Supporting Online Material

Mechanistic Studies on Intramolecular C-H Trifluoromethoxylation of (Hetero)arenes *via* OCF_3-Migration

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Materials and Methods

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere, magnetically stirred, and monitored by thin layer chromatography (TLC) using Agela Technologies 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 SiliaFlash® Silica Gel 40-63μm 60Å particle size using a forced flow of eluent at 0.3–0.5 bar pressure.[1] All air- and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen. Diethyl ether and THF were distilled from deep purple sodium benzophenone ketyl. Methylene chloride, chloroform and acetonitrile were dried over CaH_2 and distilled. Nitromethane was dried over 4Å molecular sieves. All other chemicals were used as received. All deuterated solvents were purchased from Cambridge Isotope Laboratories. NMR spectra were recorded on either a Bruker Ascend 700 spectrometer operating at 700 MHz for ^{1}H acquisitions and 175 MHz for ^{13}C acquisitions, a Bruker 500 Advance spectrometer operating at 500 MHz, 125 MHz, and 470 MHz for ^{1}H, ^{13}C, and ^{19}F acquisitions, respectively, a Bruker 400 Nanobay spectrometer operating at 400 MHz, 100 MHz, and 376 MHz for ^{1}H, ^{13}C, and ^{19}F acquisitions, respectively. Chemical shifts were referenced to the residual proton solvent peaks (^{1}H: $CDCl_3$, δ 7.26; $(CD_3)_2SO$, δ 2.50; CD_3OD, δ 3.31; CD_3CN, δ 1.94), solvent ^{13}C signals ($CDCl_3$, δ 77.16; $(CD_3)_2SO$, δ 39.52; CD_3OD, δ 49.00),[2] dissolved or external neat $PhCF_3$ (^{19}F, δ –63.3 relative to $CFCl_3$).[3] Signals are listed in ppm, and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. High-resolution mass spectra were performed at Mass Spectrometry Services at the Univ. of Illinois at Urbana-Champaign and were obtained using Waters Q-TOF Ultima ESI mass spectrometer. Concentration under reduced pressure was performed by rotary evaporation at 25–30 ºC at appropriate pressure. Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds.

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

[2] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics.* **2010**, *29*, 2176–2179.

[3] Wang, X.; Xu, Y.; Mo, F.; Ji, G.; Qiu, D.; Feng, J.; Ye, Y.; Zhang, S.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc*. **201**3, *135*, 10330–10333.

Experimental Data

Standard procedure for the synthesis of *N*-aryl-*N*-hydroxylamines

Under N_2 atmosphere, a suspension of aryl nitro compound (1.00 equiv) and Rh/C (5 mol%) in THF (0.20 M) was cooled to 0 °C. Hydrazine monohydrate (1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C until the TLC analysis indicated a complete consumption of the starting material. The reaction mixture was filtered through a short pad of celite and concentrated *in vacuo*. The residue was used directly for the next step without further purification unless otherwise stated.

Standard procedure for the synthesis of protected *N*-aryl-*N*-hydroxylamines

To a stirred suspension of *N*-aryl-*N*-hydroxylamine (1.00 equiv) and $NaHCO_3$ (1.20 equiv) in Et_2O (0.20 M) at 0 °C under N_2 was slowly added a solution of protecting group precursor (1.20 equiv) in Et_2O (0.24 M) via a syringe pump (at a rate of 10 mL/h). The reaction was stirred at 0 °C until the TLC analysis indicated a complete consumption of the starting material. The reaction mixture was filtered through a short pad of celite and concentrated *in vacuo*. The residue was purified by chromatography on silica gel.

Standard procedure for *O*-trifluoromethylation of protected *N*-aryl-*N*-hydroxylamines

Under N_2 atmosphere, to a mixture of protected *N*-aryl-*N*-hydroxylamine (1.00 equiv) and Cs_2CO_3 (10 mol%) in $CHCl_3$ (0.100 M) was added Togni reagent II (1.20 equiv) and the reaction mixture was stirred at rt for 14–23h. The reaction mixture was then washed with sat. aq. $NaHCO_3$* and the organic layer was collected, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel.

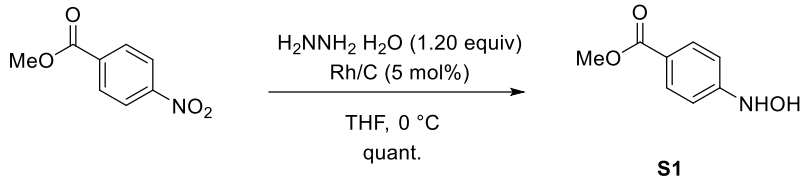
*The wash with sat. aq. $NaHCO_3$ was not necessary in case of compounds of low polarity, which could be easily separated from 2-iodobenzoic acid by means column chromatography.

Standard procedure for the synthesis of *ortho*-OCF_3 aniline derivatives *via* OCF_3-migration

A solution of protected *N*-aryl-*N*-(trifluoromethoxy)amine (0.400 mmol) in $MeNO_2$ (0.400 mL, 1.00 M) was heated at an appropriate temperature (50 °C, 80 °C, 120 °C or 140 °C) under N_2 atmosphere for 11–48h. The reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel.

Reaction procedures

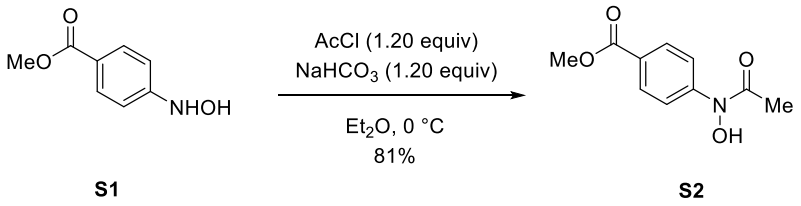
Methyl 4-(hydroxyamino)benzoate (S1)



Under N_2 atmosphere, a suspension of methyl 4-nitrobenzoate (5.00 g, 27.6 mmol, 1.00 equiv) and Rh/C (159 mg, 1.38 mmol, 5 mol%) in THF (300 mL, 0.0920 M) was cooled to 0 °C. Hydrazine monohydrate (1.52 g, 30.4 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 5h. The reaction mixture was filtered through a short pad of celite, the celite was washed with EtOAc and the combined organic layers were concentrated *in vacuo* to afford 4.62 g of the title compound as a yellow solid (quant yield).

R_f = 0.23 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ): 8.95 (s, 1H), 8.64 (d, *J* = 1.5 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.77(s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, δ): 166.2, 156.0, 130.4, 119.1, 111.2, 51.4. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_8H_{10}NO_3$ ($[M + H]^+$), 168.0661, found, 168.0667.

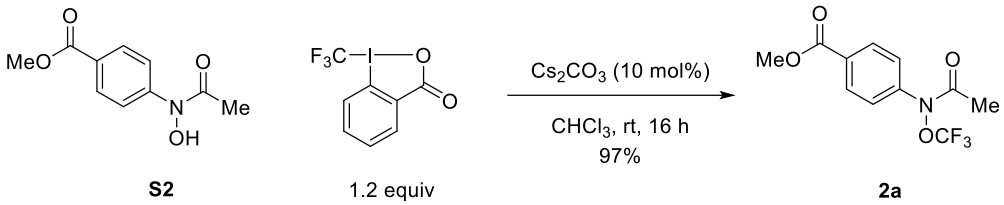
Methyl 4-(*N*-hydroxyacetamido)benzoate (S2)



To a stirred suspension of methyl 4-(hydroxyamino)benzoate (**S1**) (0.900 g, 5.38 mmol, 1.00 equiv) and $NaHCO_3$ (0.540 g, 6.46 mmol, 1.20 equiv) in Et_2O (30.0 mL, 0.179 M) at 0 °C under N_2 was slowly added a solution of acetyl chloride (0.510 g, 6.46 mmol, 1.20 equiv) in Et_2O (30.0 mL, 0.215 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 1:1 (v/v)), to afford 0.910 g of the title compound as a light yellow solid (81% yield).

R_f = 0.13 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 10.83 (s, 1H), 7.96 (d, *J* = 9.0 Hz, 2H), 7.83 (d, *J* = 9.0 Hz, 2H), 3.83 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ): 170.8, 165.7, 145.4, 129.8, 124.6, 118.4, 52.0, 22.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_{12}NO_4$ ($[M + H]^+$), 210.0766, found, 210.0766.

Methyl 4-(*N*-(trifluoromethoxy)acetamido)benzoate (2a)

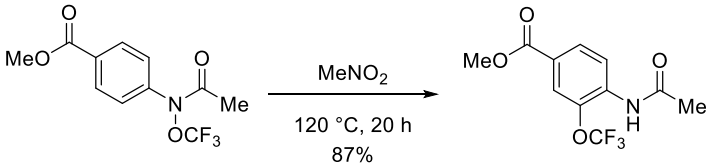


S2 1.2 equiv **2a**

Under N_2 atmosphere, to a mixture of methyl 4-(*N*-hydroxyacetamido)benzoate (**S2**) (335 mg, 1.60 mmol, 1.00 equiv) and Cs_2CO_3 (52.1 mg, 0.160 mmol, 10 mol%) in $CHCl_3$ (16.0 mL, 0.100 M) was added Togni reagent II (607 mg, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 16 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:CH_2Cl_2 (7:3 to 0:1 (v/v)), to afford 428 mg of the title compound a slightly yellow oil (97% yield).

R_f = 0.44 (CH_2Cl_2). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.13–8.09 (m, 2H), 7.49–7.45 (m, 2H), 3.93 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 172.3, 166.2, 143.9, 130.6, 129.9, 124.0, 122.8 (q, J = 264.1 Hz), 52.5, 21.9. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –65.00 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{11}H_{11}NO_4F_3$ ([M + H]$^+$), 278.0640, found, 278.0637.

Methyl 4-acetamido-3-(trifluoromethoxy)benzoate (3a)

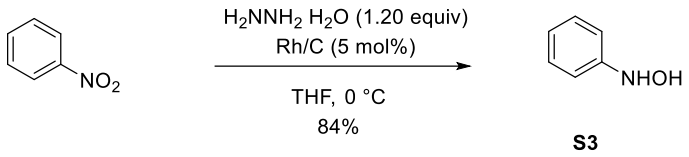


2a **3a**

A solution of methyl 4-(*N*-(trifluoromethoxy)acetamido)benzoate (**2a**) (111 mg, 0.400 mmol) in $MeNO_2$ (0.400 mL, 1.00 M) was heated at 120 °C under N_2 atmosphere for 20 h. The reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 7:3 (v/v)), to afford 97.1 mg of the title compound as a white solid (87% yield).

R_f = 0.51 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.56 (d, J = 8.6 Hz, 1H), 7.97 (d, J = 8.6 Hz, 1H), 7.93 (s, 1H), 7.56 (br. s, 1H), 3.92 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.5, 165.6, 137.2, 134.7, 129.3, 125.8, 121.5, 120.8, 120.6 (q, J = 258.9 Hz), 52.5, 25.2. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –58.1 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{11}H_{11}NO_4F_3$ ([M + H]$^+$), 278.0640, found, 278.0643.

***N*-Phenyl-*N*-hydroxylamine (S3)**

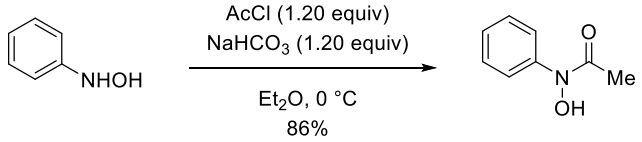


S3

Under N_2 atmosphere, a suspension of nitrobenzene (1.00 g, 8.10 mmol, 1.00 equiv) and Rh/C (40.5 mg, 0.352 mmol, 5 mol%) in THF (25.0 mL, 0.324 M) was cooled to 0 °C. Hydrazine monohydrate (0.487 g, 9.72 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 1 h and then slowly warmed up to rt and stirred at rt for 4 h. The reaction mixture was filtered through a short pad of celite and concentrated *in vacuo.* Recrystallization from CH_2Cl_2/hexanes at –20 °C afforded 0.740 g of the title compound as a white solid (84% yield).

R_f = 0.25 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ): 8.25 (s, 1H), 8.21 (s, 1H), 7.14 (t, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 7.9 Hz, 2H), 6.72 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, δ): 152.1, 128.4, 119.2, 112.9.

***N*-Hydroxy-*N*-phenylacetamide (S4)**

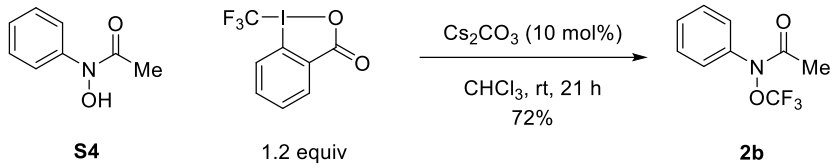


S3 **S4**

To a stirred suspension of *N*-phenylhydroxylamine (**S3**) (0.500 g, 4.58 mmol, 1.00 equiv) and $NaHCO_3$ (0.462 g, 5.50 mmol, 1.20 equiv) in Et_2O (15.0 mL, 0.305 M) at 0 °C under N_2 was slowly added a solution of acetyl chloride (0.432 g, 5.50 mmol, 1.20 equiv) in Et_2O (15.0 mL, 0.367 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The combined organic layers were washed with water, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 3:2 (v/v)), to afford 0.59 g of the title compound as a white solid (86% yield).

R_f = 0.27 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ): 10.61 (s, 1H), 7.59 (d, *J* = 6.0 Hz, 2H), 7.35 (t, *J* = 6.0 Hz, 2H), 7.13 (t, *J* = 6.0 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, δ): 169.9, 141.7, 128.4, 124.7, 120.3, 22.5.

***N*-Phenyl-*N*-(trifluoromethoxy)acetamide (2b)**

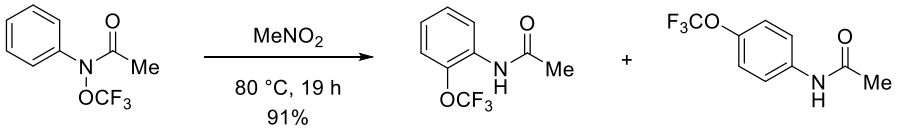


S4 1.2 equiv **2b**

Under N_2 atmosphere, to a mixture of *N*-hydroxy-*N*-phenylacetamide (**S4**) (400 mg, 2.65 mmol, 1.00 equiv) and Cs_2CO_3 (86.2 mg, 0.265 mmol, 10 mol%) in $CHCl_3$ (26.5 mL, 0.100 M) was added Togni reagent II (1.00 g, 3.18 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 21 h. The reaction mixture concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (19:1 to 9:1 (v/v)), to afford 420 mg of the title compound a slightly yellow oil (72% yield).

R_f = 0.63 (hexanes/EtOAc 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, δ): 7.49–7.41 (m, 2H), 7.41–7.31 (m, 3H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 172.4, 140.4, 129.5, 129.4, 126.3, 122.9 (q, *J* = 263.0 Hz), 22.0. ^{19}F NMR (376 MHz, $CDCl_3$, (376 MHz, $CDCl_3$, 25 ºC, δ): –64.8 (s). 25 ºC, δ): –64.8 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_9H_9NO_2F_3$ ([M + H]$^+$), 220.0585, found, 220.0580.

***N*-(2-(Trifluoromethoxy)phenyl)acetamide (3b) and *N*-(4-(trifluoromethoxy)phenyl)acetamide (3b-II)**



2b **3b**, 82% **3b-II**, 9%

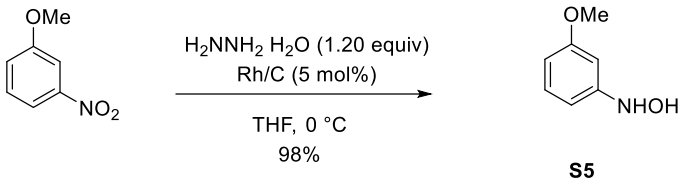
A solution of *N*-phenyl-*N*-(trifluoromethoxy)acetamide (**2b**) (128 mg, 100 µL, 0.584 mmol) in $MeNO_2$ (0.584 mL, 1.00 M) was heated at 80 °C under N_2 atmosphere for 19 h. The reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 1:1 (v/v)), to afford 105 mg of **3b** (82% yield) and 11.2 mg of **3b-II** (9% yield).

Data for **3b**: white solid; R_f = 0.36 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.39 (d, *J* = 8.2 Hz, 1H), 7.39 (br. s, 1H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.25–7.24 (m, 1H), 7.12–7.08 (m, 1 H), 2.23 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.4, 138.1, 130.7, 127.7, 124.3, 122.1, 120.7 (q, *J* = 257.7 Hz), 120.4, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –58.4 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_9H_9NO_2F_3$ ([M + H]$^+$), 220.0585, found, 220.0583.

Data for **3b-II**: white solid; R_f = 0.33 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, δ): 7.53 (d, *J* = 8.9 Hz, 2H), 7.18 (app d, *J* = 8.9 Hz, 3H), 2.19 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.4, 145.4, 136.6, 121.9, 121.1, 120.6 (q, *J* = 255.5 Hz), 24.7. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –58.8 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for

$C_9H_9NO_2F_3$ ([M + H]$^+$), 220.0585, found, 220.0583.

***N*-(3-Methoxyphenyl)hydroxylamine (S5)**

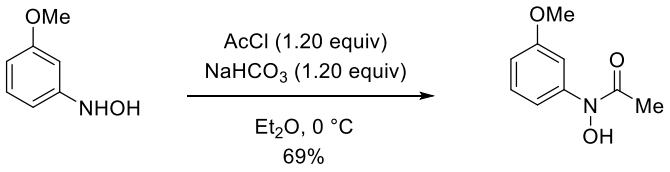


S5

Under N_2 atmosphere, a suspension of 1-methoxy-3-nitrobenzene (1.00 g, 6.53 mmol, 1.00 equiv) and Rh/C (50 mg, mmol, 5 mmol%) in THF (25.0 mL, 0.261 M) was cooled to 0 °C. Hydrazine monohydrate (0.360 g, 7.19 mmol, 1.10 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 2 h. The reaction mixture was filtered through a short pad of celite, the celite was washed with EtOAc and the combined organic layers were concentrated *in vacuo* to afford 0.89 g of the title compound as a white solid (98% yield).

R_f = 0.47 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 25 ºC, δ): 8.26 (d, *J* = 2.2 Hz, 1H), 8.23 (s, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.38-6.41 (m, 2H), 6.30 (dd, *J* = 8.0, 2.3 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, 25 ºC, δ): 159.8, 153.5, 129.1, 105.5, 104.6, 98.5, 54.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_7H_{10}NO_2$ ([M + H]$^+$), 140.0712, found, 140.0714.

***N*-Hydroxy-*N*-(3-methoxyphenyl)acetamide (S6)**

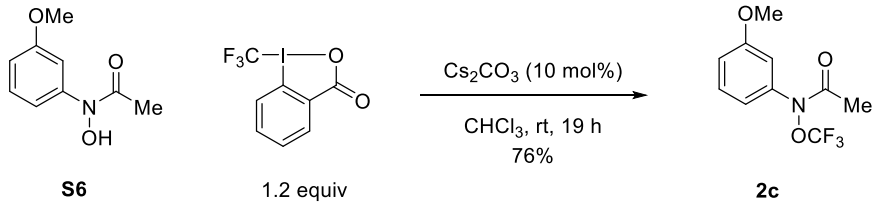


S5 **S6**

To a stirred suspension of *N*-(3-methoxyphenyl)hydroxylamine (**S5**) (0.900 g, 6.47 mmol, 1.00 equiv) and $NaHCO_3$ (0.650 g, 7.76 mmol, 1.20 equiv) in Et_2O (30.0 mL, 0.216 M) at 0 °C under N_2 was slowly added a solution of acetyl chloride (0.610 g, 7.76 mmol, 1.20 equiv) in Et_2O (30.0 mL, 0.259 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (5:1 to 4:1 (v/v)), to afford 0.810 g of the title compound as a brown liquid (69% yield).

R_f = 0.26 (hexanes/EtOAc 5:1 (v/v)). ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ): 10.61 (s, 1H), 7.30–7.20 (m, 3H), 6.74–6.71 (m, 1H), 3.74 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, δ): 169.9, 159.2, 142.8, 129.2, 112.3, 109.8, 106.0, 55.1, 22.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_9H_{12}NO_3$ ([M + H]$^+$), 182.0817, found, 182.0816.

***N*-(3-Methoxyphenyl)-*N*-(trifluoromethoxy)acetamide (2c)**

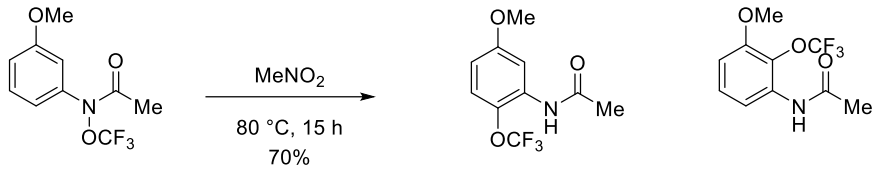


S6 1.2 equiv **2c**

Under N_2 atmosphere, to a mixture of *N*-hydroxy-*N*-(3-methoxyphenyl)acetamide (**S6**) (290 mg, 1.60 mmol, 1.00 equiv) and Cs_2CO_3 (52.1 mg, 0.160 mmol, 10 mol%) in $CHCl_3$ (16.0 mL, 0.100 M) was added Togni reagent II (607 mg, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 19 h. The reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:CH_2Cl_2 (1:1 to 3:7 (v/v)), to afford 290 mg of the title compound as a yellow oil (76% yield).

R_f = 0.34 (hexanes/CH_2Cl_2 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 7.35 (t, *J* = 8.2 Hz, 1H), 6.99–6.96 (m, 1H), 6.94 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.93–6.90 (m, 1H), 3.83 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 172.4, 160.4, 141.4, 130.2, 122.9 (q, *J* = 262.7 Hz), 118.5, 115.2, 112.0, 55.6, 22.0. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –64.8 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_{11}NO_3F_3$ ($[M + H]^+$), 250.0691, found, 250.0687.

***N*-(5-Methoxy-2-(trifluoromethoxy)phenyl)acetamide (3c) and *N*-(3-methoxy-2-(trifluoromethoxy)phenyl)acetamide (3c-II)**



2c **3c**, 55% **3c-II**, 15%

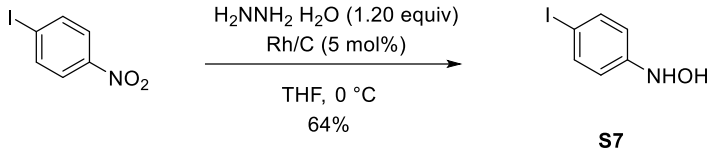
A solution of *N*-(3-methoxyphenyl)-*N*-(trifluoromethoxy)acetamide (**2c**) (99.7 mg, 0.400 mmol) in $MeNO_2$ (0.400 mL, 1.00 M) was heated at 80 °C under N_2 atmosphere for 15 h. The reaction mixture was purified by preparative TLC using hexanes:EtOAc (4:1 (v/v)) for development (prep TLC was developed four times). The purification afforded 55.3 mg of **3c** and 14.9 mg of **3c-II** (70% overall yield).

Data for **3c**: white solid; R_f = 0.77 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, δ): 8.02 (d, *J* = 2.0 Hz, 1H), 7.48 (br. s, 1H), 7.12 (dd, *J* = 9.2, 1.1 Hz, 1H), 6.59 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.79 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.5, 158.5, 131.8, 131.6, 121.7, 120.8 (q, *J* = 256.8 Hz), 109.9, 106.8, 55.8, 24.9. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –58.7 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_{11}NO_3F_3$ ($[M + H]^+$), 250.0691, found, 250.0690.

Data for **3c-II**: white solid; R_f = 0.70 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 7.93 (d, *J* = 8.2 Hz, 1H), 7.40 (br. s, 1H), 7.23 (t, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 8.2

Hz, 1H), 3.87 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.4, 152.7, 132.9, 128.2, 127.6, 121.1 (q, *J* = 258.7 Hz), 113.8, 108.0, 56.3, 24.9. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –57.9 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_{11}NO_3F_3$ ([M + H]$^+$), 250.0691, found, 250.0692.

_N_-(4-Iodophenyl)hydroxylamine (S7)

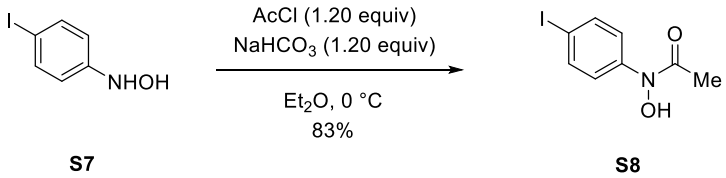


S7

Under N_2 atmosphere, a suspension of 1-iodo-4-nitrobenzene (2.00 g, 8.03 mmol, 1.00 equiv) and Rh/C (46.1 mg, 0.400 mmol, 5 mol%) in THF (30.0 mL, 0.268 M) was cooled to 0 °C. Hydrazine monohydrate (0.482 g, 9.64 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 2 h. The reaction mixture was filtered through a short pad of celite and concentrated *in vacuo*. Recrystallization from CH_2Cl_2/hexanes at –20 °C afforded 1.20 g of the title compound as a yellow solid (64% yield).

R_f = 0.26 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ): 8.41 (s, 2H), 7.46 (d, *J* = 2.7 Hz, 1H), 7.44 (d, *J* = 2.7 Hz, 1H), 6.67 (d, *J* = 2.6 Hz, 1H), 6.65 (d, *J* = 2.6 Hz, 1H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, δ): 152.4, 137.3, 115.8, 81.1.

_N_-Hydroxy-_N_-(4-iodophenyl)acetamide (S8)

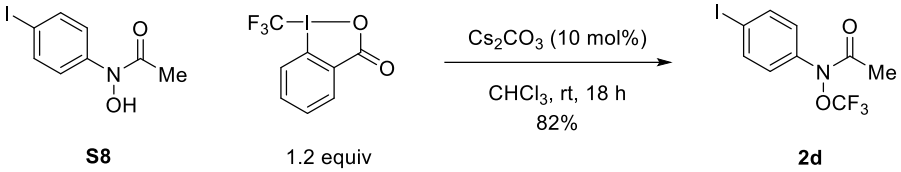


S7 **S8**

To a stirred suspension of *N*-(4-iodophenyl)hydroxylamine (**S7**) (1.00 g, 4.25 mmol, 1.00 equiv) and $NaHCO_3$ (0.430 g, 5.11 mmol, 1.20 equiv) in Et_2O (30.0 mL, 0.412 M) at 0 °C under N_2 was slowly added a solution of acetyl chloride (0.400 g, 5.11 mmol, 1.20 equiv) in Et_2O (20.0 mL, 0.256 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, water was added and the aqueous layer was extracted with EtOAc (4 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Recrystallization from Et_2O/hexanes afforded 0.980 g of the title compound as light brown solid (83% yield).

R_f = 0.18 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 10.69 (s, 1H), 7.72–7.67 (m, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ): 170.1, 141.4, 137.0, 121.8, 88.4, 22.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_8H_9NO_2I$ ([M + H]$^+$), 277.9678, found, 277.9684.

***N*-(4-Iodophenyl)-*N*-(trifluoromethoxy)acetamide (2d)**

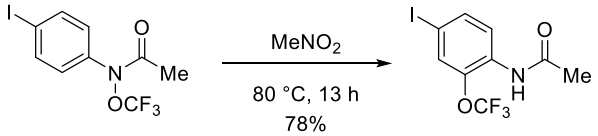


S8 1.2 equiv **2d**

Under N_2 atmosphere, to a mixture of *N*-hydroxy-*N*-(4-iodophenyl)acetamide (**S8**) (200 mg, 0.722 mmol, 1.00 equiv) and Cs_2CO_3 (23.5 mg, 0.0720 mmol, 10 mol%) in $CHCl_3$ (7.20 mL, 0.100 M) was added Togni reagent II (274 mg, 0.867 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 18 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:CH_2Cl_2 (1:1 (v/v)), to afford 205 mg of the title compound a slightly yellow oil (82% yield).

R_f = 0.48 (hexanes/CH_2Cl_2 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 7.79–7.76 (m, 2H), 7.14–7.11 (m, 2H), 2.27 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 172.5, 140.1, 138.6, 127.2, 122.8 (q, *J* = 263.5 Hz), 94.4, 21.9. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –64.9 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_9H_8NO_2F_3I$ ([M + H]$^+$), 345.9552, found, 345.9549.

***N*-(4-Iodo-2-(trifluoromethoxy)phenyl)acetamide (3d)**

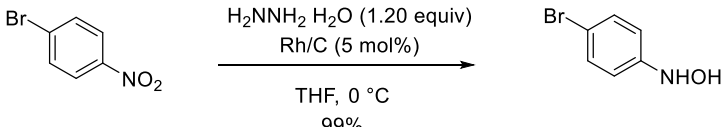


2d **3d**

A solution of *N*-(4-iodophenyl)-*N*-(trifluoromethoxy)acetamide (**2d**) (138 mg, 0.400 mmol) in $MeNO_2$ (0.400 mL, 1.00 M) was heated at 80 °C under N_2 atmosphere for 13 h. The reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 2:3 (v/v)), to afford 108 mg of the title compound as a beige solid (78% yield).

R_f = 0.46 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.19 (d, *J* = 8.6 Hz, 1H), 7.59 (dd, *J* = 8.8, 1.5 Hz, 1H), 7.56 (s, 1H), 7.36 (br. s, 1H), 2.22 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.3, 138.0, 136.8, 130.7, 129.2, 123.4, 120.6 (q, *J* = 259.1 Hz), 85.6, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –58.3 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_9H_8NO_2F_3I$ ([M + H]$^+$), 345.9552, found, 345.9548.

***N*-(4-Bromophenyl)hydroxylamine (S9)**

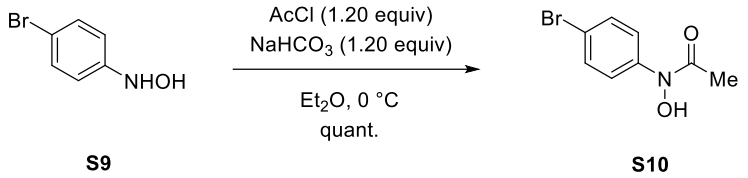


S9

Under N_2 atmosphere, a suspension of 1-bromo-4-nitrobenzene (3.00 g, 14.9 mmol, 1.00 equiv) and Rh/C (85.3 mg, 0.740 mmol, 5 mol%) in THF (100 mL, 0.149 M) was cooled to 0 °C. Hydrazine monohydrate (0.892 g, 16.2 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 2.5 h. The reaction mixture was filtered through a short pad of celite and concentrated *in vacuo* to afford 2.78 g of the title compound as a brown solid (99% yield).

R_f = 0.30 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ): 8.42 (s, 1H), 8.40 (s, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, δ): 151.4, 131.1, 114.8, 110.1. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C_6H_7NOBr ($[M + H]^+$), 187.9711, found, 187.9714.

_N_-(4-Bromophenyl)-_N_-hydroxyacetamide (S10)

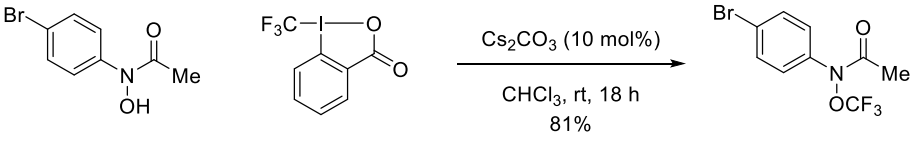


S9 **S10**

To a stirred suspension of *N*-(4-bromophenyl)hydroxylamine (**S9**) (1.00 g, 5.32 mmol, 1.00 equiv) and $NaHCO_3$ (0.540 g, 6.38 mmol, 1.20 equiv) in Et_2O (25.0 mL, 0.213 M) at 0 °C under N_2 was slowly added a solution of acetyl chloride (0.500 g, 6.38 mmol, 1.20 equiv) in Et_2O (30.0 mL, 0.213 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated *in vacuo* to afford 1.23 g of the title compound as a brown solid (quant yield).

R_f = 0.14 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 10.72 (s, 1H), 7.61 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ): 170.2, 140.9, 131.2, 121.6, 116.2, 22.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_8H_9NO_2Br$ ($[M + H]^+$), 229.9817, found, 229.9818.

_N_-(4-Bromophenyl)-_N_-(trifluoromethoxy)acetamide (2e)



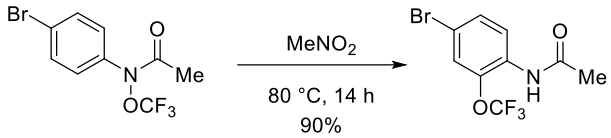
S10 1.2 equiv **2e**

Under N_2 atmosphere, to a mixture of *N*-(4-bromophenyl)-*N*-hydroxyacetamide (**S10**) (368 mg, 1.60 mmol, 1.00 equiv) and Cs_2CO_3 (52.1 mg, 0.160 mmol, 10 mol%) in $CHCl_3$ (16.0 mL, 0.100 M) was added Togni reagent II (607 mg, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 18 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:CH_2Cl_2 (1:1 to 1:3 (v/v)), to afford 384 mg of the title

compound a slightly yellow oil (81% yield).

R_f = 0.47 (hexanes/CH_2Cl_2 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 7.59–7.55 (m, 2H), 7.23–7.28 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 172.5, 139.3, 132.6, 127.2, 122.9, 122.8 (q, J = 263.3 Hz), 21.8. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –64.9 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_9H_8NO_2F_3Br$ ([M + H]$^+$), 297.9690, found, 297.9694.

_N_-(4-Bromo-2-(trifluoromethoxy)phenyl)acetamide (3e)

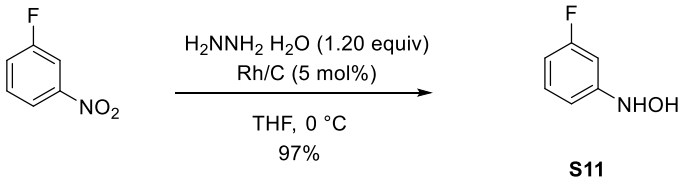


2e **3e**

A solution of *N*-(4-bromophenyl)-*N*-(trifluoromethoxy)acetamide (**2e**) (119 mg, 0.400 mmol) in $MeNO_2$ (0.400 mL, 1.00 M) was heated at 80 °C under N_2 atmosphere for 14 h. The reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (17:1 to 7:3 (v/v)), to afford 107 mg of the title compound as a beige solid (90% yield).

R_f = 0.42 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, δ): 8.32 (d, J = 9.2 Hz, 1H), 7.42–7.41 (m, 1H), 7.40 (s, 1H), 7.37 (br. s, 1H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 168.3, 138.2, 130.8, 129.9, 123.6, 123.1, 120.6 (q, J = 259.2 Hz), 115.9, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –58.2 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_9H_8NO_2F_3Br$ ([M + H]$^+$), 297.9690, found, 297.9692.

_N_-(3-Fluorophenyl)hydroxylamine (S11)



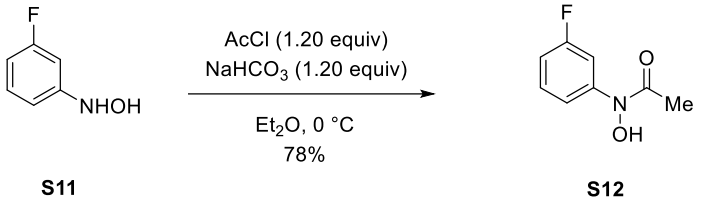
S11

Under N_2 atmosphere, a suspension of 1-fluoro-3-nitrobenzene (1.00 g, 7.09 mmol, 1.00 equiv) and Rh/C (50.0 mg, 0.435 mmol, 6 mol%) in THF (25.0 mL, 0.284 M) was cooled to 0 °C. Hydrazine monohydrate (0.390 g, 7.80 mmol, 1.10 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 1 h. The reaction mixture was filtered through a short pad of celite. The celite was washed with EtOAc and the combined organic layers were concentrated *in vacuo* to afford 0.87 g of the title compound as a white solid (97% yield).

R_f = 0.28 (hexanes/EtOAc 4:1 (v/v)). ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.50 (s, 1H), 8.45 (d, J = 2.1 Hz, 1H), 7.17–7.14 (m, 1H), 6.61–6.58 (m, 2H), 6.50–6,48 (m, 1H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ): 163.0 (d, J = 238.8 Hz), 154.4 (d, J = 10.2 Hz), 130.0 (d, J = 9.6 Hz), 108.7 (d, J = 2.3 Hz), 105.1 (d, J = 21.4 Hz), 99.3 (d, J = 25.5 Hz). ^{19}F NMR (376 MHz, $(CD_3)_2SO$, 25 ºC, δ): –117.3 (s). Mass Spectrometry:

HRMS (ESI-TOF) (m/z): calcd for C_6H_7NOF ($[M + H]^+$), 128.0512, found, 128.0513.

_N_-(3-Fluorophenyl)-_N_-hydroxyacetamide (S12)

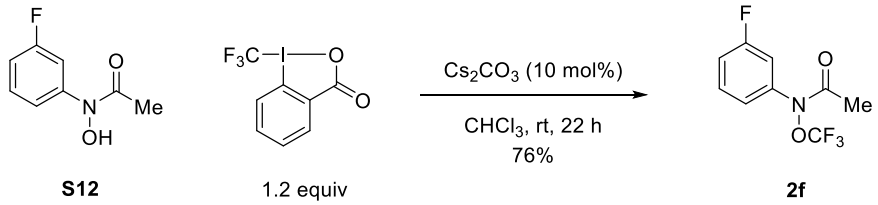


S11 **S12**

To a stirred suspension of *N*-(3-fluorophenyl)hydroxylamine (**S11**) (0.800 g, 6.29 mmol, 1.00 equiv) and $NaHCO_3$ (0.634 g, 7.55 mmol, 1.20 equiv) in Et_2O (35.0 mL, 0.180 M) at 0 °C under N_2 was slowly added a solution of acetyl chloride (0.593 g, 7.55 mmol, 1.20 equiv) in Et_2O (30.0 mL, 0.252 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 1:1 (v/v)), to afford 0.830 g of the title compound as a yellow liquid (78% yield).

R_f = 0.52 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ): 10.77 (s, 1H), 7.54–7.50 (m, 2H), 7.50–7.37 (m, 1H), 7.00–7.6.94 (m, 1H), 2.23 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, δ): 170.4, 161.80 (d, *J* = 240.2 Hz), 143.1 (d, *J* = 10.7 Hz), 130.1 (d, *J* = 9.2 Hz), 115.0, 110.7 (d, *J* = 20.9 Hz), 106.3 (d, *J* = 27.7 Hz), 22.7. ^{19}F NMR (376 MHz, $(CD_3)_2SO$, 25 ºC, δ): –114.5 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_8H_9NO_2F$ ($[M + H]^+$), 170.0617, found, 170.0617.

_N_-(3-Fluorophenyl)-_N_-(trifluoromethoxy)acetamide (2f)



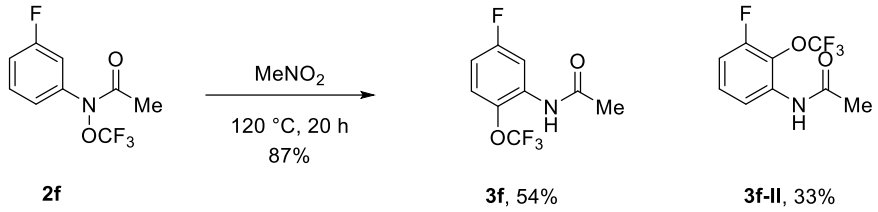
S12 1.2 equiv **2f**

Under N_2 atmosphere, to a mixture of *N*-(3-fluorophenyl)-*N*-hydroxyacetamide (**S12**) (243 mg, 1.44 mmol, 1.00 equiv) and Cs_2CO_3 (46.9 mg, 0.144 mmol, 10 mol%) in $CHCl_3$ (14.4 mL, 0.100 M) was added Togni reagent II (546 mg, 1.73 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 22 h. The reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:CH_2Cl_2 (1:1 to 1:3 (v/v)), to afford 287 mg of the title compound as a slightly yellow oil (76% yield).

R_f = 0.55 (hexanes/CH_2Cl_2 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 7.41 (td, *J* = 8.2, 6.0 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.13 (dt, *J* = 9.4, 2.2 Hz, 1H), 7.08 (td, *J* = 8.2, 1.7 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 172.5, 162.7 (d, *J* = 246.8 Hz), 141.6 (d, *J* = 9.8 Hz), 130.5 (d, *J* = 8.8 Hz), 122.8 (q, *J* = 263.4 Hz), 121.0, 115.9 (d, *J* = 20.9 Hz), 112.9 (d, *J* = 24.0 Hz),

21.9. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –65.0 (s), –111.2 (s). Mass Spectrometry: HRMS (EI-TOF) (m/z): calcd for $C_9H_7NO_2F_4$ ($[M]^+$), 237.0413, found, 237.0417.

_N_-(5-Fluoro-2-(trifluoromethoxy)phenyl)acetamide (3f) and _N_-(3-fluoro-2-(trifluoromethoxy)phenyl)acetamide (3f-II)



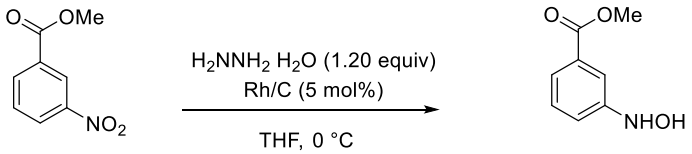
2f **3f**, 54% **3f-II**, 33%

A solution of *N*-(3-fluorophenyl)-*N*-(trifluoromethoxy)acetamide (**2f**) (95.9 mg, 0.400 mmol) in $MeNO_2$ (0.400 mL, 1.00 M) was heated at 120 °C under N_2 atmosphere for 20 h. The reaction mixture was purified by preparative TLC using hexanes:EtOAc (7:3 (v/v)) for development. The purification afforded 51.2 mg of **3f** and 31.5 mg of **3f-II** (87% overall yield).

Data for **3f**: white solid; R_f = 0.67 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.25 (d, *J* = 9.0 Hz, 1H), 7.47 (br. s, 1H), 7.23–7.18 (m, 1H), 6.83–6.73 (m, 1H), 2.23 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.4, 161.0 (d, *J* = 243.9 Hz), 133.7, 132.2 (d, *J* = 12.1 Hz), 121.8 (d, *J* = 9.7 Hz), 120.7 (q, *J* = 258.0 Hz), 110.6 (d, *J* = 24.1 Hz), 109.1 (d, *J* = 29.6 Hz), 25.0. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –58.5 (s), –111.9 (q). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_9H_8NO_2F_4$ ($[M + H]^+$), 238.0491, found, 238.0492.

Data for **3f-II**: white solid; R_f = 0.56 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.15 (d, *J* = 7.7 Hz, 1H), 7.41 (br. s, 1 H), 7.29–7.23 (m, 1 H), 6.93 (t, *J* = 9.0 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.4, 155.2 (d, *J* = 250.3 Hz), 133.5, 128.6 (d, *J* = 8.5 Hz), 126.3 (d, *J* = 13.8 Hz), 121.0 (q, *J* = 259.9 Hz), 117.3, 111.9 (d, *J* = 18.3 Hz), 24.9. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –58.9 (d), –127.3 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_9H_8NO_2F_4$ ($[M + H]^+$), 238.0491, found, 238.0490.

Methyl 3-(hydroxyamino)benzoate (S13)



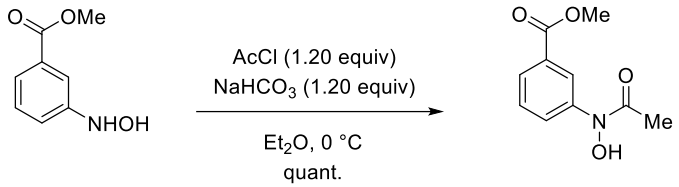
S13

Under N_2 atmosphere, a suspension of methyl 3-nitrobenzoate (2.00 g, 11.0 mmol, 1.00 equiv) and Rh/C (63.0 mg, 0.550 mmol, 5 mol%) in THF (40.0 mL, 0.275 M) was cooled to 0 °C. Hydrazine monohydrate (0.663 g, 13.3 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 2.5 h. The reaction mixture was filtered through a short pad of celite, the celite was washed with EtOAc and the

combined organic layers were concentrated *in vacuo* to afford 1.82 g of the title compound as a light yellow solid (99% yield).

R_f = 0.19 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ): 8.51 (s, 1H), 8.49 (d, *J* = 2.1 Hz, 1H), 7.45 (s, 1H), 7.35–7.28 (m, 2H), 7.07–7.04 (m, 1H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, δ): 166.6, 152.4, 130.0, 128.9, 119.9, 117.5, 113.2, 52.1. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_8H_{10}NO_3$ ($[M + H]^+$), 168.0661, found, 168.0666.

Methyl 3-(*N*-hydroxyacetamido)benzoate (S14)

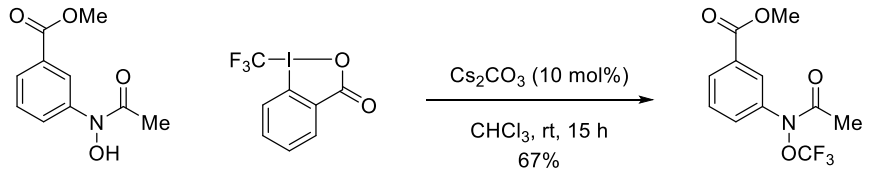


S13 **S14**

To a stirred suspension of methyl 3-(hydroxyamino)benzoate (**S13**) (1.00 g, 5.98 mmol, 1.00 equiv) and $NaHCO_3$ (0.600 g, 7.18 mmol, 1.20 equiv) in Et_2O (30.0 mL, 0.199 M) at 0 °C under N_2 was slowly added a solution of acetyl chloride (0.560 g, 7.18 mmol, 1.20 equiv) in Et_2O (30.0 mL, 0.239 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated *in vacuo* to afford 1.25 g of the title compound as a yellow solid (quant yield).

R_f = 0.10 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 10.80 (s, 1H), 8.26 (s, 1H), 7.95–7.90 (m, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 3.86 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ): 170.4, 166.0, 141.9, 129.8, 128.9, 124.9, 124.2, 120.1, 52.3, 22.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_{12}NO_4$ ($[M + H]^+$), 210.0766, found, 210.0764.

Methyl 3-(*N*-(trifluoromethoxy)acetamido)benzoate (2g)

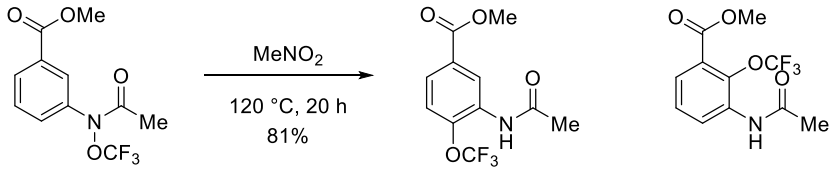


S14 1.2 equiv **2g**

Under N_2 atmosphere, to a mixture of methyl 3-(*N*-hydroxyacetamido)benzoate (**S14**) (335 mg, 1.60 mmol, 1.00 equiv) and Cs_2CO_3 (52.1 mg, 0.160 mmol, 10 mol%) in $CHCl_3$ (16.0 mL, 0.100 M) was added Togni reagent II (607 mg, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 15 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:CH_2Cl_2 (1:3 to 0:1 (v/v)), to afford 298 mg of the title compound as a slightly yellow oil (67% yield).

R_f = 0.50 (CH_2Cl_2). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, δ): 8.07–8.04 (m, 2H), 7.59–7.56 (m, 1H), 7.55–7.50 (m, 1H), 3.94 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 172.7, 166.0, 140.6, 131.7, 130.0, 129.9, 129.5, 126.5, 122.8 (q, *J* = 263.7 Hz), 52.6, 21.8. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –64.9 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{11}H_{11}NO_4F_3$ ([M + H]$^+$), 278.0640, found, 278.0640.

Methyl 3-acetamido-4-(trifluoromethoxy)benzoate (3g) and methyl 3-acetamido-2-(trifluoromethoxy)benzoate (3g-II)



2g **3g**, 43% **3g-II**, 38%

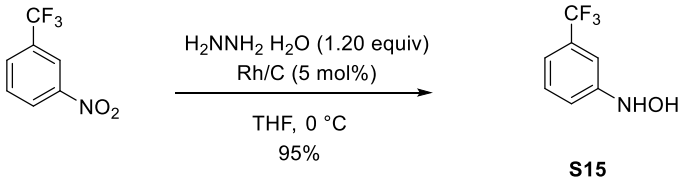
A solution of methyl 3-(*N*-(trifluoromethoxy)acetamido)benzoate (**2g**) (111 mg, 0.400 mmol) in $MeNO_2$ (0.400 mL, 1.00 M) was heated at 120 °C under N_2 atmosphere for 20 h. The reaction mixture was purified by preparative TLC using Et_2O for development. The purification afforded 90.4 mg of a 1.14:1 mixture of **3g** and **3g-II** (81% overall yield).

Compounds **3g** and **3g-II** were further separated for characterization by preparative TLC (eluting twenty times with hexanes:Et_2O (7:3 (v/v)).

Data for **3g**: white solid; R_f = 0.59 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, δ): 9.02 (br. s, 1H), 7.82 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.41 (br. s, 1H), 7.31 (dd, *J* = 8.7, 1.6 Hz, 1H), 3.92 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.4, 166.0, 141.2, 130.3, 129.4, 125.9, 123.4, 120.5 (q, *J* = 259.1 Hz), 119.5, 52.6, 24.9. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –57.8 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{11}H_{11}NO_4F_3$ ([M + H]$^+$), 278.0640, found, 278.0640.

Data for **3g-II**: white solid; R_f = 0.56 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.56 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.51 (br. s, 1H), 7.39 (t, *J* = 8.0 Hz, 1 H), 3.93 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.5, 165.0, 136.5, 132.8, 128.1, 126.6, 126.2, 126.1, 120.8 (q, *J* = 258.6 Hz), 52.7, 24.9. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –57.5 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{11}H_{11}NO_4F_3$ ([M + H]$^+$), 278.0640, found, 278.0639.

***N*-(3-(Trifluoromethyl)phenyl)hydroxylamine (S15)**

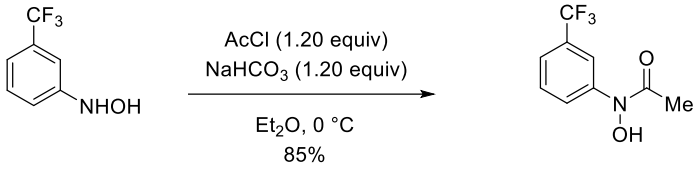


S15

Under N_2 atmosphere, a suspension of 1-nitro-3-(trifluoromethyl)benzene (1.00 g, 5.21 mmol, 1.00 equiv) and Rh/C (50 mg, 0.225 mmol, 5 mol%) in THF (25.0 mL, 0.208 M) was cooled to 0 °C. Hydrazine monohydrate (0.314 g, 5.73 mmol, 1.10 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 2 h. The reaction mixture was filtered through a short pad of celite, the celite was washed with EtOAc and the combined organic layers were concentrated *in vacuo* to afford 0.88 g of the title compound as a yellow solid (95% yield).

R_f = 0.30 (hexanes/EtOAc 4:1 (v/v)). ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.66 (s, 1H), 8.58 (s, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.09 (s, 1H), 7.07–7.03 (m, 2H). ^{13}C NMR (175 MHz, $(CD_3)_2SO$, δ): 152.7, 129.4 (q, *J* = 30.6 Hz), 124.4 (q, *J* = 270.6 Hz), 116.3, 115.2 (d, *J* = 3.8 Hz), 111.9, 108.5 (q, *J* = 4.0 Hz). ^{19}F NMR (376 MHz, $(CD_3)_2SO$, 25 ºC, δ): –63.4 (s).

_N_-Hydroxy-_N_-(3-(trifluoromethyl)phenyl)acetamide (S16)

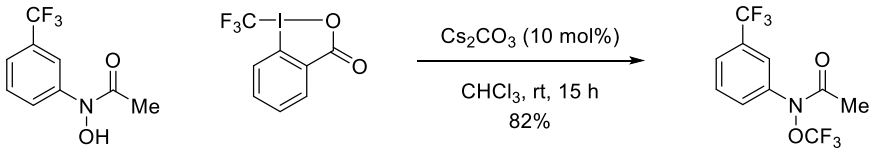


S15 **S16**

To a stirred suspension of *N*-(3-(trifluoromethyl)phenyl)hydroxylamine (**S15**) (0.720 g, 4.06 mmol, 1.00 equiv) and $NaHCO_3$ (0.410 g, 4.88 mmol, 1.20 equiv) in Et_2O (20.0 mL, 0.203 M) at 0 °C under N_2 was slowly added a solution of acetyl chloride (0.380 g, 4.88 mmol, 1.20 equiv) in Et_2O (25.0 mL, 0.192 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 1:1 (v/v)), to afford 0.760 g of the title compound as a yellow solid (85% yield).

R_f = 0.19 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ): 10.88 (s, 1H), 8.03 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, δ): 170.7, 142.2, 129.8, 129.1 (q, *J* = 31.6 Hz), 126.2 (d, *J* = 270.9 Hz), 122.9 (d, *J* = 9.6 Hz), 120.6 (d, *J* = 29.7 Hz), 115.5, 22.6. ^{19}F NMR (376 MHz, $(CD_3)_2SO$, 25 ºC, δ): –63.1 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_9H_9NO_2F_3$ ($[M + H]^+$), 220.0585, found, 220.0589.

_N_-(Trifluoromethoxy)-_N_-(3-(trifluoromethyl)phenyl)acetamide (2h)

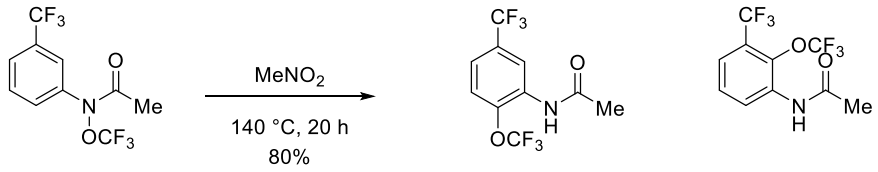


S16 1.2 equiv **2h**

Under N_2 atmosphere, to a mixture of *N*-hydroxy-*N*-(3-(trifluoromethyl)phenyl)acetamide (**S16**) (351 mg, 1.60 mmol, 1.00 equiv) and Cs_2CO_3 (52.1 mg, 0.160 mmol, 10 mol%) in $CHCl_3$ (16.0 mL, 0.100 M) was added Togni reagent II (607 mg, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 15 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:CH_2Cl_2 (1:1 to 0:1 (v/v)), to afford 378 mg of the title compound as a slightly yellow oil (82% yield).

R_f = 0.50 (hexanes/CH_2Cl_2 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, δ): 7.66 (s, 1H), 7.64–7.60 (m, 1H), 7.60–7.56 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 172.8, 140.8, 132.0 (q, *J* = 33.0 Hz), 129.9, 128.3, 125.4 (q, *J* = 3.1 Hz), 123.5 (q, *J* = 271.1 Hz), 122.8 (q, *J* = 264.0 Hz), 121.7, 21.8. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –63.3 (s), –65.0 (s). Mass Spectrometry: HRMS (EI-TOF) (m/z): calcd for $C_{10}H_7NO_2F_6$ ([M]$^+$), 287.0381, found, 287.0389.

_N_-(2-(Trifluoromethoxy)-5-(trifluoromethyl)phenyl)acetamide (3h) and _N_-(2-(trifluoromethoxy)-3-(trifluoromethyl)phenyl)acetamide (3h-II)



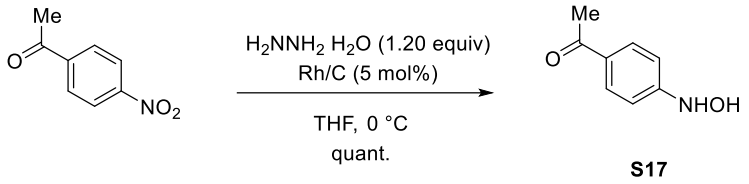
2h **3h**, 47% **3h-II**, 33%

A solution of *N*-(trifluoromethoxy)-*N*-(3-(trifluoromethyl)phenyl)acetamide (**2h**) (115 mg, 0.400 mmol) in $MeNO_2$ (0.400 mL, 1.00 M) was heated at 140 °C under N_2 atmosphere for 20 h. The reaction mixture was purified by preparative TLC using hexanes:EtOAc (4:1 (v/v)) for development (prep TLC was developed twice). The purification afforded 53.5 mg of **3h** and 37.4 mg of **3h-II** (80% overall yield).

Data for **3h**: white solid; R_f = 0.66 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.79 (br. s, 1H), 7.55 (br. s, 1H), 7.32–7.39 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.6, 139.9, 131.1, 129.9 (q, *J* = 33.1 Hz), 123.5 (q, *J* = 270.8 Hz), 121.1, 120.5 (q, *J* = 259.6 Hz), 120.1, 119.2, 24.9. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –58.0 (s), –63.2 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_8NO_2F_6$ ([M + H]$^+$), 288.0459, found, 288.0457.

Data for **3h-II**: white solid; R_f = 0.43 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.52 (br. s, 1H), 7.50 (br. s, 1H), 7.39–7.46 (m, 2H), 2.23 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.5, 135.7, 133.1, 128.3, 126.7, 125.2 (q, *J* = 32.0 Hz), 122.6 (d, *J* = 5.3 Hz), 122.5 (q, *J* = 271.6 Hz), 120.7 (q, *J* = 260.3 Hz), 24.7. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –55.7 (d), –61.1 (q). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_8NO_2F_6$ ([M + H]$^+$), 288.0459, found, 288.0463.

1-(4-(Hydroxyamino)phenyl)ethan-1-one (S17)

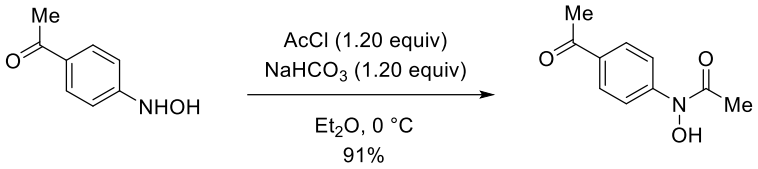


S17

Under N_2 atmosphere, a suspension of 1-(4-nitrophenyl)ethan-1-one (3.00 g, 18.2 mmol, 1.00 equiv) and Rh/C (104 mg, 0.908 mmol, 5 mol%) in THF (90.0 mL, 0.202 M) was cooled to 0 °C. Hydrazine monohydrate (1.09 g, 21.8 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 3.5 h. The reaction mixture was filtered through a short pad of celite and concentrated *in vacuo* to afford 2.80 g of the title compound as a yellow solid (quant yield).

R_f = 0.27 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.99 (s, 1H), 8.67 (s, 1H), 7.79 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ): 195.6, 155.9, 129.8, 127.7, 110.9, 26.1.

***N*-(4-Acetylphenyl)-*N*-hydroxyacetamide (S18)**

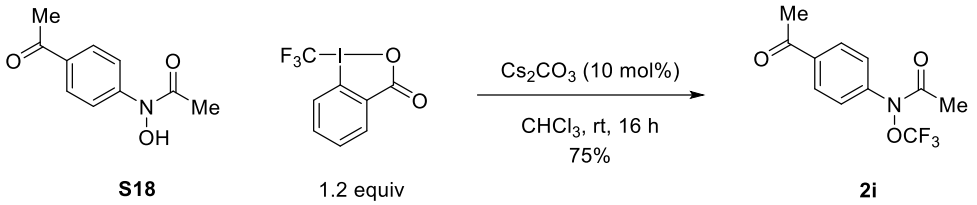


S17 **S18**

To a stirred suspension of 1-(4-(hydroxyamino)phenyl)ethan-1-one (**S17**) (0.200 g, 1.32 mmol, 1.00 equiv) and $NaHCO_3$ (0.130 g, 1.59 mmol, 1.20 equiv) in Et_2O (10.0 mL, 0.132 M) at 0 °C under N_2 was slowly added a solution of acetyl chloride (0.130 g, 1.59 mmol, 1.20 equiv) in Et_2O (5.00 mL, 0.318 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (2:1 to 1:1 (v/v)), to afford 0.230 g of the title compound as a white solid (91% yield).

R_f = 0.13 (hexanes/EtOAc 2:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 10.84 (s, 1H), 7.96 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 8.9 Hz, 2H), 2.54 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ): 196.6, 170.8, 145.3, 132.2, 128.9, 118.3, 26.5, 22.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_{12}NO_3$ ($[M + H]^+$), 194.0817, found, 194.0820.

***N*-(4-Acetylphenyl)-*N*-(trifluoromethoxy)acetamide (2i)**

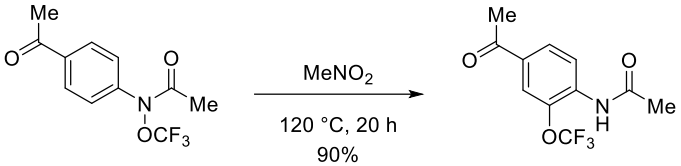


S18 1.2 equiv **2i**

Under N_2 atmosphere, to a mixture of methyl *N*-(4-acetylphenyl)-*N*-hydroxyacetamide (**S18**) (309 mg, 1.60 mmol, 1.00 equiv) and Cs_2CO_3 (52.1 mg, 0.160 mmol, 10 mol%) in $CHCl_3$ (16.0 mL, 0.100 M) was added Togni reagent II (607 mg, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 16 h. The reaction mixture was then washed with sat. aq. $NaHCO_3$ (30 mL) and the layers were separated. The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 7:3 (v/v)), to afford 314 mg of the title compound a slightly yellow oil (75% yield).

R_f = 0.62 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.03–8.00 (m, 2H), 7.50–7.48 (m, 2H), 2.61 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 196.9, 172.3, 143.9, 136.5, 129.3, 124.0, 122.7 (q, *J* = 264.2 Hz), 26.8, 21.9. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –65.00 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{11}H_{11}NO_3F_3$ ([M + H]$^+$), 262.0691, found, 262.0691.

***N*-(4-Acetyl-2-(trifluoromethoxy)phenyl)acetamide (3i)**

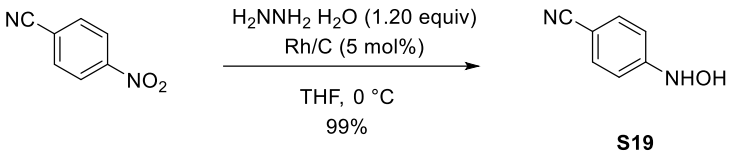


2i **3i**

A solution of *N*-(4-acetylphenyl)-*N*-(trifluoromethoxy)acetamide (**2i**) (104 mg, 0.400 mmol) in $MeNO_2$ (0.400 mL, 1.00 M) was heated at 120 °C under N_2 atmosphere for 20 h. The reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 3:2 (v/v)), to afford 93.6 mg of the title compound as a white solid (90% yield).

R_f = 0.46 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.59 (d, *J* = 8.6 Hz, 1H), 7.89–7.86 (m, 2H), 7.58 (br. s, 1H), 2.59 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 195.7, 168.6, 137.6, 134.8, 132.9, 128.4, 120.8, 120.6 (q, *J* = 259.1 Hz), 119.8, 26.5, 25.1. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –58.0 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{11}H_{11}NO_3F_3$ ([M + H]$^+$), 262.0691, found, 262.0692.

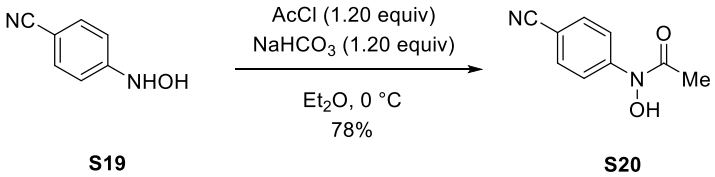
4-(Hydroxyamino)benzonitrile (S19)



Under N_2 atmosphere, a suspension of 4-nitrobenzonitrile (2.00 g, 13.5 mmol, 1.00 equiv) and Rh/C (77.6 mg, 0.680 mmol, 5 mol%) in THF (40.0 mL, 0.338 M) was cooled to 0 °C. Hydrazine monohydrate (0.810 g, 16.2 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 1 h and then slowly warmed up to rt and stirred at rt for 1 h. The reaction mixture was filtered through a short pad of celite and concentrated *in vacuo* to afford 1.80 g of the title compound as a yellow solid (99% yield).

R_f = 0.14 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 9.10 (s, 1H), 8.76 (s, 1H), 7.57–7.52 (m, 2H), 7.85 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ): 155.4, 133.1, 120.1, 111.8, 90.1.

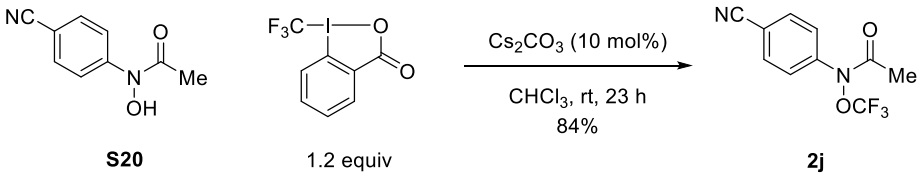
***N*-(4-Cyanophenyl)-*N*-hydroxyacetamide (S20)**



To a stirred suspension of 4-(hydroxyamino)benzonitrile (**S19**) (0.500 g, 3.73 mmol, 1.00 equiv) and $NaHCO_3$ (0.380 g, 4.47 mmol, 1.20 equiv) in Et_2O (25.0 mL, 0.149 M) at 0 °C under N_2 was slowly added a solution of acetyl chloride (0.350 g, 4.47 mmol, 1.20 equiv) in Et_2O (10.0 mL, 0.447 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined, concentrated *in vacuo*. Recrystallization from Et_2O/hexanes afforded 0.510 g of the title compound as a light pink solid (78% yield).

R_f = 0.32 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 10.92 (s, 1H), 7.88 (d, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 9.0 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ): 171.1, 145.1, 132.9, 118.9, 118.8, 105.7, 22.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_9H_9N_2O_2$ ($[M + H]^+$), 177.0664, found, 177.0665.

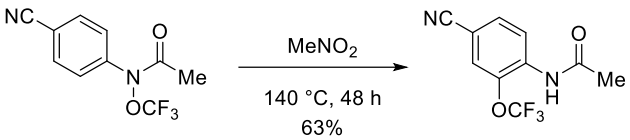
***N*-(4-Cyanophenyl)-*N*-(trifluoromethoxy)acetamide (2j)**



Under N_2 atmosphere, to a mixture of *N*-(4-cyanophenyl)-*N*-hydroxyacetamide (**S20**) (200 mg, 1.14 mmol, 1.00 equiv) and Cs_2CO_3 (37.0 mg, 0.114 mmol, 10 mol%) in $CHCl_3$ (11.4 mL, 0.100 M) was added Togni reagent II (432 mg, 1.37 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 23 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:CH_2Cl_2 (1:2 to 0:1 (v/v)), to afford 234 mg of the title compound an off-white solid (84% yield).

R_f = 0.66 (CH_2Cl_2). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 7.74–7.70 (m, 2H), 7.55–7.51 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 172.4, 143.6, 133.1, 123.8, 122.7 (q, *J* = 265.2 Hz), 118.1, 111.6, 21.9. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –65.2 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_8N_2O_2F_3$ ($[M + H]^+$), 245.0538, found, 245.0541.

***N*-(4-Cyano-2-(trifluoromethoxy)phenyl)acetamide (3j)**

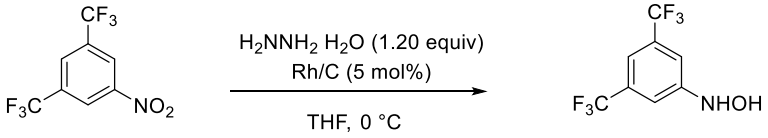


2j **3j**

A solution of *N*-(4-cyanophenyl)-*N*-(trifluoromethoxy)acetamide (**2j**) (97.7 mg, 0.400 mmol) in $MeNO_2$ (0.400 mL, 1.00 M) was heated at 120 °C under N_2 atmosphere for 48 h. The reaction mixture was purified by preparative TLC using hexanes:EtOAc (7:3 (v/v)) for development. The purification afforded 61.4 mg of the title compound as a white crystalline solid (63% yield). 20.0 mg (20%) of the starting material was recovered.

Data for **3j:** R_f = 0.64 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.66 (d, *J* = 8.6 Hz, 1H), 7.61 (br. s, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.54 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.6, 137.1, 135.0, 132.0, 123.7, 121.8, 120.5 (q, *J* = 260.2 Hz), 117.6, 107.2, 25.2. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –58.4 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_8N_2O_2F_3$ ($[M + H]^+$), 245.0538, found, 245.0539.

***N*-(3,5-bis(Trifluoromethyl)phenyl)hydroxylamine (S21)**



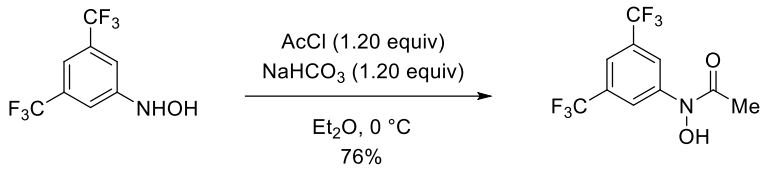
S21

Under N_2 atmosphere, a suspension of 1-nitro-3,5-bis(trifluoromethyl)benzene (1.00 g, 3.86 mmol, 1.00 equiv) and Rh/C (30.00 mg, 0.261 mmol, 5 mol%) in THF (25 mL, 0.154 M) was cooled to 0 °C. Hydrazine monohydrate (0.232 g, 4.63 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 2h. The reaction mixture was filtered through a short pad of celite, the celite was

washed with EtOAc and the combined organic layers were concentrated *in vacuo* to afford 0.940 g of the title compound as a yellow solid (quant yield).

R_f = 0.48 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 9.11 (s, 1H), 8.94 (s, 1H), 7.31 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ): 153.5, 130.7 (q, *J* = 25.7 Hz), 123.5 (q, *J* = 216.9 Hz), 111.8, 111.0 (q, *J* = 3.0 Hz). ^{19}F NMR (376 MHz, $(CD_3)_2SO$, 25 ºC, δ): –63.8 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_8H_6NOF_6$ ([M + H]$^+$), 246.0354, found, 246.0363.

_N_-(3,5-bis(Trifluoromethyl)phenyl)-N-hydroxyacetamide (S22)

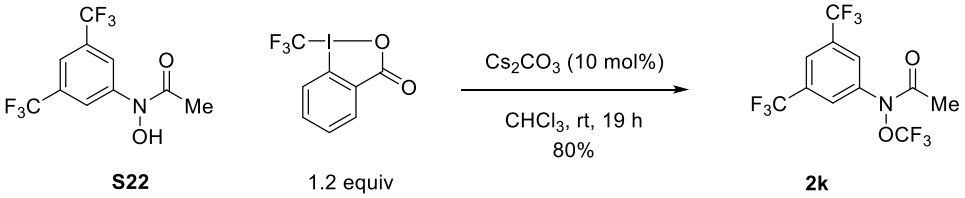


S21 **S22**

To a stirred suspension of methyl N-(3,5-bis(trifluoromethyl)phenyl)hydroxylamine (**S21**) (1.00 g, 4.08 mmol, 1.00 equiv) and $NaHCO_3$ (0.411 g, 4.90 mmol, 1.20 equiv) in Et_2O (20.0 mL, 0.204 M) at 0 °C under N_2 was slowly added a solution of acetyl chloride (0.384 g, 4.09 mmol, 1.20 equiv) in Et_2O (25.0 mL, 0.196 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 3:1 (v/v)), to afford 0.890 g of the title compound as a light white long needle solid (76% yield).

R_f = 0.36 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 11.17 (s, 1H), 8.32 (s, 2H), 7.84 (s, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ): 171.6, 143.0, 130.6 (q, *J* = 26.5 Hz), 123.2 (q, *J* = 217.0 Hz), 118.5, 116.9, 22.7. ^{19}F NMR (376 MHz, $CDCl_3$, (376 MHz, $CDCl_3$, 25 ºC, δ): –63.6 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_8NO_2F_6$ ([M + H]+), 288.0459, found, 288.0457.

_N_-(3,5-bis(Trifluoromethyl)phenyl)-_N_-(trifluoromethoxy)acetamide (2k)



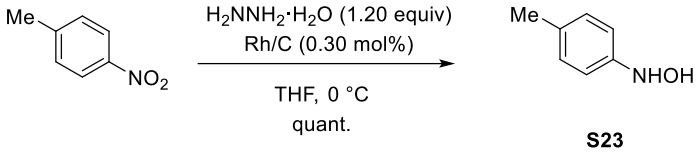
S22 1.2 equiv **2k**

Under N_2 atmosphere, to a mixture of *N*-(3,5-bis(trifluoromethyl)phenyl)-*N*-hydroxyacetamide (**S22**) (459 mg, 1.60 mmol, 1.00 equiv) and Cs_2CO_3 (52.1 mg, 0.160 mmol, 10 mol%) in $CHCl_3$ (16.0 mL, 0.100 M) was added Togni reagent II (607 g, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred

at rt for 19 h. The reaction mixture was then washed with sat. aq. $NaHCO_3$ (30 mL) and the layers were separated. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (19:1 to 9:1 (v/v)), to afford 454 mg of the title compound a slightly yellow oil (80% yield).

R_f = 0.61 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 7.86 (s, 2H), 7.84 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 172.8, 141.4, 132.8 (q, *J* = 34.0 Hz), 123.8 (d, *J* = 3.2 Hz), 122.8 (q, *J* = 270.8 Hz), 122.7 (q, *J* = 265.4 Hz), 121.7 (m), 21.7. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –63.5 (s), –65.1 (s).

_N_-(_p_-Tolyl)hydroxylamine (S23)

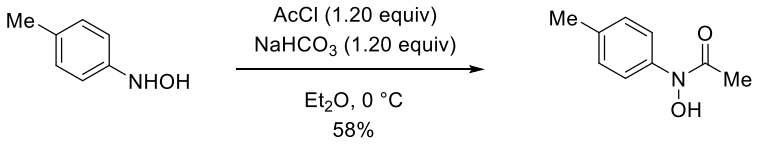


S23

Under N_2 atmosphere, a suspension of 1-methyl-4-nitrobenzene (2.50 g, 18.3 mmol, 1.00 equiv) and Rh/C (104.8 mg, 0.910 mmol, 0.30 mol%) in THF (91.0 mL, 0.200 M) was cooled to 0 °C. Hydrazine monohydrate (1.11 g, 21.9 mmol, 1.20 equiv) was added dropwise. The reaction mixture was stirred at 0 °C for 2.5 h, filtered through a short pad of celite and concentrated *in vacuo* to afford 2.25 g of the title compound as a brown solid (quant yield).

R_f = 0.20 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.20 (d, *J* = 2.3 Hz, 1H), 8.06 (s, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 8.2 Hz, 2H), 2.19 (s, 1H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ): 149.7, 128.8, 127.8, 113.3, 20.2. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_7H_{10}NO$ ($[M + H]^+$), 124.0762, found, 124.0761.

_N_-Hydroxy-_N_-(_p_-tolyl)acetamide (S24)



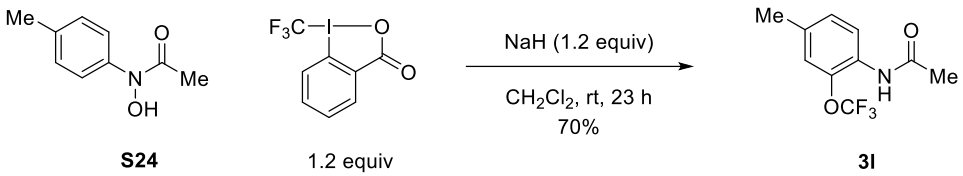
S23 **S24**

To a stirred suspension of *N*-(*p*-tolyl)hydroxylamine (**S23**) (0.200 g, 1.62 mmol, 1.00 equiv) and $NaHCO_3$ (164 mg, 1.95 mmol, 1.20 equiv) in Et_2O (10.0 mL, 0.162 M) at 0 °C under N_2 was slowly added a solution of acetyl chloride (153 mg, 1.95 mmol, 1.20 equiv) in Et_2O (5.00 mL, 0.390 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 2:1 (v/v), to afford 0.156 g of the title compound as a yellow solid (58% yield).

R_f = 0.27 (hexanes/EtOAc 2:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 10.51 (s,

1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 2.28 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, δ): 169.5, 139.3, 133.8, 128.8, 120.3, 22.3, 20.4. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_9H_{12}NO_2$ ($[M + H]^+$), 166.0868, found, 166.0867.

_N_-(4-Methyl-2-(trifluoromethoxy)phenyl)acetamide (3l)

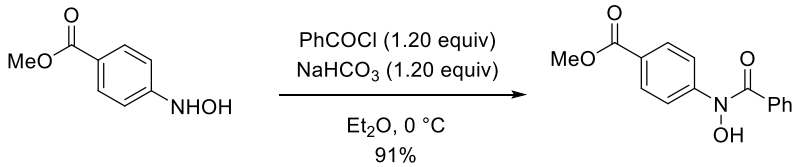


S24 1.2 equiv **3l**

Under N_2 atmosphere, to a mixture of *N*-hydroxy-*N*-(p-tolyl)acetamide (**S24**) (78.2 mg, 0.473 mmol, 1.00 equiv) and NaH (13.6 mg, 0.568 mmol, 1.20 equiv) in CH_2Cl_2 (4.73 mL, 0.100 M) was added Togni reagent II (179 mg, 0.568 mmol, 1.2 equiv) and the reaction mixture was stirred at rt for 23 h. The reaction mixture diluted with CH_2Cl_2 (30 mL) and washed with water (30 mL). The layers were separated, the organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by preparative TLC using hexanes:EtOAc (4:1 (v/v)) for development (prep TLC was developed twice). The purification afforded 76.8 mg of the title compound as a white solid (70% yield).

R_f = 0.42 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.21 (d, *J* = 8.2 Hz, 1H), 7.31 (br. s, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 7.05 (br. s, 1H), 2.33 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.3, 138.2, 134.7, 128.2, 128.0, 122.2, 120.9, 120.7 (q, *J* = 257.4 Hz), 24.8, 21.0. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –58.0 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_{11}NO_2F_3$ ($[M + H]^+$), 234.0742, found, 234.0737.

Methyl 4-(*N*-hydroxybenzamido)benzoate (S25)



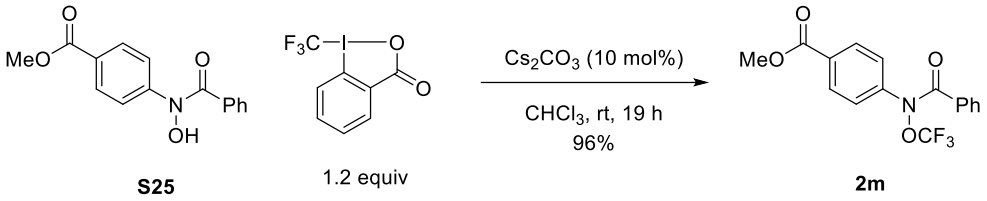
S1 **S25**

To a stirred suspension of methyl 4-(hydroxyamino)benzoate (**S1**) (1.00 g, 5.98 mmol, 1.00 equiv) and $NaHCO_3$ (0.603 g, 7.18 mmol, 1.20 equiv) in Et_2O (30.0 mL, 0.199 M) at 0 °C under N_2 was slowly added a solution of acetyl chloride (1.01 g, 7.18 mmol, 1.20 equiv) in Et_2O (30.0 mL, 0.239 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 (v/v)), to afford 1.47 g of the title compound as a light yellow solid (91% yield).

R_f = 0.20 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ): 10.93 (s, 1H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.52–7.44 (m, 3 H), 3.85

(s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, δ): 168.6, 165.7, 145.9, 135.2, 130.6, 129.8, 128.4, 127.9, 125.5, 120.0, 52.1. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{15}H_{14}NO_4$ ($[M + H]^+$), 272.0923, found, 272.0925.

Methyl 4-(*N*-(trifluoromethoxy)benzamido)benzoate (2m)

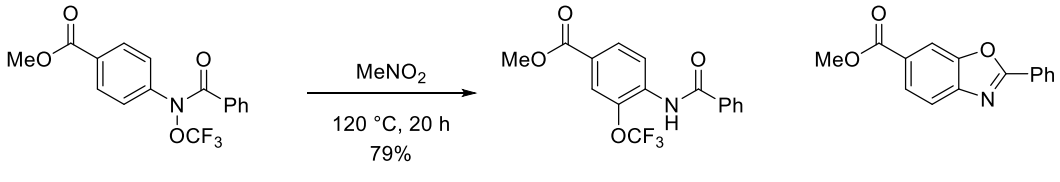


S25 **2m**

Under N_2 atmosphere, to a mixture of methyl 4-(*N*-hydroxybenzamido)benzoate (**S25**) (434 mg, 1.60 mmol, 1.00 equiv) and Cs_2CO_3 (52.1 mg, 0.160 mmol, 10 mol%) in $CHCl_3$ (16.0 mL, 0.100 M) was added Togni reagent II (607 mg, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 19 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:CH_2Cl_2 (1:1 to 0:1 (v/v)), to afford 521 mg of the title compound a slightly yellow oil (96% yield).

R_f = 0.67 (CH_2Cl_2). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.03 (d, *J* = 8.6 Hz, 2H), 7.65–7.61 (m, 2H), 7.47–7.41 (m, 3H), 7.32 (t, *J* = 7.7 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 170.7, 165.9, 145.2, 132.5, 132.1, 131.1, 131.0, 129.2, 128.6, 127.2, 122.8 (q, *J* = 265.8 Hz), 52.6. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –64.4 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{16}H_{13}NO_4F_3$ ($[M + H]^+$), 340.0797, found, 340.0801.

Methyl 4-benzamido-3-(trifluoromethoxy)benzoate (3m)



2m **3m**, 79% **3m'**, 4%

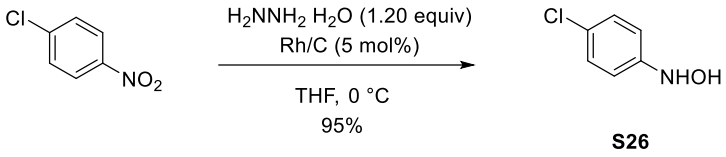
A solution of methyl 4-(*N*-(trifluoromethoxy)benzamido)benzoate (**2m**) (136 mg, 0.400 mmol) in $MeNO_2$ (0.400 mL, 1.00 M) was heated at 120 °C under N_2 atmosphere for 20 h. The reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 7:3 (v/v)), to afford 107 mg of the title compound as a white solid (79% yield). The reaction also afforded methyl methyl 2-phenylbenzo[*d*]oxazole-6-carboxylate (**3m'**) as a white solid (4% yield).

Data for **3m**: R_f = 0.72 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.74 (d, *J* = 8.6 Hz, 1H), 8.37 (br. s, 1H), 8.04 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.98 (s, 1H), 7.90–7.84 (m, 2H), 7.63–7.58 (m, 1H), 7.56–7.51 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ):

165.6, 165.5, 137.7, 135.0, 134.2, 132.8, 129.5, 129.3, 127.2, 126.0, 121.7, 120.8, 120.7 (q, J = 259.1 Hz), 52.5. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –58.1 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{16}H_{13}NO_4F_3$ ($[M + H]^+$), 340.0797, found, 340.0793.

Data for **3m'**: R_f = 0.73 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.36–8.25 (m, 3H), 8.10 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.65– 7.49 (m, 3H), 3.97 (s, 3 H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 166.8, 165.7, 150.6, 146.2, 132.4, 129.2, 128.1, 127.3, 126.8, 126.6, 119.7, 112.4, 52.5. These spectroscopic data correspond to previously reported data.[4]

_N_-(4-Chlorophenyl)hydroxylamine (S26)

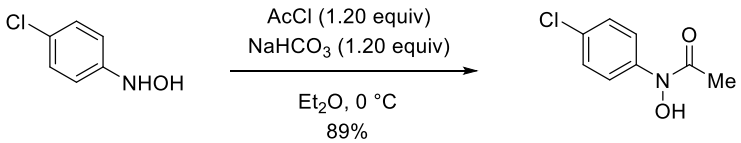


S26

Under N_2 atmosphere, a suspension of 1-chloro-4-nitrobenzene (2.00 g, 12.7 mmol, 1.00 equiv) and Rh/C (72.9 mg, 0.635 mmol, 5 mol%) in THF (40.0 mL, 0.318 M) was cooled to 0 °C. Hydrazine monohydrate (0.762 g, 15.2 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 2.5 h. The reaction mixture was filtered through a short pad of celite and concentrated *in vacuo* to afford 1.72 g of the title compound as a yellow solid (95% yield).

R_f = 0.27 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ): 8.43 (d, J = 2.2 Hz, 1H), 8.40 (s, 1H), 7.19 (d, J = 8.8 Hz, 2H), 6.87–6.83 (m, 2H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, δ): 151.0, 128.3, 122.6, 114.4.

_N_-(4-Chlorophenyl)-_N_-hydroxyacetamide (S27)



S26 **S27**

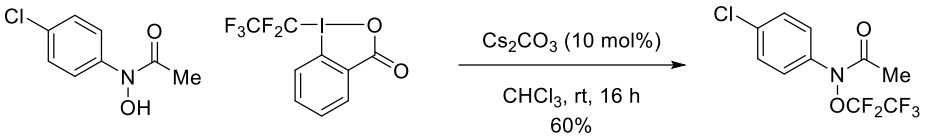
To a stirred suspension of *N*-(4-chlorophenyl)hydroxylamine (**S26**) (1.00 g, 6.97 mmol, 1.00 equiv) and $NaHCO_3$ (0.700 g, 8.36 mmol, 1.20 equiv) in Et_2O (20.0 mL, 0.349 M) at 0 °C under N_2 was slowly added a solution of acetyl chloride (0.660 g, 8.36 mmol, 1.20 equiv) in Et_2O (20.0 mL, 0.418 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated *in vacuo*. Recrystallization from Et_2O/hexanes afforded 1.15 g of the title compound

[4] Ueda, S., Nagasawa, H. *Angew. Chem. Int. Ed*., **2008**, *47*, 6411–6413.

as a yellow solid (89% yield).

R_f = 0.13 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 10.72 (s, 1H), 7.67 (d, *J* = 8.9 Hz, 2H), 7.44–7.38 (m, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ): 170.1, 140.5, 128.3, 128.1, 121.4, 22.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_8H_9NO_2Cl$ ([M + H]$^+$), 186.0322, found, 186.0321.

***N*-(4-Chlorophenyl)-*N*-(perfluoroethoxy)acetamide (6)**

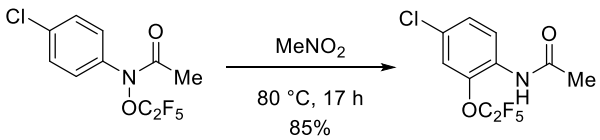


S27 2.0 equiv **6**

Under N_2 atmosphere, to a mixture of *N*-(4-chlorophenyl)-*N*-hydroxyacetamide (**S27**) (177 mg, 0.956 mmol, 1.00 equiv) and Cs_2CO_3 (31.1 mg, 0.0956 mmol, 10 mol%) in $CHCl_3$ (9.56 mL, 0.100 M) was added 1-(perfluoroethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one [5] (700 mg, 1.91 mmol, 2.00 equiv) and the reaction mixture was stirred at rt for 16 h. The reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:CH_2Cl_2 (19:1 to 1:1 (v/v)), to afford the title compound a yellow oil (173 mg, 0.570 mmol, 60% yield).

R_f = 0.51 (hexanes/CH_2Cl_2 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 7.45–7.38 (m, 2H), 7.36–7.28 (m, 2H), 2.25 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 172.8, 139.3, 135.0, 129.7, 127.0, 116.4 (qt, *J* = 283.5, 40.3 Hz), 116.2 (tq, *J* = 276.6, 40.8 Hz), 21.8. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –85.0, –93.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_8ClF_5NO_2$ ([M + H]$^+$), 304.0164, found, 304.0151.

***N*-(4-Chloro-2-(perfluoroethoxy)phenyl)acetamide (8)**



6 **8**

A solution of *N*-(4-chlorophenyl)-*N*-(perfluoroethoxy)acetamide (**6**) (50.0 mg, 0.165 mmol) in $MeNO_2$ (0.165 mL, 1.00 M) was heated at 80 °C under N_2 atmosphere for 17 h. The reaction mixture was purified by preparative TLC using hexanes:EtOAc (9:1 (v/v)) for development (the PLC was developed twice). The purification afforded the title compound as a beige solid (86.2 mg, 0.340 mmol, 85% yield).

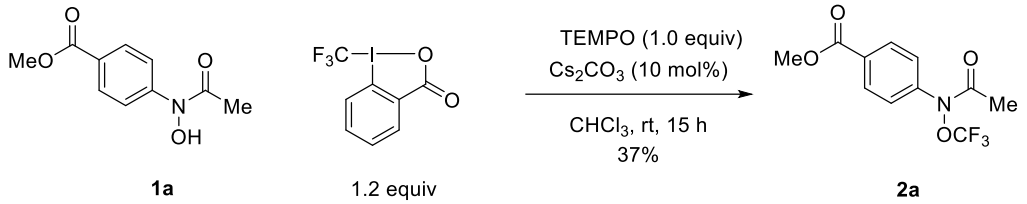
R_f = 0.30 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 8.33 (d,

[5] The reagent was prepared according to the procedure described in Li, Y.; Studer, A. *Angew. Chem. Int. Ed*. **2012**, *51*, (33), 8221-8224.

J = 9.54 Hz, 1H), 7.32–7.26 (m, 2H), 2.18 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 168.2, 137.3, 129.9, 129.1, 128.2, 123.0, 122.0, 116.7 (qt, *J* = 283.2, 43.1 Hz), 114.4 (tq, *J* = 278.3, 43.0 Hz), 24.7. ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC, δ): –86.4, –88.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_8ClF_5NO_2$ ($[M + H]^+$), 304.0164, found, 304.0151.

Mechanistic studies

O-trifluoromethylation in the presence of a radical trap (TEMPO)



1a 1.2 equiv **2a**

Under N_2 atmosphere, to a mixture of methyl 4-(*N*-hydroxyacetamido)benzoate (**1a**) (10.5 mg, 0.0502 mmol, 1.00 equiv), TEMPO (7.8 mg, 0.0500 mmol, 1.00 equiv) and Cs_2CO_3 (1.60 mg, 5.00 µmol, 10 mol%) in $CHCl_3$ (0.500 mL) was added Togni reagent II (19.0 mg, 0.0600 mmol, 1.2 equiv) and the reaction mixture was stirred at rt for 15 h. Trifluorotoluene (6.14 µL, 0.0500 mmol, 1.00 equiv) and $CDCl_3$ (0.250 mL) were added and the reaction mixture was analyzed by ^{19}F NMR. The ^{19}F NMR analysis indicated that the yield of *O*-trifluoromethylation of **1a** in the presence of TEMPO (37%) was much lower than in the absence of the radical trap (97%). In addition, the formation of 2,2,6,6-tetramethyl-1-(trifluoromethoxy)piperidine (80%) resulting from recombination of TEMPO and CF_3· was observed (Figure S1).

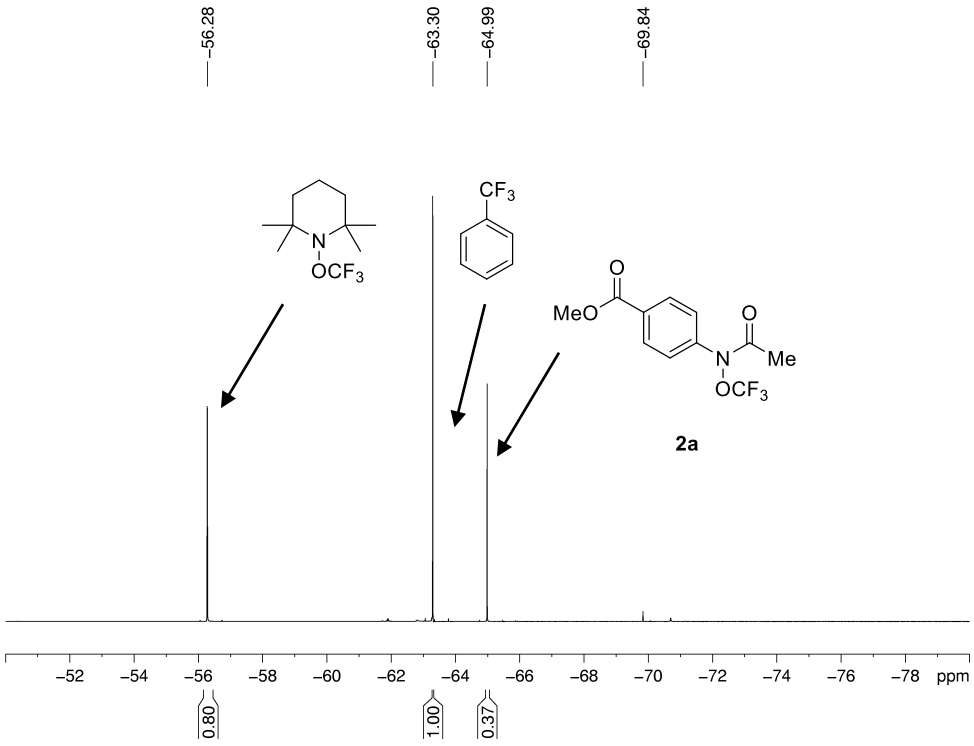
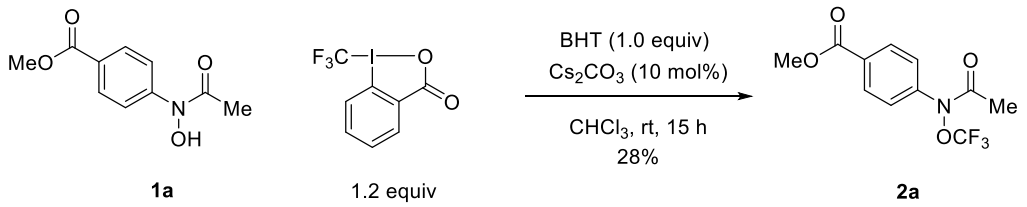


Figure S1. ^{19}F NMR spectrum of the reaction mixture.

***O*-trifluoromethylation in the presence of a radical trap (BHT)**



Under N_2 atmosphere, to a mixture of methyl 4-(*N*-hydroxyacetamido)benzoate (**1a**) (10.5 mg, 0.0502 mmol, 1.00 equiv), BHT (11.0 mg, 0.0500 mmol, 1.00 equiv) and Cs_2CO_3 (1.60 mg, 5.00 μmol, 10 mol%) in $CHCl_3$ (0.500 mL) was added Togni reagent II (19.0 mg, 0.0600 mmol, 1.2 equiv) and the reaction mixture was stirred at rt for 15 h. Trifluorotoluene (6.14 μL, 0.0500 mmol, 1.00 equiv) and $CDCl_3$ (0.250 mL) were added and the reaction mixture was analyzed by ^{19}F NMR. The ^{19}F NMR analysis indicated that the yield of *O*-trifluoromethylation of **1a** in the presence of BHT (28%) was much lower than in the absence of the radical trap (97%). In addition, the formation of 2,6-di-*tert*-butyl-4-(2,2,2-trifluoroethyl)phenol (56%) resulting from benzylic trifluoromethylation of BHT was observed. (Figure S2).

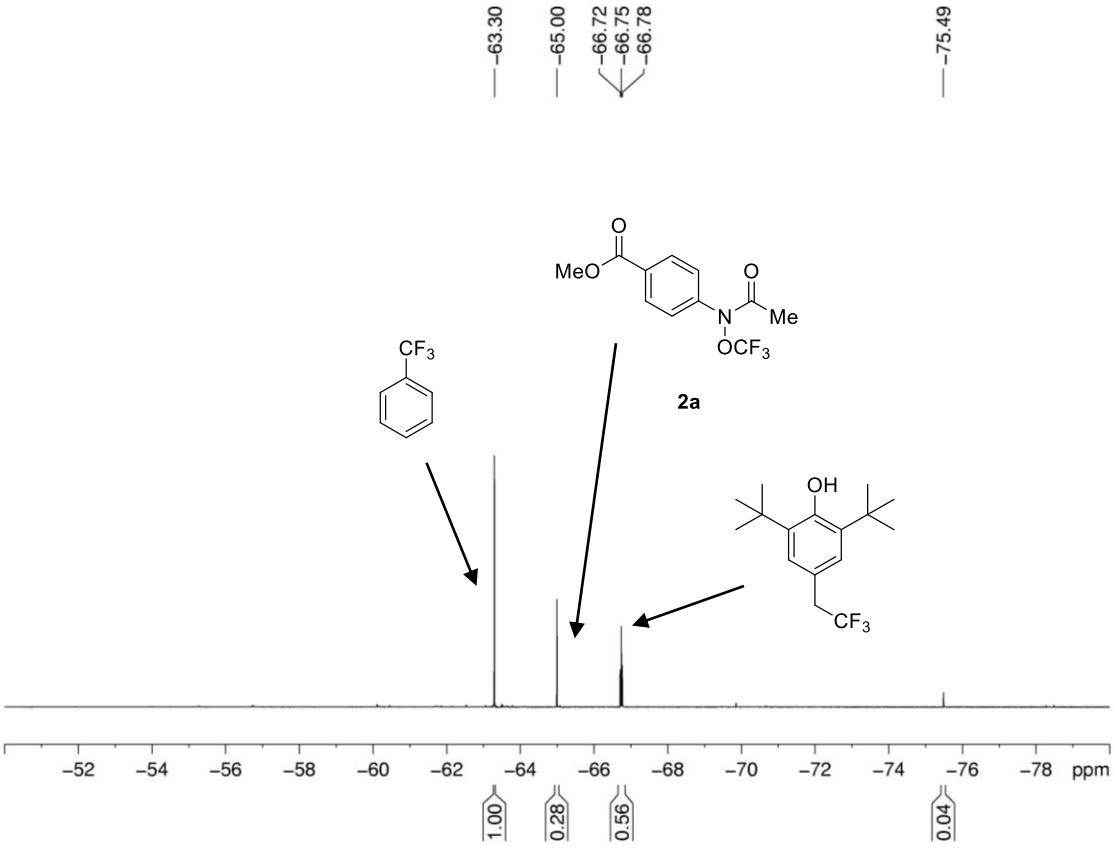
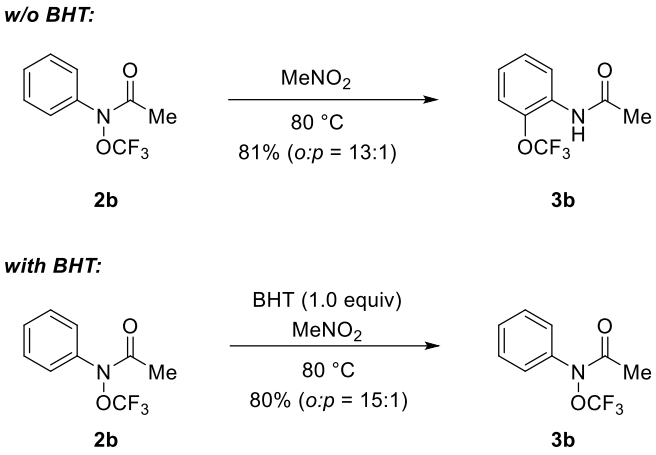


Figure S2. ^{19}F NMR spectrum of the reaction mixture.

O-CF_3 migration in the presence of a radical trap



Reaction without BHT: Under N_2 atmosphere, a solution of *N*-phenyl-*N*-(trifluoromethoxy)acetamide (11.0 mg, 50.2 μmol) (**2b**) in $MeNO_2$ (50.0 μL, 1.00 M) was heated at 80 °C for 12 h. Trifluorotoluene (6.14 μL, 50.0 μmol, 1.00 equiv) and $CDCl_3$ (0.350 mL) were added and the reaction mixture was analyzed by ^{19}F NMR (Figure S3).

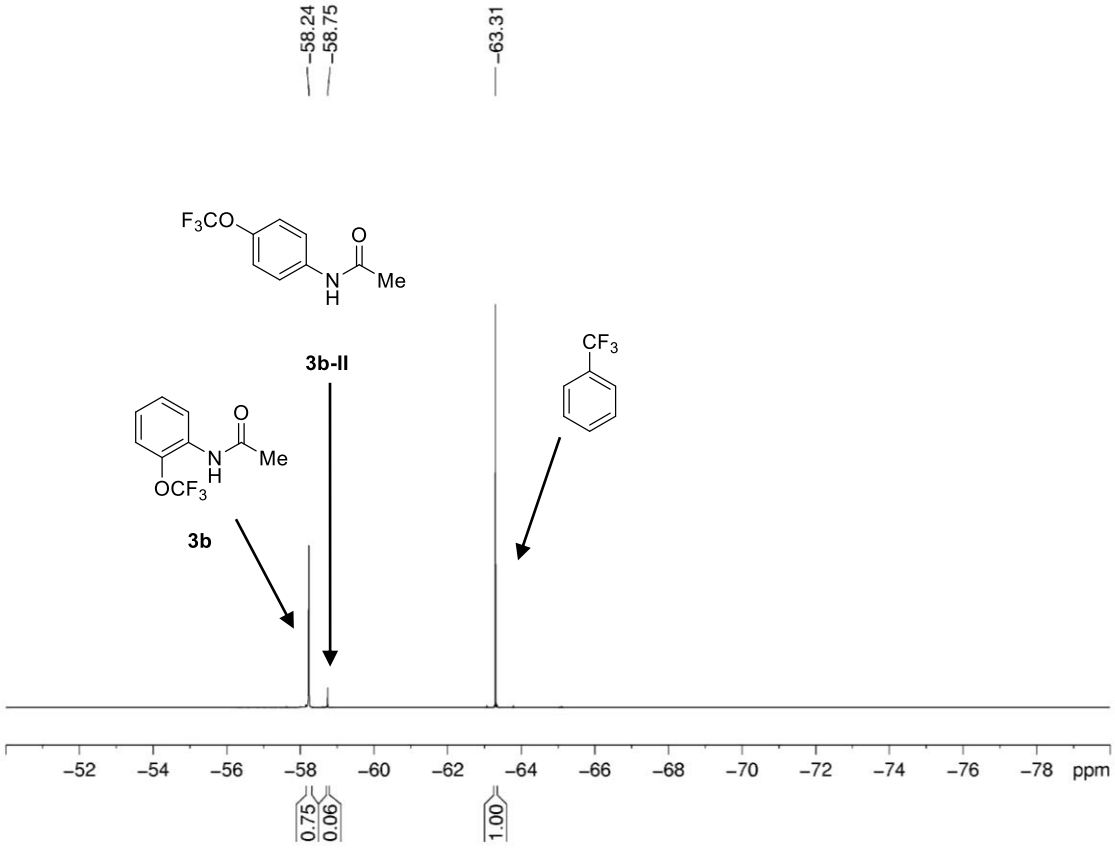


Figure S3. ^{19}F NMR spectrum of the reaction mixture w/o BHT.

Reaction with BHT: Under N_2 atmosphere, a solution of *N*-phenyl-*N*-(trifluoromethoxy)acetamide (**2b**) (11.0 mg, 50.2 μmol, 1.00 equiv) and BHT (11.0 mg, 50.0 μmol, 1.00 equiv) in $MeNO_2$ (50.0 μL, 1.00 M) was heated at 80 °C for 12 h. Trifluorotoluene (6.14 μL, 50.0 μmol, 1.00 equiv) and $CDCl_3$ (0.350 mL) were added and the reaction mixture was analyzed by ^{19}F NMR (Figure S4).

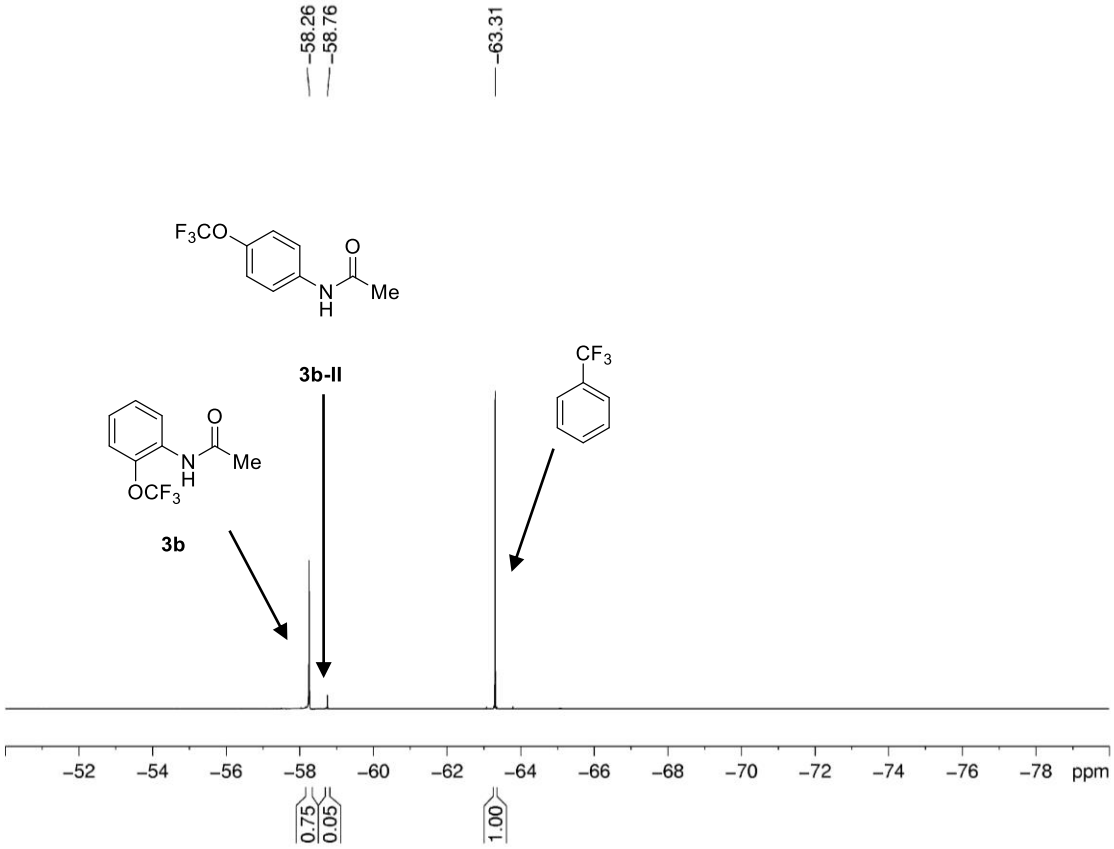
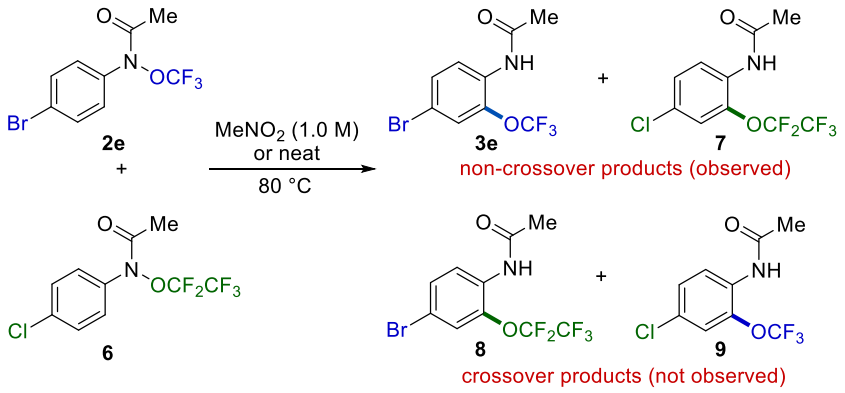


Figure S4. ^{19}F NMR spectrum of the reaction mixture with BHT.

Crossover experiments



A mixture of *N*-(4-chlorophenyl)-*N*-(perfluoroethoxy)acetamide (**6**) (7.6 mg, 0.025 mmol, 1.0 equiv) and *N*-(4-bromophenyl)-*N*-(trifluoromethoxy)acetamide (**2e**) (7.5 mg, 0.025 mmol, 1.0 equiv) was heated at 80 °C for 6h (i) in $MeNO_2$ (25 µL); (ii) neat. Trifluorotoluene (3.1 µL, 0.025 mmol, 1.0 equiv) and $CDCl_3$ (0.400 mL) were added and the reaction mixture was analyzed by ^{19}F NMR and GCMS. No crossover products were observed (Figure S5 and S6).

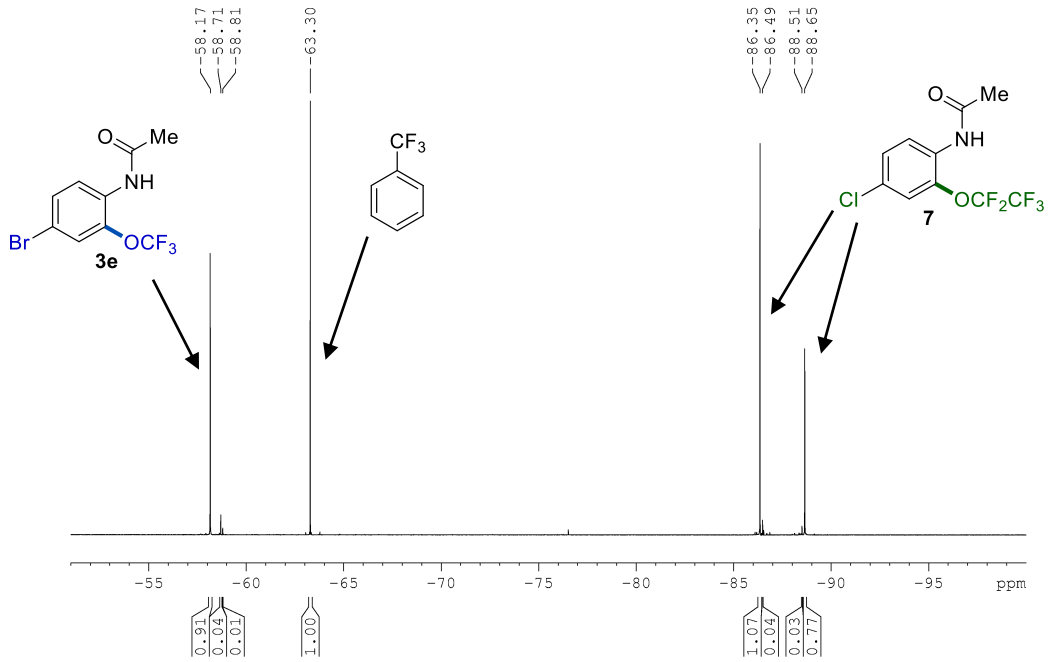


Figure S5. ^{19}F NMR spectrum of the crossover experiment (i) in $MeNO_2$.

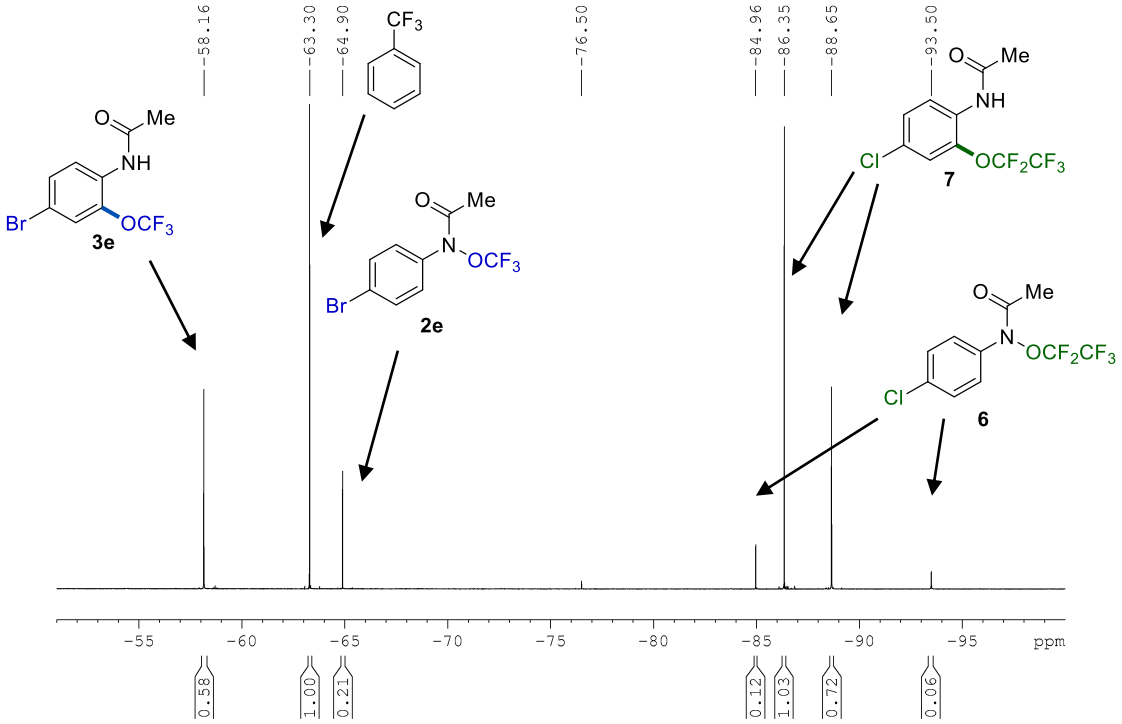


Figure S6. ^{19}F NMR spectrum of the crossover experiment (ii) neat.

Decomposition of trifluoromethoxide

While running the rearrangement reactions, in certain cases we observed that trifluoromethoxide was underwent decomposition as evidenced by detection of fluorophosgene and BF_4^- by ^{19}F NMR (Figure S7).

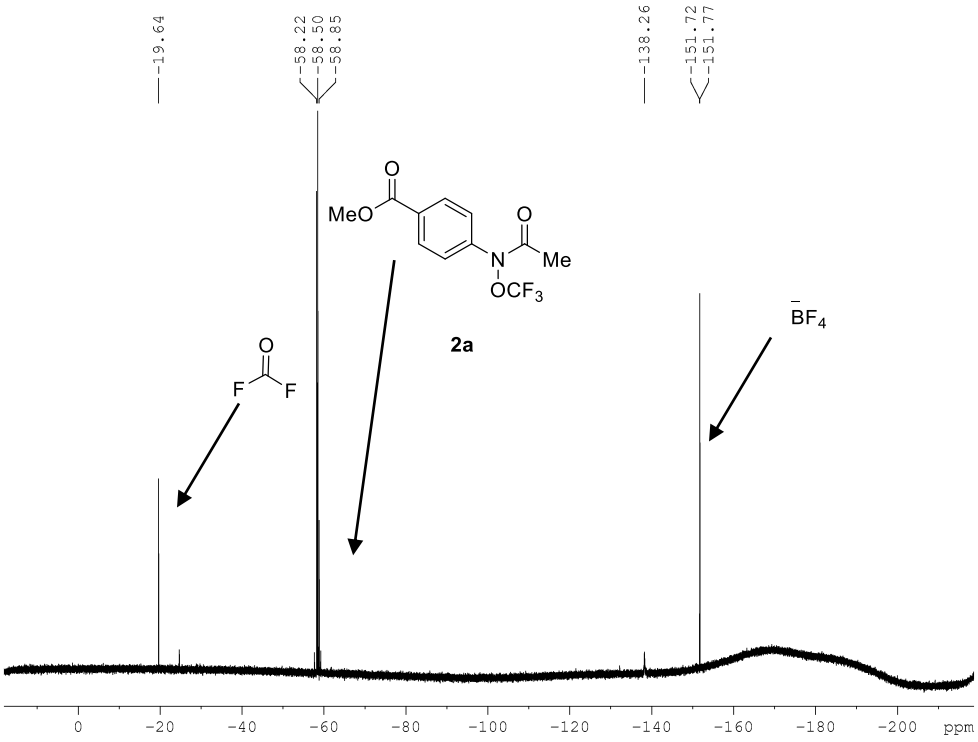
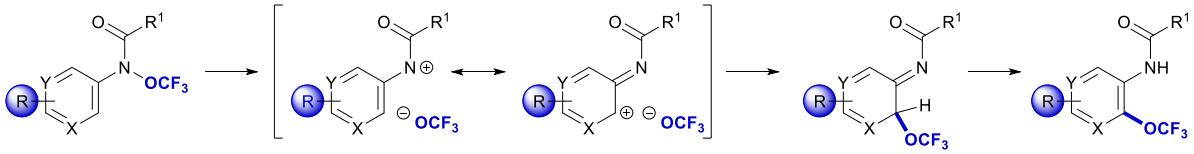


Figure S7. ^{19}F NMR spectrum of the rearrangement reaction showing the decomposition of trifluoromethoxide.

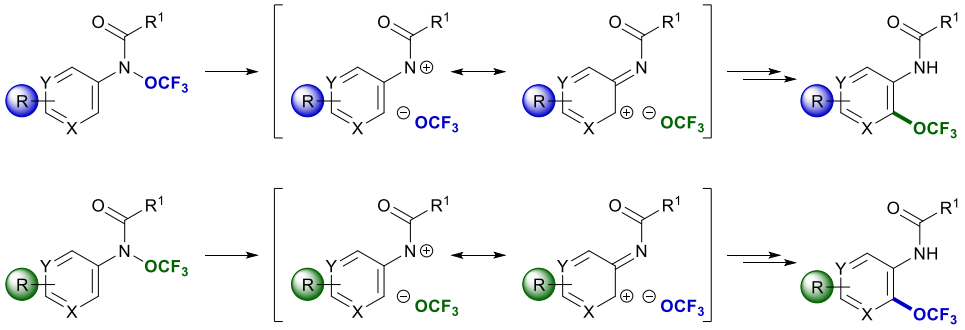
Possible mechanisms for the OCF_3-migration reaction

a. Intramolecular mechanism: tight ion pair



b. Intermolecular mechanisms

i. Counterion swap: nitrenium ions exchange OCF_3 anions (expect formation of crossover products)



ii. Trifluoromethoxide attack on *O*-trifluoromethylated *N*-hydroxylamine derivative (expect formation of crossover products)

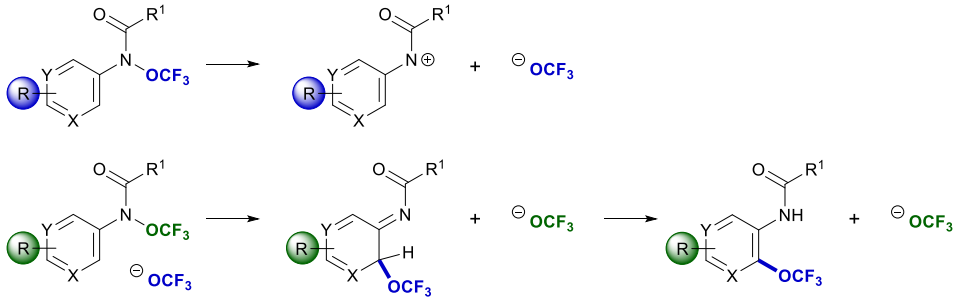


Figure S8. Possible OCF_3-migration mechanisms.

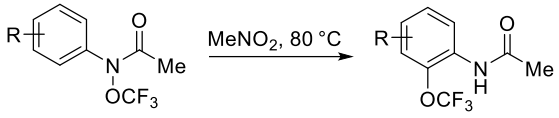
Kinetic Experiments

Sample Preparation

All samples were prepared inside a glovebox under nitrogen atmosphere. *N*-Aryl-*N*-(trifluoromethoxy)-acetamides were weighed into in a 5 mm thin wall precision screw-cap NMR tube (purchased from Wilmad-labglass) and dissolved in degassed anhydrous nitromethane (0.7 mL, at 0.01 – 0.1 M). $PhCF_3$ (4 μL) was used as internal standard which was added into NMR tubes with a 10 μL micro-syringe outside of glovebox. $PhCF_3$ (4 μL) in deuterium $MeNO_2$-d_3 (0.7 mL) was prepared for pre-shimming the ^{19}F probe.

General methods for data acquisition

All kinetic experiments (^{19}F NMR) were performed on a Bruker 400 Nanobay spectrometer (400 MHz without proton decoupling). The ^{19}F probe was pre-shimmed with the standard sample prior to data acquisition. Raw data from the spectra were processed using TopSpin 3.1 and plots for kinetic were generated and analyzed with SigmaPlot 12.0. All kinetic experiments were performed in triplicate.



Method A (substrates with fast-kinetic)

The sample was inserted into the pre-shimmed NMR spectrometer at 25 °C and the signal collected was named as the initial concentration. Then, the NMR spectrometer was warmed up to 80 °C, tuned and shimmed with the standard sample at 80 °C. The sample was inserted into the spectrometer and at the same time a digital stopwatch was used to record the time. Data was acquired right after the sample was inserted into the NMR spectrometer, each data point was collected manually with an interval time between 15 s up to 5 minutes and the reaction was monitored for at least three half-lives.

The data were fitted with the equation:

(1) $\ln [S] = \text{constant} - kt$, whereas the [S] is the concentration of the substrates at different time, k is the rate constant, t is the time.

Method B (substrates with slow-kinetic)

The sample was inserted into the pre-shimmed NMR spectrometer at 25 °C and the signal collected was named as the initial concentration. Then, the sample was heated in an oil bath at 80 °C. Every 0.5-3 hours, the reaction was cooled in an ice-bath and ^{19}F NMR data was acquired. This procedure was repeated for at least 6 times until 10-15 % of the substrate was converted.

The data were fitted with the equation:

(2) $[P] = k[S]_o t$, whereas the [P] is the concentration of products, $[S]_o$ is the concentration of the

substrate before the reaction begins, k is the rate constant, t is time.

Substrates and Data collected with Method A

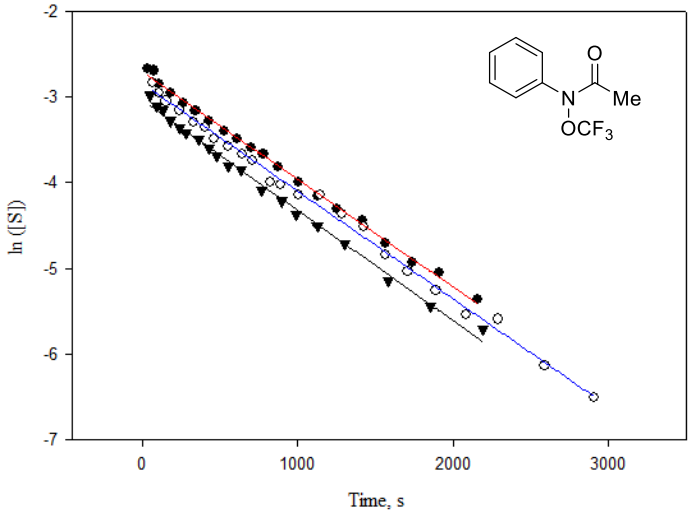
***N*-Phenyl-*N*-(trifluoromethoxy)acetamide (2b)**

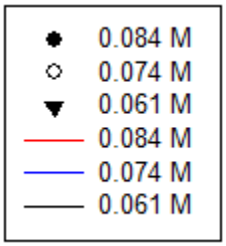
Trial	Concentration mole/L	k s^{-1}
1	0.084	0.0013
2	0.074	0.0013
3	0.061	0.0013
average		0.0013

Trial 1: ln[S] = -2.7065 – 0.0013 t
R^2 = 0.9969

Trial 2: ln[S] = -2.8432 – 0.0013 t
R^2 = 0.9955

Trial 3: ln[S] = -3.0350 – 0.0013 t
R^2 = 0.9947





Trial 1, 0.084 M				Trial 2, 0.074 M				Trial 3, 0.061 M			
Time,s	Integrals	[S], mol/L	Ln [S]	Time,s	Integrals	[S], mol/L	Ln [S]	Time,s	Integrals	[S], mol/L	Ln [S]
0	1.8036	0.0839962	-2.47698	0	1.5851	0.0735939	-2.60919	0	1.3109	0.06105049	-2.79605
16.2	1.5565	0.0724884	-2.62433	36.27	1.3535	0.0628411	-2.76715	15.7	1.191	0.05546657	-2.89197
32.8	1.4856	0.0691865	-2.67095	65.39	1.2738	0.0591407	-2.82784	49.7	1.0929	0.05089791	-2.97793
72.3	1.4573	0.0678685	-2.69018	110.87	1.1314	0.0525293	-2.94638	94.1	0.9631	0.04485294	-3.10437
108.5	1.2416	0.0578231	-2.85037	153.17	1.0209	0.0473989	-3.04916	132.5	0.9156	0.0426408	-3.15494
185.3	1.1177	0.0520529	-2.9555	241.01	0.9194	0.0426864	-3.15387	180	0.8124	0.03783463	-3.27453
267.5	0.9908	0.046143	-3.07601	329.25	0.8029	0.0372775	-3.28937	240	0.746	0.03474229	-3.3598
343.9	0.9098	0.0423707	-3.1613	403.12	0.752	0.0349143	-3.35486	278.3	0.7032	0.03274903	-3.41888
427.6	0.8065	0.0375599	-3.28182	465.11	0.6574	0.0305221	-3.4893	364.5	0.6515	0.03034129	-3.49525
527.3	0.7147	0.0332846	-3.40266	556.14	0.6027	0.0279825	-3.57618	427.9	0.5879	0.02737934	-3.59797
609.9	0.6563	0.0305648	-3.48791	645.93	0.5506	0.0255636	-3.66659	480.5	0.5421	0.02524637	-3.67907
698.2	0.5921	0.0275749	-3.59085	710.36	0.5108	0.0237157	-3.74162	553	0.4781	0.0222658	-3.8047
779.4	0.5479	0.0255165	-3.66843	824.28	0.3965	0.0184089	-3.99492	632.7	0.4596	0.02140423	-3.84417
870.5	0.4724	0.0220003	-3.8167	887.02	0.3868	0.0179586	-4.01969	769.1	0.3625	0.01688214	-4.0815
1008.8	0.3956	0.0184237	-3.99412	1008.58	0.3423	0.0158925	-4.14191	898.5	0.3183	0.01482369	-4.21153
1130.8	0.3344	0.0155735	-4.16219	1147.7	0.3417	0.0158646	-4.14366	991.7	0.2713	0.01263483	-4.3713
1252.1	0.2882	0.0134219	-4.31087	1281.94	0.2747	0.0127539	-4.36192	1125.7	0.2378	0.01107469	-4.50309
1417.5	0.2546	0.0118571	-4.43483	1426.27	0.2365	0.0109804	-4.51165	1302.7	0.1928	0.00897897	-4.71287
1563.8	0.1926	0.0089697	-4.71391	1564.93	0.1691	0.0078511	-4.84711	1580.6	0.1249	0.00581677	-5.14701
1736.6	0.155	0.0072186	-4.9311	1709.13	0.1404	0.0065186	-5.0331	1855.5	0.0924	0.0043032	-5.4484
1911.9	0.1378	0.0064175	-5.04872	1890.46	0.1117	0.0051861	-5.26178	2192.5	0.0714	0.0033252	-5.70623
2157.3	0.1008	0.0046944	-5.36138	2082.8	0.0839	0.0038954	-5.54797				
				2288.81	0.08002	0.0037152	-5.59532				
				2590.01	0.0465	0.0021589	-6.13814				
				2904.08	0.032	0.0014857	-6.51186				

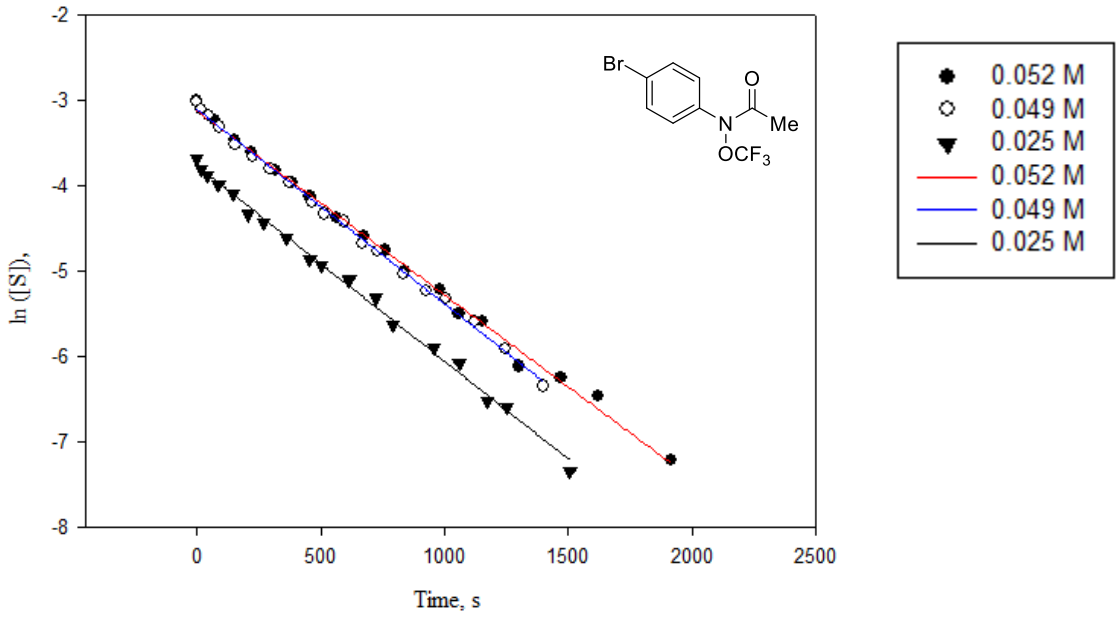
_N_-(4-Bromophenyl)-_N_-(trifluoromethoxy)acetamide (2e)

Trial	Concentration mole/L	k s^{-1}
1	0.052	0.0022
2	0.049	0.0023
3	0.025	0.0023
average		0.00227

Trial 1: ln[S] = -3.1249 – 0.0022 t
R^2 = 0.9962

Trial 2: ln[S] = -3.7676 – 0.0023 t
R^2 = 0.9957

Trial 3: ln[S] = -3.7676 – 0.0023 t
R^2 = 0.9957



Trial 1, 0.051 M				Trial 2, 0.049 M				Trial 3, 0.025 M			
Time,s	Integrals	[S], mol/L	Ln [S]	Time,s	Integrals	[S], mol/L	Ln [S]	Time,s	Integrals	[S], mol/L	Ln [S]
0	1.0633	0.0494863	-3.00606	0	1.0536	0.0490677	-3.01456	0	0.5431	0.02529294	-3.67723
71.96	0.8495	0.039536	-3.23054	15.4	0.9623	0.0448157	-3.1052	16.4	0.478	0.02226114	-3.80491
153.76	0.6711	0.0312332	-3.46627	46.7	0.8886	0.0413834	-3.18488	42.9	0.441	0.020538	-3.88548
219.96	0.5817	0.0270725	-3.60924	90.6	0.7825	0.0364421	-3.31203	87	0.3968	0.01847954	-3.99109
316.35	0.4698	0.0218646	-3.82289	154.6	0.6412	0.0298616	-3.51118	144.6	0.3566	0.01660737	-4.09791
387.18	0.4098	0.0190722	-3.95952	223.2	0.5488	0.0255584	-3.66679	205.6	0.2817	0.01311917	-4.33368
455.16	0.3468	0.0161402	-4.12644	296.2	0.4783	0.0222751	-3.80429	268.8	0.256	0.01192229	-4.42935
562.69	0.271	0.0126124	-4.37307	370.1	0.4067	0.0189406	-3.96645	360.6	0.2134	0.00993834	-4.61135
674.62	0.2179	0.0101411	-4.59116	462.7	0.3248	0.0151264	-4.19131	456	0.1652	0.0076936	-4.86737
760.22	0.1843	0.0085774	-4.75863	514.7	0.2833	0.0131937	-4.32802	503.8	0.1548	0.00720926	-4.93239
838.64	0.1442	0.0067111	-5.00399	592.6	0.2591	0.0120667	-4.41731	615.3	0.1306	0.00608223	-5.10238
980.45	0.1173	0.0054592	-5.21046	668.3	0.2007	0.0093469	-4.67271	724.6	0.1055	0.00491329	-5.31581
1058.62	0.0873	0.004063	-5.50584	728	0.1822	0.0084853	-4.76942	793.1	0.0765	0.00356271	-5.63723
1152.71	0.0805	0.0037465	-5.58694	832.1	0.1392	0.0064827	-5.03861	958.4	0.0593	0.00276169	-5.89191
1302.66	0.0474	0.002206	-6.11657	925.7	0.1153	0.0053697	-5.22699	1059.2	0.0496	0.00230994	-6.07053
1470.46	0.0413	0.0019221	-6.25433	1006.8	0.1046	0.0048714	-5.32438	1174.8	0.0315	0.001467	-6.52454
1621.58	0.0334	0.0015544	-6.46664	1122.7	0.0807	0.0037583	-5.58378	1252.3	0.0295	0.00137386	-6.59013
1915.66	0.0159	0.00074	-7.20887	1244.9	0.0583	0.0027151	-5.90892	1507.4	0.0139	0.00064734	-7.34263
				1399	0.0376	0.0017511	-6.34752				

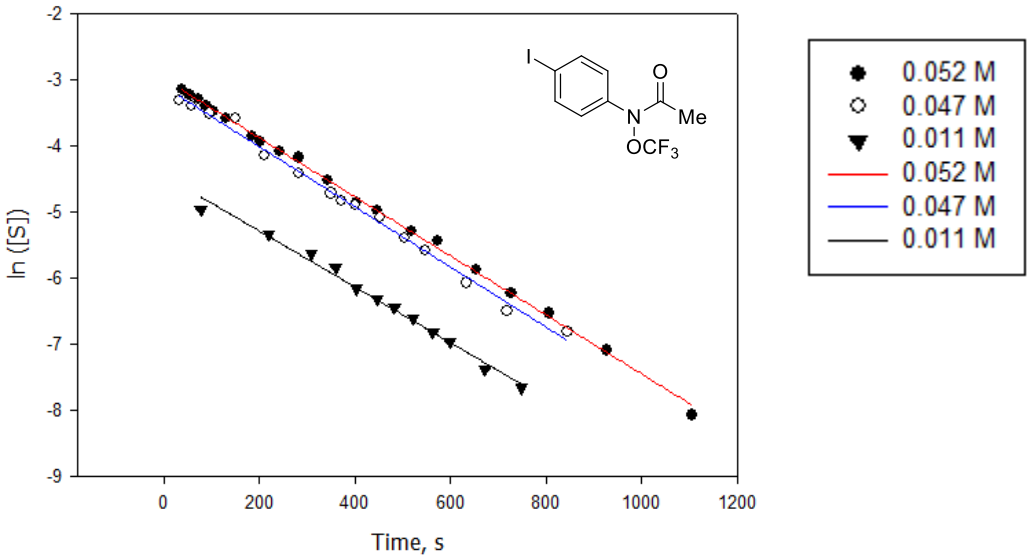
_N_-(4-Iodophenyl)-_N_-(trifluoromethoxy)acetamide (2d)

Trial	Concentration mole/L	k s^{-1}
1	0.052	0.0045
2	0.047	0.0046
3	0.011	0.0042
average		0.0044

Trial 1: ln[S] = -2.9864 – 0.0045 t
R^2 = 0.9986

Trial 2: ln[S] = -3.1016 – 0.0046 t
R^2 = 0.9941

Trial 3: ln[S] = -4.4443 – 0.0042 t
R^2 = 0.9891



Trial 1, 0.052 M				Trial 2, 0.047 M				Trial 3, 0.011 M			
Time,s	Integrals	[S], mol/L	Ln [S]	Time,s	Integrals	[S], mol/L	Ln [S]	Time,s	Integrals	[S], mol/L	Ln [S]
0	1.1102	0.0517036	-2.96223	0	1.0052	0.0468136	-3.06158	0	0.1956	0.00910328	-4.69912
17.3	0.9824	0.0457518	-3.08452	13.3	0.8442	0.0393156	-3.23613	19.16	0.1744	0.00811662	-4.81384
37	0.9243	0.043046	-3.14549	31.4	0.7809	0.0363676	-3.31408	77.3	0.1513	0.00704154	-4.95593
53.9	0.8512	0.0396416	-3.22788	57.7	0.7237	0.0337037	-3.39015	219.36	0.1035	0.00481692	-5.33562
71.8	0.7938	0.0369684	-3.29769	95	0.6421	0.0299035	-3.50978	308.03	0.0769	0.00357895	-5.63269
88.3	0.7262	0.0338202	-3.3867	151.1	0.5943	0.0276774	-3.58714	359.25	0.0624	0.00290411	-5.84163
105.2	0.6651	0.0309747	-3.47459	209.8	0.3425	0.0159507	-4.13825	402.42	0.0453	0.00210827	-6.16189
131	0.5947	0.027696	-3.58647	282.8	0.2611	0.0121598	-4.40962	447.15	0.0384	0.00178715	-6.32713
185.8	0.4535	0.0211201	-3.85753	350	0.1916	0.0089231	-4.71911	482.16	0.0343	0.00159633	-6.44005
202.5	0.4154	0.0193458	-3.94528	372.5	0.1704	0.0079358	-4.83637	520.49	0.0291	0.00135432	-6.60445
241.4	0.3588	0.0167098	-4.09176	400.5	0.16	0.0074514	-4.89935	563.11	0.0234	0.00108904	-6.82246
281.4	0.3295	0.0153453	-4.17695	451.2	0.1333	0.006208	-5.08192	597.77	0.0202	0.00094011	-6.96951
341.7	0.2352	0.0109536	-4.51409	504.2	0.0968	0.0045081	-5.40188	672.32	0.0134	0.00062364	-7.37994
403.6	0.1681	0.0078287	-4.84996	547.3	0.0811	0.0037769	-5.57884	747.69	0.0101	0.00047006	-7.66266
447.3	0.1477	0.0068786	-4.97934	633.3	0.0494	0.0023006	-6.07457				
518	0.1073	0.0049971	-5.29889	718.4	0.0323	0.0015043	-6.49946				
573	0.0934	0.0043498	-5.43763	844.7	0.0235	0.0010944	-6.81752				
653.4	0.0608	0.0028315	-5.86693								
727	0.0426	0.0019839	-6.22267								
806.2	0.0313	0.0014577	-6.53091								
927.2	0.0178	0.000829	-7.09532								
1106.1	0.0067	0.000312	-8.07242								

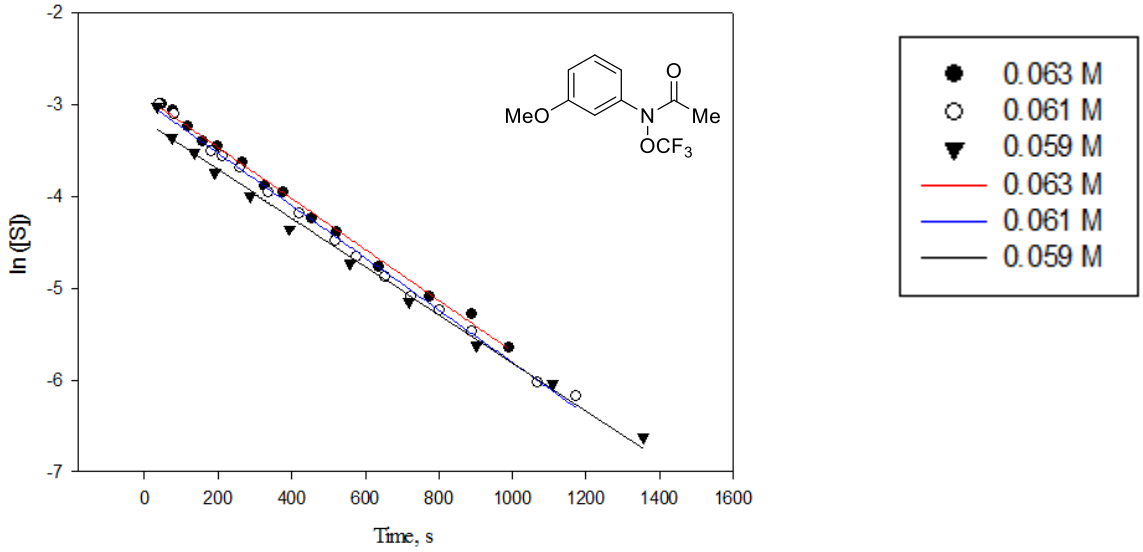
_N_-(3-Methoxyphenyl)-_N_-(trifluoromethoxy)acetamid (2c)

Trial	Concentration mole/L	k s^{-1}
1	0.063	0.0028
2	0.061	0.0028
3	0.059	0.0026
average		0.0027

Trial 1: ln[S] = -2.9146 – 0.0028 t
R^2 = 0.9962

Trial 2: ln[S] = -2.9631 – 0.0028 t
R^2 = 0.9966

Trial 3: ln[S] = -3.1884 – 0.0026 t
R^2 = 0.9912



Trial 1, 0.063 M				Trial 2, 0.061 M				Trial 3, 0.059 M			
Time,s	Integrals	[S], mol/L	Ln [S]	Time,s	Integrals	[S], mol/L	Ln [S]	Time,s	Integrals	[S], mol/L	Ln [S]
0	1.3477	0.0627643	-2.76837	0	1.3056	0.0608037	-2.80011	0	1.2665	0.05894291	-2.83119
13.2	1.2172	0.0566867	-2.87021	14.4	1.1567	0.0538692	-2.9212	25.26	1.156	0.05380024	-2.92248
45.6	1.0793	0.0502645	-2.99046	38.9	1.0667	0.0496777	-3.0022	34.18	1.042	0.04849468	-3.0263
76.4	1.0052	0.0468136	-3.06158	81.7	0.9602	0.0447179	-3.10738	74.56	0.7422	0.03454199	-3.36558
117.6	0.8386	0.0390548	-3.24279	183.3	0.6408	0.029843	-3.51181	135.74	0.6299	0.02931555	-3.52964
159	0.7194	0.0335035	-3.39611	213.7	0.6066	0.0282502	-3.56665	190.93	0.5108	0.02377263	-3.73922
200	0.6811	0.0317198	-3.45081	260.8	0.5341	0.0248738	-3.69394	287.89	0.3941	0.01834141	-3.99859
265.4	0.5674	0.0264246	-3.63346	337.5	0.4107	0.0191269	-3.95666	393.02	0.2752	0.01280781	-4.3577
328.3	0.44	0.0204914	-3.88775	421.7	0.3243	0.0151031	-4.19285	558.15	0.1894	0.00881468	-4.73134
378.6	0.4107	0.0191269	-3.95666	518.4	0.2434	0.0113355	-4.47982	719.92	0.1242	0.00578027	-5.15331
456.3	0.3105	0.0144604	-4.23634	576.3	0.2021	0.0094121	-4.66576	902.86	0.0773	0.00359754	-5.6275
524	0.2656	0.0123694	-4.39253	652.5	0.1631	0.0075958	-4.88016	1110.03	0.0509	0.00236889	-6.04534
638	0.1825	0.0084993	-4.76777	724.5	0.1312	0.0061102	-5.0978	1356.2	0.0284	0.00132174	-6.62881
775.4	0.1324	0.0061661	-5.0887	802	0.1136	0.0052905	-5.24184				
891.6	0.1092	0.0050856	-5.28134	891.1	0.0901	0.0041961	-5.4736				
991.2	0.0759	0.0035348	-5.64511	1068.2	0.0518	0.0024124	-6.02713				
				1174.6	0.0446	0.0020771	-6.17679				

Substrates and Data collected with Method B

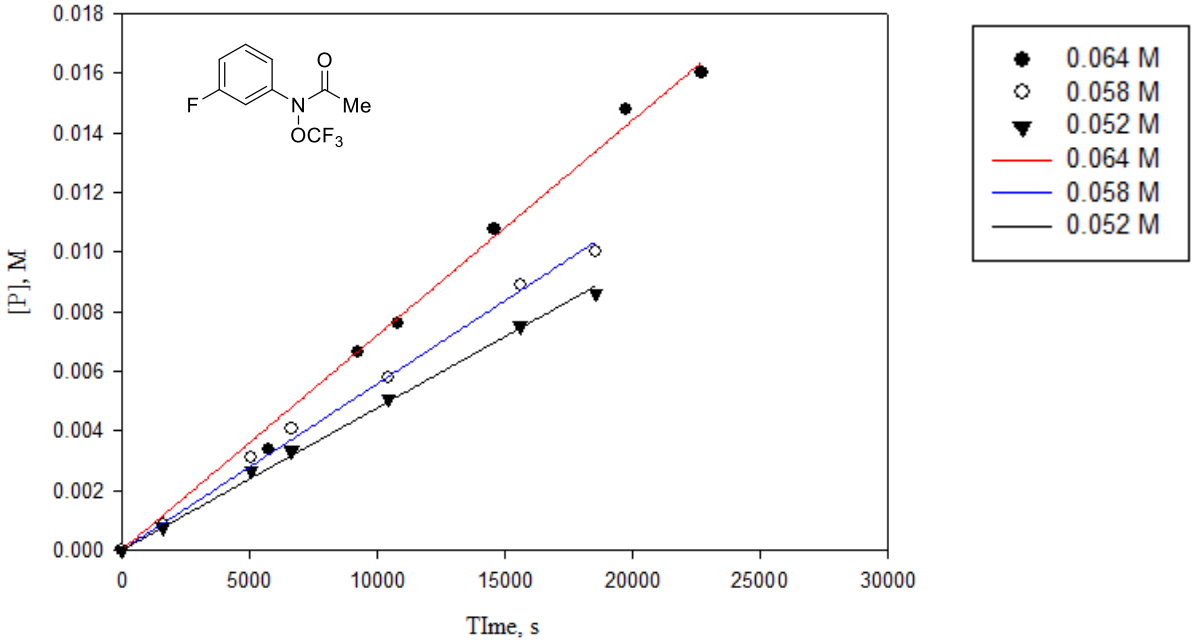
***N*-(3-Fluorophenyl)-*N*-(trifluoromethoxy)acetamide (2f)**

Trial	Concentration mole/L	k[S_o] $mole \cdot L^{-1}s^{-1}$	k s^{-1}
1	0.064	7.2084×10^{-7}	1.13×10^{-5}
2	0.058	5.5806×10^{-7}	9.62×10^{-6}
3	0.052	4.7753×10^{-7}	9.18×10^{-6}
average			9.64×10^{-6}

Trial 1: $[P] = 7.2084 \times 10^{-7} t$, $R^2 = 0.9943$

Trial 2: $[P] = 5.5806 \times 10^{-7} t$, $R^2 = 0.9960$

Trial 3: $[P] = 4.7753 \times 10^{-7} t$, $R^2 = 0.9974$



Trial 1, 0.064 M			Trial 2, 0.058 M			Trial 3, 0.052 M			Trial 4, 0.029 M		
Time, s	Integrals	[P], mol/L	Time, s	Integrals	[P], mol/L	Time, s	Integrals	[P], mol/L	Time, s	Integrals	[P], mol/L
0	0	0	0	0	0	0	0	0	0	0	0
5755.52	0.0722	0.003362	1591.08	0.0187	0.000871	1591.08	0.0164	0.000764	5913	0.031	0.001444
9237.92	0.1428	0.00665	5064.33	0.067	0.00312	5064.33	0.0576	0.002683	9956.26	0.037	0.001723
10819.75	0.1634	0.00761	6646.19	0.087	0.004052	6646.19	0.0715	0.00333	12819.04	0.0462	0.002152
14586.48	0.2316	0.010786	10412.92	0.124	0.005775	10412.92	0.1091	0.005081	15571.47	0.0588	0.002738
19771.26	0.3178	0.0148	15597.7	0.1907	0.008881	15597.7	0.1612	0.007507	19914.97	0.0722	0.003362
22715.86	0.3439	0.016016	18542.3	0.2151	0.010018	18542.3	0.185	0.008616	28506.87	0.0981	0.004569

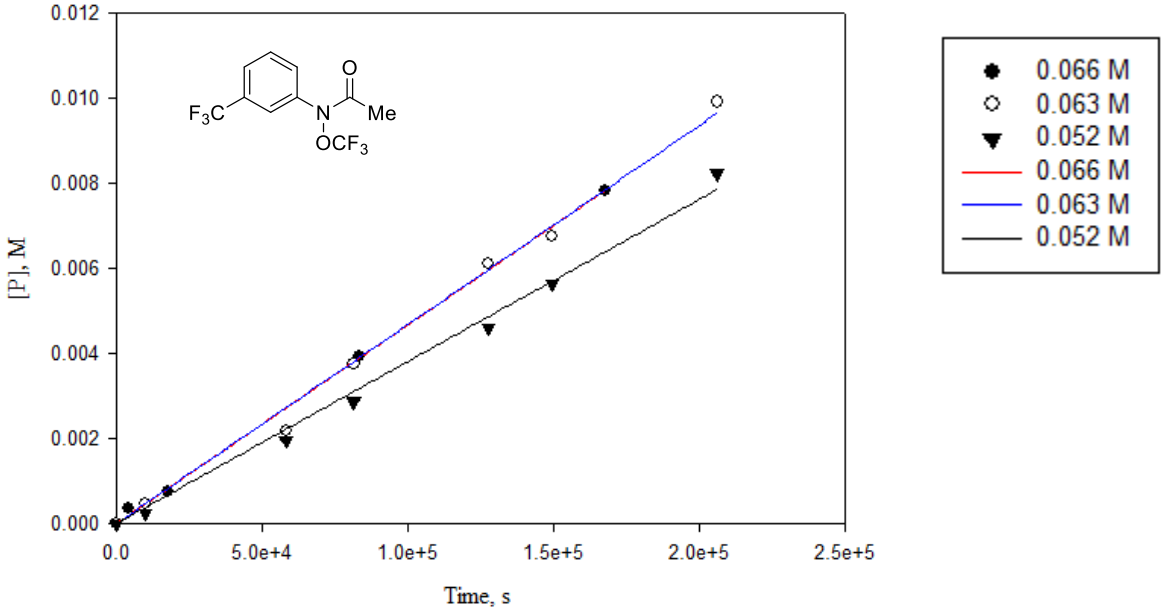
***N*-(Trifluoromethoxy)-*N*-(3-(trifluoromethyl)phenyl)acetamide (2h)**

Trial	Concentration mole/L	k[S_o] mole·$L^{-1}s^{-1}$	k s^{-1}
1	0.066	4.6687×10^{-8}	7.08×10^{-7}
2	0.063	4.6767×10^{-8}	7.41×10^{-7}
3	0.052	3.8088×10^{-8}	7.30×10^{-7}
average			7.26×10^{-7}

Trial 1: $[P] = 4.6687\times10^{-8}\,t$, $R^2 = 0.9991$

Trial 2: $[P] = 4.6767\times10^{-8}\,t$, $R^2 = 0.9942$

Trial 3: $[P] = 3.8088\times10^{-8}\,t$, $R^2 = 0.9934$



Trial 1, 0.066 M			Trial 2, 0.063 M			Trial 3, 0.052 M		
Time, s	Integrals	[P], mol/L	Time, s	Integrals	[P], mol/L	Time, s	Integrals	[P], mol/L
0	0	0	0	0	0	0	0	0
4043.26	0.0078	0.000363	9928.54	0.0101	0.0004704	9928.54	0.0051	0.000238
17625.88	0.016	0.000745	58082.14	0.0468	0.0021795	58082.14	0.0419	0.001951
83294.9	0.0846	0.00394	81401.94	0.0803	0.0037397	81401.94	0.0614	0.002859
167843.4	0.1678	0.007815	127444.6	0.1309	0.0060962	127444.6	0.099	0.004611
			149657.9	0.1448	0.0067435	149657.9	0.1209	0.00563
			206043.3	0.2129	0.0099151	206043.3	0.1766	0.008225

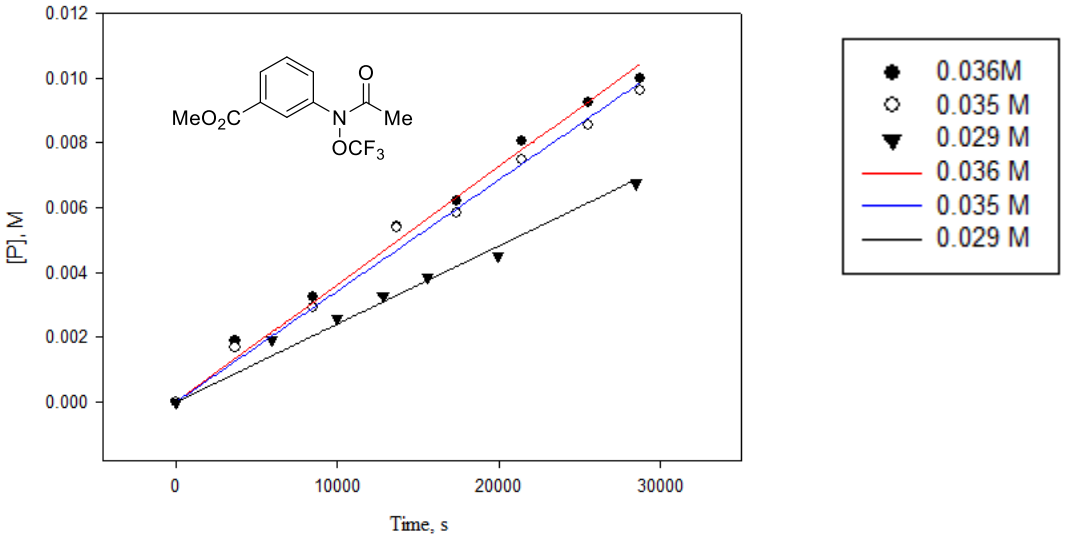
Methyl 3-(*N*-(trifluoromethoxy)acetamido)benzoate (2g)

Trial	Concentration mole/L	k[S_o] $mole \cdot L^{-1}s^{-1}$	k s^{-1}
1	0.036	3.63×10^{-7}	9.33×10^{-6}
2	0.035	3.43×10^{-7}	9.80×10^{-6}
3	0.029	2.41×10^{-7}	8.30×10^{-6}
average			9.1×10^{-6}

Trial 1: $[P] = 3.6334\times10^{-7}\,t$
$R^2 = 0.9902$

Trial 2: $[P] = 3.4299\times10^{-7}\,t$
$R^2 = 0.9898$

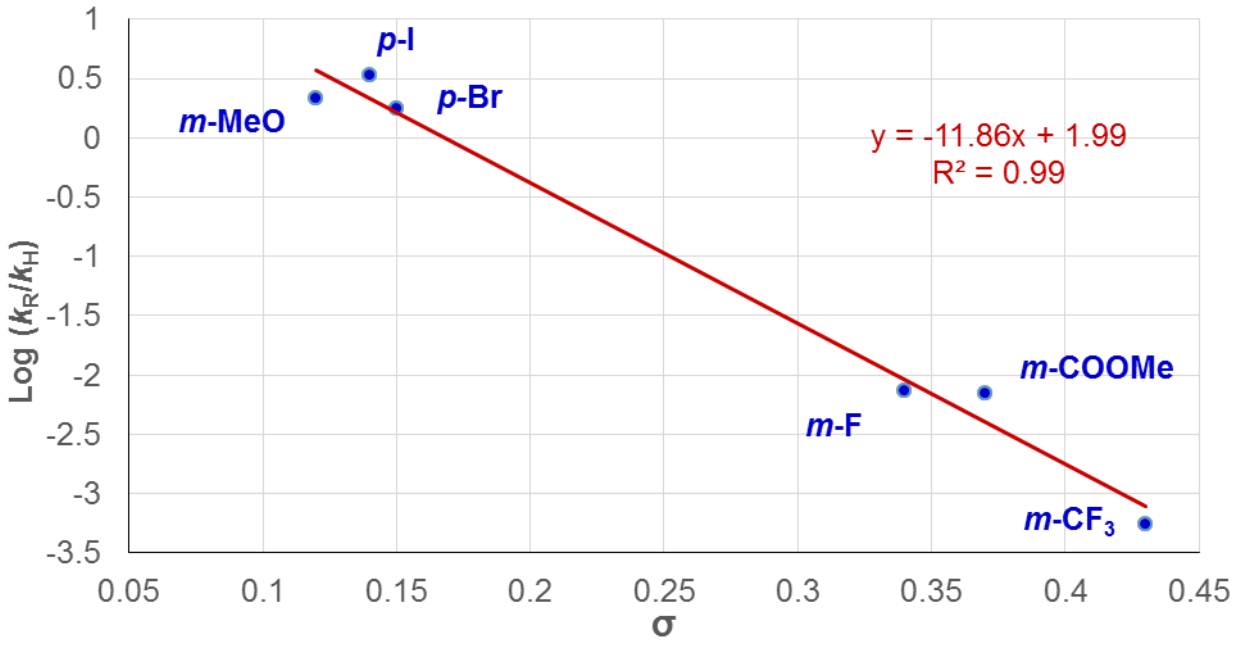
Trial 3: $[P] = 2.4121\times10^{-7}\,t$
$R^2 = 0.9838$



Trial 1, 0.036 M			Trial 2, 0.035 M			Trial 3, 0.029 M		
Time, s	Integrals	[P], mol/L	Time, s	Integrals	[P], mol/L	Time, s	Integrals	[P], mol/L
0	0	0	0	0	0	0	0	0
3668.98	0.0362	0.001686	3668.98	0.0409	0.0019048	5913	0.041	0.001909
8476.46	0.0628	0.002925	8476.46	0.0697	0.003246	9956.26	0.057	0.002655
13657.94	0.1158	0.005393	13657.94	0.1164	0.0054209	12819.04	0.0665	0.003097
17385.47	0.1254	0.00584	17385.47	0.1336	0.0062219	15571.47	0.0778	0.003623
21424.71	0.1609	0.007493	21424.71	0.1733	0.0080708	19914.97	0.0957	0.004457
25524.67	0.1838	0.00856	25524.67	0.1985	0.0092444	28506.87	0.1385	0.00645
28759.45	0.2063	0.009608	28759.45	0.2143	0.0099803			

The Hammett Plot

substituent[6]	log (k_R/k_H)	σ_p^+ or σ_m
m-MeO	0.333214679	0.12
p-I	0.529509324	0.14
p-Br	0.247784484	0.15
m-F	-2.129866318	0.34
m-COOMe	-2.15490196	0.37
m-CF_3	-3.253006732	0.43



[6] Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

Activation Energy of OCF_3 Migration of 2b

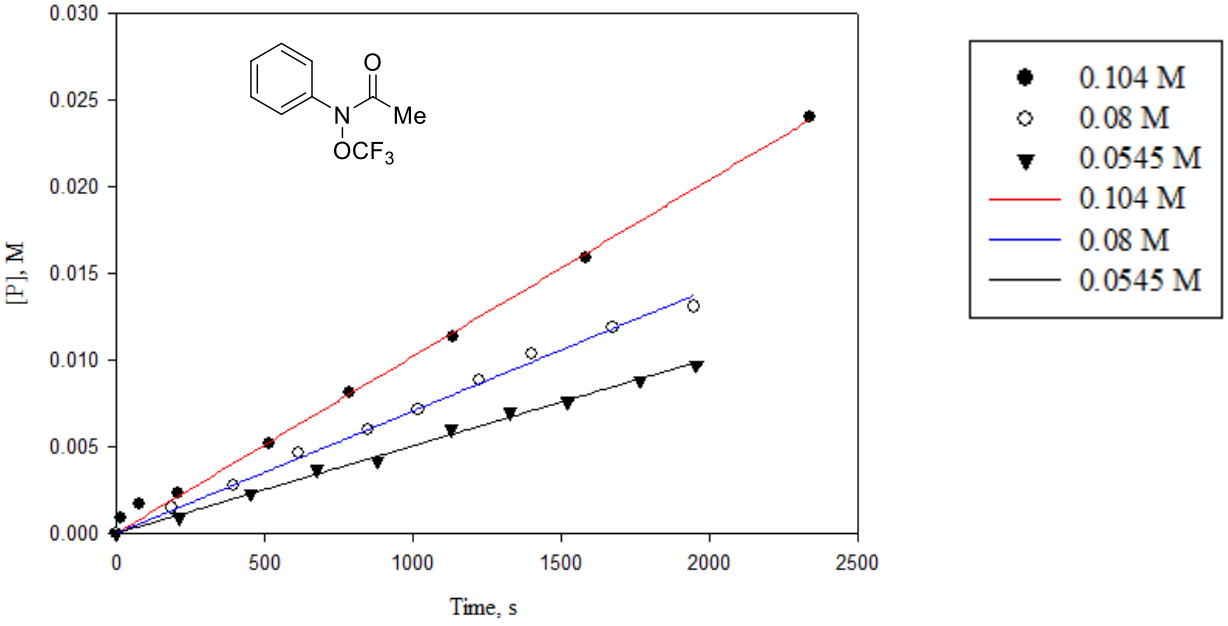
***N*-Phenyl-*N*-(trifluoromethoxy)acetamide (2b) at 60 ˚C**

Trial	Concentration mole/L	$k[S_o]$ $mole \cdot L^{-1}s^{-1}$	k s^{-1}
1	0.104	1.02×10^{-5}	1.08×10^{-4}
2	0.08	7.05×10^{-6}	8.81×10^{-5}
3	0.0545	5.05×10^{-6}	9.27×10^{-5}
average			9.30×10^{-5}

Trial 1: $[P] = 1.02\times10^{-5}\,t$
$R^2 = 0.9971$

Trial 2: $[P] = 7.05\times10^{-6}\,t$
$R^2 = 0.9954$

Trial 3: $[P] = 5.05\times10^{-6}\,t$
$R^2 = 0.9963$



Trial 1, 0.104 M			Trial 2, 0.080 M			Trial 3, 0.0545		
Time, s	Integrals	[P], mol/L	Time, s	Integrals	[P], mol/L	Time, s	Integrals	[P], mol/L
0	0	0	0	0	0	0	0	0
17	0.0185	0.000859	185.7	0.0316	0.0014671	215	0.0197	0.000915
79.5	0.0368	0.001709	394.4	0.0589	0.0027346	453.1	0.0499	0.002317
206.8	0.0501	0.002326	614.8	0.1004	0.0046614	678.5	0.0793	0.003682
515.8	0.1122	0.005209	847.4	0.1295	0.0060125	880.3	0.0895	0.004155
784.6	0.1753	0.008139	1017.4	0.1536	0.0071314	1130.3	0.1291	0.005994
1133.2	0.2443	0.011343	1225.3	0.1909	0.0088632	1328.4	0.1503	0.006978
1583.2	0.3419	0.015874	1402.2	0.223	0.0103536	1523.1	0.1636	0.007596
2336.3	0.5173	0.024018	1674	0.2559	0.0118811	1764.3	0.1901	0.008826
			1946.1	0.2818	0.0130836	1955.6	0.2096	0.009731

The experimental activation energy for the OCF_3-migration process of substrate **2b** was calculated using Arrhenius equation and based on the kinetic data of substrate **2b** at 80 ºC and 60 ºC.

Arrhenius equation:

$$k = A\, e^{-Ea/(RT)}$$

Where k is the rate constant of the reaction, R is the universal gas constant, 1.987 cal K^{-1} mol^{-1}, T is the absolute temperature, A is constant.

$k_1 = 0.0013\ s^{-1}$ at $T_1 = 353$ K

$k_2 = 9.3 \times 10^{-5}\ s^{-1}$ at $T_2 = 333$ K

$E_a = [RT_1T_2/(T_1-T_2)]x[\ln(k_1/k_2)] = 30.8$ kcal/mol

Computational Details

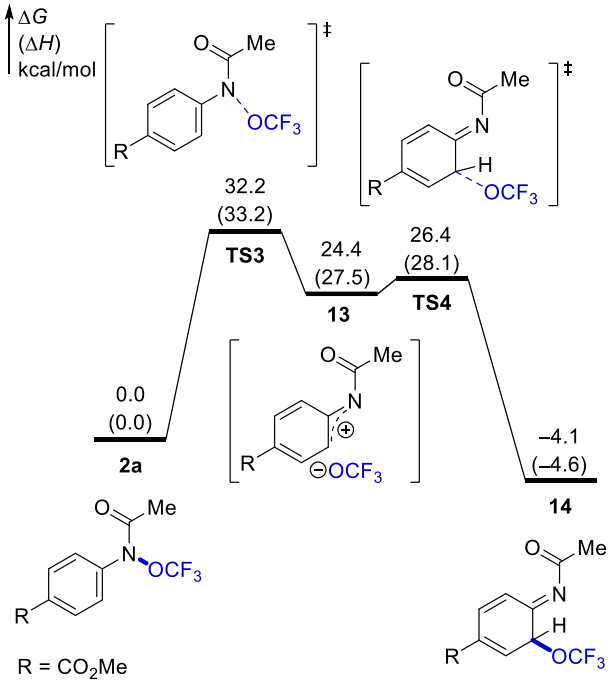
All DFT calculations were performed with the Gaussian 09 software package. Geometries were optimized using the M06-2X functional and the 6-31+G(d) basis set in solution. The SMD solvation model and $MeNO_2$ solvent were used in the calculations. Single point energies were calculated using M06-2X and 6-311++G(d,p) and the SMD solvation model in $MeNO_2$. Reported Gibbs free energies and enthalpies in solution include thermal corrections computed at 298 K.

Complete Reference of Gaussian 09

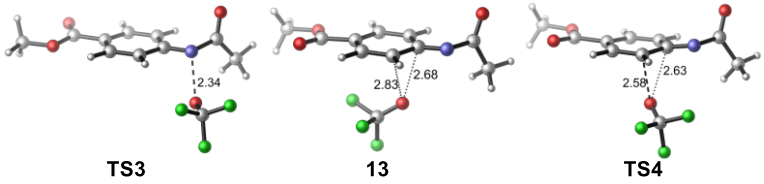
Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Reaction Energy Profile of the OCF_3 Migration of 2a

a. Reaction energy profile of the OCF_3-migration of **2a**

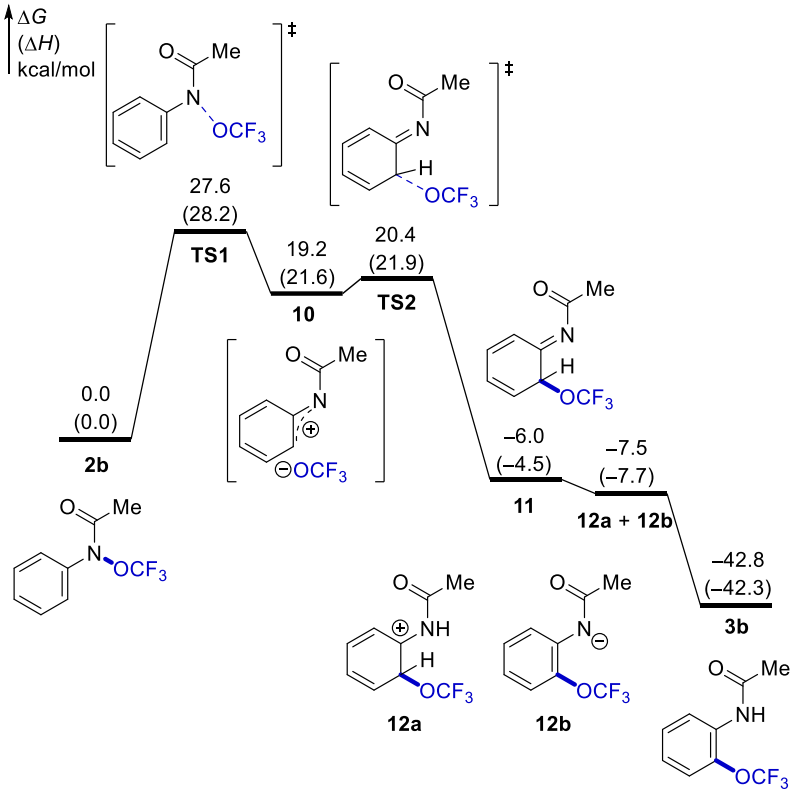


b. Optimized geometries of the ion-pair intermediate **13** and the transition states of N–O cleavage (**TS3**) and C–O formation (**TS4**)

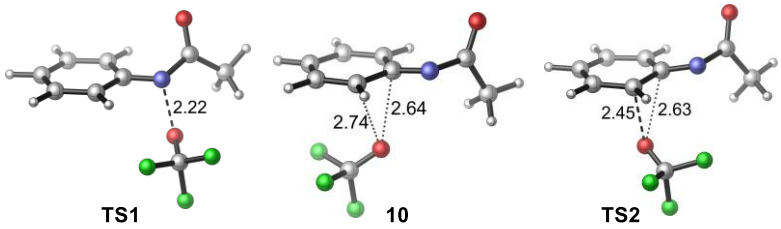


Reaction Energy Profile of the OCF_3 Migration of 2b

a. Reaction energy profile of the OCF_3-migration of **2b**



b. Optimized geometries of the ion-pair intermediate **10** and the transition states of N–O cleavage (**TS1**) and C–O formation (**TS2**)



Potential Energy Surface of OCF_3 Migration of 2b

The concerted OCF_3 migration transition state that directly connects **2b** and the dearomatized intermediate **11** cannot be located in the geometry optimization. To evaluate if such concerted pathway exists and competes with the stepwise process, the potential energy surface of the OCF_3 migration was constructed at the M06-2X/6-31+G(d)/SMD($MeNO_2$) level of theory and is shown in Fig. S9. The stationary points in the stepwise pathway (**2b**, **TS1**, **10**, **TS2**, and **11**) are labeled on the surface. The potential energy surface clearly indicates that the concerted reaction pathway, in which the C-O bond formation and the N-O bond cleavage take place simultaneously, requires a much higher barrier than the stepwise pathway (**TS1** and **TS2**). The stepwise pathway described in Fig. 4 in the main text is thus more favorable than the concerted process.

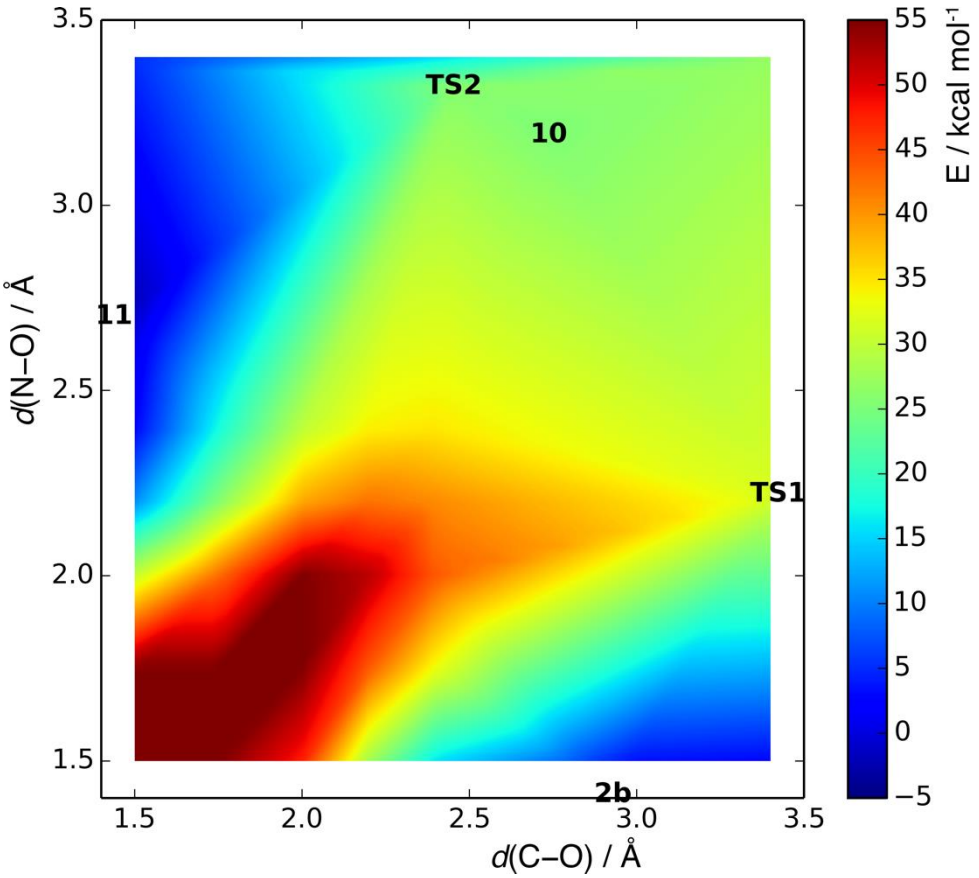


Figure S9. Potential Energy Surface of OCF_3 Migration from **2b** to Form **11**.

Cartesian Coordinates and Energies of Optimized Structures

2b
M06-2X/6-31+G(d) SCF energy: -852.18829646 a.u.
M06-2X/6-31+G(d) enthalpy: -852.009108 a.u.
M06-2X/6-31+G(d) free energy: -852.065810 a.u.
M06-2X/6-311++G(d,p) SCF energy: -852.41585217 a.u.
M06-2X/6-311++G(d,p) enthalpy: -852.236664 a.u.
M06-2X/6-311++G(d,p) free energy: -852.293366 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	3.646896	-0.868537	-0.055226
C	2.972674	-0.713078	1.155733
C	1.654319	-0.257627	1.167219
C	1.036398	0.058465	-0.038797
C	1.701196	-0.086011	-1.257021
C	3.010097	-0.561059	-1.260261
H	4.671127	-1.230156	-0.062009
H	3.467409	-0.954449	2.091971
H	1.105459	-0.142302	2.097959
H	1.195085	0.170087	-2.184427
H	3.536430	-0.681837	-2.202562
N	-0.317482	0.546043	-0.009626
C	-0.651716	1.907299	-0.060949
O	-1.731831	2.269954	-0.477471
C	0.402594	2.826343	0.492107
H	-0.015399	3.832444	0.537010
H	0.716081	2.511314	1.491203
H	1.284932	2.824161	-0.156273
O	-1.185022	-0.244862	-0.785035
C	-1.982919	-0.996113	0.020351
F	-1.285364	-1.878197	0.746058
F	-2.697608	-0.261490	0.872731
F	-2.810491	-1.661468	-0.777053

TS1
M06-2X/6-31+G(d) SCF energy: -852.13763527 a.u.
M06-2X/6-31+G(d) enthalpy: -851.962090 a.u.
M06-2X/6-31+G(d) free energy: -852.019775 a.u.
M06-2X/6-311++G(d,p) SCF energy: -852.36722909 a.u.
M06-2X/6-311++G(d,p) enthalpy: -852.191684 a.u.
M06-2X/6-311++G(d,p) free energy: -852.249369 a.u.
Imaginary frequency: -225.7874 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-3.444921	-1.229497	0.328566

C	-3.131397	-0.082139	1.089244
C	-1.994629	0.628233	0.803742
C	-1.141259	0.188581	-0.272022
C	-1.476823	-0.994288	-1.017966
C	-2.629921	-1.682239	-0.722284
H	-4.348544	-1.783419	0.568946
H	-3.786420	0.222074	1.898304
H	-1.717307	1.502866	1.385227
H	-0.810730	-1.299166	-1.818646
H	-2.909714	-2.566377	-1.284220
N	-0.028519	0.802586	-0.611846
C	0.196386	2.176149	-0.290704
O	-0.641682	2.945256	-0.715538
C	1.468343	2.583154	0.372144
H	1.563647	3.666187	0.280532
H	1.442726	2.291648	1.425434
H	2.317786	2.074099	-0.087685
O	1.337846	-0.125083	0.867953
C	2.027562	-0.944773	0.216953
F	2.899470	-1.704535	0.986380
F	1.314711	-1.909789	-0.490562
F	2.856800	-0.401951	-0.756967

10

M06-2X/6-31+G(d) SCF energy: -852.14798139 a.u.
M06-2X/6-31+G(d) enthalpy: -851.971486 a.u.
M06-2X/6-31+G(d) free energy: -852.032054 a.u.
M06-2X/6-311++G(d,p) SCF energy: -852.37577142 a.u.
M06-2X/6-311++G(d,p) enthalpy: -852.199276 a.u.
M06-2X/6-311++G(d,p) free energy: -852.259844 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.849207	2.392008	0.414323
C	0.846976	2.007452	-0.938146
C	-0.084560	1.098806	-1.357941
C	-1.102835	0.600925	-0.426210
C	-1.019380	0.992958	0.985960
C	-0.068534	1.881251	1.374712
H	1.597455	3.105000	0.751672
H	1.590287	2.406895	-1.618364
H	-0.136326	0.740970	-2.382360
H	-1.736366	0.583565	1.692749
H	0.009789	2.203785	2.406919
N	-2.031879	-0.129614	-0.921551
C	-3.086468	-0.654256	-0.134934
O	-4.106353	-0.017249	0.002453
C	-2.822255	-2.034706	0.383035
H	-3.748422	-2.457995	0.774971

H	-2.412598	-2.669095	-0.408525
H	-2.071936	-1.970654	1.180384
O	0.872239	-1.098867	-0.023196
C	2.095844	-0.961814	0.044631
F	2.566862	0.030699	0.927444
F	2.827669	-2.085896	0.460053
F	2.756159	-0.616134	-1.148966

TS2

M06-2X/6-31+G(d) SCF energy: -852.14696982 a.u.
M06-2X/6-31+G(d) enthalpy: -851.971587 a.u.
M06-2X/6-31+G(d) free energy: -852.030645 a.u.
M06-2X/6-311++G(d,p) SCF energy: -852.37715583 a.u.
M06-2X/6-311++G(d,p) enthalpy: -852.201773 a.u.
M06-2X/6-311++G(d,p) free energy: -852.260831 a.u.
Imaginary frequency: -91.6548 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-0.323001	3.115790	0.261881
C	0.296440	2.539901	-0.843265
C	0.053946	1.208021	-1.106580
C	-0.968482	0.478361	-0.342795
C	-1.510148	1.102814	0.870294
C	-1.191271	2.390873	1.142523
H	-0.127806	4.161204	0.487506
H	0.984887	3.113555	-1.452904
H	0.506939	0.686403	-1.945036
H	-2.186443	0.534563	1.503313
H	-1.597015	2.895979	2.012288
N	-1.369890	-0.631640	-0.839347
C	-2.393326	-1.403642	-0.239699
O	-3.555528	-1.157520	-0.475546
C	-1.877528	-2.554058	0.570082
H	-2.720597	-3.109438	0.984204
H	-1.271134	-3.207392	-0.065736
H	-1.234416	-2.180464	1.374474
O	1.449421	0.252981	0.666837
C	2.176497	-0.629438	0.183205
F	2.938808	-0.258055	-0.934497
F	3.145381	-1.153057	1.042396
F	1.527468	-1.780928	-0.277553

11

M06-2X/6-31+G(d) SCF energy: -852.19432148 a.u.
M06-2X/6-31+G(d) enthalpy: -852.015340 a.u.
M06-2X/6-31+G(d) free energy: -852.074457 a.u.

M06-2X/6-311++G(d,p) SCF energy: -852.42276525 a.u.
M06-2X/6-311++G(d,p) enthalpy: -852.243784 a.u.
M06-2X/6-311++G(d,p) free energy: -852.302901 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.277127	3.164504	0.094759
C	0.744412	2.304385	0.182349
C	0.546848	0.855555	-0.153046
C	-0.890656	0.367678	-0.047676
C	-1.926542	1.378090	-0.296398
C	-1.626113	2.689721	-0.222839
H	-0.126765	4.226341	0.263247
H	1.759844	2.618881	0.408448
H	0.828187	0.729152	-1.211428
H	-2.948432	1.044587	-0.456091
H	-2.410872	3.428894	-0.358462
N	-1.099074	-0.865248	0.200616
C	-2.388909	-1.409566	0.263878
O	-3.040779	-1.376540	1.290753
C	-2.825640	-2.114254	-0.990670
H	-3.814599	-2.552573	-0.848932
H	-2.845611	-1.400709	-1.822247
H	-2.102283	-2.895994	-1.244506
O	1.403831	0.046149	0.669352
C	2.283371	-0.732641	0.035567
F	3.198236	-0.024585	-0.656620
F	2.932627	-1.459294	0.943693
F	1.714889	-1.573850	-0.843822

12a
M06-2X/6-31+G(d) SCF energy: -852.63294428 a.u.
M06-2X/6-31+G(d) enthalpy: -852.440587 a.u.
M06-2X/6-31+G(d) free energy: -852.497443 a.u.
M06-2X/6-311++G(d,p) SCF energy: -852.86314667 a.u.
M06-2X/6-311++G(d,p) enthalpy: -852.670789 a.u.
M06-2X/6-311++G(d,p) free energy: -852.727645 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.128249	3.200069	-0.227776
C	-1.002109	2.181641	-0.297340
C	-0.559150	0.806221	0.071660
C	0.925753	0.551033	0.025809
C	1.783308	1.664371	0.196986
C	1.256091	2.924428	0.067752
H	-0.436513	4.223632	-0.408979
H	-2.058735	2.317488	-0.509816
H	-0.770576	0.732408	1.159940

H	2.845910	1.524020	0.326551
H	1.937924	3.767471	0.142376
N	1.302461	-0.712485	-0.103683
C	2.628332	-1.260018	-0.012249
O	3.568137	-0.559691	0.263562
C	2.663735	-2.728828	-0.282981
H	3.690684	-3.083435	-0.202562
H	2.027335	-3.252531	0.438784
H	2.272565	-2.929840	-1.286196
O	-1.261539	-0.210995	-0.639850
C	-2.238863	-0.861720	0.031866
F	-3.167770	-0.028470	0.510916
F	-2.814786	-1.707002	-0.809319
F	-1.753285	-1.555161	1.070451
H	0.570867	-1.393799	-0.314817

12b

M06-2X/6-31+G(d) SCF energy: -851.76611029 a.u.
M06-2X/6-31+G(d) enthalpy: -851.599994 a.u.
M06-2X/6-31+G(d) free energy: -851.655866 a.u.
M06-2X/6-311++G(d,p) SCF energy: -851.99322525 a.u.
M06-2X/6-311++G(d,p) enthalpy: -851.827109 a.u.
M06-2X/6-311++G(d,p) free energy: -851.882981 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.634780	3.117565	-0.019463
C	-1.326889	1.953884	-0.350914
C	-0.633596	0.759066	-0.475538
C	0.763375	0.629647	-0.304115
C	1.428888	1.834935	0.033537
C	0.747333	3.041166	0.168159
H	-1.163715	4.059915	0.084806
H	-2.400309	1.961347	-0.519382
H	2.500796	1.799814	0.183513
H	1.307777	3.938276	0.420609
N	1.355759	-0.591291	-0.560046
C	2.510326	-0.918448	0.035438
O	3.119297	-0.298175	0.940042
C	3.117855	-2.230928	-0.441087
H	4.127821	-2.043812	-0.823531
H	3.215661	-2.918379	0.406880
H	2.522424	-2.708294	-1.222619
O	-1.367533	-0.381356	-0.872036
C	-1.923031	-1.098033	0.106089
F	-2.927977	-0.445228	0.728386
F	-2.441956	-2.207714	-0.427427
F	-1.064707	-1.463358	1.069414

3b

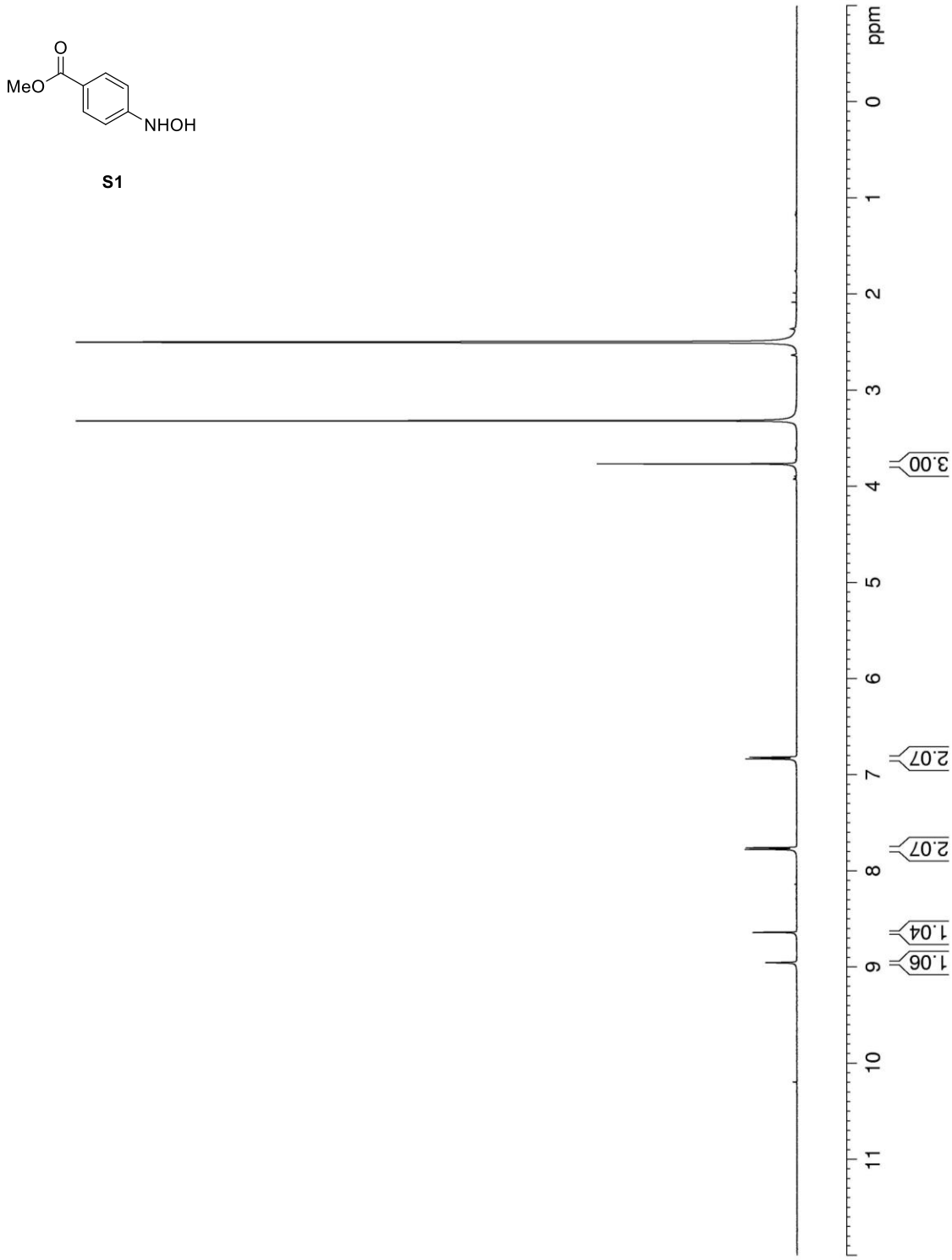
M06-2X/6-31+G(d) SCF energy: -852.25509523 a.u.
M06-2X/6-31+G(d) enthalpy: -852.074635 a.u.
M06-2X/6-31+G(d) free energy: -852.132194 a.u.
M06-2X/6-311++G(d,p) SCF energy: -852.48453400 a.u.
M06-2X/6-311++G(d,p) enthalpy: -852.304074 a.u.
M06-2X/6-311++G(d,p) free energy: -852.361633 a.u.

Cartesian coordinates

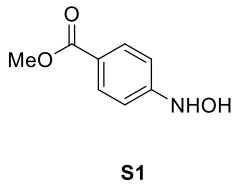
ATOM	X	Y	Z
C	-0.721261	3.104587	0.045951
C	-1.378913	1.925372	0.391698
C	-0.653880	0.747892	0.459427
C	0.727722	0.689781	0.223169
C	1.375497	1.885578	-0.116459
C	0.648489	3.071838	-0.207289
H	-1.275416	4.035601	-0.016893
H	-2.442429	1.908833	0.610296
H	2.439663	1.879278	-0.306372
H	1.172635	3.985574	-0.472028
N	1.364949	-0.548887	0.366987
C	2.634426	-0.892194	-0.022943
O	3.399112	-0.111700	-0.575892
C	3.031888	-2.312903	0.292271
H	3.431447	-2.772958	-0.615247
H	3.832203	-2.289196	1.038865
H	2.206880	-2.917506	0.674622
O	-1.297910	-0.439841	0.854044
C	-1.946501	-1.115059	-0.116433
F	-1.135300	-1.464953	-1.125620
F	-2.448514	-2.222968	0.420838
F	-2.954635	-0.414029	-0.650033
H	0.811998	-1.286890	0.789624

Spectroscopic Data

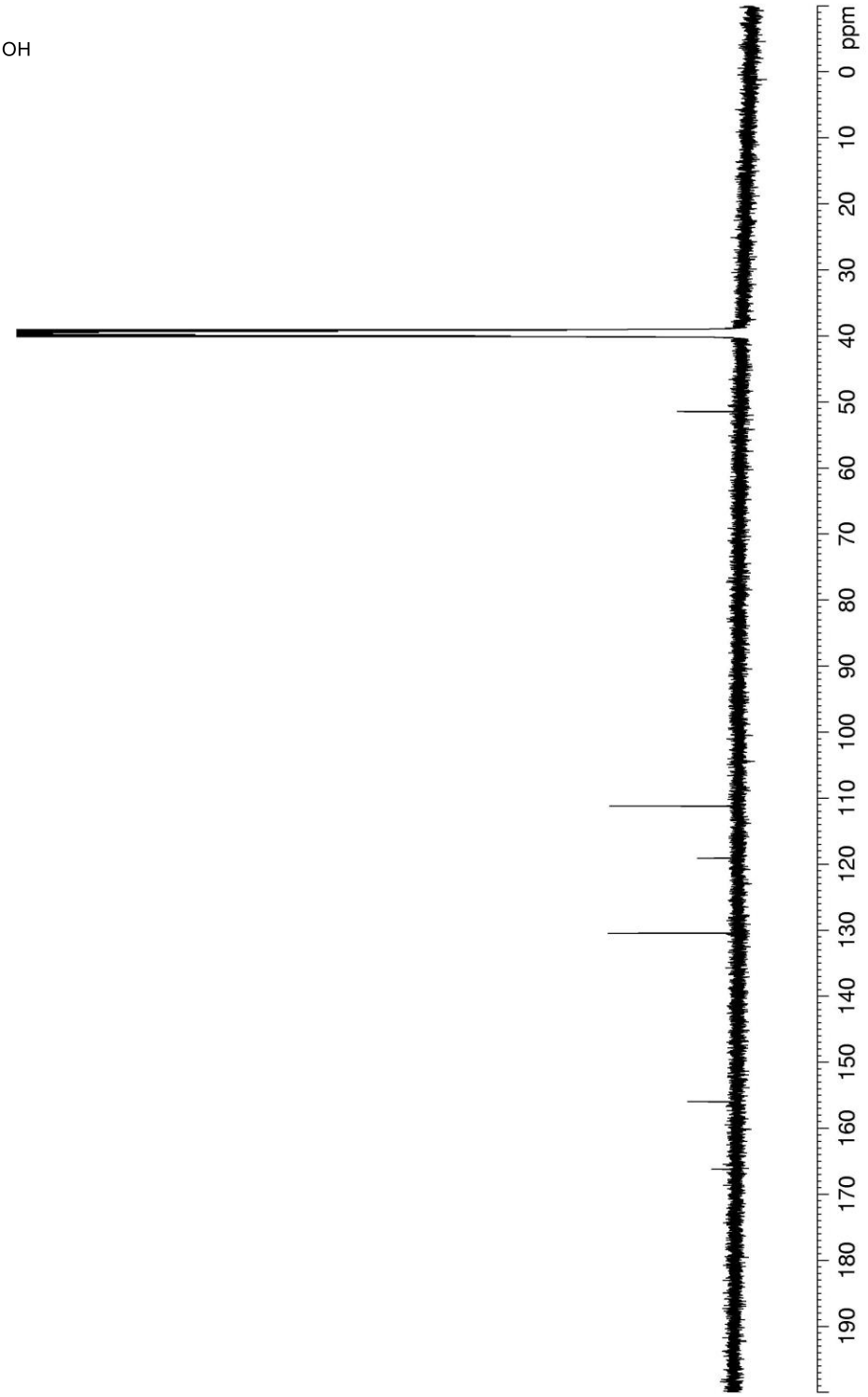
^{1}H NMR ($(CD_3)_2SO$, 25 °C) of **S1**



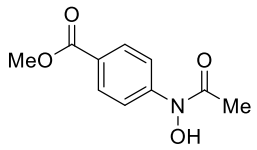
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S1**



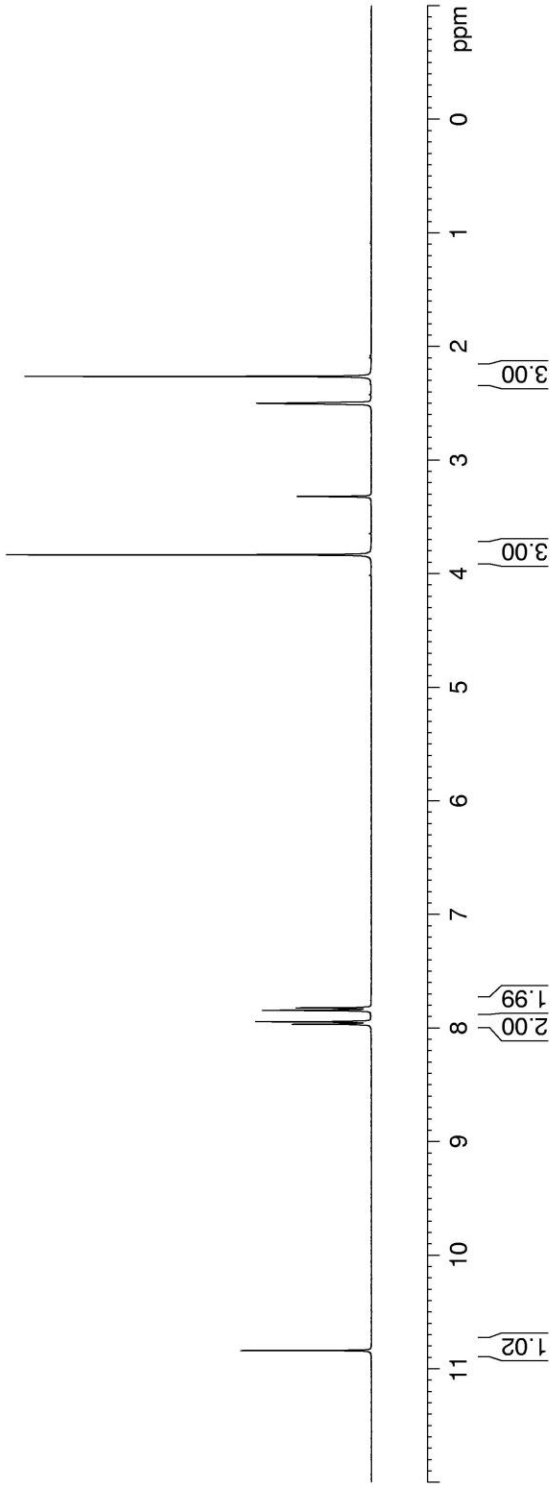
S1



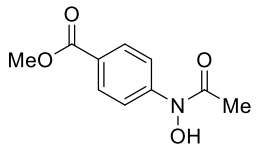
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S2**



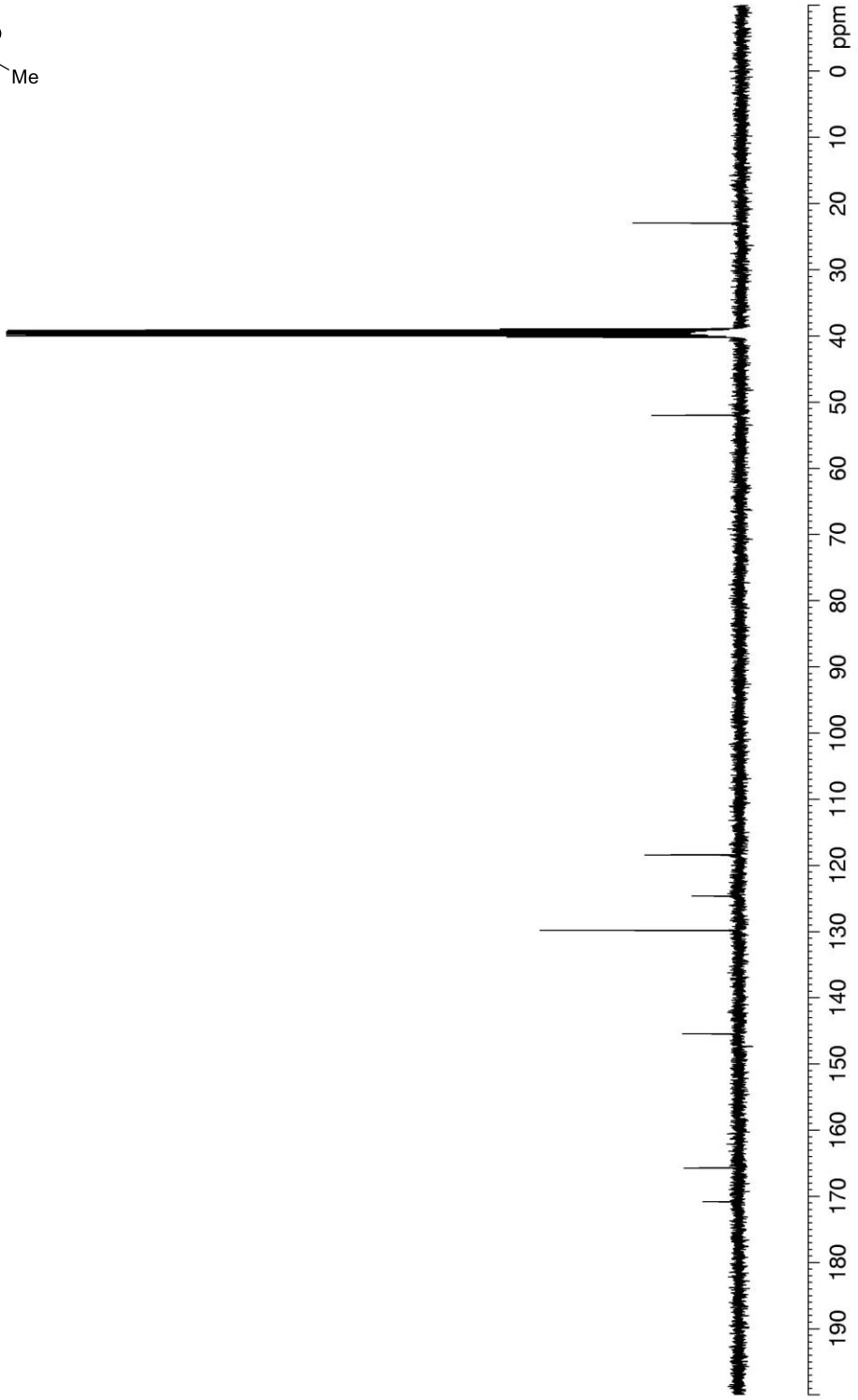
S2



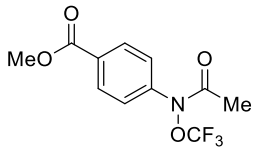
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S2**



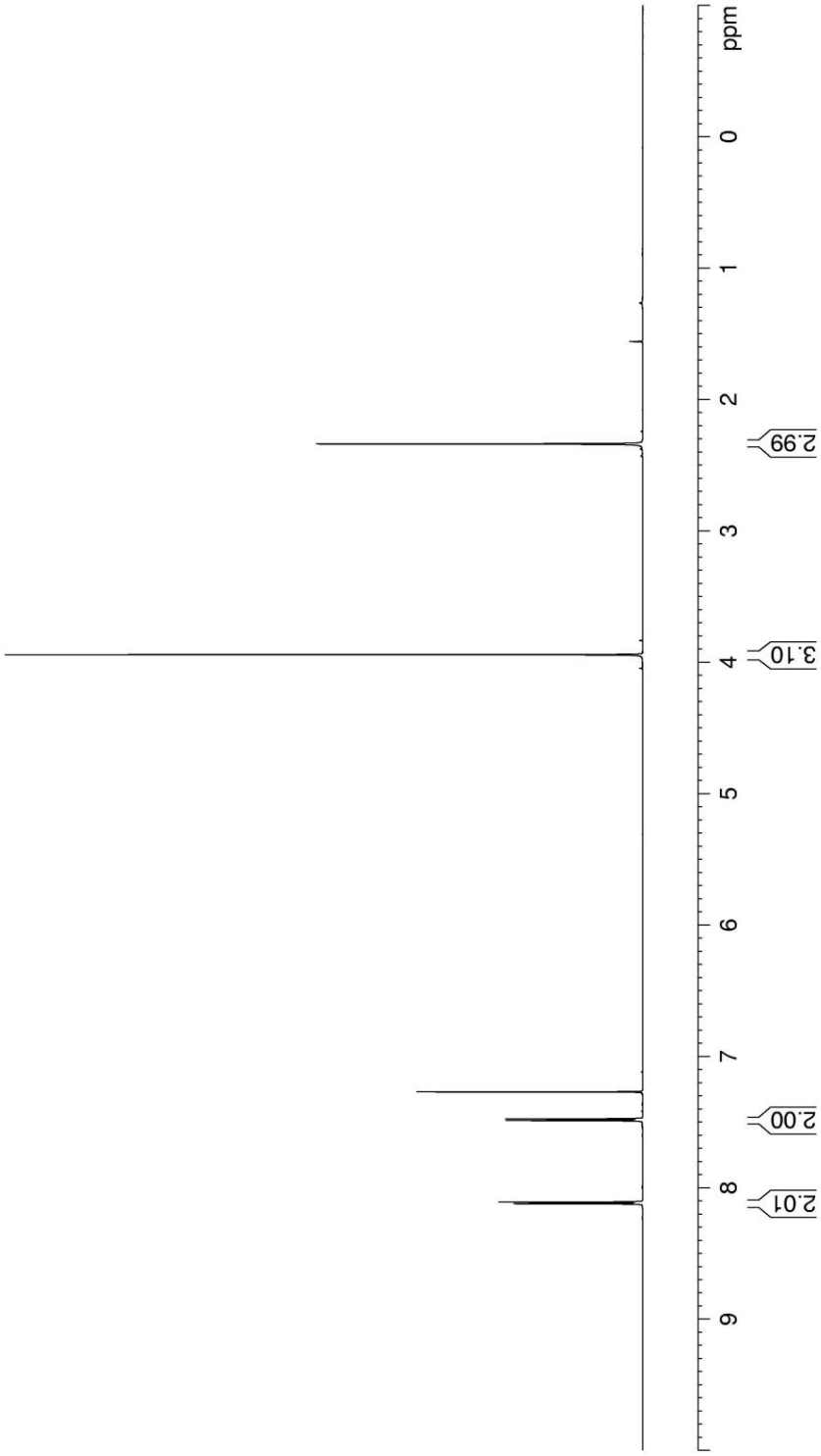
S2



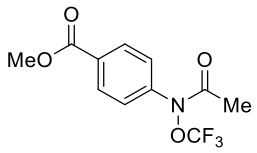
^{1}H NMR ($CDCl_3$, 25 ºC) of **2a**



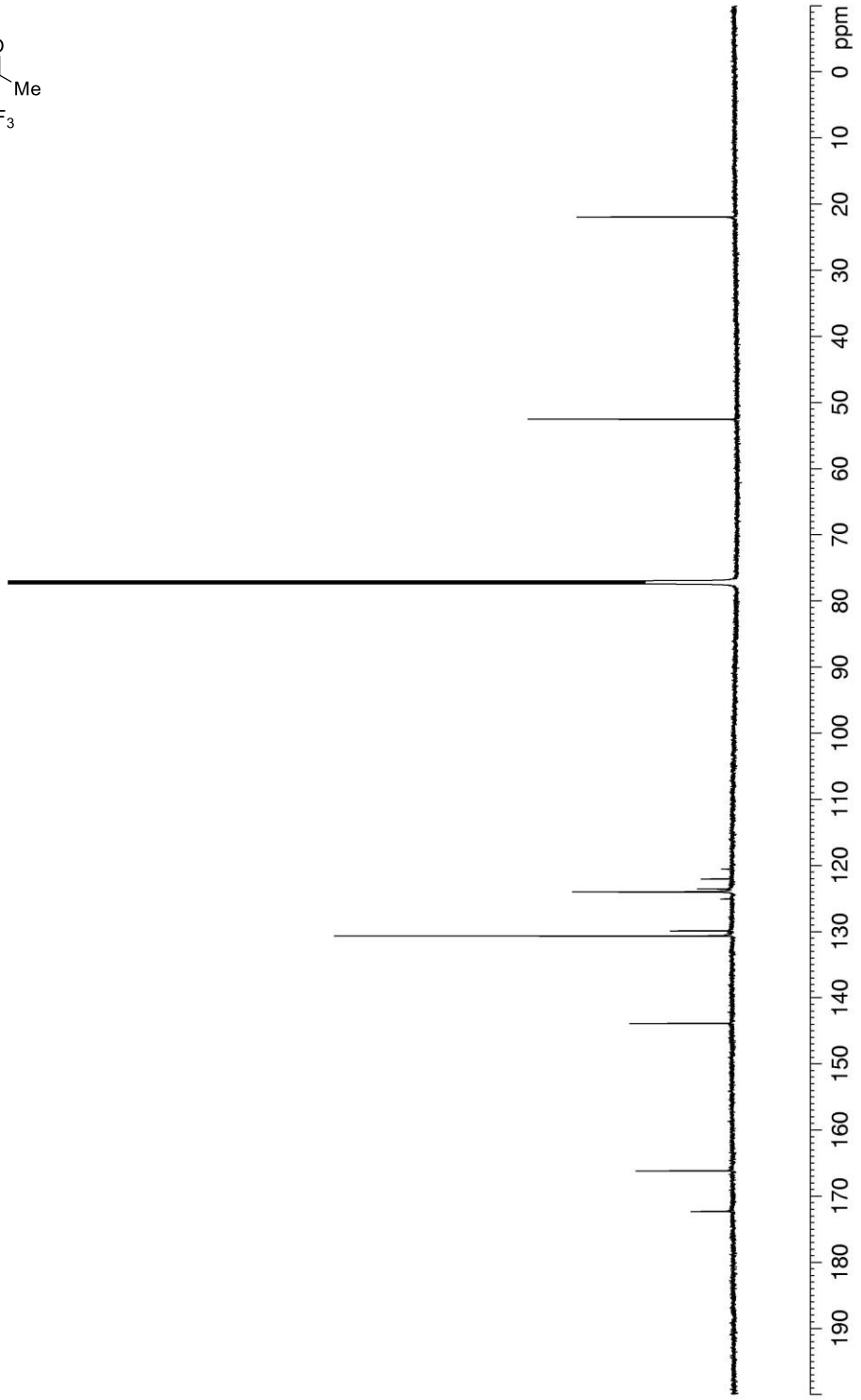
2a



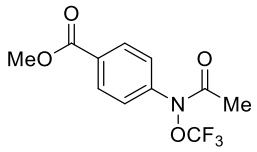
^{13}C NMR ($CDCl_3$, 25 ºC) of **2a**



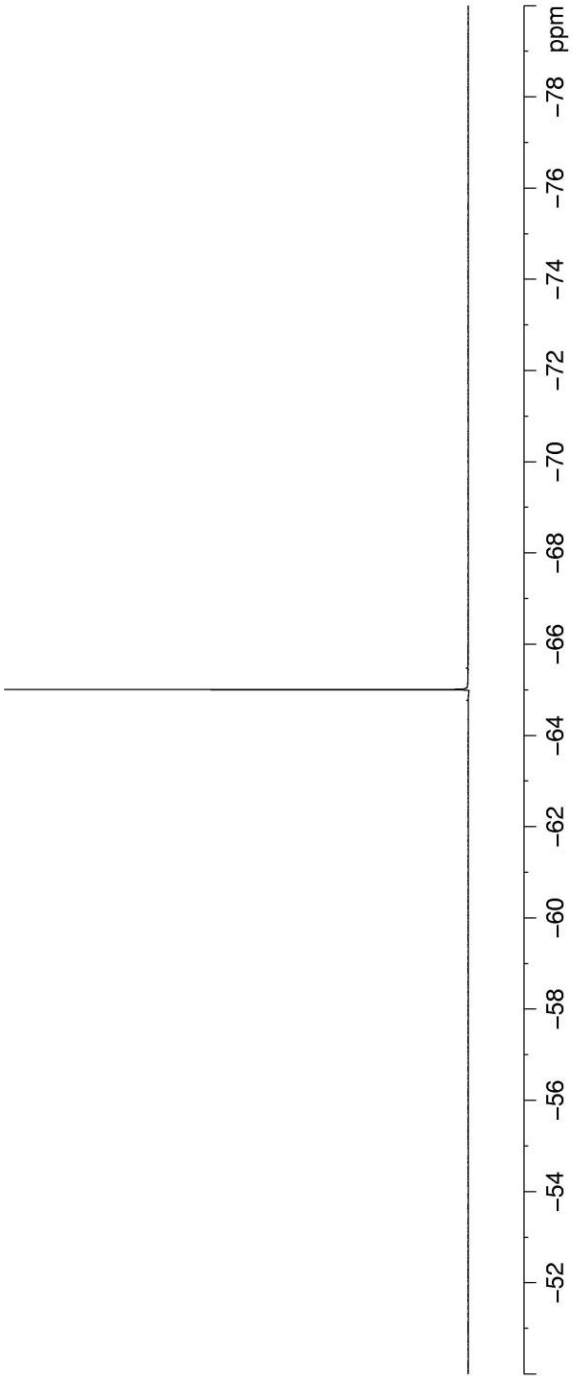
2a



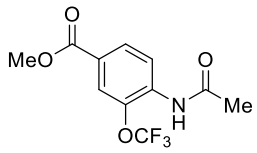
^{19}F NMR ($CDCl_3$, 25 ºC) of **2a**



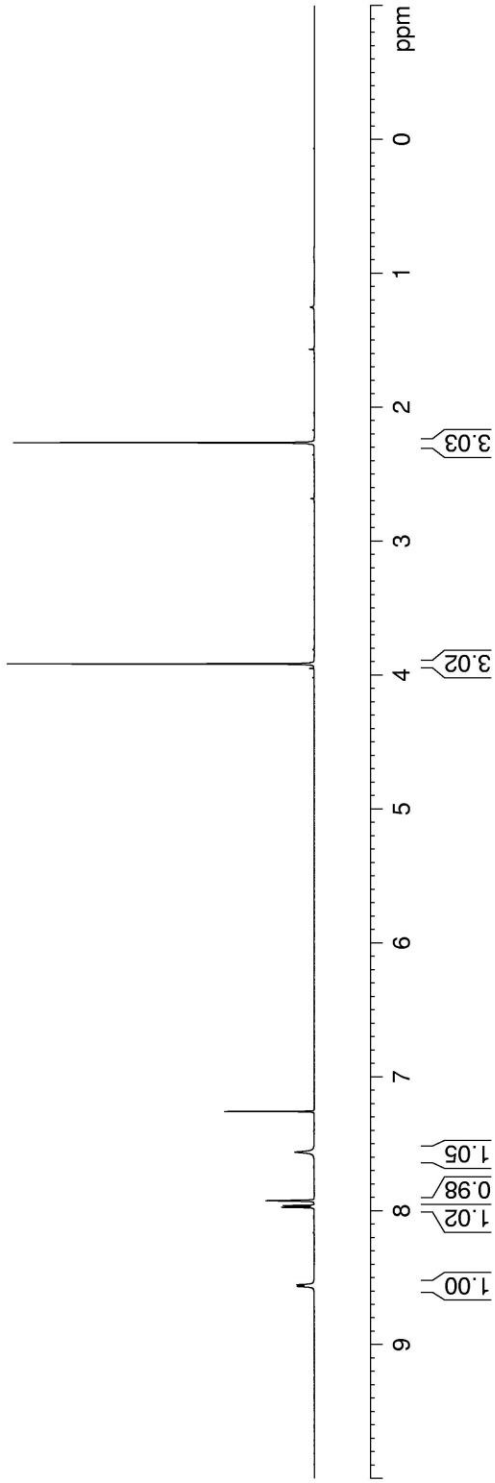
2a



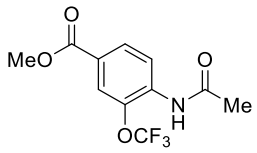
^{1}H NMR ($CDCl_3$, 25 ºC) of **3a**



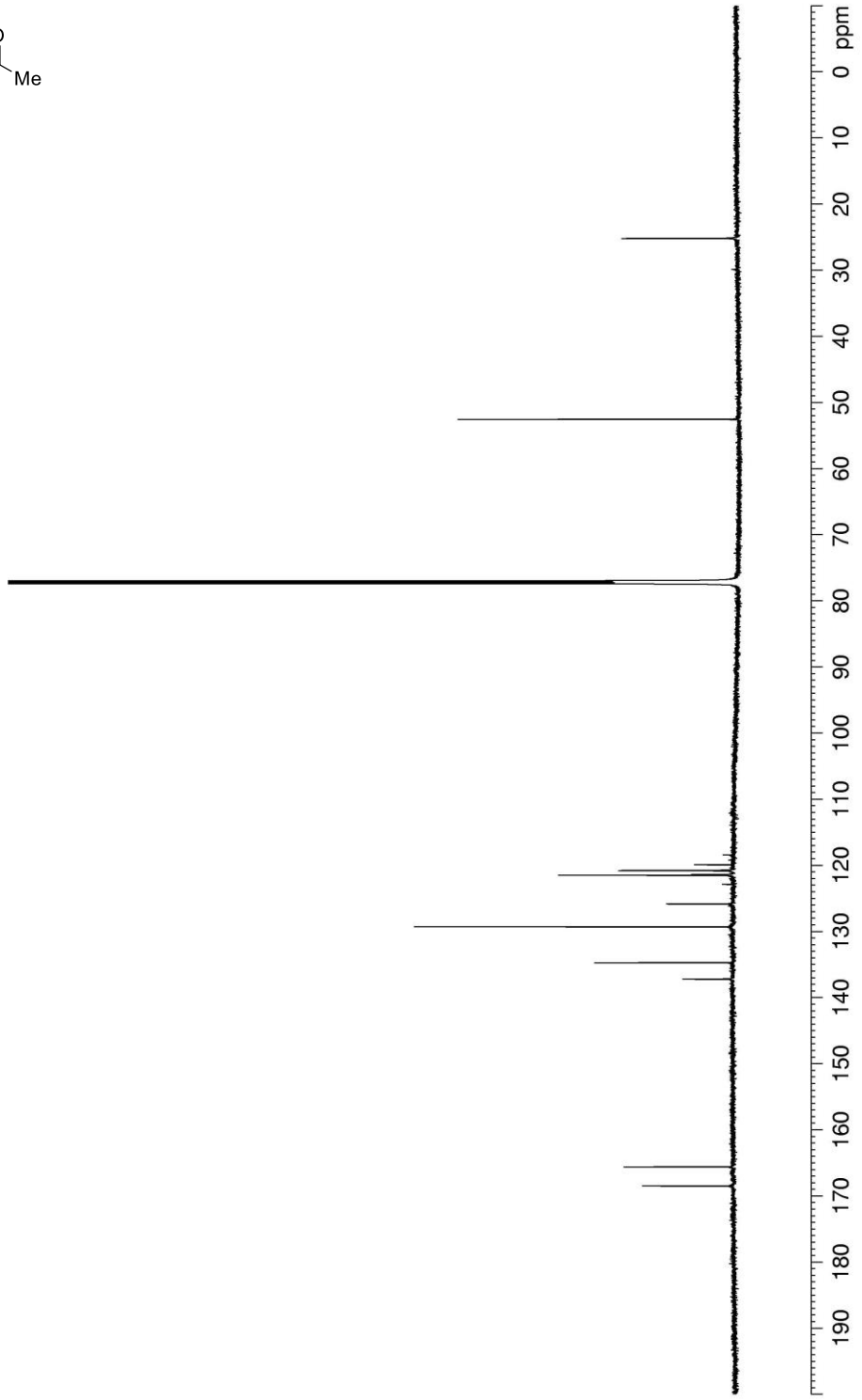
3a



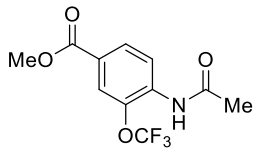
^{13}C NMR ($CDCl_3$, 25 ºC) of **3a**



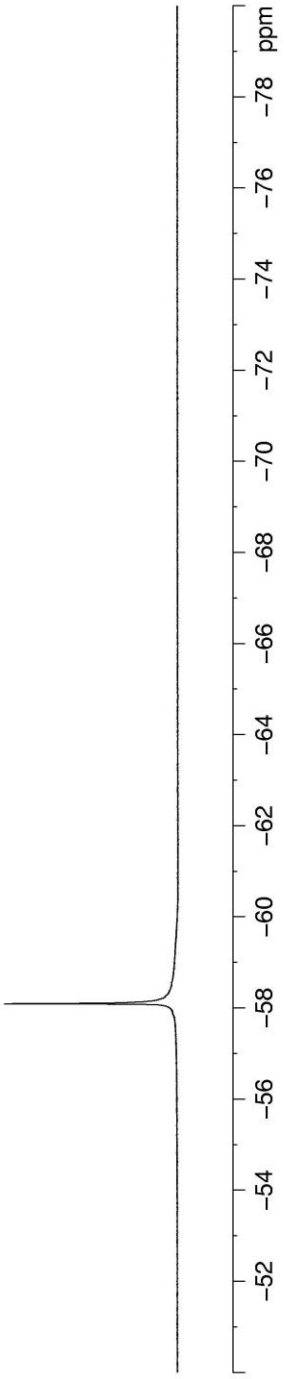
3a



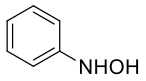
^{19}F NMR ($CDCl_3$, 25 ºC) of **3a**



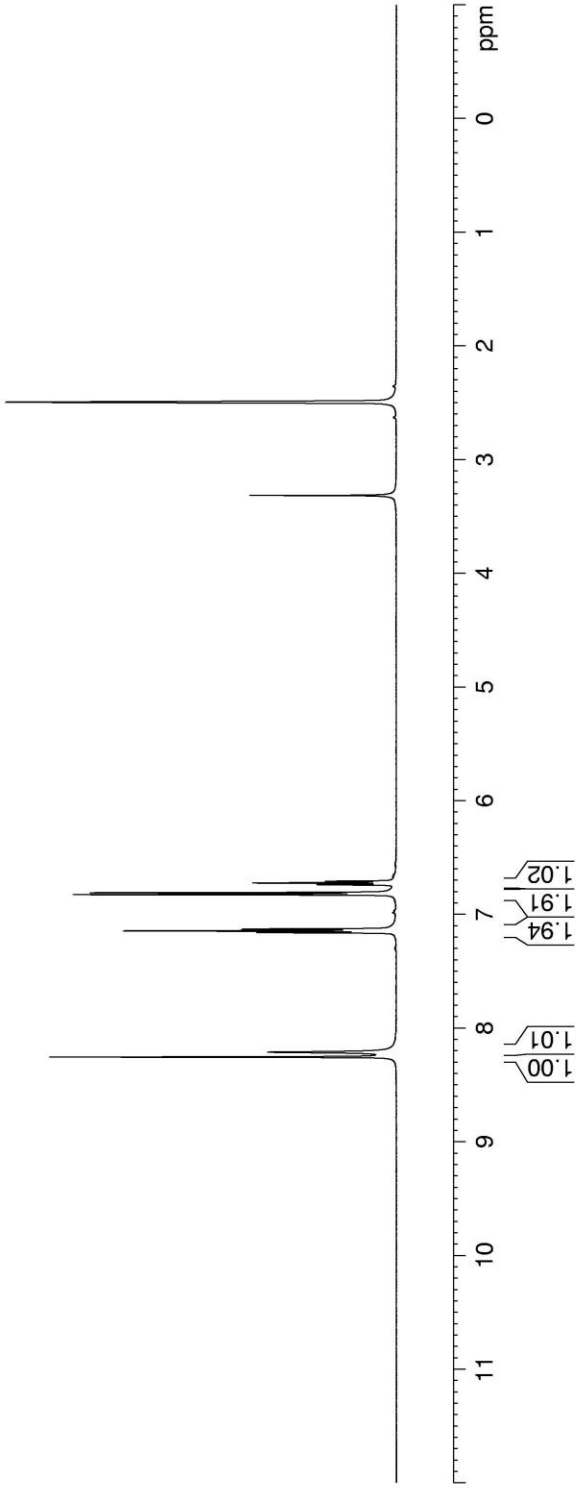
3a



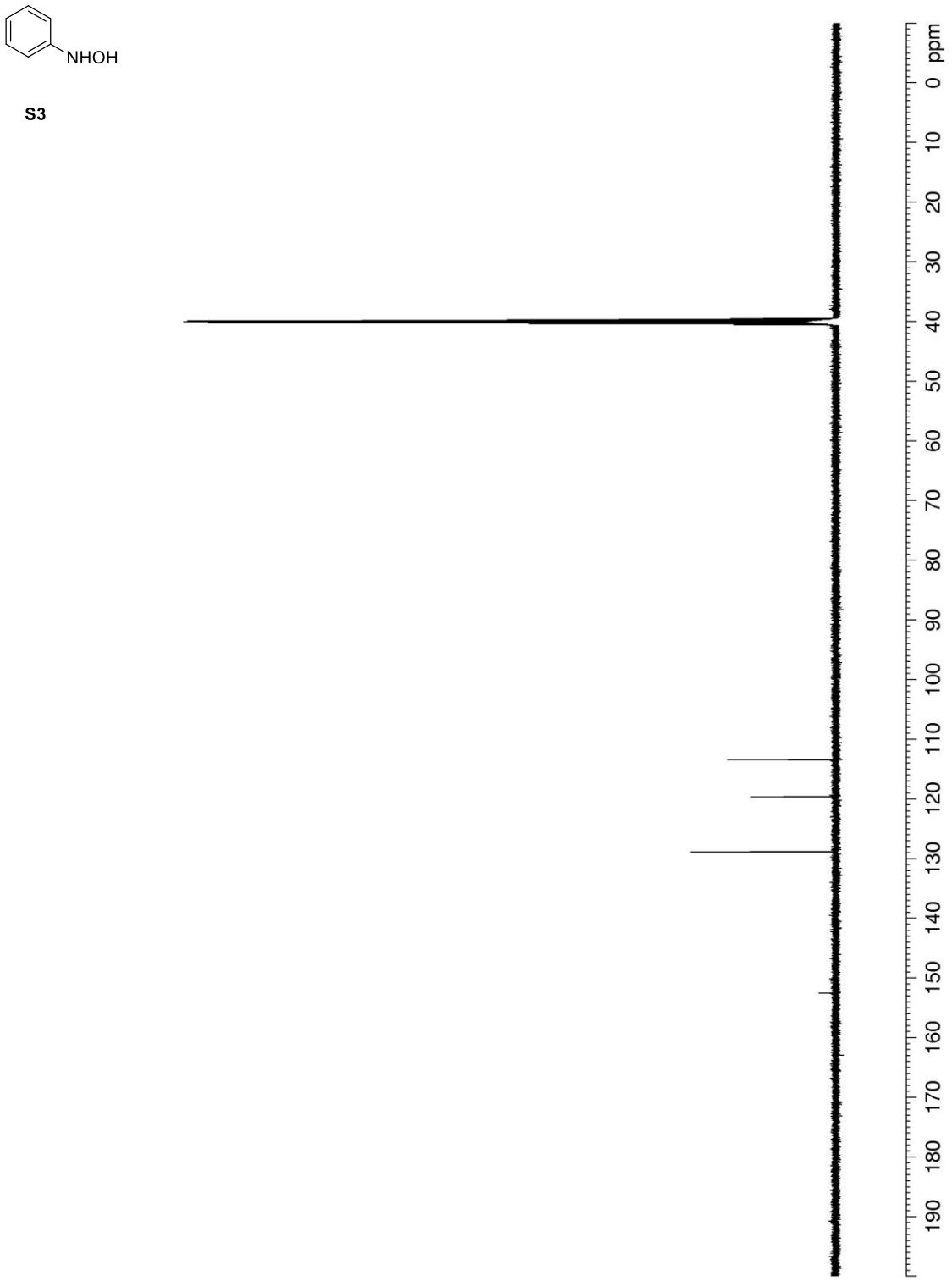
^{1}H NMR ($(CD_3)_2SO$, 25 ºC) of **S3**



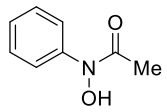
S3



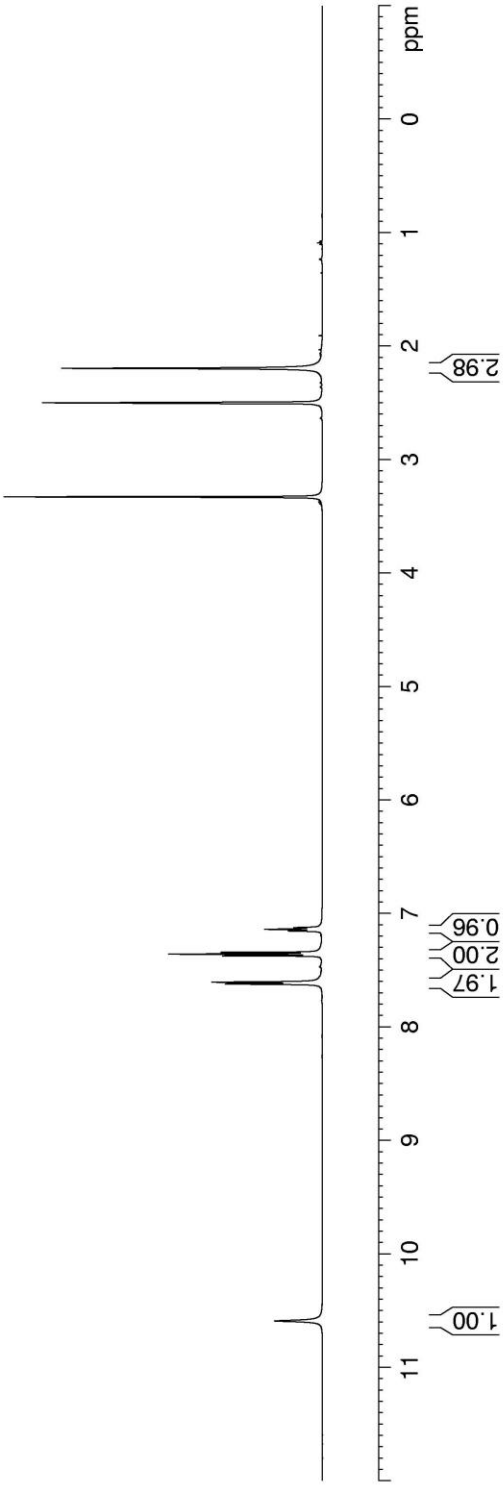
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S3**



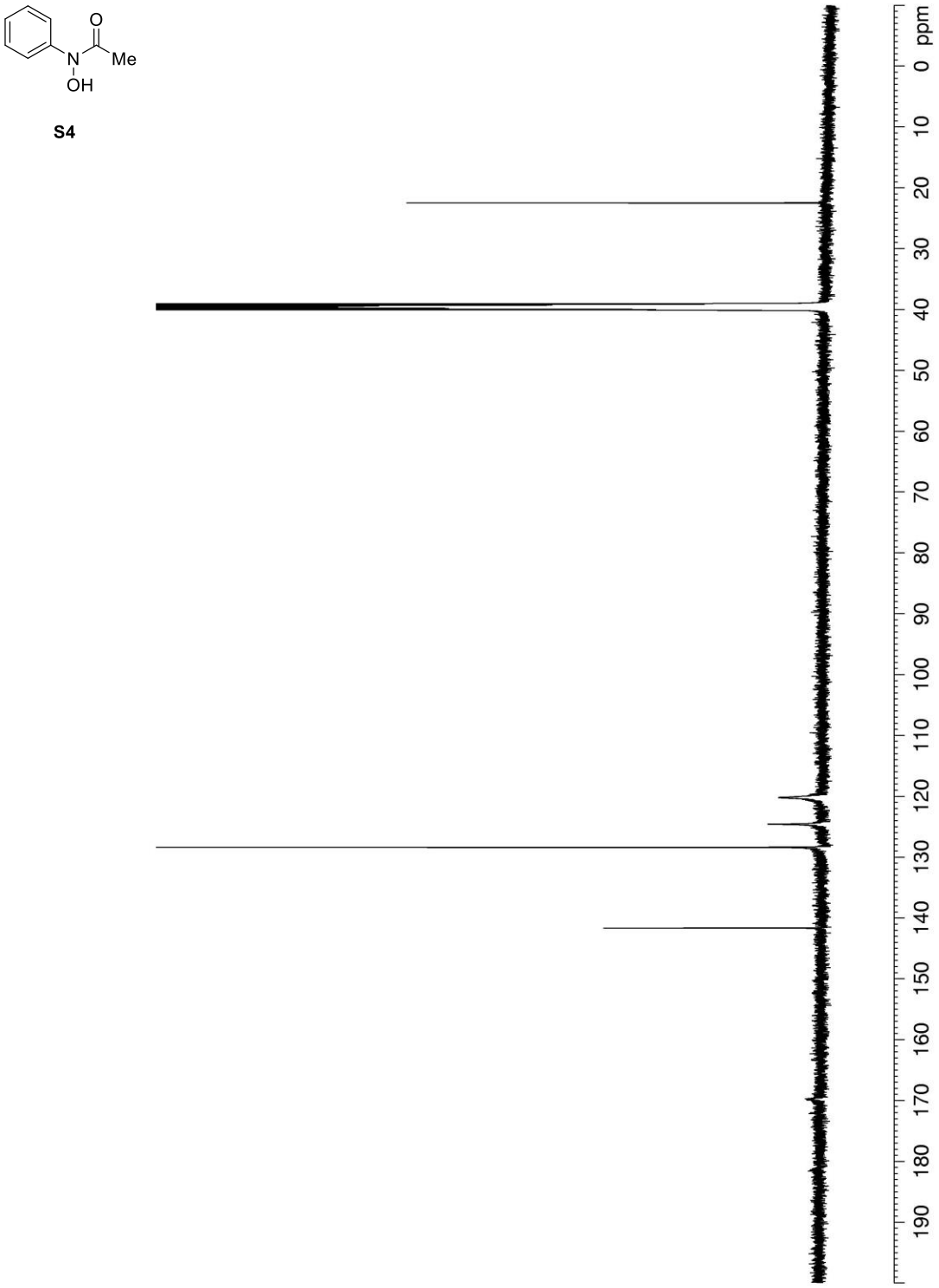
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S4**



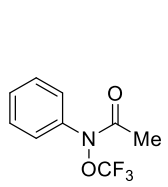
S4



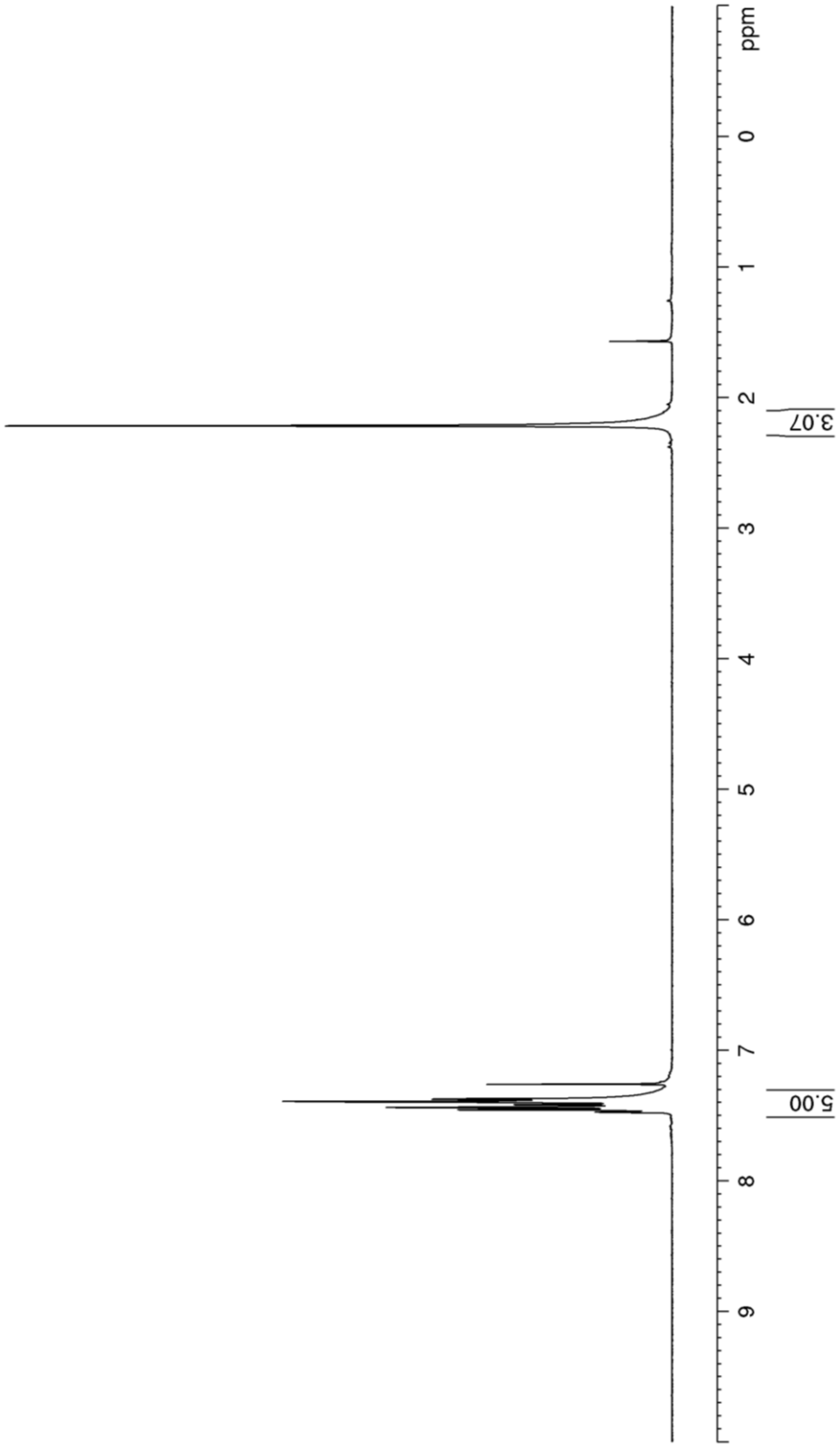
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S4**



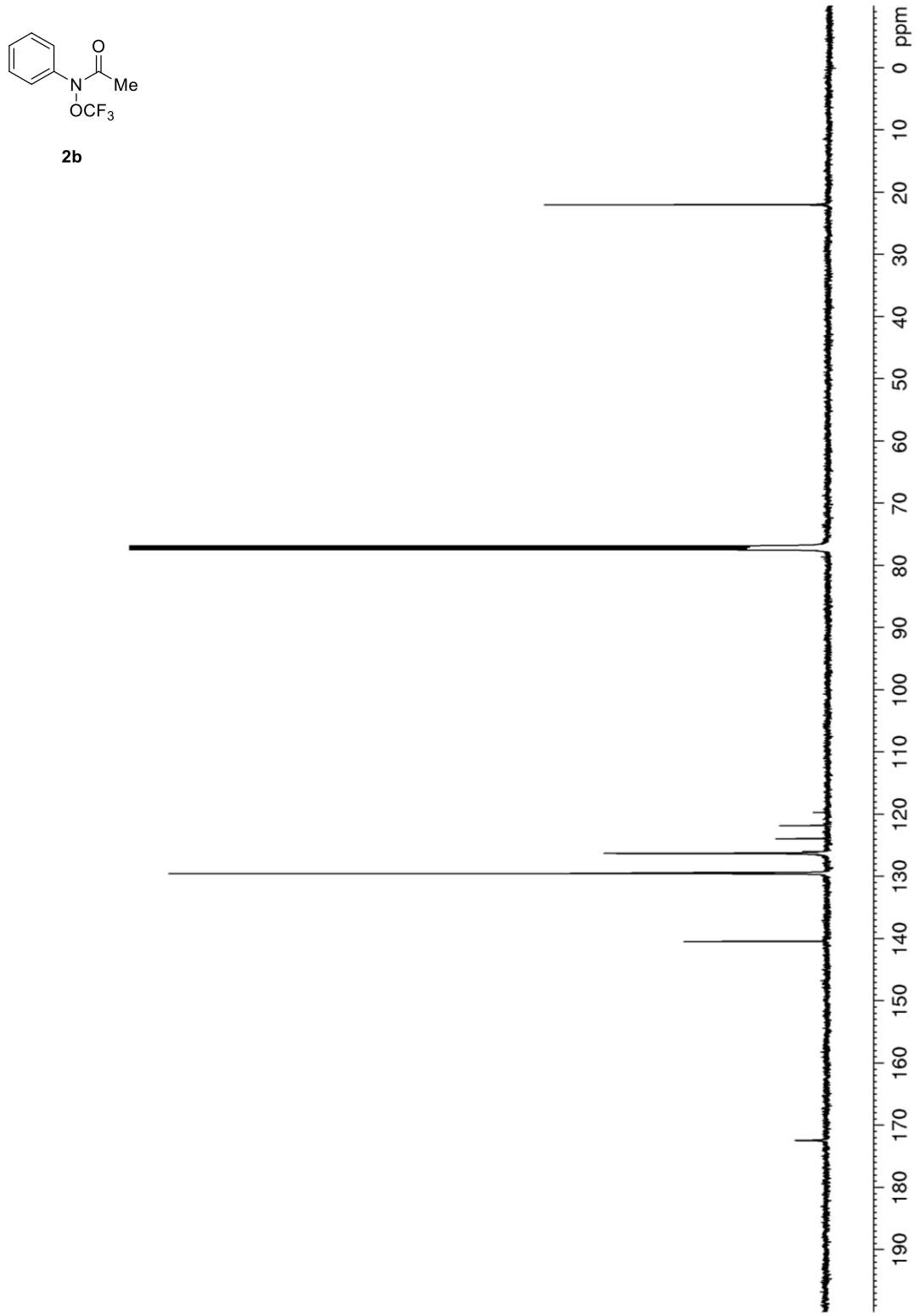
^{1}H NMR ($CDCl_3$, 25 ºC) of **2b**



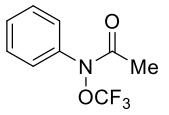
2b



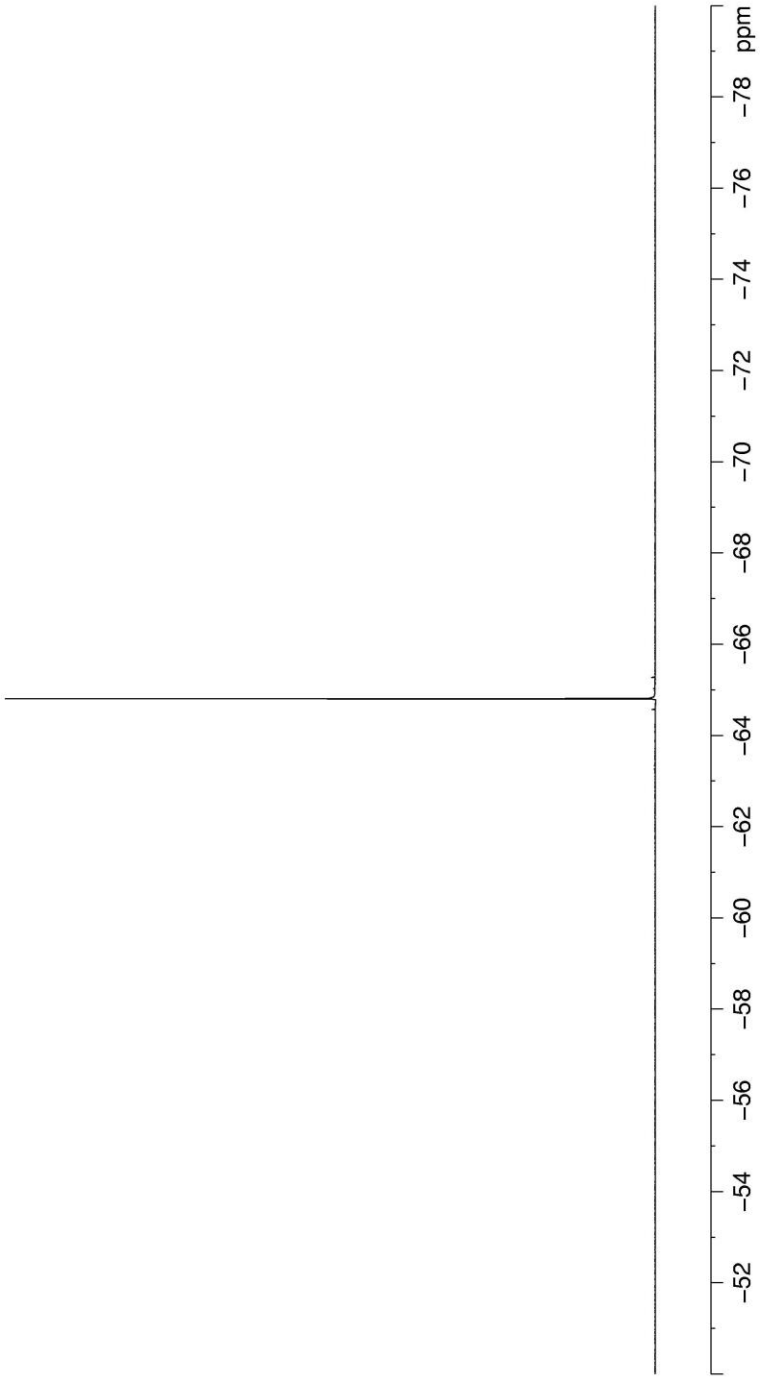
^{13}C NMR ($CDCl_3$, 25 ºC) of **2b**



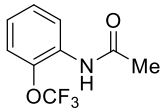
^{19}F NMR ($CDCl_3$, 25 ºC) of **2b**



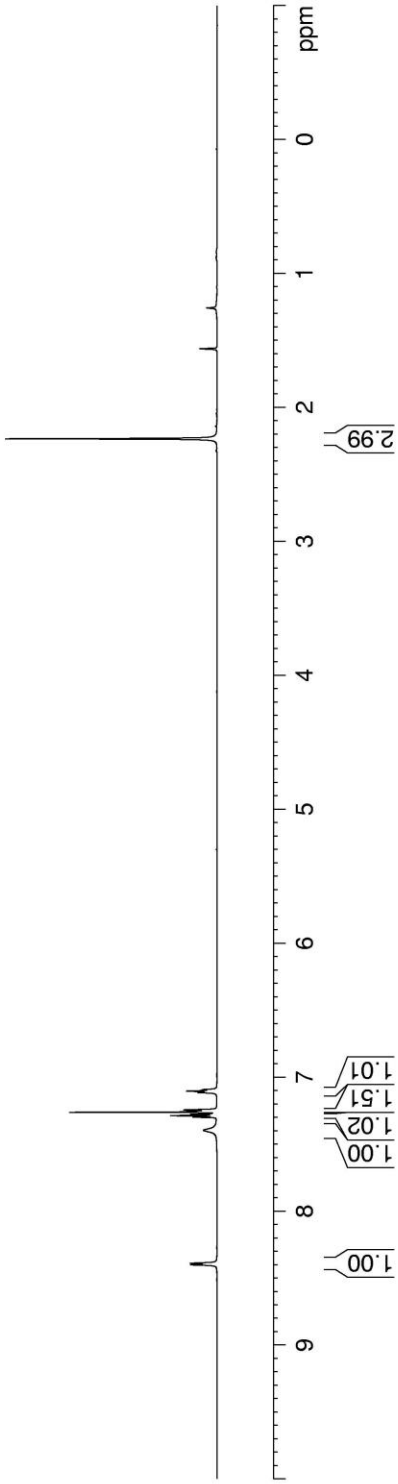
2b



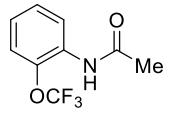
^{1}H NMR ($CDCl_3$, 25 ºC) of **3b**



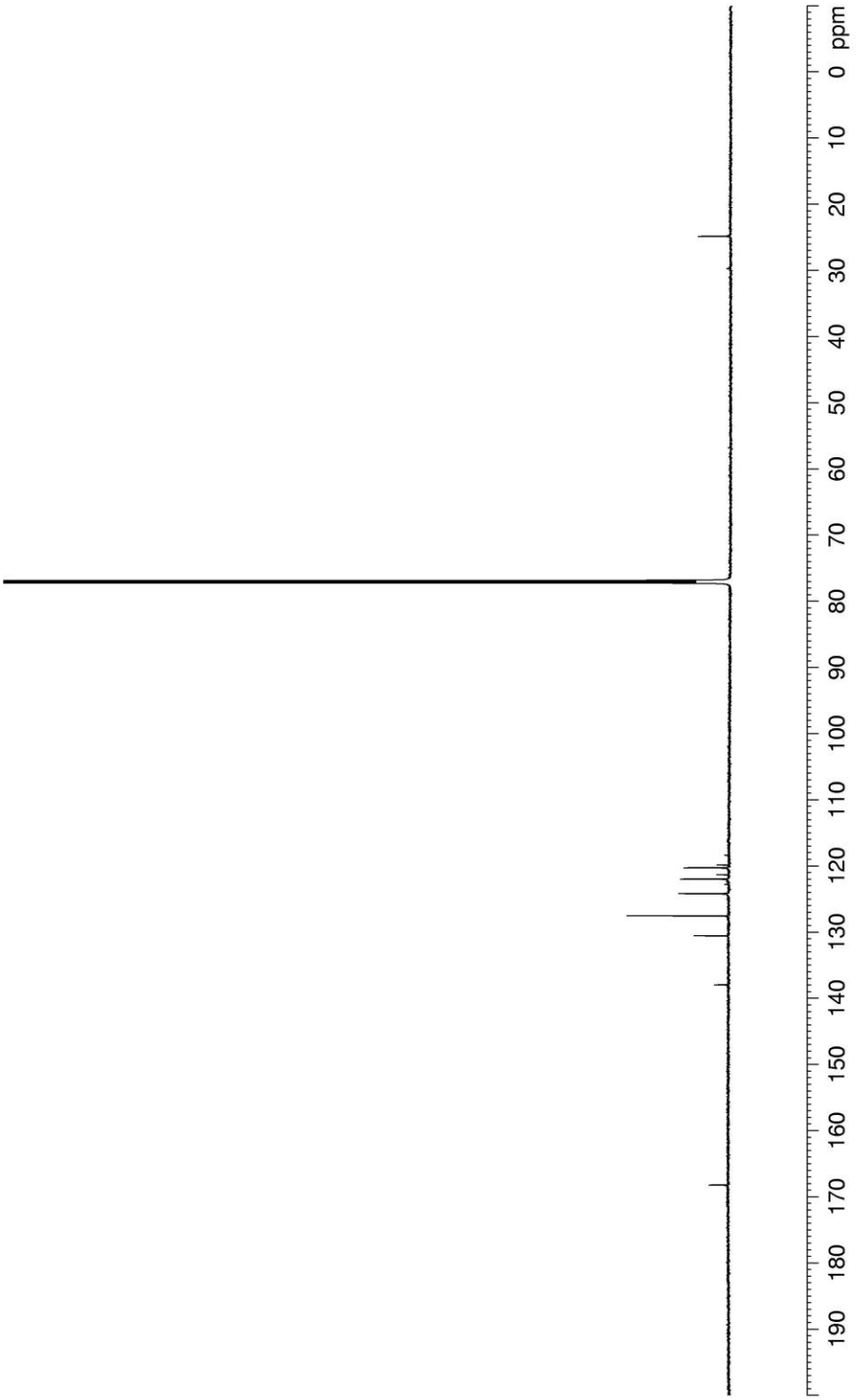
3b



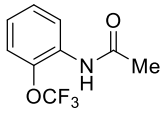
^{13}C NMR ($CDCl_3$, 25 ºC) of **3b**



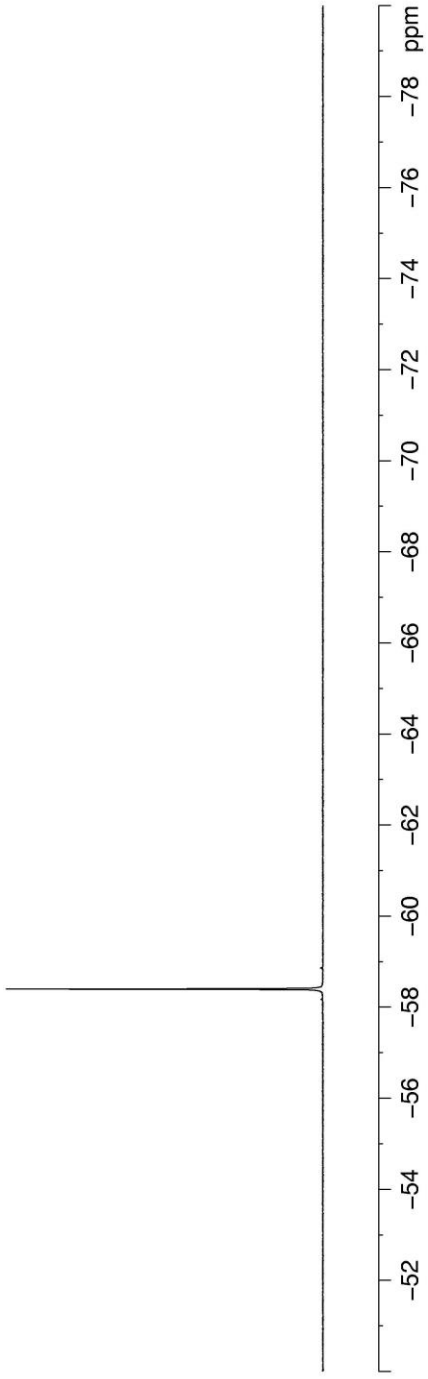
3b



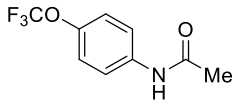
^{19}F NMR ($CDCl_3$, 25 ºC) of **3b**



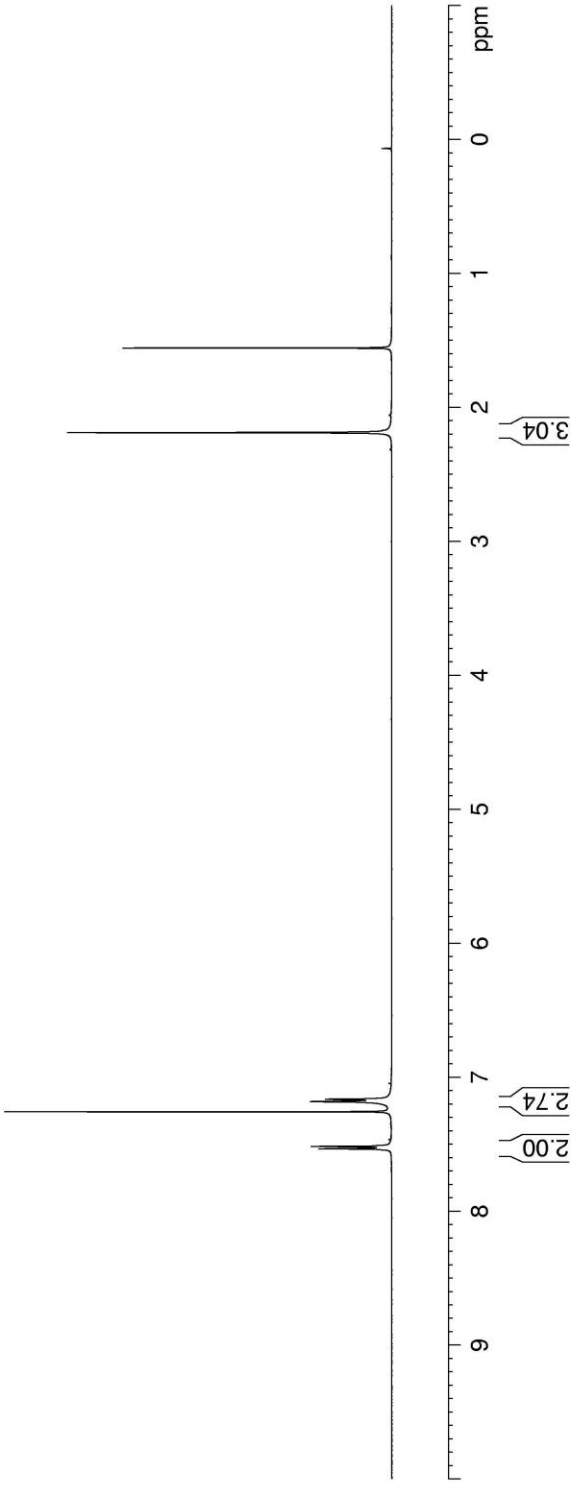
3b



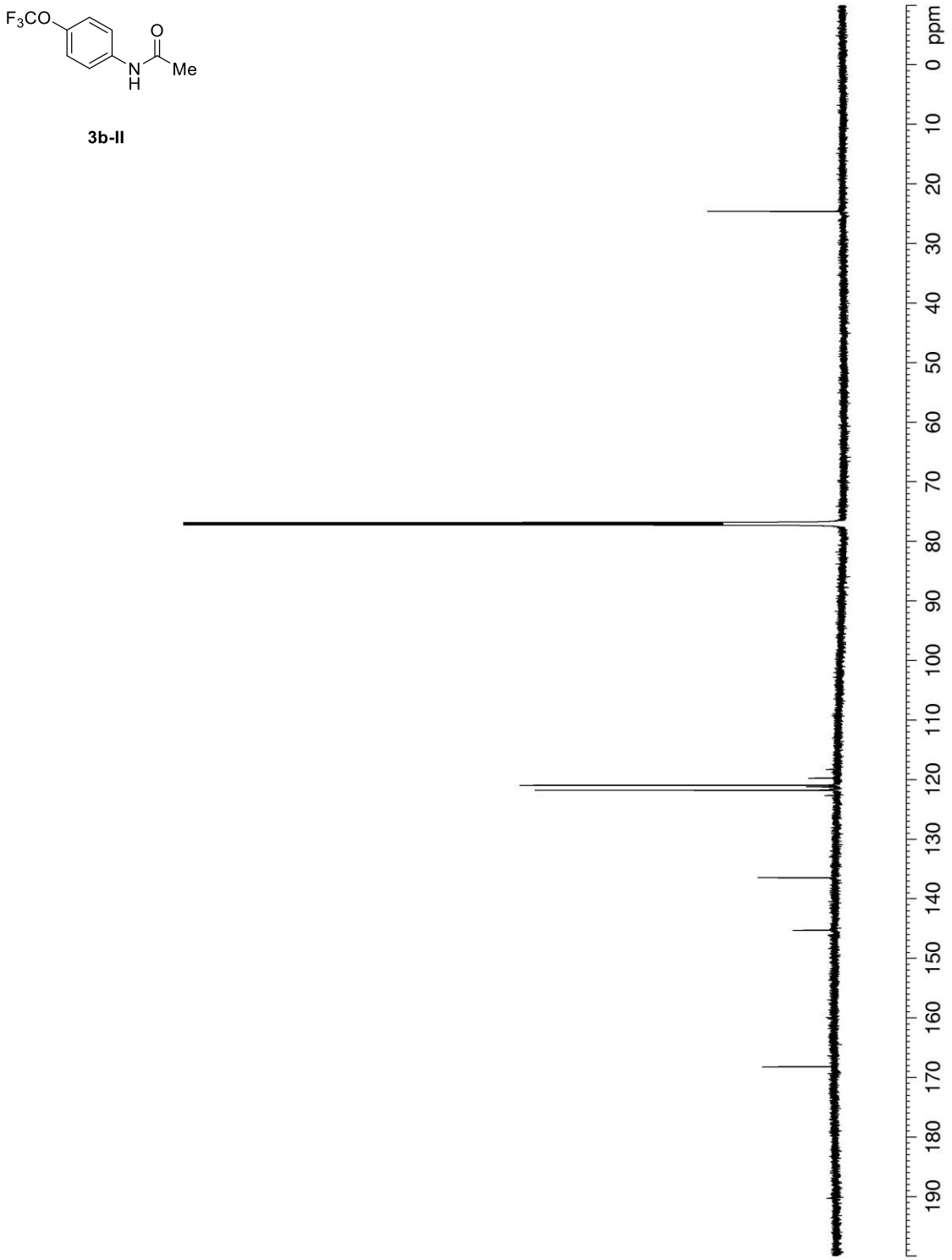
^{1}H NMR ($CDCl_3$, 25 ºC) of **3b-II**



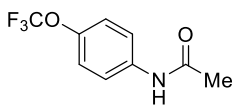
3b-II



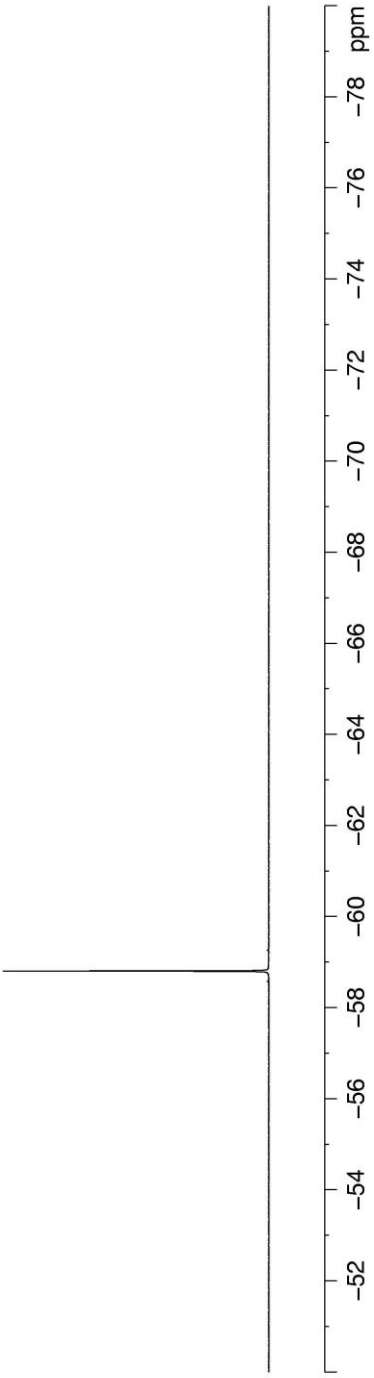
^{13}C NMR ($CDCl_3$, 25 ºC) of **3b-II**



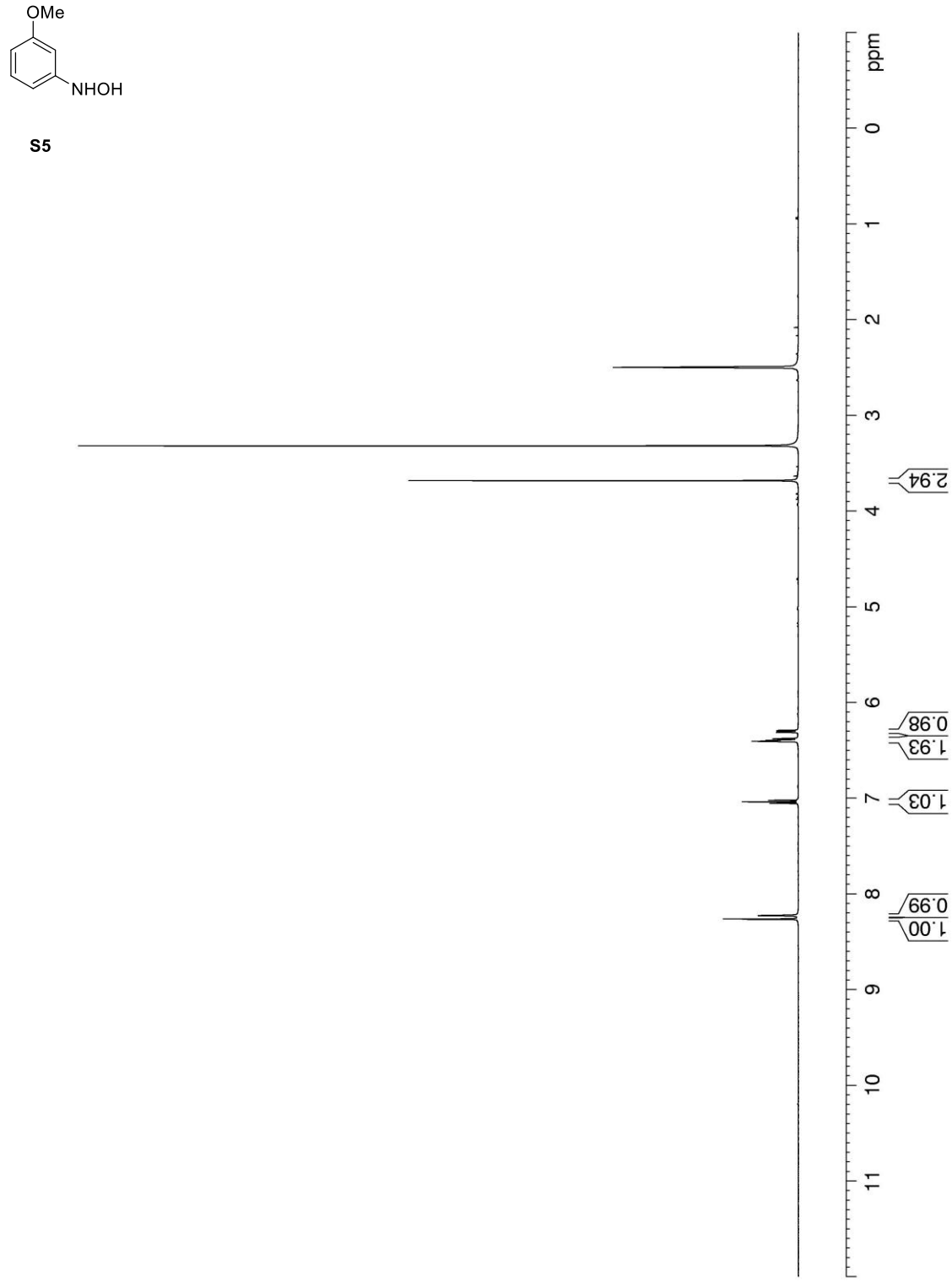
^{19}F NMR ($CDCl_3$, 25 ºC) of **3b-II**



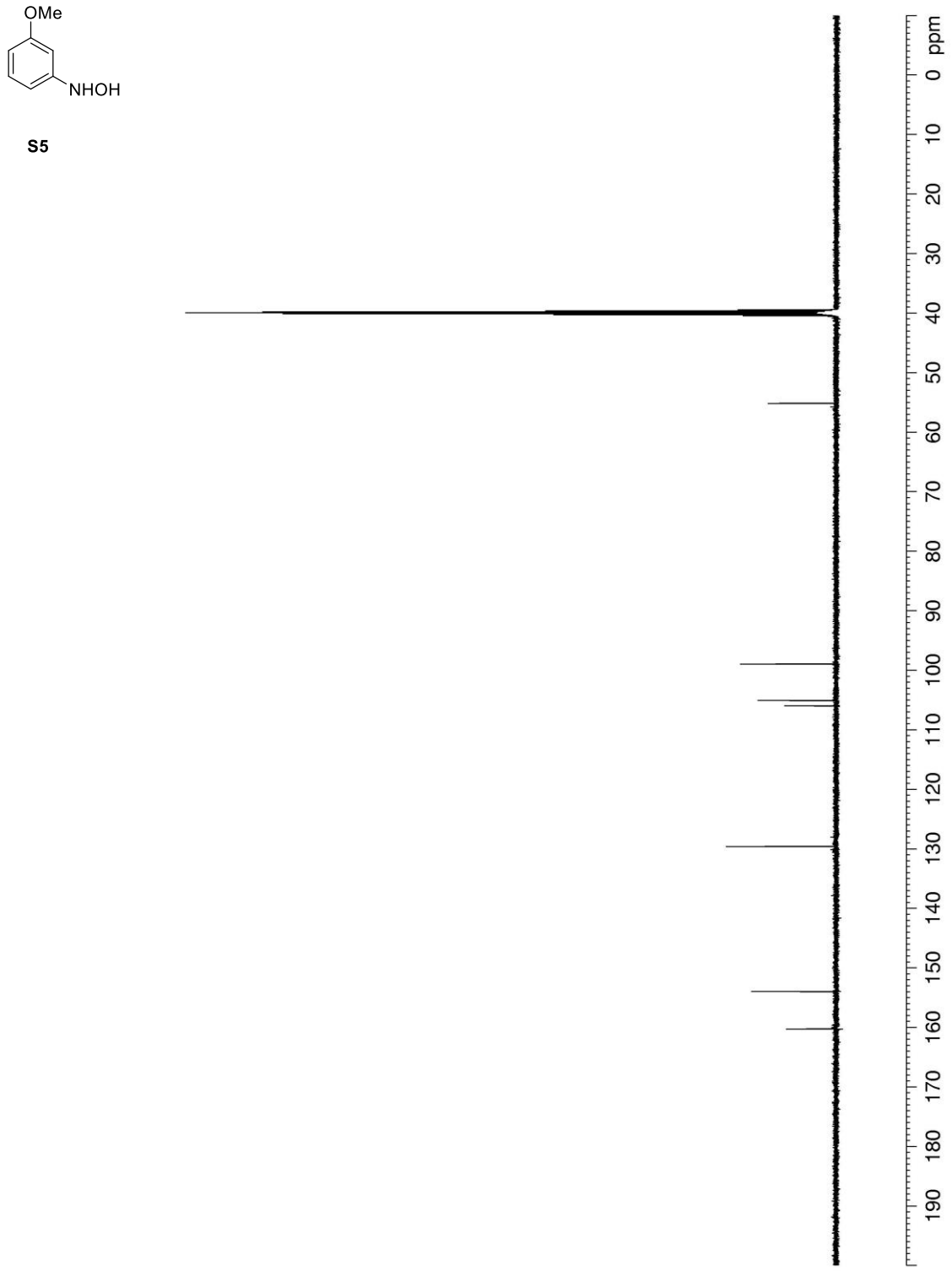
3b-II



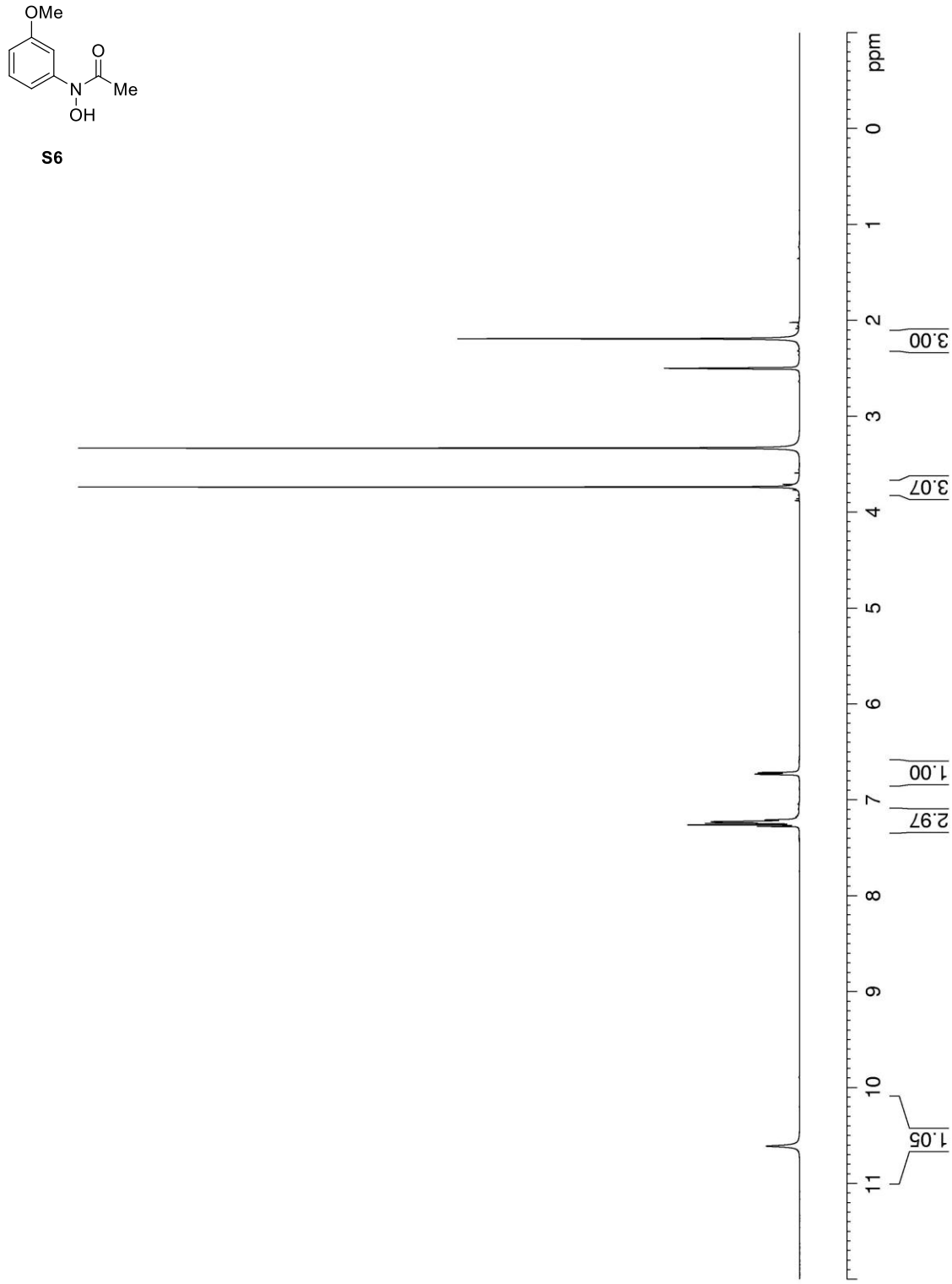
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S5**



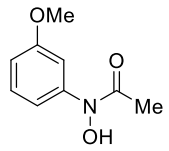
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S5**



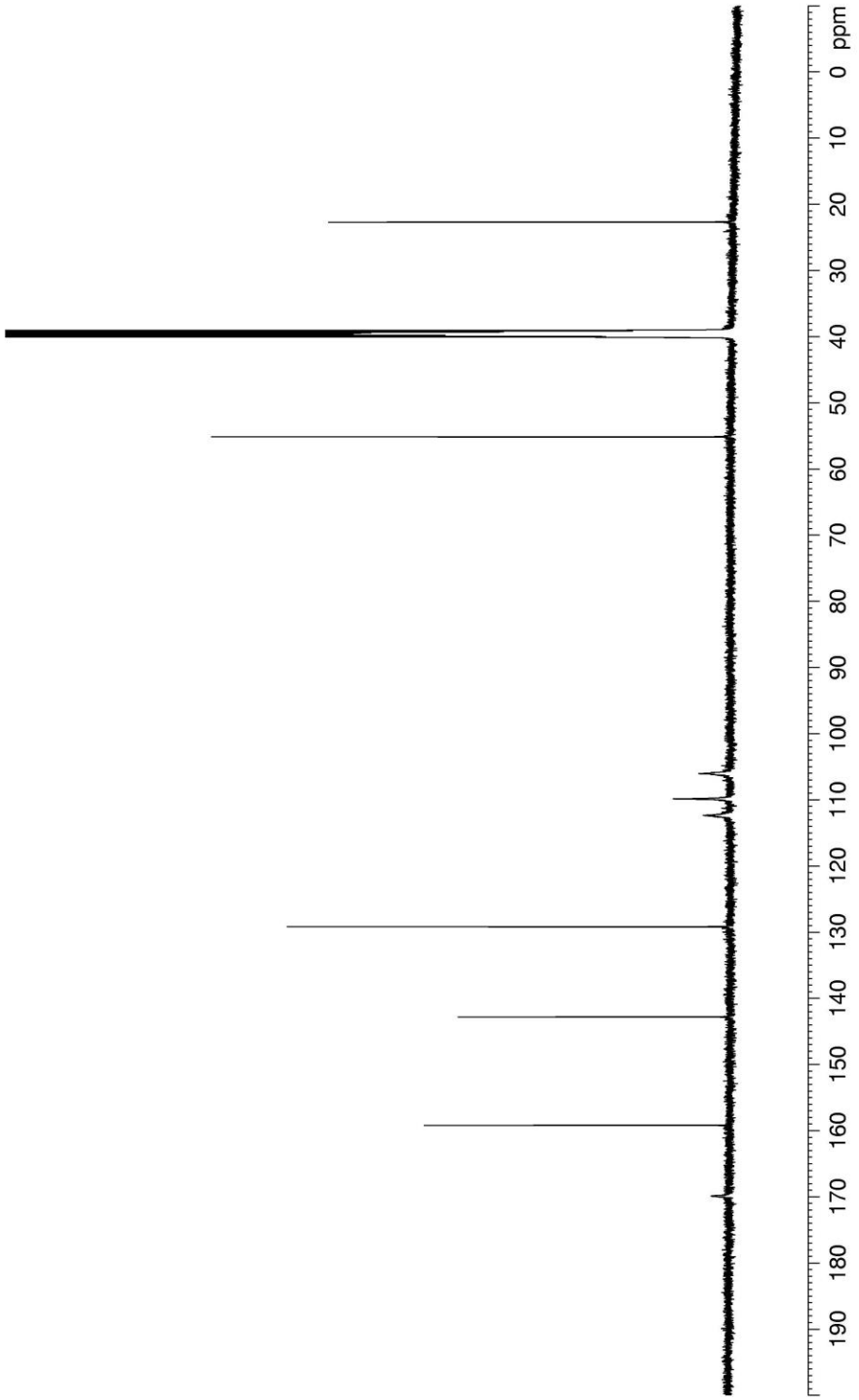
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S6**



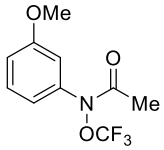
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S6**



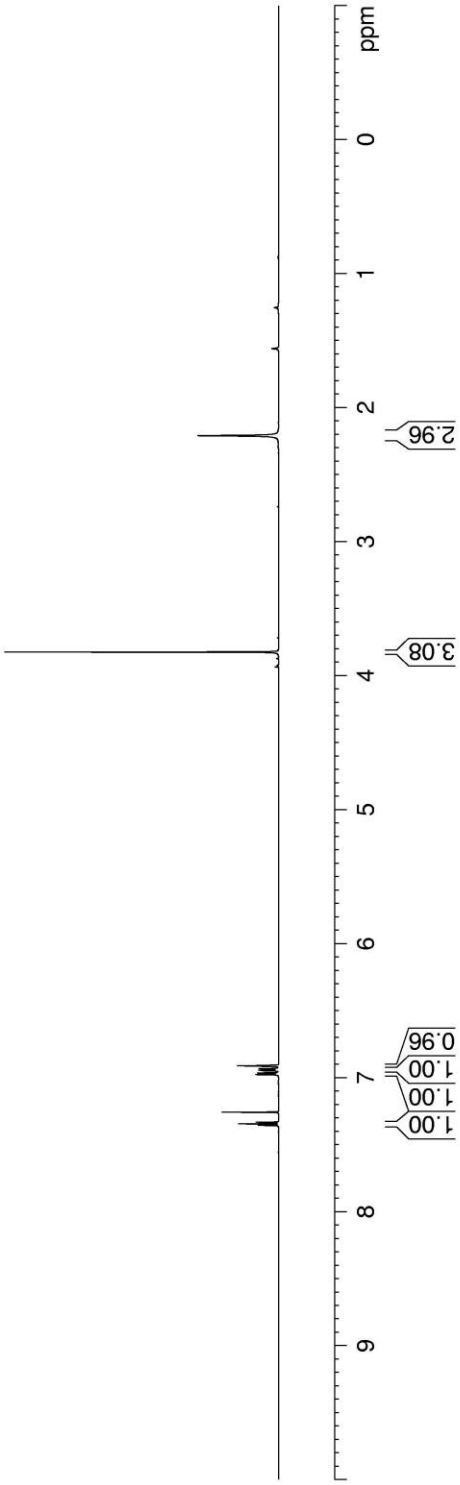
S6



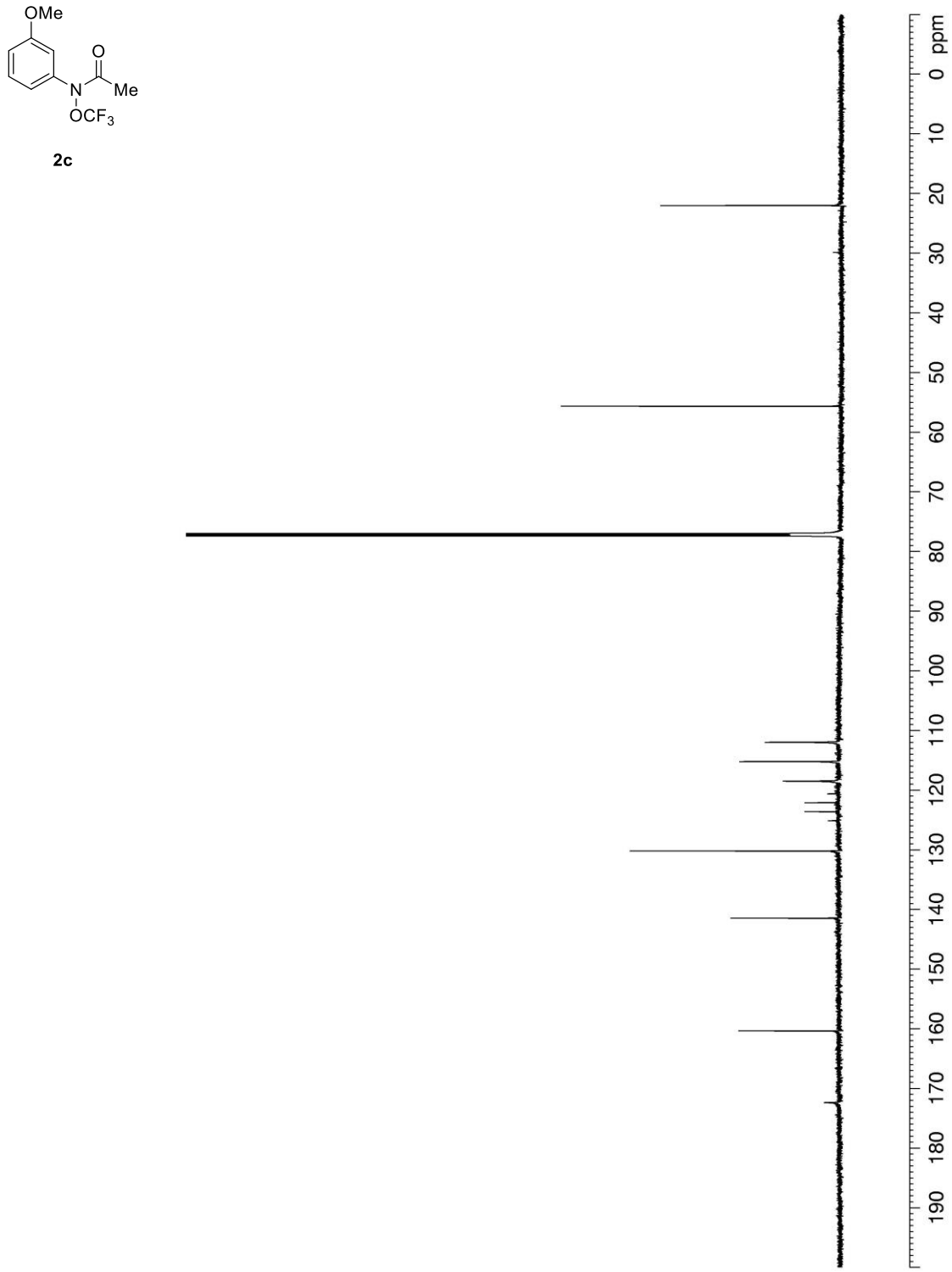
^{1}H NMR ($CDCl_3$, 25 ºC) of **2c**



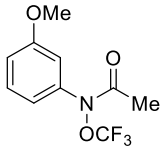
2c



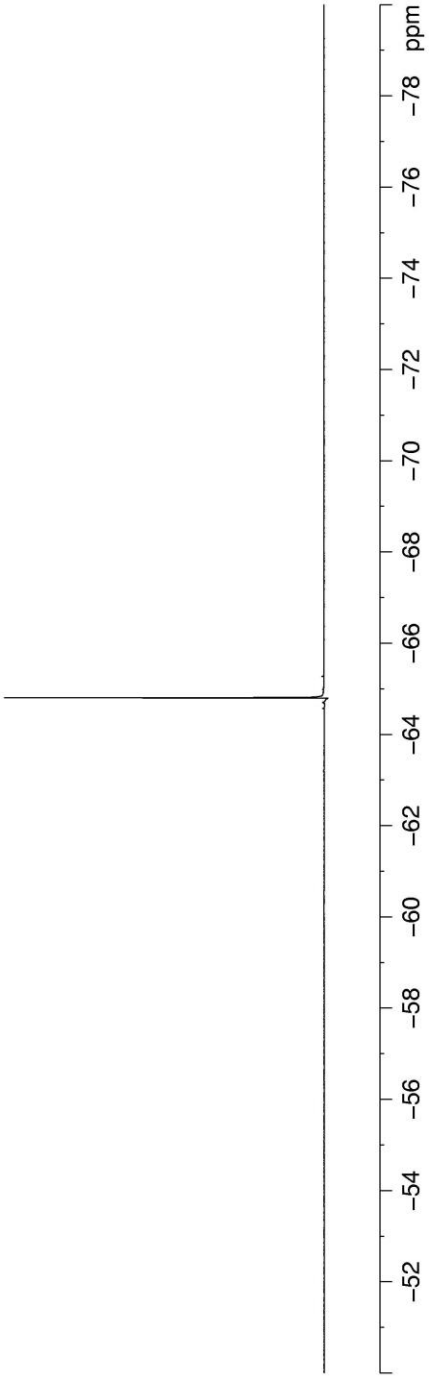
^{13}C NMR ($CDCl_3$, 25 ºC) of **2c**



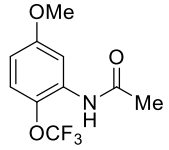
^{19}F NMR ($CDCl_3$, 25 ºC) of **2c**



2c



^{1}H NMR ($CDCl_3$, 25 ºC) of **3c**



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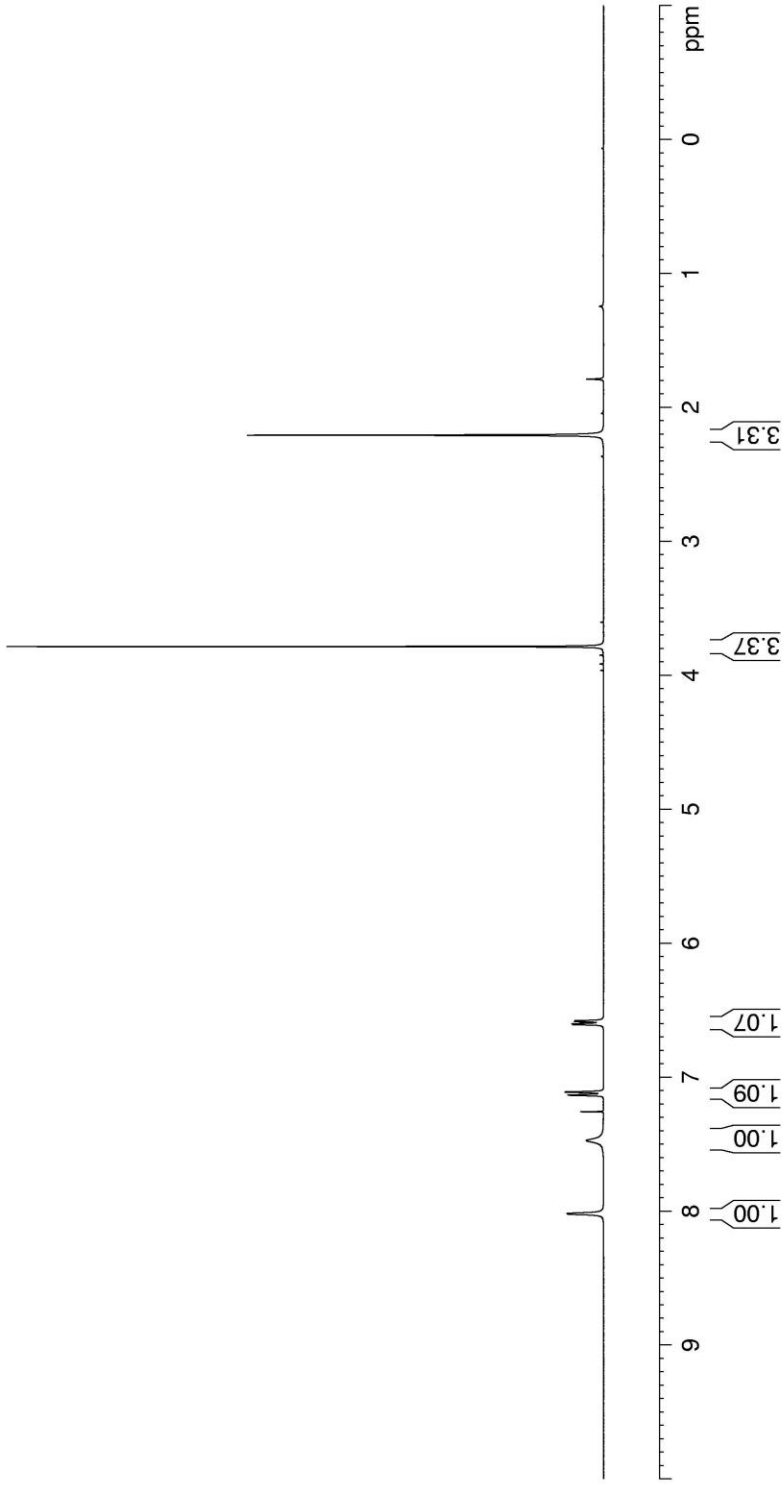
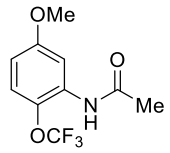
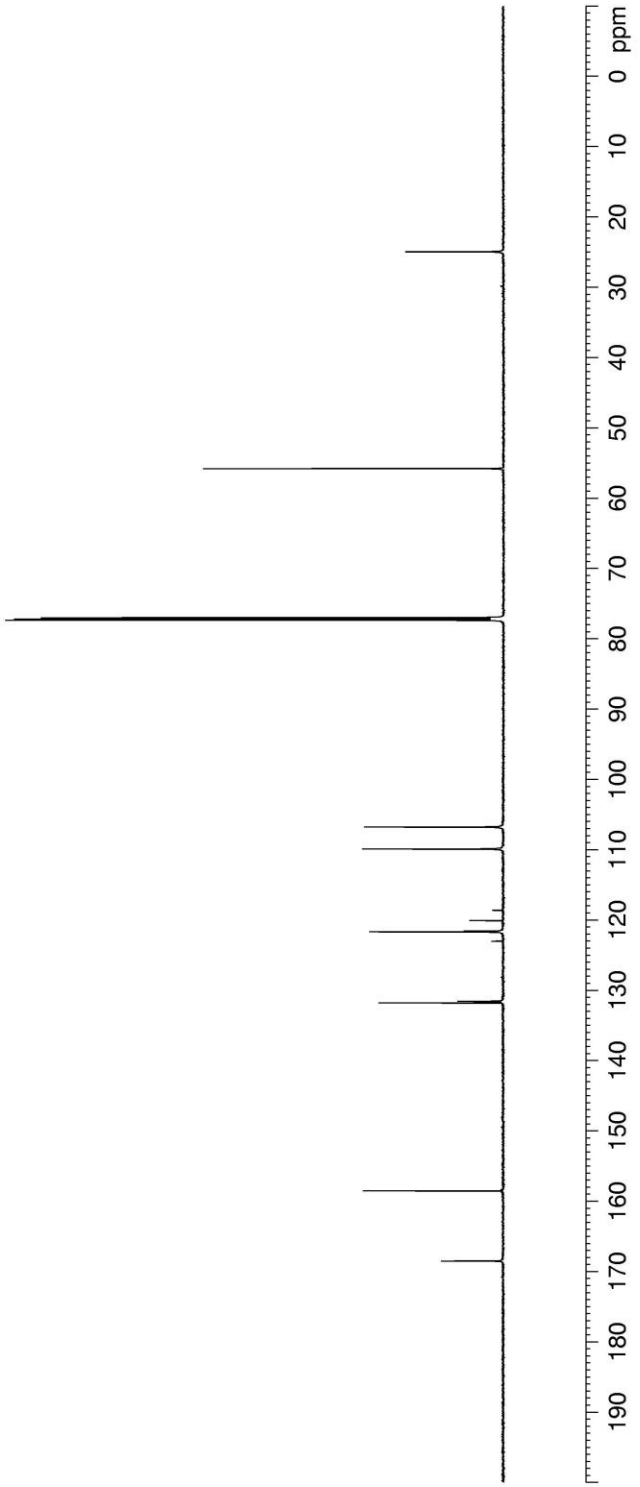


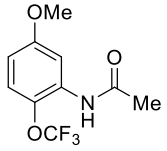
^{13}C NMR ($CDCl_3$, 25 ºC) of **3c**



3c



^{19}F NMR ($CDCl_3$, 25 ºC) of **3c**



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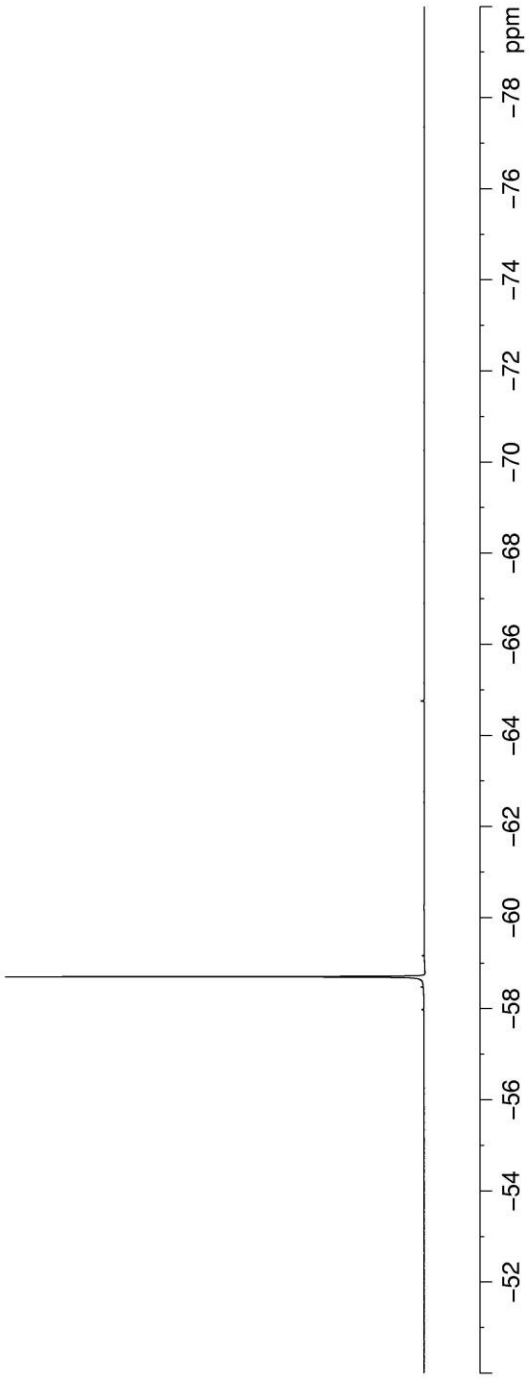
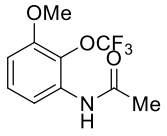
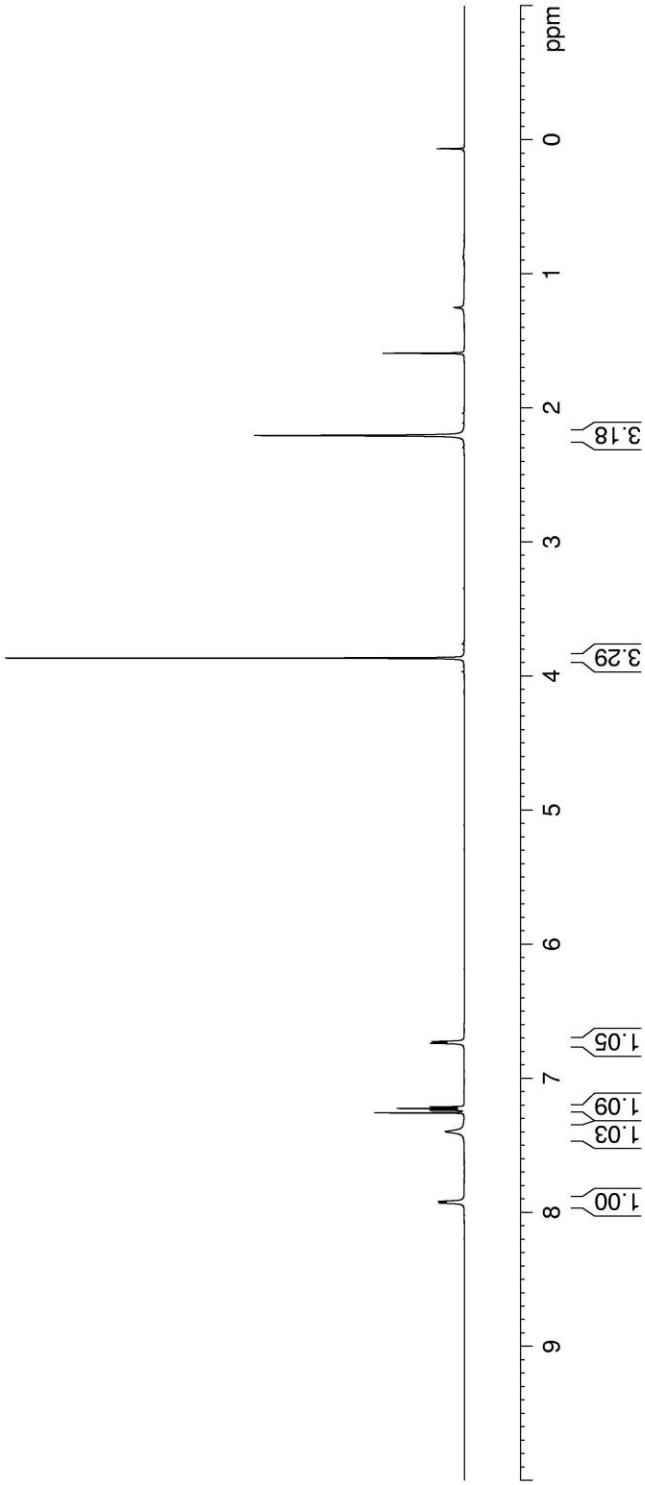


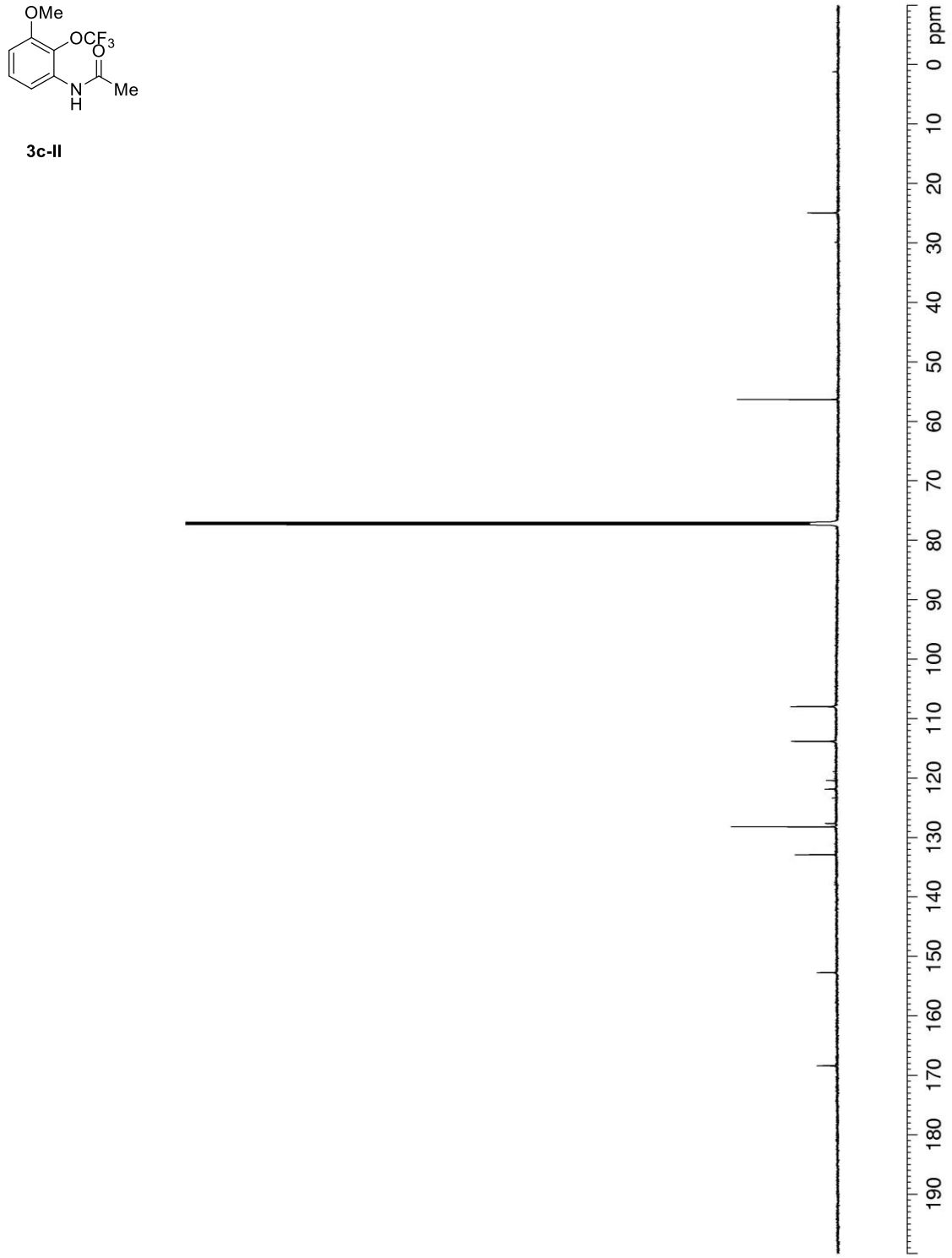
^{1}H NMR ($CDCl_3$, 25 ºC) of **3c-II**



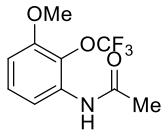
3c-II



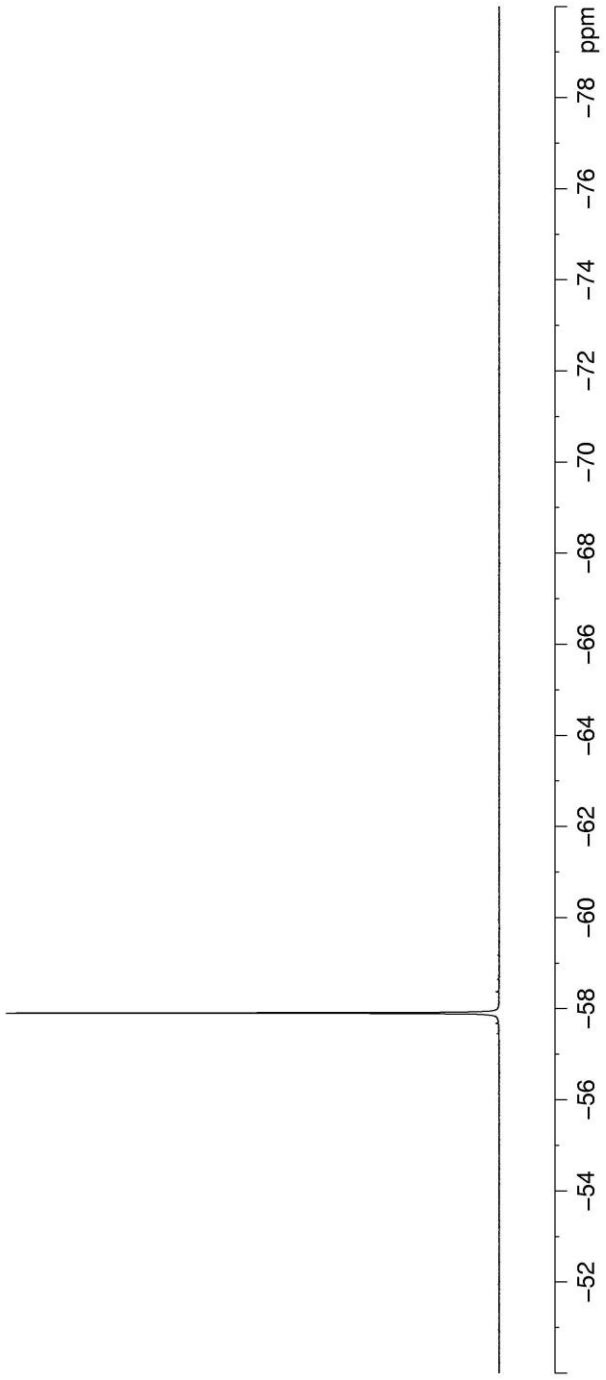
^{13}C NMR ($CDCl_3$, 25 ºC) of **3c-II**



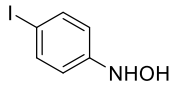
^{19}F NMR ($CDCl_3$, 25 ºC) of **3c-II**



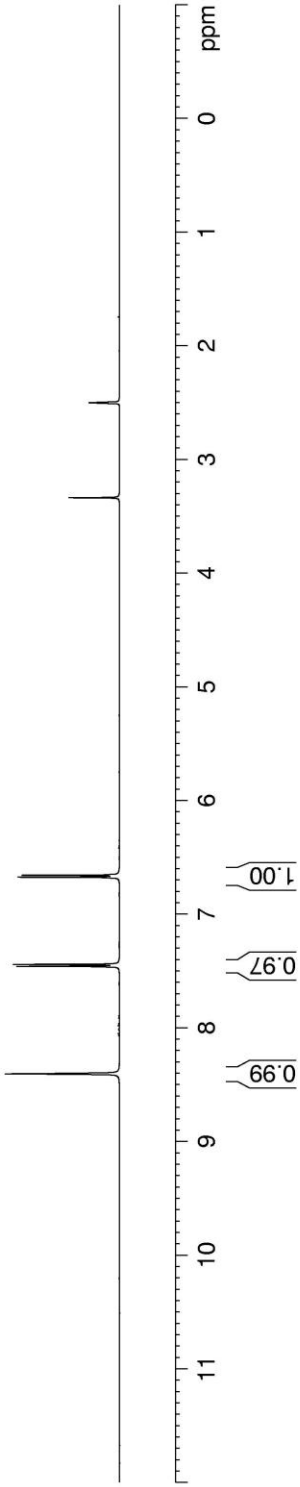
3c-II



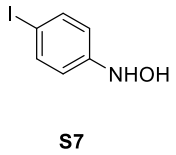
^{1}H NMR ($(CD_3)_2SO$, 25 ºC) of **S7**



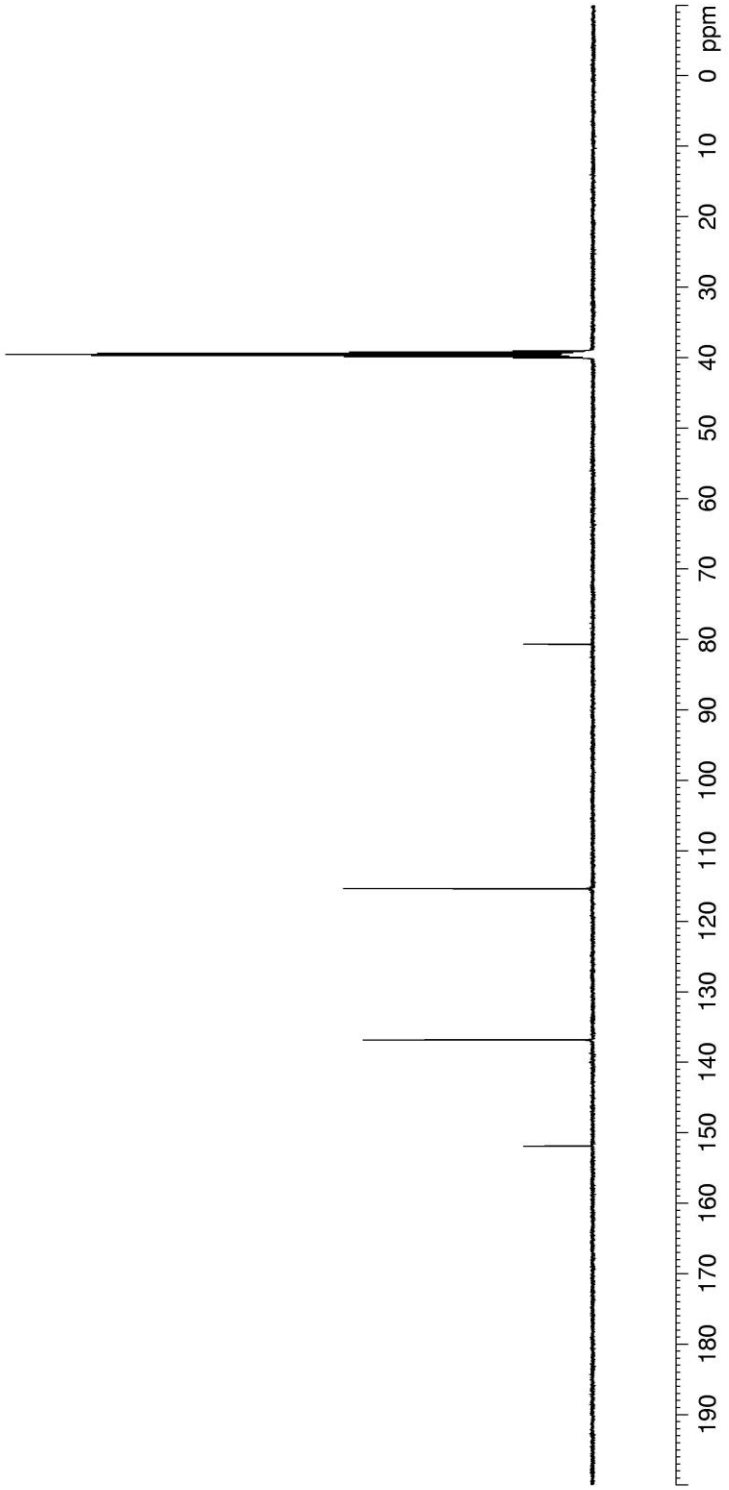
S7



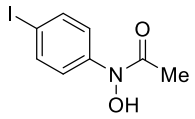
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S7**



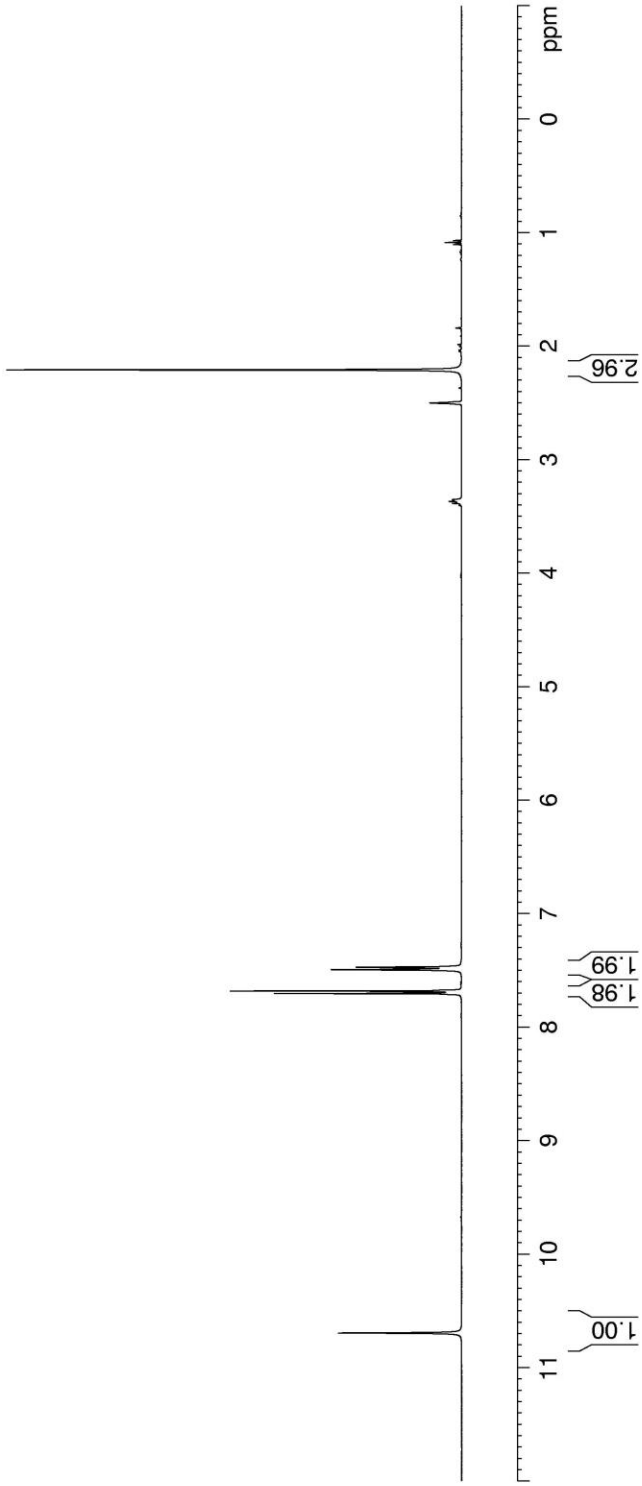
S7



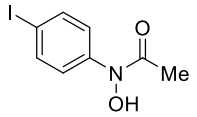
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S8**



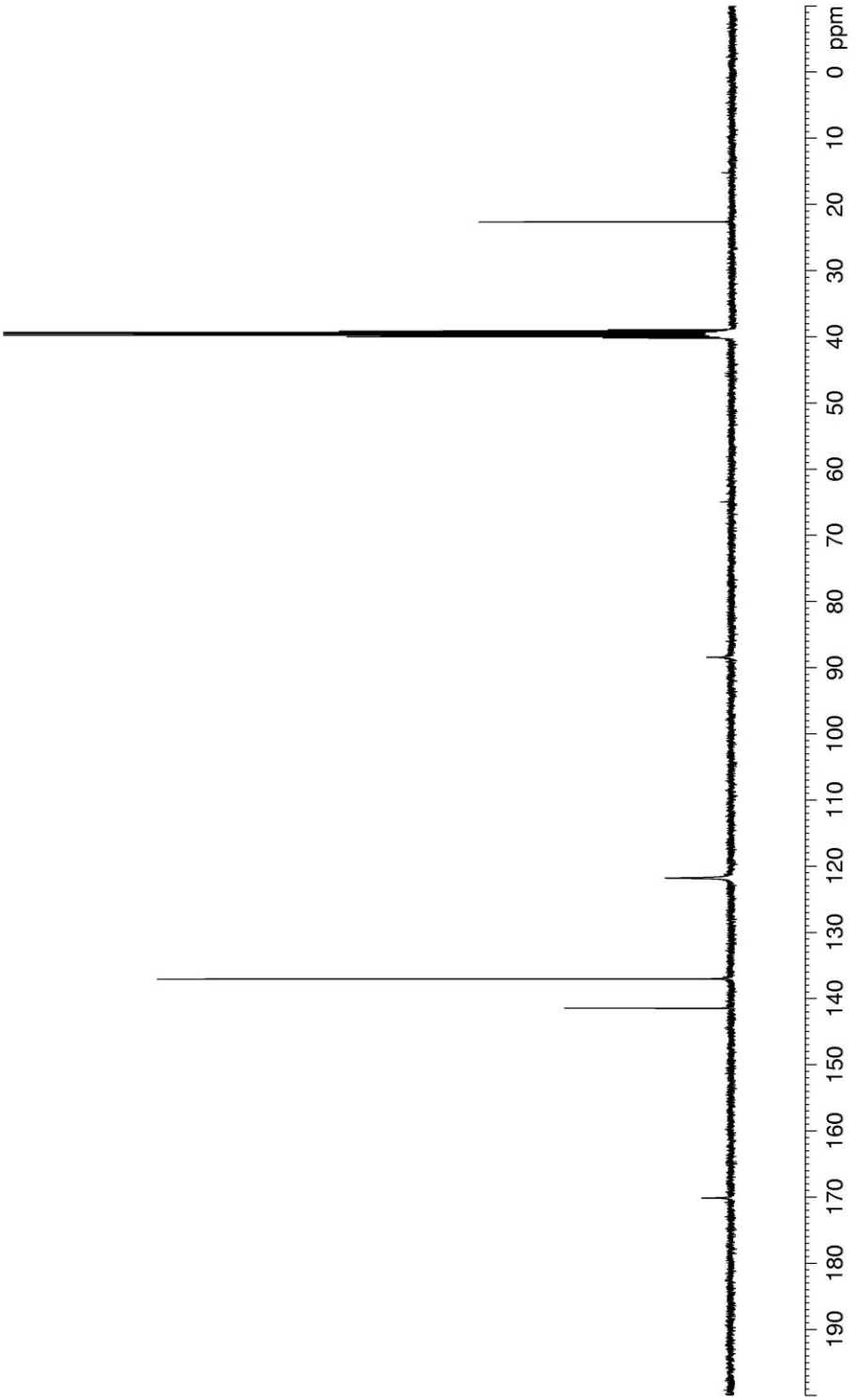
S8



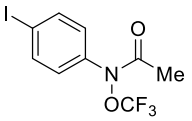
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S8**



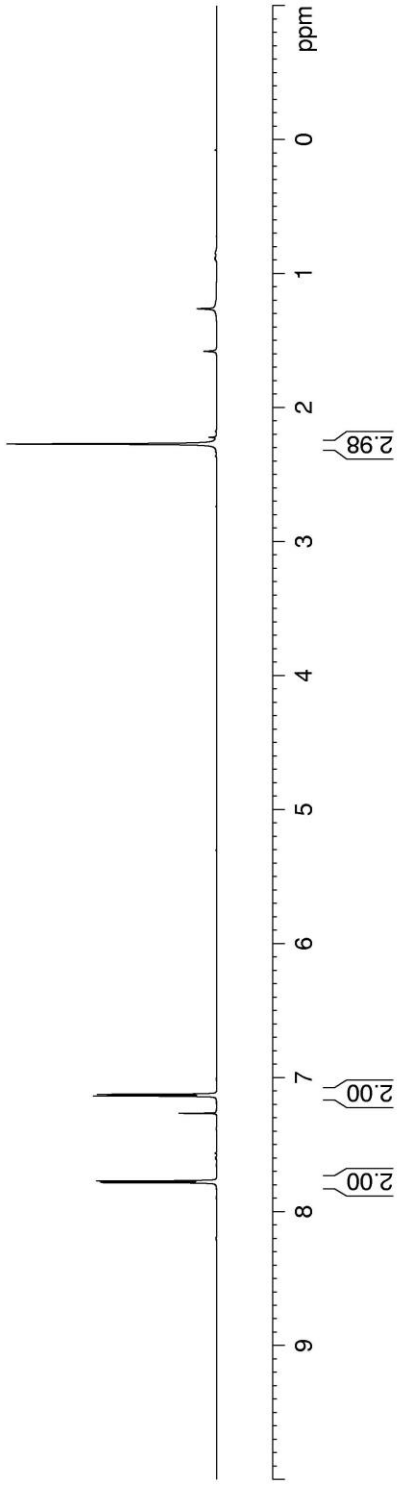
S8



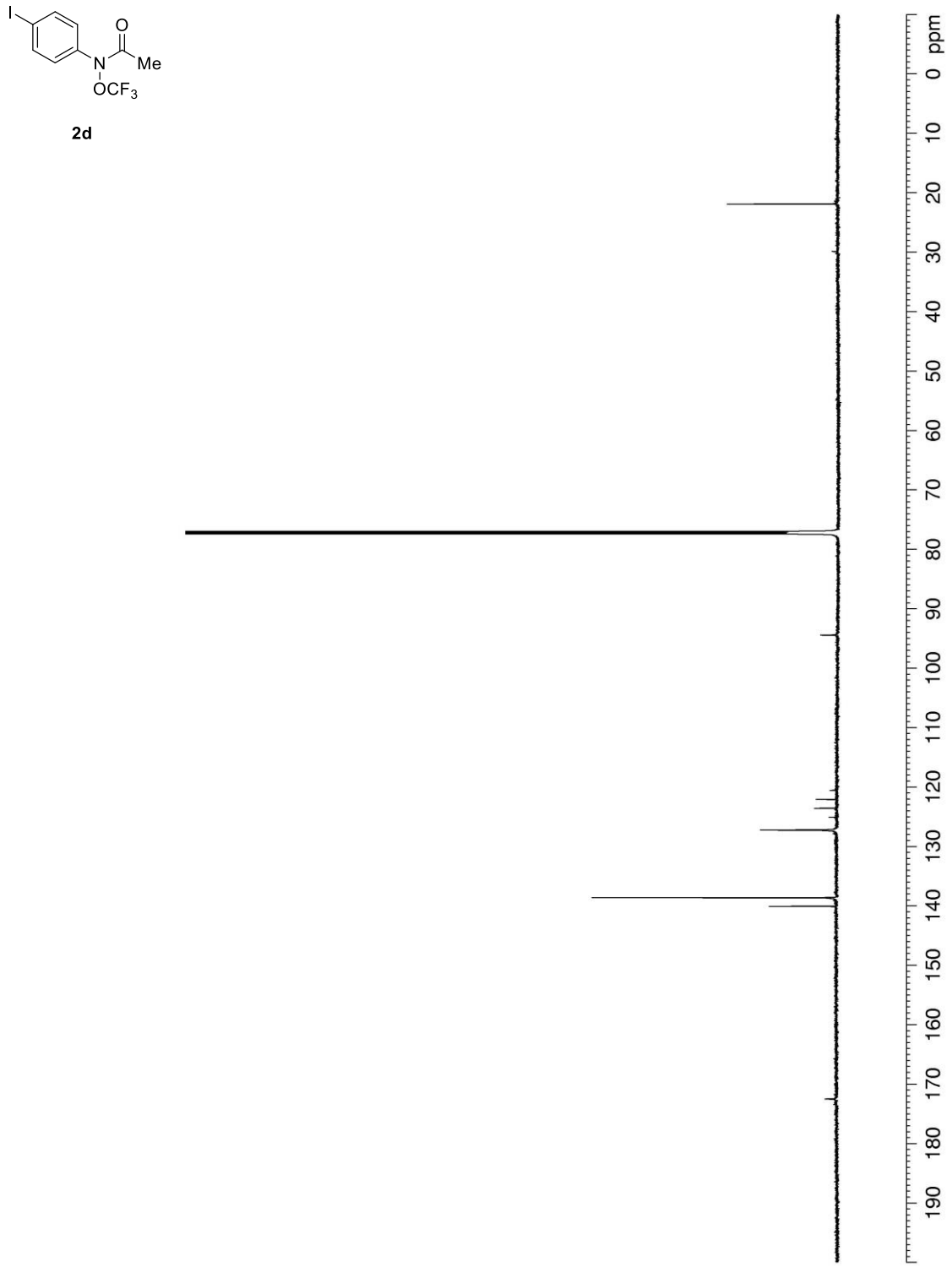
^{1}H NMR ($CDCl_3$, 25 ºC) of **2d**



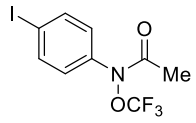
2d



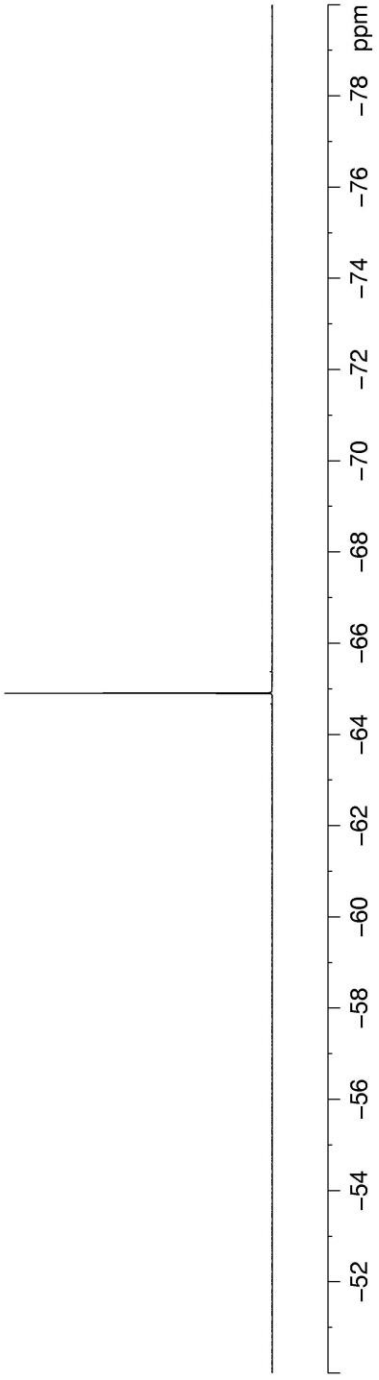
^{13}C NMR ($CDCl_3$, 25 ºC) of **2d**



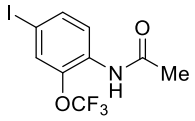
^{19}F NMR ($CDCl_3$, 25 ºC) of **2d**



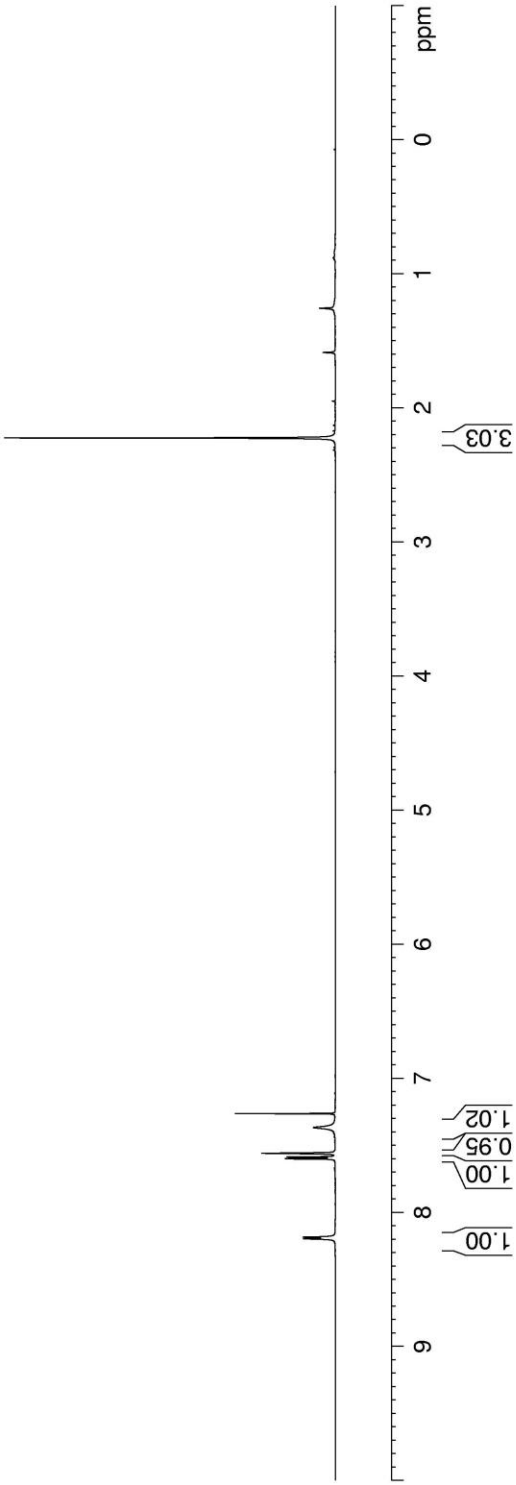
2d



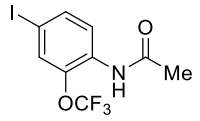
^{1}H NMR ($CDCl_3$, 25 ºC) of **3d**



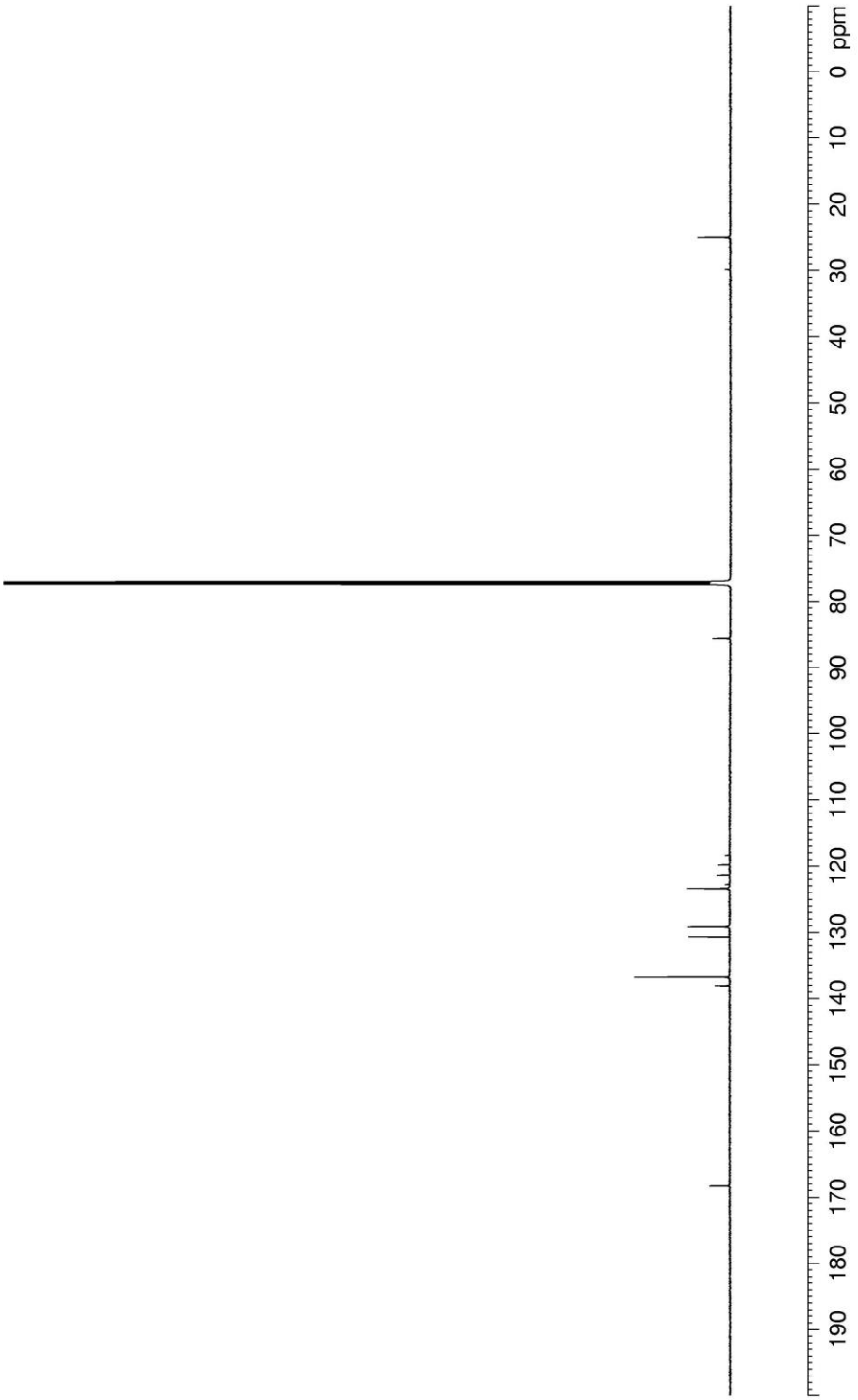
3d



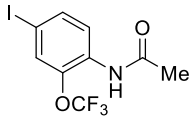
^{13}C NMR ($CDCl_3$, 25 ºC) of **3d**



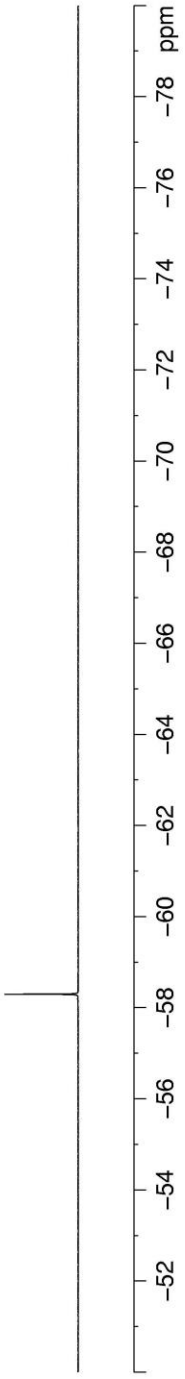
3d



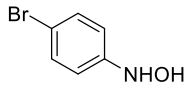
^{19}F NMR ($CDCl_3$, 25 ºC) of **3d**



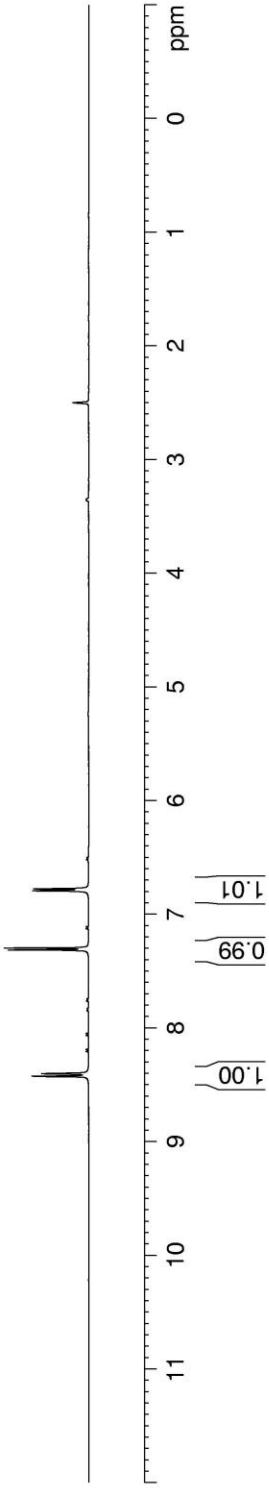
3d



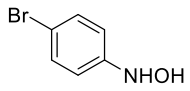
^{1}H NMR ($(CD_3)_2SO$, 25 ºC) of **S9**



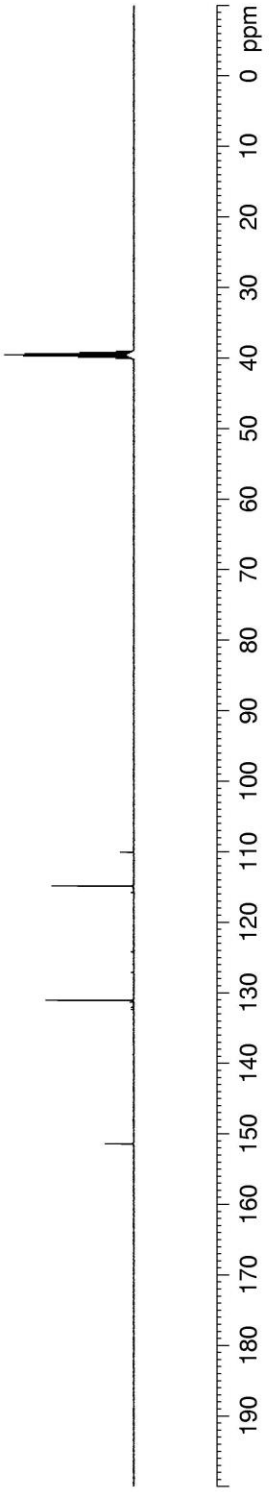
S9



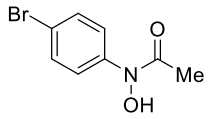
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S9**



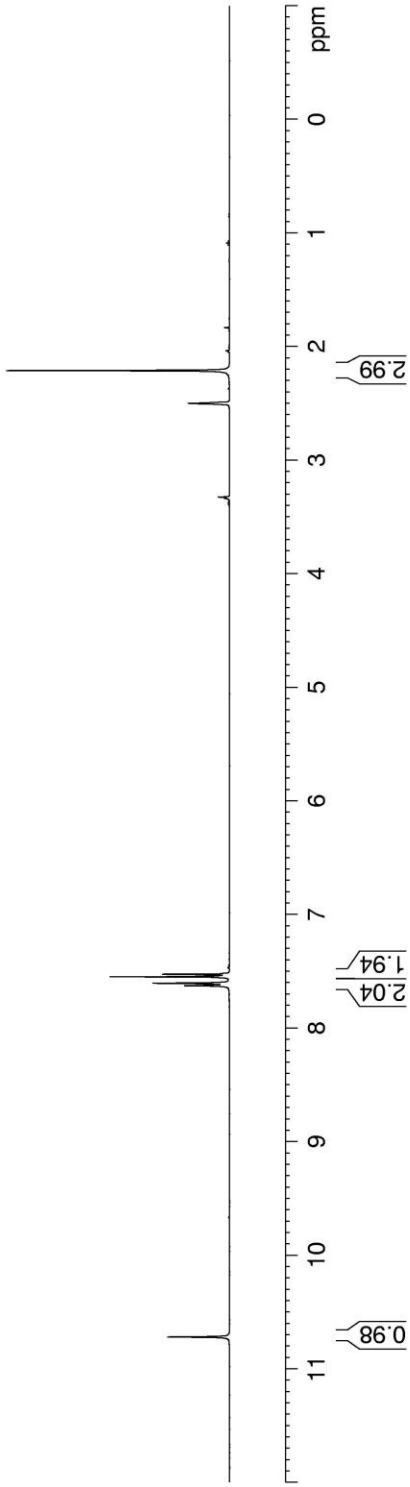
S9



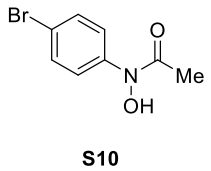
^{1}H NMR ($(CD_3)_2SO$, 25 ºC) of **S10**



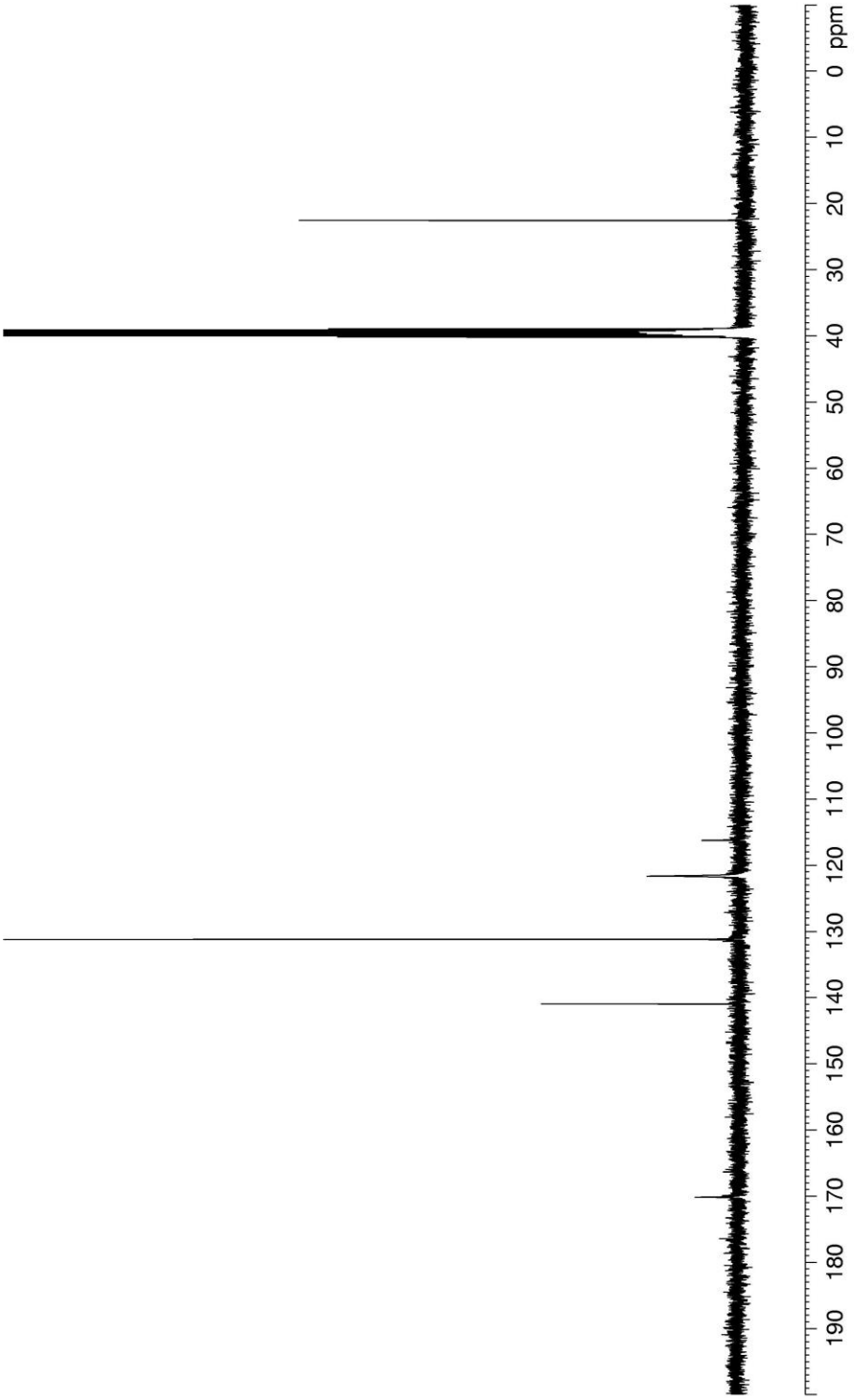
S10



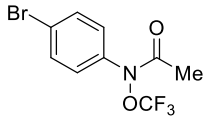
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S10**



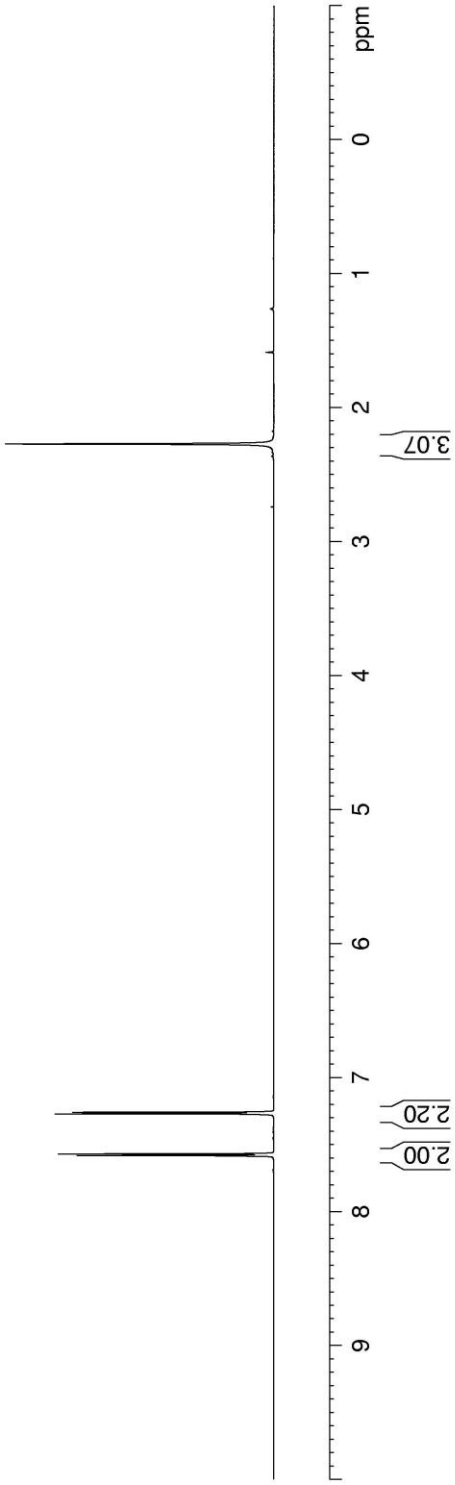
S10



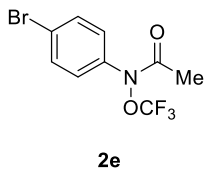
^{1}H NMR ($CDCl_3$, 25 ºC) of **2e**



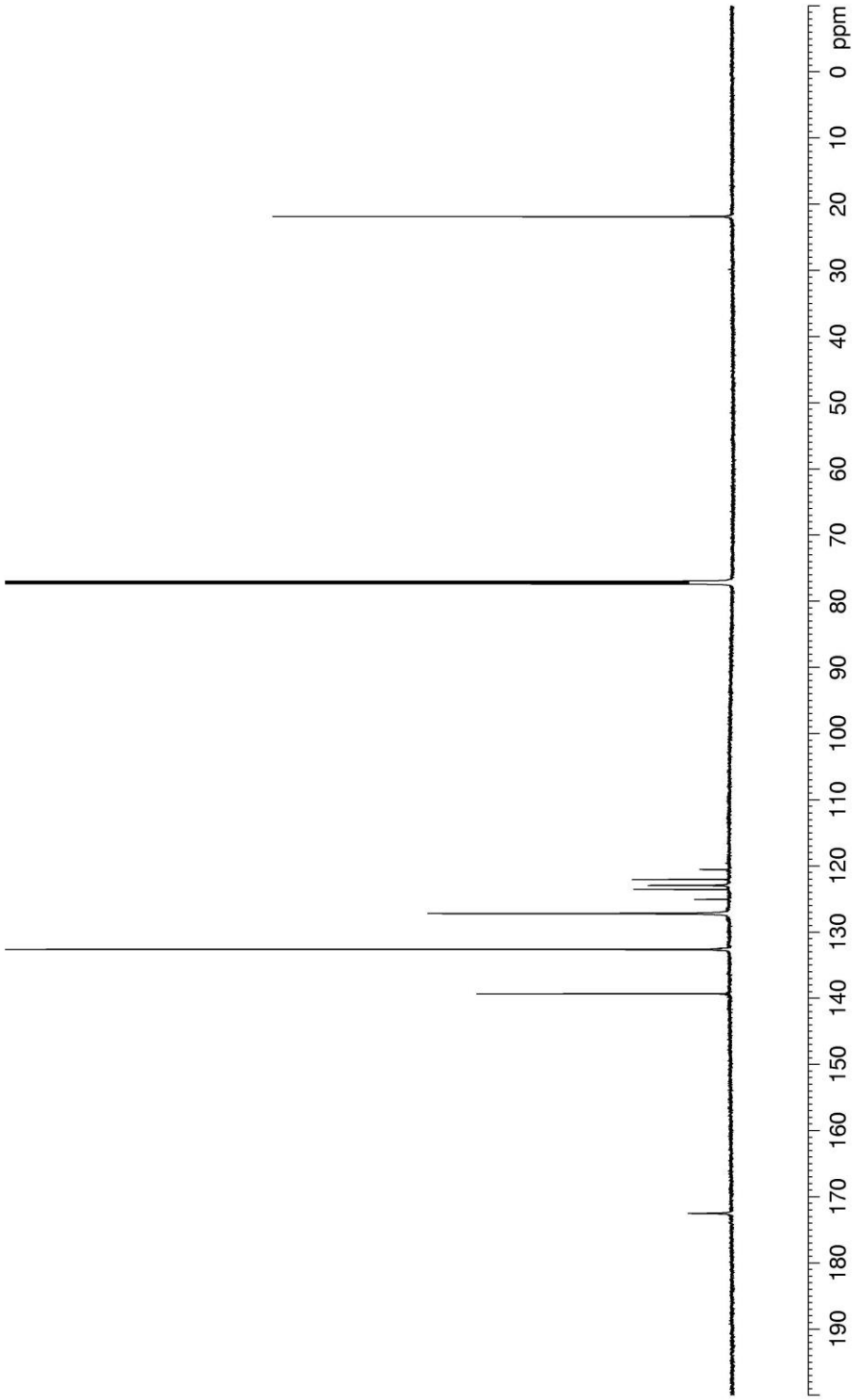
2e



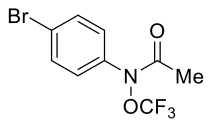
^{13}C NMR ($CDCl_3$, 25 ºC) of **2e**



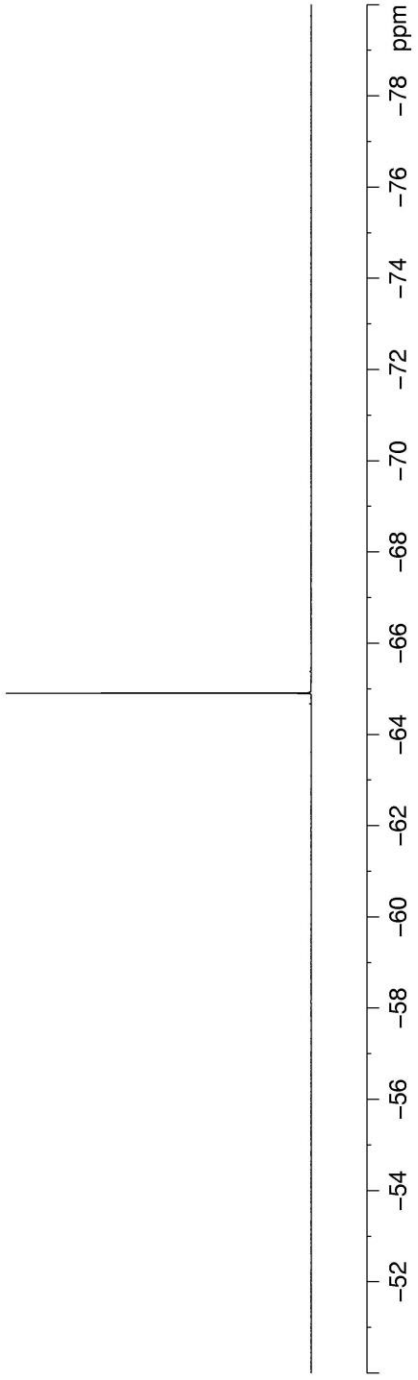
2e



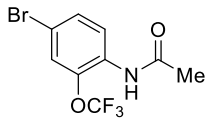
^{19}F NMR ($CDCl_3$, 25 ºC) of **2e**



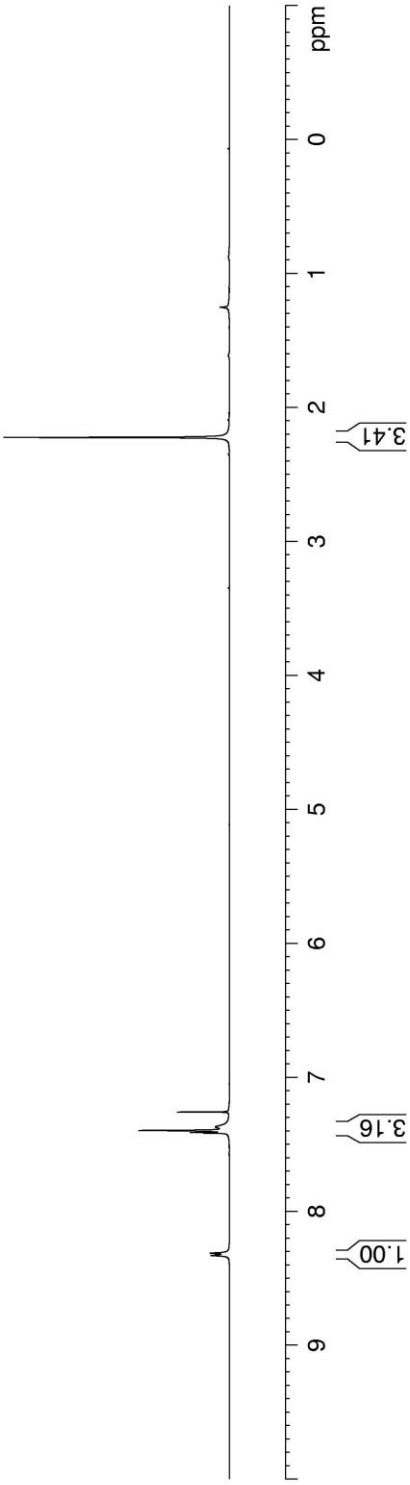
2e



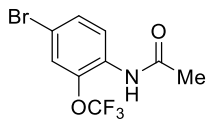
^{1}H NMR ($CDCl_3$, 25 ºC) of **3e**



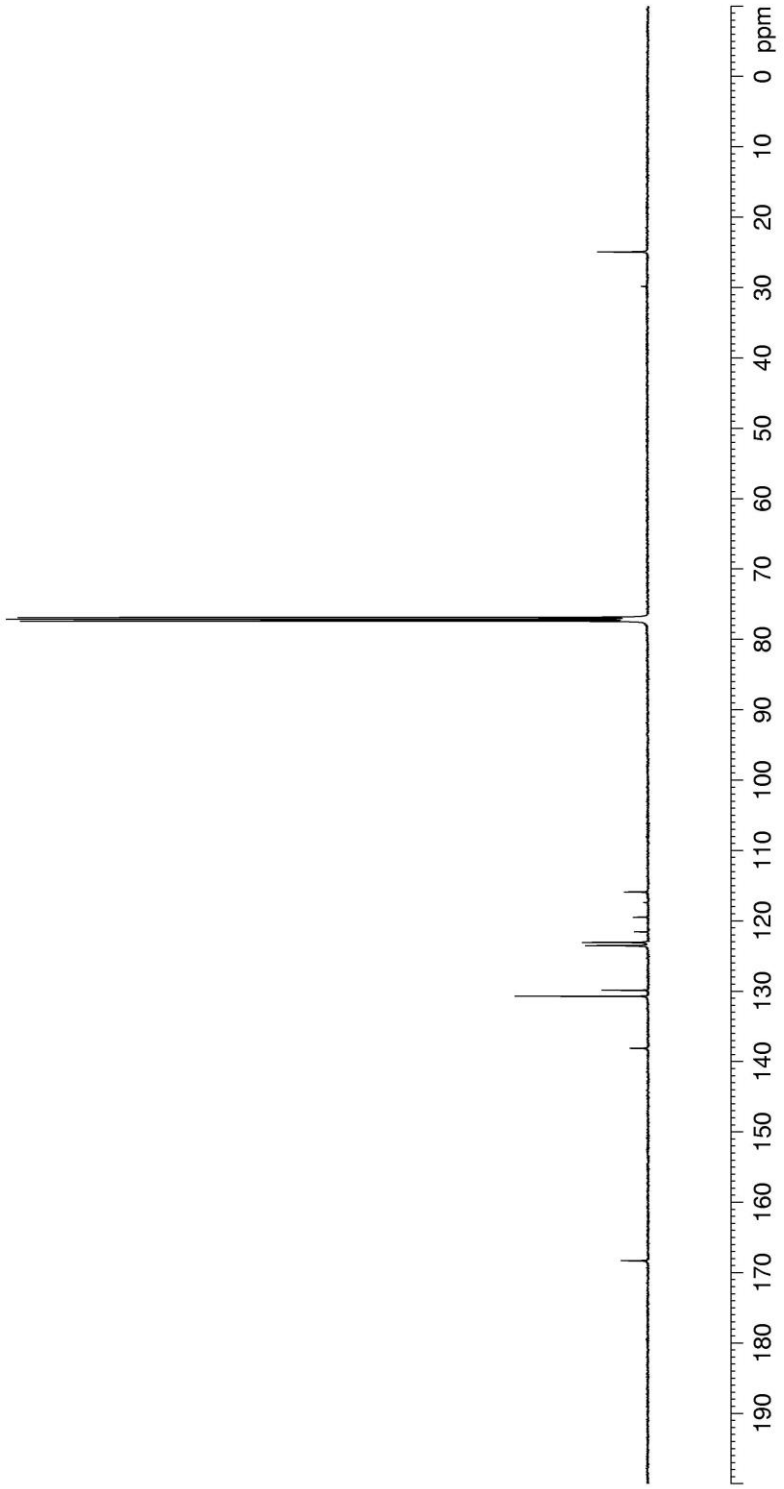
3e



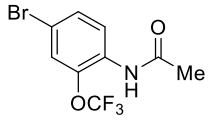
^{13}C NMR ($CDCl_3$, 25 ºC) of **3e**



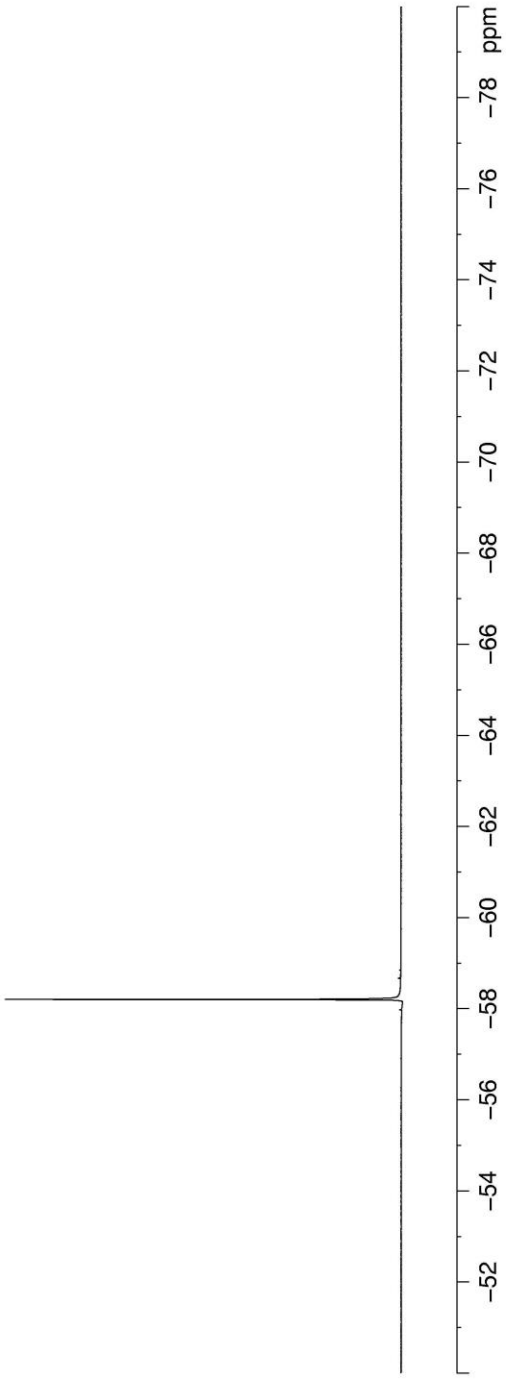
3e



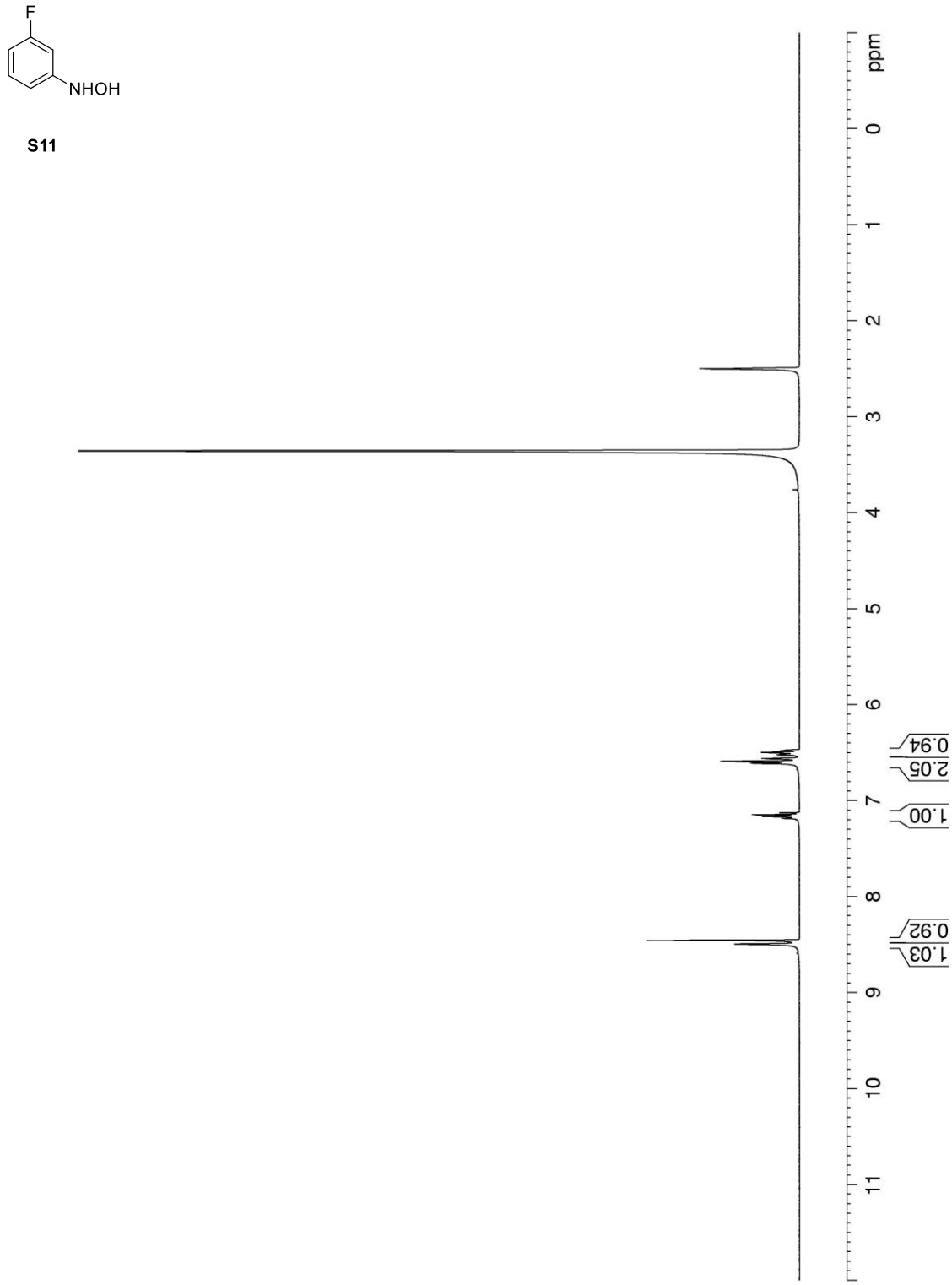
^{19}F NMR ($CDCl_3$, 25 ºC) of **3e**



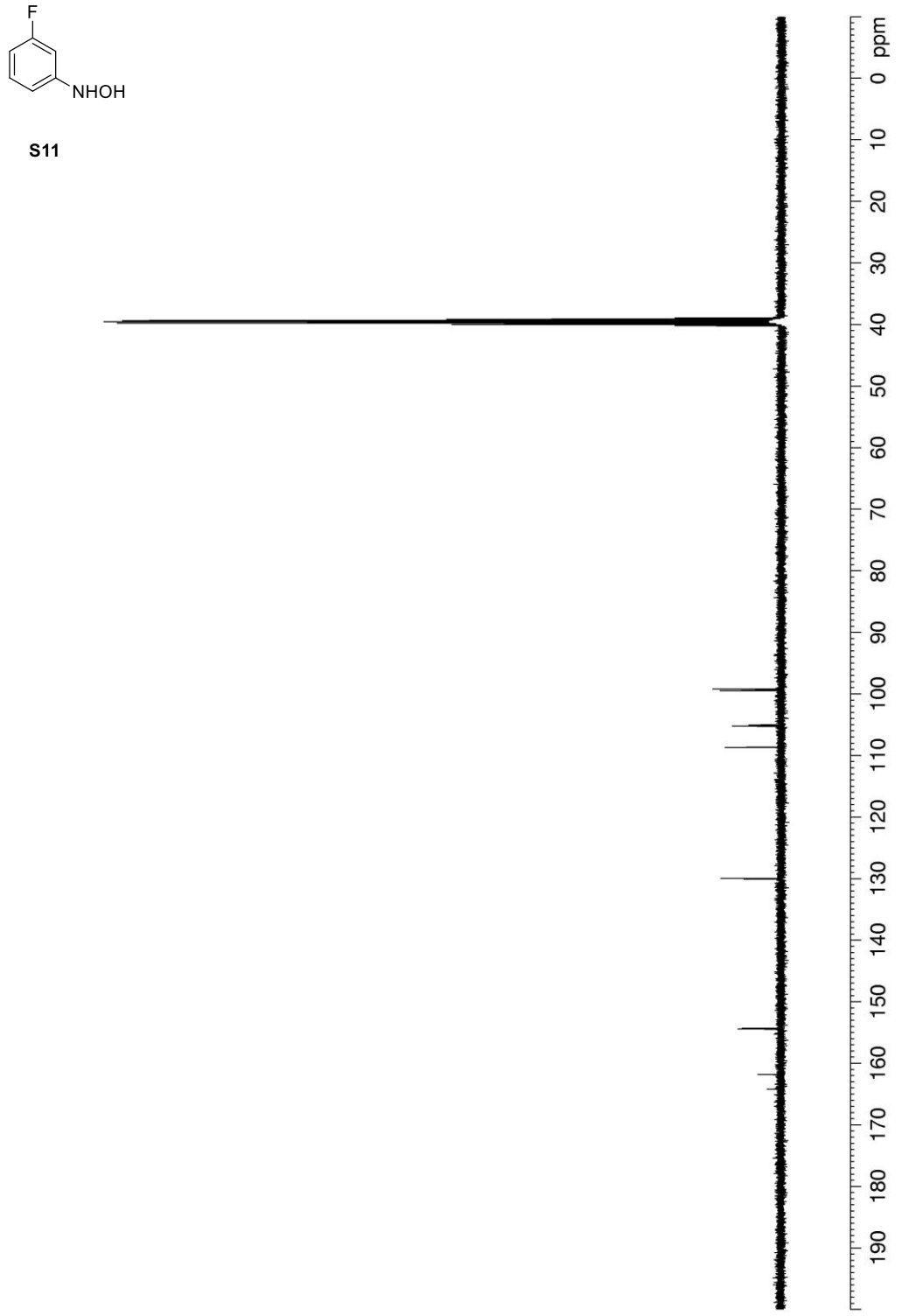
3e



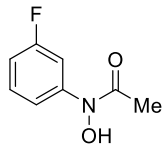
^{1}H NMR ($(CD_3)_2SO$, 25 ºC) of **S11**



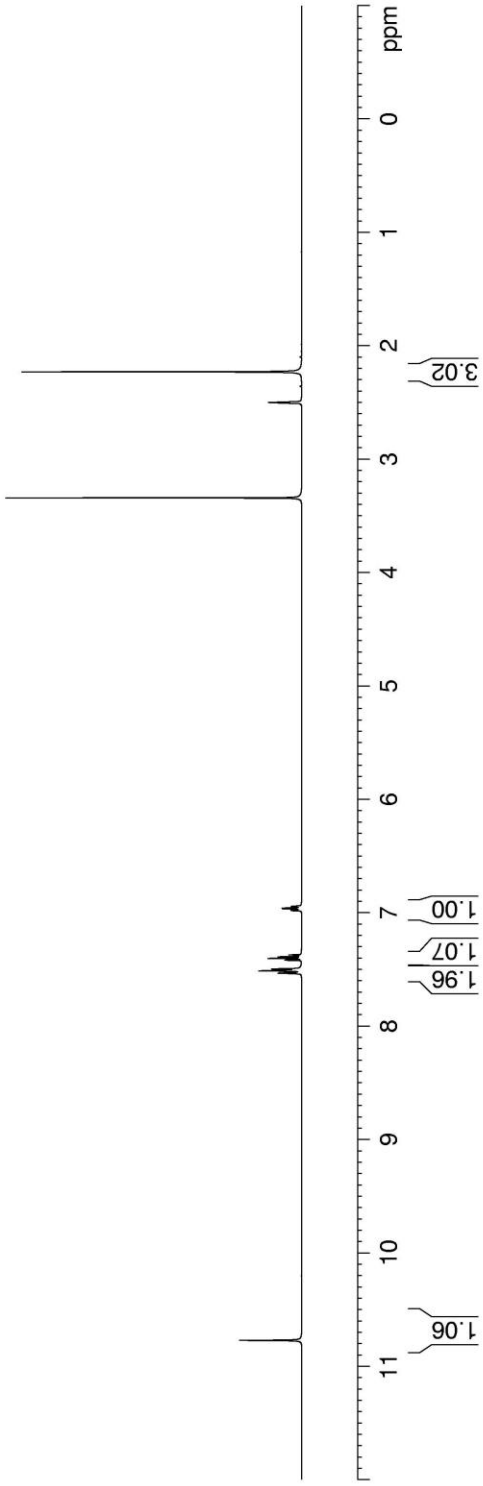
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S11**



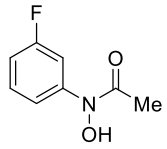
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S12**



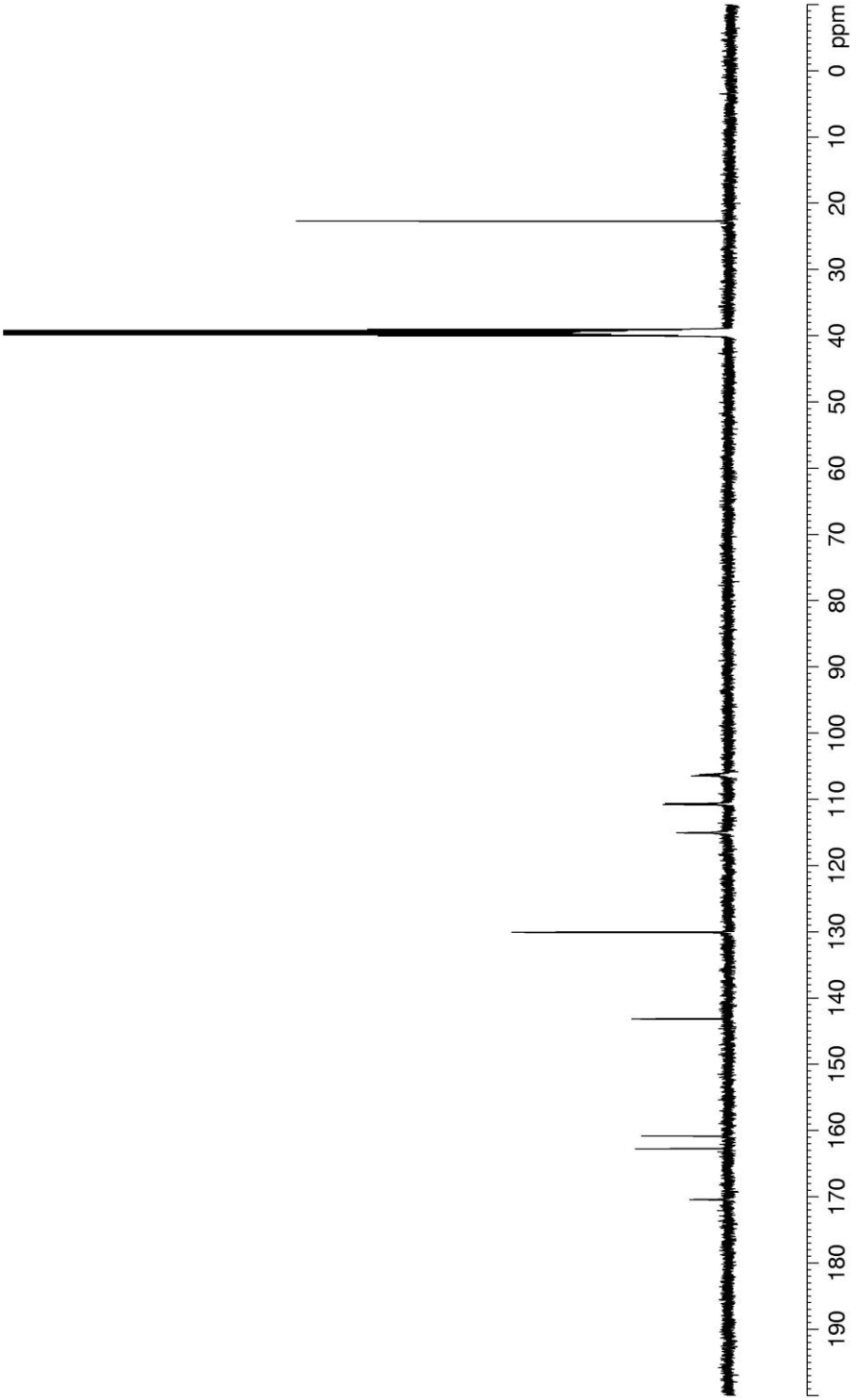
S12



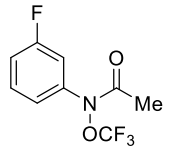
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S12**



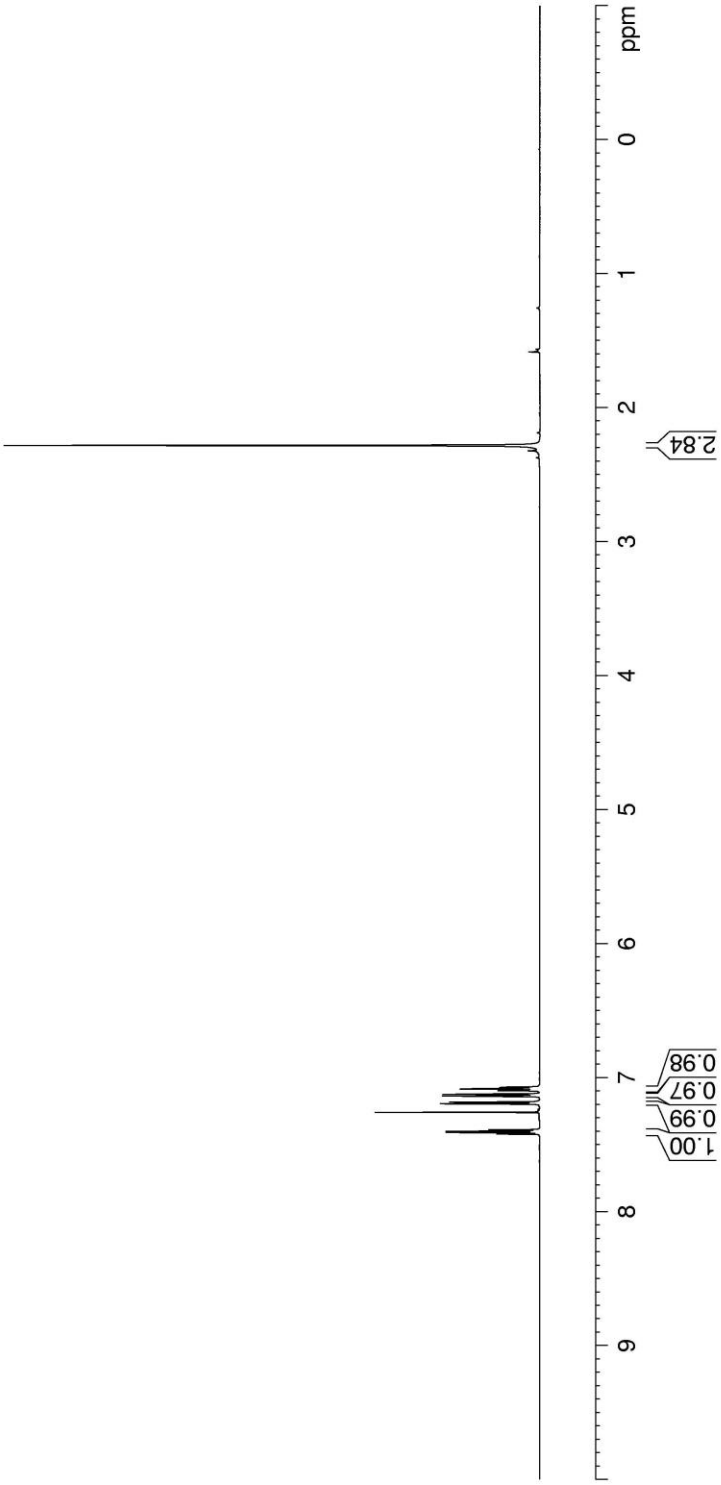
S12



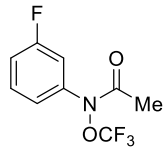
^{1}H NMR ($CDCl_3$, 25 ºC) of **2f**



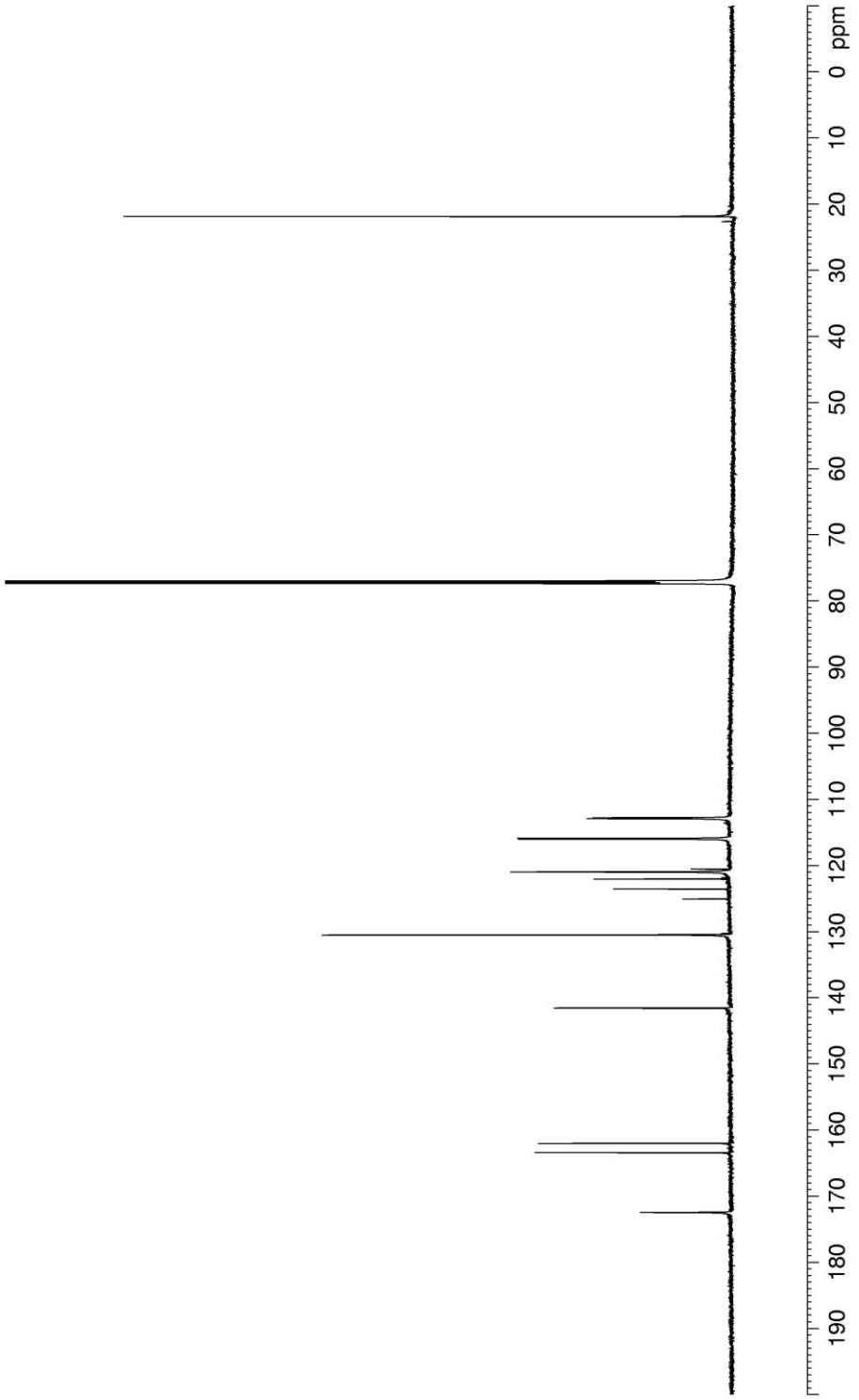
2f



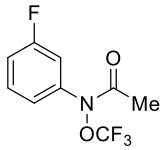
^{13}C NMR ($CDCl_3$, 25 ºC) of **2f**



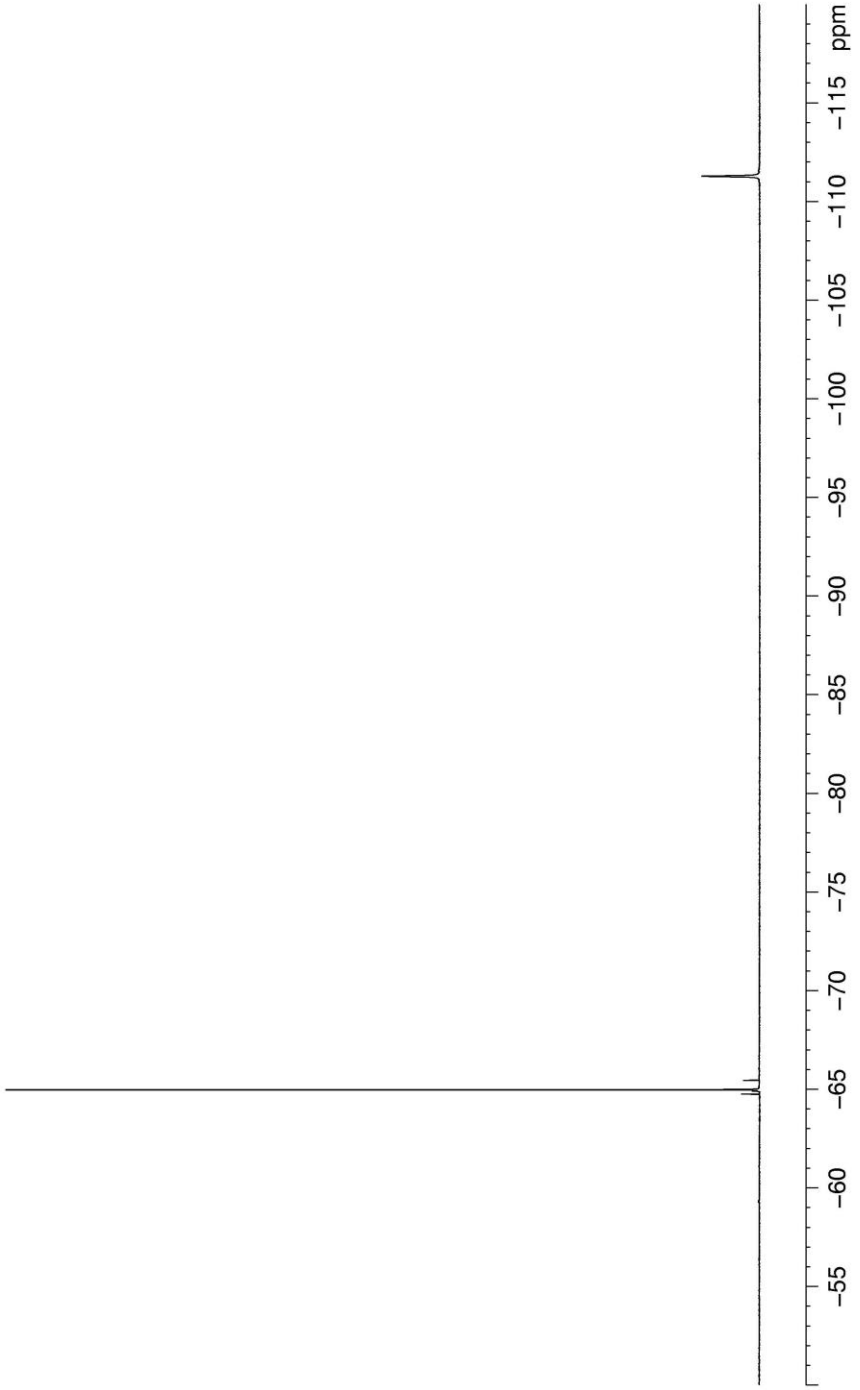
2f



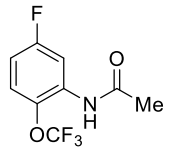
^{19}F NMR ($CDCl_3$, 25 ºC) of **2f**



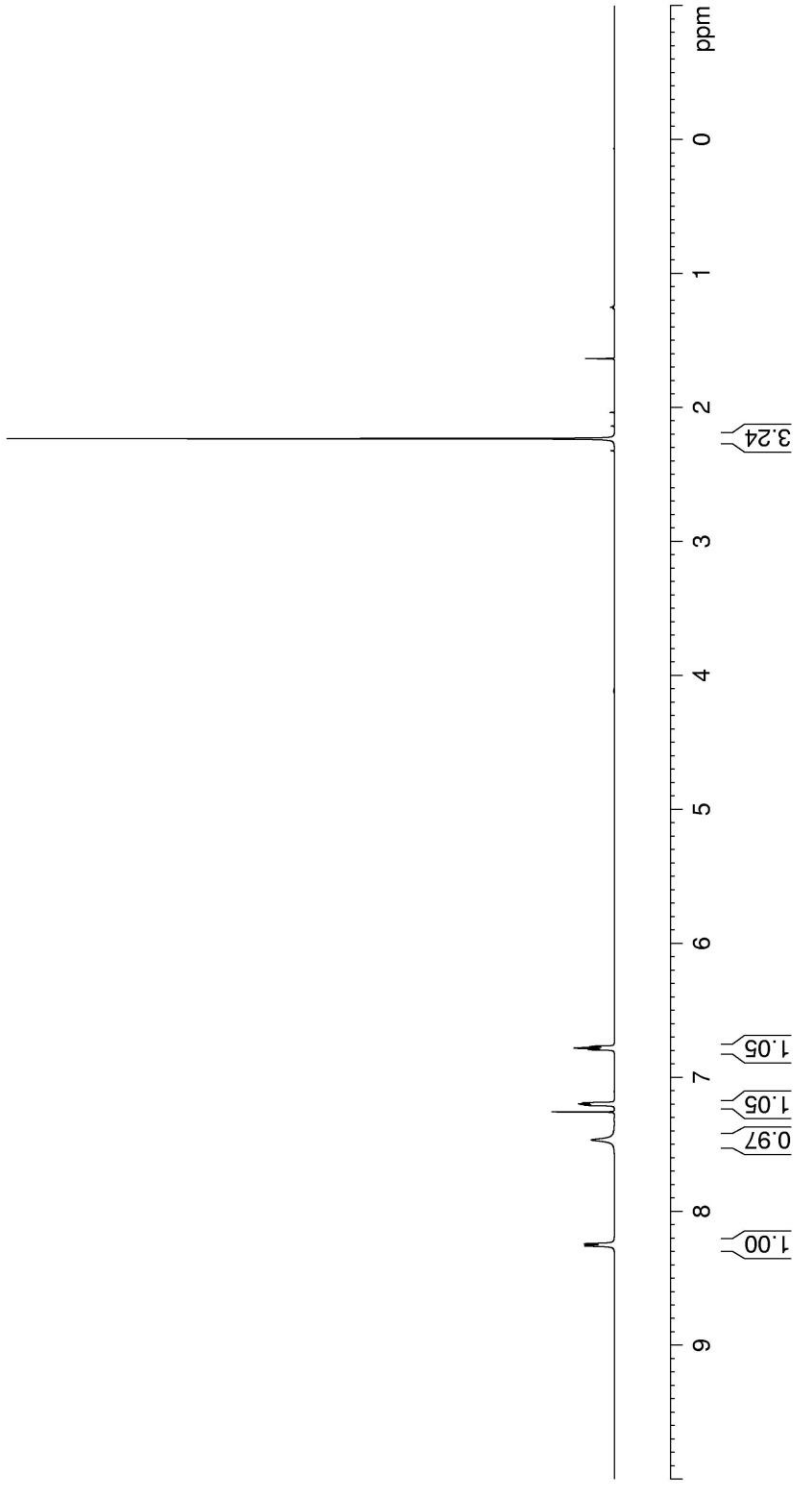
2f



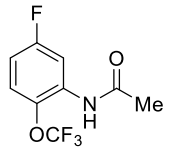
^{1}H NMR ($CDCl_3$, 25 ºC) of **3f**



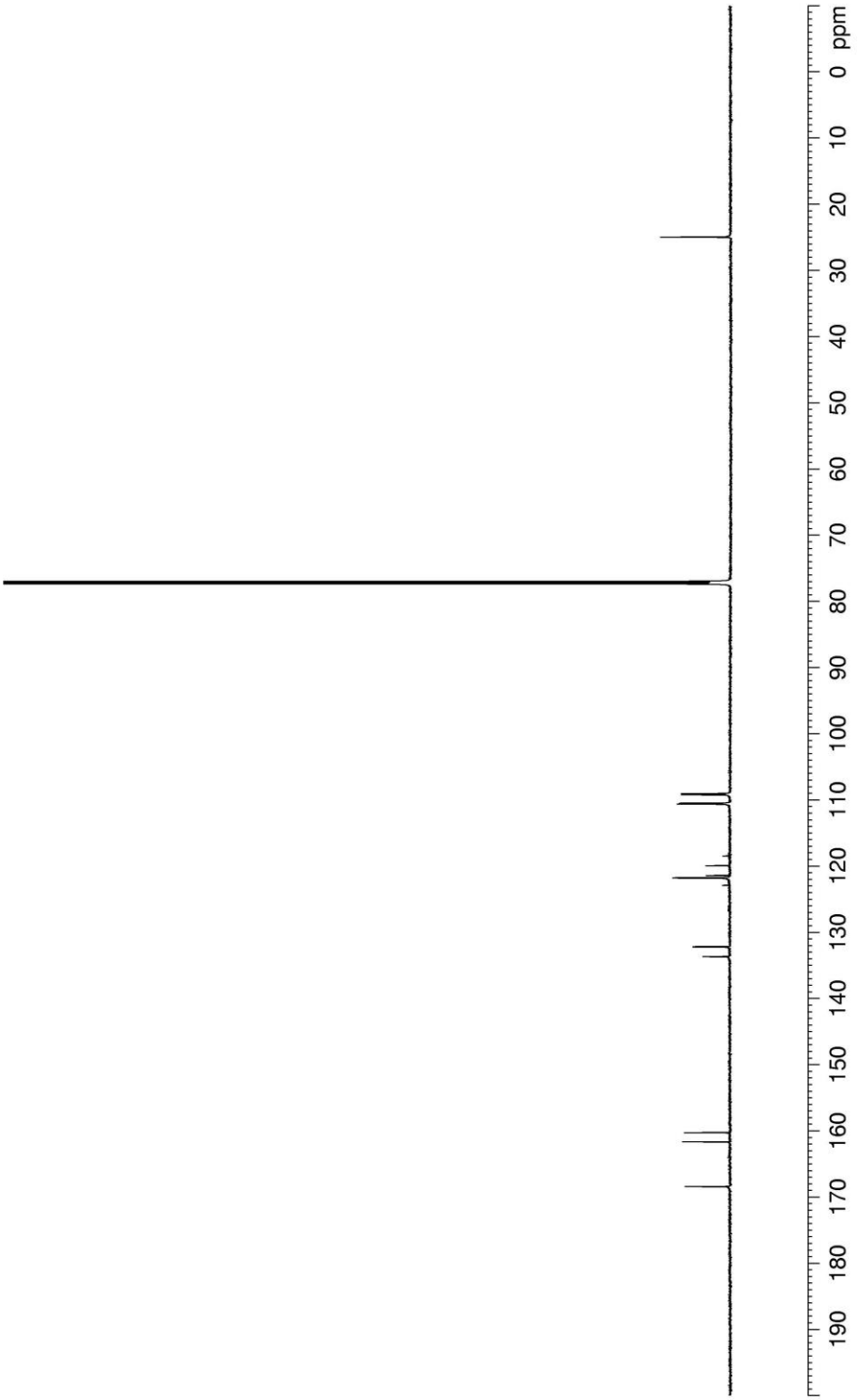
3f



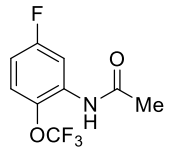
^{13}C NMR ($CDCl_3$, 25 ºC) of **3f**



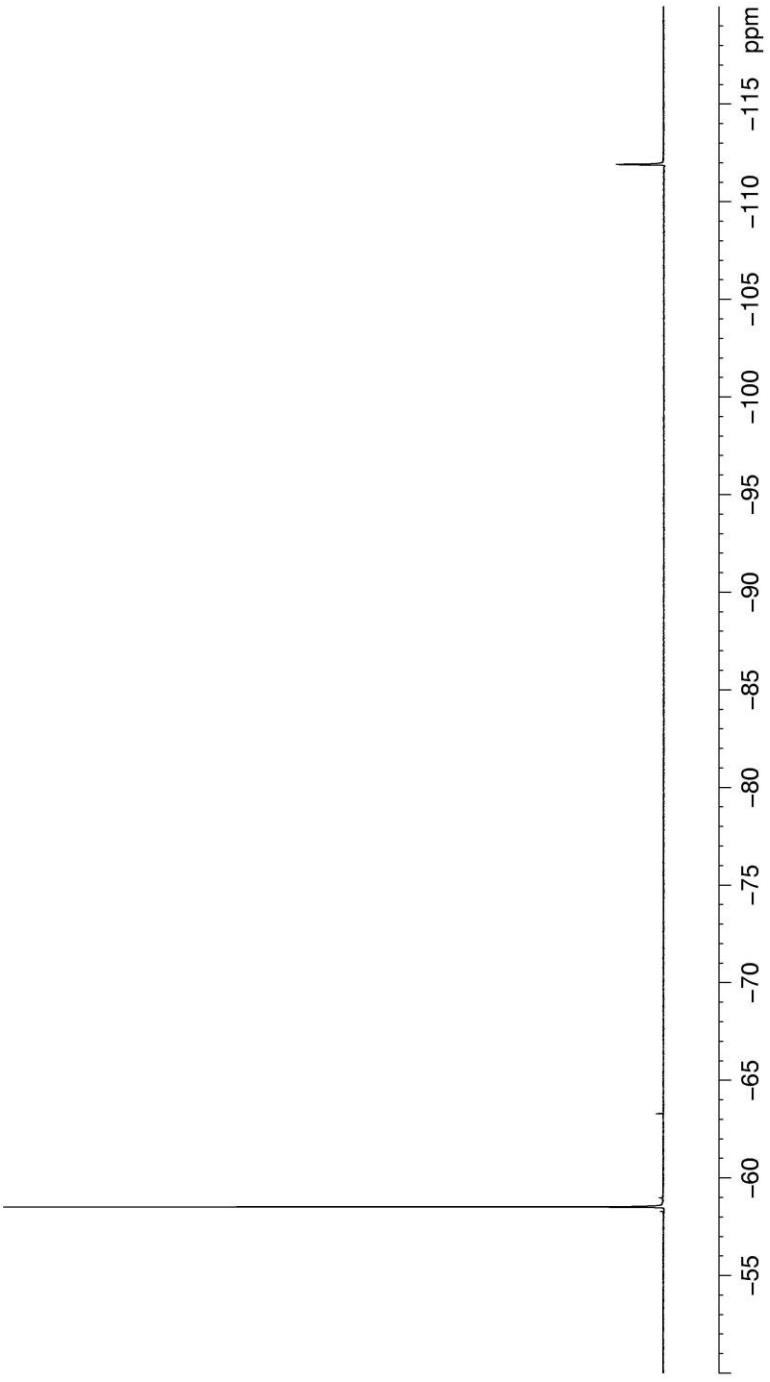
3f



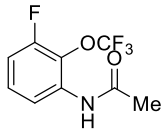
^{19}F NMR ($CDCl_3$, 25 ºC) of **3f**



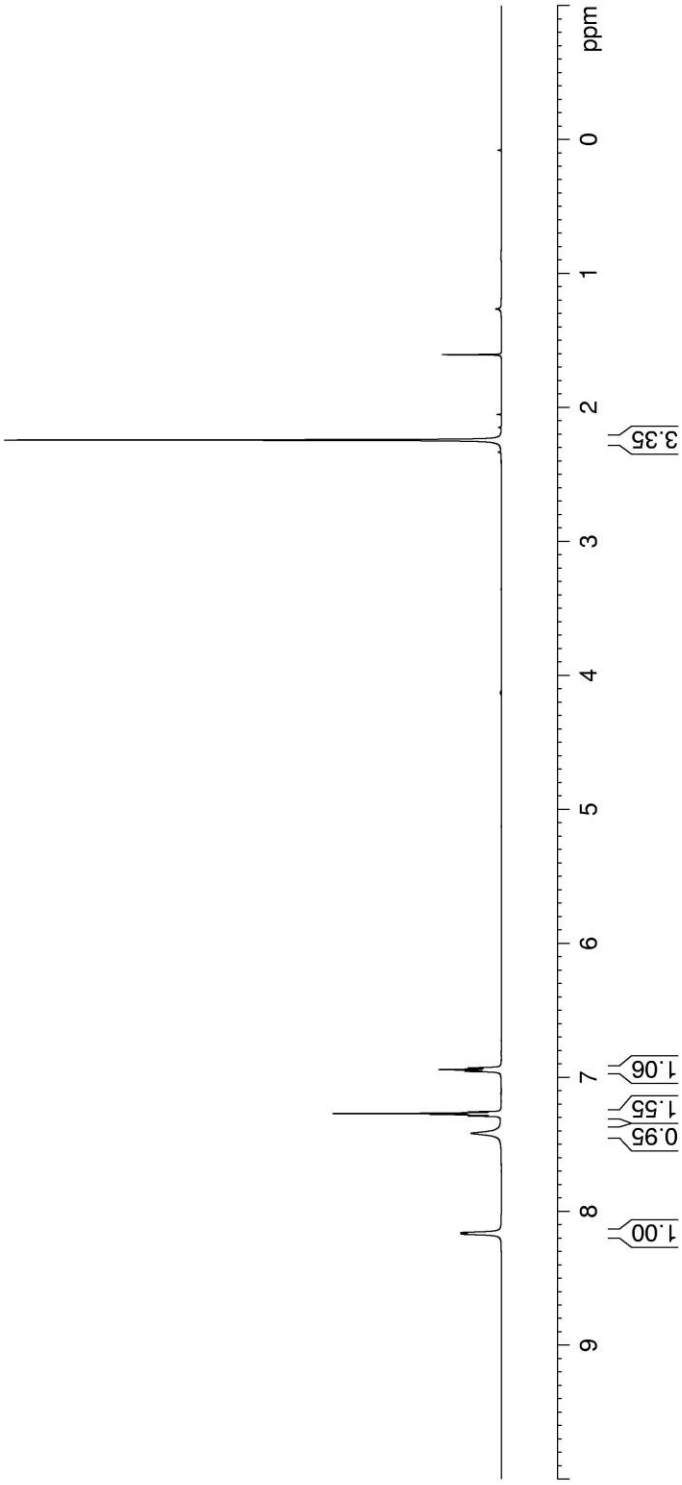
3f



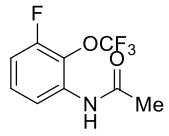
^{1}H NMR ($CDCl_3$, 25 ºC) of **3f-II**



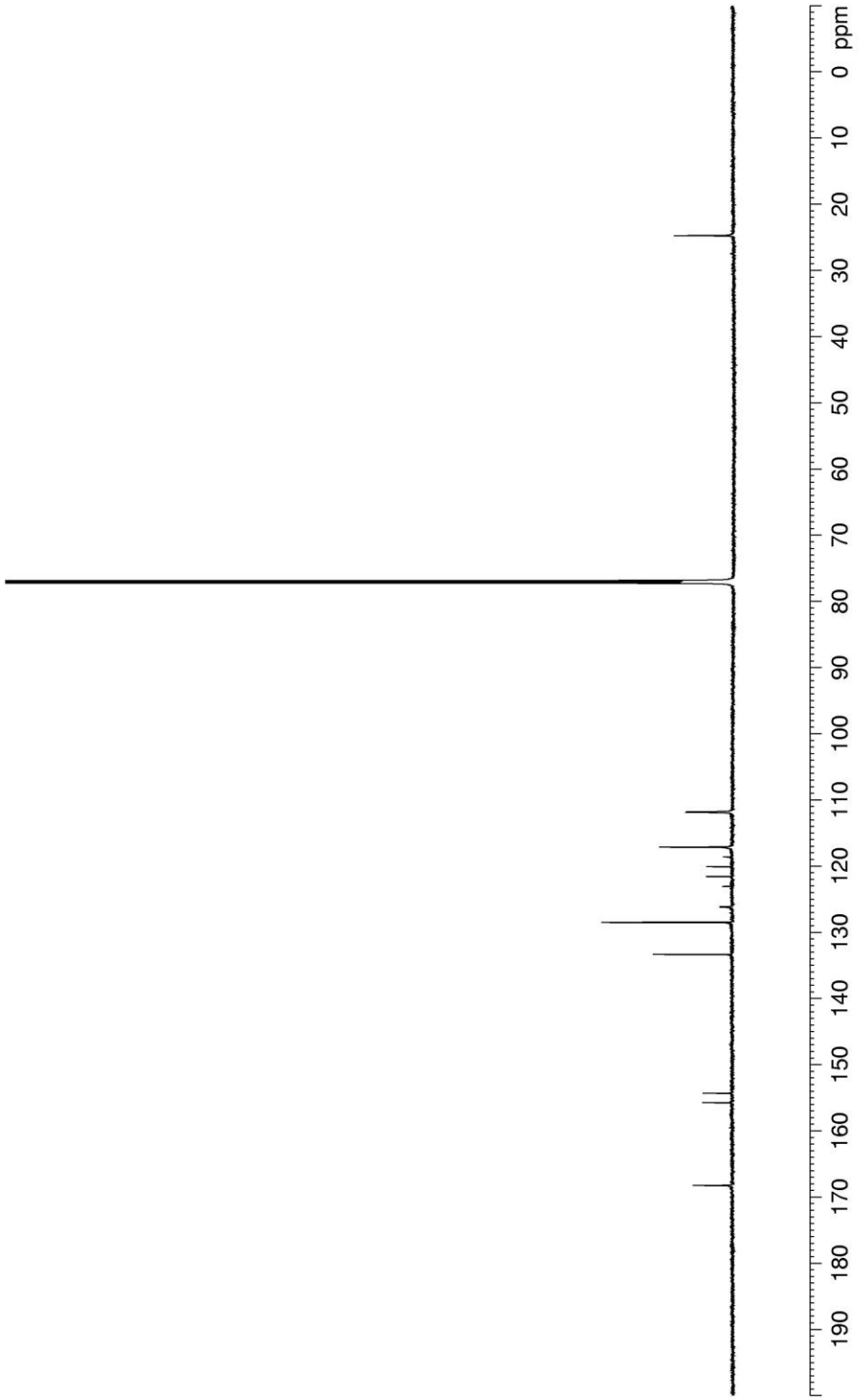
3f-II



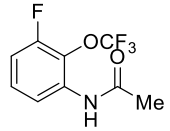
^{13}C NMR ($CDCl_3$, 25 ºC) of **3f-II**



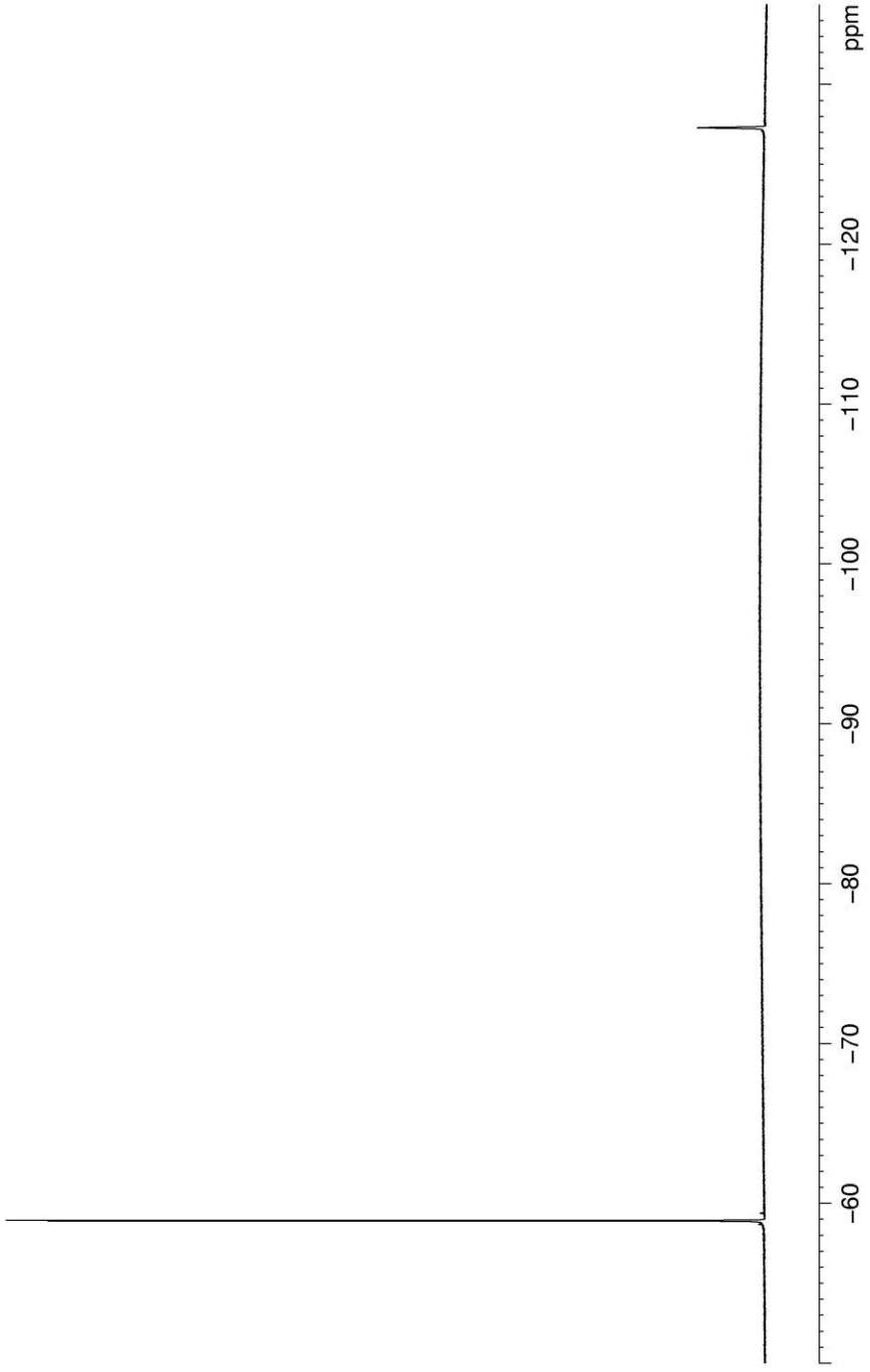
3f-II



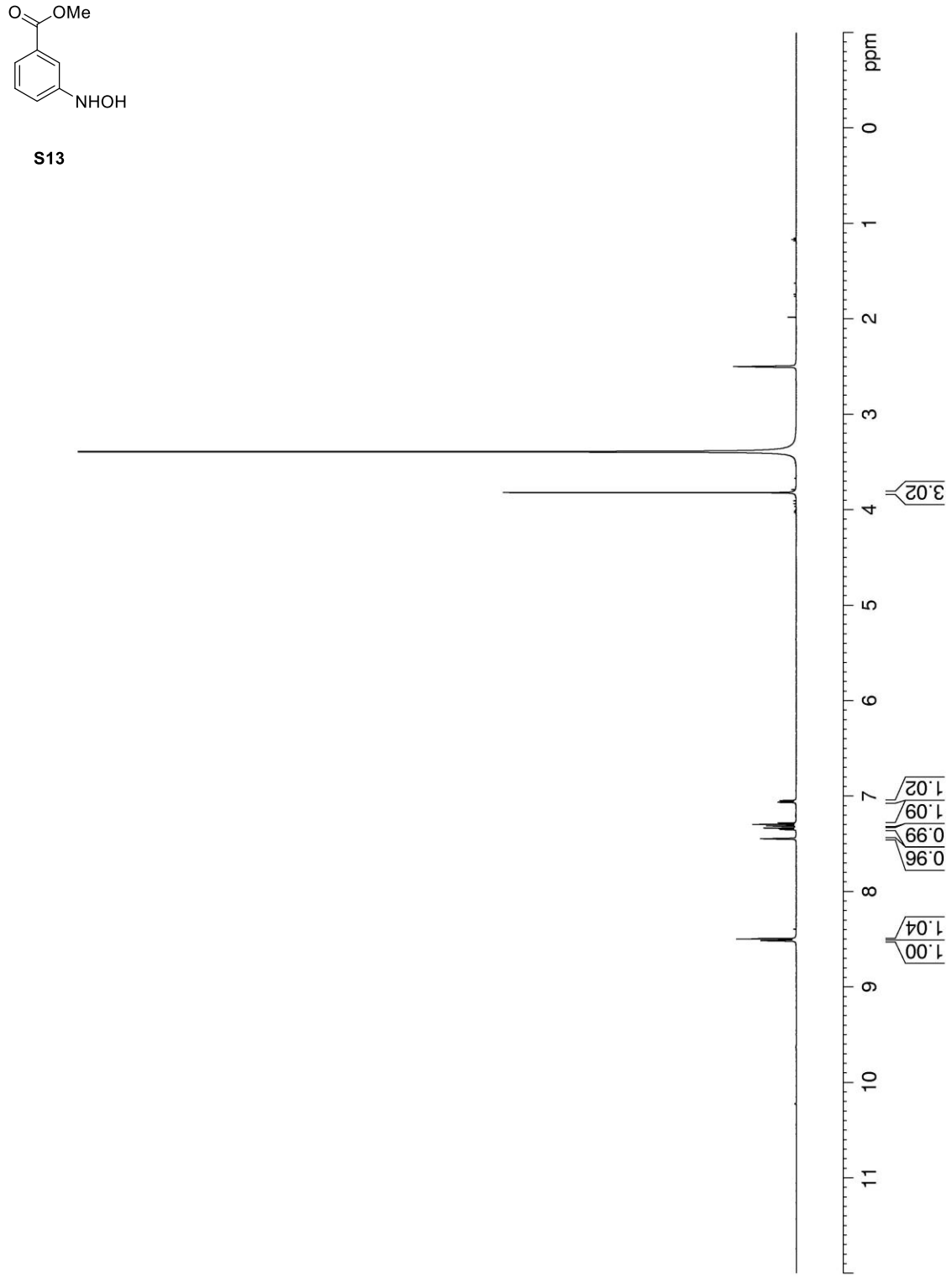
^{19}F NMR ($CDCl_3$, 25 ºC) of **3f-II**



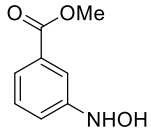
3f-II



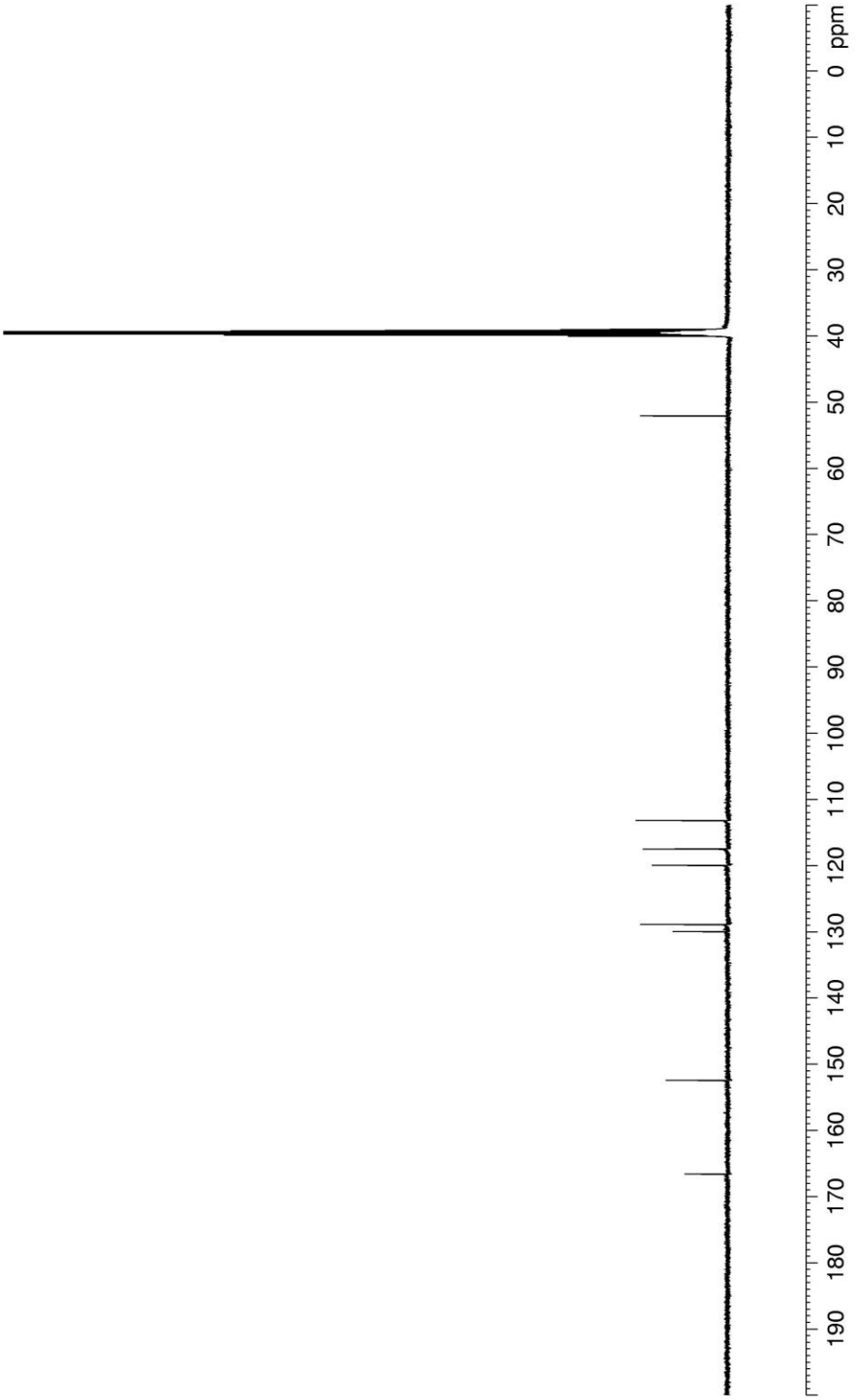
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S13**



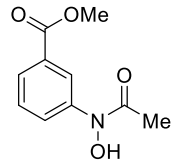
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S13**



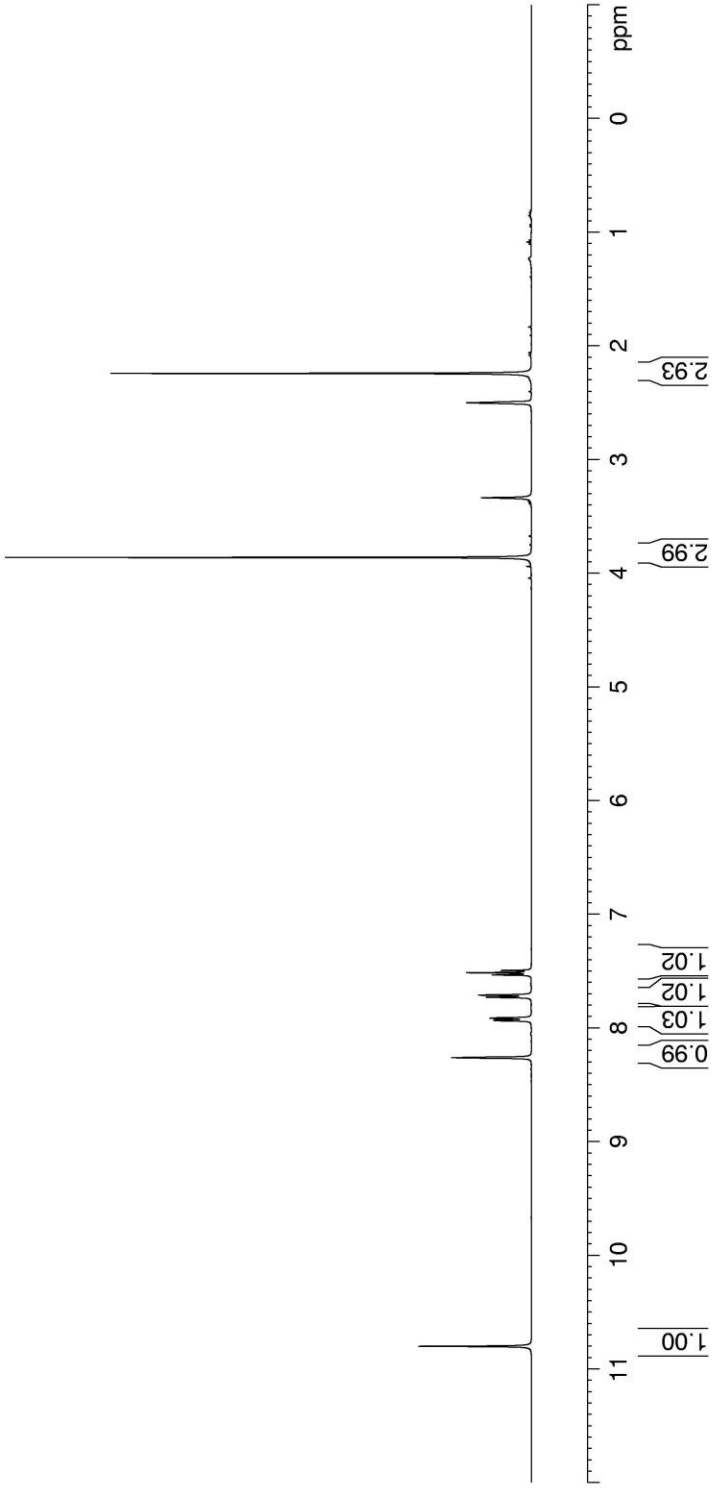
S13



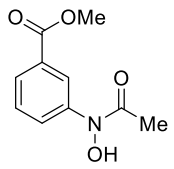
^{1}H NMR ($(CD_3)_2SO$, 25 ºC) of **S14**



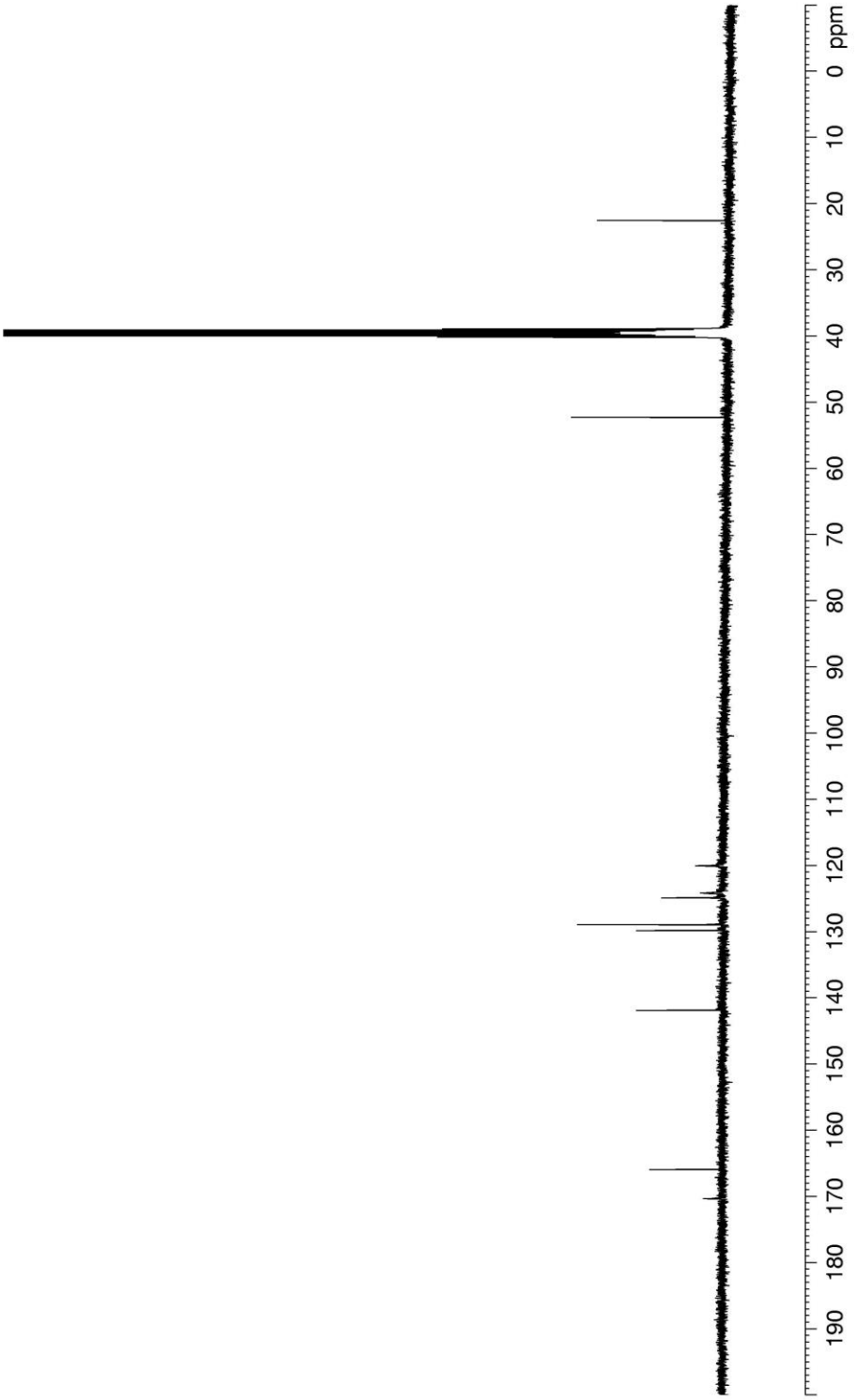
S14



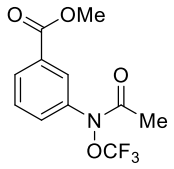
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S14**



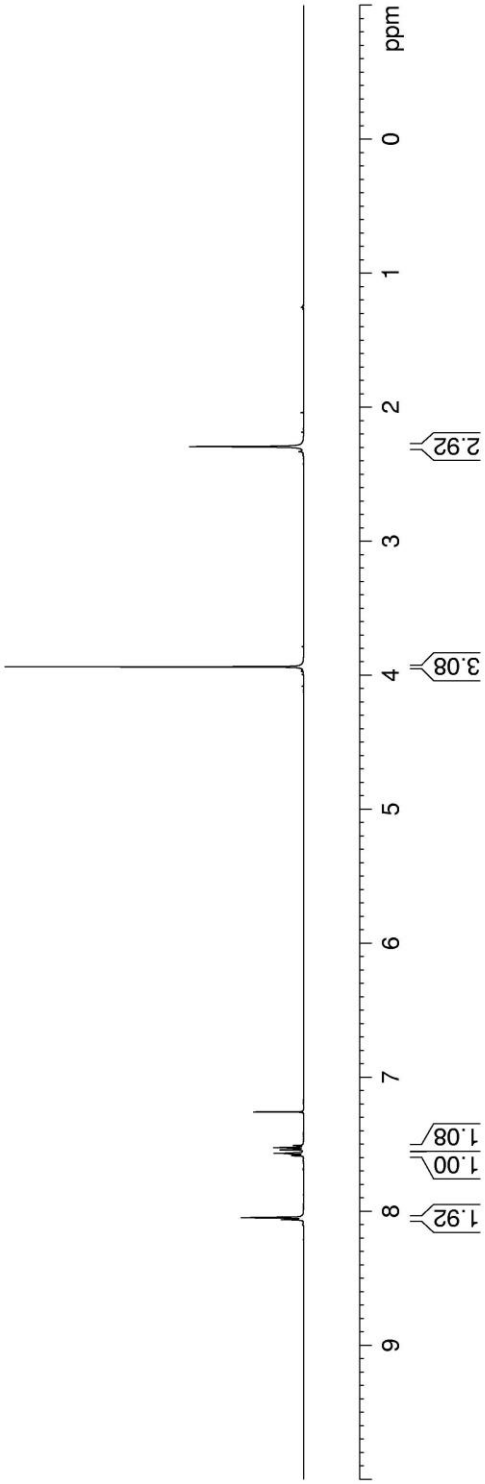
S14



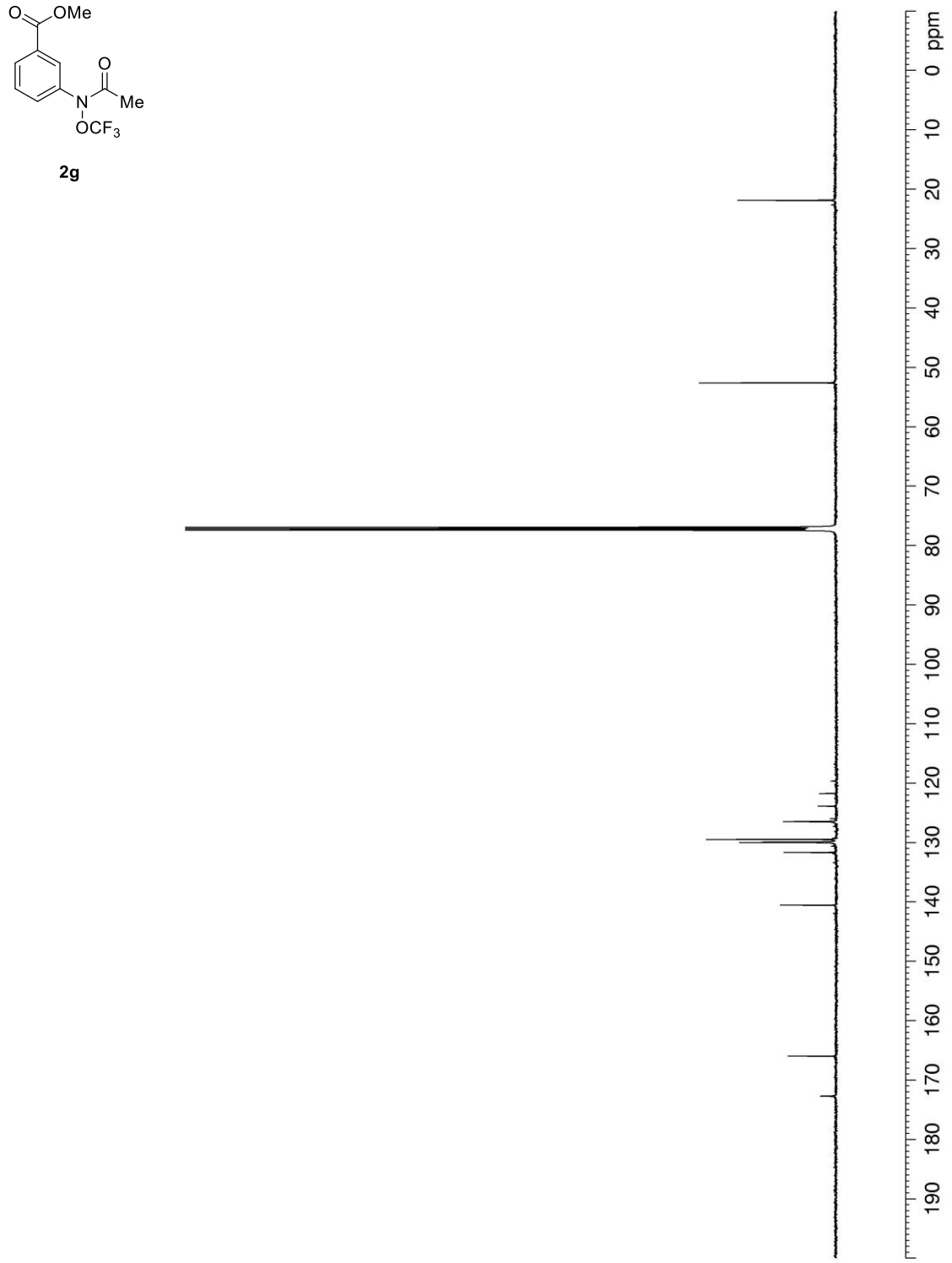
^{1}H NMR ($CDCl_3$, 25 ºC) of **2g**



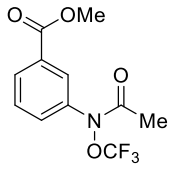
2g



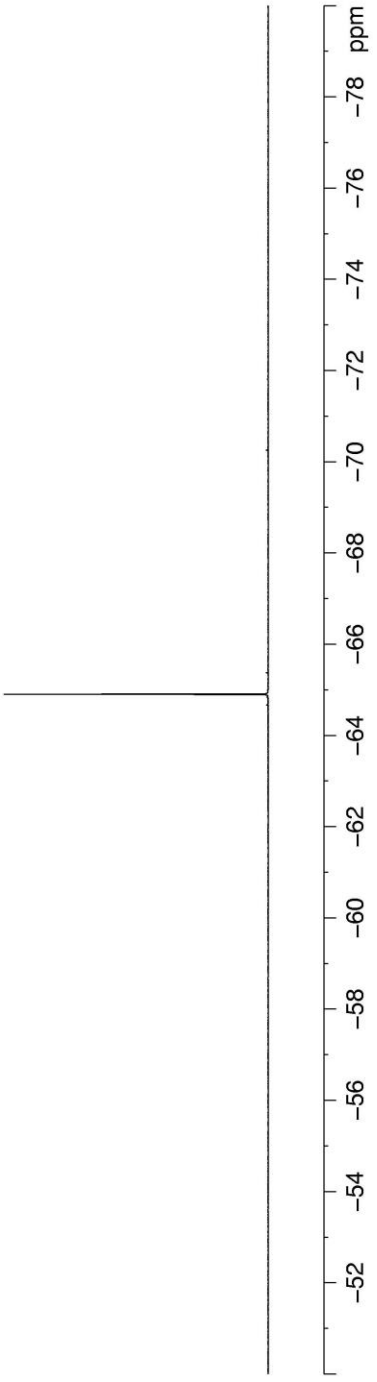
^{13}C NMR ($CDCl_3$, 25 ºC) of **2g**



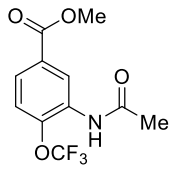
^{19}F NMR ($CDCl_3$, 25 ºC) of **2g**



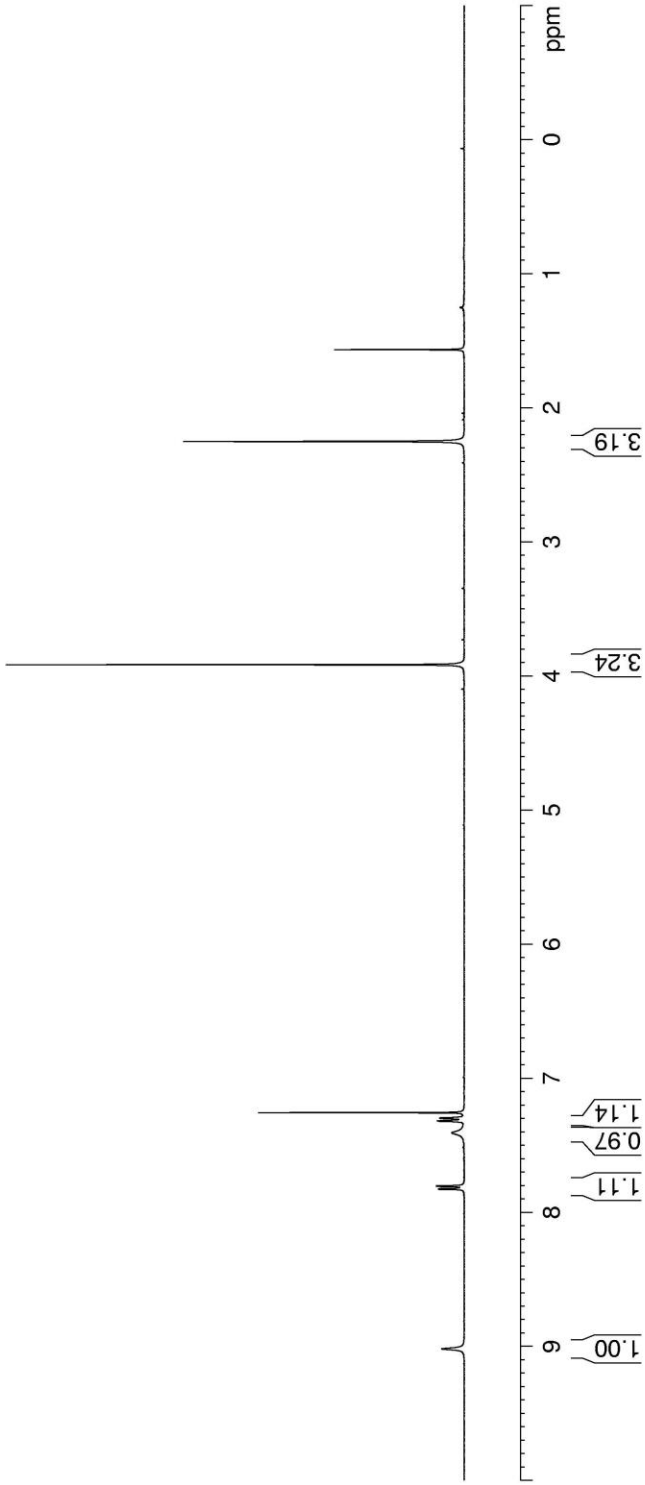
2g



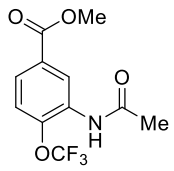
^{1}H NMR ($CDCl_3$, 25 ºC) of **3g**



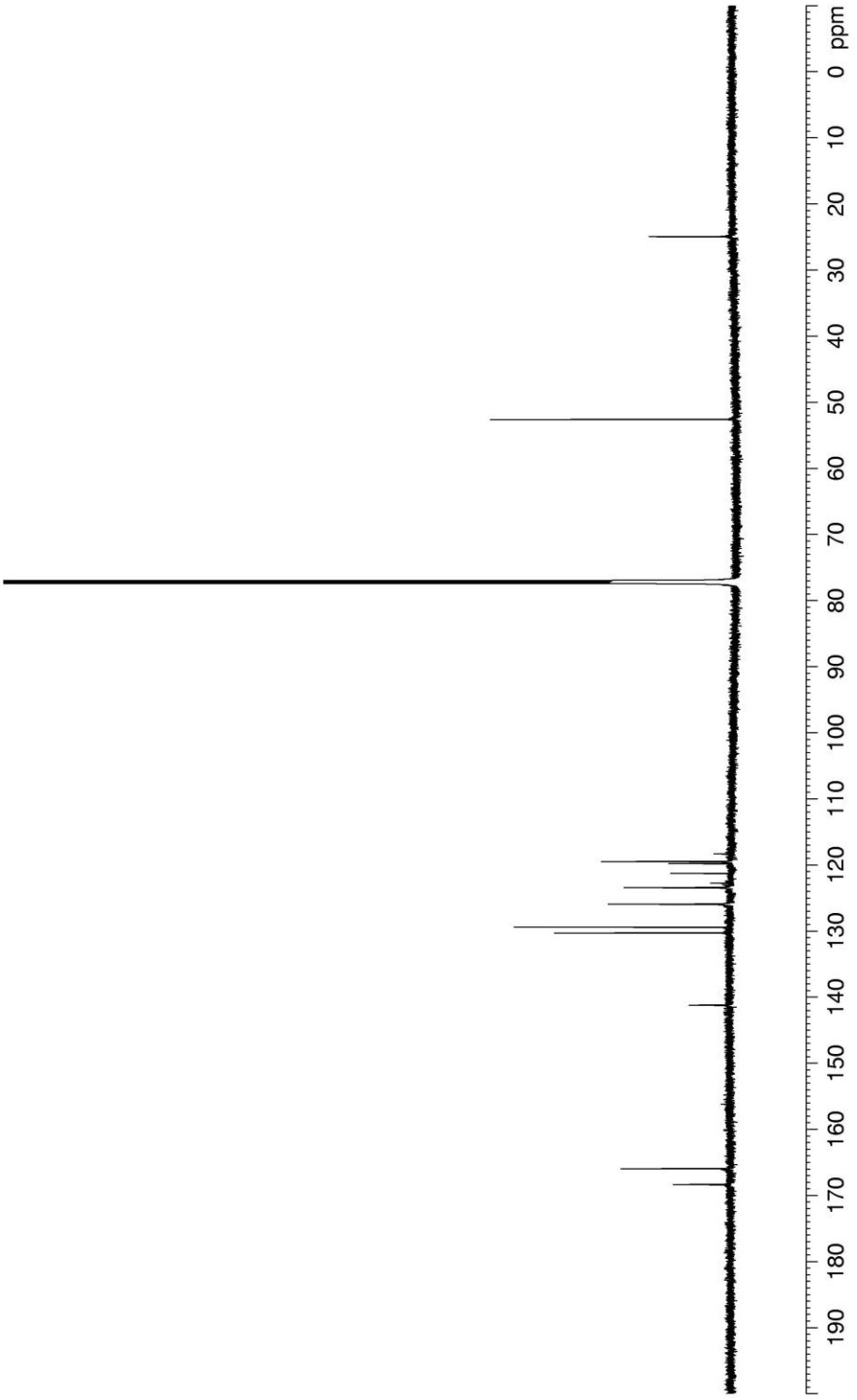
3g



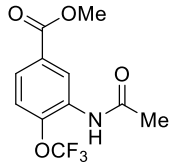
^{13}C NMR ($CDCl_3$, 25 ºC) of **3g**



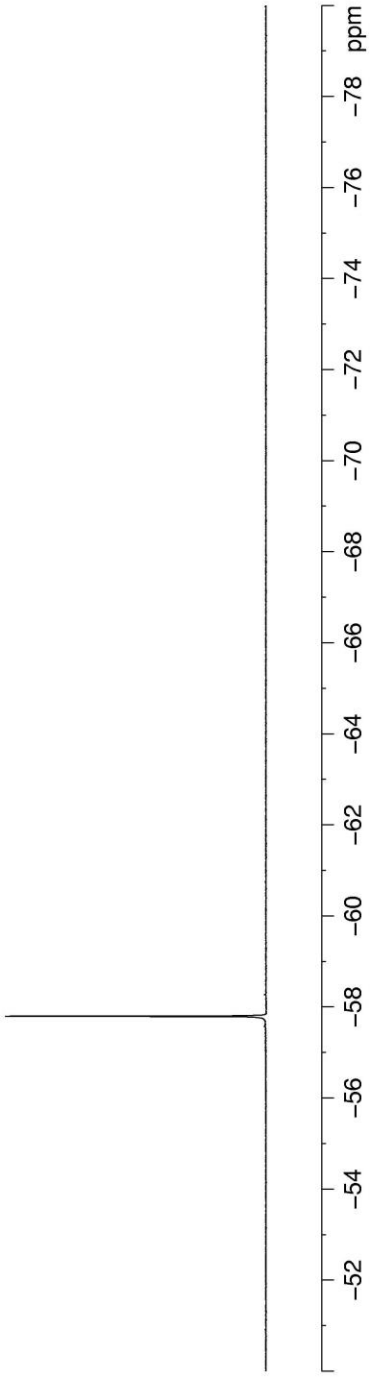
3g



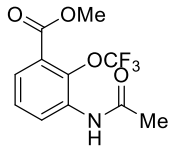
^{19}F NMR ($CDCl_3$, 25 ºC) of **3g**



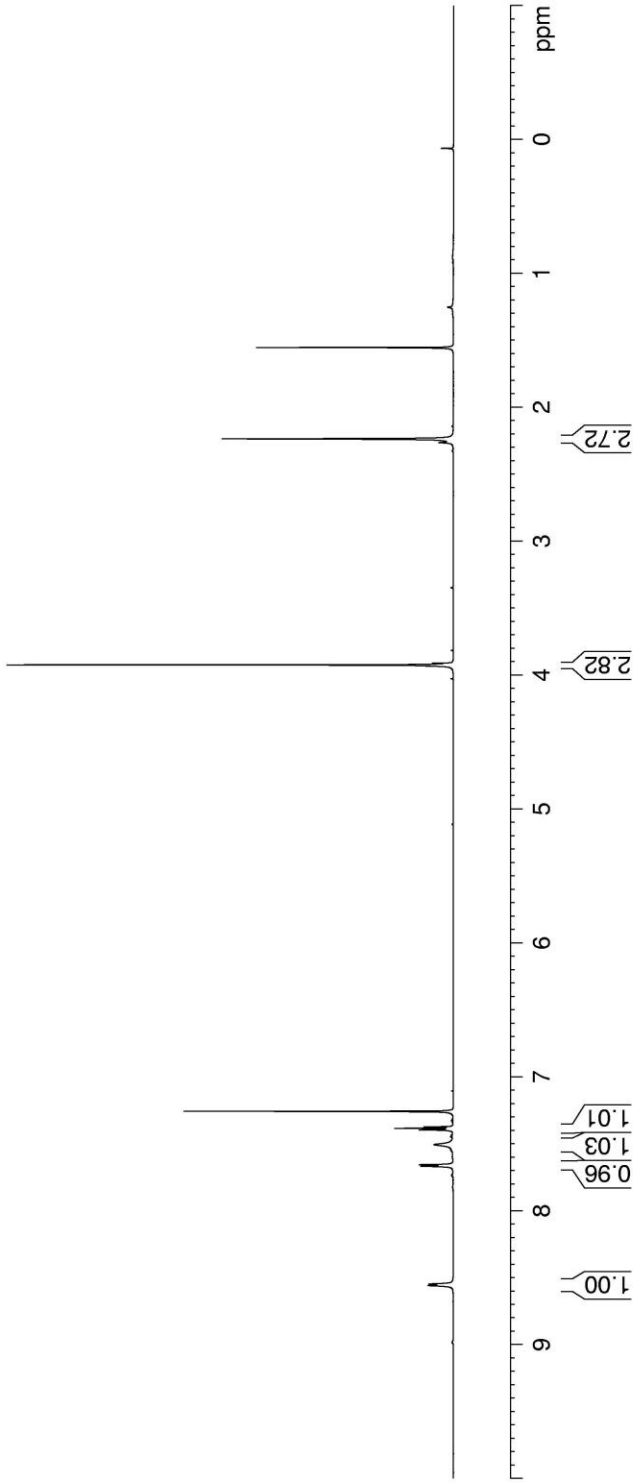
3g



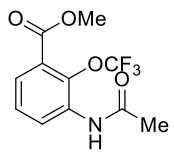
^{1}H NMR ($CDCl_3$, 25 ºC) of **3g-II**



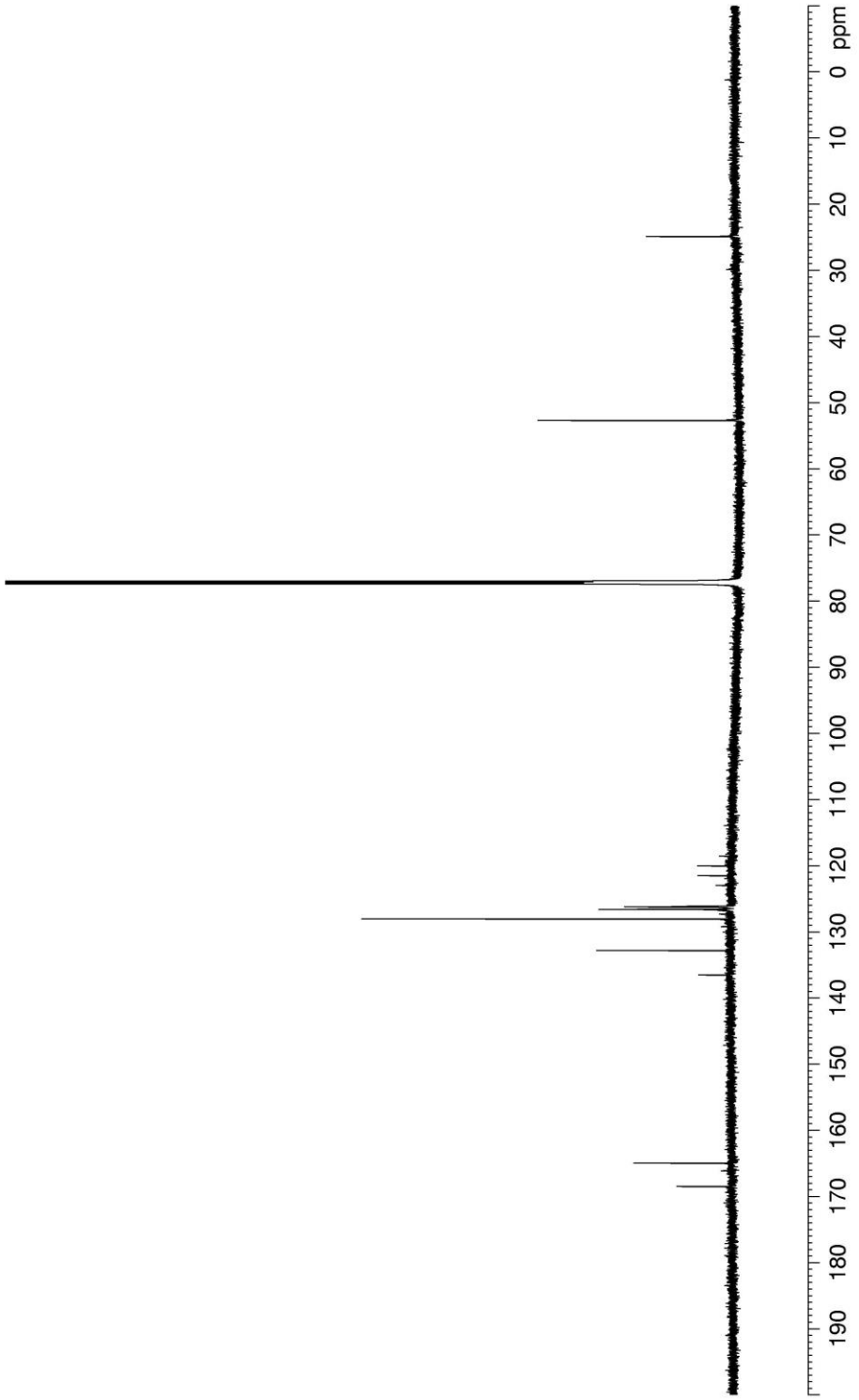
3g-II



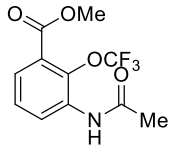
^{13}C NMR ($CDCl_3$, 25 ºC) of **3g-II**



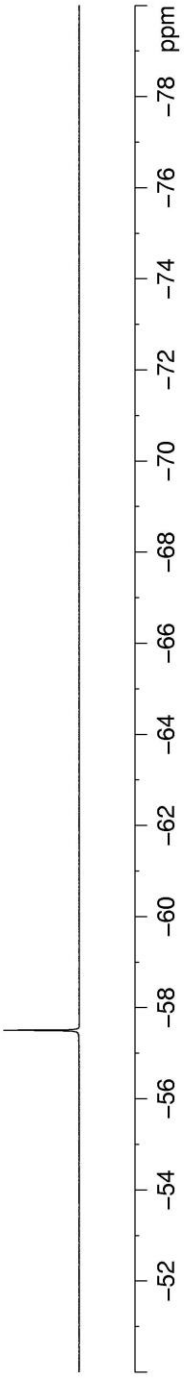
3g-II



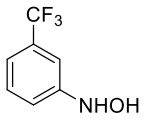
^{19}F NMR ($CDCl_3$, 25 ºC) of **3g-II**



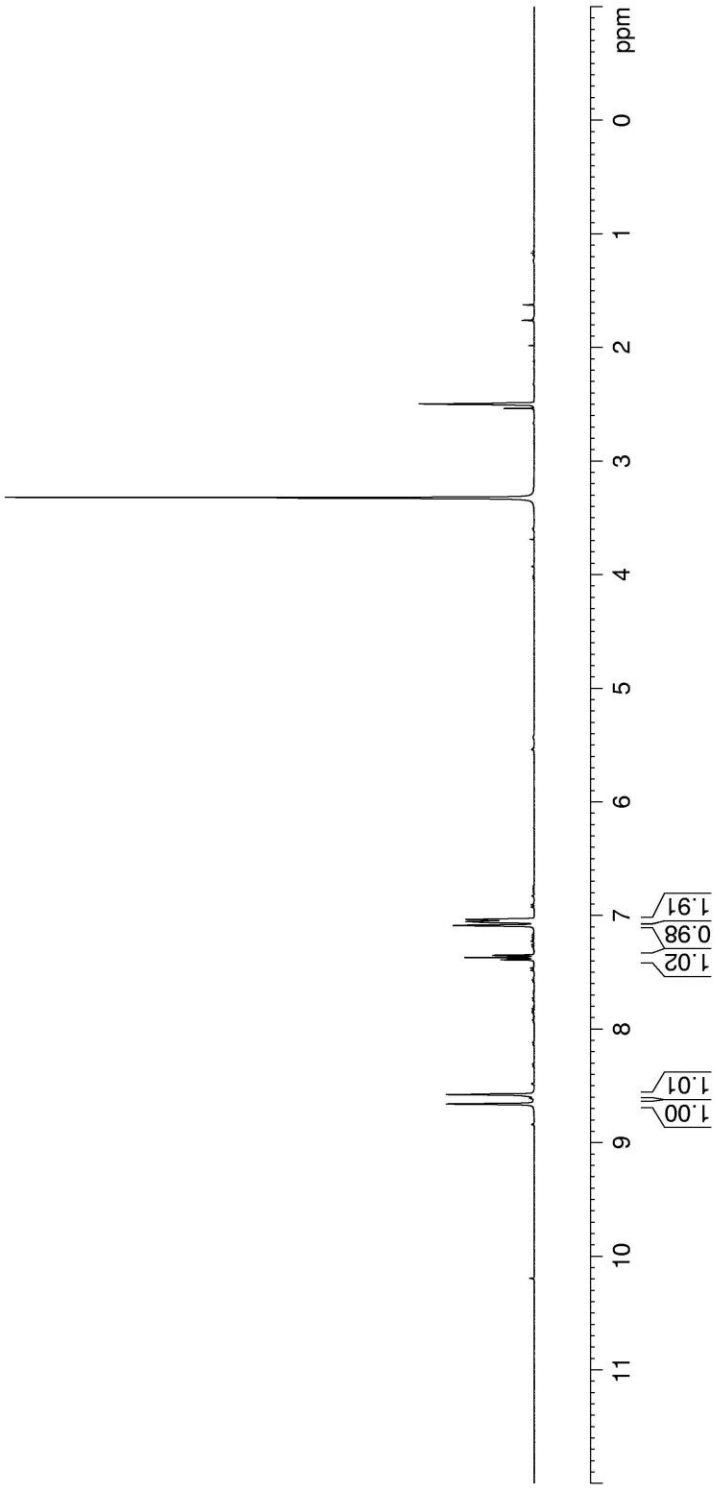
3g-II



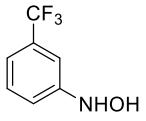
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S15**



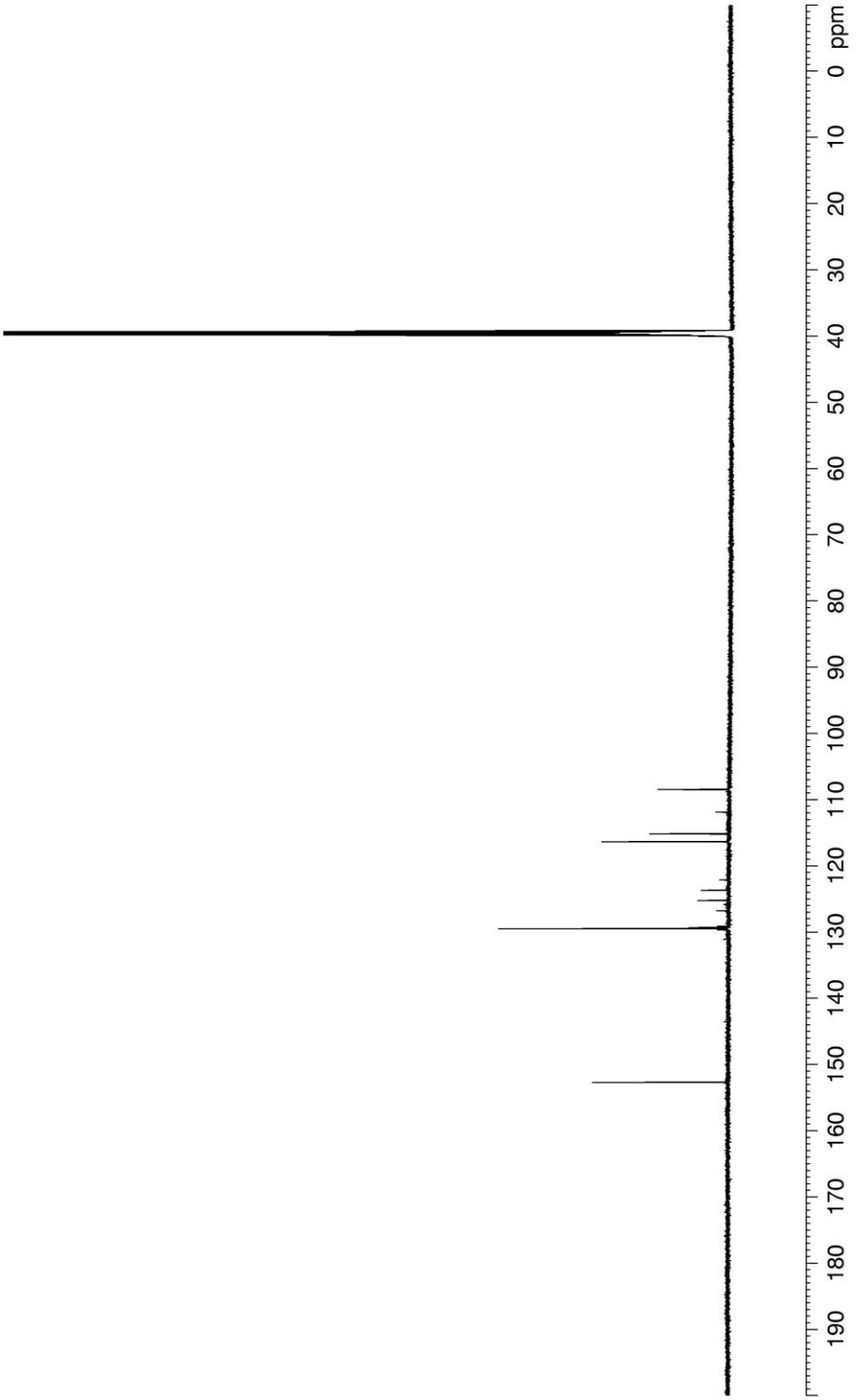
S15



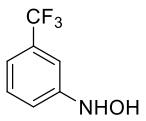
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S15**



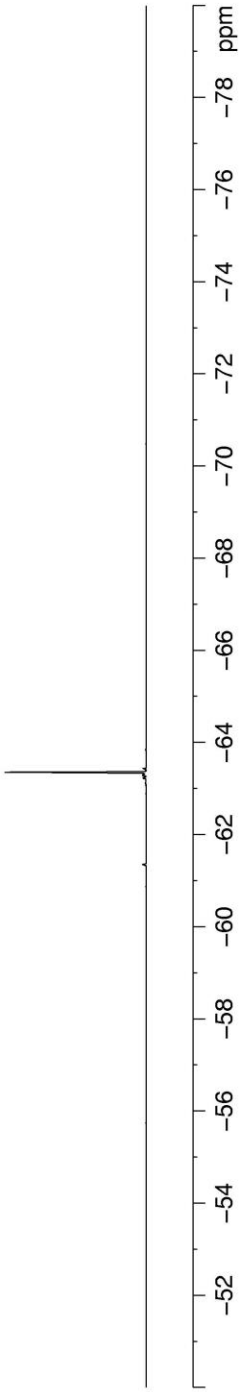
S15



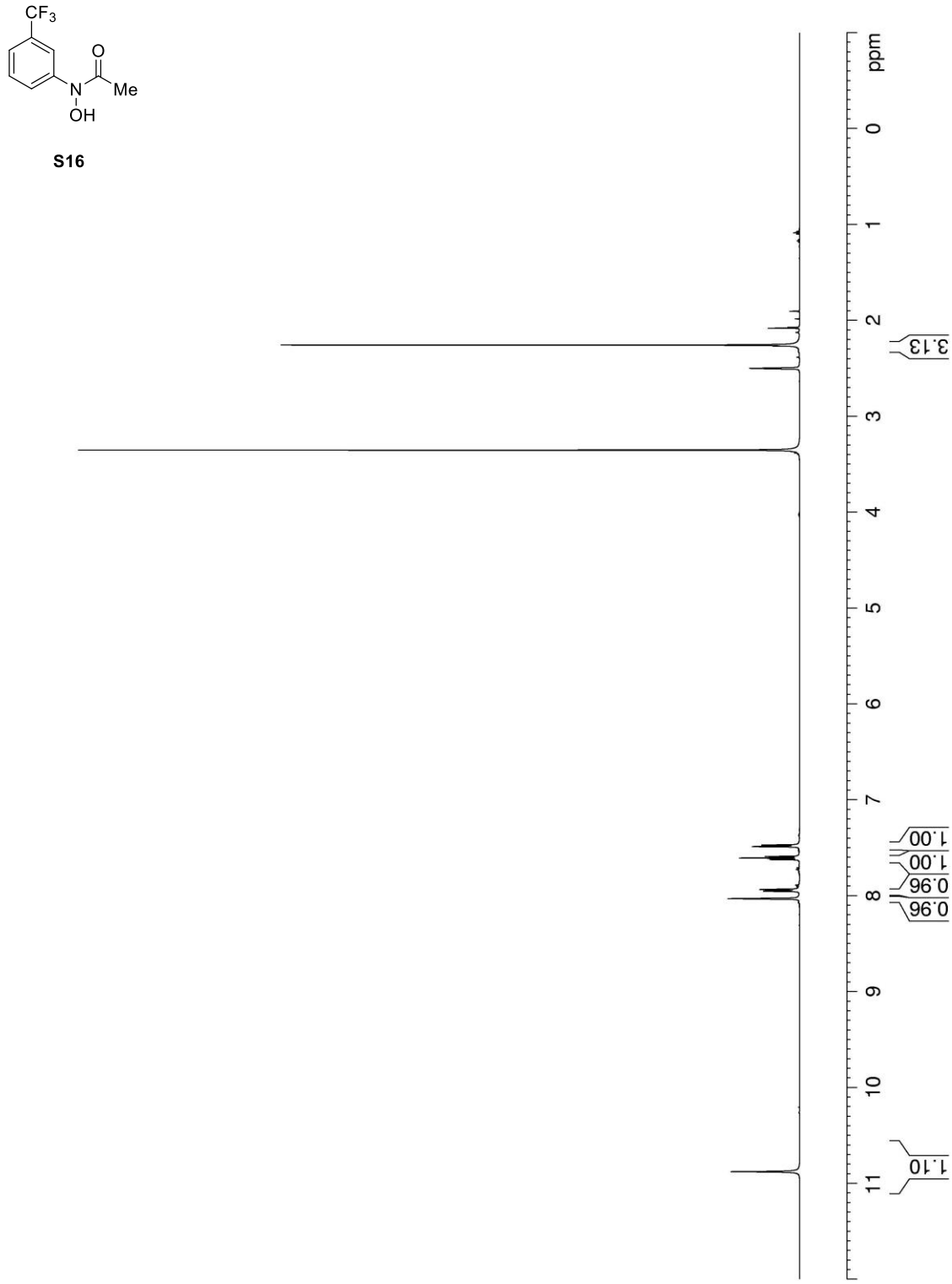
^{19}F NMR ($(CD_3)_2SO$, 25 ºC) of **S15**



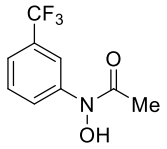
S15



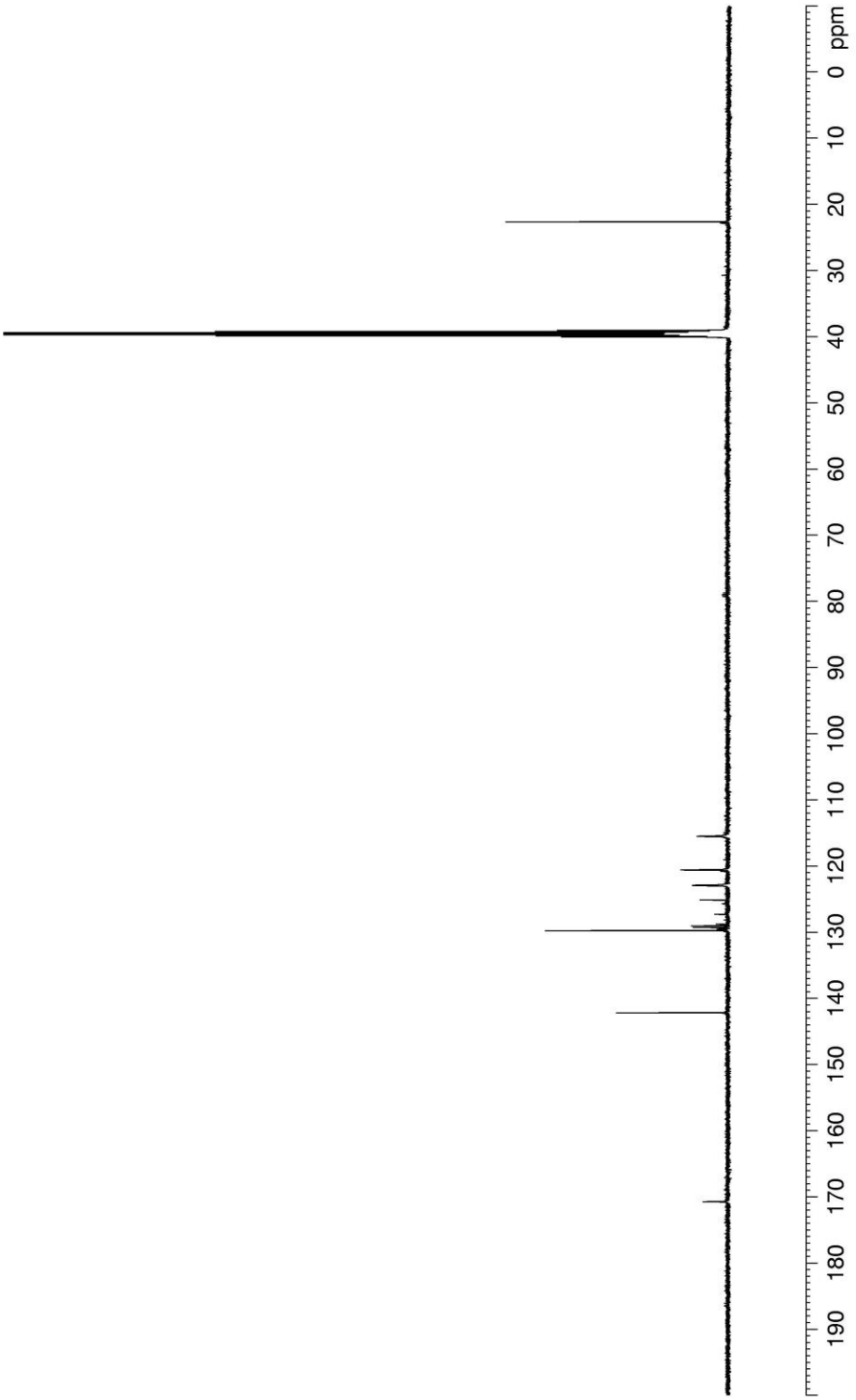
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S16**



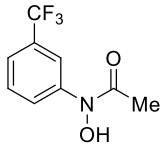
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S16**



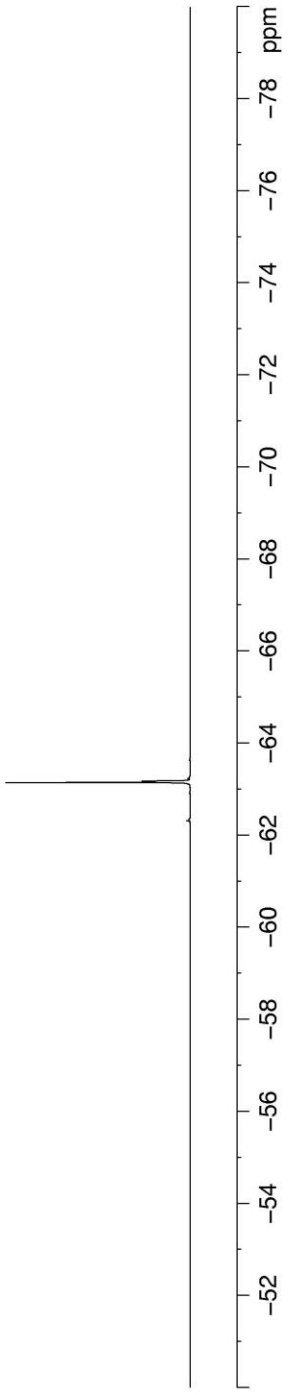
S16



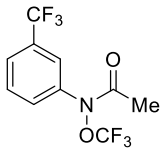
^{19}F NMR ($(CD_3)_2SO$, 25 ºC) of **S16**



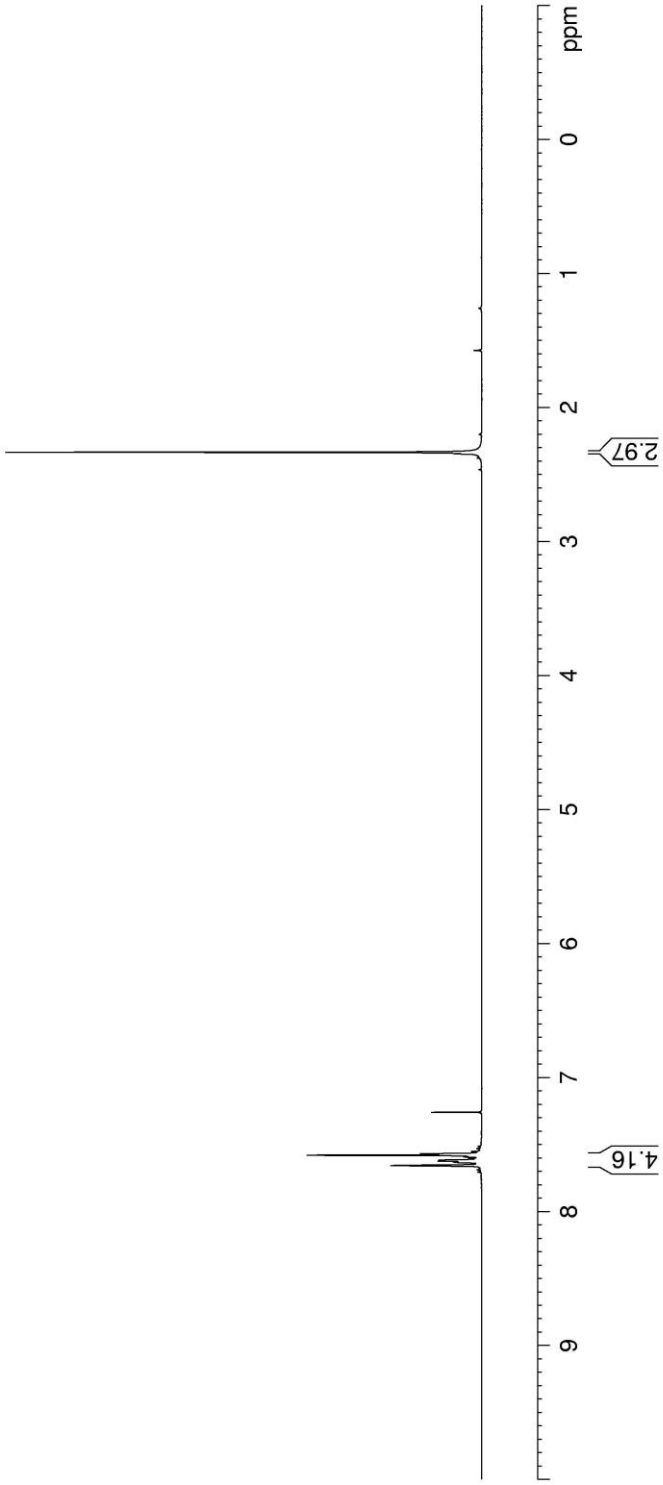
S16



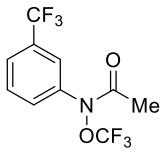
^{1}H NMR ($CDCl_3$, 25 ºC) of **2h**



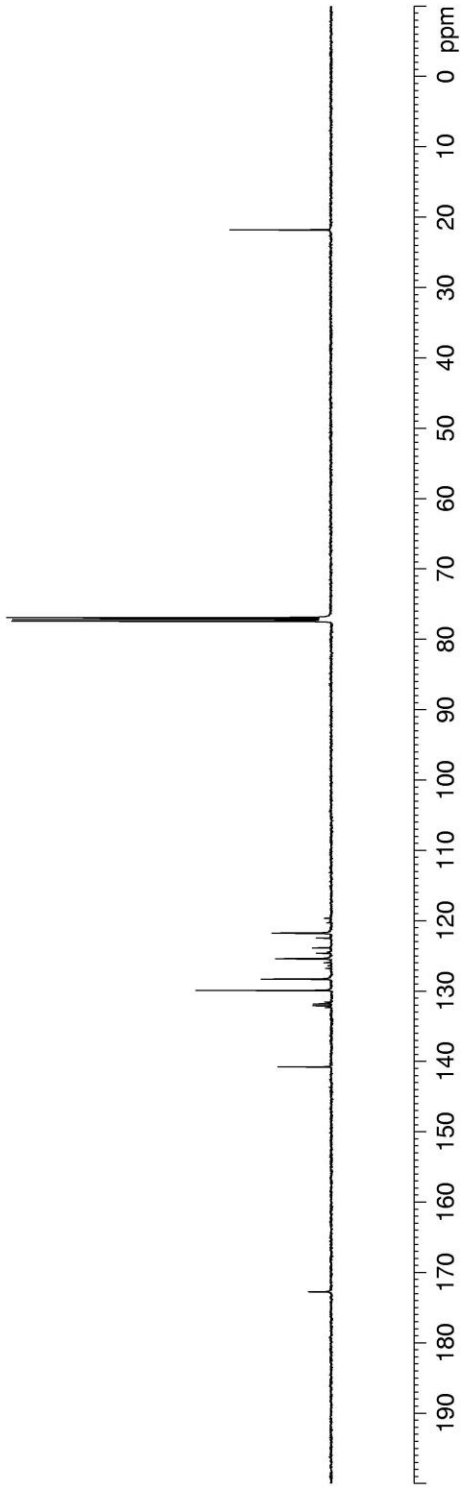
2h



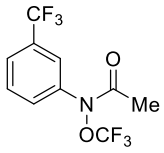
^{13}C NMR ($CDCl_3$, 25 ºC) of **2h**



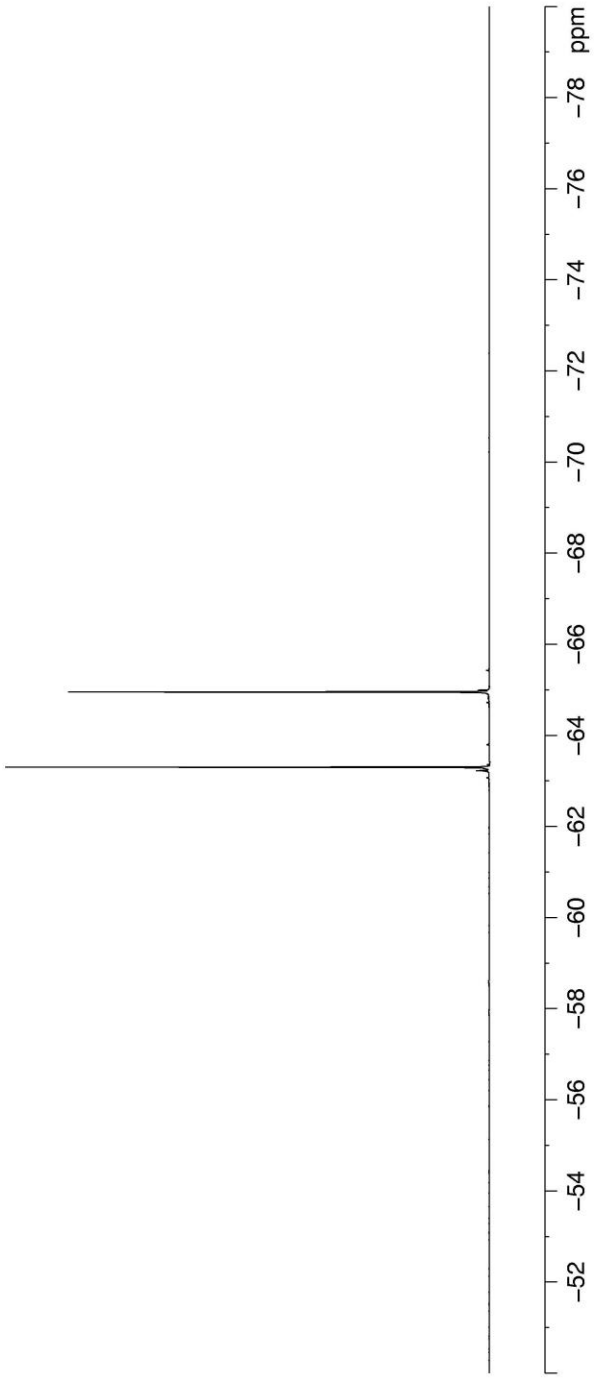
2h



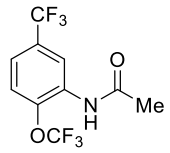
^{19}F NMR ($CDCl_3$, 25 ºC) of **2h**



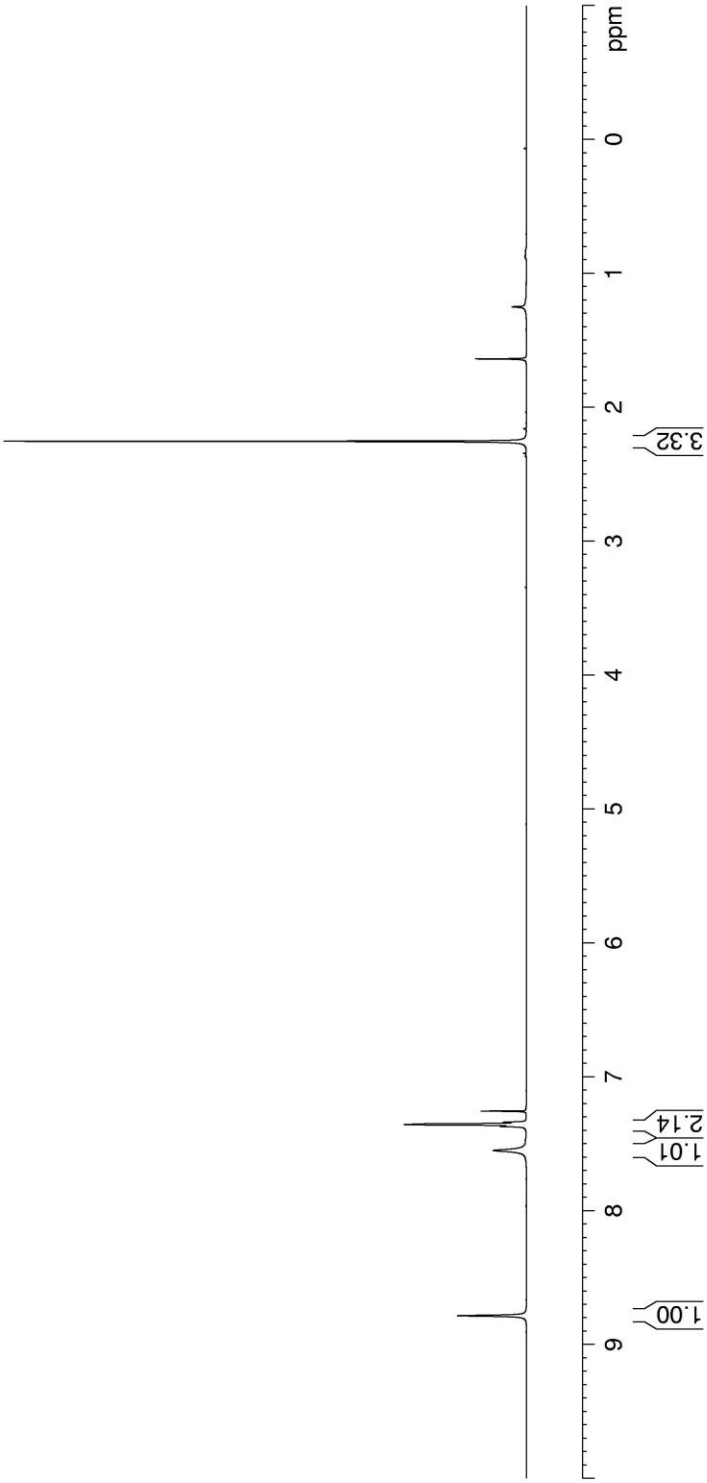
2h



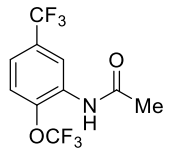
^{1}H NMR ($CDCl_3$, 25 ºC) of **3h**



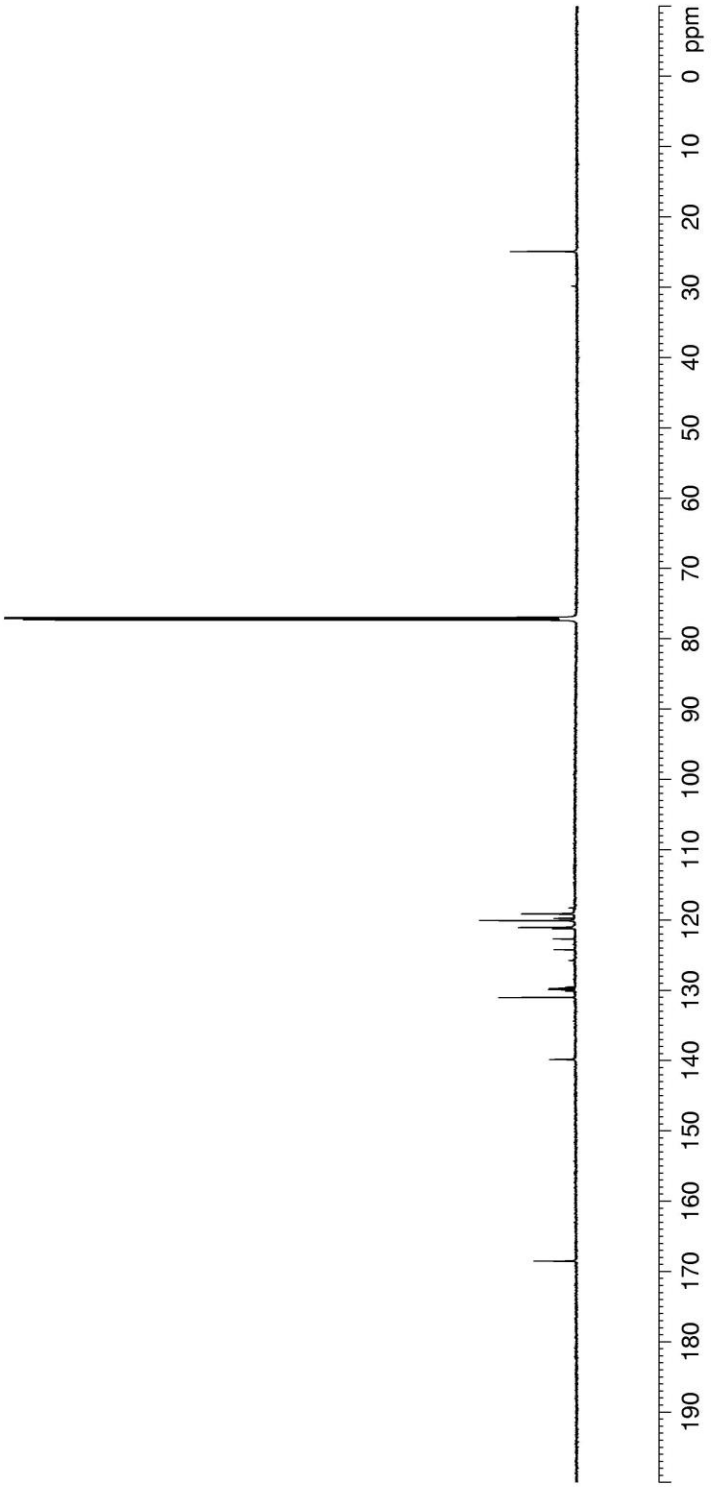
3h



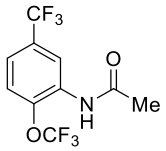
^{13}C NMR ($CDCl_3$, 25 ºC) of **3h**



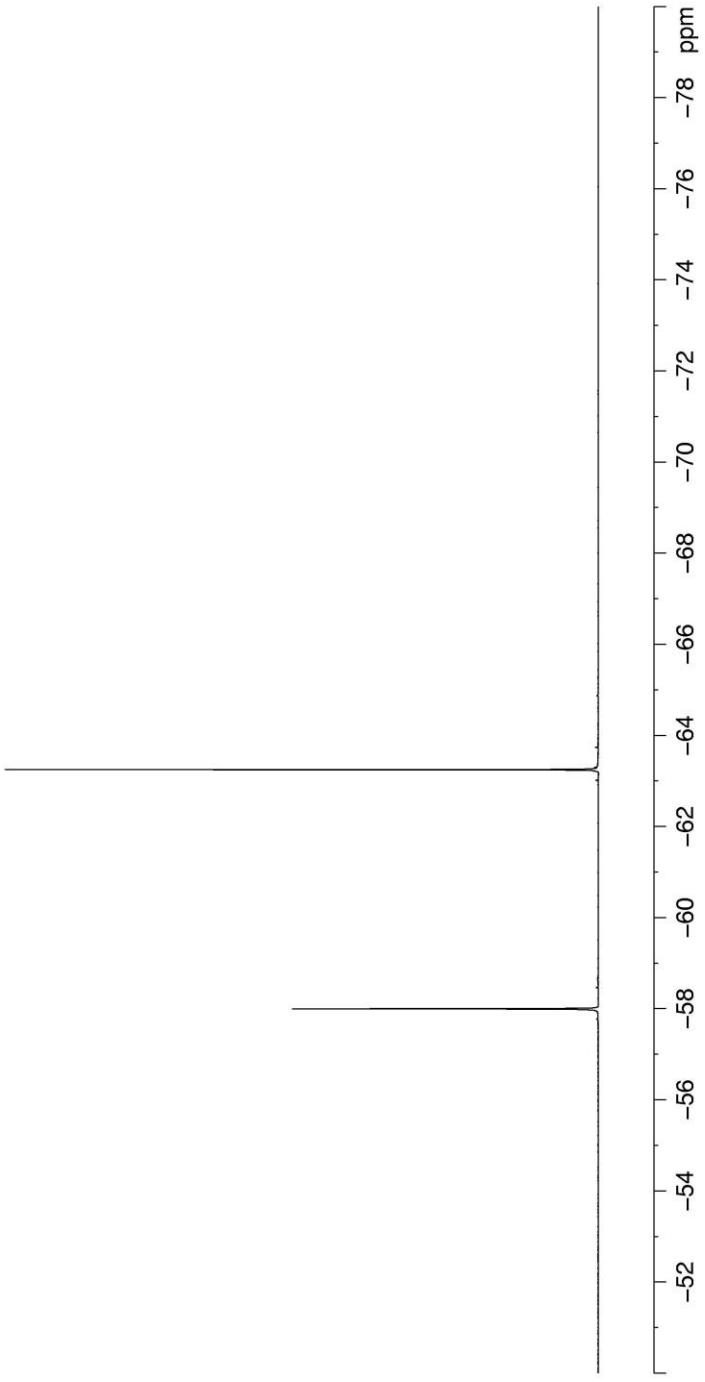
3h



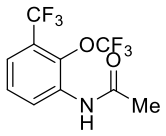
^{19}F NMR ($CDCl_3$, 25 ºC) of **3h**



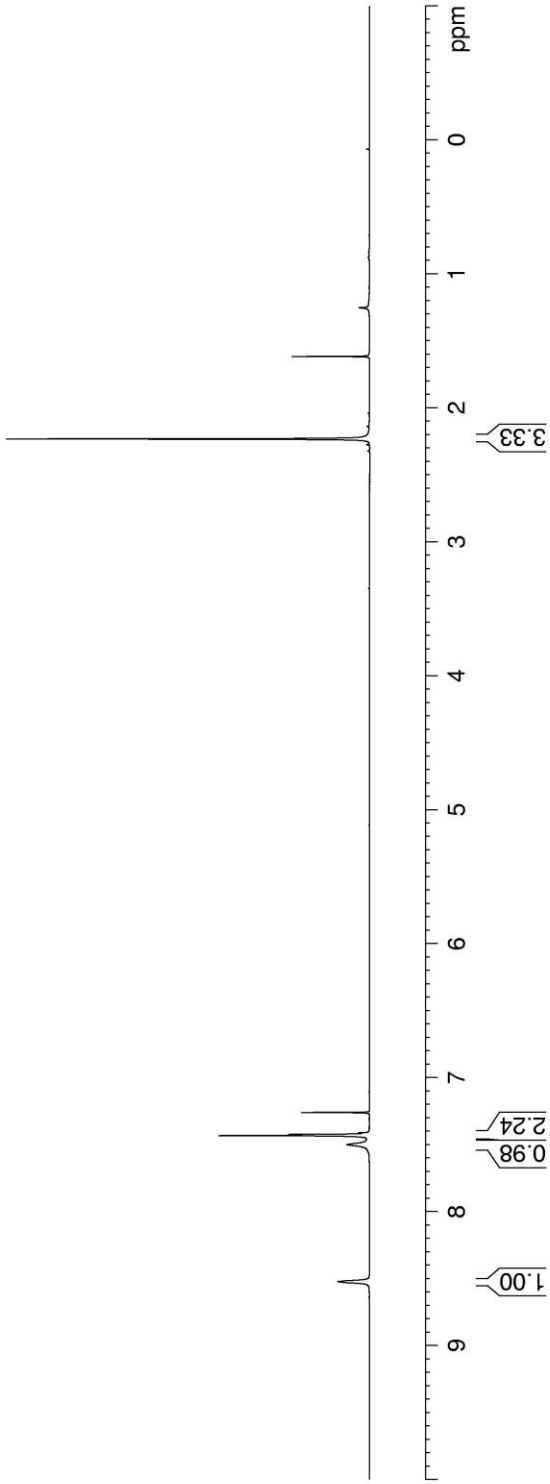
3h



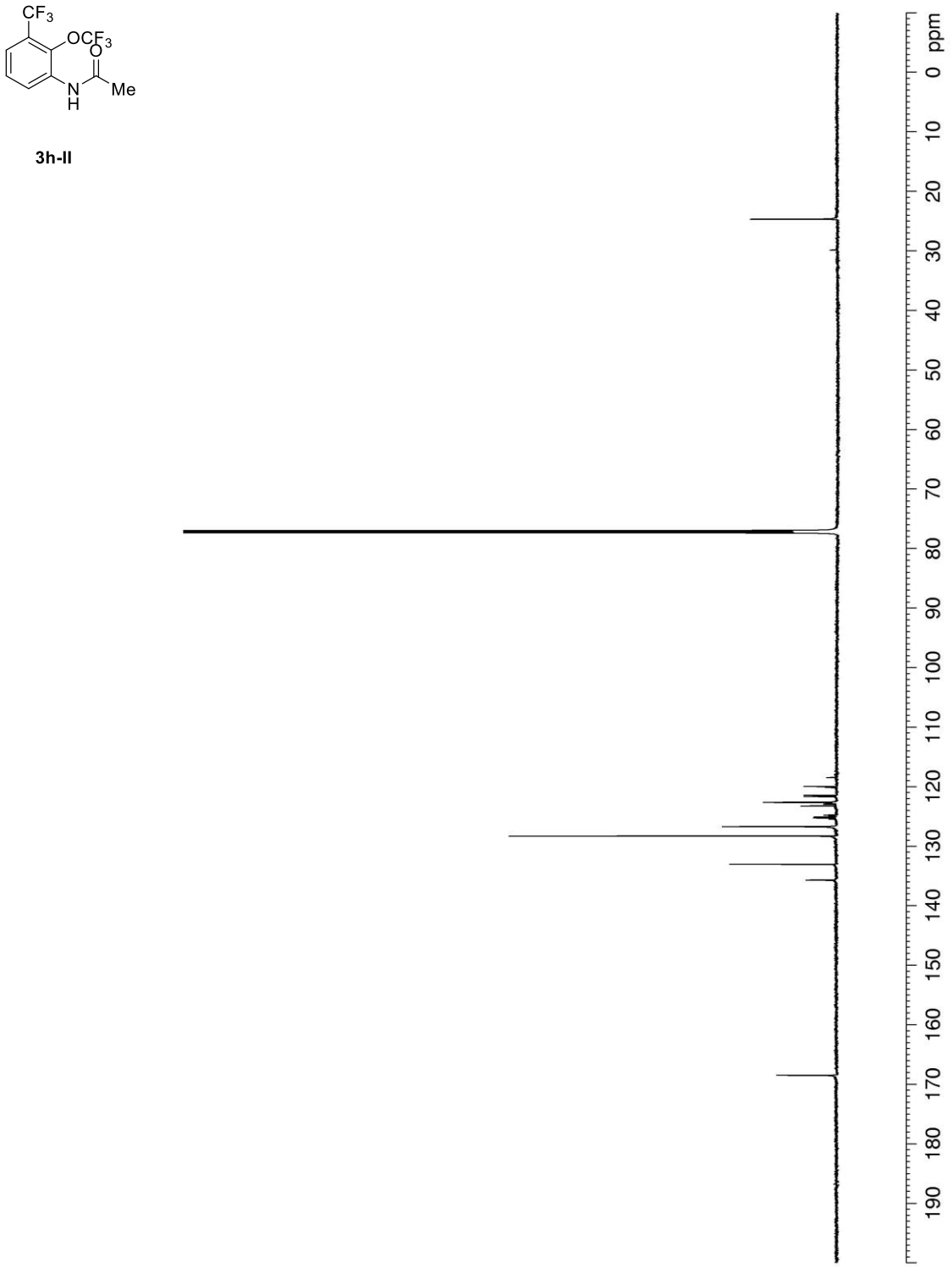
^{1}H NMR ($CDCl_3$, 25 ºC) of **3h-II**



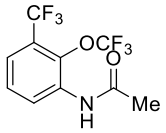
3h-II



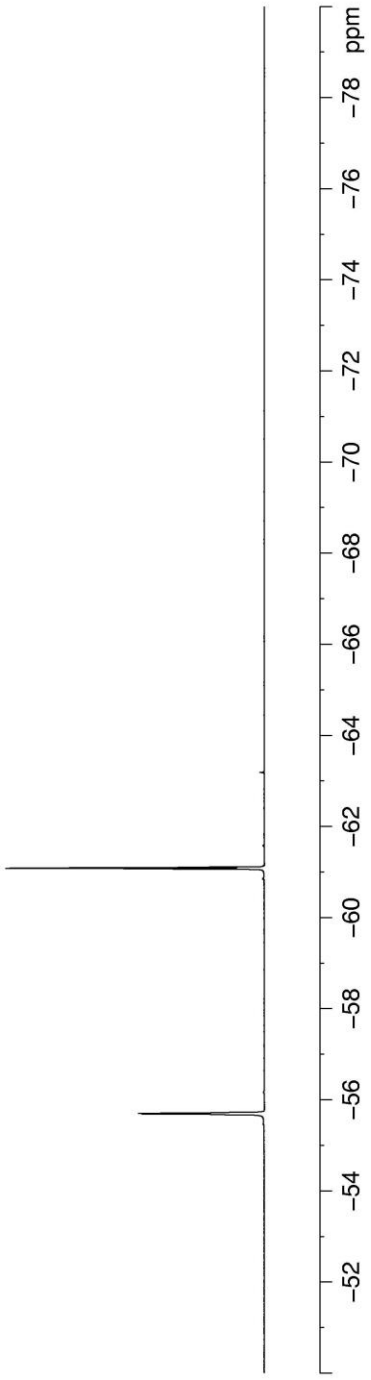
^{13}C NMR ($CDCl_3$, 25 ºC) of **3h-II**



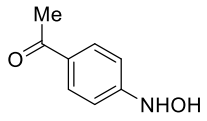
^{19}F NMR ($CDCl_3$, 25 ºC) of **3h-II**



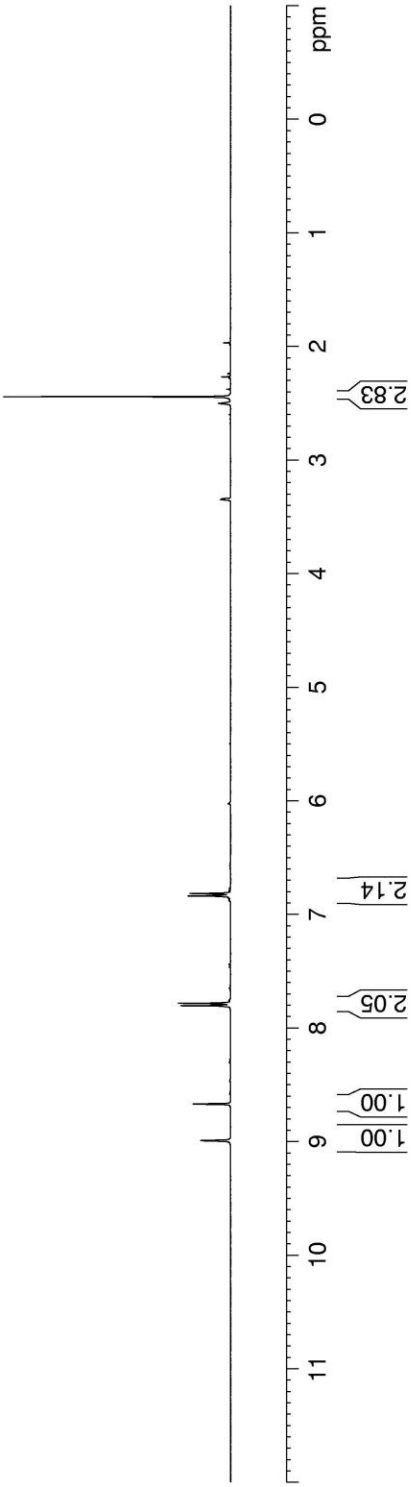
3h-II



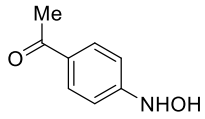
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S17**



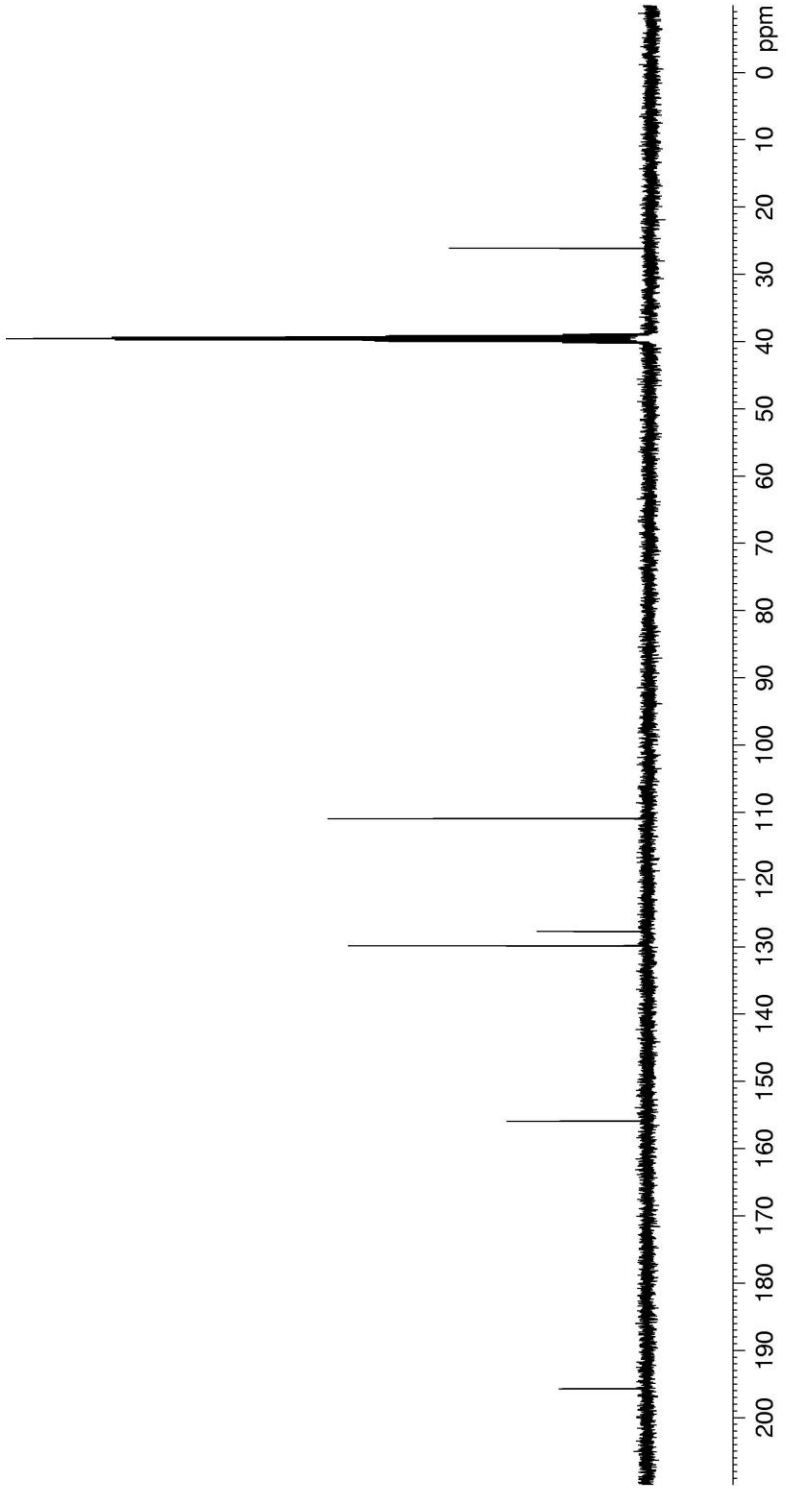
S17



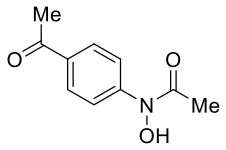
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S17**



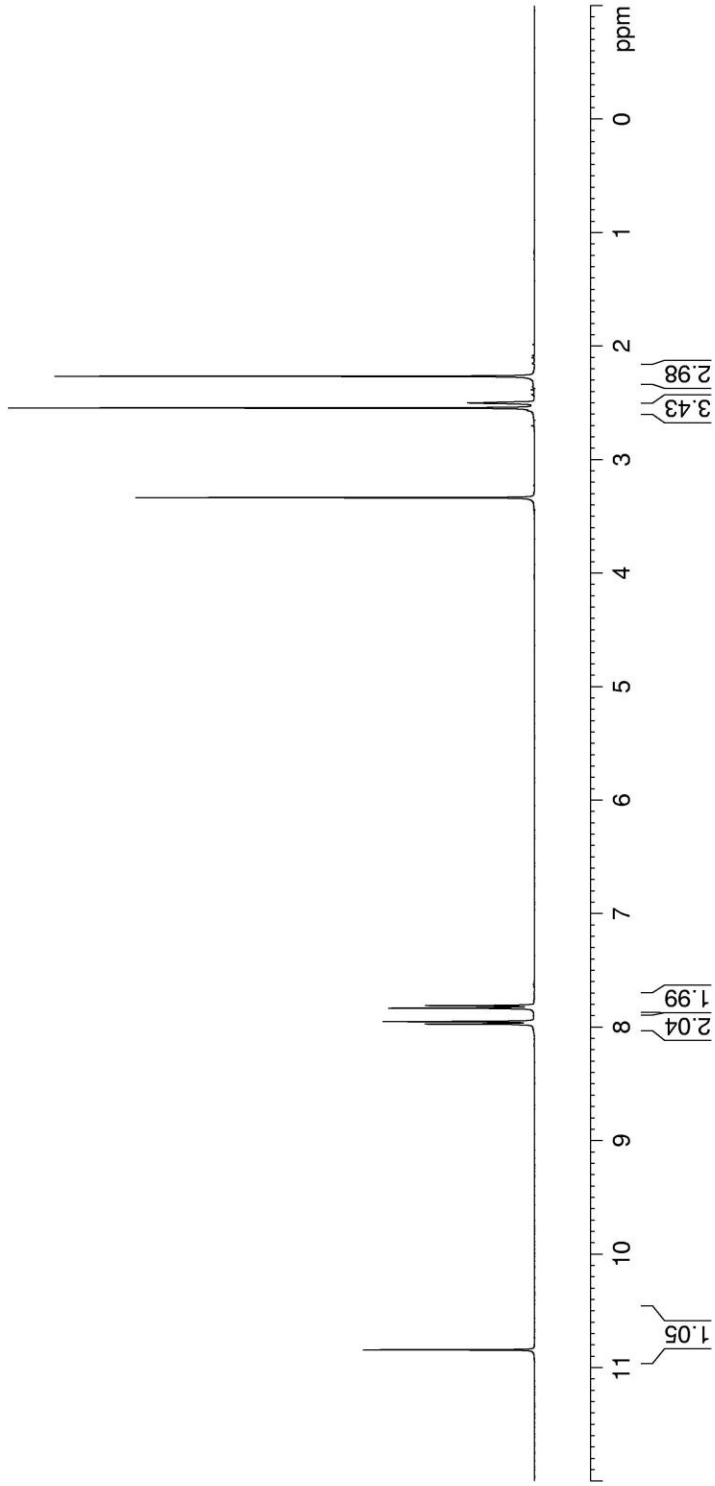
S17



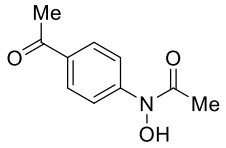
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S18**



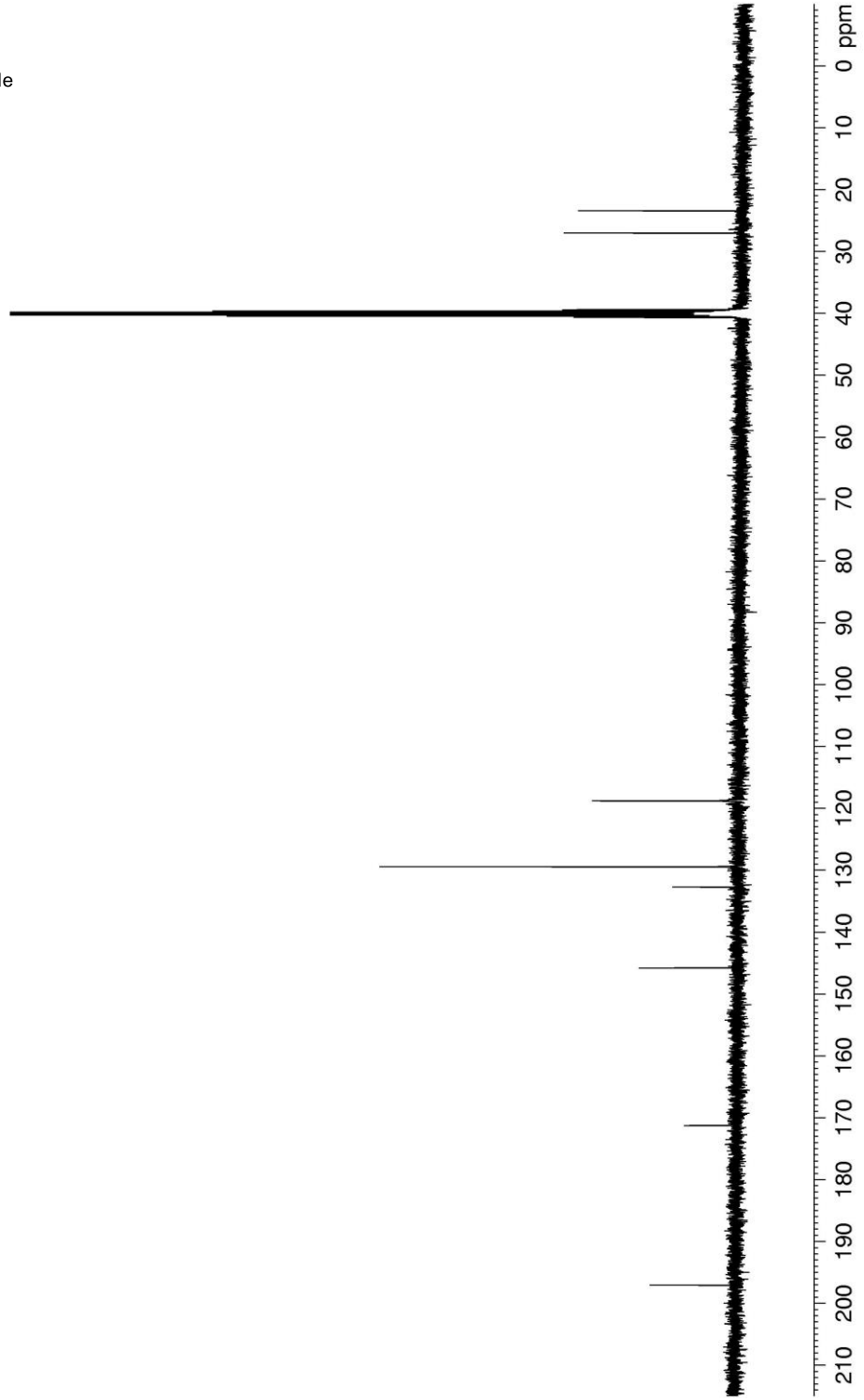
S18



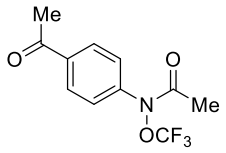
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S18**



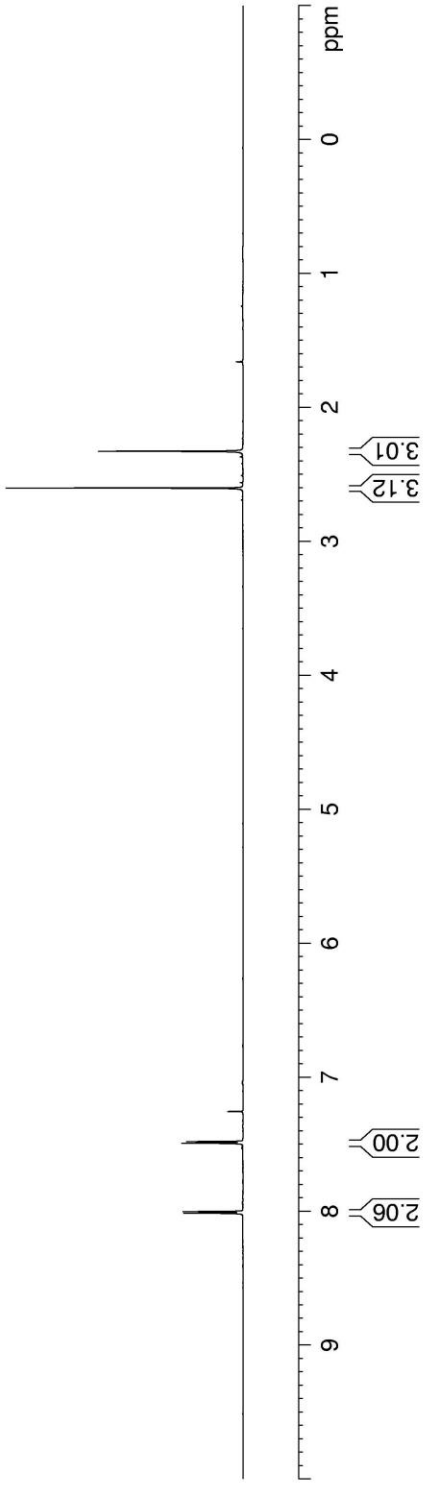
S18



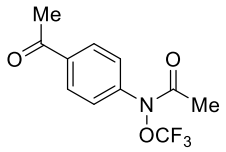
^{1}H NMR ($CDCl_3$, 25 ºC) of **2i**



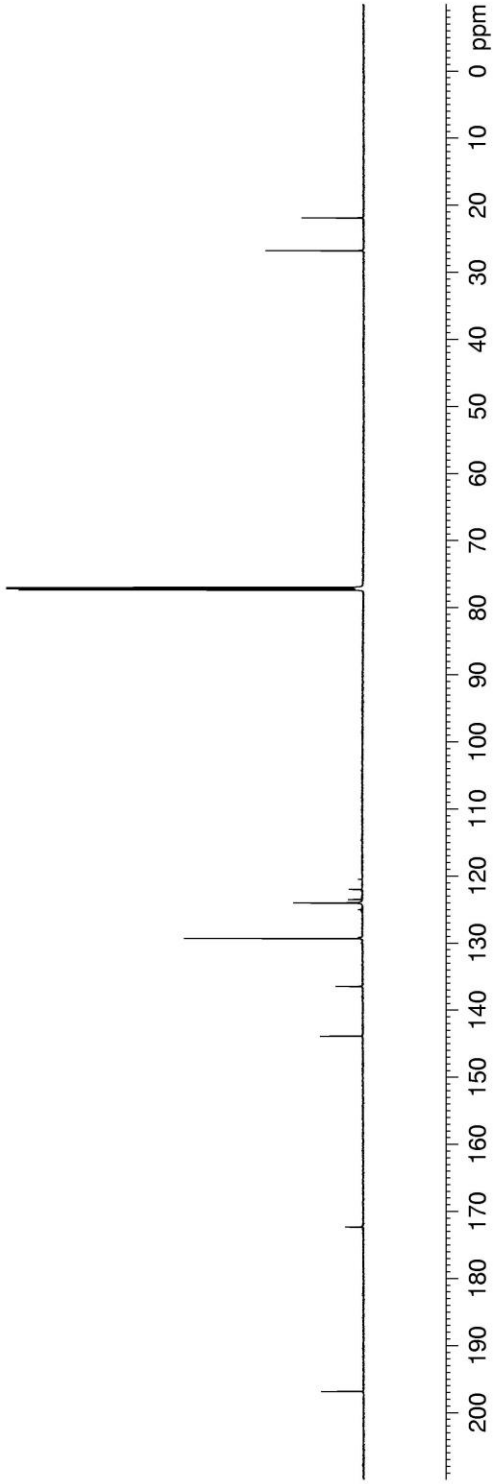
2i



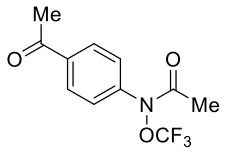
^{13}C NMR ($CDCl_3$, 25 ºC) of **2i**



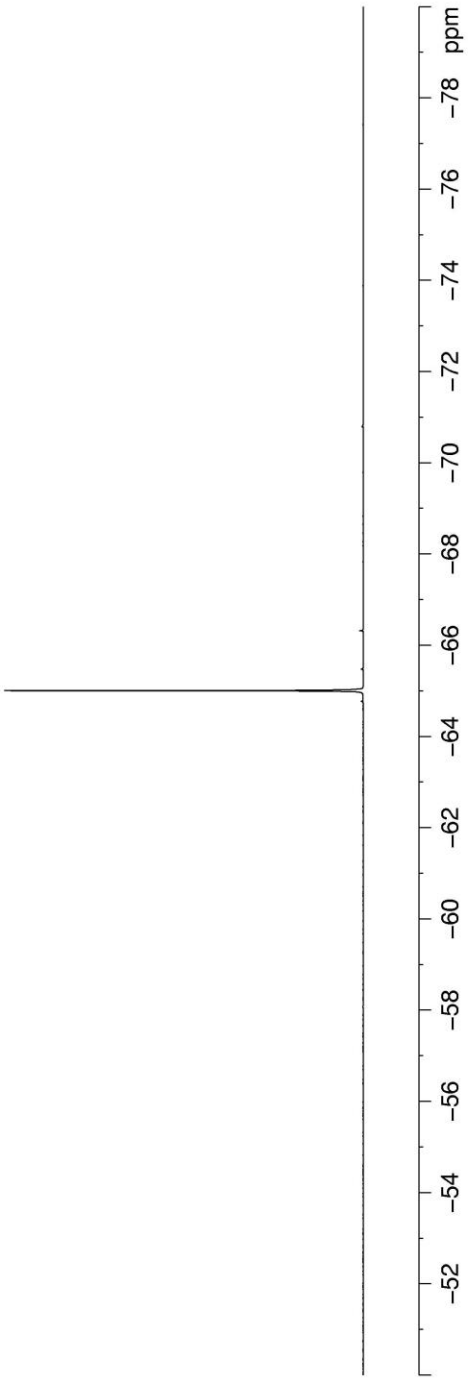
2i



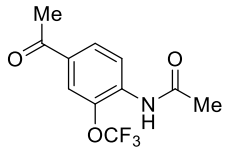
^{19}F NMR ($CDCl_3$, 25 ºC) of **2i**



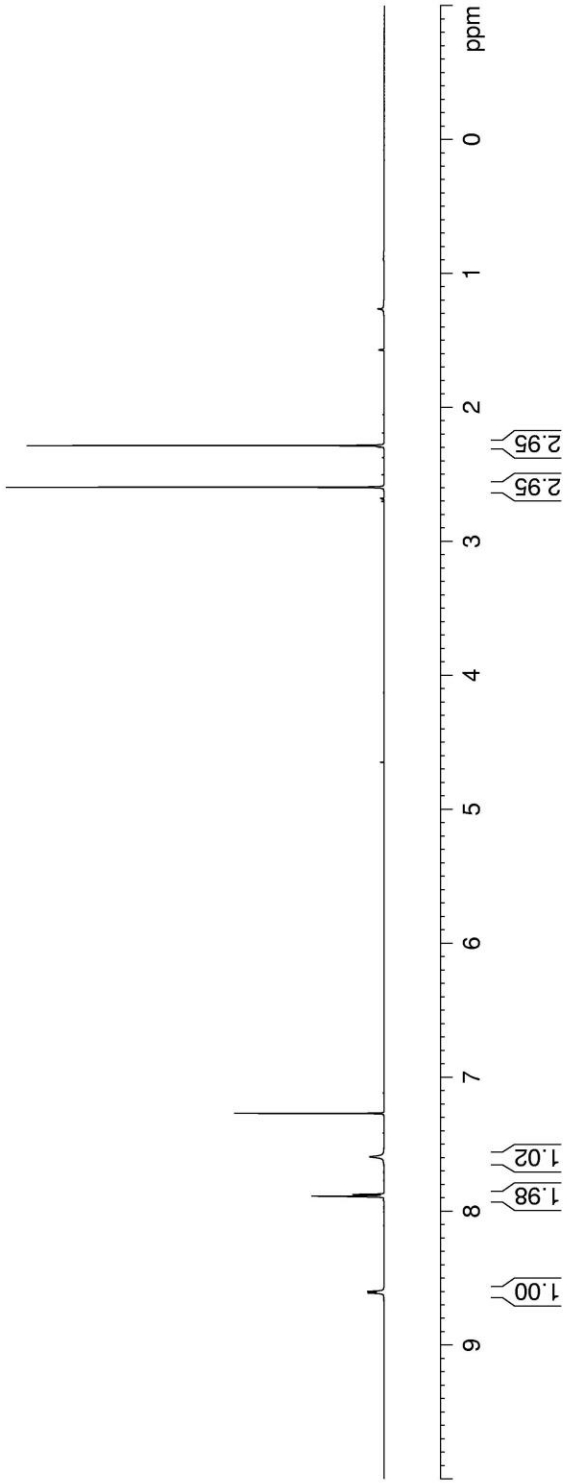
2i



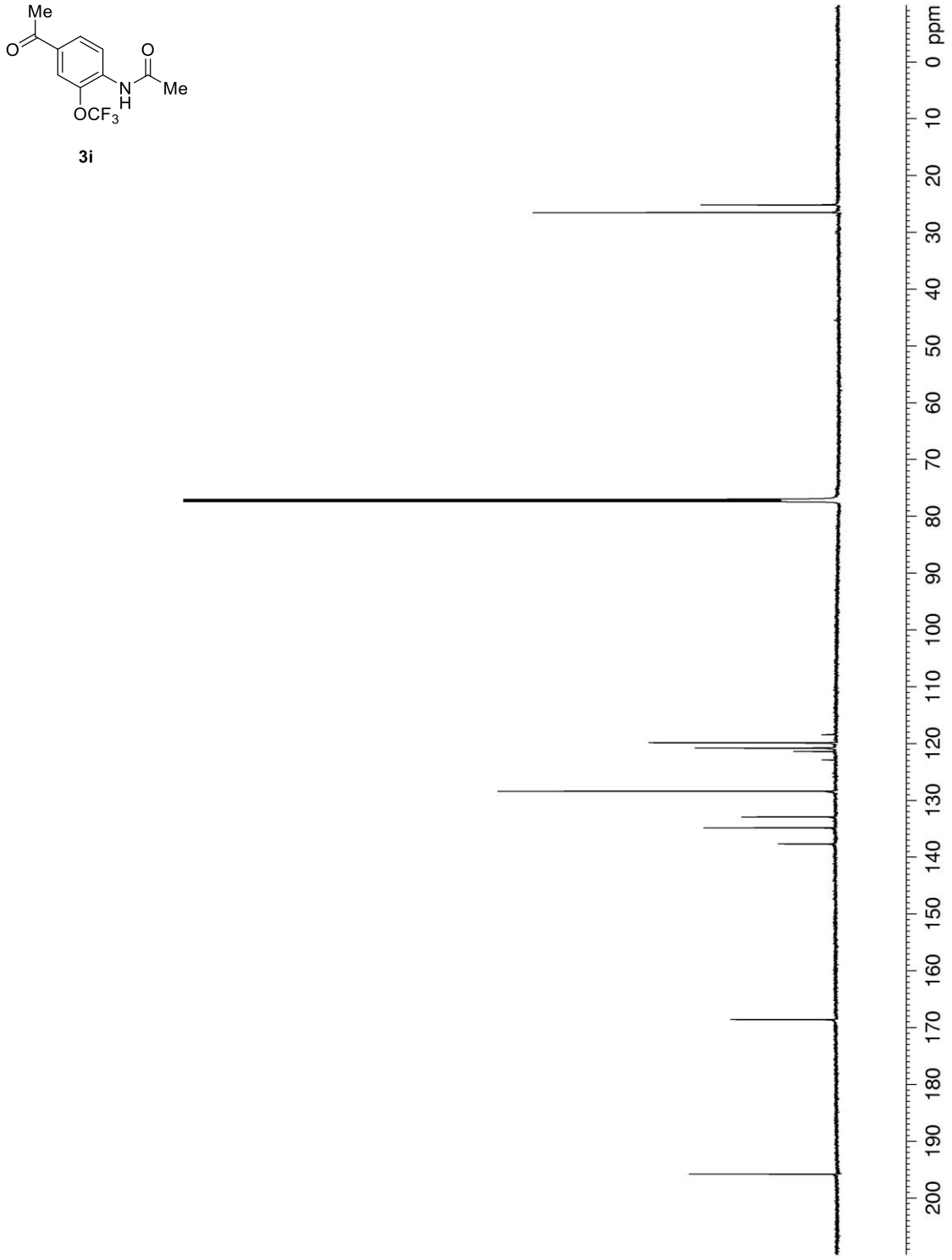
^{1}H NMR ($CDCl_3$, 25 ºC) of **3i**



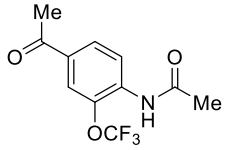
3i



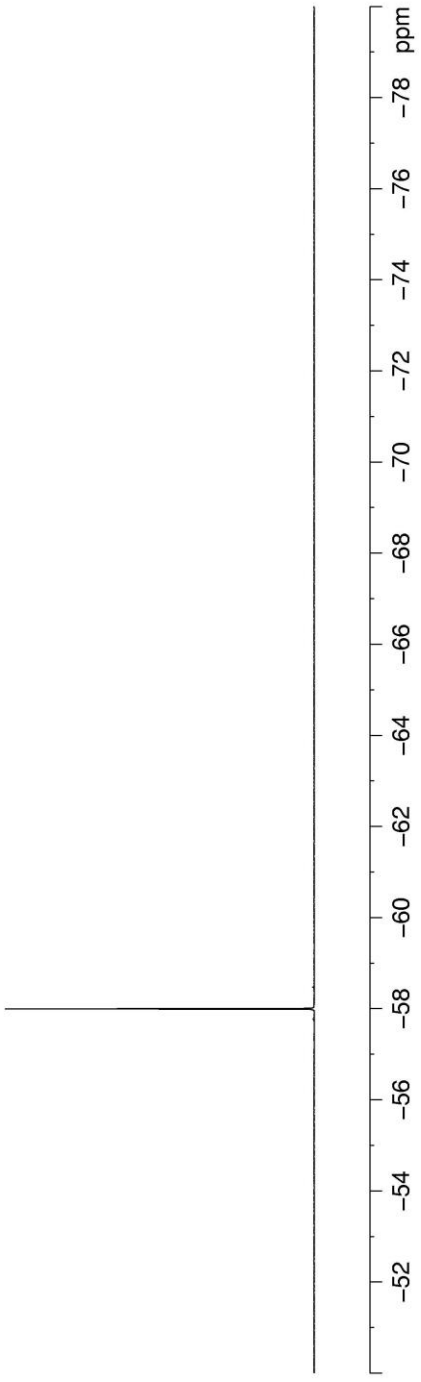
^{13}C NMR ($CDCl_3$, 25 ºC) of **3i**



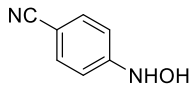
^{19}F NMR ($CDCl_3$, 25 ºC) of **3i**



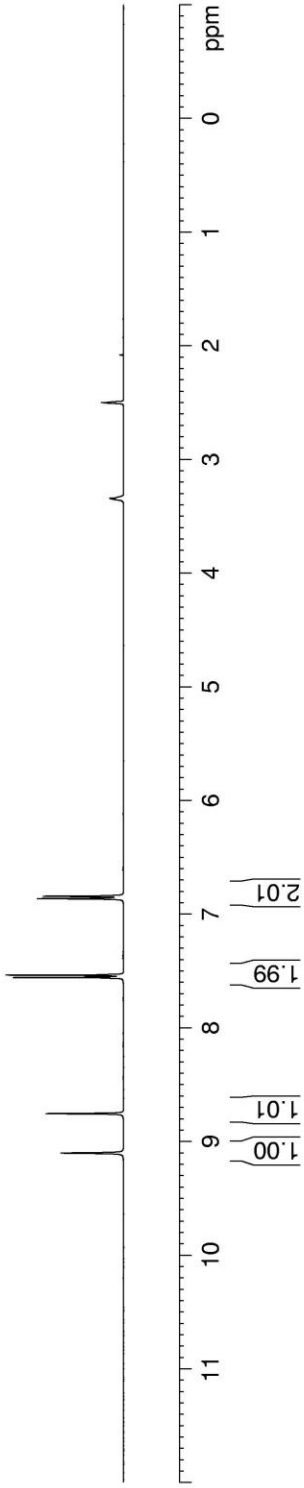
3i



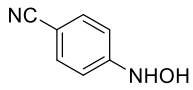
^{1}H NMR ($(CD_3)_2SO$, 25 ºC) of **S19**



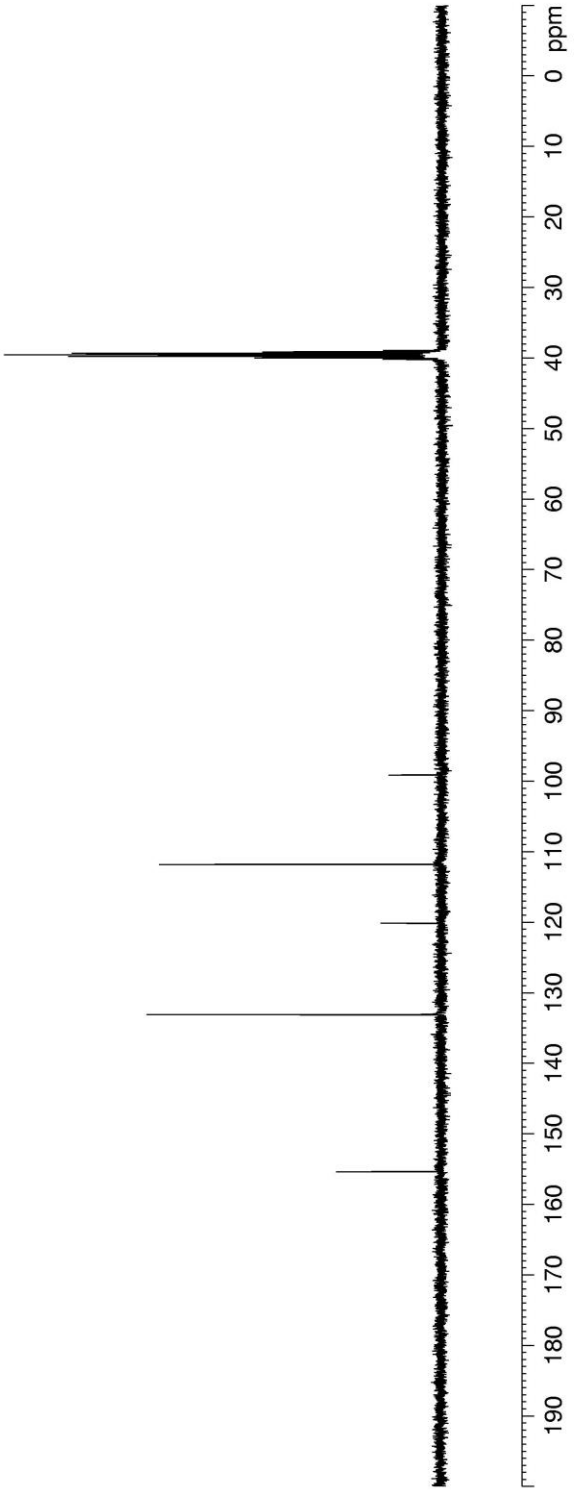
S19



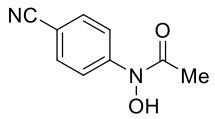
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S19**



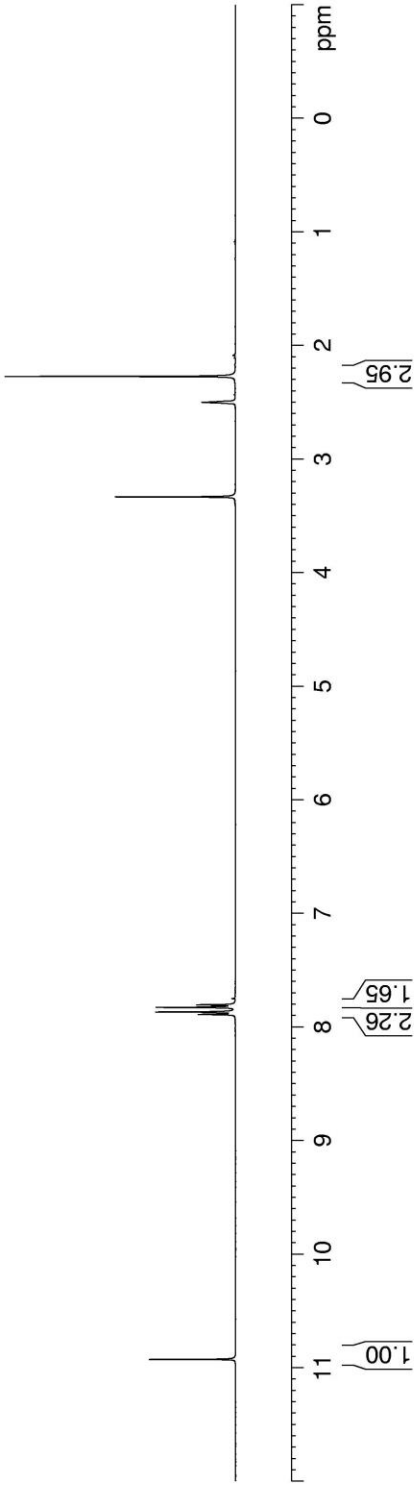
S19



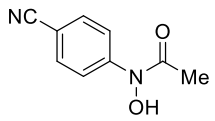
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S20**



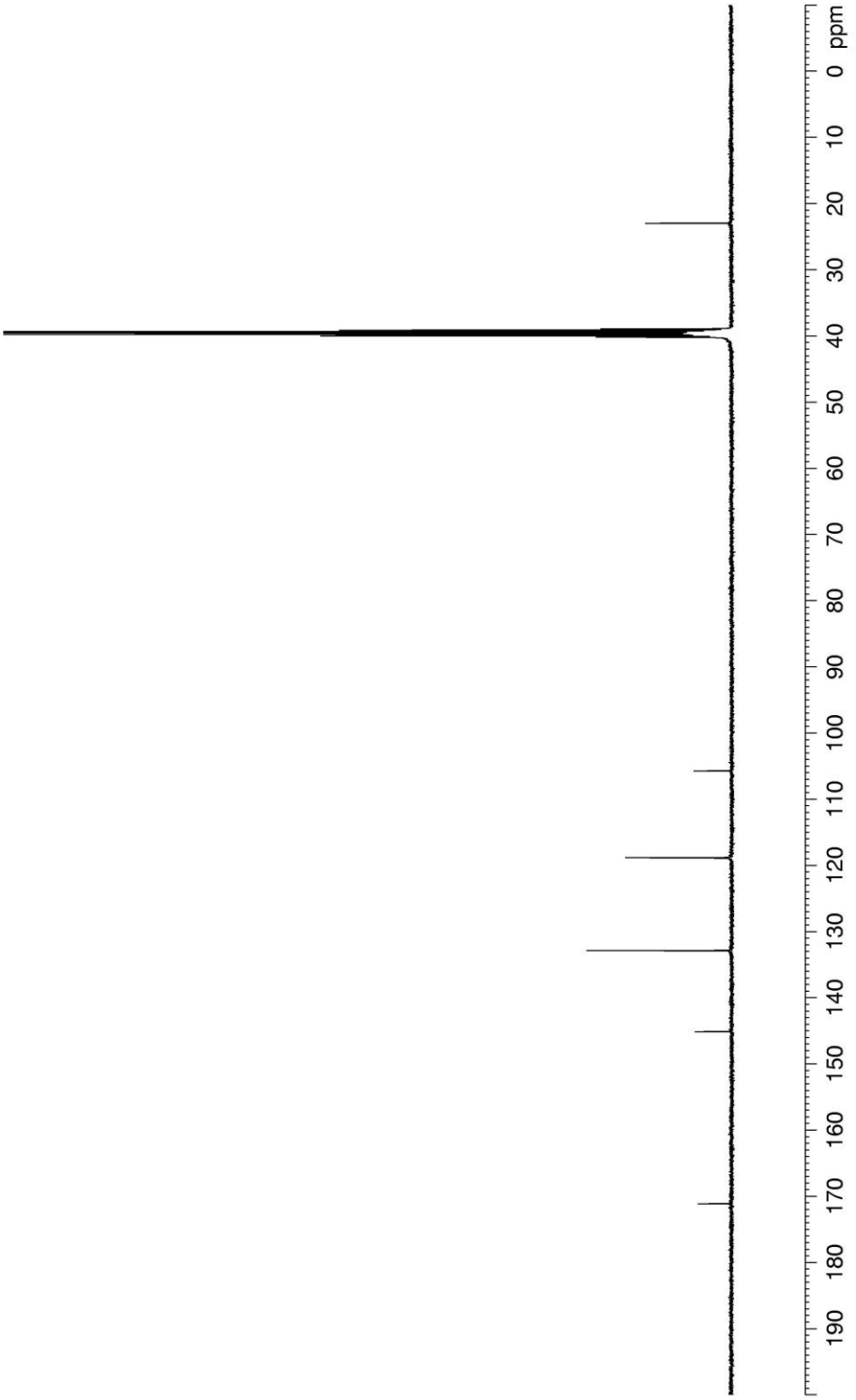
S20



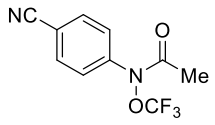
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S20**



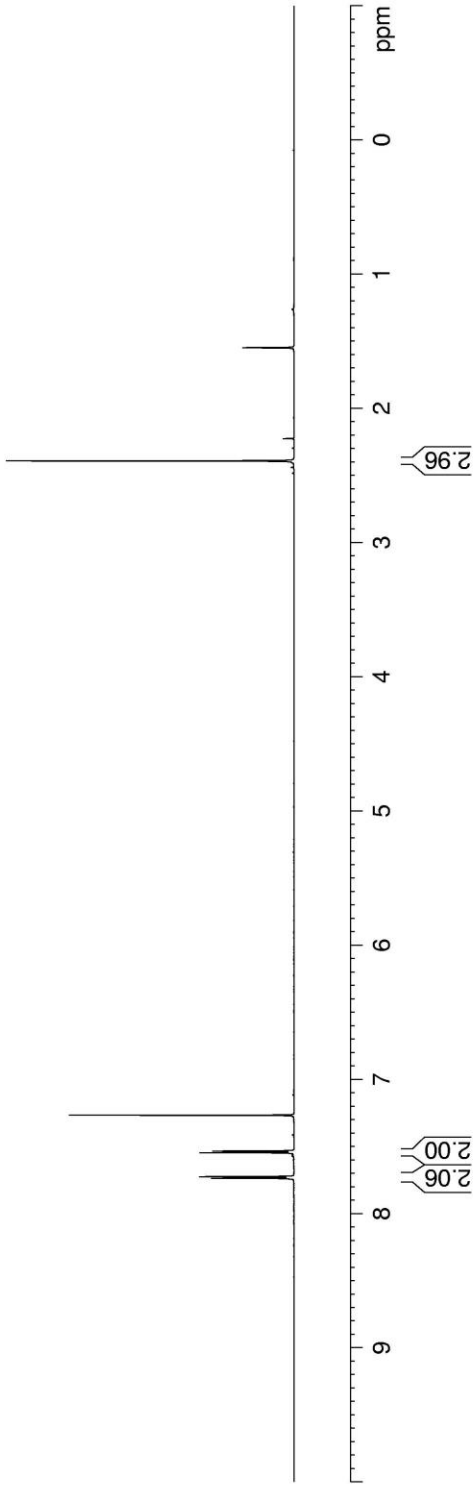
S20



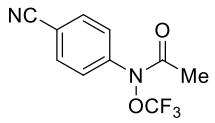
^{1}H NMR ($CDCl_3$, 25 ºC) of **2j**



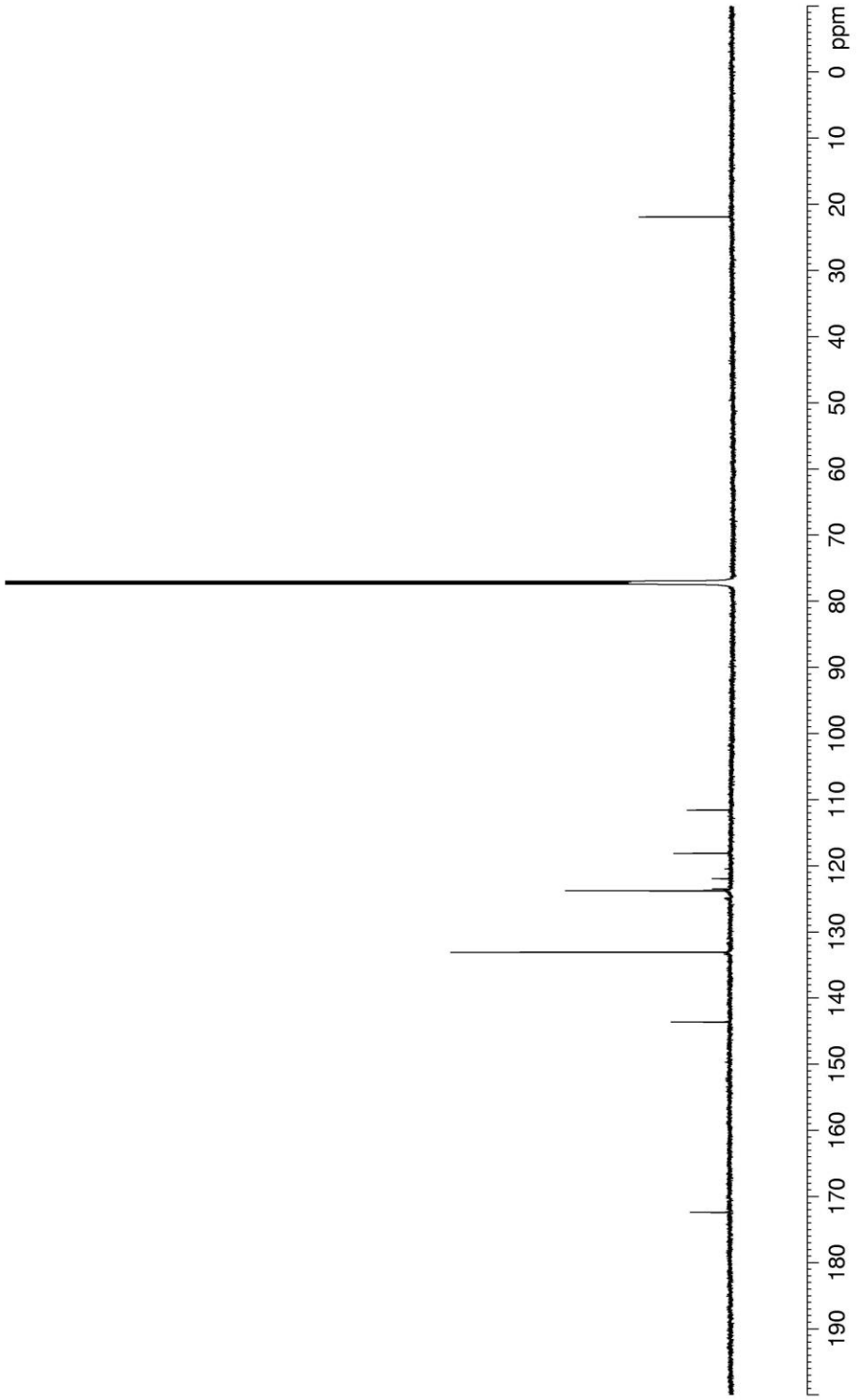
2j



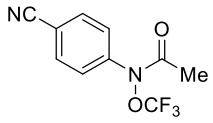
^{13}C NMR ($CDCl_3$, 25 ºC) of **2j**



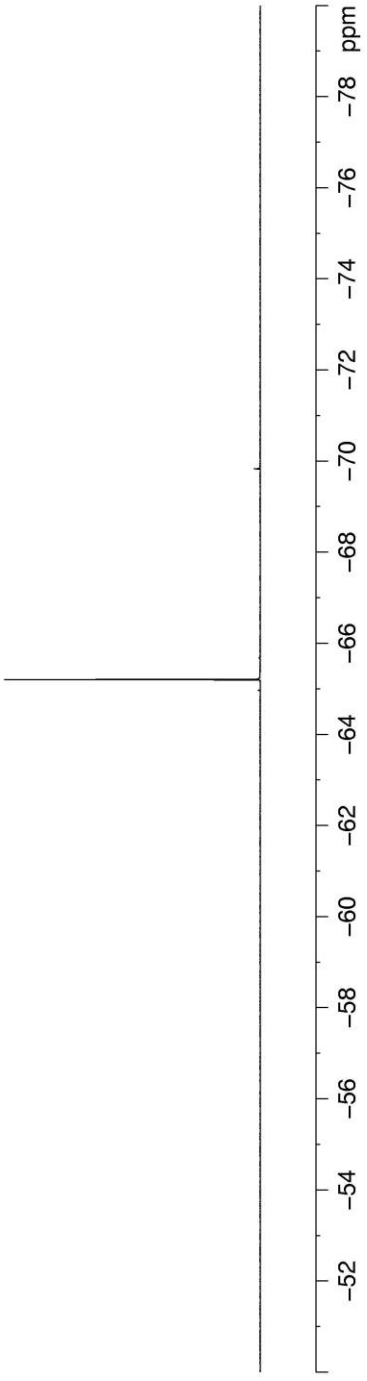
2j



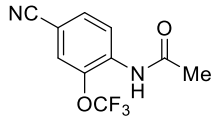
^{19}F NMR ($CDCl_3$, 25 ºC) of **2j**



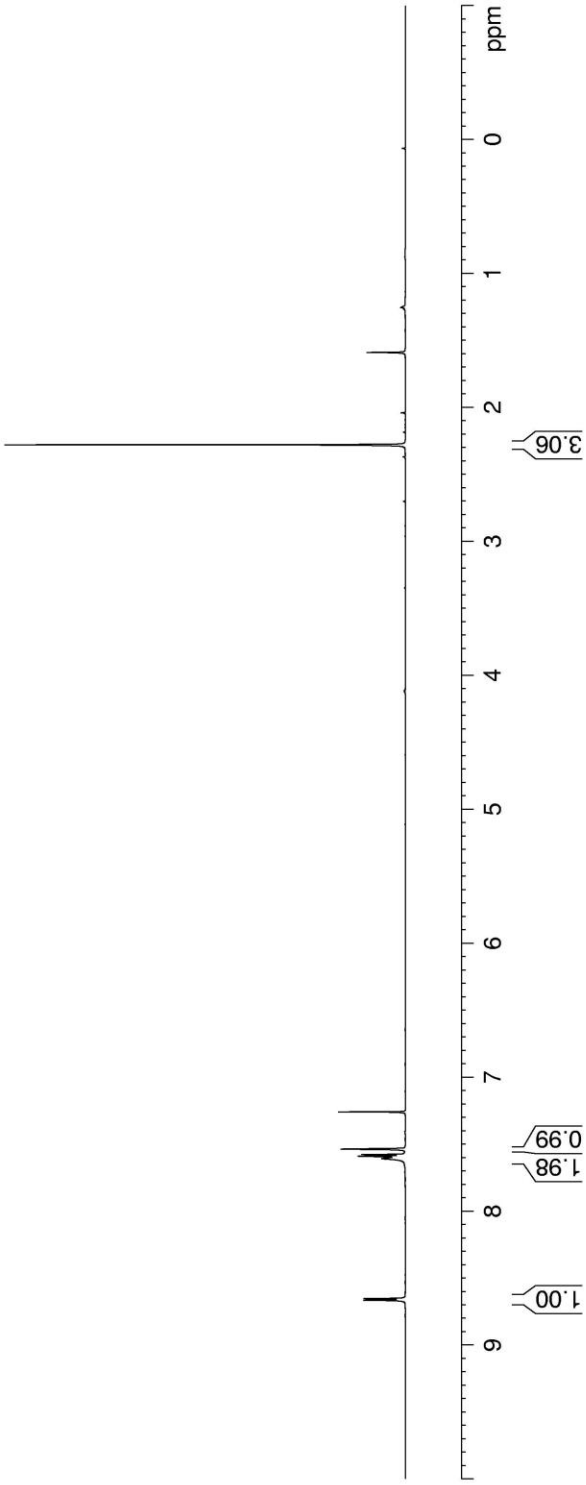
2j



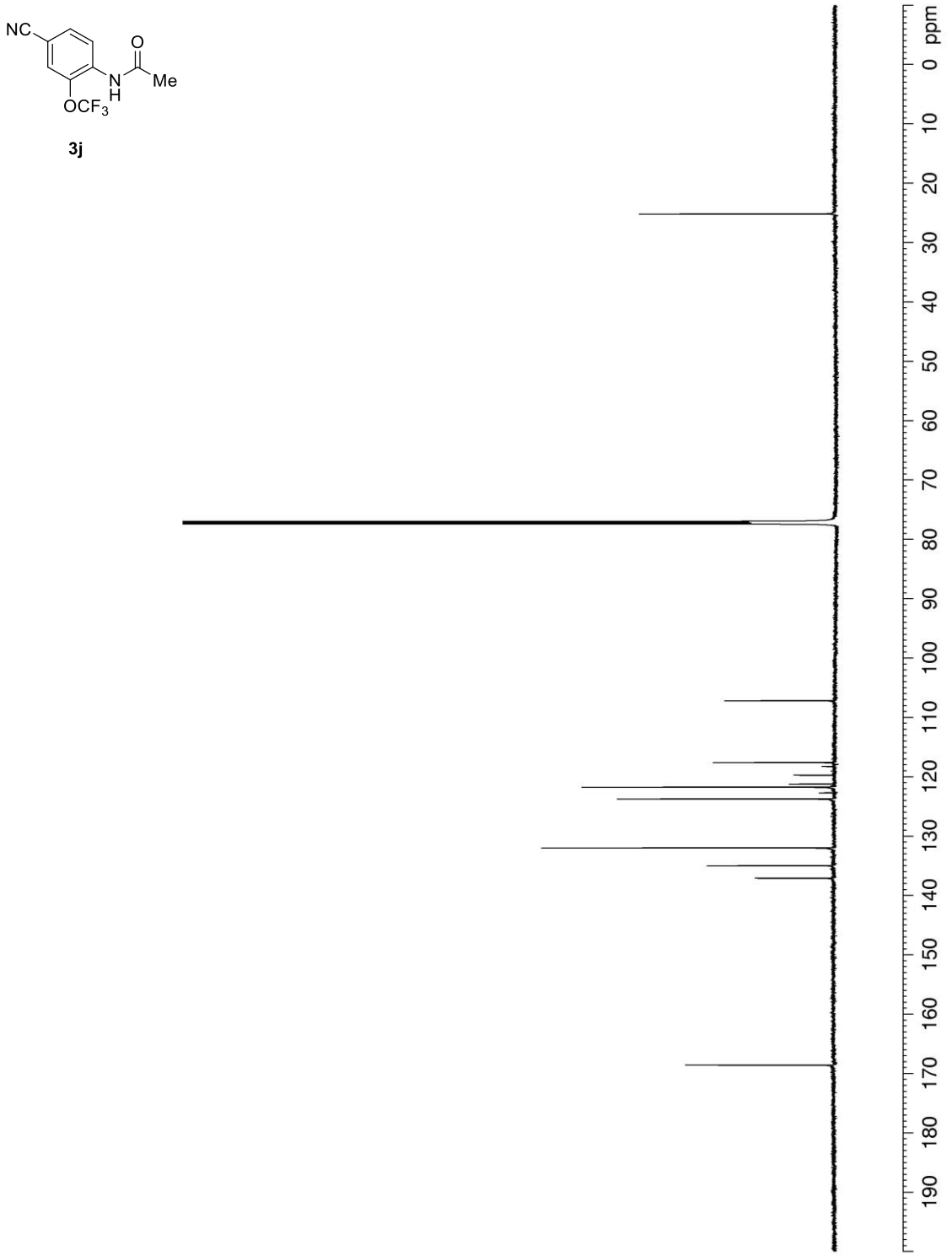
^{1}H NMR ($CDCl_3$, 25 ºC) of **3j**



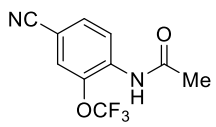
3j



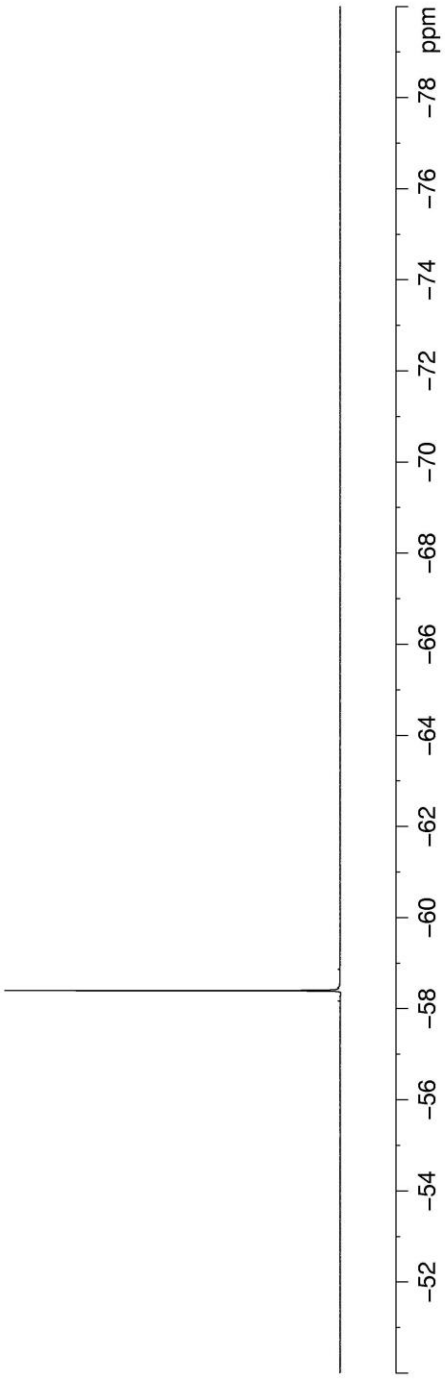
^{13}C NMR ($CDCl_3$, 25 ºC) of **3j**



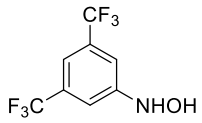
^{19}F NMR ($CDCl_3$, 25 ºC) of **3j**



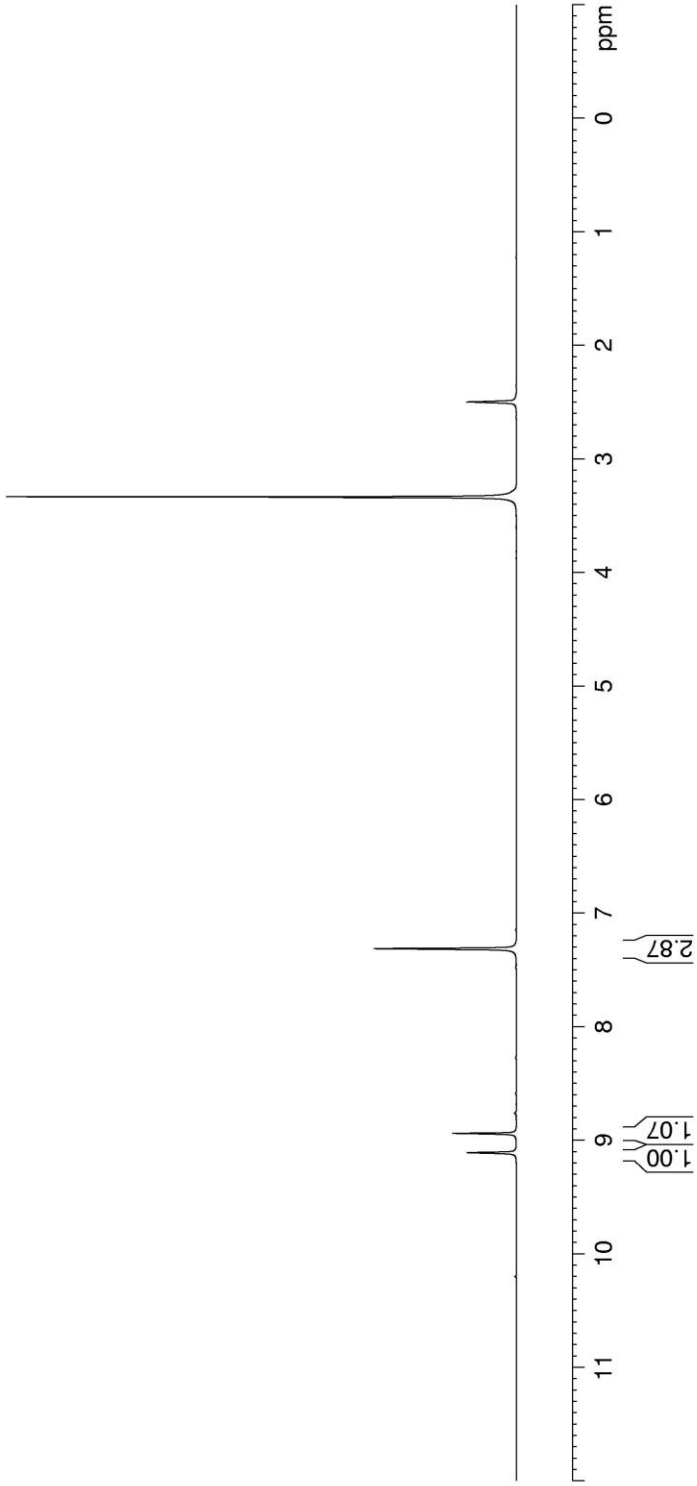
3j



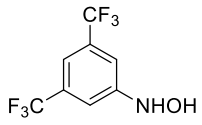
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S21**



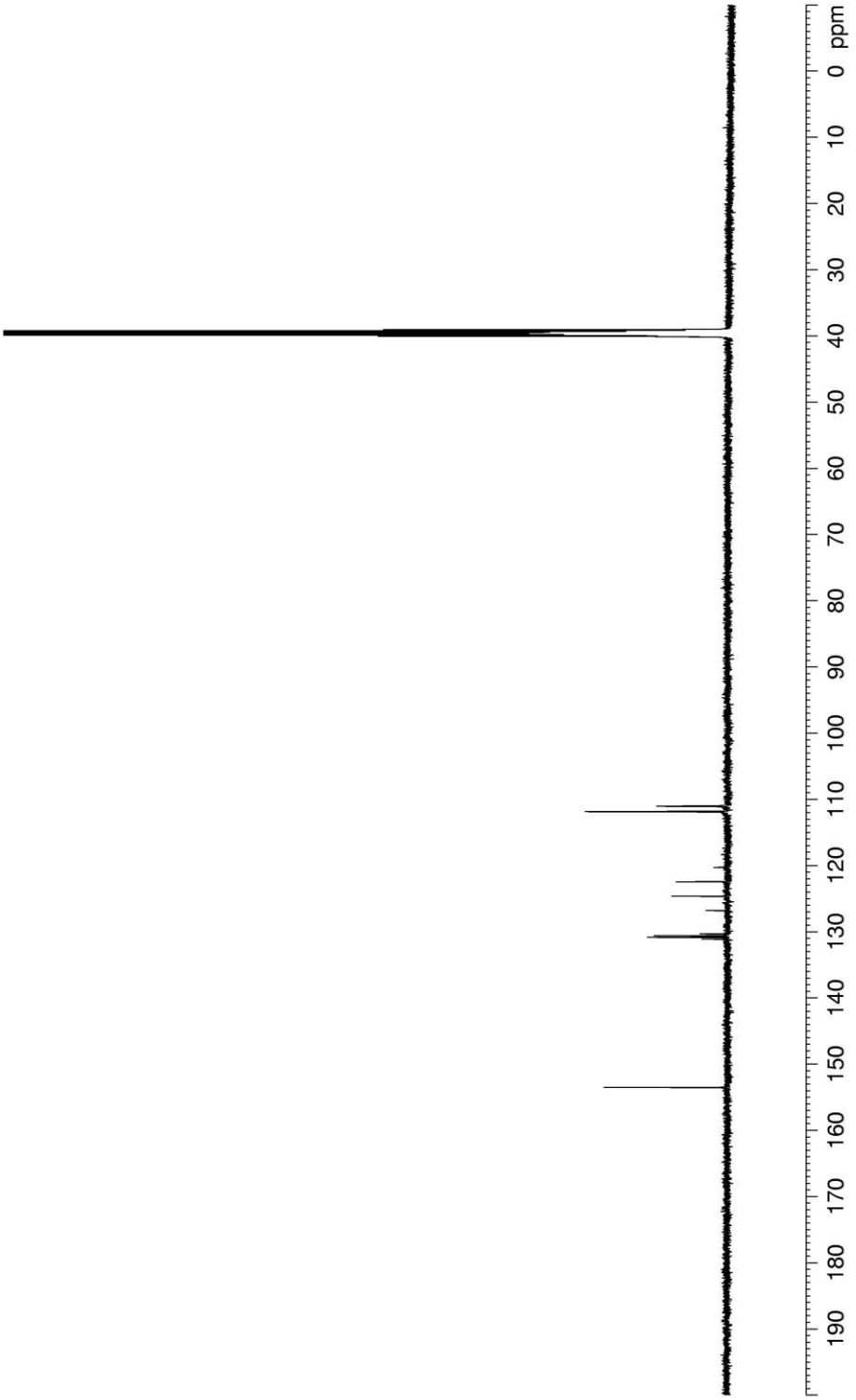
S21



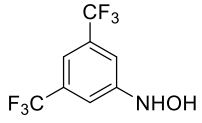
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S21**



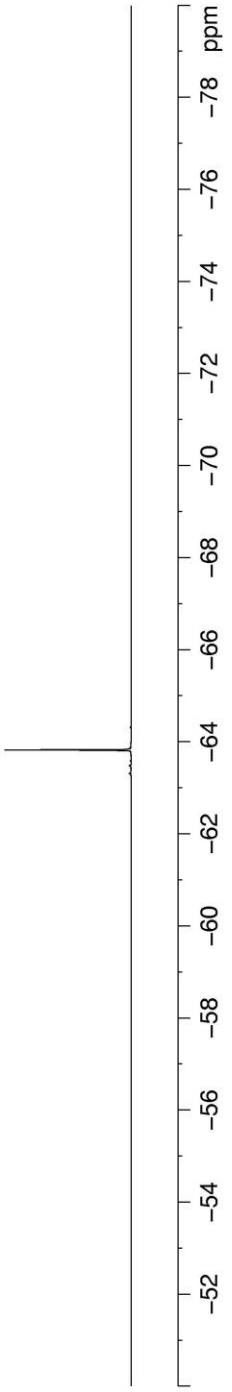
S21



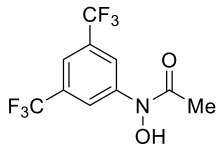
^{19}F NMR ($(CD_3)_2SO$, 25 ºC) of **S21**



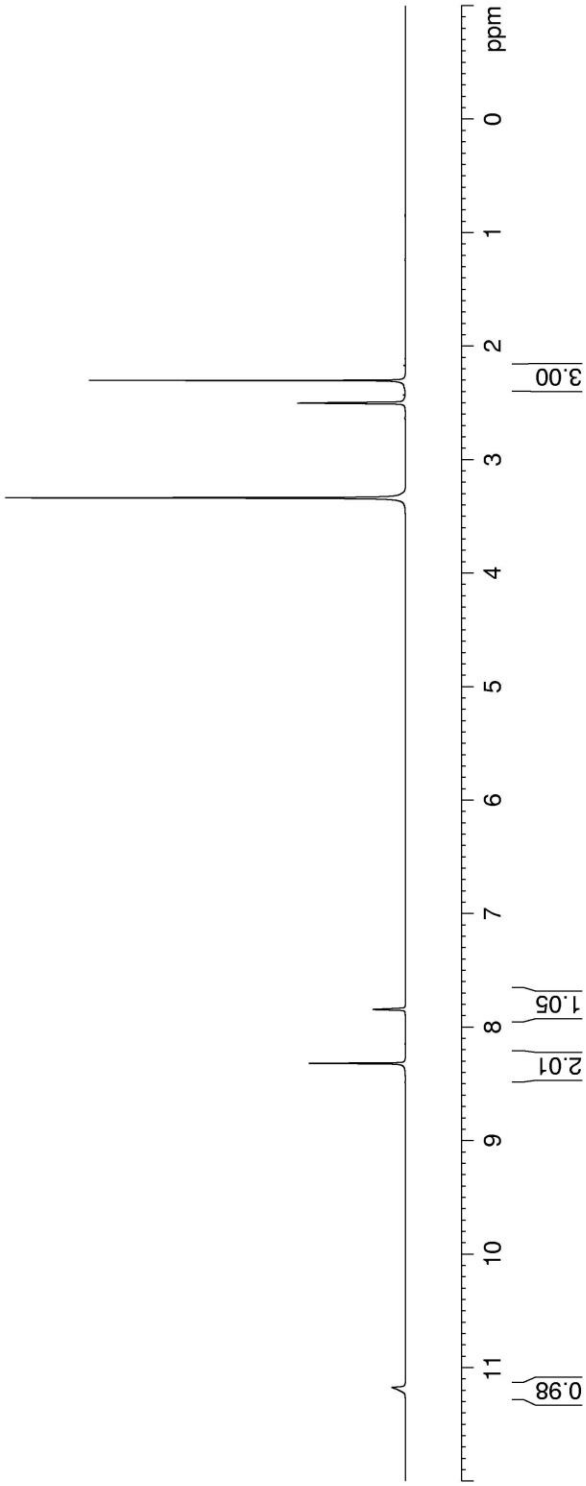
S21



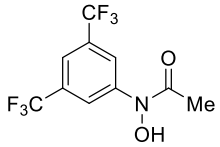
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S22**



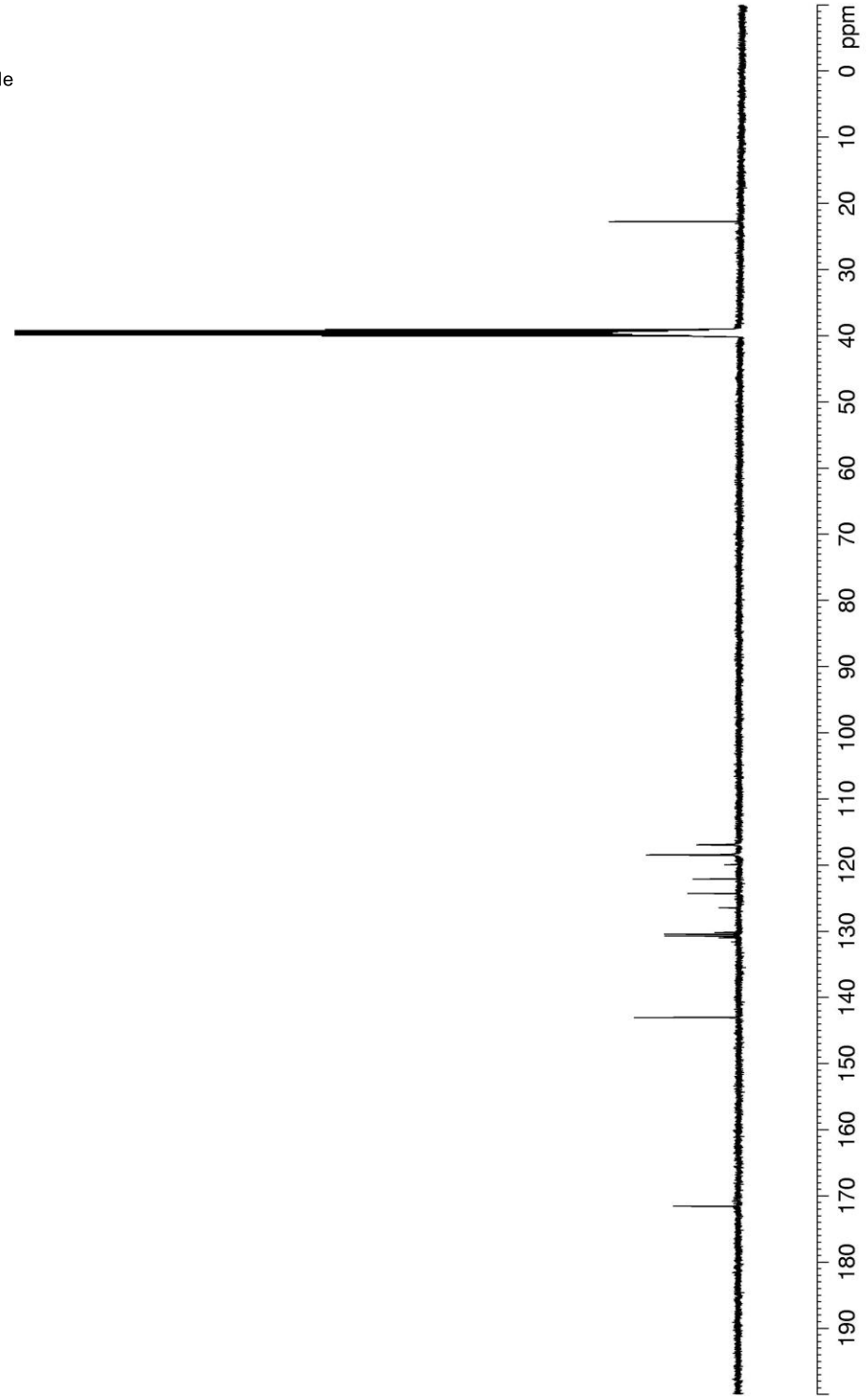
S22



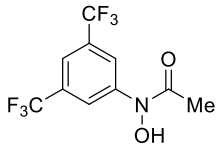
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S22**



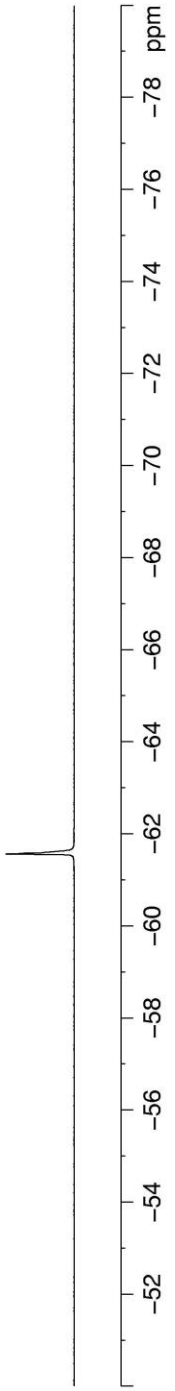
S22



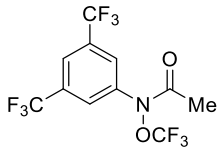
^{19}F NMR ((CD$_3$)$_2$SO, 25 ºC) of **S22**



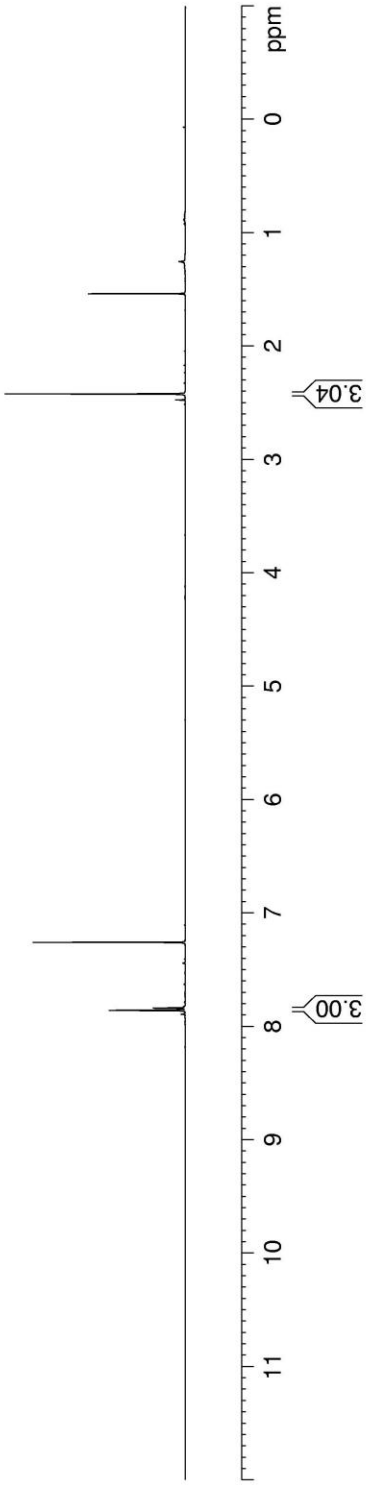
S22



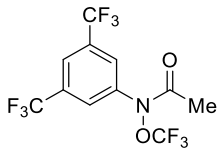
^{1}H NMR ($CDCl_3$, 25 ºC) of **2k**



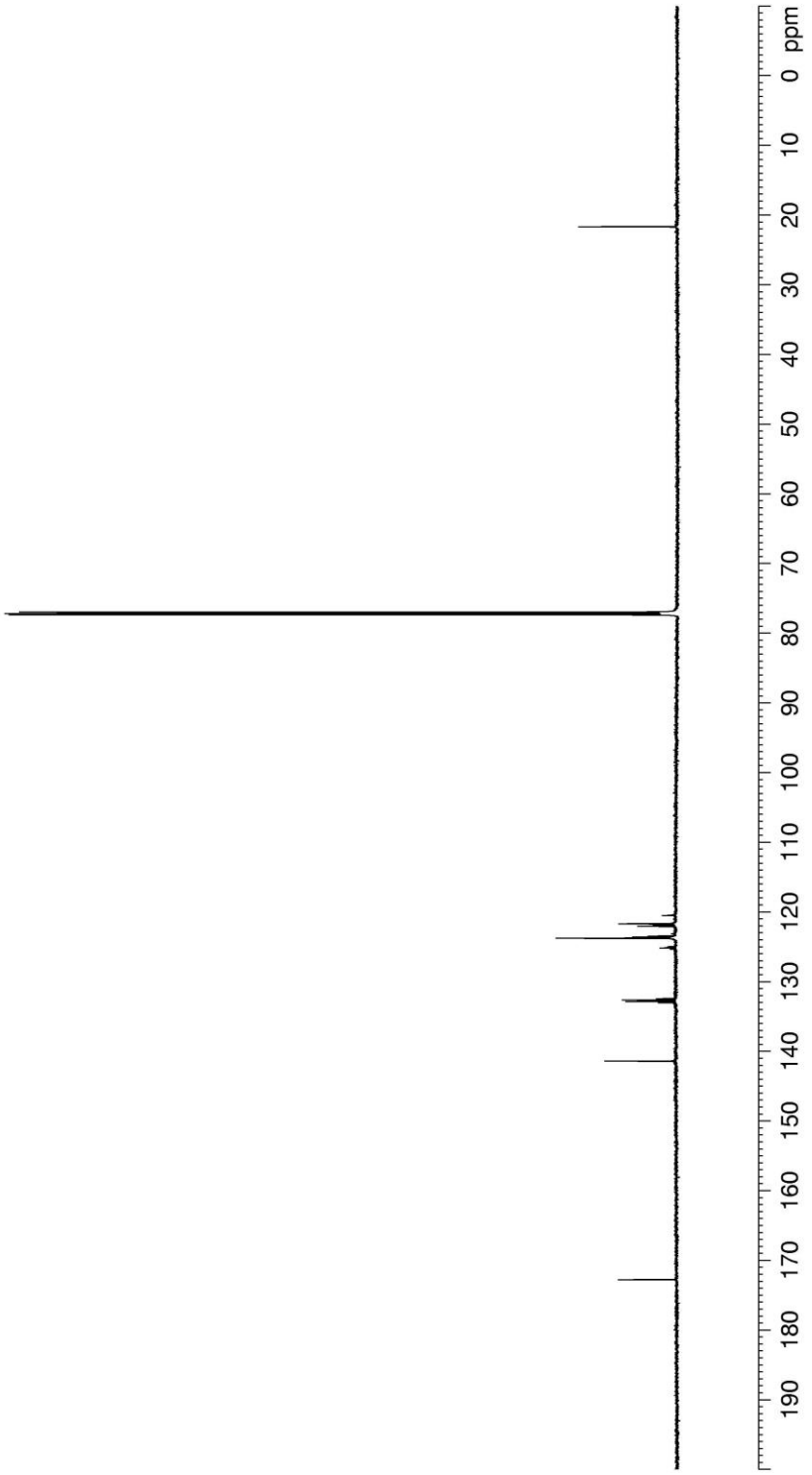
2k



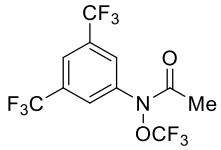
^{13}C NMR ($CDCl_3$, 25 ºC) of **2k**



2k



^{19}F NMR ($CDCl_3$, 25 ºC) of **2k**



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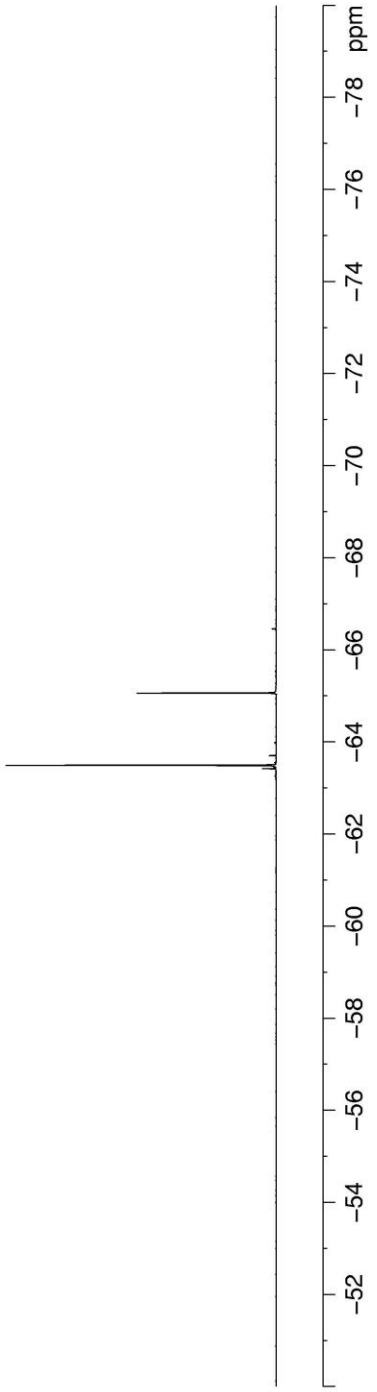
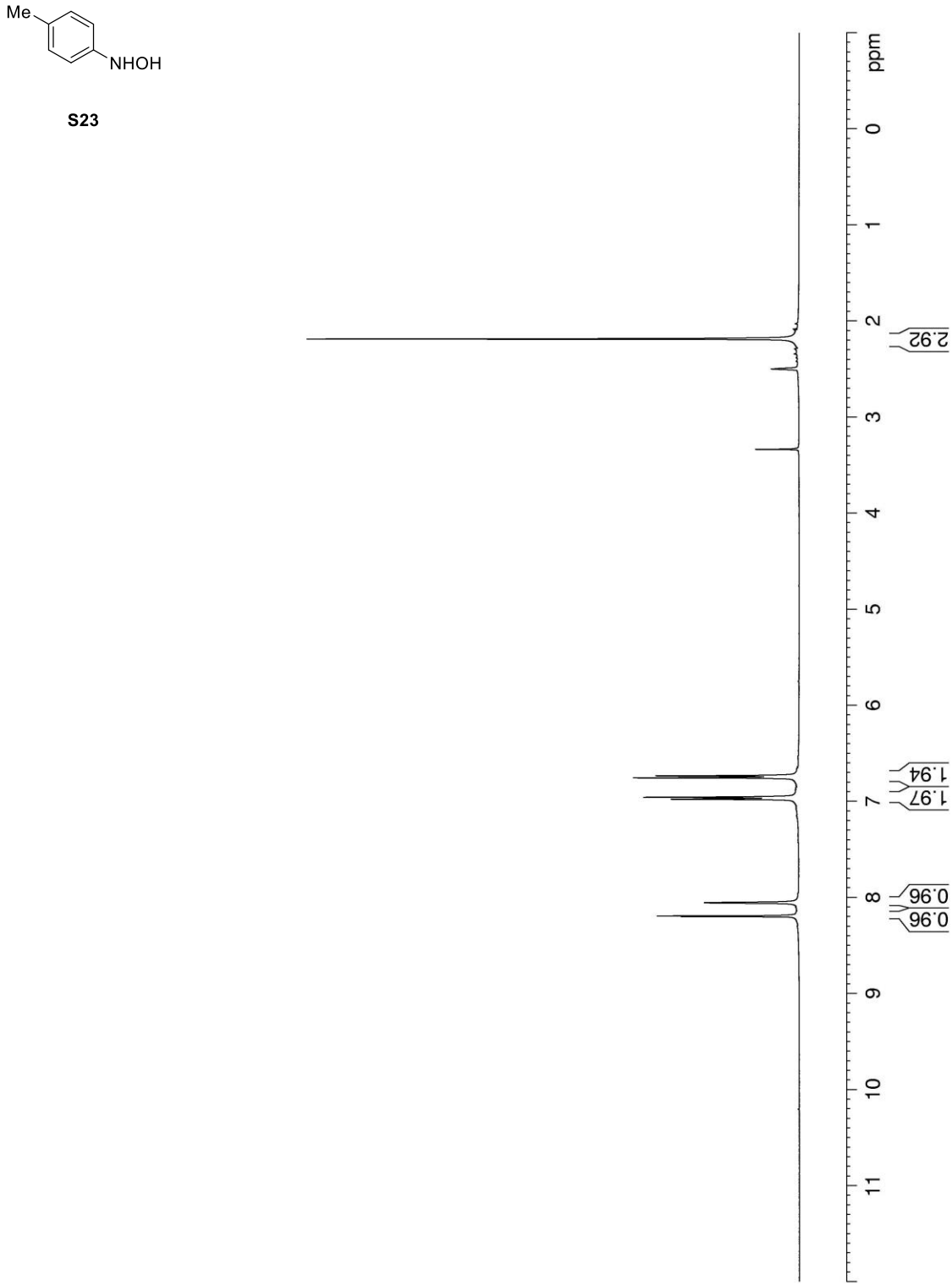
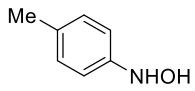


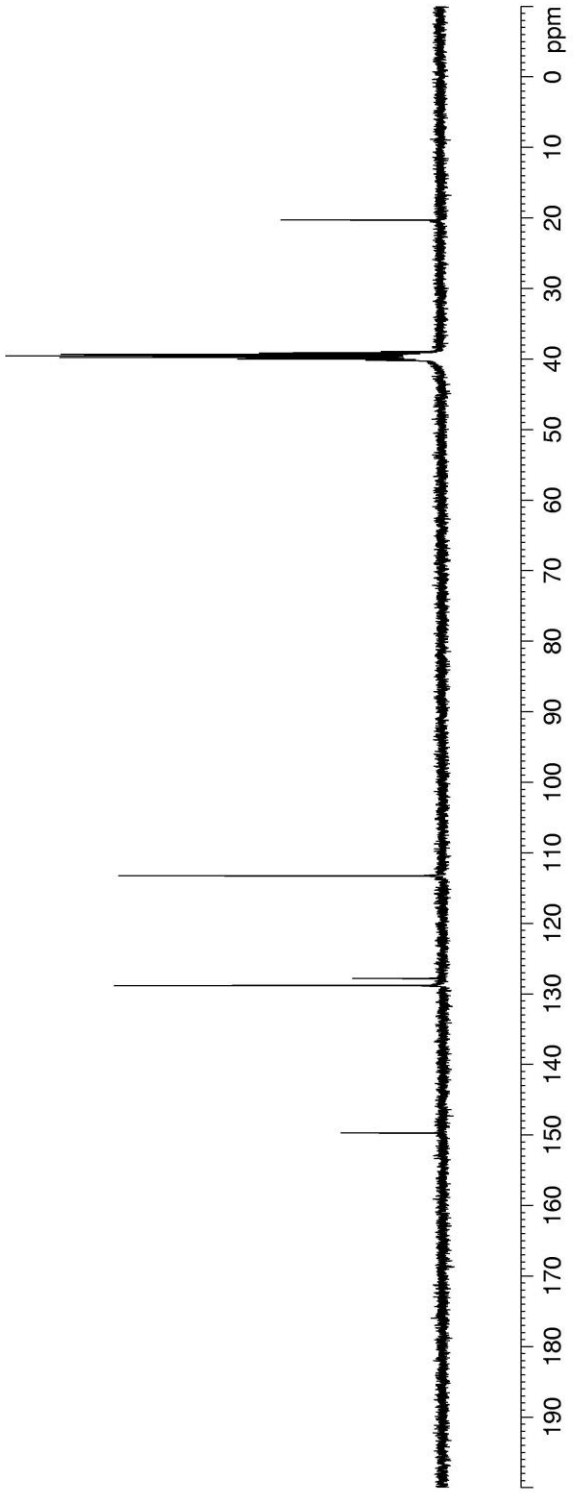
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S23**



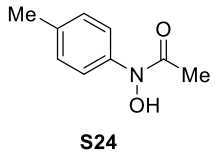
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S23**



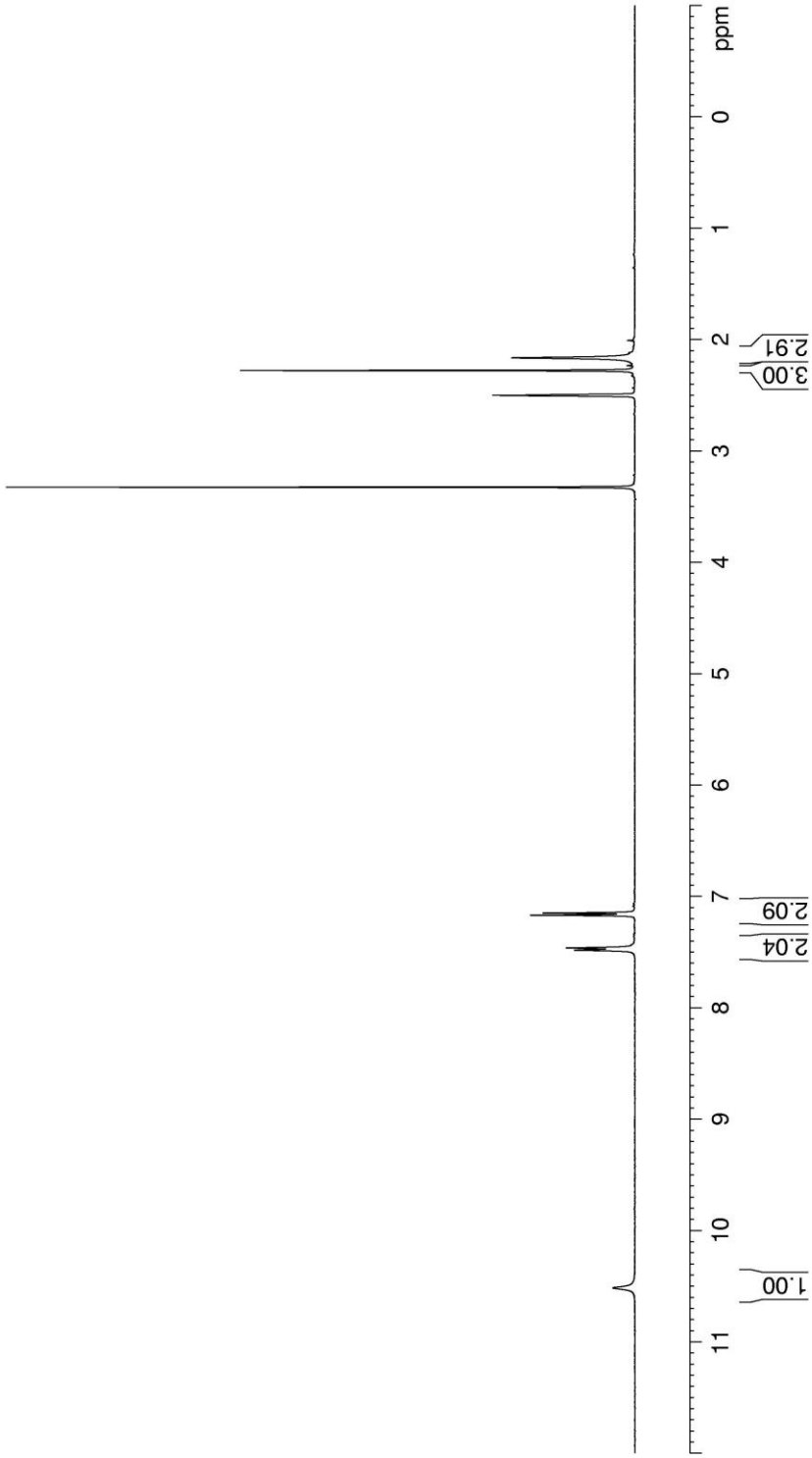
S23



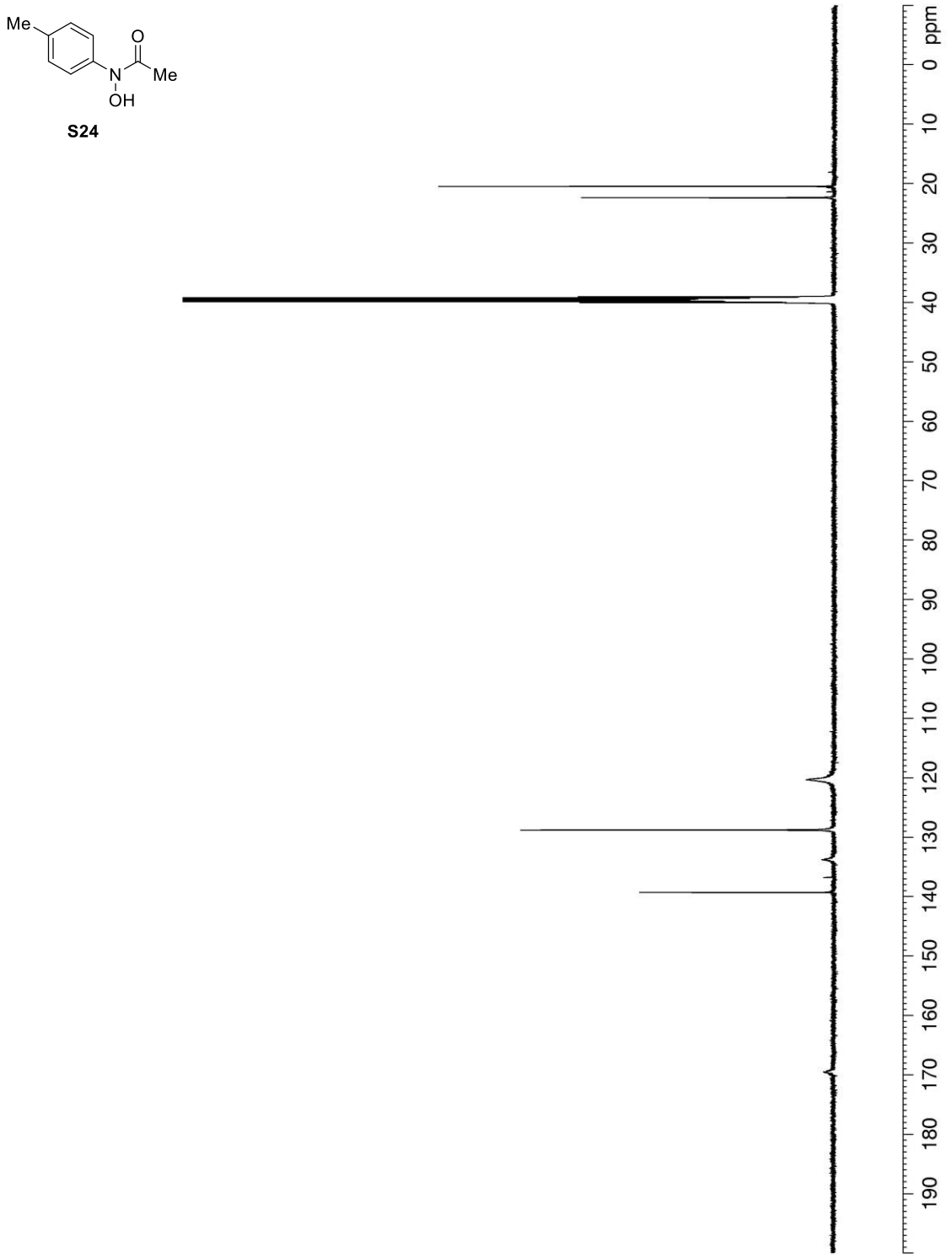
^{1}H NMR ($(CD_3)_2SO$, 25 ºC) of **S24**



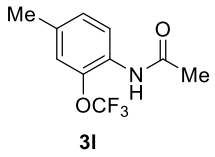
S24



^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S24**



^{1}H NMR ($CDCl_3$, 25 ºC) of **3l**



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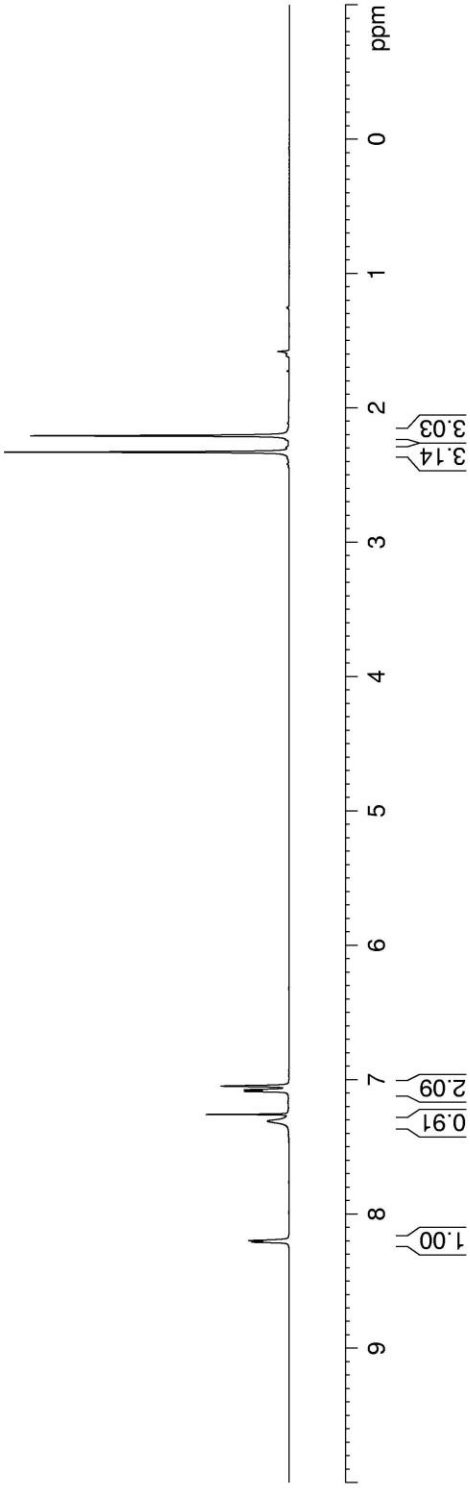
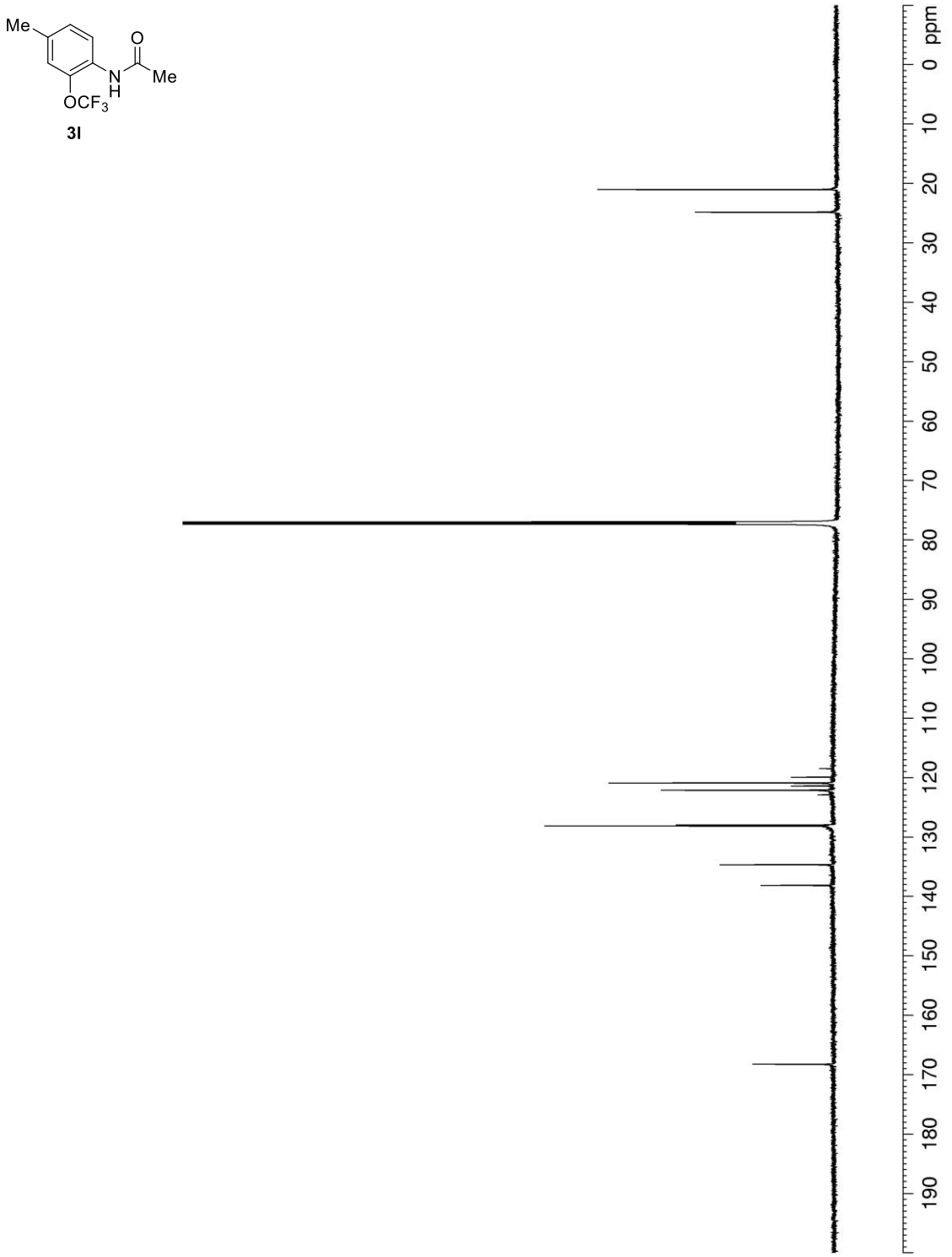
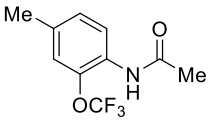


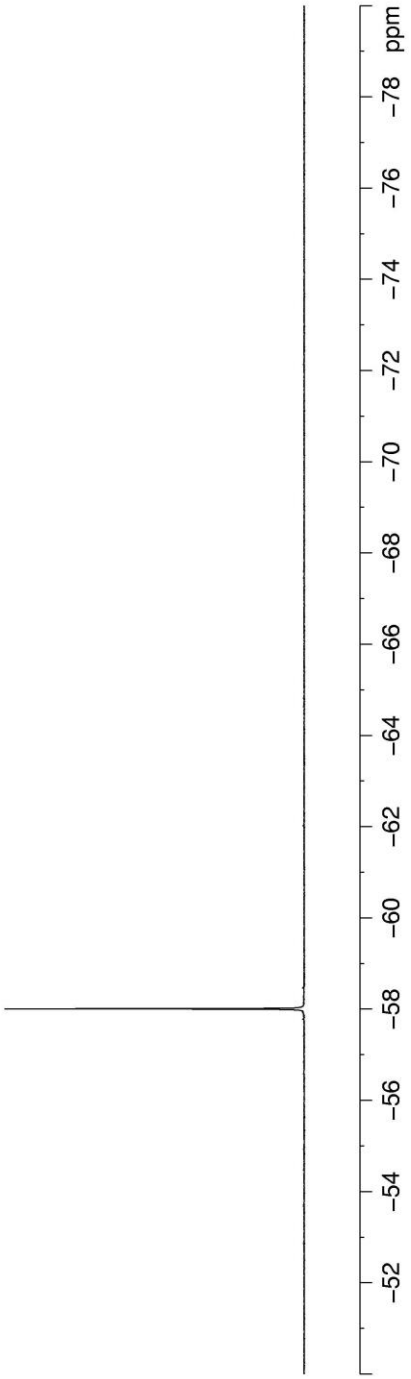
^{13}C NMR ($CDCl_3$, 25 ºC) of **3l**



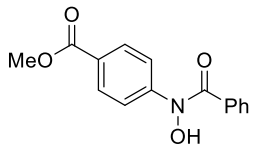
^{19}F NMR ($CDCl_3$, 25 ºC) of **3l**



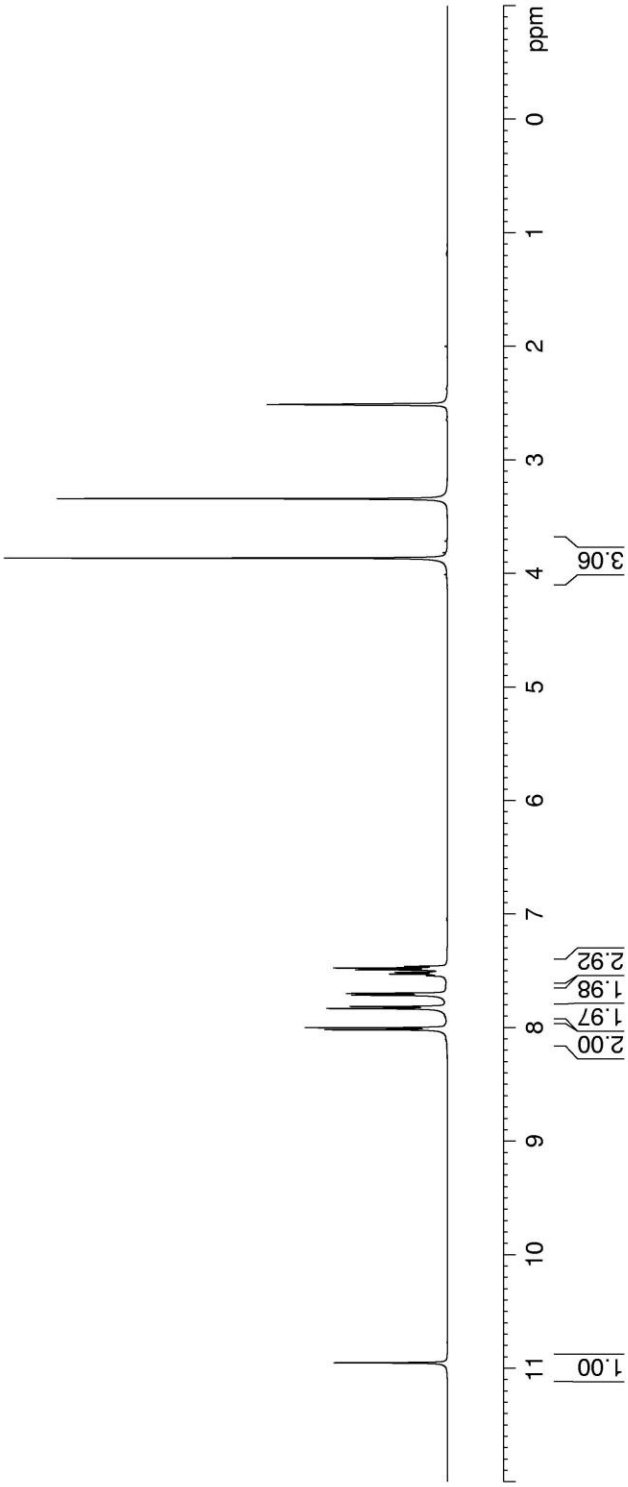
3l



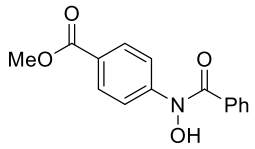
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S25**



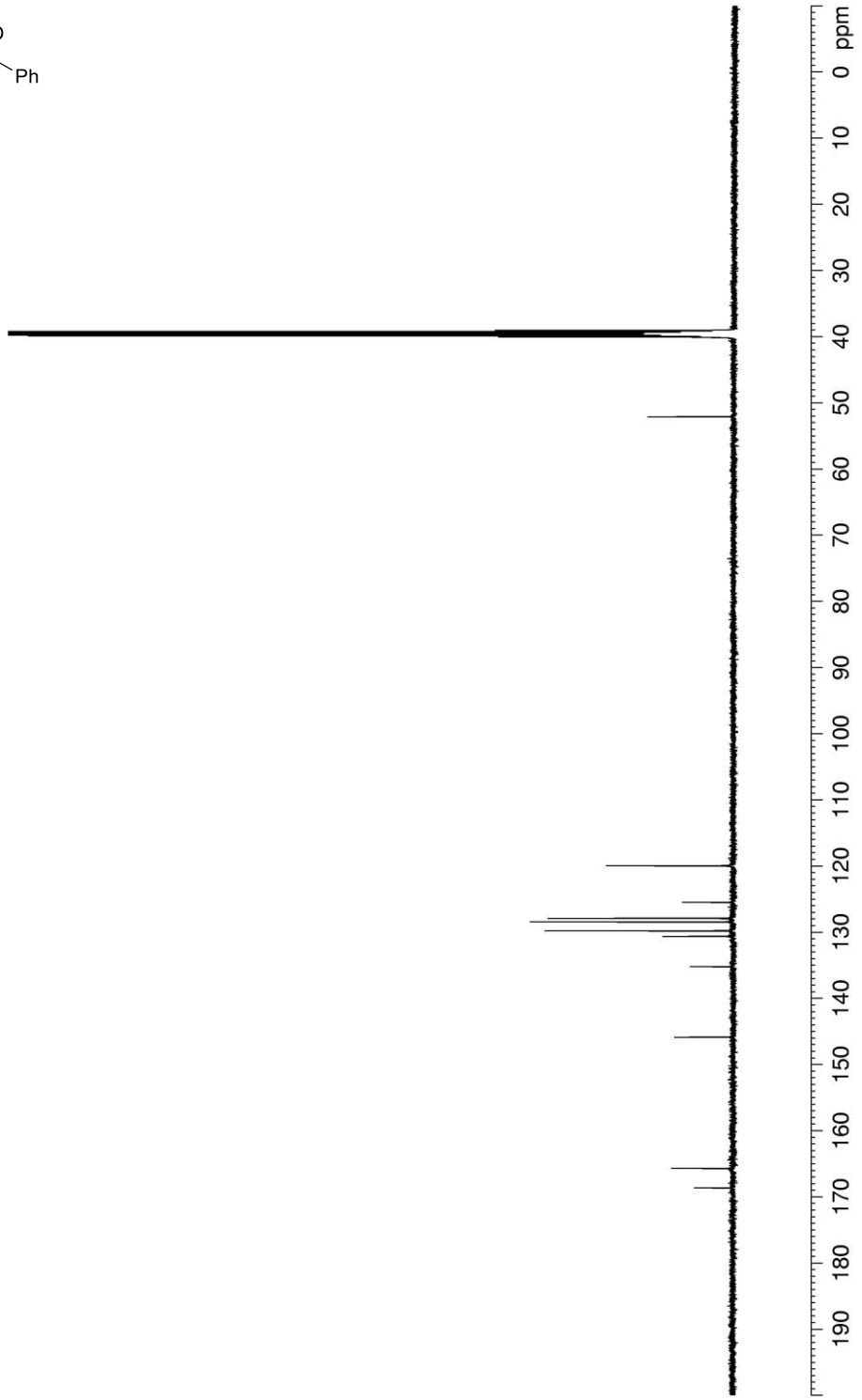
S25



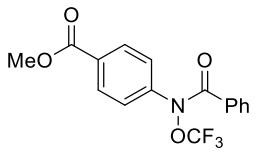
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S25**



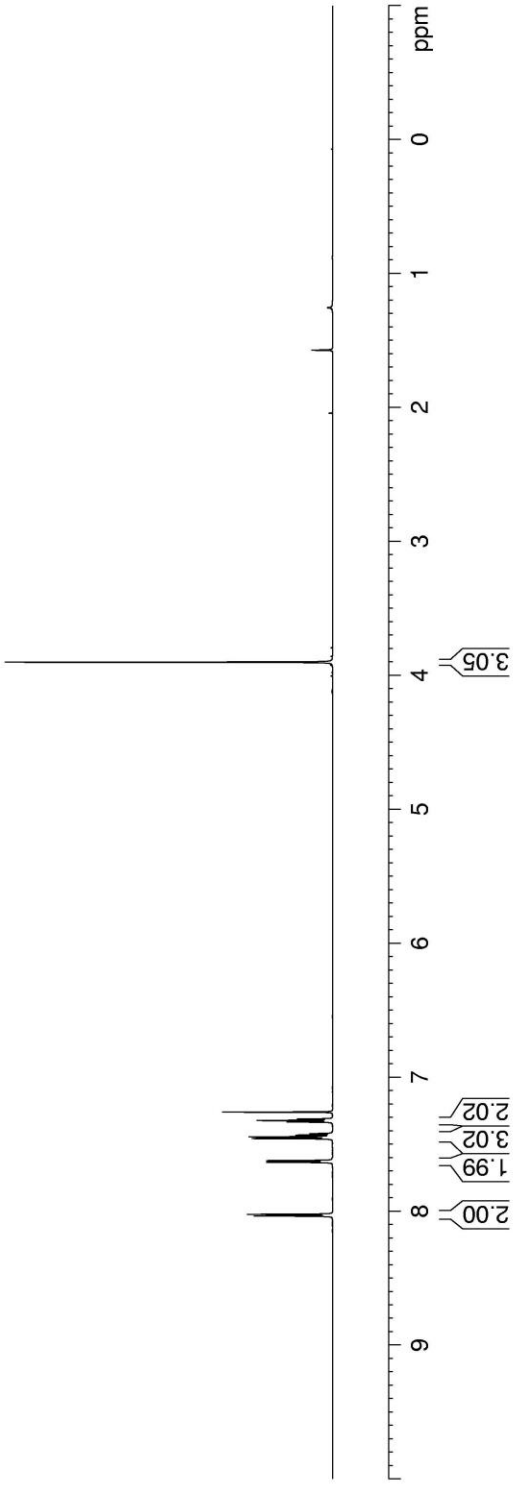
S25



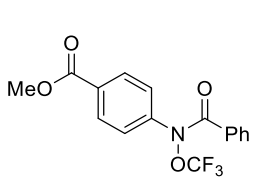
^{1}H NMR ($CDCl_3$, 25 ºC) of **2m**



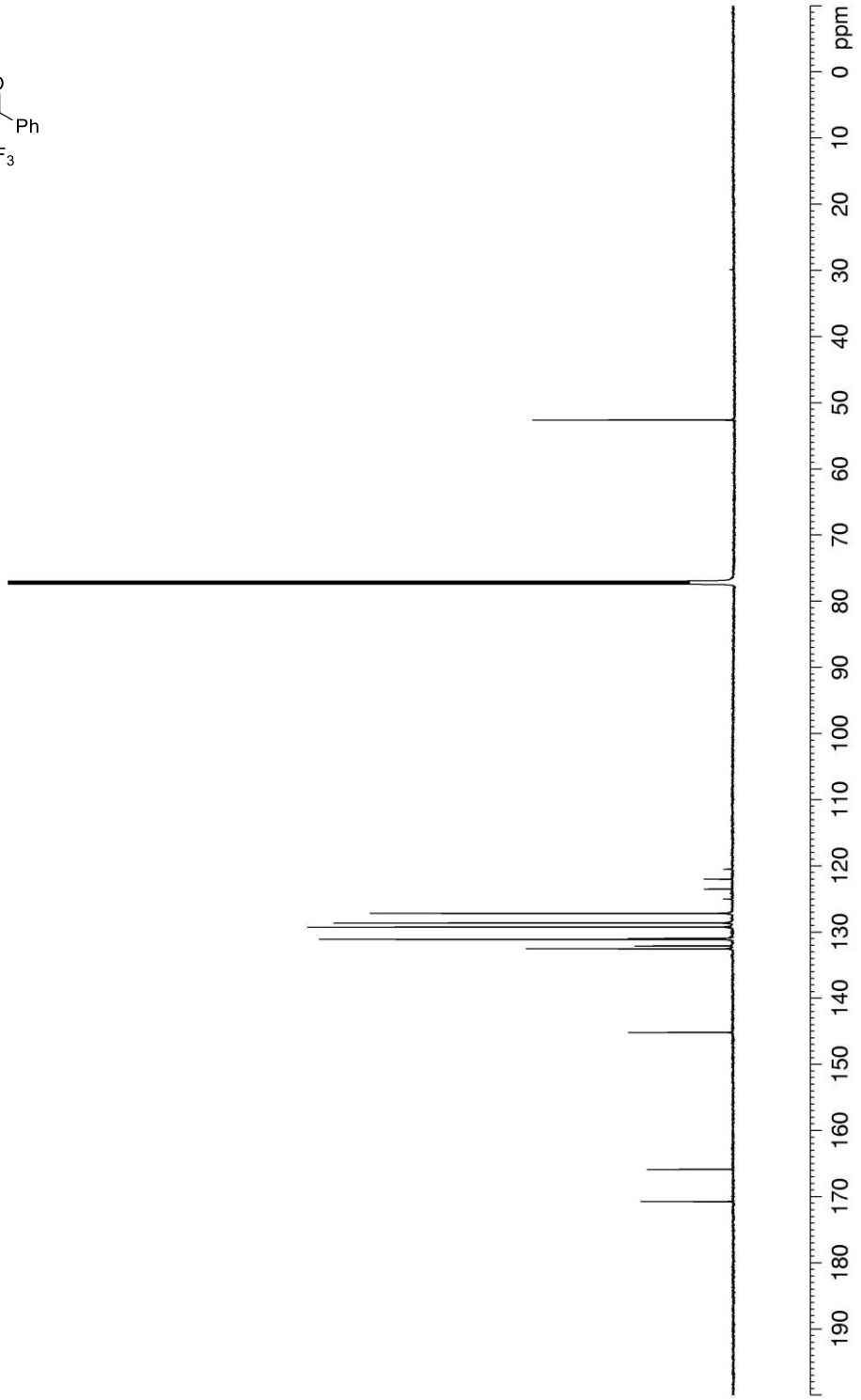
2m



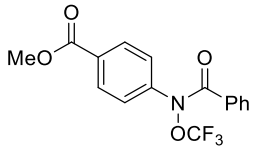
^{13}C NMR ($CDCl_3$, 25 ºC) of **2m**



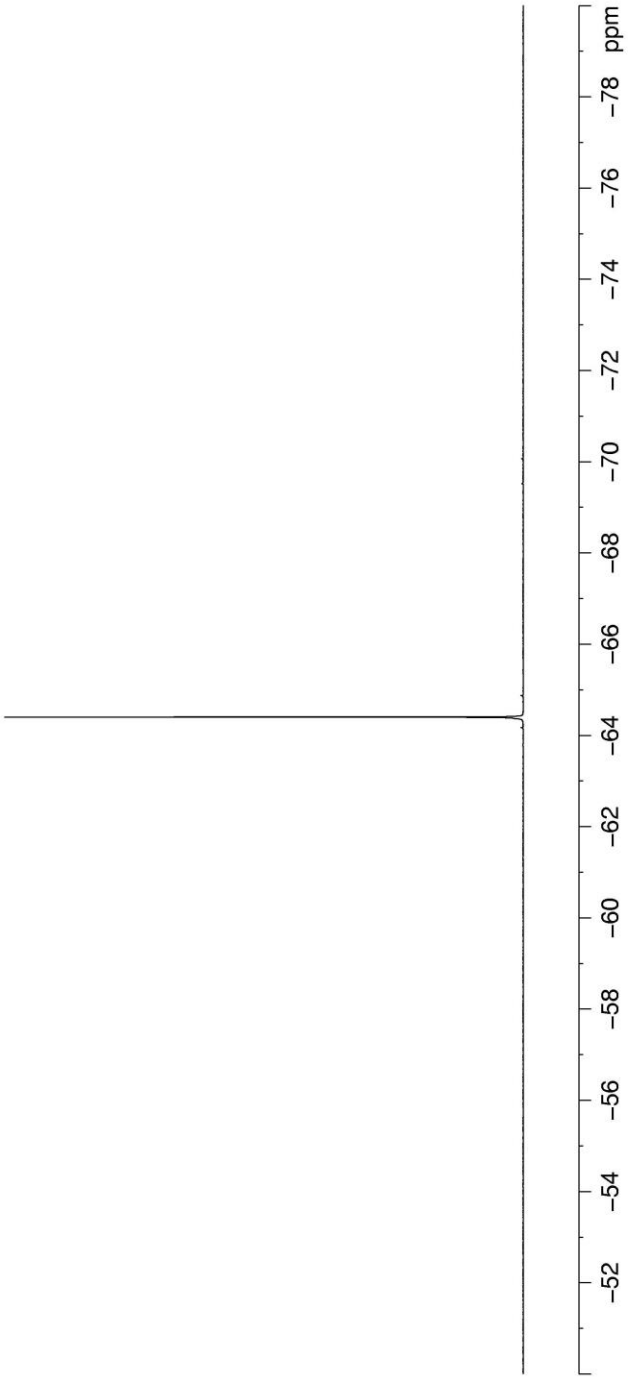
2m



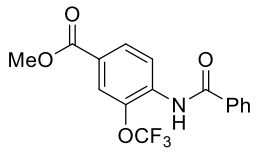
^{19}F NMR ($CDCl_3$, 25 ºC) of **2m**



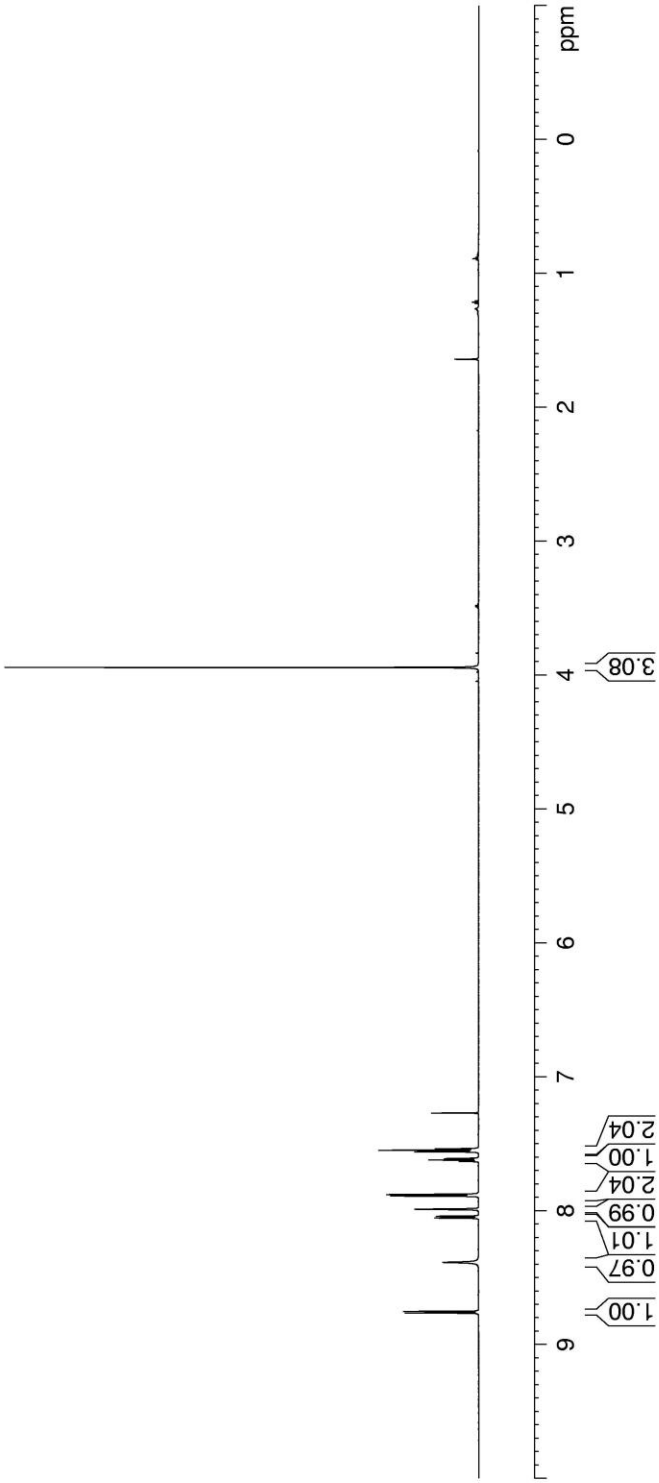
2m



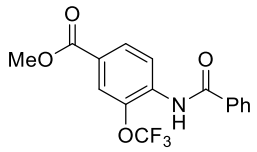
^{1}H NMR ($CDCl_3$, 25 ºC) of **3m**



3m



^{13}C NMR ($CDCl_3$, 25 ºC) of **3m**



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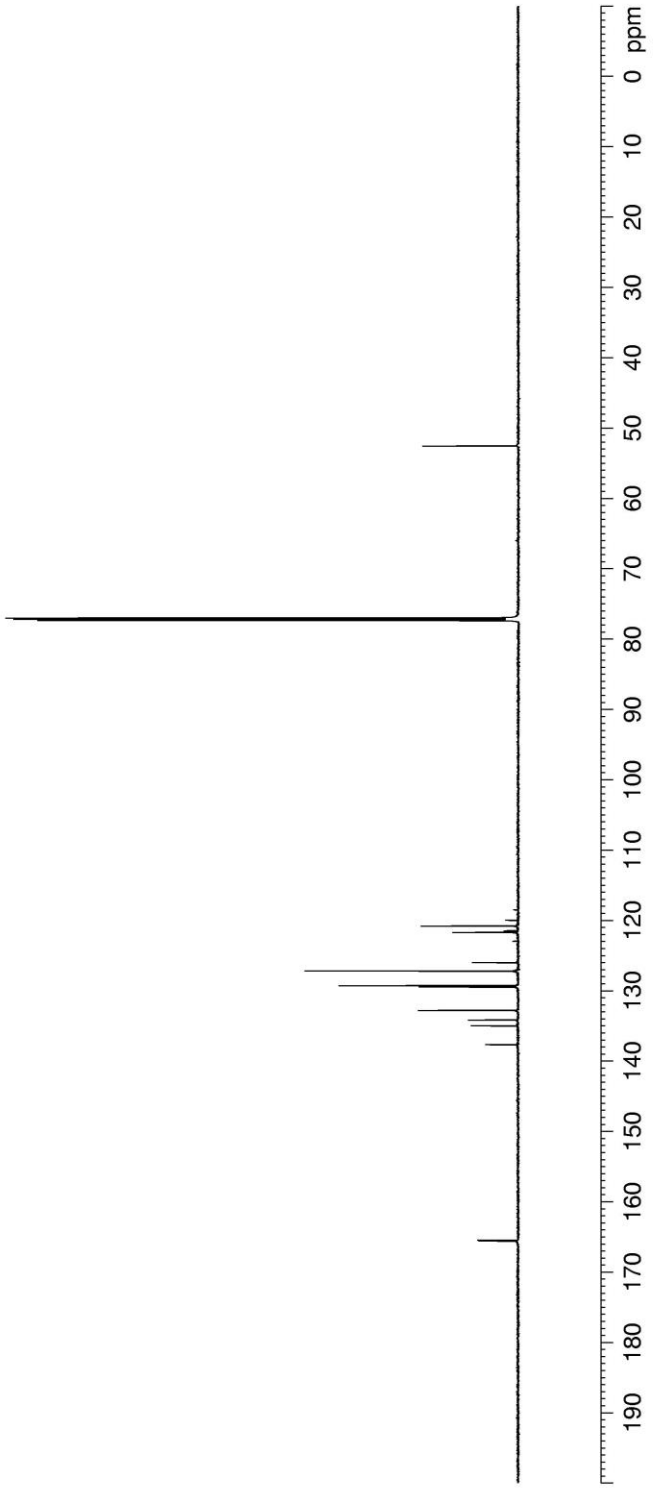
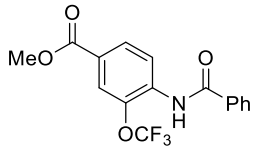
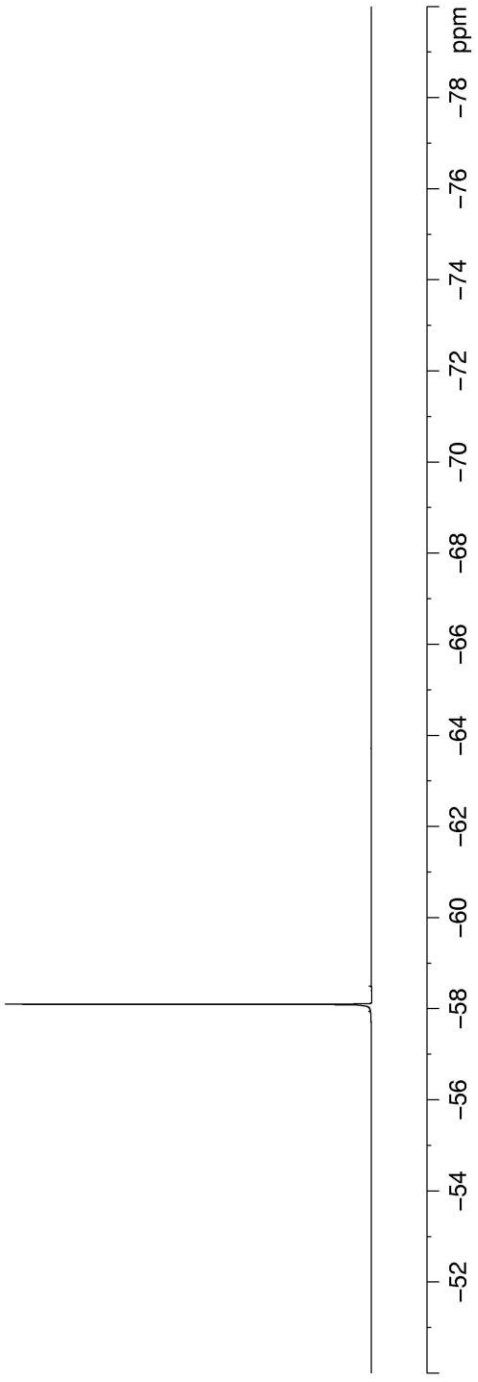


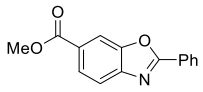
^{19}F NMR ($CDCl_3$, 25 ºC) of **3m**



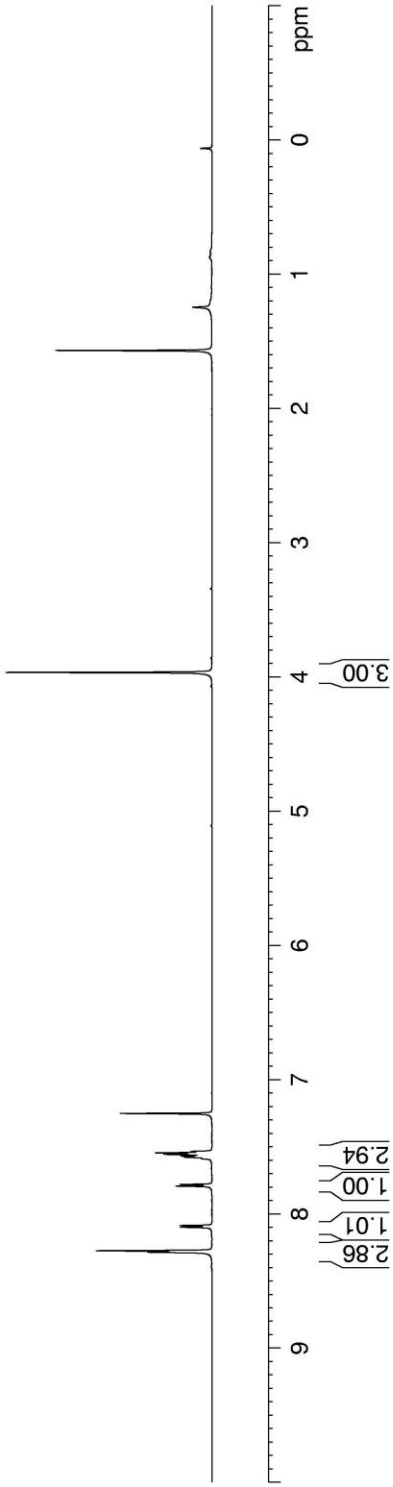
3m



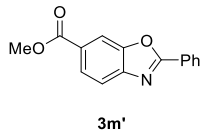
^{1}H NMR ($CDCl_3$, 25 ºC) of **3m'**



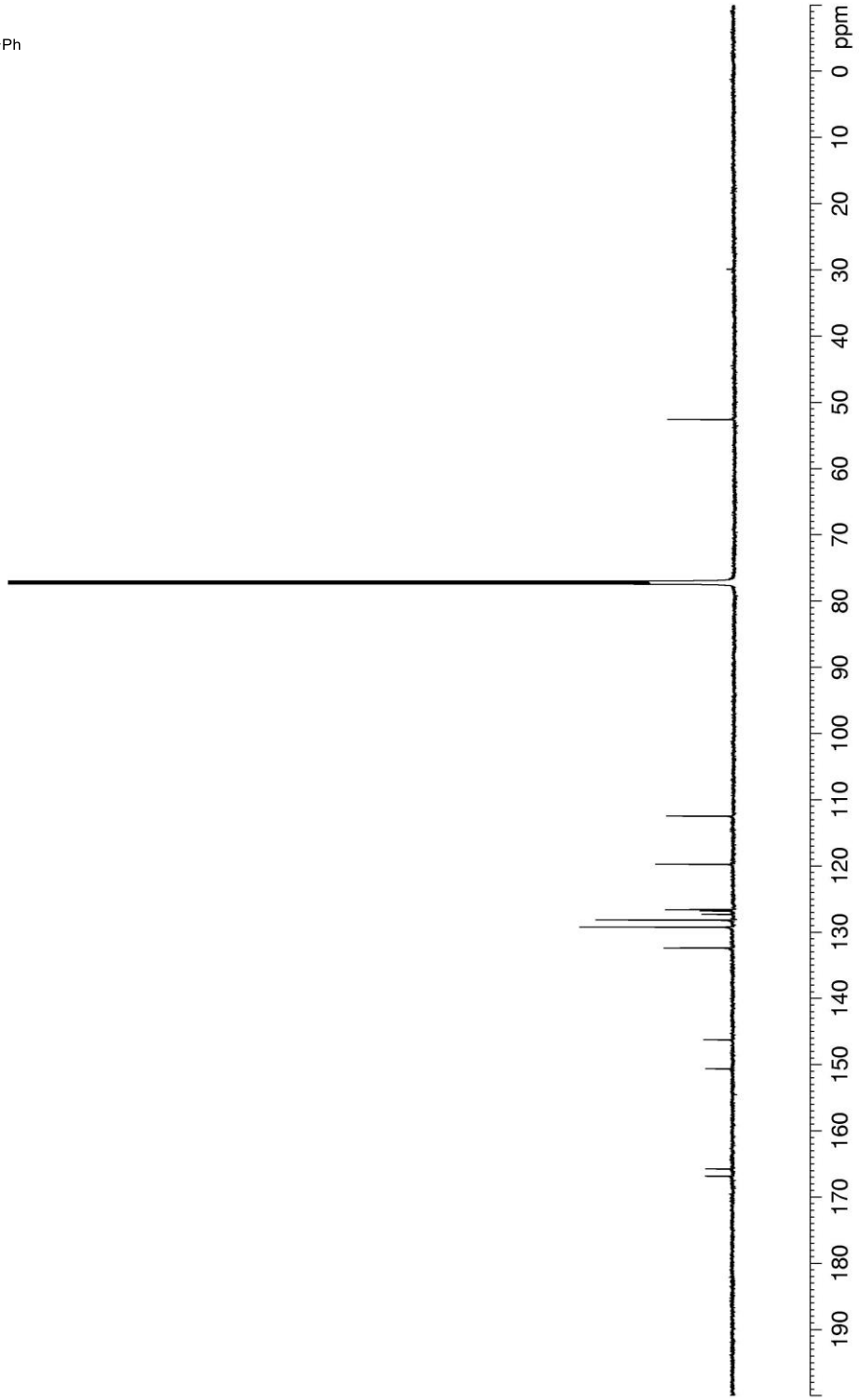
3m'



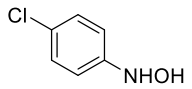
^{13}C NMR ($CDCl_3$, 25 ºC) of **3m'**



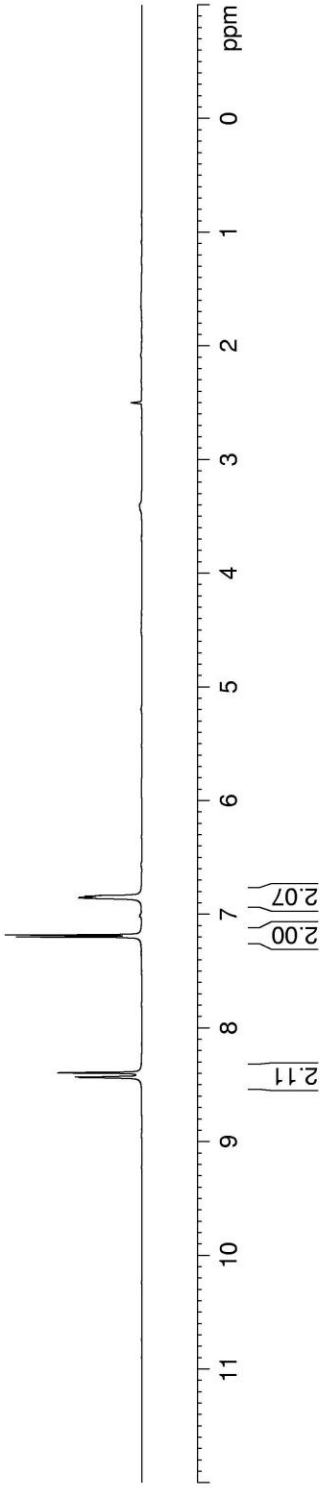
3m'



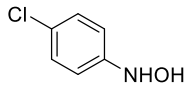
^{1}H NMR ($(CD_3)_2SO$, 25 ºC) of **S26**



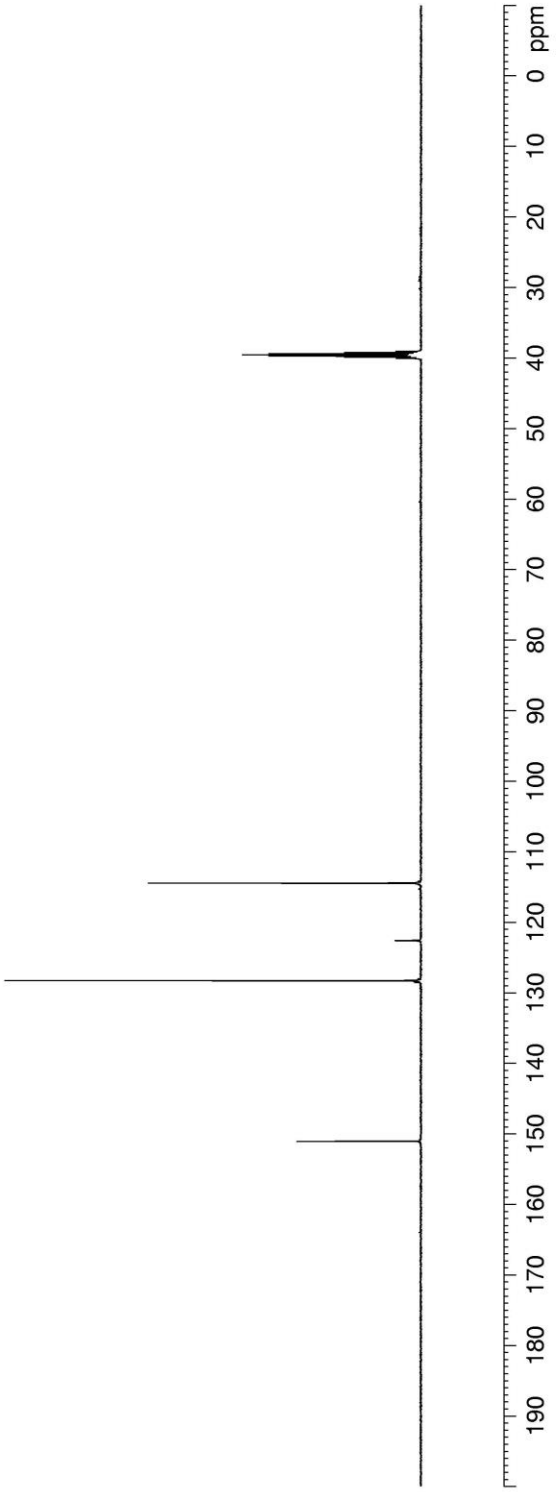
S26



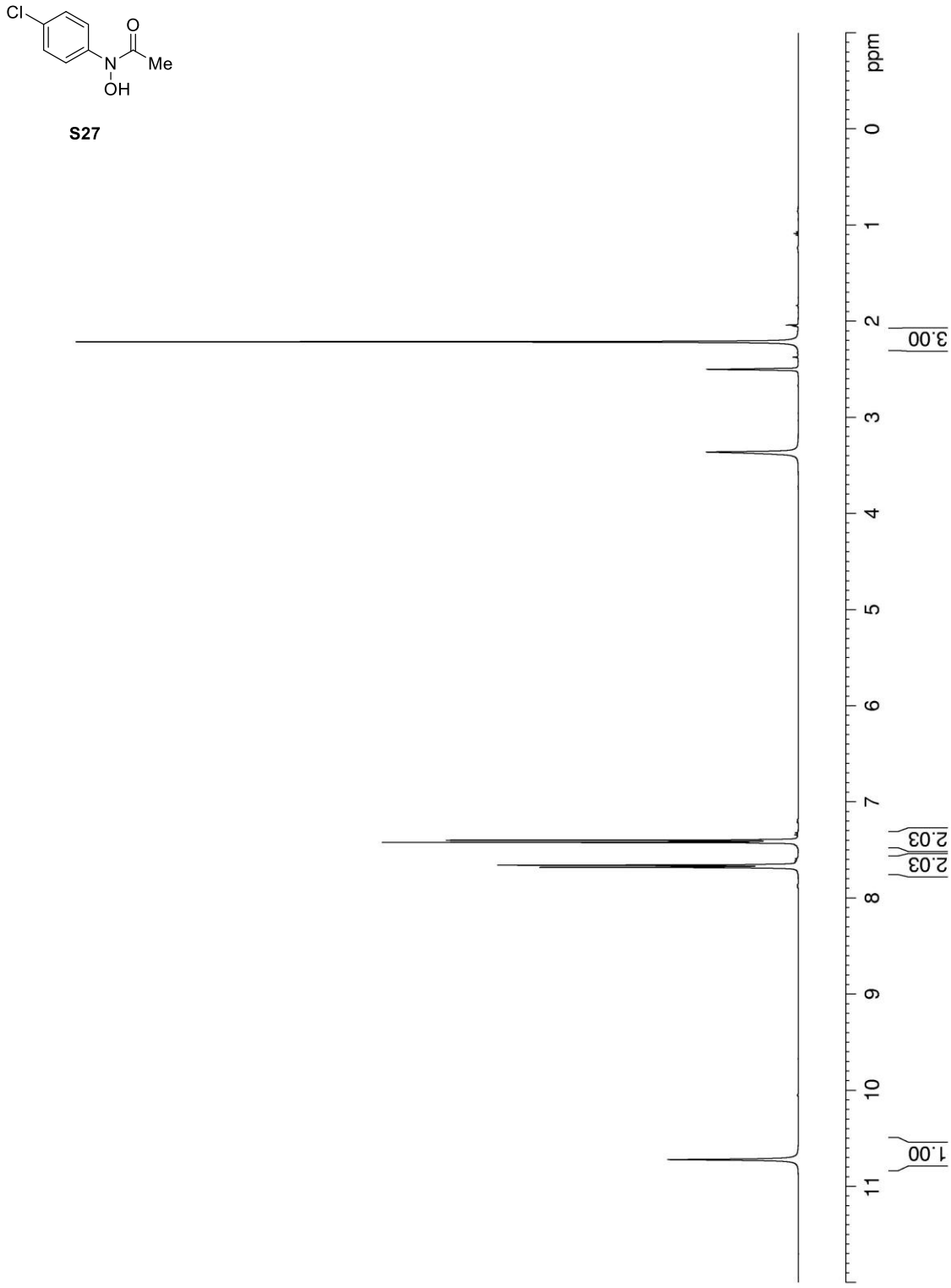
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S26**



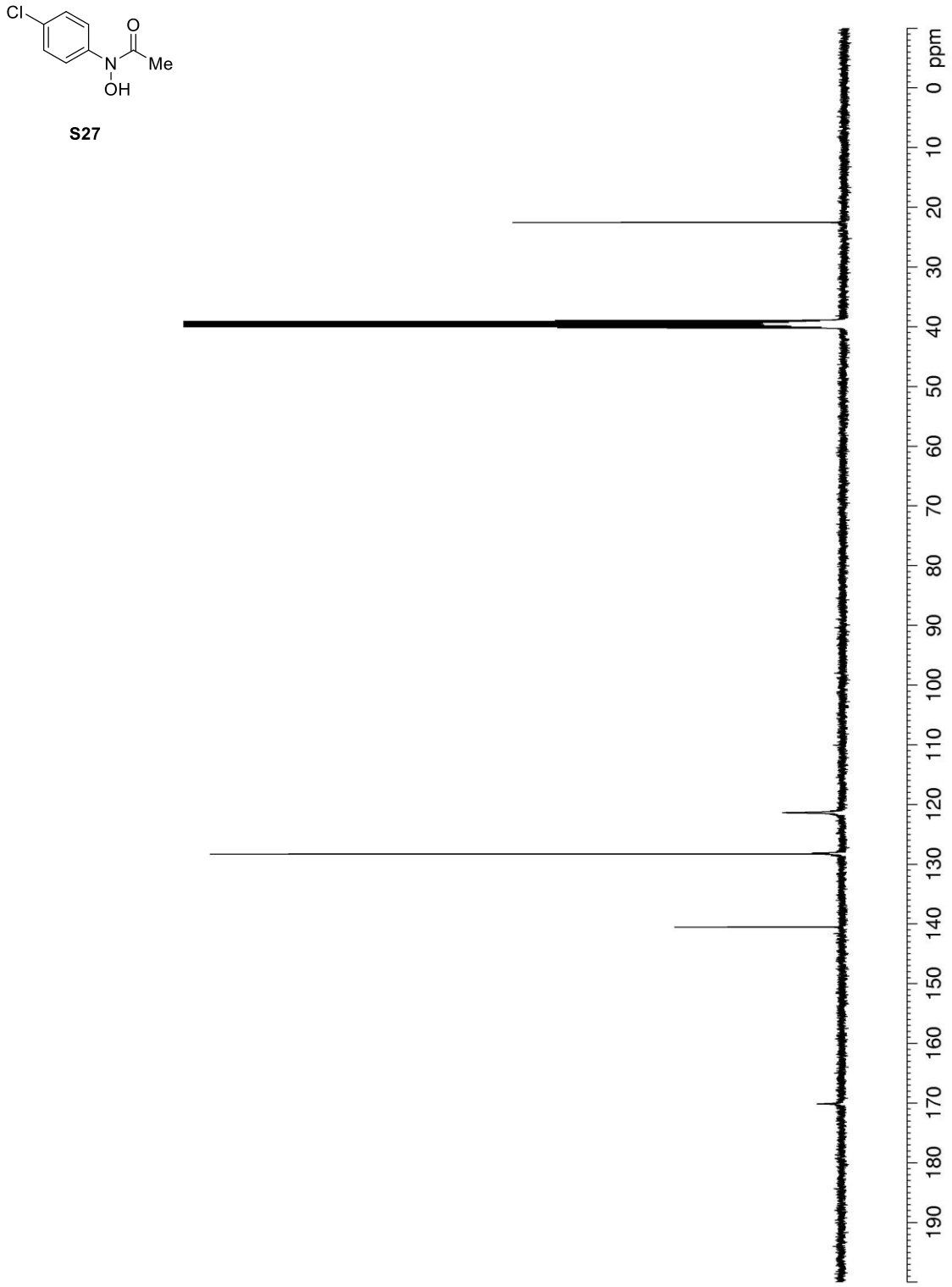
S26



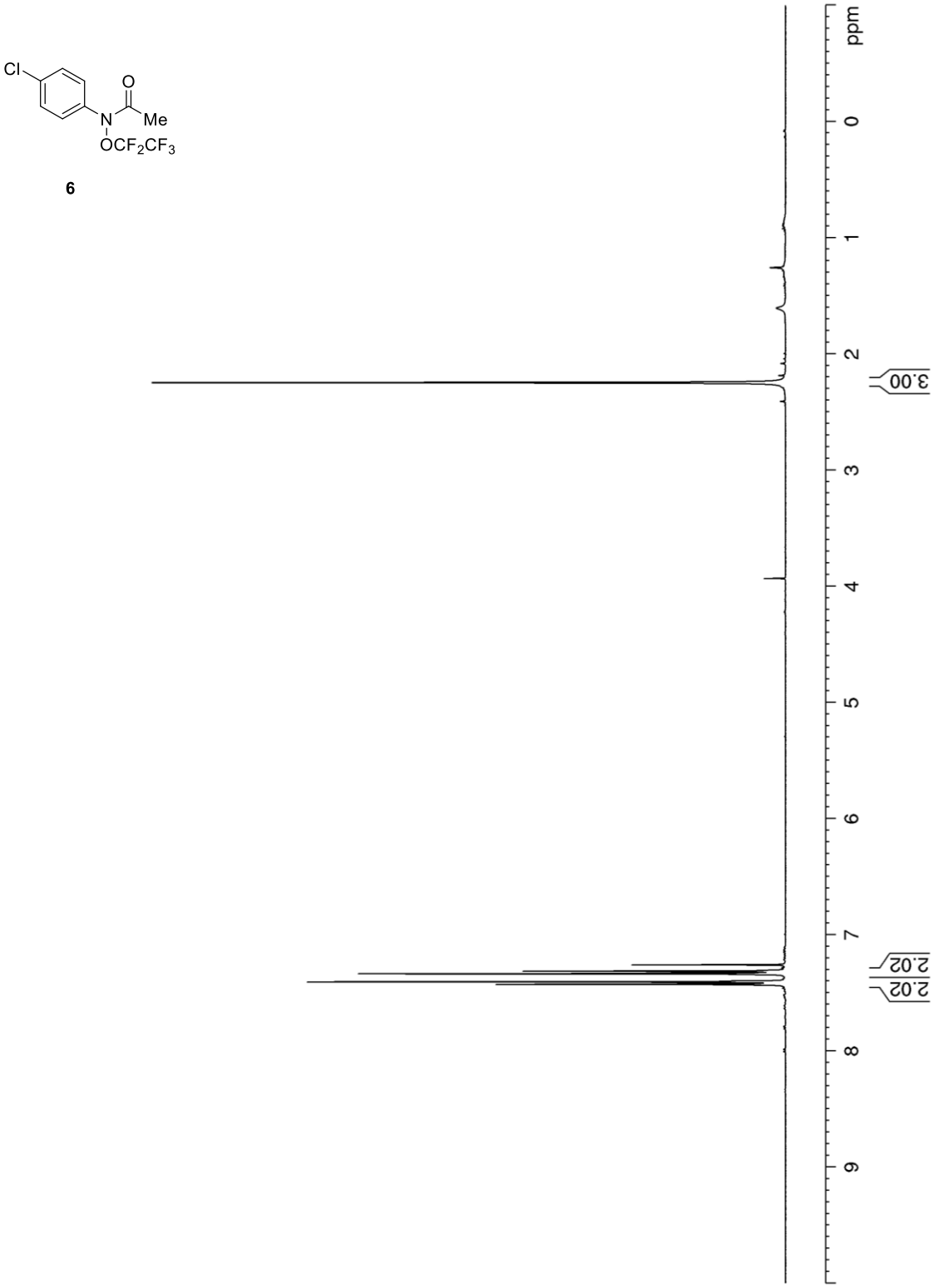
^{1}H NMR ((CD$_3$)$_2$SO, 25 ºC) of **S27**



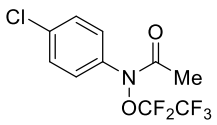
^{13}C NMR ($(CD_3)_2SO$, 25 ºC) of **S27**



^{1}H NMR ($CDCl_3$, 25 ºC) of **6**



^{13}C NMR ($CDCl_3$, 25 ºC) of **6**



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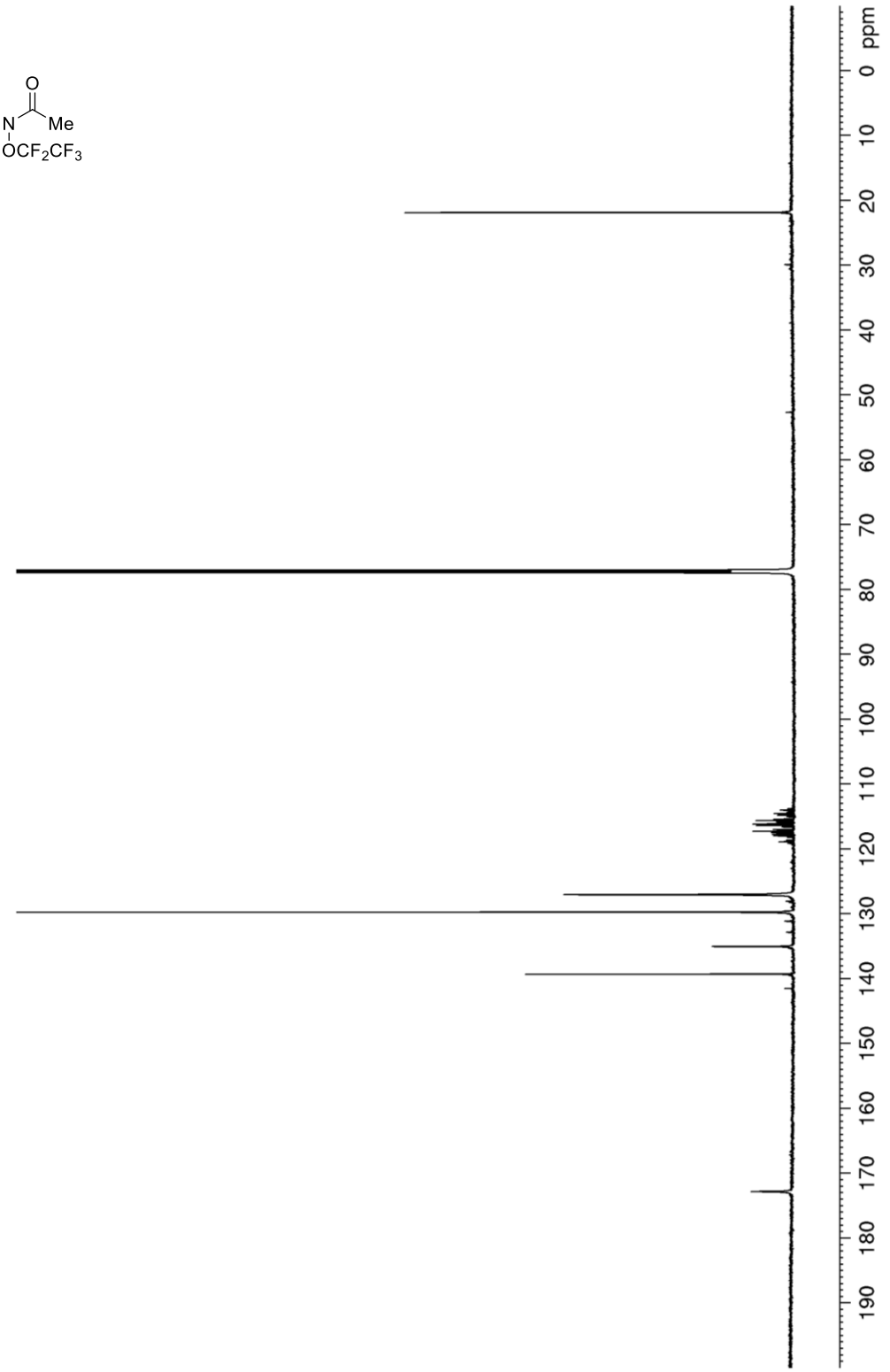
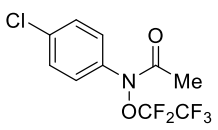


^{19}F NMR ($CDCl_3$, 25 ºC) of **6**



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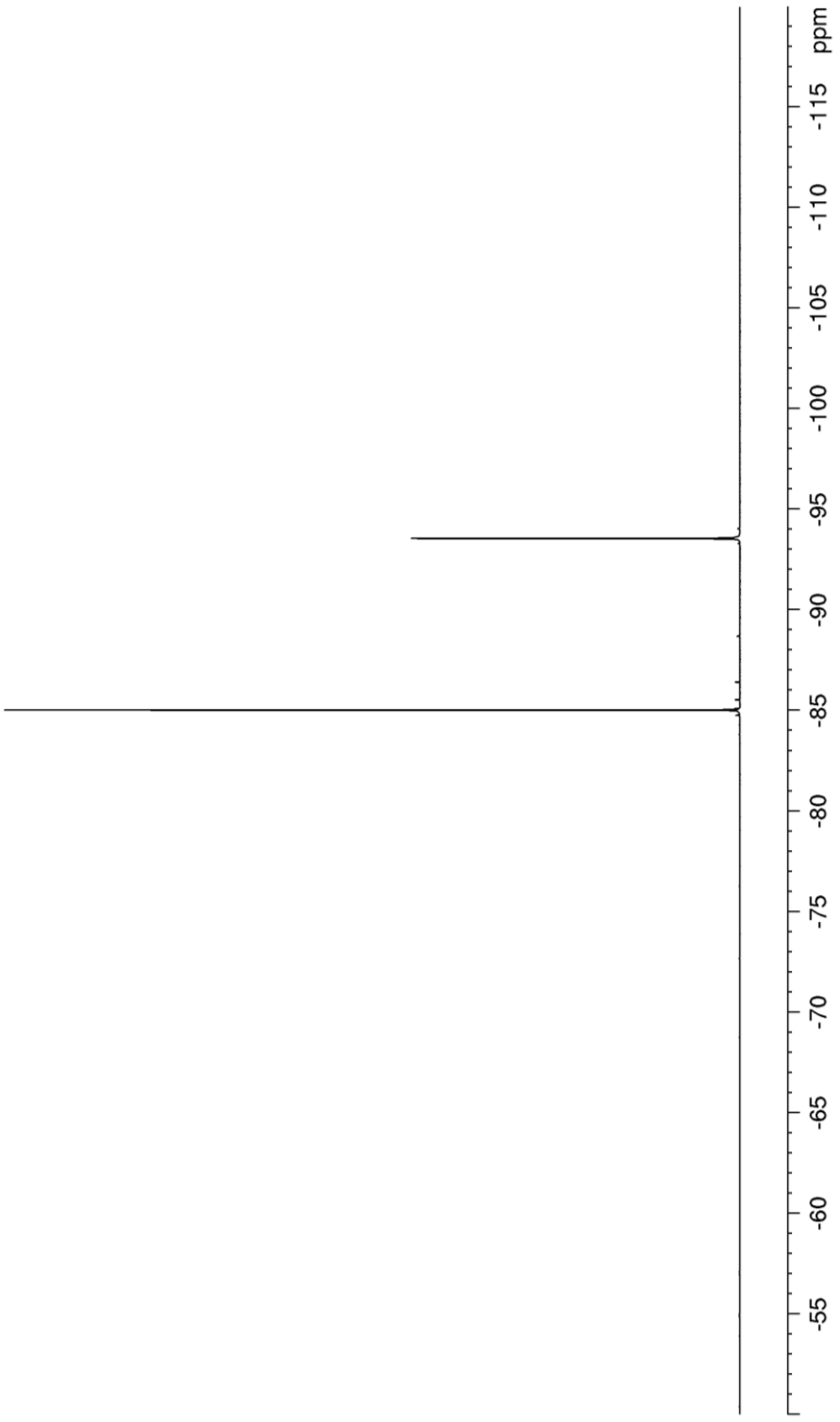
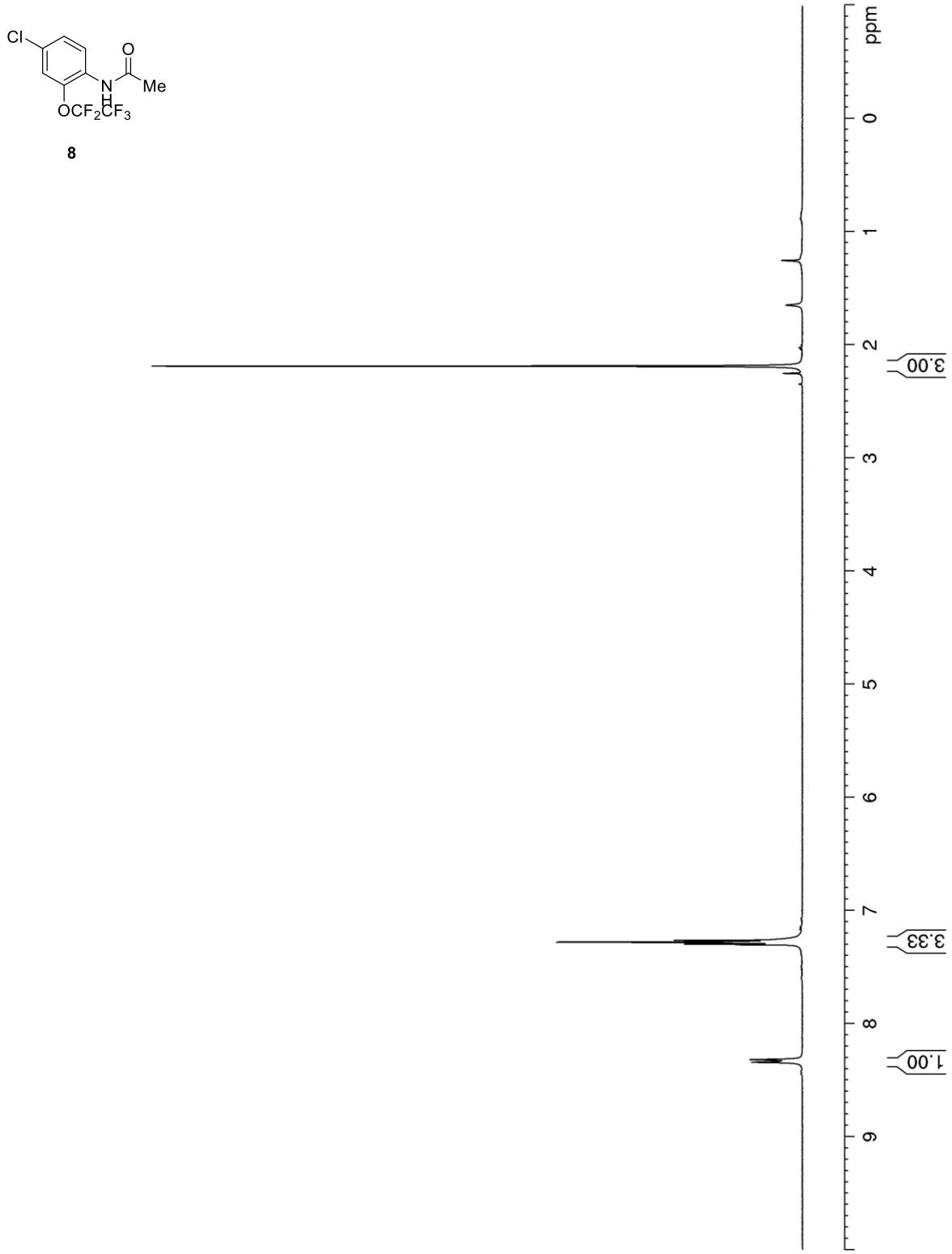
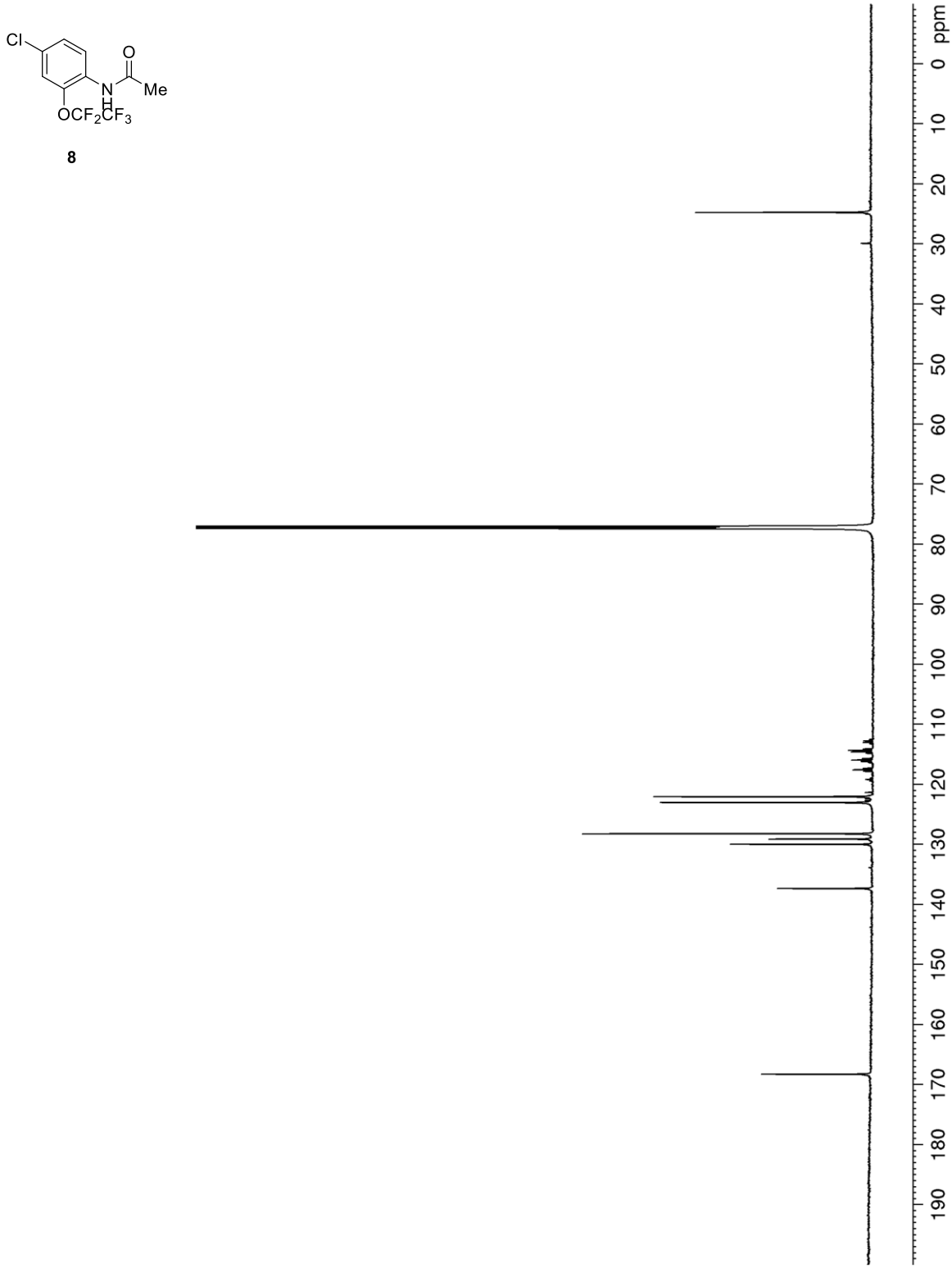


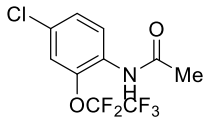
^{1}H NMR ($CDCl_3$, 25 ºC) of **8**



^{13}C NMR ($CDCl_3$, 25 ºC) of **8**



^{19}F NMR ($CDCl_3$, 25 ºC) of **8**



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