Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Oxidation of α-Trifluoromethyl and Non-Fluorinated Alcohols via the Merger of Oxoammonium Cations and Photoredox Catalysis

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Electronic Supporting Information

General Information:

General Considerations: All chemical transformations requiring inert atmospheric conditions or vacuum distillation utilized Schlenk line techniques with a 3- or 4-port dual-bank manifold. Nitrogen was used to provide such an atmosphere. Reaction progress was monitored by ^{1}H NMR and/or thin layer chromatography on silica gel plates (60 Å porosity, 250 µm thickness). Mixtures of hexanes/ethyl acetate acted as eluent and plates were visualized using UV light. Silica plugs utilized Dynamic Adsorbents Inc. Flash Silica Gel (60 Å porosity, 32-63 µm).

Spectra: All NMR spectra (^{1}H, ^{13}C, ^{19}F) were obtained using either a Brüker Avance Ultra Shield 300 MHz NMR or Brüker DRX-400 400 MHz NMR. ^{1}H NMR spectra used either deuterated chloroform (*d*-$CDCl_3$), deuterated dimethyl sulfoxide (DMSO-d_6), or deuterated methanol (MeOD) as a solvent. All chemical shifts are reported in parts per million downfield from tetramethylsilane. Spectra obtained using *d*-$CDCl_3$ were referenced to the residual non-deuterated solvent peak of 7.26 ppm, DMSO-d_6 spectra were referenced to the residual non-deuterated solvent peak of 2.50 ppm, and MeOD spectra were referenced to the residual non-deuterated solvent peak of 3.31 ppm.[1] ^{13}C NMR spectra were referenced to the carbon shift of the solvent (*d*-$CDCl_3$ = δ 77.16, d_6-DMSO = δ 39.52, MeOD δ = 49.00). ^{19}F spectra were obtained using hexafluorobenzene as a reference standard (C_6F_6 = δ -164.9). High-resolution mass spectra were performed on a JEOL AccuTOF-DART SVP 100 in positive direct analysis in real time (DART) ionization method, using PEG as the internal standard. Other mass spectra were obtained using an Agilent Technologies 7820A Gas Chromatograph attached to a 5975 Mass Spectrometer.

Chemicals: Deuterated solvents were purchased from Cambridge Isotope Laboratories. Deuterated chloroform was stored over 4 Å molecular sieves and K_2CO_3. Deuterated dimethylsulfoxide was used without any further preparation. Na_2SO_4, CH_2Cl_2, EtOAc, hexane, Et_2O, THF, MeCN, acetone, pyridine, $Na_2S_2O_8$, DBN, and 2,6-lutidine were purchased from Sigma-Aldrich. Hexafluorobenezene and (trifluoromethyl)trimethylsilane (TMS-CF_3) were purchased from Oakwood Chemicals. Tetrabutylammonium fluoride (1 M in THF) was purchased from Sigma-Aldrich and used without further purification. Alcohols and aldehydes purchased from commercial sources were either distilled or recrystallized prior to use. 4-acetamido-2,2,6,6-tetramethylpiperidin-1-yl)oxyl (ACT) was prepared according to a previous protocol published by our group.[2] The photocatalyst tris(2,2'-bipyridine)ruthenium(II) hexafluorophosphate $Ru(bpy)_3(PF_6)_2$ was prepared in house using a recent publication.[3]

Photochemistry Equipment: Irradiation of reaction vessels was accomplished using blue LEDs. LEDs were configured as outlined in the Photochemical Reactor Design section of previous

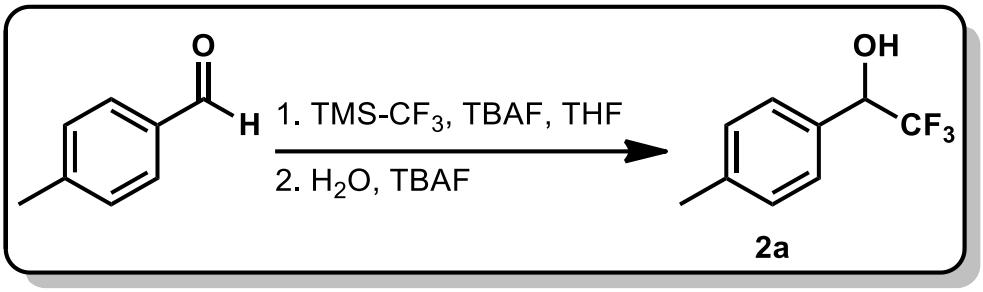
[1] Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512-7515.
[2] Mercadante, M. A.; Kelly, C. B.; Bobbitt, J. M.; Tilley, L. J.; Leadbeater, N. E. *Nat. Protoc.* **2013**, *8*, 666-676.
[3] Kelly, C. B.; Patel, N. R.; Primer, D. N.; Jouffroy, M.; Tellis, J. C.; Molander, G. A. *Nat. Protoc.* **2017**, *12*, 472-492.

articles.[4] A fan was employed to ensure reactions remained at or near rt when using LEDs. Photoreactor set-ups consisted of the following:

- Blue LEDs: 39.4 inch strips, 470 nm blue light, 32918 mcd ft-1
- Power Supply: 12V DC power supply - 60 Watt
- Connectors: LC2 Locking male connector CPS adapter cable
- Clip Fan: 2-Speed clip fan, 6-inch
- Pyrex crystallizing dishes (150 × 75 mm)
- Aluminum foil, duct tape

[4] (a) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 764-767. (b) Jouffroy, M.; Kelly, C. B.; Molander, G. *Org. Lett.* **2016**, *18*, 876-879.

Representative Procedure for the Preparation of α-CF_3 Alcohols



Note: the synthesis of α-CF_3 alcohols was adopted from Kelly et. al.[5]

2,2,2-trifluoro-1-(*p*-tolyl)ethanol,[6] (2a):

To a 100 mL round-bottom flask equipped with a stir bar was charged THF (24 mL, 0.83 M), 4-tolualdehyde (2.403 g, 0.020 mol, 0.83 M, 1 equiv.) and (trifluoromethyl)trimethylsilane (3.128 g, 0.022 mol, 1.1 equiv.). The flask was sealed with a rubber septum and placed under a N_2 atmosphere via an inlet needle. The reaction mixture was stirred using a magnetic stir plate and cooled to 0°C using an ice-water bath over the course of 10 minutes. After this time, TBAF (1 M in THF, 0.2 mL, 0.0002 mol, 0.01 equiv.) was added to the solution dropwise via a syringe.

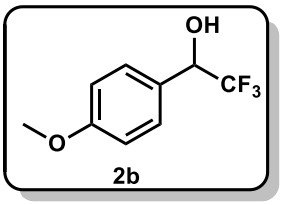
After 10 minutes, the ice bath was removed and the solution was stirred overnight at room temperature. To cleave the resulting silyl ether intermediate, the reaction mixture was cooled to 0°C using an ice bath for 10 minutes. Water (2 mL, 0.110 mol, 5.5 equiv.) was added via syringe, followed by TBAF (1 M in THF, 2 mL, 0.002 mol, 0.1 equiv). Following 10 minutes of stirring at 0°C, the ice bath was removed and the mixture was allowed to stir overnight at room temperature. The contents of the flask were then transferred to a 250 mL separatory funnel. Brine (~ 100 mL) and Et_2O (~150 mL) were added and the layers were separated. The aqueous layer was back-extracted with Et_2O (3 x 75 mL). The combined organic layers were then dried over Na_2SO_4. The solvent was removed in vacuo using a rotary evaporator to afford the crude product 2a, which was purified by vacuum distillation (bp = 87-89 °C, p = 1.5 mm Hg) to give pure α-CF_3 alcohol **2a** (3.046 g, 80%) as a clear, colorless oil.

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 4.98 (q, J = 6.8 Hz, 1H), 2.55 (s, 1H), 2.38 (s, 3H).
^{13}C NMR: (101 MHz, $CDCl_3$) δ 139.71, 131.23, 129.47, 127.48, 128.67 – 120.25 (q, J = 282.0 Hz), 72.86 (q, J = 31.9 Hz), 21.31.
^{19}F NMR: (377 MHz, $CDCl_3$) δ -81.50 (d, *J* = 6.6 Hz).

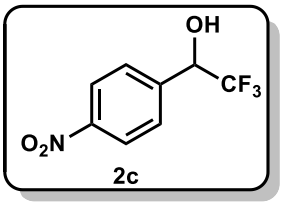
[5] Kelly, C. B.; Colthart, A. M.; Constant, B. D.; Corning, S. R.; Dubois, L. N. E.; Genovese, J. T.; Radziewicz, J. L.; Sletten, E. M.; Witaker, K. R.; Tilley, L. J. *Org. Lett.* **2011**, *13*, 1646-1649.
[6] Kelly, C. B.; Mercadante, M. A.; Hamlin, T. A. Fletcher, M. H.; Leadbeater, N. E. *J. Org. Chem.* **2012**, *77*, 8131-8141.

GC-MS: (EI) 190 ([M]$^+$, 26%) 121 (100%) 93 (65%) 92 (10%) 91 (81%) 77 (49%) 69 (33%) 65 (20%) 63 (13%) 51 (14%).

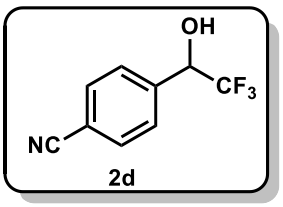
2,2,2-trifluoro-1-(4-methoxyphenyl)ethanol,[6] 2b (3.171 g, 77%), was prepared according to the general procedure from 4-methoxybenzaldehyde (2.723 g, 0.020 mol) followed by vacuum distillation (bp = 70°C, p = 0.01 mm Hg). The desired α-CF_3 alcohol, **2b**, was isolated as a light yellow oil. **^{1}H NMR:** (300 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, J = 8.7 Hz, 2H), 6.99 – 6.88 (m, J = 8.8 Hz, 2H), 4.96 (q, J = 6.8 Hz, 1H), 3.82 (s, 3H), 2.59 (s, 1H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 160.55, 128.92, 126.32 (d, J = 1.3 Hz), 128.68 – 120.27 (q, J = 281.9 Hz), 114.17, 72.57 (q, J = 32.1 Hz), 55.41.**^{19}F NMR:** (377 MHz, $CDCl_3$) δ -81.51 (d, *J* = 6.8 Hz). **GC-MS:** (EI) 206 ([M]$^+$, 29%) 137 (100%) 109 (43%) 94 (42%) 77 (40%) 69 (30%) 66 (19%) 65 (13%) 63 (10%) 51 (12%)



2,2,2-trifluoro-1-(4-nitrophenyl)ethanol,[6] 2c (2.025 g, 46%), was prepared according to the general procedure from 4-nitrobenzaldehyde (3.022 g, 0.020 mol) **with the following modification**: the crude product was washed with DCM in order to give desired α-CF_3 alcohol, **2c**, as a pure, light yellow solid. **^{1}H NMR:** (400 MHz, DMSO-d_6) δ 8.36 – 8.19 (m, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.18 (s, 1H), 5.43 (q, *J* = 7.3 Hz, 1H). **^{13}C NMR:** (101 MHz, DMSO-d_6) δ 147.85, 143.02, 128.94, 123.35, 128.85 – 120.41 (q, *J* = 283.1 Hz), 69.57 (q, *J* = 30.7 Hz). **^{19}F NMR:** (377 MHz, DMSO-d_6) δ -78.84 (d, *J* = 7.4 Hz). **GC-MS:** (EI) 221 ([M]$^+$, 6%) 152 (100%) 127 (22%) 106 (11%) 105 (18%) 94 (15%) 78 (15%) 77 (26%) 69 (6%) 51 (14%)

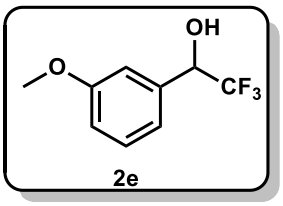


4-(2,2,2-trifluoro-1-hydroxyethyl)benzonitrile,[7] 2d (3.071 g, 76%), was prepared according to the general procedure from 4-formylbenzonitrile (2.623 g, 0.020 mol) **with the following modification**: the crude product was filtered over a plug of silica gel, eluting with 4 column volumes of Et_2O. The desired α-CF_3 alcohol, **2d**, was isolated as a white solid. **^{1}H NMR:** (400 MHz, DMSO-d_6) δ 7.92 – 7.85 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H), 7.11 (s, 1H), 5.35 (q, J = 7.3 Hz, 1H). **^{13}C NMR:** (101 MHz, MeOD) δ 142.38, 133.15, 129.68, 130.05 – 121.17 (q, J = 282.0 Hz), 119.35, 113.80, 72.27 (q, J = 31.5 Hz). **^{19}F NMR:** (377 MHz, MeOD) δ -79.22 (d, *J* = 6.9 Hz). **GC-MS:** (EI) 201 ([M]$^+$, 10%) 132 (100%) 104 (63%) 102 (14%) 77 (39%) 76 (11%) 75 (11%) 69 (12%) 51 (16%) 50 (11%)

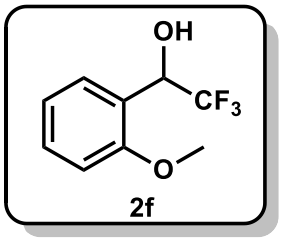


[7] Xu, Q. Zhou, H. Geng, X. Chen, P. *Tetrahedron*, **2009**, *65*, 2232-2238.

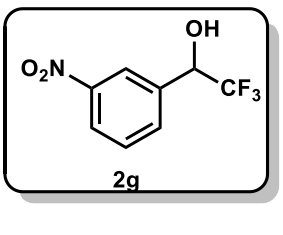
2,2,2-trifluoro-1-(3-methoxyphenyl)ethanol,[6] 2e (2.459 g, 60%), was prepared according to the general procedure from 3-methoxybenzaldehyde (2.723 g, 0.020 mol) followed by vacuum distillation (bp = 88-90°C, p = 2 mm Hg). The desired α-CF_3 alcohol, **2e**, was isolated as a clear colorless oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 1H), 7.07 – 7.01 (m, 2H), 6.95 (ddd, J = 8.3, 2.6, 1.1 Hz, 1H), 4.97 (q, J = 6.7 Hz, 1H), 3.82 (s, 3H), 2.83 (s, 1H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 159.84, 135.62, 129.82, 128.54 – 120.08 (q, J = 282.1 Hz), 119.92 (d, J = 1.1 Hz), 115.25, 113.13, 72.87 (q, J = 32.0 Hz), 55.45.**^{19}F NMR:** (377 MHz, $CDCl_3$) δ -81.30 (d, *J* = 6.7 Hz). **GC-MS:** (EI) 206 ($[M]^+$, 51%) 137 (53%) 109 (100%) 94 (50%) 78 (10%) 77 (55%) 69 (14%) 66 (20%) 65 (19%) 63 (14%) 51 (16%) 50 (10%)



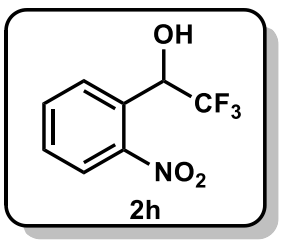
2,2,2-trifluoro-1-(2-methoxyphenyl)ethanol,[6] 2f (3.229 g, 78%), was prepared according to the general procedure from 2-methoxybenzaldehyde (2.723 g, 0.020 mol) followed by vacuum distillation (bp = 75-77°C, p = 0.5 mm Hg). The desired α-CF_3 alcohol, **2f**, was isolated as a clear colorless liquid. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 2H), 7.02 (td, J = 7.5, 1.1 Hz, 1H), 6.96 (dd, J = 8.2, 1.1 Hz, 1H), 5.28 (p, J = 6.9 Hz, 1H), 3.88 (s, 3H), 3.70 (br s, 1H).**^{13}C NMR:** (101 MHz, $CDCl_3$) δ 157.65, 130.66, 129.34, 122.27, 121.16, 129.03 – 120.59 (q, J = 283.0 Hz), 111.41, 69.69 (q, *J* = 32.8 Hz), 55.82. **^{19}F NMR:** (377 MHz, $CDCl_3$) δ -81.04 (d, *J* = 7.1 Hz). **GC-MS:** (EI) 206 ($[M]^+$, 28%) 137 (100%) 122 (12%) 121 (33%) 109 (21%) 107 (87%) 94 (22%) 91 (10%) 79 (18%) 77 (46%) 76 (10%) 69 (47%) 65 (18%) 63 (12%) 51 (22%) 50 (13%)



2,2,2-trifluoro-1-(3-nitrophenyl)ethanol,[6] 2g (3.741 g, 85%), was prepared according to the general procedure from 3-nitrobenzaldehyde (3.022 g, 0.020 mol) **with the following modification**: the crude product was filtered over a plug of silica gel, eluting with 4 column volumes of Et_2O. The desired α-CF_3 alcohol, **2g**, was isolated as a yellow solid. **^{1}H NMR:** (400 MHz, DMSO-*d*$_6$) δ 8.37 (s, 1H), 8.26 (ddd, J = 8.2, 2.4, 1.1 Hz, 1H), 7.96 (d, J = 7.7 Hz, 1H), 7.73 (t, J = 8.0 Hz, 1H), 7.21 (d, J = 5.2 Hz, 1H), 5.46 (m, 1H). **^{13}C NMR:** (101 MHz, MeOD) δ 149.65, 139.38, 134.93, 130.65, 124.79, 123.48, 130.11 – 121.70 (q, J = 281.3 Hz), 71.91 (q, J = 31.7 Hz). **^{19}F NMR:** (377 MHz, MeOD) δ -79.54 (d, *J* = 6.9 Hz). **GC-MS:** (EI) 221 ($[M]^+$, 3%) 152 (100%) 127 (18%) 106 (12%) 105 (28%) 78 (18%) 77 (29%) 69 (9%) 51 (20%) 50 (11%)

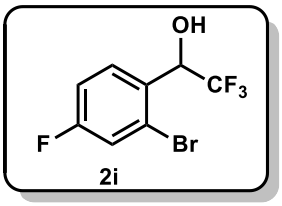


2,2,2-trifluoro-1-(2-nitrophenyl)ethanol,[6] 2h (2.786 g, 63%) was prepared according to the general procedure from 2-nitrobenzaldehyde (3.022 g, 0.020 mol) followed by vacuum distillation (bp = 98-100°C, p = 0.6 mm Hg). The desired α-CF_3 alcohol, **2h**, was isolated as a clear yellow oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 8.04 – 7.92 (m, 2H), 7.71 (td, J = 7.7, 1.4 Hz, 1H), 7.60 – 7.52 (m, 1H), 6.15 (q, J = 6.2 Hz, 1H), 3.42 (br s, 1H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 148.55, 133.83, 130.36, 129.55, 129.07, 125.08,



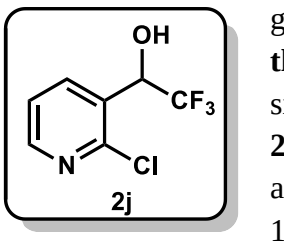
128.19 – 119.76 (q, J = 282.6 Hz), 66.89 (q, J = 32.8 Hz). **^{19}F NMR:** (377 MHz, $CDCl_3$) δ -80.50 (d, *J* = 6.4 Hz). **GC-MS:** (EI) 221 ($[M]^+$, 1%) 152 (24%) 134 (47%) 127 (62%) 123 (82%) 121 (60%) 105 (29%) 104 (53%) 97 (10%) 95 (17%) 92 (14%) 78 (17%) 77 (100%) 76 (21%) 75 (32%) 74 (14%) 69 (76%) 65 (16%) 63 (15%) 52 (16%) 51 (57%) 50 (37%)

1-(2-bromo-4-fluorophenyl)-2,2,2-trifluoroethanol,[6] 2i (3.923 g, 72%) was prepared according to the general procedure from 2-bromo-4-fluorobenzaldehyde (4.060 g, 0.020 mol) followed by vacuum distillation (bp = 63-65°C, p = 0.1 mm Hg). The desired α-CF_3 alcohol, **2i**, was isolated as a clear colorless oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 8.8, 5.9 Hz, 1H), 7.34 (dd, J = 8.2, 2.7 Hz, 1H), 7.11 (td, J = 8.3, 2.6 Hz, 1H), 5.57 (q, J = 6.3 Hz, 1H), 3.06 (s, 1H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 162.89 (d, J = 253.6 Hz), 130.68 (dd, J = 8.9, 1.5 Hz), 129.89, 124.16 (d, J = 9.5 Hz), 120.23 (d, J = 24.7 Hz), 128.47 – 120.03 (q, J = 282.8 Hz), 115.43 (d, J = 21.3 Hz), 70.78 (q, J = 32.6 Hz). **^{19}F NMR:** (377 MHz, $CDCl_3$) δ -80.85 (d, *J* = 6.1 Hz), -112.36 (q, *J* = 7.5 Hz). **GC-MS:** (EI) 274 ($[M]^+$, 18%) 272 ($[M]^+$, 18%) 205 (95%) 203 (100%) 175 (12%) 145 (10%) 123 (27%) 96 (98%) 95 (58%) 94 (20%) 75 (29%) 74 (10%) 69 (17%)



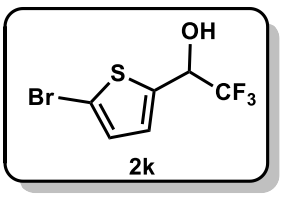
2i

1-(2-chloropyridin-3-yl)-2,2,2-trifluoroethanol, 2j (3.306 g, 78%) was prepared according to the general procedure from 2-chloronicotinaldehyde (2.831 g, 0.020 mol) **with the following modification**: the crude product was filtered over a plug of silica gel, eluting with 4 column volumes of Et_2O. The desired α-CF_3 alcohol, **2j**, was isolated as a tan solid. The desired α-CF_3 alcohol, **2j**, was isolated as a tan powder. **^{1}H NMR:** (400 MHz, DMSO-d_6) δ 8.47 (dd, *J* = 4.7, 2.0 Hz, 1H), 8.10 (d, J = 8.3 Hz, 1H), 7.56 (dd, *J* = 7.8, 4.7 Hz, 1H), 7.29 (d, *J* = 4.2 Hz, 1H), 5.45 (dd, J = 6.9, 4.2 Hz, 1H). **^{13}C NMR:** (101 MHz, DMSO-d_6) δ 150.50, 149.17, 138.99, 130.30, 123.69, 128.80 – 120.35 (q, *J* = 283.4 Hz), 67.19 (q, *J* = 31.4 Hz). **^{19}F NMR:** (377 MHz, DMSO-d_6) δ -79.08 (d, J = 6.7 Hz). **GC-MS:** (EI) 211 ($[M]^+$, 13%) 144 (35%) 142 (100%) 106 (59%) 78 (70%) 69 (14%) 52 (11%) 51 (30%) 50 (13%). **HRMS:** (DART) calculated for $C_7H_6ClF_3NO$ $[M+H]^+$: 212.0079, observed 212.0051.



2j

1-(5-bromothiophen-2-yl)-2,2,2-trifluoroethanol,[8] 2k (3.299 g, 63%), was prepared according to the general procedure from 5-bromothiophene-2-carbaldehyde (3.821 g, 0.020 mol) followed by vacuum distillation (bp = 94-95°C, p = 0.01 mm Hg). The desired α-CF_3 alcohol, **2k**, was isolated as a clear colorless oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 23.6, 3.2 Hz, 2H), 5.18 (q, *J* = 6.6, 1H), 2.91 (s, 1H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 137.58, 129.93, 128.07, 127.70 – 119.29 (q, *J* = 282.0 Hz), 114.51, 69.52 (q, *J* = 34.0 Hz). **^{19}F NMR:** (377

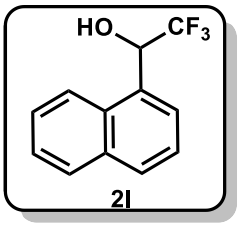


2k

[8] Baloglu, E.; Ghosh, S.; Lobera, M.; Schmidit, D. R. EP2533783, **2015**.

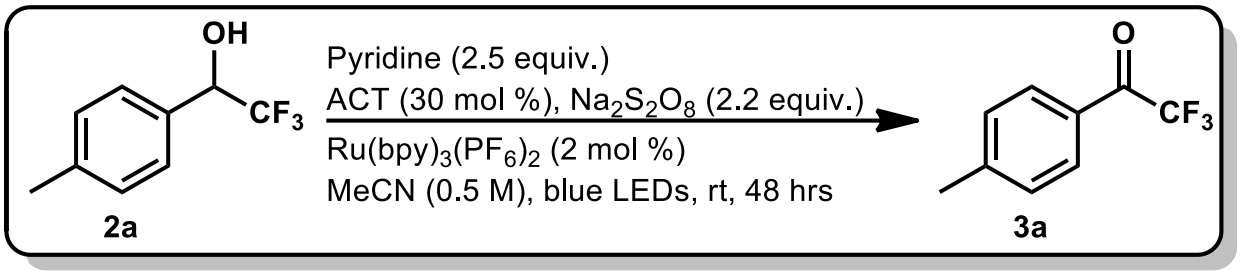
MHz, $CDCl_3$) δ -81.88 (d, *J* = 5.7 Hz). **GC-MS:** (EI) 262 ($[M]^+$, 40%) 260 ($[M]^+$, 40%) 193 (100%) 191 (99%) 111 (11%) 84 (72%) 82 (12%) 69 (16%) 57 (10%)

2,2,2-trifluoro-1-(naphthalene-1-yl)ethanol,[9] 2l (3.375 g, 75%) was prepared according to the general procedure from 1-naphthaldehyde (3.124 g, 0.020 mol) followed by vacuum distillation (bp = 116-118°C, p = 0.1 mm Hg). The desired α-CF_3 alcohol, **2l**, was isolated as a clear colorless oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.1 Hz, 1H), 7.95 – 7.89 (m, 2H), 7.84 (d, J = 7.3 Hz, 1H), 7.61 – 7.49 (m, 3H), 5.85 (q, J = 6.5 Hz, 1H), 3.07 (s, 1H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 133.75, 131.16, 130.24, 130.01 (d, J = 1.1 Hz), 129.08, 126.91, 126.01, 125.88 (d, J = 1.3 Hz), 125.26, 122.85 (d, J = 1.3 Hz), 129.00 – 120.57 (q, J = 282.7 Hz), 69.00 (q, J = 32.3 Hz).**^{19}F NMR:** (377 MHz, $CDCl_3$) δ -79.87 (d, *J* = 6.4 Hz). **GC-MS:** (EI) 227 ($[M]^+$, 12%) 226 ($[M]^+$, 82%) 158 (14%) 157 (100%) 130 (16%) 129 (98%) 128 (94%) 127 (61%) 126 (15%) 77 (12%) 69 (6%)



[9] Fujiu, M.; Nakamura, Y.; Serizawa, H.; Aikawa, K.; Ito, S.; Mikami, K. *E. J. Org. Chem.* **2012**, *36*, 7043-7047.

Representative Procedure for the Preparation of Trifluoromethyl Ketones

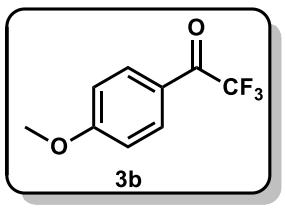


2,2,2-trifluoro-1-(4-tolyl)ethanone,[6] (3a):

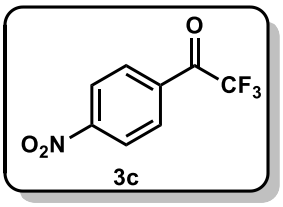
To a 20-mL vial equipped with a stir bar was added **2a** (0.380 g, 0.002 mol, 1 equiv), pyridine (0.396 g, 0.005 mol, 2.5 equiv), ACT (0.128 g, 0.0006 mol, 0.3 equiv), and MeCN (4 mL, 0.5 M). Upon addition of the solvent, $Na_2S_2O_8$ (1.047 g, 0.0044 mol, 2.2 equiv) and the photocatalyst $Ru(bpy)_3(PF_6)_2$ (0.034 g, 0.00004 mol, 0.02 equiv) were added. The vial was sealed with a cap and irradiated in the aforementioned LED reactor for 48 h. After this time, Et_2O (15 mL) was added and the solution was stirred for 10 minutes. After this time, the resulting mixture was filtered through a coarse porosity fritted glass funnel. The solution was then transferred to a separatory funnel, diluted with Et_2O (60 mL) and deionized water (75 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 × 50 mL). The organic layers were then combined and washed with 0.5 M aqueous HCl (3 × 50 mL), deionized water (50 mL), and finally brine (100 mL). The organic layer was then dried over sodium sulfate and the solvent removed in vacuo to afford the pure trifluoromethyl ketone **3a** as a clear yellow oil (0.305 g, 81%).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 180.26 (q, J = 34.8 Hz), 147.17, 130.38 (q, J = 2.1 Hz), 129.95, 127.61, 121.27 – 112.58 (q, J = 291.4 Hz), 22.03. **^{19}F NMR:** (377 MHz, $CDCl_3$) δ -74.42. **GC-MS:** (EI) 188 ($[M]^+$, 43%) 120 (26%) 119 (99%) 92 (17%) 91 (100%) 90 (16%) 89 (32%) 69 (17%) 65 (64%) 63 (31%) 62 (12%) 51 (12%) 50 (13%)

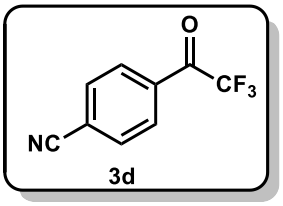
2,2,2-trifluoro-1-(4-methoxyphenyl)ethanone,[6] 3b (0.332 g, 81%) was prepared according to the general procedure from **2b** (0.412 g, 0.002 mol). The desired trifluoromethyl ketone **3b** was isolated as a clear yellow oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.3 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 3.91 (s, 3H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 179.07 (q, J = 34.4 Hz), 165.56, 132.86 (q, J = 2.2 Hz), 122.94, 114.57, 121.41 – 112.72 (q, J = 291.4 Hz), 55.81. **^{19}F NMR:** (377 MHz, $CDCl_3$) δ -74.07. **GC-MS:** (EI) 204 ($[M]^+$, 16%) 135 (100%) 107 (13%) 92 (31%) 77 (41%) 69 (8%) 64 (18%) 63 (17%)



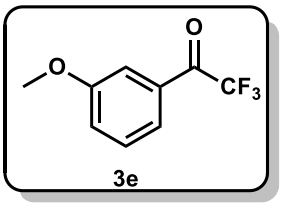
2,2,2-trifluoro-1-(4-nitrophenyl)ethanone,[6] 3c (0.330 g, 75%) was prepared according to the general procedure from **2c** (0.442 g, 0.002 mol). The desired trifluoromethyl ketone **3c** was isolated as an off white powder. **^{1}H NMR:** (400 MHz, DMSO-d_6, hydrate) δ 8.28 (d, *J* = 8.9 Hz, 2H), 7.95 (s, 2H), 7.88 (d, *J* = 8.7 Hz, 2H). **^{13}C NMR:** (101 MHz, DMSO-d_6, hydrate) δ 148.07, 145.44, 128.97, 122.96, 127.45 – 118.84 (q, J = 288.7 Hz), 92.27 (q, J = 31.5 Hz). **^{19}F NMR:** (377 MHz, DMSO-d_6) δ -84.97. **GC-MS:** (EI) 219 ([M]$^+$, 1%) 150 (100%) 123 (10%) 104 (47%) 95 (11%) 92 (24%) 76 (39%) 75 (18%) 74 (14%) 69 (10%) 50 (23%)



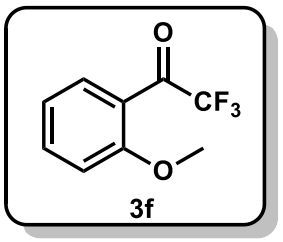
4-(2,2,2-trifluoroacetyl)benzonitrile, 3d (0.347 g, 87%) was prepared according to the general procedure from **2d** (0.402 g, 0.002 mol). The desired trifluoromethyl ketone **3d** was isolated as a light yellow solid. **^{1}H NMR:** (300 MHz, DMSO-d_6, hydrate) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.87 (s, 2H), 7.78 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR:** (101 MHz, DMSO-d_6, hydrate) δ 143.66, 131.85, 128.41, 127.48 – 118.86 (q, *J* = 289.2 Hz), 118.52, 112.00, 92.22 (q, *J* = 31.4 Hz). **^{19}F NMR:** (377 MHz, DMSO-d_6) δ -85.03. **GC-MS:** (EI) 199 ([M]$^+$, 4%) 131 (20%) 130 (100%) 103 (14%) 102 (100%) 76 (32%) 75 (55%) 74 (15%) 69 (19%) 51 (32%) 50 (31%). **HRMS:** (DART) calculated for $C_9H_4F_3NO$ [M+H]$^+$: 199.0239, observed 199.0248.



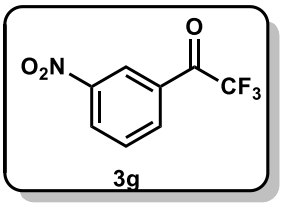
2,2,2-trifluoro-1-(3-methoxyphenyl)ethanone,[6] 3e (0.366 g, 90%) was prepared according to the general procedure from **2e** (0.412 g, 0.002 mol). The desired trifluoromethyl ketone **3e** was isolated as a yellow oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.65 (dq, *J* = 7.7, 1.4 Hz, 1H), 7.56 (s, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.28 – 7.22 (m, 1H), 3.87 (s, 3H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 180.51 (q, J = 35.1 Hz), 160.14, 131.23, 130.24, 122.85 (q, *J* = 2.7 Hz), 122.38, 114.14 (q, *J* = 1.8 Hz), 121.13 – 112.45 (q, J = 291.3 Hz), 55.64. **^{19}F NMR:** (377 MHz, $CDCl_3$) δ -74.31. **GC-MS:** (EI) 204 ([M]$^+$, 100%) 136 (20%) 135 (99%) 107 (94%) 92 (74%) 77 (87%) 76 (16%) 74 (10%) 69 (15%) 64 (36%) 63 (36%) 50 (15%)



2,2,2-trifluoro-1-(2-methoxyphenyl)ethanone,[6] 3f (0.340 g, 83%) was prepared according to the general procedure from **2f** (0.412 g, 0.002 mol). The desired trifluoromethyl ketone **3f** was isolated as a yellow-orange oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.7 Hz, 1H), 7.58 (ddd, J = 8.3, 7.4, 1.8 Hz, 1H), 7.07 – 7.00 (m, 2H), 3.91 (s, 3H).**^{13}C NMR:** (101 MHz, $CDCl_3$) δ 183.11 (q, J = 36.5 Hz), 159.96, 135.97, 131.40 (q, J = 1.7 Hz), 121.84, 120.80, 112.23, 120.66 – 111.99 (q, J = 291.0 Hz), 55.96. **^{19}F NMR:** (377 MHz, $CDCl_3$) δ -77.23. **GC-MS:** (EI) 204 ([M]$^+$, 70%) 136 (34%) 135 (96%) 120 (23%) 92 (90%) 79 (13%) 78 (11%) 77 (100%) 76 (14%) 75 (11%) 74 (10%) 69 (17%) 64 (32%) 63 (35%) 51 (14%) 50 (16%)

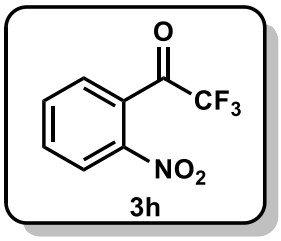


2,2,2-trifluoro-1-(3-nitrophenyl)ethanone,[6] 3g (0.363 g, 83%) was prepared according to the general procedure from **2g** (0.442 g, 0.002 mol). The desired trifluoromethyl ketone **3g** was isolated as an off yellow solid. **^{1}H NMR:** (400 MHz, MeOD) δ 8.45 (s, 1H), 8.30 (ddd, J = 8.2, 2.3, 1.1 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H).**^{13}C NMR:** (101 MHz, MeOD) δ 149.66, 138.73, 135.36 (d, J = 1.3 Hz), 130.64, 125.50, 124.21 (d, J = 1.1 Hz), 128.35 – 119.79 (q, J = 287.3 Hz), 97.19 (q, J = 31.3 Hz).**^{19}F NMR:** (377 MHz, MeOD) δ -84.12. **GC-MS:** (EI) 219 ([M]$^{+}$, 1%) 151 (11%) 150 (100%) 123 (15%) 104 (64%) 95 (19%) 92 (10%) 76 (68%) 75 (28%) 74 (17%) 69 (14%) 50 (34%)



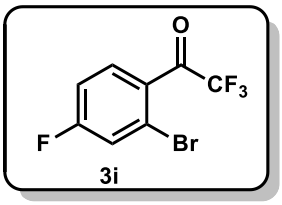
3g

2,2,2-trifluoro-1-(2-nitrophenyl)ethanone,[6] 3h (0.338 g, 76%) was prepared according to the general procedure from **2h** (0.442 g, 0.002 mol). The desired trifluoromethyl ketone **3h** was isolated as a yellow oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 8.31 (dd, J = 8.2, 1.2 Hz, 1H), 7.88 (td, J = 7.5, 1.3 Hz, 1H), 7.81 (td, J = 7.9, 1.5 Hz, 1H), 7.55 (dd, J = 7.4, 1.5 Hz, 1H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 184.15 (q, *J* = 38.7 Hz), 146.28, 135.36, 132.92, 130.36, 128.70, 124.59, 119.90-111.24 (q, *J* = 290.6 Hz). **^{19}F NMR:** (377 MHz, $CDCl_3$) δ -78.96. **GC-MS:** (EI) 219 ([M]$^{+}$, 1%) 151 (10%) 150 (100%) 123 (17%) 104 (13%) 95 (22%) 78 (14%) 76 (72%) 75 (28%) 74 (26%) 69 (61%) 52 (12%) 51 (64%) 50 (56%)



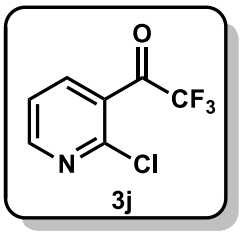
3h

1-(2-bromo-4-fluorophenyl)-2,2,2-trifluoroethanone,[6] 3i (0.437 g, 81%) was prepared according to the general procedure from **2i** (0.546 g, 0.002 mol). The desired trifluoromethyl ketone **3i** was isolated as a yellow oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.78 (ddd, J = 8.7, 5.6, 1.4 Hz, 1H), 7.51 (dt, J = 8.4, 3.0 Hz, 1H), 7.19 (ddd, J = 8.8, 7.4, 2.4 Hz, 1H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 180.73 (q, J = 36.5 Hz), 164.84 (d, J = 261.1 Hz), 132.57 (dq, J = 9.8, 3.3 Hz), 128.27 (d, J = 3.6 Hz), 124.19 (d, J = 10.0 Hz), 123.29 (d, J = 24.6 Hz), 115.12 (d, J = 21.7 Hz), 120.23 – 111.53 (q, J = 291.9 Hz). **^{19}F NMR:** (377 MHz, $CDCl_3$) δ -75.66 (s, 3 F), -104.62 (q, *J* = 6.1, 5.5 Hz, 1 F). **GC-MS:** (EI) 272 ([M]$^{+}$, 8%) 270 ([M]$^{+}$, 9%) 203 (100%) 201 (100%) 175 (57%) 173 (58%) 122 (10%) 94 (74%) 93 (18%) 74 (19%) 69 (15%) 68 (13%) 50 (15%)

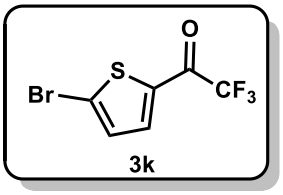


3i

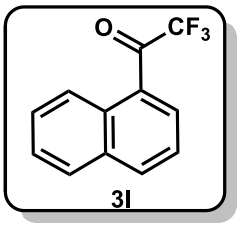
1-(2-chloropyridin-3-yl)-2,2,2-trifluoroethanone,[10] 3j (0.333 g, 80%) was prepared according to the general procedure from **2j** (0.423 g, 0.002 mol). The desired trifluoromethyl ketone **3j** was isolated as an off white solid. **^{1}H NMR:** (400 MHz, DMSO-d_6, hydrate) δ 8.44 (dd, *J* = 4.7, 1.9 Hz, 1H), 8.21 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.91 (s, 2H), 7.49 (dd, *J* = 7.8, 4.6 Hz, 1H). **^{13}C NMR:** (101 MHz, DMSO-d_6, hydrate) δ 150.12, 149.15, 140.66, 132.21, 127.65 – 119.02 (q, *J* = 289.8 Hz), 122.56, 92.15 (q, *J* = 32.5 Hz). **^{19}F NMR:** (377 MHz, DMSO-d_6) δ -83.95. **GC-MS:** (EI) 209 ([M]$^+$, 5%) 142 (33%) 140 (100%) 114 (22%) 112 (69%) 85 (11%) 76 (42%) 69 (19%) 51 (13%) 50 (23%)



1-(5-bromothiophen-2-yl)-2,2,2-trifluoroethanone,[11] 3k (0.401 g, 77%) was prepared according to the general procedure from **2k** (0.522 g, 0.002 mol). The desired trifluoromethyl ketone **3k** was isolated as a yellow oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.70 (dq, J = 4.4, 1.5 Hz, 1H), 7.21 (d, J = 4.2 Hz, 1H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 172.66 (q, J = 37.3 Hz), 137.87, 136.96 (q, J = 3.1 Hz), 132.54, 128.07, 120.63 – 111.97 (q, J = 290.3 Hz). **^{19}F NMR:** (377 MHz, $CDCl_3$) δ -75.37. **GC-MS:** (EI) 260 ([M]$^+$, 35%) (EI) 258 ([M]$^+$, 34%) 191 (100%) 189 (98%) 163 (12%) 161 (12%) 119 (10%) 117 (10%) 82 (39%) 81 (15%) 69 (12%)

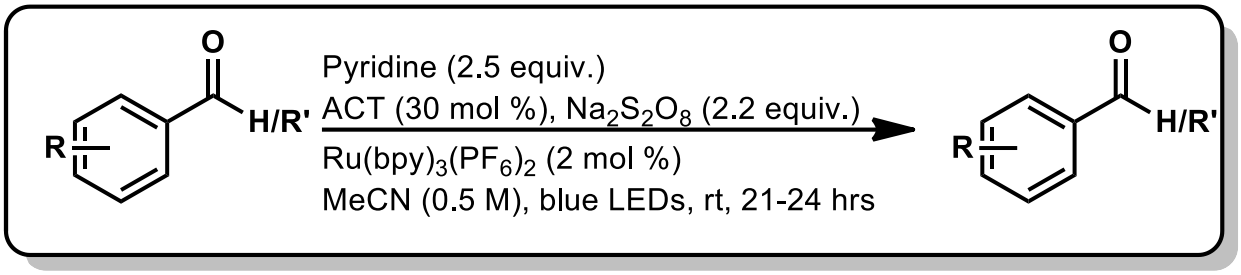


2,2,2-trifluoro-1-(naphthalen-1-yl)ethanone,[12] 3l (0.374 g, 83%) was prepared according to the general procedure from **2l** (0.452 g, 0.002 mol). The desired trifluoromethyl ketone **3l** was isolated as an orange oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 8.85 (d, J = 8.7 Hz, 1H), 8.21 (d, J = 7.5, Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.70 (t, J = 7.2 Hz, 1H), 7.64 – 7.53 (m, 2H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 182.42 (q, J = 33.8 Hz), 136.29, 134.08, 131.78 (q, J = 3.9 Hz), 131.30, 129.60, 129.10, 127.24, 126.44, 125.30, 124.24, 121.15 – 112.42 (q, J = 292.9 Hz). **^{19}F NMR:** (377 MHz, $CDCl_3$) δ -73.20. **GC-MS:** (EI) 225 ([M]$^+$, 11%) 224 ([M]$^+$, 77%) 156 (24%) 155 (100%) 128 (26%) 127 (99%) 126 (44%) 101 (18%) 77 (27%) 75 (19%) 74 (16%) 69 (8%) 63 (23%) 51 (10%)

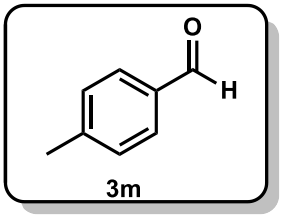


[10] Kremlev, M. M.; Mushta, A. I.; Tyrra, W.; Naumann, D.; Fischer, H. T. M.; Yagupolskii, Y. L. *J. Fluorine Chem.* **2007**, *128*, 1385-1389.
[11] Rudzinski, D. M.; Kelly, C. B.; Leadbeater, N. E. *Chem. Comm.* **2012**, *48*, 9610-9612.
[12] Czerwinski, P.; Molga, E.; Cavallo, L.; Poater, A.; Michalak, M. *Chem. Eur. J.* **2016**, *22*, 8089-8094.

Representative Procedure for the Oxidation of Non-fluorinated alcohols



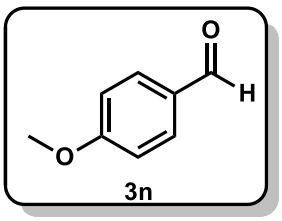
4-tolualdehyde,[13] (3m):



To a 20-mL vial equipped with a stir bar was added 4-tolylmethanol (0.244 g, 0.002 mol, 1 equiv), pyridine (0.396 g, 0.005 mol, 2.5 equiv), ACT (0.128 g, 0.0006 mol, 0.3 equiv), and MeCN (4 mL, 0.5 M). Upon addition of the solvent, $Na_2S_2O_8$ (1.047 g, 0.0044 mol, 2.2 equiv) and the photocatalyst $Ru(bpy)_3(PF_6)_2$ (0.034 g, 0.00004 mol, 0.02 equiv) were added. The vial was sealed with a cap and irradiated in the aforementioned LED reactor for 21 h. After this time, Et_2O (15 mL) was added and the solution was stirred for 10 minutes. After this time, the resulting mixture was filtered through a coarse porosity fritted glass funnel. The solution was then transferred to a separatory funnel, diluted with Et_2O (60 mL) and deionized water (75 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 × 50 mL). The organic layers were then combined and washed with 0.5 M aqueous HCl (3 × 50 mL), deionized water (50 mL), and finally brine (100 mL). The organic layer was then dried over sodium sulfate and the solvent removed in vacuo to afford the pure aldehyde **3m** as a clear yellow liquid (0.155 g, 64%).

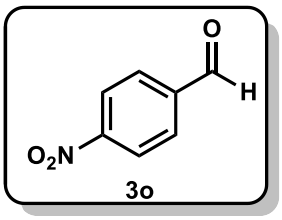
^{1}H NMR: (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.78 (d, J = 7.8 Hz 2H), 7.33 (d, J = 7.8 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 192.03, 145.61, 134.30, 129.91, 129.78, 21.93. **GC-MS:** (EI) 120 ($[M]^+$, 83%) 119 ($[M]^+$, 100%) 92 (11%) 91 (100%) 89 (13%) 65 (29%) 63 (18%) 39 (14%)

4-methoxybenzaldehyde,[13] 3n (0.182 g, 67%) was prepared according to the general procedure from (4-methoxyphenyl)methanol (0.276 g, 0.002 mol). The desired aldehyde **3n** was isolated as a clear yellow liquid. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 190.88, 164.72, 132.08, 130.10, 114.42, 55.69. **GC-MS:** (EI) 136 ($[M]^+$, 72%) 135 ($[M]^+$, 100%) 107 (16%) 92 (18%) 77 (29%) 65 (11%) 64 (10%) 63 (13%)



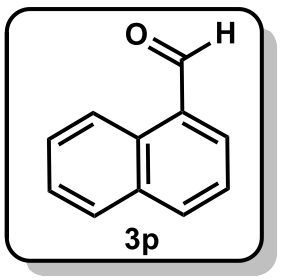
[13] Zhang, G.; Han, X.; Luan, Y.; Wang, Y.; Wen, X.; Ding, C. *Chem. Comm.* **2013**, *49*, 7908-7910.

4-nitrobenzaldehyde,[13] 3o (0.203 g, 67%) was prepared according to the general procedure from (4-nitrophenyl)methanol (0.306 g, 0.002 mol). The desired aldehyde **3o** was isolated as a pale yellow powder. **^{1}H NMR:** (400 MHz, DMSO-d6) δ 10.17 (s, 1H), 8.41 (d, J = 8.7 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H). **^{13}C NMR:** (101 MHz, DMSO-d6) δ 192.32, 150.62, 140.06, 130.62, 124.26. **GC-MS:** (EI) 151 ([M]$^+$, 98%) 150 ([M]$^+$, 100%) 105 (22%) 104 (20%) 92 (14%) 77 (78%) 76 (27%) 75 (19%) 74 (25%) 65 (13%) 51 (63%) 50 (38%)



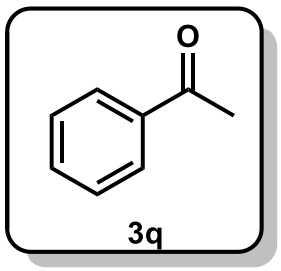
3o

1-naphthaldehyde,[13] 3p (0.253 g, 81%) was prepared according to the general procedure from naphthalen-1-ylmethanol (0.316 g, 0.002 mol). The desired aldehyde **3o** was isolated as an orange liquid. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 9.26 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 8.4, 1H), 7.98 (dd, J = 7.0, 1.3 Hz, 1H), 7.92 (d, J = 8.3 Hz 1H), 7.69 (ddd, J = 8.5, 6.9, 1.4 Hz, 1H), 7.65 – 7.57 (m, 2H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 193.62, 136.74, 135.39, 133.85, 131.54, 130.66, 129.17, 128.58, 127.07, 124.99 (d, J = 1.2 Hz). **GC-MS:** (EI) 157 ([M]$^+$, 11%) 156 ([M]$^+$, 93%) 155 ([M]$^+$, 58%) 128 (100%) 127 (95%) 126 (30%) 102 (11%) 101 (11%) 77 (17%) 75 (17%) 74 (15%) 63 (14%) 51 (13%) 50 (10%)



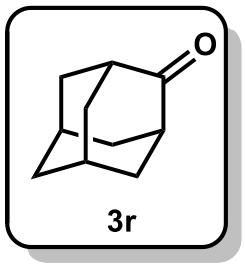
3p

Acetophenone,[13] 3q (0.196 g, 82%) was prepared according to the general procedure from 1-phenylethanol (0.244 g, 0.002 mol) **with the following modification:** the reaction was irradiated and stirred for 24 hours. The desired ketone **3r** was isolated as a clear, colorless liquid. **^{1}H NMR:** (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 2.59 (s, 3H). **^{13}C NMR:** (75 MHz, $CDCl_3$) δ 198.16, 137.19, 133.14, 128.61, 128.34, 26.63. **GC-MS:** (EI) 120 ([M]$^+$, 66%) 106 (16%) 105 (100%) 78 (12%) 77 (100%) 51 (40%) 50 (19%) 43 (14%)



3q

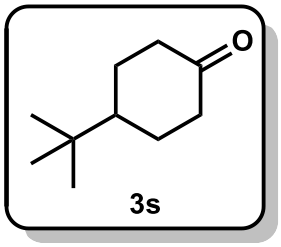
2-adamantanone,[14] 3r (0.257 g, 86%) was prepared according to the general procedure from 2-adamantanol (0.304 g, 0.002 mol) **with the following modification:** the reaction was irradiated and stirred for 24 hours. The desired ketone **3r** was isolated as a yellow powder. **^{1}H NMR:** (300 MHz, $CDCl_3$) δ 2.54 (s, 2H), 2.19 – 1.88 (m, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 218.55, 47.11, 39.38, 36.43, 27.58. **GC-MS:** (EI) 150 ([M]$^+$, 100%) 117 (17%) 81 (40%) 80 (78%) 79 (93%) 72 (12%) 67 (13%) 54 (10%) 41 (18%)



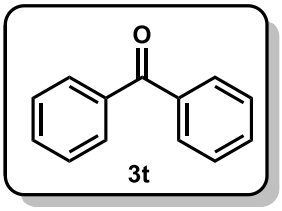
3r

[14] Wang, L.; Shang, S.; Li, G.; Ren, L.; Lv, Y.; Gao, S. *J. Org. Chem.* **2016**, *81*, 2189-2193.

4-(tert-butyl)cyclohexanone,[15] 3s (0.258 g, 84%) was prepared according to the general procedure from 4-(tert butyl)cyclohexanone (0.312 g, 0.002 mol) **with the following modification:** the reaction was irradiated and stirred for 24 hours. The desired ketone **3t** was isolated as an off white powder. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 2.41 – 2.21 (m, 4H), 2.13 – 2.00 (m, 2H), 1.50 – 1.35 (m, 3H), 0.90 (s, 9H). **^{13}C NMR:** (75 MHz, $CDCl_3$) δ 212.69, 46.85, 41.44, 32.59, 27.73. **GC-MS:** (EI) 154 ($[M]^+$, 18%) 98 (72%) 97 (13%) 83 (27%) 70 (10%) 69 (19%) 57 (100%) 55 (30%) 43 (16%) 41 (48%) 39 (17%)

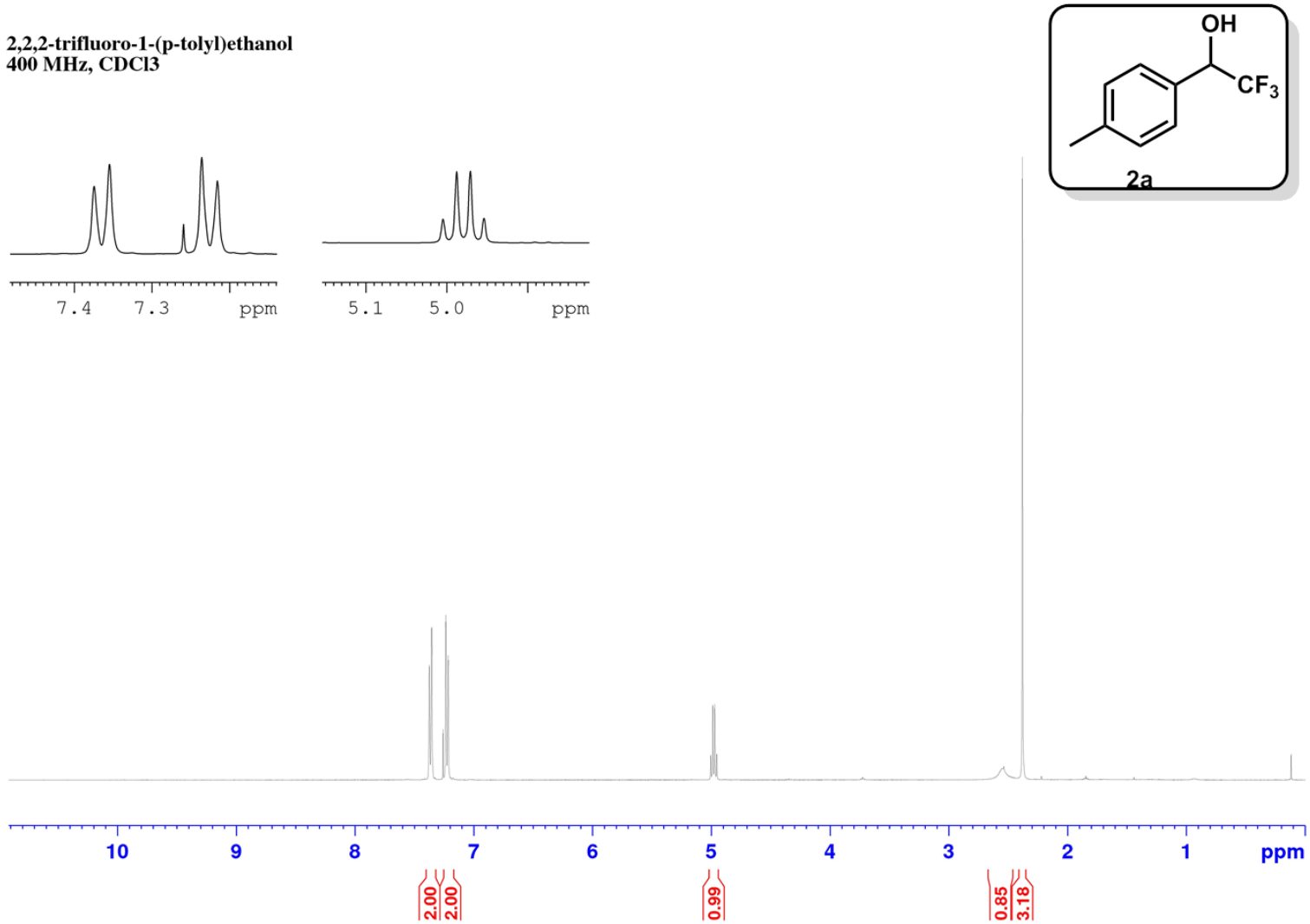


Benzophenone,[13] 3t (0.332 g, 91%) was prepared according to the general procedure from diphenylmethanol (0.368 g, 0.002 mol) **with the following modification:** the reaction was irradiated and stirred for 24 hours. The desired ketone **3t** was isolated as an off white powder. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.0 Hz, 4H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 4H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 196.85, 137.75, 132.53, 130.18, 128.40. **GC-MS:** (EI) 183 ($[M]^+$, 10%) 182 ($[M]^+$, 67%) 181 ($[M]^+$, 11%) 106 (8%) 105 (100%) 77 (65%) 51 (25%) 50 (9%)

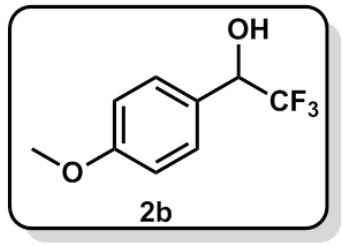


[15] Wei, Y.; Rao, B.; Cong, X.; Zeng, X. *J. Am. Chem. Soc.* **2015**, *137*, 9250-9253.

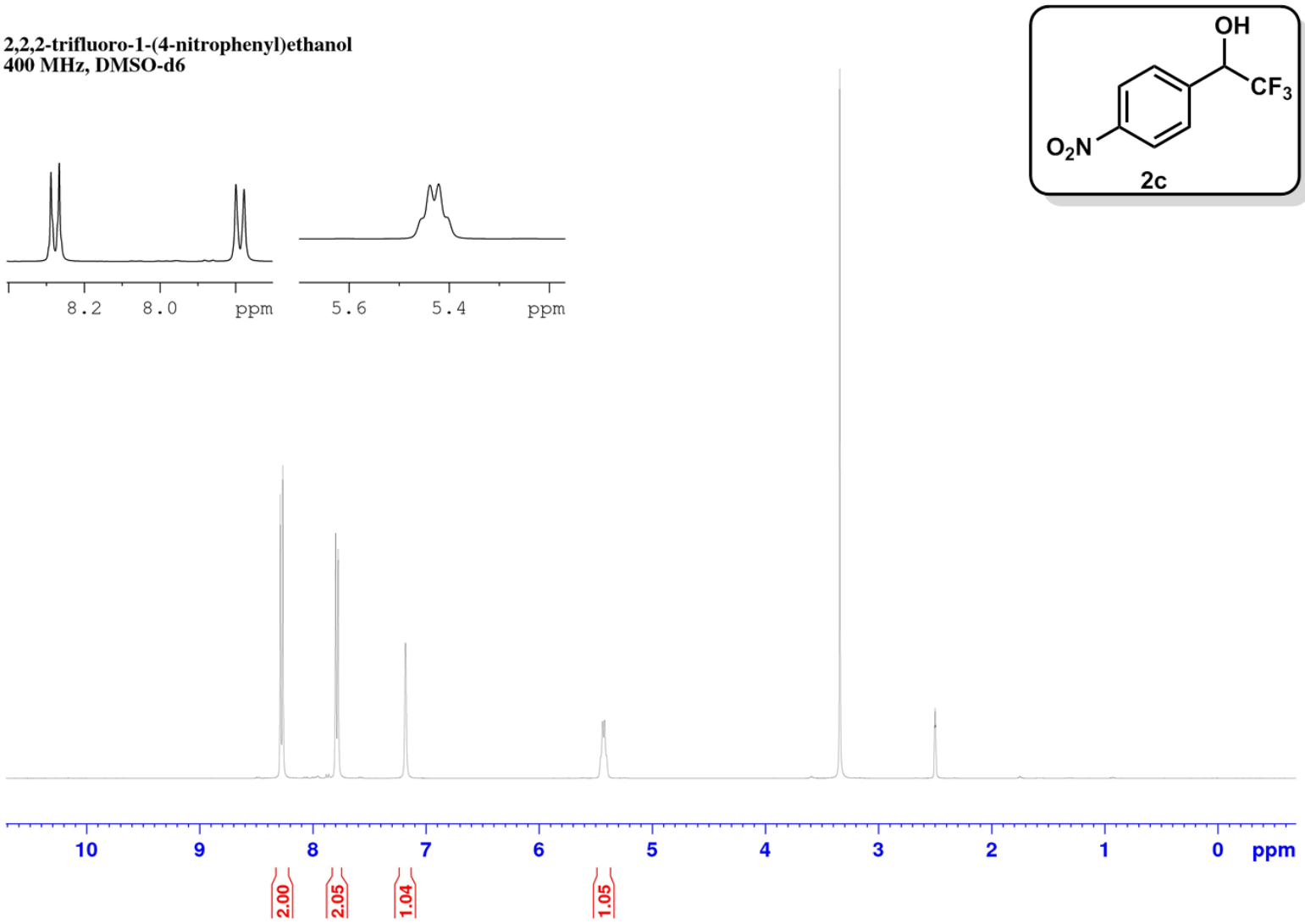
^{1}H NMR Spectra of Synthesized α-CF_3 alcohols



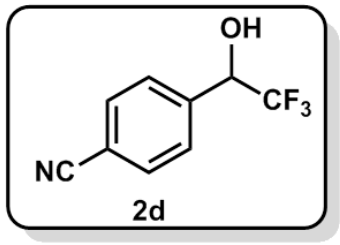
2,2,2-trifluoro-1-(4-methoxyphenyl)ethanol
400 MHz, CDCl3

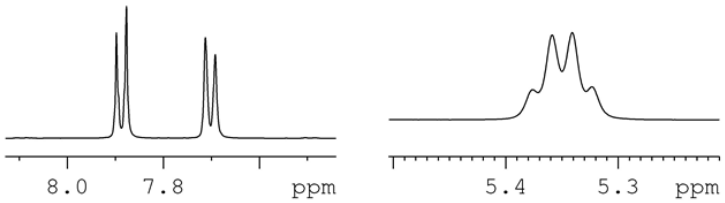


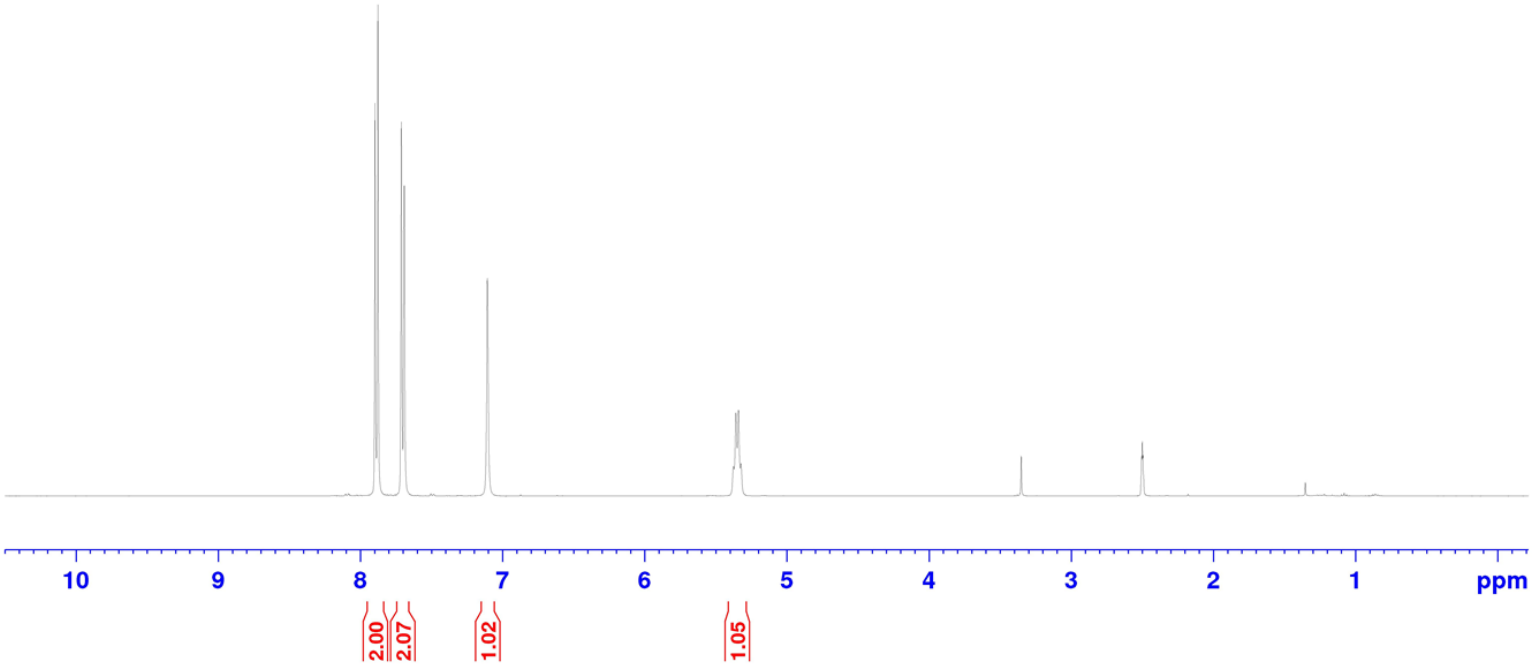
2,2,2-trifluoro-1-(4-nitrophenyl)ethanol
400 MHz, DMSO-d6



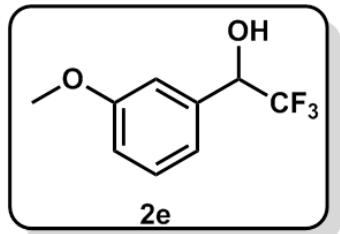
4-(2,2,2-trifluoro-1-hydroxyethyl)benzonitrile
400 MHz, DMSO-d6



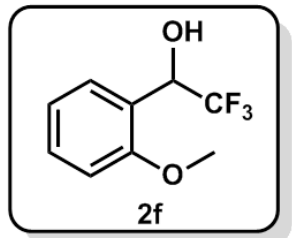


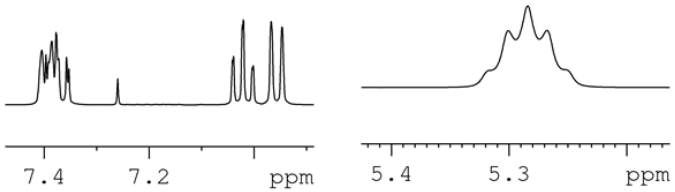


2,2,2-trifluoro-1-(3-methoxyphenyl)ethanol
400 MHz, CDCl3

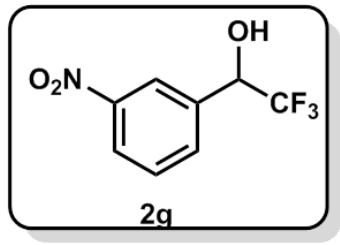


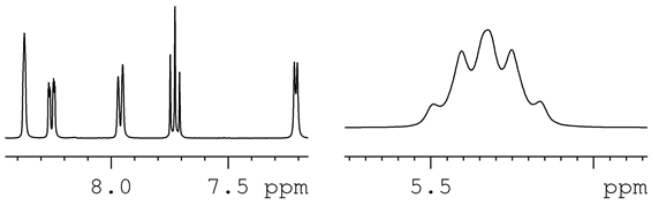
2,2,2-trifluoro-1-(2-methoxyphenyl)ethanol
400 MHz, CDCl3

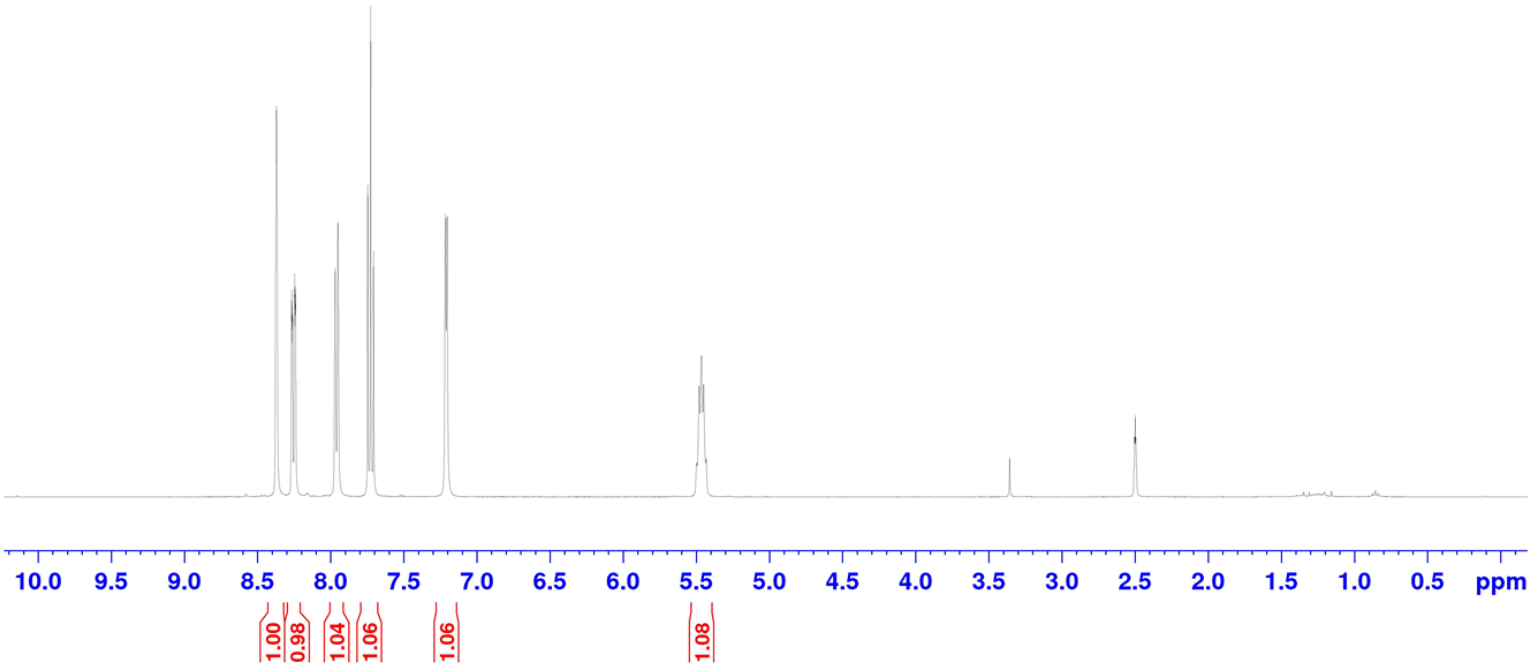




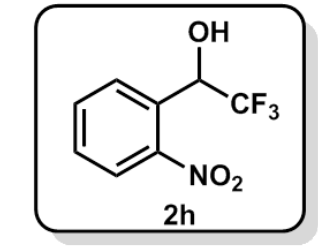
2.2.2-trifluoro-1-(3-nitrophenyl)ethanol
400 MHz, DMSO-d6

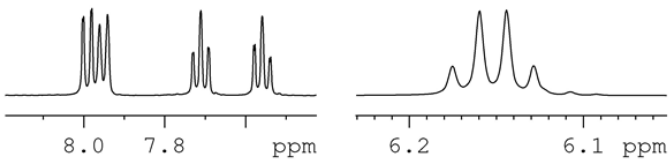


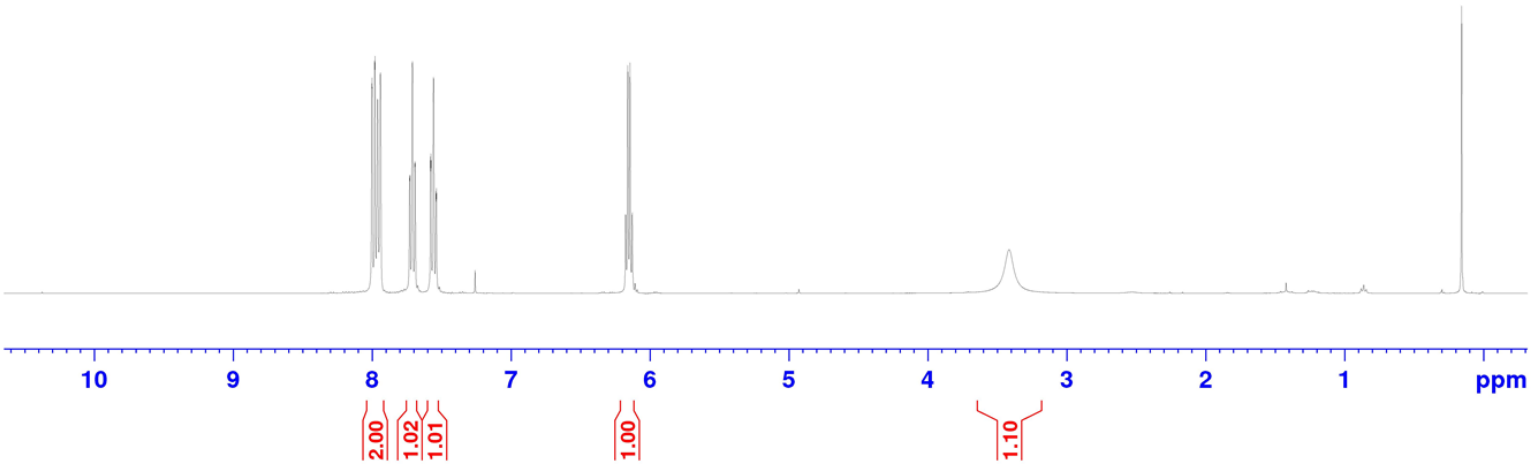




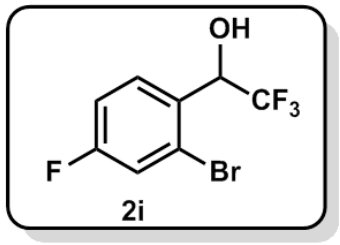
2,2,2-trifluoro-1-(2-nitrophenyl)ethanol
400 MHz, CDCl3

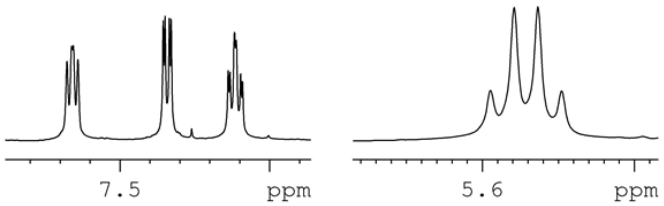


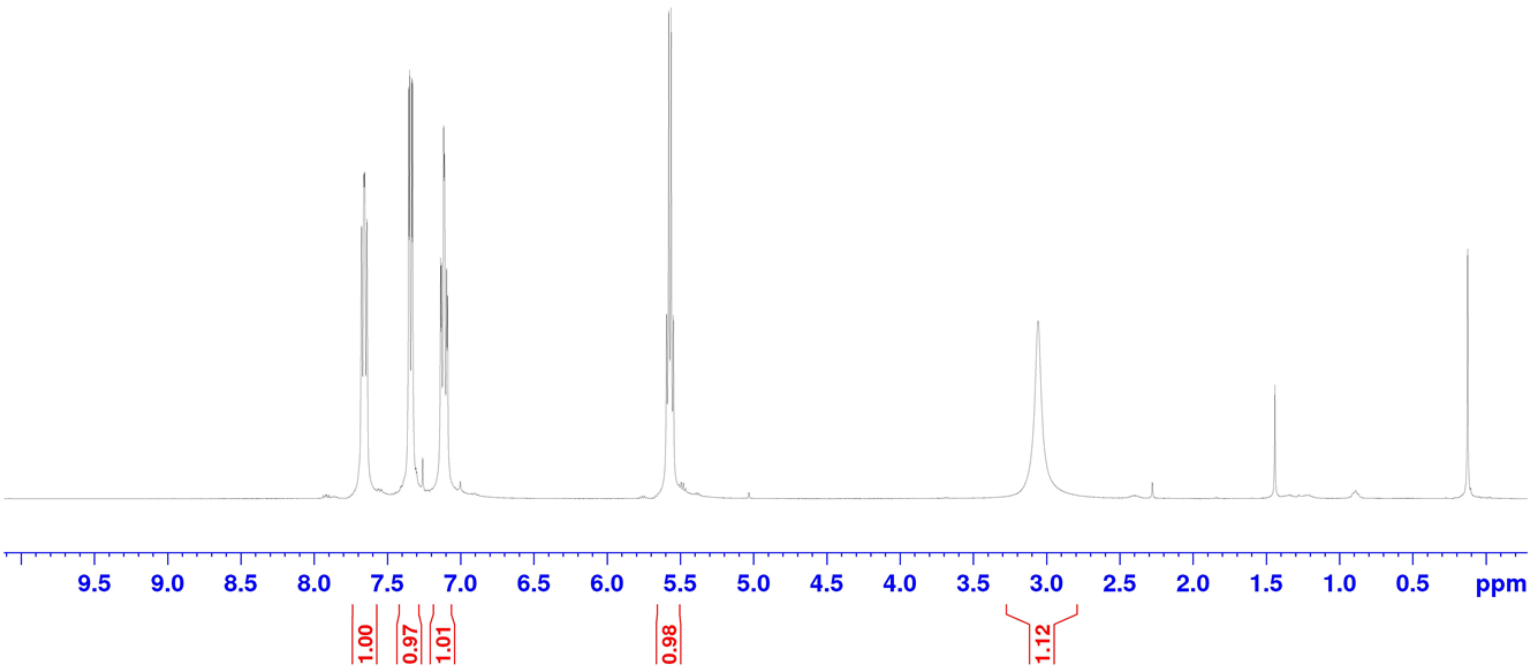




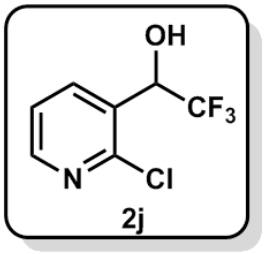
1-(2-bromo-4-fluorophenyl)-2,2,2-trifluoroethanol
400 MHz, CDCl3

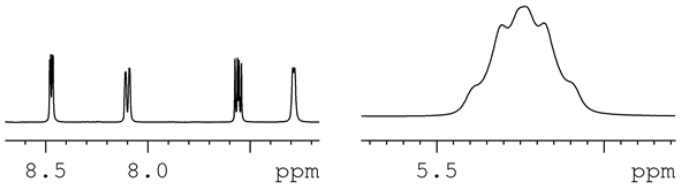


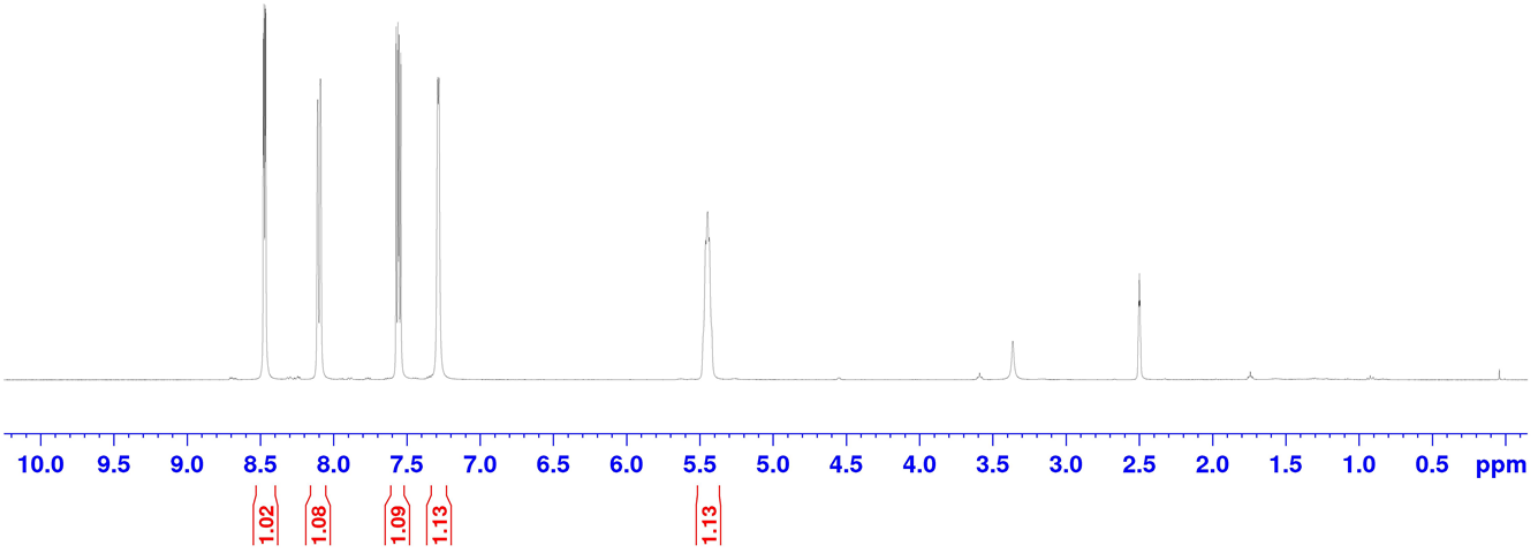




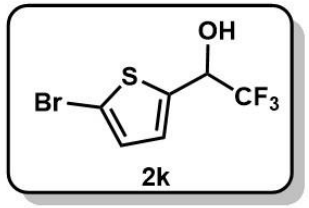
1-(2-chloropyridin-3-yl)-2,2,2-trifluoroethanol
400 MHz, DMSO-d6

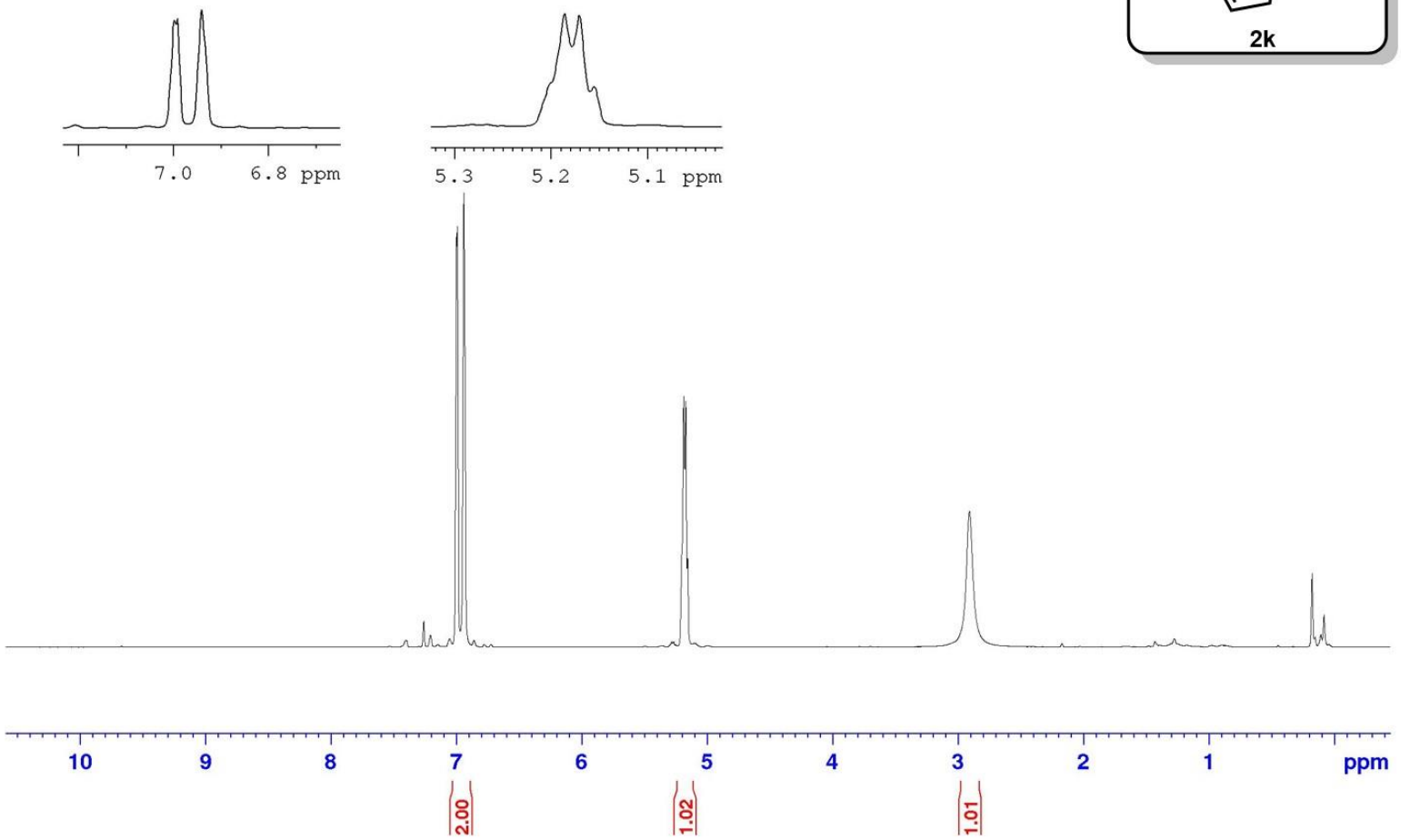




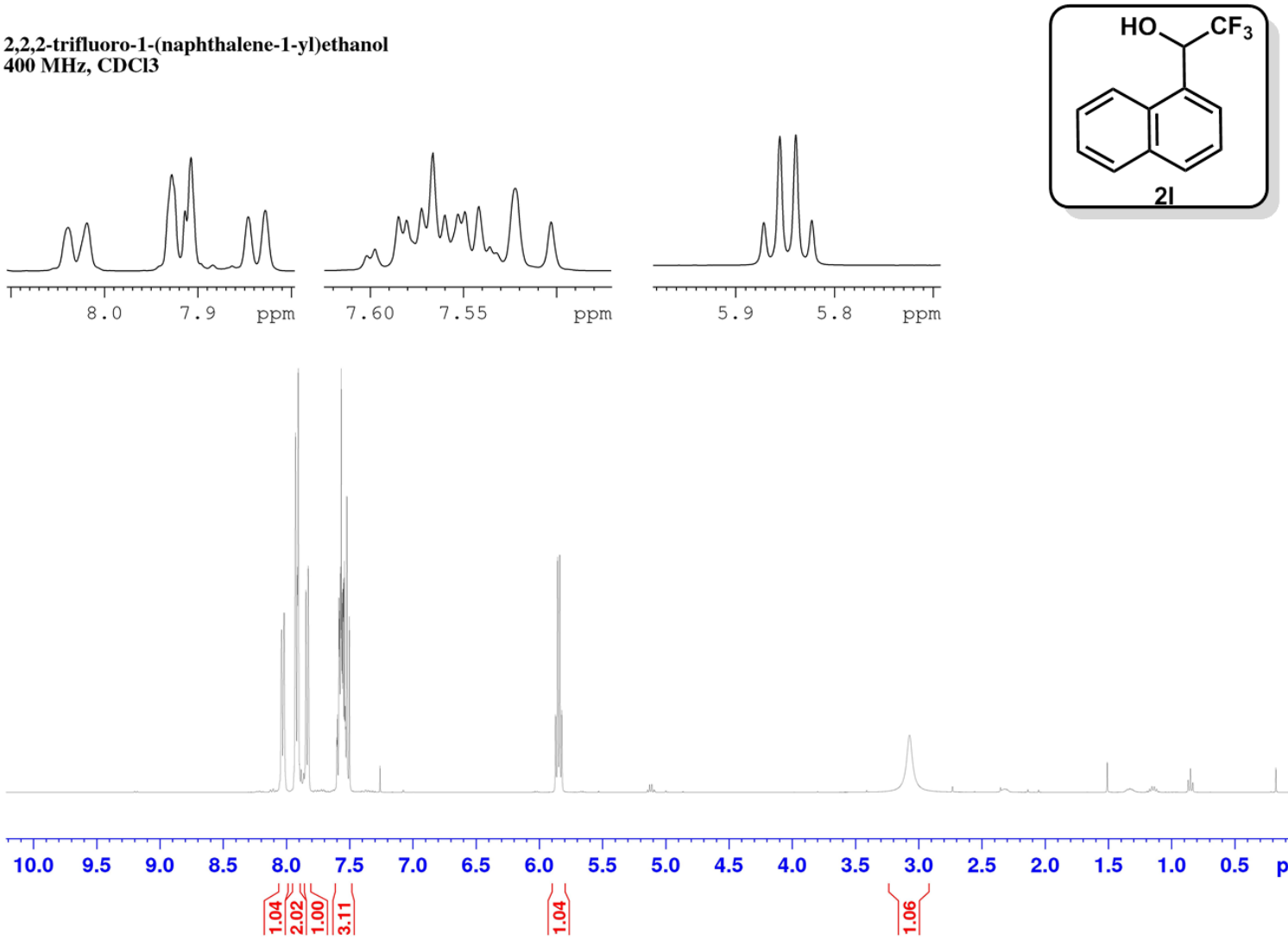


1-(5-bromothiophen-2-yl)-2,2,2-trifluoroethanol
400 MHz, CDCl3

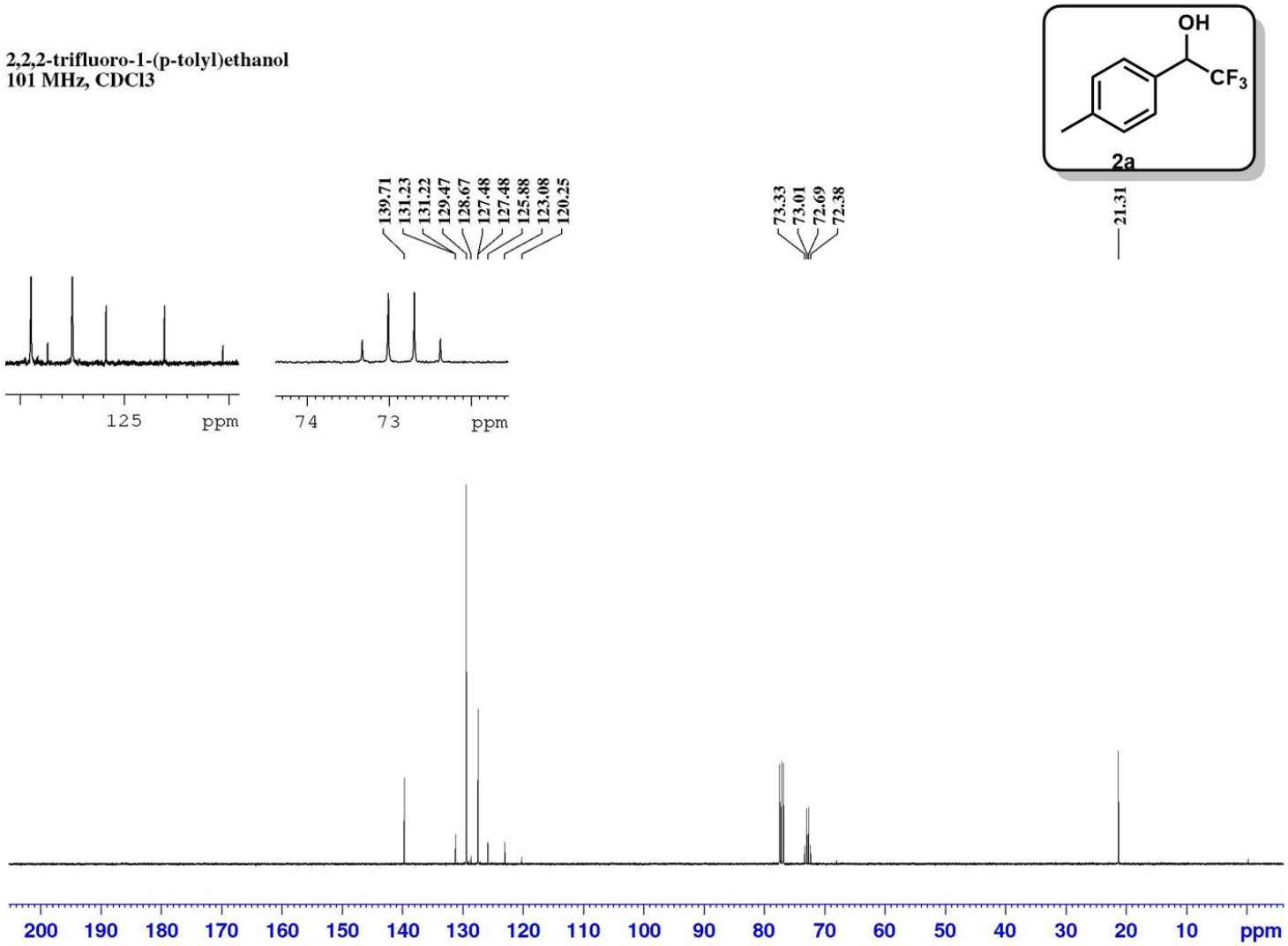




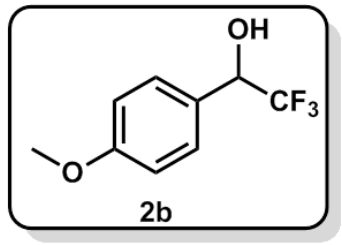
2,2,2-trifluoro-1-(naphthalene-1-yl)ethanol
400 MHz, CDCl3

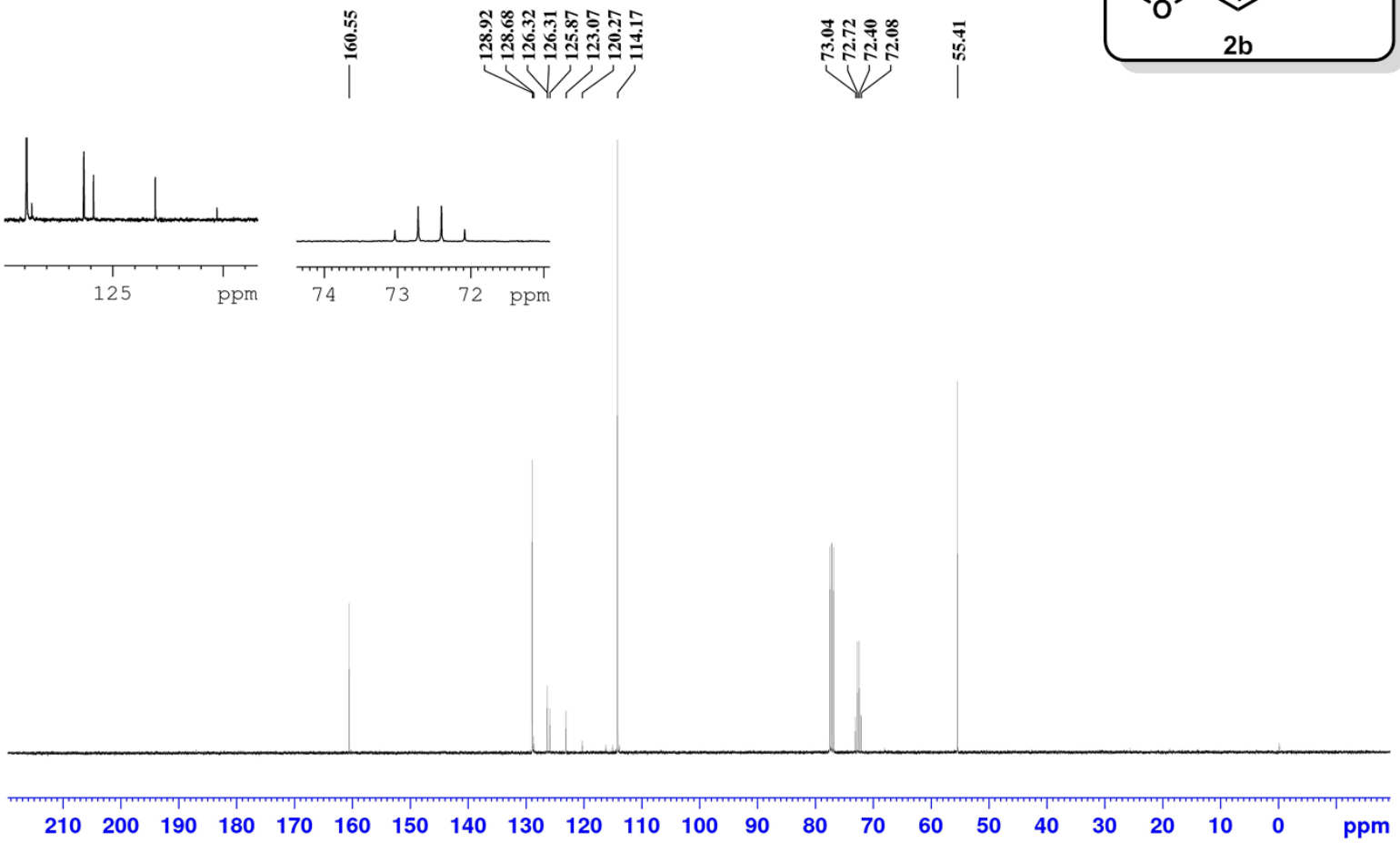


^{13}C NMR Spectra of Synthesized α-CF_3 alcohols

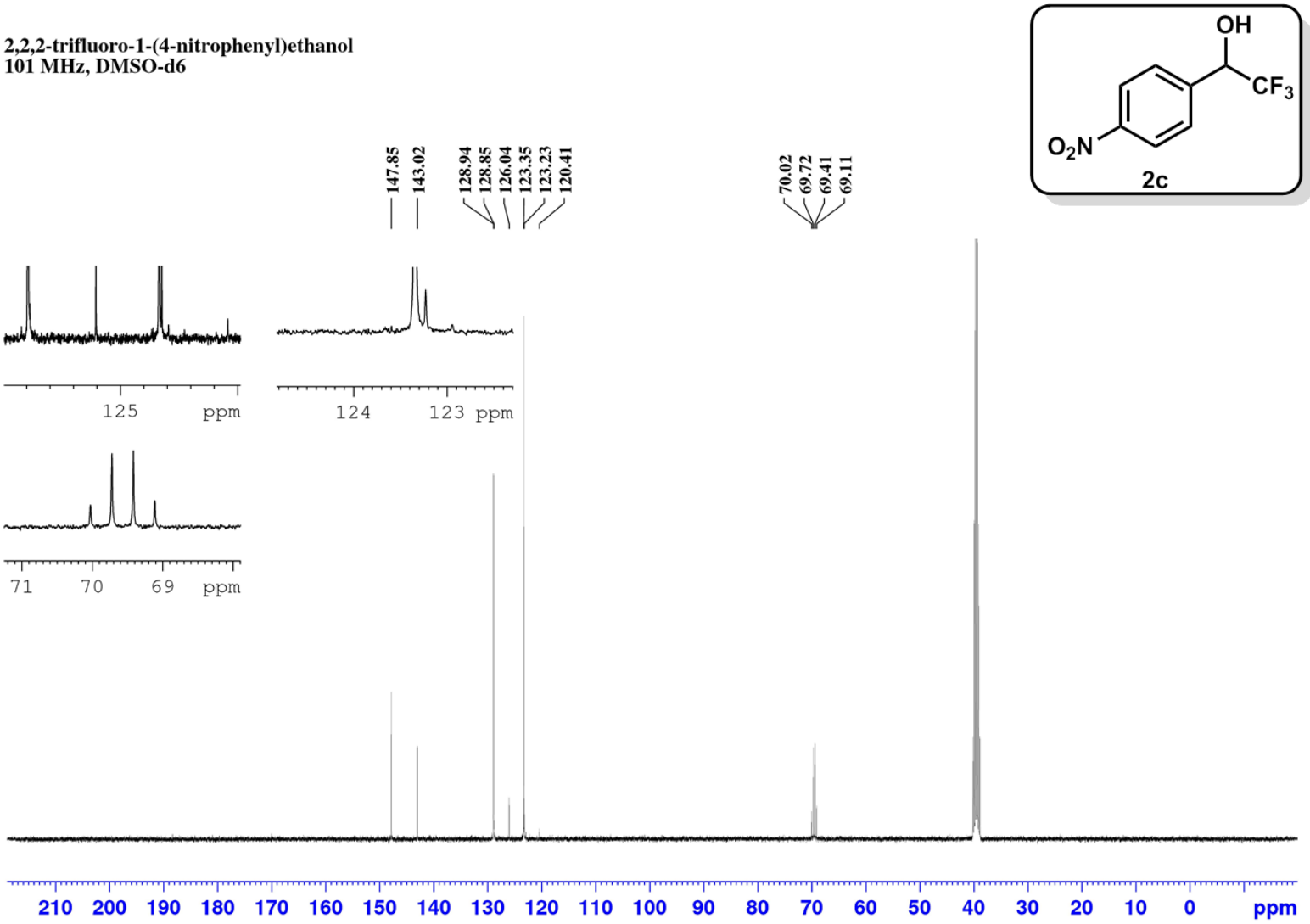


2.2.2-trifluoro-1-(4-methoxyphenyl)ethanol
101 MHz, CDCl3

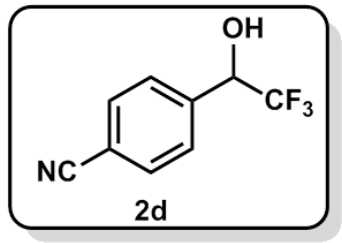


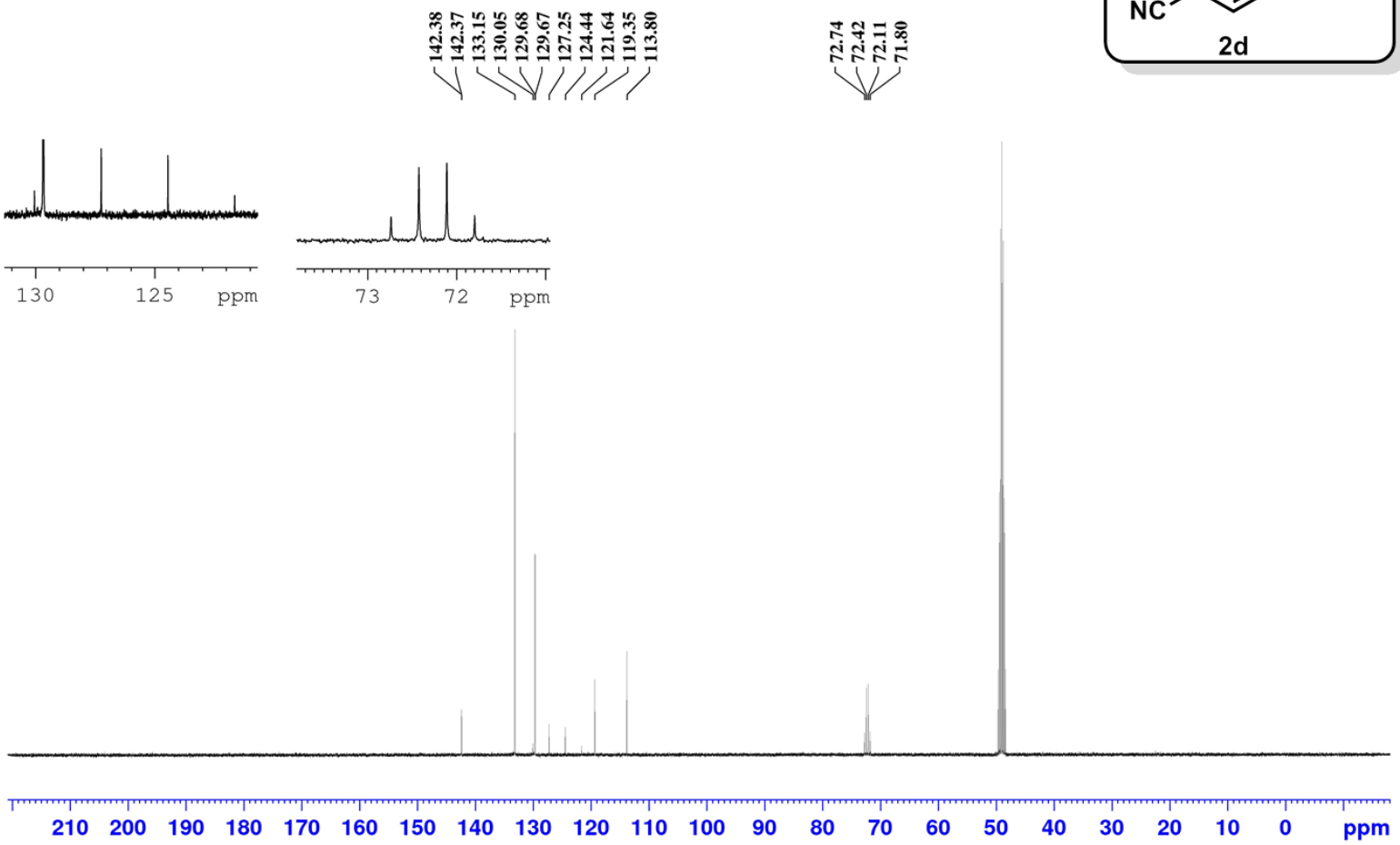


2,2,2-trifluoro-1-(4-nitrophenyl)ethanol
101 MHz, DMSO-d6

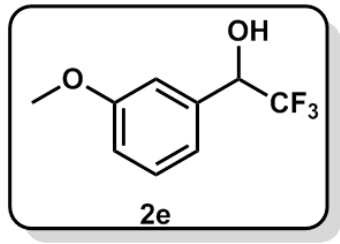


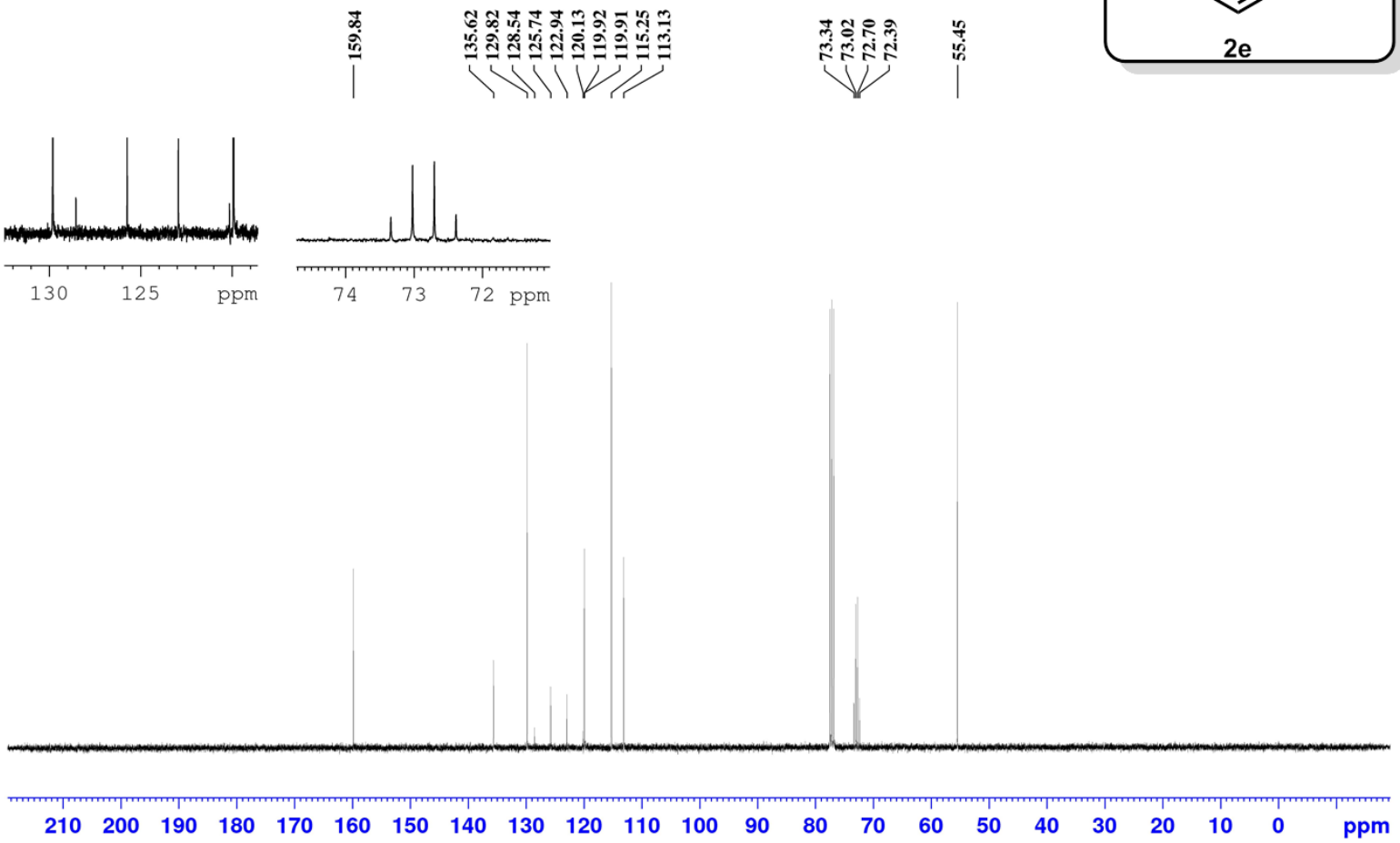
4-(2,2,2-trifluoro-1-hydroxyethyl)benzonitrile
101 MHz, MeOD



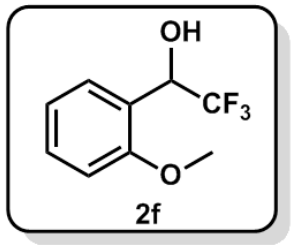


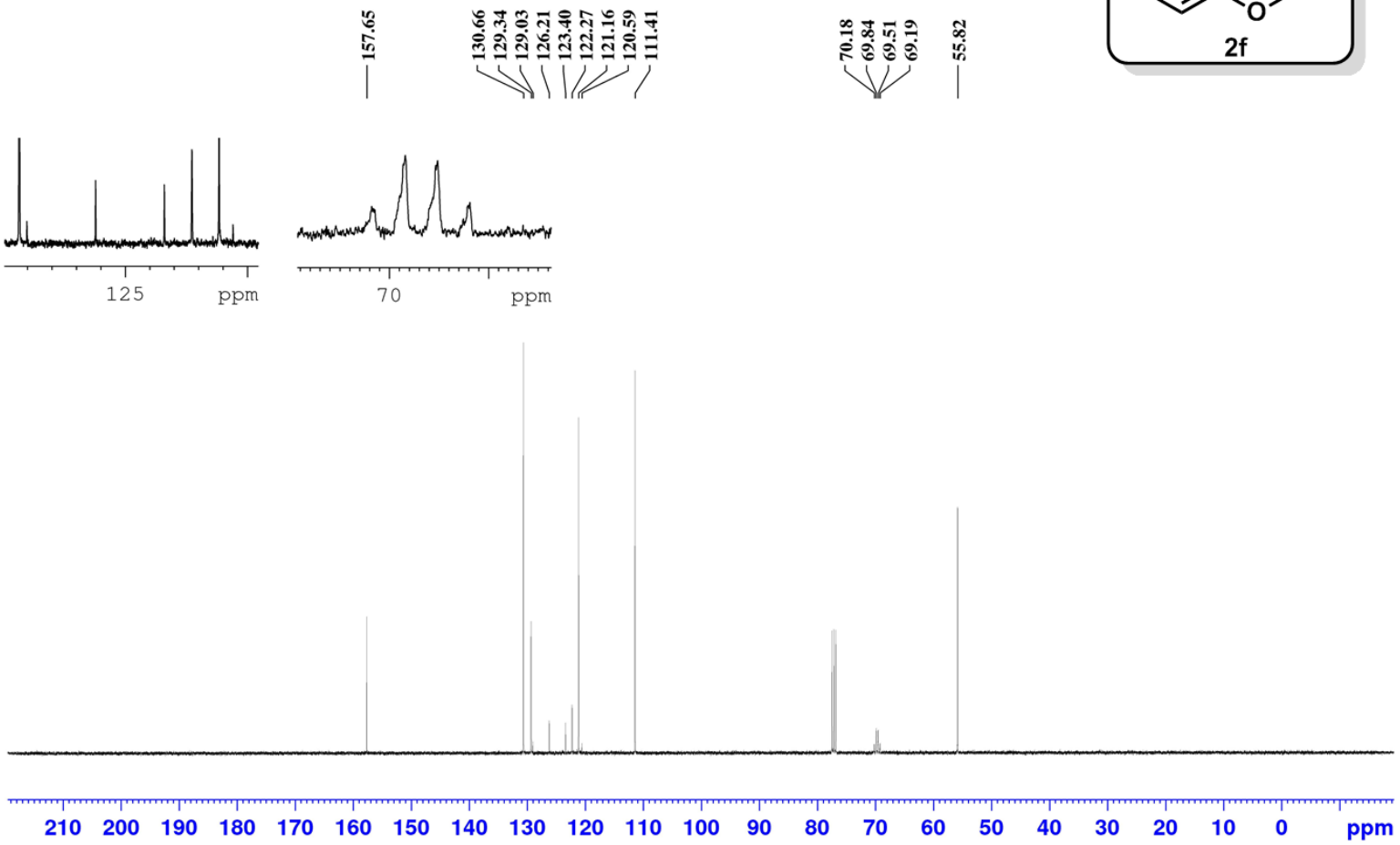
2,2,2-trifluoro-1-(3-methoxyphenyl)ethanol
101 MHz, CDCl3



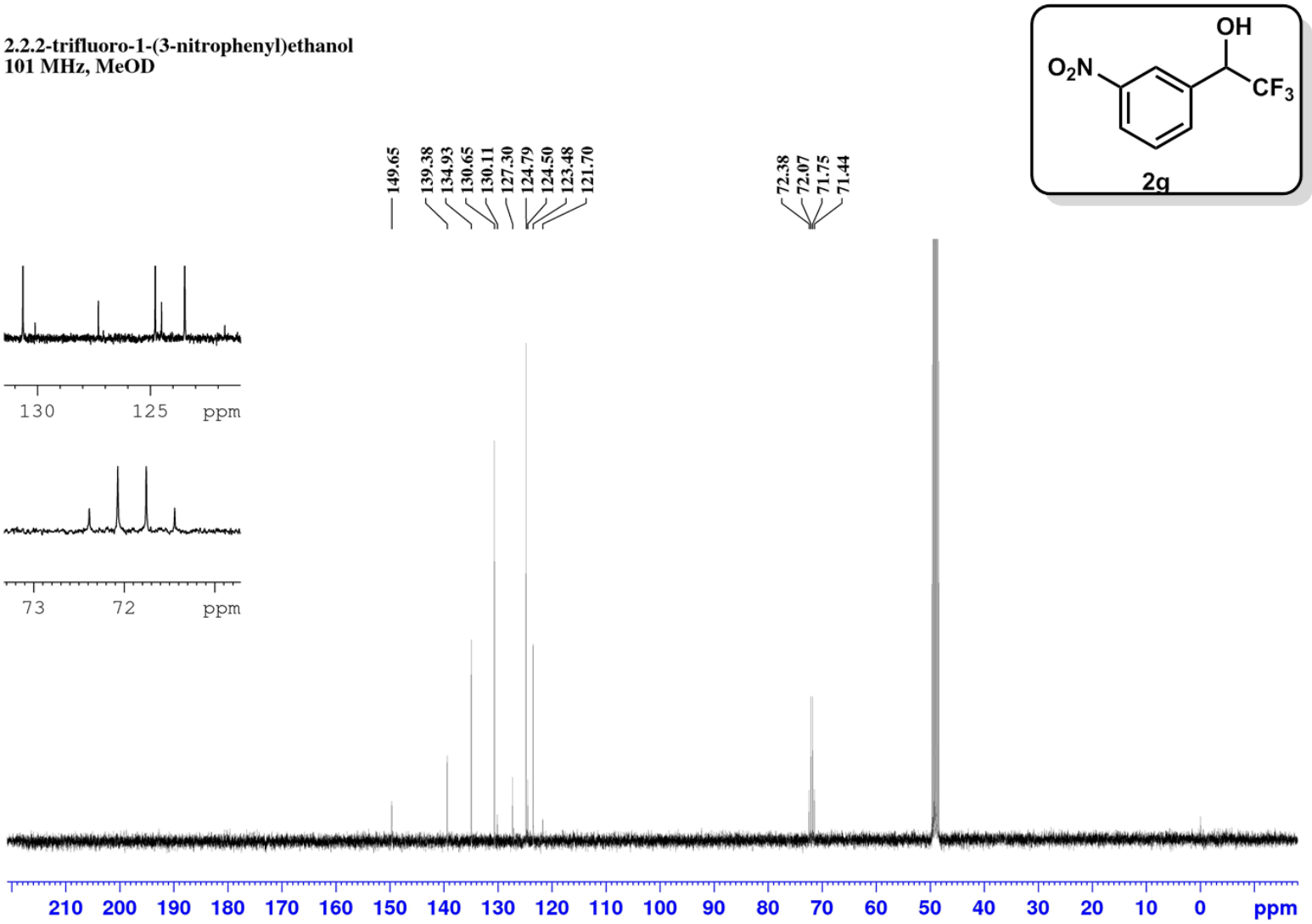


2,2,2-trifluoro-1-(2-methoxyphenyl)ethanol
101 MHz, CDCl3

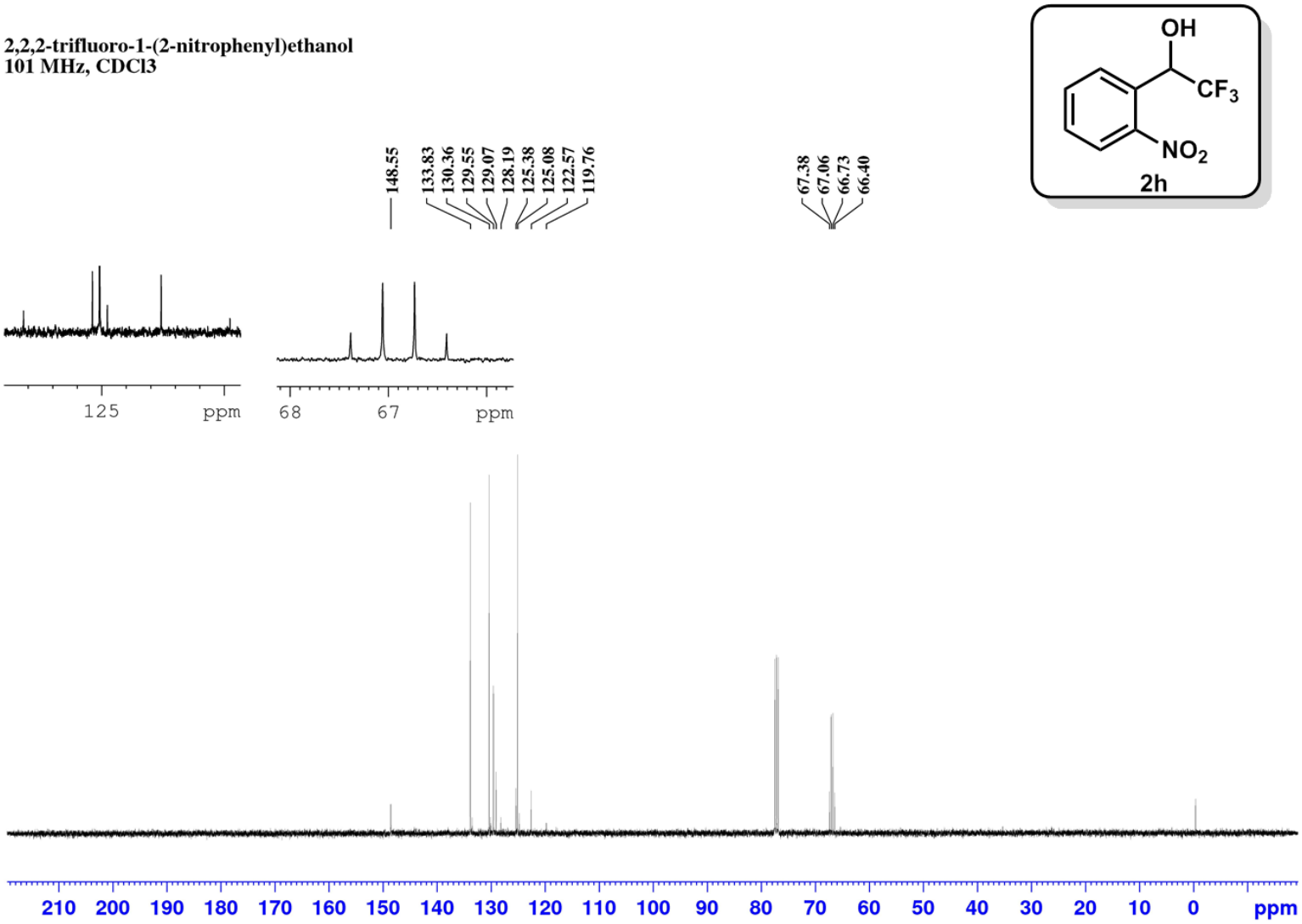




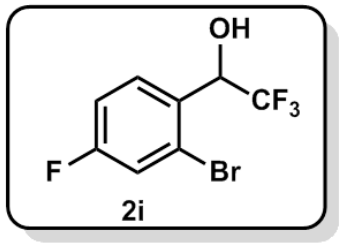
2.2.2-trifluoro-1-(3-nitrophenyl)ethanol
101 MHz, MeOD

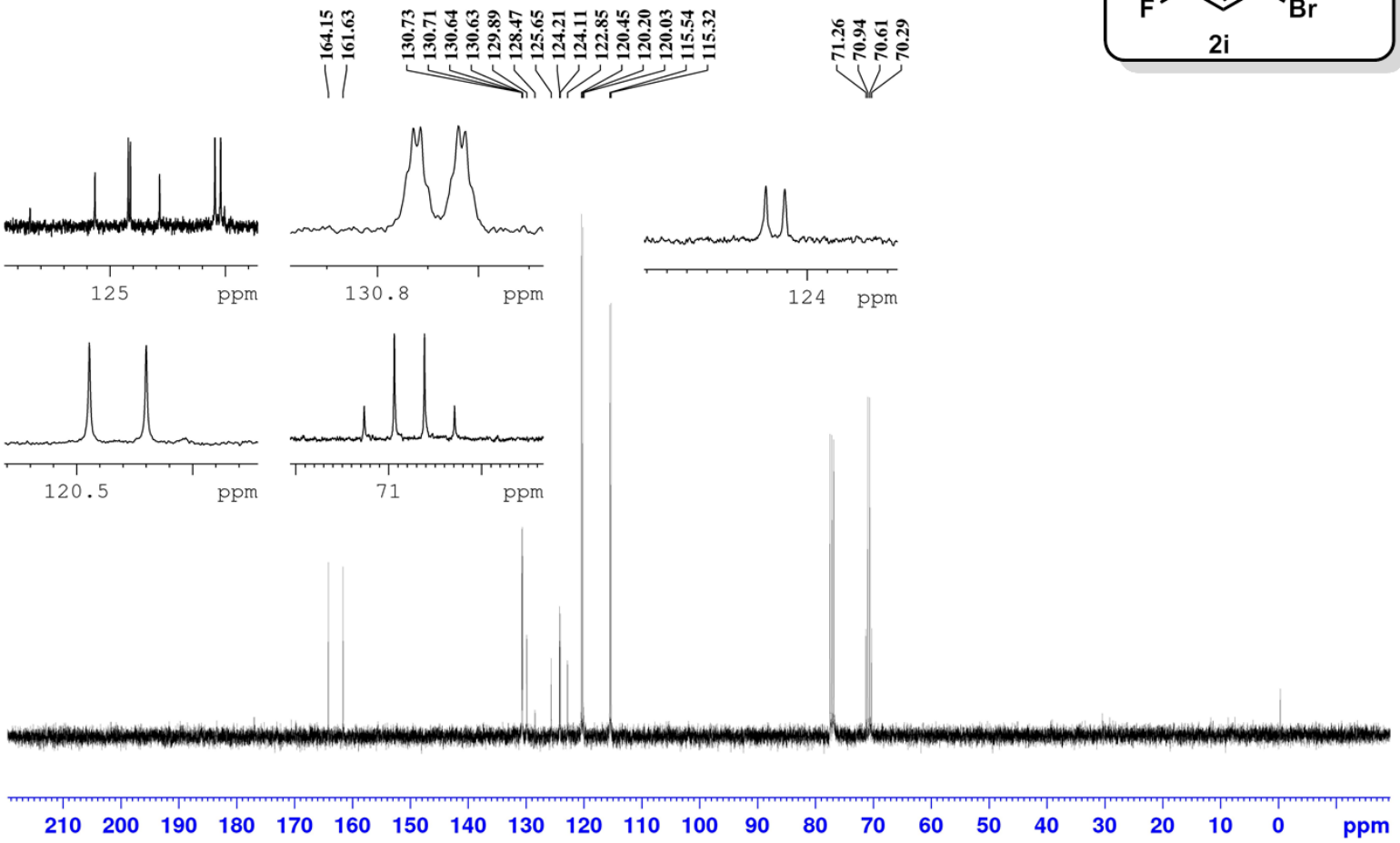


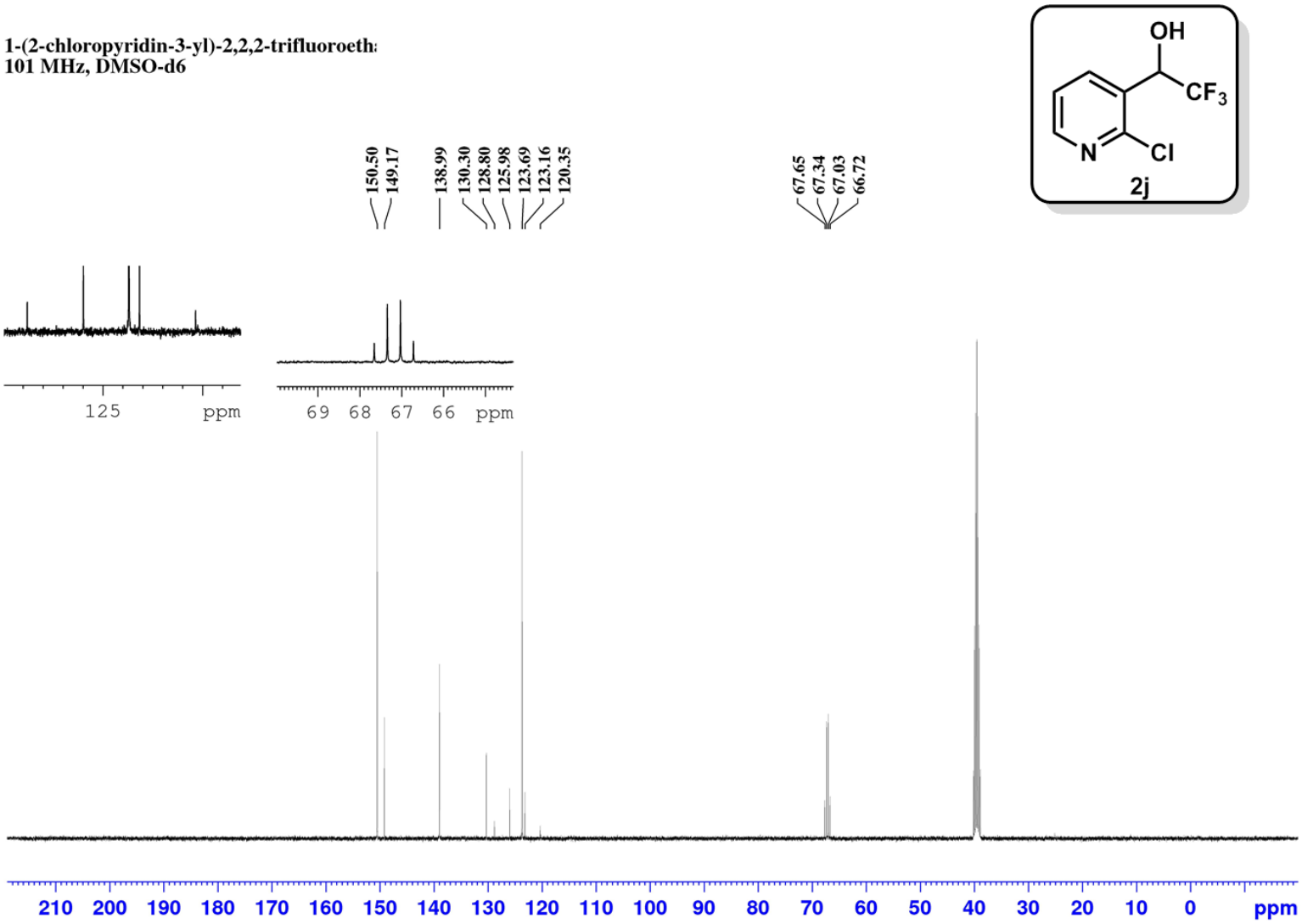
2,2,2-trifluoro-1-(2-nitrophenyl)ethanol
101 MHz, CDCl3



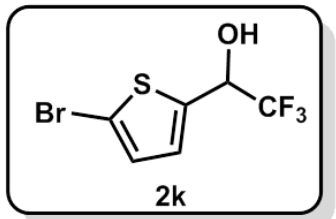
1-(2-bromo-4-fluorophenyl)-2,2,2-trifluoroethanol
101 MHz, CDCl3

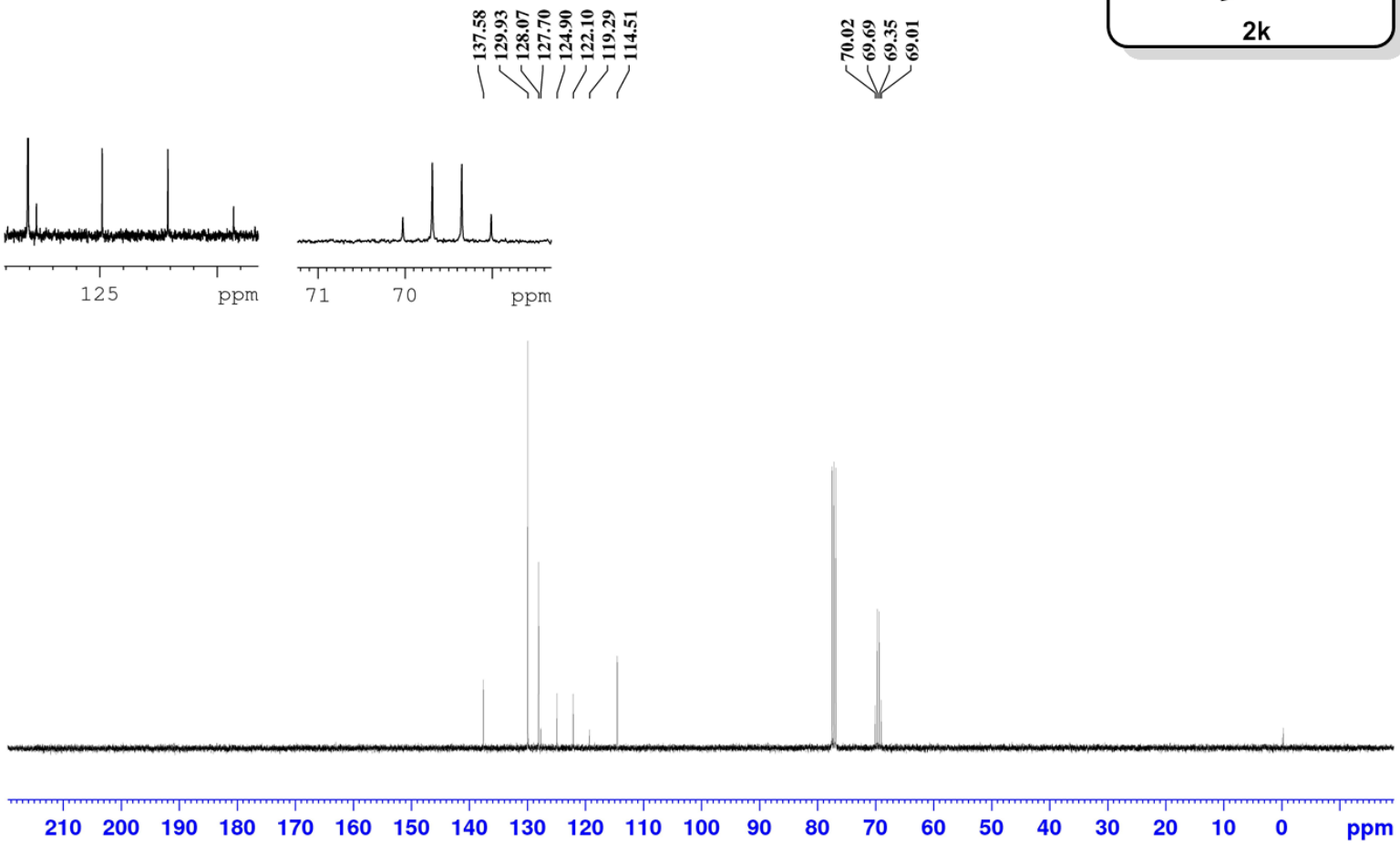




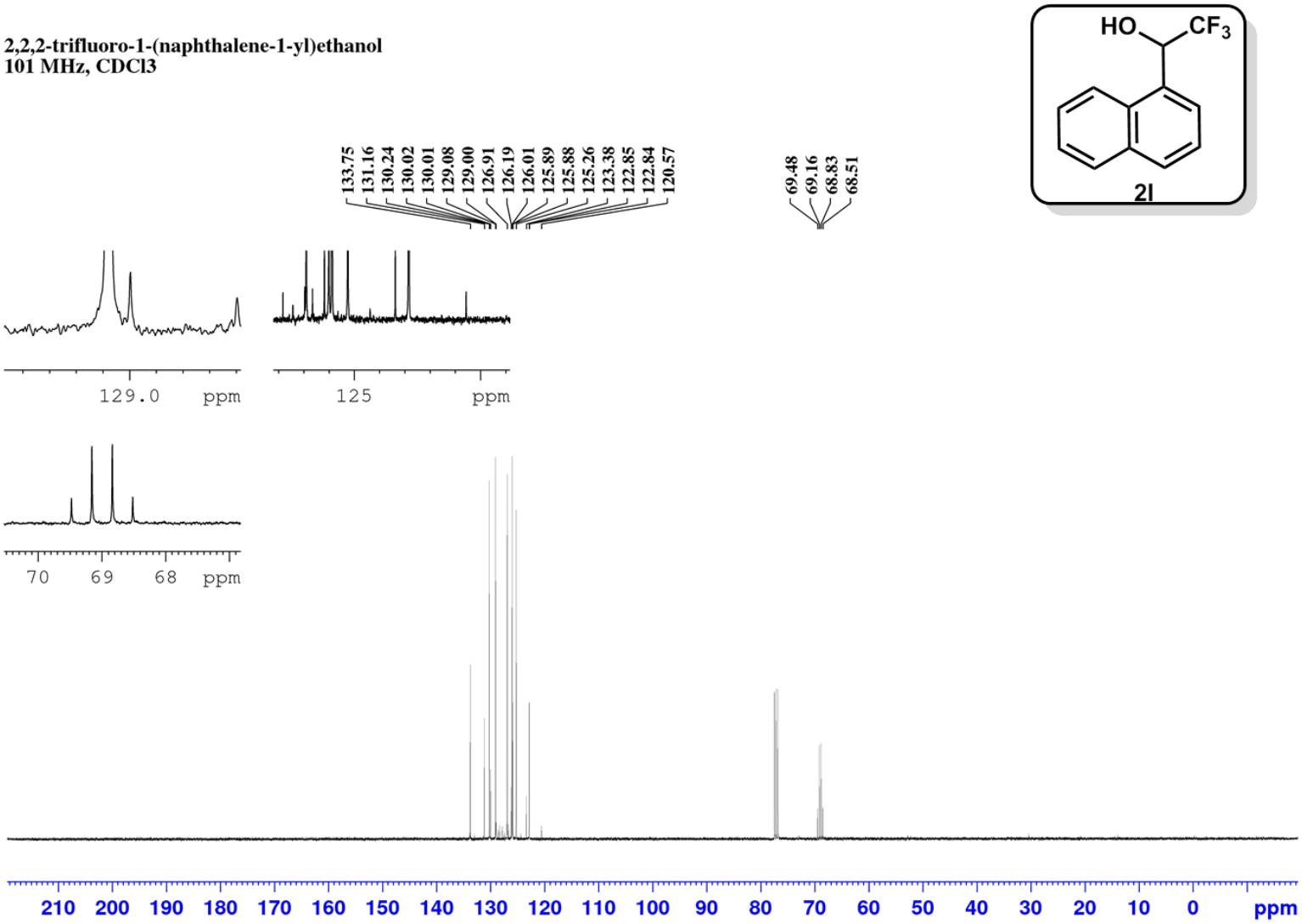

1-(2-chloropyridin-3-yl)-2,2,2-trifluoroeth
101 MHz, DMSO-d6
150.50
149.17
138.99
130.30
128.80
125.98
123.69
123.16
120.35
67.65
67.34
67.03
66.72
OH
CF3
N
Cl
2j
125
ppm
69
68
67
66
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

1-(5-bromothiphen-2-yl)-2,2,2-trifluoroethanol
101 MHz, CDCl3

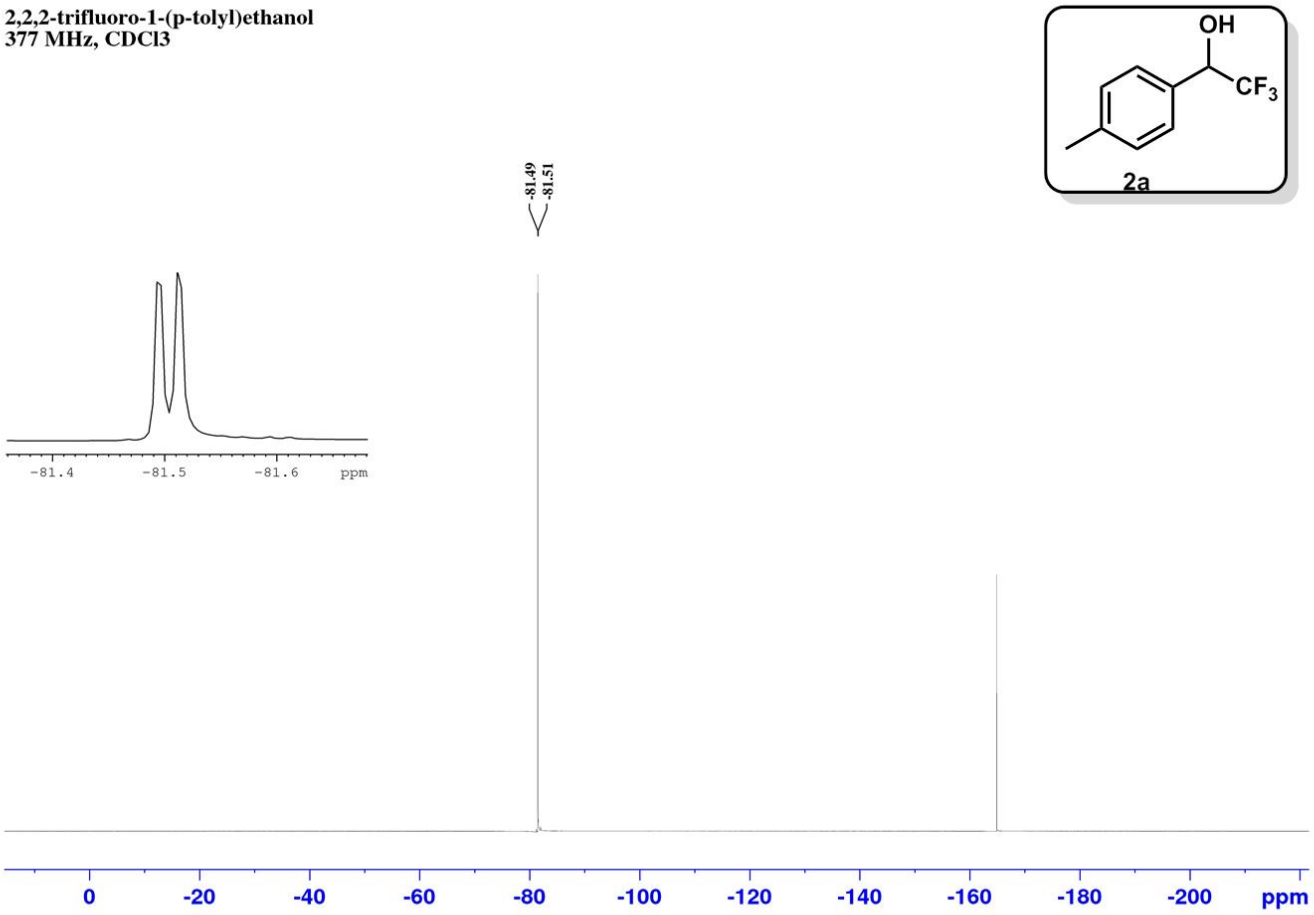




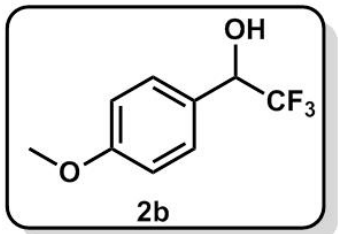
2,2,2-trifluoro-1-(naphthalene-1-yl)ethanol
101 MHz, CDCl3

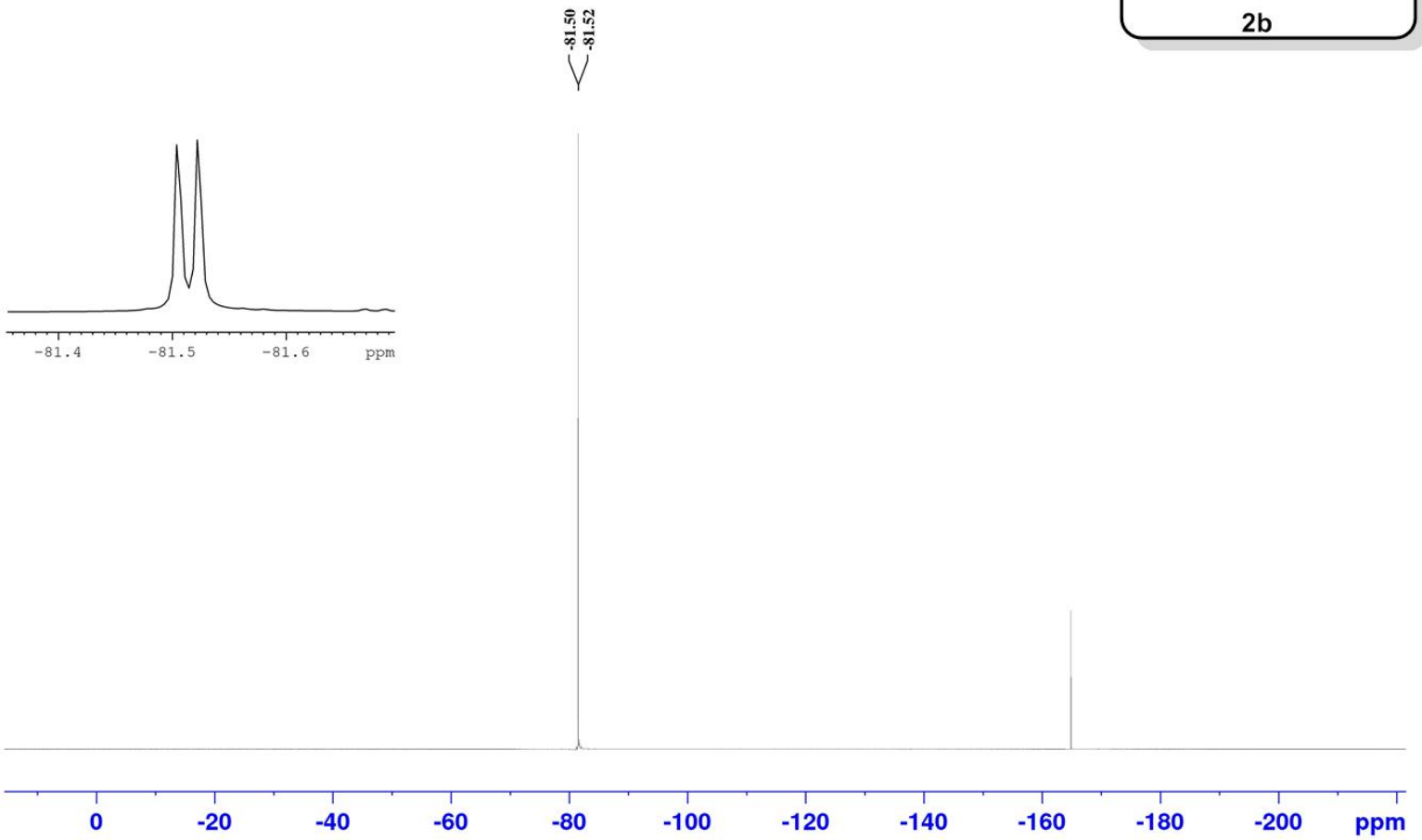


^{19}F NMR Spectra of Synthesized α-CF_3 alcohols

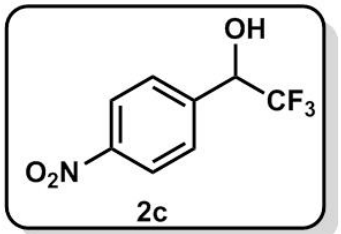


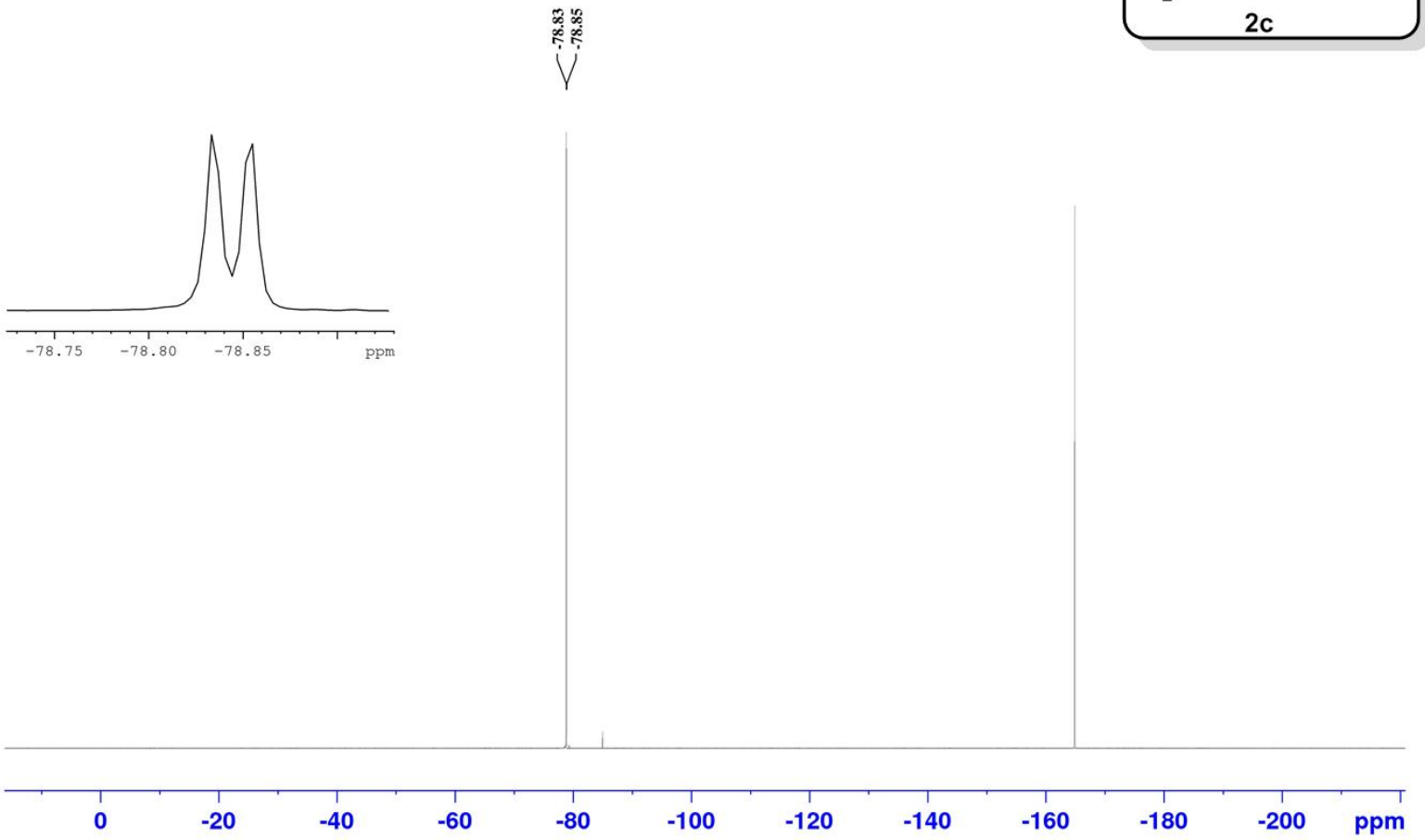
2,2,2-trifluoro-1-(4-methoxyphenyl)ethanol
377 MHz, CDCl3



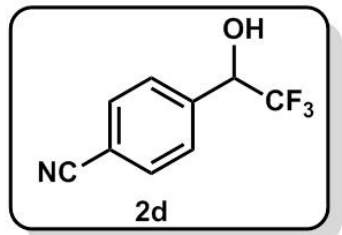


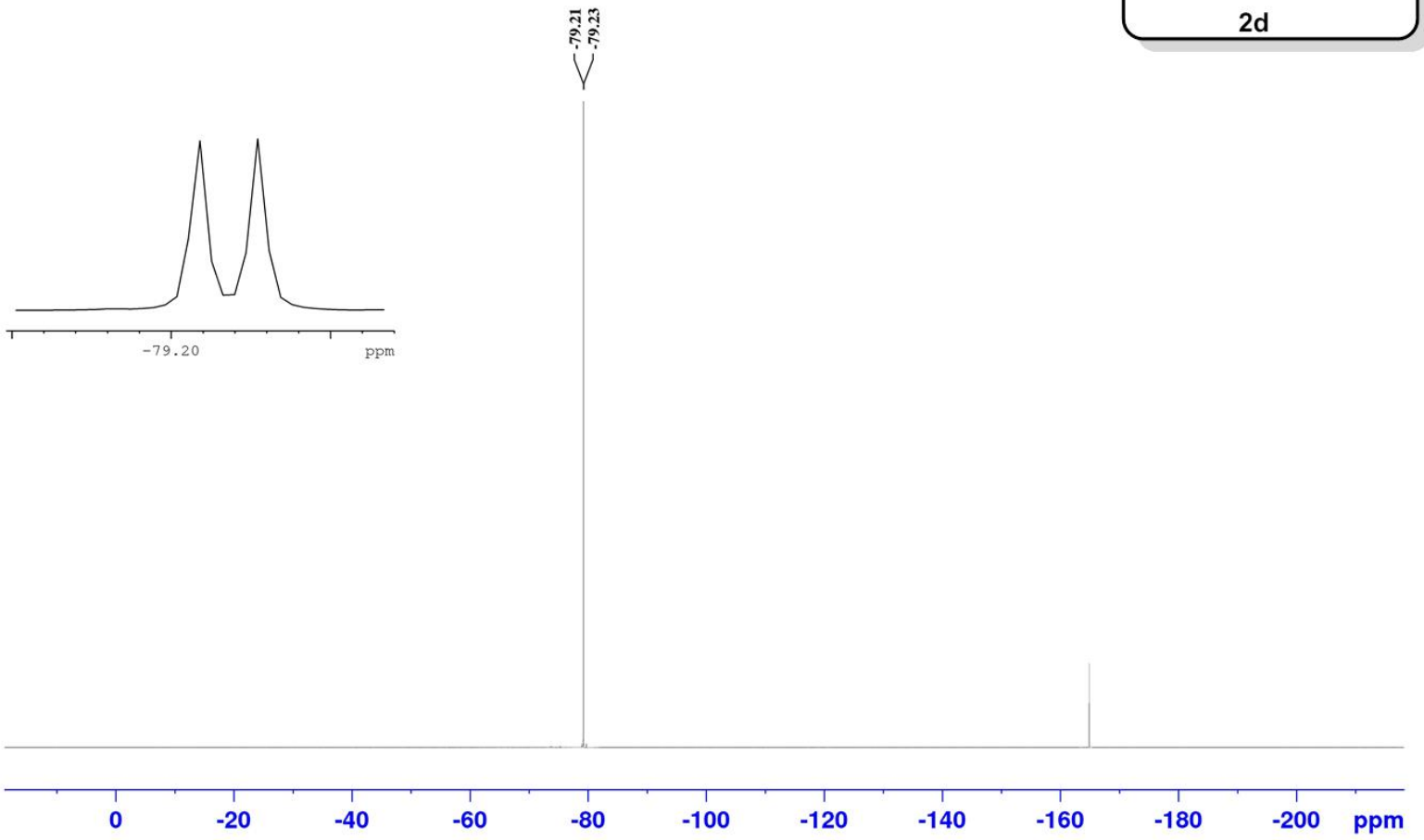
2,2,2-trifluoro-1-(4-nitrophenyl)ethanol
377 MHz, DMSO-d6



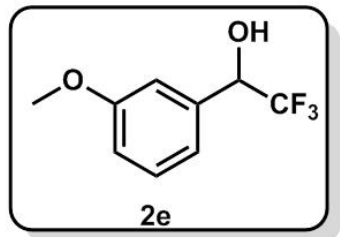


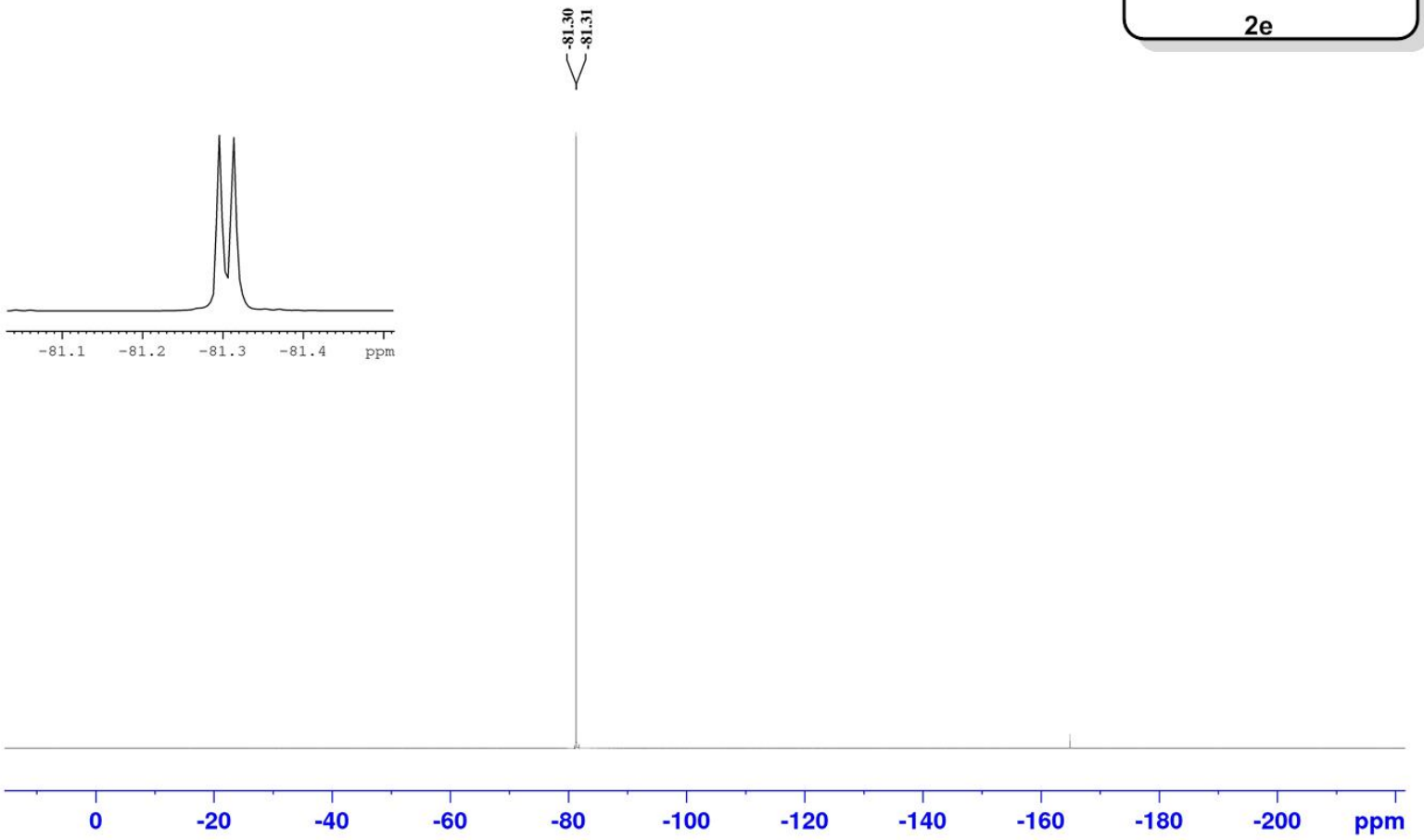
4-(2,2,2-trifluoro-1-hydroxyethyl)benzonitrile
377 MHz, MeOD



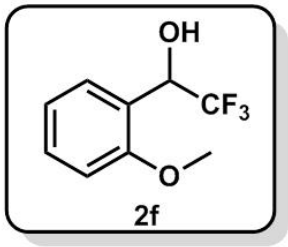


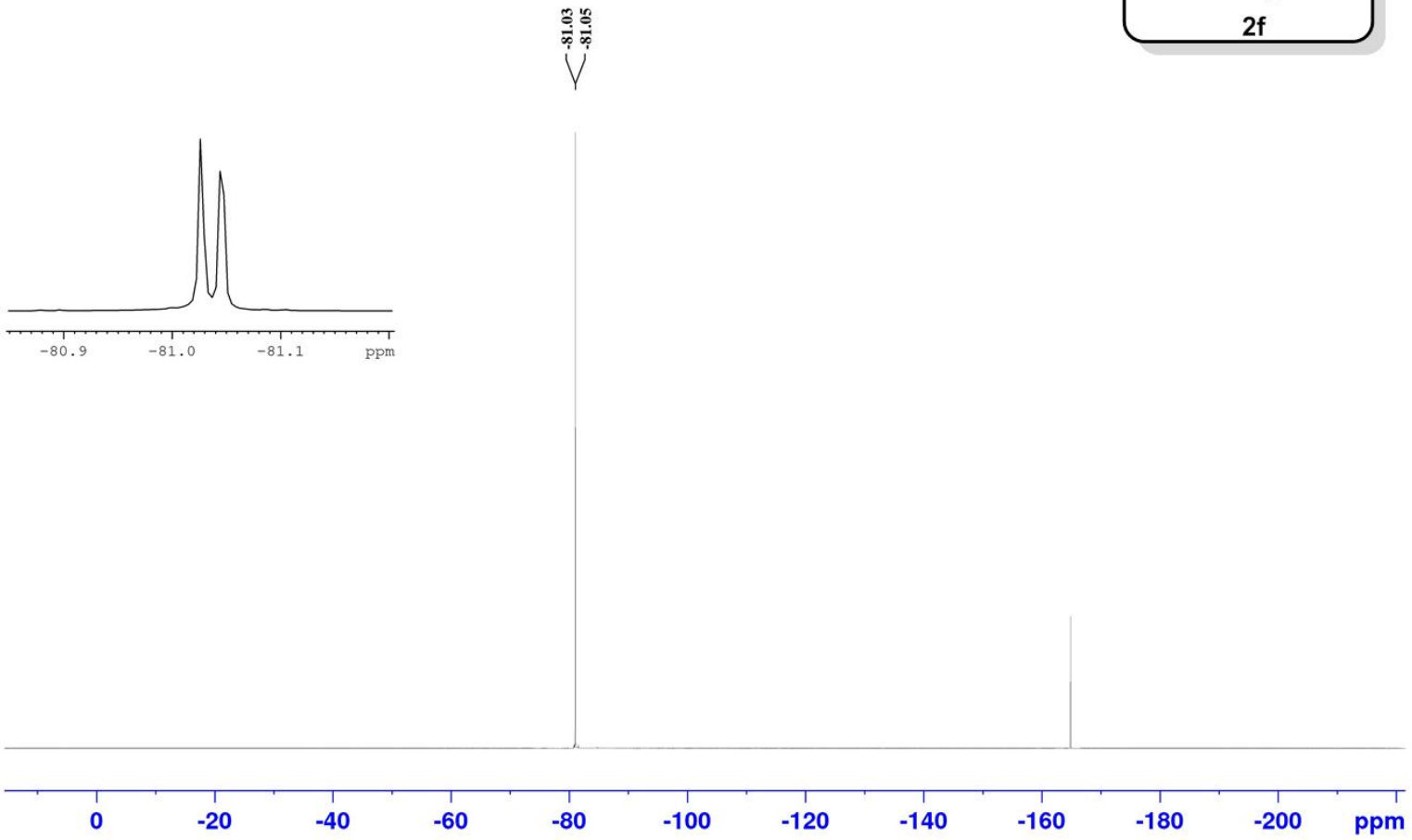
2,2,2-trifluoro-1-(3-methoxyphenyl)ethanol
377 MHz, CDCl3



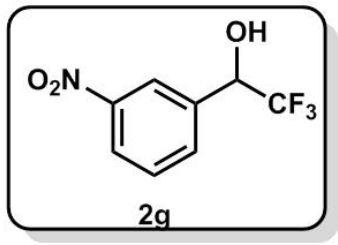


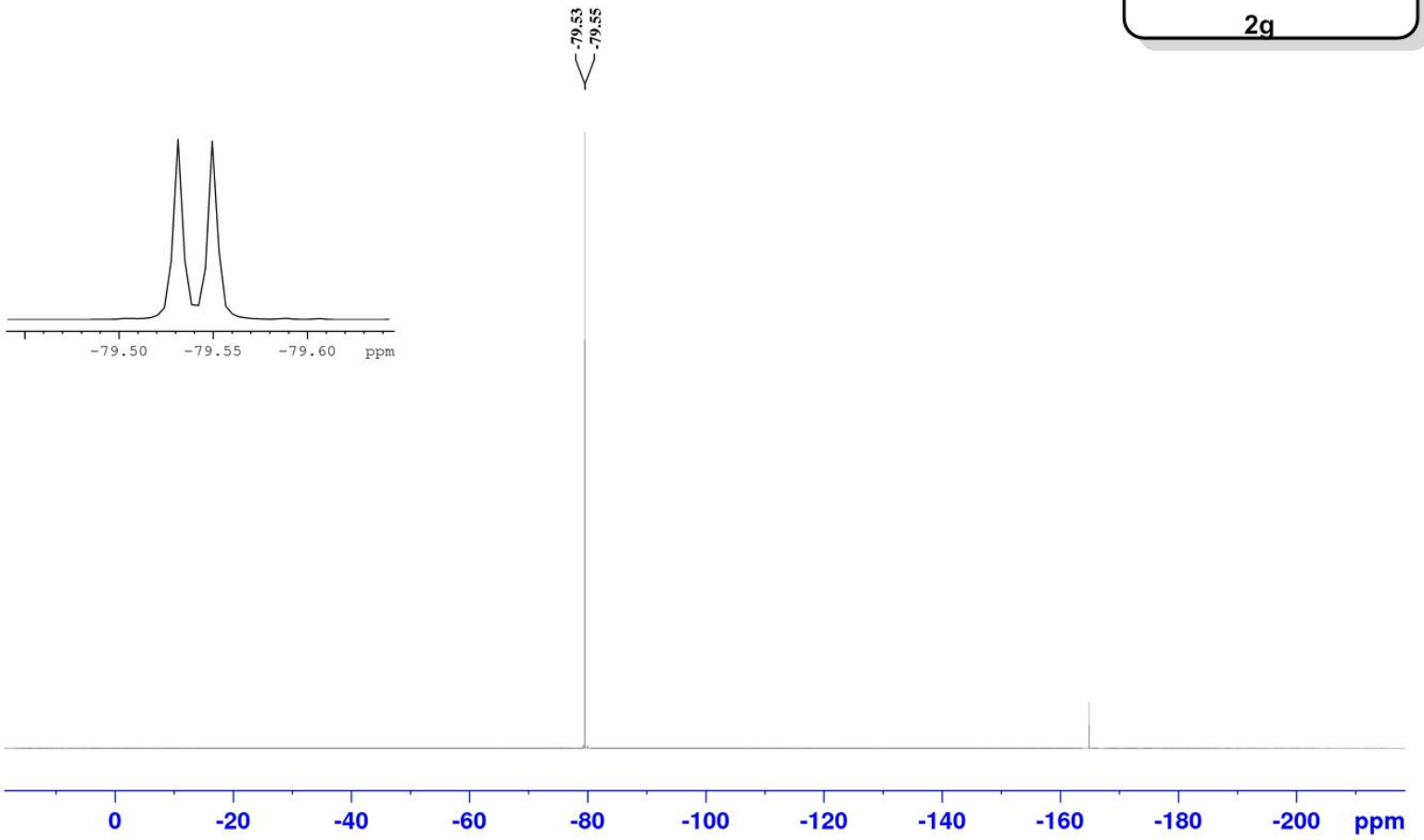
2,2,2-trifluoro-1-(2-methoxyphenyl)ethanol
377 MHz, CDCl3



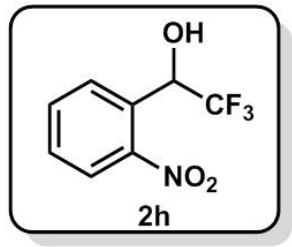


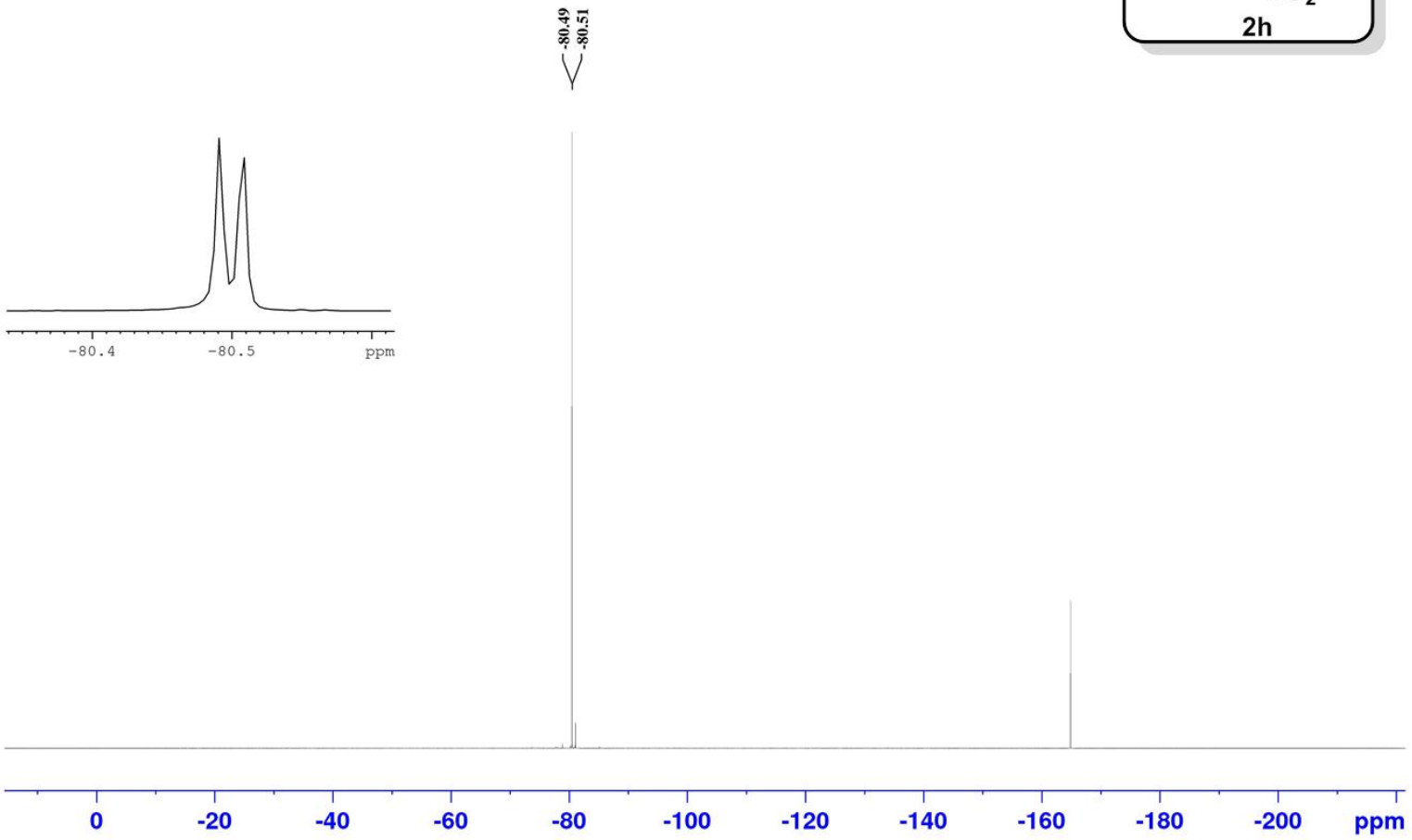
2,2,2-trifluoro-1-(3-nitrophenyl)ethanol
377 MHz, MeOD



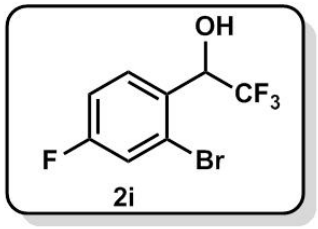


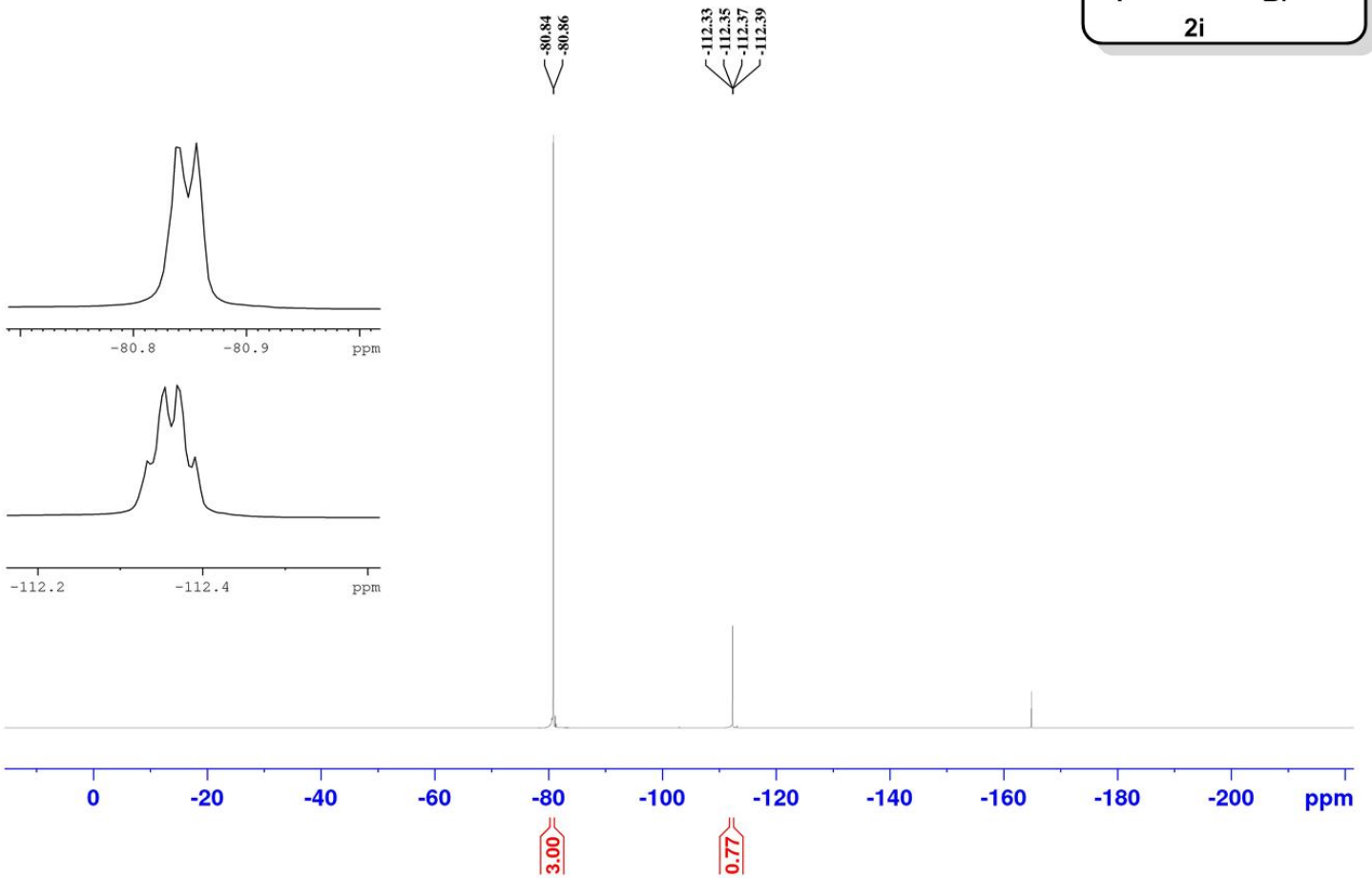
2,2,2-trifluoro-1-(2-nitrophenyl)ethanol
377 MHz, CDCl3



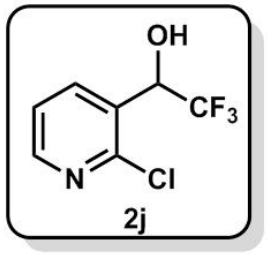


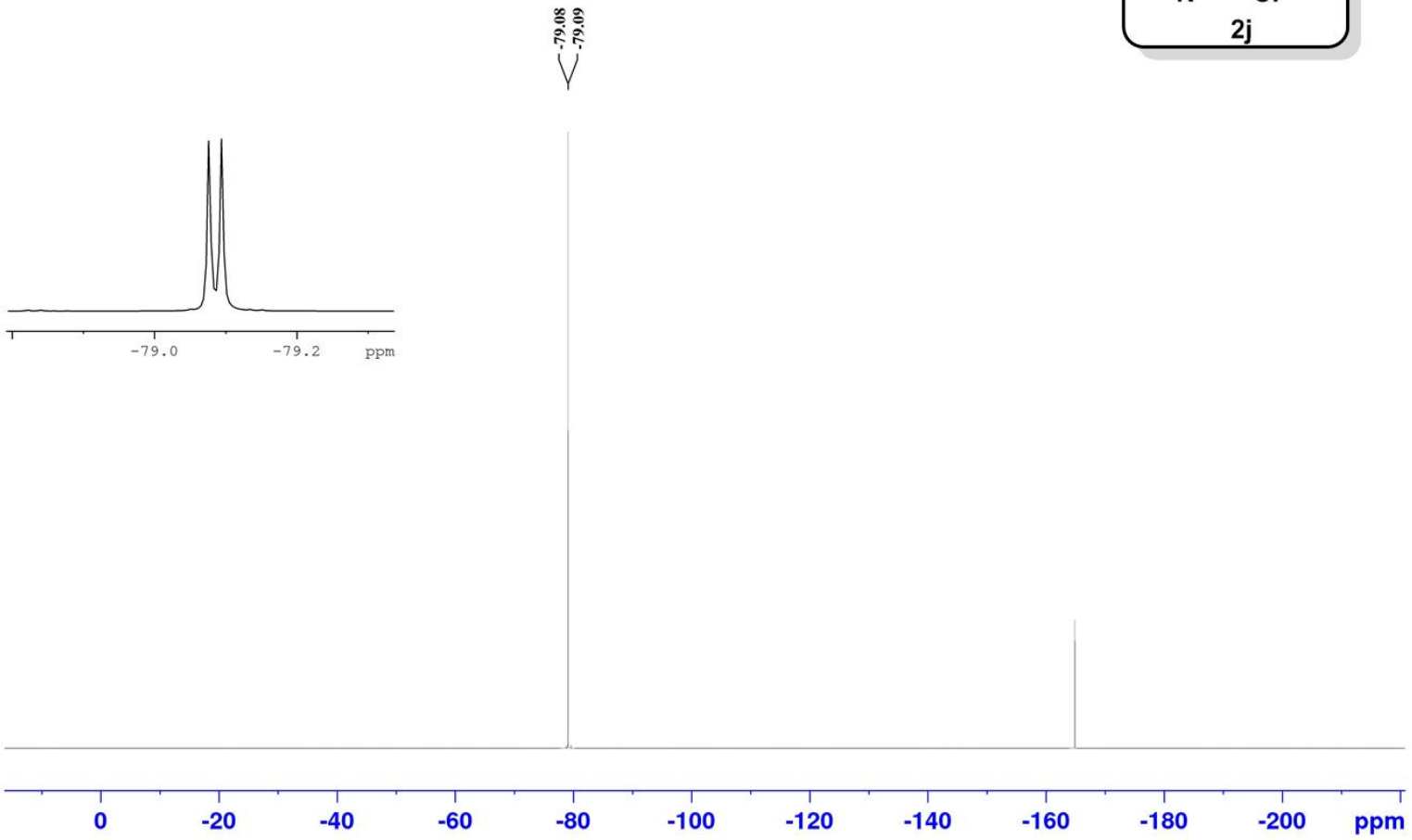
1-(2-bromo-4-fluorophenyl)-2,2,2-trifluoroethanol
377 MHz, CDCl3



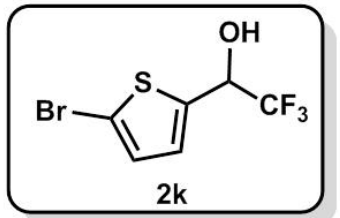


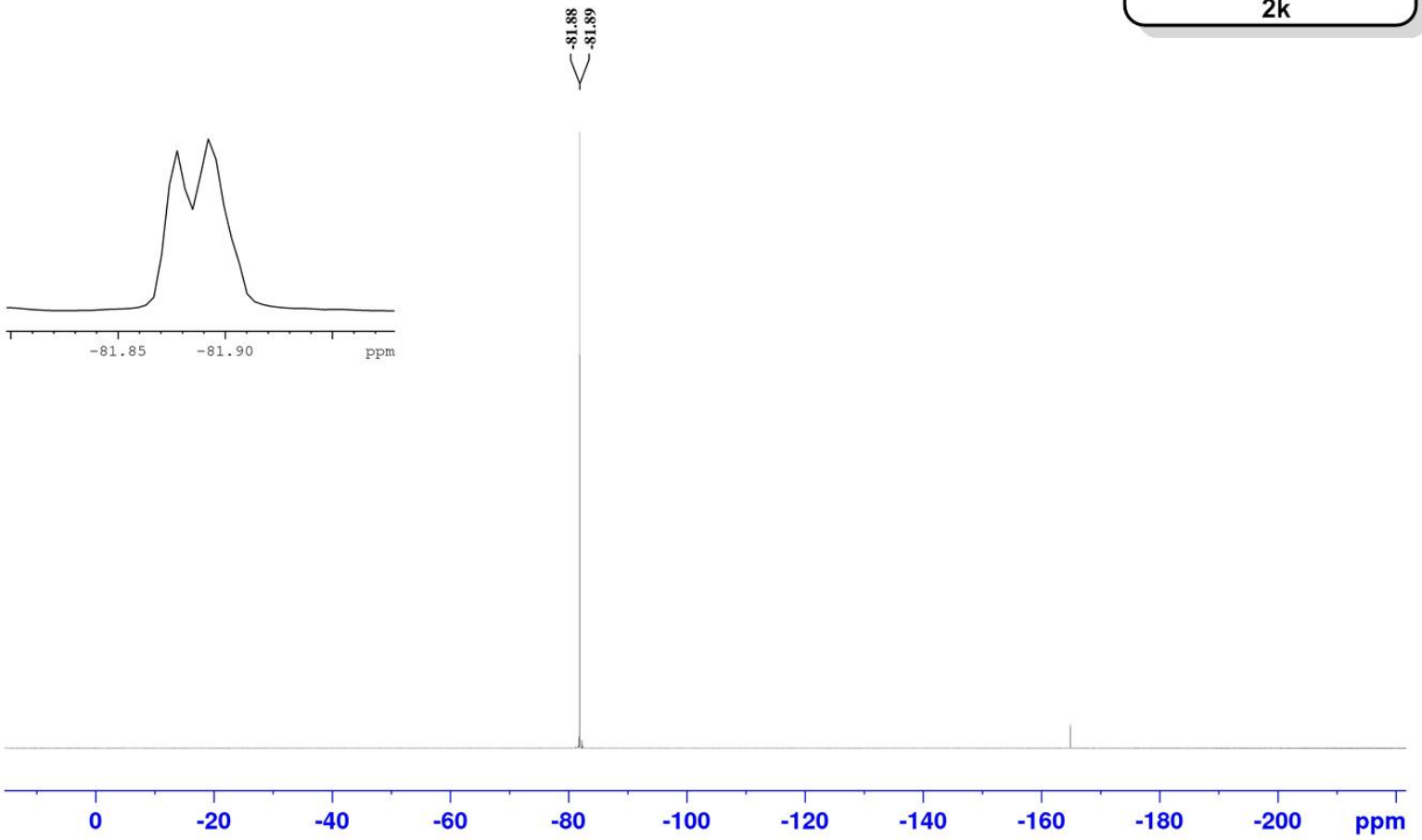
1-(2-chloropyridin-3-yl)-2,2,2-trifluoroethanol
377 MHz, DMSO-d6



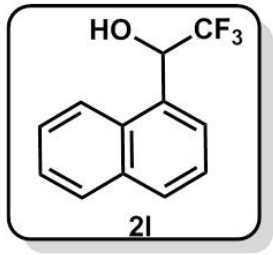


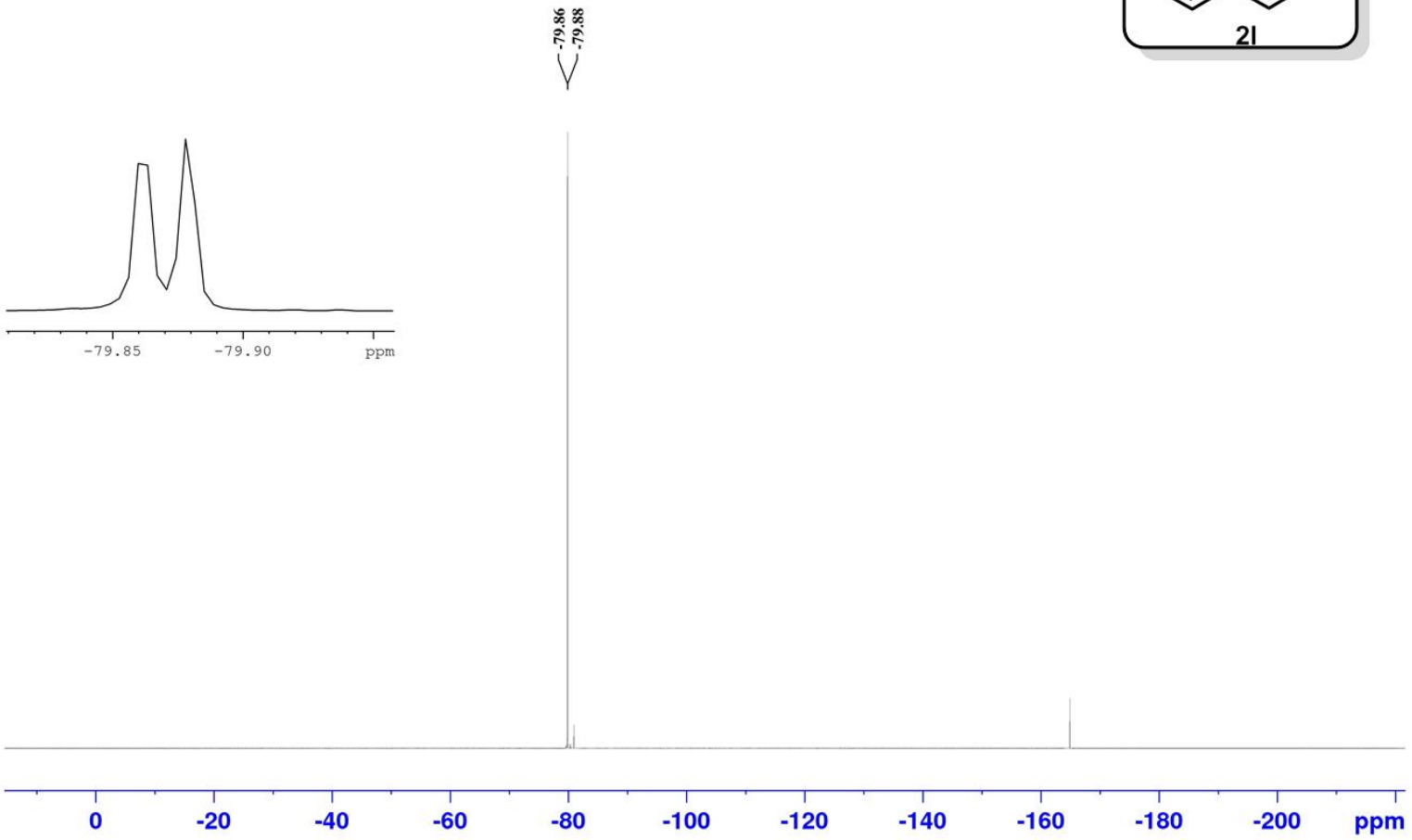
1-(5-bromothiophen-2-yl)-2,2,2-trifluoroethanol
377 MHz, CDCl3



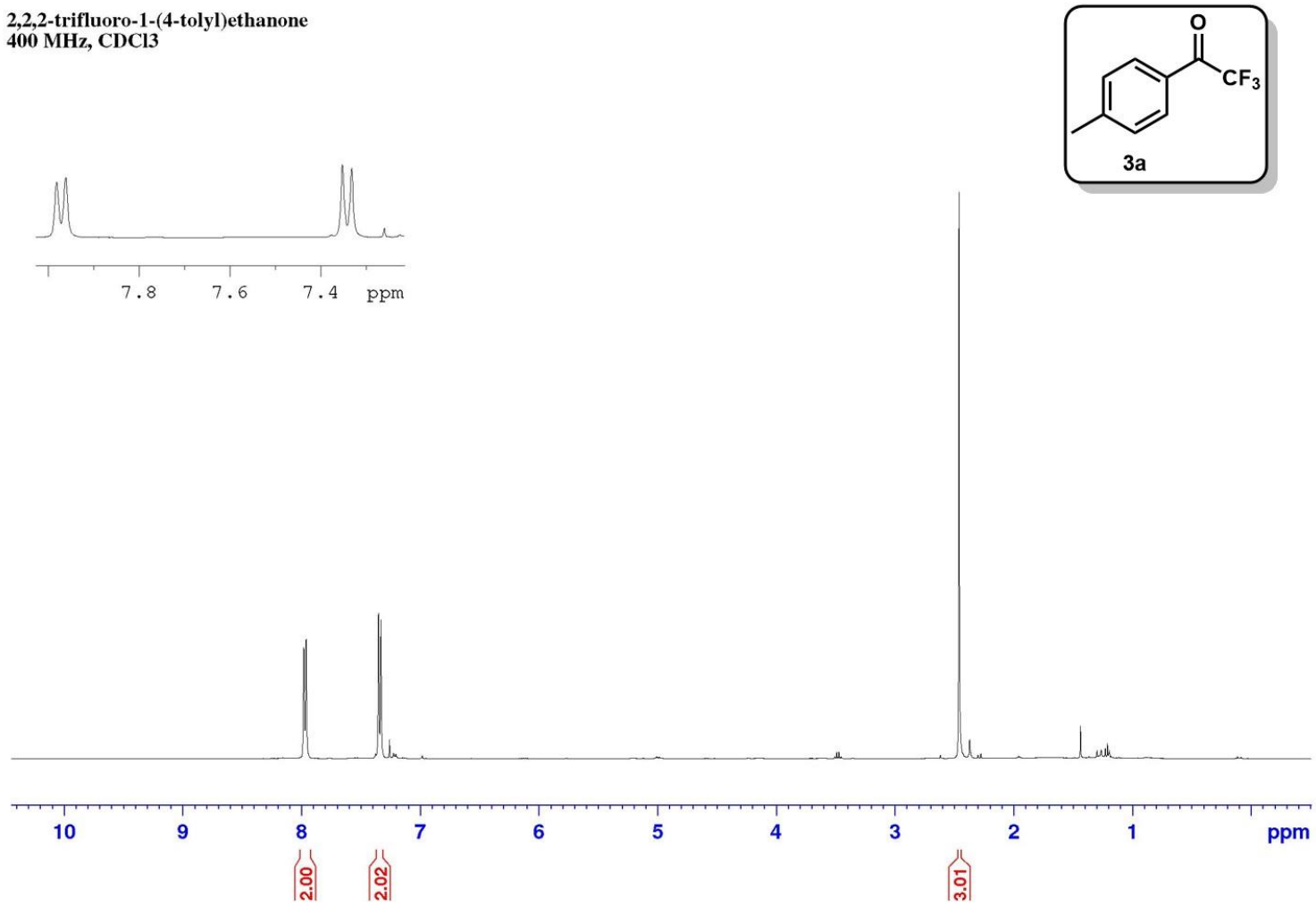


2,2,2-trifluoro-1-(naphthalene-1-yl)ethanol
377 MHz, CDCl3

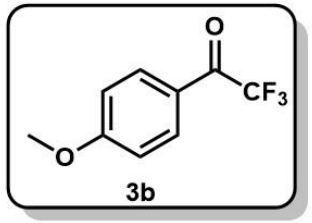


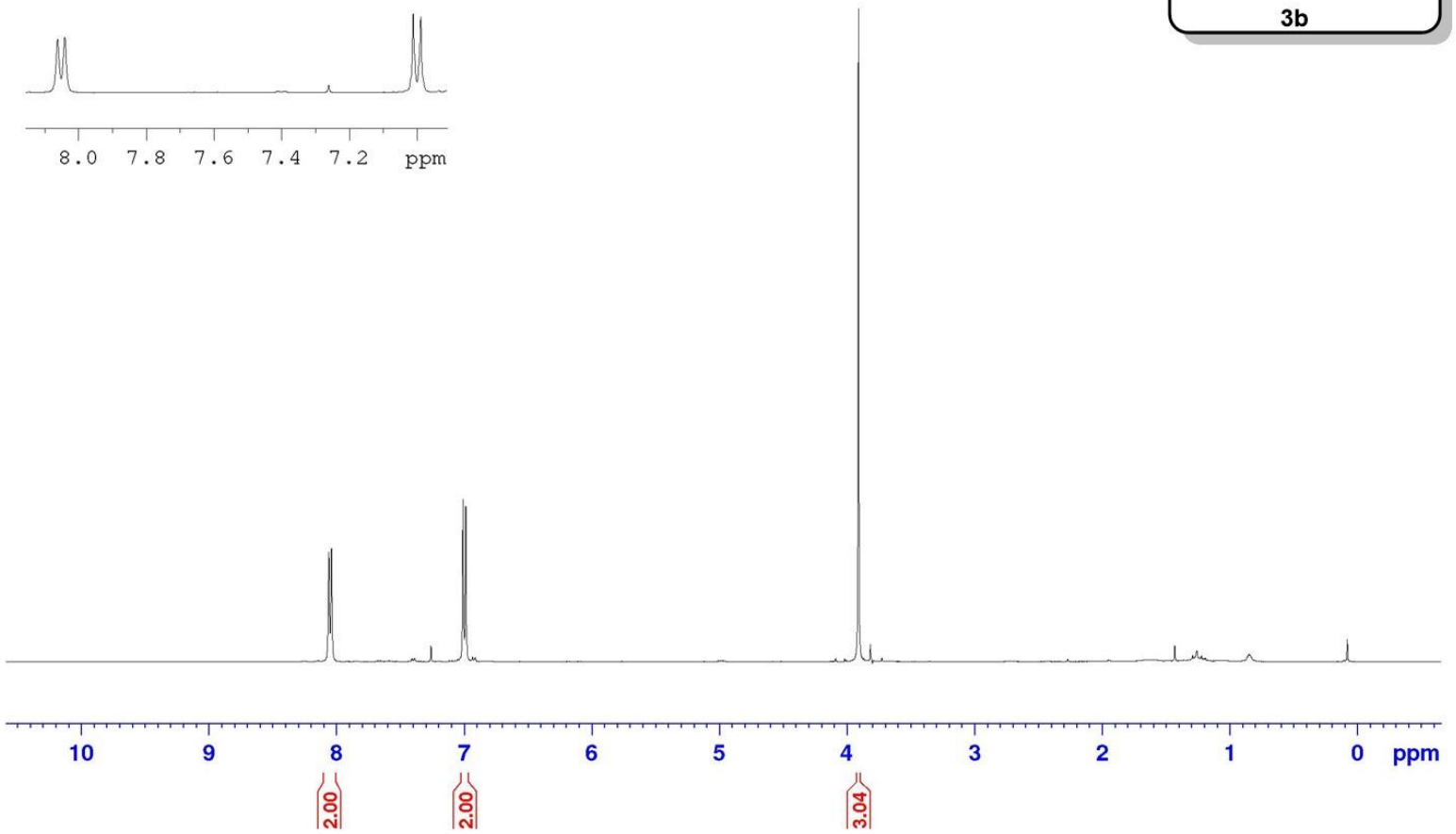


^{1}H NMR Spectra of Synthesized Trifluoromethyl Ketones

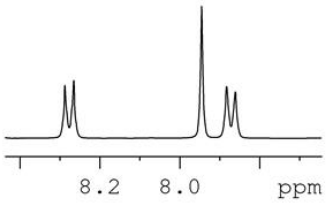


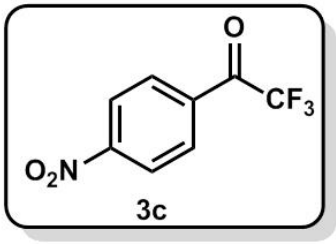
2,2,2-trifluoro-1-(4-methoxyphenyl)ethanone
400 MHz, CDCl3



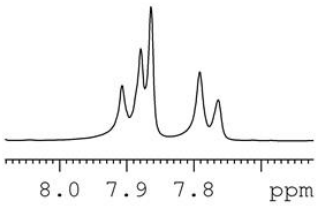


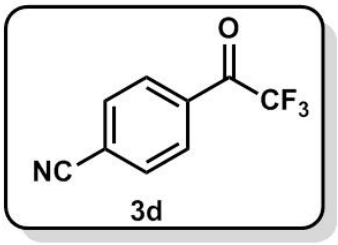
2,2,2-trifluoro-1-(4-nitrophenyl)ethanone (Hydrate)
400 MHz, DMSO-d6

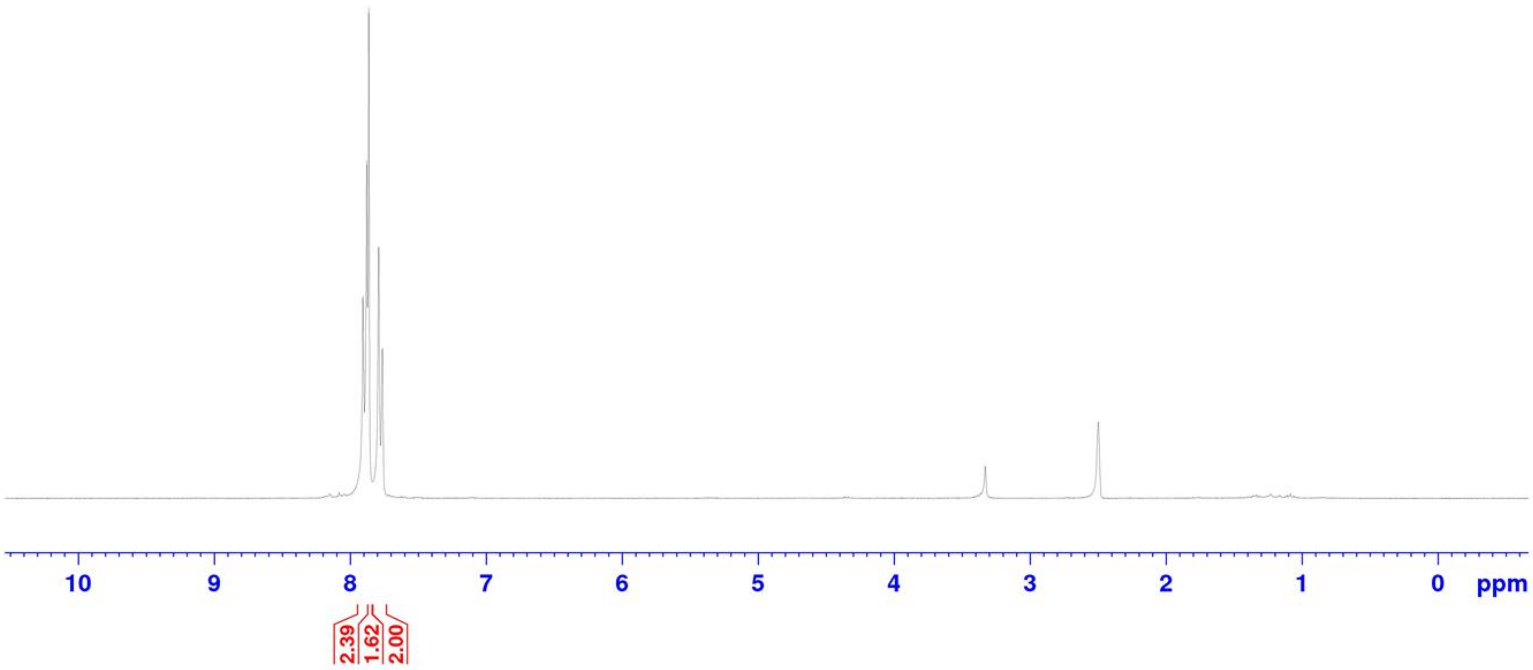




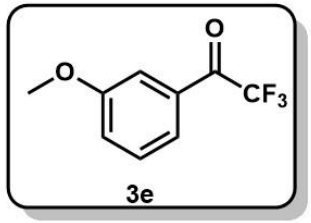
4-(2,2,2-trifluoroacetyl)benzonitrile
(Hydrate)
300 MHz, DMSO-d6

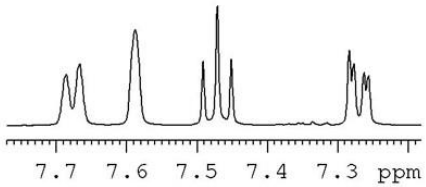




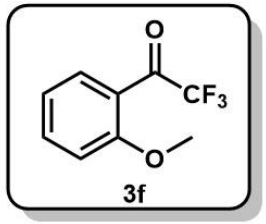


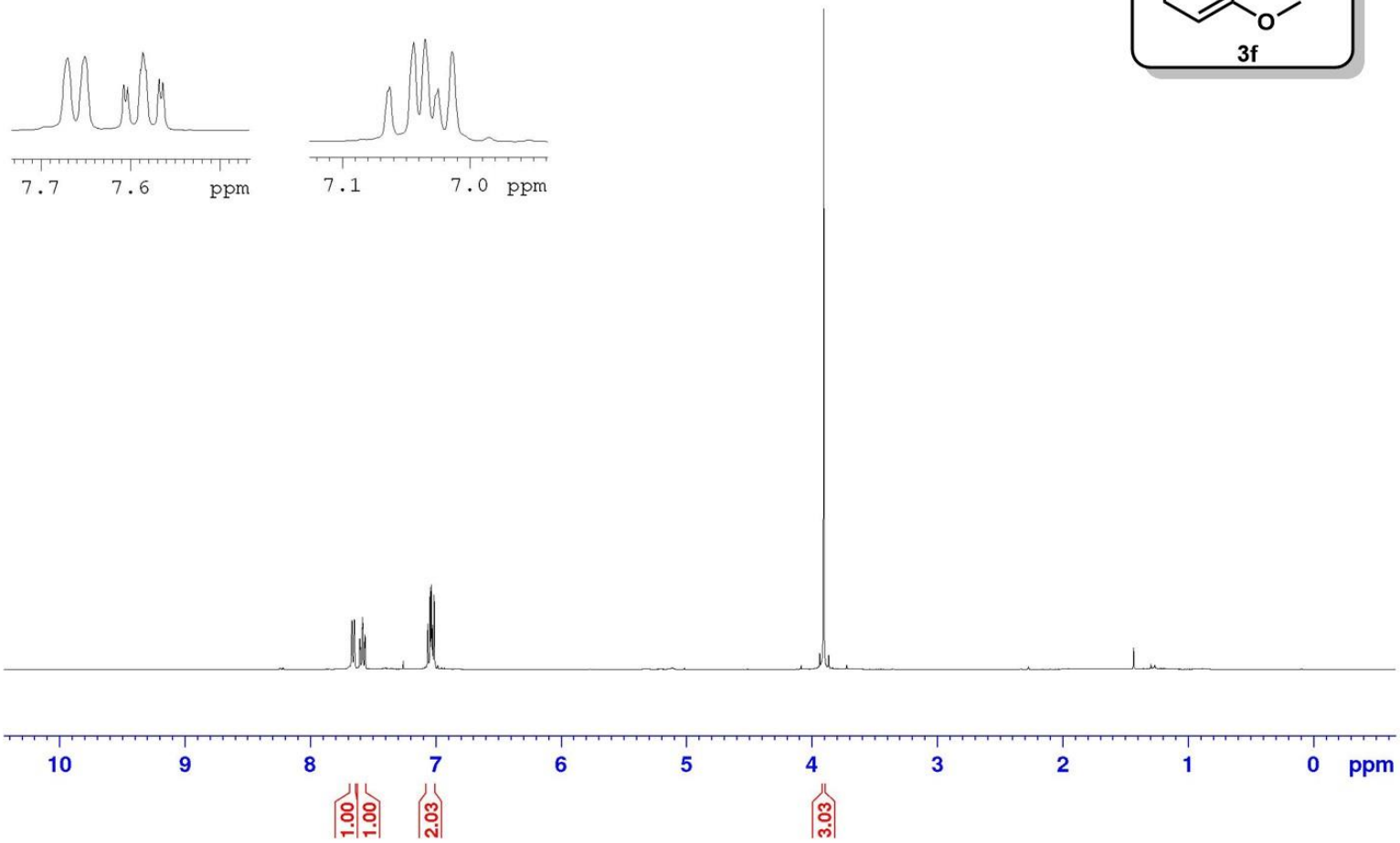
2,2,2-trifluoro-1-(3-methoxyphenyl)ethanone
400 MHz, CDCl3



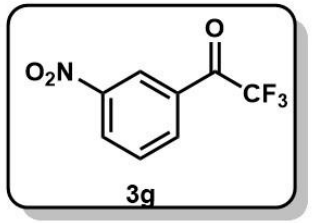


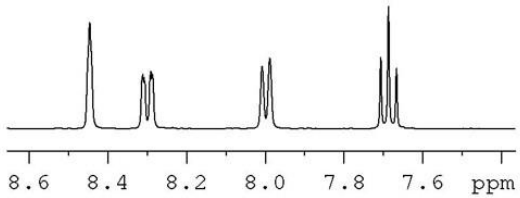
2,2,2-trifluoro-1-(2-methoxyphenyl)ethanone
400 MHz, CDCl3



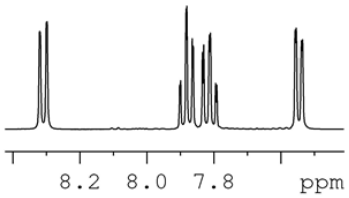


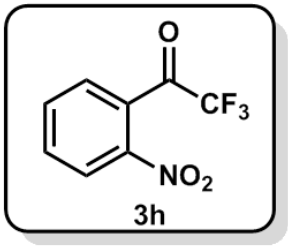
2,2,2-trifluoro-1-(3-nitrophenyl)ethanone
400 MHz, MeOD

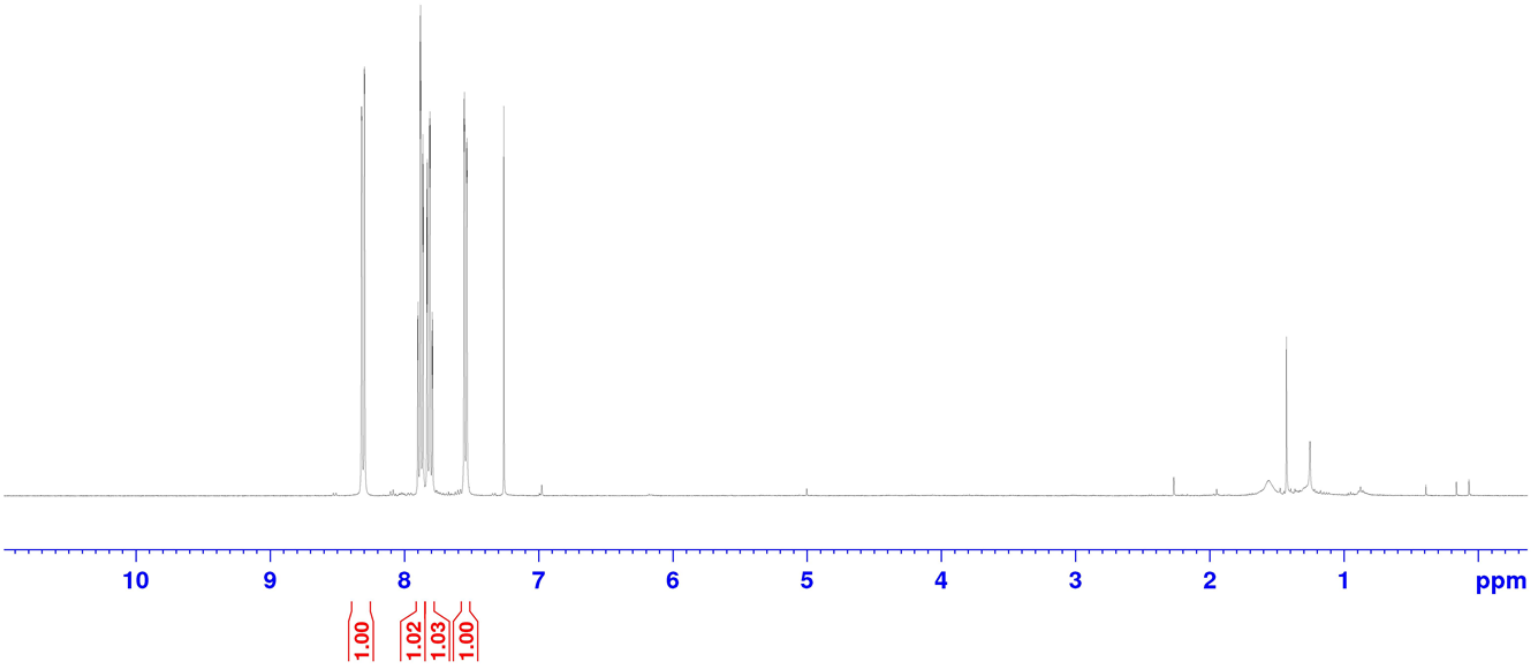




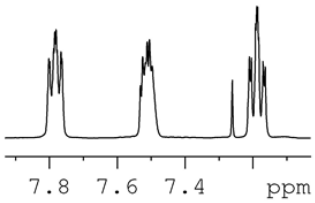
2,2,2-trifluoro-1-(2-nitrophenyl)ethanone
400 MHz, CDCl3

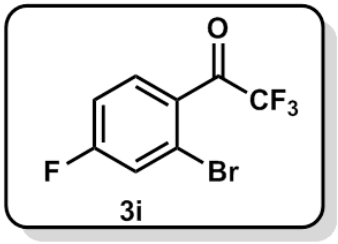


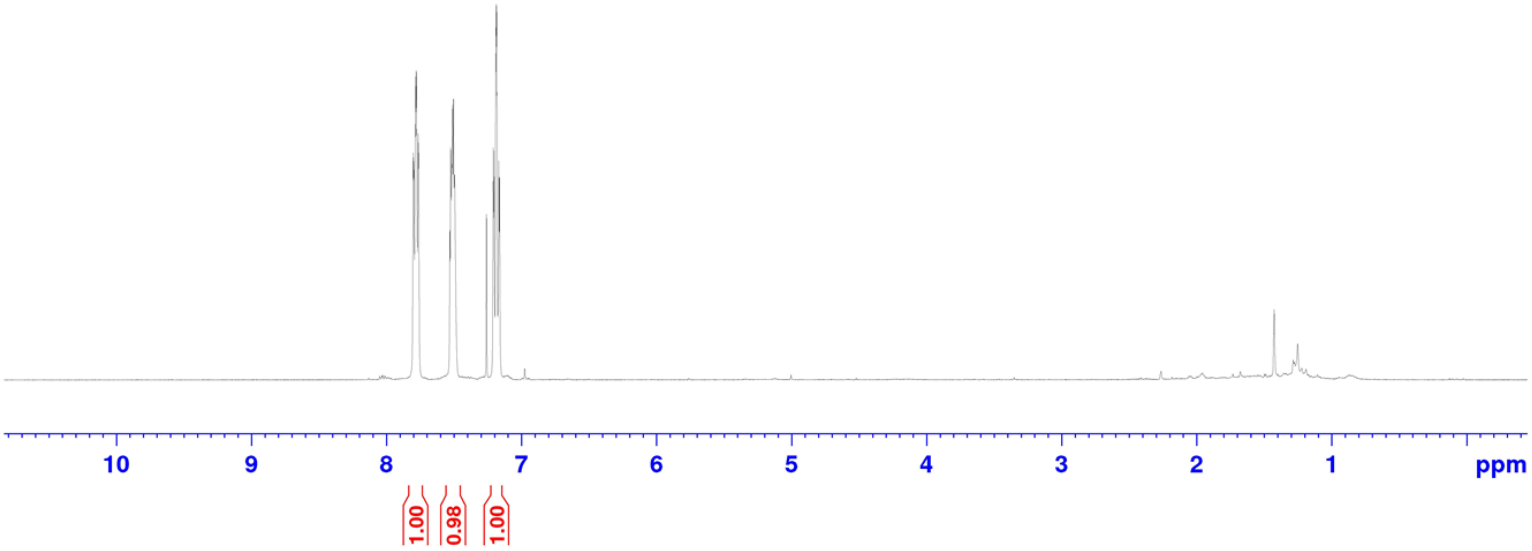




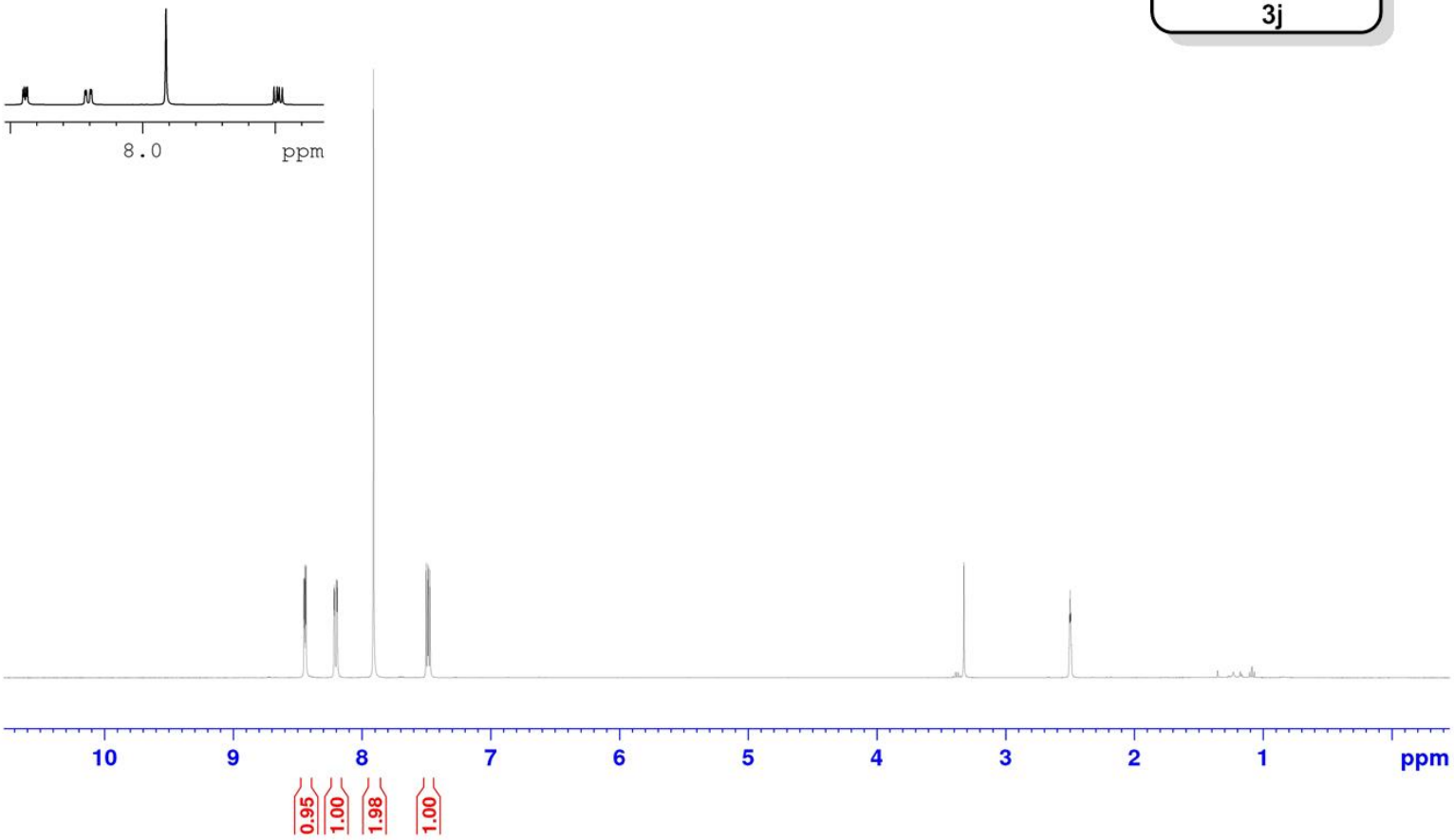
1-(2-bromo-4-fluorophenyl)-2,2,2-trifluoroethanone
400 MHz, CDCl3

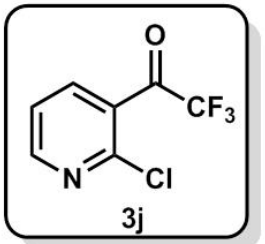




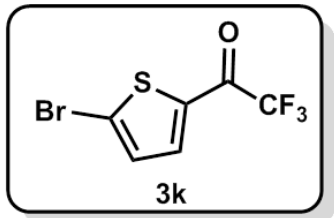


1-(2-chloropyridin-3-yl)-2,2,2-trifluoroethanone (Hydrate)
400 MHz, DMSO-d6

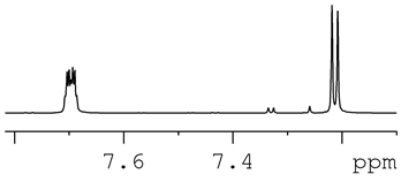


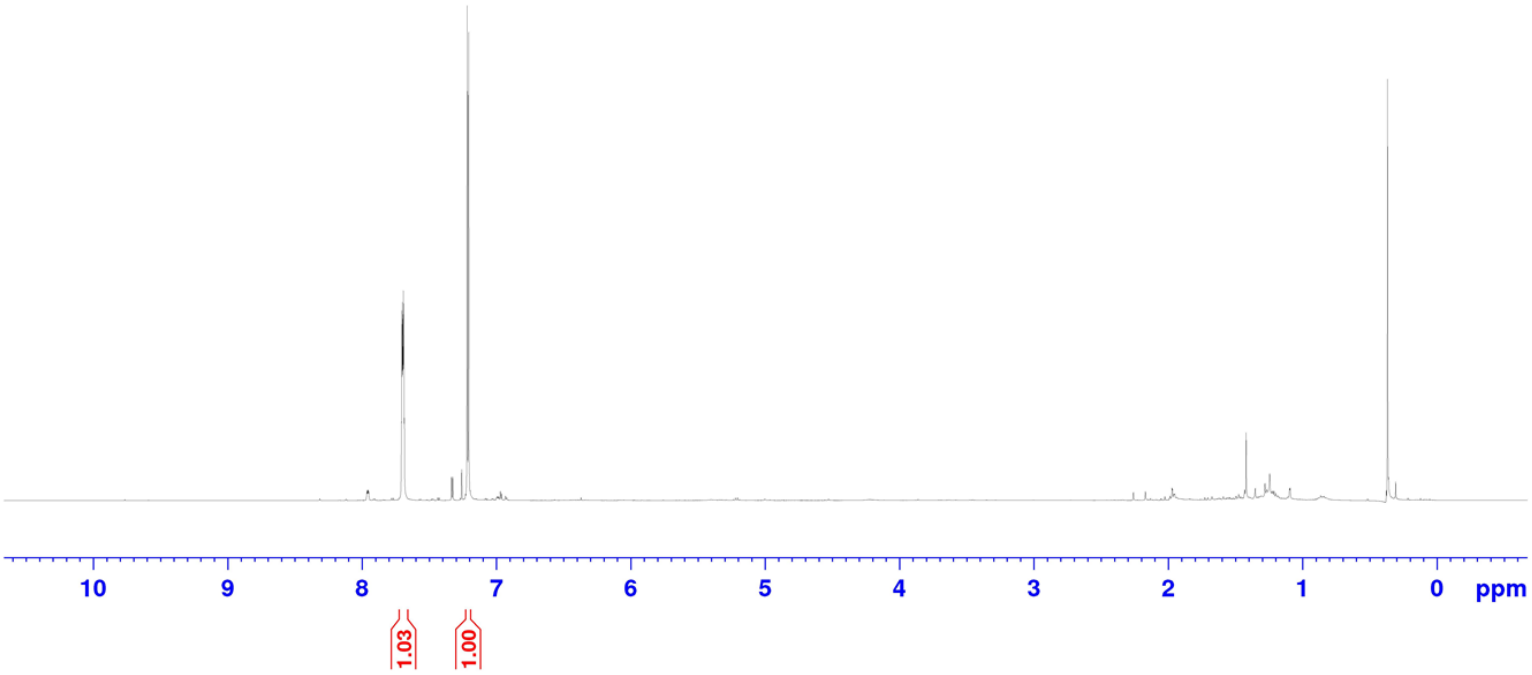


1-(5-bromothiophen-2-yl)-2,2,2-trifluoroethar
400 MHz, CDCl3

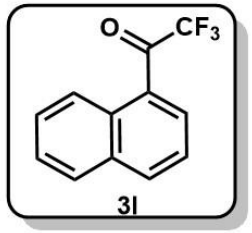


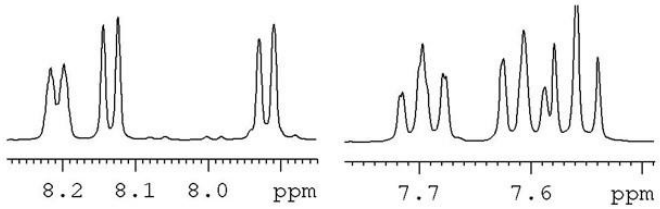
3k

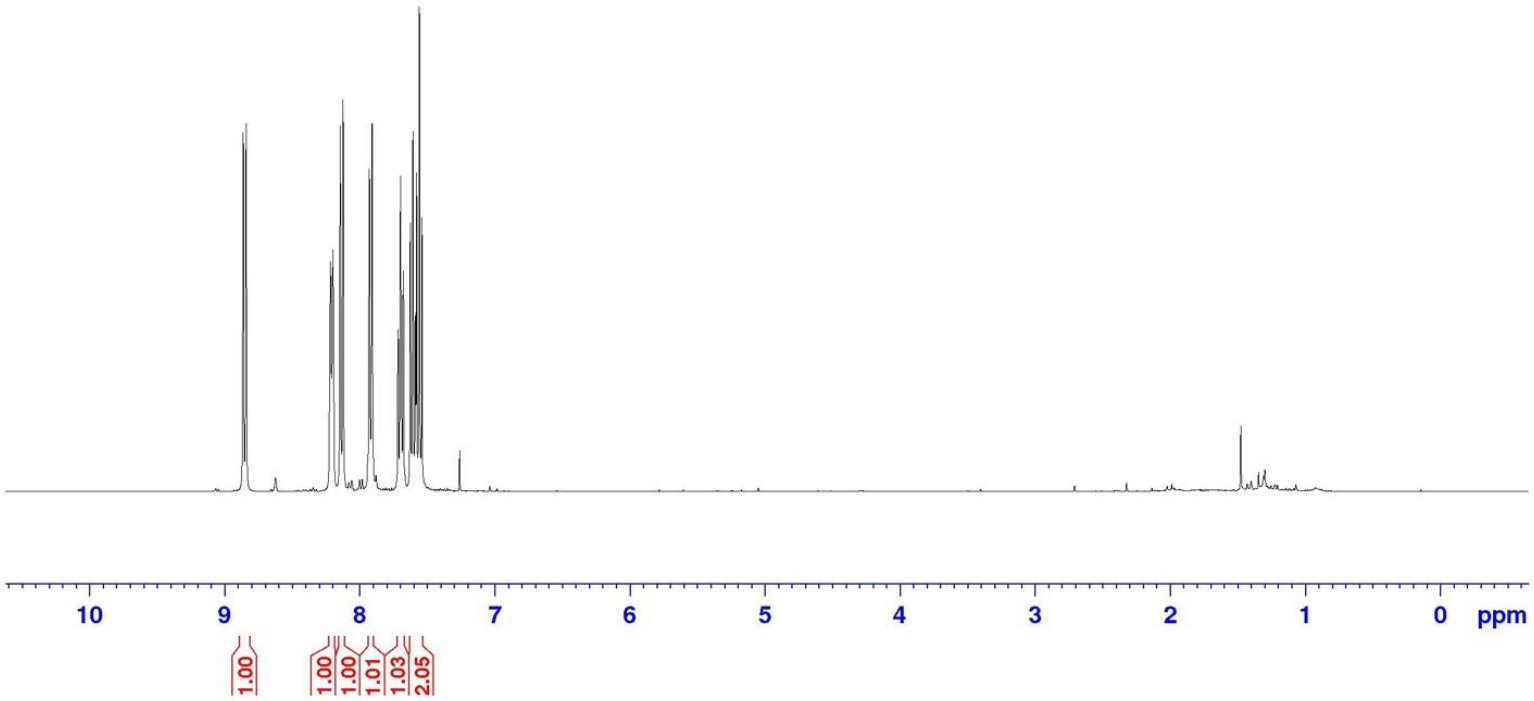




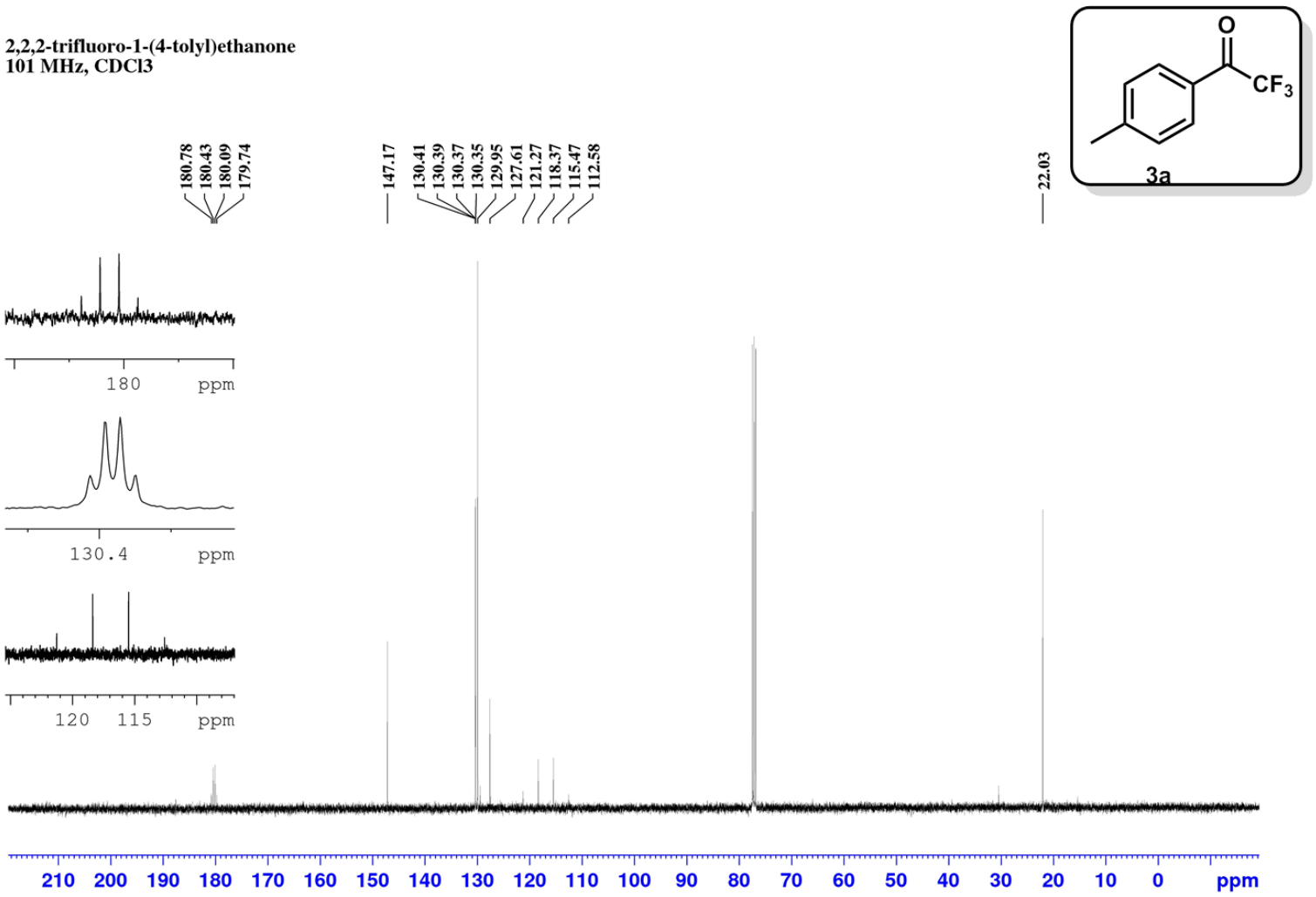
2,2,2-trifluoro-1-(naphthalen-1-yl)ethanone
400 MHz, CDCl3



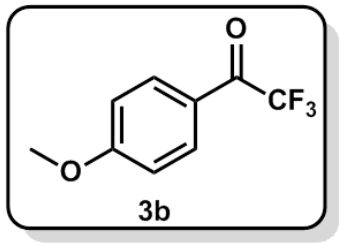


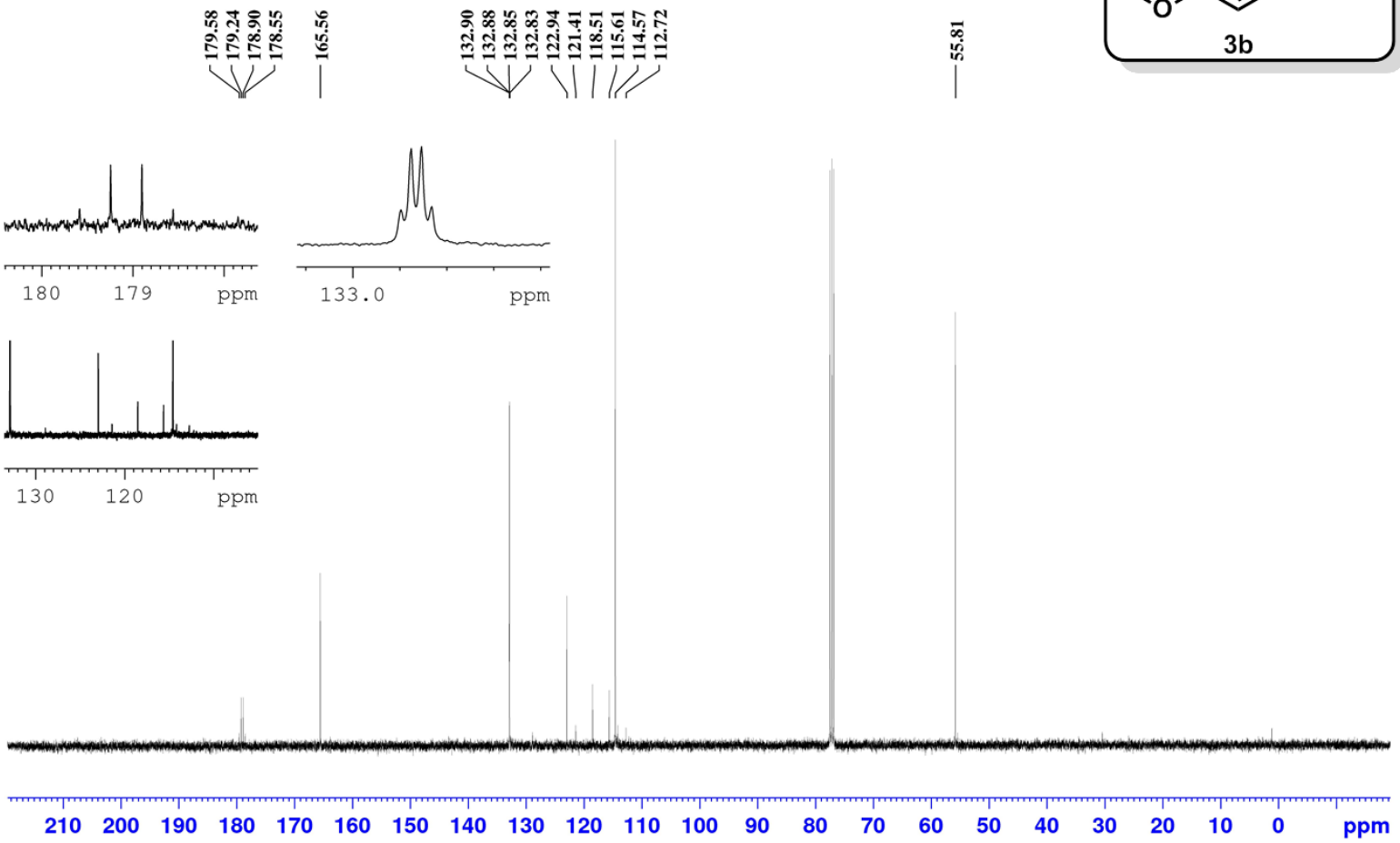


^{13}C NMR Spectra of Synthesized Trifluoromethyl Ketones

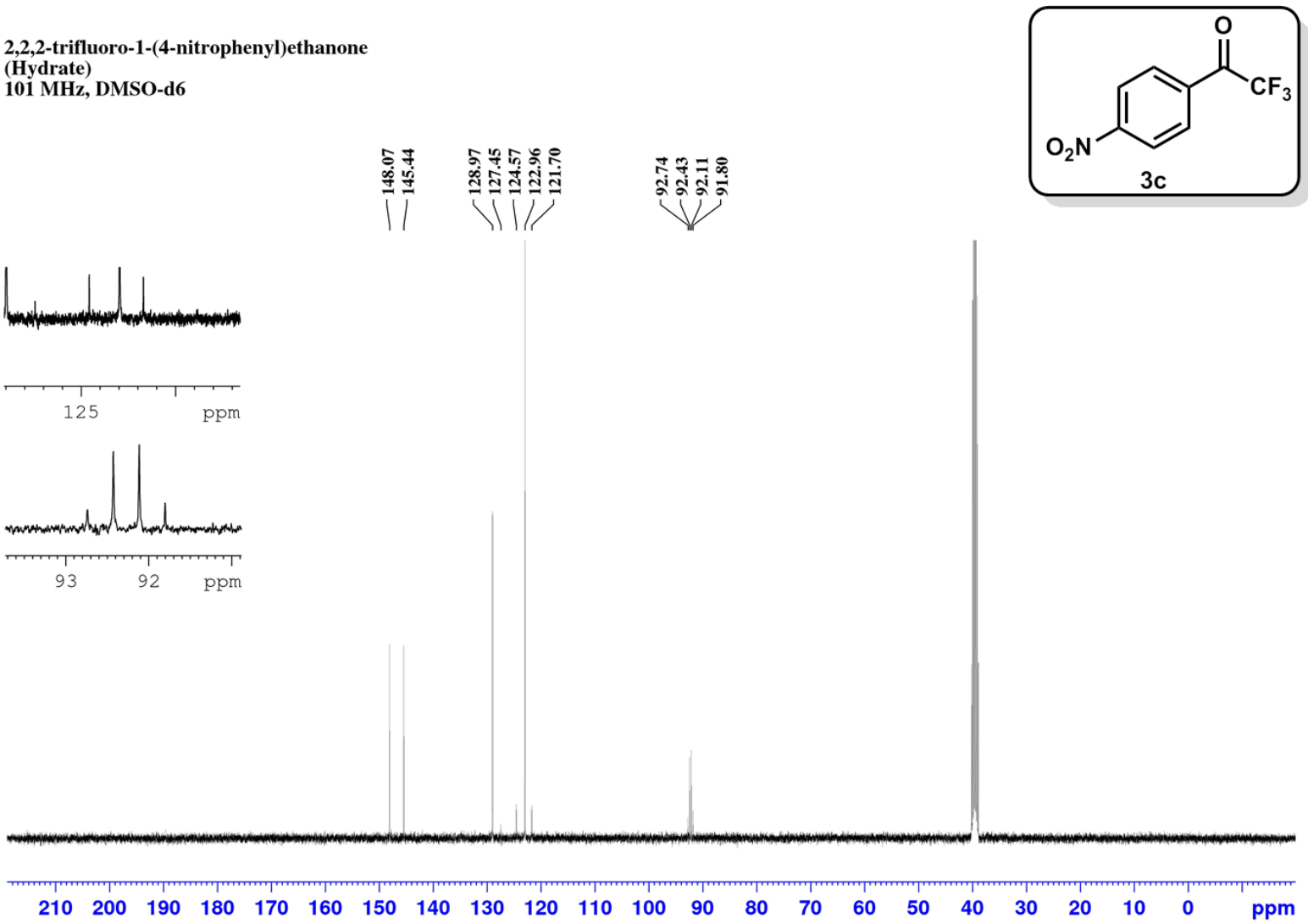


2,2,2-trifluoro-1-(4-methoxyphenyl)ethanone
101 MHz, CDCl3

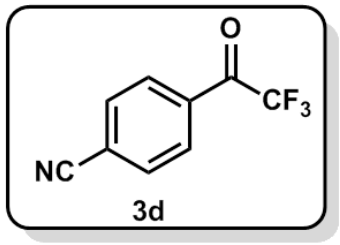


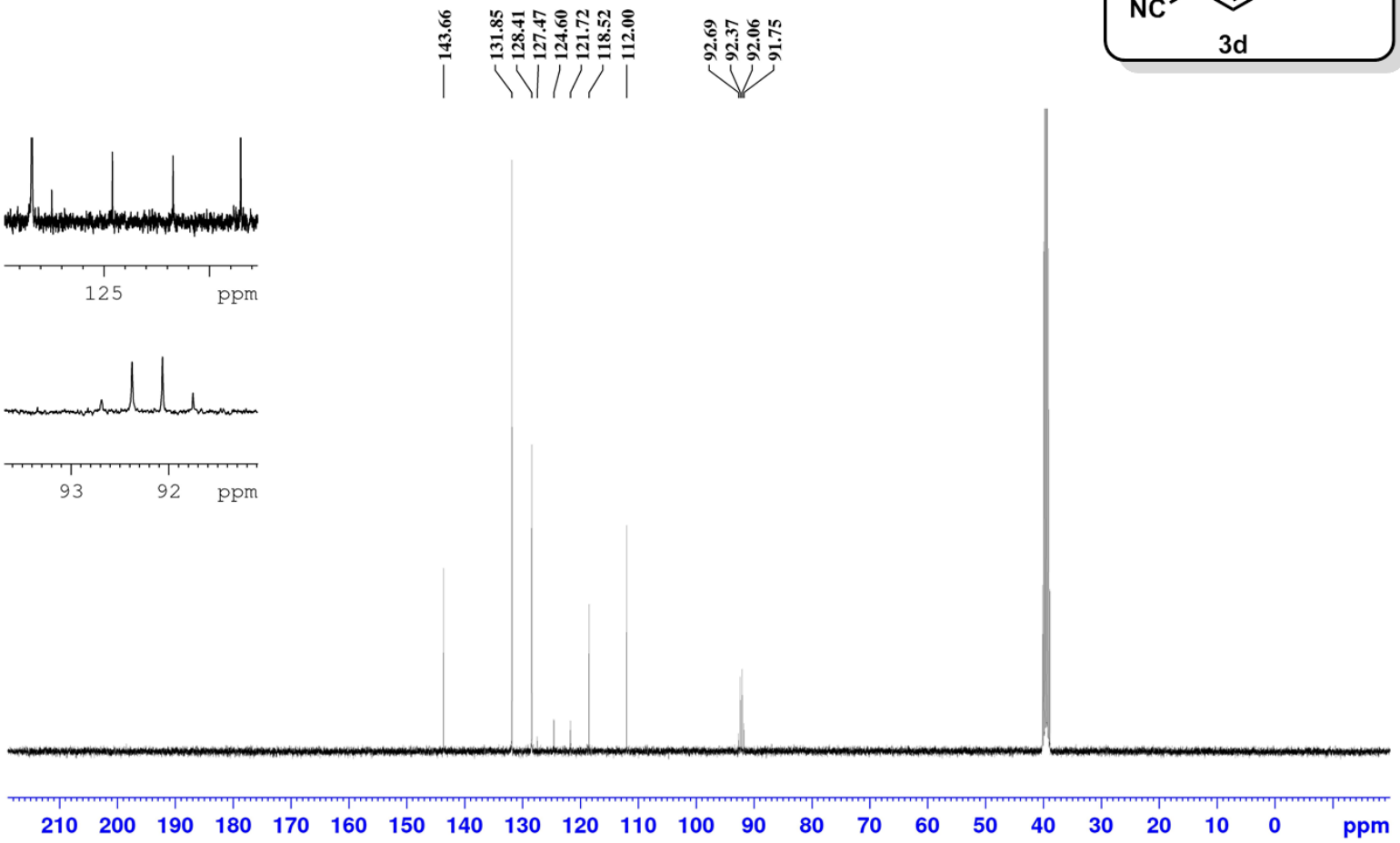


2,2,2-trifluoro-1-(4-nitrophenyl)ethanone
(Hydrate)
101 MHz, DMSO-d6

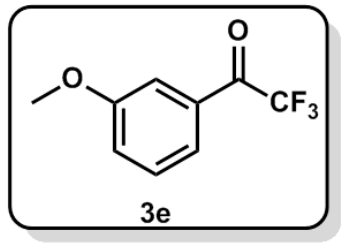


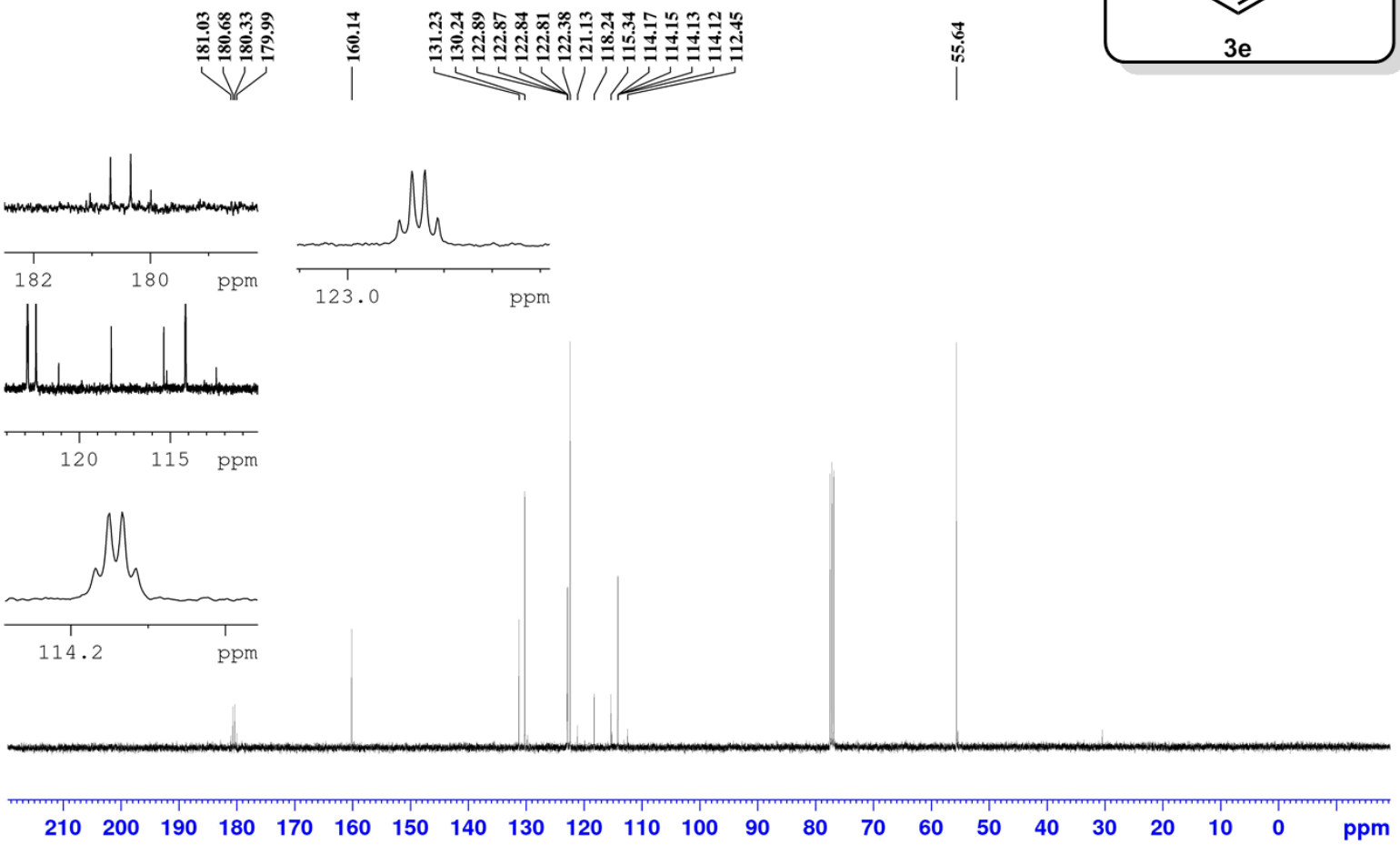
4-(2,2,2-trifluoroacetyl)benzonitrile
(Hydrate)
101 MHz, DMSO-d6



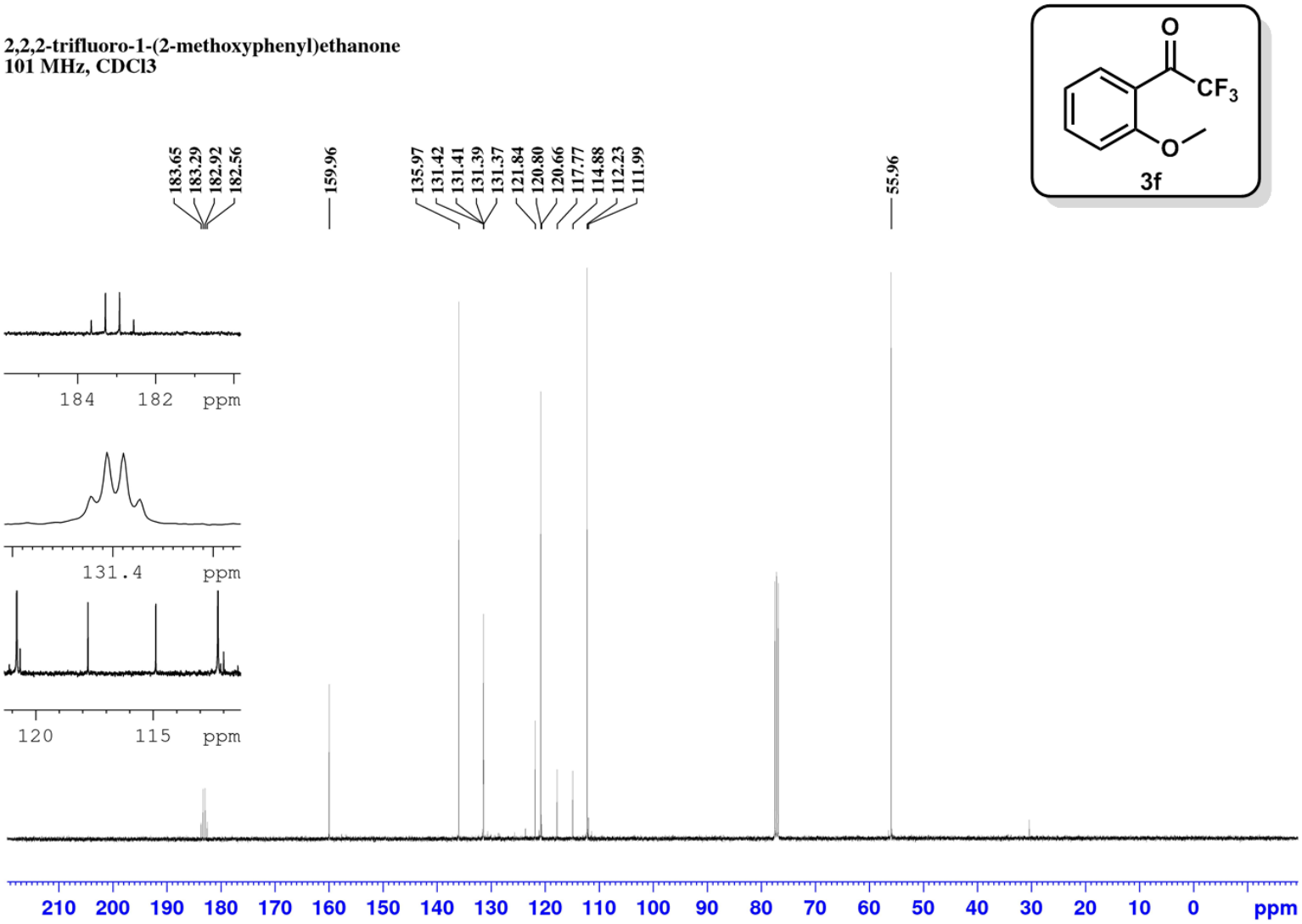


2,2,2-trifluoro-1-(3-methoxyphenyl)ethanone
101 MHz, CDCl3

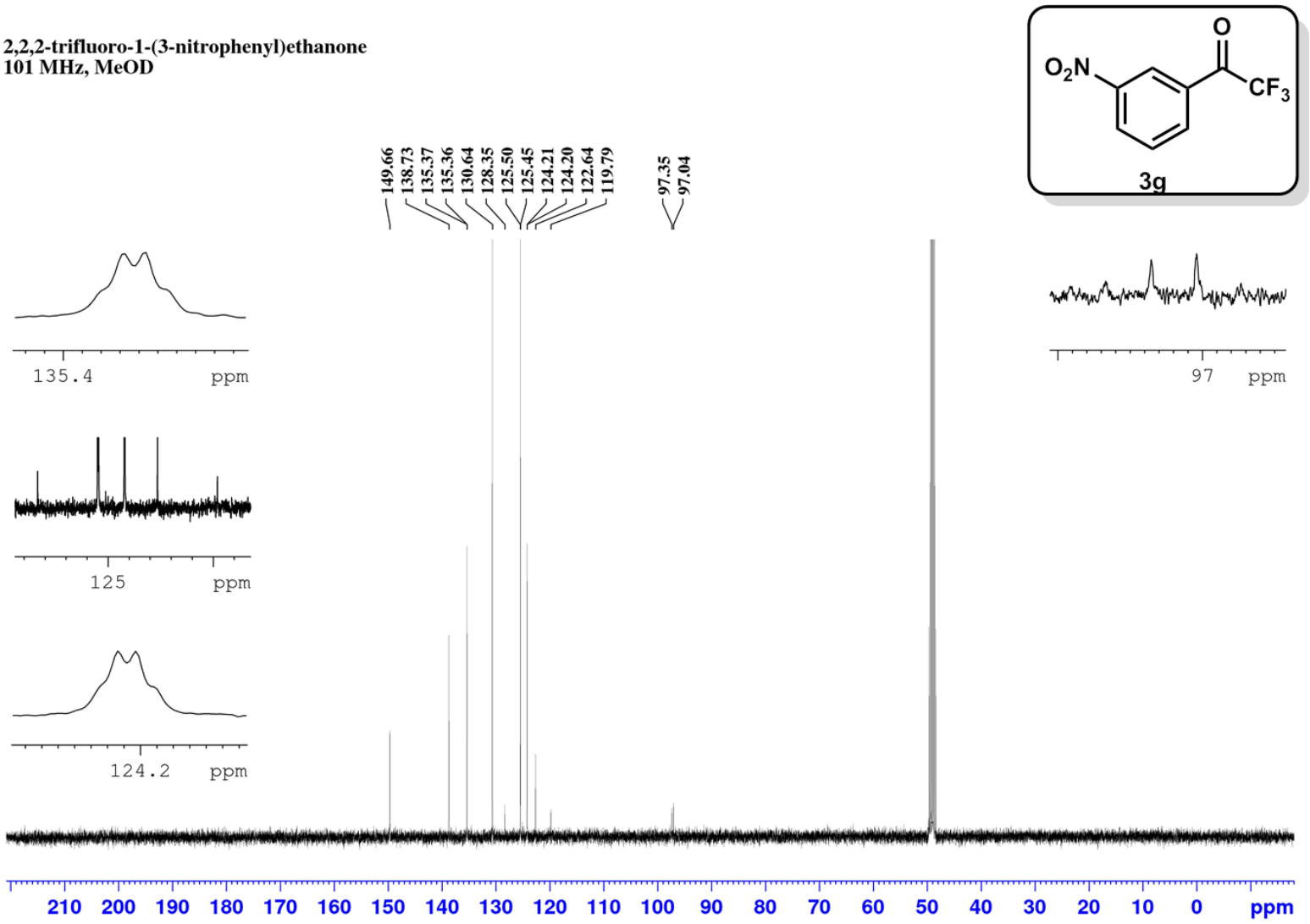




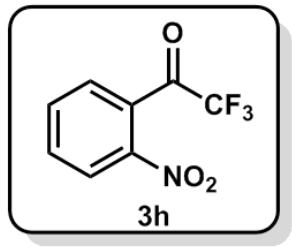
2,2,2-trifluoro-1-(2-methoxyphenyl)ethanone
101 MHz, CDCl3

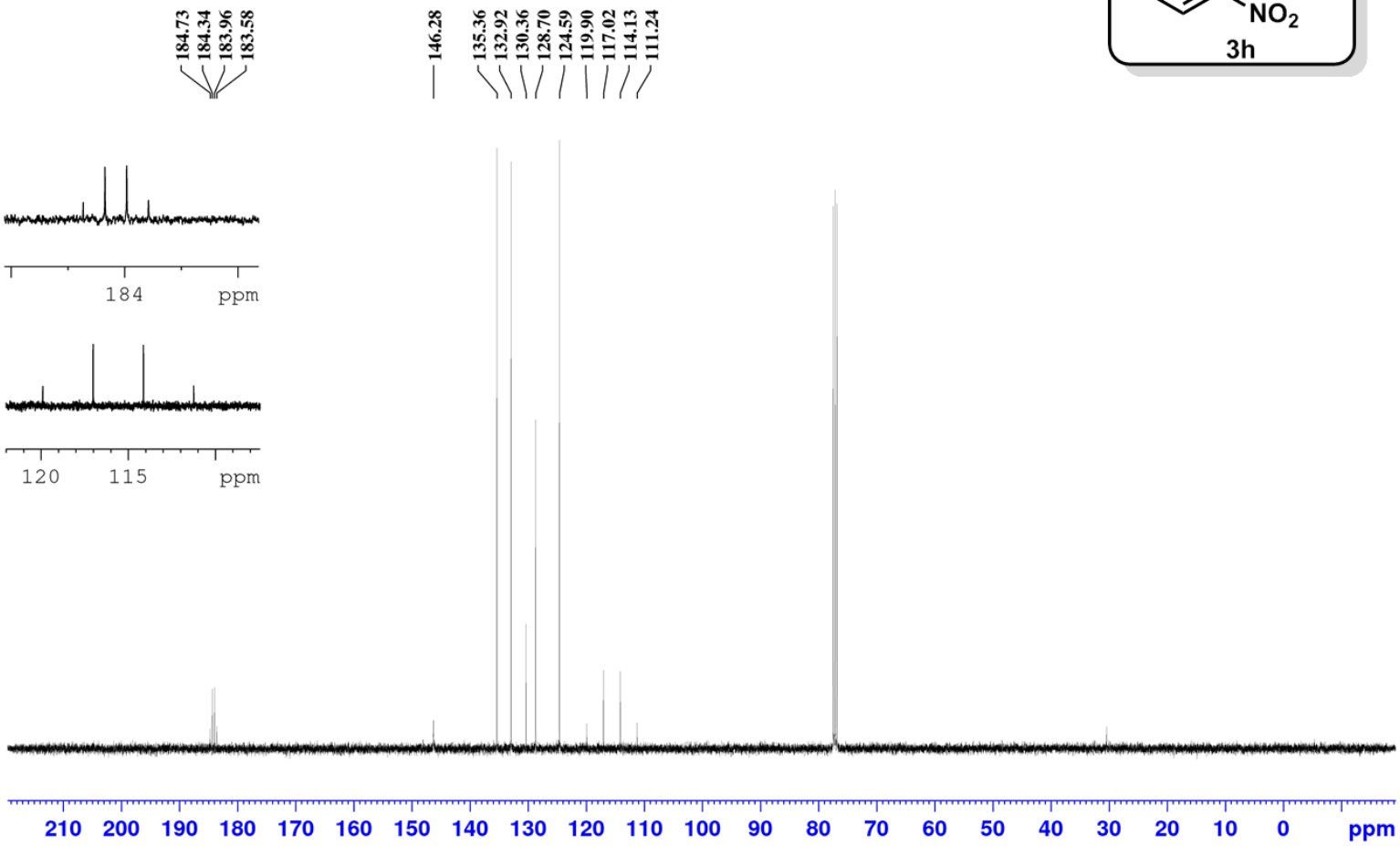


2,2,2-trifluoro-1-(3-nitrophenyl)ethanone
101 MHz, MeOD

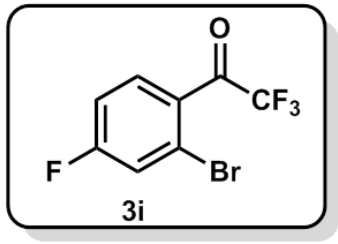


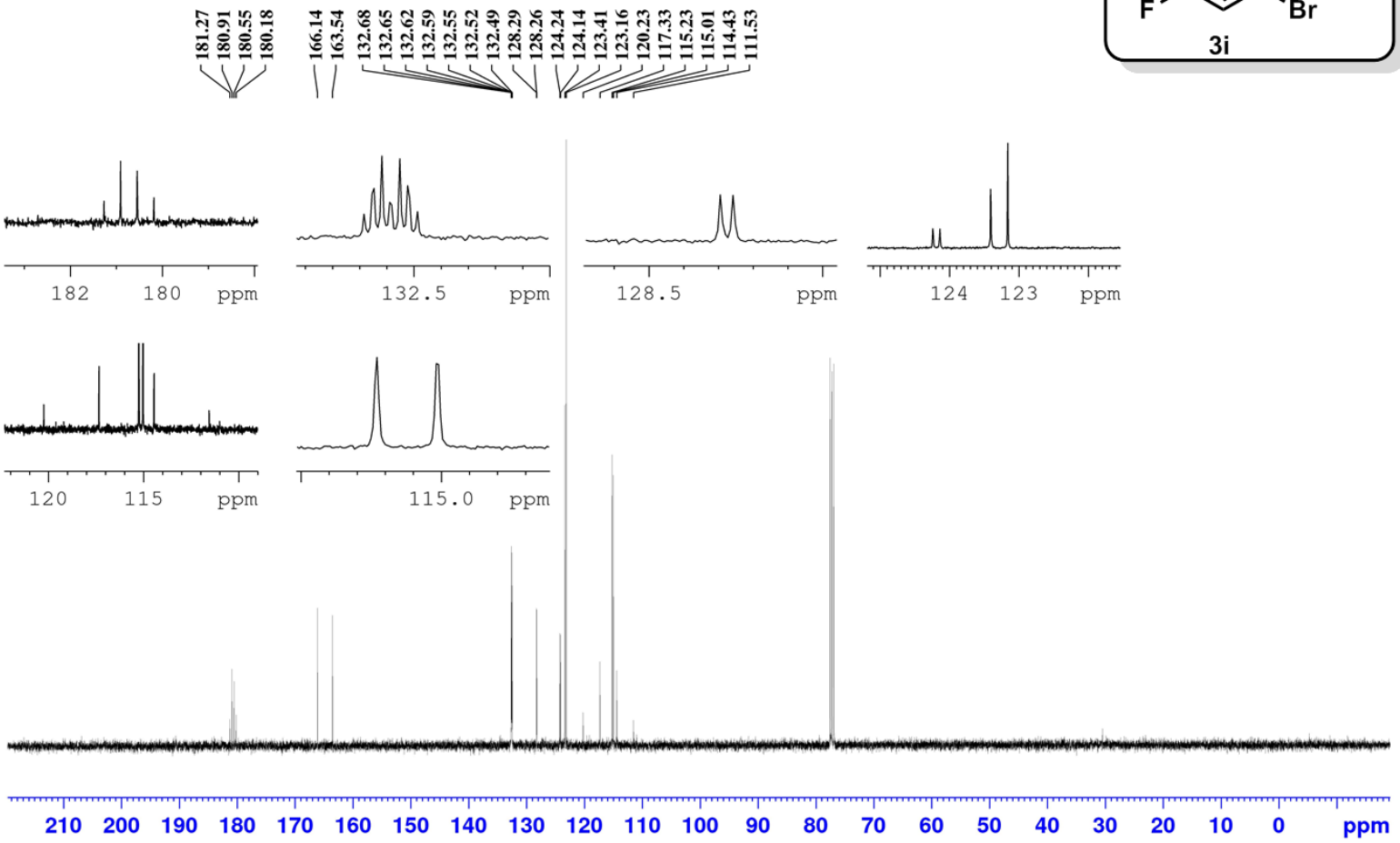
2,2,2-trifluoro-1-(2-nitrophenyl)ethanone
101 MHz, CDCl3



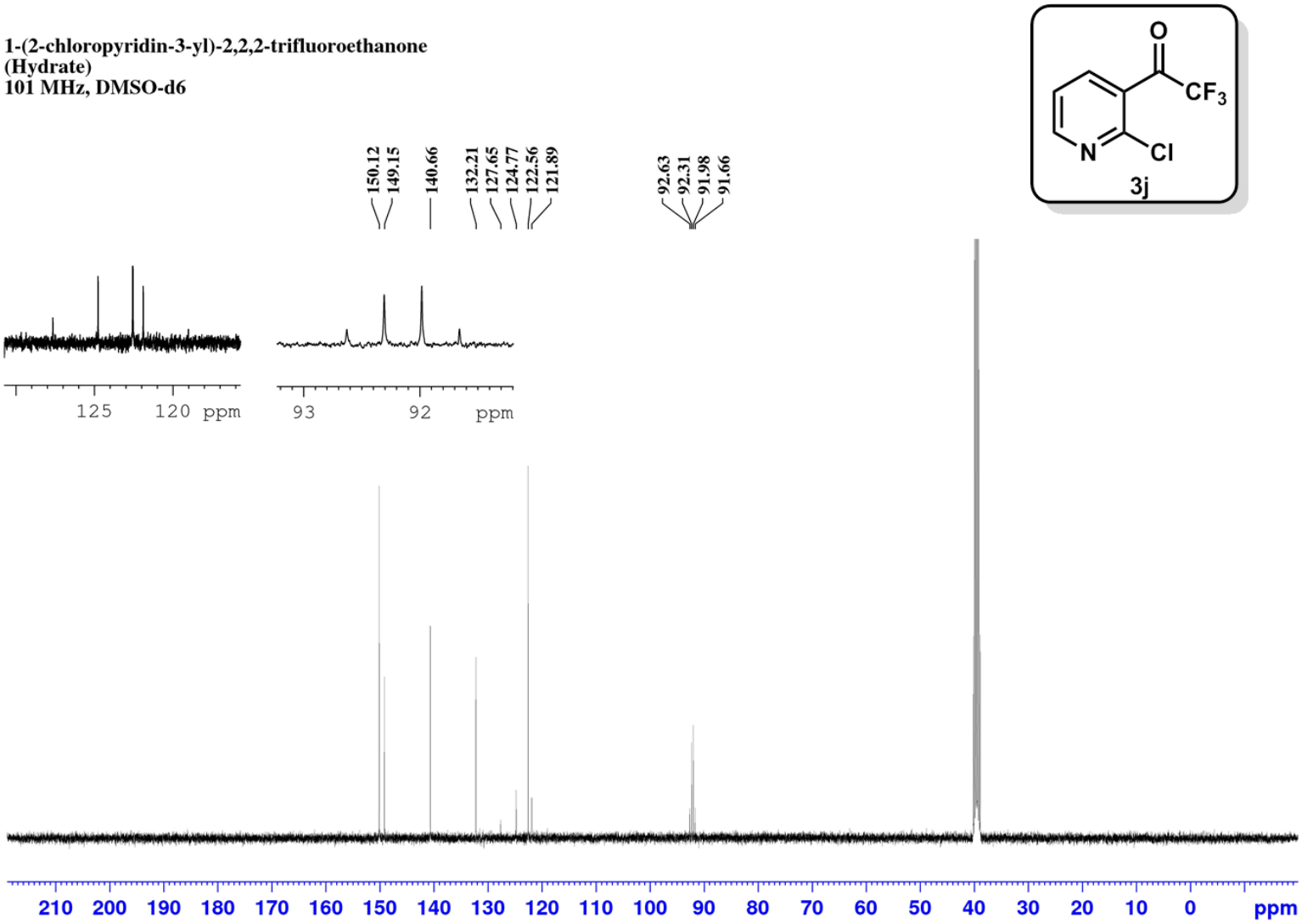


1-(2-bromo-4-fluorophenyl)-2,2,2-trifluoroethanone
101 MHz, CDCl3

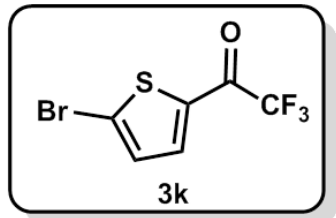




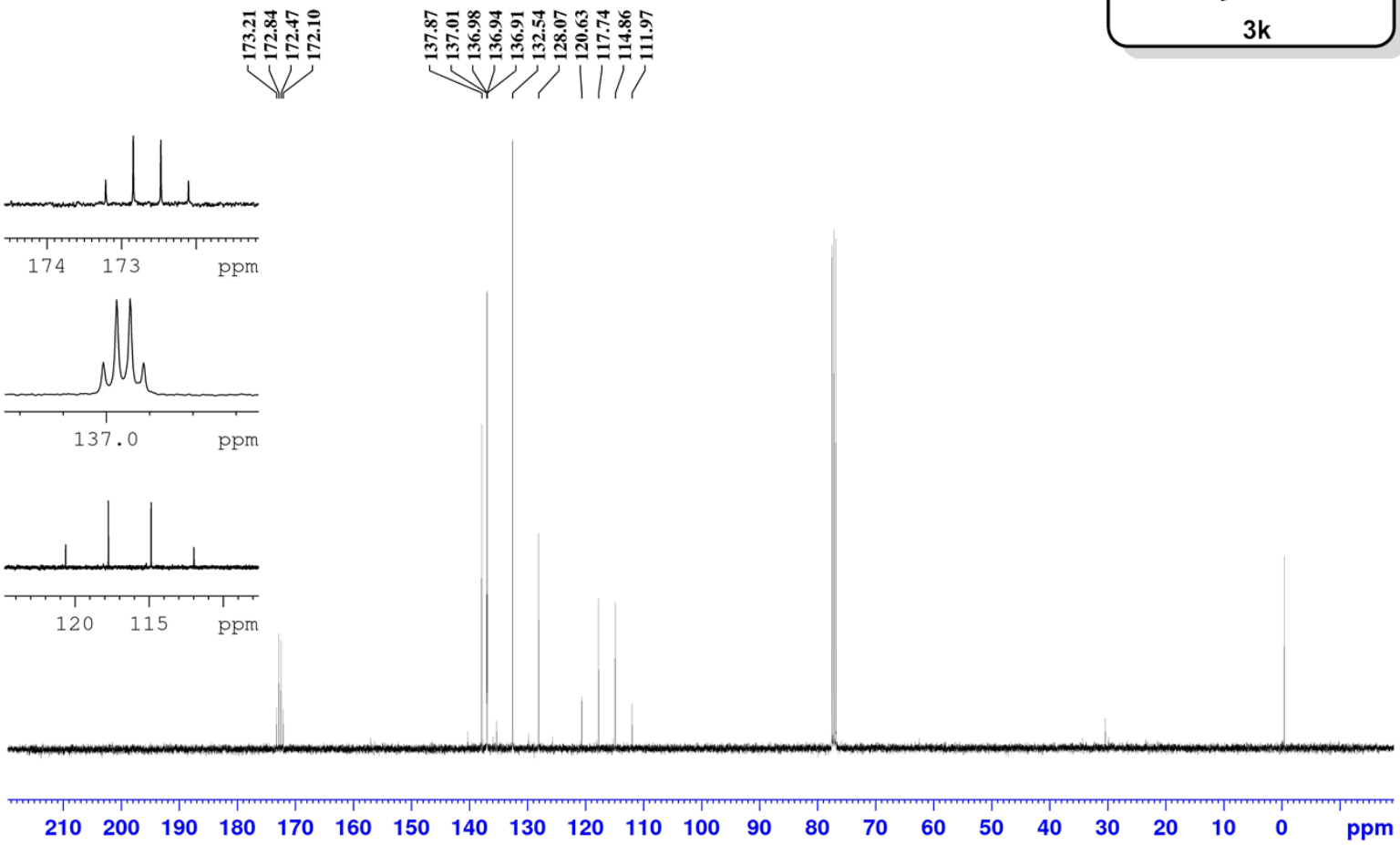
1-(2-chloropyridin-3-yl)-2,2,2-trifluoroethanone (Hydrate)
101 MHz, DMSO-d6



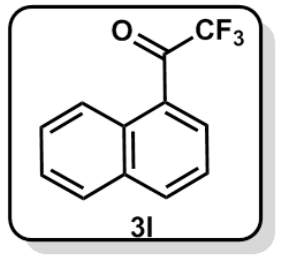
1-(5-bromothiophen-2-yl)-2,2,2-trifluoroethanone
101 MHz, CDCl3

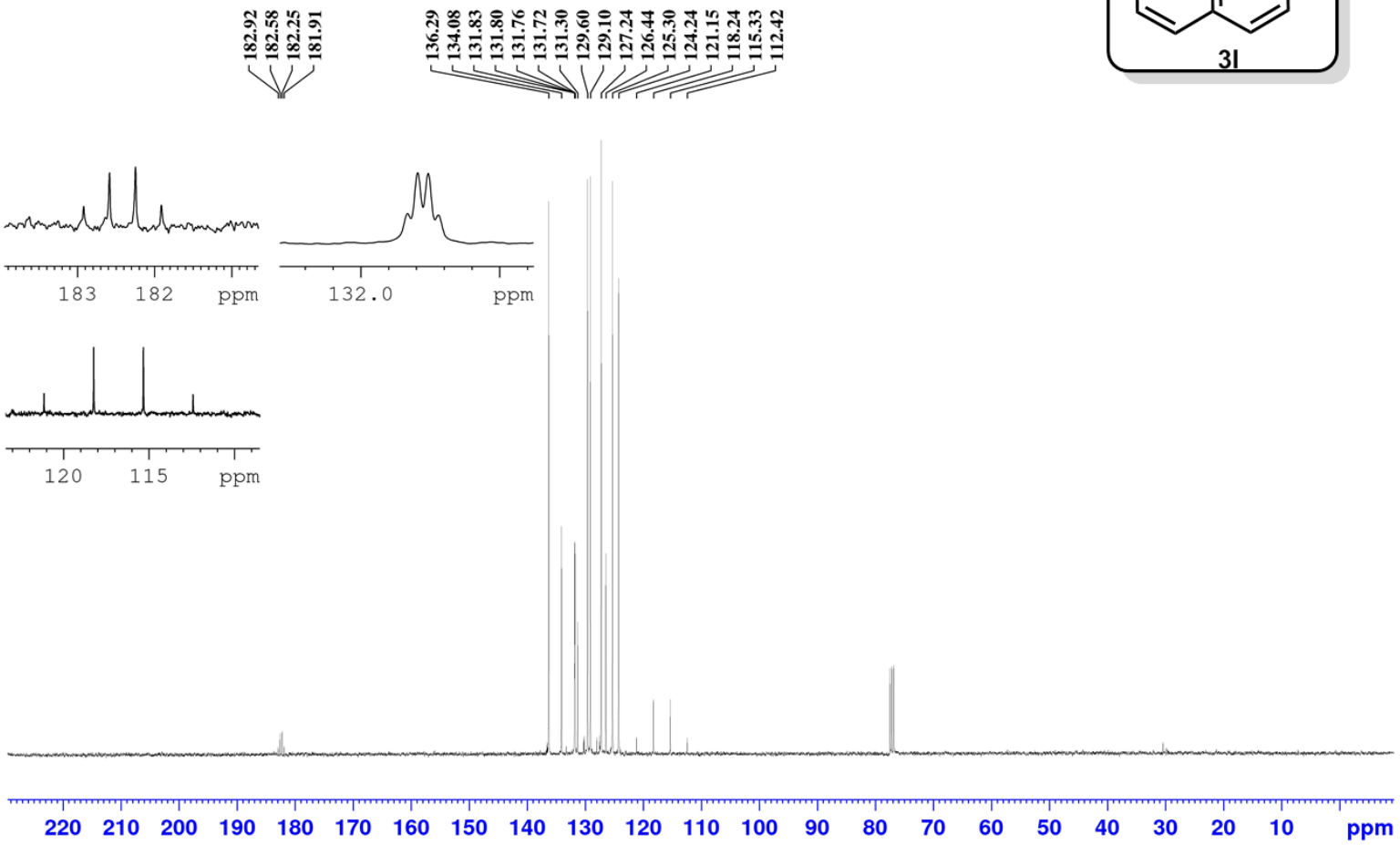


3k

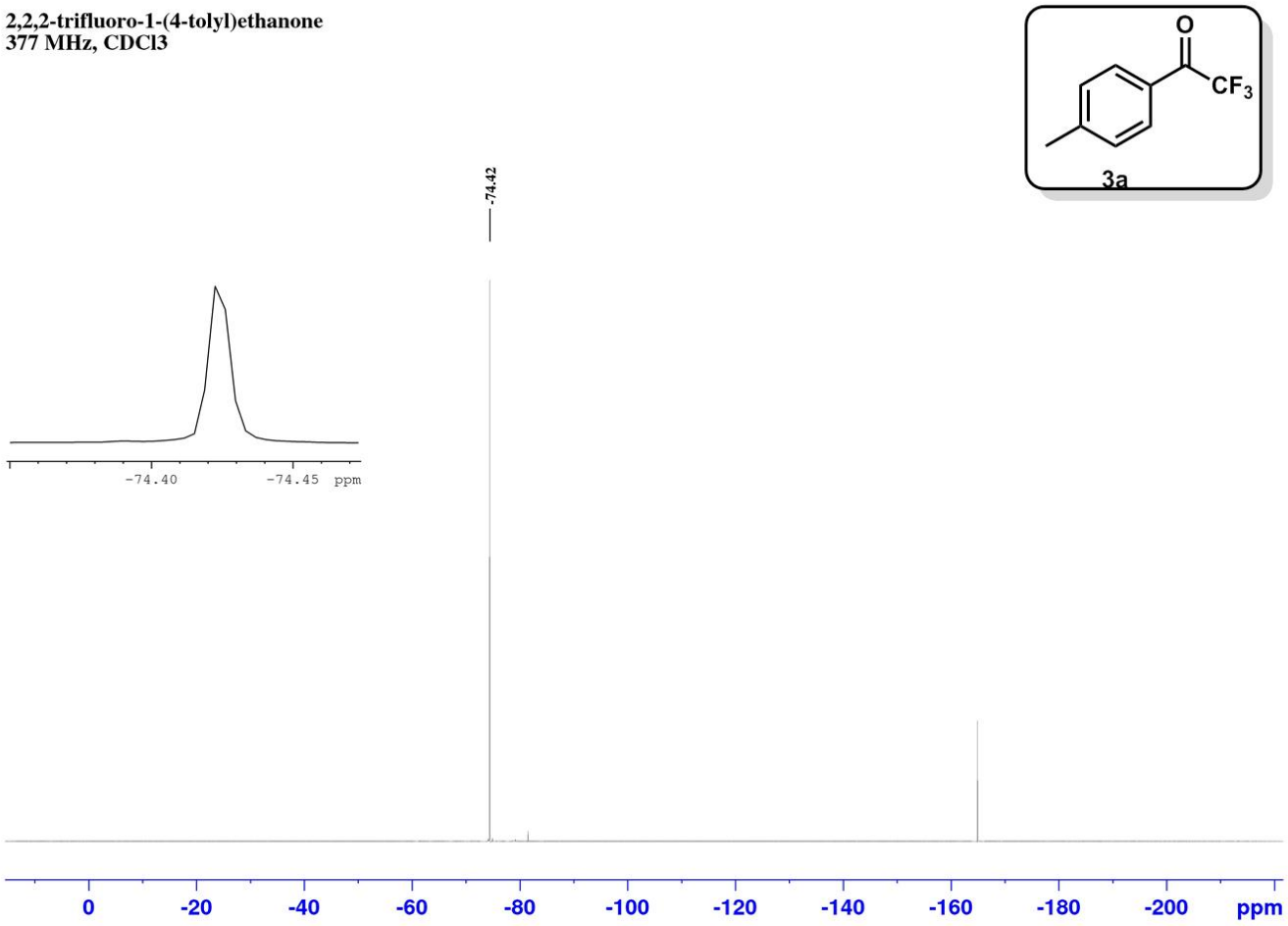


2,2,2-trifluoro-1-(naphthalen-1-yl)ethanone
101 MHz, CDCl3

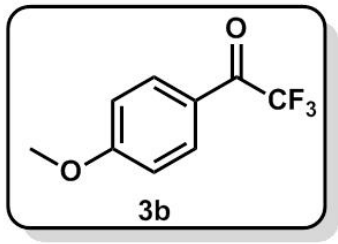


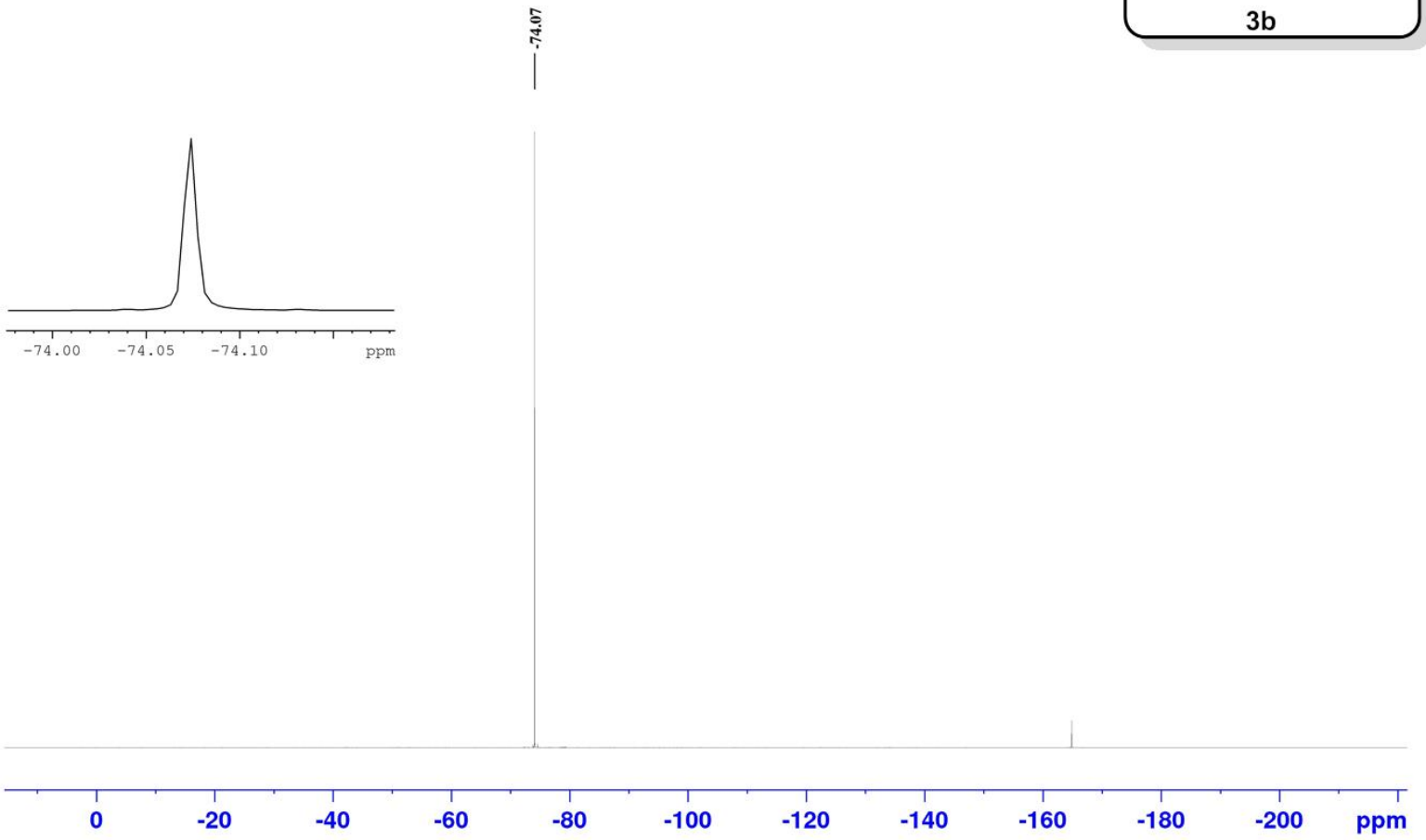


^{19}F NMR Spectra of Synthesized α-CF_3 alcohols

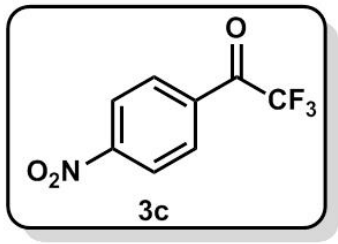


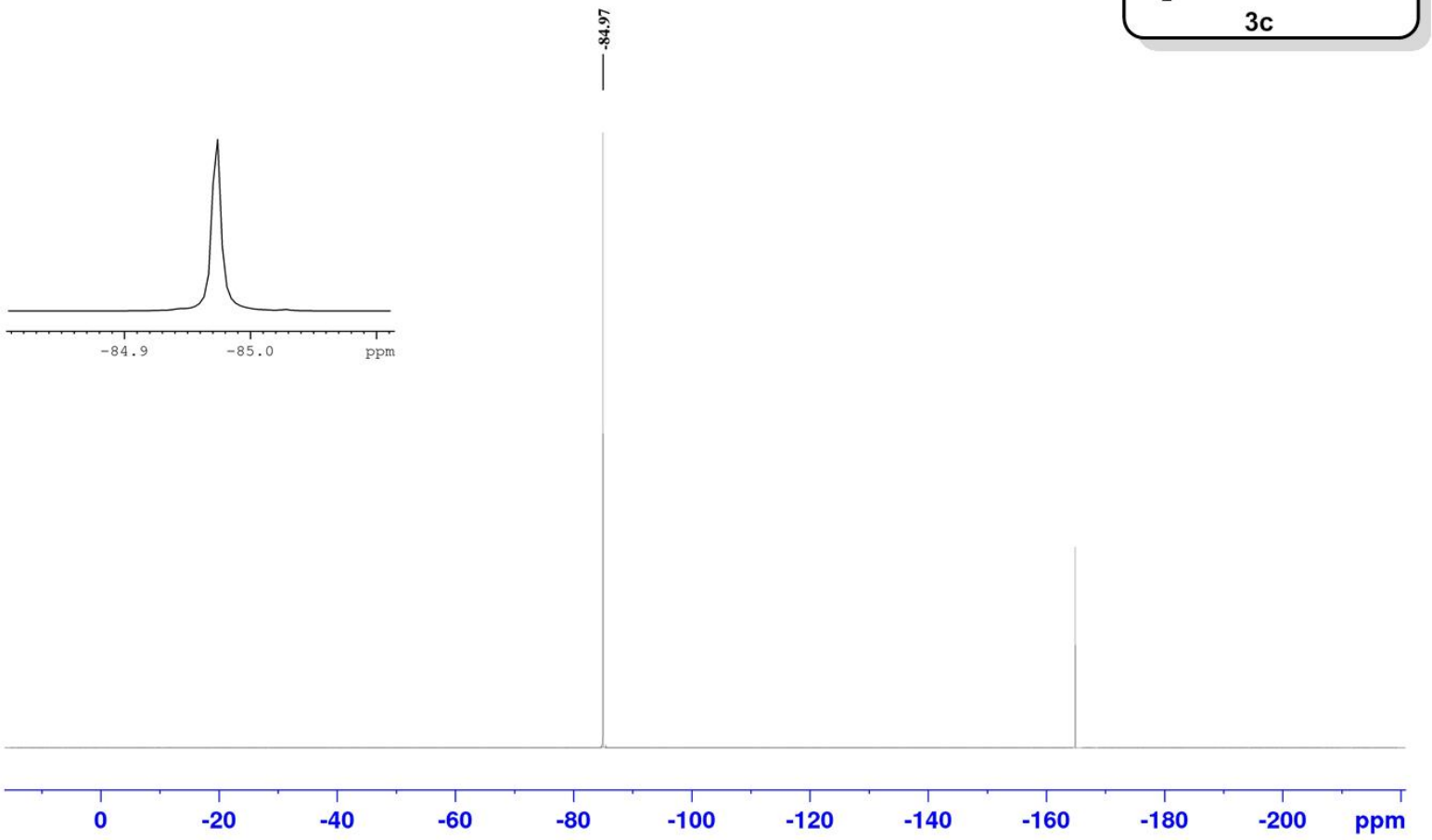
2,2,2-trifluoro-1-(4-methoxyphenyl)ethanone
377 MHz, CDCl3



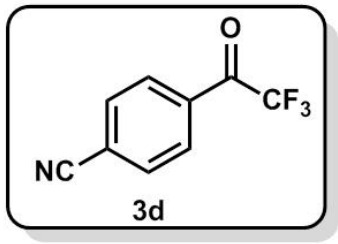


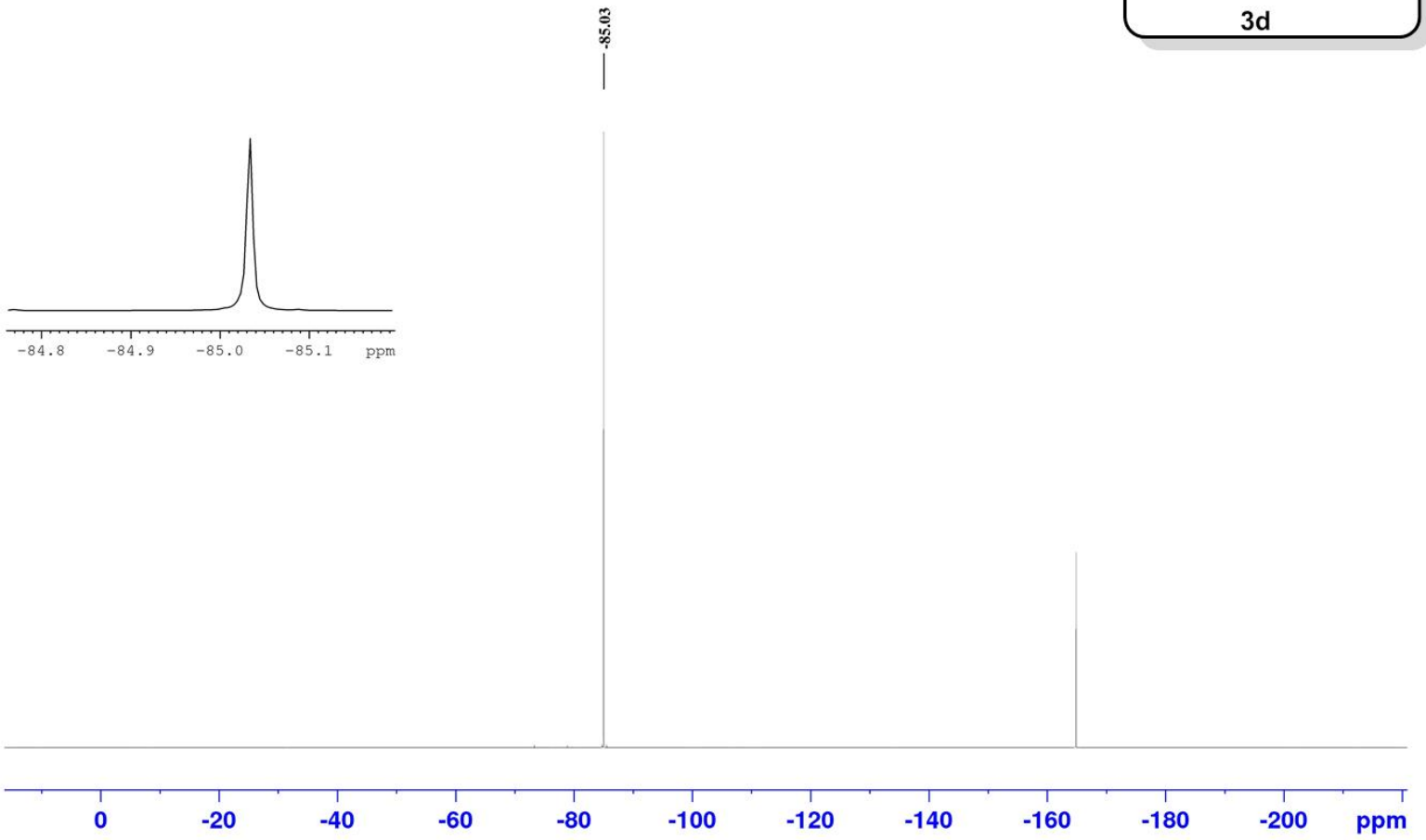
2,2,2-trifluoro-1-(4-nitrophenyl)ethanone
377 MHz, DMSO-d6



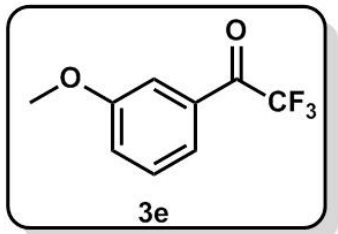


4-(2,2,2-trifluoroacetyl)benzonitrile
377 MHz, DMSO-d6

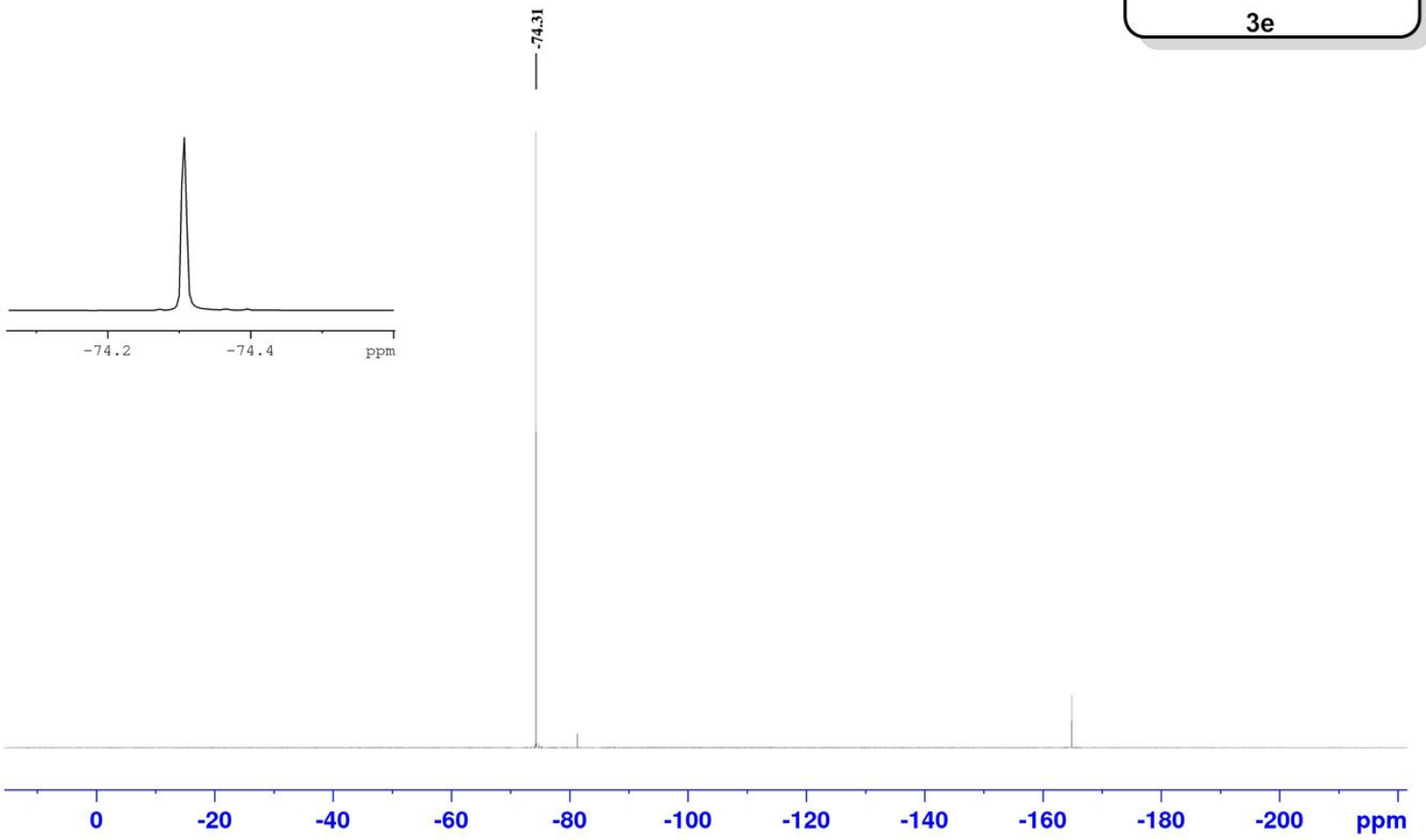




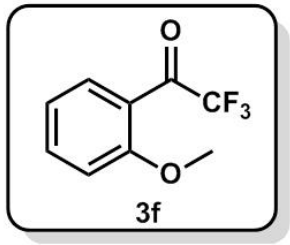
2,2,2-trifluoro-1-(3-methoxyphenyl)ethanone
377 MHz, CDCl3

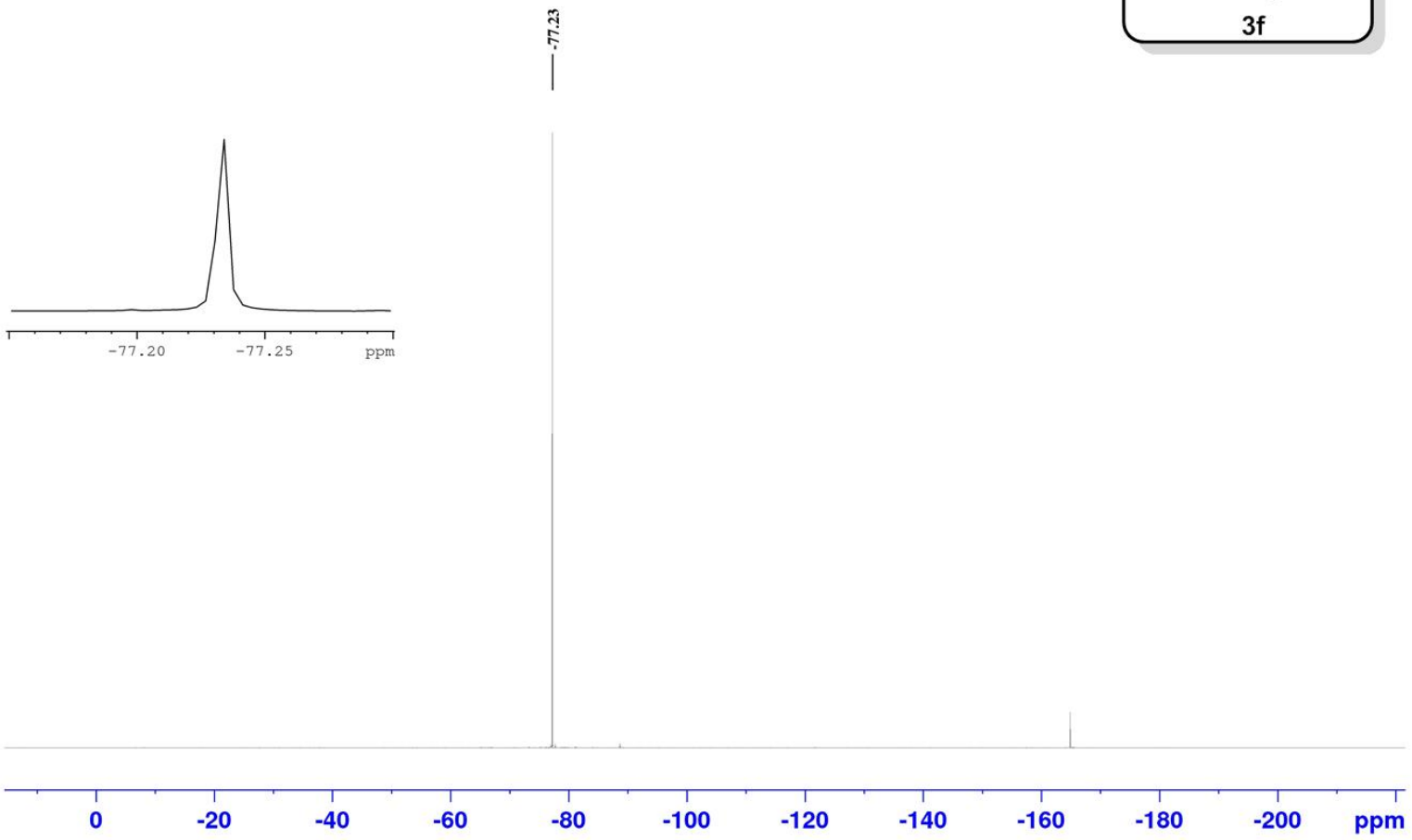


3e

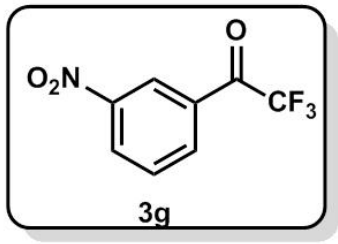


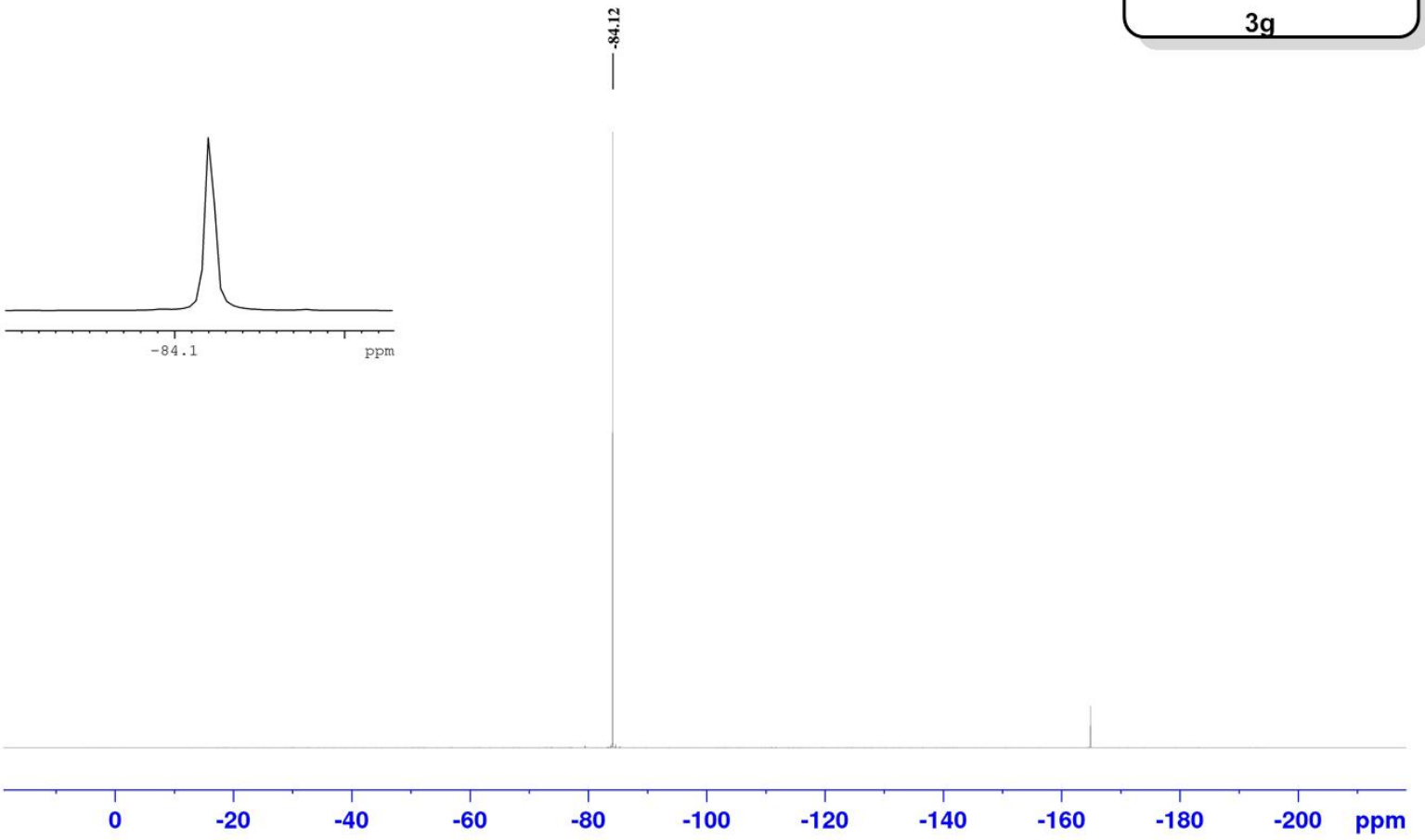
2,2,2-trifluoro-1-(2-methoxyphenyl)ethanone
377 MHz, CDCl3



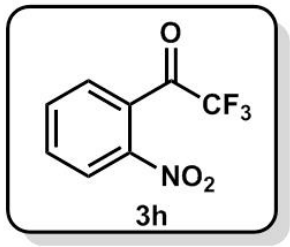


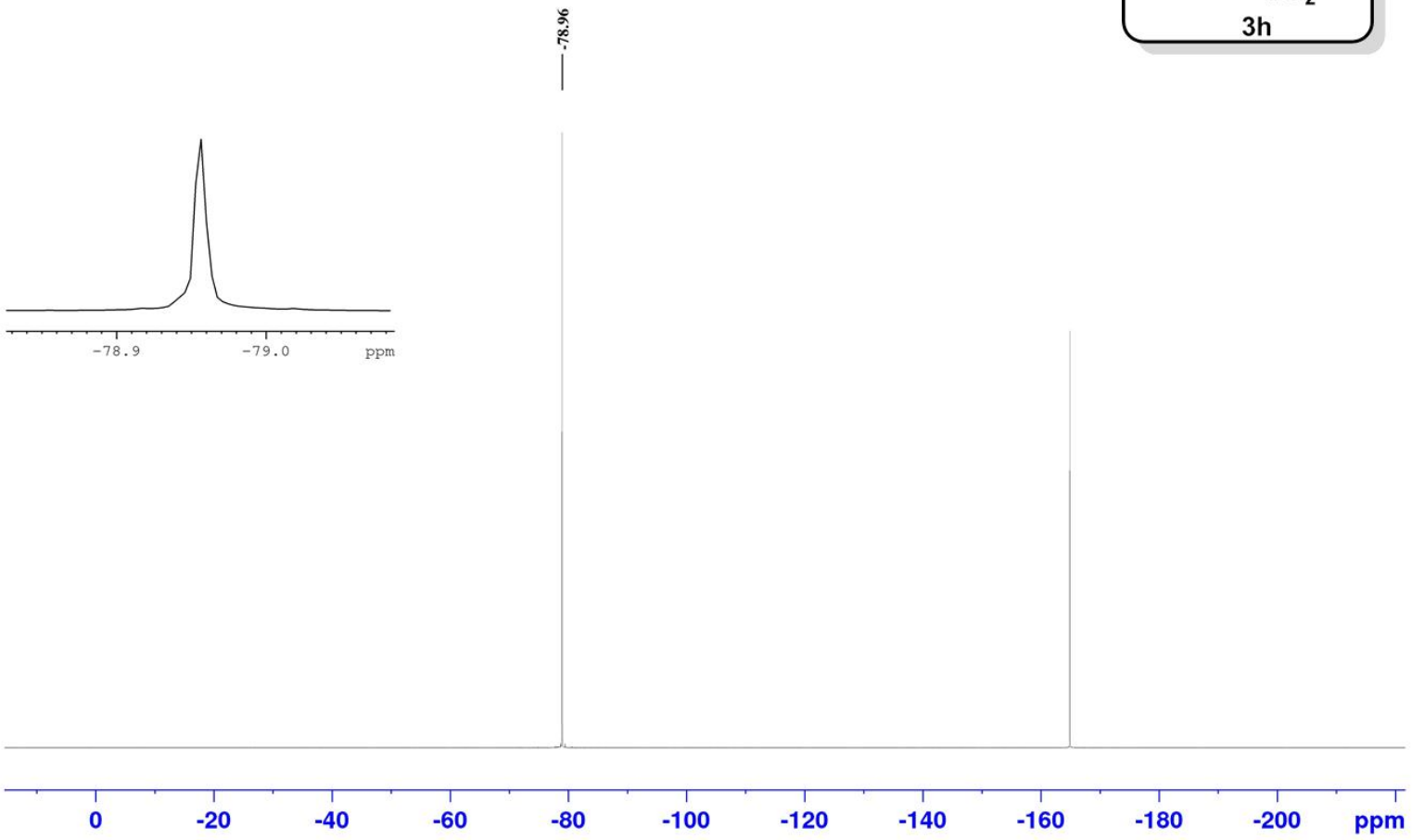
2,2,2-trifluoro-1-(3-nitrophenyl)ethanone
377 MHz, MeOD



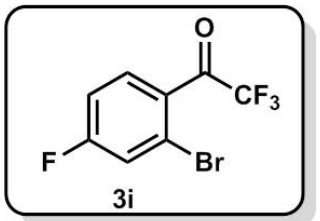


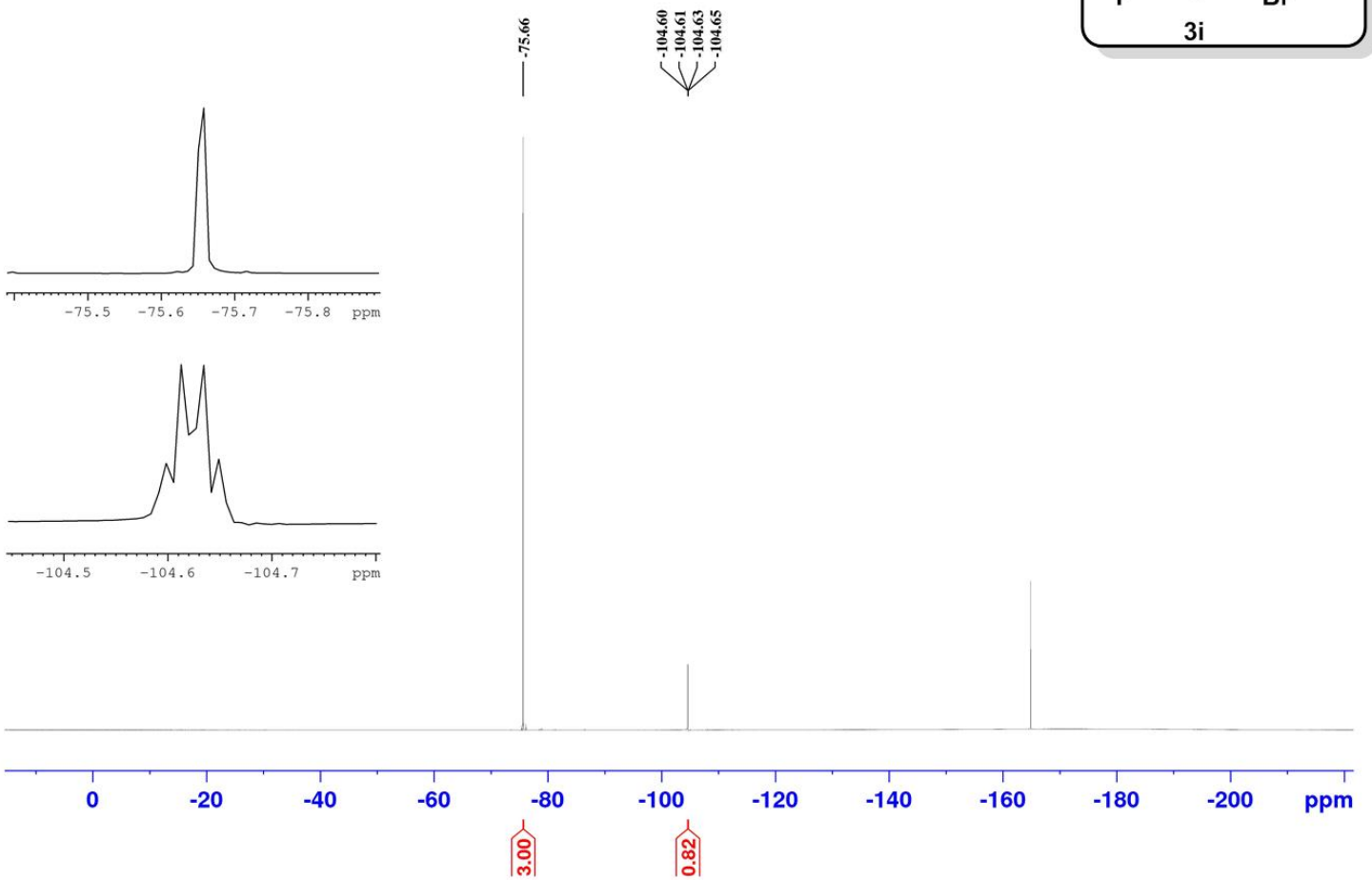
2,2,2-trifluoro-1-(2-nitrophenyl)ethanone
377 MHz, CDCl3



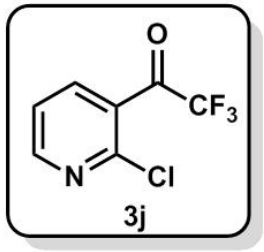


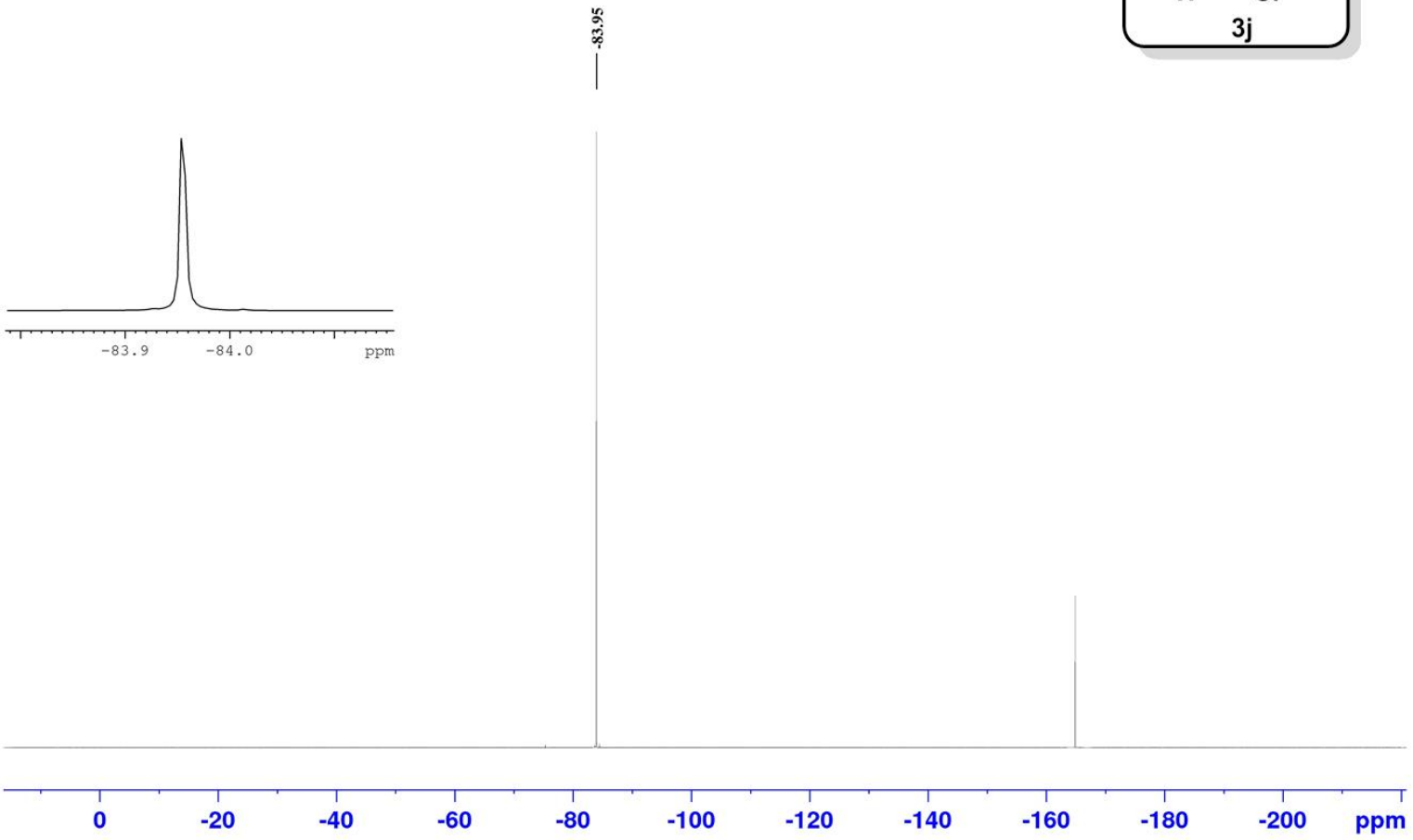
1-(2-bromo-4-fluorophenyl)-2,2,2-trifluoroethanone
377 MHz, CDCl3



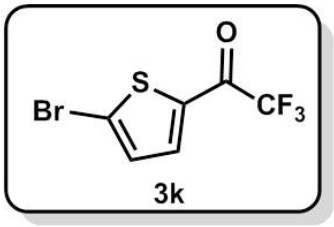


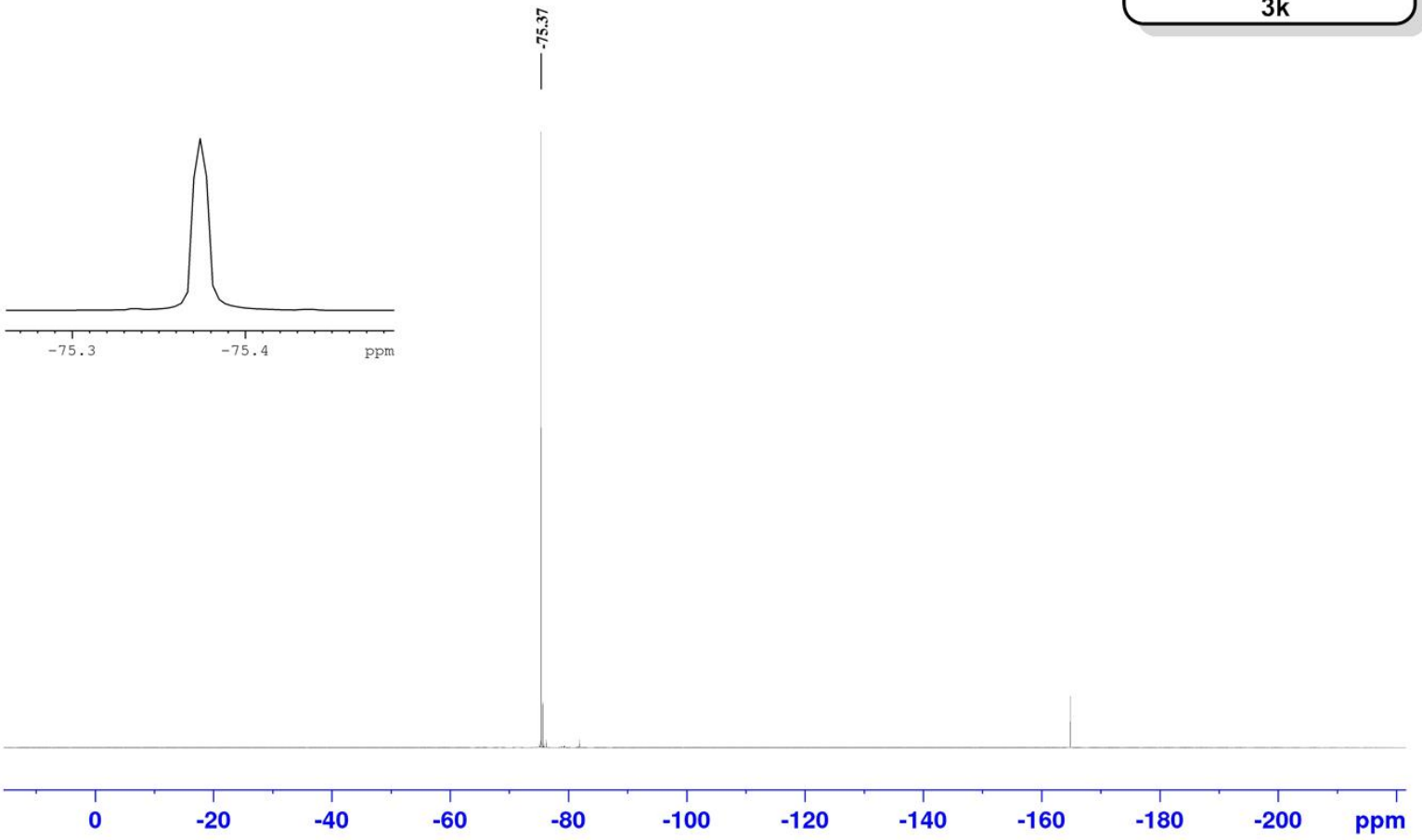
1-(2-chloropyridin-3-yl)-2,2,2-trifluoroethanone
377 MHz, DMSO-d6



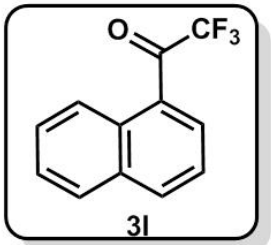


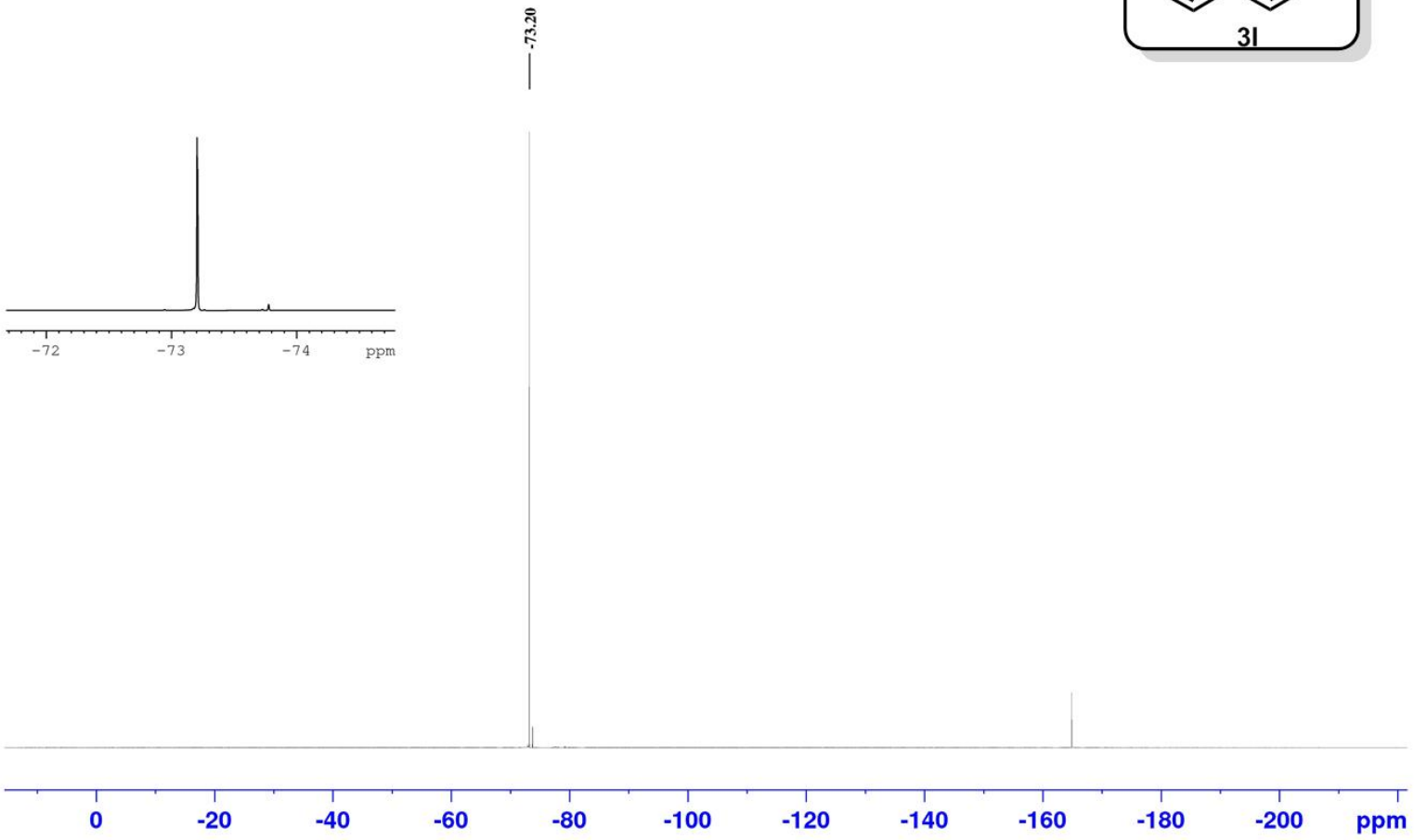
1-(5-bromothiophen-2-yl)-2,2,2-trifluoroethanone
377 MHz, CDCl3



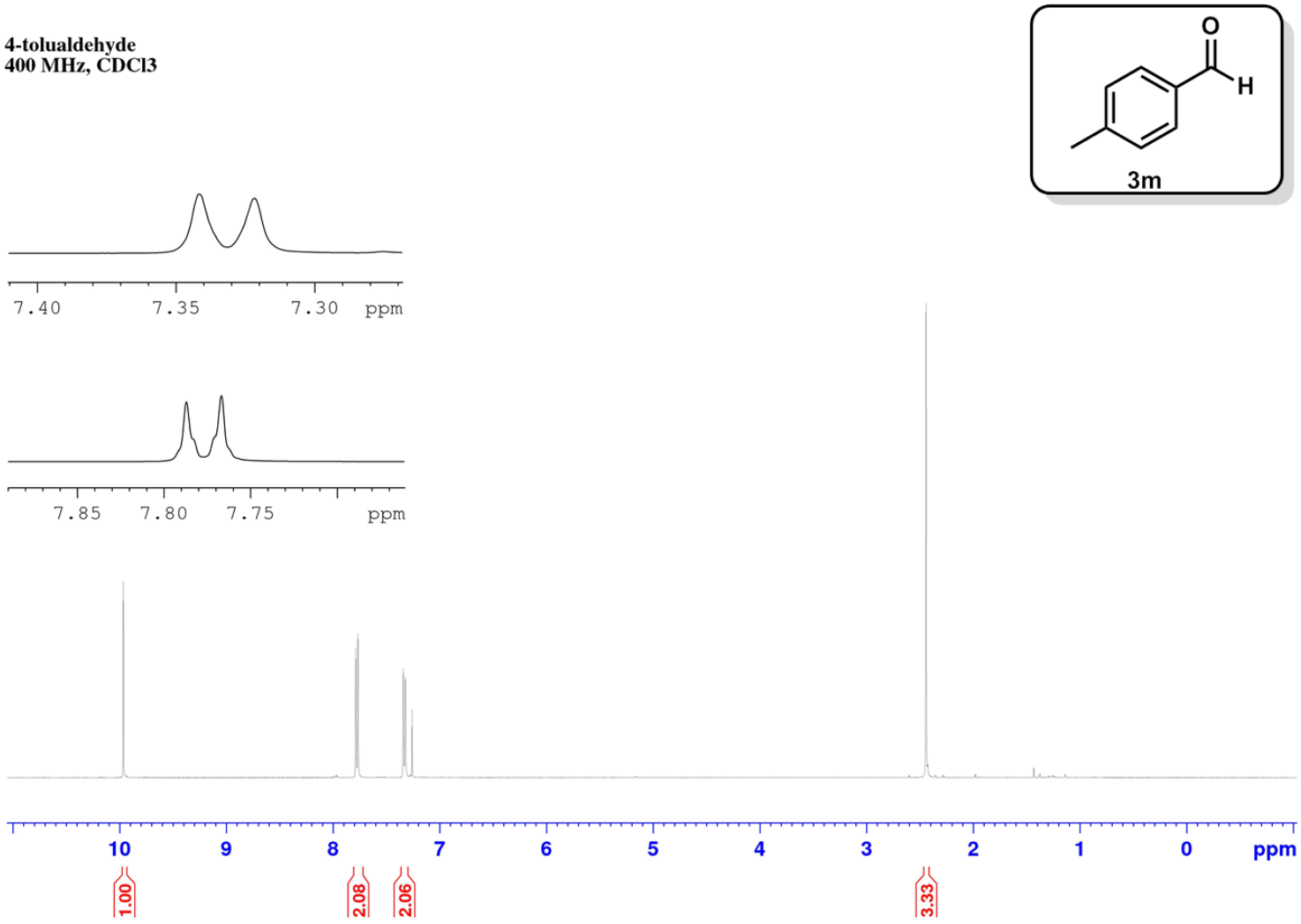


2,2,2-trifluoro-1-(naphthalen-1-yl)ethanone
377 MHz, CDCl3

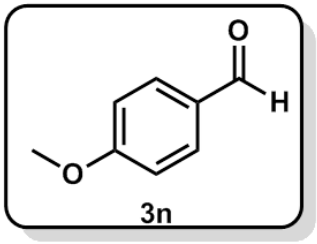




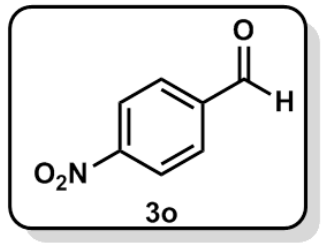
^{1}H NMR Spectra of Synthesized Non-fluorinated Aldehydes and Ketones

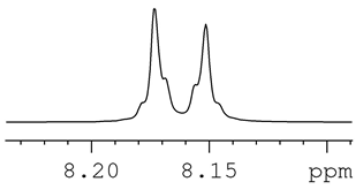


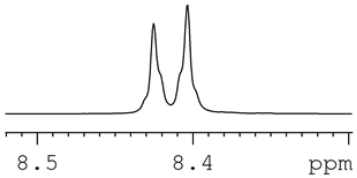
4-methoxybenzaldehyde
400 MHz, CDCl3



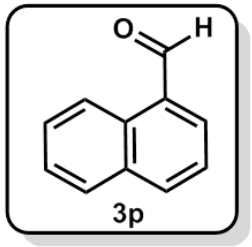
4-nitrobenzaldehyde
400 MHz, DMSO-d6

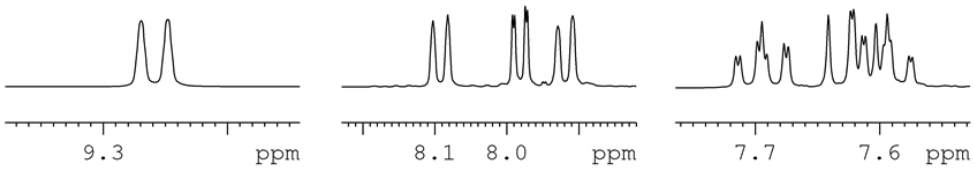


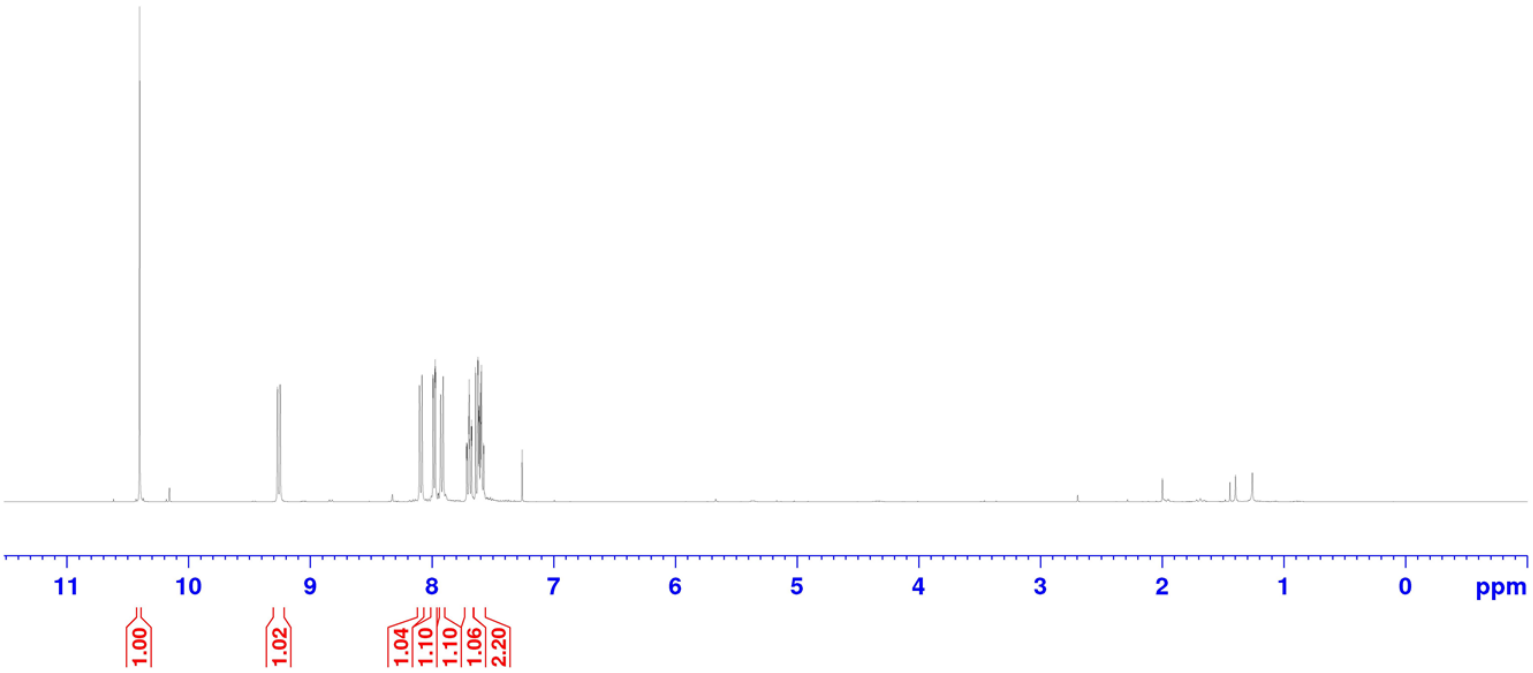


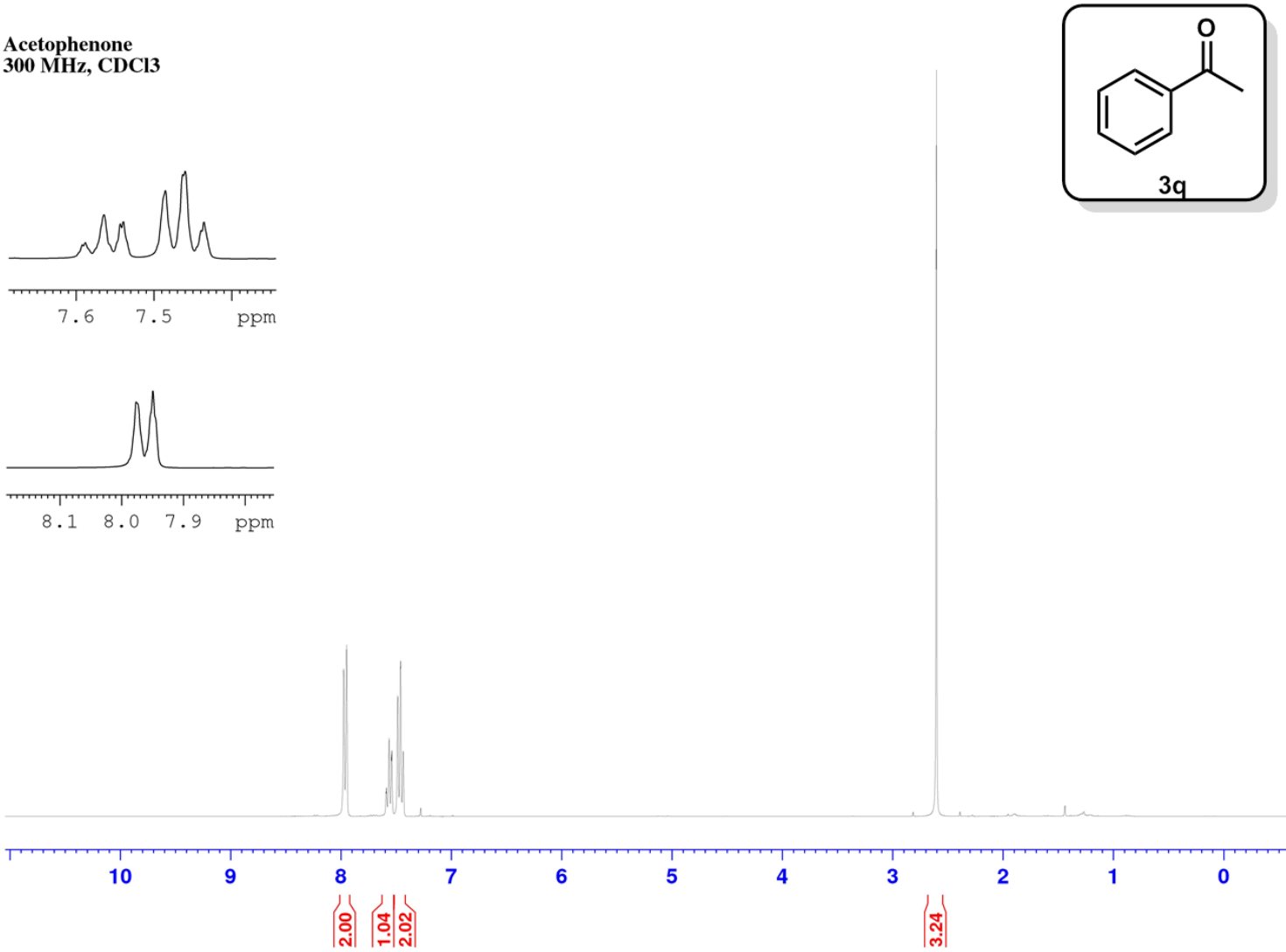


1-naphthaldehyde
400 MHz, CDCl3

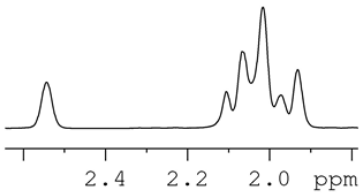


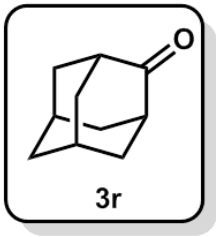




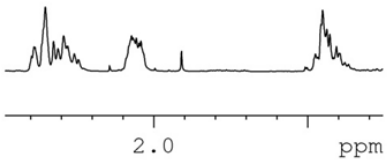

Acetophenone
300 MHz, CDCl3
O
3q
7.6
7.5
ppm
8.1
8.0
7.9
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.04
2.02
3.24

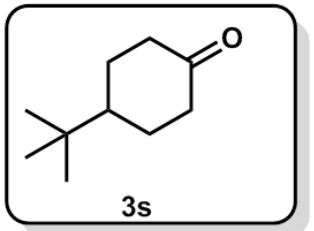
2-adamantanone
400 MHz, CDCl3



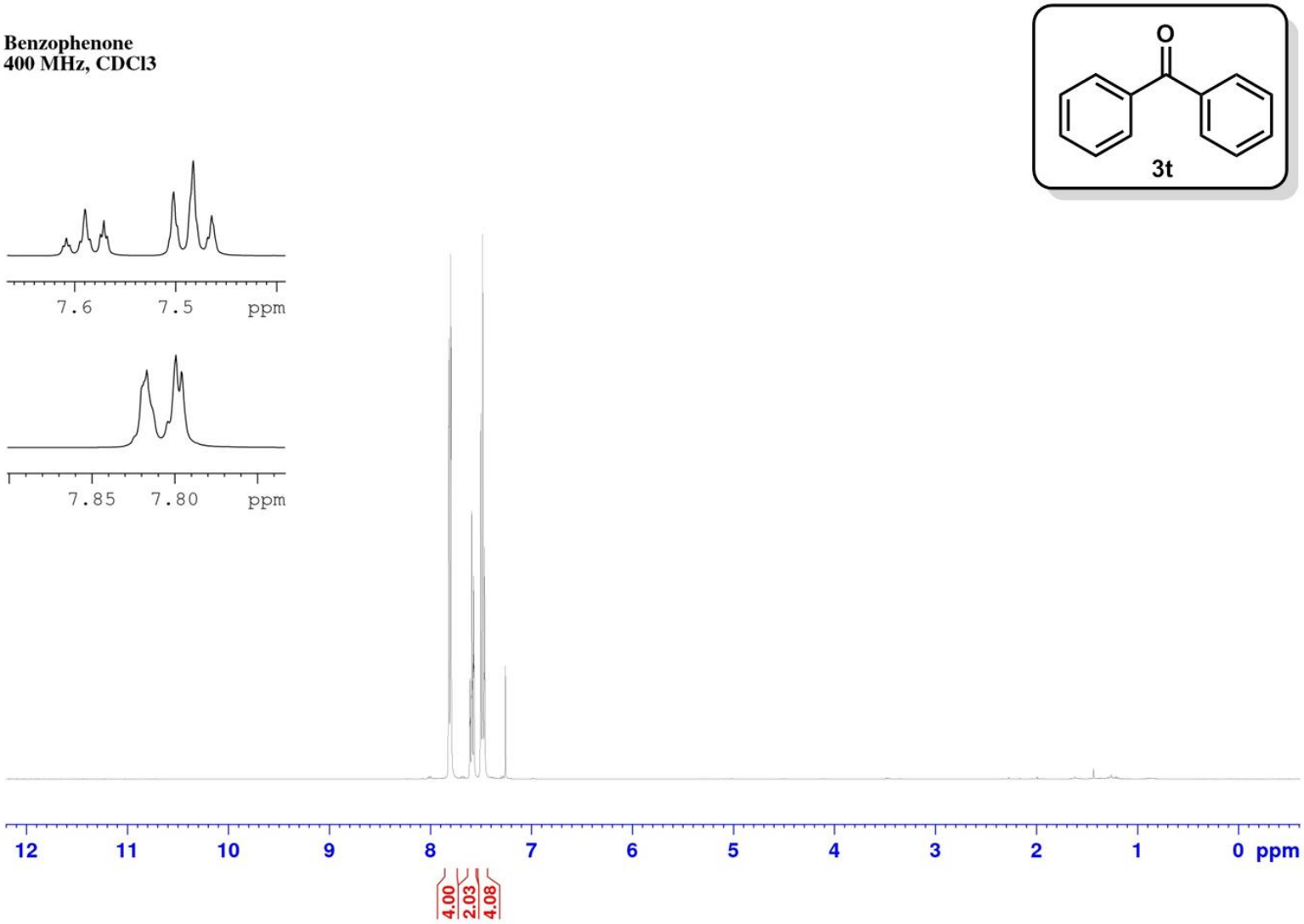


4-(tert-butyl)cyclohexanone
400 MHz, CDCl3

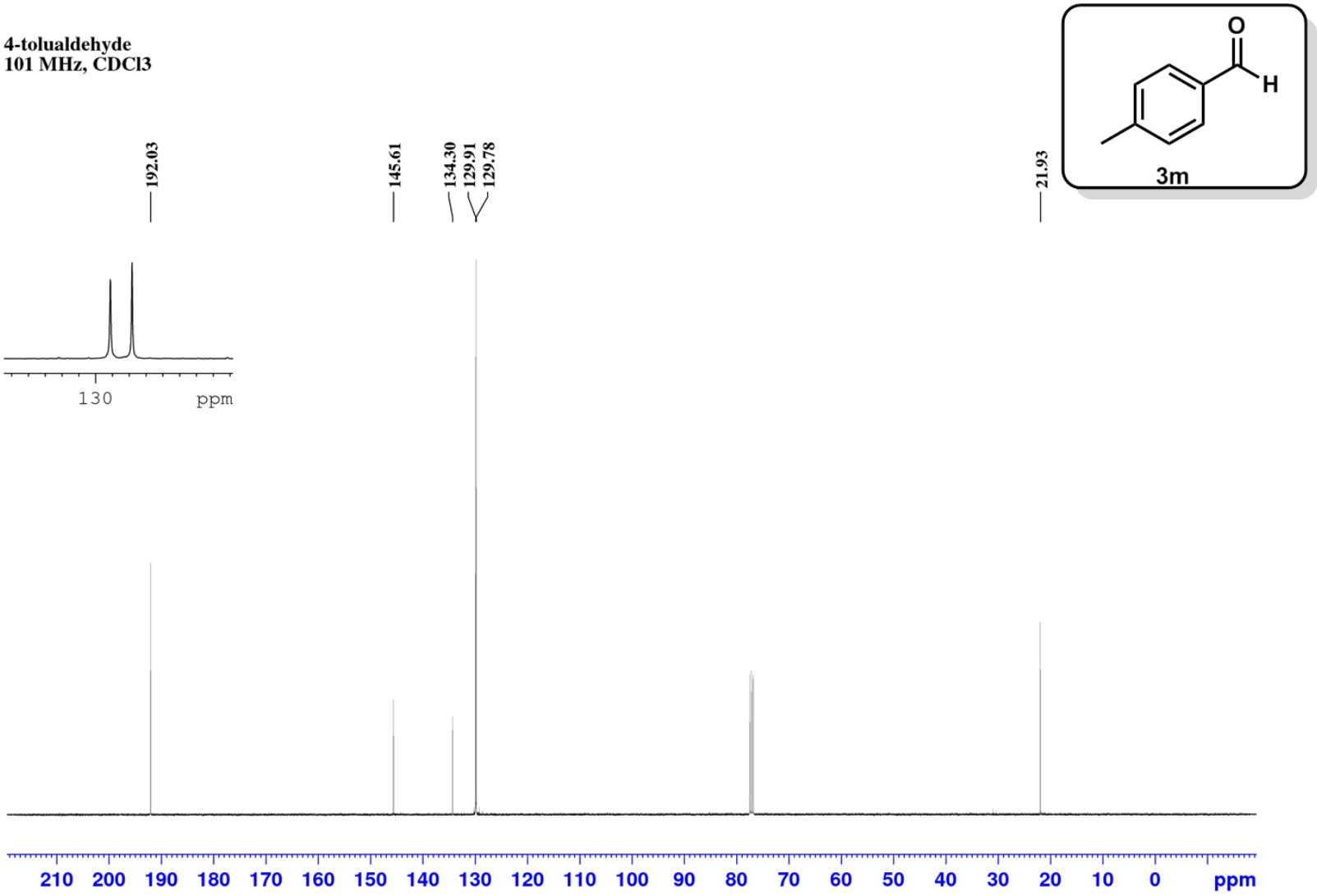




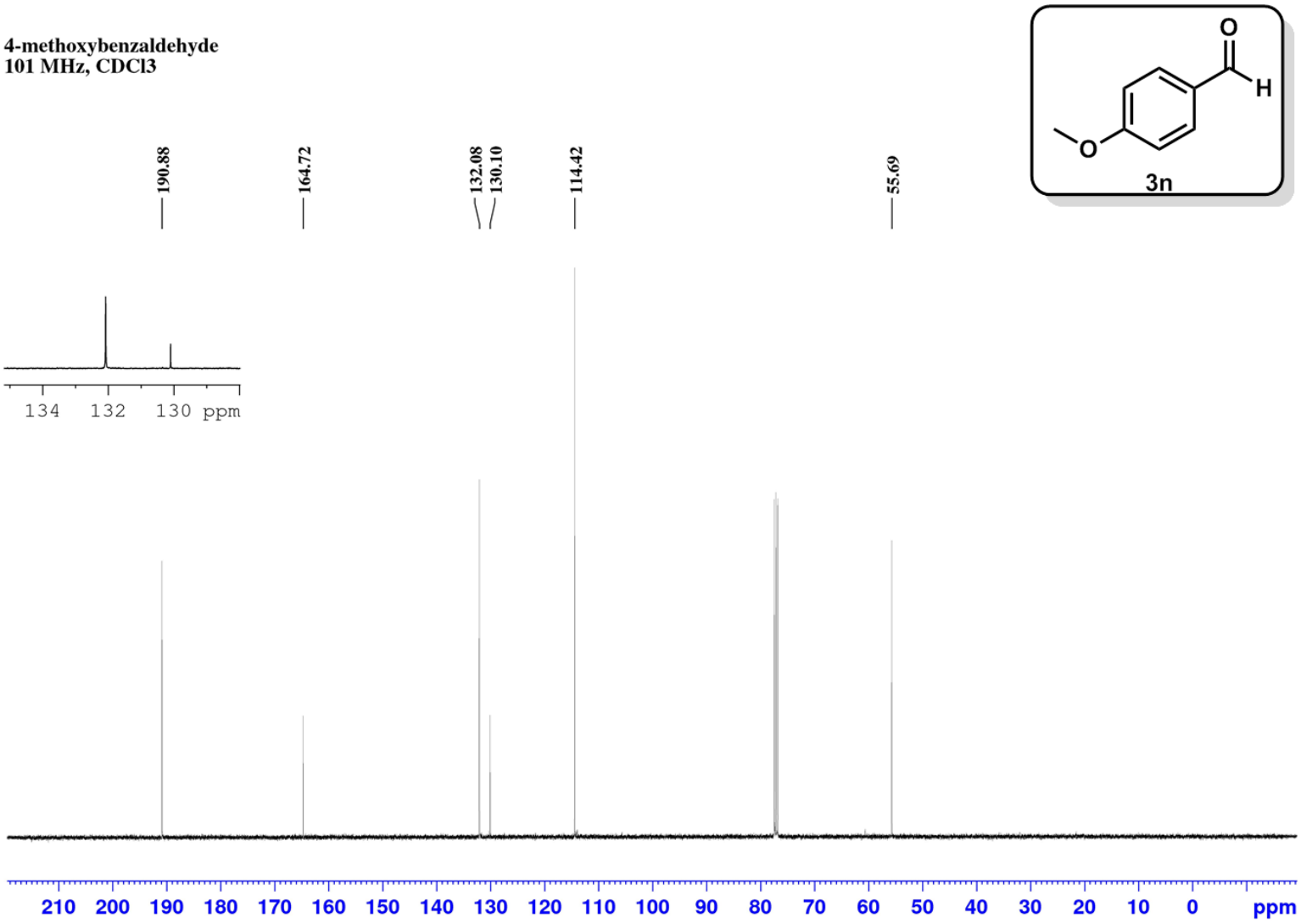
Benzophenone
400 MHz, CDCl3



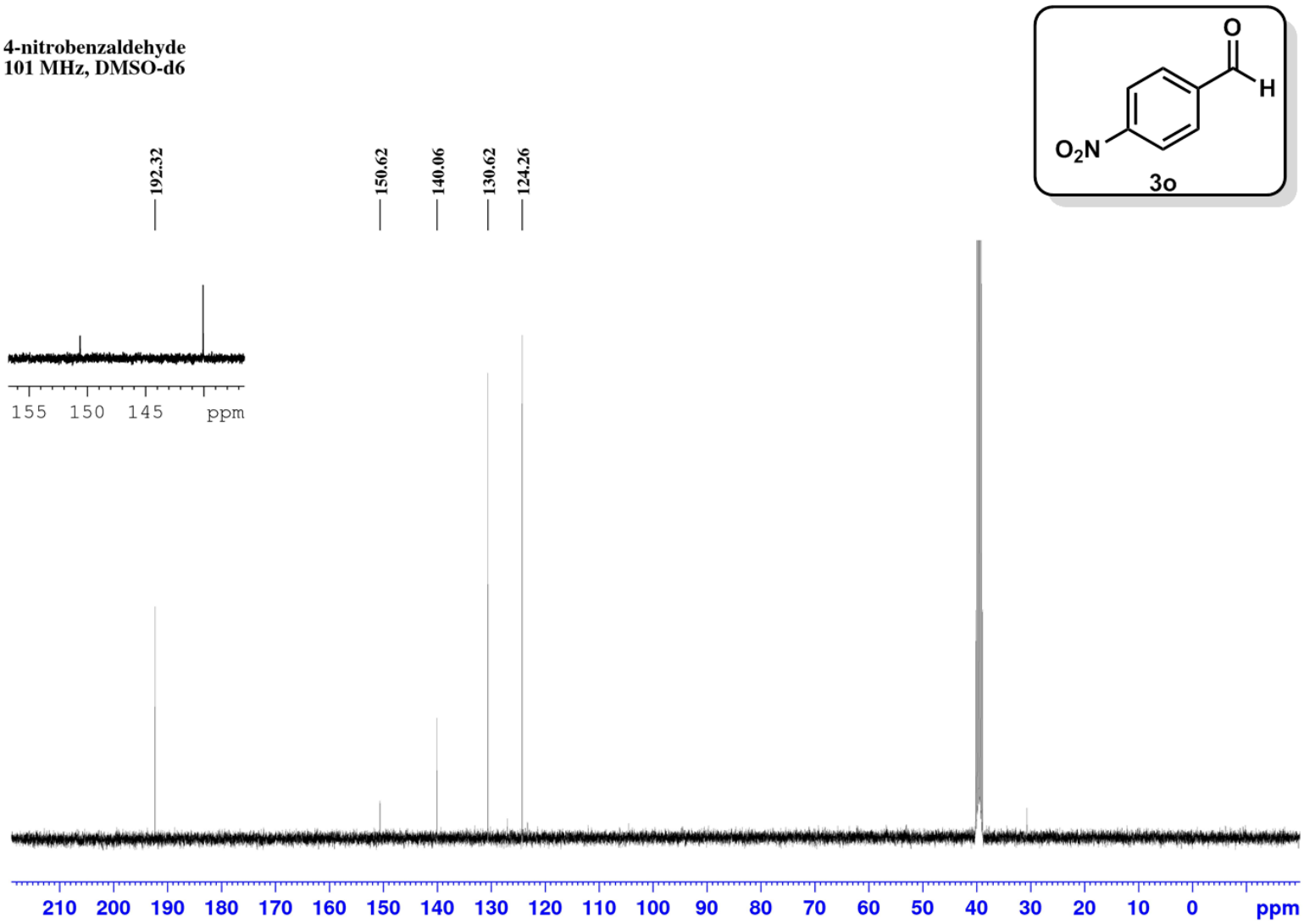
^{13}C NMR Spectra of Synthesized Non-fluorinated Aldehydes and Ketones



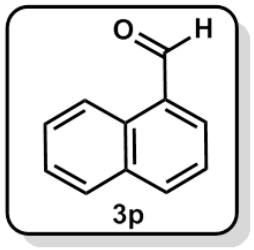
4-methoxybenzaldehyde
101 MHz, CDCl3

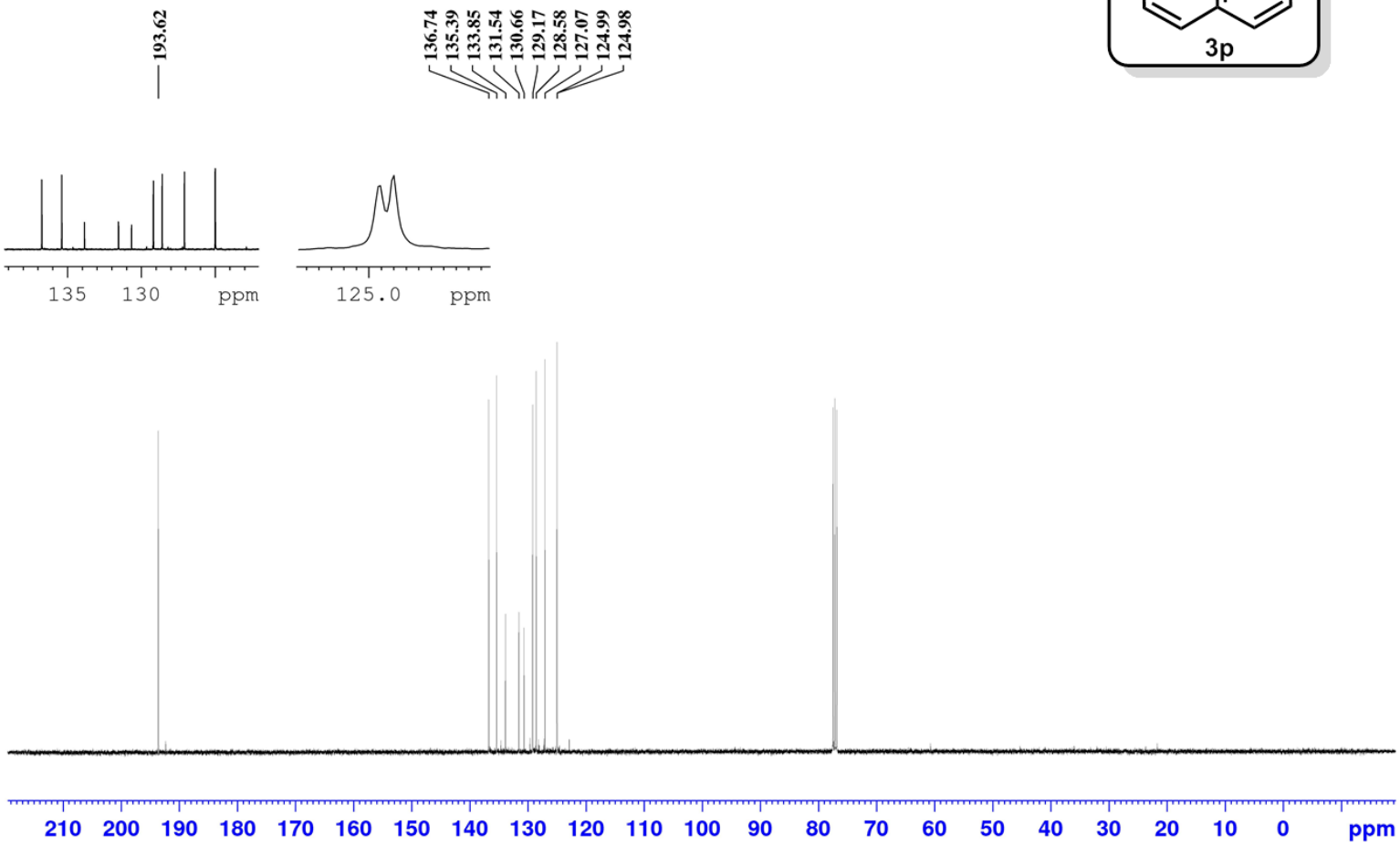


4-nitrobenzaldehyde
101 MHz, DMSO-d6

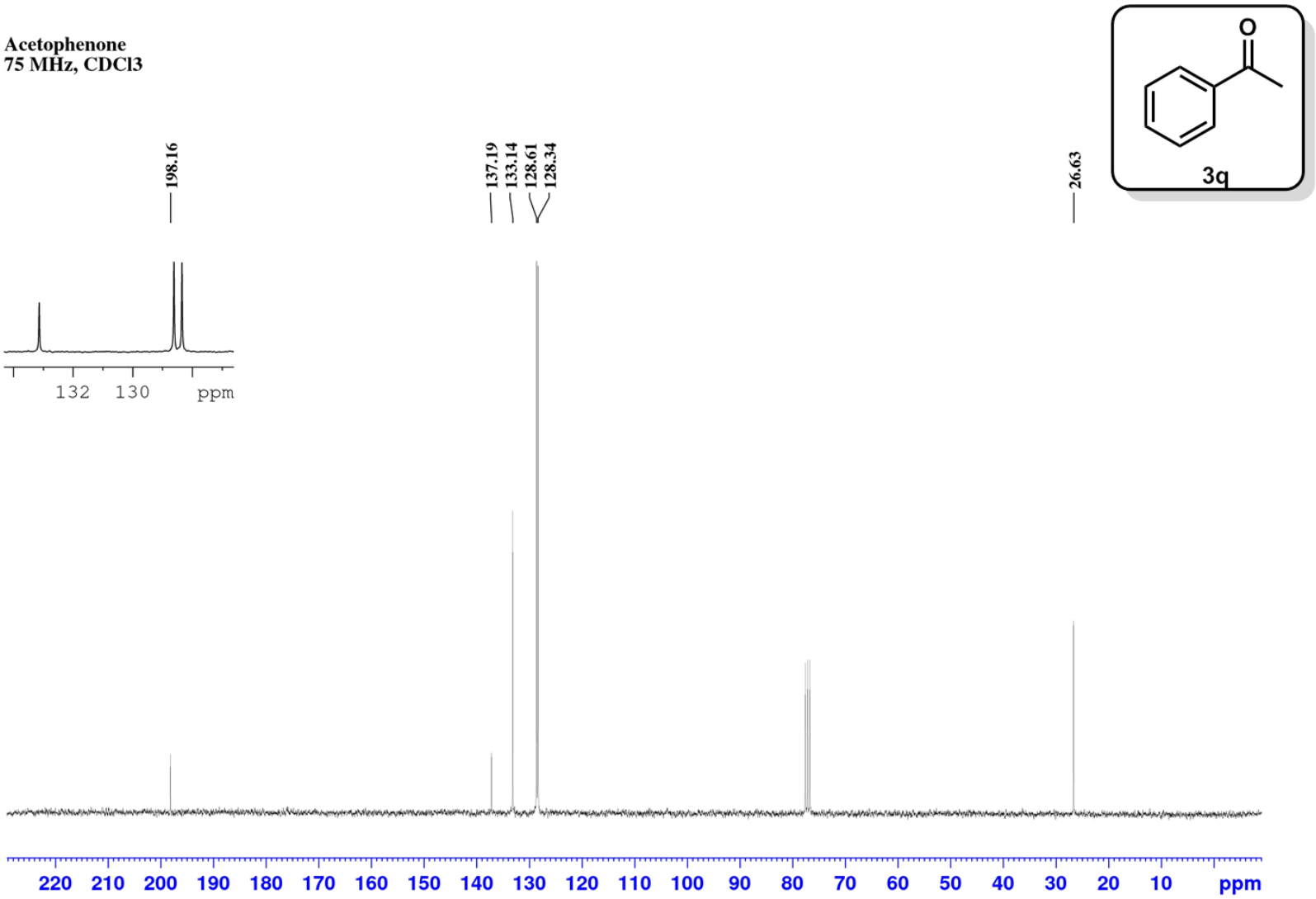


1-naphthaldehyde
101 MHz, CDCl3

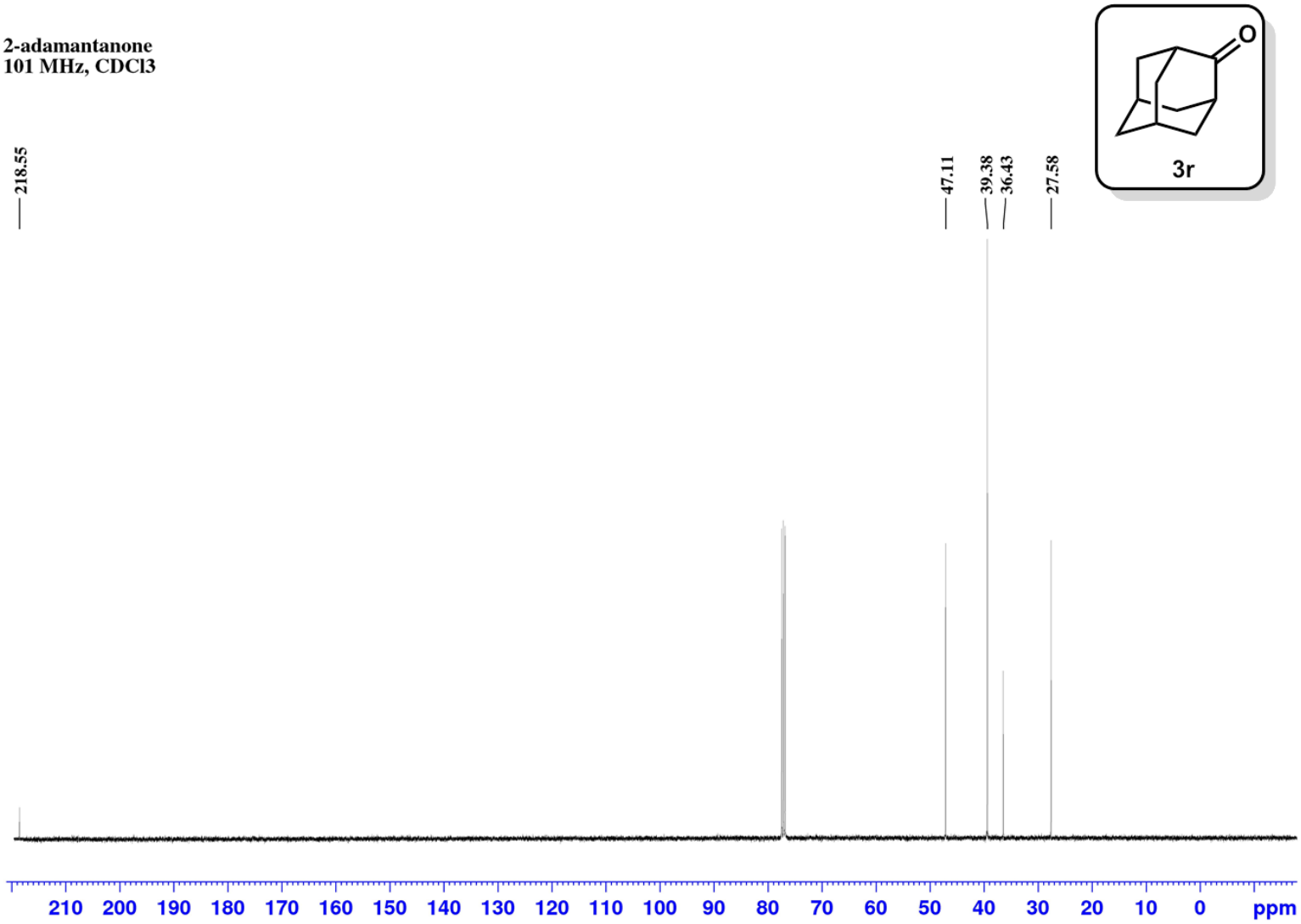




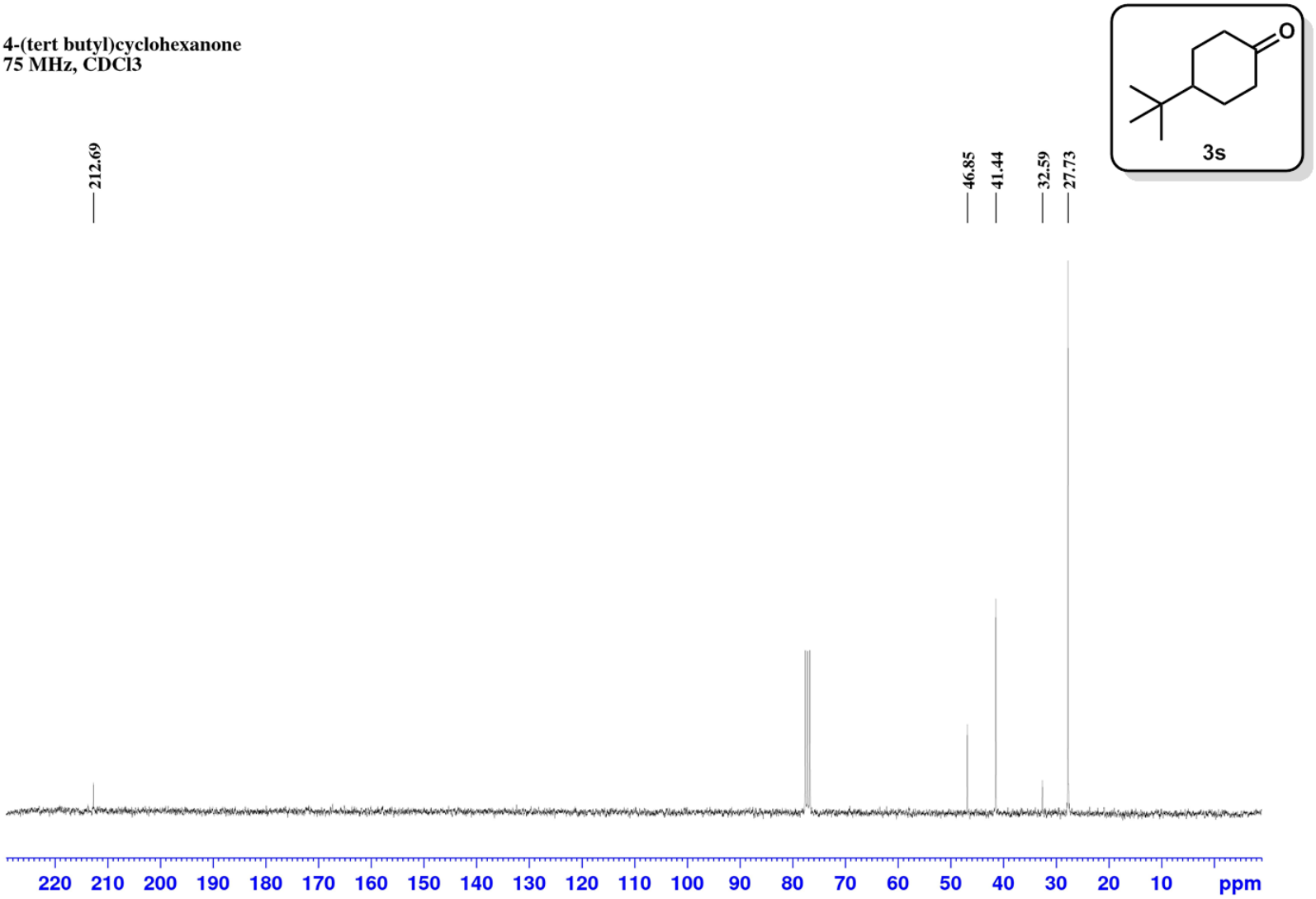
Acetophenone
75 MHz, CDCl3



2-adamantanone
101 MHz, CDCl3



4-(tert butyl)cyclohexanone
75 MHz, CDCl3



Benzophenone
101 MHz, CDCl3