Visible-light-Driven Catalytic Oxidation of Aldehydes and Alcohols to Nitriles by 4-Acetamido-TEMPO using Ammonium Carbamate as a Nitrogen Source

Jyoti Nandi,[a] and Nicholas E. Leadbeater*,[a]

[a]*Department of Chemistry, University of Connecticut, 55 N. Eagleville Road, Storrs, Connecticut 06269, USA*

Supporting Information

Key to Abbreviated Terms:

$CDCl_3$: Deuterated chloroform
TEMPO: 2,2,6,6-tetramethylpiperidine-1-oxyl
ACT: 4-Acetamido-2,2,6,6-tetramethylpiperidine-1-oxyl
$MesAcr^+BF_4^-$: 9-Mesityl-10-methylacridinium tetrafluoroborate
Bpy: 2,2′-Bipyridyl
TLC: Thin layer chromatography
SCE: Saturated calomel electrode
SET: Single electron transfer
LED: Light-emitting diode
HAT: Hydrogen atom transfer
DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene
DMAP: 4-(Dimethylamino)pyridine
Et_2O: Diethyl ether
EtOAc: Ethyl acetate
DCM: Dichloromethane
MeCN: Acetonitrile
DMF: Dimethylformamide
HMDS: Hexamethyldisilazane

General Considerations:

General: NMR Spectra (^{1}H, ^{13}C, ^{19}F) were performed at 300 K on either a Brüker Avance Ultra Shield 300 MHz NMR or Brüker DRX-400 400 MHz NMR. ^{1}H-NMR spectra were referenced to residual non-deuterated chloroform (7.26 ppm) in $CDCl_3$. ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.16 ppm). ^{19}F-NMR spectra were referenced to hexafluorobenzene (-164.9 ppm).[1] 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. Reactions were monitored by an Agilent Technologies 7820A Gas Chromatograph attached to a 5975 Mass Spectrometer, ^{1}H-NMR, and/or by TLC on silica gel plates (60Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/ethyl acetate as the eluent and visualized using permanganate stain, *p*-anisaldehyde stain, Seebach's Stain, and/or UV light. Flash chromatography and silica plugs utilized Dynamic Adsorbents Inc. Flash Silica Gel (60Å porosity, 32-63 μm).

Chemicals: Deuterated chloroform ($CDCl_3$) was purchased from Cambridge Isotope Laboratories and stored over 4Å molecular sieves and K_2CO_3. Sodium sulfate, DCM, EtOAc, hexane, pentane, diethyl ether, THF, MeCN, acetone, pyridine, $(NH_4)_2S_2O_8$, $MesAcr^{+}BF_4^{-}$ and 2,6-lutidine were purchased from Sigma-Aldrich. Hexafluorobenzene was purchased from Synquest Laboratories and/or Oakwood Chemicals. Aldehydes were either purchased from commercial suppliers (and distilled/recrystallized before use). The oxoammonium salt 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium tetrafluoroborate (Bobbitt's salt, **1a**) and 4-Acetamido-2,2,6,6-tetramethylpiperidine-1-oxyl (ACT, **1b**) was prepared according to a reported protocol.[2] 4-Acetamido-2,2,6,6-tetramethylpiperidine-*N*-hydroxyammonium tetrafluoroborate salt (**1c**) was synthesized according to a literature procedure.[3] The photocatalyst, $Ru(bpy)_3(PF_6)_2$ was prepared in laboratory by literature procedures.[4] The larger pellets of ammonium carbamate were crushed in mortal-pestle prior to use.

Photochemistry: Irradiation of reaction vessels was accomplished using blue LED strips. LEDs were configured as outlined in the *Photochemical Reactor Design* section of previous articles.[5] A fan was employed to ensure reactions remained at or near rt when using LEDs.

Information for LED-based Photoreactor Components:

- *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

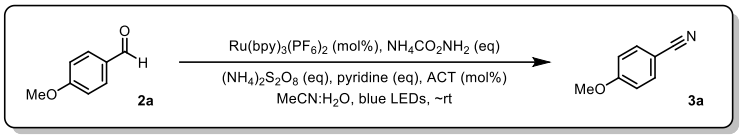
1. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.
2. Mercadante, M. A.; Kelly, C. B.; Bobbitt, J. M.; Tilley, L. J.; Leadbeater, N. E. *Nat. Protoc.* **2013**, *8*, 666.
3. Miller, S. A.; Bisset, K. A.; Leadbeater, N. E.; Eddy, N. A. *Eur. J. Org. Chem.* 10.1002/ejoc.201801718.
4. Kelly, C. B.; Patel, N. R.; Primer, D. N.; Jouffroy, M.; Tellis, J. C.; Molander, G. A. *Nat. Protoc.* **2017**, *12*, 472.
5. For information on these reactors and their construction see the supporting information of: Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 764.

Optimization & Control Studies for Nitrile Synthesis from Aldehydes:

Procedure for optimization and control studies:

To a 1-dram reaction vial equipped with a stirbar was added the photocatalyst, primary oxidant and $NH_4CO_2NH_2$, followed by the solvent. Then, the vial was charged with aldehyde (0.0005 mol, 1 eq), pyridine and $(NH_4)_2S_2O_8$. The vial was sealed with a cap and a piece of parafilm. It was irradiated in blue LED reactor for 24 h unless noted otherwise. The temperature of the reaction was maintained at approximately room temperature by using a fan over the light set up. After this time, the reaction mixture was quenched with EtOAc and transferred to a separatory funnel. It was diluted with EtOAc (30 ml) and 2 M aqueous HCl (30 ml). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 20 ml). The organic layers were then combined and washed with 2 M aqueous HCl (2 × 20 ml). The organic layer was then dried over sodium sulfate and the solvent was removed *in vacuo* to afford the crude product. Conversion to nitrile was determined by integration of signals in the ^{1}H-NMR spectrum of the crude product mixture in acetone-D_6.

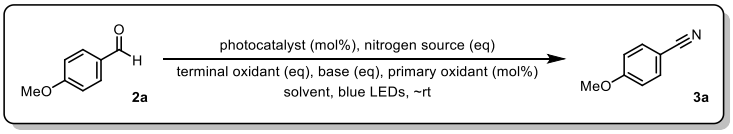
Table S1: Optimization of the ACT/Photoredox Dual Catalytic Process



Entry	$Ru(bpy)_3(PF_6)_2$ (mol%)	ACT (mol%)	$NH_4CO_2NH_2$ (eq)	Pyridine (eq)	$(NH_4)_2S_2O_8$ (eq)	MeCN:H_2O (ml)	Product (%)[a]	Aldehyde (%)[a]
1	2	20	4	2.5	2.2	0.95:0.05	95	2
2	2	20	4	2.5	2.2	0.99:0.01	75	21
3	2	20	4	2.5	2.2	0.50:0.50	22	66
4	2	20	4	2.5	2.2	0.80:0.20	34	52
5	2	20	4	2.5	2.2	1:0	77	18
6	2	20	4	2.5	2.2	0:1	10	82
7	2	20	4	0	2.2	0.95:0.05	79	13
8	2	20	4	10[b]	2.2	0.95:0.05	74	13
9	2	20	4	1.5	2.2	0.95:0.05	86	10
10	2	20	4	4	2.2	0.95:0.05	96	1
11	2	20	4	2.5[c]	2.2	0.95:0.05	14	81
12	1	20	4	2.5	2.2	0.95:0.05	86	11
13	5	20	4	2.5	2.2	0.95:0.05	92	5
14	2	10	4	2.5	2.2	0.95:0.05	86	11
15	2	40	4	2.5	2.2	0.95:0.05	88	10
17	2	20	4	2.5	1.5	0.95:0.05	80	17
18	2	20	4	2.5	4	0.95:0.05	89	6
19	2	20	1.5	2.5	2.2	0.95:0.05	77	10
20	2	20	2.5	2.5	2.2	0.95:0.05	90	7
21	2	20	6	2.5	2.2	0.95:0.05	93	4

[a] Conversion determined by integration of signals in the ^{1}H-NMR spectrum of the crude product mixture in acetone-D_6. [b] 10 mol% of pyridine was used. [c] Acetic acid was used instead of pyridine.

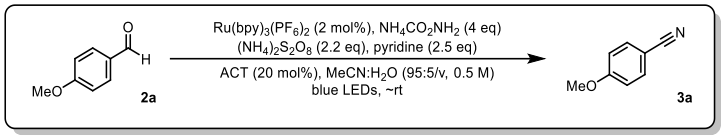
Table S2: Optimization of the ACT/Photoredox Dual Catalytic Process



Entry	Photocatalyst (mol%)	Primary oxidant (mol%)	Nitrogen source (eq)	Base (eq)	Terminal oxidant (eq)	Solvent	Product (%)[a]	Aldehyde (%)[a]
1	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	95	2
2	$(Ir[dF(CF_3)PP]_2(dtbpy))PF_6$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	32	65
3[b]	Eosin Y, 5	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	17	77
4	9-mesityl-10-methylacridinium BF_4^-, 5	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	6	88
5	$Ru(bpy)_3(PF_6)_2$, 2	Bobbitt's salt, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	62	30
6	$Ru(bpy)_3(PF_6)_2$, 2	TEMPO, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	90	5
7[c]	$Ru(bpy)_3(PF_6)_2$, 2	**1c**, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	51	45
8[d]	$Ru(bpy)_3(PF_6)_2$, 2	**1d**, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	90	6
9	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	HMDS, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	68	23
10	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	HMDS, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	38	55
11	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	Aq. NH_3, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	91	2
12	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	DBU, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	76	11
13	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	2,6-lutidine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	86	10
14	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	DMAP, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	27	70
15	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	^tBuOOH, 2.2	MeCN:H_2O 95:5 (0.5M)	83	7
16	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	Oxygen balloon	MeCN:H_2O 95:5 (0.5M)	2	91
17	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$Na_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	92	4
18	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$K_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	65	31
19	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	NaOCl. $5H_2O$, 2.2	MeCN:H_2O 95:5 (0.5M)	90	4
20	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	6	81
21	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	DCE:H_2O 95:5 (0.5M)	37	60
22	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	DCM:H_2O 95:5 (0.5M)	37	61
23	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	DMF:H_2O 95:5 (0.5M)	33	46
24	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	Toluene:H_2O 95:5 (0.5M)	12	86
25[e]	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	92	5
26[f]	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	92	5
27[g]	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 95:5 (0.5M)	71	26
28	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 90:10 (0.1M)	60	31
29	$Ru(bpy)_3(PF_6)_2$, 2	ACT, 20	$NH_4CO_2NH_2$, 4	Pyridine, 2.5	$(NH_4)_2S_2O_8$, 2.2	MeCN:H_2O 19:1 (0.25M)	84	13
30[h]	**$Ru(bpy)_3(PF_6)_2$, 2**	**ACT, 20**	**$NH_4CO_2NH_2$, 4**	**Pyridine, 2.5**	**$(NH_4)_2S_2O_8$, 2.2**	**MeCN:H_2O 95:5 (0.74M)**	**95**	**2**

[a] Conversion determined by integration of signals in the ^{1}H-NMR spectrum of the crude product mixture in acetone-D_6. [b] Green LED strips was used in place of blue LED strips. [c] **1c**: 4-Acetamido-2,2,6,6-tetramethylpiperidine-*N*-hydroxyammonium tetrafluoroborate salt. [d] **1d**: 4-Acetamido-2,2,6,6-tetramethylpiperidine-*N*-hydroxylamine. [e] Blue LED lamp was used in place of blue LED strips. [f] White LED strips was used in place of blue LED strips. [g] Household bulb was used in place of blue LED strips. [h] Reaction performed with 0.001 mol of **2a** instead of 0.0005 mol.

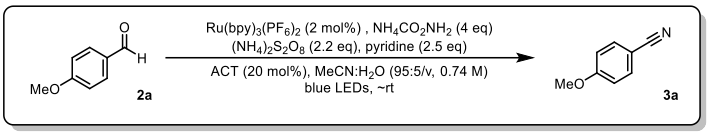
Table S3: Control Studies for the ACT/Photoredox Dual Catalytic Process



Entry	Omitted component	Conversion to a (%)[a]
1	none	95
2	$Ru(bpy)_3(PF_6)_2$	0
3[b]	ACT	11
4	light	0
5	$(NH_4)_2S_2O_8$	0
6	$NH_4CO_2NH_2$	23

[a] Conversion determined by integration of signals in the ^{1}H-NMR spectrum of the crude product mixture in acetone-D_6. [b] Mixture of oxidized products formed including trace amount of product, carboxylic acid and amide along with several unidentified products.

Procedure for the Photo-oxidation of Aldehydes to Nitriles



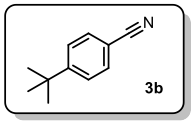
4-methoxybenzonitrile, 3a

To a 2-dram reaction vial equipped with a stirbar was added the $Ru(bpy)_3(PF_6)_2$ (0.017 g, 0.00002 mol, 0.02 eq), ACT (0.043 g, 0.0002 mol, 0.2 eq) and $NH_4CO_2NH_2$ (0.312 g, 0.004 mol, 4 eq) was added followed by 1.3 ml of MeCN and 0.06 ml of water (95:5/v, 0.74 M in aldehyde). Then, the vial was charged with *p*-anisaldehyde, **2a** (0.136 g, 0.001 mol, 1 eq), pyridine (0.198 g, 0.0025 mol, 2.5 eq) and $(NH_4)_2S_2O_8$ (0.502 g, 0.0022 mol, 2.2 eq). The vial was sealed with a cap and a piece of parafilm. It was irradiated in blue LED reactor for 24 h unless noted otherwise. The temperature of the reaction was maintained at approximately room temperature by using a fan over the light set up. After this time, the reaction mixture was quenched with Et_2O, filtered through a coarse porosity fritted glass funnel, and transferred into a separatory funnel. It was diluted with Et_2O (30 ml) and 2 M aqueous HCl (30 ml). The layers were separated, and the aqueous layer was extracted with Et_2O (3 × 20 ml). The organic layers were then combined and washed with 2 M aqueous HCl (2 × 20 ml), saturated aqueous sodium bicarbonate (2 × 20 ml), and finally with brine (20 ml). The organic layer was then dried over sodium sulfate and the solvent was evaporated *in vacuo* to ~20 ml. To eliminate any unreacted aldehyde, 25 ml of 1 M aqueous sodium metabisulfite solution was added to the organic layer and stirred for 3-4 h. The reaction mixture was transferred into separatory funnel and the aqueous layer was extracted with EtOAc (3 × 20 ml). The organic layers were combined, dried over sodium sulfate, and concentrated *in vacuo* to afford the crude product.

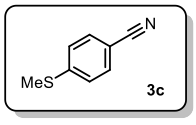
To further purify the product from any polar impurities, the resulting crude mixture was adhered to silica gel using 1.5 weight equivalents of SiO_2 (relative to the theoretical yield). The dry-packed material was gently added atop a silica gel plug. The plug was washed with an excess of hexanes (≈ 5 column volumes). The desired product was eluted off the plug *via* a 90:10 by volume mixture of hexanes: EtOAc (3-4 column volumes). The solvent was removed *in vacuo* by rotary evaporation affording the pure nitrile **3a** (0.120 g, 90%) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.58 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H).

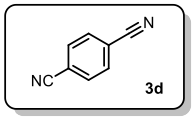
^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 162.98, 134.11, 119.34, 114.88, 104.12, 55.66.



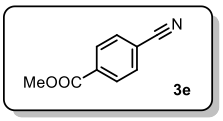
4-(*tert*-butyl)benzonitrile, 3b (0.156 g, 98%) was prepared according to the general procedure from 4-(*tert*-butyl)benzaldehyde, **2b** (0.162 g, 0.001 mol) **with the following modification:** no further purification was needed after work-up. The desired nitrile, **3b** was isolated as a clear, orangish-yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.57 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 1.32 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 156.70, 132.01, 126.23, 119.19, 109.37, 35.31, 30.99.



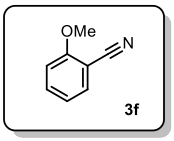
4-(methylthio)benzonitrile, 3c (0.107 g, 72%) was prepared according to the general procedure from 4-(methylthio)benzaldehyde, **2c** (0.152 g, 0.001 mol) **with the following modifications:** 1) 5 eq of pyridine (0.395 g, 0.005 mol) was used; 2) No further purification was needed after work-up. The desired nitrile, **3c** was isolated as an off-white solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.52 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 2.50 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 146.22, 132.24, 125.60, 119.05, 107.75, 14.78.



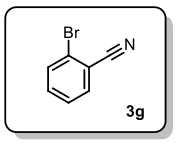
Terephthalonitrile, 3d (0.077 g, 60%) was prepared according to the general procedure from 4-cyanobenzaldehyde, **2d** (0.131 g, 0.001 mol) **with the following modification:** no further purification was needed after work-up. The desired nitrile, **3d** was isolated as an off-white solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.79 (s, 4H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 132.92, 117.12, 116.85.



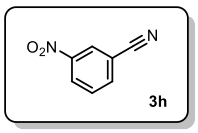
Methyl 4-cyanobenzoate, 3e (0.130 g, 81%) was prepared according to the general procedure from methyl 4-formylbenzoate, **2e** (0.164 g, 0.001 mol) **with the following modification:** no further purification was needed after work-up. The desired nitrile, **3e** was isolated as an off-white solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 8.11 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 3.94 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 165.48, 134.00, 132.29, 130.16, 118.01, 116.46, 52.78.



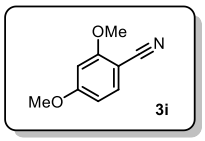
2-methoxybenzonitrile, 3f (0.113 g, 85%) was prepared according to the general procedure from 2-methoxybenzaldehyde, **2f** (0.136 g, 0.001 mol) **with the following modifications:** 1) 5 eq of pyridine (0.395 g, 0.005 mol) was used; 2) No further purification was needed after work-up. The desired nitrile, **3f** was isolated as a pale-yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.52 (ddd, *J* = 7.4, 4.5, 2.7 Hz, 2H), 7.01-6.93 (m, 2H), 3.90 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 161.25, 134.48, 133.73, 120.80, 116.55, 111.38, 101.74, 56.03.



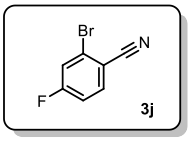
2-bromobenzonitrile, 3g (0.158 g, 87%) was prepared according to the general procedure from 2-bromobenzaldehyde, **2g** (0.185 g, 0.001 mol) **with the following modifications:** 1) 5 eq of pyridine (0.395 g, 0.005 mol) was used; 2) No further purification was needed after work-up. The desired nitrile, **3g** was isolated as a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$ in TMS) δ ppm 7.72-7.64 (m, 2H), 7.49-7.39 (m, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 134.41, 134.01, 133.30, 127.75, 125.39, 117.22, 115.95.



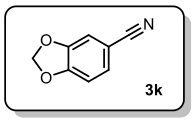
3-nitrobenzonitrile, 3h (0.078 g, 53%) was prepared according to the general procedure from 3-nitrobenzaldehyde, **2h** (0.151 g, 0.001 mol) **with the following modifications:** 1) No aldehyde elimination was needed after work-up; 2) Silica gel plug was performed with 85:15/v mixture of hexanes: EtOAc in place of 90:10. The desired nitrile, **3h** was isolated as an off-white flake. ^{1}H-NMR (400 MHz, $CDCl_3$ in TMS) δ ppm 8.54 (t, *J* = 1.9 Hz, 1H), 8.48 (ddd, *J* = 8.3, 2.3, 1.1 Hz, 1H), 8.00 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 148.30, 137.72, 130.78, 127.62, 127.29, 116.62, 114.18.



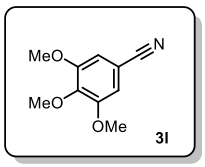
2,4-dimethoxybenzonitrile, 3i (0.141 g, 86%) was prepared according to the general procedure from 2,4-dimethoxybenzaldehyde, **2i** (0.166 g, 0.001 mol) **with the following modification:** no further purification was needed after work-up. The desired nitrile, **3i** was isolated as a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.08 (dd, *J* = 9.1, 3.1 Hz, 1H), 7.04 (d, *J* = 3.0 Hz, 1H), 6.89 (d, *J* = 9.1 Hz, 1H), 3.87 (s, 3H), 3.77 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 155.85, 153.29, 120.92, 117.74, 116.48, 112.75, 101.93, 56.53, 56.07.



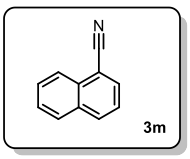
2-bromo-4-fluorobenzonitrile, 3j (0.184 g, 92%) was prepared according to the general procedure from 2-bromo-4-fluorobenzaldehyde, **2j** (0.203 g, 0.001 mol) **with the following modifications:** 1) 5 eq of pyridine (0.395 g, 0.005 mol) was used; 2) No further purification was needed after work-up. The desired nitrile, **3j** was isolated as an off-white solid. ^{1}H-NMR (400 MHz, $CDCl_3$ in TMS) δ ppm 7.68 (dd, *J* = 8.7, 5.5 Hz, 1H), 7.45 (dd, *J* = 8.0, 2.5 Hz, 1H), 7.16 (ddd, *J* = 8.7, 7.7, 2.5 Hz, 1H).^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 164.60 (d, *J* = 261.1 Hz), 136.13 (d, *J* = 9.7 Hz), 126.83 (d, *J* = 10.2 Hz), 121.32 (d, *J* = 25.3 Hz), 116.55, 115.81 (d, *J* = 22.5 Hz), 112.40 (d, *J* = 3.8 Hz).



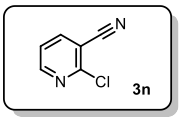
3,4-(methylenedioxy)benzonitrile, 3k (0.066 g, 45%) was prepared according to the general procedure from piperonal, **2k** (0.150 g, 0.001 mol) **with the following modifications:** 1) 5 eq of pyridine (0.395 g, 0.005 mol) was used; 2) No further purification was needed after the elimination of aldehyde. The desired nitrile, **3k** was isolated as an off-white solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm 7.24-7.18 (m, 1H), 7.03 (d, *J* = 1.6 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.07 (s, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm 151.67, 148.17, 128.37, 119.04, 111.56, 109.27, 105.11, 102.35.



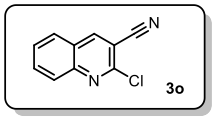
3,4,5-trimethoxybenzonitrile, 3l (0.173 g, 90%) was prepared according to the general procedure from 3,4,5-trimethoxybenzaldehyde, **2l** (0.196 g, 0.001 mol) **with the following modifications:** 1) 5 eq of pyridine (0.395 g, 0.005 mol) was used; 2) No further purification was needed after work-up. The desired nitrile, **3l** was isolated an off-white solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 6.83 (t, *J* = 2.0 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 6H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 153.62, 142.41, 118.99, 109.53, 106.75, 61.06, 56.44.



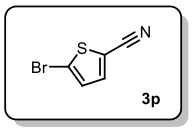
1-naphthonitrile, 3m (0.124 g, 81%) was prepared according to the general procedure from 1-naphthaldehyde, **2m** (0.156 g, 0.001 mol) **with the following modification:** no further purification was needed after work-up. The desired nitrile, **3m** was isolated as a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 8.22 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.90 (t, *J* = 7.9 Hz, 2H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 133.39, 133.05, 132.74, 132.49, 128.77, 128.71, 127.67, 125.27, 125.04, 117.93, 110.33.



2-chloro-3-pyridinecarbonitrile, 3n (0.042 g, 30%) was prepared according to the general procedure from 2-chloro-3-pyridinecarboxaldehyde **2n** (g, 0.001 mol) **with the following modifications:** 1) 5 eq of pyridine (0.395 g, 0.005 mol) was used; 2) Ran for 18 h instead of 24 h; 3) No aldehyde elimination was needed after work-up; 4) Silica gel plug was performed with 85:15/v mixture of hexanes: EtOAc in place of 90:10. The desired nitrile, **3n** was isolated as an off-white solid. ^{1}H-NMR (400 MHz, $CDCl_3$ in TMS) δ ppm 8.62 (dd, *J* = 4.9, 2.0 Hz, 1H), 8.02 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.40 (dd, *J* = 7.7, 4.9 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 152.99, 152.96, 142.70, 122.32, 114.68, 111.09.

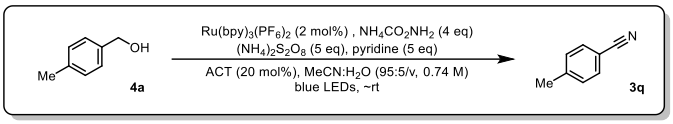


2-chloroquinoline-3-carbonitrile, 3o (0.147 g, 78%) was prepared according to the general procedure from 2-chloroquinoline-3-carboxaldehyde, **2o** (0.192 g, 0.001 mol) **with the following modifications:** 1) 5 eq of pyridine (0.395 g, 0.005 mol) was used; 2) The aqueous layer was extracted with EtOAc in place of Et_2O; 3) No further purification was needed after an elimination of the aldehyde. The desired nitrile, **3o** was isolated as an off-white solid. ^{1}H-NMR (400 MHz, $CDCl_3$ in TMS) δ ppm 8.57 (s, 1H), 8.09 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.96-7.87 (m, 2H), 7.71 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 148.38, 148.37, 144.95, 134.03, 129.02, 128.84, 128.21, 125.25, 115.17, 108.02.



5-bromothiophene-2-carbonitrile, 3p (0.131 g, 70%) was prepared according to the general procedure from 5-bromothiophene-2-carboxaldehyde, **2p** (0.191 g, 0.001 mol) **with the following modifications:** 1) 5 eq of pyridine (0.395 g, 0.005 mol) was used; 2) No further purification was needed after the elimination of aldehyde. The desired nitrile, **3p** was isolated as a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$ in TMS) δ ppm 7.39 (d, *J* = 4.0 Hz, 1H), 7.10 (d, *J* = 4.1 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 138.04, 130.79, 120.22, 113.18, 111.40.

One-Pot Procedure for the Photo-oxidation of Alcohols to Nitriles

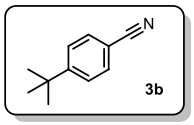


4-methylbenzonitrile, 3q

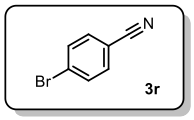
To a 2-dram reaction vial equipped with a stirbar was added the $Ru(bpy)_3(PF_6)_2$ (0.017 g, 0.00002 mol, 0.02 eq), ACT (0.043 g, 0.0002 mol, 0.2 eq) and $NH_4CO_2NH_2$ (0.312 g, 0.004 mol, 4 eq) was added followed by 1.3 ml of MeCN and 0.06 ml of water (95:5/v, 0.74 M in aldehyde). Then, the vial was charged with 4-methylbenzyl alcohol, **4a** (0.122 g, 0.001 mol, 1 eq), pyridine (0.395 g, 0.005 mol, 5 eq) and $(NH_4)_2S_2O_8$ (1.141 g, 0.005 mol, 5 eq). The vial was sealed with a cap and a piece of parafilm. It was irradiated in blue LED reactor for 24 h unless noted otherwise. The temperature of the reaction was maintained at approximately room temperature by using a fan over the light set up. After this time, the reaction mixture was quenched with Et_2O, filtered through a coarse porosity fritted glass funnel, and transferred into a separatory funnel. It was diluted with Et_2O (30 ml) and 2 M aqueous HCl (30 ml). The layers were separated, and the aqueous layer was extracted with Et_2O (3 × 20 ml). The organic layers were then combined and washed with 2 M aqueous HCl (2 × 20 ml), saturated aqueous sodium bicarbonate (2 × 20 ml), and finally with brine (20 ml). The organic layer was then dried over sodium sulfate and the solvent was removed *in vacuo* by rotary evaporation affording the pure nitrile **3q** (0.097 g, 83%) as yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.51 (d, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 2.40 (s, 3H).

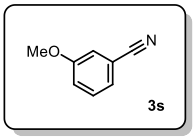
^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 143.74, 132.03, 129.86, 119.15, 109.29, 21.82.



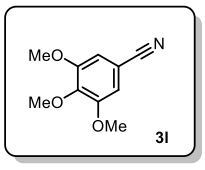
4-(*tert*-butyl)benzonitrile, 3b (0.143 g, 90%) was prepared according to the general procedure from 4-(*tert*-butyl)benzyl alcohol, **4b** (0.164 g, 0.001 mol). The desired nitrile, **3b** was isolated as a clear, yellowish-orange oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.56 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 1.31 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 156.64, 131.95, 126.18, 119.13, 109.31, 35.25, 30.93.



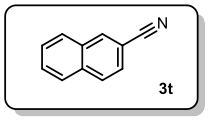
4-bromobenzonitrile, 3r (0.160 g, 88%) was prepared according to the general procedure from 4-bromobenzyl alcohol, **4c** (0.187 g, 0.001 mol) **with the following modification:** silica gel plug was performed with 90:10/v mixture of hexanes: EtOAc after work-up to afford the desired nitrile, **3r** as an off-white solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.67-7.59 (m, 2H), 7.55-7.49 (m, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 133.54, 132.79, 128.15, 118.18, 111.41.



3-methoxybenzonitrile, 3s (0.100 g, 75%) was prepared according to the general procedure from 3-methoxybenzyl alcohol, **4d** (0.138 g, 0.001 mol). The desired nitrile, **3s** was isolated as a pale, yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.42-7.34 (m, 1H), 7.26 (t, *J* = 6.2 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 2H), 3.84 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 159.78, 130.45, 124.62, 119.45, 118.86, 116.97, 113.35, 55.66.



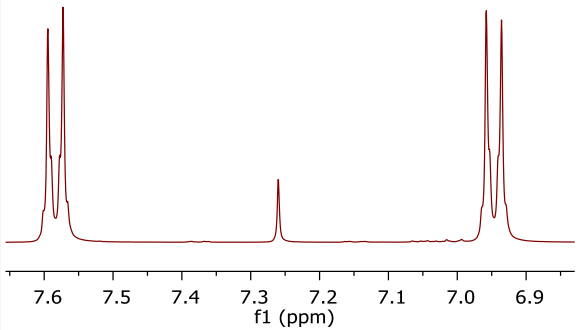
3,4,5-trimethoxybenzonitrile, 3l (0.162 g, 84%) was prepared according to the general procedure from 3,4,5-trimethoxybenzyl alcohol, **4e** (0.198 g, 0.001 mol). The desired nitrile, **3l** was isolated as an off-white solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 6.82 (t, *J* = 2.5 Hz, 2H), 3.85 (s, 3H), 3.83 (s, 6H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 153.58, 142.36, 118.95, 109.49, 106.70, 61.01, 56.40.

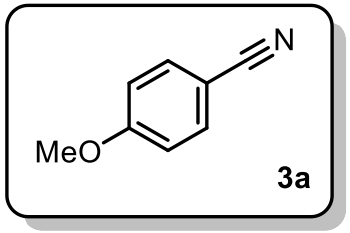


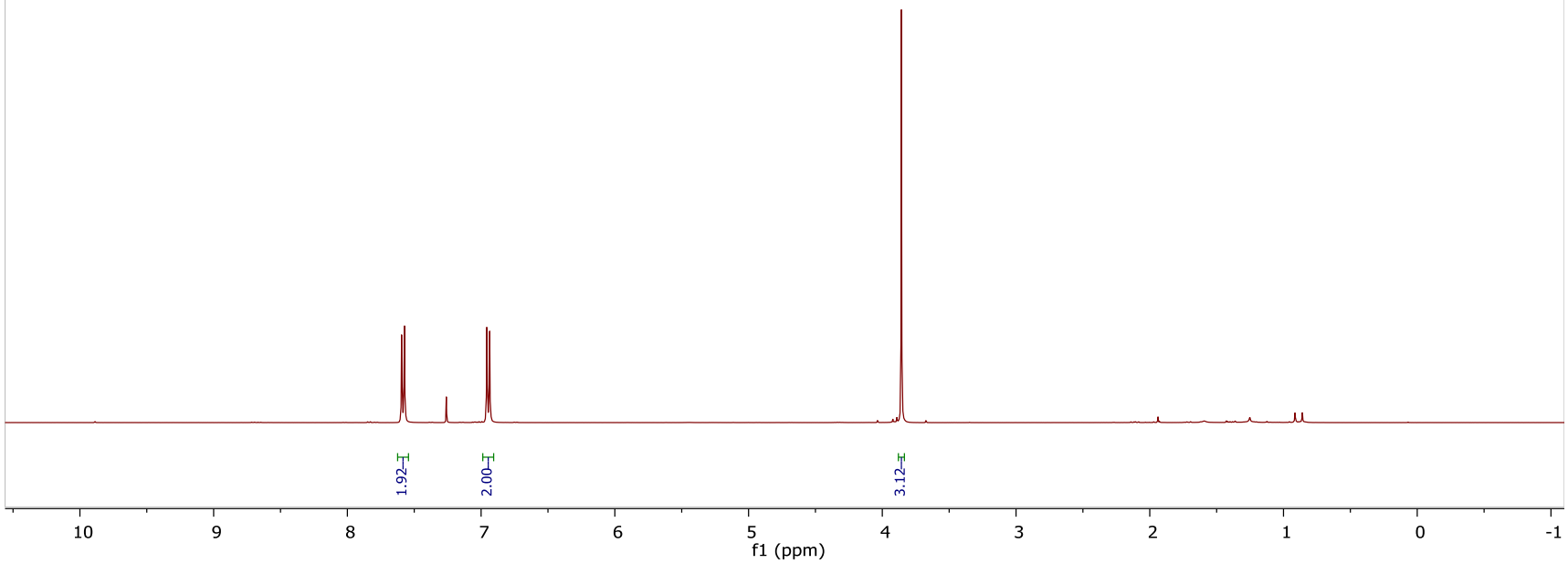
2-naphthalonitrile, 3t (0.133 g, 87%) was prepared according to the general procedure from 2-naphthalenemethanol, **4f** (0.158 g, 0.001 mol) **with the following modification:** ran for 48 h instead of 24 h to obtain complete conversion to product. The desired nitrile, **3t** was isolated as an orange solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 8.19 (s, 1H), 7.87 (t, *J* = 8.0 Hz, 3H), 7.61 (dt, *J* = 17.6, 7.7 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 134.68, 134.18, 132.28, 129.24, 129.10, 128.45, 128.10, 127.71, 126.36, 119.30, 109.41.

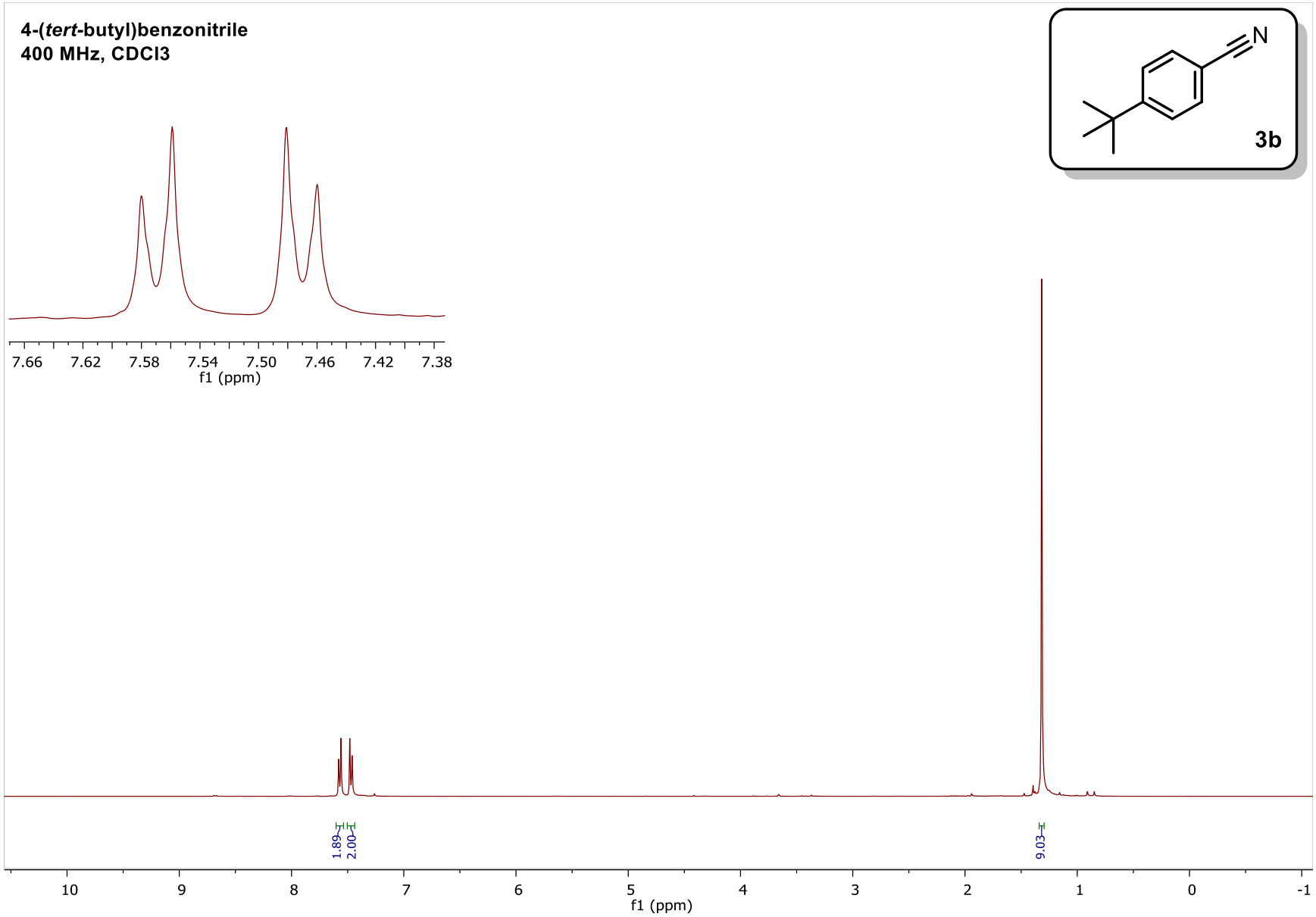
^{1}H-NMR Spectra of Synthesized Compounds

4-methoxybenzonitrile
400 MHz, CDCl3

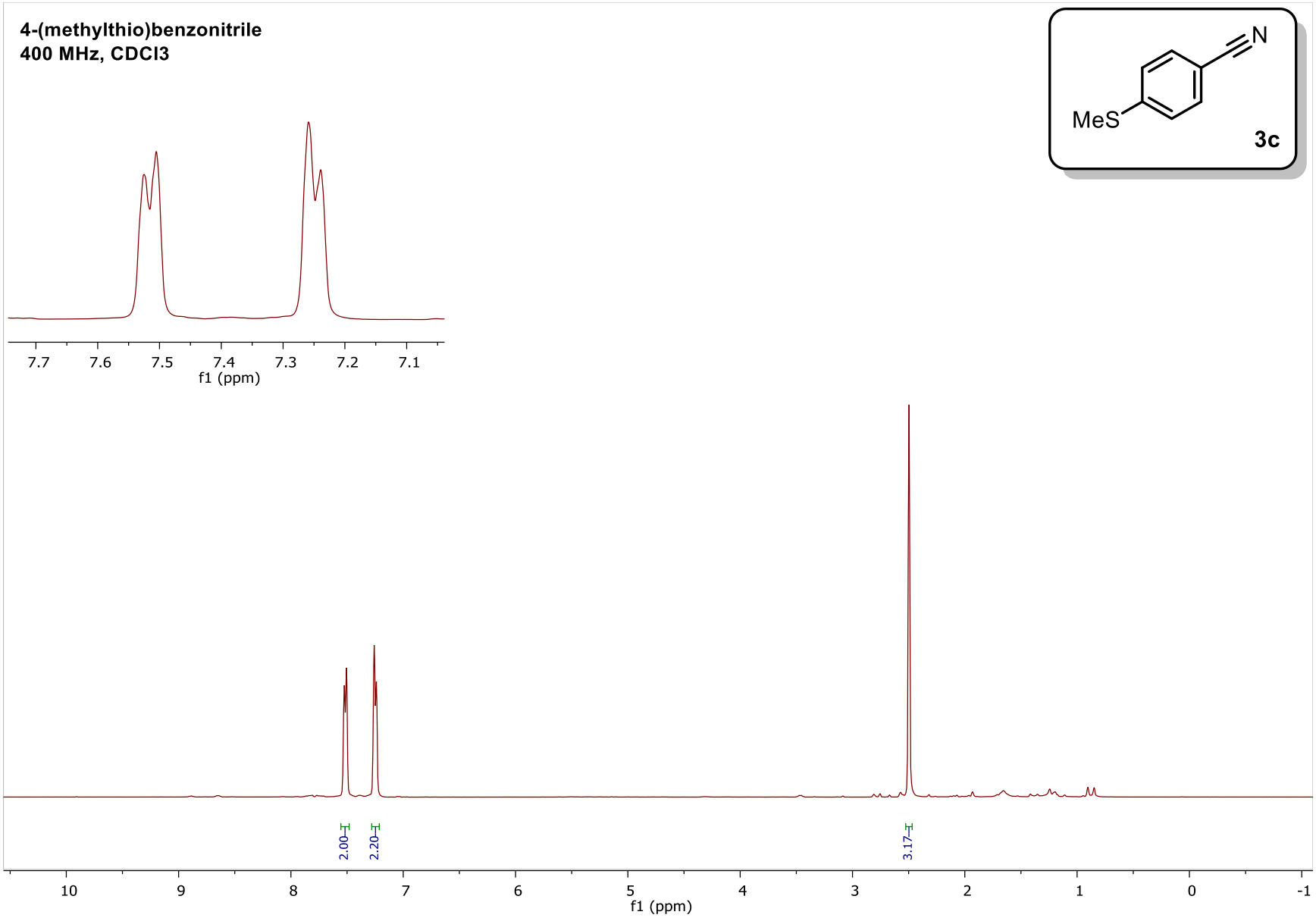




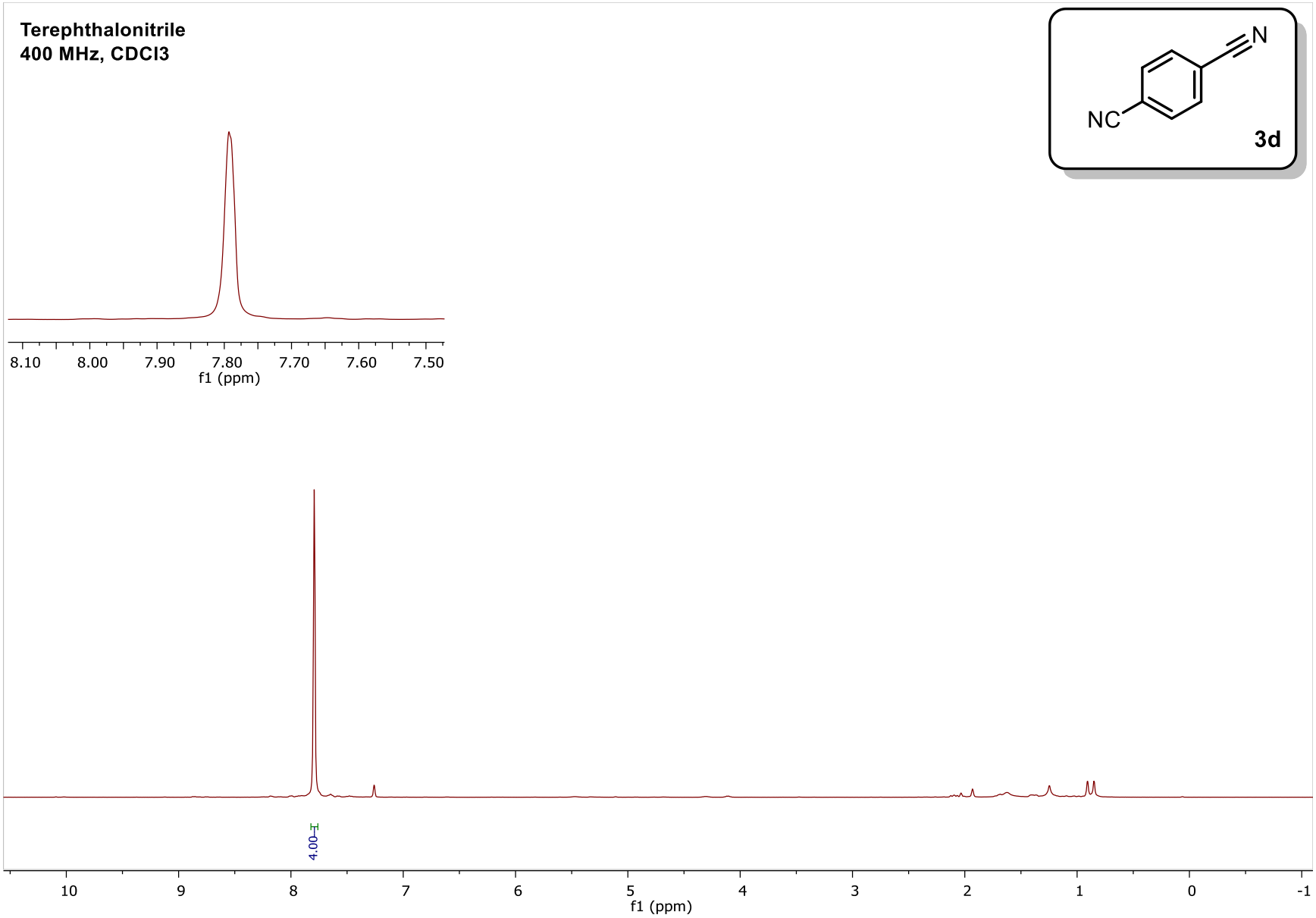


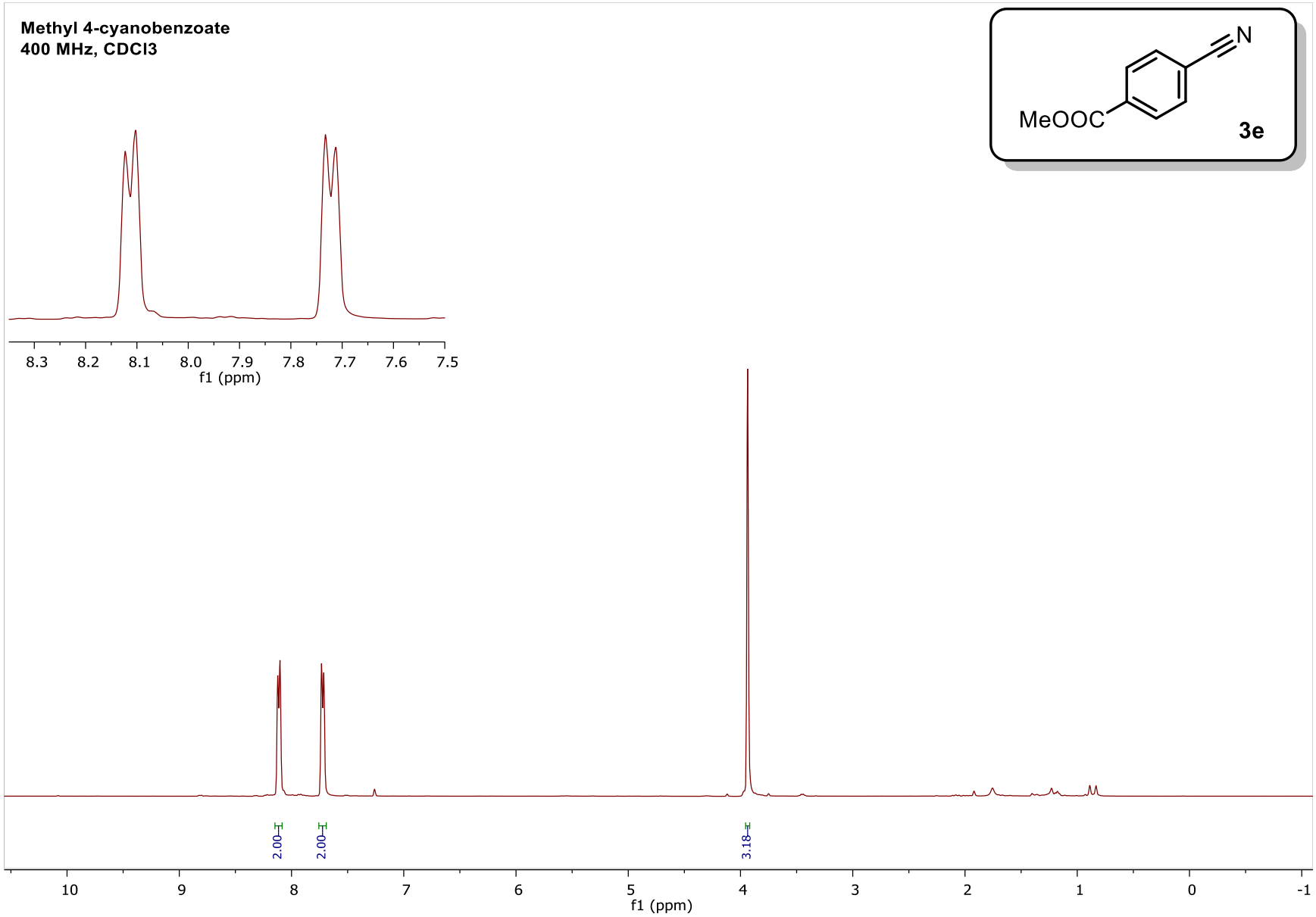

4-(*tert*-butyl)benzonitrile
400 MHz, CDCl3
N
3b
7.66
7.62
7.58
7.54
7.50
7.46
7.42
7.38
f1 (ppm)
1.89
2.00
9.03
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

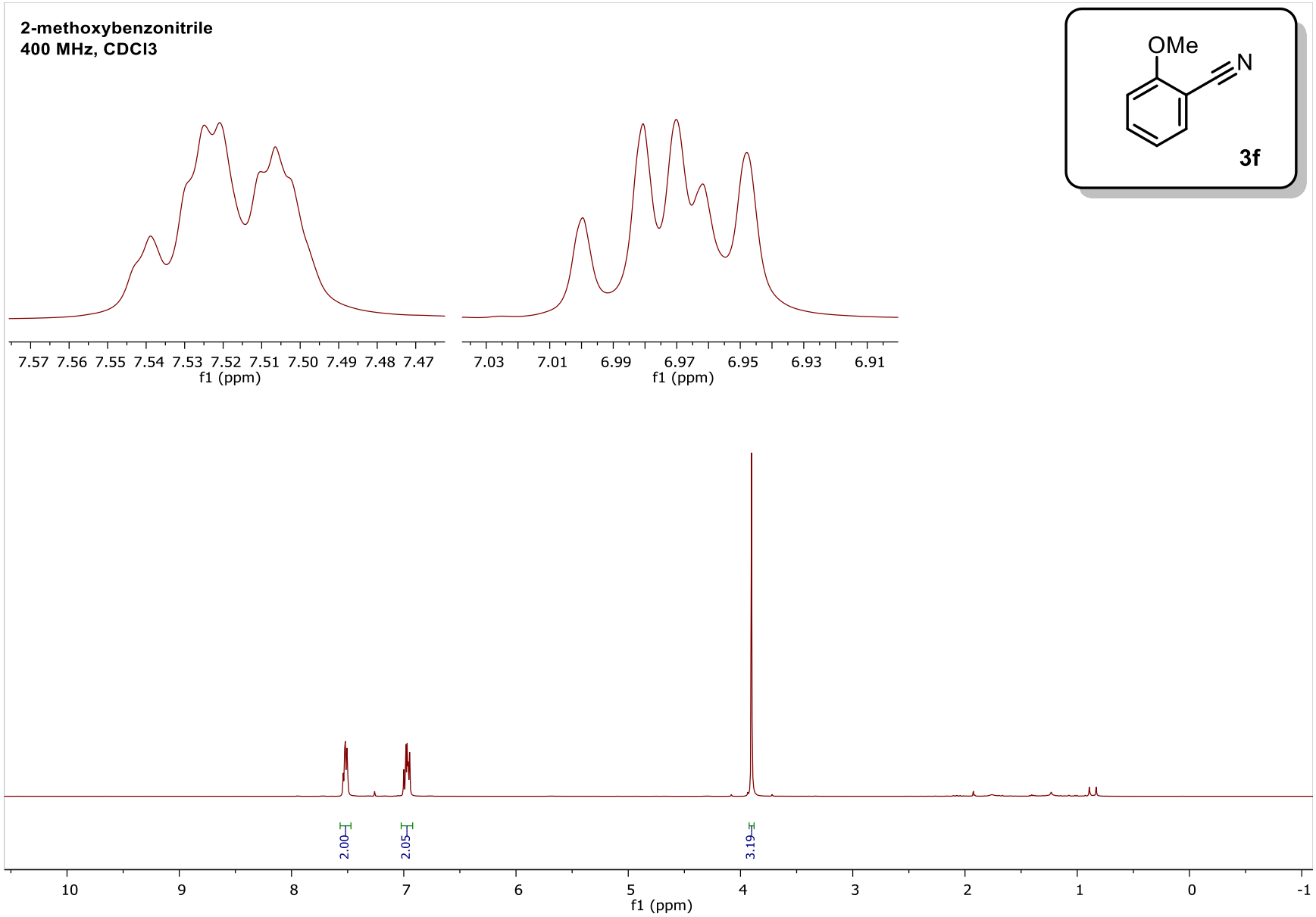
4-(methylthio)benzonitrile
400 MHz, CDCl3

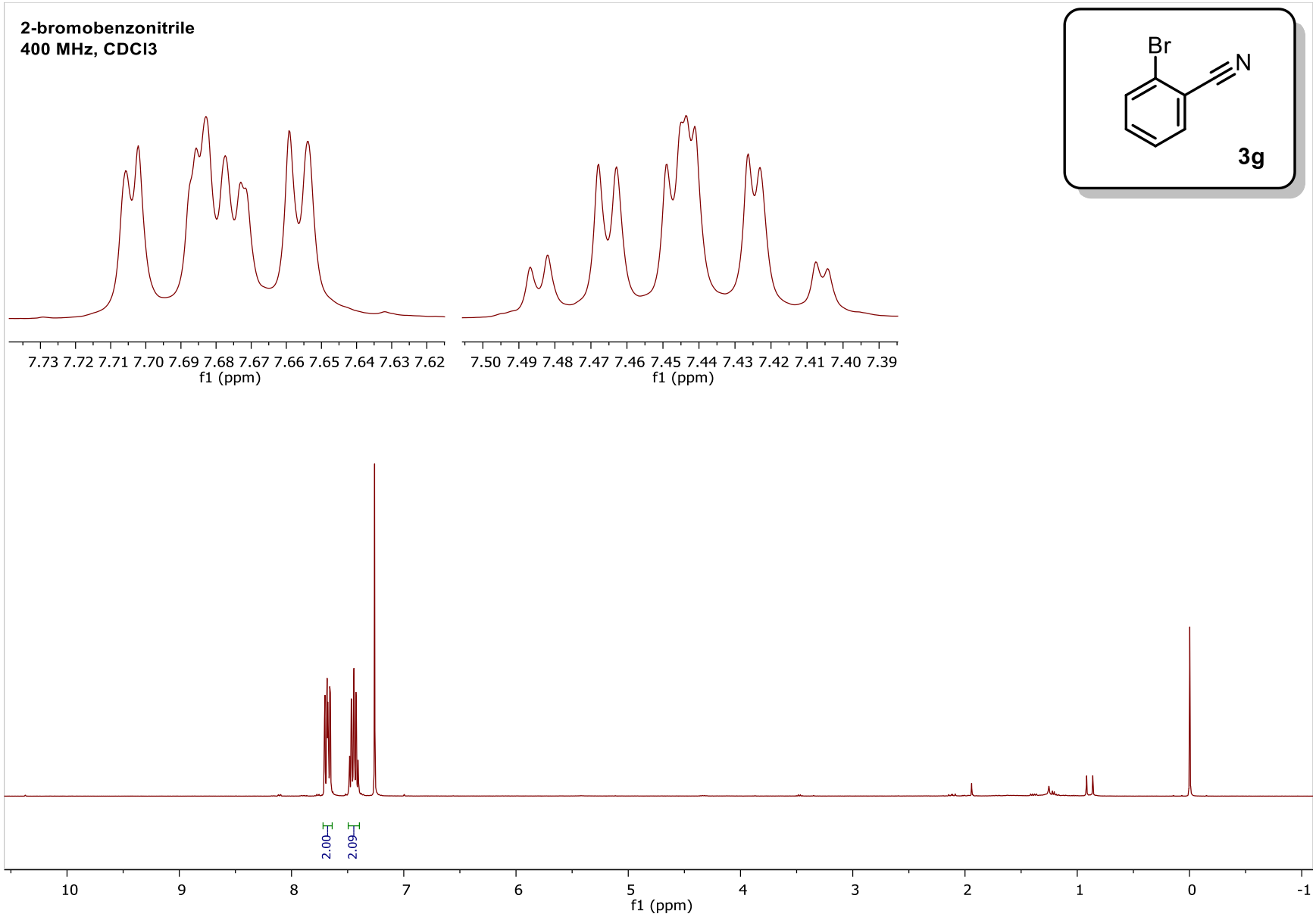


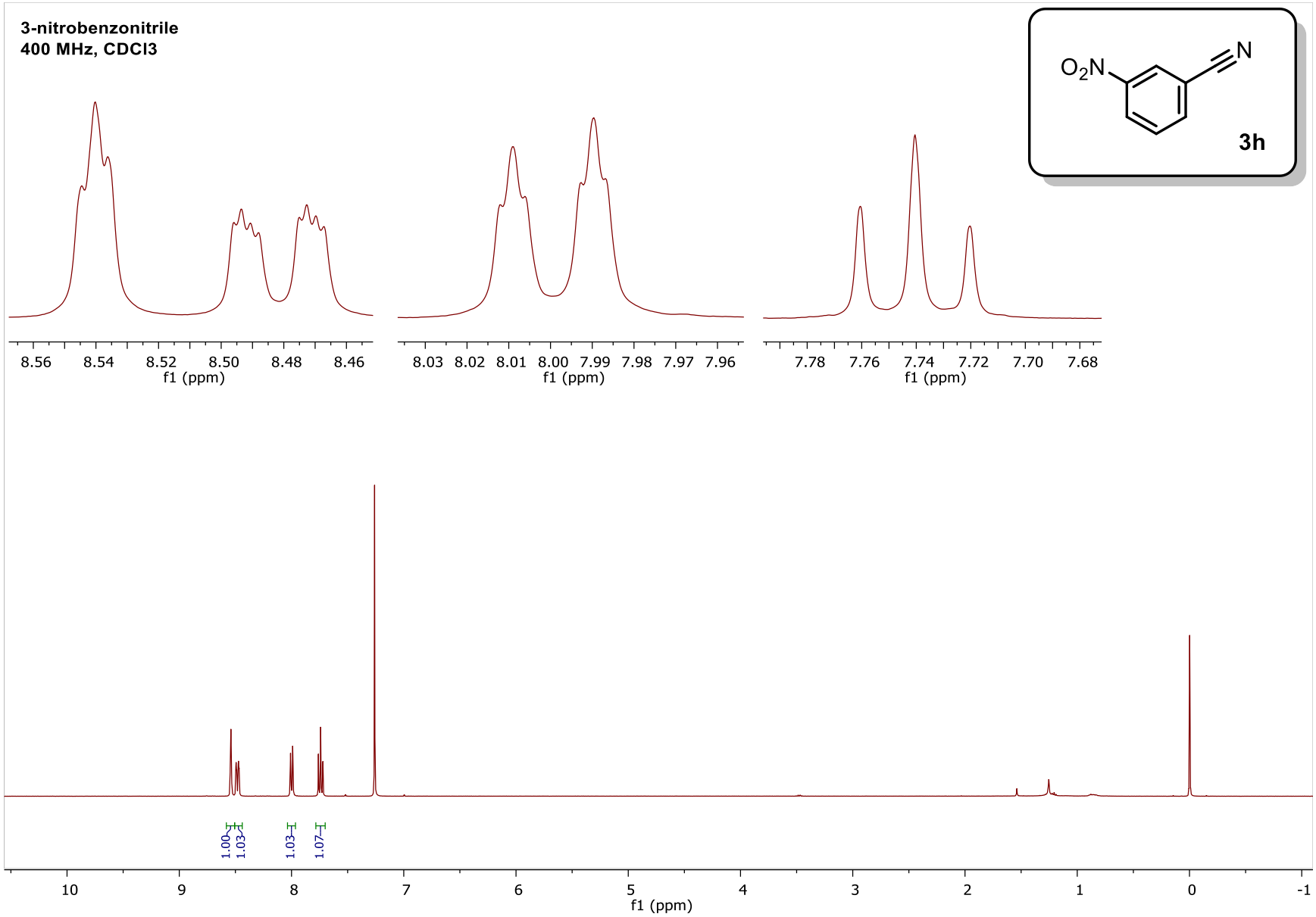
Terephthalonitrile
400 MHz, CDCl3



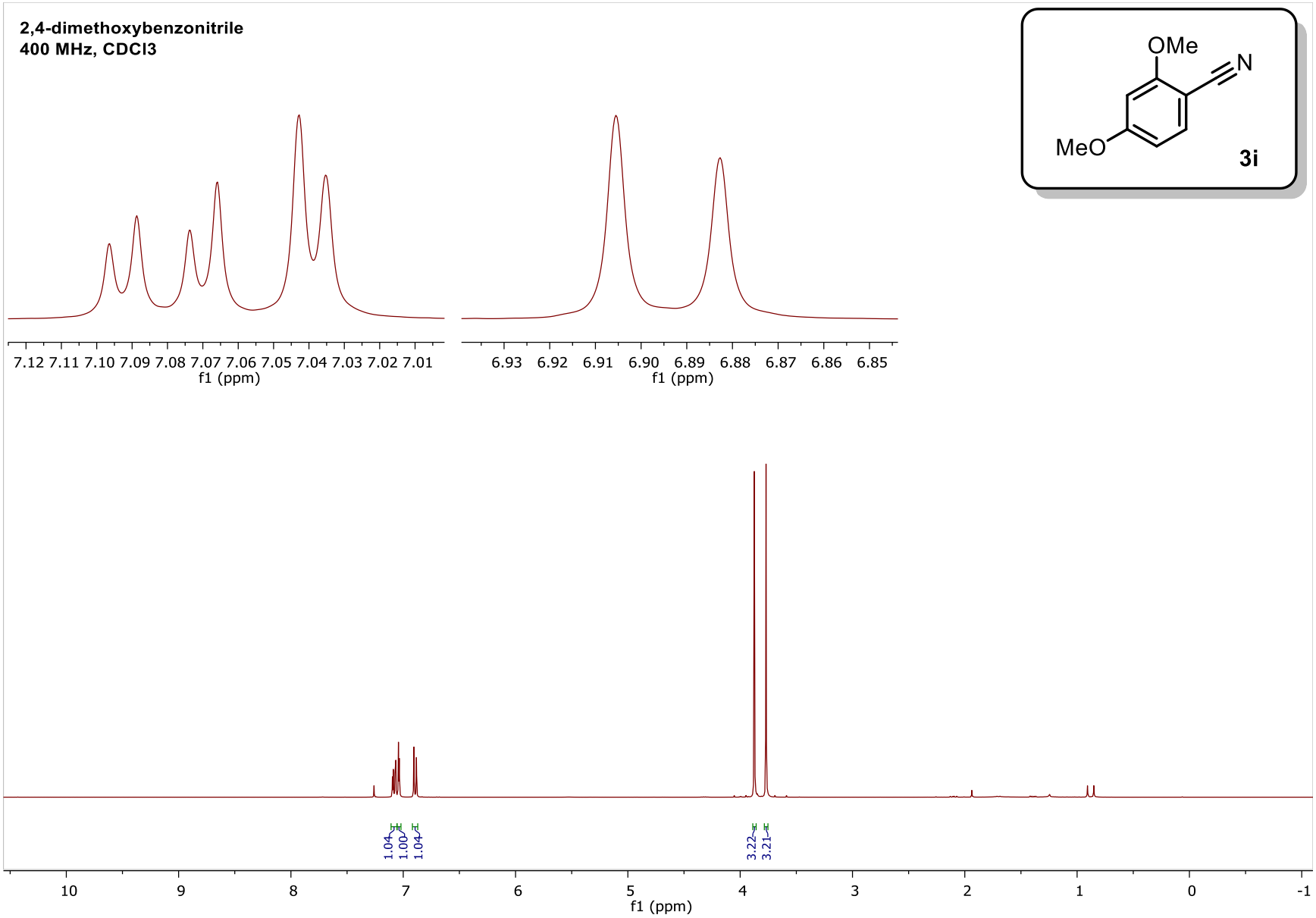

Methyl 4-cyanobenzoate
400 MHz, CDCl3
N
MeOOC
3e
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
f1 (ppm)
2.00
2.00
3.18
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

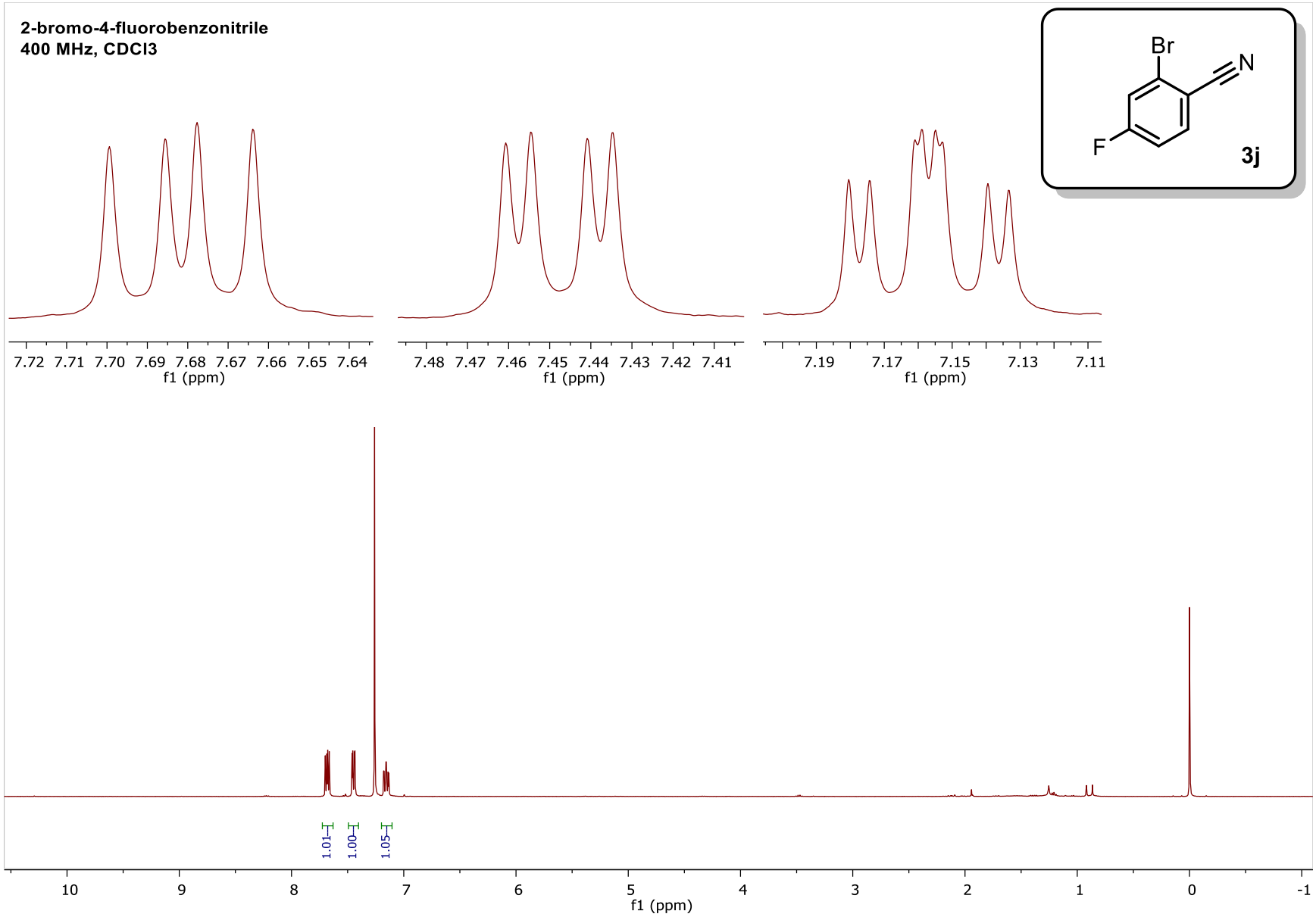

2-methoxybenzonitrile
400 MHz, CDCl3
OMe
N
3f
7.57 7.56 7.55 7.54 7.53 7.52 7.51 7.50 7.49 7.48 7.47
f1 (ppm)
7.03 7.01 6.99 6.97 6.95 6.93 6.91
f1 (ppm)
2.00
2.05
3.19
10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

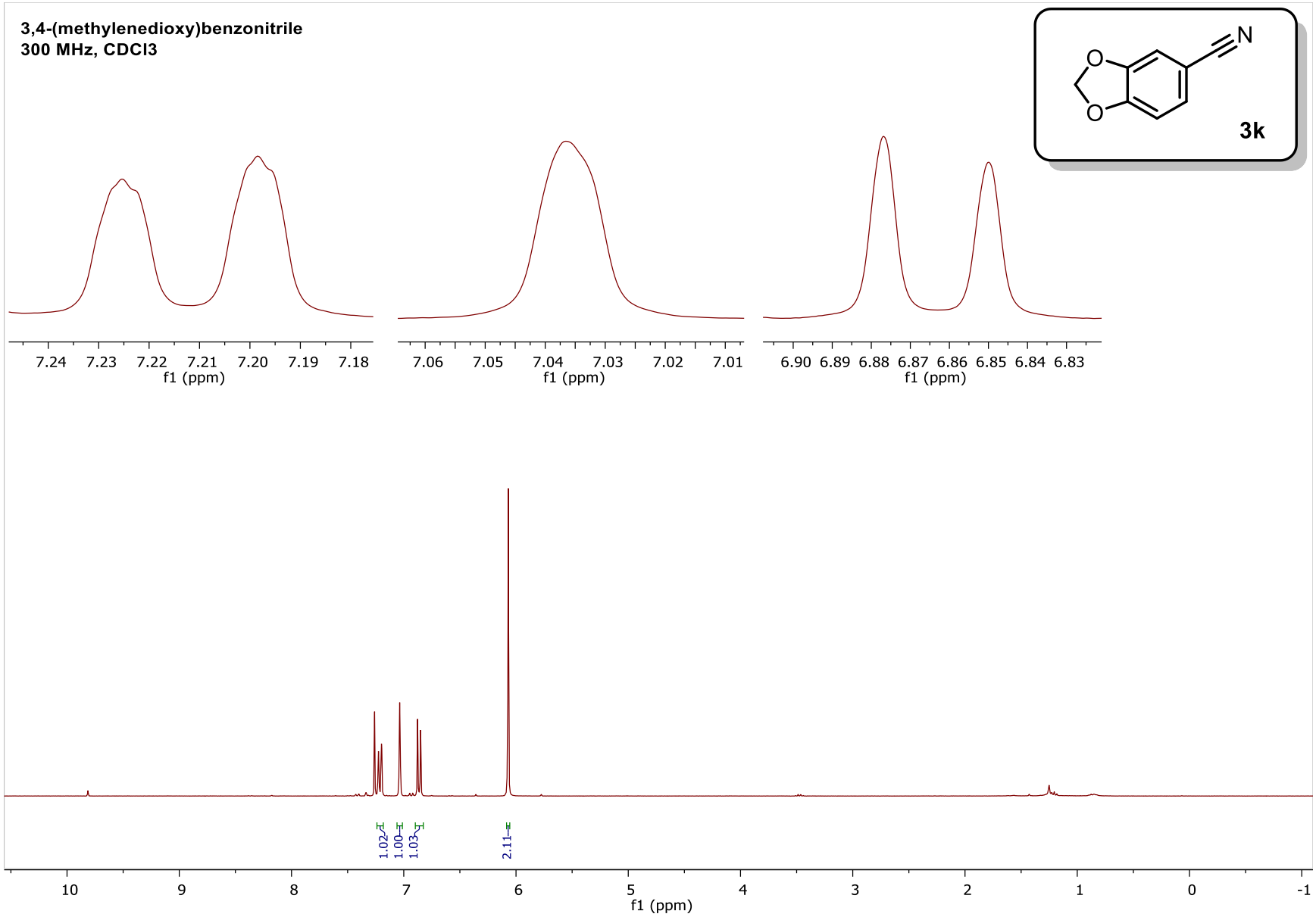

2-bromobenzonitrile
400 MHz, CDCl3
Br
N
3g
7.73 7.72 7.71 7.70 7.69 7.68 7.67 7.66 7.65 7.64 7.63 7.62
f1 (ppm)
7.50 7.49 7.48 7.47 7.46 7.45 7.44 7.43 7.42 7.41 7.40 7.39
f1 (ppm)
2.00
2.09
10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


3-nitrobenzonitrile
400 MHz, CDCl3
O2N
N
3h
8.56 8.54 8.52 8.50 8.48 8.46
f1 (ppm)
8.03 8.02 8.01 8.00 7.99 7.98 7.97 7.96
f1 (ppm)
7.78 7.76 7.74 7.72 7.70 7.68
f1 (ppm)
1.00
1.03
1.03
1.07
10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

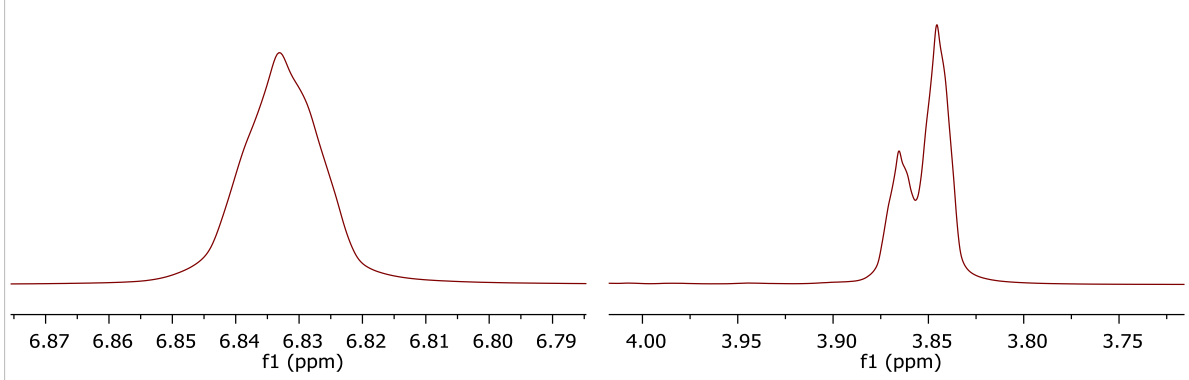
2,4-dimethoxybenzonitrile
400 MHz, CDCl3

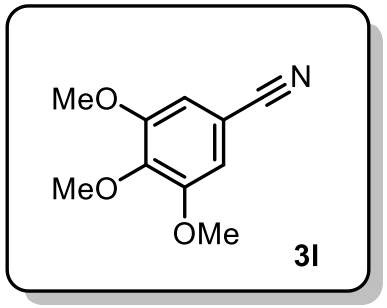


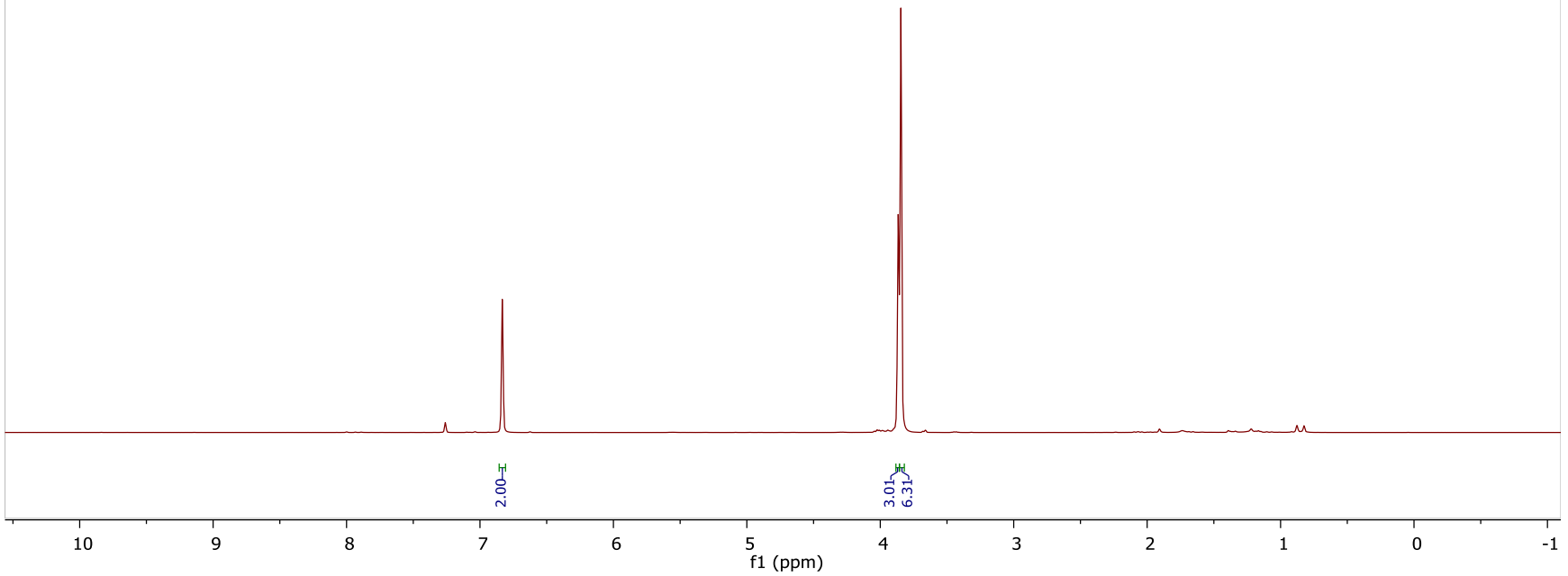

2-bromo-4-fluorobenzonitrile
400 MHz, CDCl3
Br
N
F
3j
7.72 7.71 7.70 7.69 7.68 7.67 7.66 7.65 7.64
f1 (ppm)
7.48 7.47 7.46 7.45 7.44 7.43 7.42 7.41
f1 (ppm)
7.19 7.17 7.15 7.13 7.11
f1 (ppm)
1.01
1.00
1.05
10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

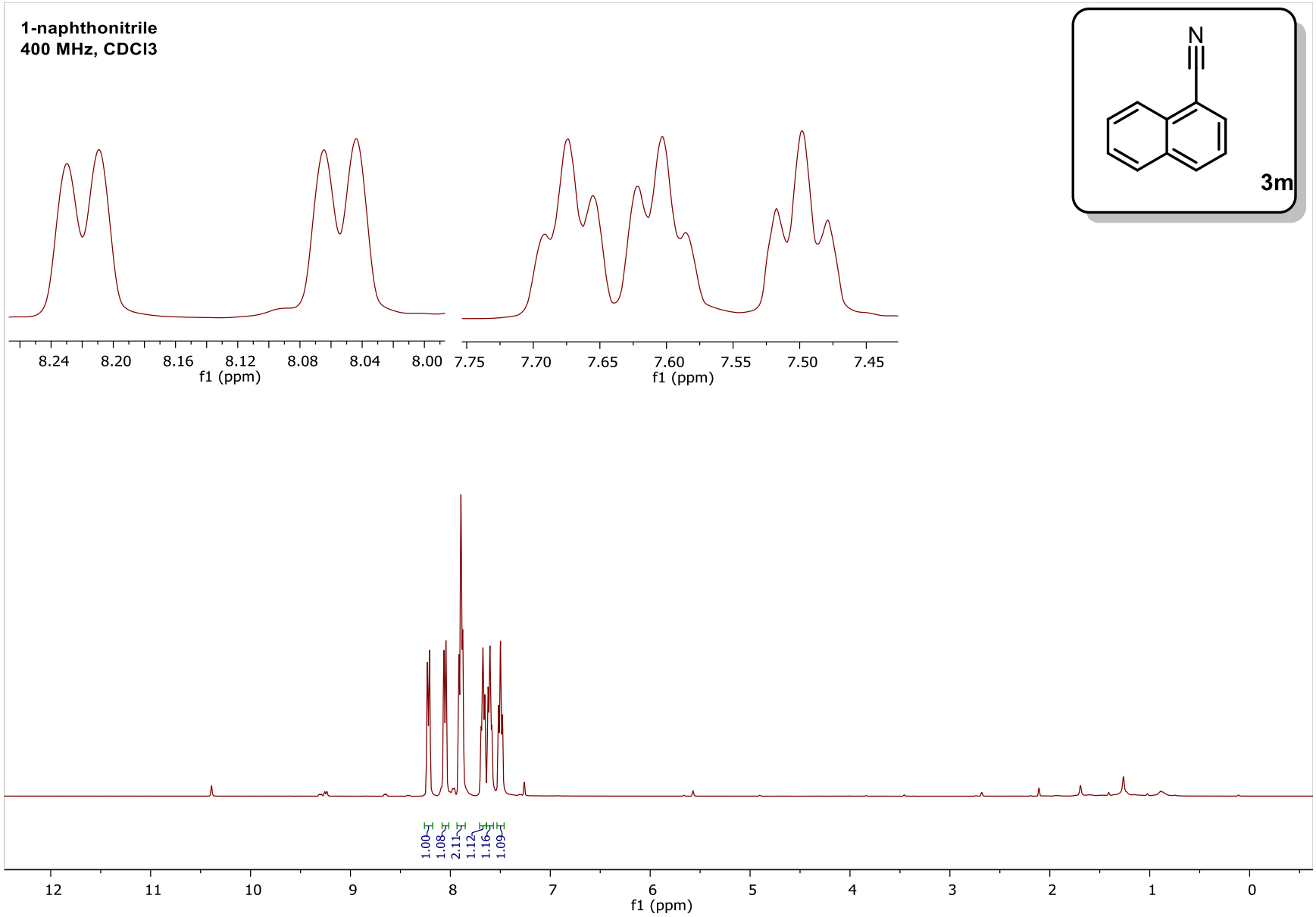

3,4-(methylenedioxy)benzonitrile
300 MHz, CDCl3
N
O
O
3k
7.24 7.23 7.22 7.21 7.20 7.19 7.18
f1 (ppm)
7.06 7.05 7.04 7.03 7.02 7.01
f1 (ppm)
6.90 6.89 6.88 6.87 6.86 6.85 6.84 6.83
f1 (ppm)
1.02
1.00
1.03
2.11
10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

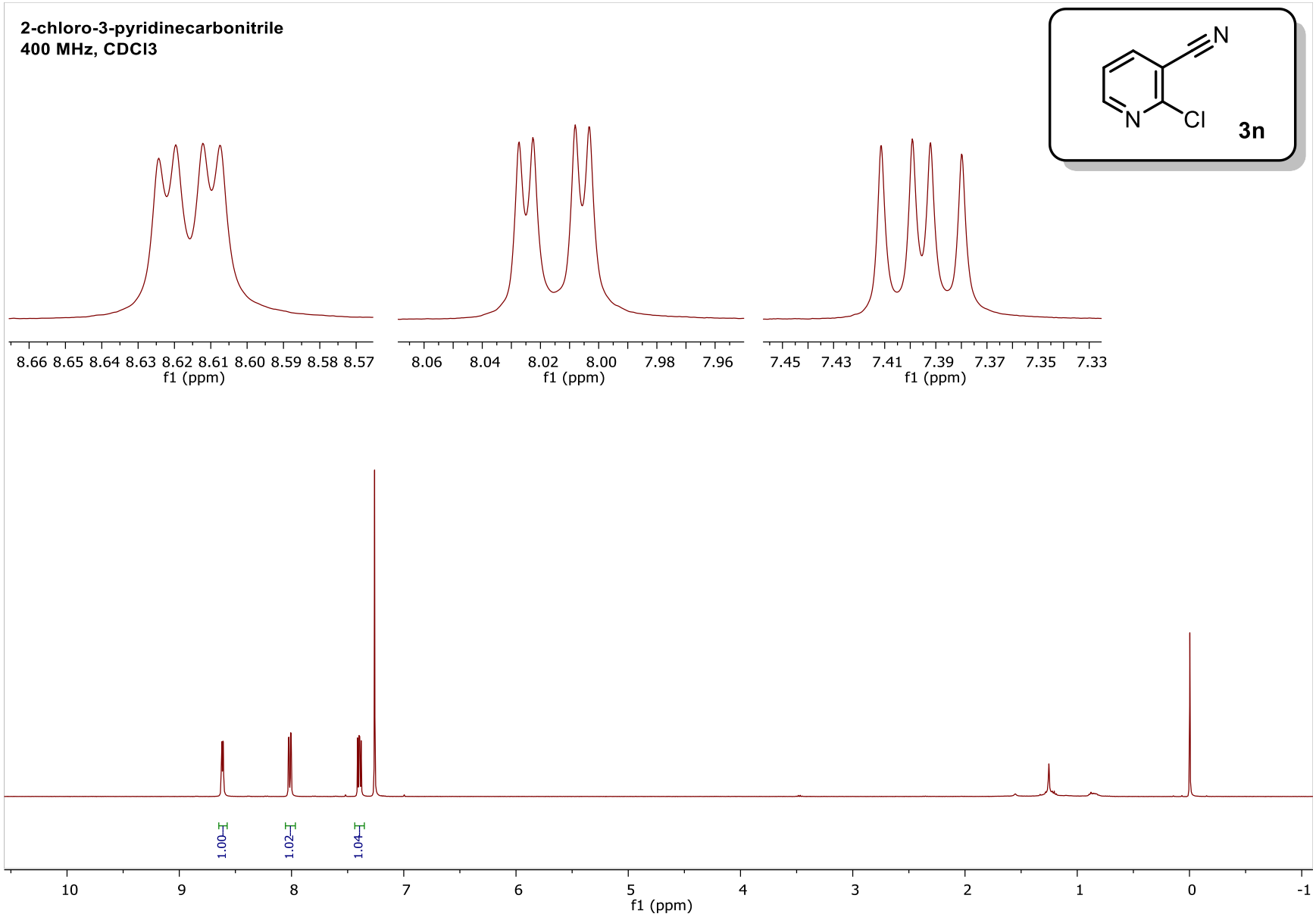
3,4,5-trimethoxybenzonitrile
400 MHz, CDCl3

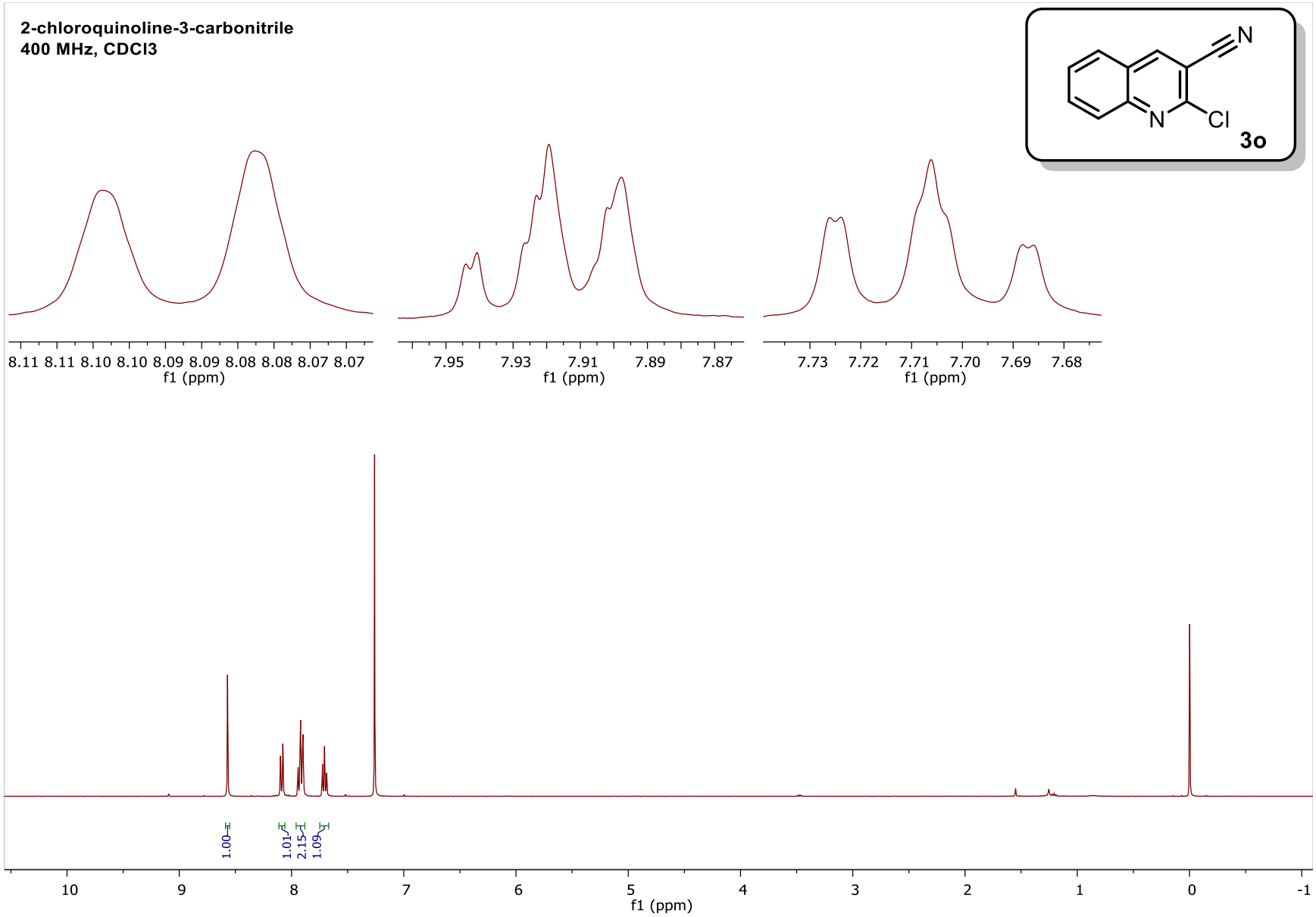




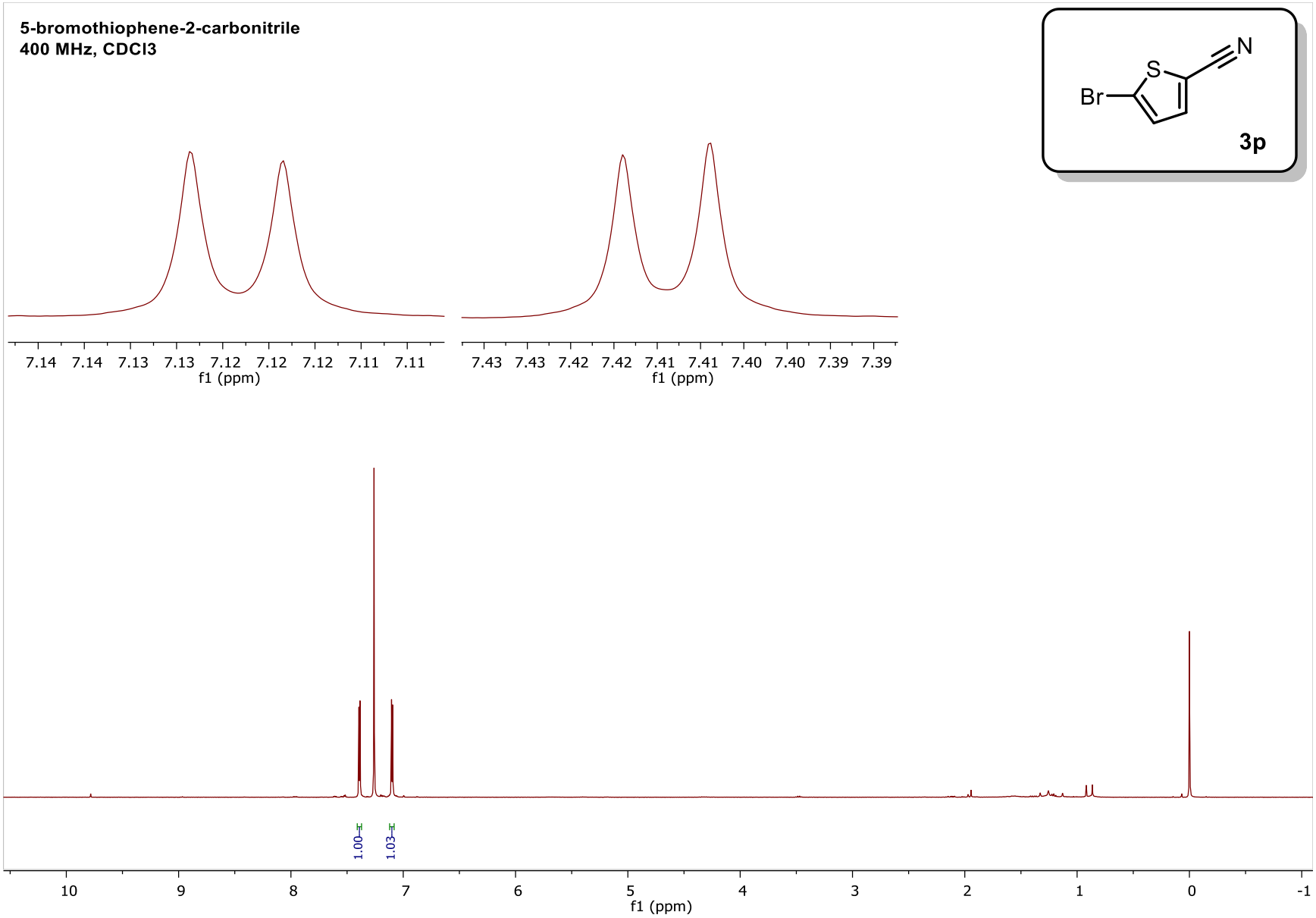


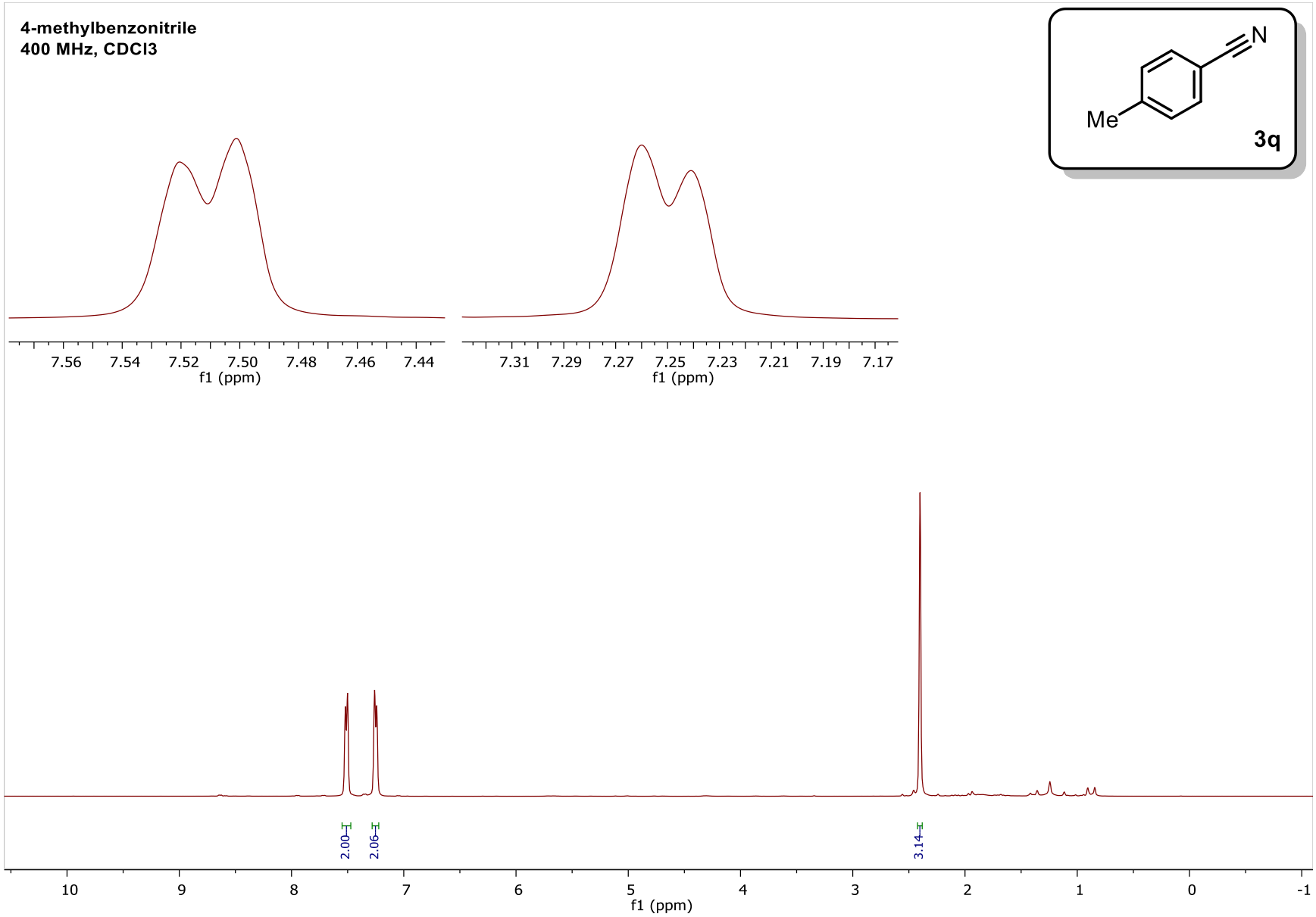

1-naphthonitrile
400 MHz, CDCl3
N
3m
8.24
8.20
8.16
8.12
8.08
8.04
8.00
f1 (ppm)
7.75
7.70
7.65
7.60
7.55
7.50
7.45
f1 (ppm)
1.00
1.08
2.11
1.12
1.16
1.09
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


2-chloro-3-pyridinecarbonitrile
400 MHz, CDCl3
N
N
Cl
3n
8.66 8.65 8.64 8.63 8.62 8.61 8.60 8.59 8.58 8.57
f1 (ppm)
8.06 8.04 8.02 8.00 7.98 7.96
f1 (ppm)
7.45 7.43 7.41 7.39 7.37 7.35 7.33
f1 (ppm)
1.00
1.02
1.04
10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

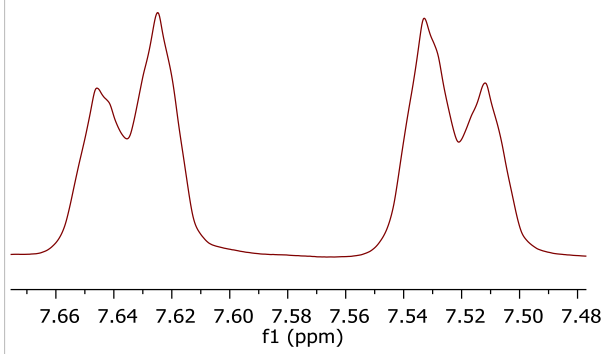

2-chloroquinoline-3-carbonitrile
400 MHz, CDCl3
N
N
Cl
3o
8.11 8.11 8.10 8.10 8.09 8.09 8.08 8.08 8.07 8.07
f1 (ppm)
7.95 7.93 7.91 7.89 7.87
f1 (ppm)
7.73 7.72 7.71 7.70 7.69 7.68
f1 (ppm)
1.00
1.01
2.15
1.09
10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

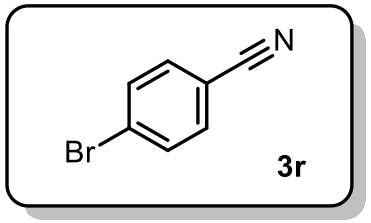
5-bromothiophene-2-carbonitrile
400 MHz, CDCl3

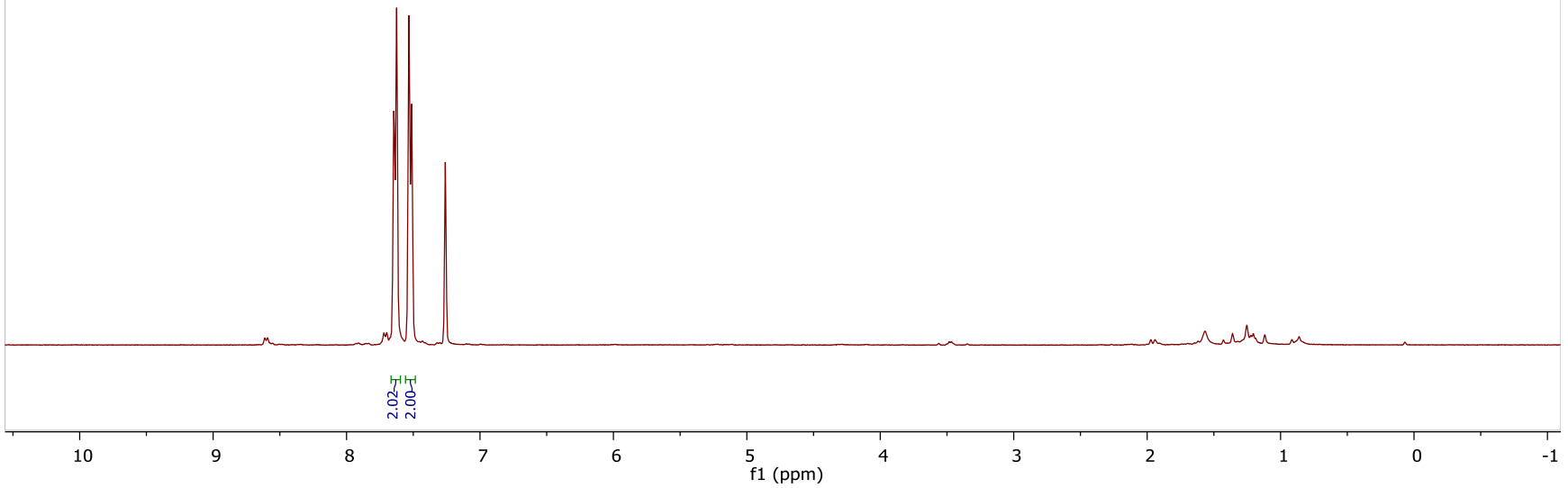


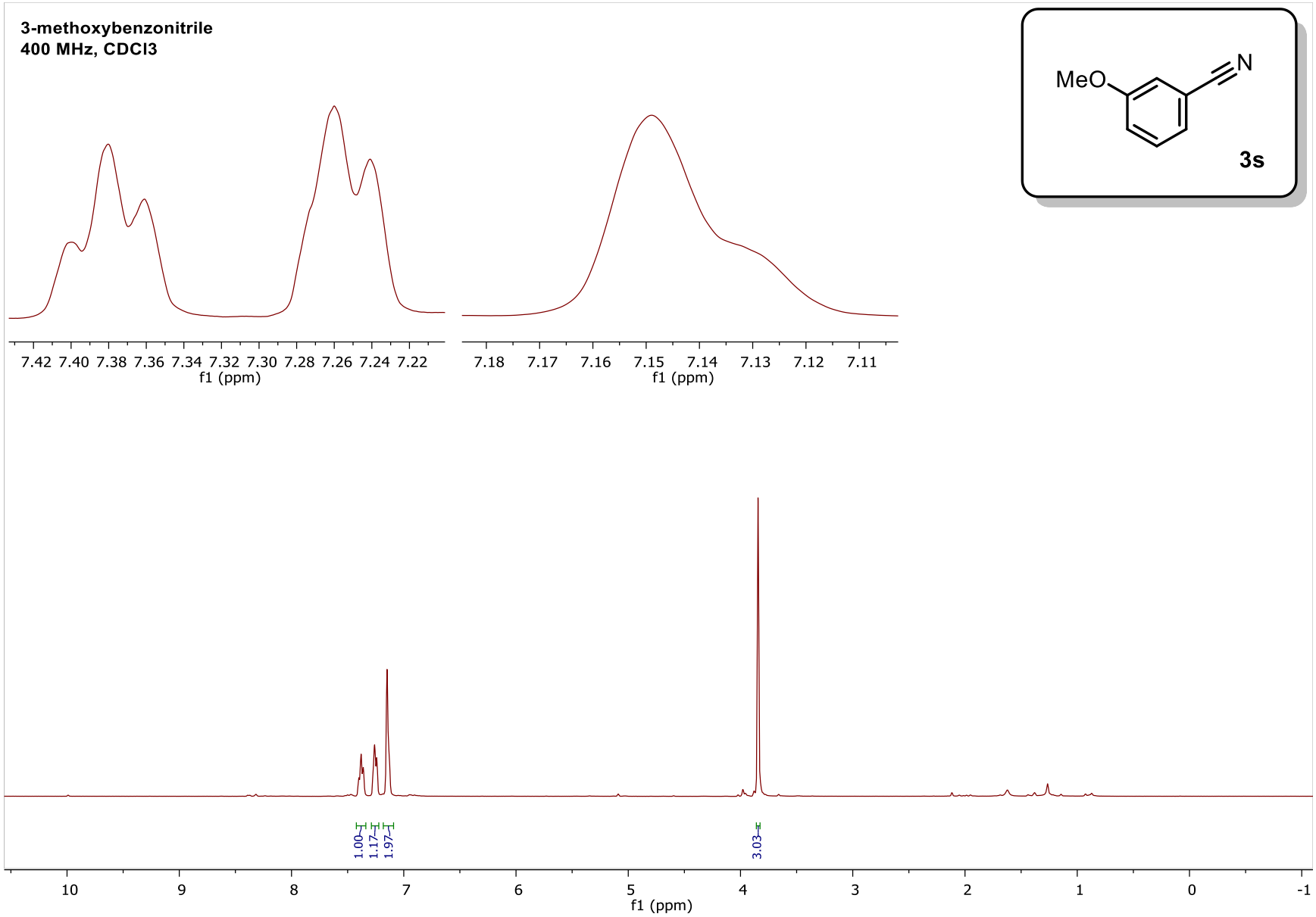

4-methylbenzonitrile
400 MHz, CDCl3
N
Me
3q
7.56
7.54
7.52
7.50
7.48
7.46
7.44
f1 (ppm)
7.31
7.29
7.27
7.25
7.23
7.21
7.19
7.17
f1 (ppm)
2.00
2.06
3.14
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

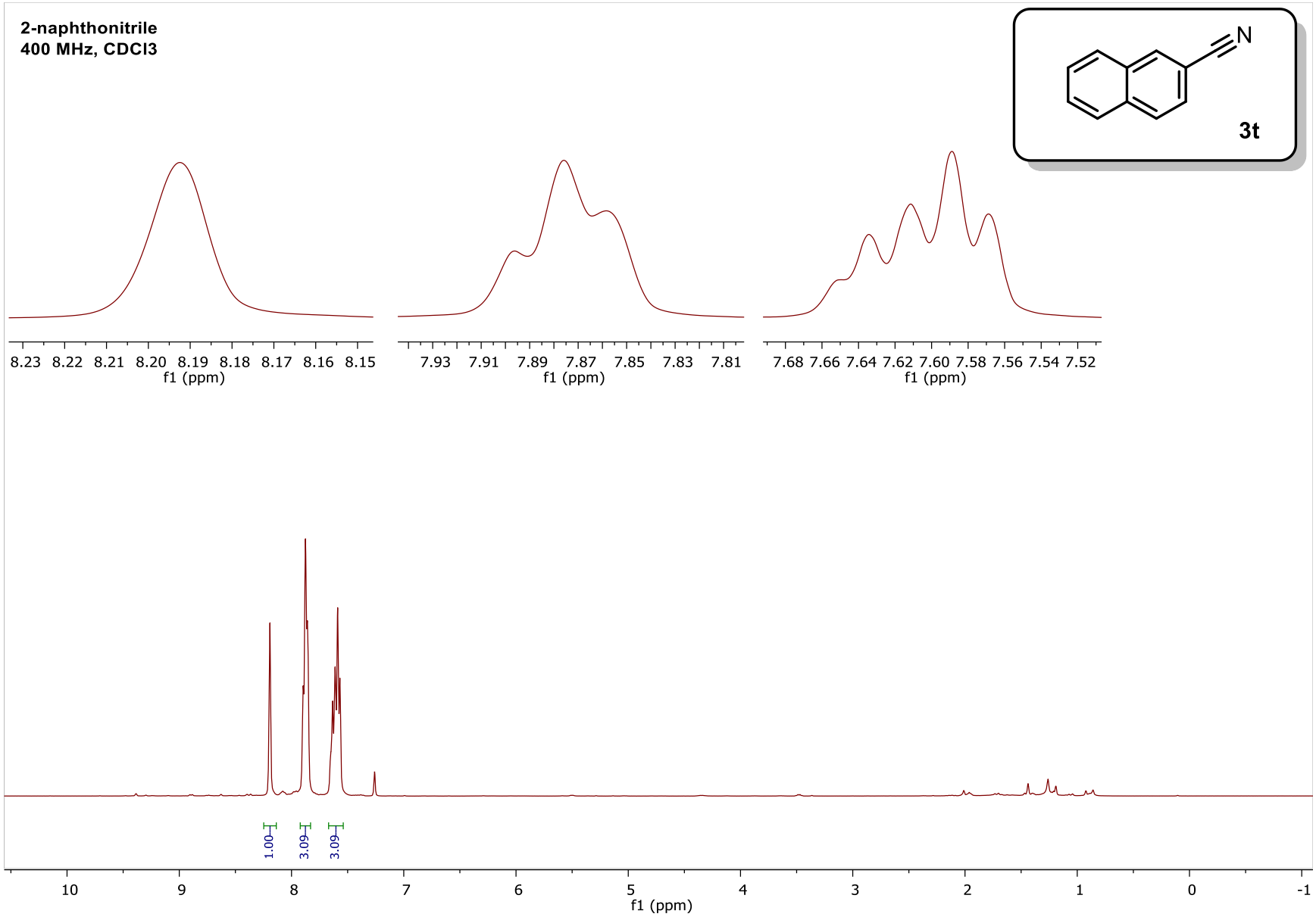
4-bromobenzonitrile
400 MHz, CDCl3



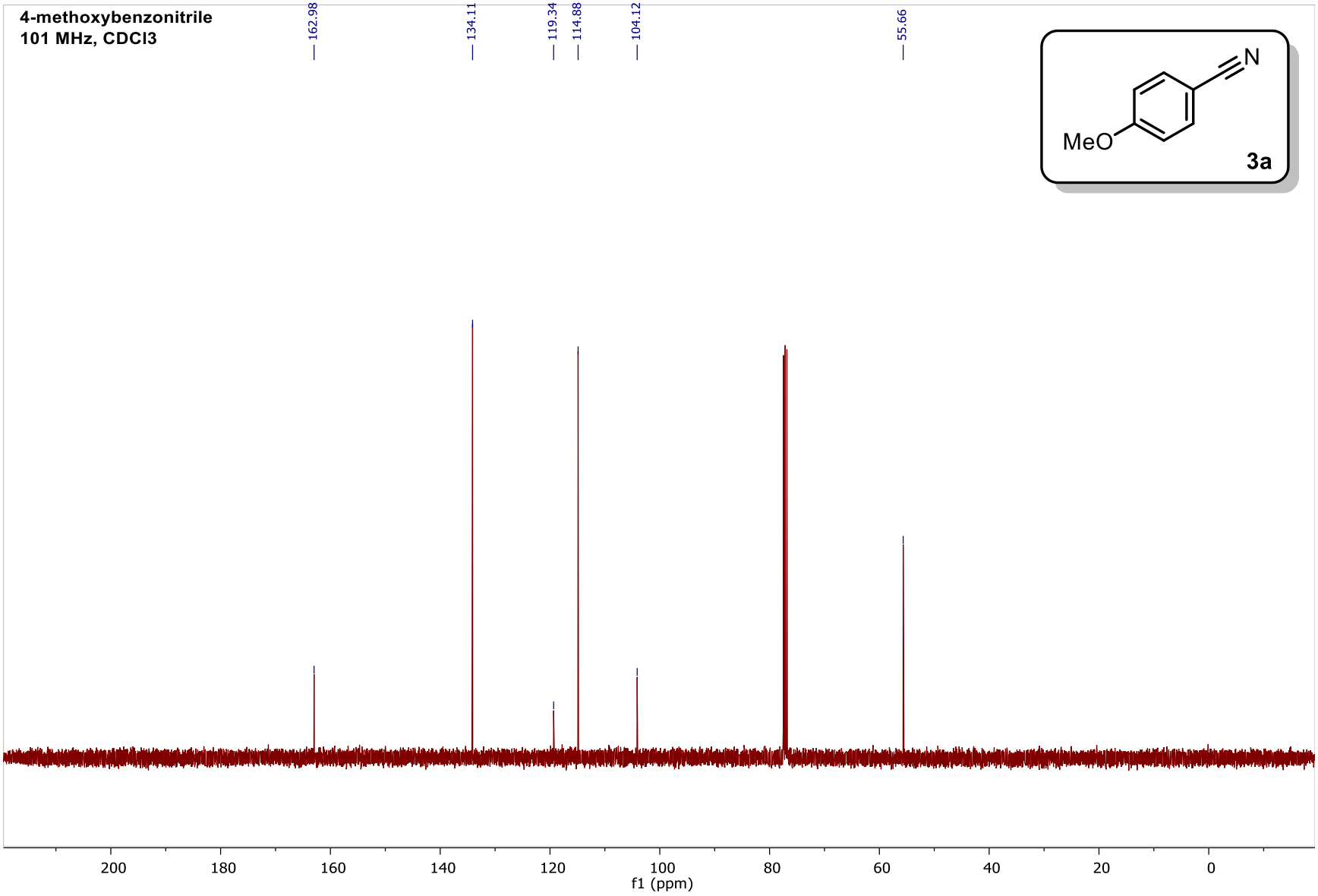


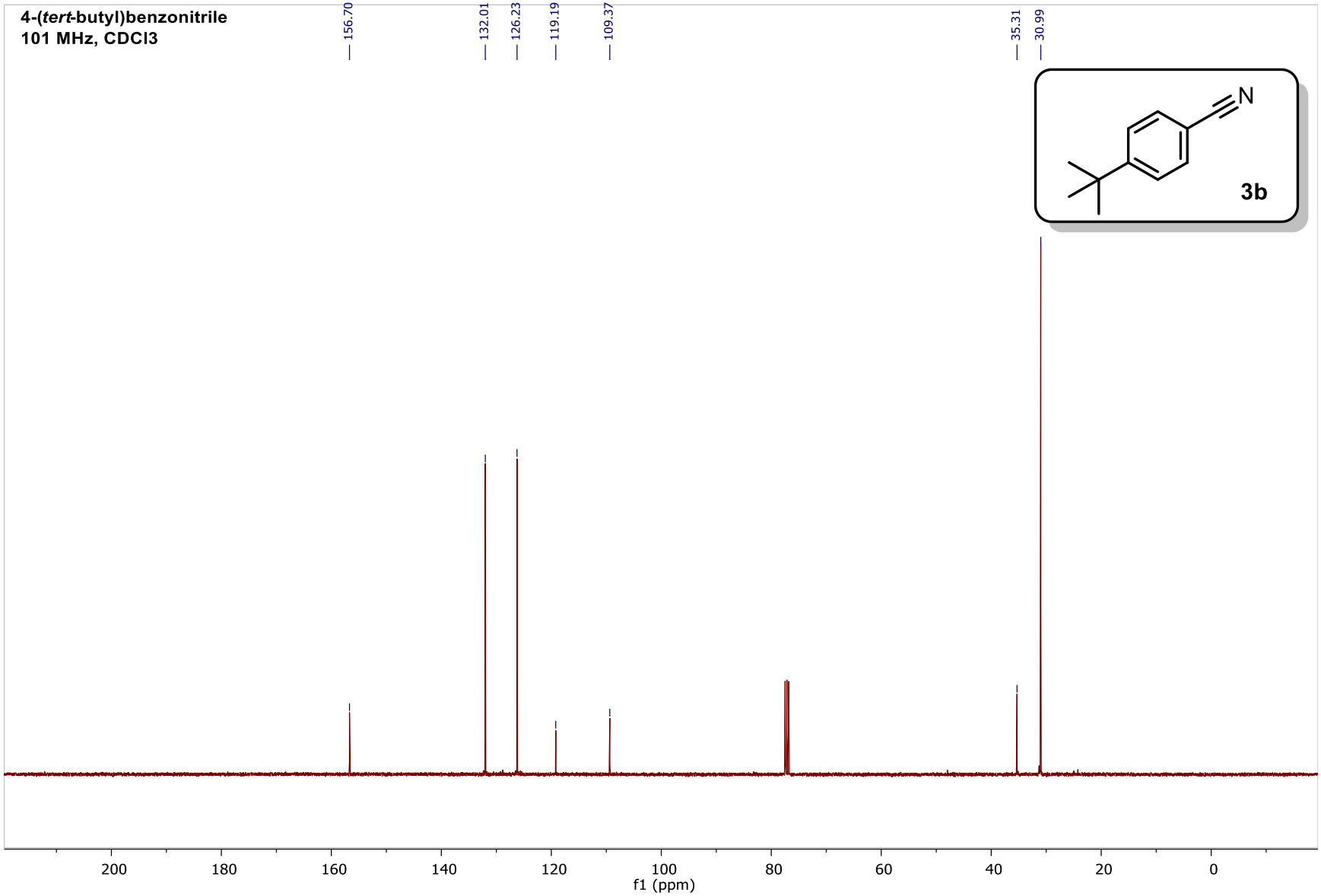


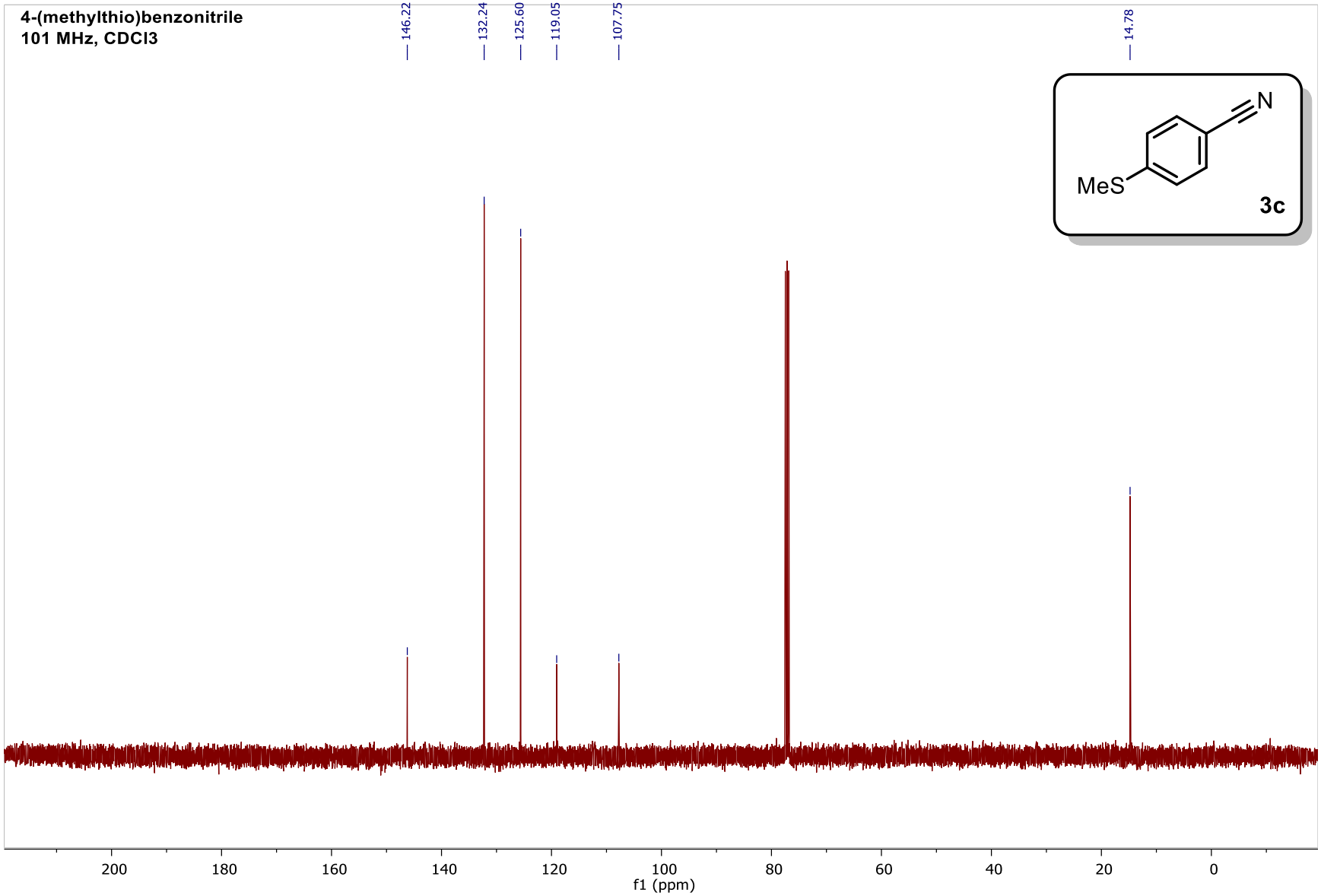

3-methoxybenzonitrile
400 MHz, CDCl3
MeO
N
3s
7.42 7.40 7.38 7.36 7.34 7.32 7.30 7.28 7.26 7.24 7.22
f1 (ppm)
7.18 7.17 7.16 7.15 7.14 7.13 7.12 7.11
f1 (ppm)
1.00
1.17
1.97
3.03
10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

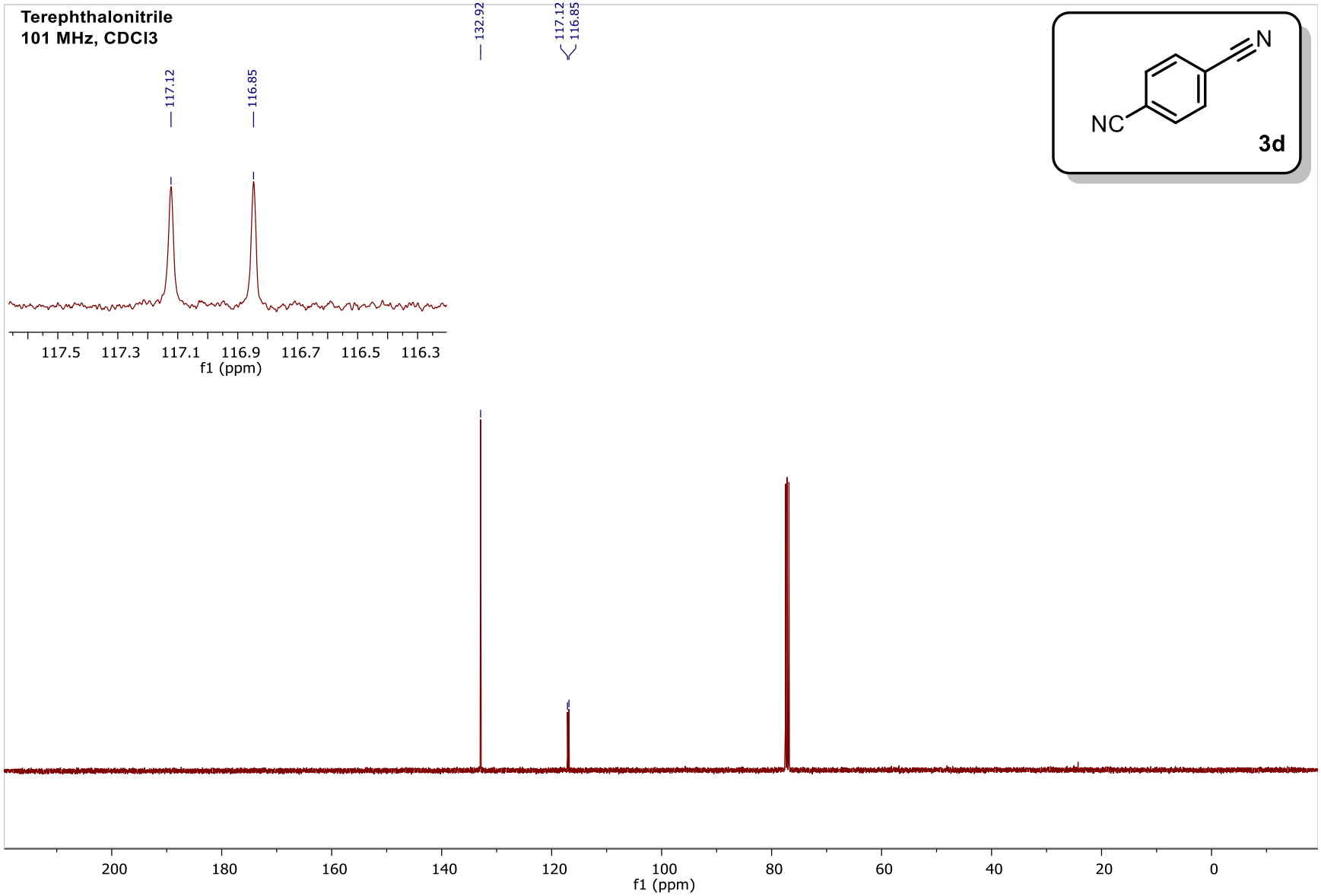

2-naphthonitrile
400 MHz, CDCl3
N
3t
8.23 8.22 8.21 8.20 8.19 8.18 8.17 8.16 8.15
f1 (ppm)
7.93 7.91 7.89 7.87 7.85 7.83 7.81
f1 (ppm)
7.68 7.66 7.64 7.62 7.60 7.58 7.56 7.54 7.52
f1 (ppm)
1.00
3.09
3.09
10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

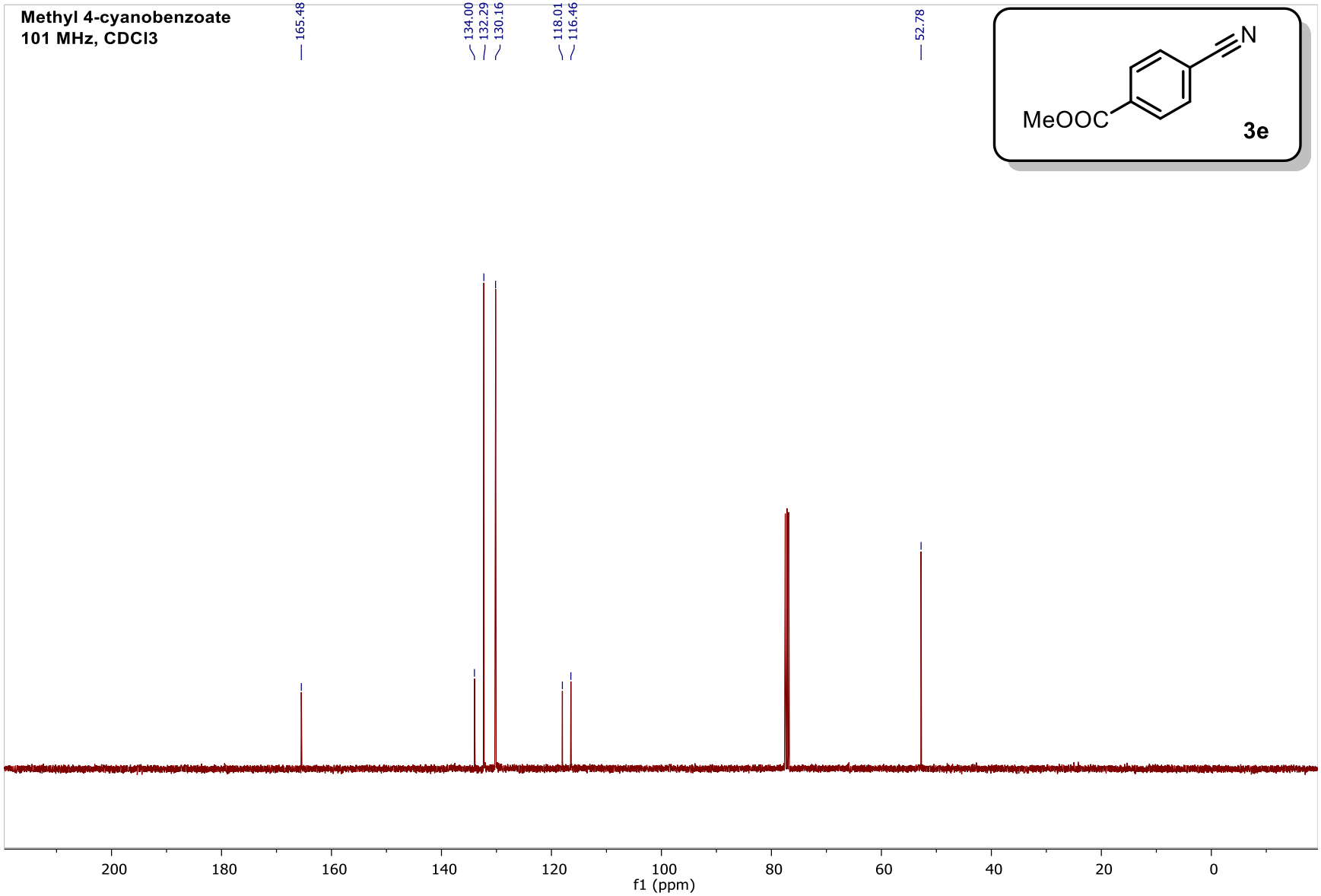
^{13}C-NMR Spectra of Synthesized Compounds

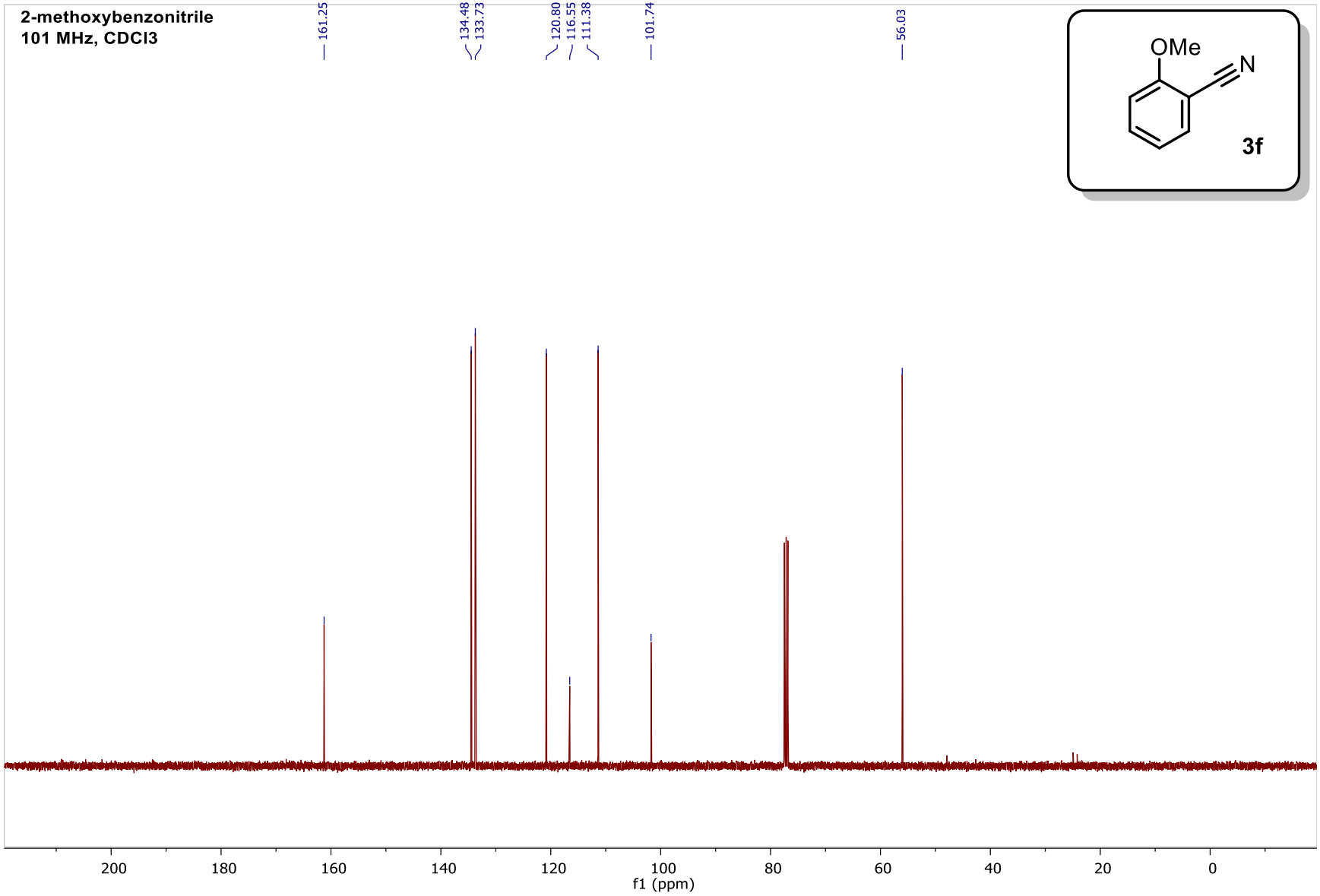


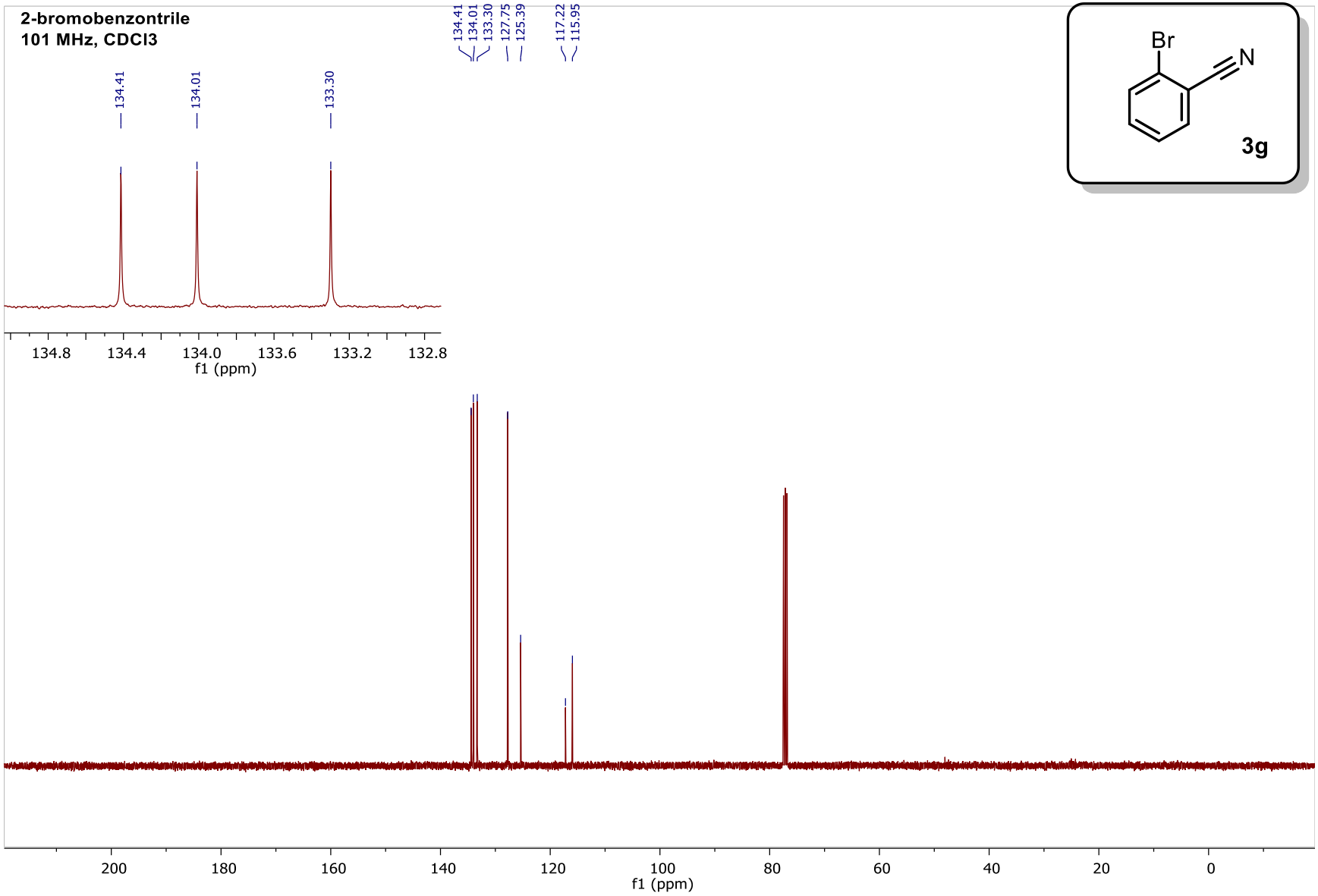

4-(*tert*-butyl)benzonitrile
101 MHz, CDCl3
156.70
132.01
126.23
119.19
109.37
35.31
30.99
N
3b
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

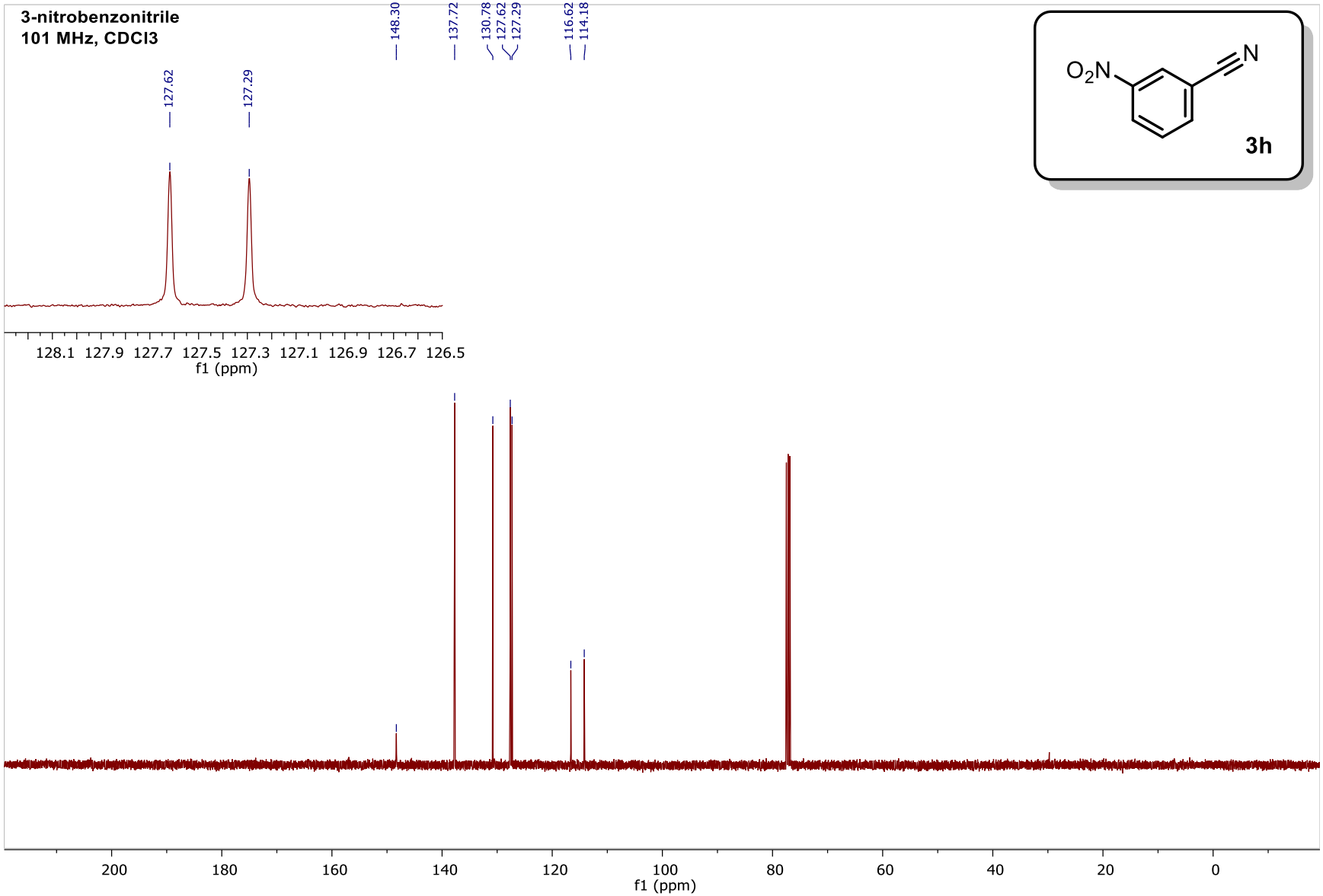

4-(methylthio)benzonitrile
101 MHz, CDCl3
146.22
132.24
125.60
119.05
107.75
14.78
N
MeS
3c
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

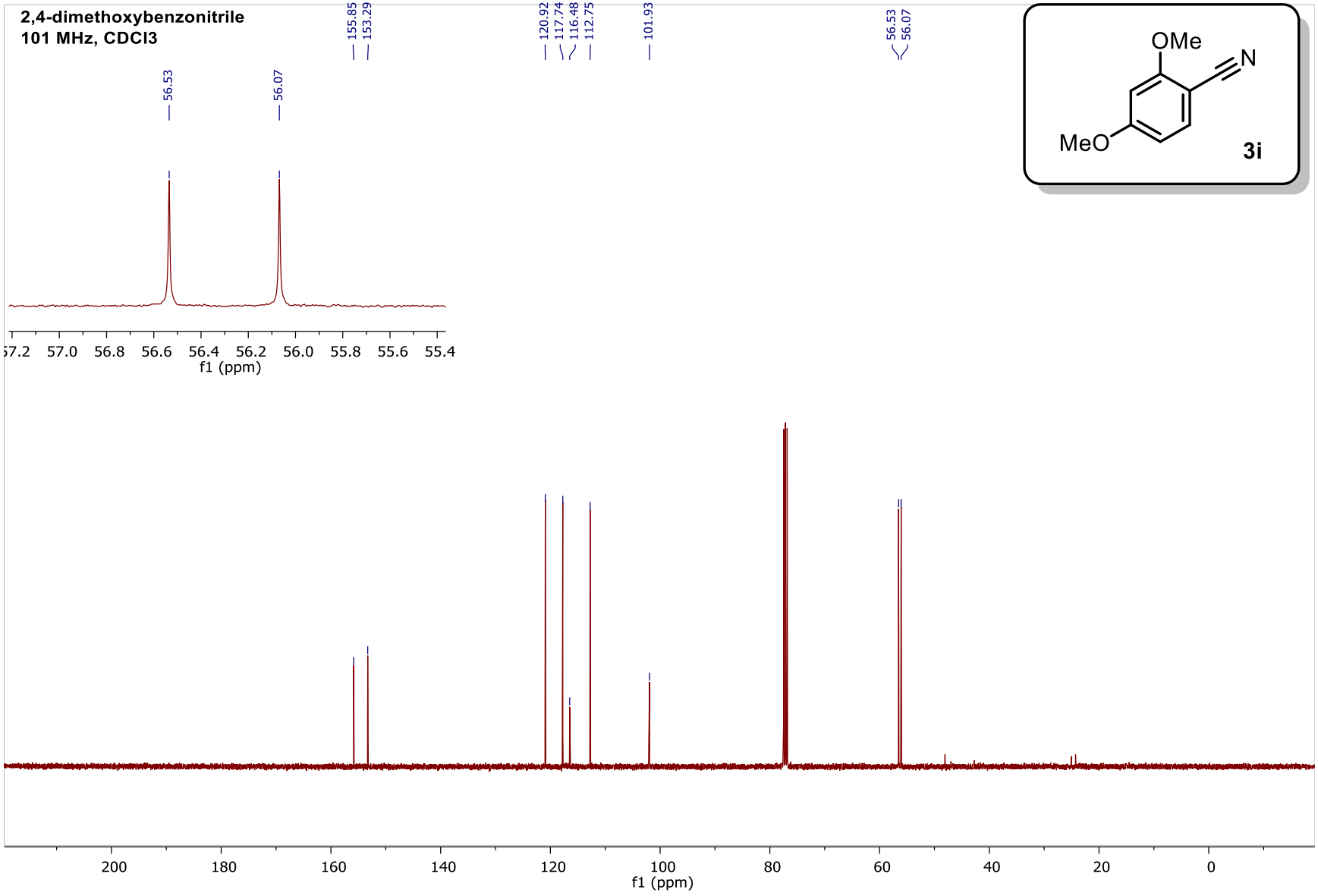

Terephthalonitrile
101 MHz, CDCl3
132.92
117.12
116.85
117.12
116.85
117.5
117.3
117.1
116.9
116.7
116.5
116.3
f1 (ppm)
N
NC
3d
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

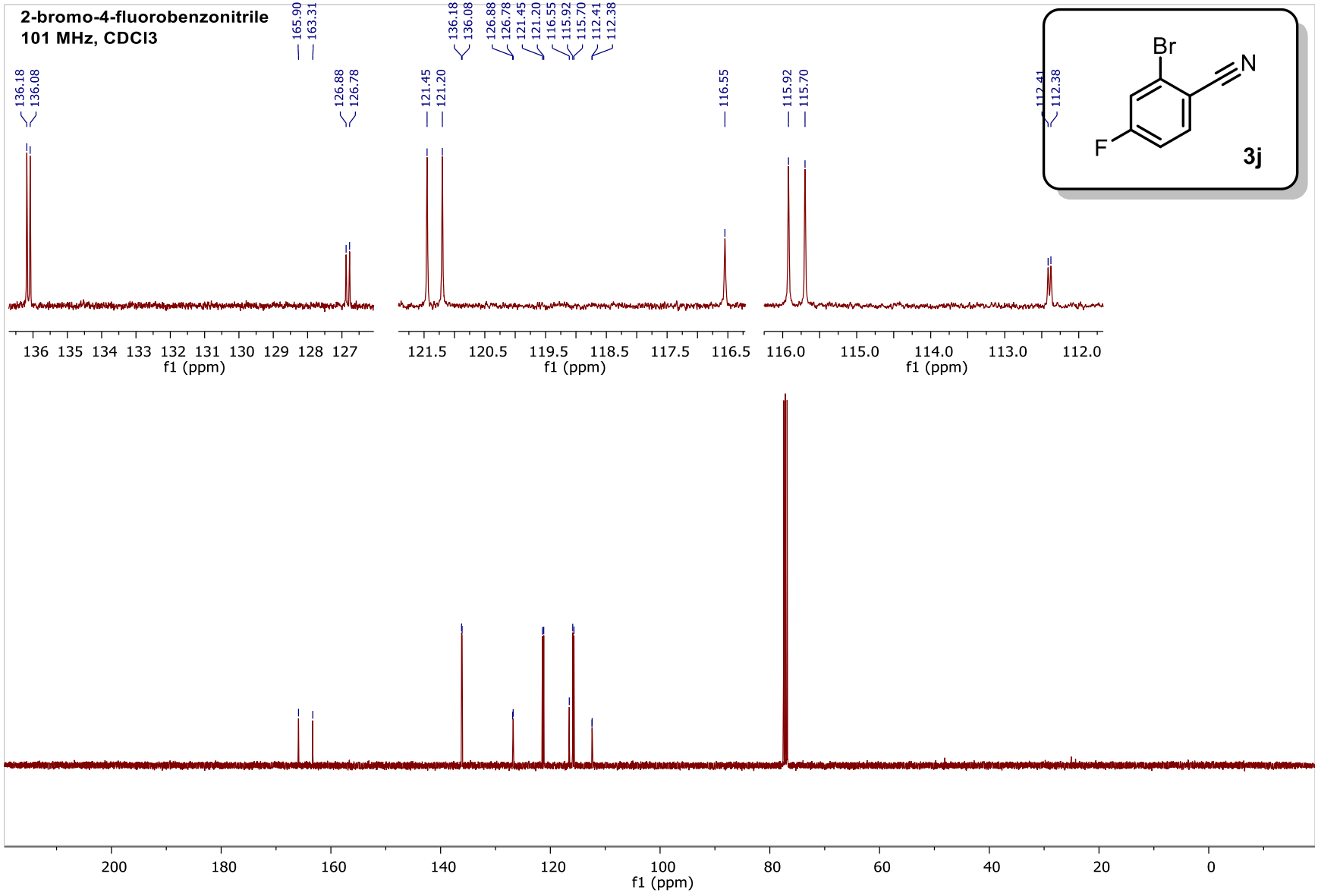

Methyl 4-cyanobenzoate
101 MHz, CDCl3
165.48
134.00
132.29
130.16
118.01
116.46
52.78
N
MeOOC
3e
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

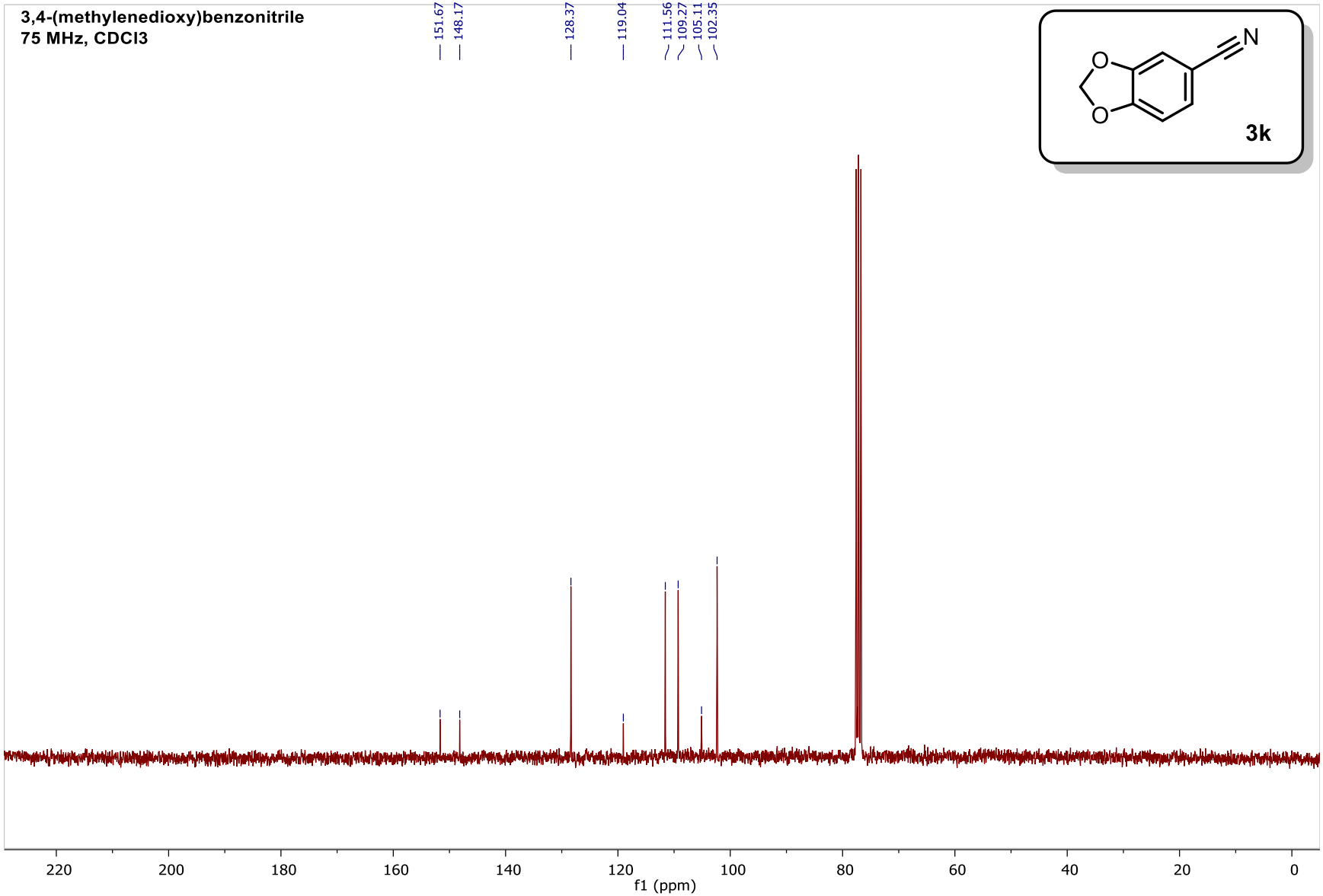

2-methoxybenzonitrile
101 MHz, CDCl3
161.25
134.48
133.73
120.80
116.55
111.38
101.74
56.03
OMe
N
3f
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

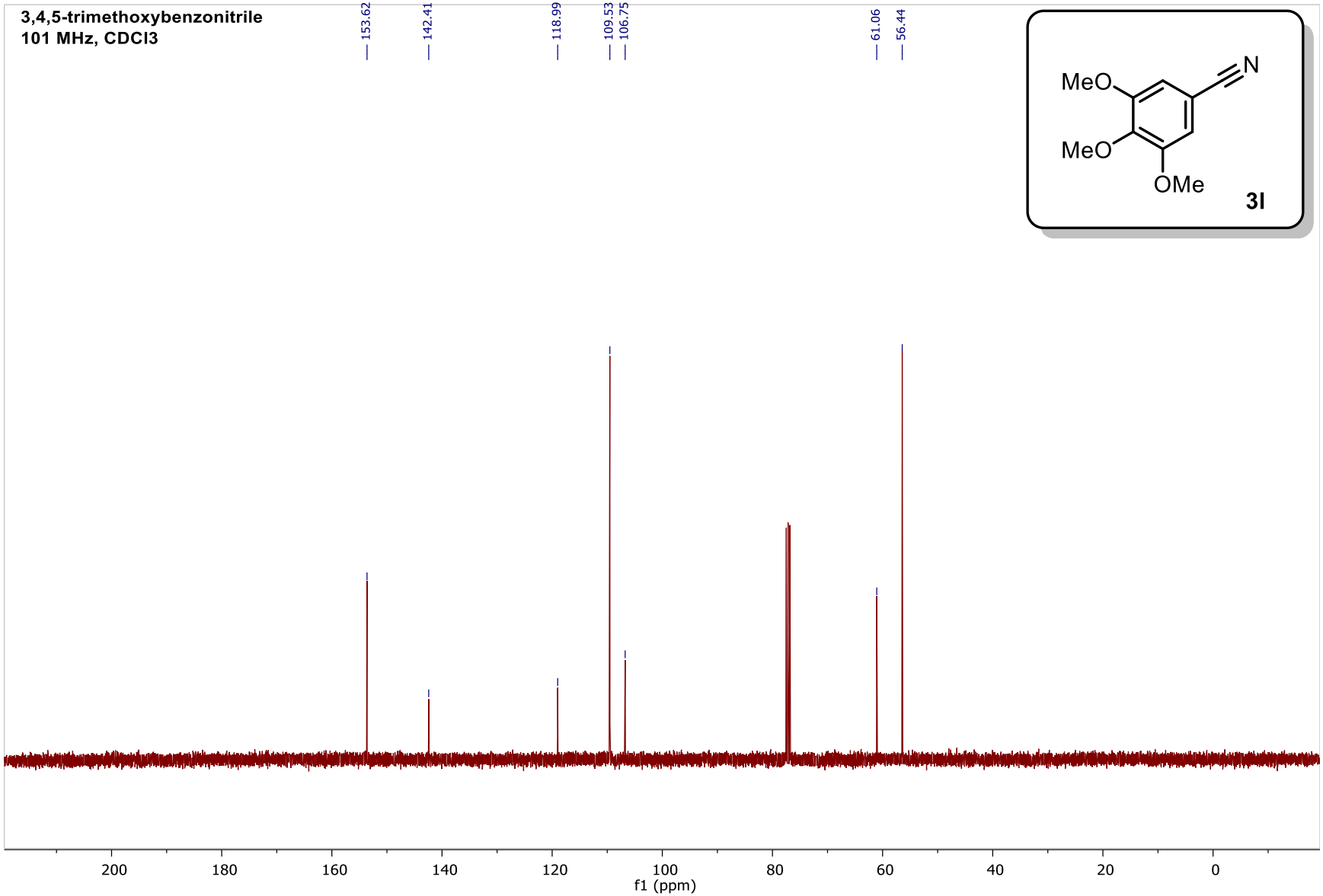

2-bromobenzontrile
101 MHz, CDCl3
134.41
134.01
133.30
127.75
125.39
117.22
115.95
Br
N
3g
134.8
134.4
134.0
133.6
133.2
132.8
f1 (ppm)
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

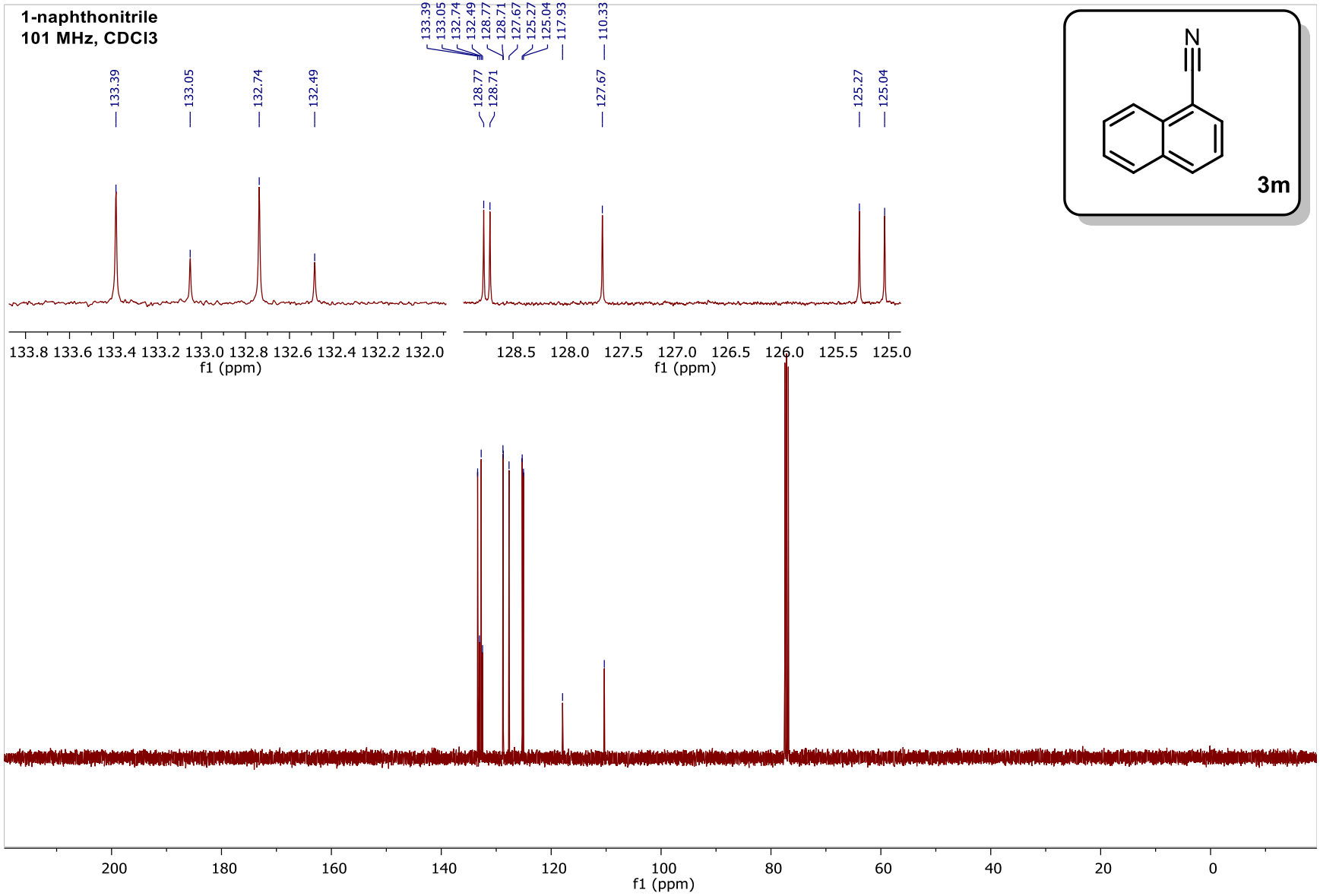

3-nitrobenzonitrile
101 MHz, CDCl3
148.30
137.72
130.78
127.62
127.29
116.62
114.18
127.62
127.29
128.1 127.9 127.7 127.5 127.3 127.1 126.9 126.7 126.5
f1 (ppm)
O2N
N
3h
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

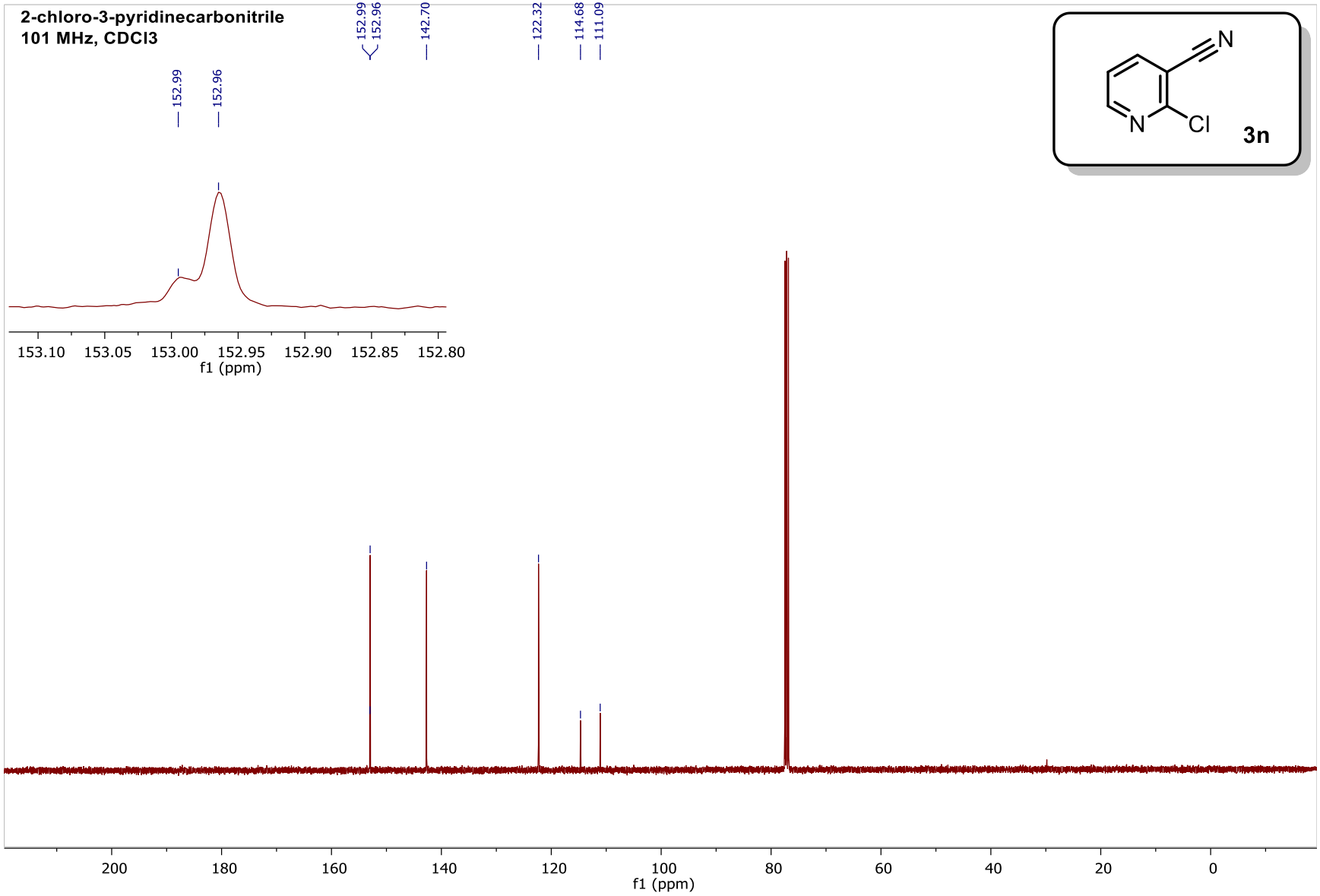

2,4-dimethoxybenzonitrile
101 MHz, CDCl3
155.85
153.29
120.92
117.74
116.48
112.75
101.93
56.53
56.07
56.53
56.07
OMe
N
MeO
3i
57.2 57.0 56.8 56.6 56.4 56.2 56.0 55.8 55.6 55.4
f1 (ppm)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

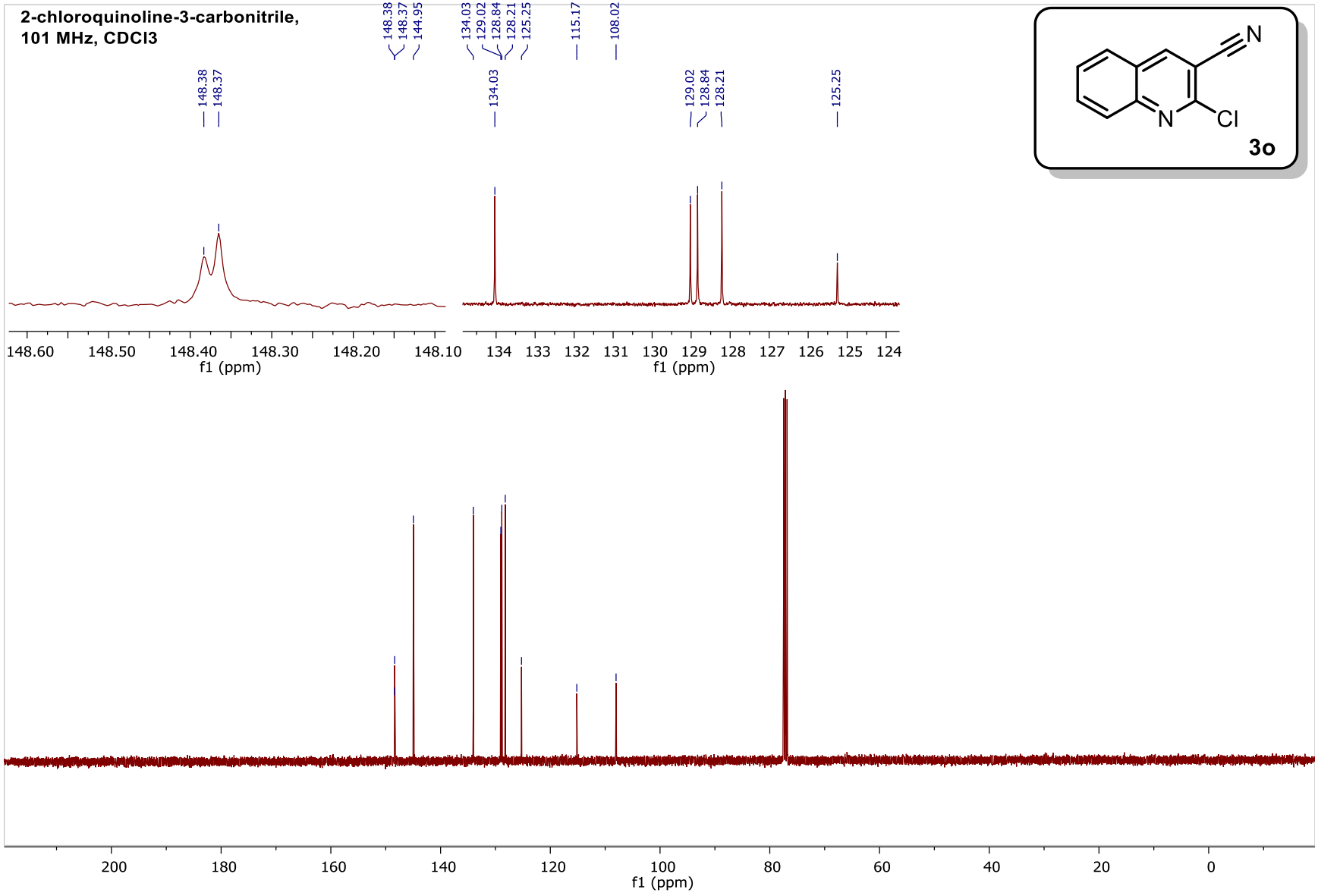

2-bromo-4-fluorobenzonitrile
101 MHz, CDCl3
165.90
163.31
136.18
136.08
126.88
126.78
121.45
121.20
116.55
115.92
115.70
112.41
112.38
Br
N
F
3j
f1 (ppm)

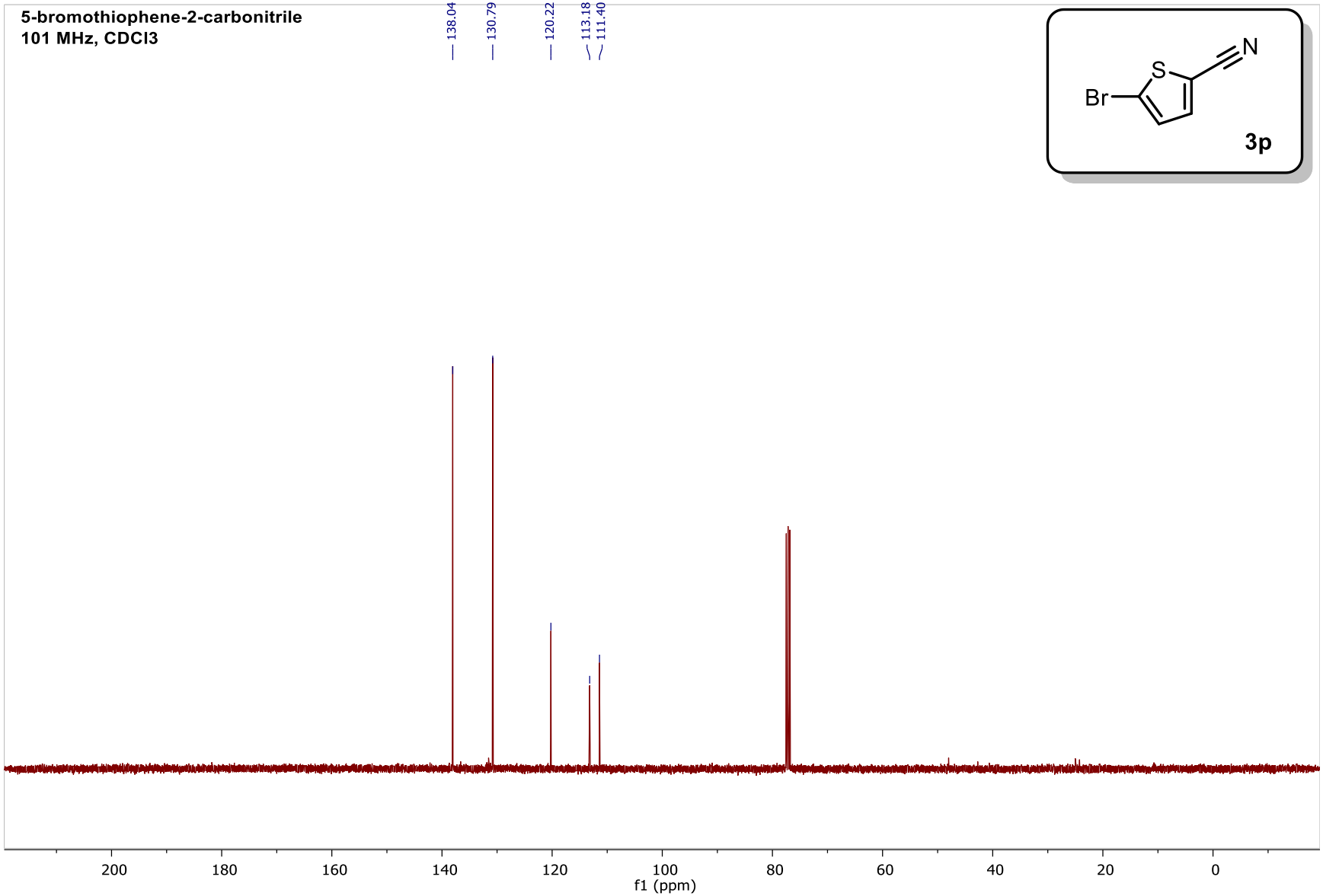

3,4-(methylenedioxy)benzonitrile
75 MHz, CDCl3
151.67
148.17
128.37
119.04
111.56
109.27
105.11
102.35
N
O
O
3k
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

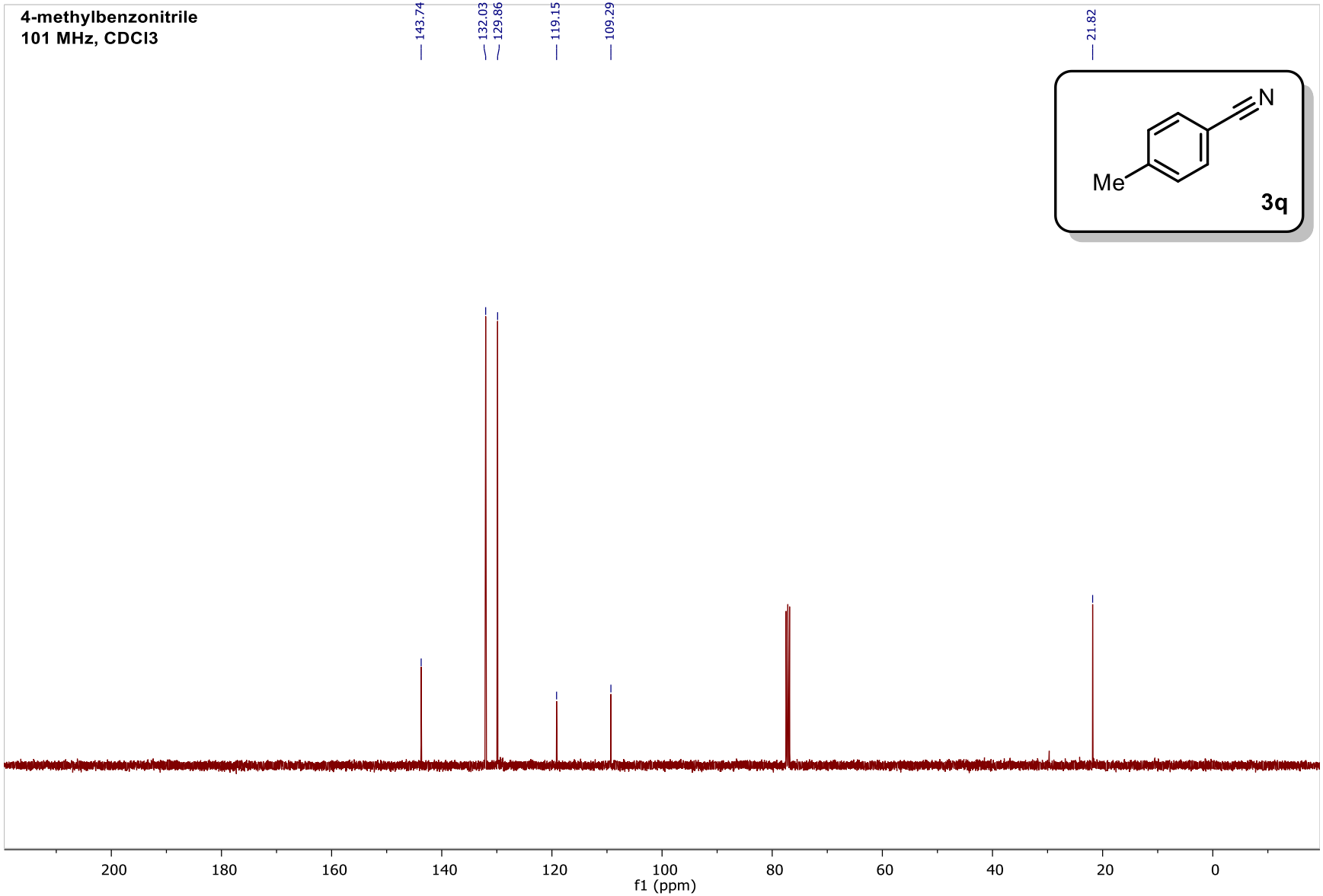

3,4,5-trimethoxybenzonitrile
101 MHz, CDCl3
153.62
142.41
118.99
109.53
106.75
61.06
56.44
MeO
MeO
OMe
N
3l
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

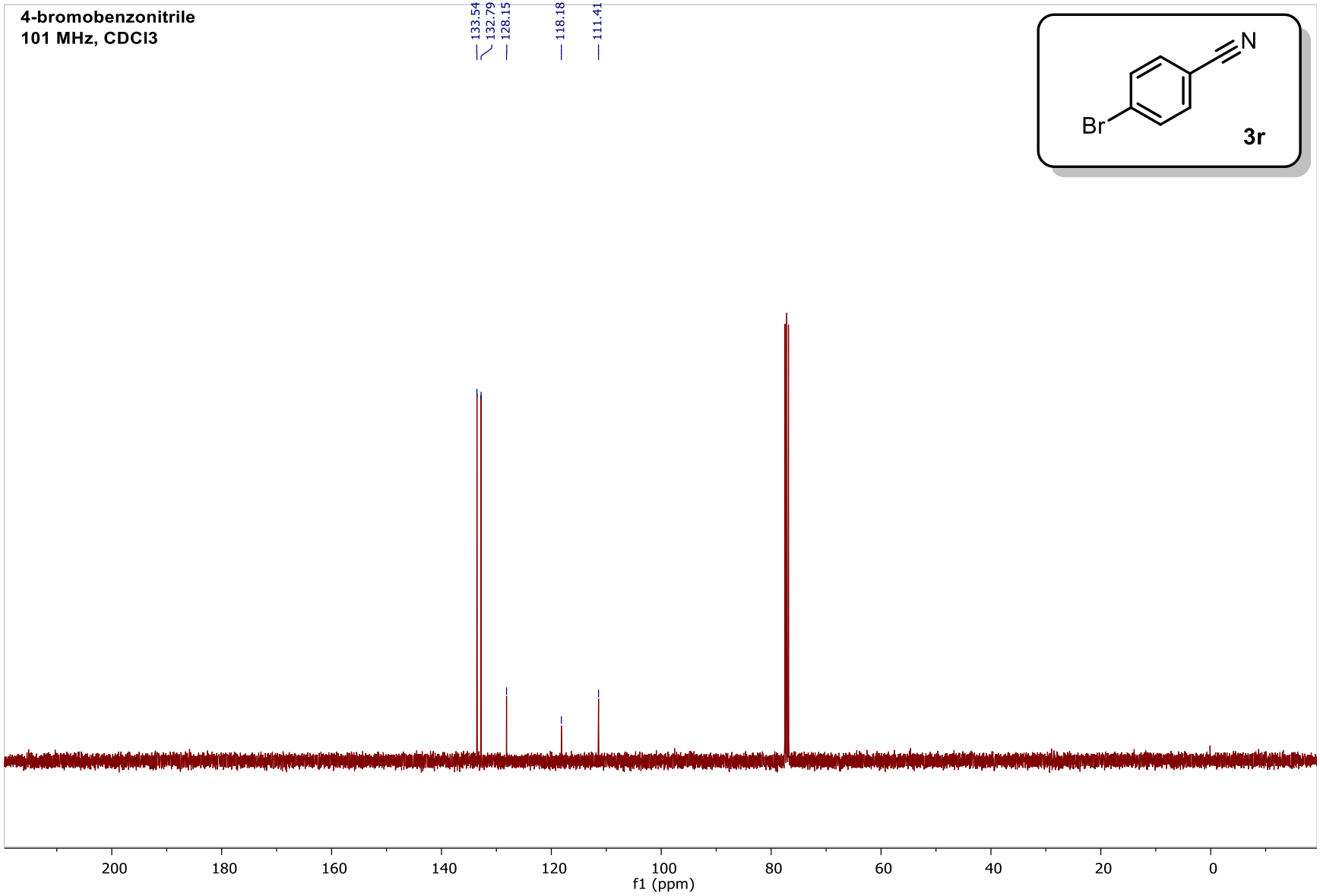

1-naphthonitrile
101 MHz, CDCl3
133.39
133.05
132.74
132.49
128.77
128.71
127.67
125.27
125.04
117.93
110.33
N
3m
f1 (ppm)
f1 (ppm)
f1 (ppm)

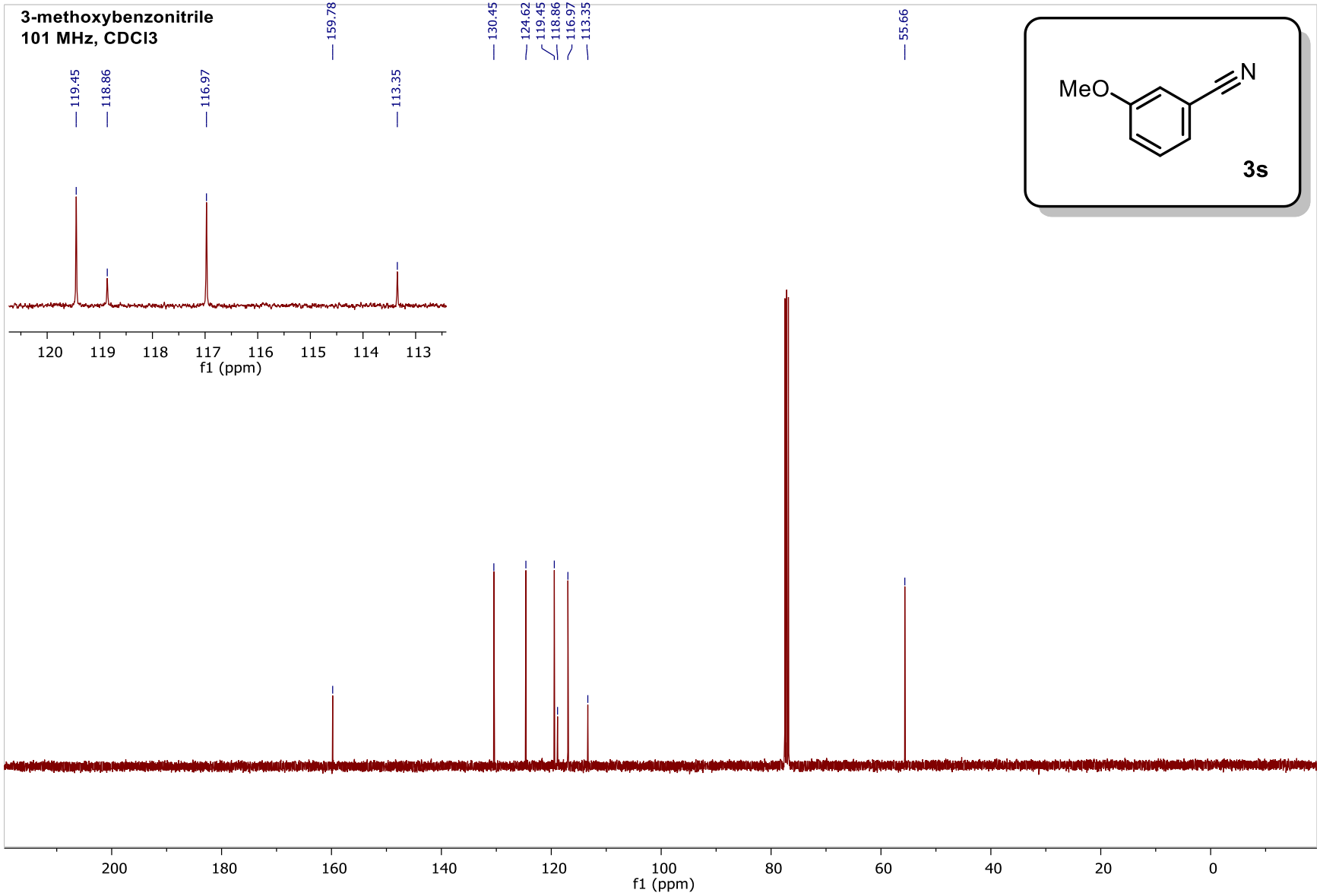

2-chloro-3-pyridinecarbonitrile
101 MHz, CDCl3
152.99
152.96
142.70
122.32
114.68
111.09
N
N
Cl
3n
153.10
153.05
153.00
152.95
152.90
152.85
152.80
f1 (ppm)
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

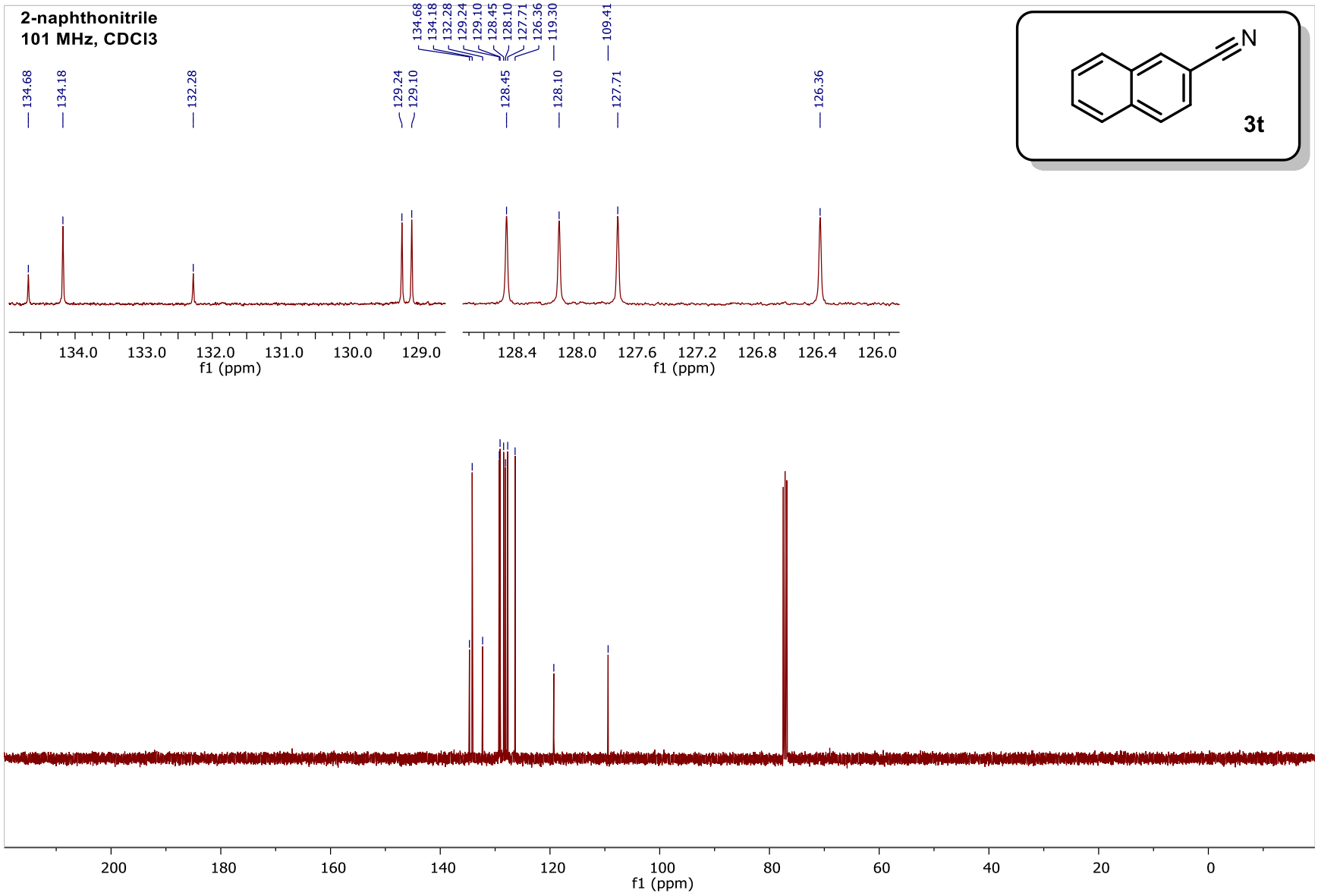

2-chloroquinoline-3-carbonitrile,
101 MHz, CDCl3
148.38
148.37
144.95
134.03
129.02
128.84
128.21
125.25
115.17
108.02
N
N
Cl
3o
f1 (ppm)
f1 (ppm)
f1 (ppm)


5-bromothiophene-2-carbonitrile
101 MHz, CDCl3
138.04
130.79
120.22
113.18
111.40
Br
S
N
3p
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


4-methylbenzonitrile
101 MHz, CDCl3
143.74
132.03
129.86
119.15
109.29
21.82
N
Me
3q
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


4-bromobenzonitrile
101 MHz, CDCl3
133.54
132.79
128.15
118.18
111.41
N
Br
3r
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


3-methoxybenzonitrile
101 MHz, CDCl3
159.78
130.45
124.62
119.45
118.86
116.97
113.35
55.66
MeO
N
3s
f1 (ppm)
f1 (ppm)


2-naphthonitrile
101 MHz, CDCl3
134.68
134.18
132.28
129.24
129.10
128.45
128.10
127.71
126.36
119.30
109.41
N
3t
f1 (ppm)
f1 (ppm)
f1 (ppm)