SUPPORTING INFORMATION

Metal-free and Atom-efficient Protocol for Diarylation of Selenocyanate by Diaryliodonium Salts

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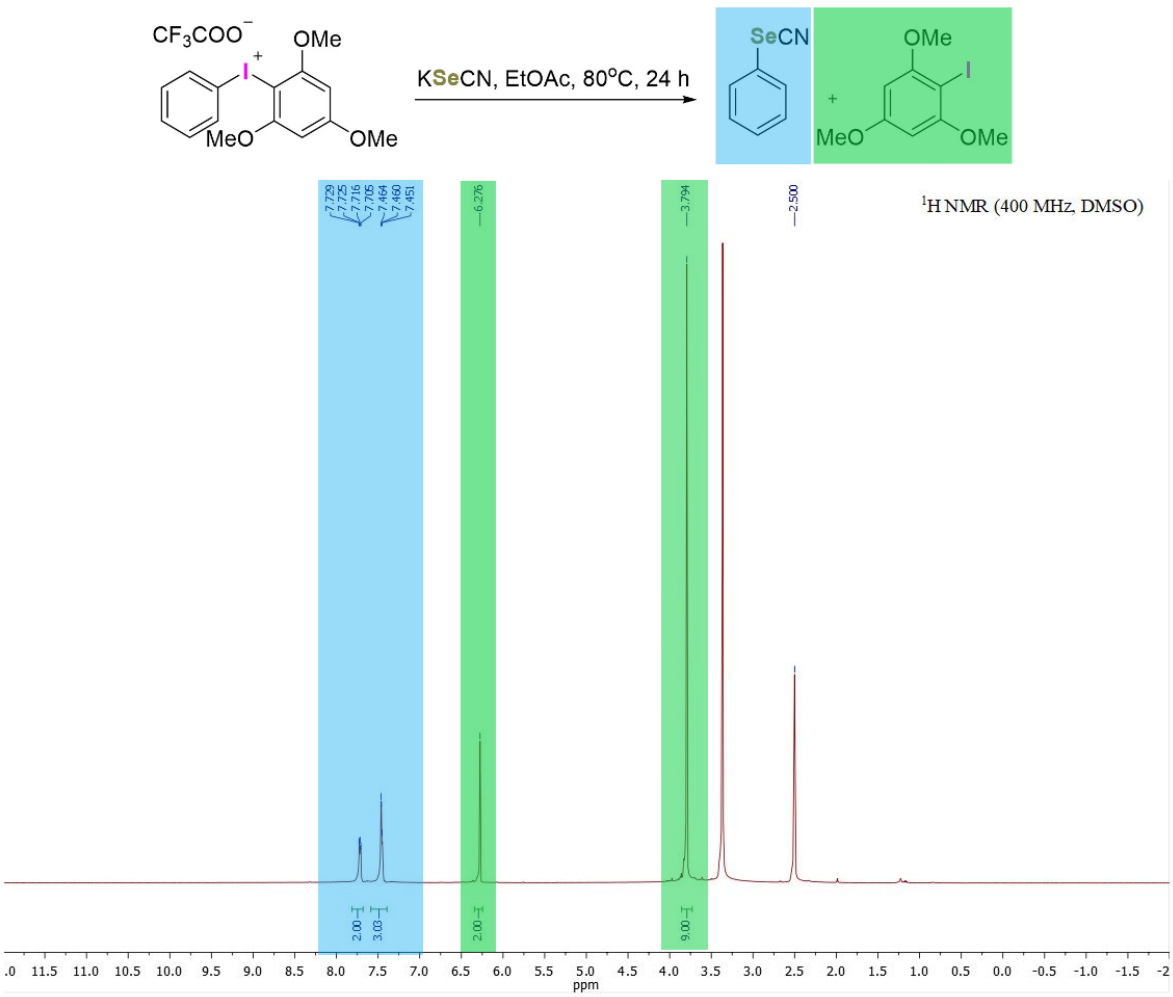
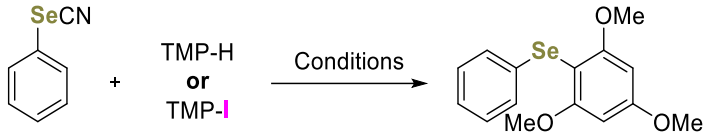


Figure S1. NMR spectra of reaction mass after arylation of KSeCN by IS **1a**.

Table S1. Arylation of PhSeCN: control experiments.[a]

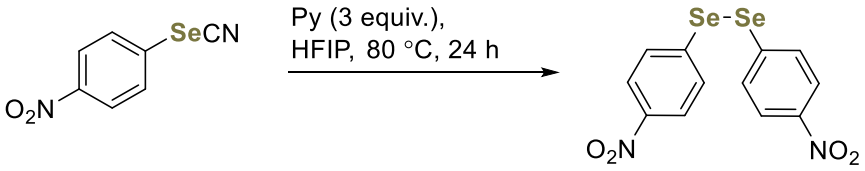


2a

Entry	Arene	Solvent, (solvent ratio)	Temperature, °C	Time, h	Yield, %[b]
1	TMP–H	HFIP/CH_2Cl_2 (1/1)	r.t	10	trace
2	TMP–H	HFIP	r.t	10	trace
3	TMP–H	HFIP	60	1.5	~5
4	TMP–H	HFIP	60	24	15
5	TMP–I	HFIP	r.t	24	trace
6	TMP–I	HFIP	60	1.5	<5
7	TMP–I	HFIP	60	24	15

[a]Reaction conditions: phenylselenocyanate (0.25 mmol), TMP–H or TMP–I (0.3 mmol), solvent (1.5 mL);

[b]Isolated yield.



3b, 90%

Reaction conditions: (**A**) 4-nitrophenylselenocyanate (1 equiv., 0.25 mmol), pyridine (3 equiv.), 24 h, 80 °C.

Figure S2. Control experiment of diselenide formation.[a]

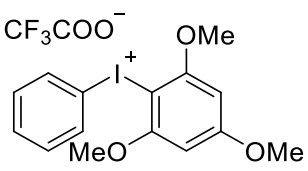
General information and synthetic procedures

General information. Reagents and solvents were obtained from commercial sources and used without further purification. HFIP was distilled and stored over the molecular sieves (4 Å). Iodonium salts were obtained by the previously reported procedures.[1] Thin layer chromatography (TLC) was performed using precoated plates purchased from Macherey–Nagel (silica gel 60, 0.20 mm). Column chromatography was performed on 63–200 μm silica gel purchased from Macherey–Nagel. Melting points were measured on a BUCHI M-560 apparatus in capillaries and are not corrected. NMR spectra were recorded on Bruker Avance III HD (400 MHz). ^{1}H NMR spectra were recorded at 400 MHz, ^{13}C NMR spectra were recorded at 100 MHz, ^{77}Se NMR spectra were recorded at 76 MHz and ^{19}F NMR spectra were recorded at 376 MHz. Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C chemical shifts are referenced relative to the residual solvent signal. High-resolution mass spectra (HRMS) were recorded using atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) methods for **2a**–**k**, **3a**,**b** on a Shimadzu LCMS-9030 Q-TOF mass spectrometer coupled with LC-30 UHPLC system.

X-ray structure determinations. X-ray diffraction data were collected at 100 K on a XtaLAB Synergy, Single source at home/near, HyPix diffractometer using Cu Kα (λ = 1.54184 Å; **2g**,**i** and **3b**). The structures were solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package incorporated in the OLEX2 program package[4] using Least Squares minimization. XRD data and structural refinement parameters are summarized in **Table S2**. Hydrogen atoms in all structures are placed in ideal calculated positions accordingly to neutron diffraction statistical data[5] and refined as colliding atoms with parameters of relative isotropic displacement. Supplementary crystallographic data have been deposited at Cambridge Crystallographic Data Centre (CCDC structures 2250168, 2250169, 2250170) and can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif.

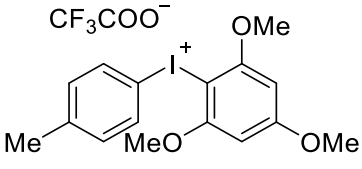
General procedure for synthesis of diarylselenides 2a–k, 3a,b (GP1). Screw cap tube was charged with a mixture of iodonium salt **1** (0.25 mmol, 1 equiv.) and KSeCN (40 mg, 0.275 mmol, 1.1 equiv.), whereupon EtOAc (2 mL) was added and the resulting mixture was heated to 80 °C and stirred for 24 h. The mixture was concentrated under a reduced pressure at 45 °C and pyridine (60 μL, 3 equiv.) in previously distilled and dried over molecular sieves (4 Å) HFIP (1.5 mL) was added to the formed residue. The resulting mixture was heated at 80 °C for 24 h until the full conversion of arylselenocyanate (monitored by TLC with 8:2, v/v, hexane: EtOAc was used as eluent). The reaction mixture was then diluted with water (10 mL) and the product was extracted by dichloromethane (3×10 mL). Organic layers were combined, dried over Na_2SO_4, and concentrated under a reduced pressure at 45 °C. Selanes **2** were isolated by flash column chromatography (hexane:EtOAc 9:1, v/v).

General procedure for the preparation of diaryliodonium trifluoroacetates 1a–n. (GP2). Diaryliodonium trifluoroacetates **1a–q** was obtained using previously reported procedure.[1] In a round-bottom flask equipped with a magnetic stirring bar and condenser, aryl iodide (2.0 mmol, 1 equiv.) was dissolved in acetonitrile (2 mL). *m*CPBA (2.4 mmol, 0.538 g, 1.2 equiv.) was added in one portion, followed by the dropwise addition of trifluoroacetic acid (2 mmol, 154 μL, 1 equiv.). The reaction was placed in an oil bath set to 55 °C and stirred 50 minutes (the reaction was monitored by TLC using hexane/EtOAc 3:1 as eluent by disappearance of the iodoarene). 1,3,5-trimethoxybenzene (2 mmol, 0.336 g, 1 equiv.) or 1,3-dimethoxybenzene (2 mmol, 0.336 g, 1 equiv.) was added and reaction mixture was stirred at 55 °C for another 15 minutes. The reaction mixture was concentrated under the reduced pressure. To the residue diethyl ether was added (15 mL) and stirred for 15 min. The precipitated trifluoroacetate salt was collected by vacuum filtration and washed with diethyl ether (3 × 10 mL). The product was dried under reduced pressure.

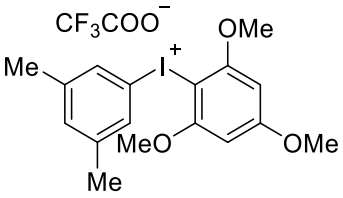


phenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (1a).[1] The reaction of iodobenzene (2 mmol, 223 μL), *m*CPBA (77%,

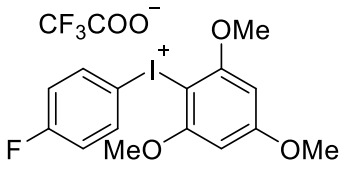
2.4 mmol, 538 mg), 1,3,5-trimethoxybenzene (2 mmol, 336 mg) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 881 mg (91%) as a slightly pink solid; mp 155–157 °C (mp lit. 153–155 °C).[1] ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 (d, J = 7.6 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 6.46 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.2, 159.4, 157.7 (d, $J_{C\text{-}F}$ = 30 Hz), 134.3, 131.6, 117.4 (q, $J_{C\text{-}F}$ = 300 Hz), 116.2, 92.1, 87.1, 57.3, 56.2. ^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6) δ −73.4.



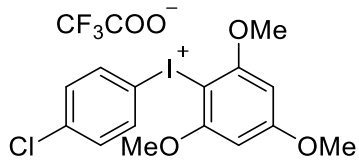
***p*-tolyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (1b)**.[1] The reaction of 4-iodotoluene (2 mmol, 436 mg), *m*CPBA (77%, 2.4 mmol, 538 mg), 1,3,5-trimethoxbenzene (2 mmol, 336 mg) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 935 mg (93%) as a colorless solid; mp 161–163 °C (mp lit. 161–163 °C).[1] ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.79 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 6.45 (s, 2H), 3.94 (s, 6H), 3.86 (s, 3H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.1, 159.3, 157.7 (q, $J_{C\text{-}F}$ = 30 Hz), 141.9, 134.4, 132.1, 117.4 (q, $J_{C\text{-}F}$ = 300 Hz), 112.6, 92.0, 87.3, 57.3, 56.1, 20.8. ^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6) δ −73.4.



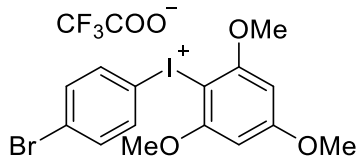
(3,5-dimethylphenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (1c).[1] The reaction of 1-iodo-3,5-dimethylbenzene (2 mmol, 289 μL), *m*CPBA (77%, 2.4 mmol, 538 mg), 1,3,5-trimethoxbenzene (2 mmol, 336 mg) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 953 mg (89%) as a colorless solid; mp 186–187 °C (mp lit. 187–189 °C).[6] ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.55 (s, 2H), 7.24 (s, 1H), 6.46 (s, 2H), 3.95 (s, 6H), 3.86 (s, 3H), 2.28 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.1, 159.4, 157.6 (q, $J_{C\text{-}F}$ = 30 Hz), 141.1, 133.1, 131.8, 117.4 (q, $J_{C\text{-}F}$ = 300 Hz), 115.7, 92.1, 86.8, 57.3, 56.2, 20.7. ^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6) δ −73.4.



(4-fluorophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (1d).[1] The reaction of 1-fluoro-4-iodobenzene (2 mmol, 231 μL), *m*CPBA (77%, 2.4 mmol, 538 mg), 1,3,5-trimethoxbenzene (2 mmol, 336 mg) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 892 mg (88%) as a colorless solid; mp 167–169 °C (mp lit. 165–169 °C).[1] ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99–7.96 (m, 2H), 7.35–7.31 (m, 2H), 6.46 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.2, 163.6 (d, $J_{C\text{-}F}$ = 249 Hz), 159.3, 157.7 (q, $J_{C\text{-}F}$ = 30 Hz), 137.2 (d, $J_{C\text{-}F}$ = 9 Hz), 119.0 (d, $J_{C\text{-}F}$ = 23 Hz), 117.0 (q, $J_{C\text{-}F}$ = 266 Hz), 110.4 (d, $J_{C\text{-}F}$ = 3 Hz), 92.1, 87.5, 57.4, 56.2. ^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6) δ −73.4, −107.5 (m).

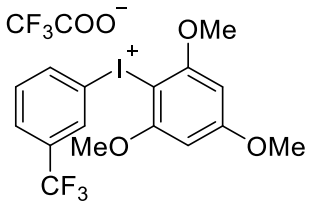


(4-chlorophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (1e).[1] The reaction of 1-chloro-4-iodobenzene (2 mmol, 476 mg), *m*CPBA (77%, 2.4 mmol, 538 mg), 1,3,5-trimethoxbenzene (2 mmol, 336 mg) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 812 mg (79%) as a colorless solid; mp 168–171 °C (mp lit. 168–172 °C).[1] ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 6.47 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.3, 159.4, 157.7 (q, $J_{C\text{-}F}$ `= 29 Hz), 136.7, 136.1, 131.5, 117.4 (q, $J_{C\text{-}F}$ = 300 Hz), 114.0, 92.1, 87.3, 57.4, 56.2. ^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6) δ −73.4.

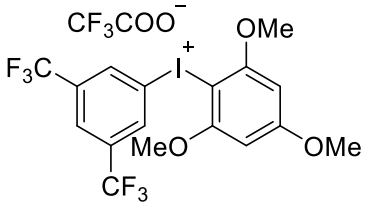


(4-bromophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (1f).[1] The reaction of 1-bromo-4-iodobenzene (2 mmol, 566 mg), *m*CPBA (77%, 2.4 mmol, 538 mg), 1,3,5-trimethoxbenzene (2 mmol, 336 mg) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 910 mg (81%) as a colorless solid; mp 171–174 °C (mp lit. 171–173 °C).[1] ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 6.47 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.3, 159.4, 157.7 (d, $J_{C\text{-}F}$ = 31 Hz),

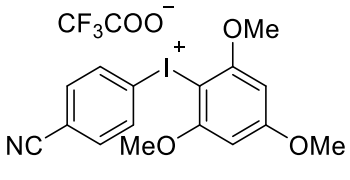
136.2, 134.4, 125.5, 117.4 (d, $J_{C\text{-}F}$ = 299 Hz), 114.7, 92.1, 87.2, 57.4, 56.2. $^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d_6) δ −73.4.



(3-(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (1g).[1] The reaction of 3-iodobenzenetrifluoride (2 mmol, 288 μL), *m*CPBA (77%, 2.4 mmol, 538 mg), 1,3,5-trimethoxbenzene (2 mmol, 336 mg) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 800 mg (71%) as a colorless solid; mp 155–157 °C (mp lit. 142–144°°C).[6] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34 (s, 1H), 8.14 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H), 6.48 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 166.4, 159.4, 157.7 (q, $J_{C\text{-}F}$ = 30 Hz), 138.1, 132.7, 131.1 (q, $J_{C\text{-}F}$ = 33 Hz), 130.8 (q, $J_{C\text{-}F}$ = 4 Hz), 128.3 (q, $J_{C\text{-}F}$ = 4 Hz), 123.0 (q, $J_{C\text{-}F}$ = 272 Hz), 117.4 (q, $J_{C\text{-}F}$ = 299 Hz), 116.4, 92.2, 87.2, 57.3, 56.2. $^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d_6) δ −61.3, −73.4.

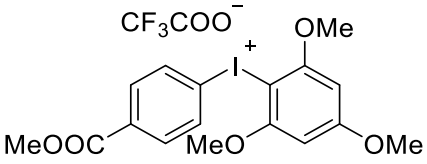


(3,5-bis(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (1h).[1] The reaction of 3,5-bis(trifluoromethyl)iodobenzene (2 mmol, 465 μL), *m*CPBA (77%, 2.4 mmol, 538 mg), 1,3,5-trimethoxbenzene (2 mmol, 336 mg) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 855 mg (69%) as a colorless solid; mp 151–153 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.60 (s, 2H), 8.44 (s, 1H), 6.49 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 166.6, 159.4, 157.8 (q, $J_{C\text{-}F}$ = 30 Hz), 135.0, 132.1 (q, $J_{C\text{-}F}$ = 34 Hz), 125.7, 122.2 (q, $J_{C\text{-}F}$ = 272 Hz), 117.3, 117.3 (q, $J_{C\text{-}F}$ = 299 Hz), 92.2, 87.4, 57.3, 56.3. $^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d_6) δ −61.3, −73.5. HRMS (ESI) *m/z* calcd. for $[M]^+$ $C_{17}H_{14}F_6IO_3^+$: 506.9889, found 506.9886.

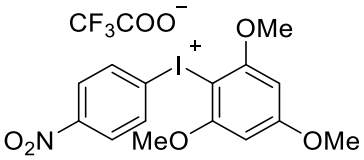


(4-cyanophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (1i).[1] The reaction of 4-iodobenzonitrile (2 mmol, 458 mg), *m*CPBA (77%, 2.4 mmol, 538 mg), 1,3,5-

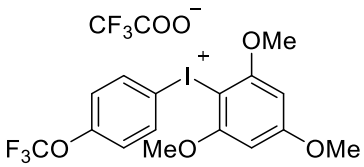
trimethoxbenzene (2 mmol, 336 mg) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 783 mg (72%) as a colorless solid; mp 166–167 °C (mp lit. 166–167 °C).[1] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 6.49 (s, 2H), 3.93 (s, 6H), 3.88 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.5, 159.5, 157.9 (q, $J_{C\text{-}F}$ = 31 Hz), 134.9, 134.8, 121.2, 117.6, 117.3 (q, $J_{C\text{-}F}$ = 300 Hz), 114.1, 107.1, 92.2, 87.2, 57.4, 56.2. ^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6) δ −73.4.



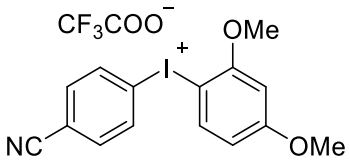
(4-(methoxycarbonyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (1j).[1] The reaction of methyl 4-iodobenzoate (2 mmol, 524 mg), *m*CPBA (77%, 2.4 mmol, 538 mg), 1,3,5-trimethoxbenzene (2 mmol, 336 mg) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 835 mg (77%) as a colorless solid; mp 150–153 °C (mp lit. 152–155 °C).[7] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 6.48 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H), 3.85 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.4, 165.2, 159.4, 157.8 (q, $J_{C\text{-}F}$ = 30 Hz), 134.6, 132.1, 131.8, 121.1, 117.4 (q, $J_{C\text{-}F}$ = 300 Hz), 92.2, 87.1, 57.4, 56.2, 52.7. ^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6) δ −73.4.



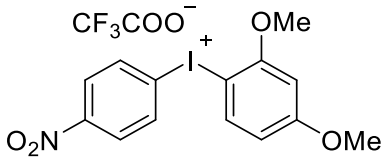
(4-nitrophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (1k).[1] The reaction of 1-iodo-4-nitrobenzene (2 mmol, 498 mg), *m*CPBA (77%, 2.4 mmol, 538 mg), 1,3,5-trimethoxbenzene (2 mmol, 336 mg) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 518 mg (45%) as a colorless solid; mp 143–144 °C (mp lit. 144–147 °C).[7] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 (d, J = 9.2 Hz, 2H), 8.14 (d, J = 9.2 Hz, 2H), 6.49 (s, 2H), 3.94 (s, 6H), 3.88 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.5, 159.5, 157.7 (q, $J_{C\text{-}F}$ = 30 Hz), 149.1, 135.4, 126.1, 122.5, 117.4 (q, $J_{C\text{-}F}$ = 299 Hz), 92.2, 87.2, 57.5, 56.3. ^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6) δ −73.4.



(4-(trifluoromethoxy)phenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (1l).[1] The reaction of 1-iodo-4-(trifluoromethoxy)benzene (2 mmol, 576 mg), *m*CPBA (77%, 2.4 mmol, 538 mg), 1,3,5-trimethoxbenzene (2 mmol, 336 mg) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 518 mg (45%) as a colorless solid; mp 142–144 °C (mp lit. 144–147 °C).[6] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 6.48 (s, 2H), 3.95 (s, 6H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.3, 159.4, 157.7 (q, $J_{C\text{-}F}$ = 30 Hz), 150.2 (d, $J_{C\text{-}F}$ = 2 Hz), 136.7, 123.9, 119.9 (q, $J_{C\text{-}F}$ = 256 Hz), 117.4 (q, $J_{C\text{-}F}$ = 300 Hz), 113.8, 92.1, 87.3, 57.4, 56.2. ^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6) δ −56.9, −73.4.

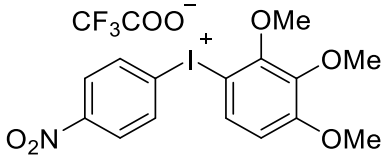


(4-cyanophenyl)(2,4-dimethoxyphenyl)iodonium trifluoroacetate (1m).[1] The reaction of 4-iodobenzonitrile (2 mmol, 458 mg), *m*CPBA (77%, 2.4 mmol, 538 mg), 1,3-dimethoxbenzene (2 mmol, 262 μL) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 713 mg (70%) as a colorless solid; mp 128–130 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.29 (d, J = 8.4 Hz, 2H), 8.18 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 2.4 Hz, 1H), 6.69 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz 1H), 3.96 (s, 3H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, Acetone-d_6) δ 166.3, 161.0 (q, $J_{C\text{-}F}$ = 33 Hz), 160.0, 139.7, 136.2, 135.2, 123.2, 118.2, 117.8 (q, $J_{C\text{-}F}$ = 295 Hz), 115.7, 109.7, 100.5, 98.2, 57.5, 56.4. ^{19}F{^{1}H} NMR (376 MHz, Acetone-d_6) δ −73.4.

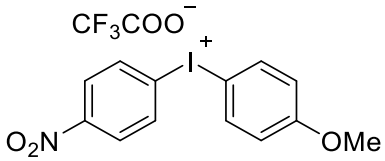


(4–nitrophenyl)(2,4–dimethoxyphenyl)iodonium trifluoroacetate (1n).[1] The reaction of 1-iodo-4-nitrobenzene (2 mmol, 498 mg), *m*CPBA (77%, 2.4 mmol, 538 mg), 1,3-dimethoxbenzene (2 mmol, 262 μL) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 494 mg (64%) as a colorless solid; mp 141–143 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30–8.20 (m, 5H), 6.82 (d, J = 2.4 Hz, 1H), 6.72 (dd, J_1 = 8.8, J_2 = 2.4 Hz, 1H), 3.92 (s, 3H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.0, 158.3, 157.8 (q, $J_{C\text{-}F}$ = 30 Hz), 149.2, 138.6,

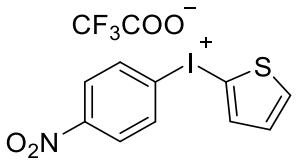
135.8, 126.0, 122.7, 117.3 (q, $J_{C\text{-}F}$ = 299 Hz), 109.1, 99.8, 96.2, 57.2, 56.1. $^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d_6) δ −73.4. HRMS (ESI) *m/z* calcd. for $[M - CF_3COO^-]^+$ $C_{14}H_{13}INO_4^+$: 385.9884, found 385.9886.



(4-nitrophenyl)(2,3,4-trimethoxyphenyl)iodonium trifluoroacetate (1o).[1] The reaction of 1-iodo-4-nitrobenzene (2 mmol, 498 mg), *m*CPBA (77%, 2.4 mmol, 538 mg), 1,2,3-trimethoxbenzene (2 mmol, 336 mg) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 772 mg (73%) as a colorless solid; mp 139–141 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.33 (d, *J* = 8.8 Hz, 2H), 8.28 (d, *J* = 9.2 Hz, 2H), 8.10 (d, *J* = 9.2 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.76 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 158.4, 157.9 (q, $J_{C\text{-}F}$ = 30 Hz), 151.5, 149.3, 141.2, 136.0, 132.1, 126.2, 123.0, 117.3 (q, $J_{C\text{-}F}$ = 299 Hz), 110.7, 103.0, 62.1, 60.9, 56.6. $^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d_6) δ −73.4.

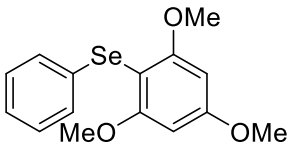


(4-methoxyphenyl)(4-nitrophenyl)iodonium trifluoroacetate (1p).[1] The reaction of 1-iodo-4-nitrobenzene (2 mmol, 498 mg), *m*CPBA (77%, 2.4 mmol, 538 mg), anisole (2 mmol, 217 μL) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 486 mg (52%) as a colorless solid; mp 147–148 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.42 (d, *J* = 8.4 Hz, 2H), 8.29 (d, *J* = 8.4 Hz, 2H), 8.23 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 162.2, 157.9 (q, $J_{C\text{-}F}$ = 30 Hz), 149.3, 137.6, 136.0, 126.1, 123.4, 117.6, 117.3 (q, $J_{C\text{-}F}$ = 299 Hz), 105.9, 55.8. $^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d_6) δ −73.4.

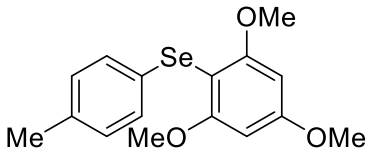


(4-nitrophenyl)(thiophen-2-yl)iodonium trifluoroacetate (1q).[1] The reaction of 1-iodo-4-nitrobenzene (2 mmol, 538 mg), *m*CPBA (77%, 2.4 mmol, 538 mg), thiophene (2 mmol, 162 μL) and trifluoroacetic acid (154 μL) according to procedure **GP2** afforded 427 mg (48%) as a colorless solid; mp 122–123 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.49 (d, *J* = 8.4 Hz, 2H), 8.30 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 3.2 Hz, 1H), 7.99 (d, *J* = 5.2 Hz, 1H), 7.20 (t, *J* = 4.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-

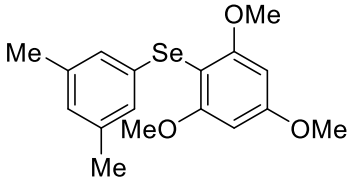
d_6) δ: 157.9 (q, $J_{C\text{-}F}$ = 30 Hz), 140.3, 137.2, 134.6, 132.0, 131.7, 129.6, 119.6, 117.3 (q, $J_{C\text{-}F}$ = 299 Hz), 101.2. $^{19}F\{^1H\}$ NMR (376 MHz, DMSO-d_6) δ −73.5.



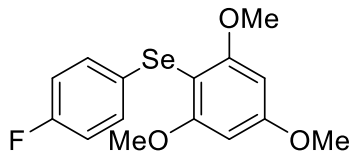
phenyl(2,4,6-trimethoxyphenyl)selane (2a).[8] The reaction of phenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1a** (0.25 mmol, 121 mg) according to general procedure **GP1** afforded 58 mg (73%) of **2a** isolated as the colorless crystalline solid; mp 105–107 °C (lit. yellow oil [8]). ^1H NMR (400 MHz, $CDCl_3$) δ 7.19–7.08 (m, 5H), 6.21 (s, 2H), 3.87 (s, 3H), 3.79 (s, 6H). $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ 163.1, 162.0, 133.7, 128.8, 125.4, 97.1, 91.2, 56.4, 55.6. $^{77}Se\{^1H\}$ NMR (76 MHz, $CDCl_3$) δ 224.4. HRMS (ESI) *m/z* calcd. for $[M+Na]^+$ $C_{15}H_{16}NaO_3Se^+$: 347.0157, found 347.0157.



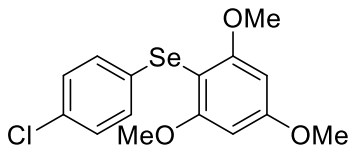
***p*-tolyl(2,4,6-trimethoxyphenyl)selane (2b)**.[8] The reaction of *p*-tolyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1b** (0.25 mmol, 125 mg) according to general procedure **GP1** afforded 32 mg (37%) of **2b** isolated as colorless oil (lit.[8] yellow oil). ^1H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 6.8 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.19 (s, 2H), 3.86 (s, 3H), 3.79 (s, 6H), 2.25 (s, 3H). $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ 163.0, 162.0, 135.2, 129.7, 129.7, 129.3, 97.7, 91.2, 56.4, 55.5, 21.1. $^{77}Se\{^1H\}$ NMR (76 MHz, $CDCl_3$) δ 157.4. HRMS (ESI) *m/z* calcd. for $[M]^+$ $C_{16}H_{18}O_3Se^+$: 338.0416, found 338.0416.



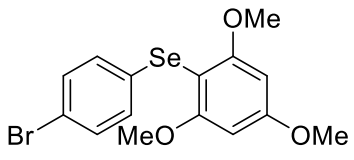
(3,5-dimethylphenyl)(2,4,6-trimethoxyphenyl)selane (2c). The reaction of (3,5-dimethylphenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1c** (0.25 mmol, 128 mg) according to general procedure **GP1** afforded 32 mg (26%) of **2c** isolated as a colorless solid; mp 102–104 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 2H), 6.71 (s, 1H), 6.20 (s, 2H), 3.87 (s, 3H), 3.79 (s, 6H), 2.19 (s, 6H). $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ 163.0, 162.1, 138.3, 133.1, 127.4, 126.5, 97.4, 91.3, 56.5, 21.4. $^{77}Se\{^1H\}$ NMR (76 MHz, $CDCl_3$) δ 219.7. HRMS (APCI) *m/z* calcd. for $[M+H]^+$ $C_{17}H_{21}O_3Se^+$: 353.0656, found 353.0651.



(4-fluorophenyl)(2,4,6-trimethoxyphenyl)selane (2d). The reaction of (4-fluorophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1d** (0.25 mmol, 126 mg) according to general procedure **GP1** afforded 34 mg (40%) of **2d** isolated as the colorless solid; mp 80–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.17 (m, 2H), 6.83–6.87 (m, 2H), 6.19 (s, 2H), 3.86 (s, 3H), 3.79 (s, 6H). $^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) δ 163.1, 161.8, 161.6 (d, $J_{C\text{-}F}$ = 242 Hz), 131.2 (d, $J_{C\text{-}F}$ = 8 Hz), 127.8 (d, $J_{C\text{-}F}$ = 3 Hz), 115.9 (d, $J_{C\text{-}F}$ = 21 Hz), 97.7, 91.2, 56.4, 55.5. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ −117.7. $^{77}Se\{^{1}H\}$ NMR (76 MHz, $CDCl_3$) δ 223.1. HRMS (APCI) *m/z* calcd. for $[M+H]^+$ $C_{15}H_{16}FO_3Se^+$: 343.0249, found 343.0245.



(4-chlorophenyl)(2,4,6-trimethoxyphenyl)selane (2e). The reaction of (4-chlorophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1e** (0.25 mmol, 130 mg) according to general procedure **GP1** afforded 50 mg (57%) of **2e** isolated as the colorless solid; mp 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.05 (m, 4H), 6.20 (s, 2H), 3.87 (s, 3H), 3.79 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3, 161.9, 132.1, 131.3, 130.3, 128.9, 96.9, 91.3, 56.4, 55.6. $^{77}Se\{^{1}H\}$ NMR (76 MHz, $CDCl_3$) δ 227.2. HRMS (APCI) *m/z* calcd. for $[M+H]^+$ $C_{15}H_{16}ClO_3Se^+$: 358.9953, found 358.9946.



(4-bromophenyl)(2,4,6-trimethoxyphenyl)selane (2f).[8] The reaction of (4-bromophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1f** (0.25 mmol, 141 mg) according to general procedure **GP1** afforded 69 mg (68%) of **2f** isolated as a colorless solid; mp 108−109 °C from hexane: EtOAc (mp lit.[8] 100–102 °C from hexane: EtOAc). HRMS (APCI) *m/z* calcd. for $[M+H]^+$ $C_{15}H_{16}BrO_3Se^+$: 402.9443, found 402.9438. The formation and purity of **2f** was confirm by GCMS (EI) m/z 402 that was process instantly after isolation of **2f**.

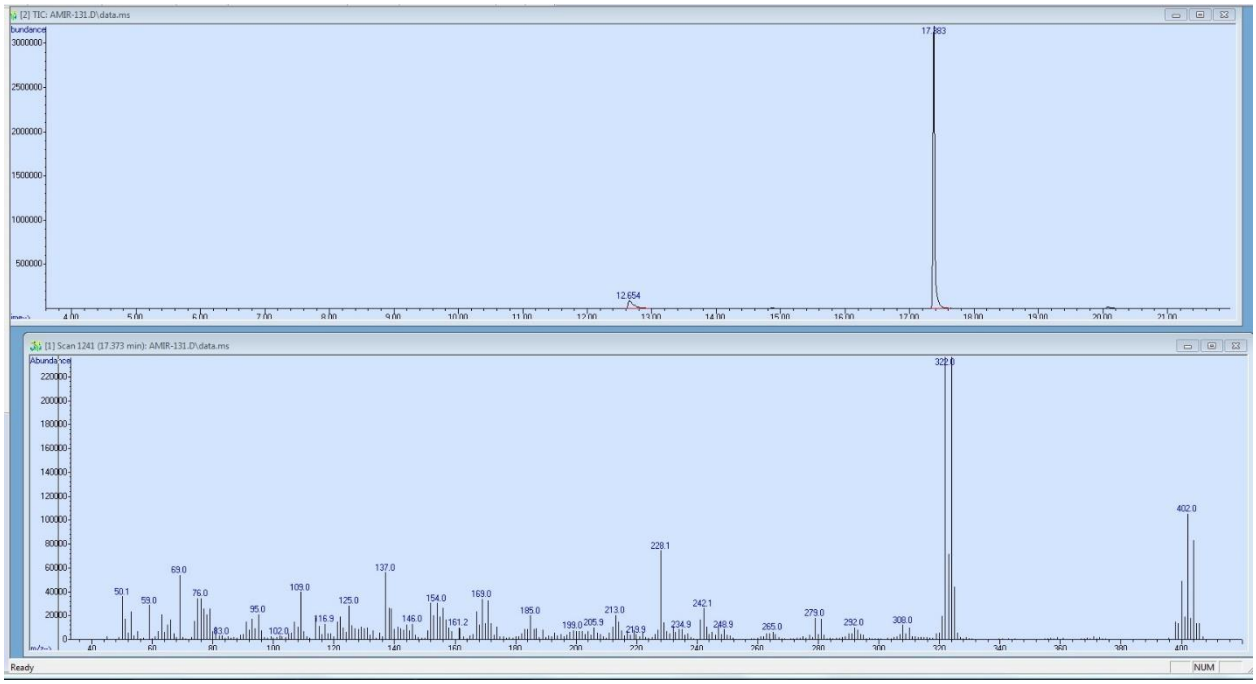
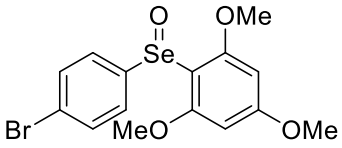
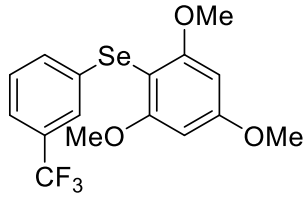


Figure S3. Chromatogram and mass spectrum of **2f**.

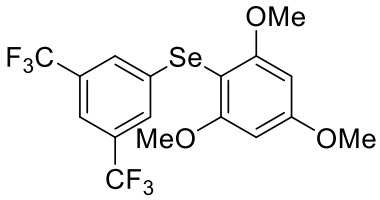


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.56 (m, 4H), 6.04 (s, 2H), 3.81 (s, 3H), 3.68 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 165.3, 161.9, 141.0, 131.8, 128.1, 124.4, 110.6, 91.4, 56.1, 55.7. $^{77}Se\{^{1}H\}$ NMR (76 MHz, $CDCl_3$) δ 839.8. Compound **2f** is unstable on air and during storage undergoes oxidation to corresponding selenoxide. An ^{77}Se $\{^{1}H\}$ NMR spectra revealed chemical shift of selenoxide on 839.8 ppm.[9] Additionally, the molecular ion of selenoxide was detected in HRMS (APCI) spectra of **2f**: *m/z* calcd. $[M_{selenoxide}+H]^+$ $C_{15}H_{16}BrO_4Se^+$: 418.9392, found 418.9386.

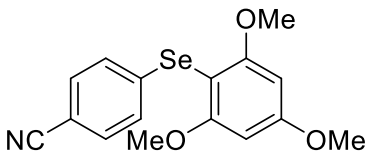


(3-trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)selane (2g). The reaction of (3-(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1g** (0.25 mmol, 138 mg) according to general procedure **GP1** afforded 24 mg (23%) of **2g** isolated as a colorless solid; mp 113−114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.33 (d, J = 7.6 Hz 2H), 7.23 (t, J = 7.8 Hz, 1H), 6.22 (s, 2H), 3.88 (s, 3H), 3.79 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.5, 161.9, 135.0, 131.9 (q, $J_{C\text{-}F}$ = 1.1 Hz), 131.0 (q, $J_{C\text{-}F}$ = 32 Hz), 129.0, 125.5 (q, $J_{C\text{-}F}$ = 4 Hz), 124.0 (q, $J_{C\text{-}F}$ = 271 Hz), 122.1 (q, $J_{C\text{-}F}$ = 4 Hz), 96.1, 91.3, 56.4, 55.6. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ

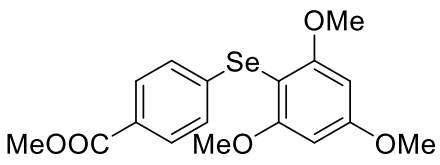
−62.7. ^{77}Se{^{1}H} NMR (76 MHz, $CDCl_3$) δ 239.2. HRMS (APCI) *m/z* calcd. for $[M+H]^+$ $C_{16}H_{16}F_3O_3Se^+$: 393.0217, found 393.0212.



(3,5-bis(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)selane (2h). The reaction of (3,5-bis(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1h** (0.25 mmol, 155 mg) according to general procedure **GP1** afforded 62 mg (54%) of **2h** isolated as the light yellow solid; mp 103−104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.59 (m, 3H), 6.23 (s, 2H), 3.89 (s, 3H), 3.80 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.9, 161.8, 137.1, 131.6 (q, $J_{C\text{-}F}$ = 33 Hz), 128.5 (m), 123.3 (q, $J_{C\text{-}F}$ = 271.3 Hz), 119.0 (m), 94.9, 91.4, 56.3, 55.6. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −63.0. ^{77}Se{^{1}H} NMR (76 MHz, $CDCl_3$) δ 257.3. HRMS (APCI) *m/z* calcd. for $[M+H]^+$ $C_{15}H_{16}NO_5Se^+$: 461.0091, found 461.0088.

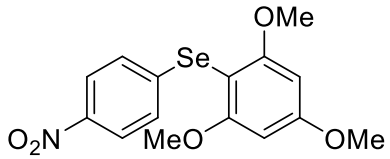


4-((2,4,6-trimethoxyphenyl)selanyl)benzonitryl (2i). The reaction of (4-cyanophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1i** (0.25 mmol, 127 mg) according to general procedure **GP1** afforded 73 mg (83%) of **2i** isolated as a pale yellow solid; mp 128−130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.23 (s, 2H), 3.89 (s, 3H), 3.79 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.8, 162.0, 142.4, 132.1, 128.3, 119.5, 108.2, 95.0, 91.3, 56.4, 55.6. ^{77}Se{^{1}H} NMR (76 MHz, $CDCl_3$) δ 253.7. HRMS (APCI) *m/z* calcd. for $[M+H]^+$ $C_{16}H_{16}NO_3Se^+$: 350.0295, found 350.0291.

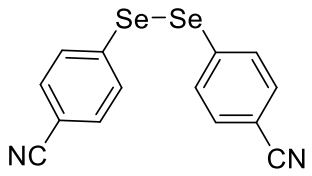


methyl 4-((2,4,6-trimethoxyphenyl)selanyl)benzoate (2j). The reaction of (4-(methoxycarbonyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1j** (0.25 mmol, 136 mg) according to general procedure **GP1** afforded 73 mg (76%) of **2j** isolated as a colorless solid; mp 125–127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.23 (s, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 3.79 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.3, 163.5, 162.0, 141.6, 129.8, 127.7, 126.9, 95.7, 91.3, 56.4, 55.6, 52.1. ^{77}Se{^{1}H} NMR (76

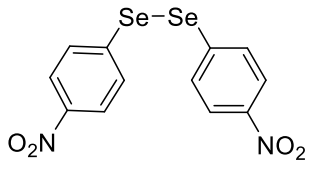
MHz, $CDCl_3$) δ 242.5. HRMS (ESI) *m/z* calcd. for $[M+H]^+$ $C_{16}H_{16}NO_3Se^+$: 383.0398, found 383.0392.



(4-nitrophenyl)(2,4,6-trimethoxyphenyl)selane (2k). The reaction of (4-nitrophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1k** (0.25 mmol, 132 mg) according to general procedure **GP1** afforded 85 mg (92%) of **2k** isolated as a bright yellow solid; mp 134−135 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.2 Hz, 2H), 7.21 (d, *J* = 9.2 Hz, 2H), 6.24 (s, 2H), 3.90 (s, 3H), 3.80 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.9, 162.0, 145.6, 145.5, 127.9, 123.7, 94.9, 91.3, 56.5, 55.7. $^{77}Se\{^1H\}$ NMR (76 MHz, $CDCl_3$) δ 260.0. HRMS (APCI) *m/z* calcd. for $[M+H]^+$ $C_{15}H_{16}NO_5Se^+$: 370.0194, found 370.0189.

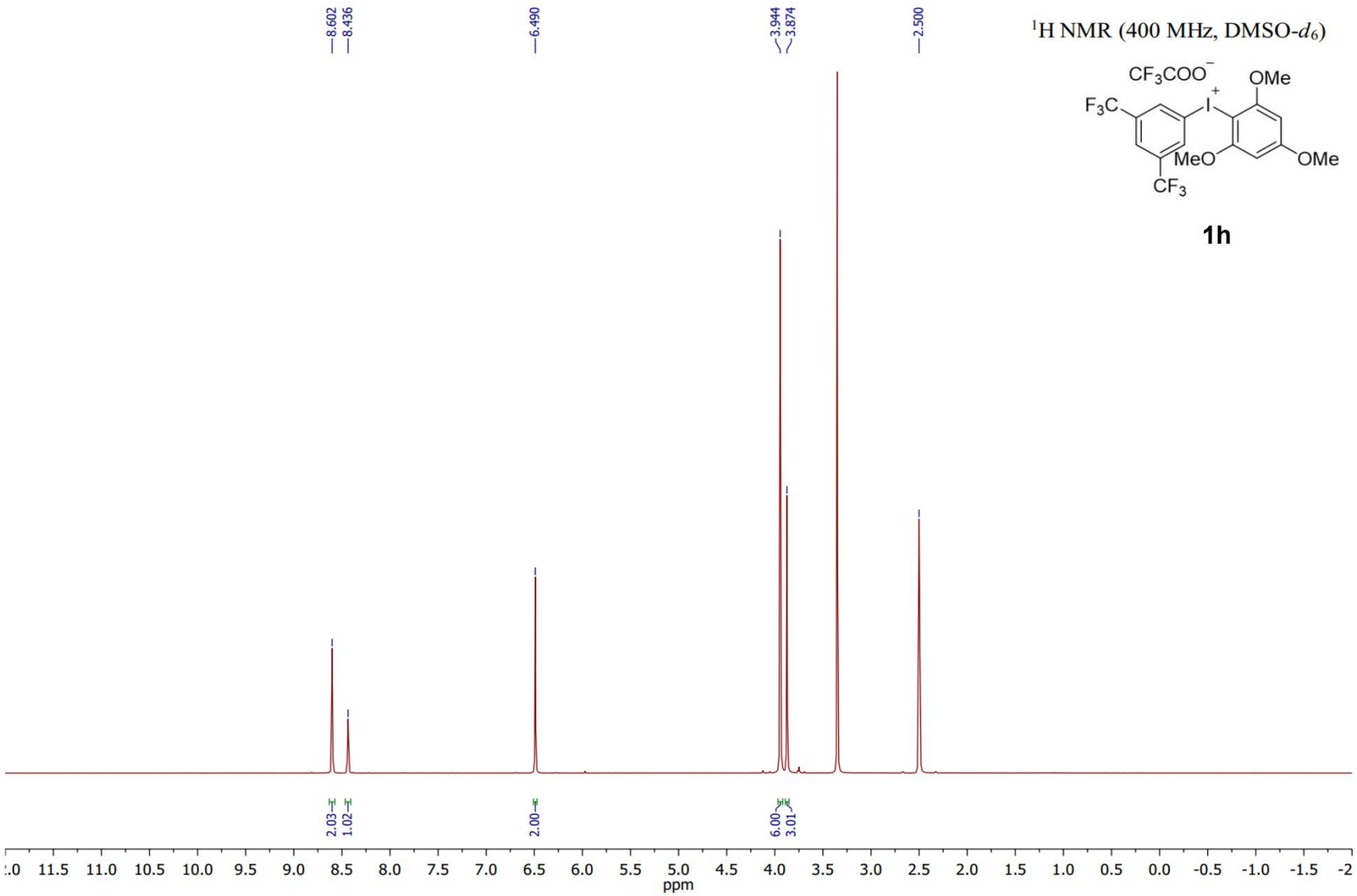


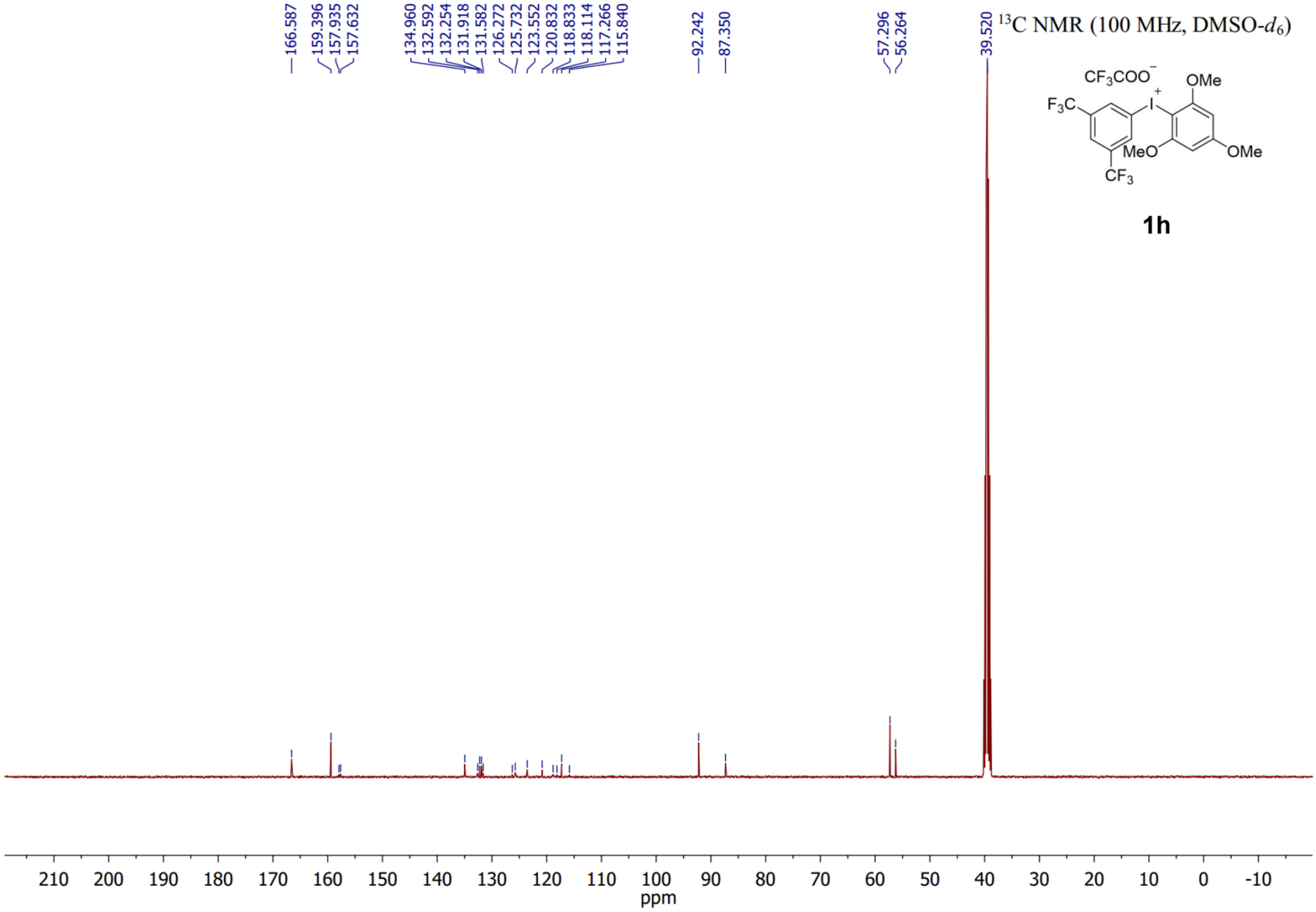
4,4'-diselanediyldibenzonitrile (3a).[10] The reaction of (4-cyanophenyl)(2,4-dimethoxyphenyl)iodonium trifluoroacetate **1m** (0.25 mmol, 120 mg) according to general procedure **GP1** afforded 34 mg (76%) of **3a** isolated as a brown solid; mp 152−154 °C (mp lit.[10] 156–158 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 4H), 7.54 (d, *J* = 8.0 Hz, 4H). $^{13}C\{^1H\}$ NMR (100MHz, $CDCl_3$) δ 136.5, 132.8, 130.7, 118.3, 111.5. $^{77}Se\{^1H\}$ NMR (76 MHz, $CDCl_3$) δ 456.0. HRMS (ESI) *m/z* calcd. for $[M]^+$ $C_{14}H_8N_2NaSe_2^+$: 386.8910, found 386.8913.



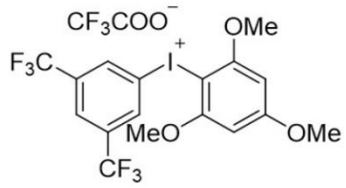
1,2-bis(4-nitrophenyl)diselane (3b).[11] The reaction of (4-nitrophenyl)(2,4-dimethoxyphenyl)iodonium trifluoroacetate **1n** (0.25 mmol, 125 mg) according to general procedure **GP1** afforded 45 mg (89%) of **3b** isolated as a brown solid; mp 179−181 °C (mp lit.[11] 179–180 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, 4H), 7.75 (d, *J* = 8.8 Hz, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.5, 138.7, 130.5, 124.4. $^{77}Se\{^1H\}$ NMR (76 MHz, $CDCl_3$) δ 456.2. HRMS (ESI) *m/z* calcd. for $[M]^+$ $C_{12}H_8N_2O_4Se_2^+$: 403.8815, found 403.8812.

NMR spectra of **1h**, **m**–**q**

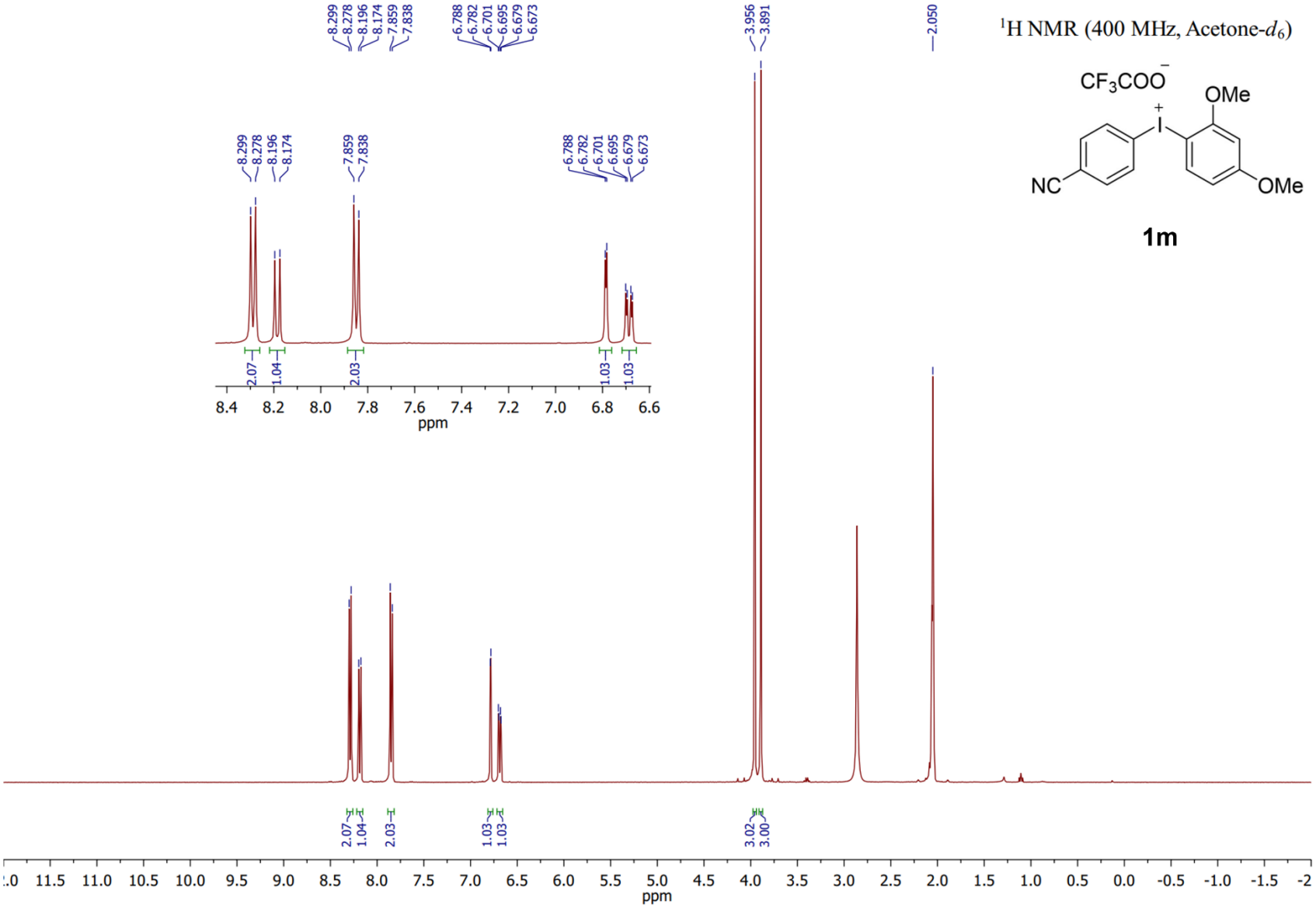


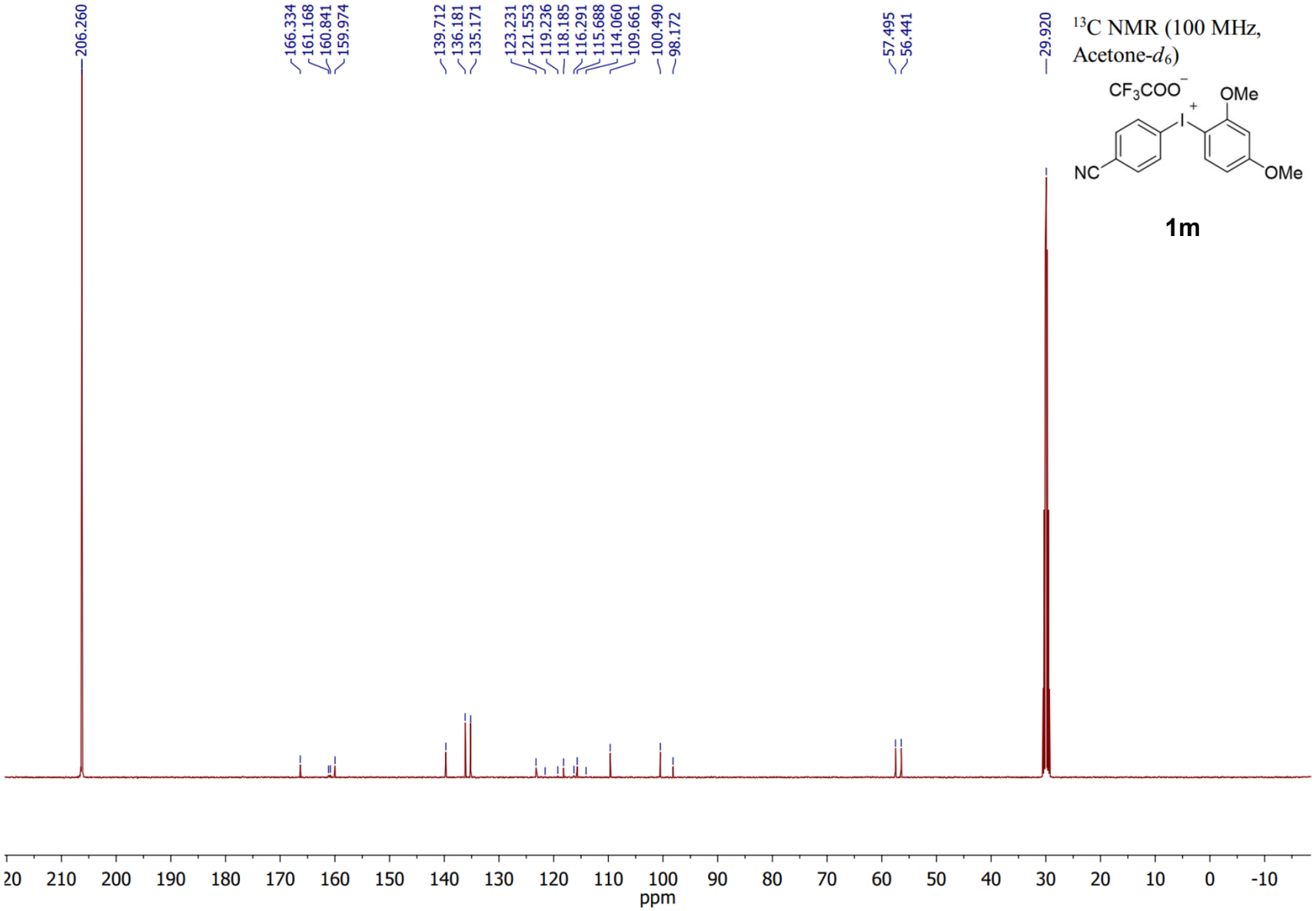

166.587
159.396
157.935
157.632
134.960
132.592
132.254
131.918
131.582
126.272
125.732
123.552
120.832
118.833
118.114
117.266
115.840
92.242
87.350
57.296
56.264
39.520
^{13}C NMR (100 MHz, DMSO-d_6)
CF_3COO^-
OMe
F_3C
I
MeO
OMe
CF_3
1h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

^{19}F NMR (376 MHz, DMSO-d_6)

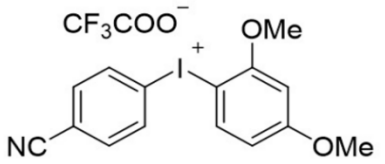


1h

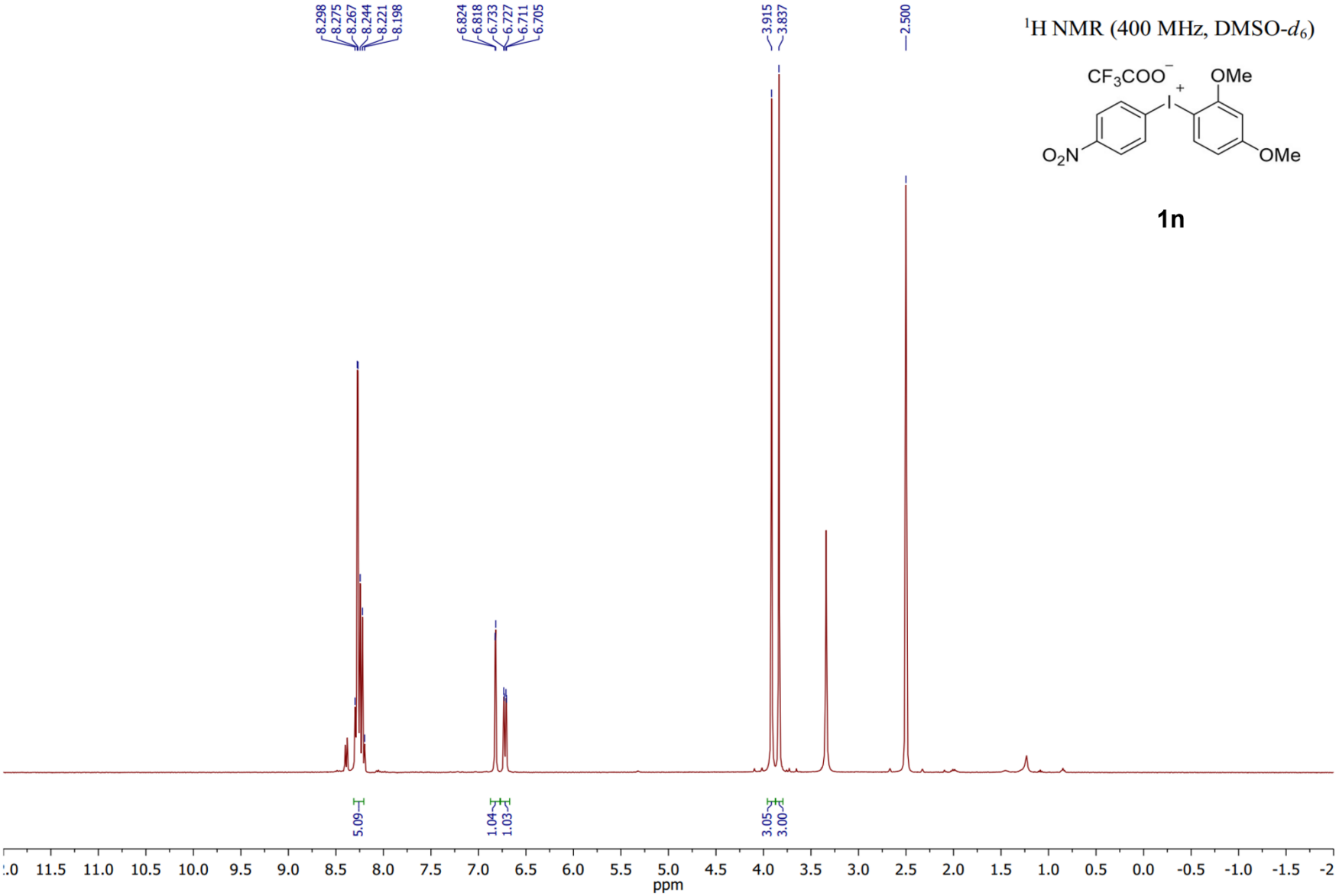

8.299
8.278
8.196
8.174
7.859
7.838
6.788
6.782
6.701
6.695
6.679
6.673
3.956
3.891
2.050
2.07
1.04
2.03
1.03
1.03
3.02
3.00
ppm
^{1}H NMR (400 MHz, Acetone-d_6)
CF_3COO^-
OMe
NC
OMe
1m


206.260
166.334
161.168
160.841
159.974
139.712
136.181
135.171
123.231
121.553
119.236
118.185
116.291
115.688
114.060
109.661
100.490
98.172
57.495
56.441
29.920
^{13}C NMR (100 MHz, Acetone-d_6)
CF_3COO^-
OMe
NC
OMe
1m
ppm

^{19}F NMR (376 MHz, Acetone-d_6)

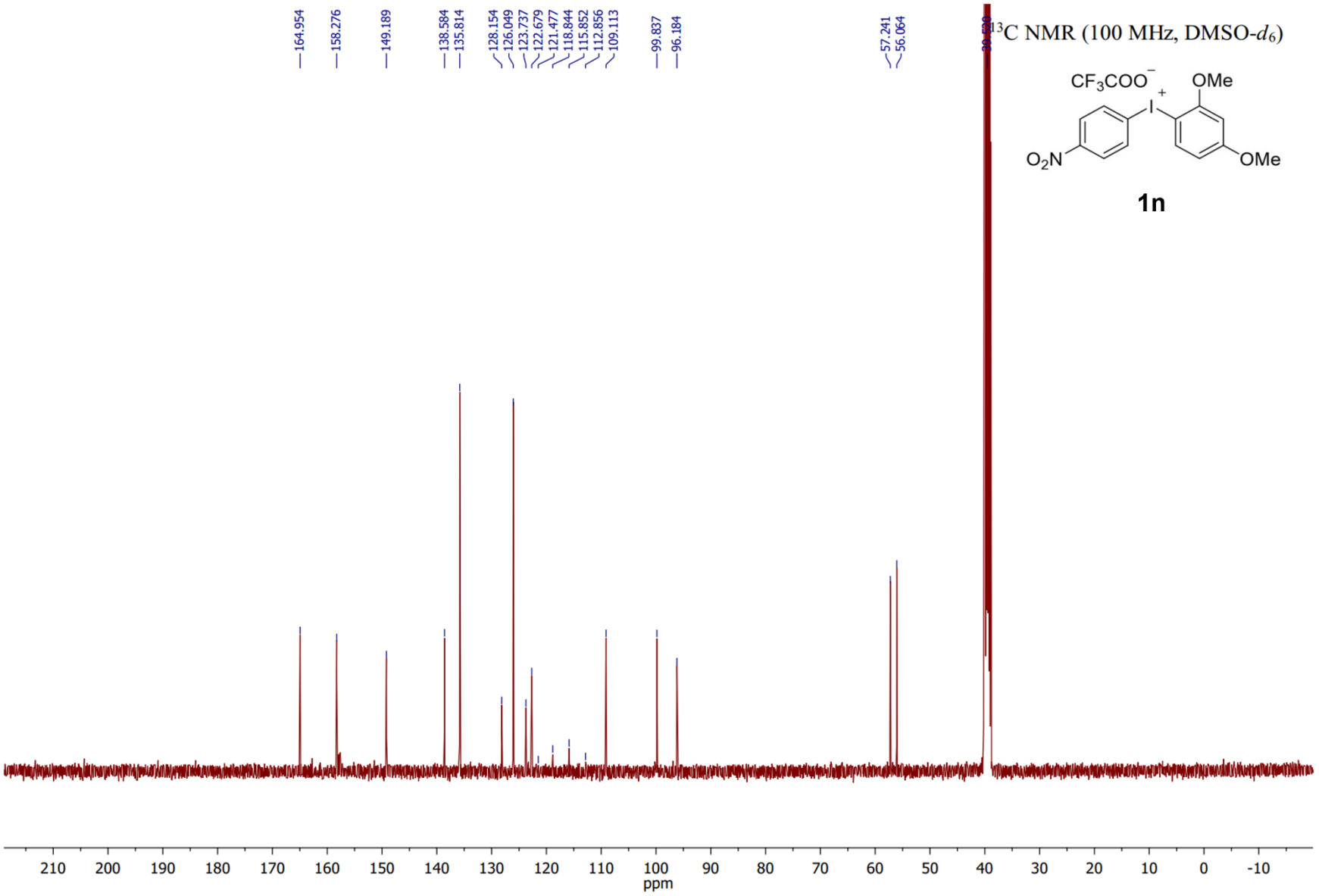


1m

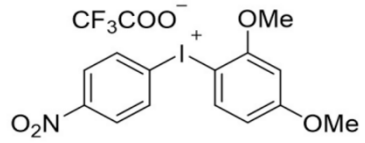


^{1}H NMR (400 MHz, DMSO-d_6)

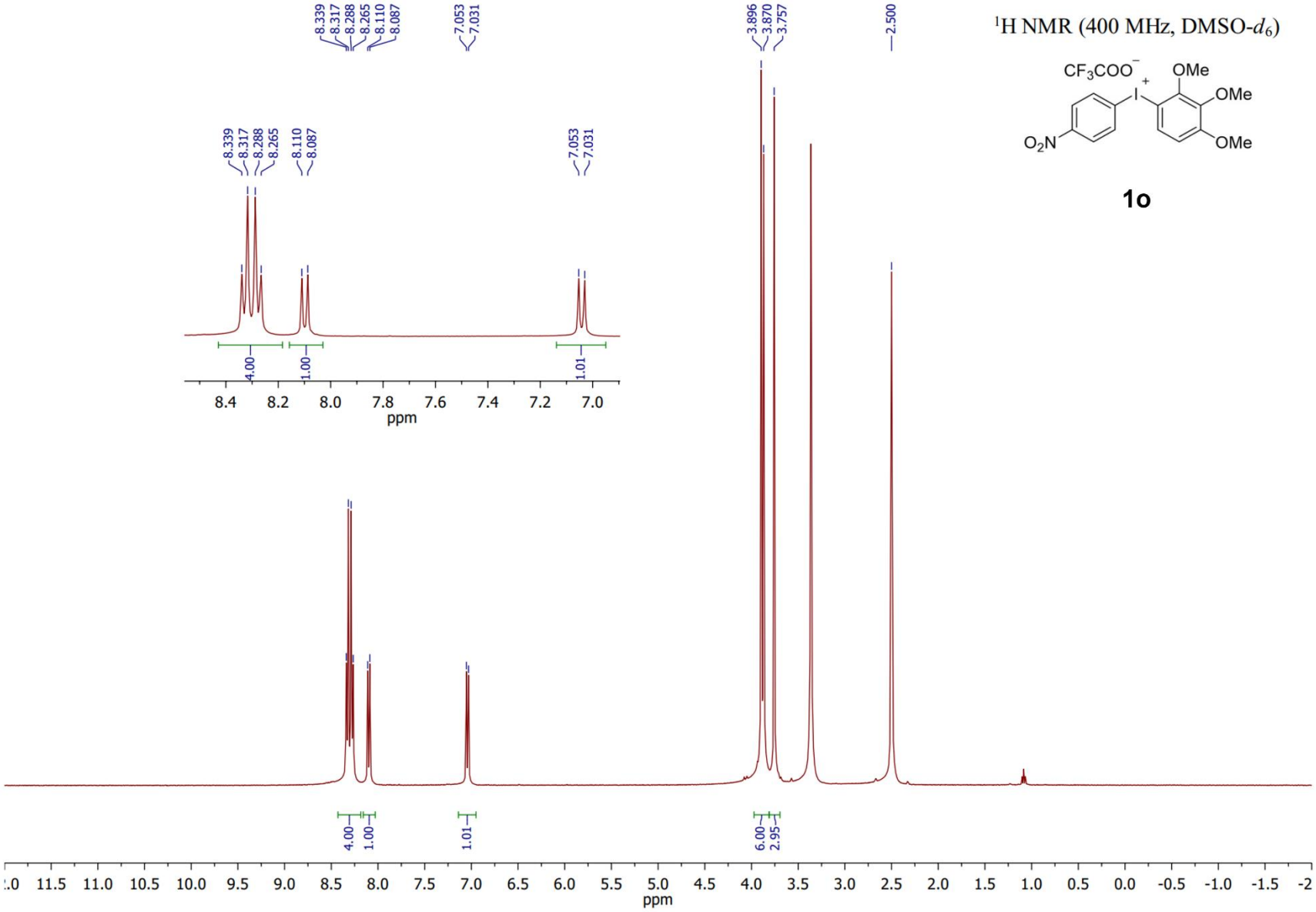
1n

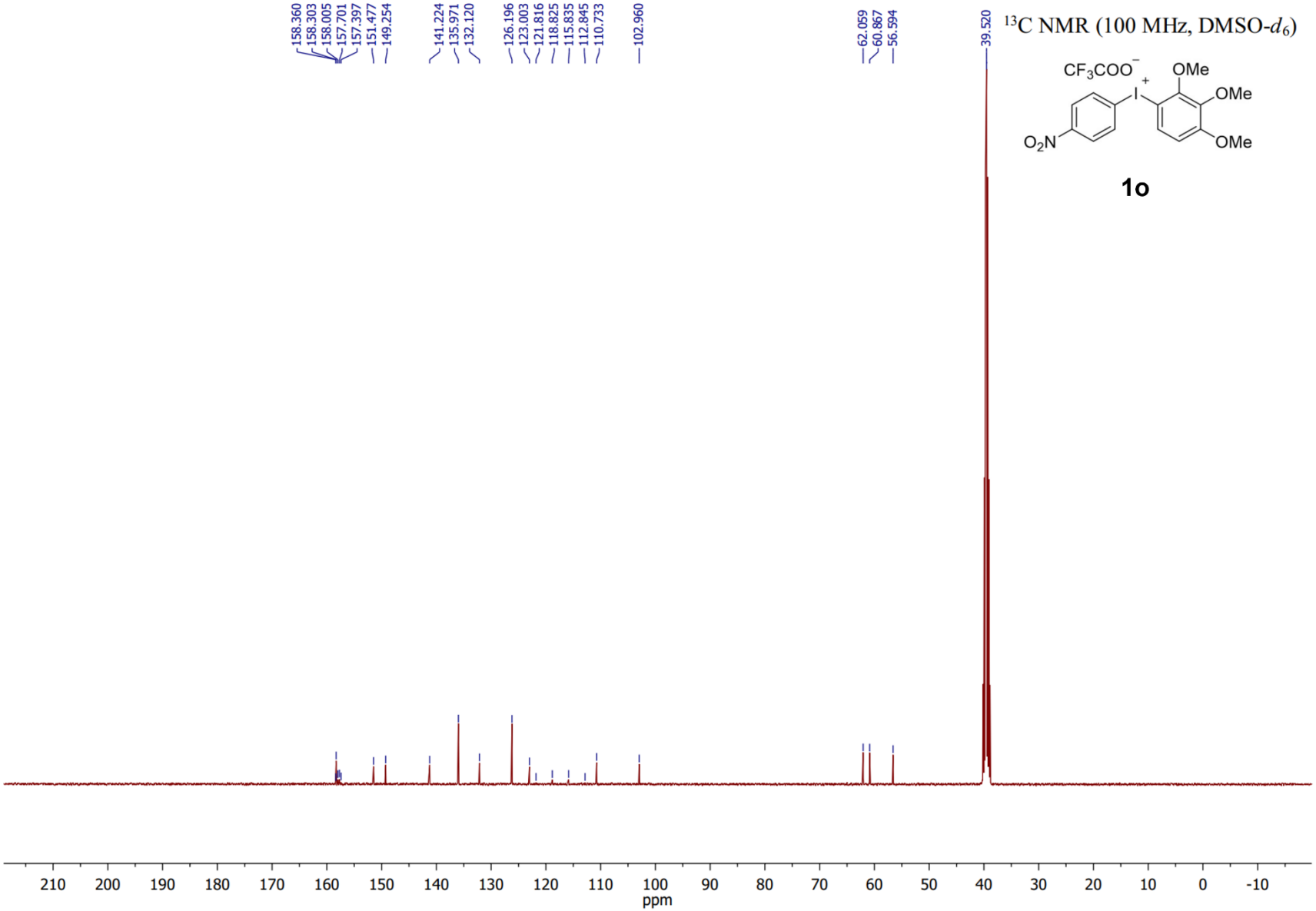

164.954
158.276
149.189
138.584
135.814
128.154
126.049
123.737
122.679
121.477
118.844
115.852
112.856
109.113
99.837
96.184
57.241
56.064
39.520
^{13}C NMR (100 MHz, DMSO-d_6)
CF_3COO^-
OMe
O_2N
OMe
1n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

^{19}F NMR (376 MHz, DMSO-d_6)

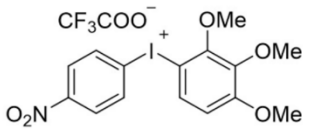


1n

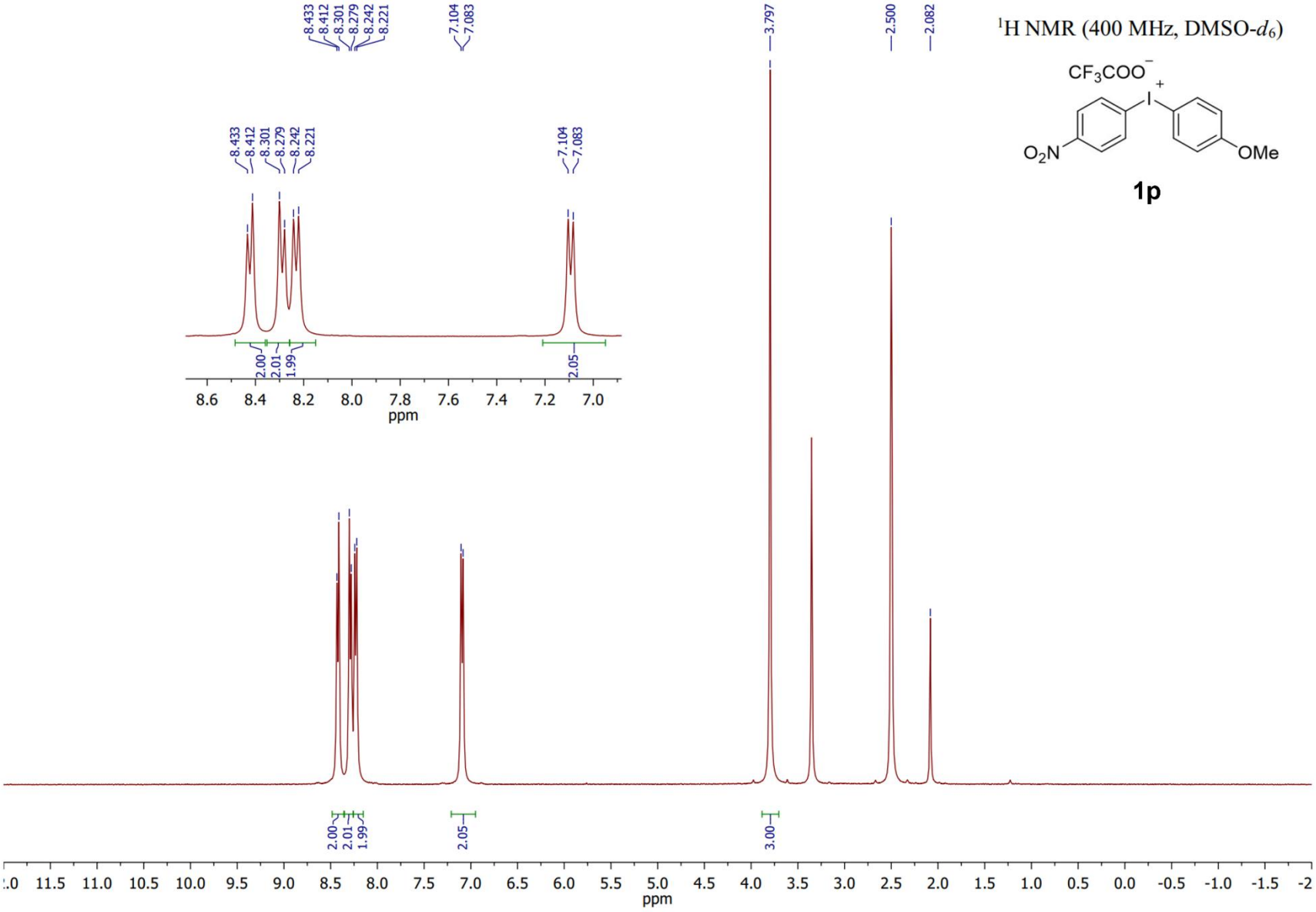

^{1}H NMR (400 MHz, DMSO-d_6)
CF_3COO^-
O_2N
OMe
OMe
OMe
1o
8.339
8.317
8.288
8.265
8.110
8.087
7.053
7.031
3.896
3.870
3.757
2.500
4.00
1.00
1.01
6.00
2.95
ppm

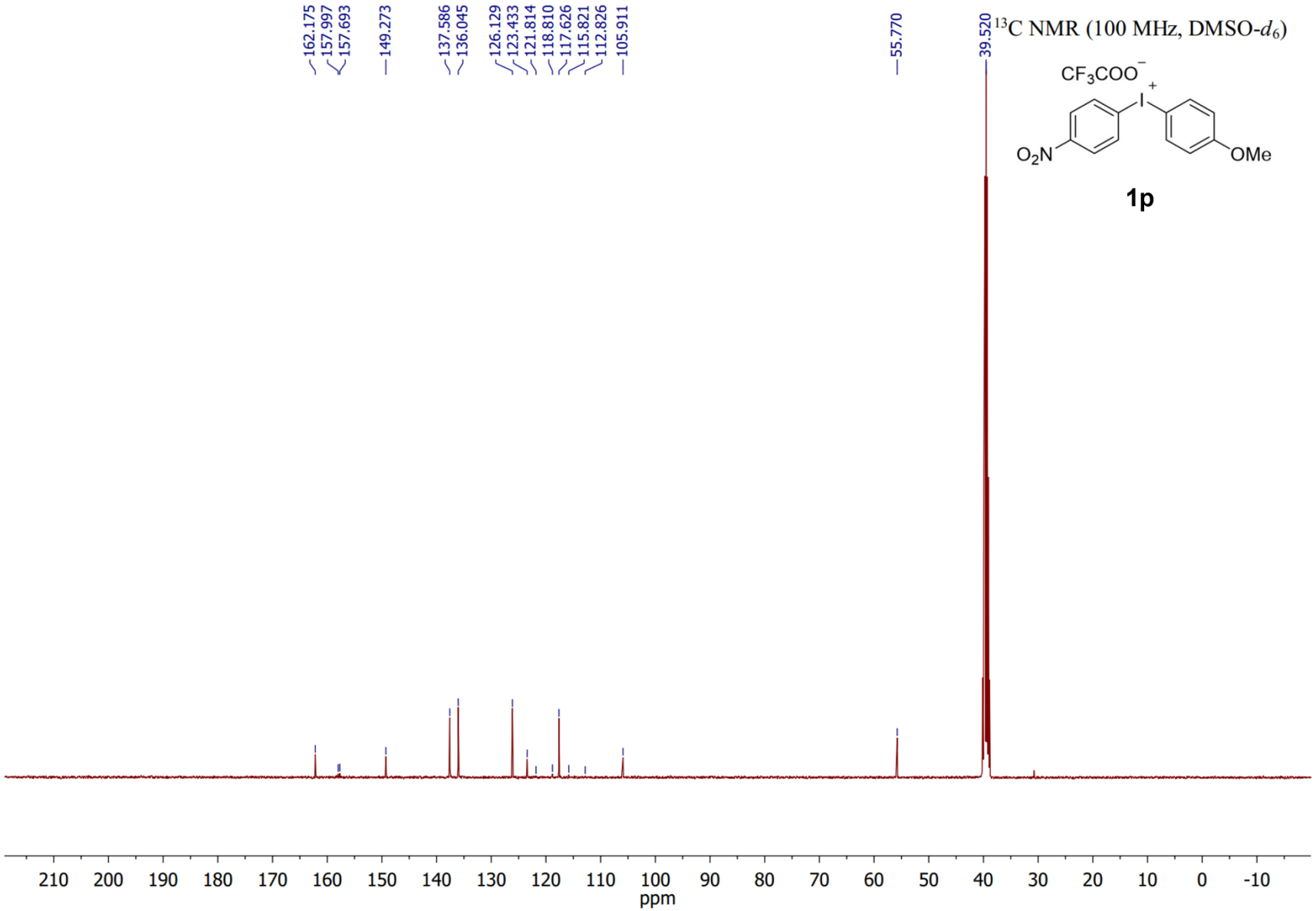

158.360
158.303
158.005
157.701
157.397
151.477
149.254
141.224
135.971
132.120
126.196
123.003
121.816
118.825
115.835
112.845
110.733
102.960
62.059
60.867
56.594
39.520
^{13}C NMR (100 MHz, DMSO-d_6)
CF_3COO^-
OMe
OMe
OMe
O_2N
1o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

^{19}F NMR (376 MHz, DMSO-d_6)

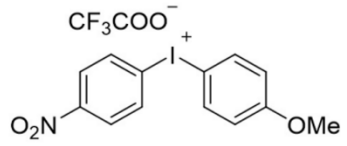


1o

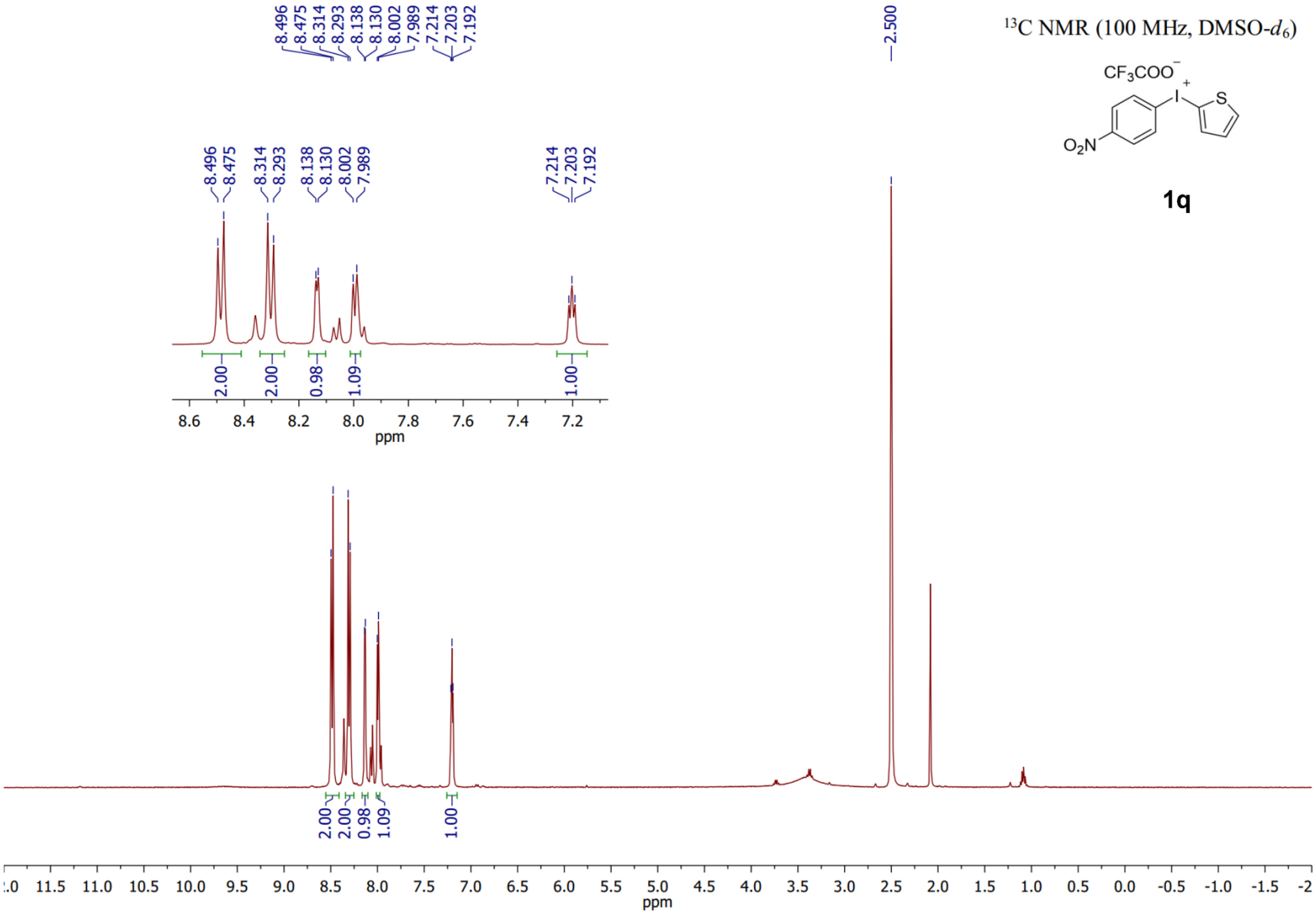

^{1}H NMR (400 MHz, DMSO-d_6)
CF_3COO^-
O_2N
OMe
1p
8.433
8.412
8.301
8.279
8.242
8.221
7.104
7.083
3.797
2.500
2.082
2.00
2.01
1.99
2.05
3.00
ppm

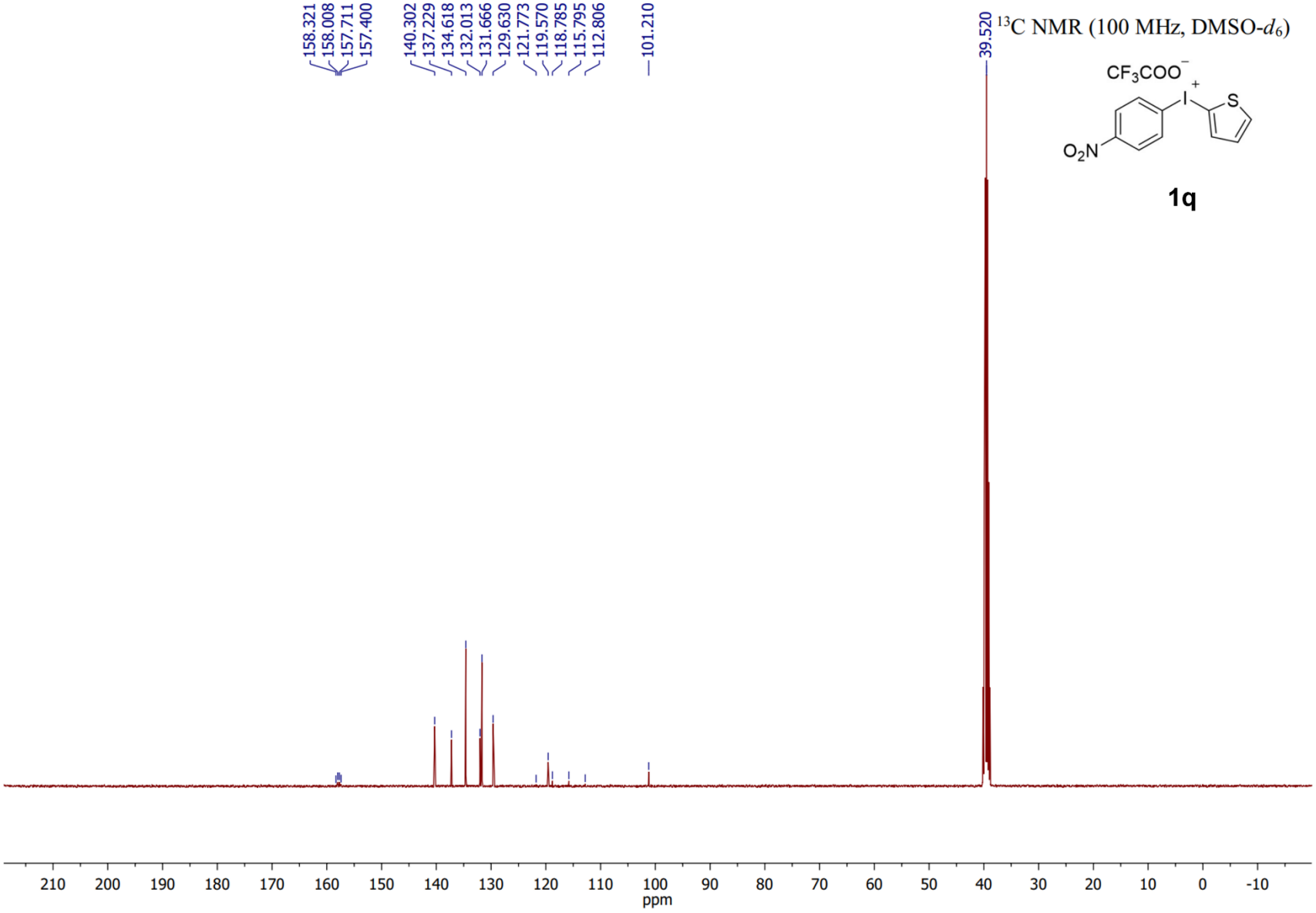

162.175
157.997
157.693
149.273
137.586
136.045
126.129
123.433
121.814
118.810
117.626
115.821
112.826
105.911
55.770
39.520
^{13}C NMR (100 MHz, DMSO-d_6)
CF_3COO^-
O_2N
OMe
1p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

^{19}F NMR (376 MHz, DMSO-d_6)

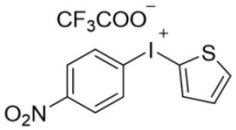


1p


8.496
8.475
8.314
8.293
8.138
8.130
8.002
7.989
7.214
7.203
7.192
2.500
^{13}C NMR (100 MHz, DMSO-d_6)
CF_3COO^-
O_2N
S
1q
2.00
2.00
0.98
1.09
1.00
ppm

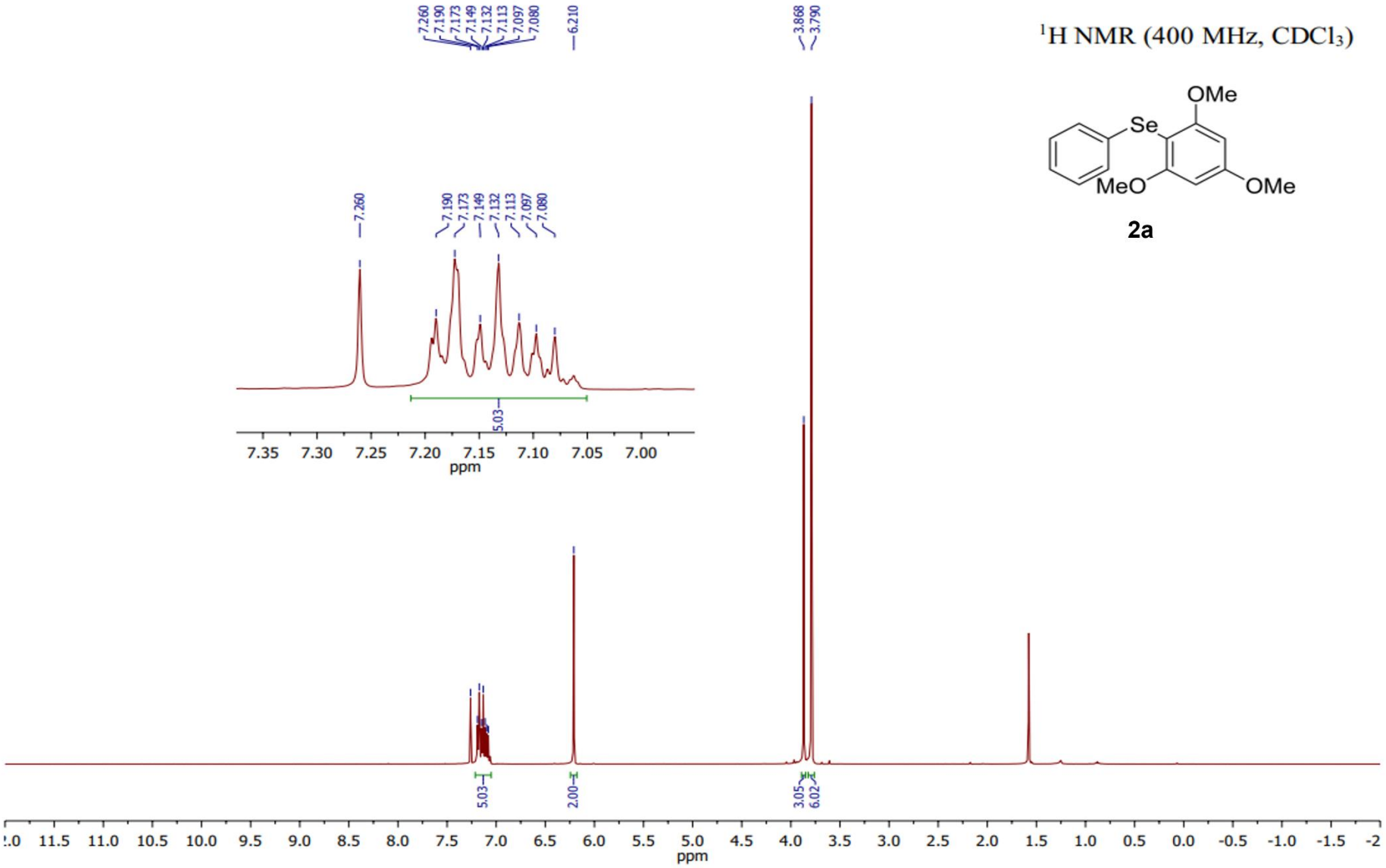

158.321
158.008
157.711
157.400
140.302
137.229
134.618
132.013
131.666
129.630
121.773
119.570
118.785
115.795
112.806
101.210
39.520
^{13}C NMR (100 MHz, DMSO-d_6)
CF_3COO^-
O_2N
1q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

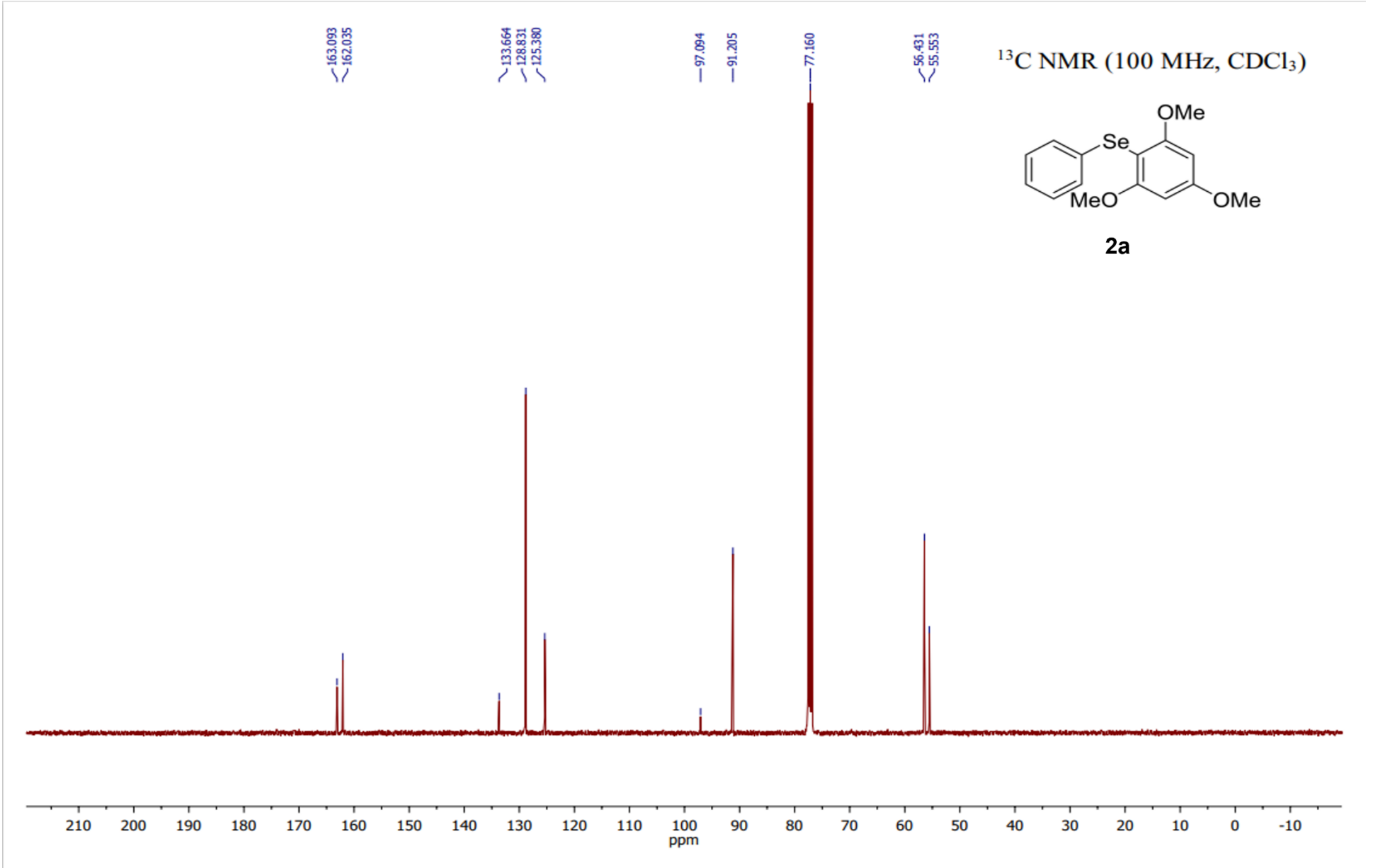
^{19}F NMR (376 MHz, DMSO-d_6)



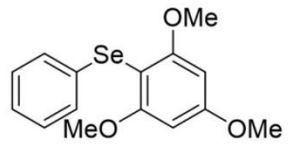
1q

NMR spectra of **2a**–**k**

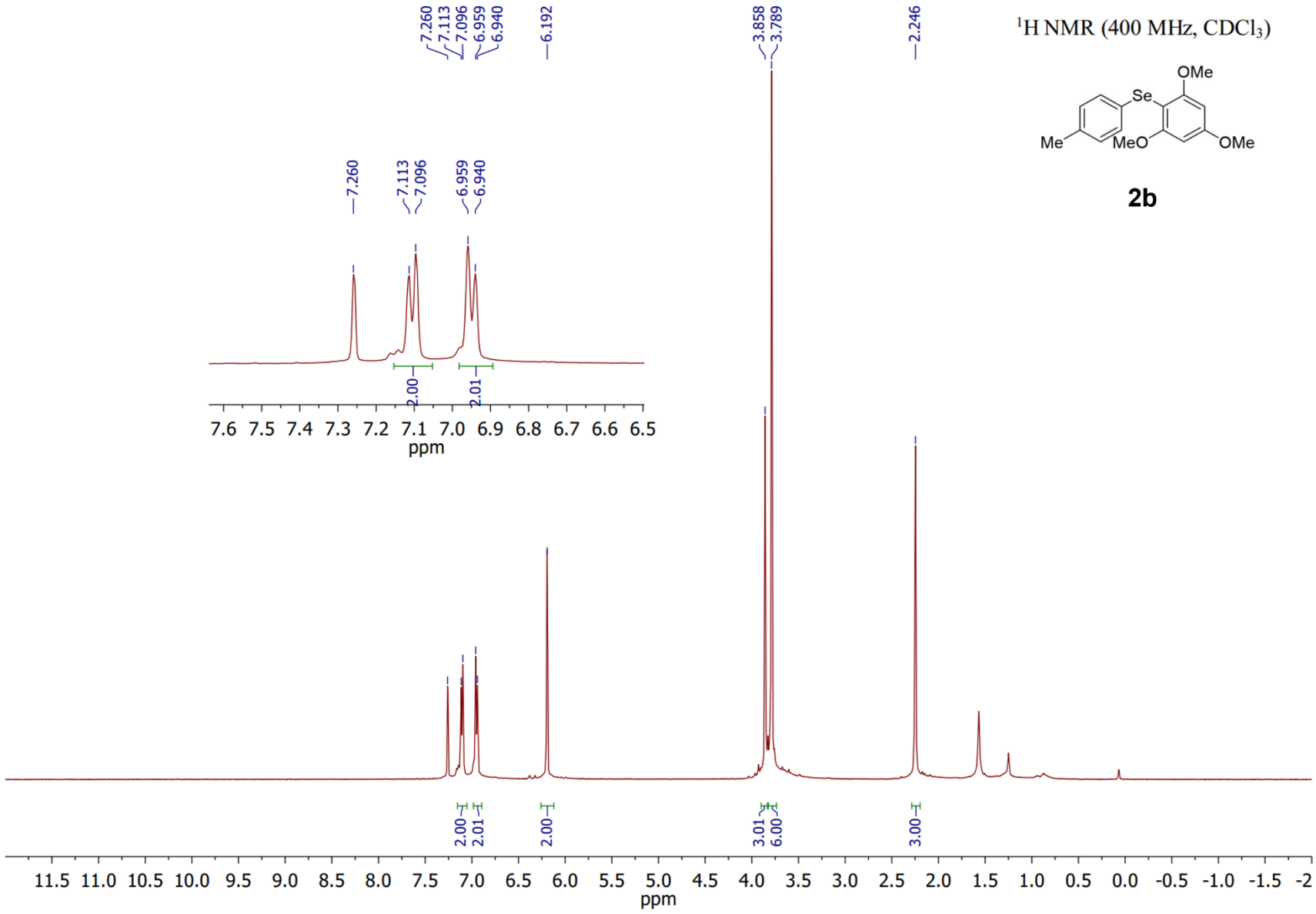



163.093
162.035
133.664
128.831
125.380
97.094
91.205
77.160
56.431
55.553
^{13}C NMR (100 MHz, $CDCl_3$)
OMe
Se
MeO
OMe
2a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

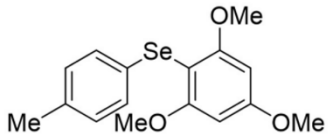
^{77}Se NMR (76 MHz, $CDCl_3$)



2a

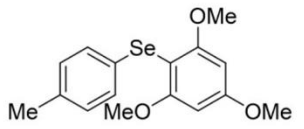

7.260
7.113
7.096
6.959
6.940
6.192
3.858
3.789
2.246
^{1}H NMR (400 MHz, $CDCl_3$)
OMe
Se
Me
MeO
OMe
2b
2.00
2.01
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5
ppm
2.00
2.01
2.00
3.01
6.00
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2
ppm

^{13}C NMR (100 MHz, $CDCl_3$)

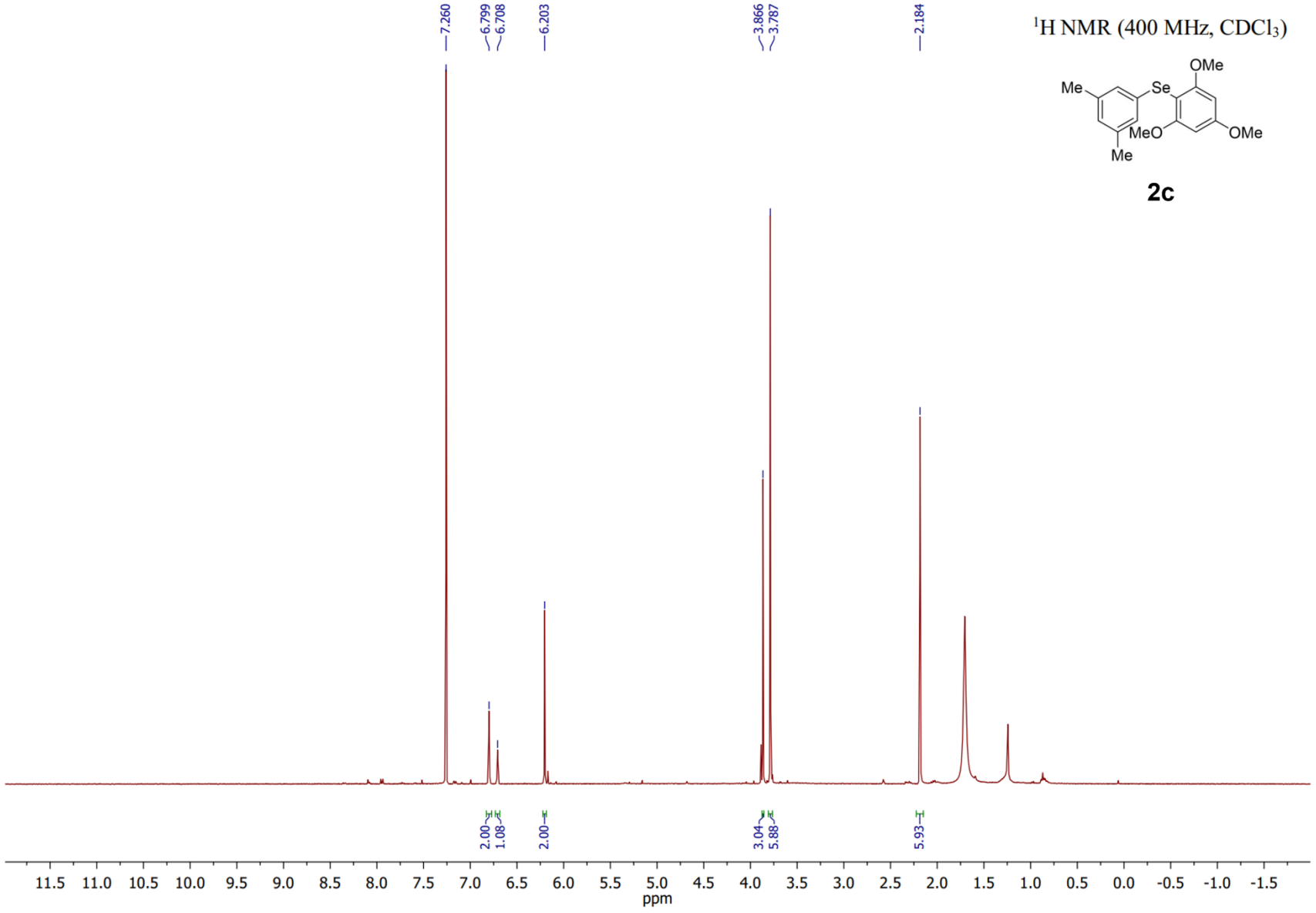


2b

^{77}Se NMR (76 MHz, $CDCl_3$)



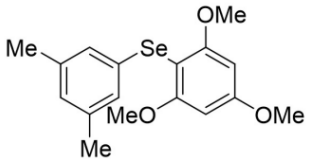
2b



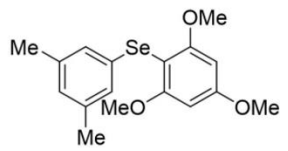
^{1}H NMR (400 MHz, $CDCl_3$)

2c

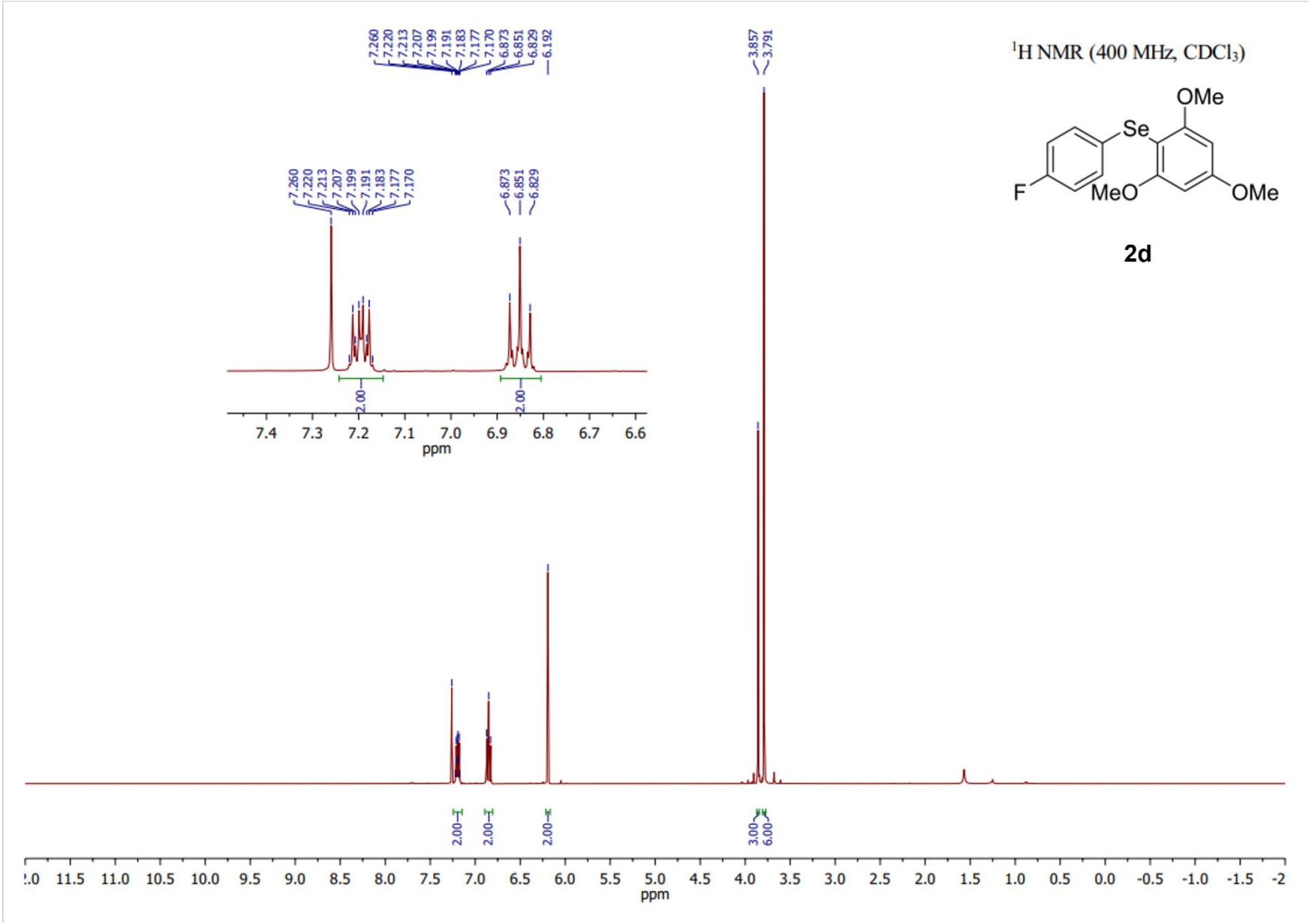
^{13}C NMR (100 MHz, $CDCl_3$)

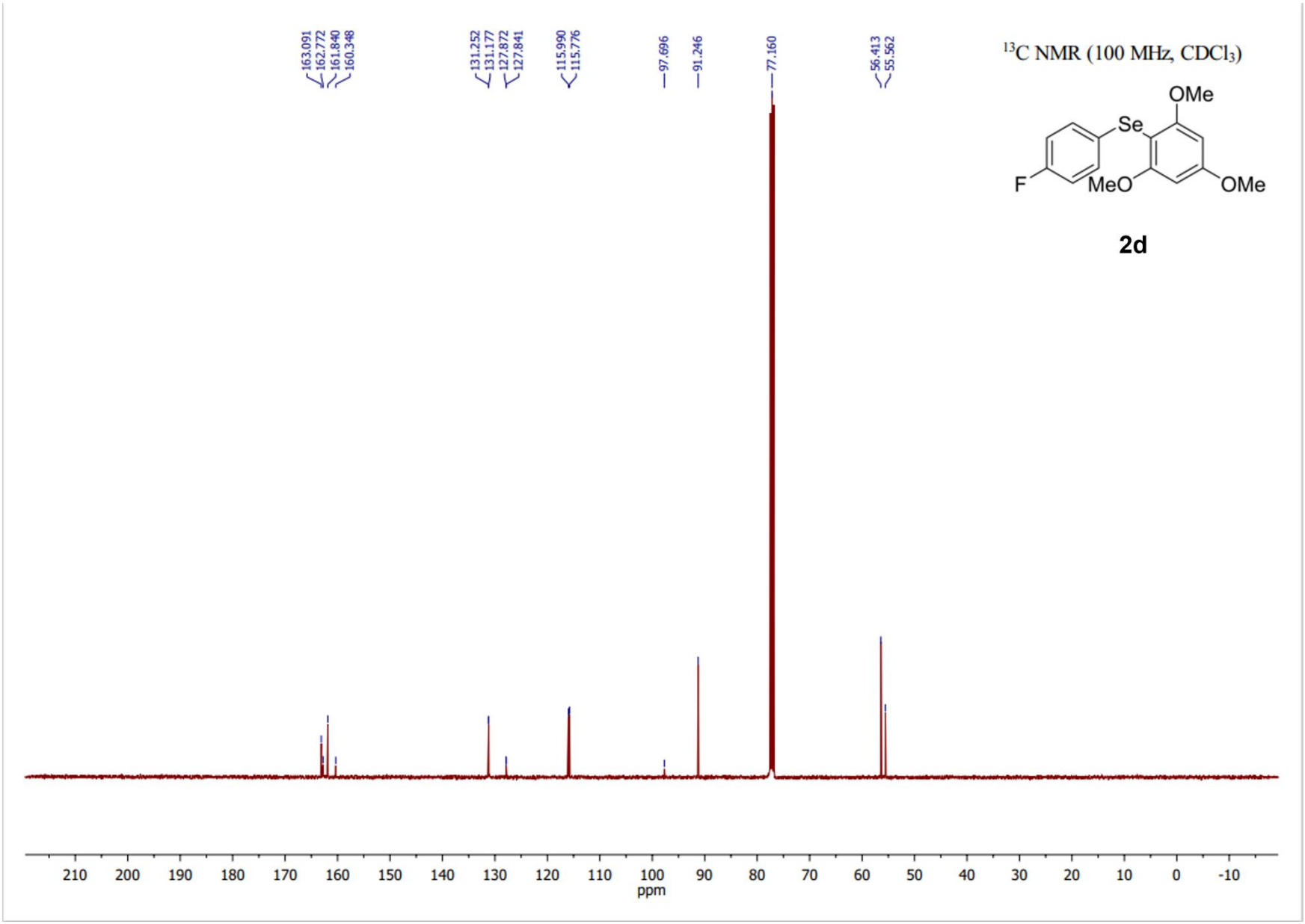


^{77}Se NMR (76 MHz, $CDCl_3$)

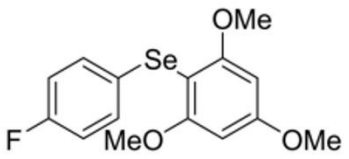


2c


^{1}H NMR (400 MHz, $CDCl_3$)
OMe
Se
F
MeO
OMe
2d
7.260
7.220
7.213
7.207
7.199
7.191
7.183
7.177
7.170
6.873
6.851
6.829
6.192
3.857
3.791
2.00
2.00
ppm
2.00
2.00
2.00
3.00
6.00
ppm

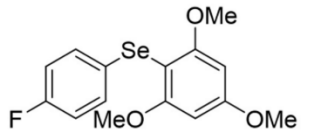

163.091
162.772
161.840
160.348
131.252
131.177
127.872
127.841
115.990
115.776
97.696
91.246
77.160
56.413
55.562
^{13}C NMR (100 MHz, $CDCl_3$)
OMe
Se
F
MeO
OMe
2d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

^{19}F NMR (376 MHz, $CDCl_3$)

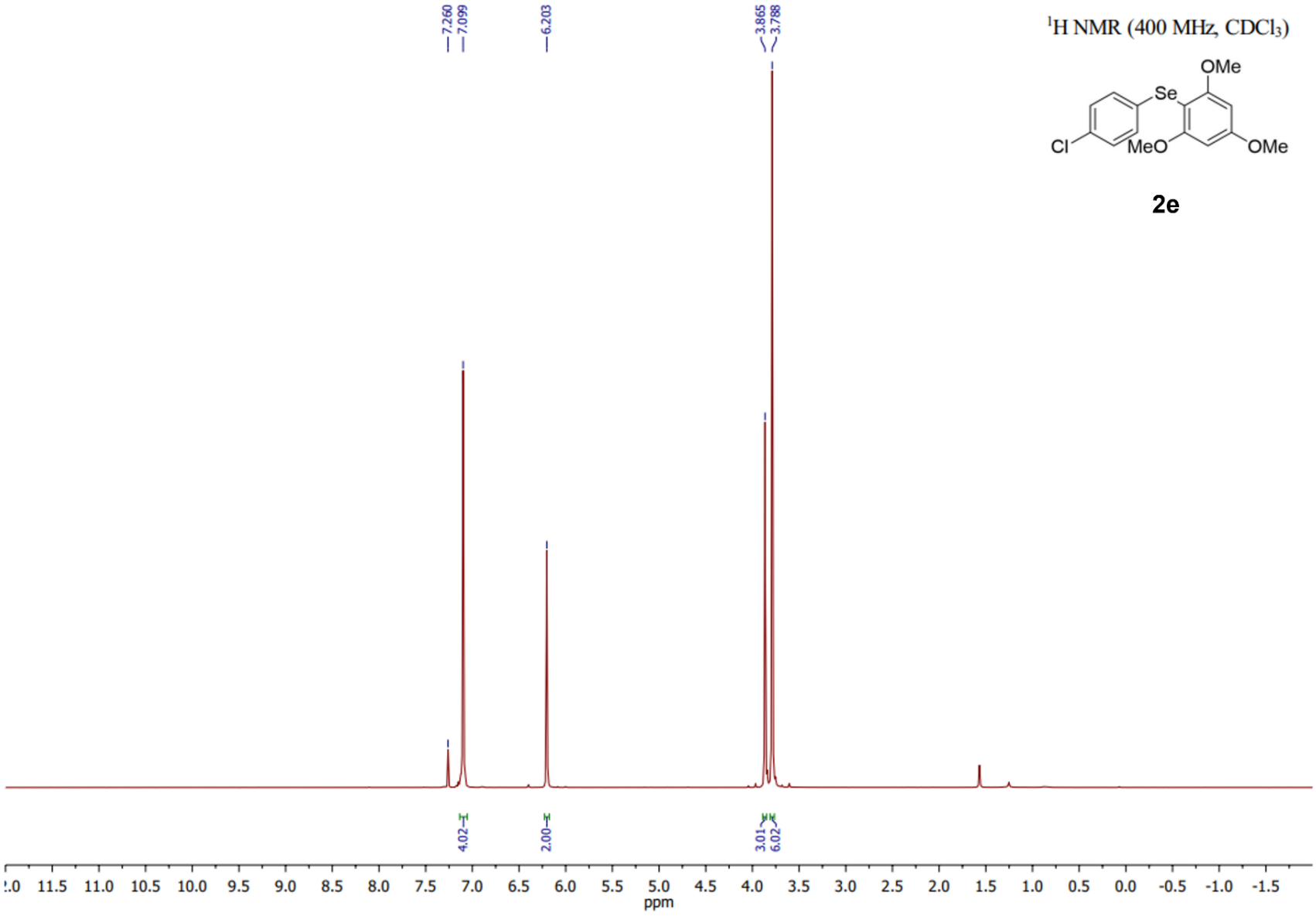


2d

^{77}Se NMR (76 MHz, $CDCl_3$)

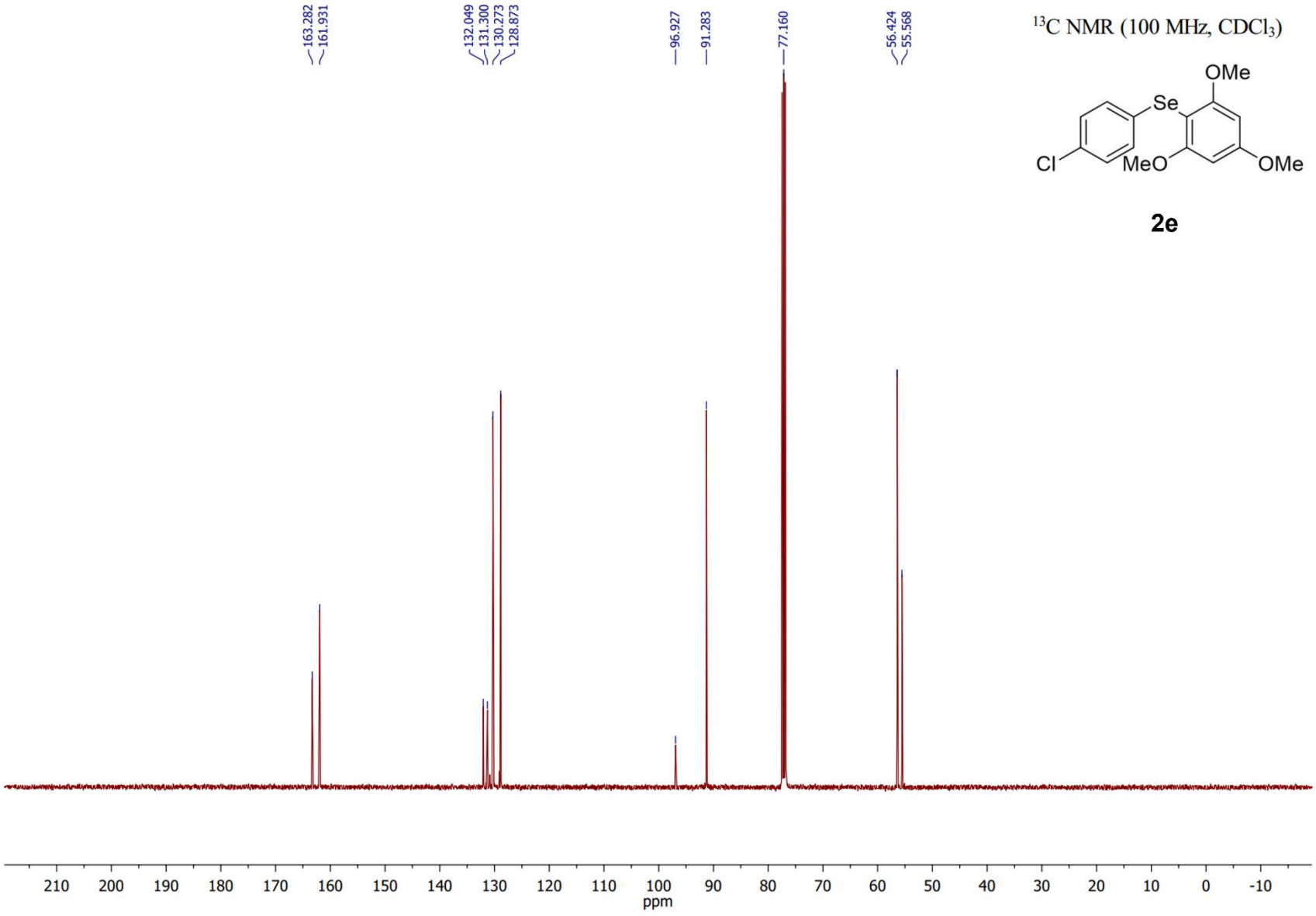


2d

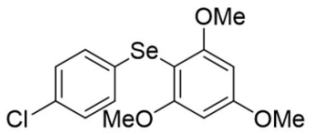


^{1}H NMR (400 MHz, $CDCl_3$)

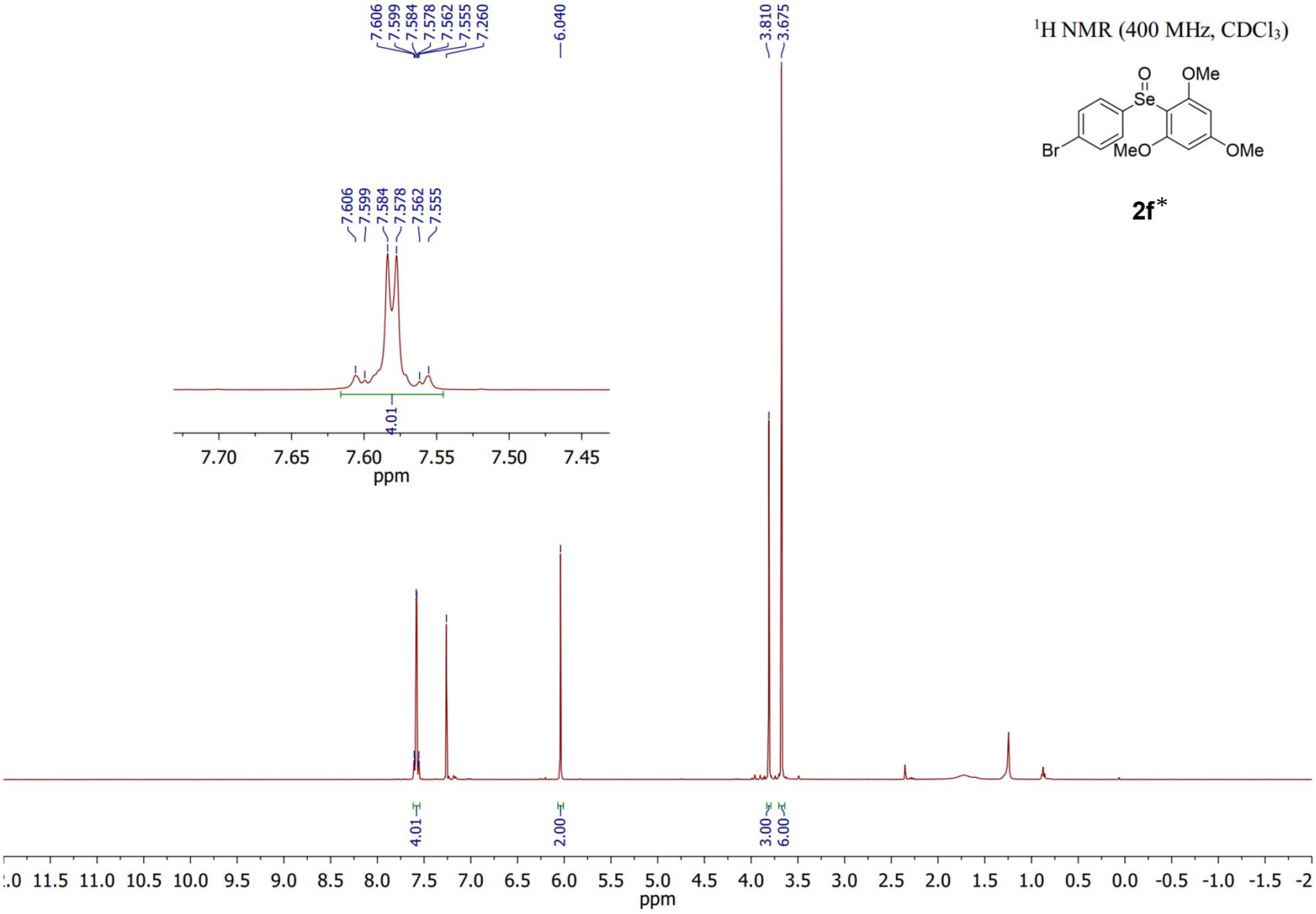
2e

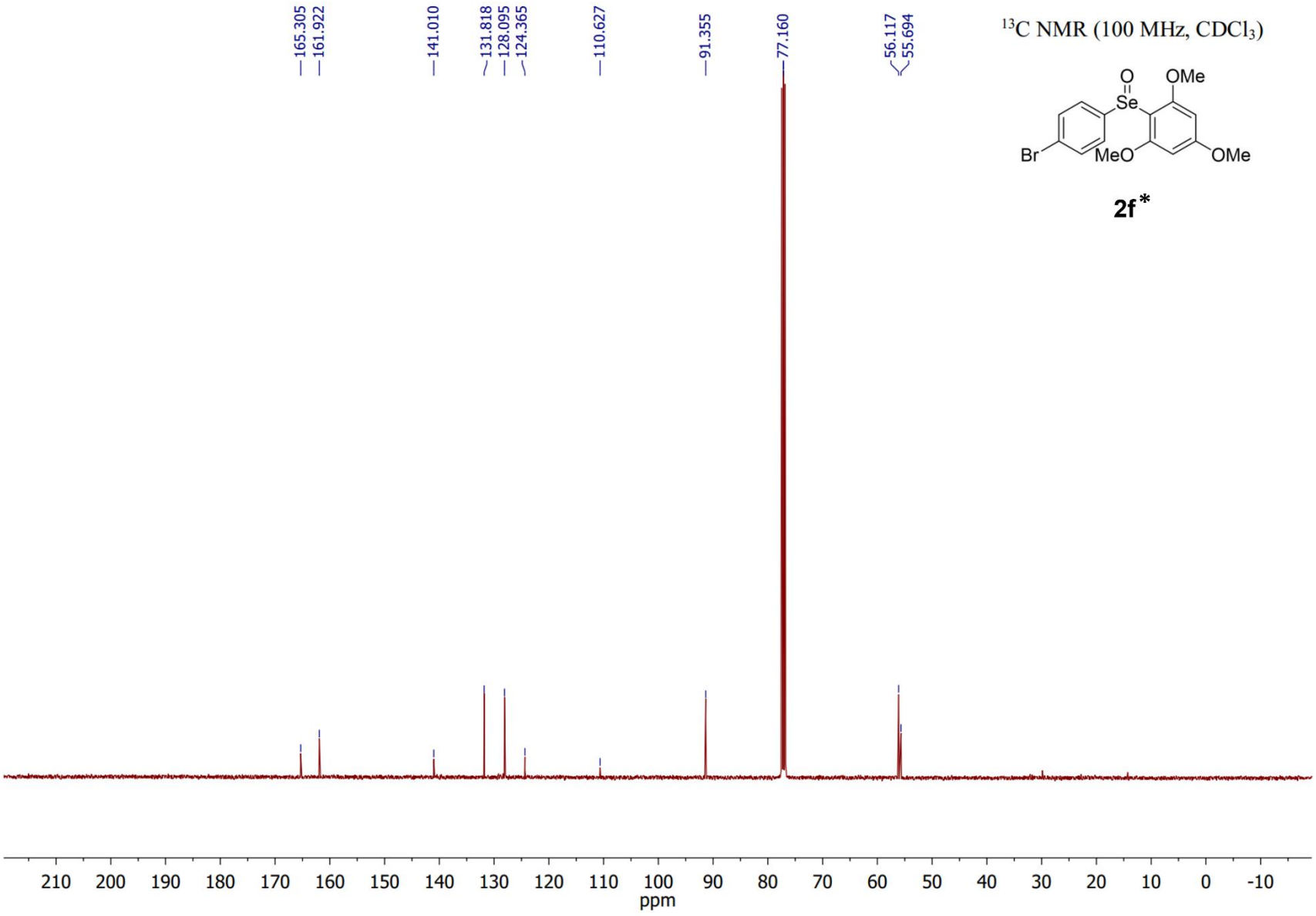

163.282
161.931
132.049
131.300
130.273
128.873
96.927
91.283
77.160
56.424
55.568
^{13}C NMR (100 MHz, $CDCl_3$)
OMe
Se
Cl
MeO
OMe
2e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

^{77}Se NMR (76 MHz, $CDCl_3$)

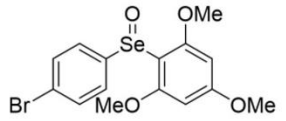


2e

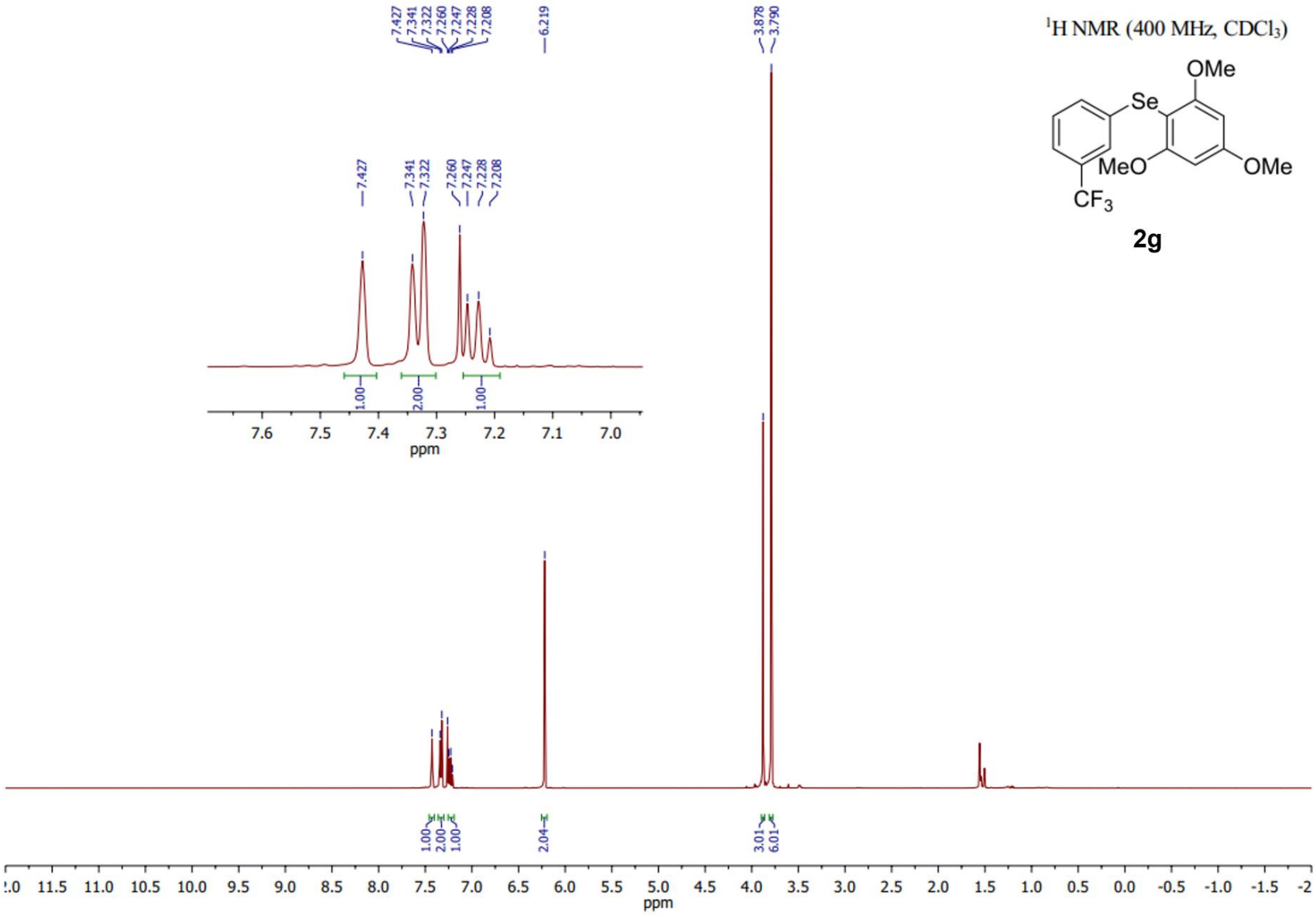

7.606
7.599
7.584
7.578
7.562
7.555
7.260
6.040
3.810
3.675
4.01
2.00
3.00
6.00
ppm
^{1}H NMR (400 MHz, CDCl$_3$)
O
Se
OMe
Br
MeO
OMe
2f*

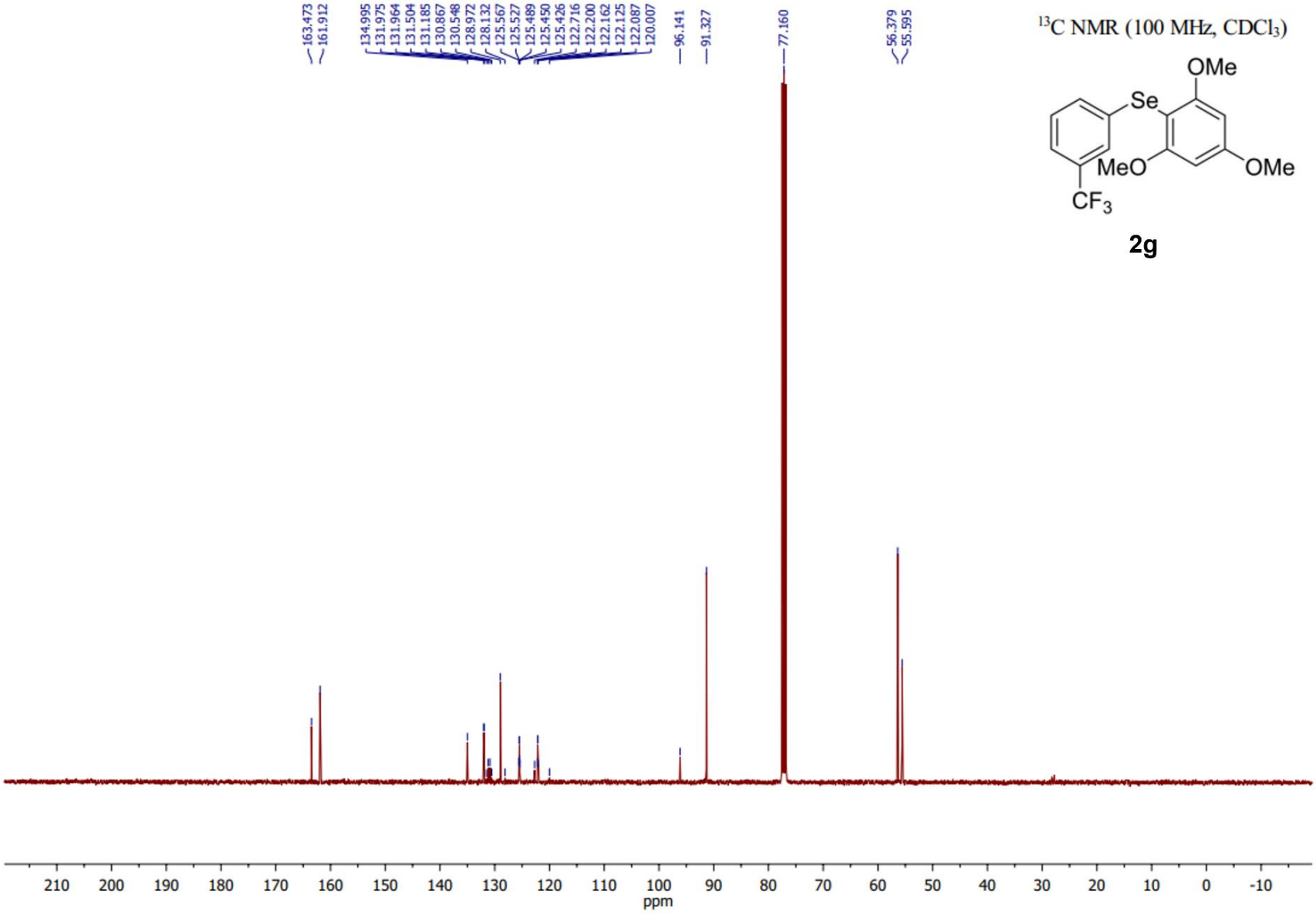

165.305
161.922
141.010
131.818
128.095
124.365
110.627
91.355
77.160
56.117
55.694
^{13}C NMR (100 MHz, $CDCl_3$)
O
Se
OMe
Br
MeO
OMe
2f*
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

^{77}Se NMR (76 MHz, $CDCl_3$)



2f*

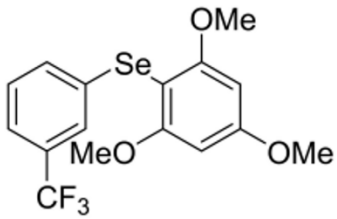

^{1}H NMR (400 MHz, $CDCl_3$)
OMe
Se
MeO
OMe
CF_3
2g
7.427
7.341
7.322
7.260
7.247
7.228
7.208
6.219
3.878
3.790
1.00
2.00
1.00
2.04
3.01
6.01
ppm



^{13}C NMR (100 MHz, $CDCl_3$)

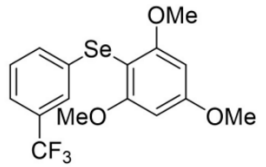
2g

^{19}F NMR (376 MHz, $CDCl_3$)

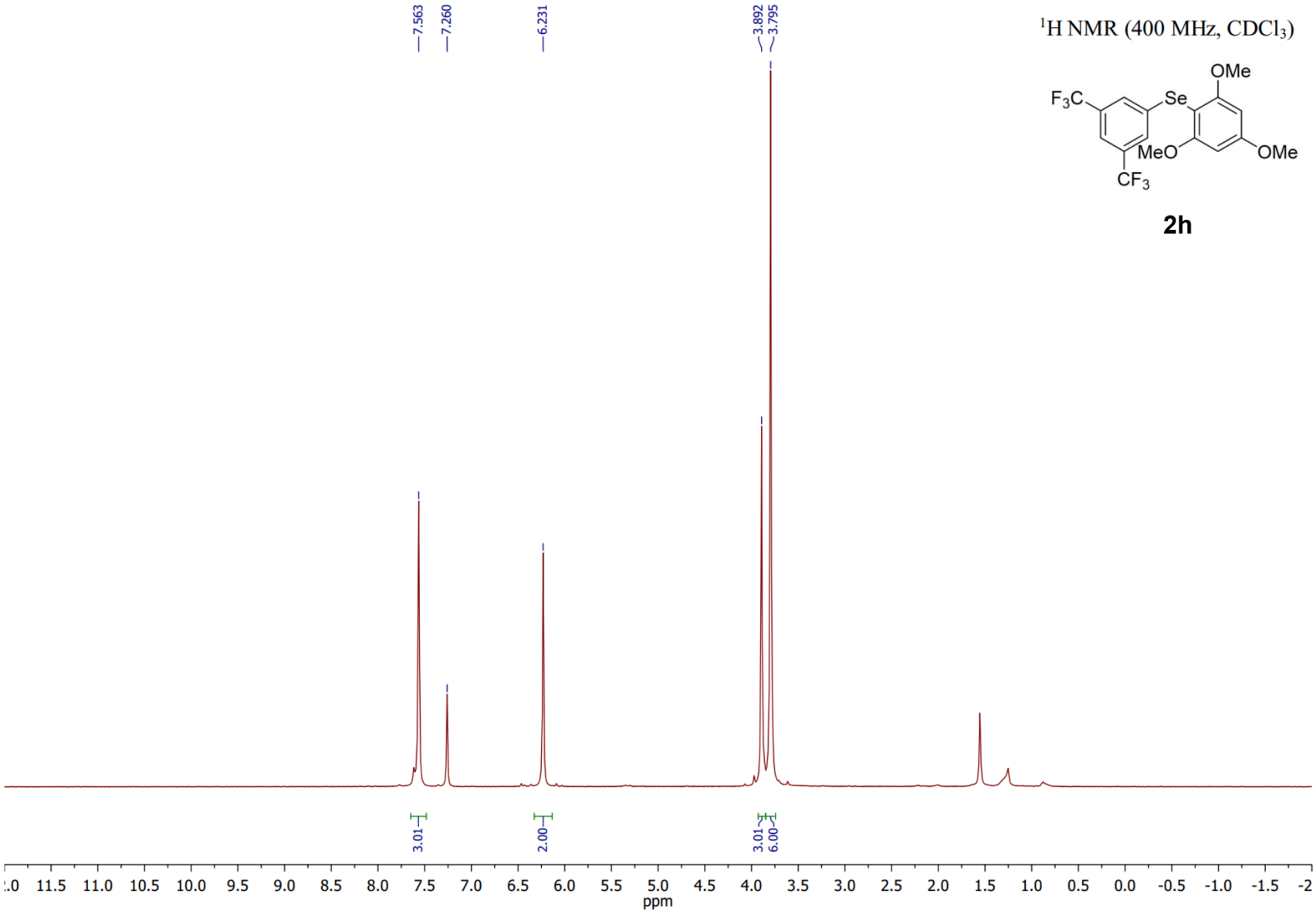


2g

^{77}Se NMR (76 MHz, $CDCl_3$)

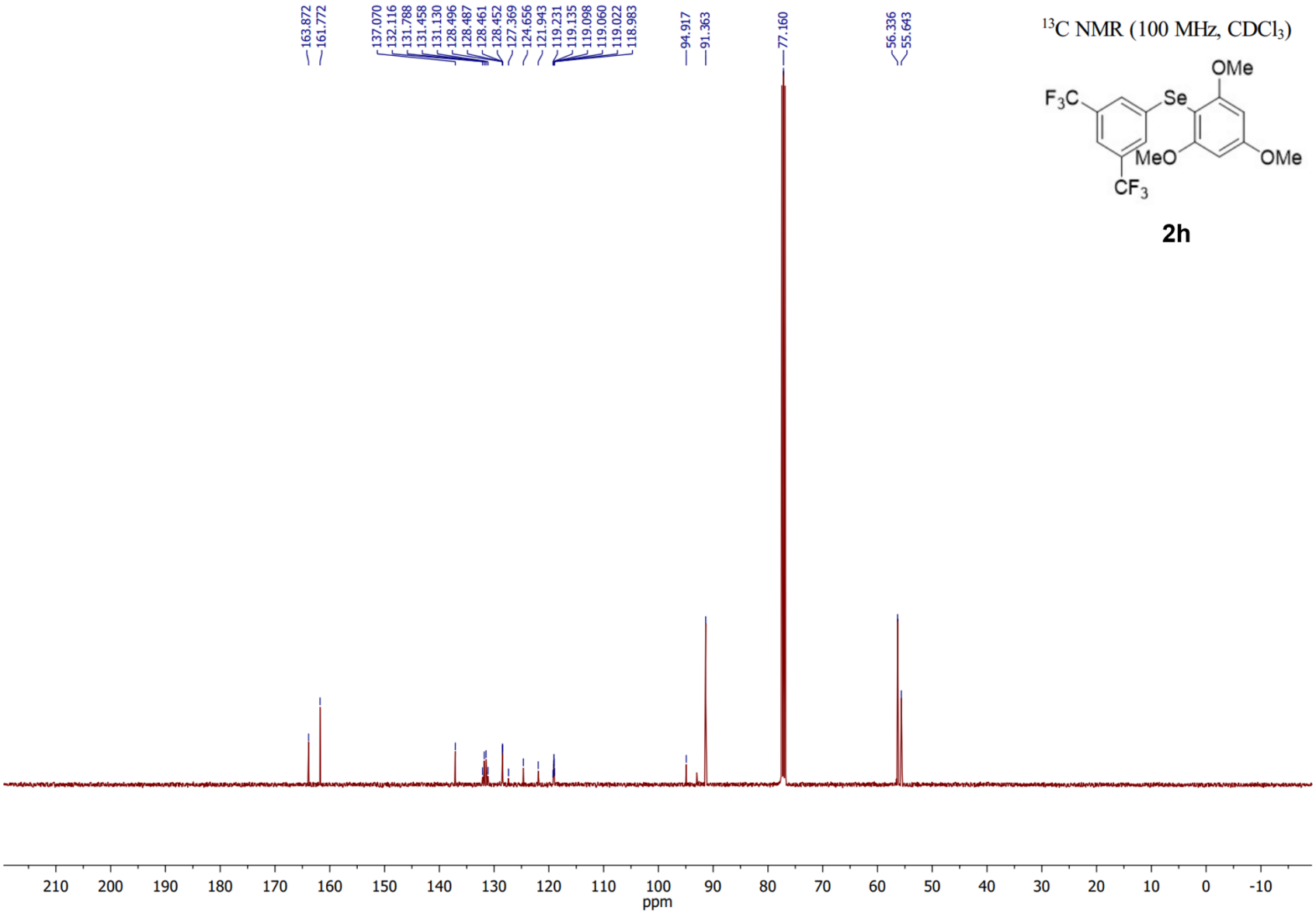


2g



^{1}H NMR (400 MHz, $CDCl_3$)

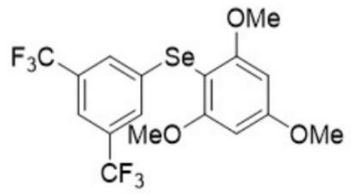
2h



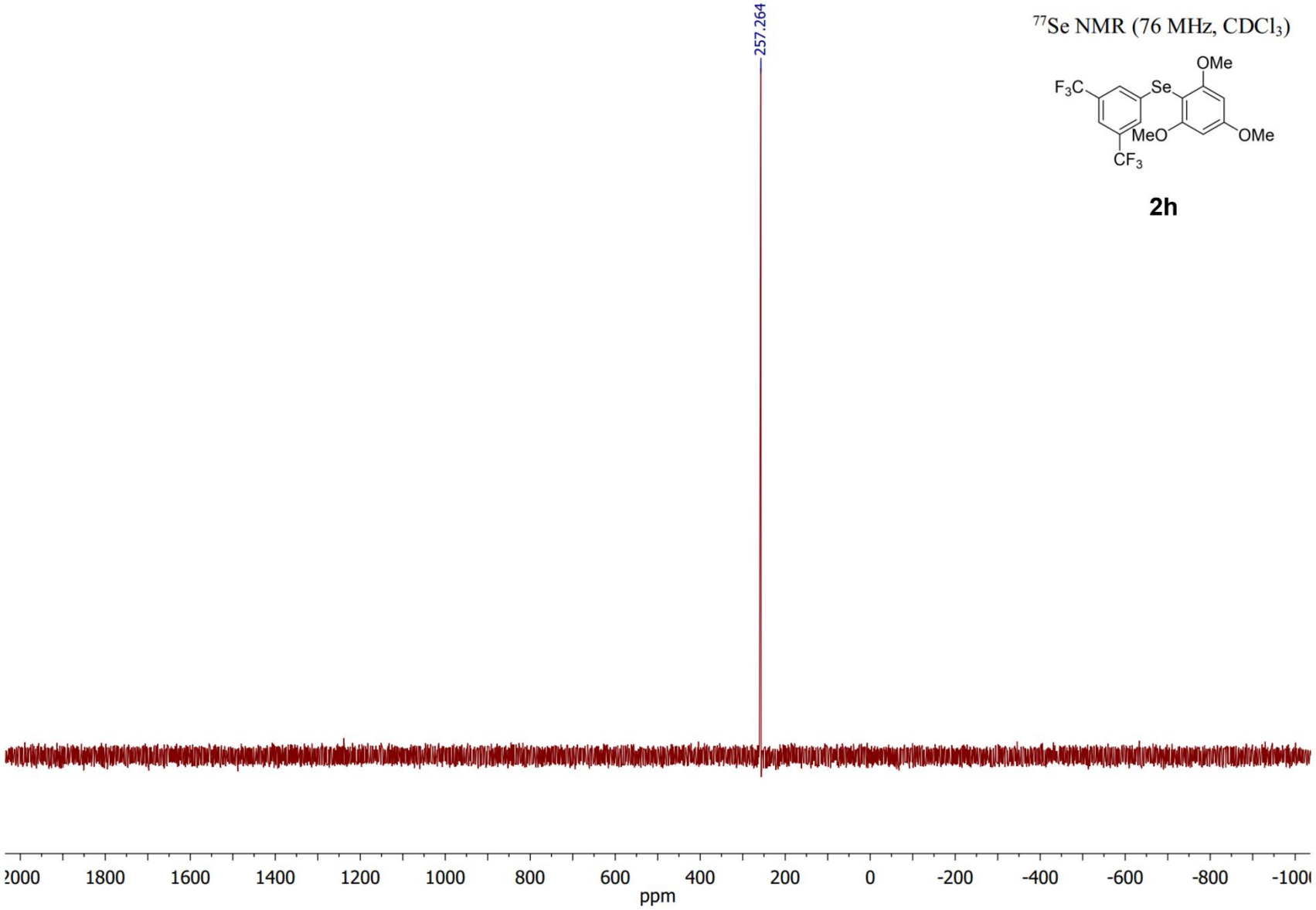
^{13}C NMR (100 MHz, $CDCl_3$)

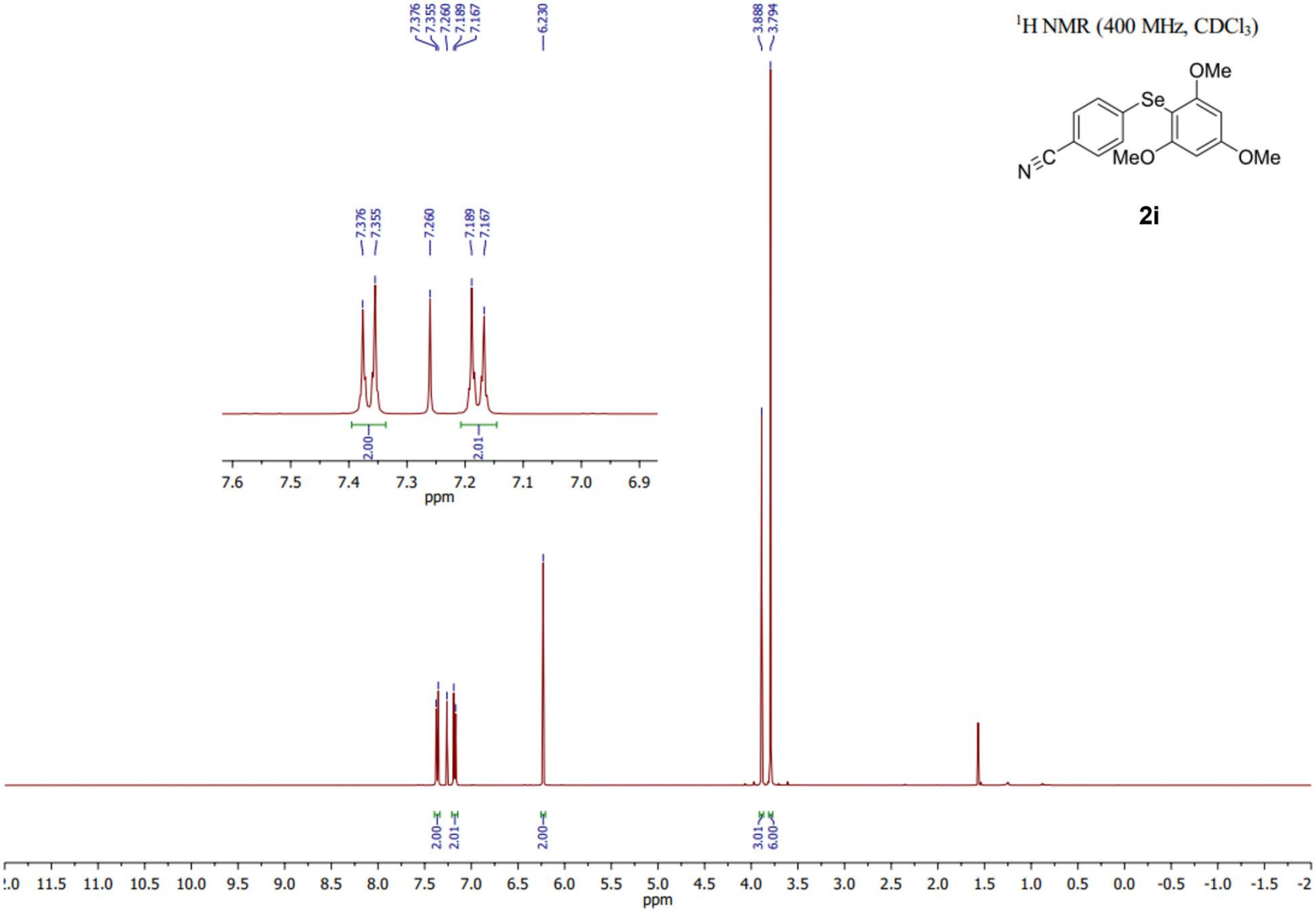
2h

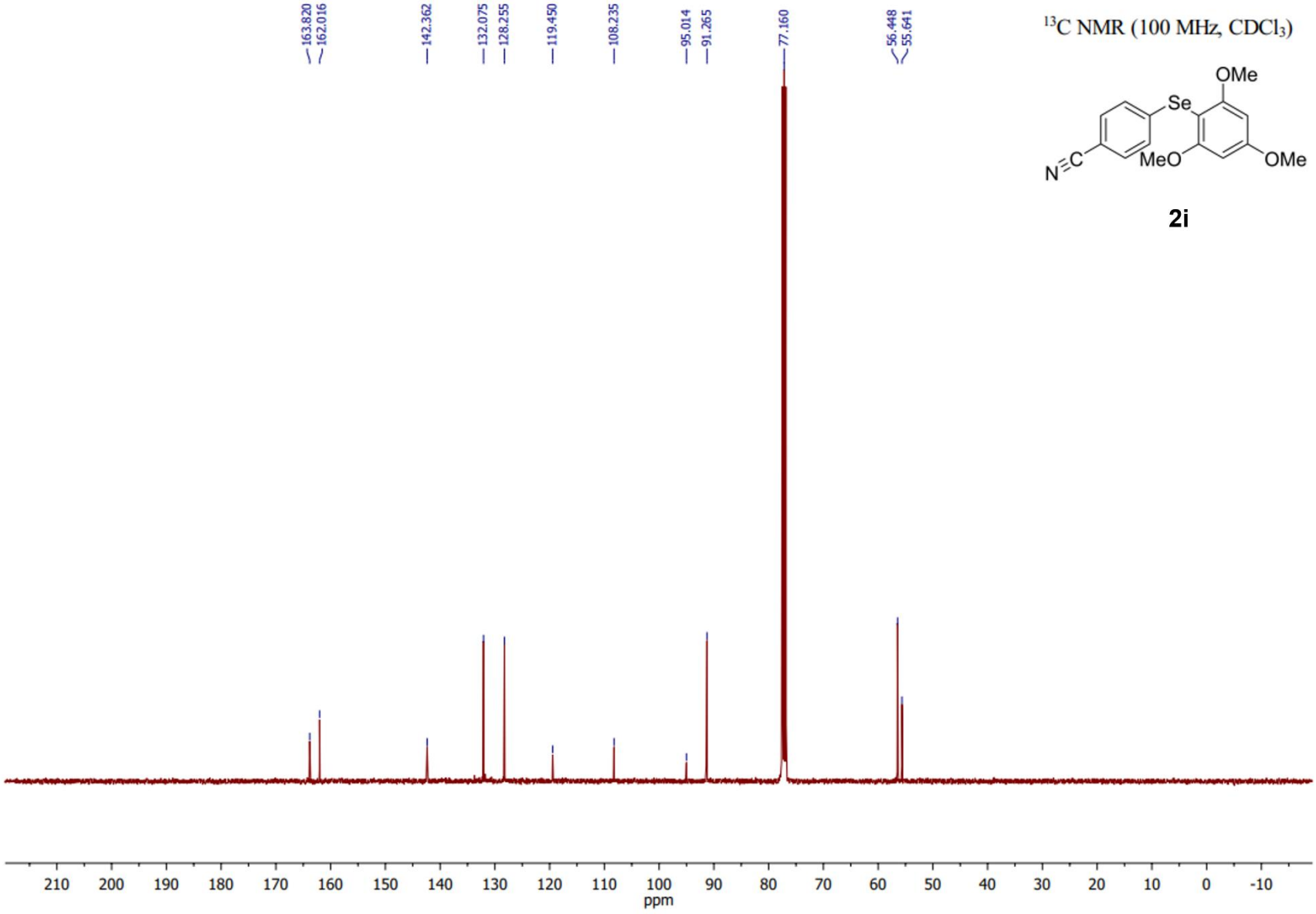
^{19}F NMR (376 MHz, $CDCl_3$)



2h


257.264
^{77}Se NMR (76 MHz, $CDCl_3$)
OMe
F_3C
Se
MeO
OMe
CF_3
2h
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
-1000
ppm

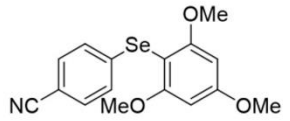

^{1}H NMR (400 MHz, $CDCl_3$)
OMe
Se
N≡C
MeO
OMe
2i
7.376
7.355
7.260
7.189
7.167
6.230
3.888
3.794
2.00
2.01
ppm
2.00
2.01
2.00
3.01
6.00
ppm



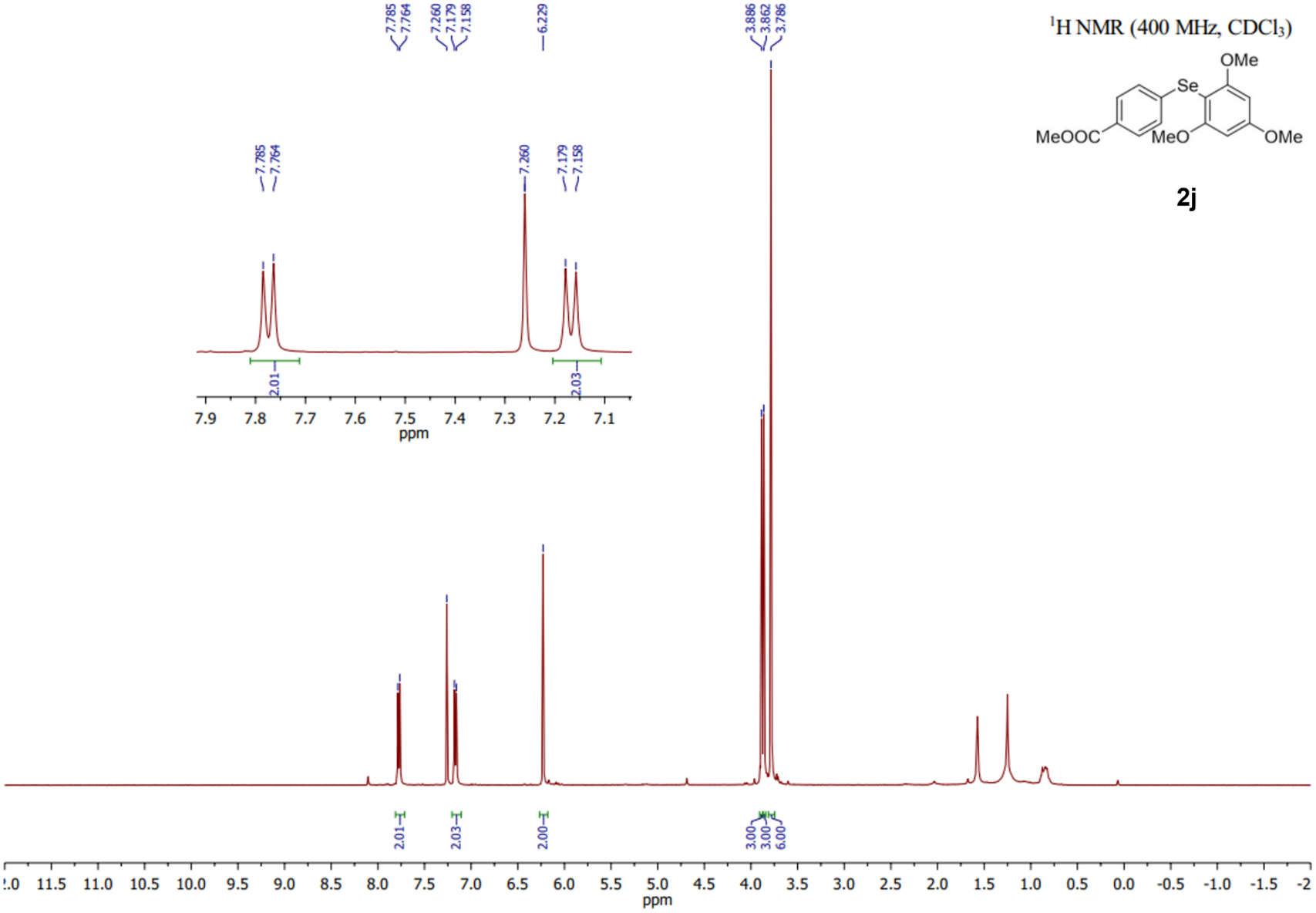
^{13}C NMR (100 MHz, $CDCl_3$)

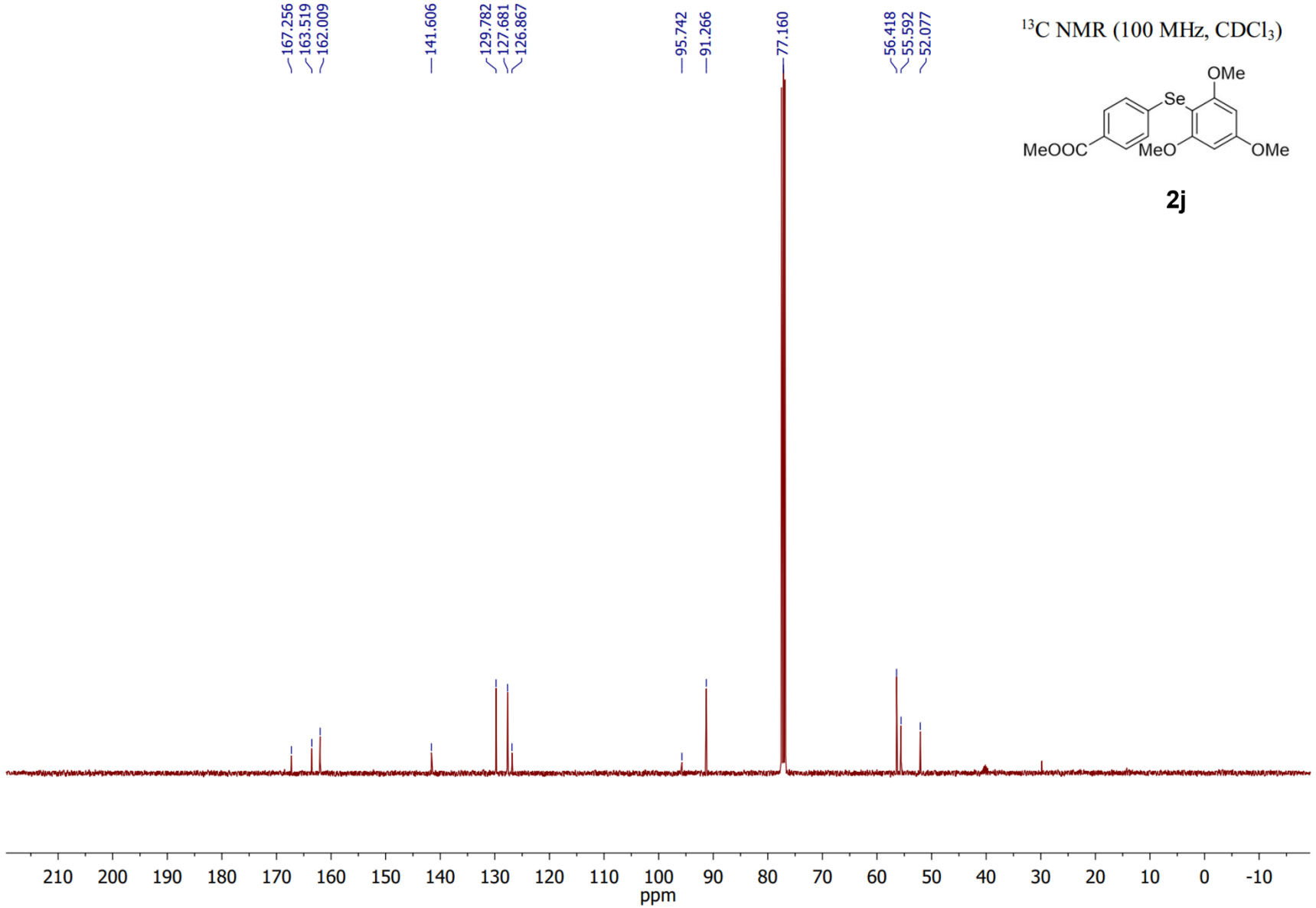
2i

^{77}Se NMR (76 MHz, $CDCl_3$)



2i

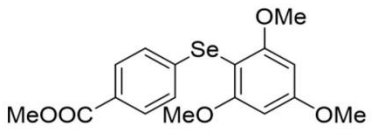

^{1}H NMR (400 MHz, CDCl$_3$)
OMe
Se
MeOOC
MeO
OMe
2j
7.785
7.764
7.260
7.179
7.158
6.229
3.886
3.862
3.786
2.01
2.03
2.00
3.00
3.00
6.00
ppm



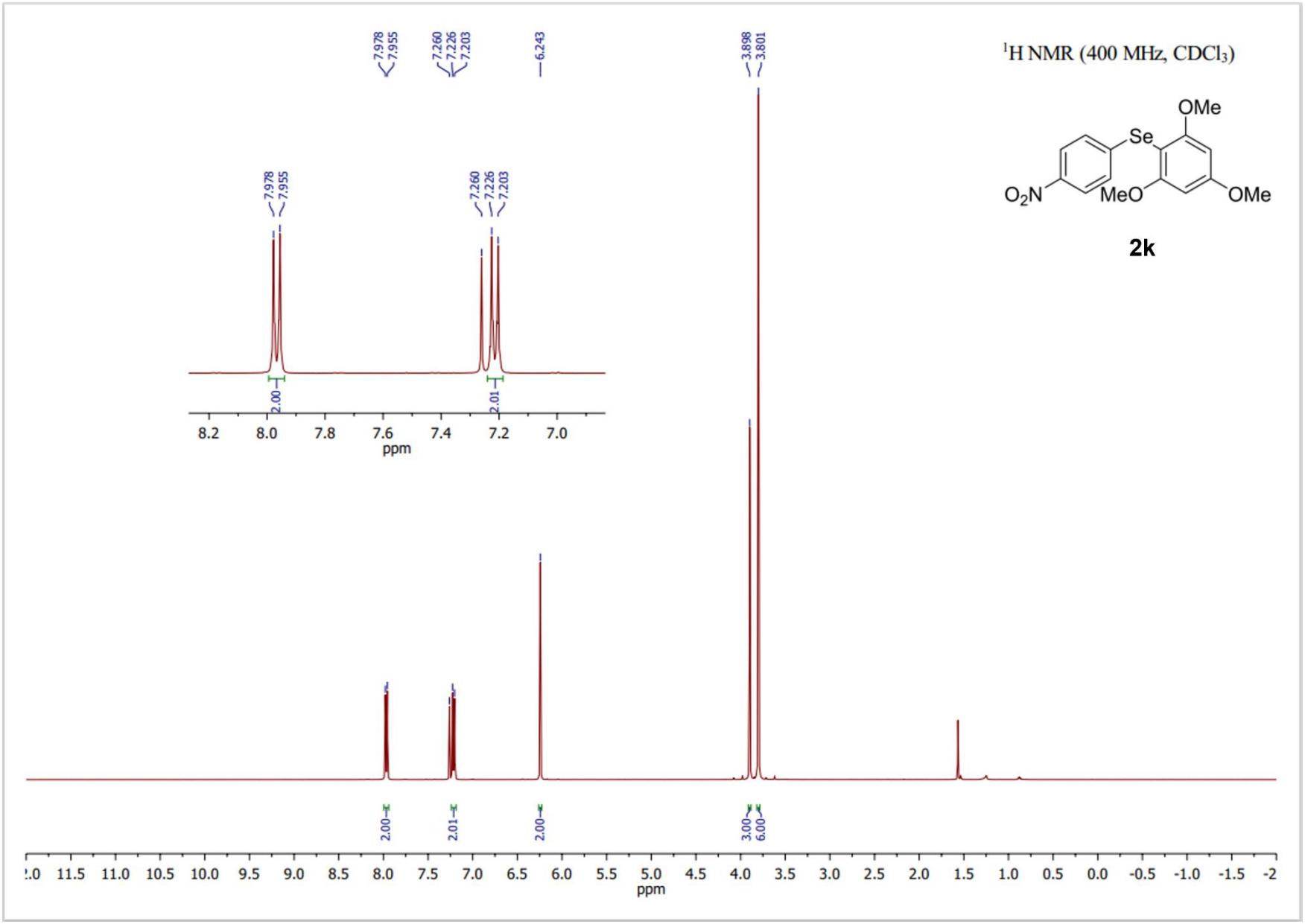
^{13}C NMR (100 MHz, $CDCl_3$)

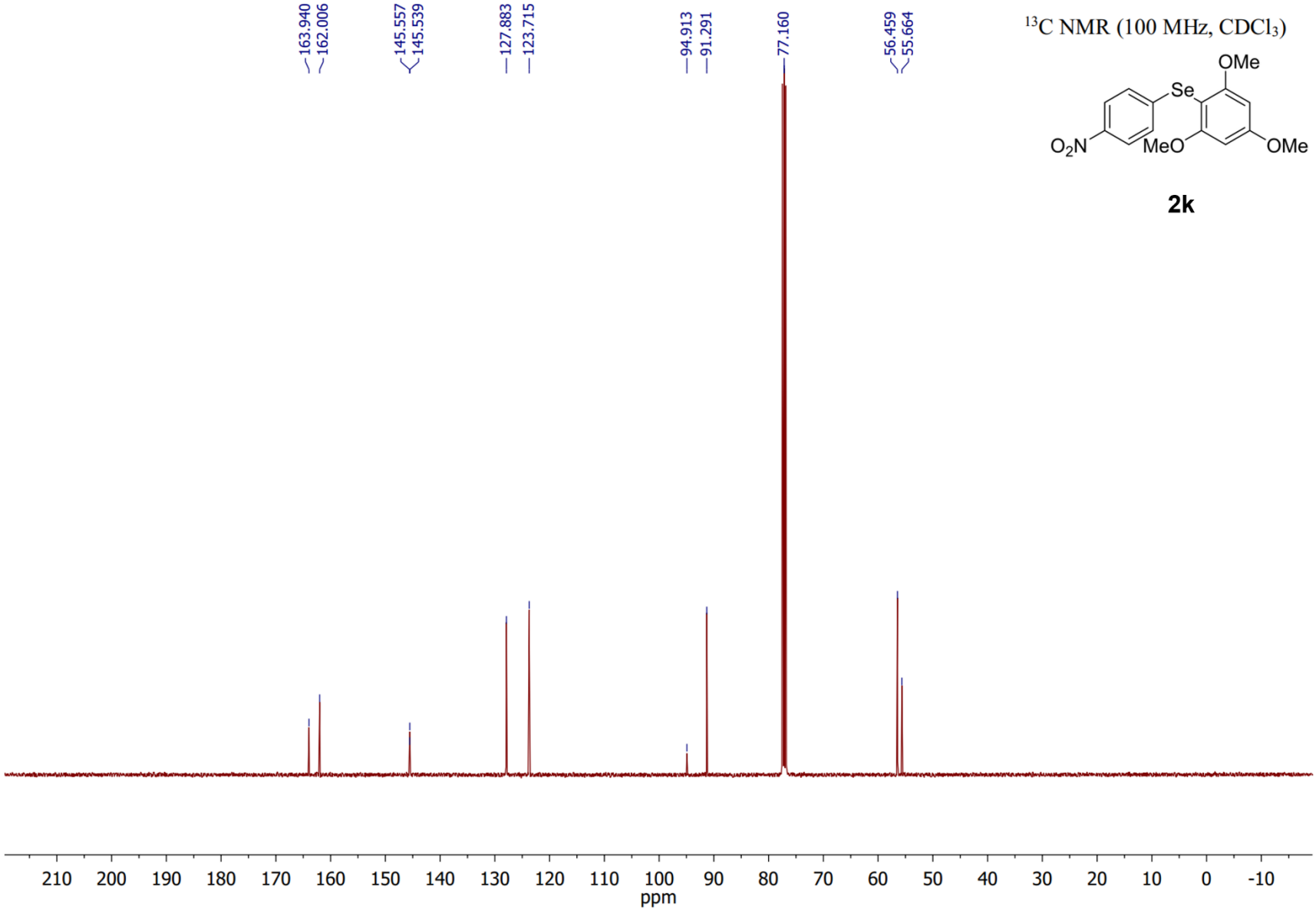
2j

^{77}Se NMR (76 MHz, $CDCl_3$)



2j

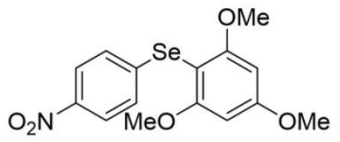

^{1}H NMR (400 MHz, $CDCl_3$)
OMe
Se
O_2N
MeO
OMe
2k
7.978
7.955
7.260
7.226
7.203
6.243
3.898
3.801
2.00
2.01
2.00
3.00
6.00
ppm



^{13}C NMR (100 MHz, $CDCl_3$)

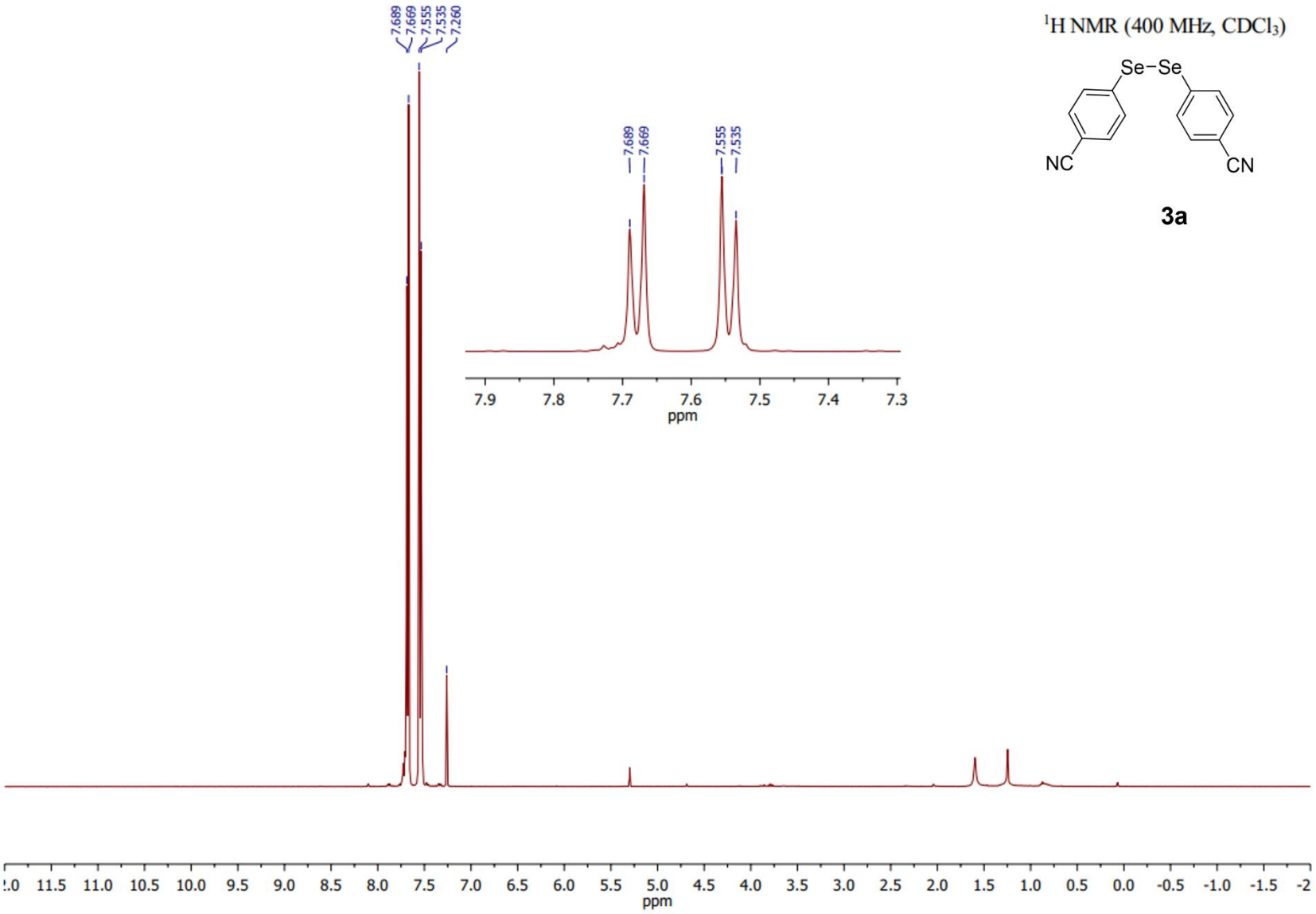
2k

^{77}Se NMR (76 MHz, $CDCl_3$)



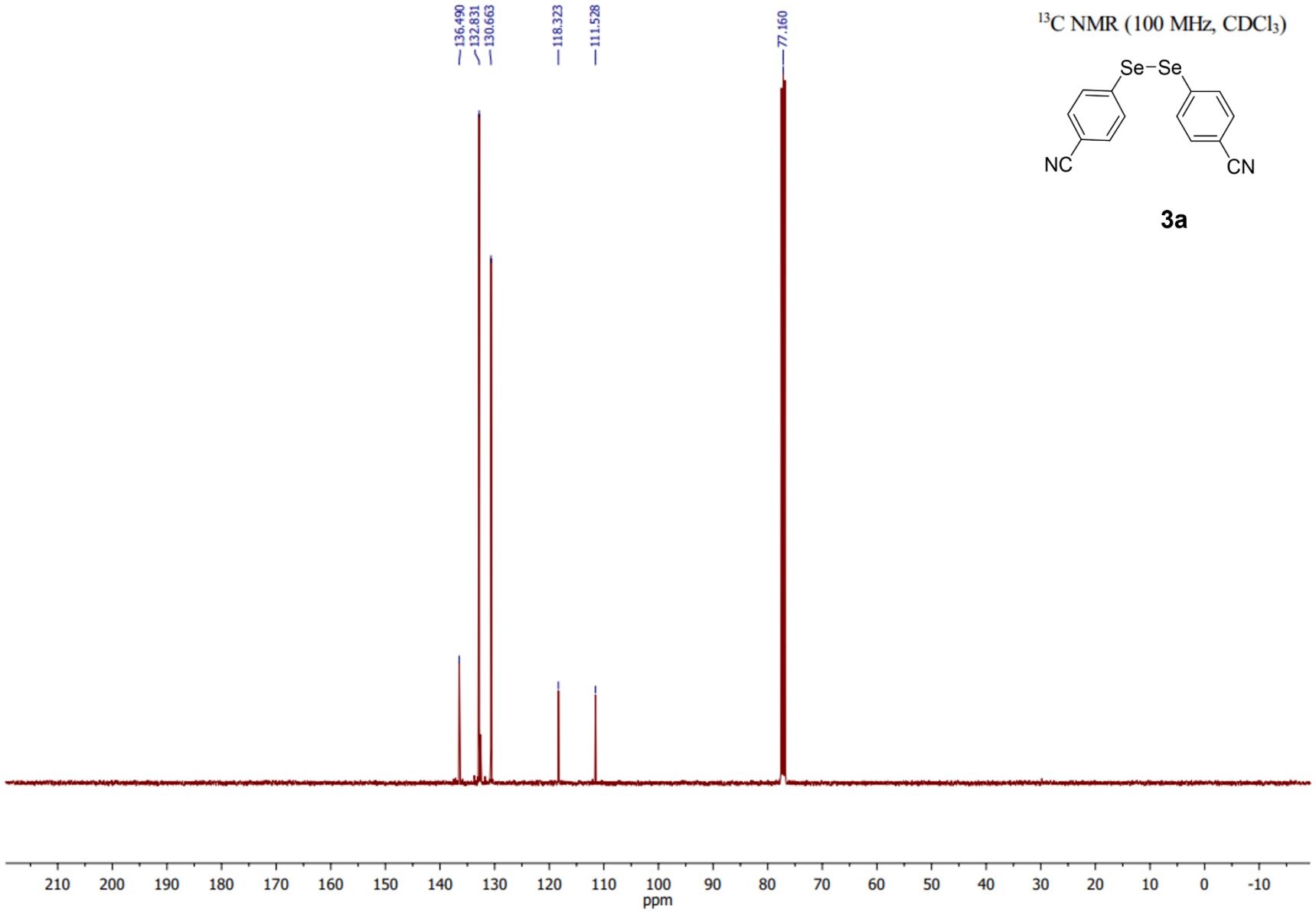
2k

NMR spectra of **3a**,**b**



^{1}H NMR (400 MHz, $CDCl_3$)

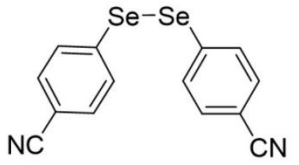
3a



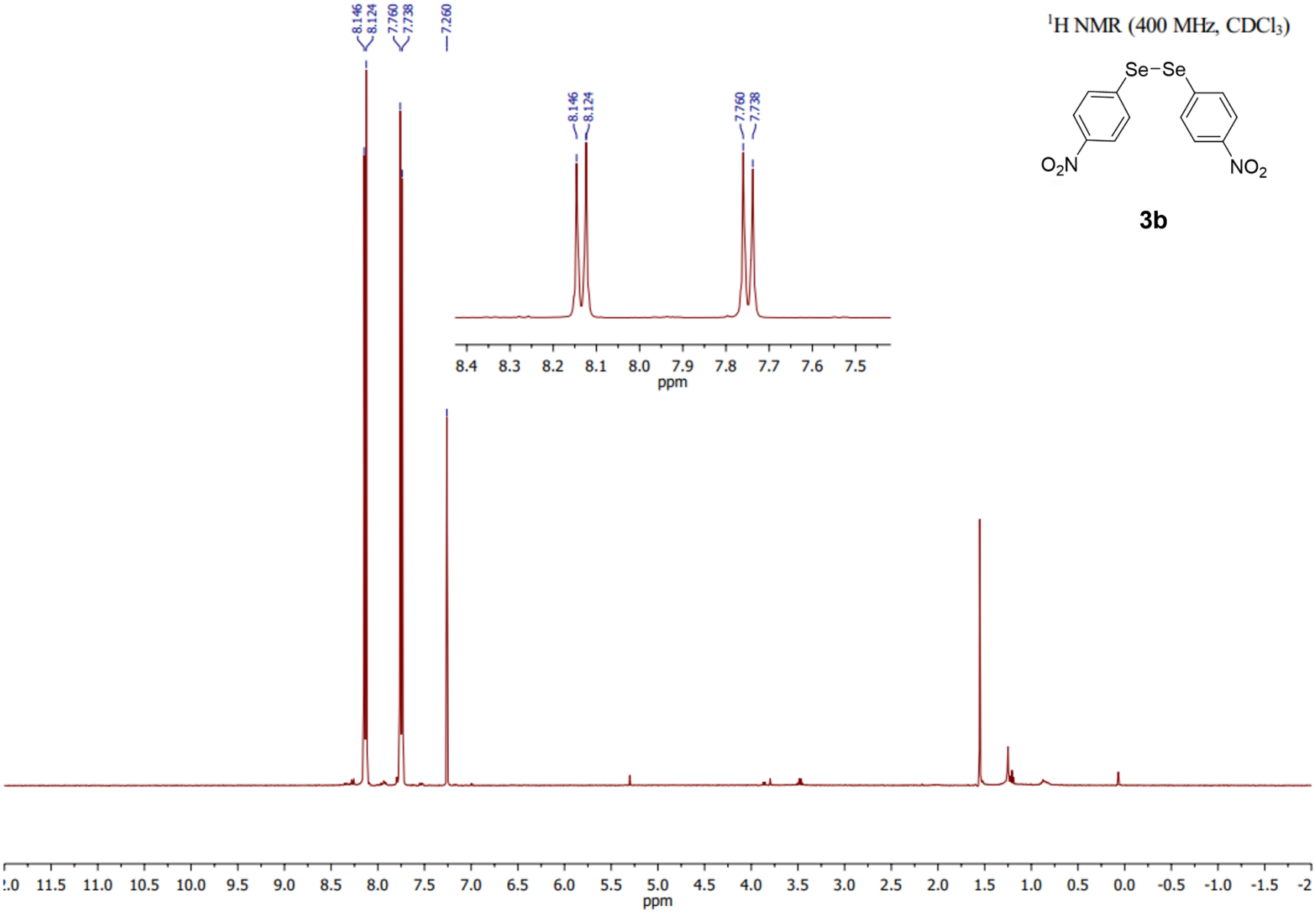
^{13}C NMR (100 MHz, $CDCl_3$)

3a

^{77}Se NMR (76 MHz, $CDCl_3$)

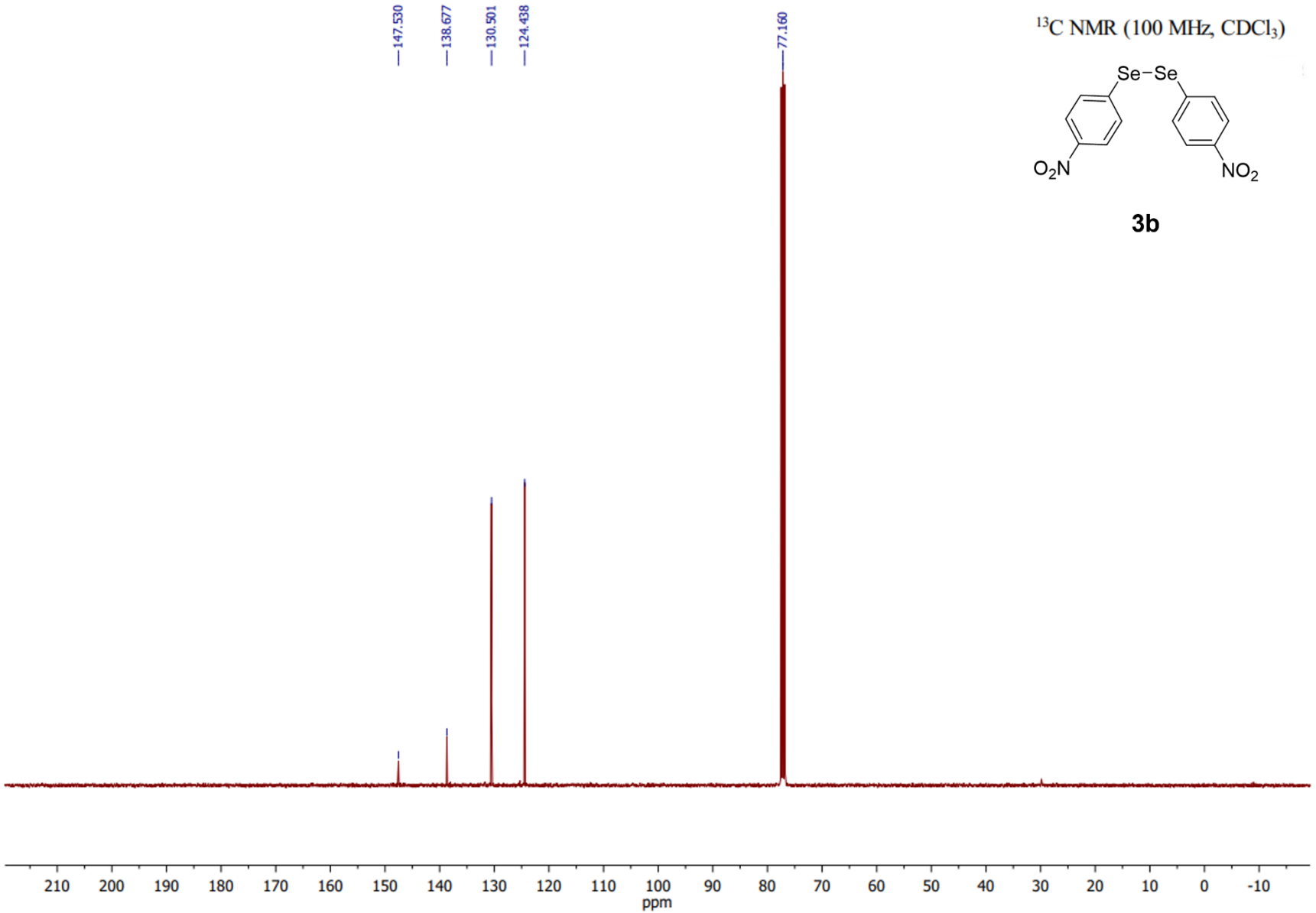


3a

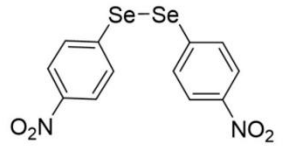


^{1}H NMR (400 MHz, $CDCl_3$)

3b


147.530
138.677
130.501
124.438
77.160
^{13}C NMR (100 MHz, $CDCl_3$)
Se–Se
O_2N
NO_2
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

^{77}Se NMR (76 MHz, $CDCl_3$)



3b

Table S2. Crystal data and structure refinement for **2g**, **2i**, and **3b**.

Identification code	**2g**	**2i**	**3b**
CCDC number	2250168	2250169	2250170
Empirical formula	$C_{16}H_{15}F_3O_3Se$	$C_{16}H_{15}NO_3Se$	$C_{12}H_8N_2O_4Se_2$
Formula weight	391.24	348.25	402.12
Temperature, K	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
a, Å	8.4142(2)	14.6406(9)	7.19910(10)
b, Å	25.3815(4)	4.3593(3)	14.1649(2)
c, Å	8.4387(2)	23.6861(19)	12.8571(2)
α, °	90	90	90
β, °	119.088(3)	104.016(8)	90.3270(10)
γ, °	90	90	90
Volume, $Å^3$	1574.90(7)	1466.71(19)	1311.08(3)
Z	4	4	4
ρ_{calc}, g/cm^3	1.650	1.577	2.037
μ, mm^{-1}	3.646	3.554	7.214
F(000)	784.0	704.0	776.0
Crystal size, mm^3	0.2 × 0.18 × 0.15	0.21 × 0.18 × 0.15	0.2 × 0.18 × 0.17
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection, °	6.966 to 134.99	6.222 to 134.98	12.498 to 159.478
Index ranges	$-10 \le h \le 10$, $-29 \le k \le 30$, $-8 \le l \le 10$	$-17 \le h \le 17$, $-5 \le k \le 4$, $-28 \le l \le 28$	$-9 \le h \le 6$, $-17 \le k \le 17$, $-16 \le l \le 16$
Reflections collected	18825	25265	3717
Independent reflections	2812 [R_{int} = 0.0495, R_{sigma} = 0.0299]	2641 [R_{int} = 0.1605, R_{sigma} = 0.0788]	1350 [R_{int} = 0.0178, R_{sigma} = 0.0148]
Data/restraints/parameters	2812/0/211	2641/0/193	1350/0/91
Goodness-of-fit on F^2	1.257	1.076	1.040
Final R indexes [I≥2σ (I)]	R_1 = 0.0767, wR_2 = 0.1803	R_1 = 0.0709, wR_2 = 0.1714	R_1 = 0.0293, wR_2 = 0.0817
Final R indexes [all data]	R_1 = 0.0778, wR_2 = 0.1807	R_1 = 0.0925, wR_2 = 0.1883	R_1 = 0.0300, wR_2 = 0.0824
Largest diff. peak/hole, $e \cdot Å^{-3}$	1.42/–0.85	2.12/–0.92	0.91/–0.79

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