Supporting information

Photocatalyzed Arylation of Isonitriles by Diaryliodonium Salts towards N-Substituted Benzamides

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Table of content

1. General information

Reagents were used as received from their commercial supplier (abcr, Acros Organics, Alfa Aesar, Sigma Aldrich, TCI, fluorochem, BLD pharm). The solvents were used as received expect MeCN which was dried using standard methods.[1] Unless otherwise stated, all yields refer to isolated yields of compounds estimated to be >95 % pure as determined by ^{1}H NMR spectroscopy.

Thin layer chromatography was performed on fluorescence indicator marked precoated silica gel 60 plates (Macherey-Nagel, ALUGRAM Xtra SIL G/UV254) and visualized by UV light (254 nm/365 nm). Column chromatography was performed on silica gel (0.040 – 0.063 mm) with the solvents given in the procedures.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AVANCE III HD (400 MHz), Bruker AVANCE III (500 MHz). The following abbreviations were used to describe splitting patterns: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin. = quintet, sext. = sextet, sept. = septet, m = multiplet. Coupling constants *J* are given in Hertz. Chemical shifts for ^{1}H NMR spectra were reported as δ (parts per million) relative to the residual signal of $CDCl_3$ at 7.26 ppm (s), DMSO-d_6 at 2.50 ppm (s), Acetone-d_6 at 2.05 ppm (quin.). Chemical shifts for ^{13}C NMR spectra were reported as δ (parts per million) relative to the signal of $CDCl_3$ at 77.2 ppm (t), DMSO-d_6 at 39.5 ppm (sept.), Acetone-d_6 at 29.8 ppm (sept.).

HR-ESI mass spectra were recorded on a Bruker impact II. EI mass spectra were obtained from an Agilent 7890B GC System with an Agilent 5977A MSD mass spectrometer. All signals were reported with the quotient from mass to charge m/z. A solvent for HR-ESI mass spectra measurements specified for each compound.

Melting points were determined on a Büchi M-5600 Melting Point apparatus or on a melting point apparatus SMP30 with a heating rate of 2 °C/min. The melting points were reported in °C. Most of the iodonium salts underwent changes in appearance (e.g. softening) before final melting/decomposition.

Photochemical experiments were carried out with a homemade setup (Fig. S1A). The reaction mixture was irradiated by 20 W blue LED (455 nm) coiled around a glass tube. Water cooled to 14 °C was supplied between the glass tube and the screw cap tube with the reaction mixture. The screw cap tube is inside a glass tube (Fig. S1B).

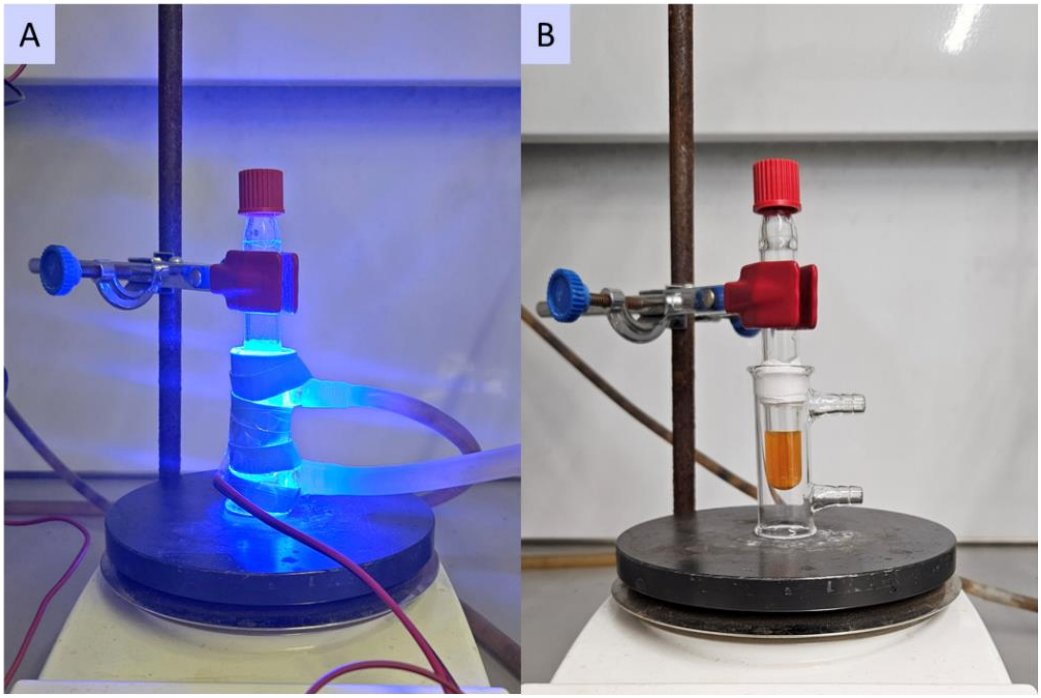


Figure S1. Overview of the reaction setup. (A) Photoreactor with power on. (B) A screw cap tube arrangement inside the glass tube

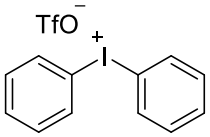
2. Synthesis of Iodonium salts *1 and 3*

General procedure (GP1): according to the literature procedure.[2] Iodoarene (1.0 equiv., 10.0 mmol) was dissolved in DCM (50 mL) and *m*CPBA was added (1.13 equiv., 11.3 mmol, 2.89 g, 70 %) neat. Then arene (1.13 equiv., 11.3 mmol) was added and the reaction mixture was stirred for 5 min. Afterwards the reaction mixture was cooled in ice-water bath and TfOH (3.0 equiv., 30.0 mmol, 2.66 mL) was added dropwise. The mixture was allowed to stir overnight at room temperature. Then the solvent was removed under reduced pressure. The product was precipitated by Et_2O and stored at – 30 °C for 1 h. Then the precipitate was filtered, washed with cold Et_2O (3 × 15 mL) and dried under vacuum to give diaryliodonium triflate ***1*** *or* ***2***.

General procedure (GP2): according to the modified literature procedure.[3] Iodoarene (1.0 equiv., 10.0 mmol) was dissolved in $CHCl_3$ (10 mL). Then *m*CPBA (1.1 equiv., 11.0 mmol, 2.71 g, 70 %) and *p*-TsOH·H_2O (1.0 equiv., 10.0 mmol, 2.09 g) were added neat. The reaction mixture was allowed to stir for 2 h at room temperature. Then the solvent was removed under reduced pressure and the product was precipitated by Et_2O. The precipitate was filtered and washed with Et_2O (3 × 10 mL). The product was dried under vacuum to give [hydroxy(tosyloxy)iodo]arene. Then prepared [hydroxy(tosyloxy)iodo]arene (1.0 equiv., 2.0 mmol) was suspended in MeCN. BF_3·Et_2O (4.0 equiv., 8.0 mmol, 1.02 mL) was added dropwise to the mixture. After full dissolution of the substrate arylboronic acid (1.1 equiv., 2.2 mmol) was added and the reaction mixture was stirred overnight. TfOH (3.0 equiv., 6.0 mmol, 0.9 mL) was added dropwise and stirring was continued for 30 min. The solvent was removed under reduced pressure and the product was isolated by column chromatography on silica (gradient elution: DCM:MeOH – 100:1 → 10:1) to give diaryliodonium triflate ***1***.

General procedure (GP3): according to the literature procedure.[4] Iodoarene (1.0 equiv., 5.0 mmol) and *p*-TsOH·H_2O (1.05 equiv., 5.25 mmol, 0.90 g, 70 %) was dissolved in MeCN (50 mL) and *m*CPBA was added (1.13 equiv., 11.3 mmol, 2.89 g, 70 %) neat. The reaction mixture was stirred at 77 °C for 30 min. Then 1,3,5-trimethoxybenzene (1.05 equiv., 5.25 mmol, 0.88 g) was added and the reaction mixture was stirred at 77 °C for 5 min. The solvent was removed under reduced pressure. The product was precipitated by Et_2O, washed with cold Et_2O (3 × 15 mL) and dried in the air at room temperature to give aryl(2,4,6-trimethoxyphenyl)iodonium tosylate. Afterwards aryl(2,4,6-trimethoxyphenyl)iodonium tosylate was dissolved in DCM (50 mL). The resulted solution was washed with cooled aqueous solution of NaOTf (1 M, 100 mL) prepared by mixing

solutions of NaOH (100 mmol, 4.0 g) in H_2O (50 mL) and TfOH (100 mmol, 8.8 mL) in H_2O (50 mL). Combined organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was precipitated by Et_2O, filtered, washed with cold Et_2O (3 × 15 mL) and dried in the air at room temperature to give aryl(2,4,6-trimethoxyphenyl)iodonium triflate ***1*** *or* ***3***. *Not recommended to dry under vacuum since for some salts decomposition occurred!*

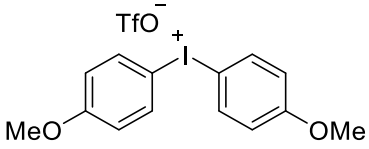


1a: according to ***GP1*** iodobenzene (10.0 mmol, 1.2 mL) reacted with benzene (11.3 mmol, 1.0 mL) to give diphenyliodonium triflate ***1a*** as a white solid, 4.10 g (95 %). mp = 170 – 172 °C (lit. 169 – 173 °C).[4] The analytical data is in accordance with previously published.[4]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.25 (d, J = 8.0 Hz, 4H), 7.67 (t, J = 6.8 Hz, 2H), 7.53 (t, J = 6.8 Hz, 4H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 135.2, 132.1, 131.8, 120.7 (q, J = 320.0 Hz), 116.5.

^{19}F NMR (376 MHz, DMSO-d_6) δ -77.7.

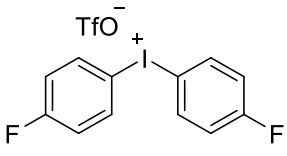


1b: Preparation of ***1b*** is based on the previously reported procedure.[4] Anisole (3.5 equiv., 20.0 mmol, 2.2 mL), *m*CPBA (70 %, 2.0 equiv., 14.3 mmol, 3.53 g) and *p*-TsOH·H_2O (3.4 equiv., 19.4 mmol, 3.69 g) was dissolved in DCM (50 mL). Iodine (1.0 equiv., 5.7 mmol, 1.43 g) was added. Solution was stirred overnight at room temperature. Then the solvent was removed under reduced pressure, the product was precipitated by Et_2O, filtered and washed with Et_2O (3 × 15 mL). Obtained bis(4-methoxyphenyl)iodonium tosylate was dried in the air at room temperature. Afterwards bis(4-methoxyphenyl)iodonium tosylate was suspended in DCM (50 mL). The resulted suspension was washed with cooled aqueous solution of NaOTf (1 M, 100 mL) prepared by mixing solutions of NaOH (100 mmol, 4.0 g) in H_2O (50 mL) and TfOH (100 mmol, 8.8 mL) in H_2O (50 mL). Combined organic layer was dried over $MgSO_4$ and solvent was removed under reduced pressure. The product was precipitated by Et_2O, filtered, washed with cold Et_2O (3 × 15 mL) and dried under vacuum to give bis(4-methoxyphenyl)iodonium triflate ***1b*** as a white solid, 3.10 g (63 %). mp = 131 – 133 °C (lit. 116 – 125 °C).[4] The analytical data is in accordance with previously published.[4]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.13 (d, J = 8.4 Hz, 4H), 7.06 (d, J = 8.4 Hz, 4H), 3.79 (s, 6H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 161.9, 136.9, 120.7 (q, J = 320.0 Hz), 117.4, 106.0, 55.7.

^{19}F NMR (376 MHz, DMSO-d_6) δ -77.7.

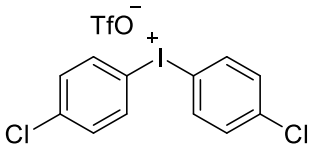


1c: Preparation of ***1c*** is based on the previously reported procedure.[2] Iodine (1.0 equiv., 10.0 mmol, 1.43 g) and *m*CPBA (3.0 equiv., 30.0 mmol, 3.2 g, 70 %,) was dissolved in DCM (84 mL). Afterwards the reaction mixture was cooled in ice-water bath and fluorobenzene (10.0 equiv., 100.0 mmol, 9.39 mL) was added. After 5 min of stirring TfOH (3.8 equiv., 38.0 mmol, 3.36 mL) was added dropwise. The mixture allowed to stir overnight at room temperature. The solvent was removed under reduced pressure. The product was precipitated by Et_2O, stored at - 30 °C for 1 h, filtered, washed with cold Et_2O (3 × 15 mL) and dried under vacuum to give bis(4-fluorophenyl)iodonium triflate ***1c*** as a white solid, 5.25 g (56 %). mp = 166 – 168 °C (lit. 168 – 170 °C).[5] The analytical data is in accordance with previously published.[5]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.32 (dd, J = 9.2, 5.2 Hz, 4H), 7.42 (t, J = 8.8 Hz, 4H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 164.0 (d, J = 250.0 Hz), 138.06 (d, J = 9.0 Hz), 120.7 (q, J = 320.0 Hz), 119.3 (d, J = 23.0 Hz), 111.2 (d, J = 3.0 Hz).

^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8, -106.6 – 106.6 (m).

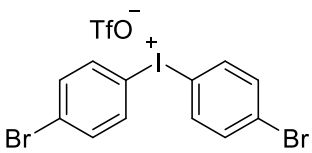


1d: according to ***GP1*** 1-chloro-4-iodobenzene (10.0 mmol, 2.39 g) reacted with chlorobenzene (11.3 mmol, 1.2 mL) to give bis(4-chlorophenyl)iodonium triflate ***1d*** as a white solid, 4.39 g (88 %). mp = 189 – 190 °C (lit. 183 – 185 °C).[4] The analytical data is in accordance with previously published.[4]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 (d, J = 8.0 Hz, 4H), 7.63 (d, J = 8.0 Hz, 4H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 137.5, 137.0, 131.8, 120.7 (q, J = 320.0 Hz), 114.7.

^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8.



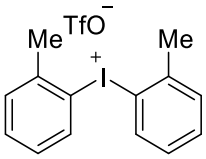
1e: according to ***GP1*** 1-bromo-4-iodobenzene (10.0 mmol, 2.83 g) reacted with bromobenzene (11.3 mmol, 1.2 mL) for 2 h to give bis(4-

bromophenyl)iodonium triflate ***1e*** as a white solid, 5.30 g (90 %). mp = 210 – 212 °C (lit. 181 – 184 °C).[4] The analytical data is in accordance with previously published.[4]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 (d, J = 8.4 Hz, 4H), 7.77 (d, J = 8.4 Hz, 4H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 137.1, 134.7, 126.4, 120.7 (q, J = 320.3 Hz), 115.4.

^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8.

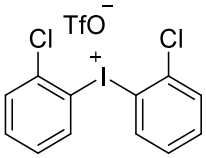


1f: according to ***GP2*** 1-iodo-2-methylbenzene (10.0 mmol, 2.18 g) reacted with *m*CPBA (70 %, 11.0 mmol, 2.71 g) and *p*-TsOH·H_2O (11.0 mmol, 2.09 g) to give hydroxy(2-methylphenyl)iodonium tosylate as a white solid 3.98 g (98 %). Reaction of hydroxy(2-methylphenyl)iodonium tosylate (2.0 mmol, 0.81 g) with (2-methylphenyl)boronic acid (2.2 mmol, 0.30 g) afforded bis(2-methylphenyl)iodonium triflate ***1f*** as a white solid, 0.44 g (48 %). mp = 175 – 178 °C (lit. 170 – 171 °C).[6] The analytical data is in accordance with previously published.[6]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.32 (d, J = 8.4 Hz, 2H), 7.60 – 7.56 (m, 4H), 7.32 – 7.28 (m, 2H), 2.61 (s, 6H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 140.6, 137.2, 132.8, 131.6, 129.3, 120.7 (q, J = 320.0 Hz), 120.6, 25.0.

^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8.



1g: according to ***GP2*** 1-chloro-2-iodobenzene (10.0 mmol, 2.38 g) reacted with *m*CPBA (70 %, 11.0 mmol, 2.71 g) and *p*-TsOH·H_2O (11.0 mmol, 2.09 g) to give hydroxy(2-chlorophenyl)iodonium tosylate as a white solid 4.14 g (97 %). Reaction of hydroxy(2-chlorophenyl)iodonium tosylate (2.0 mmol, 0.85 g) with (2-chlorophenyl)boronic acid (2.2 mmol, 0.34 g) afforded bis(2- chlorophenyl)iodonium triflate ***1g*** as a white solid, 0.67 g (67 %). mp = 193 – 195 °C.

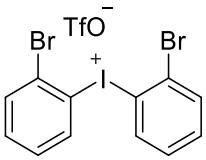
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.53 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 139.0, 136.0, 134.8, 130.5, 130.2, 120.7 (q, J = 320.0 Hz), 119.6.

^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8.

HRMS (positive mode, MeCN) calcd. for $C_{12}H_8Cl_2I^+$ ($[M+H]^+$) 348.9043 (found 348.9043).

HRMS (negative mode, MeCN) calcd. for $CF_3O_3S^-$ ($[M+H]^-$) 148.9525 (found 148.9524).



1h: according to ***GP2*** 1-bromo-2-iodobenzene (10.0 mmol, 2.38 g) reacted with *m*CPBA (70 %, 11.0 mmol, 2.71 g) and *p*-TsOH·H_2O (11.0 mmol, 2.09 g) to give hydroxy(2-bromophenyl)iodonium tosylate as a white solid 4.62 g (98 %). Reaction of hydroxy(2-bromophenyl)iodonium tosylate (2.0 mmol, 0.94 g) with (2-bromophenyl)boronic acid (2.2 mmol, 0.44 g) afforded bis(2-bromophenyl)iodonium triflate ***1h*** as a white solid, 0.76 g (65 %) mp = 209 – 210 °C.

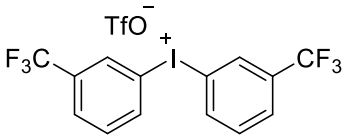
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.50 (d, *J* = 7.6 Hz, 2H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 139.2, 134.7, 133.9, 130.6, 127.0, 122.9, 120,7 (q, *J* = 320.0 Hz).

^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8.

HRMS (positive mode, MeCN) calcd. for $C_{12}H_8Br_2I^+$ ($[M+H]^+$) 438.8012 (found 438.8014).

HRMS (negative mode, MeCN) calcd. for $CF_3O_3S^-$ ($[M+H]^-$) 148.9525 (found 148.9527).

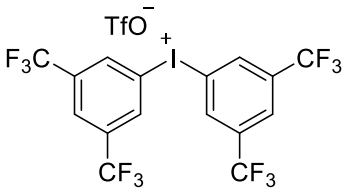


1i: Preparation of ***1i*** is based on the previously reported procedure.[4] Iodine (1.0 equiv., 2.84 mmol, 0.72 g) and $NaIO_4$ (1.5 equiv., 4.3 mmol, 0.92 g) were added to $H_2SO_{4conc.}$ (10 mL) and stirred at 75 °C for 1 h. Reaction mixture was cooled with ice-water bath and benzotrifluoride (9.1 equiv., 26 mmol, 3.8 mL) was added dropwise and obtained mixture was stirred overnight at room temperature. Then ice was added to the reaction mixture (total volume after melting was approximately 50 mL). TfOH (7.0 equiv., 20.0 mmol, 1.77 mL) was added. Resulted mixture was extracted with DCM (3 × 20 mL) and combined organic phase was dried over Mg_2SO_4 and solvent was removed under reduced pressure. The product was precipitated by Et_2O (2 mL) and hexane (18 mL), filtered and washed with hexane (3 × 10 mL). Afterwards the precipitate dried under vacuum to give bis(3-(trifluoromethyl)phenyl)iodonium triflate ***1i*** as a white solid, 1.83 g (45 %). mp = 109 – 110 °C (lit. 95 – 102 °C).[4] The analytical data is in accordance with previously published.[4]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.83 (s, 2H), 8.62 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.79 (t, *J* = 8.0 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 139.4, 132.8, 132.0 (q, *J* = 4.0 Hz), 131.3 (q, *J* = 33.0 Hz), 129.1 (q, *J* = 3.0 Hz), 122.9 (q, *J* = 271.7 Hz), 120.7 (q, *J* = 320.0 Hz), 117.2.

^{19}F NMR (376 MHz, DMSO-d_6) δ -61.3, -77.8.

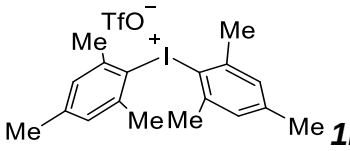


1j: Preparation of ***1j*** is based on the previously reported procedure.[7] A 100 mL round-bottom flask was charged with the mixture of TfOH (3 mL) and iodine (1.0 equiv., 0.66 mmol, 0.17 g). Then $NaIO_4$ (1.5 equiv., 1 mmol, 0.2 g) was added to the mixture under stream of argon, reaction vessel was flushed with argon and stirred at room temperature for 48 h. Afterwards, the reaction mixture was cooled in ice-water bath and 1,3-bis(trifluoromethyl)benzene (9.1 equiv., 6.0 mmol, 0.95 mL) was added dropwise. The obtained mixture was allowed to stir at room temperature for 24 h. Then ice was added to the reaction mixture (total volume after melting was approximately 50 mL). The reaction mixture was extracted with EtOAc (3 × 20 mL). Combined organic phase were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The mixture of hexane (10 mL) and Et_2O (2 mL) was added to the residue. The product was filtered, washed with hexane (3 × 10 mL) and dried under vacuum to give bis(3,5-bis(trifluoromethyl)phenyl)iodonium triflate as a white solid, 0.79 mg (49 %). mp = 254 – 255 °C (dec.) (lit. 198 – 203 °C).[7] The analytical data is in accordance with previously published.[7]

^{1}H NMR (400 MHz, Acetone-d_6) δ 9.21 (s, 4H), 8.43 (s, 2H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 137.8 (q, J = 4.0 Hz), 134.4 (q, J = 34.0 Hz), 127.7 (sept. J = 3.8 Hz), 123.1 (q, J = 271.3 Hz), 121.8 (q, J = 318.3 Hz), 116.5.

^{19}F NMR (376 MHz, Acetone d_6) δ -63.4, -79.1.



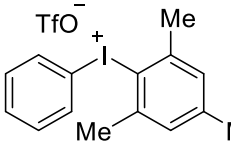
1k: Preparation of ***1k*** is based on the previously reported procedure.[4] A 100 mL round-bottom flask was charged with iodine (1.0 equiv., 2.5 mmol, 0.64 g), Oxone (4.0 equiv., 10.0 mmol, 6.17 g) and mesitylene (4.3 equiv., 10.8 mmol, 1.5 mL). MeCN was added (10 mL). Afterwards, $H_2SO_{4conc.}$ (2 mL) was added to the mixture. The reaction mixture was allowed to stir overnight. Then the solution of TfOH (4.0 equiv., 10.0 mmol, 0.88 mL) in water (10 mL) was added. Reaction mixture was extracted with DCM (3 × 20 mL) and combined organic phase was dried over Mg_2SO_4.The solvent was removed under reduced pressure. The product was precipitated by Et_2O (2 mL) and hexane (18 mL), filtered and washed with hexane (3 × 5 mL). Afterwards, the precipitate was dried under vacuum to give dimesityliodonium triflate ***1k***

as an off-white solid, 1.20 g (47 %). mp = 197 – 198 °C (dec.) (lit. 189 – 191 °C).[4] The analytical data is in accordance with previously published.[4]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.19 (s, 4H), 2.46 (s, 12H), 2.29 (s, 6H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 142.8, 141.9, 130.3, 120.7 (J = 320.0 Hz), 118.9, 25.3, 20.4.

^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8.

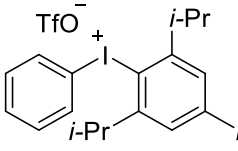


3a: Preparation of ***3a*** is based on the previously reported procedure.[8] Mesitylene (1.1 equiv., 11.0 mmol, 1,53 mL) was added to the suspension of iodosobenzene diacetate (1.0 equiv., 10.0 mmol, 3.22 g) in DCM (20 mL). Then the reaction mixture was cooled with ice-water bath and TfOH (1.1 equiv., 11.0 mmol, 0.97 mL) was added dropwise to a stirred solution. The cooling bath was removed and the reaction was stirred for 2 h at room temperature. The solvent was removed under reduced pressure, The product was precipitated by Et_2O. The solid was filtered and washed with Et_2O (3 × 15 mL). The solid was dried under vacuum to give mesityl(phenyl)iodonium triflate ***3a*** as a white solid, 4.60 g (97 %). mp = 150 – 151 °C (lit. 149 – 150 °C).[9] The analytical data is in accordance with previously published.[8]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 (d, J = 7.2 Hz, 2H), 7.65 – 7.61 (m, 1H), 7.52 – 7.48 (m, 2H), 7.22 (s, 2H), 2.60 (s, 6H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 143.1, 141.6, 134.5, 131.9, 131.8, 129.8, 122.6, 120.7 (q, J = 320.3 Hz), 114.5, 26.3, 20.5.

^{19}F NMR (376 MHz, DMSO-d_6) δ -77.7.

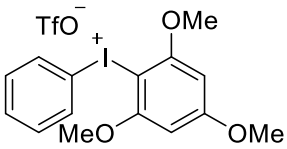


3b: according to ***GP1*** iodobenzene (10 mmol, 1.2 mL) reacted with 1,3,5-triisopropylbenzene (11.0 mmol, 2.7 mL) to give phenyl(2,4,6-triisopropylphenyl)iodonium triflate ***3b*** as a white solid, 3.00 g (54 %). mp = 171 – 172 °C (lit. 169 – 170 °C).[8] The analytical data is in accordance with previously published.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.0 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.17 (s, 2H), 3.26 (sept., J = 6.8 Hz, 2H), 2.96 (sept., J = 6.8 Hz, 1H), 1.27 (d, J = 6.8 Hz, 6H), 1.23 (d, J = 6.8 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 152.5, 132.7, 132.5, 132.0, 125.4, 120.7, 120.5 (q, J = 318.3 Hz), 113.0, 39.7, 34.3, 24.4, 23.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -78.3.

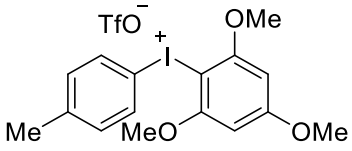


3c: according to ***GP3*** iodobenzene (5.0 mmol, 0.56 mL) reacted with 1,3,5-trimethoxybenzene (5.25 mmol, 0.88 g) to give phenyl(2,4,6-trimethoxyphenyl)iodonium triflate ***3c*** as a white solid, 2.00 g (77 %). mp = 107 – 108 °C (dec.) (lit. 114 – 116 °C). The analytical data is in accordance with previously published.[10]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 6.47 (s, 2H), 3.95 (s, 6H), 3.87 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 166.2, 159.4, 134.3, 131.7, 131.6, 120.7 (q, *J* = 320.0 Hz), 116.1, 92.1, 87.0, 57.3, 56.1.

^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8.

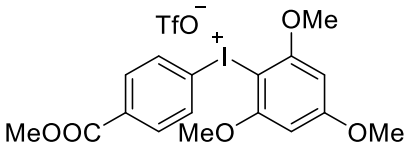


3d: according to ***GP3*** 1-iodo-4-methylbenzene (5.0 mmol, 1.09 g) reacted with 1,3,5-trimethoxybenzene (5.25 mmol, 0.88 g) to give 4-methylphenyl(2,4,6-trimethoxyphenyl)iodonium tosylate as a white solid, 2.67 g (96 %). 4-Methylphenyl(2,4,6-trimethoxyphenyl)iodonium tosylate (4.8 mmol ,2.66 g) was washed with the solution of NaOTf to give 4-methylphenyl(2,4,6-trimethoxyphenyl)iodonium triflate ***3d*** as a white solid, 2.20 g (85 %). mp = 73 – 74 °C (dec.). The analytical data is in accordance with previously published.[11]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.80 (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 NMR (100 MHz, DMSO-d_6) δ 166.1, 159.3, 142.0, 134.5, 132.2, 120.7 (q, *J* = 320.3 Hz), 112.5, 92.0, 87.2, 57.3, 56.2, 20.8.

^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8.



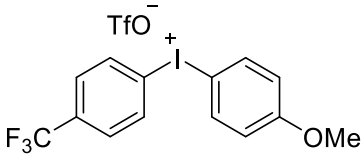
3e: according to ***GP3*** methyl 4-iodobenzoate (5.0 mmol, 1.31 g) reacted with 1,3,5-trimethoxybenzene (5.25 mmol, 0.88 g) to give (4-(methoxycarbonyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium tosylate as a white solid, 2.64 g (88 %). (4-(Methoxycarbonyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium tosylate (4.4 mmol, 2.63 g) was washed with the solution of NaOTf to give (4-(methoxycarbonyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium triflate ***3e*** as a white solid,

2.10 g (83 %). mp = 98 – 100 °C (dec.) (lit. 120 – 122 °C).[12] The analytical data is in accordance with previously published.[12]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 8.0 Hz, 2H), 6.48 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H), 3.85 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 166.4, 165.2, 159.4, 134.6, 132.2, 131.9, 120.9, 120.7 (q., J = 320.3 Hz), 107.1, 92.2, 86.9, 57.4, 56.2, 55.0, 52.7, 15.2.

^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8.



3f: according to ***GP1*** 4-iodobenzotrifluoride (5.0 mmol, 0.75 mL) reacted with anisole (5.0 mmol, 0.55 mL) to give (4-methoxyphenyl)(4-(trifluoromethyl)phenyl)iodonium triflate ***3f*** as an off-green solid, 0.76 g (29 %). mp = 148 – 149 °C (lit. 149.6 °C).[13] The analytical data is in accordance with previously published.[13]

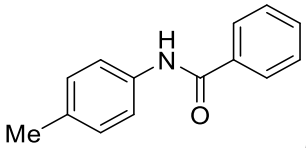
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.39 (d, J = 8.0 Hz, 2H), 8.22 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 162.2, 137.6, 135.6, 131.7 (q., J = 31.3 Hz), 128.3 (q., J = 3.0 Hz), 123.5 (q., J = 271.7 Hz), 121.3, 120.7 (q., J = 320.0 Hz), 117.6, 55, 105.6, 55.8.

^{19}F NMR (376 MHz, DMSO-d_6) δ -61.6, -77.8.

3. Synthesis of Amides *2, 4, 5*

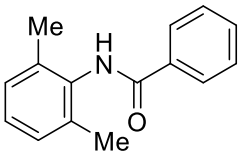
General procedure (GP4): a transparent tube with screw cap was charged with iodonium salt ***1*** or ***3*** (1.0 equiv., 0.2 mmol or 2.0 equiv., 0.4 mmol), Na_2CO_3 (1.7 equiv., 0.34 mmol, 36 mg or 3.4 equiv., 0.68 mmol, 72 mg), isocyanide (1.0 equiv., 0.2 mmol) and $[Ru(bpy)_3](PF_6)_2$ (2.0 mol. %, 0.002 mmol, 2 mg). Afterwards MeCN (2 mL) and H_2O (200 µL) were added. The suspension was bubbled with argon for 20 min and closed under stream of argon. Then the tube was allowed to stir under 20 W blue LED (455 nm) irradiation for 10 h under water cooling (14 °C). After the reaction was completed, water was added (15 mL) and the water layer was extracted with DCM (4 × 15 mL). The combined organic layers were dried over Mg_2SO_4, filtered and the solvent was removed under reduced pressure. The product was isolated by column chromatography on silica to afford the crude product ***2*** or ***4, 5***. The crude product ***2*** or ***4, 5*** was refluxed with hexane (1 mL), cooled to -30 °C, decanted and washed with hexane (2 × 1 mL). Solid was dried under vacuum to give amide ***2*** or ***4, 5***.



2aa: according to ***GP4*** 1-isocyano-4-methylbenzene (0.2 mmol, 12 mg) reacted with diphenyliodonium triflate ***1a*** (0.2 mmol, 86 mg) followed by column chromatography (gradient elution: hexane → hexane:EtOAc – 10:1) to give *N*-(4-tolyl)benzamide ***2aa*** as a beige solid, 26 mg (31 %). mp = 155 – 157 °C (lit. 158 – 159 °C).[14] The analytical data is in accordance with previously published.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 3H(Ar+NH)), 7.55 – 7.51 (m, 3H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H).

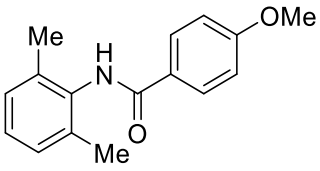
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 135.5, 135.2, 134.4, 131.9, 129.7, 128.9, 127.1, 120.4, 21.1.



2ba: according to ***GP4*** 2-isocyano-1,3-dimethylbenzene (0.2 mmol, 26 mg) reacted with diphenyliodonium triflate ***1a*** (0.2 mmol, 86 mg) followed by column chromatography (gradient elution: hexane:EtOAc – 10:1 → 7:1) to give *N*-(2,6-dimethylphenyl)benzamide ***2ba*** as an yellowish solid, 15 mg (33 %). mp = 156 – 157 °C (lit. 155 – 157 °C).[15] The analytical data is in accordance with previously published.[16] This amide was also mentioned as ***4a*** in the selectivity study for clarity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.50 – 7.47 (m, 3H), 7.17 – 7.10 (m, 3H), 2.27 (s, 6H).

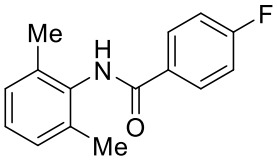
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 135.7, 134.6, 134.0, 131.9, 128.9, 128.4, 127.5, 127.4, 18.6.



2bb: according to ***GP4*** 2-isocyano-1,3-dimethylbenzene (0.2 mmol, 26 mg) reacted with bis(4-methoxyphenyl)iodonium triflate ***1b*** (0.2 mmol, 98 mg) followed by column chromatography (gradient elution: hexane:EtOAc – 10:1 → 7:1) (0.4 mmol, 196 mg) to give *N*-(2,6-dimethylphenyl)-4-methoxybenzamide ***2bb*** as a beige solid, 14 mg (27 %). mp = 169 – 170 °C (lit. 168 – 170 °C).[17] The analytical data is in accordance with previously published.[17] This amide was also mentioned as ***5b*** in the selectivity study for clarity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.36 (br s, 1H), 7.16 – 7.09 (m, 3H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 3H), 2.27 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 162.6, 135.7, 134.2, 129.2, 128.4, 127.4, 126.8, 114.0, 55.6, 18.6.



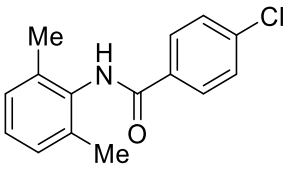
2bc: according to ***GP4*** 2-isocyano-1,3-dimethylbenzene (0.2 mmol, 26 mg) reacted with bis(4-fluorophenyl)iodonium triflate ***1c*** (0.2 mmol, 93 mg) followed by column chromatography (gradient elution: hexane:EtOAc – 10:1 → 7:1) to give *N*-(2,6-dimethylphenyl)-4-fluorobenzamide ***2bc*** as a pinkish solid, 21 mg (43 %). mp = 180 – 181 °C (lit. 179 – 181 °C).[17] The analytical data is in accordance with previously published.[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.0, 5.6 Hz, 2H), 7.47 (br s, 1H), 7.17 – 7.10 (m, 5H), 2.25 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0 (d, *J* = 251.0 Hz), 165.0, 135.7, 133.9, 130.7 (d, *J* = 3.0 Hz), 129.7 (d, *J* = 9.0 Hz), 128.4, 127.7, 115.9 (d, *J* = 21.0 Hz), 18.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -107.6 – -107.7 (m).

HRMS (positive mode, MeCN) calcd. for $C_{15}H_{15}FNO^+$ ($[M+H]^+$) 244.1133 (found 244.1135).

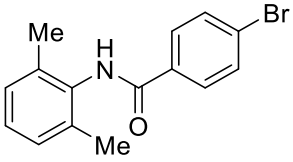


2bd: according to ***GP4*** 2-isocyano-1,3-dimethylbenzene (0.2 mmol, 26 mg) reacted with bis(4-chlorophenyl)iodonium triflate ***1d*** (0.2 mmol, 100 mg) followed by column chromatography (gradient elution: hexane:EtOAc – 10:1 → 7:1) to give 4-chloro-*N*-(2,6-dimethylphenyl)benzamide ***2bd*** as an yellowish solid, 22 mg (42 %). mp = 180 – 181 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.50 (br s, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.10 (m, 3H), 2.24 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 138.2, 135.6, 133.8, 132.9, 129.1, 128.8, 128.5, 127.7, 18.6.

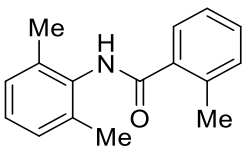
HRMS (positive mode, MeCN) calcd. for $C_{15}H_{15}ClNO^+$ ($[M+H]^+$) 260.0837 (found 260.0834).



2be: according to ***GP4*** 2-isocyano-1,3-dimethylbenzene (0.2 mmol, 26 mg) reacted with bis(4-bromophenyl)iodonium triflate ***1e*** (0.2 mmol, 118 mg) followed by column chromatography (gradient elution: hexane:EtOAc – 10:1 → 7:1) to give 4-bromo-*N*-(2,6-dimethylphenyl)benzamide ***2be*** as a white solid, 33 mg (54 %). mp = 189 – 191 °C (lit. 190 – 192 °C).[17] The analytical data is in accordance with previously published.[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.59 – 7.56 (m, 3H), 7.17 – 7.09 (m, 3H), 2.23 (s, 6H).

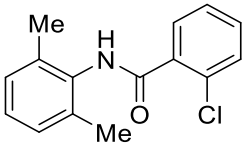
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 135.6, 133.8, 133.3, 132.1, 129.0, 128.4, 127.7, 126.6, 18.6.



2bf: according to ***GP4*** 2-isocyano-1,3-dimethylbenzene (0.2 mmol, 26 mg) reacted with bis(2-methylphenyl)iodonium triflate ***1f*** (0.2 mmol, 92 mg) followed by column chromatography (gradient elution: hexane:EtOAc – 10:1 → 7:1) to give *N*-(2,6-dimethylphenyl)-2-methylbenzamide ***2bf*** as an yellowish solid, 17 mg (36 %). mp = 135 – 136 °C (lit. 138 – 140 °C).[17] The analytical data is in accordance with previously published.[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.2 Hz 1H), 7.30 – 7.25 (m, 2H), 7.18 – 7.11 (m, 3H), 7.08 (br s, 1H), 2.54 (s, 3H), 2.34 (s, 6H).

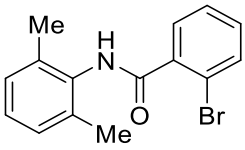
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 136.7, 136.4, 135.7, 133.7, 131.4, 130.3, 128.5, 127.7, 126.8, 126.0, 20.1, 18.8.



2bg: according to ***GP4*** 2-isocyano-1,3-dimethylbenzene (0.2 mmol, 26 mg) reacted with bis(2- chlorophenyl)iodonium triflate ***1g*** (0.2 mmol, 100 mg) followed by column chromatography (gradient elution: hexane:EtOAc – 10:1 → 7:1) to give 2-chloro-*N*-(2,6-dimethylphenyl)benzamide ***2bg*** as a white solid, 35 mg (67 %). mp = 148 – 150 °C. The analytical data is in accordance with previously published.[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.2 Hz, 1H), 7.49 – 7.36 (m, 4H), 7.17 – 7.11 (m, 3H), 2.35 (s, 6H).

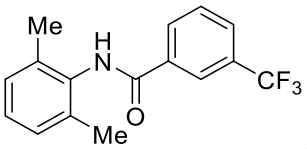
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 135.8, 135.3, 133.5, 131.7, 130.7, 130.6, 130.5, 128.5, 127.8, 127.4, 18.9.



2bh: according to ***GP4*** 2-isocyano-1,3-dimethylbenzene (0.2 mmol, 26 mg) reacted with bis(2-bromophenyl)iodonium triflate ***1h*** (0.2 mmol, 118 mg) followed by column chromatography (gradient elution: hexane:EtOAc – 10:1 → 7:1) to give 2-bromo-*N*-(2,6-dimethylphenyl) benzamide ***2bh*** as a white solid, 39 mg (64 %). mp = 172 – 173 °C (lit. 166 – 168 °C).[19] The analytical data is in accordance with previously published.[19]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (t, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.18 – 7.11 (m, 3H), 2.37 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 138.0, 135.9, 133.7, 133.4, 131.6, 130.0, 128.5, 127.9, 127.8, 119.4, 19.0.



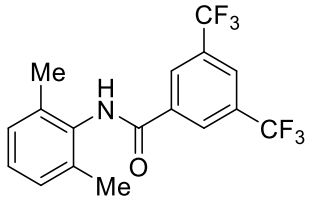
2bi: according to ***GP4*** 2-isocyano-1,3-dimethylbenzene (0.2 mmol, 26 mg) reacted with bis(3-(trifluoromethyl)phenyl)iodonium triflate ***1i*** (0.2 mmol, 113 mg) followed by column chromatography (gradient elution: hexane → hexane:EtOAc – 10:1) to give *N*-(2,6-dimethylphenyl)-3-(trifluoromethyl)benzamide ***2bi*** as an yellowish solid, 32 mg (55 %). mp = 234 – 236 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.18 – 7.10 (m, 3H), 2.25 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 135.6, 135.4, 133.5, 131.5 (q, *J* = 32.6 Hz), 130.6, 129.5, 128.6 (q, *J* = 4.0 Hz), 128.5, 127.9, 124.4 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 271.0 Hz), 18.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7.

HRMS (positive mode, MeCN) calcd. for $C_{16}H_{15}F_3NO^+$ ($[M+H]^+$) 294.1100 (found 294.1105).



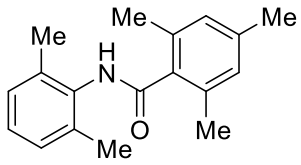
2bj: according to ***GP4*** 2-isocyano-1,3-dimethylbenzene (0.2 mmol, 26 mg) reacted with bis(3,5-bis(trifluoromethyl)phenyl)iodonium triflate ***1j*** (0.4 mmol, 281 mg) followed by column chromatography (gradient elution: hexane → hexane:EtOAc – 10:1) to give *N*-(2,6-dimethylphenyl)-3,5-bis(trifluoromethyl)benzamide ***2bj*** as a white solid, 30 mg (42 %). mp = 176 – 177 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 2H), 8.07 (s, 1H), 7.59 (br s, 1H), 7.19 – 7.11 (m, 3H), 2.26 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 136.6, 135.5, 133.1, 132.8 (q, *J* = 33.6 Hz), 128.6, 128.2, 127.7 (d, *J* = 2.0 Hz), 125.5 (p, *J* = 3.5 Hz), 123.0 (q, *J* = 271.3 Hz), 18.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9.

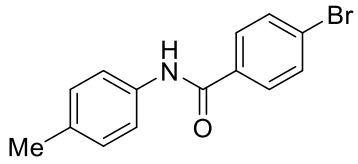
HRMS (positive mode, MeCN) calcd. for $C_{17}H_{14}F_6NO^+$ ($[M+H]^+$) 360.0975 (found 360.0983).



2bk: according to ***GP4*** 2-isocyano-1,3-dimethylbenzene (0.2 mmol, 26 mg) reacted with dimesityliodonium triflate ***1k*** (0.2 mmol, 103 mg) followed by column chromatography (gradient elution: hexane:EtOAc – 10:1 → 7:1) to give *N*-(2,6-dimethylphenyl)-2,4,6-trimethylbenzamide ***2bk*** as a beige solid, 10 mg (19 %). mp = 192 – 193 °C (lit. 197 – 199 °C).[20] The analytical data is in accordance with previously published.[20] This amide was also mentioned as ***5a*** in the selectivity study for clarity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.11 (m, 3H), 6.96 (br s, 1H), 6.91 (s, 2H), 2.47 (s, 6H), 2.39 (s, 6H), 2.31 (s, 3H).

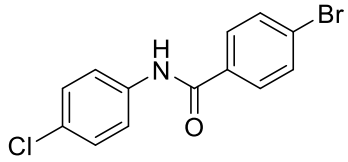
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 138.9, 135.3, 135.0, 134.7, 133.6, 128.8, 128.7, 127.6, 21.2, 20.1, 19.7.



2ce: according to ***GP4*** 1-isocyano-4-methylbenzene (0.2 mmol, 24 mg) reacted with bis(4-bromophenyl)iodonium triflate ***1e*** (0.2 mmol, 118 mg) followed by column chromatography (gradient elution: hexane:EtOAc – 10:1 → 7:1) to give 4-bromo-*N*-(*p*-tolyl)benzamide ***2ce*** as a brown solid, 13 mg (22 %). mp = 186 – 187 °C (lit. 180 – 181 °C).[21] The analytical data is in accordance with previously published.[21]

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.23 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H).

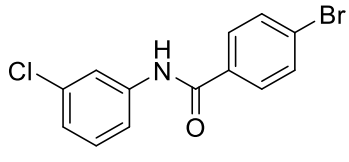
^{13}C NMR (100 MHz, DMSO-d_6) δ 164.3, 136.4, 134.1, 132.8, 131.4, 129.8, 129.1, 125.2, 120.4, 20.5.



2de: according to ***GP4*** 1-chloro-4-isocyanobenzene (0.2 mmol, 27 mg) reacted with bis(4-bromophenyl)iodonium triflate ***1e*** (0.4 mmol, 235 mg) followed by column chromatography (gradient elution: hexane:EtOAc – 10:1 → 7:1) to give 4-bromo-*N*-(4-chlorophenyl)benzamide ***2de*** as an off-white solid, 20 mg (32 %). mp = 219 – 220 °C. The analytical data is in accordance with previously published.[21]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (br s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 136.3, 133.5, 132.3, 130.0, 129.3, 128.8, 127.0, 121.6.

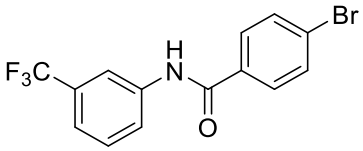


2ee: according to ***GP4*** 1-isocyano-3-chlorobenzene (0.2 mmol, 28 mg) reacted with bis(4-bromophenyl)iodonium triflate ***1e*** (0.4 mmol, 235 mg) followed by column chromatography (hexane:EtOAc – 15:1) to give 4-bromo-*N*-(3-chlorophenyl)benzamide ***2ee*** as a white solid, 8 mg (13 %). mp = 120 – 121 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (br s, 1H), 7.75 – 7.72 (m, 3H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 138.9, 135.0, 133.5, 132.3, 130.3, 128.8, 127.1, 125.0, 120.5, 118.3.

HRMS (positive mode, MeCN) calcd. for $C_{13}H_9BrClNNaO^+$ ([M+H]$^+$) 331.9454 (found 331.9444).



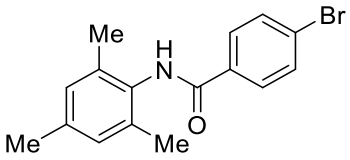
2fe: according to ***GP4*** 1-isocyano-3-(trifluoromethyl)benzene (0.2 mmol, 34 mg) reacted with bis(4-bromophenyl)iodonium triflate ***1e*** (0.2 mmol, 118 mg) followed by column chromatography (hexane:EtOAc – 15:1) to give 4-bromo-*N*-(3-(trifluoromethyl)phenyl)benzamide ***2fe*** as a white solid, 5 mg (7 %). mp = 98 – 100 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.85 (d, *J* = 6.4 Hz, 2H(Ar+NH)), 7.76 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 138.3, 133.3, 132.4, 131.7 (q, *J* = 32.5 Hz), 129.9, 128.8, 127.2, 123.4, 122.8 (q, *J* = 271.5 Hz), 121.5 (q, *J* = 3.8 Hz), 117.1 (q, *J* = 3.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8.

HRMS (positive mode, MeCN) calcd. for $C_{14}H_9BrF_3NNaO^+$ ([M+H]$^+$) 365.9717 (found 365.9715).

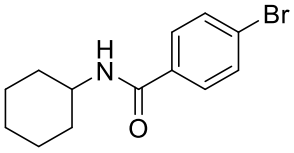


2ge: according to ***GP4*** 2-isocyano-1,3-dimethylbenzene (0.2 mmol, 29 mg) reacted with bis(4-bromophenyl)iodonium triflate ***1e*** (0.4 mmol, 235 mg) followed by column chromatography (gradient elution: hexane:EtOAc – 10:1 → 7:1) to give 4-bromo-*N*-mesitylbenzamide ***2ge*** as a white solid, 46 mg (73 %). mp = 222 – 223 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.37 (br s, 1H), 6.93 (s, 2H), 2.30 (s, 3H), 2.21 (s, 6H).

^{13}C NMR (100 MHz, CDCl3) δ 165.3, 137.4, 135.4, 133.5, 132.1, 131.1, 129.2, 129.0, 126.6, 21.1, 18.5.

HRMS (positive mode, MeCN) calcd. for $C_{16}H_{17}BrNO^+$ ([M+H]$^+$) 318.0489 (found 244.1135).

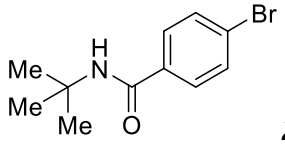


2he: according to ***GP4*** isocyanocyclohexane (0.2 mmol, 22 mg) reacted with bis(4-bromophenyl)iodonium triflate ***1e*** (0.4 mmol, 235 mg) followed by column chromatography (gradient elution: hexane → hexane:EtOAc – 10:1) to give 4-bromo-*N*-cyclohexylbenzamide ***2he*** as an off-white solid, 27 mg (48 %). mp = 200 –

201 °C (lit. 180 – 181 °C).[22] The analytical data is in accordance with previously published.[22]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 5.96 (d, *J* = 4.4 Hz, 1H), 4.00 – 3.90 (m, 1H), 2.02 (d, *J* = 12.0 Hz, 2H), 1.78 – 1.73 (m, 2H), 1.66 (s, 1H), 1.42 (q, *J* = 12.4 Hz, 2H), 1.27 – 1.18 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 134.0, 131.8, 128.6, 126.0, 49.0, 33.3, 25.7, 25.0.

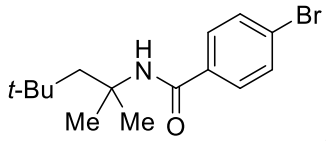


2ie: according to ***GP4*** 2-isocyano-2-methylpropane (0.2 mmol, 17 mg) reacted with bis(4-bromophenyl)iodonium triflate ***1e*** (0.2 mmol, 118 mg) followed by column chromatography (hexane:EtOAc – 15:1) to give 4-bromo-*N*-(*tert*-butyl)benzamide ***2ie*** as a white solid, 13 mg (25 %). mp = 135 – 136 °C (lit. 132 – 133 °C).[23] The analytical data is in accordance with previously published.[23]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 5.88 (br s, 1H), 1.46 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 134.9, 131.8, 128.5, 125.8, 52.0, 29.0.

HRMS (positive mode, MeCN) calcd. for $C_{11}H_{15}BrNNaO^+$ ([M+H]$^+$) 278.0156 (found 278.0151).

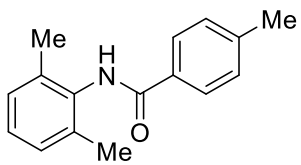


2je: according to ***GP4*** 2-isocyano-2,4,4-trimethylpentane (0.2 mmol, 28 mg) reacted with bis(4-bromophenyl)iodonium triflate ***1e*** (0.2 mmol, 118 mg) followed by column chromatography (hexane:EtOAc – 15:1) to give 4-bromo-*N*-(2,4,4-trimethylpentan-2-yl)benzamide ***2je*** as a white solid, 6 mg (10 %). mp = 85 – 87 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 4H), 5.88 (s, 1H), 1.85 (s, 2H), 1.52 (s, 6H), 1.04 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 135.2, 131.9, 128.4, 125.8, 55.9, 51.8, 31.9, 31.7, 29.4.

HRMS (positive mode, MeCN) calcd. for $C_{15}H_{22}BrNNaO^+$ ([M+H]$^+$) 334.0774 (found 334.0782).

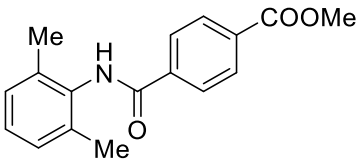


4d: according to ***GP4*** 1-isocyano-4-methylbenzene (0.2 mmol, 12 mg) reacted with 4-methylphenyl(2,4,6-trimethoxyphenyl)iodonium triflate ***3d***

(0.2 mmol, 106.8 mg) followed by column chromatography (gradient elution: hexane → hexane:EtOAc – 10:1 → 7/1) to give *N*-(2,6-dimethylphenyl)-4-methylbenzamide ***4d*** as an off-white solid, 13 mg (26 %). mp = 158 – 159 °C (lit. 162 – 164 °C).[17]The analytical data is in accordance with previously published.[24]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.35 (br s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.10 (m, 3H), 2.44 (s, 3H), 2.28 (s, 6H).

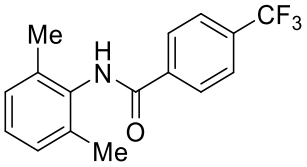
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 142.5, 135.7, 134.1, 131.8, 129.6, 128.4, 127.5, 127.4, 21.7, 18.7.



4e: according to ***GP4*** 1-isocyano-4-methylbenzene (0.2 mmol, 12 mg) reacted with (4-(methoxycarbonyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium triflate ***3e*** (0.2 mmol, 115.6 mg) followed by column chromatography (gradient elution: hexane → hexane:EtOAc – 10:1 → 7/1) to give methyl 4-((2,6-dimethylphenyl)carbamoyl)benzoate ***4e*** as an off-white solid, 24 mg (42 %). mp = 198 – 199 °C (lit. 192 – 194 °C).[25] The analytical data is in accordance with previously published.[25]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.54 (br s, 1H), 7.18 – 7.12 (m, 3H), 3.96 (s, 3H), 2.27 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 165.2, 138.5, 135.6, 133.6, 133.1, 130.1, 128.5, 127.8, 127.4, 52.6, 18.6.



4f: according to ***GP4*** 1-isocyano-4-methylbenzene (0.2 mmol, 12 mg) reacted with (4-methoxyphenyl)(4-(trifluoromethyl)phenyl)iodonium triflate ***3f*** (0.2 mmol, 106.8 mg) followed by column chromatography (hexane → hexane:EtOAc – 10:1) to give *N*-(2,6-dimethylphenyl)-4-(trifluoromethyl)benzamide ***4f*** as a white solid, 19 mg (32 %). mp = 206 – 207 °C (lit. 205 – 207 °C).[17] The analytical data is in accordance with previously published.[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.71 – 7.68 (m, 3H), 7.20 – 7.14 (m, 1H), 7.11 (d, *J* = 7.2 Hz, 2H), 2.24 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 137.7, 135.6, 133.6 (q, *J* = 32.6 Hz), 133.6, 128.5, 127.9, 127.8, 125.9 (q, *J* = 3.6 Hz), 123.8 (q, *J* = 271.0 Hz), 18.54.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9.

4. Control Experiments

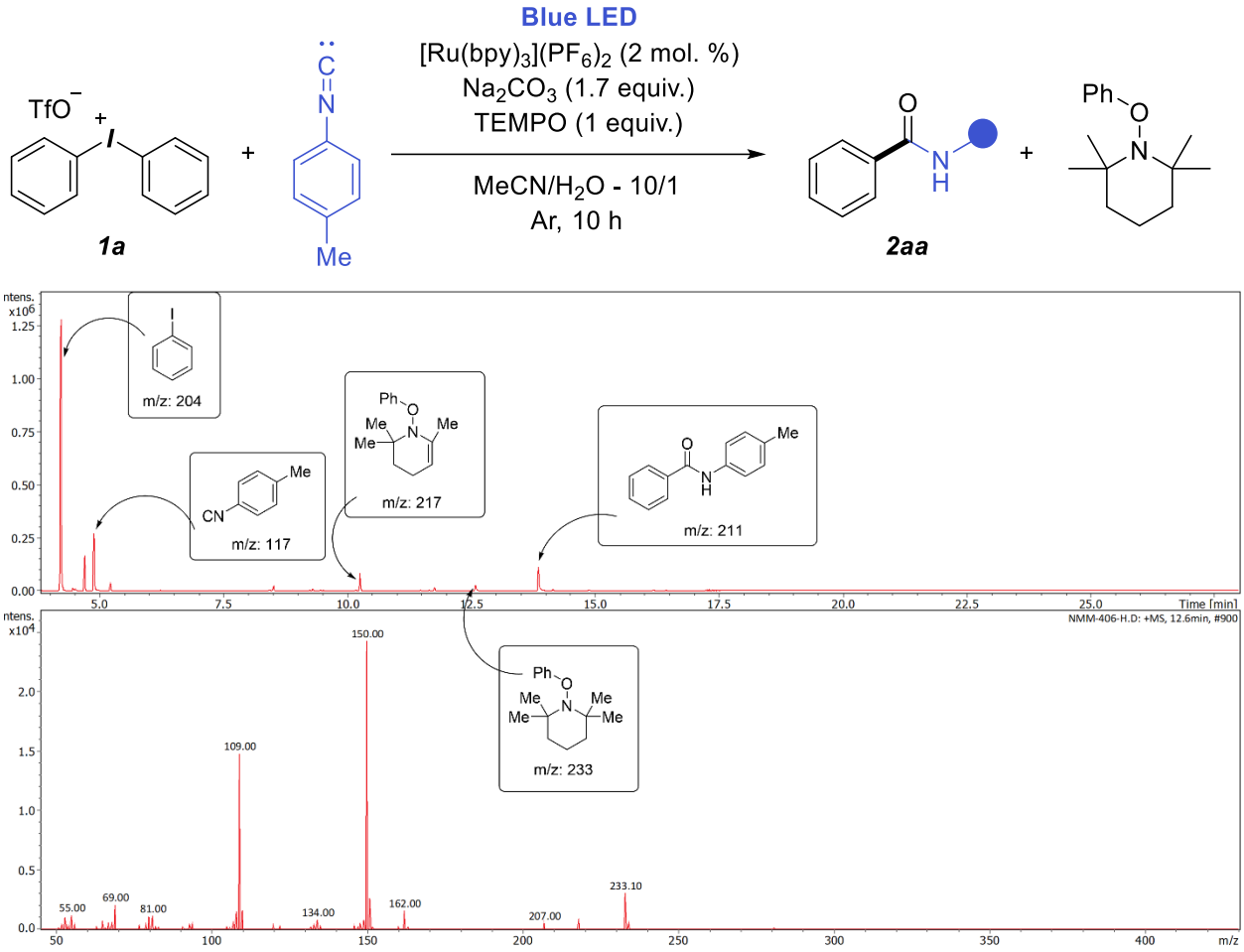


Figure S2. Radical trapping experiment.

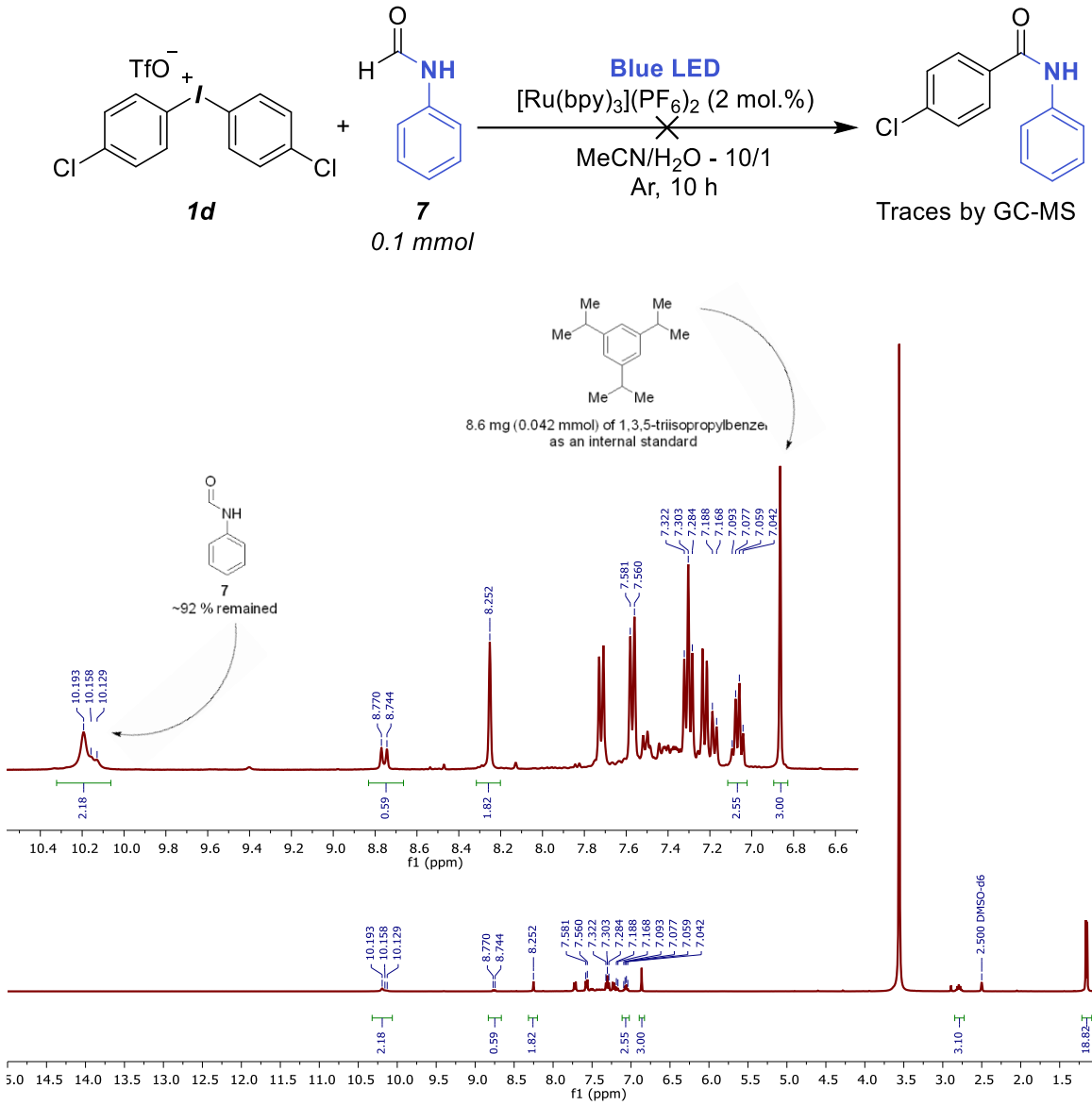


Figure S3. Experiment with formamide ***7*** as a substrate.

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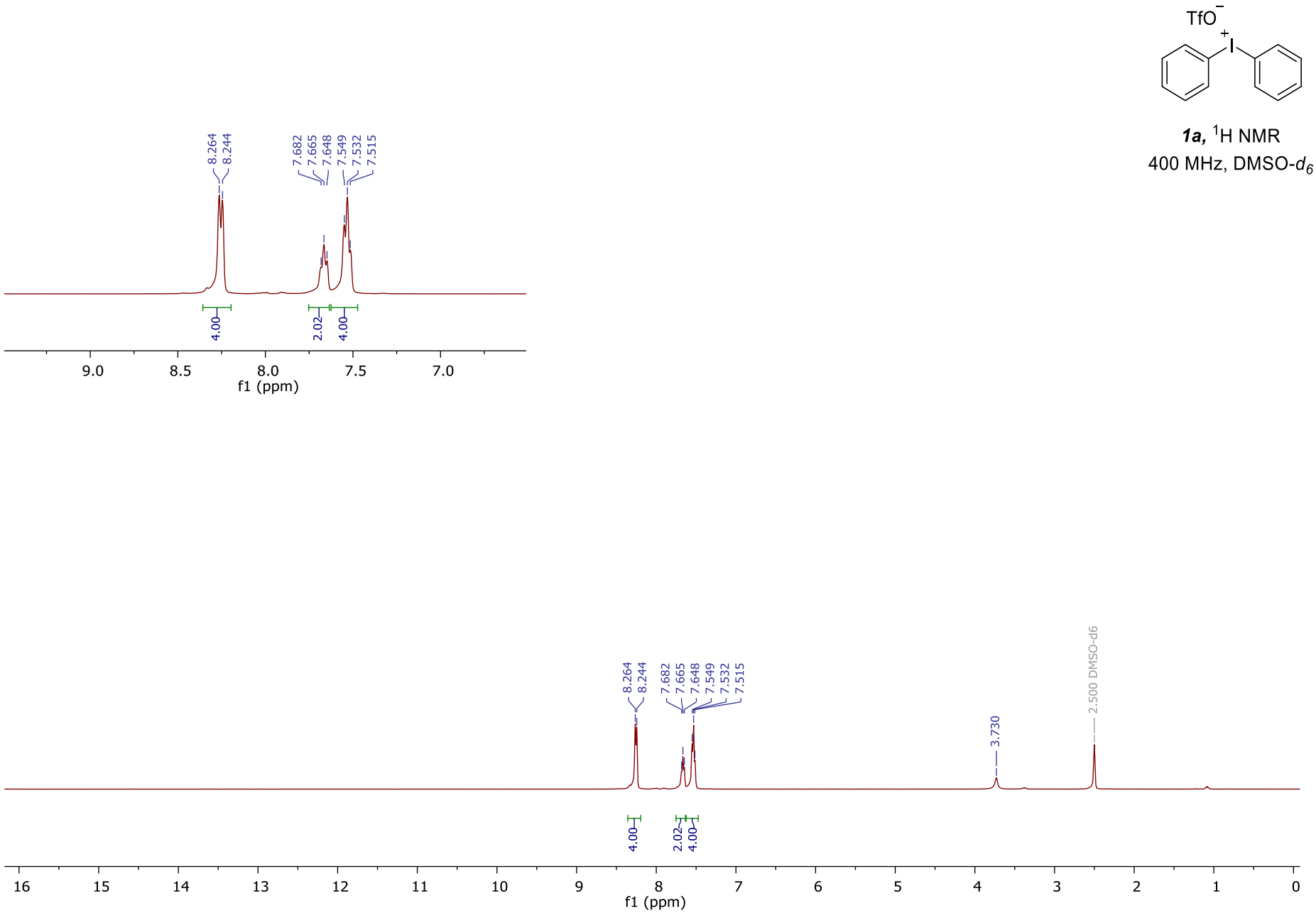
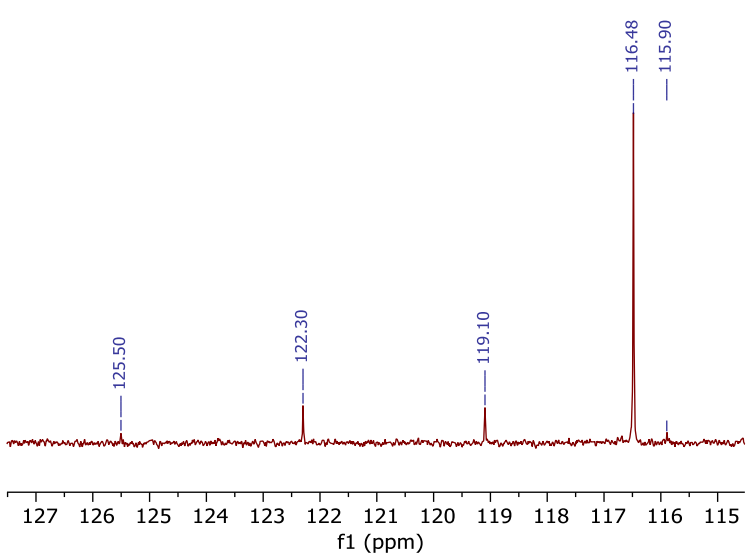
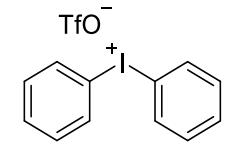
Spectral data

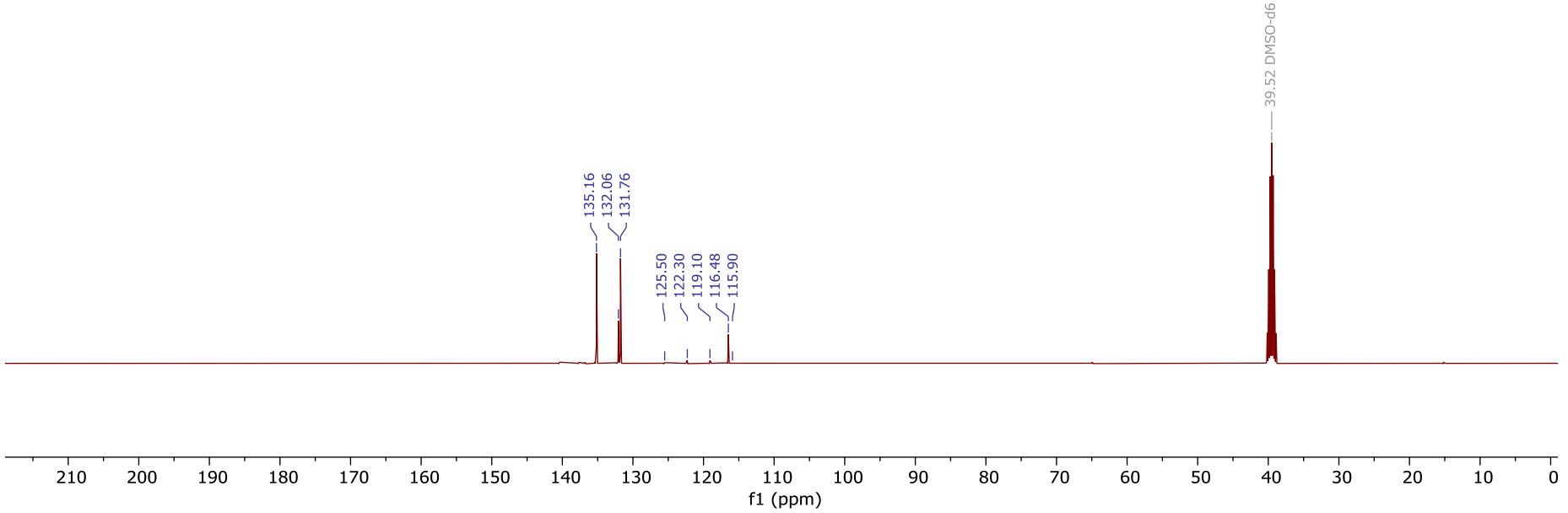


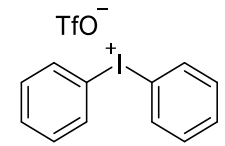
1a, ^{1}H NMR
400 MHz, DMSO-d_6



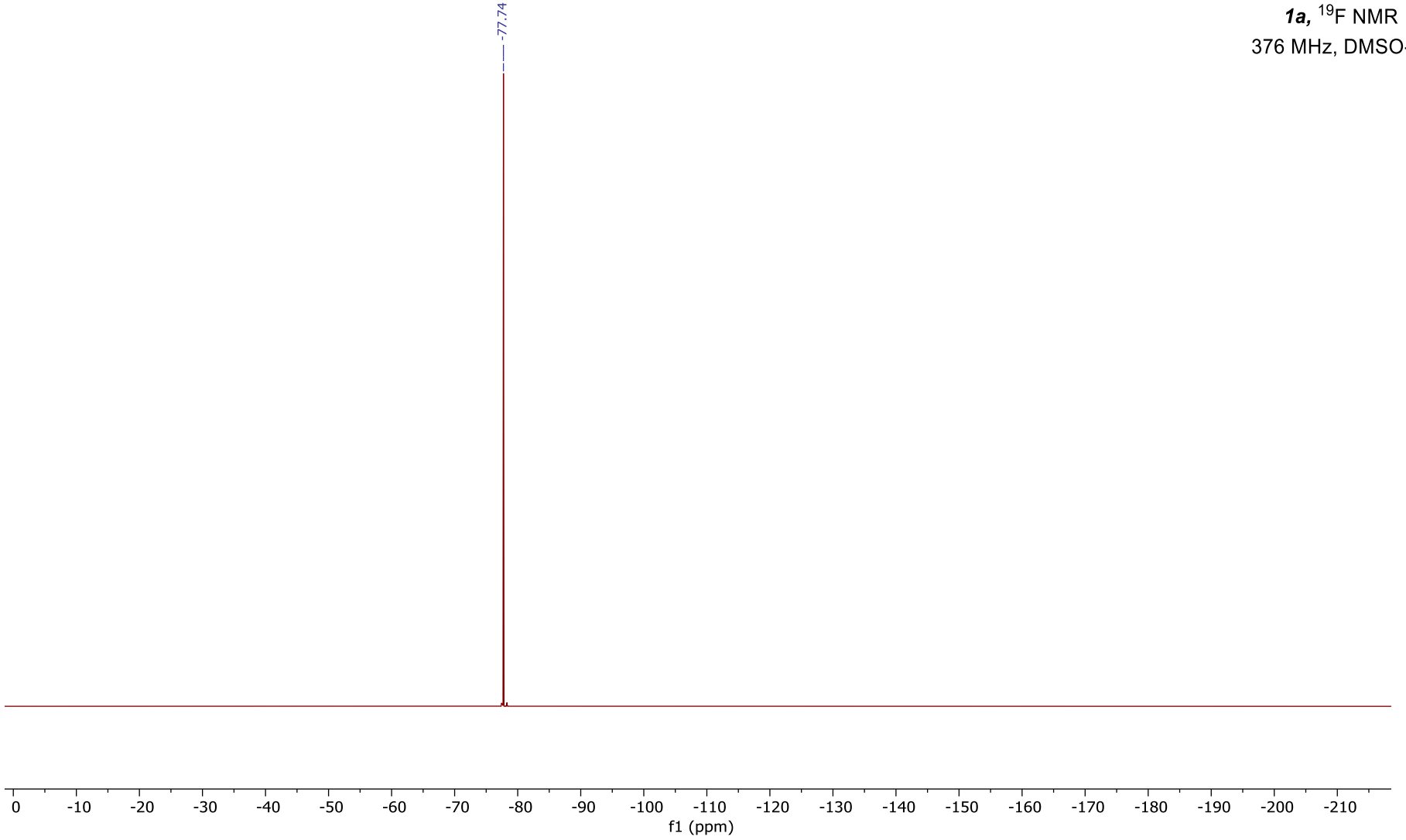


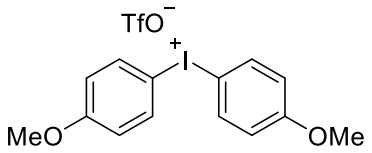
1a, ^{13}C NMR
100 MHz, DMSO-d_6



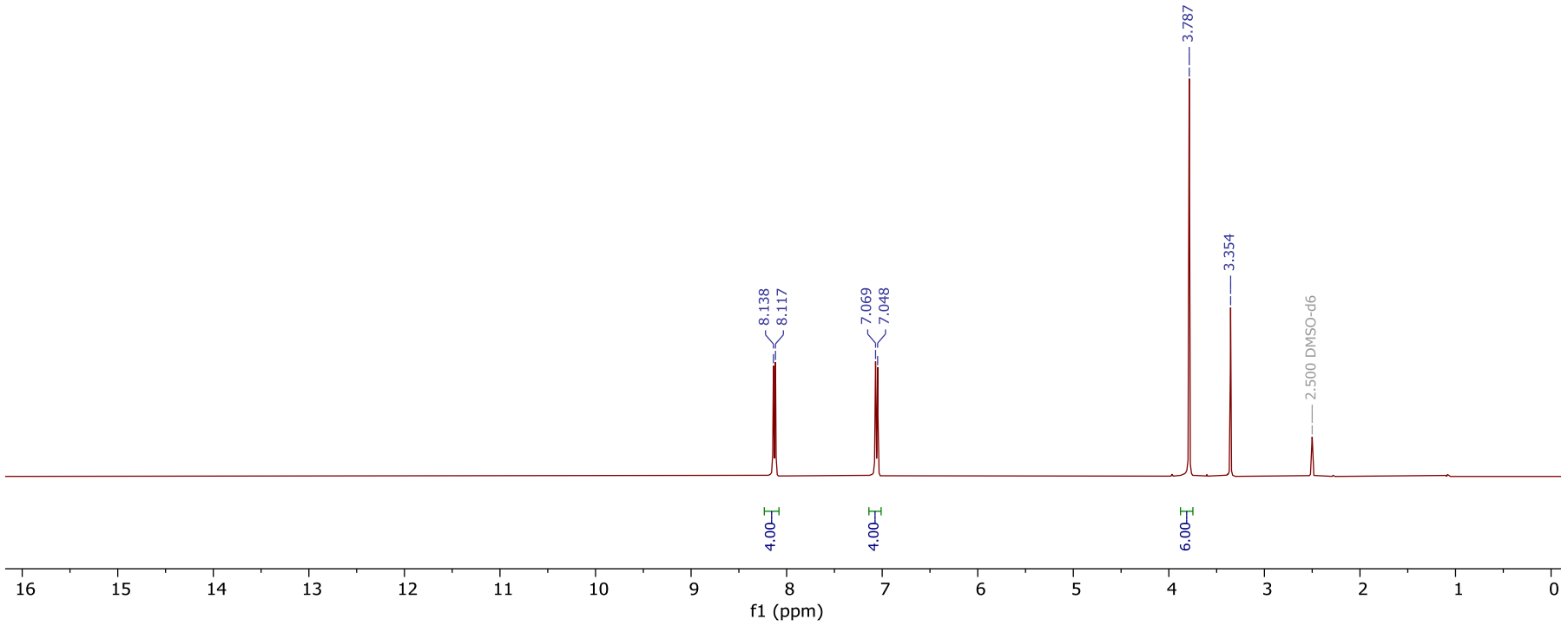


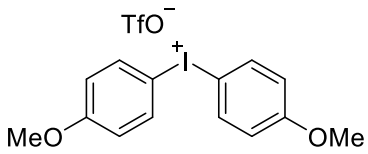
1a, ^{19}F NMR
376 MHz, DMSO-d_6



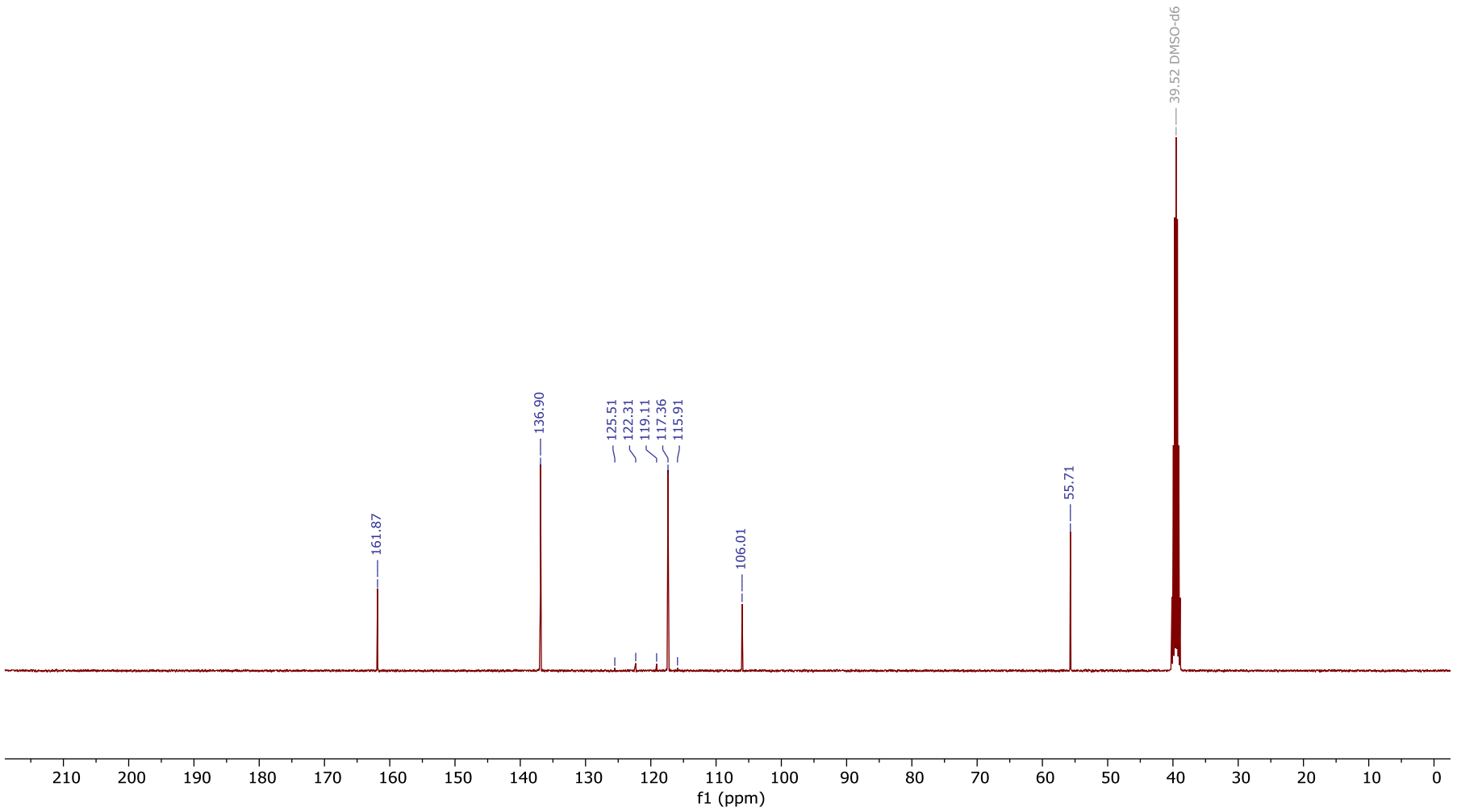


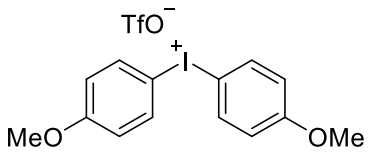
1b, ^{1}H NMR
400 MHz, DMSO-d_6



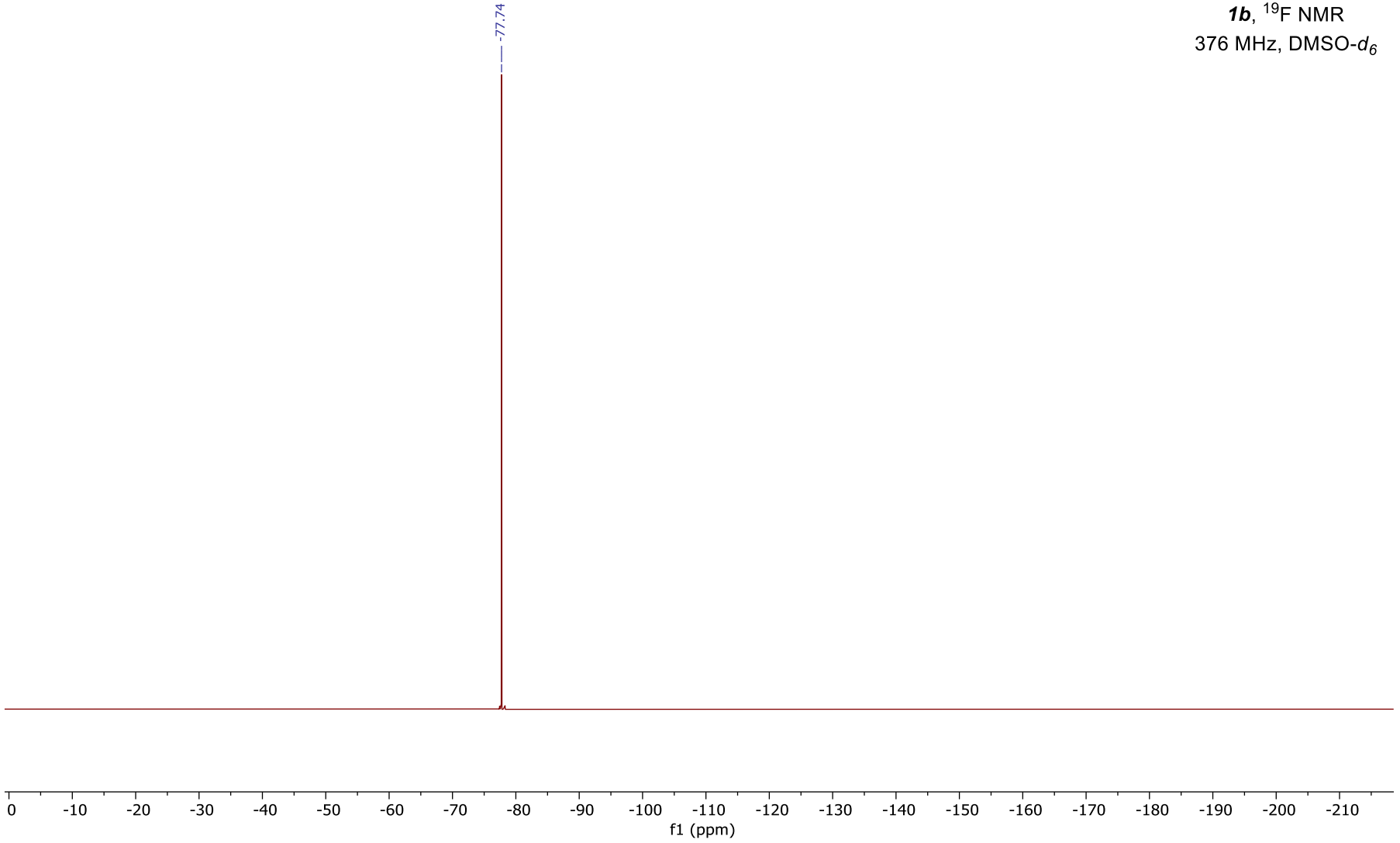


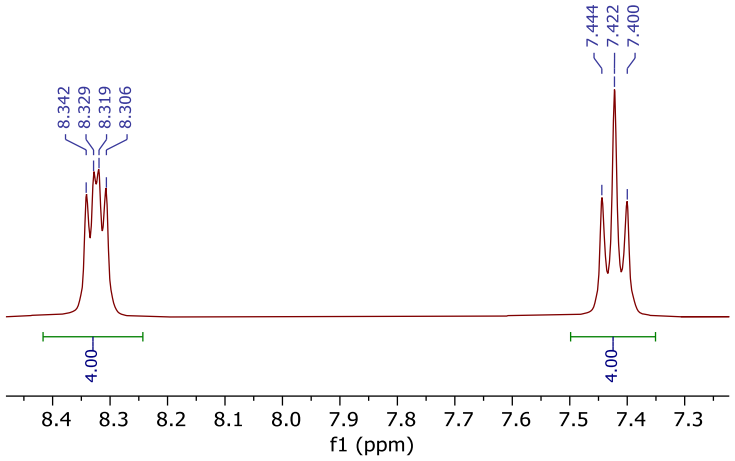
1b, ^{13}C NMR
100 MHz, DMSO-d_6

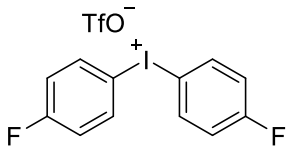




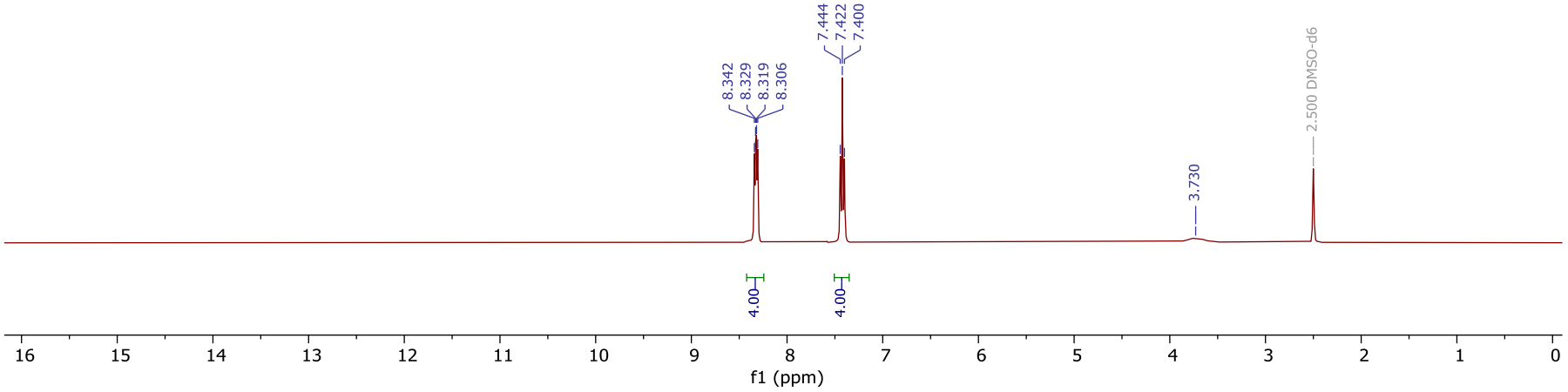
1b, ^{19}F NMR
376 MHz, DMSO-d_6

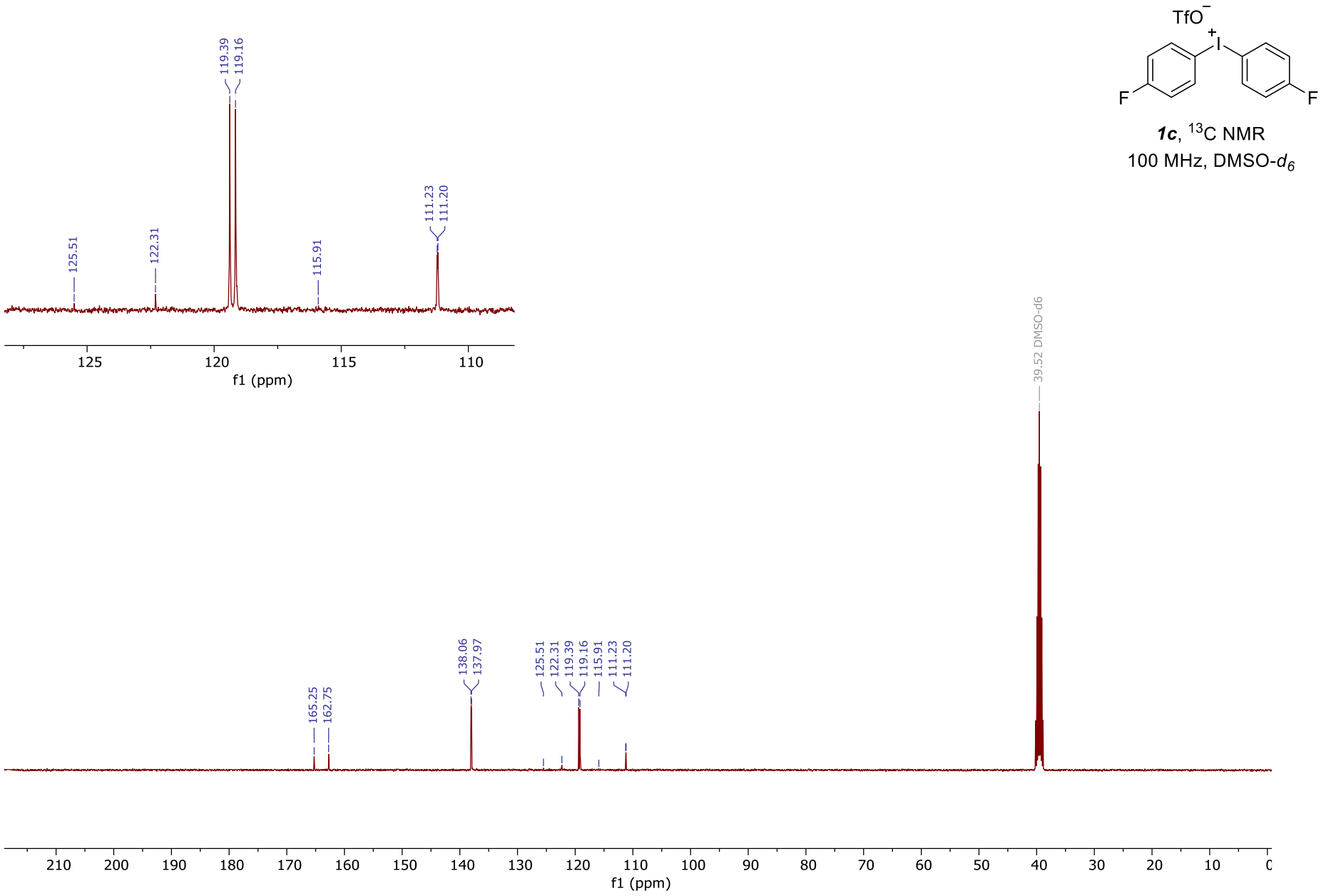


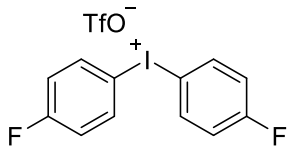




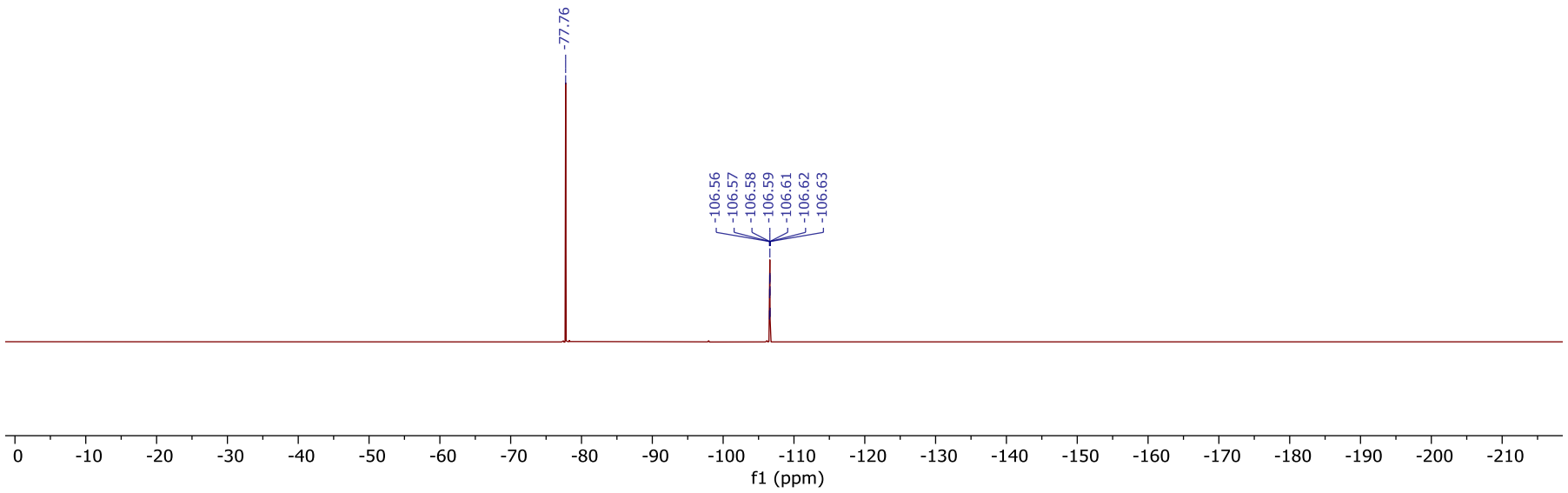
1c, ^{1}H NMR
400 MHz, DMSO-d_6

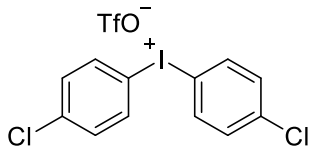



TfO
F
F
1c, 13C NMR
100 MHz, DMSO-d6
125.51
122.31
119.39
119.16
115.91
111.23
111.20
125
120
115
110
f1 (ppm)
39.52 DMSO-d6
165.25
162.75
138.06
137.97
125.51
122.31
119.39
119.16
115.91
111.23
111.20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

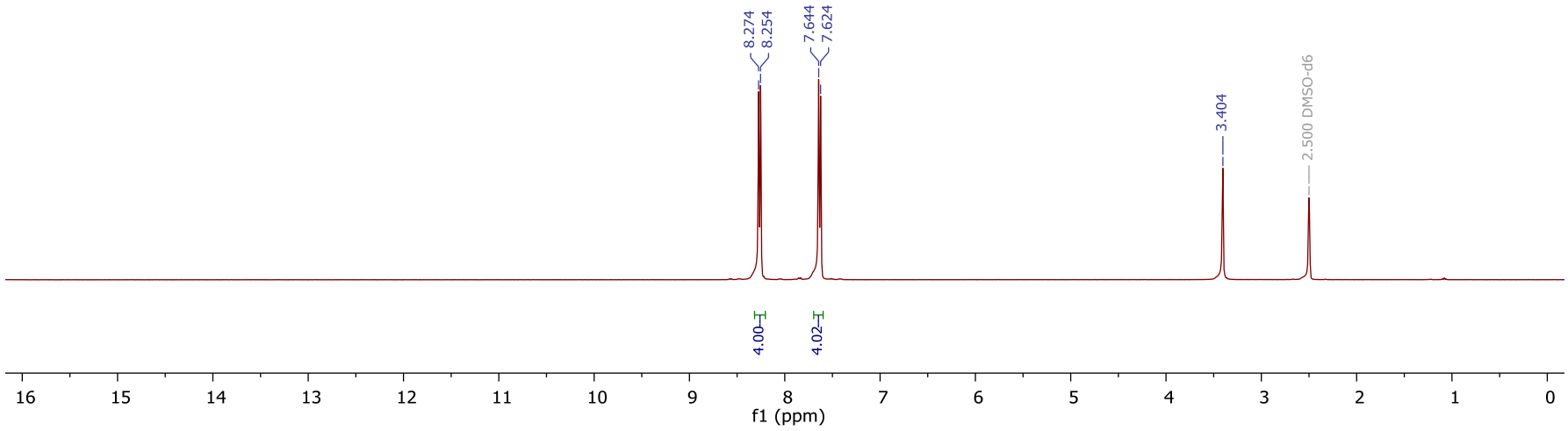


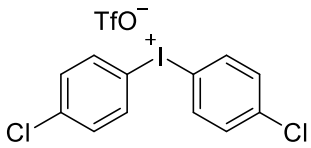
1c, ^{19}F NMR
376 MHz, DMSO-d_6



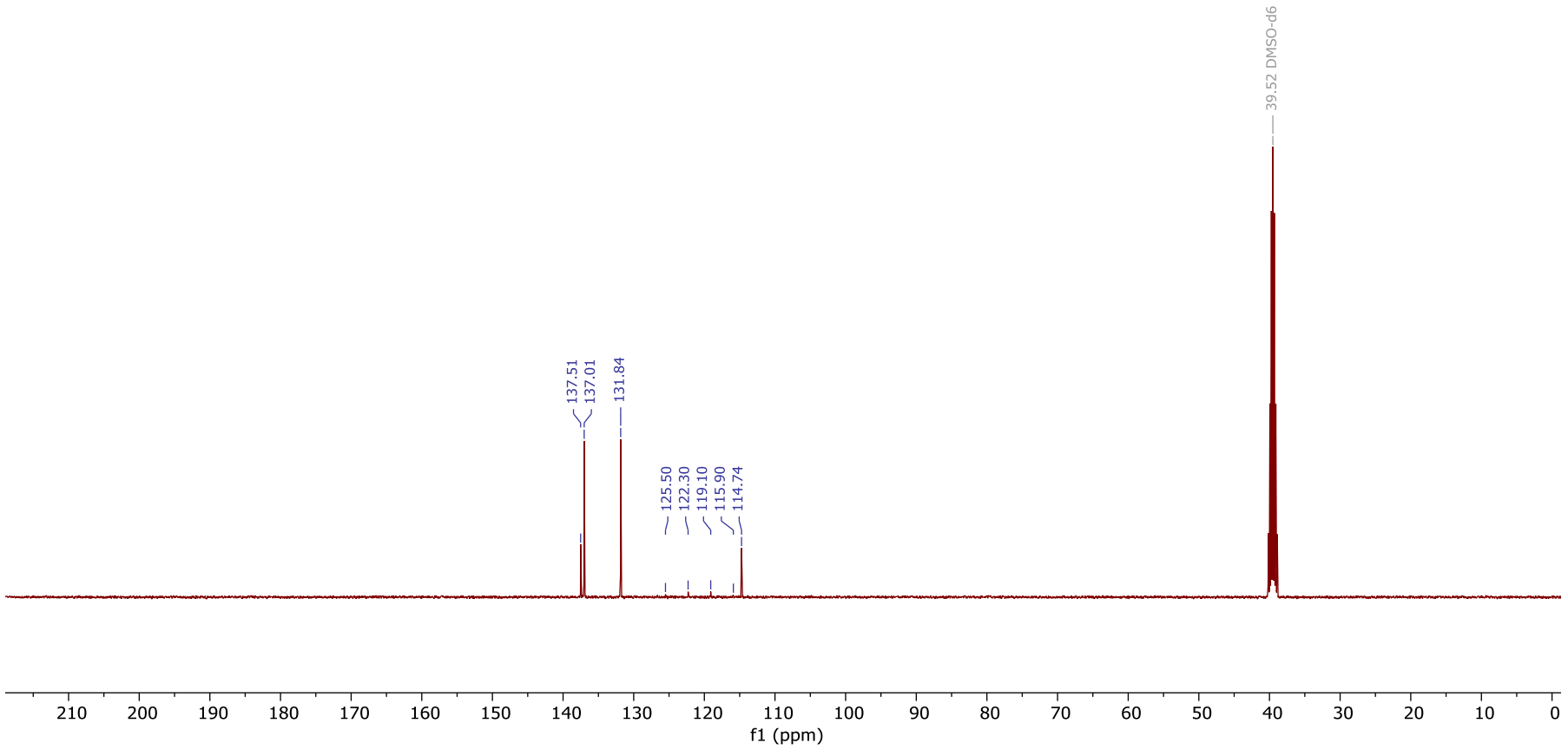


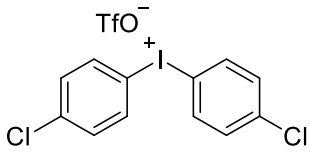
1d, ^{1}H NMR
400 MHz, DMSO-d_6



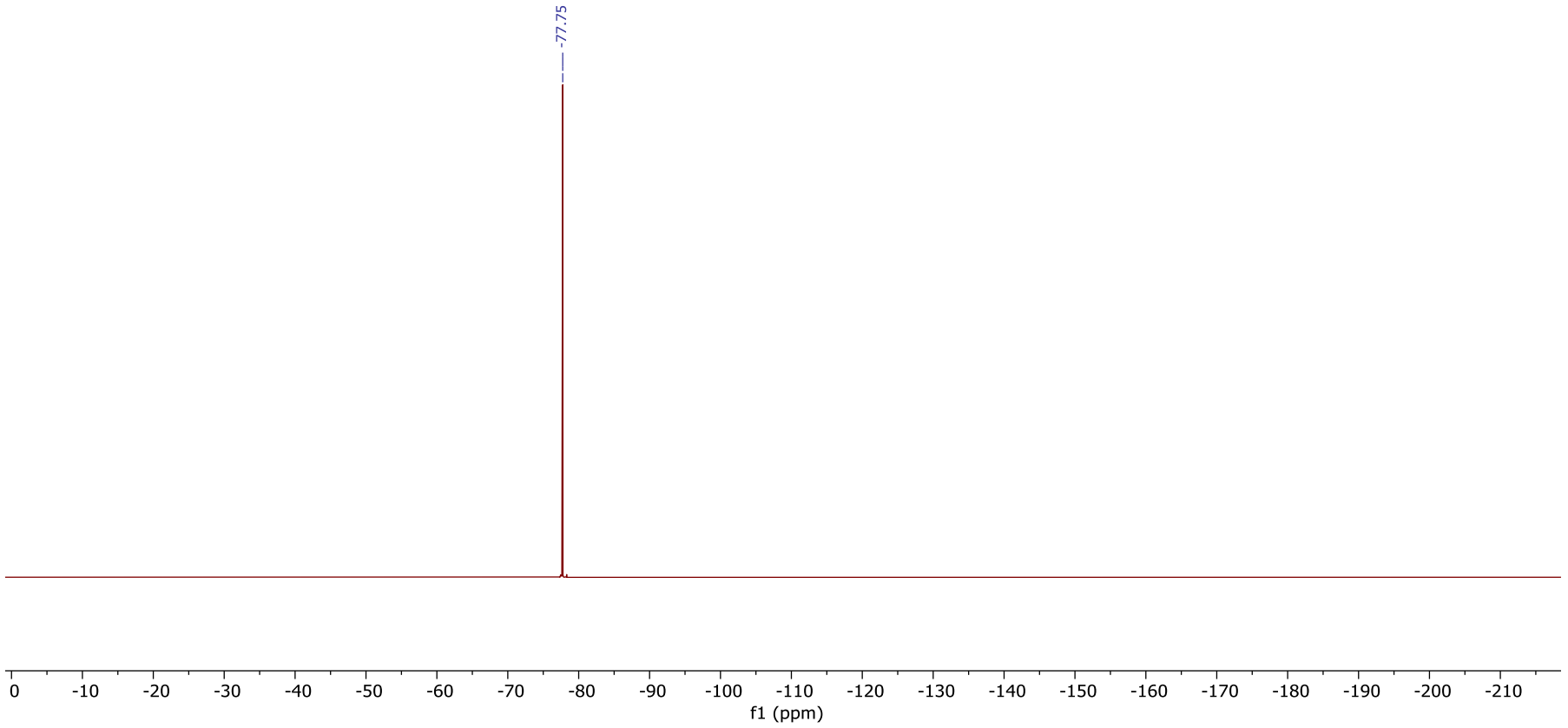


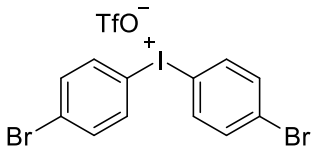
1d, ^{13}C NMR
100 MHz, DMSO-d_6



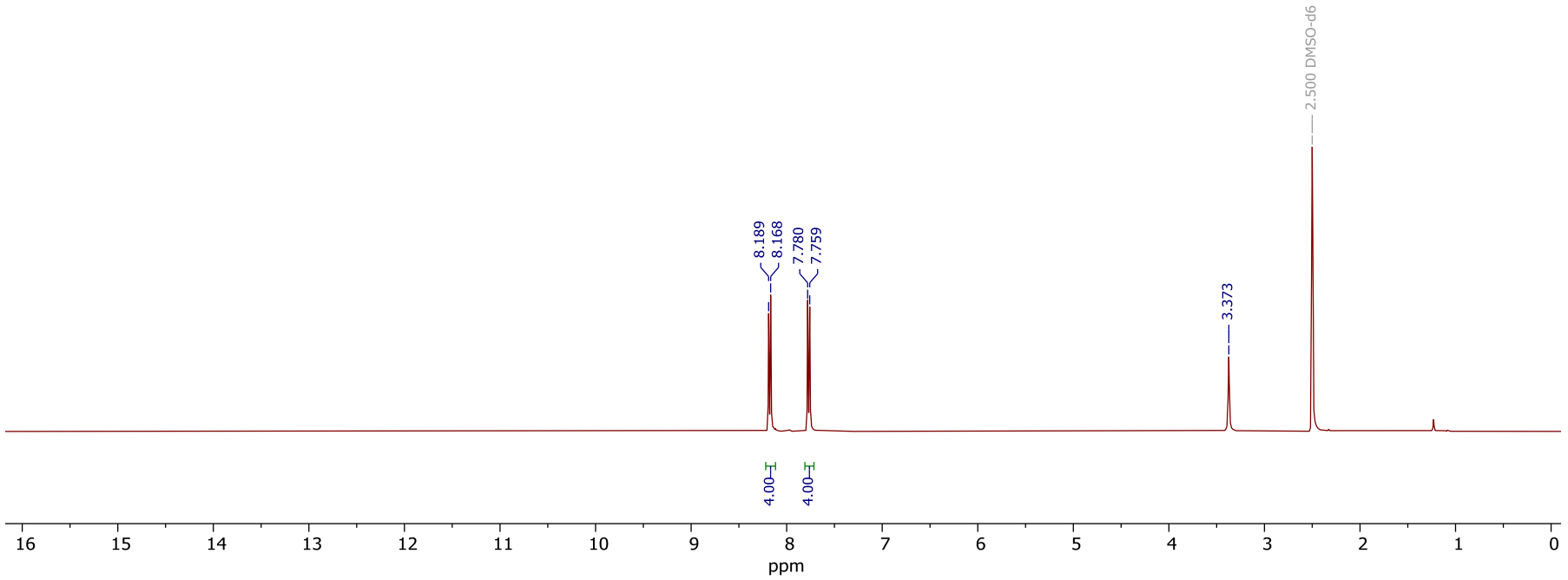


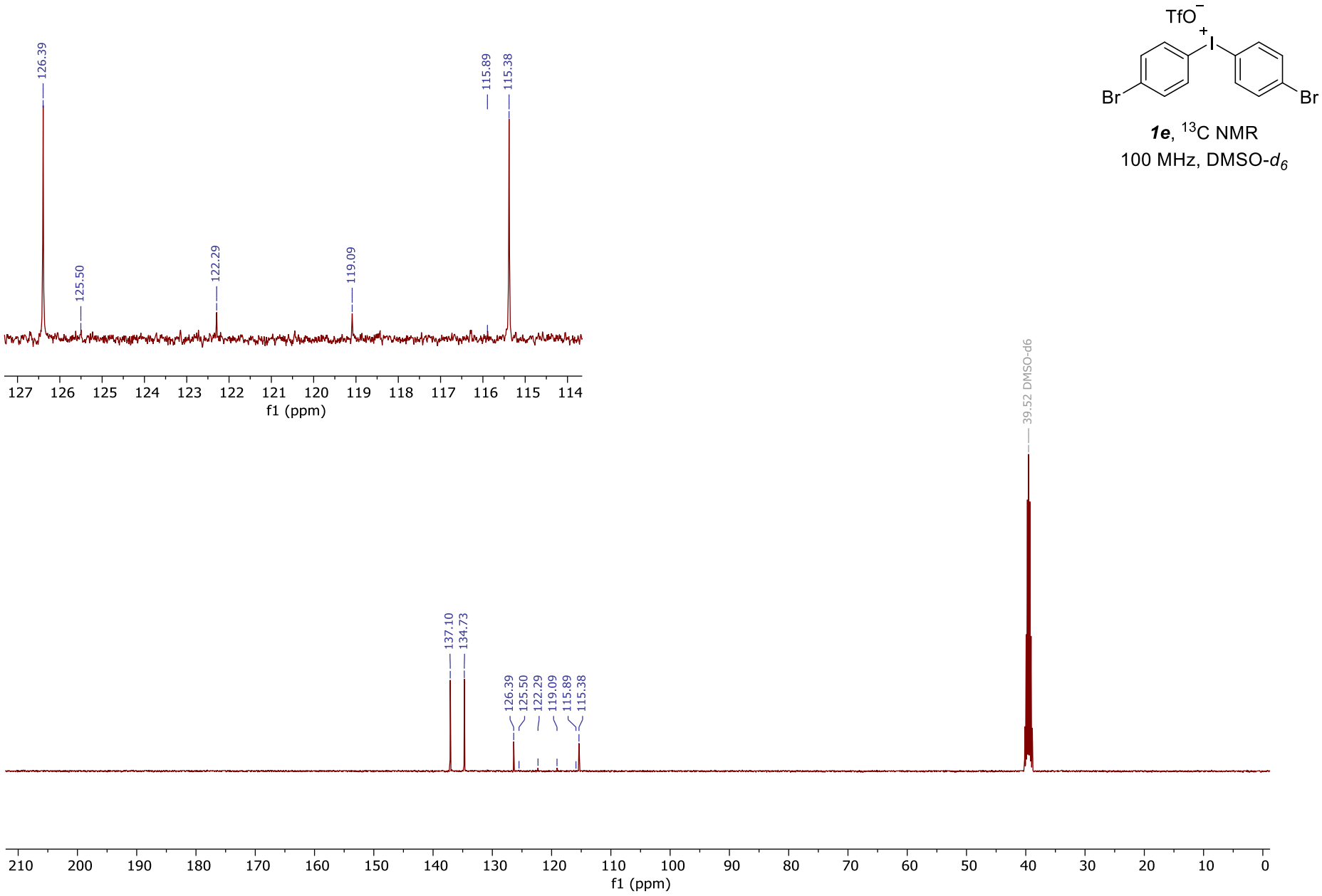
1d, ^{19}F NMR
376 MHz, DMSO-d_6

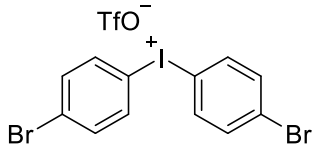




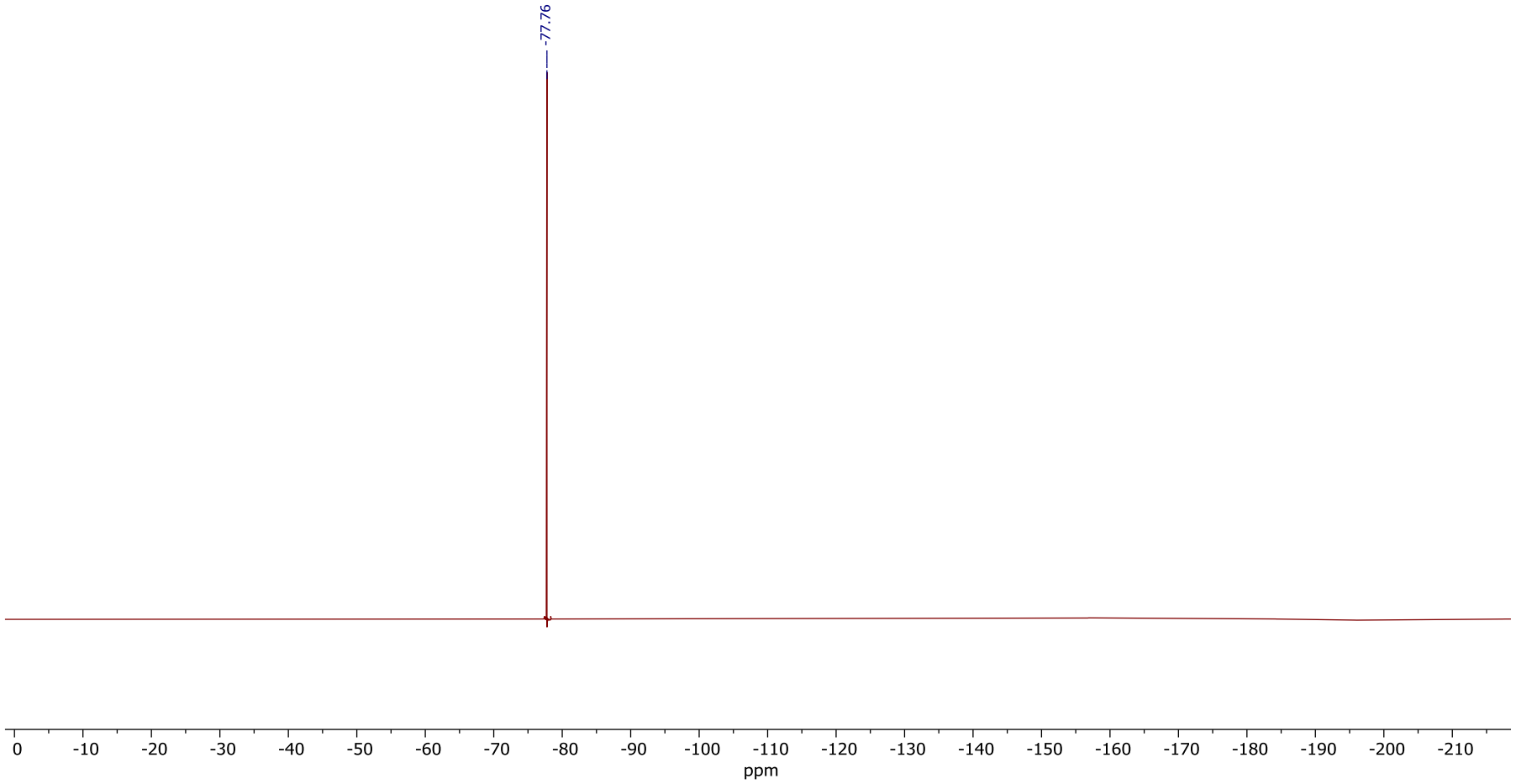
1e, ^{1}H NMR
400 MHz, DMSO-d_6

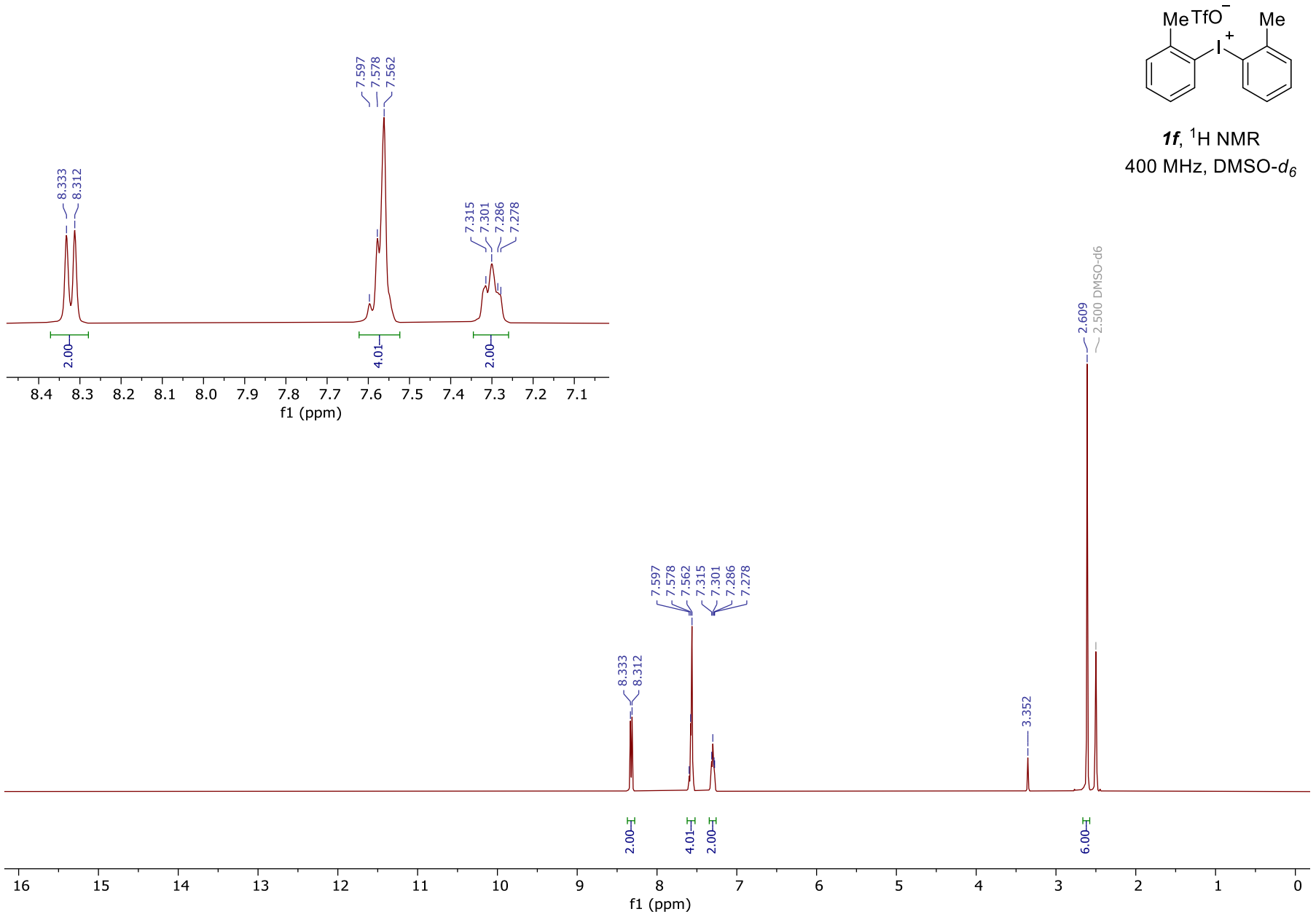


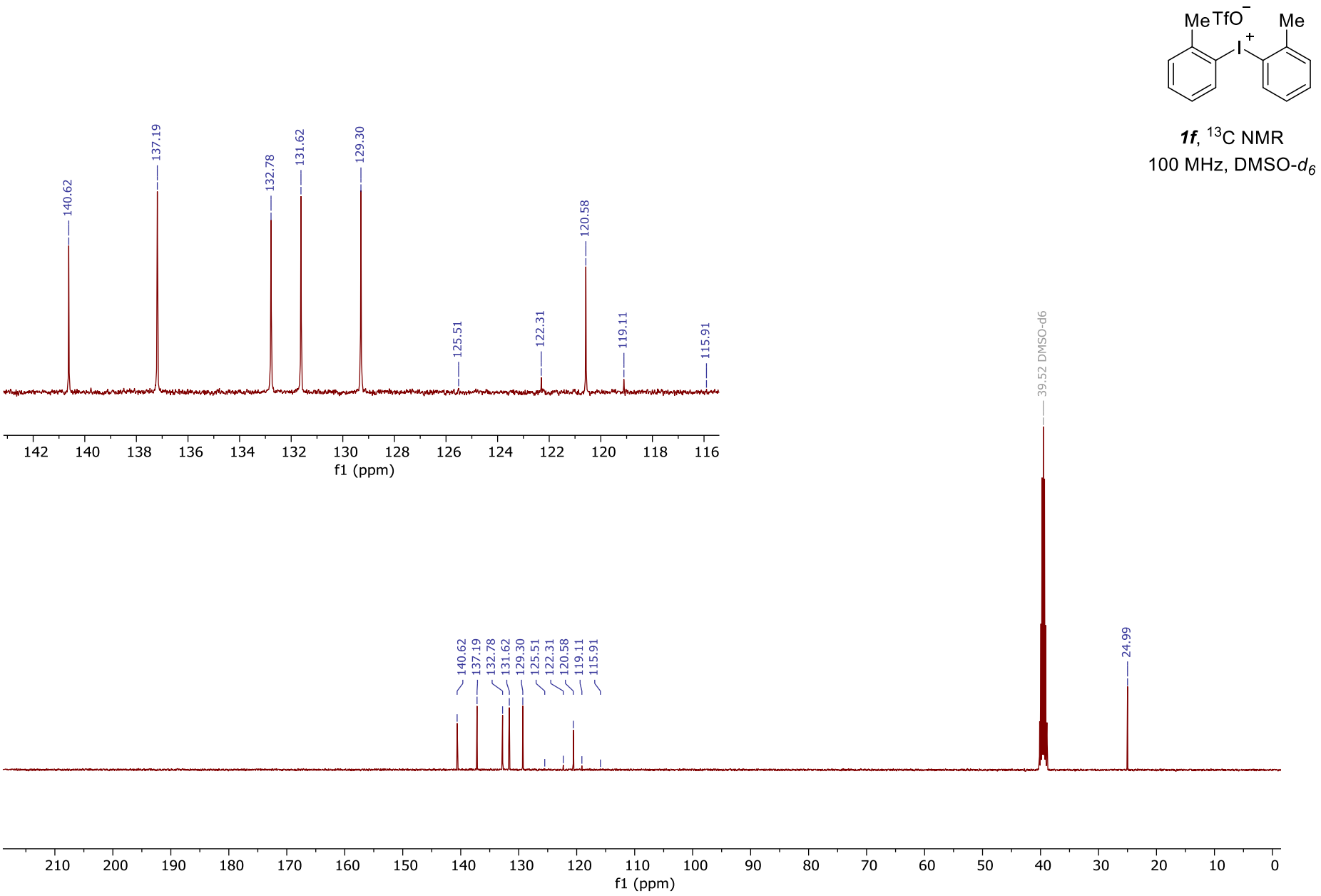

TfO
I
Br
Br
1e, 13C NMR
100 MHz, DMSO-d6
126.39
125.50
122.29
119.09
115.89
115.38
f1 (ppm)
39.52 DMSO-d6
137.10
134.73
126.39
125.50
122.29
119.09
115.89
115.38
f1 (ppm)

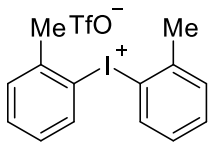


1e, ^{19}F NMR
376 MHz, DMSO-d_6

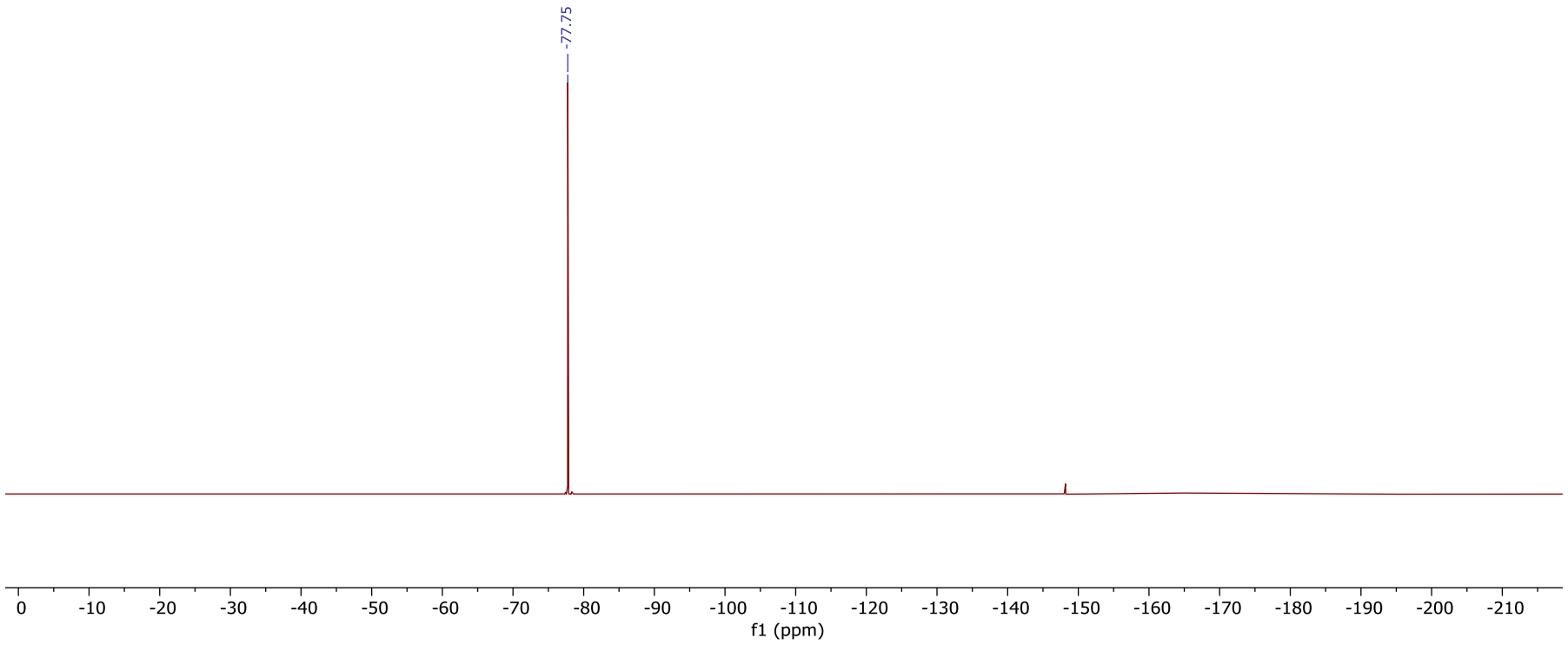


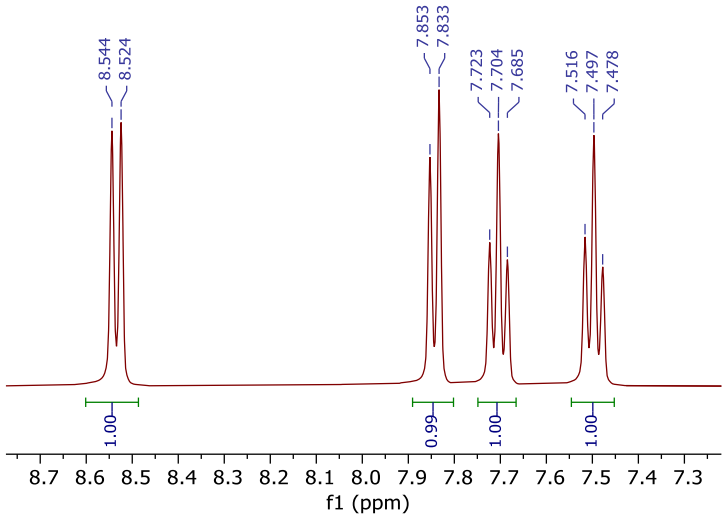

Me TfO⁻ Me
I+
1f, 1H NMR
400 MHz, DMSO-d6
8.333
8.312
7.597
7.578
7.562
7.315
7.301
7.286
7.278
2.00
4.01
2.00
8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
2.609
2.500 DMSO-d6
3.352
6.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

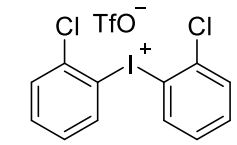

Me
TfO
Me
1f, 13C NMR
100 MHz, DMSO-d6
140.62
137.19
132.78
131.62
129.30
125.51
122.31
120.58
119.11
115.91
39.52 DMSO-d6
24.99
f1 (ppm)



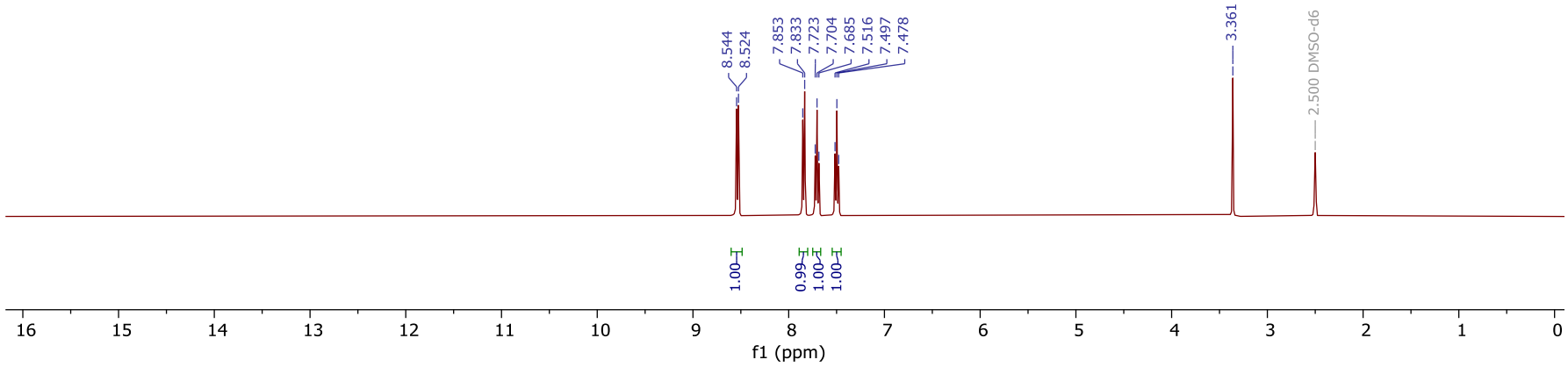
1f, ^{19}F NMR
376 MHz, DMSO-d_6

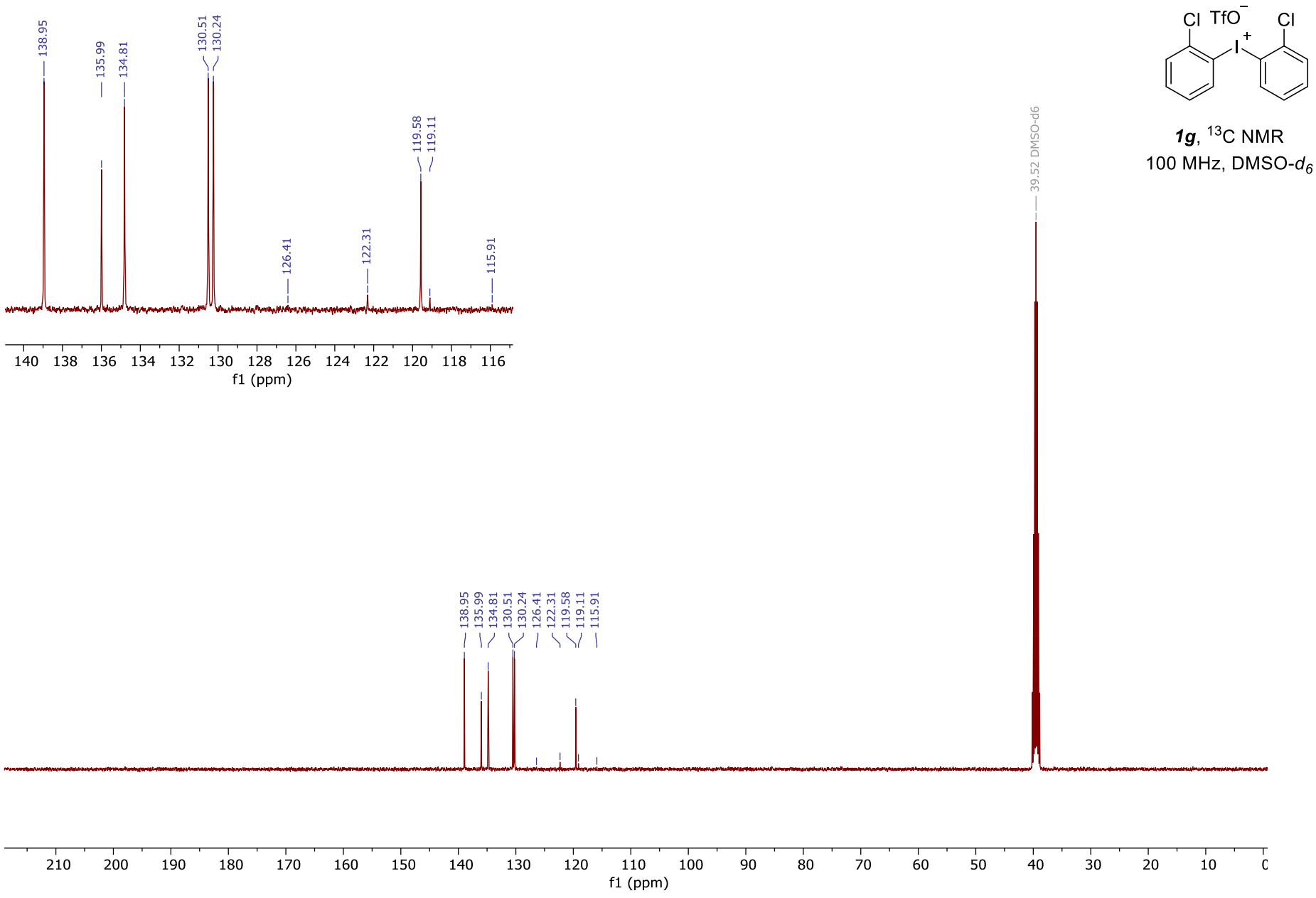


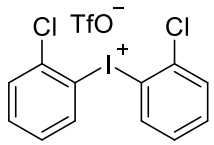




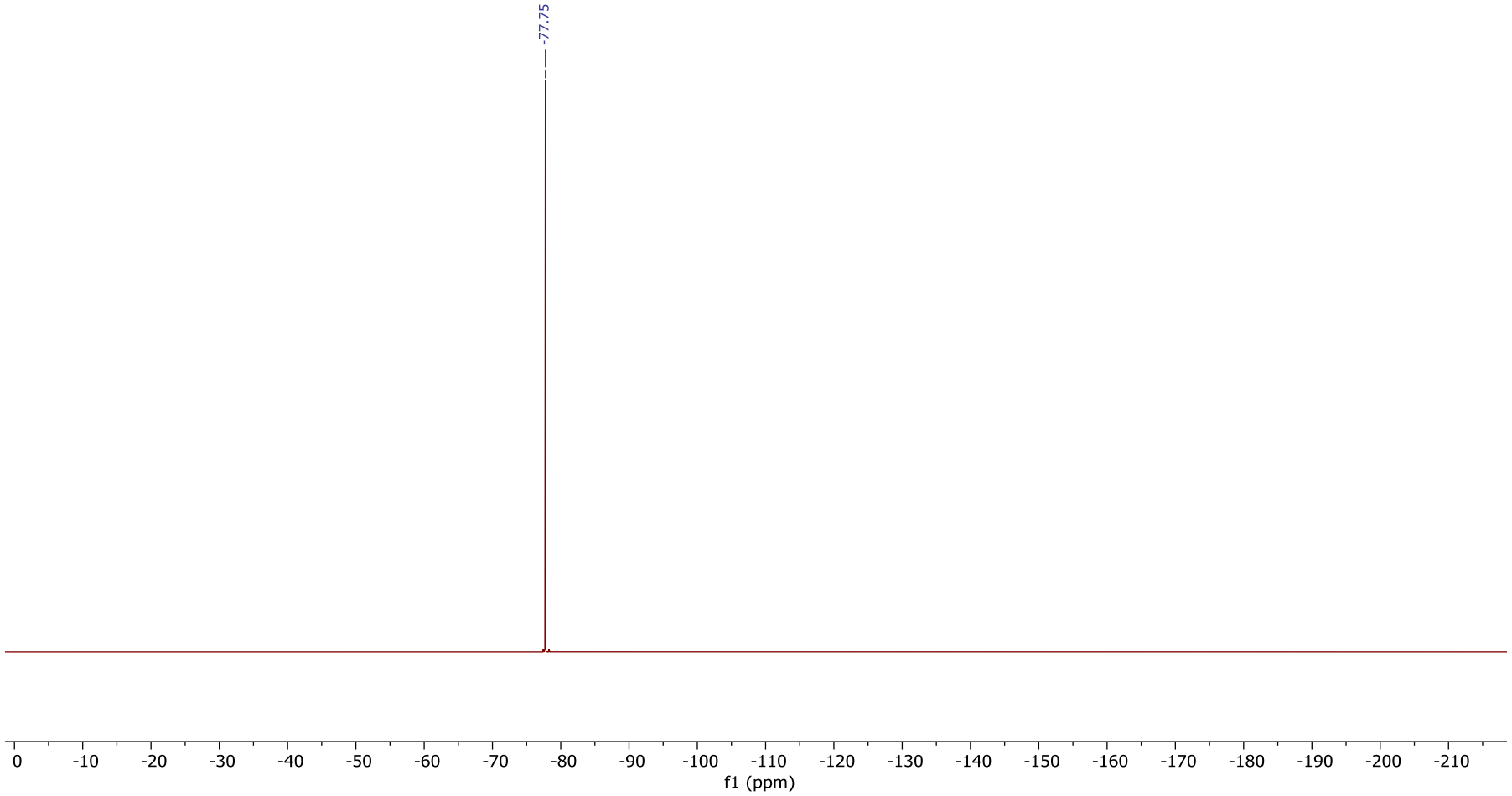
1g, ^{1}H NMR
400 MHz, DMSO-d_6

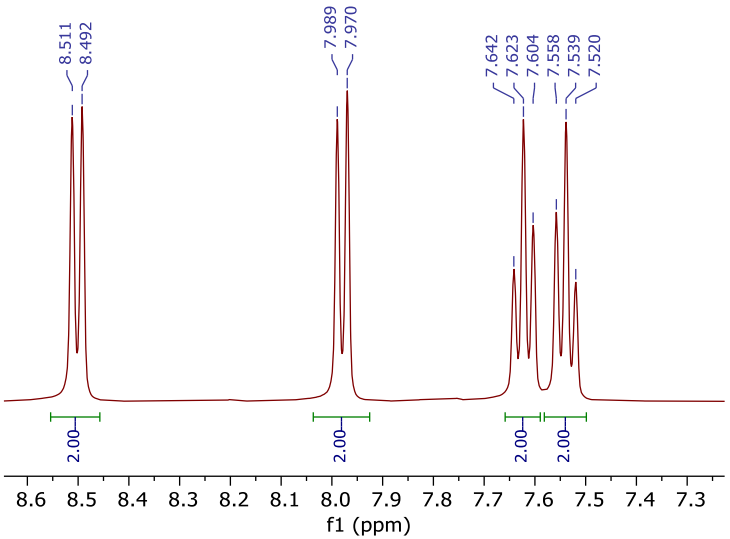


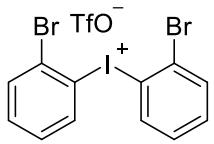

Cl
TfO
Cl
I
+
1g, 13C NMR
100 MHz, DMSO-d6
138.95
135.99
134.81
130.51
130.24
126.41
122.31
119.58
119.11
115.91
39.52 DMSO-d6
f1 (ppm)



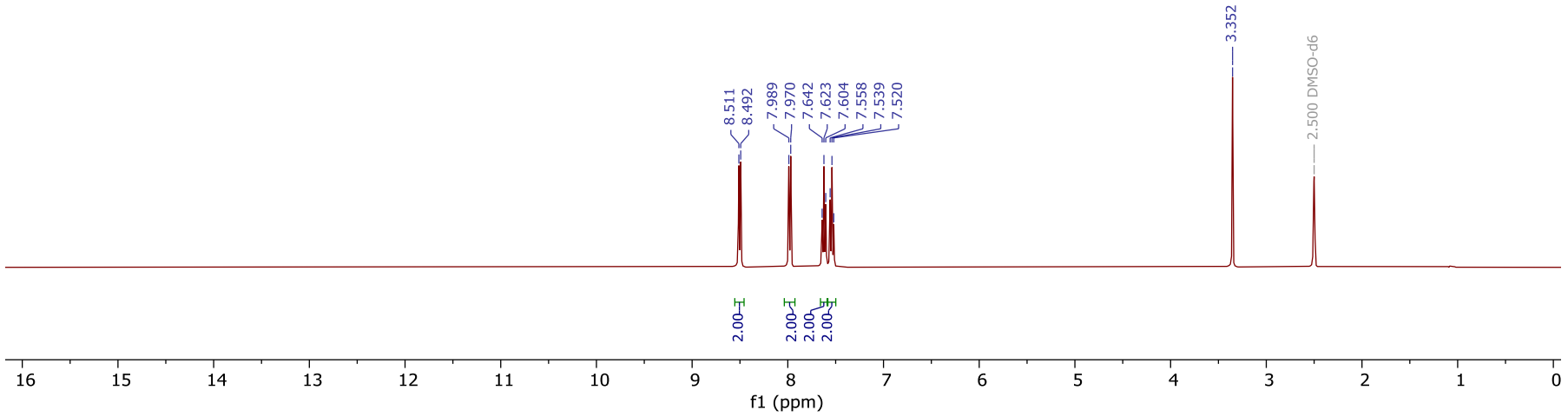
1g, ^{19}F NMR
376 MHz, DMSO-d_6

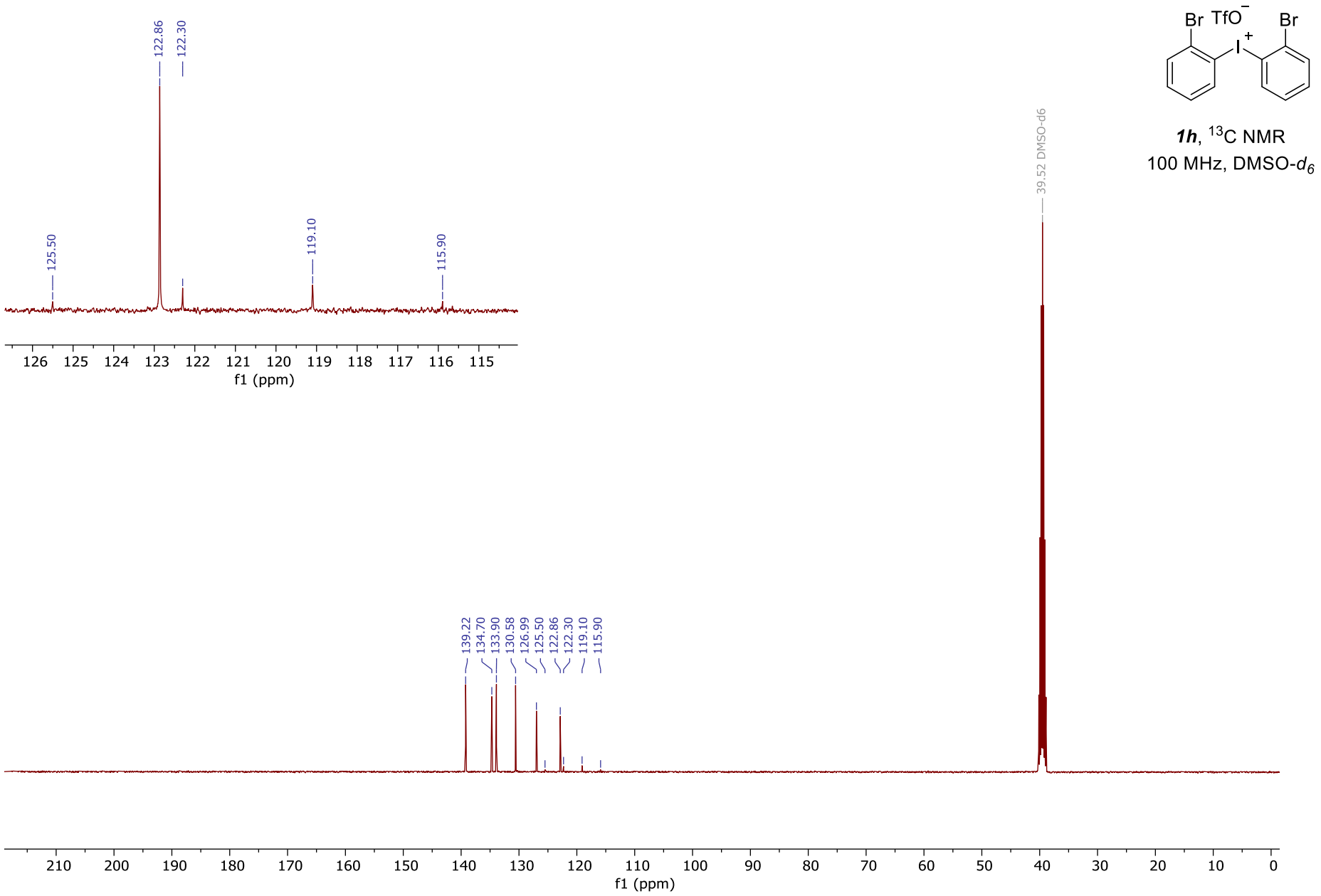


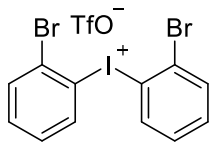




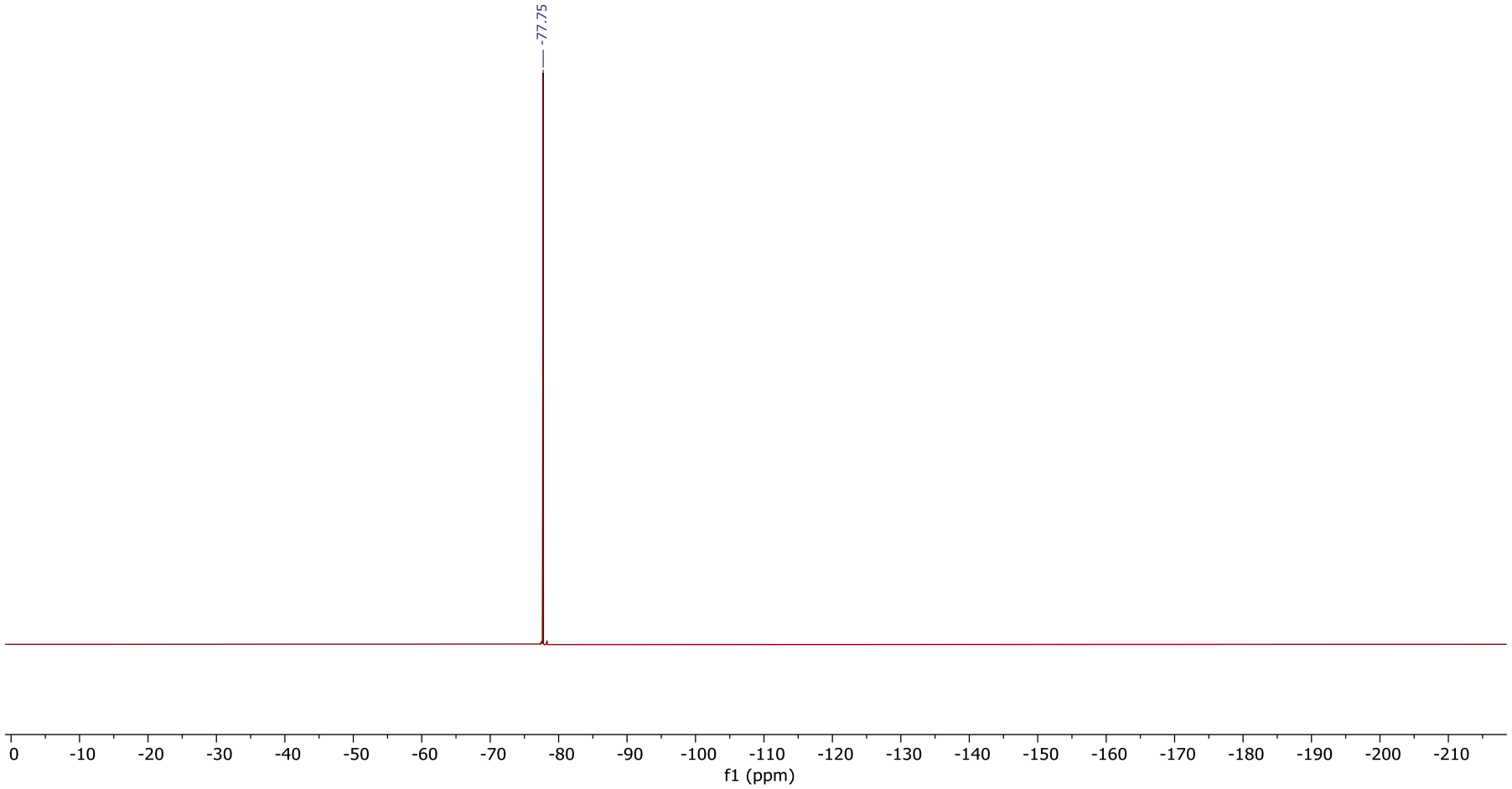
1h, ^{1}H NMR
400 MHz, DMSO-d_6

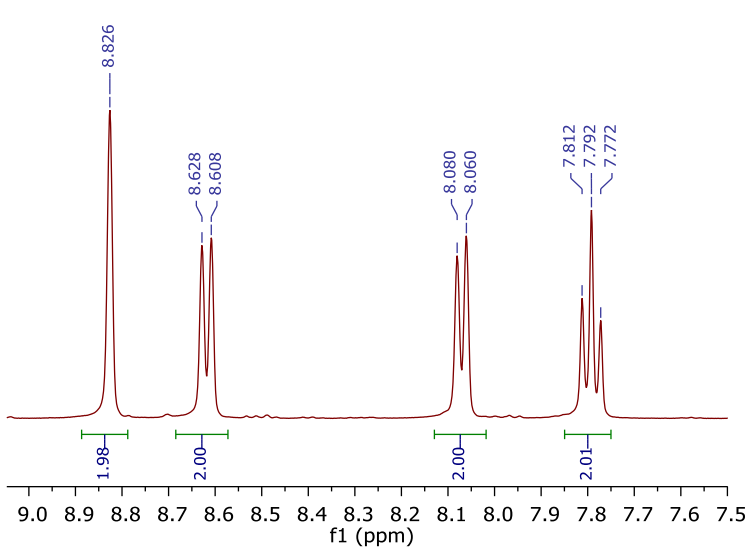


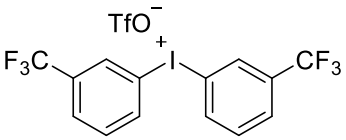

Br TfO⁻ Br
I+
1h, 13C NMR
100 MHz, DMSO-d6
39.52 DMSO-d6
139.22
134.70
133.90
130.58
126.99
125.50
122.86
122.30
119.10
115.90
f1 (ppm)



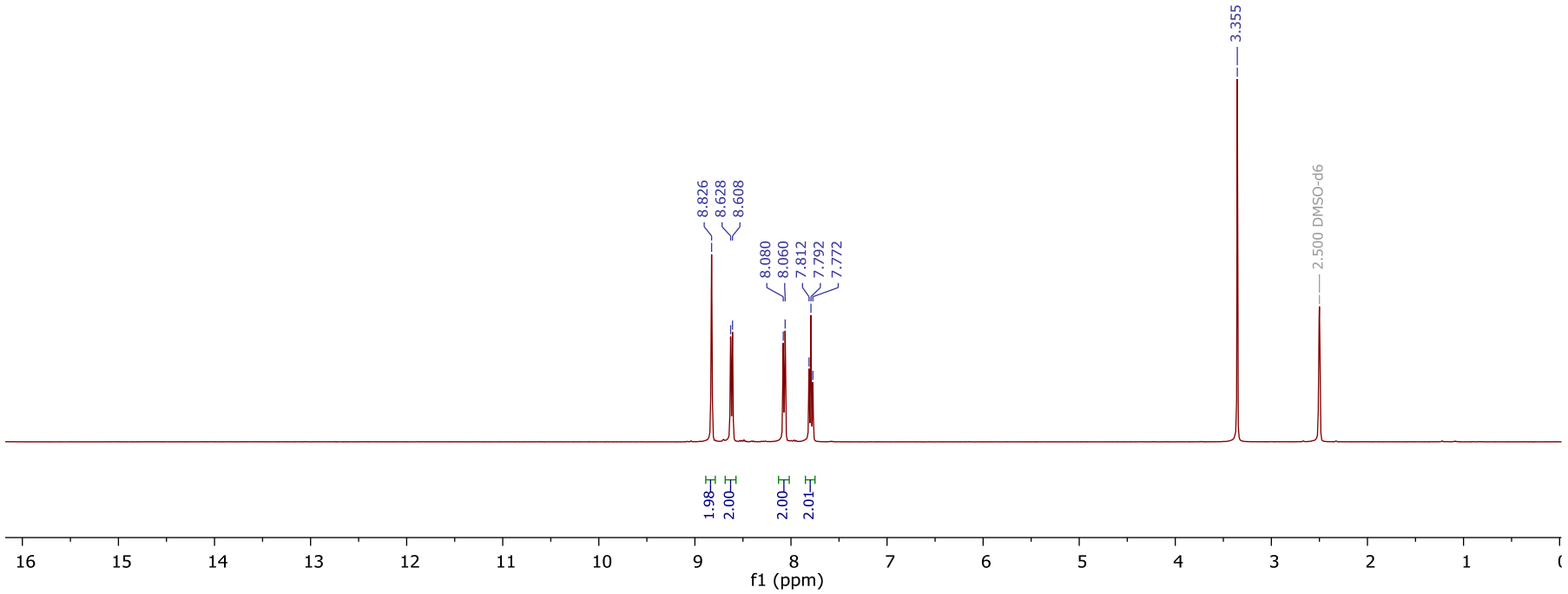
1h, ^{19}F NMR
376 MHz, DMSO-d_6

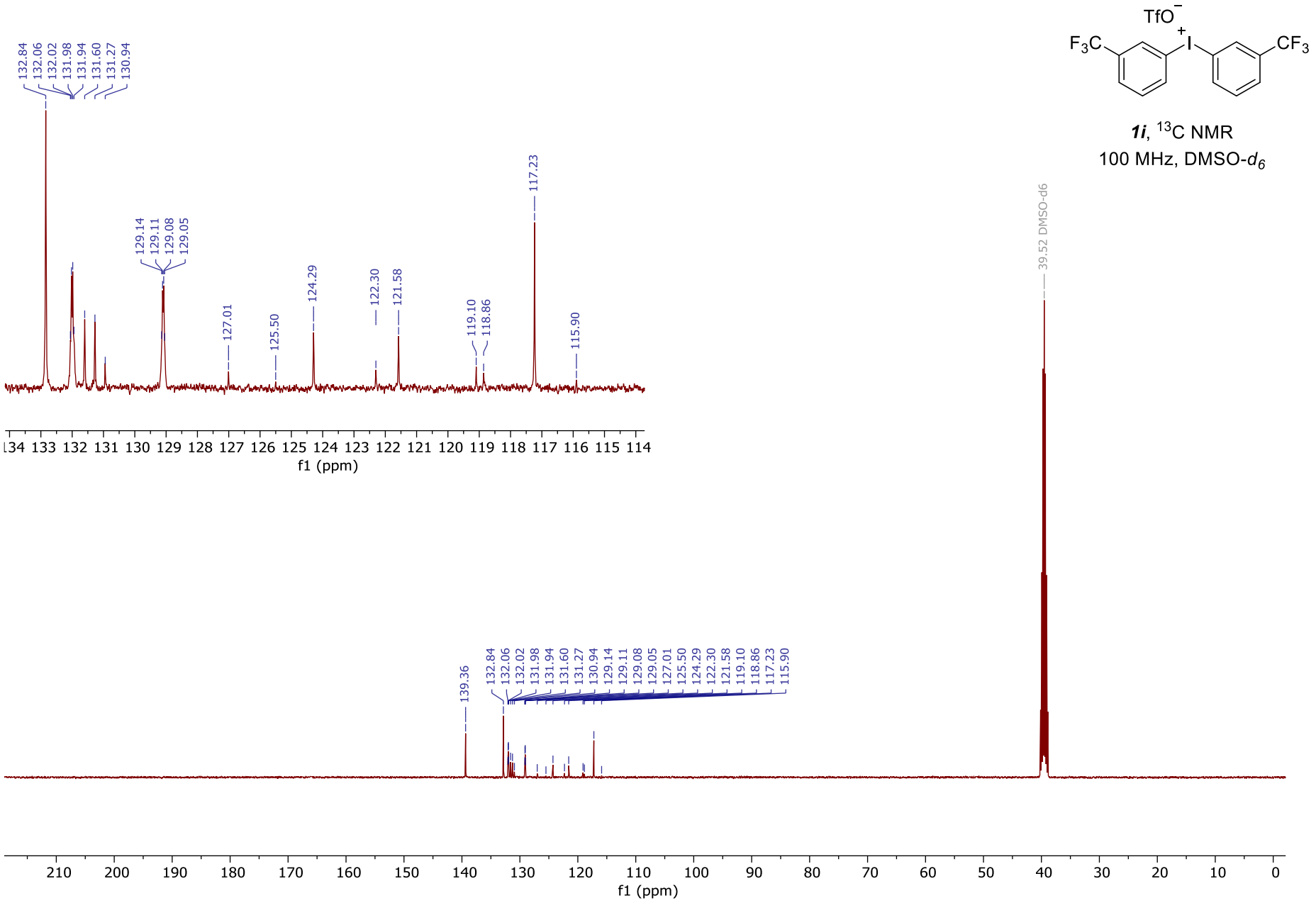


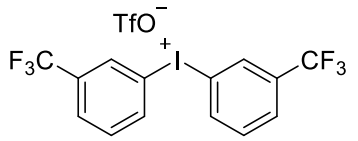




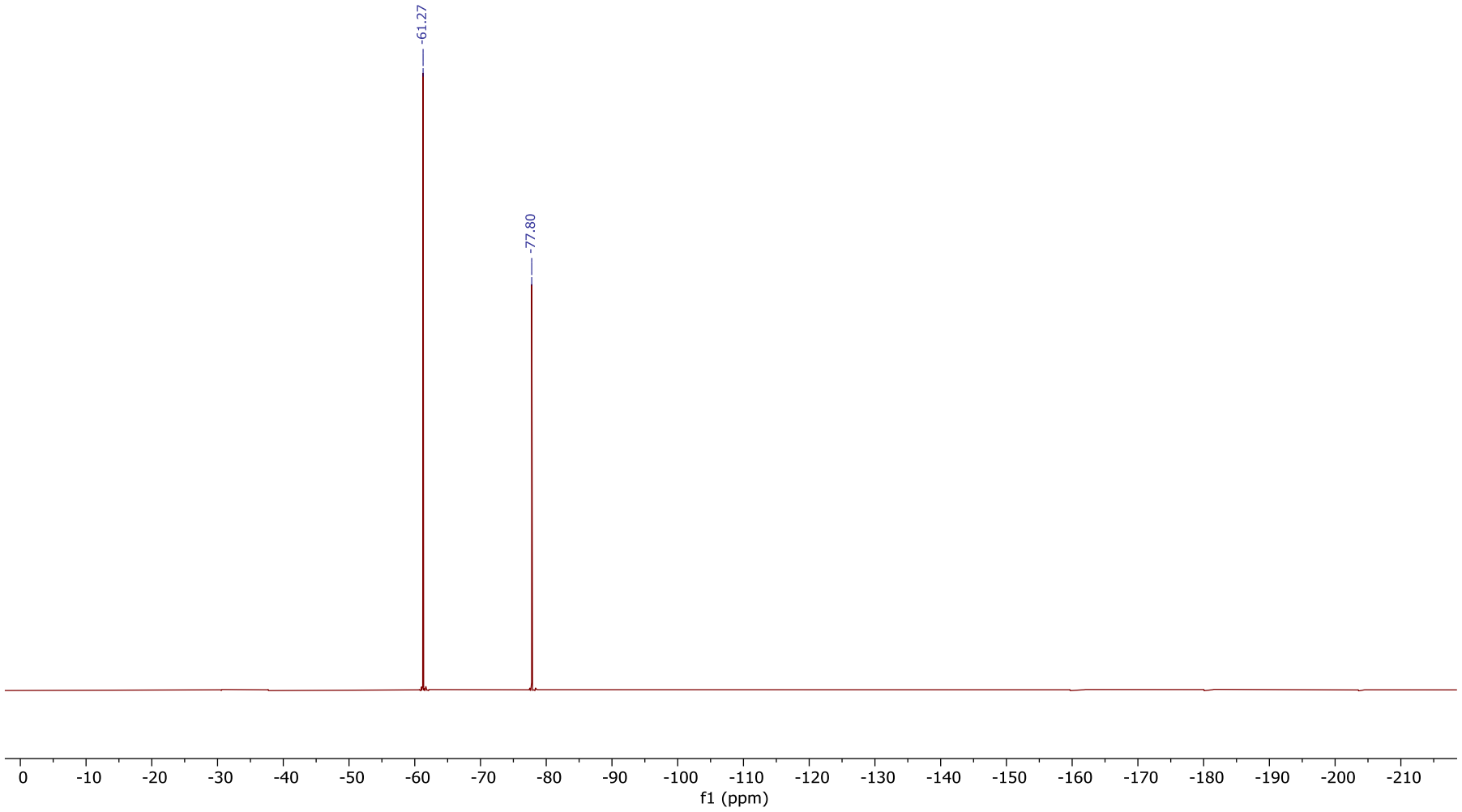
1i, ^{1}H NMR
400 MHz, DMSO-d_6

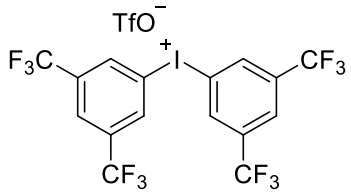



TfO⁻
F3C
I+
CF3
1i, 13C NMR
100 MHz, DMSO-d6
132.84
132.06
132.02
131.98
131.94
131.60
131.27
130.94
129.14
129.11
129.08
129.05
127.01
125.50
124.29
122.30
121.58
119.10
118.86
117.23
115.90
39.52 DMSO-d6
139.36
f1 (ppm)

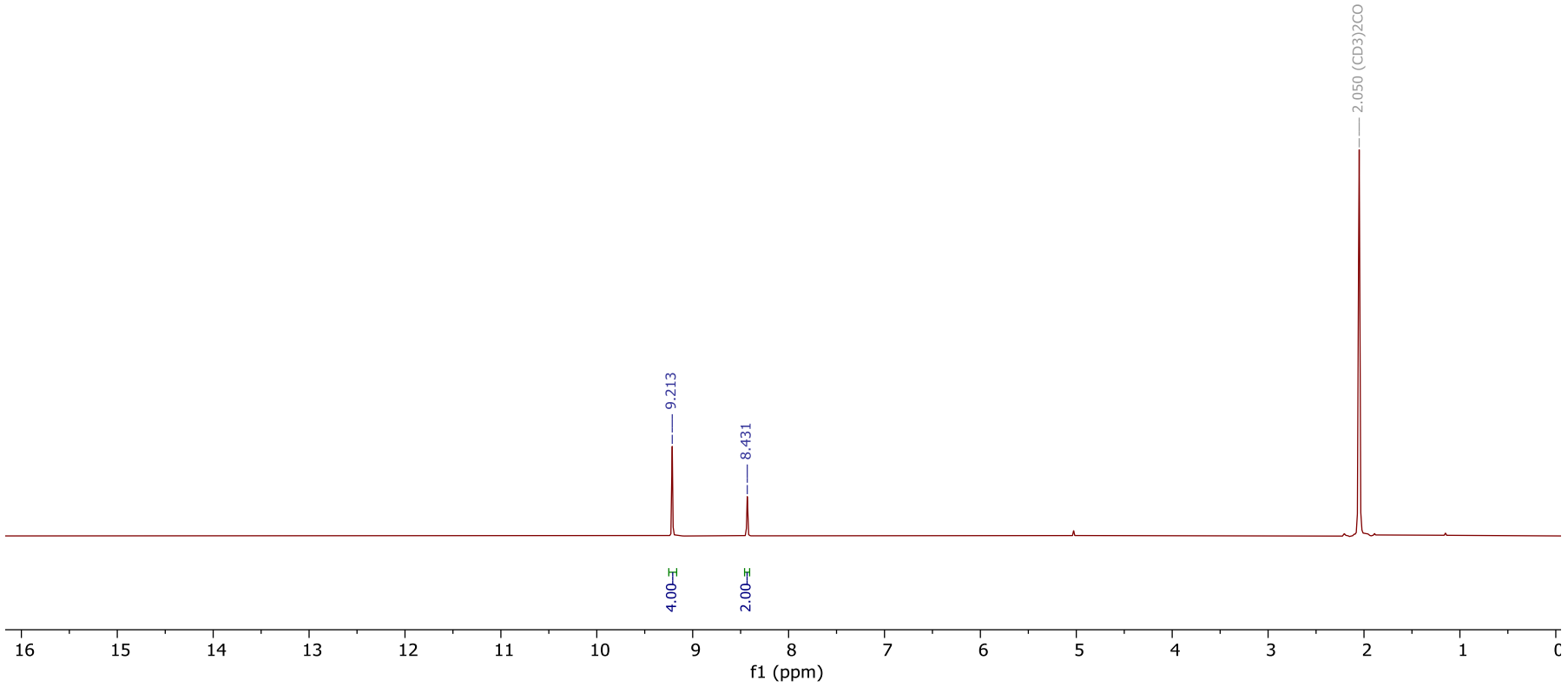


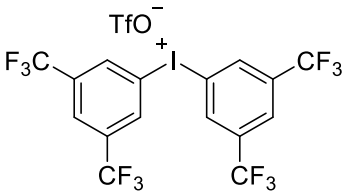
1i, ^{19}F NMR
376 MHz, DMSO-d_6





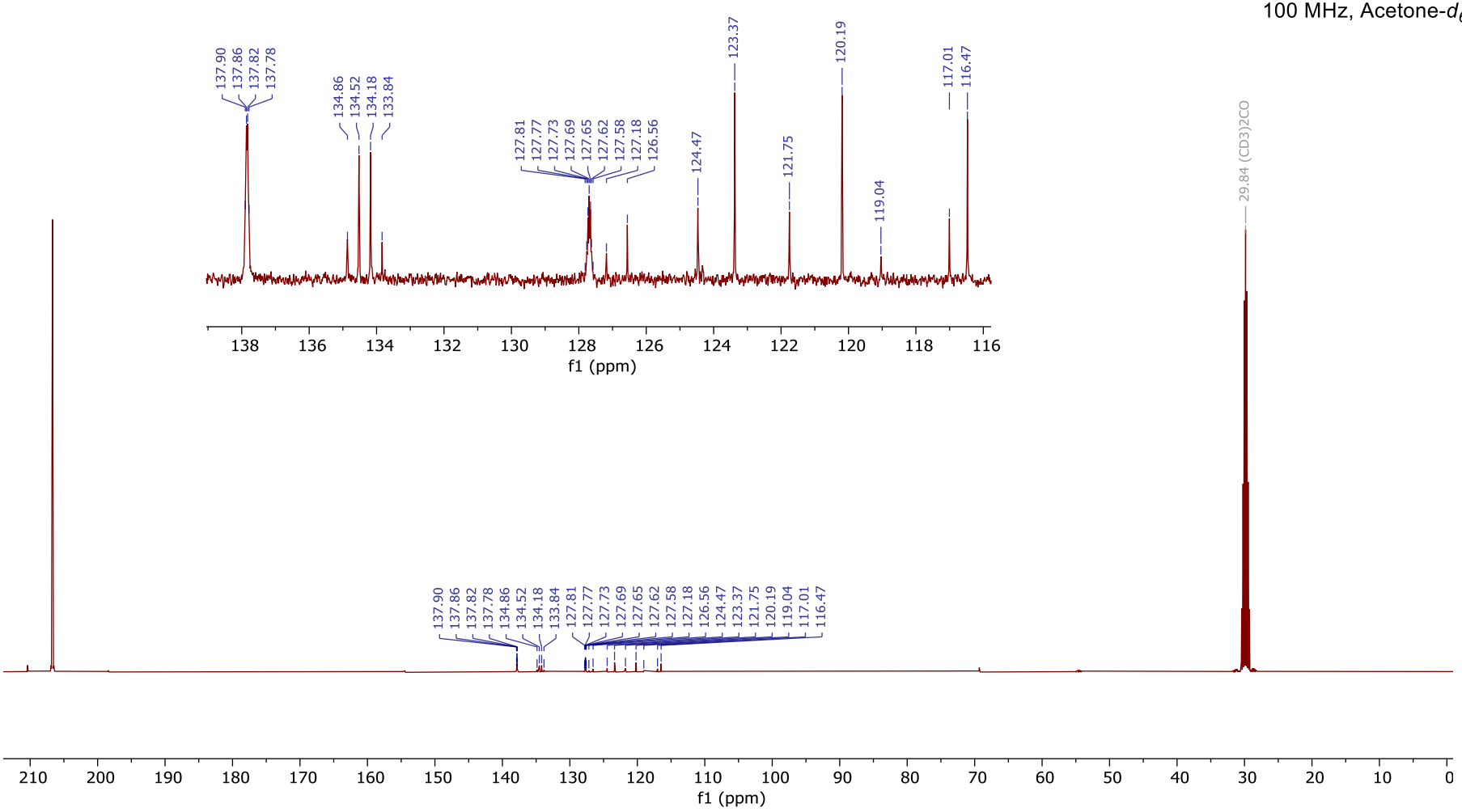
1j, ^{1}H NMR
400 MHz, Acetone-d_6

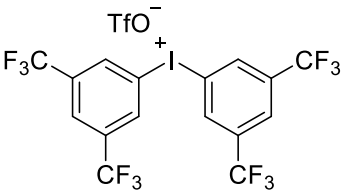




1j, ^{13}C NMR

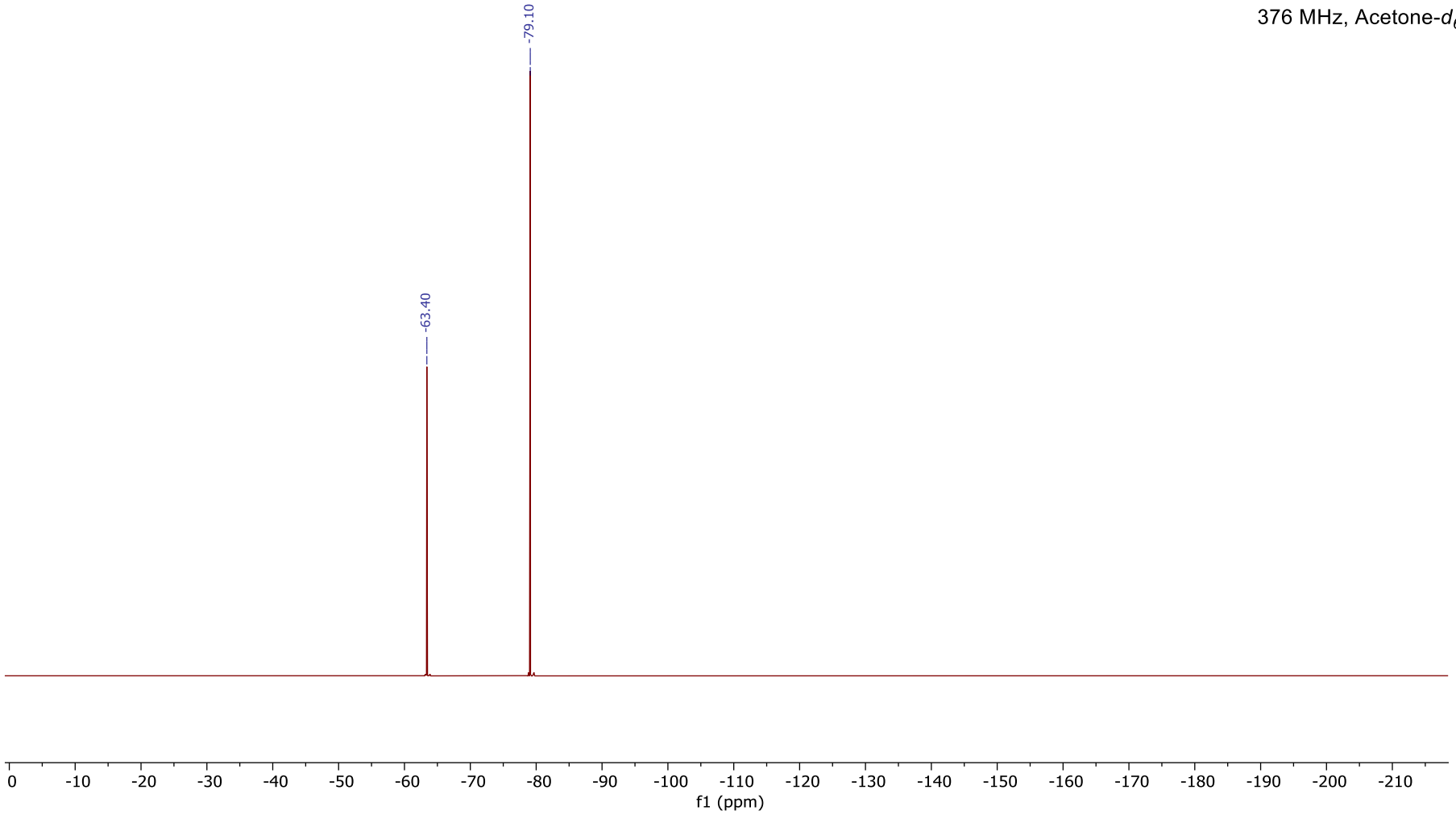
100 MHz, Acetone-d_6

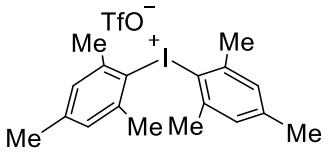




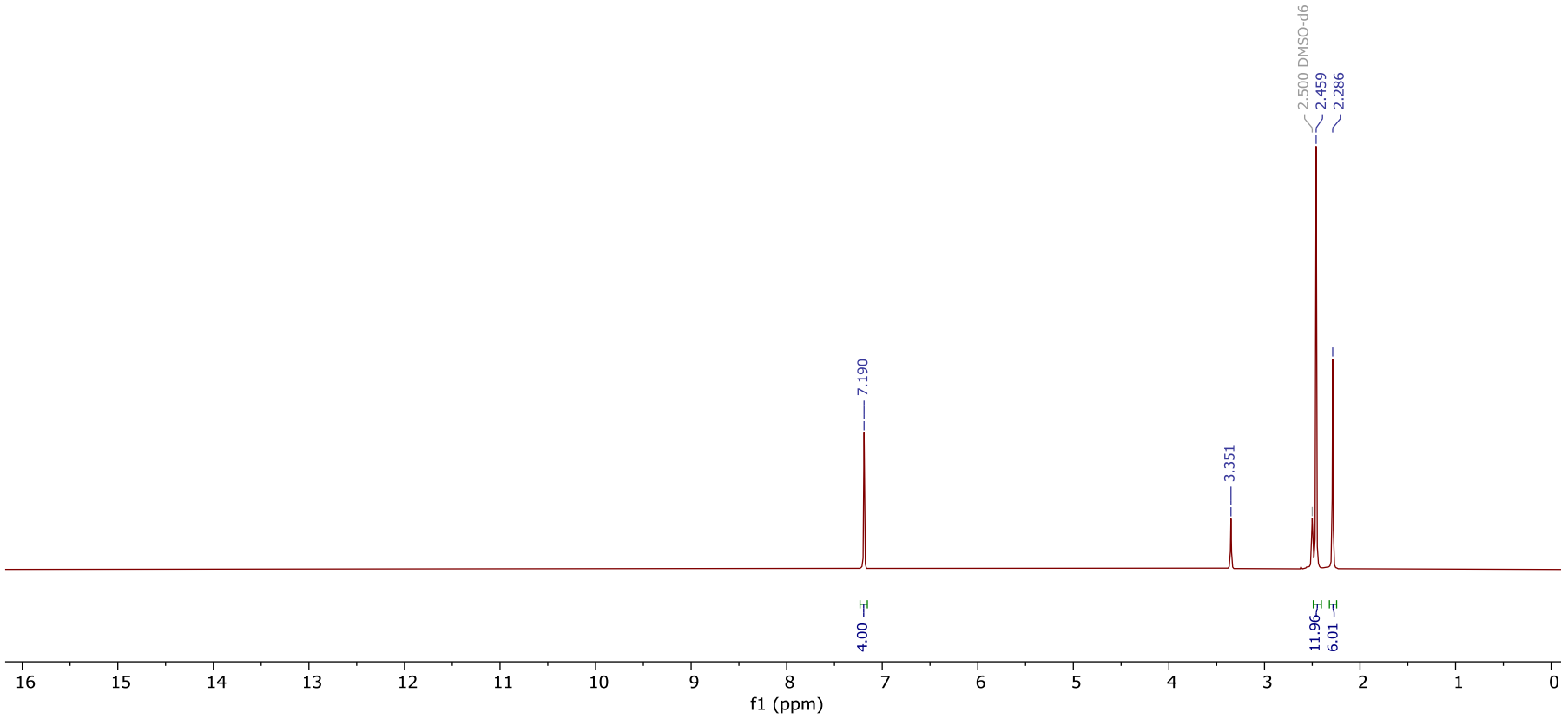
1j, ^{19}F NMR

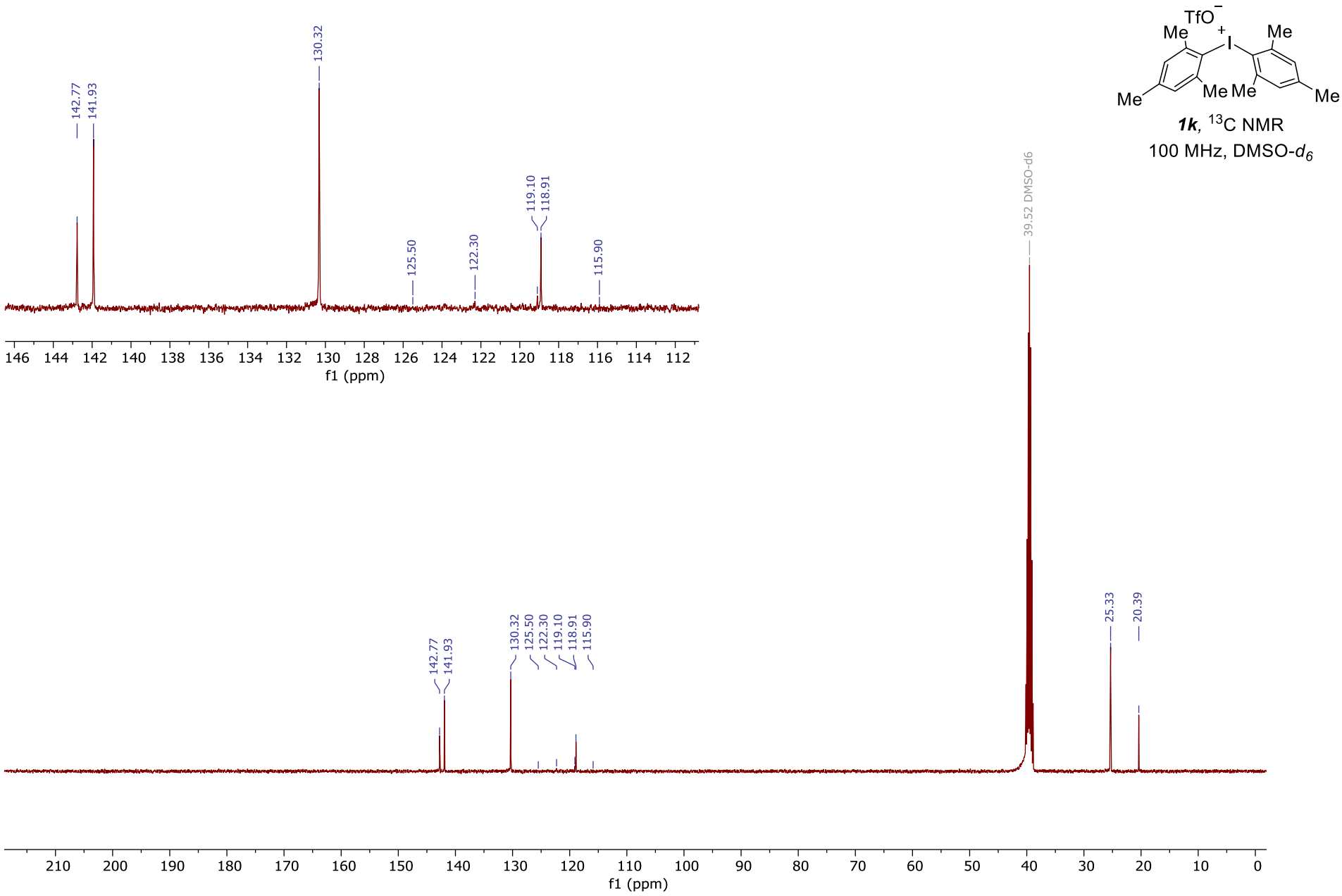
376 MHz, Acetone-d_6

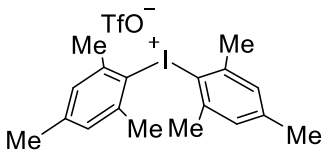




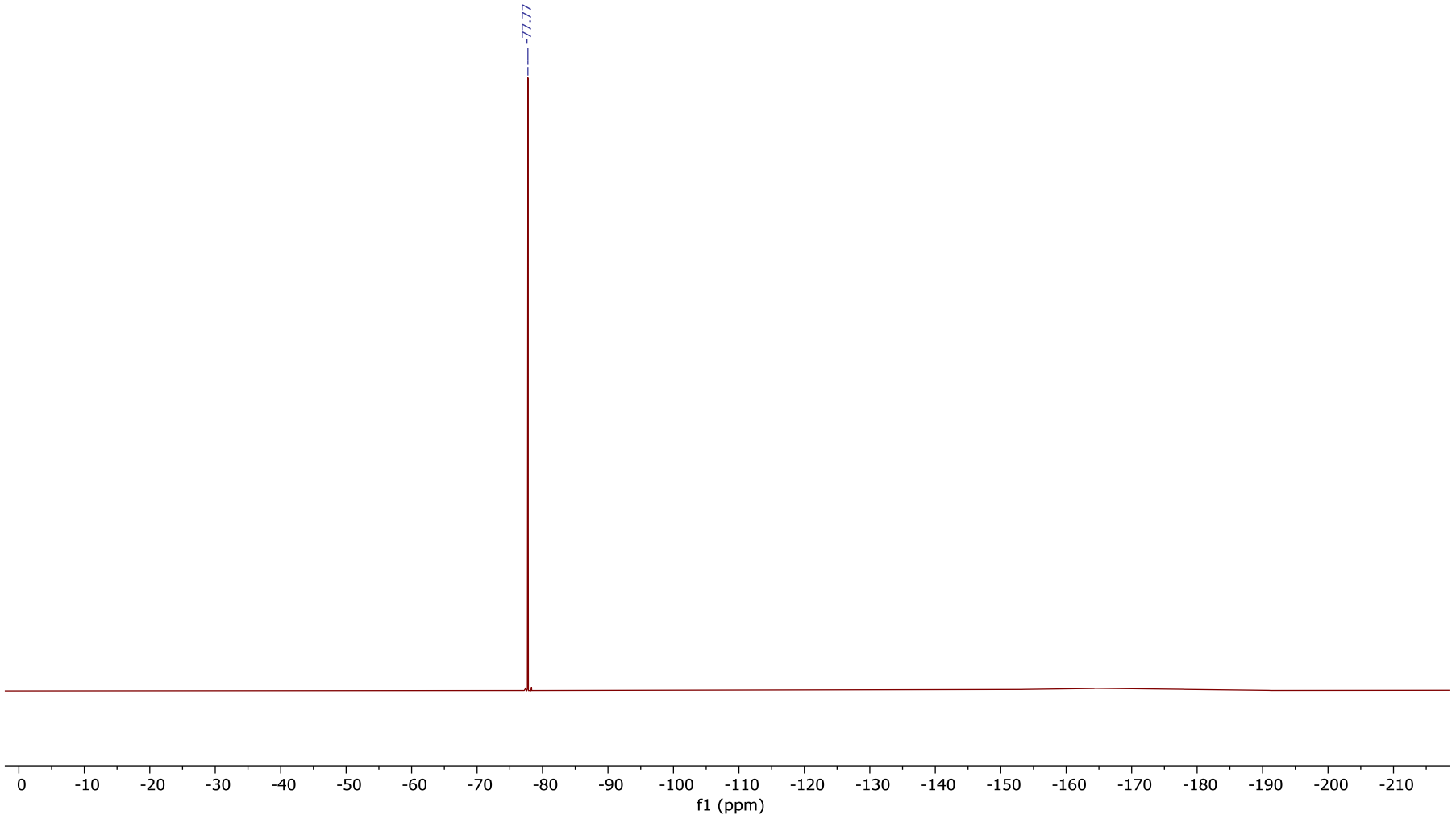
1k, ^{1}H NMR
400 MHz, DMSO-d_6

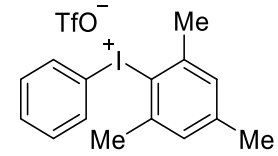



TfO⁻
Me
Me
I
Me
Me
Me
Me
Me
1k, ^{13}C NMR
100 MHz, DMSO-d_6
142.77
141.93
130.32
125.50
122.30
119.10
118.91
115.90
39.52 DMSO-d6
25.33
20.39
f1 (ppm)

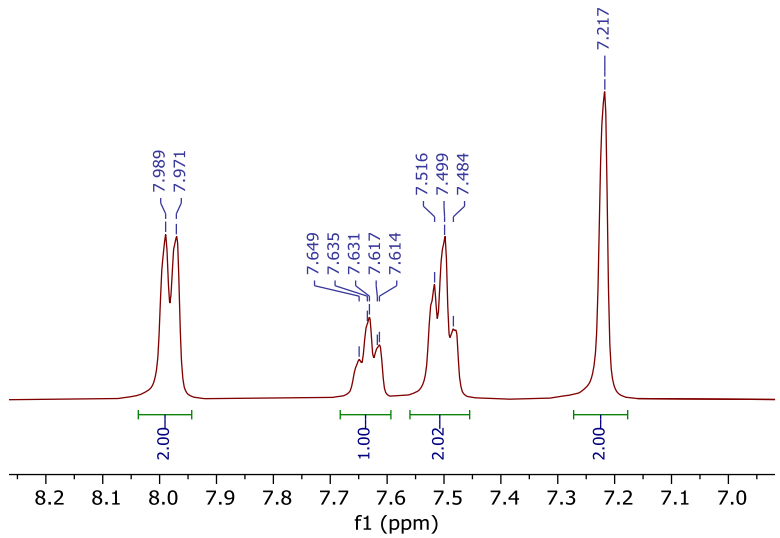


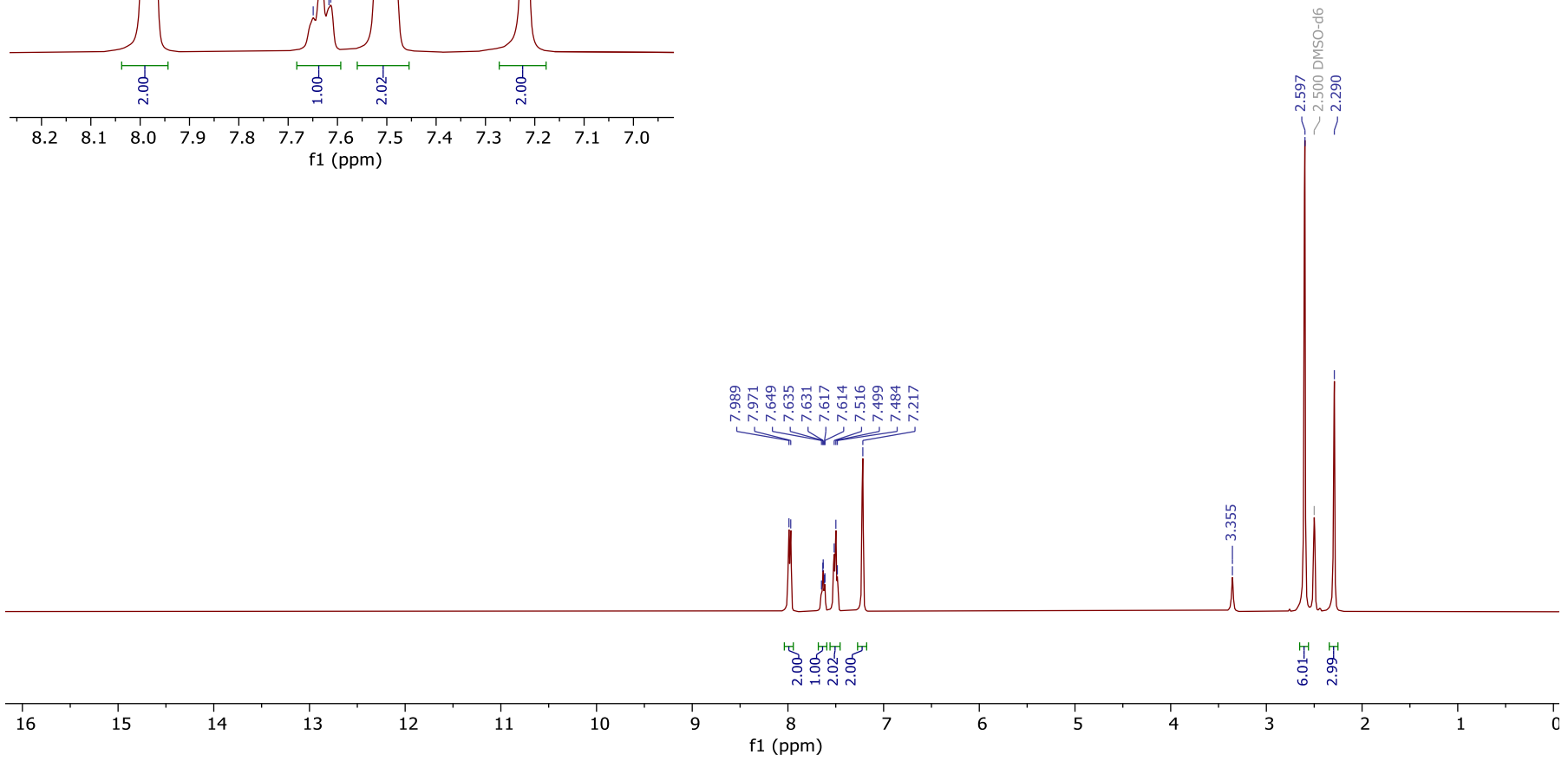
1k, ^{19}F NMR
376 MHz, DMSO-d_6

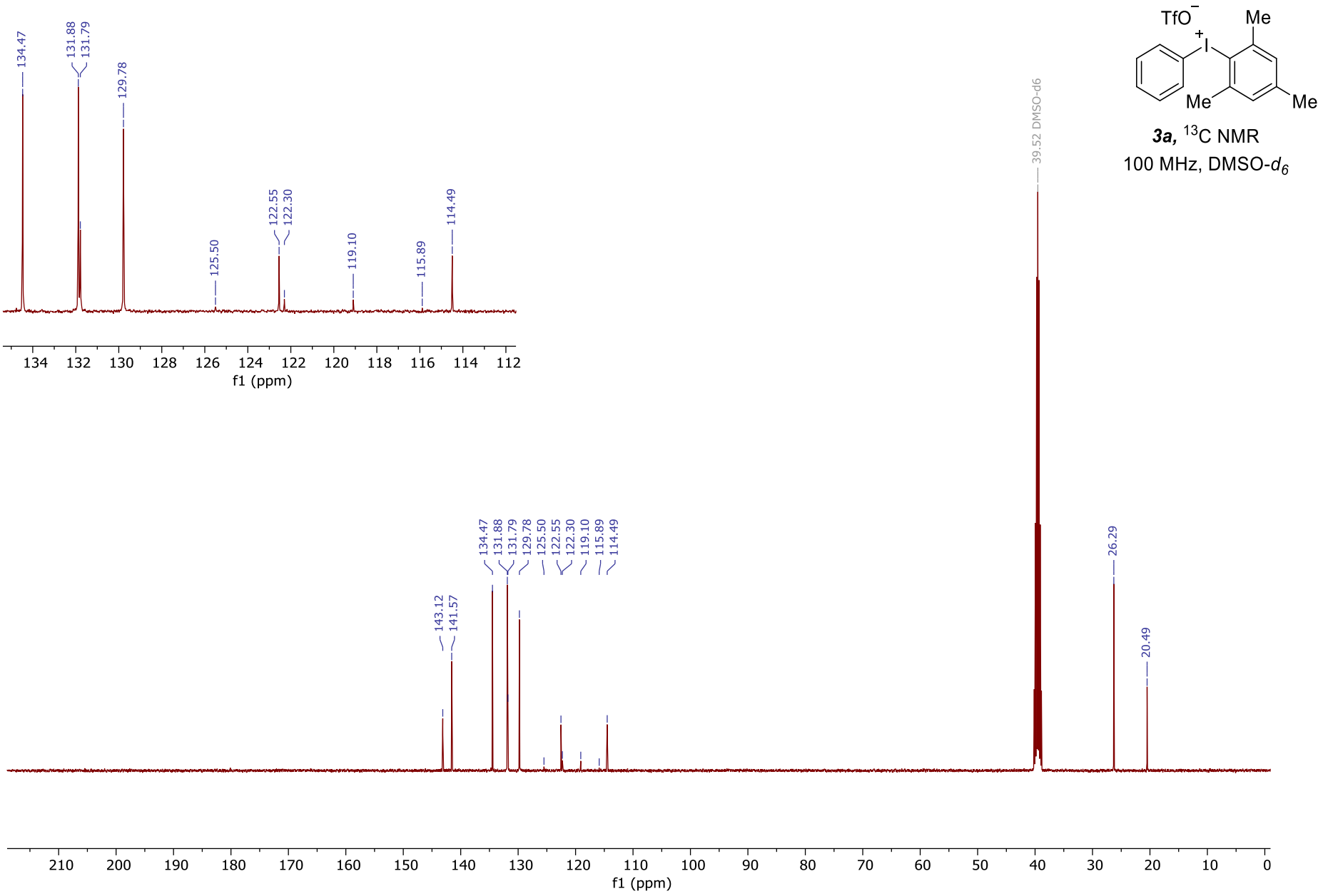


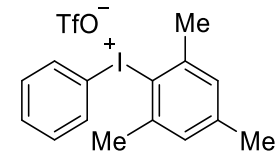


3a, ^{1}H NMR
400 MHz, DMSO-d_6

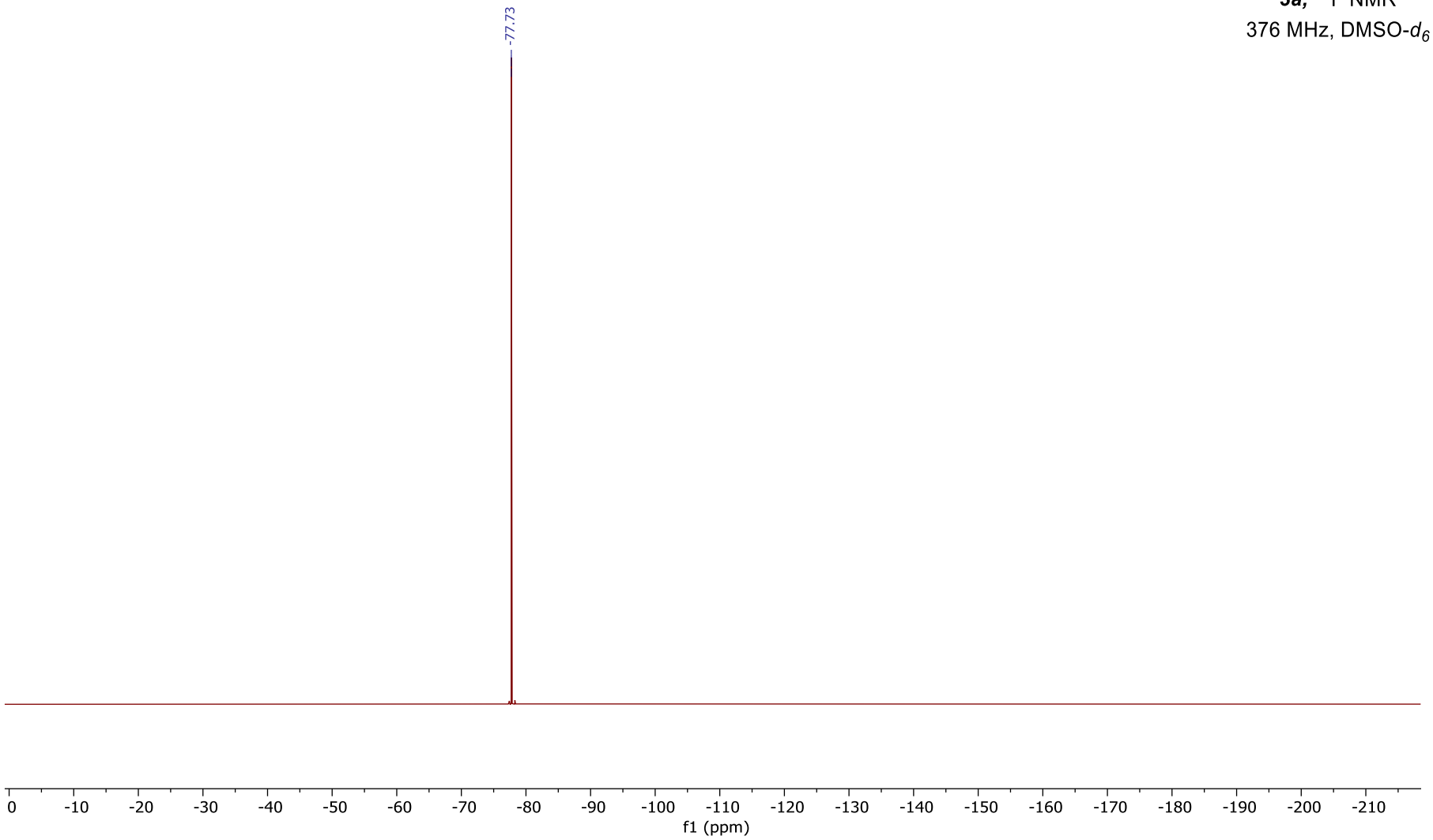


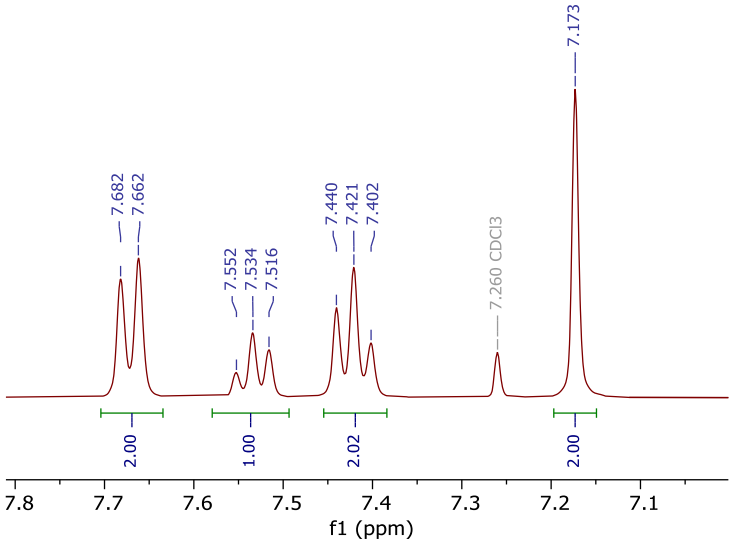


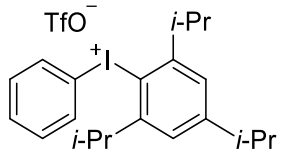

TfO
Me
Me
Me
3a, 13C NMR
100 MHz, DMSO-d6
134.47
131.88
131.79
129.78
125.50
122.55
122.30
119.10
115.89
114.49
39.52 DMSO-d6
26.29
20.49
143.12
141.57
f1 (ppm)



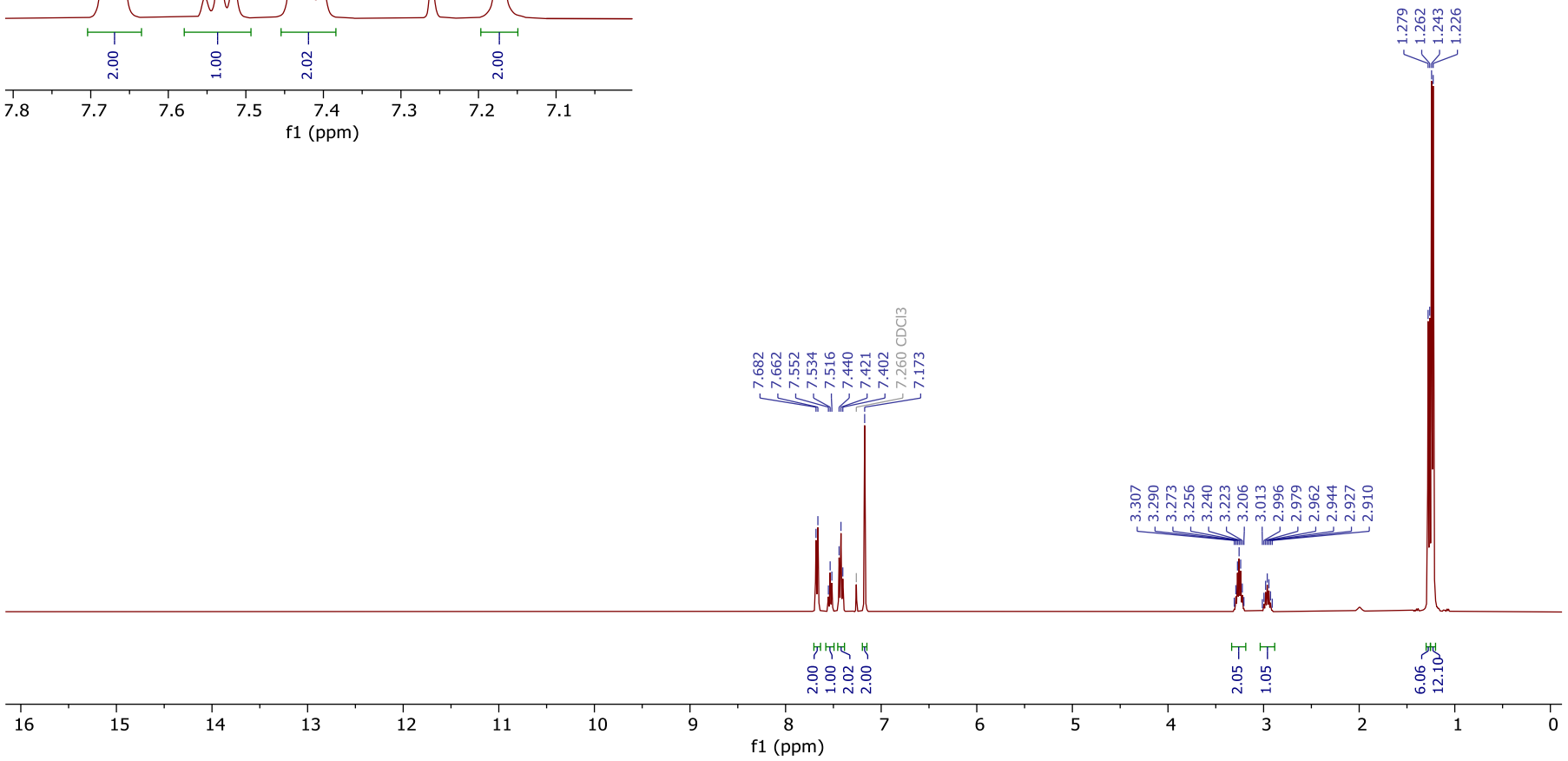
3a, ^{19}F NMR
376 MHz, DMSO-d_6

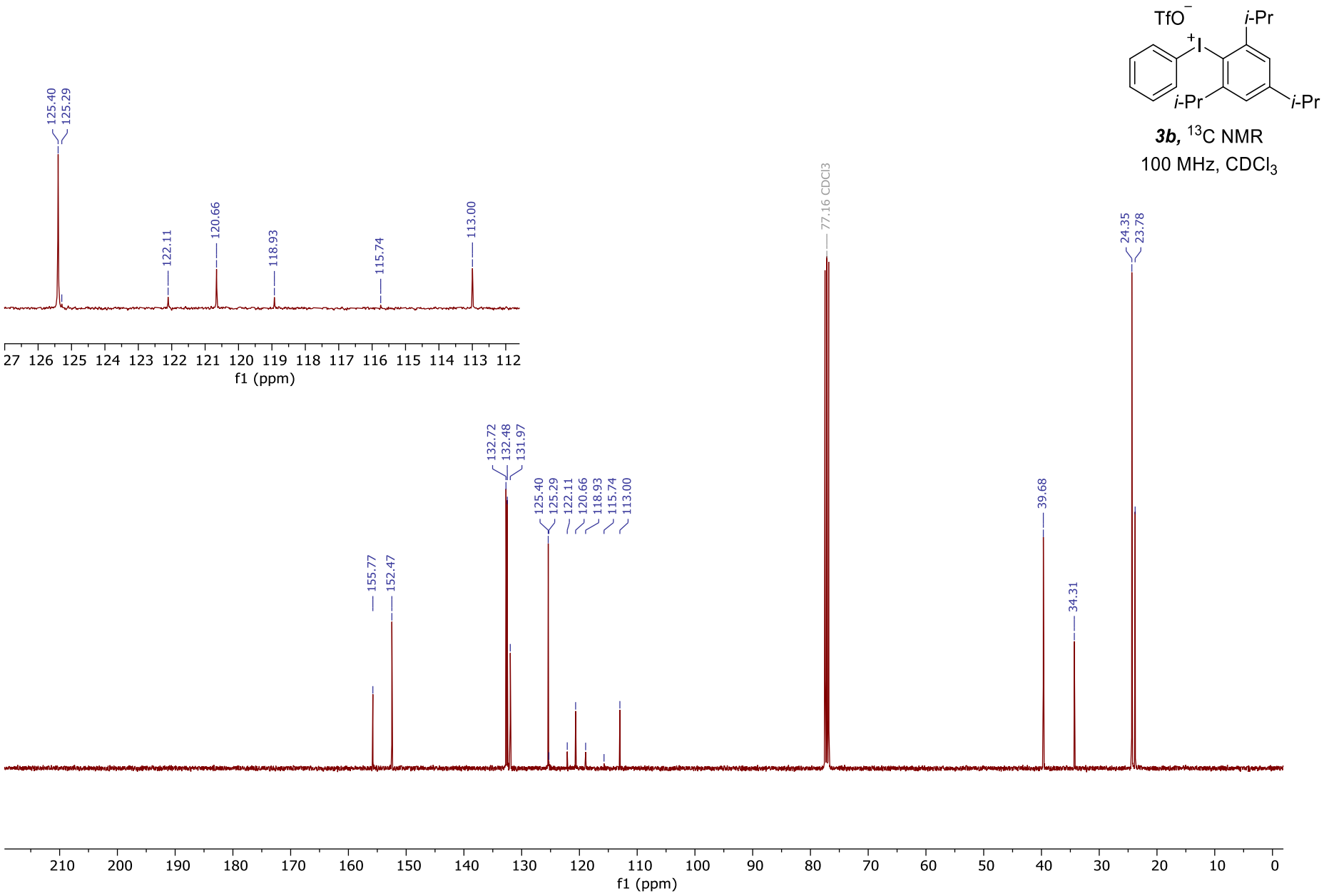


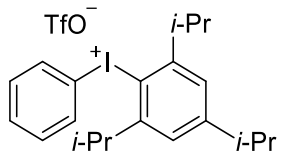




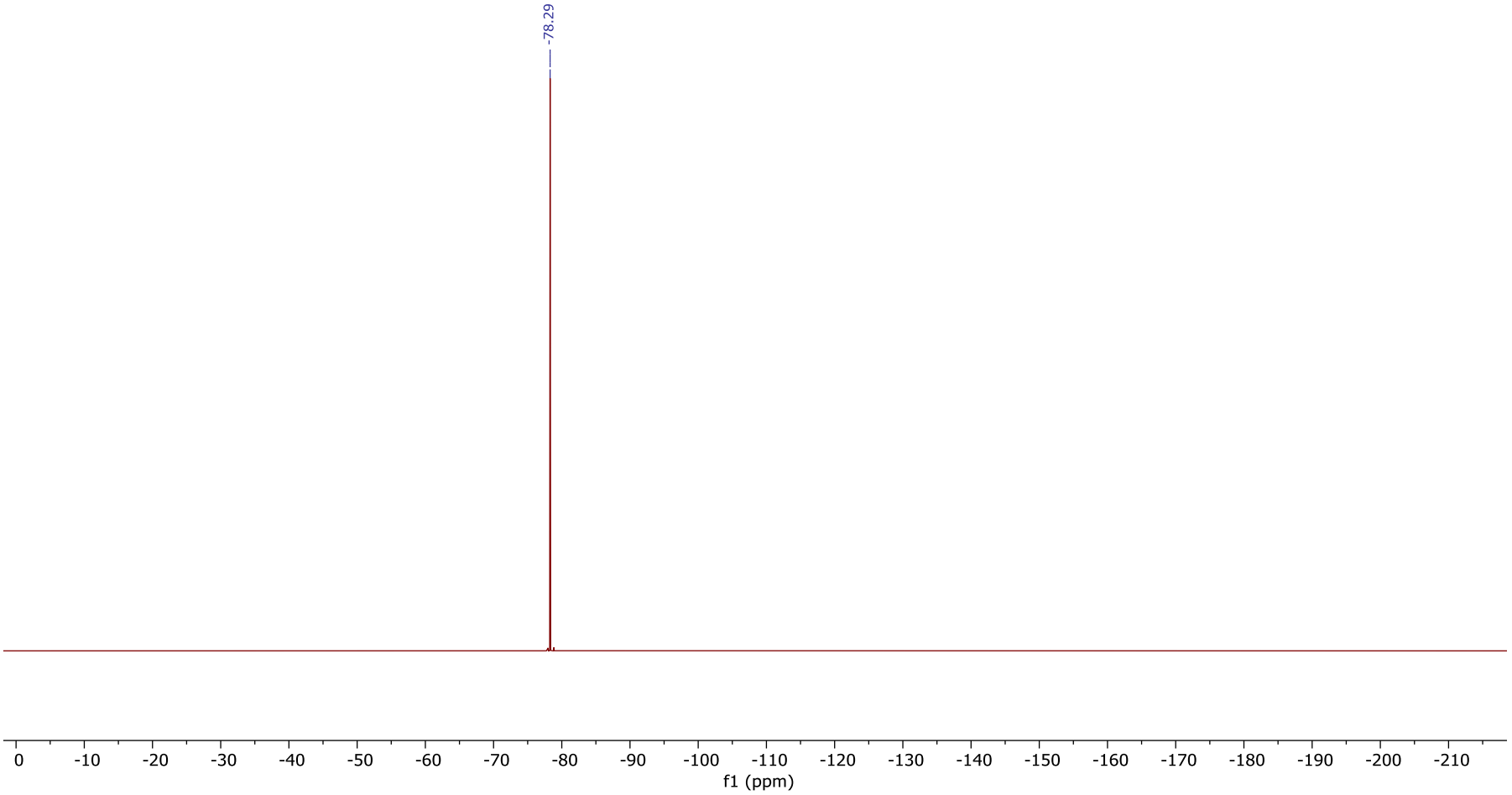
3b, ^{1}H NMR
400 MHz, $CDCl_3$

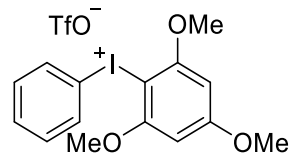



TfO⁻
i-Pr
i-Pr
i-Pr
3b, 13C NMR
100 MHz, CDCl3
125.40
125.29
122.11
120.66
118.93
115.74
113.00
77.16 CDCl3
24.35
23.78
132.72
132.48
131.97
125.40
125.29
122.11
120.66
118.93
115.74
113.00
155.77
152.47
39.68
34.31
f1 (ppm)
f1 (ppm)

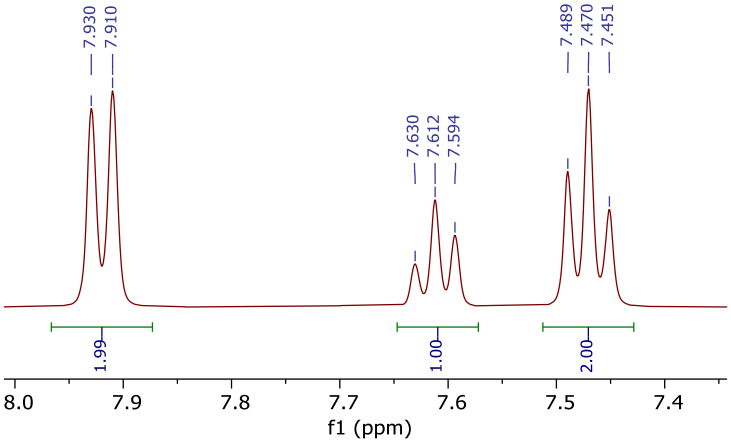


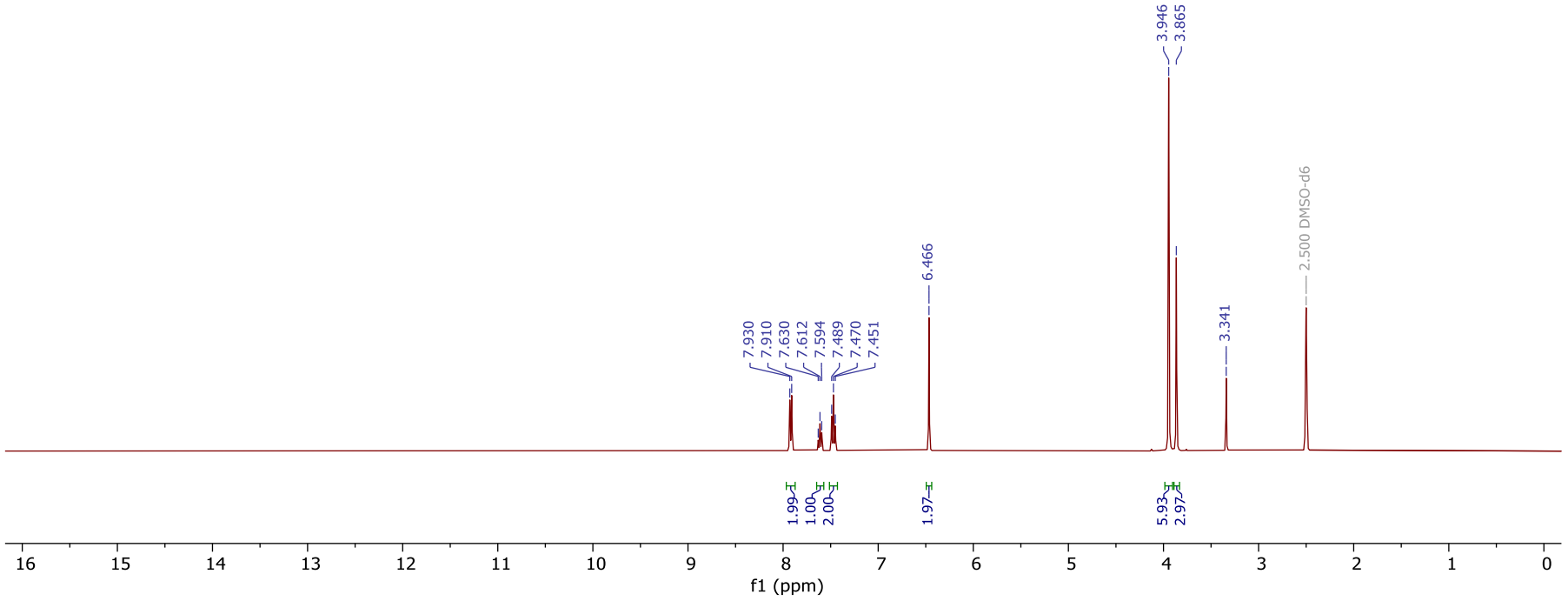
3b, ^{19}F NMR
376 MHz, $CDCl_3$

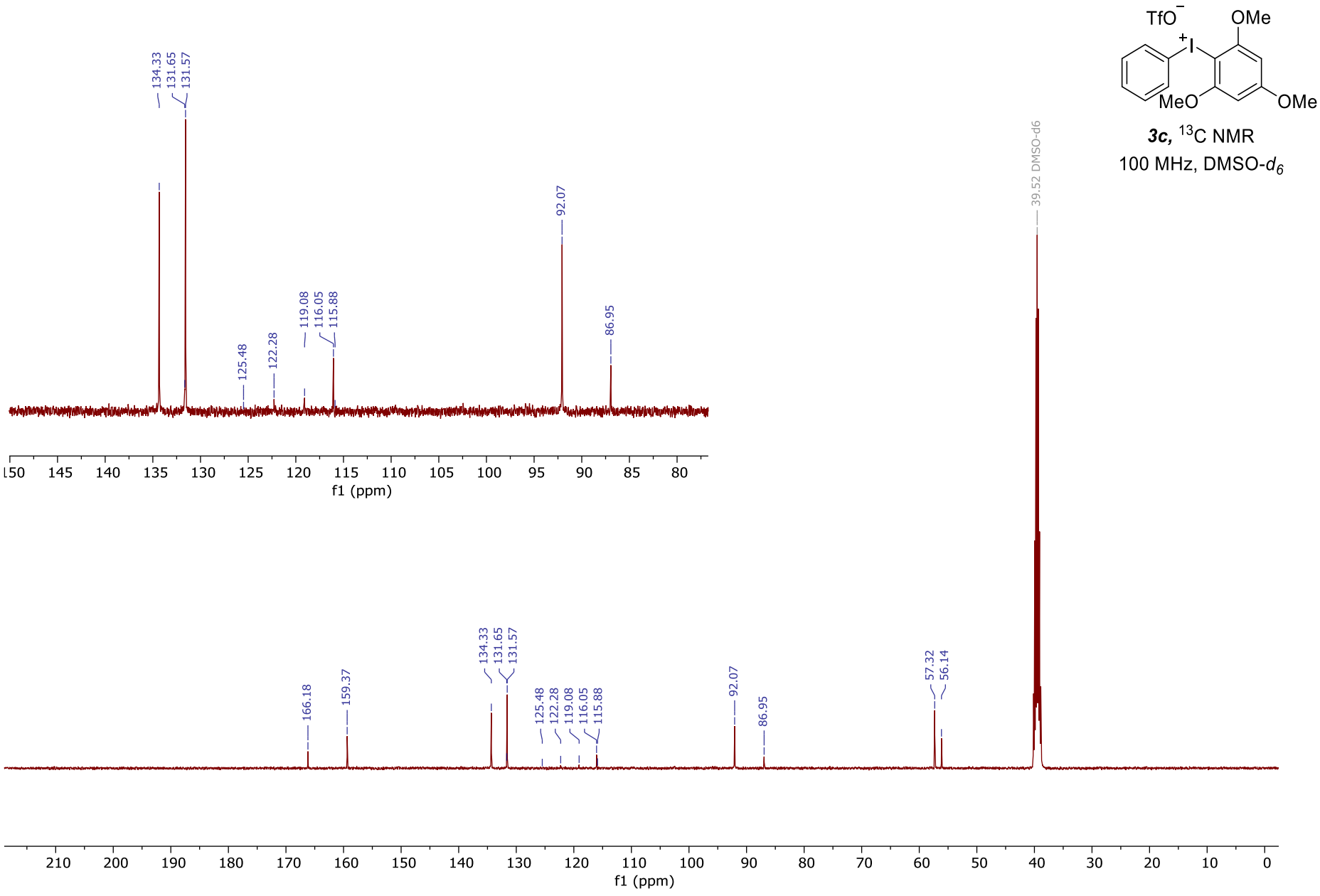


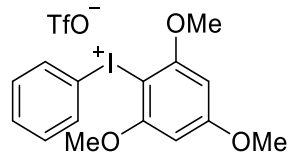


3c, ^{1}H NMR
400 MHz, DMSO-d_6

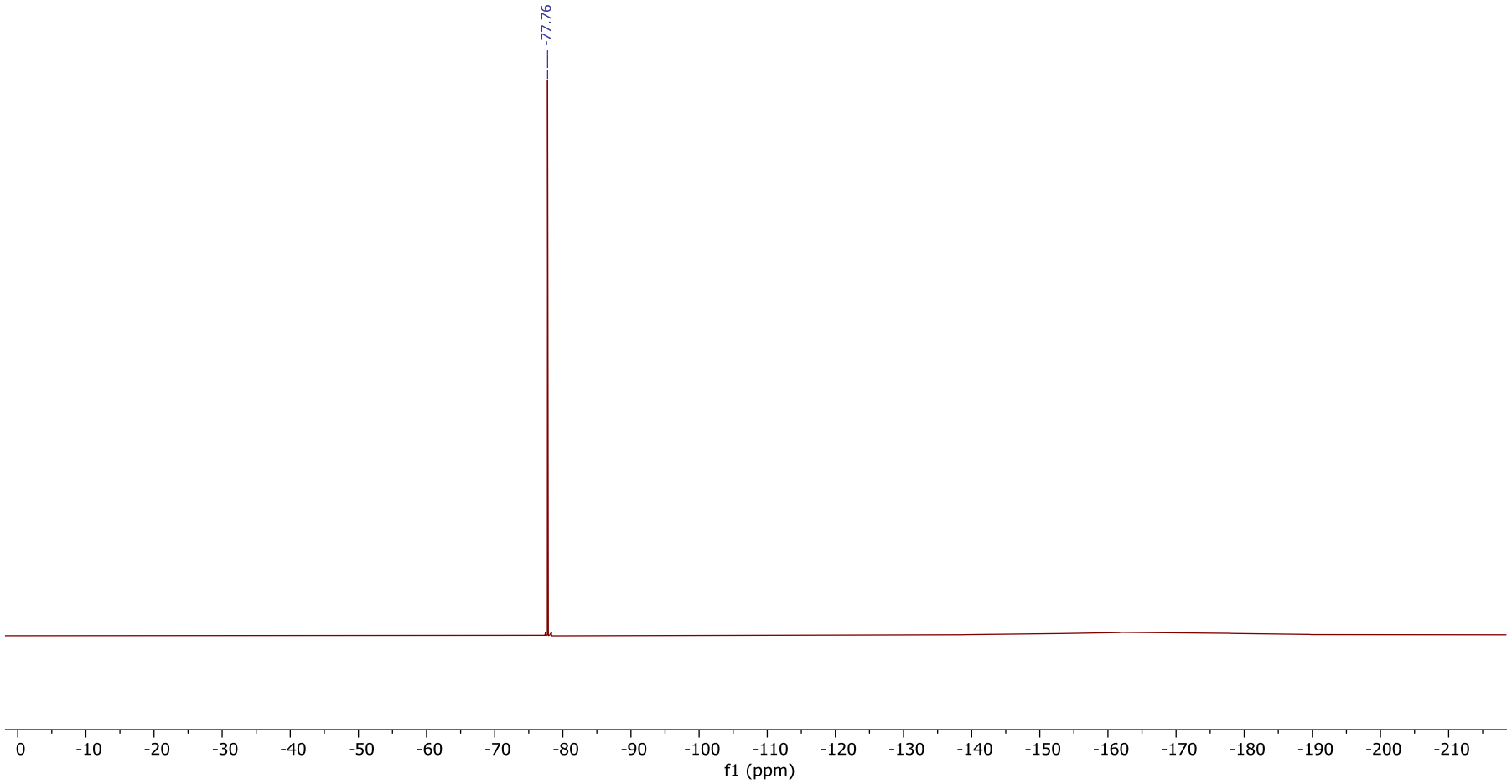


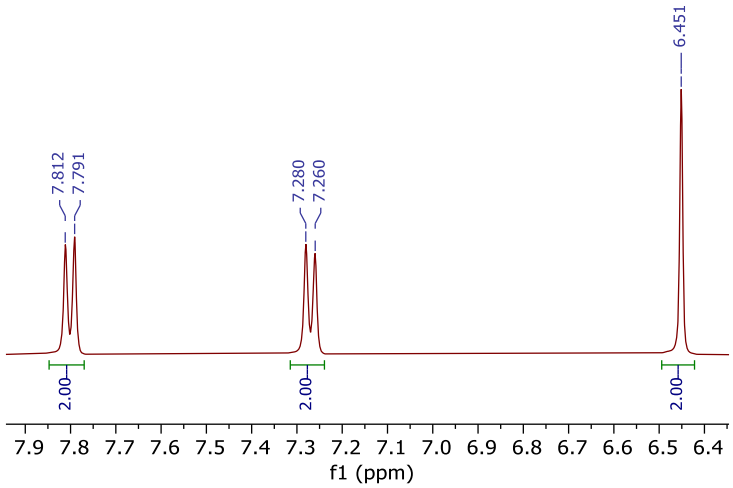


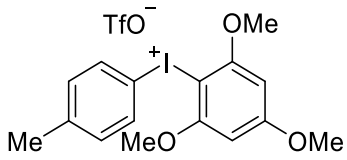

TfO
OMe
MeO
OMe
3c, 13C NMR
100 MHz, DMSO-d6
134.33
131.65
131.57
125.48
122.28
119.08
116.05
115.88
92.07
86.95
39.52 DMSO-d6
166.18
159.37
57.32
56.14
f1 (ppm)



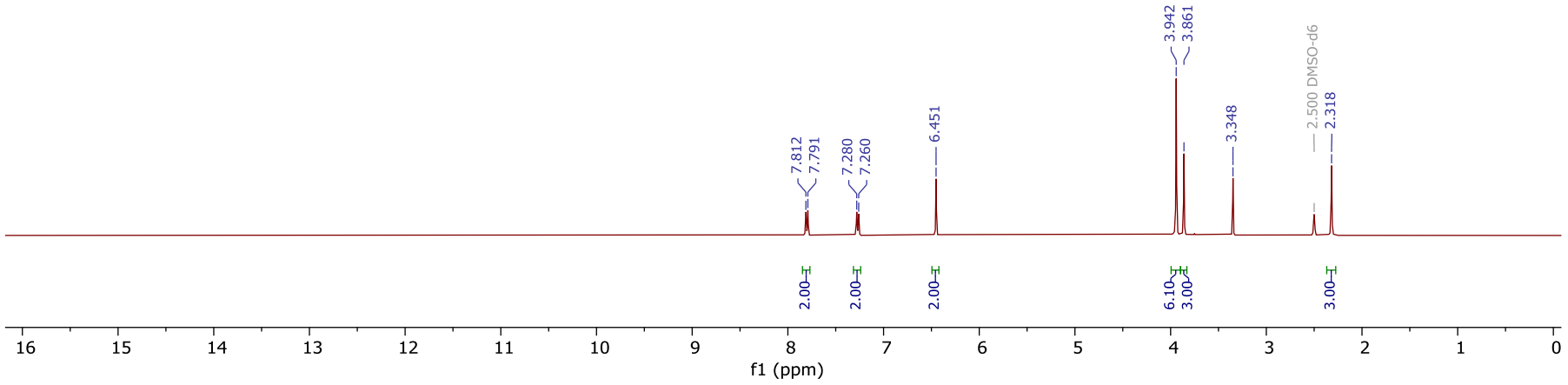
3c, ^{19}F NMR
376 MHz, DMSO-d_6

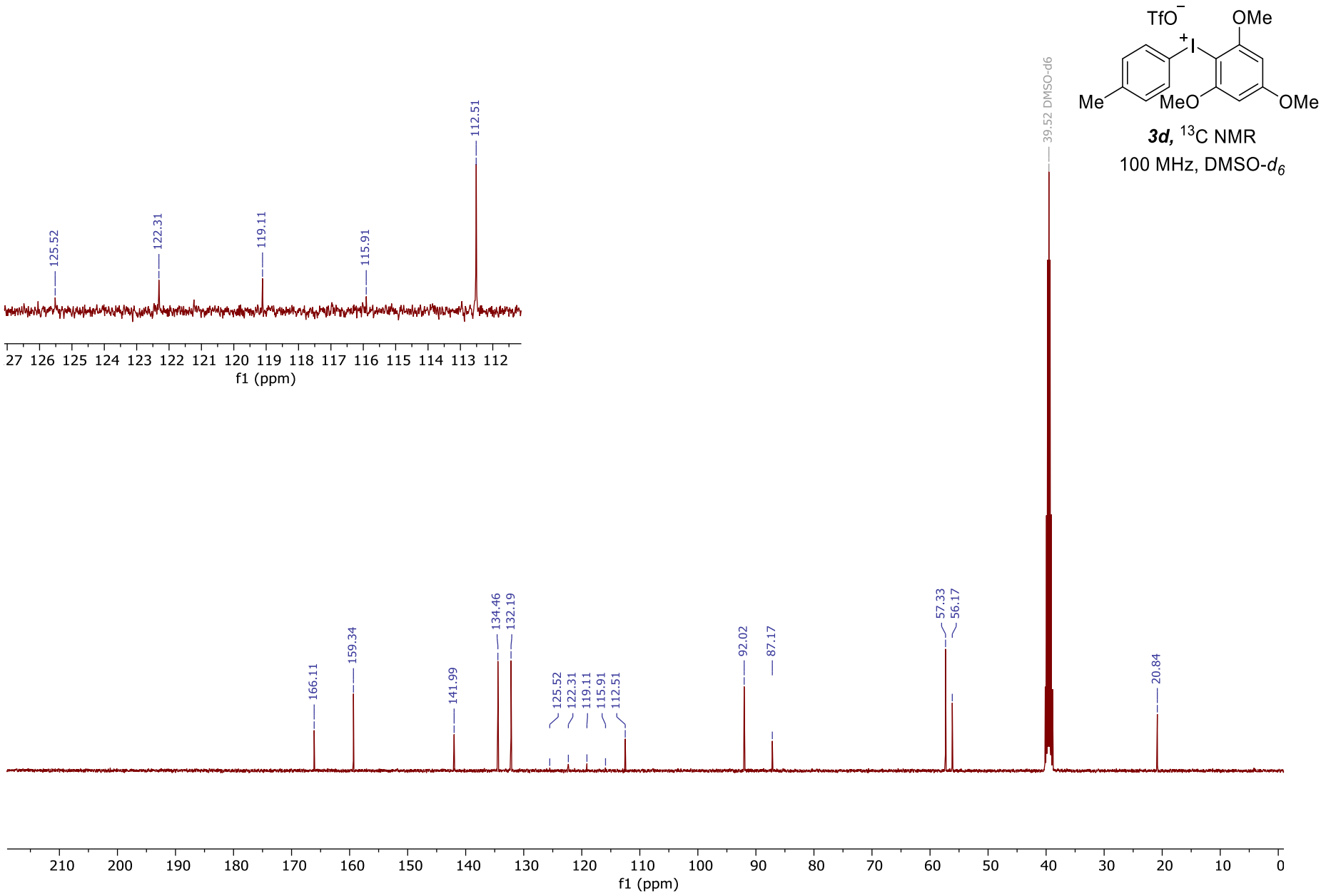


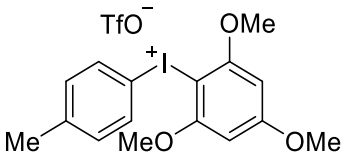




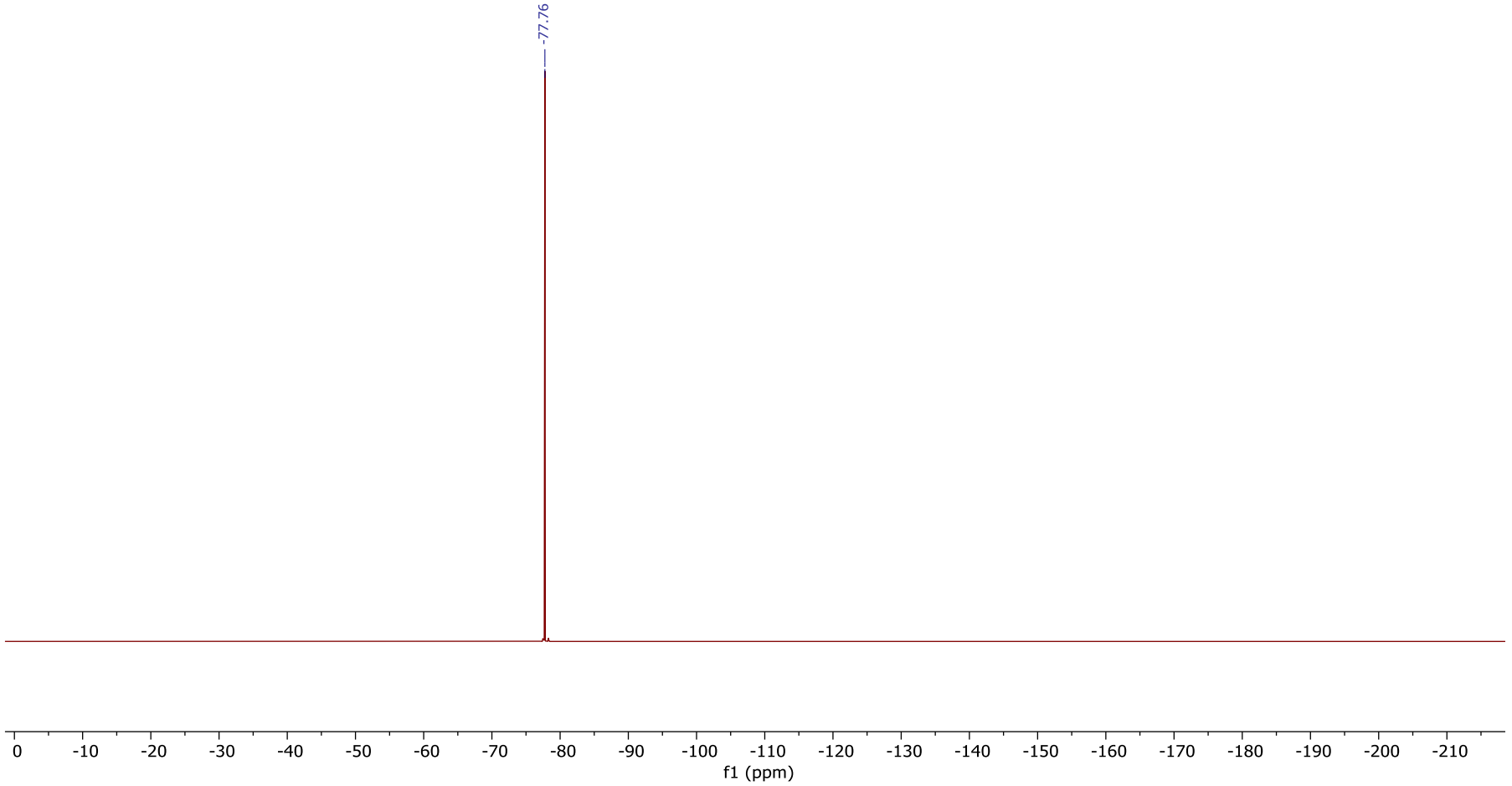
3d, ^{1}H NMR
400 MHz, DMSO-d_6

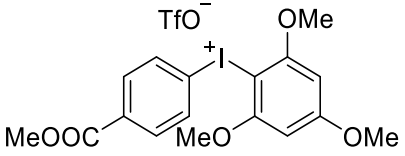



TfO⁻
OMe
Me
MeO
OMe
3d, 13C NMR
100 MHz, DMSO-d6
39.52 DMSO-d6
125.52
122.31
119.11
115.91
112.51
f1 (ppm)
166.11
159.34
141.99
134.46
132.19
125.52
122.31
119.11
115.91
112.51
92.02
87.17
57.33
56.17
20.84
f1 (ppm)

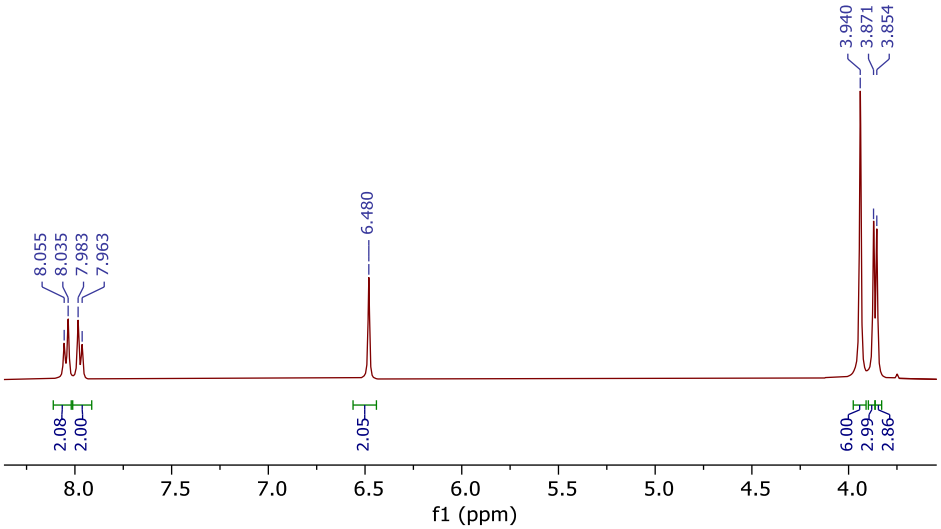


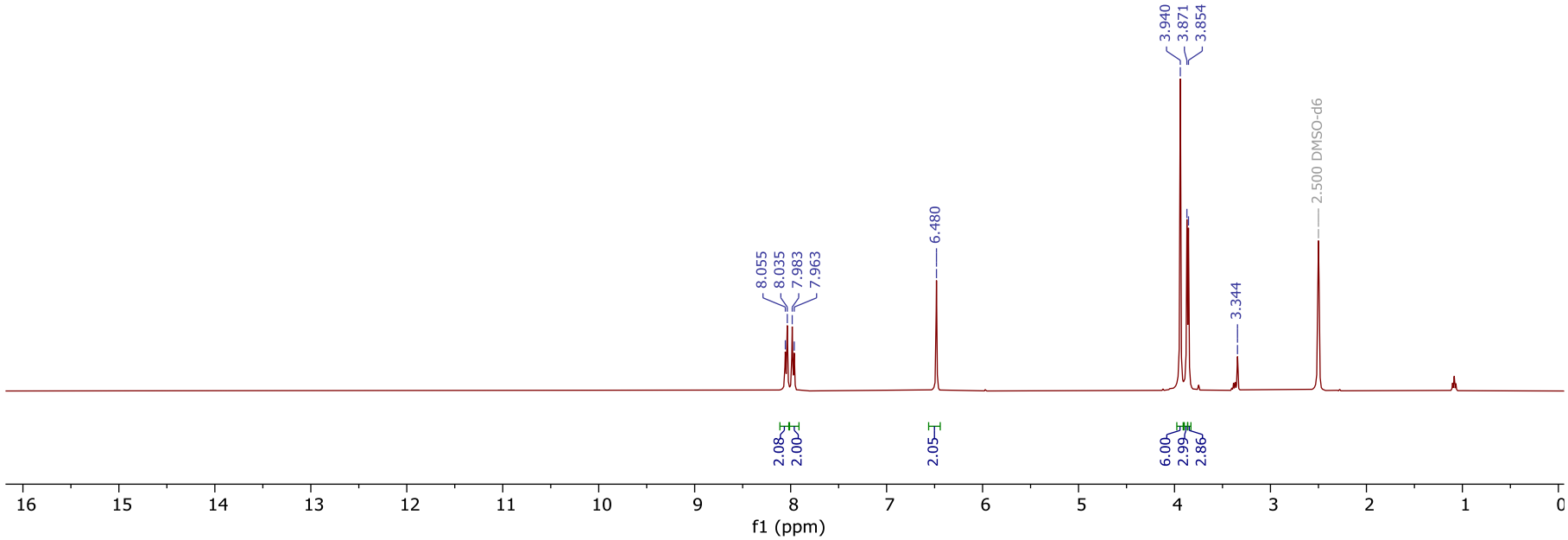
3d, ^{19}F NMR
376 MHz, DMSO-d_6

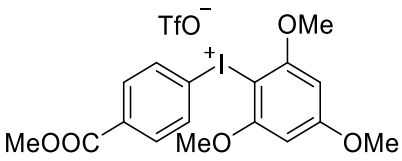




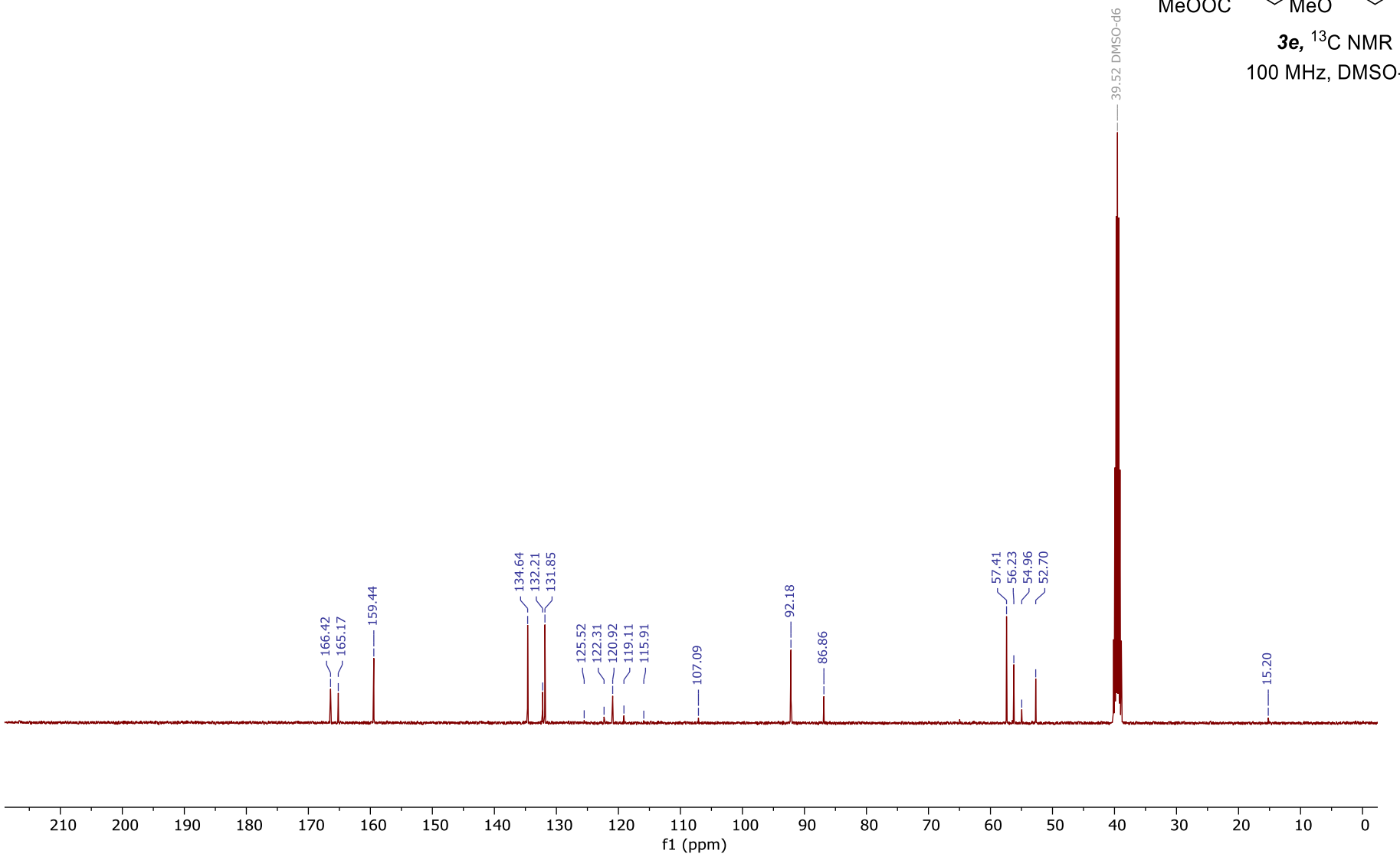
3e, ^{1}H NMR
400 MHz, DMSO-d_6

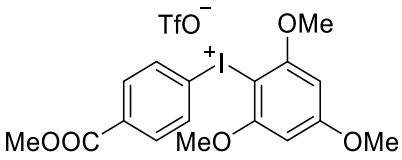




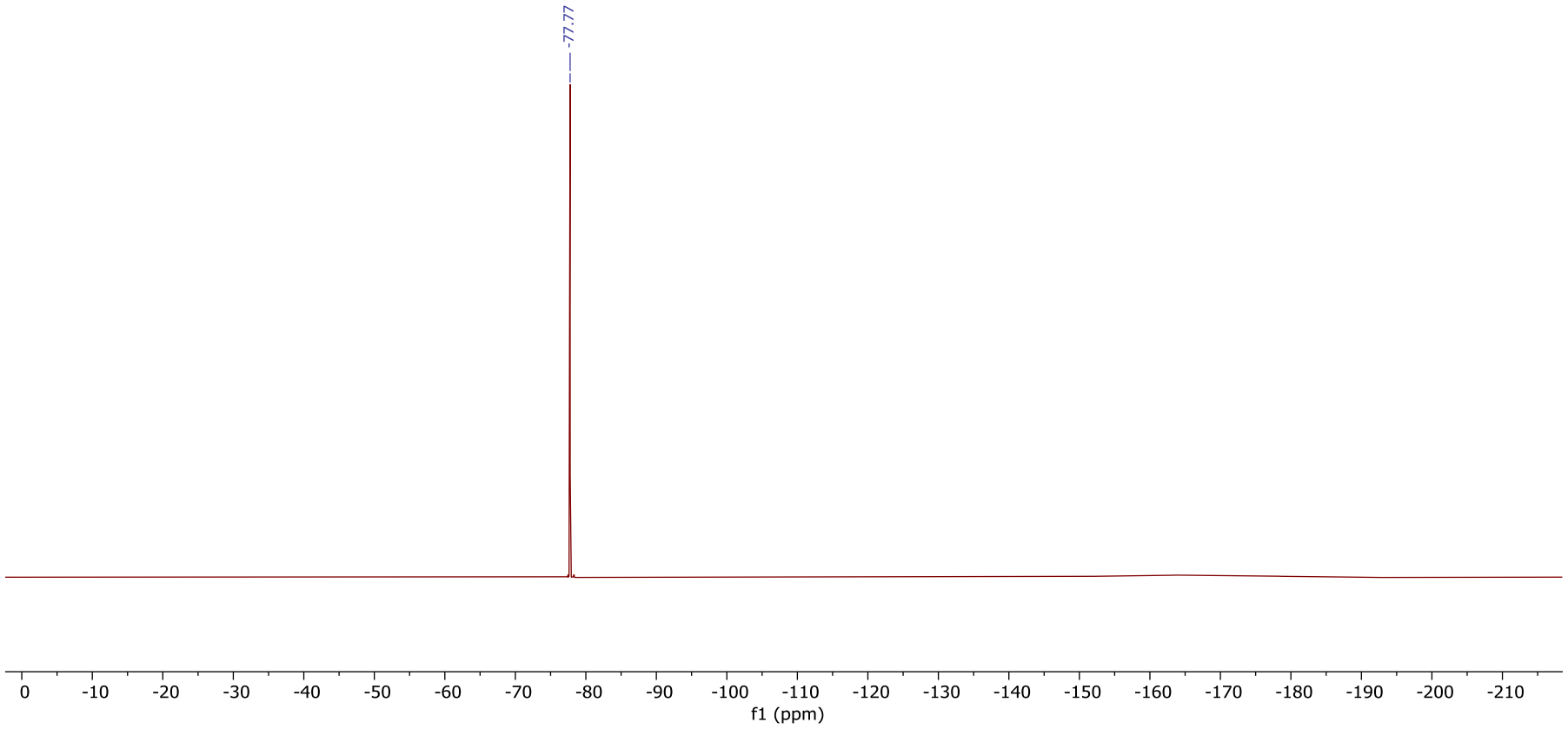


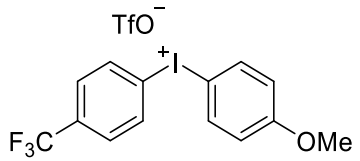
3e, ^{13}C NMR
100 MHz, DMSO-d_6



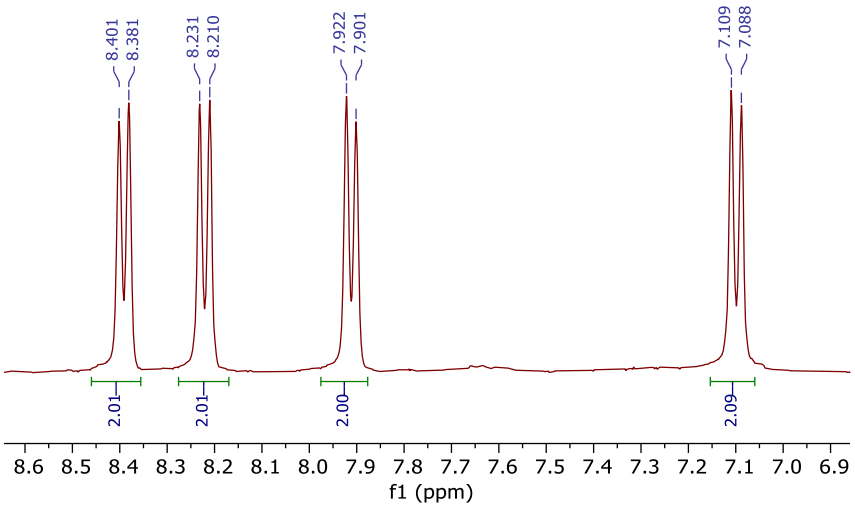


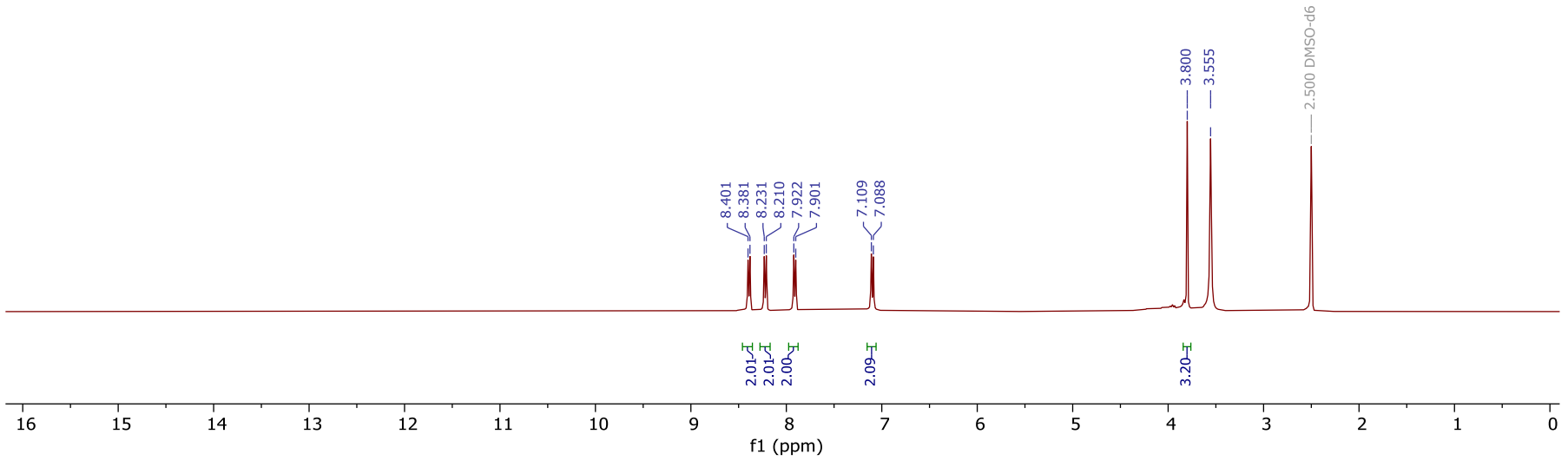
3e, ^{19}F NMR
376 MHz, DMSO-d_6

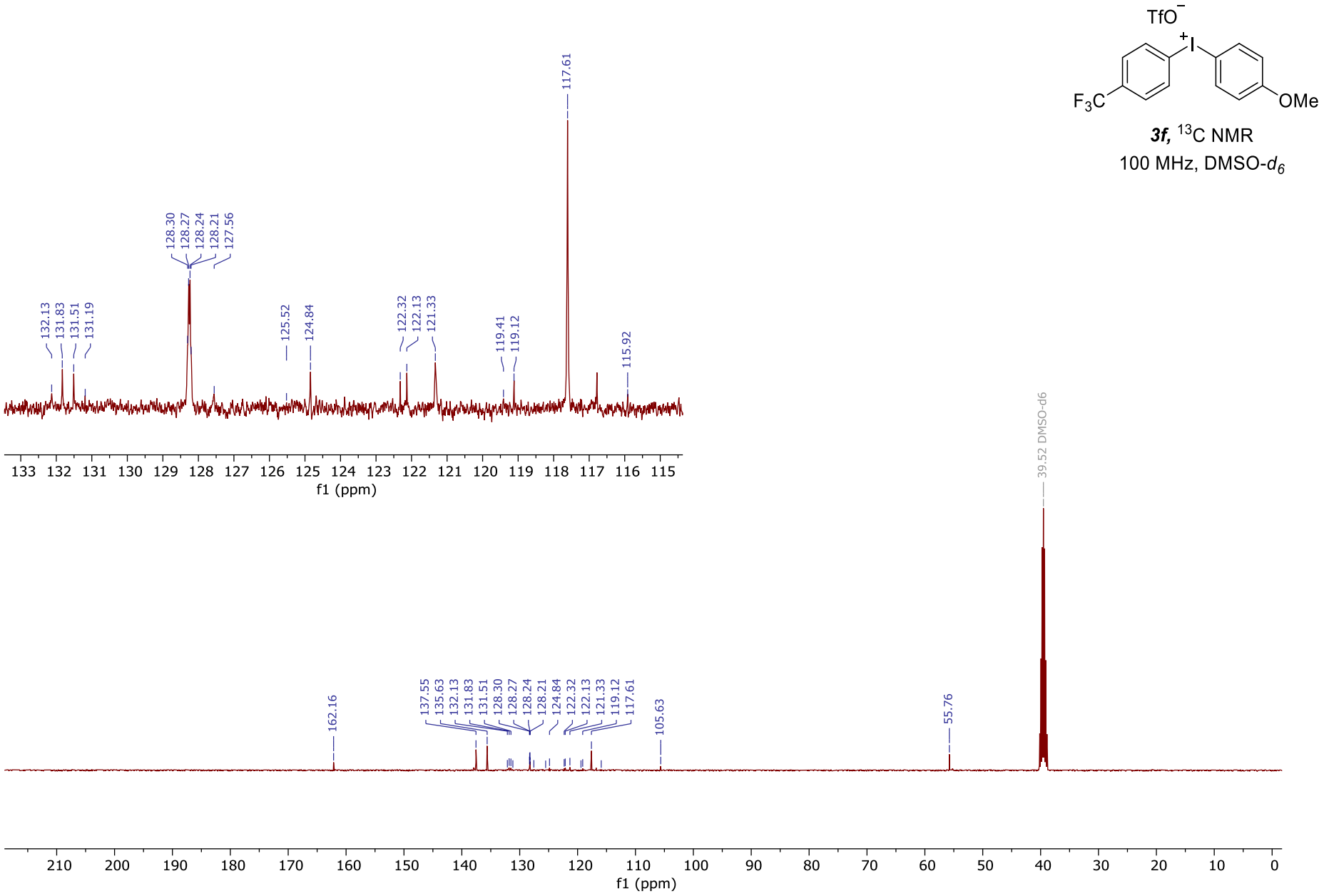


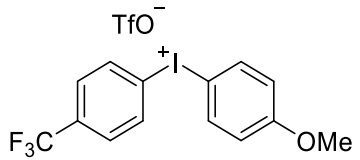


3f, ^{1}H NMR
400 MHz, DMSO-d_6

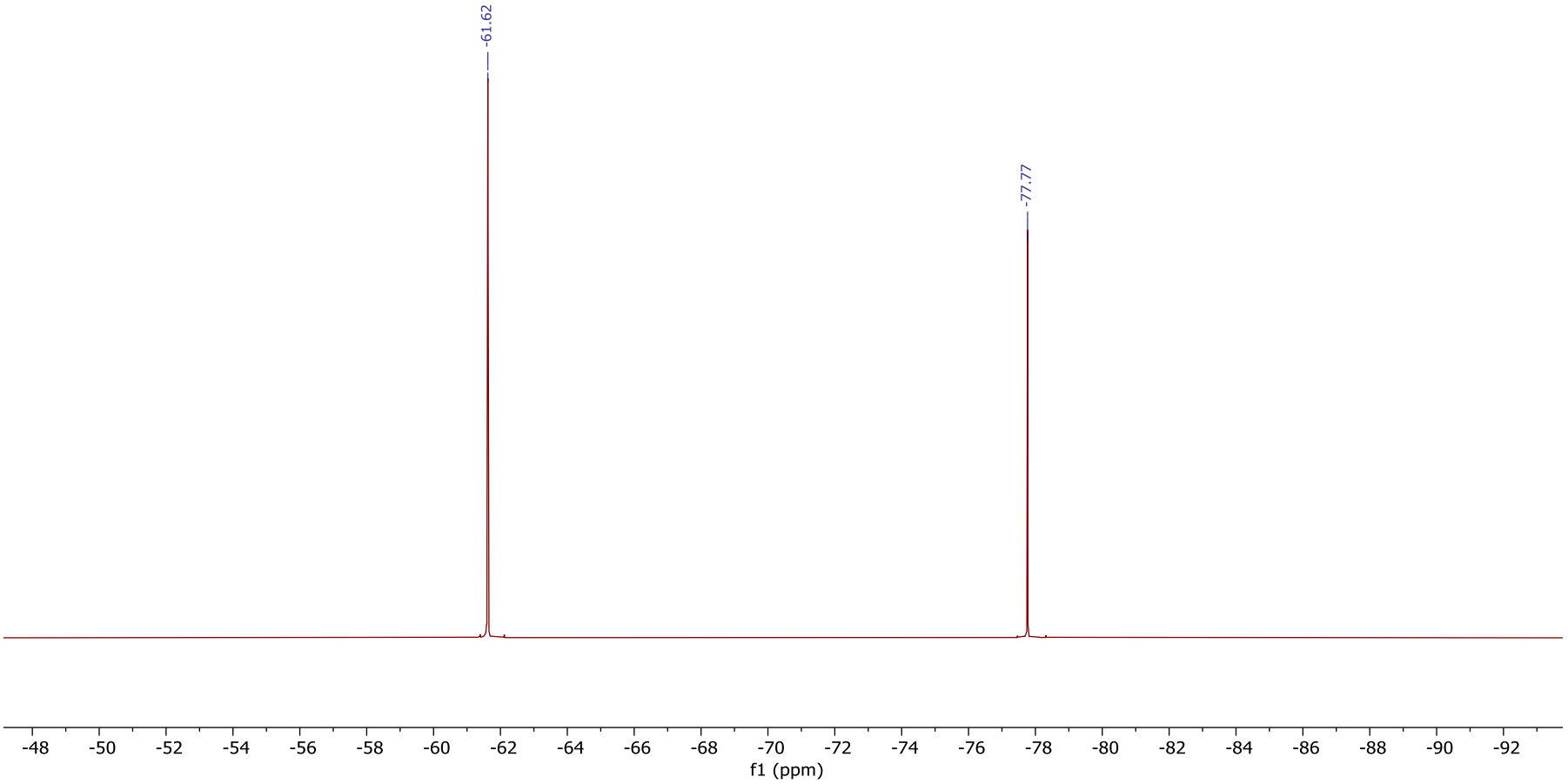


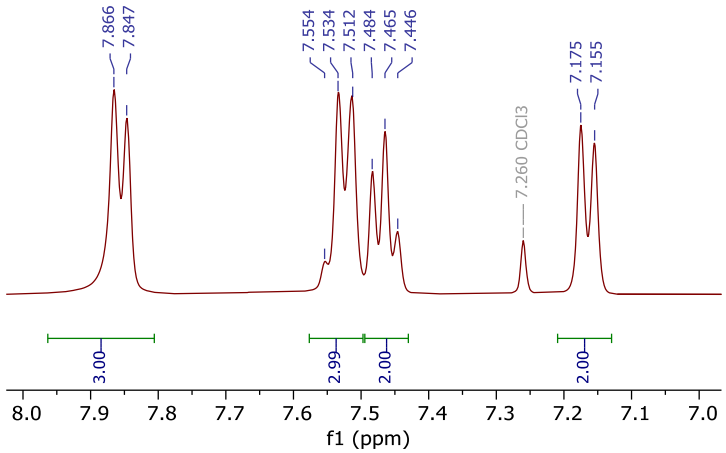


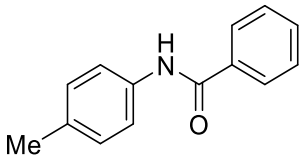

TfO⁻
I⁺
F3C
OMe
3f, 13C NMR
100 MHz, DMSO-d6
117.61
128.30
128.27
128.24
128.21
127.56
132.13
131.83
131.51
131.19
125.52
124.84
122.32
122.13
121.33
119.41
119.12
115.92
133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115
f1 (ppm)
39.52 DMSO-d6
162.16
137.55
135.63
132.13
131.83
131.51
128.30
128.27
128.24
128.21
124.84
122.32
122.13
121.33
119.12
117.61
105.63
55.76
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



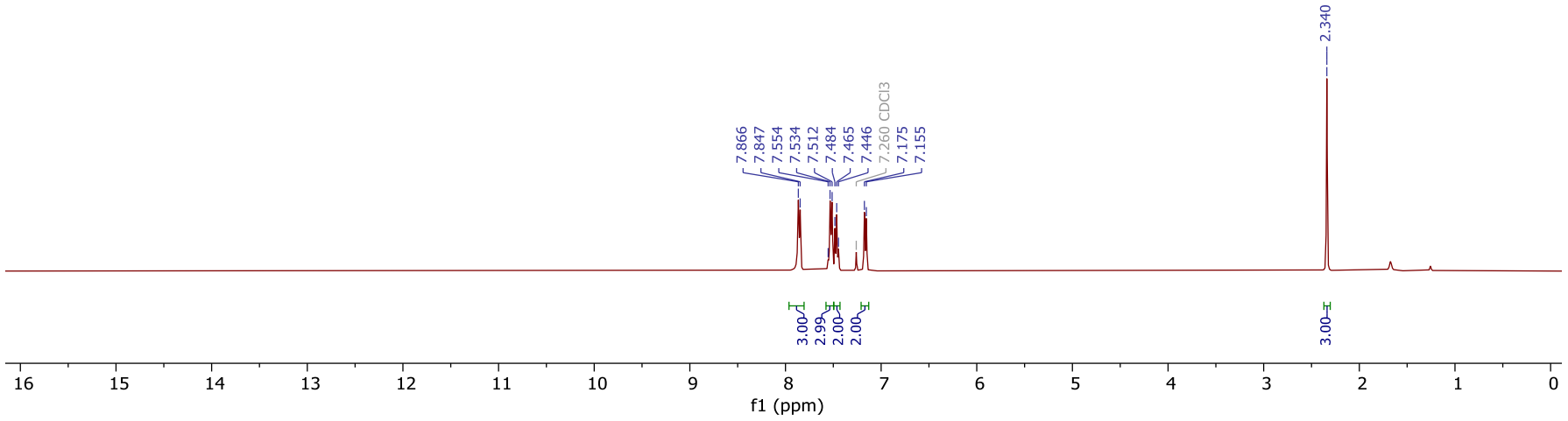
3f, ^{19}F NMR
376 MHz, DMSO-d_6

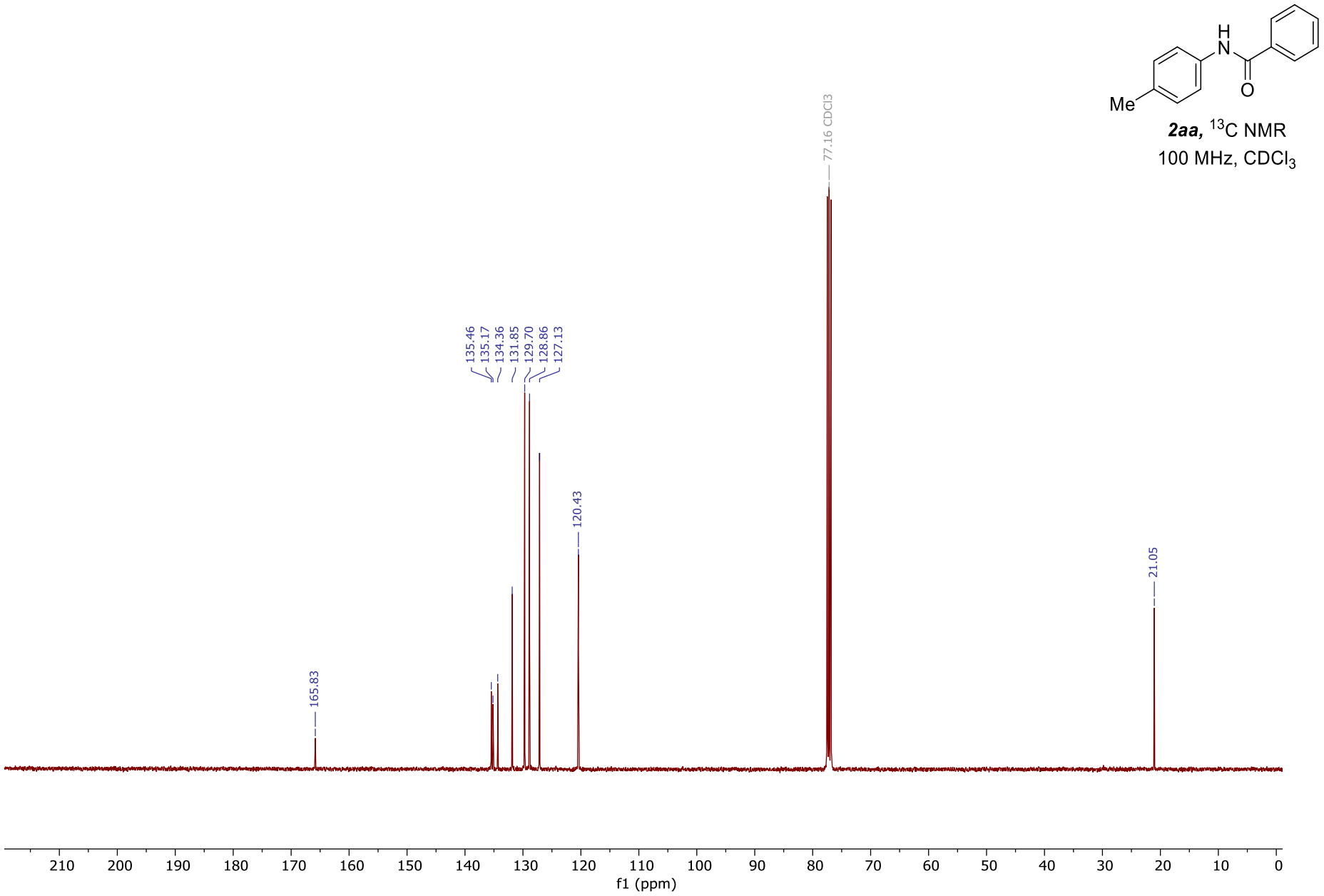


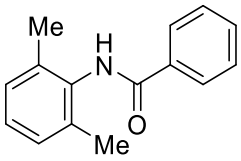




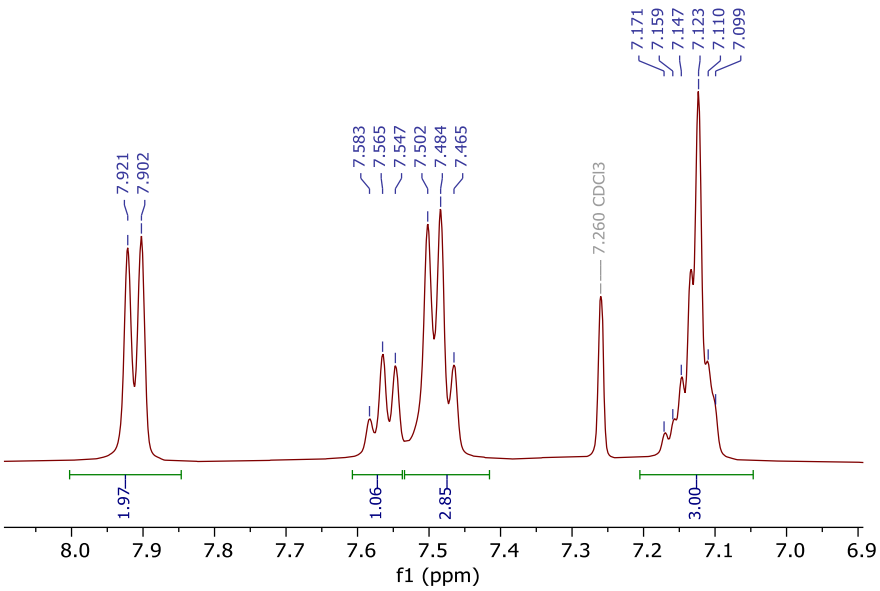
2aa, ^{1}H NMR
400 MHz, $CDCl_3$

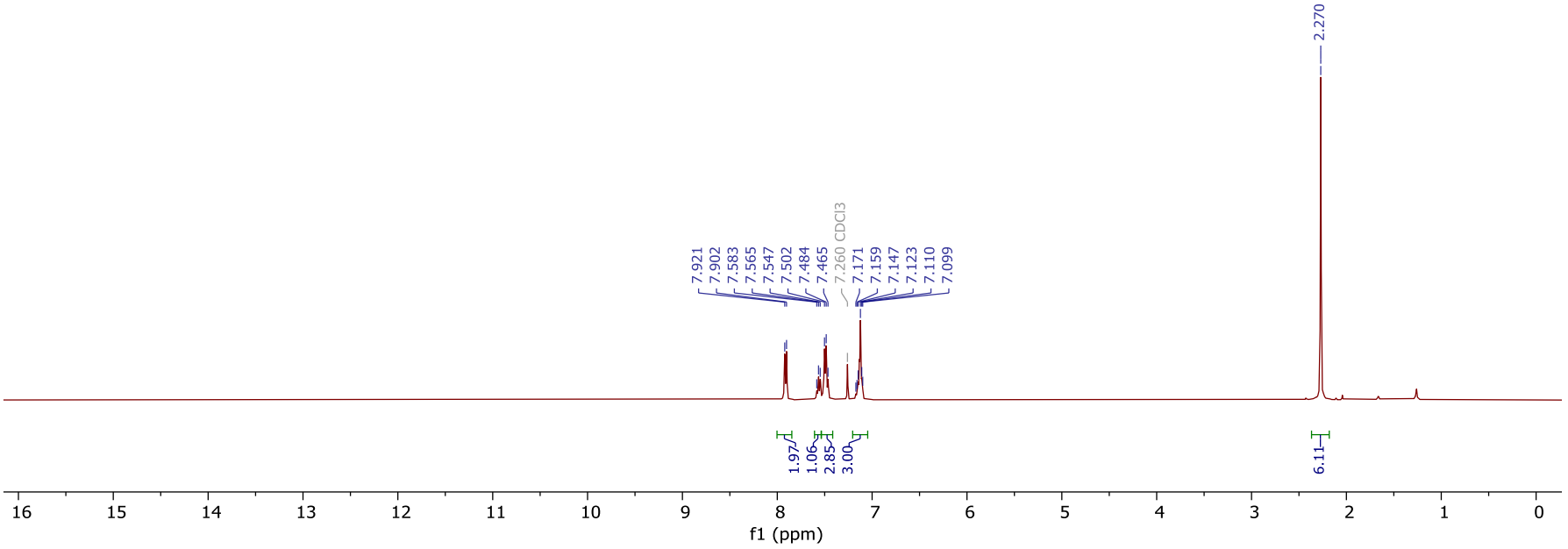


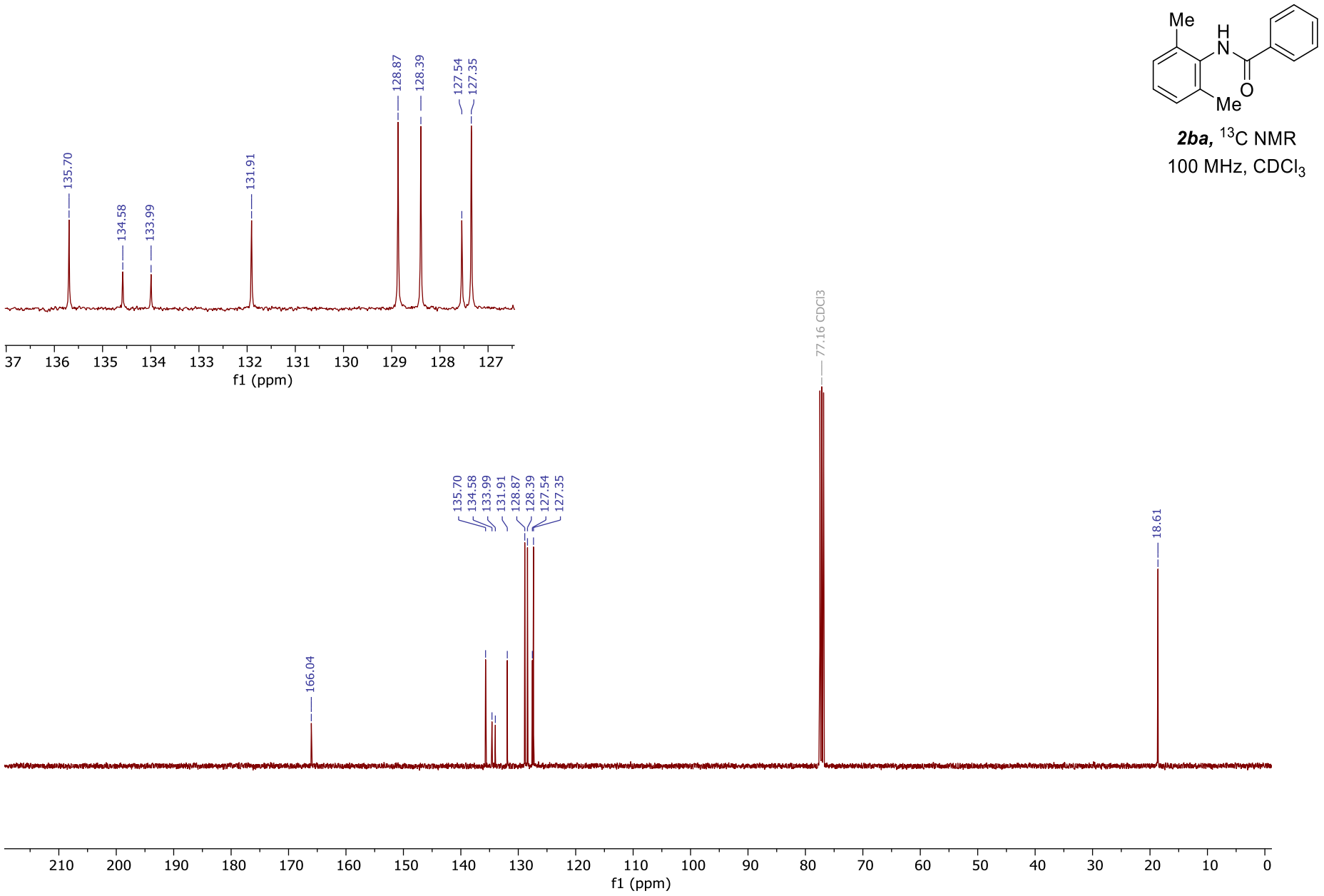

Me
H
N
O
2aa, 13C NMR
100 MHz, CDCl3
77.16 CDCl3
135.46
135.17
134.36
131.85
129.70
128.86
127.13
120.43
165.83
21.05
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

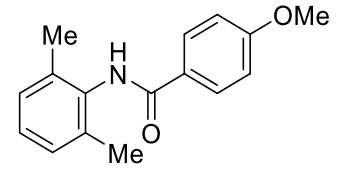


2ba, ^{1}H NMR
400 MHz, $CDCl_3$

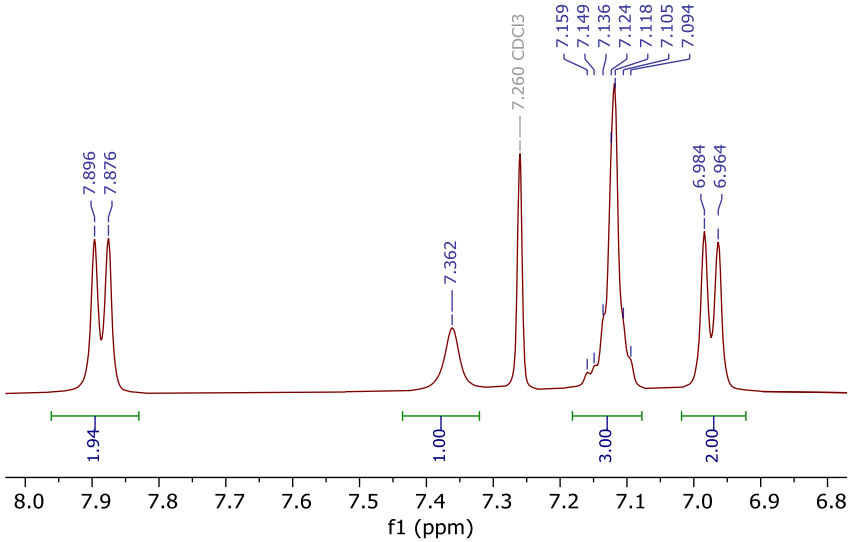


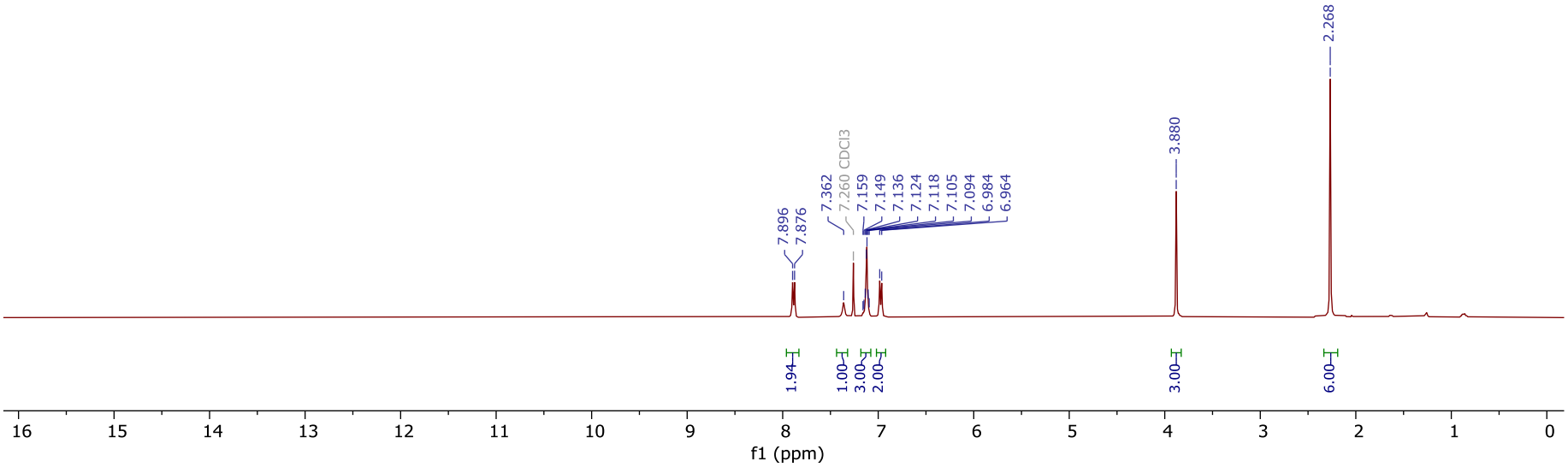


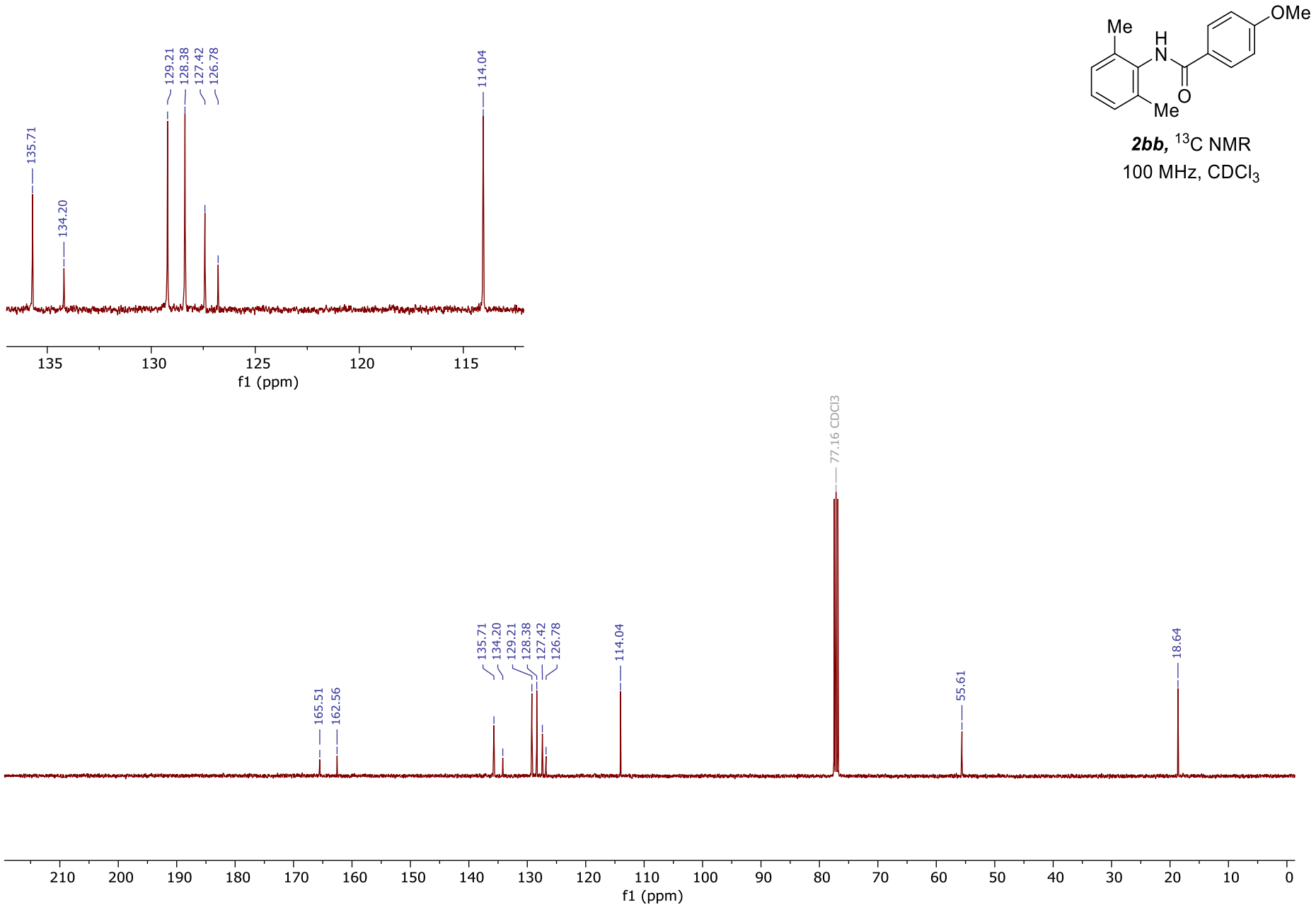

Me
H
N
O
Me
2ba, 13C NMR
100 MHz, CDCl3
135.70
134.58
133.99
131.91
128.87
128.39
127.54
127.35
77.16 CDCl3
18.61
166.04
f1 (ppm)



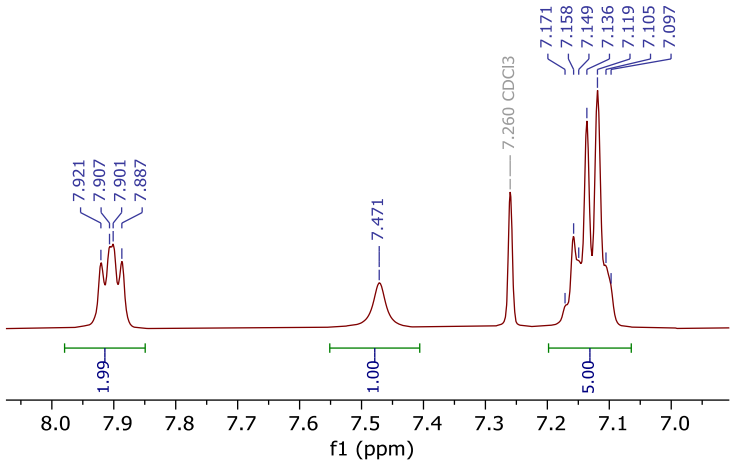
2bb, ^{1}H NMR
400 MHz, $CDCl_3$

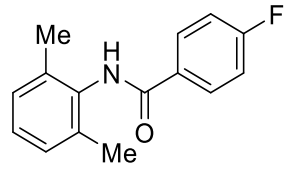




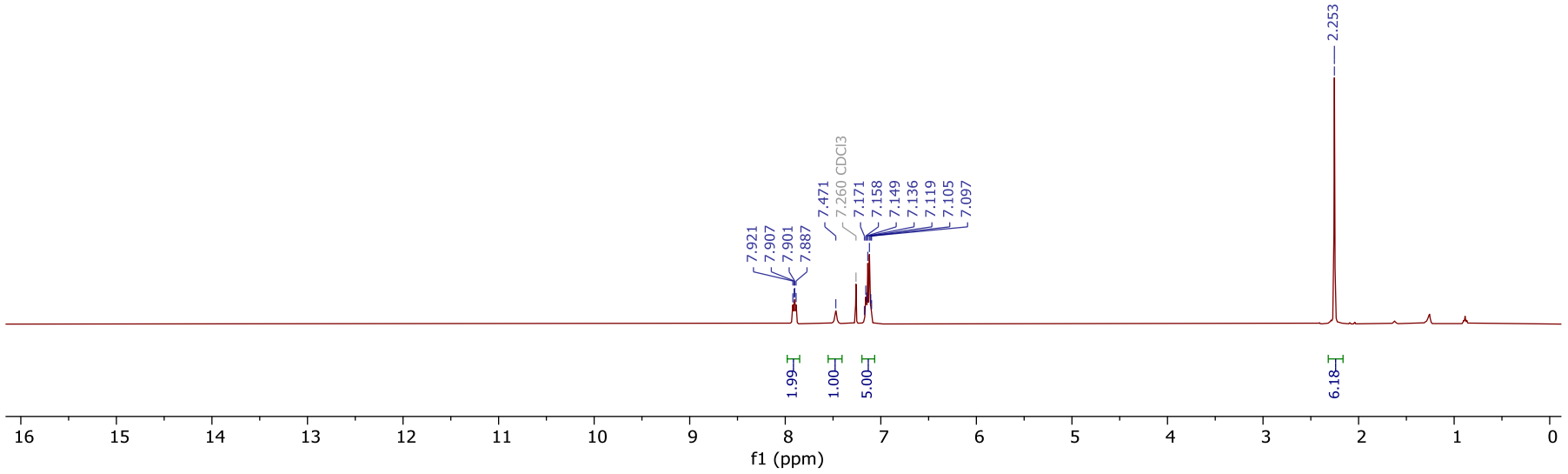


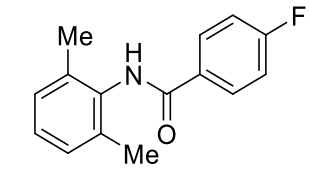
2bb, ^{13}C NMR
100 MHz, $CDCl_3$



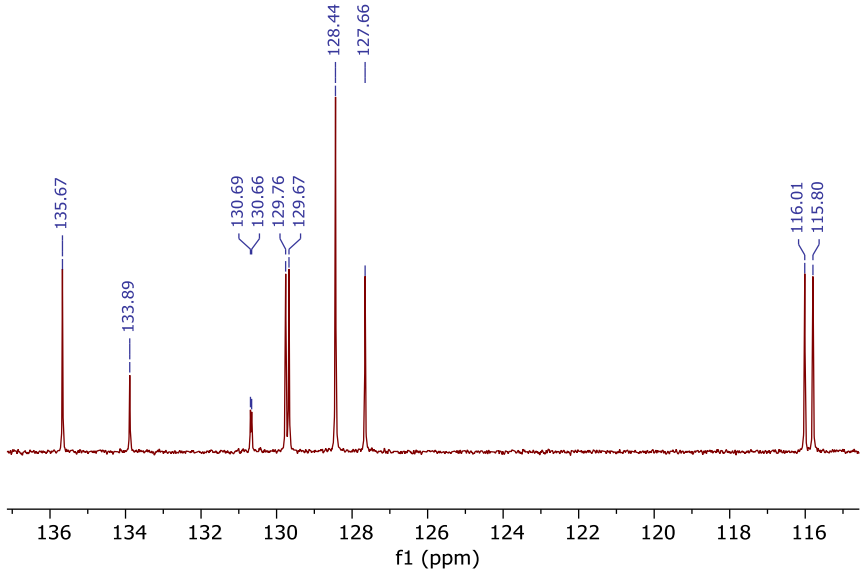


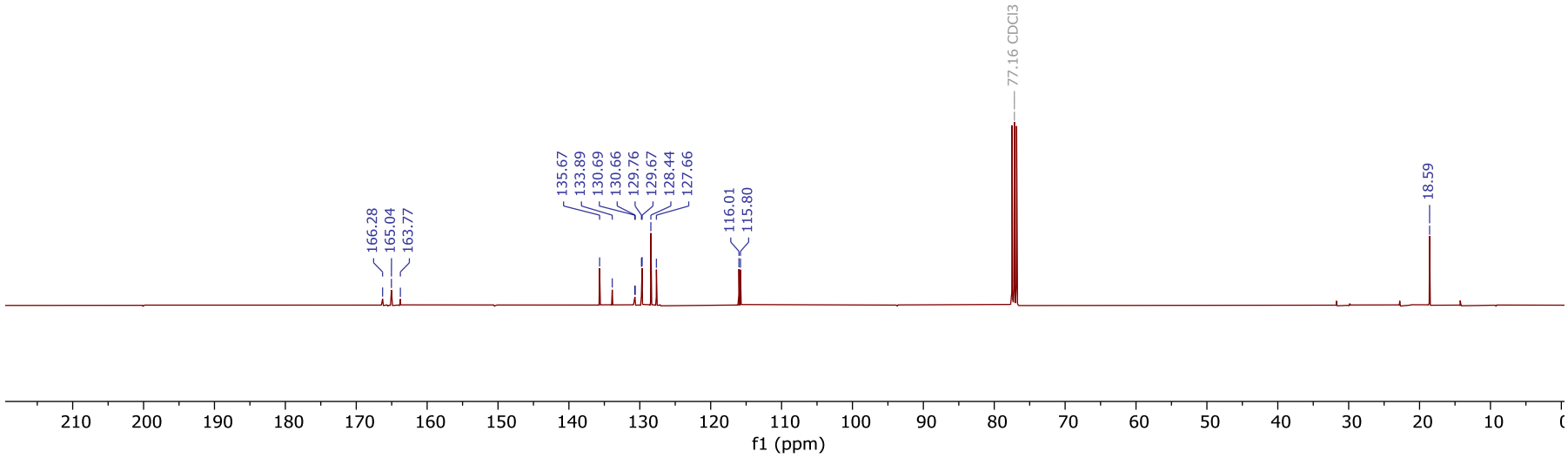
2bc, ^{1}H NMR
400 MHz, $CDCl_3$

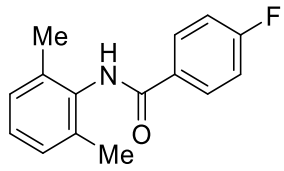




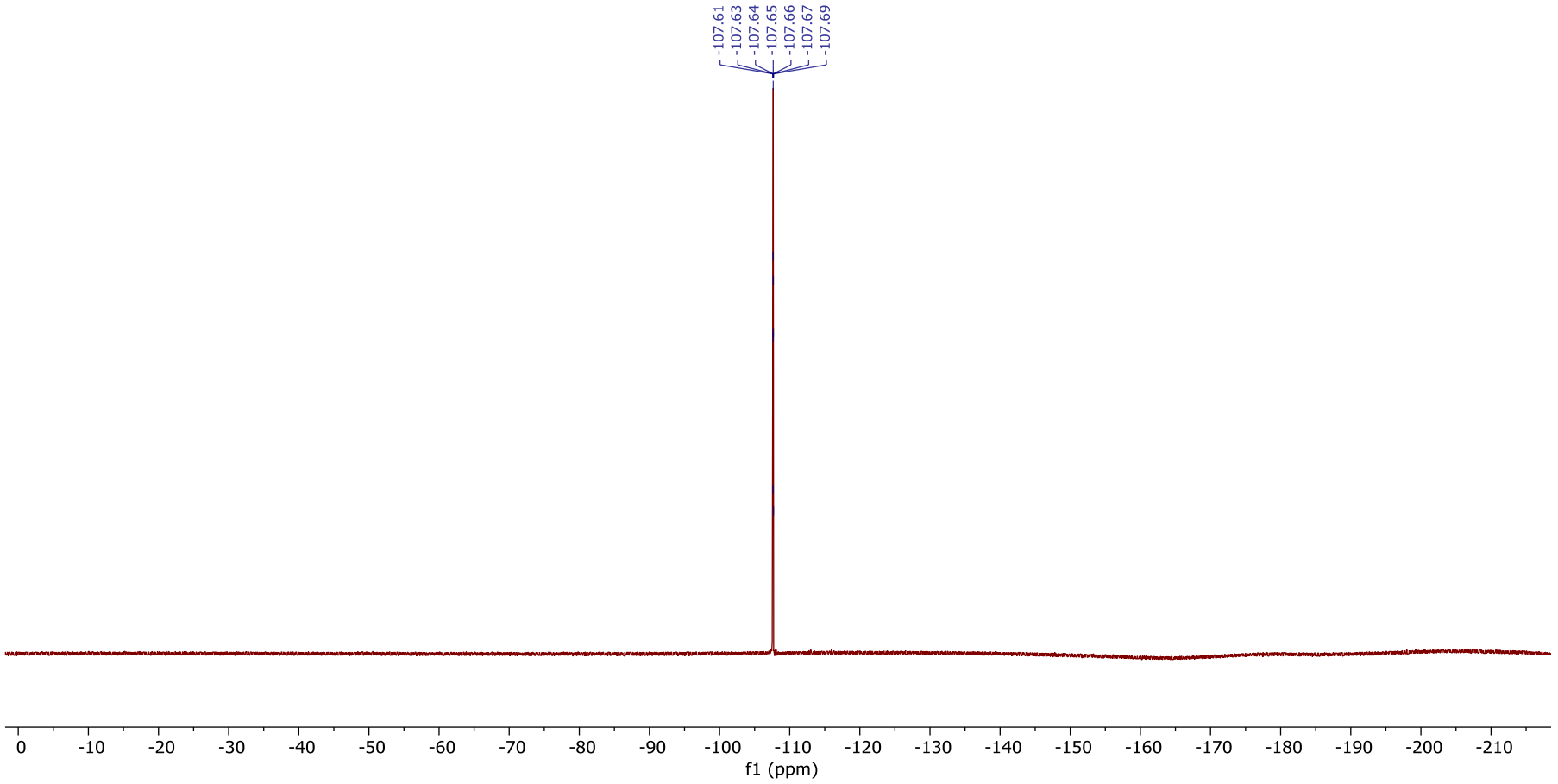
2bc, ^{13}C NMR
100 MHz, $CDCl_3$

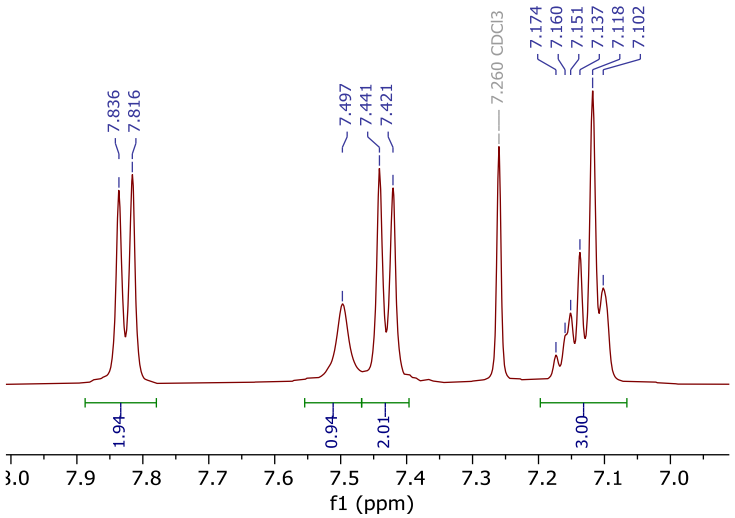


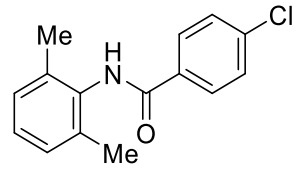




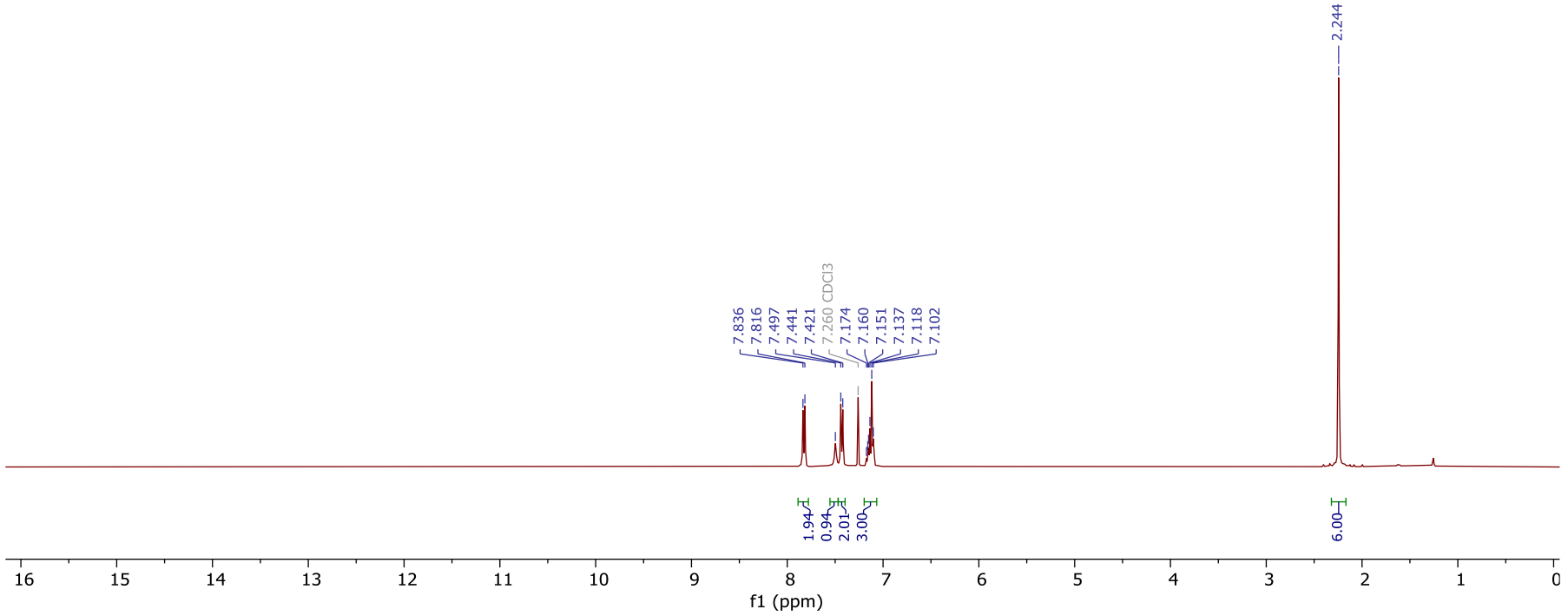
2bc, ^{19}F NMR
376 MHz, $CDCl_3$

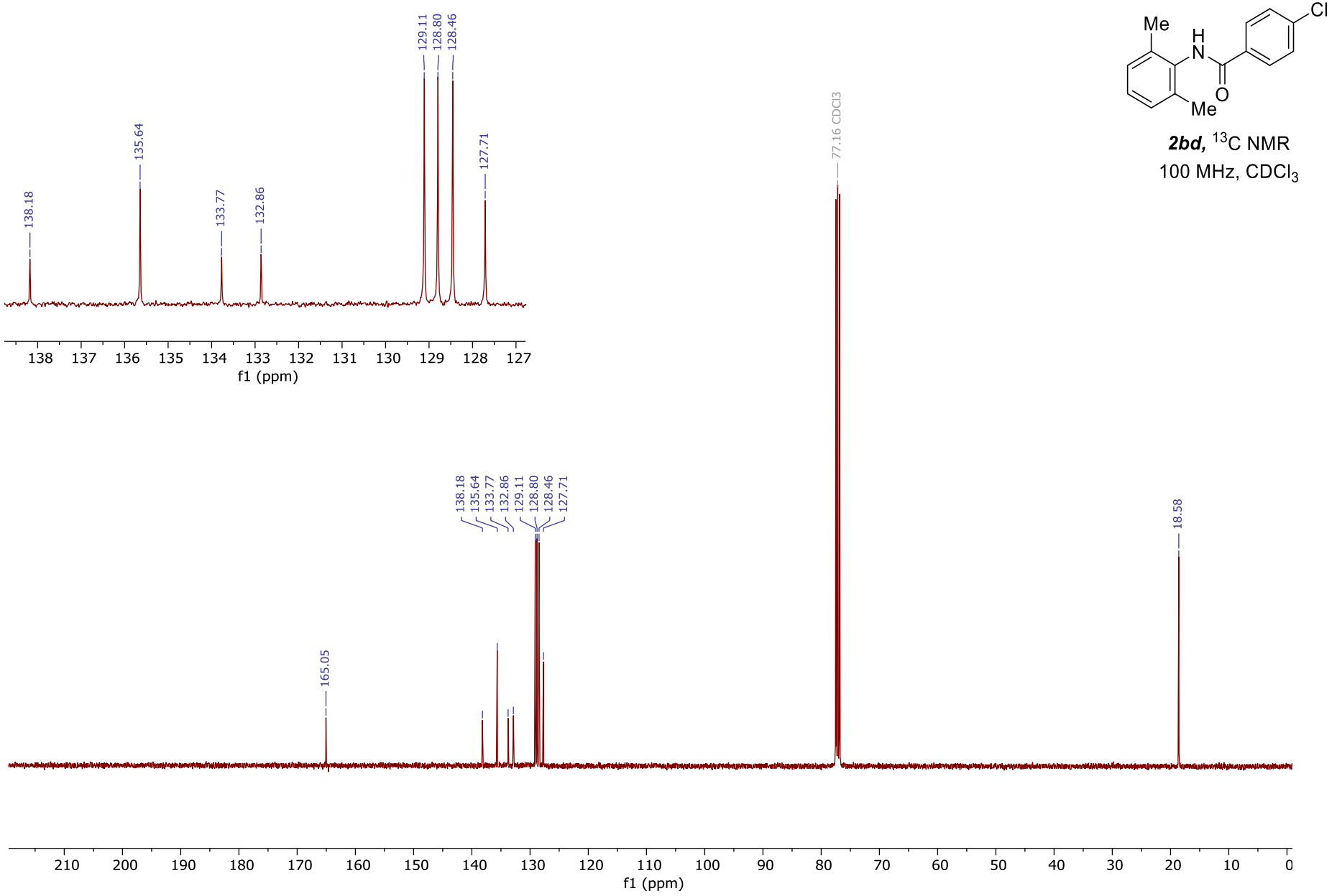


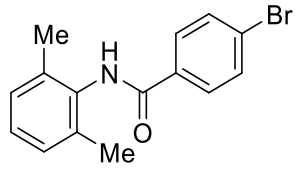




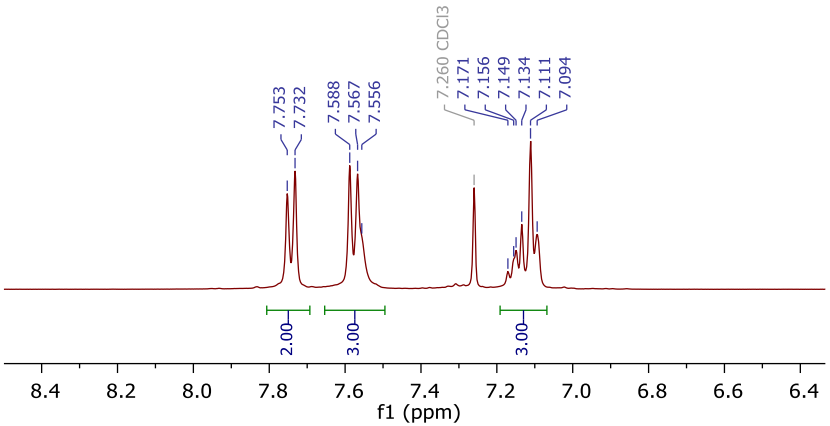
2bd, ^{1}H NMR
400 MHz, $CDCl_3$

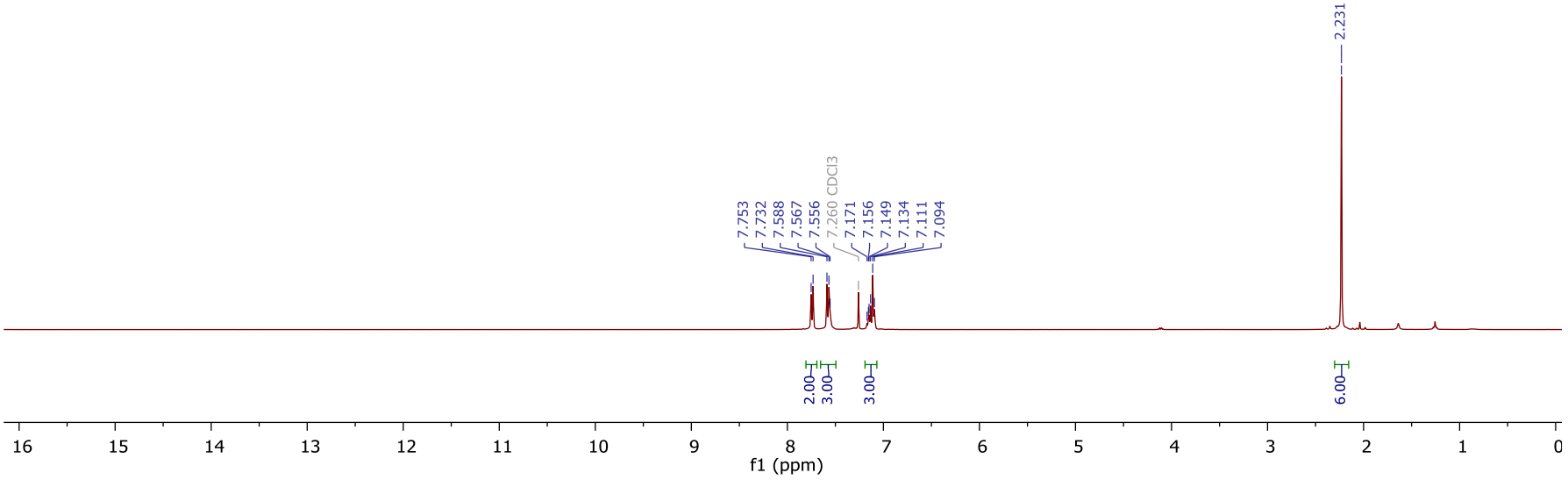


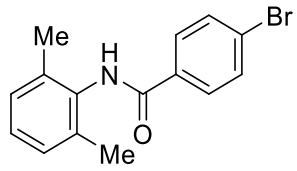

Me
H
N
O
Cl
Me
2bd, 13C NMR
100 MHz, CDCl3
138.18
135.64
133.77
132.86
129.11
128.80
128.46
127.71
77.16 CDCl3
18.58
165.05
f1 (ppm)



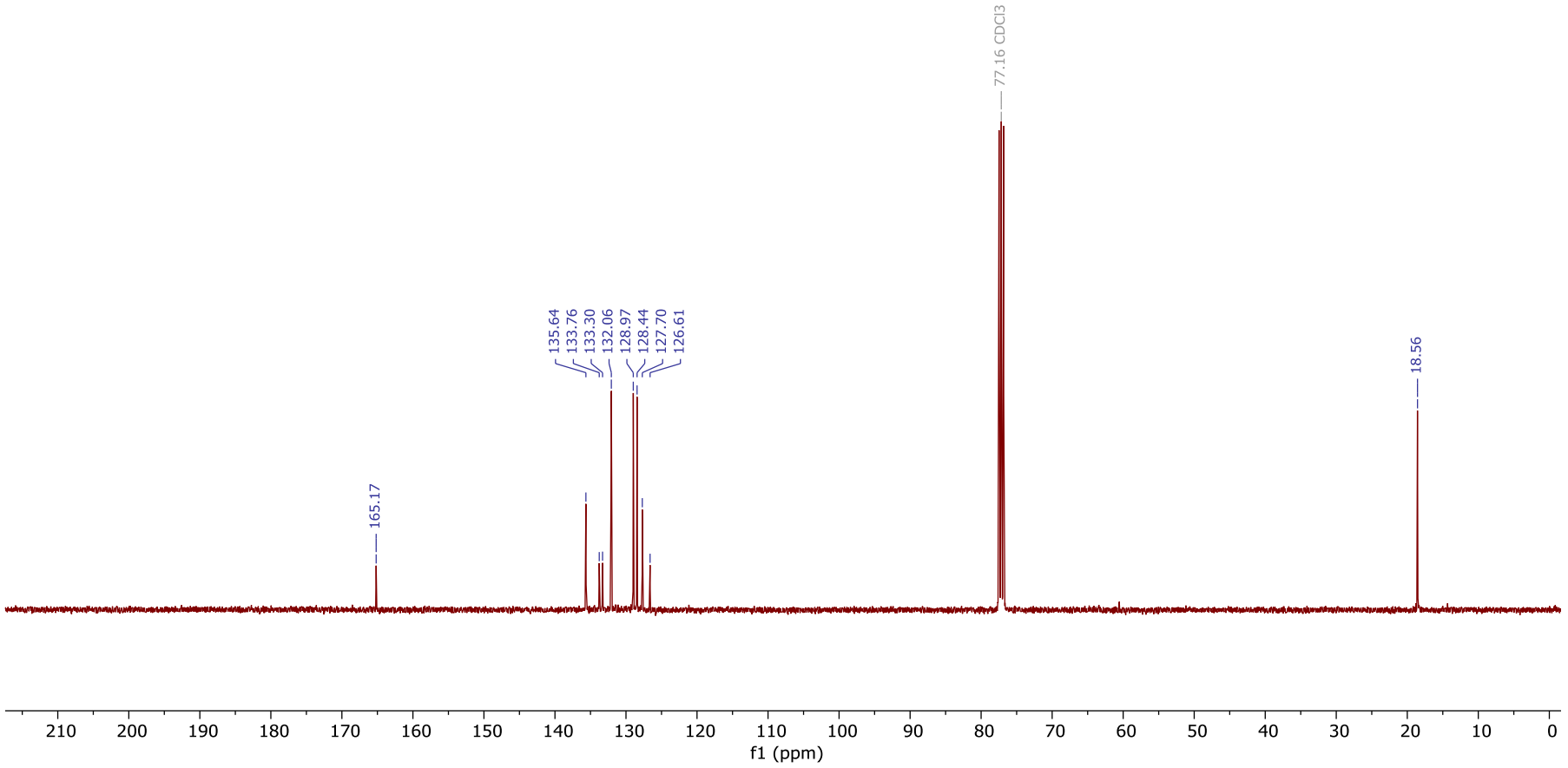
2be, ^{1}H NMR
400 MHz, $CDCl_3$

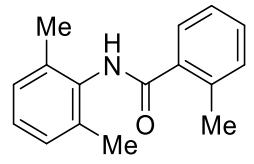




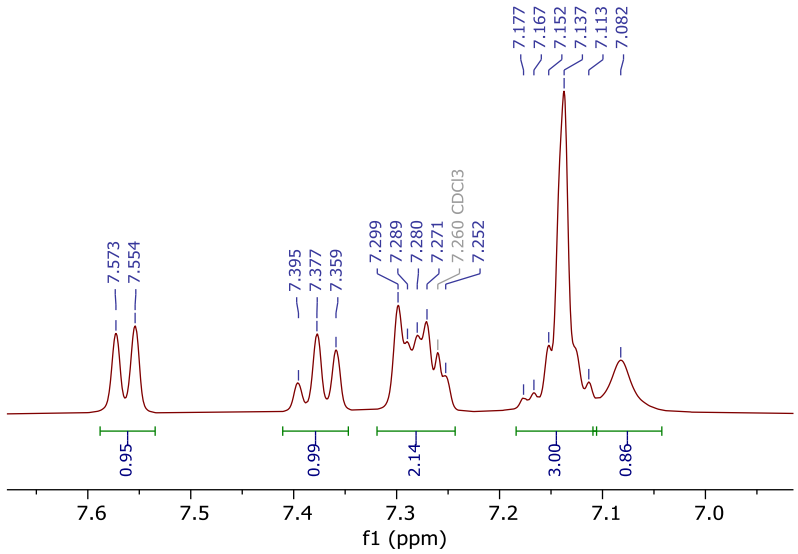


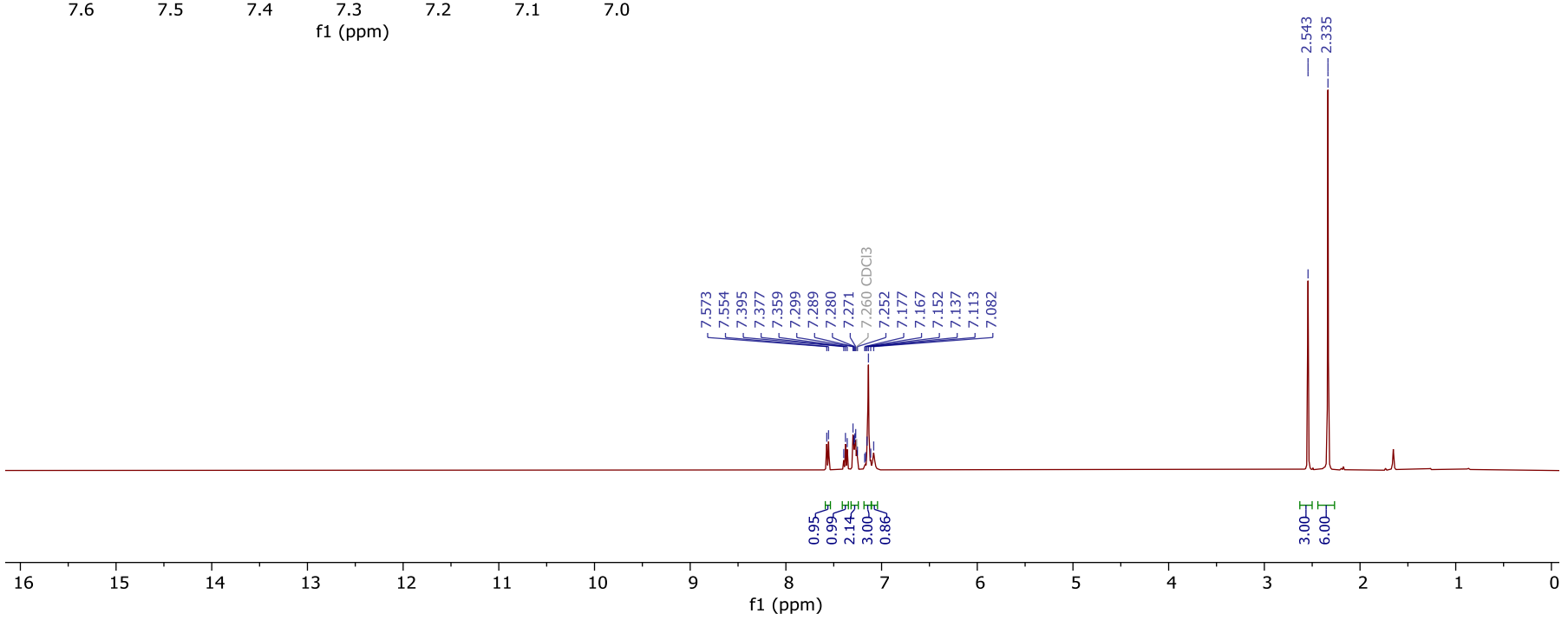
2be, ^{13}C NMR
100 MHz, $CDCl_3$

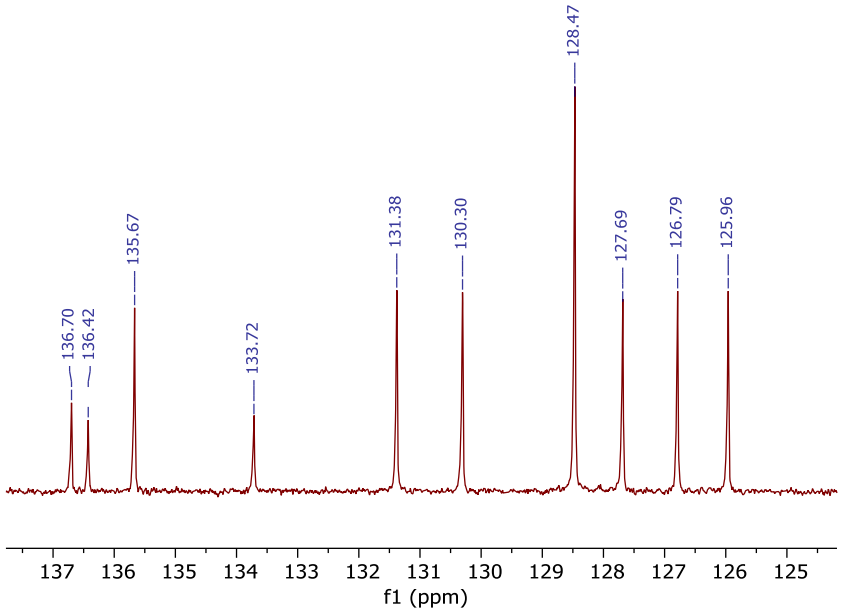


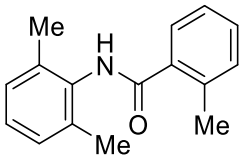


2bf, ^{1}H NMR
400 MHz, $CDCl_3$

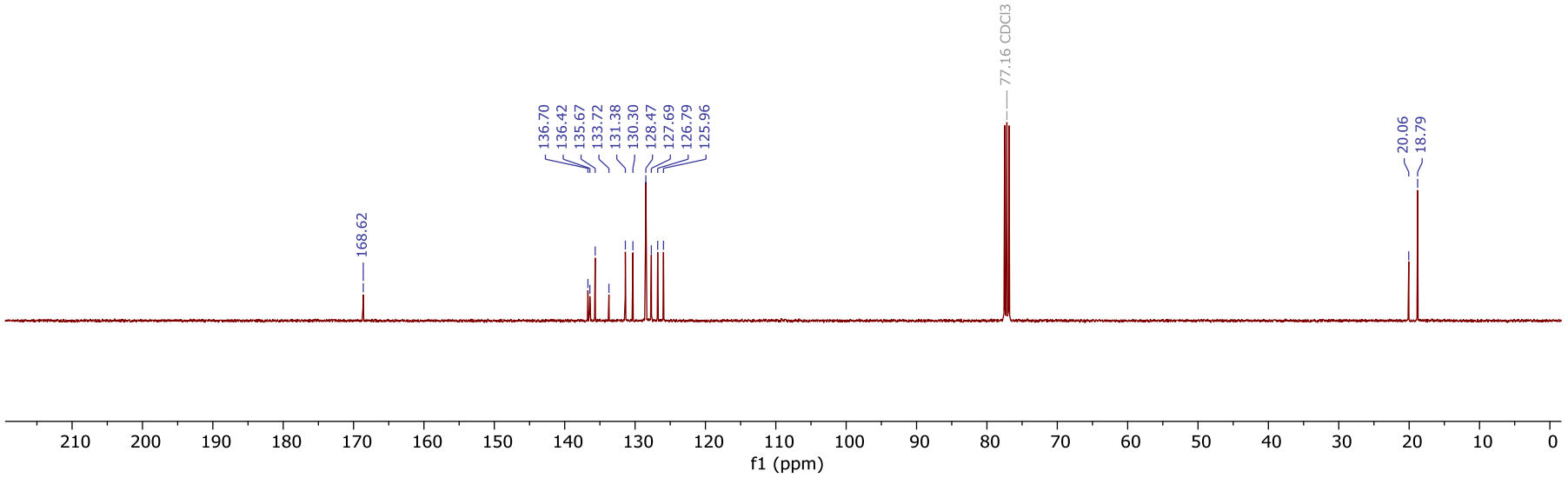


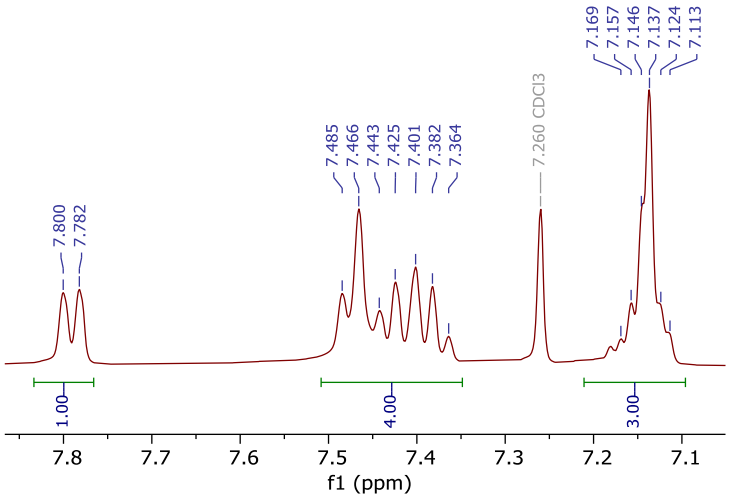


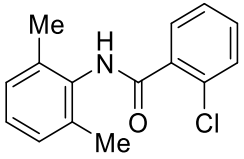




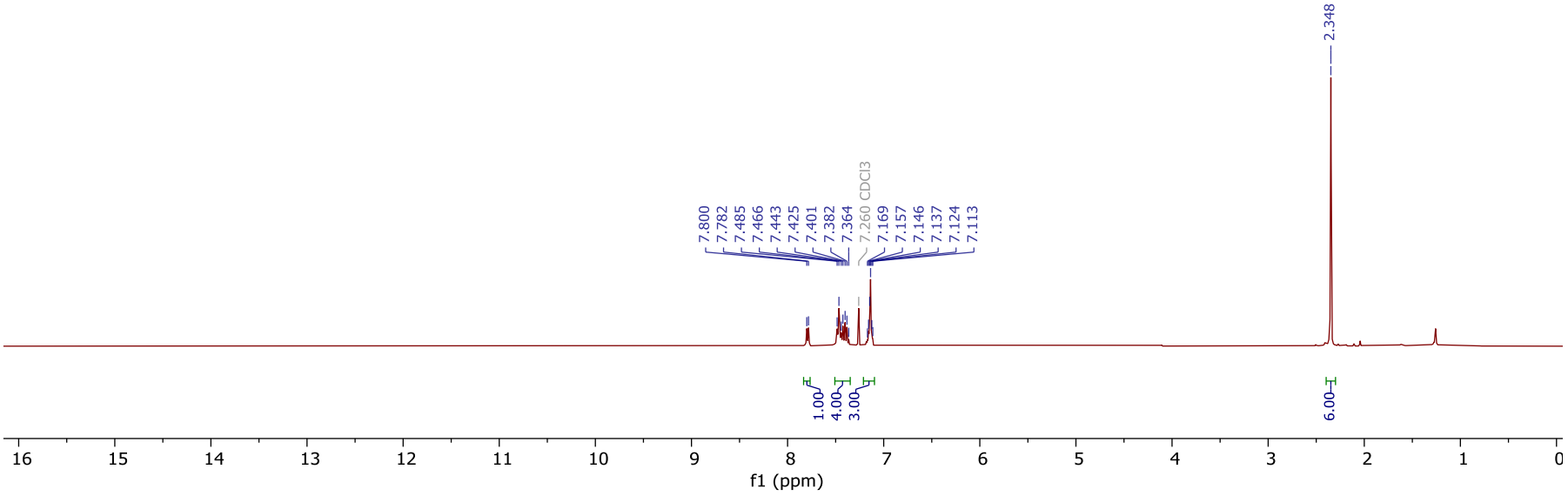
2bf, ^{13}C NMR
100 MHz, $CDCl_3$

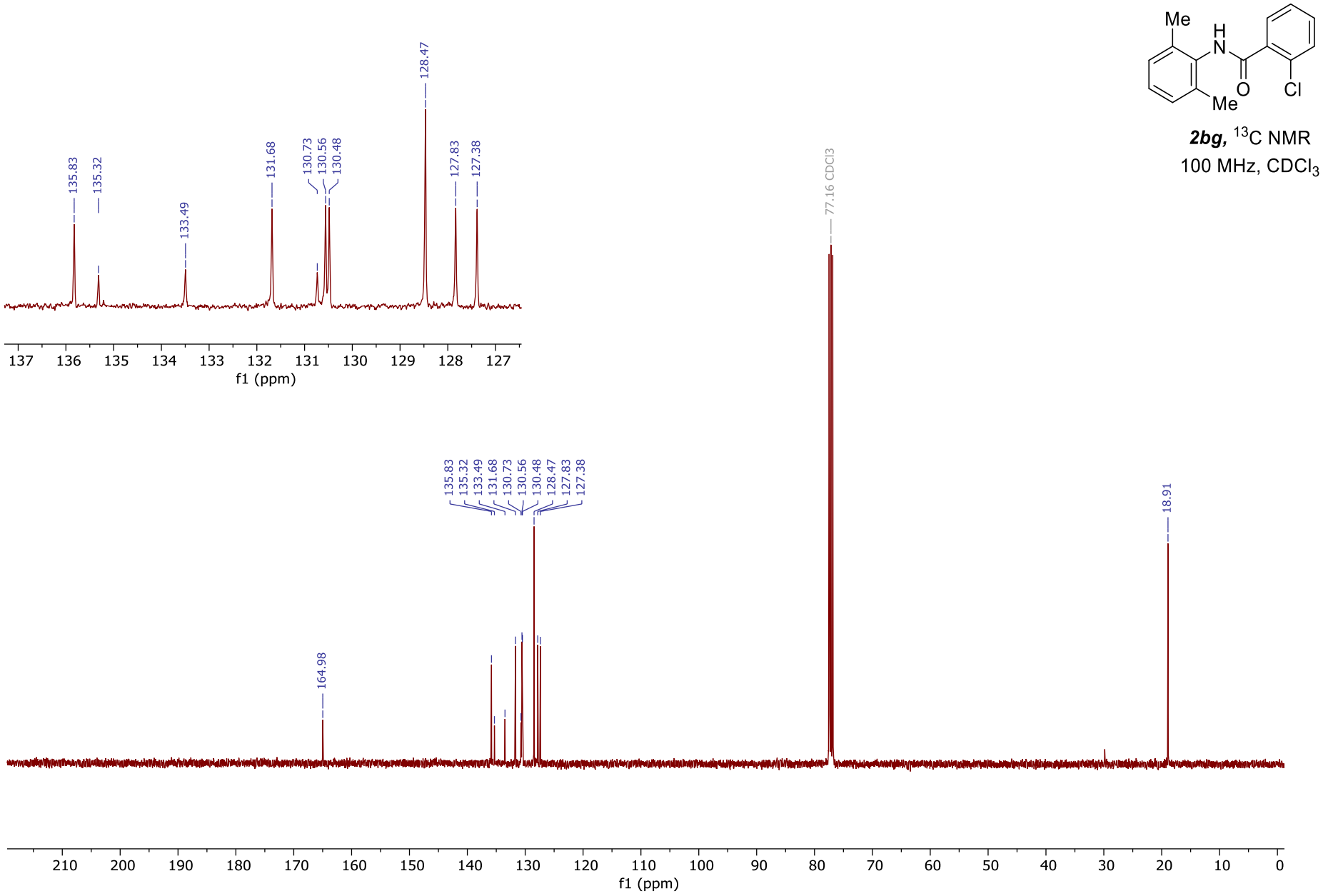


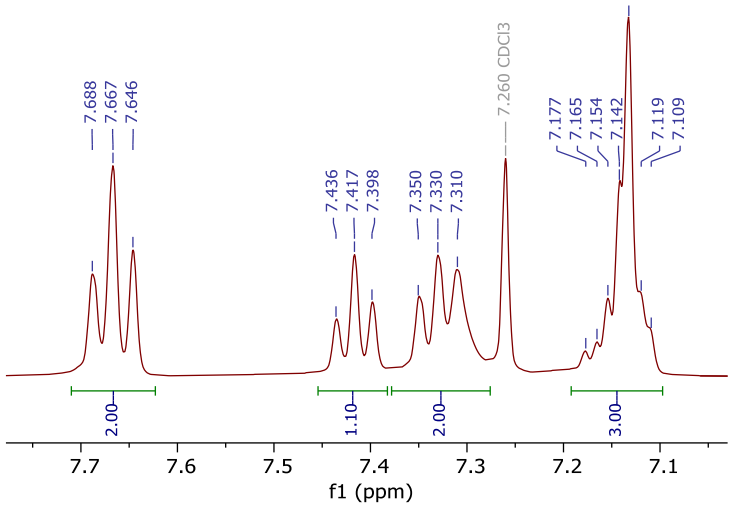


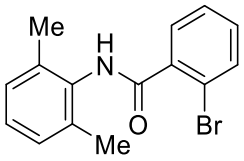


2bg, ^{1}H NMR
400 MHz, $CDCl_3$

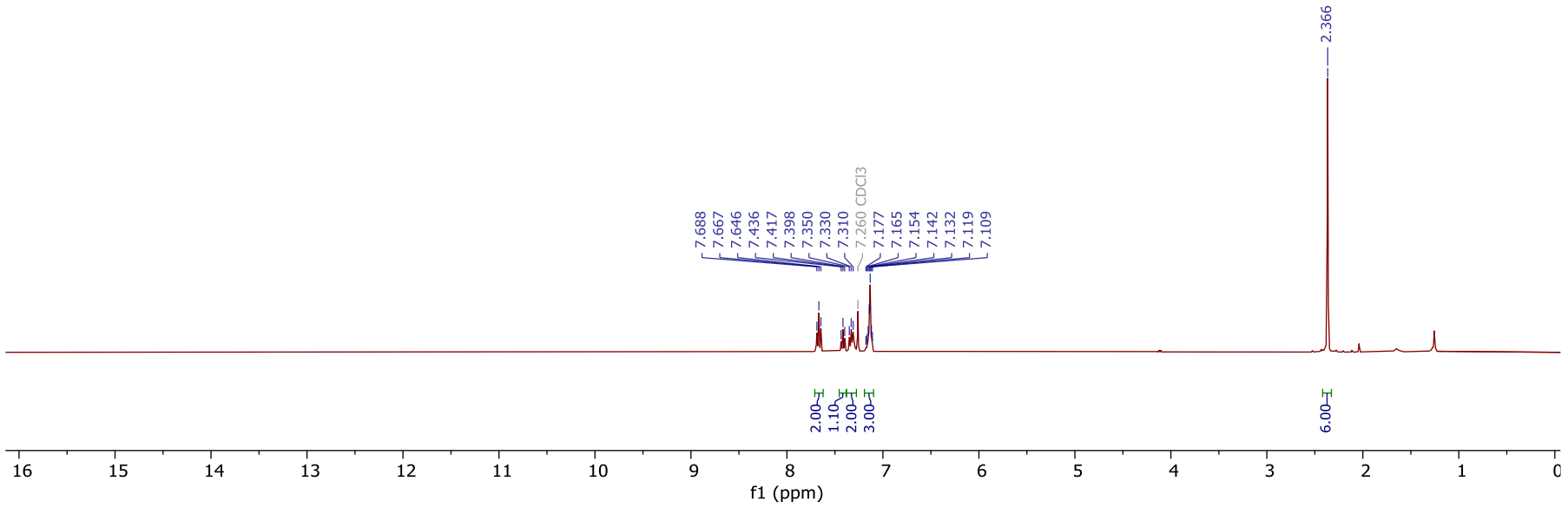


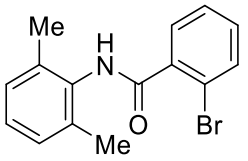

Me
H
N
O
Cl
Me
2bg, 13C NMR
100 MHz, CDCl3
135.83
135.32
133.49
131.68
130.73
130.56
130.48
128.47
127.83
127.38
77.16 CDCl3
18.91
164.98
f1 (ppm)



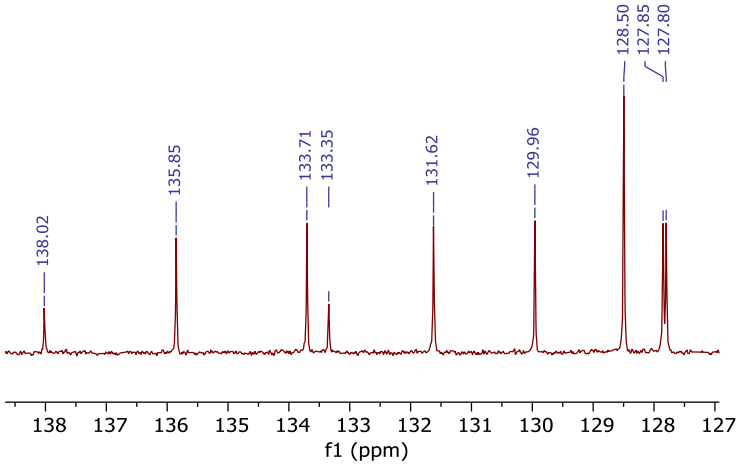


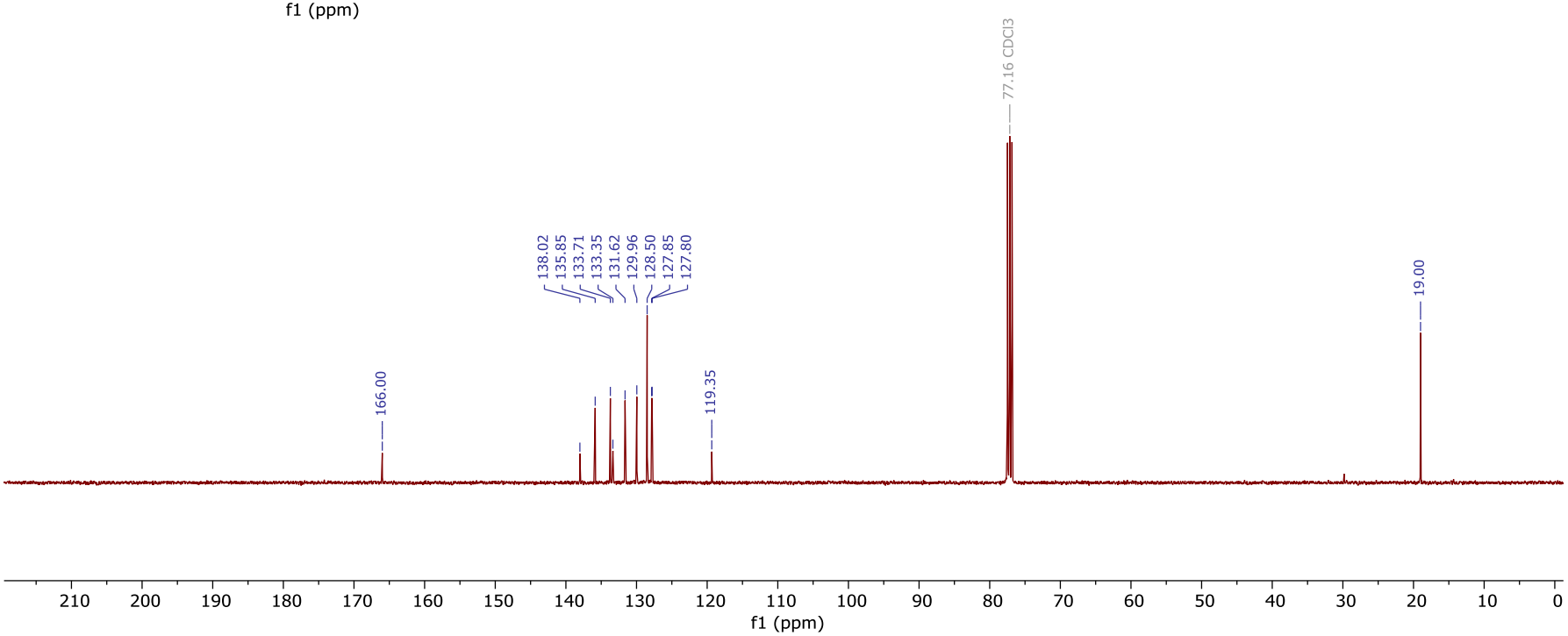
2bh, ^{1}H NMR
400 MHz, $CDCl_3$

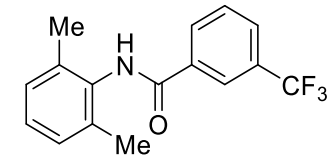




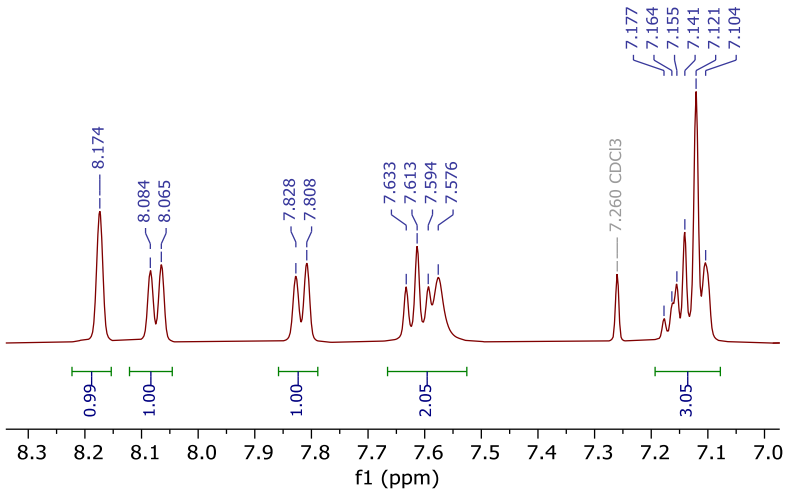
2bh, ^{13}C NMR
100 MHz, $CDCl_3$

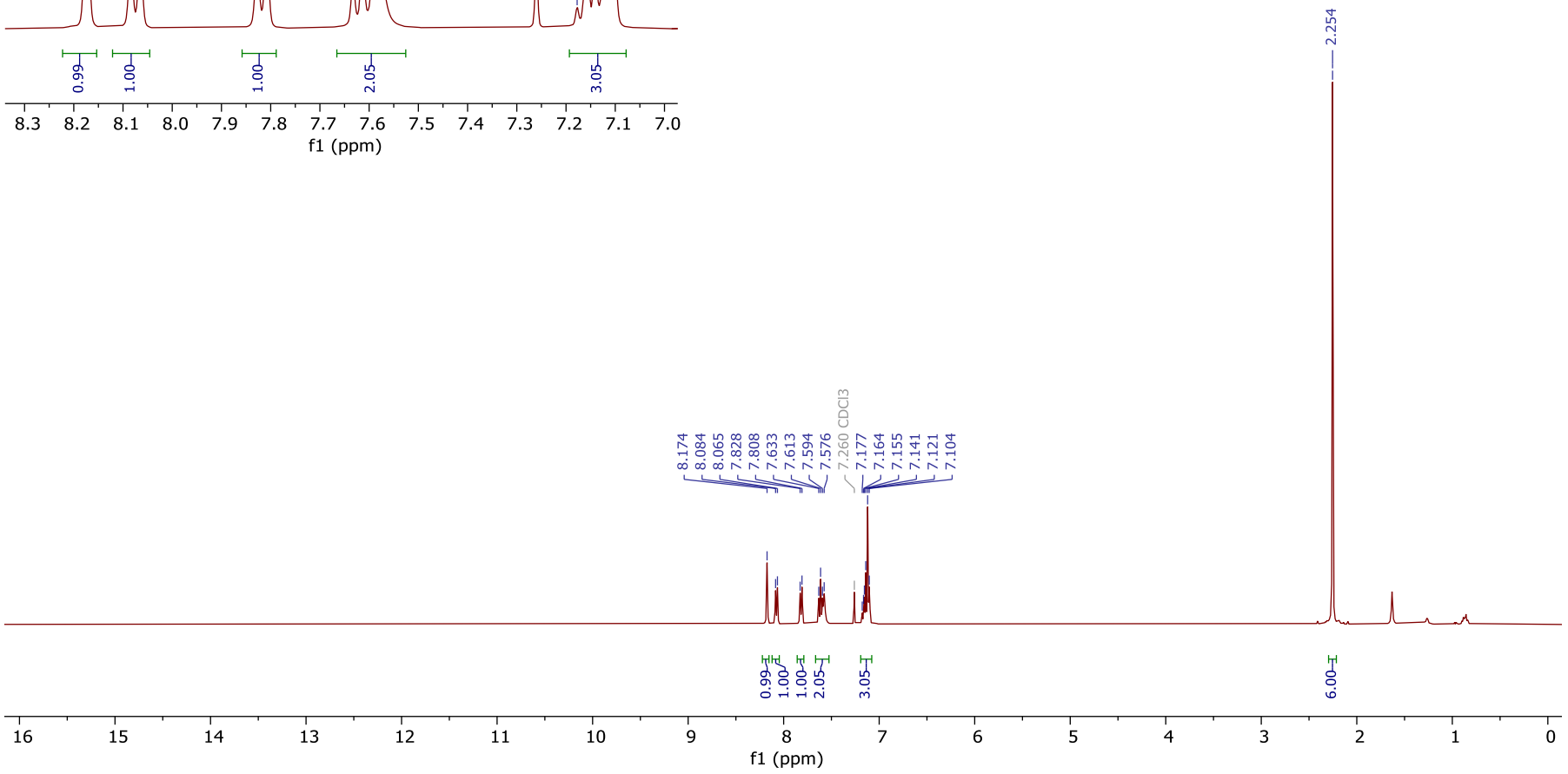


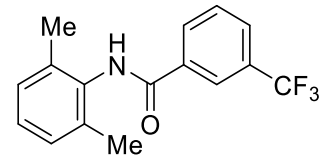




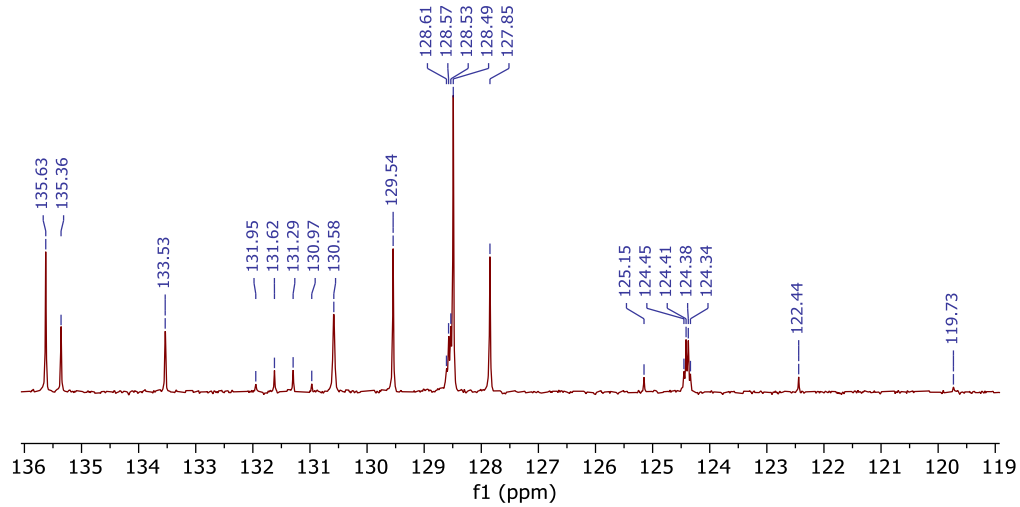
2bi, ^{1}H NMR
400 MHz, $CDCl_3$

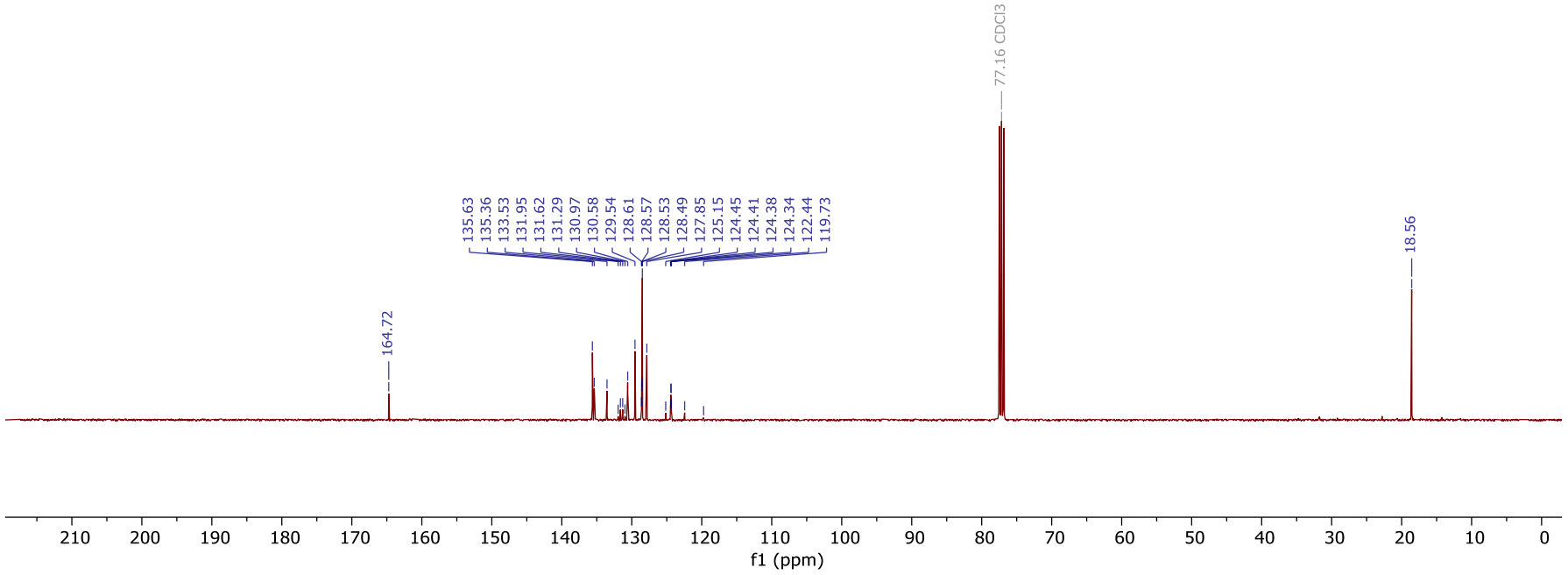


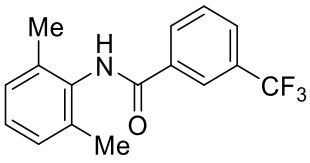




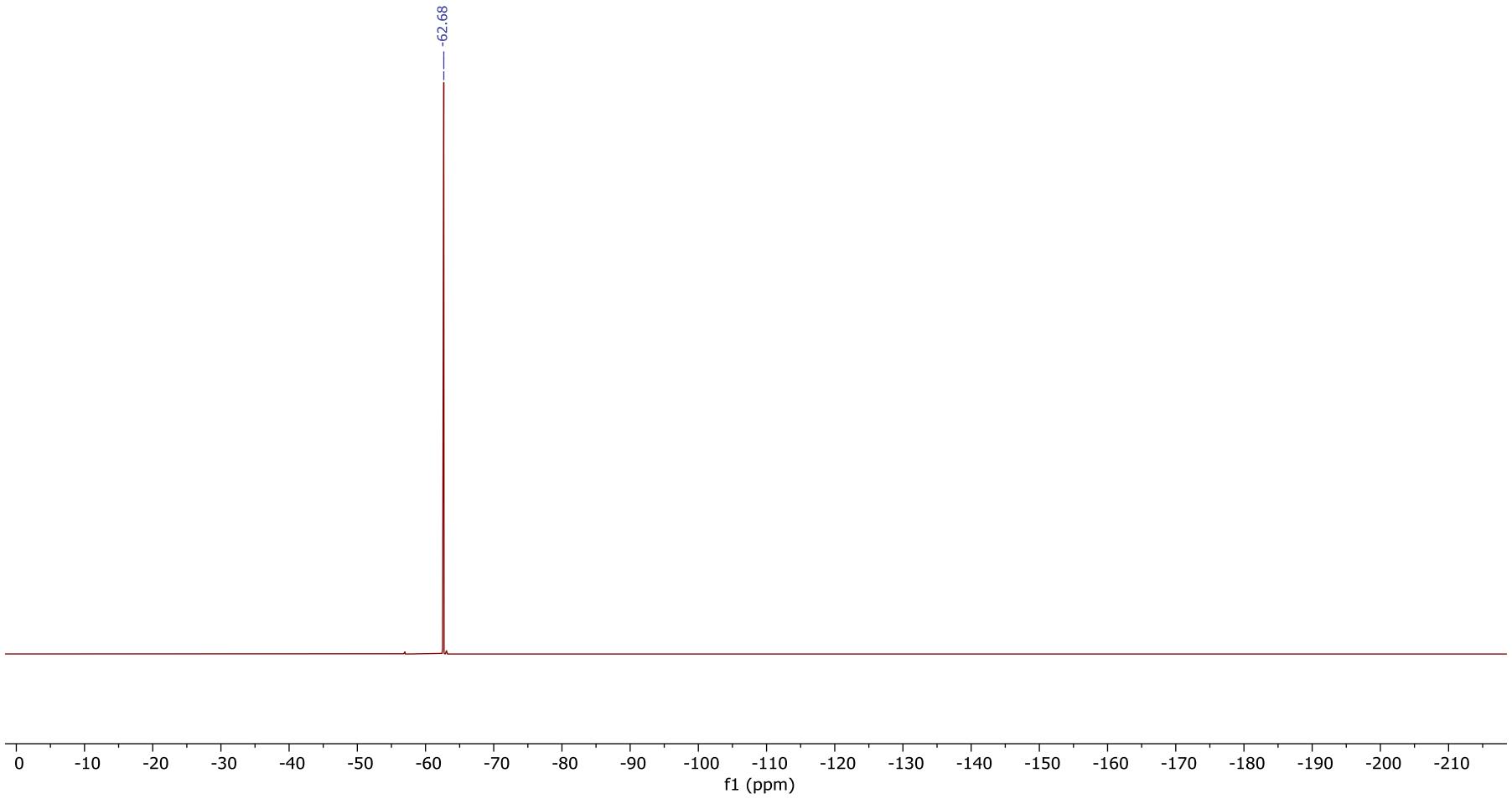
2bi, ^{13}C NMR
100 MHz, $CDCl_3$

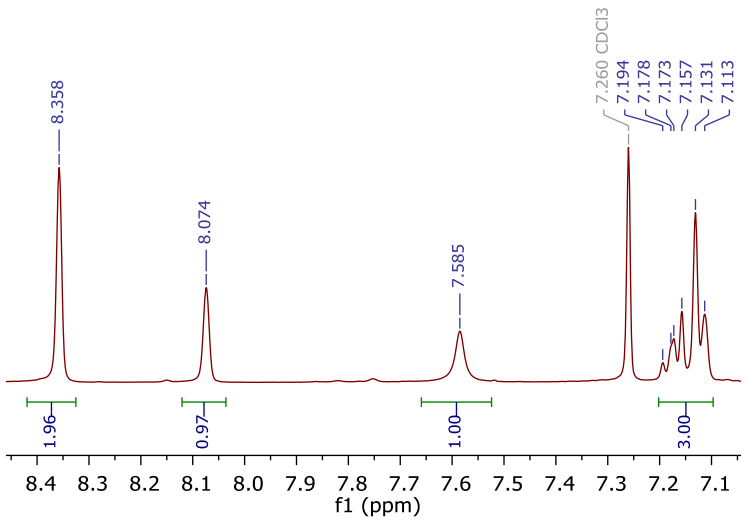


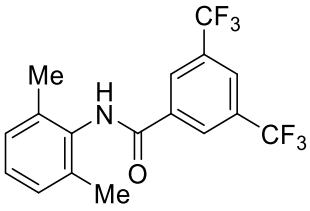




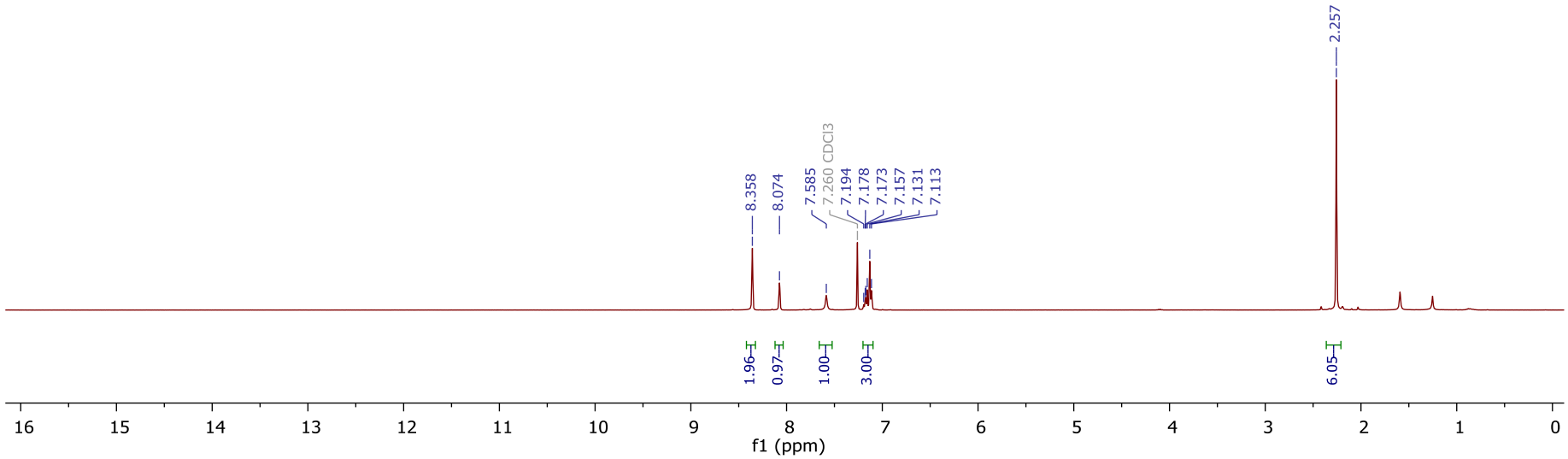
2bi, ^{19}F NMR
376 MHz, $CDCl_3$

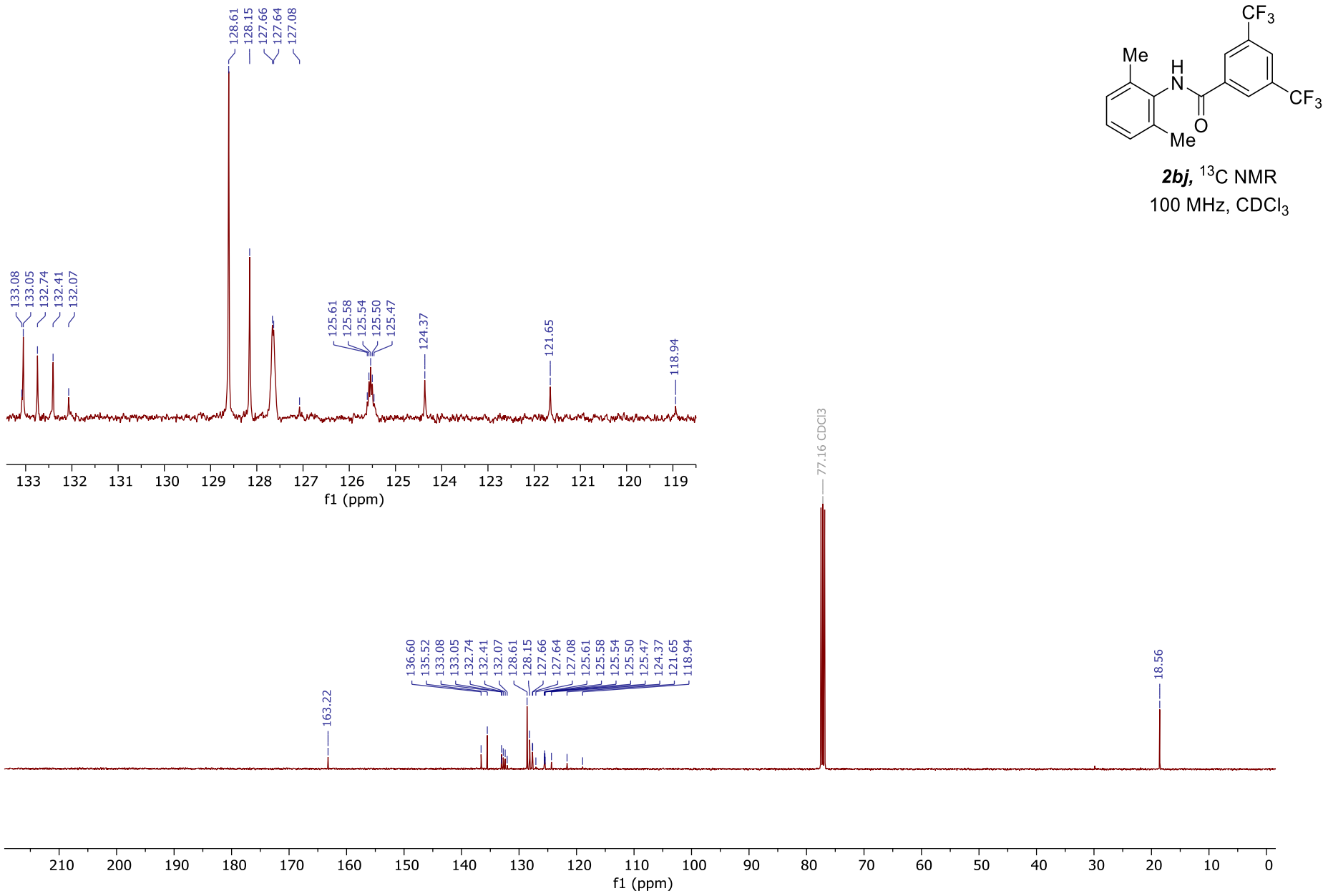




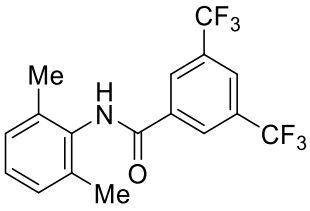


2bj, ^{1}H NMR
400 MHz, $CDCl_3$

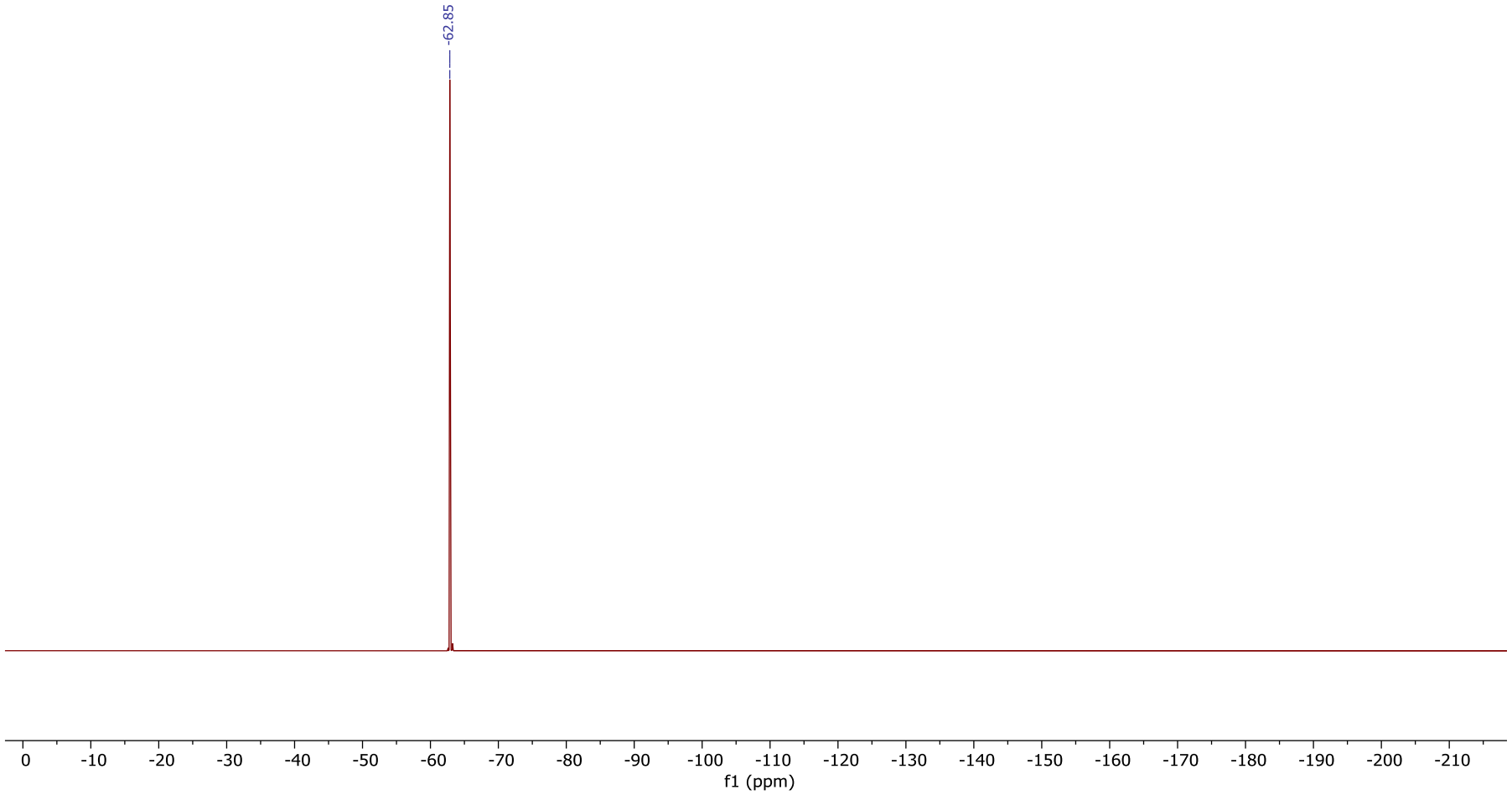


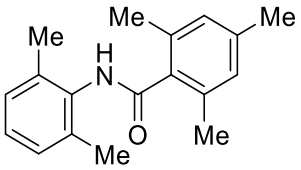


2bj, ^{13}C NMR
100 MHz, $CDCl_3$

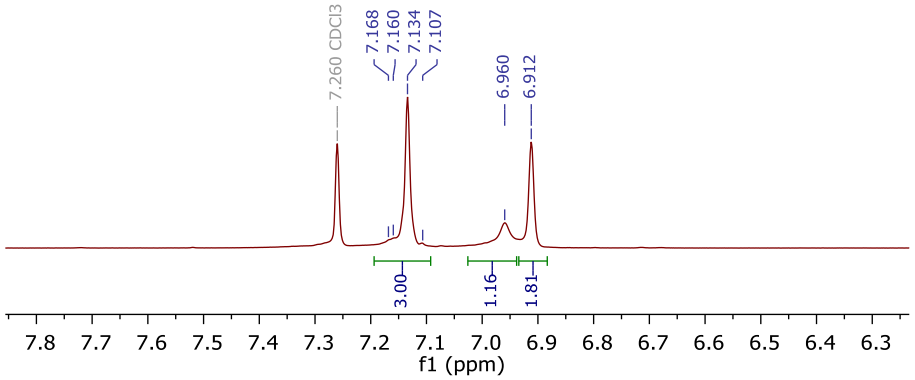


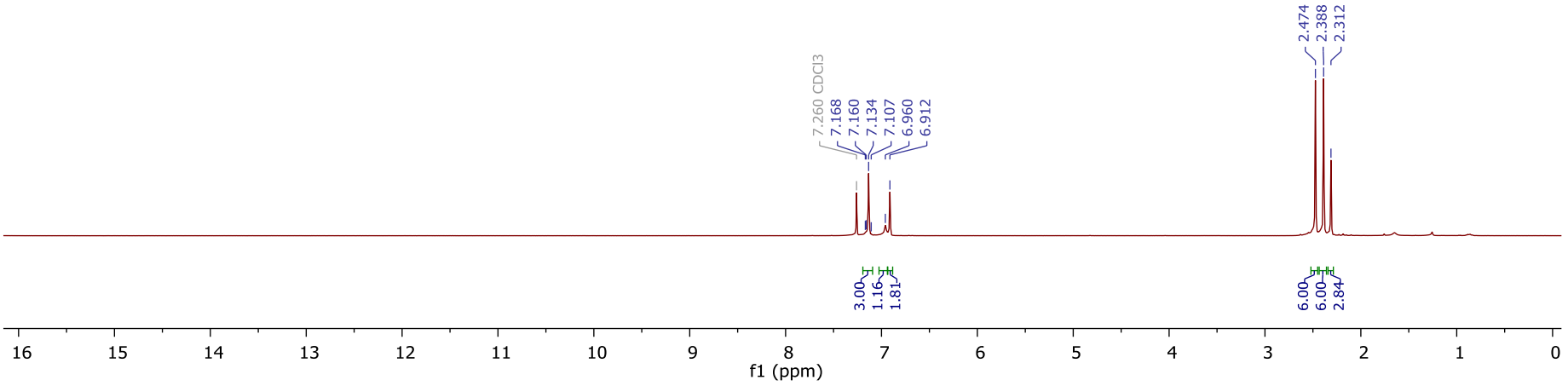
2bj, ^{19}F NMR
376 MHz, $CDCl_3$

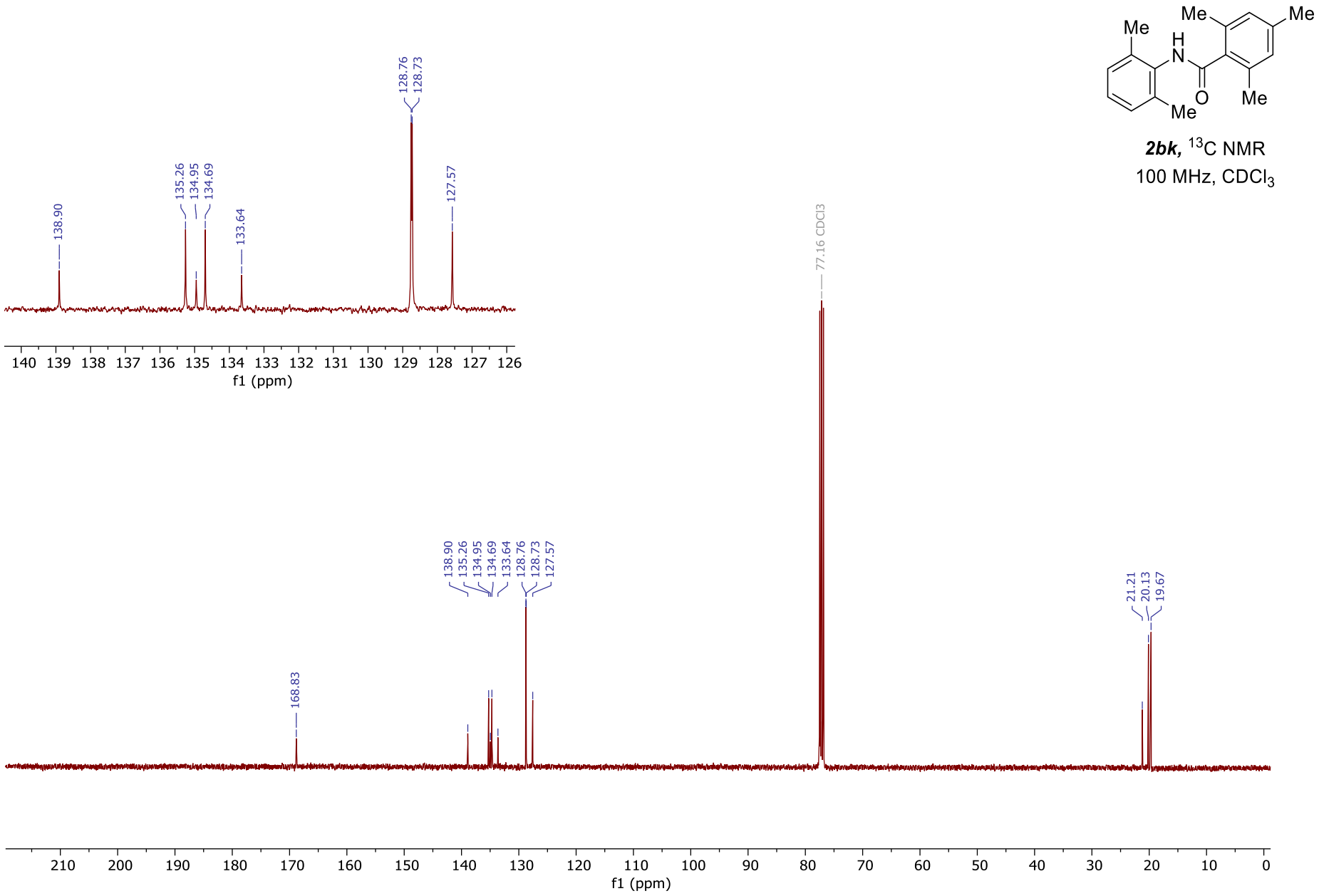


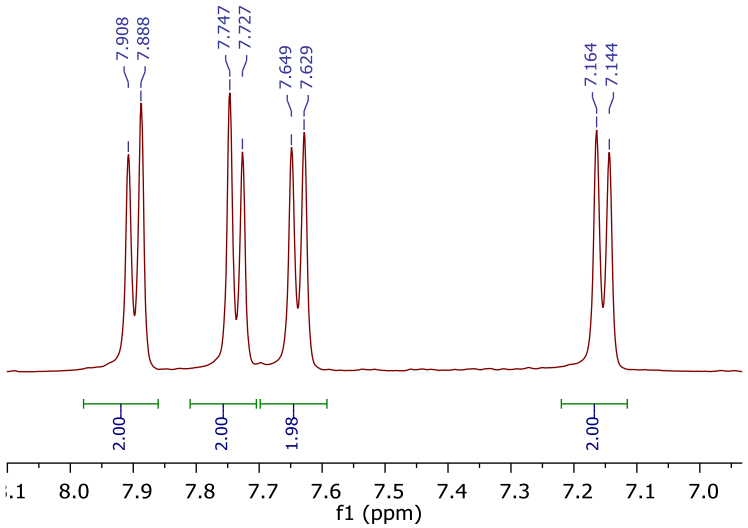


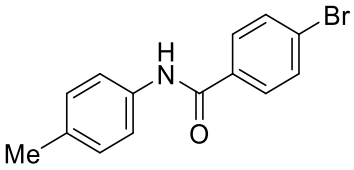
2bk, ^{1}H NMR
400 MHz, $CDCl_3$



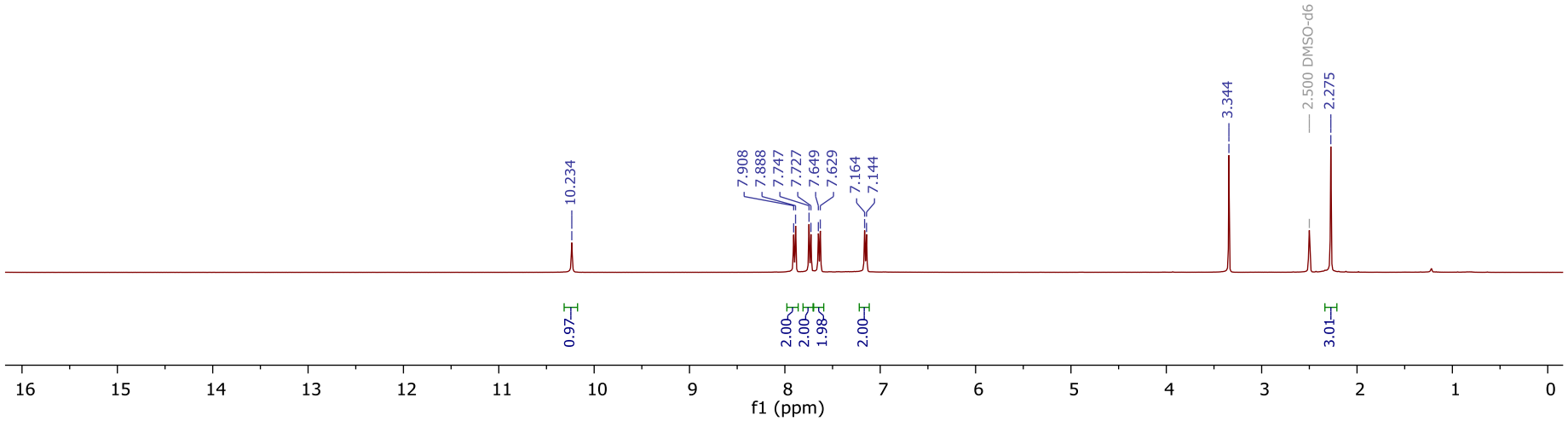


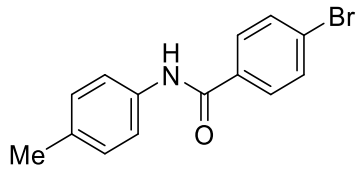

Me
Me
Me
H
N
O
Me
Me
2bk, 13C NMR
100 MHz, CDCl3
138.90
135.26
134.95
134.69
133.64
128.76
128.73
127.57
77.16 CDCl3
168.83
21.21
20.13
19.67
f1 (ppm)



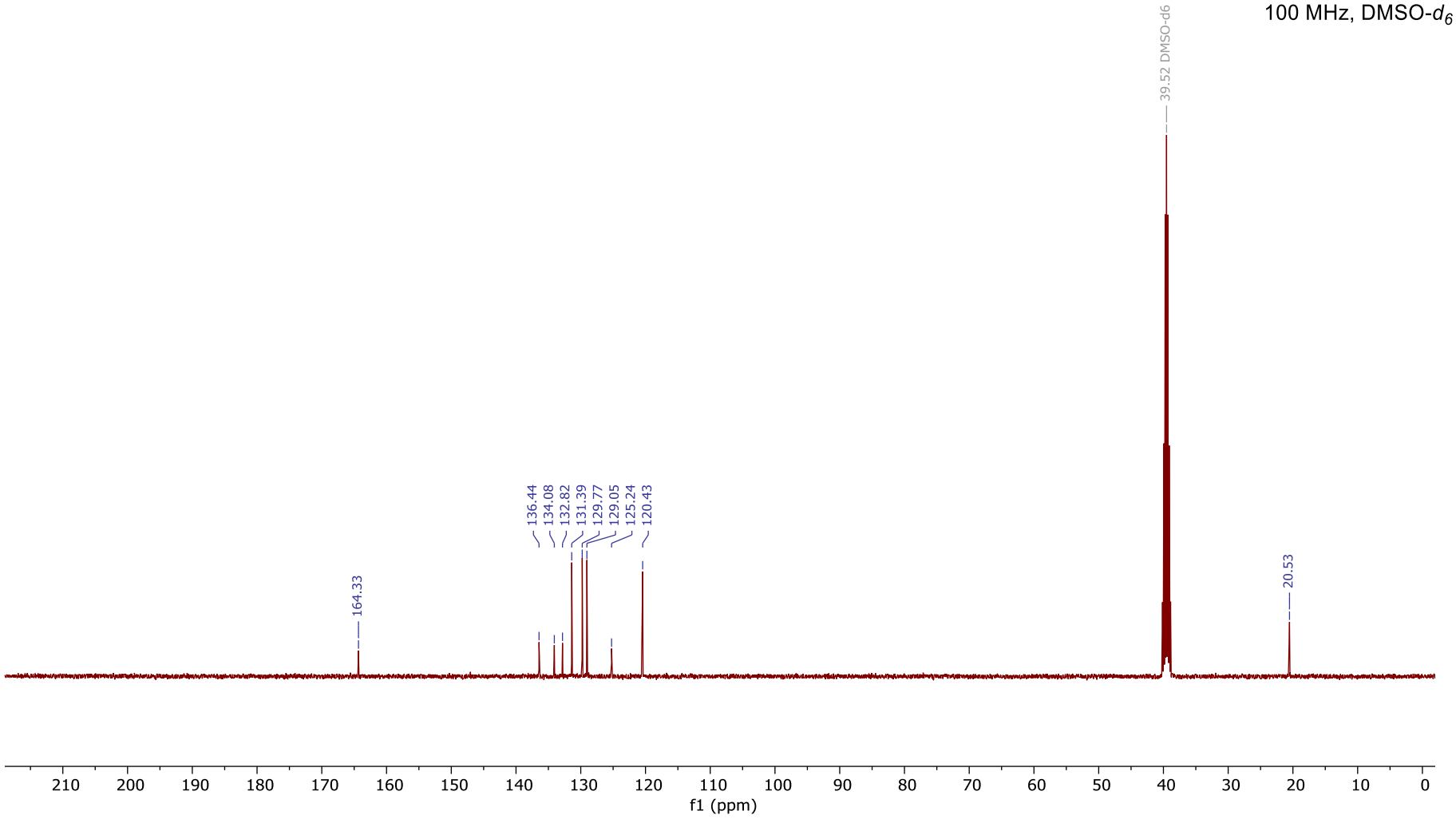


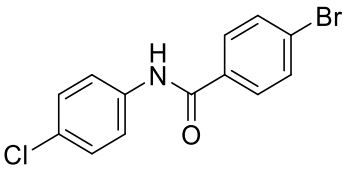
2ce, ^{1}H NMR
400 MHz, DMSO-d_6



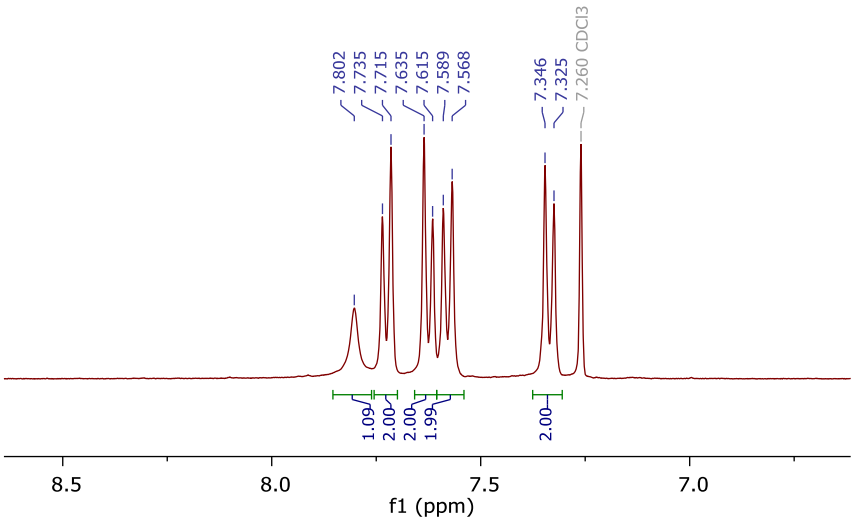


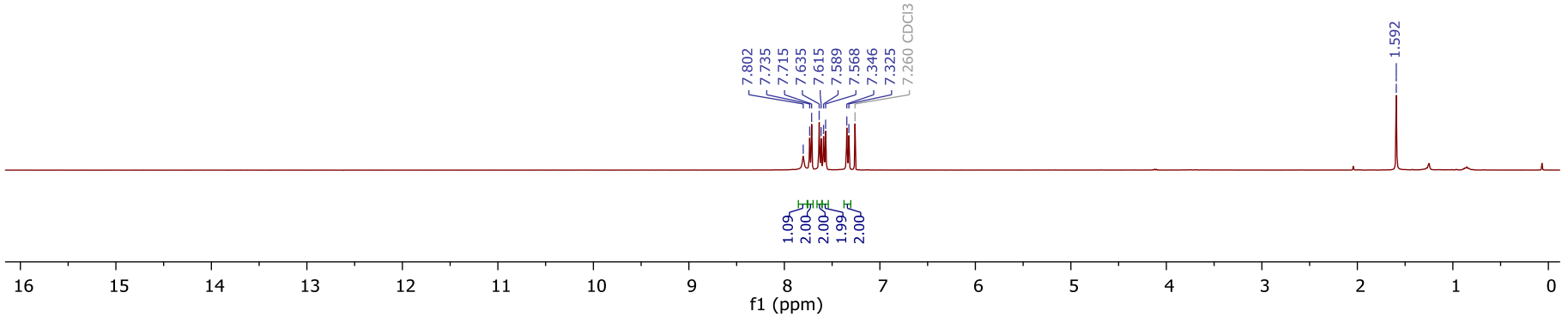
2ce, ^{13}C NMR
100 MHz, DMSO-d_6

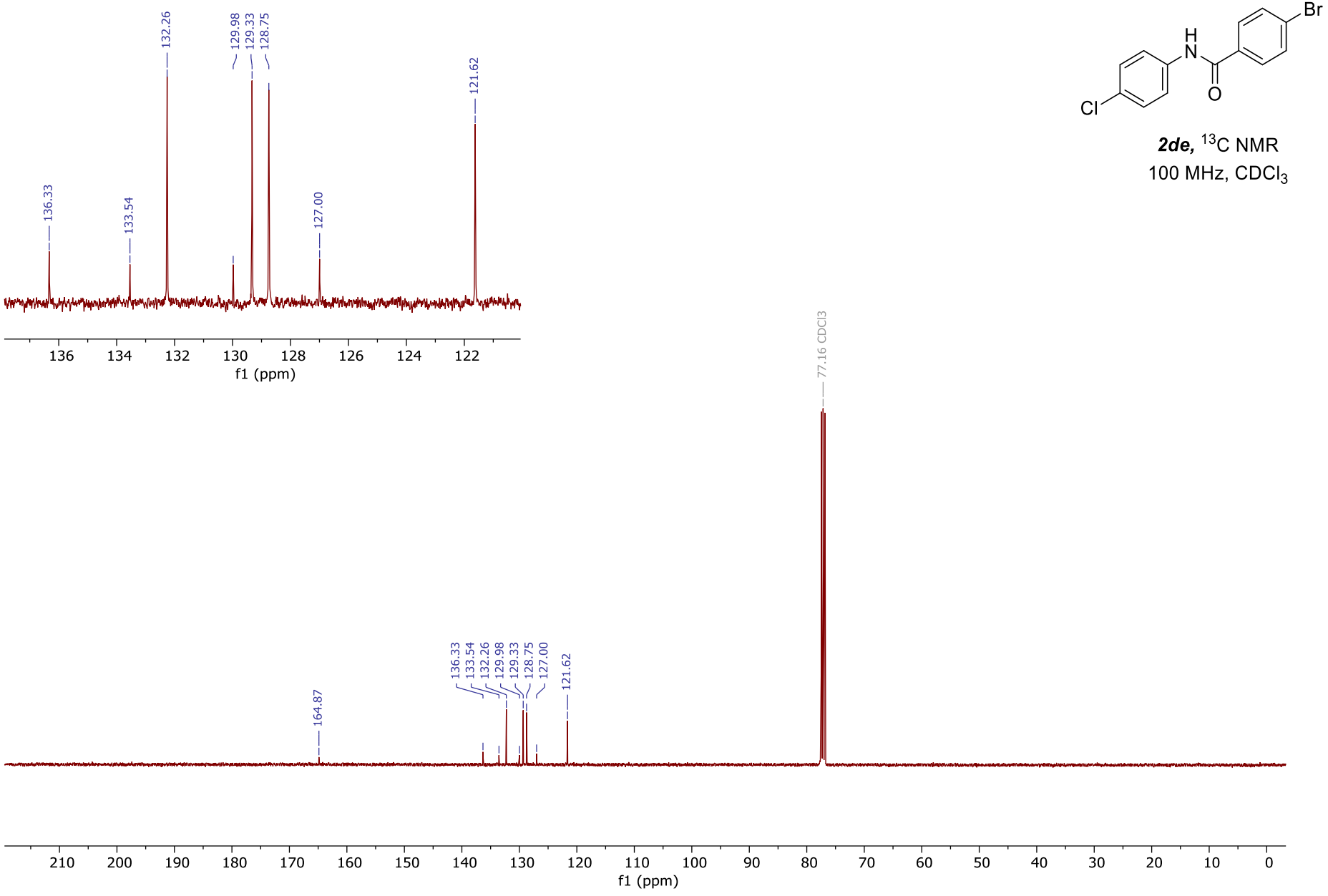


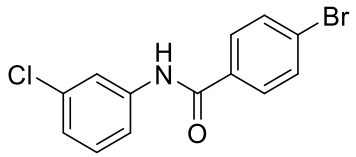


2de, ^{1}H NMR
400 MHz, $CDCl_3$

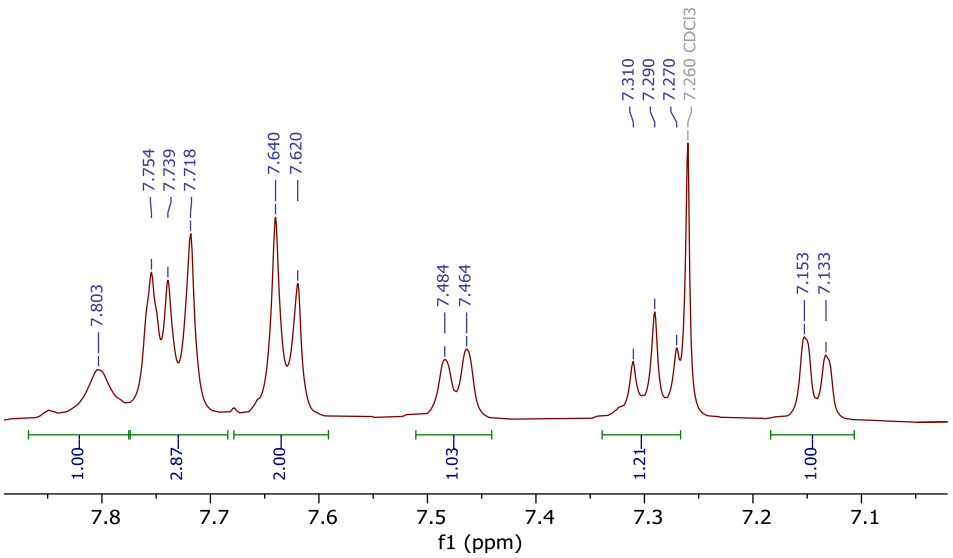


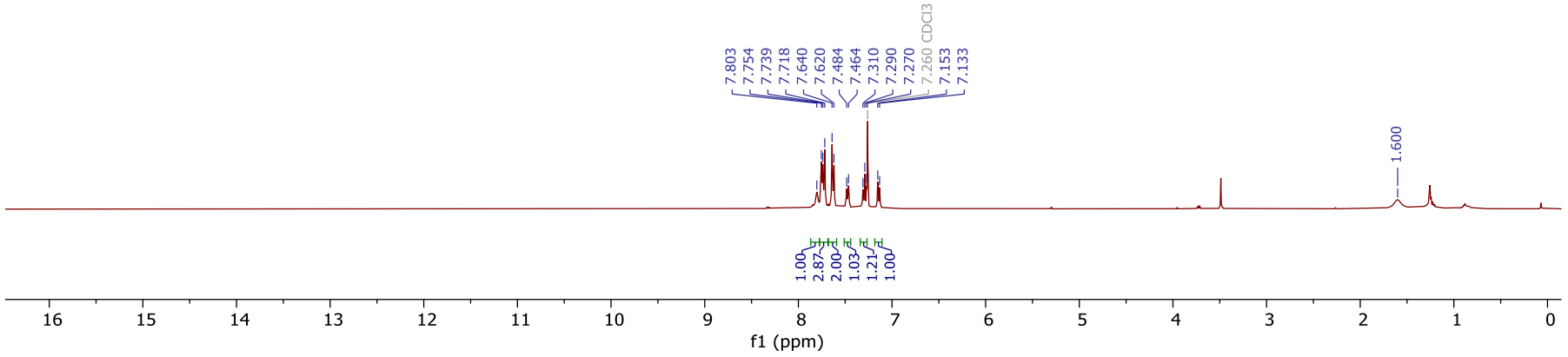


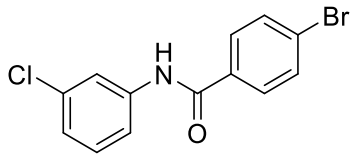

Br
H
N
O
Cl
2de, 13C NMR
100 MHz, CDCl3
136.33
133.54
132.26
129.98
129.33
128.75
127.00
121.62
77.16 CDCl3
164.87
f1 (ppm)



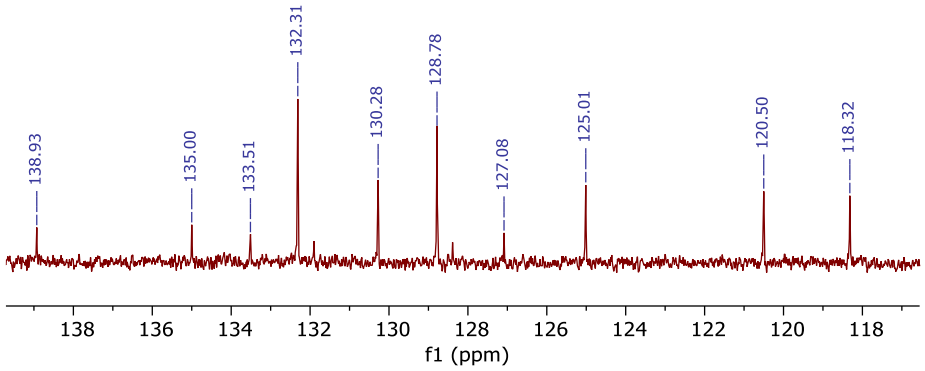
2ee, ^{1}H NMR
400 MHz, $CDCl_3$

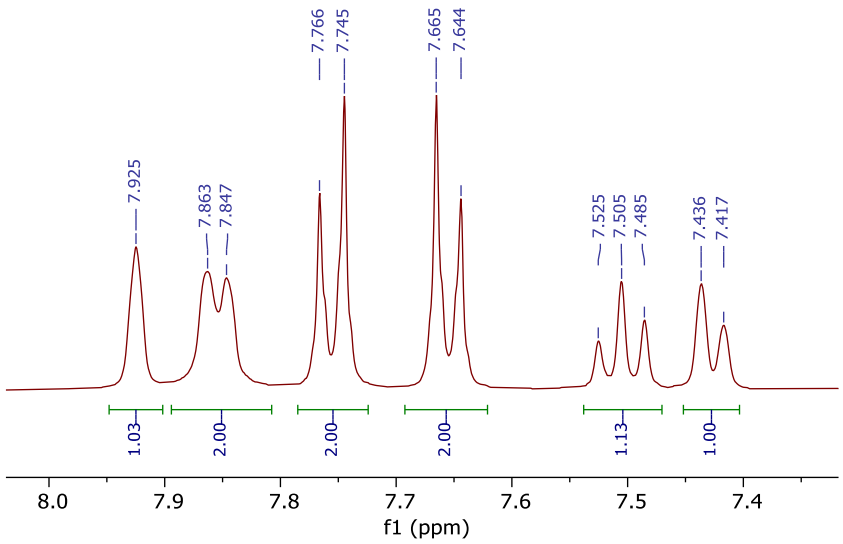


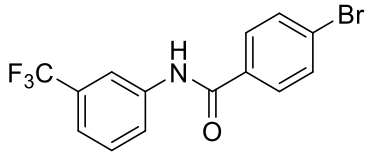




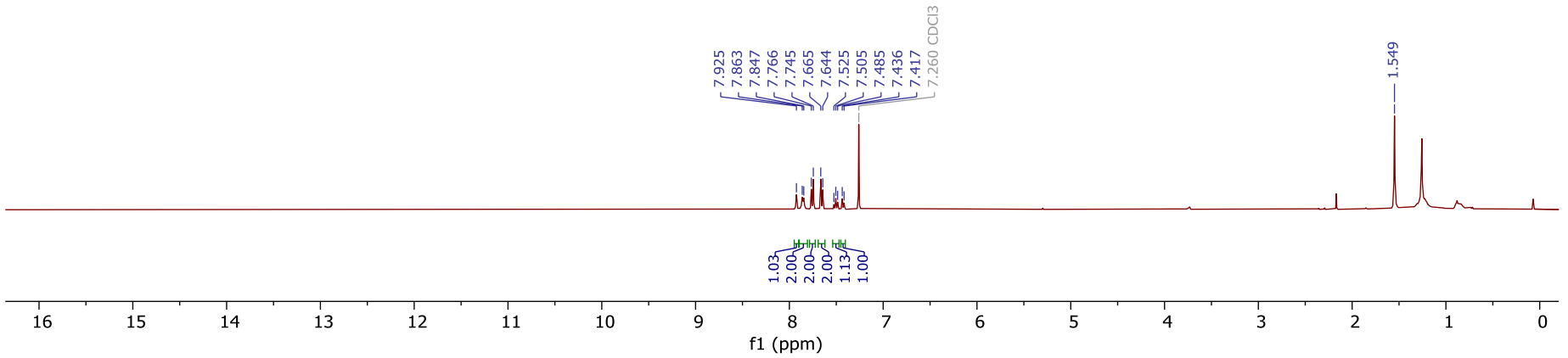
2ee, ^{13}C NMR
100 MHz, $CDCl_3$

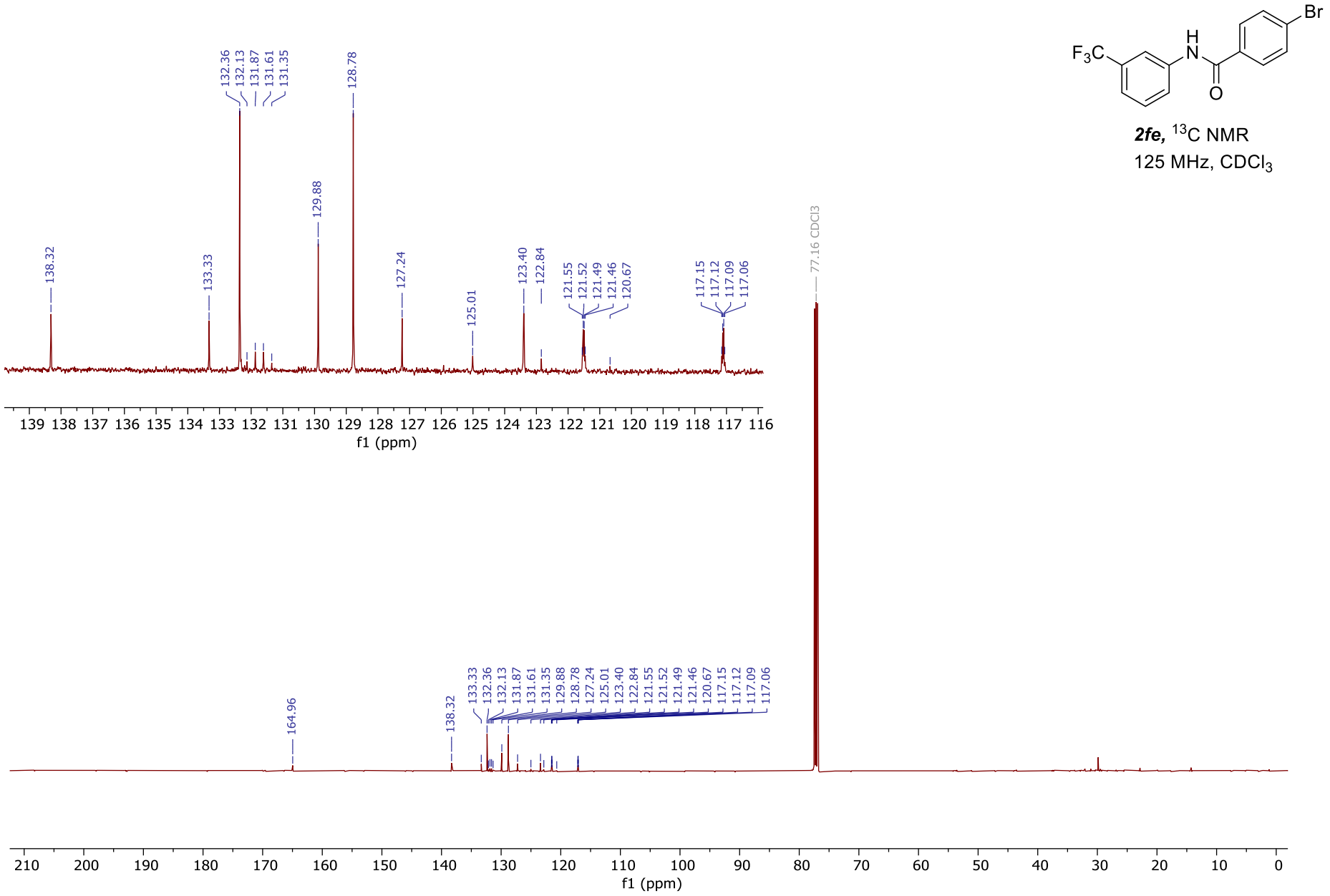


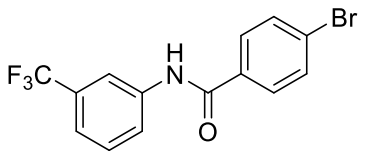




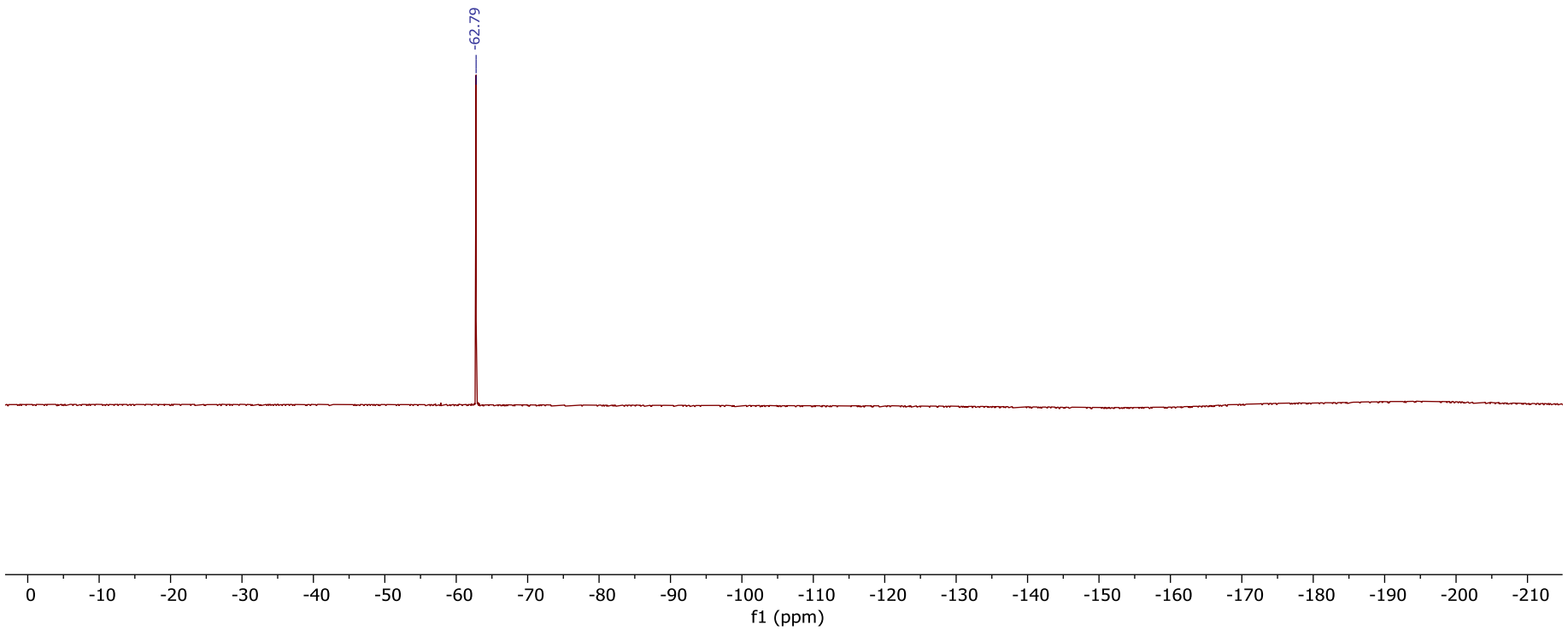
2fe, ^{1}H NMR
400 MHz, $CDCl_3$

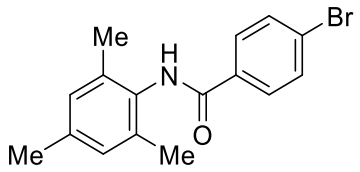



Br
H
N
F3C
O
2fe, 13C NMR
125 MHz, CDCl3
138.32
133.33
132.36
132.13
131.87
131.61
131.35
129.88
128.78
127.24
125.01
123.40
122.84
121.55
121.52
121.49
121.46
120.67
117.15
117.12
117.09
117.06
77.16 CDCl3
164.96
f1 (ppm)

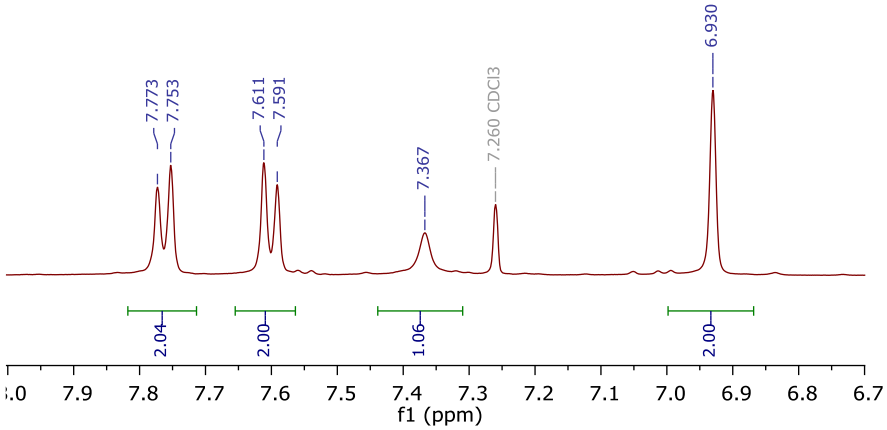


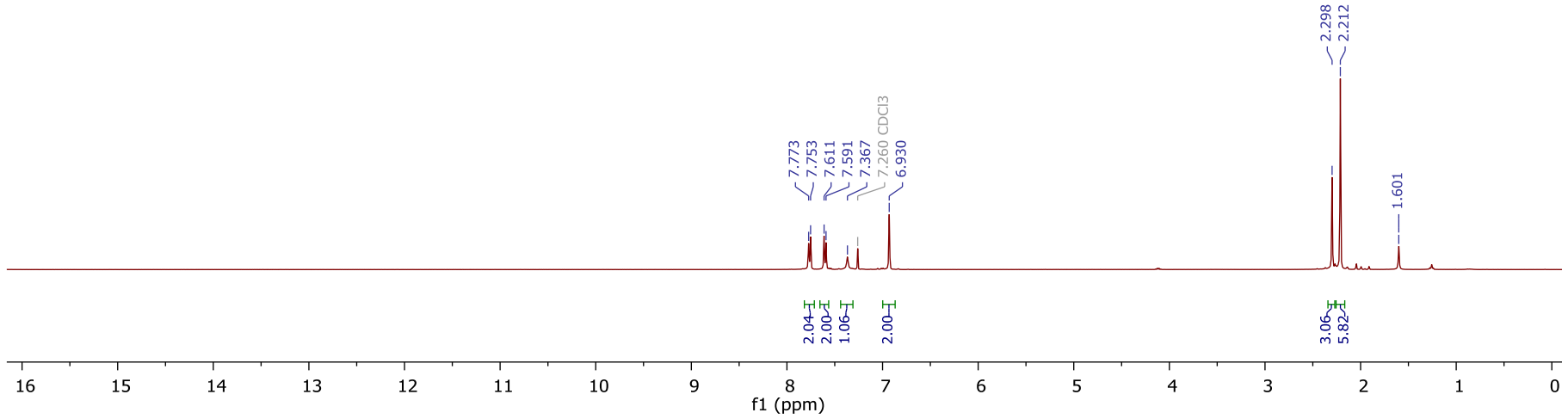
2fe, ^{19}F NMR
376 MHz, $CDCl_3$

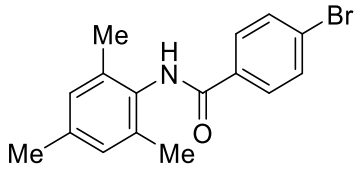




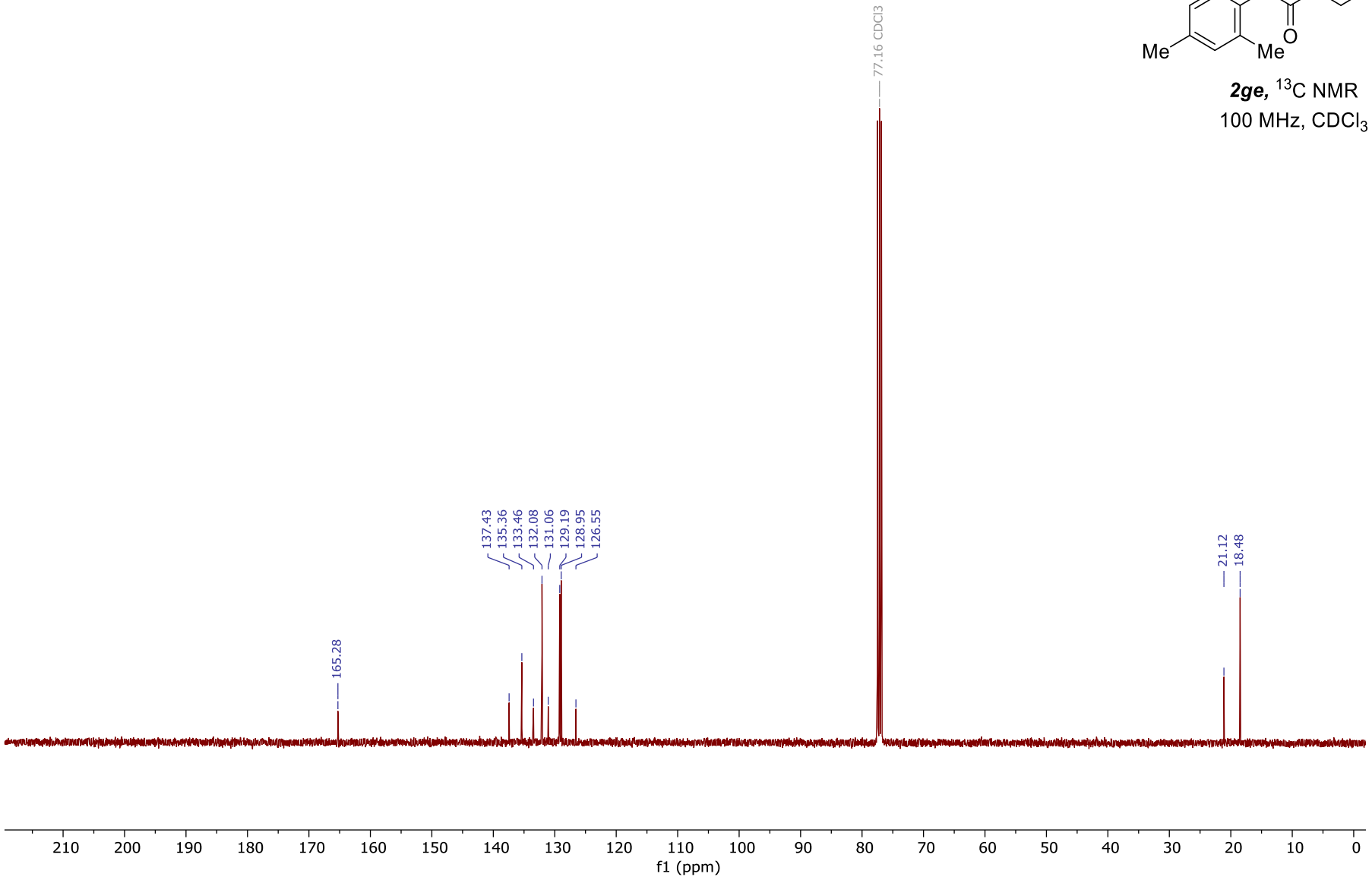
2ge, ^{1}H NMR
400 MHz, $CDCl_3$

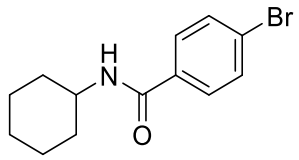




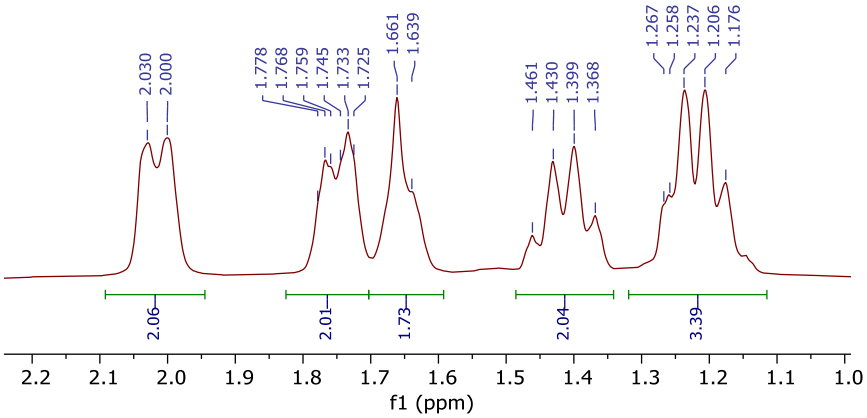


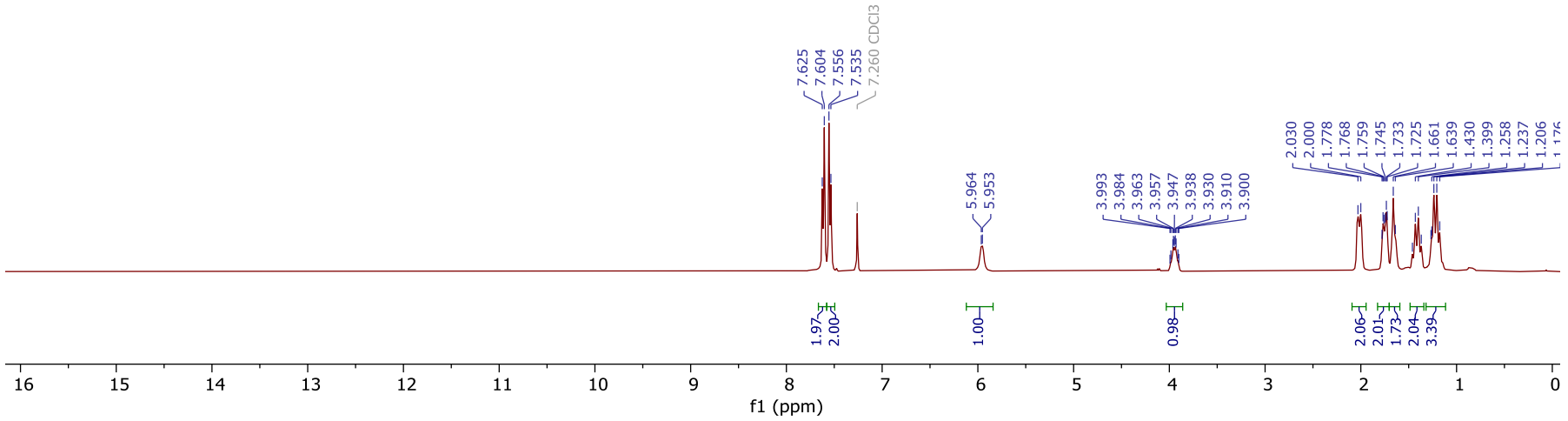
2ge, ^{13}C NMR
100 MHz, $CDCl_3$

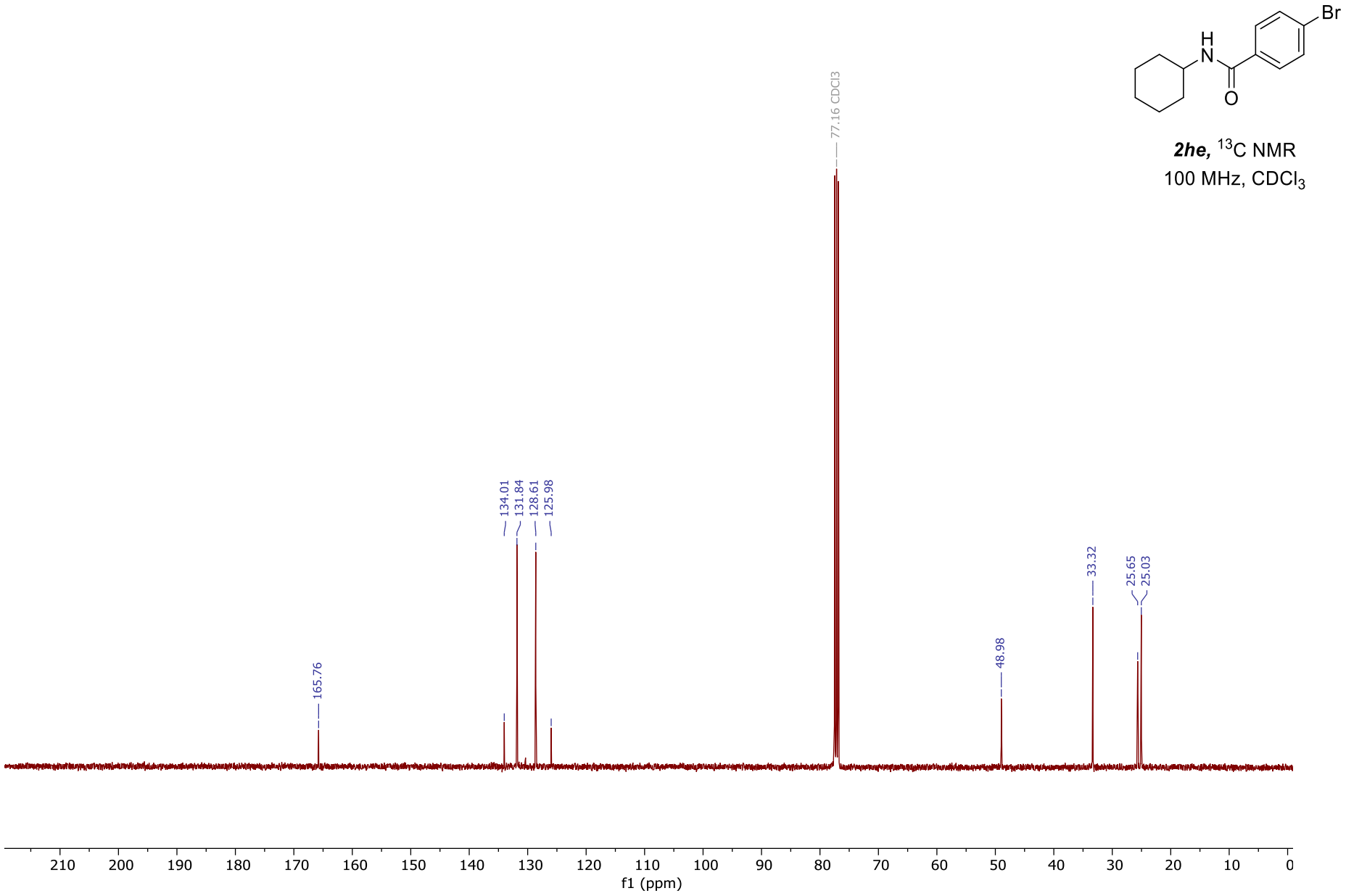




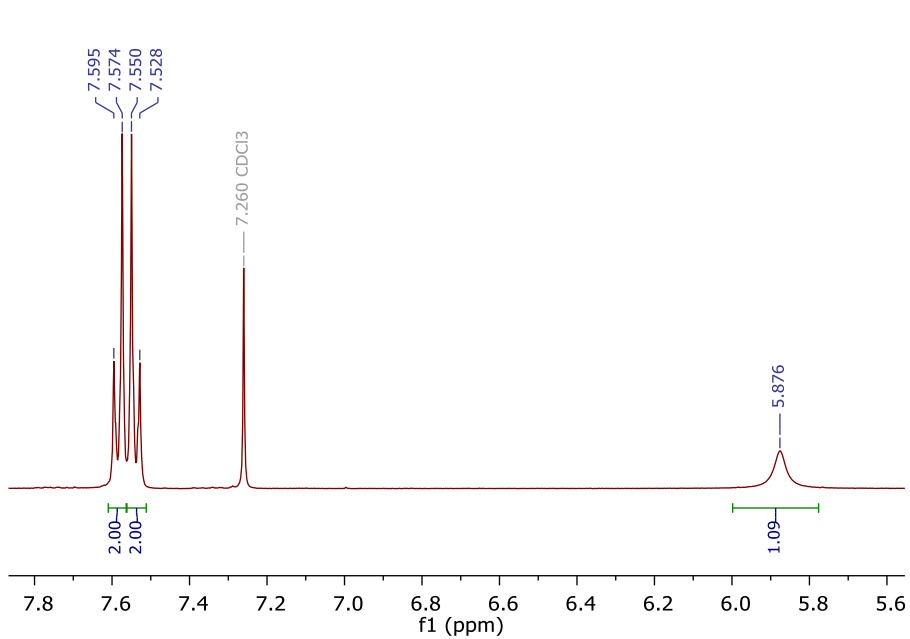
2he, ^{1}H NMR
400 MHz, $CDCl_3$

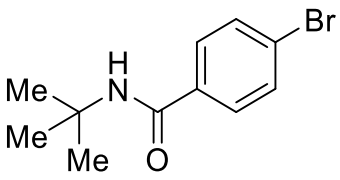




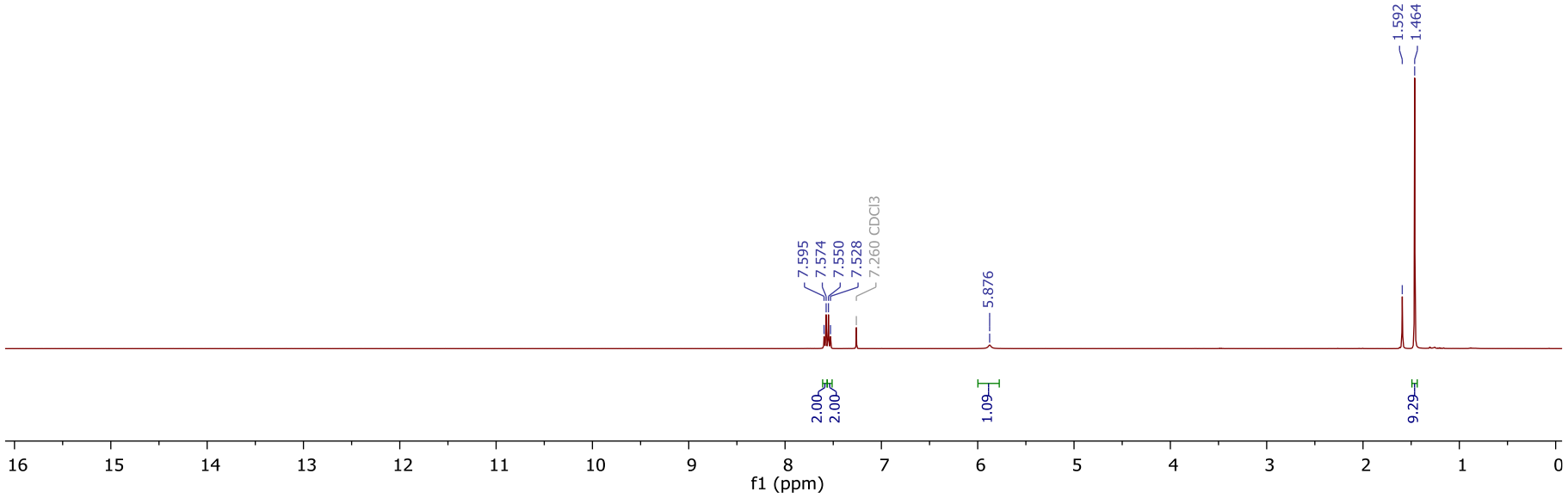


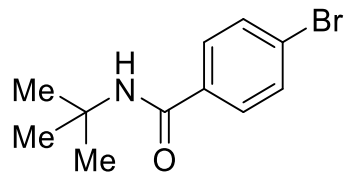
2he, ^{13}C NMR
100 MHz, $CDCl_3$



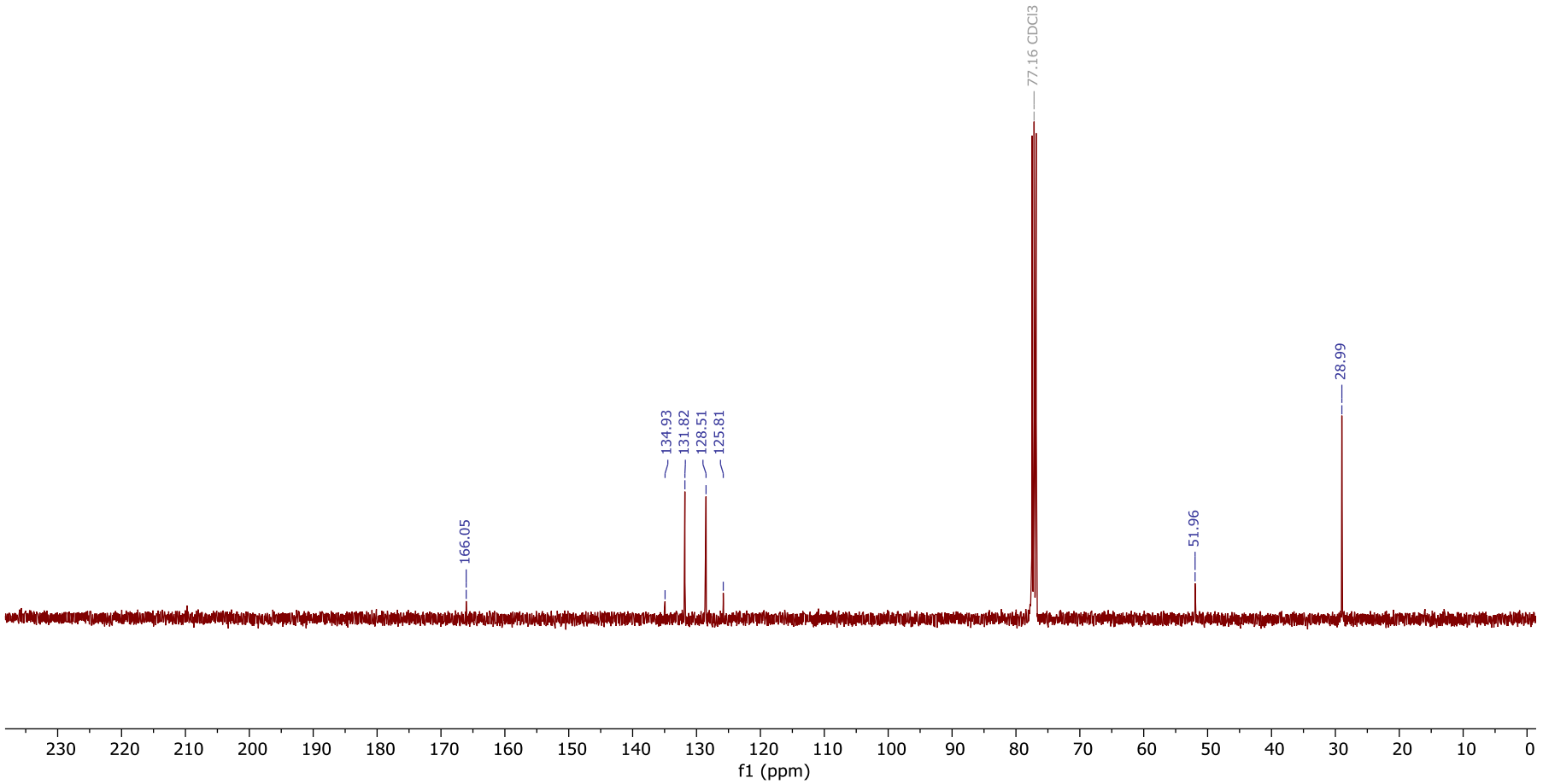


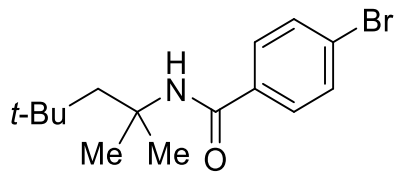
2ie, ^{1}H NMR
400 MHz, $CDCl_3$



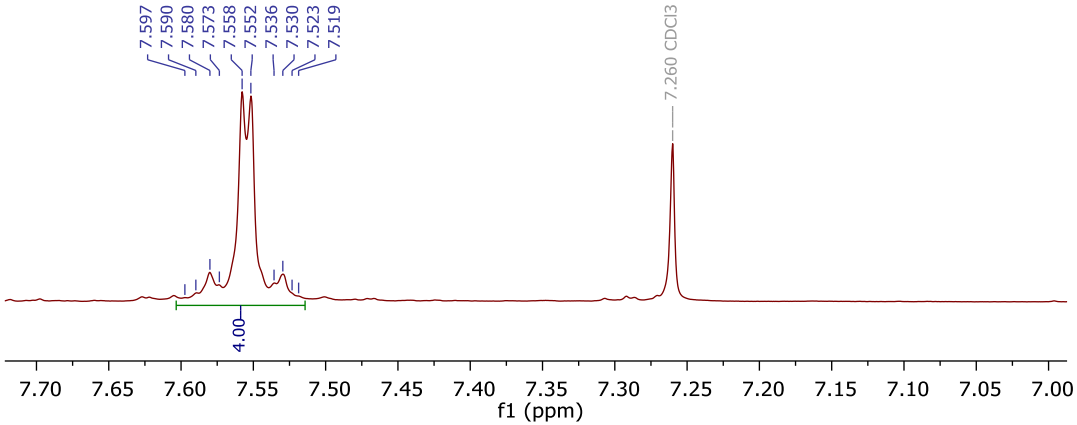


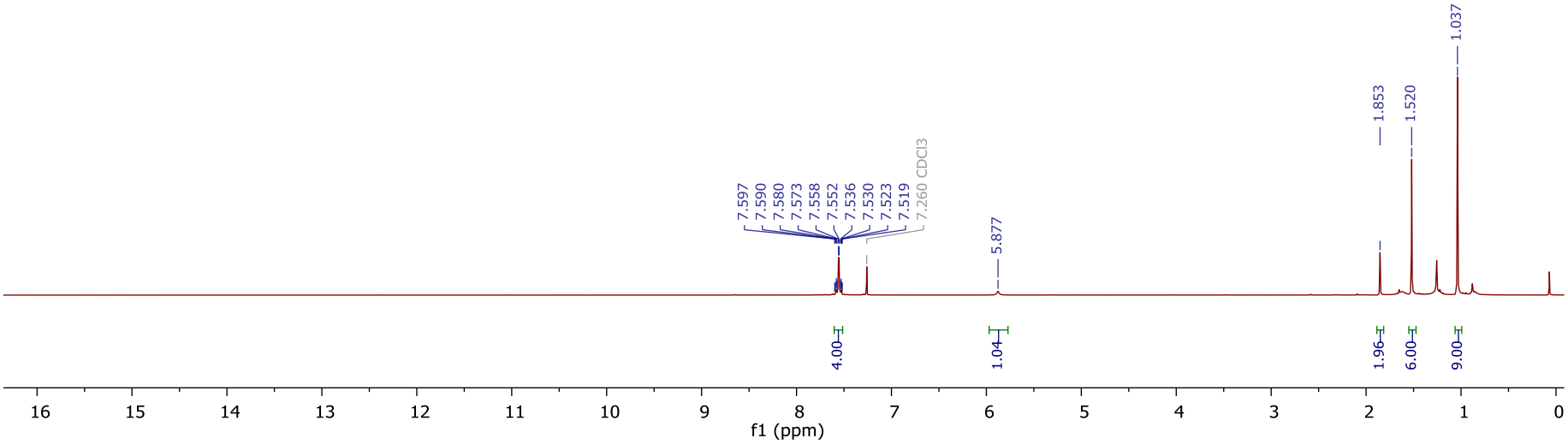
2ie, ^{13}C NMR
100 MHz, $CDCl_3$

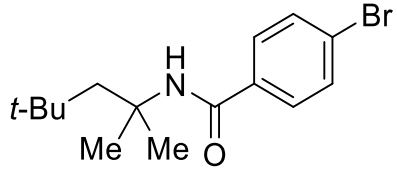




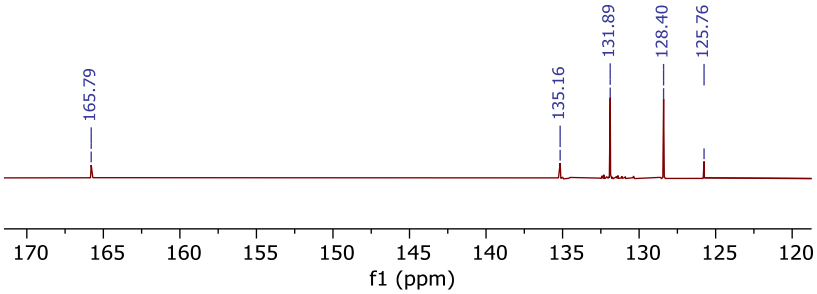
2je, ^{1}H NMR
400 MHz, $CDCl_3$

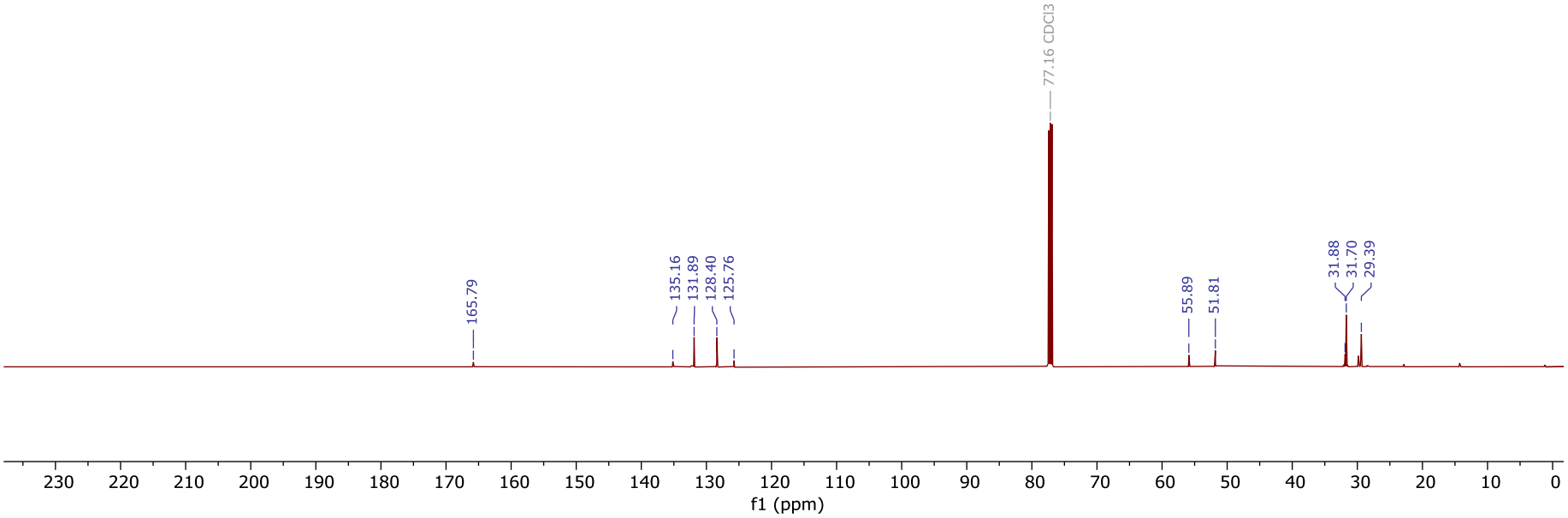


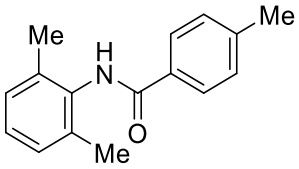




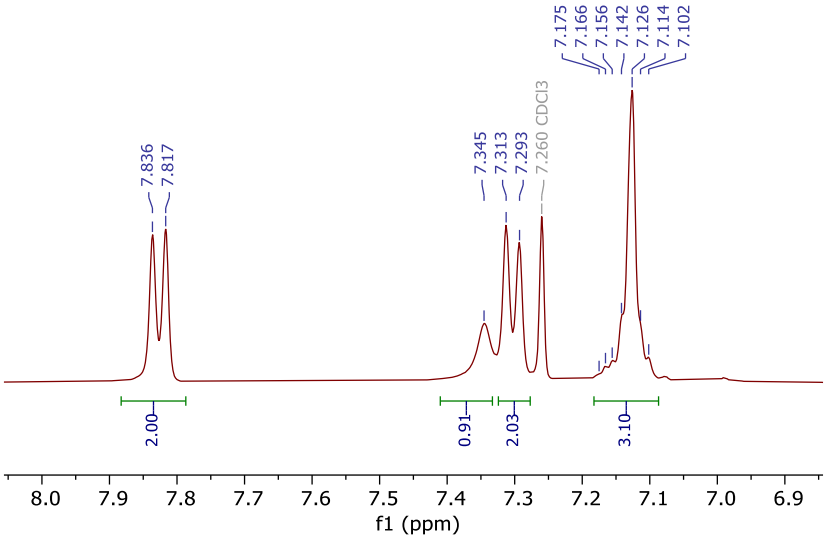
2je, ^{13}C NMR
125 MHz, $CDCl_3$

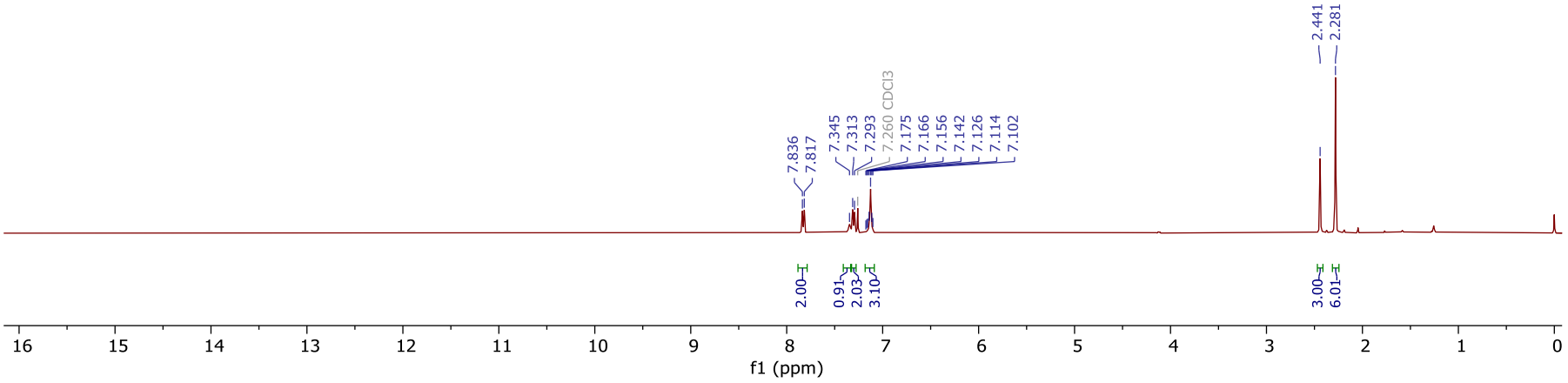


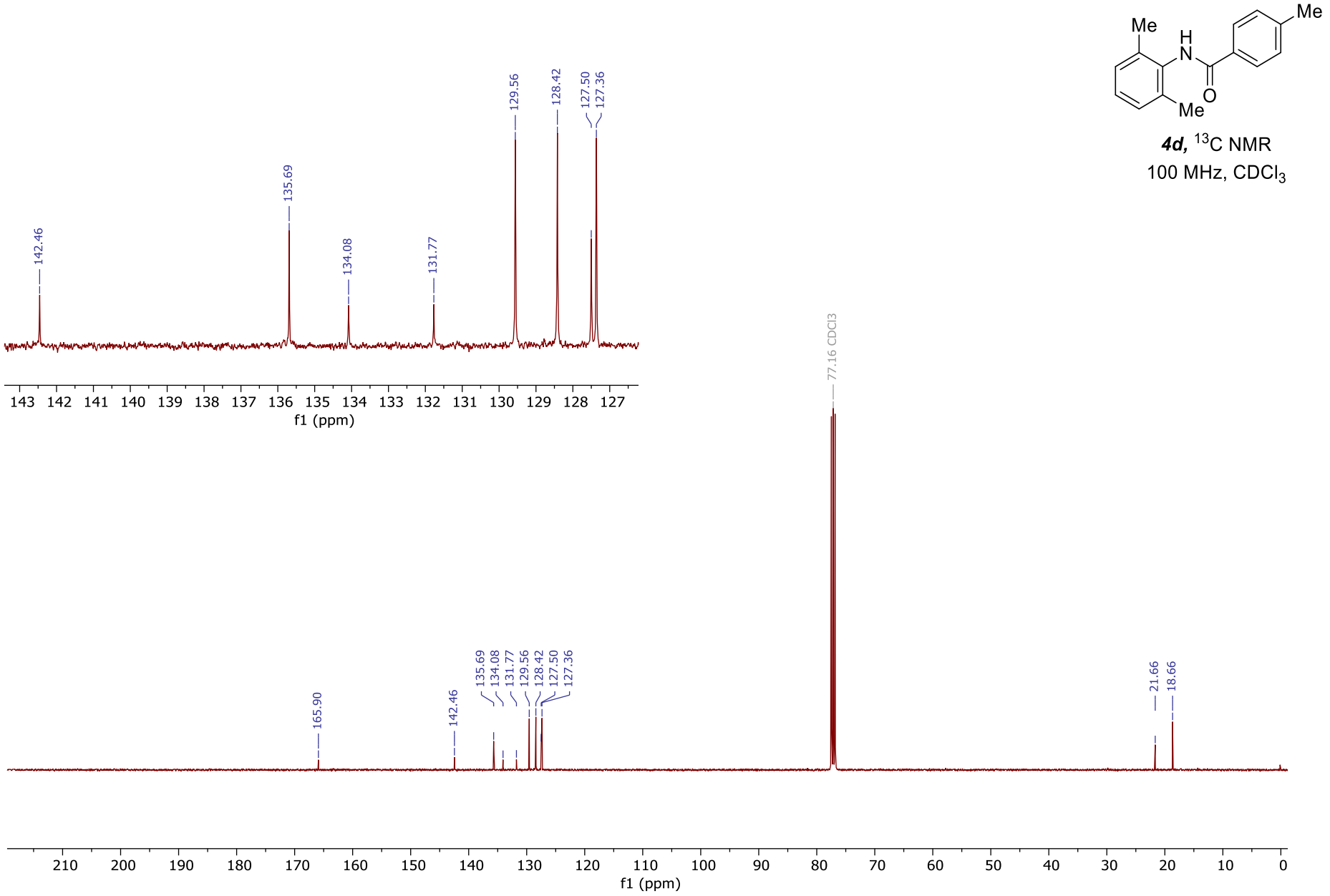


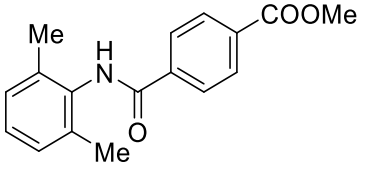


4d, ^{1}H NMR
400 MHz, $CDCl_3$

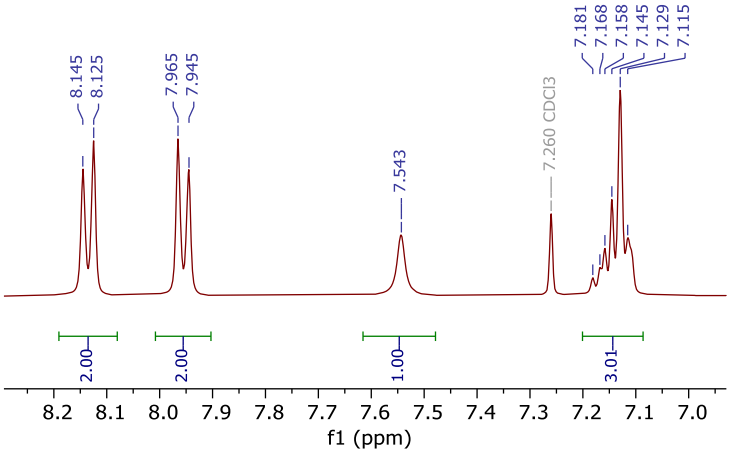


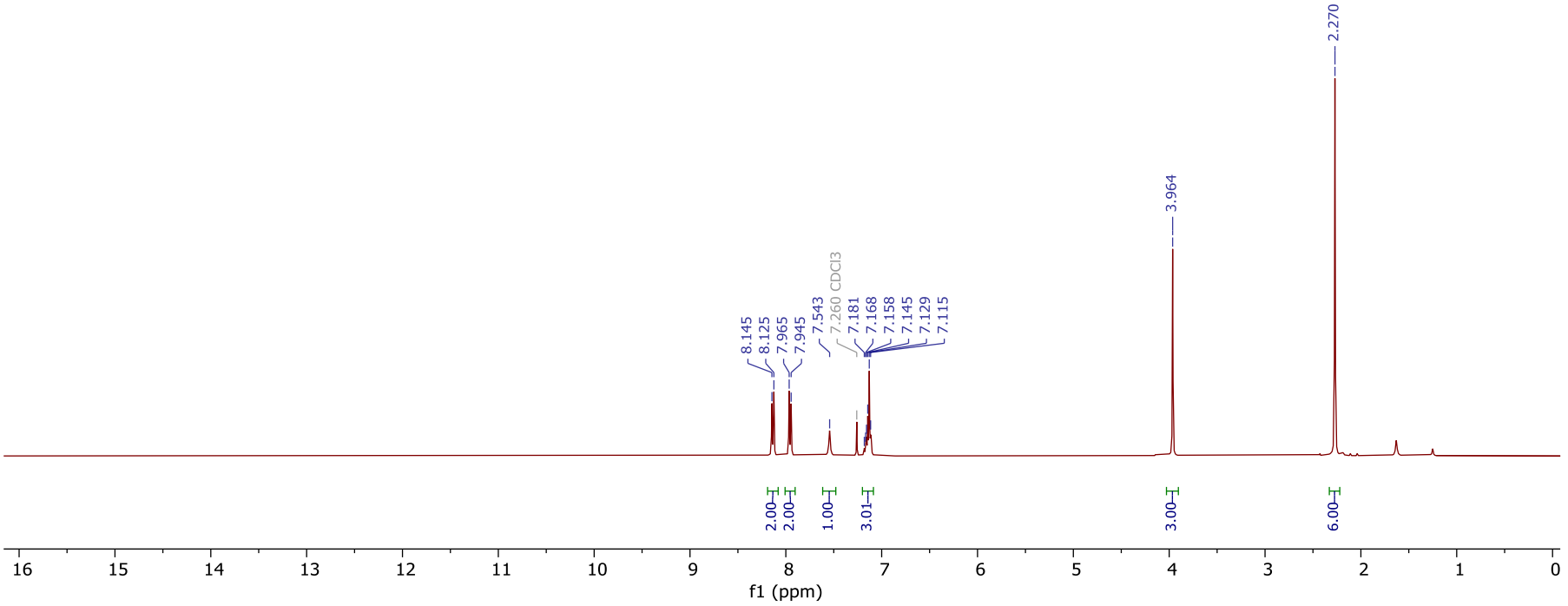


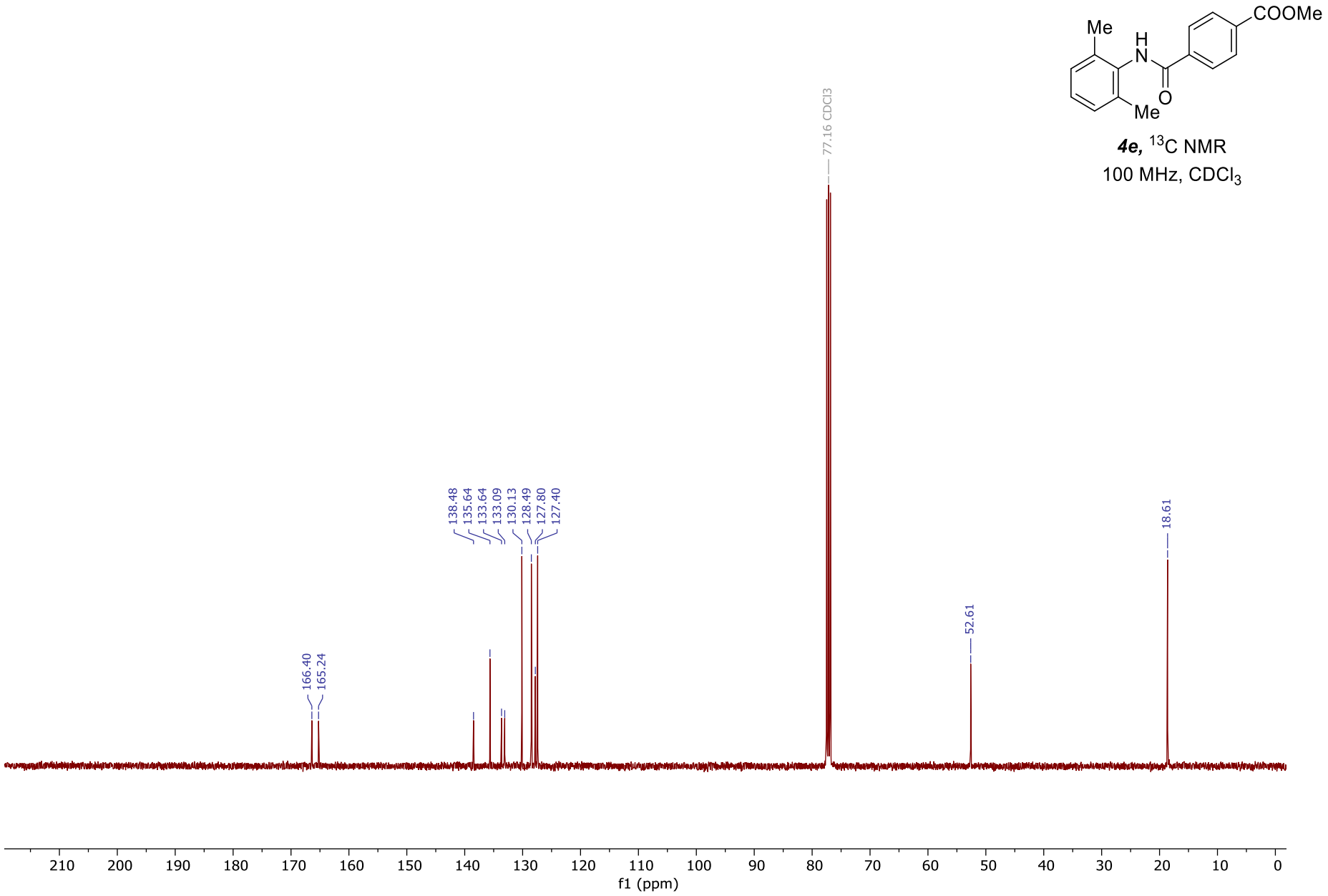

Me
H
N
O
Me
Me
4d, 13C NMR
100 MHz, CDCl3
142.46
135.69
134.08
131.77
129.56
128.42
127.50
127.36
143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127
f1 (ppm)
77.16 CDCl3
165.90
142.46
135.69
134.08
131.77
129.56
128.42
127.50
127.36
21.66
18.66
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

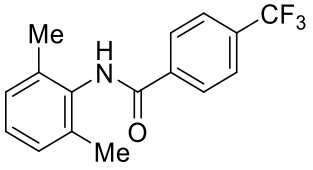


4e, ^{1}H NMR
400 MHz, $CDCl_3$

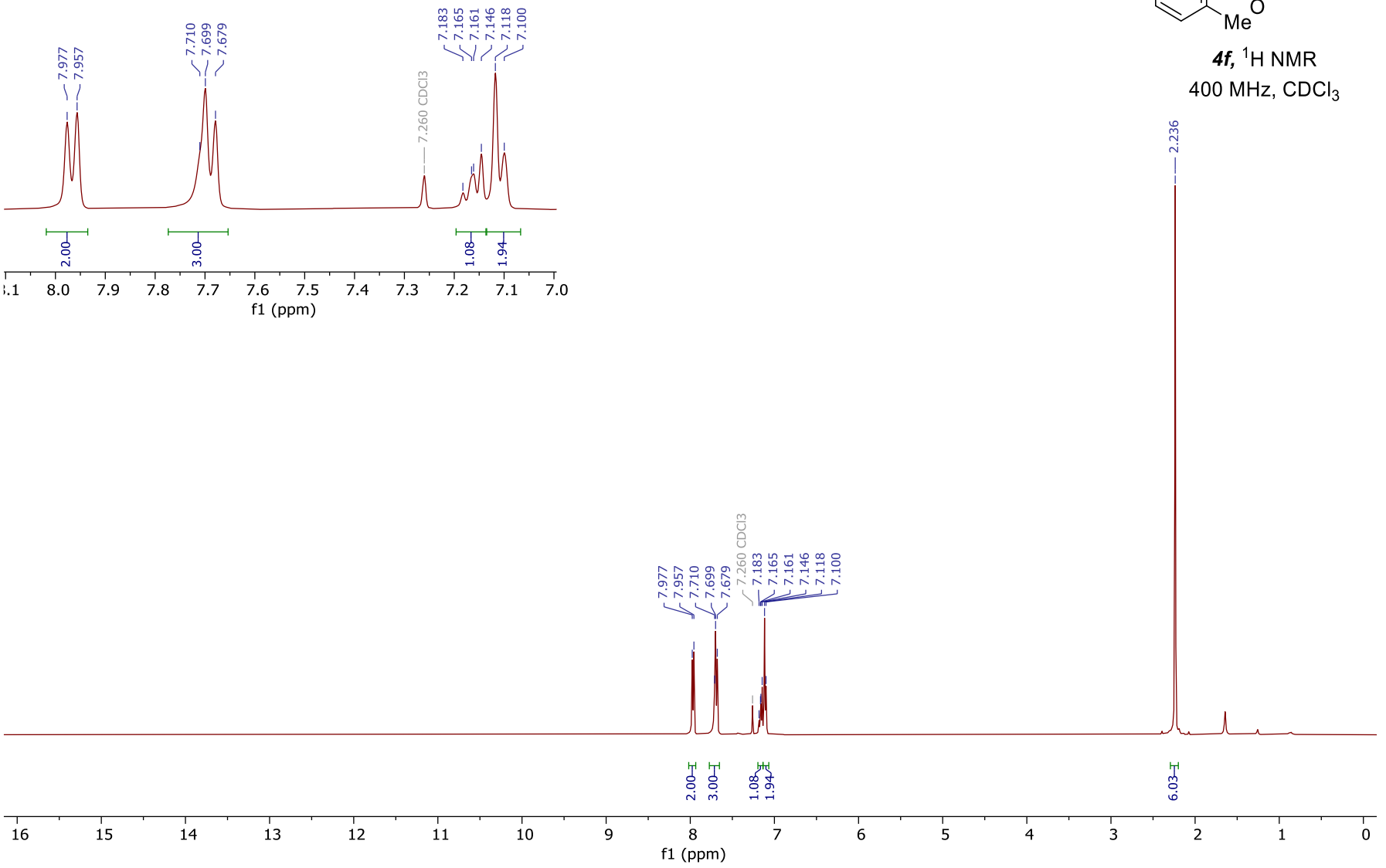


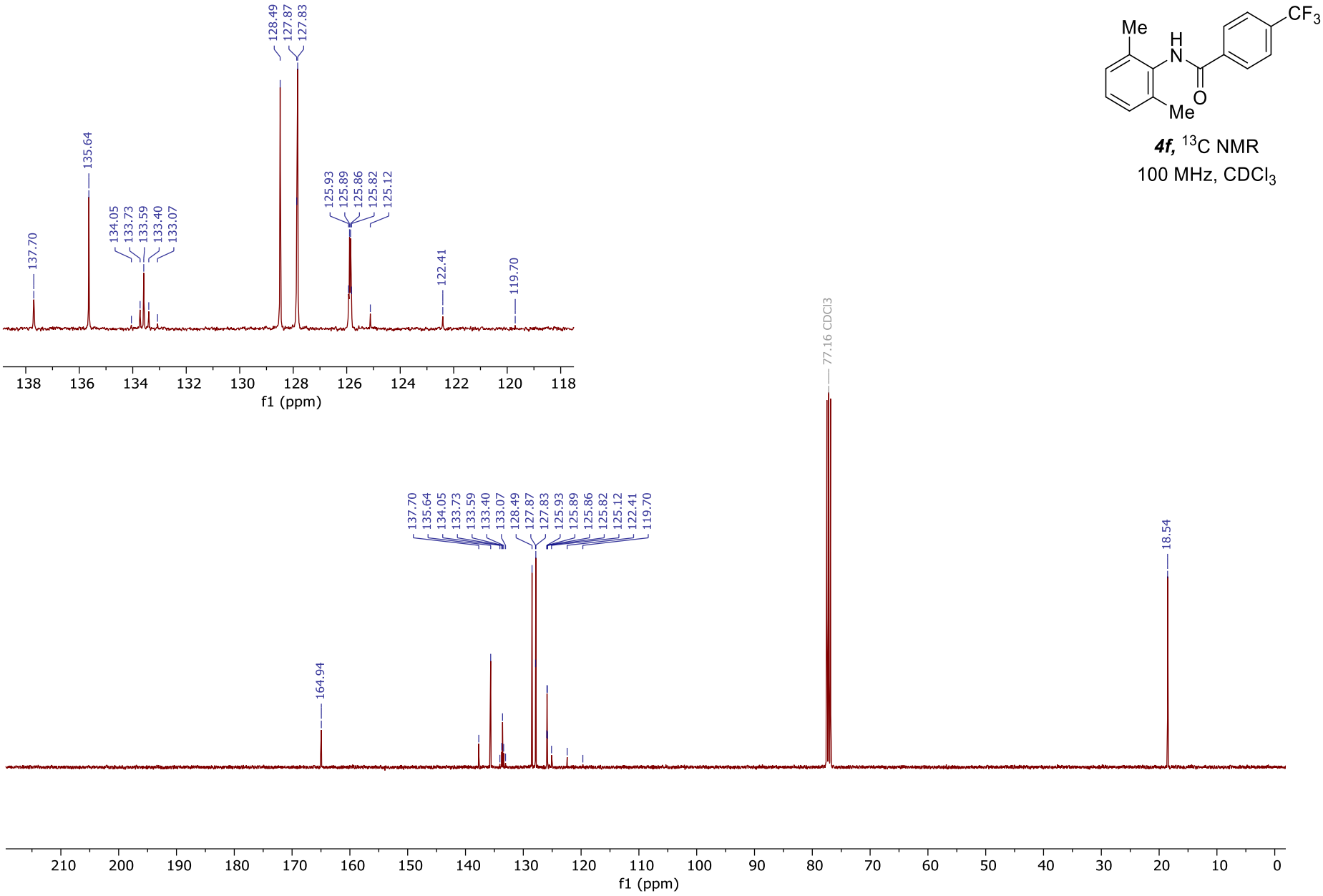


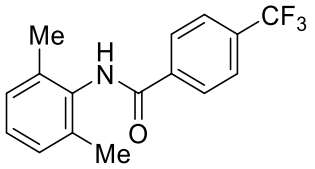

Me
H
N
O
Me
COOMe
4e, 13C NMR
100 MHz, CDCl3
77.16 CDCl3
138.48
135.64
133.64
133.09
130.13
128.49
127.80
127.40
166.40
165.24
52.61
18.61
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4f, ^{1}H NMR
400 MHz, $CDCl_3$




Me
H
N
O
Me
CF3
4f, 13C NMR
100 MHz, CDCl3
128.49
127.87
127.83
135.64
134.05
133.73
133.59
133.40
133.07
125.93
125.89
125.86
125.82
125.12
137.70
122.41
119.70
138
136
134
132
130
128
126
124
122
120
118
f1 (ppm)
77.16 CDCl3
18.54
164.94
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4f, ^{19}F NMR
376 MHz, $CDCl_3$