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SUPPORTING INFORMATION

Title: *N*-Sulfonylcarboxamide as an Oxidizing Directing Group for Ruthenium-Catalyzed C–H Activation/Annulation

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Table of Contents

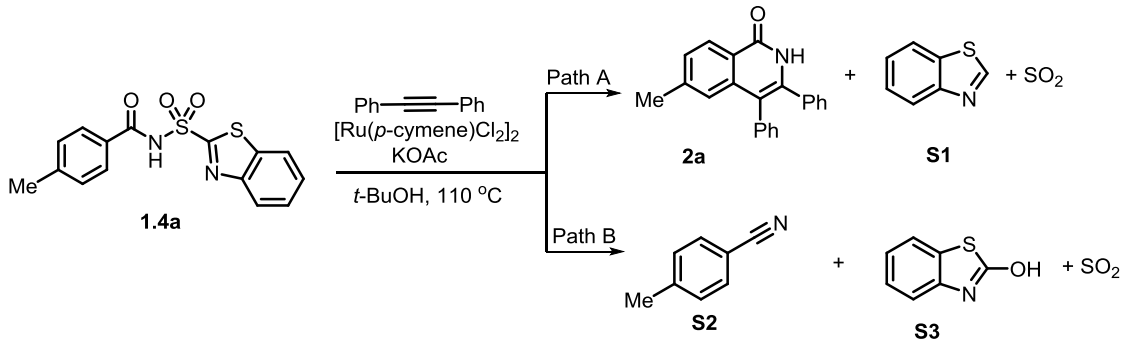
General information.

Reagents and starting materials were obtained from commercial sources and used as received. The solvents were purified and dried by standard procedures prior to use. Flash chromatography was carried out using silica gel (230−400 mesh). Thin layer chromatography (TLC) was performed on silica gel and was visualized by UV lamp or staining with $KMnO_4$. NMR spectra were recorded on 300 and 400 MHz spectrometers with chemical shift values (δ) in parts per million using the residual chloroform, dimethylsulfoxide, methanol or acetone signal as the internal standard. Conversion of starting material was detected with UPLC Waters Acquity, column: Acquity UPLC BEH-C18, 1.7 μm, 2.1mm x 50 mm, column temperature (30.0±5.0) ^oC, gradient: 0.01% TFA in water/CH_3CN 90%/10% – 5%/95%; flow: 0.500 mL/min; time: 8 min; detector: PDA, 220 – 320 nm, SQ detector with an electrospray ion source (ESI/APCI). Gas chromatographic (GC) analysis was performed on Agilent Technologies gas chromatographer with triple-axis detector, heating range 80- 280 ^oC, column 30 m x 0.25 mm, 0.25 μm, 7 inch cage. Exact molecular masses (HRMS) were detrmined on a hybrid quadrupole time-of-flight mass spectrometer equipped with an electrospray ion source.

1. By-product analysis

1.1. Annulation of *N*-betsylcarboxamide 1.4a.

In the Ru-catalyzed reaction of *N*-betsylcarboxamide **1.4a** with diphenylacetylene the expected annulation product **2a** formed together with by-products **S1, S2** and **S3** according to UPLC-MS analysis of the reaction mixture (Scheme S1, figure S1). These by-products were islolated and their strucutures proved by comparision the physicochemical characterization with the literature data.



Scheme S1. The two possible reaction pathways for the reaction of *N*-sulfonylcarboxamide **1.4a**

The formation of benzothiazole (**S1**) can be explained by decomposition of sulfinate by-product resulting from the annulation of starting material **1.4a** (Scheme S1, path A). The formation of tolunitrile (**S2**) and 2-hydroxybenzthiazole (**S3**) could be explained by the competitive pathway which invloves Smiles rearrangement of deprotonated *N*-betsylcarboxamide **1.4a**.[1]

[1] Sulfur-Mediated Rearrangements II, Michael Reggelin (auth.), Ernst Schaumann (eds.), Springer-Verlag Berlin Heidelberg, 2007.

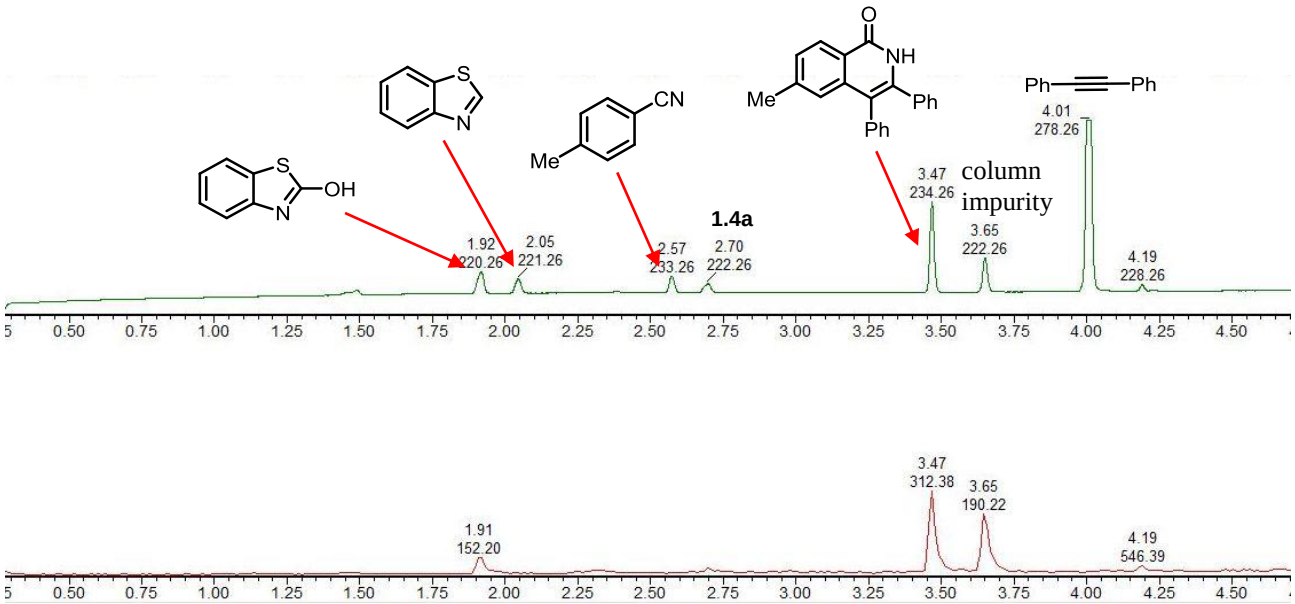


Figure S1. Liquid chromatogramm of reaction mixture presented in Scheme S1.

Benzothiazole (S1)

^{1}H NMR (300 MHz, DMSO-d_6) δ= 9.40 (s, 1H), 8.23 – 8.13 (m, 1H), 8.12 – 8.07 (m, 1H), 7.59 – 7.52 (m, 1H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H).

^{13}C-NMR (75 MHz, DMSO-d_6): δ= 156.0 (CH), 152.9 (C_q), 133.5 (C_q), 126.1 (CH), 125.4 (CH), 123.0 (CH), 122.4 (CH).

GC/MS m/z = 135.1 [M^+]

Analytical data are in accordance with those reported in the literature.[2]

***p*-Tolunitrile (S2)**

^{1}H NMR (300 MHz, DMSO-d_6) δ= 7.72 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 2.39 (s, 3H).

Analytical data are in accordance with those reported in the literature.[3]

2-Hydroxybenzothiazole (S3)

^{1}H NMR (300 MHz, DMSO-d_6) δ= 11.86 (br s, 1H), 7.58 – 7.53 (m, 1H), 7.31 – 7.24 (m, 1H), 7.16 – 7.08 (m, 2H).

HRMS (ESI/TOF) calcd for C_7H_6NOS $[M+H]^+$ 152.0170, found 152.0169.

Analytical data are in accordance with those reported in the literature.[4]

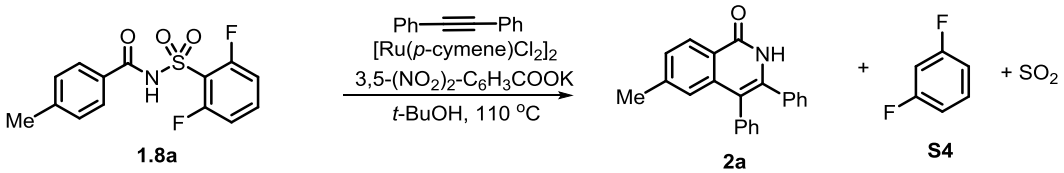
[2] Itoh, T.; Mase, T. *Org. Lett.* **2007**, *9*, 3687-3689.

[3] Wang, E. C.*; Huang, K. S.; Chen, H. M.; Wu, C. C.; Lin, G. J. *J. Chin. Chem. Soc.* **2004**, *5*, 619-627.

[4] Yamada, N.; Koyasu, T.; Sonami, M.; Aoi, M.; Tashiro, S.; Sheikh, Md. C.; Ishida, Y.; Kawashima, W.; Yoshimura, T; Morita, T. *Phosphorus, Sulfur and Silicon and the Related Elements*, **2010**, *185*, 1142-1153.

1.2. Annulation of *N*-(2,6-difluorobenzenesulfonyl)carboxamide 1.8a

When 2,6-difluorobenzenesulfonamide was used as a directing group in compound **1.8a** (Scheme S2), reaction mixture was studied with fluorine NMR to determine fluorinated by-products.



Scheme S2. Annulation of substrate **1.8a**.

These studies revealed 1,3-difluorobenzene (**S4)** as the only by-product for the synthesis of isoquinolone **1.8a**. Thus, ^{19}F-NMR spectra were recorded for 1,3-difluorobenzene (Figure S2, (a), starting material (b), reaction mixture after 2 h (c)). Pure **S4** was spiked together with reaction mixture after 2 h to make sure that newly formed signal belongs to expected by-product (Figure S2, (d)). ^{19}F-NMR spectra of reaction mixtures were also recorded after 4 and 24 h (Figure S2 (e) and (f)).

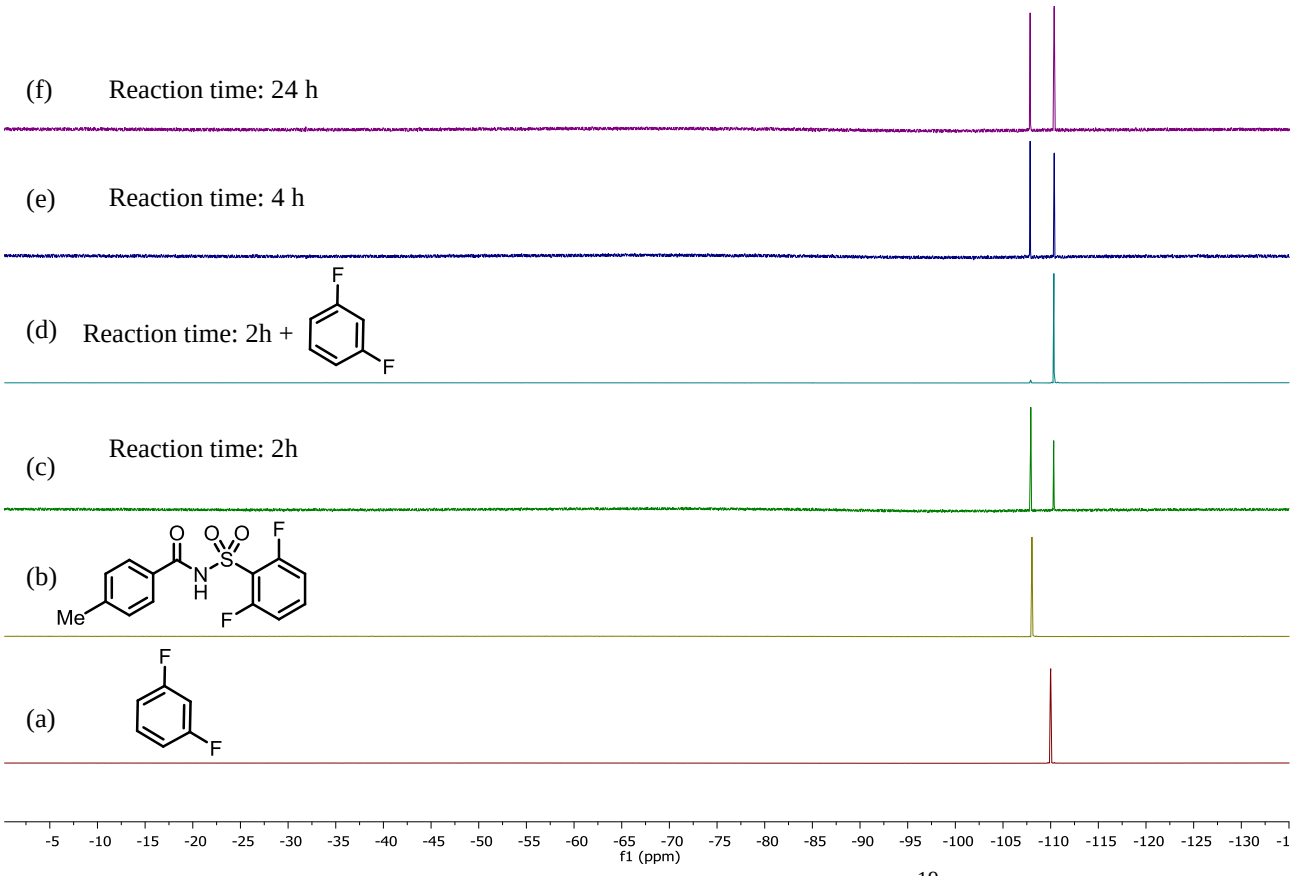


Figure S2. Studies of the reaction mixture showed in scheme S2 using ^{19}F NMR.

Reaction mixture was tested with GC after 2 h and the presence of 1,3-difluorobenzene was determined (see figure S3).

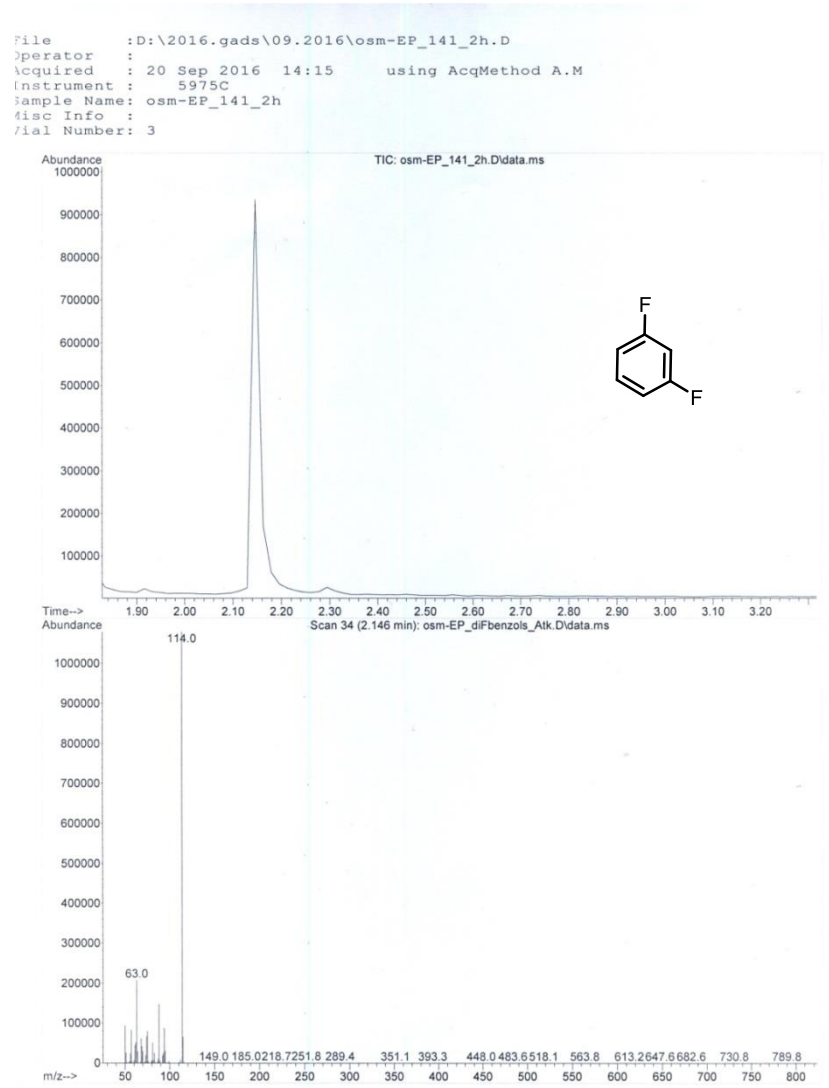
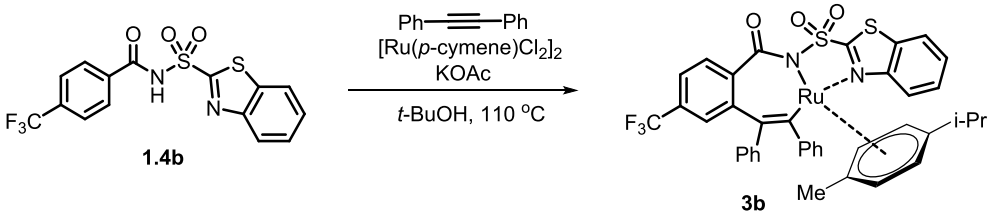


Figure S3. GC-MS analysis of the reaction mixture presented in Scheme S2.

1.3. Isolation of ruthenacycle 3b.

When a substrate **1.4b** was subjected to the C-H activation/annulation reaction conditions, seven membered cycloruthenated complex **3b** was isolated (Scheme S3).

Description of synthesis: N-Acyl sulfonamide **1.4b** (200 mg, 0.52 mmol), diphenylacetylene (185 mg, 1.04 mmol), potassium acetate (15.3 mg, 0.16 mmol) and $[Ru(cymene)Cl_2]_2$ (31.7 mg, 0.05 mmol) in 10 mL of *t*-butanol. After 24 h, additional catalyst amount was added (31.7 mg, 0.05 mmol) and stirred for 24 h. Reaction mixture was separated by column chromatography on silica gel (DCM:Hex:EtOAc 1:4:1-1:1:1) to yield intermediate **3b**. Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of a solution of **3b** in CH_3CN at room temperature (ORTEP drawing is presented in Figure S4).



Scheme S3. Formation of ruthenacycle intermediate.

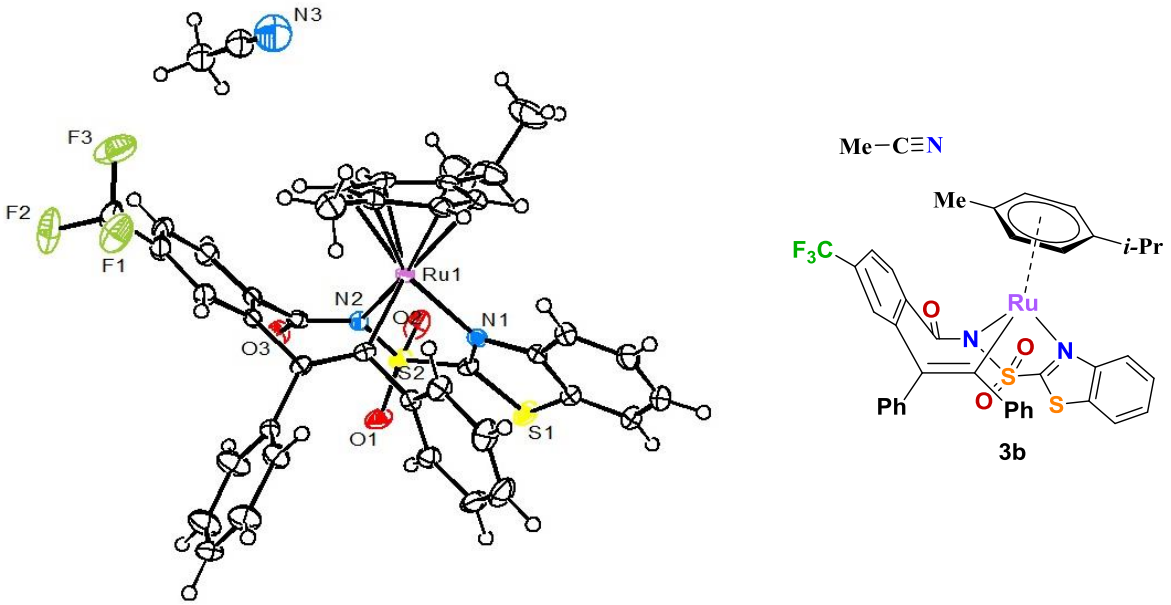
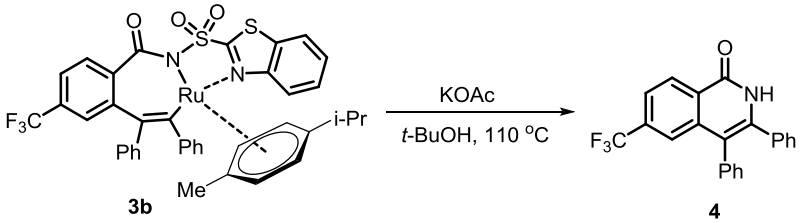


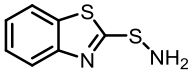
Figure S4. An ORTEP drawing of isolated ruthenacycle **3b**.

When isolated intermediate **3b** (35 mg) was heated in *t*-butanol (2 mL) at 110 °C in the prescence of KOAc (0.3 eq, 1.3 mg), product **4** slow generation was observed using UPLC-MS (Scheme S4).



Scheme S4. Product **4** formation from intermediate **3b**.

2. Substrate synthesis

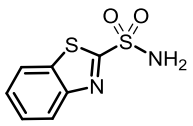


2-Benzothiazolesulfenamide S5. Round bottomed flask equipped with a dropping funnel was charged with concentrated ammonia in water (25 %, 150 mL) and cooled to 0 °C in an ice-salt bath. A solution of 2-mercaptobenzothiazole (10.55 g, 59.8 mmol) in H_2O (35 mL) containing NaOH (2.5 g, 63.0 mmol) was added via dropping funnel and simultaneously NaOCl (13 %, 24 mL) solution was dropped through a syringe for 1 h and temperature was maintained at -5 – 0 °C. Stirring was continued for 1 h and then the white product was filtered and rinsed with sufficient amount of ice-H_2O to remove all $NH_3 \cdot H_2O$. Yield 7.40 g (68%) white substance (mp= 126-129 °C).

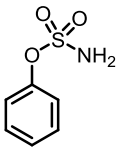
UPLC-MS (ESI) calcd for $C_7H_7N_2S_2$ $[M+H]^+$ 183.28, found 183.26.

^{1}H-NMR (300 MHz, DMSO-d_6): δ= 8.00 (ddd, J = 7.9, 1.4, 0.6 Hz, 1H), 7.73 (ddd, J = 8.1, 1.2, 0.6 Hz, 1H), 7.47 – 7.36 (m, 1H), 7.34 – 7.23 (m, 1H), 4.94 (s, 2H)

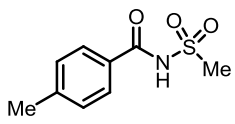
^{13}C-NMR (100 MHz, DMSO-d_6): δ= 182.3 (C_q), 154.8 (C_q), 134.4 (C_q), 126.0 (CH), 123.3 (CH), 121.6 (CH), 120.9 (CH).



Benzothiazole-2-sulfonamide S6. 2-Benzothiazolesulfenamide **S5** (7.40 g, 40.6 mmol) was suspended in the mixture of acetone (150 mL) and H_2O (150 mL). A solution of $KMnO_4$ (9.62 g, 1.5 eq.) in H_2O (275 mL) was added with stirring over a 1h period. The reaction mixture was stirred for another 1 h, treated with decolorizing charcoal (2 g) and NaOH (10 N, 37 mL) and then stirred for 30 min. Mixture was filtered through celite for better sparation of MnO_2. The filtrate was acidified with concentrated HCl and the product was extracted with ethylacetate (4x100 mL) and dried over Na_2SO_4. Crude product was recrystallized from dichloroethane, yielding 4.09 g (47 %) light brown solid (mp= 172-173 ^oC).
HR-MS (ESI/TOF) calcd for $C_7H_7N_2O_2S_2$ $[M+H]^+$ 214.9949, found 214.9951.
^{1}H-NMR (300 MHz, DMSO-d_6): δ= 8.35 (s, 2H), 8.29 – 8.23 (m, 1H), 8.20 – 8.12 (m, 1H), 7.74 – 7.56 (m, 2H).
^{13}C-NMR (100 MHz, DMSO-d_6): δ= 169.4 (C_q), 151. 8 (C_q), 135.7 (C_q), 127.6 (CH), 127.5 (CH), 124.2 (CH), 123.2 (CH).



Phenyl sulfamate S7.[5] Formic acid (2.5 mL, 65.6 mmol, 1.5 eq.) was added dropwise to neat $ClSO_2NCO$ (5.7 mL, 65.6 mmol, 1.5 eq.) at 0 ^oC with rapid stirring. Vigorous gas evolution was observed during the addition process and within 5 min the mixture solidified. To the solid mass was then added 34 mL of CH_3CN, and the resulting solution was stirred for 1 h at 0 °C and 8 h at 25 °C. The reaction was cooled to 0 °C and a solution of 4.12 g of phenol (43.8 mmol) in 34 mL of DMA was added dropwise. After stirring for 15 h at 25 °C, the solution was diluted with 50 mL of Et_2O and 50 mL of H_2O. The biphasic solution was separated and the ethereal layer was washed with 1 x 50 mL of H_2O and 2 x 50 mL of saturated aqueous NaCl. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the residue by chromatography on silica gel (Hex:EtOAc 1:1) afforded the product **S7** as a white solid (5.0 g, 66 %).
^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.49 – 7.36 (m, 2H), 7.36 – 7.29 (m, 3H), 4.98 (s, 2H).
Analytical data are in accordance with those reported in the literature.[6]

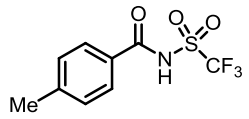


Representative procedure for *N*-acylsulfonamides. Synthesis of 4-methyl-*N*-(methylsulfonyl)benzamide (1.1). Methanesulfonamide (553 mg, 5.82 mmol, 1 eq.) and 2.43 mL Et_3N (3 eq.) were dissolved in 25 mL of dry DCM and cooled in water-ice bath. 4-Methylbenzoyl chloride (776 µL, 900 mg, 5.82 mmol, 1 eq.) was added and resulting mixture was allowed to warm up to room temperature and stirred for 6 h at room temperature under an argon atmosphere. After conversion of all sulfonamide (UPLC/MS), solvent was evaporated, crude mixture was dissolved in EtOAc and washed 3x15 mL with 5% $KHSO_4$, once with brine (15 mL) and dried over sodium sulfate. After filtration and evaporation of the solvent in vacuo, the crude product was purified with flash chromatography, eluent: 1-5% MeOH/DCM. Yield: 942 mg (76 %) white solid (mp= 158-163 ^oC).
HR-MS (ESI/TOF) calcd for $C_9H_{10}NO_3S$ $[M-H]^-$ 212.0381, found 212.0384.

[5] *Procedure:* Guthikonda, K.; Du Bois, J. *J. Am. Chem. Soc.*, **2002**, *124*, 13672-13673

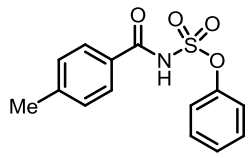
[6] Yamamoto, H.; Ho, E.; Sasaki, I.; Mitsutake, M.; Takagi, Y.; Imagawa, H.; Nishizawa, M. *Eur. J. Org. Chem.* **2011**, *13*, 2417–2420

^{1}H NMR (300 MHz, DMSO-d_6): δ= 12.02 (s, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 3.36 (s, 3H), 2.38 (s, 3H).
^{13}C NMR (100 MHz, DMSO-d_6): δ= 166.3 (C_q), 143.6 (C_q), 129.1 (CH), 129.0 (C_q), 128.5, (CH), 41.4 (CH_3), 21.1 (CH_3).



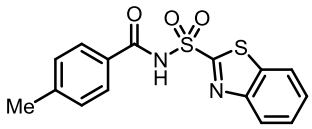
4-Methyl-*N*-((trifluoromethyl)sulfonyl)benzamide (1.2)

Prepared by analogy to compound **1.1** from trifluoromethanesulfonamide (300 mg, 2.01 mmol), 0.84 mL Et_3N, 4-methylbenzoyl chloride (268 μL, 311 mg, 2.01 mmol) in DCM, reaction mixture was stirred for 2 h at room temperature. Crude product was purified with flash chromatography, eluent: 1-7% MeOH/DCM, yield: 284 mg (53 %), yellowish solid (mp= 93-98 ^{o}C).
HR-MS (ESI/TOF) calcd for $C_9H_7F_3NO_3S$ $[M-H]^-$ 266.0099, found 266.0099.
^{1}H NMR (300 MHz, DMSO-d_6): δ= 7.81 (d, J = 8.2 Hz, 1H), 7.19 (d, J = 7.9 Hz, 1H), 2.33 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): δ= 169.6 (C_q), 141.0 (C_q), 134.4 (C_q), 128.7 (CH), 128.5 (CH), 120.4 (q, J=325 Hz, CF_3), 21.1 (CH_3).
^{19}F NMR (376 MHz, DMSO-d_6): -77.17 (s).



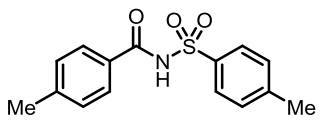
Phenyl (4-methylbenzoyl)sulfamate (1.3)

Prepared by analogy to compound **1.1** from phenyl sulfamate **S7** (356 mg, 2.06 mmol), 0.86 mL Et_3N, 4-methylbenzoyl chloride (369 μL, 318 mg, 2.06 mmol) in DCM, reaction mixture was stirred for 4 h at room temperature. Crude product was purified byflash chromatography (1-7% MeOH/DCM) to yield **1.3** (450 mg, 75 %)as a white solid (mp= 137-140 ^{o}C).
HR-MS (ESI/TOF) calcd for $C_{14}H_{14}NO_4S$ $[M+H]^+$292.0644, found 292.0644.
^{1}H NMR (400 MHz, Methanol-d_4): δ= 7.76 (d, J = 8.3 Hz, 2H), 7.44 – 7.34 (m, 2H), 7.35 – 7.24 (m, 5H), 2.39 (s, 3H).
^{13}C NMR (100 MHz, Methanol-d_4): δ=169.1 (C_q), 151.9 (C_q), 145.3 (C_q), 131.3 (C_q), 130.9 (CH), 130.3 (CH), 129.6 (CH), 128.3 (CH), 123.1 (CH), 21.6 (CH_3).



***N*-(Benzo[d]thiazol-2-ylsulfonyl)-4-methylbenzamide (1.4a)**.

Prepared by analogy to compound **1.1** from sulfonamide **S6** (785mg, 3.66 mmol), 1.53 mL Et_3N, 4-methylbenzoyl chloride (488 μL, 566 mg, 3.66 mmol) in DCM, reaction mixture was stirred for 6 h at room temperature. The crude product was recrystallized from EtOH. Yield 850 mg (70%) white crystaline substance (mp= 166-168 ^{o}C).
HR-MS (ESI/TOF) calcd for $C_{15}H_{13}N_2O_3S_2$ $[M+H]^+$ 333.0368, found 333.0364
^{1}H NMR (400 MHz, DMSO-d_6): δ=8.30 (m, 1H), 8.18 (m, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.68 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H),
^{13}C NMR (100 MHz, DMSO-d_6): δ=166.4 (C_q), 151.5 (C_q), 144.1 (C_q), 136.3 (C_q), 129.2 (CH), 128.8 (CH), 128.6 (C_q), 127.9 (CH), 127.7 (CH), 124.6 (CH), 123.3 (CH), 21.2 (CH_3), one C missing due to the overlap.



4-Methyl-*N*-tosylbenzamide (1.5)

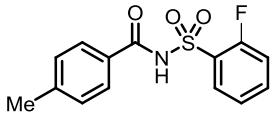
Prepared by analogy to compound **1.1** from *p*-toluenesulfonamide (500 mg, 2.92 mmol), 1.22 mL Et_3N, 4-methylbenzoyl chloride (390 μL,

452 mg, 2.92 mmol) in DCM, reaction mixture was stirred for 1 h at room temperature. Crude product was purified with flash chromatography, eluent: 1-5% MeOH/DCM. Yield: 574 mg (68 %) white solid (mp= 142-145 ^{o}C)

HR-MS (ESI/TOF) calcd for $C_{15}H_{16}NO_3S$ $[M+H]^+$ 290.0851, found 290.0854

^{1}H NMR (300 MHz, $CDCl_3$) δ=9.28 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ=164.4 (C_q), 145.3 (C_q), 144.5 (C_q), 135.7 (C_q), 129.72 (CH), 129.69 (CH), 128.8 (CH), 128.5 (C_q), 128.0 (CH), 21.8 (CH_3), 21.7 (CH_3).



***N*-((2-Fluorophenyl)sulfonyl)-4-methylbenzamide (1.6)**

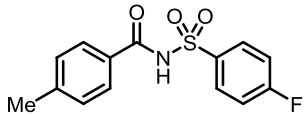
Prepared by analogy to compound **1.1** from 2-fluorobenzenesulfonamide (500 mg, 2.85 mmol), 1.19 mL Et_3N, 4-methylbenzoyl chloride (380 µL, 441 mg, 2.85 mmol) in DCM, reaction mixture was stirred for 15h (overnight) at room temperature. Crude product was washed with EtOAc:Hex 1:2 mixture to yield 663 mg (79 %) white solid (mp= 152-155 ^{o}C).

HR-MS (ESI/TOF) calcd for $C_{14}H_{13}NO_3S$ $[M+H]^+$ 294.0600, found 294.0603.

^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ= 12.81 (br. s, 1H), 8.00 (td, *J* = 7.8, 1.9 Hz, 1H), 7.84 – 7.72 (m, 3H), 7.51 – 7.40 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ= 165.5 (C_q), 158.2 (CF, d, *J* = 255.0 Hz), 144.0 (C_q), 136.5 (CH, d, *J* = 8.5 Hz), 131.3 (C_q), 129.2 (CH), 128.6 (CH), 128.4 (C_q), 127.3 (CH, d, *J* = 12.8 Hz), 125.0 (CH, d, *J* = 3.7 Hz), 117.3 (CH, d, *J* = 20.6 Hz), 21.1 (CH_3).

^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ= -110.9 (m).



***N*-((4-Fluorophenyl)sulfonyl)-4-methylbenzamide (1.7)**

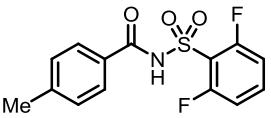
Prepared by analogy to compound **1.1** from 4-fluorobenzenesulfonamide (500 mg, 2.85 mmol), 1.19 mL Et_3N, 4-methylbenzoyl chloride (380 µL, 441 mg, 2.85 mmol) in DCM, reaction mixture was stirred for 16 h (overnight) at room temperature. Crude product was washed with EtOAc:Hex 1:2 mixture to yield 601 mg (72 %)white solid (mp= 183-186^{o}C).

HR-MS (ESI/TOF) calcd for $C_{14}H_{13}NO_3S$ $[M+H]^+$ 294.0600, found 294.0595.

^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ=12.47 (br. s., 1H), 8.13 – 8.00 (m, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.41 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ= 165.3 (C_q), 164.8 (CF, d, *J* = 252.6 Hz), 143.8 (C_q), 135.8 (C_q, d, *J* = 3.0 Hz), 131.0 (CH, d, *J* = 9.9 Hz), 129.2 (CH), 128.6 (C_q), 128.5 (CH), 116.4 (CH, d, *J* = 23.0 Hz), 21.1 (CH_3).

^{19}F NMR (376 MHz, DMSO-*d*6): δ= -104.9 (tt, *J* = 8.9, 5.2 Hz).

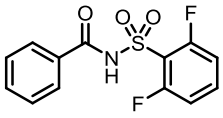


***N*-((2,6-Difluorophenyl)sulfonyl)-4-methylbenzamide (1.8a)**

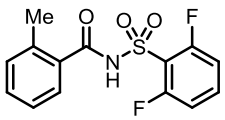
Prepared by analogy to compound **1.1** from 2,6-difluorobenzene-sulfonamide (200 mg, 1.04 mmol), 0.43 mL Et_3N, 4-methylbenzoyl chloride (137 µL, 160 mg, 1.04 mmol) in DCM, reaction mixture was stirred for 16 h (overnight) at room temperature. Crude product was purified with column chromatography, eluent EtOAc to yield 285 mg (88 %) white solid (mp=154-157 ^{o}C).

HR-MS (ESI/TOF) calcd for $C_{14}H_{12}F_2NO_3S$ $[M+H]^+$ 312.0506, found 312.0489.

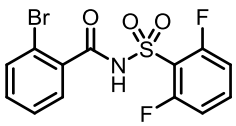
^{1}H NMR (400 MHz, DMSO-d_6): δ= 13.04 (br. s., 1H), 7.86 – 7.74 (m, 3H), 7.37 – 7.29 (m, 4H), 2.36 (s, 3H).
^{13}C NMR (100 MHz, DMSO-d_6): δ=166.1 (C_q), 159.0 (CF, dd, *J* = 258.3, 3.4 Hz), 144.1 (C_q), 136.4 (CH, t, *J* = 11.3 Hz), 129.4 (CH), 128.6 (CH), 128.3 (C_q), 117.4 (C_q, t, *J* = 15.0 Hz), 113.5 (CH, dd, *J* = 22.6, 3.4 Hz), 21.1 (CH_3).
^{19}F NMR (376 MHz, DMSO-d_6): δ= -108.04 (dd, *J* = 10.1, 6.1 Hz).



_N_-((2,6-Difluorophenyl)sulfonyl)benzamide (1.8b)
Prepared by analogy to compound **1.1** from 2,6-difluorobenzenesulfonamide (800 mg, 4.14 mmol), 1.73 mL Et_3N, benzoyl chloride (481 µL, 582 mg, 4.14 mmol) in DCM, reaction mixture was stirred for 4 h at room temperature. Crude product was recrystallized from *i*PrOH to yield 1.07 g (87 %) white solid (mp= 162-164 ^{o}C).
HR-MS (ESI/TOF) calcd for $C_{13}H_{10}F_2NO_3S$ $[M+H]^+$ 298.0349, found 298.0344.
^{1}H NMR (300 MHz, DMSO-d_6): δ=7.97 – 7.86 (m, 1H), 7.79 (tt, *J* = 8.5, 6.1 Hz, 1H), 7.72 – 7.59 (m, 1H), 7.58 – 7.45 (m, 2H), 7.34 (t, *J* = 9.1 Hz, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): δ=166.3 (C_q), 159.0 (CF, dd, *J* = 258.4, 3.4 Hz), 136.5 (CH, t, *J* = 11.2 Hz), 133.6 (CH), 131.1 (C_q), 128.7 (CH), 128.5 (CH), 117.3 (C_q, t, *J* = 15.0 Hz), 113.5 (CH, dd, *J* = 22.6, 3.5 Hz).
^{19}F NMR (376 MHz, DMSO-d_6): δ= -108.0 (dd, *J* = 9.7, 6.0 Hz).

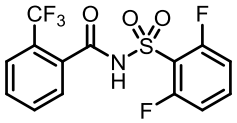


_N_-((2,6-Difluorophenyl)sulfonyl)-2-methylbenzamide (1.8c)
Prepared by analogy to compound **1.1** from 2,6-difluorobenzenesulfonamide (210 mg, 1.09 mmol), 0.46 mL Et_3N, *o*-toluoyl chloride (143 µL, 170 mg, 1.09 mmol) in DCM, reaction mixture was stirred for 4 h at room temperature. Crude product was recrystallized from *i*PrOH to yield 300mg (89 %) white solid (mp= 173-175 ^{o}C).
HR-MS (ESI/TOF) calcd for $C_{14}H_{11}F_2NO_3SNa$ $[M+Na]^+$ 334.0325, found 334.0321.
^{1}H NMR (400 MHz, $CDCl_3$): δ=8.68 (s, 1H), 7.61 (tt, *J* = 8.5, 5.9 Hz, 1H), 7.48 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.42 (td, *J* = 7.5, 1.4 Hz, 1H), 7.26 (t, *J* = 7.1 Hz, 2H), 7.09 (t, *J* = 8.6 Hz, 2H), 2.40 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ=166.6 (C_q), 160.3 (CF, dd, *J* = 261.7, 3.0 Hz), 138.6 (C_q), 136.1 (CH, t, *J* = 11.2 Hz), 132.4 (CH), 132.1 (CH), 131.5 (C_q), 127.5 (CH), 126.3 (CH), 117.0 (C_q, t, *J* = 14.5 Hz), 113.4 (CH, dd, *J* = 23.1, 3.5 Hz), 20.2 (CH_3).
^{19}F NMR (376 MHz, $CDCl_3$): δ=-106.27 (dd, *J* = 8.9, 6.1 Hz).



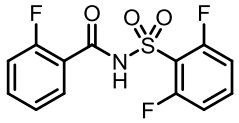
2-Bromo-_N_-((2,6-difluorophenyl)sulfonyl)benzamide (1.8d)
Prepared by analogy to compound **1.1** from 2,6-difluorobenzenesulfonamide (200 mg, 1.04 mmol), 0.43 mL Et_3N, 2-bromobenzoyl chloride (136 µL, 227 mg, 1.04 mmol) in DCM, reaction mixture was stirred for 5 h at room temperature. Crude product was purified by column chromatography on silica gel (Hex:EtOAc 2:1-1:1) to yield 310 mg (80 %) as an oily substance.
HR-MS (ESI/TOF) calcd for $C_{13}H_8BrF_2NO_3SNa$ $[M+Na]^+$397.9274, found 397.9273.
^{1}H NMR (400 MHz, $CDCl_3$): δ=9.19 (br.s, 1H), 7.66 – 7.56 (m, 3H), 7.42 – 7.31 (m, 2H), 7.12 – 7.04 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ=164.7 (C_q), 160.3 (CF, dd, *J* = 262.6, 2.9 Hz), 136.4 (CH, t, *J* = 11.2 Hz), 134.1 (CH), 133.7 (C_q), 133.3 (CH), 130.5 (CH), 128.0 (CH), 119.5 (C_q), 116.6 (C_q, t, *J* = 14.3 Hz), 113.4 (CH, dd, *J* = 23.0, 3.3 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ= -106.81 (s).



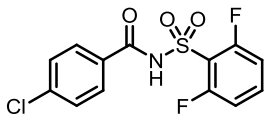
***N*-((2,6-Difluorophenyl)sulfonyl)-2-(trifluoromethyl)benzamide (1.8e)**

Prepared by analogy to compound **1.1** from 2,6-difluorobenzenesulfonamide (200 mg, 1.04 mmol), 0.43 mL Et_3N, 2-(trifluoromethyl)benzoyl chloride (153 μL, 216 mg, 1.04 mmol) in DCM, reaction mixture was stirred for 3 h at room temperature. Crude product was recrystallized from *i*PrOH to yield 278 mg (74 %) white solid (mp= 175-178^{o}C).
HR-MS (ESI/TOF) calcd for $C_{14}H_8F_5NO_3SNa$ $[M+Na]^+$388.0043, found 388.0031.
^{1}H NMR (400 MHz, DMSO-d_6): δ= 7.87 – 7.70 (m, 4H), 7.65 – 7.58 (m, 1H), 7.37 (t, *J* = 9.1 Hz, 2H).
^{13}C NMR (100 MHz, DMSO-d_6): δ=166.4 (C_q), 159.33 (CF, dd, *J* = 259.0, 3.4 Hz), 136.82 (CH, t, *J* = 11.4 Hz), 132.6 (CH and C_q overlaps), 131.3 (CH), 128.6 (CH), 126.6 (CH, q, *J* = 4.8 Hz), 126.0 (C_q, q, *J* = 31.9 Hz), 123.3 (CF_3, q, *J* = 273.7 Hz), 116.5 (C_q, t, *J* = 3.7 Hz), 113.4 (CH, dd, *J* = 22.7, 3.4 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ= -59.08 (s), -105.76 (tt, *J* = 6.2, 2.3 Hz).



***N*-((2,6-Difluorophenyl)sulfonyl)-2-fluorobenzamide (1.8f)**

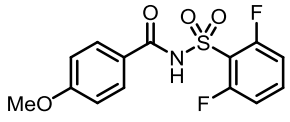
Prepared by analogy to compound **1.1** from 2,6-difluorobenzenesulfonamide (200 mg, 1.04 mmol), 0.43 mL Et_3N, 2-fluorobenzoyl chloride (123 μL, 164 mg, 1.04 mmol) in DCM, reaction mixture was stirred for 15 h (overnight) at room temperature. Crude product was washed with EtOAc:Hex 1:4 to yield 251 mg (77 %) white solid (mp= 125-128 ^{o}C).
HR-MS (ESI/TOF) calcd for $C_{13}H_{18}F_3NO_3S$ $[M+H]^+$ 316.0255, found 316.0247.
^{1}H NMR (400 MHz, DMSO-d_6): δ=7.82 (tt, *J* = 8.5, 6.1 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.41 – 7.26 (m, 4H).
^{13}C NMR (100 MHz, DMSO-d_6): δ=163.9 (C_q), 159.4 (CF, d, *J* = 252.9 Hz), 159.1 (CF, dd, *J* = 258.7, 3.4 Hz), 136.7 (CH, t, *J* = 11.3 Hz), 134.4 (CH, d, *J* = 8.6 Hz), 130.2 (CH, d, *J* = 1.9 Hz), 124.6 (CH, d, *J* = 3.5 Hz), 121.4 (C_q, d, *J* = 13.1 Hz), 117.0 (C_q, t, *J* = 14.8 Hz), 116.5 (CH, d, *J* = 21.1 Hz), 113.5 (CH, dd, *J* = 22.6, 3.5 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ= -105.96 (dd, *J* = 9.2, 5.9 Hz), -111.37 (s).



4-Chloro-*N*-((2,6-difluorophenyl)sulfonyl)benzamide (1.8g)

Prepared by analogy to compound **1.1** from 2,6-difluorobenzenesulfonamide (200 mg, 1.04 mmol), 0.43 mL Et_3N, 4-chlorobenzoyl chloride (132 μL, 181 mg, 1.04 mmol) in DCM, reaction mixture was stirred for 3 h at room temperature. Crude product was recrystallized from *i*PrOH to yield 251 mg (77 %) white solid (mp= 198-201^{o}C).
HR-MS (ESI/TOF) calcd for $C_{13}H_7ClF_2NO_3S$ $[M-H]^-$ 329.9803, found 329.9809.
^{1}H NMR (400 MHz, DMSO-d_6): δ= 7.95 – 7.90 (m, 2H), 7.79 (tt, *J* = 8.5, 6.1 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.38 – 7.28 (m, 2H).
^{13}C NMR (100 MHz, DMSO-d_6): δ=165.4 (C_q), 159.0 (CF, dd, *J* = 258.4, 3.4 Hz), 138.5 (C_q), 136.5 (t, *J* = 11.2 Hz), 130.5 (CH), 130.0 (C_q), 128.8 (CH), 117.24 (t, *J* = 15.6 Hz), 113.52 (CH, dd, *J* = 22.6, 3.4 Hz).

^{19}F NMR (376 MHz, DMSO-d_6): δ= -107.93 (dd, J = 9.7, 6.2 Hz).



***N*-((2,6-Difluorophenyl)sulfonyl)-4-methoxybenzamide (1.8h)**

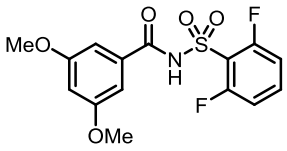
Prepared by analogy to compound **1.1** from 2,6-difluorobenzene-sulfonamide (220 mg, 1.14 mmol), 0.48 mL Et_3N, 4-methoxybenzoyl chloride (154 µL, 194 mg, 1.14 mmol) in DCM, reaction mixture was stirred for 15h (overnight) at room temperature. Crude product was washed with EtOAc:Hex 1:2 to yield 305 mg (82 %) white solid (mp= 161-164 ^{o}C).

HR-MS (ESI/TOF) calcd for $C_{14}H_{12}F_2NO_4S$ $[M+H]^+$ 328.0455, found 328.0453.

^{1}H NMR (400 MHz, DMSO-d_6): δ=12.97 (br. s, 1H), 7.97 – 7.87 (m, 3H), 7.78 (tt, J = 8.5, 6.1 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.07 – 7.00 (m, 2H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ=165.4 (C_q), 163.4 (C_q), 159.0 (CF, dd, J = 258.2, 3.5 Hz), 136.3 (CH, t, J = 11.2 Hz), 130.8 (CH), 123.1 (C_q), 117.5 (C_q, t, J = 14.8 Hz), 114.0 (CH), 113.5 (CH, dd, J = 22.6, 3.4 Hz), 55.6 (CH_3).

^{19}F NMR (376 MHz, DMSO-d_6): δ=-108.08 (ddd, J = 9.8, 6.3, 3.3 Hz).



***N*-((2,6-Difluorophenyl)sulfonyl)-3,5-dimethoxybenzamide (1.8i)**

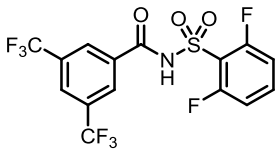
Prepared by analogy to compound **1.1** from 2,6-difluorobenzene-sulfonamide (200 mg, 1.04 mmol), 0.43 mL Et_3N, 3,5-dimethoxybenzoyl chloride (208 mg, 1.04 mmol) in DCM, reaction mixture was stirred for 15h (overnight) at room temperature. Crude product was recrystallized from *i*PrOH to yield 330 mg (89 %) white solid (mp= 191-195 ^{o}C).

HR-MS (ESI/TOF) calcd for $C_{15}H_{14}F_2NO_5S$ $[M+H]^+$ 358.0561, found 358.0561.

^{1}H NMR (400 MHz, DMSO-d_6): δ= 7.79 – 7.67 (m, 1H), 7.28 (t, J = 9.3 Hz, 2H), 7.10 (d, J = 2.3 Hz, 2H), 6.71 (t, J = 2.3 Hz, 1H), 3.77 (s, 6H).

^{13}C NMR (100 MHz, DMSO-d_6): δ=166.3 (C_q), 160.3 (C_q), 159.1 (CF, dd, J = 257.6, 3.7 Hz), 135.7 (CH), 134.1 (C_q), 118.3 (C_q), 113.3 (CH, dd, J = 22.8, 3.3 Hz), 106.0 (CH), 105.5 (CH), 55.5 (OCH_3).

^{19}F NMR (376 MHz, DMSO-d_6): δ= -107.92 (dd, J = 10.0, 6.2 Hz).



***N*-((2,6-Difluorophenyl)sulfonyl)-3,5-bis(trifluoromethyl)benz-amide (1.8j)**

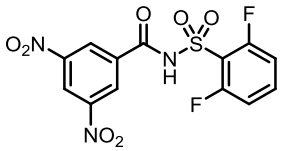
Prepared by analogy to compound **1.1** from 2,6-difluorobenzenesulfonamide (200 mg, 1.04 mmol), 0.43 mL Et_3N, 3,5-bis(trifluoromethyl)-benzoyl chloride (188 µL, 286 mg, 1.04 mmol) in DCM, reaction mixture was stirred for 6 h at room temperature. Crude product was recrystallized from *i*PrOH to yield 413 mg (92 %) white solid (mp=dec. above 200 ^{o}C).

HR-MS (ESI/TOF) calcd for $C_{15}H_6F_8NO_3S$ $[M-H]^-$ 431.9941, found 431.9950.

^{1}H NMR (400 MHz, DMSO-d_6): δ= 8.52 (s, 2H), 8.37 (s, 1H), 7.73 (tt, J = 8.5, 6.0 Hz, 1H), 7.28 (t, J = 9.0 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ=164.2 (C_q), 159.2 (CF, dd, J = 258.1, 3.7 Hz), 136.1 (CH, t, J = 11.3 Hz), 134.8 (C_q), 130.6 (C_q, q, J = 33.5 Hz), 129.3 (CH, m), 126.4 (CH, hept, J=3.4 Hz), 123.0 (C_q, q, J = 273.1 Hz), 117.9 (C_q, t, J = 15.3 Hz), 113.4 (CH, dd, J = 22.7, 3.5 Hz).

^{19}F NMR (376 MHz, DMSO-d_6): δ= -61.47 (s), -107.72 (dd, J = 9.6, 6.1 Hz)



***N*-((2,6-Difluorophenyl)sulfonyl)-3,5-dinitrobenzamide (1.8k)**

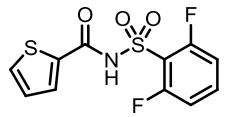
Prepared by analogy to compound **1.1** from 2,6-difluorobenzene-sulfonamide (200 mg, 1.04 mmol), 0.43 mL Et_3N, 3,5-dinitrobenzoyl chloride (239 mg, 1.04 mmol) in DCM, reaction mixture was stirred for 6 h at room temperature. Crude product was washed with EtOAc:Hex 1:4 to yield 302 mg (75 %) light yellow solid (mp= 262-265 ^oC).

HR-MS (ESI/TOF) calcd for $C_{13}H_6F_2N_3O_7S$ $[M-H]^-$ 385.9895, found 385.9908.

^1H NMR (400 MHz, DMSO-d_6): δ=9.00 (d, *J* = 2.2 Hz, 2H), 8.93 (t, *J* = 2.2 Hz, 1H), 7.62 (tt, *J* = 8.4, 6.0 Hz, 1H), 7.19 (t, *J* = 8.7 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ=163.7 (C_q), 159.2 (CF, dd, *J* = 257.2, 4.1 Hz), 148.1 (C_q), 136.8 (C_q), 135.3 (CH, t, *J* = 11.3 Hz), 128.4 (CH), 121.6 (CH), 118.8 (C_q), 113.2 (dd, *J* = 23.0, 3.3 Hz).

^{19}F NMR (376 MHz, DMSO-d_6): δ=-107.63 (dd, *J* = 9.7, 6.0 Hz).



***N*-((2,6-Difluorophenyl)sulfonyl)thiophene-2-carboxamide (1.8l)**

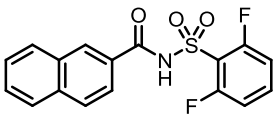
Prepared by analogy to compound **1.1** from 2,6-difluorobenzenesulfonamide (175 mg, 0.91 mmol), 0.38 mL Et_3N, thiophene-2-carbonyl chloride (97 µL, 133 mg, 0.91 mmol) in DCM, reaction mixture was stirred for 4 h at room temperature. Crude product was recrystallized from *i*PrOH to yield 187 mg (68 %) white solid (mp=196-198 ^oC).

HR-MS (ESI/TOF) calcd for $C_{11}H_8F_2NO_3S_2$ $[M+H]^+$ 303.9914, found 303.9914.

^1H NMR (400 MHz, DMSO-d_6): δ=8.09 (d, *J* = 3.8 Hz, 1H), 7.97 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.77 (tt, *J* = 8.5, 6.1 Hz, 1H), 7.32 (t, *J* = 9.2 Hz, 2H), 7.21 (dd, *J* = 5.0, 3.8 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6): δ=160.4 (C_q), 159.0 (CF, dd, *J* = 258.6, 3.4 Hz), 136.6 (CH, t, *J* = 11.3 Hz), 135.9 (C_q), 135.3 (CH), 132.8 (CH), 128.7 (CH), 117.25 (C_q, t, *J* = 14.7 Hz), 113.53 (CH, dd, *J* = 22.4, 3.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ= -105.93 (dd, *J* = 8.8, 5.9 Hz).



***N*-((2,6-Difluorophenyl)sulfonyl)-2-naphthamide (1.8m)**

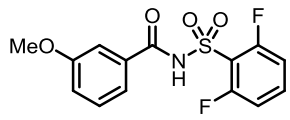
Prepared by analogy to compound **1.1** from 2,6-difluorobenzenesulfonamide (203 mg, 1.05 mmol), 0.44 mL Et_3N, 2-naphthoyl chloride (200 mg, 1.05 mmol) in DCM, reaction mixture was stirred for 15h (overnight) at room temperature. Crude product was washed with EtOAc:Hex 1:2 to yield 300 mg (82 %) white solid (mp=179-182 ^oC).

HR-MS (ESI/TOF) calcd for $C_{17}H_{12}F_2NO_3S$ $[M+H]^+$348.0506, found 348.0500.

^1H NMR (300 MHz, DMSO-d_6): δ=8.65 (d, *J* = 1.8 Hz, 1H), 8.09 – 8.04 (m, 1H), 8.01 (dd, *J* = 8.4, 5.9 Hz, 2H), 7.89 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.80 (tt, *J* = 8.5, 6.0 Hz, 1H), 7.66 (dddd, *J* = 19.6, 8.2, 6.9, 1.4 Hz, 2H), 7.35 (t, *J* = 9.1 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ=166.4 (C_q), 159.14 (CF, dd, *J* = 258.4, 3.4 Hz), 136.5 (t, *J* = 11.1 Hz), 135.0, 131.8, 130.1 (C_q), 129.4 (CH), 128.9 (C_q), 128.4 (CH), 128.3 (C_q), 127.7 (CH), 127.2 (CH), 124.1 (CH), 117.4 (t, *J* = 15.0 Hz), 113.5 (dd, *J* = 22.6, 3.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ= -106.03 (dd, *J* = 9.0, 6.0 Hz).



***N*-((2,6-difluorophenyl)sulfonyl)-3-methoxybenzamide (1.8n)**

Prepared by analogy to compound **1.1** from 2,6-difluorobenzenesulfonamide (190 mg, 0.98 mmol), 0.41 mL Et_3N, 3-

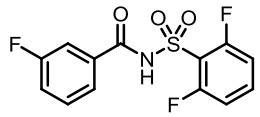
methoxybenzoyl chloride (168 mg, 0.98 mmol) in DCM, reaction mixture was stirred for 15 h (overnight) at room temperature. Crude product was recrystallized from *i*PrOH to yield 225 mg (70 %) white solid (mp= 154-157 ^{o}C).

HR-MS (ESI/TOF) calcd for $C_{14}H_{12}F_2NO_4S$ $[M+H]^+$ 328.0455, found 328.0453

^{1}H NMR (400 MHz, $CDCl_3$): 9.36 (s, 1H), 7.60 (tt, *J* = 8.5, 5.9 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.13 (dt, *J* = 7.1, 2.3 Hz, 1H), 7.07 (t, *J* = 8.6 Hz, 2H), 3.81 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ=164.8 (C_q), 160.3 (CF, dd, *J* = 262.1, 2.9 Hz), 160.2 (C_q), 136.2 (t, *J* = 11.3 Hz), 132.0 (C_q), 130.2 (CH), 120.9 (CH), 120.0 (CH), 116.9 (C_q, t, *J* = 14.5 Hz), 113.4 (CH, dd, *J* = 23.0, 3.4 Hz), 112.6 (CH).

^{19}F NMR (376 MHz, $CDCl_3$): δ= -106.01 (dd, *J* = 8.7, 5.8 Hz).



***N*-((2,6-difluorophenyl)sulfonyl)-3-fluorobenzamide (1.8o)**

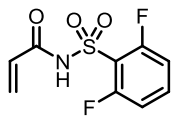
Prepared by analogy to compound **1.1** from 2,6-difluorobenzenesulfonamide (207 mg, 1.07 mmol), 0.45 mL Et_3N, 3-fluorobenzoyl chloride (170 mg, 1.07 mmol) in DCM, reaction mixture was stirred for 15 h (overnight) at room temperature. Crude product was recrystallized from *i*PrOH to yield 250 mg (74 %) white solid (mp=172-175 ^{o}C).

HR-MS (ESI/TOF) calcd for $C_{13}H_7F_3NO_3S$ $[M-H]^-$ 314.0099, found 314.0110

^{1}H NMR (400 MHz, $CDCl_3$): 9.39 (s, 1H), 7.66 – 7.58 (m, 2H), 7.55 (dt, *J* = 9.0, 2.1 Hz, 1H), 7.47 (td, *J* = 8.0, 5.4 Hz, 1H), 7.31 (tdd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 7.09 (t, *J* = 8.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ= 163.7 (C_q, d, *J* = 2.7 Hz), 162.9 (CF, d, *J* = 249.6 Hz), 160.3 (CF, dd, *J* = 262.3, 2.9 Hz), 136.4 (CH, t, *J* = 11.2 Hz), 132.9 (C_q, d, *J* = 7.2 Hz), 131.0 (CH, d, *J* = 7.9 Hz), 123.5 (CH, d, *J* = 3.2 Hz), 121.2 (CH, d, *J* = 21.3 Hz), 116.7 (C_q, t, *J* = 14.5 Hz), 115.5 (CH, d, *J* = 23.5 Hz), 113.5 (CH, dd, *J* = 22.9, 3.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ= -105.96 (dd, *J* = 9.0, 5.8 Hz), -110.25 (td, *J* = 8.5, 5.3 Hz).



***N*-((2,6-Difluorophenyl)sulfonyl)acrylamide (1.8p)**

Prepared by analogy to compound **1.1** from 2,6-difluorobenzenesulfonamide (320 mg, 1.66 mmol), 0.70 mL Et_3N, acryloyl chloride (135 μL, 150 mg, 1.66 mmol) in DCM, reaction mixture was stirred for 4 h at room temperature. Crude product was purified by column chromatography on silica gel (Hex:EtOAc 2:1-1:1-pure EtOAc) to yield 250 mg (78 %) colorless solid (mp= 112-115 ^{o}C).

HR-MS (ESI/TOF) calcd for $C_9H_6F_2NO_3S$ $[M-H]^-$ 246.0036, found 246.0039.

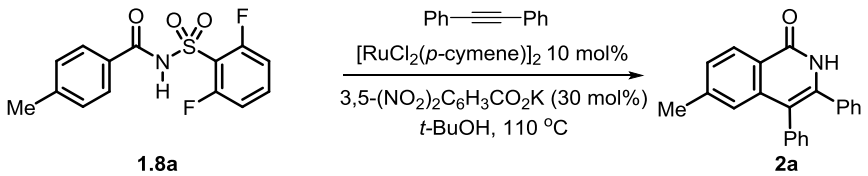
^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ=11.34 (br s, 1H), 7.80 (tt, *J* = 8.5, 6.0 Hz, 1H), 7.25 (t, *J* = 8.7 Hz, 2H), 6.40 (d, *J* = 8.4 Hz, 1H), 6.39 (d, *J* = 3.3 Hz, 1H), 5.90 (dd, *J* = 8.4, 3.3 Hz, 1H).

^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ=164.0 (C_q),160.8 (CF, dd, *J* = 259.4, 3.4 Hz), 137.2 (CH, t, *J* = 11.3 Hz), 131.8 (CH), 129.6 (CH_2), 118.3 (C_q, t, *J* = 14.9 Hz), 114.1 (CH, dd, *J* = 23.0, 3.6 Hz).

^{19}F NMR (376 MHz, $(CD_3)_2CO$): δ= -108.30 (dd, *J* = 9.1, 6.0 Hz).

3. Investigation of the concentration effect of the annulation of N-sulfonylcarboxamide 1.8a

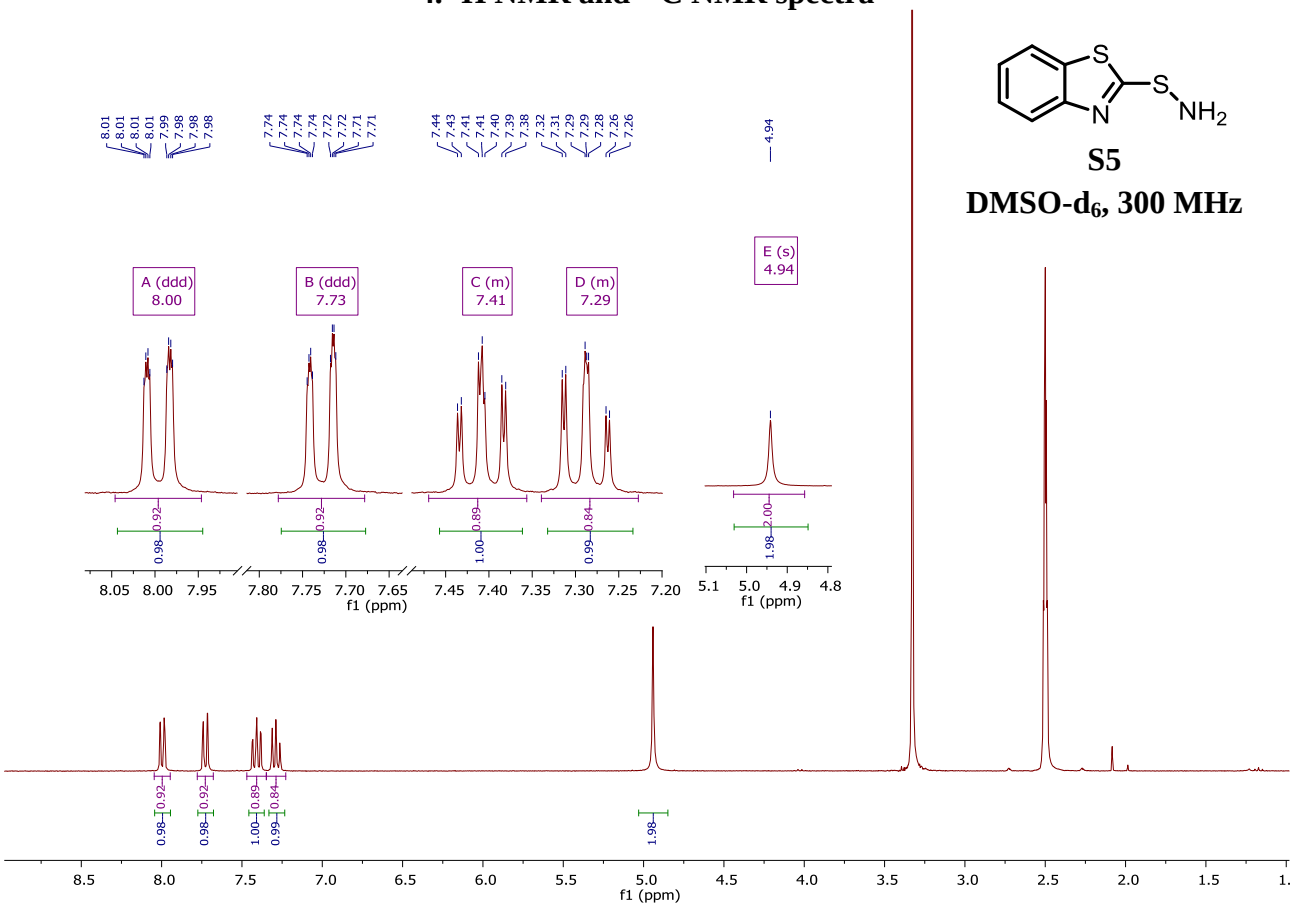
Test reactions were performed to investigate the effect of the concentration to annulation reaction (scheme 5).

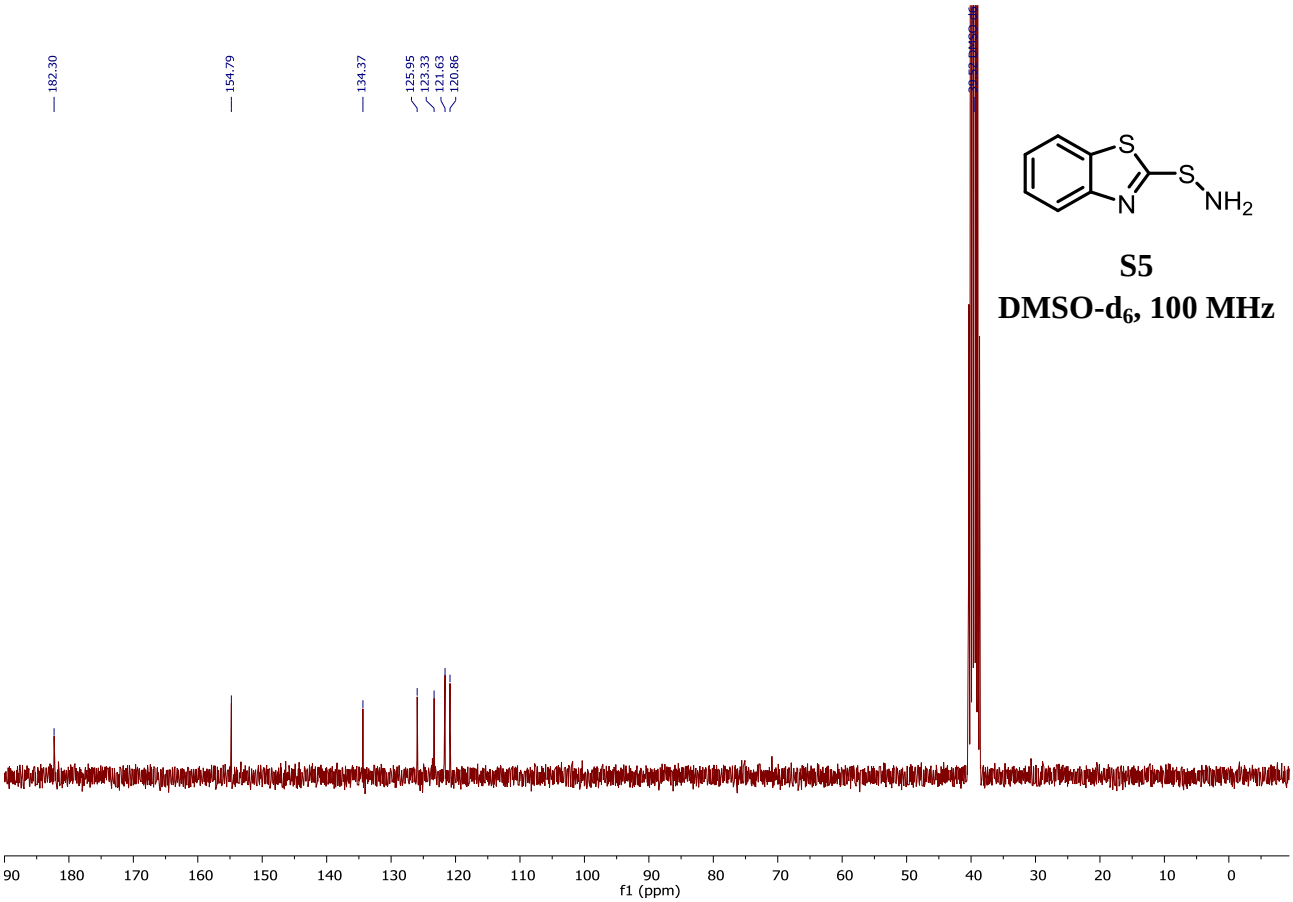


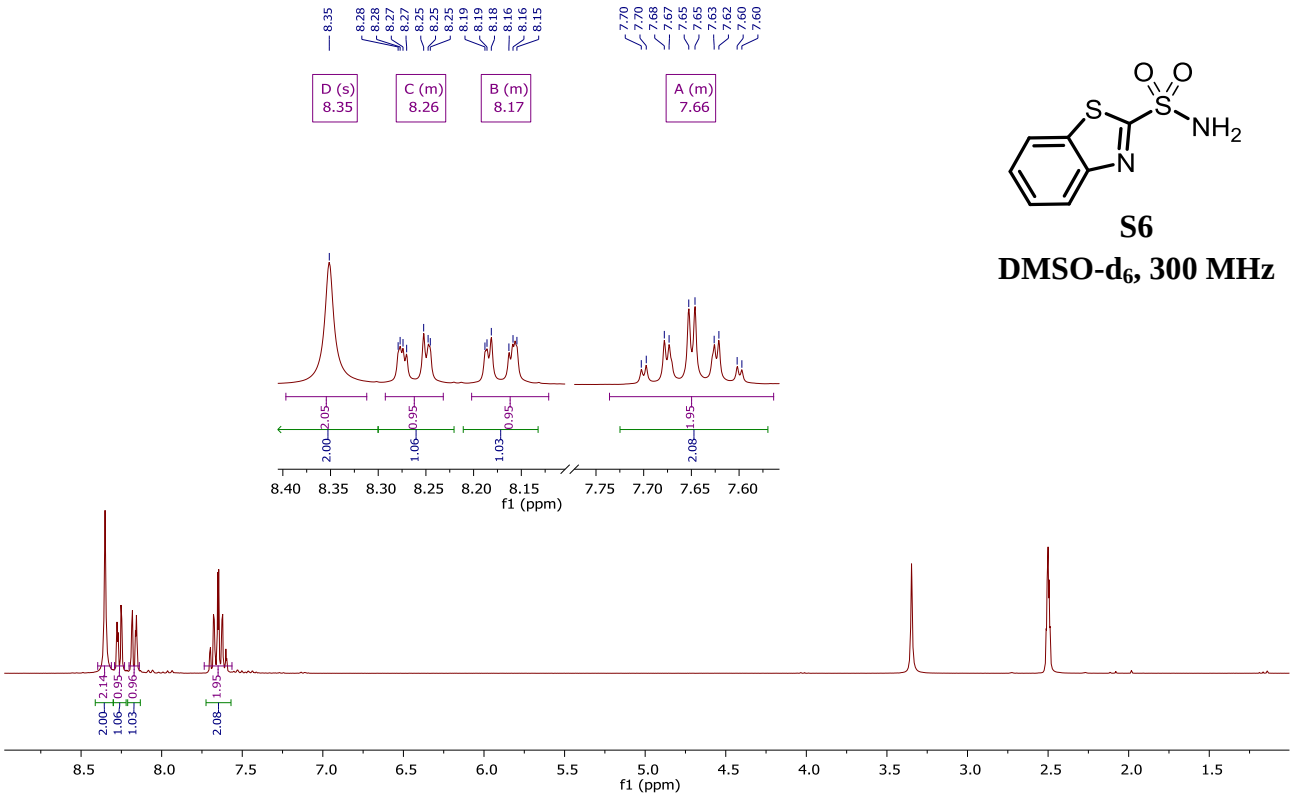
Scheme 5. C-H activation/annulation reaction of substrate **1.8a**

When the concentration of the substrate **1.8a** was c=0.1 M, the NMR yield was 47 % using 1,3,5-trimethoxybenzene as an internal standart. If the concentration of the same substrate was lowered till c=0.04 M, NMR yield was 74 %. When mixture was diluted even more, respectively, c=0.01 M, product **2a** NMR yield dropped to 63 %.

4. ^{1}H NMR and ^{13}C NMR spectra

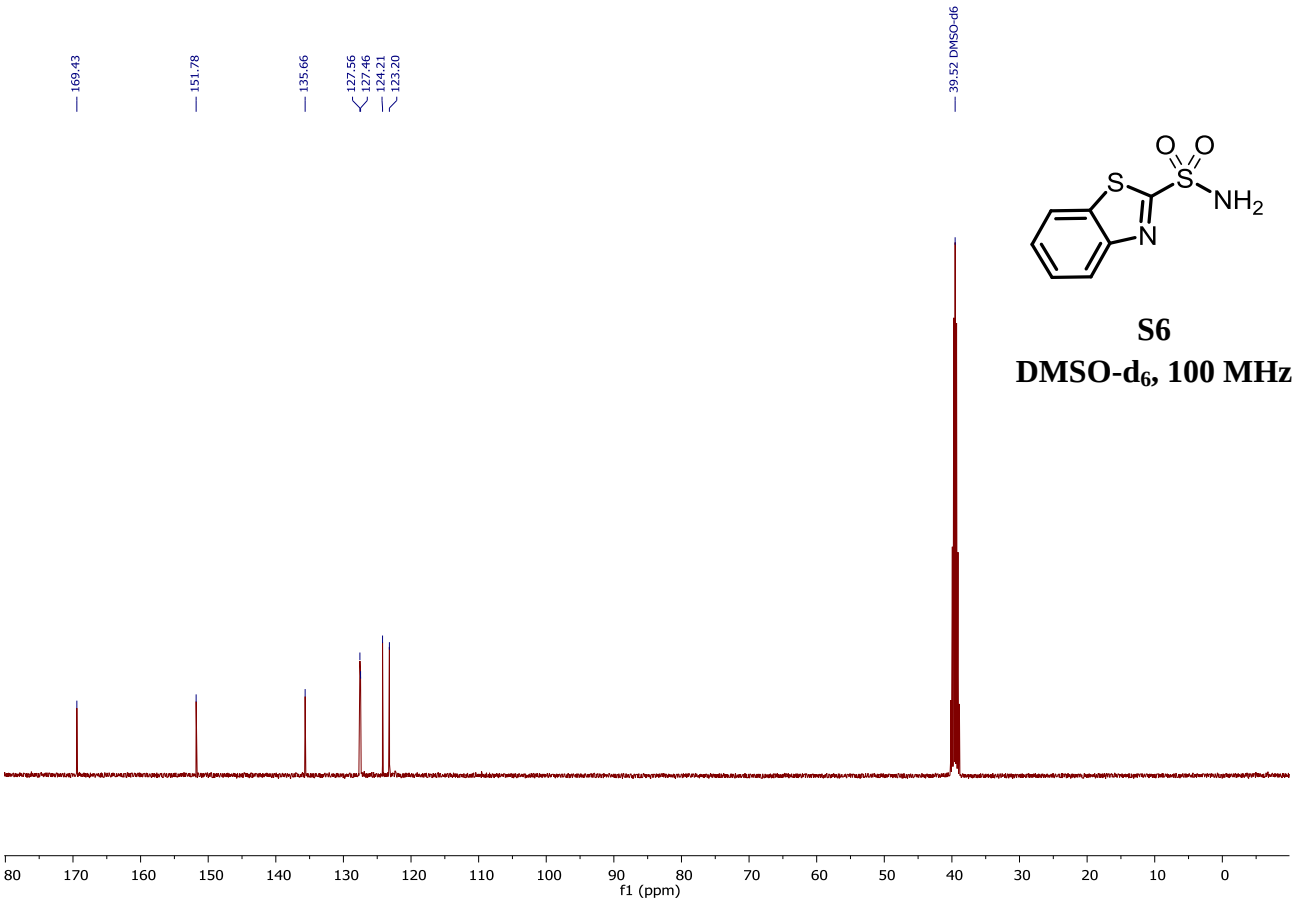






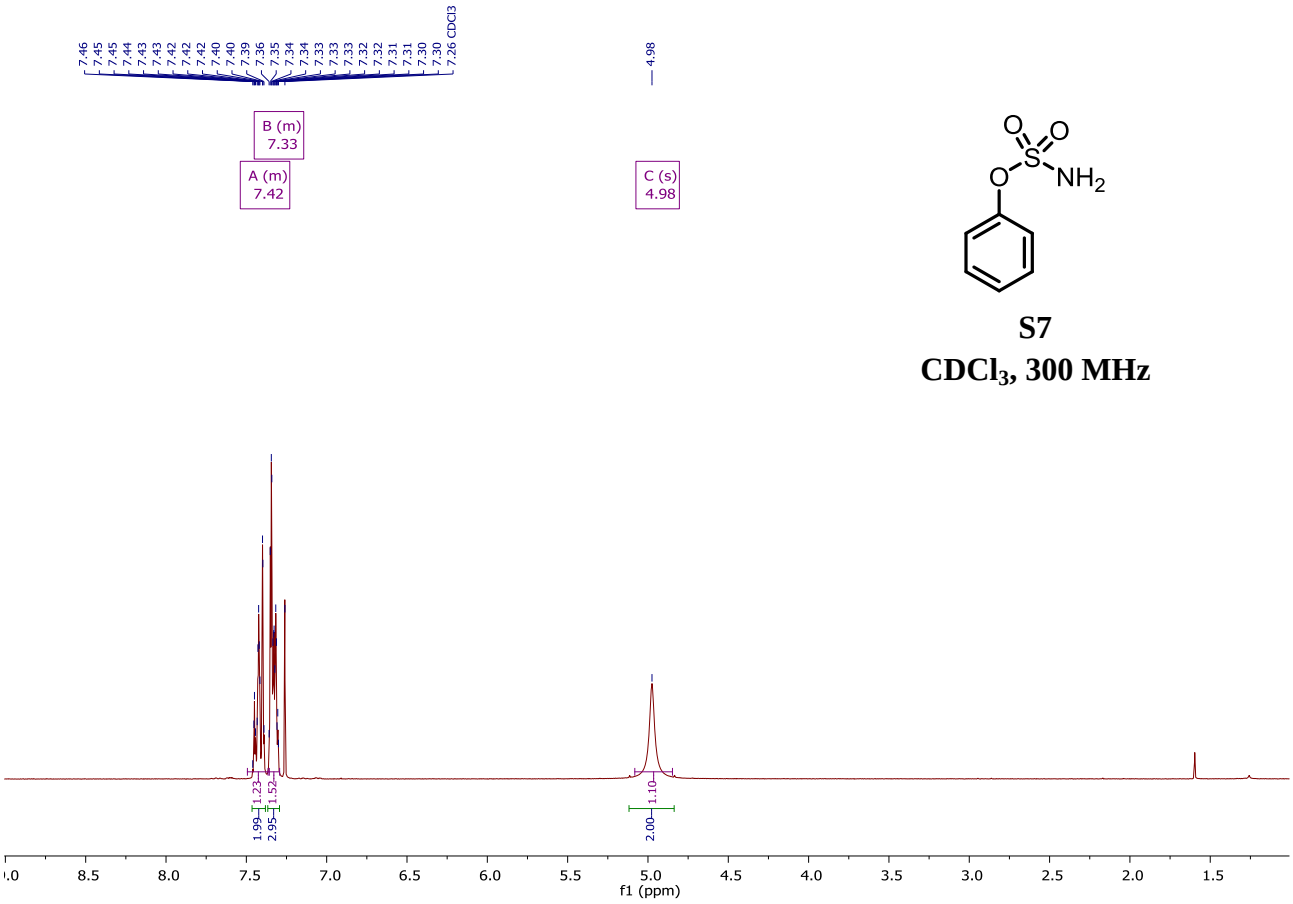
S6

DMSO-d_6, 300 MHz



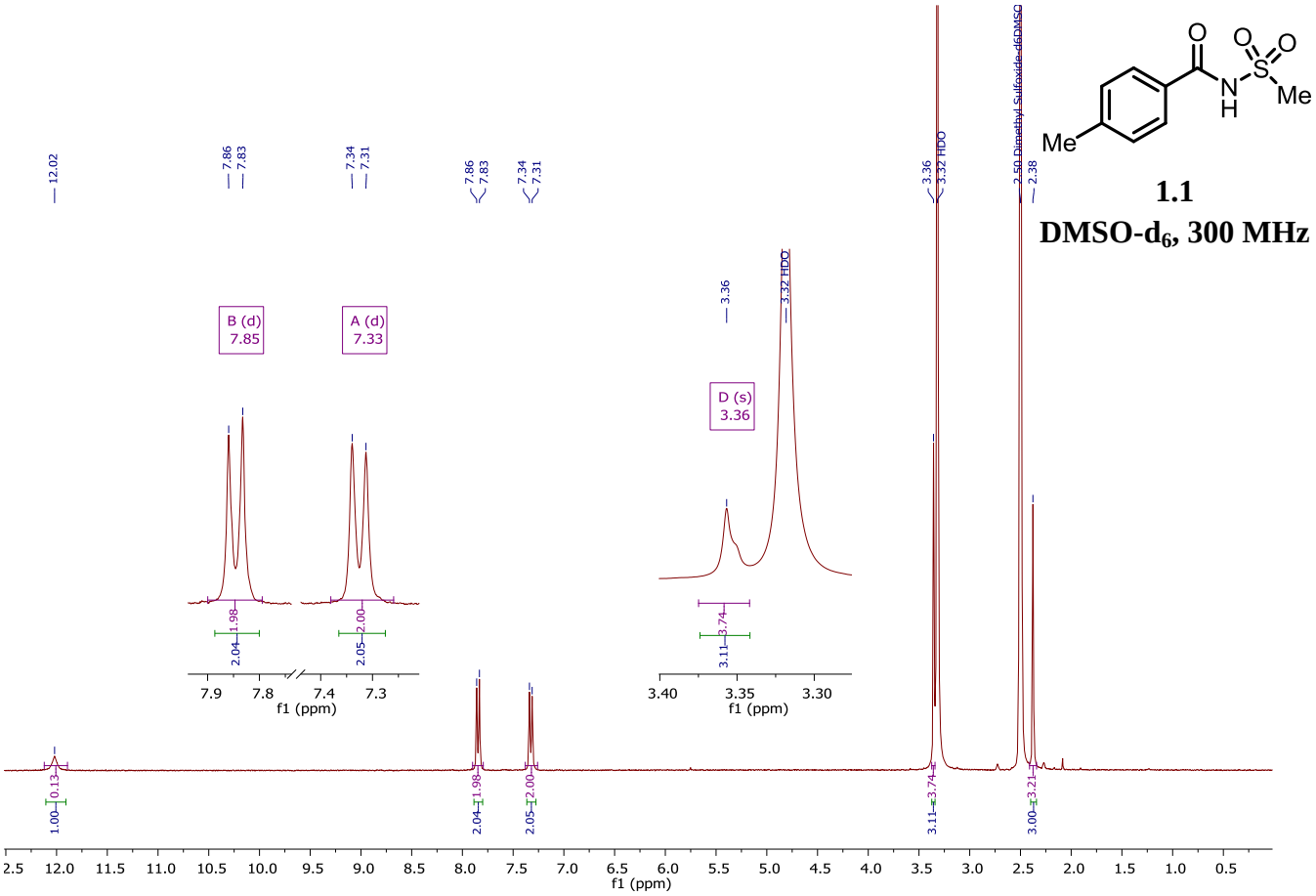
S6

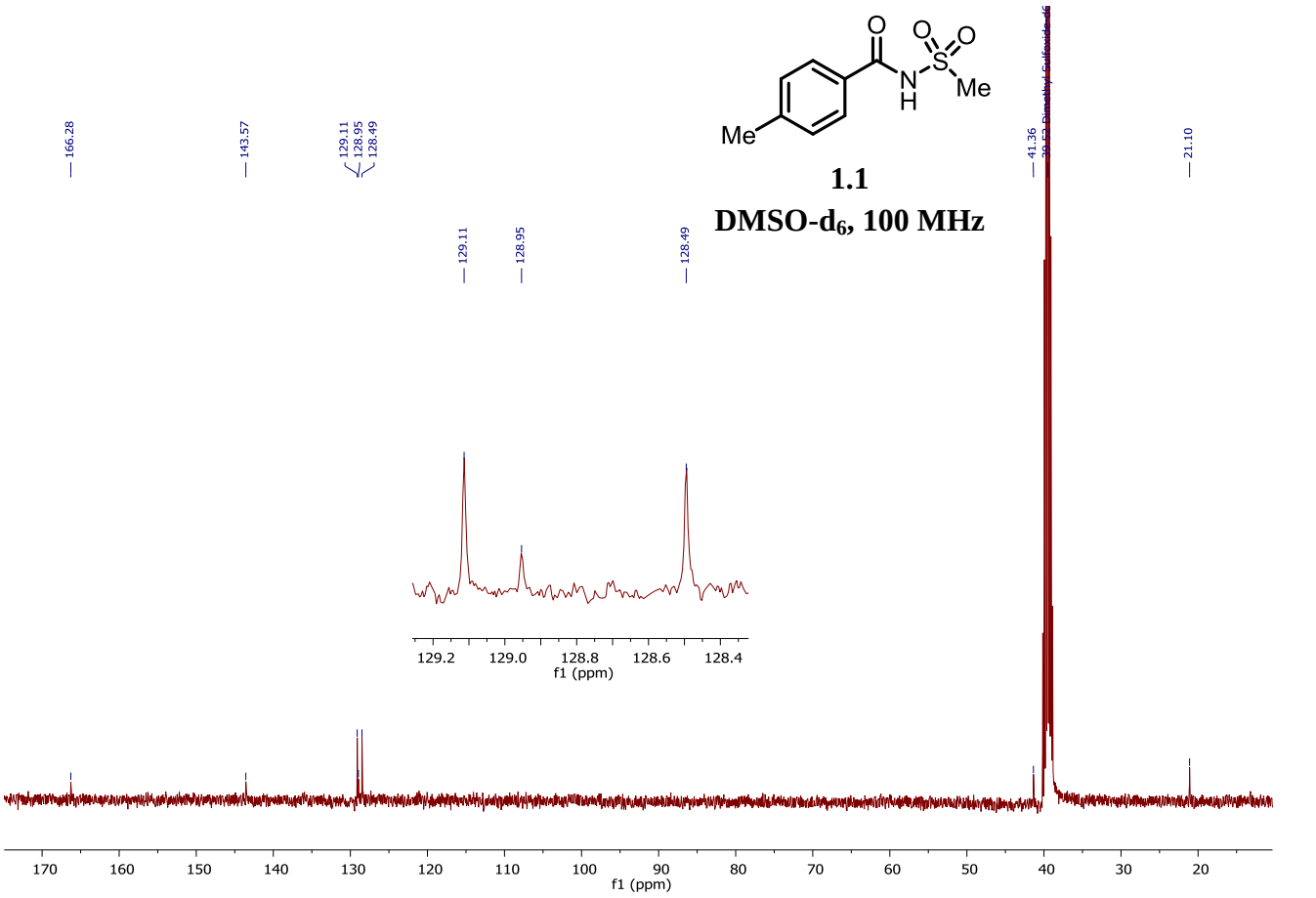
DMSO-d_6, 100 MHz

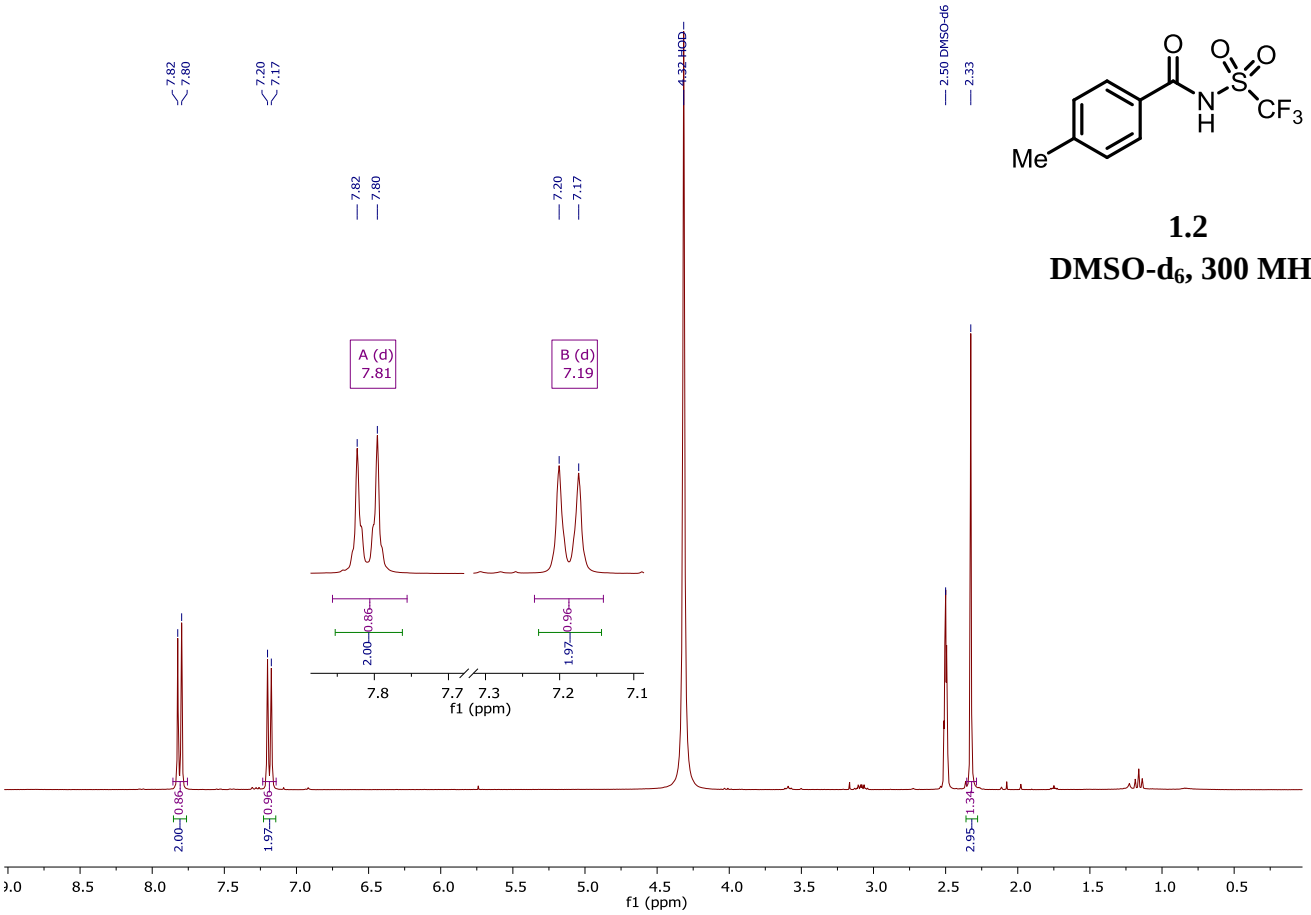


S7

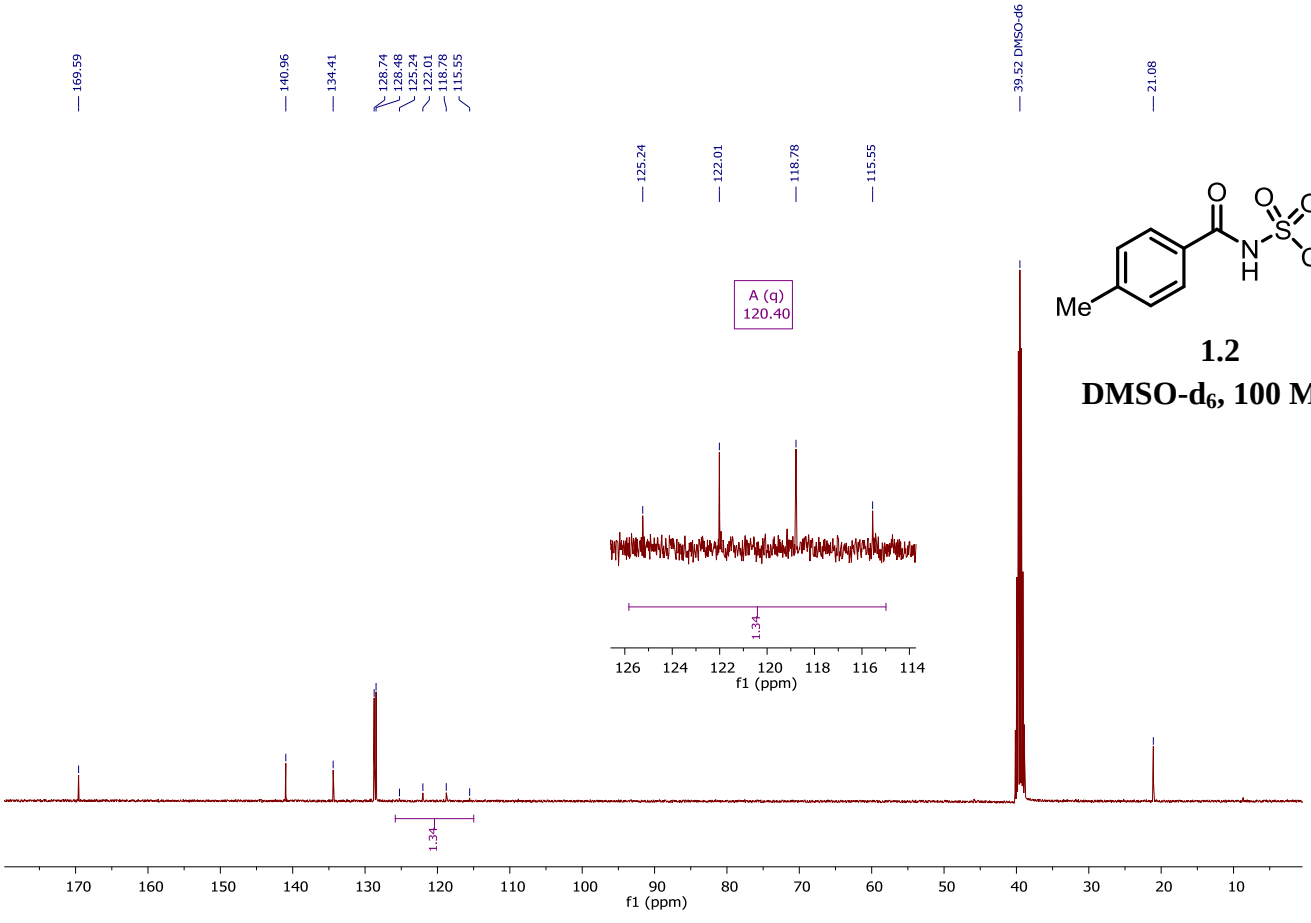
$CDCl_3$, 300 MHz


1.1
DMSO-d6, 300 MHz
B (d) 7.85
A (d) 7.33
D (s) 3.36
f1 (ppm)

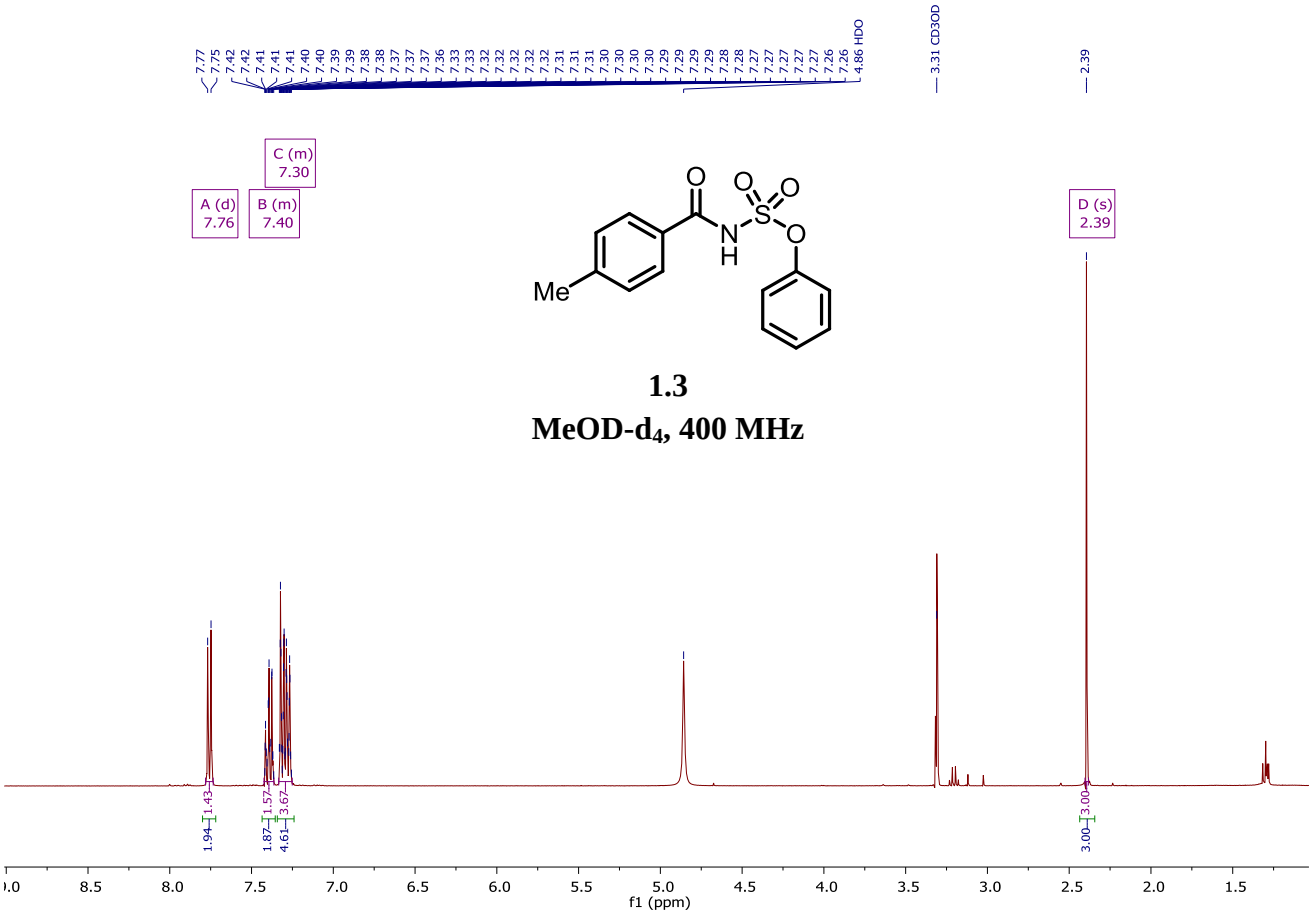

1.1
DMSO-d6, 100 MHz
f1 (ppm)



1.2
DMSO-d$_6$, 300 MHz

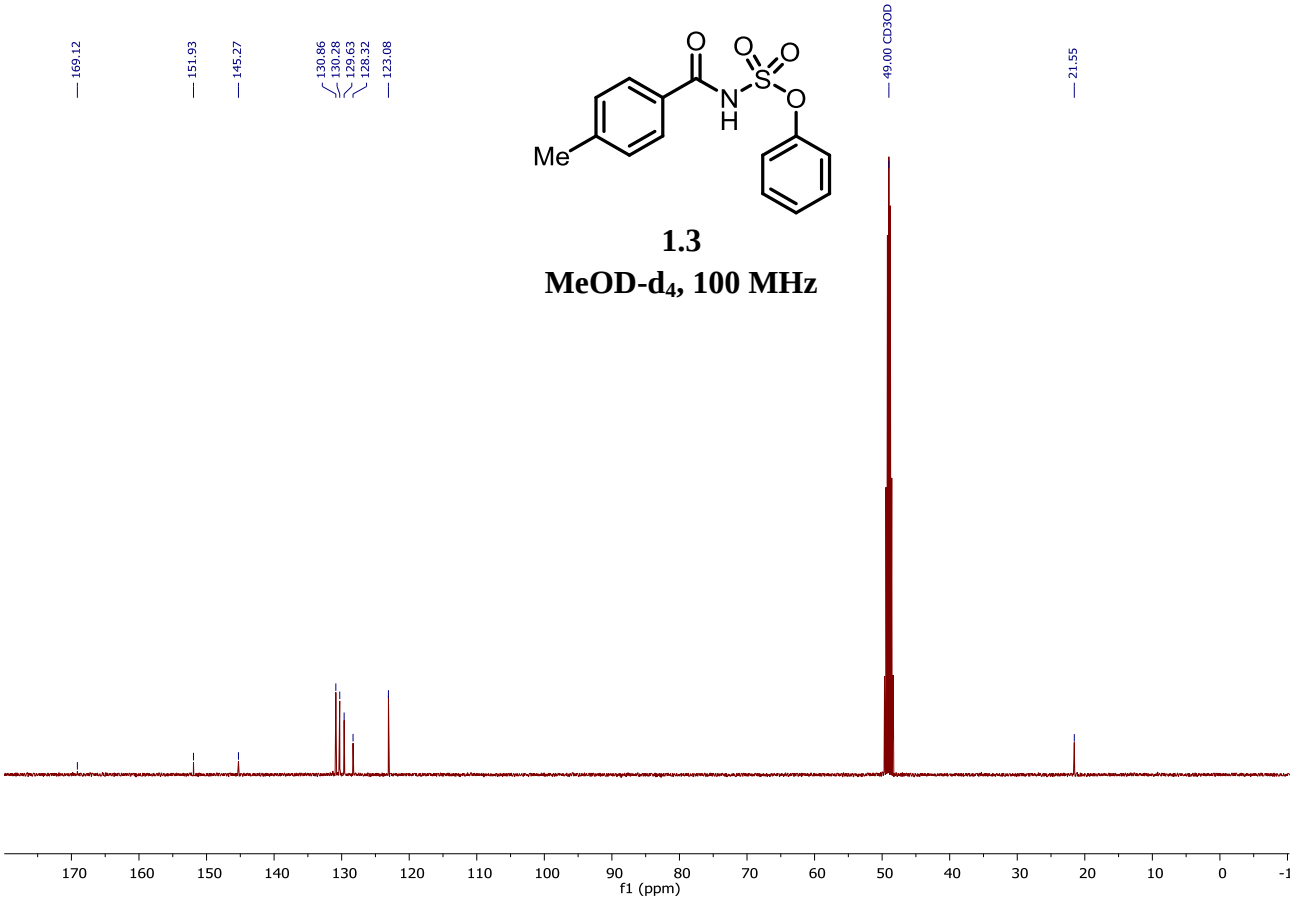


1.2
DMSO-d$_6$, 100 MHz



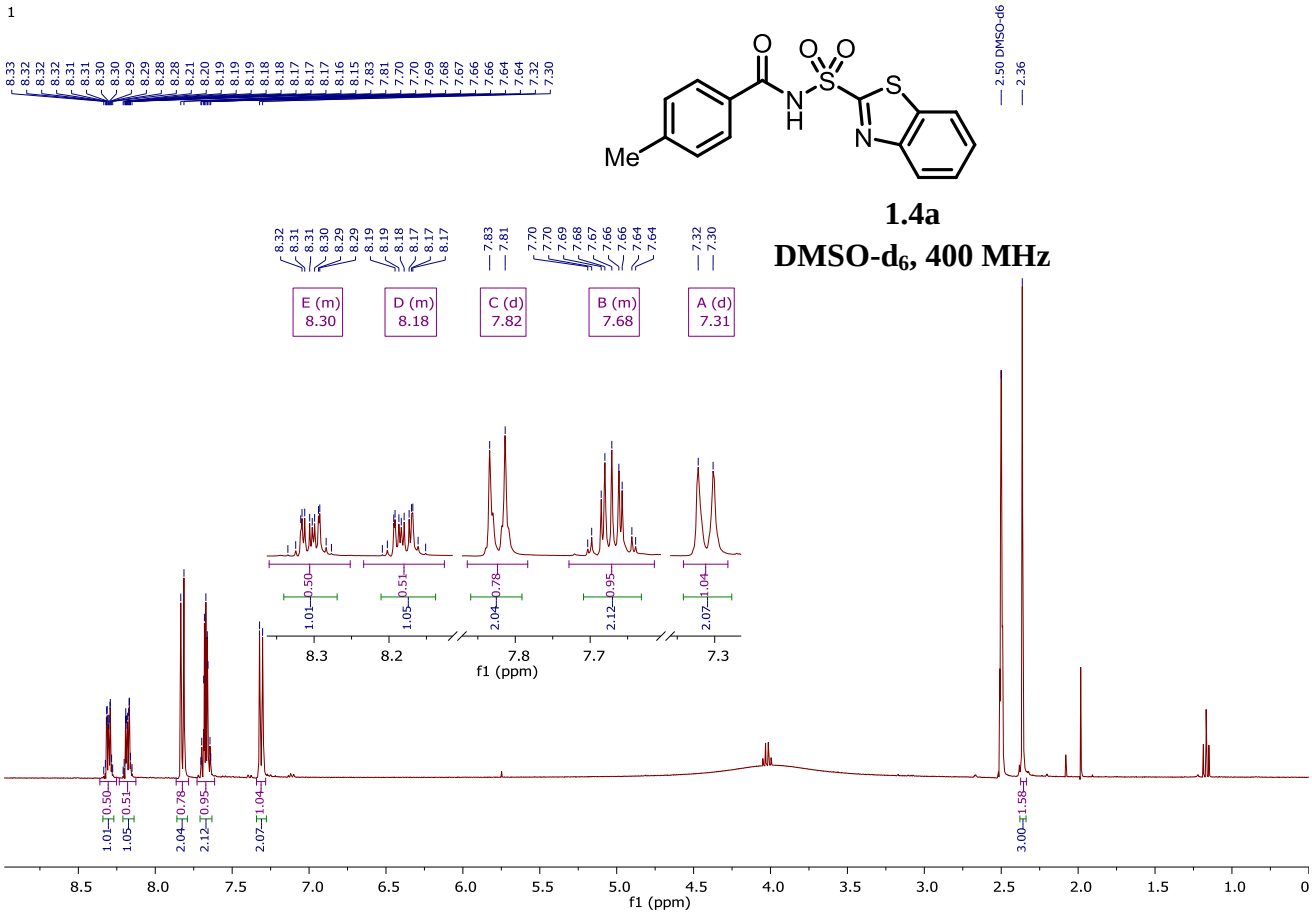
1.3

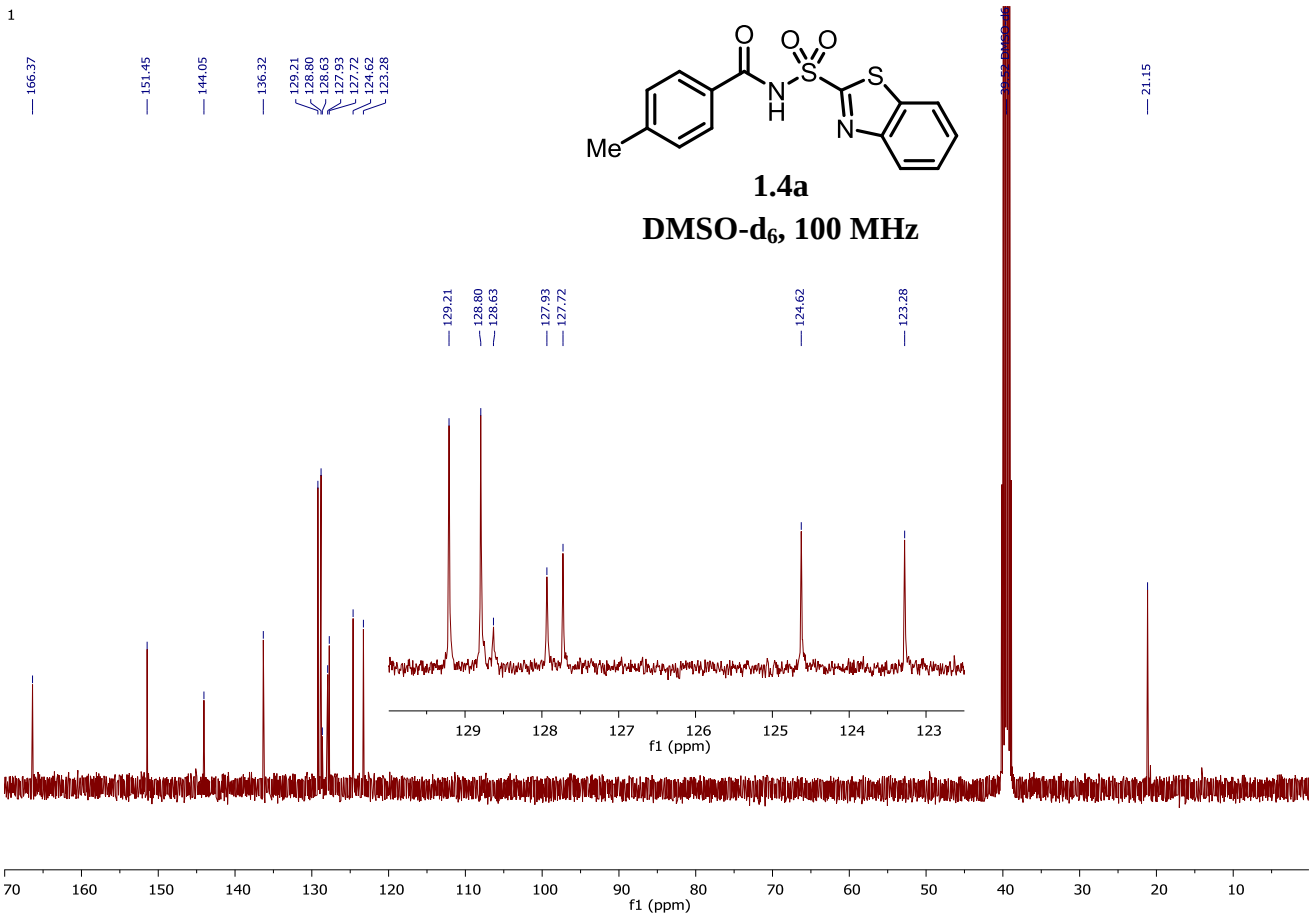
MeOD-d_4, 400 MHz

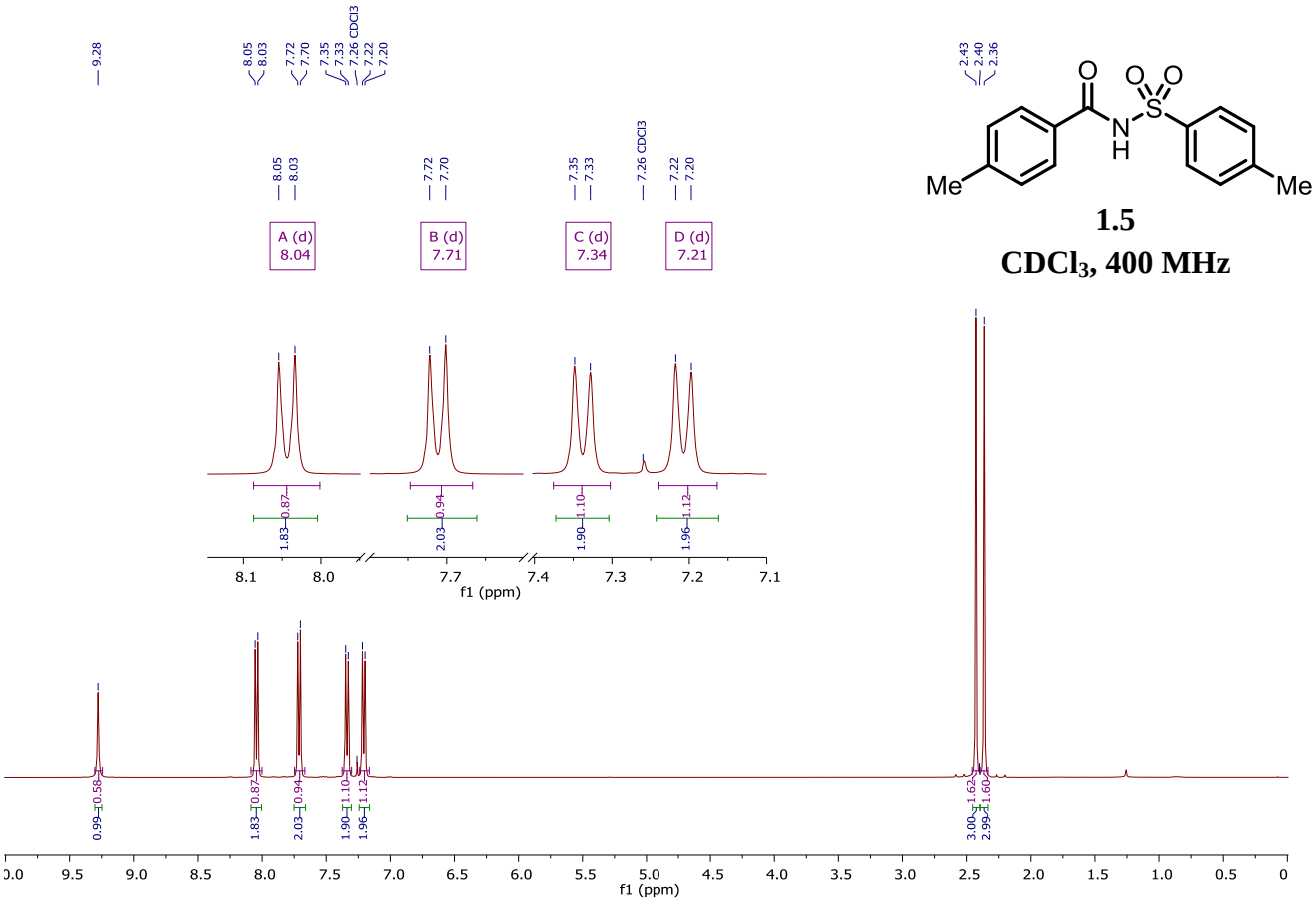


1.3

MeOD-d_4, 100 MHz

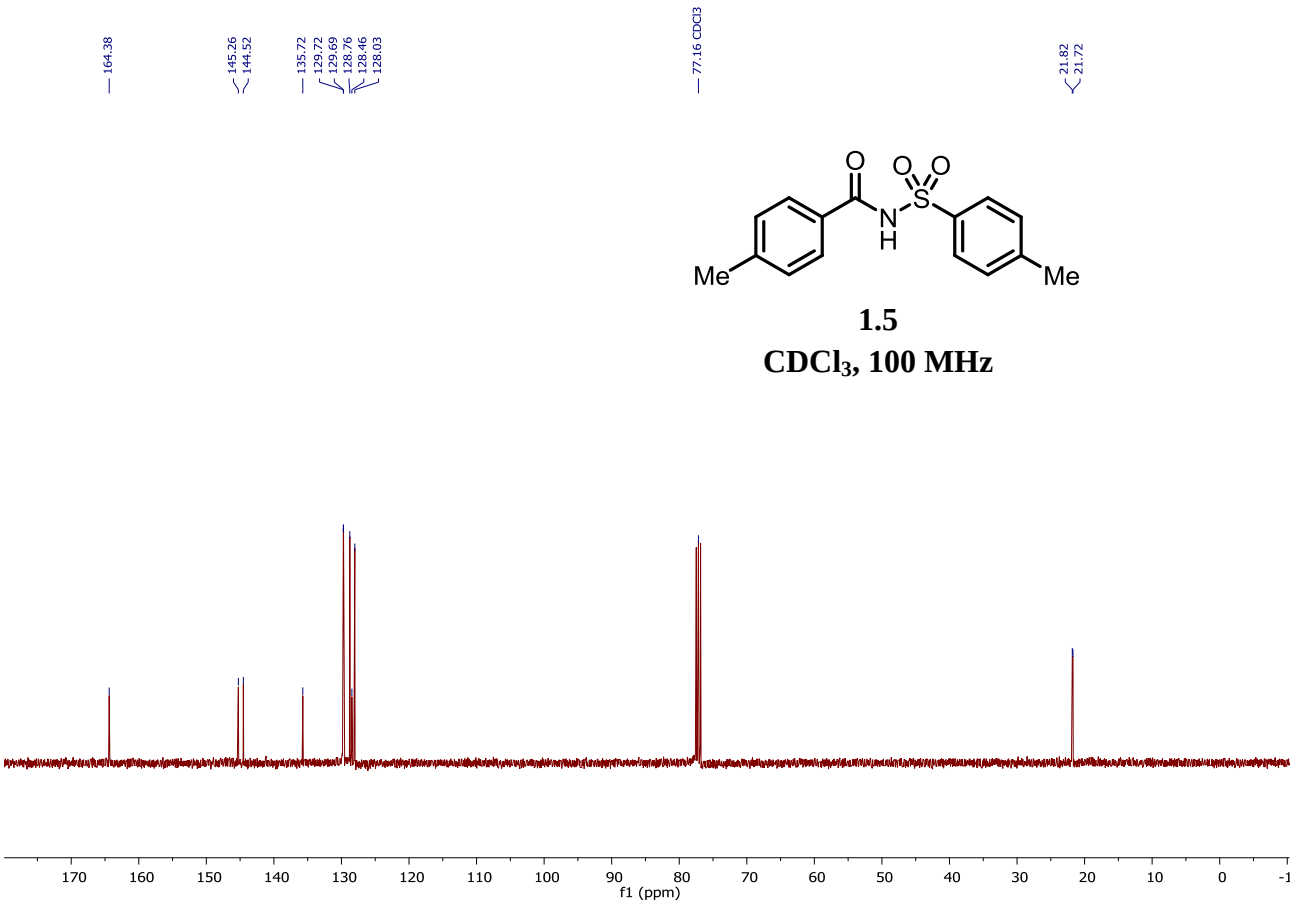

1.4a
DMSO-d6, 400 MHz
E (m) 8.30
D (m) 8.18
C (d) 7.82
B (m) 7.68
A (d) 7.31
f1 (ppm)


1.4a
DMSO-d6, 100 MHz
f1 (ppm)



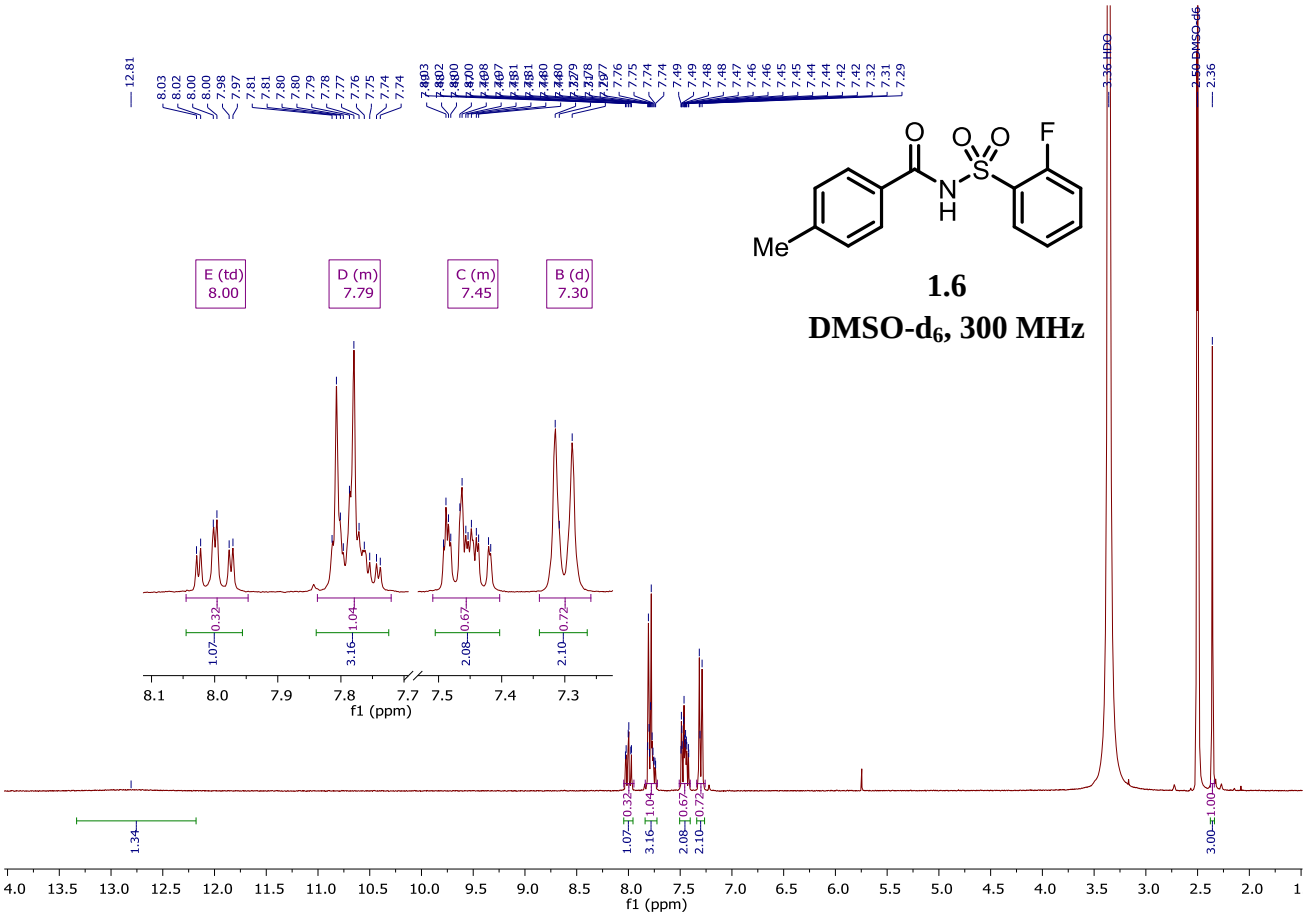
1.5

$CDCl_3$, 400 MHz



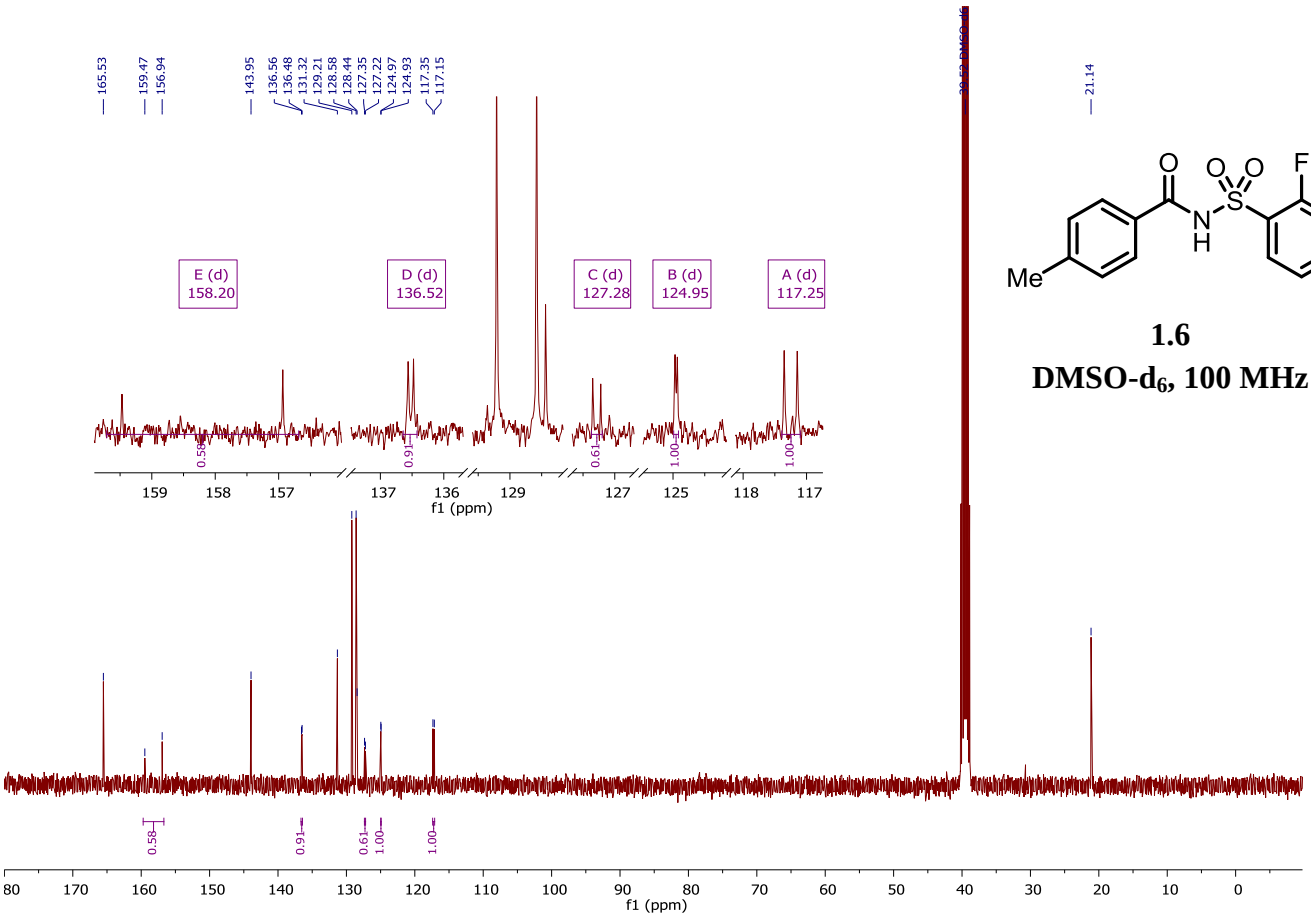
1.5

$CDCl_3$, 100 MHz



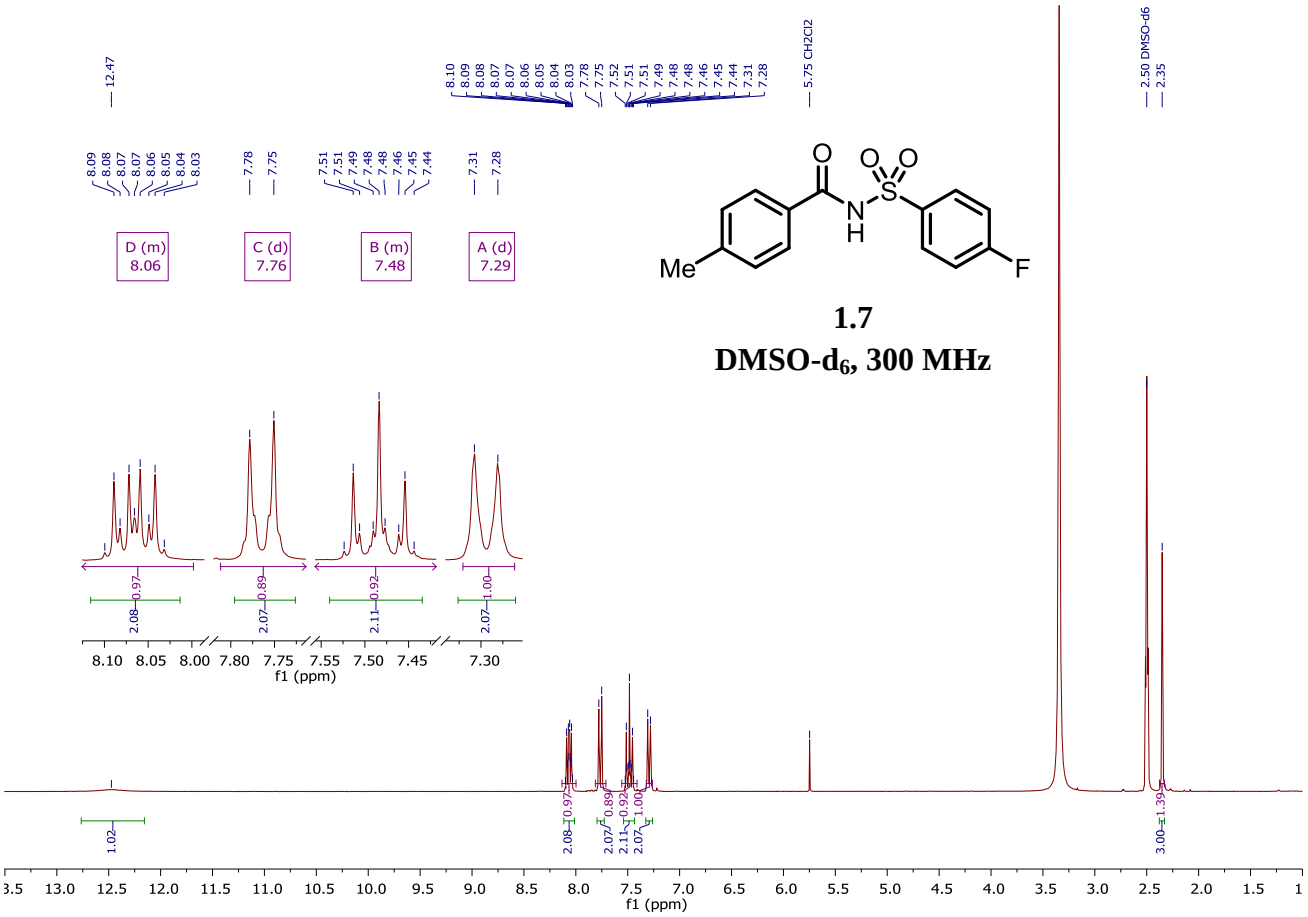
1.6

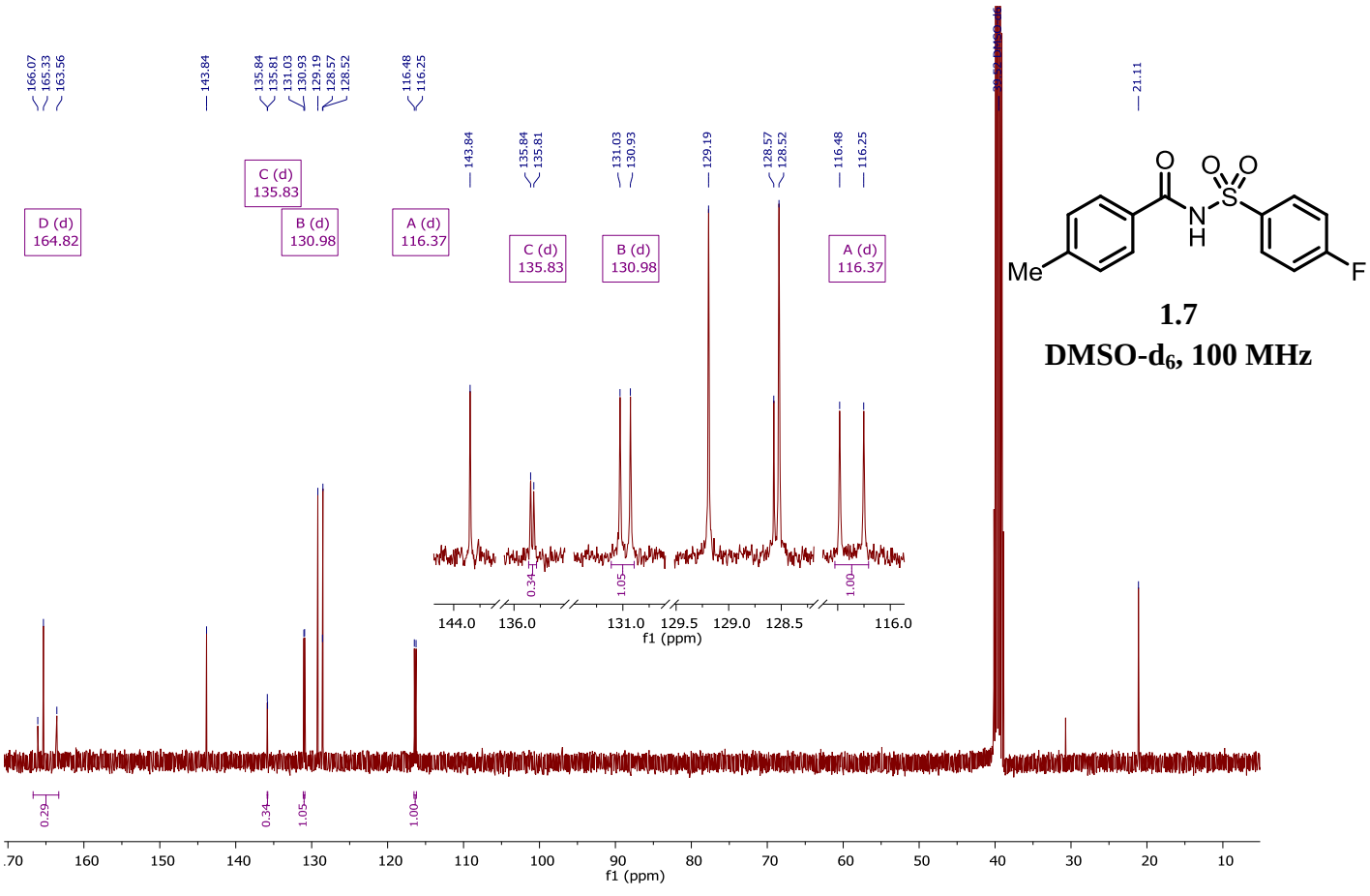
DMSO-d_6, 300 MHz

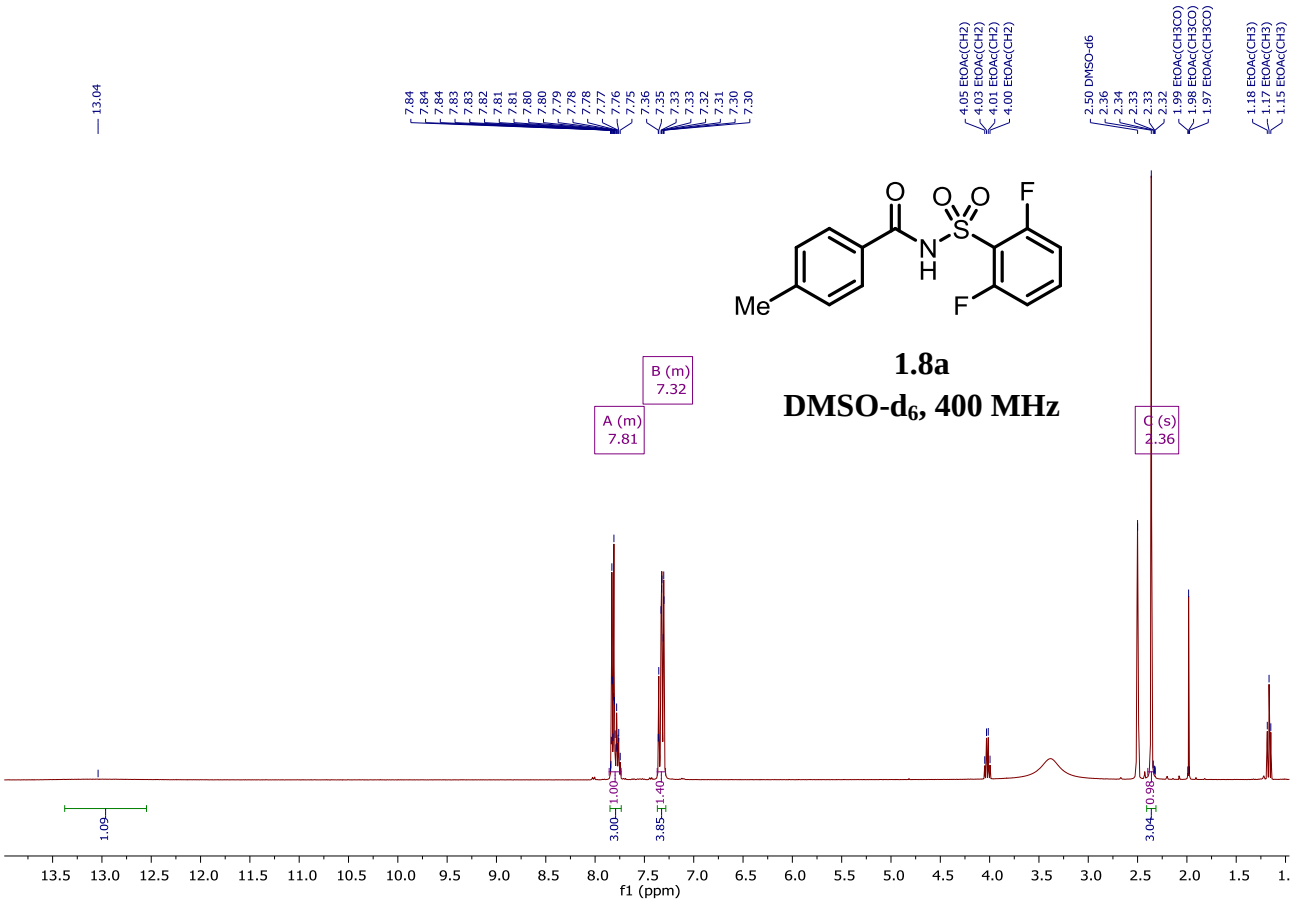


1.6

DMSO-d_6, 100 MHz

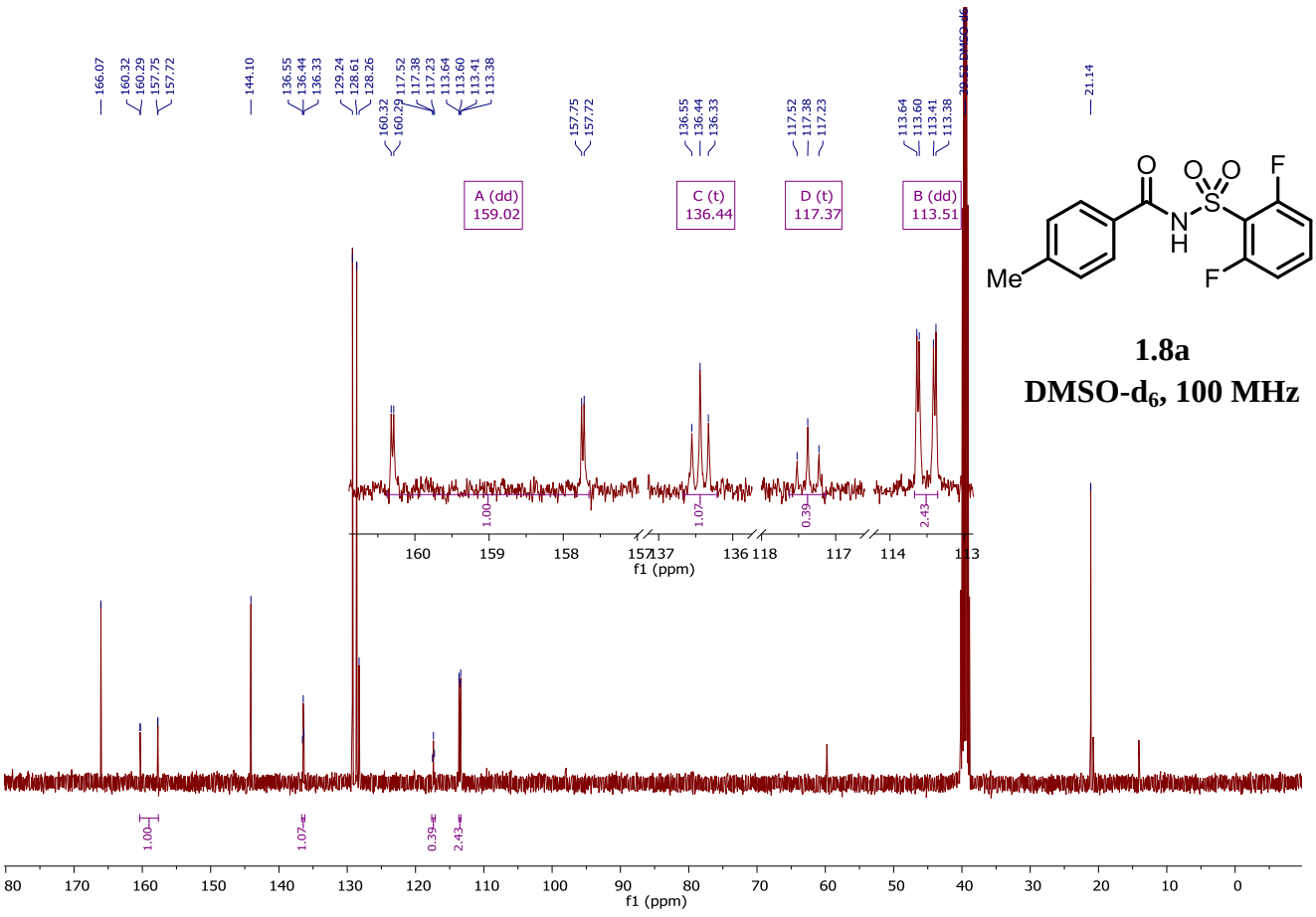

12.47
8.10 8.09 8.08 8.07 8.07 8.06 8.05 8.04 8.03 7.78 7.75 7.52 7.51 7.51 7.49 7.48 7.48 7.46 7.45 7.44 7.31 7.28
5.75 CH2Cl2
2.50 DMSO-d6
2.35
D (m) 8.06
C (d) 7.76
B (m) 7.48
A (d) 7.29
Me
F
1.7
DMSO-d6, 300 MHz
f1 (ppm)


166.07 165.33 163.56 143.84 135.84 135.81 131.03 130.93 129.19 128.57 128.52 116.48 116.25
21.11
D (d) 164.82
C (d) 135.83
B (d) 130.98
A (d) 116.37
Me
F
1.7
DMSO-d6, 100 MHz
f1 (ppm)



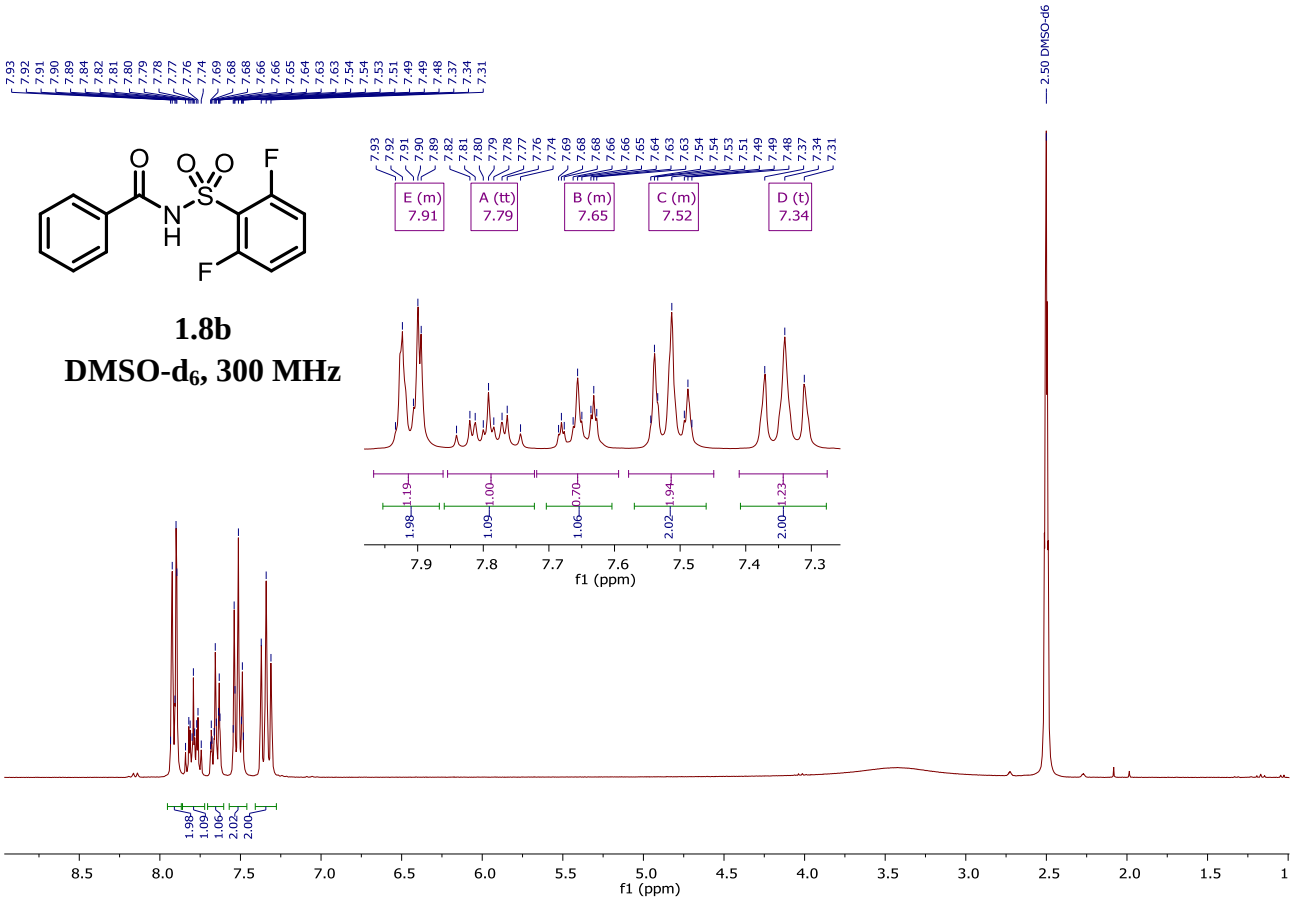
1.8a

DMSO-d_6, 400 MHz



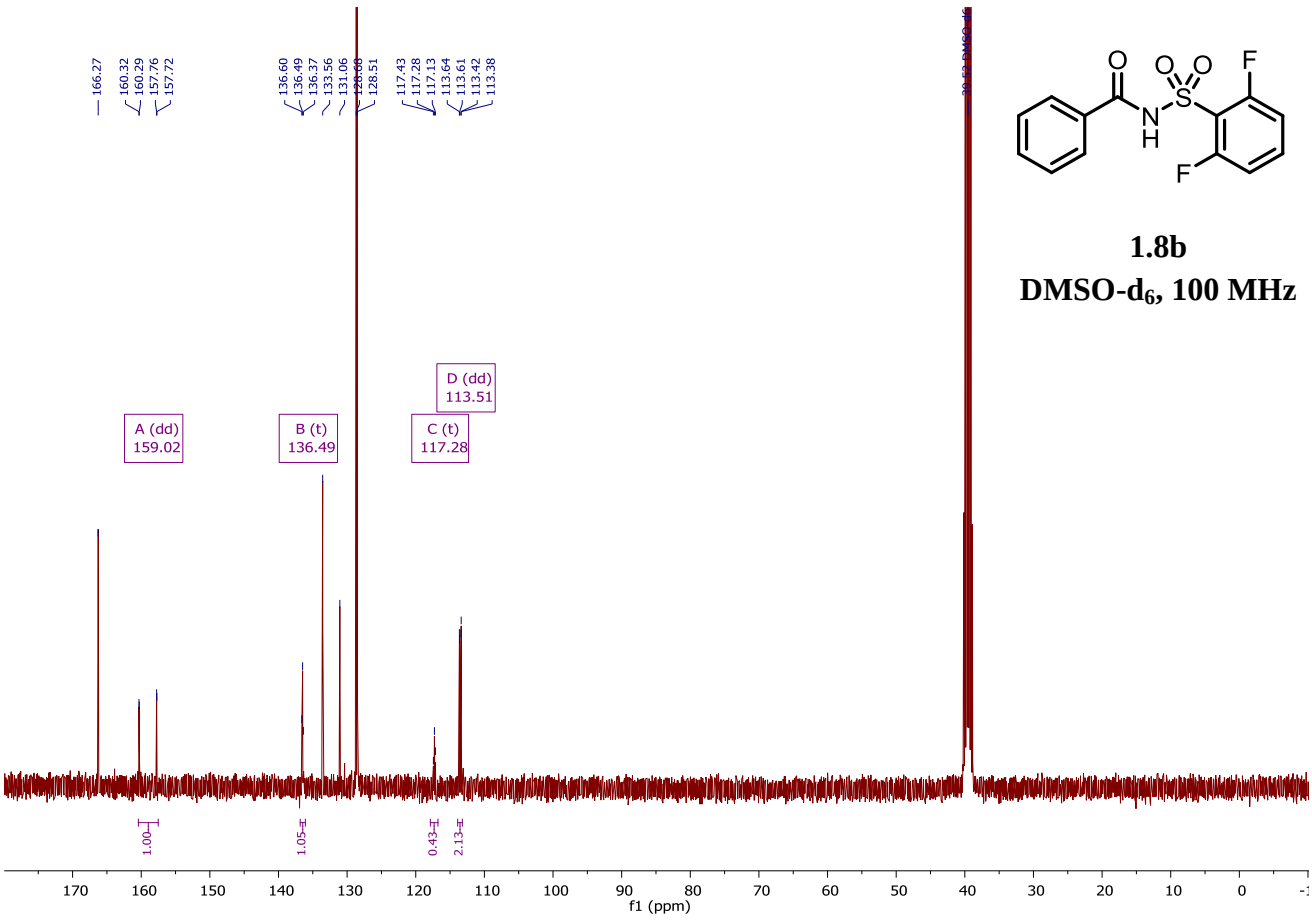
1.8a

DMSO-d_6, 100 MHz



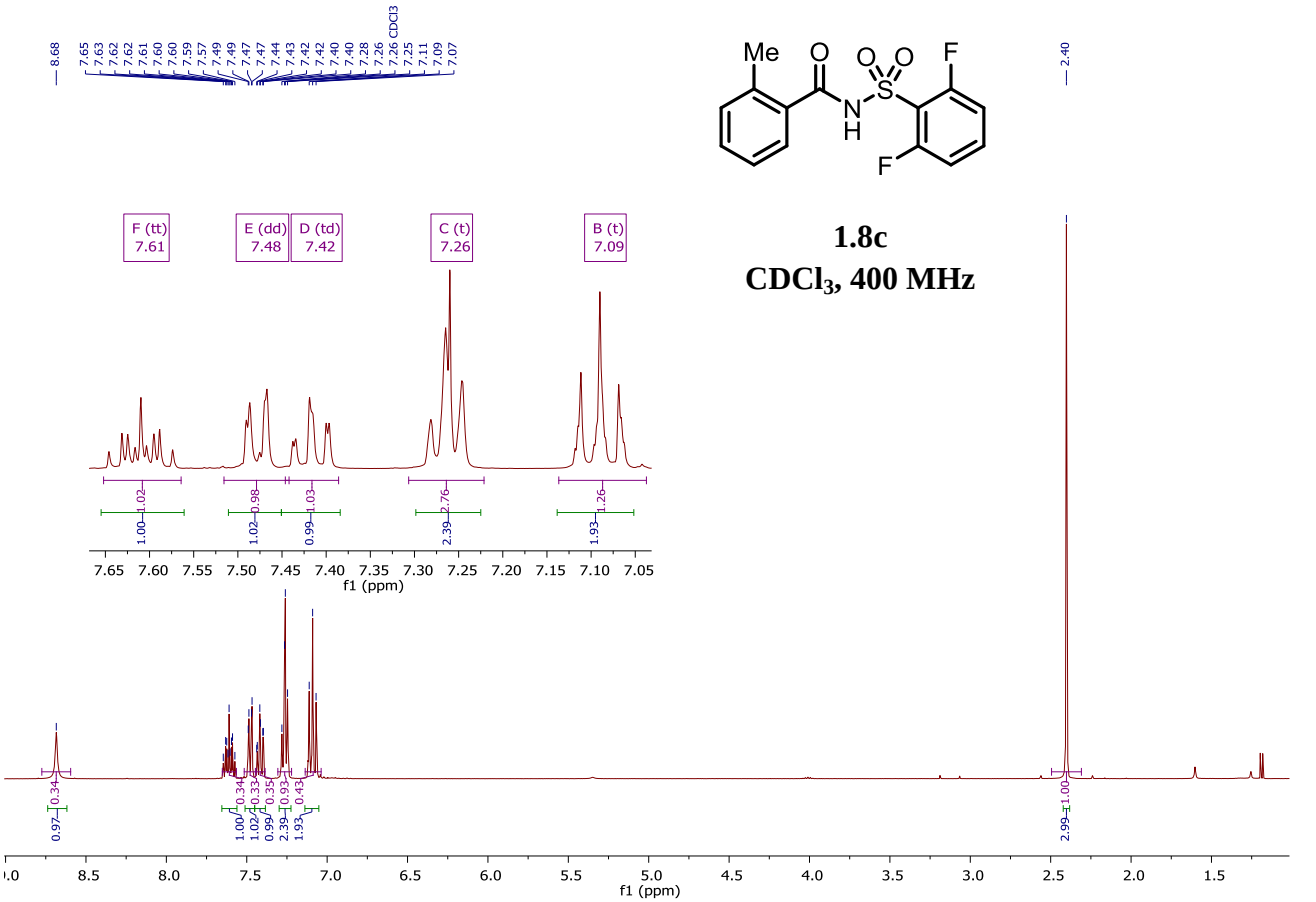
1.8b

DMSO-d$_6$, 300 MHz



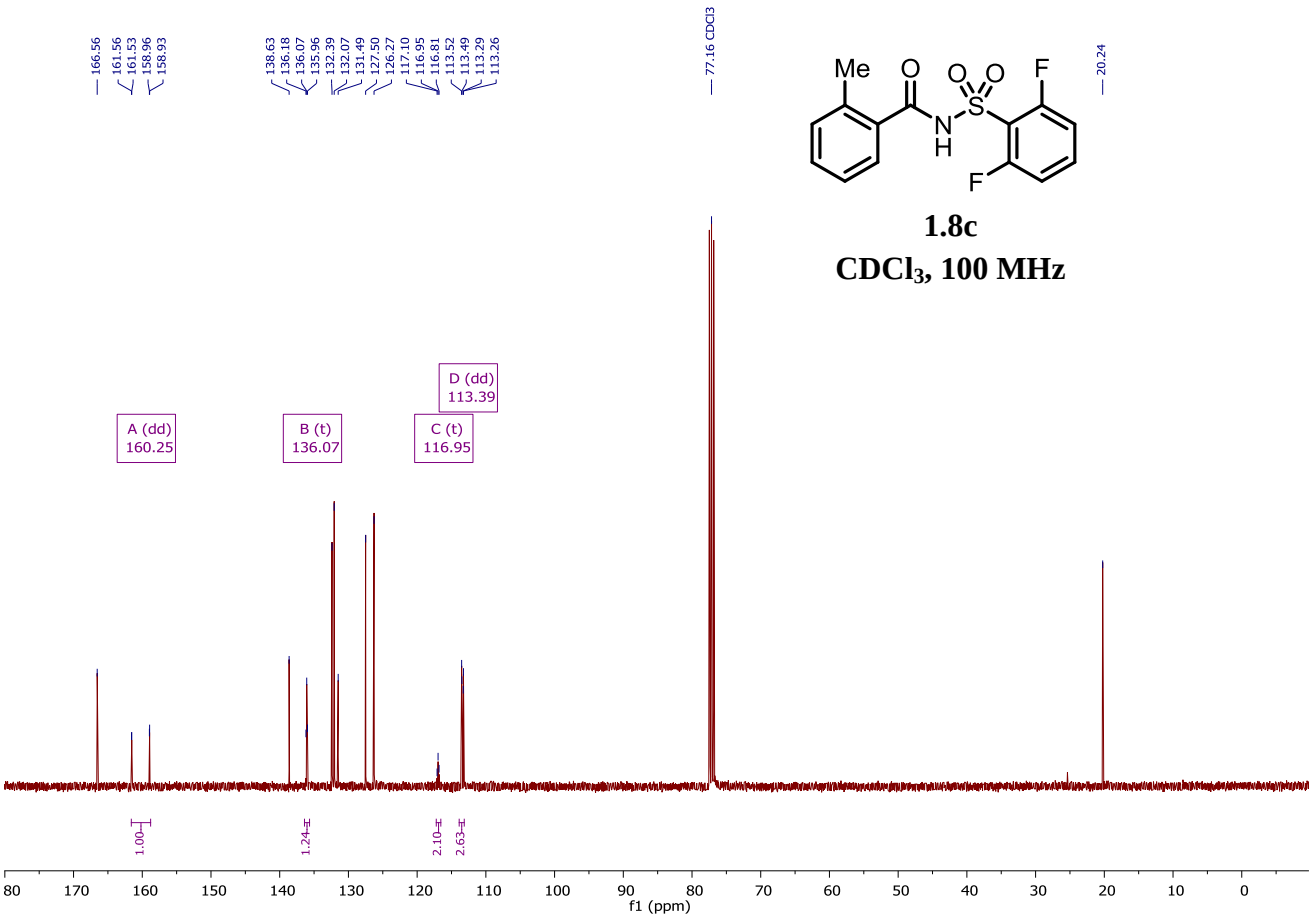
1.8b

DMSO-d$_6$, 100 MHz



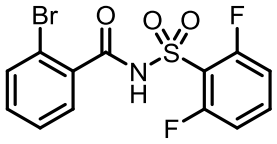
1.8c

$CDCl_3$, 400 MHz



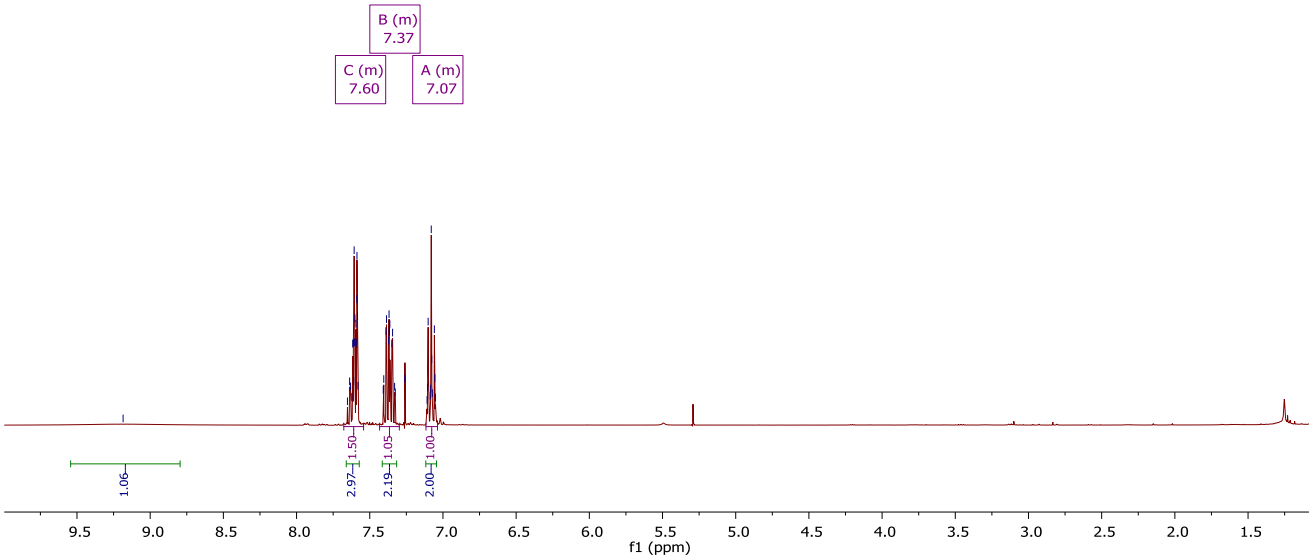
1.8c

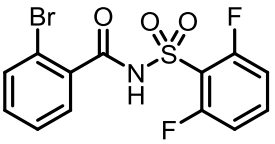
$CDCl_3$, 100 MHz



1.8d

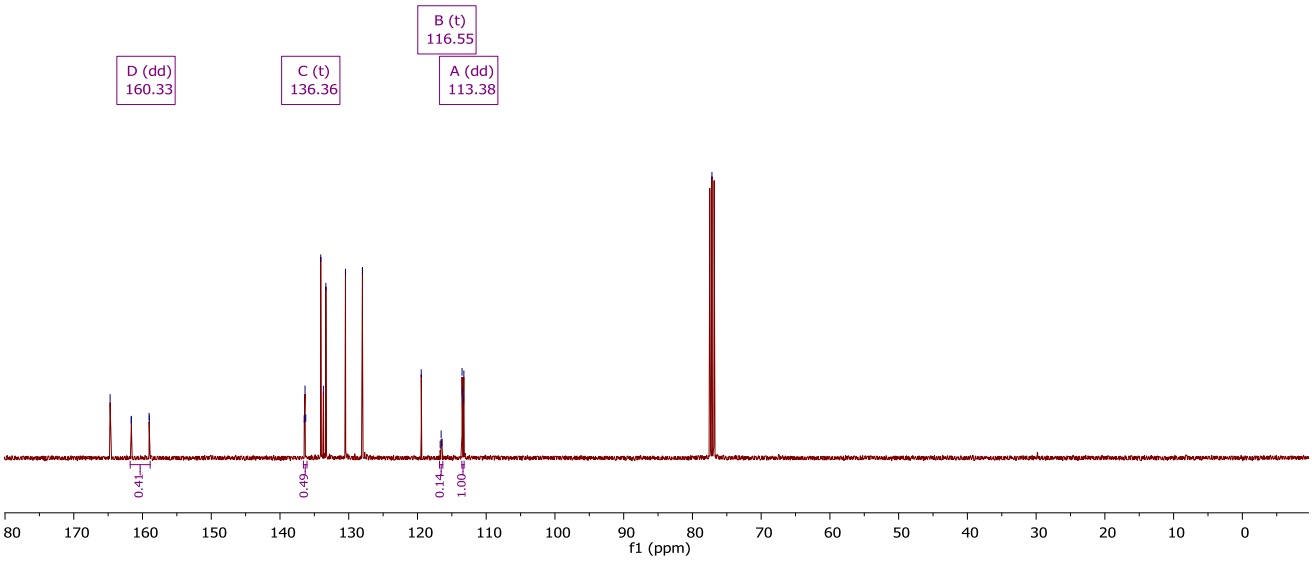
$CDCl_3$, 400 MHz

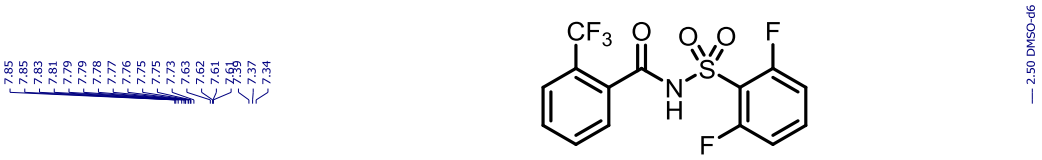




1.8d

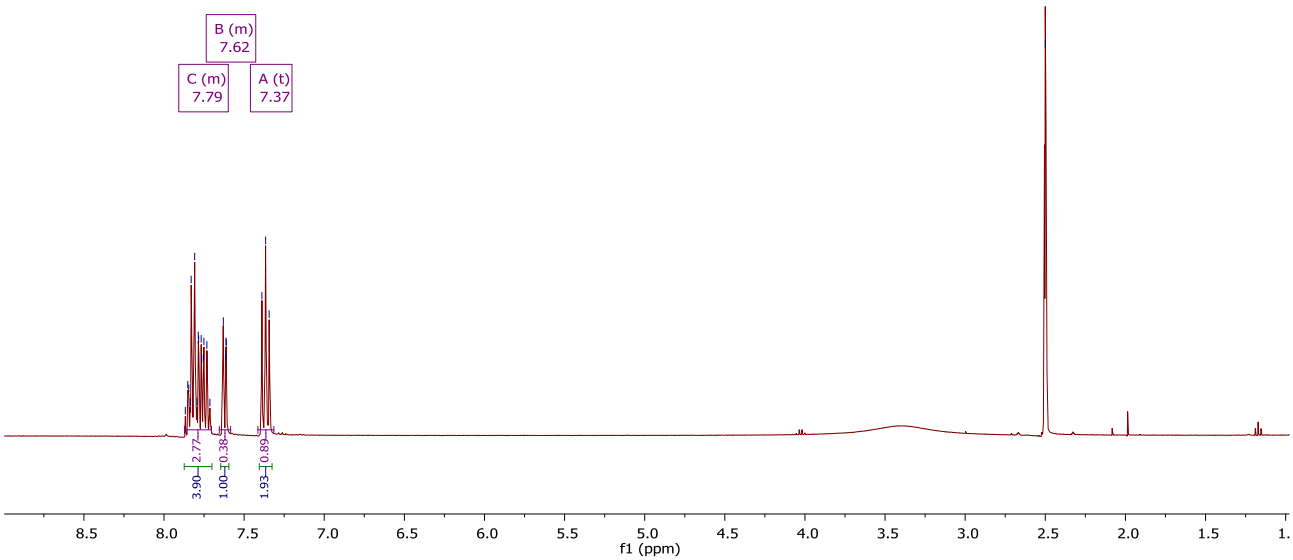
$CDCl_3$, 100 MHz

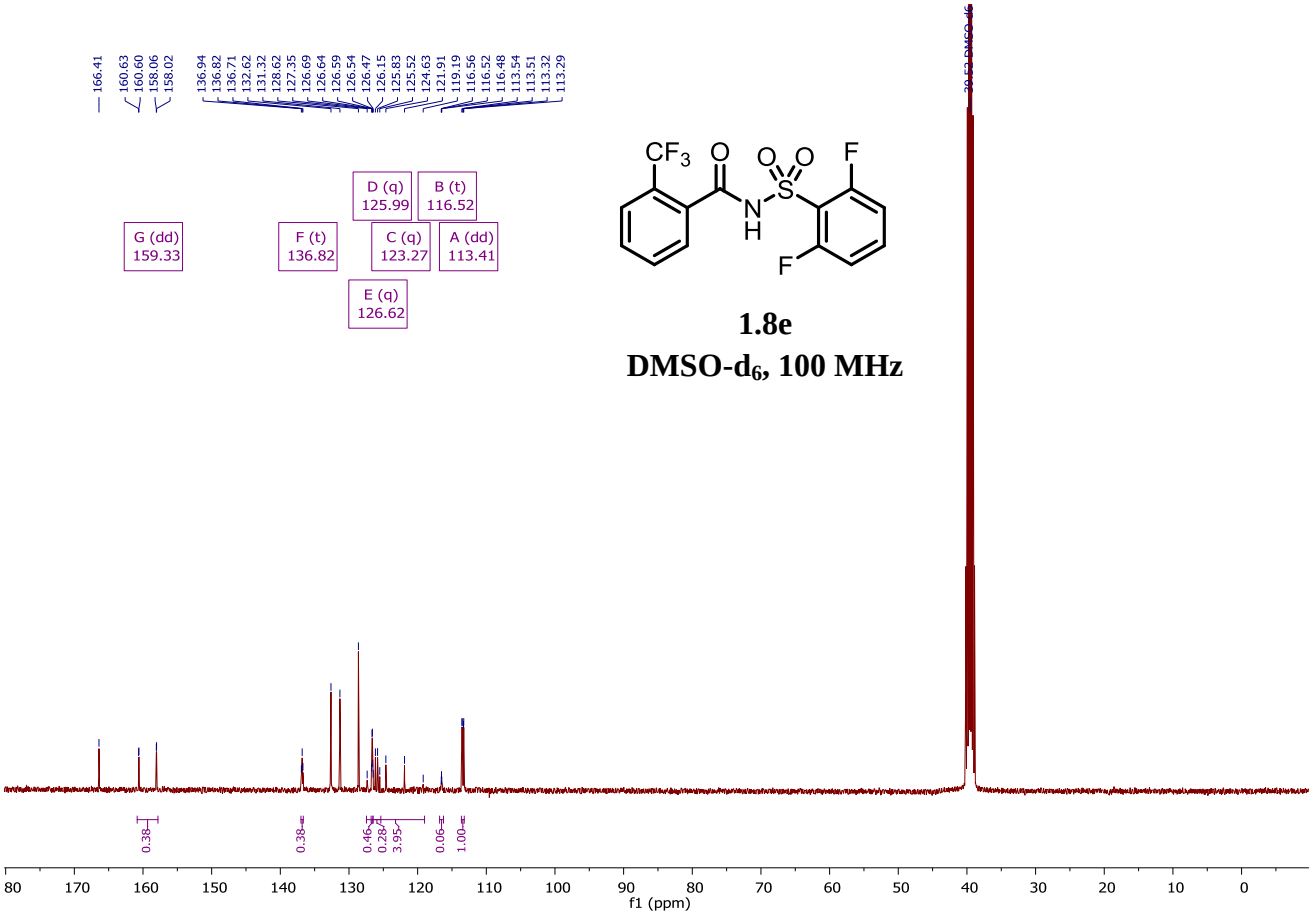




1.8e

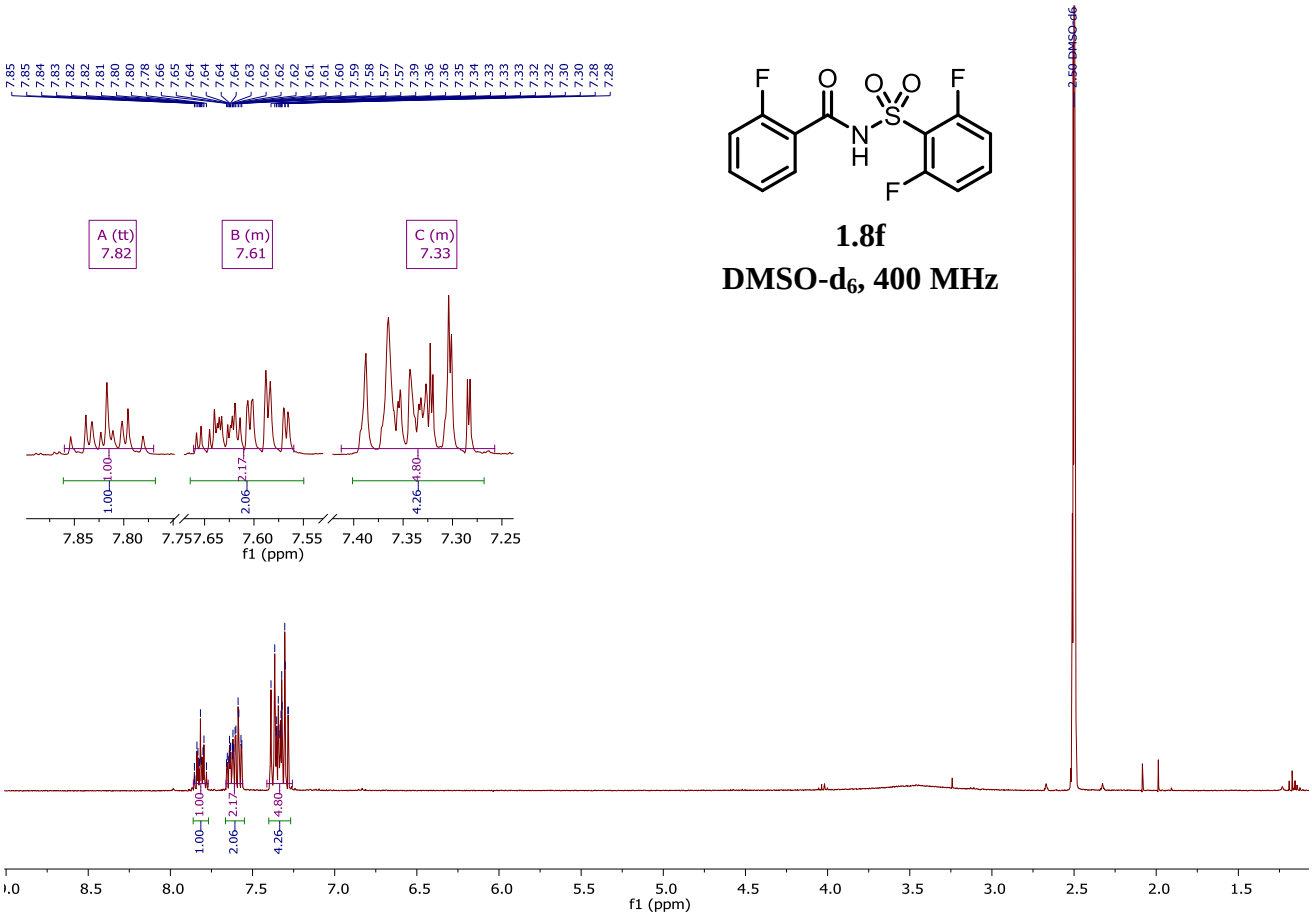
DMSO-d_6, 400 MHz





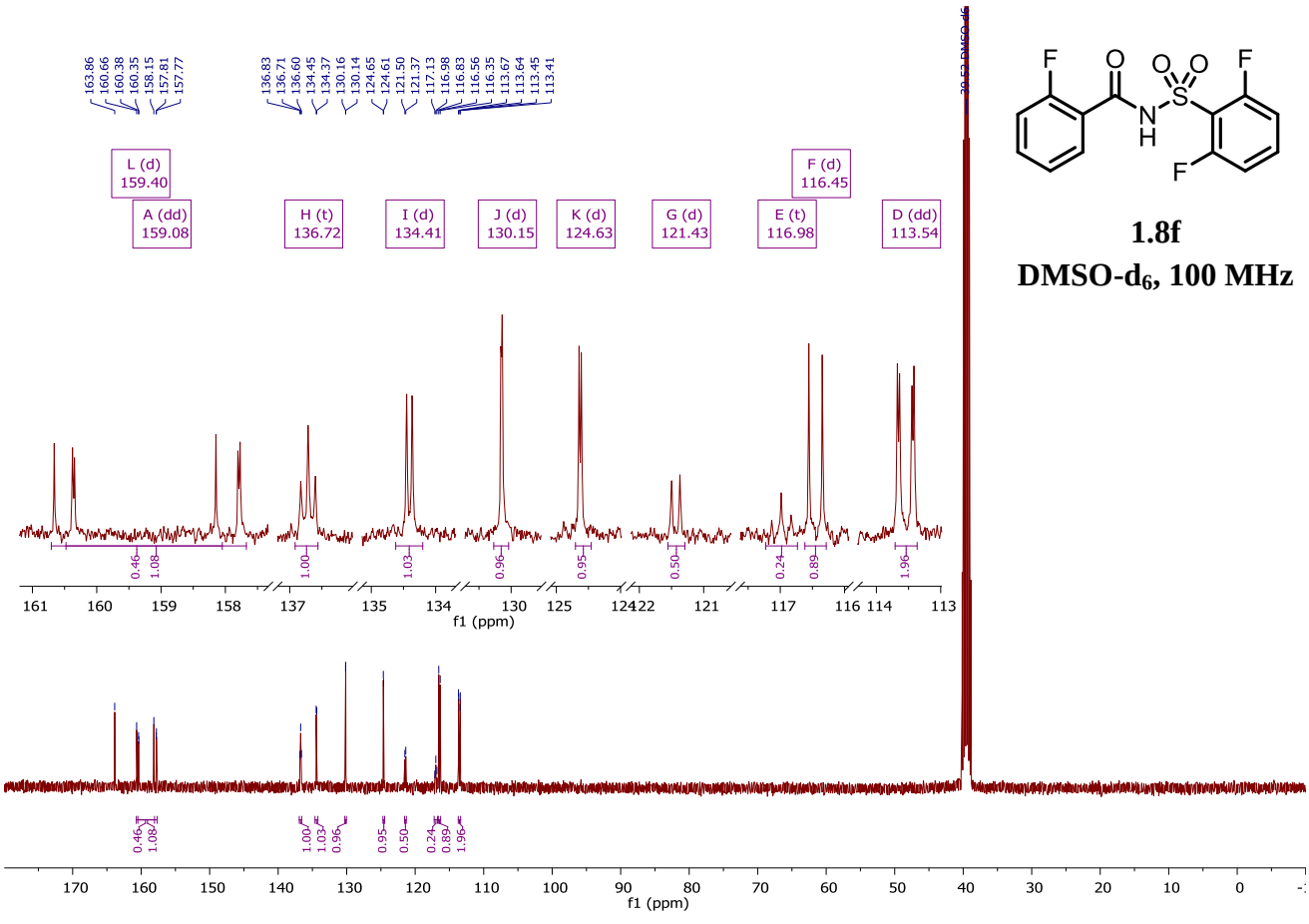
1.8e

DMSO-d_6, 100 MHz



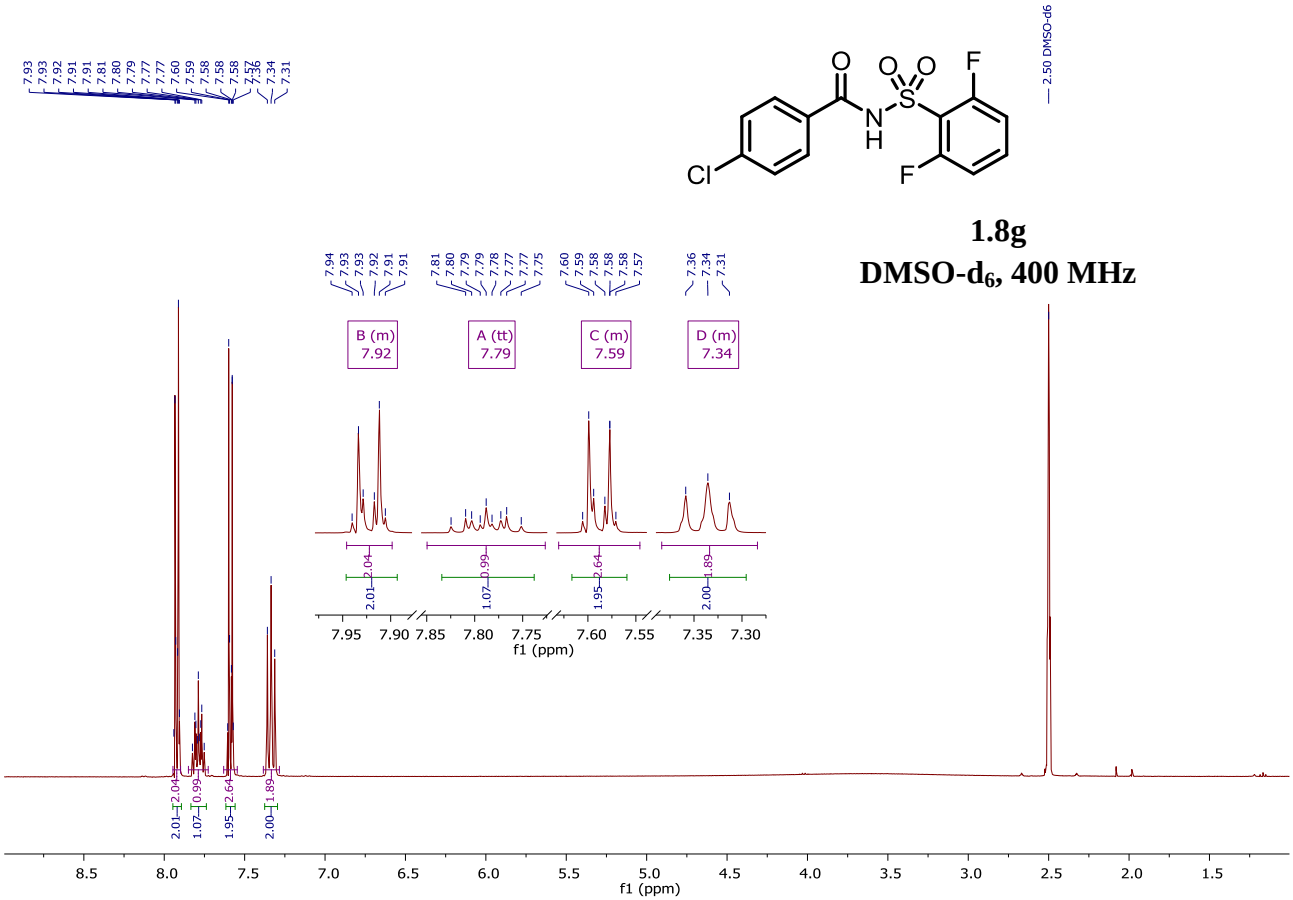
1.8f

DMSO-d_6, 400 MHz



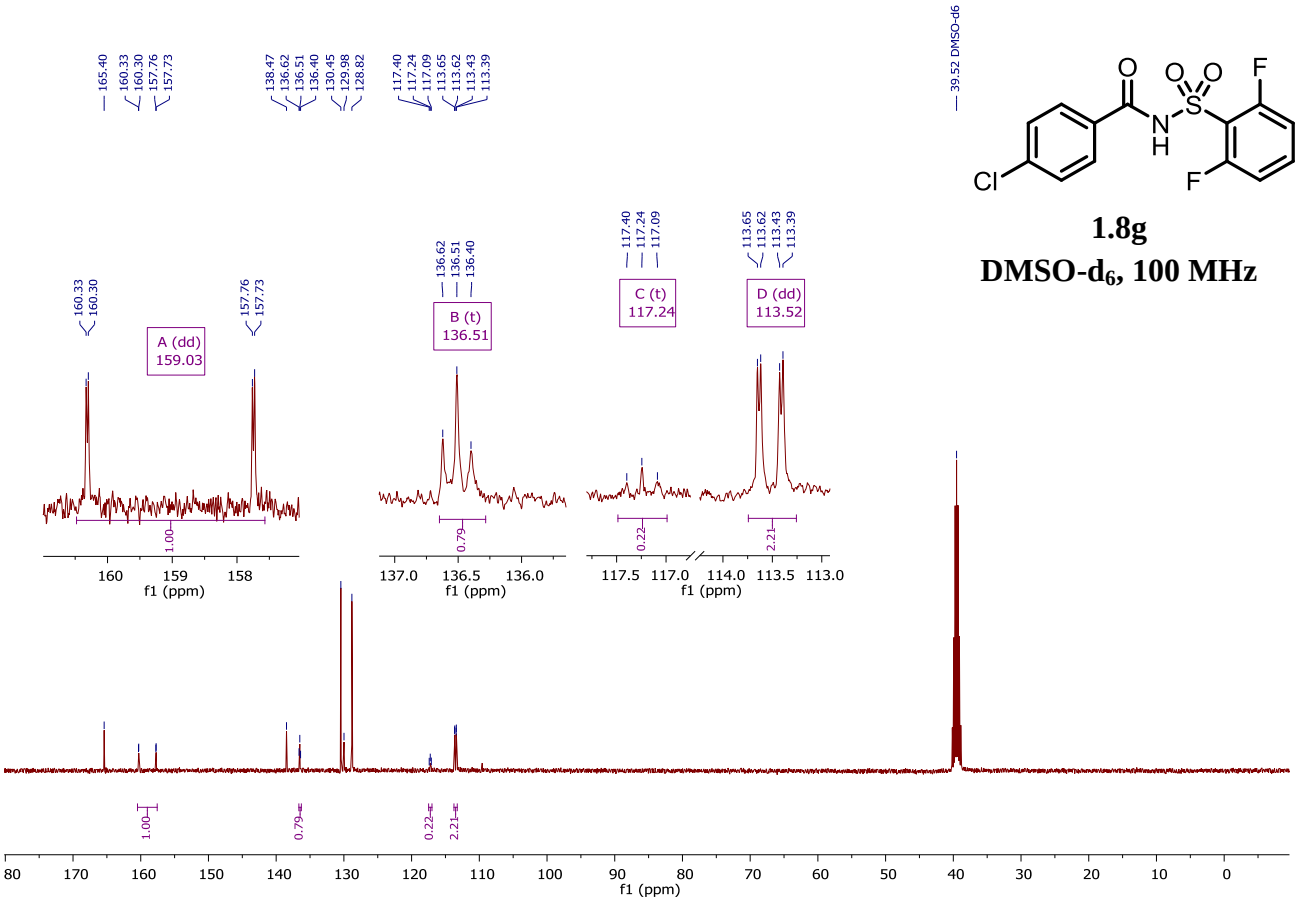
1.8f

DMSO-d_6, 100 MHz



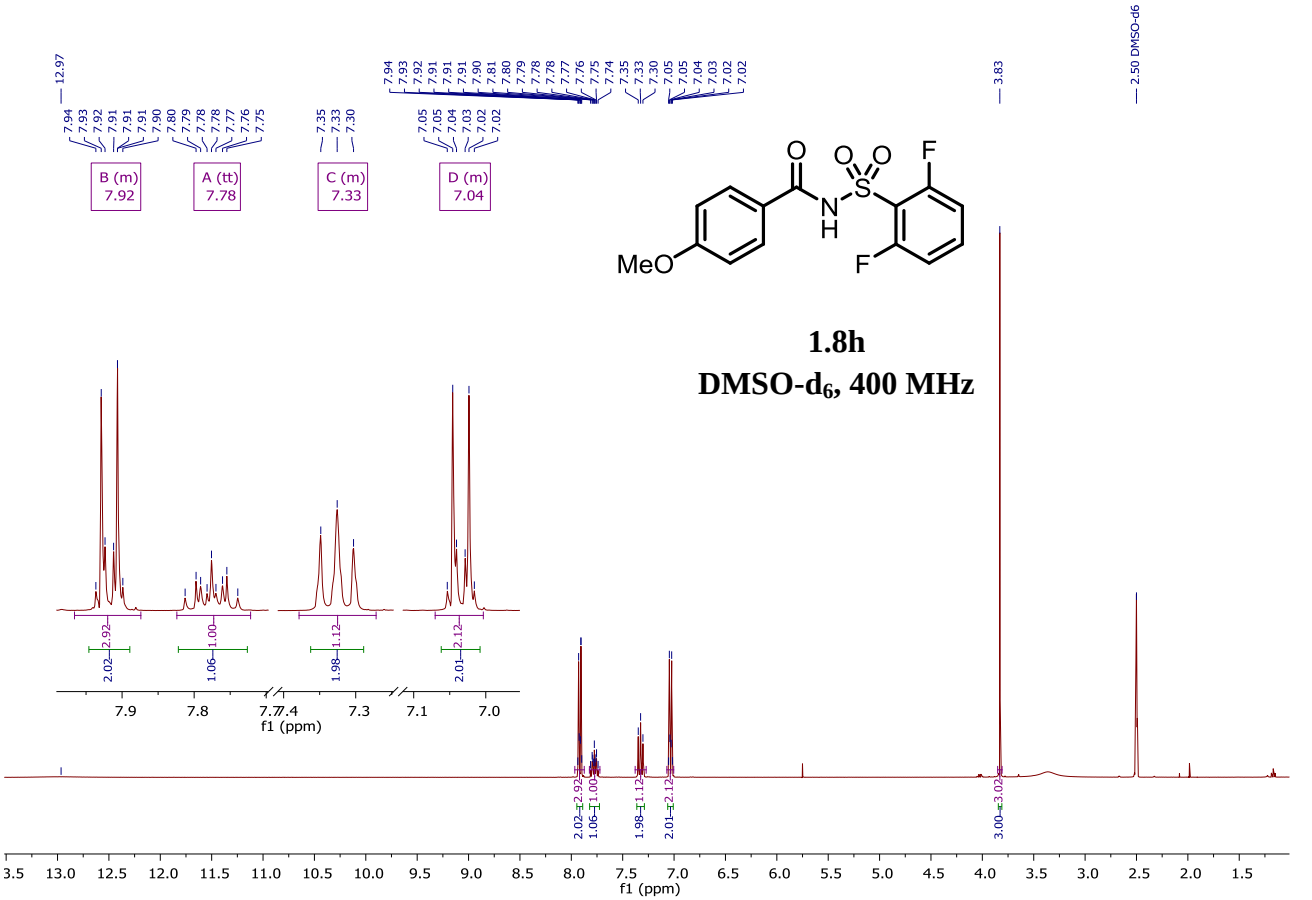
1.8g

DMSO-d$_6$, 400 MHz



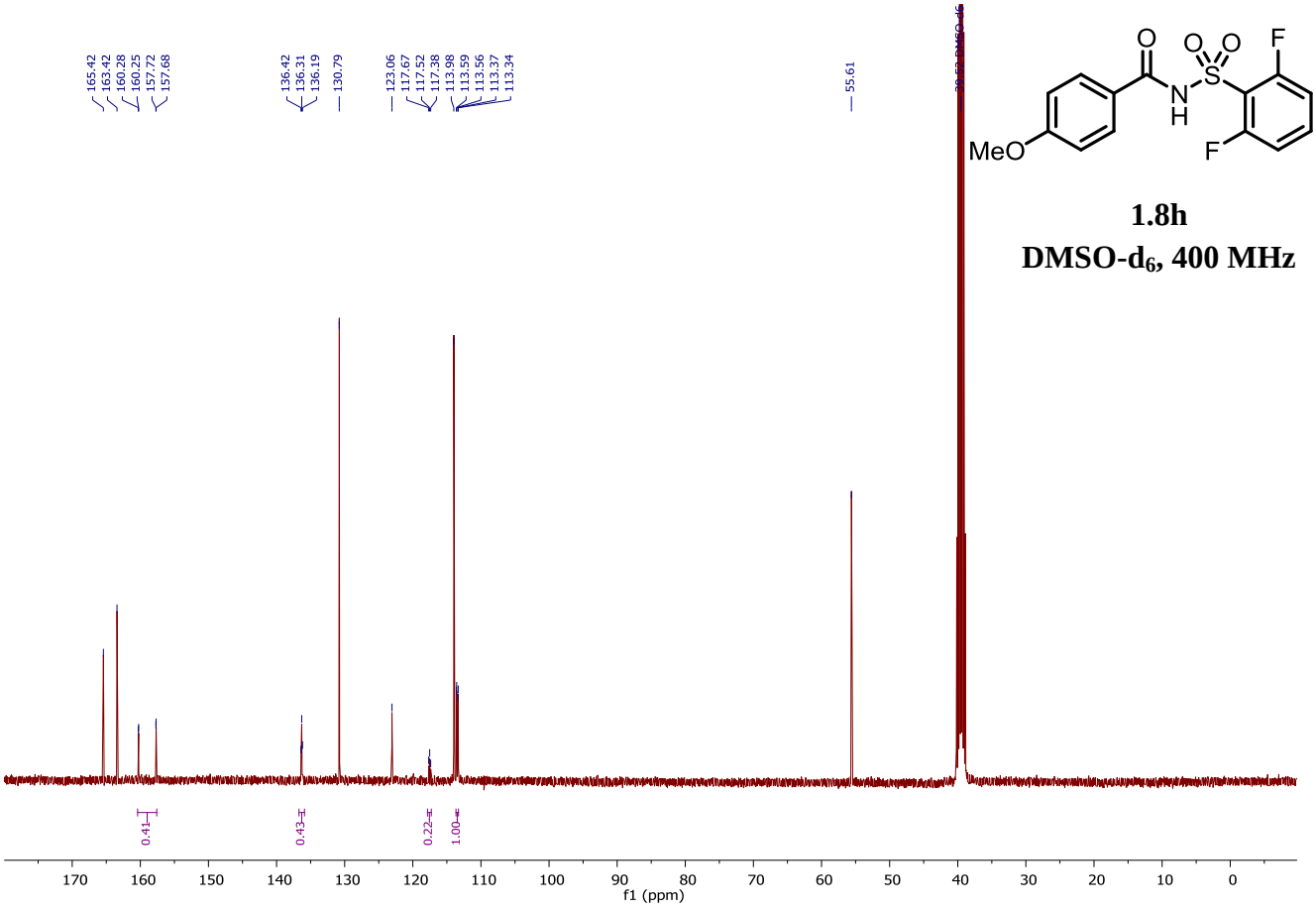
1.8g

DMSO-d$_6$, 100 MHz



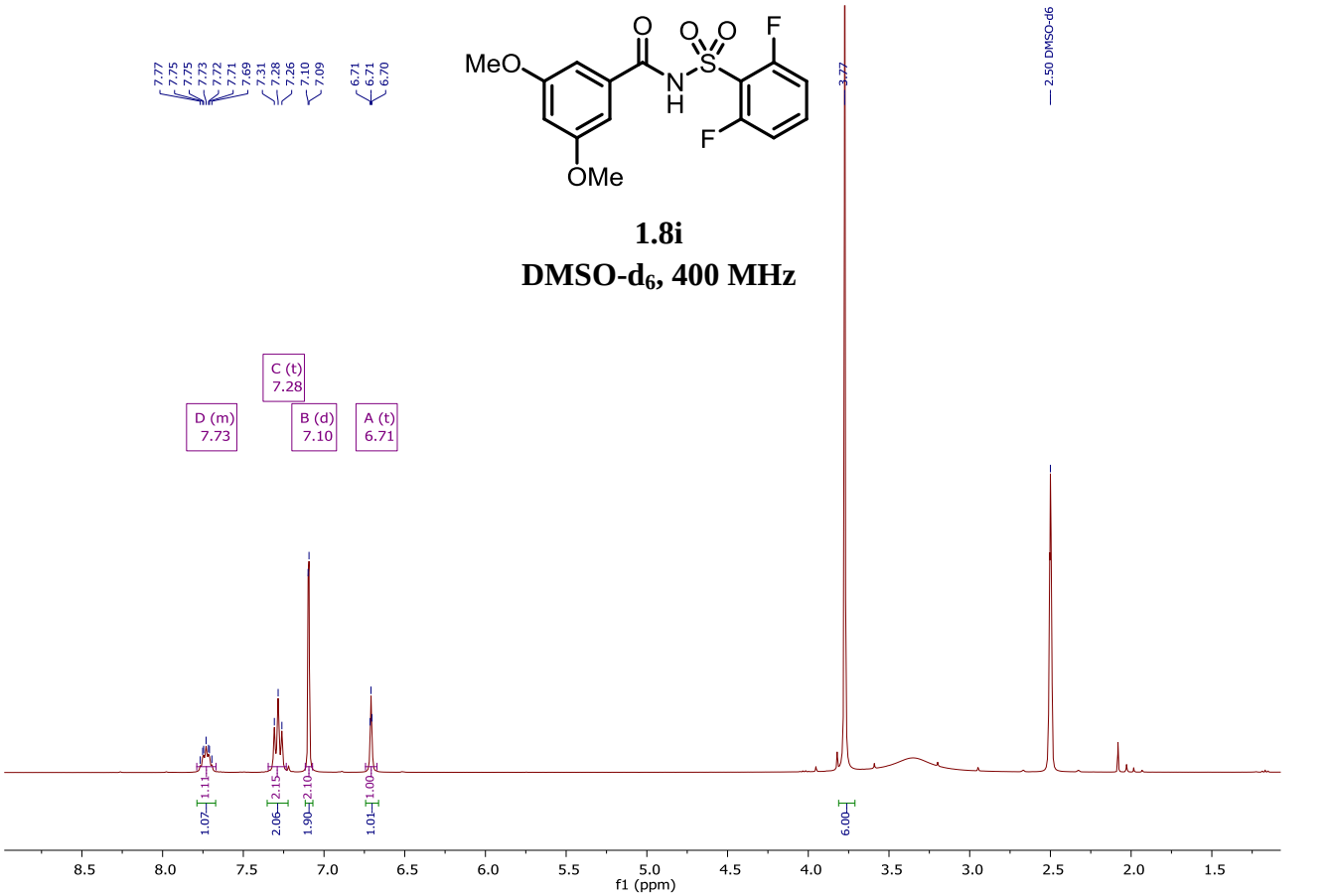
1.8h

DMSO-d_6, 400 MHz

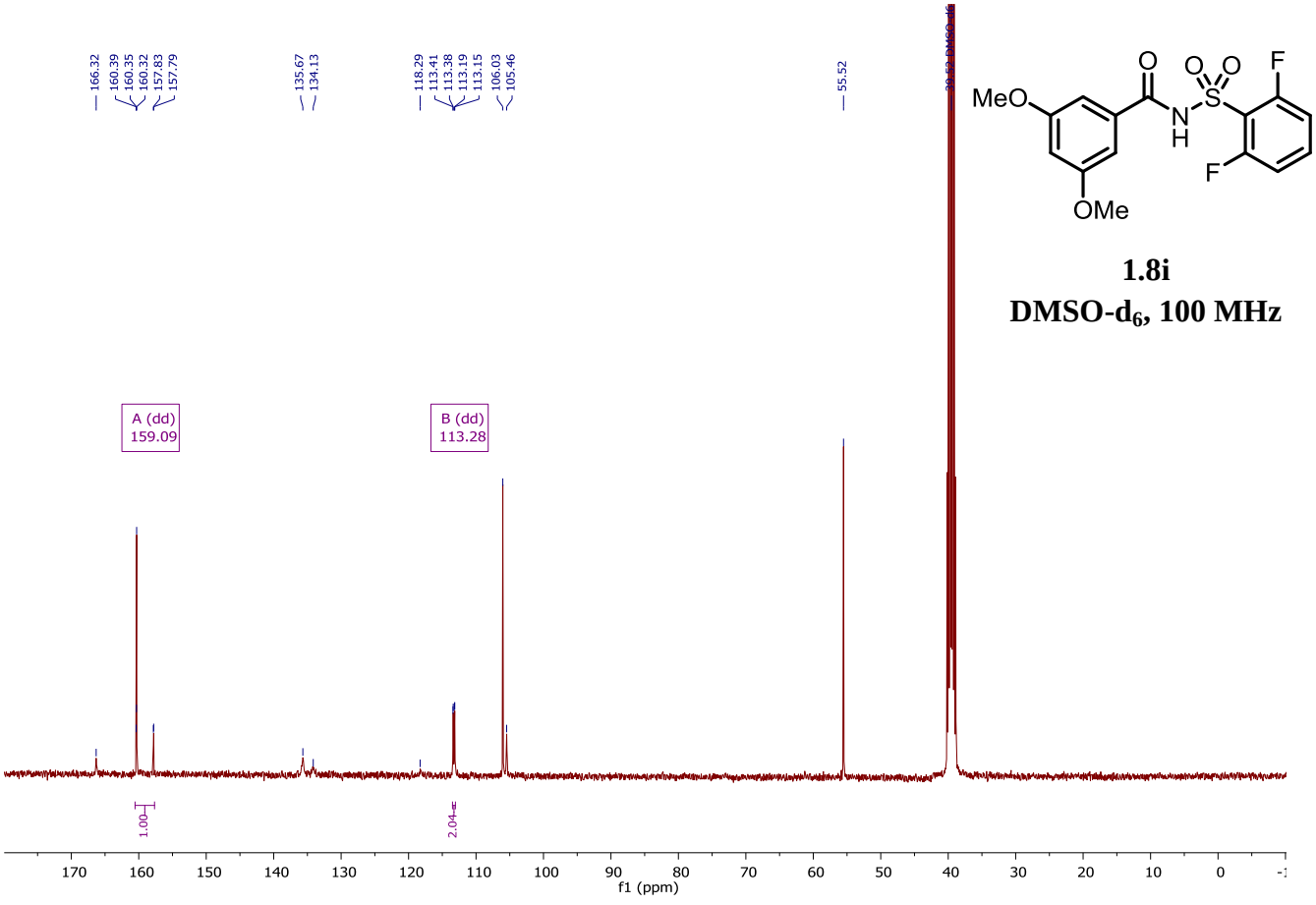


1.8h

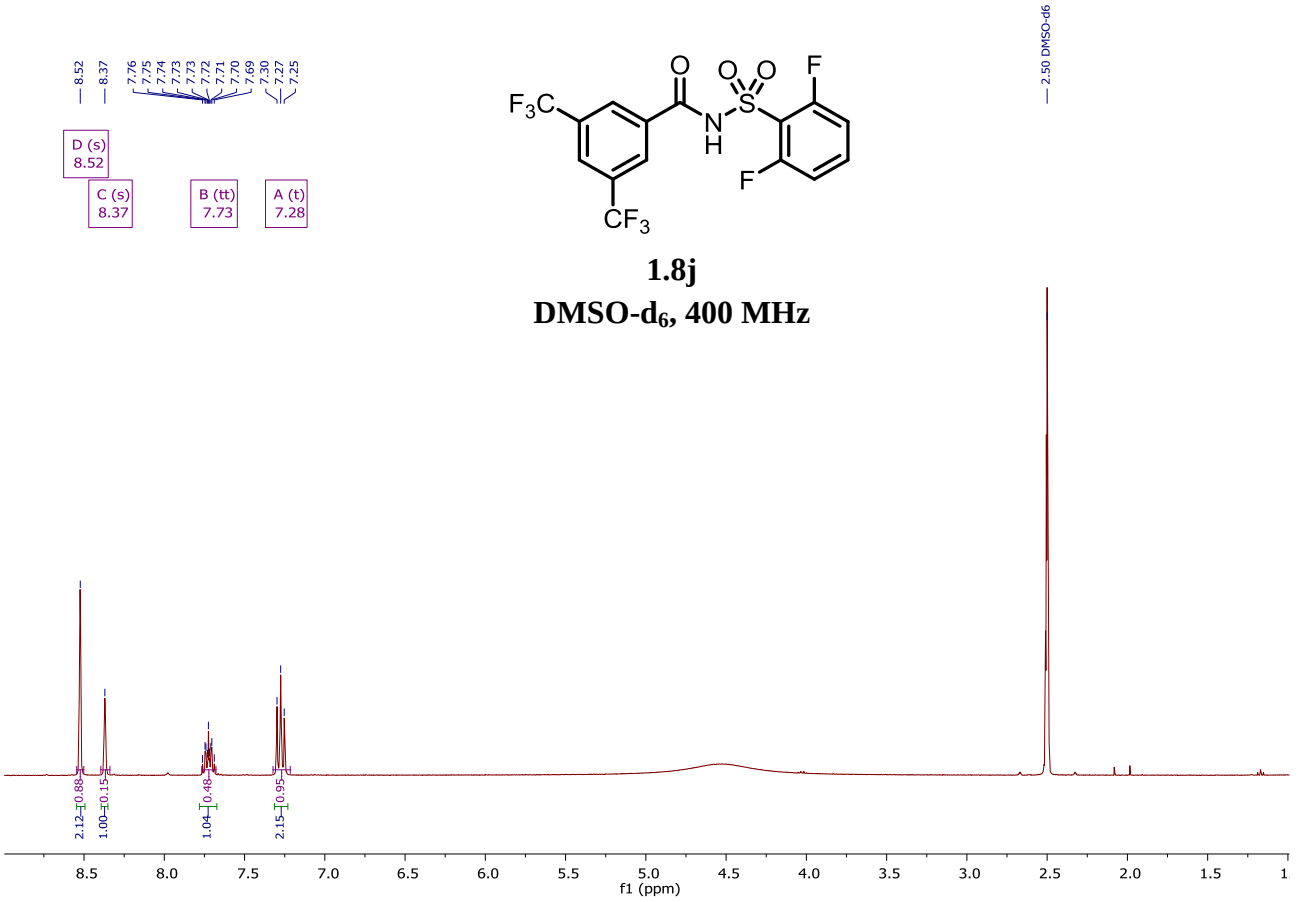
DMSO-d_6, 400 MHz



1.8i
DMSO-d_6, 400 MHz

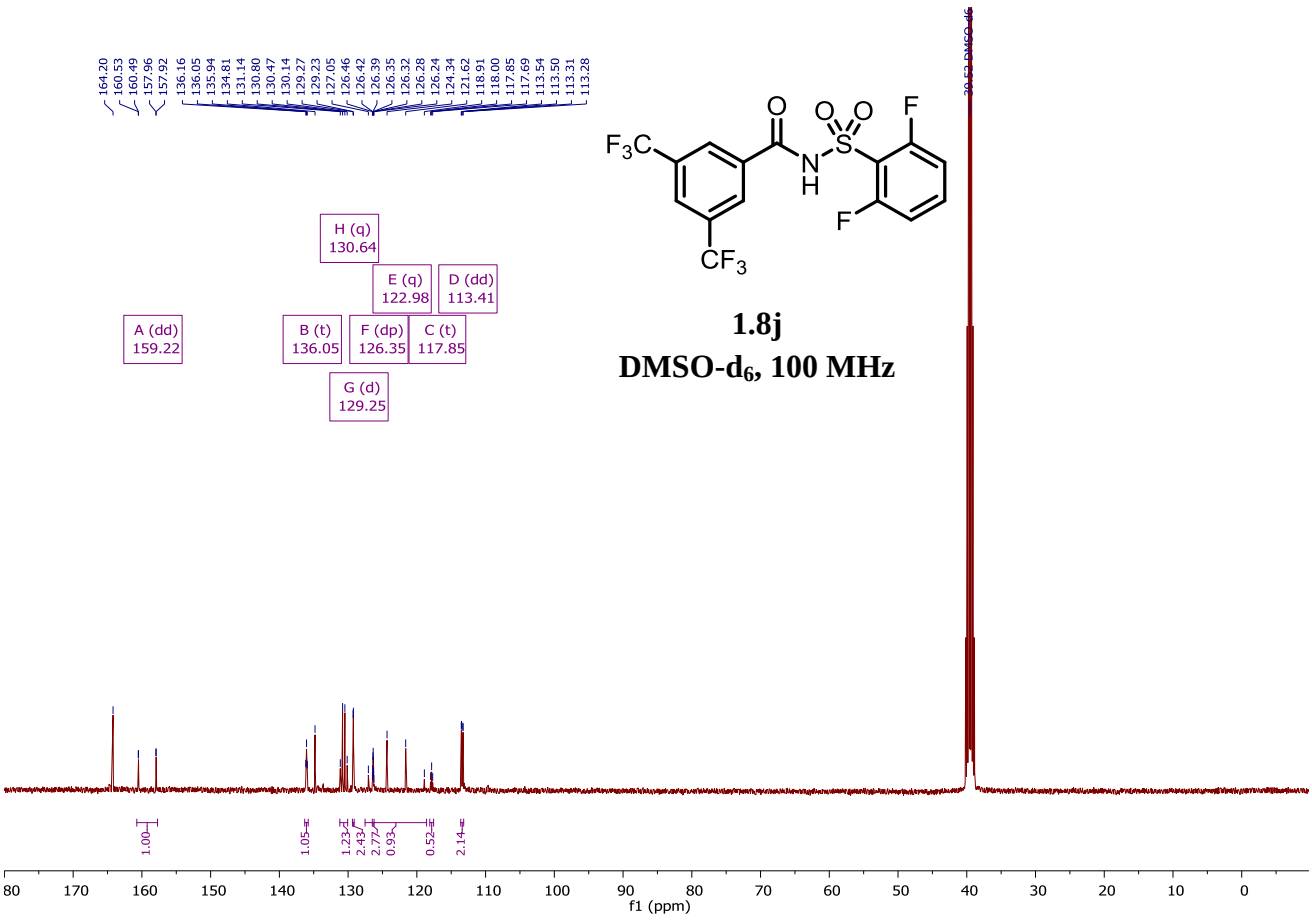


1.8i
DMSO-d_6, 100 MHz



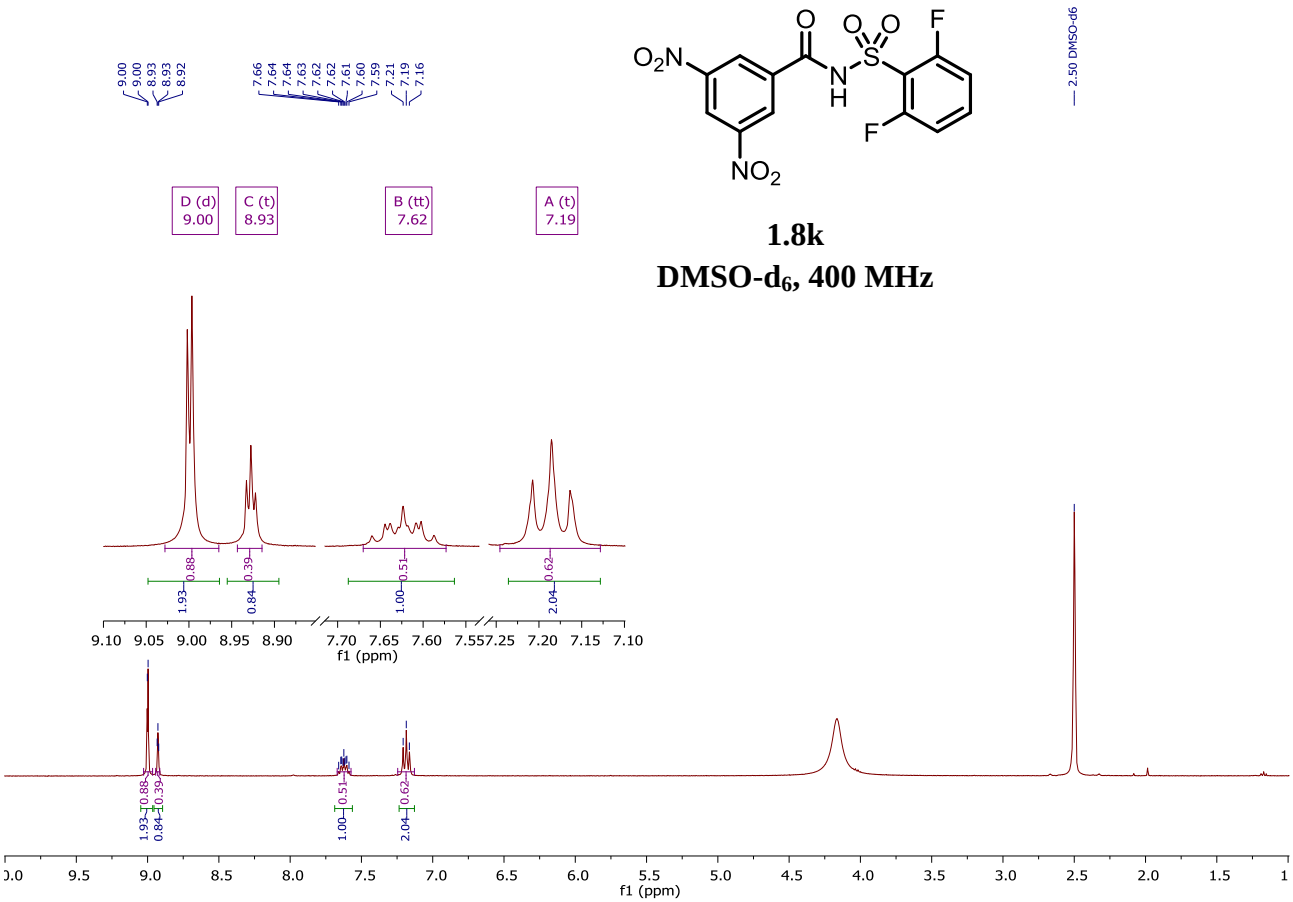
1.8j

DMSO-d_6, 400 MHz



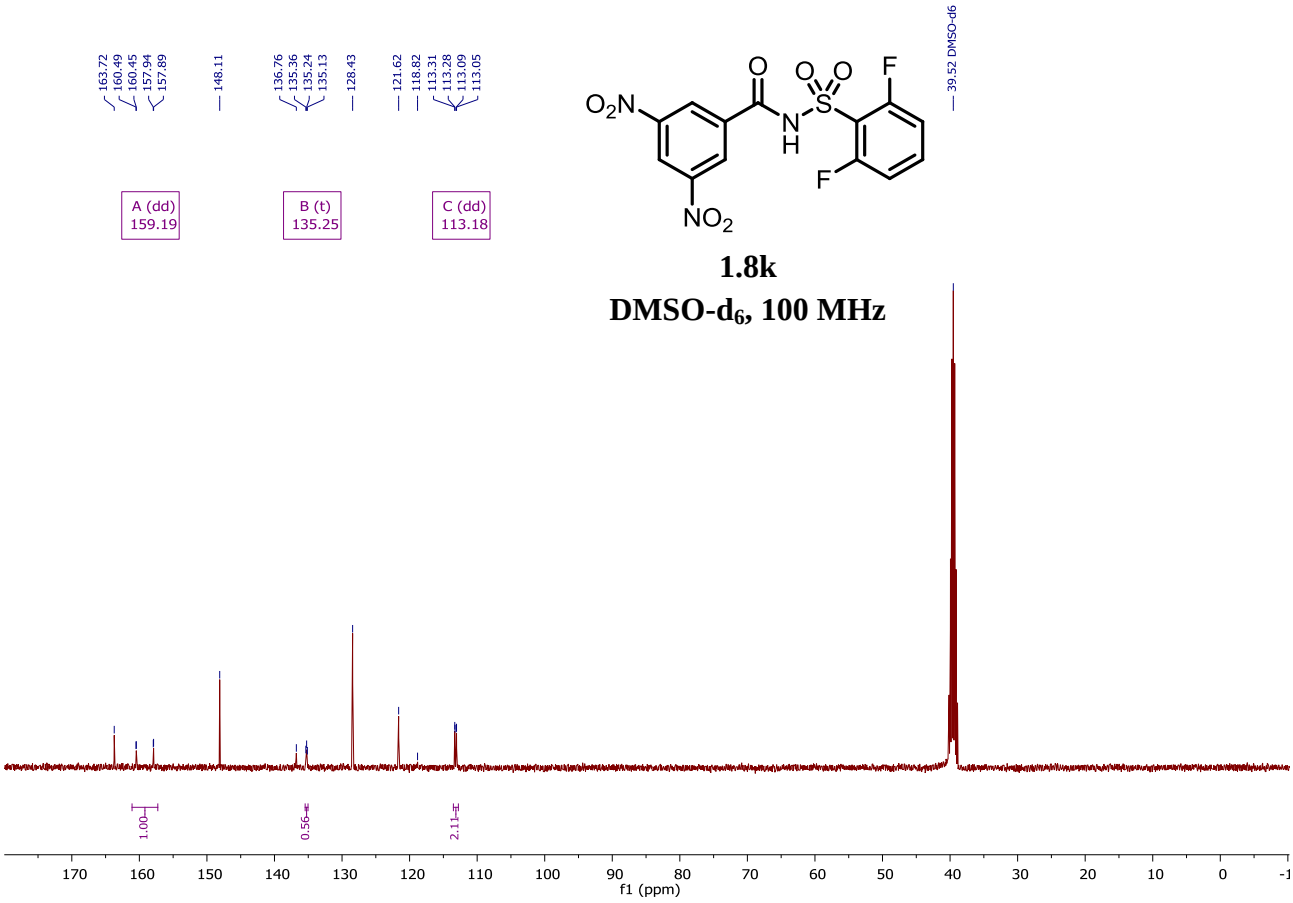
1.8j

DMSO-d_6, 100 MHz



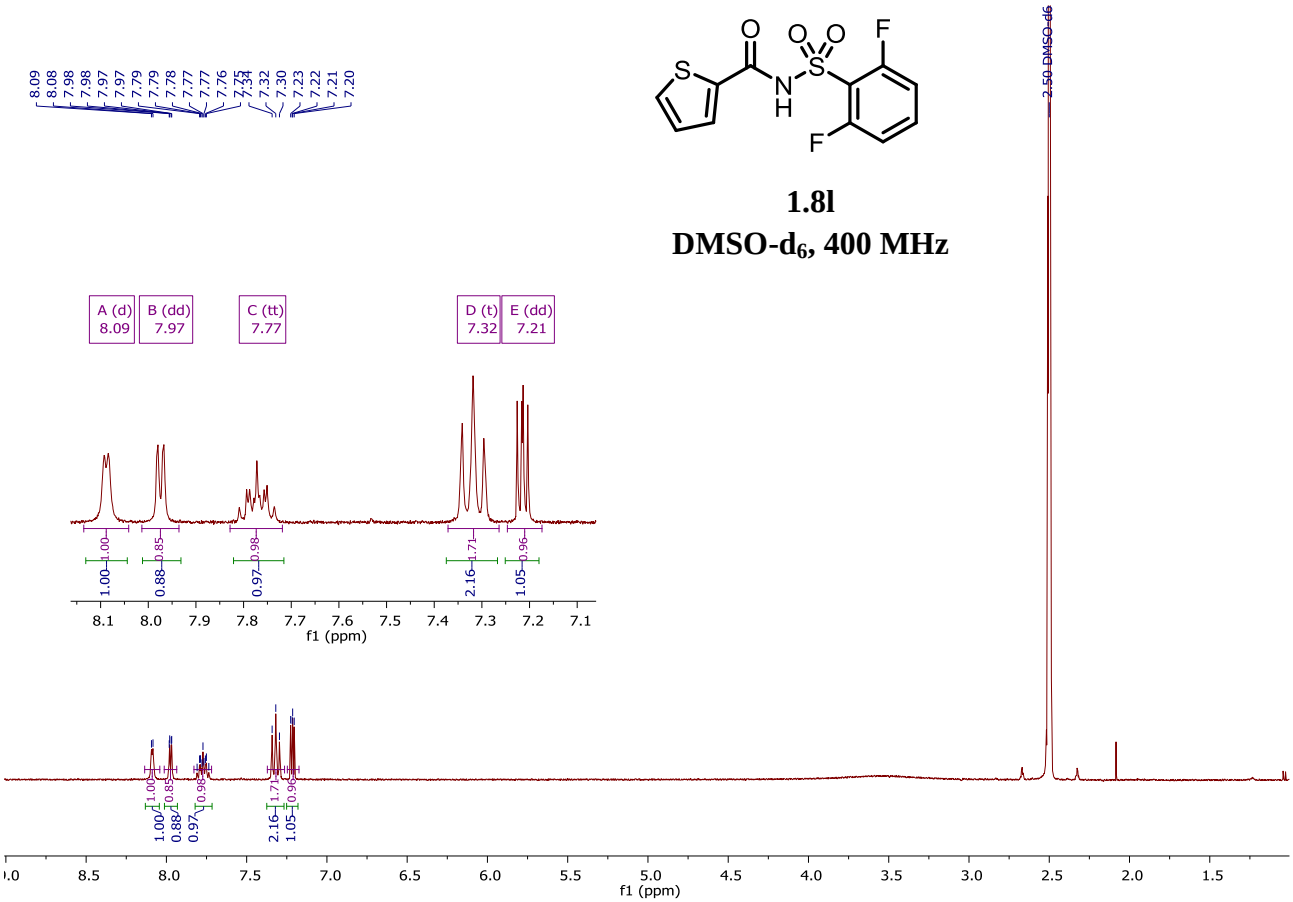
1.8k

DMSO-d_6, 400 MHz



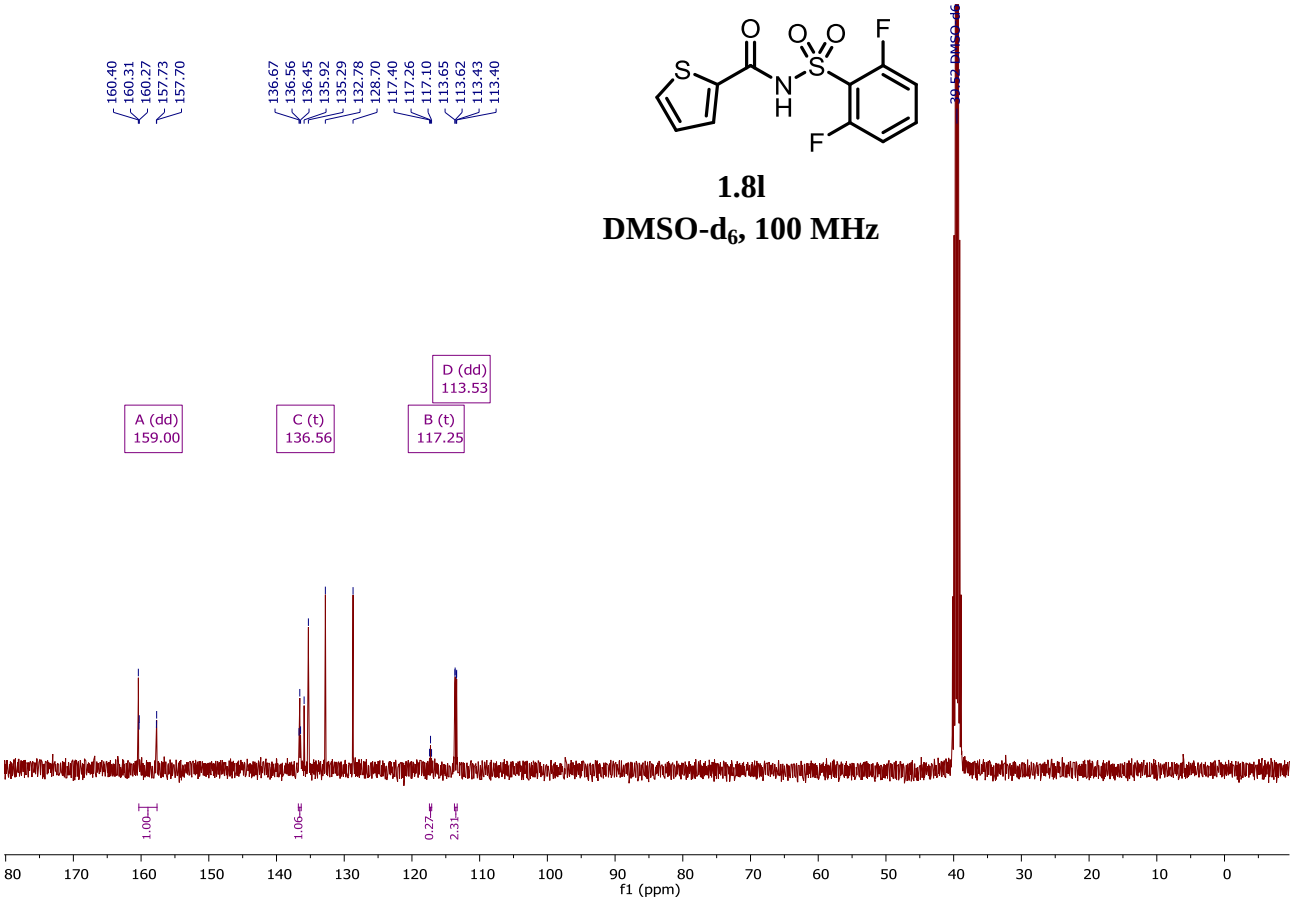
1.8k

DMSO-d_6, 100 MHz



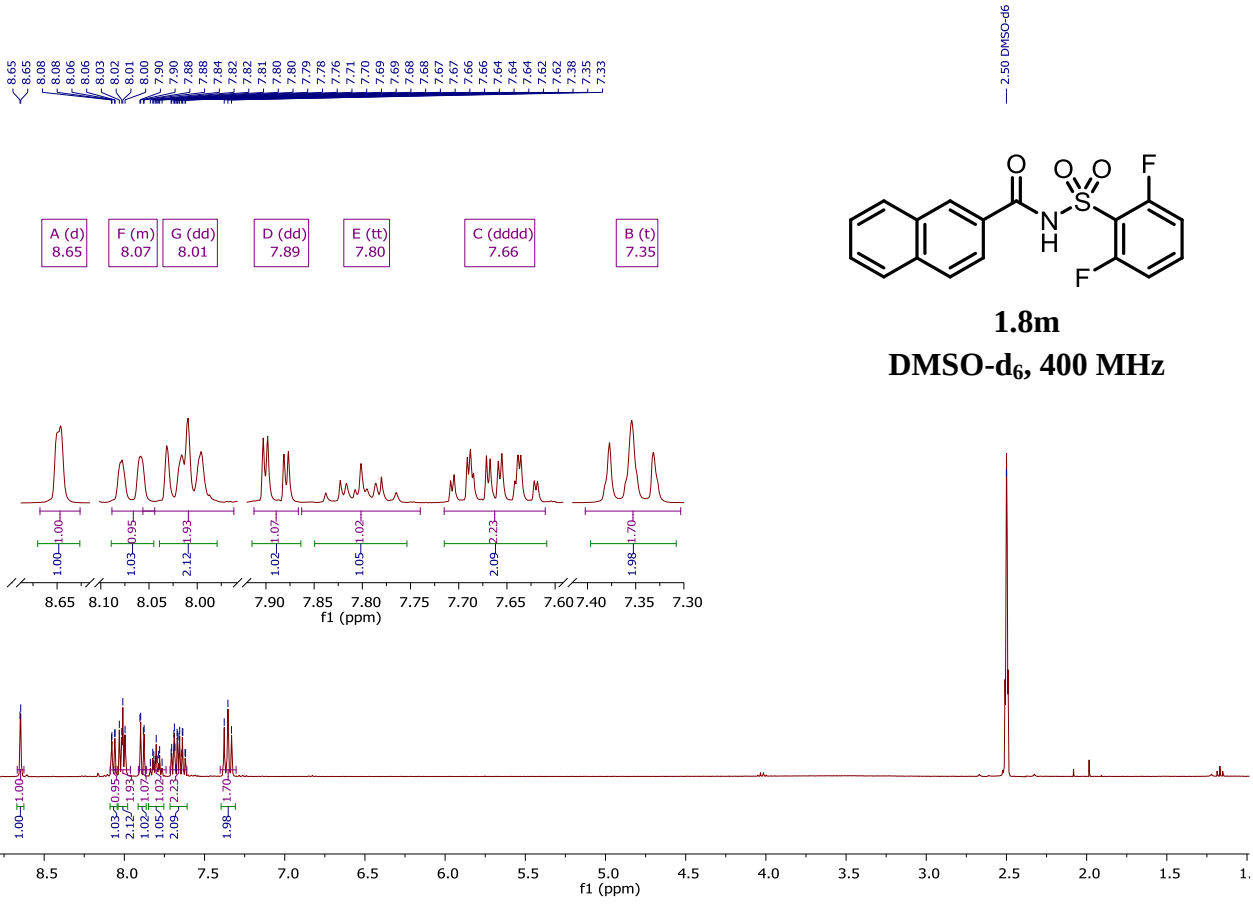
1.8l

DMSO-d_6, 400 MHz



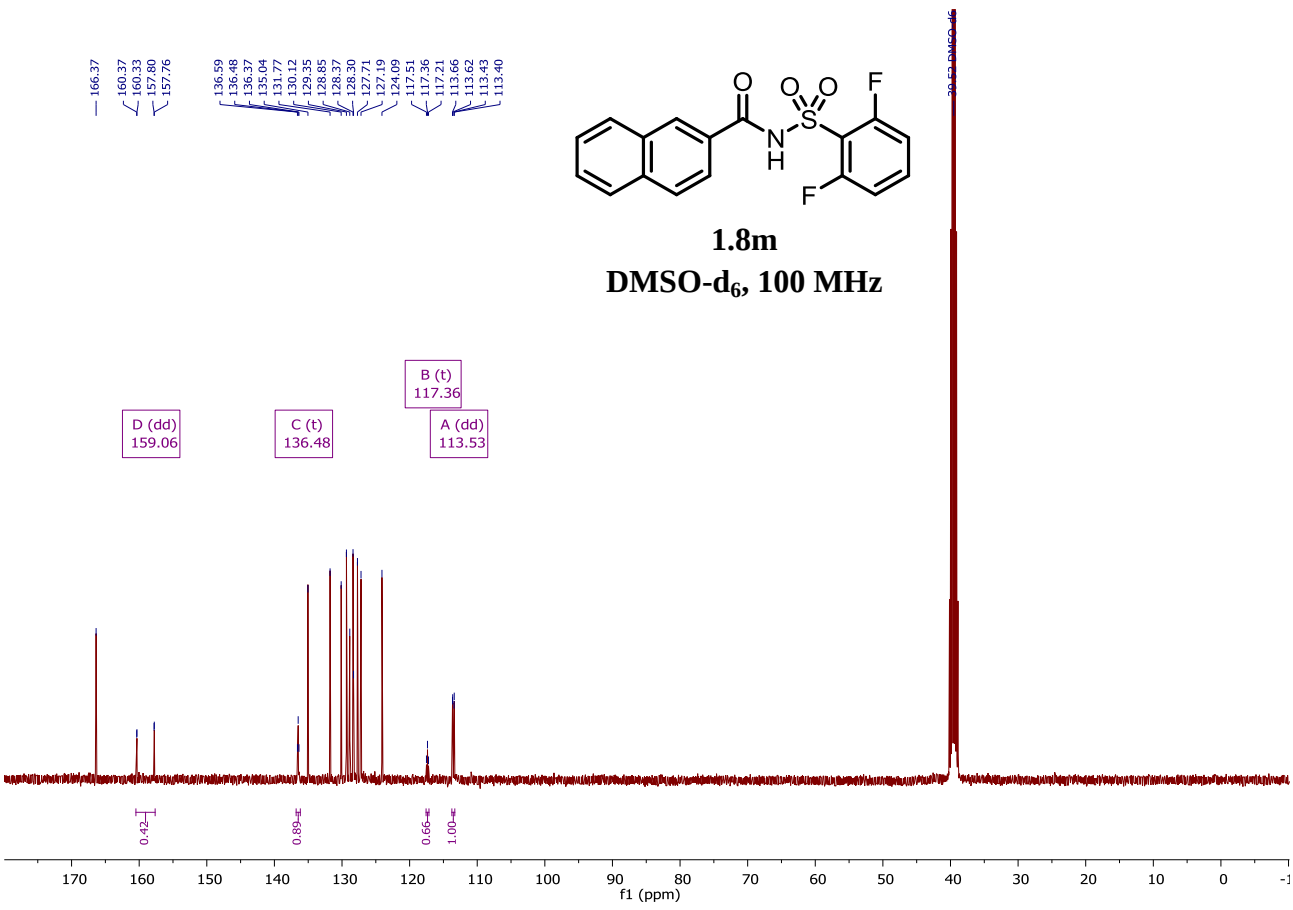
1.8l

DMSO-d_6, 100 MHz



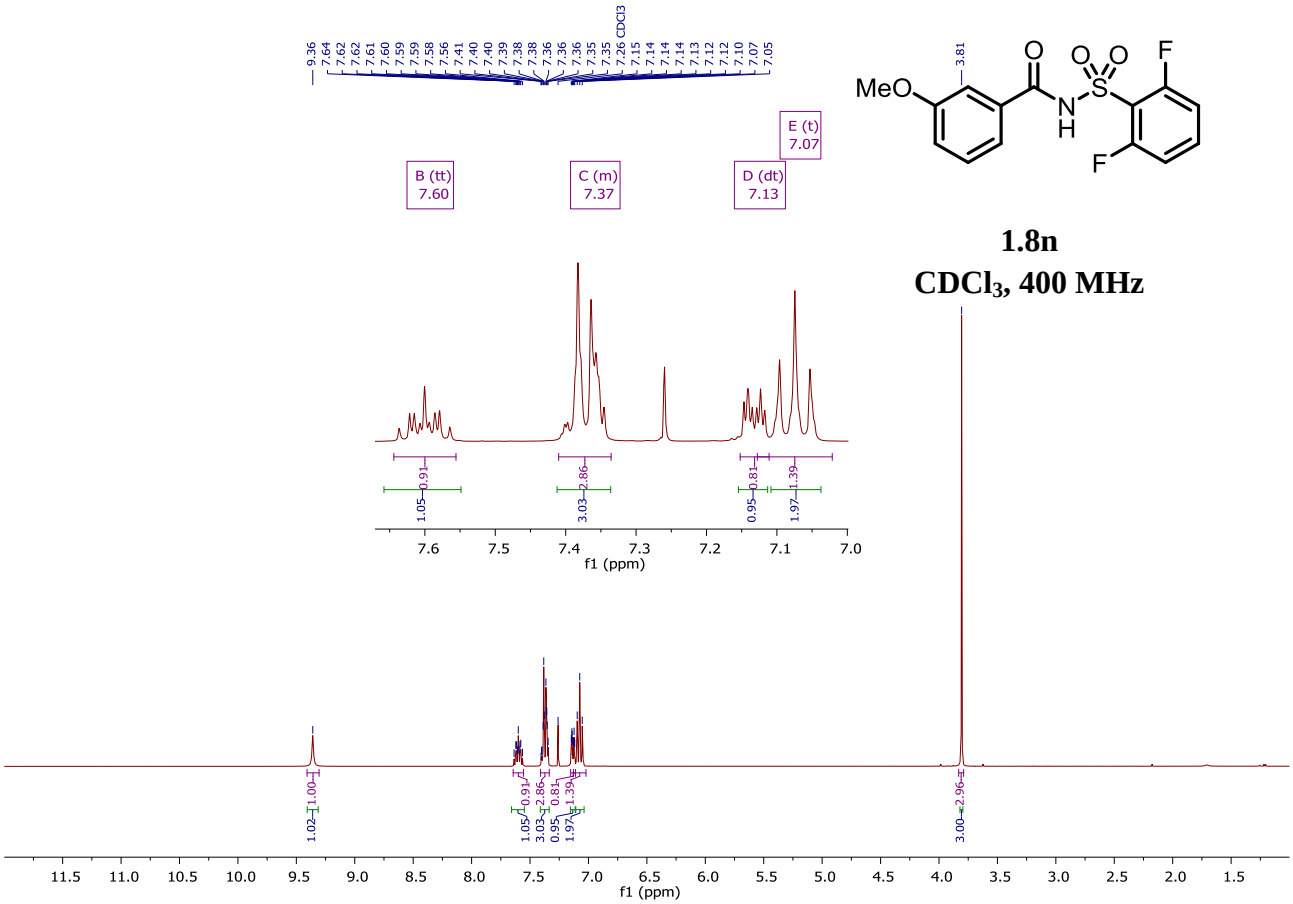
1.8m

DMSO-d_6, 400 MHz



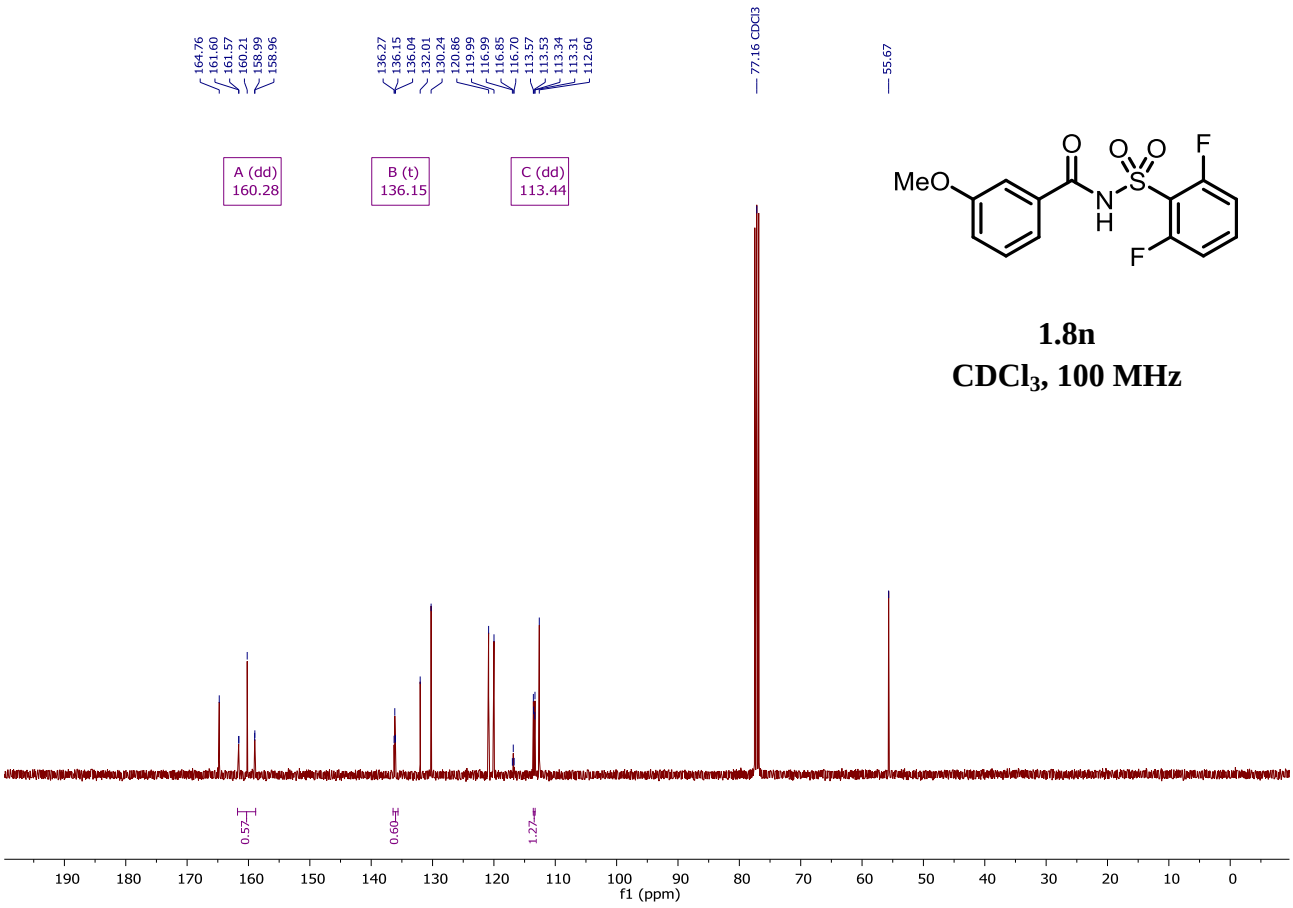
1.8m

DMSO-d_6, 100 MHz



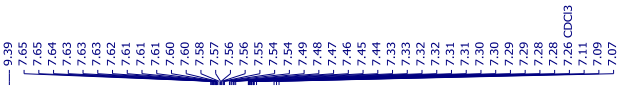
1.8n

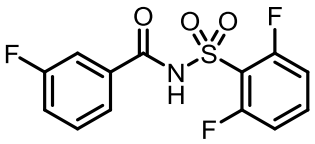
$CDCl_3$, 400 MHz



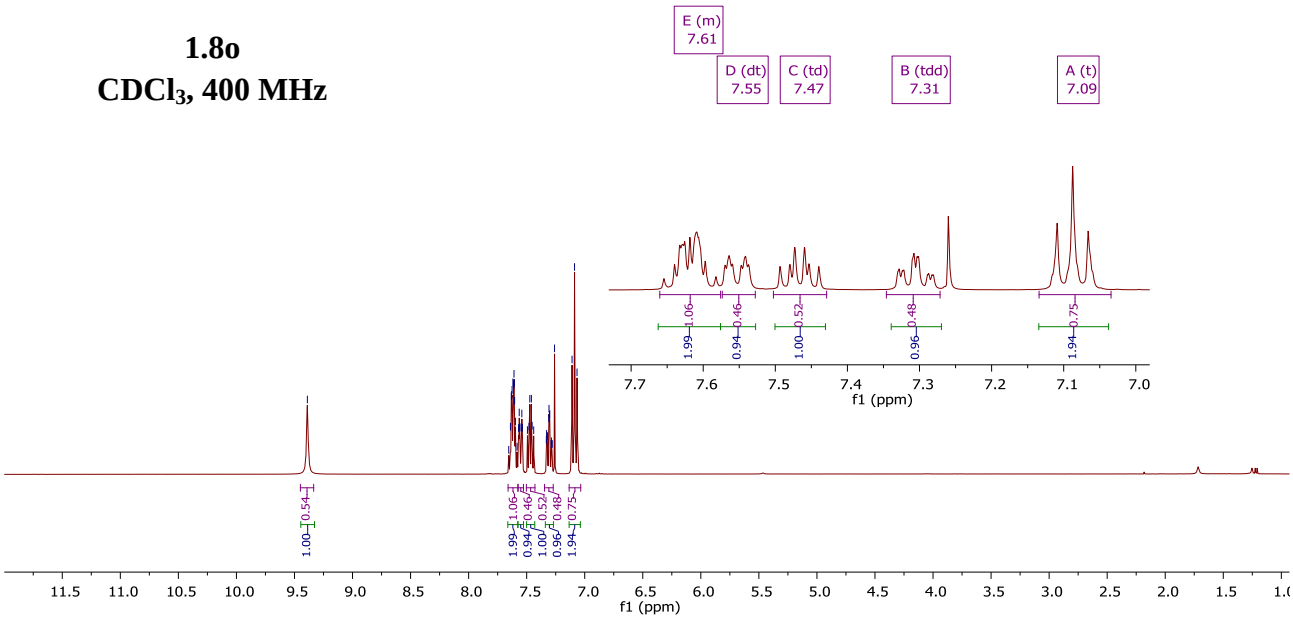
1.8n

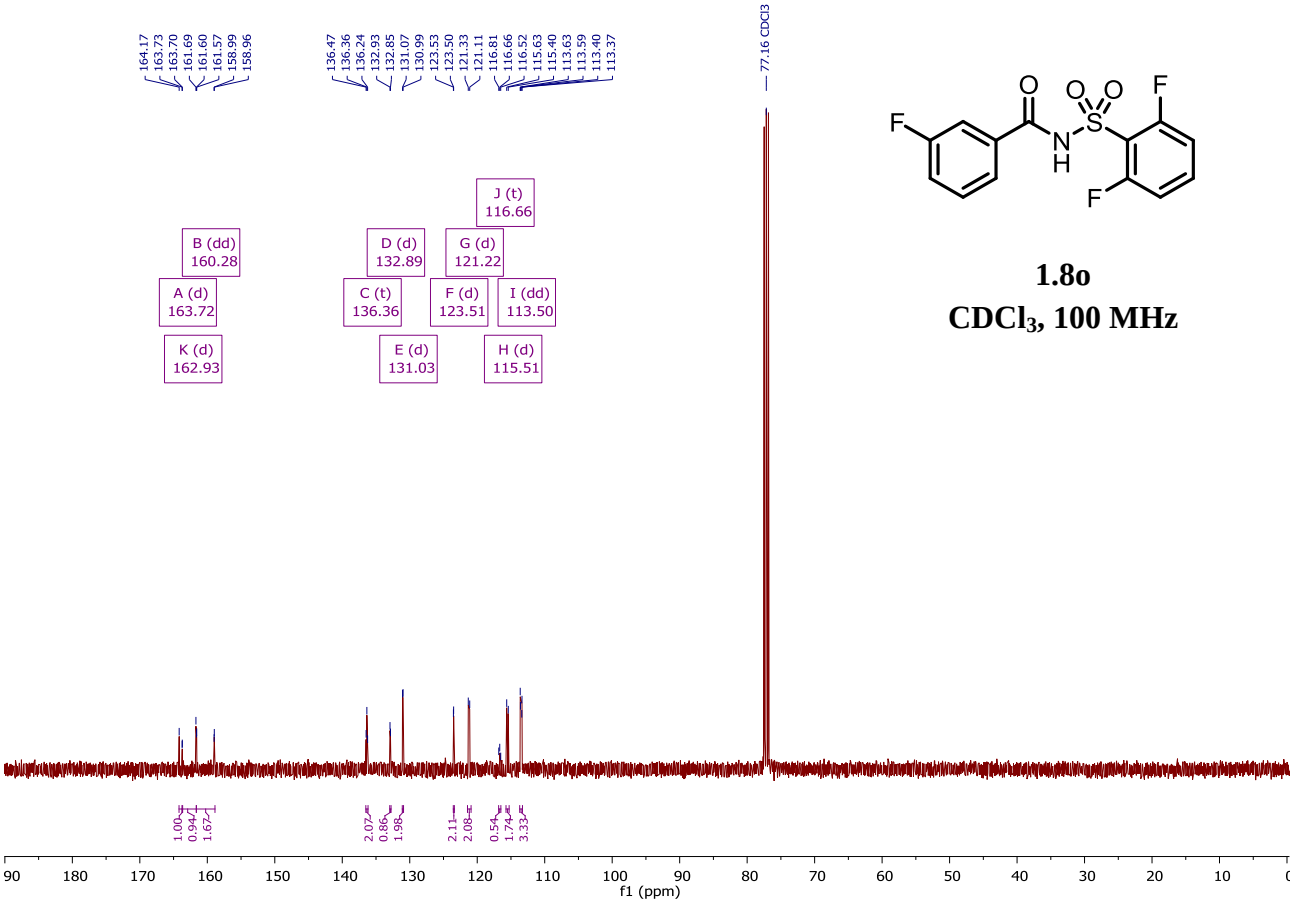
$CDCl_3$, 100 MHz



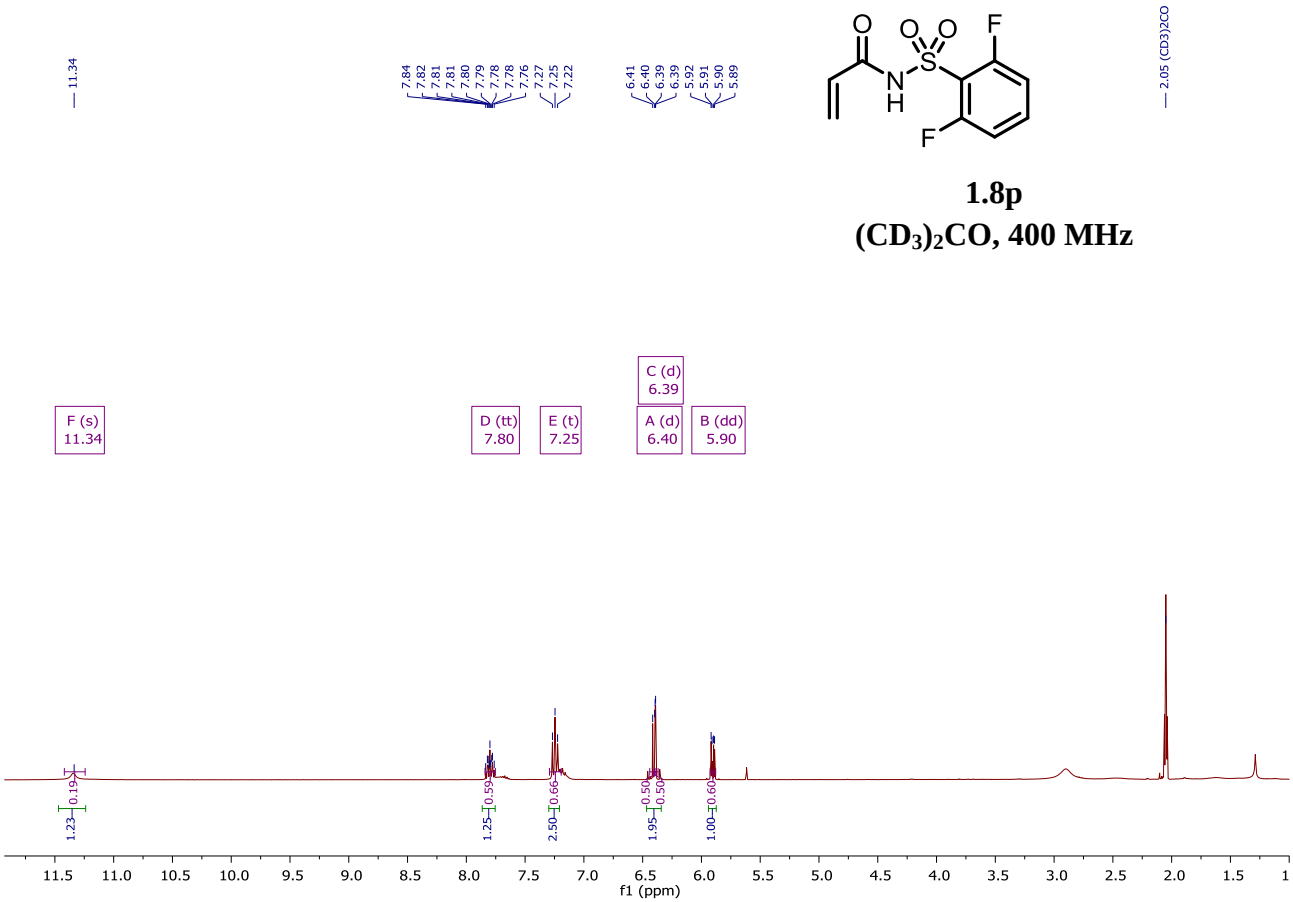


1.8o
$CDCl_3$, 400 MHz

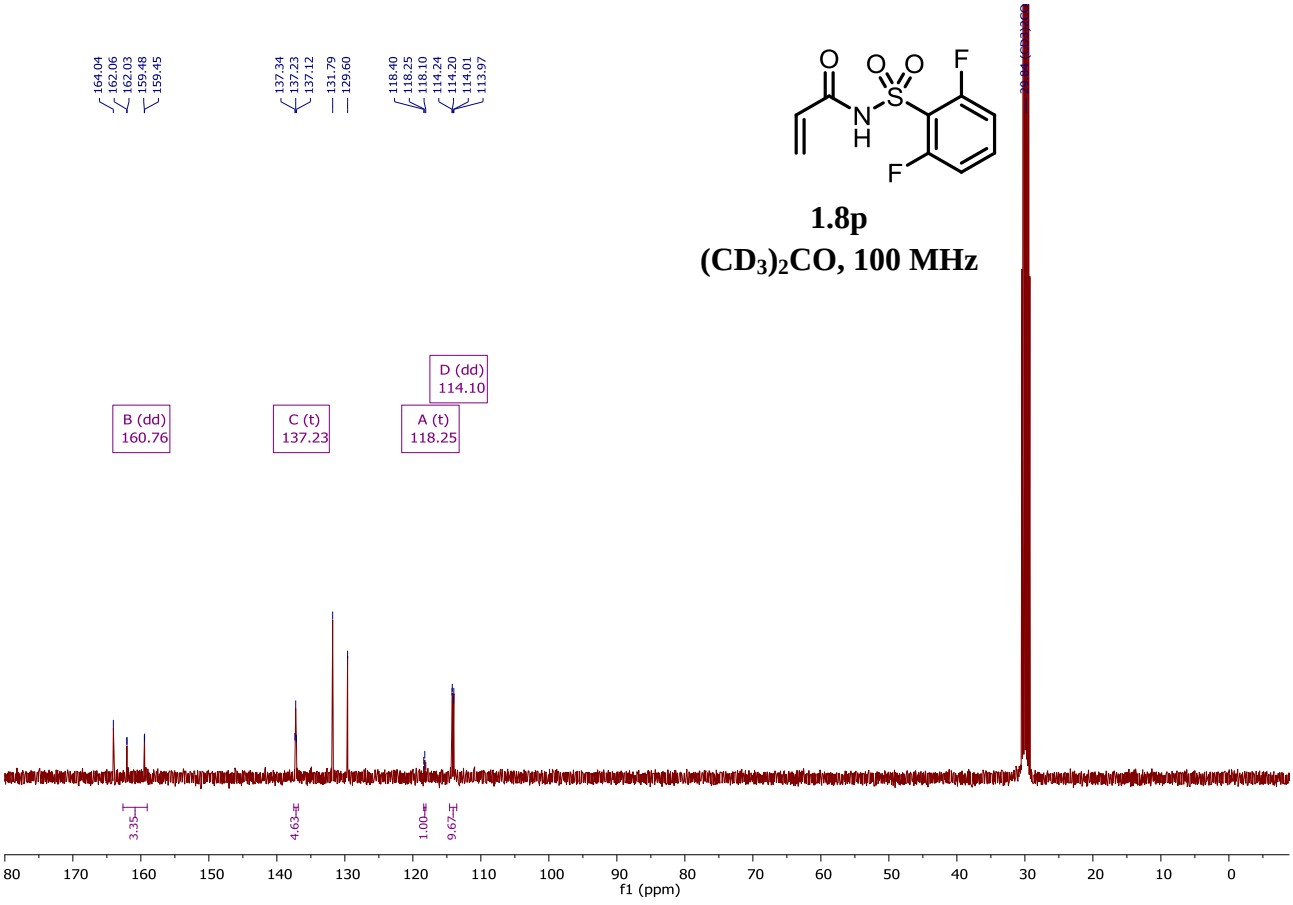




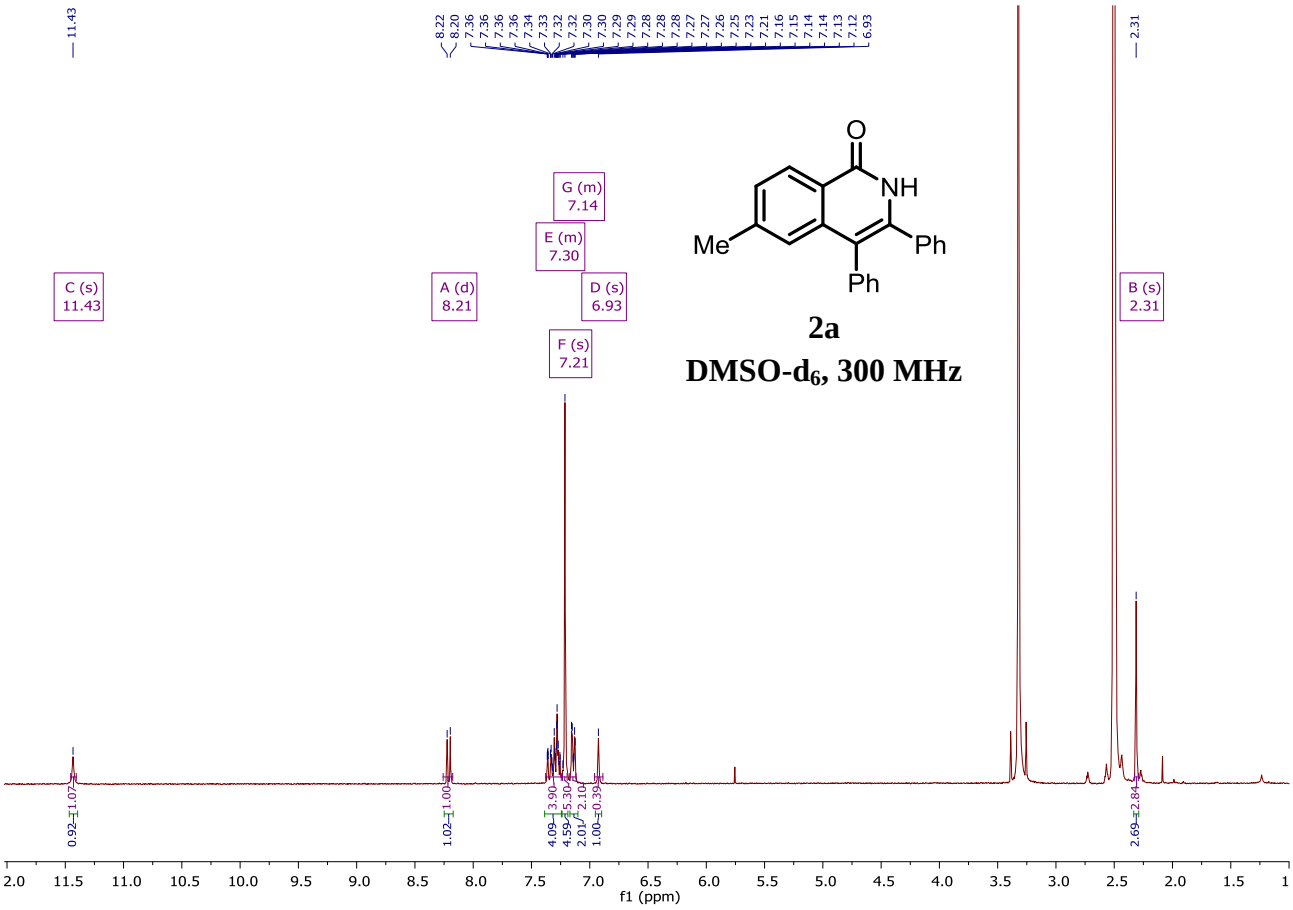
1.8o
$CDCl_3$, 100 MHz

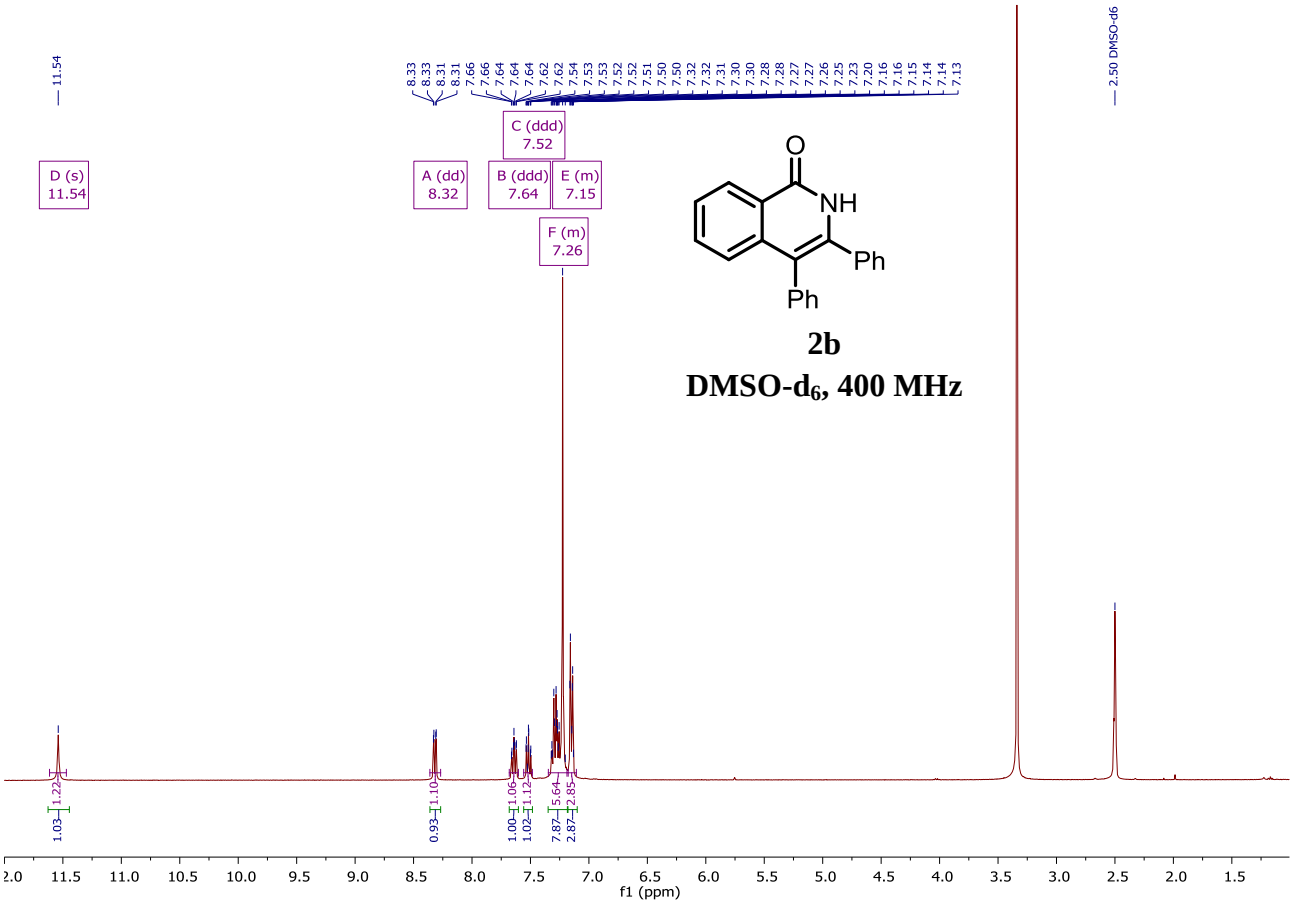


1.8p
$(CD_3)_2CO$, 400 MHz



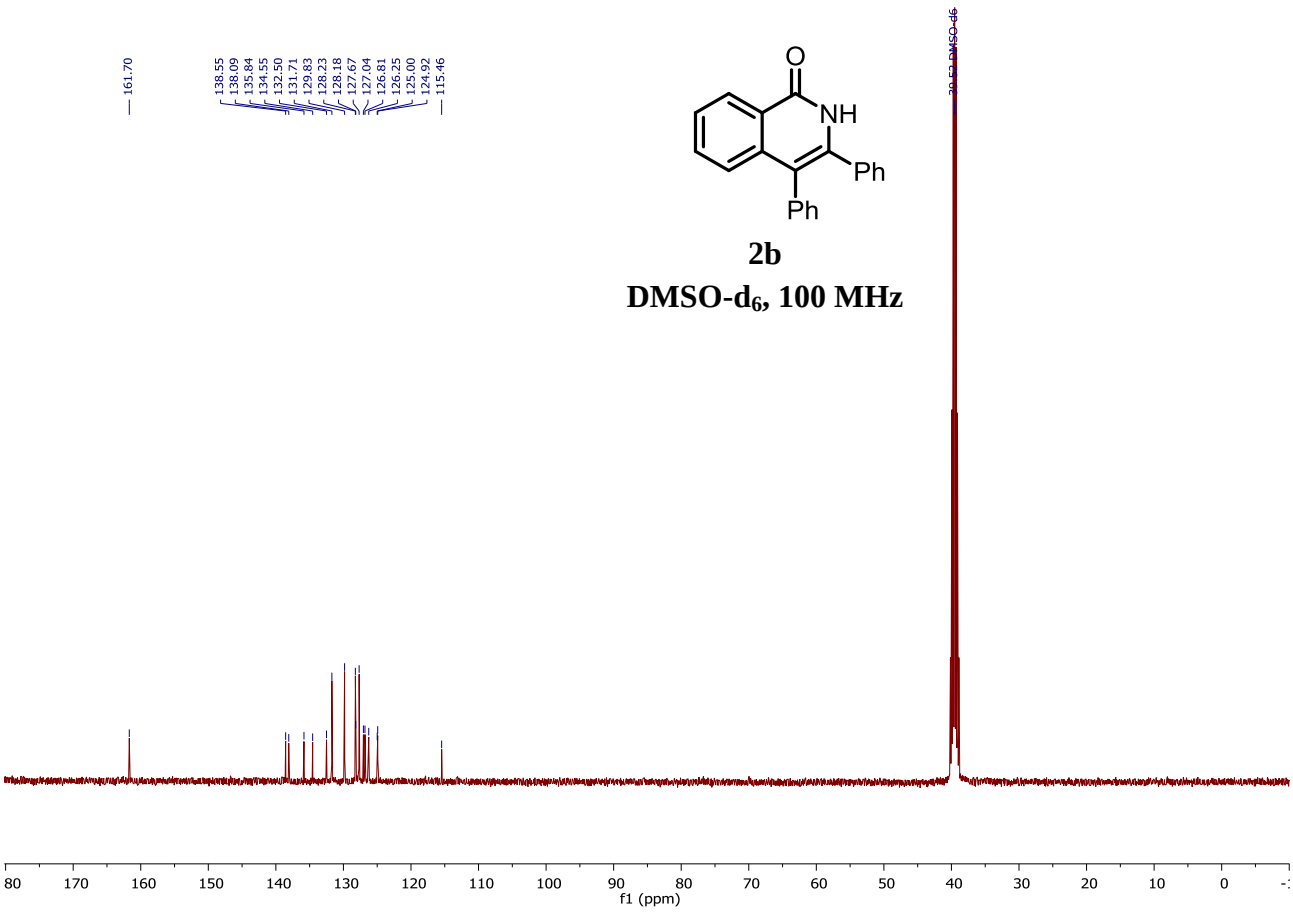
1.8p
$(CD_3)_2CO$, 100 MHz


11.43
8.22
8.20
7.36
7.36
7.36
7.34
7.33
7.32
7.32
7.30
7.30
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.26
7.25
7.23
7.21
7.16
7.15
7.14
7.14
7.13
7.12
6.93
2.31
G (m)
7.14
E (m)
7.30
C (s)
11.43
A (d)
8.21
D (s)
6.93
F (s)
7.21
B (s)
2.31
O
NH
Me
Ph
Ph
2a
DMSO-d6, 300 MHz
0.92
1.07
1.02
1.00
4.09
3.90
4.59
5.30
2.01
2.10
1.00
0.39
2.69
2.84
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1
f1 (ppm)



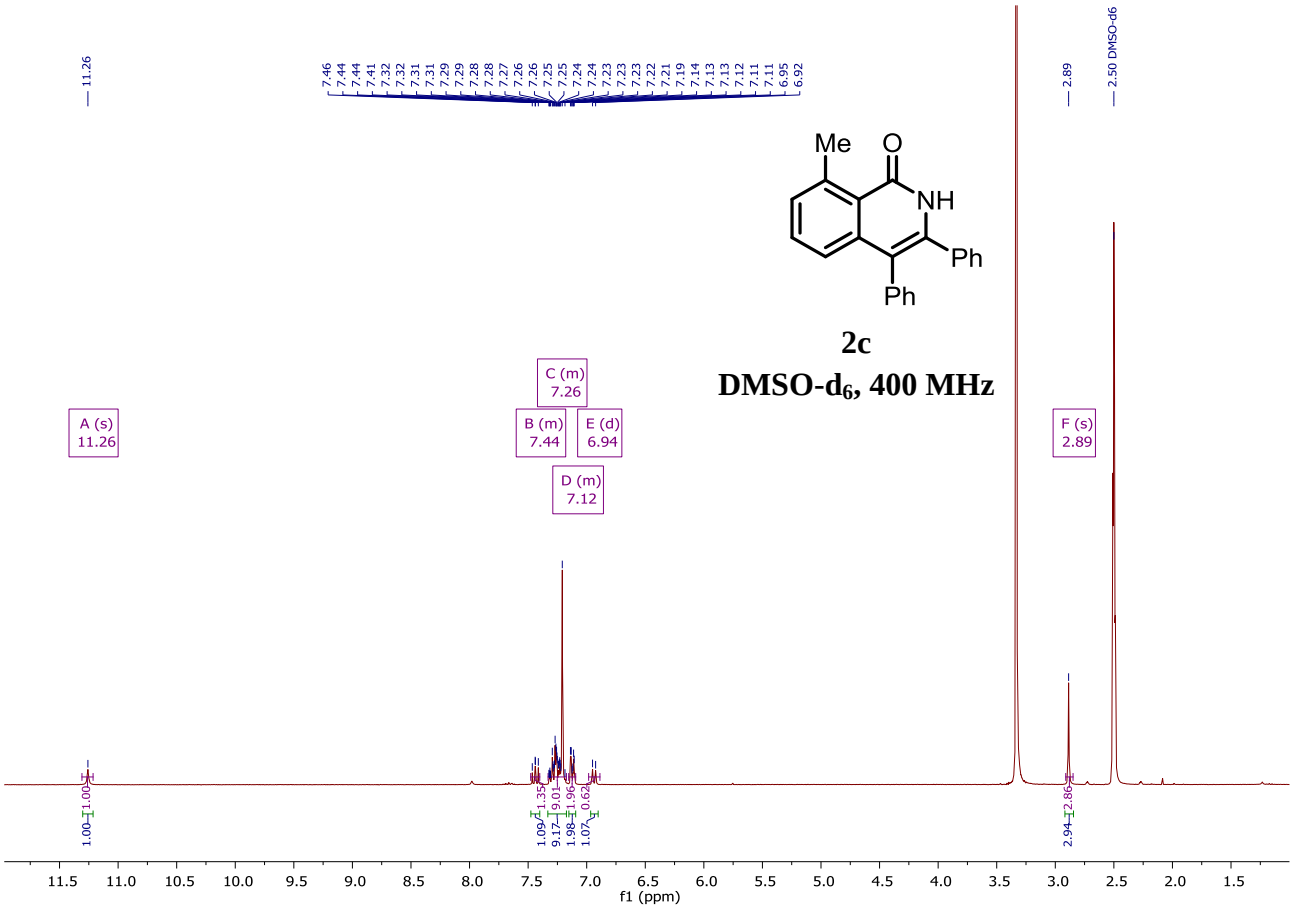
2b

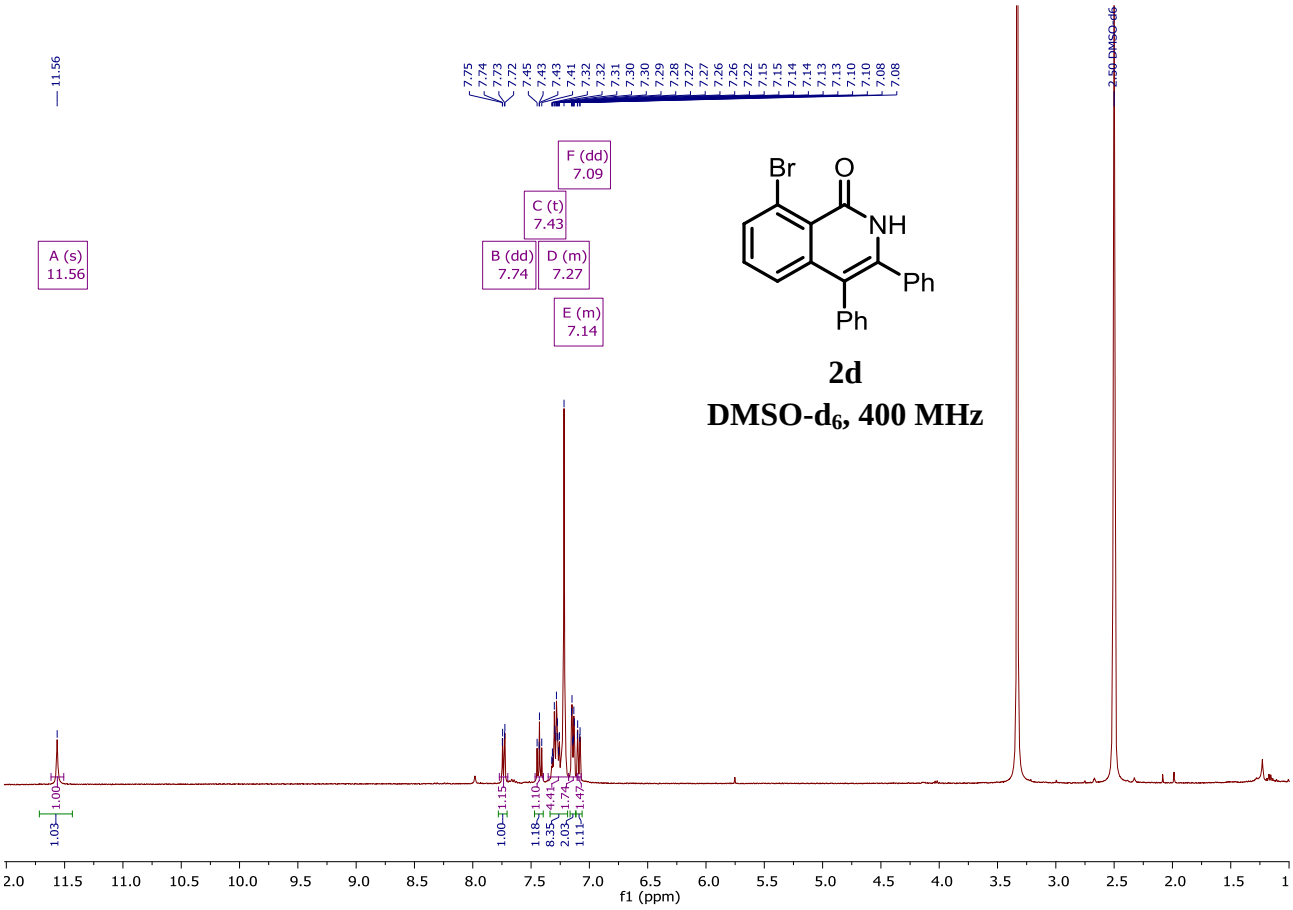
DMSO-d_6, 400 MHz

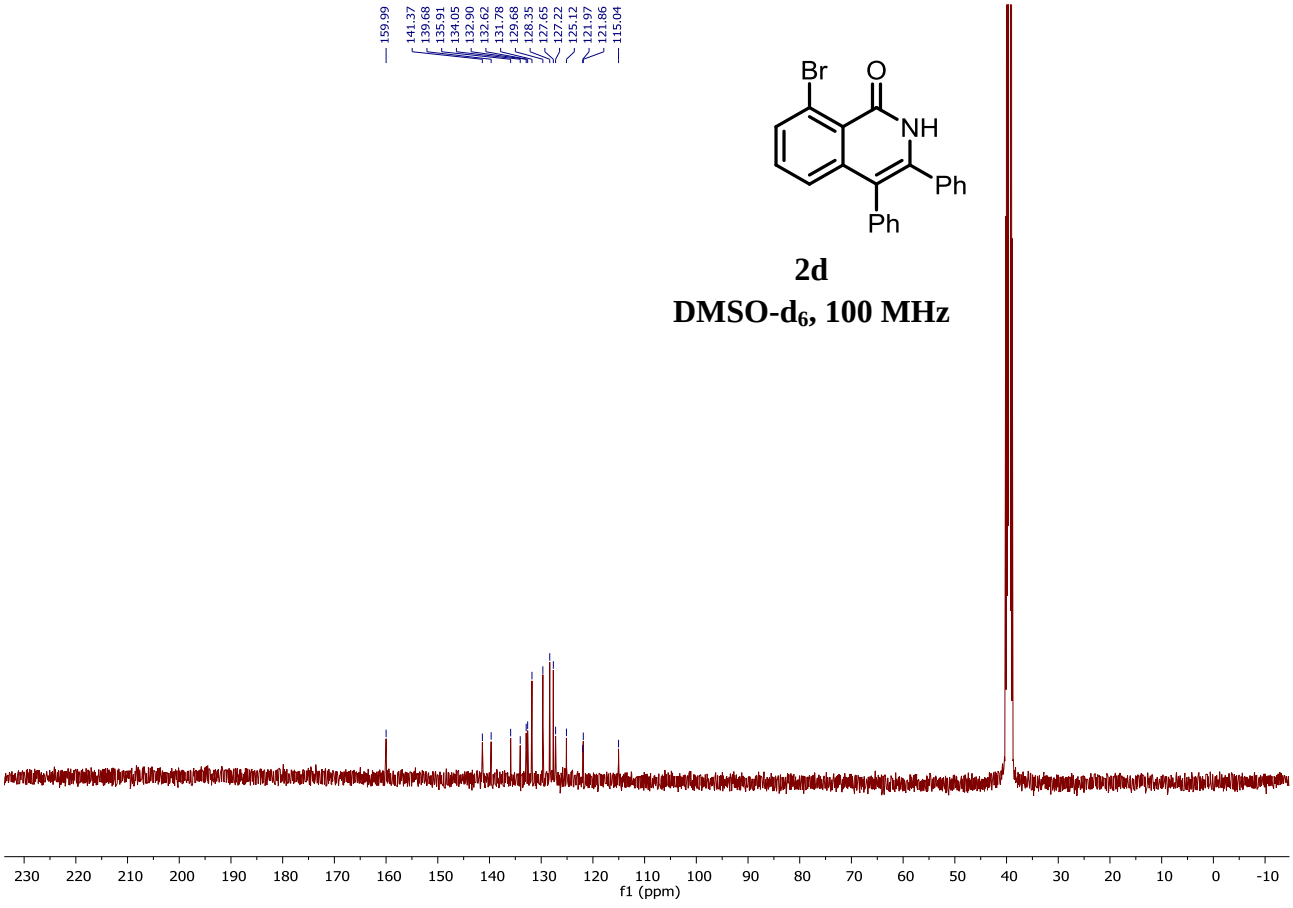


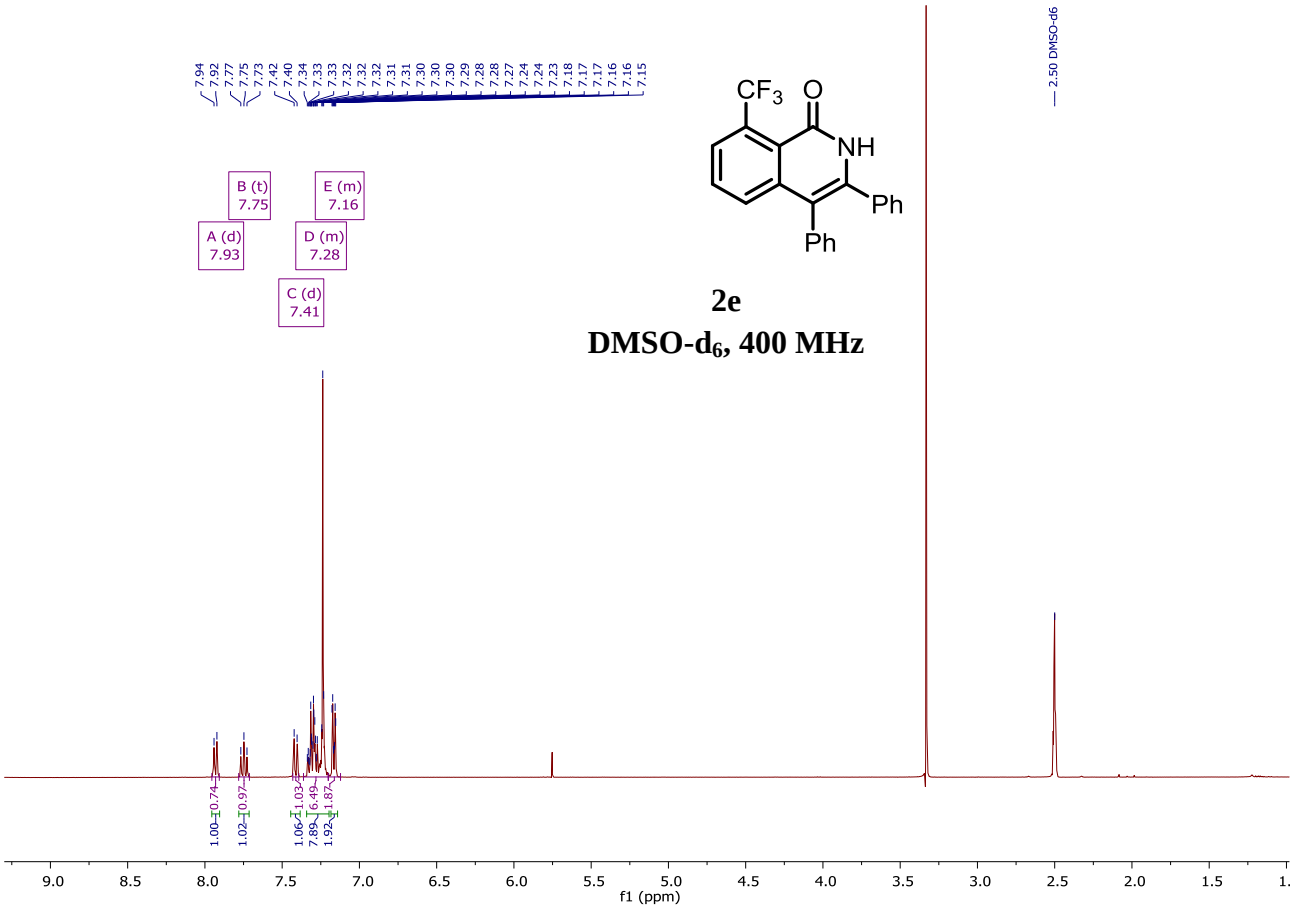
2b

DMSO-d_6, 100 MHz


11.26
7.46
7.44
7.44
7.41
7.32
7.32
7.31
7.31
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.23
7.22
7.21
7.19
7.14
7.13
7.13
7.12
7.11
7.11
6.95
6.92
2.89
2.50 DMSO-d6
Me
O
NH
Ph
Ph
2c
DMSO-d6, 400 MHz
A (s)
11.26
C (m)
7.26
B (m)
7.44
E (d)
6.94
D (m)
7.12
F (s)
2.89
1.00
1.00
1.09
1.35
9.17
9.01
1.98
1.96
1.07
0.62
2.94
2.86
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

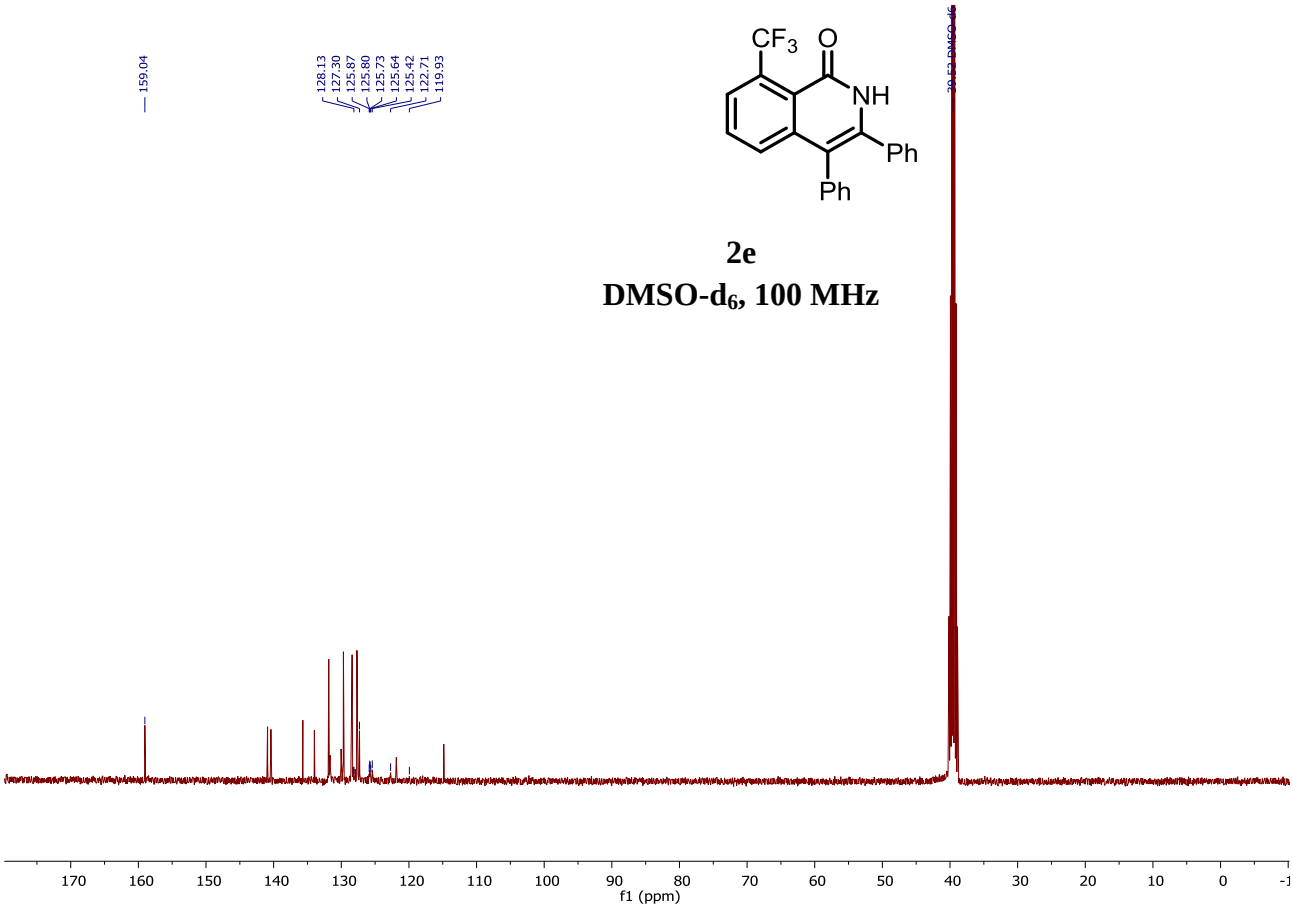

11.56
7.75
7.74
7.73
7.72
7.45
7.43
7.43
7.41
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.27
7.27
7.26
7.26
7.22
7.15
7.15
7.14
7.14
7.13
7.13
7.10
7.10
7.08
7.08
2.50 DMSO-d6
A (s)
11.56
B (dd)
7.74
C (t)
7.43
D (m)
7.27
E (m)
7.14
F (dd)
7.09
Br
O
NH
Ph
Ph
2d
DMSO-d6, 400 MHz
f1 (ppm)


159.99
141.37
139.68
135.91
134.05
132.90
132.62
131.78
129.68
128.35
127.65
127.22
125.12
121.97
121.86
115.04
Br
O
NH
Ph
Ph
2d
DMSO-d6, 100 MHz
f1 (ppm)



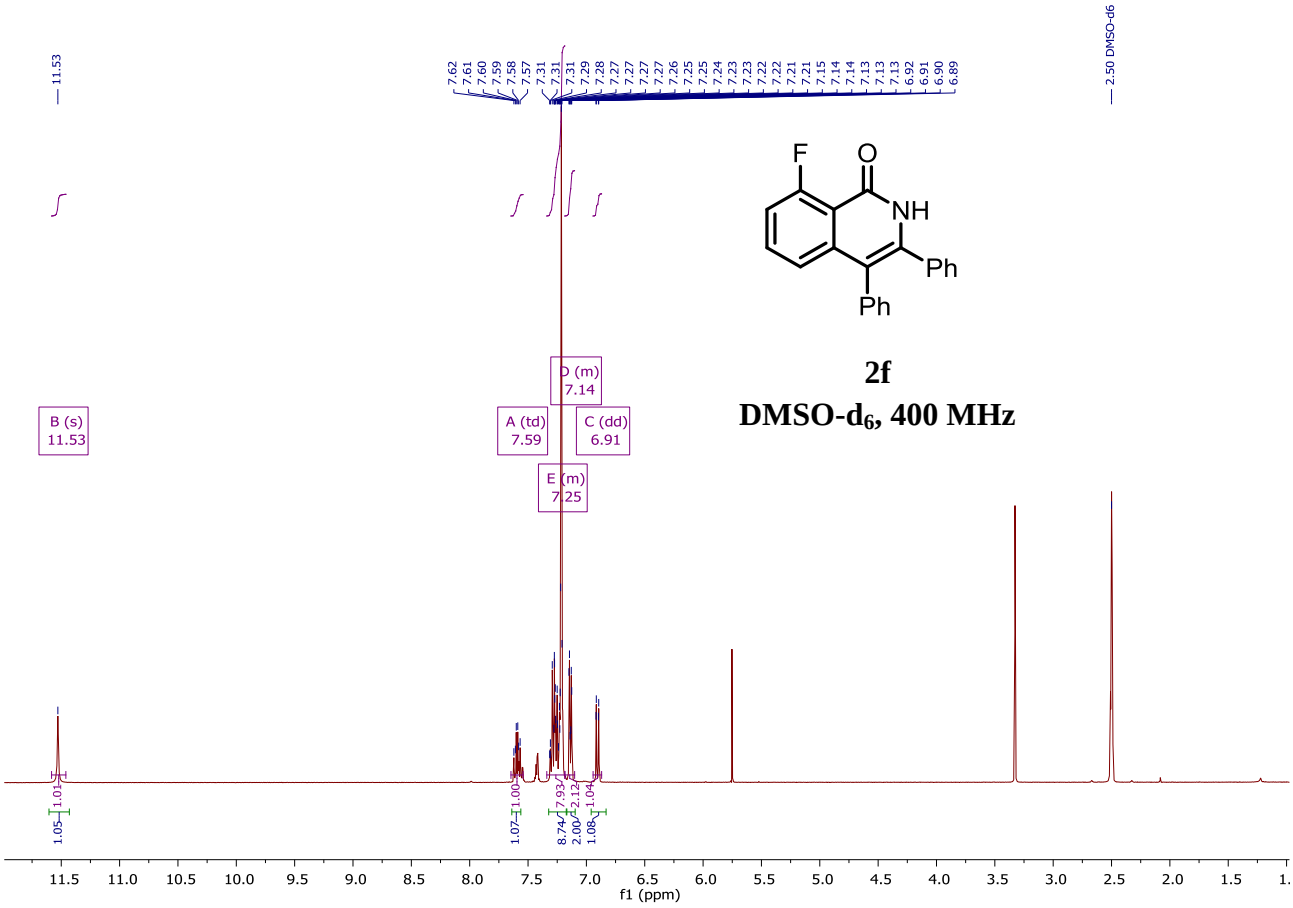
2e

DMSO-d_6, 400 MHz



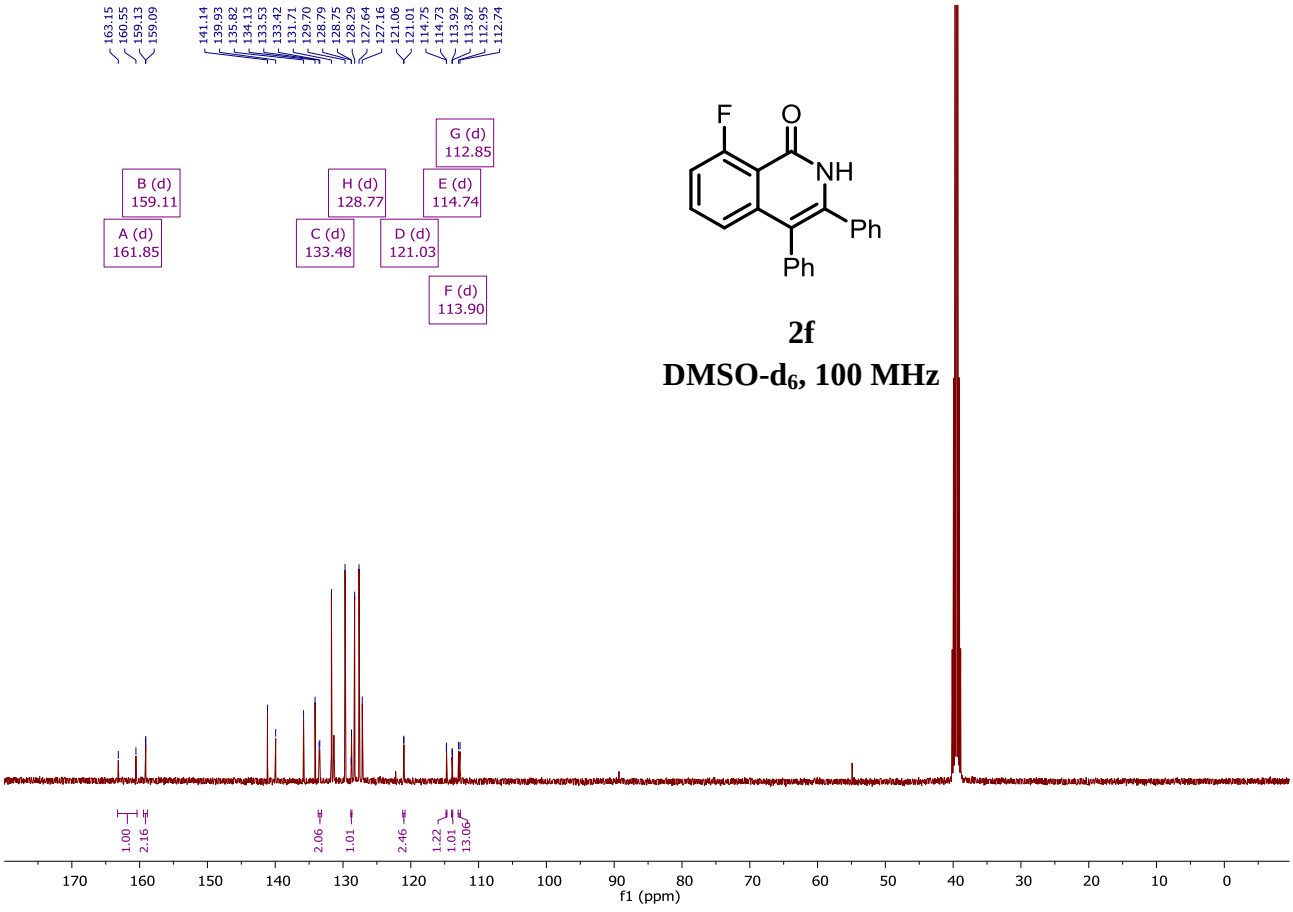
2e

DMSO-d_6, 100 MHz



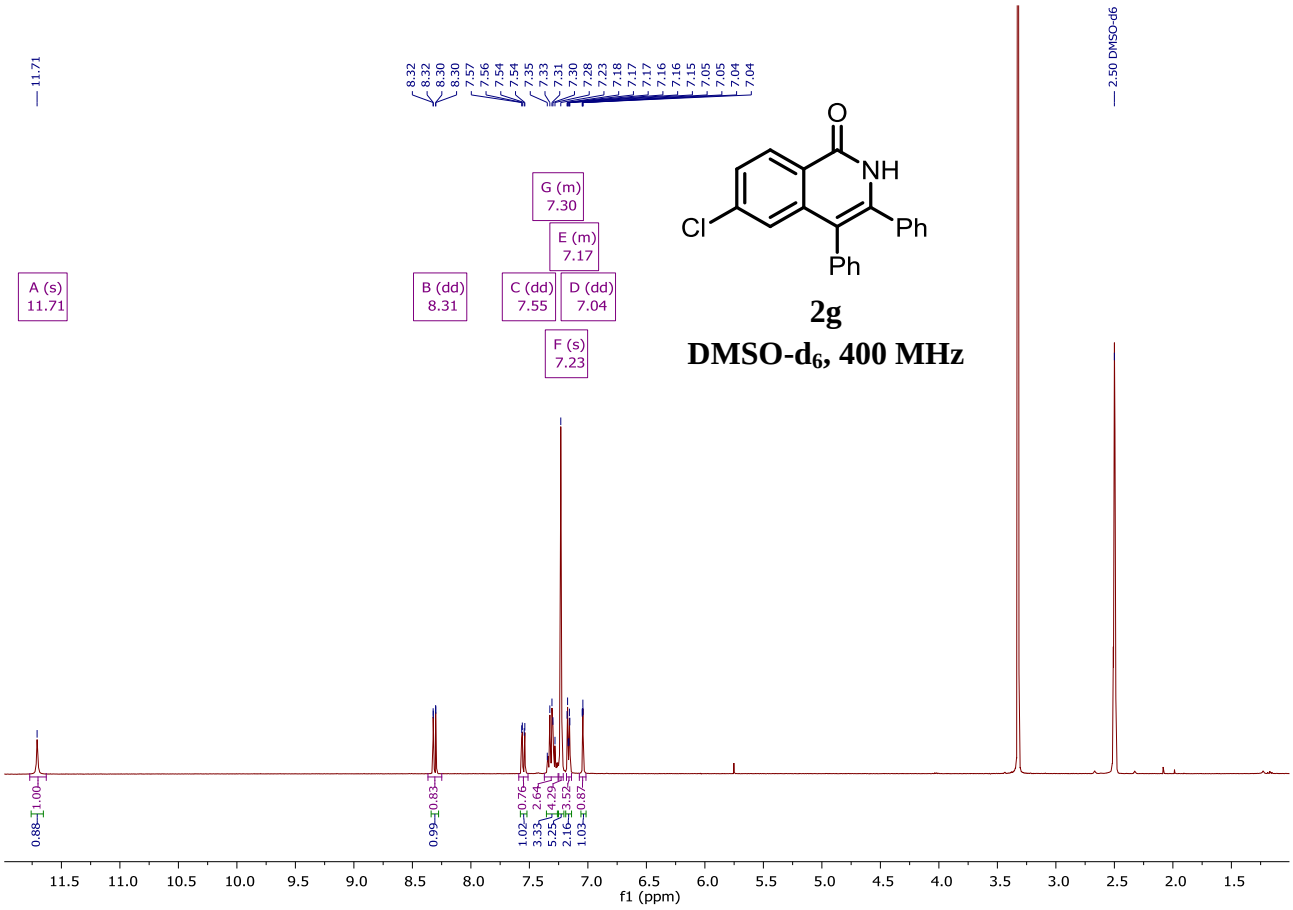
2f

DMSO-d_6, 400 MHz



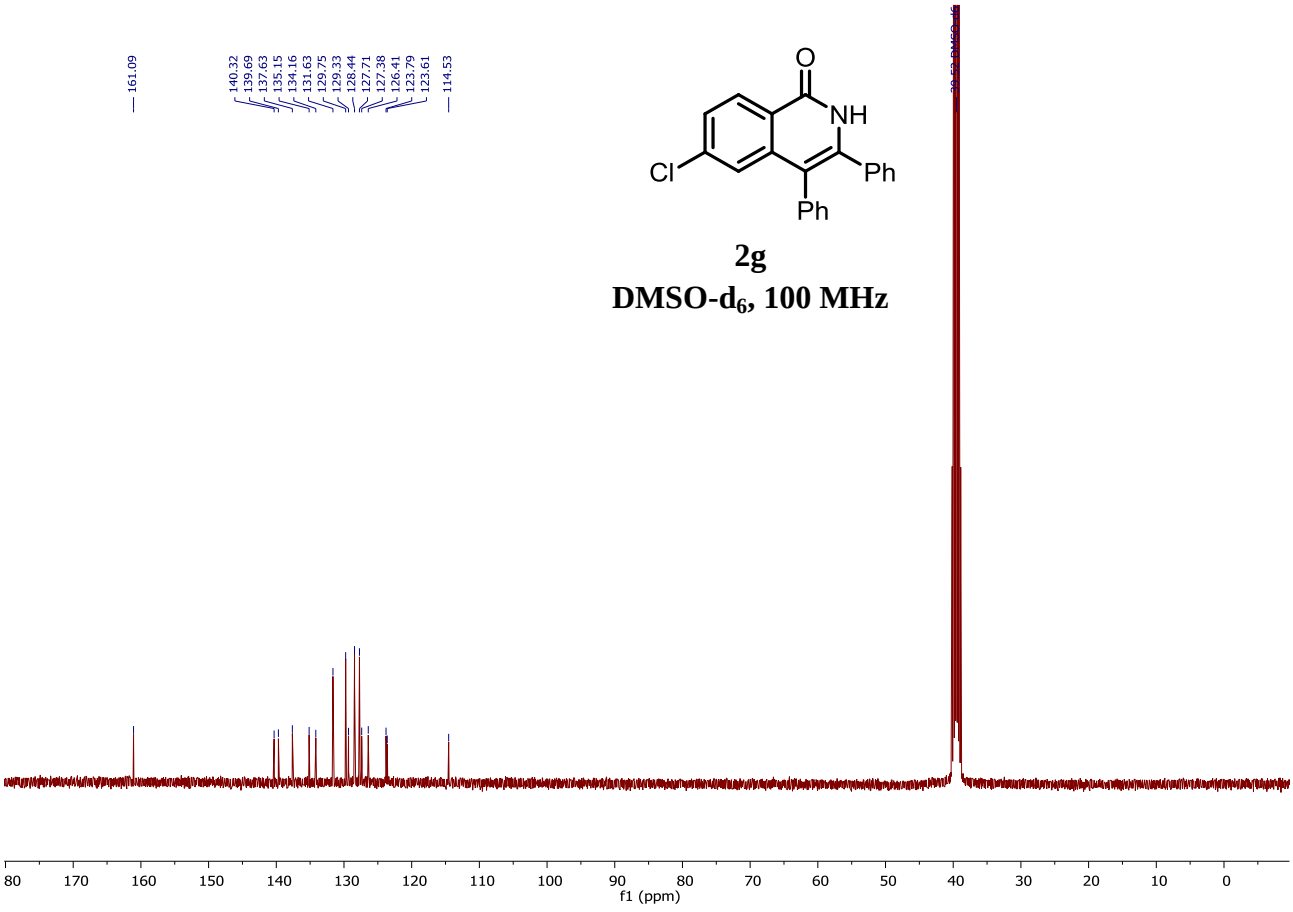
2f

DMSO-d_6, 100 MHz



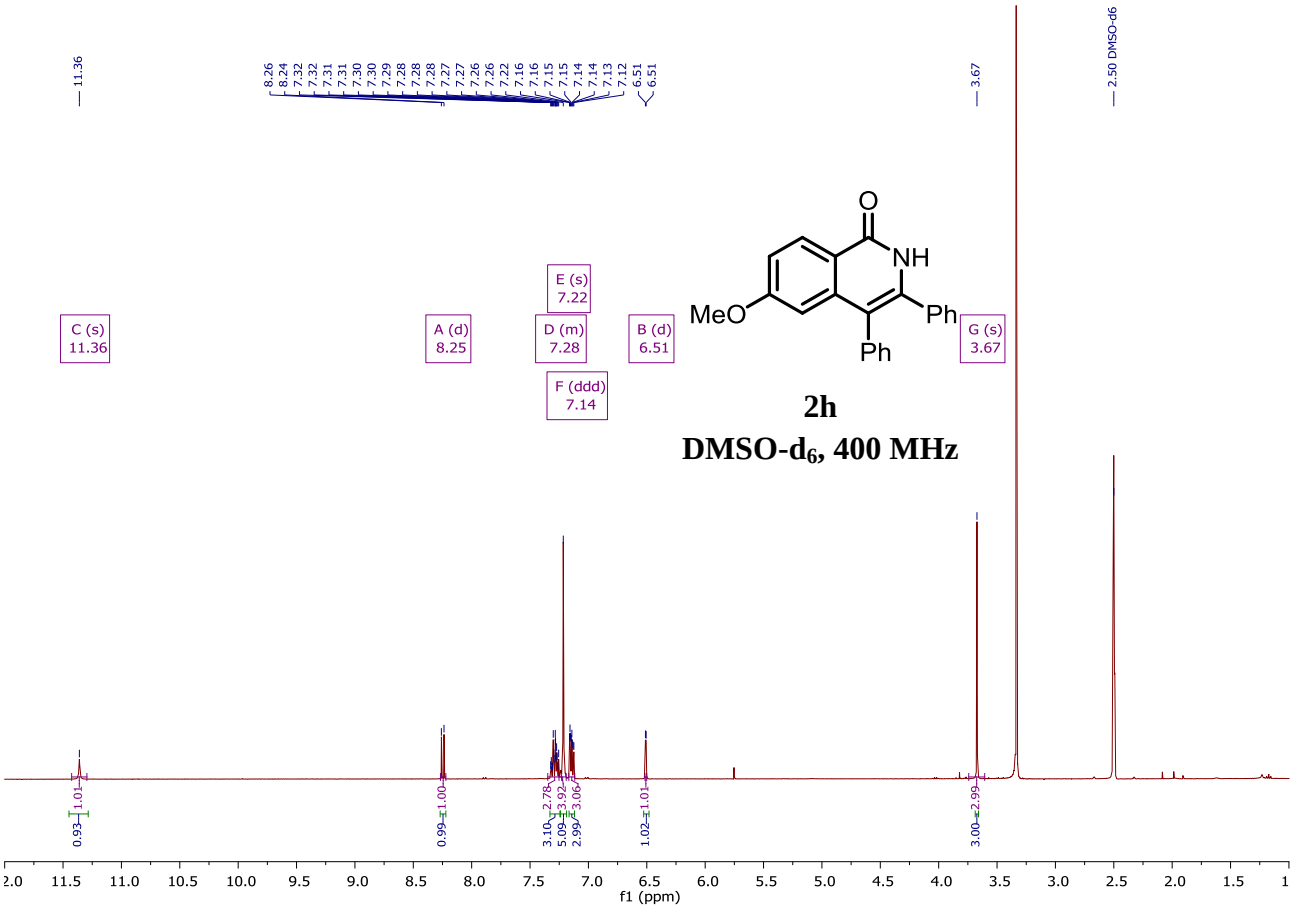
2g

DMSO-d_6, 400 MHz



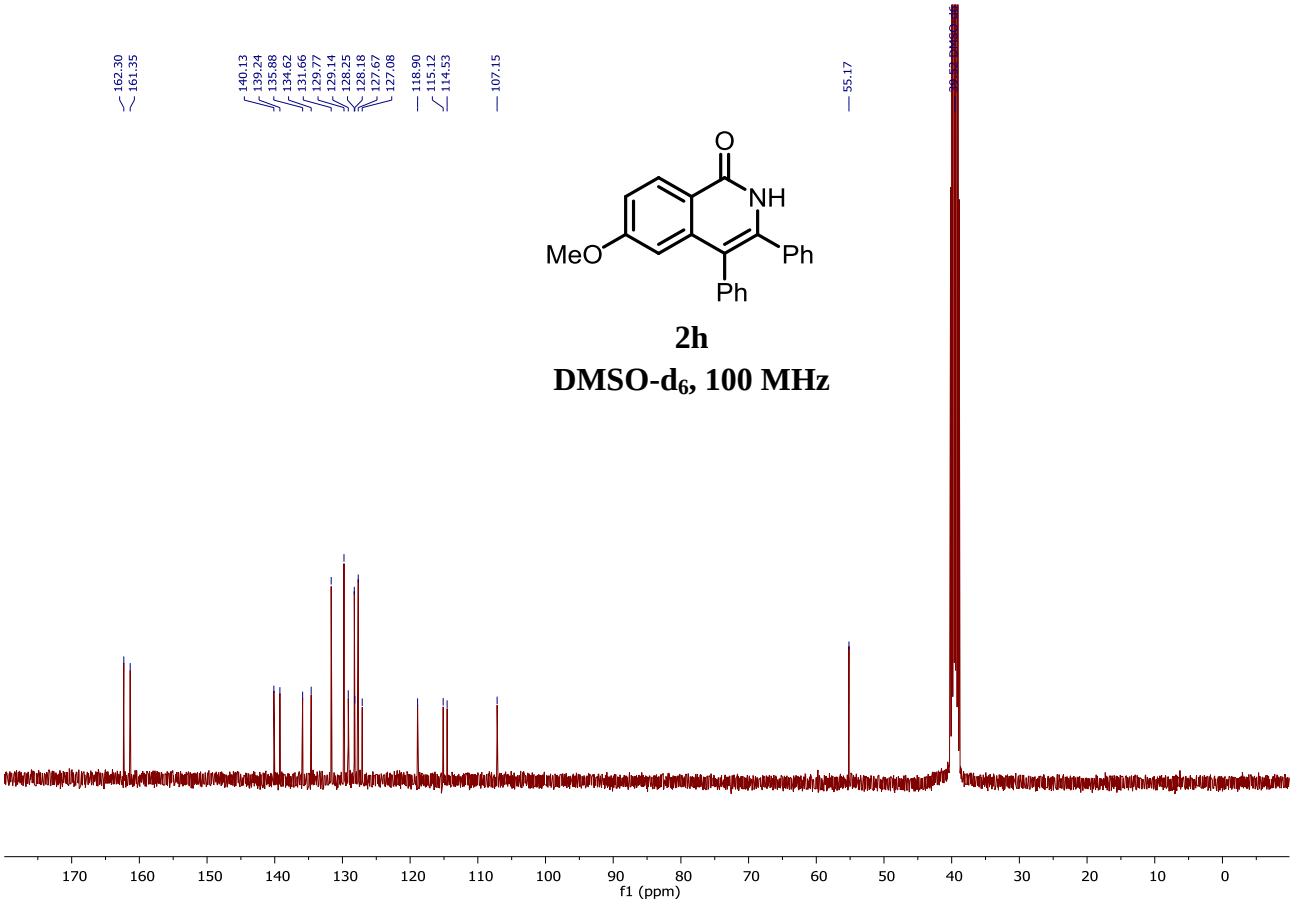
2g

DMSO-d_6, 100 MHz



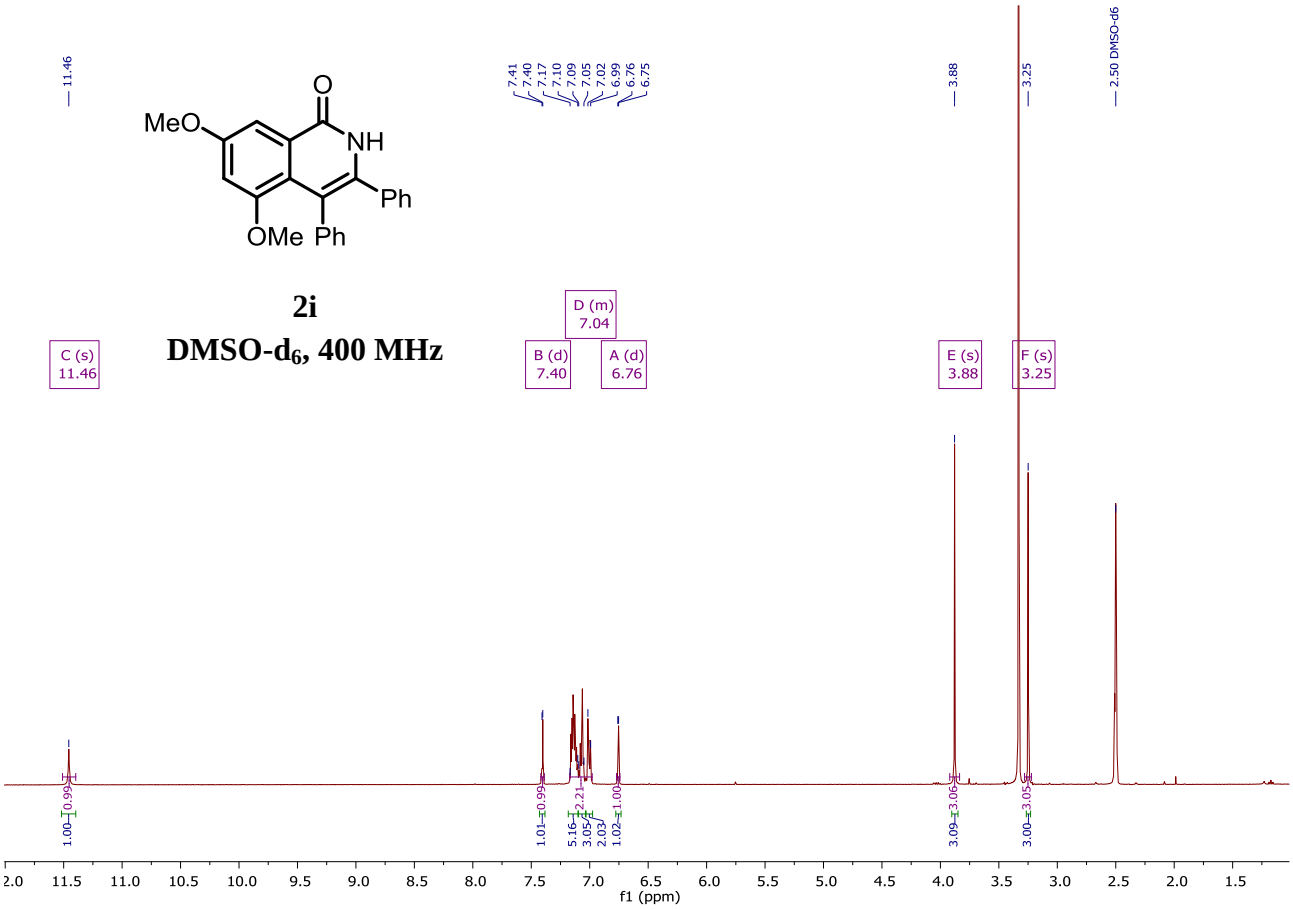
2h

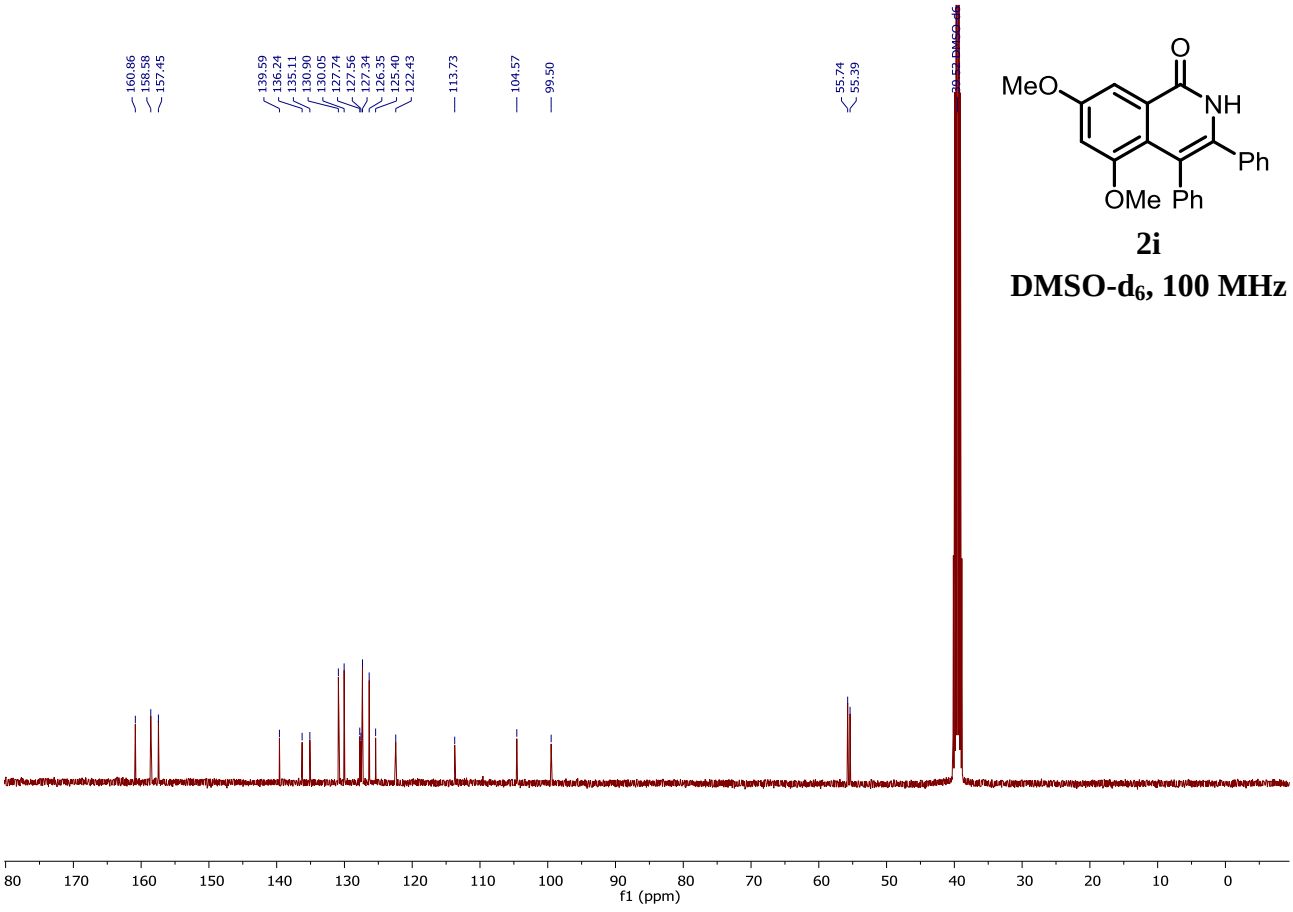
DMSO-d_6, 400 MHz

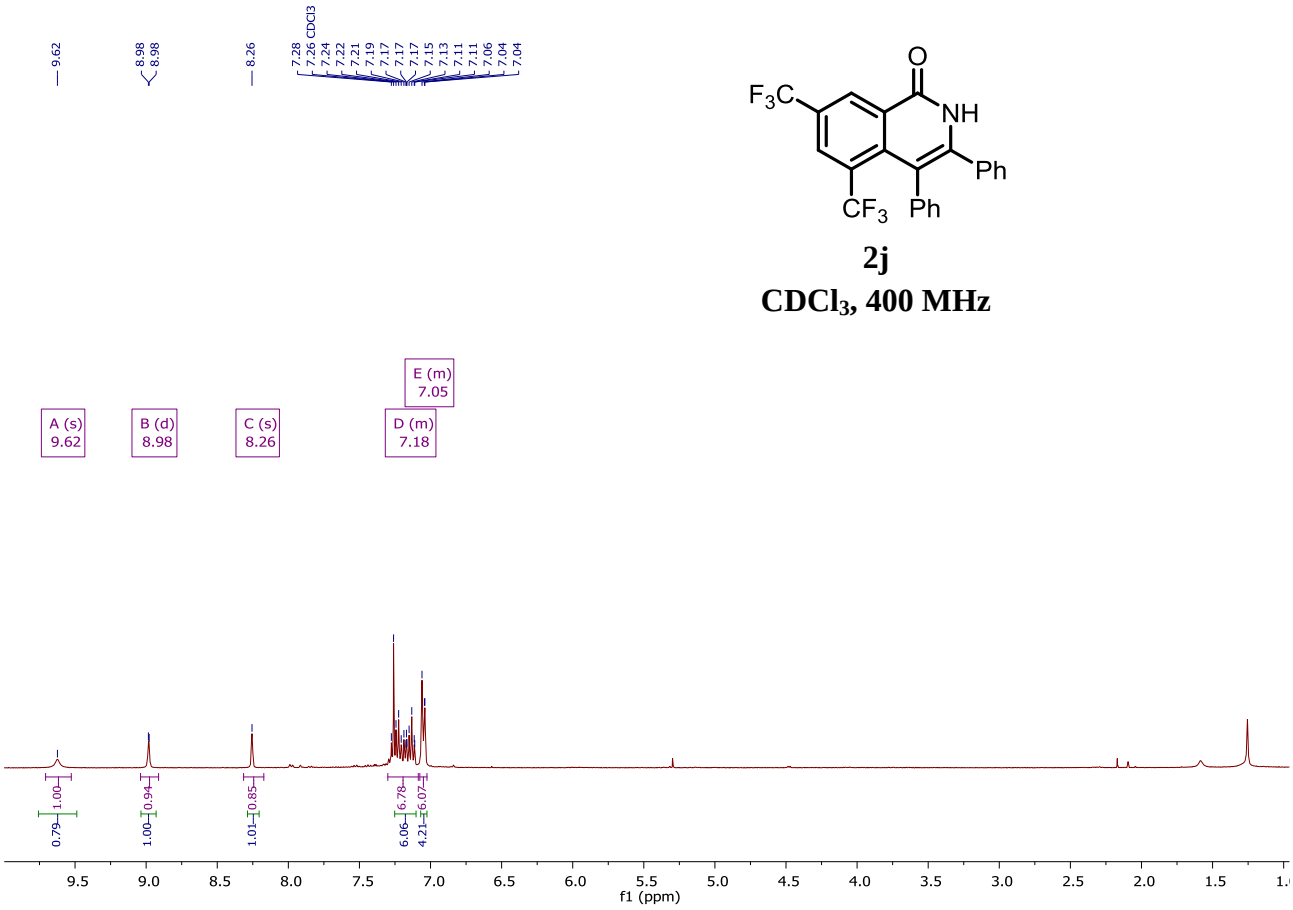


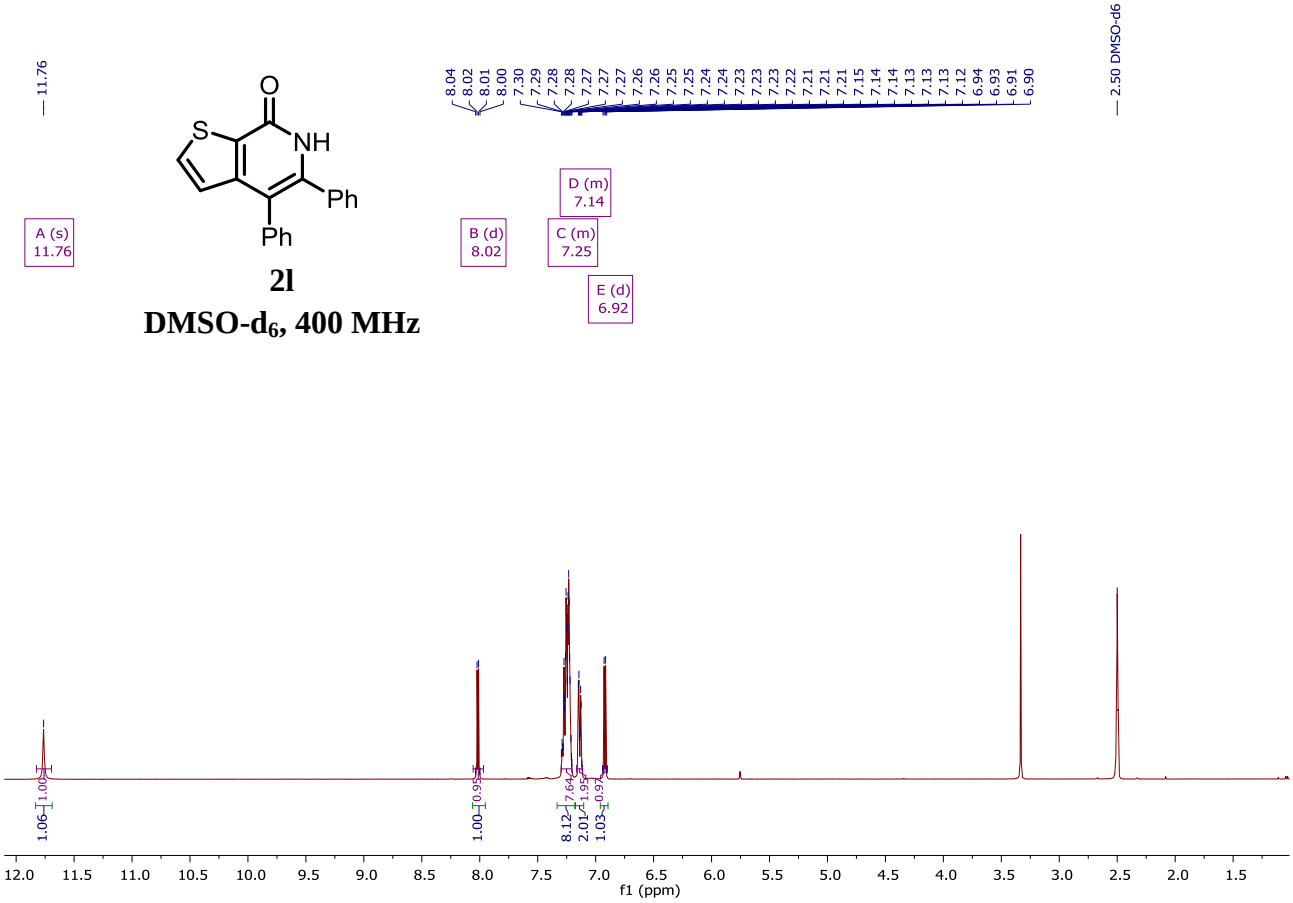
2h

DMSO-d_6, 100 MHz


11.46
7.41
7.40
7.17
7.10
7.09
7.05
7.02
6.99
6.76
6.75
3.88
3.25
2.50 DMSO-d6
MeO
O
NH
Ph
OMe Ph
2i
DMSO-d6, 400 MHz
D (m) 7.04
C (s) 11.46
B (d) 7.40
A (d) 6.76
E (s) 3.88
F (s) 3.25
1.00
0.99
1.01
0.99
5.16
2.21
3.05
2.03
1.02
1.00
3.09
3.06
3.00
3.05
f1 (ppm)

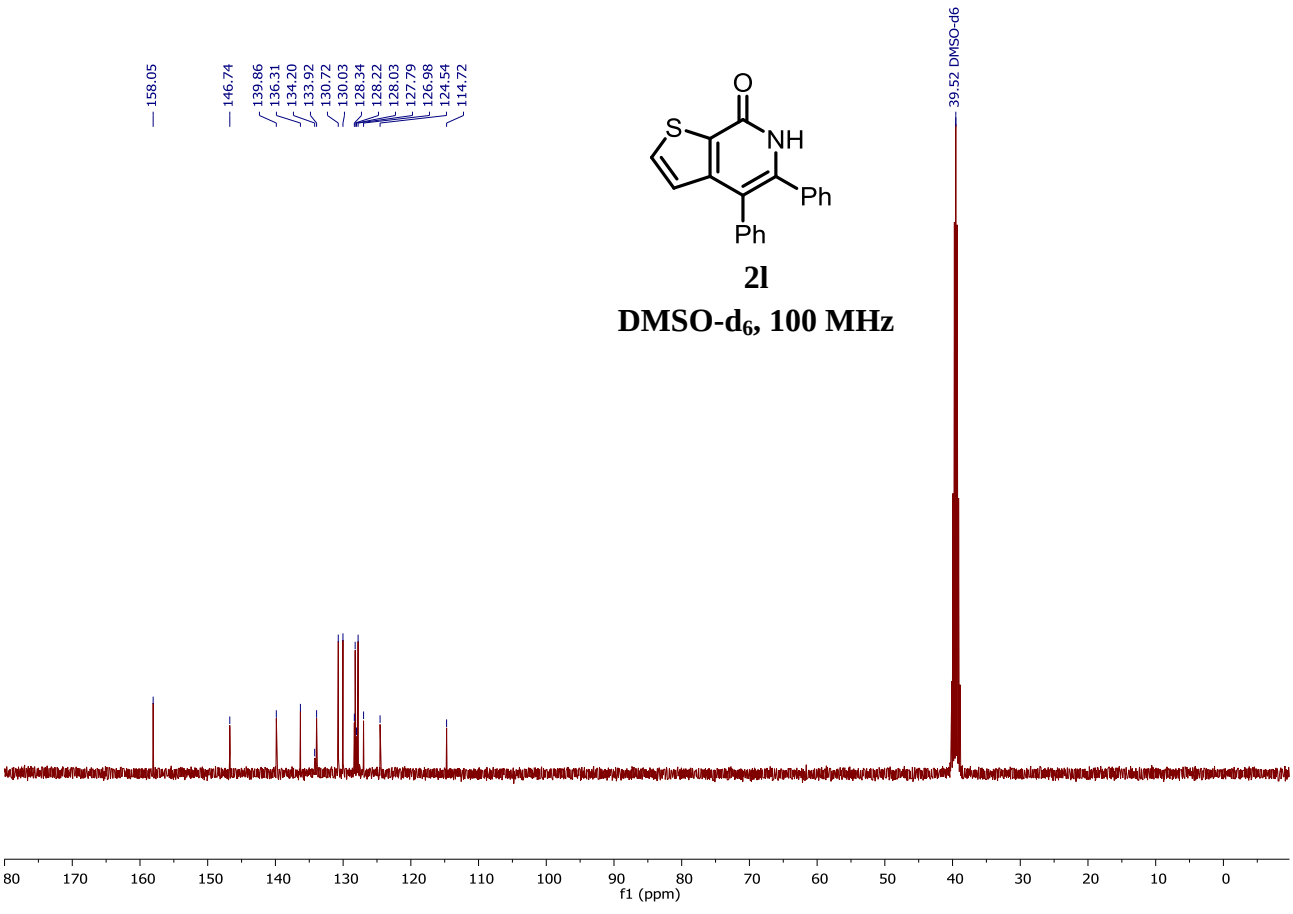

160.86
158.58
157.45
139.59
136.24
135.11
130.90
130.05
127.74
127.56
127.34
126.35
125.40
122.43
113.73
104.57
99.50
55.74
55.39
39.52 DMSO-d6
MeO
O
NH
Ph
OMe Ph
2i
DMSO-d6, 100 MHz
f1 (ppm)


9.62
8.98
8.98
8.26
7.28
7.26 CDCl3
7.24
7.22
7.21
7.19
7.17
7.17
7.17
7.15
7.13
7.11
7.11
7.06
7.04
7.04
F3C
O
NH
Ph
CF3
Ph
2j
CDCl3, 400 MHz
A (s)
9.62
B (d)
8.98
C (s)
8.26
D (m)
7.18
E (m)
7.05
0.79
1.00
1.00
0.94
1.01
0.85
6.06
6.78
4.21
6.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)



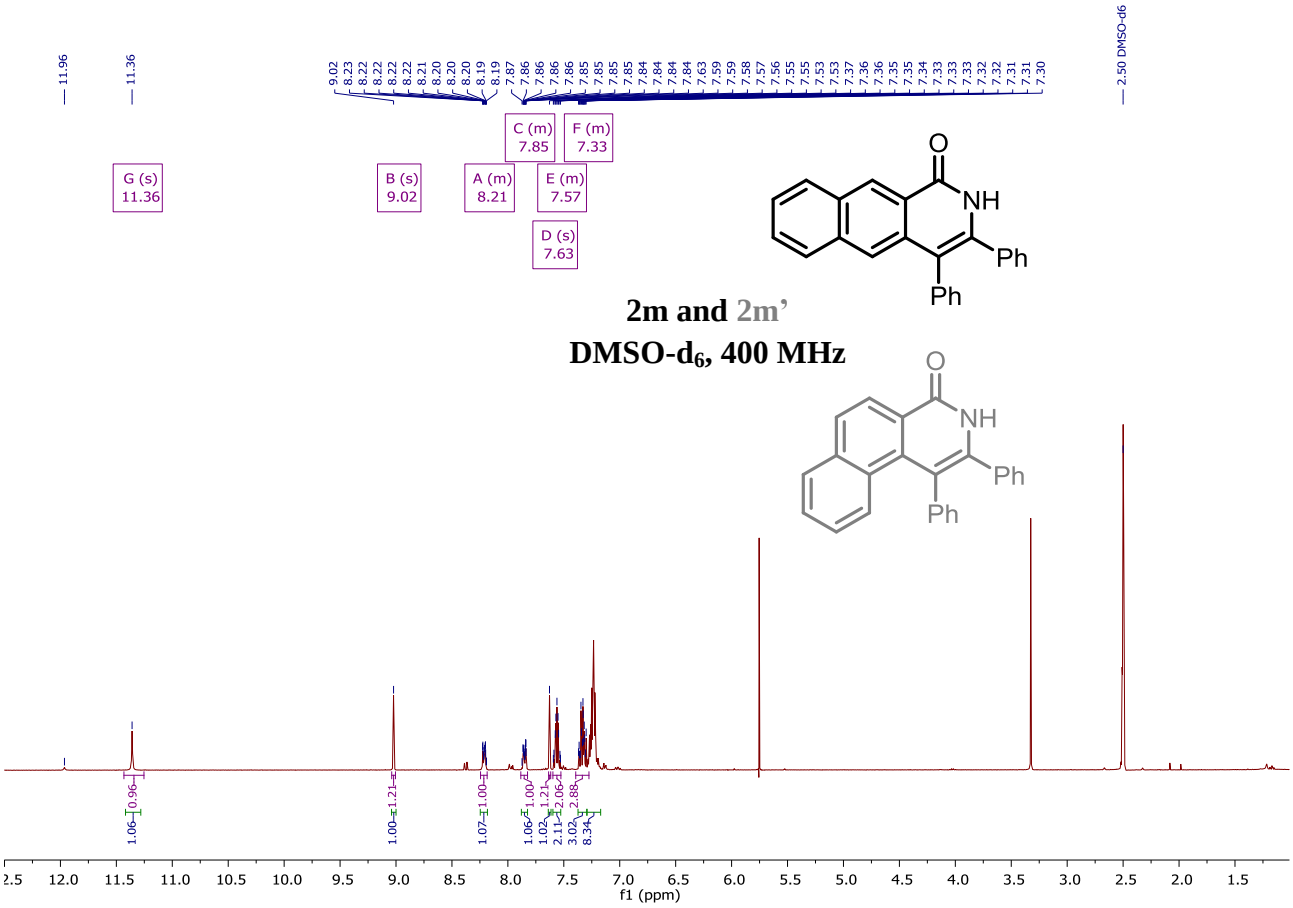
2l

DMSO-d_6, 400 MHz



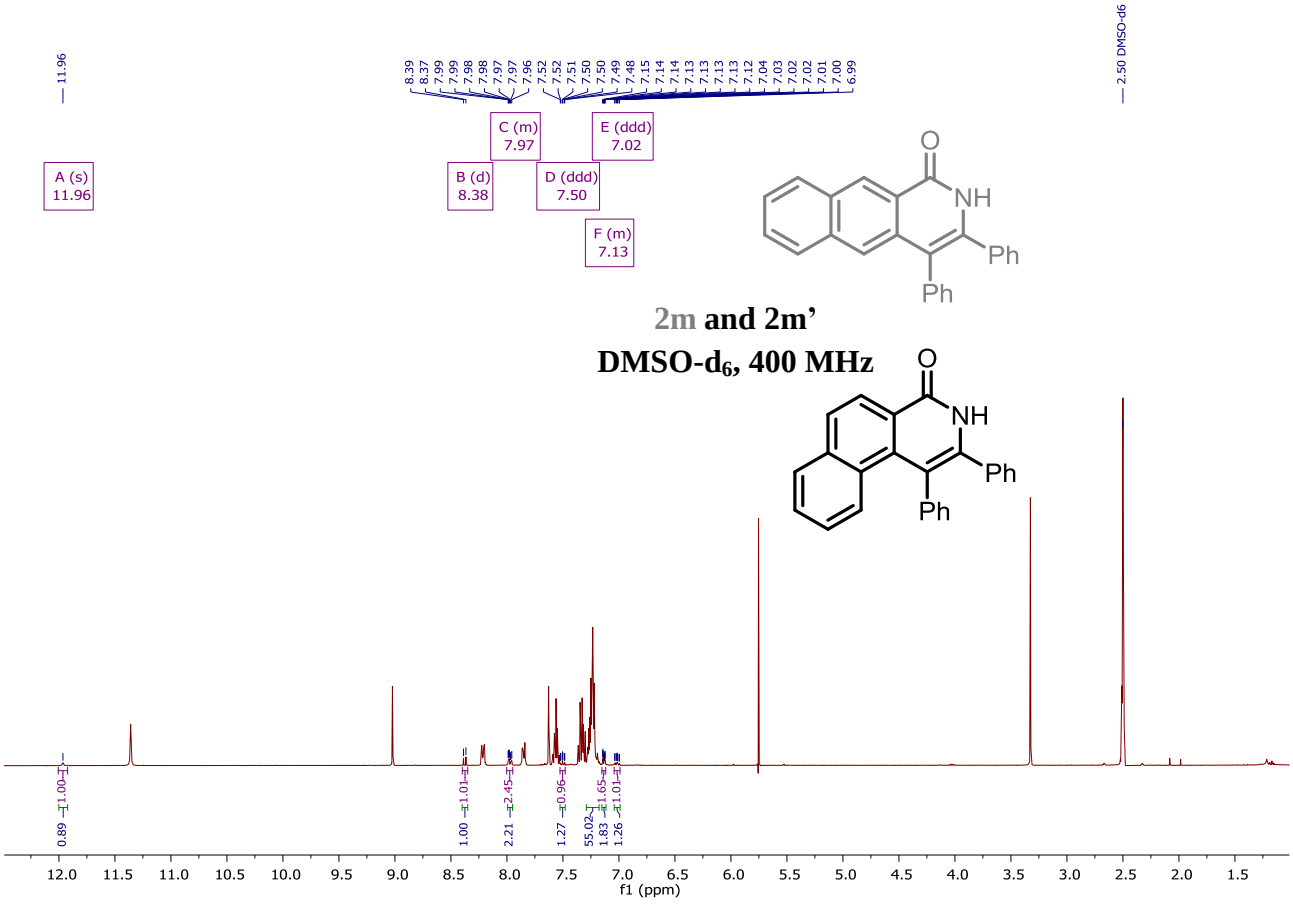
2l

DMSO-d_6, 100 MHz



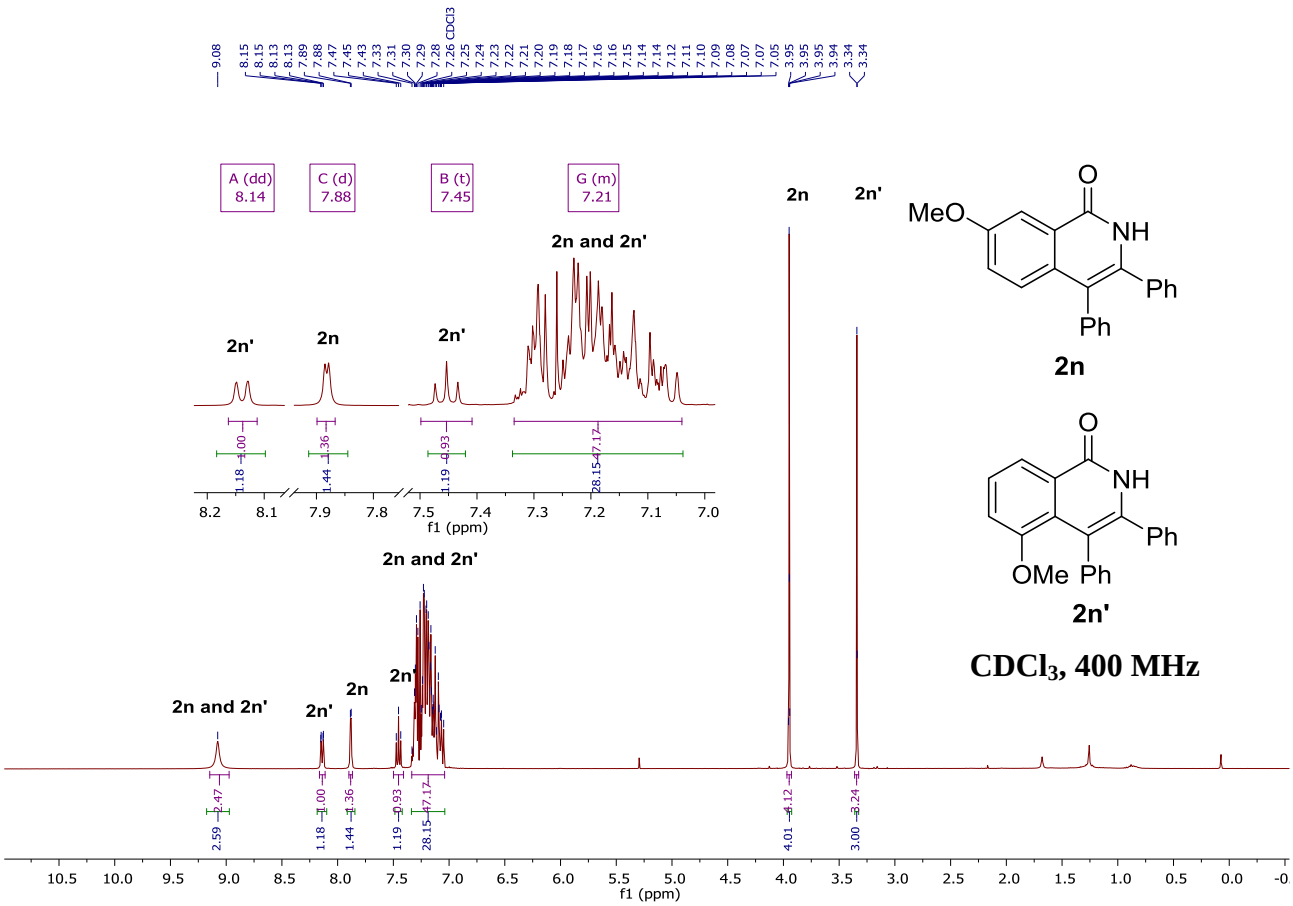
2m and 2m'

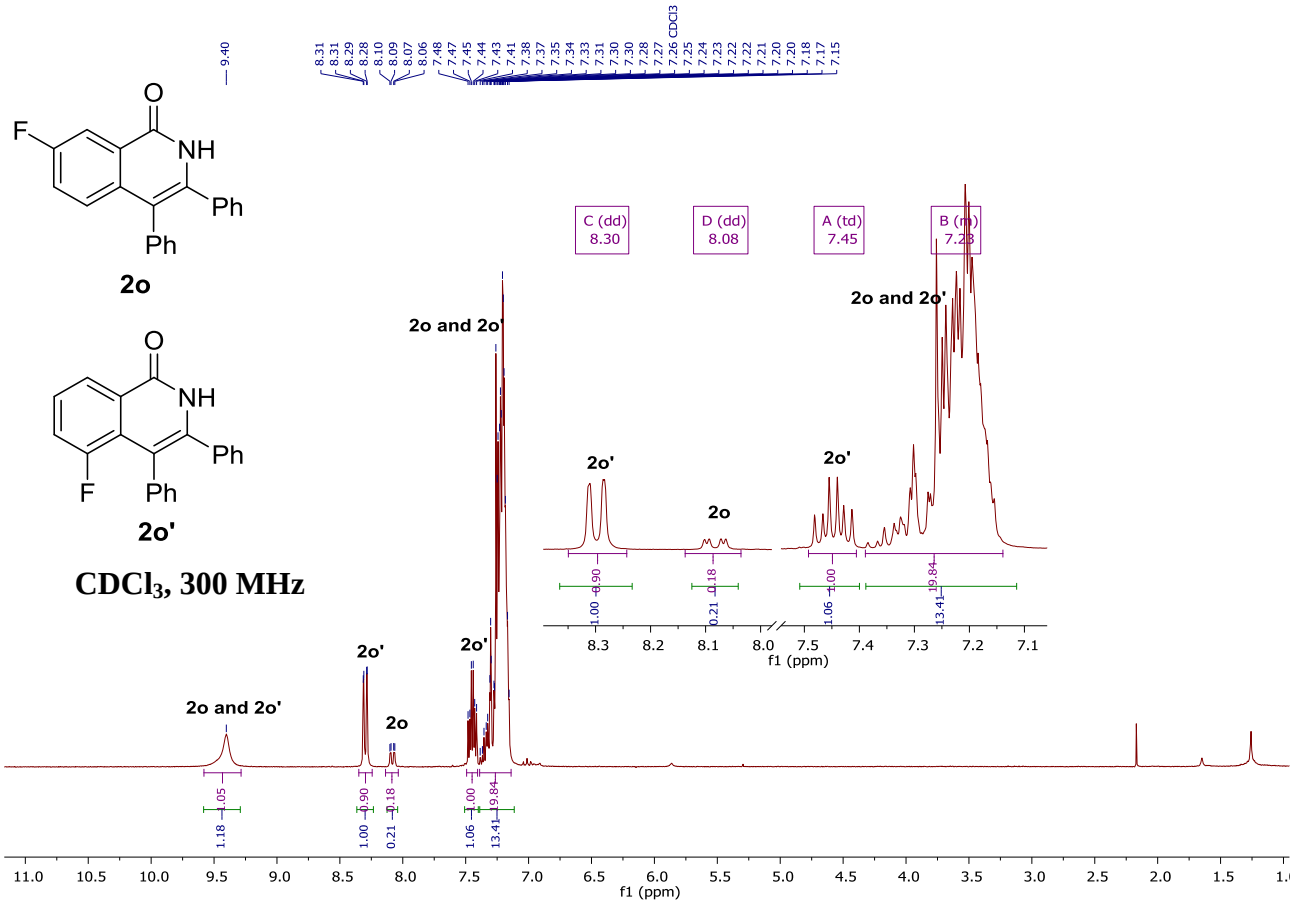
DMSO-d_6, 400 MHz

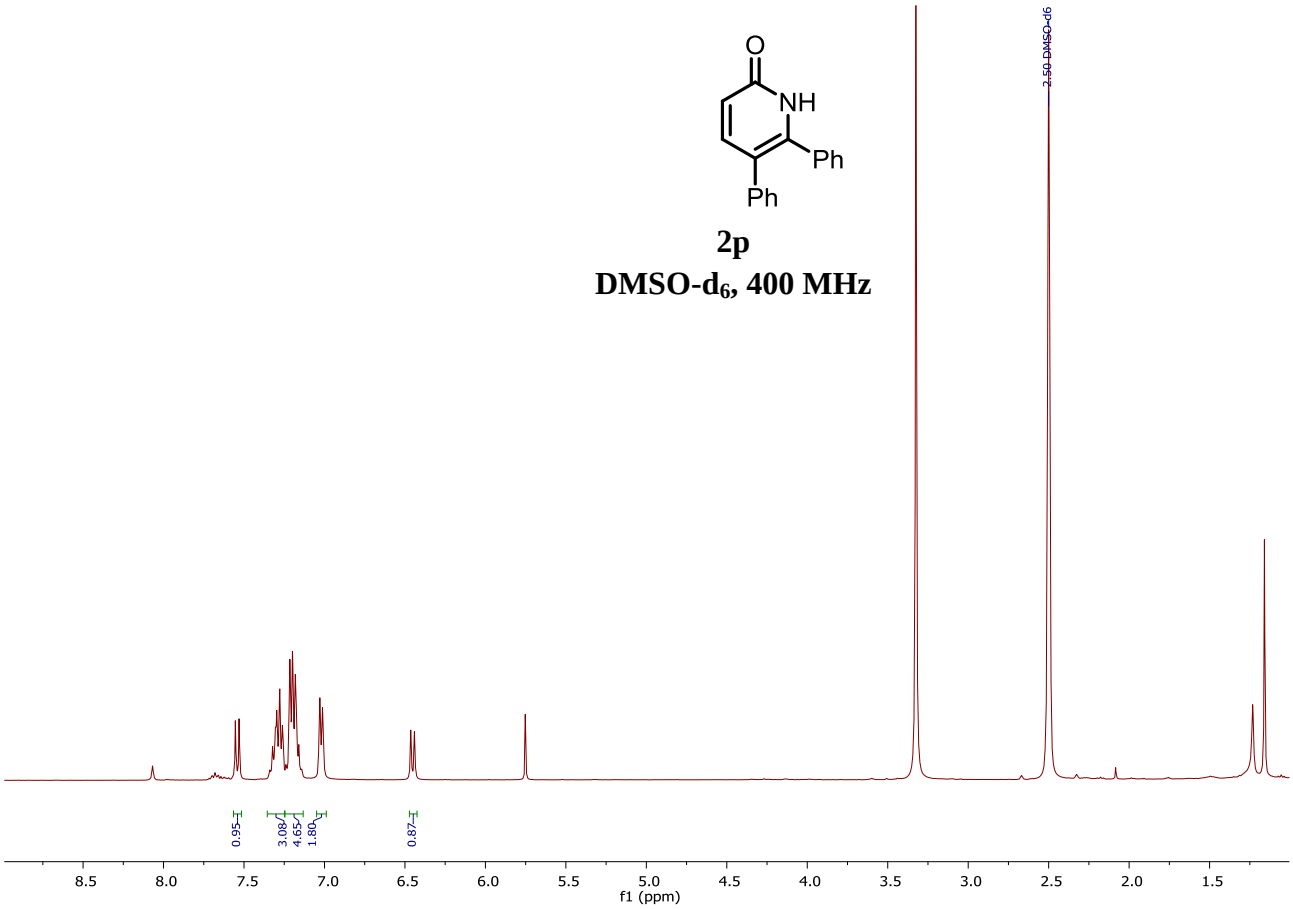


2m and 2m'

DMSO-d_6, 400 MHz

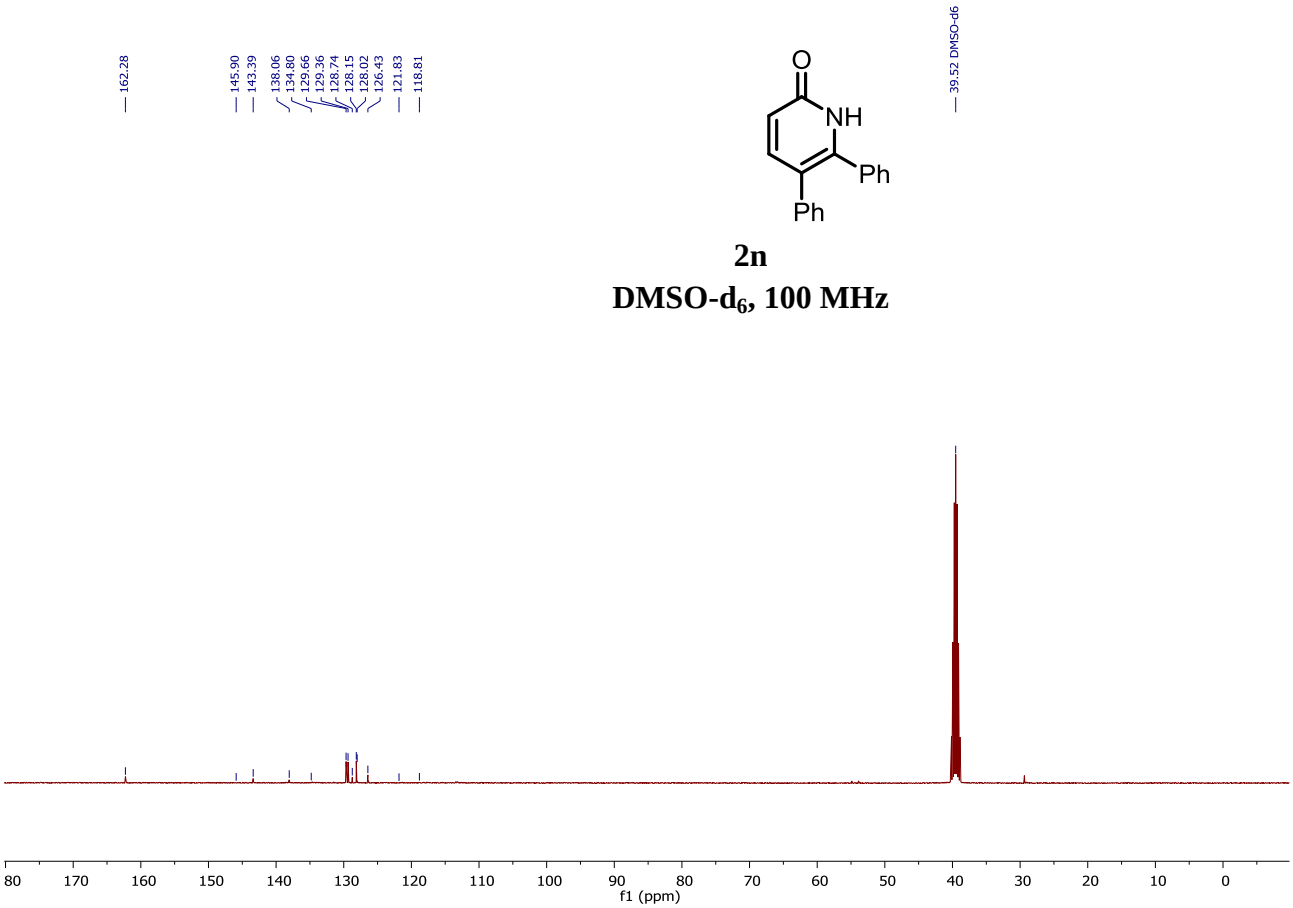

A (dd)
8.14
C (d)
7.88
B (t)
7.45
G (m)
7.21
2n and 2n'
2n'
2n
2n'
2n and 2n'
2n
2n'
2n and 2n'
2n'
2n
2n'
MeO
NH
Ph
Ph
2n
OMe
Ph
2n'
CDCl3, 400 MHz
f1 (ppm)


2o
2o'
CDCl3, 300 MHz
2o and 2o'
2o'
2o
2o'
2o and 2o'
C (dd) 8.30
D (dd) 8.08
A (td) 7.45
B (m) 7.23
f1 (ppm)



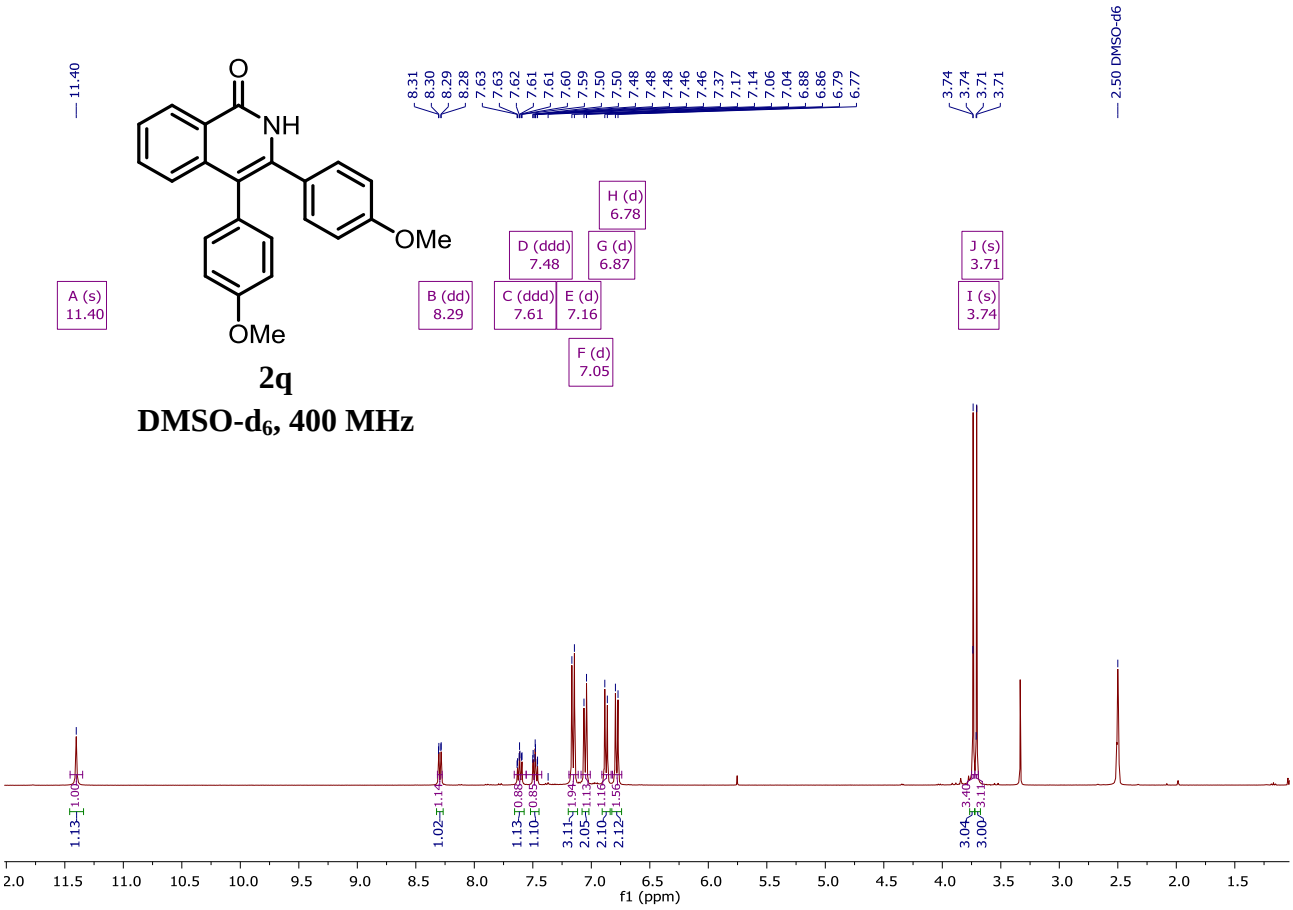
2p

DMSO-d_6, 400 MHz



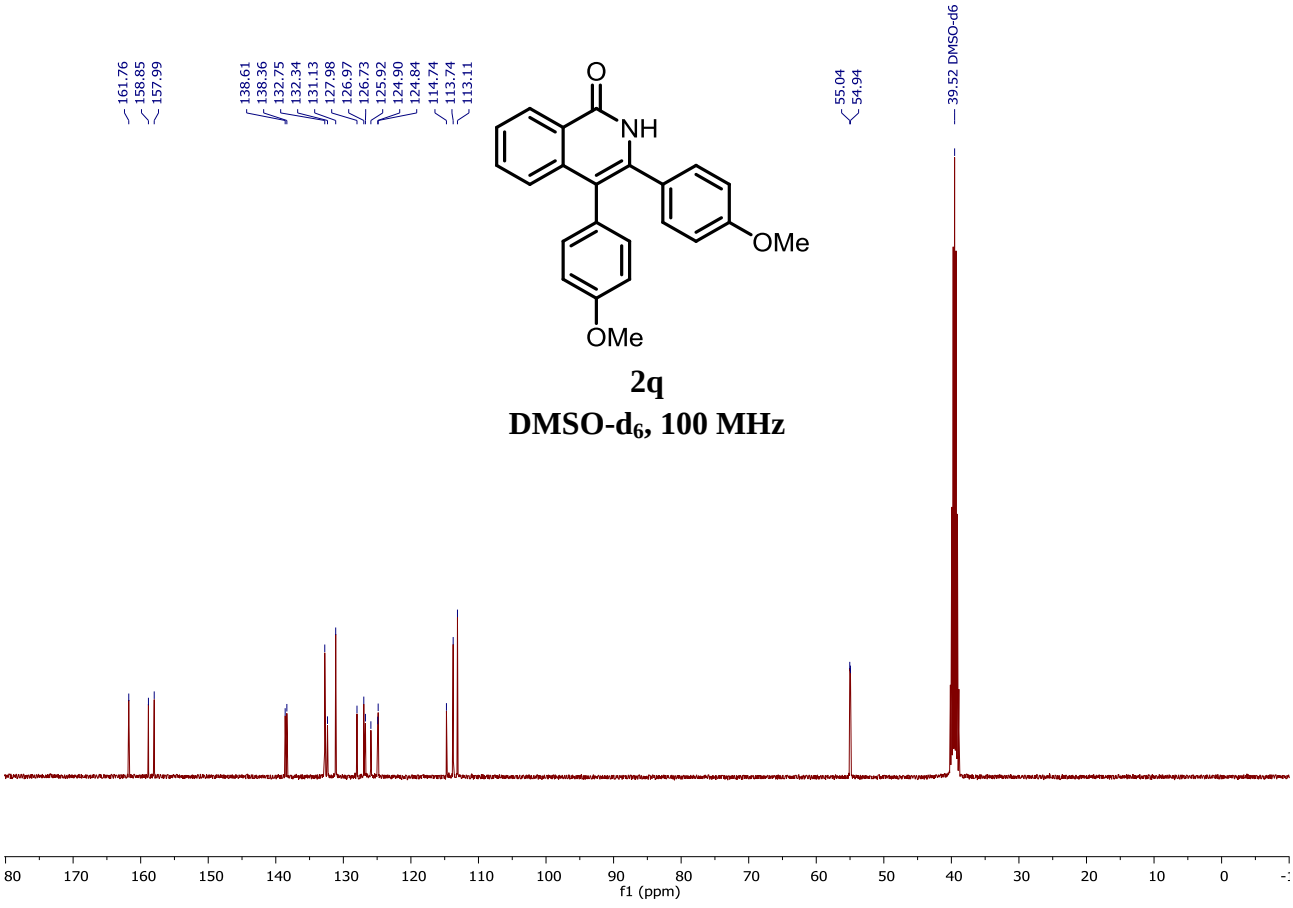
2n

DMSO-d_6, 100 MHz



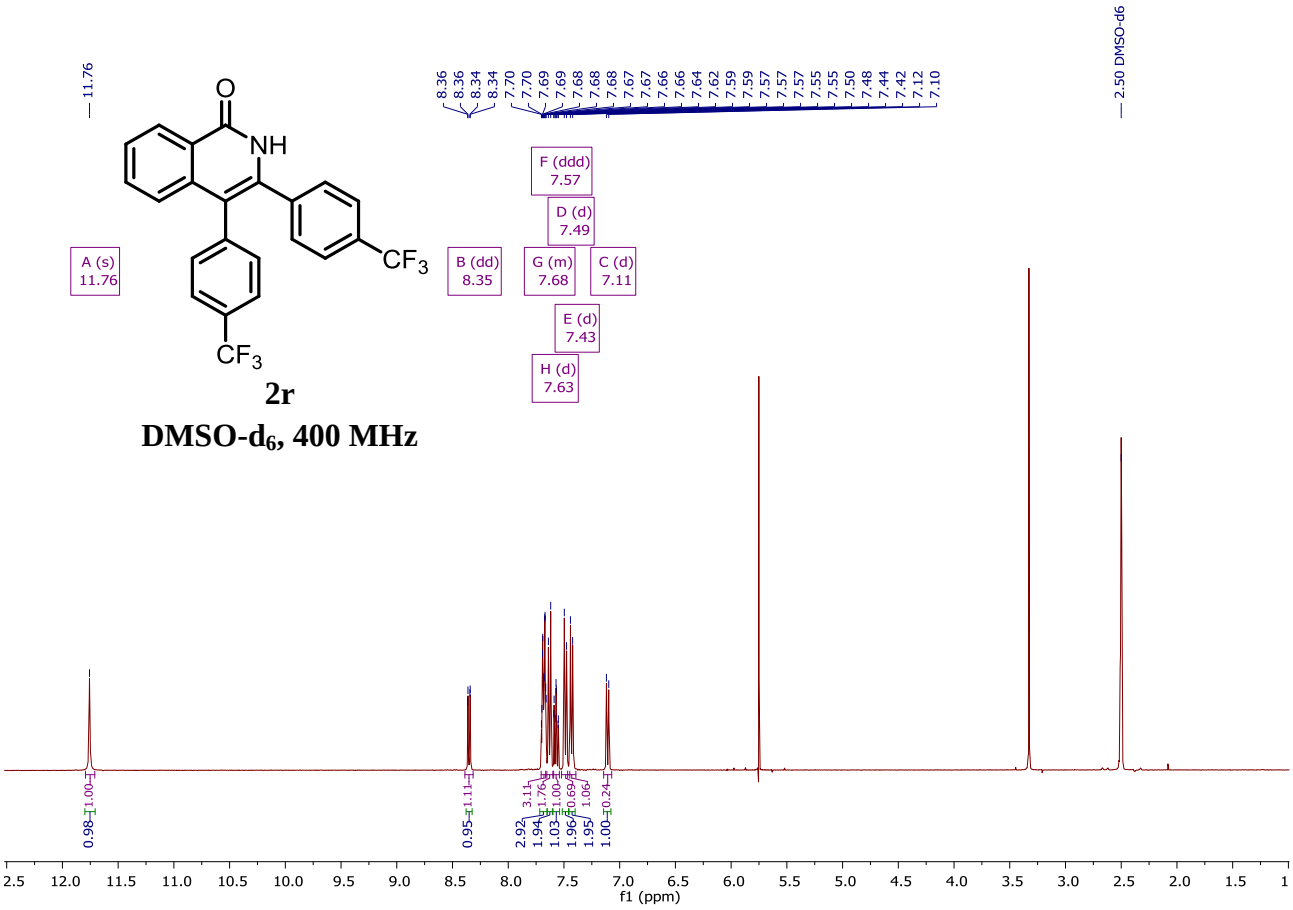
2q

DMSO-d_6, 400 MHz



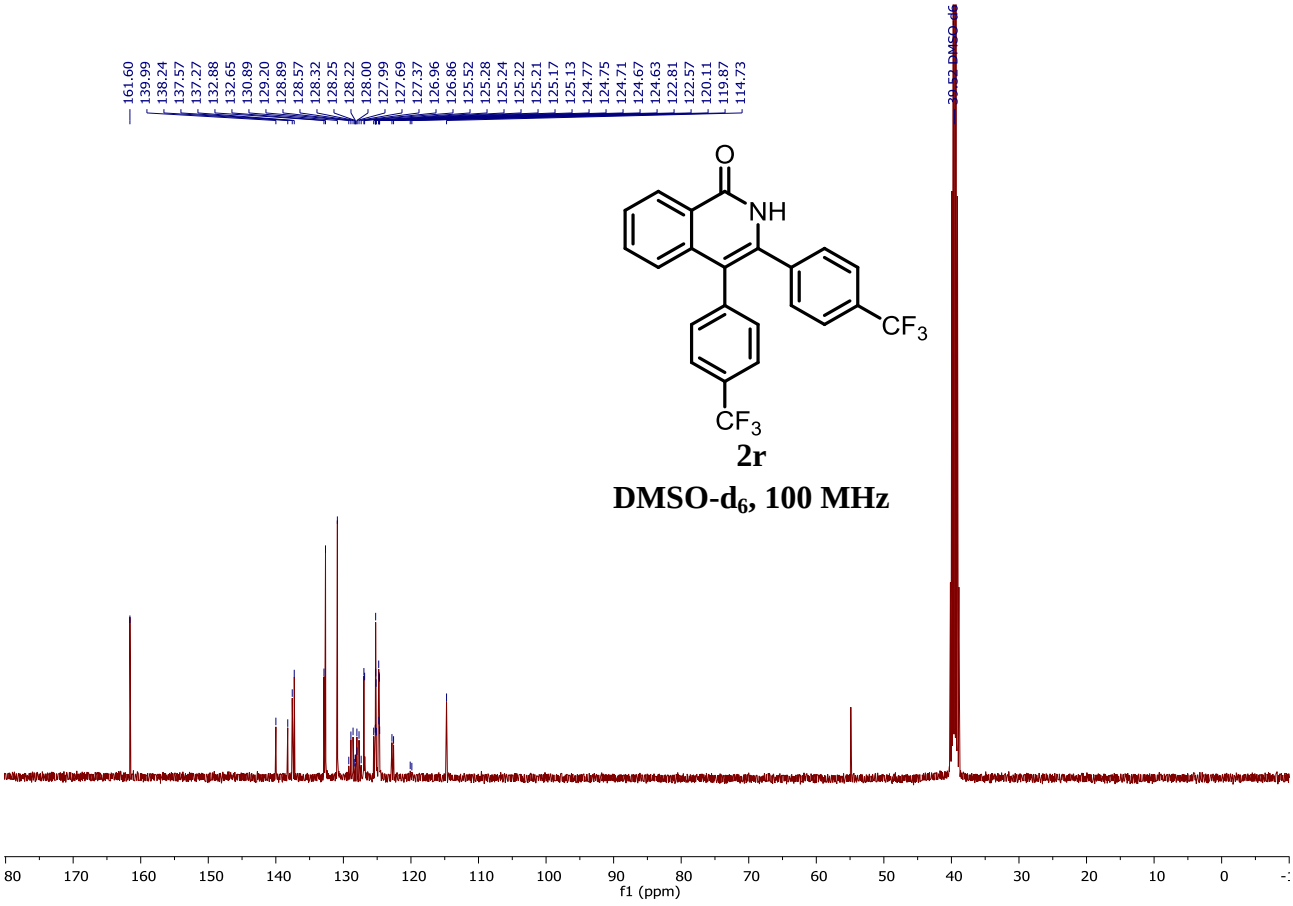
2q

DMSO-d_6, 100 MHz



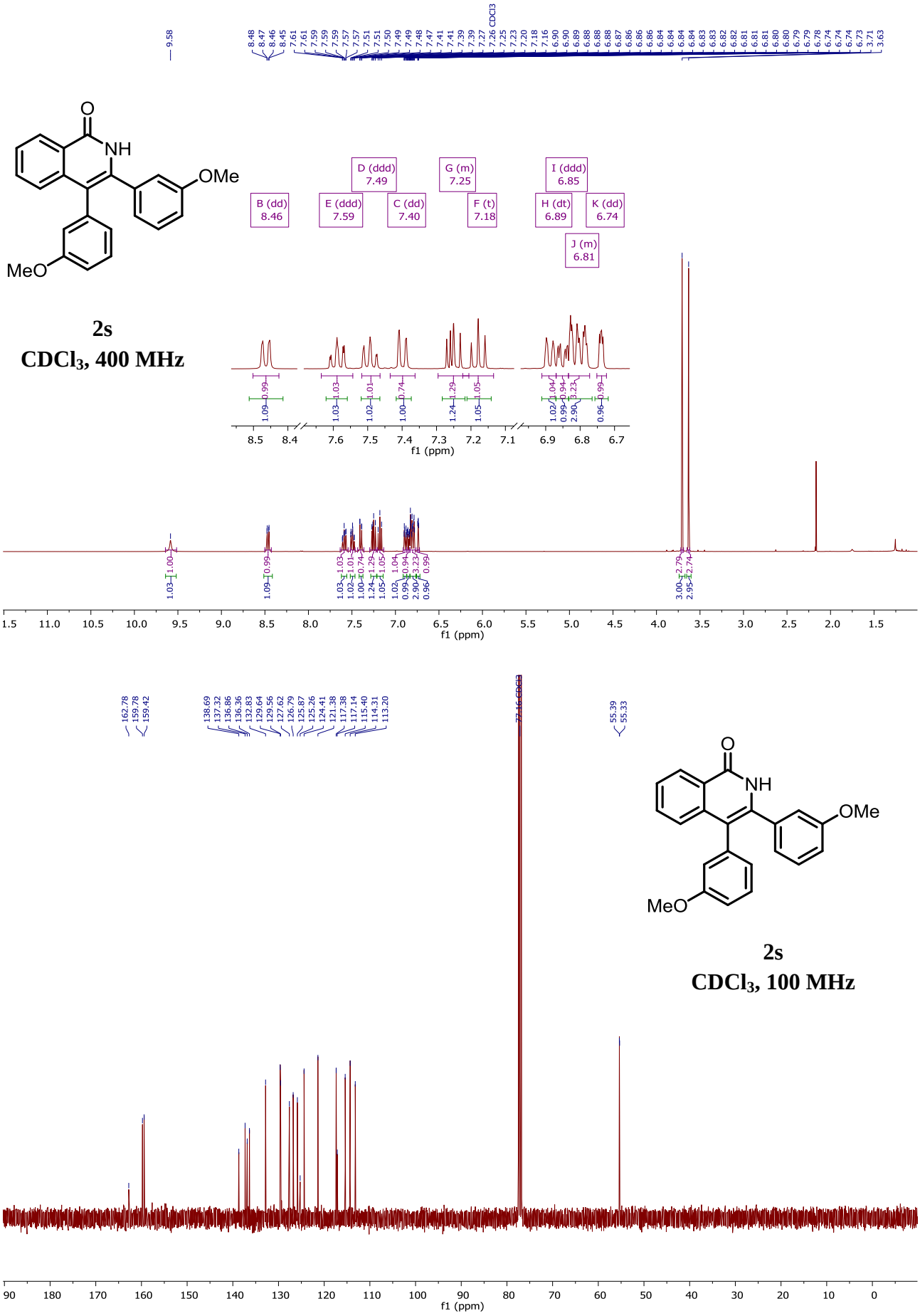
2r

DMSO-d_6, 400 MHz



2r

DMSO-d_6, 100 MHz

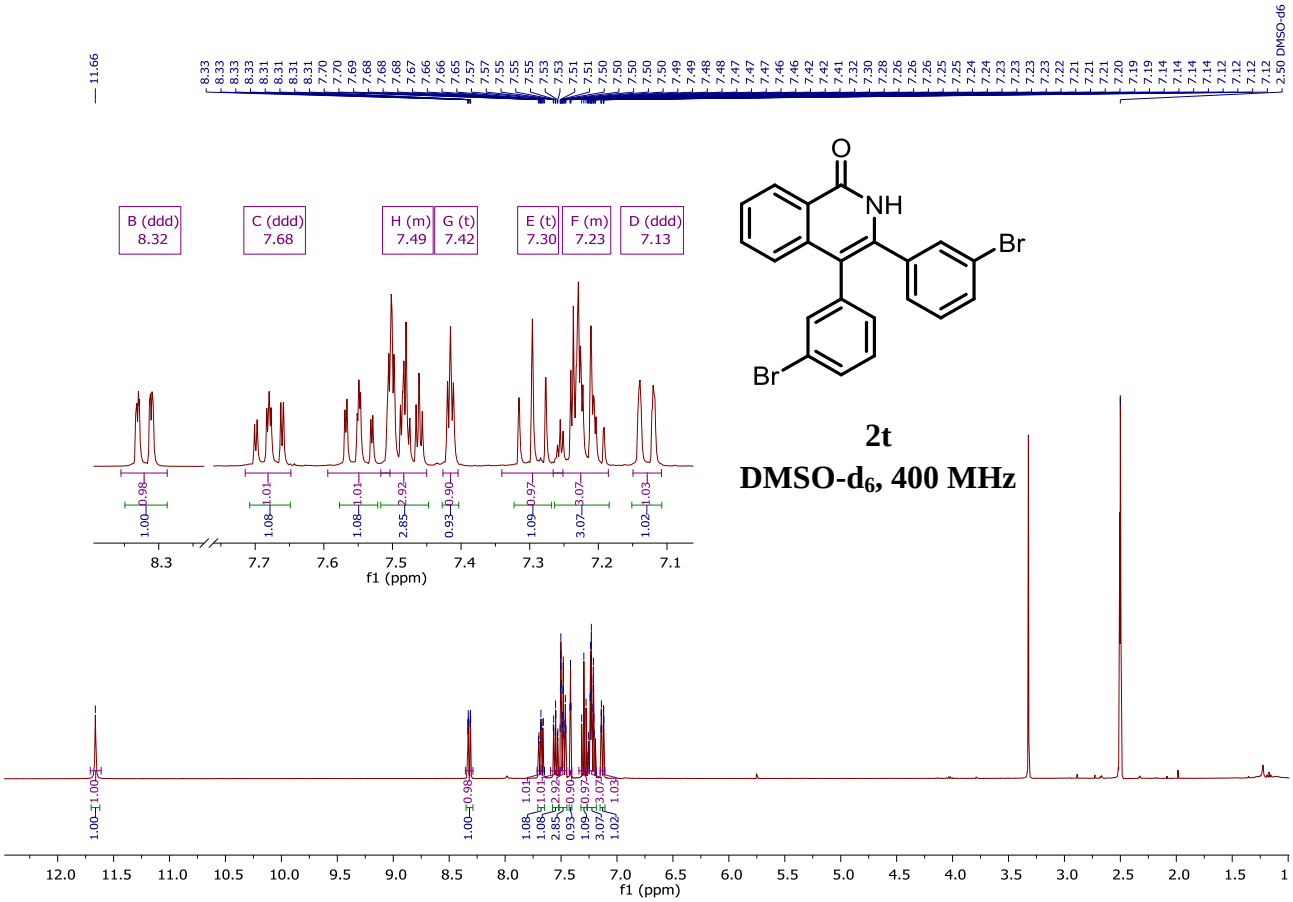


2s

$CDCl_3$, 400 MHz

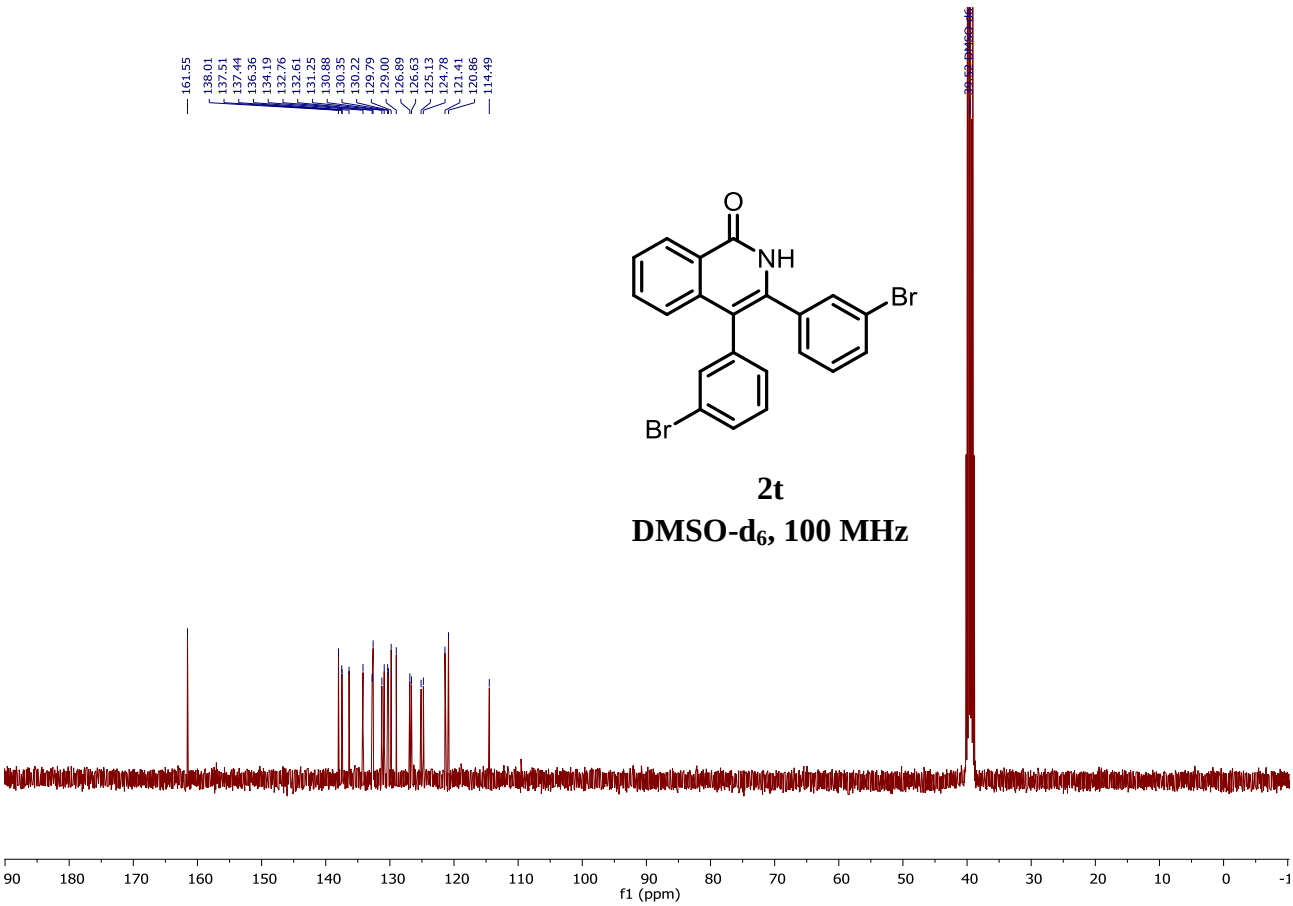
2s

$CDCl_3$, 100 MHz



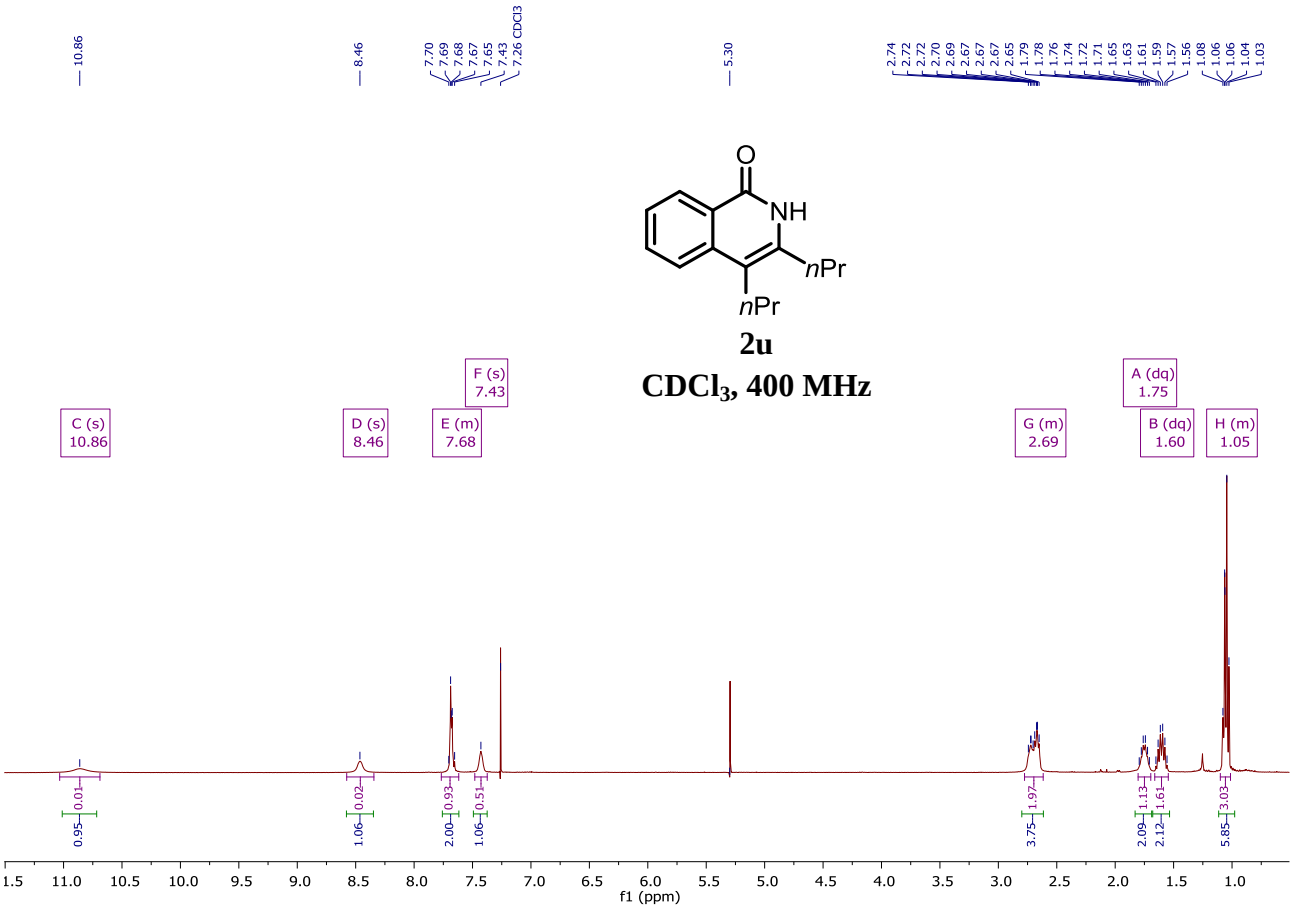
2t

DMSO-d_6, 400 MHz



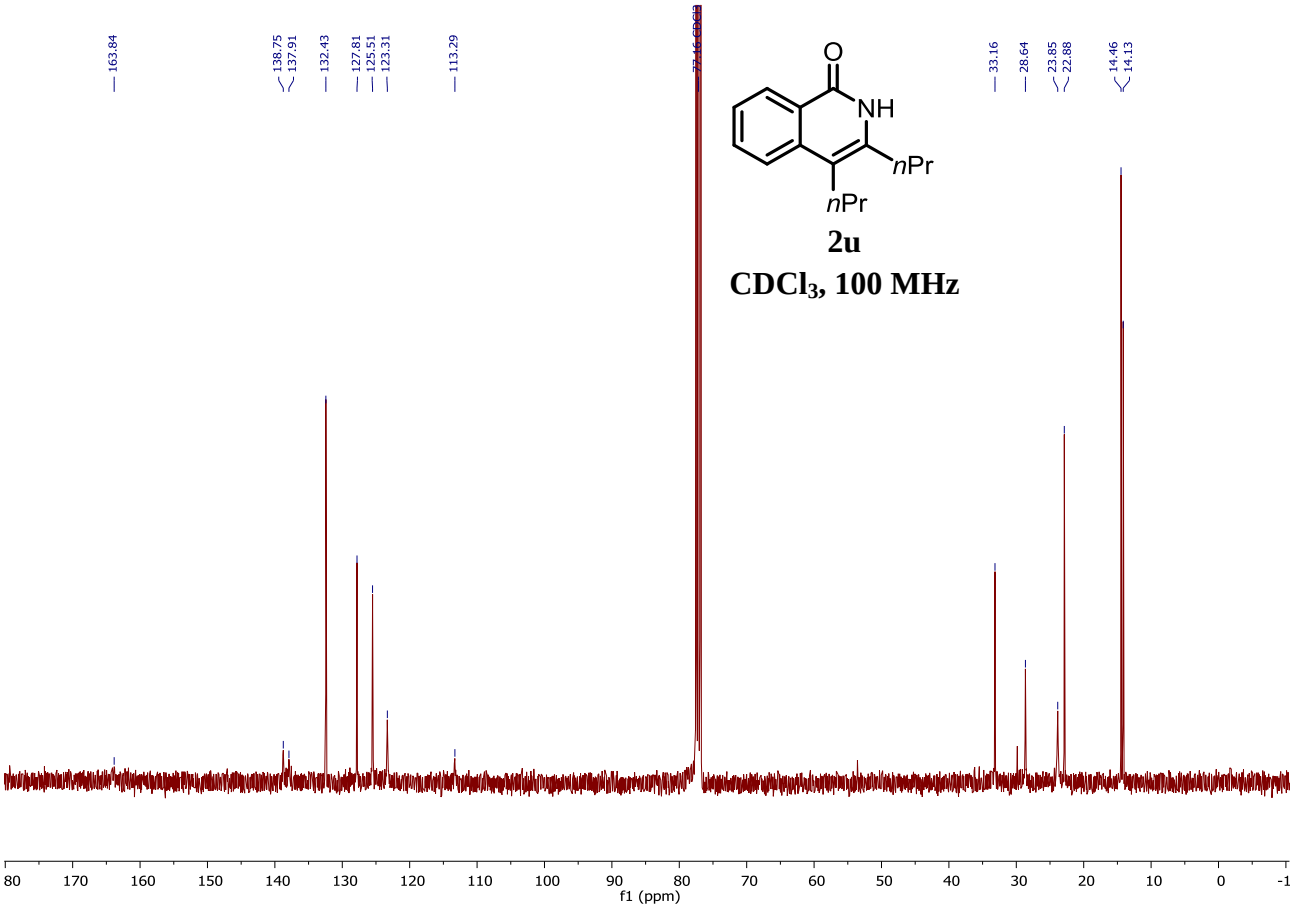
2t

DMSO-d_6, 100 MHz



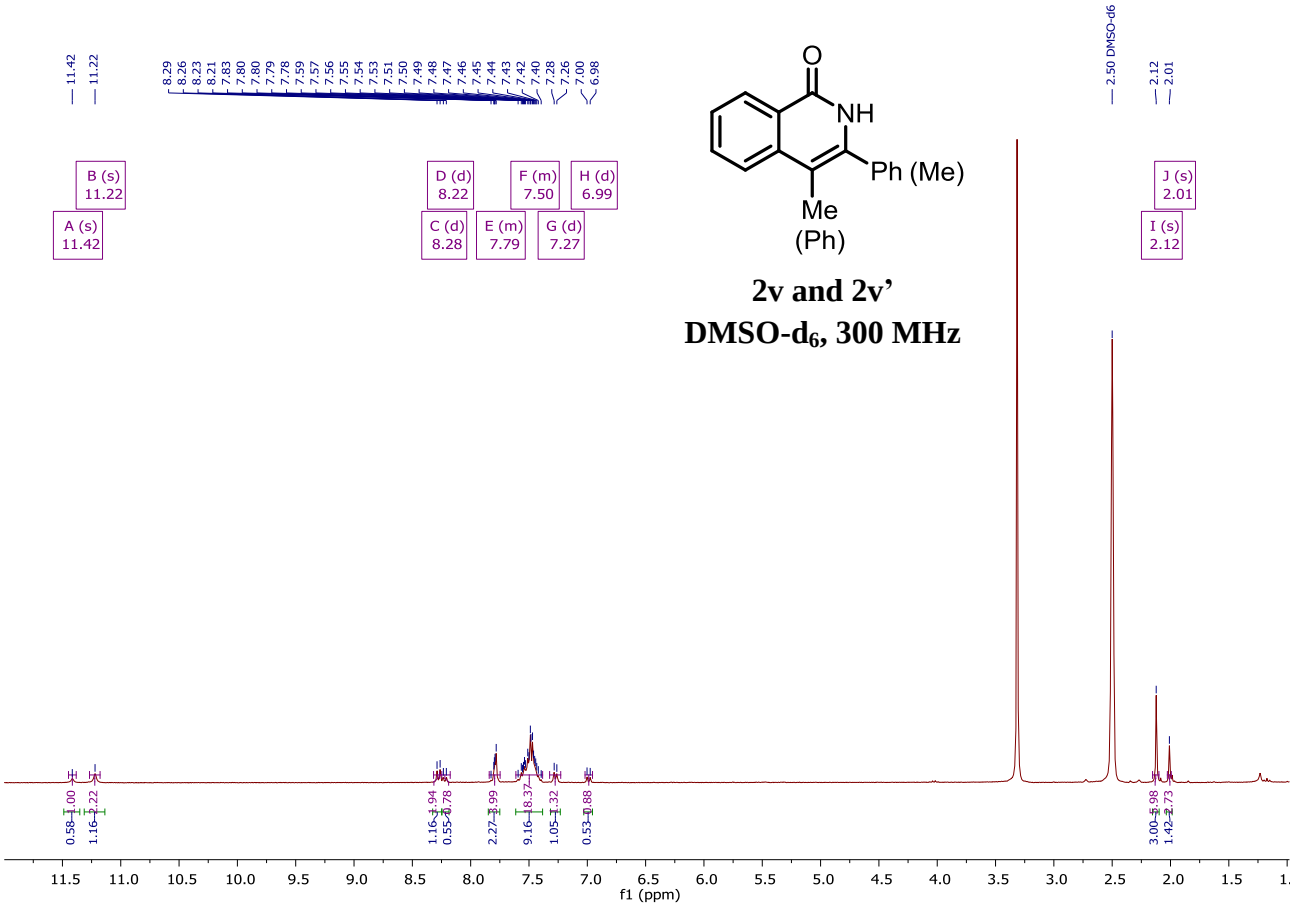
2u

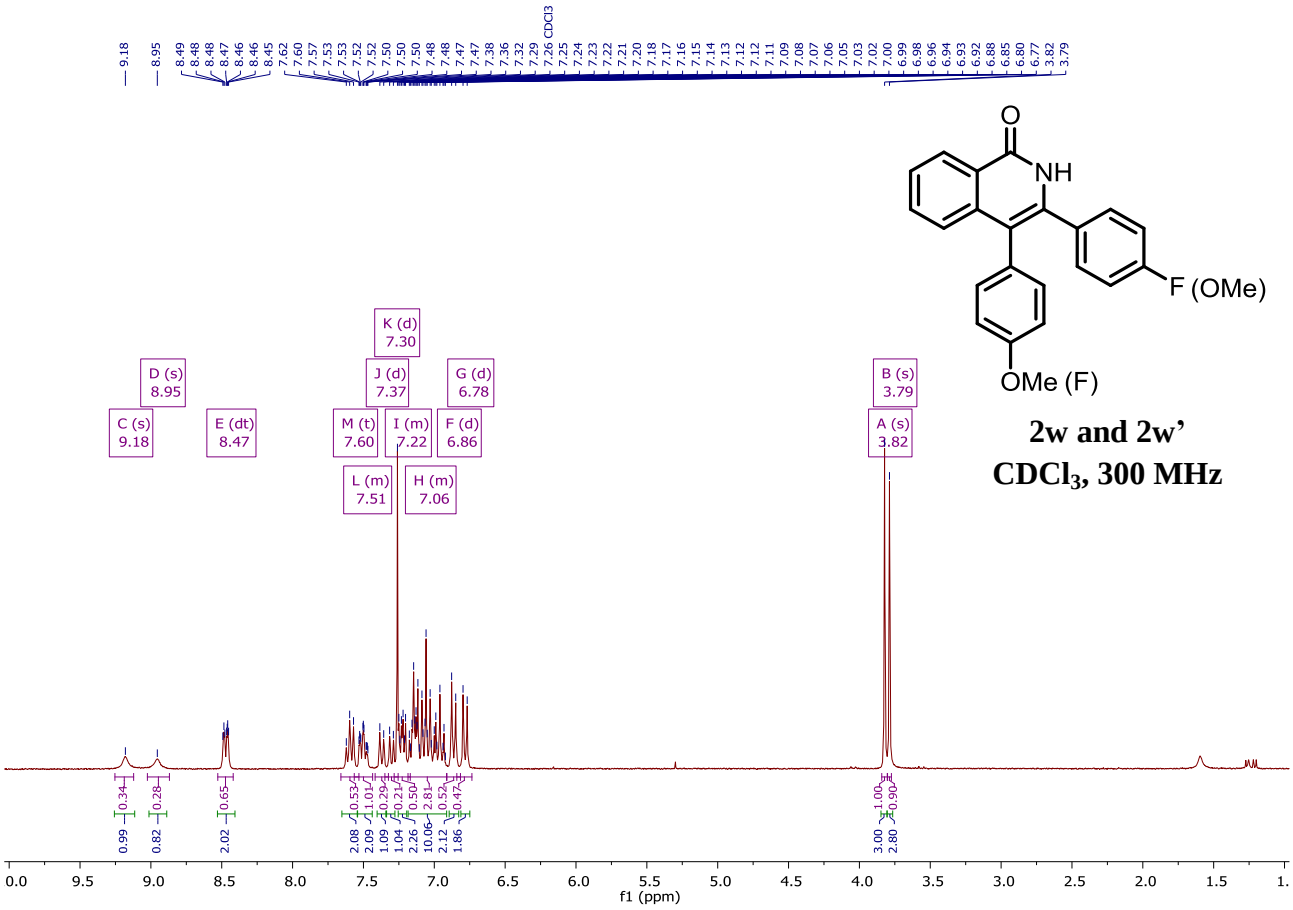
$CDCl_3$, 400 MHz



2u

$CDCl_3$, 100 MHz


11.42
11.22
8.29
8.26
8.23
8.21
7.83
7.80
7.80
7.79
7.78
7.59
7.57
7.56
7.55
7.54
7.53
7.51
7.50
7.49
7.48
7.47
7.46
7.45
7.44
7.43
7.42
7.40
7.28
7.26
7.00
6.98
2.50 DMSO-d6
2.12
2.01
B (s) 11.22
A (s) 11.42
D (d) 8.22
C (d) 8.28
F (m) 7.50
E (m) 7.79
H (d) 6.99
G (d) 7.27
J (s) 2.01
I (s) 2.12
O
NH
Ph (Me)
Me
(Ph)
2v and 2v'
DMSO-d6, 300 MHz
0.58
1.00
1.16
2.22
1.16
1.94
0.55
0.78
2.27
2.99
9.16
8.37
1.05
1.32
0.53
0.88
3.00
5.98
1.42
2.73
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


O
NH
F (OMe)
OMe (F)
2w and 2w'
CDCl3, 300 MHz
C (s) 9.18
D (s) 8.95
E (dt) 8.47
M (t) 7.60
L (m) 7.51
I (m) 7.22
H (m) 7.06
K (d) 7.30
J (d) 7.37
F (d) 6.86
G (d) 6.78
A (s) 3.82
B (s) 3.79
f1 (ppm)