Supporting Information

Tricomponent Decarboxysulfonylative Cross-Coupling Facilitates Direct Construction of Aryl Sulfones and Reveals a Mechanistic Dualism in the Acridine/Copper Photocatalytic System

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Materials and experimental details

Materials: Acetonitrile was thoroughly degassed under the atmosphere of argon for 10 min and dried over 3Å molecular sieves before use. DABSO,[1] 5-(5-methylthiophen-2-yl)-5-oxopentanoic acid (**S1**),[2] 5-((2*S*,3*S*,4*R*)-3,4-bis((*tert*-butoxycarbonyl)amino)tetrahydrothiophen-2-yl)pentanoic acid (**S2**),[3,4] 5-oxo-5-(((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methoxy)pentanoic acid (**S3**),[5] (4*R*)-4-((3*S*,7*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3,7-diacetoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoic acid (**S4**),[6] (4*R*)-4-((3*R*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,7,12-triacetoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoic acid (**S5**),[7] potassium cyclohexanesulfinate (**17**)[8] were prepared as previously described. DABSO was used within one month after preparation, because lower yields of sulfone products were observed with older DABSO batches. All other chemicals were used as commercially available.

Experimental equipment: Glovebox work was carried out in a nitrogen-filled LC Technology Solutions LCPW-220 glovebox. For convenience, the reactions were set up in the glovebox and stirred in a fume hood. The reactions can also be set up outside the glovebox with comparable yields. In this case, a pressure tube containing the solid reactants was fitted with a septum and degassed for 5 min by passing argon through two needles connected to an argon supply line and a gas bubbler, with subsequent addition of degassed and dry acetonitrile. When the reaction was set up outside a glovebox with DABSO as a sulfur dioxide source, DABSO was added after purging the pressure tube argon, immediately before adding acetonitrile. 10 mL pressure tubes were used for 0.3 mmol scale reactions. The reaction pressure tubes were placed in an oil bath at a 2–3 cm distance from a 36 W purple LED light (λ_{max} = 400 nm) while ensuring efficient stirring.

Purification: Column chromatography was performed using CombiFlash Rf-200 (Teledyne-Isco) automated flash chromatography system, as well as manually. Thin layer chromatography was carried out on silica gel-coated glass plates (Merck Kieselgel 60 F254). Plates were visualized under ultraviolet light (254 nm) and using a potassium permanganate stain.

Characterization: ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at 500 MHz (^{1}H), 125 MHz (^{13}C), 202 MHz (^{31}P), 470.5 MHz (^{19}F), and 160.4 MHz (^{11}B) on Bruker AVANCE III 500 instruments in $CDCl_3$ or other specified deuterated solvents with and without tetramethylsilane (TMS) as an internal standard at 25 °C, unless otherwise specified. Chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane (^{1}H and ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B), and $CFCl_3$ (^{19}F). Coupling constants (*J*) are in Hz. Proton multiplicity is assigned using the following abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint.), septet (sept.), multiplet (m), broad (br).

Infrared measurements were carried out neat on a Bruker Vector 22 FT-IR spectrometer fitted with a Specac diamond attenuated total reflectance (ATR) module. UV/Vis absorption spectra were recorded on a Carey 5000i spectrophotometer.

General procedures

General procedure for the decarboxysulfonylation with carboxylic acid as a limiting reagent (GP1)

To a 10 mL pressure tube equipped with a stirbar, carboxylic acid (0.3 mmol), aryl halide (0.6 mmol, 2 equiv.), acridine **A1** (0.03 mmol, 10 mol%), $CuOTf{\cdot}½PhCH_3$ (0.03 mmol, 10 mol%), *trans-*

N,*N'*-dimethylcyclohexane-1,2-diamine (**L1**) (0.045 mmol, 15 mol%), DABCO (0.21 mmol, 0.7 equiv.), and potassium metabisulfite (0.36 mmol, 1.2 equiv.) were added. The reaction vessel was capped with a septum that is connected to an argon line and a gas-bubbler. Degassed acetonitrile (3 mL) was then added, and the reaction mixture was stirred for 5 min at rt. The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while vigorously stirring (e.g., 1000 rpm) at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel to give sulfone product.

General procedure for the decarboxysulfonylation with aryl halide as a limiting reagent (GP2)

To a 10 mL pressure tube equipped with a stirbar, aryl halide (0.3 mmol), carboxylic acid (0.6 mmol, 2 equiv.), acridine **A1** (0.03 mmol, 10 mol%), CuOTf·½$PhCH_3$ (0.03 mmol, 10 mol%), *trans-N*,*N'*-dimethylcyclohexane-1,2-diamine (**L1**) (0.045 mmol, 15 mol%), cesium carbonate (0.45 mmol, 1.5 equiv.), and DABSO (0.72 mmol, 2.4 equiv.) were added. The reaction vessel was capped with a septum that is connected to an argon line and a gas-bubbler. Degassed acetonitrile (4.5 mL) was then added, and the reaction mixture was stirred for 5 min at rt. The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while vigorously stirring (e.g., 1000 rpm) at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel to give sulfone product.

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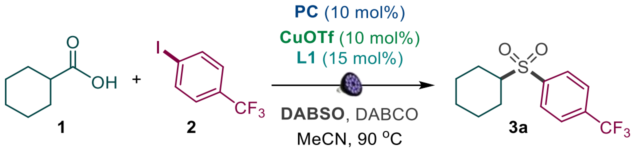
Additional experimental studies

Table S1. Performance of other photocatalysts in the direct decarboxysulfonylative construction of alkyl (hetero)aryl sulfones.[a]



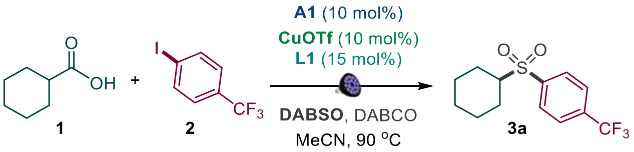
Entry	Photocatalyst	Yield, %
1	Eosin Y at 450 nm	0
2	Eosin Y at 420 nm	0
3	Eosin Y at 400 nm	0
4	Eosin Y disodium salt at 450 nm	0
5	4CzIPN at 450 nm	0
6	4CzIPN at 420 nm	0
7	4CzIPN at 400 nm	0
8	$[\text{Acr-Mes}]^+(\text{ClO}_4)^-$ at 400 nm	0
9	$[\text{Acr-Mes}]^+(\text{ClO}_4)^-$ at 450 nm	0[b]
10	Ir(ppy)_3 at 450 nm	0[b]
11	$\text{Ir(ppy)}_2\text{(pq)}$ at 450 nm	0[b]
12	$(\text{Ir[dF(CF}_3\text{)ppy]}_2\text{(dtbpy))PF}_6$ at 450 nm	0[b]
13	$\text{Ru(bpm)}_2\text{Cl}_2$ at 450 nm	0[b]
14	Ru(*p*-CF_3-bpy)$_3$(BF_4)$_2$ at 450 nm	0[b]
15	TiO_2, anatase	0[c]

[a] Reaction conditions: carboxylic acid (0.3 mmol), DABSO (0.36 mmol), aryl iodide (0.6 mmol), **A1** (10 mol%), CuOTf·½PhMe (10 mol%), **L1** (15 mol%), MeCN (3 mL), LED light (400 nm), 90 °C, 14 h. Yield was determined by ^{1}H NMR spectroscopy with 1,4-dimethoxybenzene as an internal standard. [b] 2 mol% photocatalyst was used. [c] nanopowder, <25 nm particle size, 30 mg. 4CzIPN: 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene, $[\text{Acr-Mes}]^+(\text{ClO}_4)^-$: 10-Methyl-9-(2,4,6-trimethylphenyl)acridinium perchlorate, Ir(ppy)_3: Tris(2-phenylpyridine)iridium(III), $\text{Ir(ppy)}_2\text{(pq)}$: bis(2-phenylpyridine)(2-phenylquinoline)iridium(III), $(\text{Ir[dF(CF}_3\text{)ppy]}_2\text{(dtbpy))PF}_6$: [4,4′-Bis(1,1-dimethylethyl)-2,2′-bipyridine-*N1*,*N1*′]-bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyri-dinyl-*N*]phenyl-C]iridium(III) hexafluorophosphate, $\text{Ru(bpm)}_2\text{Cl}_2$: Tris(2,2′-bipyrimide)ru-thenium(II) dichloride, Ru(*p*-CF_3-bpy)$_3$(BF_4)$_2$: Tris(2,2′-(*p*CF_3)-bipyridine)ruthenium(II) tetra-fluoroborate.

Influence of various reaction parameters on the photocatalytic direct decarboxysulfonylative construction of alkyl (hetero)aryl sulfones

Investigation of the influence of changes in key reaction parameters indicated that ±10 °C variations in the reaction temperature had a relatively small impact on the reaction efficiency (entries 2, 3, Table S2). Similarly, ±20% variations in the solvent volume did not significantly affect the yield (entries 4, 5). However, the reaction (both with DABSO and potassium metabisulfite) was sensitive to moisture (entries 6 and 7, Table S2), indicating that dry solvent and anhydrous conditions should be used for efficient conversion. Additionally, the reaction was sensitive to the reduction in light intensity and the presence of air (entries 8 and 9, Table S2), pointing to the importance of using sufficient light irradiation and efficient degassing of the reaction mixture, as described in the Experimental equipment and General procedure sections. Finally, given the heterogeneity of the reaction mixture, efficient stirring (e.g., 1000 rpm) was necessary to ensure optimal reaction performance (entry 10).

Table S2. Influence of various reaction parameters on the reaction performance.[a]



Entry	Change in the reaction conditions	Yield, %[a]
1	none	97
2	100 °C	89
3	80 °C	78
4	20% increase in solvent volume	87
5	20% decrease in solvent volume	79
6	With added water (5 equiv.)	49
7	With added water (5 equiv.) using method A ($K_2S_2O_5$)	60
8	Reduced light intensity[b]	51
9	Under air[c]	24
10	Reduced stirring rate[d]	51

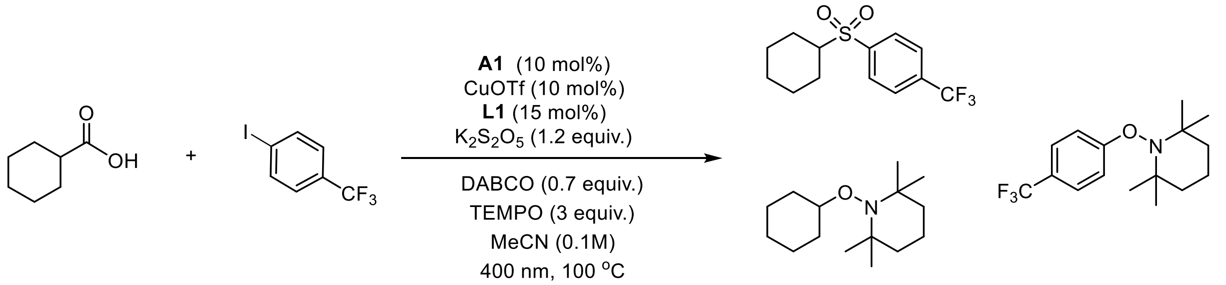
[a] Reaction conditions: carboxylic acid (0.3 mmol), DABSO (0.36 mmol), aryl iodide (0.6 mmol), **A1** (10 mol%), CuOTf·½PhMe (10 mol%), **L1** (15 mol%), MeCN (3 mL), LED light (400 nm), 90 °C, 14 h. Yield was determined by ^{1}H NMR spectroscopy with 1,4-dimethoxybenzene as an internal standard. [b] LED light was positioned 8 cm away from the reaction. [c] Air (60 mL) was passed through the reaction vessel prior to the start of the experiment. [d] The reaction was stirred at 500 rpm, one-half the standard stirring rate.

Mechanistic studies

Quantum yield measurement

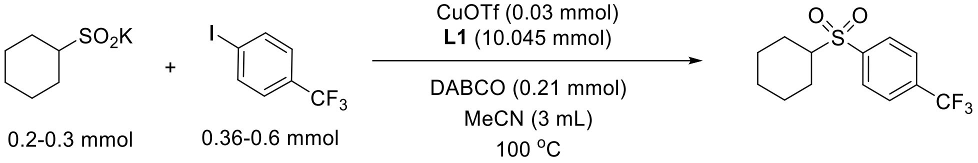
The photon flux of the photochemical setup was determined using the phenylglyoxylic acid chemical actinometer system.[9] Incident photon flux: 0.32 μmol photons per second. The three-component reaction of cyclohexanecarboxylic acid, 1-iodo-4-(trifluoromethyl)benzene and potassium metabisulfite was carried out as described in GP1. Yield was determined by ^{1}H NMR spectroscopy, using 1,3,5-trimethoxybenzene as an internal standard. $\Phi = 0.06$.

Radical trapping experiment with TEMPO



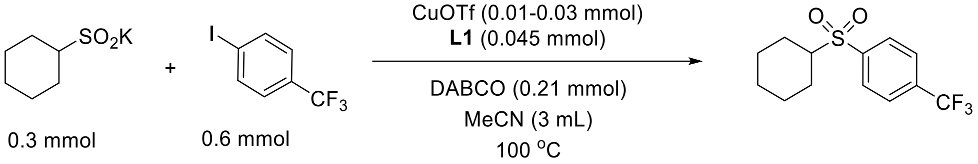
According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , TEMPO (140 mg, 0.9 mmol, 3 equiv.) and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction vessel was cooled to room temp, and 1,3,5-trimethoxybenzene (0.1 mmol) were added. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the ^{1}H NMR data was recorded.

Variable time normalization analysis (VTNA) studies



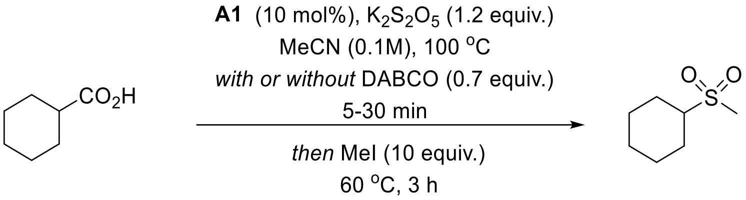
To a 10 mL pressure tube equipped with a stirbar, potassium cyclohexanesulfinate (0.2–0.3 mmol), aryl halide (0.36–0.6 mmol), CuOTf·½PhCH$_3$ (0.03 mmol), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (**L1**) (0.045 mmol), DABCO (0.21 mmol), and 1,3,5-trimethoxybenzene (0.1 mmol) were added. Acetonitrile (3 mL) was then added. The tube was sealed with a GL18 screw cap with a septum, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C. After every 5 minutes, an aliquot (0.1 mL) was withdrawn, diluted with ethyl acetate (1 mL) and washed with a saturated aqueous solution of EDTA (1 mL). The organic layer was concentrated. and the ^{1}H NMR data was recorded. Four identical experiments were carried out, and each reaction was used to withdraw 3 aliquots.

Kinetic study of the rate order in copper(I) triflate



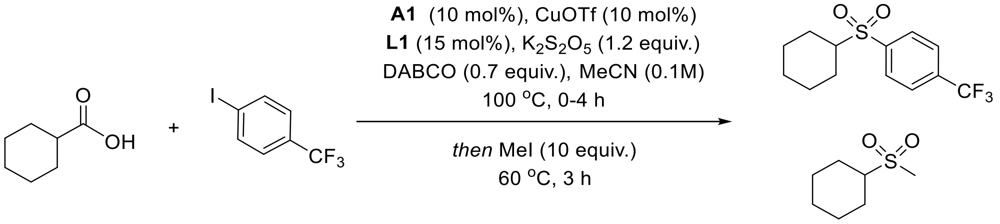
To a 10 mL pressure tube equipped with a stirbar, potassium cyclohexanesulfinate (0.3 mmol), aryl halide (0.6 mmol), CuOTf·½PhCH$_3$ (0.01–0.03 mmol), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (**L1**) (0.045 mmol), DABCO (0.21 mmol), and 1,3,5-trimethoxybenzene (0.1 mmol) were added. Acetonitrile (3 mL) was then added. The tube was sealed with a GL18 screw cap with a septum, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C. After every 5 minutes, an aliquot (0.1 mL) was withdrawn, diluted with ethyl acetate (1 mL) and washed with a saturated aqueous solution of EDTA (1 mL). The organic layer was concentrated. and the ^{1}H NMR data was recorded. Two identical experiments were carried out, and each reaction was used to withdraw 3 aliquots.

Kinetic study of the decarboxylative sulfination



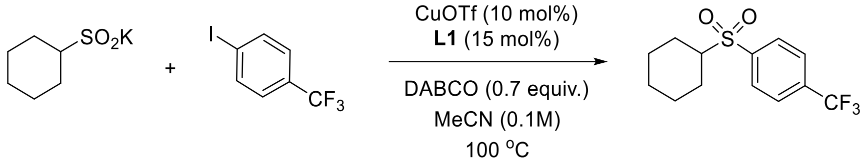
To a 10 mL pressure tube equipped with a stirbar, cyclohexanecarboxylic acid (0.3 mmol), acridine **A1** (0.03 mmol, 10 mol%), potassium metabisulfite (0.36 mmol, 1.2 equiv.) were added with or without DABCO (0.21 mmol). Acetonitrile (3 mL) was then added. The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 ˚C. After 5 minutes, irradiation was discontinued, and methyl iodide (3 mmol) and 1,3,5-trimethoxybenzene (0.1 mmol) were added. The reaction was allowed to stir for another 3 hours at 60 ˚C in dark. The reaction was diluted with ethyl acetate (5 mL) and washed with water (3 mL). The organic layer was concentrated and the ^{1}H NMR data was recorded. The reaction was repeated for 10, 20, 30 minutes.

Kinetic study of the decarboxysulfonylation



To a 10 mL pressure tube equipped with a stirbar, cyclohexanecarboxylic acid (0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (0.6 mmol, 2 equiv.), acridine **A1** (0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (0.03 mmol, 10 mol%), *trans*-*N*,*N'*-dimethylcyclohexane-1,2-diamine (0.045 mmol, 15 mol%), DABCO (0.21 mmol, 0.7 equiv.), potassium metabisulfite (0.36 mmol, 1.2 equiv.), and 1,3,5-trimethoxybenzene (0.1 mmol) were added were added. Acetonitrile (3 mL) was then added. The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C. After 5 minutes, irradiation was discontinued, an aliquot (0.1 mL) was withdrawn, diluted with ethyl acetate (1 mL) and washed with a saturated aqueous solution of EDTA (1 mL), while methyl iodide (3 mmol) was added to the remaining reaction mixture. The reaction was allowed to stir for another 3 hours at 60 ˚C in dark. The reaction was diluted with ethyl acetate (5 mL) and extracted with water (3 mL). The organic layers before and after methylation step were concentrated and the ^{1}H NMR data was recorded and compared. The reaction was repeated for 60, 120, 180, 240 minutes.

Kinetic study of the cross-coupling of sulfinate salt 17 and aryl iodide 2



To a 10 mL pressure tube equipped with a stirbar, potassium cyclohexanesulfinate (0.3 mmol), aryl halide (0.6 mmol), CuOTf·½PhCH$_3$ (0.03 mmol), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (**L1**) (0.045 mmol), DABCO (0.21 mmol), and 1,3,5-trimethoxybenzene (0.1 mmol) were added. Acetonitrile (3 mL) was then added. The tube was sealed with a GL18 screw cap with a septum, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C. After 30, 60, 120 and 280 minutes, an aliquot (0.1 mL) was withdrawn, diluted with ethyl acetate (1 mL) and washed with a saturated aqueous solution of EDTA (1 mL). The organic layer was concentrated and the ^{1}H NMR data was recorded.

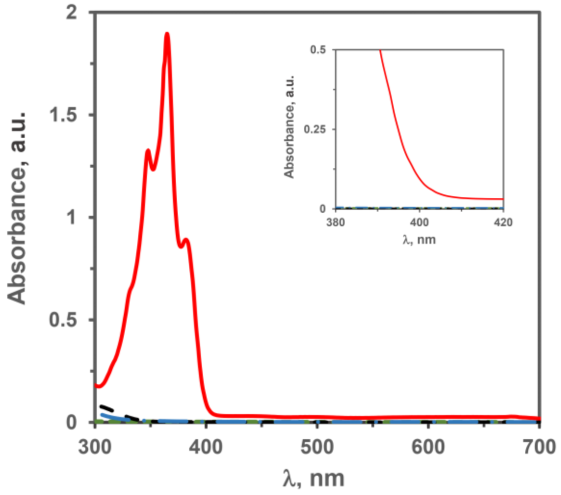
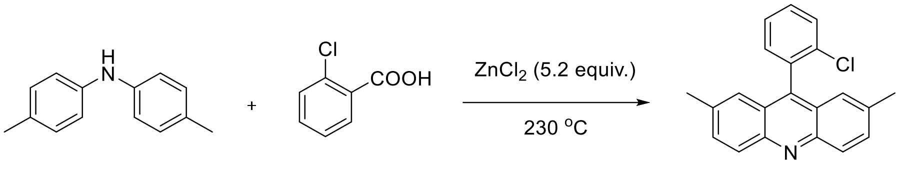


Figure S1. UV/vis spectra of 0.5 mM solutions of Cu(MeCN)$_4$BF$_4$ (—·), Cu(MeCN)$_4$BF$_4$/**L4** (·····), CuO$_2$STol (– –), and acridine **A1** (—) in acetonitrile. The spectral data indicate that, in contrast to the acridine photocatalyst, the copper complexes do not have appreciable absorption at 400 nm, with the ratios of molar absorptivity at 400 nm $\varepsilon_{A1}/\varepsilon_{Cu}$ = 37, 25, and 53 for Cu(MeCN)$_4$BF$_4$, Cu(MeCN)$_4$BF$_4$/**L4**, and CuO$_2$STol, respectively.

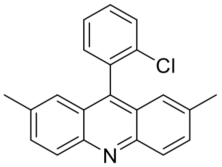
Acridine catalyst

9-(2-Chlorophenyl)-2,7-dimethylacridine (A1)



A1

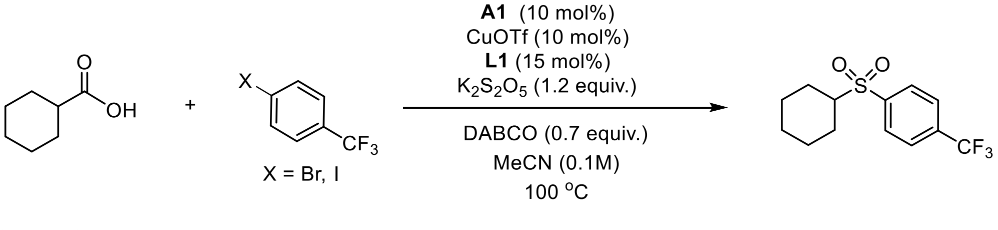
To a 35 mL pressure vessel, di-*p*-tolylamine (0.71 g, 3.6 mmol), 2-chlorobenzoic acid (1.6 g, 10 mmol, 3 equiv.), and zinc chloride (2.6 g, 19 mmol, 5.2 equiv.) were added. The reaction was allowed to stir at 200 °C in a sand bath for 14 h. After completion, the reaction was quenched with a saturated solution of ammonium hydroxide (50 mL) and then extracted with ethyl acetate (3 x 75 mL). The organic layer was washed with brine, separated, and dried over Na_2SO_4. Removal of the solvent and purification by silica gel chromatography (hexane/ ethyl acetate 9 : 1 v/v) afforded acridine **A1** as a yellow solid (0.77 g, 68%).



m.p.: 167–170 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.20 (2 H, d, *J* = 8.8 Hz), 7.70 (1 H, dd, *J* = 8.0, 1.2 Hz), 7.64–7.49 (4 H, m), 7.36 (1 H, dd, *J* = 7.4, 1.8 Hz), 7.21 (2 H, s), 2.48 (6 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 147.3, 141.7, 135.8, 135.4, 134.3, 132.5, 132.1, 129.91, 129.87, 129.5, 126.9, 125.1, 124.0, 22.1 ppm. – IR: 3035, 1653, 1621, 1543, 1520, 1501, 1417, 1402, 1379, 1268, 1213, 1184 cm^{-1}. – HRMS: calcd for $C_{21}H_{16}ClN$: 318.1044, found 318.1045 [M+H$^+$].

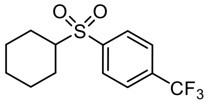
Sulfone products

1-(Cyclohexylsulfonyl)-4-(trifluoromethyl)benzene (3a)



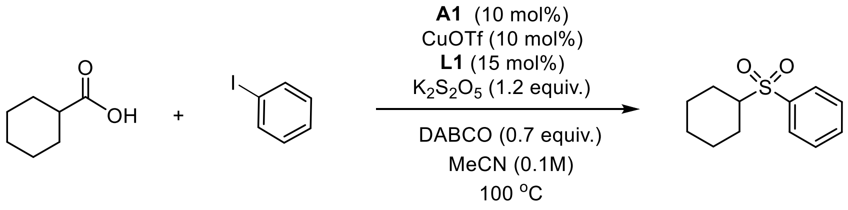
From aryl iodide: According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **3a** (72 mg, 82%) as a colorless solid.

From aryl bromide: According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 1-bromo-4-(trifluoromethyl)benzene (114 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **3a** (78 mg, 89%) as a colorless solid.

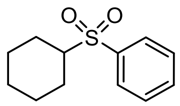


m.p.: 50–53 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.03 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 2.95 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.14–2.04 (m, 2H), 1.90 (dt, *J* = 13.1, 3.2 Hz, 2H), 1.75–1.67 (m, 1H), 1.44 (qd, *J* = 12.5, 3.5 Hz, 2H), 1.31–1.12 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 141.0, 135.3 (q, *J* = 32.8 Hz), 129.7, 126.2 (q, *J* = 3.8 Hz), 123.2 (q, *J* = 273.2 Hz), 63.6, 25.4, 25.0, 25.0 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.2 ppm. – IR: 2938, 2850, 1608, 1454, 1402, 1316, 1270 cm^{-1}. – HRMS calcd for $C_{13}H_{15}F_3O_2S$: 293.0818, found 293.0816 [M+H$^+$].

(Cyclohexylsulfonyl)benzene (3b)[10]

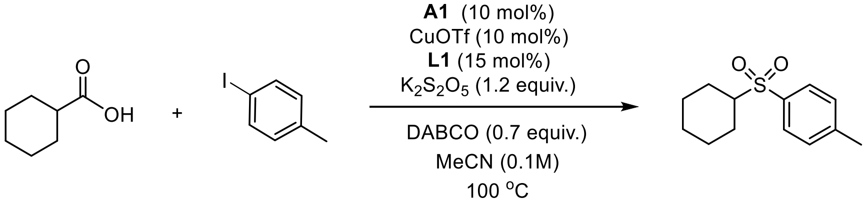


According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), iodobenzene (122 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **3b** (48 mg, 72%) as a colorless solid.

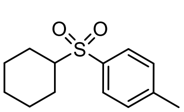


m.p.: 75–78 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.91–7.87 (m, 2H), 7.70–7.65 (m, 1H), 7.58 (dd, *J* = 8.4, 7.1 Hz, 2H), 2.92 (tt, *J* = 12.1, 3.4 Hz, 1H), 2.08 (ddq, *J* = 12.2, 3.8, 2.1 Hz, 2H), 1.87 (ddd, *J* = 11.5, 5.3, 2.5 Hz, 2H), 1.71–1.66 (m, 1H), 1.43 (qd, *J* = 12.5, 3.5 Hz, 2H), 1.29–1.12 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 137.3, 133.5, 129.0, 129.0, 63.5, 25.5, 25.1, 25.1 ppm. – IR: 2937, 2854, 1583, 1479, 1445, 1304, 1278, 1261, 1141cm^{-1}.

1-(Cyclohexylsulfonyl)-4-methylbenzene (3c)[11]



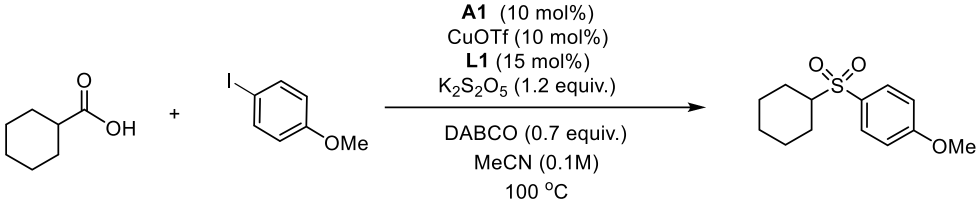
According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 1-iodo-4-methylbenzene (131 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **3c** (50 mg, 70%) as a colorless solid.



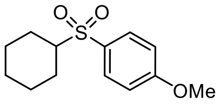
m.p.: 85–87 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.78–7.74 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.89 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.47 (s, 2H), 2.08 (ddq, *J* = 12.1, 3.8, 2.1 Hz, 2H), 1.87 (dt, *J* = 12.1, 3.0 Hz, 2H), 1.68 (dddd, *J* = 11.1, 4.9, 2.9, 1.6 Hz, 1H), 1.41

(qd, *J* = 12.5, 3.5 Hz, 2H), 1.29–1.08 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 144.4, 134.3, 129.6, 129.1, 63.5, 25.6, 25.1, 25.1, 21.6 ppm. – IR: 2932, 2855, 1595, 1451, 1400, 1313, 1299, 1267 cm^{-1}.

1-(Cyclohexylsulfonyl)-4-methoxybenzene (3d)

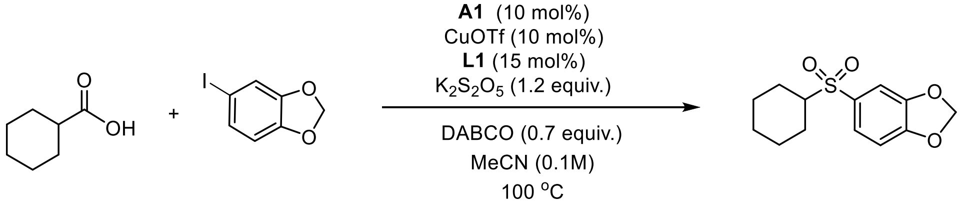


According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 1-iodo-4-methoxybenzene (140 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans*-*N*,*N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **3d** (50 mg, 66%) as a colorless solid.



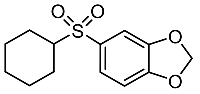
m.p.: 89–92 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.83–7.79 (m, 2H), 7.06–7.01 (m, 2H), 2.88 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.13–2.05 (m, 2H), 1.87 (dt, *J* = 12.7, 3.1 Hz, 2H), 1.68 (dtd, *J* = 12.0, 3.3, 1.5 Hz, 1H), 1.40 (qd, *J* = 12.5, 3.5 Hz, 2H), 1.29–1.09 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 163.6, 131.2, 128.8, 114.2, 63.7, 55.7, 25.7, 25.2, 25.1 ppm. – IR: 2932, 2856, 1593, 1577, 1497, 1452, 1313, 1294, 1257, 1217 cm^{-1}. – HRMS calcd for $C_{13}H_{18}O_3S$: 225.1049, 225.1045 found [M+H$^+$].

5-(Cyclohexylsulfonyl)benzo[*d*][1,3]dioxole (3e)



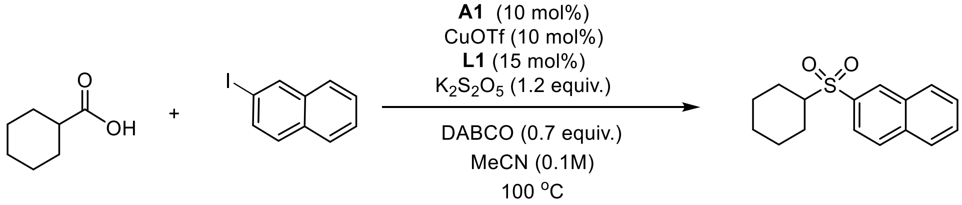
According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 5-iodobenzo[*d*][1,3]dioxole (149 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans*-*N*,*N'*-dimethylcyclohexane-1,2-

diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **3e** (50 mg, 62%) as a colorless solid.

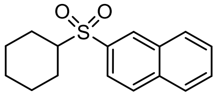


m.p.: 107–109 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.44 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.28 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.12 (s, 2H), 2.88 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.11–2.06 (m, 2H), 1.88 (dt, *J* = 12.4, 2.9 Hz, 2H), 1.72–1.67 (m, 1H), 1.41 (qd, *J* = 12.5, 3.5 Hz, 2H), 1.29–1.10 (m, 3H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 152.1, 148.2, 130.6, 125.0, 109.0, 108.4, 102.4, 63.8, 25.7, 25.1, 25.1 ppm. – IR: 2924, 2854, 1601, 1502, 1476, 1452, 1425, 1358, 1304, 1258, 1239, 1130, 1107, 1033 cm^{-1}. – HRMS calcd for $C_{13}H_{16}O_4S$: 269.0842, found 269.0846 [M+H$^+$].

2-(Cyclohexylsulfonyl)naphthalene (3f) [12]



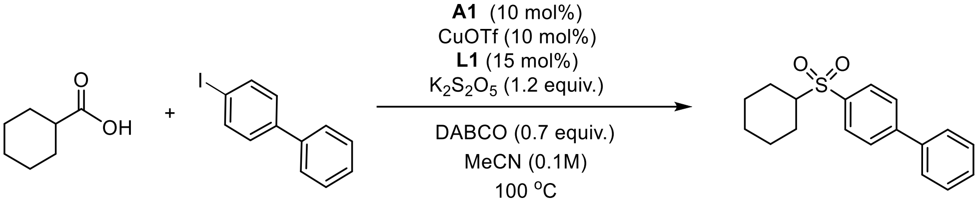
According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 2-iodonaphthalene (152 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½$PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **3f** (61 mg, 74%) as a colorless solid.



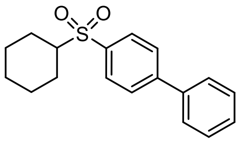
m.p.: 92–95 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.47 (d, *J* = 1.7 Hz, 1H), 8.02 (dd, *J* = 8.6, 2.5 Hz, 2H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.87 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.72–

7.63 (m, 2H), 3.01 (tt, *J* = 12.1, 3.4 Hz, 1H), 2.16–2.10 (m, 2H), 1.87 (dt, *J* = 13.2, 3.2 Hz, 2H), 1.68 (dt, *J* = 12.6, 3.1 Hz, 1H), 1.48 (qd, *J* = 12.5, 3.6 Hz, 2H), 1.29–1.10 (m, 3H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 135.3, 134.3, 132.1, 130.8, 129.4, 129.2, 128.0, 127.6, 123.8, 63.6, 25.6, 25.1, 25.1 ppm. – IR: 3059, 2930, 2850, 1623, 1589, 1504, 1448, 1346, 1328, 1302, 1276, 1264, 1141 cm^{-1}.

4-(Cyclohexylsulfonyl)-1,1'-biphenyl (3g)

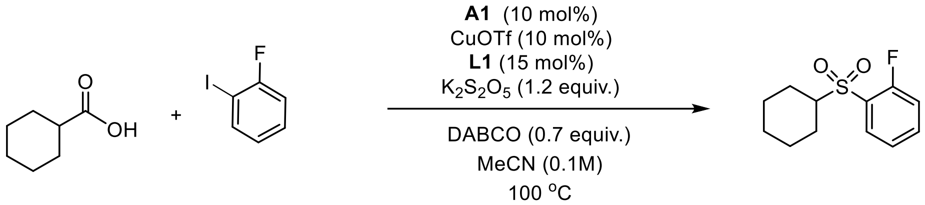


According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 4-iodo-1,1'-biphenyl (168 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½$PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **3g** (82 mg, 91%) as a colorless solid.

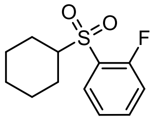


m.p.: 80–82 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.97–7.92 (m, 2H), 7.80–7.76 (m, 2H), 7.66–7.62 (m, 2H), 7.54–7.43 (m, 3H), 2.96 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.17–2.11 (m, 2H), 1.90 (dt, *J* = 12.8, 3.0 Hz, 2H), 1.73–1.67 (m, 1H), 1.47 (qd, *J* = 12.5, 3.6 Hz, 2H), 1.31–1.13 (m, 3H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 146.5, 139.2, 135.8, 129.6, 129.1, 128.6, 127.6, 127.4, 63.6, 25.6, 25.1, 25.1 ppm. – IR: 2929, 2858, 1590, 1561, 1478, 1454, 1396, 1310, 1302, 1266, 1210, 1179, 1143 cm^{-1}. – HRMS calcd for $C_{18}H_{20}O_2S$: 301.1257, found 301.1252 [M+H$^+$].

1-(Cyclohexylsulfonyl)-2-fluorobenzene (3h)

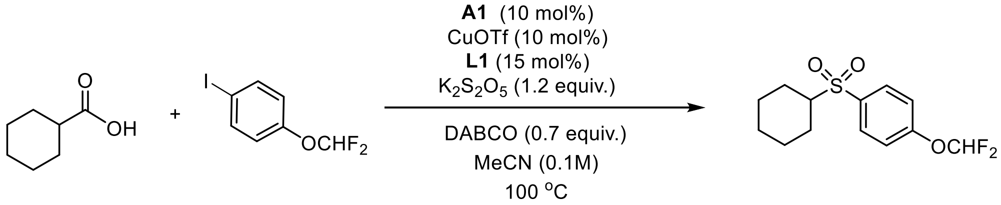


According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 1-fluoro-2-iodobenzene (133 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans*-*N*,*N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **3h** (58 mg, 80%) as a colorless solid.



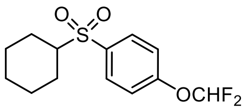
m.p.: 74–76 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.93 (td, *J* = 7.4, 1.8 Hz, 1H), 7.66 (tdd, *J* = 7.3, 5.0, 1.8 Hz, 1H), 7.35 (td, *J* = 7.6, 1.1 Hz, 1H), 7.26 (ddd, *J* = 9.6, 8.4, 1.0 Hz, 1H), 3.25–3.18 (m, 1H), 2.06–2.02 (m, 2H), 1.91 (dt, *J* = 12.1, 2.8 Hz, 2H), 1.75–1.70 (m, 1H), 1.61–1.51 (m, 2H), 1.34–1.17 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 159.8 (d, *J* = 255.8 Hz), 135.9 (d, *J* = 8.4 Hz), 131.7, 125.5 (d, *J* = 14.9 Hz), 124.6 (d, *J* = 3.8 Hz), 117.2 (d, *J* = 21.7 Hz), 63.1, 25.1, 25.0, 25.0 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -108.0 (q, *J* = 7.1, 6.7 Hz) ppm. – IR: 2927, 2858, 1594, 1577, 1469, 1445, 1314, 1298, 1280, 1260, 1219, 1159, 1140, 1120, 1068 cm^{-1}. – HRMS calcd for $C_{12}H_{15}FO_2S$: 243.0850, found 243.0852 [M+H$^+$].

1-(Cyclohexylsulfonyl)-4-(difluoromethoxy)benzene (3i)



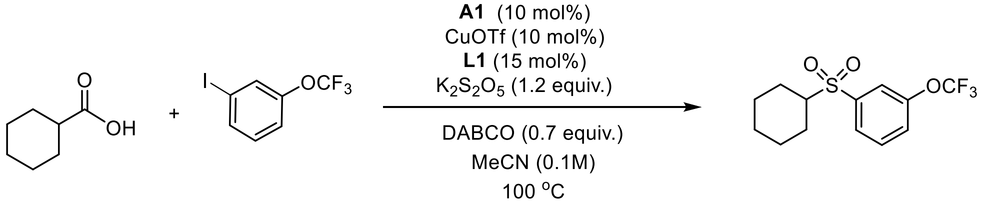
According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 1-(difluoromethoxy)-4-iodobenzene (152 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans*-*N*,*N'*-dimethylcyclohexane-

1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **3i** (68 mg, 78%) as a colorless solid.

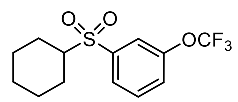


m.p.: 85–87 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.90 (dd, *J* = 8.7, 1.9 Hz, 2H), 7.31–7.28 (m, 2H), 6.65 (t, *J* = 72.5 Hz, 1H), 2.91 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.11–2.05 (m, 2H), 1.88 (dt, *J* = 11.8, 3.1 Hz, 2H), 1.72–1.67 (m, 1H), 1.41 (qd, *J* = 12.5, 3.3 Hz, 2H), 1.29–1.11 (m, 3H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 154.9, 133.9, 131.3, 119.3, 115.1 (t, *J* = 262.8 Hz), 63.6, 25.5, 25.1, 25.0 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -82.2 (d, *J* = 72.6 Hz) ppm. – IR: 2933, 2859, 1595, 1587, 1493, 1453, 1387, 1311, 1291, 1268, 1217 cm^{-1}. – HRMS calcd for $C_{13}H_{16}F_2O_3S$: 291.0861, found 291.0856 [M+H$^+$].

1-(Cyclohexylsulfonyl)-3-(trifluoromethoxy)benzene (3j)

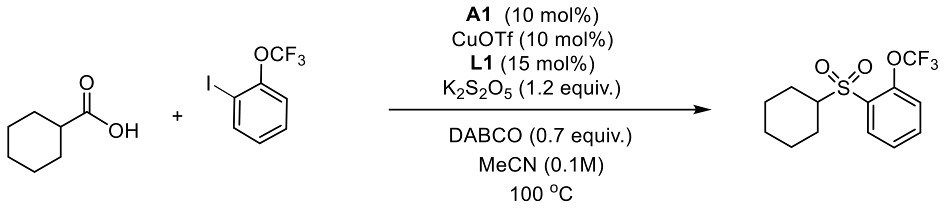


According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 1-iodo-3-(trifluoromethoxy)benzene (173 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½$PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **3j** (72 mg, 78%) as a colorless solid.

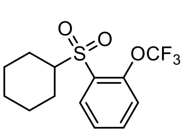


m.p.: 97–99 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.83 (dt, J = 7.8, 1.3 Hz, 1H), 7.75 (s, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.53 (ddt, J = 8.3, 2.3, 1.1 Hz, 1H), 2.94 (tt, J = 12.2, 3.5 Hz, 1H), 2.11–2.05 (m, 2H), 1.90 (dt, J = 12.7, 3.0 Hz, 2H), 1.73–1.68 (m, 1H), 1.44 (qd, J = 12.5, 3.5 Hz, 2H), 1.31–1.12 (m, 3H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 149.3, 139.5, 130.7, 127.3, 125.9, 121.7, 120.3 (q, J = 259.3 Hz), 63.6, 25.5, 25.04, 24.99 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): –58.0 ppm. – IR: 2937, 2860, 1591, 1474, 1454, 1432, 1316, 1253, 1205, 1168, 1139, 1118 cm^{-1}. – HRMS calcd for $C_{13}H_{15}F_3O_3S$: 309.0767, found 309.0768 [M+H$^+$].

1-(Cyclohexylsulfonyl)-2-(trifluoromethoxy)benzene (3k)

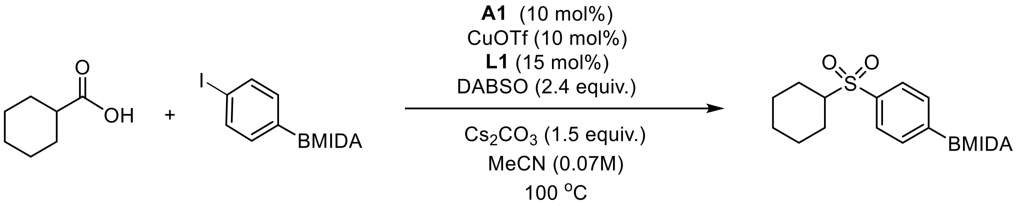


According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 1-iodo-2-(trifluoromethoxy)benzene (173 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½$PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **3k** (60 mg, 65%) as a colorless solid.

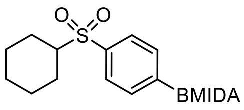


m.p.: 100–102 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.07 (dd, J = 7.8, 1.7 Hz, 1H), 7.70 (td, J = 7.9, 1.8 Hz, 1H), 7.50–7.44 (m, 2H), 3.25 (tt, J = 12.1, 3.4 Hz, 1H), 2.02–1.87 (m, 4H), 1.75–1.69 (m, 1H), 1.60–1.52 (m, 2H), 1.34–1.17 (m, 3H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 147.1, 135.3, 132.3, 129.9, 126.7, 120.23 (q, J = 261.1 Hz), 120.18, 62.8, 25.1, 25.0, 24.9 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -56.04 ppm. – IR: 2936, 2859, 1590, 1474, 1446, 1317, 1270, 1245, 1206, 1170, 1145 1065 cm^{-1}. – HRMS calcd for $C_{13}H_{15}F_3O_3S$: 309.0767, found 309.0769 [M+H$^+$].

2-(4-(Cyclohexylsulfonyl)phenyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3l)

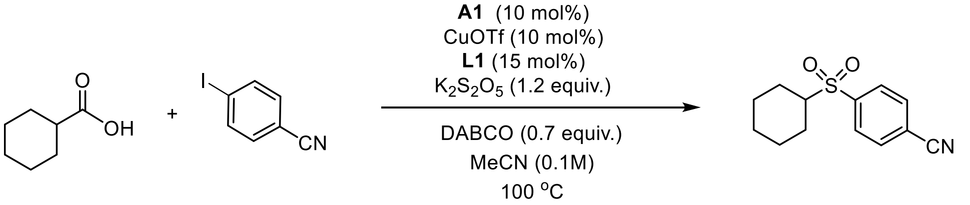


According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), 2-(4-iodophenyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (107 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:6 v/v) to give sulfone **3l** (77 mg, 68%) as a colorless solid.

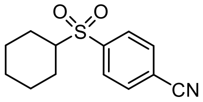


m.p.: >200 °C. – ^{1}H NMR (500 MHz, (CD$_3$)$_2$CO): 7.95–7.71 (m, 4H), 4.44 (d, *J* = 17.1 Hz, 2H), 4.25 (d, *J* = 17.1 Hz, 2H), 3.11–3.00 (m, 1H), 2.81 (d, *J* = 1.7 Hz, 3H), 2.00 (dd, *J* = 12.9, 3.3 Hz, 2H), 1.82 (dt, *J* = 13.2, 3.3 Hz, 2H), 1.65 (dddt, *J* = 14.4, 4.9, 3.2, 1.8 Hz, 1H), 1.43–1.10 (m, 5H) ppm. – ^{13}C NMR (125 MHz, (CD$_3$)$_2$CO): 168.3, 138.4, 134.6, 133.3, 128.0, 127.7, 62.5, 62.1, 47.6, 25.4, 25.0, 24.7 ppm. – IR: 3053, 3045, 2927, 2857, 1641, 1491, 1445, 905, 759, 744 cm^{-1}. – HRMS calcd for $C_{17}H_{22}BNO_6S$: 380.1334, found 380.1338 [M+H$^+$].

4-(Cyclohexylsulfonyl)benzonitrile (3m)[13]

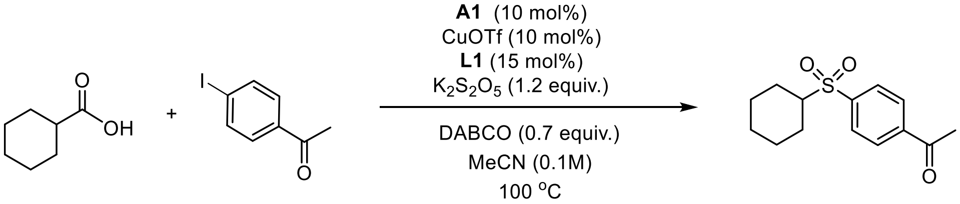


According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 4-iodobenzonitrile (137 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **3m** (63 mg, 84%) as a colorless solid.

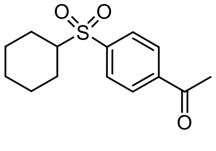


m.p.: 121–123 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.03–8.00 (m, 2H), 7.90–7.87 (m, 2H), 2.95 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.08–2.03 (m, 2H), 1.89 (dt, *J* = 13.2, 3.3 Hz, 2H), 1.70 (dt, *J* = 13.2, 3.1 Hz, 1H), 1.42 (qd, *J* = 12.5, 3.4 Hz, 2H), 1.21 (ddddd, *J* = 25.3, 22.1, 15.9, 9.8, 6.4 Hz, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 141.6, 132.8, 129.8, 117.4, 117.2, 63.6, 25.4, 25.0, 24.9 ppm. – IR: 3092, 2936, 2859, 2232, 1453, 1397, 1314, 1270, 1143 cm^{-1}. – HRMS calcd for $C_{13}H_{15}NO_2S$: 250.0896, found 2500896 [M+H$^+$].

1-(4-(Cyclohexylsulfonyl)phenyl)ethan-1-one (3n)

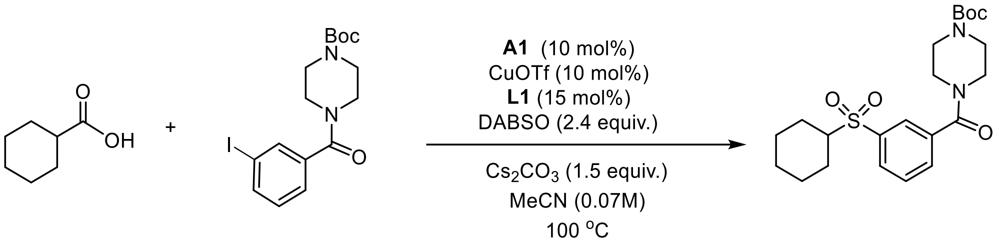


According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 1-(4-iodophenyl)ethan-1-one (148 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **3n** (54 mg, 68%) as a colorless solid.

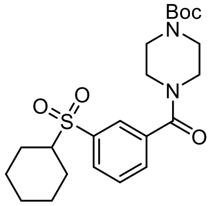


m.p.: 105–108 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.15–8.11 (m, 2H), 8.02–7.98 (m, 2H), 2.95 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.69 (s, 3H), 2.11–2.05 (m, 2H), 1.89 (dt, *J* = 12.7, 3.1 Hz, 2H), 1.73–1.67 (m, 1H), 1.43 (qd, *J* = 12.5, 3.5 Hz, 2H), 1.30–1.11 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 196.8, 141.2, 140.8, 129.5, 128.7, 63.6, 26.9, 25.5, 25.1, 25.0 ppm. – IR: 2921, 2853, 1685, 1595, 1443, 1397, 1356, 1306, 1289, 1269, 1180 cm^{-1}. – HRMS calcd for $C_{14}H_{18}O_3S$: 267.1049, found 267.1046 [M+H$^+$].

tert-Butyl 4-(3-(cyclohexylsulfonyl)benzoyl)piperazine-1-carboxylate (3o)

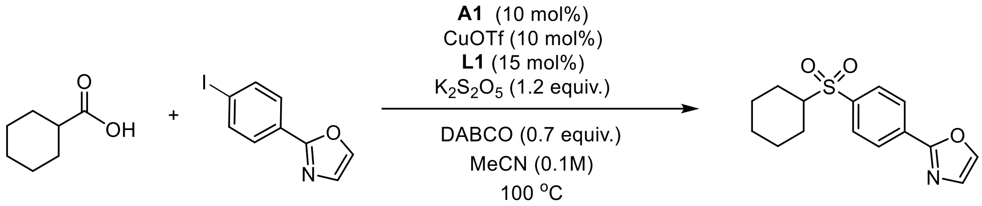


According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), *tert*-butyl 4-(3-iodobenzoyl)piperazine-1-carboxylate (125 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:6 v/v) to give sulfone **3o** (110 mg, 84%) as a colorless solid.

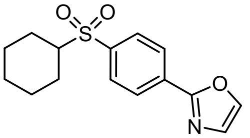


m.p.: 162–165 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.92 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 3.74 (s, 2H), 3.53–3.33 (m, 6H), 2.90 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.06–2.01 (m, 2H), 1.84 (dt, *J* = 13.1, 3.3 Hz, 2H), 1.67–1.63 (m, 1H), 1.45 (s, 9H), 1.38 (td, *J* = 12.5, 3.5 Hz, 1H), 1.26–1.07 (m, 4H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 168.5, 154.4, 138.0, 136.6, 132.2, 130.3, 129.6, 127.4, 80.5, 63.5, 47.6, 42.2, 28.3, 25.4, 24.99, 24.95 ppm. – IR: 2956, 2933, 2878, 1756, 1732, 1641, 1586, 1577, 1512, 1480, 1467, 1381 cm^{-1}. – HRMS calcd for $C_{22}H_{32}N_2O_5S$: 437.2105, found 437.2105 [M+H$^+$].

2-(4-(Cyclohexylsulfonyl)phenyl)oxazole (3p)

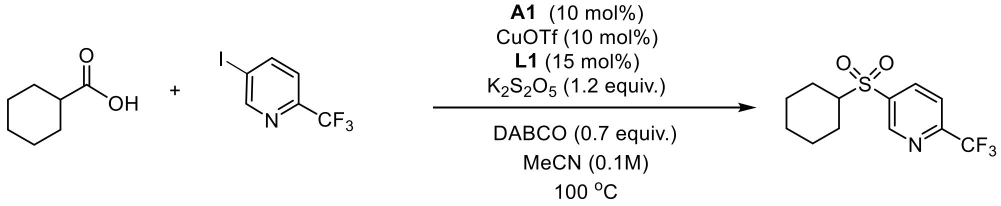


According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 2-(4-iodophenyl)oxazole (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **3p** (59 mg, 68%) as a colorless solid.

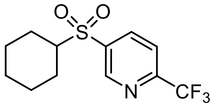


m.p.: 137–140 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.27–8.23 (m, 2H), 8.00–7.96 (m, 2H), 7.81 (d, *J* = 0.8 Hz, 1H), 7.34 (d, *J* = 0.8 Hz, 1H), 2.95 (tt, *J* = 12.1, 3.4 Hz, 1H), 2.13–2.07 (m, 2H), 1.89 (dt, *J* = 12.8, 3.1 Hz, 2H), 1.72–1.65 (m, 1H), 1.44 (qd, *J* = 12.5, 3.6 Hz, 2H), 1.30–1.10 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 160.3, 139.7, 138.5, 132.0, 129.7, 129.2, 126.7, 63.6, 25.5, 25.1, 25.0 ppm. – IR: 2934, 2920, 2854, 1731, 1686, 1604, 1581, 1552, 1507, 1482, 1451, 1405, 1367, 1328, 1308, 1290, 1275 cm^{-1}. – HRMS calcd for $C_{15}H_{17}NO_3S$: 292.1002, found 292.1005 [M+H$^+$].

5-(Cyclohexylsulfonyl)-2-(trifluoromethyl)pyridine (3q)

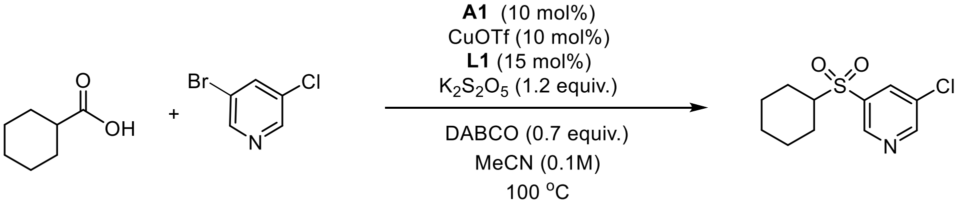


According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 5-iodo-2-(trifluoromethyl)pyridine (164 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **3q** (66 mg, 75%) as a colorless solid.

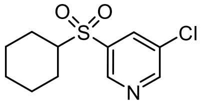


m.p.: 105–108 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 9.18 (d, *J* = 2.1 Hz, 1H), 8.38 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.92 (dd, *J* = 8.2, 0.8 Hz, 1H), 3.00 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.14–2.09 (m, 2H), 1.93 (dt, *J* = 12.6, 3.1 Hz, 2H), 1.76–1.71 (m, 1H), 1.46 (qd, *J* = 12.5, 3.6 Hz, 2H), 1.33–1.14 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 152.1 (q, *J* = 35.7 Hz), 150.2, 138.8, 136.7, 120.7 (q, *J* = 275.3 Hz), 120.7, 64.0, 25.4, 24.94, 24.86 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -68.2 ppm. – IR: 3290, 3079, 2834, 1647, 1554, 1365, 1336, 918 cm^{-1}. – HRMS calcd for $C_{12}H_{14}F_3NO_2S$: 294.0770, found 294.0762 [M+H$^+$].

3-Chloro-5-(cyclohexylsulfonyl)pyridine (3r)

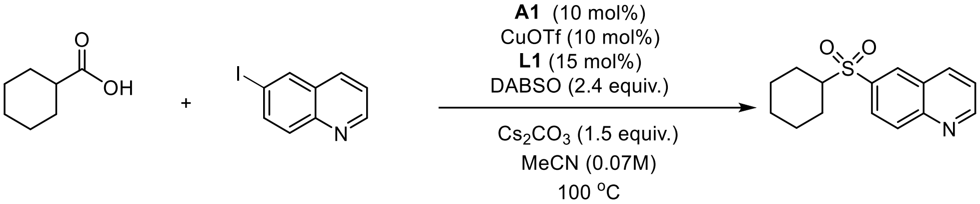


According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 3-bromo-5-chloropyridine (115 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **3r** (65 mg, 84%) as a colorless solid.

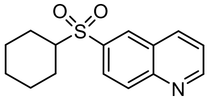


m.p.: 78–80 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.94 (d, *J* = 1.9 Hz, 1H), 8.85 (d, *J* = 2.3 Hz, 1H), 8.15 (t, *J* = 2.1 Hz, 1H), 2.97 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.14–2.08 (m, 2H), 1.92 (dt, *J* = 12.9, 3.1 Hz, 2H), 1.72 (dddd, *J* = 12.7, 5.0, 3.1, 1.6 Hz, 1H), 1.45 (qd, *J* = 12.5, 3.5 Hz, 2H), 1.32–1.13 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 153.2, 147.5, 136.3, 134.8, 132.7, 64.0, 25.4, 25.0, 24.9 ppm. – IR: 2943, 2925, 2862, 1451, 1376, 1333, 1311, 1295, 1276, 1170 cm^{-1}. – HRMS calcd for $C_{11}H_{14}ClNO_2S$: 260.0507, 260.0509 found [M+H$^+$].

6-(Cyclohexylsulfonyl)quinolone (3s)

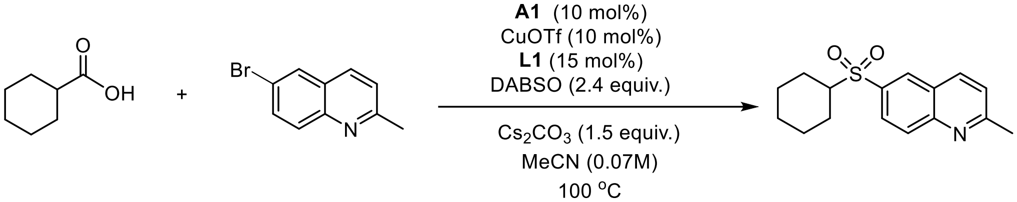


According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), 6-iodoquinoline (77 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **3s** (62 mg, 79%) as a colorless solid.



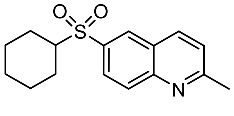
m.p.: 85–88 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 9.11 (dd, *J* = 4.0, 1.8 Hz, 1H), 8.47 (d, *J* = 2.0 Hz, 1H), 8.34 (dd, *J* = 8.4, 1.7 Hz, 1H), 8.29 (d, *J* = 8.8 Hz, 1H), 8.11 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.58 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.03 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.15–2.10 (m, 2H), 1.88 (dt, *J* = 13.7, 3.4 Hz, 2H), 1.71–1.66 (m, 1H), 1.48 (qd, *J* = 12.5, 3.5 Hz, 2H), 1.29–1.11 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 153.4, 149.8, 137.4, 135.2, 131.0, 127.5, 127.3, 122.6, 63.6, 25.6, 25.1, 25.0 ppm. – IR: 3060, 2934, 2852, 1490, 1451, 1324, 1302, 1273, 1177 cm^{-1}. – HRMS calcd for $C_{15}H_{17}NO_2S$: 276.1053, found 276.1049 [M+H$^+$].

6-(Cyclohexylsulfonyl)-2-methylquinoline (3t)



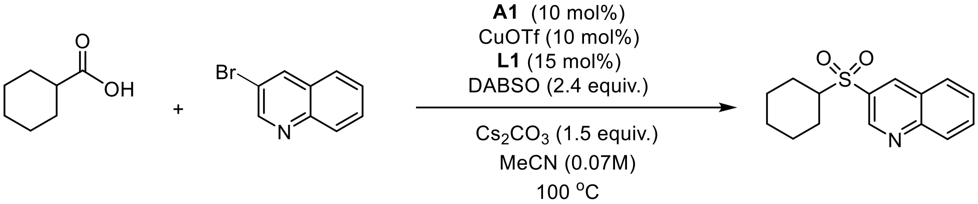
According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), 6-bromo-2-methylquinoline (67 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:3 v/v) to give sulfone **3t** (75 mg, 87%) as a colorless solid.

Gram scale synthesis: According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (1.52 g, 12 mmol, 2 equiv.), 6-bromo-2-methylquinoline (1.34 g, 6 mmol), acridine **A1** (160 mg, 0.6 mmol, 10 mol%), CuOTf·½PhCH$_3$ (320 mg, 0.6 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (120 mg, 0.9 mmol, 15 mol%), cesium carbonate (2.92 g, 9 mmol, 1.5 equiv.), and DABSO (3.46 g, 14.4 mmol, 2.4 equiv.) and acetonitrile (90 mL) was then added. The tube was sealed with a screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 24 h. The reaction mixture was then diluted with ethyl acetate (100 mL) and washed with a saturated aqueous solution of EDTA (30 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:3 v/v) to give sulfone **3t** (1.23 g, 71%) as a colorless solid.

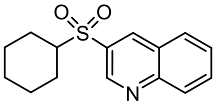


m.p.: 105–107 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.38 (d, *J* = 2.0 Hz, 1H), 8.17 (dd, *J* = 17.7, 8.6 Hz, 2H), 8.04 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 2.99 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.80 (s, 3H), 2.13–2.07 (m, 2H), 1.85 (dt, *J* = 13.4, 3.3 Hz, 2H), 1.68–1.63 (m, 1H), 1.45 (qd, *J* = 12.6, 3.5 Hz, 2H), 1.27–1.08 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 162.7, 149.5, 137.3, 134.1, 130.6, 130.0, 127.5, 125.5, 123.7, 63.6, 25.7, 25.6, 25.1, 25.0 ppm. – IR: 3017, 2931, 2854, 2399, 1715, 1614, 1594, 1589, 1519, 1484, 1463, 1453, 1434 cm^{-1}. – HRMS calcd for $C_{16}H_{19}NO_2S$: 290.1209, found 290.1208 [M+H$^+$].

3-(Cyclohexylsulfonyl)quinolone (3u)

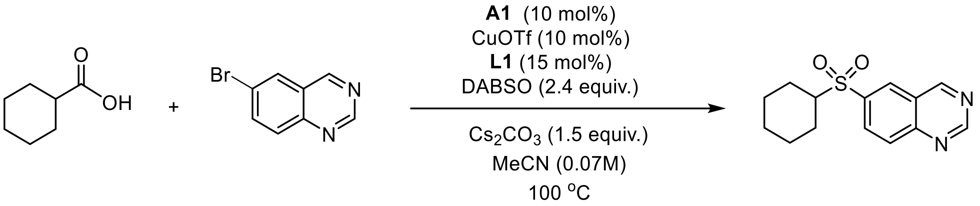


According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), 3-bromoquinoline (62 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:3 v/v) to give sulfone **3u** (65 mg, 79%) as a colorless solid.

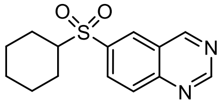


m.p.: 100–103 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 9.26 (s, 1H), 8.74 (d, *J* = 2.1 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.95 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 3.04 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.19–2.13 (m, 2H), 1.89 (dt, *J* = 13.5, 3.3 Hz, 2H), 1.70 (dd, *J* = 13.1, 3.6 Hz, 1H), 1.48 (qd, *J* = 12.6, 3.6 Hz, 2H), 1.31–1.10 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 149.7, 147.9, 138.9, 132.9, 130.3, 129.7, 129.2, 128.4, 126.3, 64.1, 25.6, 25.0, 24.9 ppm. – IR: 3061, 2965, 2924, 2893, 2875, 2234, 2114, 1509, 1485, 1364, 1265, 1195 cm^{-1}. – HRMS calcd for $C_{15}H_{17}NO_2S$: 276.1053, found 276.1049 [M+H$^+$].

6-(Cyclohexylsulfonyl)quinazoline (3v)

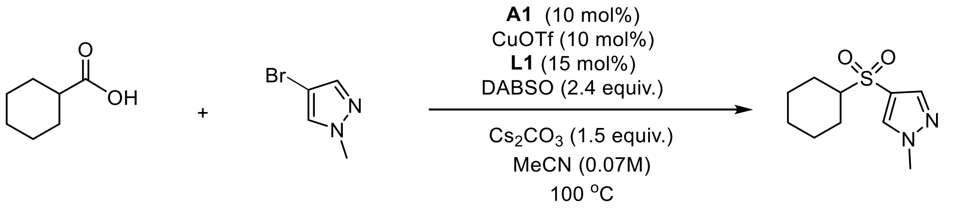


According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), 6-iodoquinazoline (63 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:3 v/v) to give sulfone **3v** (53 mg, 64%) as a colorless solid.



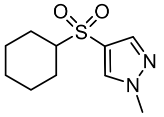
m.p.: 120–123 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 9.58 (m, 2H), 8.59 (d, *J* = 1.9 Hz, 1H), 8.31 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 3.03 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.15–2.08 (m, 2H), 1.89 (dt, *J* = 13.6, 3.3 Hz, 2H), 1.70 (dt, *J* = 12.9, 3.1 Hz, 1H), 1.48 (qd, *J* = 12.5, 3.6 Hz, 2H), 1.30–1.09 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 161.6, 157.6, 151.7, 136.9, 132.1, 130.4, 130.1, 63.7, 25.5, 25.0, 24.9 ppm. – IR: 3118, 2810, 2156, 1620, 1520, 1416, 1358, 1326, 1105, 997 cm^{-1}. – HRMS calcd for $C_{14}H_{16}N_2O_2S$: 277.1005, found 277.1008 [M+H$^+$].

4-(Cyclohexylsulfonyl)-1-methyl-1*H*-pyrazole (3w)



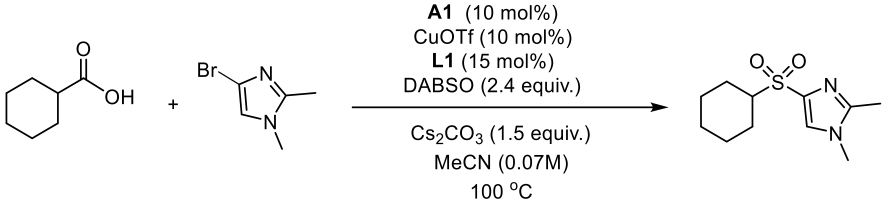
According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), 4-bromo-1-methyl-1*H*-pyrazole (48 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO

(173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:9 v/v) to give sulfone **3w** (51 mg, 75%) as a colorless solid.

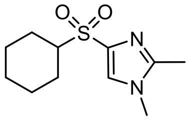


m.p.: 67–69 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.81–7.79 (m, 2H), 3.99 (s, 3H), 2.87 (tt, *J* = 12.1, 3.4 Hz, 1H), 2.21–2.15 (m, 2H), 1.90 (dp, *J* = 13.1, 3.4 Hz, 2H), 1.71 (dqd, *J* = 13.2, 3.3, 1.7 Hz, 1H), 1.40 (qd, *J* = 12.5, 3.4 Hz, 2H), 1.28 (qt, *J* = 13.0, 3.3 Hz, 2H), 1.16 (qt, *J* = 12.9, 3.5 Hz, 1H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 140.2, 133.4, 64.0, 39.7, 25.6, 25.1 ppm. – IR: 3006, 2931, 2854, 2843, 1748, 1703, 1618, 1575, 1480, 1379, 1352, 1234 cm^{-1}. – HRMS calcd for $C_{10}H_{16}N_2O_2S$: 229.1005, found 229.1004 [M+H$^+$].

4-(Cyclohexylsulfonyl)-1,2-dimethyl-1*H*-imidazole (3x)



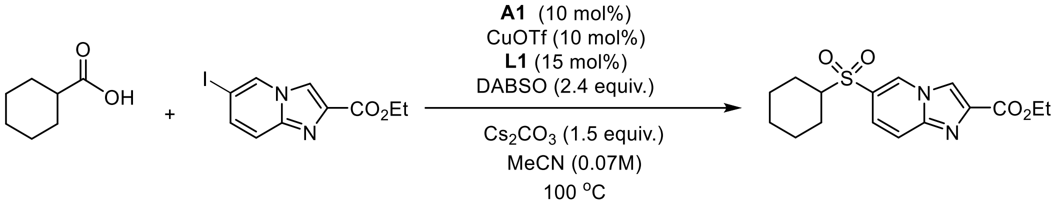
According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.3 mmol), 4-bromo-1,2-dimethyl-1*H*-imidazole (52 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:9 v/v) to give sulfone **3x** (54 mg, 75%) as a colorless solid.



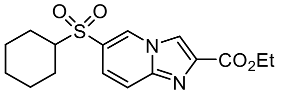
m.p.: 85–87 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.44 (s, 1H), 3.64 (s, 3H), 3.08 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.42 (s, 3H), 2.15–2.09 (m, 2H), 1.87 (dt, *J* = 12.5, 3.0 Hz, 2H), 1.71–1.66 (m, 1H), 1.49 (qd, *J* = 12.6, 3.5 Hz, 2H), 1.31–1.13 (m, 3H) ppm. – ^{13}C

NMR (125 MHz, $CDCl_3$): 147.5, 136.0, 126.6, 61.7, 33.5, 25.2, 25.2, 25.1, 13.1 ppm. – IR: 3400, 3019, 2945, 2853, 1461, 1217, 908, 755, 733 cm^{-1}. – HRMS calcd for $C_{11}H_{18}N_2O_2S$: 243.1162, found 243.1160 [M+H$^+$].

Ethyl 6-(cyclohexylsulfonyl)imidazo[1,2-*a*]pyridine-2-carboxylate (3y)

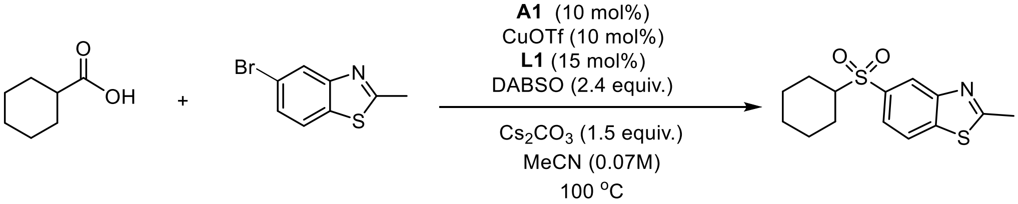


According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), ethyl 6-iodoimidazo[1,2-*a*]pyridine-2-carboxylate (95 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½$PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:9 v/v) to give sulfone **3y** (79 mg, 78%) as a colorless solid.

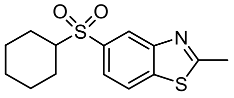


m.p.: 147–150 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.81 (s, 1H), 8.35 (s, 1H), 7.80 (d, *J* = 9.6 Hz, 1H), 7.54 (dd, *J* = 9.6, 1.8 Hz, 1H), 4.48 (q, *J* = 7.2 Hz, 2H), 3.01 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.12 (d, *J* = 12.5 Hz, 2H), 1.93–1.87 (m, 2H), 1.71 (d, *J* = 13.0 Hz, 1H), 1.52–1.42 (m, 5H), 1.31–1.12 (m, 3H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 162.4, 144.9, 139.2, 130.6, 125.7, 123.8, 119.4, 118.4, 63.8, 61.6, 25.5, 25.0, 24.9, 14.4 ppm. – IR: 3044, 2926, 2844, 1624, 1581, 1515, 1403, 1370, 2393, 1251 cm^{-1}. – HRMS calcd for $C_{16}H_{20}N_2O_4S$: 337.1217, found 337.1214 [M+H$^+$].

5-(Cyclohexylsulfonyl)-2-methylbenzo[*d*]thiazole (3z)

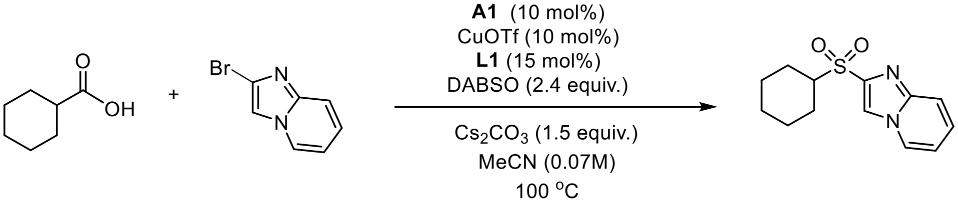


According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), 5-bromo-2-methylbenzo[*d*]thiazole (68 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:2 v/v) to give sulfone **3z** (62 mg, 70%) as a colorless solid.

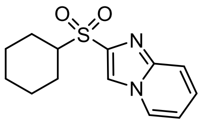


m.p.: 87–90 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.45 (d, *J* = 1.8 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.83 (dd, *J* = 8.3, 1.4 Hz, 1H), 2.96 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.90 (s, 3H), 2.12–2.08 (m, 2H), 1.85 (dt, *J* = 13.2, 3.3 Hz, 2H), 1.69–1.64 (m, 1H), 1.43 (qd, *J* = 12.5, 3.6 Hz, 2H), 1.27–1.09 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 169.8, 153.1, 141.4, 135.2, 124.3, 124.2, 123.5, 122.0, 63.8, 25.6, 25.1, 25.0, 20.4 ppm. – IR: 3394, 3050, 2982, 2933, 2852, 1620, 1565, 1457, 1367, 1338 cm^{-1}. – HRMS calcd for $C_{14}H_{17}NO_2S_2$: 296.0773, found 296.0778 [M+H$^+$].

2-(Cyclohexylsulfonyl)imidazo[1,2-*a*]pyridine (3aa)

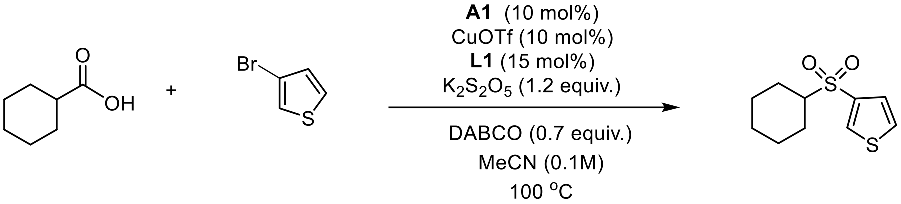


According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), 2-bromoimidazo[1,2-*a*]pyridine (59 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:3 v/v) to give sulfone **3aa** (44 mg, 56%) as a colorless solid.

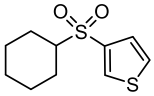


m.p.: 135–137 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.21 (d, *J* = 6.9 Hz, 1H), 8.17 (s, 1H), 7.70 (d, *J* = 9.2 Hz, 1H), 7.35 (dd, *J* = 9.2, 6.8 Hz, 1H), 6.97 (t, *J* = 6.8 Hz, 1H), 3.30 (td, *J* = 12.2, 6.1 Hz, 1H), 2.19–2.13 (m, 2H), 1.89 (dt, *J* = 13.3, 3.4 Hz, 2H), 1.71–1.68 (m, 1H), 1.58 (qd, *J* = 12.6, 3.5 Hz, 2H), 1.33–1.14 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 145.8, 142.4, 127.1, 126.6, 119.1, 116.6, 114.5, 61.9, 25.2, 25.1, 25.0 ppm. – IR: 2920, 2857, 1611, 1584, 1474, 1447, 1379, 1304, 1276, 1263, 1249, 1146 cm^{-1}. – HRMS calcd for $C_{13}H_{16}N_2O_2S$: 265.1005, found 265.1005 [M+H$^+$].

3-(Cyclohexylsulfonyl)thiophene (3ab)

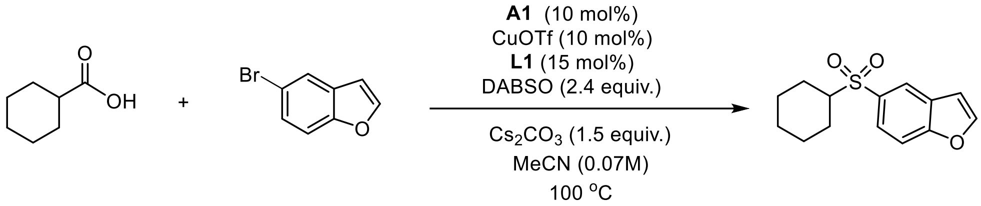


According to GP1, the reaction was carried out with cyclohexanecarboxylic acid (38 mg, 0.3 mmol), 3-bromothiophene (97 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **3ab** (62 mg, 90%) as a colorless solid.

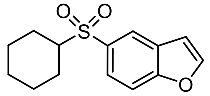


m.p.: 78–80 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.05 (dd, *J* = 3.1, 1.3 Hz, 1H), 7.48 (dd, *J* = 5.1, 3.1 Hz, 1H), 7.37 (dd, *J* = 5.2, 1.3 Hz, 1H), 2.93 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.13 (dtd, *J* = 12.3, 3.9, 2.3 Hz, 2H), 1.89 (dt, *J* = 13.3, 3.3 Hz, 2H), 1.70 (dddd, *J* = 12.7, 5.1, 3.1, 1.5 Hz, 1H), 1.44 (qd, *J* = 12.5, 3.5 Hz, 2H), 1.31–1.11 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 137.9, 133.2, 127.8, 126.9, 63.7, 25.5, 25.1, 25.1 ppm. – IR: 3061, 2969, 2869, 1775, 1735, 1587, 1497, 1445, 1395, 1289, 1224, 1201 cm^{-1}. – HRMS calcd for $C_{10}H_{14}O_2S_2$: 231.0508, found 231.0506 [M+H$^+$].

5-(Cyclohexylsulfonyl)benzofuran (3ac)

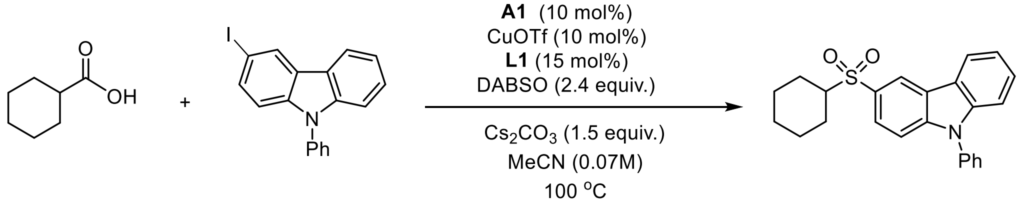


According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), 5-bromobenzofuran (58 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **3ac** (55 mg, 69%) as a colorless solid.



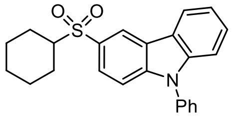
m.p.: 70–73 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.19 (d, *J* = 1.8 Hz, 1H), 7.83 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.79 (d, *J* = 2.2 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 6.92 (dd, *J* = 2.3, 0.9 Hz, 1H), 2.95 (tt, *J* = 12.1, 3.4 Hz, 1H), 2.11 (ddt, *J* = 12.8, 3.8, 1.9 Hz, 2H), 1.87 (dt, *J* = 12.6, 3.0 Hz, 2H), 1.68 (dddd, *J* = 11.0, 5.0, 3.0, 1.6 Hz, 1H), 1.44 (qd, *J* = 12.5, 3.6 Hz, 2H), 1.29–1.09 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 157.3, 147.2, 131.9, 127.9, 125.1, 123.5, 112.0, 107.2, 63.9, 25.7, 25.1, 25.1 ppm. – IR: 3047, 3024, 2955, 2923, 2846, 2767, 1733, 1466, 1384, 1355, 1238, 1226, 1142, 1087 cm^{-1}. – HRMS calcd for $C_{14}H_{16}O_3S$: 265.0893, found 265.0890 [M+H$^+$].

3-(Cyclohexylsulfonyl)-9-phenyl-9*H*-carbazole (3ad)



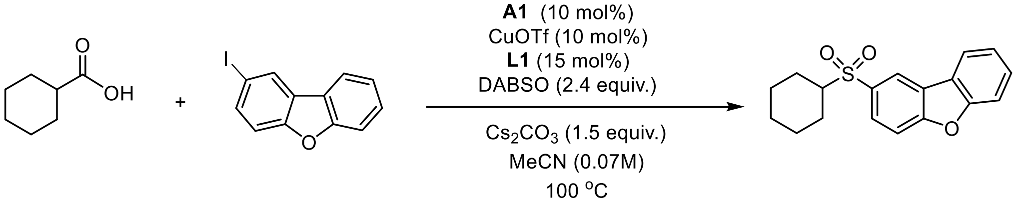
According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), 3-iodo-9-phenyl-9H-carbazole (111 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO

(173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **3ad** (62 mg, 53%) as a colorless solid.

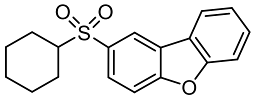


m.p.: 137–140 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.69 (d, *J* = 1.7 Hz, 1H), 8.23 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.88 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.70–7.65 (m, 2H), 7.59–7.47 (m, 5H), 7.45–7.39 (m, 2H), 3.00 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.16 (dd, *J* = 13.1, 3.6 Hz, 2H), 1.87 (dt, *J* = 13.4, 3.2 Hz, 2H), 1.68 (dt, *J* = 12.7, 3.3 Hz, 1H), 1.48 (qd, *J* = 12.6, 3.7 Hz, 2H), 1.30–1.10 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 143.4, 141.9, 136.6, 130.2, 128.4, 127.9, 127.3, 127.2, 126.4, 123.3, 122.7, 122.5, 121.2, 120.8, 110.4, 109.9, 64.1, 25.8, 25.2, 25.1 ppm. – IR: 3062, 2931, 2854, 2249, 1622, 1593, 1500, 1470, 1320 cm^{-1}. – HRMS calcd for $C_{24}H_{23}NO_2S$: 390.1522, found 390.1518 [M+H$^+$].

2-(Cyclohexylsulfonyl)dibenzo[*b*,*d*]furan (3ae)

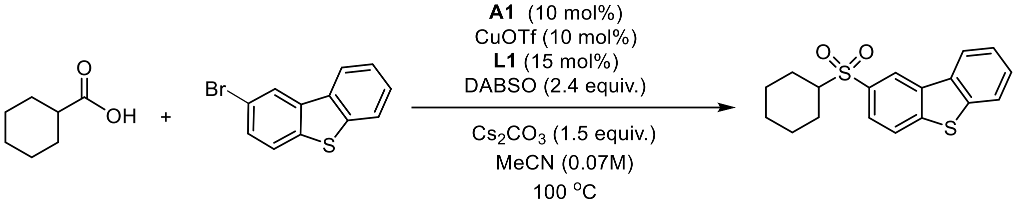


According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), 2-iododibenzo[*b*,*d*]furan (88 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **3ae** (85 mg, 90%) as a colorless solid.

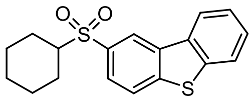


m.p.: 108–110 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.51 (d, *J* = 1.8 Hz, 1H), 8.05–8.02 (m, 1H), 7.99 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.58 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 7.45 (td, *J* = 7.5, 1.0 Hz, 1H), 3.00 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.17–2.12 (m, 2H), 1.88 (dt, *J* = 13.3, 3.3 Hz, 2H), 1.71–1.66 (m, 1H), 1.47 (qd, *J* = 12.6, 3.6 Hz, 2H), 1.30–1.10 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 158.7, 157.0, 131.7, 128.7, 127.9, 125.0, 123.8, 123.0, 122.6, 121.3, 112.2, 112.1, 63.9, 25.7, 25.1, 25.1 ppm. – IR: 2932, 2845, 1464, 1441, 1326, 1196, 1148 cm^{-1}. – HRMS calcd for $C_{18}H_{18}O_3S$: 315.1049, found 315.1047 [M+H$^+$].

2-(Cyclohexylsulfonyl)dibenzo[*b*,*d*]thiophene (3af)

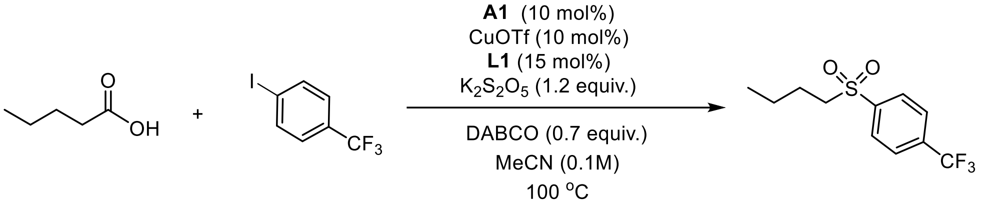


According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), 2-bromodibenzo[*b*,*d*]thiophene (79 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans*-*N*,*N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **3af** (70 mg, 71%) as a colorless solid.

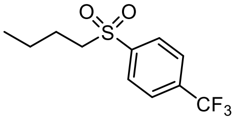


m.p.: 88–90 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.66 (d, *J* = 1.6 Hz, 1H), 8.30–8.26 (m, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.95–7.91 (m, 2H), 7.60–7.54 (m, 2H), 3.01 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.18–2.12 (m, 2H), 1.88 (dt, *J* = 12.9, 3.1 Hz, 2H), 1.72–1.66 (m, 1H), 1.49 (qd, *J* = 12.5, 3.6 Hz, 2H), 1.30–1.11 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 145.0, 139.9, 135.8, 134.5, 133.4, 128.0, 126.1, 125.2, 123.3, 123.0, 122.7, 122.2, 63.9, 25.7, 25.1, 25.1 ppm. – IR: 3059, 2933, 2856, 1583, 1452, 1426, 1407, 1301, 1267, 1227, 1139 cm^{-1}. – HRMS calcd for $C_{18}H_{18}O_2S_2$: 331.0821, found 331.0822 [M+H$^+$].

1-(Butylsulfonyl)-4-(trifluoromethyl)benzene (4a)[14]

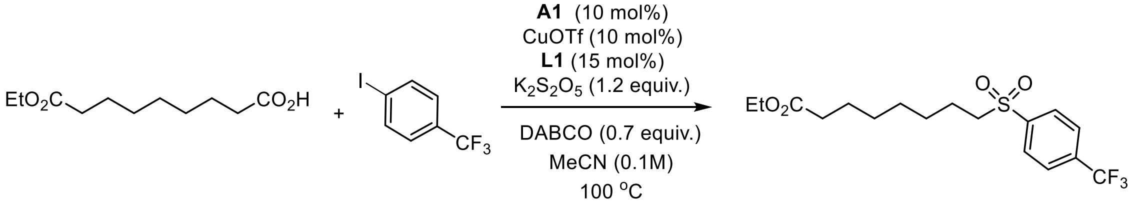


According to GP1, the reaction was carried out with pentanoic acid (31 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **4a** (60 mg, 75%) as a colorless liquid.

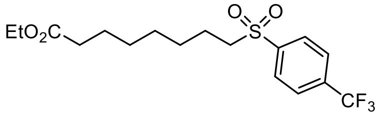


^{1}H NMR (500 MHz, CDCl$_3$): 8.08 (d, *J* = 8.1 Hz, 2 H), 7.87 (d, *J* = 8.2 Hz, 2 H), 3.19–3.07 (m, 2 H), 1.78–1.66 (m, 2 H), 1.43 (h, *J* = 7.4 Hz, 2 H), 0.93 (t, *J* = 7.4 Hz, 3 H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 142.7, 135.4 (q, *J* = 33.1 Hz), 128.8, 126.4 (q, *J* = 3.9 Hz), 123.1 (q, *J* = 273.1 Hz), 56.0, 24.5, 21.5, 13.5 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.2 ppm. – IR: 2963, 2876, 1468, 1403, 1318, 1293, 1234, 1170, 1129, 1106, 1060 cm^{-1}.

Ethyl 8-((4-(trifluoromethyl)phenyl)sulfonyl)octanoate (4b)

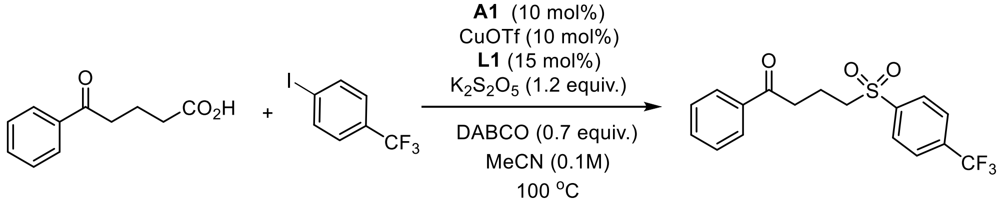


According to GP1, the reaction was carried out with 9-ethoxy-9-oxononanoic acid (65 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **4b** (92 mg, 81%) as a colorless solid.

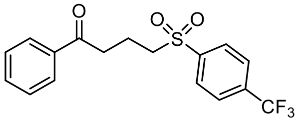


m.p.: 75–78 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.07 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.23–3.04 (m, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 1.74 (ddd, *J* = 11.7, 10.0, 6.4 Hz, 2H), 1.60 (dh, *J* = 7.5, 4.6 Hz, 2H), 1.40 (h, *J* = 7.2 Hz, 2H), 1.34–1.23 (m, 7H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 173.6, 142.7, 135.4 (q, *J* = 33.3 Hz), 128.7, 126.5 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 272.8 Hz), 60.2, 56.2, 34.2, 28.7, 28.6, 28.1, 24.7, 22.5, 14.3 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -63.1 ppm. – IR: 3035, 2945, 2878, 1614, 1533, 1426, 1315, 1255, 1247, 1124 cm^{-1}. – HRMS calcd for $C_{17}H_{23}F_3O_4S$: 381.1342, found 381.1341 [M+H$^+$].

1-Phenyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-1-one (4c)



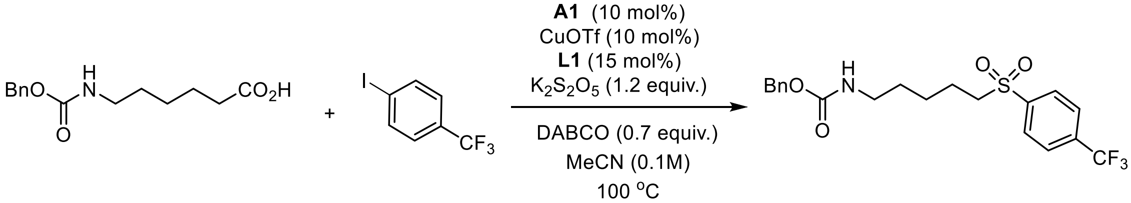
According to GP1, the reaction was carried out with 65-oxo-5-phenylpentanoic acid (58 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½$PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **4c** (85 mg, 80%) as a colorless solid.



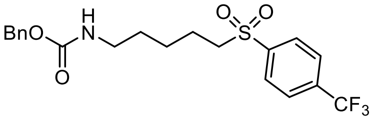
m.p.: 105–107 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.10 (d, *J* = 8.0 Hz, 2H), 7.96–7.91 (m, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 3.31 (dd, *J* = 8.2, 6.8 Hz, 2H), 3.22 (t, *J* = 6.7 Hz, 2H) ppm.

– ^{13}C NMR (125 MHz, CDCl$_3$): 198.2, 142.6, 136.3, 135.5 (q, *J* = 33.5 Hz), 133.5, 128.7, 127.9, 126.5 (q, *J* = 3.8 Hz), 123.1 (q, *J* = 273.4 Hz), 55.1, 36.1, 17.3 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3321, 2966, 2935, 2863, 1637, 1538, 1508, 1323, 1315, 1291, 1274, 1166, 1156, 1208 cm^{-1}. – HRMS calcd for $C_{17}H_{15}F_3O_3S$: 357.0767, found 357.0763 [M+H$^+$].

Benzyl (5-((4-(trifluoromethyl)phenyl)sulfonyl)pentyl)carbamate (4d)

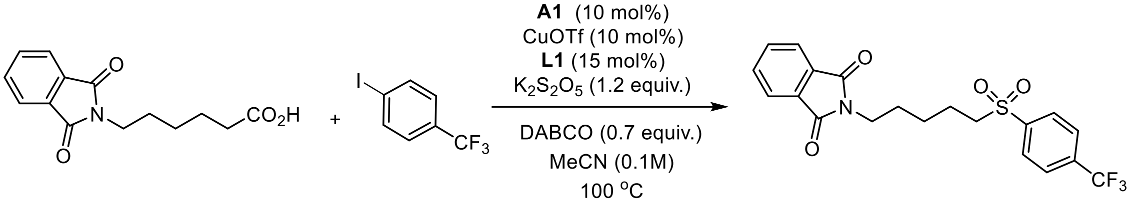


According to GP1, the reaction was carried out with 6-(((benzyloxy)carbonyl)amino)hexanoic acid (80 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **4d** (114 mg, 89%) as a colorless solid.



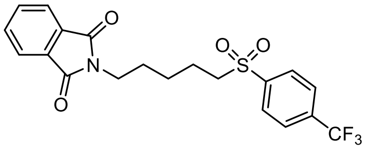
m.p.: 93–95 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.05 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.40–7.30 (m, 5H), 5.09 (s, 2H), 4.87 (s, 1H), 3.14 (dt, *J* = 25.3, 7.3 Hz, 4H), 1.76 (p, *J* = 7.6 Hz, 2H), 1.47 (dq, *J* = 34.7, 7.4 Hz, 4H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 156.4, 142.6, 136.5, 135.5 (q, *J* = 33.4 Hz), 128.7, 128.5, 128.2, 128.1, 126.5 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 272.9 Hz), 66.7, 55.9, 40.6, 29.5, 25.4, 22.3 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3052, 2988, 1736, 1427, 1264, 895, 785 cm^{-1}. – HRMS calcd for $C_{20}H_{22}F_3NO_4S$: 430.1294, found 430.1279 [M+H$^+$].

2-(5-((4-(Trifluoromethyl)phenyl)sulfonyl)pentyl)isoindoline-1,3-dione (4e)



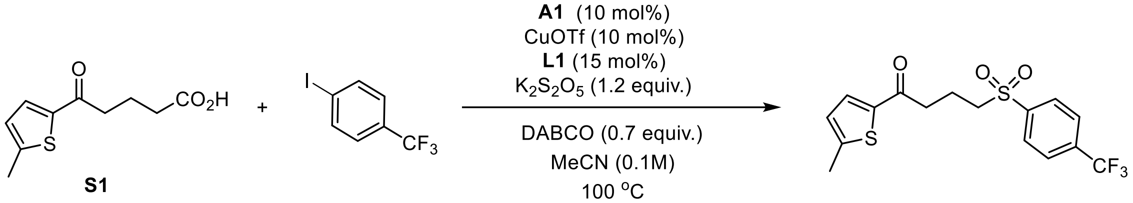
According to GP1, the reaction was carried out with 6-(1,3-dioxoisoindolin-2-yl)hexanoic acid (78 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½$PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **4e** (115 mg, 90%) as a colorless solid.

Gram scale synthesis: According to GP1, the reaction was carried out with 6-(1,3-dioxoisoindolin-2-yl)hexanoic acid (1.04 g, 4 mmol), 1-iodo-4-(trifluoromethyl)benzene (2.17 g, 8 mmol, 2 equiv.), acridine **A1** (106 mg, 0.4 mmol, 10 mol%), CuOTf·½$PhCH_3$ (213 mg, 0.4 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (80 mg, 0.6 mmol, 15 mol%), DABCO (320 mg, 2.8 mmol, 0.7 equiv.), potassium metabisulfite (986 mg, 4.8 mmol, 1.2 equiv.) and acetonitrile (40 mL) was then added. The tube was sealed with a screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 24 h. The reaction mixture was then diluted with ethyl acetate (100 mL) and washed with a saturated aqueous solution of EDTA (30 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **4e** (1.29 g, 76%) as a colorless solid.

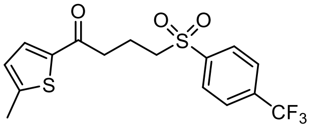


m.p.: 110–112 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.07 (d, *J* = 8.1 Hz, 2H), 7.89–7.83 (m, 4H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 3.67 (t, *J* = 7.1 Hz, 2H), 3.18–3.07 (m, 2H), 1.80 (tt, *J* = 8.0, 6.5 Hz, 2H), 1.70 (p, *J* = 7.3 Hz, 2H), 1.46 (tt, *J* = 10.1, 6.4 Hz, 2H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 142.6, 135.5 (q, *J* = 33.1 Hz), 134.0, 132.0, 126.5 (q, *J* = 3.7 Hz), 128.8, 123.3, 123.1 (q, *J* = 273.3 Hz), 55.9, 37.4, 28.0, 25.5, 22.2 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -63.1 ppm. – IR: 3383, 2980, 2924, 2878, 1652, 1455, 1355, 1341, 1268, 1204 cm^{-1}. – HRMS calcd for $C_{20}H_{18}F_3NO_4S$: 426.0981, found 426.0973 [M+H$^+$].

1-(5-Methylthiophen-2-yl)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-1-one (4f)

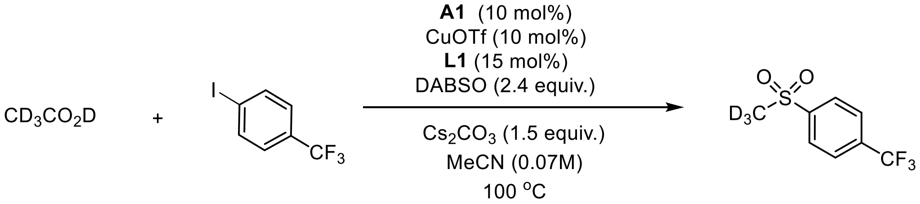


According to GP1, the reaction was carried out with 5-(5-methylthiophen-2-yl)-5-oxopentanoic acid (**S1**) (64 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **4f** (75 mg, 67%) as a colorless solid.

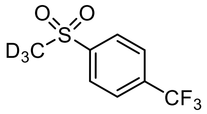


m.p.: 110–112 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.08 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 3.7 Hz, 1H), 6.80 (dd, *J* = 3.8, 1.1 Hz, 1H), 3.32–3.25 (m, 2H), 3.07 (t, *J* = 6.8 Hz, 2H), 2.54 (d, *J* = 0.9 Hz, 3H), 2.16 (dq, *J* = 8.9, 6.9 Hz, 2H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 190.7, 150.3, 142.6, 141.3, 135.5 (q, *J* = 33.4 Hz), 132.8, 128.7, 126.9, 126.5 (q, *J* = 3.8 Hz), 123.1 (q, *J* = 273.0 Hz), 55.0, 36.2, 17.6, 16.0 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3286, 3058, 3036, 2975, 2972, 1613, 1493, 1462, 1447, 0328, 1227, 1101, 981 cm^{-1}. – HRMS calcd for $C_{16}H_{15}F_3O_2S_2$: 377.0487, found 377.0489 [M+H$^+$].

1-((Methyl-*d*$_3$)sulfonyl)-4-(trifluoromethyl)benzene (4g)

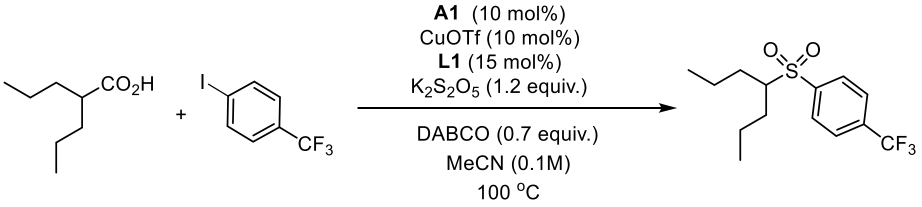


According to GP2, the reaction was carried out with deuterated acetic acid (39 mg, 0.6 mmol, 2 equiv.), 1-iodo-4-(trifluoromethyl)benzene (82 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), $CuOTf\cdot\frac{1}{2}PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **4g** (35 mg, 52%) as a colorless solid.

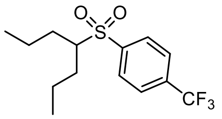


m.p.: 48–50 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.12 (2 H, d, *J* = 8.1 Hz), 7.88 (2 H, d, *J* = 8.1 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 143.9, 135.5 (q, *J* = 33.3 Hz), 128.1, 126.6 (q, *J* = 3.8 Hz), 123.1 (q, *J* = 273.2 Hz) ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.2 ppm. – ^{2}D NMR (77 MHz, CDCl$_3$): 3.05 (3 H, s) ppm. – IR: 3033, 2937, 2846, 1563, 1482, 1436, 1417, 1301, 1266, 1227, 1129 cm^{-1}. – HRMS calcd for $C_8H_4D_3F_3O_2S$: 228.0380, found [M+H$^+$].

1-(Heptan-4-ylsulfonyl)-4-(trifluoromethyl)benzene (4h)

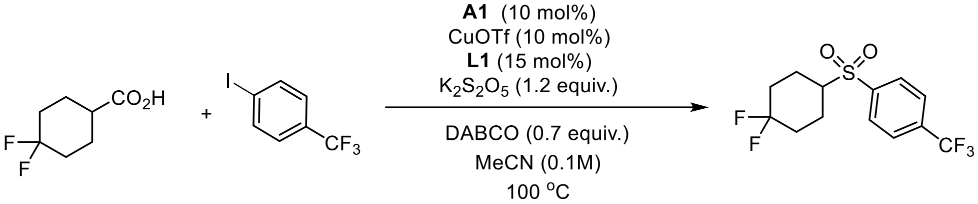


According to GP1, the reaction was carried out with 2-propylpentanoic acid (43 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), $CuOTf\cdot\frac{1}{2}PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **4h** (71 mg, 77%) as a colorless oil.

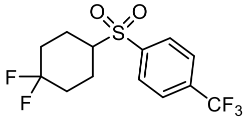


^{1}H NMR (500 MHz, CDCl$_3$): 8.05 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 2.98 (tt, *J* = 7.3, 4.8 Hz, 1H), 1.82 (dddd, *J* = 13.9, 10.3, 5.8, 4.7 Hz, 2H), 1.65–1.46 (m, 4H), 1.39 (dddd, *J* = 13.3, 10.4, 7.2, 5.8 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 6H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 141.9, 135.2 (q, *J* = 33.3 Hz), 129.5, 126.2 (q, *J* = 3.8 Hz), 123.2 (q, *J* = 273.0 Hz), 64.3, 29.9, 20.1, 20.0, 13.9 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3087, 3076, 2951, 2934, 2873, 2155, 1739, 1680, 1499, 1449, 1323, 1217 cm^{-1}. – HRMS calcd for $C_{14}H_{19}F_3O_2S$: 309.1131, found 309.1132 [M+H$^+$].

1-((4,4-Difluorocyclohexyl)sulfonyl)-4-(trifluoromethyl)benzene (4i)



According to GP1, the reaction was carried out with 4,4-difluorocyclohexane-1-carboxylic acid (49 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **4i** (76 mg, 77%) as a colorless solid.



m.p.: 55–58 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.05 (d, *J* = 8.1 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 2H), 3.03 (ddt, *J* = 11.7, 8.0, 2.6 Hz, 1H), 2.34–2.23 (m, 2H), 2.17 (ddt, *J* = 13.0, 5.0, 2.4 Hz, 2H), 1.94–1.68 (m, 4H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 140.4, 135.8 (q, *J* = 33.4 Hz), 129.6, 126.5 (q, *J* = 3.6 Hz), 123.0 (q, *J* = 273.1 Hz), 121.5 (t, *J* = 242.5 Hz), 60.8, 32.1 (t, *J* = 25.4 Hz), 22.3, 22.2 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.3, -94.5 (d, *J* = 241.1 Hz), -102.0 (dt, *J* = 242.6, 31.3 Hz) ppm. – IR: 3057, 2971, 2925, 2862, 2856, 1732, 1473, 1405, 1384, 1207, 1188, 1114, 893, 776 cm^{-1}. – HRMS calcd for $C_{13}H_{13}F_5O_2S$: 328.0556, found 328.0559 [M+H$^+$].

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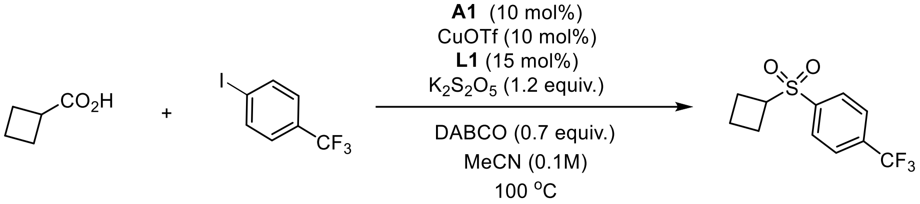
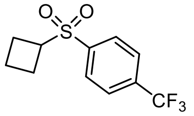
1-(Cyclobutylsulfonyl)-4-(trifluoromethyl)benzene (4j)

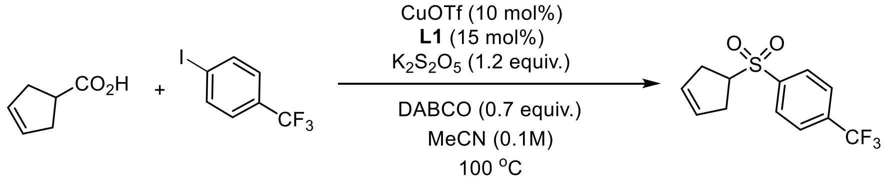


According to GP1, the reaction was carried out with cyclobutanecarboxylic acid (30 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **4j** (65 mg, 82%) as a colorless solid.

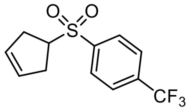


m.p.: 61–63 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.03 (d, *J* = 8.0 Hz, 2H), 7.91–7.78 (m, 2H), 3.84 (p, *J* = 8.3 Hz, 1H), 2.60 (ttd, *J* = 10.8, 8.8, 2.0 Hz, 2H), 2.22 (dtdt, *J* = 10.2, 8.1, 4.1, 2.3 Hz, 2H), 2.09–1.97 (m, 2H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 141.8, 135.3 (d, *J* = 33.0 Hz), 128.9, 126.4 (q, *J* = 3.7 Hz), 123.1 (d, *J* = 273.4 Hz), 56.8, 22.7, 16.9 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3278, 3051, 3026, 2951, 2928, 2862, 2852, 1659, 1640, 1454, 1422, 1308, 1288, 1252, 1127, 1091, 1018 cm^{-1}. – HRMS calcd for $C_{11}H_{11}F_3O_2S$: 265.0505, found 265.0501 [M+H$^+$].

1-(Cyclopent-3-en-1-ylsulfonyl)-4-(trifluoromethyl)benzene (4k)

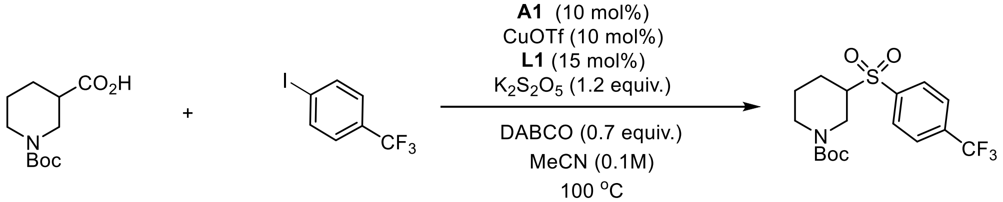


According to GP1, the reaction was carried out with cyclopent-3-ene-1-carboxylic acid (34 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **4k** (75 mg, 91%) as a colorless solid.

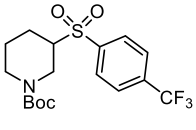


m.p.:–°C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.08 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 5.65 (s, 2H), 3.90 (tt, *J* = 9.5, 6.2 Hz, 1H), 3.01–2.85 (m, 2H), 2.79–2.61 (m, 2H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 142.1, 135.4 (q, *J* = 33.0 Hz), 129.2, 128.2, 126.4 (q, *J* = 3.9 Hz), 123.1 (q, *J* = 273.0 Hz), 62.0, 33.8 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 2935, 2870, 2343, 1516, 1265, 1128, 897 cm^{-1}. – HRMS calcd for $C_{12}H_{11}F_3O_2S$: 277.0505, found 277.0501 [M+H$^+$].

tert-Butyl 3-((4-(trifluoromethyl)phenyl)sulfonyl)piperidine-1-carboxylate (4l)



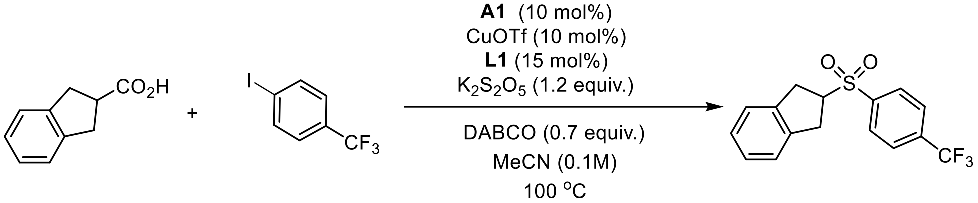
According to GP1, the reaction was carried out with 1-(*tert*-butoxycarbonyl)piperidine-3-carboxylic acid (69 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans*-*N*,*N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **4l** (80 mg, 68%) as a colorless solid.



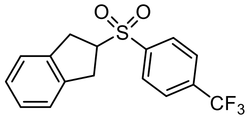
m.p.: 70–73 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.06 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 4.13 (d, *J* = 106.2 Hz, 2H), 3.15–2.89 (m, 2H), 2.71 (s, 1H), 2.24 (d, *J* = 12.9 Hz, 1H), 1.91–1.62 (m, 2H), 1.57–1.24 (m, 10H) ppm. – ^{13}C NMR (125 MHz,

$CDCl_3$): 154.2, 140.9, 135.7 (q, *J* = 33.3 Hz),, 129.5, 126.5 (q, *J* = 3.9 Hz), 123.1 (q, *J* = 273.3 Hz), 80.4, 60.3, 43.6, 28.2, 23.9, 23.4 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -63.1 ppm. – IR: 3096, 3013, 2976, 2925, 1748, 1658, 1456, 1375, 1311, 1299, 1228, 1122 cm^{-1}. – HRMS calcd for $C_{17}H_{22}F_3NO_4S$: 394.1294, found 3941294 [M+H$^+$].

2-((4-(Trifluoromethyl)phenyl)sulfonyl)-2,3-dihydro-1*H*-indene (4m)

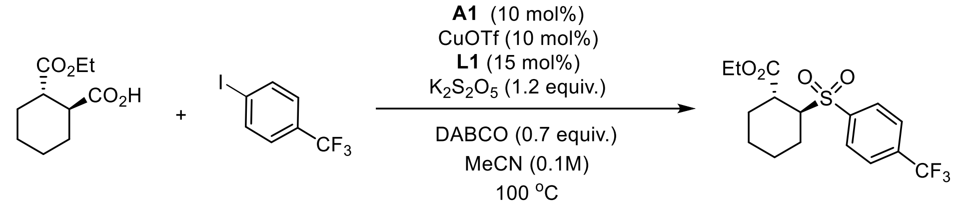


According to GP1, the reaction was carried out with 2,3-dihydro-1H-indene-2-carboxylic acid (49 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **4m** (73 mg, 75%) as a colorless solid.

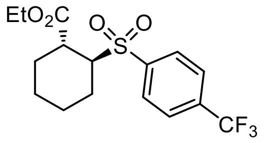


m.p.: 115–117 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.09 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 1.7 Hz, 4H), 4.07 (tt, *J* = 8.8, 7.5 Hz, 1H), 3.51 (dd, *J* = 16.3, 7.5 Hz, 2H), 3.25 (dd, *J* = 16.3, 8.8 Hz, 2H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 141.8, 139.2, 135.5 (q, *J* = 33.0 Hz), 129.3, 127.3, 126.3 (q, *J* = 3.7 Hz), 124.4, 123.1 (d, *J* = 272.9 Hz), 63.7, 33.8 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -63.1 ppm. – IR: 3035, 2954, 2923, 2861, 1739, 1511, 1415, 1404, 1258, 1237, 1194, 1155, 1016 cm^{-1}. – HRMS calcd for $C_{16}H_{13}F_3O_2S$: 327.0661, 327.0658 found [M+H$^+$].

Ethyl (1*R**,2*S**)-2-((4-(trifluoromethyl)phenyl)sulfonyl)cyclohexane-1-carboxylate (4n)

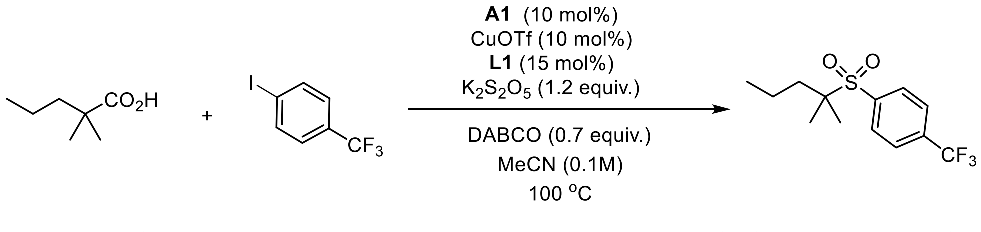


According to GP1, the reaction was carried out with (1*S**,2*S**)-2-(ethoxycarbonyl)cyclohexane-1-carboxylic acid (60 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½$PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N*,*N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **4n** (60mg, 55%) as a colorless solid.



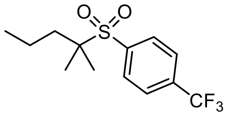
m.p.: 79–81 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.06 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 4.16 (qd, *J* = 7.1, 3.9 Hz, 2H), 3.54 (ddd, *J* = 12.1, 10.9, 4.1 Hz, 1H), 2.63 (td, *J* = 11.4, 4.3 Hz, 1H), 2.15–2.03 (m, 2H), 1.87 (dtd, *J* = 13.0, 3.6, 1.6 Hz, 1H), 1.79–1.68 (m, 1H), 1.58–1.38 (m, 2H), 1.36–1.15 (m, 5H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 173.7, 141.1, 135.5 (q, *J* = 32.9 Hz), 129.9, 126.2 (q, *J* = 3.6 Hz), 123.2 (q, *J* = 273.0 Hz), 63.8, 61.2, 42.7, 30.1, 25.2, 24.1, 23.9, 14.1 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -63.1 ppm. – IR: 3322, 2954, 2837, 2478, 2215, 2071, 1649, 1457, 1325, 1161, 1121 cm^{-1}. – HRMS calcd for $C_{16}H_{19}F_3O_4S$: 365.1029, found 365.1031 [M+H$^+$].

1-((2-Methylpentan-2-yl)sulfonyl)-4-(trifluoromethyl)benzene (4o)



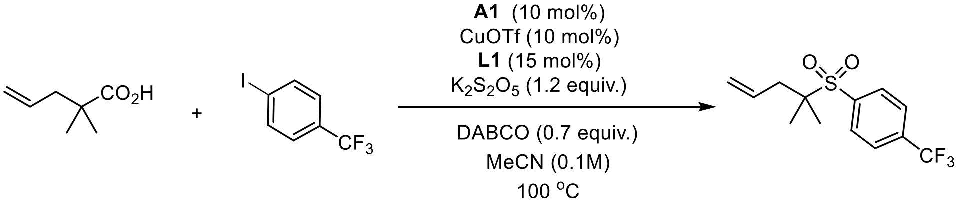
According to GP1, the reaction was carried out with 2,2-dimethylpentanoic acid (39 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½$PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N*,*N'*-dimethylcyclohexane-

1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **4o** (71mg, 81%) as a colorless solid.

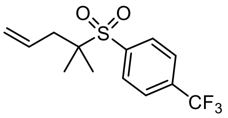


m.p.: 63–65 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.04 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 1.72–1.65 (m, 2H), 1.44–1.30 (m, 8H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 139.4, 135.2 (q, *J* = 33.1 Hz), 131.2, 125.8 (q, *J* = 3.9 Hz), 123.2 (q, *J* = 272.9 Hz), 63.7, 37.0, 20.6, 17.1, 14.5 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3083, 3013, 2576, 2195, 1607, 1510, 1245, 1178, 1133, 1081 cm^{-1}. – HRMS calcd for $C_{13}H_{17}F_3O_2S$: 295.0974, found 295.0971 [M+H$^+$].

1-((2-Methylpent-4-en-2-yl)sulfonyl)-4-(trifluoromethyl)benzene (4p)

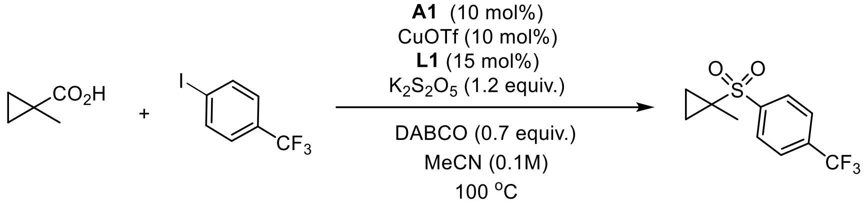


According to GP1, the reaction was carried out with 2,2-dimethylpent-4-enoic acid (38 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **4p** (54 mg, 62%) as a colorless oil.

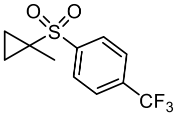


^{1}H NMR (500 MHz, $CDCl_3$): 8.05 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 5.76 (ddt, *J* = 17.3, 10.0, 7.4 Hz, 1H), 5.28–5.04 (m, 2H), 2.48 (dt, *J* = 7.5, 1.1 Hz, 2H), 1.32 (s, 6H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 139.1, 135.4 (q, *J* = 33.5 Hz), 131.2, 131.1, 125.9 (q, *J* = 3.5 Hz), 123.2 (q, *J* = 273.0 Hz), 120.5, 63.1, 39.3, 20.5 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -63.1 ppm. – IR: 3113, 3084, 2943, 2913, 2854, 1739, 1606, 1577, 1566, 1488, 1413, 1176, 1116, 1077, 1046, 991 cm^{-1}. – HRMS calcd for $C_{13}H_{15}F_3O_2S$: 293.0818, found 293.0819 [M+H$^+$].

1-((1-Methylcyclopropyl)sulfonyl)-4-(trifluoromethyl)benzene (4q)

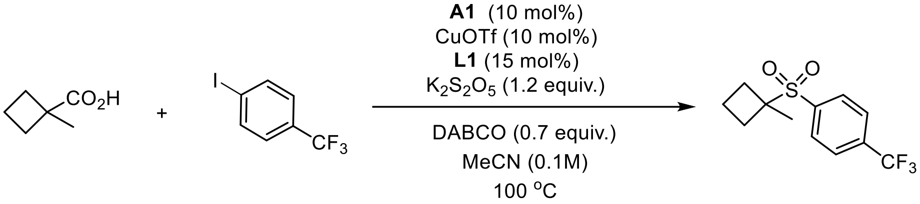


According to GP1, the reaction was carried out with 1-methylcyclopropane-1-carboxylic acid (30 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), $CuOTf\cdot\frac{1}{2}PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **4q** (45 mg, 57%) as a colorless oil.

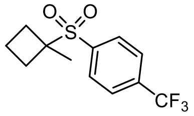


^{1}H NMR (500 MHz, $CDCl_3$): 8.04 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 1.70–1.63 (m, 2H), 1.38 (s, 3H), 0.92–0.86 (m, 2H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 142.0, 135.1 (d, *J* = 33.2 Hz), 129.3, 126.2 (q, *J* = 3.7 Hz), 123.2 (d, *J* = 273.0 Hz), 37.3, 18.0, 13.2 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -63.1 ppm. – IR: 3335, 2933, 2927, 1854, 1712, 1515, 1453, 1382, 1366, 1278, 1268, 1153, 1124, 1053 cm^{-1}. – HRMS calcd for $C_{11}H_{11}F_3O_2S$: 265.0505, found 265.0501 [M+H$^+$].

1-((1-Methylcyclobutyl)sulfonyl)-4-(trifluoromethyl)benzene (4r)

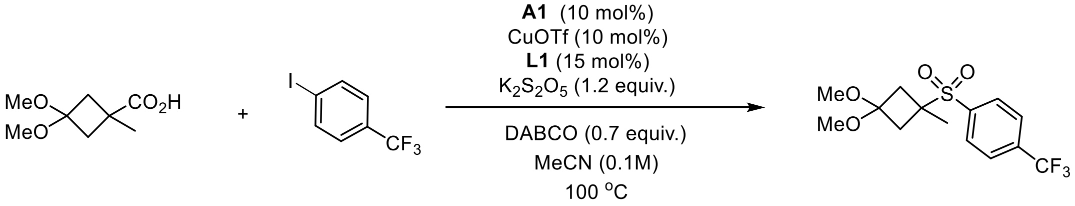


According to GP1, the reaction was carried out with 1-methylcyclobutane-1-carboxylic acid (34 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **4r** (71 mg, 85%) as a colorless oil.



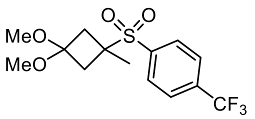
^{1}H NMR (500 MHz, CDCl$_3$): 8.02 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 2.98–2.88 (m, 2H), 2.11–2.00 (m, 2H), 1.86 (tt, *J* = 7.9, 5.0 Hz, 2H), 1.47 (s, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 139.7, 135.2 (q, *J* = 33.2 Hz), 130.1, 126.1 (q, *J* = 3.6 Hz), 123.2 (q, *J* = 273.2 Hz), 61.7, 28.3, 21.4, 14.4 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3042, 3007, 2932, 2854, 1606, 1571, 1338, 1238, 1114, 1106 cm^{-1}. – HRMS calcd for $C_{12}H_{13}F_3O_2S$: 279.0661, found 279.0660 [M+H$^+$].

1-((3,3-Dimethoxy-1-methylcyclobutyl)sulfonyl)-4-(trifluoromethyl)benzene (4s)



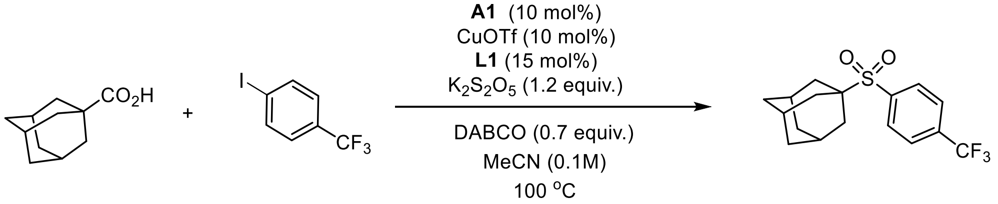
According to GP1, the reaction was carried out with 3,3-dimethoxy-1-methylcyclobutane-1-carboxylic acid (52 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL).

The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **4s** (66 mg, 65%) as a colorless solid.

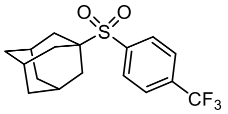


m.p.: 72–75 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.03 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 3.17 (d, *J* = 1.4 Hz, 6H), 3.03–2.88 (m, 2H), 2.18–2.03 (m, 2H), 1.52 (s, 3H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 139.6, 135.4 (q, *J* = 33.4 Hz), 130.2, 126.2 (q, *J* = 3.9 Hz), 123.1 (q, *J* = 273.2 Hz), 97.1, 54.0, 48.7, 48.6, 39.2, 21.5 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -63.1 ppm. – IR: 3087, 2959, 2936, 2874, 1605, 1499, 1365, 1315, 1299, 1159, 1123, 1060, 1031, 986 cm^{-1}. – HRMS calcd for $C_{14}H_{17}F_3O_4S$: 339.0872, found 339.0878 [M+H$^+$].

1-((4-(Trifluoromethyl)phenyl)sulfonyl)adamantine (4t)



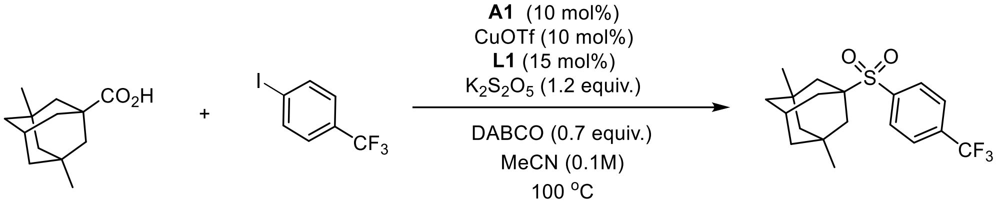
According to GP1, the reaction was carried out with adamantane-1-carboxylic acid (54 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½$PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **4t** (55 mg, 53%) as a colorless solid.



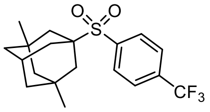
m.p.: 132–135 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.99 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H), 2.20–2.12 (m, 3H), 1.96 (d, *J* = 3.0 Hz, 6H), 1.72 (dt, *J* = 12.9, 2.8 Hz, 3H), 1.64 (dq, *J* = 12.8, 2.1 Hz, 3H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 138.5, 135.2 (q, *J* = 33.2 Hz), 131.1, 125.7 (q, *J* = 3.6 Hz), 123.2 (q, *J* = 273.0 Hz), 61.3, 35.6, 34.9, 28.1

ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 2911, 2855, 1455, 1402, 1322, 1289, 1260, 1170, 1149 cm^{-1}. – HRMS calcd for $C_{17}H_{19}F_3O_2S$: 345.1131, found 345.1136 [M+H$^+$].

1,3-Dimethyl-5-((4-(trifluoromethyl)phenyl)sulfonyl)adamantine (4u)

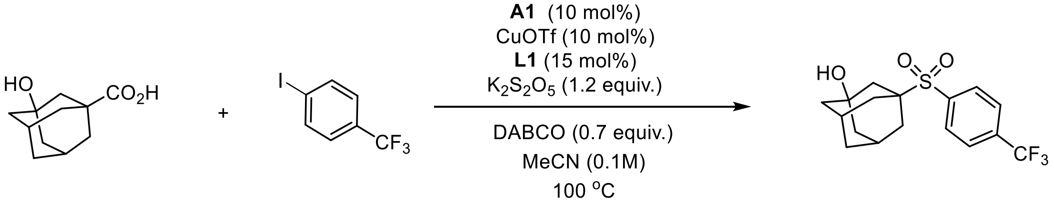


According to GP1, the reaction was carried out with (1r,3R,5S,7r)-3,5-dimethyladamantane-1-carboxylic acid (62 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N*,*N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **4u** (68 mg, 61%) as a colorless solid.

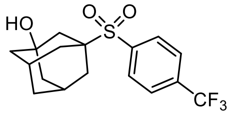


m.p.: 128–130 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.99 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H), 2.24 (p, *J* = 3.2 Hz, 1H), 1.78 (d, *J* = 3.2 Hz, 2H), 1.64–1.54 (m, 4H), 1.33 (d, *J* = 3.0 Hz, 4H), 1.23–1.09 (m, 2H), 0.89 (s, 6H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 138.7, 135.2 (q, *J* = 33.2 Hz), 131.1, 125.8 (q, *J* = 4.0 Hz), 123.3 (q, *J* = 273.1 Hz), 63.1, 49.9, 41.9, 40.7, 33.8, 31.8, 30.1, 29.2 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 2922, 2853, 1733, 1456, 1404, 1320, 1304, 1289, 1263, 1170, 1139, 1128, 1116, 1108 cm^{-1}. – HRMS calcd for $C_{19}H_{23}F_3O_2S$: 373.1444, found 373.1443 [M+H$^+$].

3-((4-(Trifluoromethyl)phenyl)sulfonyl)adamantan-1-ol (4v)

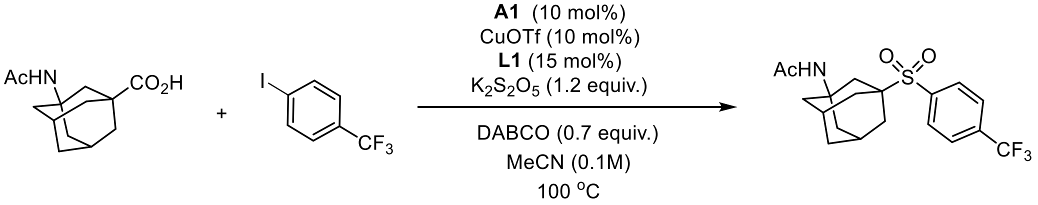


According to GP1, the reaction was carried out with (1r,3s,5*R*,7*S*)-3-hydroxyadamantane-1-carboxylic acid (59 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans*-*N*,*N*′-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:5 v/v) to give sulfone **4v** (72mg, 67%) as a colorless solid.

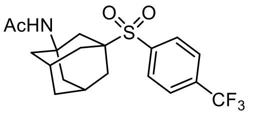


m.p.: 130–133 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.99 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 2.39 (q, *J* = 3.2 Hz, 2H), 1.86 (q, *J* = 12.3, 9.8 Hz, 6H), 1.77–1.52 (m, 7H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 138.2, 135.4 (q, *J* = 33.1 Hz), 131.1, 125.9 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 273.4 Hz), 68.7, 63.5, 43.6, 42.6, 42.6, 34.2, 33.8, 30.1 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3054, 2996, 2322, 2026, 1546, 1431, 1264, 1182 cm^{-1}. – HRMS calcd for $C_{17}H_{19}F_3O_3S$: 361.1080, found 3611073 [M+H$^+$].

N-(-3-((4-(Trifluoromethyl)phenyl)sulfonyl)adamantan-1-yl)acetamide (4w)

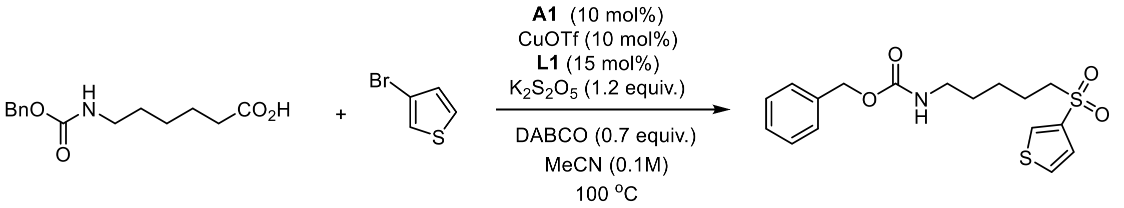


According to GP1, the reaction was carried out with (1r,3s,5*R*,7*S*)-3-acetamidoadamantane-1-carboxylic acid (71 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans*-*N*,*N*′-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:4 v/v) to give sulfone **4w** (69mg, 59%) as a colorless solid.

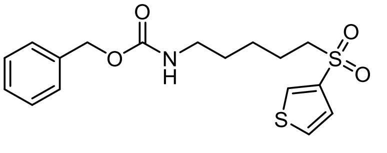


m.p.: 171–180 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.98 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H), 5.36 (s, 1H), 2.36–2.28 (m, 2H), 2.24 (s, 2H), 2.01–1.84 (m, 11H), 1.62 (ddt, *J* = 38.3, 13.0, 2.8 Hz, 2H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 169.6, 138.3, 135.4 (q, *J* = 33.2 Hz), 131.1, 125.9 (q, *J* = 3.6 Hz), 123.2 (q, *J* = 273.1 Hz), 62.4, 52.2, 40.0, 38.5, 34.5, 34.0, 29.0, 24.5 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -63.1 ppm. – IR: 2939, 2835, 2412, 1606, 1515, 1468, 1449, 1438, 1233, 1145, 1010 cm^{-1}. – HRMS calcd for $C_{19}H_{22}F_3NO_3S$: 402.1345, found 402.1344 [M+H$^+$].

Benzyl (5-(thiophen-3-ylsulfonyl)pentyl)carbamate (4x)

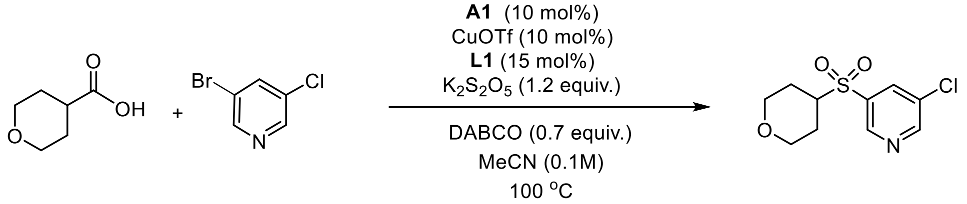


According to GP1, the reaction was carried out with 6-(((benzyloxy)carbonyl)amino)hexanoic acid (80 mg, 0.3 mmol), 3-bromothiophene (98 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½$PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **4x** (81 mg, 74%) as a colorless solid.

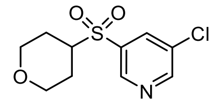


m.p.: 120–123 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.08 (1 H, dd, *J* = 3.1, 1.4 Hz), 7.48 (1 H, dd, *J* = 5.1, 3.0 Hz), 7.43– .32 (6 H, m), 5.10 (2 H, s), 4.83 (1 H, s), 3.29–3.02 (2 H, m), 1.90–1.68 (2 H, m), 1.56–1.31 (4 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 156.4, 139.7, 136.5, 132.6, 128.5, 128.4, 128.2, 128.1, 126.0, 66.7, 56.4, 40.6, 29.5, 25.4, 22.5 ppm. – IR: 3051, 2985, 1746, 1426, 1254, 898, 795 cm^{-1}. – HRMS calcd for $C_{17}H_{21}NO_4S_2$: 368.0985, found 368.0988 [M+H$^+$].

3-Chloro-5-((tetrahydro-2*H*-pyran-4-yl)sulfonyl)pyridine (4y)

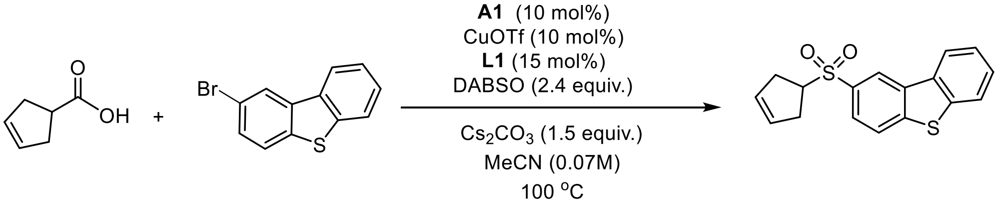


According to GP1, the reaction was carried out with tetrahydro-2*H*-pyran-4-carboxylic acid (39 mg, 0.3 mmol), 3-bromo-5-chloropyridine (115 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), $CuOTf\cdot\frac{1}{2}PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **4y** (56 mg, 72%) as a colorless solid.



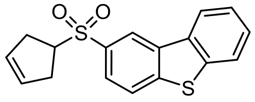
m.p.: 82–85 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.96 (1 H, d, *J* = 2.0 Hz), 8.88 (1 H ,d, *J* = 2.3 Hz), 8.16 (1 H, t, *J* = 2.1 Hz), 4.18–3.98 (2 H, m), 3.37 (2 H, td, *J* = 11.9, 2.2 Hz), 3.32–3.14 (1 H, m), 1.95 (2 H, ddd, *J* = 12.7, 4.1, 2.0 Hz), 1.89–1.77 (2 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 153.6, 147.6, 136.3, 66.4, 61.2, 25.4 ppm. – IR: 2983, 2935, 2866, 1454, 1386, 1323, 1310, 1285, 1276, 1175 cm^{-1}. – HRMS calcd for $C_{10}H_{12}ClNO_3S$: 262.0299, found 262.0292 [M+H$^+$].

2-(Cyclopent-3-en-1-ylsulfonyl)dibenzo[*b*,*d*]thiophene (4z)



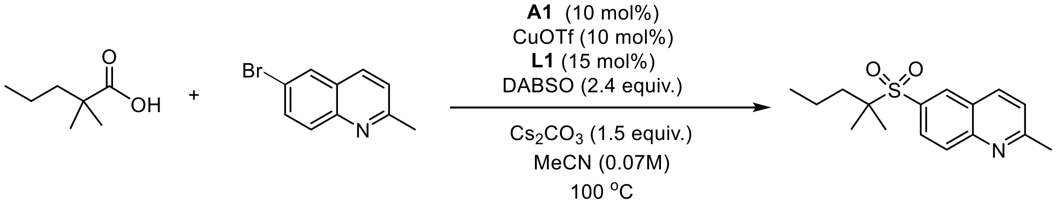
According to GP2, the reaction was carried out with cyclopent-3-ene-1-carboxylic acid (67 mg, 0.6 mmol, 2 equiv.), 2-bromodibenzo[*b*,*d*]thiophene (79 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), $CuOTf\cdot\frac{1}{2}PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO

(173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 v/v) to give sulfone **4z** (67 mg, 71%) as a colorless solid.

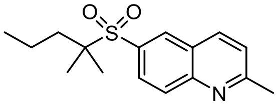


m.p.: 73–75 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.72 (1 H, dd, *J* = 1.8, 0.6 Hz), 8.39–8.22 (1 H, m), 8.05 (1 H, dd, *J* = 8.4, 0.6 Hz), 7.97 (1 H, dd, *J* = 8.4, 1.8 Hz), 7.95–7.91 (1 H, m), 7.61–7.54 (2 H, m), 5.66 (2 H, d, *J* = 0.8 Hz), 4.05–3.87 (1 H, m), 3.06–2.93 (2 H, m), 2.69 (2 H, dddd, *J* = 18.0, 9.6, 3.0, 1.7 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 145.1, 139.9, 135.9, 134.6, 134.5, 128.3, 128.0, 125.6, 125.3, 123.6, 123.0, 122.2, 62.4, 34.0 ppm. – IR: 3039, 2953, 2866, 1573, 1462, 1436, 1417, 1307, 1264, 1228, 1149 cm^{-1}. – HRMS calcd for $C_{17}H_{14}O_2S_2$: 315.0508, found 315.0508 [M+H$^+$].

2-Methyl-6-((2-methylpentan-2-yl)sulfonyl)quinoline (4aa)

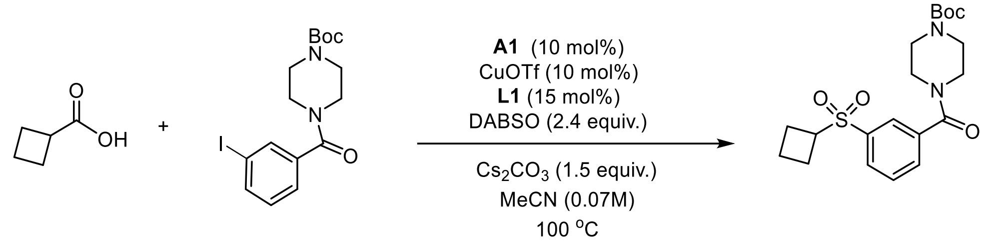


According to GP2, the reaction was carried out with 2,2-dimethylpentanoic acid (78 mg, 0.6 mmol, 2 equiv.), 6-bromo-2-methylquinoline (67 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N*,*N*′-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:2 v/v) to give sulfone **4aa** (60 mg, 69%) as a colorless solid.

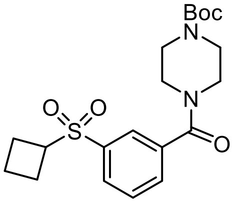


m.p.: 95–97 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.40 (1 H, d, *J* = 2.0 Hz), 8.21 (1 H, d, *J* = 8.5 Hz), 8.17 (1 H, d, *J* = 8.8 Hz), 8.08 (1 H, dd, *J* = 8.8, 2.0 Hz), 7.46 (1 H, d, *J* = 8.5 Hz), 2.83 (3 H, s), 1.77–1.67 (2 H, m), 1.35 (8 H, s), 0.94 (3 H, t, *J* = 7.3 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 162.8, 149.4, 137.3, 132.6, 132.0, 129.4, 129.2, 125.4, 123.6, 63.6, 37.1, 25.7, 20.7, 17.2, 14.6 ppm. – IR: 3027, 2935, 2844, 2389, 1755, 1624, 1584, 1569, 1519, 1485, 1467, 1455, 1433 cm^{-1}. – HRMS calcd for $C_{16}H_{21}NO_2S$: 292.1366, found 292.1368 [M+H$^+$].

tert-Butyl 4-(3-(cyclobutylsulfonyl)benzoyl)piperazine-1-carboxylate (4ab)

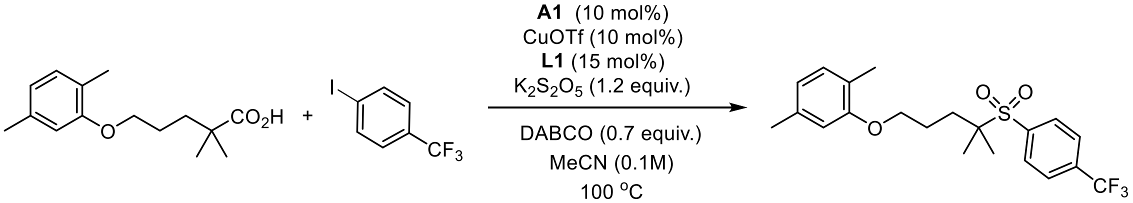


According to GP2, the reaction was carried out with cyclobutanecarboxylic acid (60 mg, 0.6 mmol, 2 equiv.), tert-butyl 4-(3-iodobenzoyl)piperazine-1-carboxylate (125 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:6 v/v) to give sulfone **4ab** (82 mg, 65%) as a colorless solid.

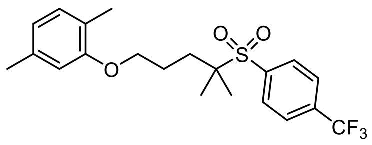


m.p.: 142–145 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.93 (1 H, dt, *J* = 7.7, 1.5 Hz), 7.87 (1 H, d, *J* = 1.7 Hz), 7.71 (1 H, dt, *J* = 7.6, 1.5 Hz), 7.64 (1 H, t, *J* = 7.7 Hz), 3.82–3.27 (8 H, m), 3.00–2.81 (2 H, m), 2.13–1.93 (2 H, m), 1.84 (2 H, dtd, *J* = 13.4, 4.9, 2.4 Hz), 1.47 (12 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 168.5, 154.5, 136.6, 136.5, 132.2, 130.8, 129.6, 127.9, 80.6, 61.7, 47.6, 43.7, 42.2, 28.3, 21.5, 14.3 ppm. – IR: 2986, 2943, 2875, 1776, 1733, 1641, 1596, 1574, 1516, 1485, 1467, 1371 cm^{-1}. – HRMS calcd for $C_{20}H_{28}N_2O_5S$: 409.1792, found 409.1795 [M+H$^+$].

1,4-Dimethyl-2-((4-methyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)pentyl)oxy)benzene (5a)

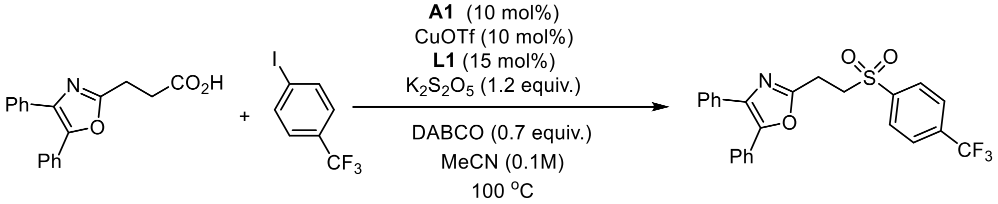


According to GP1, the reaction was carried out gemfibrozil (75 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **5a** (74 mg, 60%) as a colorless solid.

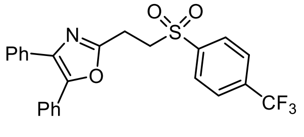


m.p.: 112–115 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.04 (d, *J* = 8.2 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 1.5 Hz, 1H), 4.04–3.88 (m, 2H), 2.33 (s, 3H), 2.09 (s, 3H), 1.93–1.89 (m, 4H), 1.40 (s, 6H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 156.6, 139.2, 136.6, 135.3 (q, *J* = 33.1 Hz), 131.1, 130.4, 125.9 (q, *J* = 4.3, 3.7 Hz), 123.4, 123.2 (q, *J* = 273.1 Hz), 121.0, 111.9, 67.2, 63.2, 32.1, 24.2, 21.4, 20.7, 15.7 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3056, 3014, 2997, 2953, 2855, 1789, 1488, 1476, 1312, 1297, 1127 cm^{-1}. – HRMS calcd for $C_{21}H_{25}F_3O_3S$: 415.1549, found 415.1552 [M+H$^+$].

4,5-Diphenyl-2-(2-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)oxazole (5b)

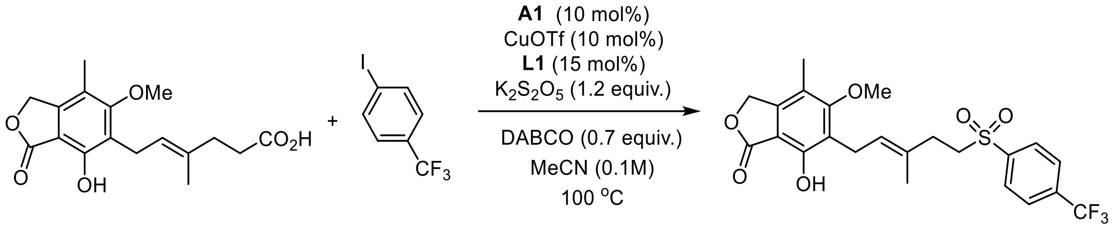


According to GP1, the reaction was carried out with oxaprozin (88 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **5b** (71 mg, 52%) as a colorless solid.

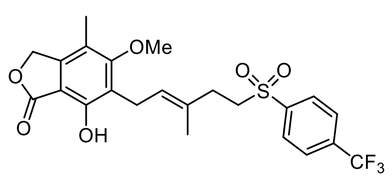


m.p.: 68–70 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.09 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.52 (ddd, *J* = 8.3, 5.2, 1.8 Hz, 4H), 7.42–7.32 (m, 6H), 3.78 (dd, *J* = 8.4, 7.0 Hz, 2H), 3.37 (dd, *J* = 8.4, 7.0 Hz, 2H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 158.5, 145.9, 142.1, 135.7 (q, *J* = 33.1 Hz), 135.2, 131.8, 128.9, 128.8, 128.7, 128.6, 128.3, 127.7, 126.5 (q, *J* = 4.2 Hz), 126.4, 123.0 (q, *J* = 273.0 Hz), 53.1, 22.2 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3210, 2843, 2831, 2604, 1440, 1119, 1025 cm^{-1}. – HRMS calcd for $C_{24}H_{18}F_3NO_3S$: 458.1032, found 458.1026 [M+H$^+$].

(*E*)-7-Hydroxy-5-methoxy-4-methyl-6-(3-methyl-5-((4-(trifluoromethyl)phenyl)sulfonyl)pent-2-en-1-yl)isobenzofuran-1(3*H*)-one (5c)

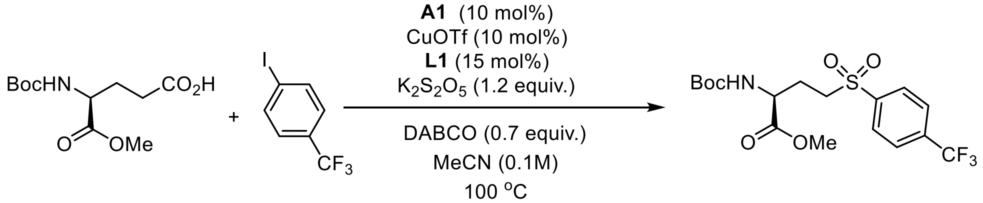


According to GP1, the reaction was carried out with mycophenolic acid (96 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans*-*N*,*N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:3 v/v) to give sulfone **5c** (94 mg, 65%) as a colorless solid.

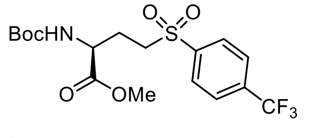


m.p.: 68–70 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.05 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.68 (s, 1H), 5.26–5.17 (m, 3H), 3.76 (s, 3H), 3.35 (d, *J* = 7.0 Hz, 2H), 3.25–3.14 (m, 2H), 2.45–2.35 (m, 2H), 2.15 (s, 3H), 1.76 (s, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 172.8, 163.6, 153.5, 144.3, 142.6, 135.4 (q, *J* = 33.3 Hz), 131.2, 128.8, 126.4 (q, *J* = 4.3 Hz), 124.6, 123.1 (q, *J* = 273.2 Hz), 121.4, 116.8, 106.4, 70.1, 61.0, 54.8, 32.0, 22.6, 16.1, 11.6 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3006, 2859, 1639, 1574, 1518, 1433, 1454, 1274, 1179, 1042, 994, 919, 802 cm^{-1}. – HRMS calcd for $C_{23}H_{23}F_3O_6S$: 484.1167, found 484.1168 [M+H$^+$].

Methyl (*S*)-2-((tert-butoxycarbonyl)amino)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butanoate (5d)

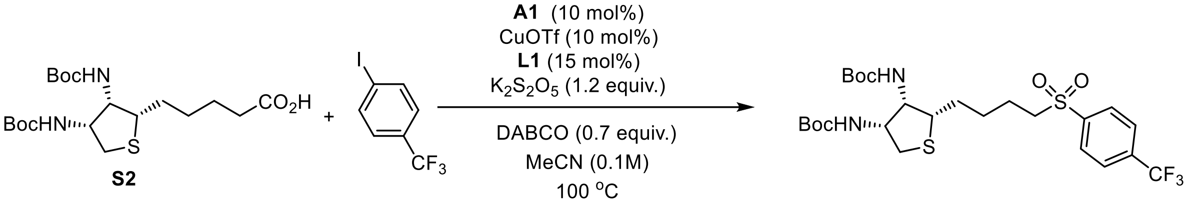


According to GP1, the reaction was carried out with (*S*)-4-((tert-butoxycarbonyl)amino)-5-methoxy-5-oxopentanoic acid (78 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **5d** (76 mg, 60%) as a colorless solid.

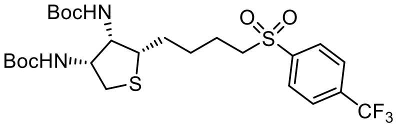


m.p.: 57–60 °C. – $[\alpha]_{23}^{D}$= +23 (c 0.5, CHCl$_3$). – ^{1}H NMR (500 MHz, CDCl$_3$): 8.07 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 5.17 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 1H), 3.76 (q, *J* = 1.8 Hz, 3H), 3.32–3.13 (m, 2H), 2.38–2.25 (m, 1H), 2.07 (tq, *J* = 13.4, 4.9 Hz, 1H), 1.42 (q, *J* = 1.6 Hz, 9H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 171.5, 155.3, 142.3, 135.7 (q, *J* = 33.1 Hz), 128.8, 126.6 (q, *J* = 3.9 Hz), 123.1 (q, *J* = 273.2 Hz), 80.6, 52.8, 52.6, 51.9, 28.2, 26.1 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 2975, 1717, 1393, 1368, 1256, 1154, 1073 cm^{-1}. – HRMS calcd for $C_{17}H_{22}F_3NO_6S$: 426.1193, found 426.1192 [M+H$^+$].

Di-*tert*-butyl ((2*S*,3*S*,4*R*)-2-(4-((4-(trifluoromethyl)phenyl)sulfonyl)butyl)tetrahydrothiophene-3,4-diyl)dicarbamate (5e)



According to GP1, the reaction was carried out with 5-((2*S*,3*S*,4*R*)-3,4-bis((*tert*-butoxycarbonyl)amino)tetrahydrothiophen-2-yl)pentanoic acid (**S2**) (125 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans*-*N*,*N*′-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **5e** (105 mg, 60%) as a yellow solid.



m.p.: 76–78 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.06 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 4.83 (dd, *J* = 92.7, 9.1 Hz, 2H), 4.40–4.08 (m, 2H), 3.46 (q, *J* = 6.2, 5.5 Hz, 1H), 3.26–3.04 (m, 3H), 2.48 (t, *J* = 10.1 Hz, 1H), 1.82–1.60 (m, 3H), 1.45 (d, *J* = 5.3 Hz, 21H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 156.1, 155.2, 142.6, 135.5 (q, *J* = 33.5 Hz), 128.8, 126.5 (q, *J* = 3.7 Hz), 125.3 (q, *J* = 272.6 Hz), 80.3, 80.0, 56.5, 56.2, 55.9, 48.0, 31.7, 30.4, 28.3, 28.2, 27.0, 22.5 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3361, 2931, 2846, 1670, 1455, 1395, 1364, 1242, 1160, 1053, 917 cm^{-1}. – HRMS calcd for $C_{25}H_{37}F_3N_2O_6S_2$: 583.2118, found 583.2111 [M+H$^+$].

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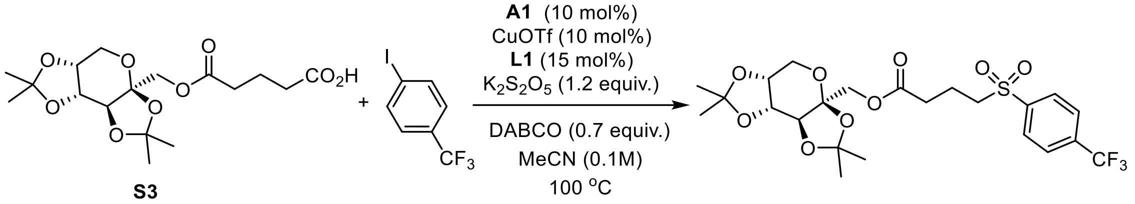
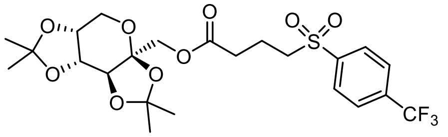
((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 4-((4-(trifluoromethyl)phenyl)sulfonyl)butanoate (5f)

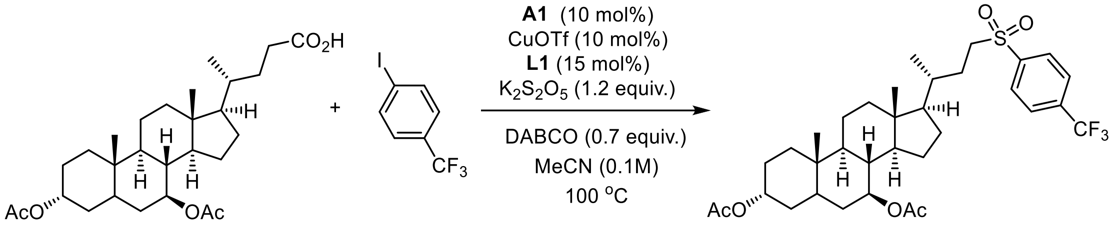


According to GP1, the reaction was carried out with 5-oxo-5-(((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methoxy)pentanoic acid (**S3**) (112 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **5f** (94 mg, 58%) as a colorless oil.



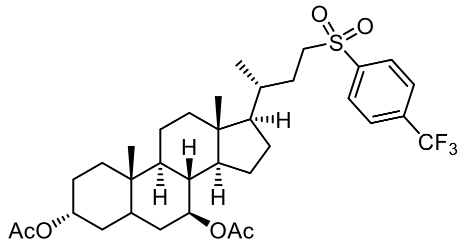
$[\alpha]_{23}^{D}$= –23.0 (c 0.5, CHCl$_3$).–^{1}H NMR (500 MHz, CDCl$_3$): 8.08 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 4.61 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.42 (d, *J* = 11.6 Hz, 1H), 4.28–4.23 (m, 2H), 4.04 (d, *J* = 11.6 Hz, 1H), 3.90 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.77 (d, *J* = 13.1 Hz, 1H), 3.26 (td, *J* = 7.1, 2.4 Hz, 2H), 2.57 (t, *J* = 7.0 Hz, 2H), 2.08 (p, *J* = 7.3 Hz, 2H), 1.55 (s, 3H), 1.48 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 171.3, 142.4, 135.6 (q, *J* = 33.1 Hz), 128.8, 126.5 (q, *J* = 3.3 Hz), 123.1 (q, *J* = 273.2 Hz), 109.1, 108.8, 101.3, 70.7, 70.6, 70.0, 65.7, 61.2, 54.9, 31.9, 26.4, 25.9, 25.2, 24.0, 18.1 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3423, 3015, 2334, 2143, 1747, 1645, 1367, 1262, 1211, 915 cm^{-1}. – HRMS calcd for $C_{23}H_{29}F_3O_9S$: 539.1557, found 539.1552 [M+H$^+$].

(3*S*,7*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7-diyl diacetate (5g)



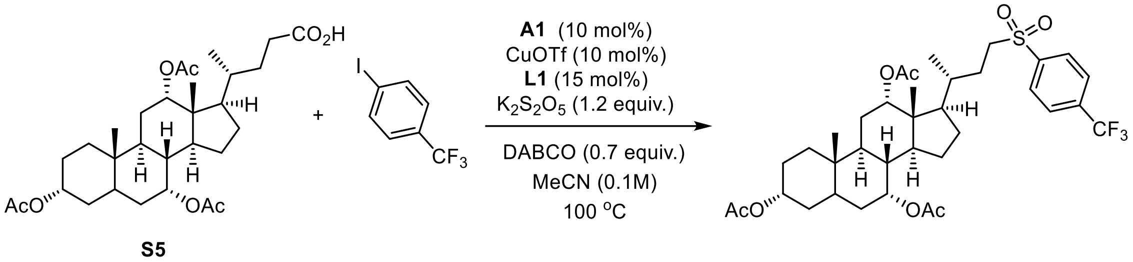
S4

According to GP1, the reaction was carried out with (4*R*)-4-((3*S*,7*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3,7-diacetoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoic acid (**S4**) (143 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), $CuOTf\cdot\frac{1}{2}PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **5g** (150 mg, 78%) as a colorless solid.

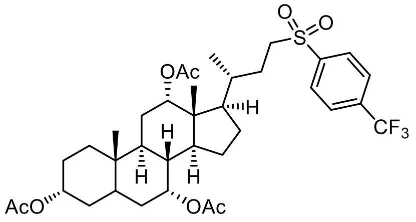


m.p.: 61–63 °C. – $[\alpha]_{23}^{D}$= +27 (c 0.2, $CHCl_3$). –^1H NMR (500 MHz, $CDCl_3$): 8.06 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 4.76 (td, *J* = 10.9, 5.2 Hz, 1H), 4.67 (tt, *J* = 10.8, 4.9 Hz, 1H), 3.14 (ddd, *J* = 15.8, 11.6, 4.2 Hz, 1H), 3.03 (ddd, *J* = 13.7, 11.0, 4.9 Hz, 1H), 2.05–2.01 (m, 3H), 2.01–1.91 (m, 4H), 1.90–1.04 (m, 22H), 1.03–0.95 (m, 4H), 0.92–0.87 (m, 3H), 0.65 (d, *J* = 1.4 Hz, 3H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 170.5, 142.8, 135.4 (q, *J* = 32.8 Hz), 128.7, 126.4 (q, *J* = 3.8 Hz), 123.1 (q, *J* = 273.0 Hz), 73.5, 55.1, 54.5, 53.5, 43.6, 42.0, 39.9, 39.8, 39.3, 34.6, 34.5, 34.0, 32.9, 28.2, 26.4, 25.5, 23.2, 21.8, 21.4, 21.1, 18.4, 12.1 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -63.1 ppm. – IR: 3340, 2995, 2933, 2875, 1813, 1657, 1507, 1456, 1446, 1391, 1248, 1175, 1130, 1055, 937, 871 cm^{-1}. – HRMS calcd for $C_{34}H_{47}F_3O_6S$: 641.3118, found 641.3101 [$M+H^+$].

(3*R*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7,12-triyl triacetate (5h)

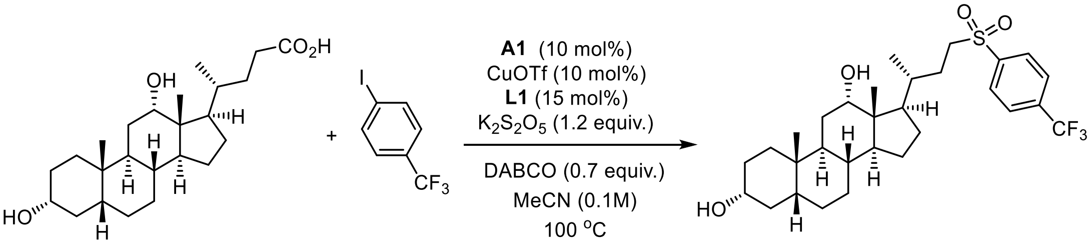


According to GP1, the reaction was carried out with (4*R*)-4-((3*R*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,7,12-triacetoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoic acid (**S5**) (161 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **5h** (130 mg, 62%) as a colorless solid.

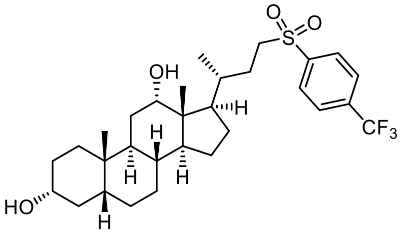


m.p.: 78–80 °C. – $[\alpha]_{23}^{D}$= +19.5 (c 0.1, CHCl$_3$). – ^{1}H NMR (500 MHz, CDCl$_3$): 8.03 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 5.04 (d, *J* = 2.9 Hz, 1H), 4.89 (q, *J* = 3.1 Hz, 1H), 4.56 (tt, *J* = 11.5, 4.3 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 1H), 3.15 (ddd, *J* = 13.3, 11.6, 4.1 Hz, 1H), 2.99 (ddd, *J* = 13.8, 11.0, 4.9 Hz, 1H), 2.14–1.55 (m, 18H), 1.53–1.36 (m, 5H), 1.29–1.17 (m, 4H), 1.15–1.00 (m, 2H), 0.93–0.88 (m, 4H), 0.77 (d, *J* = 6.0 Hz, 3H), 0.69 (s, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 170.5, 170.4, 170.3, 142.7, 135.4 (q, *J* = 33.3 Hz), 128.7, 126.4 (q, *J* = 3.9 Hz), 123.1 (q, *J* = 273.2 Hz), 75.1, 74.0, 70.6, 60.4, 53.7, 47.2, 45.1, 43.3, 40.9, 37.7, 34.7, 34.6, 34.3, 34.1, 31.2, 28.8, 28.2, 27.0, 26.9, 25.5, 22.7, 22.5, 21.6, 21.5, 21.4, 21.0, 17.6, 14.2, 12.2 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3391, 2982, 2925, 2868, 1738, 1649, 1475, 1307, 1289, 1128, 1068, 1001, 976, 931 cm^{-1}. – HRMS calcd for $C_{36}H_{49}F_3O_8S$: 699.3173, found 699.3175 [M+H$^+$].

(3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diol (5i)

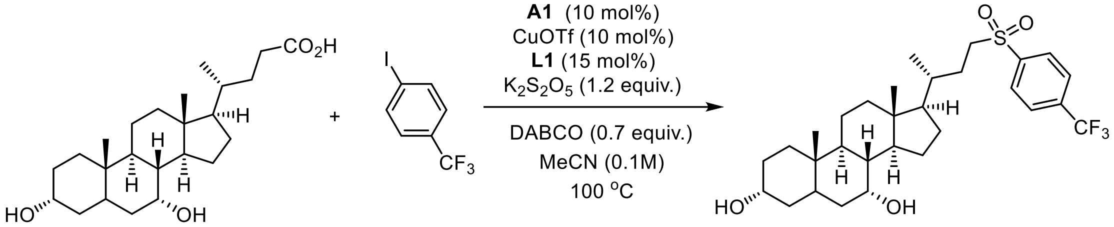


According to GP1, the reaction was carried out with deoxycholic acid (118 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans*-*N*,*N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:4 v/v) to give sulfone **5i** (88 mg, 53%) as a colorless solid.

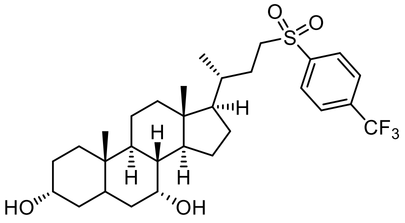


m.p.: 63–66 °C. – $[\alpha]_{23}^{D}$= +9.4 (c 0.26, CHCl$_3$). – ^{1}H NMR (500 MHz, CDCl$_3$): 8.06 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 3.92 (t, *J* = 2.9 Hz, 1H), 3.61 (td, *J* = 11.0, 10.1, 4.6 Hz, 1H), 3.18 (ddd, *J* = 14.0, 11.8, 4.3 Hz, 1H), 3.06 (ddd, *J* = 13.9, 11.0, 4.8 Hz, 1H), 1.95–0.93 (m, 27H), 0.91 (s, 3H), 0.65 (s, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 142.8, 135.4 (q, *J* = 33.1 Hz), 128.7, 126.4 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 273.3 Hz), 72.9, 71.7, 53.5, 48.2, 46.5, 42.0, 36.4, 36.0, 35.2, 34.5, 34.1, 33.6, 30.4, 28.9, 28.1, 27.3, 27.1, 26.1, 23.6, 23.1, 17.3, 12.7 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3056, 2929, 2862, 1633, 1447, 1309, 1215, 1063, 1040, 1015 cm^{-1}. – HRMS calcd for $C_{30}H_{43}F_3O_4S$: 557.2907, found 557.2909 [M+H$^+$].

(3*R*,7*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthrene-3,7-diol (5j)

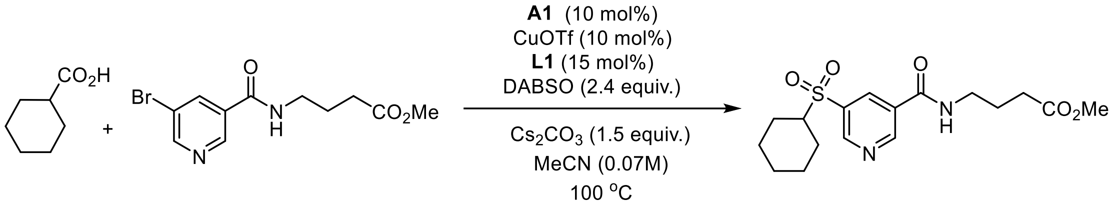


According to GP1, the reaction was carried out with chenodeoxycholic acid (118 mg, 0.3 mmol), 1-iodo-4-(trifluoromethyl)benzene (163 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:4 v/v) to give sulfone **5j** (108 mg, 65%) as a colorless solid.

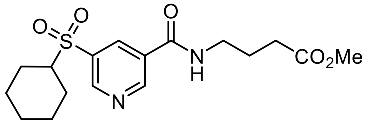


m.p.: 61–63 °C. – $[\alpha]^{D}_{23}$= +7 (c 0.6, CHCl$_3$). – ^{1}H NMR (500 MHz, CDCl$_3$): 8.07 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 3.84 (q, *J* = 3.1 Hz, 1H), 3.47 (tt, *J* = 11.1, 4.4 Hz, 1H), 3.16 (ddd, *J* = 13.4, 11.7, 4.2 Hz, 1H), 3.04 (ddd, *J* = 13.8, 11.2, 4.8 Hz, 1H), 2.21 (td, *J* = 13.0, 11.3 Hz, 1H), 2.02–1.59 (m, 7H), 1.59–1.06 (m, 14H), 1.03–0.94 (m, 1H), 0.94–0.84 (m, 7H), 0.64 (s, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 142.8, 135.4 (q, *J* = 33.4 Hz), 128.7, 126.4 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 273.4 Hz), 71.9, 68.4, 55.2, 53.5, 50.4, 42.7, 41.4, 39.8, 39.5, 39.4, 35.3, 35.0, 34.73, 34.69, 34.66, 32.8, 31.6, 30.6, 28.2, 28.0, 25.3, 23.6, 22.73, 22.65, 20.5, 18.3, 14.1, 11.8 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -63.1 ppm. – IR: 3364, 1926, 2865, 1457, 1376, 1215, 1179, 1113, 1002, 979 cm^{-1}. – HRMS calcd $C_{30}H_{43}F_3O_4S$: 557.2907, found 557.2901 [M+H$^+$].

Methyl 4-(5-(cyclohexylsulfonyl)nicotinamido)butanoate (5k)

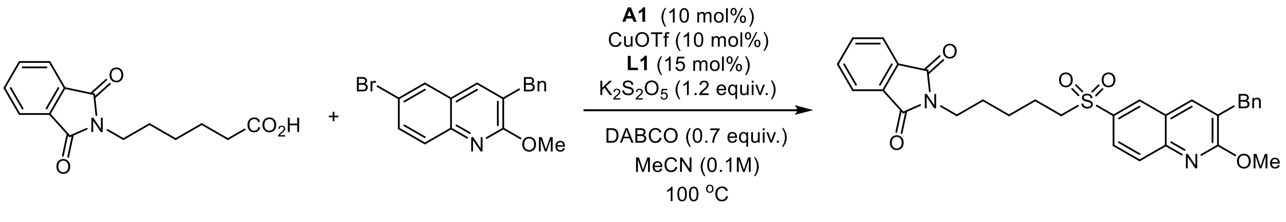


According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), methyl 4-(5-bromonicotinamido)butanoate (90 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:3 v/v) to give sulfone **5k** (81 mg, 60%) as a colorless solid.



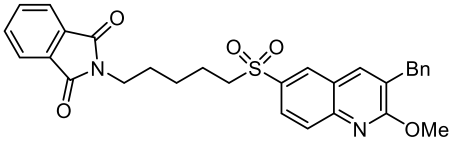
m.p.: 58–60 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 9.54–8.91 (m, 2H), 8.54 (d, *J* = 2.0 Hz, 1H), 7.62–7.41 (m, 1H), 3.69 (d, *J* = 3.5 Hz, 3H), 3.54 (q, *J* = 6.3 Hz, 2H), 2.99 (tt, *J* = 12.1, 3.4 Hz, 1H), 2.49 (t, *J* = 6.8 Hz, 2H), 2.09–1.97 (m, 4H), 1.88 (dt, *J* = 13.0, 3.4 Hz, 2H), 1.69 (dt, *J* = 12.9, 3.3 Hz, 1H), 1.40 (qd, *J* = 12.5, 3.6 Hz, 2H), 1.33–1.08 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 174.5, 163.9, 152.9, 151.6, 135.4, 133.7, 130.5, 63.8, 52.0, 40.2, 40.2, 31.9, 31.9, 25.4, 24.9, 24.9, 24.0, 23.9 ppm. – IR: 3053, 2986, 2897, 1425, 1264, 899, 735, 705 cm^{-1}. – HRMS calcd for $C_{17}H_{24}N_2O_5S$: 369.1479, found 369.1472 [M+H$^+$].

2-(5-((3-Benzyl-2-methoxyquinolin-6-yl)sulfonyl)pentyl)isoindoline-1,3-dione (5l)



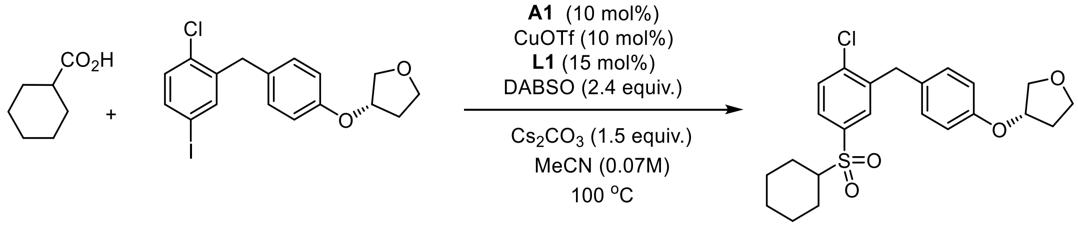
According to GP1, the reaction was carried out with 6-(1,3-dioxoisoindolin-2-yl)hexanoic acid (78 mg, 0.3 mmol), 3-benzyl-6-bromo-2-methoxyquinoline (196 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-

dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:3 v/v) to give sulfone **5l** (143 mg, 92%) as a colorless solid.



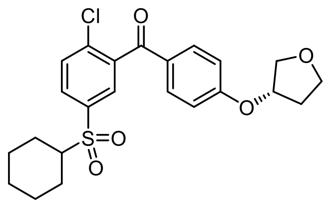
m.p.: 85–88 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.22 (t, *J* = 1.3 Hz, 1H), 7.96 (d, *J* = 1.3 Hz, 2H), 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.75–7.67 (m, 3H), 7.39–7.23 (m, 5H), 4.15 (s, 3H), 4.07 (s, 2H), 3.64 (t, *J* = 7.1 Hz, 2H), 3.18–3.09 (m, 2H), 1.82–1.72 (m, 2H), 1.66 (dq, *J* = 15.2, 7.4, 6.5 Hz, 2H), 1.43 (p, *J* = 7.9 Hz, 2H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 168.3, 163.0, 148.0, 138.3, 137.4, 134.0, 133.8, 132.0, 129.3, 128.8, 128.7, 128.3, 128.2, 126.7, 126.2, 124.7, 123.2, 56.2, 54.1, 37.5, 36.0, 28.1, 25.6, 22.5 ppm. – IR: 2975, 2845, 1649, 1590, 1556, 1531, 1488, 1398, 1338, 1165 cm^{-1}. – HRMS calcd for $C_{30}H_{28}N_2O_5S$: 529.1792, found 529.1783 [M+H$^+$].

(*S*)-3-(4-(2-Chloro-5-(cyclohexylsulfonyl)benzyl)phenoxy)tetrahydrofuran (5m)



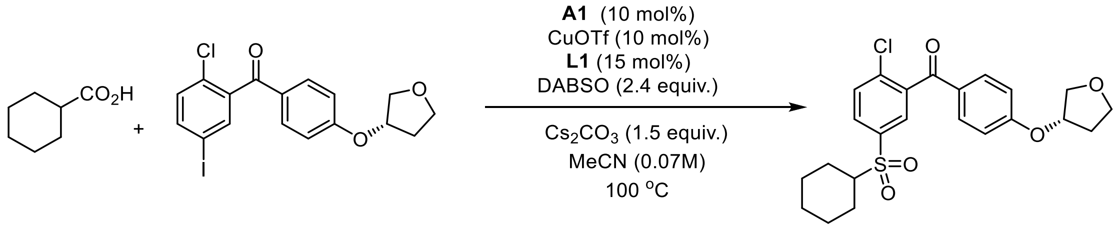
According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), (*S*)-3-(4-(2-chloro-5-iodobenzyl)phenoxy)tetrahydrofuran (124 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½$PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **5m** (107 mg, 82%) as a colorless solid.

Gram scale synthesis: According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (1.01 g, 8 mmol, 2 equiv.), (*S*)-3-(4-(2-chloro-5-iodobenzyl)phenoxy)tetrahydrofuran (1.65 g, 4 mmol), acridine **A1** (106 mg, 0.4 mmol, 10 mol%), CuOTf·½PhCH$_3$ (213 mg, 0.4 mmol, 10 mol%), *trans-N*,*N'*-dimethylcyclohexane-1,2-diamine (80 mg, 0.6 mmol, 15 mol%), cesium carbonate (1.95 g, 6 mmol, 1.5 equiv.), and DABSO (2.3 g, 9.6 mmol, 2.4 equiv.) and acetonitrile (60 mL) was then added. The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 24 h. The reaction mixture was then diluted with ethyl acetate (100 mL) and washed with a saturated aqueous solution of EDTA (30 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **5m** (1.18 mg, 68%) as a colorless solid.

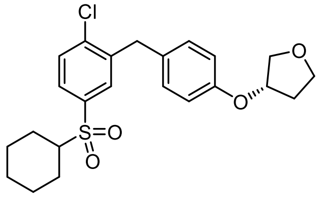


m.p.: 105–107 °C. – $[\alpha]_{23}^{D}$= +4 (c 0.8, CHCl$_3$). – ^{1}H NMR (500 MHz, CDCl$_3$): 7.66 (dd, *J* = 5.9, 2.4 Hz, 2H), 7.59–7.53 (m, 1H), 7.13–7.07 (m, 2H), 6.85–6.78 (m, 2H), 4.91 (ddt, *J* = 6.4, 4.4, 2.1 Hz, 1H), 4.11 (s, 2H), 4.02–3.95 (m, 3H), 3.90 (td, *J* = 8.3, 4.4 Hz, 1H), 2.86 (tt, *J* = 12.1, 3.5 Hz, 1H), 2.24–2.09 (m, 2H), 2.06–1.99 (m, 2H), 1.86 (dt, *J* = 13.0, 3.2 Hz, 2H), 1.68 (dt, *J* = 12.7, 3.1 Hz, 1H), 1.36 (qd, *J* = 12.5, 3.4 Hz, 2H), 1.30–1.07 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 156.2, 140.6, 140.1, 135.9, 131.3, 130.4, 130.3, 130.0, 129.9, 128.1, 115.6, 115.6, 77.3, 73.1, 67.2, 63.6, 38.4, 33.0, 25.5, 25.1, 25.1, 25.0 ppm. – IR: 2974, 2923, 2858, 1610, 1454, 1378, 1200, 1125, 880 cm^{-1}. – HRMS calcd for $C_{23}H_{27}ClO_4S$: 435.1391, found 435.1392 [M+H$^+$].

(*S*)-(2-Chloro-5-(cyclohexylsulfonyl)phenyl)(4-((tetrahydrofuran-3-yl)oxy)phenyl)methanone (5n)

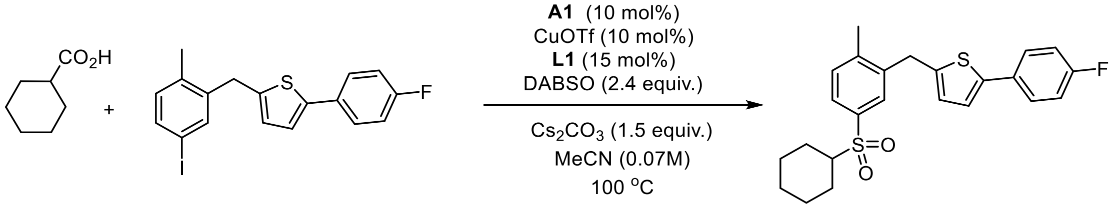


According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), (*S*)-(2-chloro-5-iodophenyl)(4-((tetrahydrofuran-3-yl)oxy)phenyl)methanone (128 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N*,*N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:1 v/v) to give sulfone **5n** (101 mg, 75%) as a colorless solid.

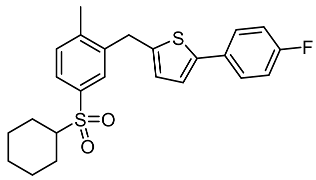


m.p.: 124–126 °C. – $[\alpha]_{23}^{D}$= +5 (c 0.6, CHCl$_3$). – ^{1}H NMR (500 MHz, CDCl$_3$): 7.91 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.84 (d, *J* = 2.2 Hz, 1H), 7.75 (dd, *J* = 9.1, 2.3 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 6.96–6.88 (m, 2H), 5.02 (ddt, *J* = 6.3, 4.2, 2.0 Hz, 1H), 4.08–3.87 (m, 4H), 2.92 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.27 (dtd, *J* = 14.3, 8.3, 6.2 Hz, 1H), 2.21–2.12 (m, 1H), 2.11–2.02 (m, 2H), 1.88 (dt, *J* = 12.8, 3.2 Hz, 2H), 1.73–1.64 (m, 1H), 1.41 (qd, *J* = 12.5, 3.2 Hz, 2H), 1.21 (dddd, *J* = 30.2, 24.8, 11.4, 3.1 Hz, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 191.7, 162.5, 139.8, 137.1, 136.2, 132.7, 131.1, 130.9, 129.3, 128.6, 115.4, 77.9, 73.0, 67.2, 63.7, 33.0, 25.5, 25.01, 24.95 ppm. – IR: 3347, 2993, 2875, 1725, 1656, 1455, 1265, 1128, 894, 735 cm^{-1}. – HRMS calcd for $C_{23}H_{25}ClO_5S$: 449.1184, found 449.1177 [M+H$^+$].

2-(5-(Cyclohexylsulfonyl)-2-methylbenzyl)-5-(4-fluorophenyl)thiophene (5o)

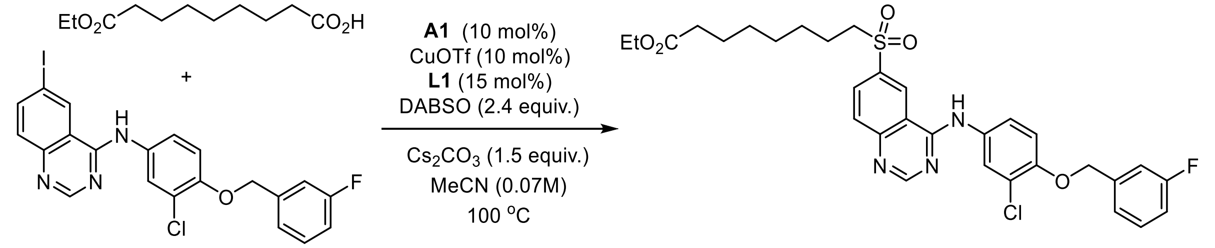


According to GP2, the reaction was carried out with cyclohexanecarboxylic acid (76 mg, 0.6 mmol, 2 equiv.), 2-(4-fluorophenyl)-5-(5-iodo-2-methylbenzyl)thiophene (122 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **5o** (82 mg, 64%) as a colorless solid.

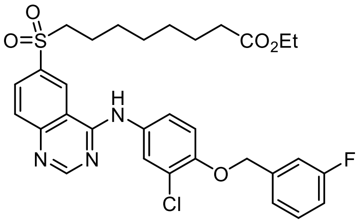


m.p.: 98–100 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.74 (d, *J* = 1.9 Hz, 1H), 7.69 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.51–7.45 (m, 2H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.08–7.02 (m, 3H), 6.70 (dd, *J* = 3.5, 1.2 Hz, 1H), 4.22 (s, 2H), 2.90 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.43 (s, 3H), 2.13–2.05 (m, 2H), 1.86 (dt, *J* = 13.3, 3.2 Hz, 2H), 1.72–1.62 (m, 1H), 1.41 (qd, *J* = 12.5, 3.5 Hz, 2H), 1.31–1.07 (m, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 162.2 (d, *J* = 246.8 Hz), 143.0, 142.0, 141.7, 139.4, 134.9, 131.2, 130.6 (d, *J* = 3.6 Hz), 129.9, 127.6, 127.1 (d, *J* = 8.1 Hz), 126.4, 122.8, 115.8 (d, *J* = 21.8 Hz), 63.6, 34.0, 25.6, 25.2, 25.1, 19.8 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -114.8 (tt, *J* = 9.0, 5.2 Hz) ppm. – IR: 3063, 3012, 2986, 2974, 2897, 2886, 1795, 1236, 1189, 1095, 967 cm^{-1}. – HRMS calcd for $C_{24}H_{25}FO_2S_2$: 429.1353, found 429.1349 [M+H$^+$].

Ethyl 8-((4-((3-chloro-4-((3-fluorobenzyl)oxy)phenyl)amino)quinazolin-6-yl)sulfonyl)octanoate (5p)



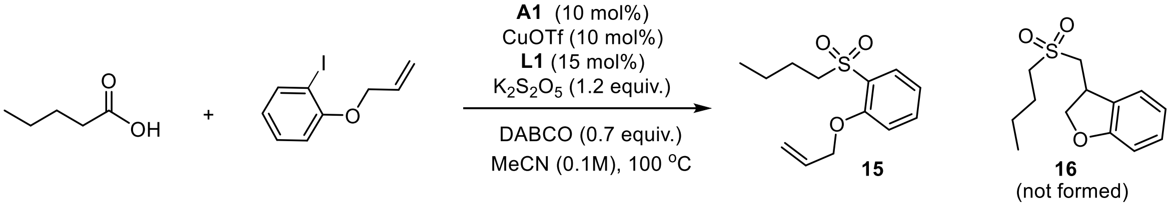
According to GP2, the reaction was carried out with 9-ethoxy-9-oxononanoic acid (130 mg, 0.6 mmol, 2 equiv.), *N*-(3-chloro-4-((3-fluorobenzyl)oxy)phenyl)-6-iodoquinazolin-4-amine (151 mg, 0.3 mmol), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½PhCH$_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N*,*N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), cesium carbonate (146 mg, 0.45 mmol, 1.5 equiv.), DABSO (173 mg, 0.72 mmol, 2.4 equiv.), and acetonitrile (4.5 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 1:9 v/v) to give sulfone **5p** (79 mg, 43%) as a colorless solid.



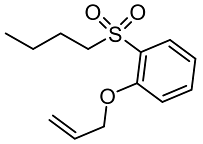
m.p.: 115–128 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.81 (d, *J* = 21.7 Hz, 2H), 8.48 (s, 1H), 8.18 (dd, *J* = 8.7, 1.8 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.92–7.87 (m, 1H), 7.58 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.38 (td, *J* = 7.9, 5.8 Hz, 1H), 7.31–7.20 (m, 2H), 7.09–6.98 (m, 2H), 5.17 (s, 2H), 4.11

(q, *J* = 7.1 Hz, 2H), 3.20–3.12 (m, 2H), 2.26 (t, *J* = 7.4 Hz, 2H), 1.75–1.62 (m, 2H), 1.57 (p, *J* = 7.2 Hz, 2H), 1.39–1.17 (m, 9H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 173.9, 163.0 (d, *J* = 246.8 Hz), 158.5, 157.8, 152.8, 151.6, 139.0 (d, *J* = 7.3 Hz), 136.1, 131.5, 130.4, 130.3, 130.2, 125.4, 123.7, 123.7, 123.5, 122.5, 122.4 (d, *J* = 3.2 Hz), 115.0 (d, *J* = 21.4 Hz), 114.1, 114.0 (d, *J* = 22.1 Hz), 70.4, 60.4, 56.3, 34.1, 28.5, 28.4, 27.9, 24.6, 22.5, 14.2 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -112.55 (td, *J* = 9.1, 5.8 Hz) ppm. – IR: 2932, 2880, 1777, 1742, 1452, 1369, 1322, 1221, 1167, 1131, 1098, 1021, 954 cm^{-1}. – HRMS calcd for $C_{31}H_{33}ClFN_3O_5S$: 614.1886, found 614.1877 [M+H$^+$].

1-(Allyloxy)-2-(butylsulfonyl)benzene (15)



According to GP1, the reaction was carried out with pentanoic acid (31 mg, 0.3 mmol), 1-(allyloxy)-2-iodobenzene (156 mg, 0.6 mmol, 2 equiv.), acridine **A1** (8 mg, 0.03 mmol, 10 mol%), CuOTf·½$PhCH_3$ (16 mg, 0.03 mmol, 10 mol%), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (6 mg, 0.045 mmol, 15 mol%), DABCO (24 mg, 0.21 mmol, 0.7 equiv.), potassium metabisulfite (74 mg, 0.36 mmol, 1.2 equiv.) , and acetonitrile (3 mL). The tube was sealed with a GL18 screw cap, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 100 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with a saturated aqueous solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ethyl acetate 2:1 v/v) to give sulfone **15** (56 mg, 67%) as a colorless liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 7.98 (1 H, dd, *J* = 7.8, 1.7 Hz), 7.58 (1 H, ddd, *J* = 8.7, 7.4, 1.7 Hz), 7.12 (1 H, td, *J* = 7.7, 1.0 Hz), 7.04 (1 H, dd, *J* = 8.4, 0.9 Hz), 6.10 (1 H, ddt, *J* = 17.2, 10.4, 5.1 Hz), 5.53 (1 H, dq, *J* = 17.2, 1.5 Hz), 5.37 (1 H, dq, *J* = 10.7, 1.5 Hz), 4.73 (2 H, dt, *J* = 5.0, 1.6 Hz), 3.51–3.26 (2 H, m), 1.68 (2 H, tt, *J* = 8.1, 6.5 Hz), 1.41 (2 H, h, *J* = 7.4 Hz), 0.90 (3 H, t, *J* = 7.4 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 156.3, 135.3, 131.8, 130.6, 127.4, 120.9, 118.5, 113.5, 69.8, 54.2, 24.5, 21.6, 13.5 ppm. – IR: 2987, 2862, 1498, 1453, 1398, 1263, 1234, 1120, 1109, 1006, 960 cm^{-1}.

Computational data

1. Software

Quantum chemical calculations were performed using the Stampede2 supercomputer at the Texas Advanced Computing Center (TACC) hosted by the University of Texas in Austin, Texas and the Expanse system operating at the San Diego Supercomputer Center (SDSC) at the University of California at San Diego supported by the Extreme Science and Engineering Discovery Environment (XSEDE). DFT geometry optimization, vibrational frequency, and IRC calculations were conducted using Gaussian 16 (rA.03).[15] The CREST[16] and Reaction Path[17] utility of the xTB software suite[18,19] were used to locate initial starting geometries for optimization via DFT. Final images of minima and transition state geometries were rendered using CYLview[20] and VMD[21]. Spin density surface was generated with isovalue 0.03. Energy decomposition analysis was performed with Q-Chem 5.3.1.[22] Routine visualization and monitoring of calculations were performed with Chemcraft.[23]

2. Details of Computational Methods

Gaussian 16 DFT calculations

Geometries of ground state minima and transition states were optimized without constraints using ωB97X-D[24] DFA and the def2-TZVP[25,26] basis set in MeCN solvent with the SMD solvation model.[27] Calculations were set to "tight" convergence criteria with an ultrafine grid. The temperature was set to 363.15 K in line with the experimental reaction conditions. Frequency calculations at the same level of theory were used to confirm the nature of the isolated stationary points. Geometries with zero imaginary frequencies were deemed minima whereas those with exactly one imaginary frequency along the chemical path of interest were deemed transition states. IRC calculations were performed to further corroborate that the located transition states connected reactants to products. The Grimme's quasi-harmonic approximation[28] was applied via GoodVibes[29] to all structures to correct for potential errors associated with low magnitude vibrational frequencies using a cut-off frequency of 50 cm^{-1}. Additionally, thermodynamic data were corrected to a solution phase standard state of 1 mol/L and temperature-corrected to 363.15 K using GoodVibes. Single point corrections of the above geometries were calculated at the PW6B95[30]-D3(BJ)[31] / def2-TZVPPD[32] / SMD (MeCN) level of theory and provided the final electronic component to the reported free energies. PW6B95-D3(BJ) and ωB97X-D were selected based on their accuracy relative to the GMTKN30 and GMTKN55 databases.[33,34]

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Optimized Geometries

Br$^-$

E(UPW6B95D3) = -2575.45465800
E(UωB97XD) = -2574.38060091
Charge = -1 Multiplicity = 1
Single point geometry:

Br	0.	0.	0.

KBr

E(UPW6B95D3) = -3175.74991499
E(UωB97XD) = -3174.25714506
Charge = 0 Multiplicity = 1

K	-1.7574123781	0.7721622367	-0.0001144260
Br	1.2707104270	0.7720330708	0.0009982357

CsBr

E(UPW6B95D3) = -2595.56554773
E(UωB97XD) = -2594.52868603
Charge = 0 Multiplicity = 1

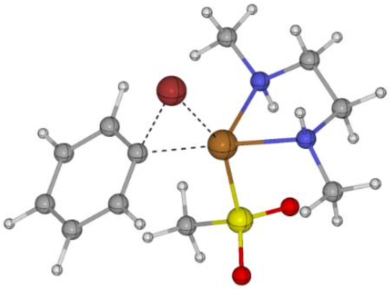
Cs	-2.2097144984	0.7721815298	-0.0002806211
Br	1.3230125746	0.7720308398	0.0010174538

Br

E(UPW6B95D3) = -2575.24461238
E(UωB97XD) = -2574.17541530
Charge = 0 Multiplicity = 2
Single point geometry:

Br	0.	0.	0.

TSA



E(UPW6B95D3) = -5307.56655158
E(UωB97XD) = -5304.25002483
Charge = 0 Multiplicity = 1

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C	3.06349	2.94383	0.75828
C	1.86282	3.28175	0.14942
C	1.13415	2.33071	-0.5505
H	3.21998	-0.32878	-0.1213
H	4.48573	1.37436	1.12616
H	3.63029	3.694	1.29472
H	1.48637	4.2956	0.20832
H	0.2105	2.60253	-1.04156
Cu	0.20607	-0.41904	-0.49609

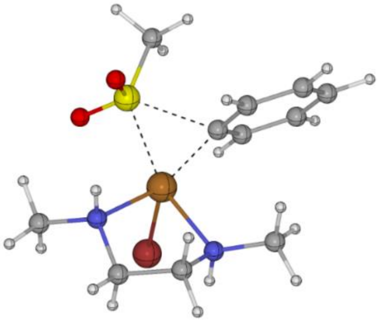
Br	1.2102	0.00906	-2.58188
O	1.13317	-1.35151	2.46598
O	-1.29595	-0.92282	2.1979
N	-0.60666	-2.3609	-0.92057
H	-0.36901	-2.49322	-1.89905
C	-2.0691	-2.2712	-0.82742
H	-2.33096	-2.29414	0.2322
H	-2.54862	-3.12477	-1.31724
C	-2.55793	-0.9767	-1.44324
H	-2.25806	-0.92315	-2.49439
H	-3.65373	-0.94948	-1.41404
N	-1.9706	0.1663	-0.74491
H	-2.2778	0.13173	0.22278
C	-0.06822	-3.49941	-0.17515
H	-0.52342	-4.44359	-0.49291
H	1.00904	-3.55512	-0.33004
H	-0.25876	-3.35803	0.88826
C	-2.36535	1.44201	-1.32642
H	-3.45285	1.52915	-1.4404
H	-2.01889	2.25498	-0.68877
H	-1.9082	1.55509	-2.31153
S	0.0841	-0.53446	1.82594
C	0.27862	1.09338	2.55543
H	1.2892	1.45779	2.37954
H	-0.45441	1.77239	2.12043
H	0.09749	0.97539	3.62552

TSB

E(UPW6B95D3) = -5307.57628113

E(UωB97XD) = -5304.26208772

Charge = 0 Multiplicity = 1



C	1.49823	0.86753	-0.57309
C	2.05118	1.29885	0.625
C	2.2923	2.65327	0.8003
C	2.0088	3.55452	-0.21913
C	1.4825	3.10436	-1.42073
C	1.23767	1.75035	-1.60998
H	2.26613	0.59128	1.41508
H	2.70676	3.00439	1.73737
H	2.20776	4.60954	-0.07741
H	1.26705	3.80322	-2.21952
H	0.85072	1.3927	-2.55579
Cu	0.34297	-0.69932	-0.49204
N	-0.7433	-2.21251	-1.44735
H	-0.65291	-1.99545	-2.43577
C	-2.1455	-1.99224	-1.06427
H	-2.27299	-2.38238	-0.05176

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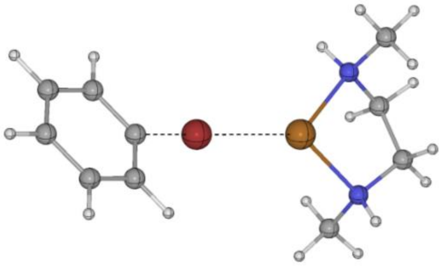
H	-2.82408	-2.54019	-1.72484
C	-2.47235	-0.51447	-1.08823
H	-2.32756	-0.1141	-2.09548
H	-3.52205	-0.36097	-0.81595
N	-1.56905	0.20137	-0.18584
H	-1.72061	-0.13039	0.76285
C	-0.33888	-3.60552	-1.24982
H	-1.03821	-4.29542	-1.7335
H	0.65679	-3.75466	-1.66102
H	-0.30489	-3.81346	-0.18042
C	-1.74849	1.64648	-0.21727
H	-2.77313	1.93458	0.04129
H	-1.06035	2.11297	0.48792
H	-1.5248	2.02077	-1.21649
S	2.37735	-1.02141	-1.50401
O	1.95396	-1.03317	-2.89237
O	2.64259	-2.28691	-0.84868
Br	0.28623	-1.62263	1.99176
C	3.94631	-0.17836	-1.46045
H	3.86829	0.79293	-1.94068
H	4.27492	-0.08775	-0.42791
H	4.61672	-0.83641	-2.01665

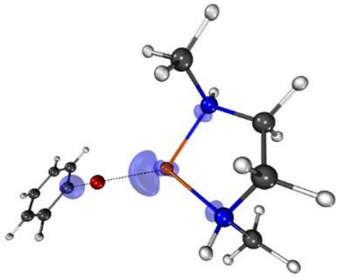
TSC

E(UPW6B95D3) = -4718.30608599

E(UωB97XD) = -4715.59953034

Charge = 0 Multiplicity = 2





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C	1.89496	-1.54967	-7.51229
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C	4.13912	-1.10657	-8.2694
C	3.70074	-1.16168	-9.5864
C	2.36496	-1.40967	-9.87081
H	0.42042	-1.79684	-9.04552
H	1.18934	-1.70031	-6.70465
H	5.18201	-0.91196	-8.05186
H	4.40953	-1.00934	-10.39159
H	2.02644	-1.45165	-10.89858
Br	3.83964	-1.21844	-5.37994
Cu	4.77703	-0.97278	-2.2151
N	6.24247	0.16363	-1.02193
C	6.19894	-0.45436	0.30481
C	5.94022	1.59299	-1.00917
H	7.1671	0.03396	-1.41072
C	4.77238	-0.7817	0.72369
H	6.64874	0.19683	1.06454
H	6.79067	-1.37042	0.26644

H	6.58353	2.14478	-0.31246
H	4.90123	1.75588	-0.72018
H	6.07575	1.9979	-2.01201
N	4.12737	-1.69202	-0.22436
H	4.79059	-1.20446	1.73587
H	4.18153	0.13485	0.7623
C	4.47846	-3.09479	-0.01644
H	3.12444	-1.59488	-0.13733
H	4.28317	-3.42121	1.01269
H	5.53542	-3.25493	-0.23277
H	3.89942	-3.71553	-0.70012

8

E(UPW6B95D3) = -2500.24245004
E(UωB97XD) = -2498.40504330
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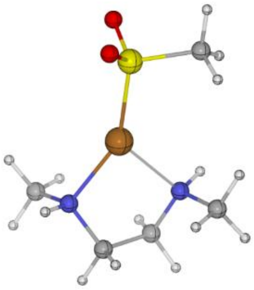

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N	1.03576	1.17498	-0.56676
N	1.25057	-1.31449	0.85163
C	2.25574	0.36624	-0.64594
C	2.43167	-0.47238	0.61094
C	1.23949	-2.54051	0.0471
C	1.21132	2.42986	0.16393
H	0.72625	1.39082	-1.50511
H	1.24736	-1.5824	1.82774
H	3.14495	0.99103	-0.78688
H	2.16958	-0.28552	-1.5164
H	3.33841	-1.07995	0.51944
H	2.55356	0.18022	1.47673
H	2.16207	-3.11664	0.17867
H	1.13023	-2.29657	-1.00941
H	0.39009	-3.15485	0.3431
H	2.02157	3.03884	-0.25388
H	1.4387	2.22552	1.21079
H	0.28341	3.00018	0.12534
S	-2.54541	0.27936	0.69548
O	-3.37018	-0.51905	-0.23967
O	-3.03606	0.25111	2.09146
C	-2.84891	1.97637	0.18135
H	-2.51311	2.10367	-0.84856
H	-3.92375	2.15789	0.25646
H	-2.30393	2.65269	0.8408

7

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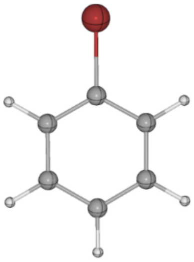
E(UωB97XD) = -2805.87214961

Charge = 0 Multiplicity = 1

C	-3.40512	-0.4285	0.00004
C	-2.01721	-0.43697	0.00057
C	-1.34101	0.77215	0.00004
C	-2.01711	1.98132	-0.00099
C	-3.40502	1.97297	-0.0015
C	-4.10035	0.77226	-0.00098
H	-3.94107	-1.3694	0.00045
H	-1.47566	-1.37348	0.00137
H	-1.47548	2.91778	-0.0014
H	-3.94088	2.91391	-0.0023
H	-5.18302	0.77231	-0.00138
Br	0.56126	0.77206	0.00074



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E(UPW6B95D3) = -5307.58388941

E(UωB97XD) = -5304.26859212

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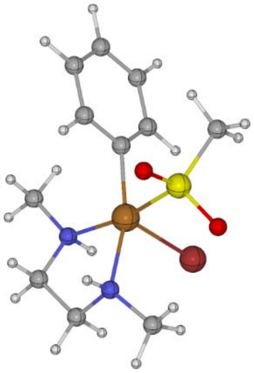
N	1.38335	-1.63506	-1.73733
N	2.90096	0.53926	-0.82934
C	0.01154	2.3506	-0.0509
C	-0.1594	3.60891	0.51625
C	0.27168	3.85372	1.81227
C	0.87719	2.84086	2.54377
C	1.05643	1.58056	1.98486
C	1.06389	-3.05789	-1.56231
C	3.22178	1.96536	-0.76472
C	2.78337	-1.47437	-2.16917
C	3.15153	-0.01453	-2.16745
H	-0.33996	2.15931	-1.0573
H	-0.63492	4.3943	-0.05903
H	0.13372	4.83329	2.25331
H	1.21429	3.02756	3.55654
H	1.53478	0.78745	2.5459
H	-0.00615	-3.17991	-1.43346
H	1.56764	-3.42025	-0.66722
H	1.3986	-3.62996	-2.43229
H	3.11671	2.3235	0.25663
H	4.24812	2.13608	-1.10047
H	2.54162	2.52267	-1.4076
H	2.9321	-1.90816	-3.16076
H	3.40727	-2.02003	-1.45875
H	2.53618	0.53961	-2.88
H	4.19972	0.11581	-2.44929
H	0.79283	-1.27424	-2.48319
H	3.48149	0.04119	-0.15394



S	-1.02952	-0.76488	0.23831
O	-1.81343	-0.19857	-0.84967
O	-1.07488	-2.20859	0.39402
Cu	1.10524	-0.25314	-0.22798
Br	2.62533	-1.70999	1.63781
C	-1.69733	-0.1367	1.76421
H	-2.66464	-0.63186	1.86556
H	-1.03638	-0.42551	2.57901
H	-1.81615	0.94142	1.7124

6

E(UPW6B95D3) = -4486.38283569
E(UωB97XD) = -4484.08130270
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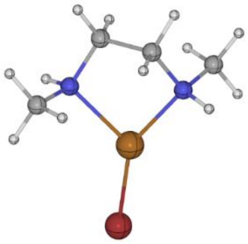

Cu	-0.31941	0.05425	-0.03107
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N	1.2952	-1.23875	0.75268
C	2.46848	0.40737	-0.65045
C	2.49486	-0.40876	0.63373
C	1.37762	-2.49687	0.01438
C	1.37555	2.4926	0.02635
H	1.09827	1.4736	-1.69743
H	1.13721	-1.44827	1.72915
H	3.3749	1.02033	-0.70785
H	2.46488	-0.26105	-1.51265
H	3.40959	-1.01327	0.65181
H	2.52599	0.26066	1.49477
H	2.25279	-3.09081	0.3054
H	1.43738	-2.30052	-1.0569
H	0.47628	-3.08117	0.19871
H	2.25748	3.06801	-0.27741
H	1.44852	2.28435	1.09377
H	0.48305	3.09465	-0.14113
Br	-2.61304	-0.25606	0.09003

Sulfone

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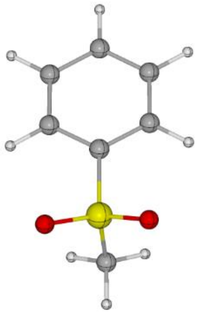
E(UωB97XD) = -820.235450149
Charge = 0 Multiplicity = 1



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C	-1.26239	1.01399	0.09259
C	-2.60424	1.07743	-0.24951
C	-3.36486	-0.08266	-0.2985
H	-3.38391	-2.21587	-0.05027

H	-0.9889	-2.34197	0.55466
H	-0.65916	1.91152	0.12876
H	-3.05487	2.0343	-0.47997
H	-4.4126	-0.02863	-0.56683
S	1.01239	-0.30941	0.83705
O	1.51777	-1.60488	0.45841
O	1.68017	0.86361	0.33241
C	0.98305	-0.2189	2.59778
H	2.02026	-0.26997	2.93144
H	0.5318	0.72561	2.89762
H	0.41555	-1.06258	2.98747

HA

E(UPW6B95D3) = -1248.56021328

E(UωB97XD) = -1246.84709124

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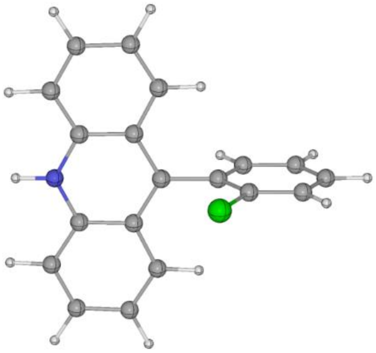

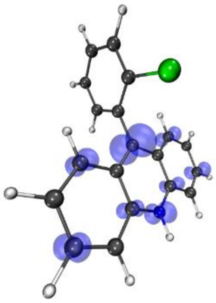

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C	-2.41383	0.01626	0.02289
C	-3.17891	1.19913	0.04613
C	-4.55835	1.16442	0.04812
C	-5.22674	-0.05859	0.02601
H	-5.01636	-2.19863	-0.01427
H	-2.66523	2.1523	0.06327
H	-5.12043	2.08975	0.06698
H	-6.30909	-0.08926	0.02717
C	-0.98997	0.00275	0.02365
C	-1.02618	-2.44649	-0.01457
C	-0.28876	-1.23637	0.00811
C	-0.37609	-3.67726	-0.03021
C	1.00706	-3.73424	-0.0195
H	1.50388	-4.6962	-0.03139
C	1.75401	-2.55773	0.00761
H	2.8359	-2.60181	0.01843
C	1.11689	-1.33379	0.02122
H	1.70296	-0.42351	0.04282
N	-2.3981	-2.38511	-0.02069
H	-2.90968	-3.25421	-0.03496
C	-0.23619	1.2792	0.01848
C	0.11207	1.95108	1.18766
C	0.15641	1.85491	-1.1894
C	0.81754	3.14394	1.16984
C	0.8625	3.04589	-1.22832
H	-0.10313	1.34767	-2.11088
C	1.19298	3.69151	-0.04594
H	1.07021	3.63722	2.0991
H	1.15419	3.46935	-2.18105

H	1.74491	4.6227	-0.06406
Cl	-0.34322	1.28444	2.73531
H	-0.9674	-4.58545	-0.04956

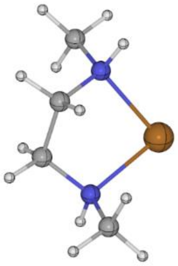
10

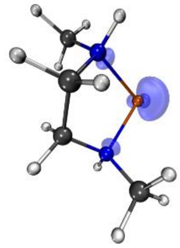
E(UPW6B95D3) = -1910.94685763

E(UωB97XD) = -1909.71305503

Charge = 0 Multiplicity = 2

Cu	-0.41551	-0.00652	-0.03425
N	1.28472	1.26616	-0.75265
N	1.28589	-1.25767	0.74812
C	2.46402	0.40669	-0.65189
C	2.4671	-0.40167	0.63899
C	1.39916	-2.50984	0.00739
C	1.39341	2.5054	0.0103
H	1.13203	1.49749	-1.72525
H	1.12628	-1.47148	1.72352
H	3.3928	0.98972	-0.70206
H	2.45713	-0.27075	-1.5076
H	3.39427	-0.98774	0.68185
H	2.47034	0.27544	1.4948
H	2.29758	-3.07695	0.28334
H	1.43512	-2.31154	-1.06479
H	0.52002	-3.12387	0.20343
H	2.29512	3.07531	-0.24839
H	1.41916	2.28988	1.07935
H	0.51708	3.12406	-0.18363





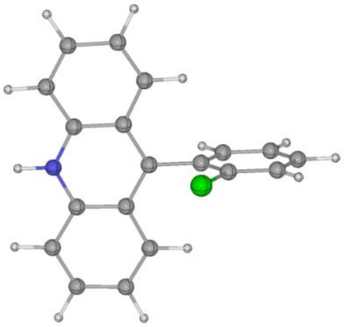
HA^+

E(UPW6B95D3) = -1248.42623740

E(UωB97XD) = -1246.71228539

Charge = 1 Multiplicity = 1

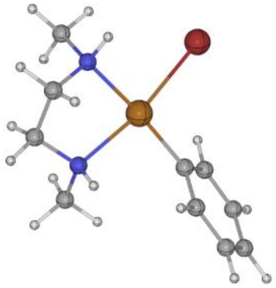
C	-4.50026	-1.25783	-0.01508
C	-3.09174	-1.22237	-0.00808
C	-2.39455	0.01213	0.02312
C	-3.1596	1.21149	0.05022
C	-4.51757	1.16196	0.04714
C	-5.19031	-0.08378	0.01294
H	-5.00529	-2.21488	-0.04073
H	-2.64301	2.16142	0.07396
H	-5.09523	2.07629	0.06931
H	-6.27267	-0.10111	0.00929
C	-0.99313	-0.00226	0.02973
C	-1.03987	-2.42861	-0.02099
C	-0.29921	-1.21981	0.01007
C	-0.38648	-3.67687	-0.04097



C	0.97502	-3.70999	-0.02446
H	1.48553	-4.66436	-0.03789
C	1.73733	-2.51716	0.01127
H	2.81726	-2.57806	0.02608
C	1.12108	-1.3062	0.02675
H	1.701	-0.39368	0.05335
N	-2.38511	-2.36861	-0.03097
H	-2.89808	-3.24393	-0.05386
C	-0.23916	1.27788	0.02747
C	0.11374	1.92865	1.20345
C	0.13124	1.84943	-1.18593
C	0.81836	3.12082	1.18337
C	0.83498	3.041	-1.21886
H	-0.13904	1.34681	-2.10619
C	1.17764	3.67538	-0.03402
H	1.08191	3.60795	2.11259
H	1.11557	3.47288	-2.17062
H	1.72872	4.60678	-0.05196
Cl	-0.33171	1.23987	2.74008
H	-0.97737	-4.58347	-0.06695

11

E(UPW6B95D3) = -4718.39591490
E(UωB97XD) = -4715.69287680
Charge = 0 Multiplicity = 2



N	-3.1888	0.37708	0.28176
N	-1.86531	-1.59588	-1.15411
C	-3.93981	-0.80171	-0.16323
C	-3.29255	-1.36534	-1.41067
C	-1.6015	-2.79417	-0.35118
C	-3.45736	0.72616	1.6757
H	-3.45295	1.16524	-0.30124
H	-1.38369	-1.70119	-2.03905
H	-3.91393	-1.53764	0.64168
H	-4.98946	-0.56142	-0.35382
H	-3.3706	-0.6434	-2.22597
H	-3.79927	-2.28535	-1.71817
H	-0.525	-2.94602	-0.29618
H	-2.07304	-3.6793	-0.78949
H	-1.98041	-2.6607	0.66193
H	-4.53011	0.84013	1.86282
H	-2.95445	1.65997	1.91985
H	-3.06987	-0.05949	2.32518
Cu	-1.11142	0.14742	-0.28731
Br	1.2077	-0.55019	-0.98167
C	-0.62297	1.91592	0.42672
C	-1.27892	3.06571	-0.02522

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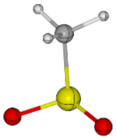
C	0.32195	2.09435	1.44138
C	-1.01015	4.32637	0.5008
H	-2.03032	2.98962	-0.80743
C	0.58652	3.34455	1.99098
H	0.87558	1.23787	1.81347
C	-0.07813	4.4697	1.51932
H	-1.53331	5.19646	0.11845
H	1.3174	3.44297	2.78676
H	0.12911	5.44659	1.94049

MeSO$_2^-$

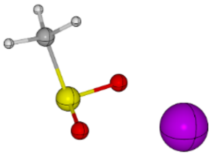
E(UPW6B95D3) = -589.312824955
E(UωB97XD) = -588.699565733
Charge = -1 Multiplicity = 1



S	0.87517	-0.31942	0.78522
O	1.55841	-1.63195	0.53467
O	1.73199	0.83586	0.35722
C	0.99967	-0.19649	2.59897
H	2.06108	-0.2636	2.85333
H	0.59163	0.75979	2.93305
H	0.44794	-1.01629	3.06397

MeSO$_2$K

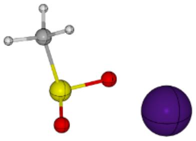
E(UPW6B95D3) = -1189.61862203
E(UωB97XD) = -1188.58756179
Charge = 0 Multiplicity = 1



K	-2.1915156326	-1.6616388771	1.5343469867
S	-1.9383317791	1.2369267546	0.1581049786
O	-2.2644960022	-0.0518613278	-0.5594828467
O	-1.7472656808	0.9402692411	1.6270295735
C	-3.5388175943	2.0746687383	0.1564823247
H	-3.8310697802	2.2874153607	-0.8731994385
H	-4.2660556125	1.4090694268	0.6283568544
H	-3.4561519183	3.0065866834	0.7182305673

MeSO$_2$Cs

E(UPW6B95D3) = -609.427507367
E(UωB97XD) = -608.855008206
Charge = 0 Multiplicity = 1

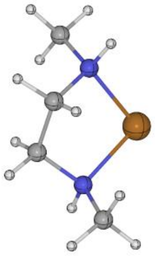


Cs	-1.9430255384	-2.0134334753	-0.3399507940
S	-2.0616089849	1.2243699526	1.4136611309
O	-0.8700151421	0.7471731892	0.6264763923
O	-2.9580410751	0.0640831089	1.7559517162
C	-3.0301004179	2.0540025906	0.1230155051
H	-2.4633831224	2.8995763502	-0.2706796396
H	-3.2168792175	1.3233978964	-0.6689524497

H	-3.9746085017	2.4030083873	0.5440841388

10^{+}

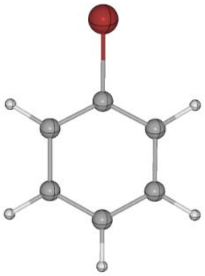
E(UPW6B95D3) = -1910.88816721
E(UωB97XD) = -1909.65764285
Charge = 1 Multiplicity = 1

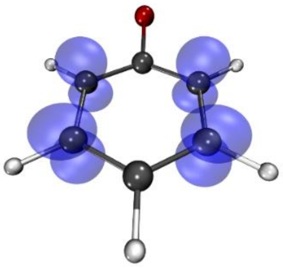


Cu	-0.2338	-0.0019	-0.00235
N	1.25777	1.27548	-0.74163
N	1.25949	-1.27438	0.74099
C	2.44641	0.41318	-0.6417
C	2.44689	-0.41035	0.64126
C	1.39596	-2.53179	0.00141
C	1.39147	2.53219	-0.00039
H	1.11032	1.49888	-1.71754
H	1.11126	-1.4968	1.717
H	3.36628	1.00708	-0.67859
H	2.44702	-0.25202	-1.5063
H	3.36757	-1.00297	0.67827
H	2.4465	0.25482	1.50587
H	2.28611	-3.08992	0.313
H	1.46981	-2.33167	-1.06745
H	0.51316	-3.14667	0.17257
H	2.28133	3.09186	-0.31007
H	1.46403	2.33101	1.06836
H	0.50811	3.1461	-0.17214

7$^{-\cdot}$

E(UPW6B95D3) = -2807.38284957
E(UωB97XD) = -2805.91082151
Charge = -1 Multiplicity = 2





C	-3.01433	-0.42598	-0.01624
C	-1.55825	-0.44106	-0.0135
C	-0.91414	0.78338	-0.0105
C	-1.54783	2.01264	-0.00986
C	-3.00398	2.01067	-0.01313
C	-3.67786	0.7949	-0.01587
H	-3.56574	-1.35855	-0.01846
H	-1.00185	-1.36775	-0.01411
H	-0.98354	2.93459	-0.00744
H	-3.54728	2.94794	-0.01282
H	-4.76531	0.79937	-0.01795
Br	1.0127	0.77535	-0.00719

Ph

E(UPW6B95D3) = -231.963727440
E(UωB97XD) = -231.564275164

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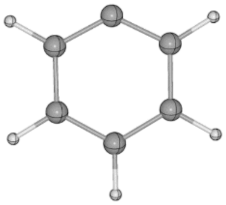
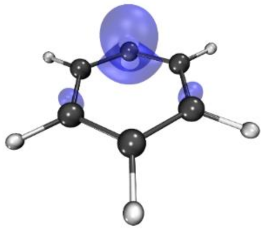
Charge = 0 Multiplicity = 2

C	-3.42311	-0.43545	0.00004
C	-2.02696	-0.44902	0.00059
C	-1.40754	0.77215	0.00004
C	-2.02685	1.99336	-0.00098
C	-3.423	1.97992	-0.00151
C	-4.11016	0.77227	-0.00099
H	-3.96736	-1.37256	0.00044
H	-1.47803	-1.38307	0.00139
H	-1.47784	2.92737	-0.00138
H	-3.96717	2.91707	-0.00232
H	-5.19315	0.77231	-0.0014



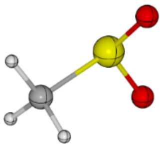


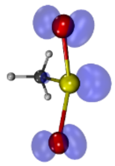
MeSO$_2$

E(UPW6B95D3) = -589.149307393
E(UωB97XD) = -588.541786025

Charge = 0 Multiplicity = 2

S	1.0089683488	-0.3228081614	0.8431534210
O	1.4824604221	-1.6467592945	0.4811560498
O	1.6713017988	0.8501600865	0.3014678858
C	1.0189128274	-0.1950659143	2.6327277780
H	2.0641042821	-0.2517967652	2.9398995202
H	0.5775157985	0.7625400421	2.8995601068
H	0.4426065225	-1.0283739934	3.0284602385



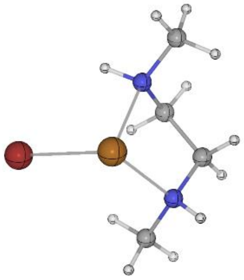


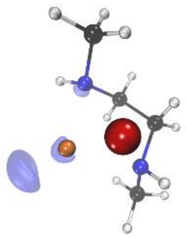
6$^-$

E(UPW6B95D3) = -4486.41015126
E(UωB97XD) = -4484.10449132

Charge = -1 Multiplicity = 2

Cu	-0.2149427550	-0.0584224822	0.5969704484
N	1.3041158758	1.2864509985	-0.4832206964
N	1.6747457229	-1.2428869767	1.0001806522
C	2.4160282123	0.3717454259	-0.7113237345
C	2.7754720147	-0.3872559570	0.5587766520
C	1.6319070391	-2.5310176686	0.3183850557
C	1.6993429163	2.5864856394	0.0322472168
H	0.7723292190	1.3948012841	-1.3364405553
H	1.7636882901	-1.4038121134	1.9940803843
H	3.3083213751	0.8977642601	-1.0775853130
H	2.1129623969	-0.3379915974	-1.4832167274
H	3.6902772740	-0.9691345051	0.3830409881
H	2.9894923797	0.3256971460	1.3577402330
H	2.5874327328	-3.0692511198	0.3803396381
H	1.3699394967	-2.3874034592	-0.7302522661
H	0.8505943681	-3.1463032399	0.7653852319
H	2.4259532730	3.0977752695	-0.6147495609





H	2.1454727843	2.4774255894	1.0226791278
H	0.8164010265	3.2185326438	0.1347532149
Br	-1.2671403500	-0.8599151493	-1.6018789813

Study of the C–Br bond dissociation in radical anion $\mathbf{7}^{-\cdot}$

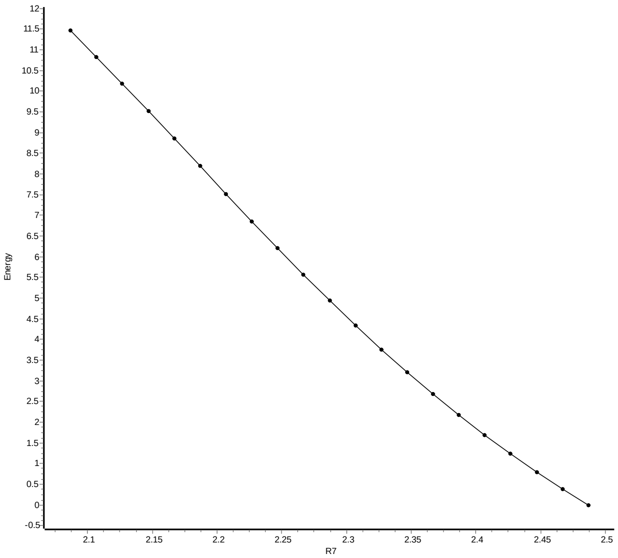


Figure S2. A scan of the C–Br bond in structure $\mathbf{7}^{-\cdot}$, indicating that the dissociation of the anion radical is barrierless.

Study of the oxidative addition to complex 10

A transition state for an oxidative addition to Cu^0 complex **10** could not be located, which is in line with the high energy of the SOMO of complex **10** (–4.2 eV, cf –6.77 eV for the HOMO) and the trigonal planar orientation of the ligand and the SOMO, predisposing the complex to react either in a halogen atom transfer (XAT) or a single electron transfer (SET), consistent with the results of the computational study.

Anion exchange

The thermodynamics of the anion exchange reaction between bromide **6** and the methanesulfinate salt was investigated computationally with the anion form $MeSO_2^-$, as well as the potassium and cesium sulfinates ($MeSO_2K$ and $MeSO_2Cs$). The Gibbs free energies of the reactions were 8.97 kcal/mol for potassium, 4.94 kcal/mol for cesium, and 6.22 kcal/mol for the free sulfinate anion.

Estimation of the activation barriers of the dissociative electron transfer (DET) between complex 10 and aryl bromide 7 and acridinyl radical HA and complex 6

The following equations, derived from Marcus-Hush theory,[35] can approximate the stepwise DET process:

$$\Delta G^{\ddagger}_{ET} = \Delta G^{\ddagger}_{0}\left(1 + \frac{\Delta G_r}{4\Delta G_0}\right)^2$$

$$\Delta G_0 = \frac{\lambda}{4}$$

$$\lambda_0 = \left(332\ \frac{kcal}{mol}\right)\left(\frac{1}{2a_1} + \frac{1}{2a_2} + \frac{1}{R}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon}\right)$$

The intrinsic barrier, ΔG_0 , is estimated by first determining the reorganization energy, λ. As the inner reorganization is expected to have a small contribution to λ, the reorganization energy is approximated by the outer reorganization energy, $\lambda_0 \approx \lambda$.

The concerted DET barrier is calculated following Savéant's model.[36] The intrinsic barrier incorporates the bond dissociation free energy (BDFE) for the accepting species:

$$\Delta G^{\ddagger}_{0} = \frac{\lambda + BDFE}{4}$$

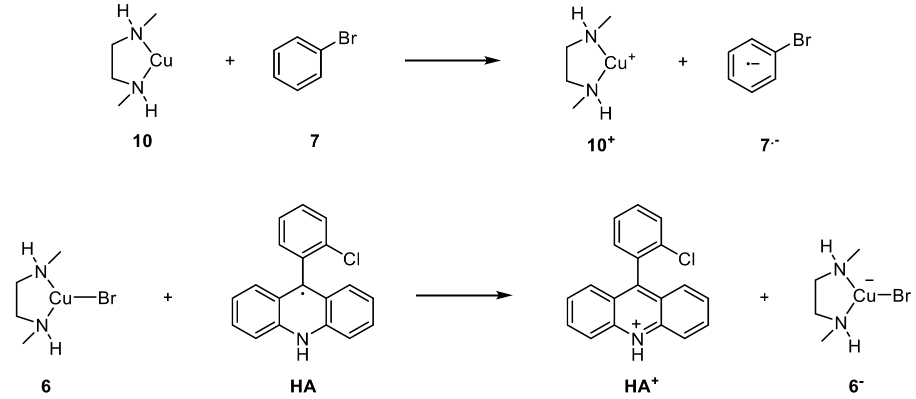


Figure S3. Estimation of the barrier for the stepwise DET process for reactants **10** and **7** and **HA** and **6**.

The estimated energy barrier for the stepwise DET was 11.0 kcal/mol for reactants **10** and **7** and 74.8 kcal/mol for **HA** and **6** (Tables S3 and S4).

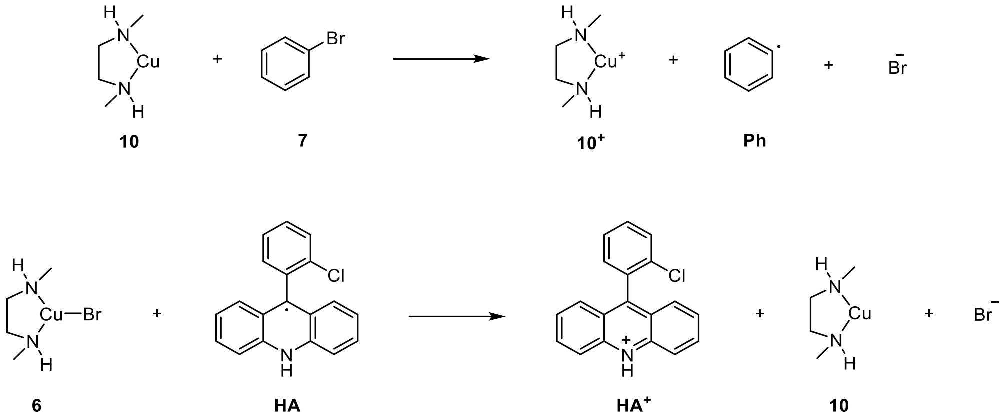


Figure S4: Estimation of the barrier for the concerted DET process for reactants **10** and **7** and **HA** and **6**.

The estimated energy barrier for the stepwise DET was 17.6 kcal/mol for reactants **10** and **7** and 95.7 kcal/mol for **HA** and **6** (Tables S3 and S4).

Table S3. DET process parameters for reactants 10 and 7.

	a_1, Å	a_2, Å	ε_{op}	ε	λ_0, kcal/mol	BDFE, kcal/mol	ΔG_r, kcal/mol	ΔG_{ET}‡, kcal/mol
Stepwise	6.47	5.74	1.81	35.69	28.77		6.85	11.0
Concerted	6.47	5.74	1.81	35.69	28.77	74.48	-18.11	17.6

Values displayed are taken from the final single point-corrected values. The stepwise and concerted for each term are displayed. a_1 is the sphere radius of the donor species; a_2 is the sphere radius of the acceptor species; ε_{op} is the square of the refractive index of the solvent (acetonitrile), ε is the dielectric constant of the solvent (acetonitrile); λ_o is the outer sphere reorganization energy; BDFE is the bond dissociation free energy of bromide **7** along the C–Br bond; ΔG_r is the free energy of the stepwise and concerted processes; ΔG_{ET}‡ is the activation barrier for the processes.

Table S4. DET process parameters for reactants HA and 6.

	a_1, Å	a_2, Å	ε_{op}	ε	λ_0, kcal/mol	BDFE, kcal/mol	ΔG_r, kcal/mol	ΔG_{ET}‡, kcal/mol
Stepwise	3.23	4.74	1.81	35.7	23.5		71.3	95.7
Concerted	3.23	4.74	1.81	35.7	23.5	110.6	66.3	74.8

Values displayed are taken from the final single point-corrected values. The stepwise and concerted for each term are displayed. a_1 is the sphere radius of the donor species; a_2 is the sphere radius of the acceptor species; ε_{op} is the square of the refractive index of the solvent (acetonitrile), ε is the dielectric constant of the solvent (acetonitrile); λ_o is the outer sphere reorganization energy; BDFE is the bond dissociation free energy of bromide **7** along the C–Br bond; ΔG_r is the free energy of the stepwise and concerted processes; $\Delta G_{ET}^{\ddagger}$ is the activation barrier for the processes.

Reduction potentials of acridine structures

The reduction potentials of the O/R **HA**$^+$/**HA**, **6**/[**10** + Br$^-$], Cu(**L4**)I/[**10** + I$^-$] couples was calculated from the difference in the free energies at the PW6B95 - D3(BJ) / def2-TZVPPD / SMD (MeCN) // ωB97X-D / def2-TZVP / SMD (MeCN) level expressed in eV, followed by subtraction of the absolute potential of the saturated calomel electrode (SCE) in MeCN.[37]

$$E^{\ominus}_{O/_{R},MeCN} = E^{\ominus}_{O/_{R},MeCN} - 4.43V$$

The calculated reduction potentials are –0.66 V for **HA**$^+$/**HA**, –3.52 V for **6**/[**10** + Br$^-$], –3.31 V for Cu(**L4**)I/[**10** + I$^-$].

Interaction/distortion-activation strain model (ASM) and energy decomposition analysis (EDA) of TSA

The Interaction/Distortion-Activation Strain Model (ASM)[38] and ALMO-EDA2[39] were used to investigate the electronic contributions to the oxidative addition between the copper complex **8** and aryl bromide **7**. The ALMO-EDA2 study was carried out using Q-Chem at the ωB97X-D / def2-TZVP (SG-2 grid) level in MeCN (SMD). The Gaussian 16 optimized geometries were used as inputs for the Q-Chem optimization, using the same level of theory as for Gaussian 16. The fragments specified for the energy decomposition analysis (EDA) of **TSA** were those representing reactants **6** and **7**.

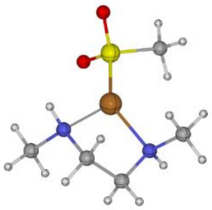
Q-Chem optimized geometries

8

E(UωB97XD) = -2498.38288749

Charge = 0 Multiplicity = 1

Cu	-0.32543	0.19665	0.37652
N	1.20338	1.29762	-0.52757
N	1.19265	-1.22308	0.83398
C	2.33506	0.36681	-0.65671
C	2.45319	-0.51330	0.57854
C	1.04529	-2.44933	0.04480
C	1.53550	2.51064	0.22843



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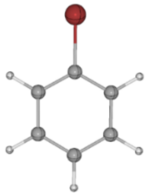
H	0.91403	1.57883	-1.45599
H	1.15638	-1.47254	1.81411
H	3.27578	0.90543	-0.81006
H	2.15782	-0.25237	-1.53701
H	3.28501	-1.21306	0.44552
H	2.67357	0.10268	1.45161
H	1.88126	-3.13855	0.20705
H	0.99593	-2.20885	-1.01750
H	0.11658	-2.94543	0.32400
H	2.39414	3.03191	-0.20774
H	1.77250	2.25653	1.26165
H	0.67525	3.17914	0.23068
S	-2.48803	0.24879	0.73854
O	-3.20531	-0.80104	-0.01746
O	-2.82920	0.28830	2.17698
C	-3.17583	1.77941	0.09837
H	-2.98975	1.83509	-0.97470
H	-4.25006	1.77083	0.29785
H	-2.70326	2.62298	0.60261

7

E(UωB97XD) = -2805.86508778

Charge = 0 Multiplicity = 1

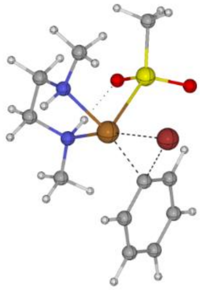


C	-3.40478	-0.42819	0.00006
C	-2.01692	-0.43682	0.00058
C	-1.34037	0.77214	0.00005
C	-2.01682	1.98117	-0.00099
C	-3.40468	1.97266	-0.00151
C	-4.10023	0.77226	-0.00099
H	-3.94047	-1.36912	0.00045
H	-1.47662	-1.37384	0.00136
H	-1.47644	2.91814	-0.00139
H	-3.94029	2.91363	-0.00230
H	-5.18293	0.77231	-0.00140
Br	0.55988	0.77206	0.00072

TSA

E(UωB97XD) = -5304.21248014

Charge = 0 Multiplicity = 1



C	1.53048	1.20840	-0.38716
C	2.37560	0.94292	0.68687
C	2.90780	2.02448	1.38549
C	2.62174	3.33318	1.00038
C	1.78802	3.57070	-0.08906
C	1.24269	2.50652	-0.80399
H	2.58509	-0.08606	0.98700

H	3.55632	1.83551	2.24001
H	3.05369	4.16899	1.54757
H	1.56224	4.59073	-0.39654
H	0.60711	2.69002	-1.66793
Cu	-0.05960	0.02661	-0.53526
Br	1.69158	-0.37929	-2.28585
N	-1.13899	0.67001	1.14755
H	-0.77010	-0.03743	1.81107
C	-2.53714	0.34944	0.87987
H	-2.96609	1.14288	0.25102
H	-3.12940	0.31523	1.80757
C	-2.62069	-0.97830	0.16319
H	-2.16743	-1.75586	0.79253
H	-3.66871	-1.25818	-0.01934
N	-1.85575	-0.89945	-1.08010
H	-2.30409	-0.21577	-1.68898
C	-0.94172	2.00154	1.68504
H	-1.53500	2.16558	2.59830
H	0.11480	2.14882	1.92919
H	-1.23519	2.75866	0.94795
C	-1.74656	-2.15995	-1.79673
H	-2.73050	-2.60539	-2.00550
H	-1.22385	-1.99818	-2.74499
H	-1.16194	-2.87009	-1.20262
S	0.68427	-2.00589	1.20588
C	0.21274	-3.75266	1.08162
H	0.70962	-4.20389	0.21590
H	0.57381	-4.20812	2.01137
H	-0.87472	-3.85460	1.00037
O	2.17766	-2.12671	1.43286
O	-0.07880	-1.58286	2.46488

Distortion/interaction activation strain model analysis

The total electronic energy for a transition state is determined by summation of the interaction and distortion energies of its fragments:

$$\Delta E^{\ddagger} = \Delta E^{\ddagger}_{int} + \Delta E^{\ddagger}_{dist}$$

where $\Delta E^{\ddagger}_{int}$ is the energy of the distorted components interaction and $\Delta E^{\ddagger}_{dist}$ is the distorted energy of each of the components of **TSA**.

$$\Delta E^{\ddagger}_{dist} = \Delta E^{\ddagger}_{dist}(\mathbf{8}) + \Delta E^{\ddagger}_{dist}(\mathbf{7})$$

$$\Delta E^{\ddagger}_{dist}(\mathbf{8}) = E_{dist}(\mathbf{8}) - E(\mathbf{8})$$

$$\Delta E^{\ddagger}_{dist}(\mathbf{7}) = E_{dist}(\mathbf{7}) - E(\mathbf{7})$$

Energy decomposition analysis

The interaction energy was further decomposed by the second generation Absolutely Localized Molecular Orbital Energy Decomposition Analysis (ALMO-EDA2).

$$\Delta E^{\ddagger}_{int} = \Delta E_{FRZ} + \Delta E_{POL} + \Delta E_{CT}$$

ΔE_{FRZ} is the difference between the energies of the isolated fragments and the energy for bringing these fragments together in the transition state without allowing intrafragment orbital relaxation nor interfragment delocalization. The ΔE_{POL} term is the energy contribution associated with polarization obtained by allowing the frozen fragment-localized orbitals to relax without interfragment orbital delocalization. ΔE_{CT} is the contribution of the interfragment MO relaxation. The ΔE_{FRZ} term can be decomposed further into three components:

$$\Delta E_{FRZ} = \Delta E_{Pauli} + \Delta E_{Elec} + \Delta E_{Disp}$$

The ΔE_{Pauli} term represents Pauli repulsion, ΔE_{Elec} refers to permanent electrostatic interactions, and ΔE_{Disp} is the attractive interactions caused by dispersion.

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X-Ray crystallographic data

1-(Cyclohexylsulfonyl)-2-fluorobenzene (3h)

CCDC 2154274

Bond precision: C—C = 0.0020 Å Wavelength = 1.54184

Cell: a = 5.7507(1) b = 16.7466(2) c = 12.2017(2)

α = 90 β = 91.744(1) γ = 90

Temperature: 100 K

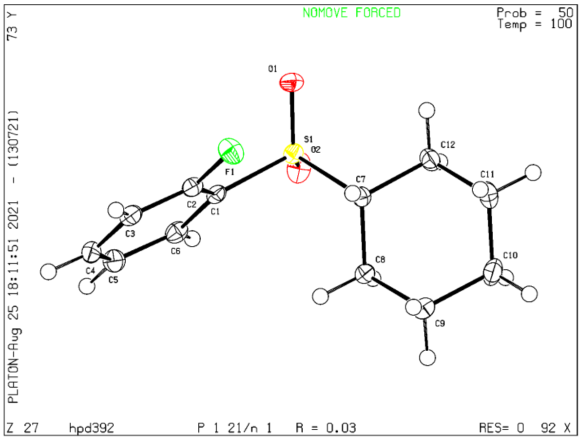
	Calculated	Reported
Volume	1174.54(3)	1174.54(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	$C_{12}H_{15}FO_2S$	$C_{12}H_{15}FO_2S$
Sum formula	$C_{12}H_{15}FO_2S$	$C_{12}H_{15}FO_2S$
M_r	242.30	242.30
D_x,g cm^{-3}	1.370	1.370
Z	4	4
Mu (mm^{-1})	2.440	2.440
F000	512.0	512.0
F000'	514.85	
h,k,l_{max}	7,21,15	7,20,14
N_{ref}	2471	2351
T_{min},T_{max}	0.849,0.929	0.878,1.000
T_{min}'	0.755	

Correction method = # Reported T Limits: T_{min} = 0.878 T_{max} = 1.000 AbsCorr = GAUSSIAN

Data completeness = 0.951 Theta(max) = 76.474

R(reflections) = 0.0333(2190) wR2(reflections) = 0.0923(2351)

S = 1.062 N_{par} = 145



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2-(4-(Cyclohexylsulfonyl)phenyl)oxazole (3p)

CCDC 2154269

Bond precision: C–C = 0.0019 Å Wavelength = 1.54184

Cell: a = 5.59474(6) b = 11.06957(9) c = 11.48371(12)

α = 99.6103(8) β = 92.4648(9) γ = 97.3808(8)

Temperature: 100 K

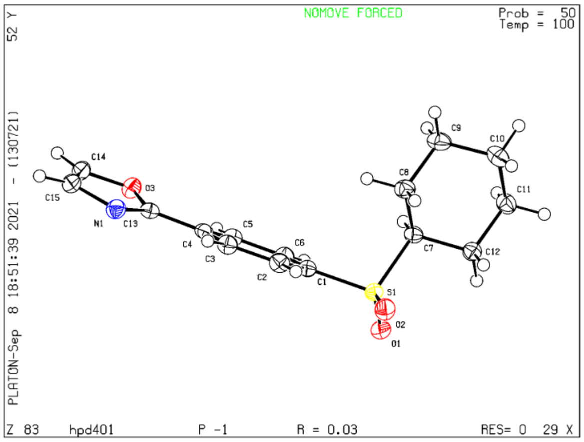
	Calculated	Reported
Volume	693.898(12)	693.899(12)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	$C_{15}H_{17}NO_3S$	$C_{15}H_{17}NO_3S$
Sum formula	$C_{15}H_{17}NO_3S$	$C_{15}H_{17}NO_3S$
M_r	291.36	291.35
D_x,g cm^{-3}	1.395	1.394
Z	2	2
Mu (mm^{-1})	2.137	2.137
F000	308.0	308.0
F000'	309.53	
h,k,l_{max}	7,13,14	7,13,14
N_{ref}	2916	2801
T_{min},T_{max}	0.752,0.895	0.751,1.000
T_{min}'	0.694	

Correction method = # Reported T Limits: T_{min} = 0.751 T_{max} = 1.000 AbsCorr = GAUSSIAN

Data completeness = 0.961 Theta(max) = 76.483

R(reflections) = 0.0313(2646) wR2(reflections) = 0.0876(2801)

S = 1.000 N_{par} = 182



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6-(Cyclohexylsulfonyl)quinolone (3s)

CCDC 2154271

Bond precision: C–C = 0.0020 Å Wavelength = 1.54184

Cell: a = 8.57740(13) b = 14.94469(19) c = 11.09695(16)

α = 90 β = 109.6212(17) γ = 90

Temperature: 100 K

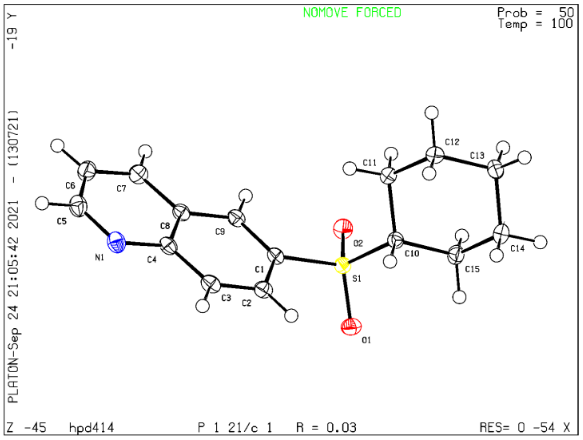
	Calculated	Reported
Volume	1339.88(4)	1339.88(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{15}H_{17}NO_2S$	$C_{15}H_{17}NO_2S$
Sum formula	$C_{15}H_{17}NO_2S$	$C_{15}H_{17}NO_2S$
M_r	275.36	275.35
D_x,g cm^{-3}	1.365	1.365
Z	4	4
Mu (mm^{-1})	2.123	2.123
F000	584.0	584.0
F000'	586.87	
h,k,l_{max}	10,18,13	10,18,13
N_{ref}	2820	2700
T_{min},T_{max}	0.824,0.944	0.850,1.000
T_{min}'	0.821	

Correction method = # Reported T Limits: T_{min} = 0.850 T_{max} = 1.000 AbsCorr = GAUSSIAN

Data completeness = 0.957 Theta(max) = 76.588

R(reflections) = 0.0348(2449) wR2(reflections) = 0.0889(2700)

S = 1.048 N_{par} = 172



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3-(Cyclohexylsulfonyl)quinolone (3u)

CCDC 2154270

Bond precision: C–C = 0.0019 Å Wavelength = 1.54184

Cell: a = 14.42366(14) b = 5.22588(5) c = 17.50239(19)

α = 90 β = 95.9585(10) γ = 90

Temperature: 100 K

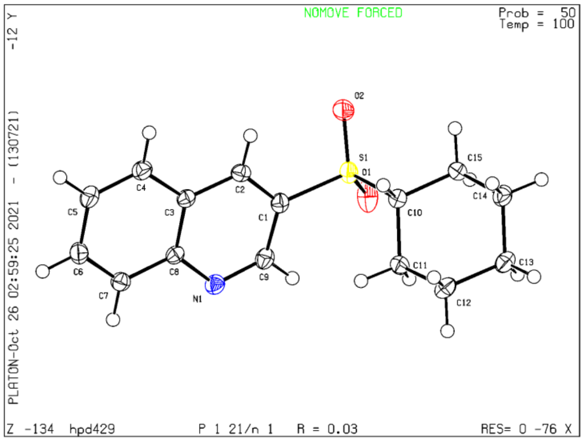
	Calculated	Reported
Volume	1312.14(2)	1312.14(2)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	$C_{15}H_{17}NO_2S$	$C_{15}H_{17}NO_2S$
Sum formula	$C_{15}H_{17}NO_2S$	$C_{15}H_{17}NO_2S$
M_r	275.36	275.35
D_x,g cm^{-3}	1.394	1.394
Z	4	4
Mu (mm^{-1})	2.168	2.168
F000	584.0	584.0
F000'	586.87	
h,k,l_{max}	18,6,22	18,6,21
N_{ref}	2751	2680
T_{min},T_{max}	0.793,0.850	0.691,1.000
T_{min}'	0.681	

Correction method = # Reported T Limits: T_{min}=0.691 T_{max}=1.000 AbsCorr = GAUSSIAN

Data completeness = 0.974 Theta(max) = 76.237

R(reflections)= 0.0317(2493) wR2(reflections)= 0.0858(2680)

S = 1.073 N_{par} = 173



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4-(Cyclohexylsulfonyl)-1,2-dimethyl-1*H*-imidazole (3x)

CCDC 2154277

Bond precision: C–C = 0.0020 Å Wavelength = 1.54184

Cell: a = 8.92184(15) b = 10.50688(15) c = 25.2850(4)

α = 90 β = 90 γ = 90

Temperature: 100 K

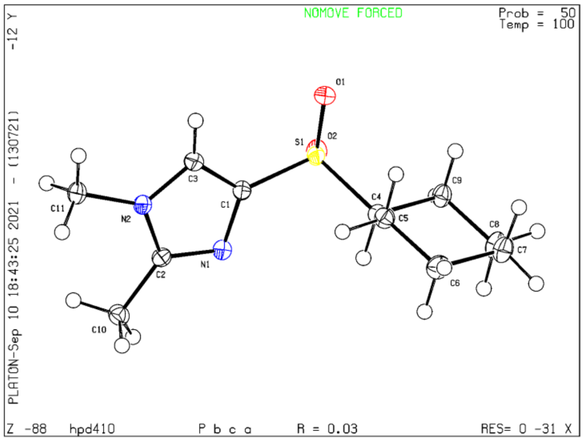
	Calculated	Reported
Volume	2370.23(6)	2370.24(6)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	$C_{11}H_{18}N_2O_2S$	$C_{11}H_{18}N_2O_2S$
Sum formula	$C_{11}H_{18}N_2O_2S$	$C_{11}H_{18}N_2O_2S$
M_r	242.33	242.33
D_x,g cm^{-3}	1.358	1.358
Z	8	8
Mu (mm^{-1})	2.337	2.337
F000	1040.0	1040.0
F000'	1045.38	
h,k,l_{max}	11,13,31	11,12,30
N_{ref}	2482	2385
T_{min},T_{max}	0.824,0.886	0.797,1.000
T_{min}'	0.743	

Correction method = # Reported T Limits: T_{min} = 0.797 T_{max} = 1.000 AbsCorr = GAUSSIAN

Data completeness = 0.961 Theta(max) = 76.242

R(reflections) = 0.0324(2193) wR2(reflections) = 0.0862(2385)

S = 1.055 N_{par} = 148



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3-(Cyclohexylsulfonyl)thiophene (3ab)

CCDC 2154273

Bond precision: C—C = 0.0030 Å Wavelength = 1.54184

Cell: a = 9.7634(1) b = 11.2655(2) c = 10.1948(1)

α = 90 β = 106.174(2) γ = 90

Temperature: 100 K

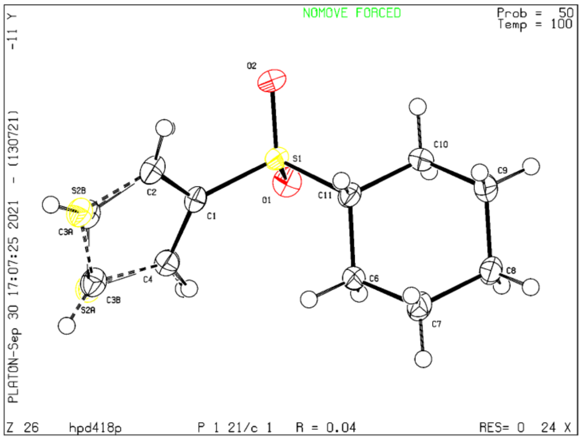
	Calculated	Reported
Volume	1076.94(3)	1076.94(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{10}H_{14}O_2S_2$	$C_{10}H_{14}O_2S_2$
Sum formula	$C_{10}H_{14}O_2S_2$	$C_{10}H_{14}O_2S_2$
M_r	230.33	230.33
D_x,g cm^{-3}	1.421	1.421
Z	4	4
Mu (mm^{-1})	4.255	4.255
F000	488.0	488.0
F000'	491.77	
h,k,l_{max}	12,14,12	12,13,12
N_{ref}	2219	2151
T_{min},T_{max}	0.738,0.805	0.740,1.000
T_{min}'	0.545	

Correction method = # Reported T Limits: T_{min} = 0.740 T_{max} = 1.000 AbsCorr = GAUSSIAN

Data completeness = 0.969 Theta(max) = 75.181

R(reflections) = 0.0357(2010) wR2(reflections) = 0.0937(2151)

S = 1.055 N_{par} = 127



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2-(Cyclohexylsulfonyl)dibenzo[*b*,*d*]furan (3ae)

CCDC 2154272

Bond precision: C—C = 0.0019 Å Wavelength = 1.54184

Cell: a = 5.4824(1) b = 10.8253(1) c = 25.2140(3)

α = 90 β = 91.633(1) γ = 90

Temperature: 100 K

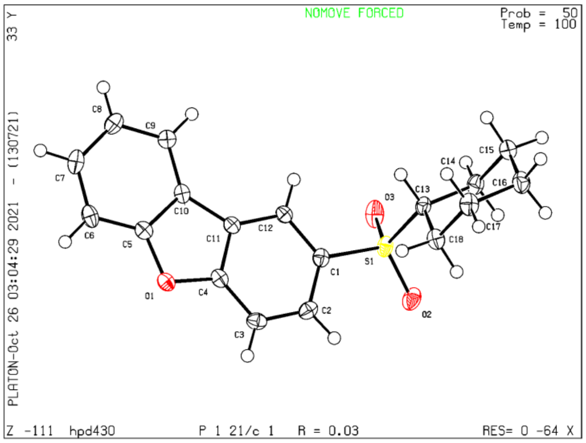
	Calculated	Reported
Volume	1495.81(4)	1495.81(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{18}H_{18}O_3S$	$C_{18}H_{18}O_3S$
Sum formula	$C_{18}H_{18}O_3S$	$C_{18}H_{18}O_3S$
M_r	314.38	314.38
D_x,g cm^{-3}	1.396	1.396
Z	4	4
Mu (mm^{-1})	2.009	2.009
F000	664.0	664.0
F000'	667.16	
h,k,l_{max}	6,13,31	6,13,31
N_{ref}	3128	3035
T_{min},T_{max}	0.811,0.915	0.672,1.000
T_{min}'	0.718	

Correction method = # Reported T Limits: T_{min} = 0.672 T_{max} = 1.000 AbsCorr = GAUSSIAN

Data completeness = 0.970 Theta(max) = 76.161

R(reflections) = 0.0345(2761) wR2(reflections) = 0.0926(3035)

S = 1.052 N_{par} = 199



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1-Phenyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-1-one (4c)

CCDC 2154279

Bond precision: C–C = 0.0021 Å Wavelength = 1.54184

Cell: a = 5.74991(7) b = 29.6978(5) c = 9.19517(14)

α = 90 β = 98.3701(14) γ = 90

Temperature: 100 K

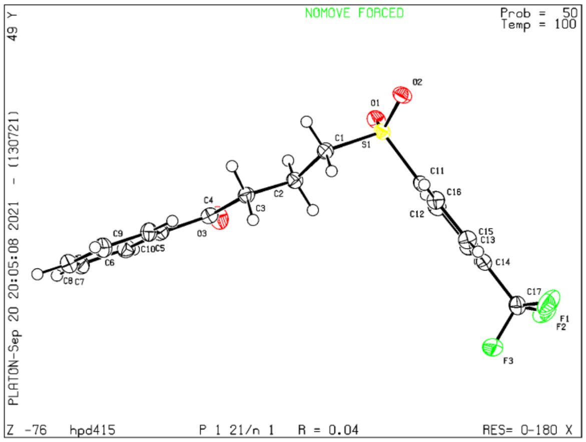
	Calculated	Reported
Volume	1553.44(4)	1553.44(4)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	$C_{17}H_{15}F_3O_3S$	$C_{17}H_{15}F_3O_3S$
Sum formula	$C_{17}H_{15}F_3O_3S$	$C_{17}H_{15}F_3O_3S$
M_r	356.35	356.35
D_x,g cm^{-3}	1.524	1.524
Z	4	4
Mu (mm^{-1})	2.295	2.295
F000	736.0	736.0
F000'	739.96	
h,k,l_{max}	7,37,11	7,36,11
N_{ref}	3268	3149
T_{min},T_{max}	0.829,0.906	0.803,1.000
T_{min}'	0.823	

Correction method = # Reported T Limits: T_{min} = 0.803 T_{max} = 1.000 AbsCorr = GAUSSIAN

Data completeness = 0.964 Theta(max) = 76.345

R(reflections) = 0.0372(2783) wR2(reflections) = 0.1022(3149)

S = 1.058 N_{par} = 218



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2-(5-((4-(Trifluoromethyl)phenyl)sulfonyl)pentyl)isoindoline-1,3-dione (4e)

CCDC 2154280

Bond precision: C–C = 0.0020 Å Wavelength = 1.54184

Cell: a = 7.8536(4) b = 8.1137(3) c = 16.1137(6)

α = 75.885(3) β = 76.455(4) γ = 73.909(4)

Temperature: 100 K

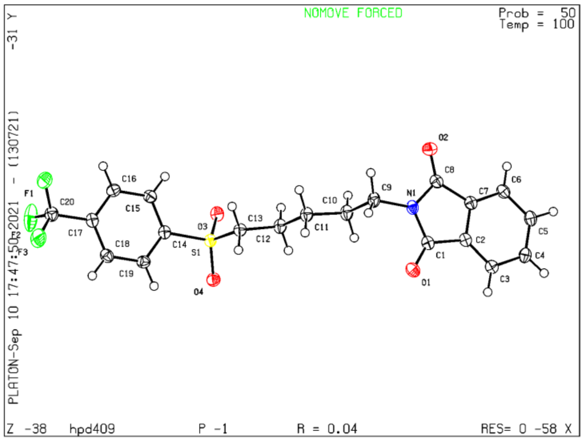
	Calculated	Reported
Volume	941.36(7)	941.36(7)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	$C_{20}H_{18}F_3NO_4S$	$C_{20}H_{18}F_3NO_4S$
Sum formula	$C_{20}H_{18}F_3NO_4S$	$C_{20}H_{18}F_3NO_4S$
M_r	425.41	425.41
D_x,g cm^{-3}	1.501	1.501
Z	2	2
Mu (mm^{-1})	2.053	2.053
F000	440.0	440.0
F000'	442.23	
h,k,l_{max}	9,10,20	9,10,20
N_{ref}	3951	3768
T_{min},T_{max}	0.768,0.871	0.632,1.000
T_{min}'	0.733	

Correction method = # Reported T Limits: T_{min} = 0.632 T_{max} = 1.000 AbsCorr = GAUSSIAN

Data completeness = 0.954 Theta(max) = 76.536

R(reflections) = 0.0432(3414) wR2(reflections) = 0.1189(3768)

S = 1.081 N_{par} = 262



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1-((4-(Trifluoromethyl)phenyl)sulfonyl)adamantine (4t)

CCDC 2154278

Bond precision: C–C = 0.0019 Å Wavelength = 1.54184

Cell: a = 6.53596(7) b = 27.0398(3) c = 8.63637(9)

α = 90 β = 97.2354(10) γ = 90

Temperature: 100 K

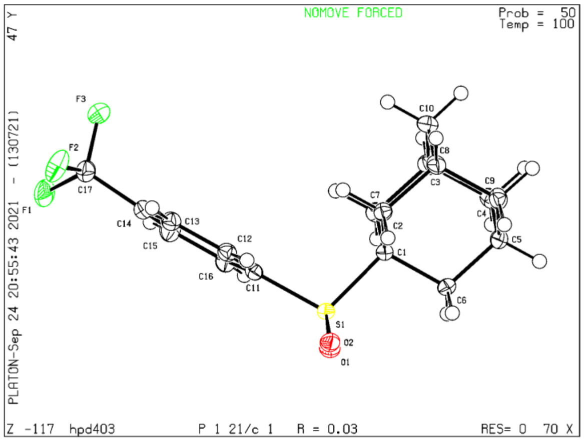
	Calculated	Reported
Volume	1514.16(3)	1514.16(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{17}H_{19}F_3O_2S$	$C_{17}H_{19}F_3O_2S$
Sum formula	$C_{17}H_{19}F_3O_2S$	$C_{17}H_{19}F_3O_2S$
M_r	344.38	344.38
D_x,g cm^{-3}	1.511	1.511
Z	4	4
Mu (mm^{-1})	2.275	2.275
F000	720.0	720.0
F000'	723.77	
h,k,l_{max}	8,34,10	8,34,10
N_{ref}	3174	3075
T_{min},T_{max}	0.819,0.892	0.807,1.000
T_{min}'	0.811	

Correction method = # Reported T Limits: T_{min} = 0.807 T_{max} = 1.000 AbsCorr = MULTI-SCAN

Data completeness = 0.969 Theta(max) = 76.350

R(reflections) = 0.0326(2779) wR2(reflections) = 0.0852(3075)

S = 1.058 N_{par} = 208



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1,3-Dimethyl-5-((4-(trifluoromethyl)phenyl)sulfonyl)adamantine (4u)

CCDC 2154275

Bond precision: C–C = 0.0040 Å Wavelength = 1.54184

Cell: a = 27.4338(3) b = 8.6962(1) c = 14.8129(2)

α = 90 β = 95.703(1) γ = 90

Temperature: 100 K

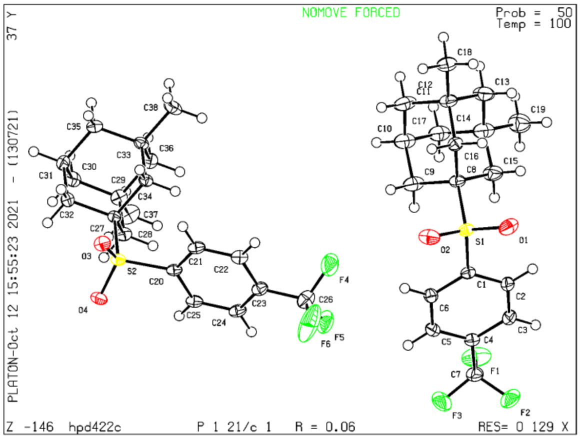
	Calculated	Reported
Volume	3516.42(7)	3516.42(7)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{19}H_{23}F_3O_2S$	$C_{19}H_{23}F_3O_2S$
Sum formula	$C_{19}H_{23}F_3O_2S$	$C_{19}H_{23}F_3O_2S$
M_r	372.43	372.43
D_x,g cm^{-3}	1.407	1.407
Z	8	8
Mu (mm^{-1})	2.001	2.001
F000	1568.0	1568.0
F000'	1575.81	
h,k,l_{max}	34,10,18	34,10,18
N_{ref}	7389	7174
T_{min},T_{max}	0.817,0.923	0.907,1.000
T_{min}'	0.676	

Correction method = # Reported T Limits: T_{min} = 0.907 T_{max} = 1.000 AbsCorr = MULTI-SCAN

Data completeness = 0.971 Theta(max) = 76.565

R(reflections) = 0.0593(6514) wR2(reflections) = 0.1372(7174)

S = 1.073 N_{par} = 443



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1,4-Dimethyl-2-((4-methyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)pentyl)oxy)benzene (5a)

CCDC 2154276

Bond precision: C—C = 0.0036 Å Wavelength = 1.54184

Cell: a = 6.6412(2) b = 18.3312(5) c = 16.9189(5)

α = 90 β = 100.876(3) γ = 90

Temperature: 100 K

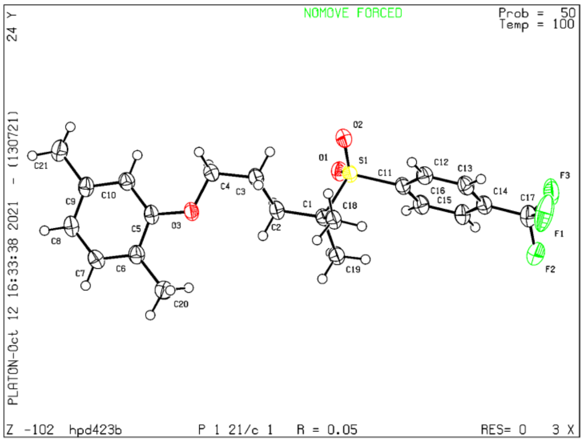
	Calculated	Reported
Volume	2022.73(10)	2022.73(10)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{21}H_{25}F_3O_3S$	$C_{21}H_{25}F_3O_3S$
Sum formula	$C_{21}H_{25}F_3O_3S$	$C_{21}H_{25}F_3O_3S$
M_r	414.47	414.47
D_x,g cm^{-3}	1.361	1.361
Z	4	4
Mu (mm^{-1})	1.835	1.835
F000	872.0	872.0
F000'	876.24	
h,k,l_{max}	8,23,21	8,23,20
N_{ref}	4245	3917
T_{min},T_{max}	0.869,0.928	0.805,1.000
T_{min}'	0.720	

Correction method = # Reported T Limits: T_{min} = 0.805 T_{max} = 1.000 AbsCorr = GAUSSIAN

Data completeness = 0.923 Theta(max) = 76.143

R(reflections) = 0.0517(3458) wR2(reflections) = 0.1261(3917)

S = 1.058 N_{par} = 257



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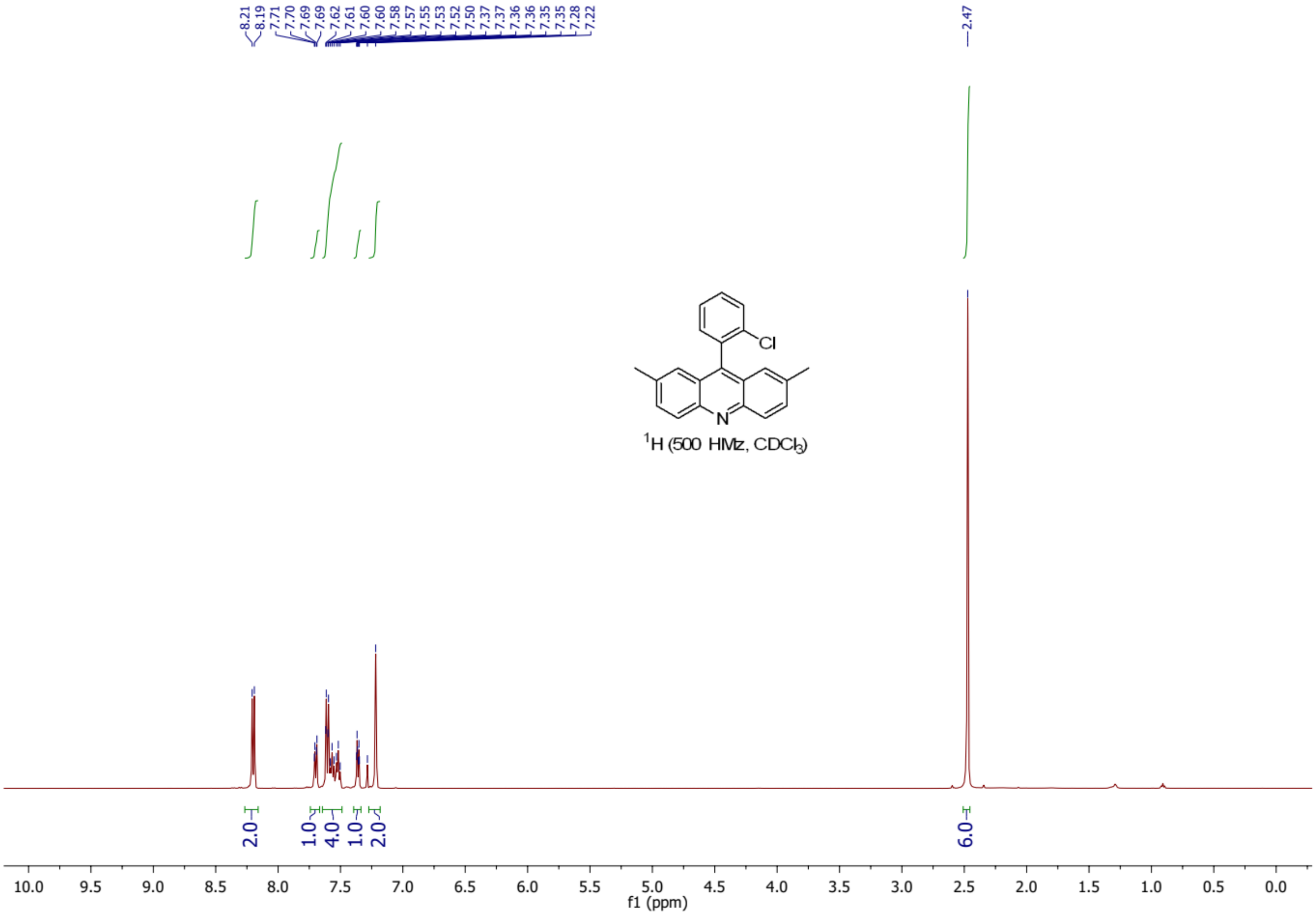
NMR Spectroscopic data

9-(2-Chlorophenyl)-2,7-dimethylacridine (A1)



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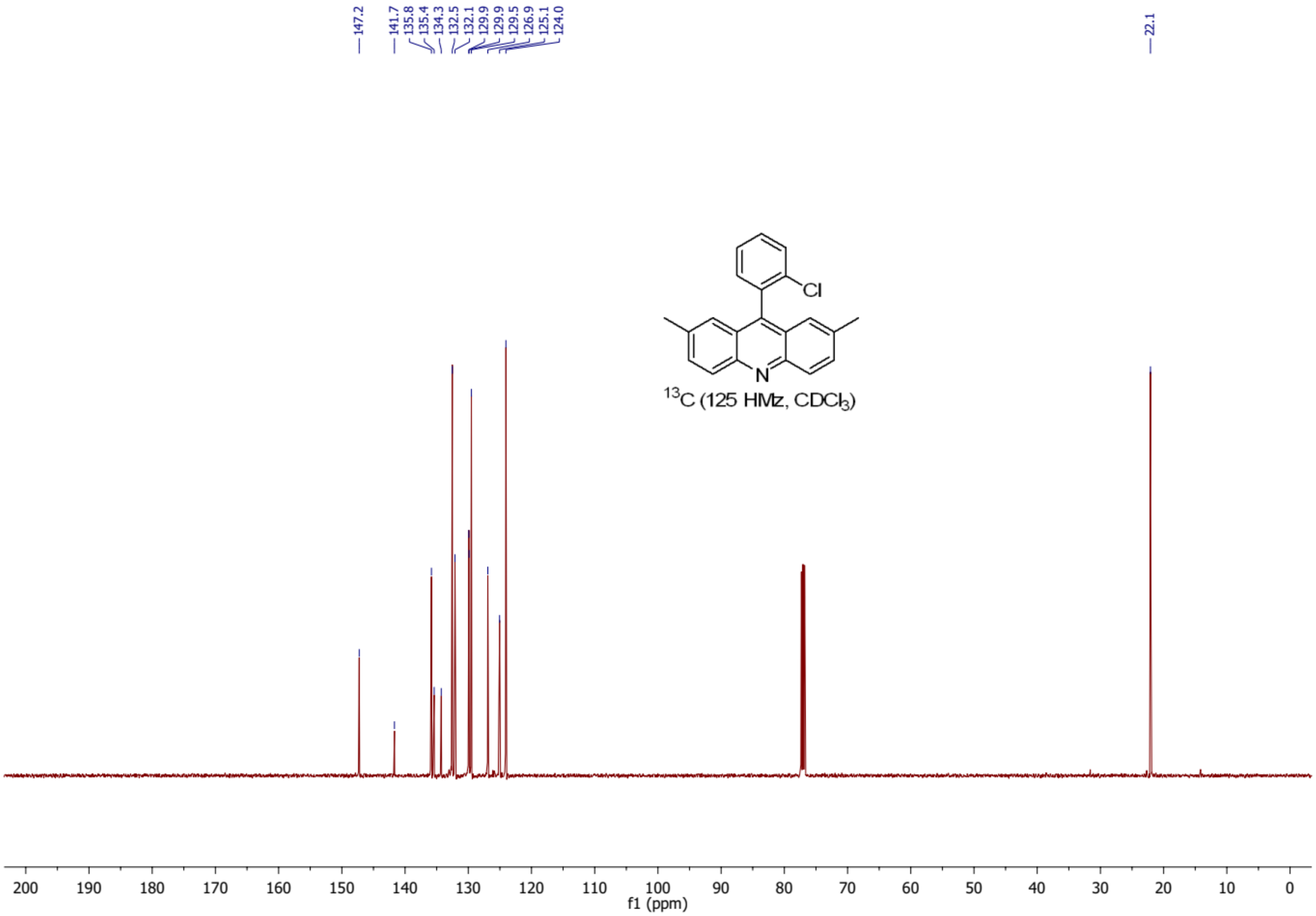
9-(2-Chlorophenyl)-2,7-dimethylacridine (A1)



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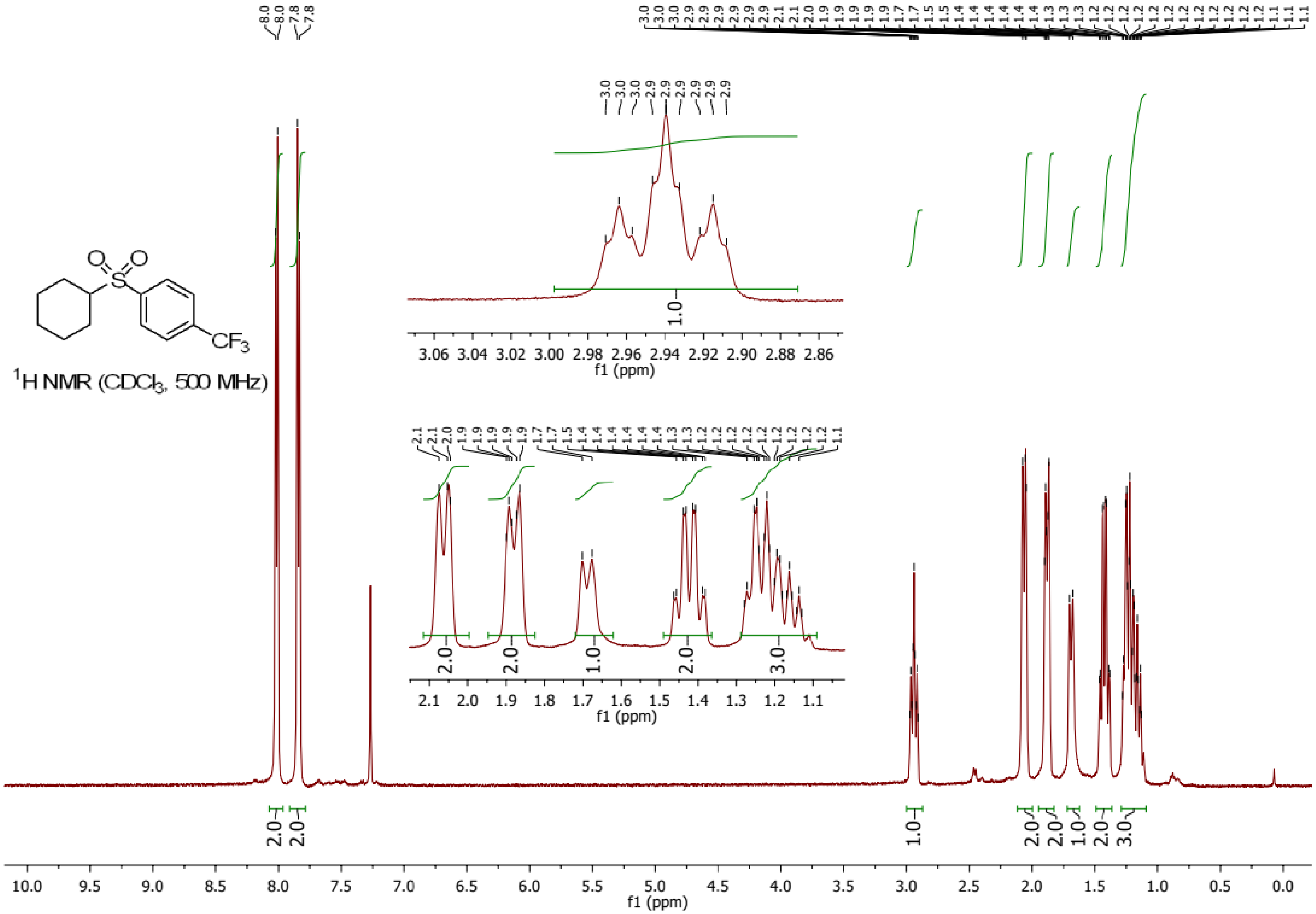
1-(Cyclohexylsulfonyl)-4-(trifluoromethyl)benzene (3a)



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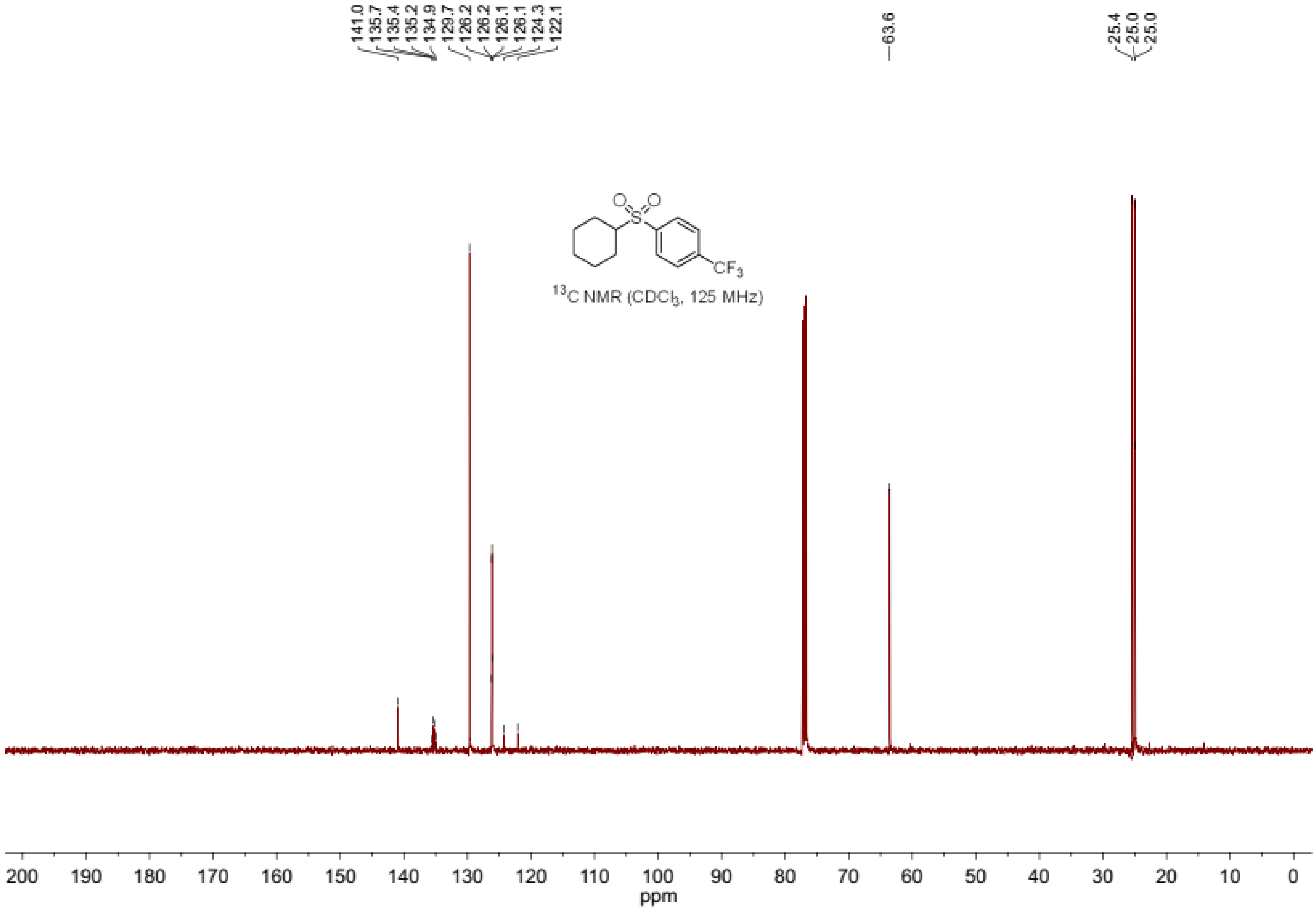
1-(Cyclohexylsulfonyl)-4-(trifluoromethyl)benzene (3a)



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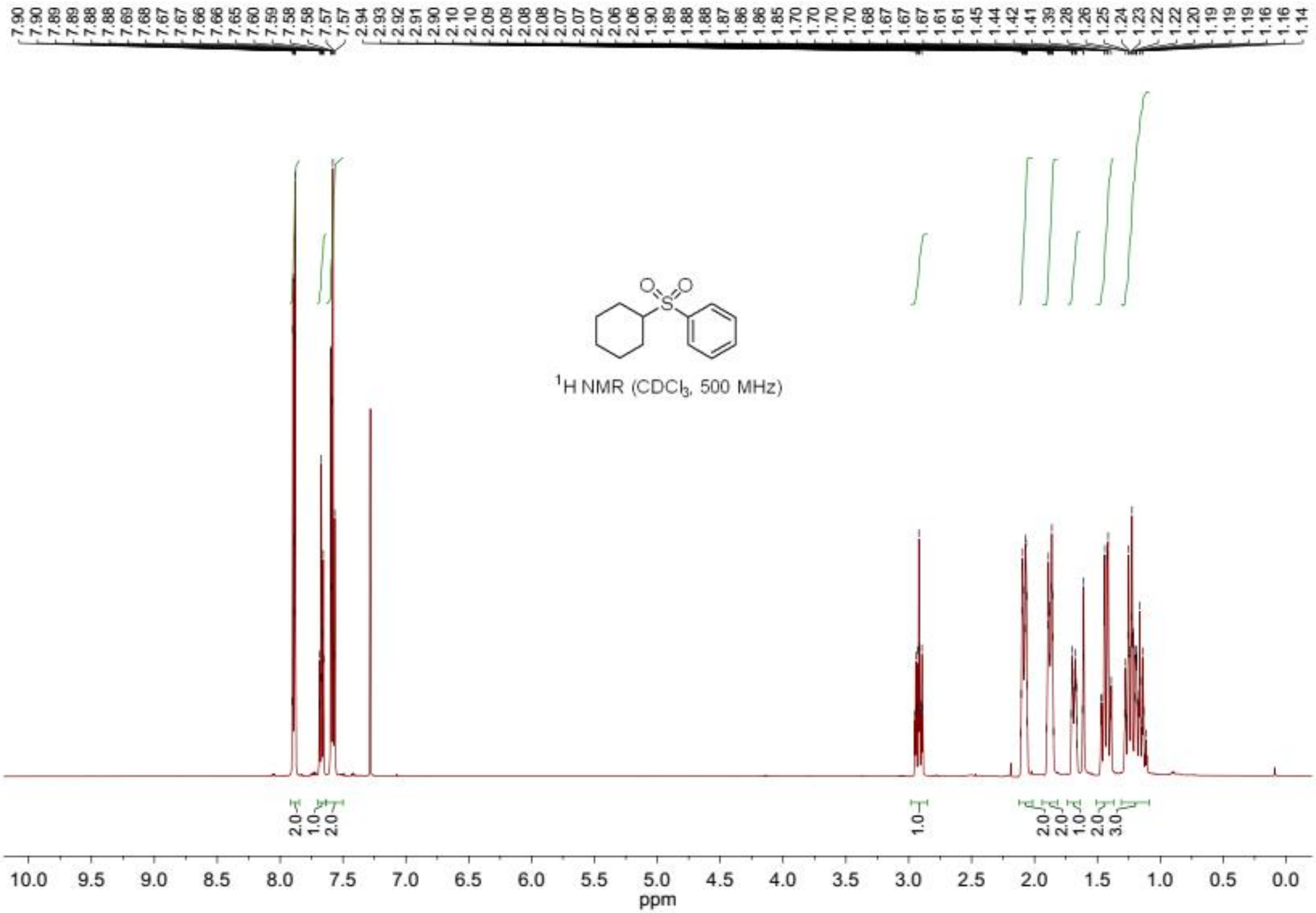
(Cyclohexylsulfonyl)benzene (3b)



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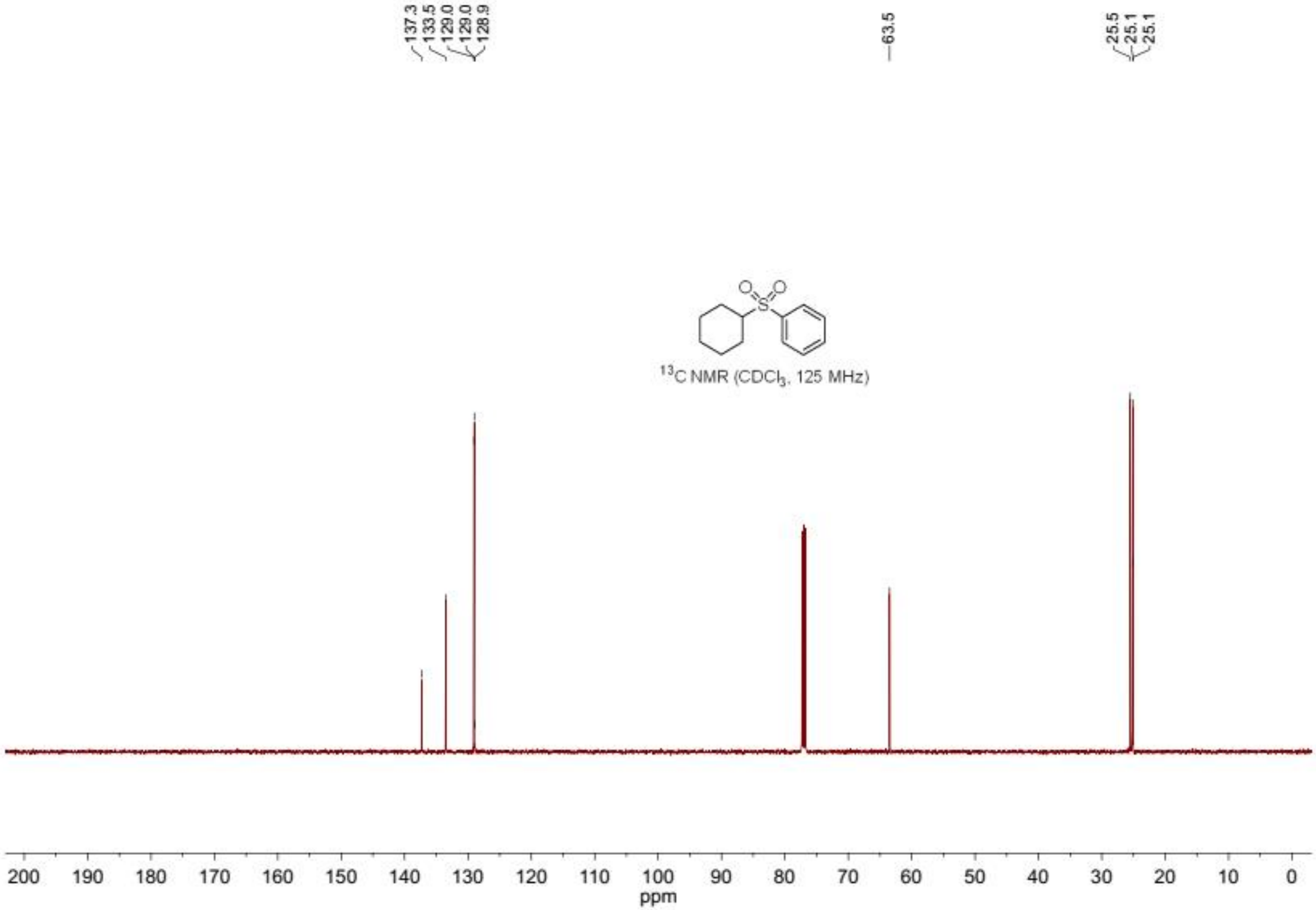
(Cyclohexylsulfonyl)benzene (3b)



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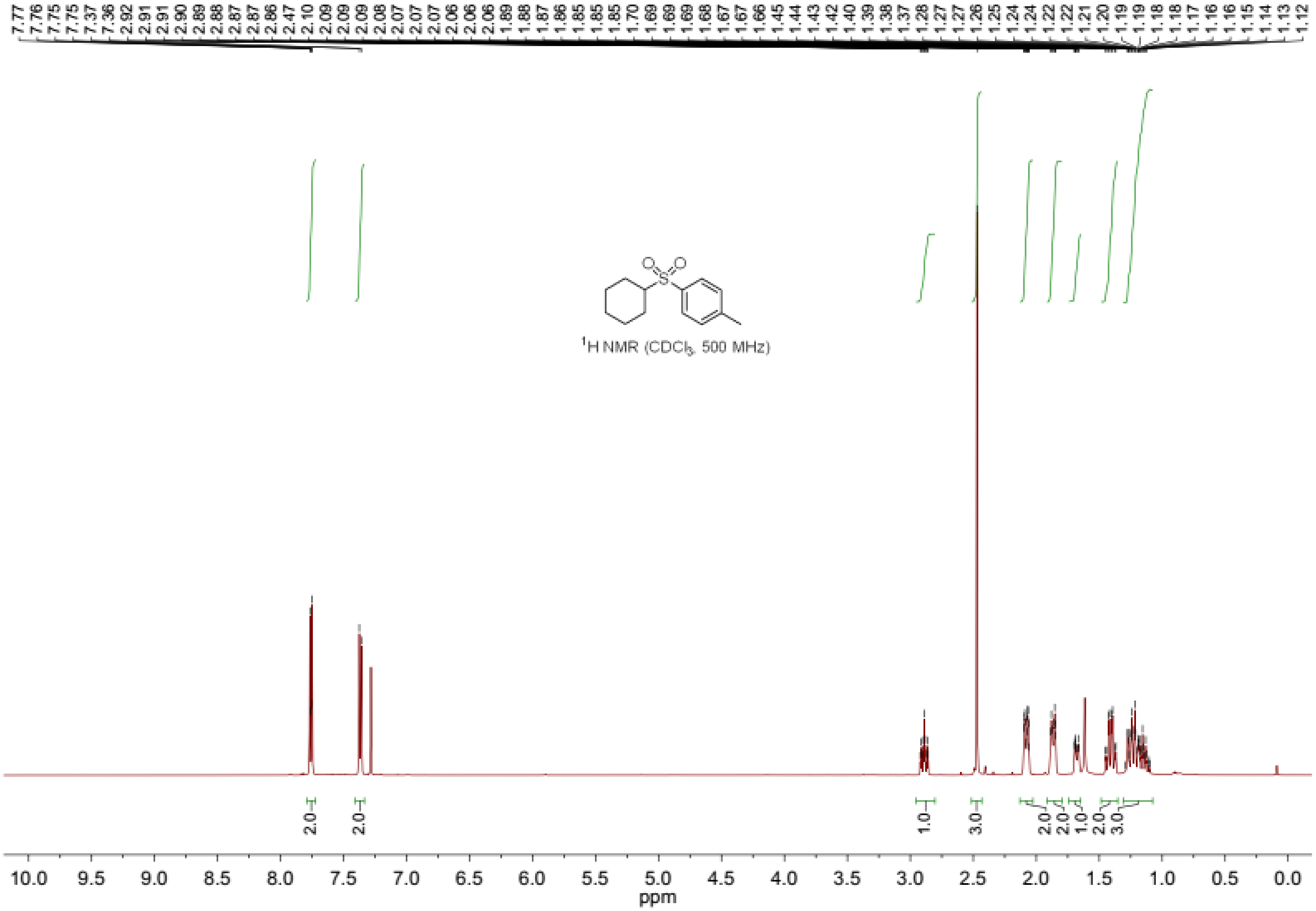
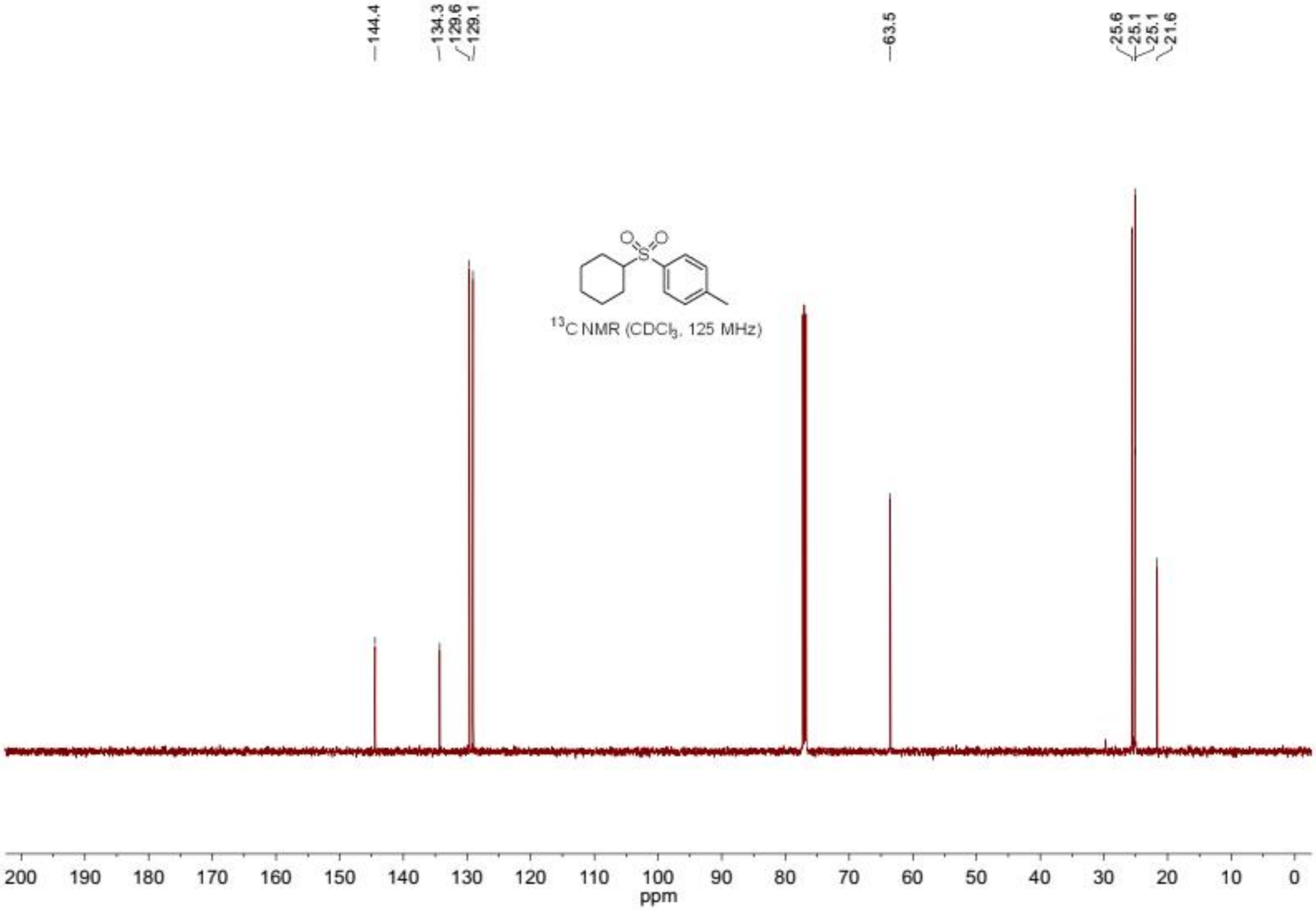
1-(Cyclohexylsulfonyl)-4-methylbenzene (3c)



1-(Cyclohexylsulfonyl)-4-methylbenzene (3c)



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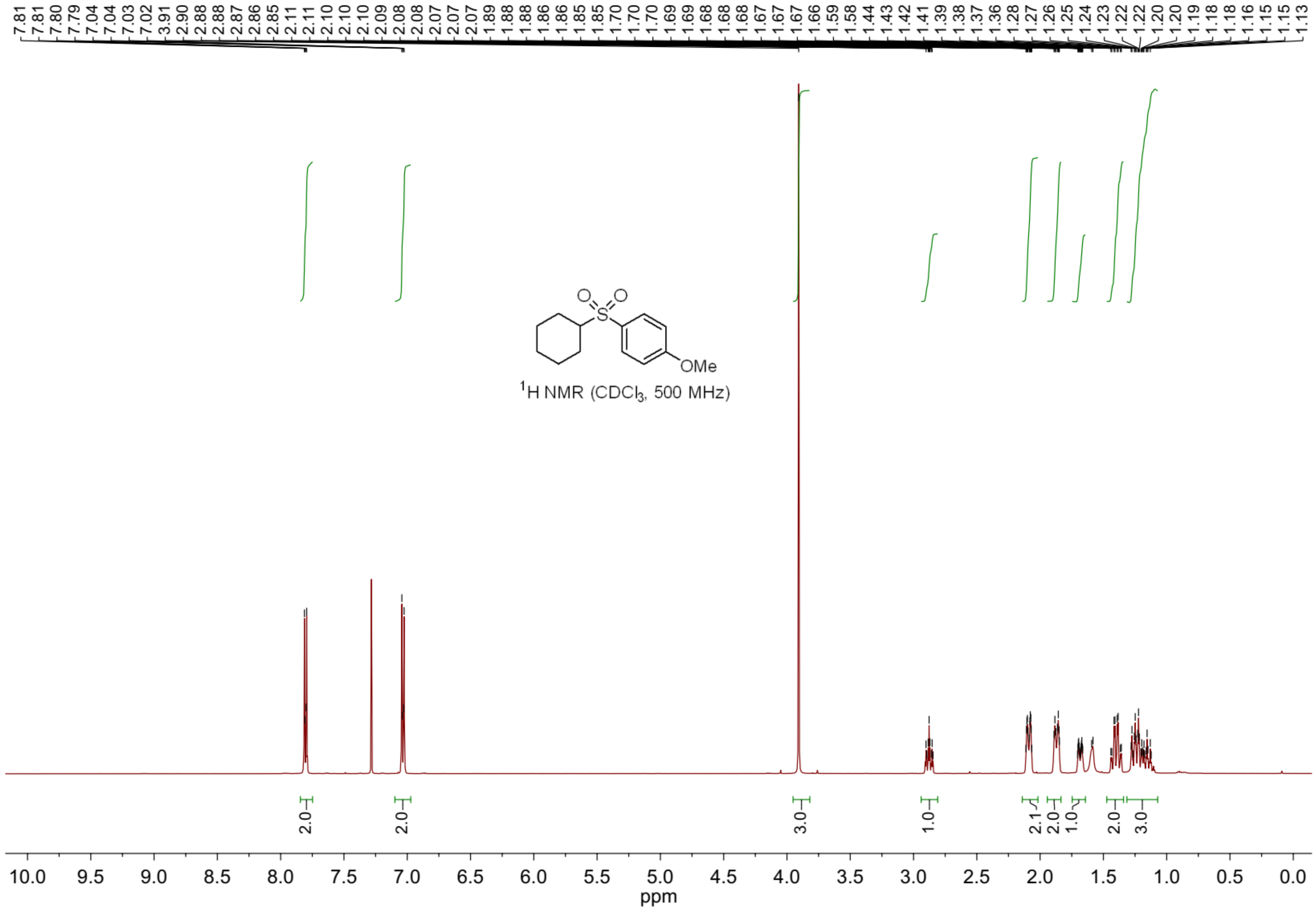
1-(Cyclohexylsulfonyl)-4-methoxybenzene (3d)



^{1}H NMR (CDCl$_3$, 500 MHz)

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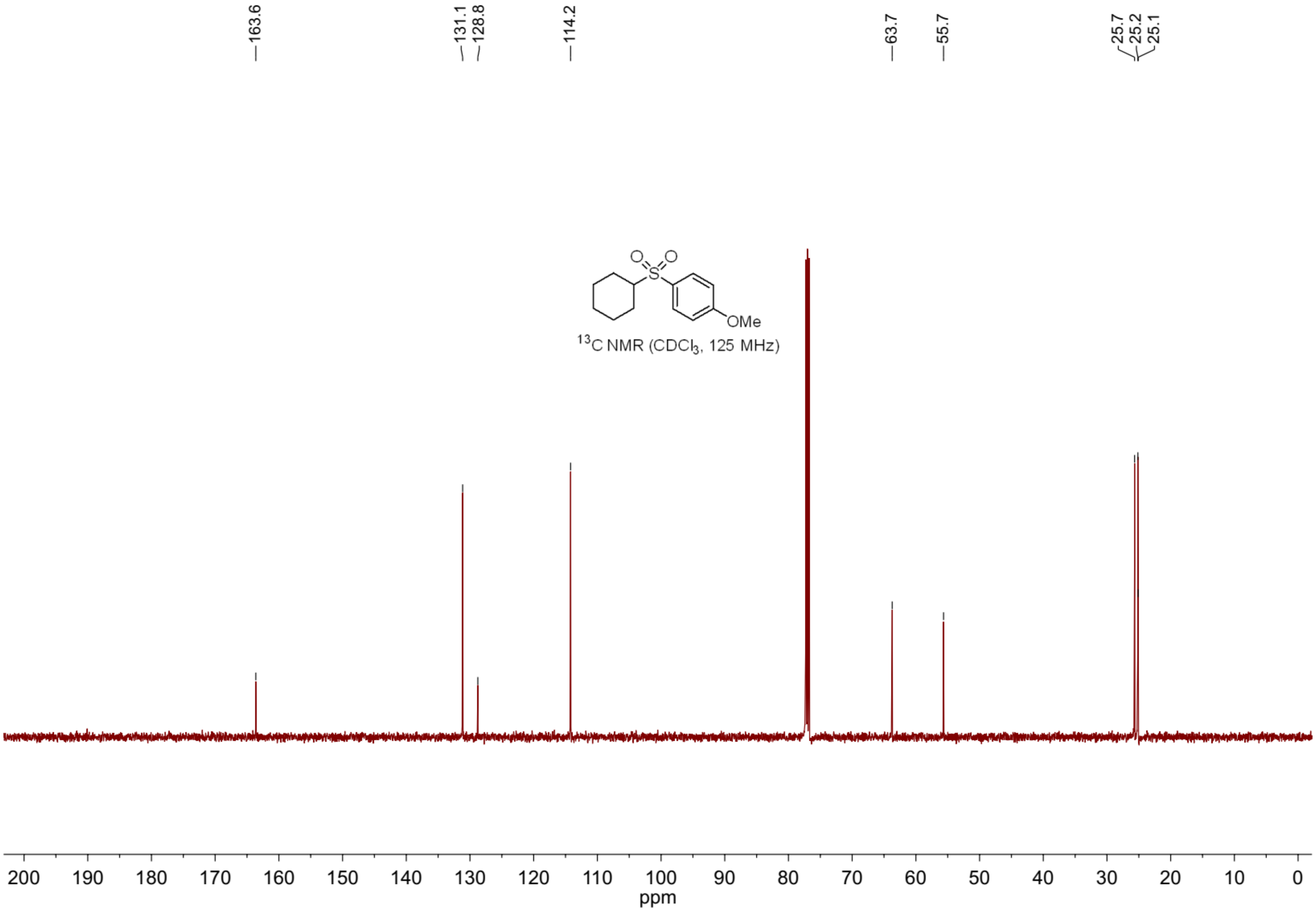
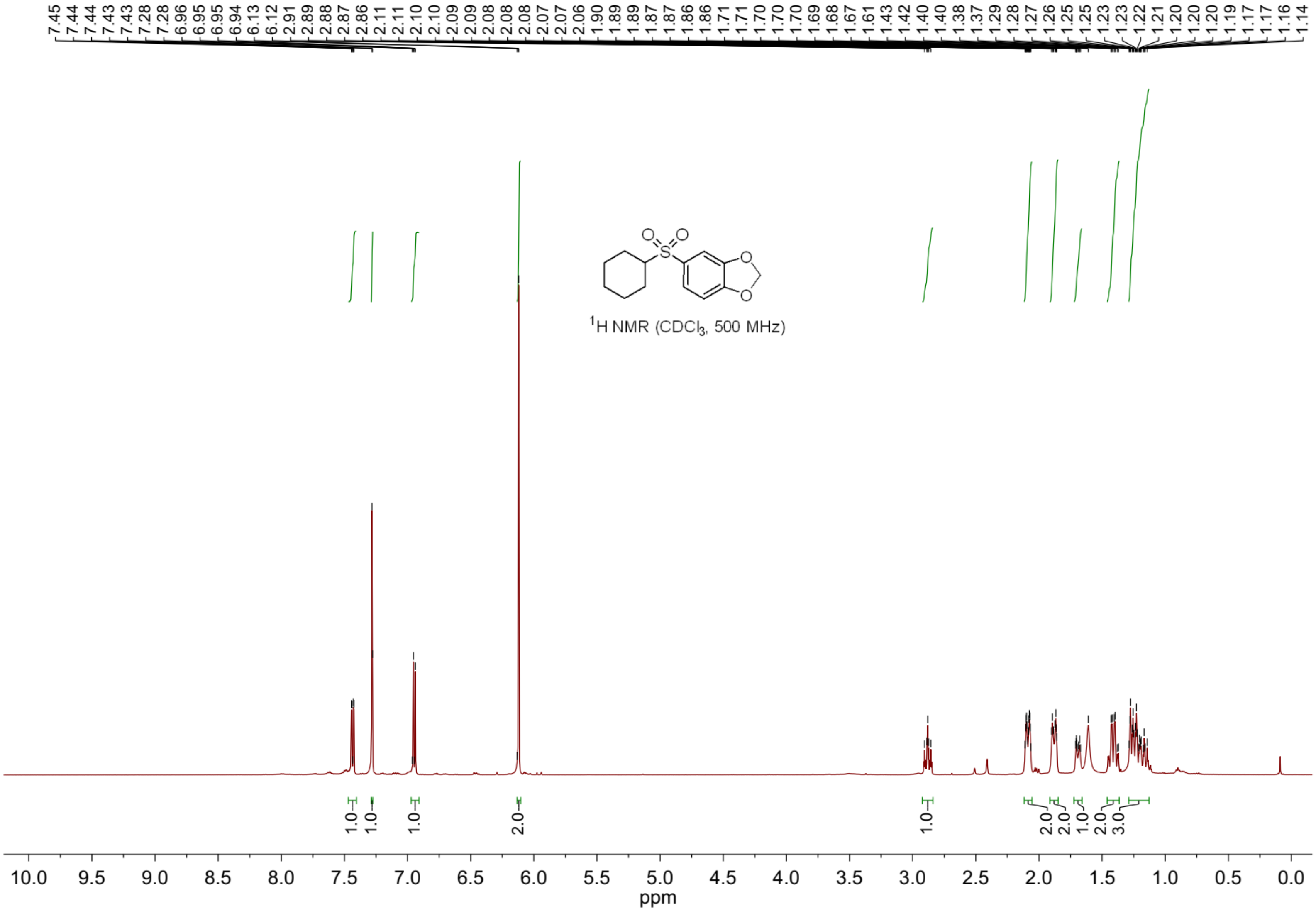
1-(Cyclohexylsulfonyl)-4-methoxybenzene (3d)



5-(Cyclohexylsulfonyl)benzo[*d*][1,3]dioxole (3e)



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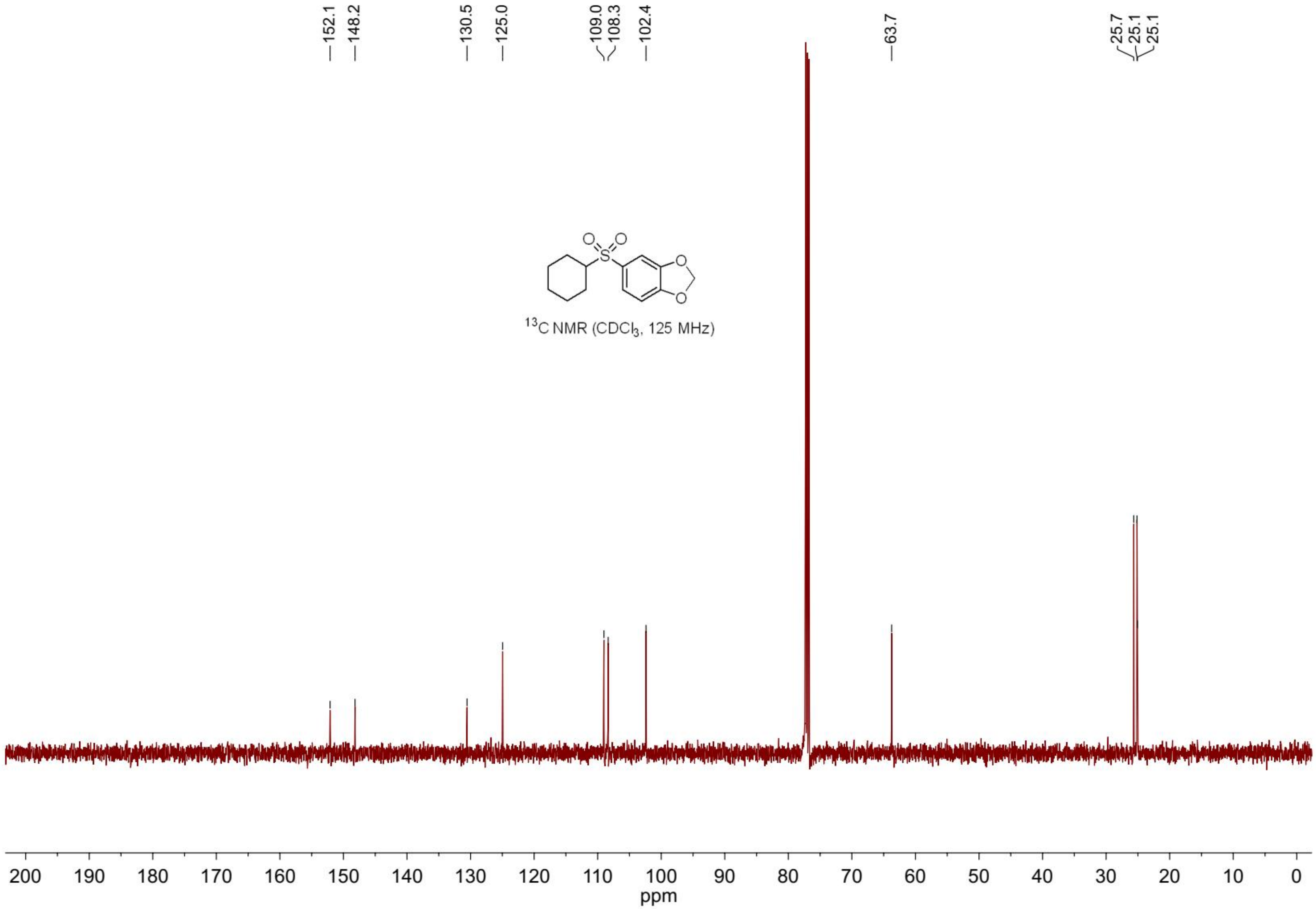
5-(Cyclohexylsulfonyl)benzo[*d*][1,3]dioxole (3e)



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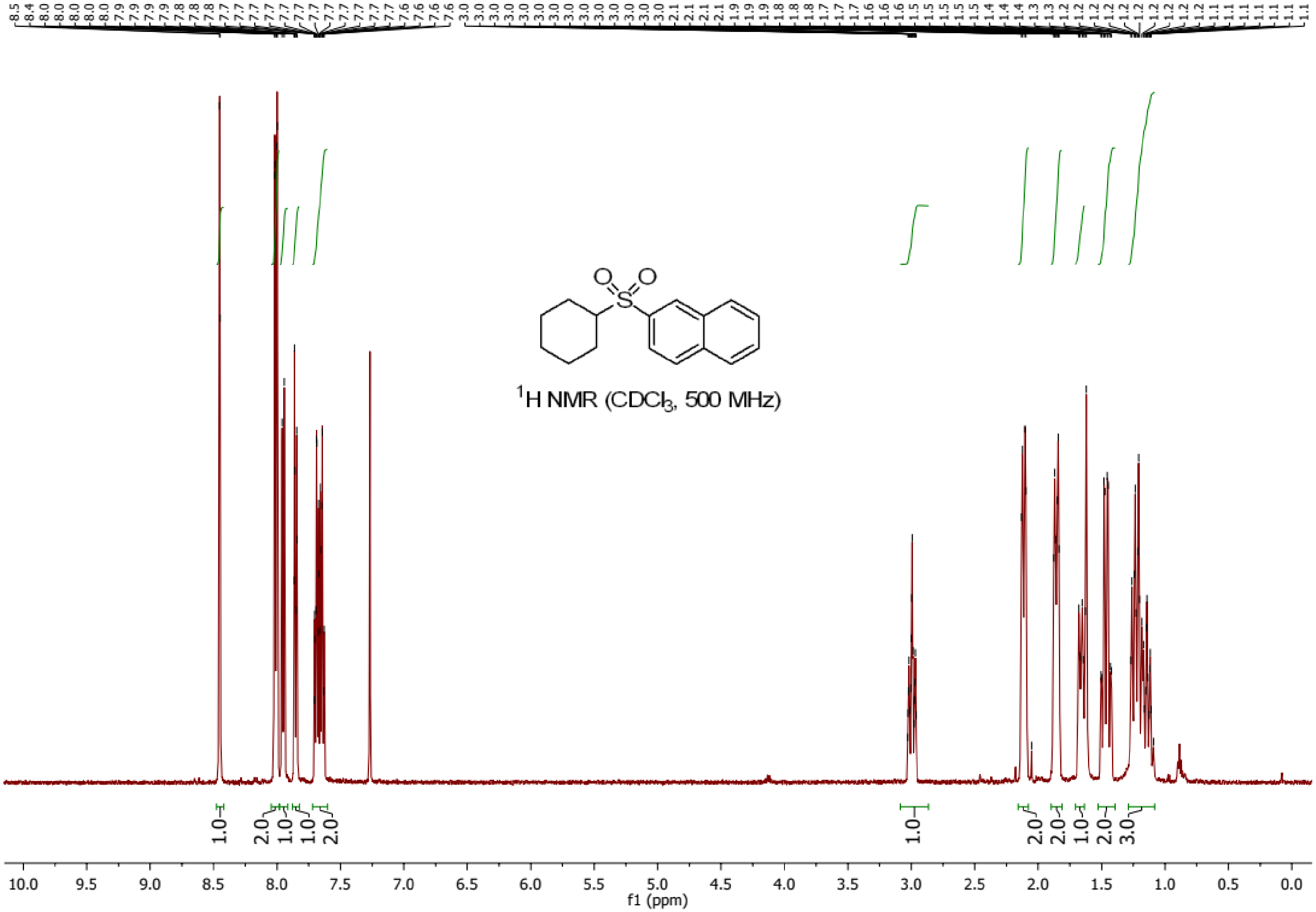
2-(Cyclohexylsulfonyl)naphthalene (3f)



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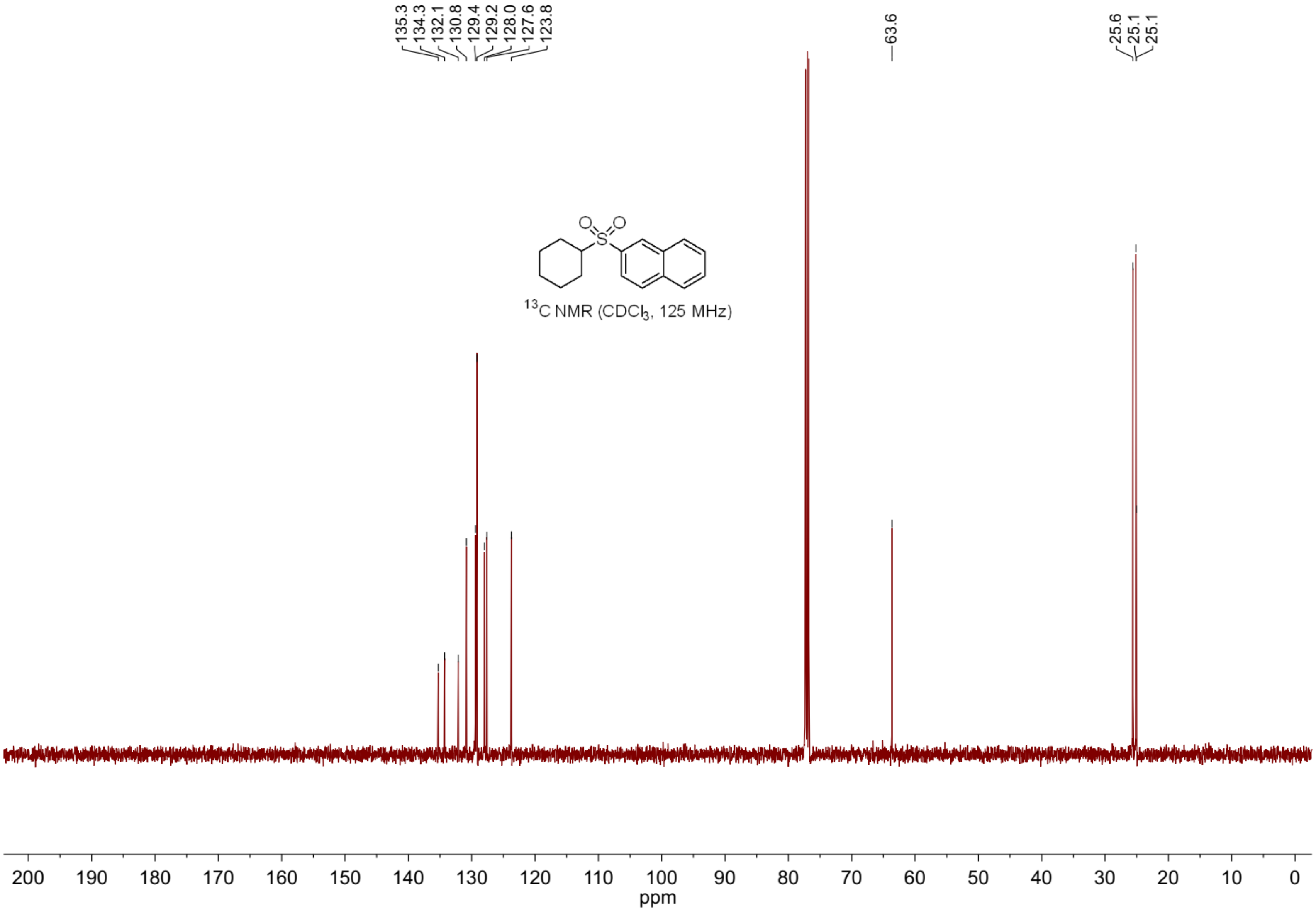
2-(Cyclohexylsulfonyl)naphthalene (3f)



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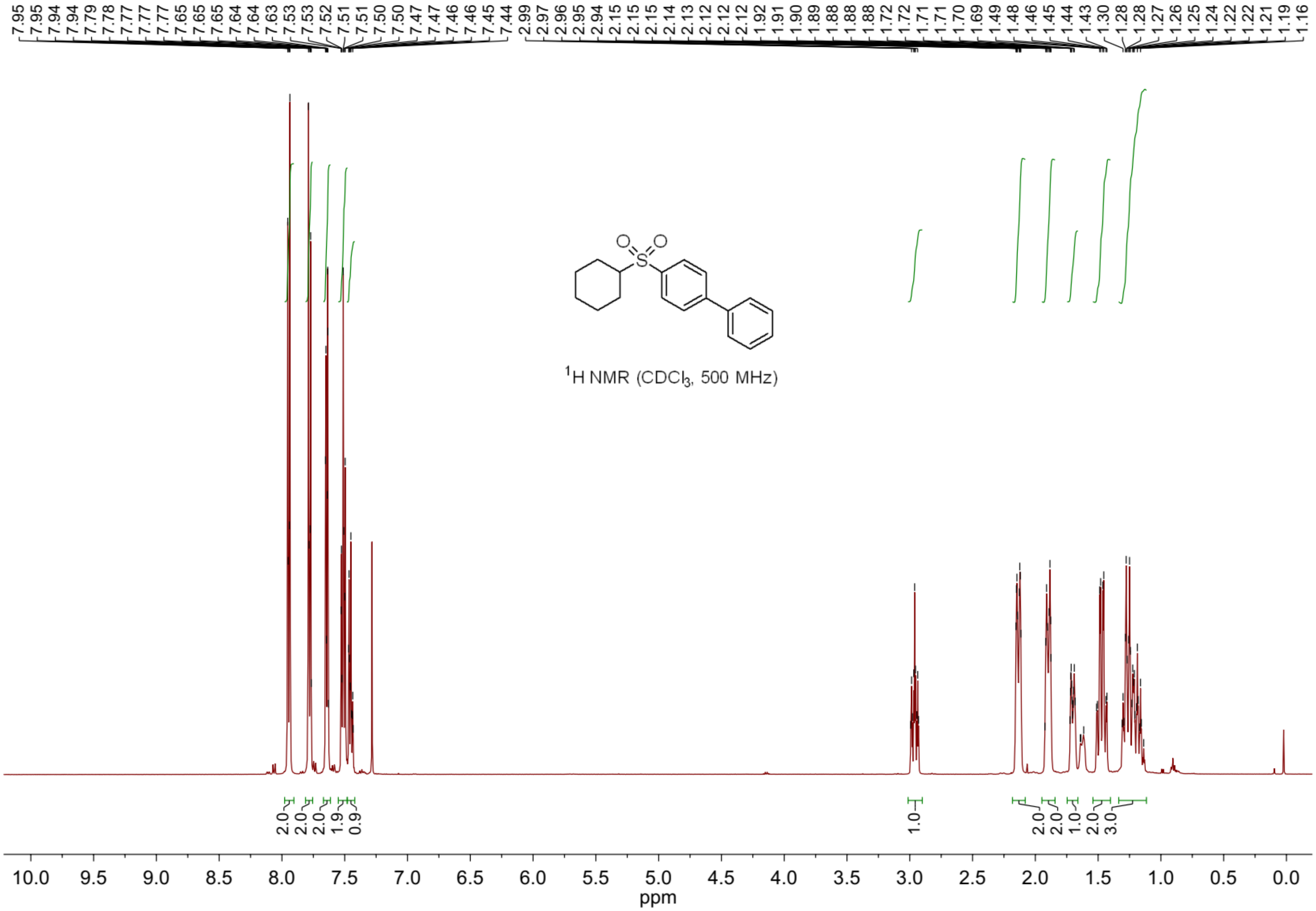
4-(Cyclohexylsulfonyl)-1,1'-biphenyl (3g)



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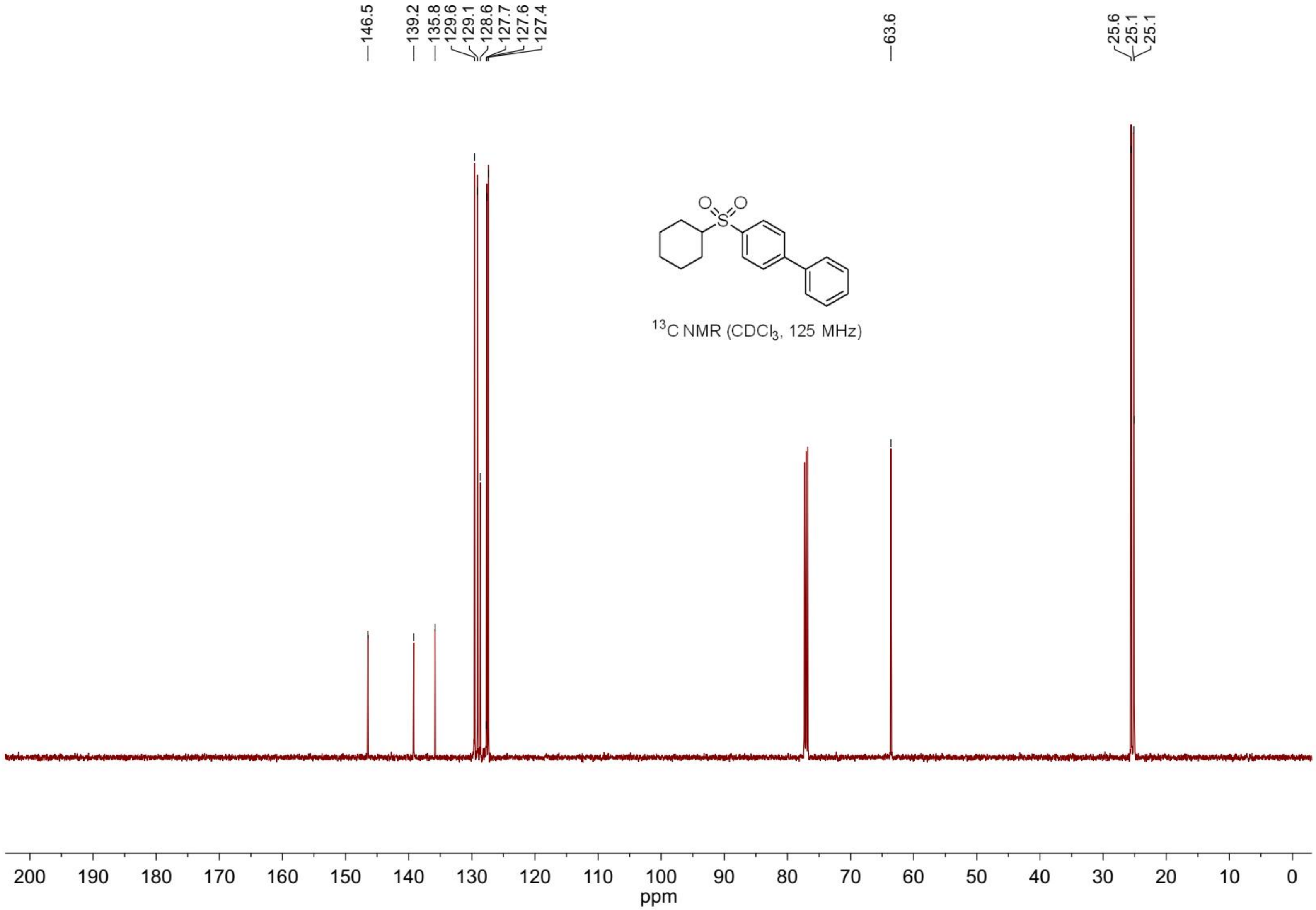
4-(Cyclohexylsulfonyl)-1,1'-biphenyl (3g)



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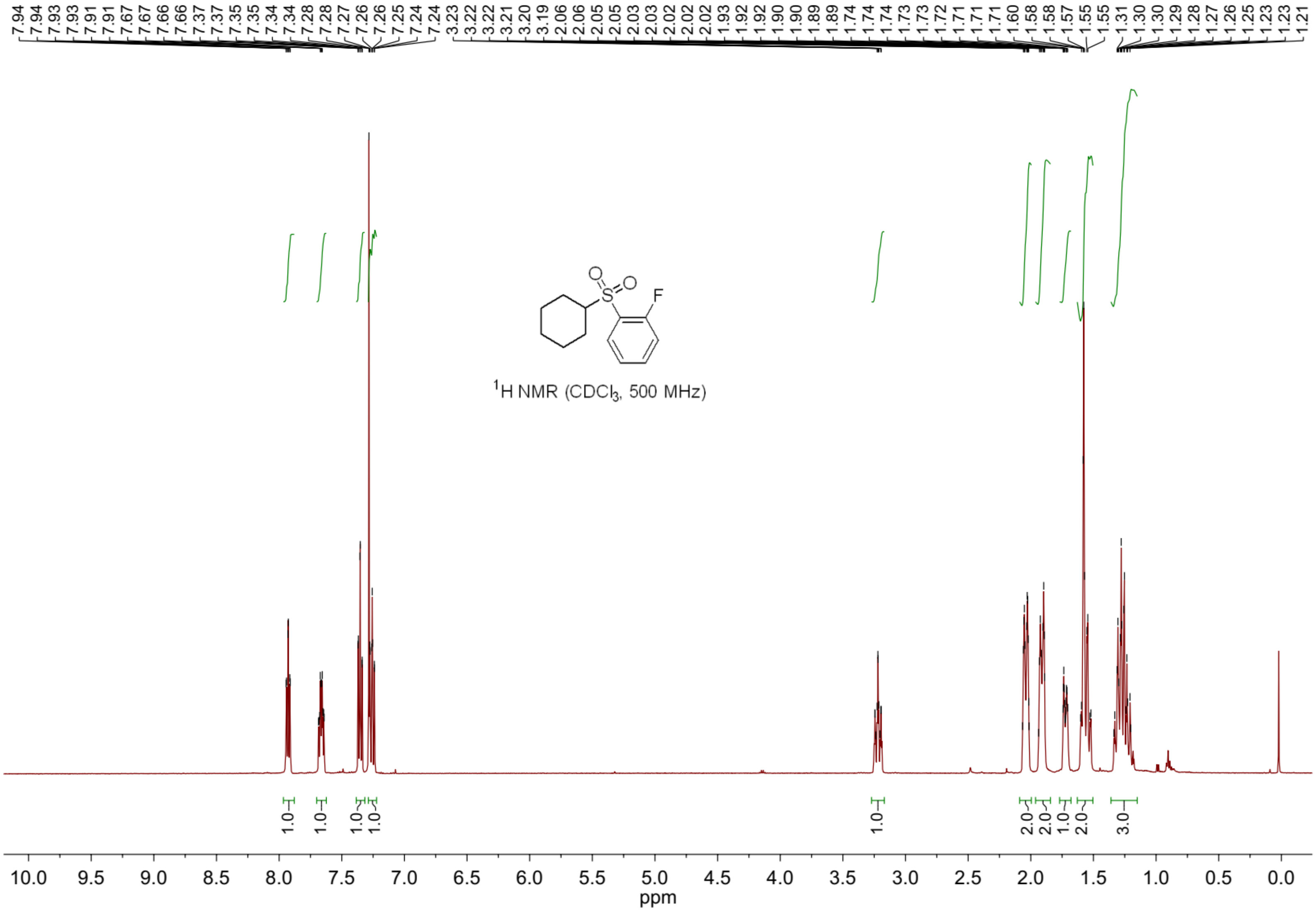
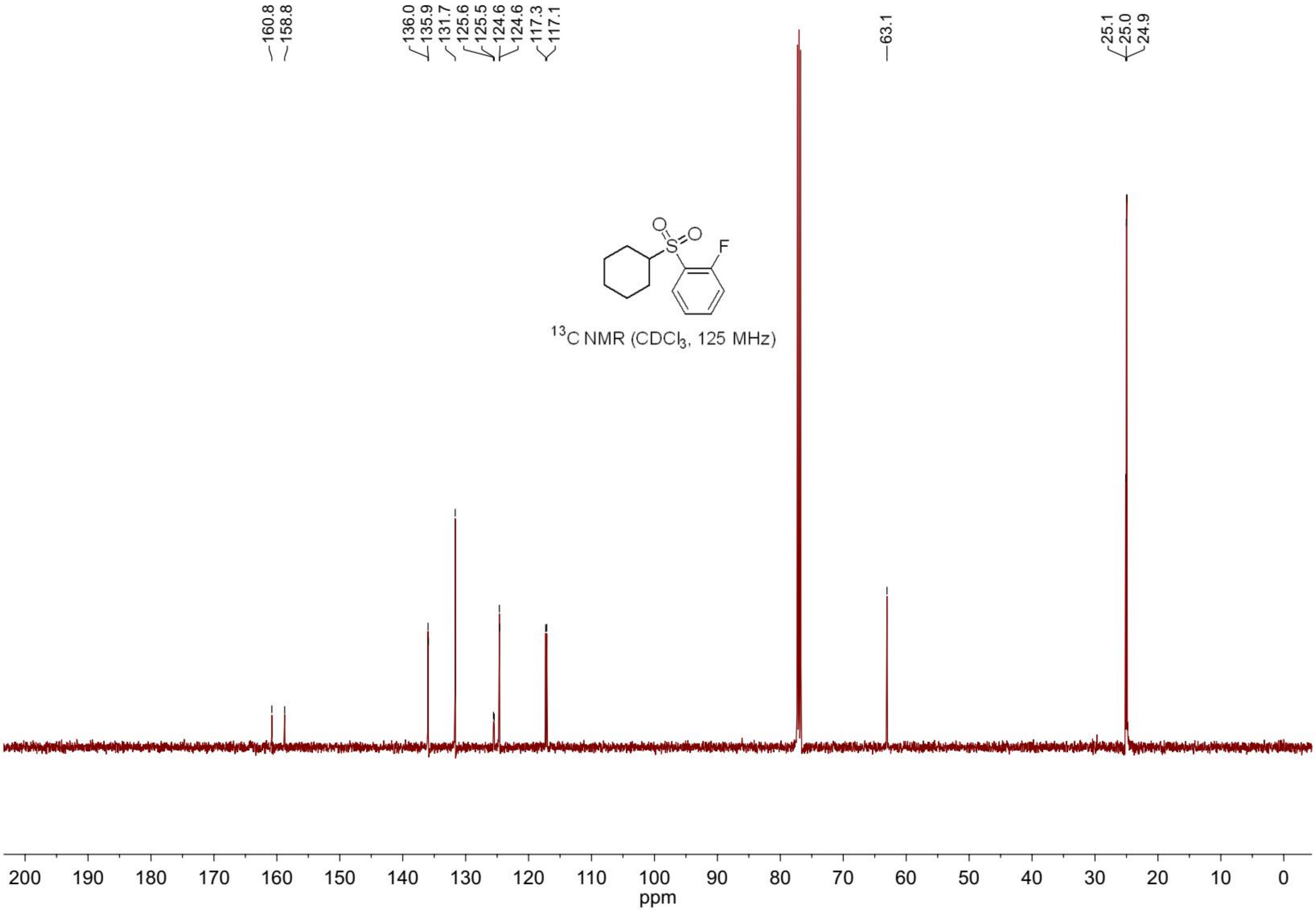
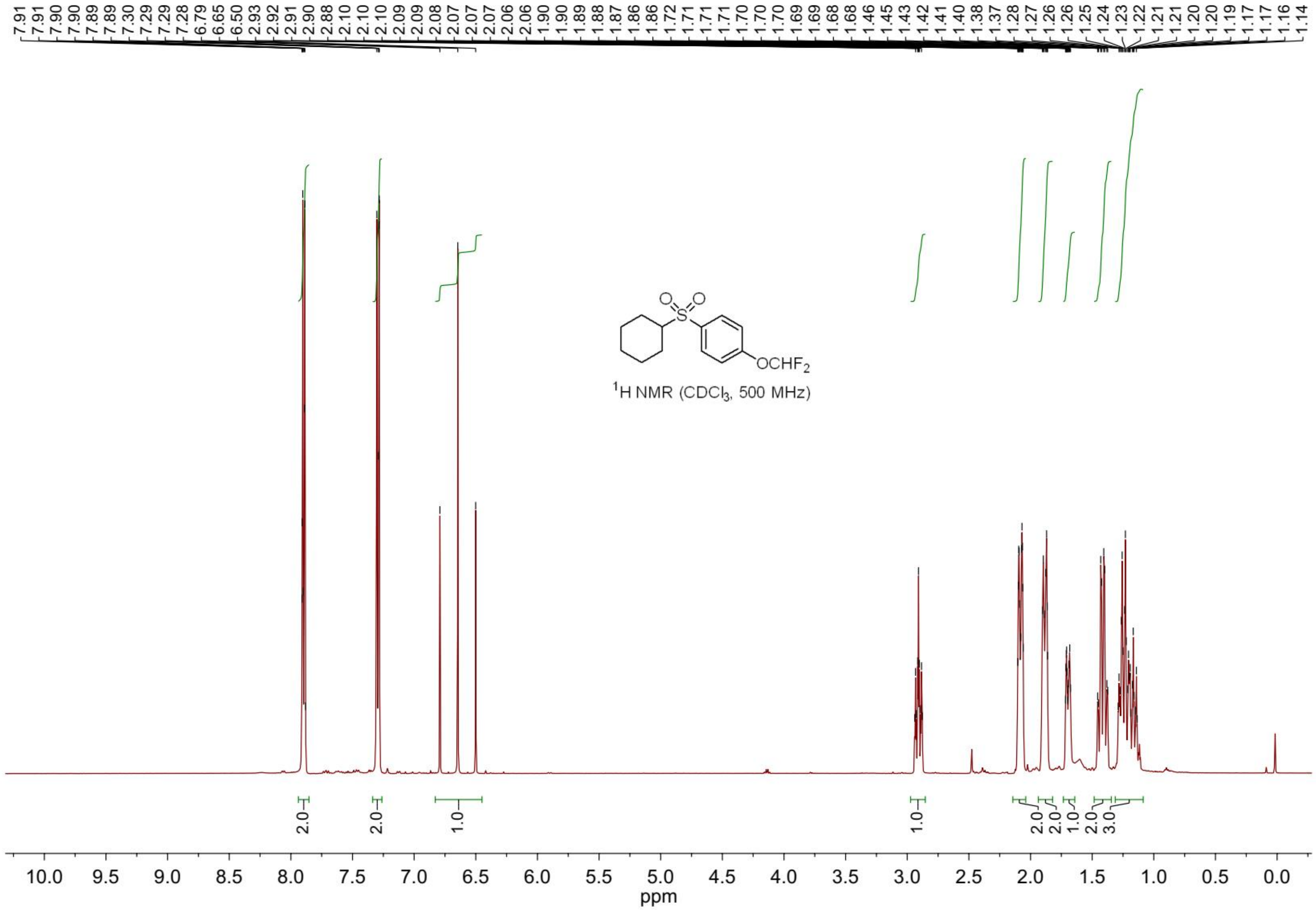
1-(Cyclohexylsulfonyl)-2-fluorobenzene (3h)



1-(Cyclohexylsulfonyl)-2-fluorobenzene (3h)



1-(Cyclohexylsulfonyl)-4-(difluoromethoxy)benzene (3i)



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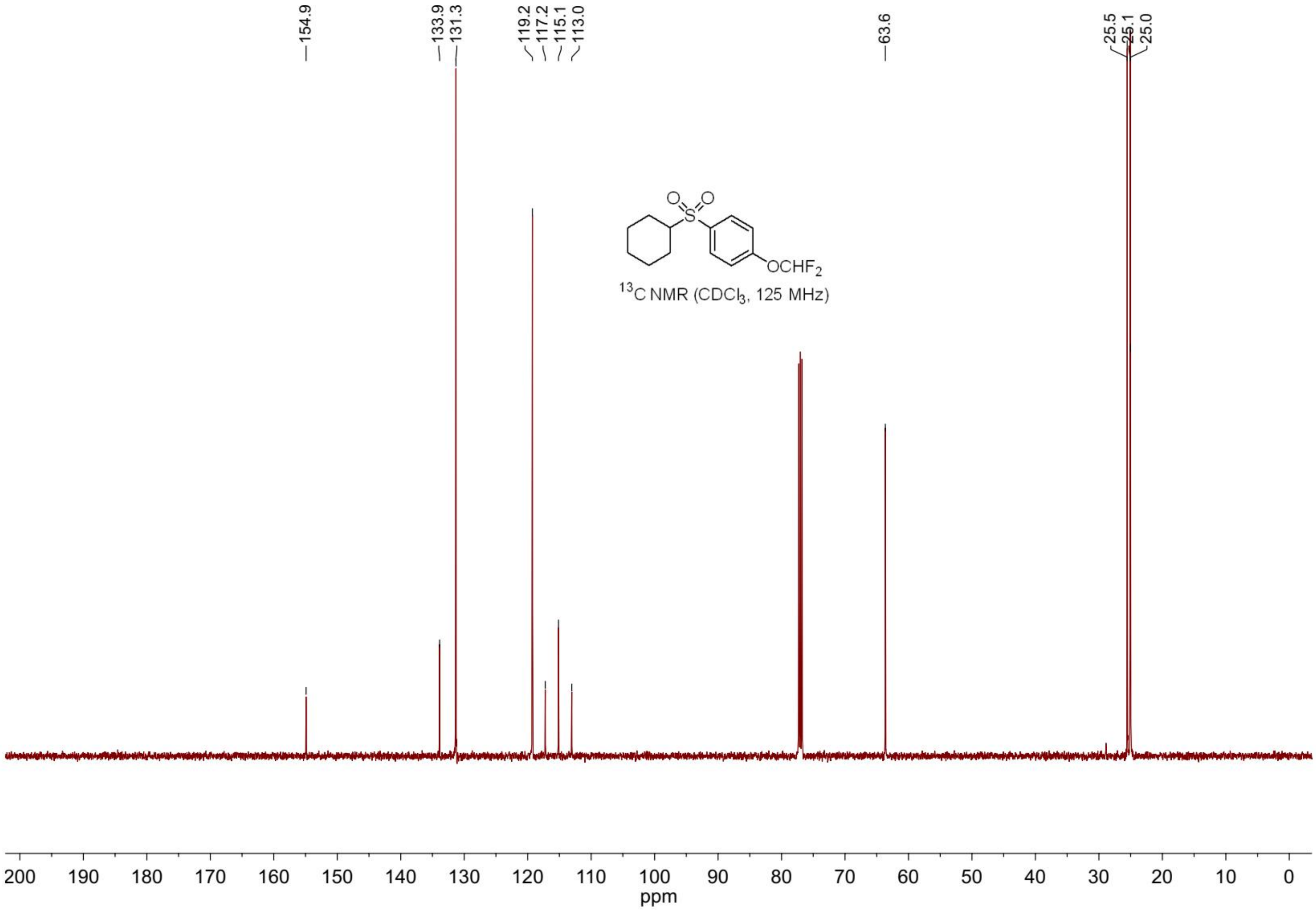
1-(Cyclohexylsulfonyl)-4-(difluoromethoxy)benzene (3i)



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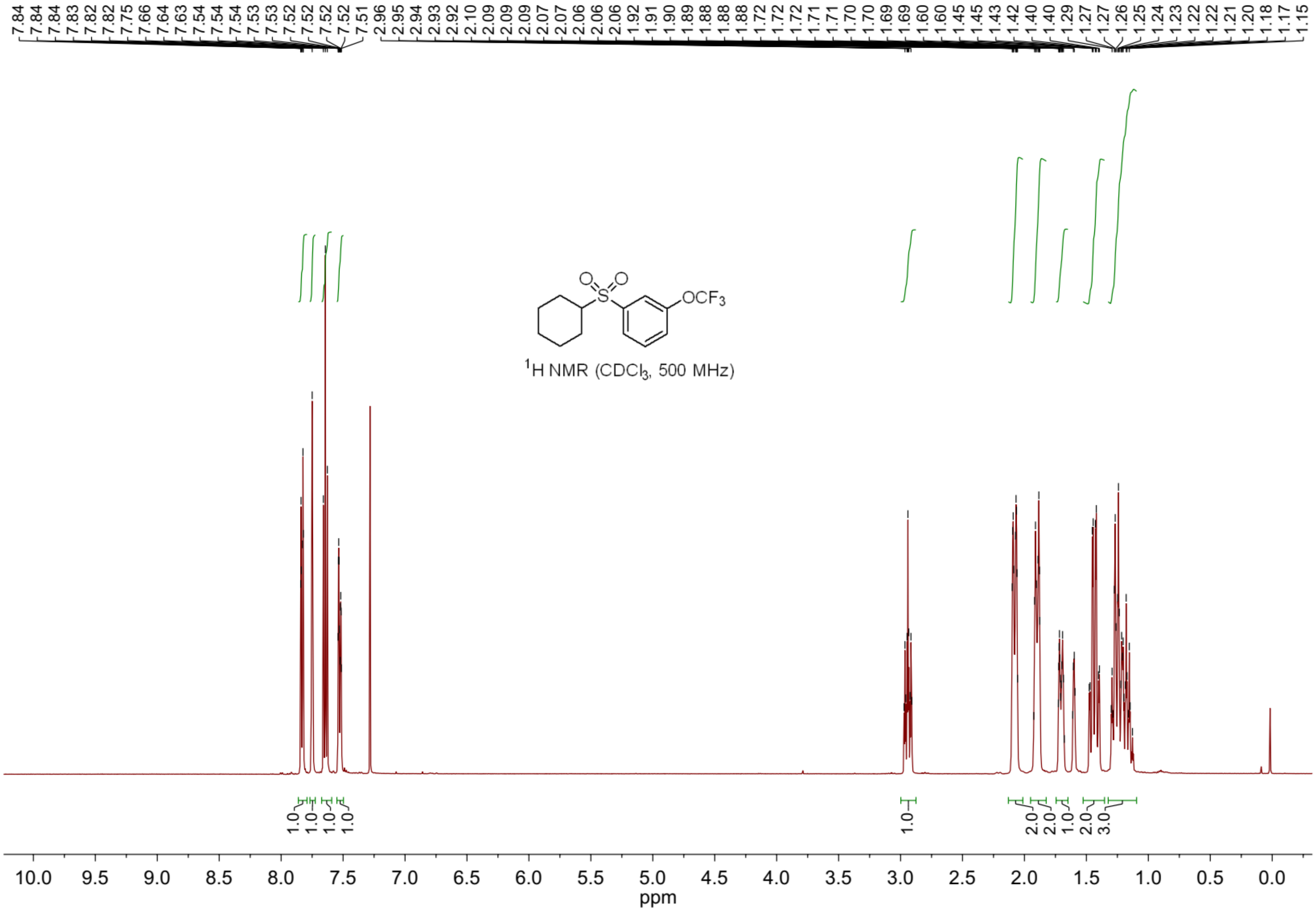
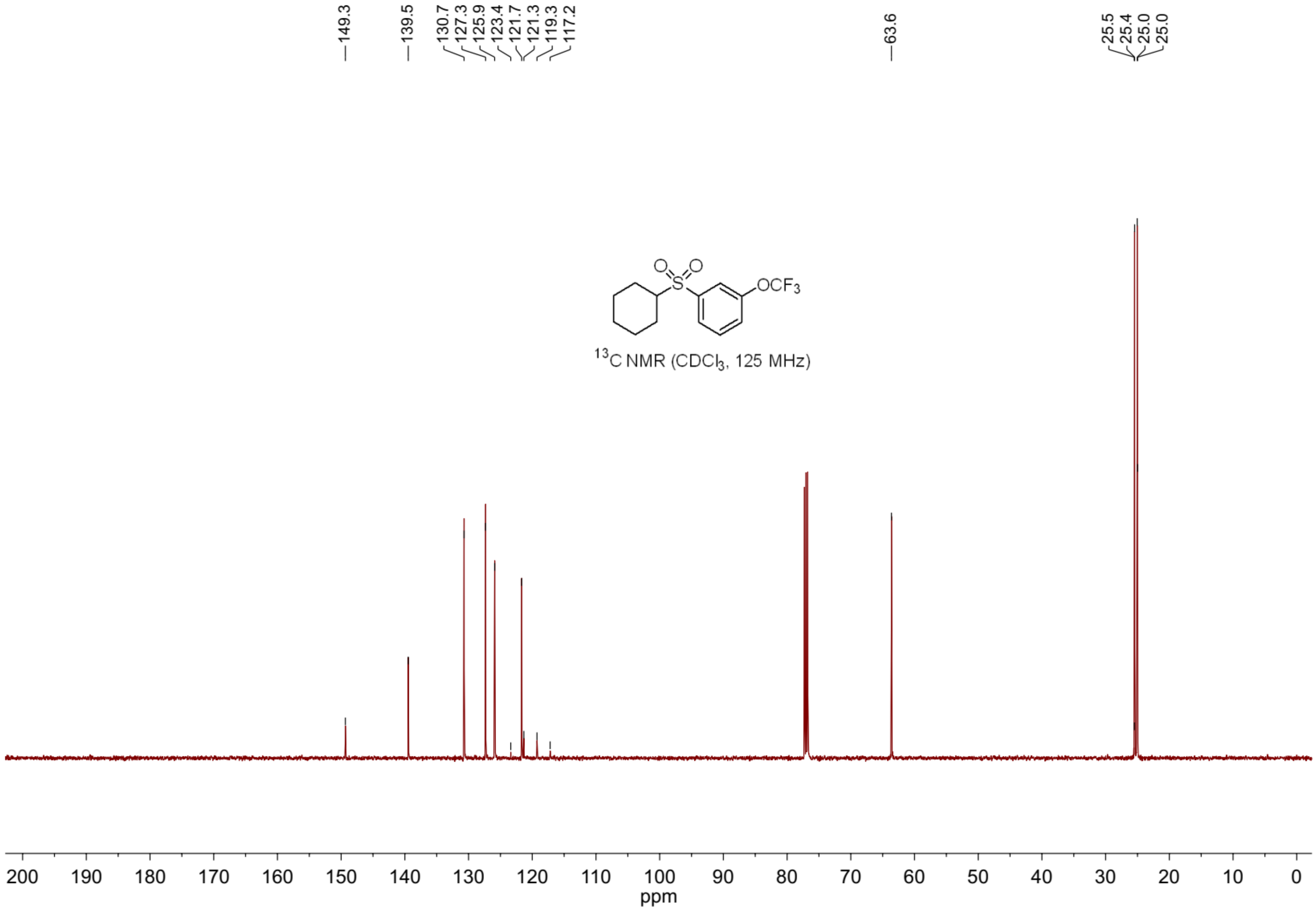
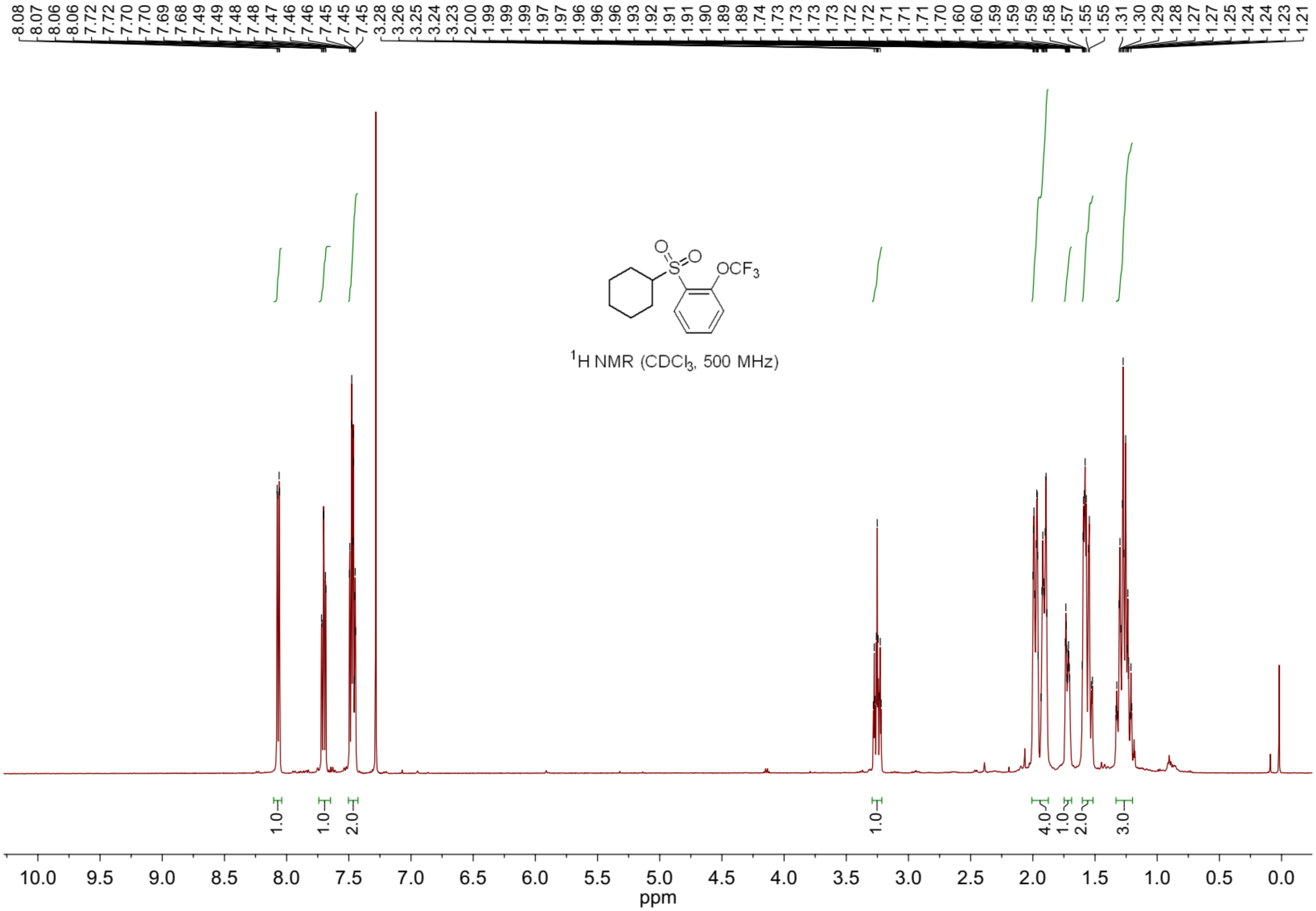
1-(Cyclohexylsulfonyl)-3-(trifluoromethoxy)benzene (3j)



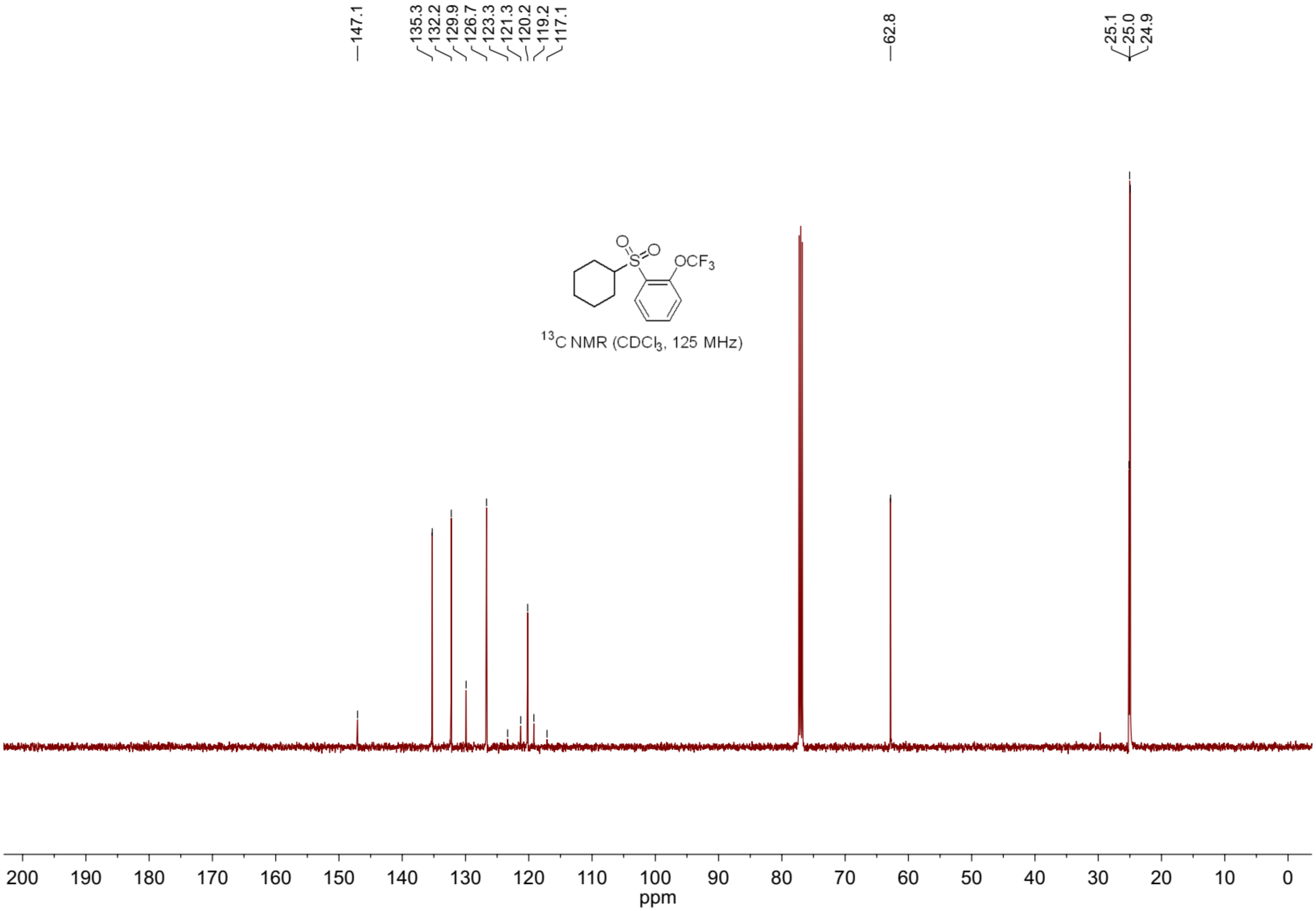
1-(Cyclohexylsulfonyl)-3-(trifluoromethoxy)benzene (3j)



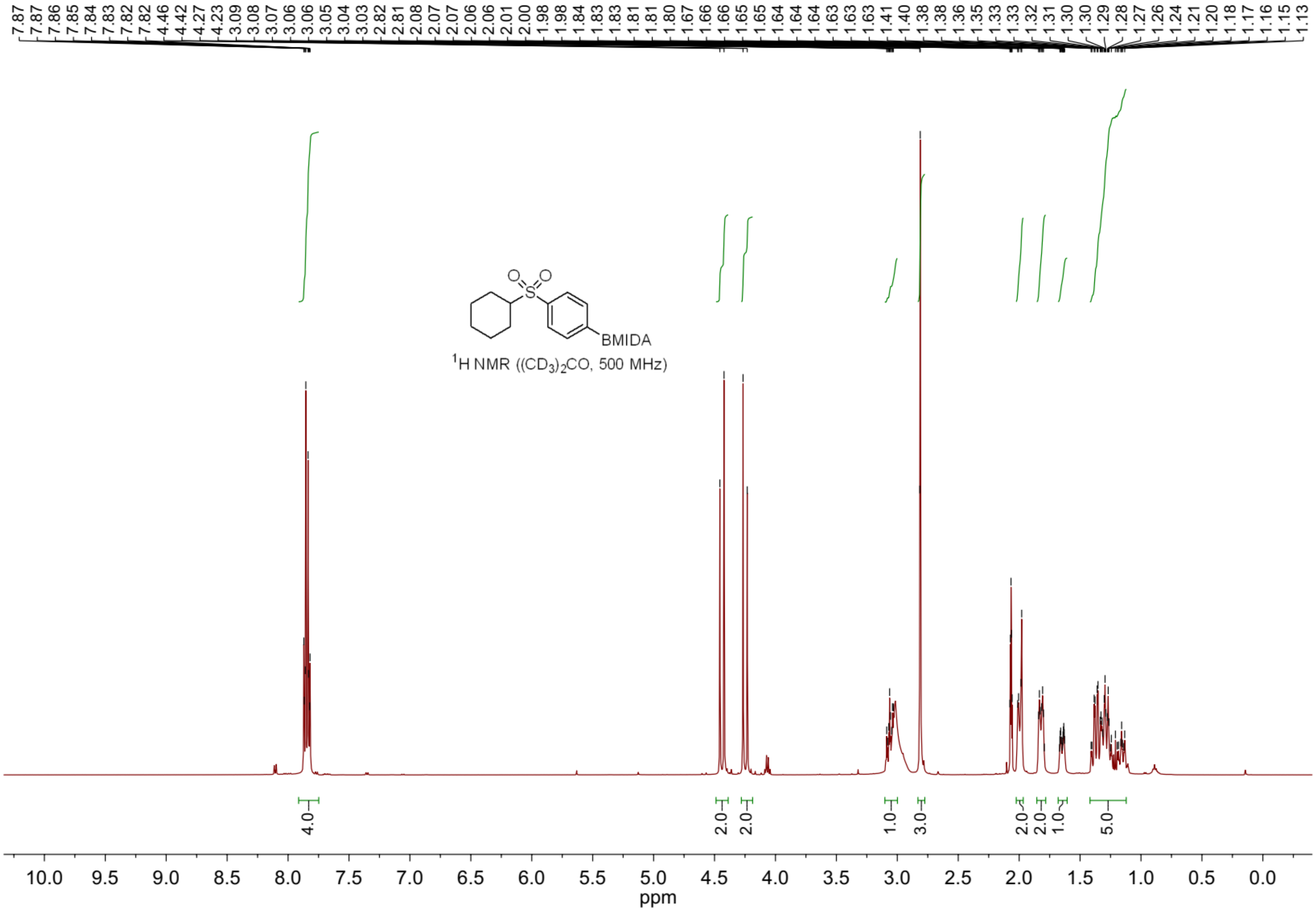
1-(Cyclohexylsulfonyl)-2-(trifluoromethoxy)benzene (3k)



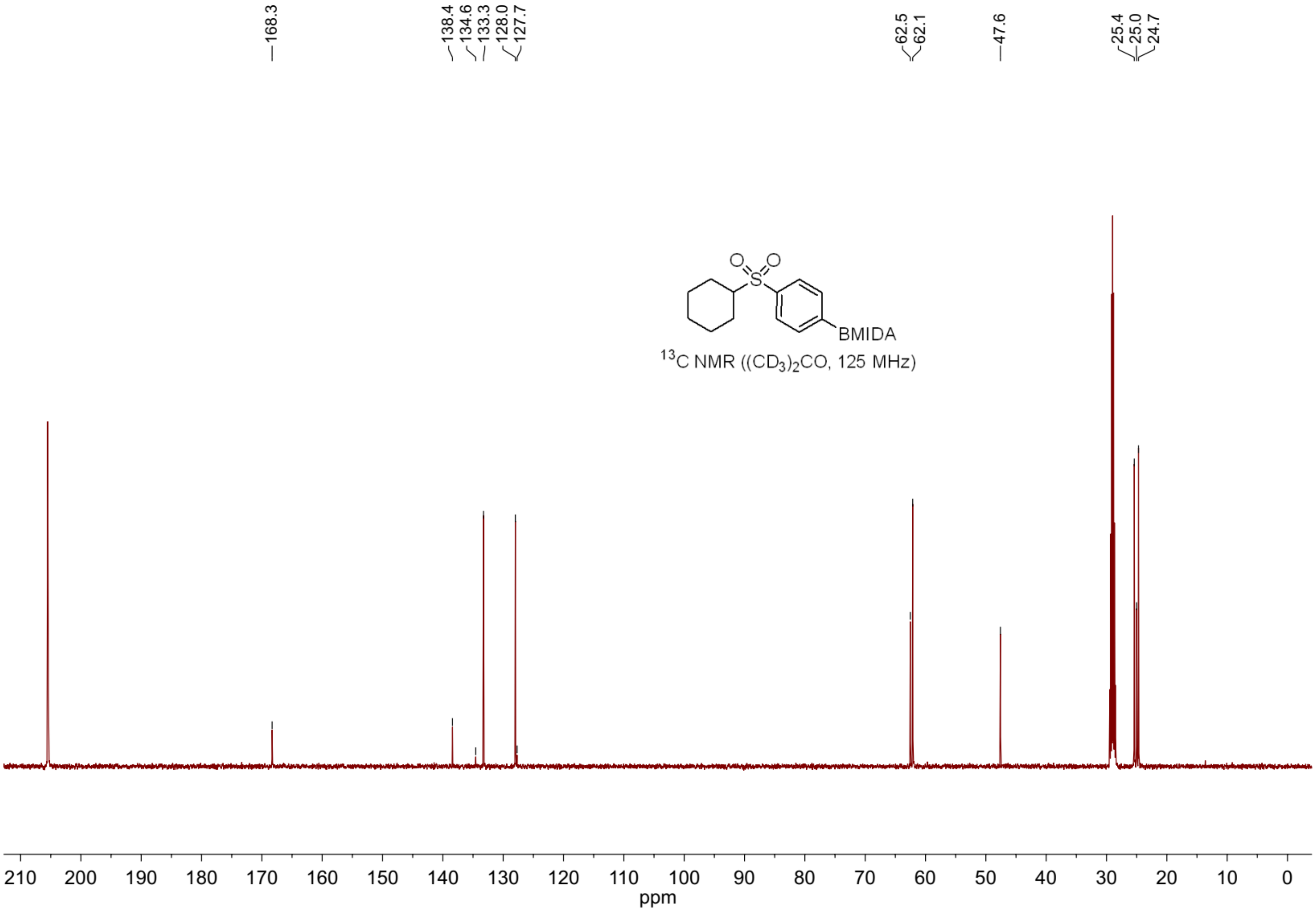
1-(Cyclohexylsulfonyl)-2-(trifluoromethoxy)benzene (3k)



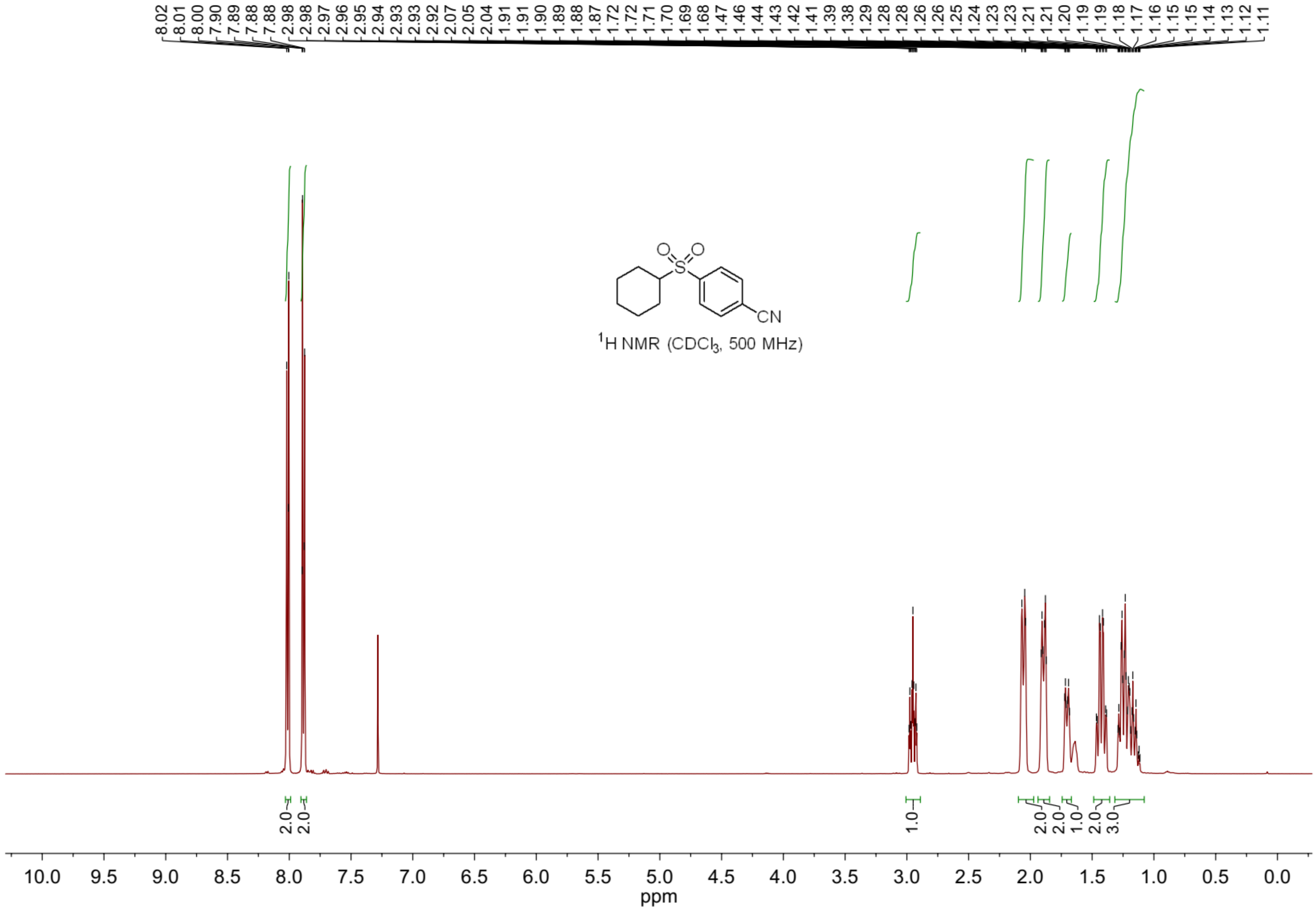
2-(4-(Cyclohexylsulfonyl)phenyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3l)



2-(4-(Cyclohexylsulfonyl)phenyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3l)



4-(Cyclohexylsulfonyl)benzonitrile (3m)



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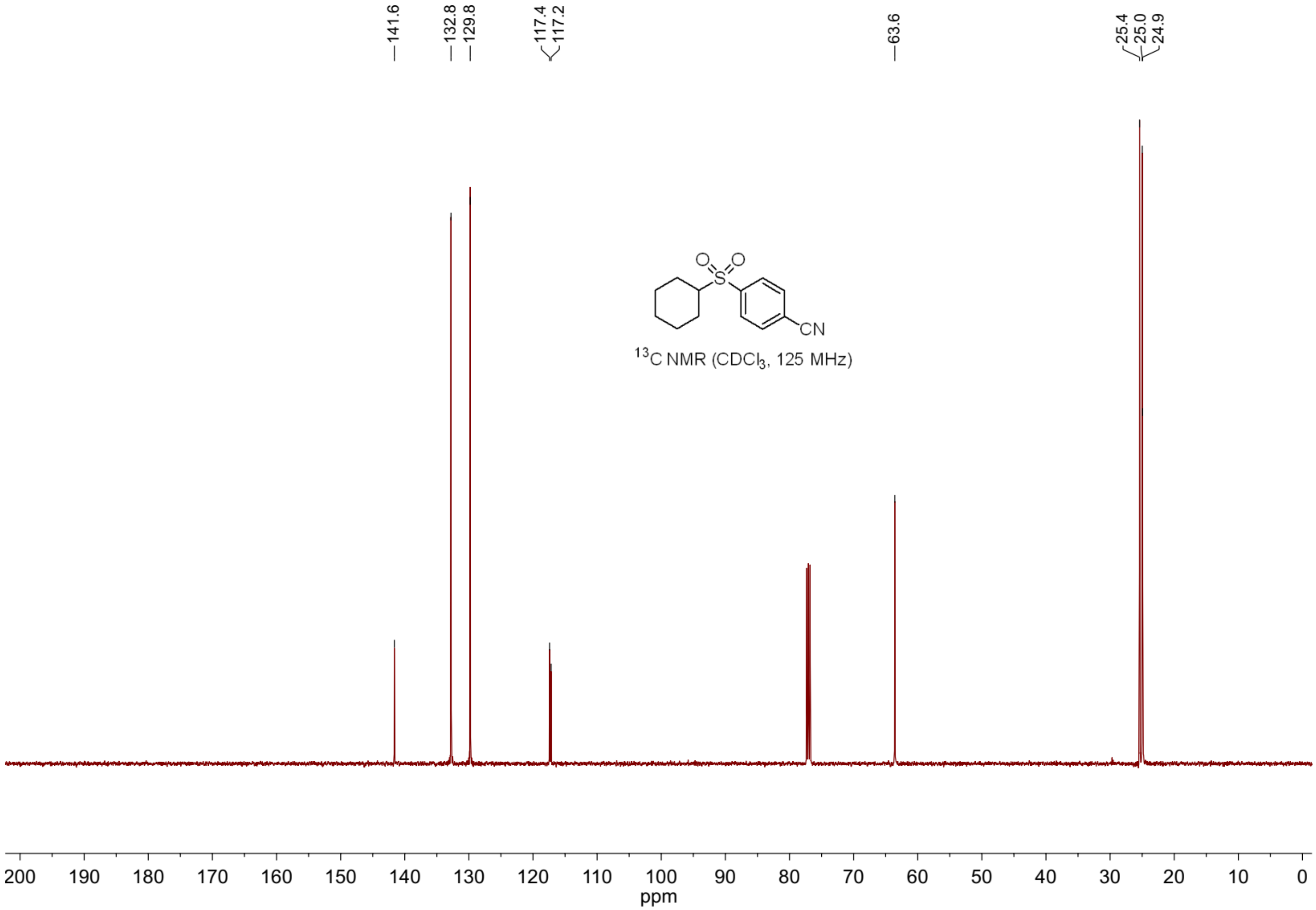
4-(Cyclohexylsulfonyl)benzonitrile (3m)



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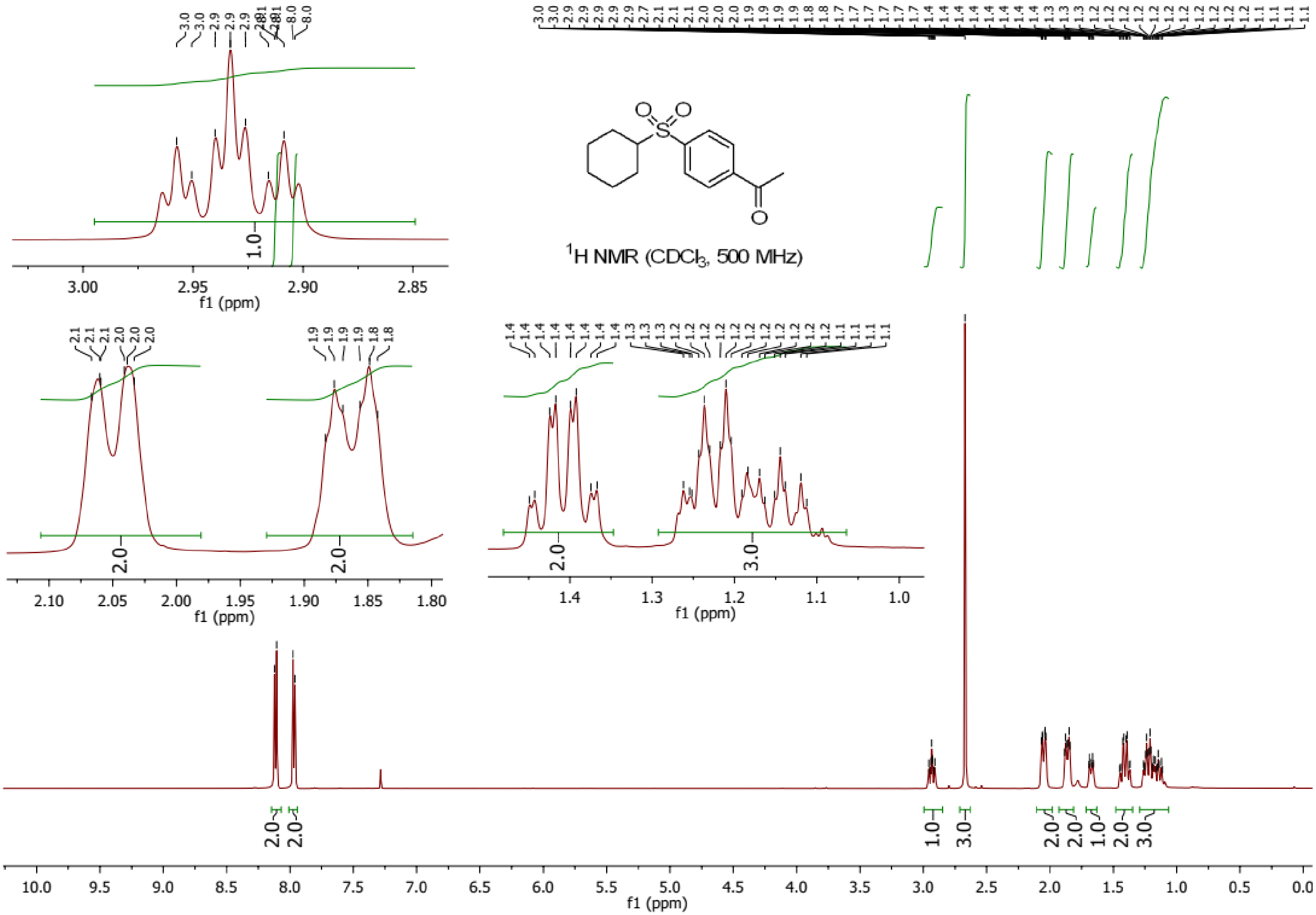
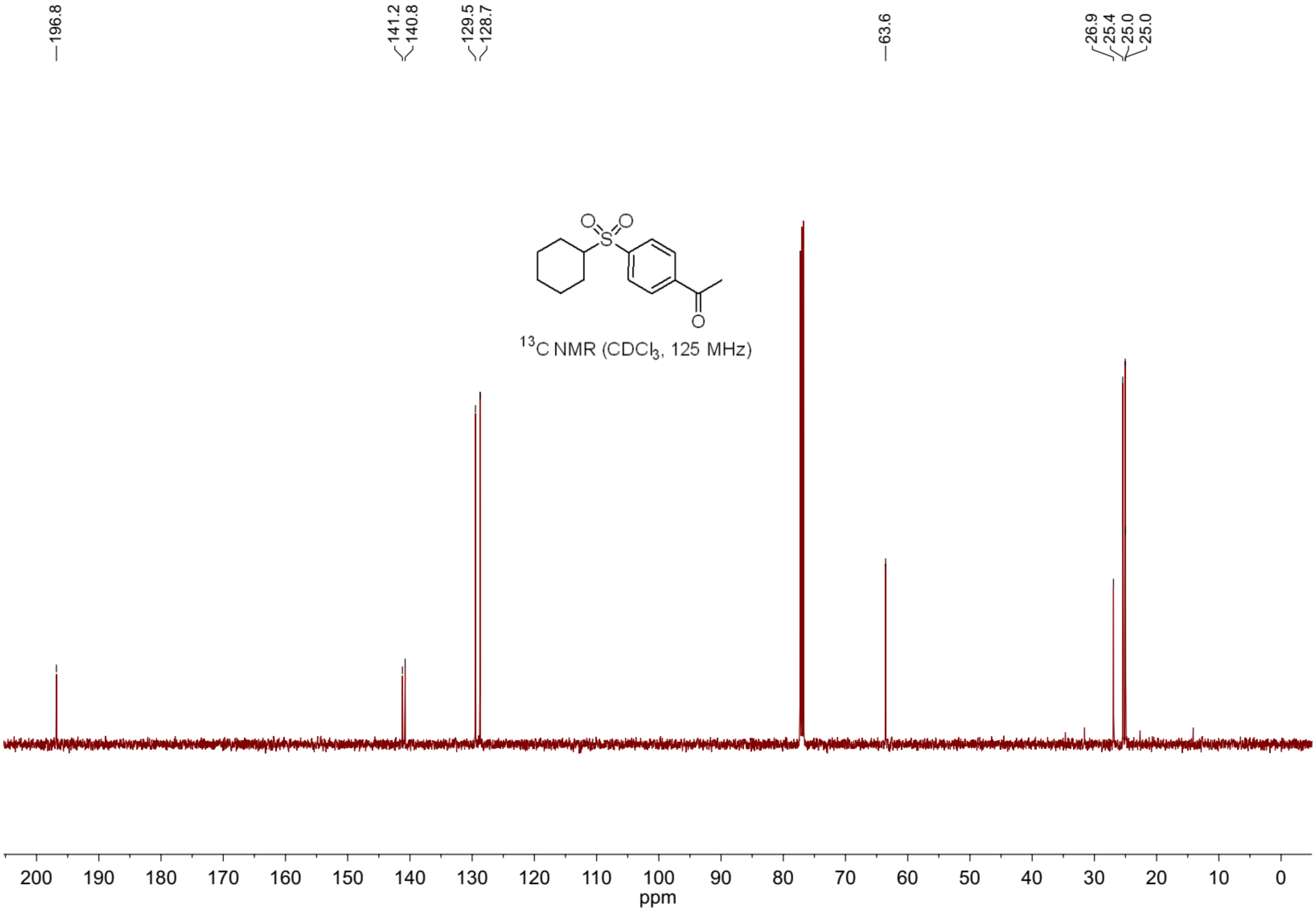
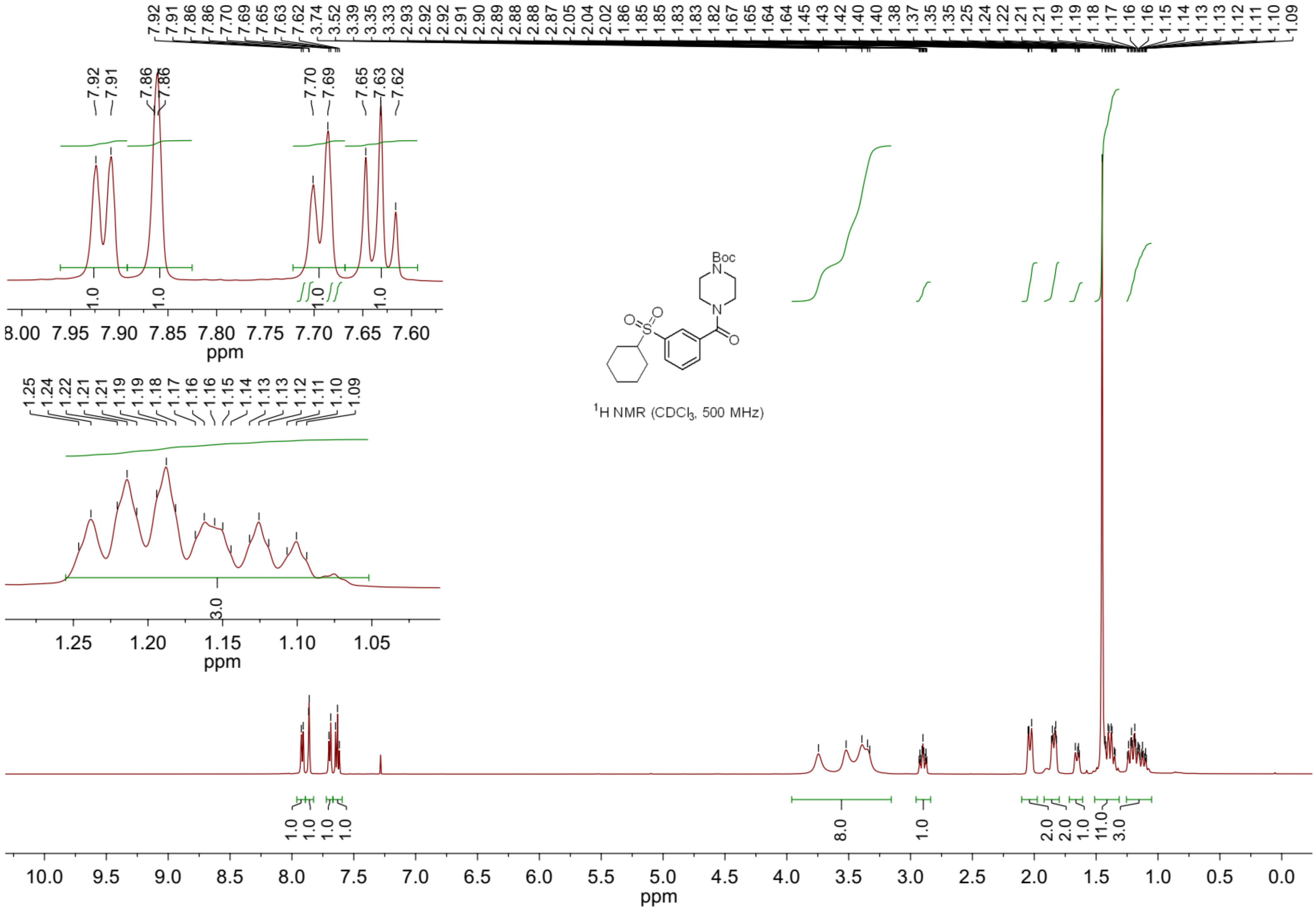
1-(4-(Cyclohexylsulfonyl)phenyl)ethan-1-one (3n)



1-(4-(Cyclohexylsulfonyl)phenyl)ethan-1-one (3n)



tert-Butyl 4-(3-(cyclohexylsulfonyl)benzoyl)piperazine-1-carboxylate (3o)



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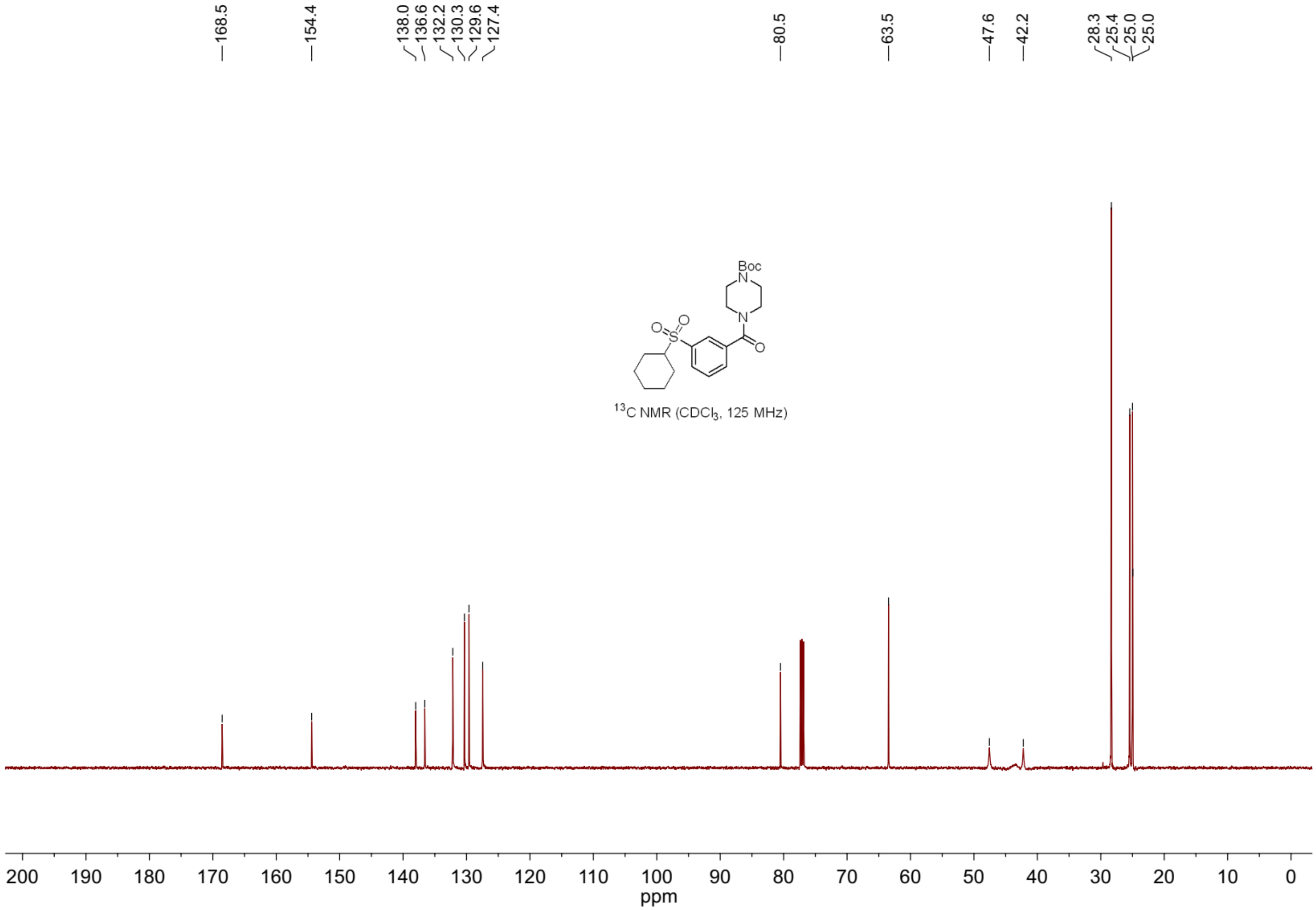
tert-Butyl 4-(3-(cyclohexylsulfonyl)benzoyl)piperazine-1-carboxylate (3o)



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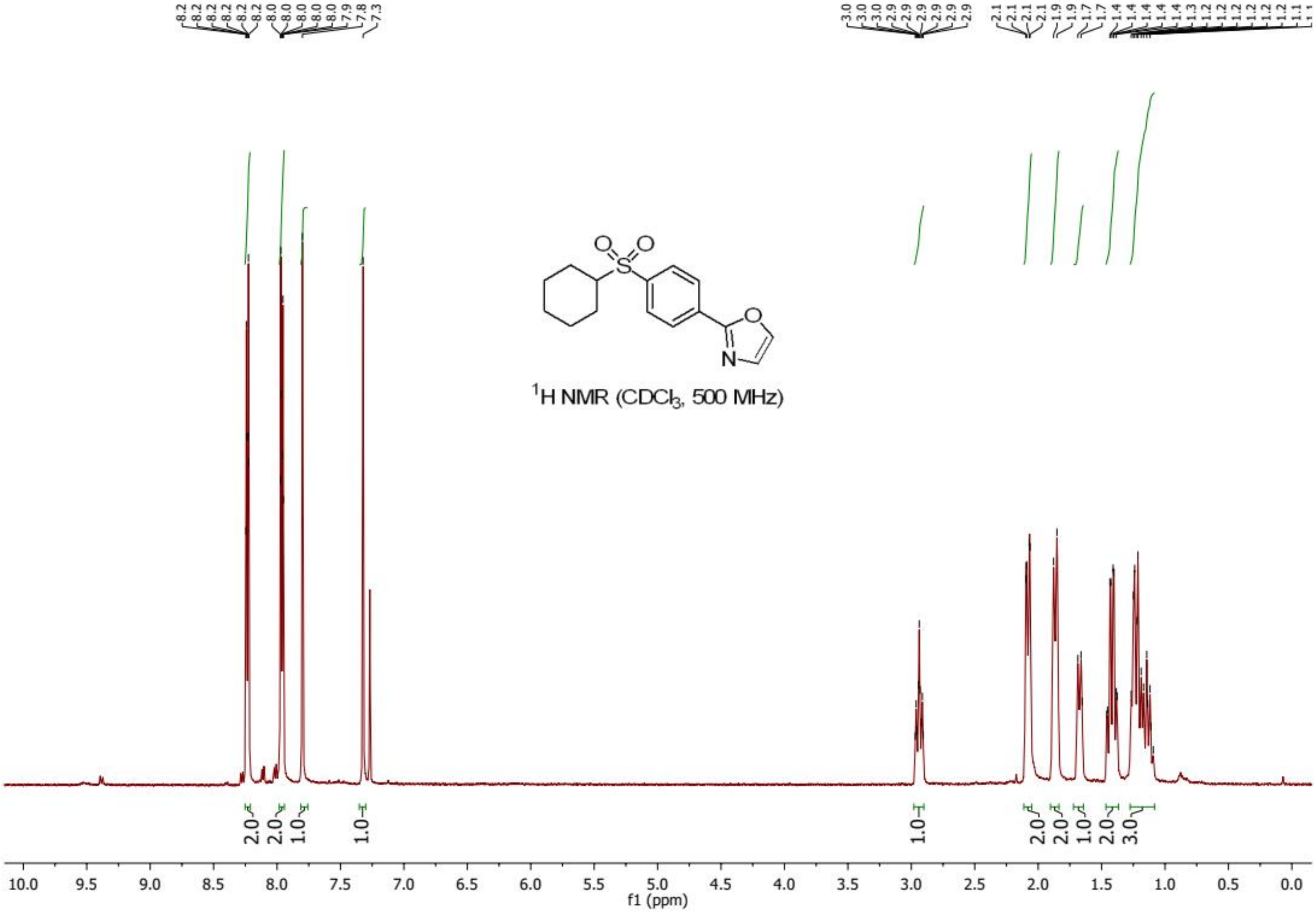
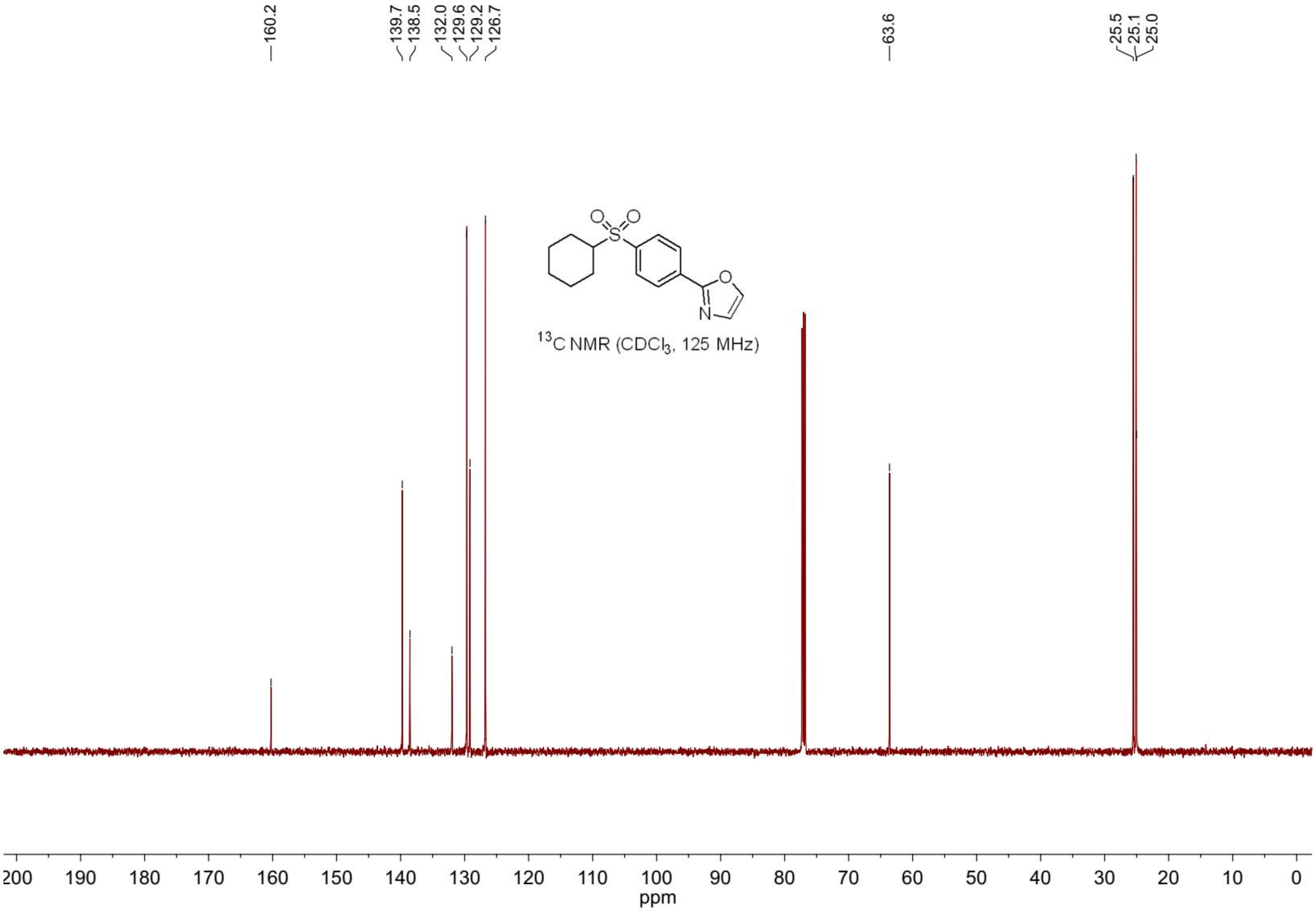
2-(4-(Cyclohexylsulfonyl)phenyl)oxazole (3p)



2-(4-(Cyclohexylsulfonyl)phenyl)oxazole (3p)



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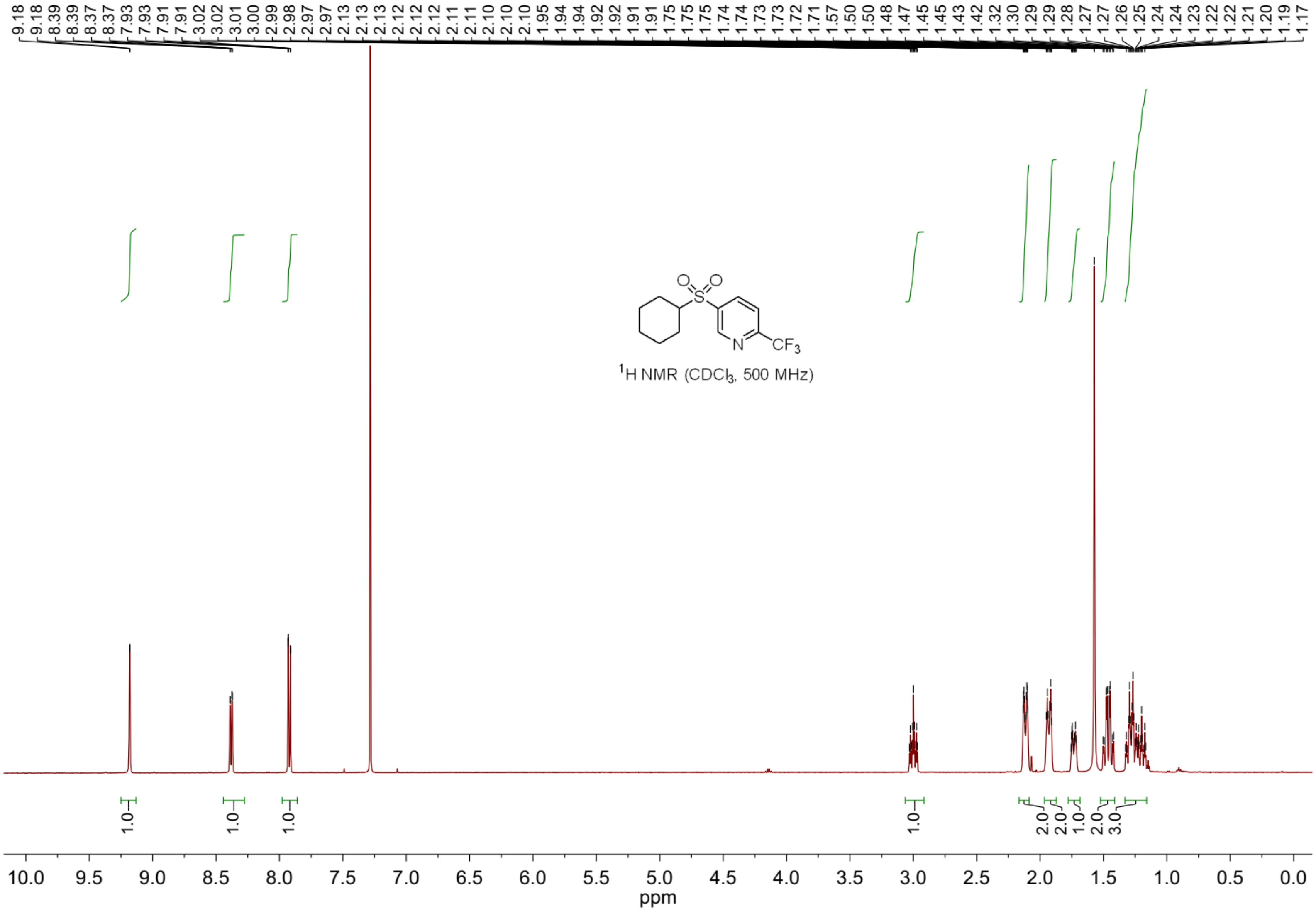
5-(Cyclohexylsulfonyl)-2-(trifluoromethyl)pyridine (3q)



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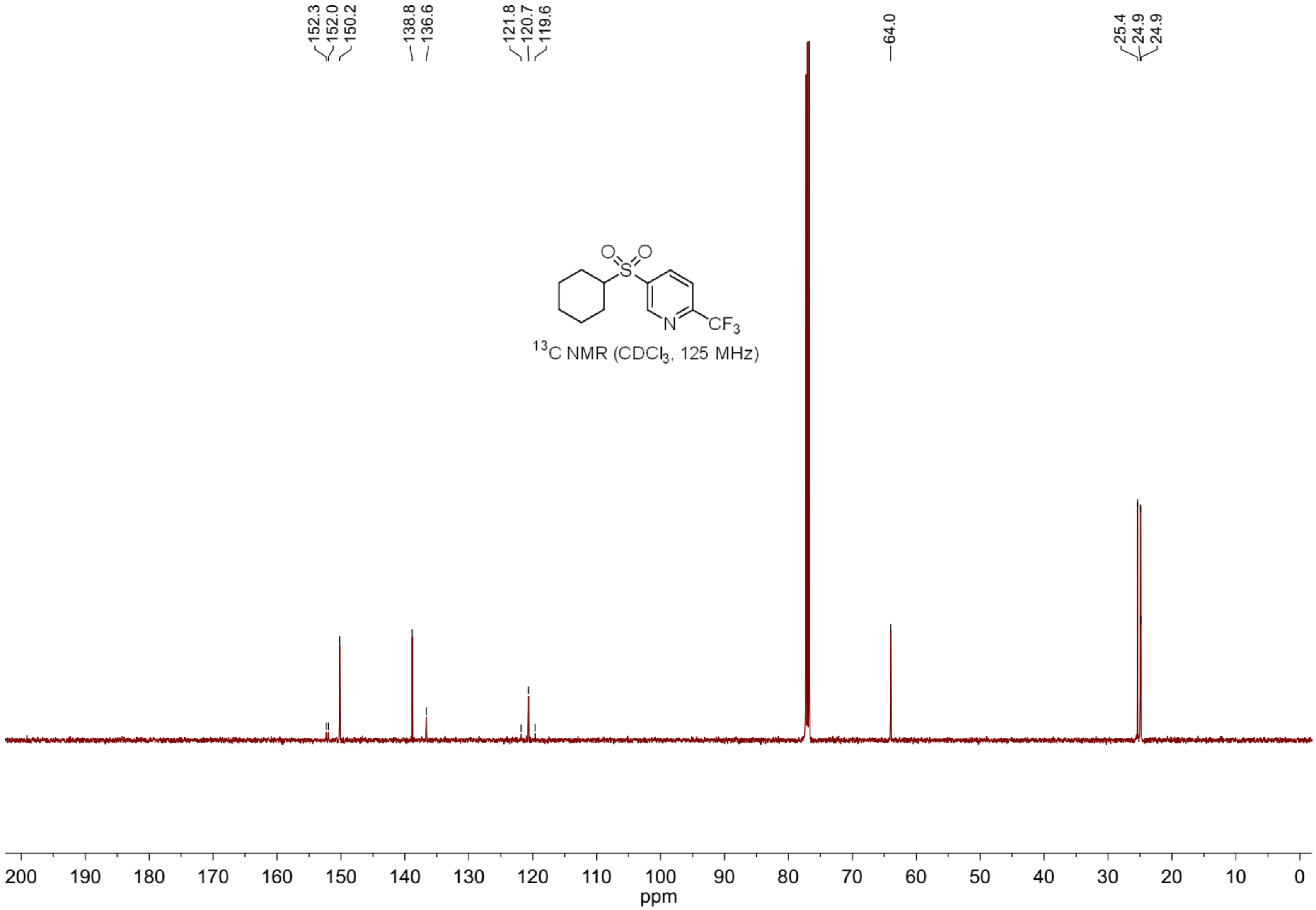
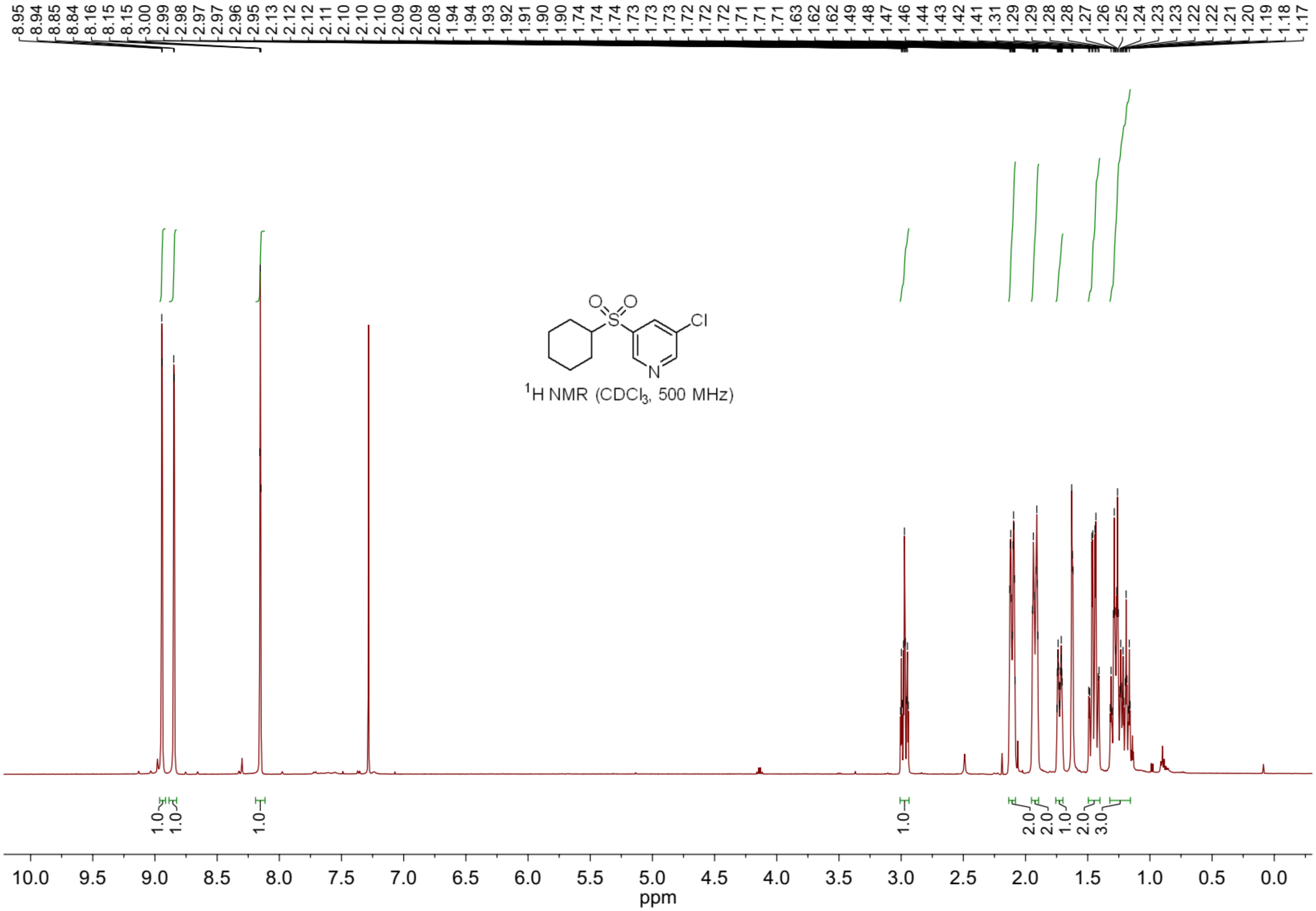
5-(Cyclohexylsulfonyl)-2-(trifluoromethyl)pyridine (3q)



3-Chloro-5-(cyclohexylsulfonyl)pyridine (3r)



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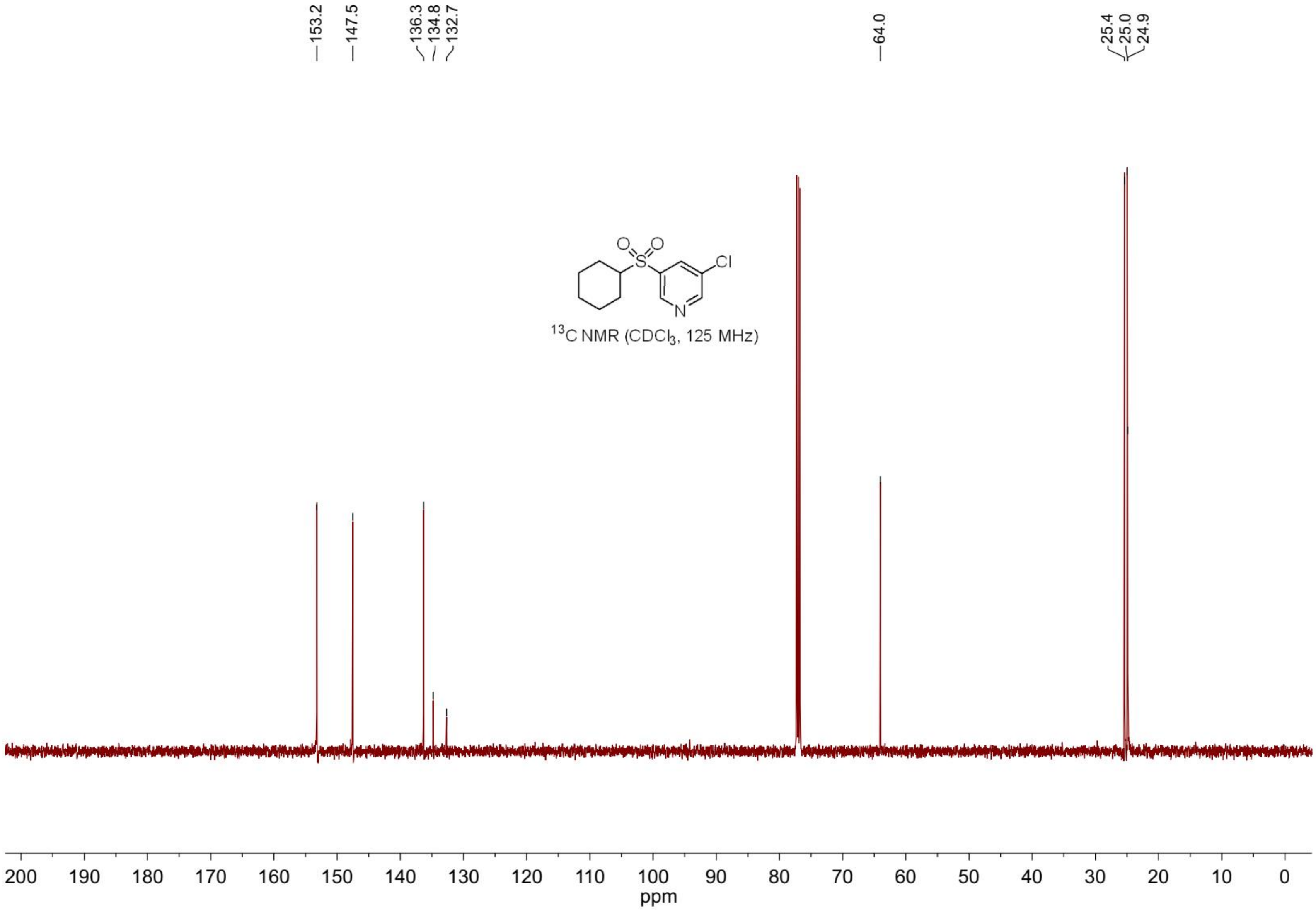
3-Chloro-5-(cyclohexylsulfonyl)pyridine (3r)



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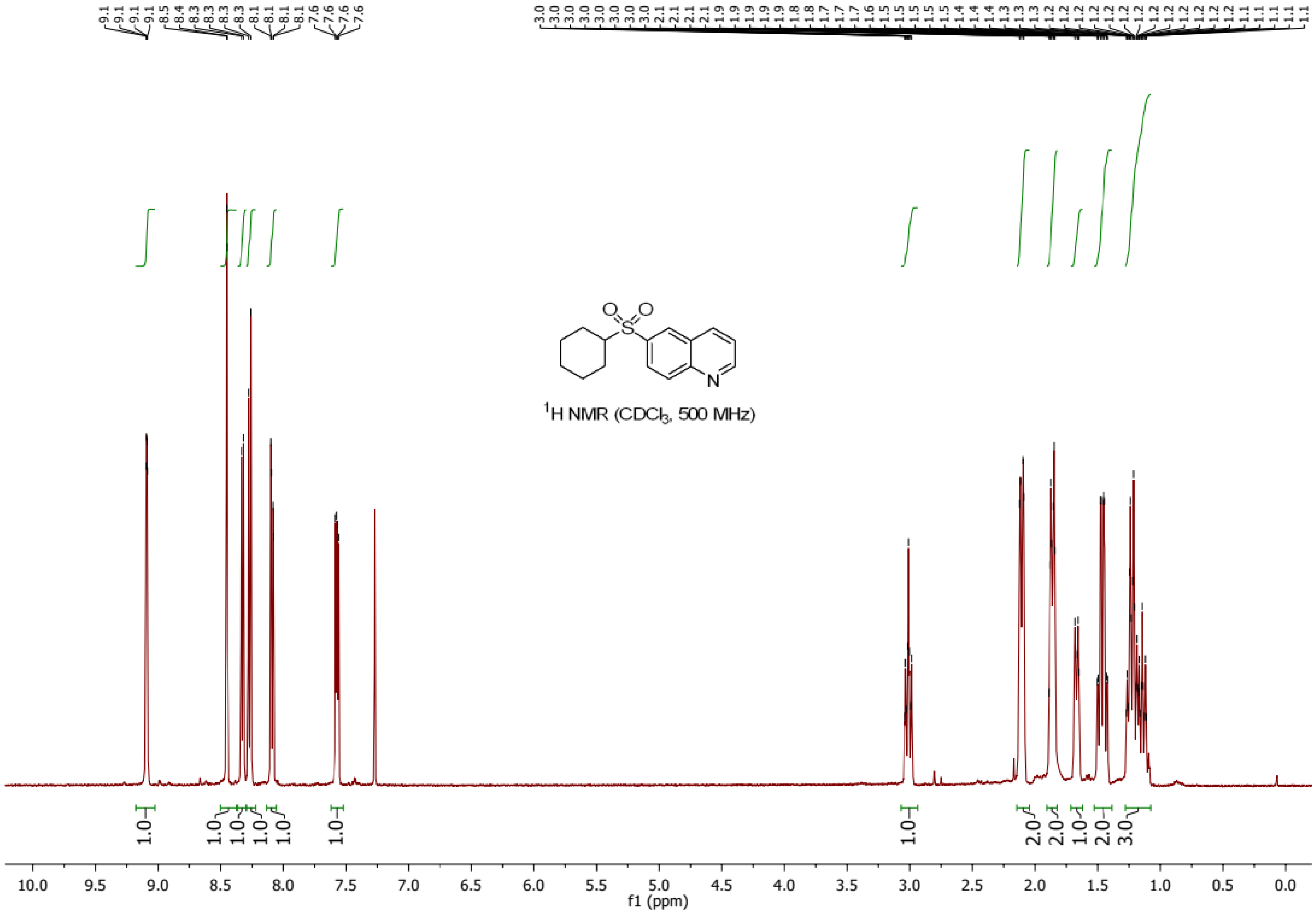
6-(Cyclohexylsulfonyl)quinolone (3s)



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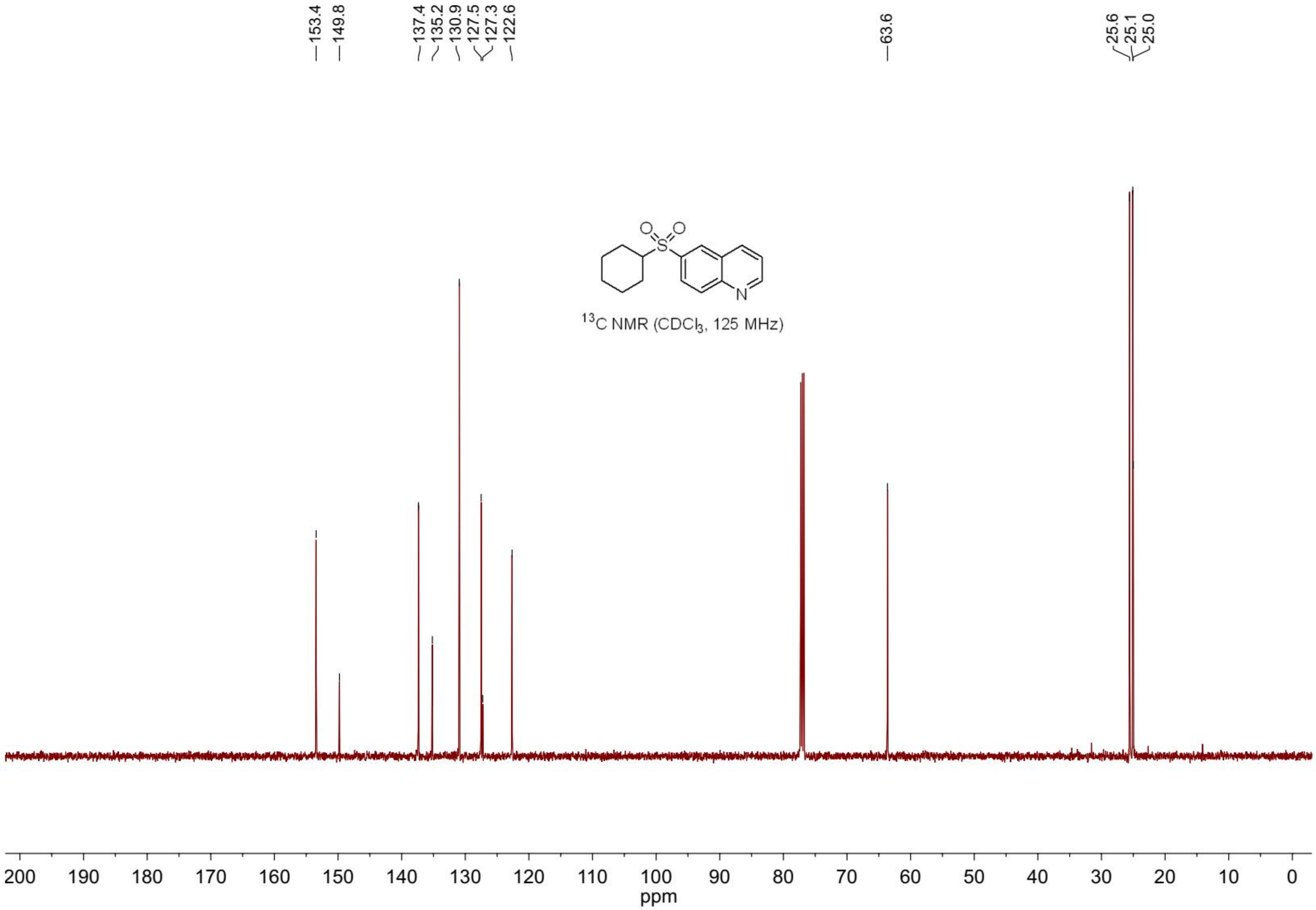
6-(Cyclohexylsulfonyl)quinolone (3s)



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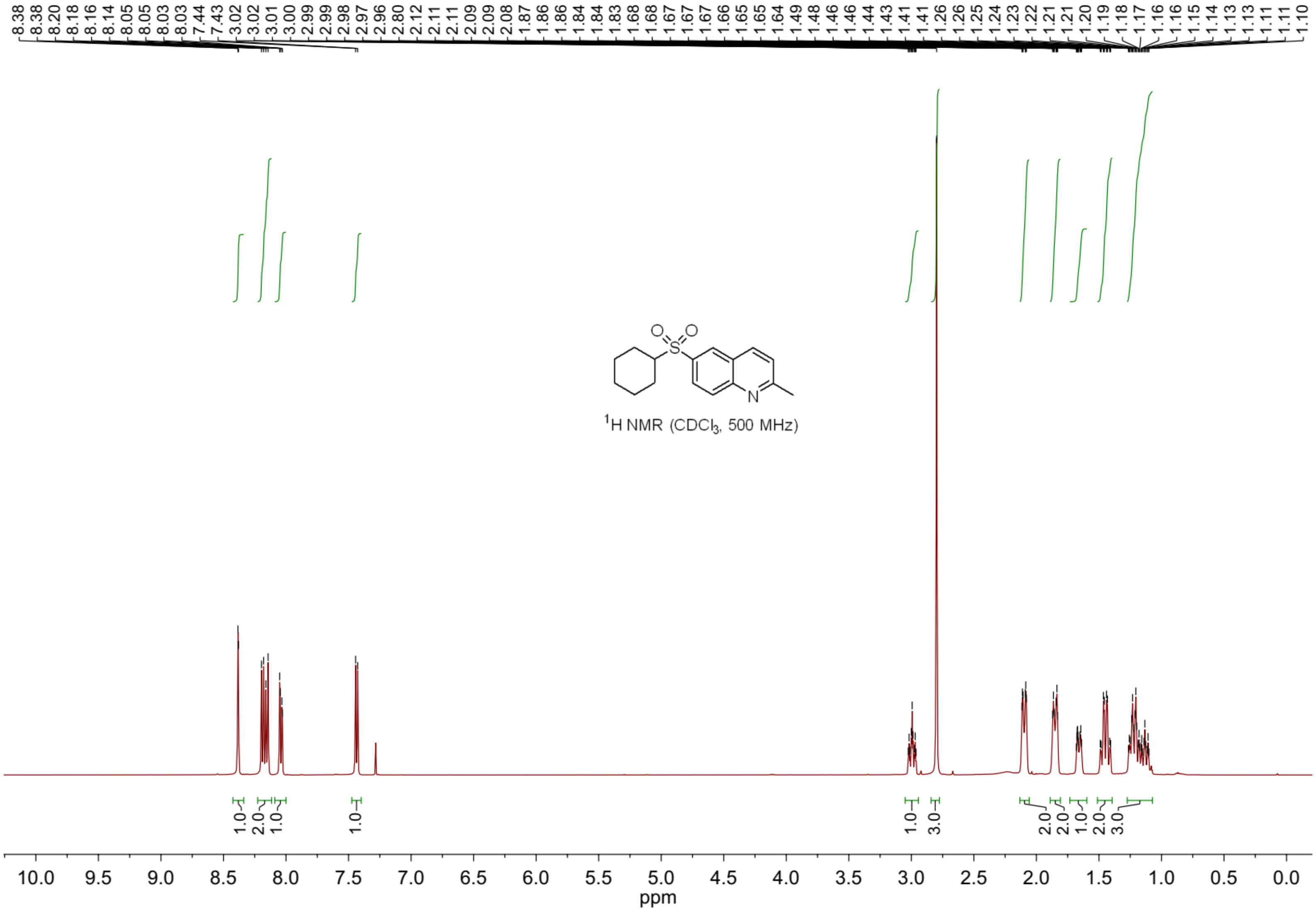
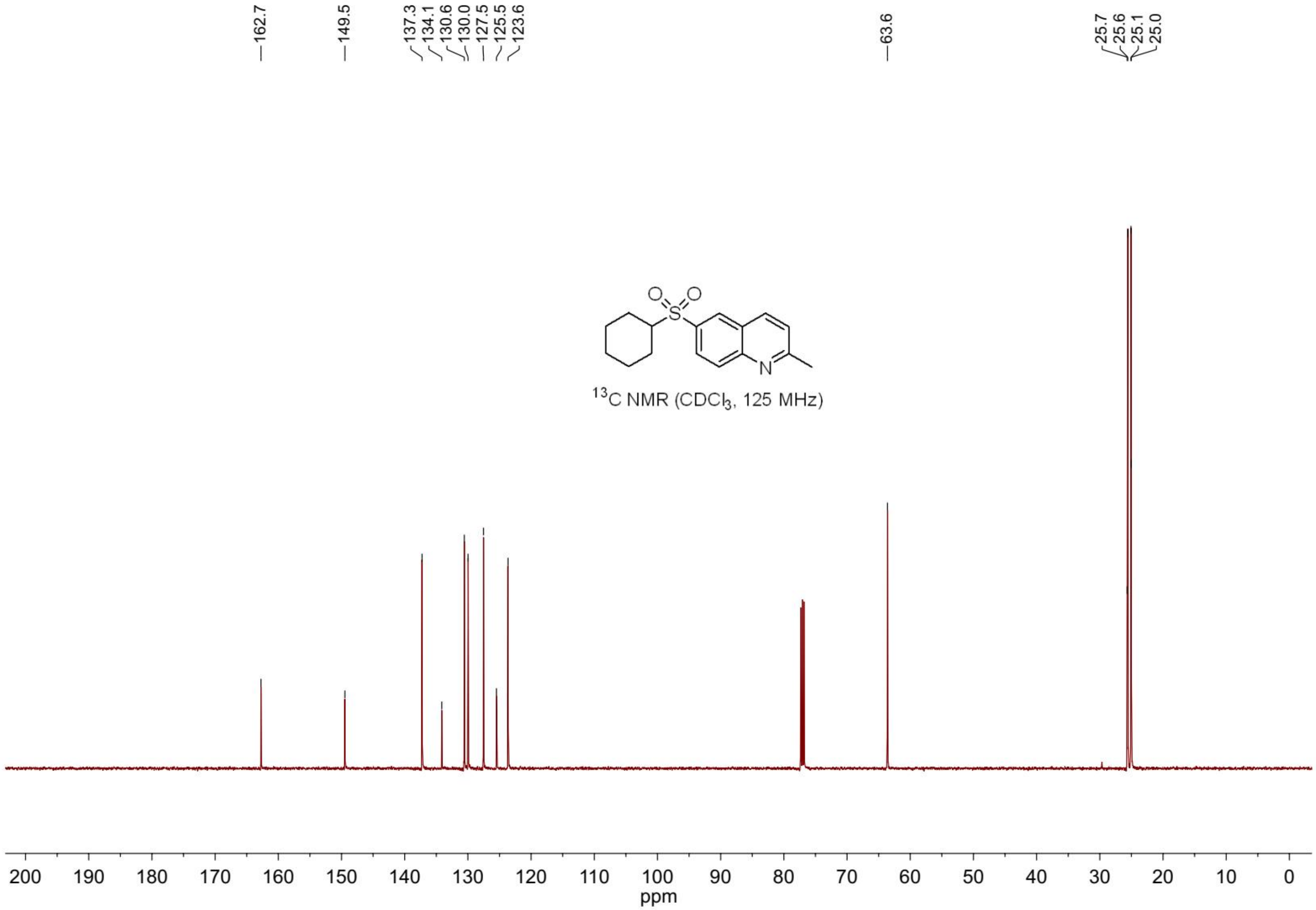
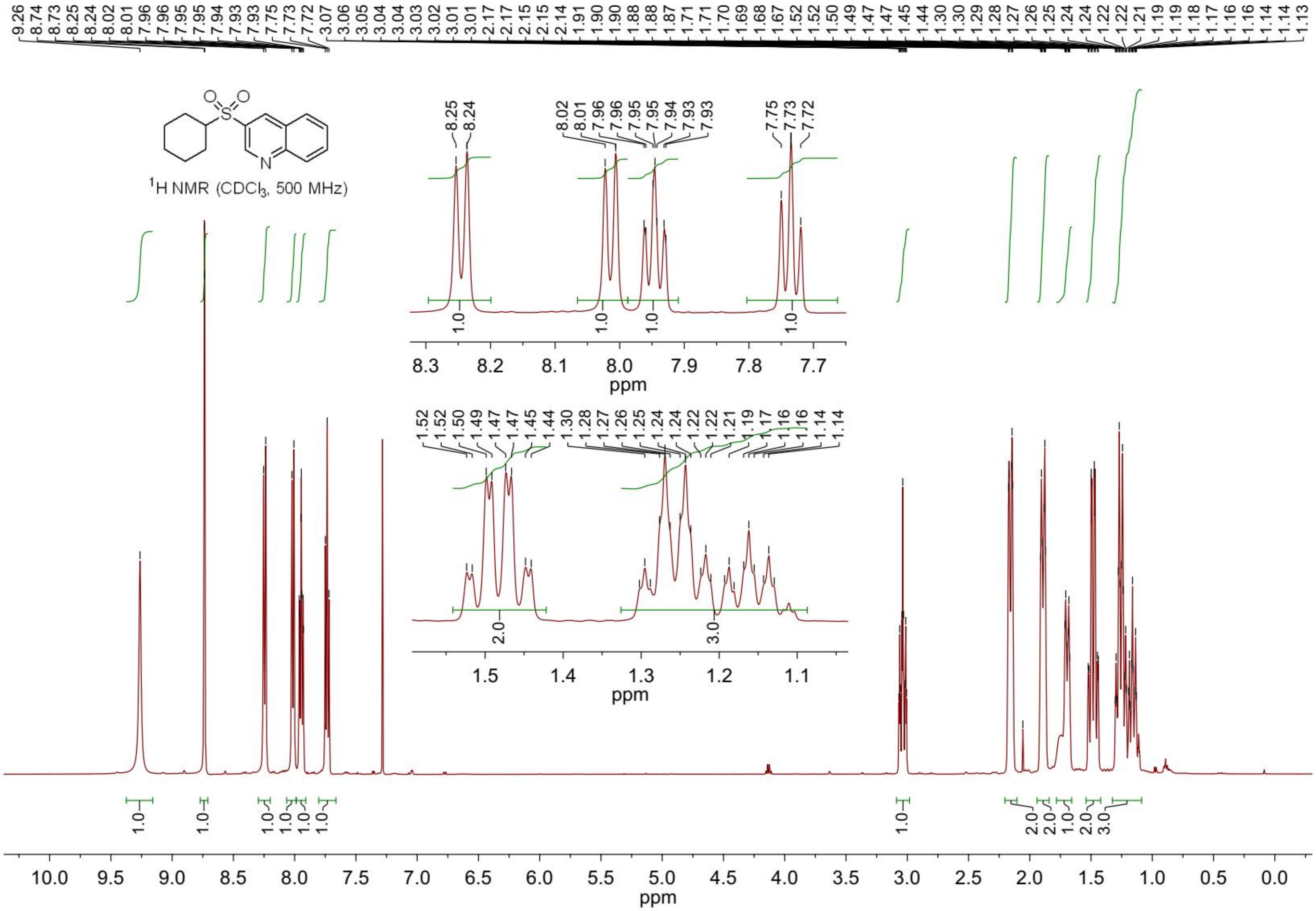
6-(Cyclohexylsulfonyl)-2-methylquinoline (3t)



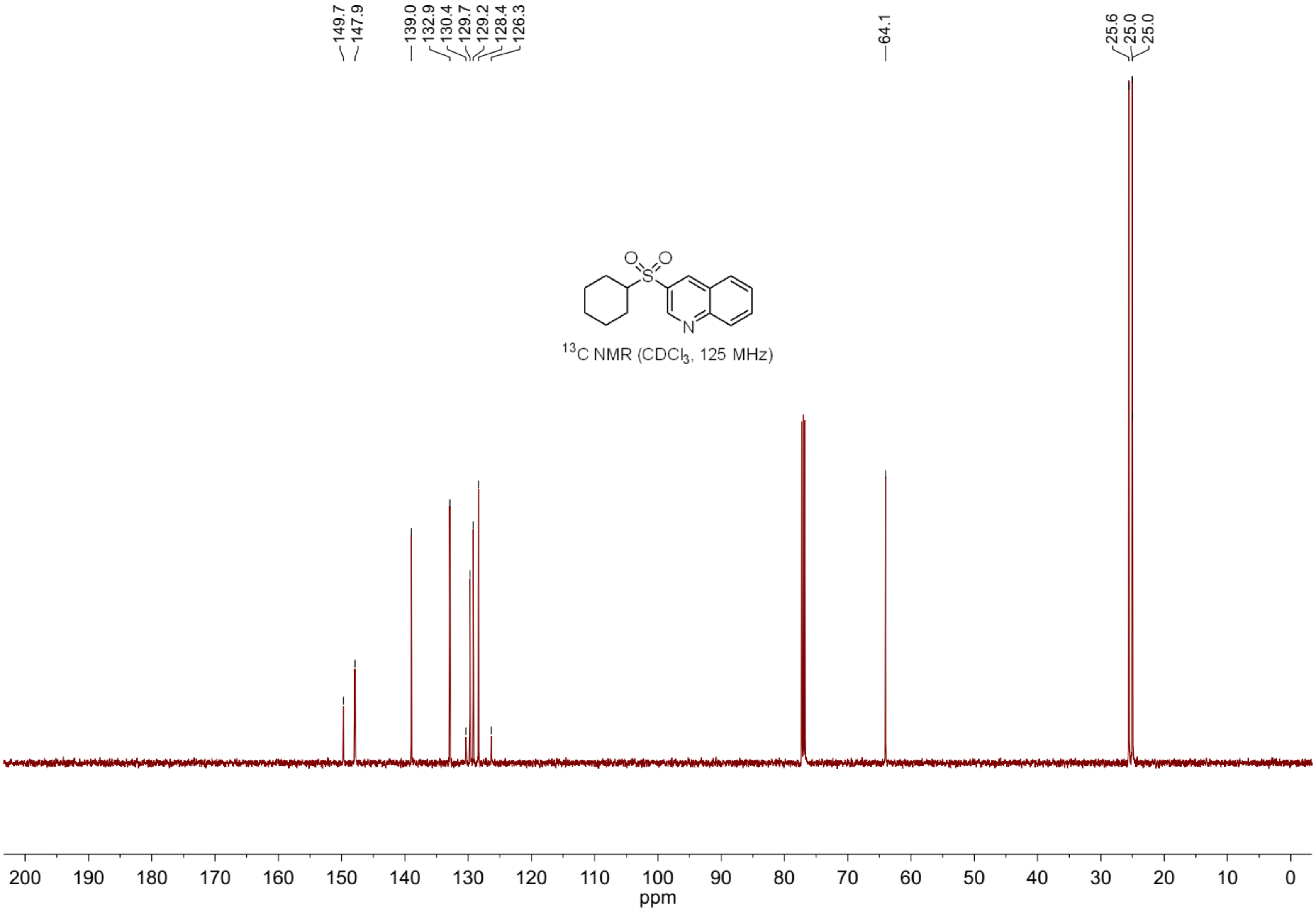
6-(Cyclohexylsulfonyl)-2-methylquinoline (3t)



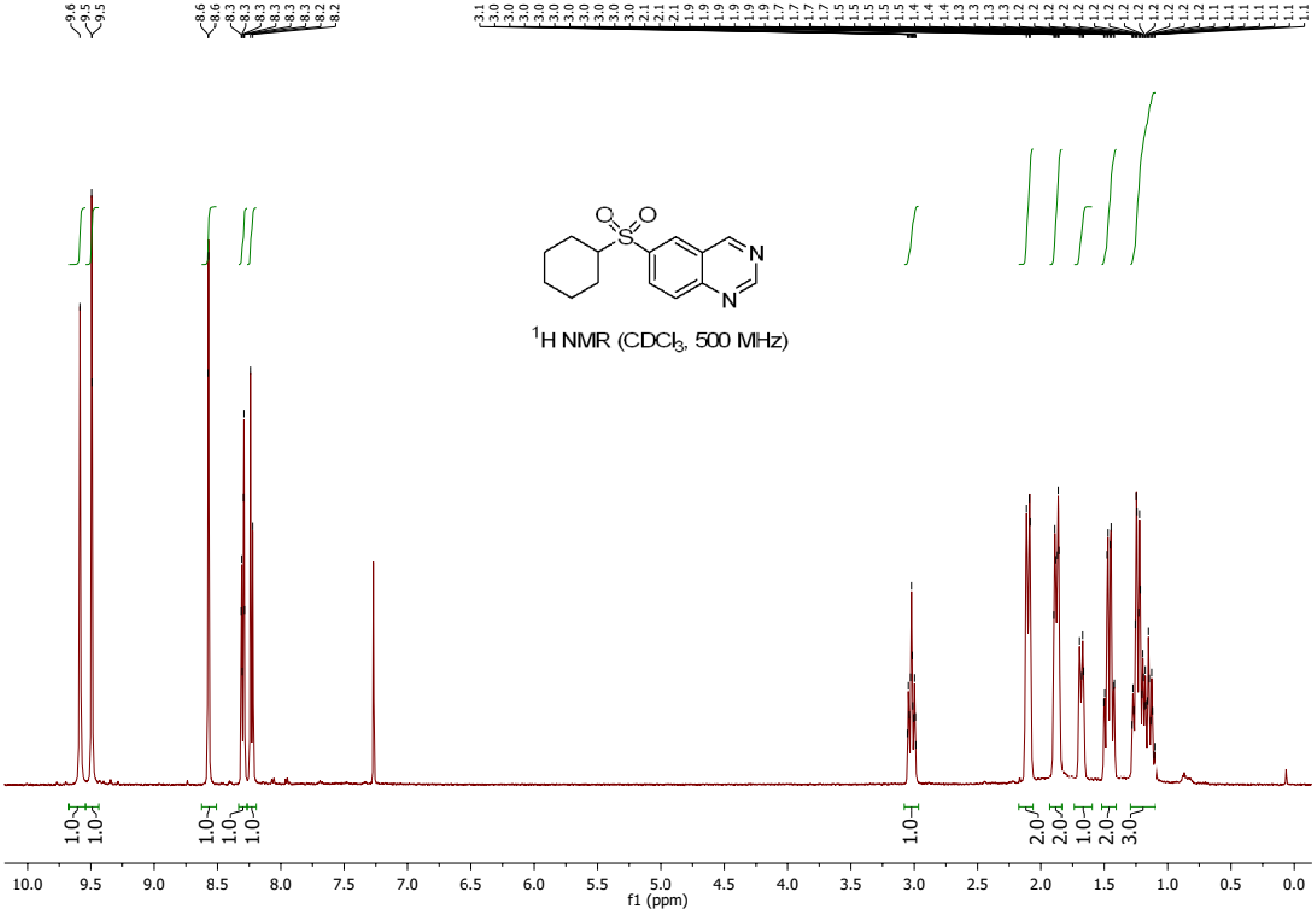
3-(Cyclohexylsulfonyl)quinolone (3u)



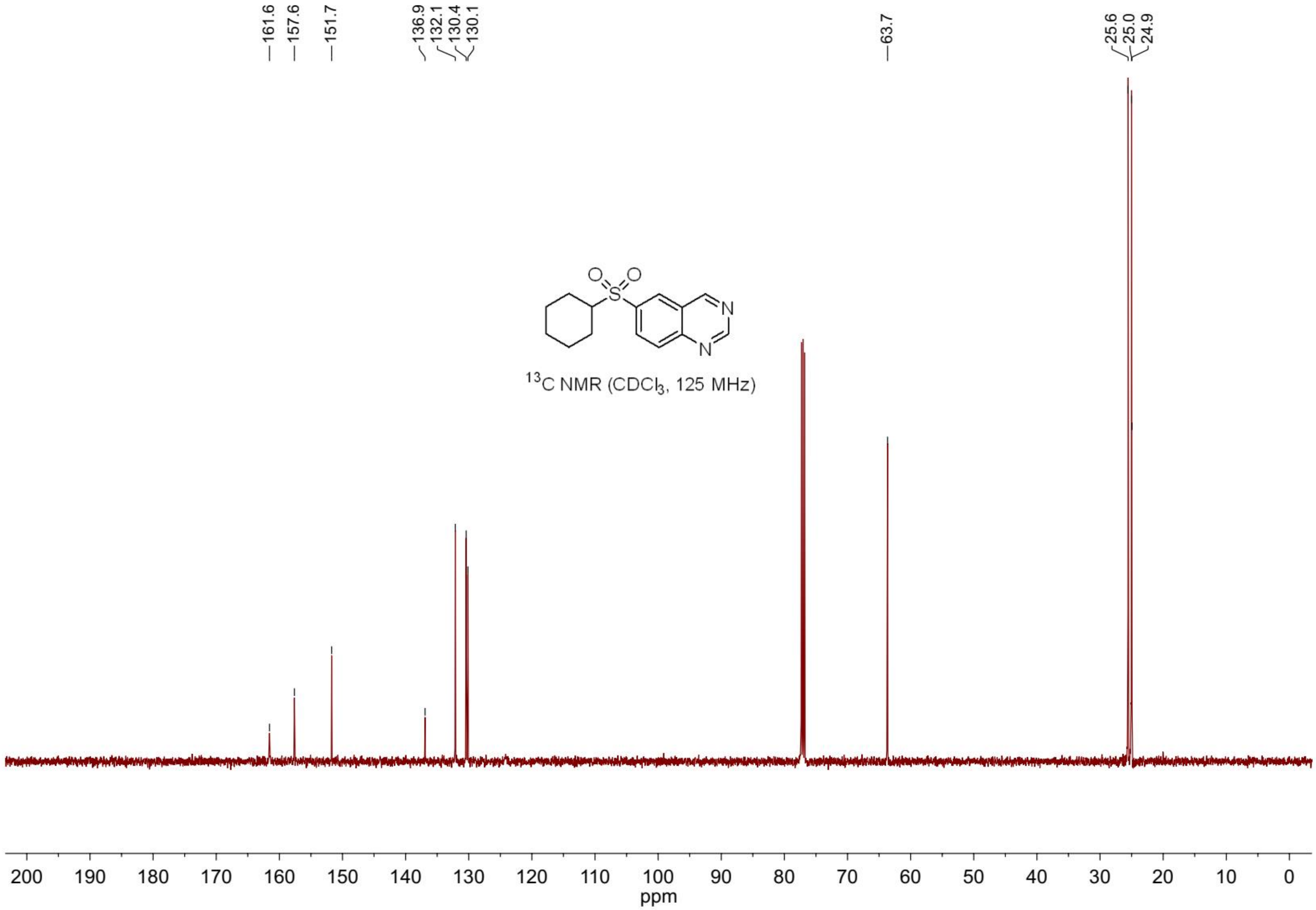
3-(Cyclohexylsulfonyl)quinolone (3u)



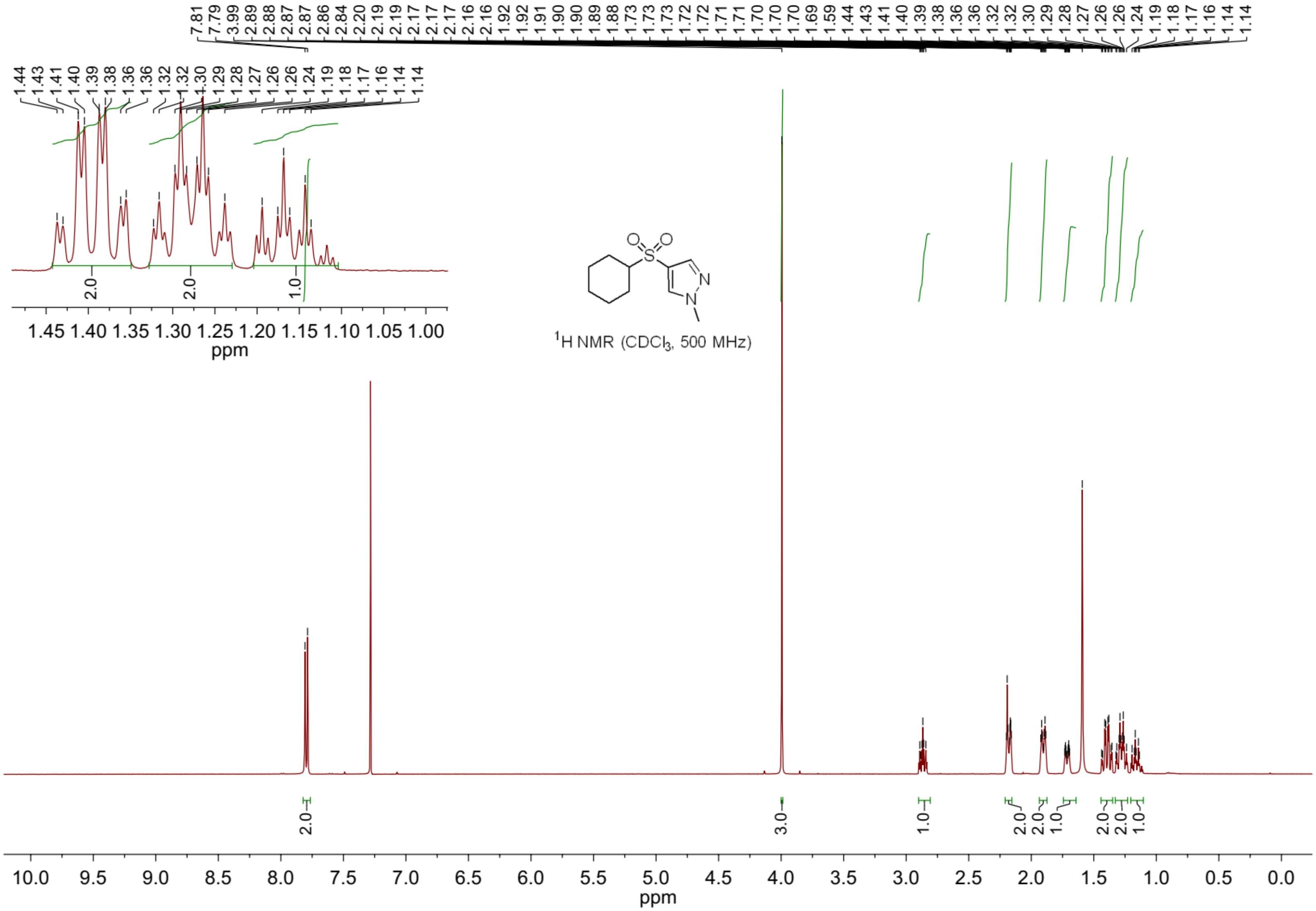
6-(Cyclohexylsulfonyl)quinazoline (3v)



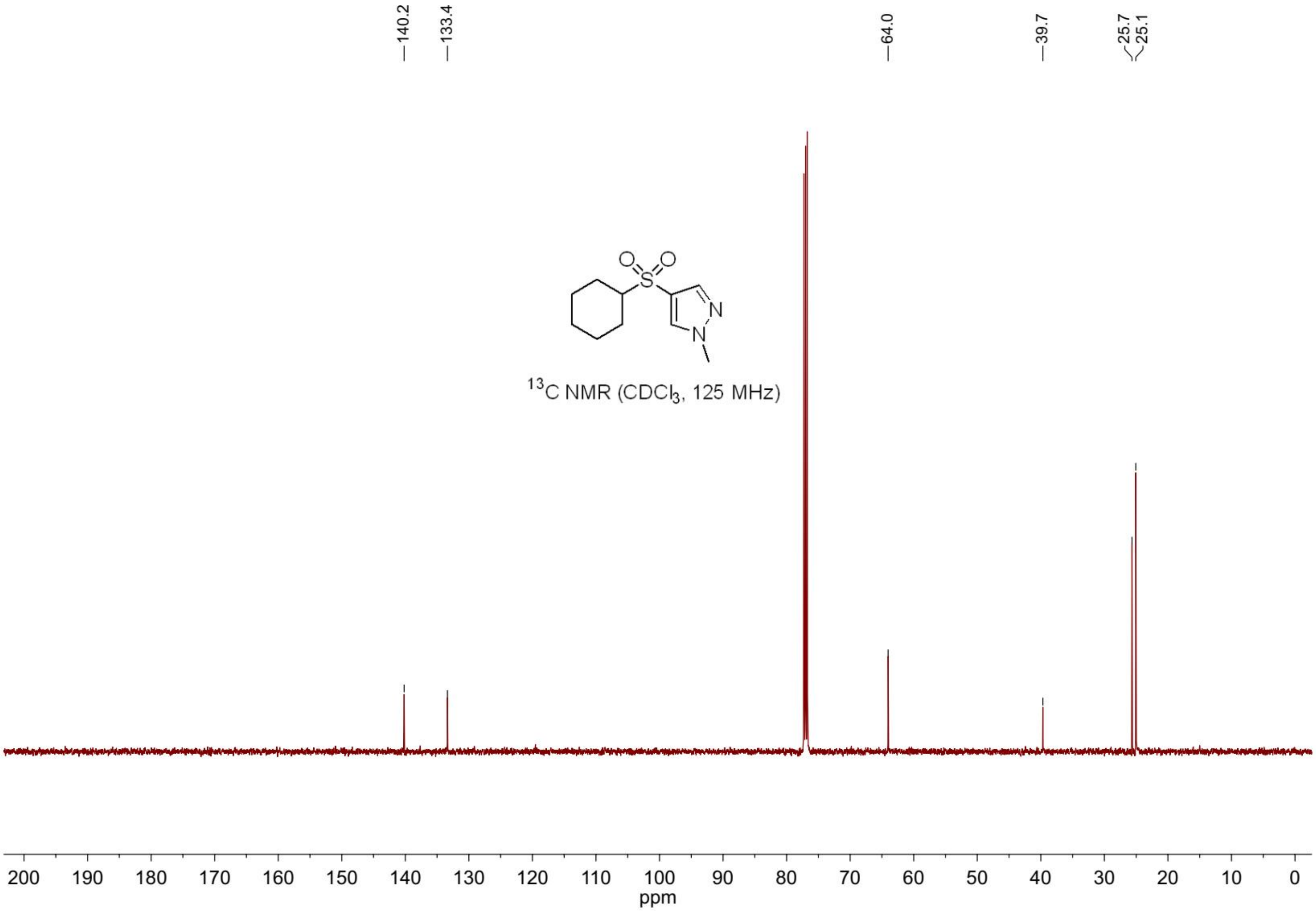
6-(Cyclohexylsulfonyl)quinazoline (3v)



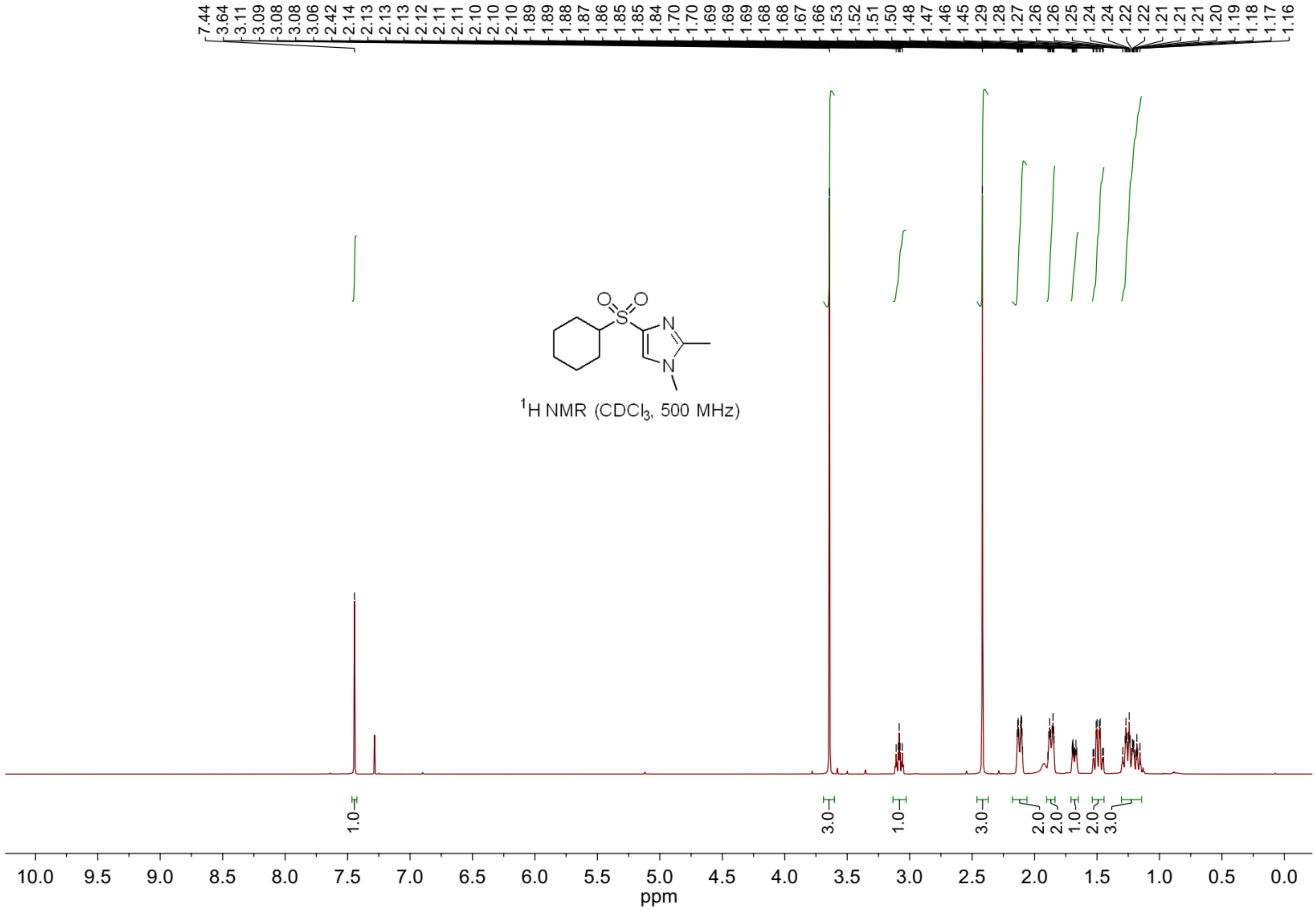
4-(Cyclohexylsulfonyl)-1-methyl-1*H*-pyrazole (3w)



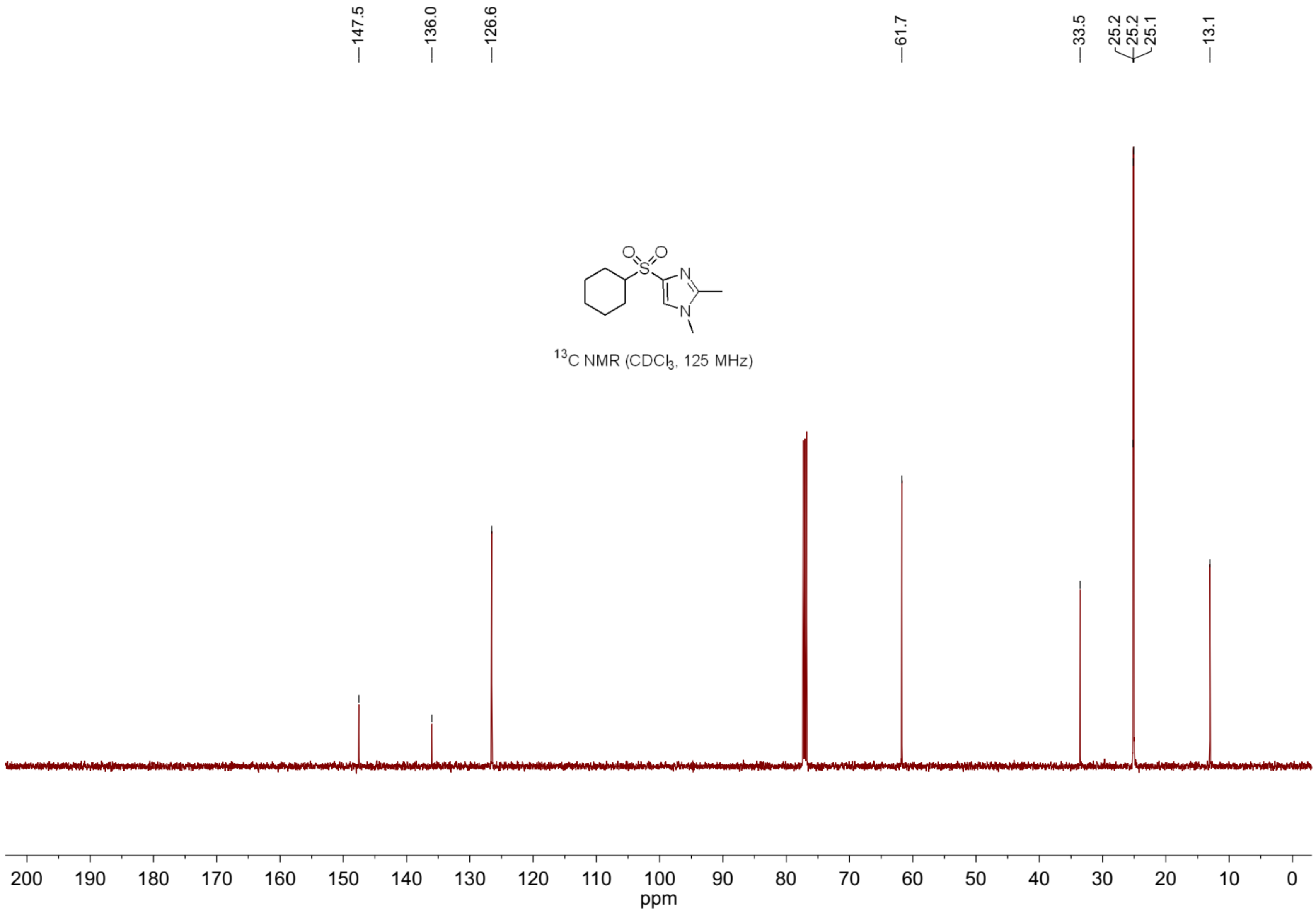
4-(Cyclohexylsulfonyl)-1-methyl-1*H*-pyrazole (3w)



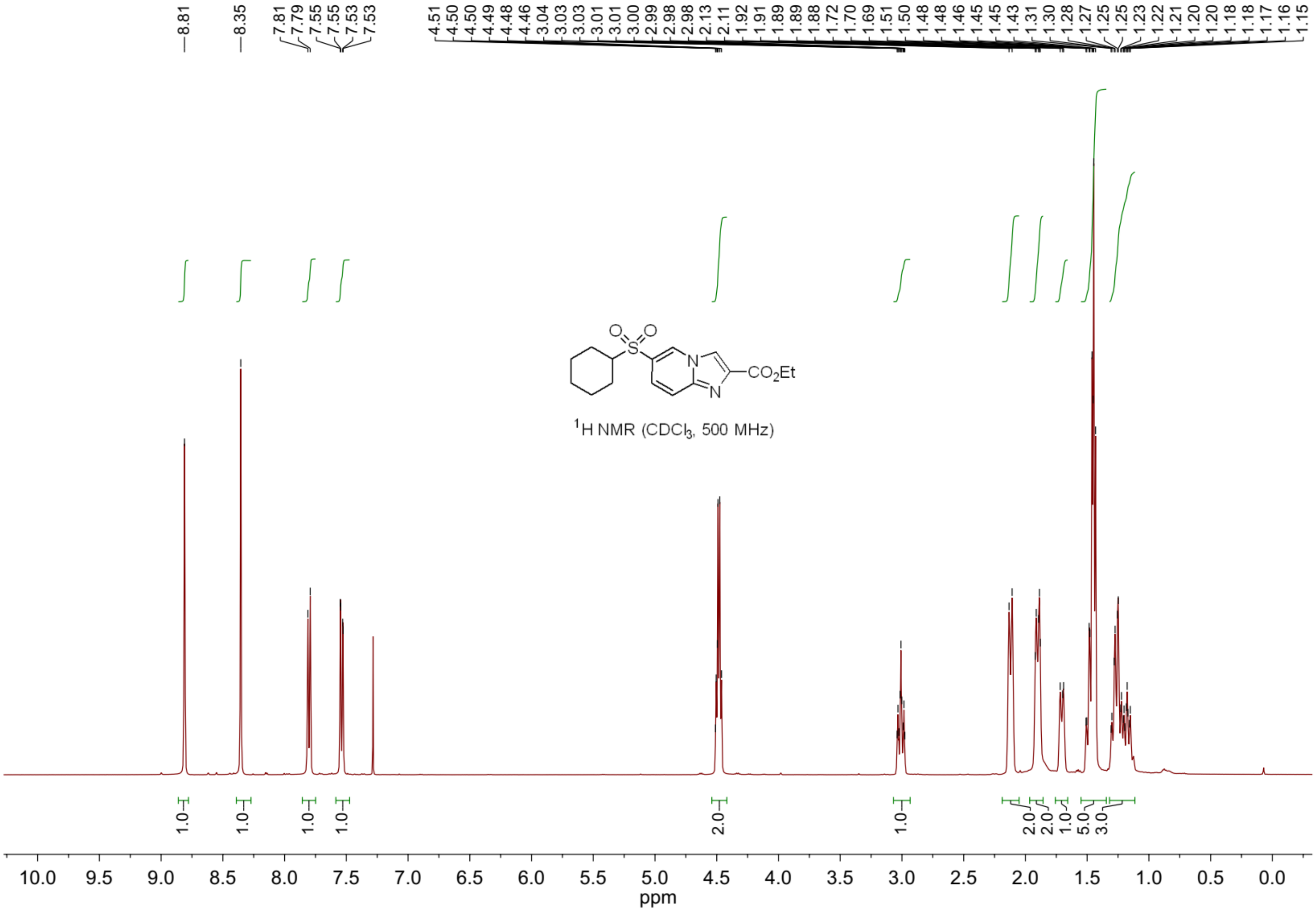
4-(Cyclohexylsulfonyl)-1,2-dimethyl-1*H*-imidazole (3x)



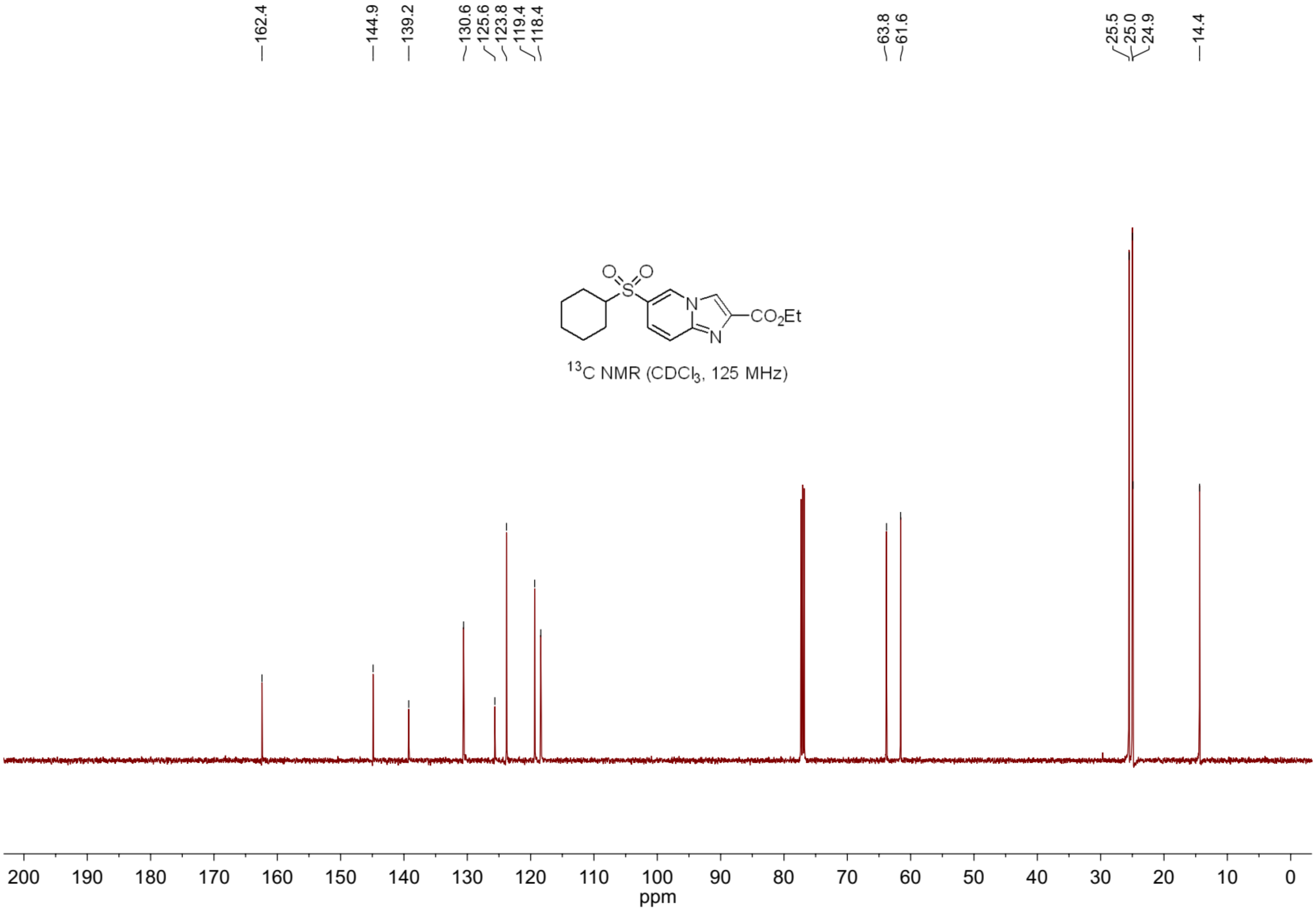
4-(Cyclohexylsulfonyl)-1,2-dimethyl-1*H*-imidazole (3x)



Ethyl 6-(cyclohexylsulfonyl)imidazo[1,2-*a*]pyridine-2-carboxylate (3y)



Ethyl 6-(cyclohexylsulfonyl)imidazo[1,2-*a*]pyridine-2-carboxylate (3y)



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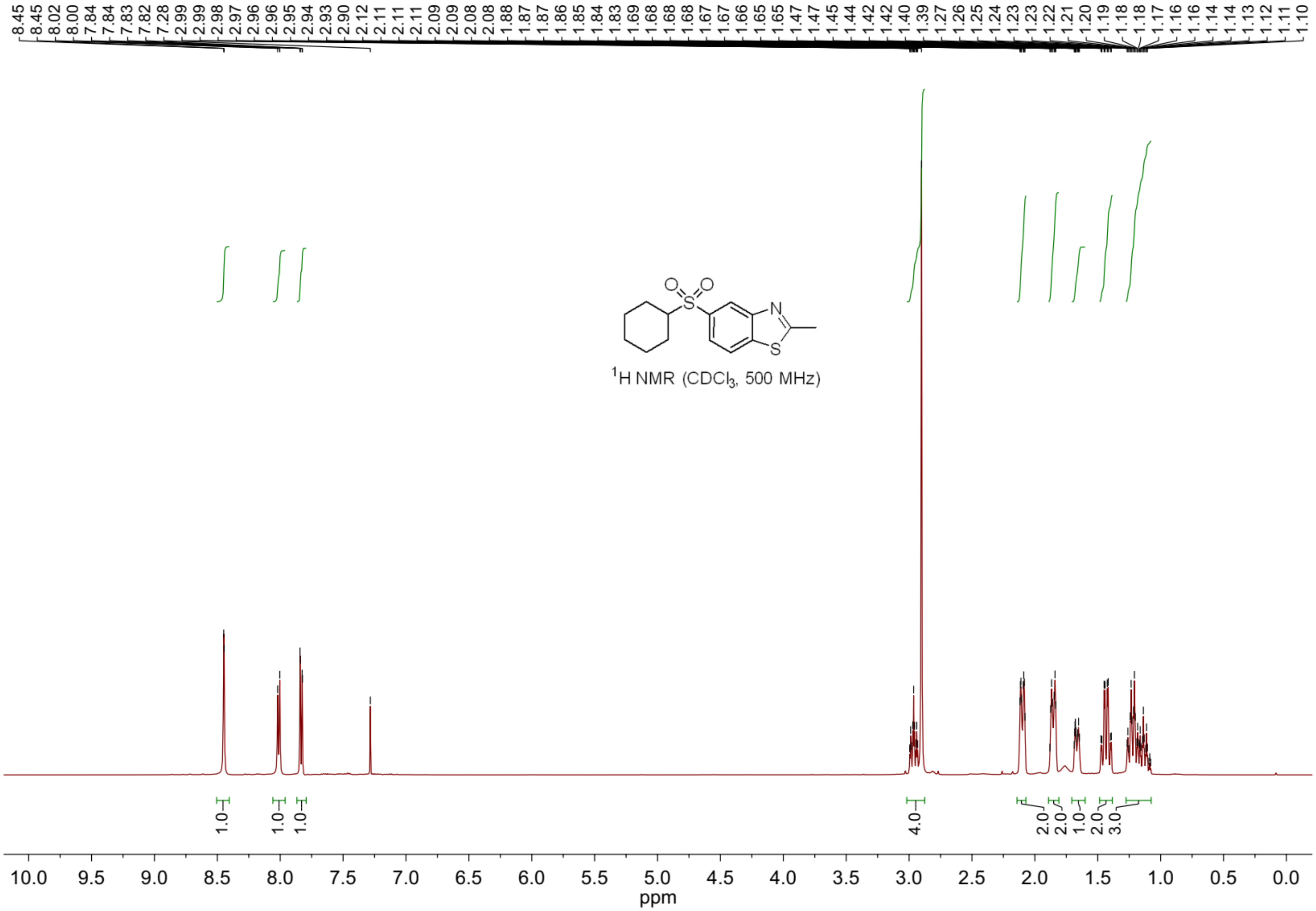
5-(Cyclohexylsulfonyl)-2-methylbenzo[*d*]thiazole (3z)



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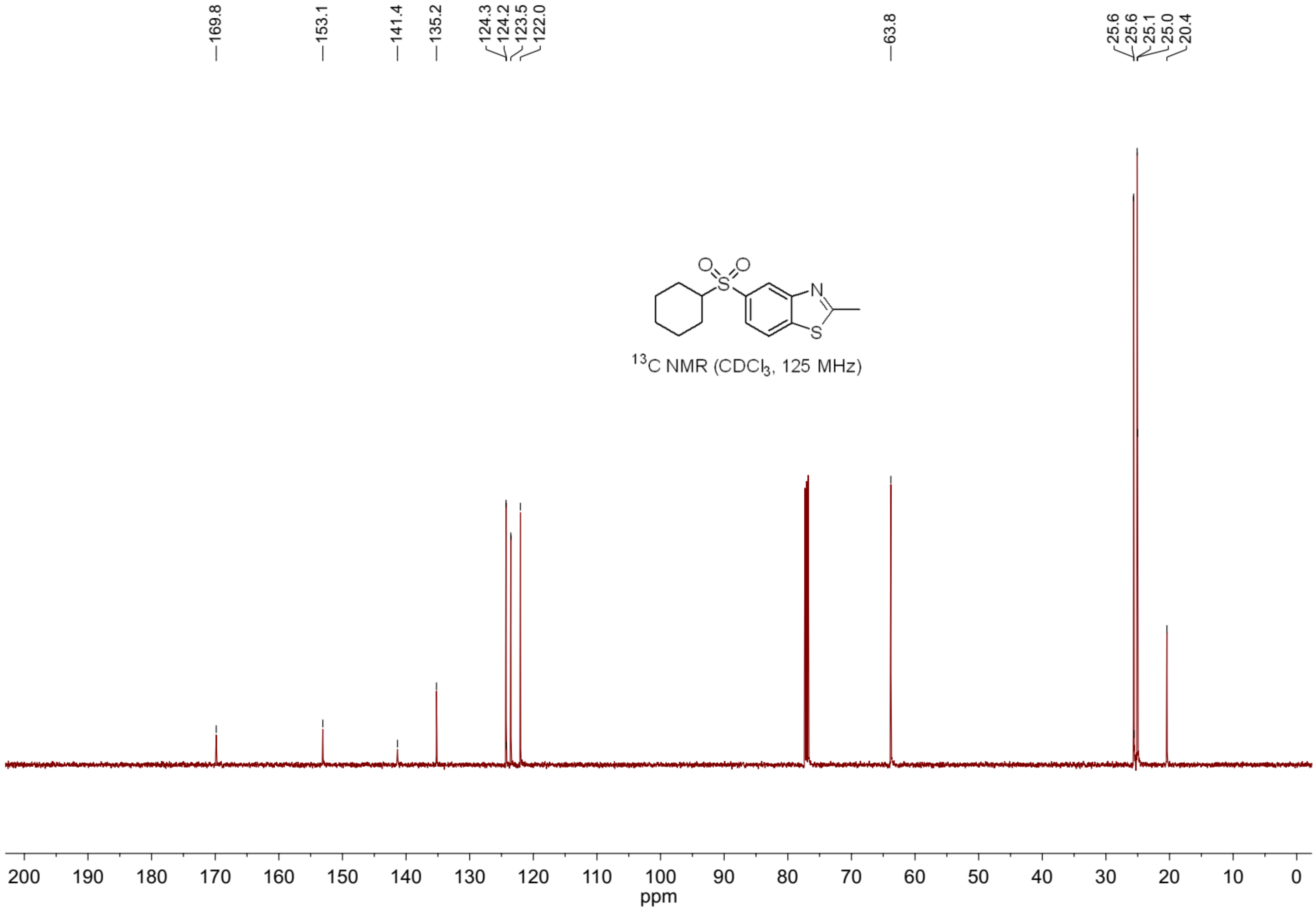
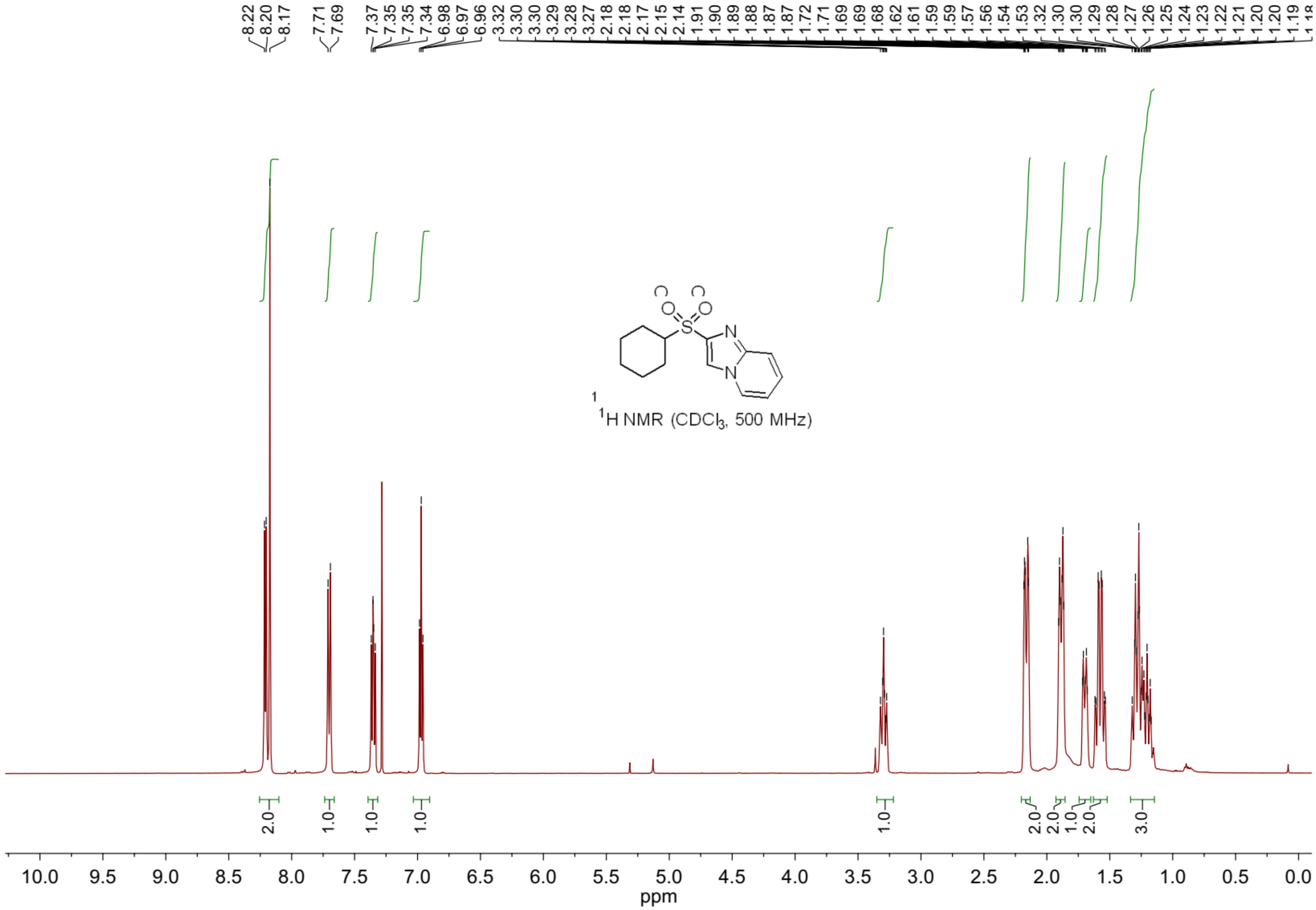
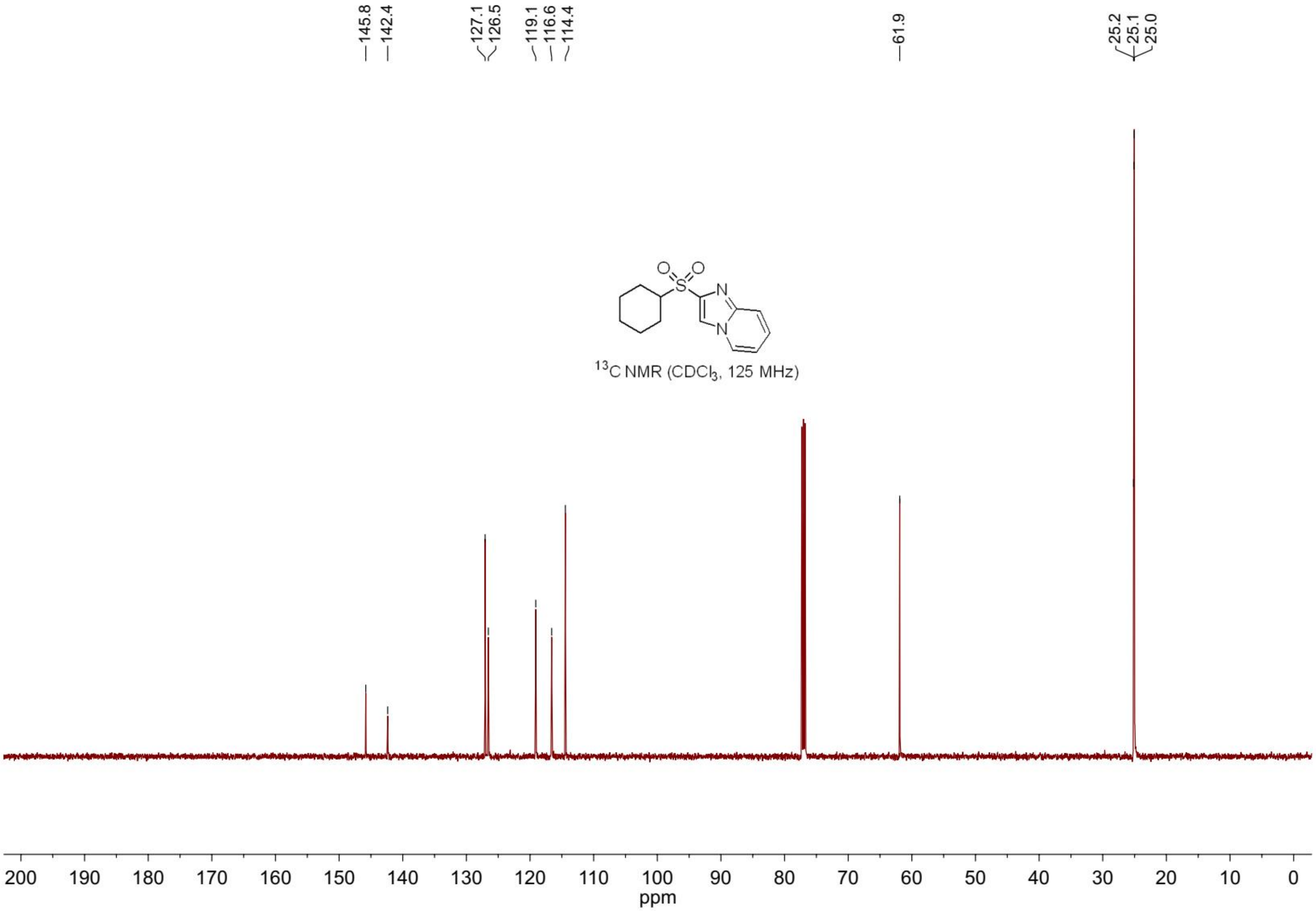
5-(Cyclohexylsulfonyl)-2-methylbenzo[*d*]thiazole (3z)



2-(Cyclohexylsulfonyl)imidazo[1,2-*a*]pyridine (3aa)



2-(Cyclohexylsulfonyl)imidazo[1,2-*a*]pyridine (3aa)



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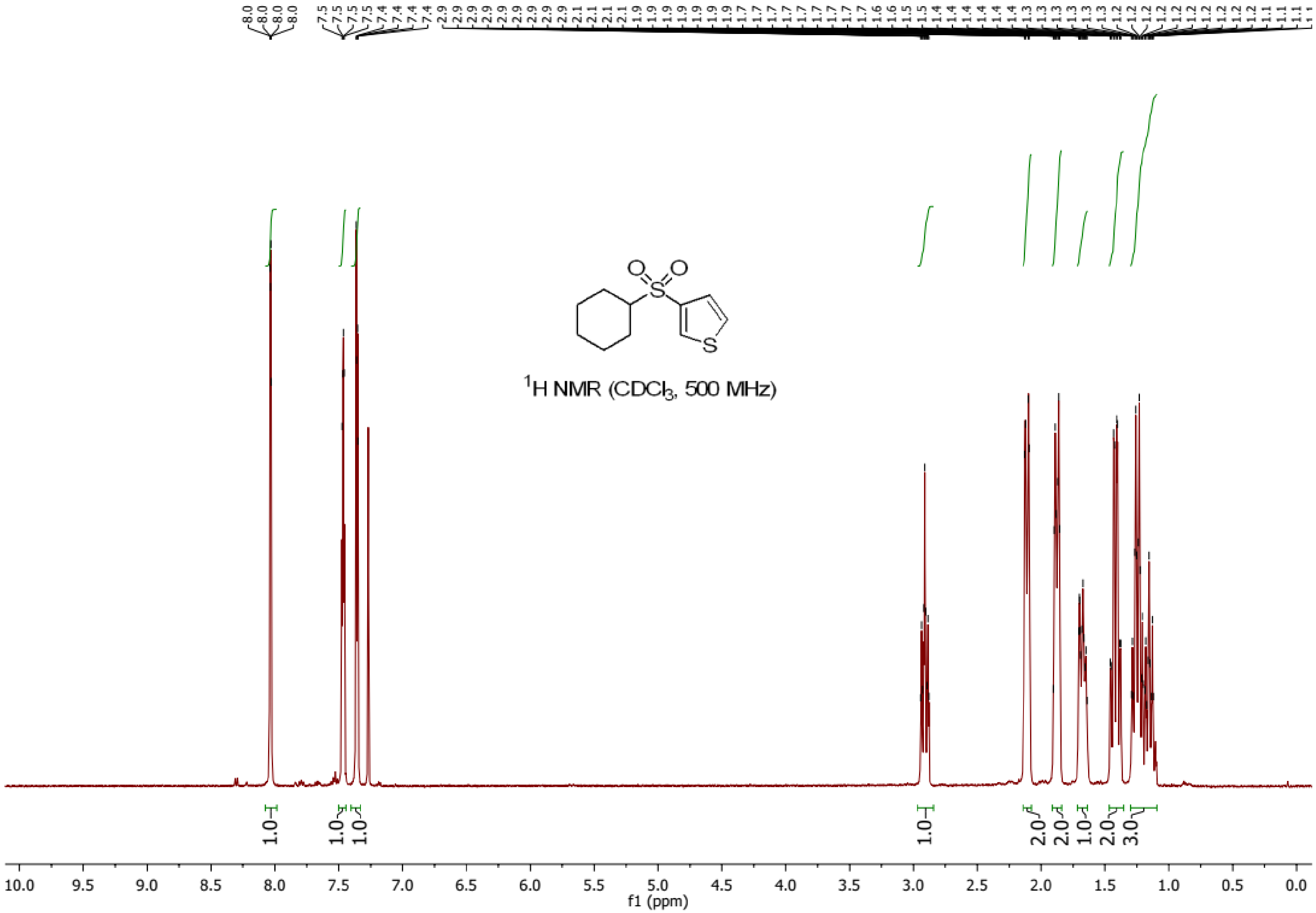
3-(Cyclohexylsulfonyl)thiophene (3ab)



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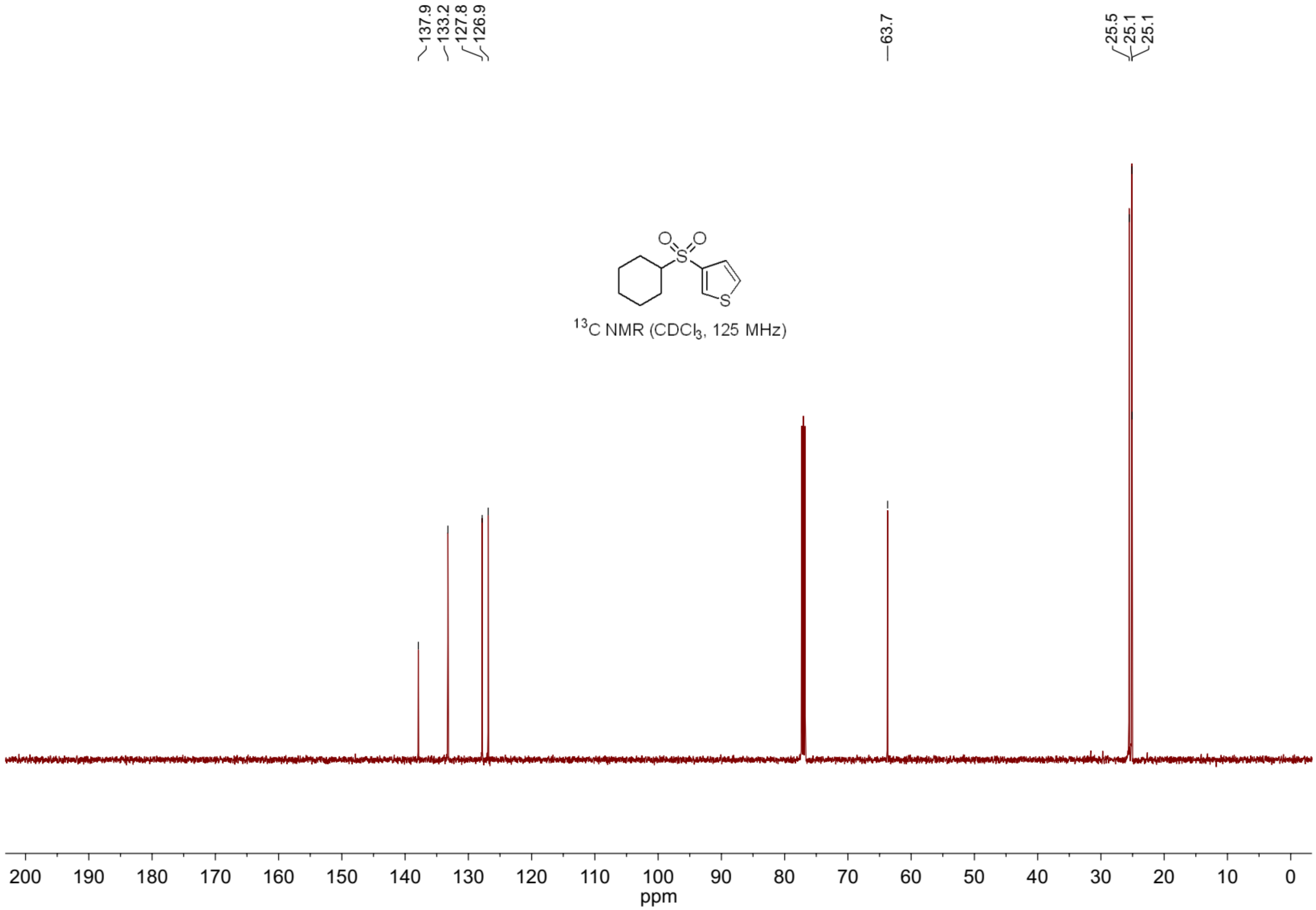
3-(Cyclohexylsulfonyl)thiophene (3ab)



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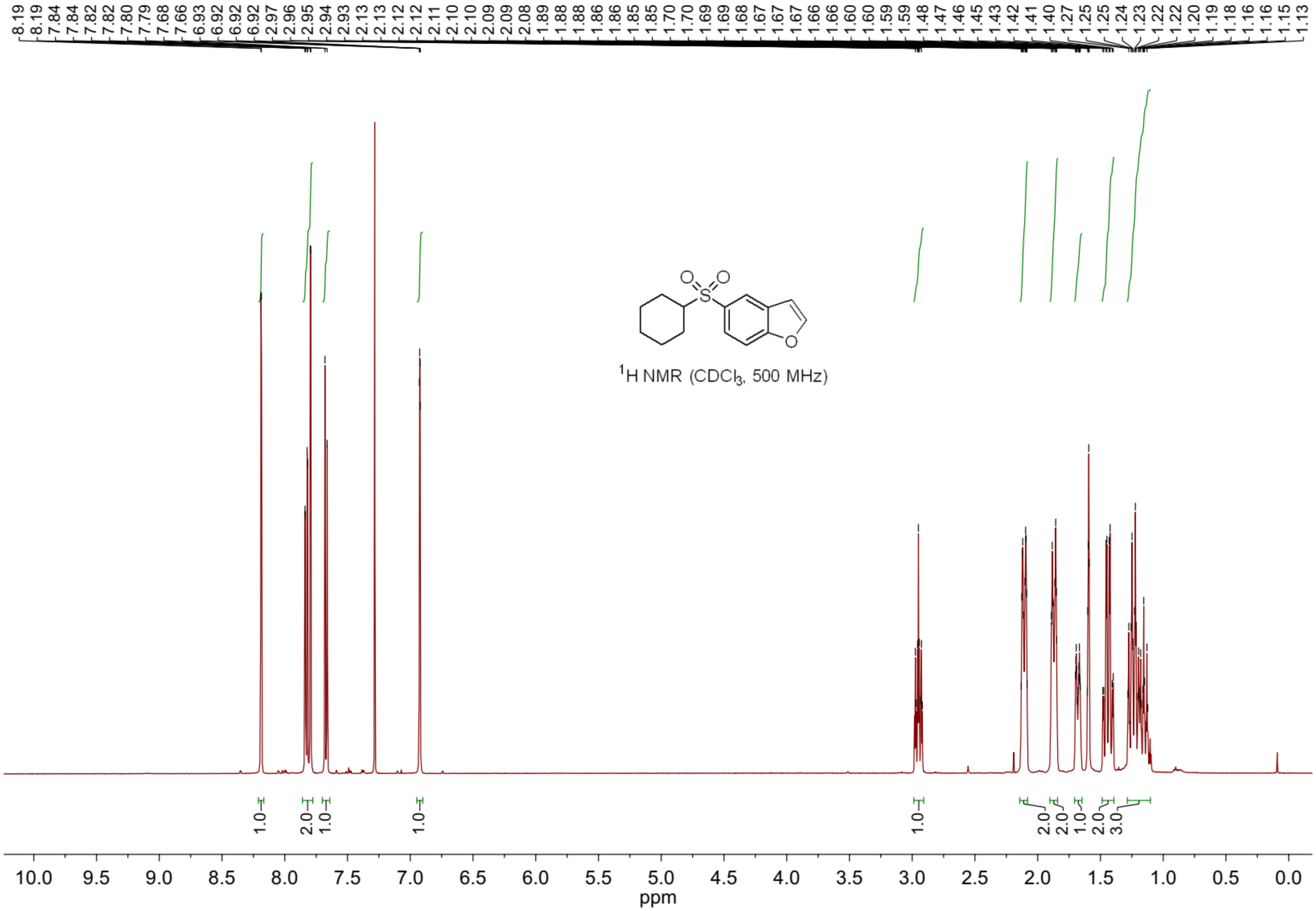
5-(Cyclohexylsulfonyl)benzofuran (3ac)



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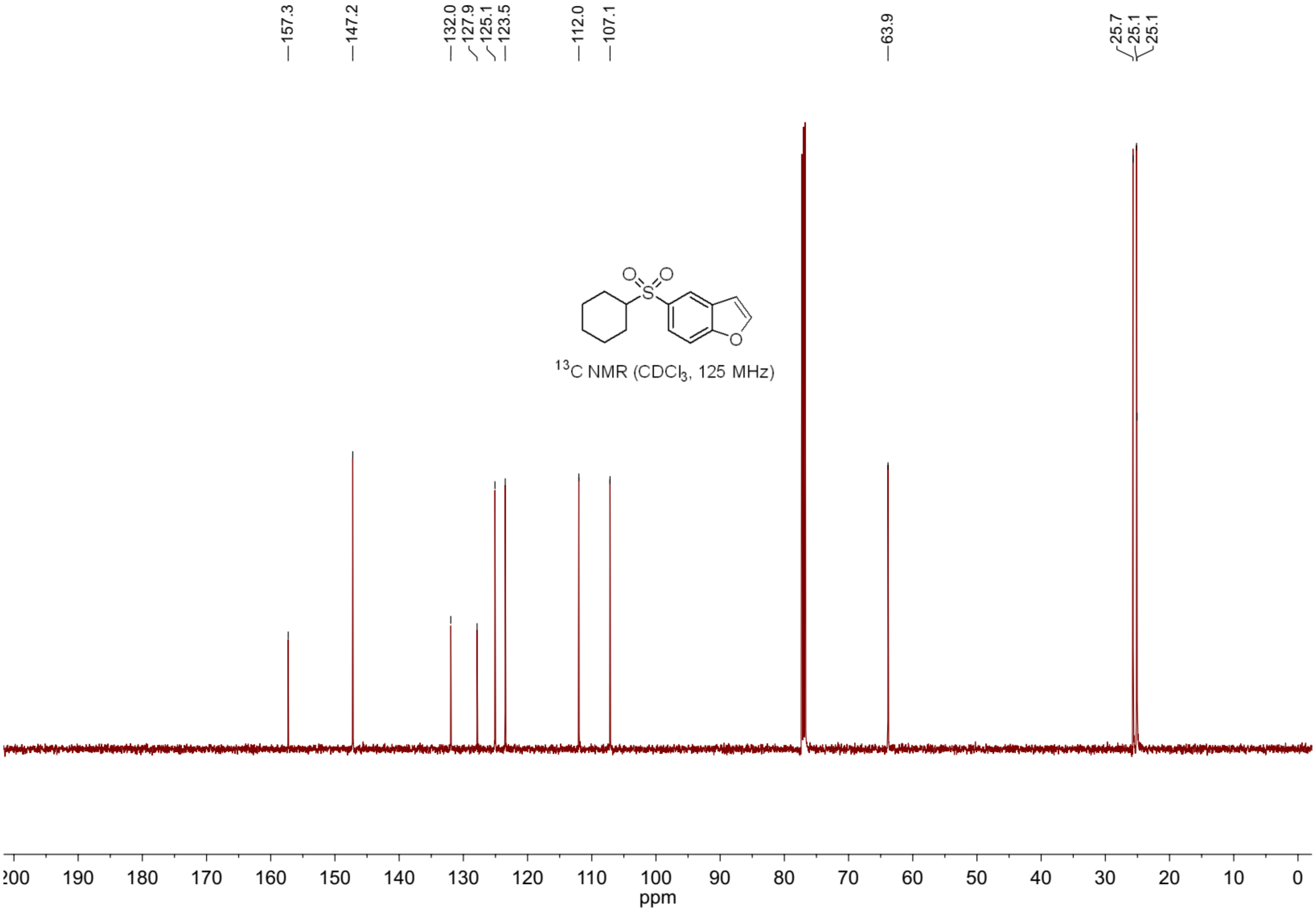
5-(Cyclohexylsulfonyl)benzofuran (3ac)



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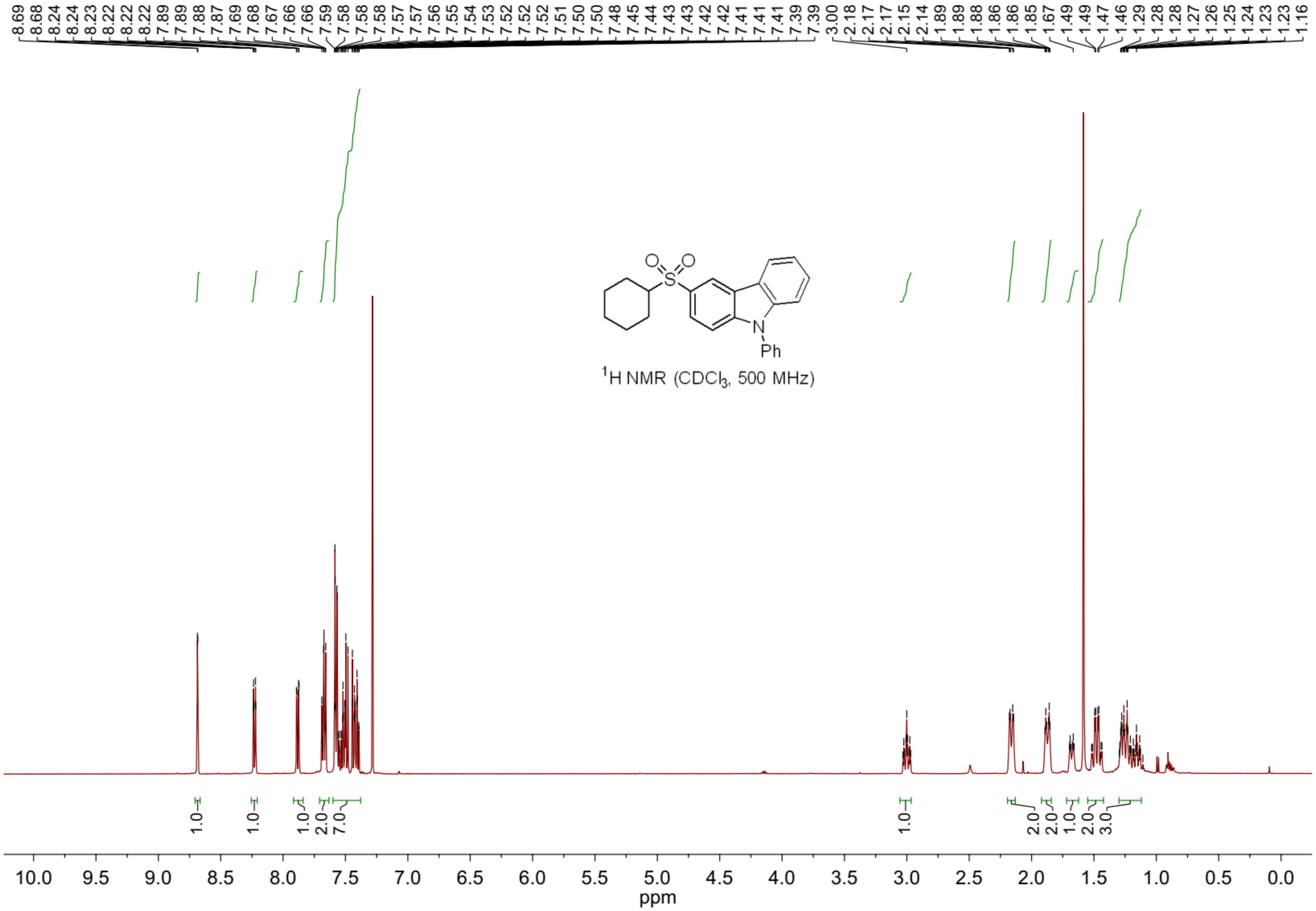
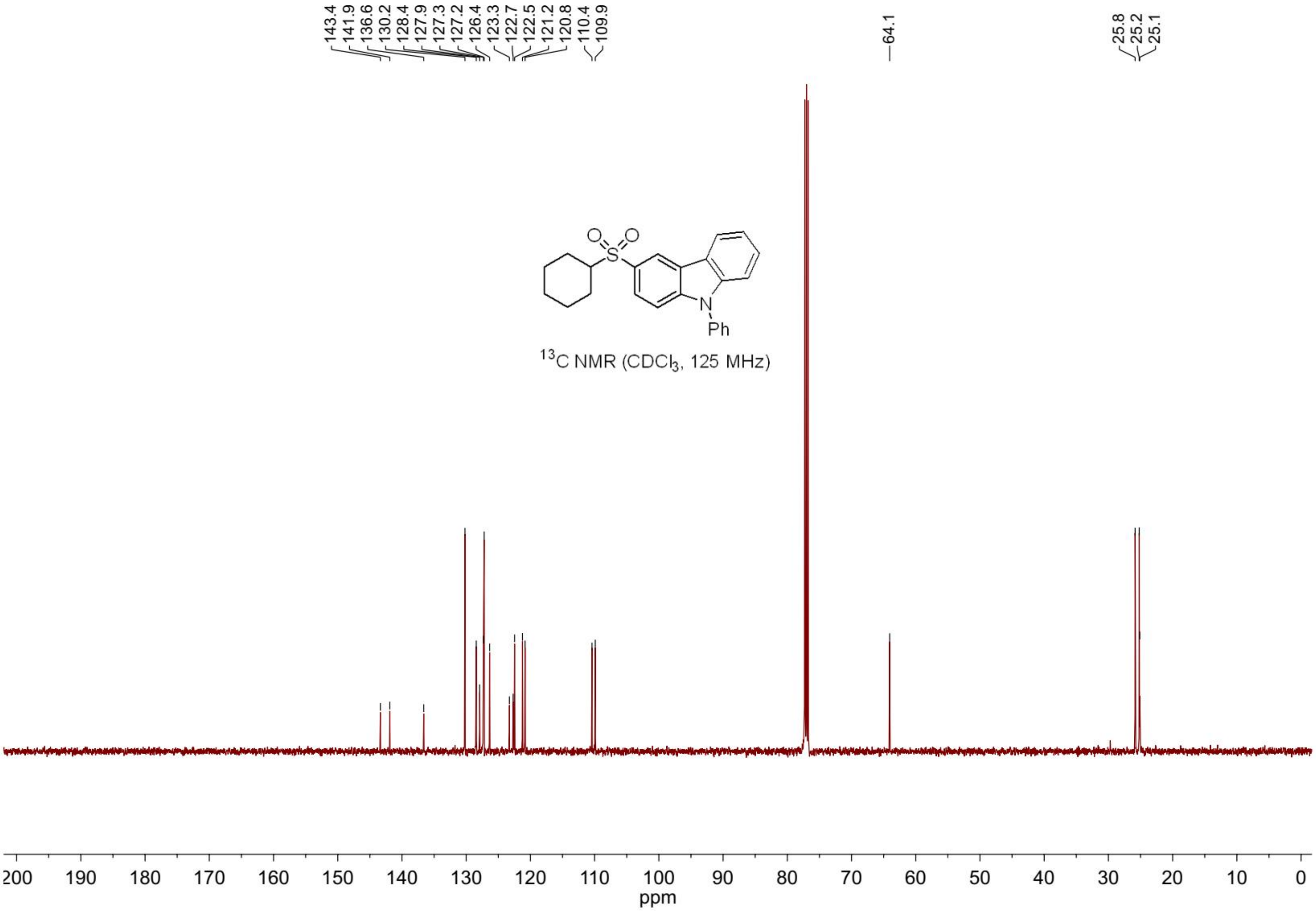
3-(Cyclohexylsulfonyl)-9-phenyl-9*H*-carbazole (3ad)



3-(Cyclohexylsulfonyl)-9-phenyl-9*H*-carbazole (3ad)



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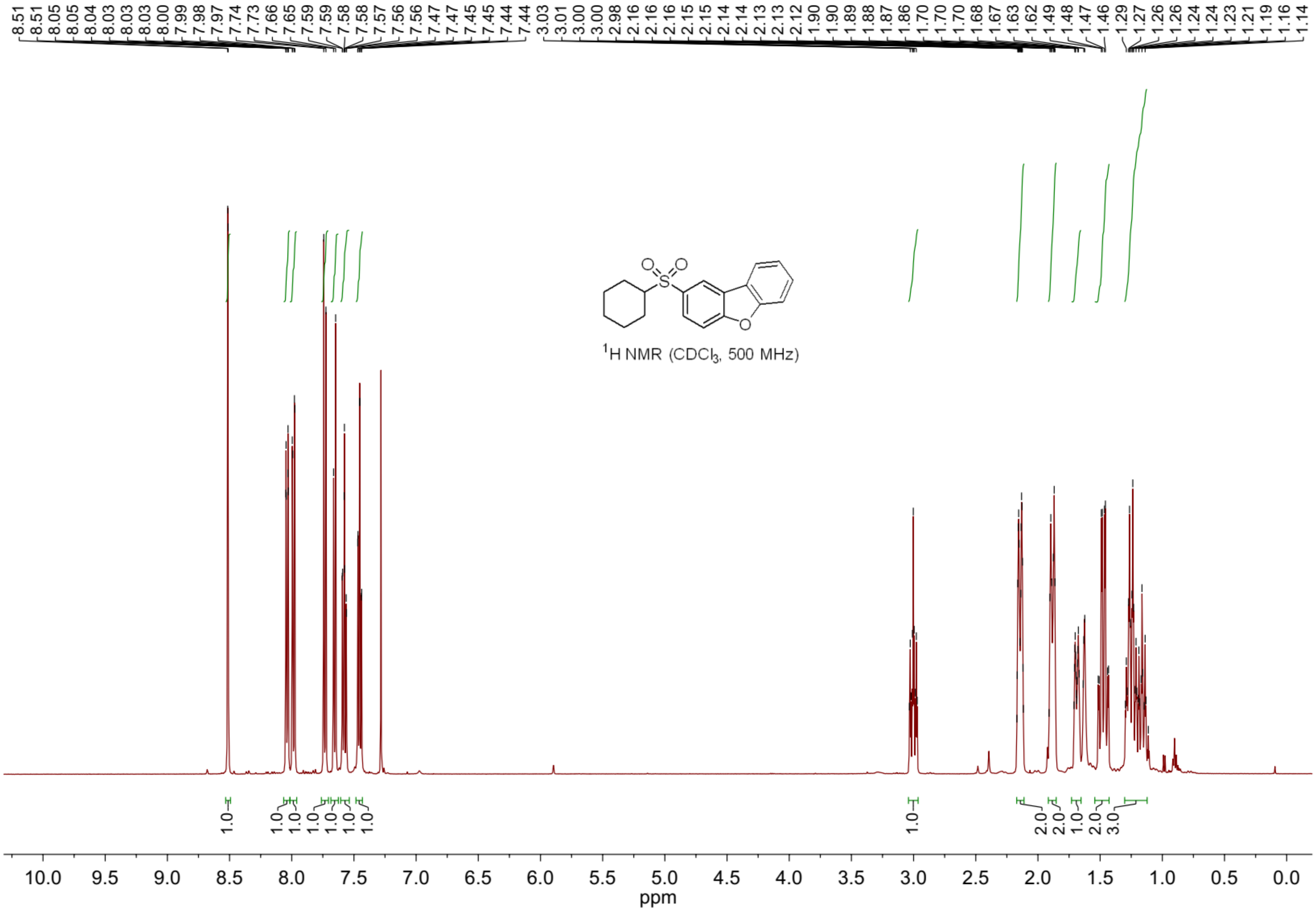
2-(Cyclohexylsulfonyl)dibenzo[*b*,*d*]furan (3ae)



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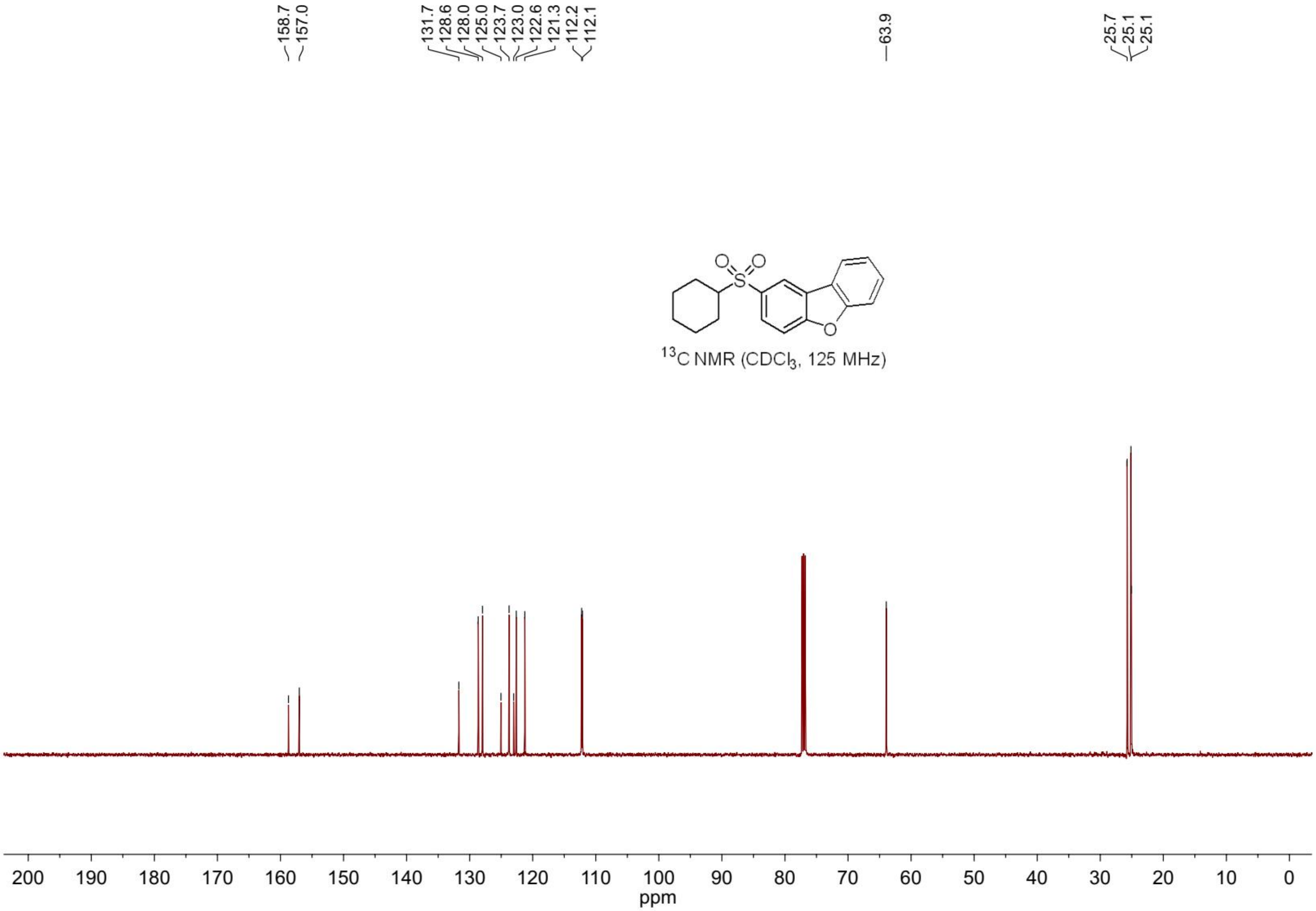
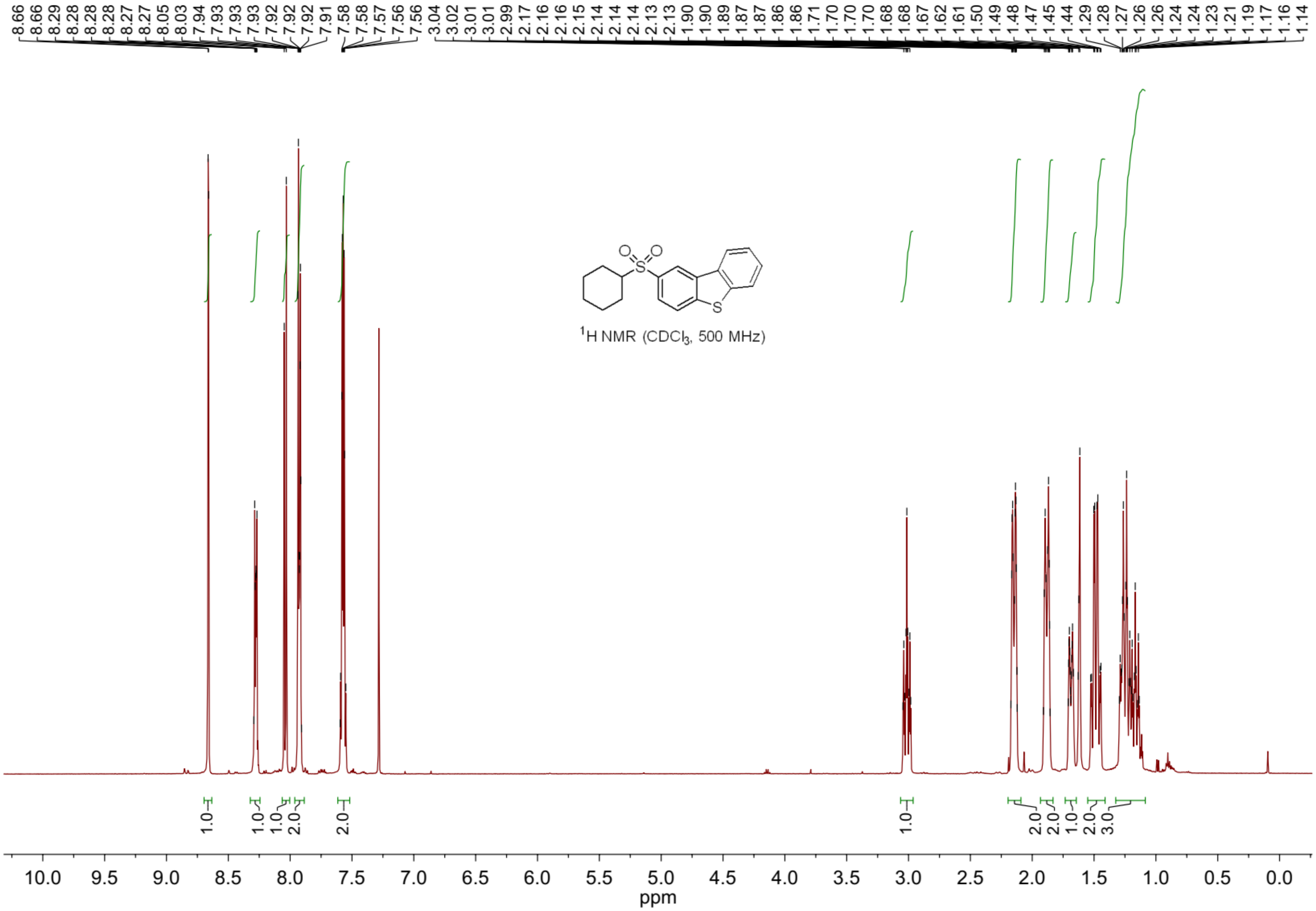
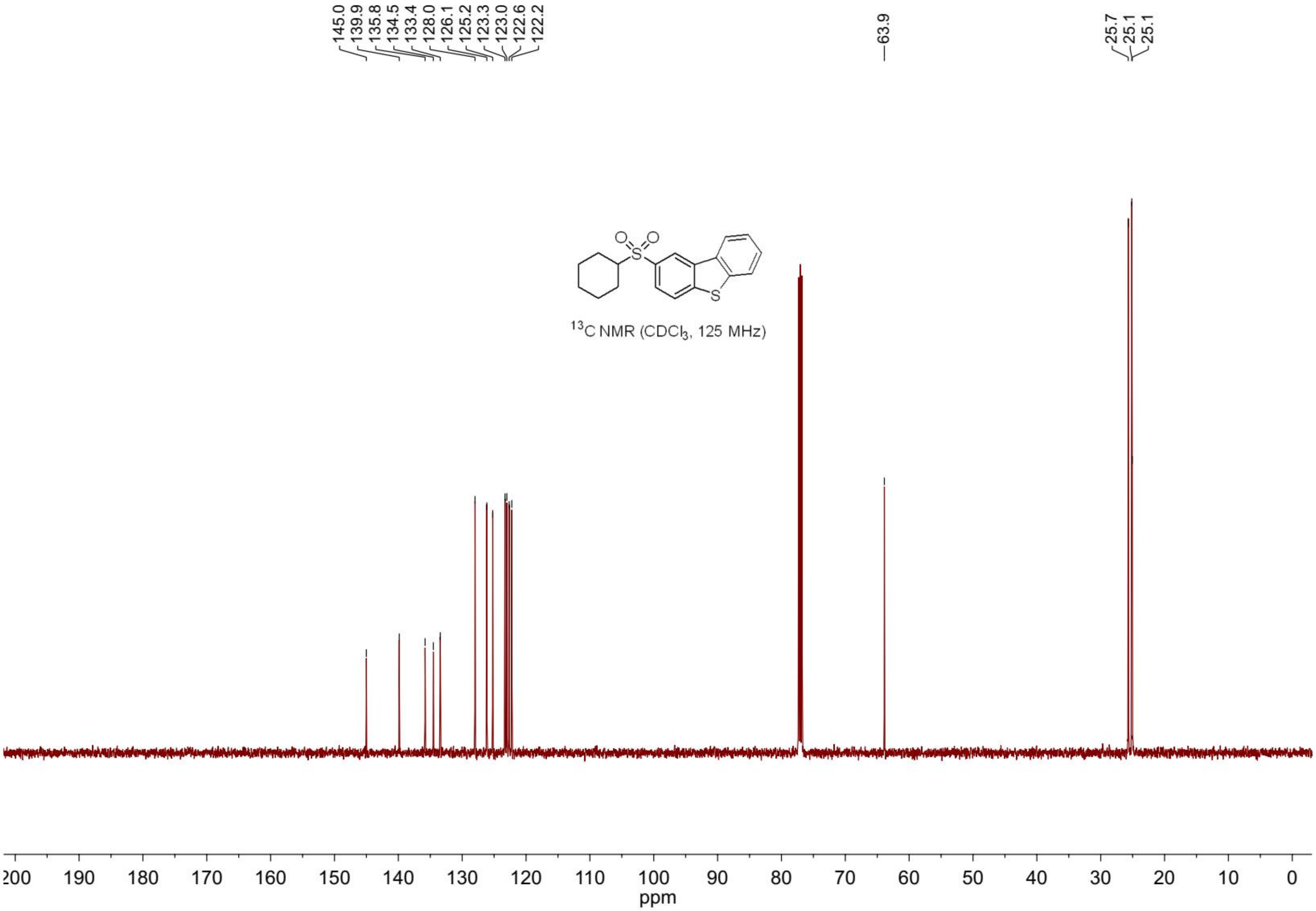
2-(Cyclohexylsulfonyl)dibenzo[*b*,*d*]furan (3ae)



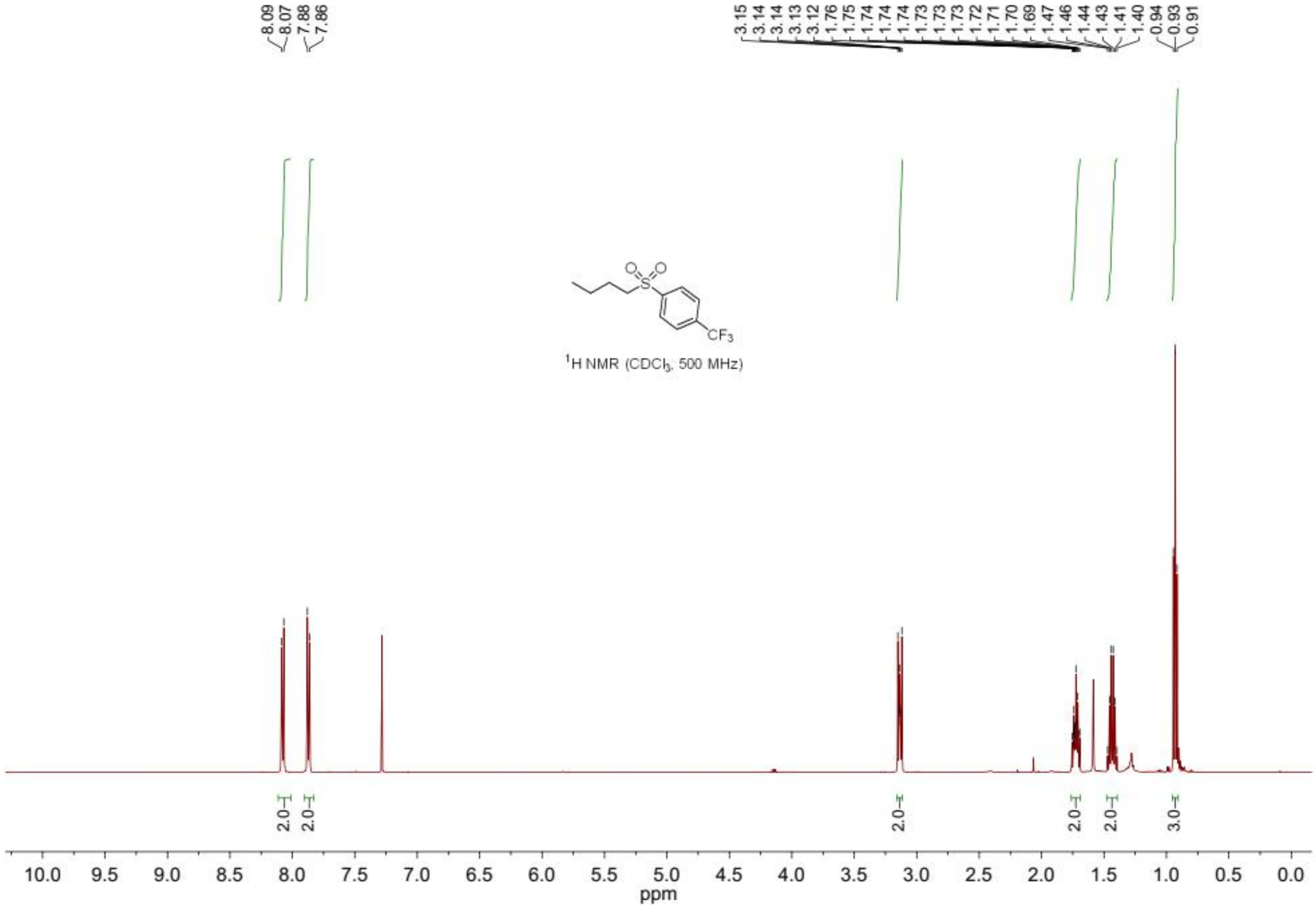
2-(Cyclohexylsulfonyl)dibenzo[*b*,*d*]thiophene (3af)



2-(Cyclohexylsulfonyl)dibenzo[*b*,*d*]thiophene (3af)



1-(Butylsulfonyl)-4-(trifluoromethyl)benzene (4a)



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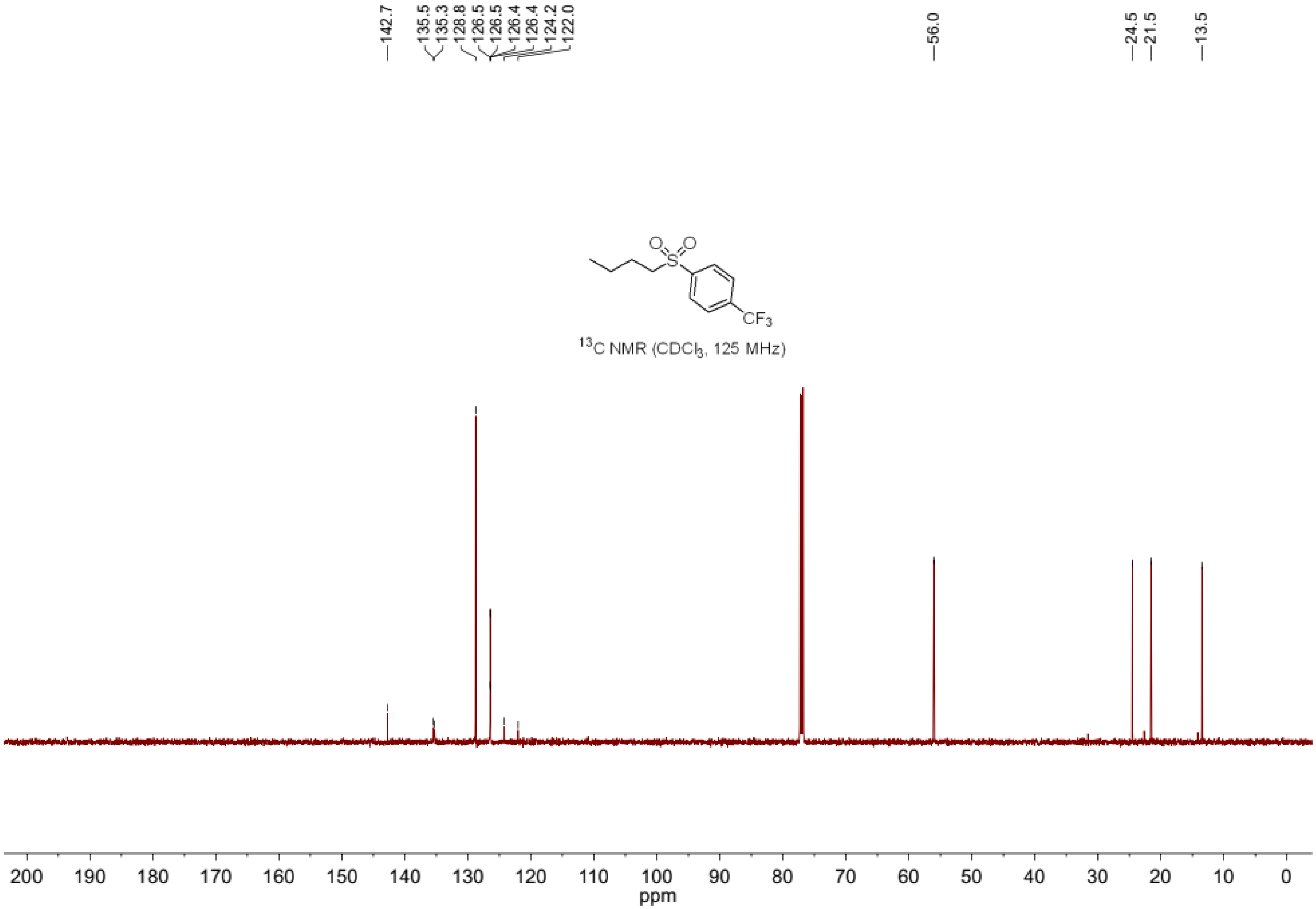
1-(Butylsulfonyl)-4-(trifluoromethyl)benzene (4a)



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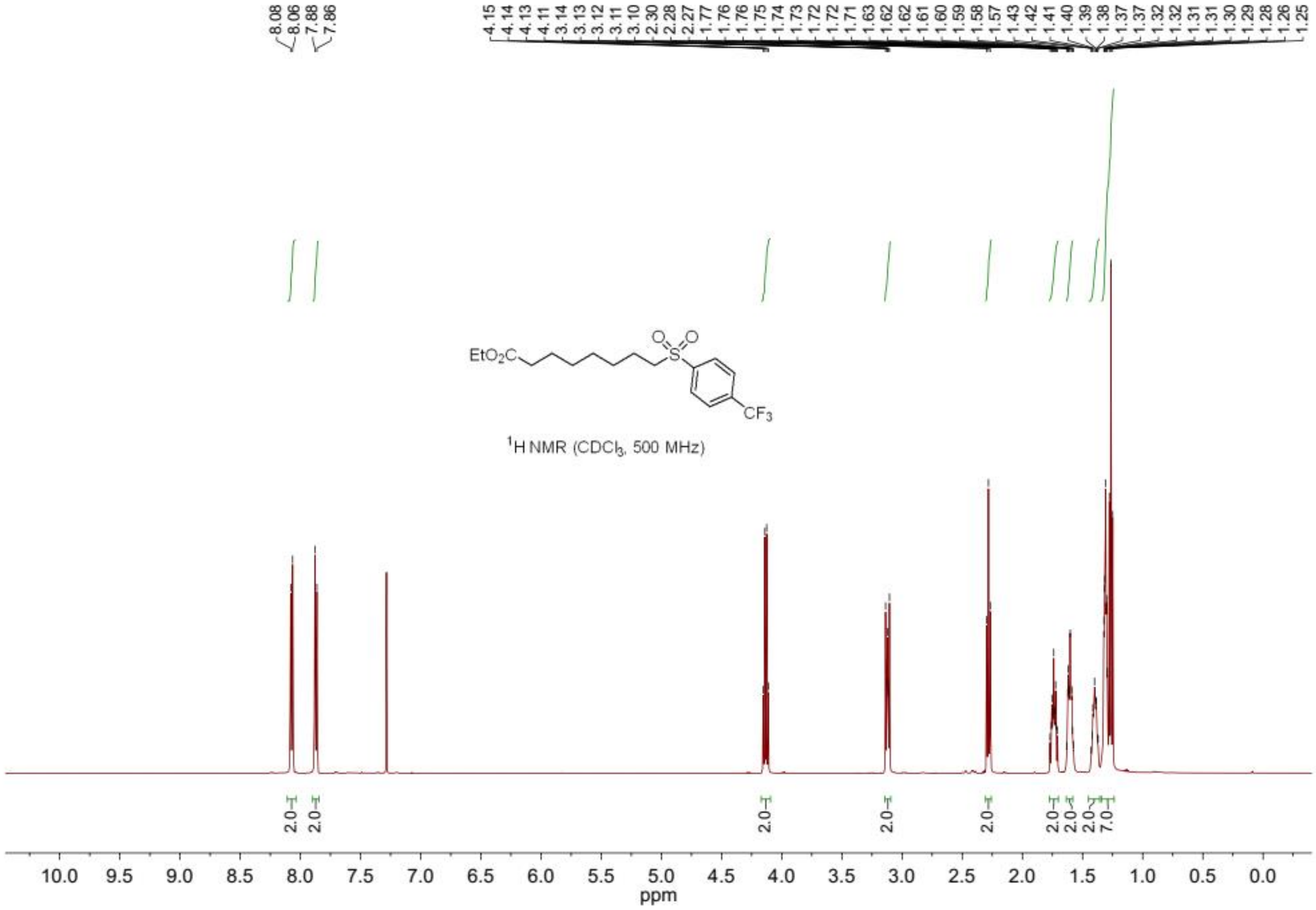
Ethyl 8-((4-(trifluoromethyl)phenyl)sulfonyl)octanoate (4b)



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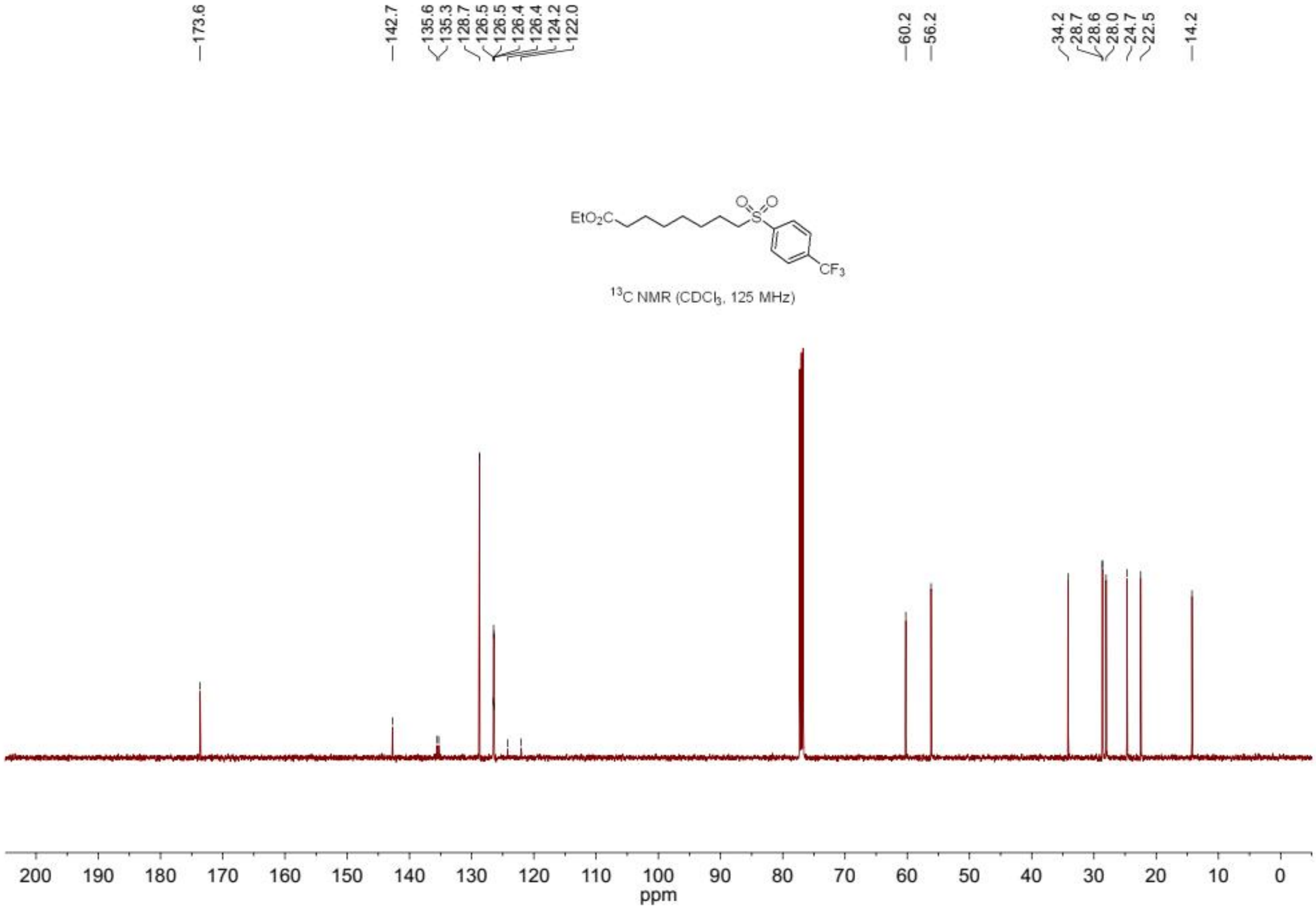
Ethyl 8-((4-(trifluoromethyl)phenyl)sulfonyl)octanoate (4b)



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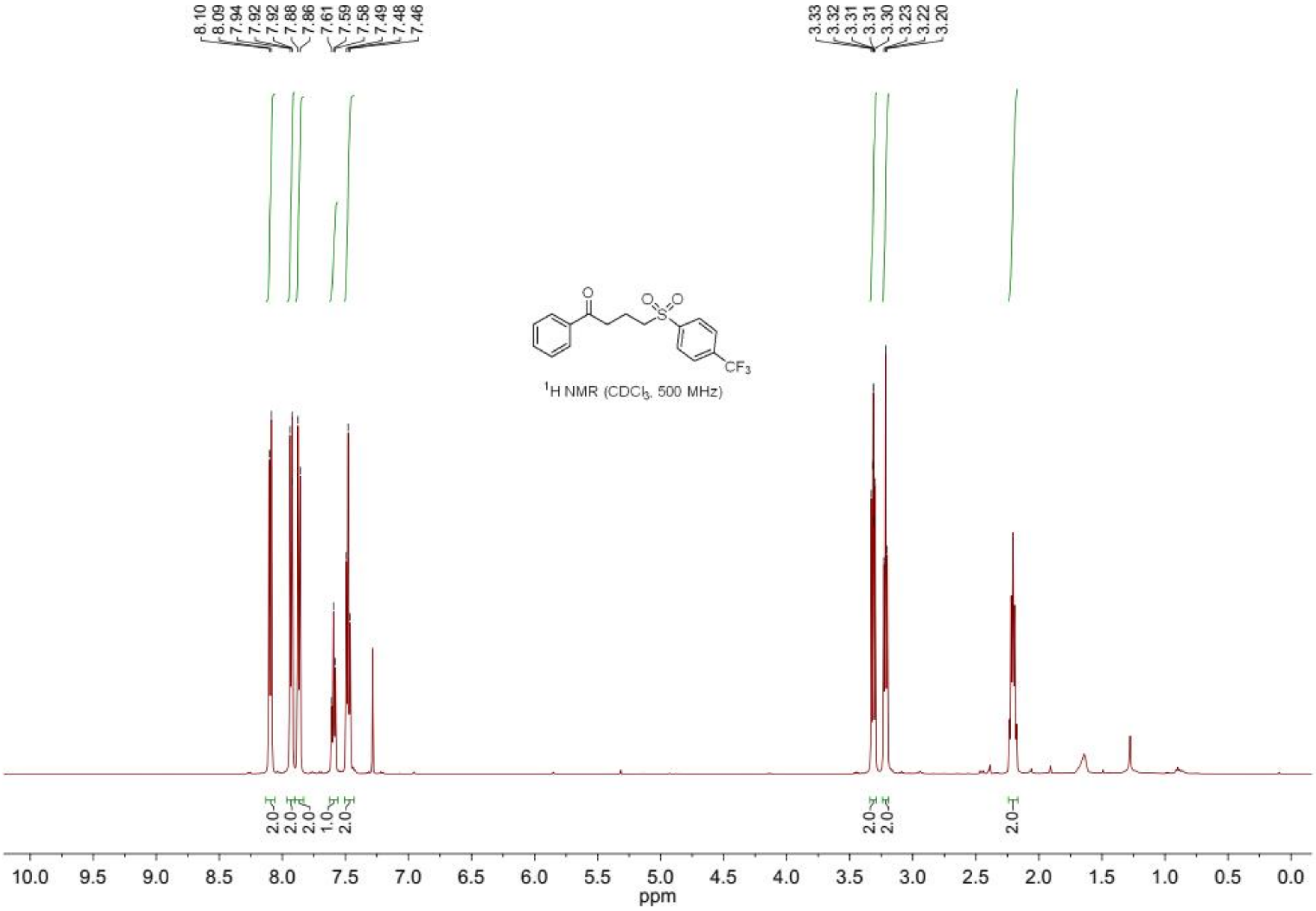
1-Phenyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-1-one (4c)



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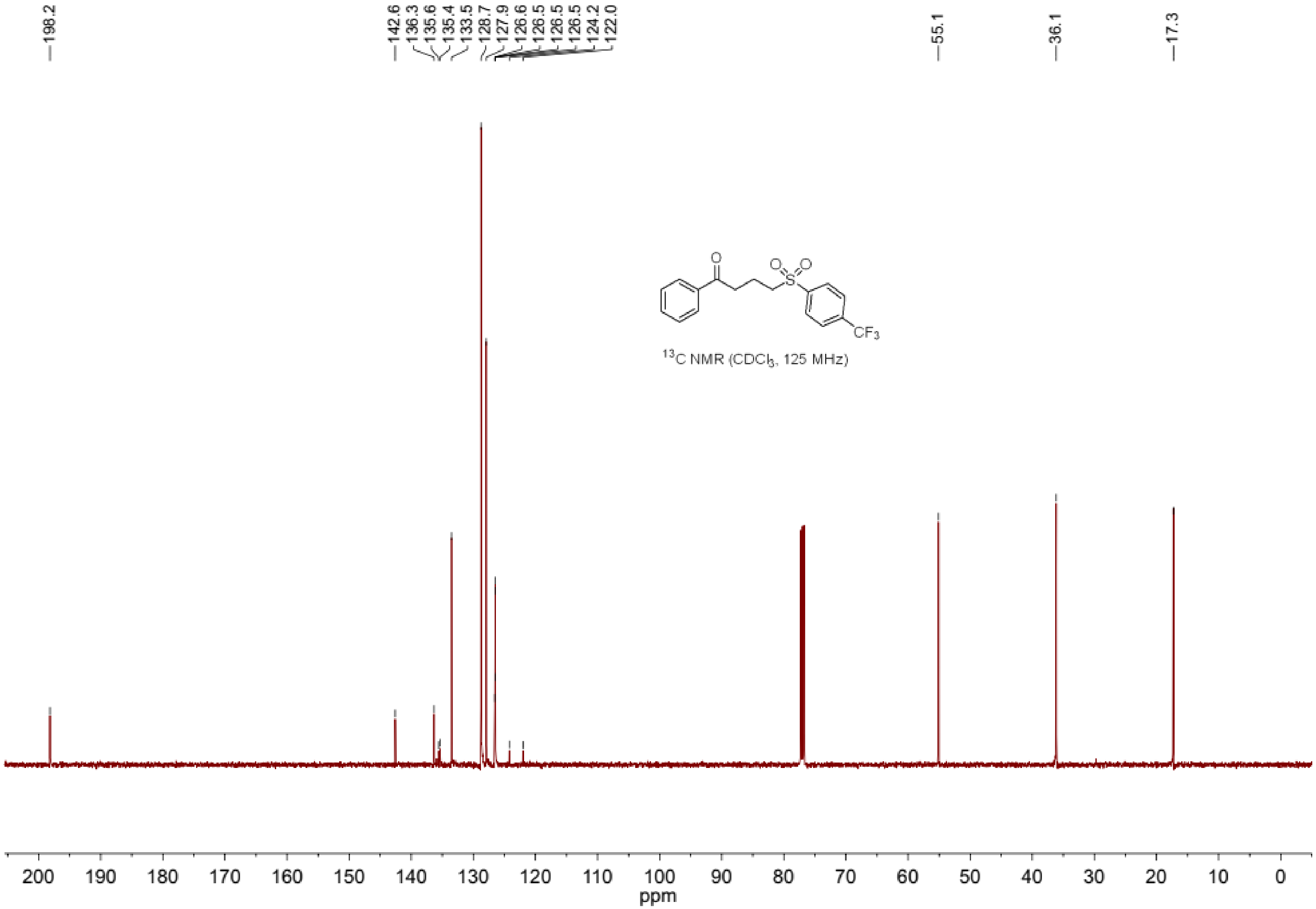
1-Phenyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-1-one (4c)



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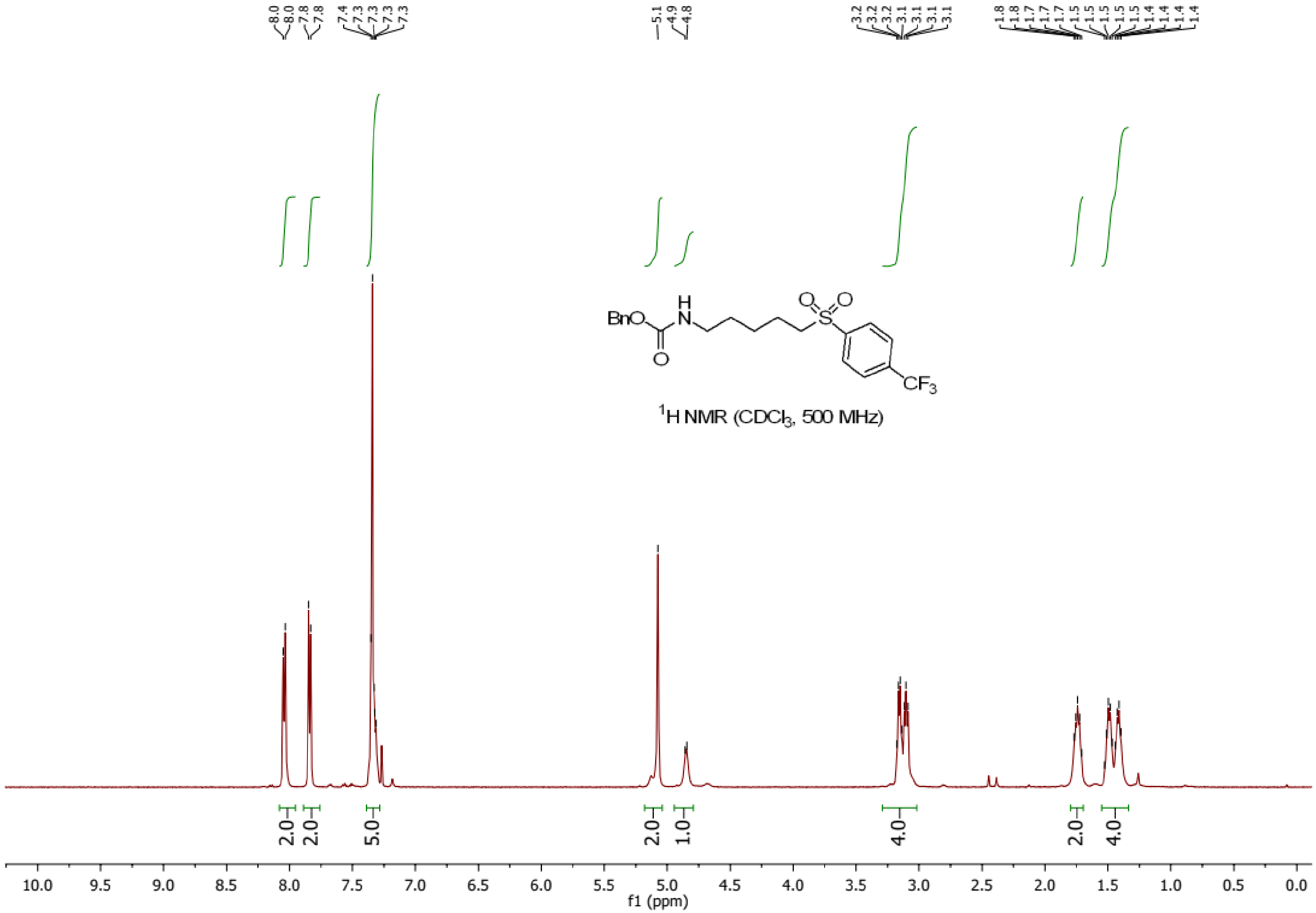
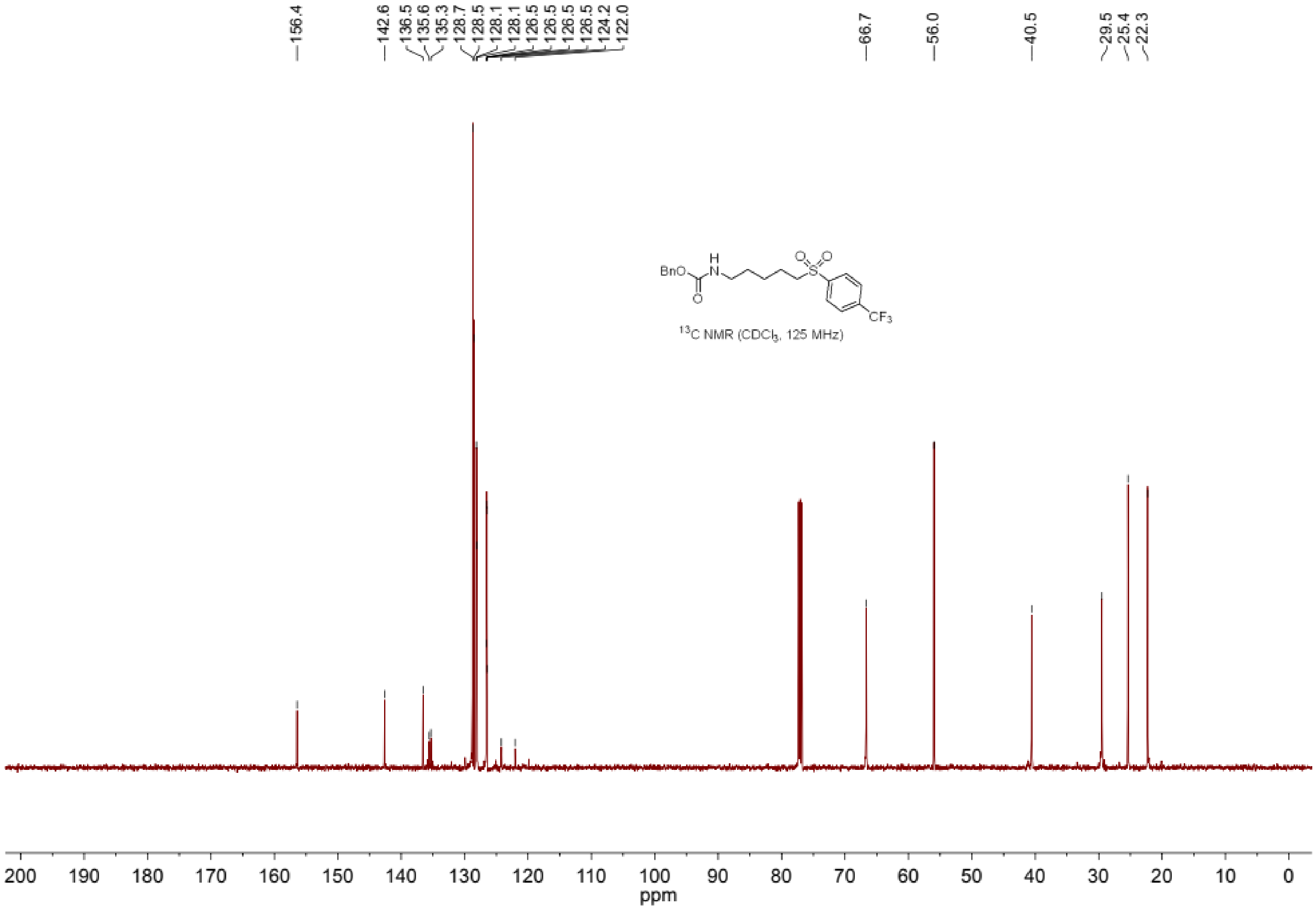
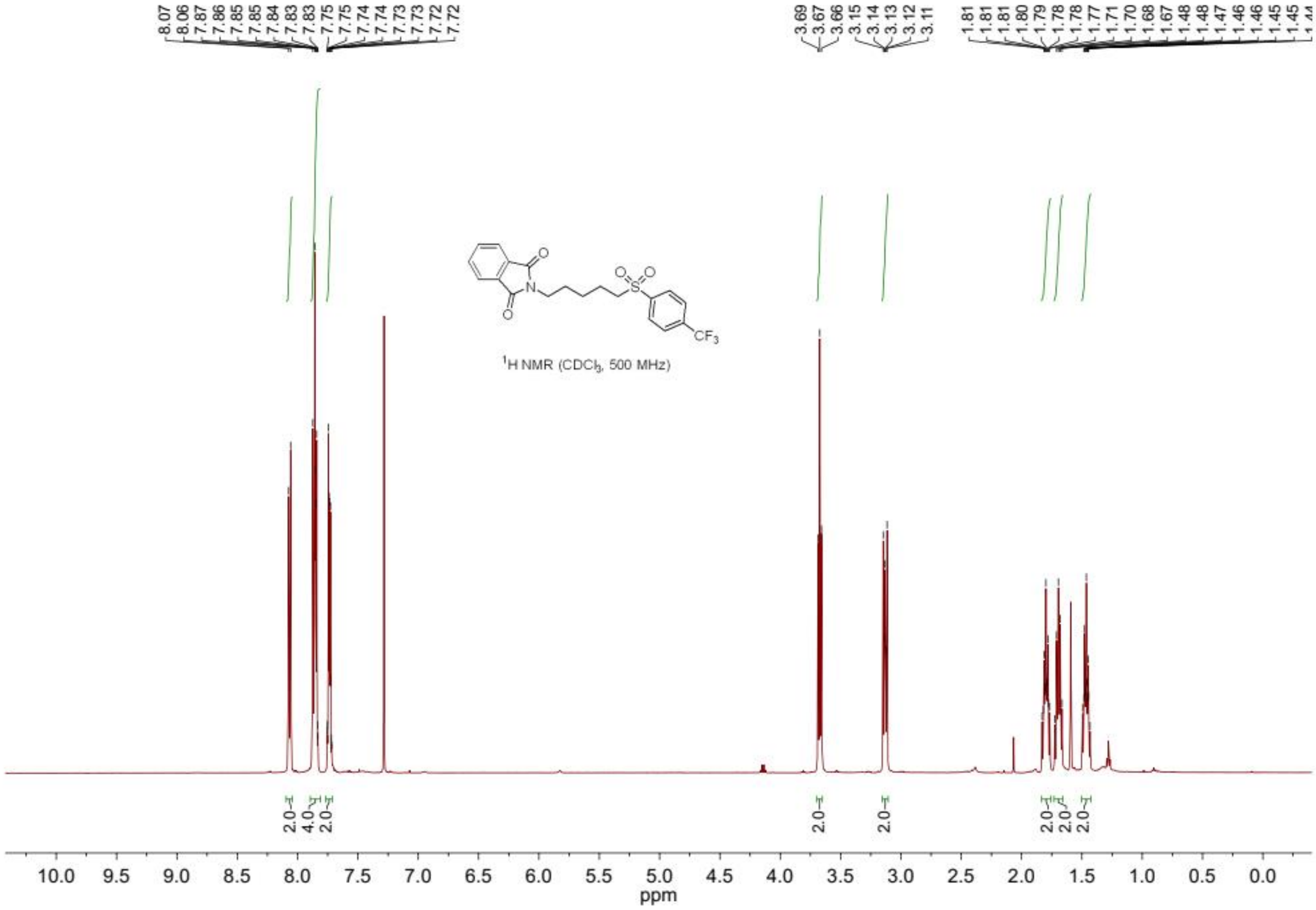
Benzyl (5-((4-(trifluoromethyl)phenyl)sulfonyl)pentyl)carbamate (4d)



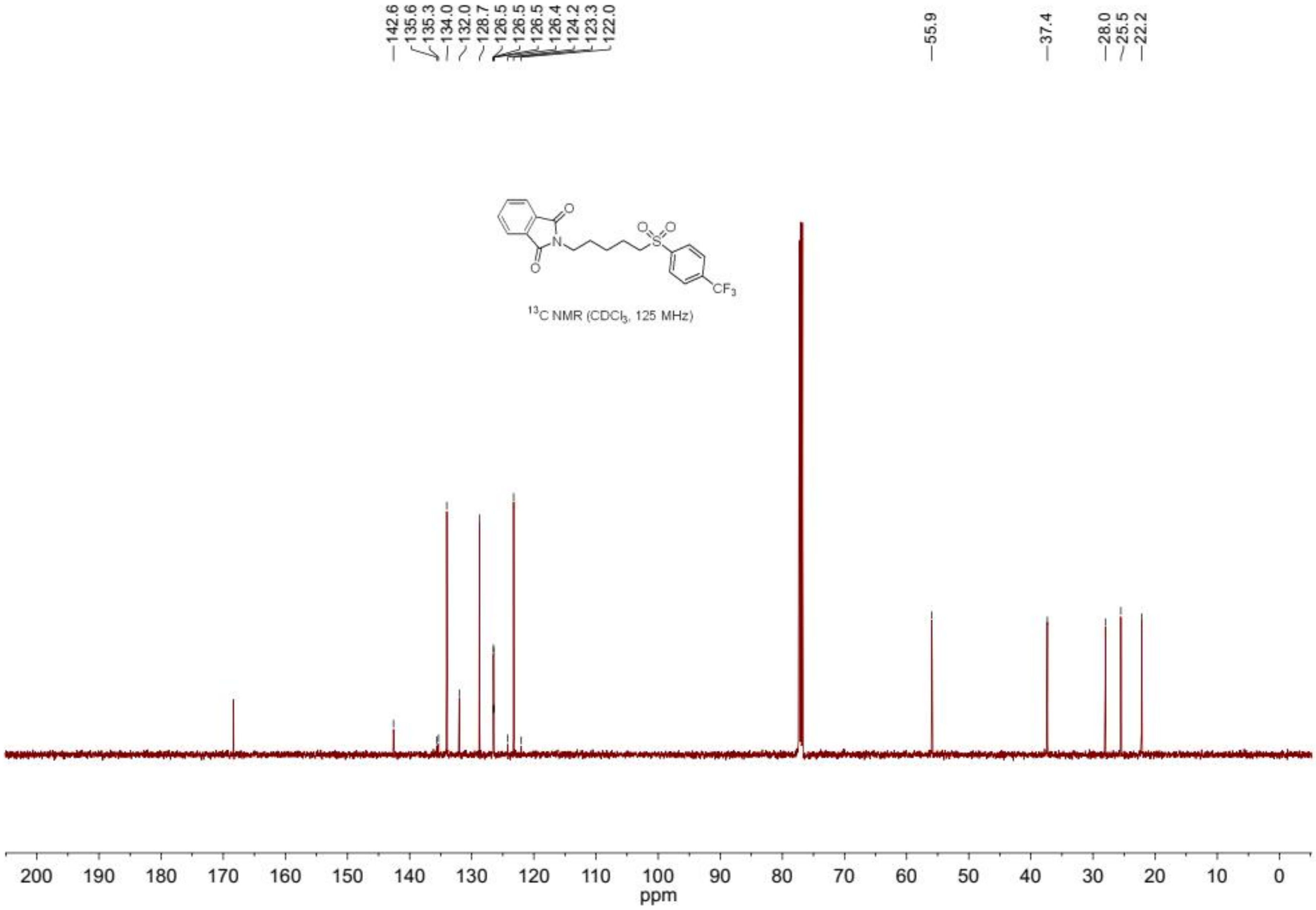
Benzyl (5-((4-(trifluoromethyl)phenyl)sulfonyl)pentyl)carbamate (4d)



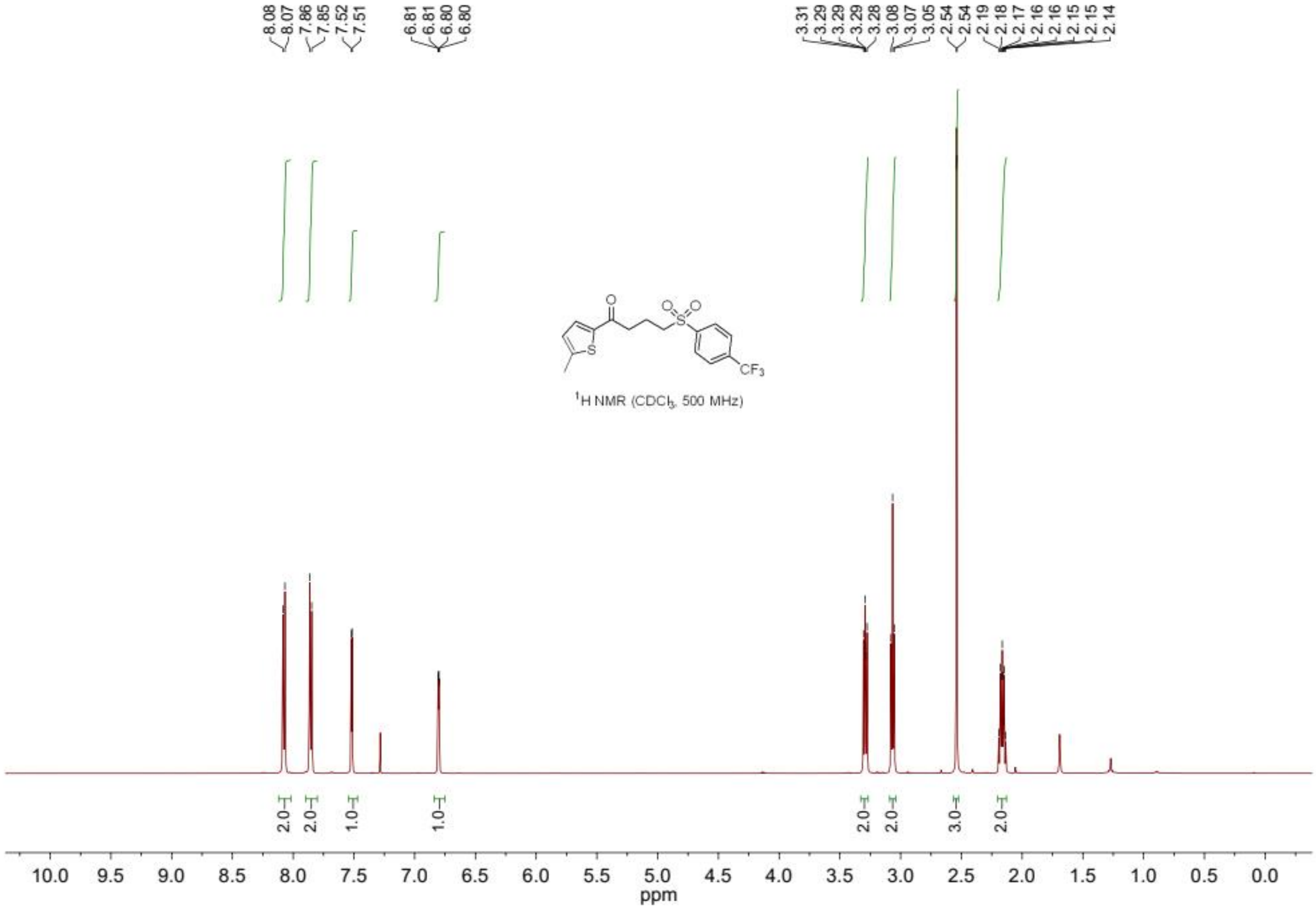
2-(5-((4-(trifluoromethyl)phenyl)sulfonyl)pentyl)isoindoline-1,3-dione (4e)



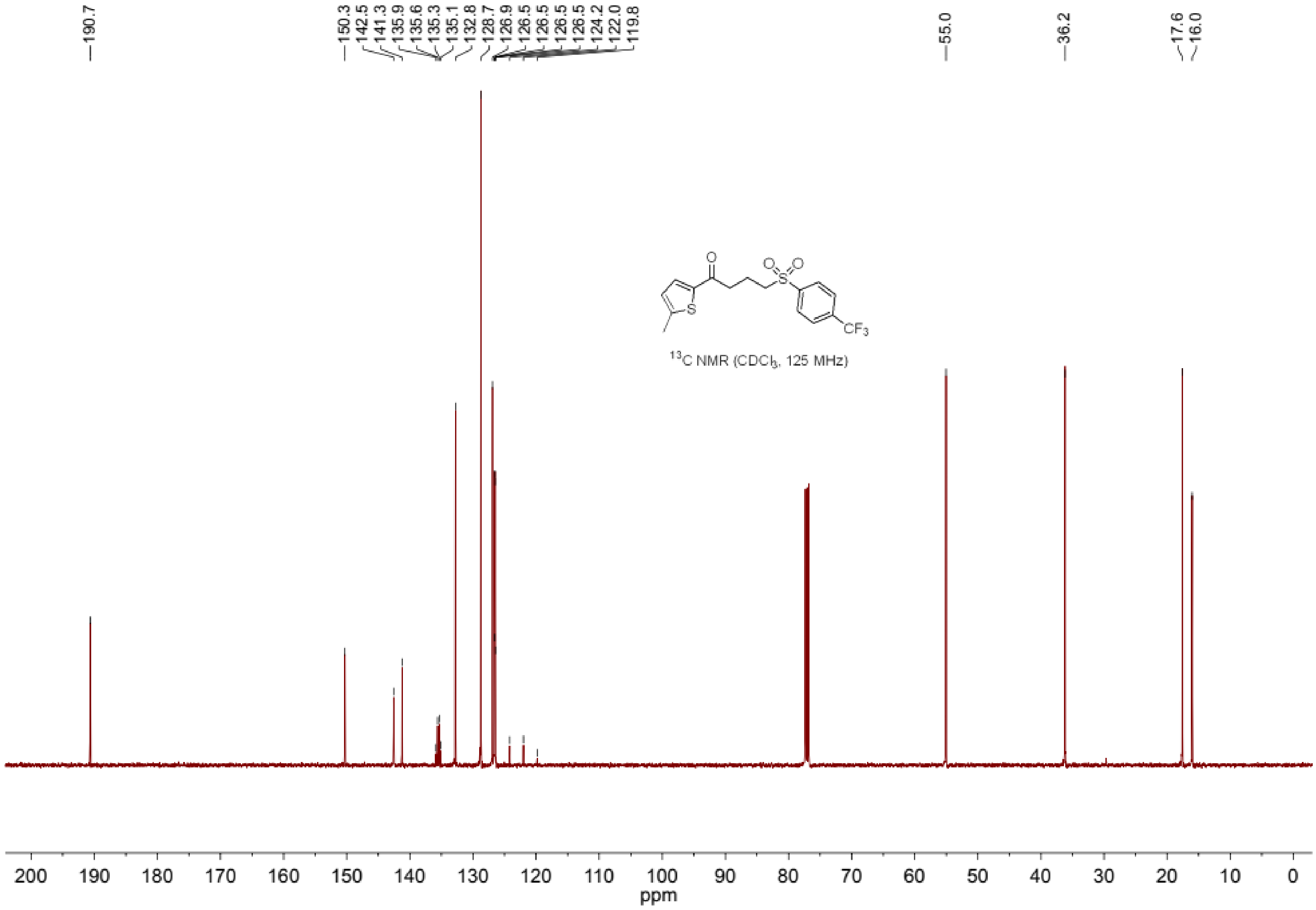
2-(5-((4-(trifluoromethyl)phenyl)sulfonyl)pentyl)isoindoline-1,3-dione (4e)



1-(5-Methylthiophen-2-yl)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-1-one (4f)



1-(5-Methylthiophen-2-yl)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-1-one (4f)



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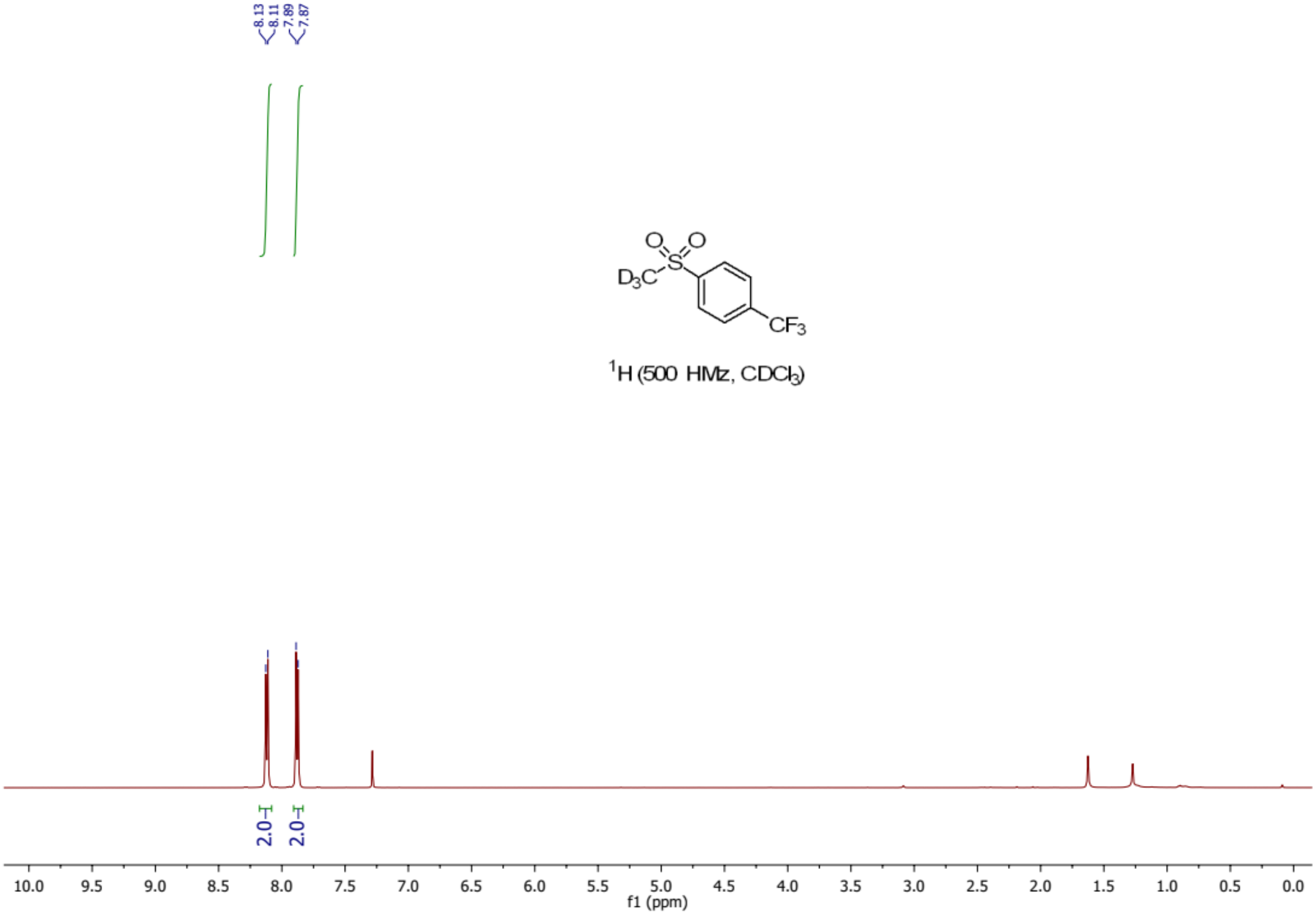
1-((Methyl-d_3)sulfonyl)-4-(trifluoromethyl)benzene (4g)



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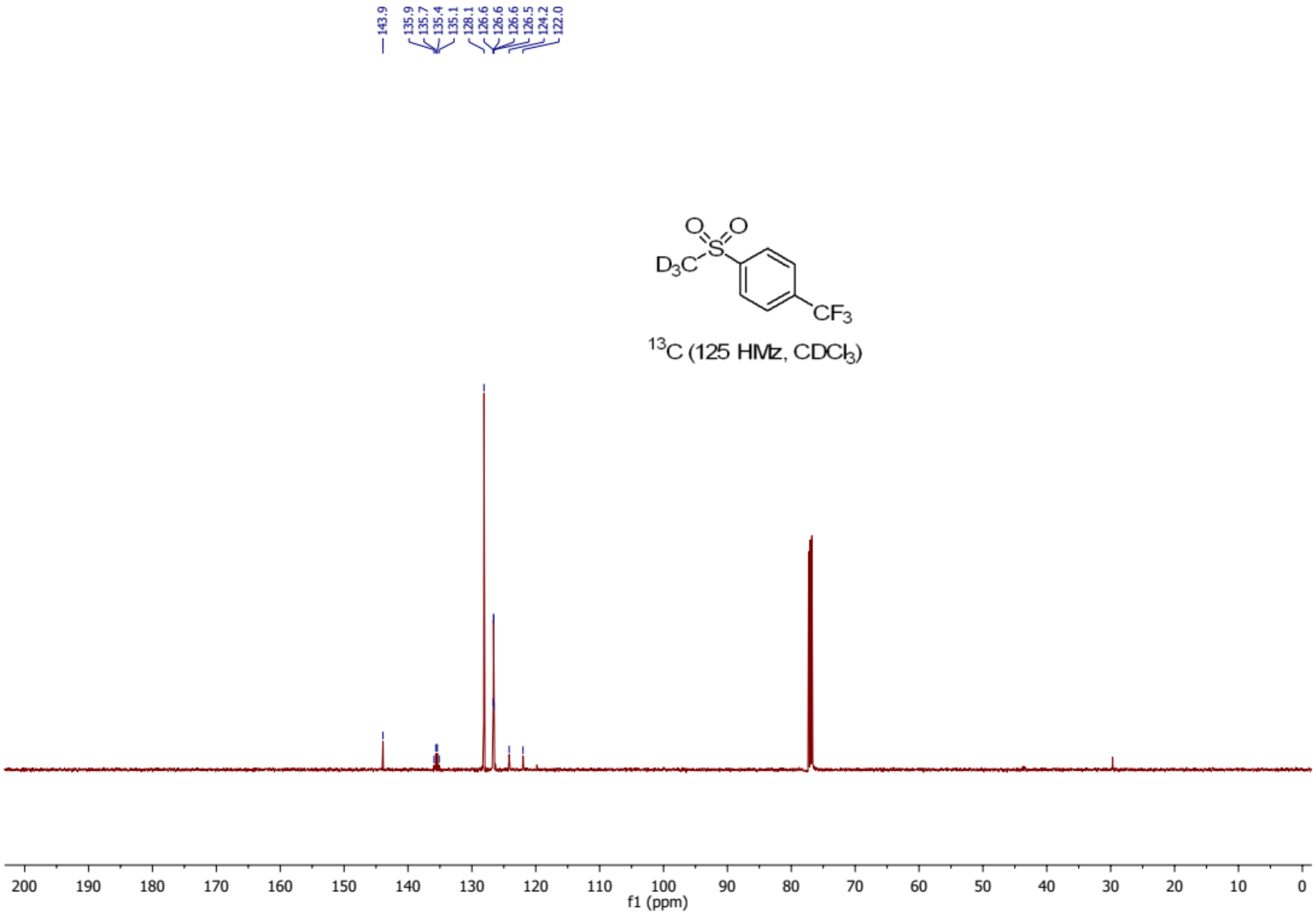
1-((Methyl-d_3)sulfonyl)-4-(trifluoromethyl)benzene (4g)



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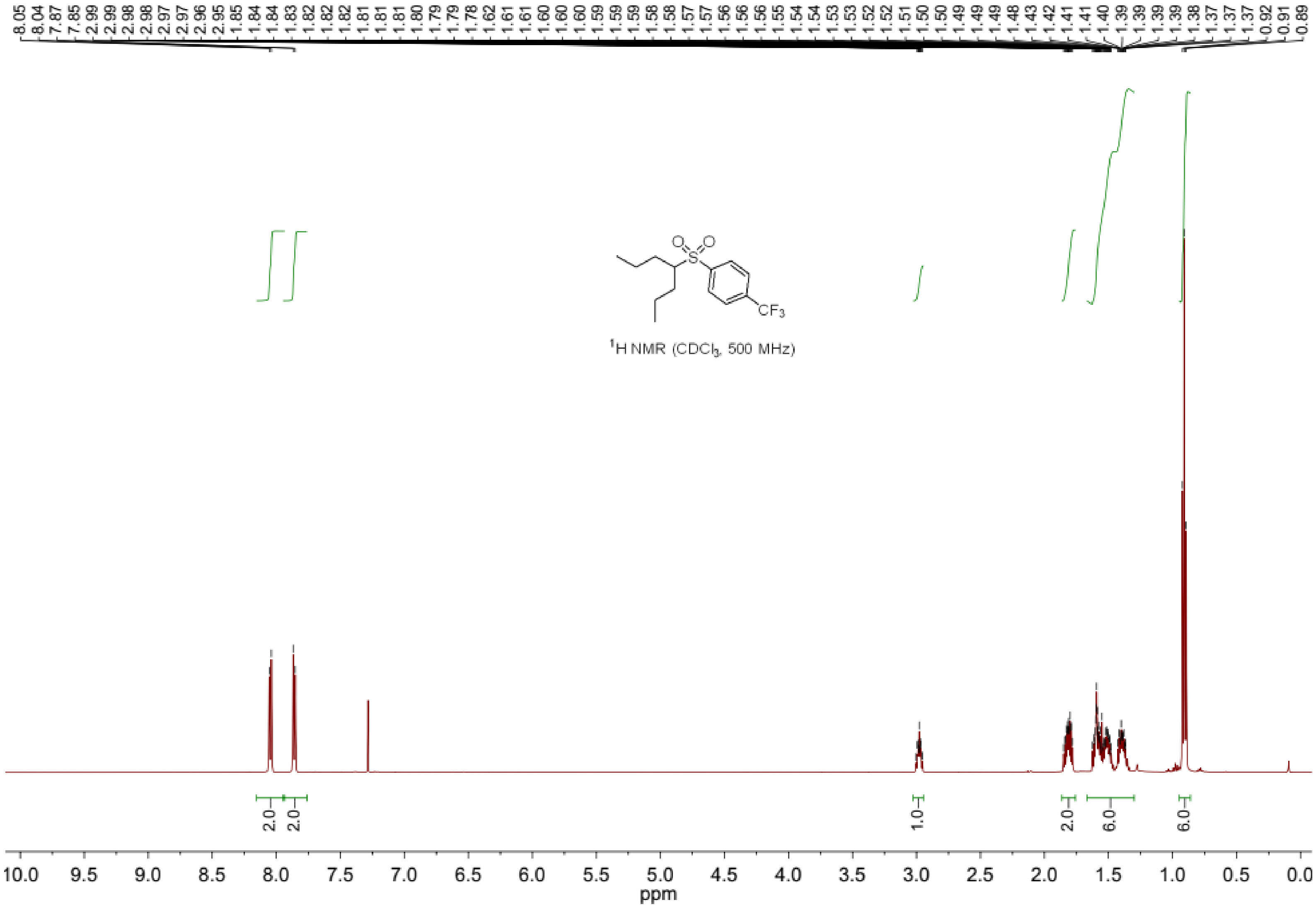
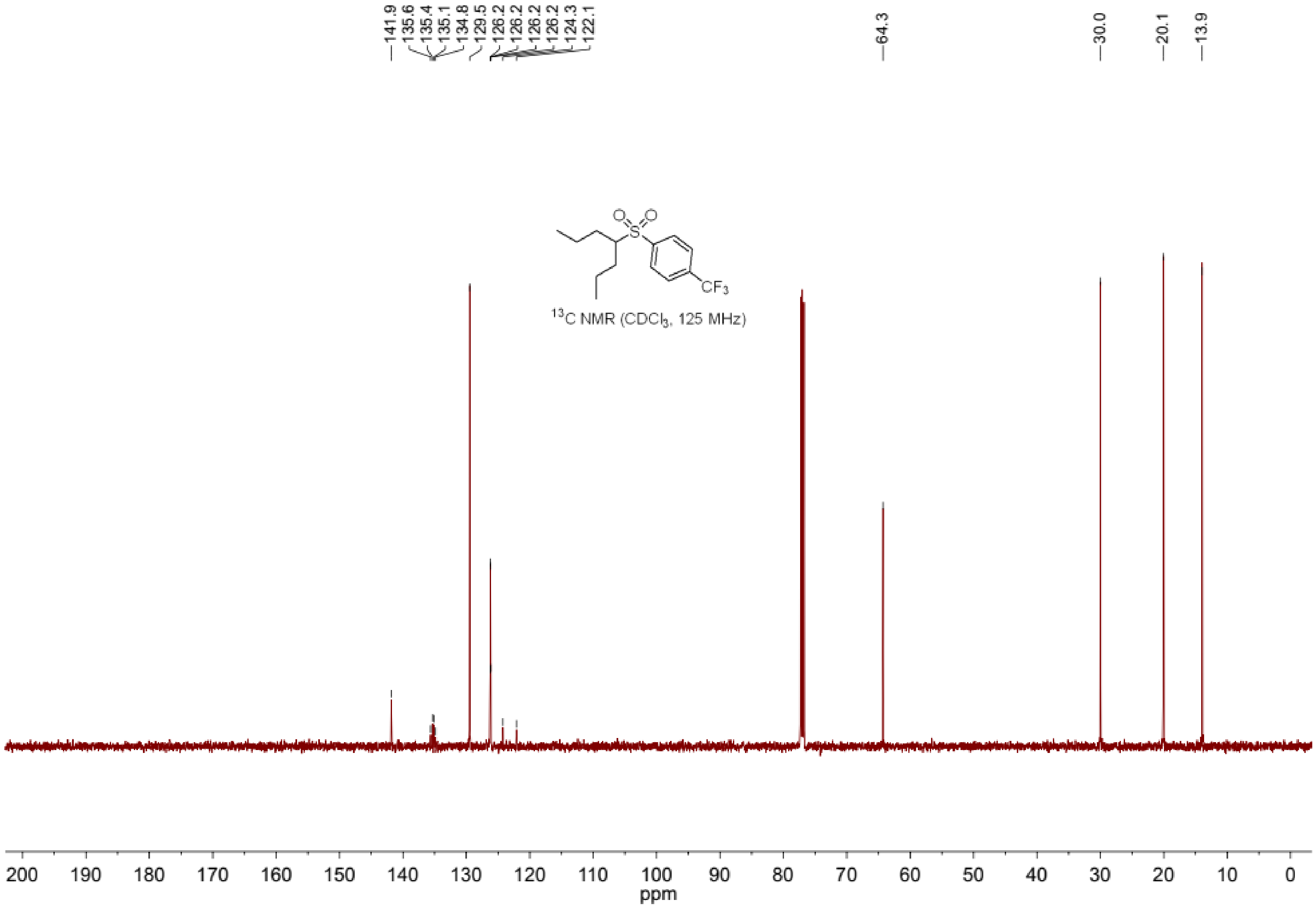
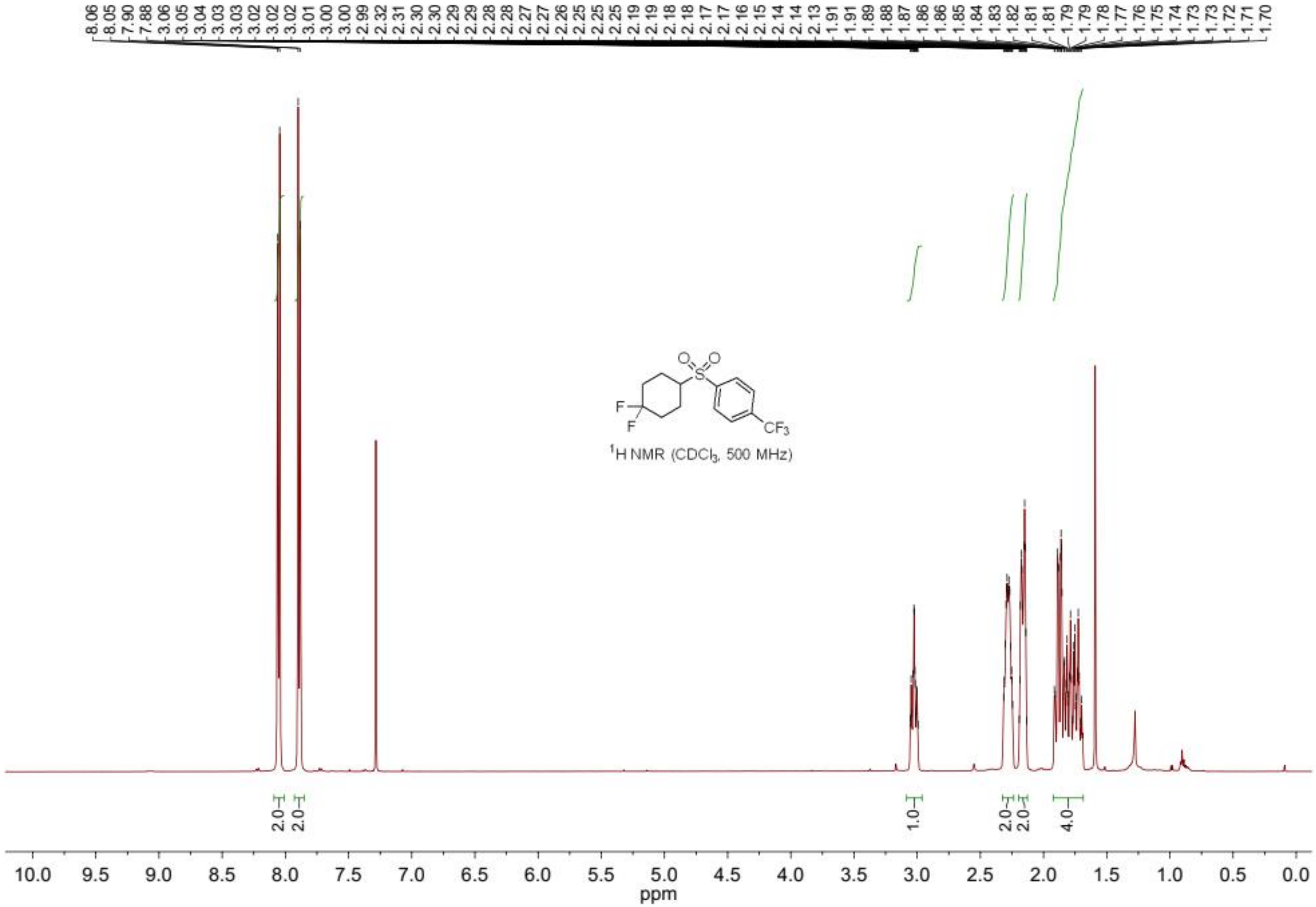
1-(Heptan-4-ylsulfonyl)-4-(trifluoromethyl)benzene (4h)



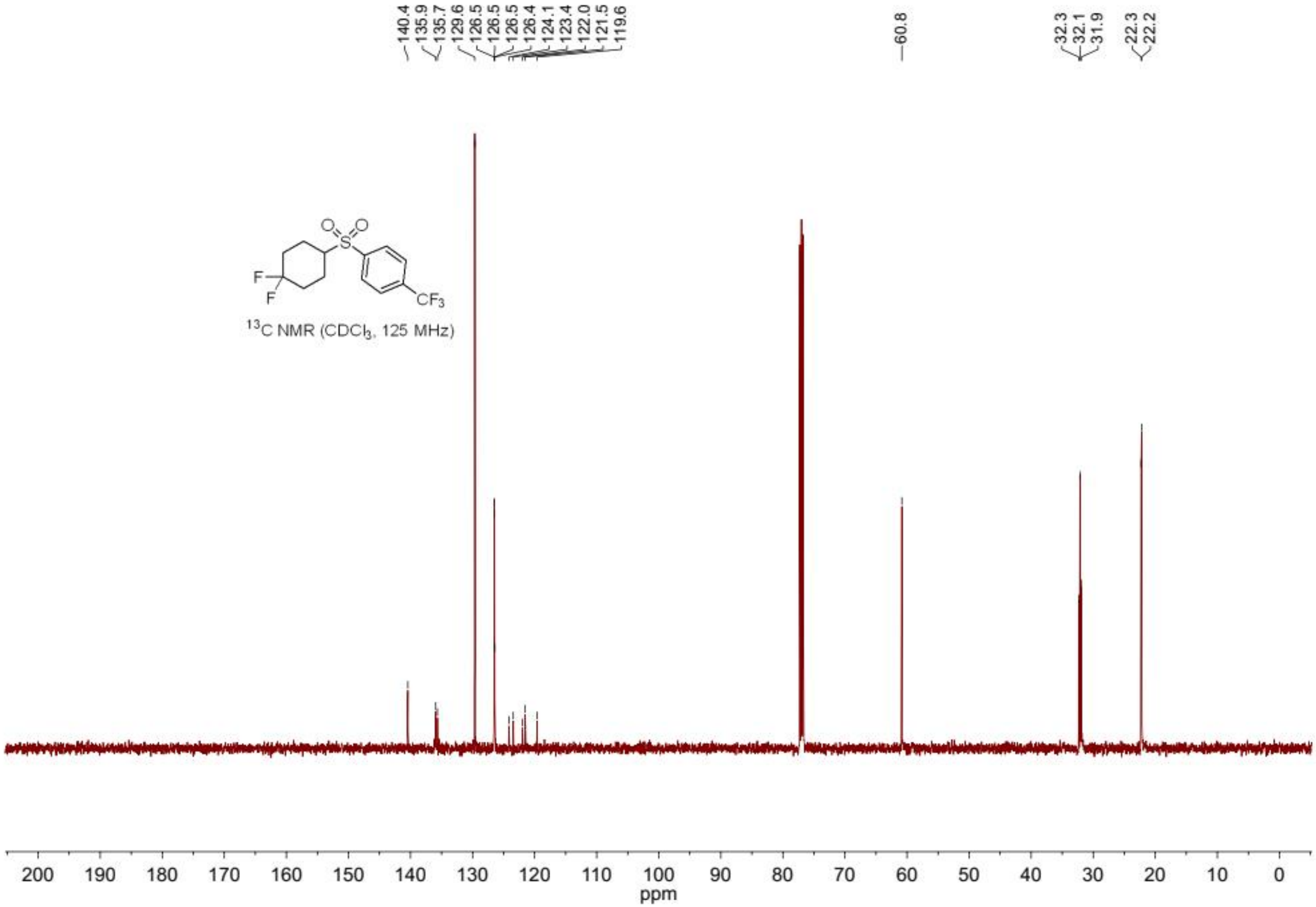
1-(Heptan-4-ylsulfonyl)-4-(trifluoromethyl)benzene (4h)



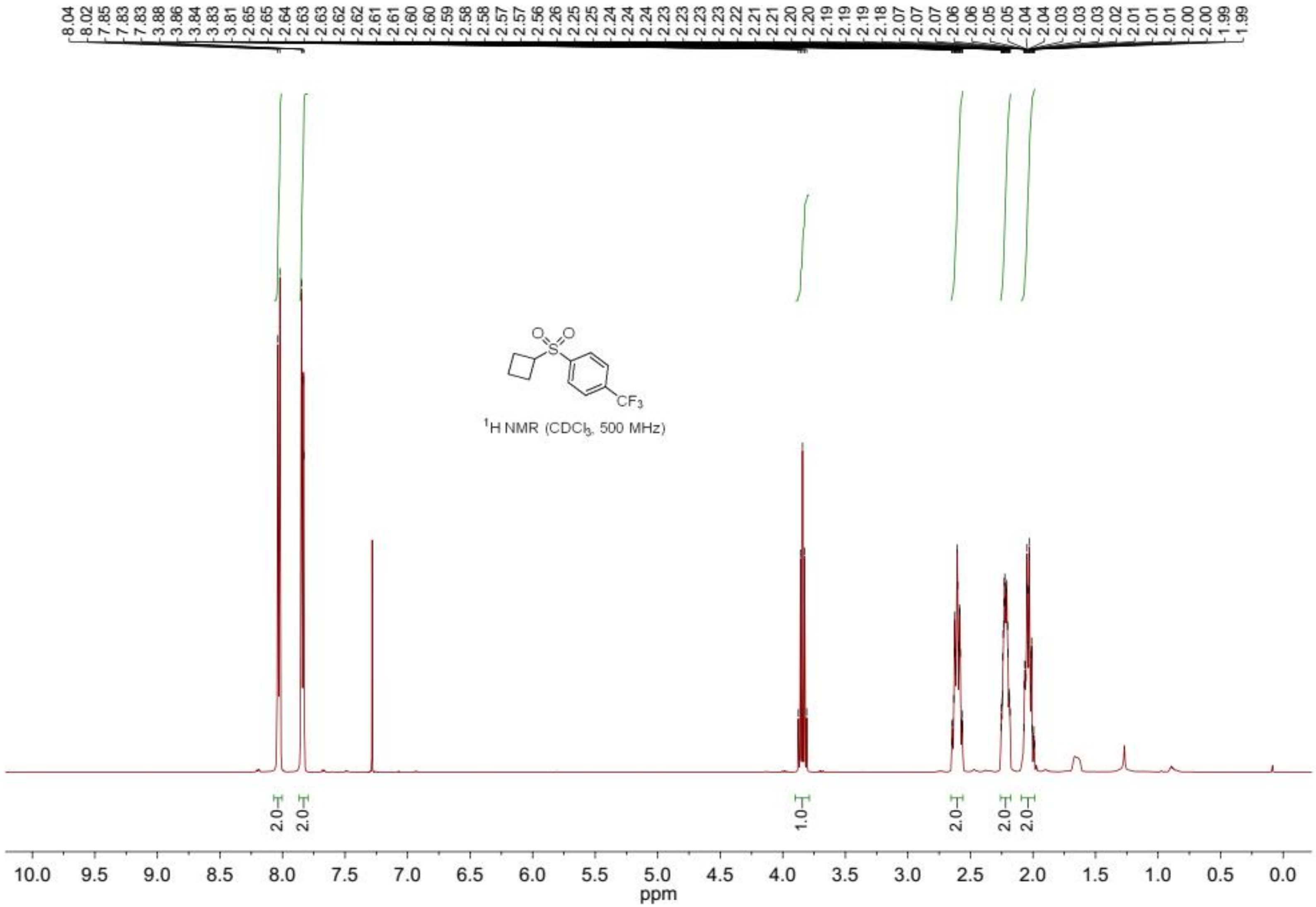
1-((4,4-Difluorocyclohexyl)sulfonyl)-4-(trifluoromethyl)benzene (4i)



1-((4,4-Difluorocyclohexyl)sulfonyl)-4-(trifluoromethyl)benzene (4i)



1-(Cyclobutylsulfonyl)-4-(trifluoromethyl)benzene (4j)



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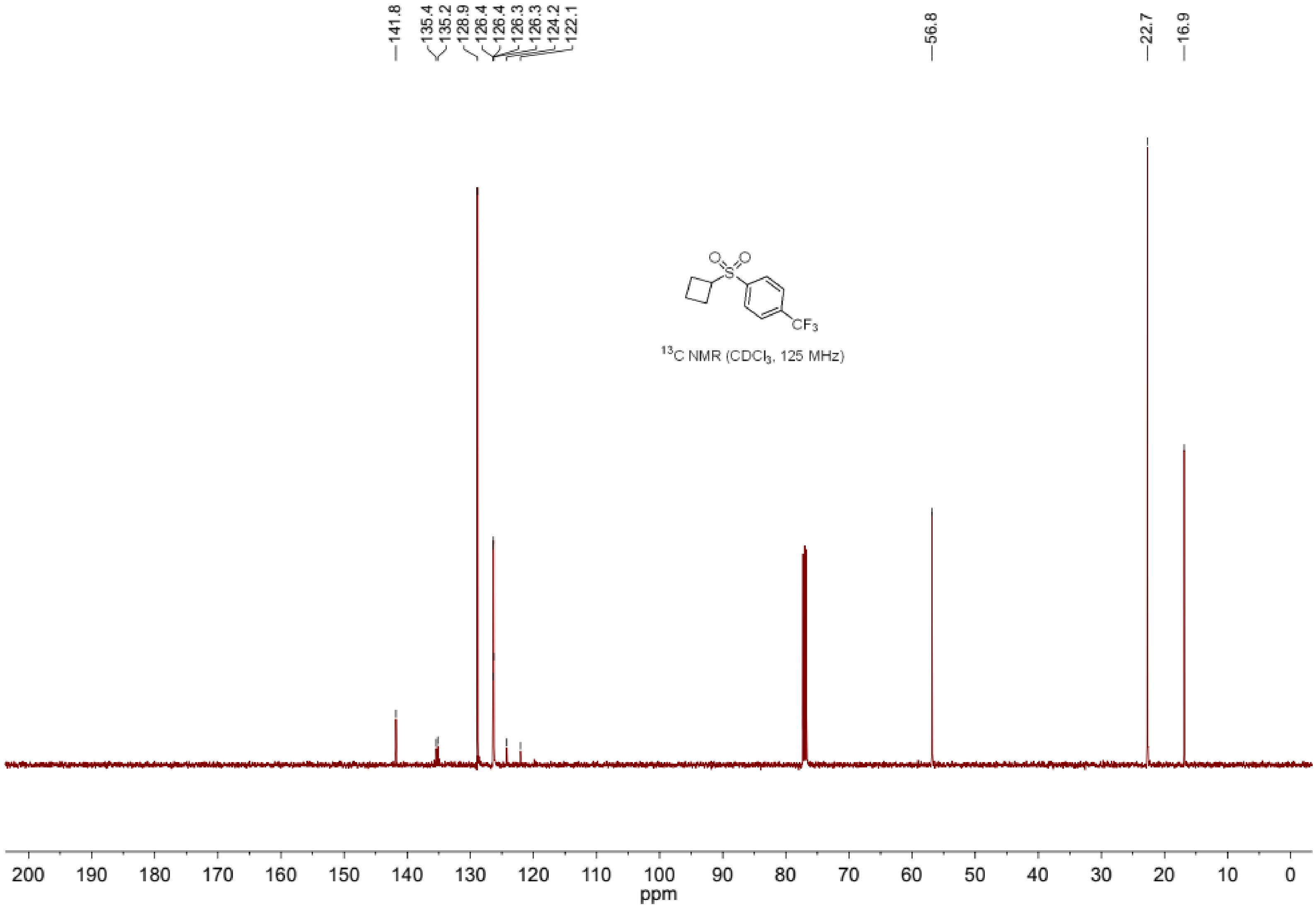
1-(Cyclobutylsulfonyl)-4-(trifluoromethyl)benzene (4j)



^{13}C NMR ($CDCl_3$, 125 MHz)

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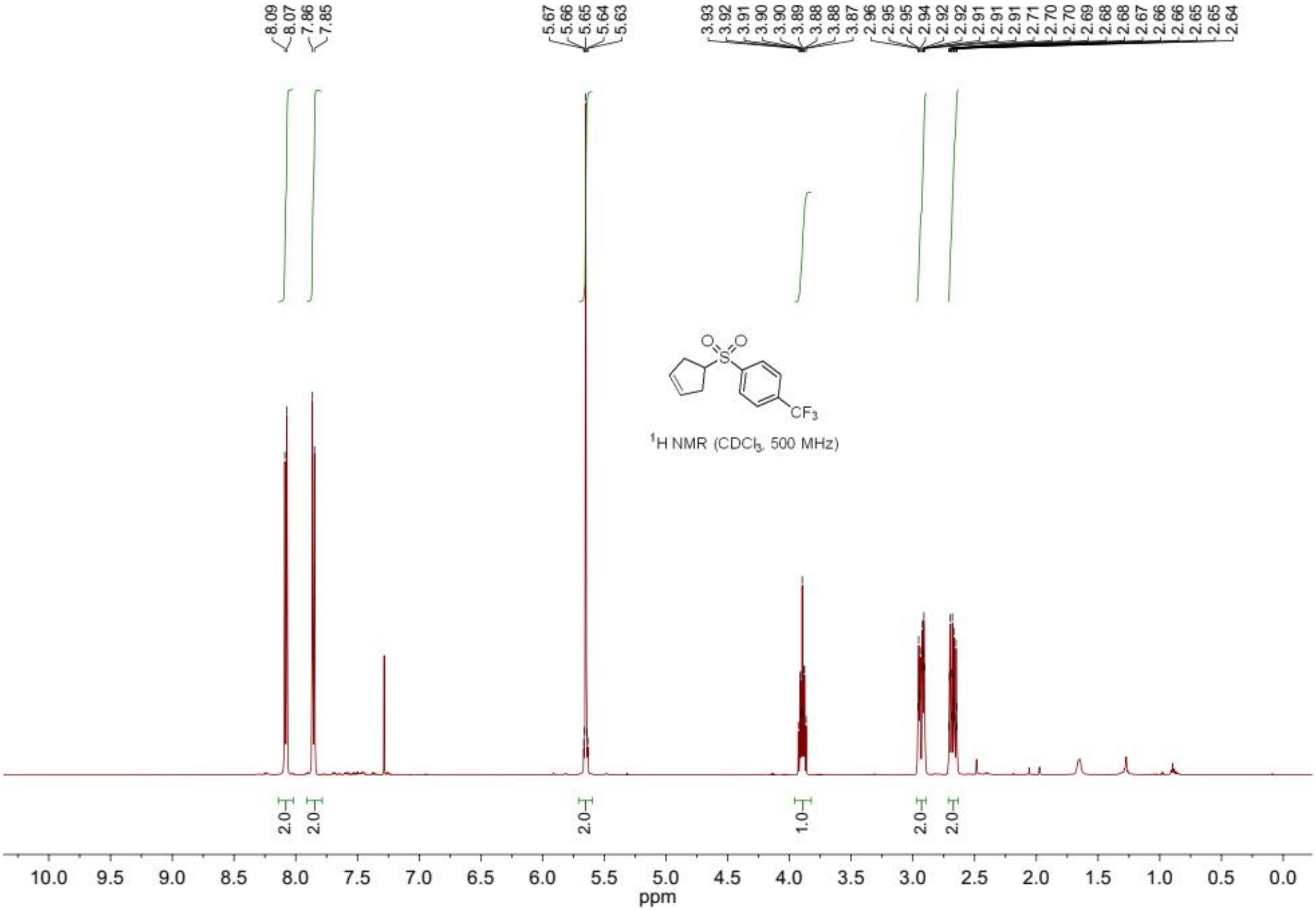
1-(Cyclopent-3-en-1-ylsulfonyl)-4-(trifluoromethyl)benzene (4k)



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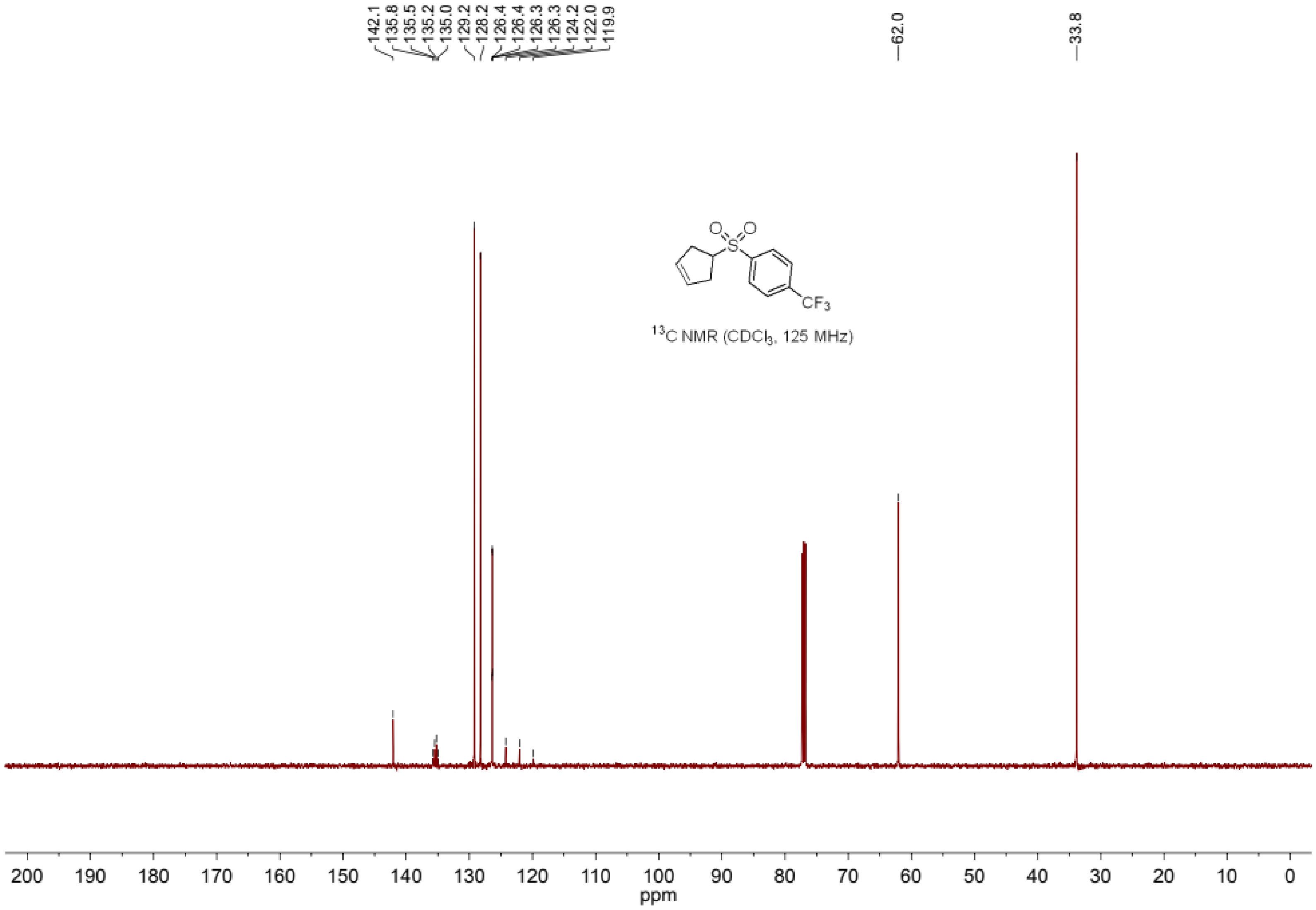
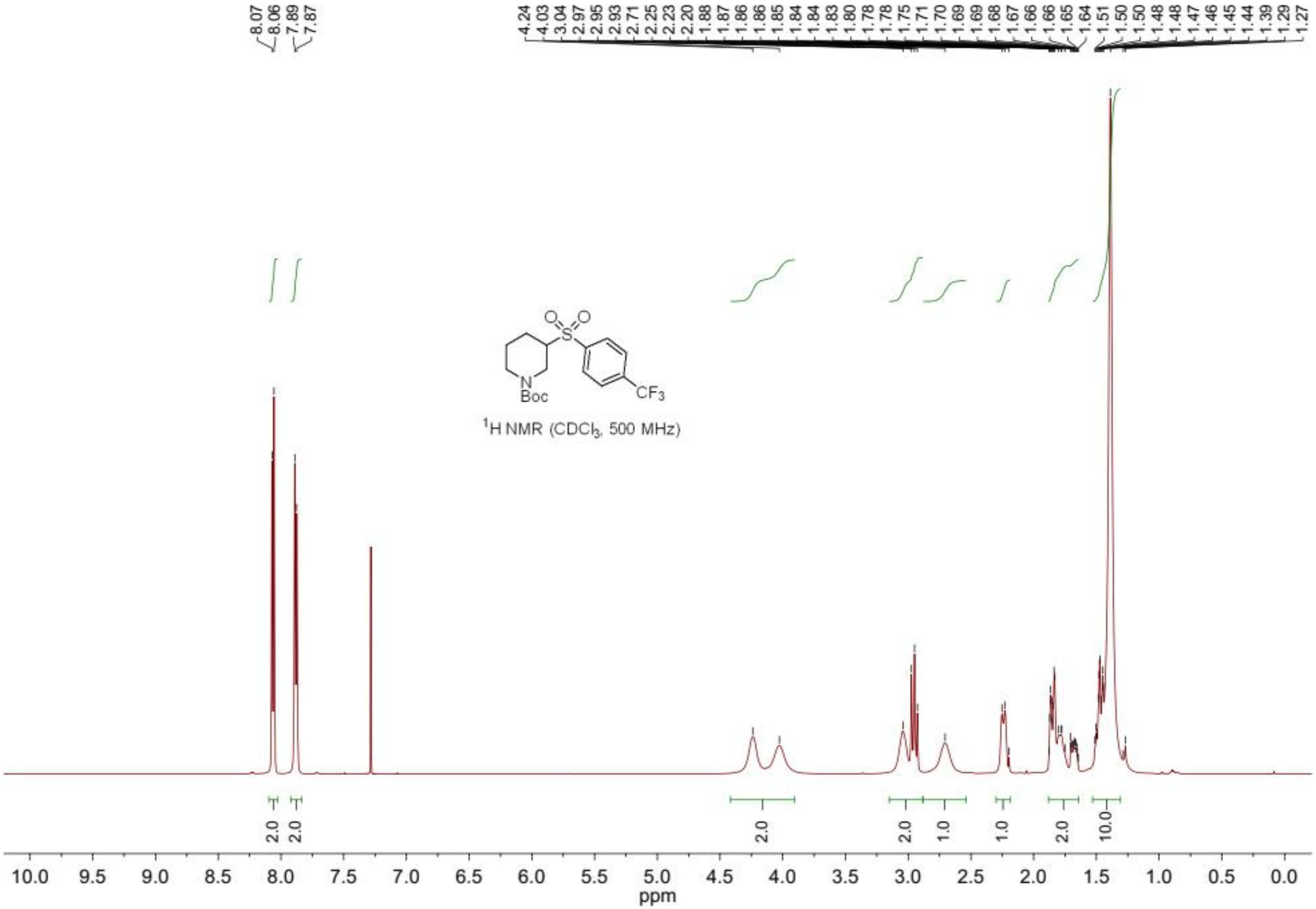
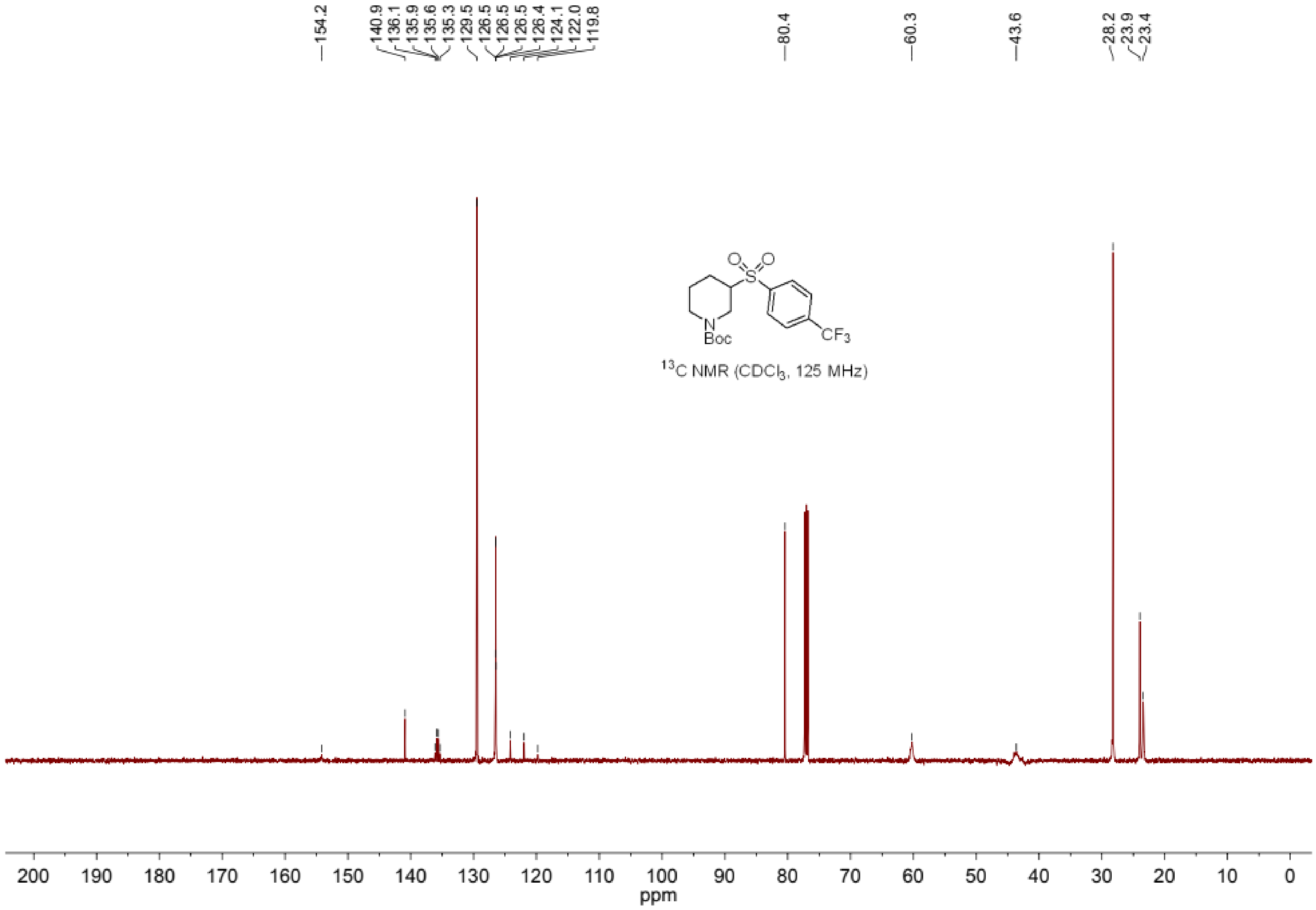
1-(Cyclopent-3-en-1-ylsulfonyl)-4-(trifluoromethyl)benzene (4k)



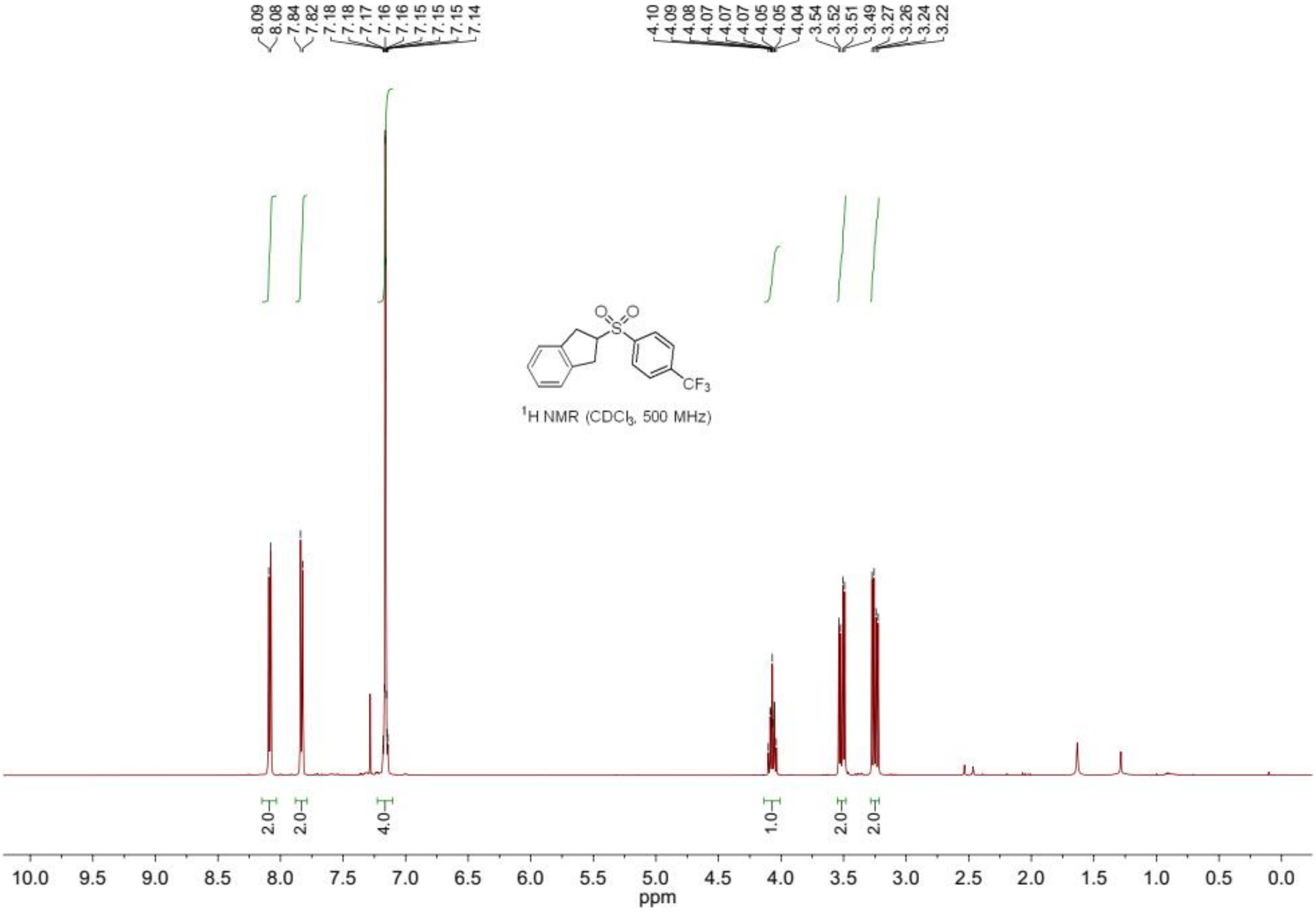
tert-Butyl 3-((4-(trifluoromethyl)phenyl)sulfonyl)piperidine-1-carboxylate (4l)



tert-Butyl 3-((4-(trifluoromethyl)phenyl)sulfonyl)piperidine-1-carboxylate (4l)



2-((4-(Trifluoromethyl)phenyl)sulfonyl)-2,3-dihydro-1*H*-indene (4m)



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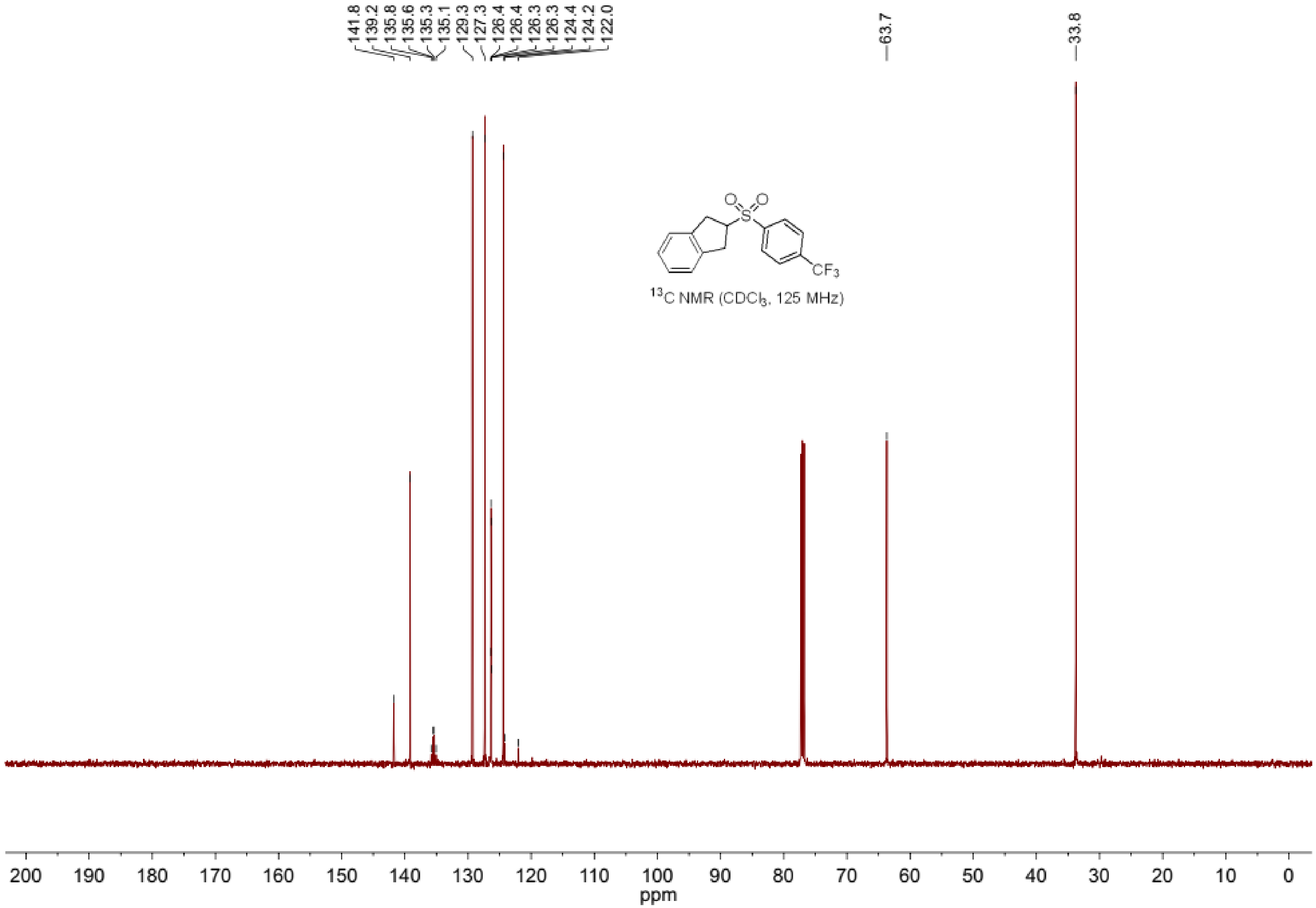
2-((4-(Trifluoromethyl)phenyl)sulfonyl)-2,3-dihydro-1*H*-indene (4m)



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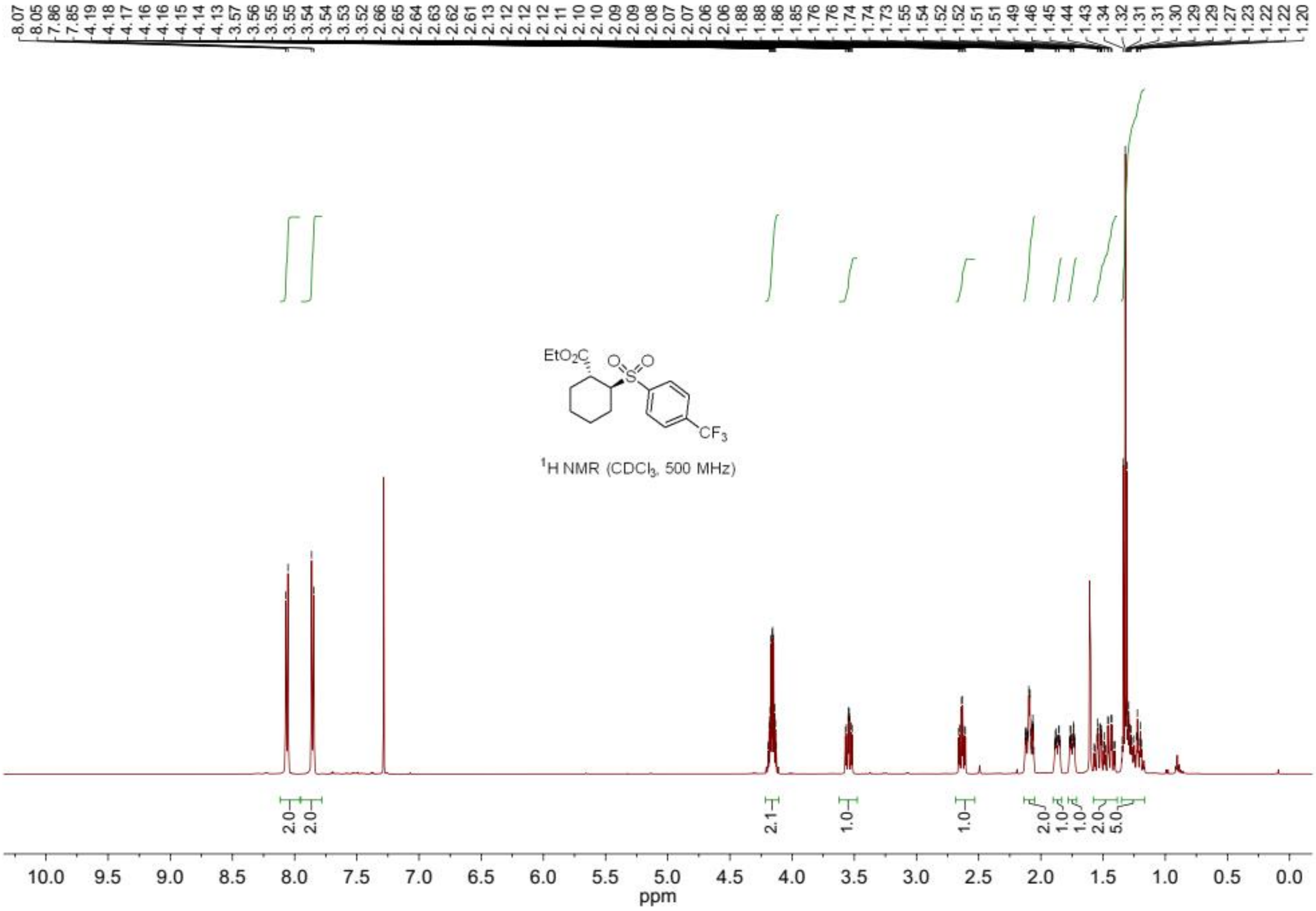
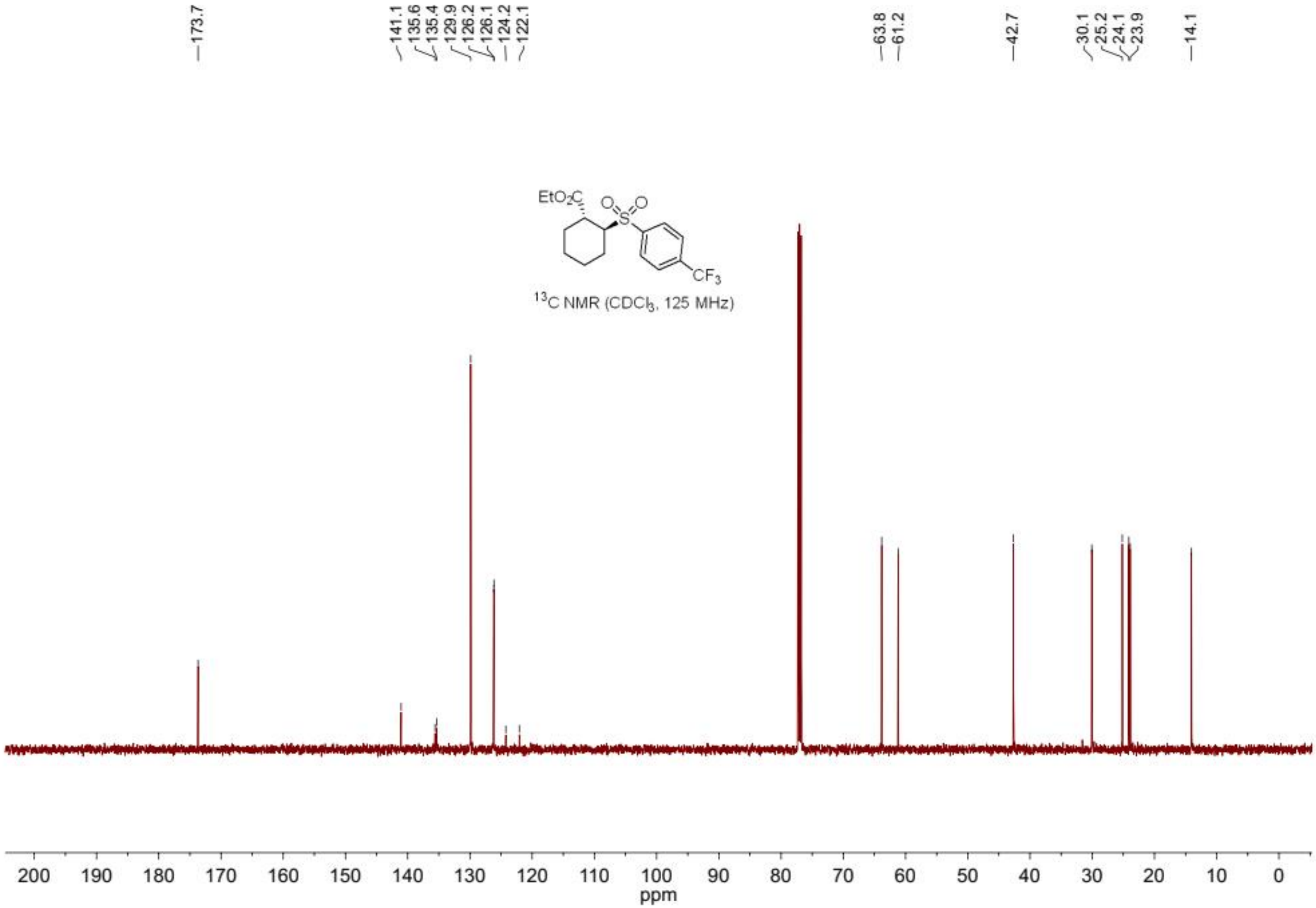
Ethyl (1*R**,2*S**)-2-((4-(trifluoromethyl)phenyl)sulfonyl)cyclohexane-1-carboxylate (4n)



Ethyl (1*R**,2*S**)-2-((4-(trifluoromethyl)phenyl)sulfonyl)cyclohexane-1-carboxylate (4n)



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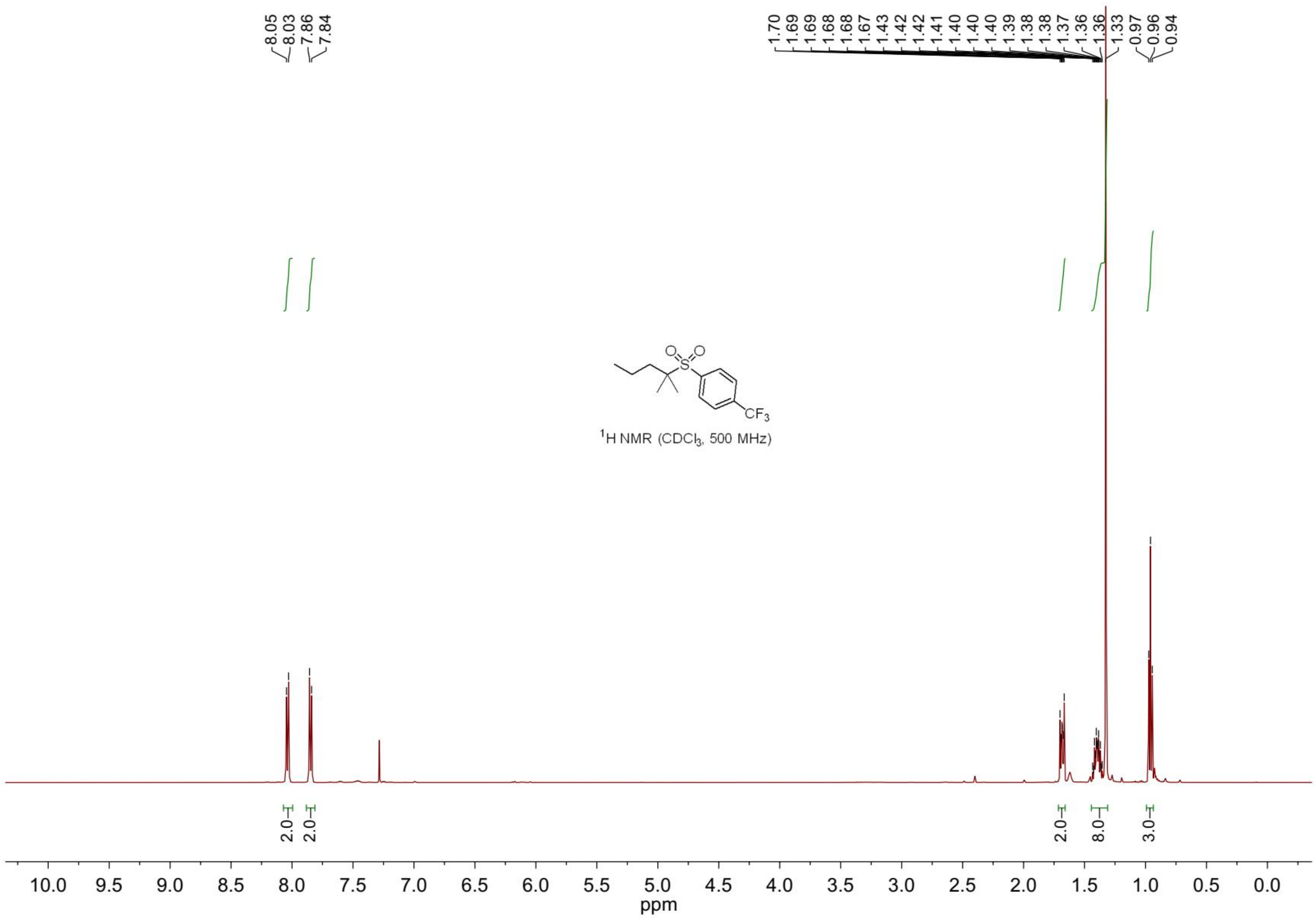
1-((2-Methylpentan-2-yl)sulfonyl)-4-(trifluoromethyl)benzene (4o)



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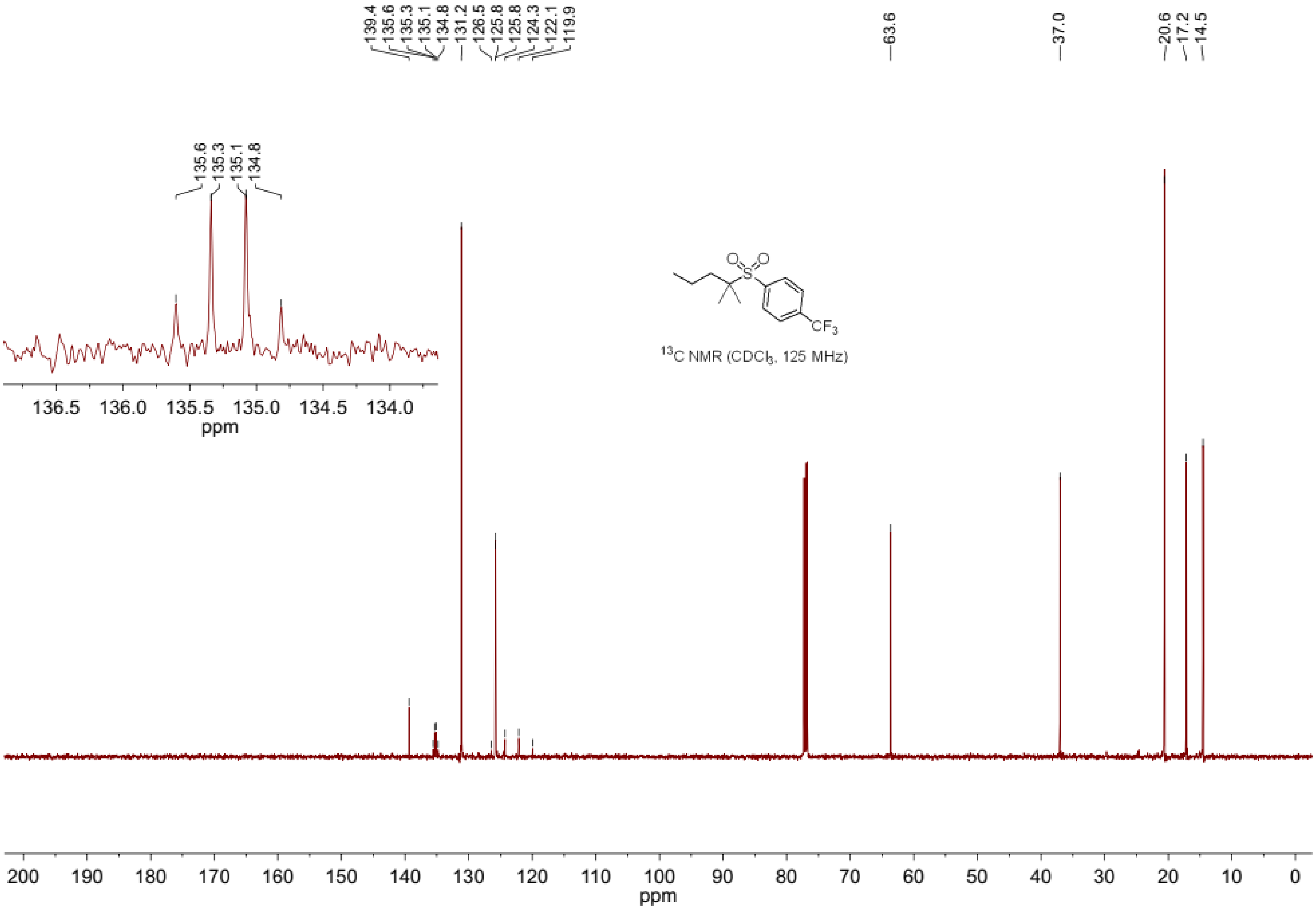
1-((2-Methylpentan-2-yl)sulfonyl)-4-(trifluoromethyl)benzene (4o)



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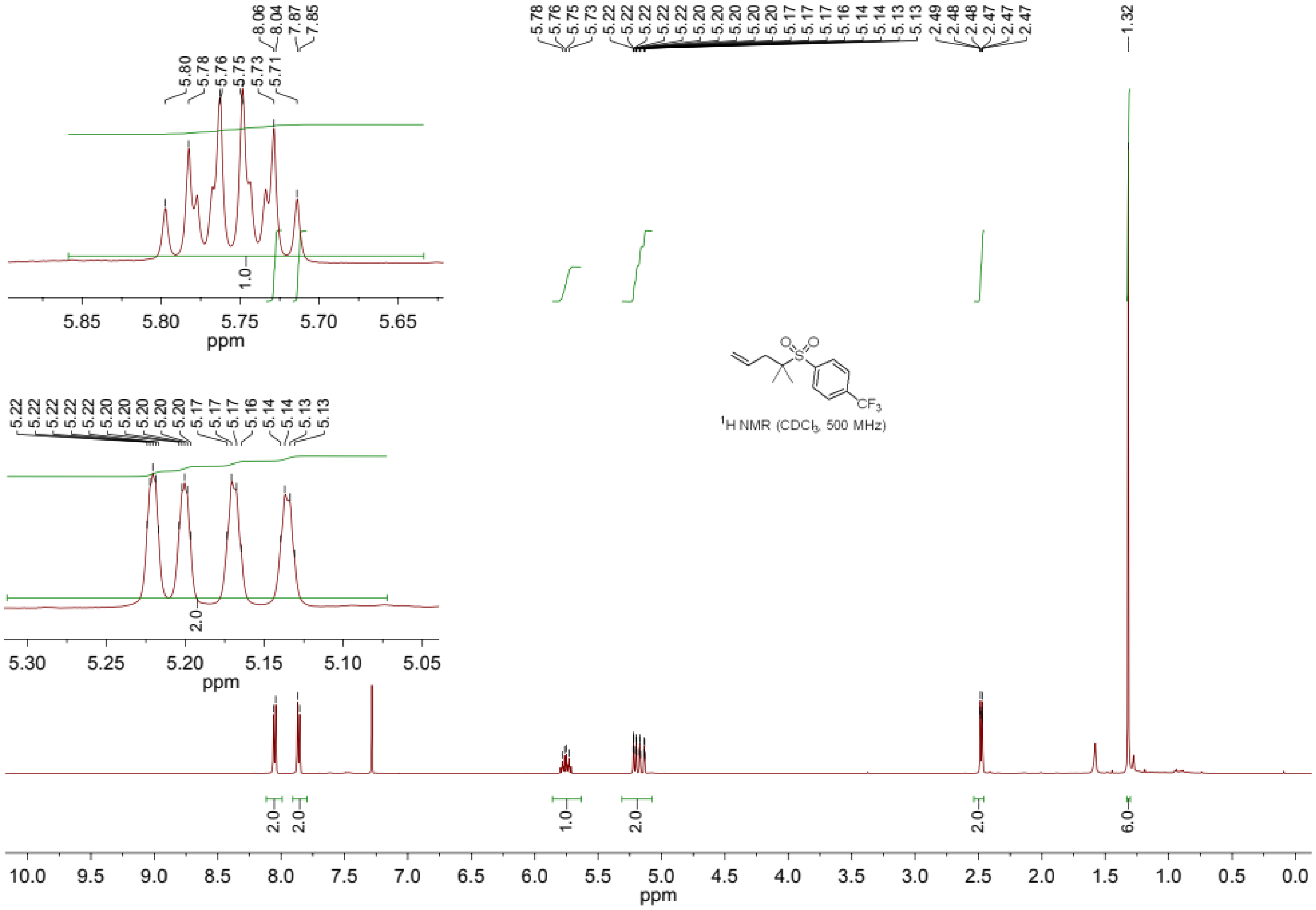
1-((2-Methylpent-4-en-2-yl)sulfonyl)-4-(trifluoromethyl)benzene (4p)



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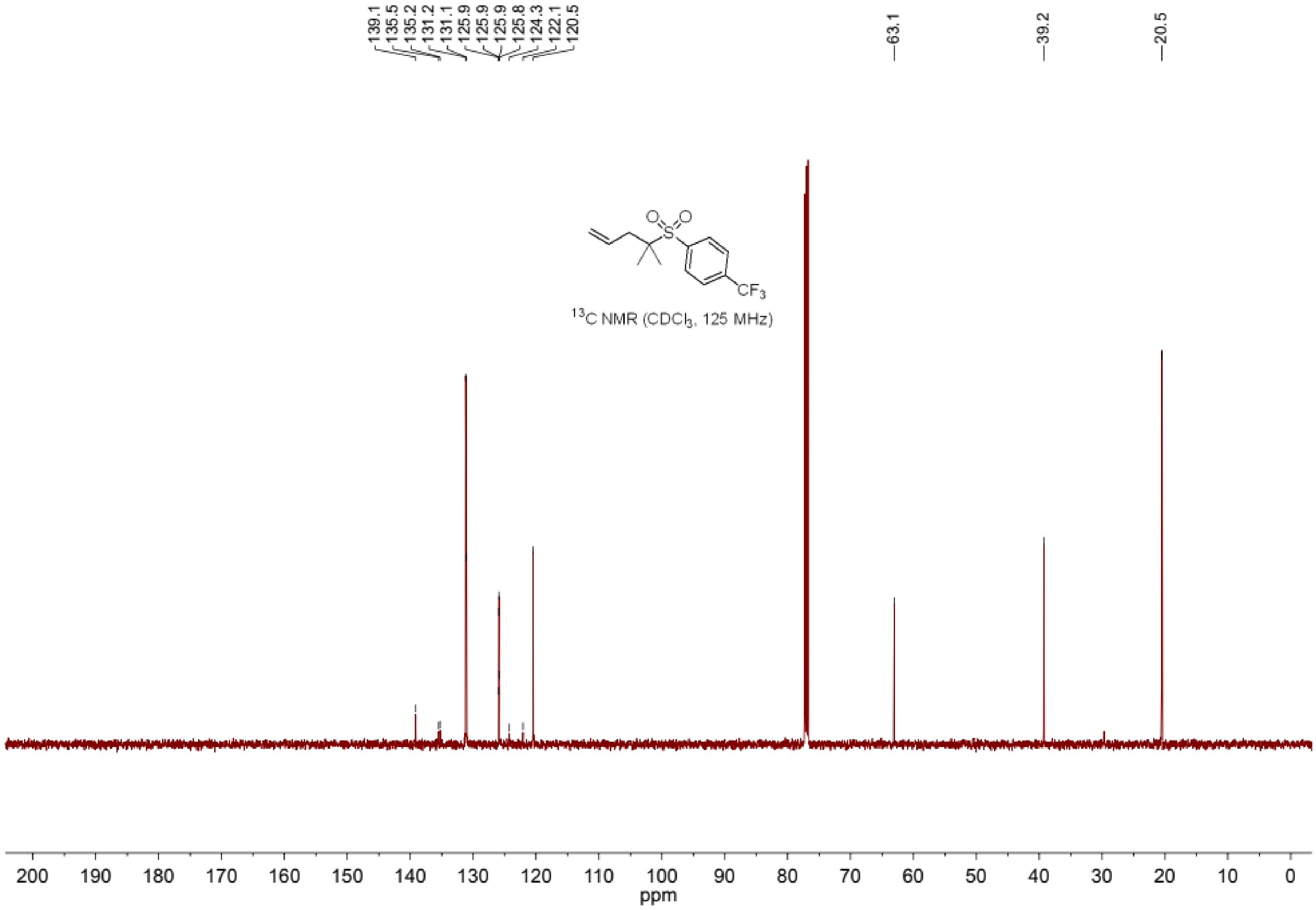
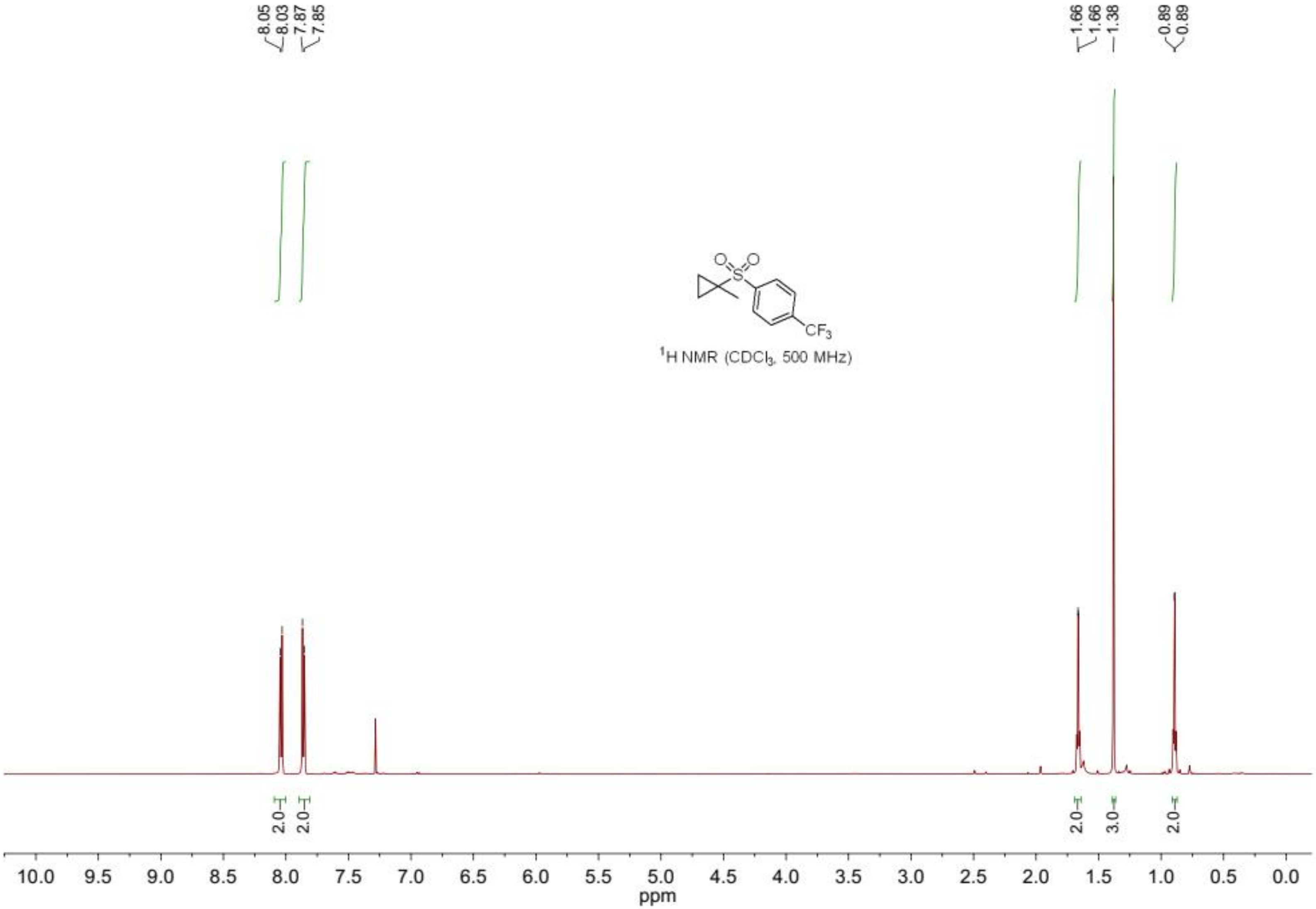
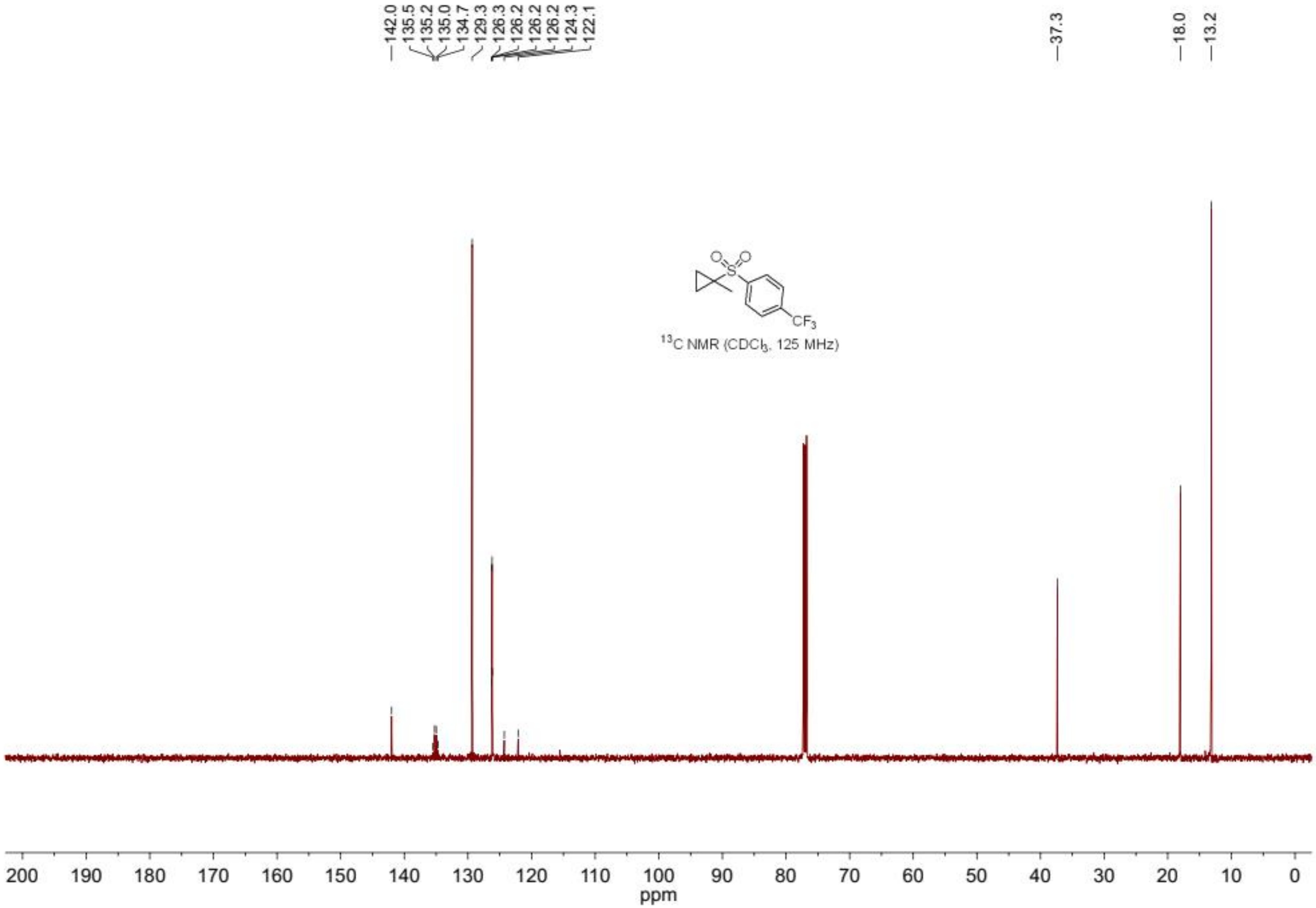
1-((2-Methylpent-4-en-2-yl)sulfonyl)-4-(trifluoromethyl)benzene (4p)



1-((1-Methylcyclopropyl)sulfonyl)-4-(trifluoromethyl)benzene (4q)



1-((1-Methylcyclopropyl)sulfonyl)-4-(trifluoromethyl)benzene (4q)



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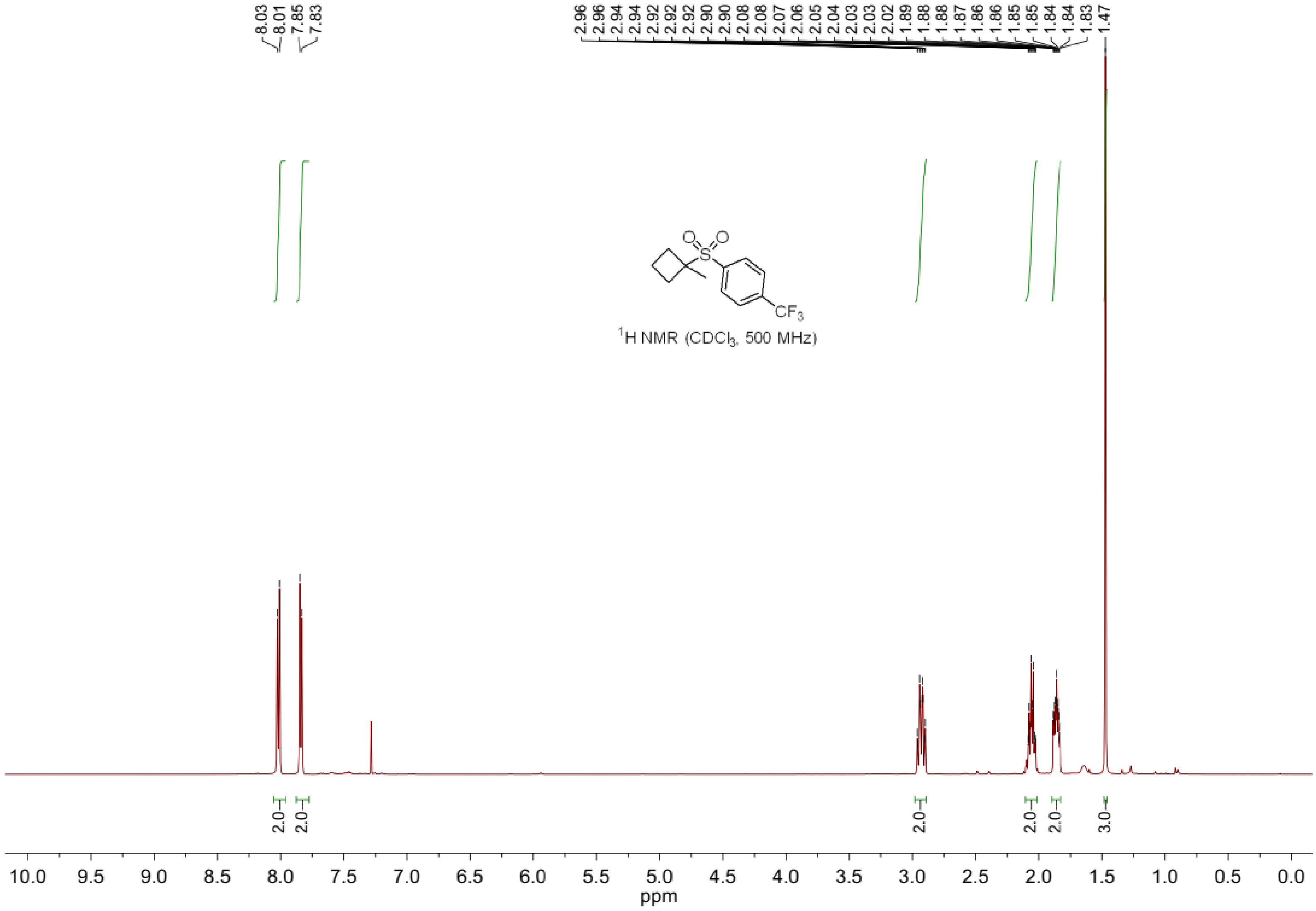
1-((1-Methylcyclobutyl)sulfonyl)-4-(trifluoromethyl)benzene (4r)



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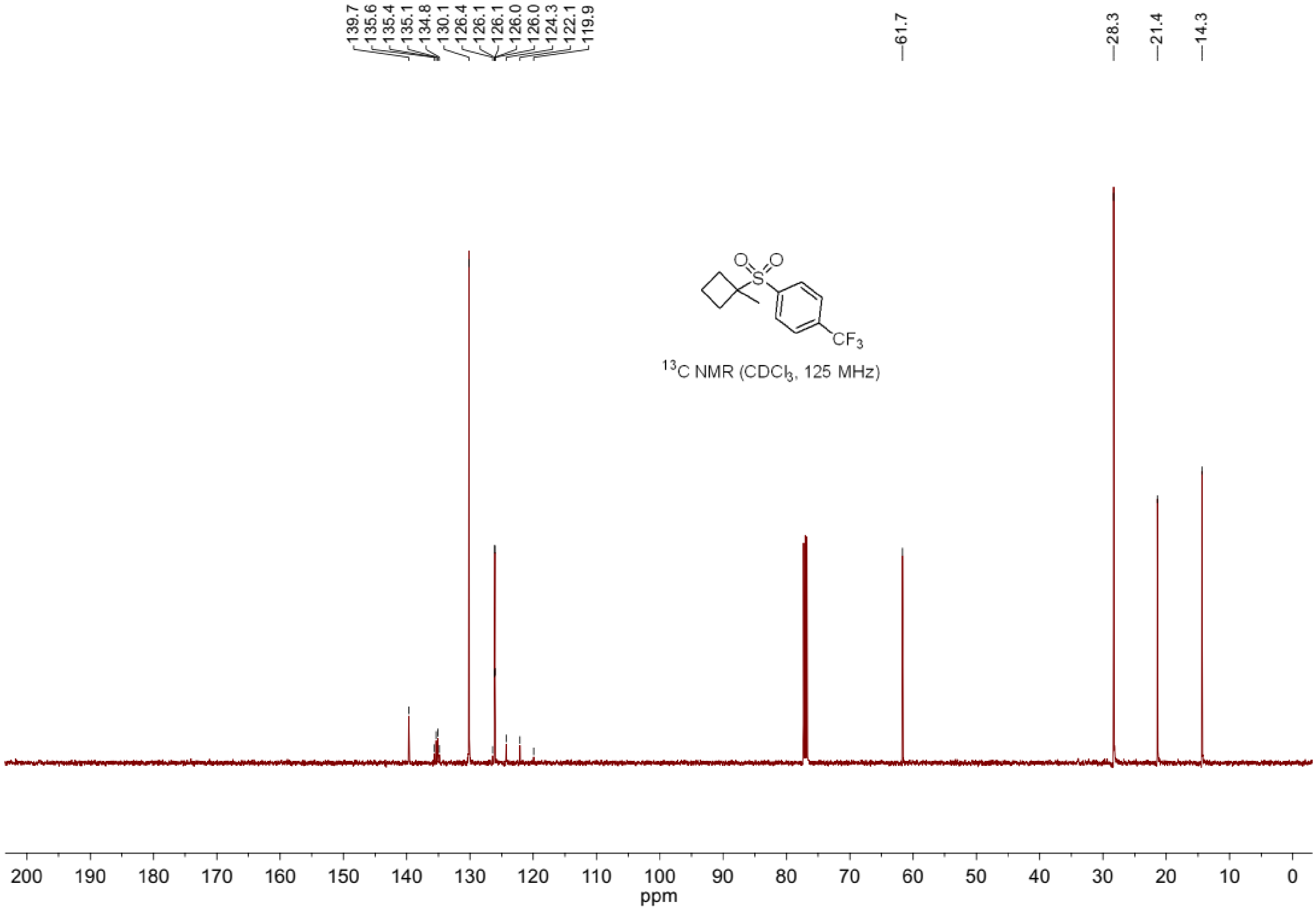
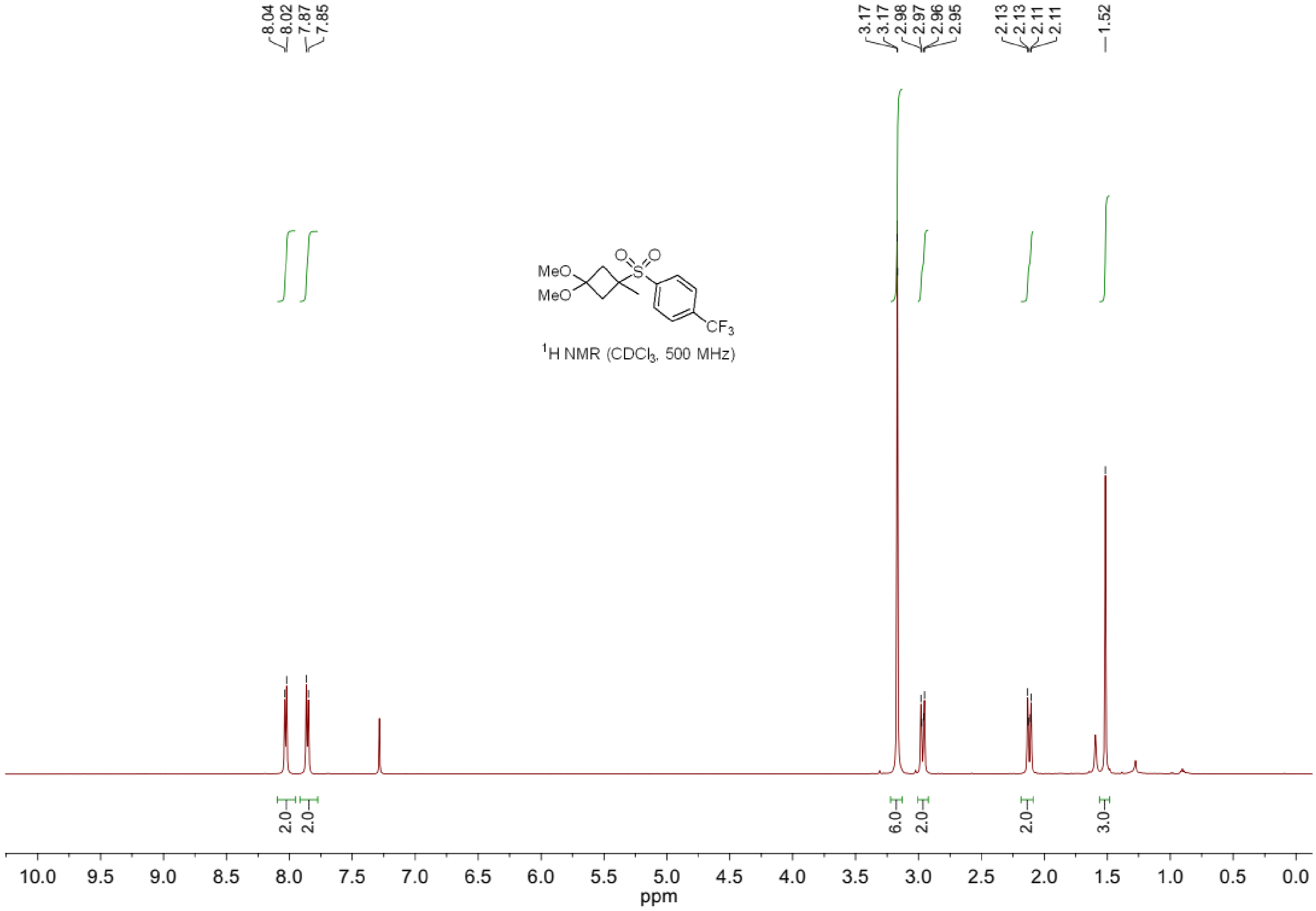
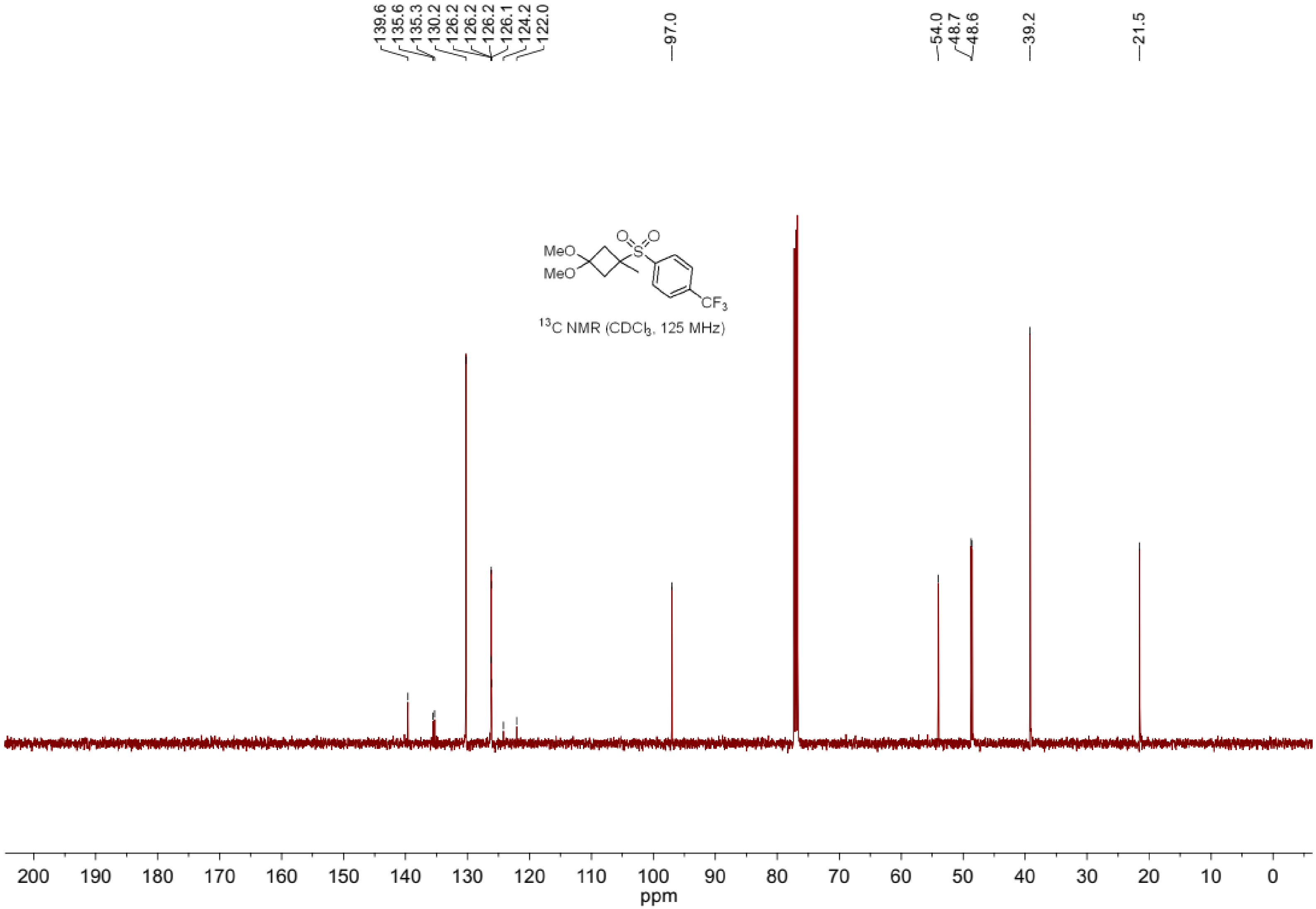
1-((1-Methylcyclobutyl)sulfonyl)-4-(trifluoromethyl)benzene (4r)



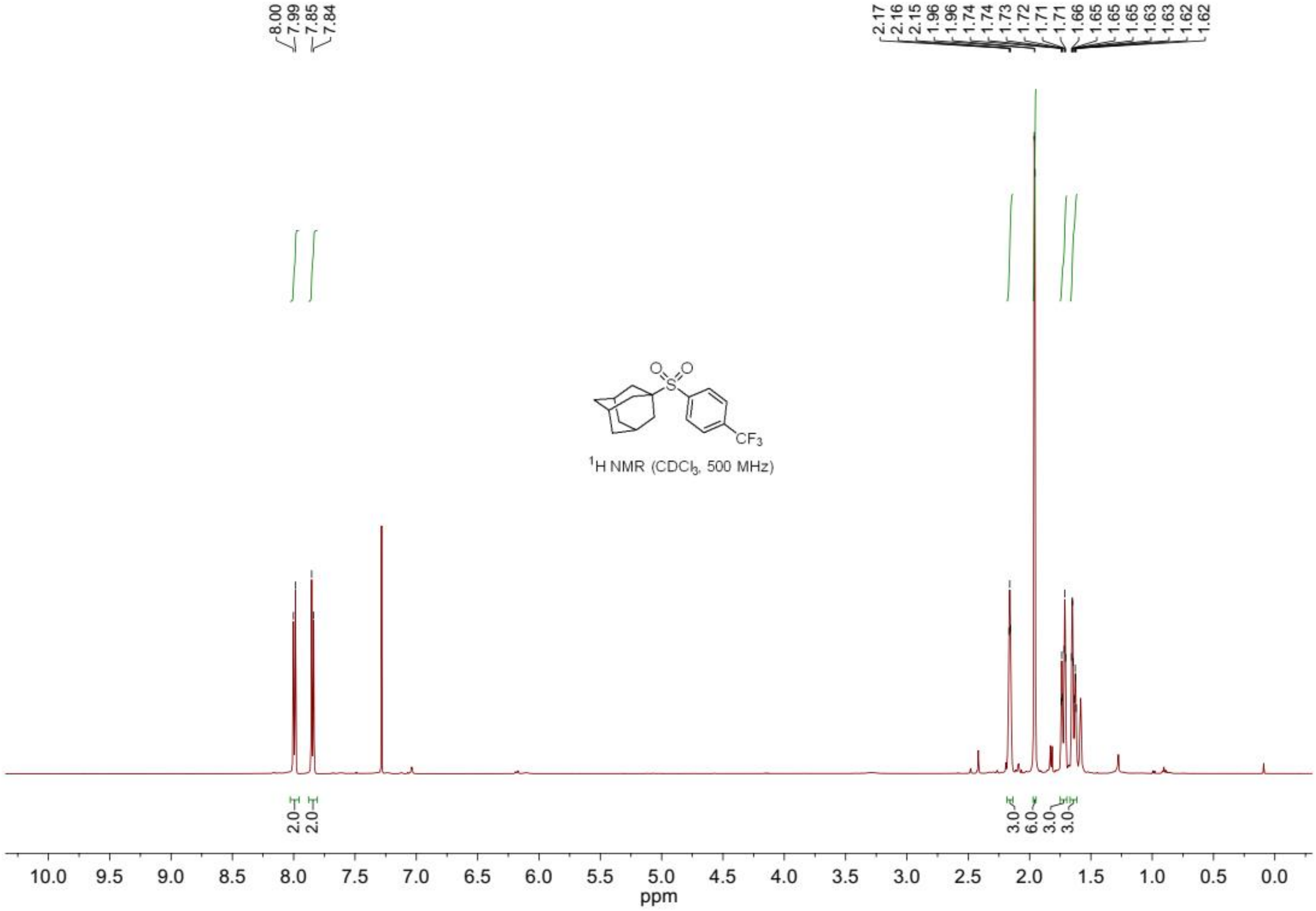
1-((3,3-Dimethoxy-1-methylcyclobutyl)sulfonyl)-4-(trifluoromethyl)benzene (4s)



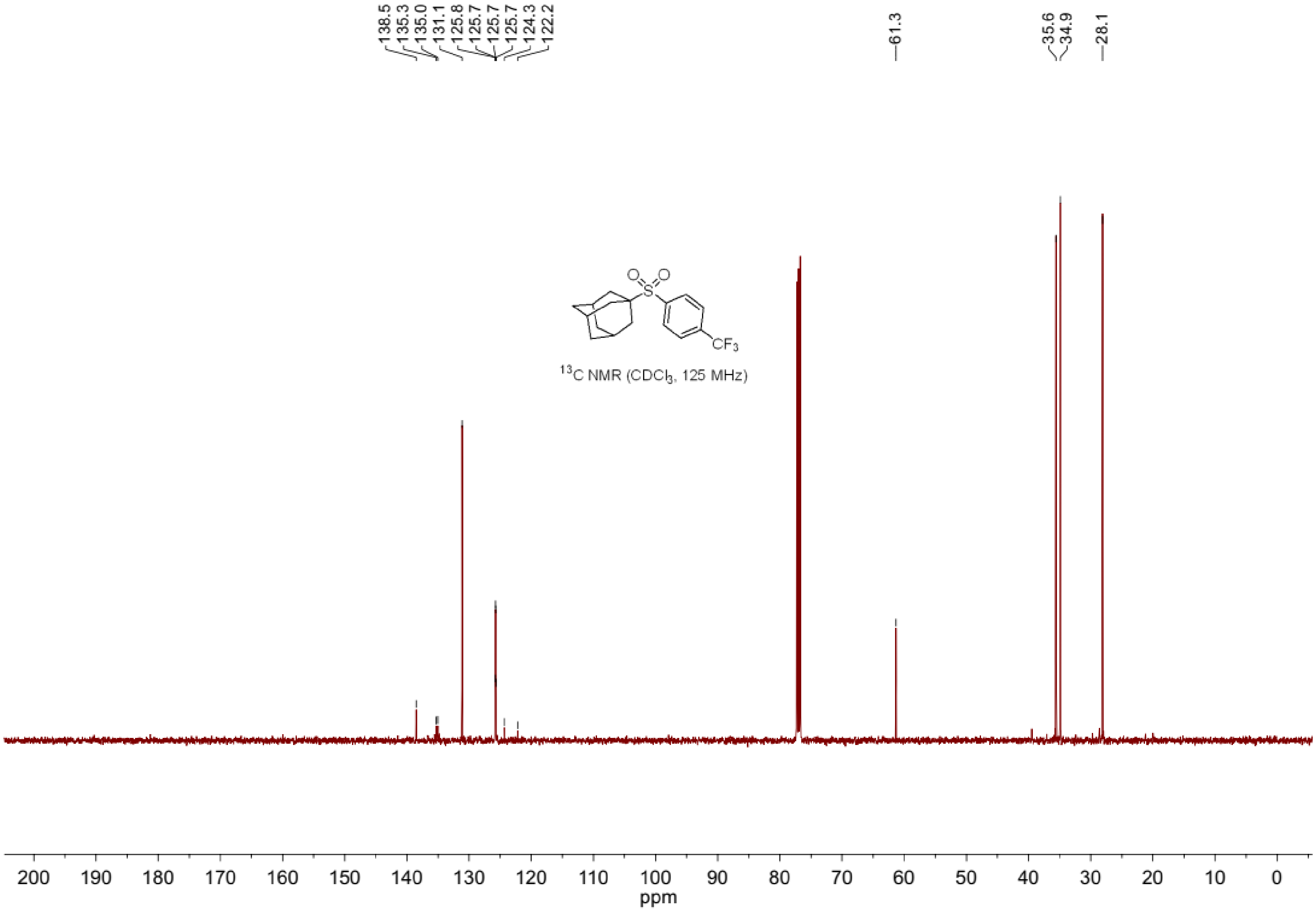
1-((3,3-Dimethoxy-1-methylcyclobutyl)sulfonyl)-4-(trifluoromethyl)benzene (4s)



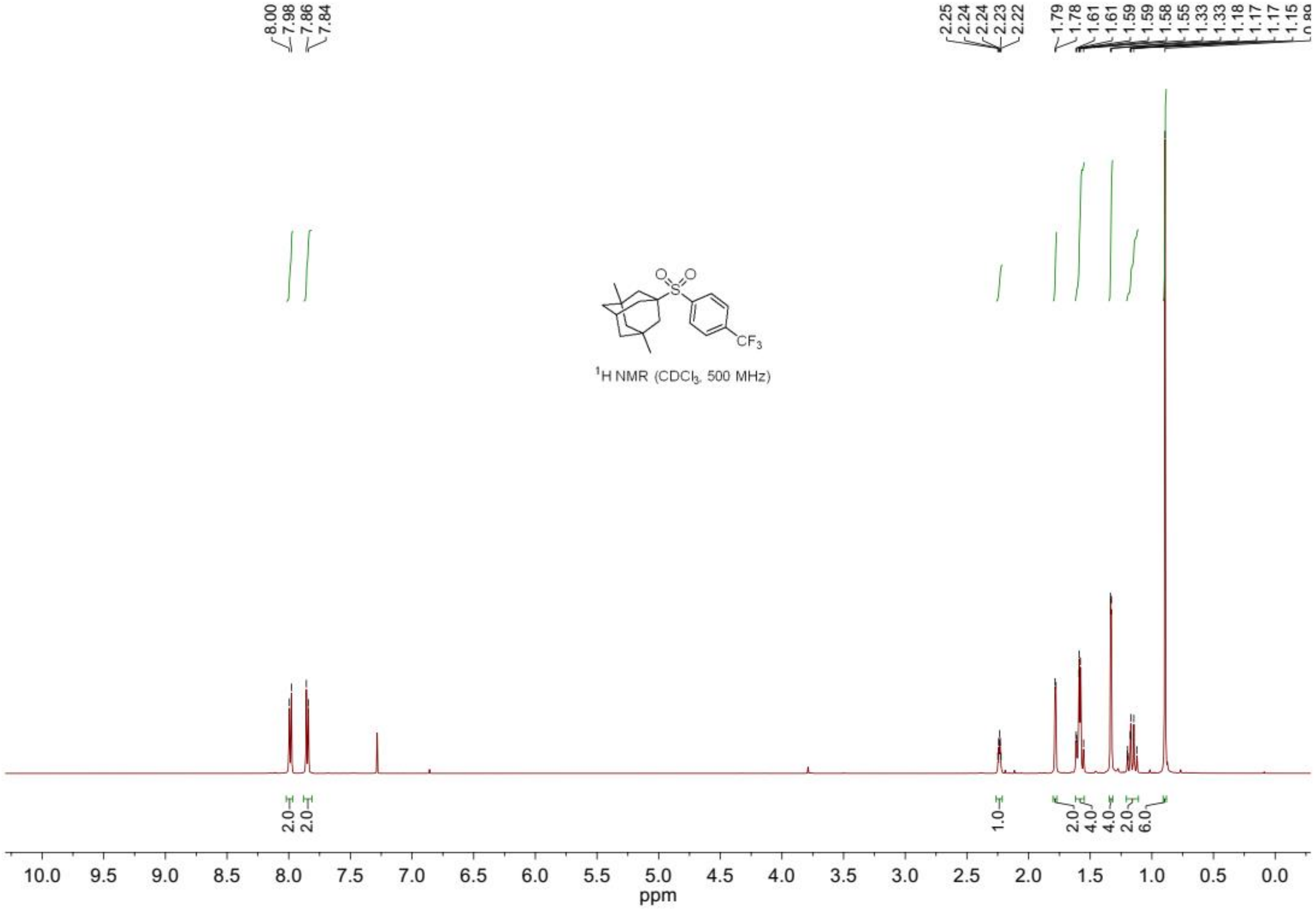
1-((4-(Trifluoromethyl)phenyl)sulfonyl)adamantine (4t)



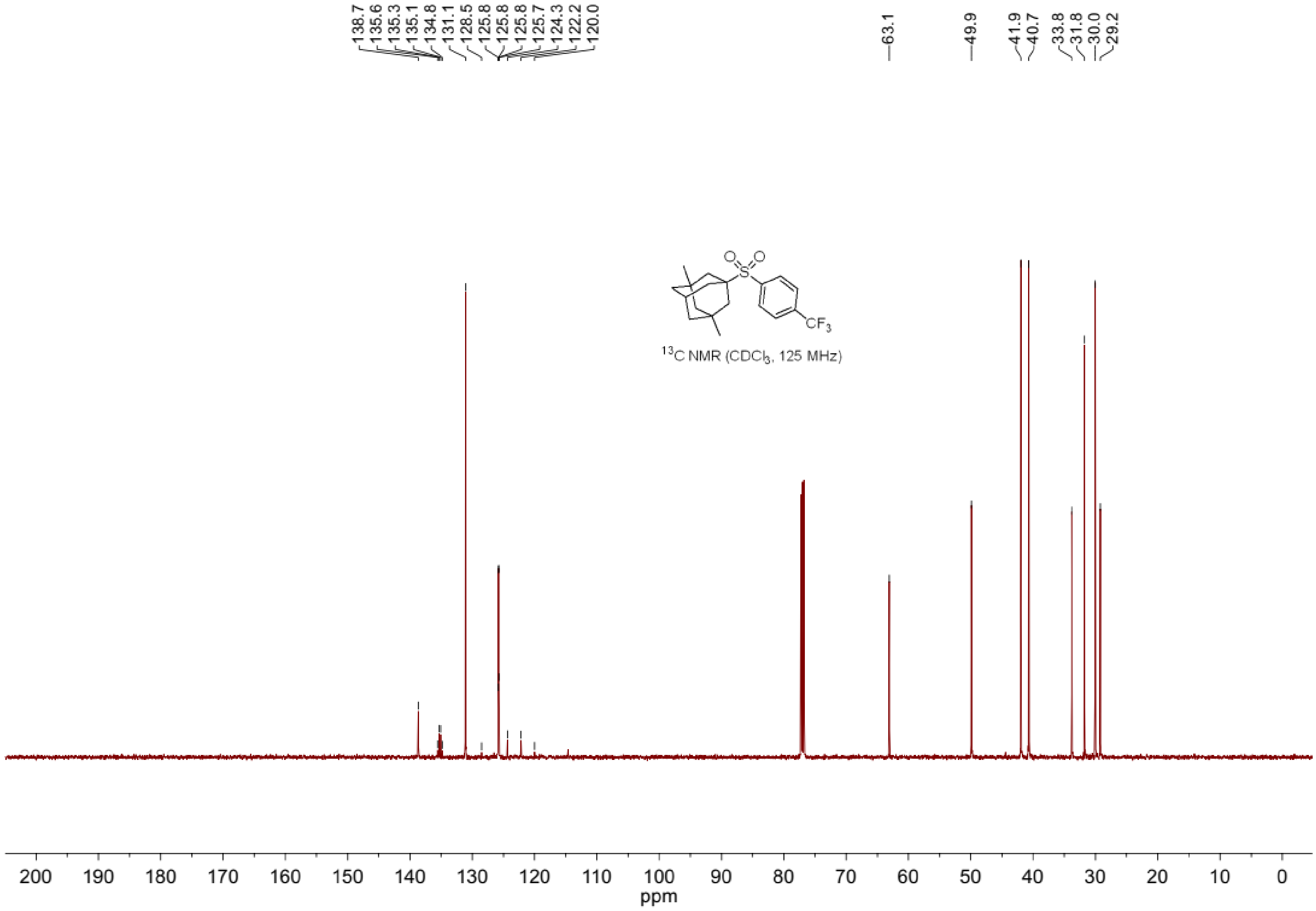
1-((4-(Trifluoromethyl)phenyl)sulfonyl)adamantine (4t)



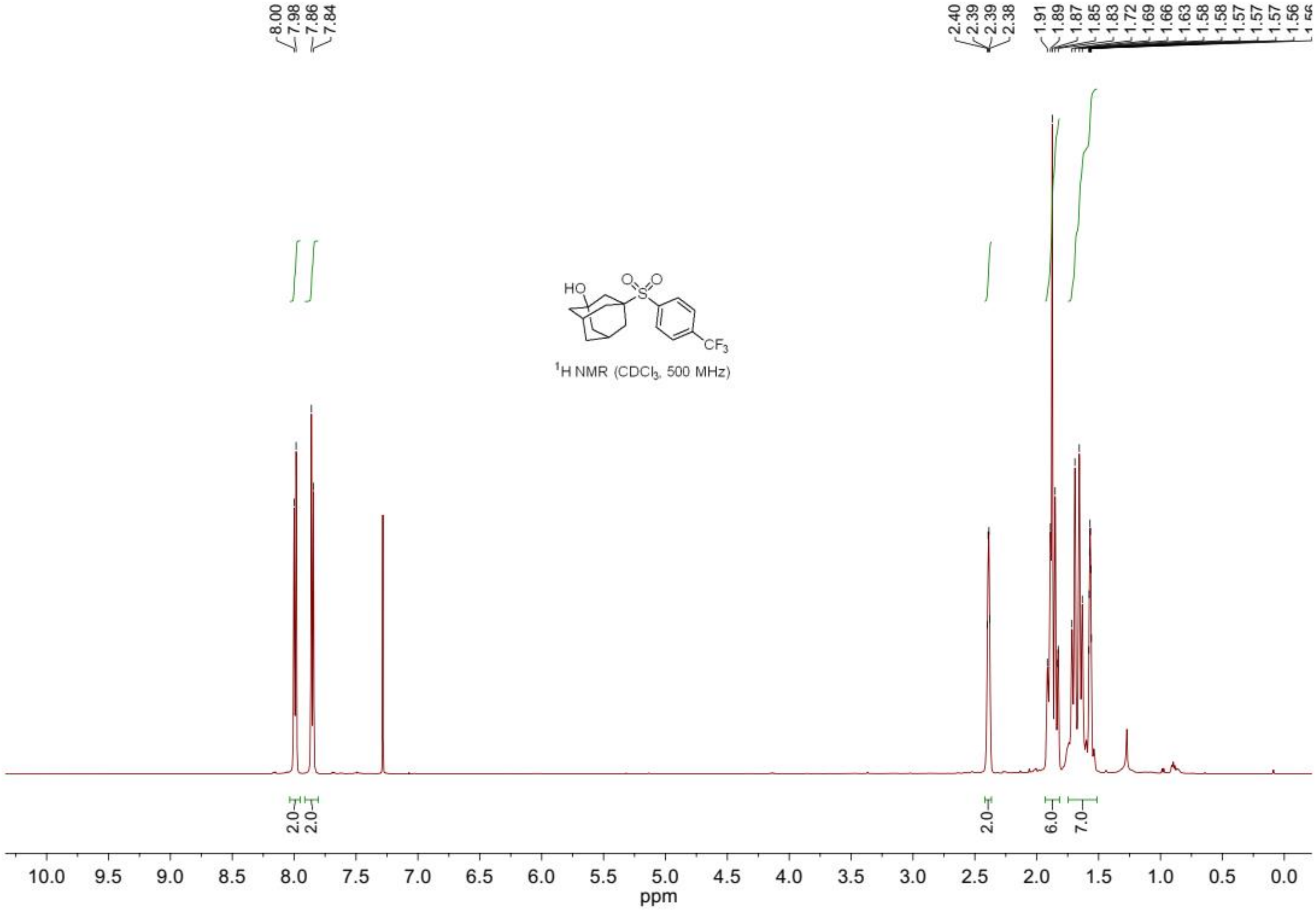
(1,3-Dimethyl-5-((4-(trifluoromethyl)phenyl)sulfonyl)adamantine (4u)



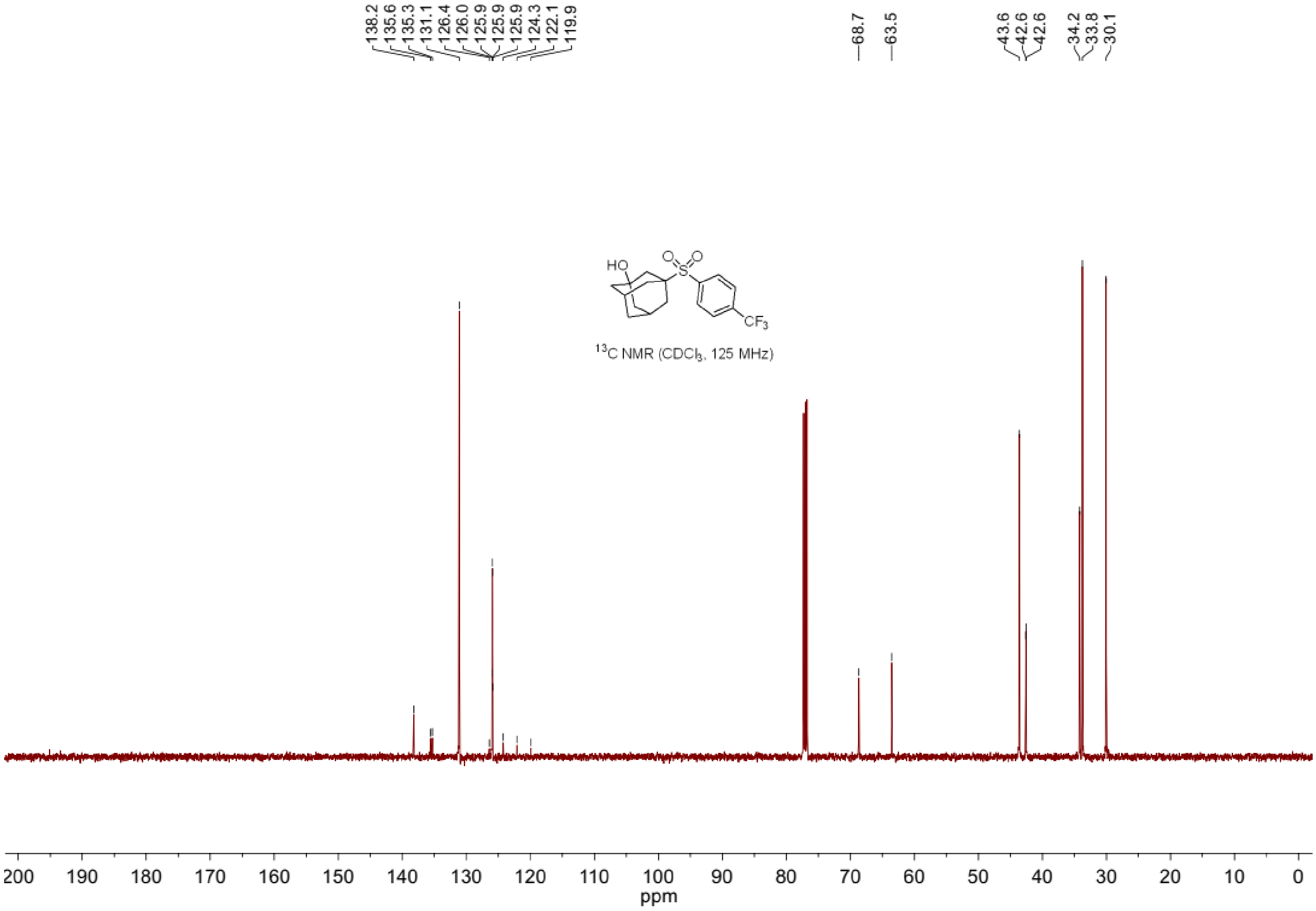
1,3-Dimethyl-5-((4-(trifluoromethyl)phenyl)sulfonyl)adamantine (4u)



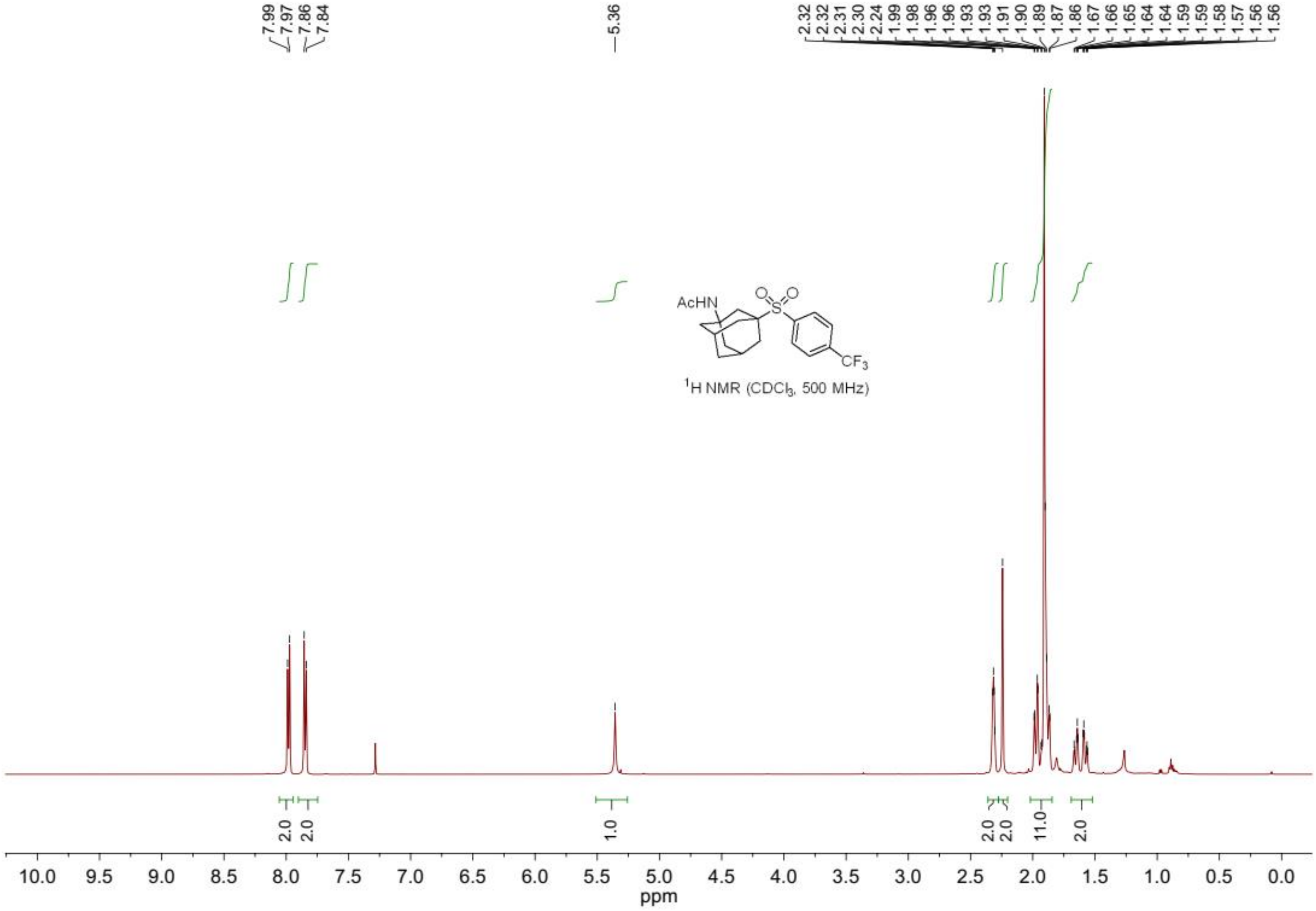
3-((4-(Trifluoromethyl)phenyl)sulfonyl)adamantan-1-ol (4v)



3-((4-(Trifluoromethyl)phenyl)sulfonyl)adamantan-1-ol (4v)



N-(-3-((4-(Trifluoromethyl)phenyl)sulfonyl)adamantan-1-yl)acetamide (4w)



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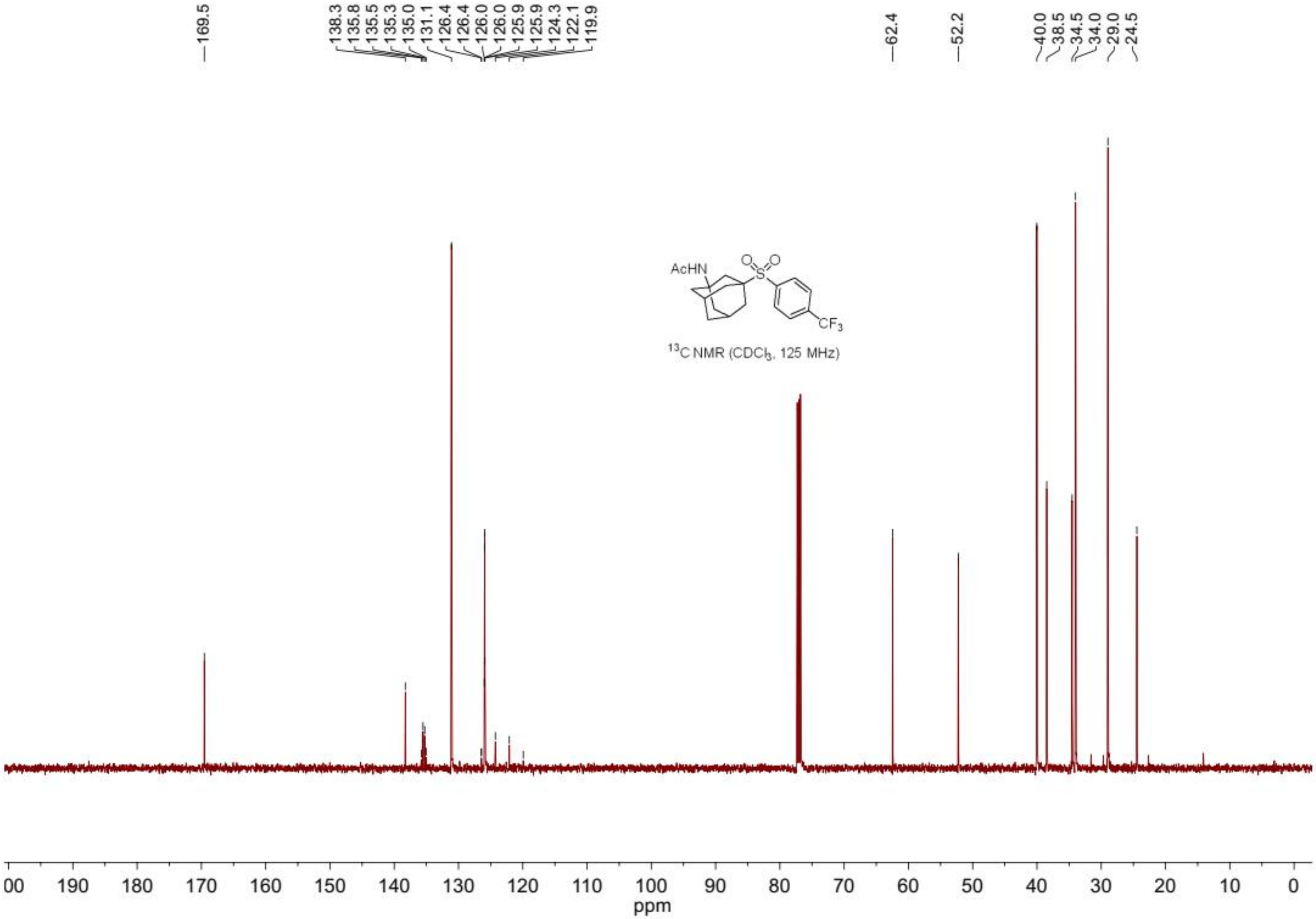
N-(-3-((4-(Trifluoromethyl)phenyl)sulfonyl)adamantan-1-yl)acetamide (4w)



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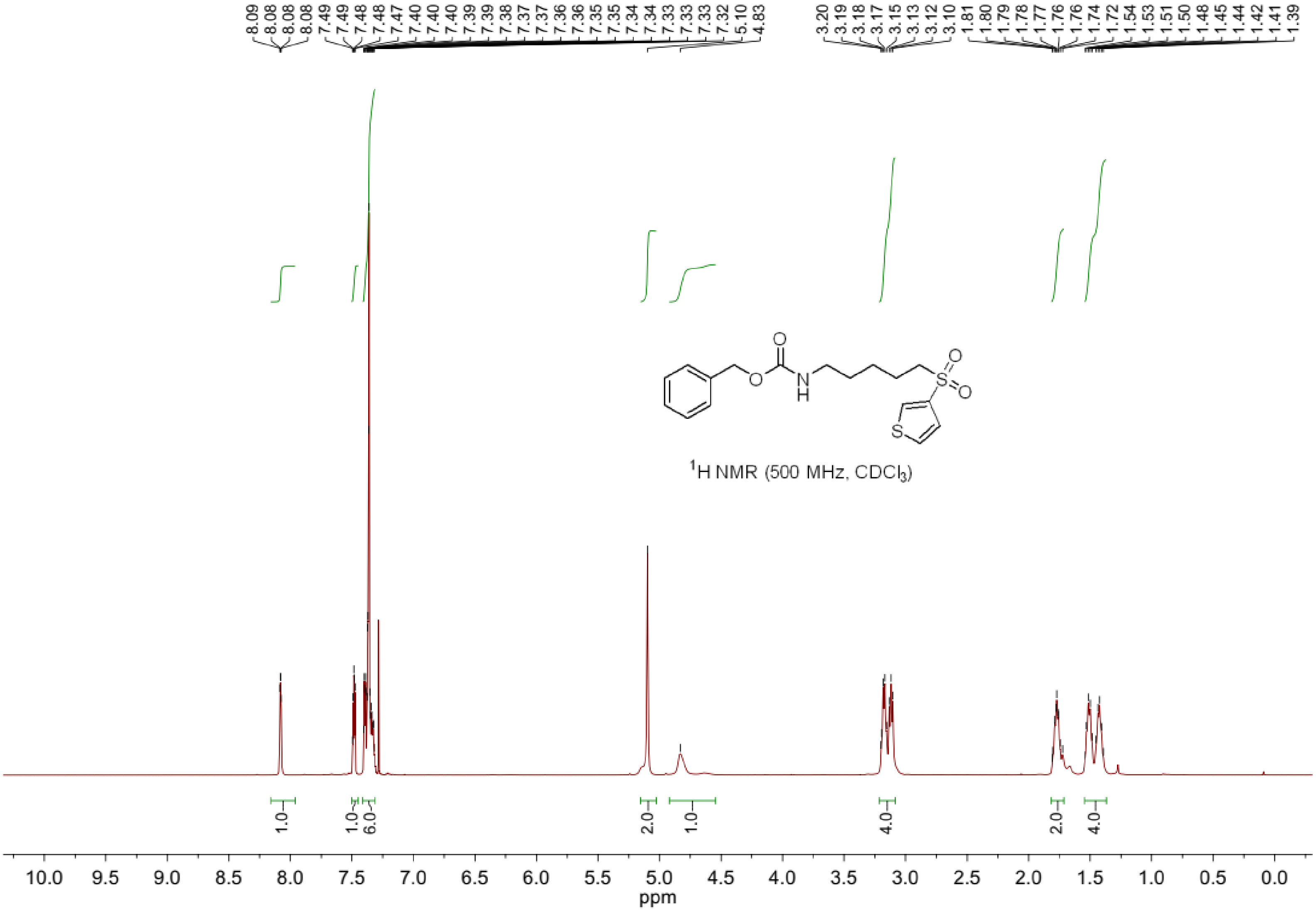
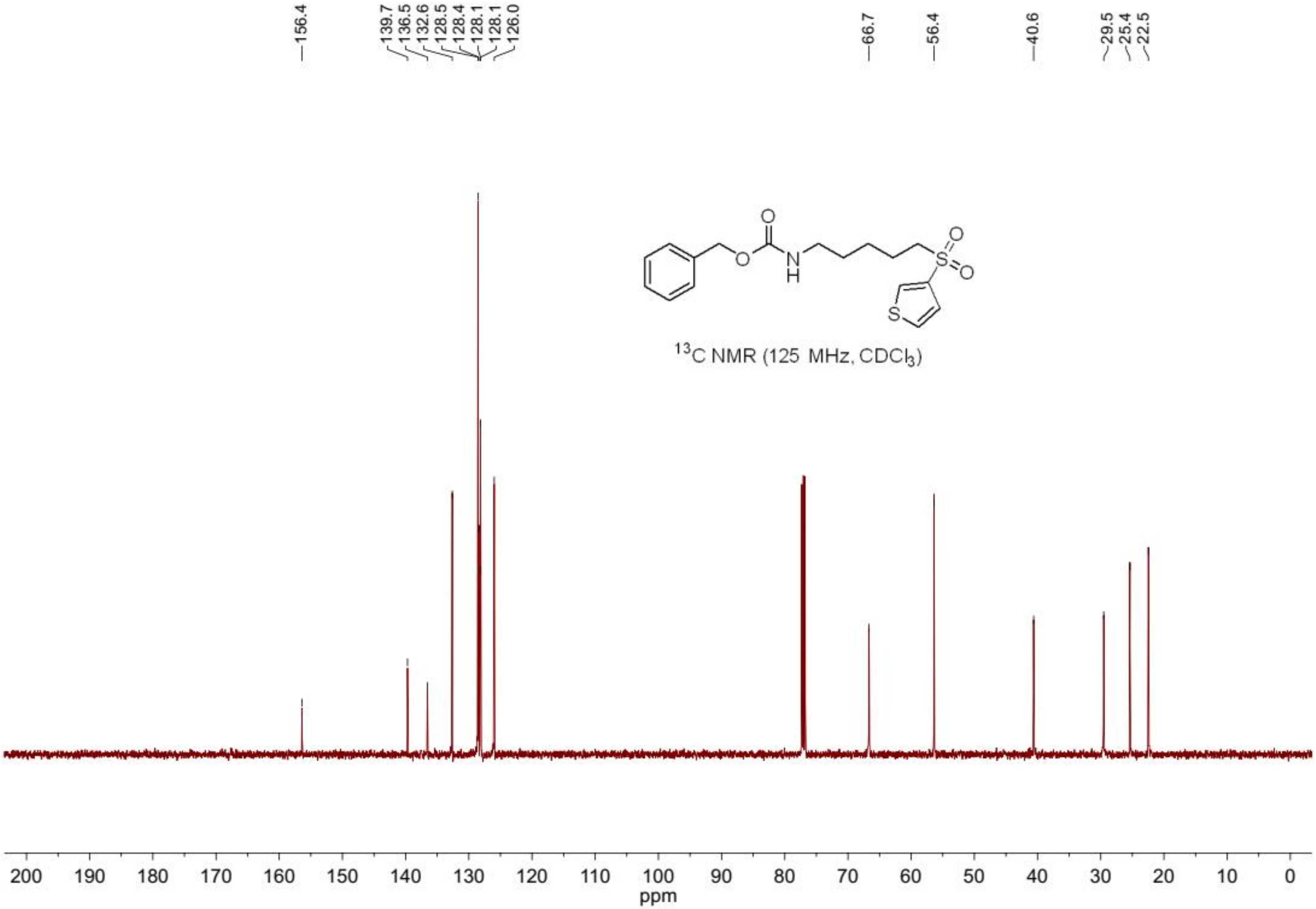
Benzyl (5-(thiophen-3-ylsulfonyl)pentyl)carbamate (4x)



Benzyl (5-(thiophen-3-ylsulfonyl)pentyl)carbamate (4x)



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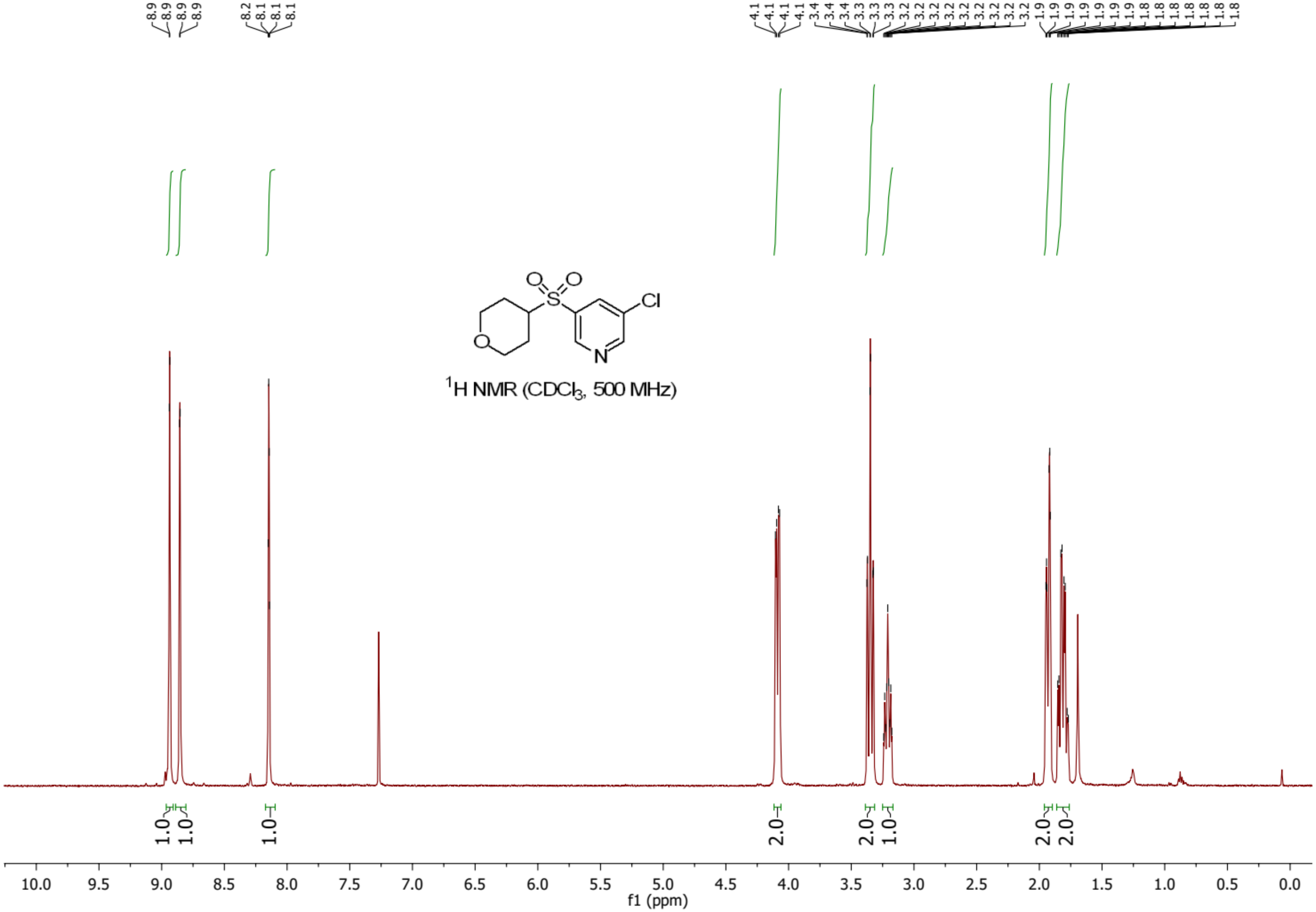
3-Chloro-5-((tetrahydro-2*H*-pyran-4-yl)sulfonyl)pyridine (4y)



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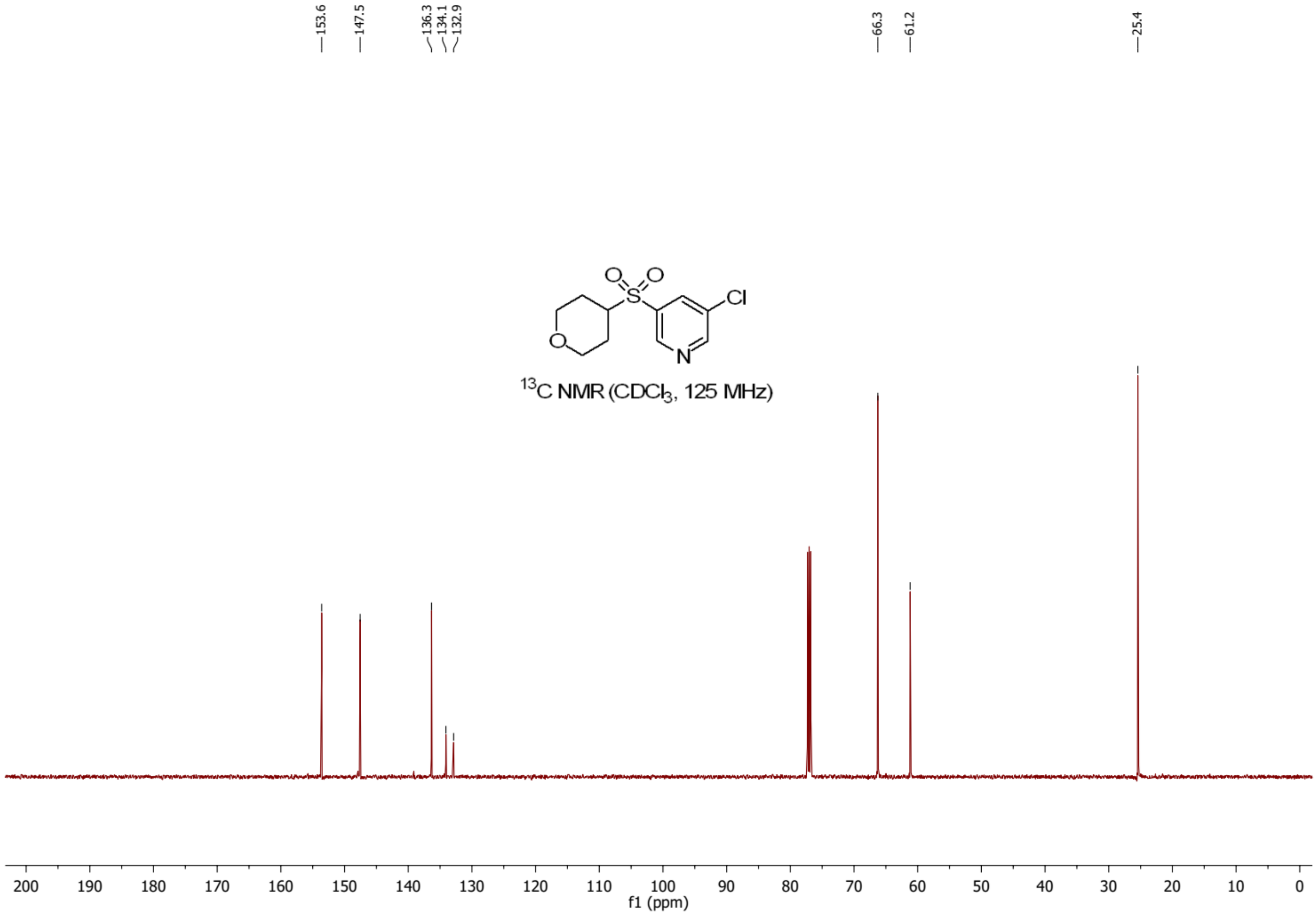
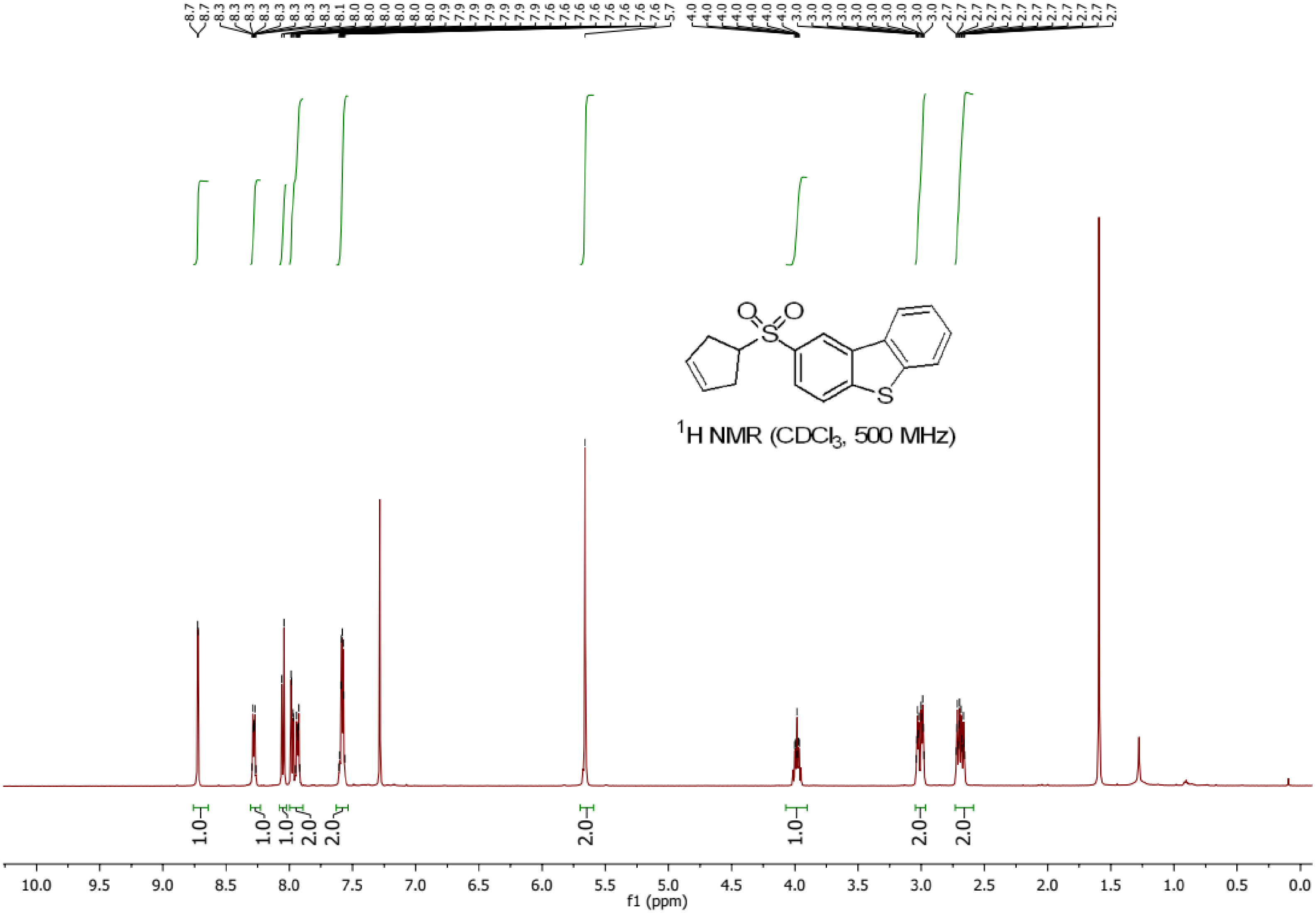
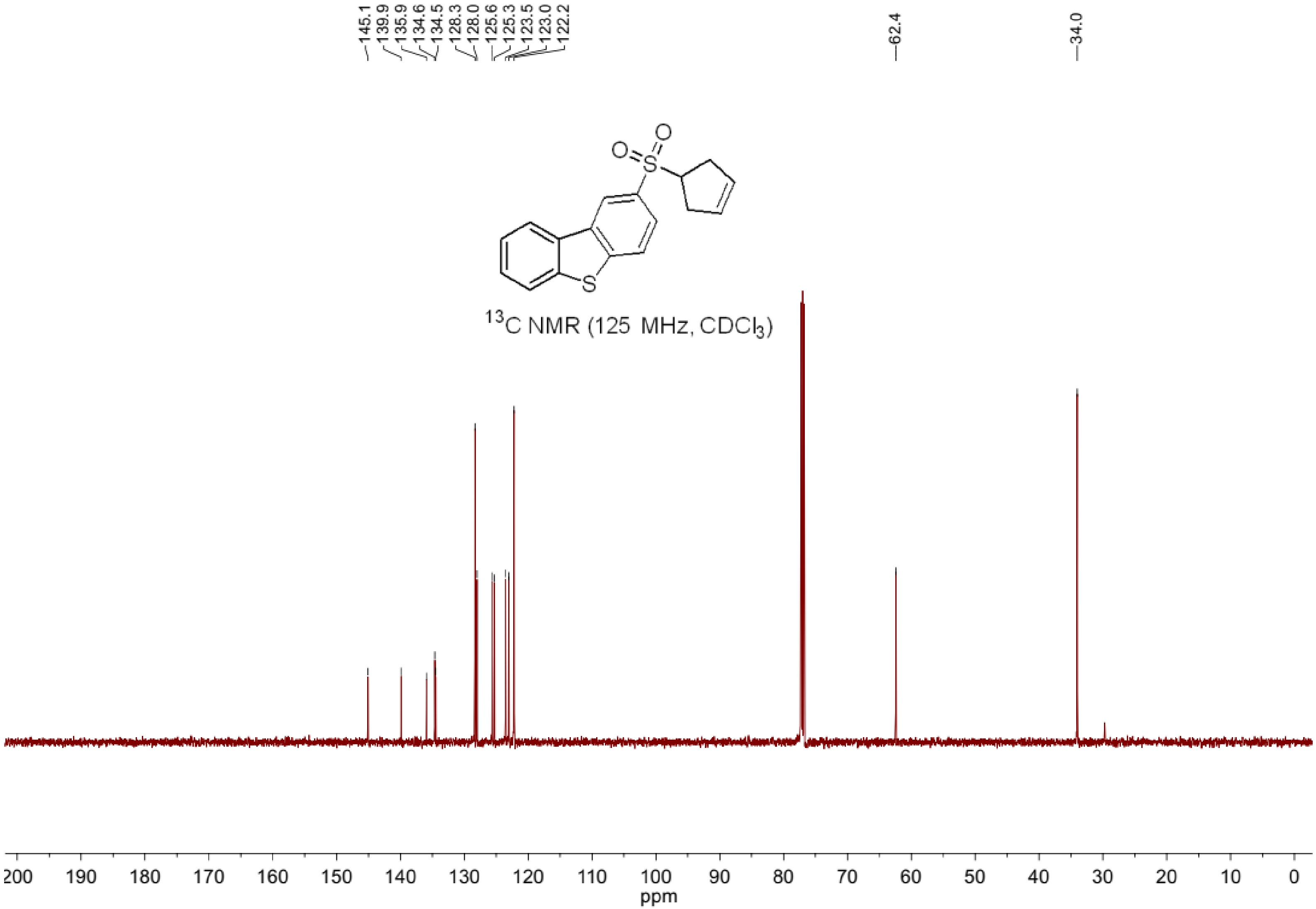
3-Chloro-5-((tetrahydro-2*H*-pyran-4-yl)sulfonyl)pyridine (4y)



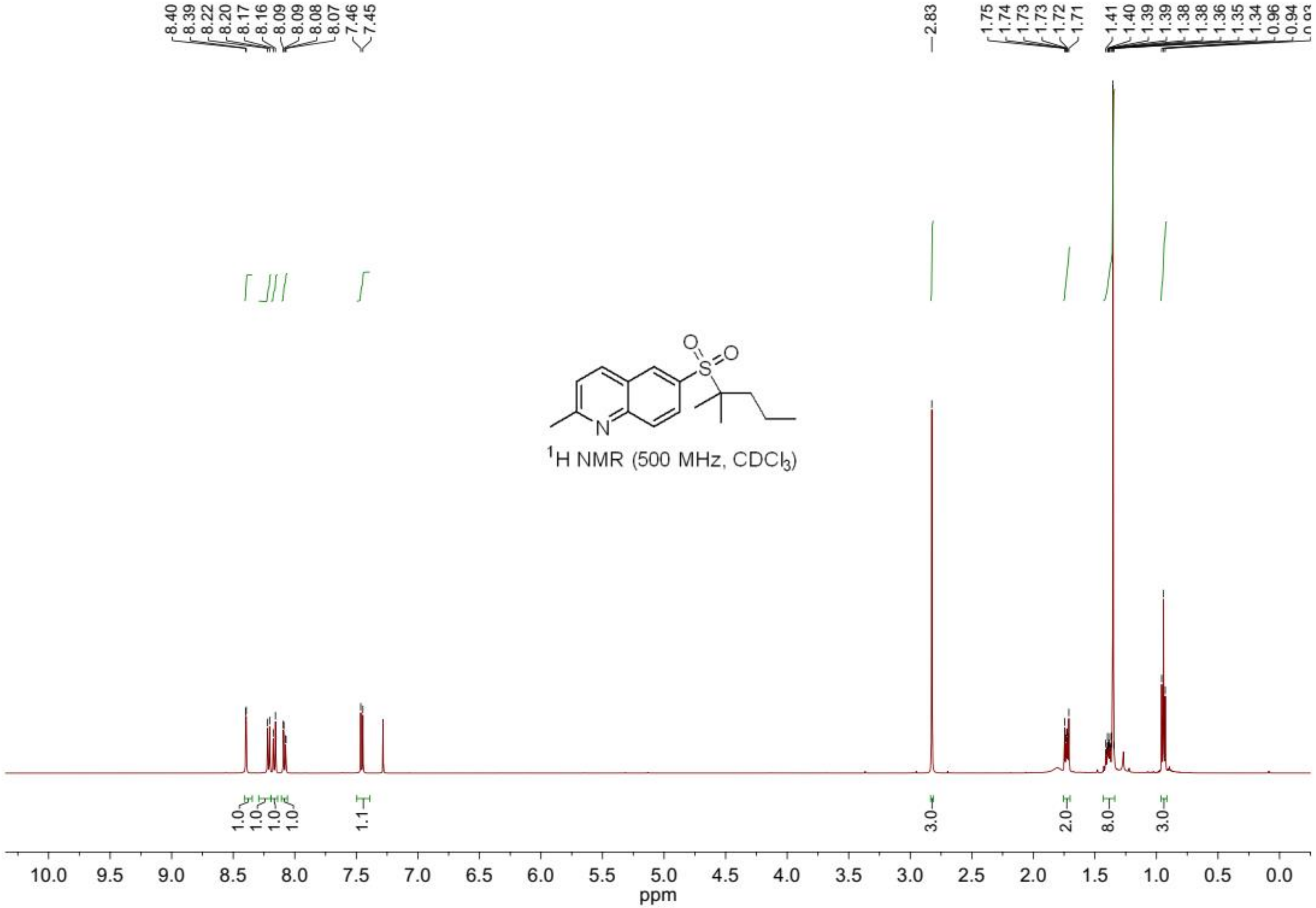
2-(Cyclopent-3-en-1-ylsulfonyl)dibenzo[*b*,*d*]thiophene (4z)



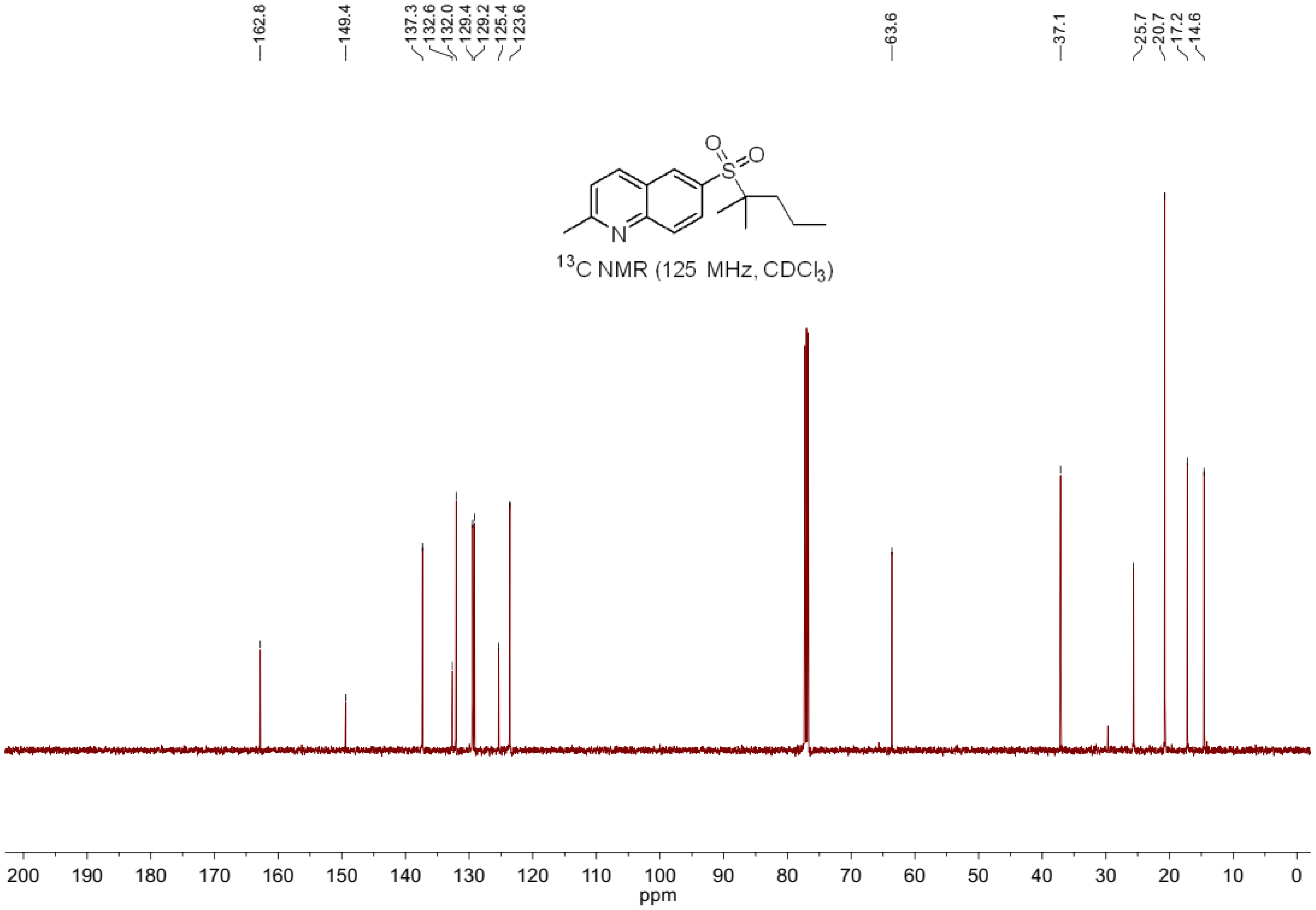
2-(Cyclopent-3-en-1-ylsulfonyl)dibenzo[*b*,*d*]thiophene (4z)



2-Methyl-6-((2-methylpentan-2-yl)sulfonyl)quinoline (4aa)



2-Methyl-6-((2-methylpentan-2-yl)sulfonyl)quinoline (4aa)



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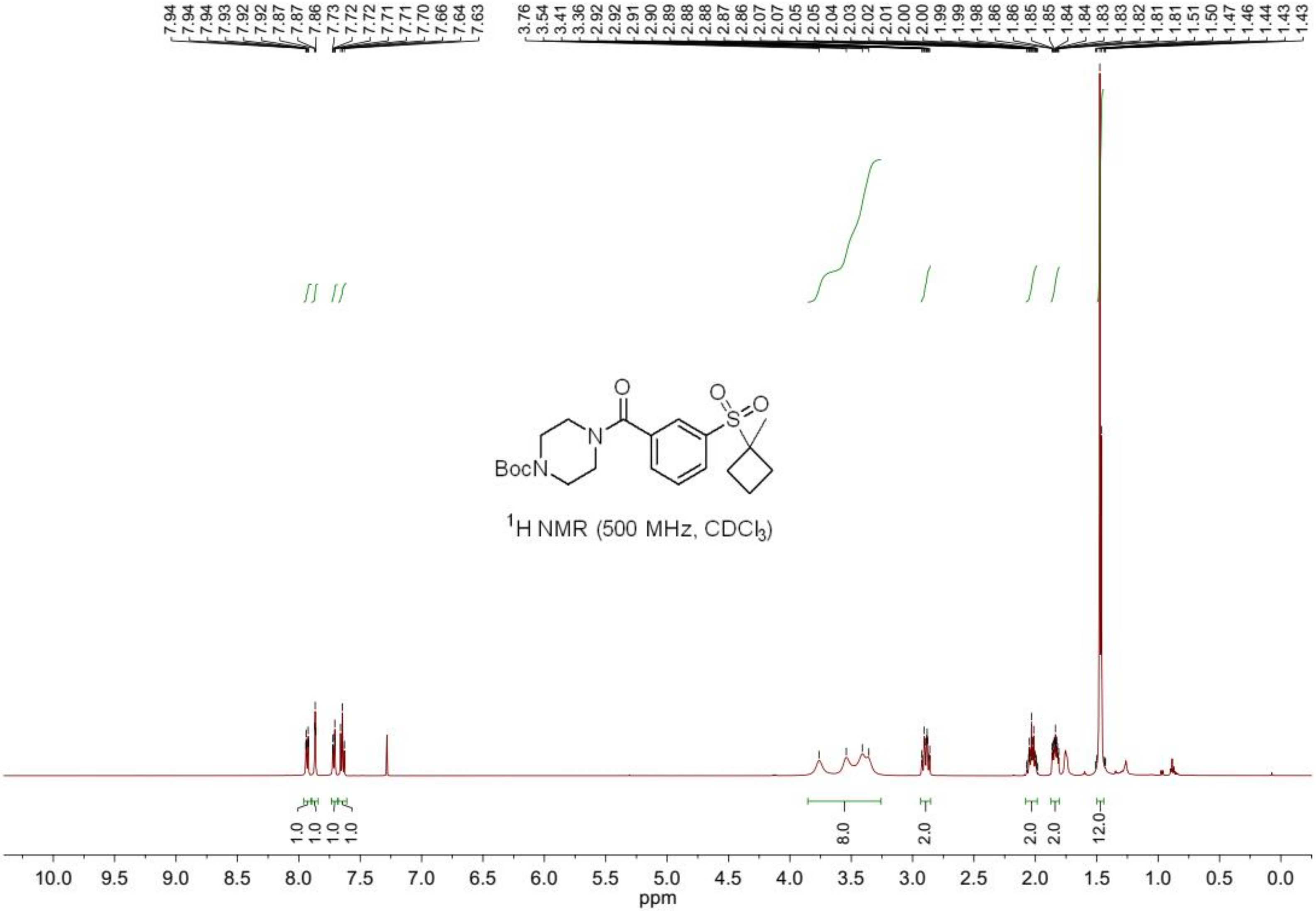
tert-Butyl 4-(3-(cyclobutylsulfonyl)benzoyl)piperazine-1-carboxylate (4ab)



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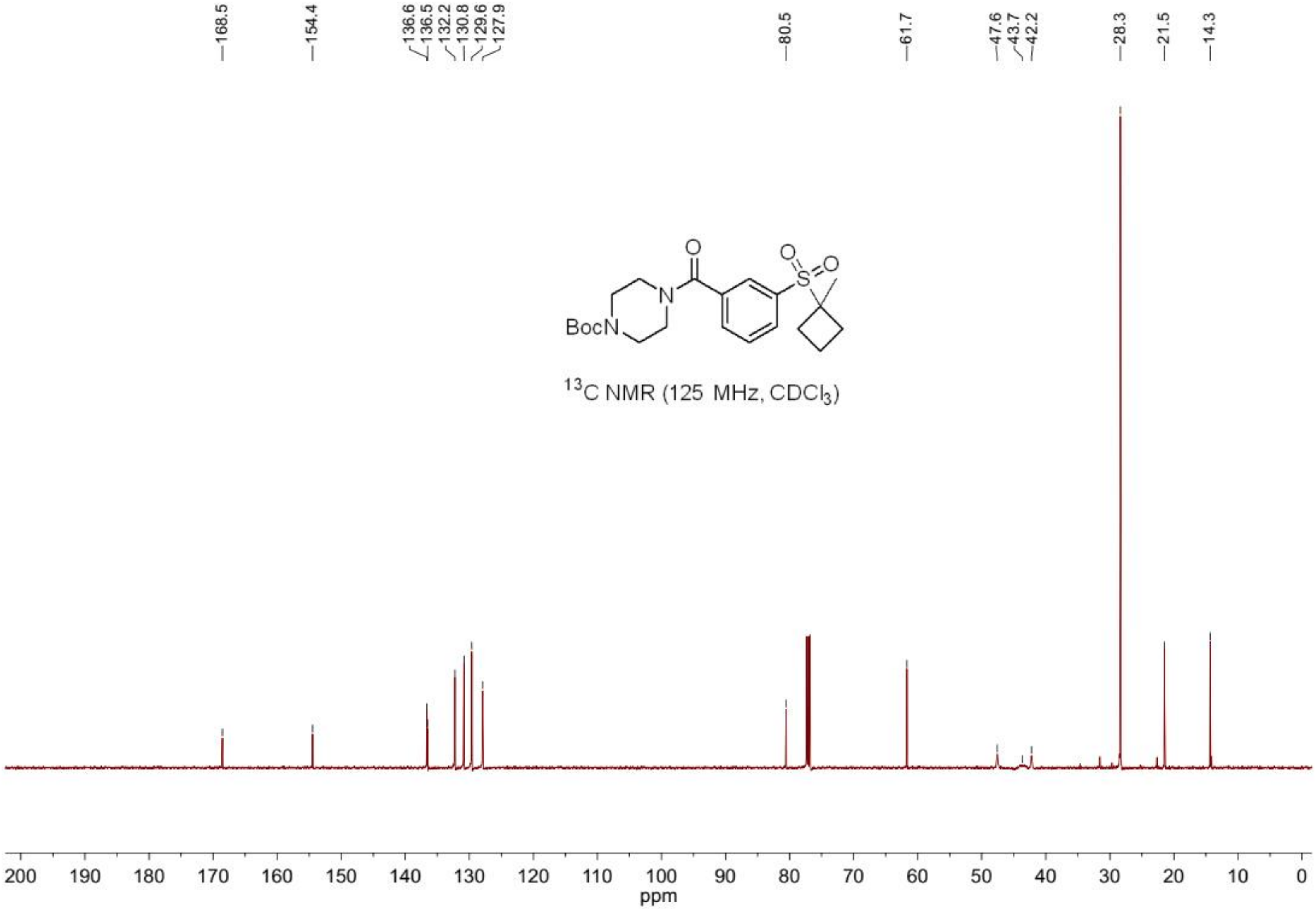
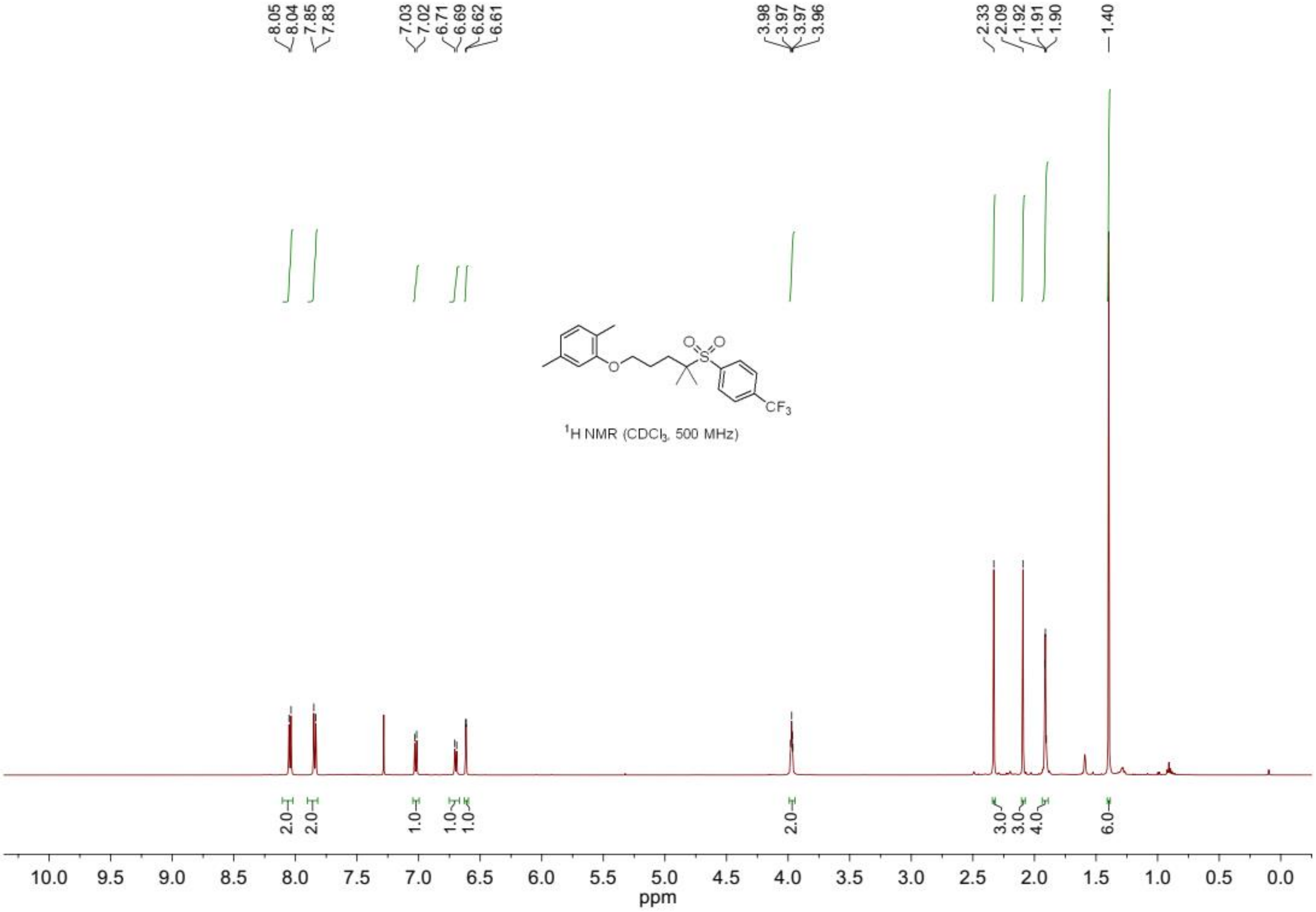
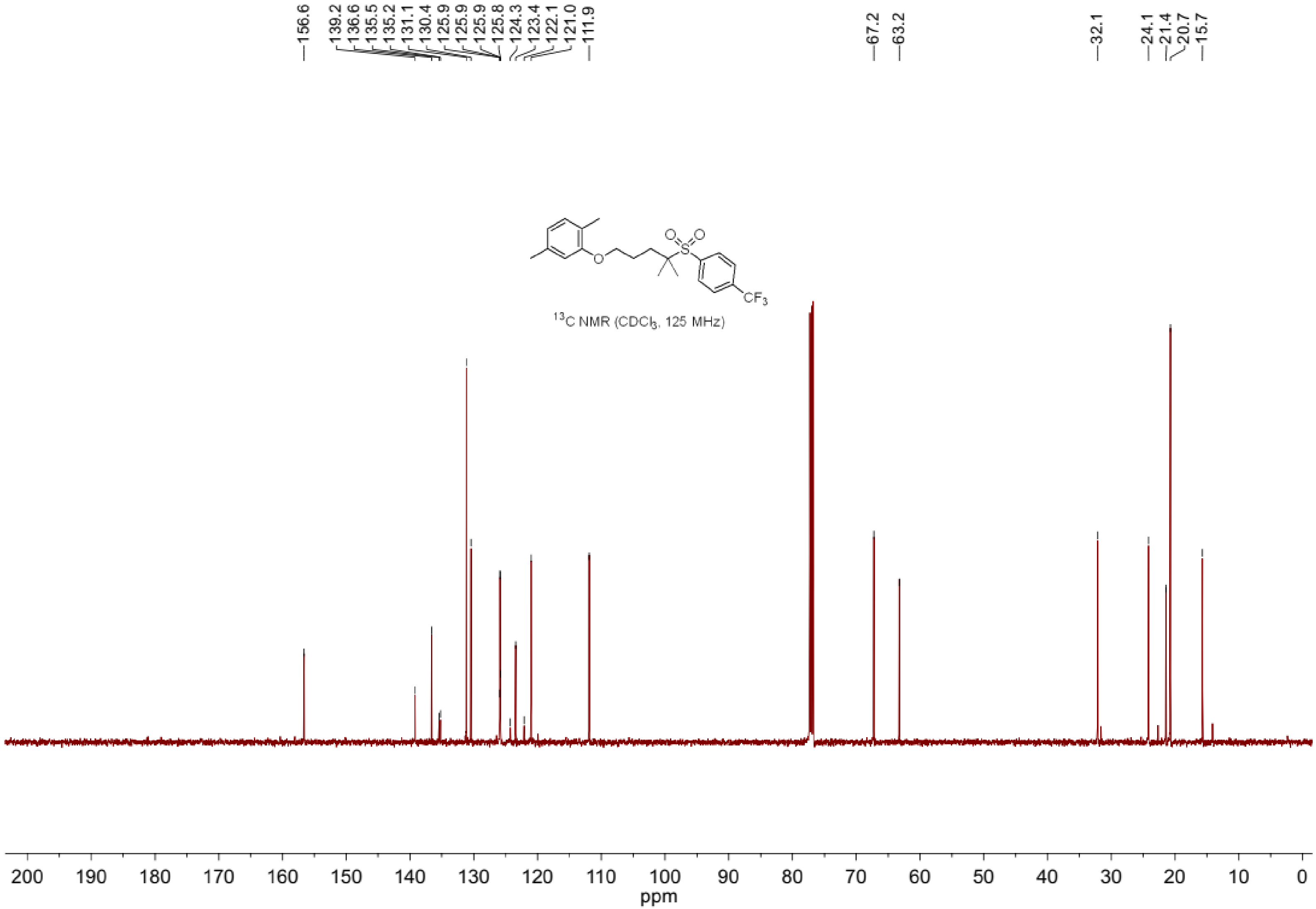
tert-Butyl 4-(3-(cyclobutylsulfonyl)benzoyl)piperazine-1-carboxylate (4ab)



1,4-Dimethyl-2-((4-methyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)pentyl)oxy)benzene (5a)



1,4-Dimethyl-2-((4-methyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)pentyl)oxy)benzene (5a)



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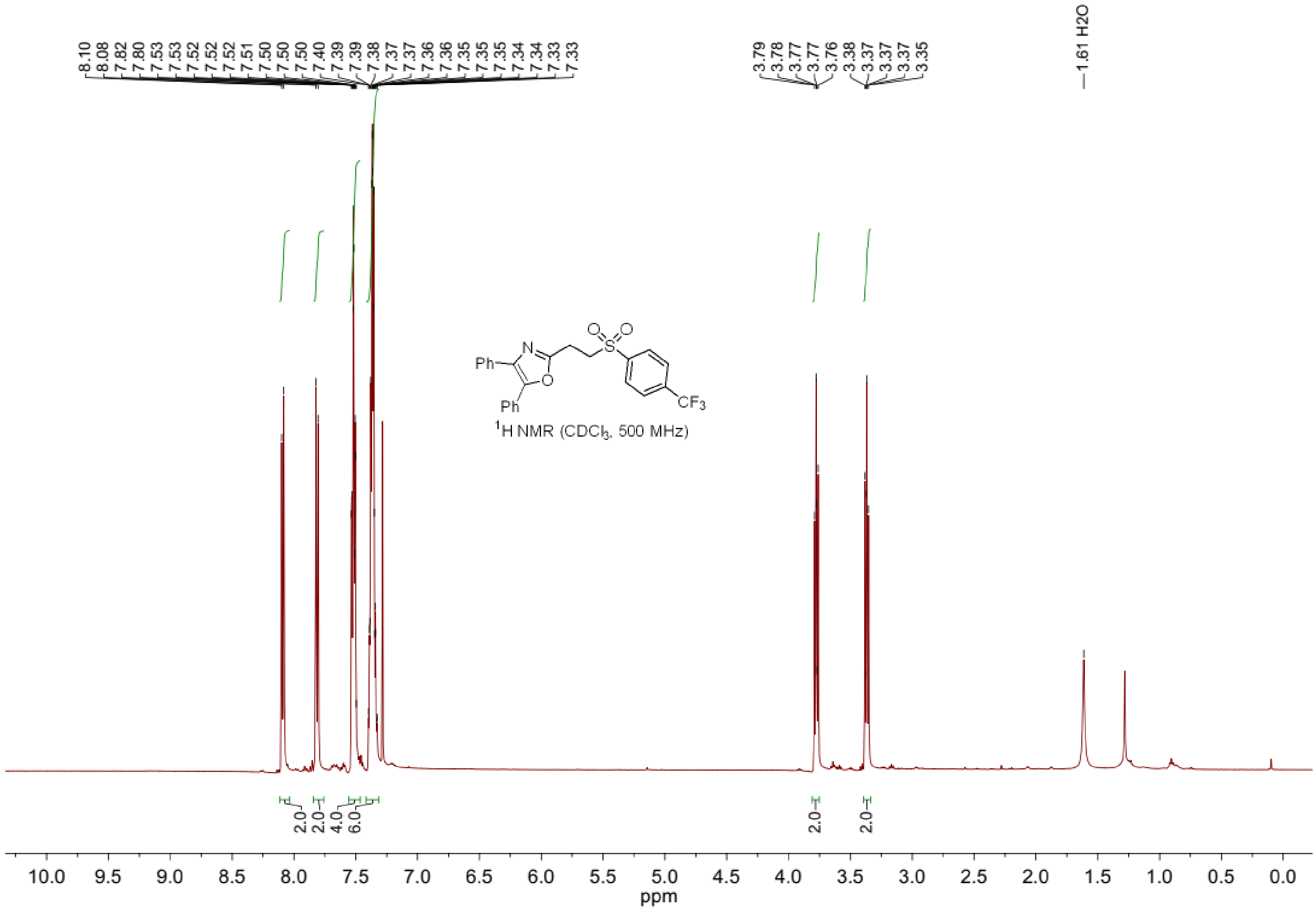
4,5-Diphenyl-2-(2-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)oxazole (5b)



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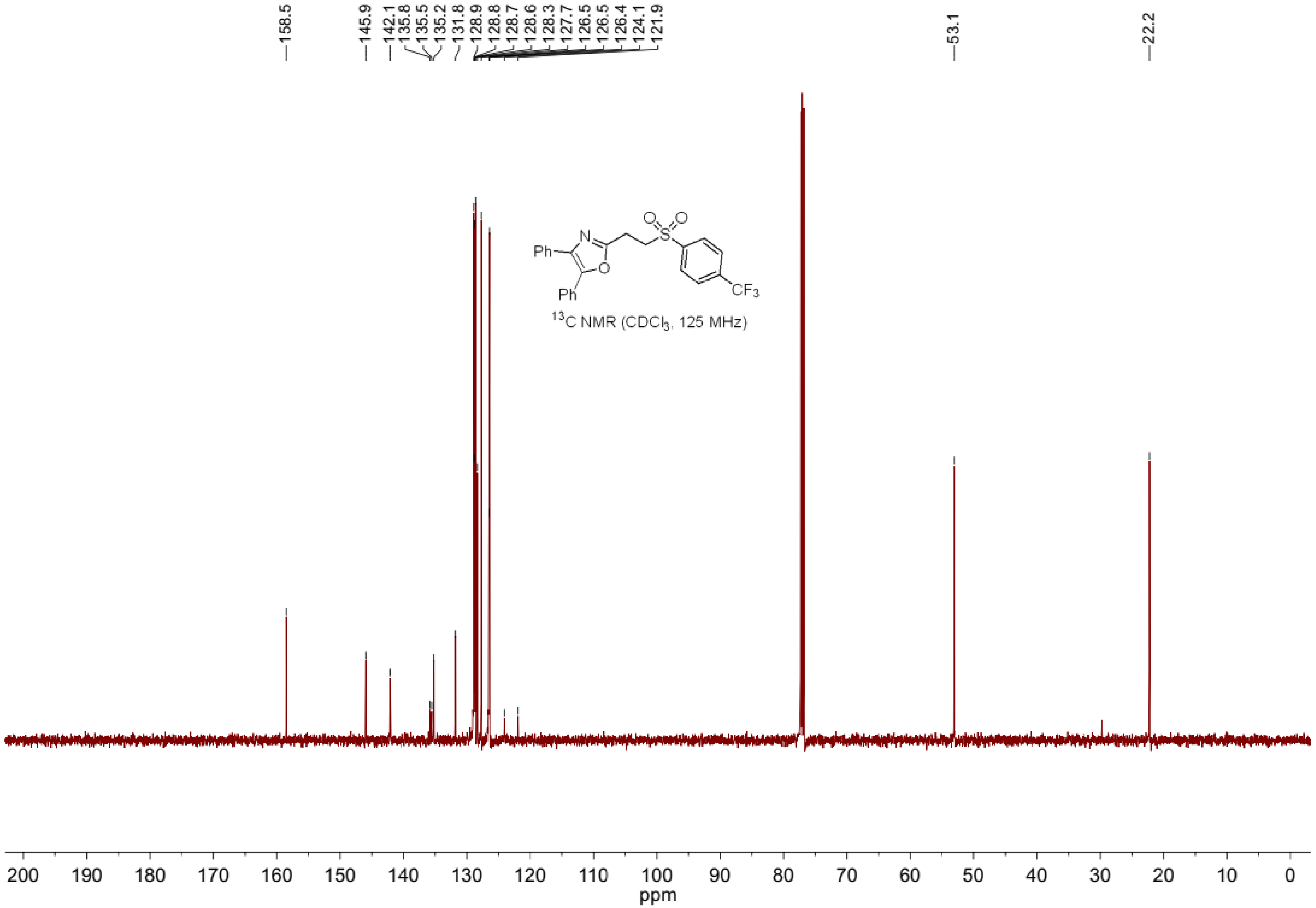
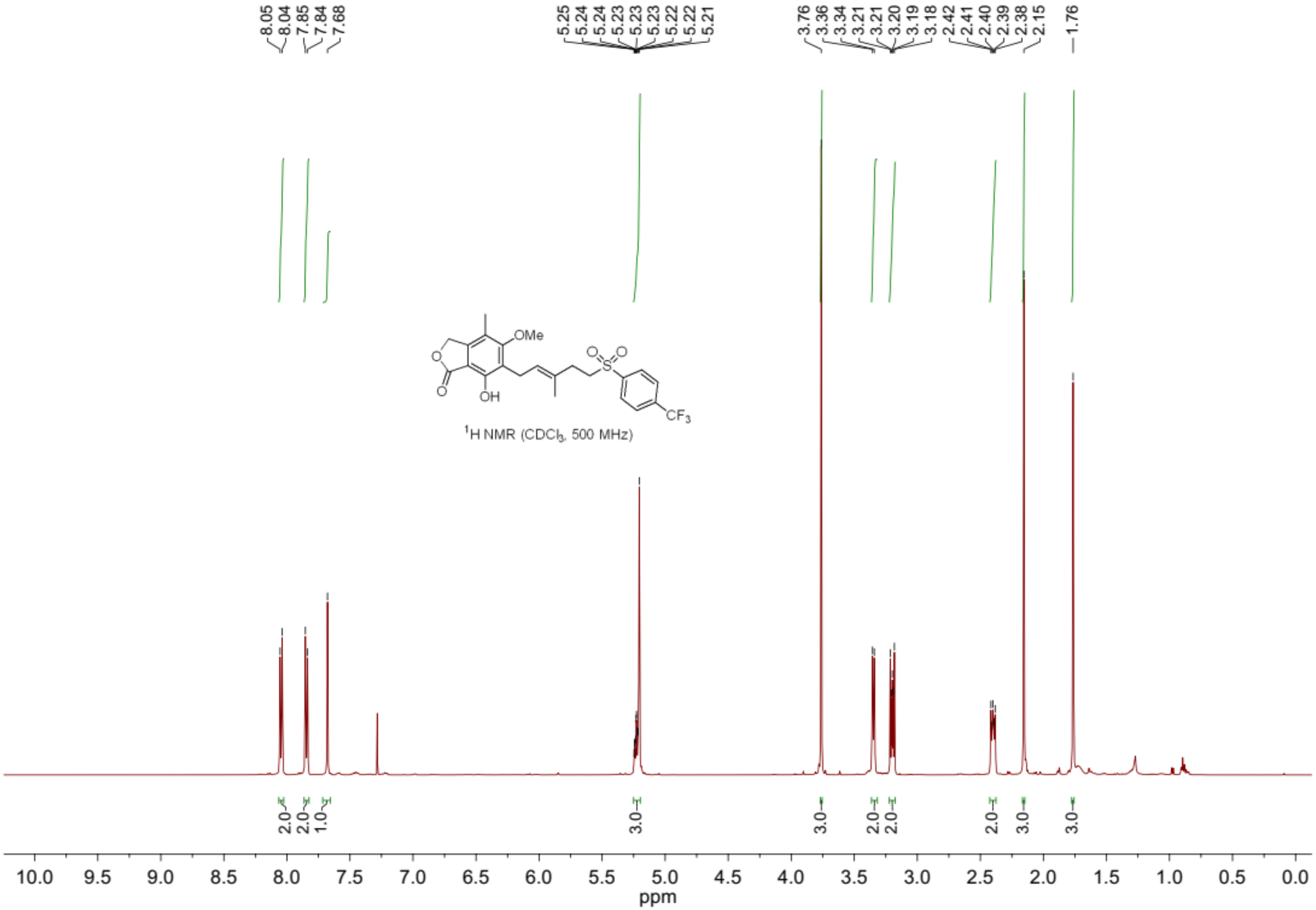
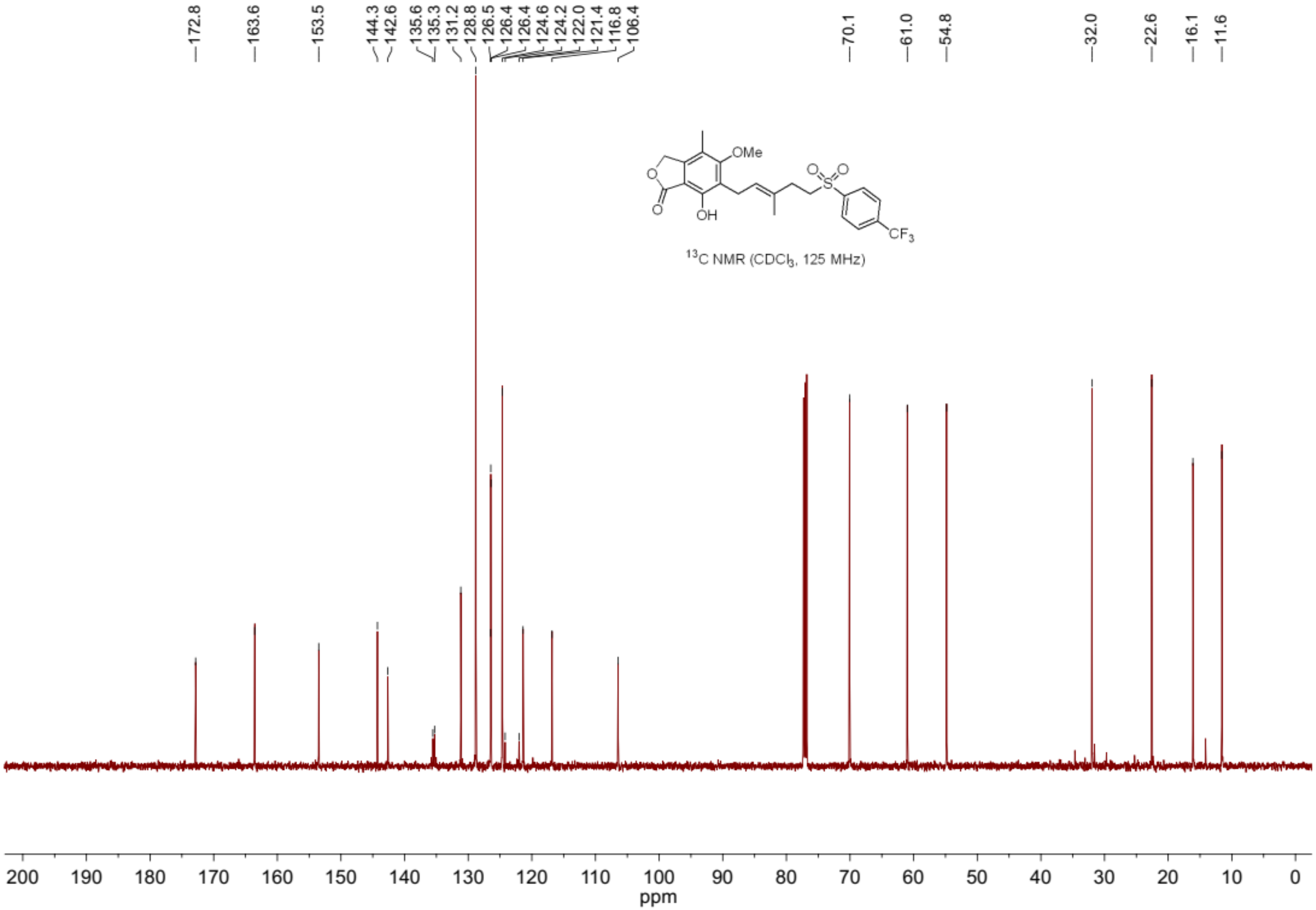
4,5-Diphenyl-2-(2-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)oxazole (5b)



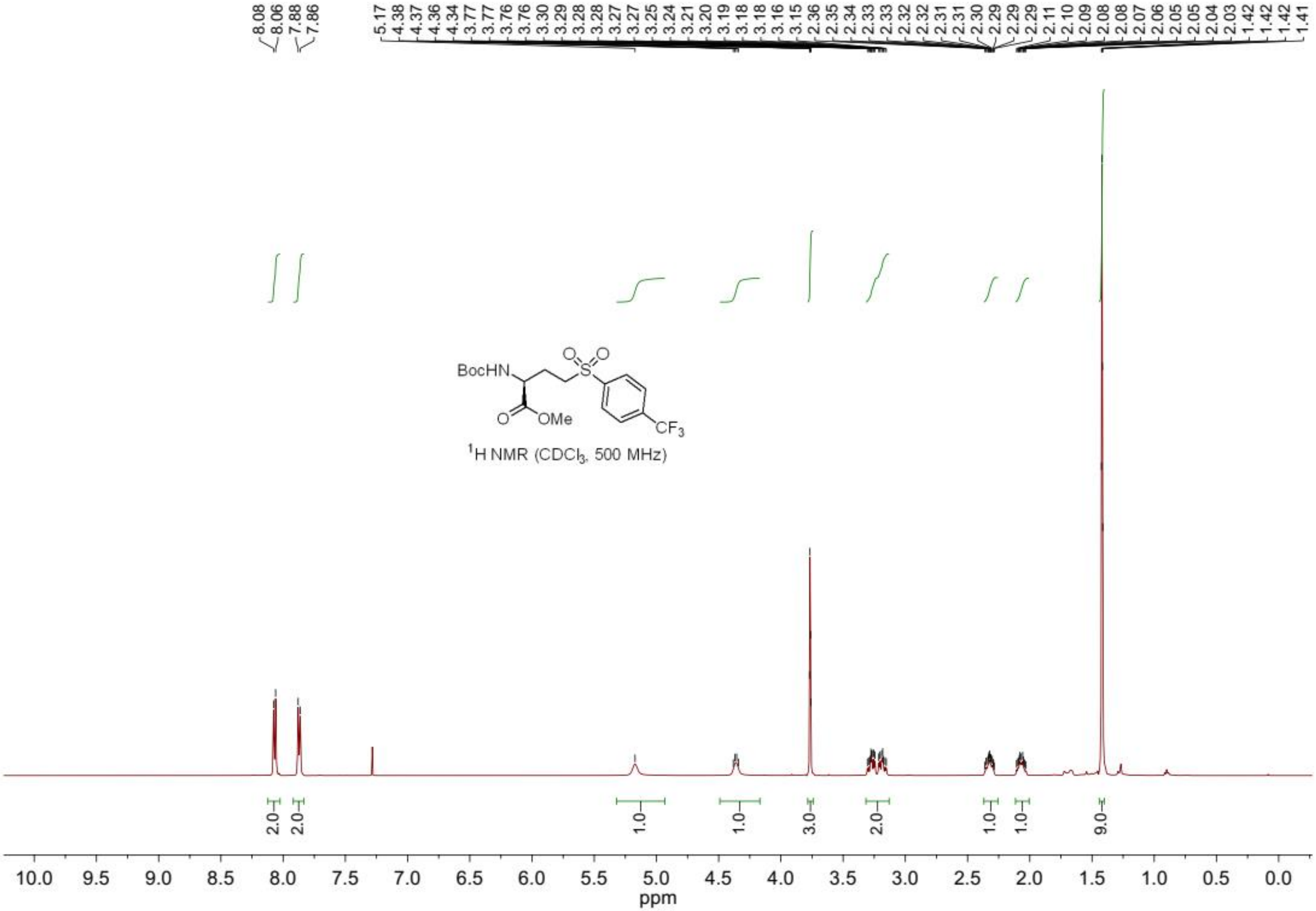
(*E*)-7-Hydroxy-5-methoxy-4-methyl-6-(3-methyl-5-((4-(trifluoromethyl)phenyl)sulfonyl)pent-2-en-1-yl)isobenzofuran-1(3*H*)-one (5c)



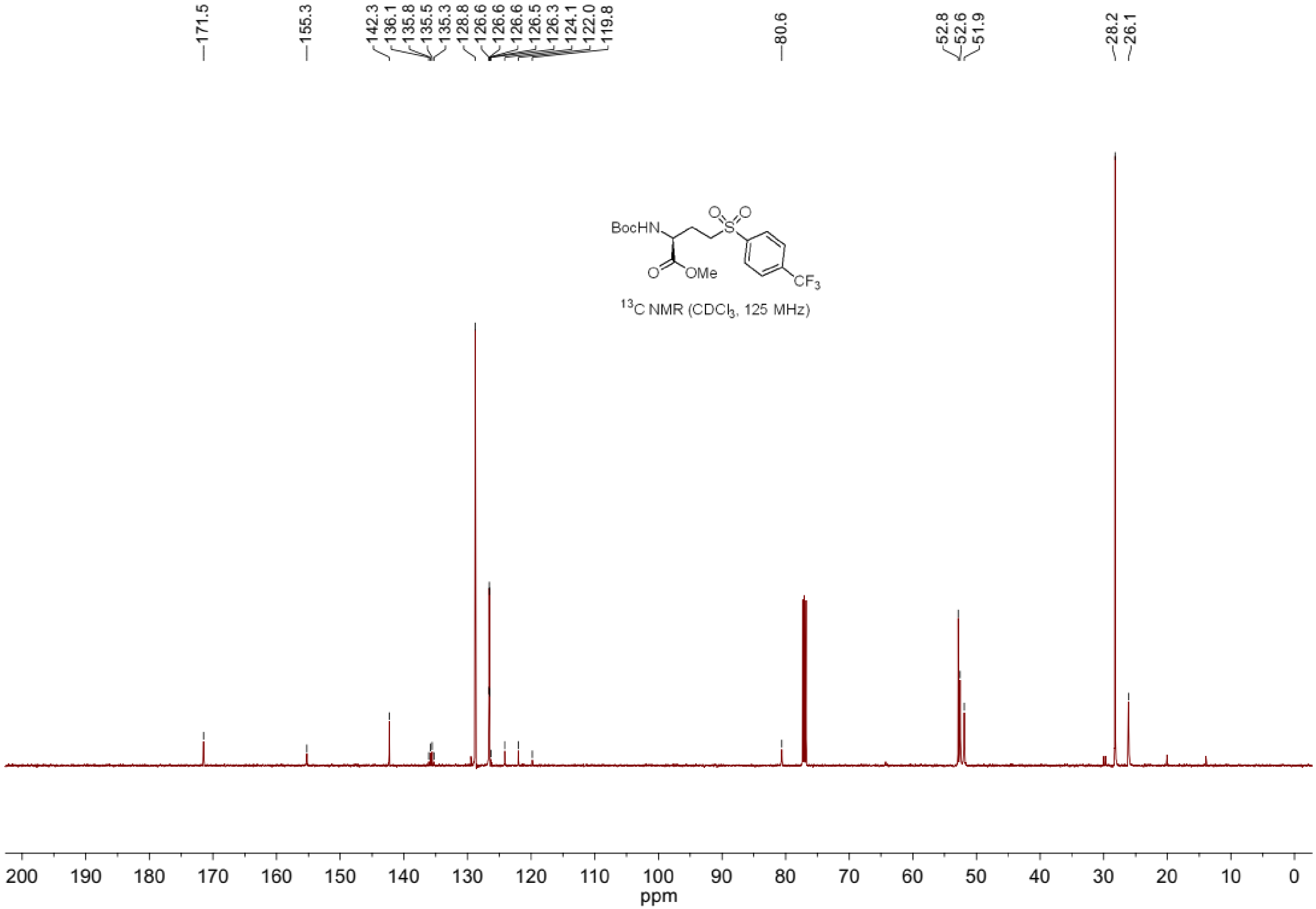
(*E*)-7-Hydroxy-5-methoxy-4-methyl-6-(3-methyl-5-((4-(trifluoromethyl)phenyl)sulfonyl)pent-2-en-1-yl)isobenzofuran-1(3*H*)-one (5c)



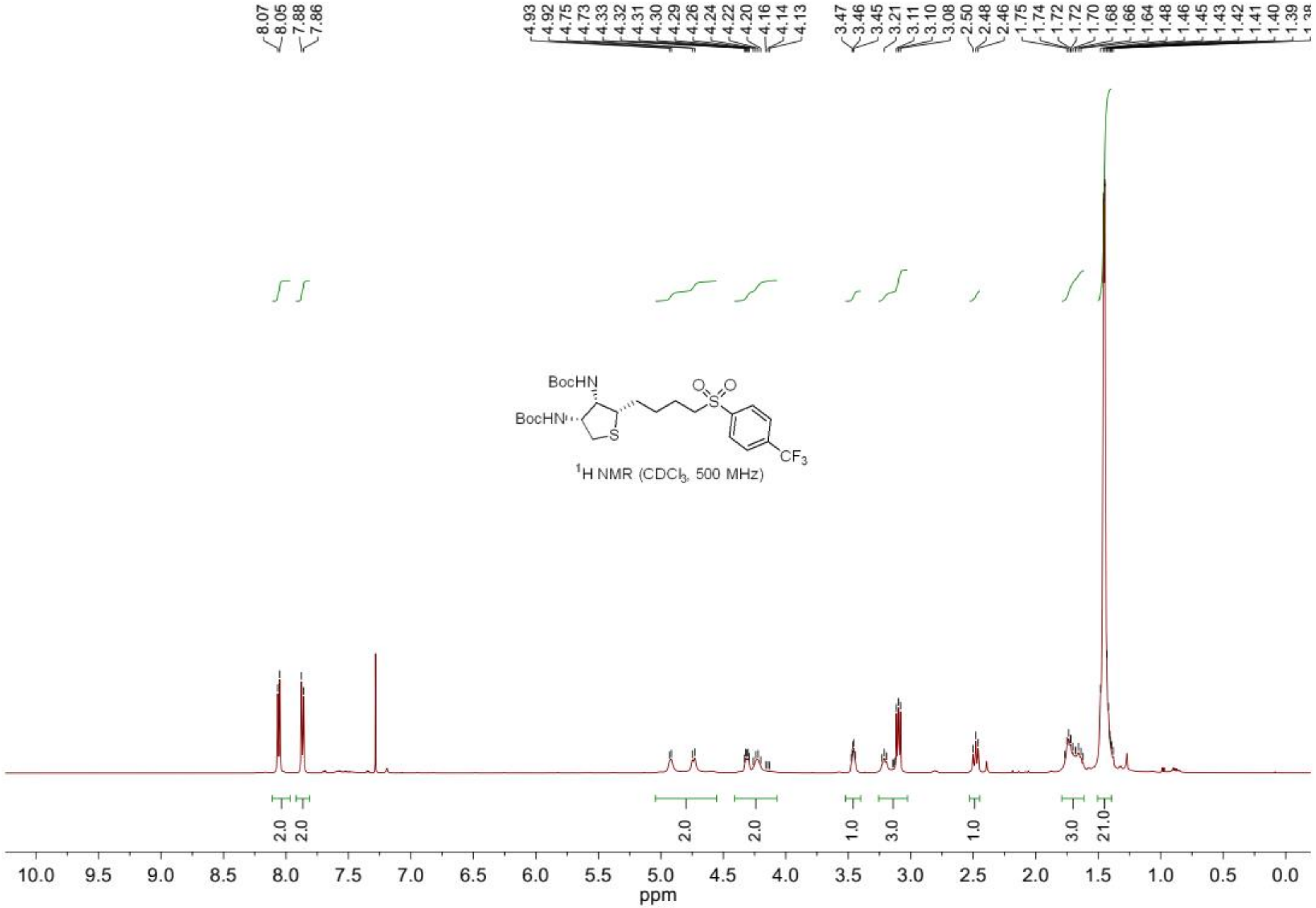
Methyl (*S*)-2-((tert-butoxycarbonyl)amino)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butanoate (5d)



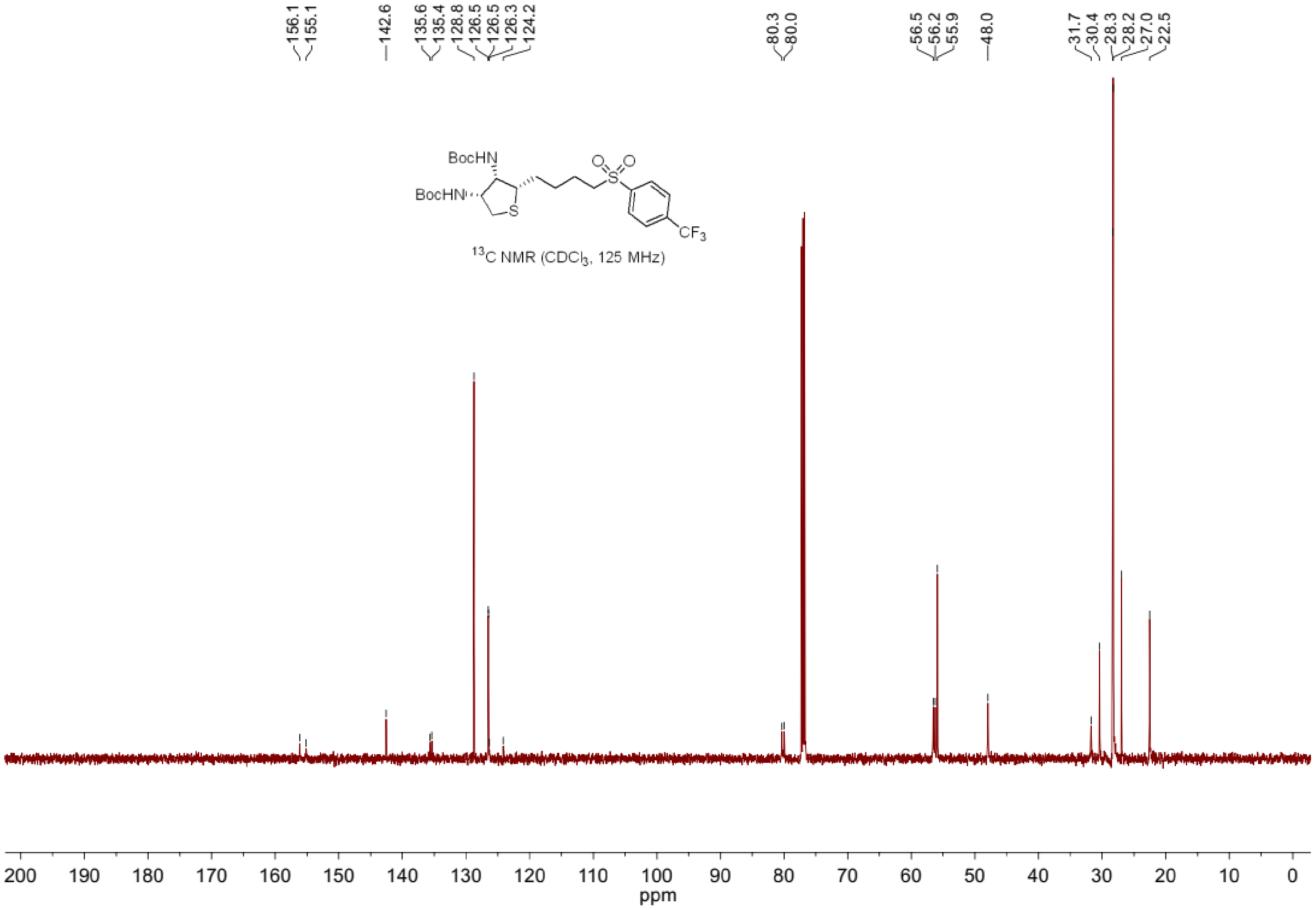
Methyl (*S*)-2-((tert-butoxycarbonyl)amino)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butanoate (5d)



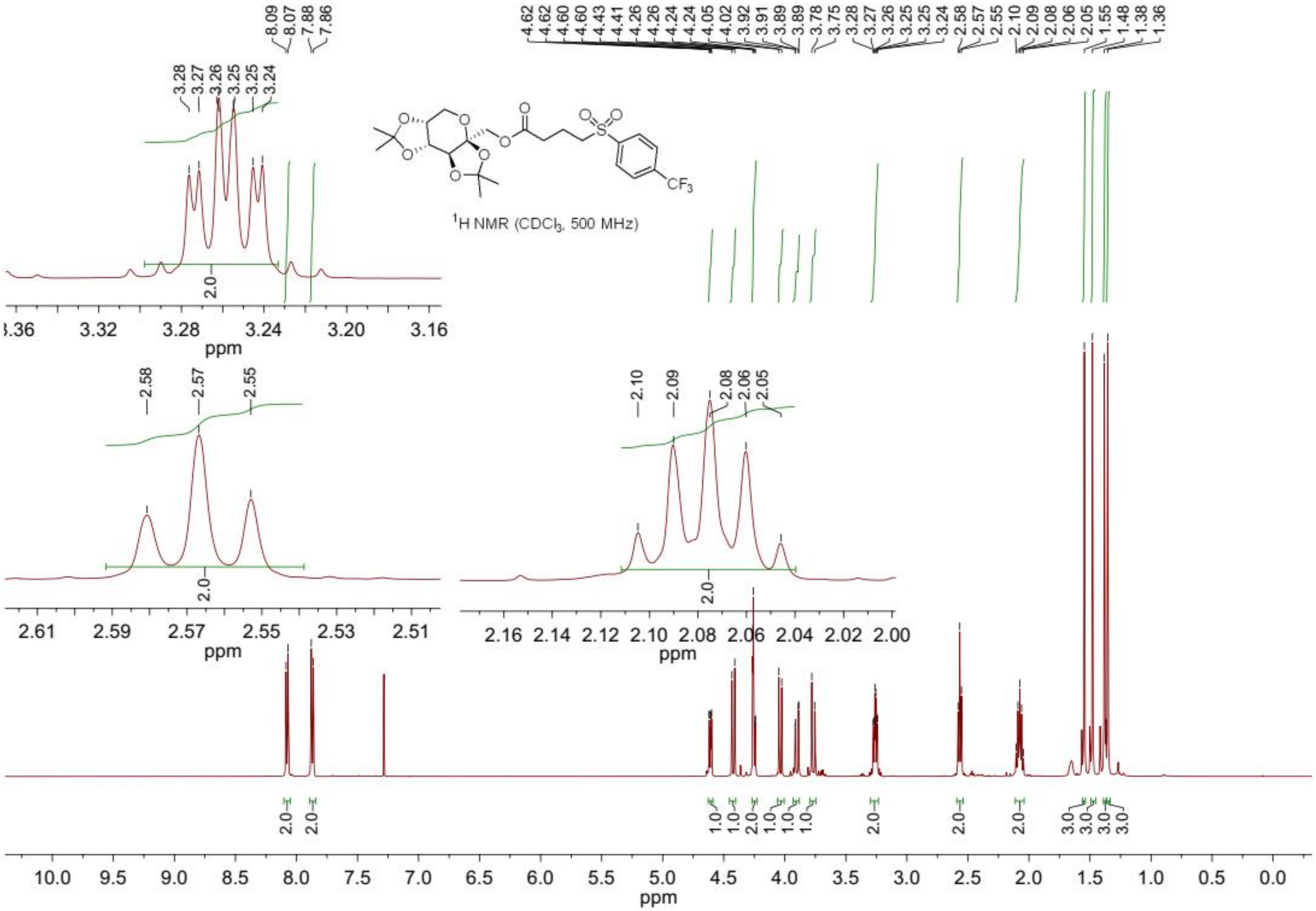
Di-*tert*-butyl ((2*S*,3*S*,4*R*)-2-(4-((4-(trifluoromethyl)phenyl)sulfonyl)butyl)tetrahydrothiophene-3,4-diyl)dicarbamate (5e)



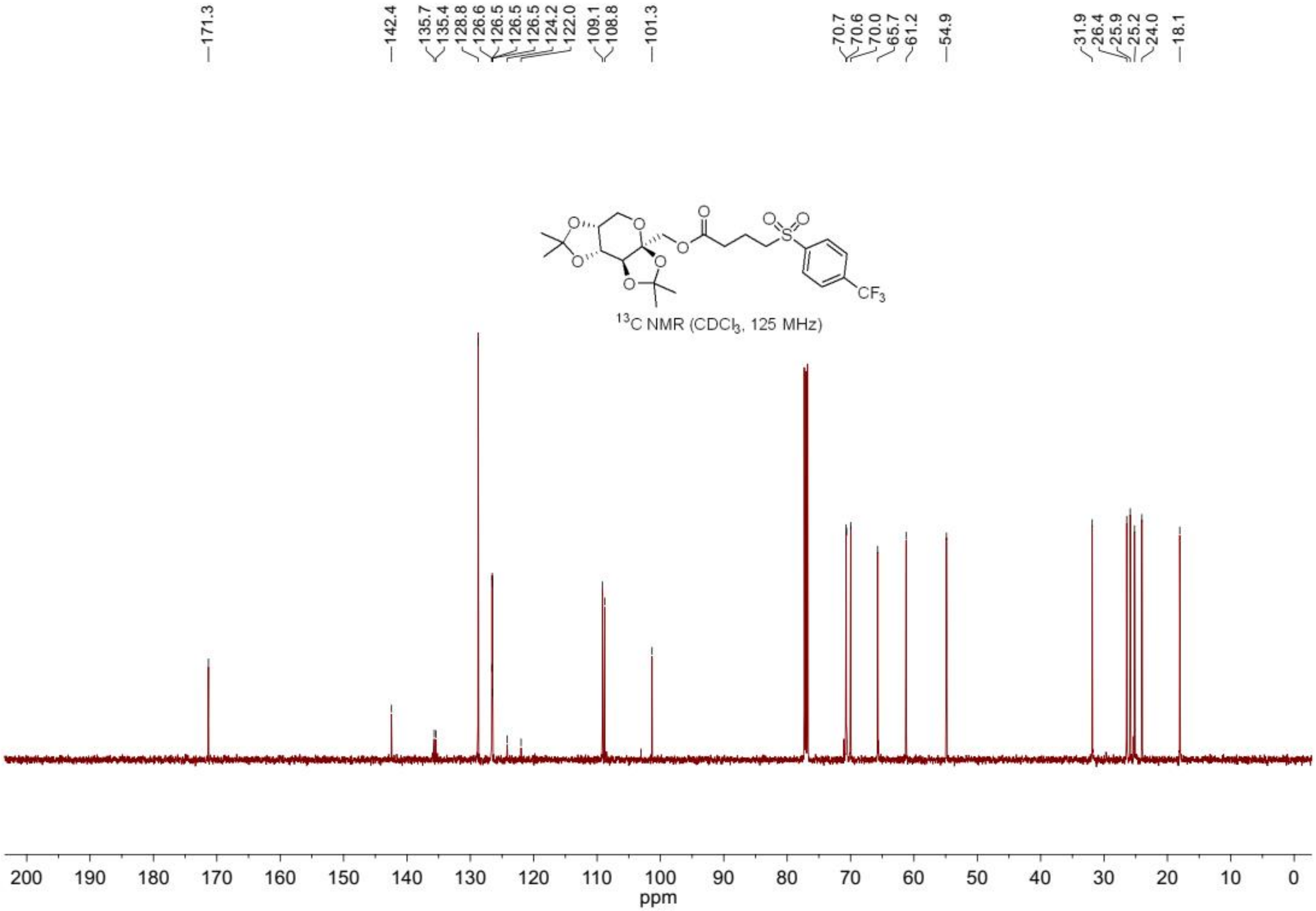
Di-*tert*-butyl ((2*S*,3*S*,4*R*)-2-(4-((4-(trifluoromethyl)phenyl)sulfonyl)butyl)tetrahydrothiophene-3,4-diyl)dicarbamate (5e)



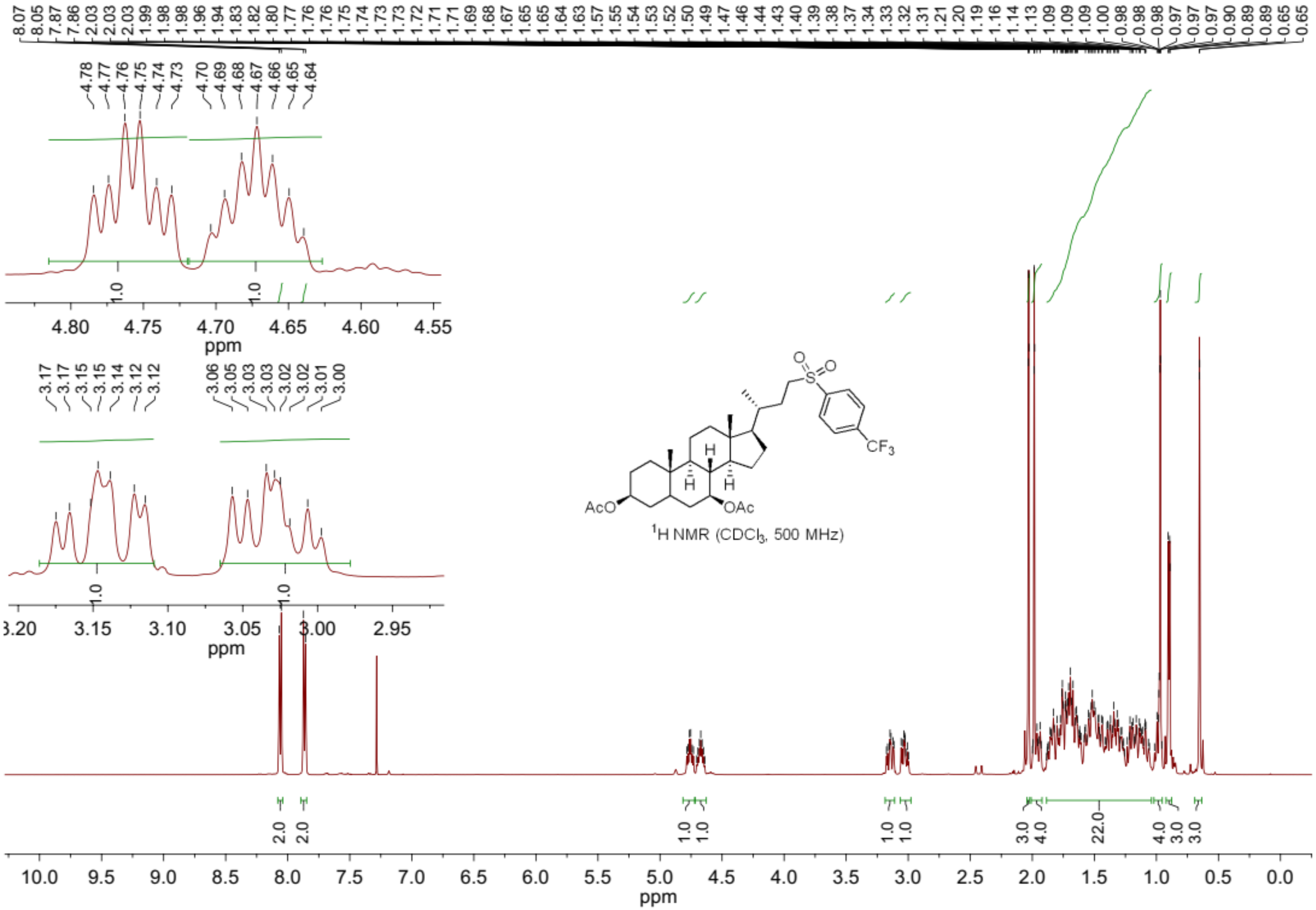
((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 4-((4-(trifluoromethyl)phenyl)sulfonyl)butanoate (5f)



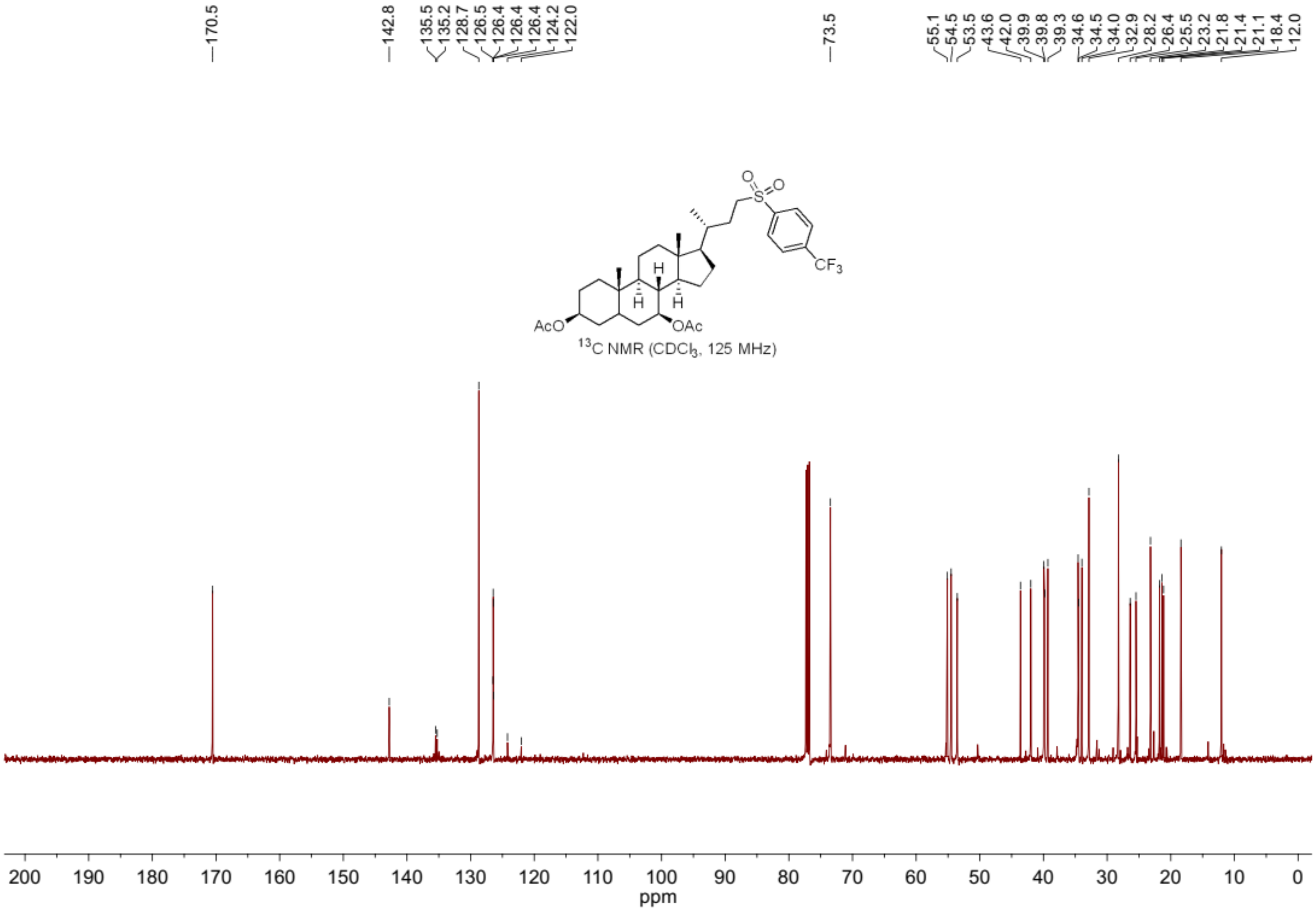
((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 4-((4-(trifluoromethyl)phenyl)sulfonyl)butanoate (5f)



(3*S*,7*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7-diyl diacetate (5g)

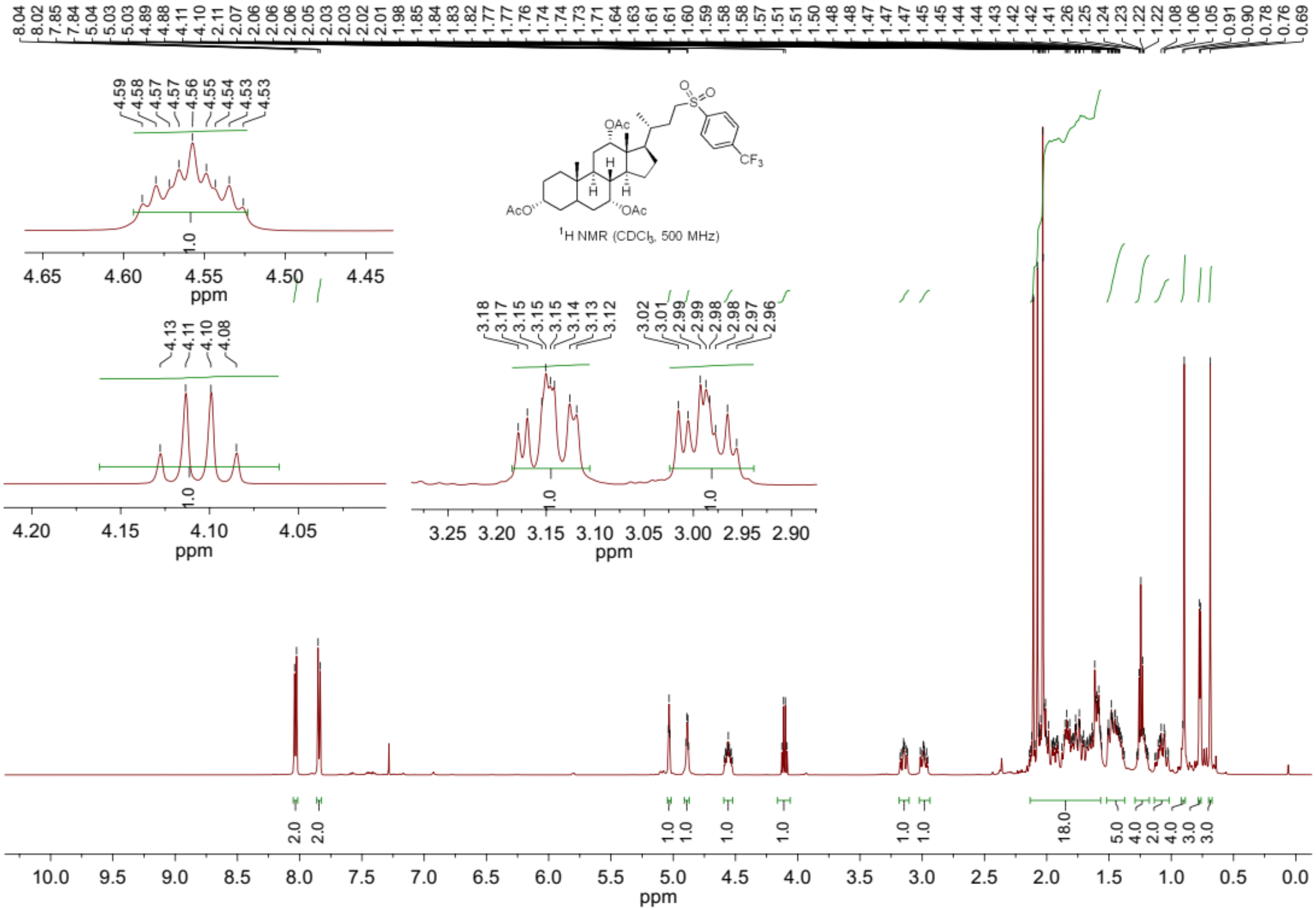


(3*S*,7*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7-diyl diacetate (5g)

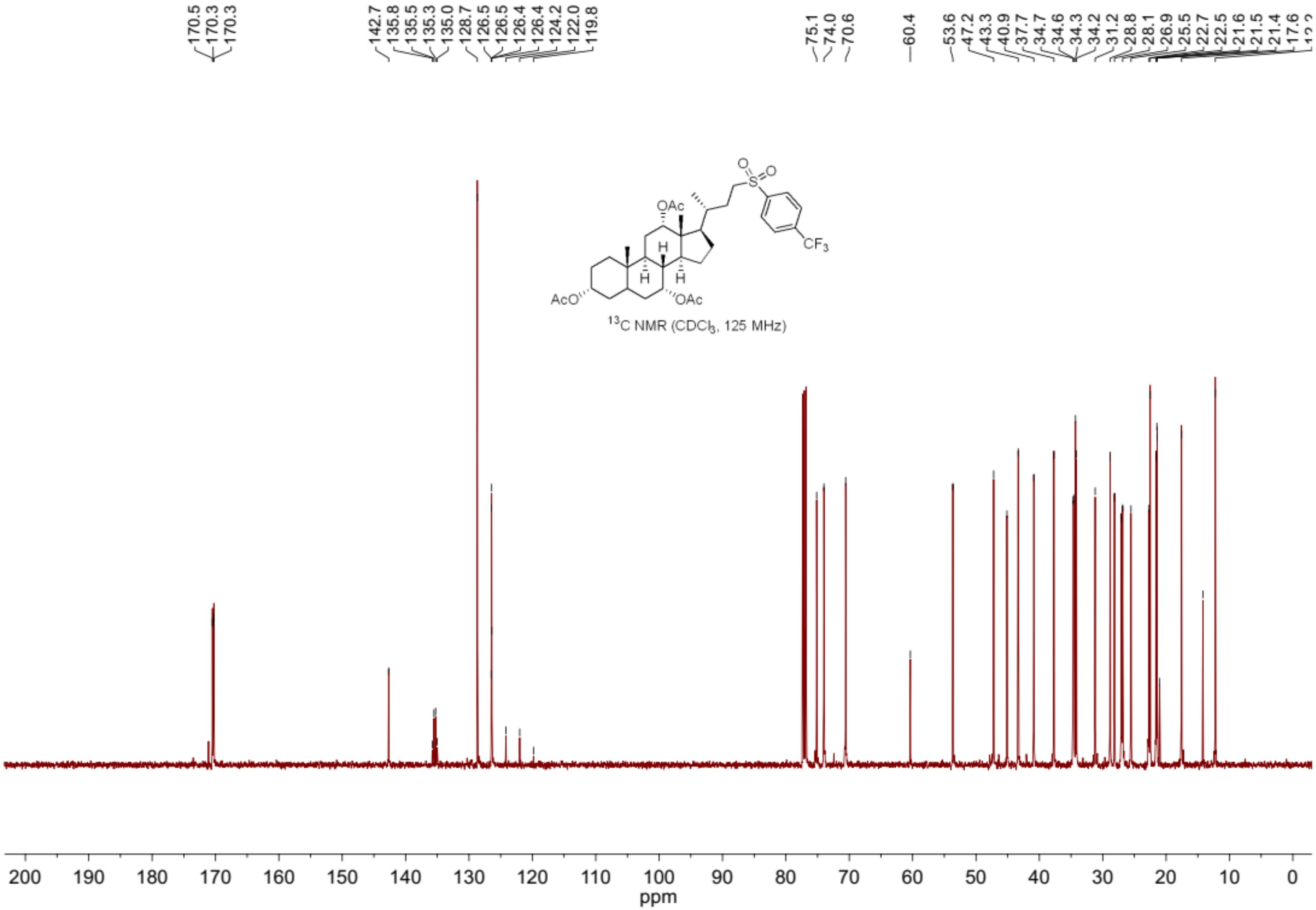


^{13}C NMR (CDCl$_3$, 125 MHz)

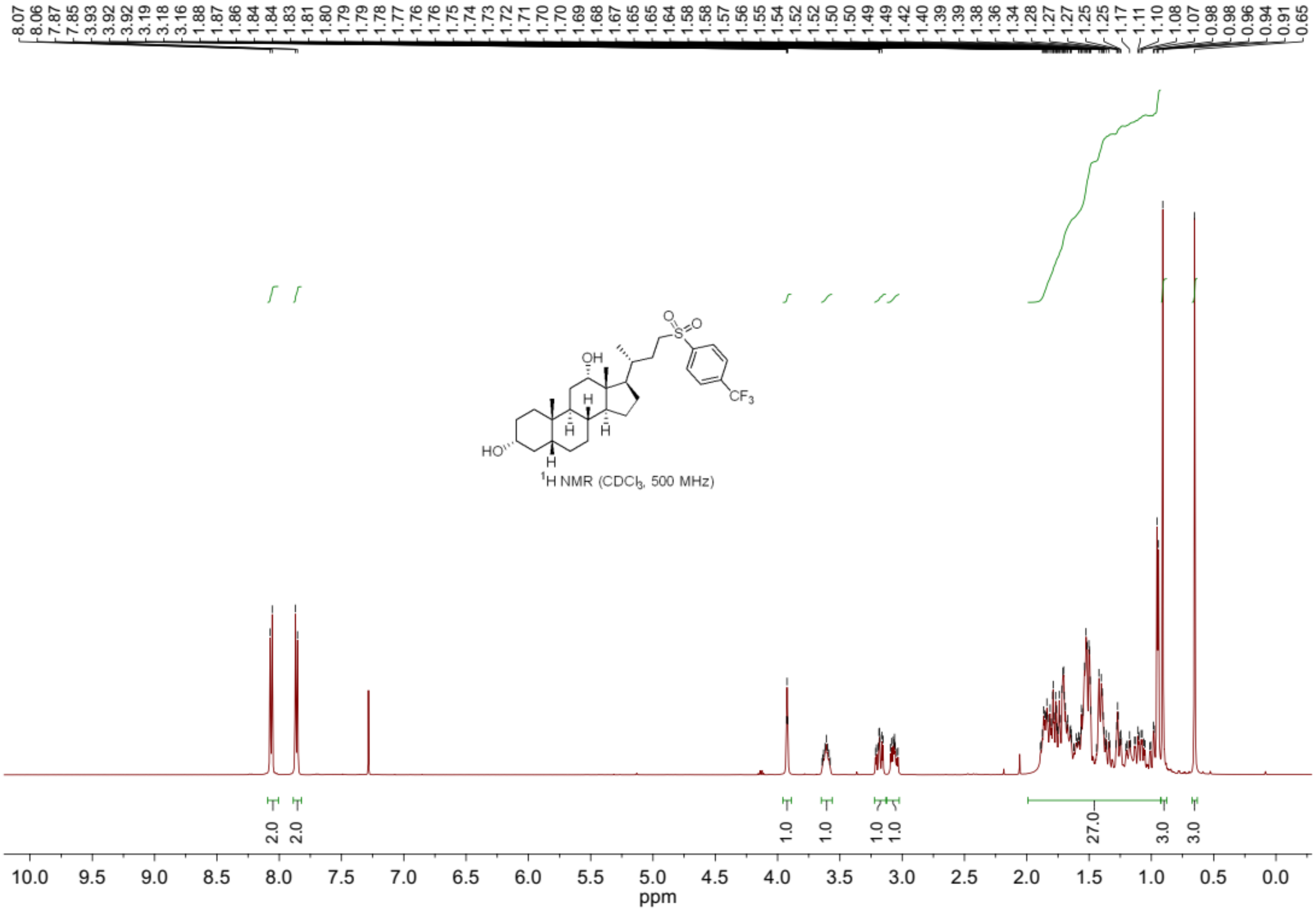
(3*R*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7,12-triyl triacetate (5h)



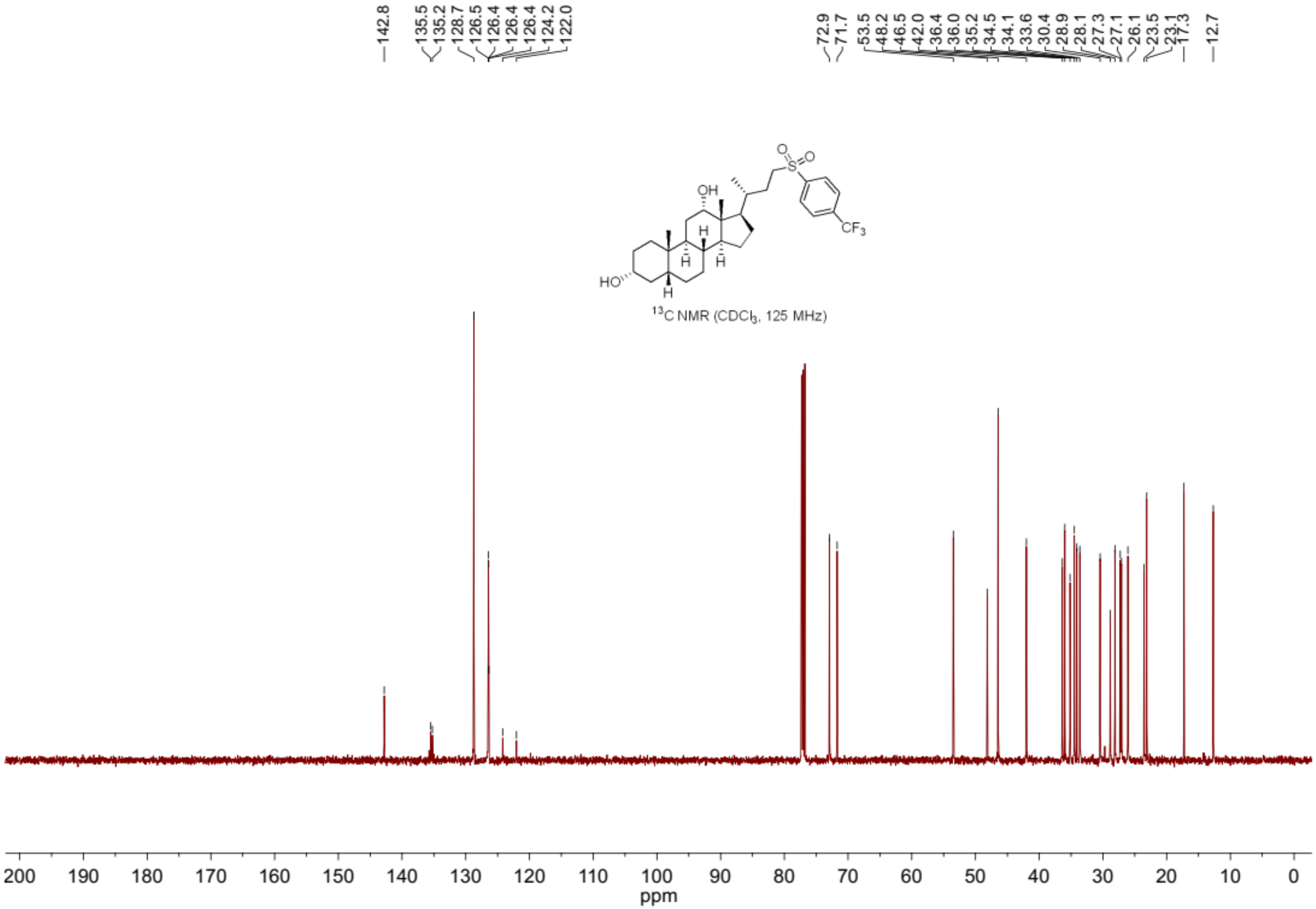
(3*R*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7,12-triyl triacetate (5h)



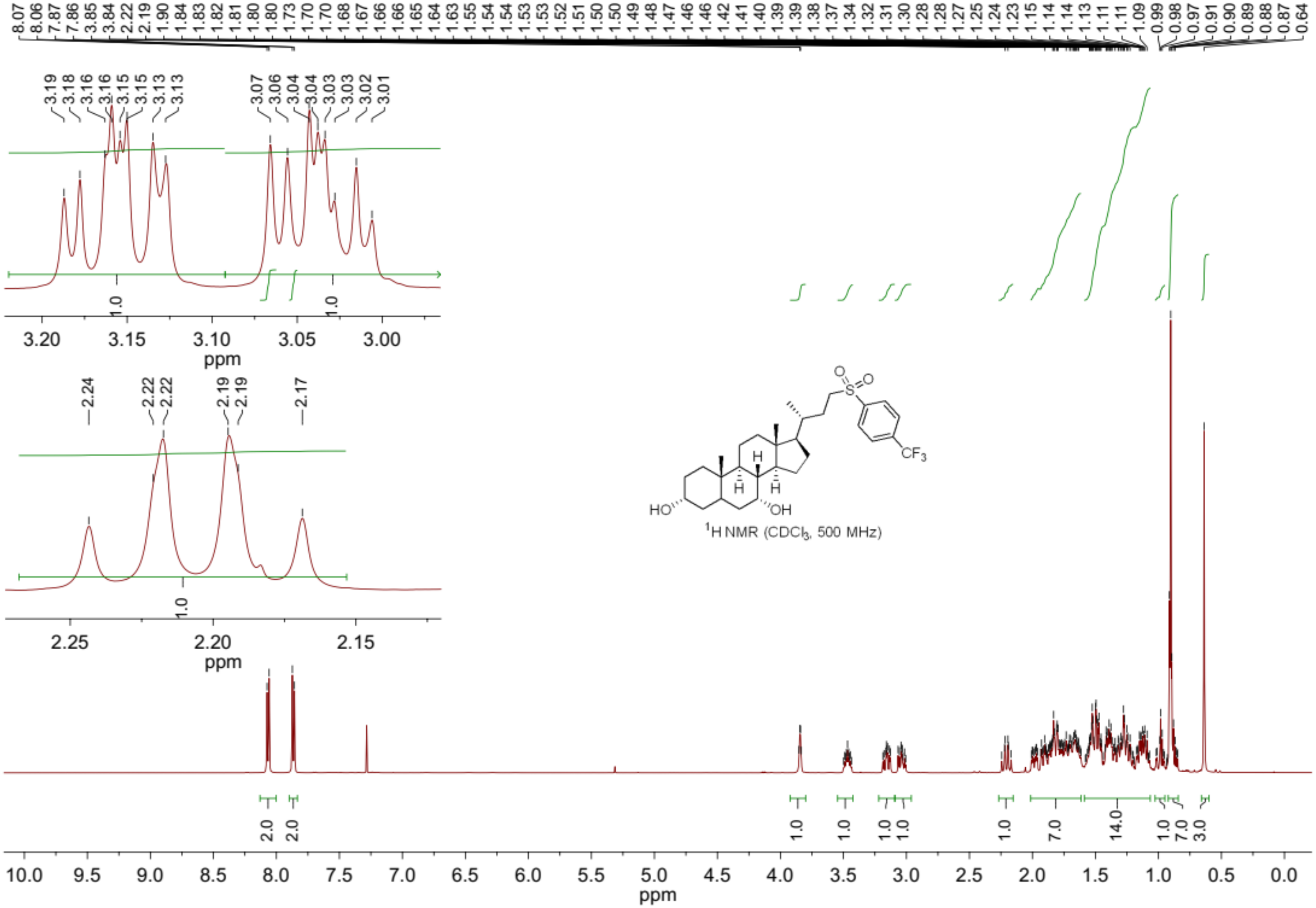
(3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diol (5i)



(3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diol (5i)



(3R,7R,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthrene-3,7-diol (5j)



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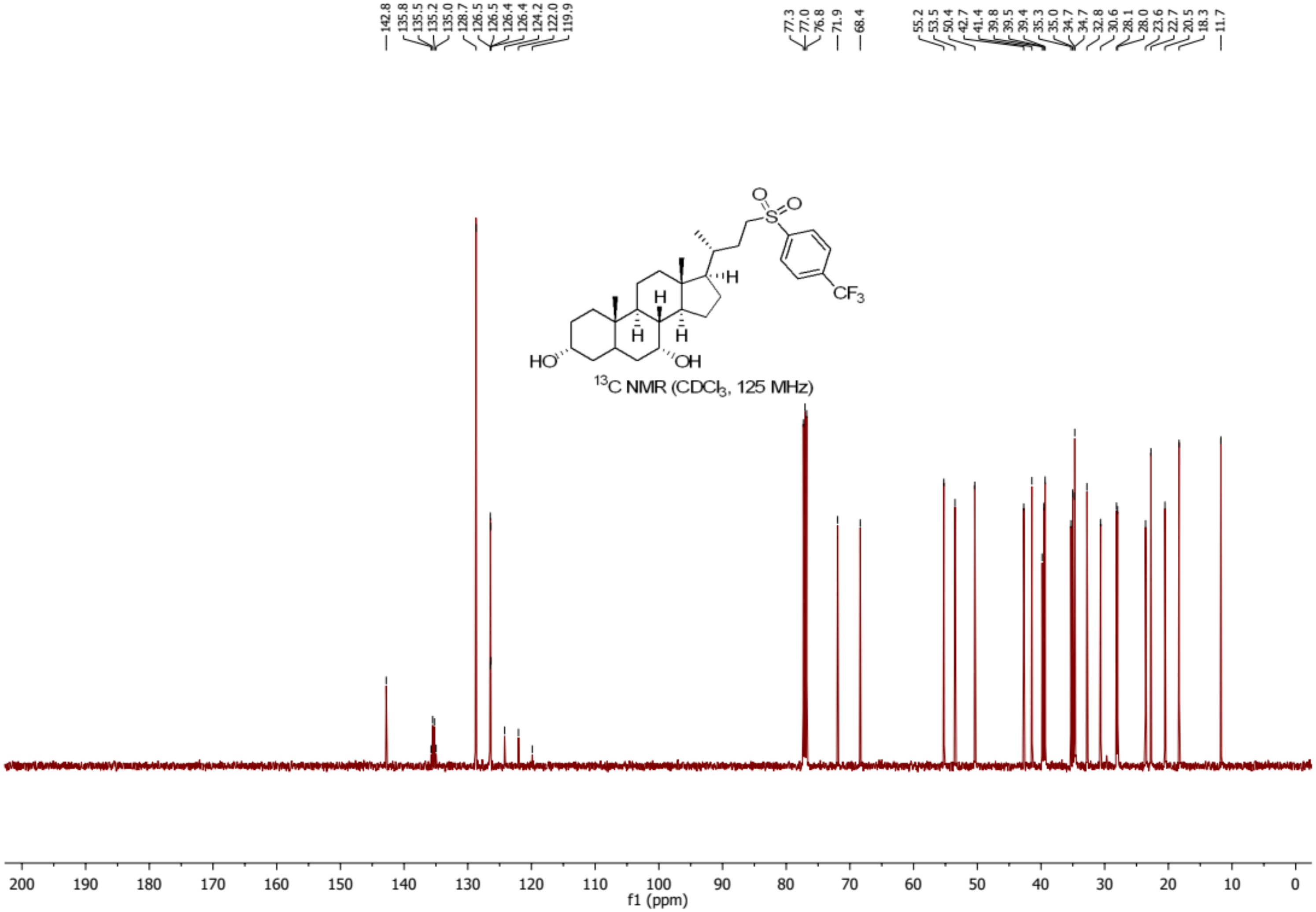
(3R,7R,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthrene-3,7-diol (5j)



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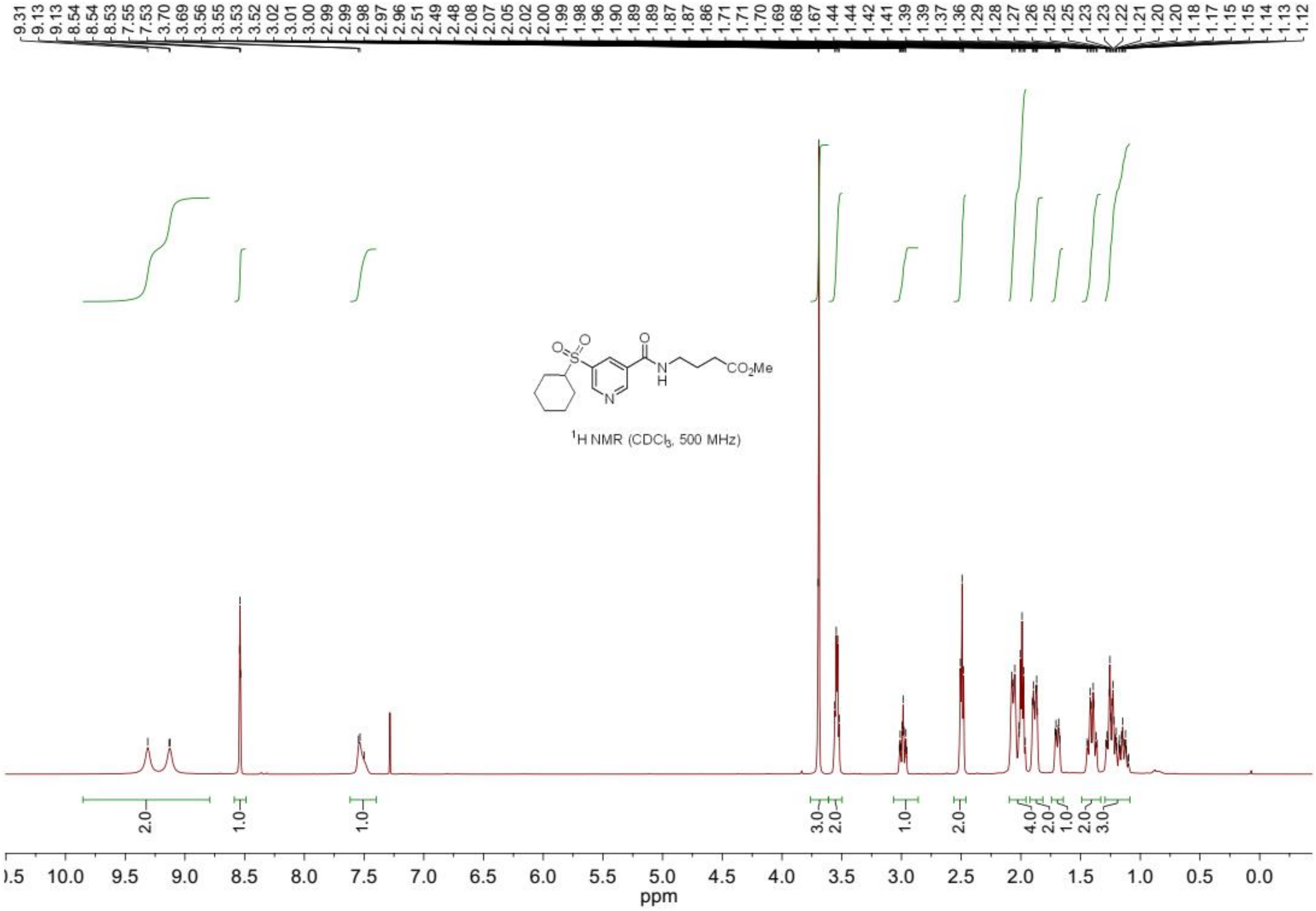
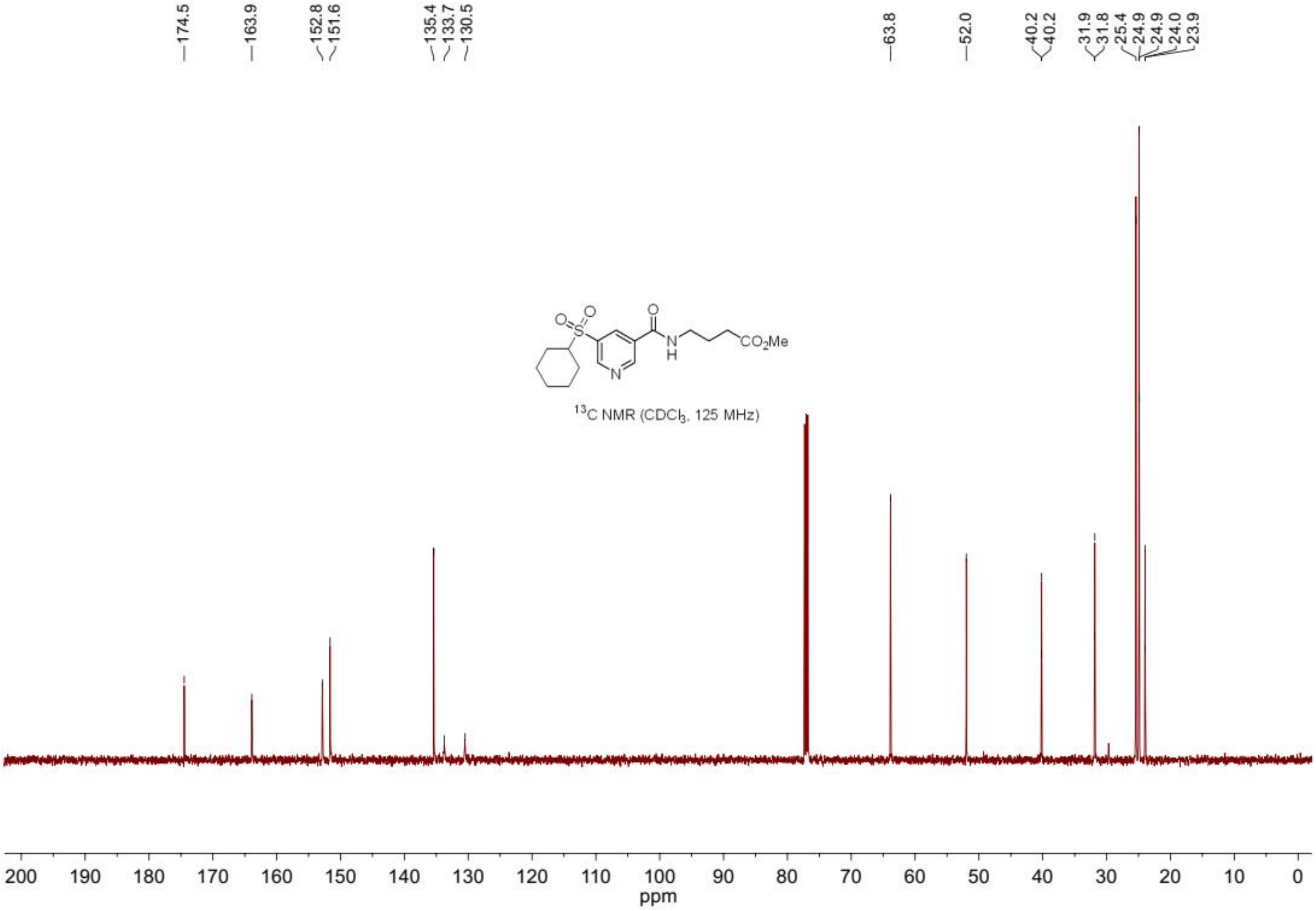
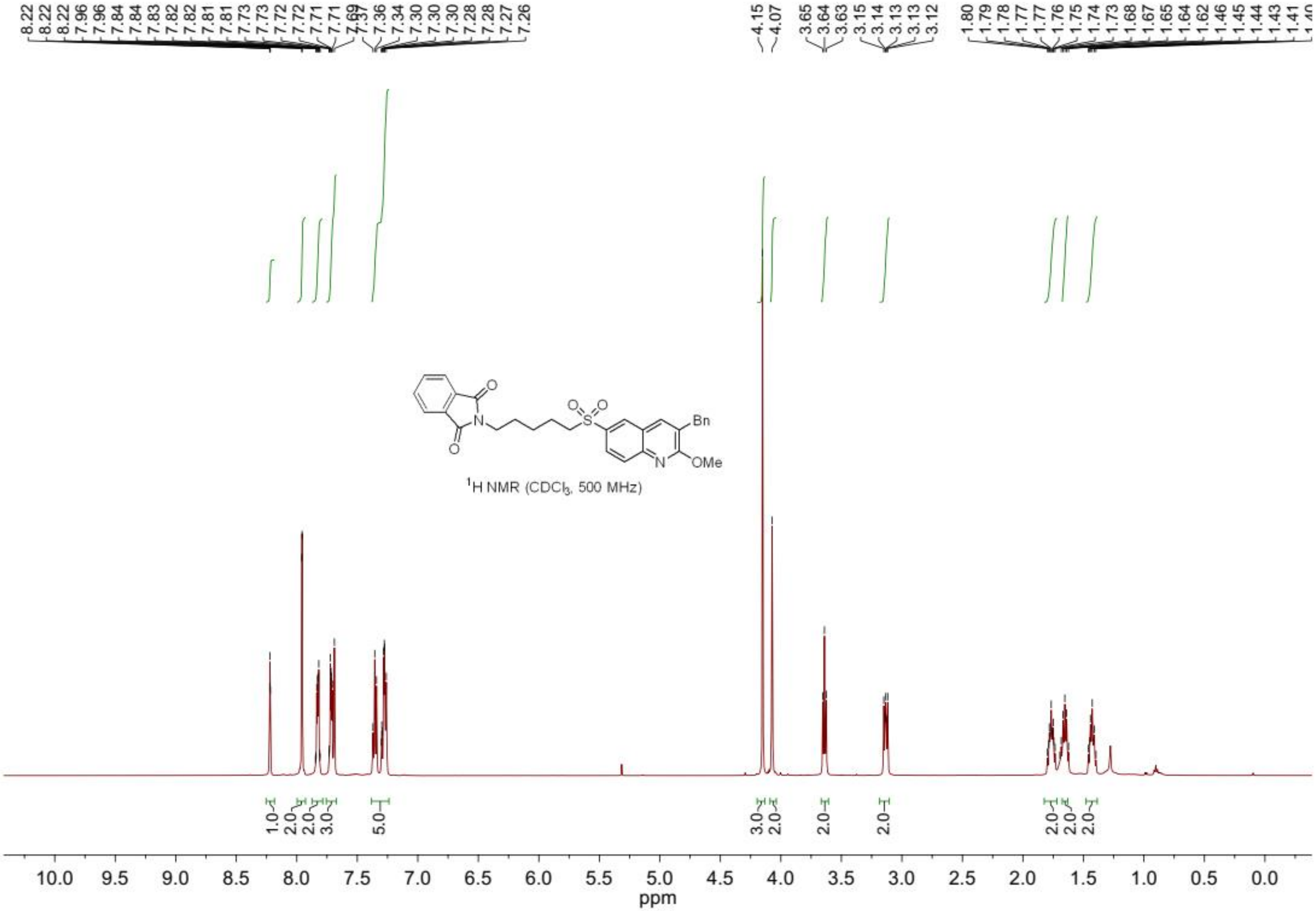
Methyl 4-(5-(cyclohexylsulfonyl)nicotinamido)butanoate (5k)



Methyl 4-(5-(cyclohexylsulfonyl)nicotinamido)butanoate (5k)



2-(5-((3-Benzyl-2-methoxyquinolin-6-yl)sulfonyl)pentyl)isoindoline-1,3-dione (5l)



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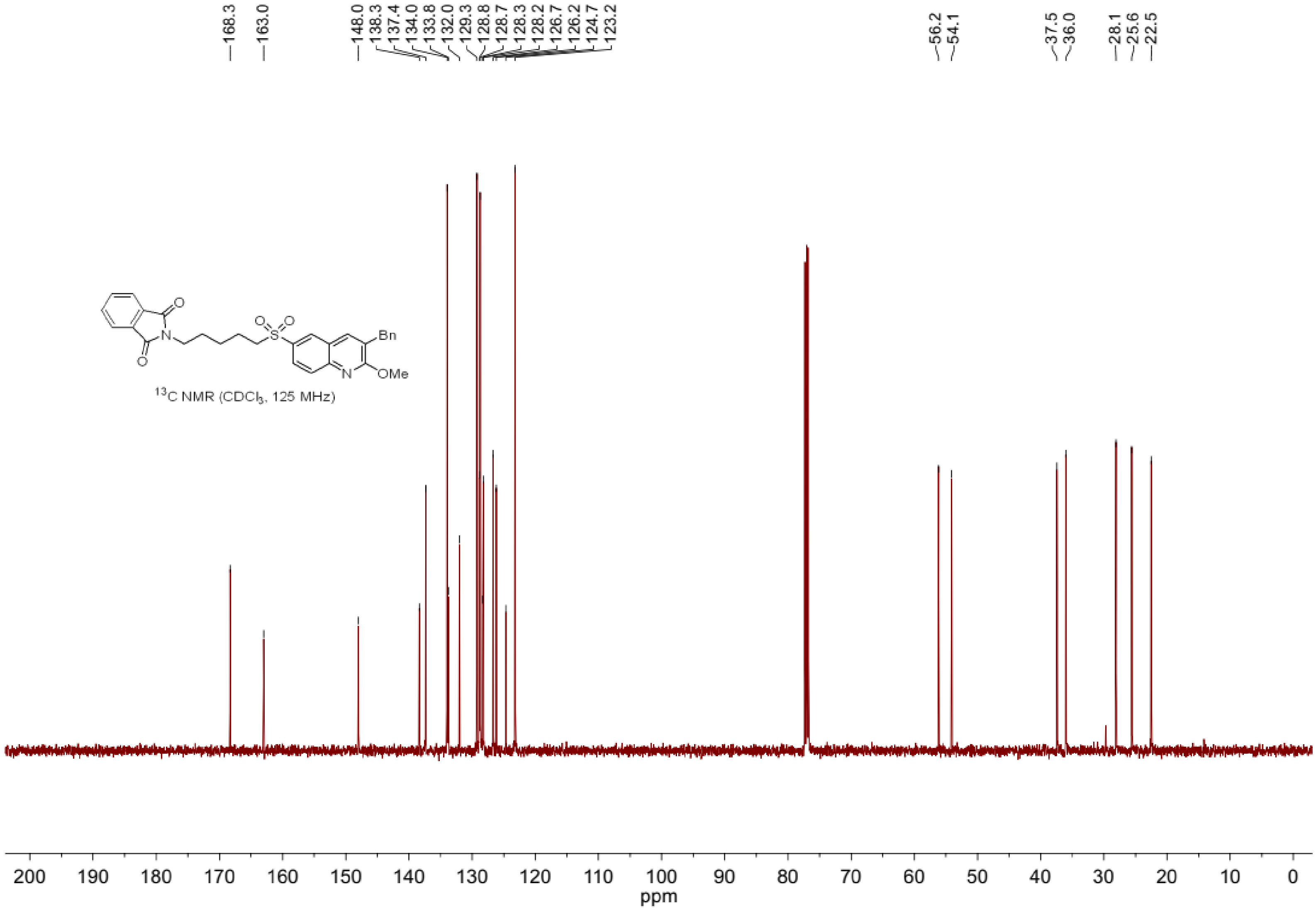
2-(5-((3-Benzyl-2-methoxyquinolin-6-yl)sulfonyl)pentyl)isoindoline-1,3-dione (5l)



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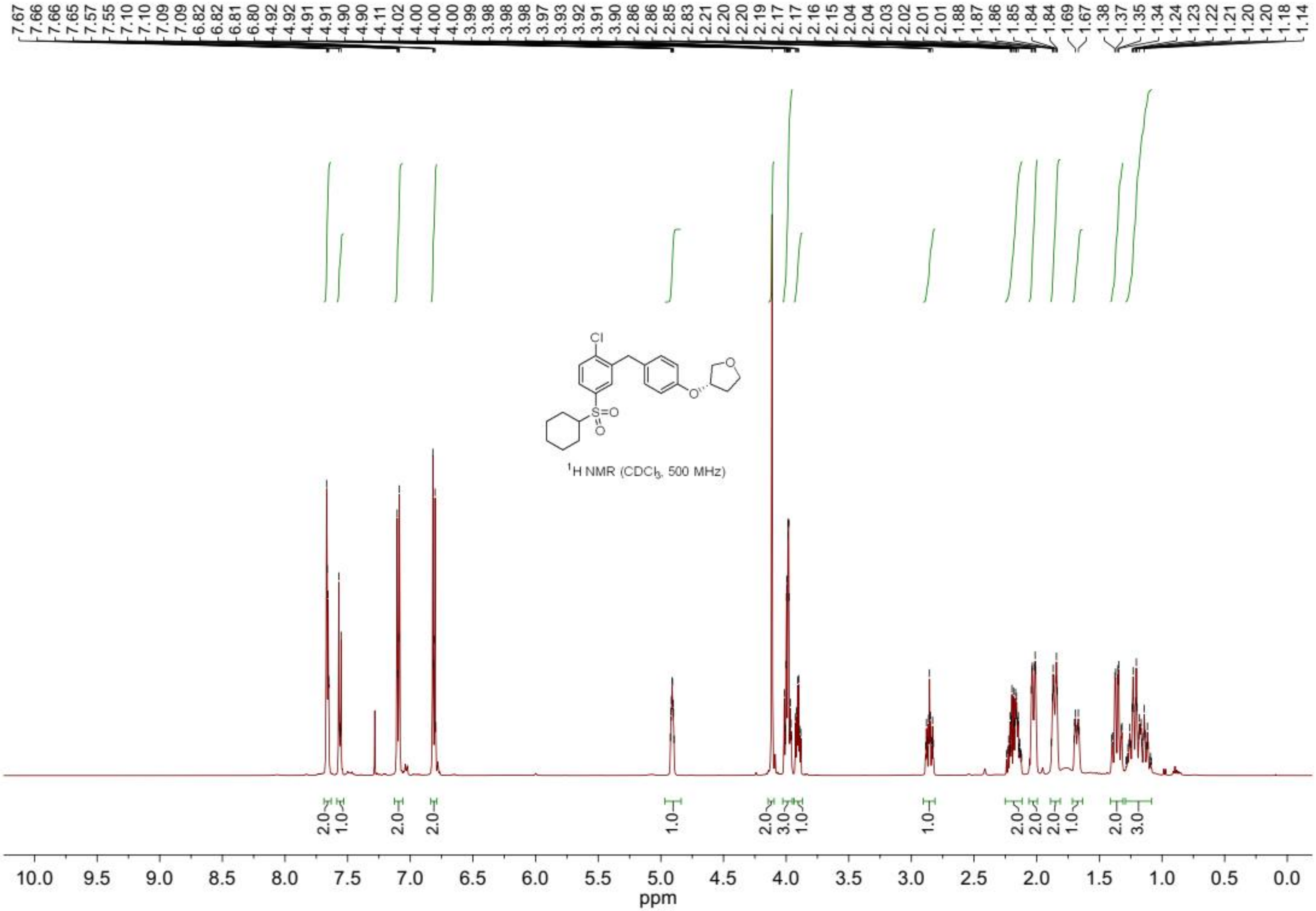
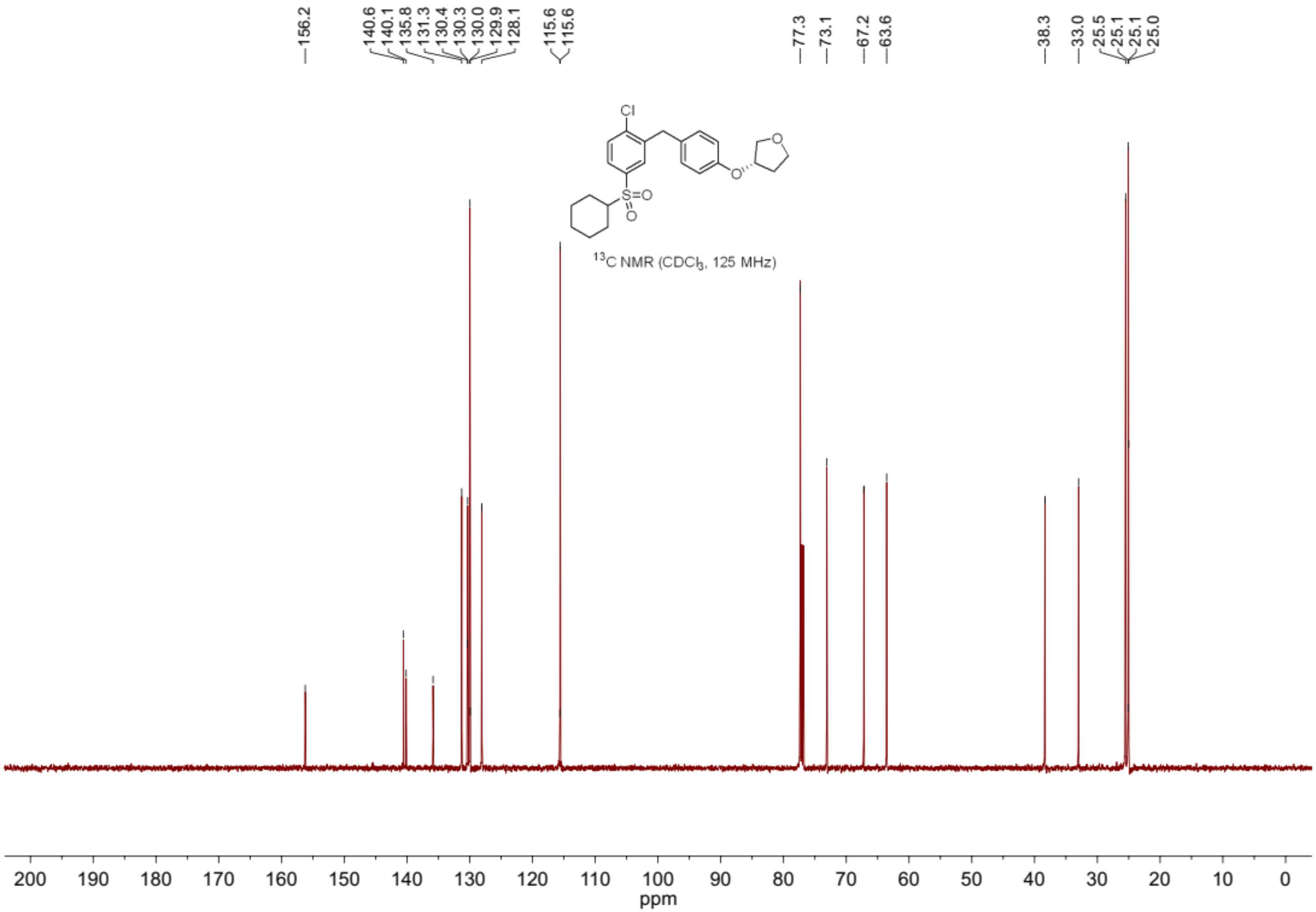
(*S*)-3-(4-(2-Chloro-5-(cyclohexylsulfonyl)benzyl)phenoxy)tetrahydrofuran (5m)



^{1}H NMR (CDCl$_3$, 500 MHz)

(*S*)-3-(4-(2-Chloro-5-(cyclohexylsulfonyl)benzyl)phenoxy)tetrahydrofuran (5m)



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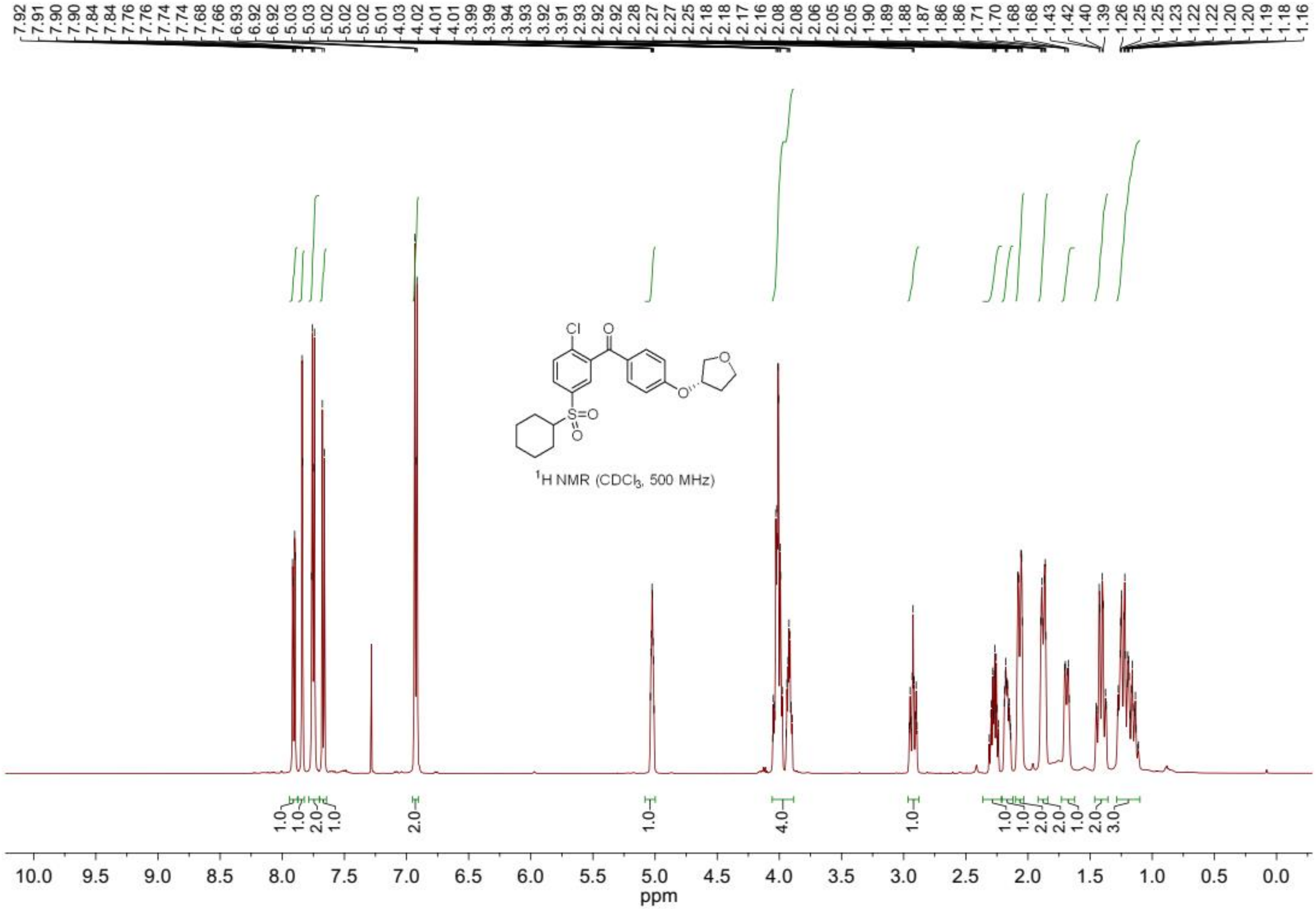
(*S*)-(2-Chloro-5-(cyclohexylsulfonyl)phenyl)(4-((tetrahydrofuran-3-yl)oxy)phenyl)methanone (5n)



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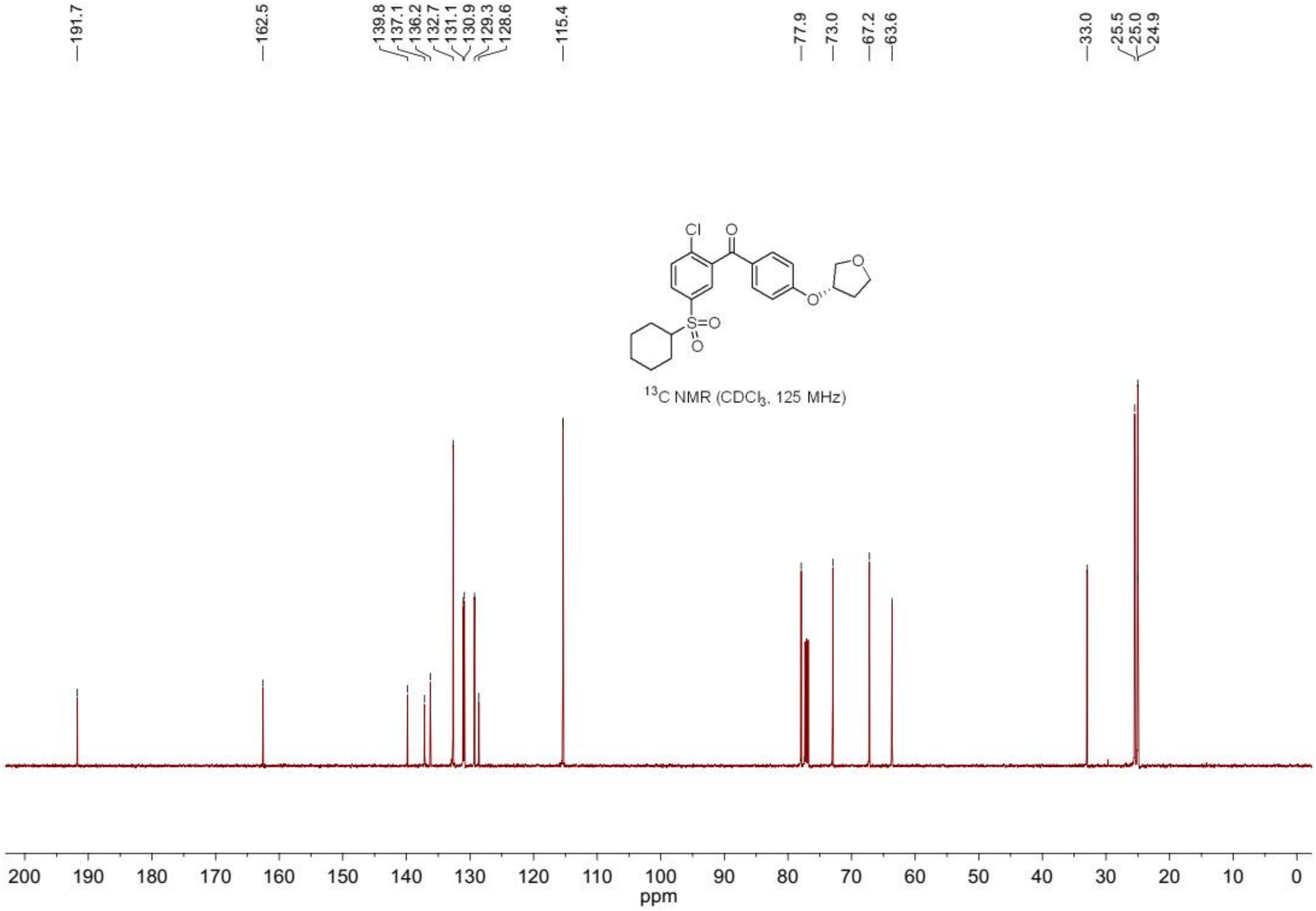
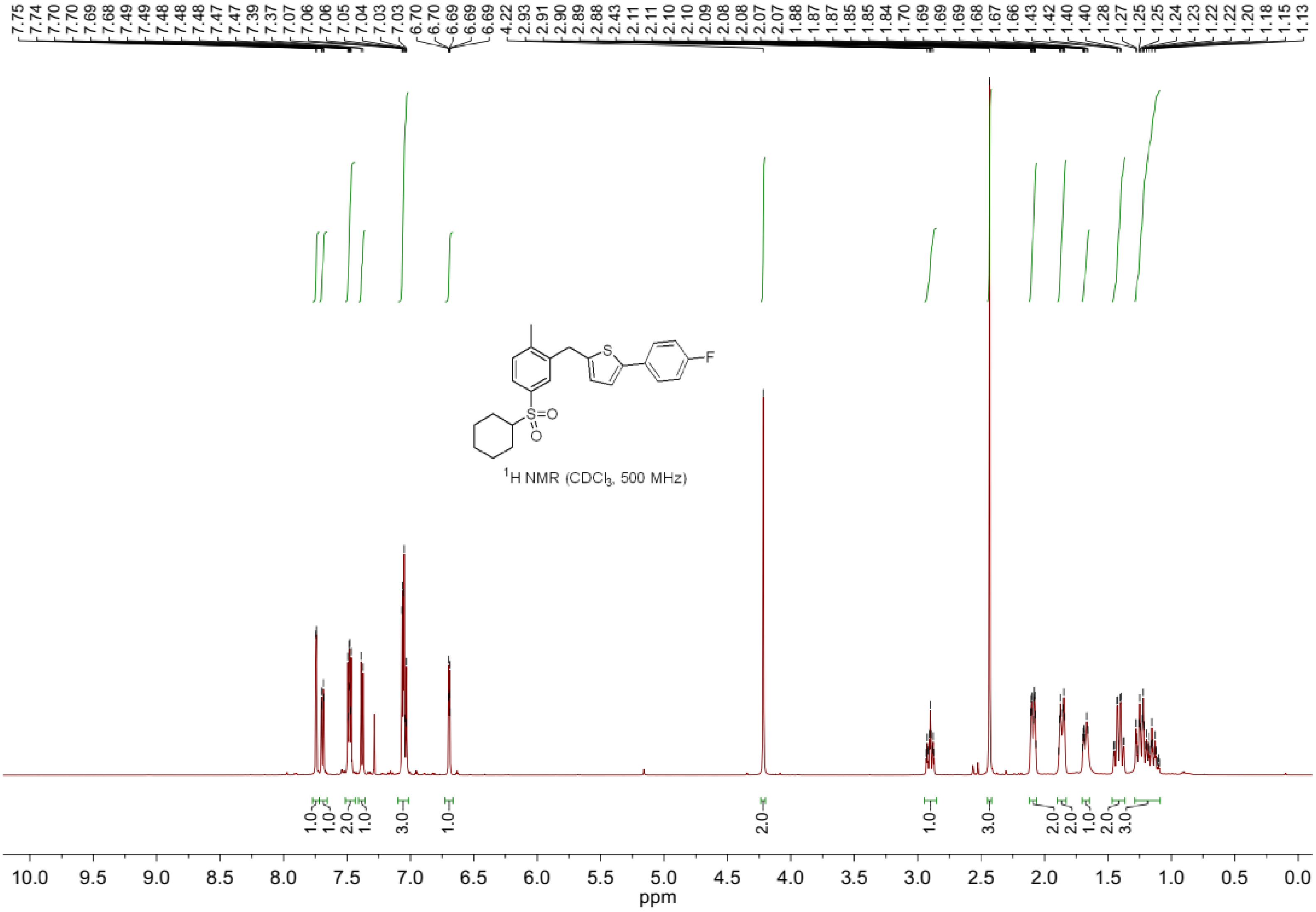
(*S*)-(2-Chloro-5-(cyclohexylsulfonyl)phenyl)(4-((tetrahydrofuran-3-yl)oxy)phenyl)methanone (5n)



2-(5-(Cyclohexylsulfonyl)-2-methylbenzyl)-5-(4-fluorophenyl)thiophene (5o)



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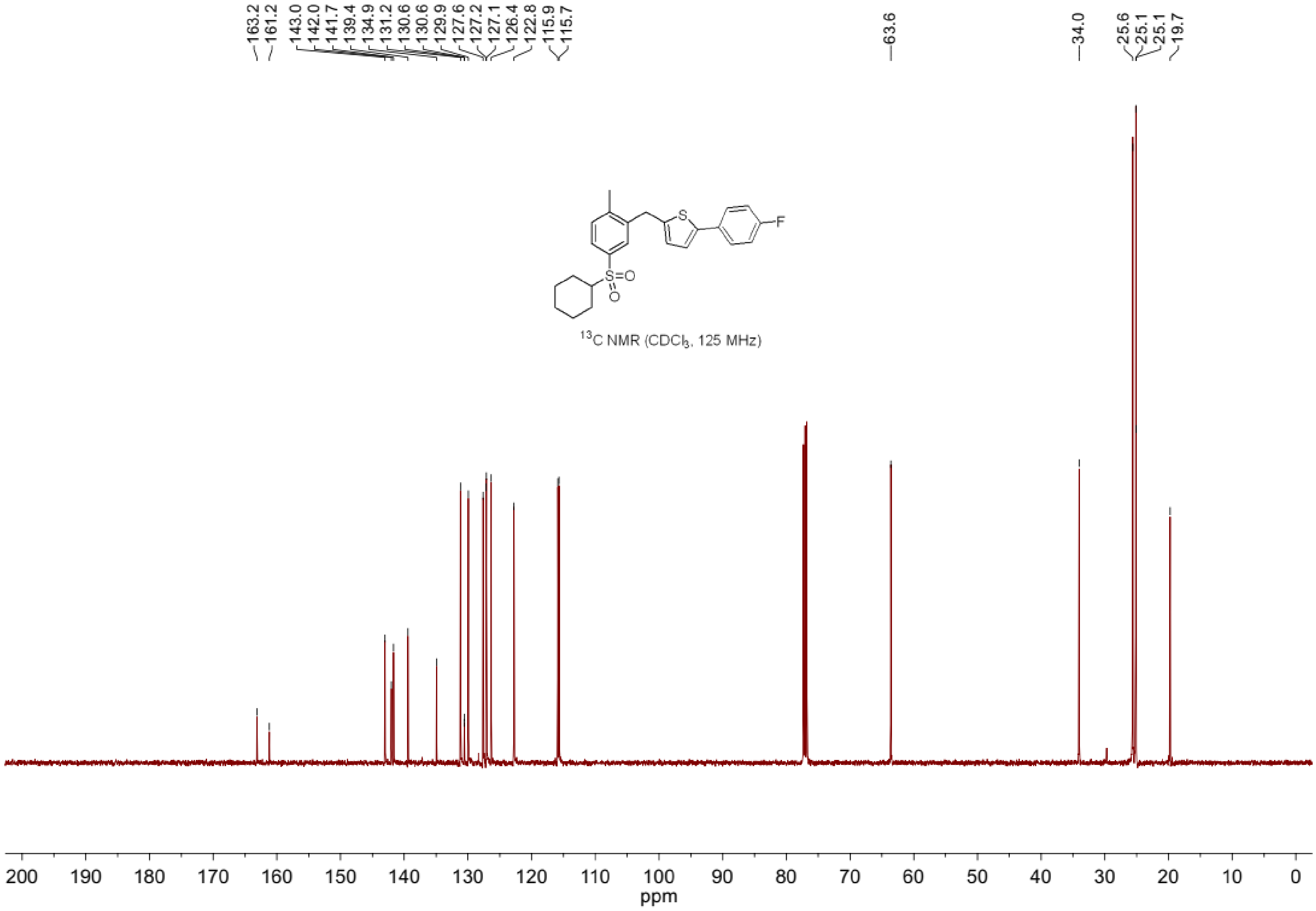
2-(5-(Cyclohexylsulfonyl)-2-methylbenzyl)-5-(4-fluorophenyl)thiophene (5o)



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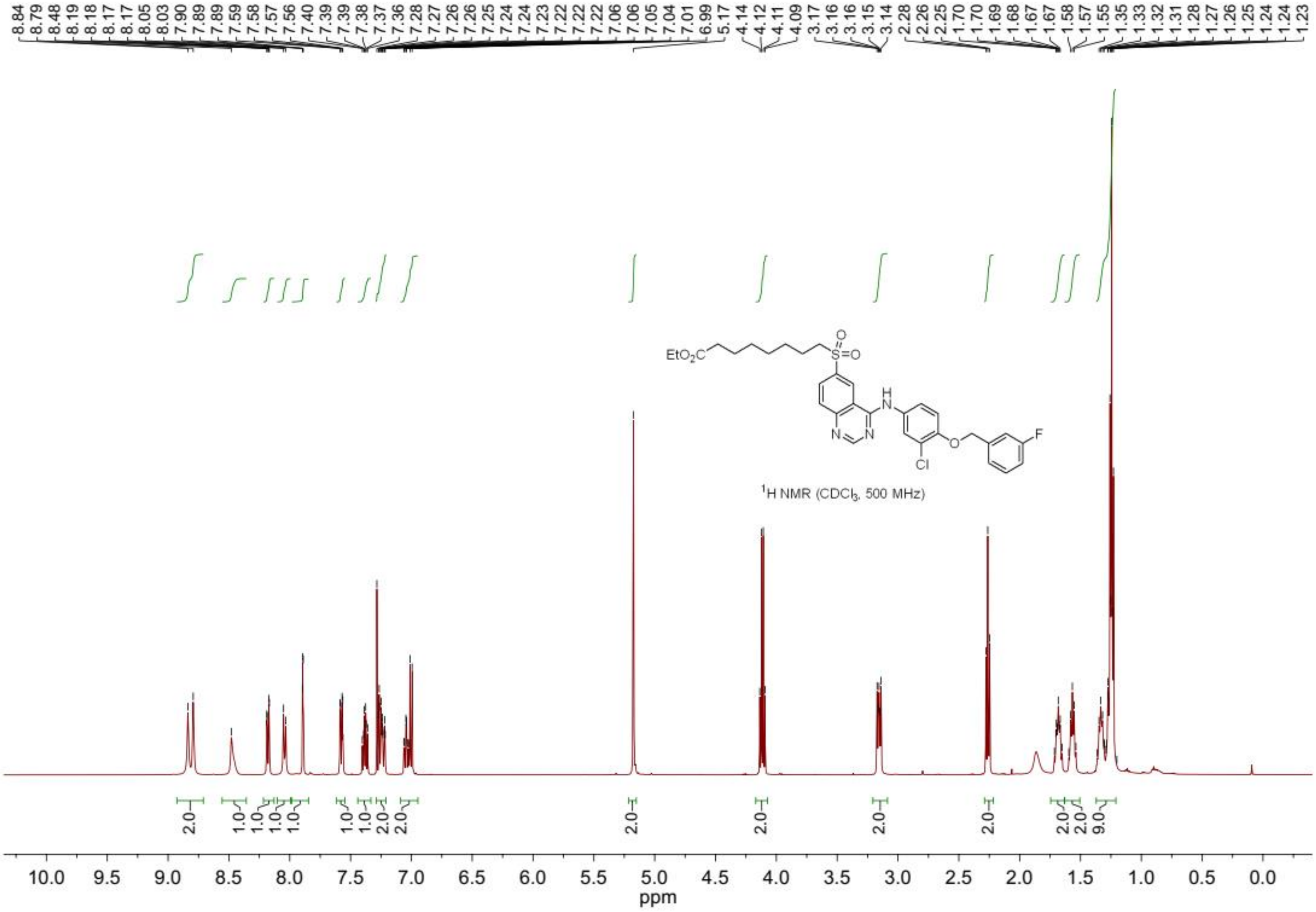
Ethyl 8-((4-((3-chloro-4-((3-fluorobenzyl)oxy)phenyl)amino)quinazolin-6-yl)sulfonyl)octanoate (5p)



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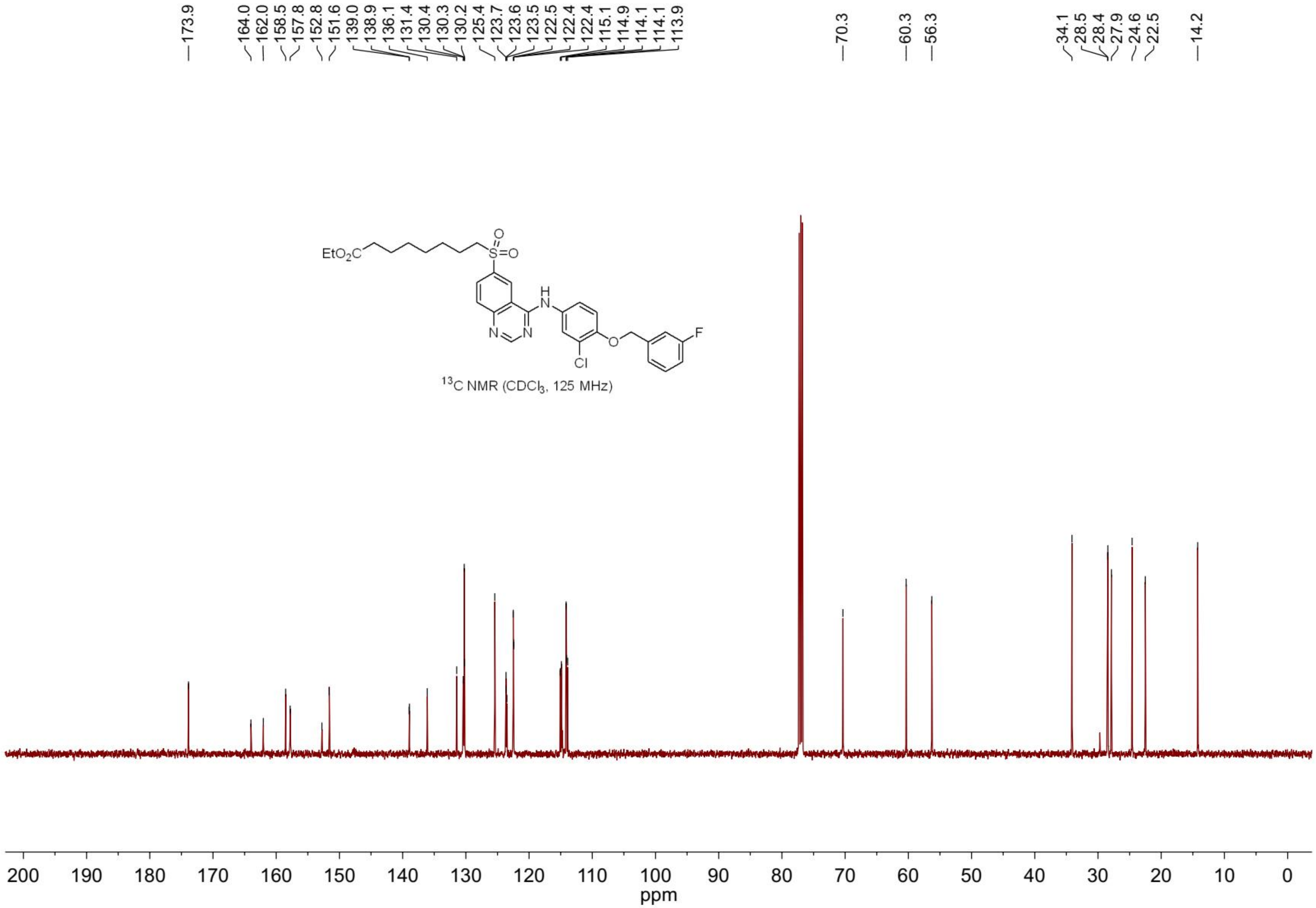
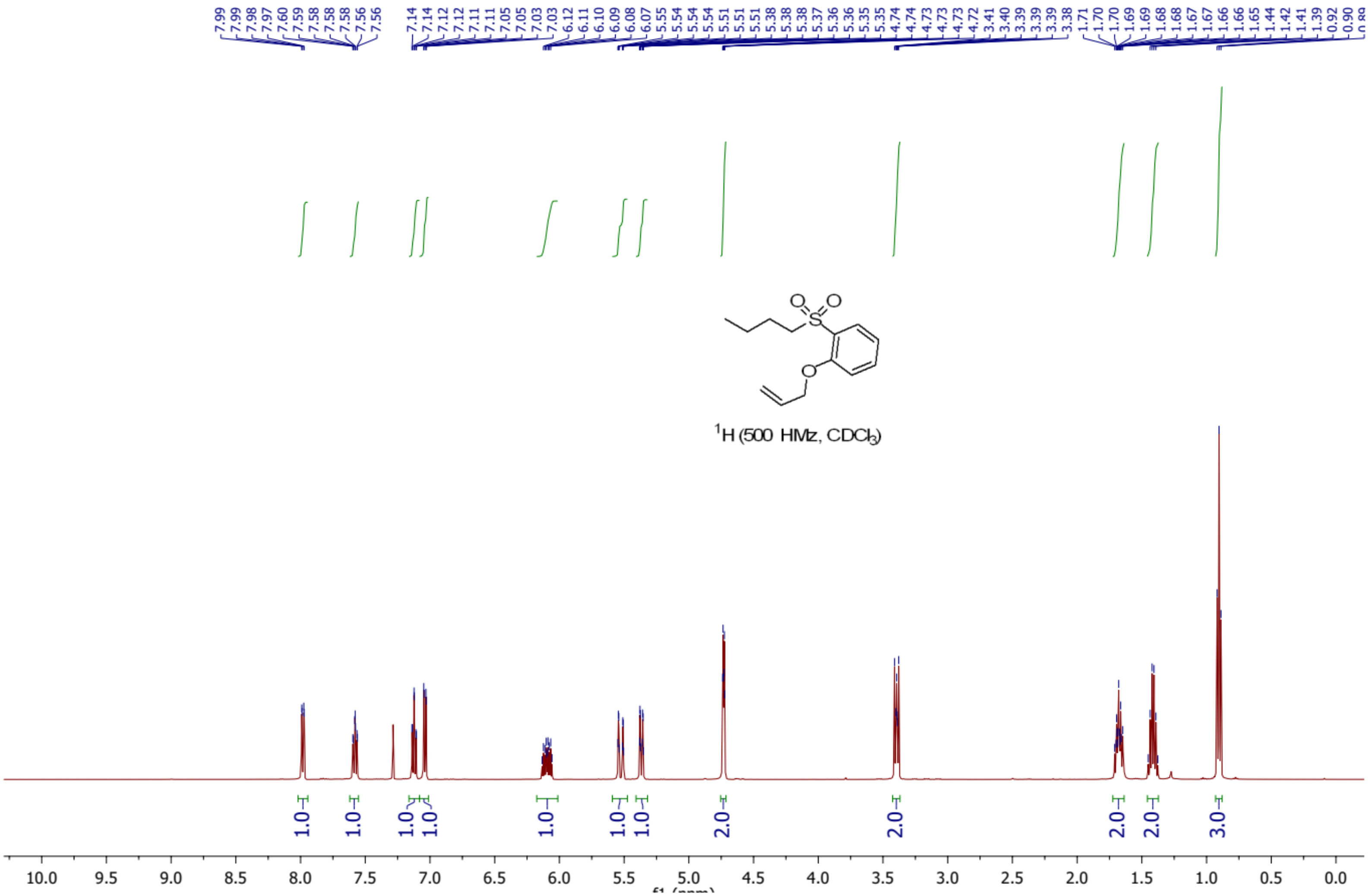
Ethyl 8-((4-((3-chloro-4-((3-fluorobenzyl)oxy)phenyl)amino)quinazolin-6-yl)sulfonyl)octanoate (5p)

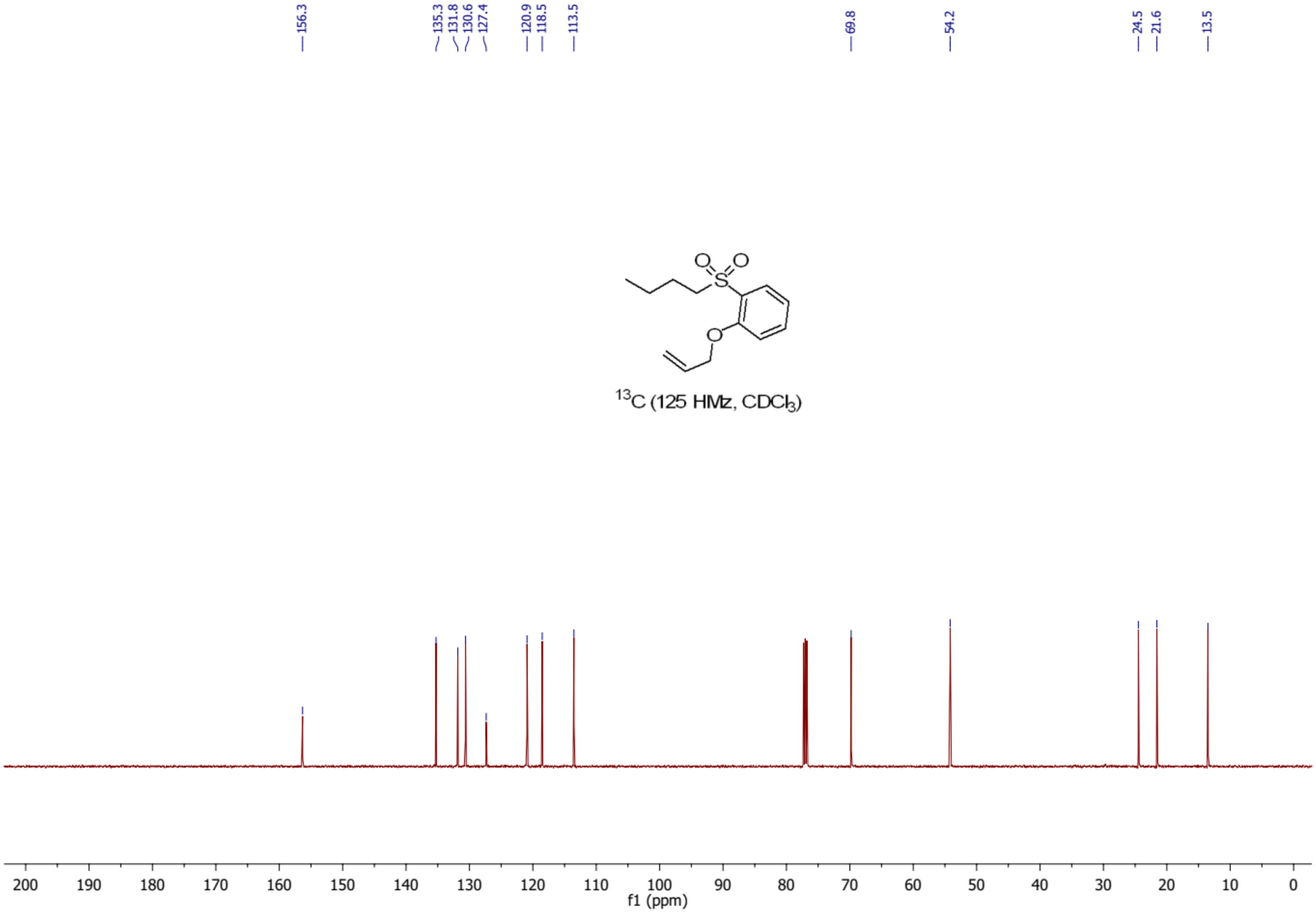


^{13}C NMR (CDCl$_3$, 125 MHz)

1-(Allyloxy)-2-(butylsulfonyl)benzene (15)



1-(Allyloxy)-2-(butylsulfonyl)benzene (15)



^{13}C (125 HMz, $CDCl_3$)

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