

Supporting Information

Visible-Light-Driven Oxidative Coupling of Arylhydrazines with

Sulfates Catalyzed by Polyoxometalates for Aryl

Sulfone Synthesis

Ahmed Th. Abdulghaffar,^{‡a,c} Chengze Zhang,^{‡a} Jianghao Yu,^{‡a} Guan Wang,^{*a} Yanrong Ren,^a Zhongyan Cao,^a Wei Chen,^{*a} Yuanqing Xu,^{*a} Hao Xu,^{*a,b} and Jingyang Niu^a

^a. *College of Chemistry and Molecular Sciences, Henan University, Kaifeng 475004, China.*

^b. *Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China.*

^c. *Chemistry Department, Faculty of Science, Fayoum University, Fayoum, 63514, Egypt.*

E-mail: wangguan@henu.edu.cn; chanwee@henu.edu.cn; xuyuanqing@henu.edu.cn; xuhao@henu.edu.cn

[‡]The authors contributed equally to this work.

Table of Contents

1.	Supporting Figures	4
2.	Supporting Tables.....	14
3.	Supporting Methods.....	16
4.	Characterization Data of Product of 3a-3y'	18
5.	References:	35
6.	NMR Spectra:	36

List of Supporting Figures

Figure S1. Representative aryl sulfones with biological activities.	4
Figure S2. Characterization of POM catalysts: (a) P-XRD patterns of HPMoV (blue line), NaHPMo (green line), and HPW (red line), (b) FT-IR spectra of the as-prepared POMs.	4
Figure S3. XPS survey analyses of (a) HPMoV, (b) NaHPMo, and (c) HPW, (d-g) XPS analysis of Mo, P, V, and W within their respective Polyoxometalate catalysts.	5
Figure S4. TGA and DTG curves of (a) HPMoV, (b) NaHPMo, and (c) HPW.	5
Figure S5. Electrochemical measurements of POMs: (a & b) EIS and i-t curve of HPMoV (blue line), NaHPMo (green line), and HPW (red line), respectively.	6
Figure S6. Reaction equipment and light source ($\lambda_{\text{peak}} = 454 \text{ nm}$).	7
Figure S7. The emission spectrum of the 40W KSA160WE-TB, with a peak wavelength of 454 nm.	7
Figure S8. Excitation spectra of the screened photosensitizers, (a) HPMoV, NaHPMo, and HPW, (b) Eosin B, (c) Eosin Y, and (d) Rhodamine B.	8
Figure S9. Emission spectra of the screened photosensitizers, (a) HPMoV, NaHPMo, and HPW, (b) Eosin B, (c) Eosin Y, and (d) Rhodamine B.	8
Figure S10. Competitive kinetics of substituted arylhydrazines (A) and sulfinates (B): Electron-donating group (EDG)/Electron-withdrawing group (EWG) effects.	9
Figure S11. Gram-scale experiments.	9
Figure S12. A comparative study of our methodology against prior methods employed in the synthesis of pharmaceutical compounds.	9
Figure S13. Radical trapping experiments.	10
Figure S14. ESI-HRMS spectrum for radical adduct A-1 with TEMPO.	10
Figure S15. ESI-HRMS spectrum for radical adduct A-2 with 1,1-diphenylethylene.	10
Figure S16. Light ON-OFF experiments.	11
Figure S17. Fluorescence excitation spectrum of NaHPMo was detected at 457 nm.	11
Figure S18. Fluorescence emission spectrum of NaHPMo excited at 381 nm.	12
Figure S19. Fluorescence emission spectra of NaHPMo with different quencher concentrations (p-methoxy phenylhydrazine hydrochloride).	12
Figure S20. Dynamic emission quenching of NaHPMo by p-methoxy phenylhydrazine hydrochloride.	13
Figure S21. EPR spectrum for a mixture of NaHPMo (3 mM), p-methoxy phenylhydrazine (100 mM), and DMPO (50 mM) in DMSO.	13

List of Supporting Tables

Table S1. Screening of photosensitizers and light sources according to UV-visible absorption of photosensitizers ^a	14
Table S2. Screening of Base ^a	14
Table S3. Screening of Solvent ^a	15
Table S4. Screening of atmosphere ^a	15

List of Supporting Methods

Instruments and reagents	16
Catalyst Preparations	16
Calculation of Apparent Quantum Efficiency (A.Q.E.)	17
Procedures for the ON-OFF Experiments	17
Investigation of mechanism by EPR	17

1. Supporting Figures

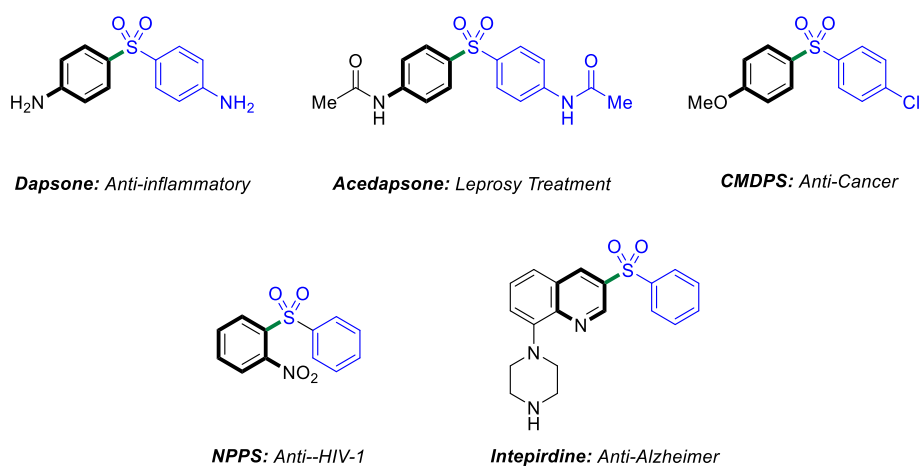


Figure S1. Representative aryl sulfones with biological activities.

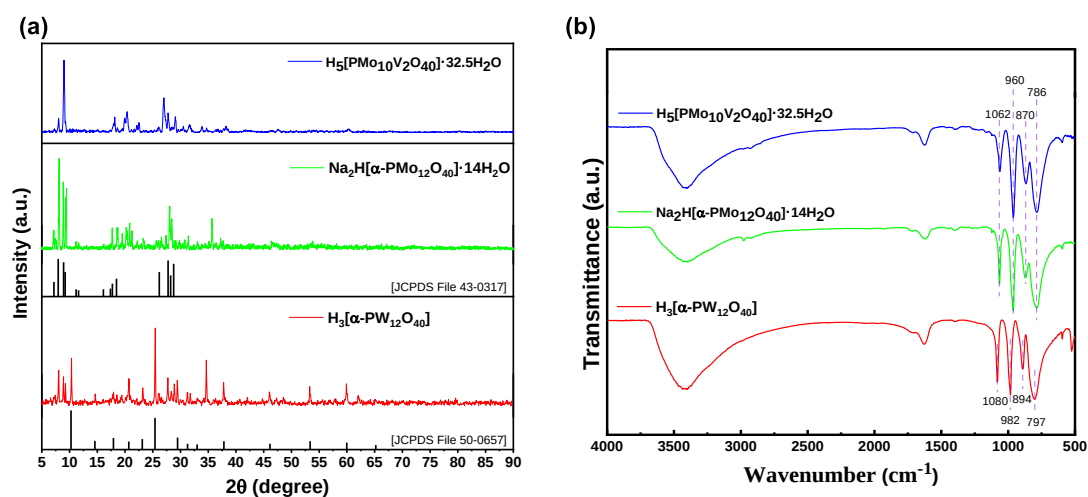


Figure S2. Characterization of POM catalysts: (a) P-XRD patterns of HPMoV (blue line), NaHPMo (green line), and HPW (red line), (b) FT-IR spectra of the as-prepared POMs.

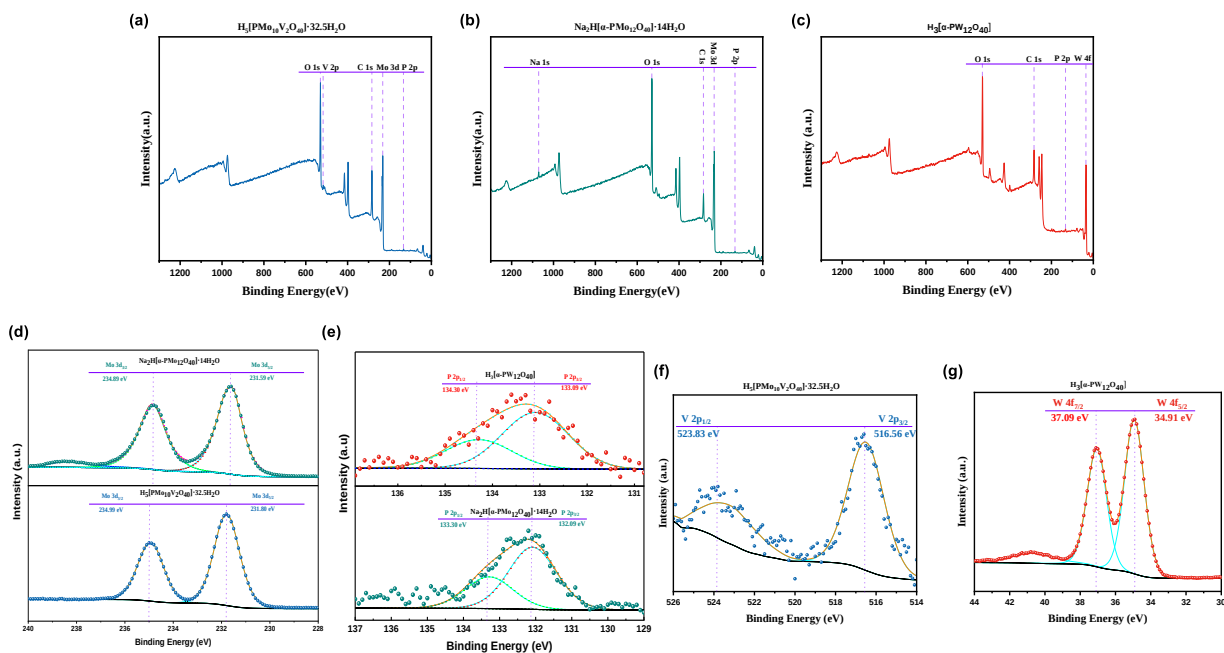


Figure S3. XPS survey analyses of (a) HPMoV, (b) NaHPMo, and (c) HPW, (d-g) XPS analysis of Mo, P, V, and W within their respective Polyoxometalate catalysts.

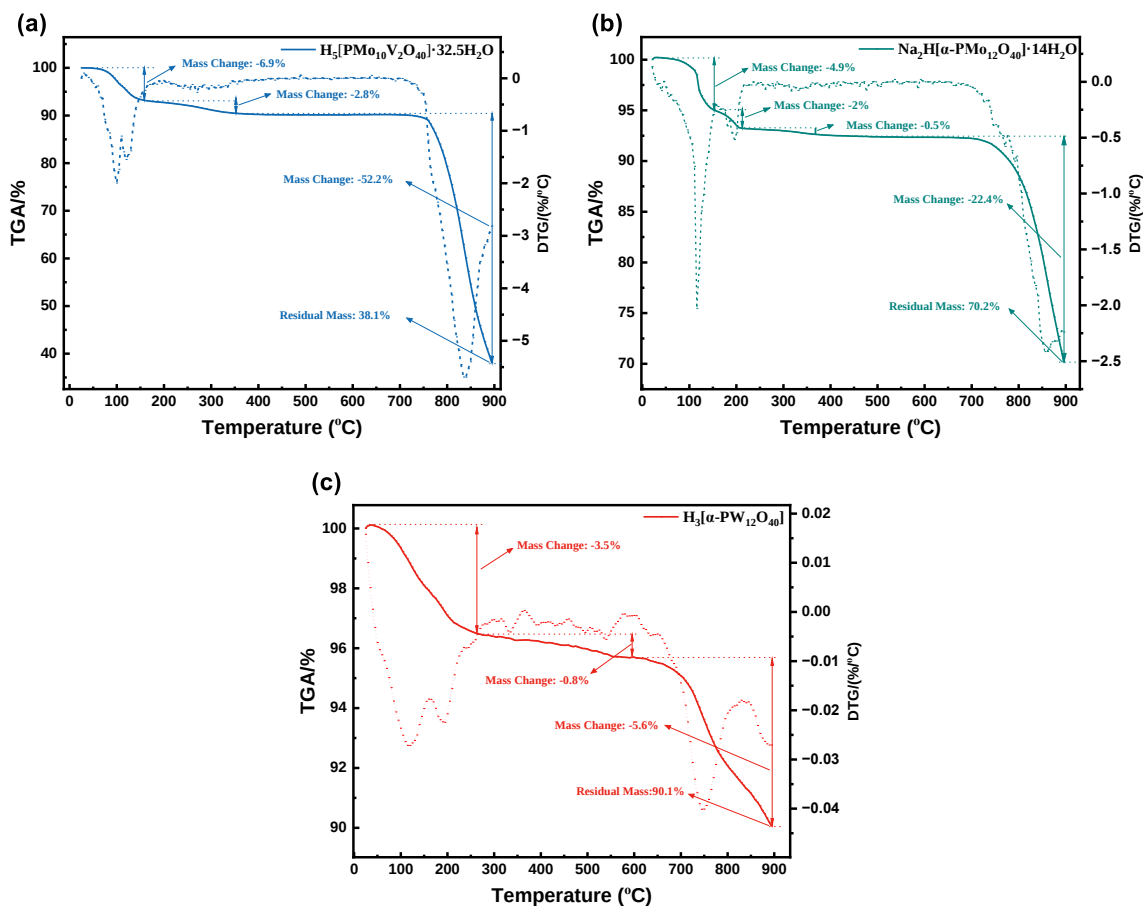


Figure S4. TGA and DTG curves of (a) HPMoV, (b) NaHPMo, and (c) HPW.

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were performed to assess the thermal stability of the synthesized POMs at a heating rate of 10 °C/min under a nitrogen atmosphere (50

mL/min), spanning a temperature range from 25 to 900 °C, as shown in Figure S4. The TGA curves for HPMoV, NaHPMo, and HPW exhibited multi-step weight loss patterns. The initial decomposition stage, occurring between 25 and 370 °C, is attributed to the removal of crystallization water, with weight losses of 9.7% for HPMoV (25-350 °C) and 7.4% for NaHPMo (25-370 °C).¹ In contrast, HPW demonstrated a weight loss of 3.5% due to surface-adsorbed water or solvents in the range of 25-260 °C.² Additionally, HPMoV and NaHPMo exhibited weight loss in the 370-890 °C range, likely corresponding to the decomposition of the Keggin unit and subsequent conversion into metal oxides such as MoO₃, V₂O₅, P₂O₅, and Na₂MoO₄, with respective weight losses of 52.2% and 22.4%, leaving residual masses of 38.1% and 70.2%, respectively. Meanwhile, HPW showed two distinct weight loss steps within the ranges of 260-600 °C and 600-890 °C, which are associated with the decomposition of the Keggin unit, conversion to metal oxides such as WO₃ and P₂O₅, and the release of gaseous products such as NO_x (0.8% and 5.6%), ultimately yielding a residual mass of 90.1%. In conclusion, the thermal stability analysis reveals significant differences in the decomposition profiles and residual masses of the synthesized POMs, highlighting their diverse thermal behaviors and loss mechanisms.

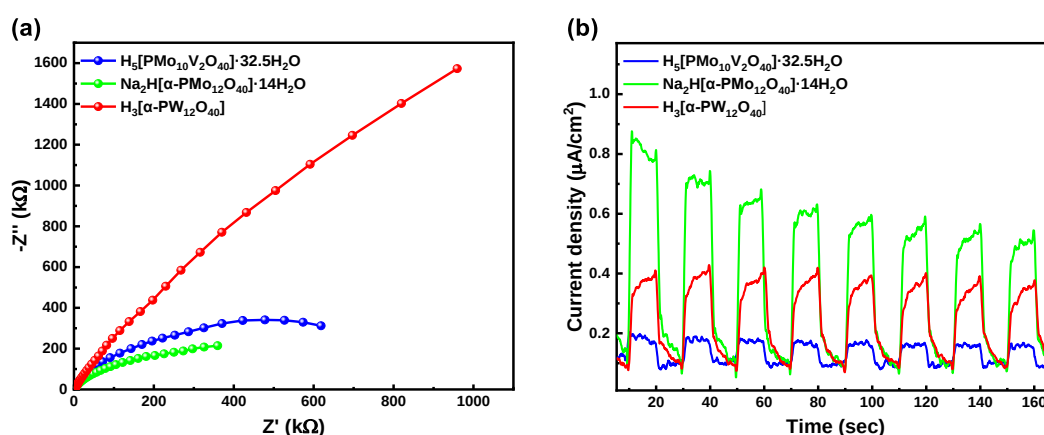
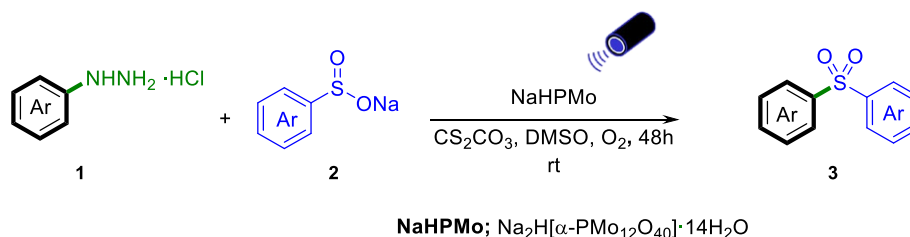


Figure S5. Electrochemical measurements of POMs: (a & b) EIS and i-t curve of HPMoV (blue line), NaHPMo (green line), and HPW (red line), respectively.

The electrochemical impedance spectroscopy (EIS) results in Figure S5a provide valuable insights into the electrochemical performance of the materials under investigation. The sizes of the Nyquist plot arcs are ranked as follows: HPW > HPMoV > NaHPMo. The smallest arc size for NaHPMo indicates the lowest interfacial charge transfer resistance, which facilitates the efficient separation of electron-hole pairs. Furthermore, the transient photocurrent-time (i-t) curves, depicted in Figure S5b, illustrate the photocatalysts' photo-response capabilities. All photocatalysts exhibit consistent photocurrent responses during light on-off cycles, with NaHPMo showing a higher photocurrent density than HPW and HPMoV. This suggests that the Keggin-type structure of NaHPMo provides a more robust photo-response capability than those of HPW and HPMoV, consistent with the previously discussed data.

General Experimental Procedure for Synthesis of Aryl Sulfones



In a 10 mL reaction vial, the following components were added: **aryldrazine hydrochloride 1** (0.3 mmol), **sodium sulfinate 2** (0.9 mmol), $\text{Na}_2\text{H}[\alpha\text{-PMo}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O}$ (0.009 mmol), Cs_2CO_3 (0.6 mmol), and anhydrous DMSO (3.0 mL). The mixture was stirred for 48 hours at 25 °C under an oxygen atmosphere (provided *via* a balloon) and illuminated with blue LED light. A thermostat with a cooling system maintained the reaction temperature at 25 °C as shown in Figure S6. Upon completion of the reaction, the crude products were purified by flash chromatography using petroleum ether/ethyl acetate as the eluent to give the desired products (**3a-3y'**).

Note: Phenylhydrazine hydrochloride (HCl adduct) is recommended over free phenylhydrazine for this reaction (resulting in 54% and 30% yields of aryl sulfones, respectively) due to its improved stability, ease of handling, and decreased sensitivity to moisture and oxygen. Furthermore, arylhydrazine hydrochlorides offer advantages in terms of cost and availability.

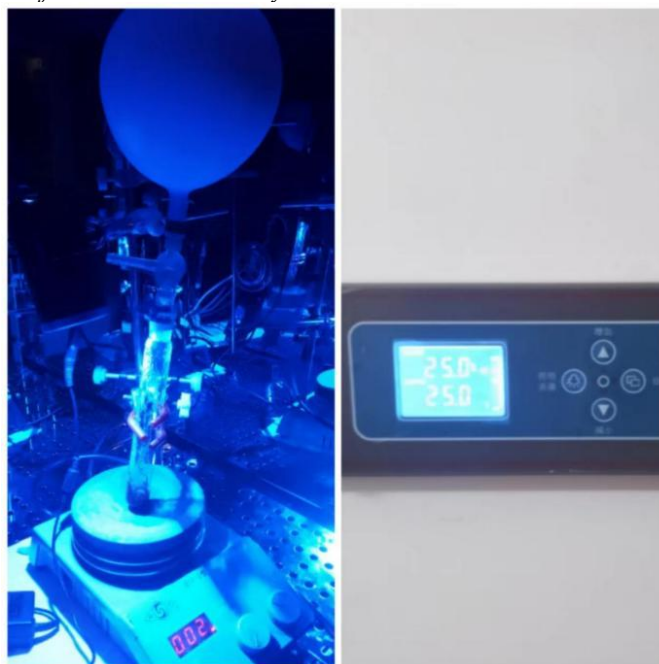


Figure S6. Reaction equipment and light source ($\lambda_{\text{peak}} = 454 \text{ nm}$).

We use the Kessil TUNA BLUE (KSA160WE-TB) light source provided by DiCon Fiberoptics, Inc. in Taiwan region. An energy spectrometer has measured the irradiance of the 40W KSA160WE-TB, finding it to be 10.9 mW/cm^2 with a peak wavelength of 454 nm (Figure S7). The irradiation is conducted within a borosilicate glass test tube, which is positioned 10 cm away from the light source. It is important to note that no light filter was used between the KSA160WE-TB and the test tube.

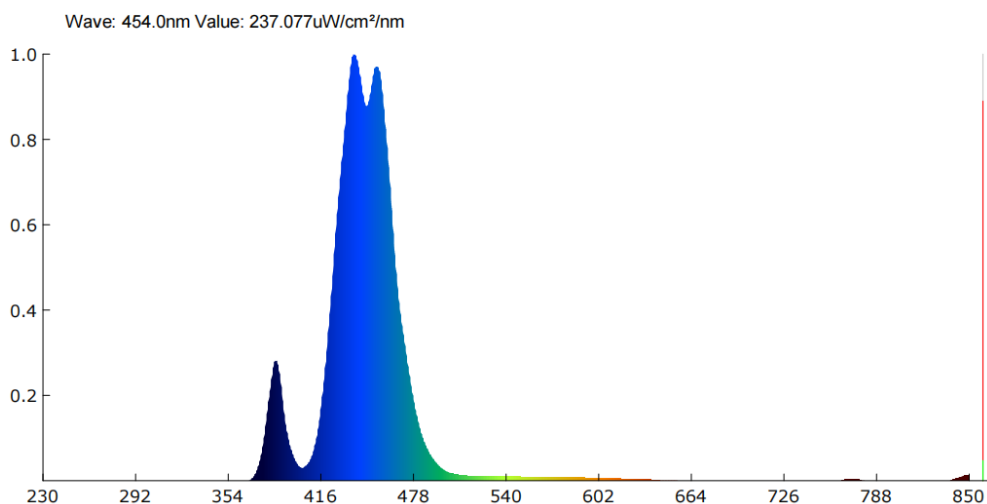


Figure S7. The emission spectrum of the 40W KSA160WE-TB, with a peak wavelength of 454 nm.

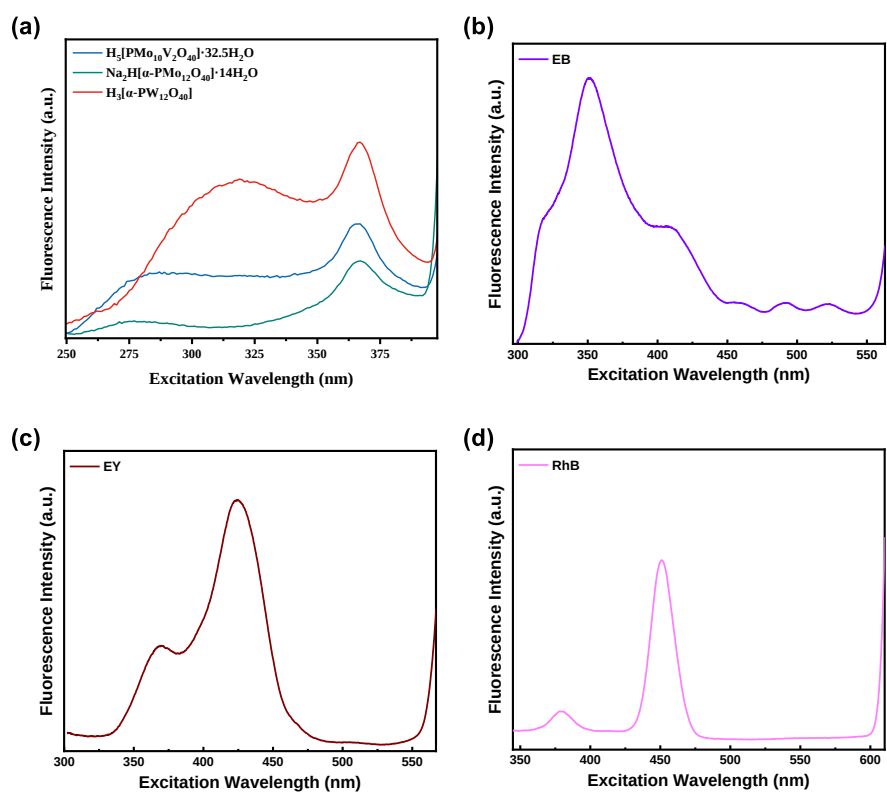


Figure S8. Excitation spectra of the screened photosensitizers, (a) HPMoV, NaHPMo, and HPW, (b) Eosin B, (c) Eosin Y, and (d) Rhodamine B.

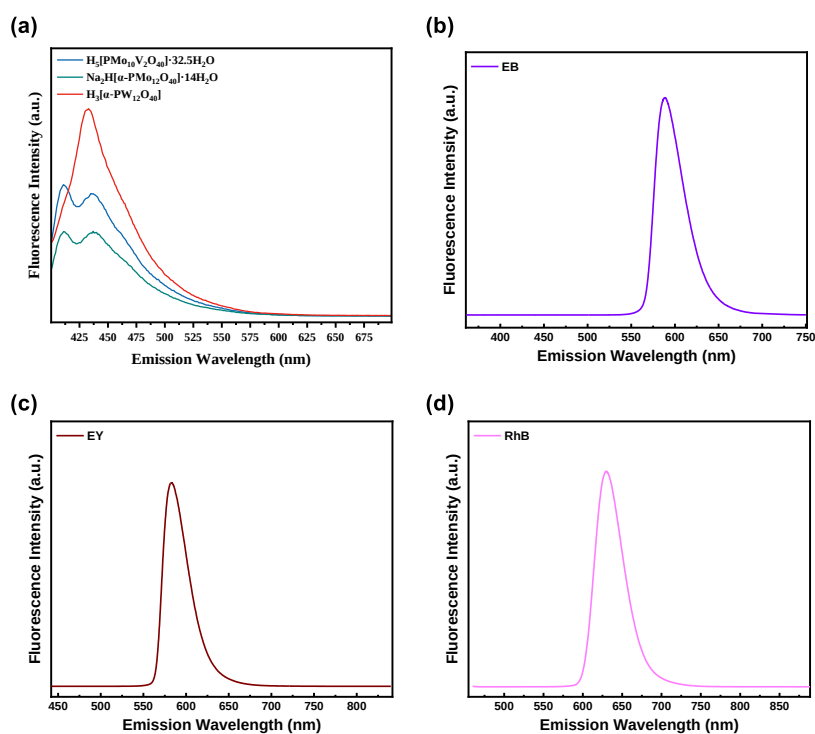


Figure S9. Emission spectra of the screened photosensitizers, (a) HPMoV, NaHPMo, and HPW, (b) Eosin B, (c) Eosin Y, and (d) Rhodamine B.

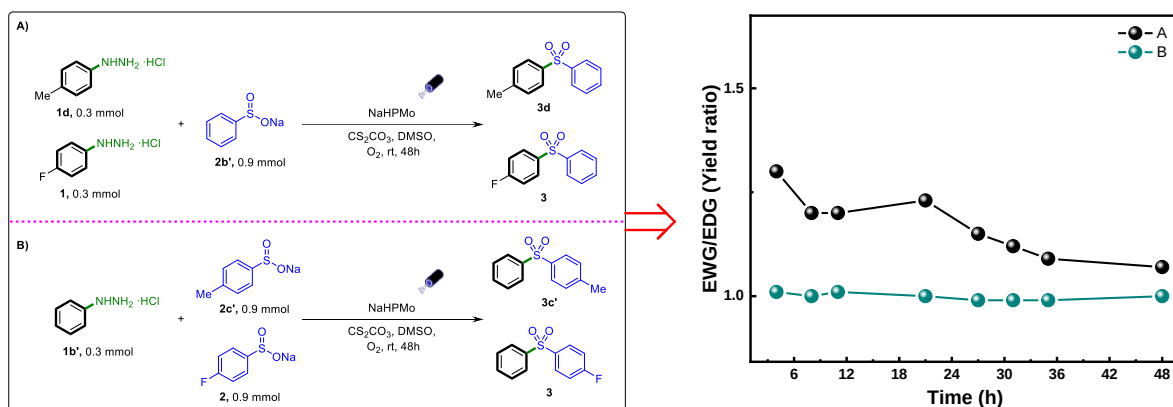


Figure S10. Competitive kinetics of substituted arylhydrazines (A) and sulfonates (B): Electron-donating group (EDG)/Electron-withdrawing group (EWG) effects.

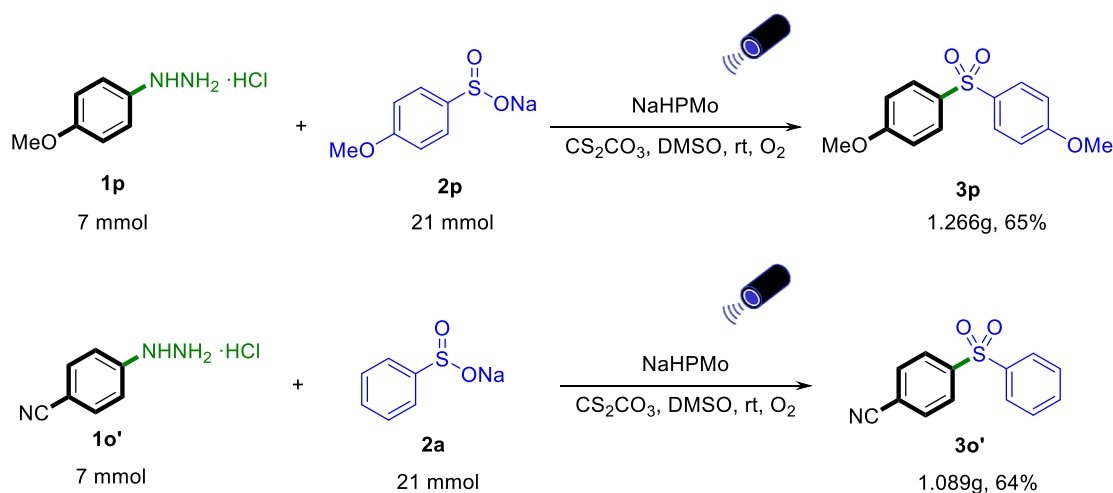


Figure S11. Gram-scale experiments.

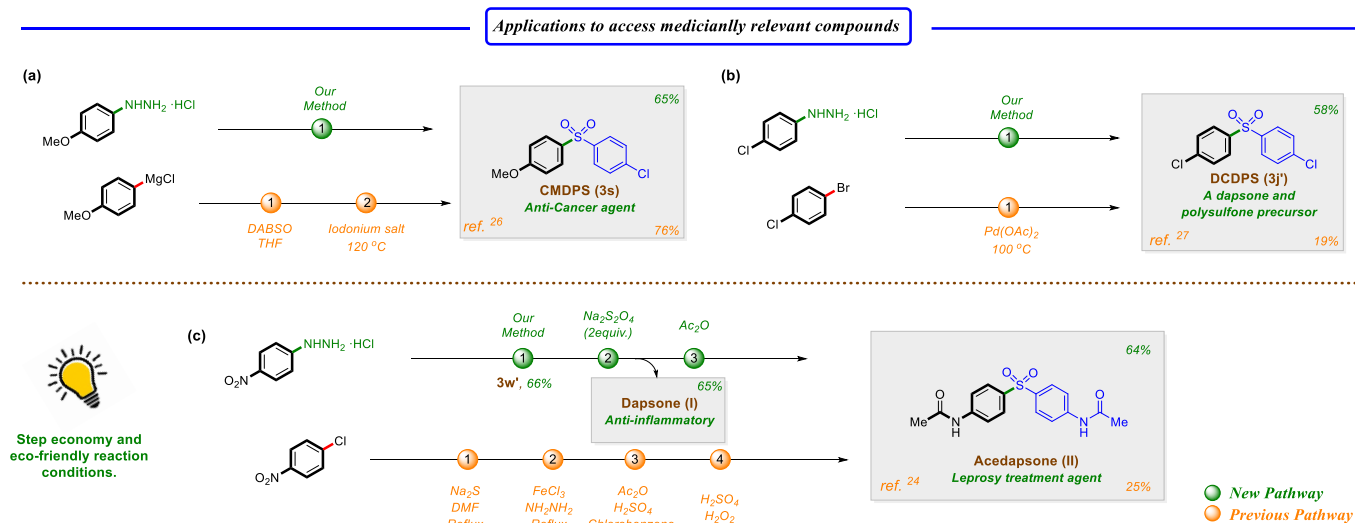


Figure S12. A comparative study of our methodology against prior methods employed in the synthesis of pharmaceutical compounds.

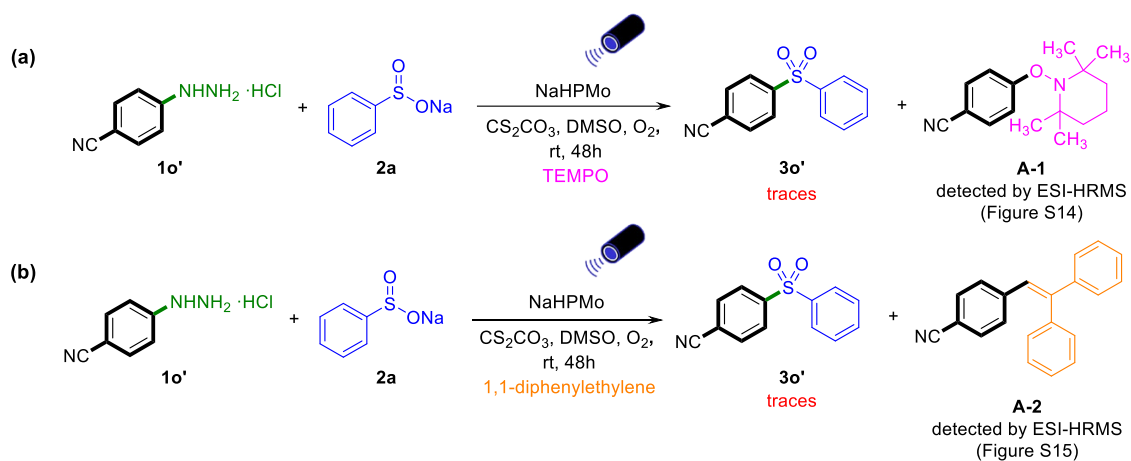


Figure S13. Radical trapping experiments.

Conditions: **1o'** (0.3 mmol), **2a** (0.9 mmol), Na₂H [α-PMo₁₂O₄₀]·14H₂O (0.009 mmol), Cs₂CO₃ (0.6 mmol), TEMPO or 1,1-diphenylethylene (0.9 mmol), anhydrous DMSO 3.0 mL, stirred for 48 h at 25 °C under O₂ and Blue LED irradiation.

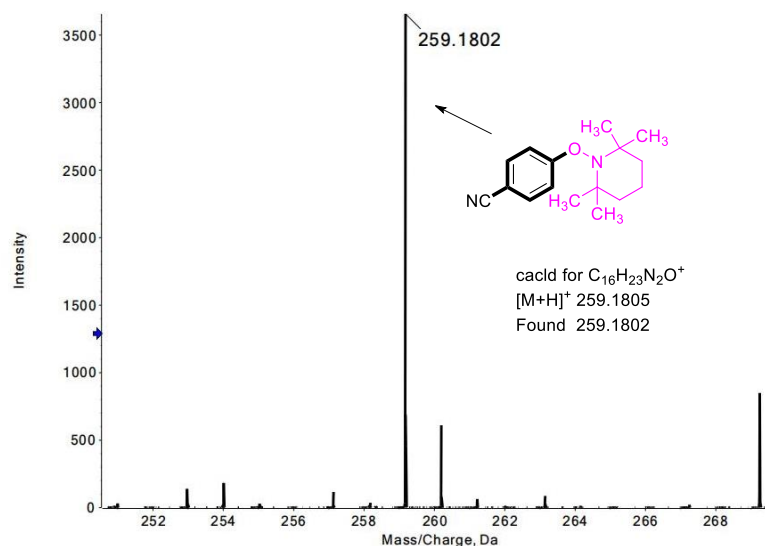


Figure S14. ESI-HRMS spectrum for radical adduct **A-1** with TEMPO.

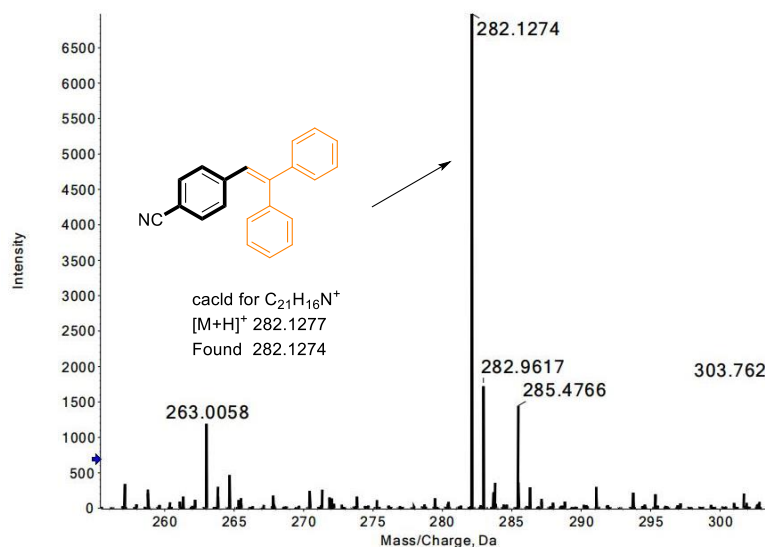


Figure S15. ESI-HRMS spectrum for radical adduct **A-2** with 1,1-diphenylethylene.

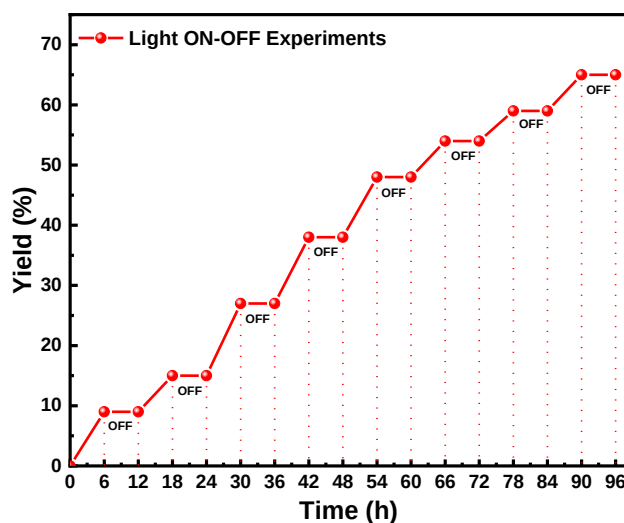


Figure S16. Light ON-OFF experiments.

Stern-Volmer Fluorescence Quenching Experiments

Firstly, the emission and excitation spectra of NaHPMo were investigated. NaHPMo (0.1 mM) solution in DMSO was chosen as the model. The fluorescence excitation spectrum was obtained with the detection wavelength of 381 nm (Figure S17), and the fluorescence emission spectrum was detected at 457 nm (Figure S18). Next, we conducted the fluorescence quenching experiments. In a typical experiment, 3.0 mL of solution of NaHPMo (0.1 mM) in DMSO was added to the appropriate amount of quencher in a quartz cuvette, 0.667 mM solution of the quencher (*p*-methoxy phenylhydrazine hydrochloride) was added into the cuvette by 100 μ L, and the emission of the sample was collected (Figure S19). The solution was excited at 381 nm (excitation maximum of NaHPMo) and the emission intensity at 457 nm (emission maximum of NaHPMo). By fitting the above measurements, a linear relationship was observed between the NaHPMo emission quenching (I_0/I) and the concentration of *p*-methoxy phenylhydrazine hydrochloride (Figure S20).

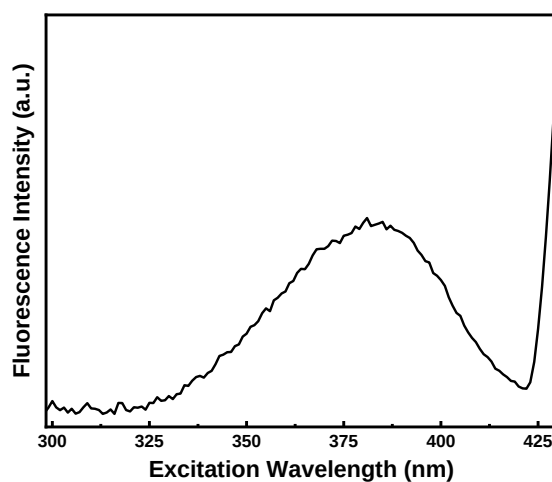


Figure S17. Fluorescence excitation spectrum of NaHPMo was detected at 457 nm.

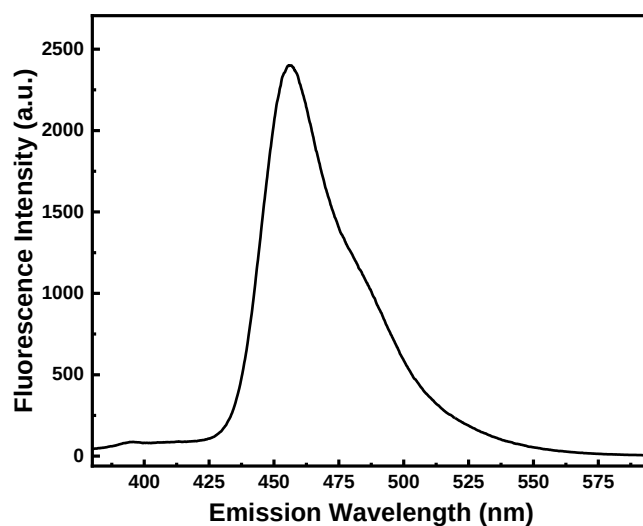


Figure S18. Fluorescence emission spectrum of NaHPMo excited at 381 nm.

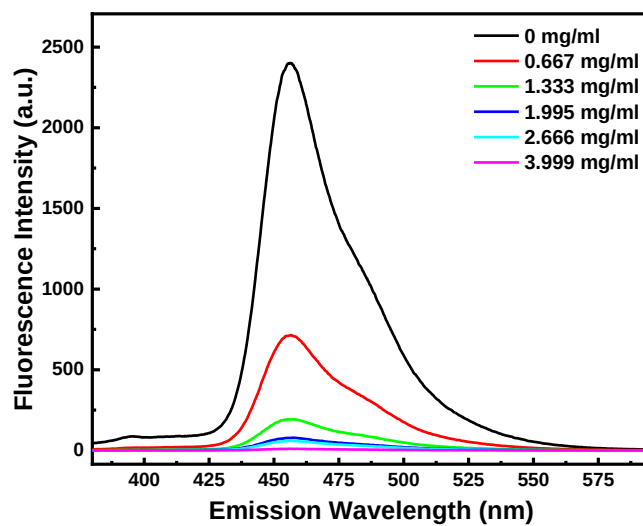


Figure S19. Fluorescence emission spectra of NaHPMo with different quencher concentrations (*p*-methoxy phenylhydrazine hydrochloride).

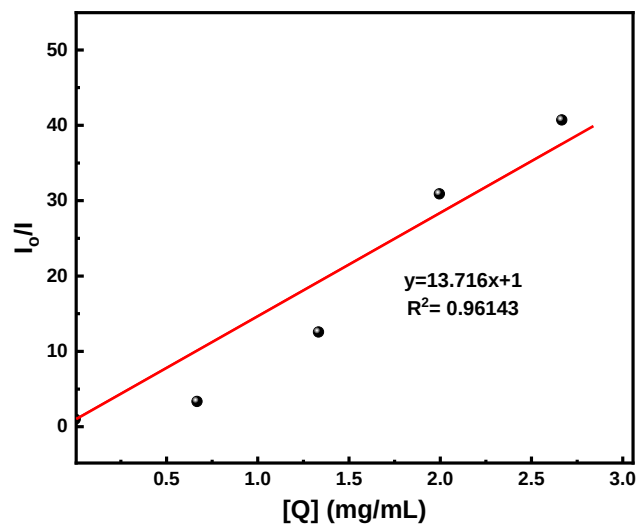


Figure S20. Dynamic emission quenching of NaHPMo by *p*-methoxy phenylhydrazine hydrochloride.

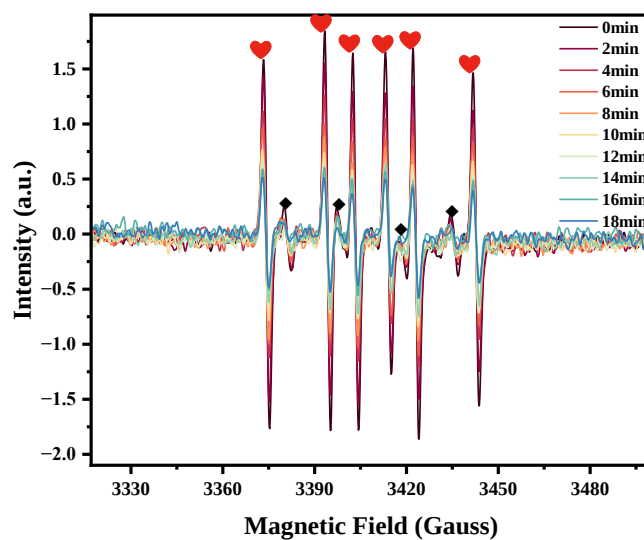
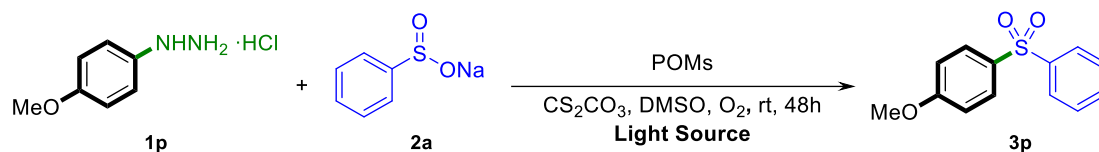


Figure S21. EPR spectrum for a mixture of NaHPMo (3 mM), *p*-methoxy phenylhydrazine (100 mM), and DMPO (50 mM) in DMSO.

2. Supporting Tables

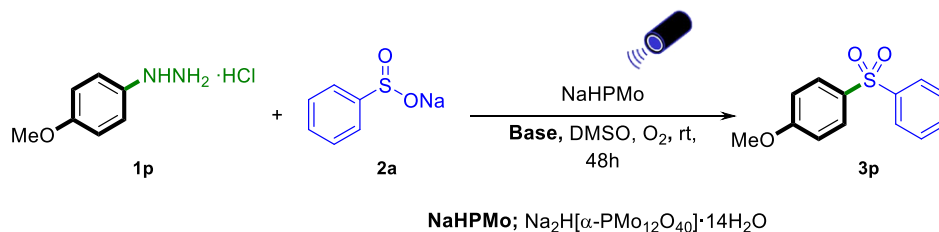
Table S1. Screening of photosensitizers and light sources according to UV-visible absorption of photosensitizers ^a



Entry	Photosensitizer	Light source	Yield (%) ^b
1	$\text{Na}_2\text{H}[\alpha\text{-PMo}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O}$	Blue LED	65
2	$\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}] \cdot 32.5\text{H}_2\text{O}$	Blue LED	44
3	$\text{H}_3[\alpha\text{-PW}_{12}\text{O}_{40}]$	Blue LED	50
4	Eosin B	395nm	8
5	Eosin Y	Blue LED	22
6	Rhodamine B	Blue LED	13
7	-	-	Traces

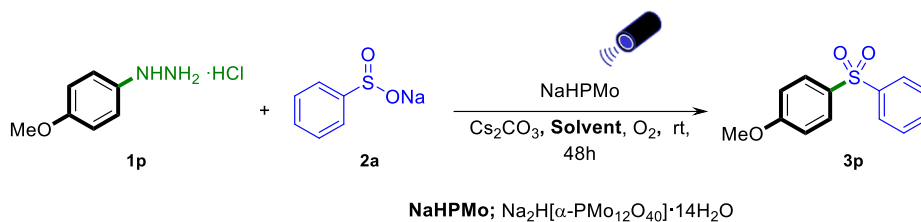
^a Reaction conditions: **1p** (0.3 mmol), **2a** (0.9 mmol), Photosensitizer (0.009 mmol), anhydrous DMSO (3.0 mL), CS_2CO_3 (0.6 mmol), stirred for 48 h at 25 °C under O_2 and irradiation of visible light. ^b Isolated yield.

Table S2. Screening of Base ^a



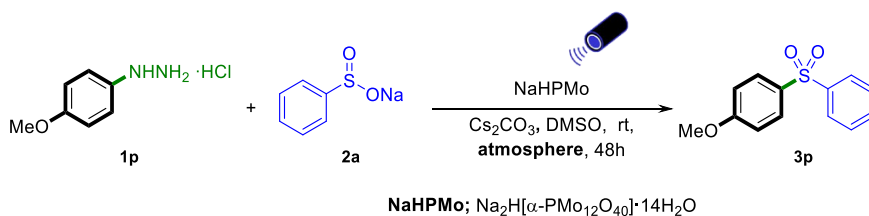
Entry	Base	Yield (%) ^b
1	Cs_2CO_3	65
2	DBU	38
3	Et_3N	NR
4	K_2CO_3	21
5	--	NR

^a Reaction conditions: **1p** (0.3 mmol), **2a** (0.9 mmol), $\text{Na}_2\text{H}[\alpha\text{-PMo}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O}$ (0.009 mmol), anhydrous DMSO (3.0 mL), Base (0.6 mmol), stirred for 48 h at 25 °C under O_2 and irradiation of Blue LED. ^b Isolated yield.

Table S3. Screening of Solvent ^a

Entry	Solvent	Yield (%) ^b
1	DMSO	65
2	DMF	39
3	CH ₃ CN	NR
4	DCM	NR
5	DCE	8
6	THF	22
7	Toluene	28

^a Reaction conditions: **1p** (0.3 mmol), **2a** (0.9 mmol), Na₂H[α-PMo₁₂O₄₀]·14H₂O (0.009 mmol), anhydrous solvent (3.0 mL), Cs₂CO₃ (0.6 mmol), stirred for 48 h at 25 °C under O₂ and irradiation of Blue LED. ^b Isolated yield.

Table S 4. Screening of atmosphere ^a

Entry	atmosphere	Yield (%) ^b
1	O₂	65
2	N ₂	Traces
3	Air	42

^a Reaction conditions: **1p** (0.3 mmol), **2a** (0.9 mmol), Na₂H[α-PMo₁₂O₄₀]·14H₂O (0.009 mmol), anhydrous DMSO (3.0 mL), Cs₂CO₃ (0.6 mmol), stirred for 48 h at 25 °C under certain atmosphere and irradiation of Blue LED. ^b Isolated yield.

3. Supporting Methods

Instruments and reagents

^1H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz or 300 MHz spectrometers. Proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) in the solvent of CDCl_3 or $\text{DMSO}-d_6$ as the internal standard (^1H NMR: TMS at 0.00 ppm, CDCl_3 at 7.26 ppm, and DMSO at 2.50 ppm; ^{13}C NMR: TMS at 0.00 ppm, CDCl_3 at 77.16 ppm, and DMSO at 39.51 ppm). Melting points were recorded on WRS-1B. Mass spectra were recorded with a Bruker Esquire 6000 using Atmospheric pressure chemical ionization (APCI) and Electrospray ionization (ESI) techniques. The structure of the products was determined by powder X-ray diffraction (XRD, Bruker D8 Advance, Germany). The X-ray photoelectron spectroscopy (XPS) was collected on an AXIS SUPRA+ with a monochromatic Al $\text{K}\alpha$ X-ray source. The thermogravimetric analyses (TGA) data were collected using the NETZSCH STA449F5/QMS 403D system, Germany. The UV–visible absorption spectra were obtained using a Agilent Cary 5000 spectrometer. The electrochemical impedance spectroscopy (EIS) and transient photocurrent-time (i-t) curve measurements were obtained on a CHI760e electrochemical workstation. Solvents and substrates were obtained from TCI, Aldrich, Bidepharm, and Macklin. Unless otherwise noted, all the materials and reagents were commercial without further purifications.

Catalyst Preparations

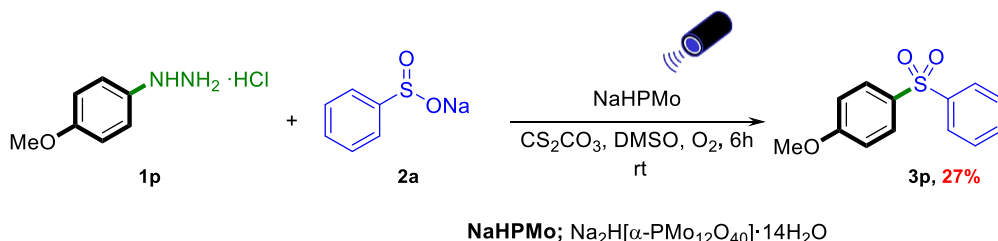
Synthesis of $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]\cdot 32.5\text{H}_2\text{O}$ (HPMoV): prepared according to the reported procedure.^{3,4} NaVO_3 (3.0 g, 0.025 mol) and MoO_3 (7.4 g, 0.051 mol) were dissolved in 80.0 mL of distilled water under stirring, followed by the addition of 340.0 μL of 85% H_3PO_4 (~ 14.7 M). Then, the mixture was refluxed at 115 $^\circ\text{C}$ for 8 h. After completion, the solution was acidified with 14.5 mL of concentrated HCl and then extracted with THF. After removing the THF, the crude crystal product was obtained, which was then recrystallized with water to obtain the crystalline product.

Synthesis of $\text{Na}_2\text{H}[\alpha\text{-PMo}_{12}\text{O}_{40}]\cdot 14\text{H}_2\text{O}$ (NaHPMo): The synthetic procedure was identical to the previous report.⁵ Na_2MoO_4 (29.0 g, 0.141 mol) was dissolved in 42.0 mL of distilled water at room temperature, then 0.7 mL of 85% H_3PO_4 (~ 14.7 M) and 28.4 mL of 70% HClO_4 (~ 11.7 M) were drop wisely added, respectively. The homogeneous solution was continuously stirred at room temperature for 8 h. After that, the solution was cooled to room temperature, and then the precipitate was separated by filtering. The crude product was recrystallized with 40 mL of Et_2O and 200 mL of H_2O to obtain the green microcrystal product.

Synthesis of $\text{H}_3[\alpha\text{-PW}_{12}\text{O}_{40}]$ (HPW): The $\alpha\text{-PW}_{12}$ was synthesized according to the reported approach,⁶ by dissolving $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ (10.0 g) in 10 mL distilled water under heat to form a clear solution. Then, 1.0 mL of 85% H_3PO_4 and 8.0 mL of concentrated HCl were added, and the mixture was stirred for 6 hours. The solid product was filtered and dissolved in 12.0 mL distilled water and transferred to a separatory funnel with 7.0 mL ether. Adding 4.0 mL concentrated HCl , the funnel was shaken. After 5 minutes, the lower layer was taken, shaken with 15.0 mL distilled water, 5.0 mL anhydrous ether, and 4.0 mL concentrated HCl . The

lower white oily solution containing $\text{H}_3[\alpha\text{-PW}_{12}\text{O}_{40}]$ ether complex was separated, treated with 10 mL water, and then heated to remove ether, yielding a white crystalline product.

Calculation of Apparent Quantum Efficiency (A.Q.E.)



The apparent quantum efficiency (A.Q.E.) was calculated from the ratio of the number of reacted electrons during the reaction to the number of incident photons as follows:

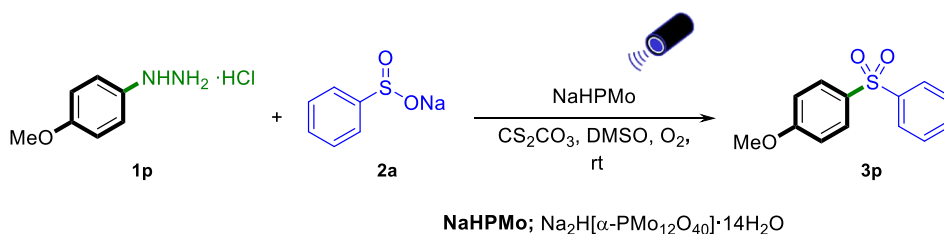
$$E_{\text{photon}} = \frac{hc}{\lambda_{\text{inc}}} = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s} \times 3 \times 10^8 \text{ ms}^{-1}}{454 \times 10^{-9} \text{ m}} = 4.38 \times 10^{-19} \text{ J}$$

$$E_{\text{total}} = Pst = 15.852 \times 10^{-3} \text{ W/cm}^2 \times 3.14 \text{ cm}^2 \times 6 \times 3600 \text{ s} = 1075.146 \text{ J}$$

$$\text{Number of incident photons} = \frac{E_{\text{total}}}{E_{\text{photon}}} = \frac{1075.146 \text{ J}}{4.38 \times 10^{-19} \text{ J}} = 24.54 \times 10^{20} = 4.076 \text{ mmol}$$

$$\text{A. Q. E (\%)} = \frac{\text{Number of product}}{\text{Number of incident photons}} \times 100 = \frac{0.081}{4.076} \times 100 = 1.99\%$$

Procedure for the ON-OFF Experiment



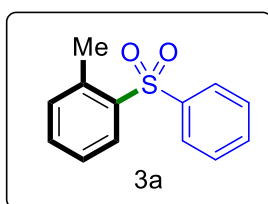
In a 10 mL reaction vial, the following components were added: **1p** (0.3 mmol), **2a** (0.9 mmol), $\text{Na}_2\text{H}[\alpha\text{-PMo}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O}$ (0.009 mmol), Cs_2CO_3 (0.6 mmol), n-dodecane (0.3 mmol), and anhydrous DMSO (3.0 mL). The resulting mixture was subjected to stirring for 6 hours at 25 °C under an oxygen atmosphere (provided via a balloon) and illuminated with blue LED light. Subsequently, upon cessation of the light source, a 20 μL aliquot of the reaction mixture was extracted for GC-FID analysis to evaluate the yield of **3p**. The mixture was then stirred for an additional 6 hours at 25 °C under the same oxygen conditions in a dark environment, followed by another 20 μL sample collection for GC-FID analysis. The remaining reaction mixture underwent alternating stirring under blue LED illumination and in the dark, with GC-FID analyses conducted every 6 hours until the total reaction time reached 96 hours, as illustrated in Figure S16.

Investigation of mechanism by EPR

Electron Paramagnetic Resonance (EPR) spectra were recorded using a JEOL JES X320 spectrometer operating in the X-band frequency range. The measurement conditions were as follows: frequency 9.6256

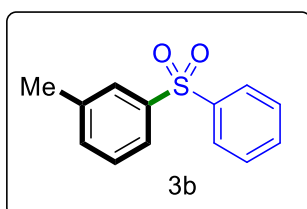
GHz, power 0.1 mW, center field 341.7 mT, sweep width 20 mT, modulation width 0.1 mT, amplitude 600, sweep time 2 minutes, and time constant 0.1 seconds. A mixture containing NaHPMo (3 mM), *p*-methoxy phenylhydrazine hydrochloride (100 mM), and DMPO (50 mM) was placed in a flat cell, which was subsequently introduced into the EPR instrument. The spectrum was recorded in situ under visible light irradiation. Following 18 minutes of irradiation with visible light (>400 nm), a sextet signal was observed (indicated by heart shapes) with $g = 2.0045$, $AN = 14.5$ G, and $AH = 21.5$ G, corresponding to a centered phenyl radical as shown in Figure S21.⁷ Additionally, a quartet signal was detected (rhombus shapes) with $g = 2.0040$, $AN = 13.0$ mT, and $AH = 11.0$ mT, attributed to a superoxide radical generated from atmospheric oxygen.⁸

4. Characterization Data of Product of 3a-3y'



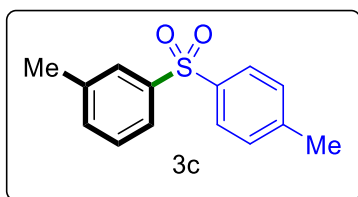
1-Methyl-2-(phenylsulfonyl) benzene (3a)⁹

Physical properties: White solid (36.2 mg, 52% yield). Melting Point 69.7-70.5 °C, (lit.⁹ mp 66-68 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.87 – 7.71 (m, 2H), 7.54 – 7.35 (m, 4H), 7.32 (td, $J = 7.6, 1.3$ Hz, 1H), 7.16 (d, $J = 7.5$ Hz, 1H), 2.36 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 141.30, 138.83, 138.01, 133.64, 133.04, 132.69, 129.44, 129.04, 127.67, 126.49, 20.20. ESI m/z : $[M+H]^+$ Calcd for C₁₃H₁₃O₂S⁺ 233.02; Found 233.01.



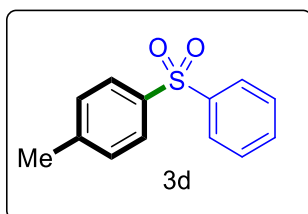
1-Methyl-3-(phenylsulfonyl) benzene (3b)⁹

Physical properties: White solid (41.1 mg, 59% yield). Melting Point 108.1-108.9 °C, (lit.⁹ mp 107-109 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.91 (m, 2H), 7.81 – 7.69 (m, 2H), 7.61 – 7.48 (m, 3H), 7.44 – 7.33 (m, 2H), 2.40 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 141.78, 141.44, 139.56, 134.01, 133.09, 129.25, 129.14, 127.96, 127.63, 124.85, 21.34. ESI m/z : $[M+H]^+$ Calcd for C₁₃H₁₃O₂S⁺ 233.06; Found 233.06.



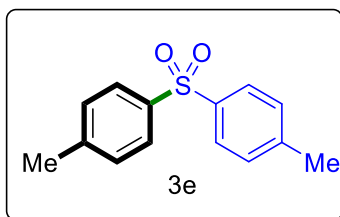
1-Methyl-3-[(4-methylphenyl) sulfonyl] benzene (3c)¹⁰

Physical properties: White solid (42.8 mg, 58% yield). Melting Point 134.3-135.9 °C, (lit.¹⁰ mp 133-135 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.71 (m, 2H), 7.70 – 7.57 (m, 2H), 7.33 – 7.18 (m, 4H), 2.30 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 144.08, 141.81, 139.49, 138.80, 133.84, 129.90, 129.10, 127.78, 127.68, 124.67, 21.56. ESI *m/z*: [M+H]⁺ Calcd for C₁₄H₁₅O₂S⁺ 247.06; Found 247.06.



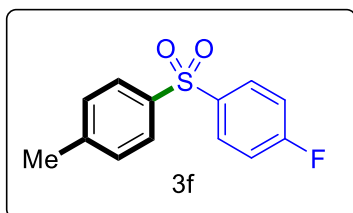
1-Methyl-4-(phenylsulfonyl) benzene (3d)⁹

Physical properties: White solid (49.4 mg, 71% yield). Melting Point 126.5-127.8 °C, (lit.⁹ mp 129-130 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.80 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.43 (dt, *J* = 14.4, 7.1 Hz, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 144.17, 142.00, 138.66, 133.00, 129.92, 129.22, 127.73, 127.50, 21.57. ESI *m/z*: [M+H]⁺ Calcd for C₁₃H₁₃O₂S⁺ 233.06; Found 233.07.



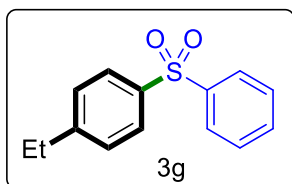
1,1'-Sulfonylbis[4-methylbenzene] (3e)¹¹

Physical properties: White solid (48 mg, 65% yield). Melting Point 159.9-160.5 °C, (lit.¹¹ mp 158-160 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.66 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 4H), 2.31 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 143.92, 139.08, 129.85, 127.56, 21.54. ESI *m/z*: [M+H]⁺ Calcd for C₁₄H₁₅O₂S⁺ 247.07; Found 247.05.



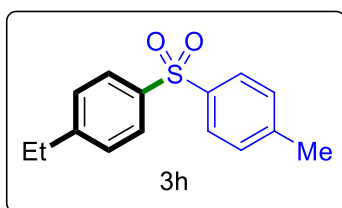
1-Fluoro-4-[(4-methylphenyl) sulfonyl] benzene (3f)¹¹

Physical properties: White solid (48.8 mg, 65% yield). Melting Point 84.5-85.6 °C, (lit.¹¹ mp 83-85 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 8.6, 5.1 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.09 (t, *J* = 8.5 Hz, 2H), 2.33 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.60, 164.06, 144.38, 138.50, 138.09, 138.06, 130.36, 130.27, 130.03, 127.64, 116.64, 116.42, 21.59. ESI *m/z*: [M+H]⁺ Calcd for C₁₃H₁₂FO₂S⁺ 251.05; Found 251.01.



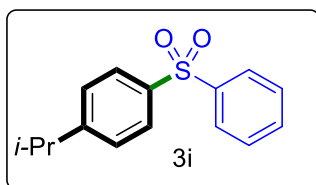
1-Phenylsulfonyl-4-ethylbenzene (3g)

Physical properties: White solid (49.5 mg, 67% yield). Melting Point 91.5-92.0 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.83 (m, 2H), 7.83 – 7.67 (m, 2H), 7.52 – 7.36 (m, 3H), 7.23 (s, 2H), 2.60 (q, J = 7.6 Hz, 2H), 1.14 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.29, 141.99, 138.81, 133.02, 129.23, 128.79, 127.81, 127.54, 28.83, 15.07. ESI m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2\text{S}^+$ 247.07; Found 247.06.



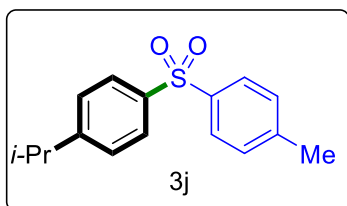
4-Ethylphenyl-4-methylphenyl sulfone (3h)

Physical properties: White solid (49.2 mg, 63% yield). Melting Point 112.1-112.8 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.69 (m, 4H), 7.29 (t, J = 7.6 Hz, 4H), 2.68 (q, J = 7.6 Hz, 2H), 2.39 (s, 3H), 1.22 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.03, 143.91, 139.23, 139.07, 129.85, 128.71, 127.66, 127.61, 28.83, 21.55, 15.09. ESI m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{17}\text{O}_2\text{S}^+$ 261.10; Found 261.10.



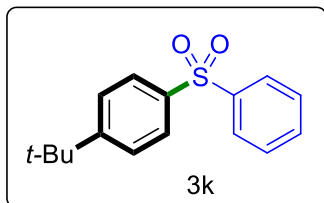
1-(1-Methylethyl)-4-(phenylsulfonyl) benzene (3i)

Physical properties: White solid (53.1 mg, 68% yield). Melting Point 58.4-59.2 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.90 (m, 2H), 7.90 – 7.68 (m, 2H), 7.61 – 7.47 (m, 3H), 7.40 – 7.31 (m, 2H), 2.94 (hept, J = 6.9 Hz, 1H), 1.23 (d, J = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.83, 141.97, 138.90, 133.02, 129.30, 129.23, 127.84, 127.57, 127.43, 34.20, 23.60. ESI m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{17}\text{O}_2\text{S}^+$ 261.10; Found 261.10.



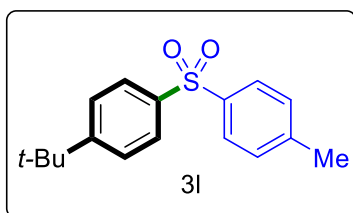
1-(1-Methylethyl)-4-[(4-methylphenyl) sulfonyl] benzene (3j)

Physical properties: White solid (53.5 mg, 65% yield). Melting Point 108.6-109.4 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.68 (m, 4H), 7.28 – 7.18 (m, 4H), 2.85 (hept, J = 6.9 Hz, 1H), 2.30 (s, 3H), 1.14 (d, J = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.60, 143.94, 139.30, 139.04, 129.86, 127.66, 127.63, 127.36, 34.18, 23.61, 21.55. ESI m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{S}^+$ 275.10; Found 275.06.



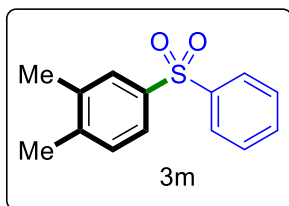
1-(1,1-Dimethylethyl)-4-(phenylsulfonyl) benzene (3k)⁹

Physical properties: White solid (51 mg, 62% yield). Melting Point 129.2-130.6 °C, (lit.⁹ mp 128-130 °C). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.81 (m, 2H), 7.81 – 7.73 (m, 2H), 7.49 – 7.36 (m, 5H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.10, 141.95, 138.55, 133.03, 129.24, 127.60, 127.54, 126.33, 35.18, 31.04. ESI m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{S}^+$ 275.10; Found 275.09.



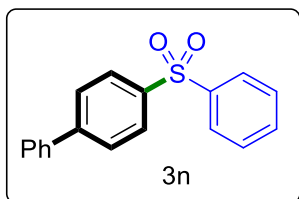
1-(1,1-Dimethylethyl)-4-[(4-methylphenyl) sulfonyl] benzene (3l)¹²

Physical properties: White solid (51.9 mg, 60% yield). Melting Point 143.4-144.8 °C, (lit.¹² mp 144-145 °C). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.66 (m, 4H), 7.44 – 7.37 (m, 2H), 7.19 (d, J = 4.4 Hz, 2H), 2.30 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.86, 143.95, 139.02, 138.95, 129.87, 127.66, 127.37, 126.26, 35.15, 31.04, 21.55. ESI m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{21}\text{O}_2\text{S}^+$ 289.12; Found 289.11.



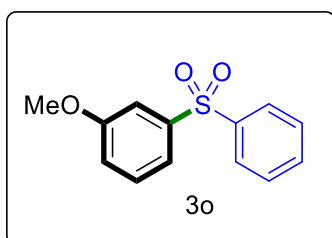
1,2-Dimethyl-4-(phenylsulfonyl) benzene (3m)¹³

Physical properties: White solid (42.1 mg, 57% yield). Melting Point 106.9-108.5 °C, (lit.¹³ mp 107.8-111.2 °C). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.90 (m, 2H), 7.70 – 7.64 (m, 2H), 7.54 – 7.45 (m, 3H), 7.24 (d, J = 7.9 Hz, 1H), 2.28 (d, J = 2.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.92, 142.15, 138.76, 138.11, 132.92, 130.42, 129.20, 128.45, 127.47, 125.26, 19.95. ESI m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2\text{S}$ 247.07; Found 247.06.



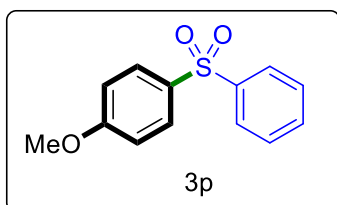
4-(Phenylsulfonyl)-1,1'-biphenyl (3n)¹⁴

Physical properties: White solid (55.6 mg, 63% yield). Melting Point 150.5-152.2 °C, (lit.¹⁴ mp 150-151 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 (td, *J* = 8.2, 7.4, 1.8 Hz, 4H), 7.64 – 7.57 (m, 2H), 7.59 – 7.30 (m, 8H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 146.20, 141.76, 140.15, 139.16, 133.24, 129.36, 129.09, 128.63, 128.23, 127.96, 127.67, 127.37. ESI *m/z*: [M+H]⁺ Calcd for C₁₈H₁₅O₂S⁺ 295.07; Found 295.05.



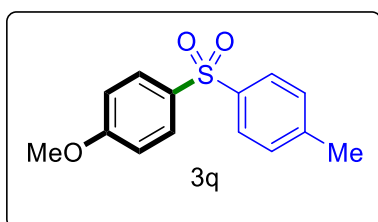
1-Methoxy-3-(phenylsulfonyl) benzene (3o)¹⁴

Physical properties: White solid (46.18 mg, 62% yield). Melting Point 89.1-90.6 °C, (lit.¹⁴ mp 89-91 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.87 (m, 2H), 7.61 – 7.37 (m, 6H), 7.07 (dd, *J* = 8.3, 2.6 Hz, 1H), 3.82 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 160.04, 142.74, 141.59, 133.19, 130.38, 129.27, 127.65, 119.94, 119.55, 112.27, 55.69. ESI *m/z*: [M+H]⁺ Calcd for C₁₃H₁₃O₃S⁺ 249.05; Found 249.03.



4-Methoxyphenyl phenyl sulfone (3p)¹⁵

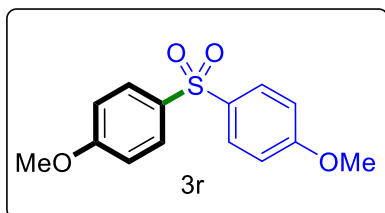
Physical properties: White solid (48.4 mg, 65% yield). Melting Point 92.5-93.8 °C, (lit.¹⁵ mp 91-93 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.69 (m, 4H), 7.56 – 7.32 (m, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.76 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.39, 142.37, 133.11, 132.85, 129.89, 129.21, 127.31, 114.52, 55.65. ESI *m/z*: [M+H]⁺ Calcd for C₁₃H₁₃O₃S⁺ 249.05; Found 249.05.



1-Methoxy-4-[(4-methylphenyl)sulfonyl]benzene (3q)⁹

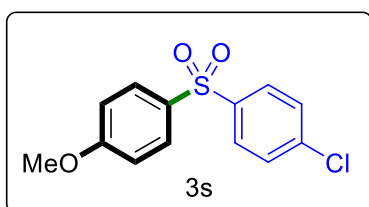
Physical properties: White solid (47.2 mg, 60% yield). Melting Point 104.4-105.3 °C, (lit.⁹ mp 103-105 °C). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.92 – 7.83 (m, 2H), 7.81 – 7.74 (m, 2H), 7.42 – 7.36 (m, 2H), 7.13 – 7.08

(m, 2H), 3.81 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.24, 143.74, 139.45, 133.57, 129.83, 129.71, 127.38, 114.45, 55.63, 21.53. ESI *m/z*: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{15}\text{O}_3\text{S}^+$ 263.07; Found 263.06.



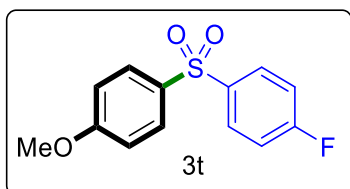
1,1'-Sulfonylbis[4-methoxybenzene] (3r)⁹

Physical properties: White solid (50.1 mg, 60% yield). Melting Point 129.1-129.9 °C, (lit.⁹ mp 128-130 °C). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.79 (m, 4H), 6.98 – 6.90 (m, 4H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.11, 133.96, 129.51, 114.43, 55.64. ESI *m/z*: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{15}\text{O}_3\text{S}^+$ 277.08; Found 277.08.



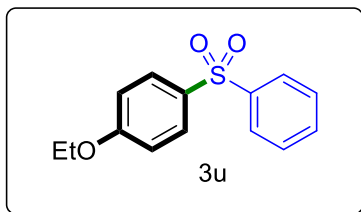
1-Chloro-4-((4-methoxyphenyl) sulfonyl) benzene (3s)⁹

Physical properties: White solid (55.1 mg, 65% yield). Melting Point 72.6-73.9 °C, (lit.⁹ mp 71-73 °C). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.80 (m, 4H), 7.52 – 7.41 (m, 2H), 7.01 – 6.95 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.59, 140.94, 139.48, 132.69, 129.90, 129.52, 128.80, 114.65, 55.69. ESI *m/z*: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_3\text{SCl}^+$ 275.10; Found 275.08.



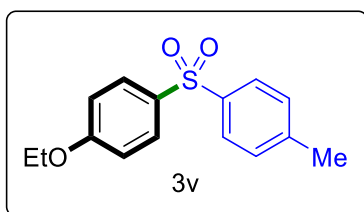
1-Fluoro-4-((4-methoxyphenyl) sulfonyl) benzene (3t)⁹

Physical properties: White solid (51.9 mg, 65% yield). Melting Point 88.5-89.8 °C, (lit.⁹ mp 88-90 °C). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.82 (m, 2H), 7.81 – 7.75 (m, 2H), 7.12 – 7.05 (m, 2H), 6.92 – 6.88 (m, 2H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.22 (d), 163.49, 138.49 (d), 132.96, 130.11 (d), 129.81, 116.48 (d), 114.62, 55.68. ESI *m/z*: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_3\text{SF}^+$ 267.04; Found 267.02.



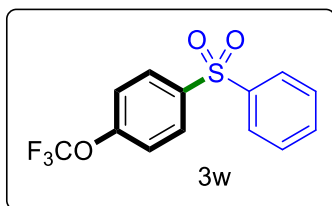
1-Ethoxy-4-(phenylsulfonyl) benzene (3u)¹⁶

Physical properties: White solid (49.57 mg, 63% yield). Melting Point 114.2-116.1 °C, (lit.¹⁶ mp 114.5-115 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.81 (ddd, *J* = 20.4, 7.4, 1.6 Hz, 4H), 7.52 – 7.35 (m, 3H), 6.91 – 6.83 (m, 2H), 3.98 (q, *J* = 7.0 Hz, 2H), 1.34 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.82, 142.44, 132.81, 129.87, 129.19, 127.30, 114.92, 64.04, 14.57. ESI *m/z*: [M+H]⁺ Calcd for C₁₄H₁₅O₃S⁺ 263.07; Found 263.06.



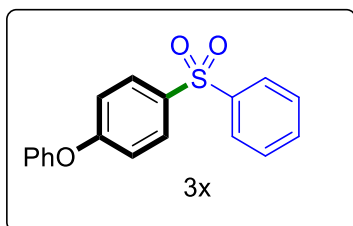
1-Ethoxy-4-[(4-methylphenyl) sulfonyl]-benzene (3v)

Physical properties: White solid (48.08 mg, 58% yield). Melting Point 159.3-160.1 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.66 (m, 4H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.89 – 6.81 (m, 2H), 3.98 (q, *J* = 7.0 Hz, 2H), 2.30 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.66, 143.70, 139.50, 133.25, 129.82, 129.69, 127.36, 114.86, 64.01, 21.52, 14.57. ESI *m/z*: [M+H]⁺ Calcd for C₁₄H₁₉O₃S⁺ 277.08; Found 277.07.



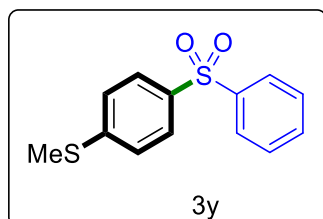
1-(Phenylsulfonyl)-4-(trifluoromethoxy) benzene (3w)¹⁷

Physical properties: White solid (58.9 mg, 65% yield). Melting Point 56.8-57.9 °C, (lit.¹⁷ mp 56.5-58.4 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.81 (m, 4H), 7.53 – 7.39 (m, 3H), 7.27 – 7.20 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 152.55, 141.09, 139.98, 133.54, 129.89, 129.47, 127.73, 121.47, 120.18 (q), 118.89. ESI *m/z*: [M+H]⁺ Calcd for C₁₃H₁₀O₃SF₃⁺ 303.02; Found 303.02.



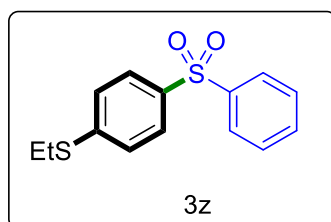
1-Phenoxy-4-(phenylsulfonyl) benzene (3x)¹²

Physical properties: White solid (60.5 mg, 65% yield). Melting point 86.0-86.8 °C, (lit.¹² mp 85-86 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.75 (m, 4H), 7.49 – 7.43 (m, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.02 (m, 2H), 6.96 (td, *J* = 9.0, 1.8 Hz, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.13, 154.91, 142.04, 135.00, 133.03, 130.21, 129.97, 129.28, 127.48, 125.10, 120.41, 117.70. ESI *m/z*: [M+H]⁺ Calcd for C₁₈H₁₅O₃S⁺ 311.07.; Found 311.06.



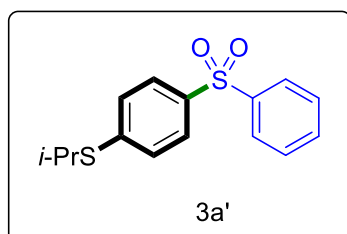
1-(Methylthio)-4-(phenylsulfonyl) benzene (3y)⁹

Physical properties: White solid (30.1 mg, 38% yield). Melting point 110.5-112.4 °C, (lit.⁹ mp 111-112 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.79 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.37 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 2.38 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 146.72, 141.88, 137.13, 133.12, 129.31, 127.96, 127.43, 125.48, 14.71. ESI *m/z*: [M+H]⁺ Calcd for C₁₃H₁₃O₂S₂⁺ 265.03.; Found 265.01.



1-(Ethylthio)-4-(phenylsulfonyl) benzene (3z)¹⁸

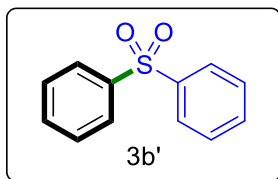
Physical properties: White solid (27.6 mg, 33% yield). Melting point 90.9-92.5 °C, (lit.¹⁸ mp 91 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.79 (m, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.39 (m, 3H), 7.23 (d, *J* = 8.3 Hz, 2H), 2.91 (q, *J* = 7.4 Hz, 2H), 1.27 (td, *J* = 7.4, 1.3 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 145.53, 141.85, 137.45, 133.11, 129.30, 128.01, 127.49, 126.62, 25.97, 13.77. ESI *m/z*: [M+H]⁺ Calcd for C₁₄H₁₅O₂S₂⁺ 278.04.; Found 278.03.



Isopropyl(4-(phenylsulfonyl)phenyl) sulfane (3a')

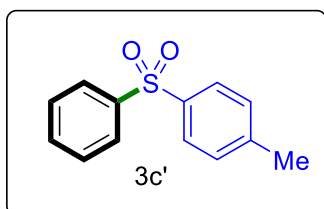
Physical properties: White solid (24.6 mg, 28% yield). Melting point 74.8-78.4 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.80 – 7.70 (m, 2H), 7.53 – 7.40 (m, 3H), 7.32 – 7.24 (m, 2H), 3.47 (h, *J* = 6.7 Hz, 1H), 1.27 (d, *J* = 6.6 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 144.77, 141.77,

137.99, 133.14, 129.30, 128.53, 127.99, 127.54, 36.58, 22.83. ESI m/z : $[M+H]^+$ Calcd for $C_{15}H_{17}O_2S_2^+$ 292.06.; Found 292.03.



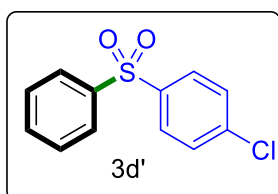
4-(Phenylsulfonyl) benzene (3b')¹⁹

Physical properties: White solid (35.35 mg, 54% yield). Melting Point 124.6-126.1 °C, (lit.¹⁹ mp 128-131 °C). 1H NMR (400 MHz, Chloroform- d) δ 7.91 – 7.83 (m, 4H), 7.53 – 7.37 (m, 6H). ^{13}C NMR (101 MHz, Chloroform- d) δ 141.60, 133.24, 129.32, 127.66. ESI m/z : $[M+H]^+$ Calcd for $C_{12}H_{11}O_2S^+$ 219.04; Found 219.01.



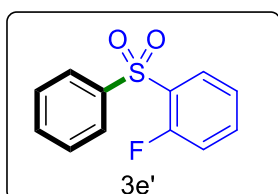
1-Methyl-4-(phenylsulfonyl) benzene (3c')²⁰

Physical properties: White solid (47.4 mg, 68% yield). Melting Point 124.8-126.1 °C, (lit.²⁰ mp 125-126 °C). 1H NMR (400 MHz, Chloroform- d) δ 7.89 – 7.82 (m, 2H), 7.78 – 7.73 (m, 2H), 7.49 – 7.39 (m, 3H), 7.22 (d, J = 8.1 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 144.17, 142.01, 138.68, 133.00, 129.93, 129.23, 127.73, 127.51, 21.57. ESI m/z : $[M+H]^+$ Calcd for $C_{13}H_{13}O_2S^+$ 233.06; Found 233.01.



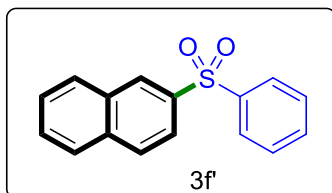
4-Chlorophenyl phenyl sulfone (3d')¹⁵

Physical properties: White solid (50.8 mg, 67% yield). Melting Point 91.1-92.5 °C, (lit.¹⁵ mp 94-95 °C). 1H NMR (400 MHz, Chloroform- d) δ 8.01 – 7.83 (m, 4H), 7.65 – 7.45 (m, 5H). ^{13}C NMR (101 MHz, Chloroform- d) δ 141.22, 140.15, 139.93, 133.46, 129.64, 129.43, 129.15, 127.67. ESI m/z : $[M+H]^+$ Calcd for $C_{12}H_{10}O_2SCl^+$ 253.00.; Found 253.09.



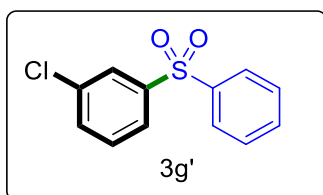
2-Fluorophenyl phenyl sulfone (3e')²¹

Physical properties: White solid (41.1 mg, 58% yield). Melting Point 105.2-106.9 °C, (lit.²¹ mp 105-106 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 (td, *J* = 7.5, 1.8 Hz, 1H), 8.01 – 7.89 (m, 2H), 7.60 – 7.43 (m, 4H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.09 – 7.00 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 160.49, 157.93, 140.87, 136.07, 135.99, 133.72, 129.75, 129.46, 129.32, 129.15, 128.17, 128.14, 124.67, 124.63, 117.42, 117.21. ESI *m/z*: [M+H]⁺ Calcd for C₁₂H₁₀O₂SF⁺ 237.03.; Found 236.99.



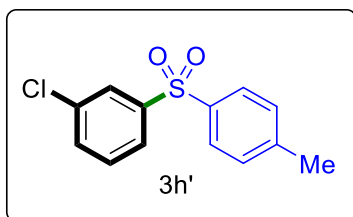
2-(Phenylsulfonyl) naphthalene (3f')²²

Physical properties: White solid (48.3 mg, 60% yield). Melting point 116.8-118.6 °C, (lit.²² mp 116.5-117.5 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 1.9 Hz, 1H), 7.98 – 7.74 (m, 6H), 7.61 – 7.38 (m, 5H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 141.65, 138.41, 135.03, 133.19, 132.23, 129.67, 129.43, 129.31, 129.17, 129.12, 127.94, 127.73, 127.66, 122.70. ESI *m/z*: [M+H]⁺ Calcd for C₁₆H₁₃O₂S⁺ 269.06.; Found 269.09.



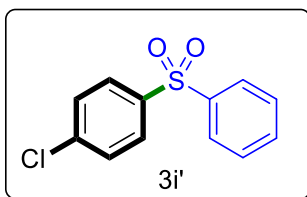
1-Chloro-3-(phenylsulfonyl) benzene (3g')¹¹

Physical properties: White solid (55.3 mg, 73% yield). Melting Point 101.3-102.1 °C, (lit.¹¹ mp 100-101 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.83 (m, 3H), 7.75 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.57 – 7.36 (m, 5H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 143.43, 140.94, 135.51, 133.59, 133.35, 130.61, 129.47, 127.82, 127.73, 125.79. ESI *m/z*: [M+H]⁺ Calcd for C₁₂H₁₀O₂SCl⁺ 253.00.; Found 253.03.



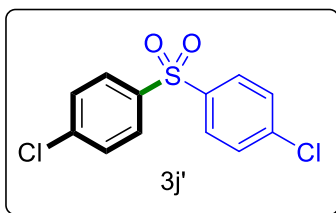
1-Chloro-3-[(4-methylphenyl) sulfonyl] benzene (3h')²³

Physical properties: White solid (45.6 mg, 57% yield). Melting Point 126.5-128.2 °C, (lit.²³ mp 127-128 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.83 (t, *J* = 1.9 Hz, 1H), 7.74 (td, *J* = 7.4, 6.8, 1.7 Hz, 3H), 7.43 (ddd, *J* = 8.0, 2.1, 1.2 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 2.33 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 150.73, 143.85, 136.43, 133.76, 130.60, 130.10, 128.04, 118.80, 112.48, 111.73, 21.49. ESI *m/z*: [M+H]⁺ Calcd for C₁₃H₁₂O₂SCl⁺ 267.02.; Found 267.05.



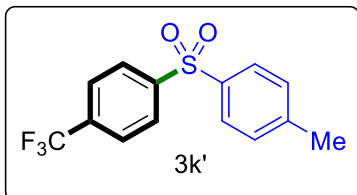
1-Chloro-(4-phenyl) sulfonyl benzene (3i')²⁰

Physical properties: White solid (42.45 mg, 56% yield). Melting Point 91.1-92.7 °C, (lit.²⁰ mp 93-95 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.83 (m, 4H), 7.65 – 7.44 (m, 5H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 141.22, 140.15, 139.93, 133.46, 129.64, 129.43, 129.15, 127.67. ESI *m/z*: [M+H]⁺ Calcd for C₁₂H₁₀O₂SCl⁺ 253.00.; Found 253.04.



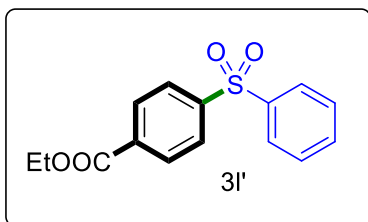
4,4'-Dichlorodiphenyl sulfone (3j')¹⁹

Physical properties: White solid (50.0 mg, 58% yield). Melting Point 147.9-148.6 °C, (lit.¹⁹ mp 148-150 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.83 (m, 4H), 7.53 – 7.45 (m, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 140.23, 139.73, 129.78, 129.13. ESI *m/z*: [M+H]⁺ Calcd for C₁₂H₉NO₂SCl₂⁺ 286.96.; Found 286.99.



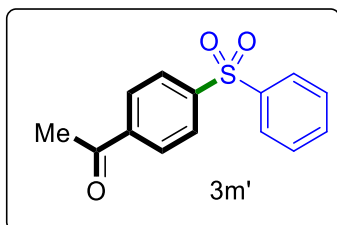
1-[(4-Methylphenyl) sulfonyl]-4-(trifluoromethyl) benzene (3k')²⁴

Physical properties: White solid (58.55 mg, 65% yield). Melting Point 123.5-125.1 °C, (lit.²⁴ mp 123-124 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 145.63, 144.97, 137.60, 134.81, 134.49, 130.19, 128.05, 127.97, 126.45, 126.41, 126.37, 126.34, 123.15 (q), 21.60. ESI *m/z*: [M+H]⁺ Calcd for C₁₄H₁₂O₂SF₃⁺ 301.04.; Found 301.03.



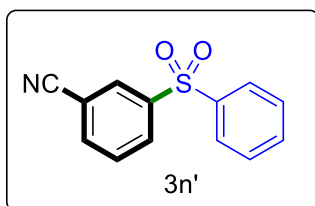
Ethyl 4-(phenylsulfonyl) benzoate (3l')¹²

Physical properties: White solid (54.9 mg, 63% yield). Melting Point 67.8-68.9 °C, (lit.¹² mp 68-69 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 7.99 (m, 2H), 7.98 – 7.83 (m, 4H), 7.54 – 7.40 (m, 3H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 164.97, 145.37, 140.85, 134.67, 133.63, 130.41, 129.46, 129.29, 127.82, 127.65, 61.72, 14.22. ESI *m/z*: [M+H]⁺ Calcd for C₁₅H₁₅O₄S⁺ 291.06.; Found 291.05.



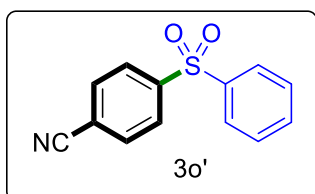
1-[4-(phenylsulfonyl) phenyl]-Ethanone (3m')²⁰

Physical properties: White solid (52.3 mg, 67% yield). Melting Point 129.8-131.4 °C, (lit.²⁰ mp 130-131 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.92 (m, 4H), 7.92 – 7.85 (m, 2H), 7.57 – 7.41 (m, 3H), 2.54 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 196.68, 145.46, 140.81, 140.37, 133.67, 129.49, 129.08, 127.99, 127.86, 26.87. ESI *m/z*: [M+H]⁺ Calcd for C₁₄H₁₃O₃S⁺ 261.05.; Found 261.05.



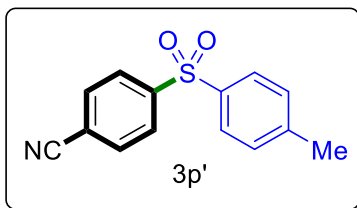
3-(Phenylsulfonyl) benzonitrile (3n')²⁵

Physical properties: White solid (46.0 mg, 63% yield). Melting Point 104-105.8 °C, (lit.²⁵ mp 103.2-103.9 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 8.02 (m, 2H), 7.88 (dd, *J* = 7.3, 1.8 Hz, 2H), 7.76 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.63 – 7.45 (m, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 143.49, 140.19, 136.31, 134.07, 131.57, 131.26, 130.46, 129.72, 127.94, 117.03, 113.95. ESI *m/z*: [M+H]⁺ Calcd for C₁₃H₁₀NO₂S⁺ 244.04.; Found 244.01.



4-(Phenylsulfonyl) benzonitrile (3o')²⁴

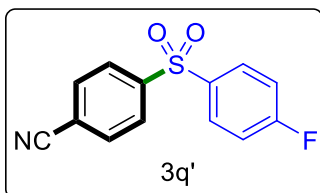
Physical properties: White solid (56.2 mg, 77% yield). Melting Point 120.8-122.5 °C, (lit.²⁴ mp 120-121 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.94 (m, 2H), 7.91 – 7.80 (m, 2H), 7.76 – 7.66 (m, 2H), 7.59 – 7.44 (m, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 145.85, 140.13, 134.06, 133.13, 129.68, 128.30, 127.99, 117.19, 116.92. ESI *m/z*: [M+H]⁺ Calcd for C₁₃H₁₀NO₂S⁺ 244.04.; Found 244.01.



4-[(4-Methylphenyl) sulfonyl] benzonitrile (3p')¹⁰

Physical properties: White solid (54.0 mg, 70% yield). Melting Point 130.4-131.9 °C, (lit.¹⁰ mp 130-132 °C).

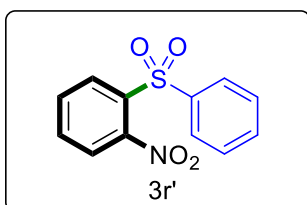
¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.92 (m, 2H), 7.78 – 7.67 (m, 4H), 7.26 (d, *J* = 8.1 Hz, 2H), 2.34 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 146.27, 145.28, 137.15, 133.05, 130.30, 128.14, 128.05, 117.22, 116.72, 21.64. ESI *m/z*: [M+H]⁺ Calcd for C₁₄H₁₂NO₂S⁺ 258.05.; Found 258.03.



4-[(4-Fluorophenyl) sulfonyl] benzonitrile (3q')²⁴

Physical properties: White solid (51.0 mg, 65% yield). Melting Point 155.8-157.1 °C, (lit.²⁴ mp 156-157 °C).

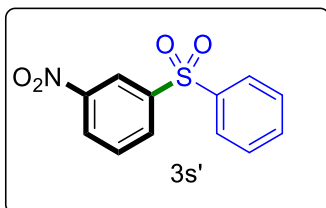
¹H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.79 (m, 4H), 7.78 – 7.62 (m, 2H), 7.20 – 7.13 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 165.95 (d), 145.72, 136.25, 136.21, 133.18, 130.92 (d), 128.22, 117.09 (d), 117.08 (d), 116.96. ESI *m/z*: [M+H]⁺ Calcd for C₁₃H₉NO₂SF⁺ 262.03.; Found 262.05.



2-Nitrophenyl phenyl sulfone (3r')²⁶

Physical properties: Yellow solid (52.1 mg, 66% yield). Melting point 137.2-140.1 °C, (lit.²⁶ mp 138-141 °C).

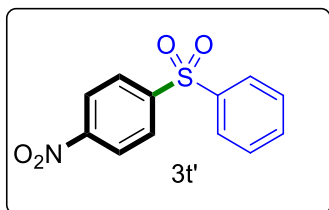
¹H NMR (400 MHz, Chloroform-*d*) δ 8.42 – 8.30 (m, 1H), 8.04 – 7.92 (m, 2H), 7.85 – 7.71 (m, 3H), 7.70 – 7.54 (m, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 148.52, 140.46, 134.66, 134.56, 133.86, 132.58, 131.62, 129.15, 128.25, 124.78. ESI *m/z*: [M+H]⁺ Calcd for C₁₂H₁₀NO₄S⁺ 264.03.; Found 264.01.



1-Nitro-3-(phenylsulfonyl) benzene (3s')²⁰

Physical properties: Yellow solid (52.1 mg, 66% yield). Melting Point 77.9-79.5 °C, (lit.²⁰ mp 78-80 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.69 (t, *J* = 2.0 Hz, 1H), 8.34 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 8.20 (dt, *J*

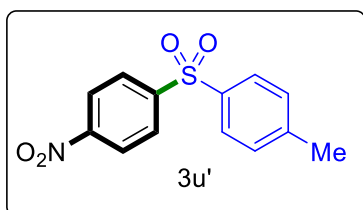
= 7.9, 1.3 Hz, 1H), 8.00 – 7.86 (m, 2H), 7.67 (t, J = 8.0 Hz, 1H), 7.61 – 7.47 (m, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 148.47, 144.02, 140.16, 134.10, 133.12, 130.77, 129.73, 128.01, 127.69, 122.94. ESI m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{10}\text{NO}_4\text{S}^+$ 264.03.; Found 264.01.



1-Nitro-4-(phenylsulfonyl) benzene (3t')²⁰

Physical properties: Yellow solid (56.1 mg, 71% yield). Melting Point 141.9-142.6 °C, (lit.²⁰ mp 141-143 °C).

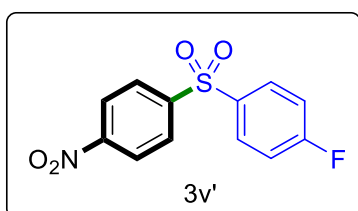
^1H NMR (400 MHz, Chloroform- d) δ 8.32 – 8.22 (m, 2H), 8.12 – 8.02 (m, 2H), 7.94 – 7.82 (m, 2H), 7.59 – 7.45 (m, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 150.38, 147.40, 140.06, 134.14, 129.71, 129.00, 128.05, 124.54. ESI m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{10}\text{NO}_4\text{S}^+$ 264.03.; Found 264.01.



1-Methyl-4-[(4-nitrophenyl) sulfonyl] benzene (3u')¹⁰

Physical properties: Yellow solid (55.7 mg, 67% yield). Melting Point 164.9-166.3 °C, (lit.¹⁰ mp 163-165 °C).

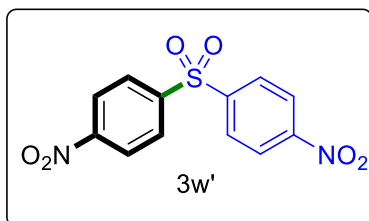
^1H NMR (400 MHz, Chloroform- d) δ 8.35 – 8.21 (m, 2H), 8.11 – 7.99 (m, 2H), 7.84 – 7.72 (m, 2H), 7.27 (d, J = 8.1 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 150.25, 147.79, 145.40, 137.05, 130.34, 128.82, 128.10, 124.48, 21.65. ESI m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_{12}\text{NO}_4\text{S}^+$ 278.04.; Found 278.01.



1-Fluoro-4-[(4-nitrophenyl) sulfonyl] benzene (3v')²⁷

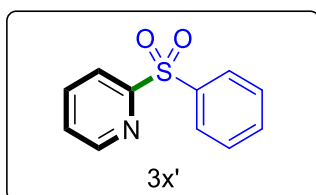
Physical properties: Yellow solid (52.3 mg, 62% yield). Melting Point 161.4-162.8 °C, (lit.²⁷ mp 161-162 °C).

^1H NMR (400 MHz, Chloroform- d) δ 8.42 – 8.11 (m, 2H), 8.24 – 7.95 (m, 2H), 8.03 – 7.86 (m, 2H), 7.18 (d, J = 2.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 166.01 (d), 150.46, 147.23, 136.13 (d), 130.98 (d), 128.93, 124.63, 117.13 (d). ESI m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_9\text{NO}_4\text{SF}^+$ 281.02.; Found 281.01.



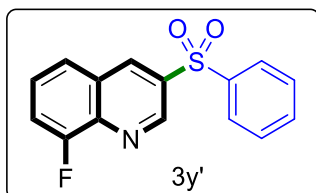
4,4'-Sulfonylbis(nitrobenzene) (3w')²⁸

Physical properties: White solid (61.0 mg, 66% yield). Melting Point 255.8-257.8 °C, (lit.²⁸ mp 256-261 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.28 (dd, *J* = 8.8, 2.1 Hz, 4H), 7.82 (dd, *J* = 8.9, 2.1 Hz, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.50, 148.74, 124.36, 123.89. ESI *m/z*: [M+H]⁺ Calcd for C₁₂H₉NO₄SF⁺ 309.01.; Found 309.05.



2-(Phenylsulfonyl)-pyridine (3x')²⁹

Physical properties: White solid (40.8 mg, 62% yield). Melting Point 88.8-90.4 °C, (lit.²⁹ mp 88-90 °C). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.69 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 8.20 – 8.09 (m, 1H), 7.99 (dd, *J* = 7.3, 2.1 Hz, 2H), 7.75 – 7.60 (m, 4H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 158.34, 151.08, 139.64, 139.62, 139.03, 134.63, 130.00, 128.94, 128.30, 128.28, 122.48. ESI *m/z*: [M+H]⁺ Calcd for C₁₁H₁₀NO₂S⁺ 220.04.; Found 220.01.

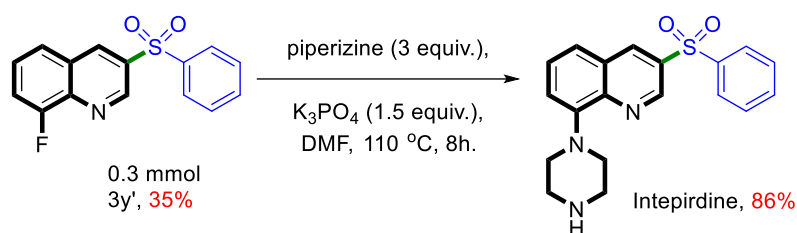


8-Fluoro-3-(phenylsulfonyl) quinoline (3y')¹⁴

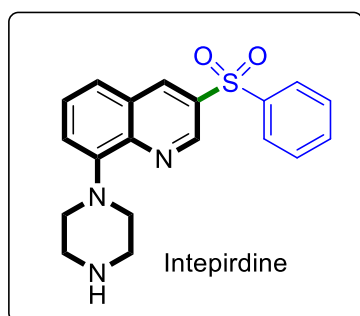
Physical properties: White solid (30.2 mg, 35% yield). Melting Point 166.8-168.1 °C, (lit.¹⁴ mp 166-168 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 9.31 (d, *J* = 2.2 Hz, 1H), 8.85 (t, *J* = 1.9 Hz, 1H), 8.11 – 7.95 (m, 2H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.50 (m, 5H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 157.87 (d), 147.35, 140.64, 139.43 (d), 136.59 (d), 136.00, 133.99, 129.71, 128.52 (d), 127.98, 127.90, 124.85 (d), 116.89 (d). ESI *m/z*: [M+H]⁺ Calcd for C₁₅H₁₁FNO₂S⁺ 288.04.; Found 288.07.

Synthesis and characterizations of pharmaceutical compounds:

a. Intepirdine.



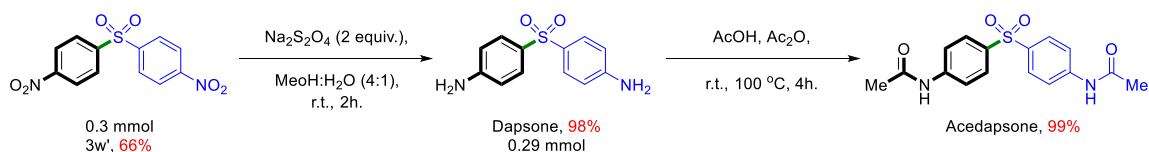
A solution containing **3y'** (86.2 mg, 0.3 mmol) in DMF (2 mL) was prepared, to which piperazine (77.5 mg, 0.9 mmol) and K₃PO₄ (882.8 mg, 0.39 mmol) were added. The mixture was stirred at 110 °C for 8 hours. After cooling, the solution was partitioned between dichloromethane (DCM) and water. The organic layer was separated, and the aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried over Na₂SO₄, and then concentrated. The resulting residue was purified by flash chromatography, using a 50:1 dichloromethane/methanol elution, which yielded 91.2 mg of Intepirdine (86%) as a yellow solid.¹⁴



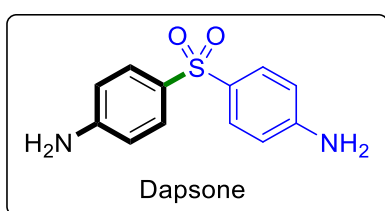
3-Phenylsulfonyl-8-(piperazin-1-yl) quinoline (Intepirdine)¹⁴

Physical properties: Yellow solid (91.2 mg, 86%). Melting point 184.2-185.6 °C, (lit.¹⁴ mp 183-185 °C). ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.24 (d, *J* = 2.4 Hz, 1H), 9.10 (d, *J* = 2.4 Hz, 1H), 8.09 (d, *J* = 7.7 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.79 – 7.63 (m, 4H), 7.40 (d, *J* = 7.6 Hz, 1H), 3.54 (t, *J* = 4.7 Hz, 4H), 3.26 (t, *J* = 4.9 Hz, 4H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 148.13, 144.73, 142.93, 141.03, 138.24, 134.69, 134.52, 130.45, 129.36, 128.07, 123.67, 120.19, 48.59, 43.39. ESI *m/z*: [M+H]⁺ Calcd for C₁₉H₂₀N₃O₂S⁺ 354.21.; Found 354.15.

b. Dapsone and Acedapsone.

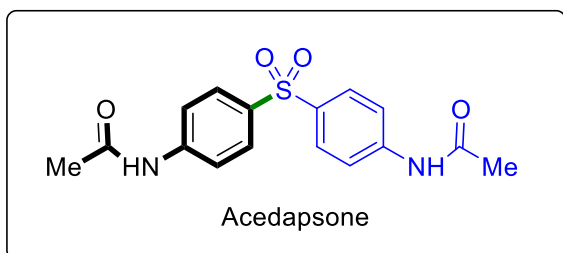


In a dried 50 mL round-bottom flask, 0.3 mmol of compound **3w'** (92.4 mg) and sodium dithionite (2 equivalents, 104.4 mg) were introduced to a 15 mL methanol/water mixture (4:1) and stirred for 2 hours. The resulting solid was filtered and washed with a small amount of methanol, followed by recrystallization using a methanol/water ratio of 9:1, yielding white crystalline dapsone in 98% yield (73 mg).³⁰ Furthermore, acedapsone was synthesized using the following methodology:³¹ dapsone (72 mg, 0.29 mmol) and acetic acid (0.750 mL) were added to a 25 mL round-bottom three-necked flask. The mixture was stirred at 70 °C, allowing the solids to dissolve gradually. Subsequently, acetic anhydride (150 μ L) was added dropwise over 0.5 hours. The reaction mixture was then heated to 100 °C and maintained at this temperature for 4 hours. The crude product was washed three times with hot water and an additional three times with alcohol. Finally, the product was dried at 100 °C for 10 hours, resulting in acedapsone as a white powder (95.4 mg, 99% yield).



4,4'-Sulfonylbis(2-aminobenzene) (Dapsone)¹³

Physical properties: White solid (73 mg, 98%). Melting Point 174.4-175.9 °C, (lit.¹³ mp 173.5-175 °C). ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.38 (s, 2H), 7.92 – 7.83 (m, 4H), 7.83 – 7.76 (m, 4H), 2.08 (s, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 153.19, 129.09, 128.72, 113.44. ESI *m/z*: [M+H]⁺ Calcd for C₁₂H₁₃N₂O₂S⁺ 249.06.; Found 249.09.



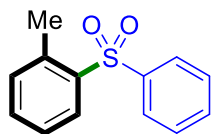
4,4'-Sulfonylbis(2-acetamidobenzene) (Acedapsone)³²

Physical properties: White solid (95.4 mg, 99%). Melting Point 290.8-292.6 °C, (lit.³² mp 295.3 °C). ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.38 (s, 2H), 7.92 – 7.83 (m, 4H), 7.83 – 7.76 (m, 4H), 2.08 (s, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 169.58, 144.09, 135.52, 128.87, 119.37, 24.61. ESI *m/z*: [M+H]⁺ Calcd for C₁₆H₁₇N₂O₂S⁺ 333.08.; Found 333.11.

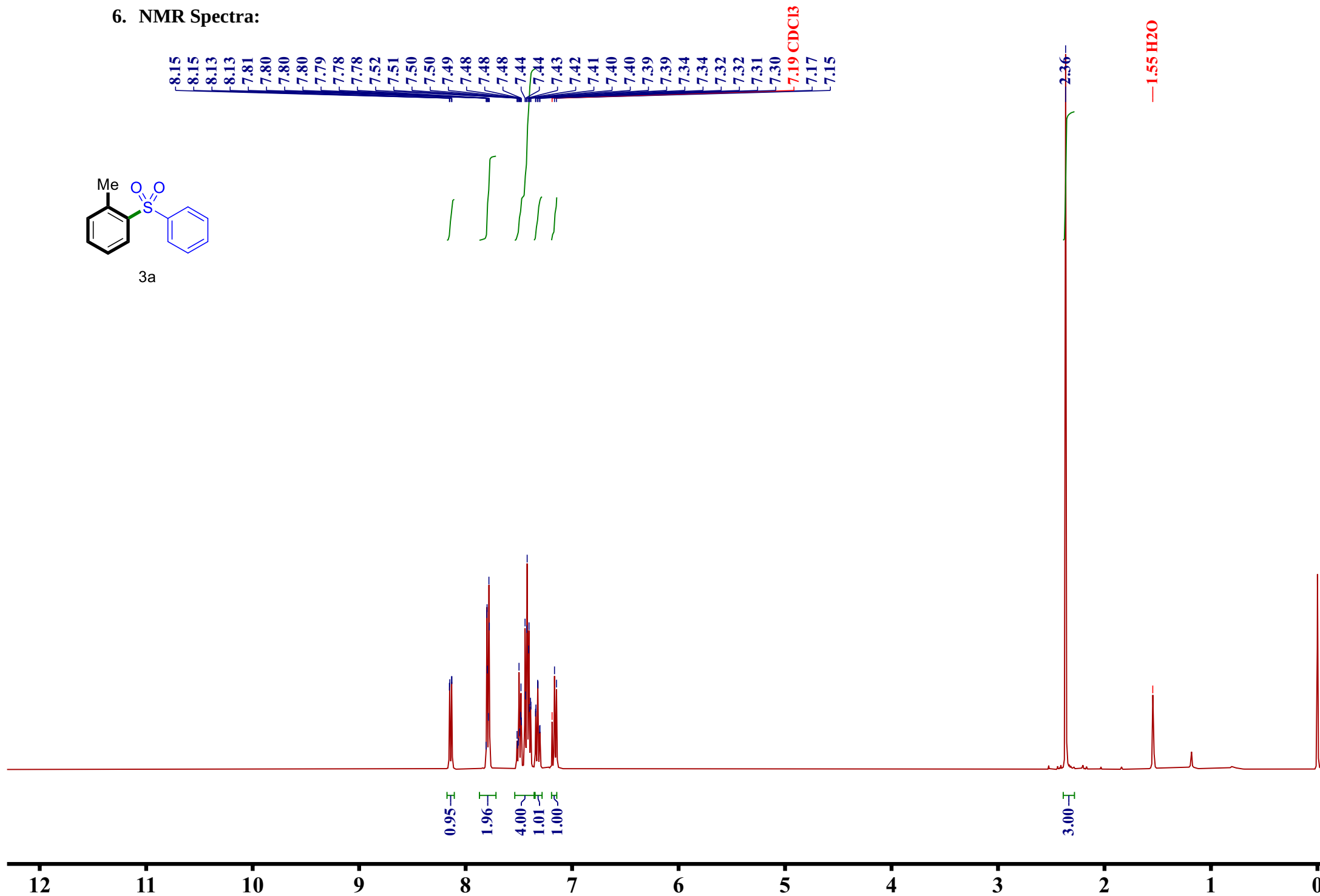
5. References:

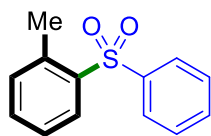
- 1 Y. Zhu, M. Zhu, L. Kang, F. Yu and B. Dai, *Ind. Eng. Chem. Res.*, 2015, **54**, 2040–2047.
- 2 G. He, H. Chen, J. Zhu, F. Bei, X. Sun and X. Wang, *J. Mater. Chem.*, 2011, **21**, 14631–14638.
- 3 G. A. Tsigdinos and C. J. Hallada, *Inorg. Chem.*, 1968, **7**, 437–441.
- 4 P. Zhao, J. Wang, G. Chen, Y. Zhou and J. Huang, *Catal. Sci. Technol.*, 2013, **3**, 1394–1404.
- 5 C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.*, 1983, **22**, 207–216.
- 6 H. Wu, *J. Biol. Chem.*, 1920, **43**, 189–220.
- 7 G. R. Buettner, *Free Radic. Biol. Med.*, 1987, **3**, 259–303.
- 8 J. R. Harbour and M. L. Hair, *J. Phys. Chem.*, 1978, **82**, 1397–1399.
- 9 H. Zhu, L. Yang, J. Meng, Z. Xie, Z.-G. Le and T. Tu, *Tetrahedron Lett.*, 2021, **63**, 152708.
- 10 M. Phanindrudu, P. Jaya, P. R. Likhar and D. K. Tiwari, *Tetrahedron*, 2020, **76**, 131263.
- 11 H. Yang, Y. Li, M. Jiang, J. Wang and H. Fu, *Chem. – Eur. J.*, 2011, **17**, 5652–5660.
- 12 N.-W. Liu, S. Liang, N. Margraf, S. Shaaban, V. Luciano, M. Drost and G. Manolikakes, *Eur. J. Org. Chem.*, 2018, **2018**, 1208–1210.
- 13 Y. Yang, Z. Chen and Y. Rao, *Chem. Commun.*, 2014, **50**, 15037–15040.
- 14 J. Zhao, S. Niu, X. Jiang, Y. Jiang, X. Zhang, T. Sun and D. Ma, *J. Org. Chem.*, 2018, **83**, 6589–6598.
- 15 A. Bhowmik, M. Yadav and R. A. Fernandes, *Org. Biomol. Chem.*, 2020, **18**, 2447–2458.
- 16 S. S. Gandhi, M. S. Gibson, M. L. Kaldas and S. M. Vines, *J. Org. Chem.*, 1979, **44**, 4705–4707.
- 17 L. Wang, J. Wei, R. Wu, G. Cheng, X. Li, J. Hu, Y. Hu and R. Sheng, *Org. Chem. Front.*, 2017, **4**, 214–223.
- 18 A. Kar, I. A. Sayyed, W. F. Lo, H. M. Kaiser, M. Beller and M. K. Tse, *Org. Lett.*, 2007, **9**, 3405–3408.
- 19 X. Li, J. Du, Y. Zhang, H. Chang, W. Gao and W. Wei, *Org. Biomol. Chem.*, 2019, **17**, 3048–3055.
- 20 X. Ge, S. Zhang, X. Chen, X. Liu and C. Qian, *Green Chem.*, 2019, **21**, 2771–2776.
- 21 G. Petrillo, M. Novi, G. Garbarino and D. Carlo, *Tetrahedron*, 1986, **42**, 4007–4016.
- 22 J. Bunnett and T. Brotherton, *J. Org. Chem.*, 1958, **23**, 904–906.
- 23 R. B. Wagh and J. M. Nagarkar, *Catal. Lett.*, 2017, **147**, 181–187.
- 24 L. Chen, J. Liang, Z. Chen, J. Chen, M. Yan and X. Zhang, *Adv. Synth. Catal.*, 2019, **361**, 956–960.
- 25 D.-L. Zhu, Q. Wu, H.-Y. Li, H.-X. Li and J.-P. Lang, *Chem. – Eur. J.*, 2020, **26**, 3484–3488.
- 26 M. Bian, F. Xu and C. Ma, *Synthesis*, 2007, **2007**, 2951–2956.
- 27 V. K. Madduluri, N. Baig, S. Chander, S. Murugesan and A. K. Sah, *Catal. Commun.*, 2020, **137**, 105931.
- 28 M. Lutz, M. Wenzler and I. Likhovorik, *Synthesis*, 2018, **50**, 2231–2234.
- 29 F. Chen, F. Chacón-Huete, H. El-Husseini and P. Forgione, *Synthesis*, 2018, **50**, 1914–1920.
- 30 W. Jianwei, W. Shanhong, Z. Baoli and C. Kai, *Chin. J. Org. Chem.*, 2014, **34**, 767.
- 31 Z. Li, G. Zhang, Y. Li and J. Yang, *J. Polym. Res.*, 2015, **22**, 75.
- 32 A. Habibi-Yangjeh, E. Pourbasheer and M. Danandeh-Jenagharad, *Bull. Korean Chem. Soc.*, 2008, **29**, 833–841.

6. NMR Spectra:

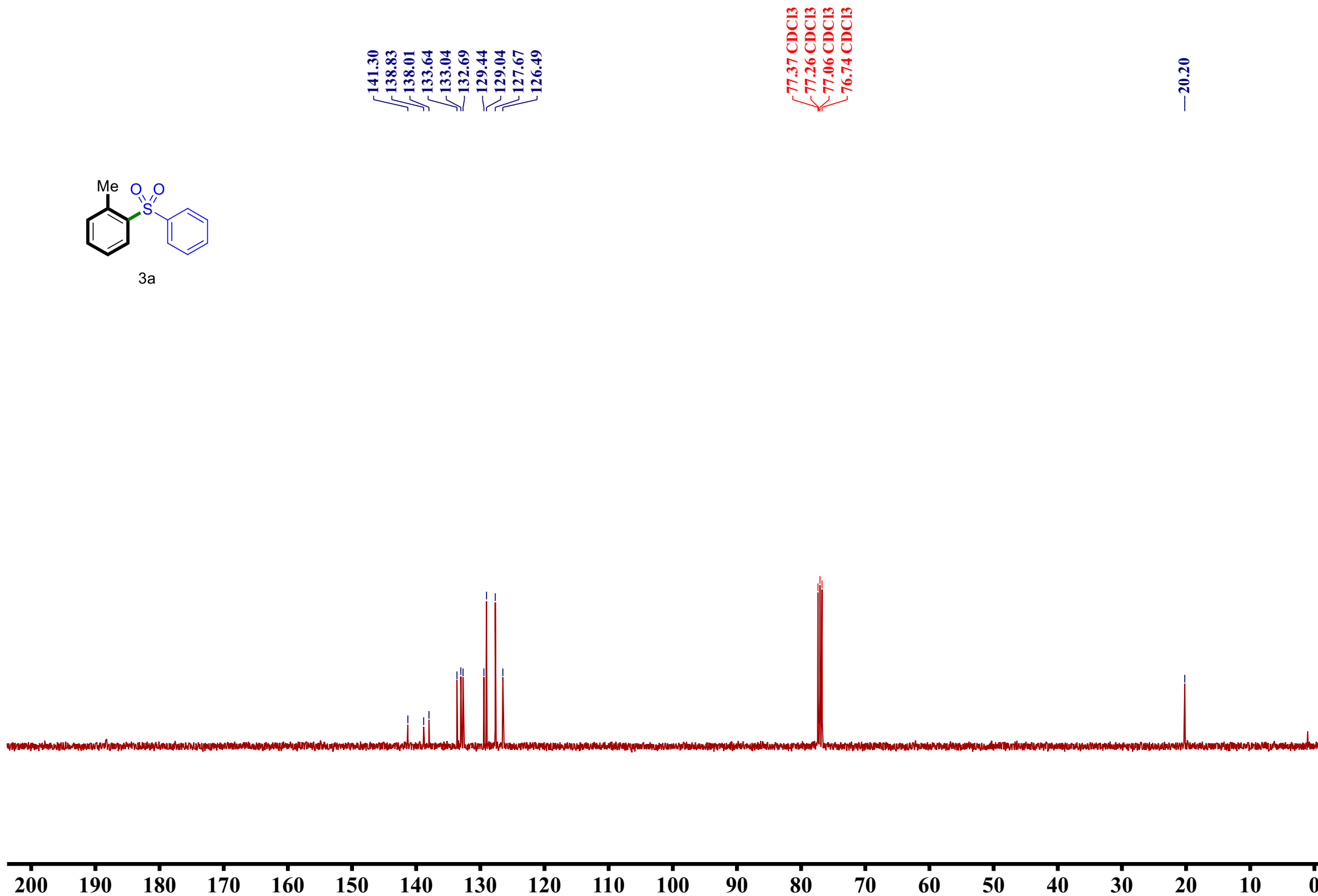


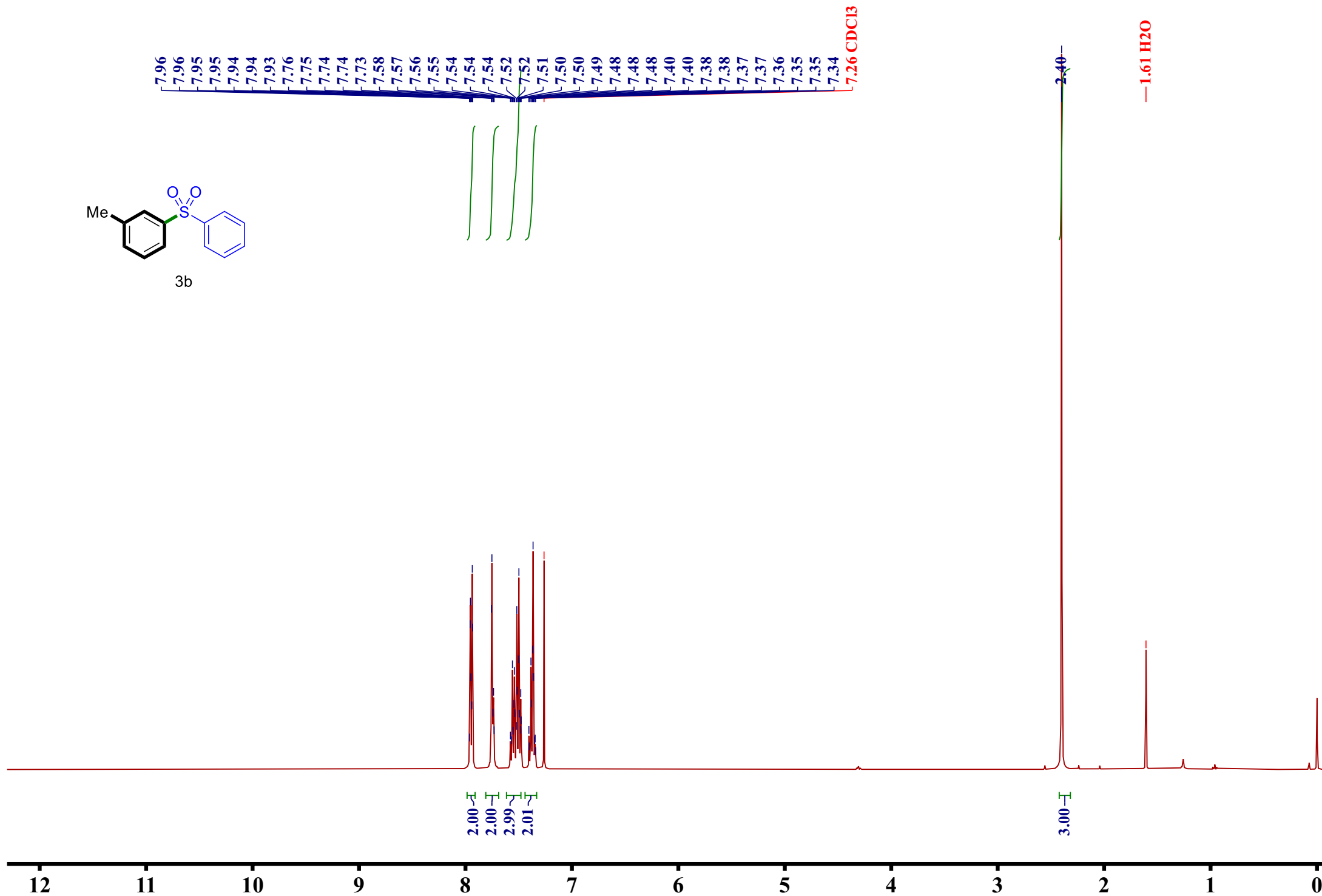
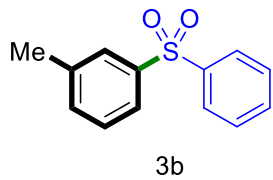
3a

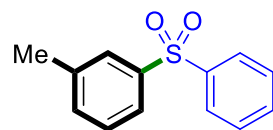




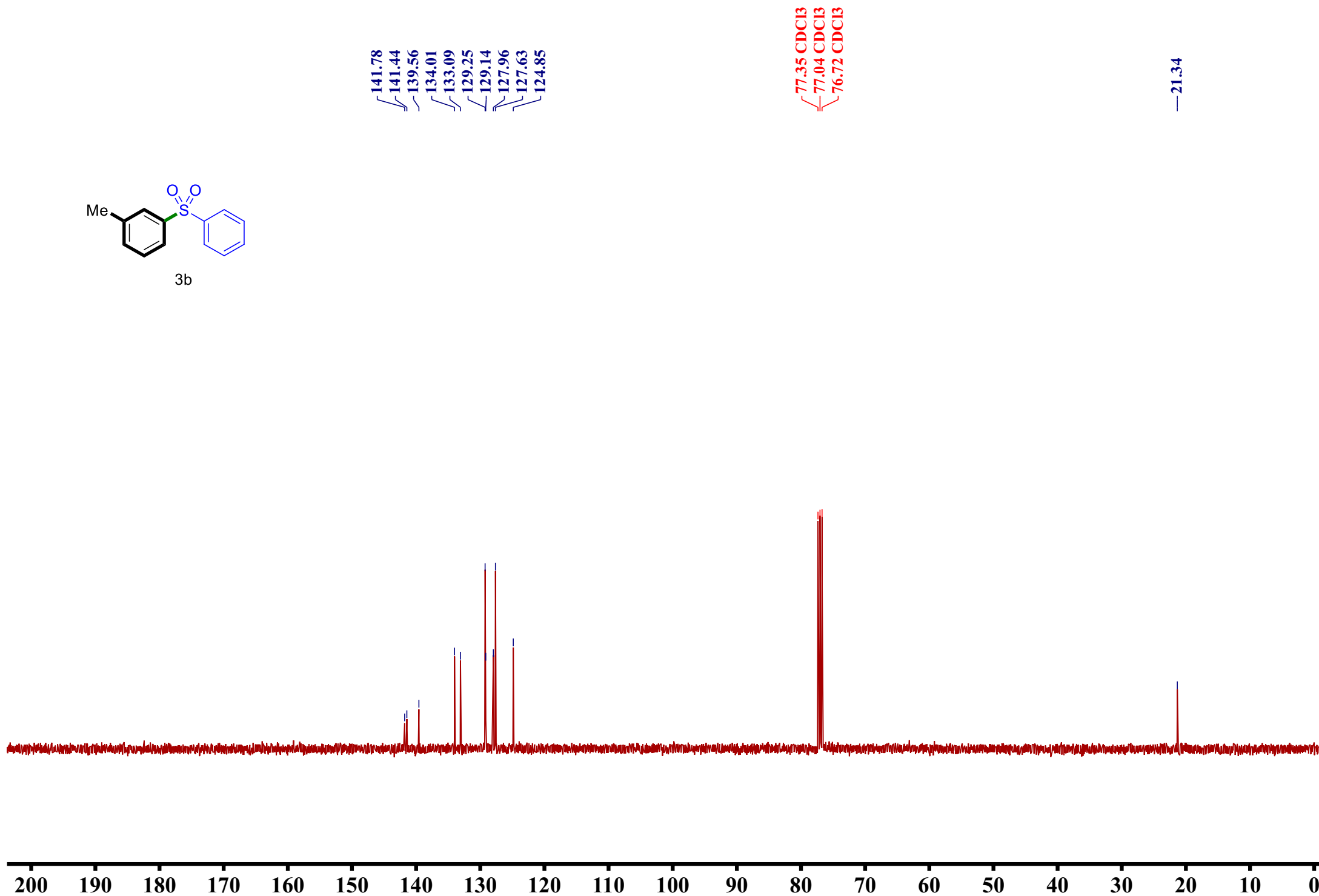
3a

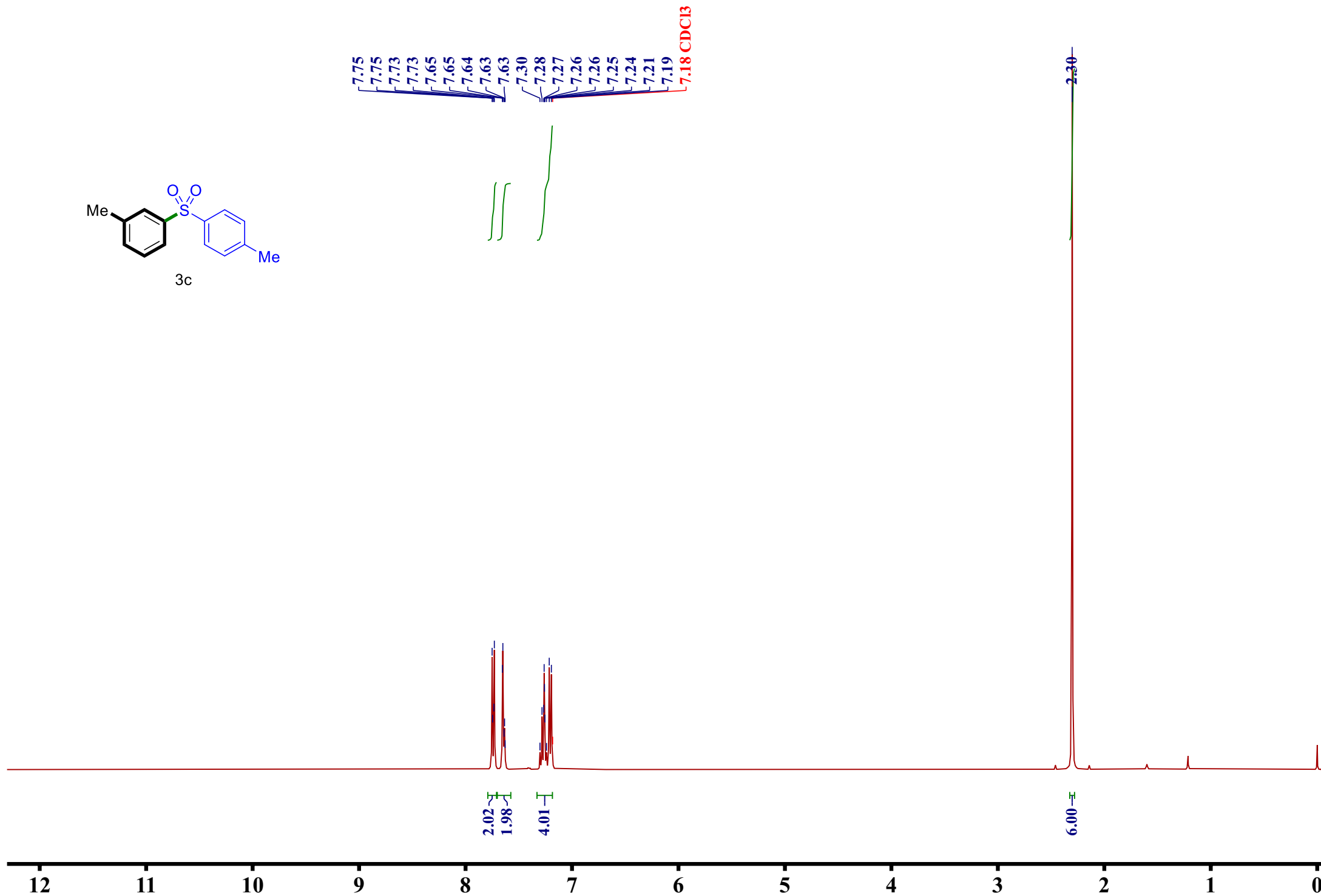
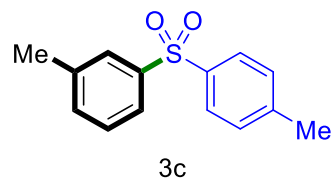


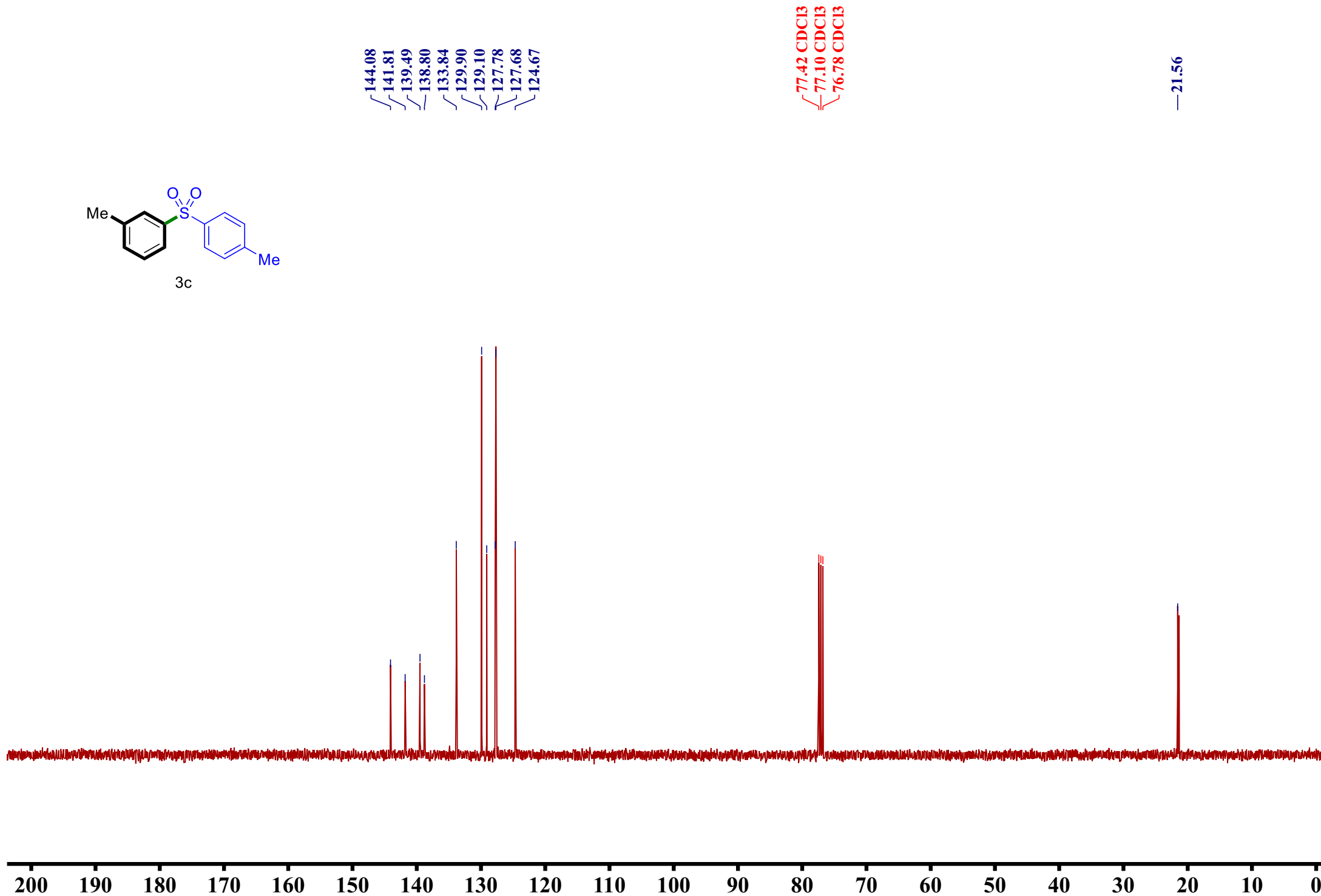
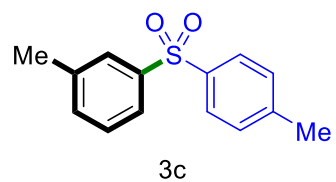


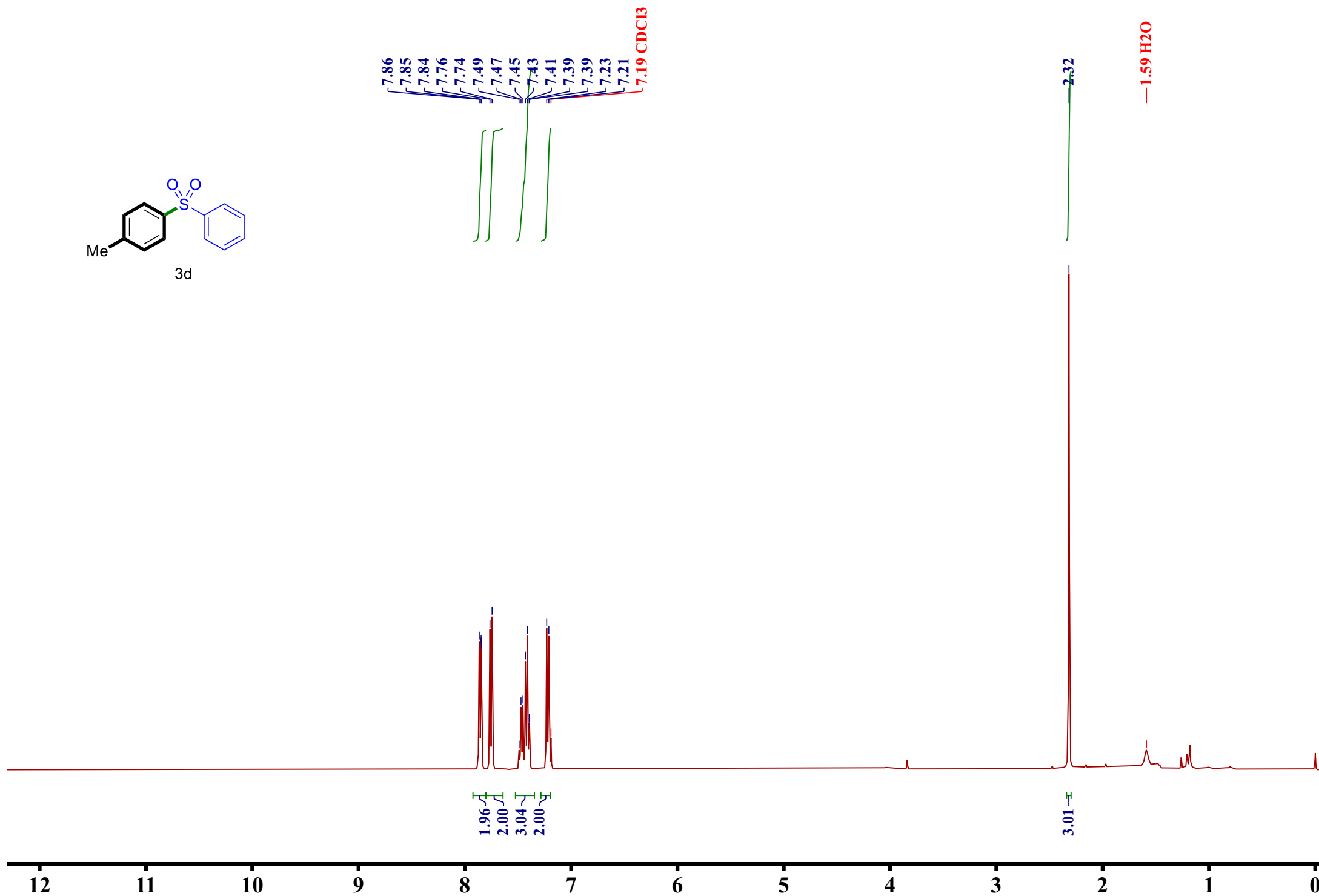
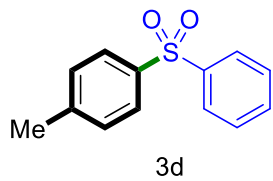


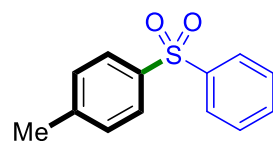
3b



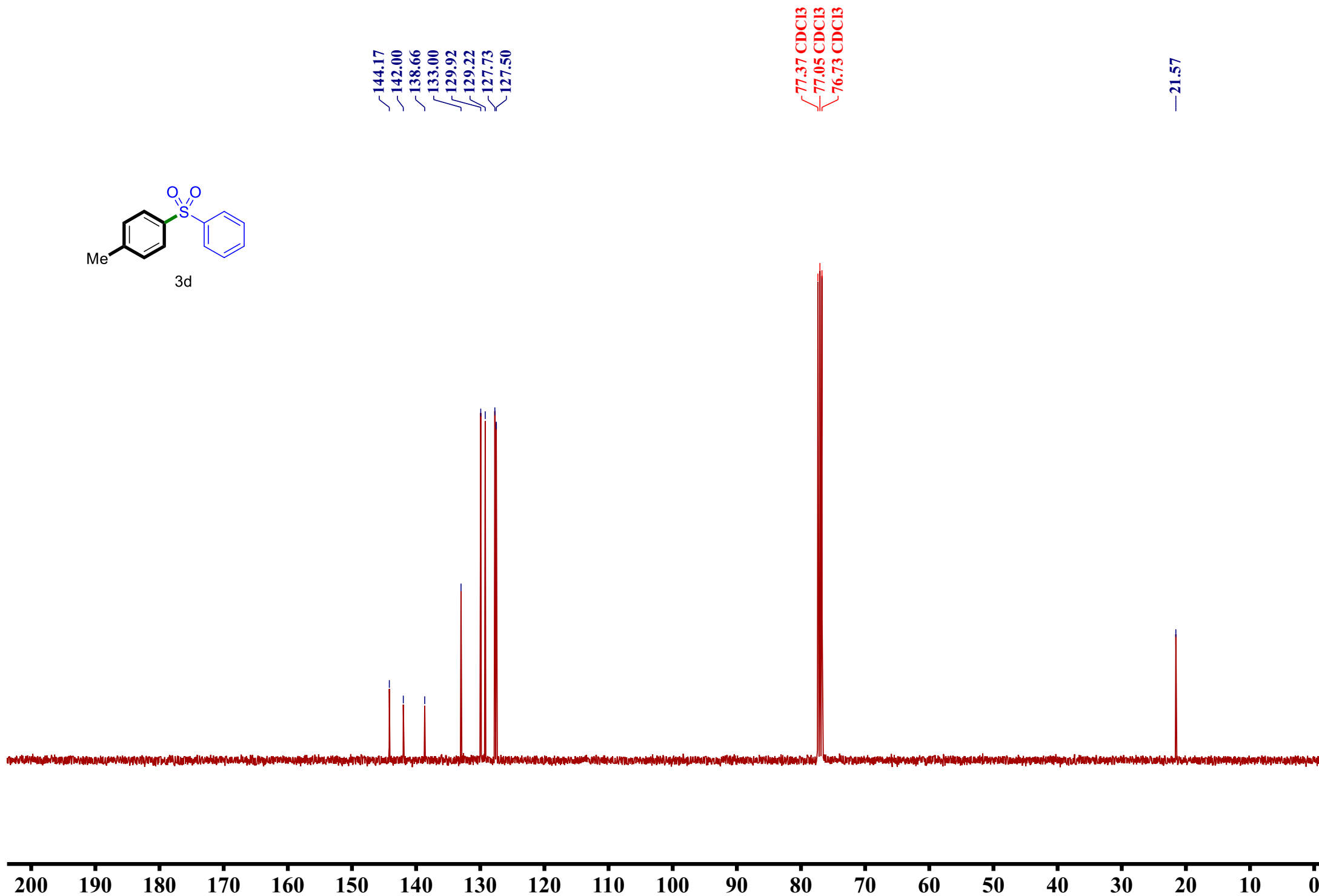


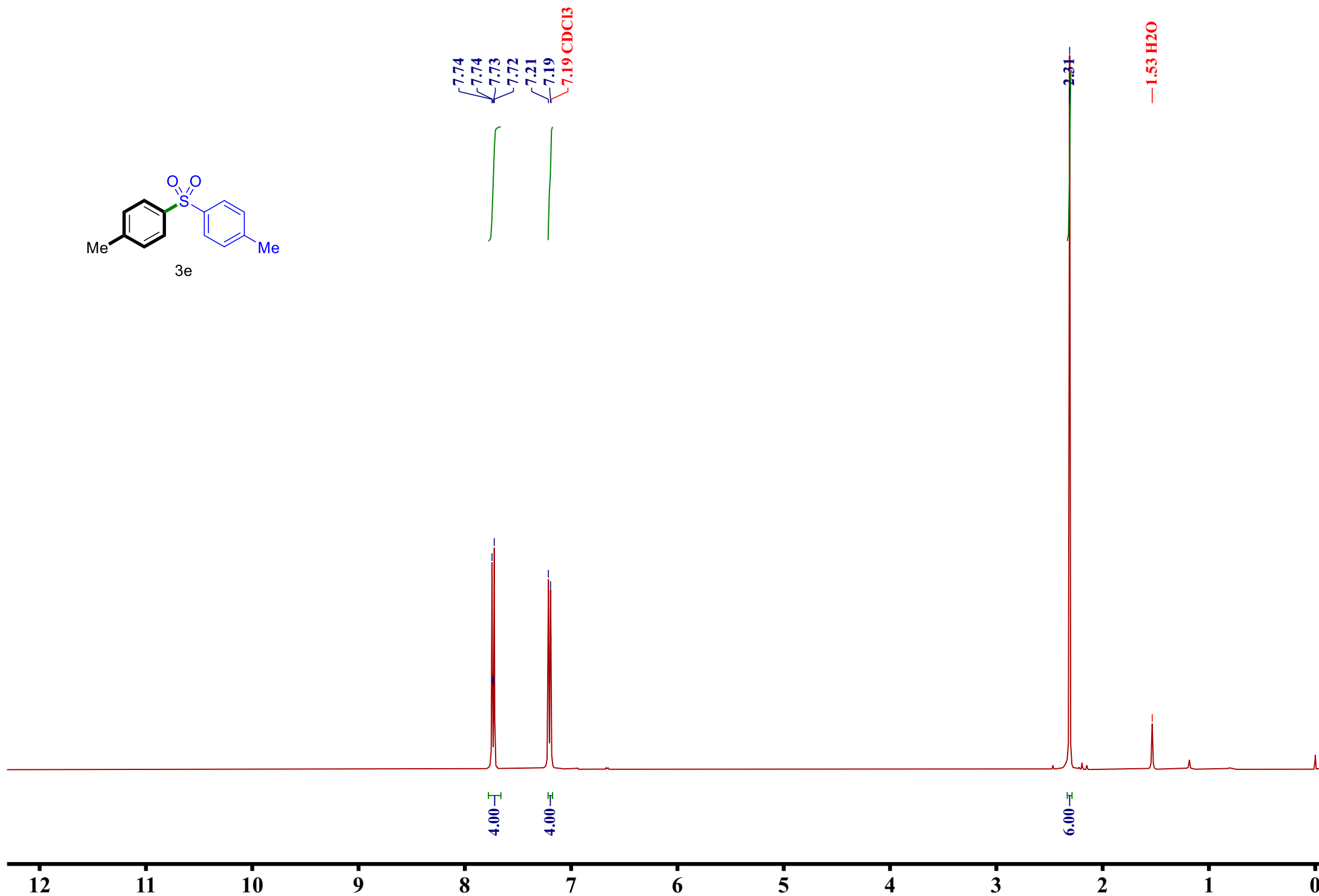
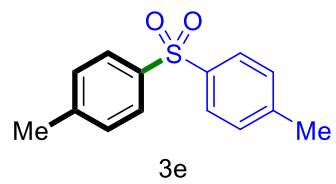


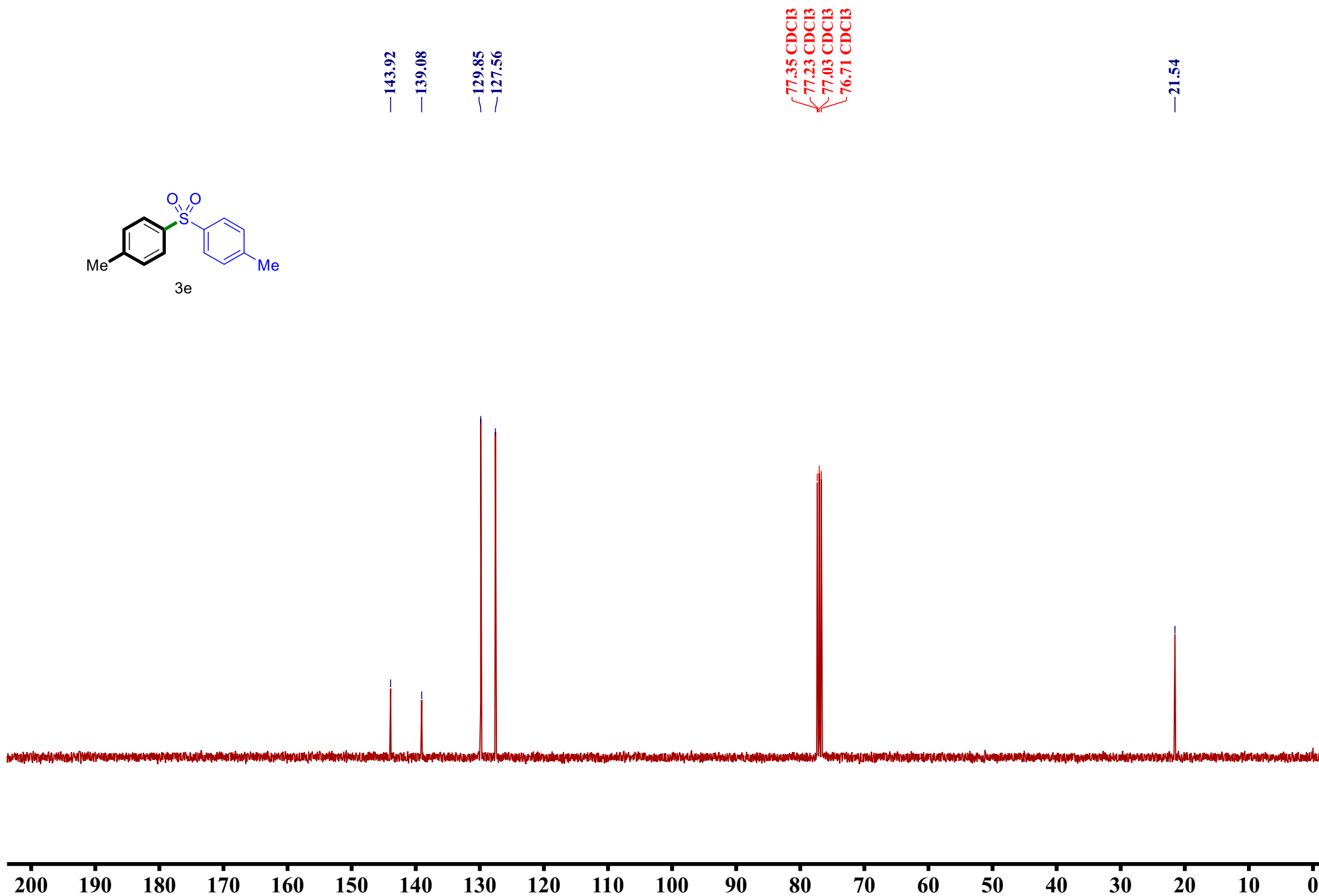
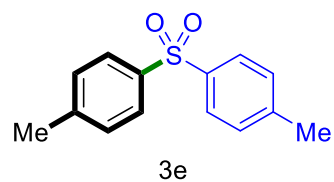


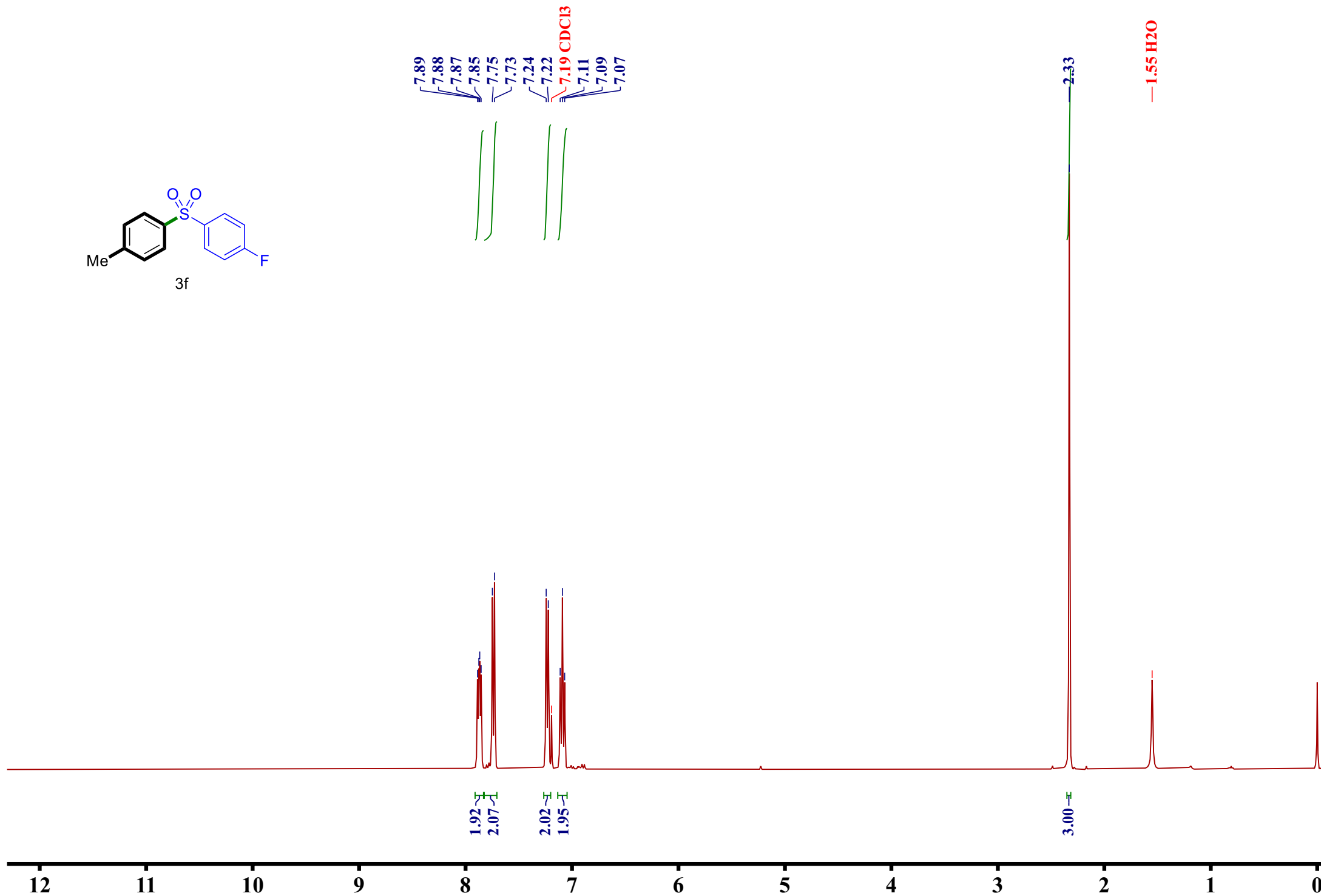
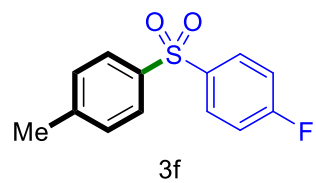


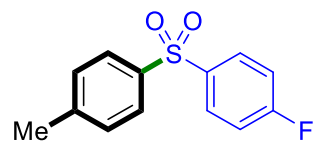
3d











3f

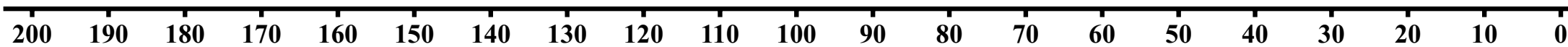
166.60
164.06

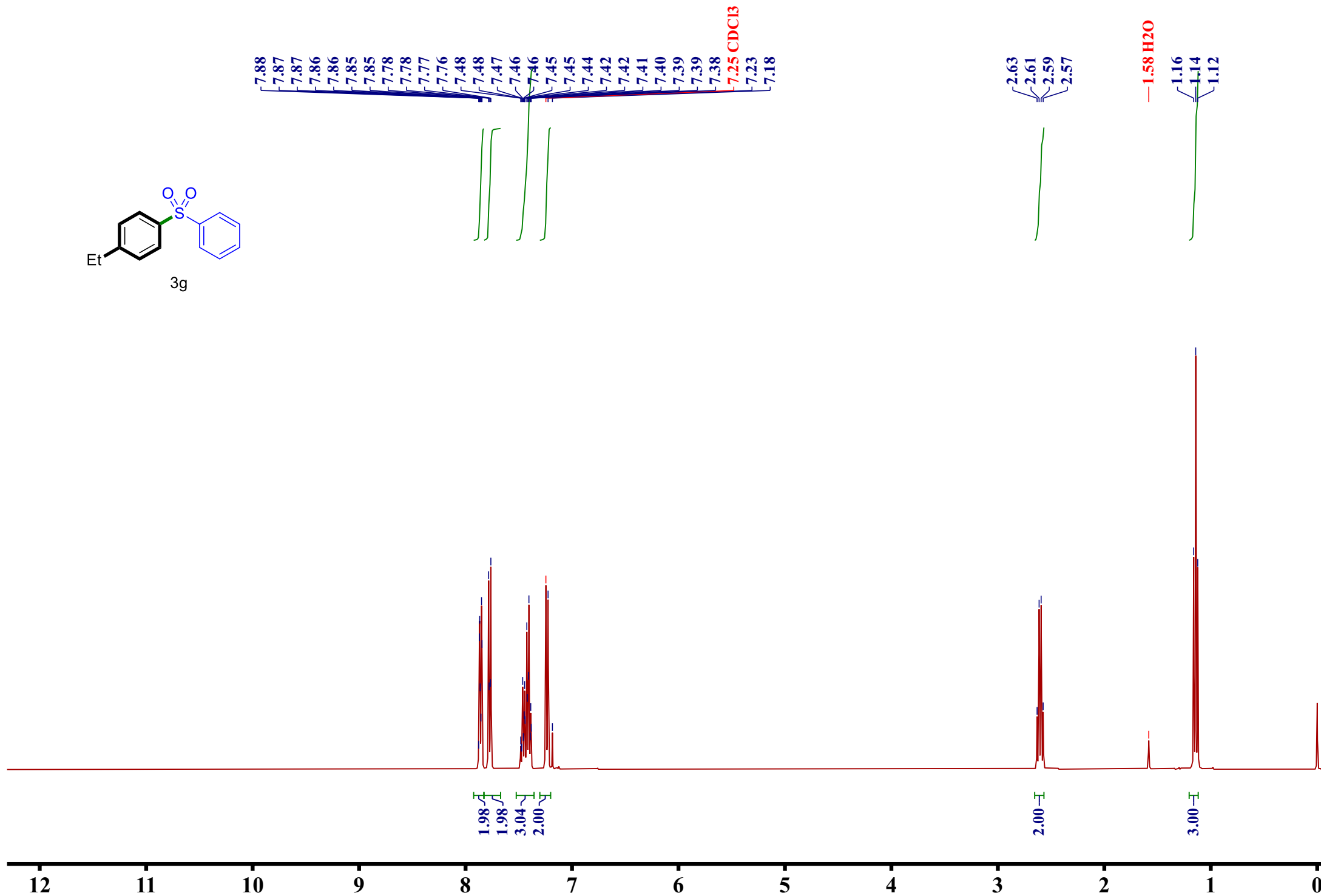
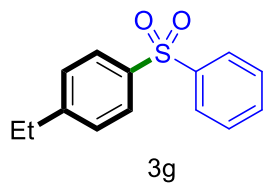
144.38
138.50
138.09
138.06
130.36
130.27
130.03
127.64

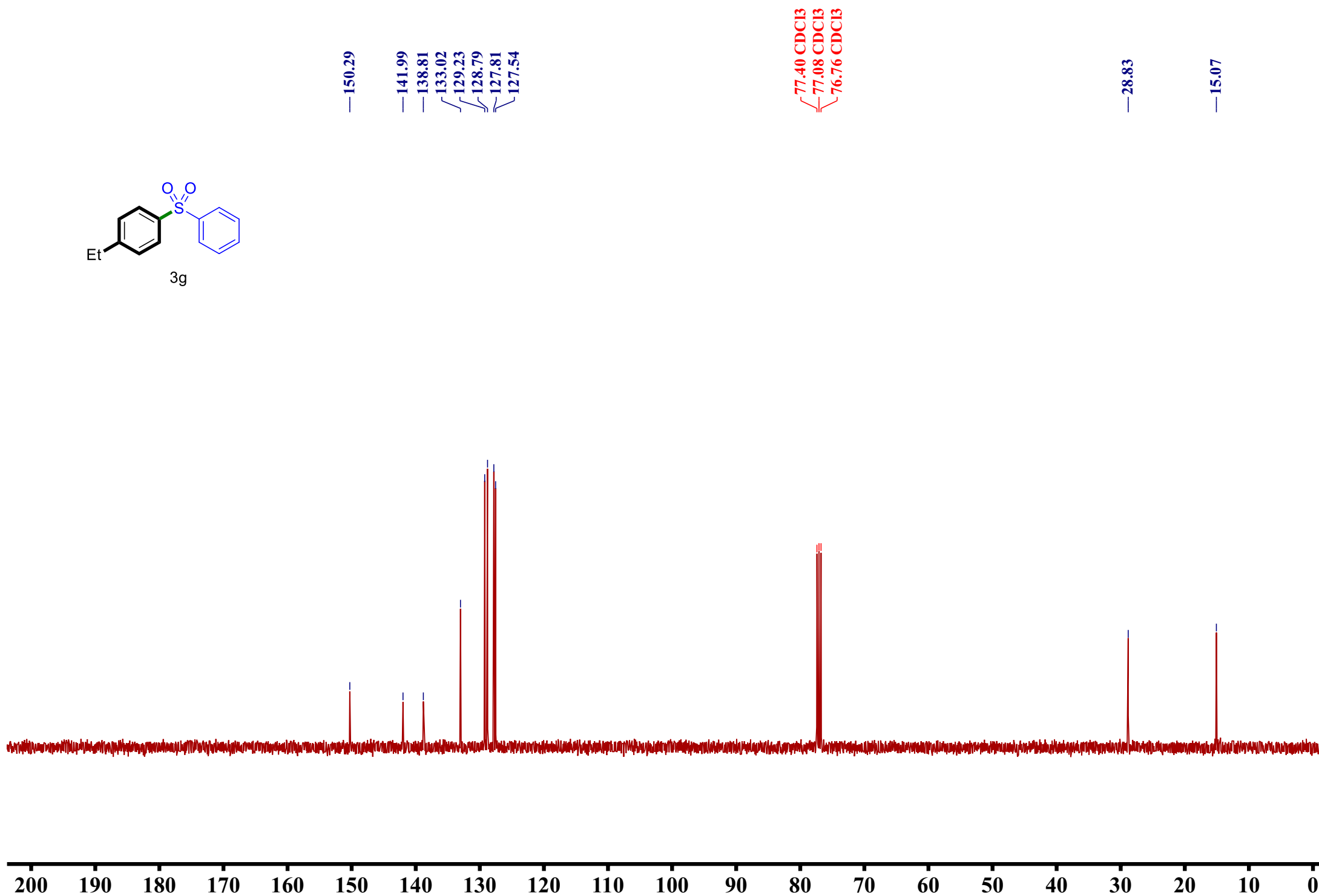
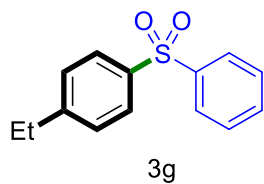
116.64
116.42

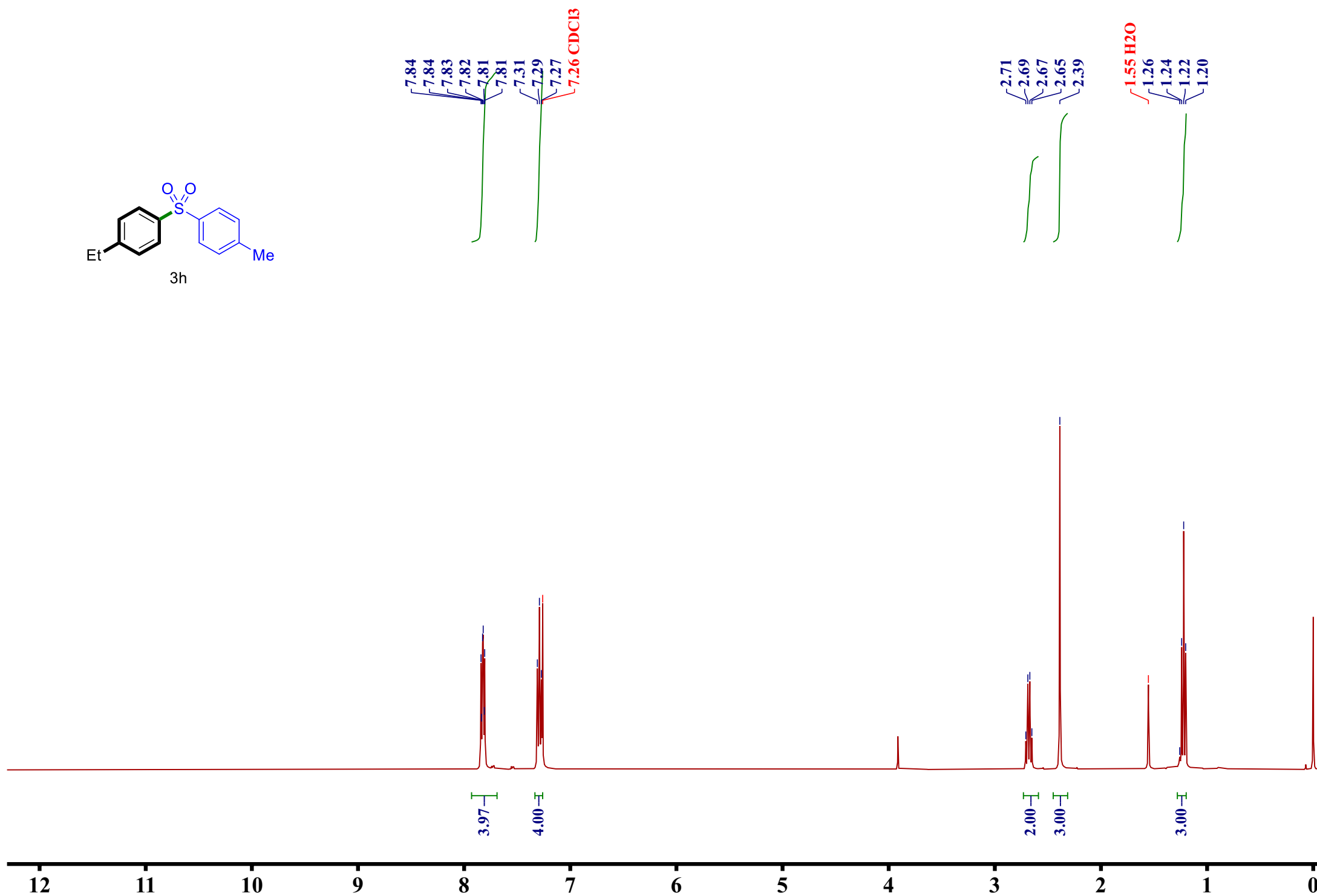
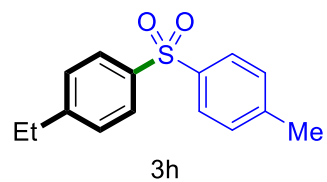
77.36 CDC13
77.04 CDC13
76.72 CDC13

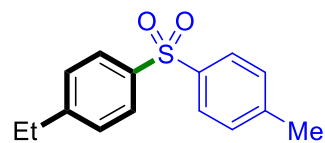
21.59



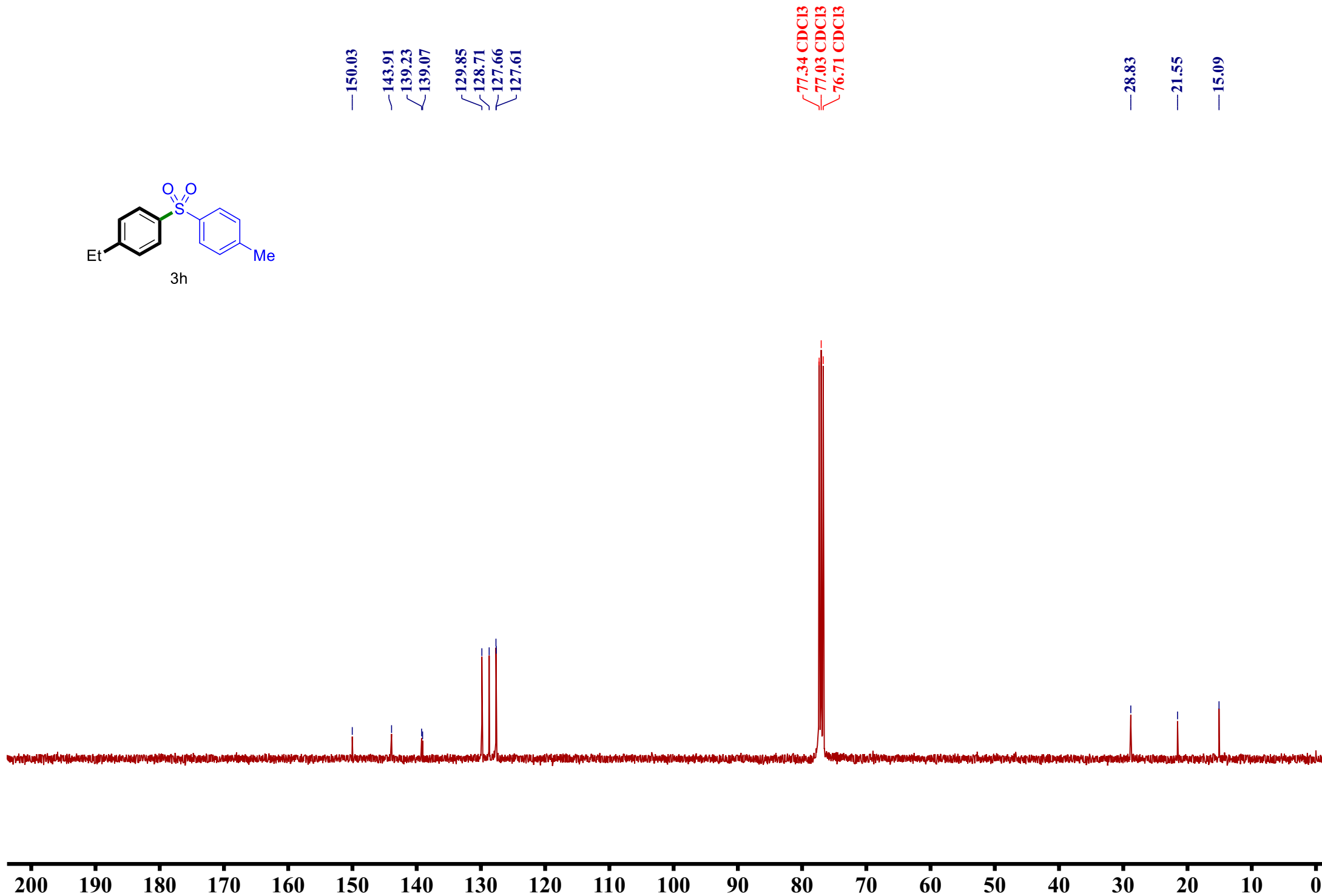


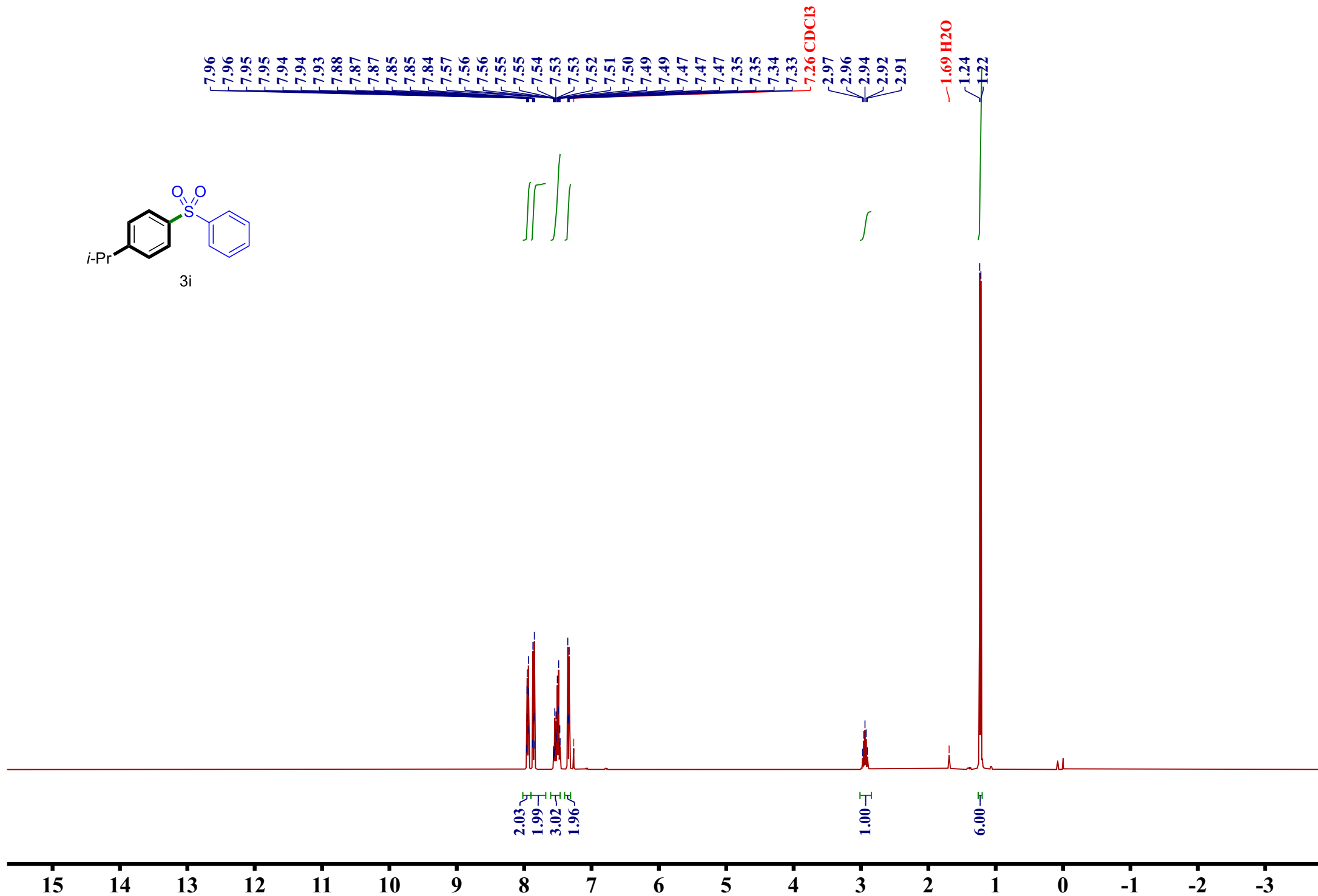
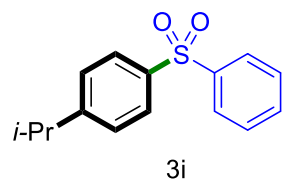


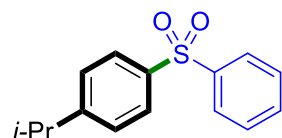




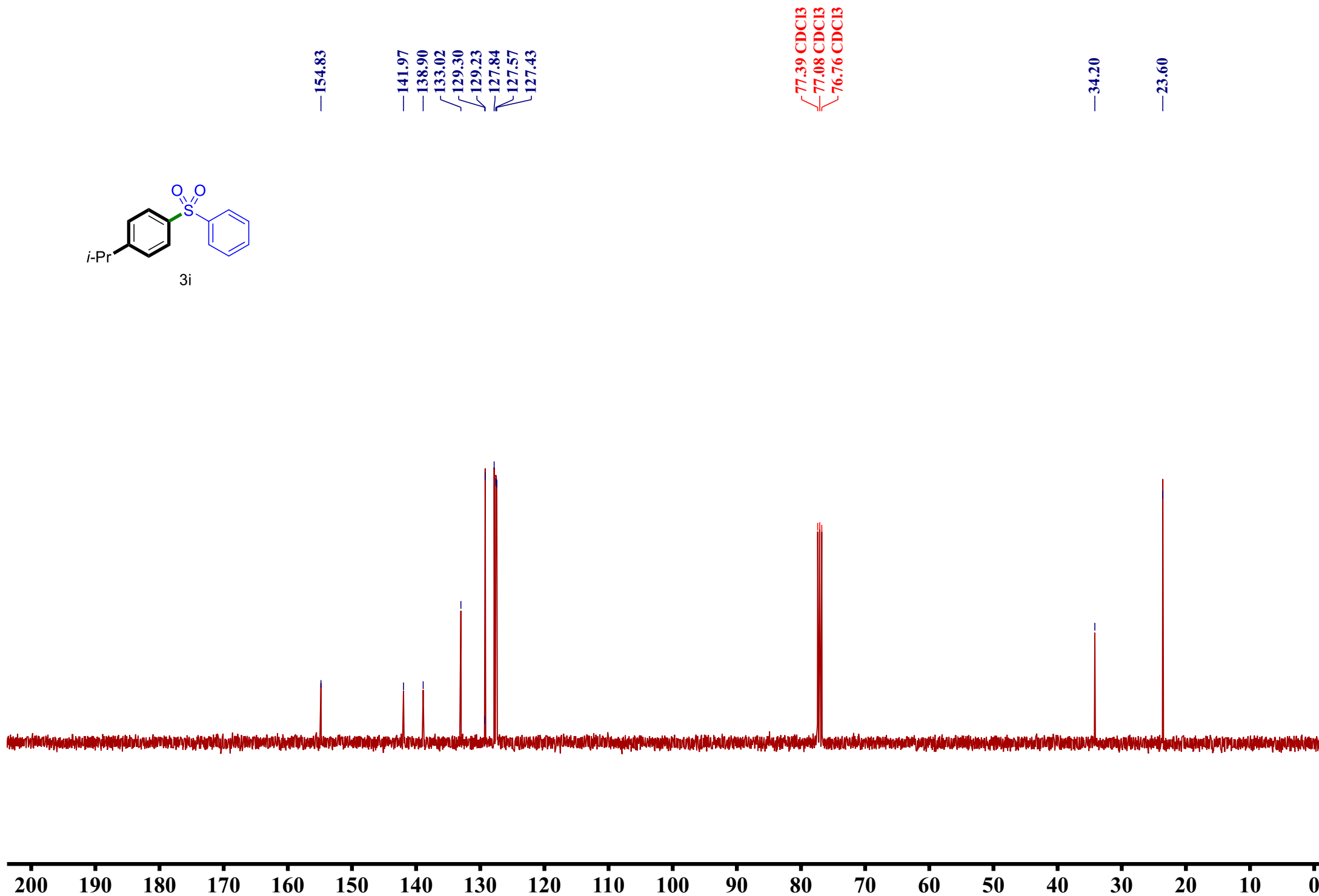
3h

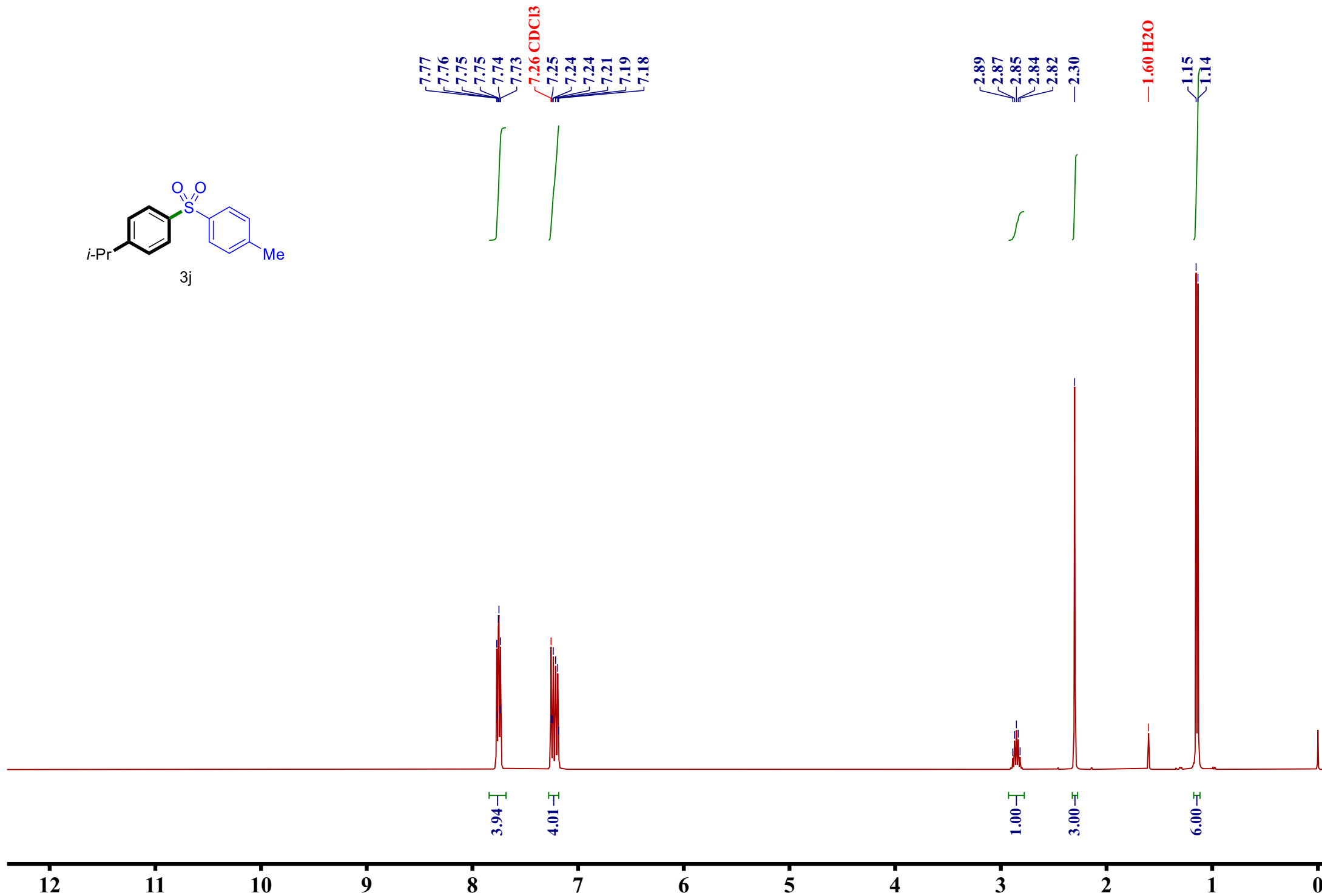
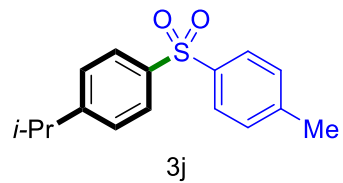


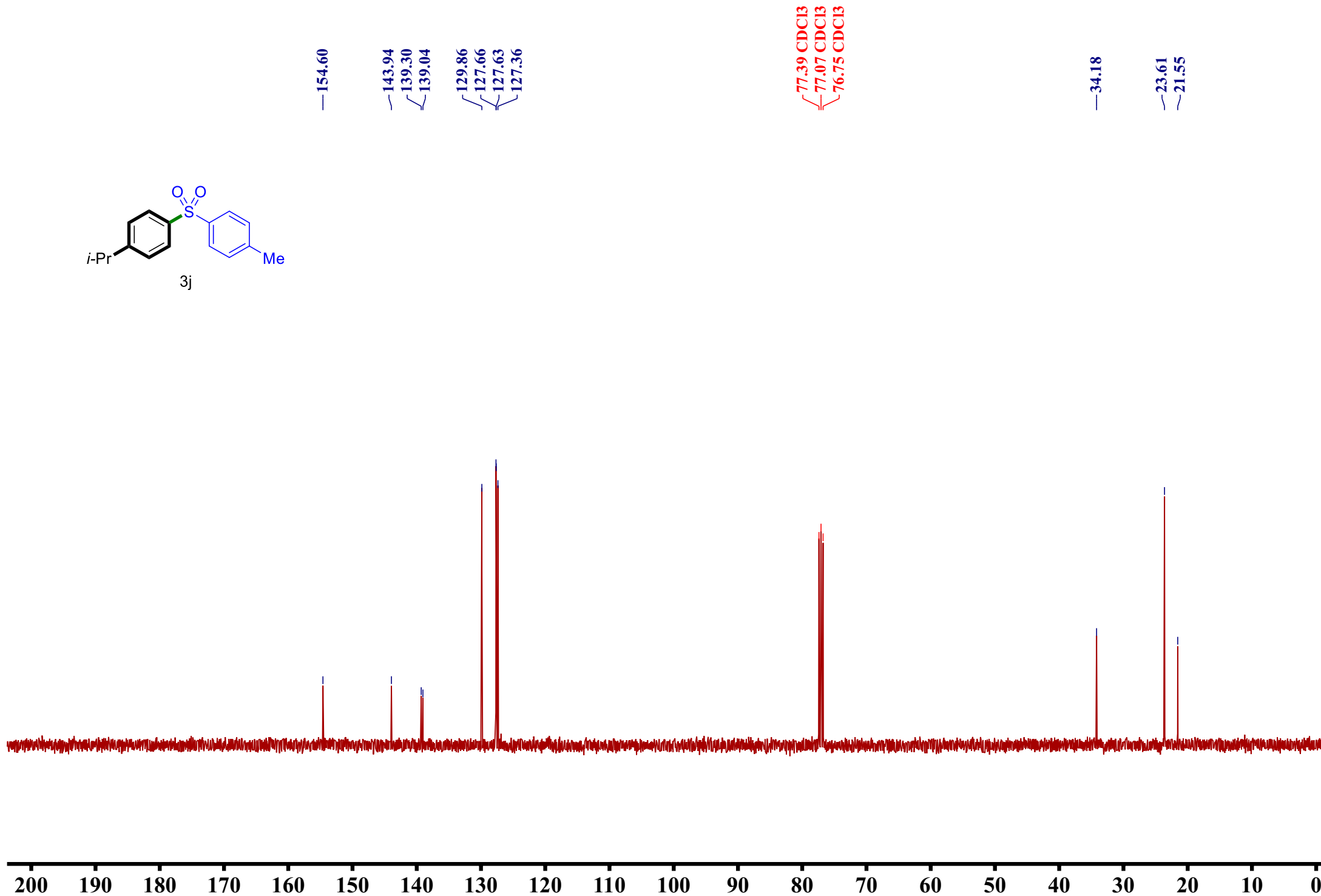
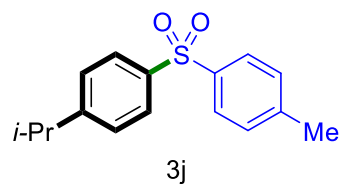


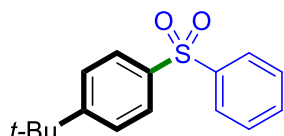


3i

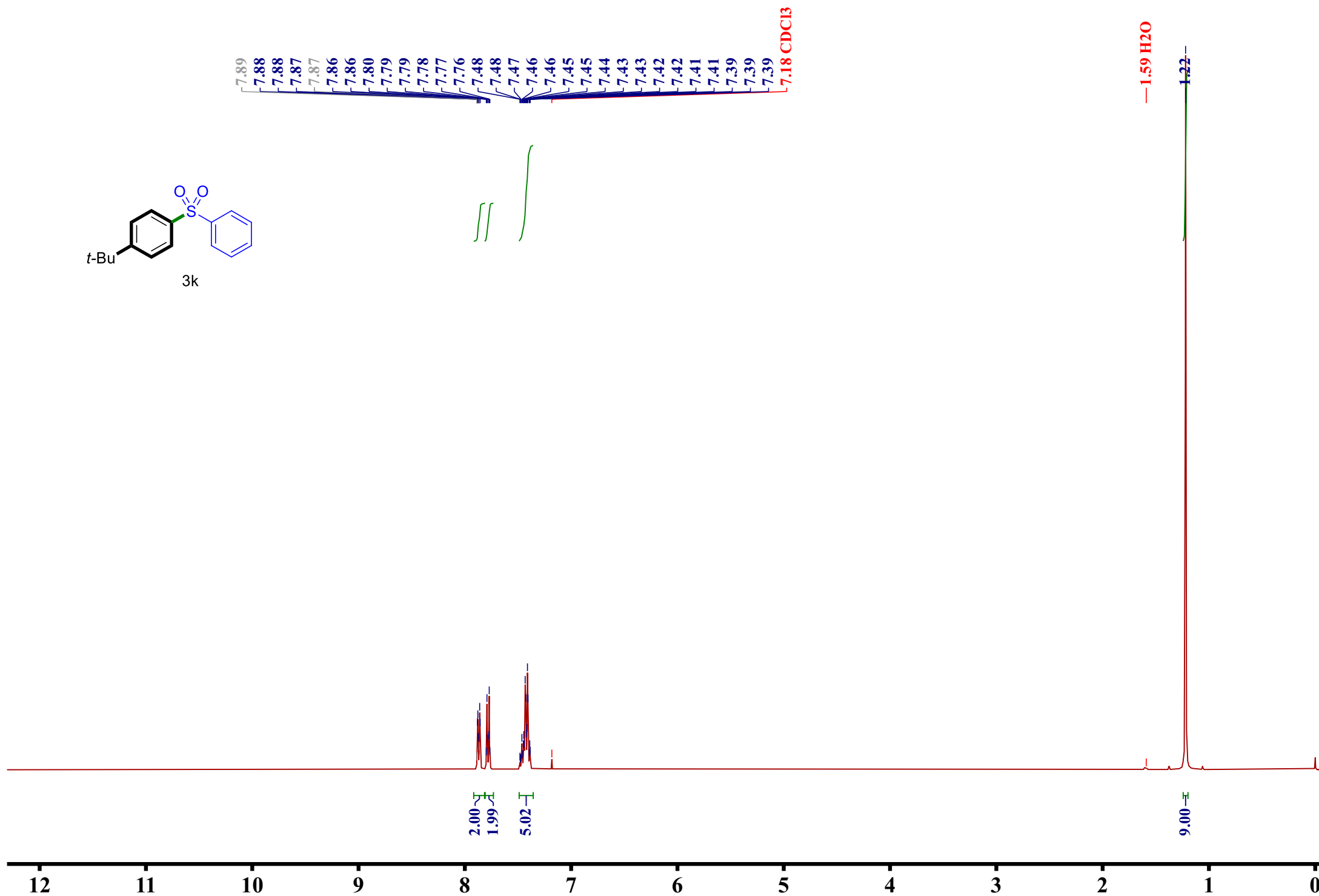


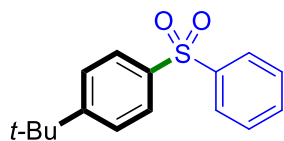




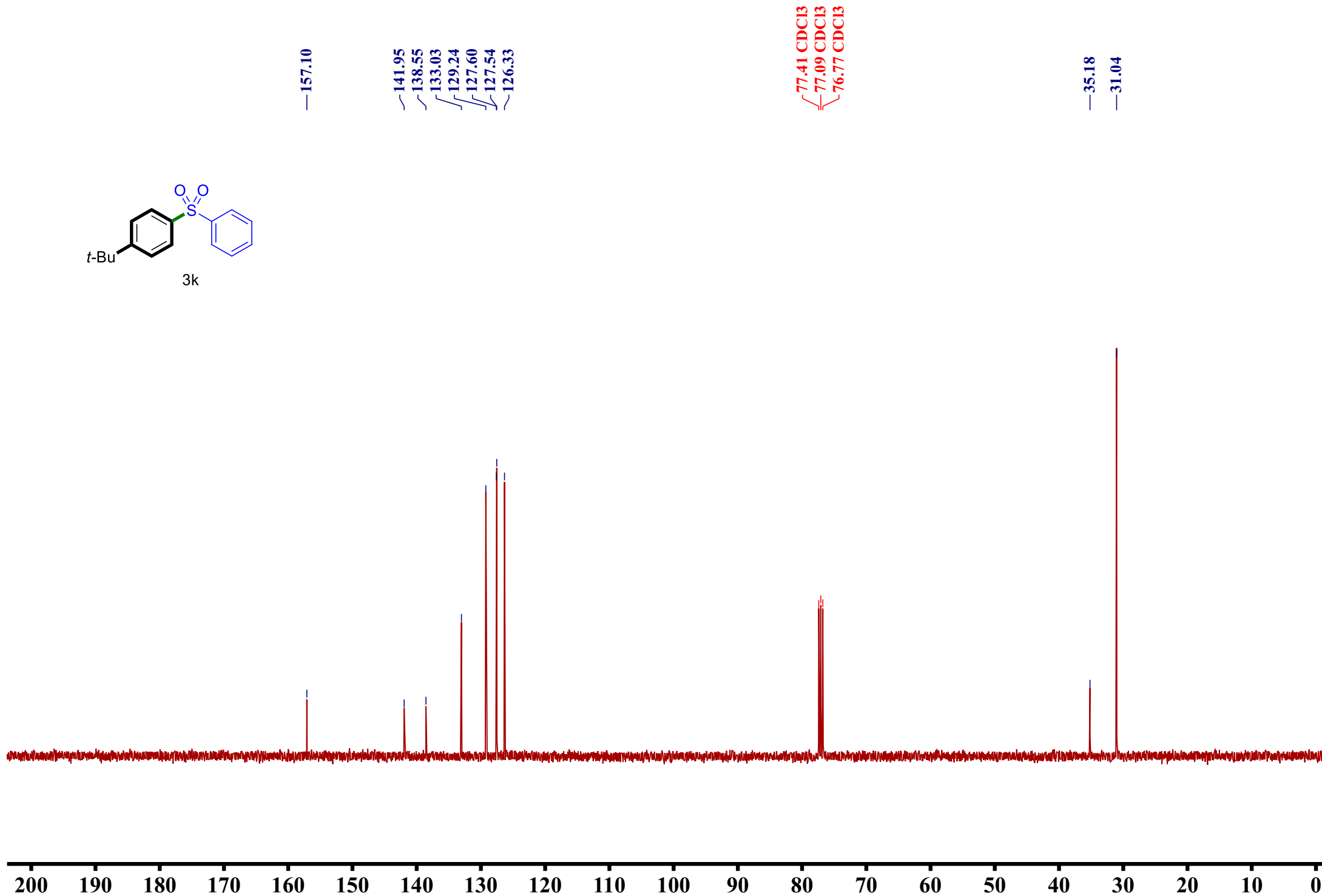


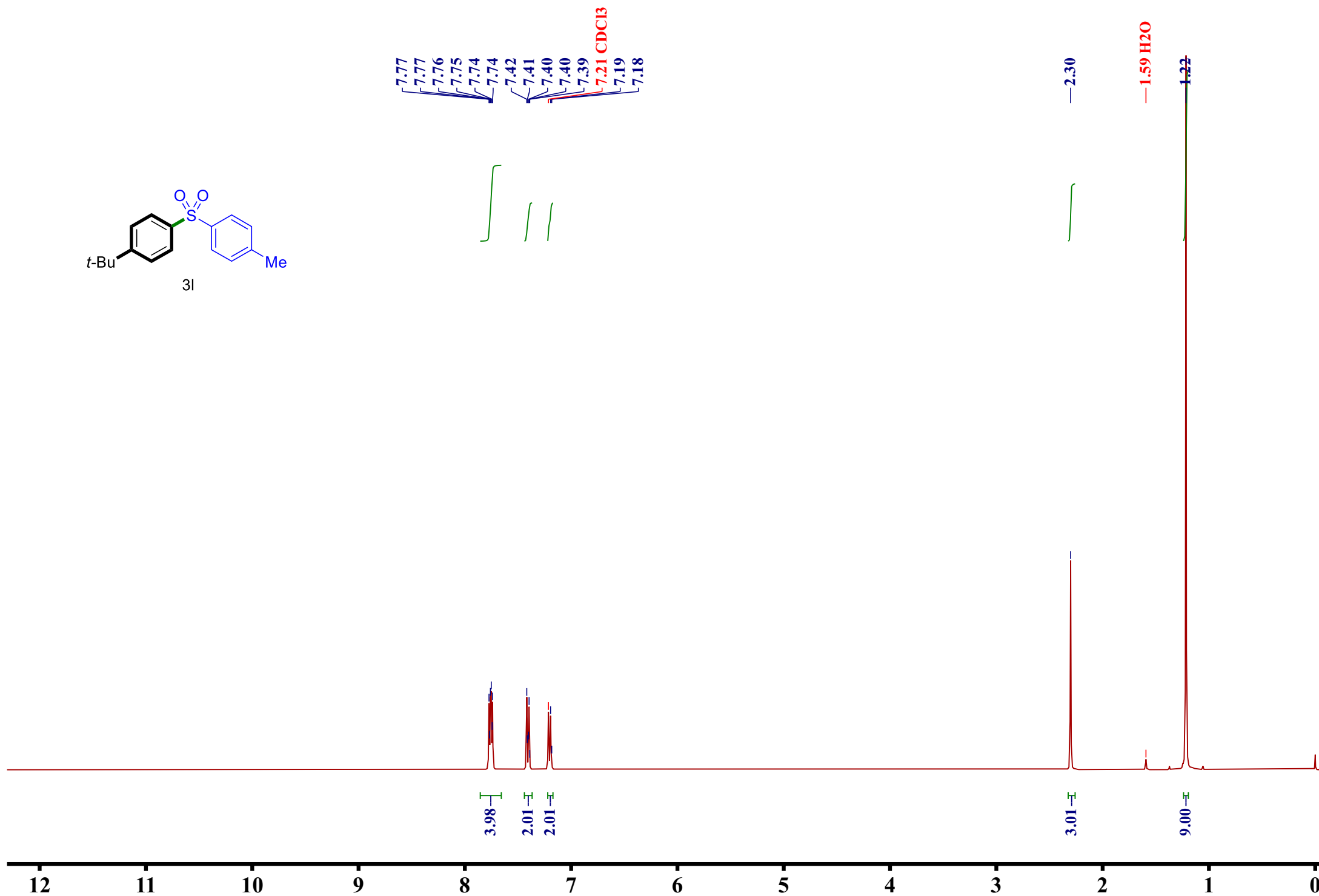
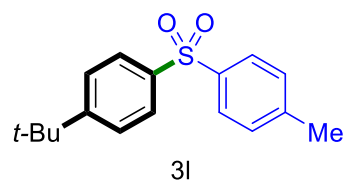
3k

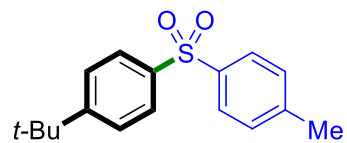




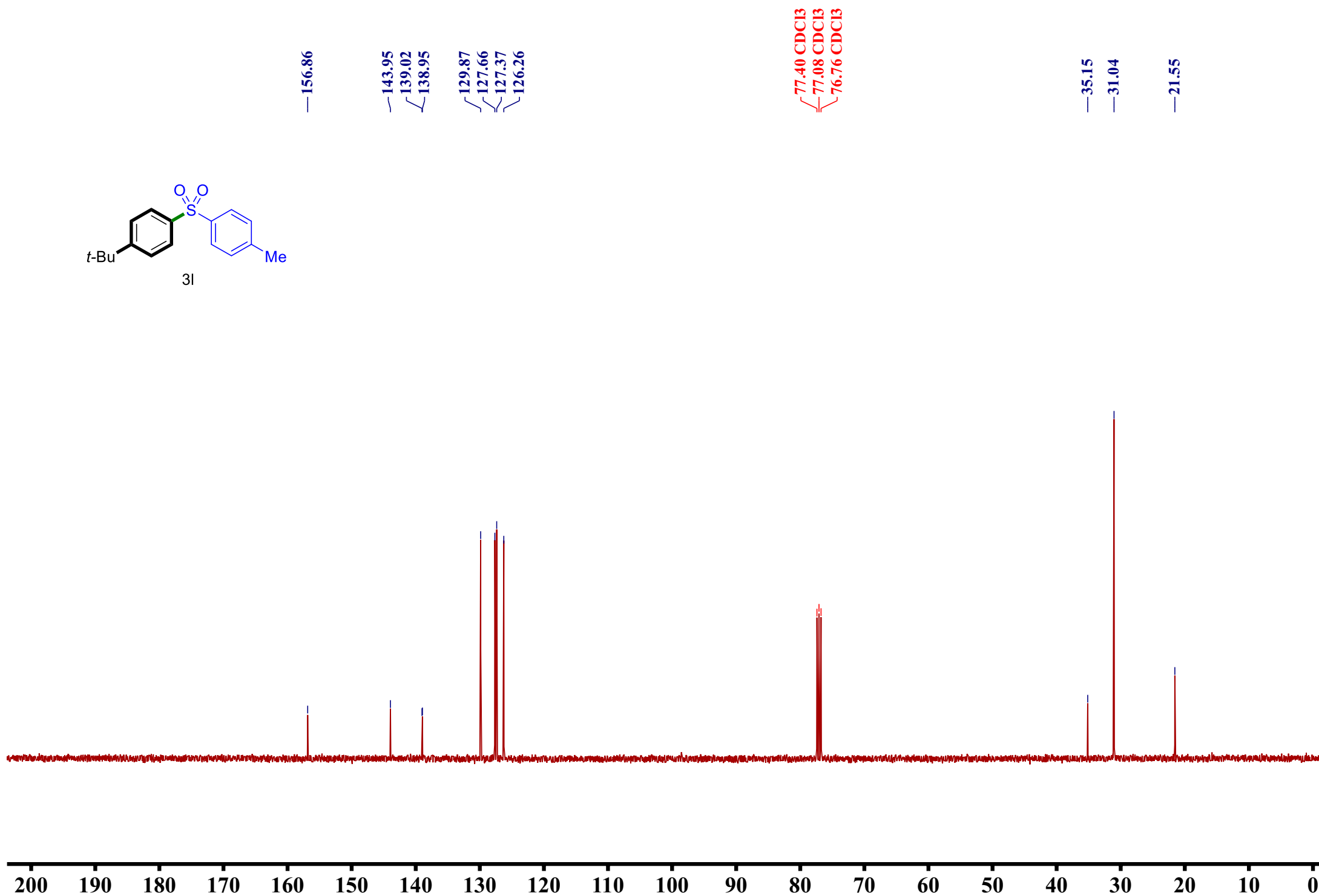
3k

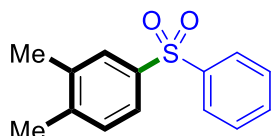






3I





3m

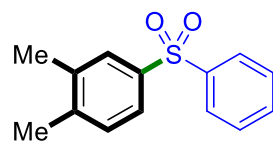
7.94
7.94
7.93
7.93
7.92
7.92
7.91
7.69
7.69
7.68
7.67
7.66
7.65
7.55
7.55
7.55
7.54
7.53
7.52
7.52
7.51
7.51
7.49
7.49
7.48
7.47
7.46
7.46
7.45
7.26 CDCl₃
7.25
7.23

2.28
2.28

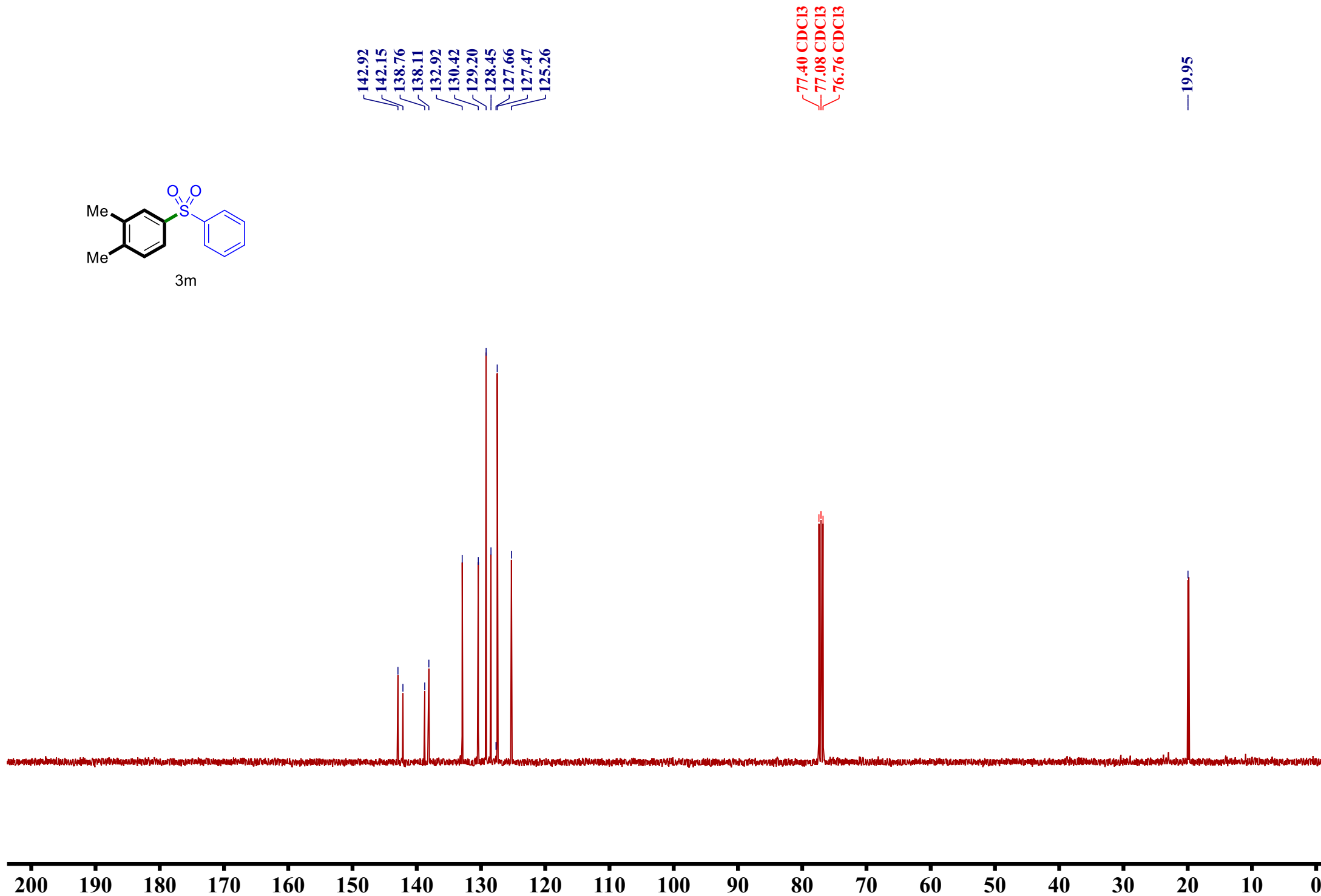
2.00
2.00
3.00
1.00

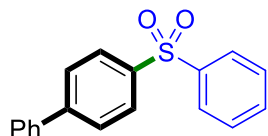
6.00

12 11 10 9 8 7 6 5 4 3 2 1 0

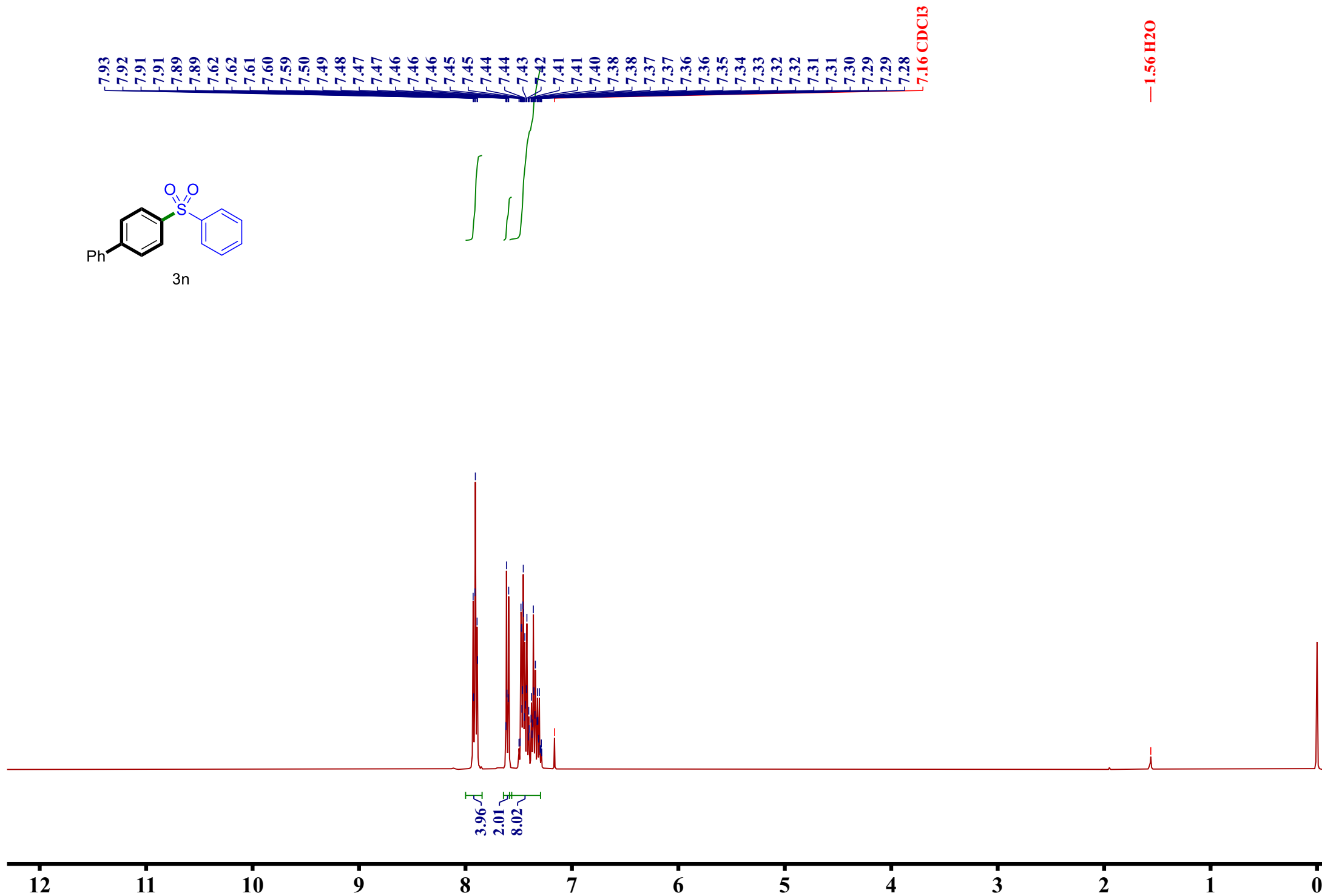


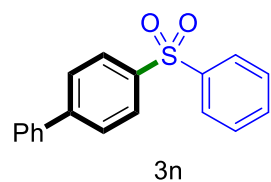
3m





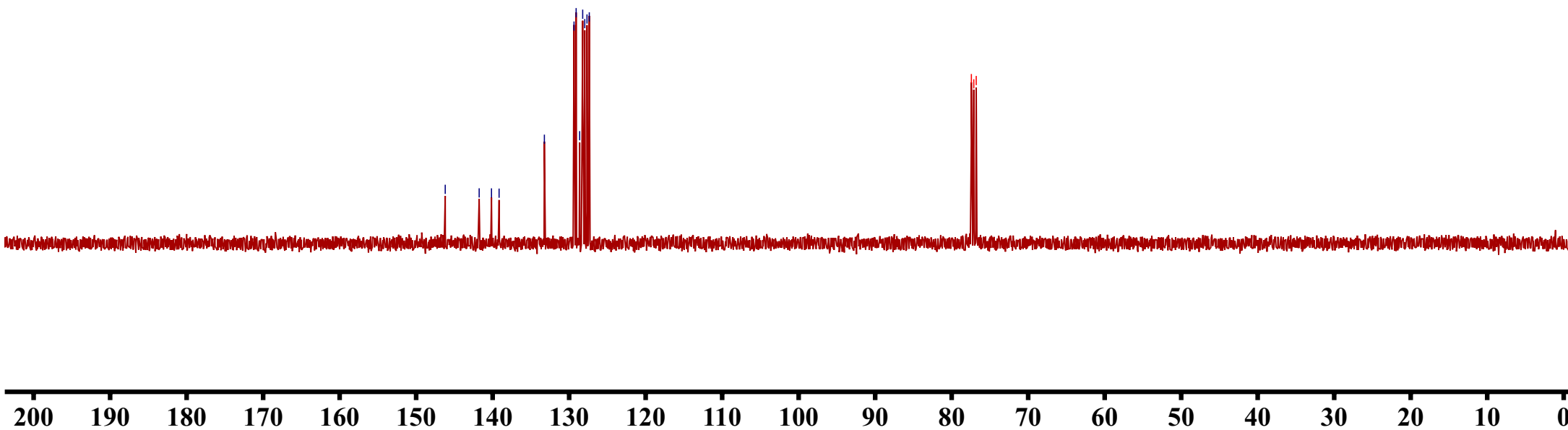
3n

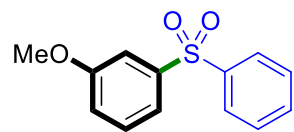




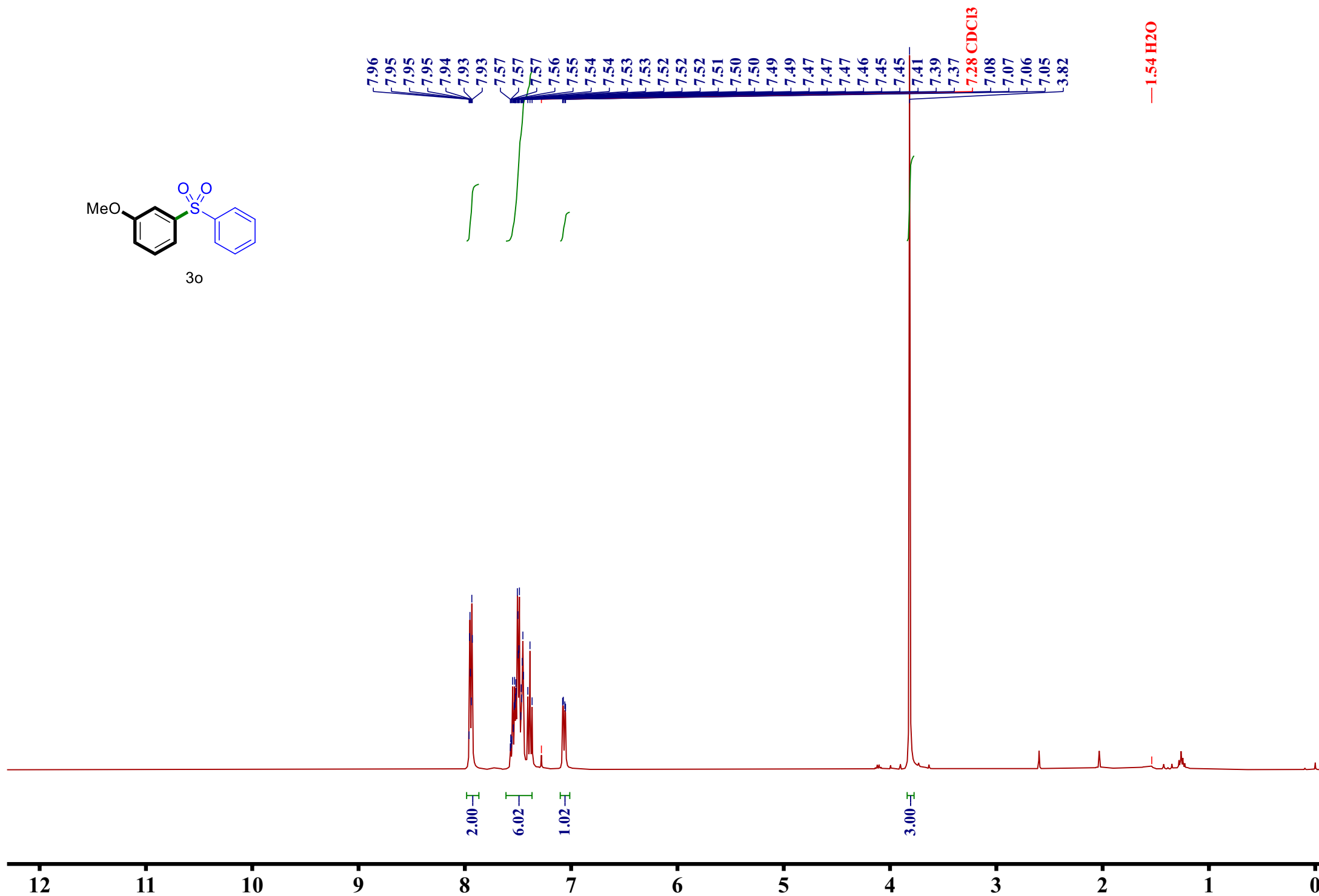
146.20
141.76
140.15
139.16
133.24
129.36
129.09
128.63
128.23
127.96
127.67
127.37

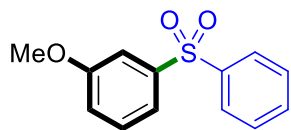
77.43 CDCl₃
77.11 CDCl₃
76.79 CDCl₃



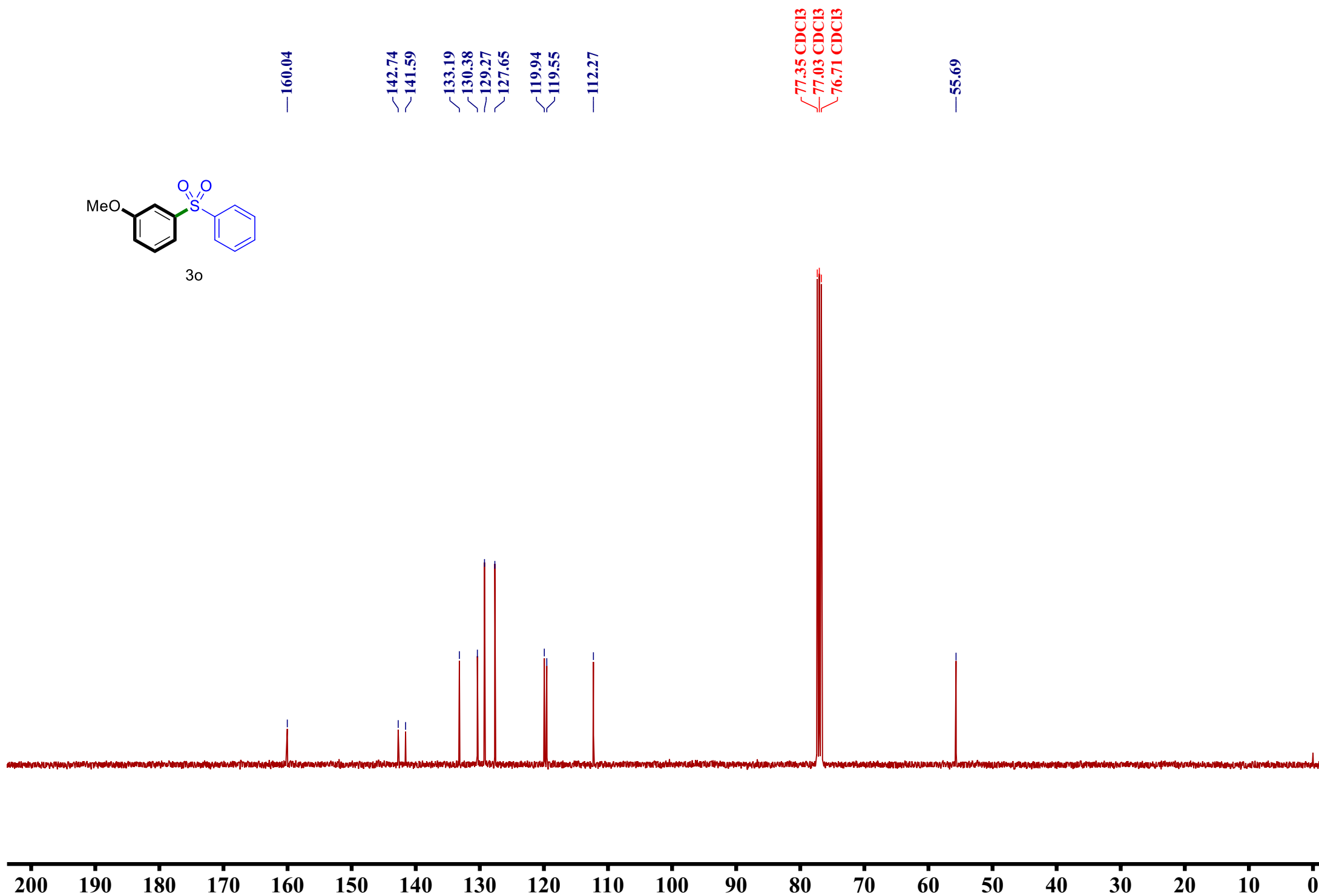


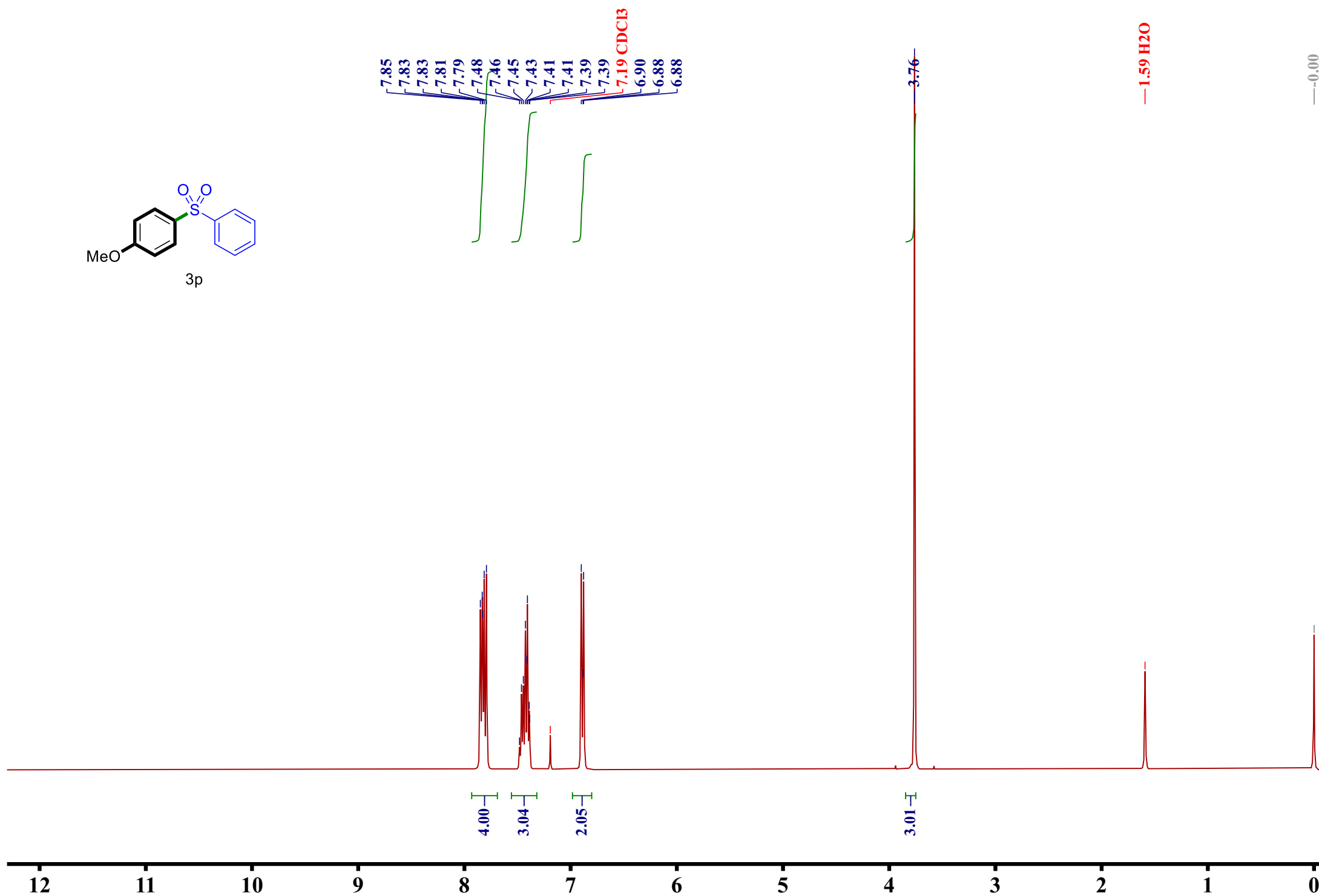
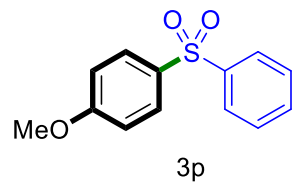
3o

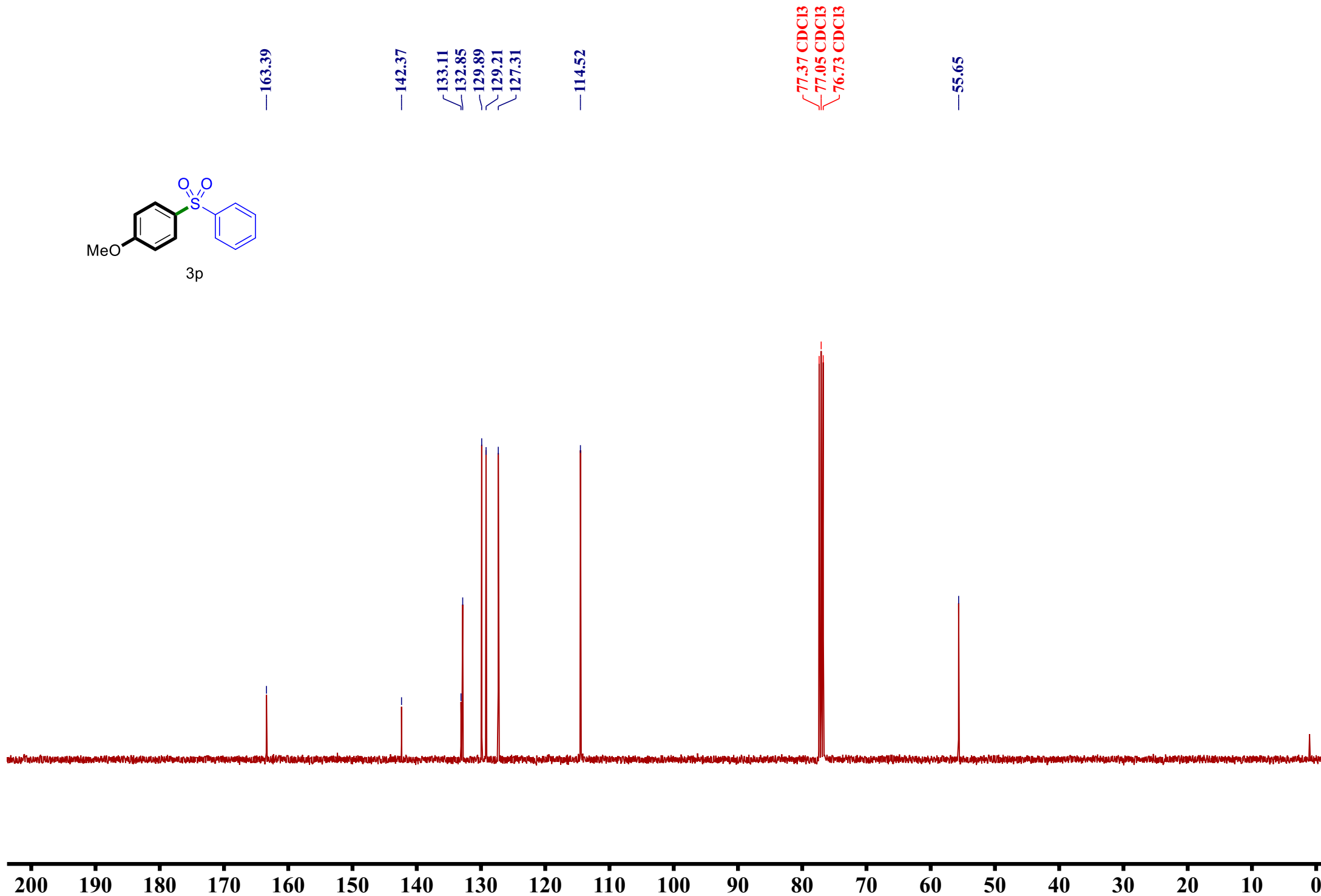
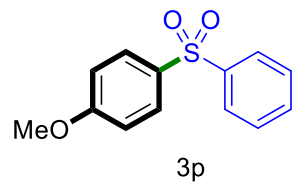


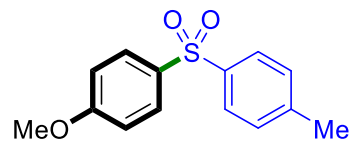


3o









3q

7.87
7.86
7.86
7.85
7.84
7.83
7.80
7.79
7.78
7.78
7.40
7.40
7.38
7.13
7.12
7.11
7.10
7.10
7.09

7.86
7.84
7.80
7.79
7.78
7.78

7.40
7.40
7.38

7.12
7.11
7.10
7.10

3.81

— 3.33 H₂O

2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.35

7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0

1.99
2.02

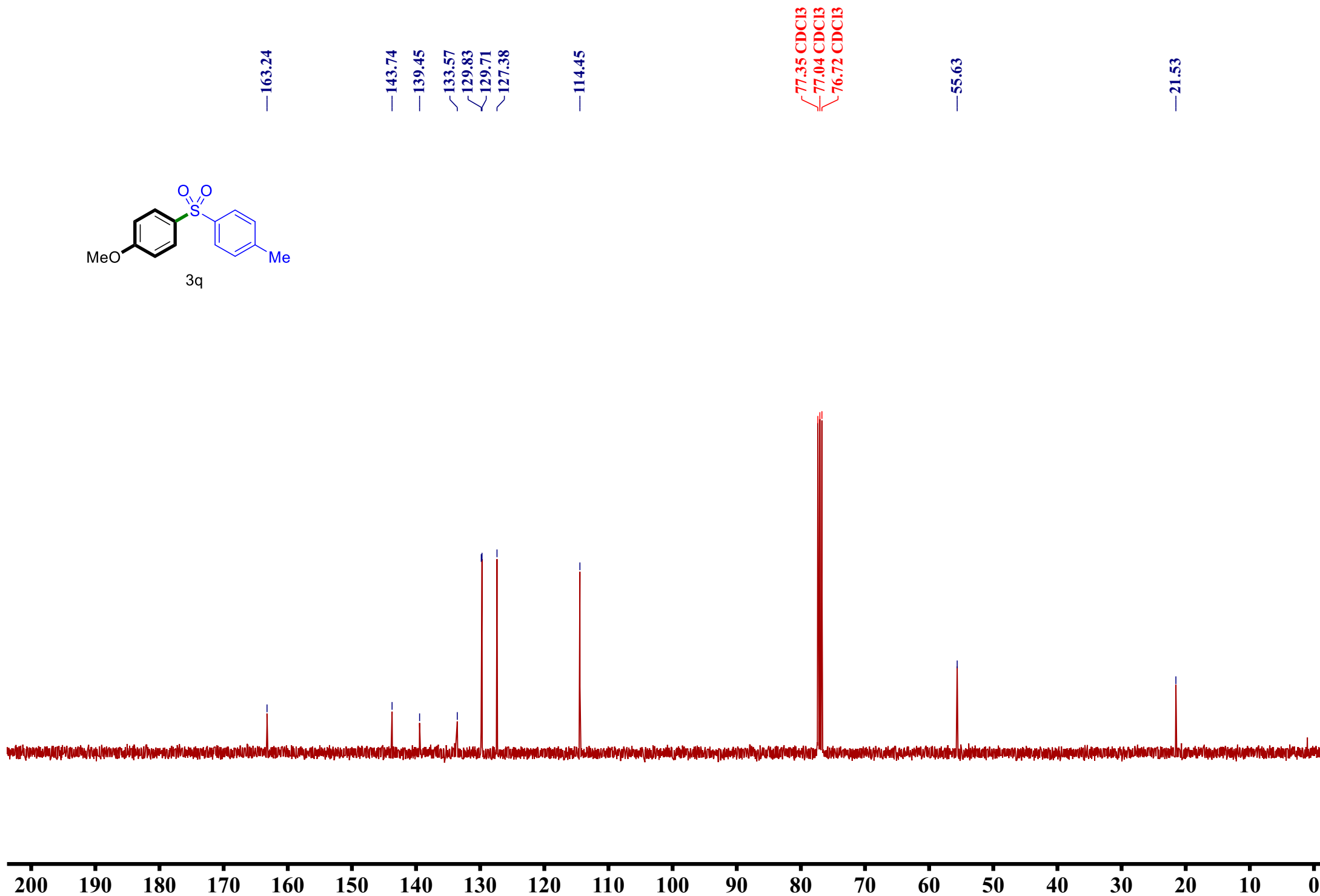
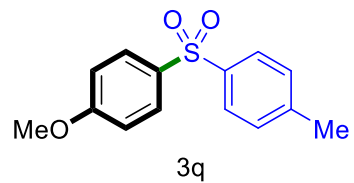
2.01

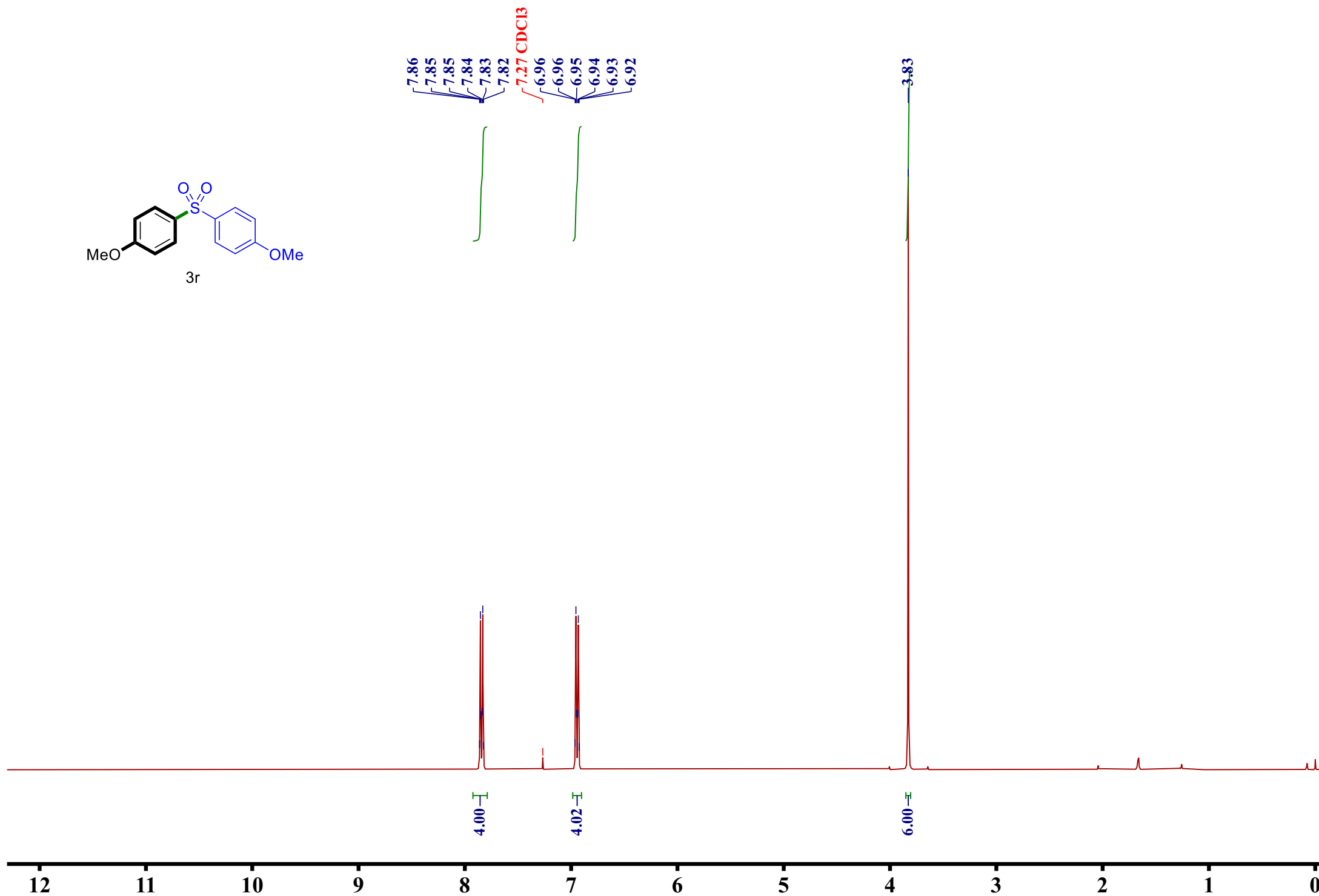
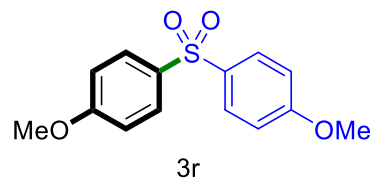
1.99

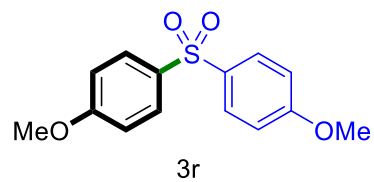
3.00

3.02

2 11 10 9 8 7 6 5 4 3 2 1 0







—163.11

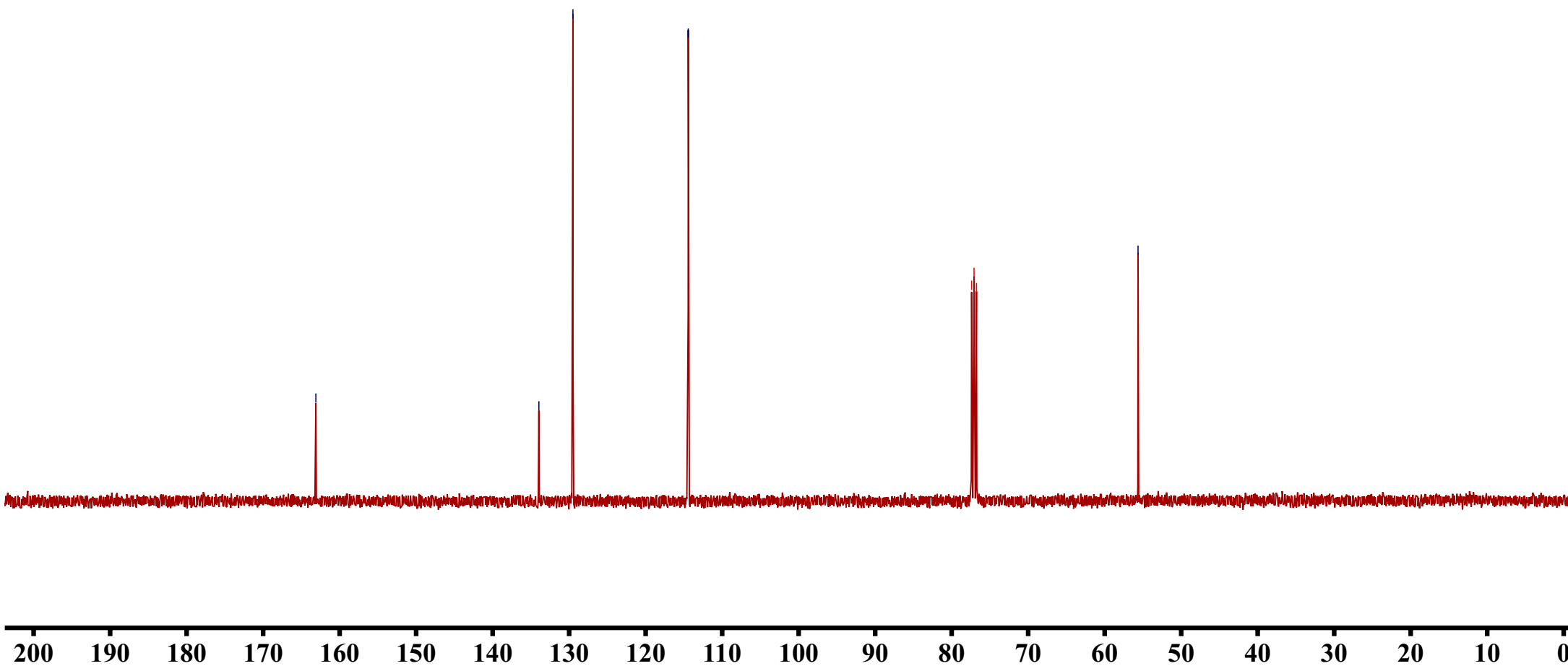
—133.96

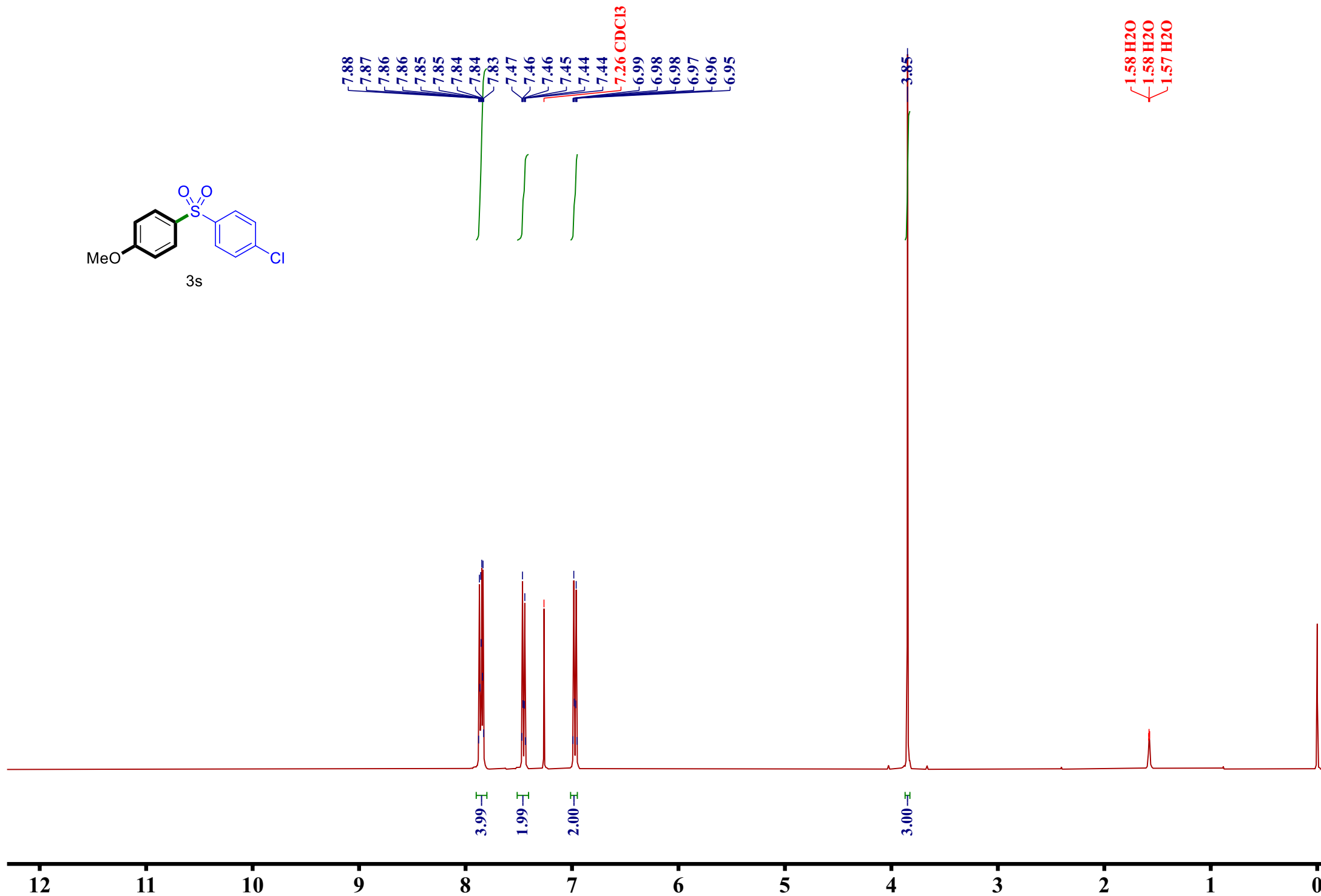
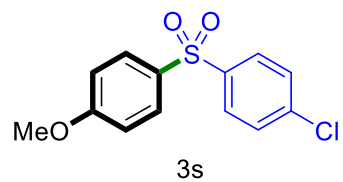
—129.51

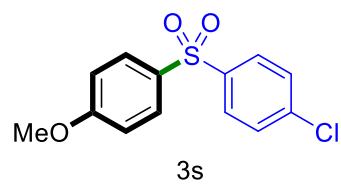
—114.43

77.39 CDC13
77.08 CDC13
76.76 CDC13

—55.64







—163.59

—140.94

—139.48

—132.69

—129.90

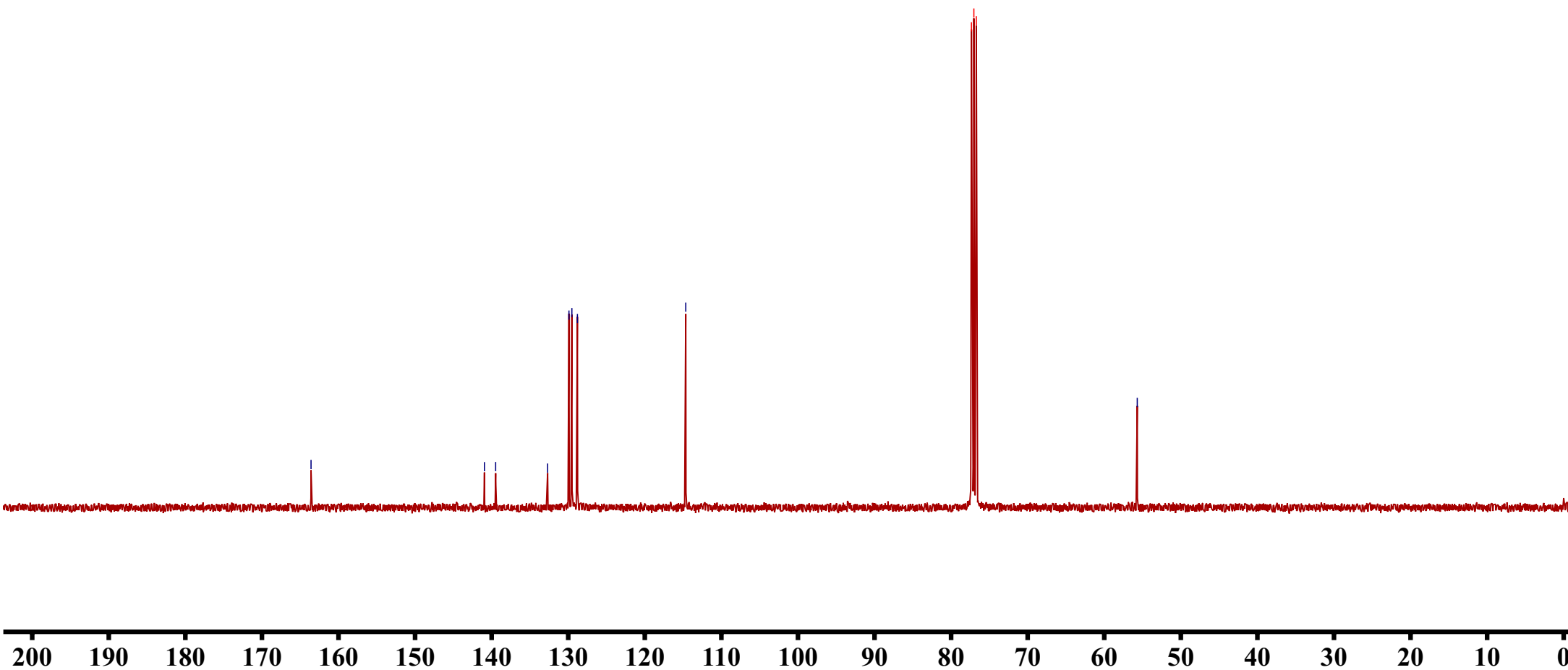
—129.52

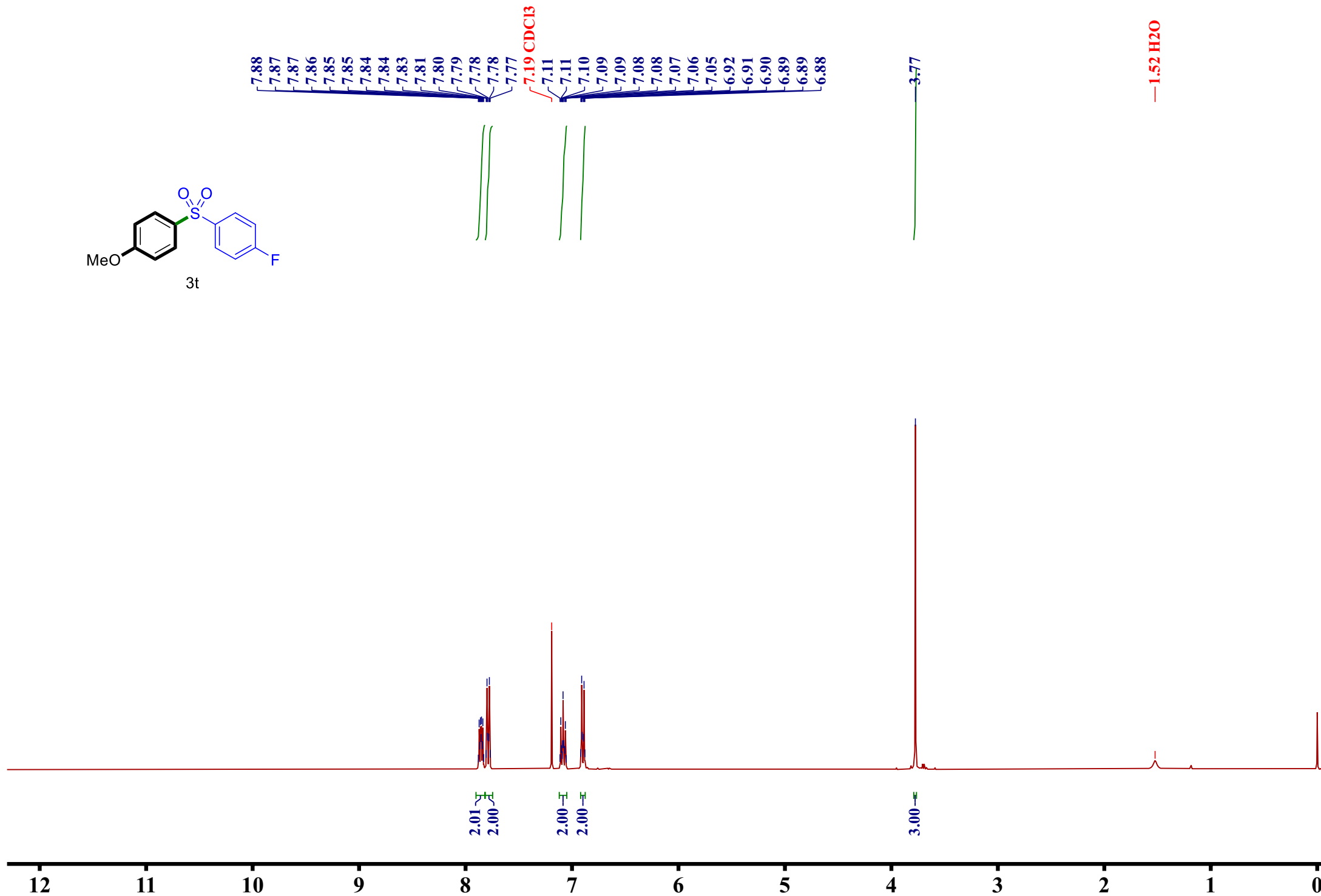
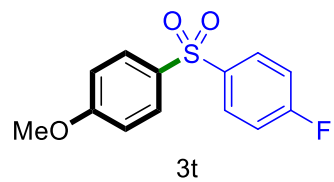
—128.80

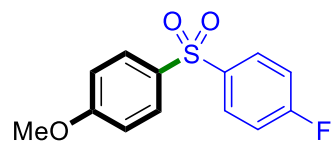
—114.65

77.35 CDC13
77.03 CDC13
76.71 CDC13

—55.69







3t

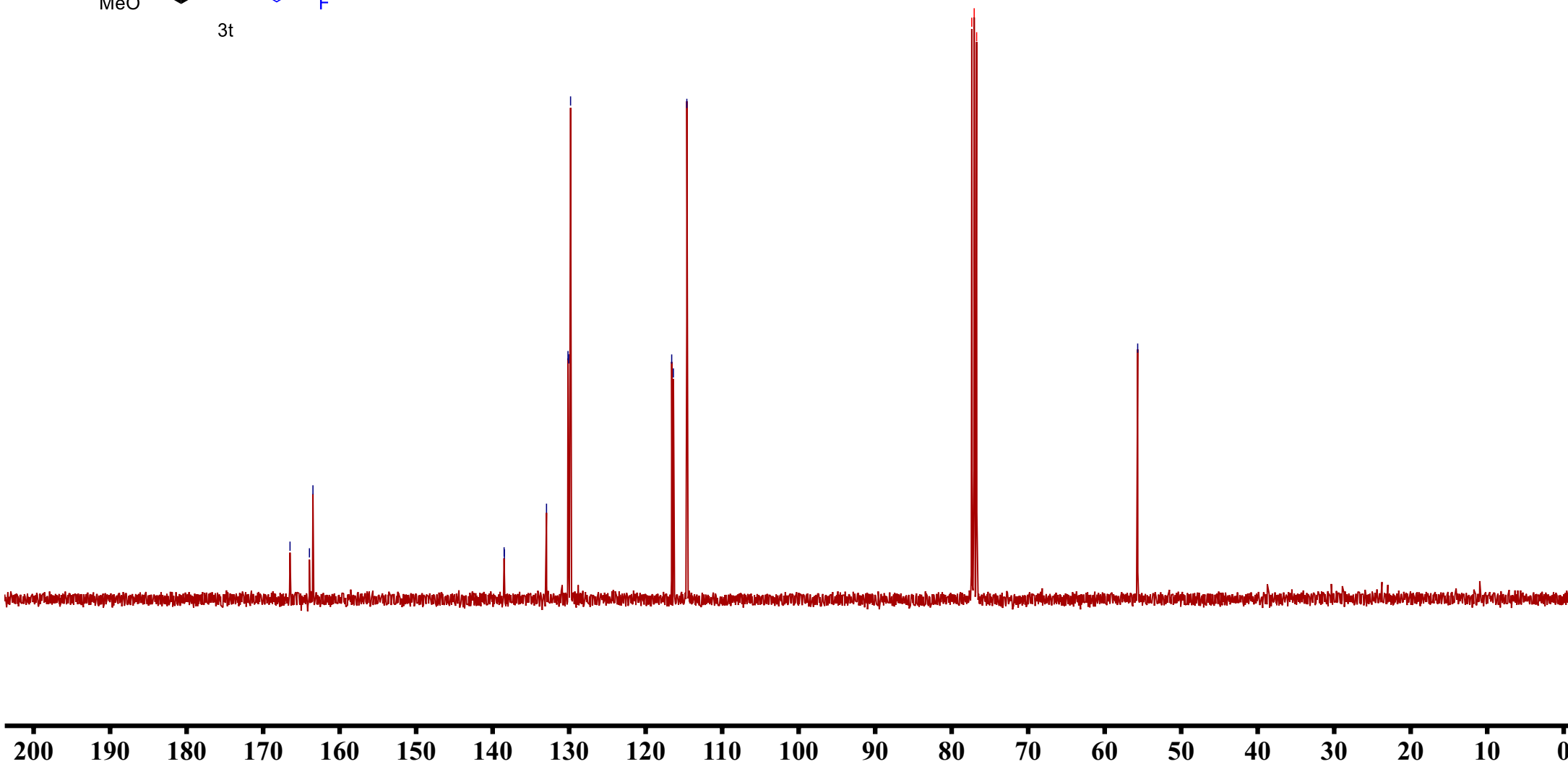
166.48
163.95
163.49

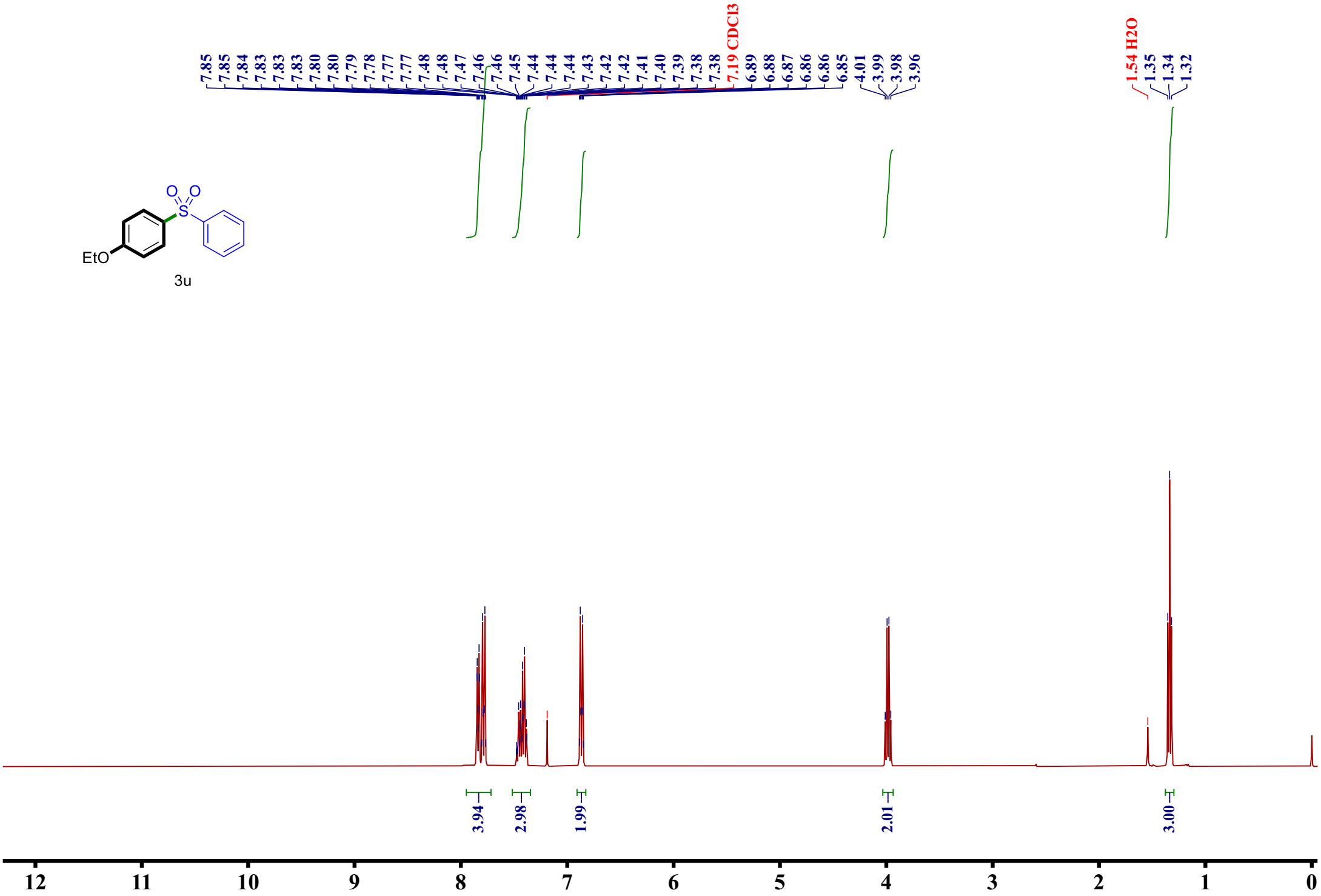
138.50
138.47
132.96
130.15
130.06
129.81

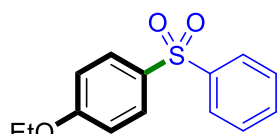
116.60
116.37
114.62

77.37 CDC13
77.05 CDC13
76.74 CDC13

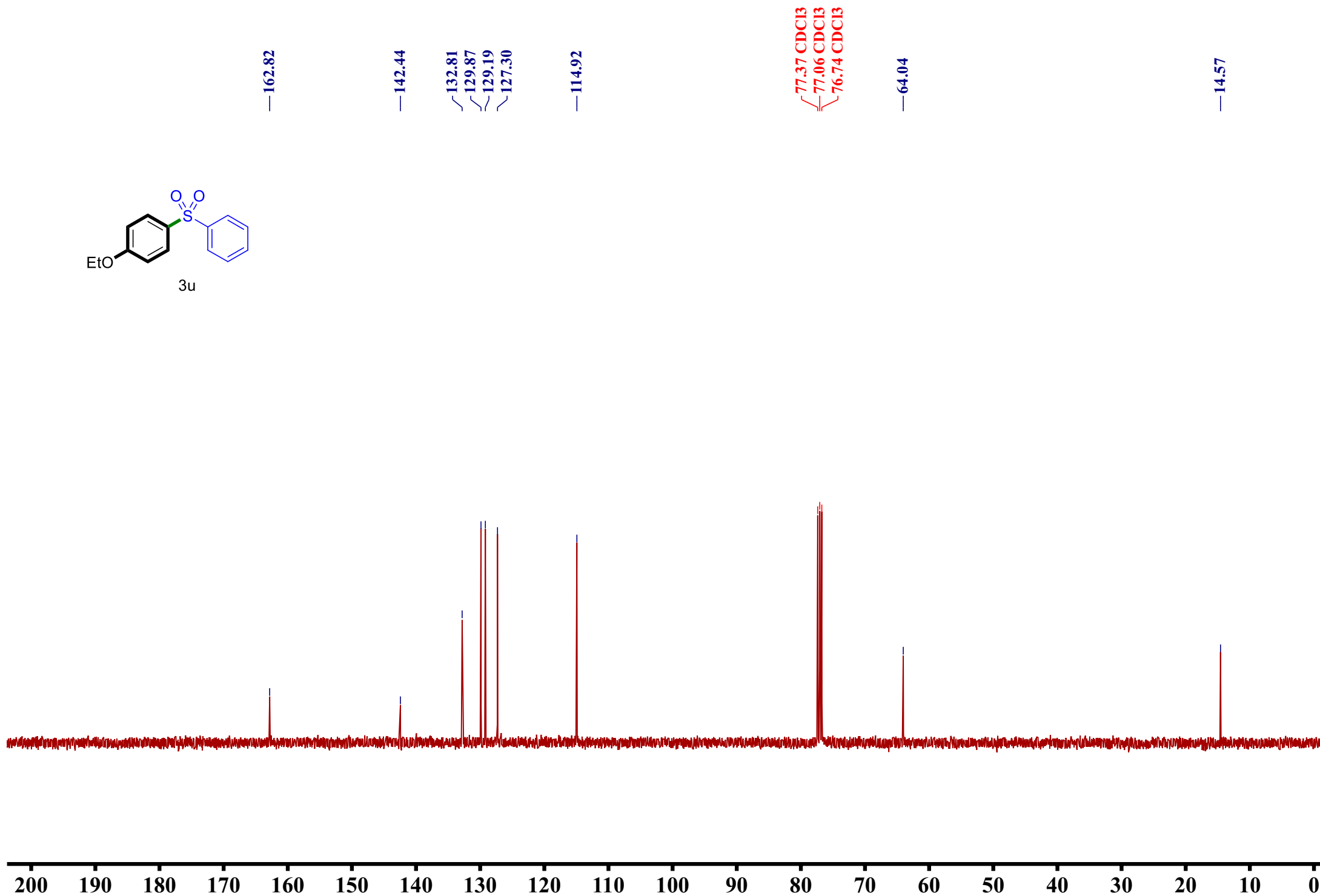
55.68

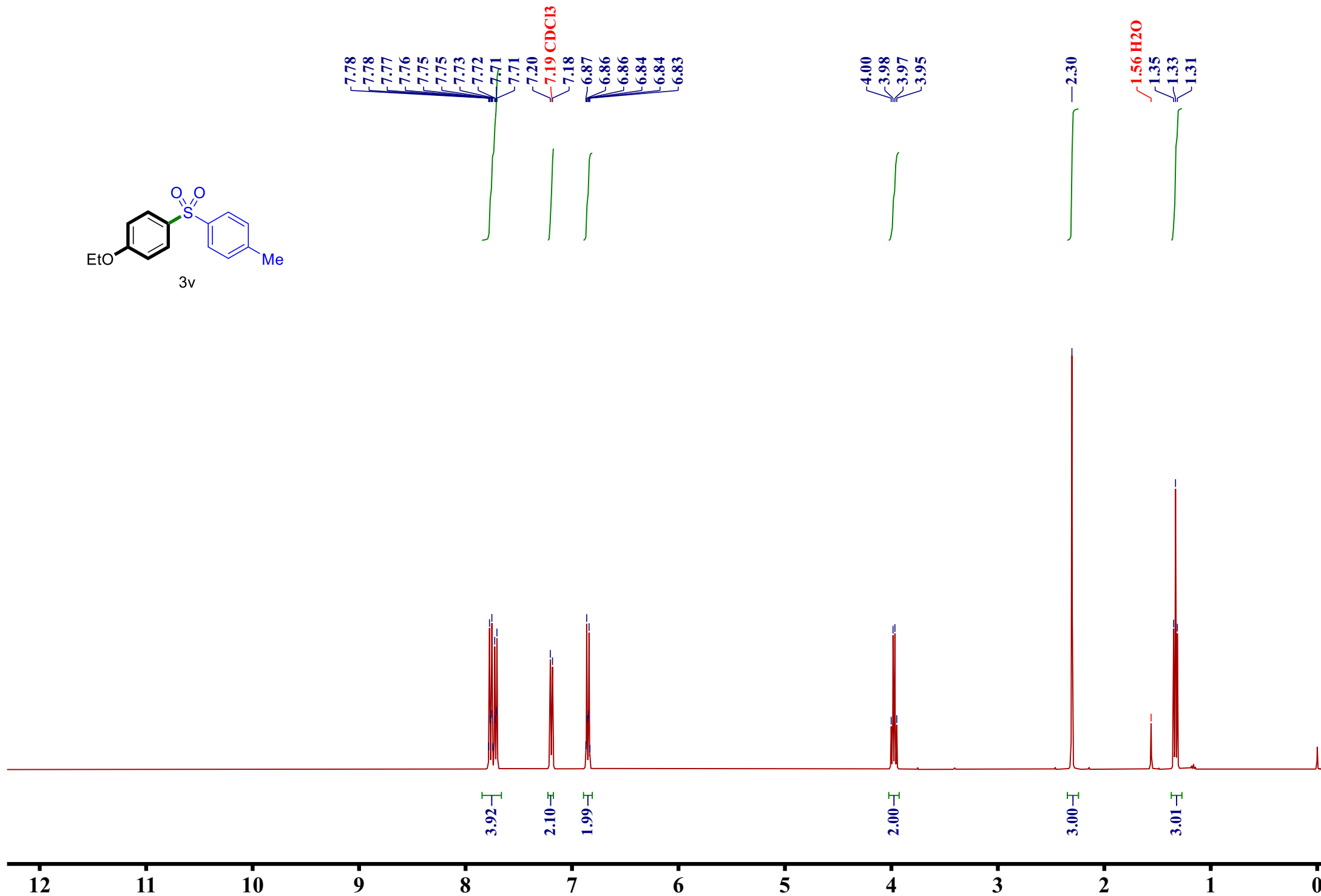
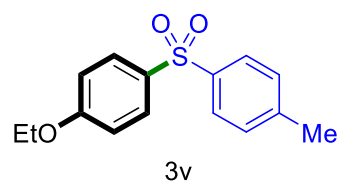


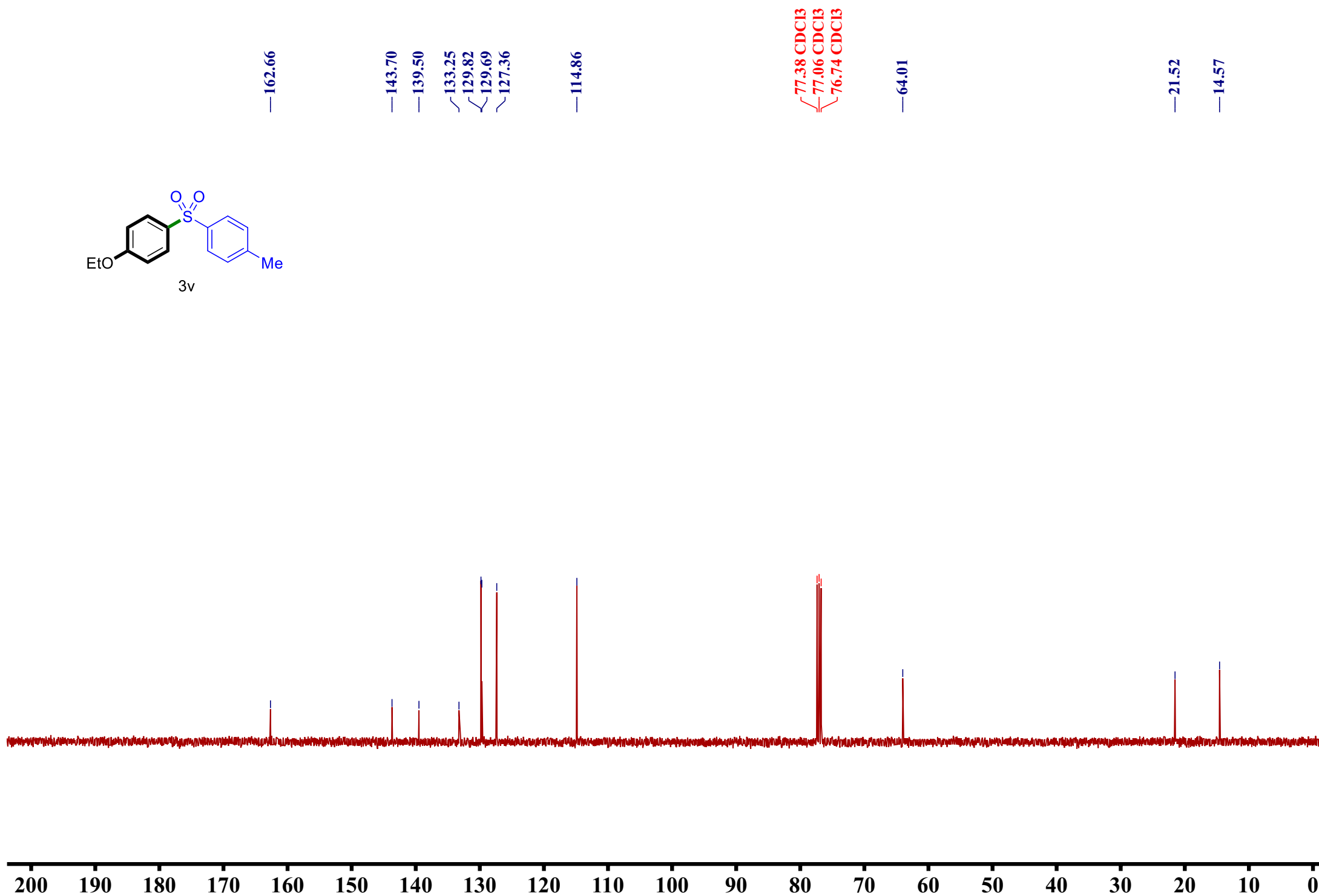
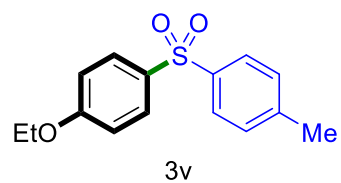


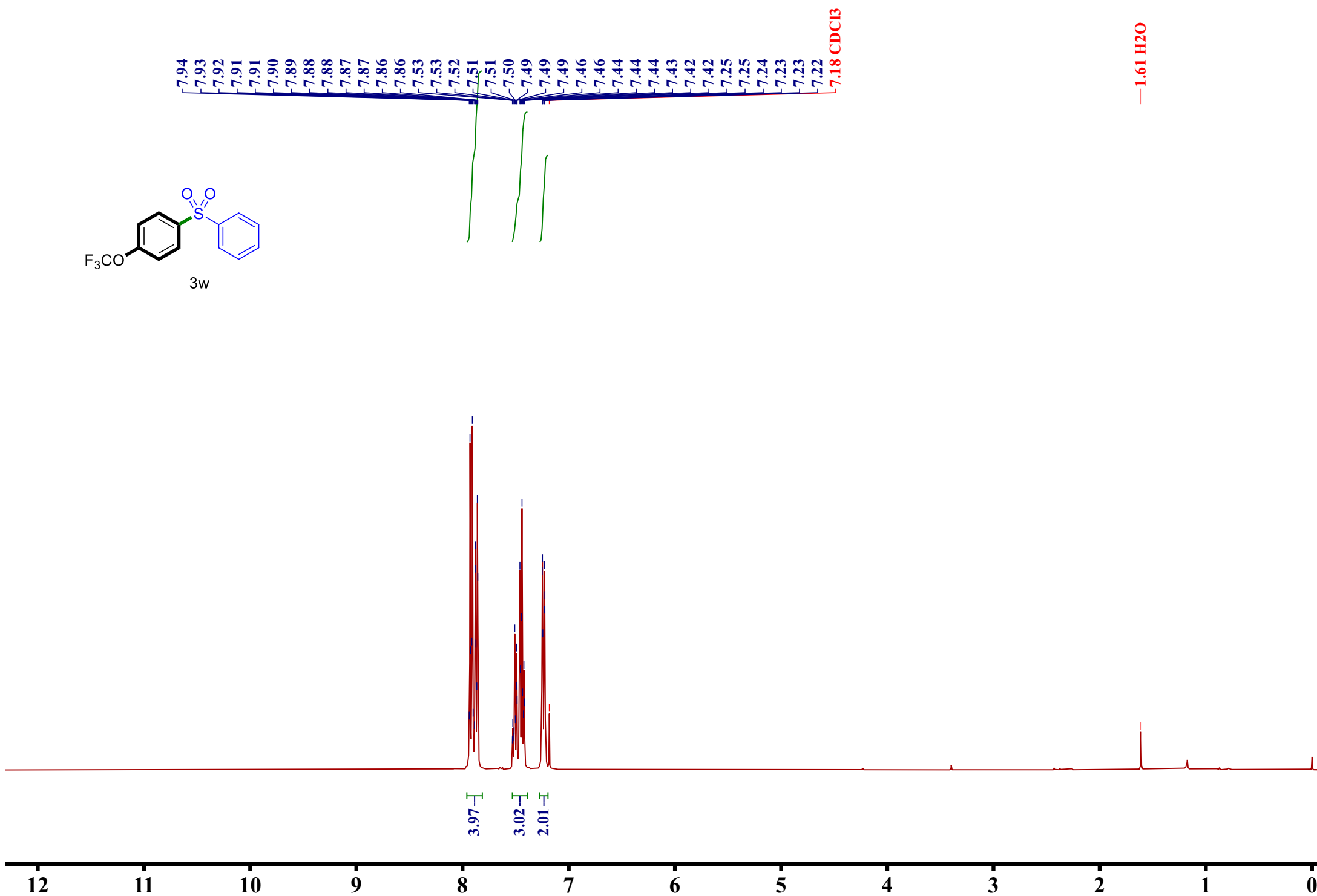
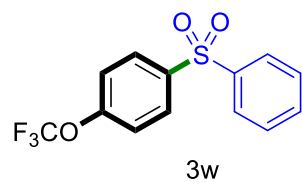


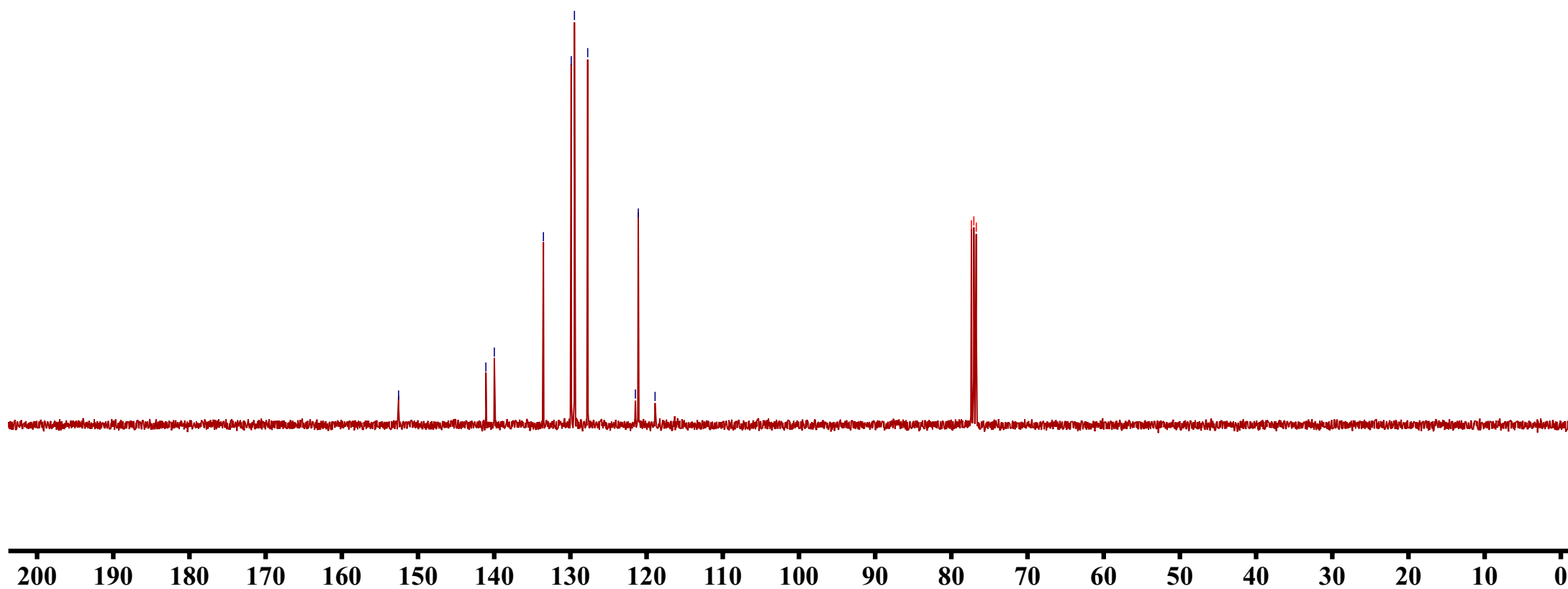
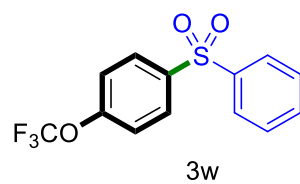
3u

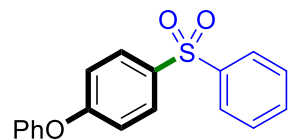




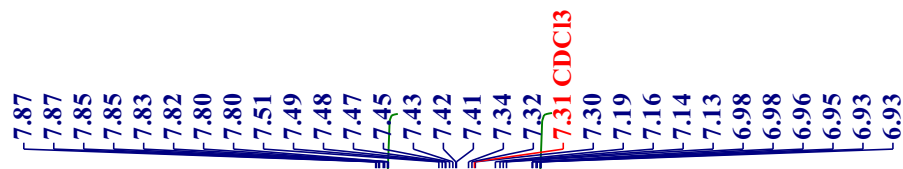




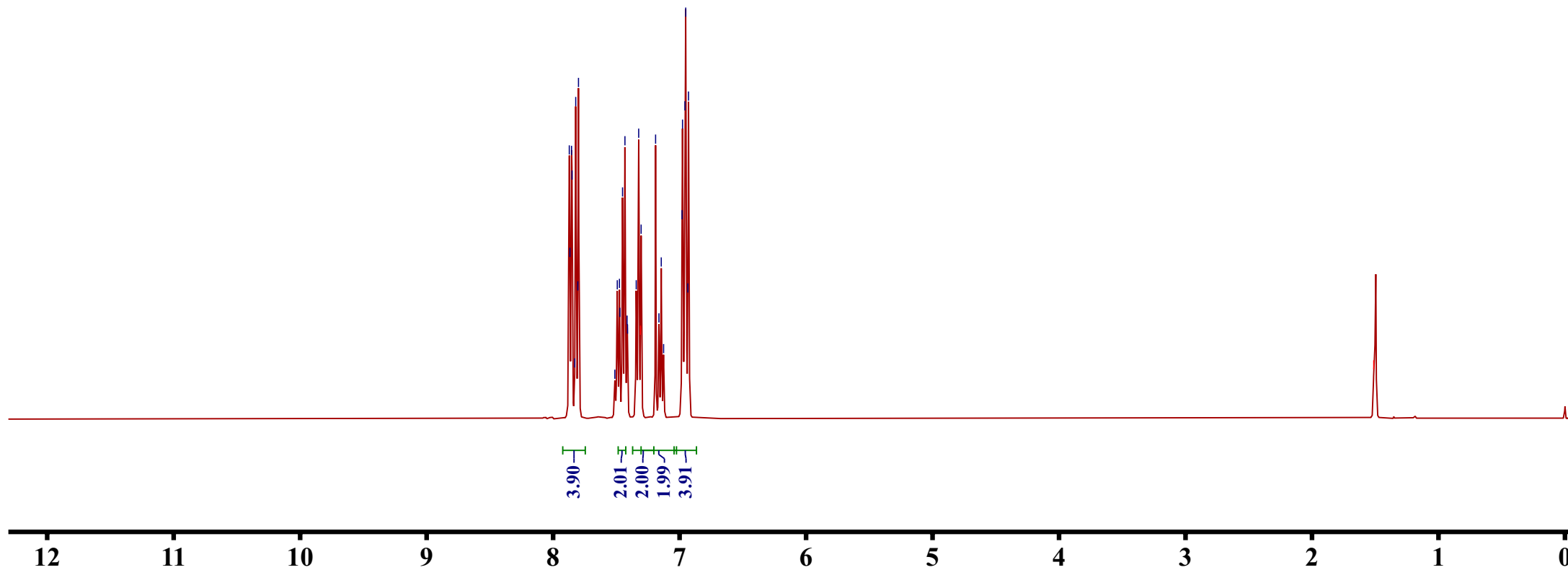


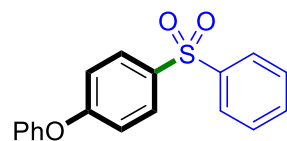


3x

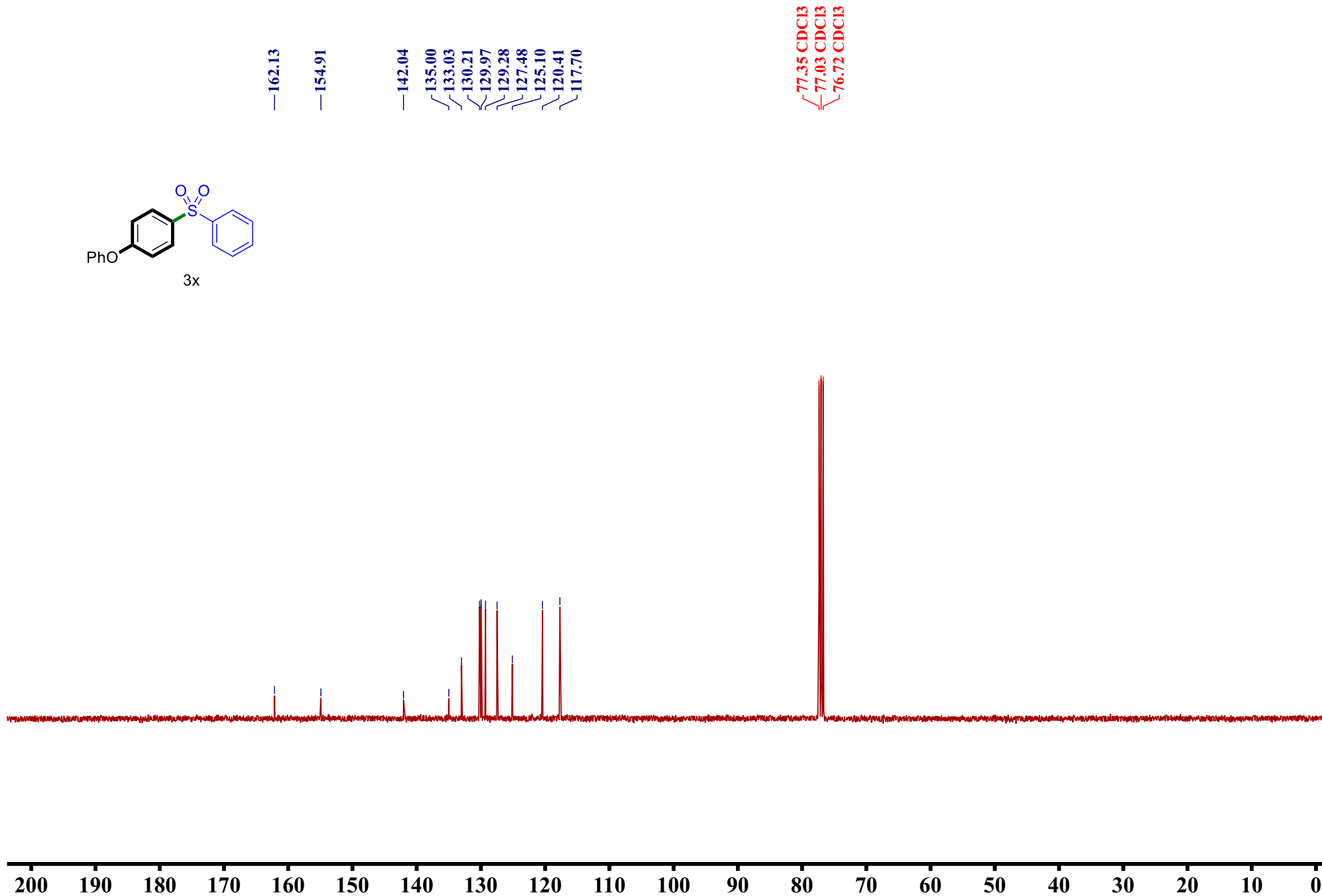


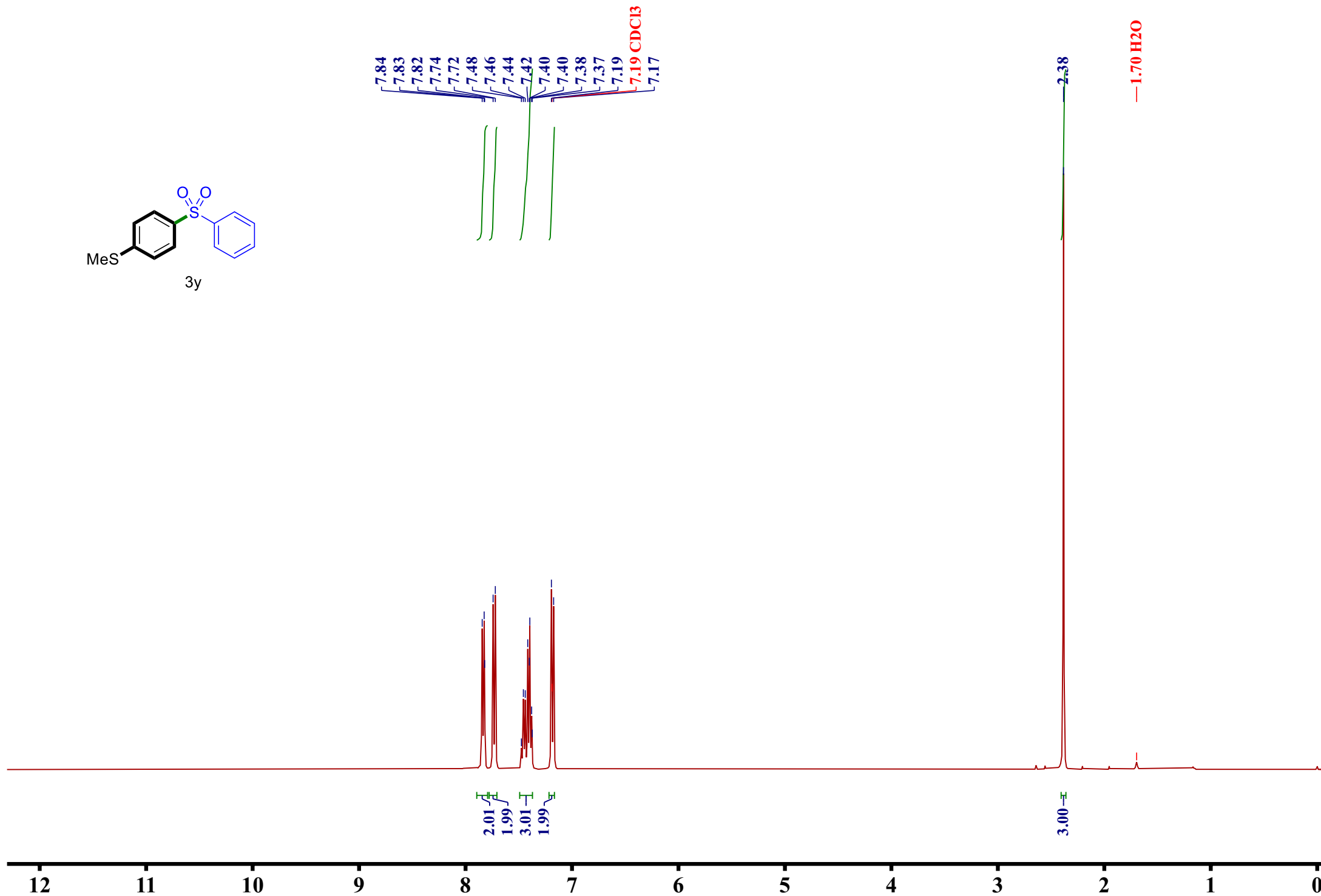
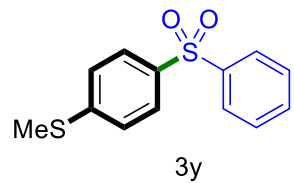
— 1.51 H2O

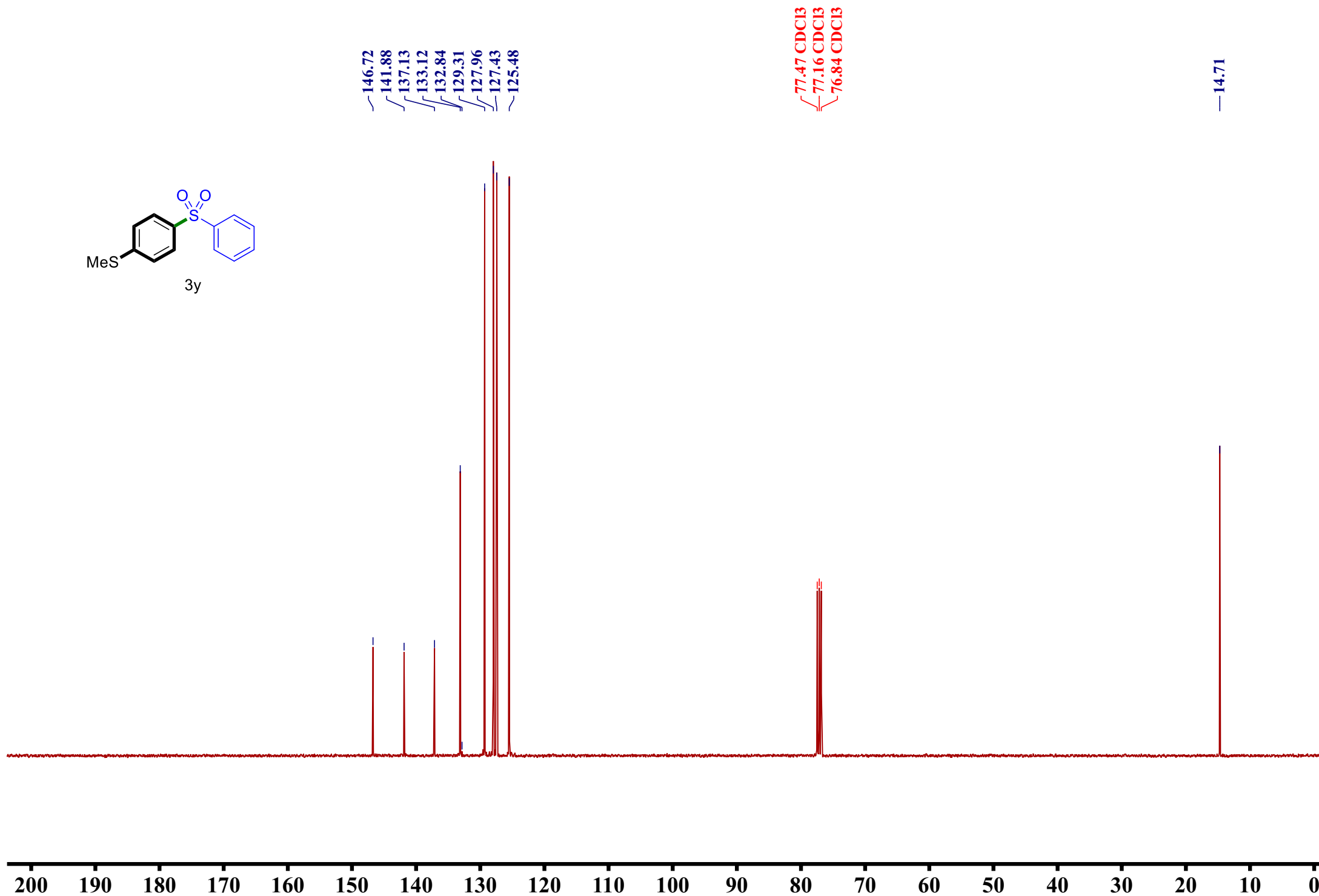
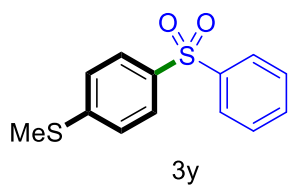


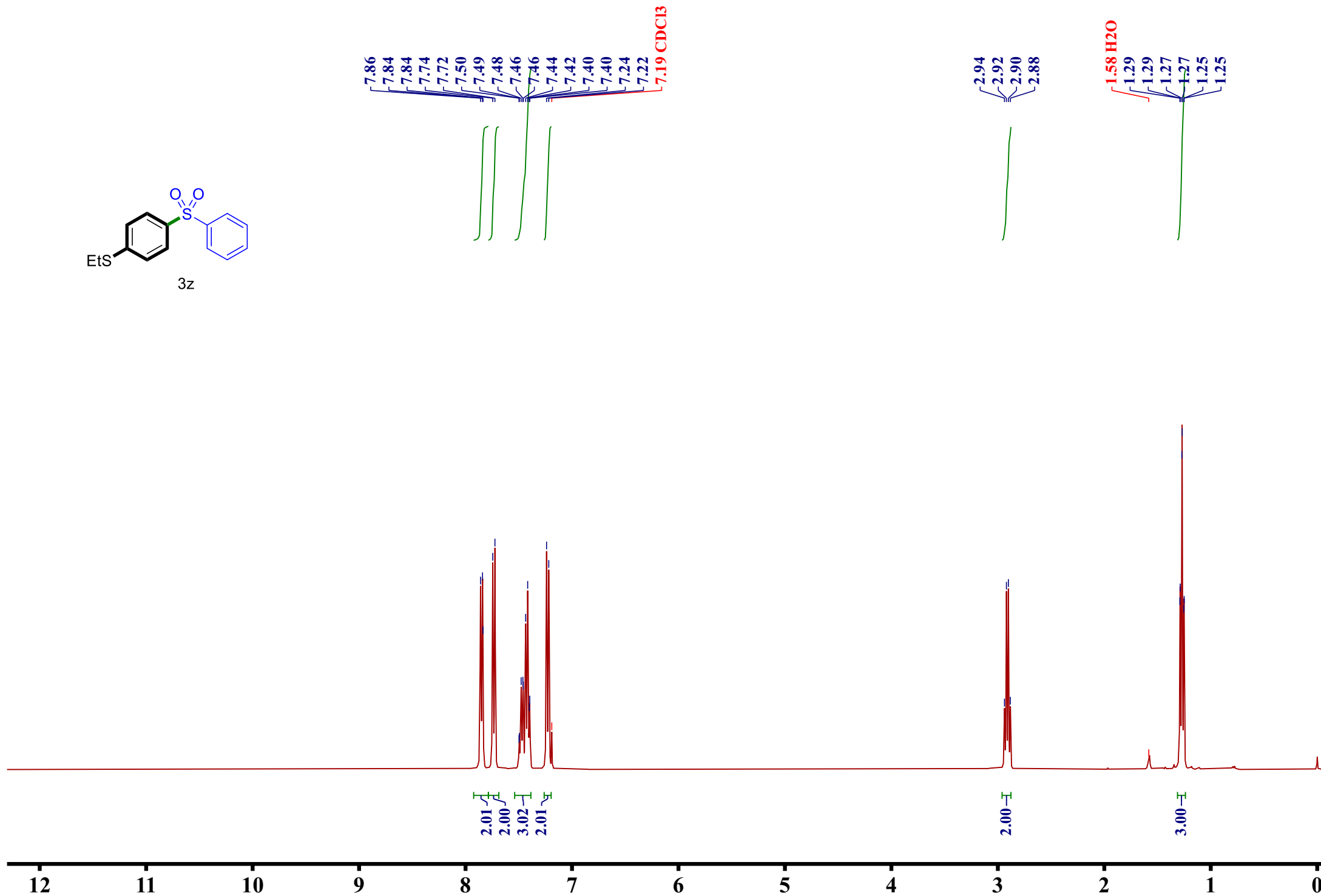
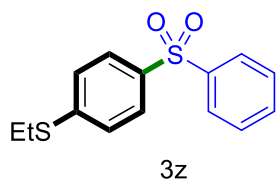


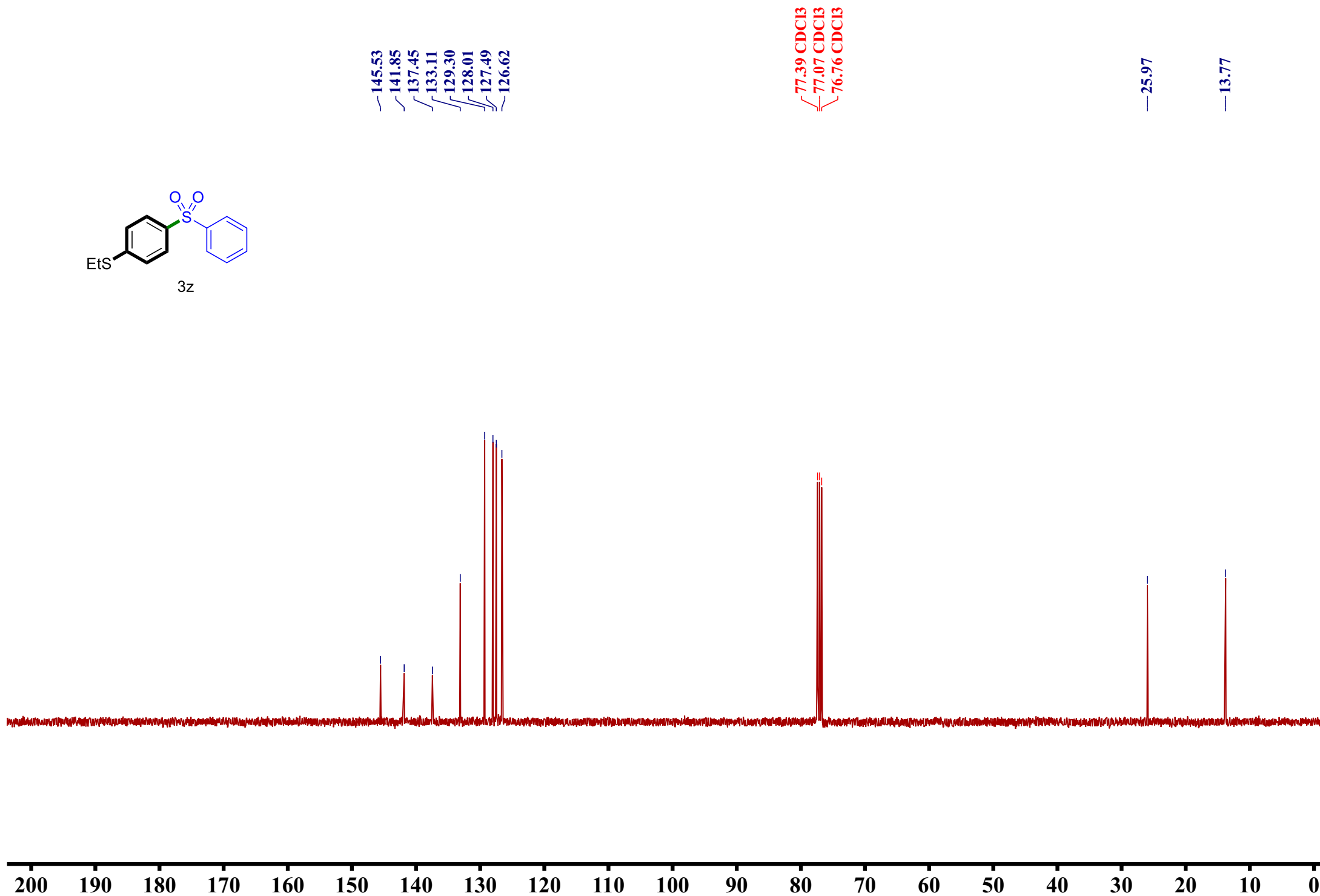
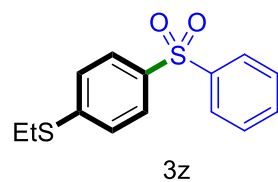
3x

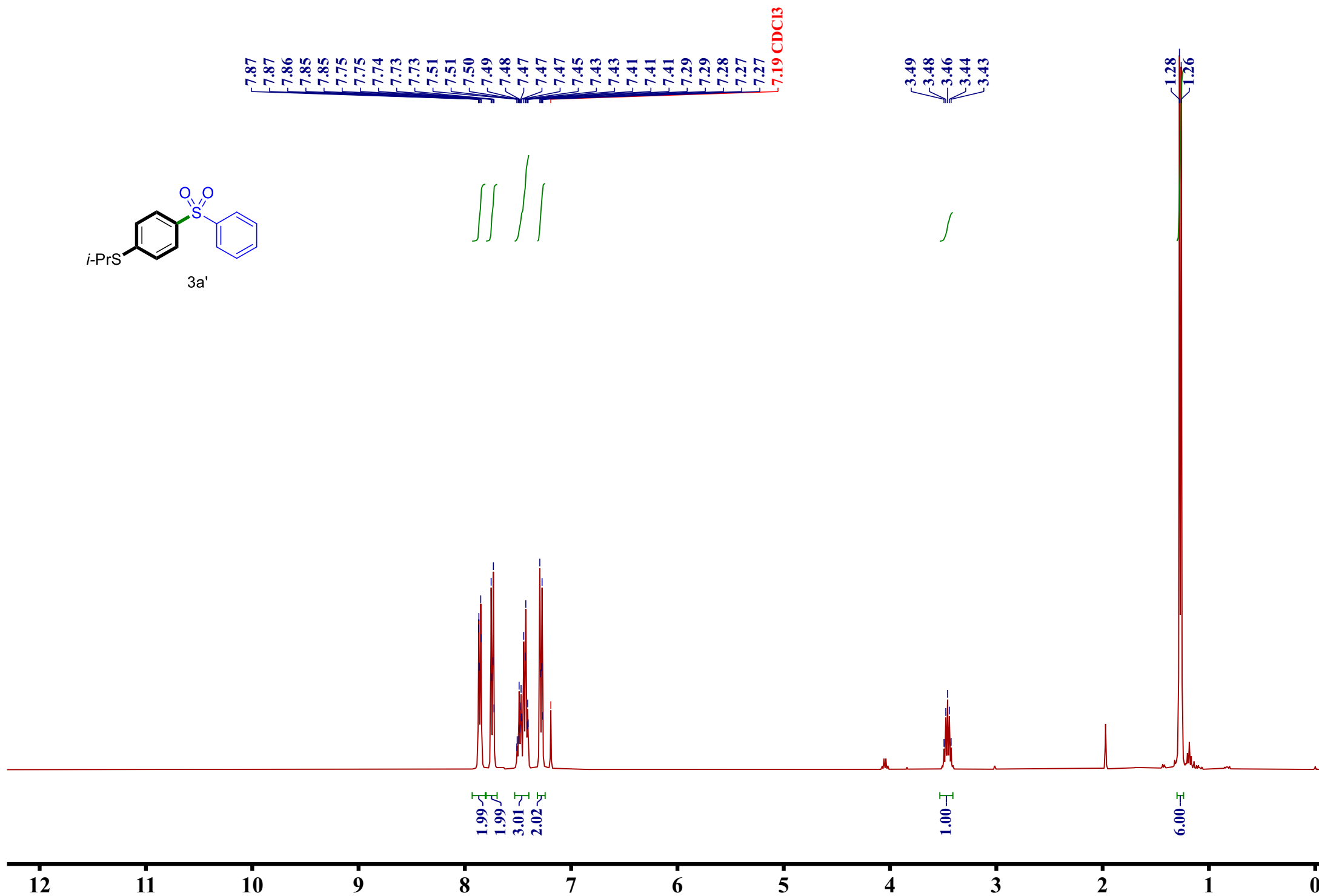
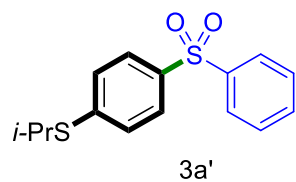


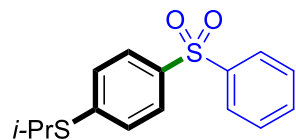




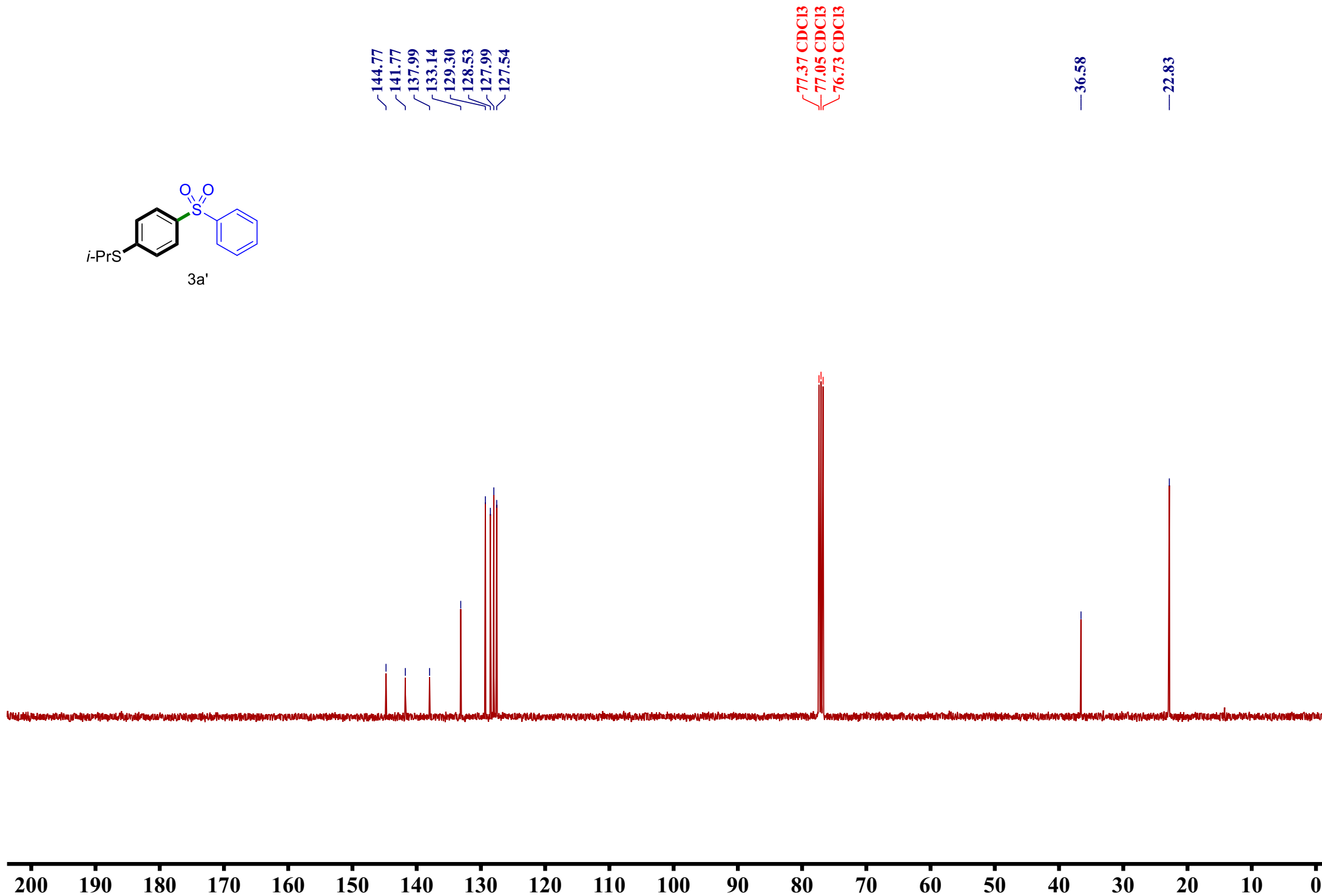


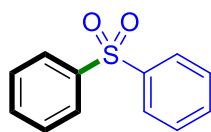




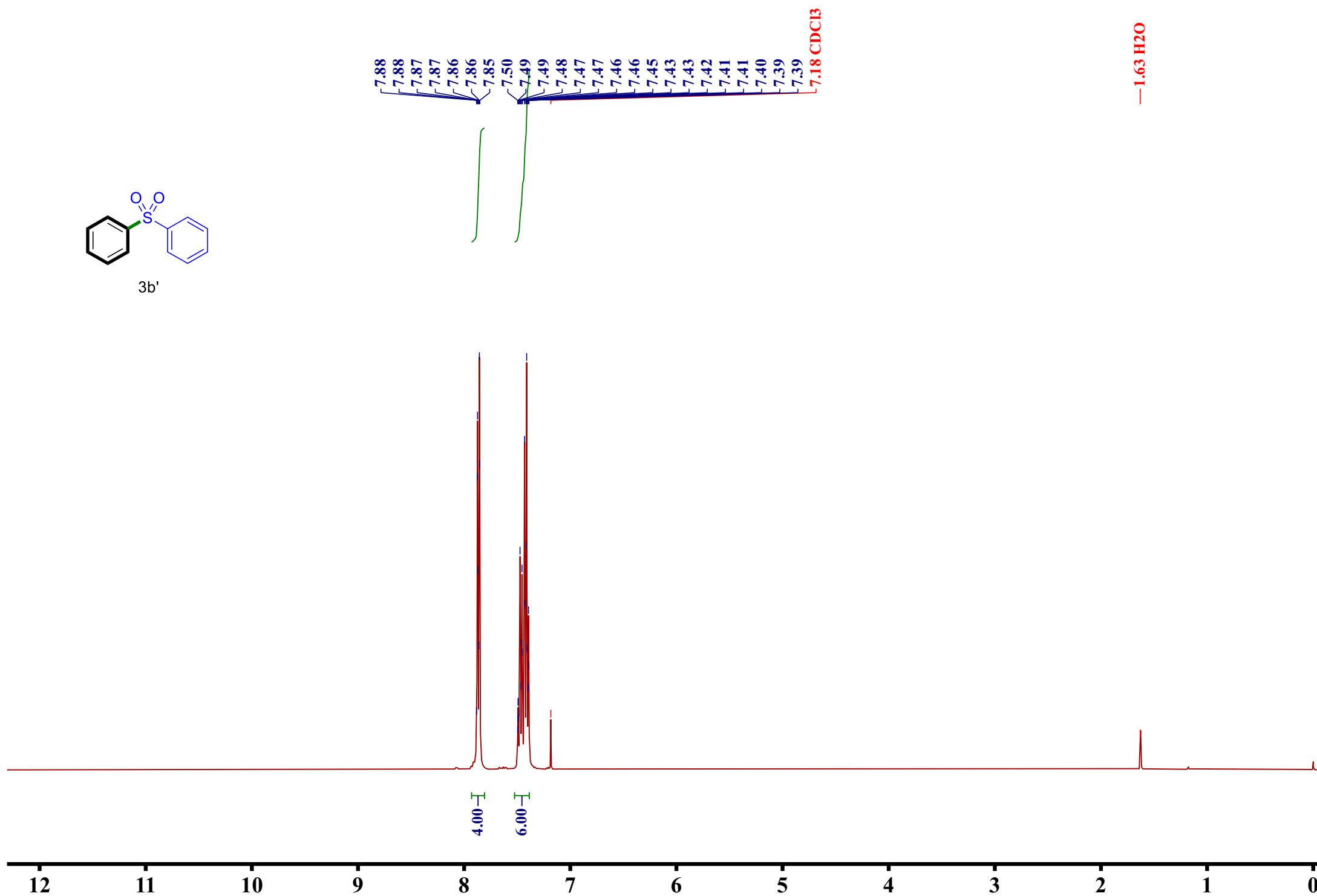


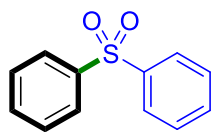
3a'



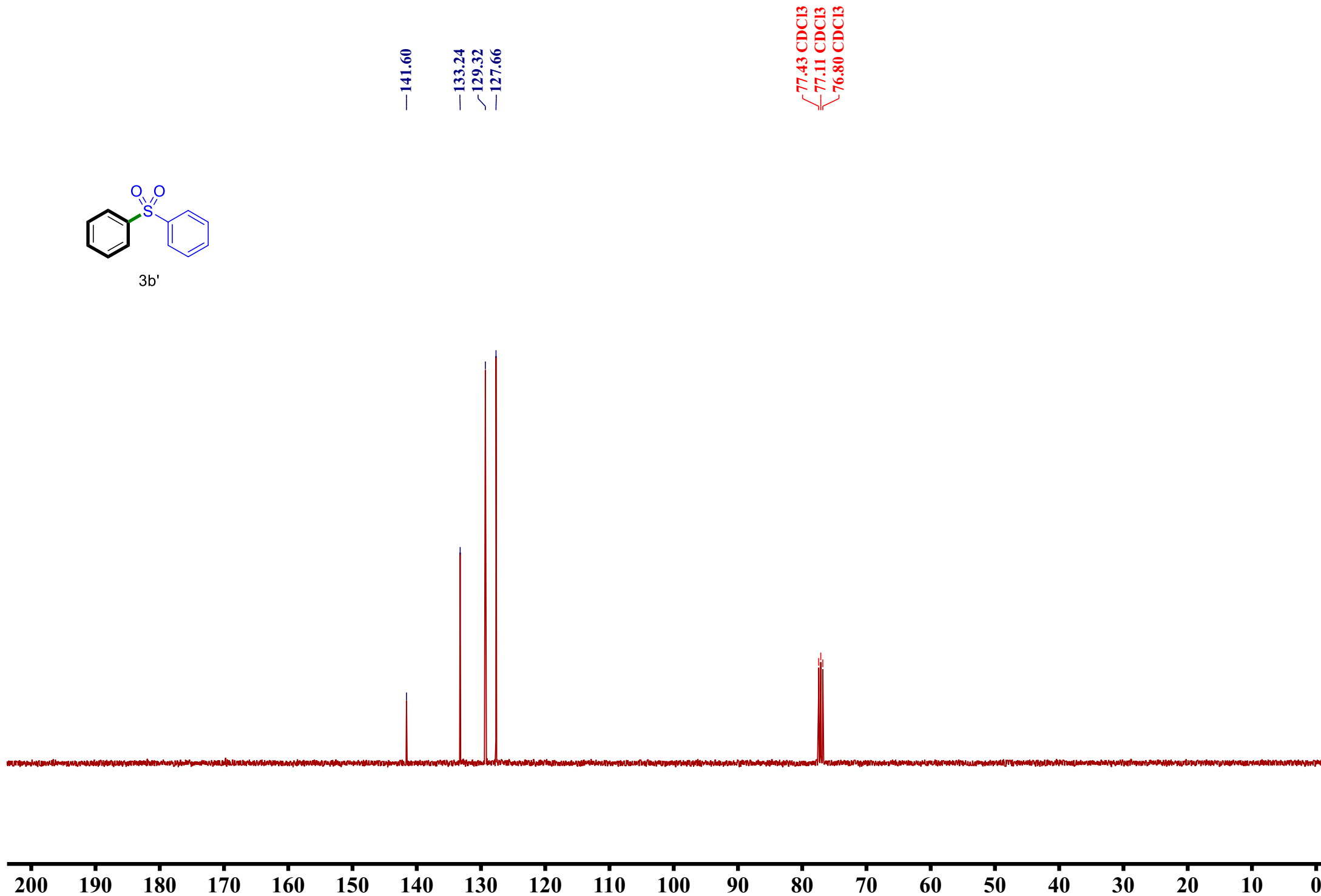


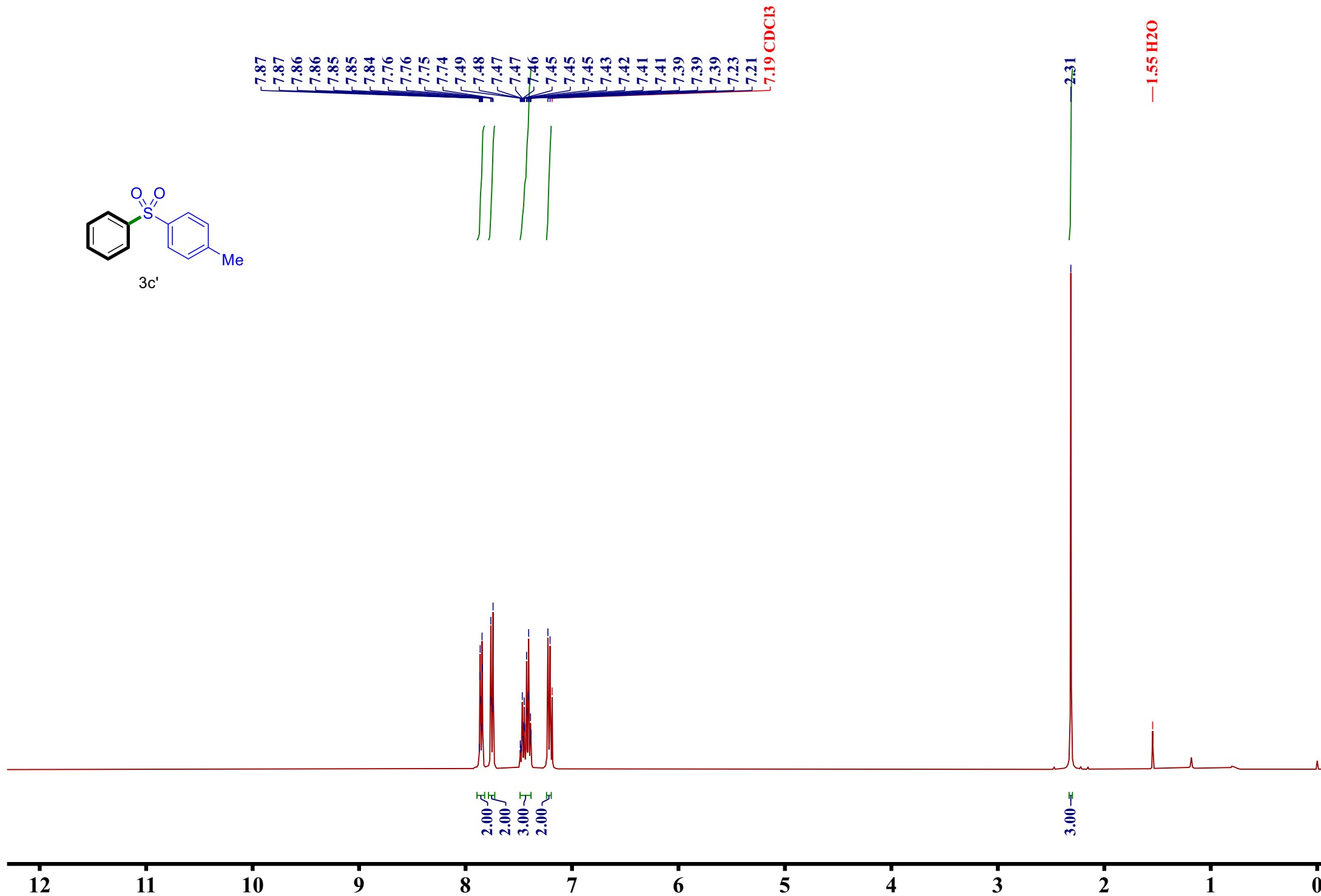
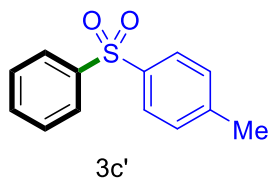
3b'

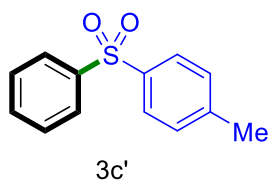




3b'



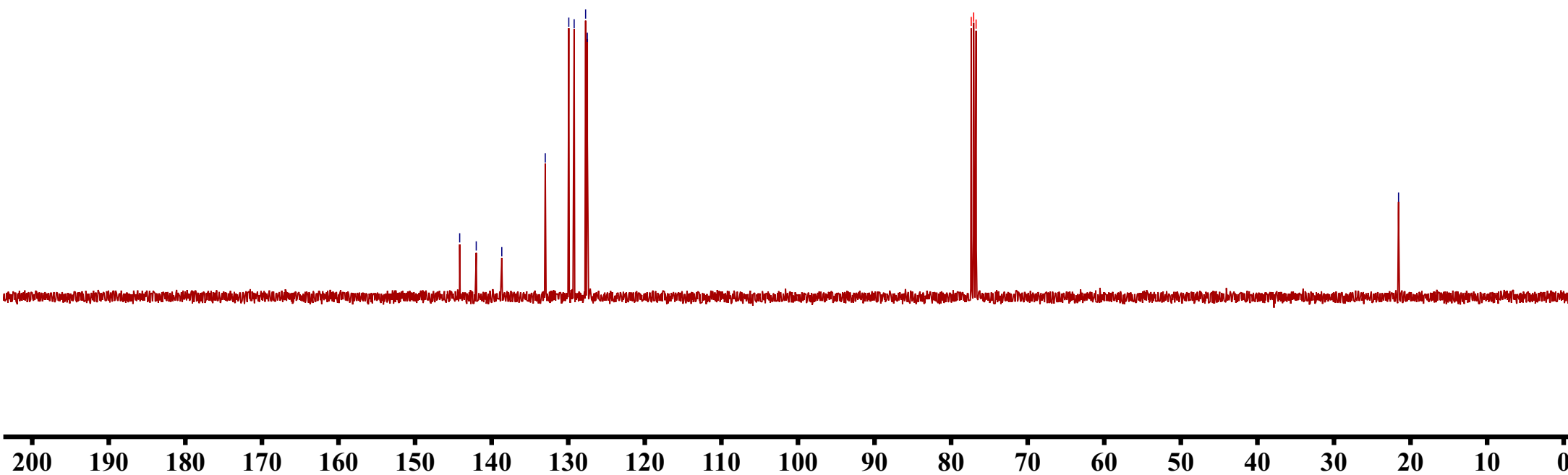


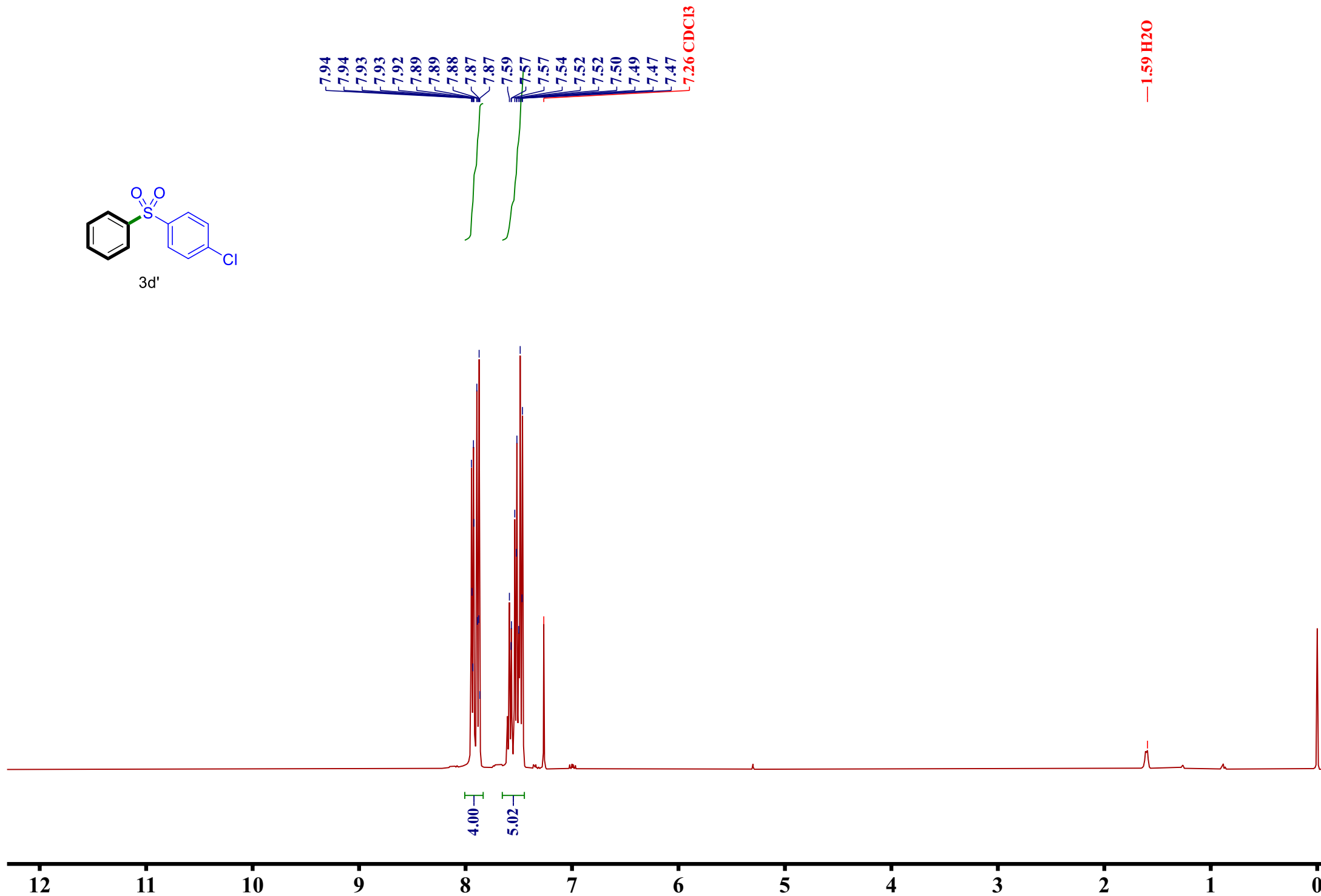
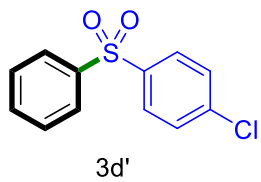


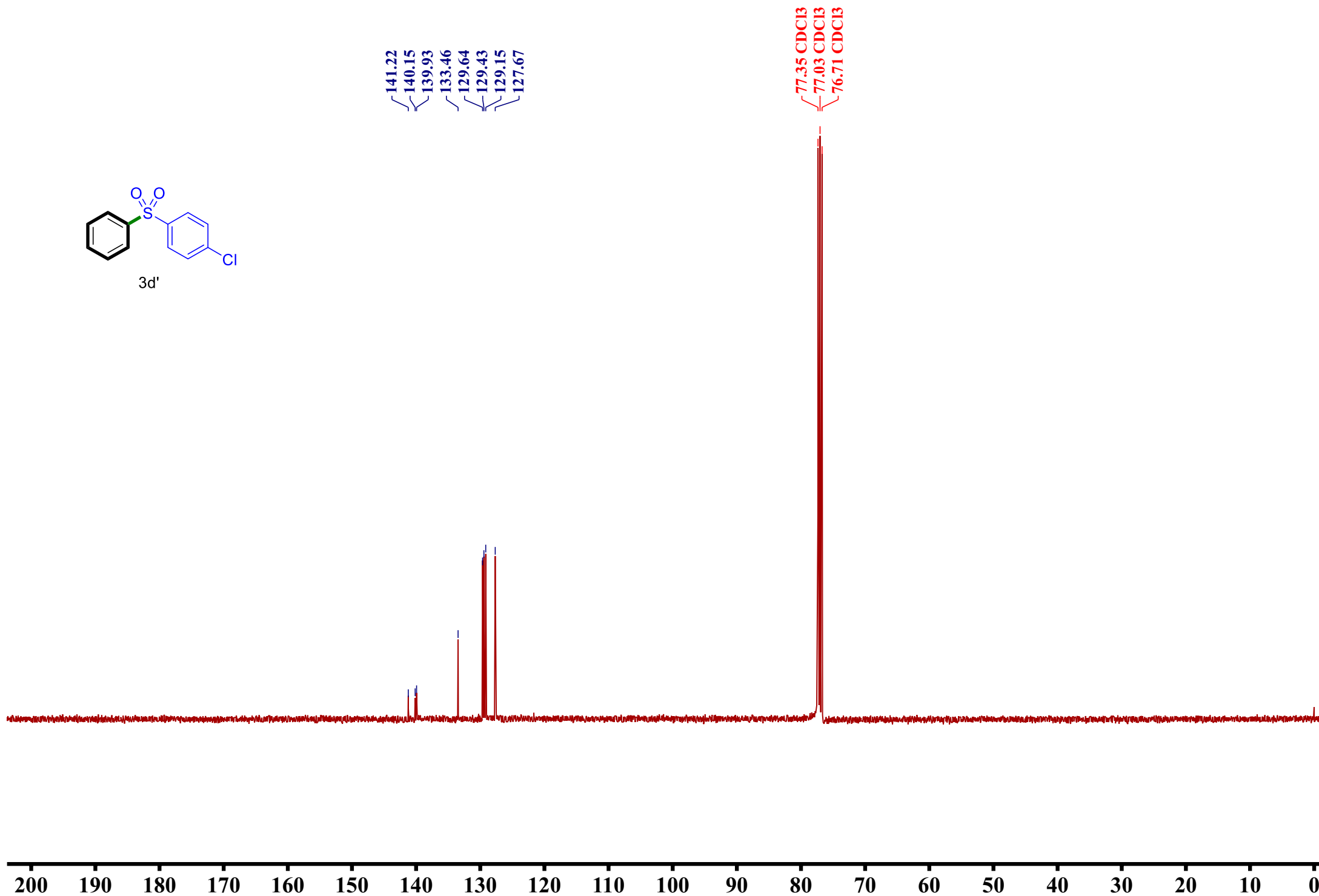
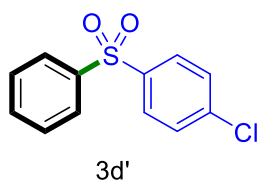
144.17
142.01
138.68
133.00
129.93
129.23
127.73
127.51

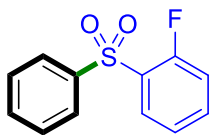
77.37 CDCl₃
77.05 CDCl₃
76.74 CDCl₃

21.57

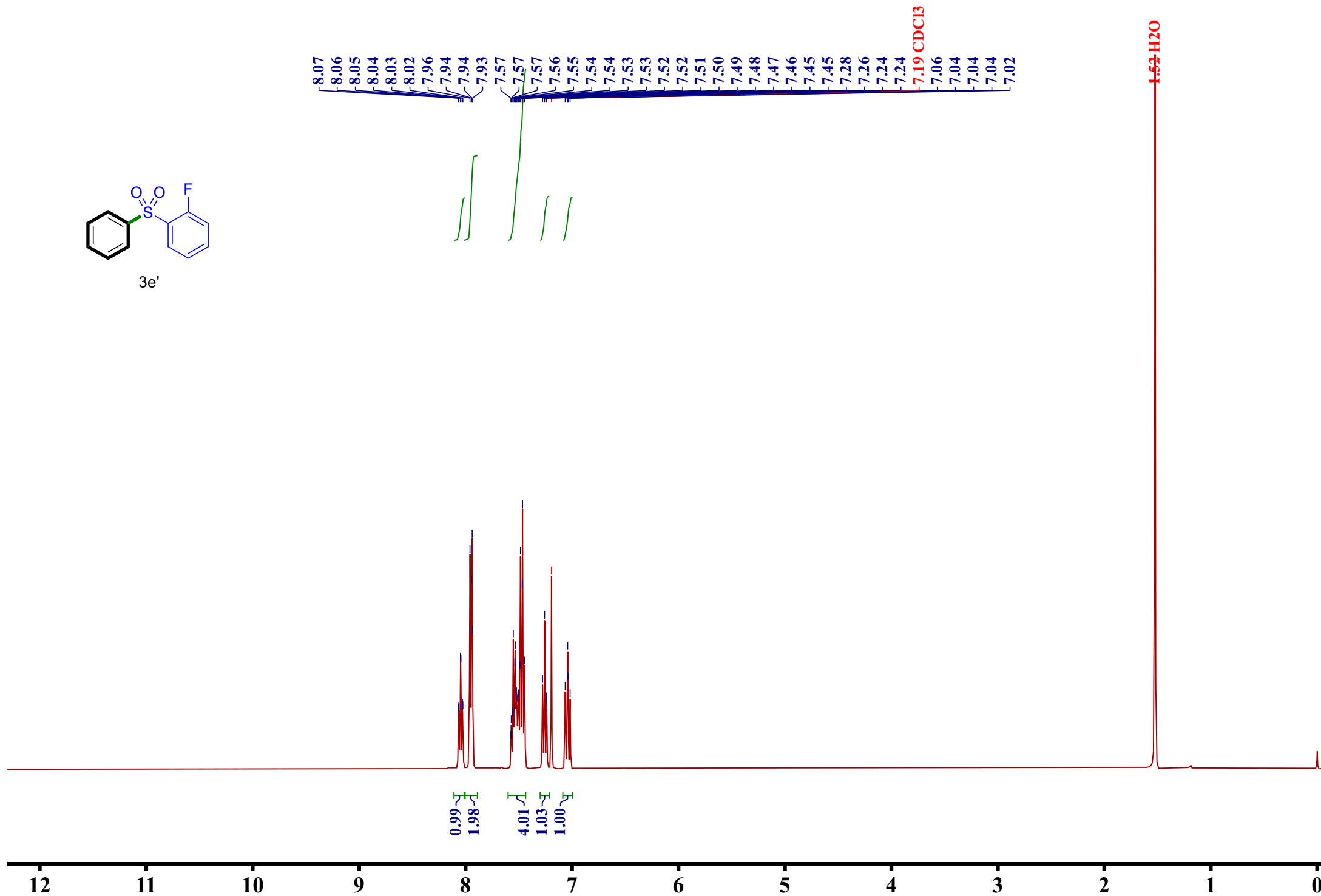


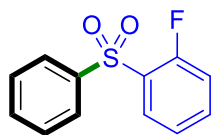




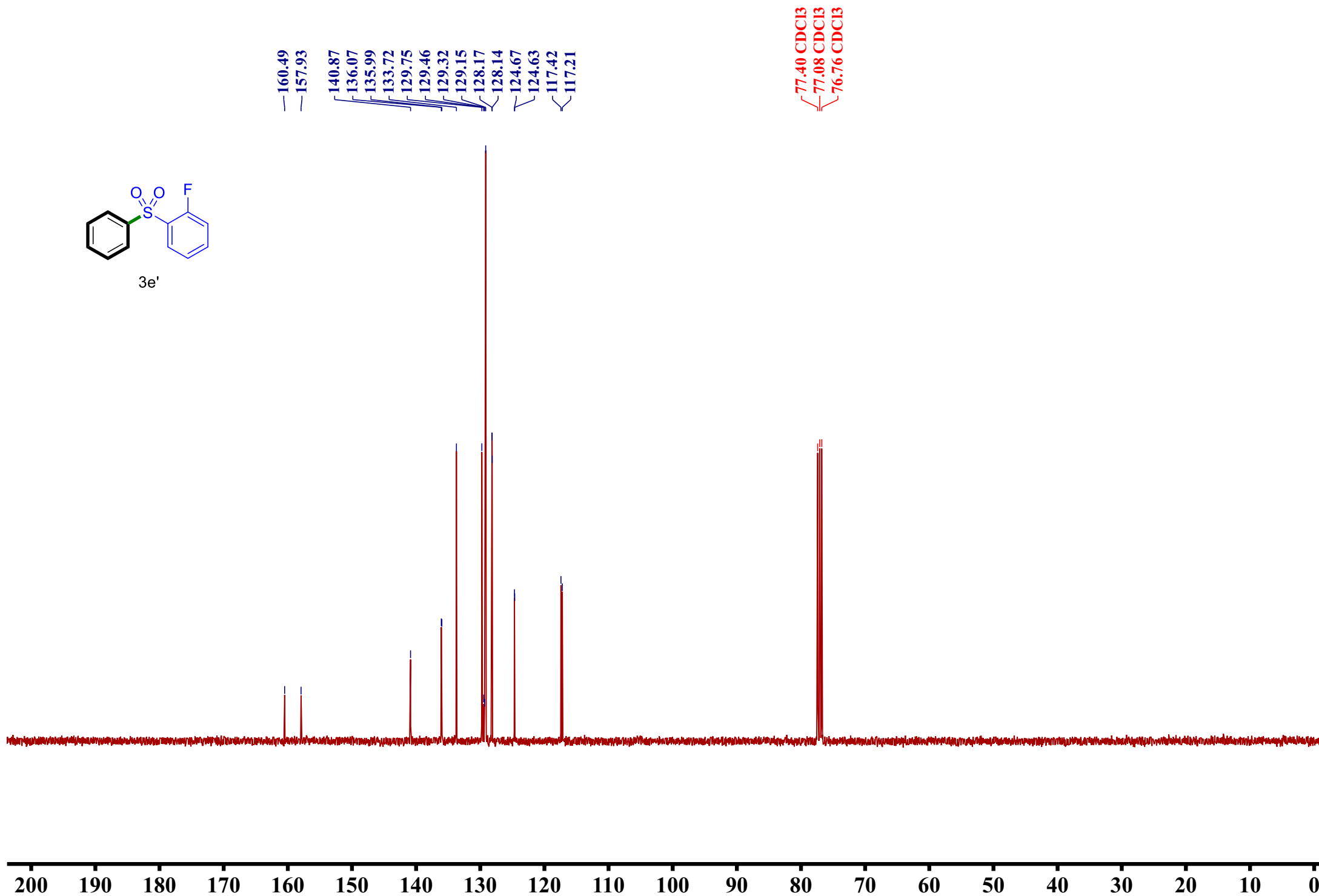


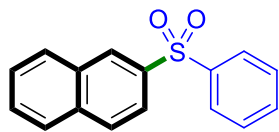
3e'



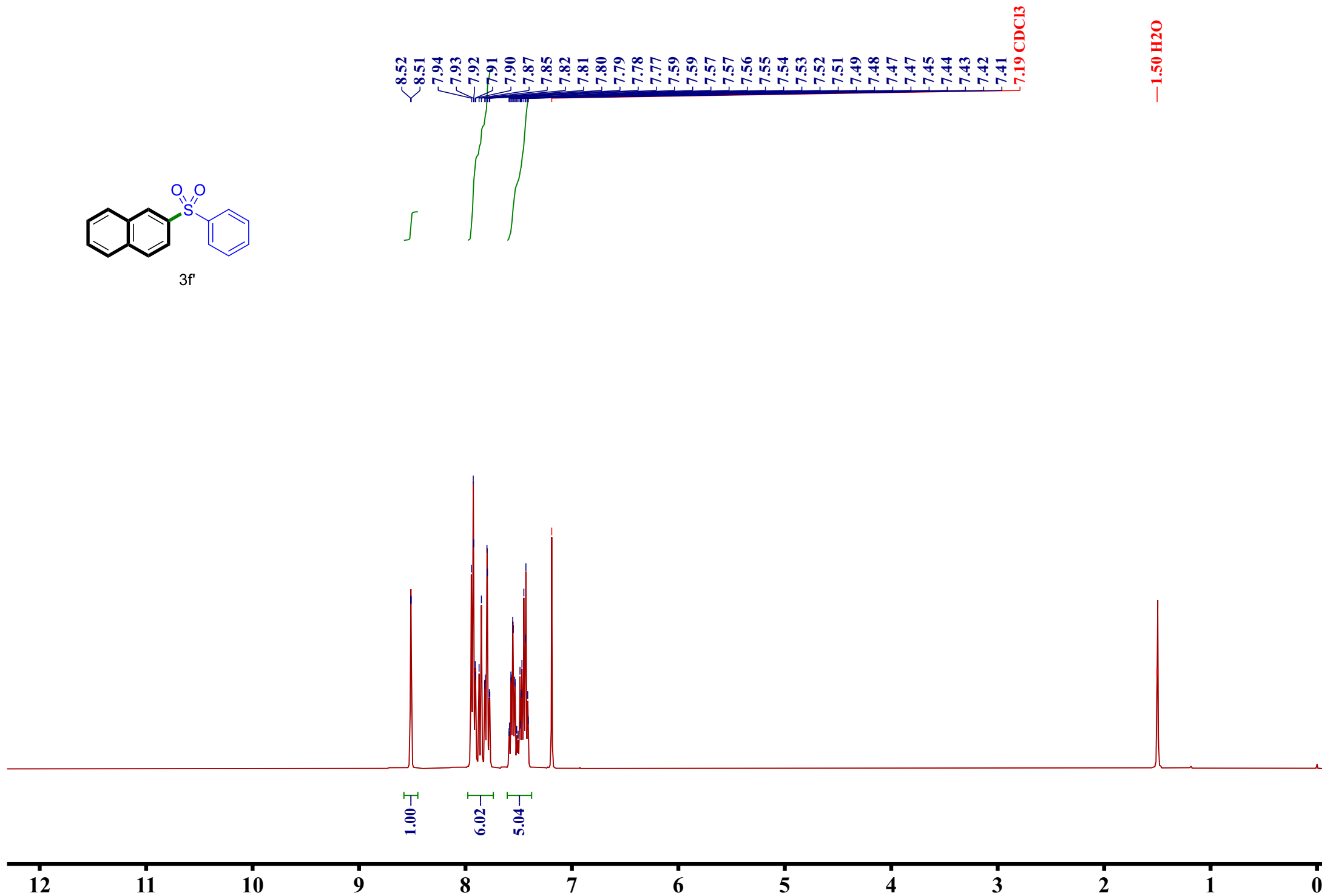


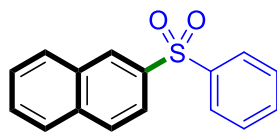
3e'





3f



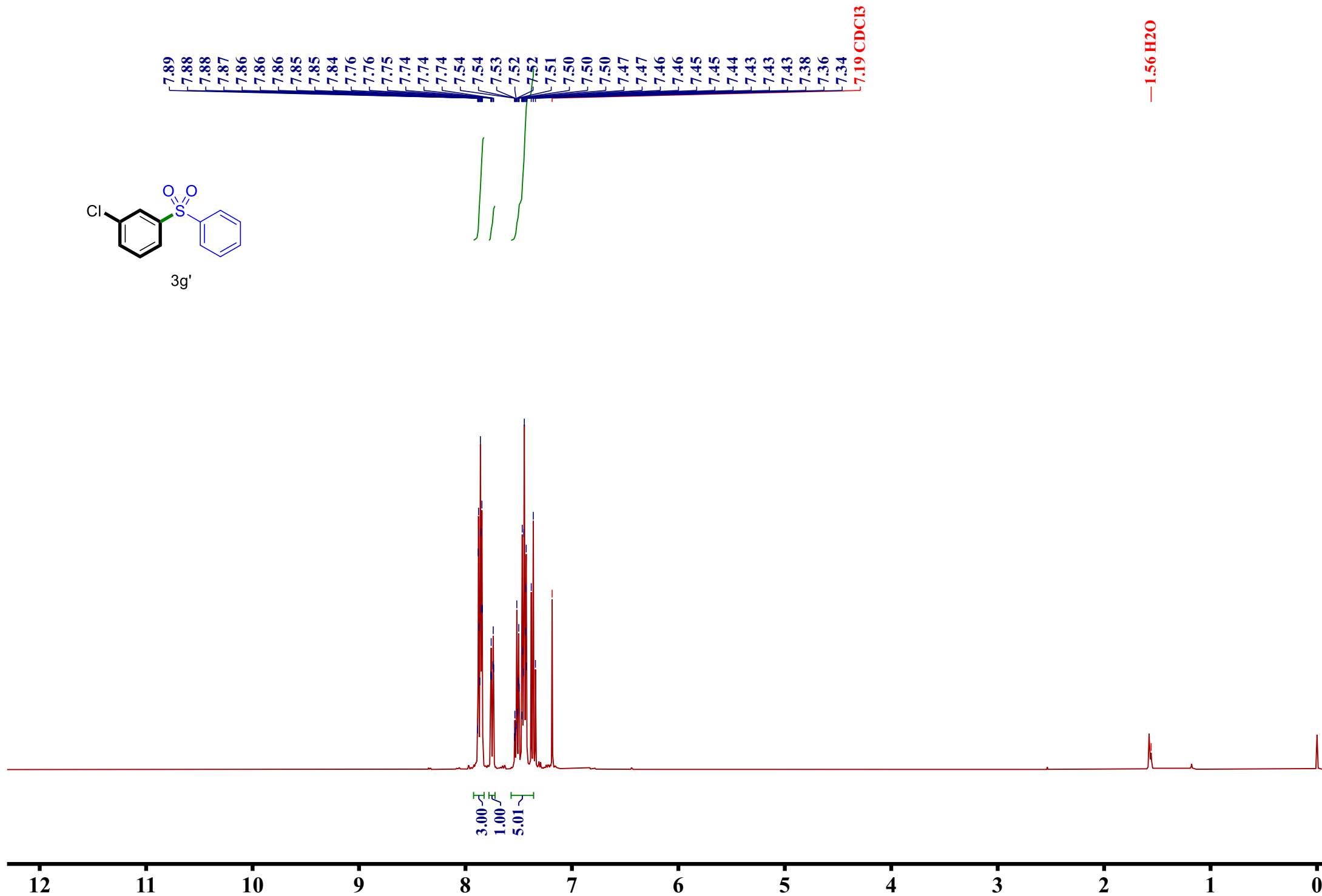
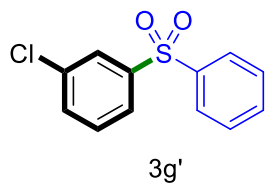


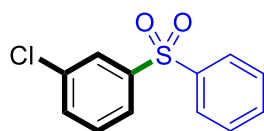
3f

141.65
138.41
135.03
133.19
132.23
129.67
129.43
129.31
129.17
129.12
127.94
127.73
127.66
122.70

77.35 CDC13
77.00 CDC13
76.71 CDC13

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

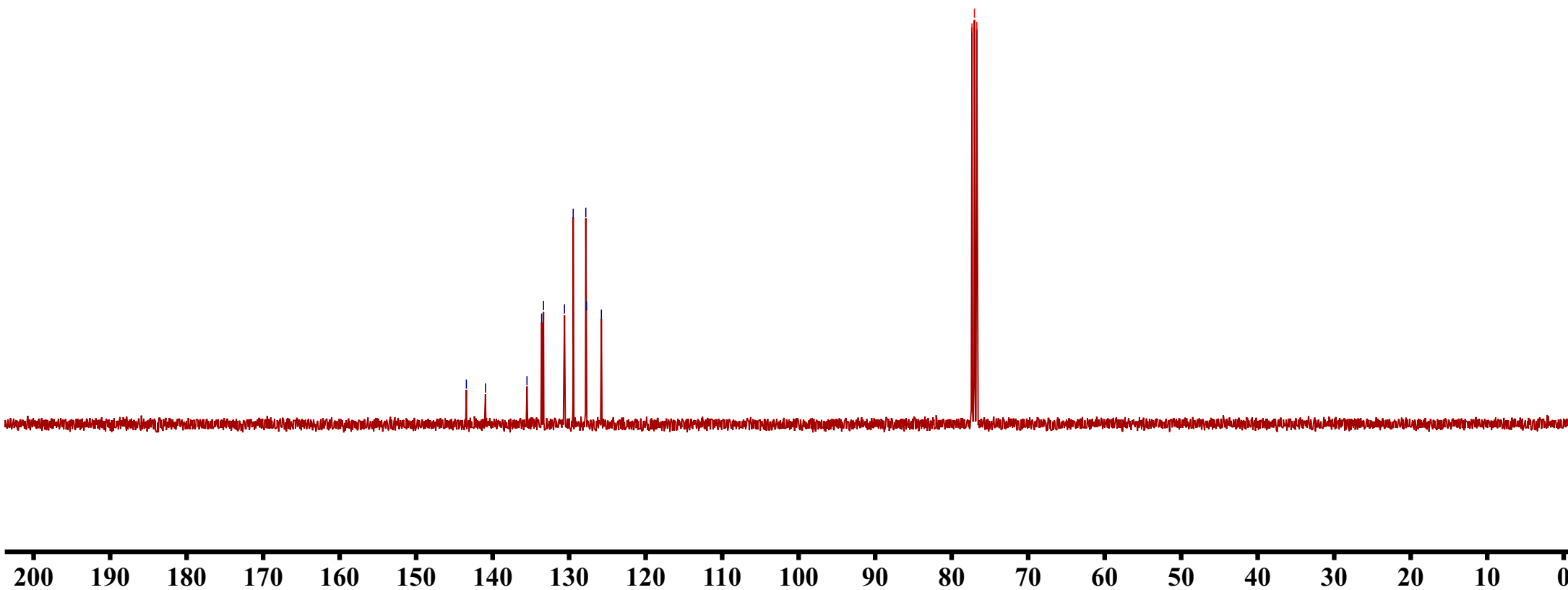


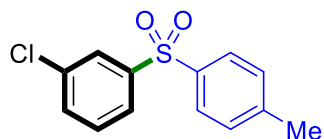


3g'

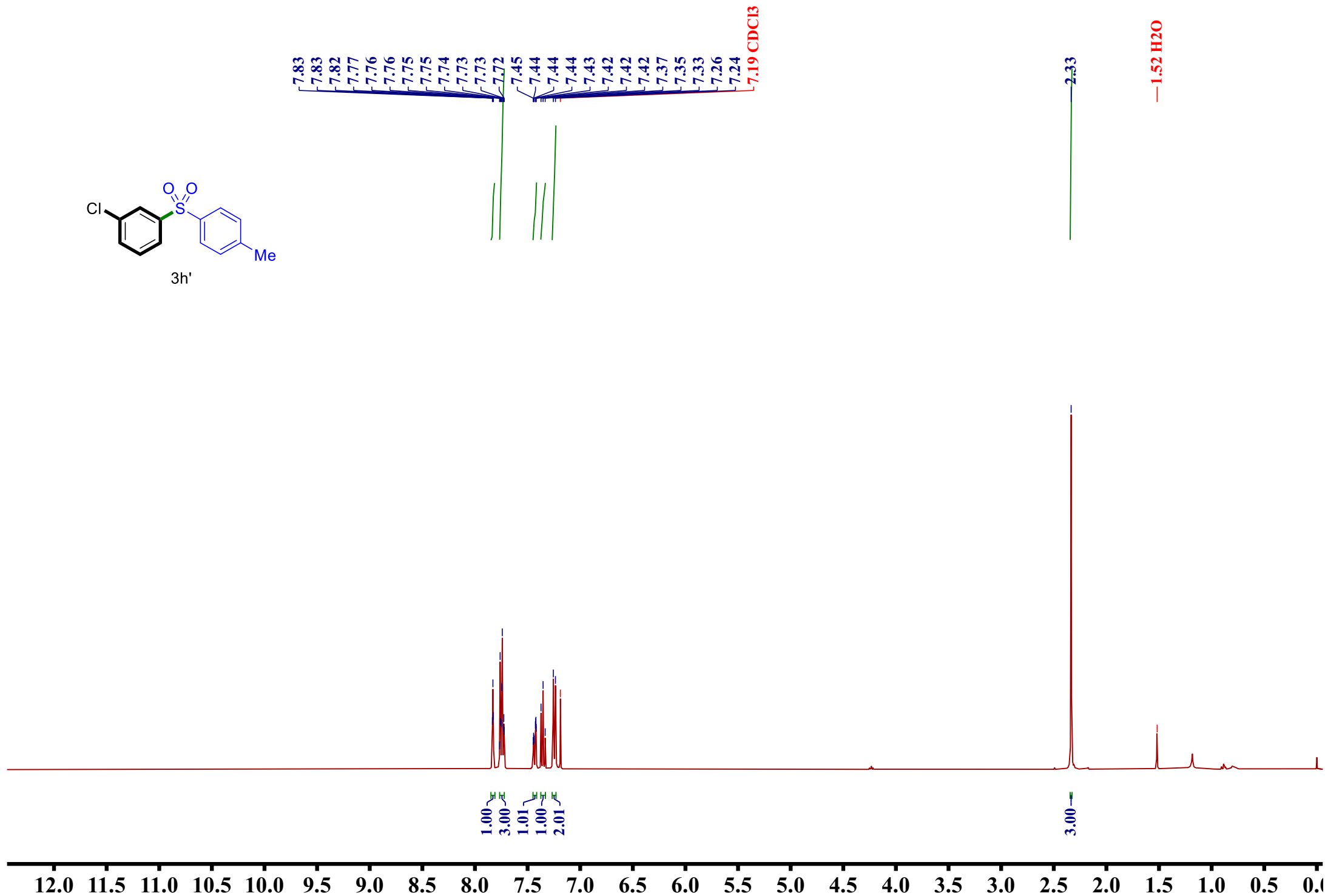
143.43
140.94
135.51
133.59
133.35
130.61
129.47
127.82
127.73
125.79

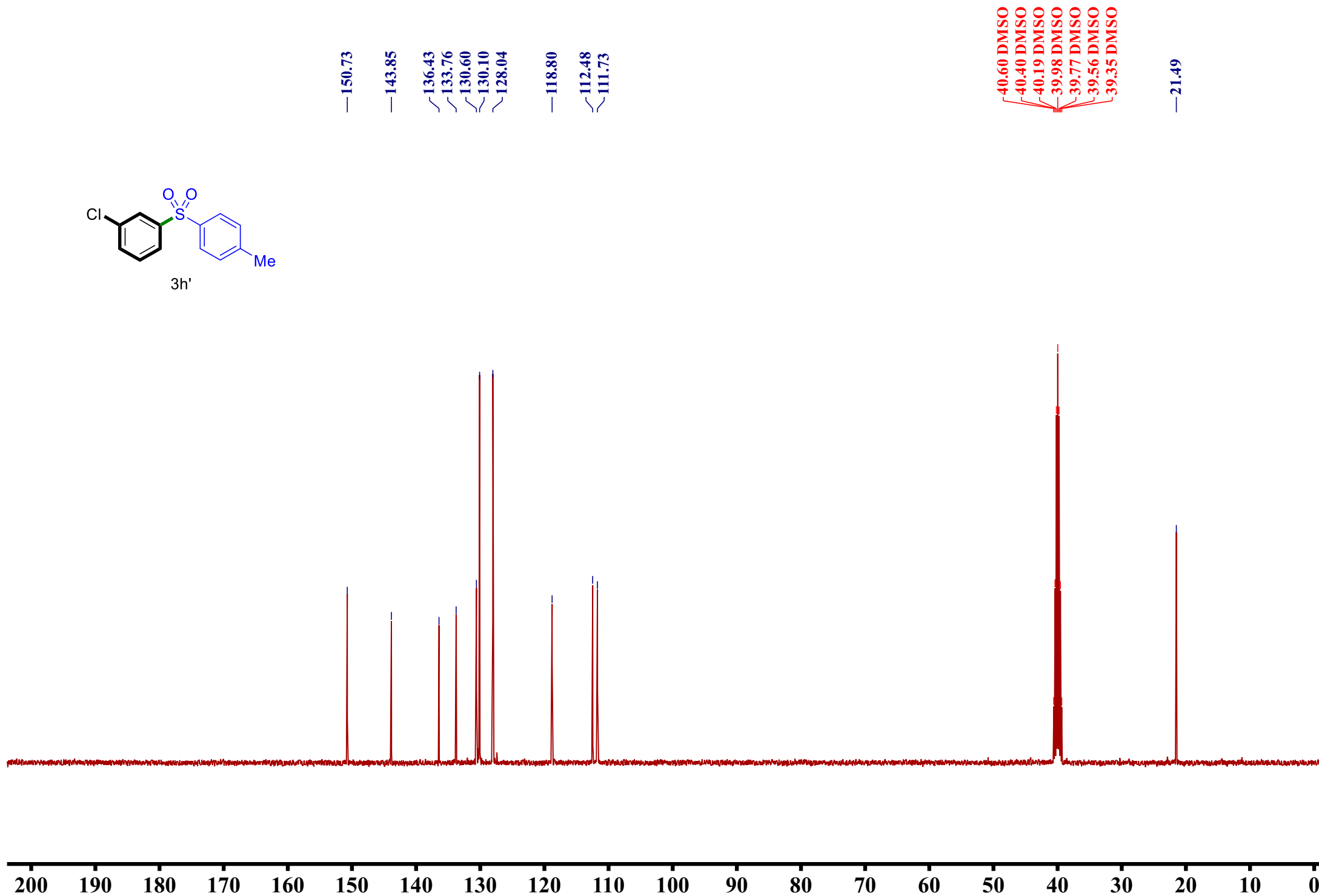
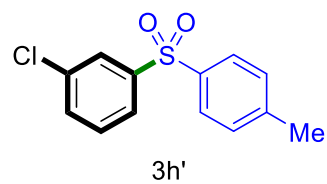
77.35 CDC13
77.03 CDC13
76.71 CDC13

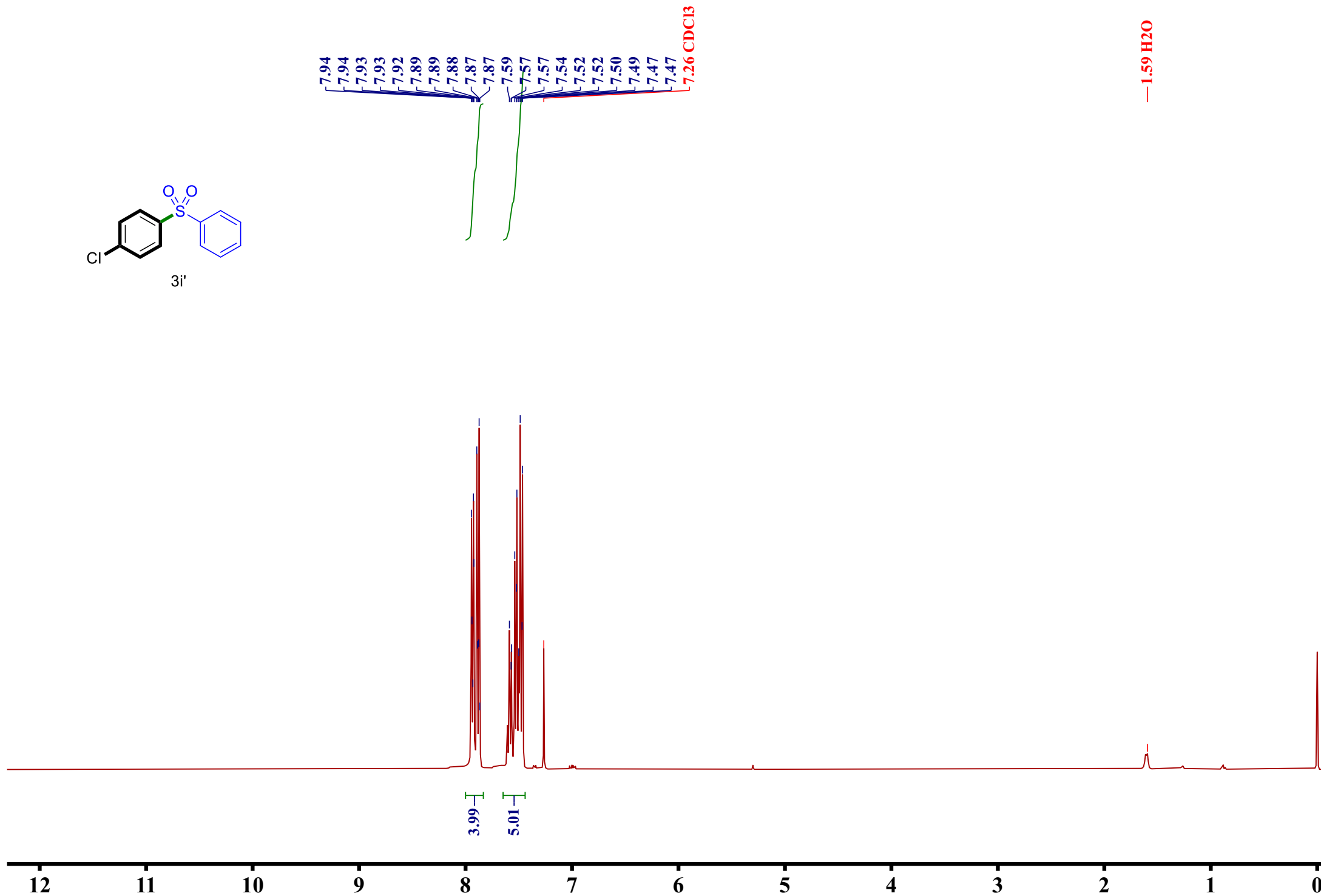
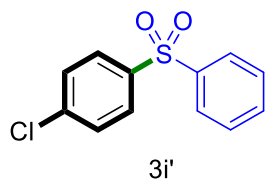


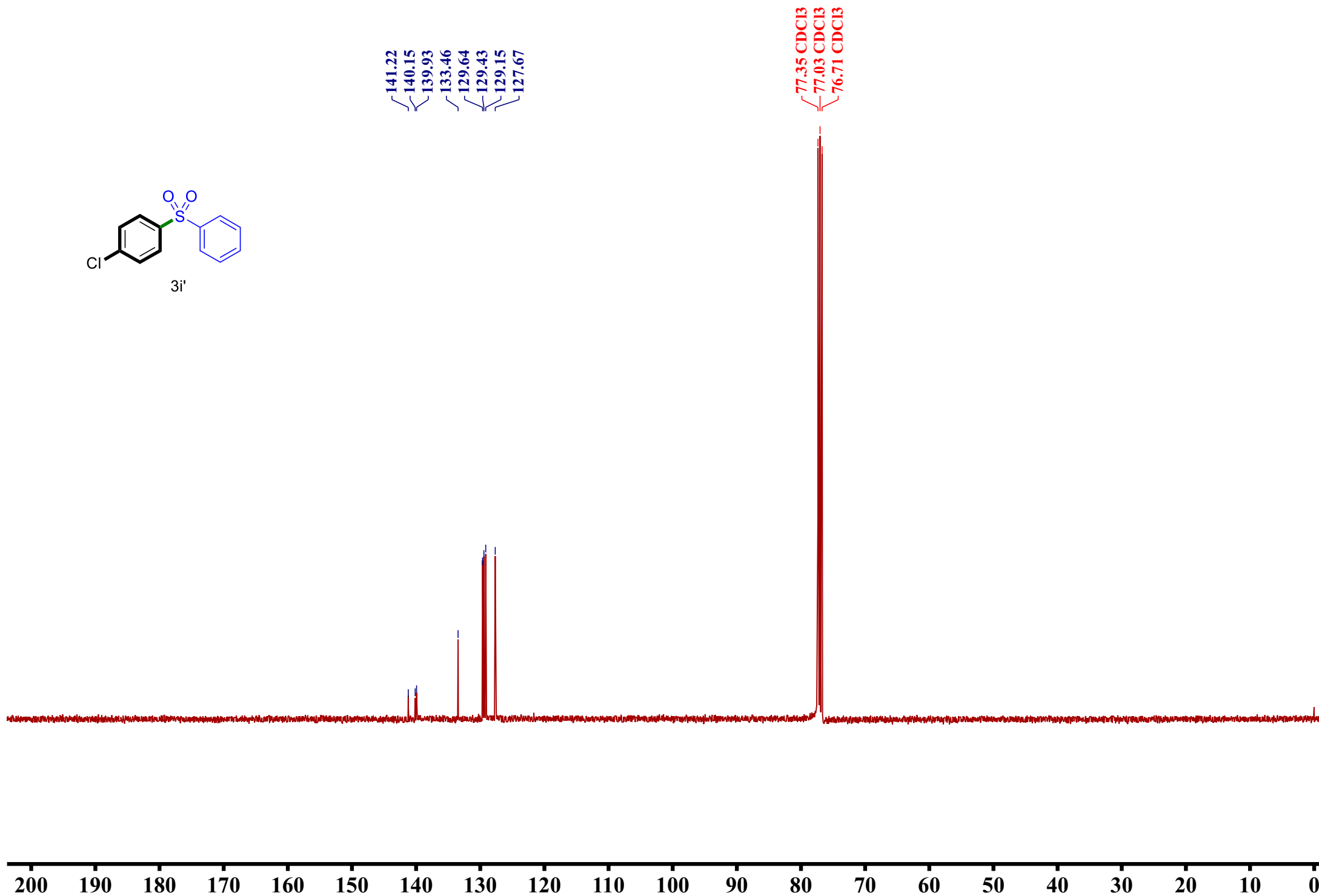
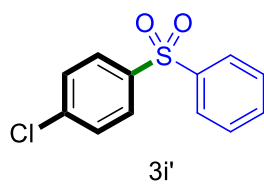


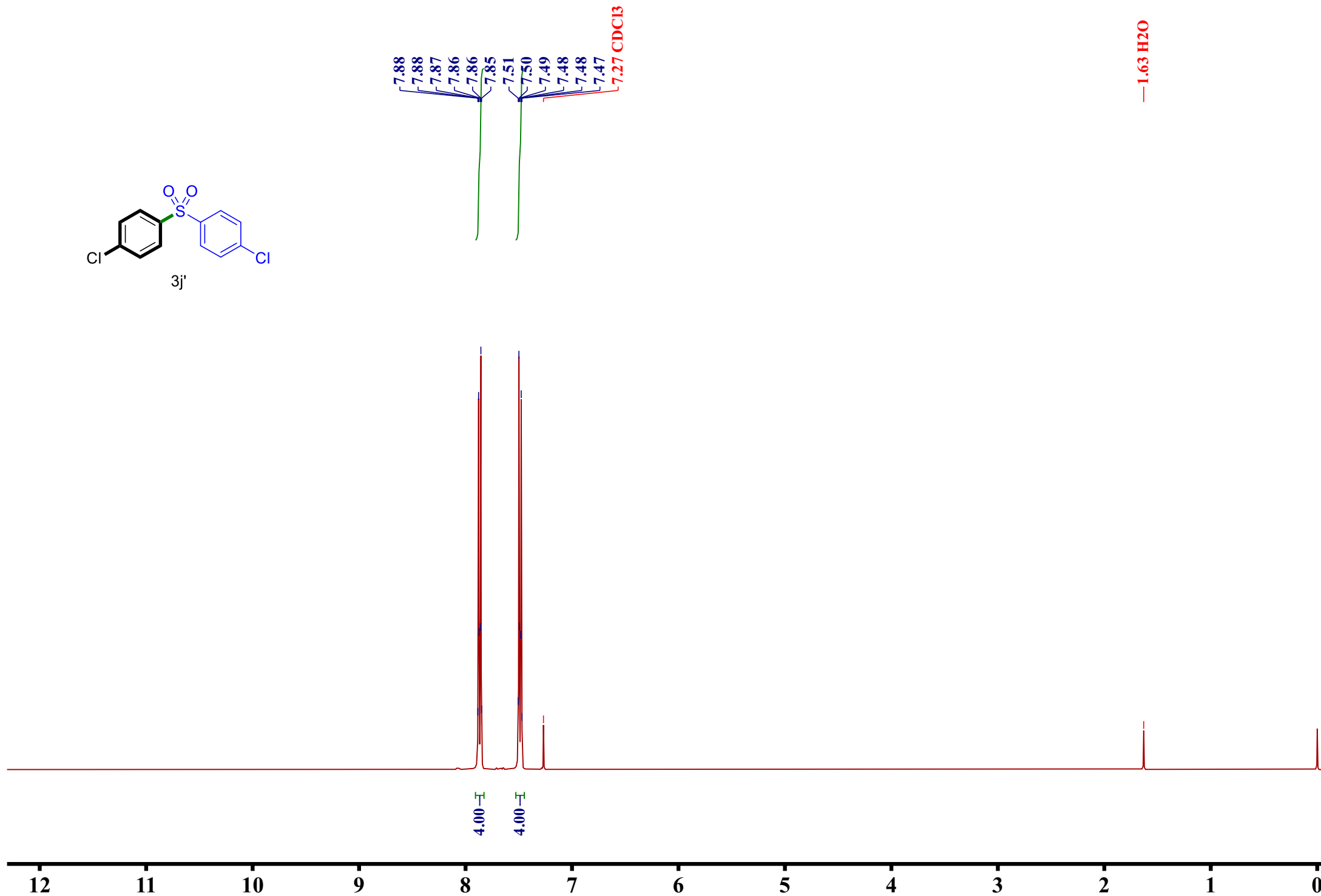
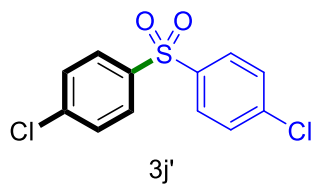
3h'

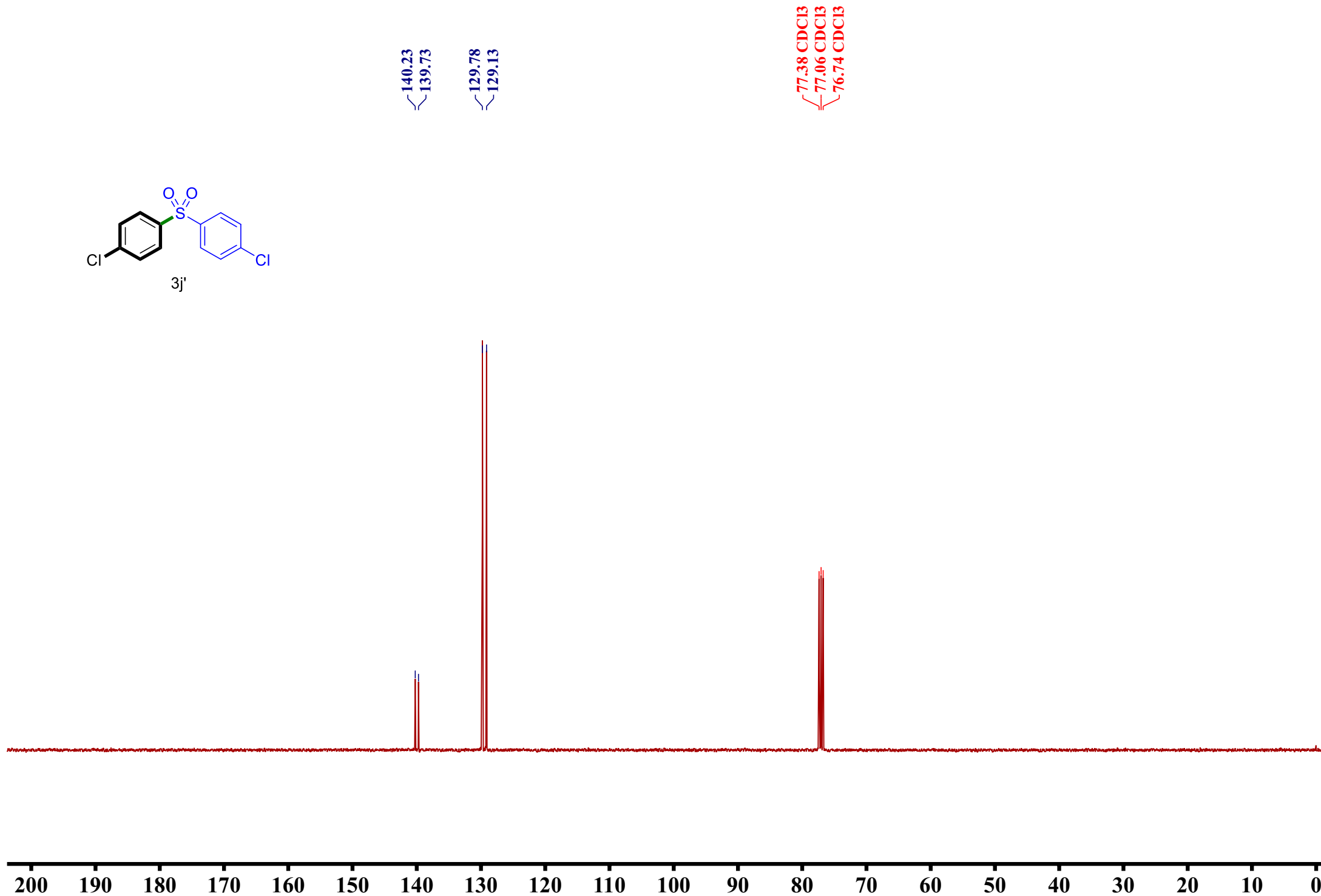
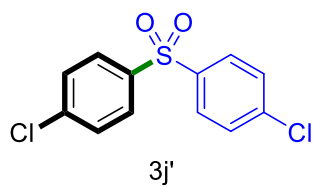


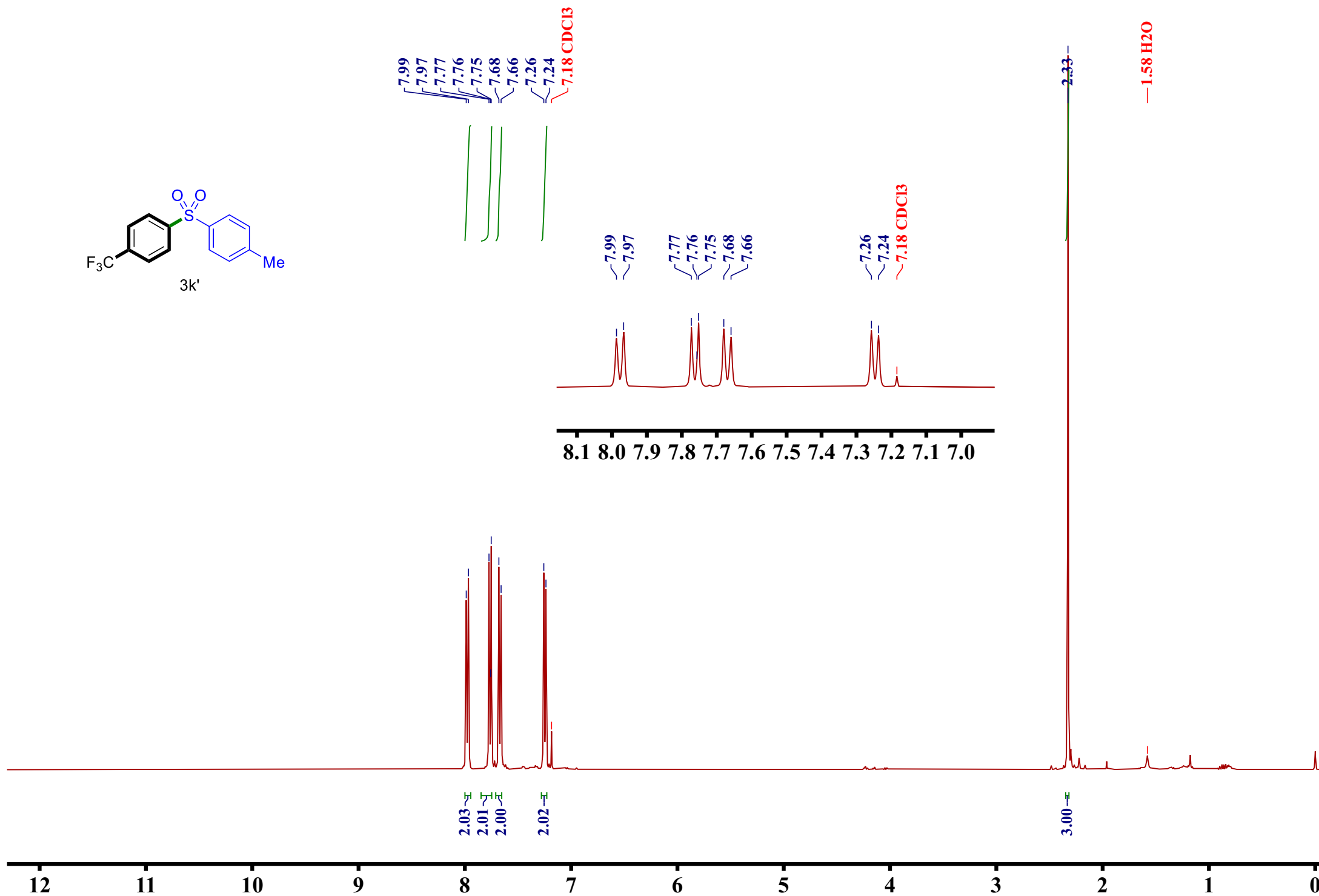
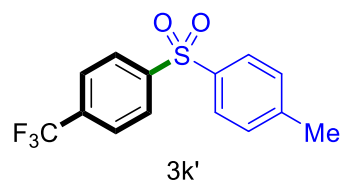


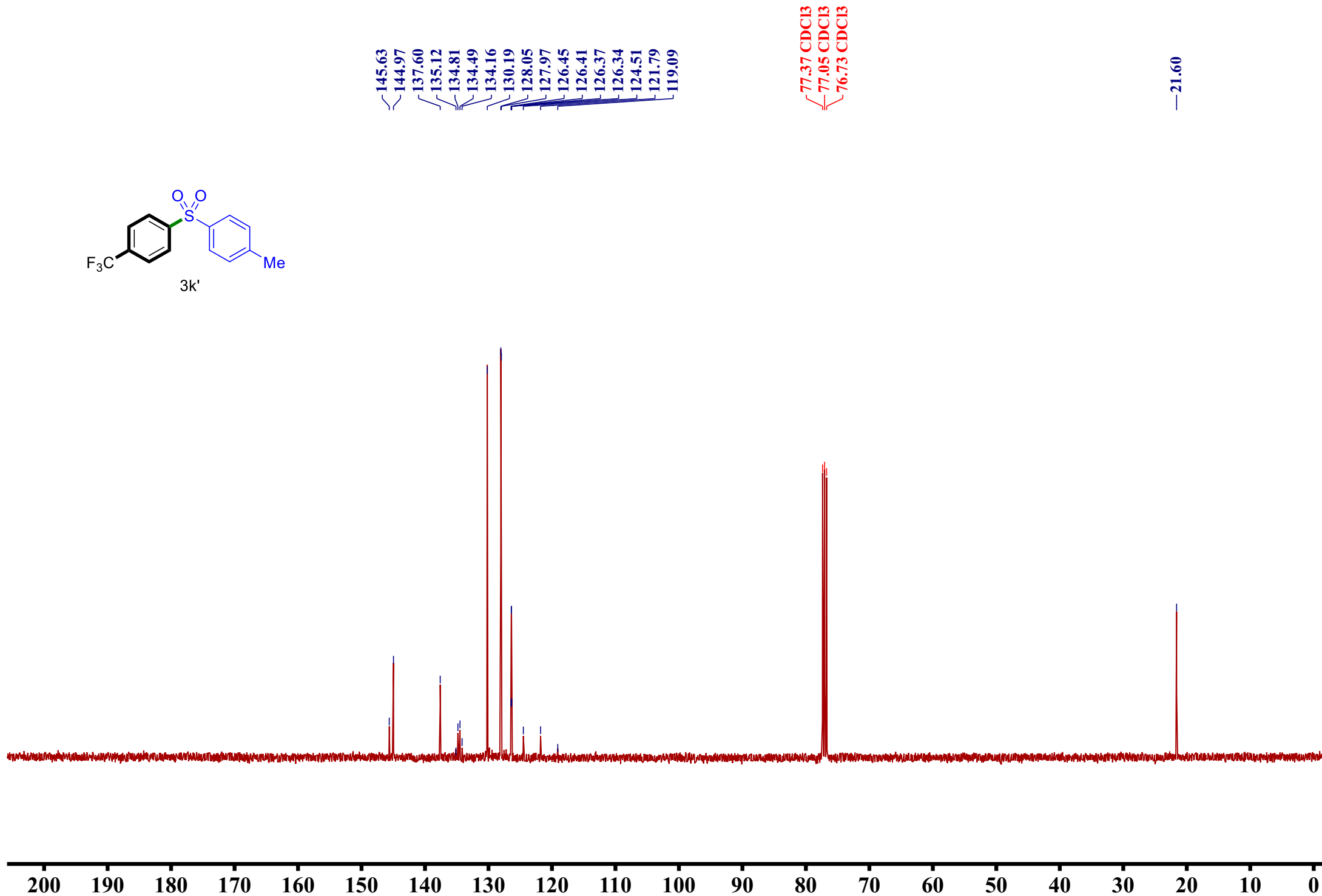
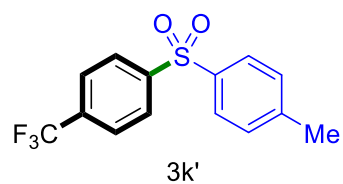


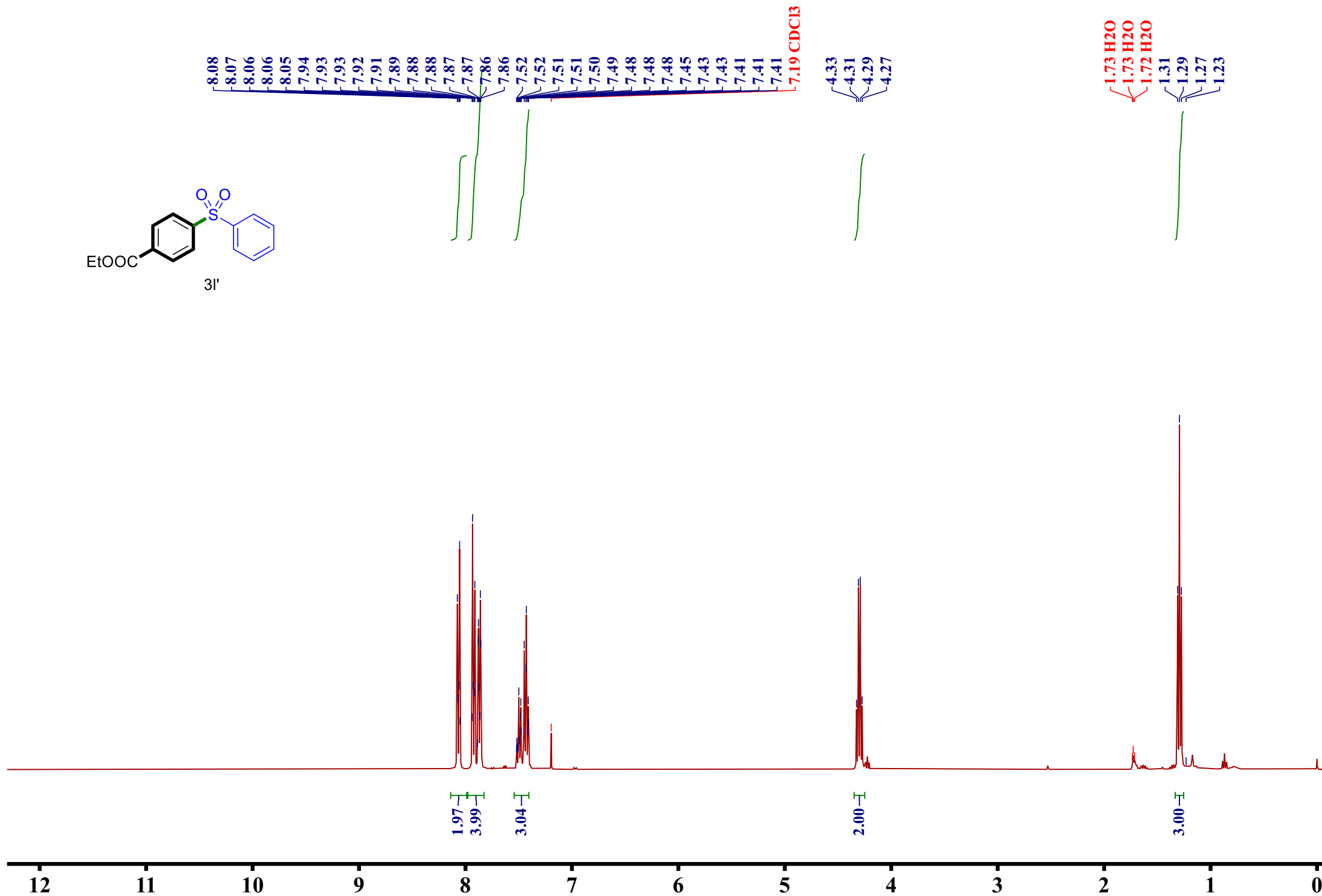
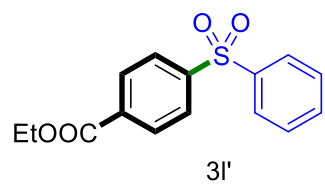


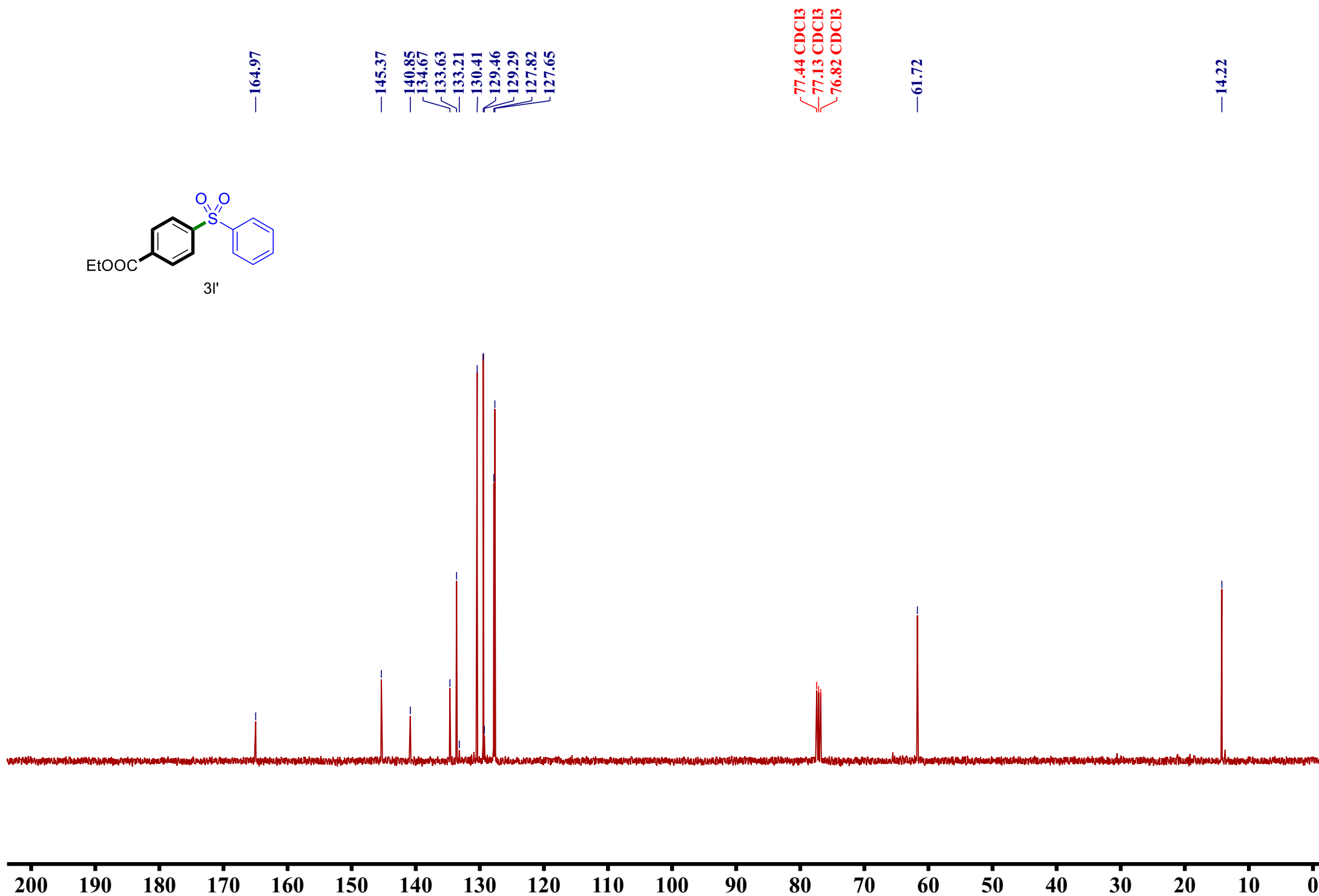
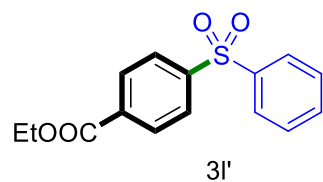


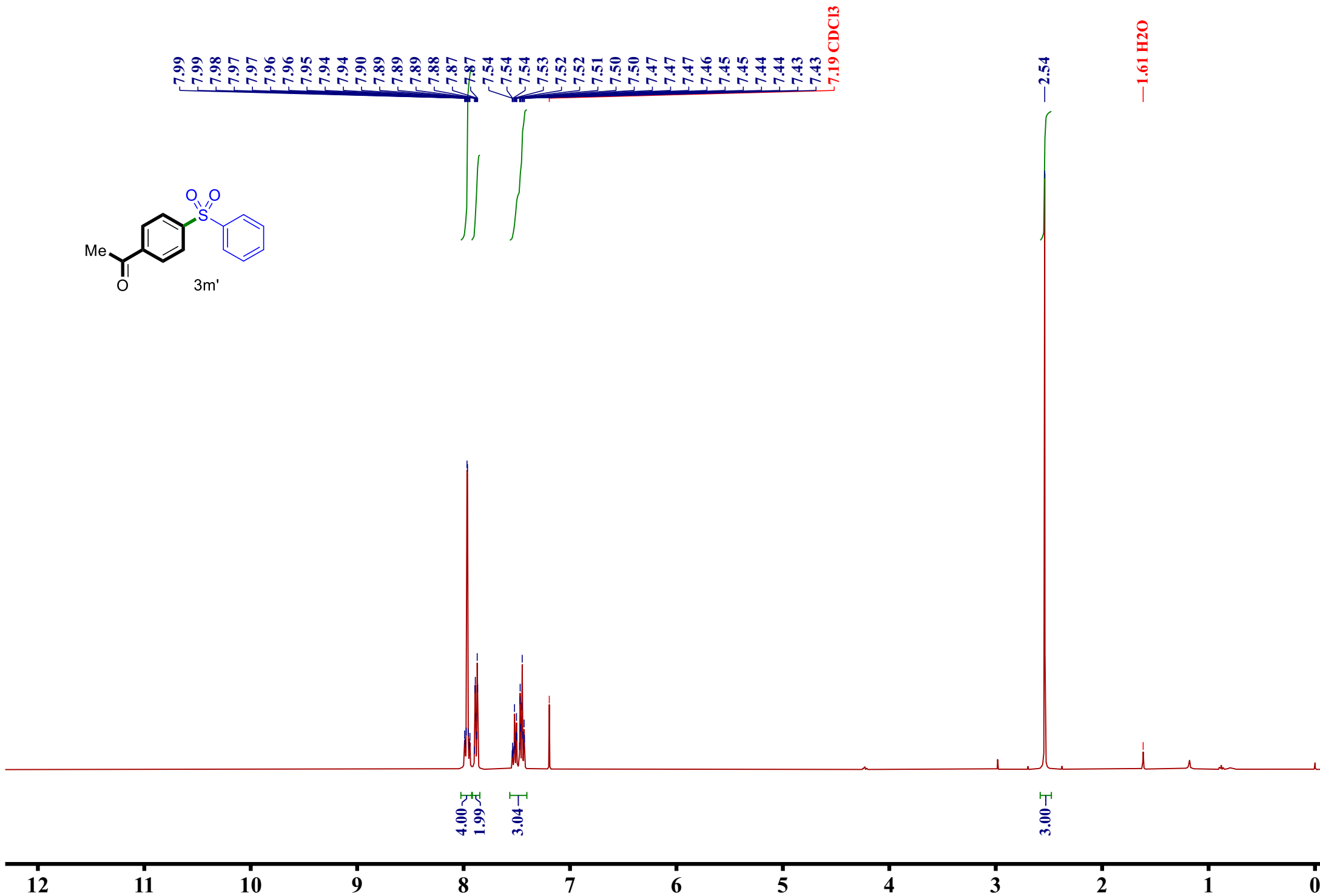
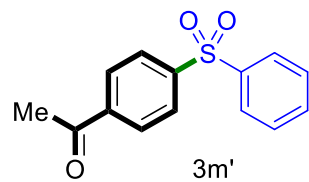


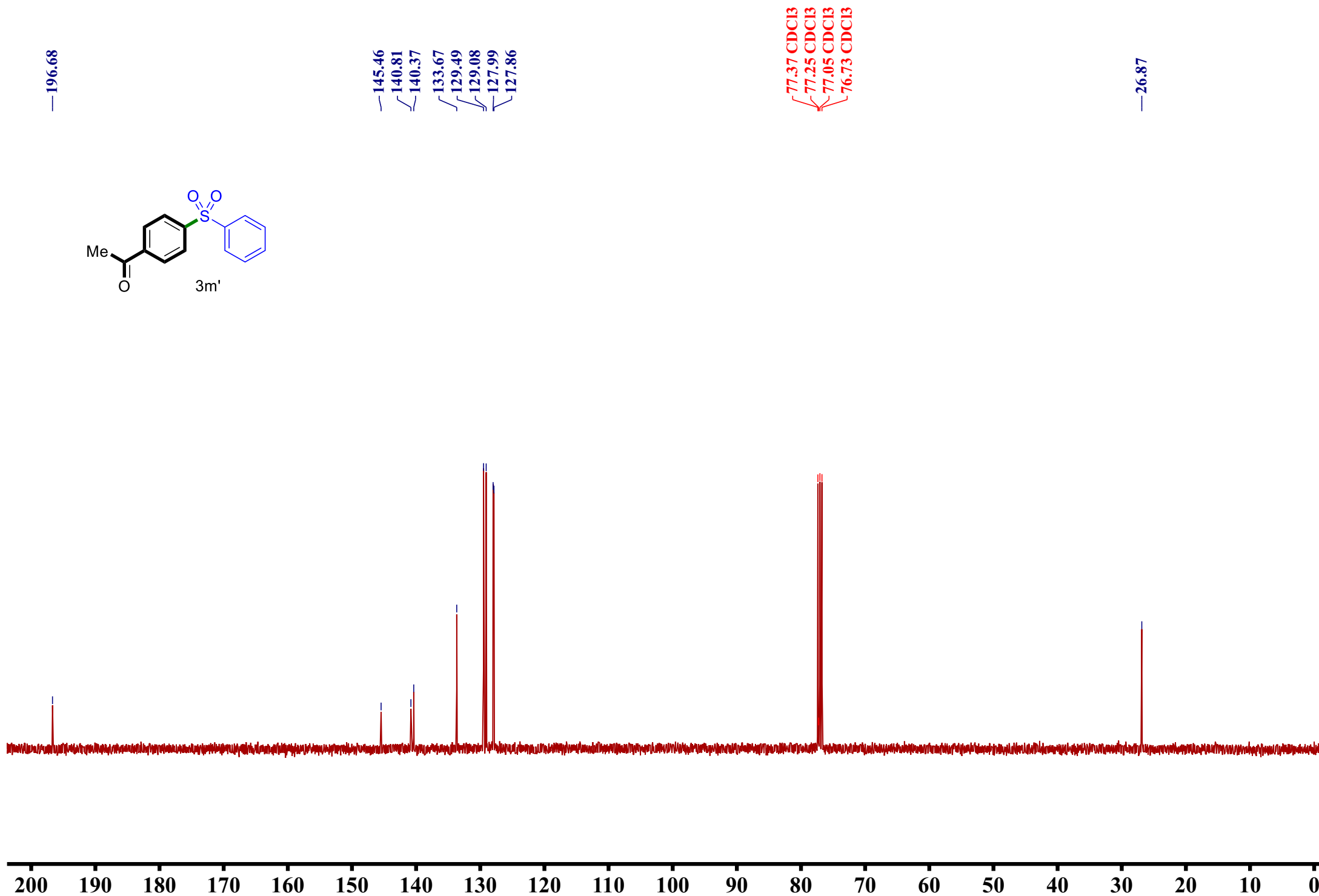
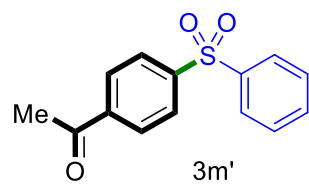


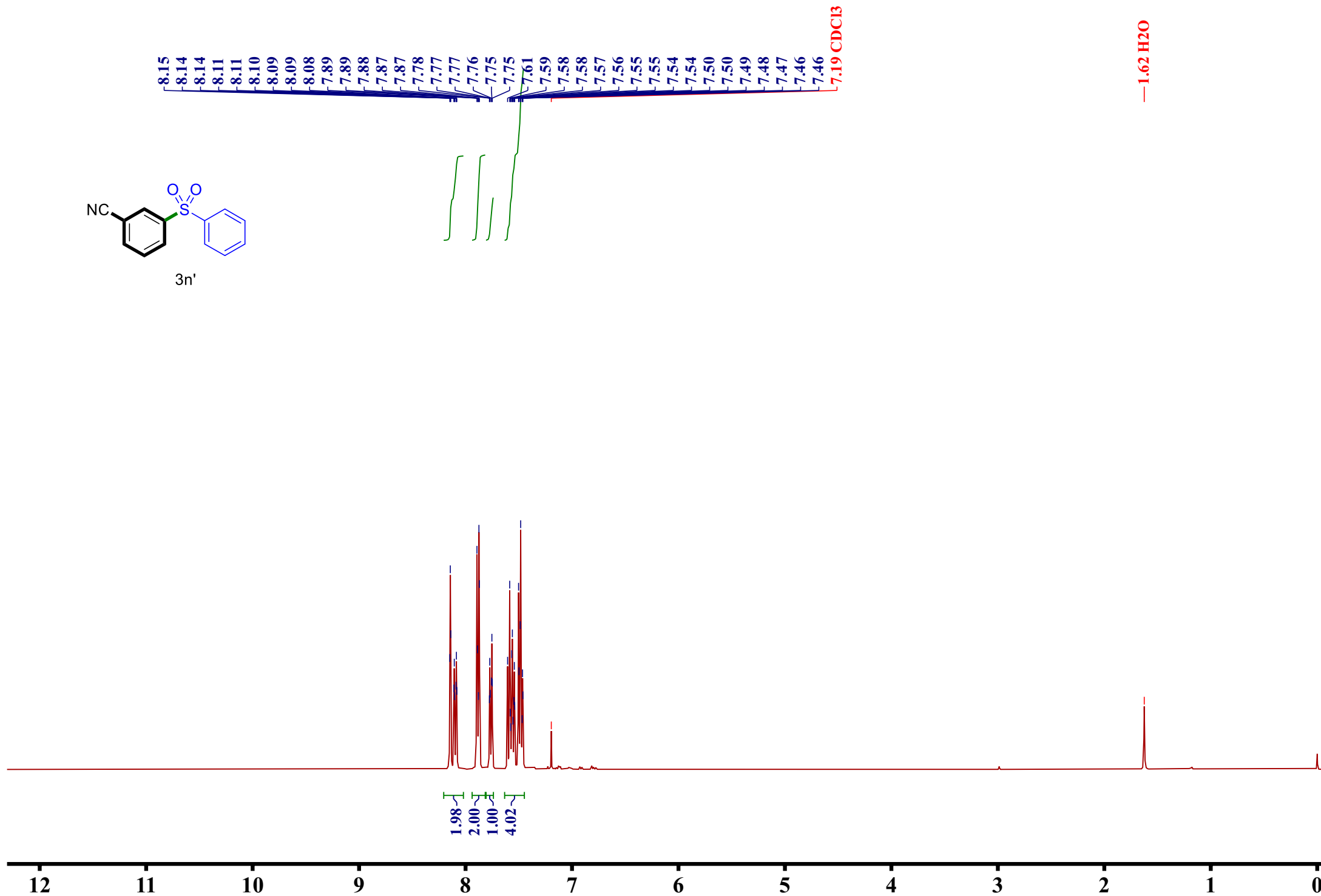
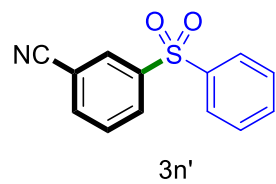


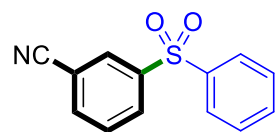








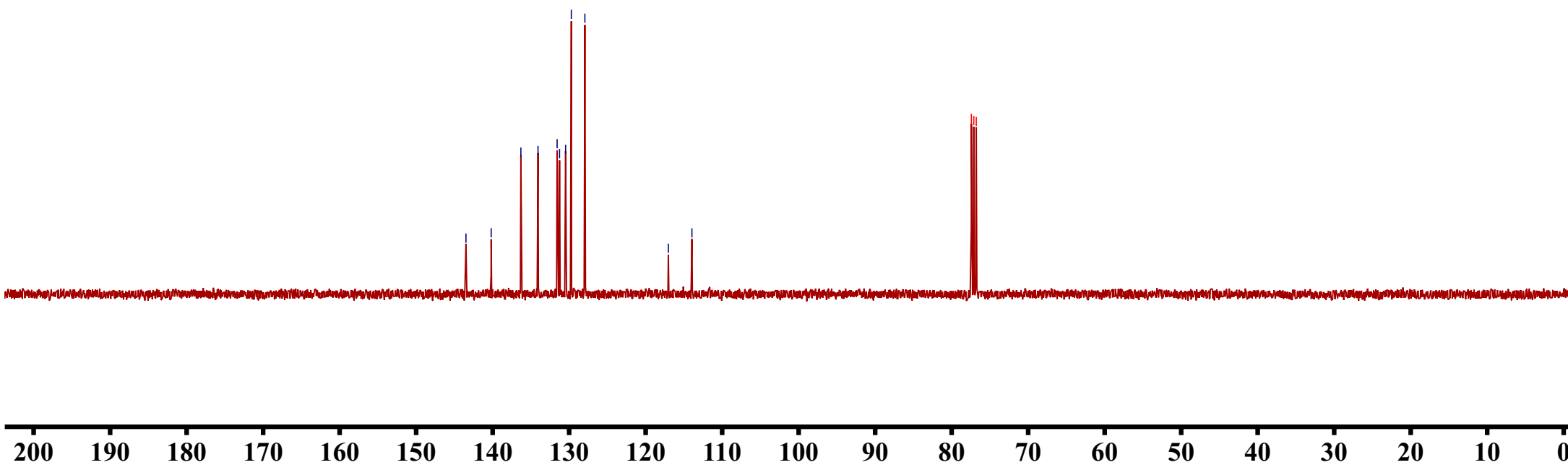


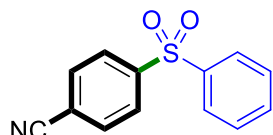


3n'

143.49
140.19
136.31
134.07
131.57
131.26
130.46
129.72
127.94
— 117.03
— 113.95

77.42 CDCl₃
77.10 CDCl₃
76.79 CDCl₃





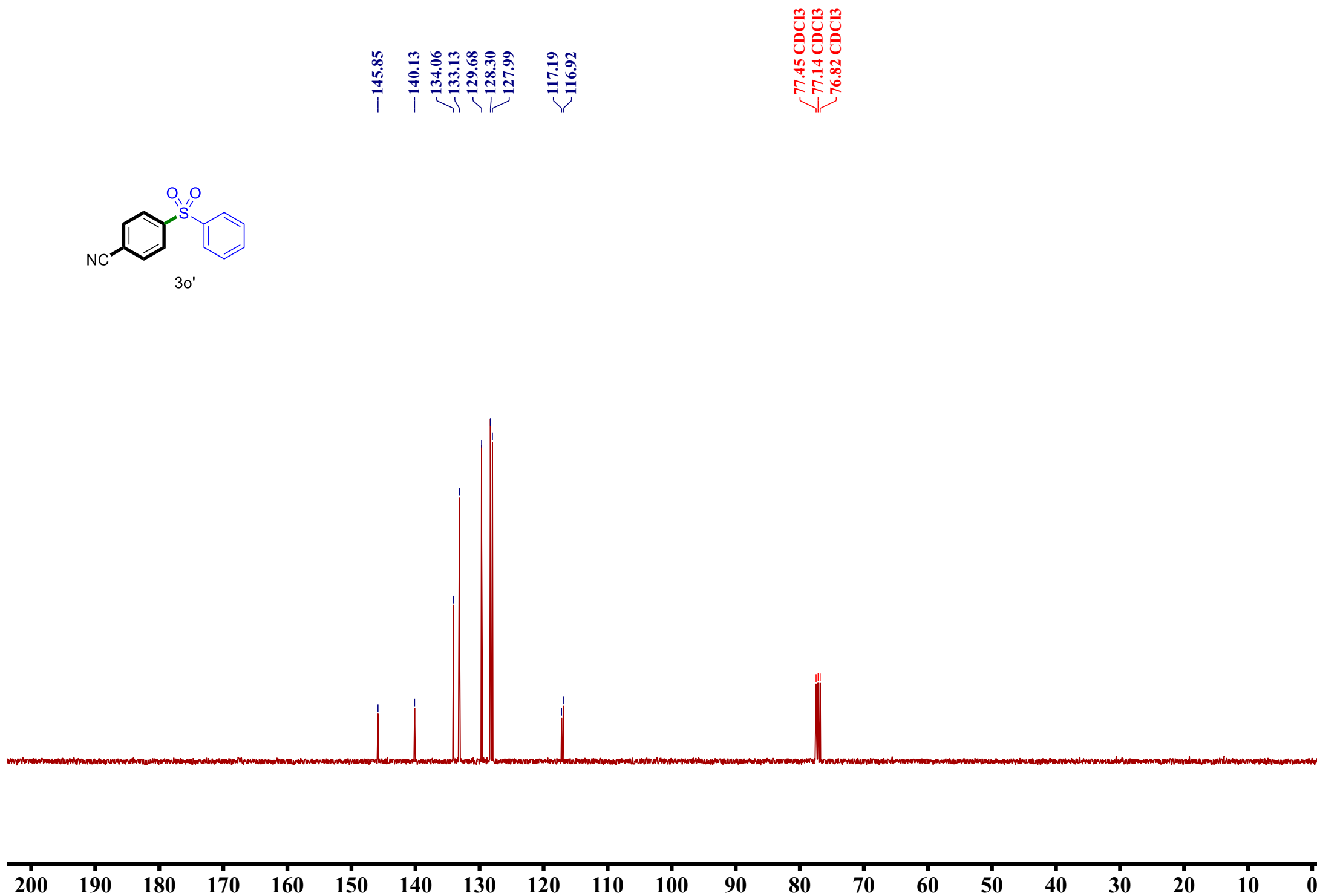
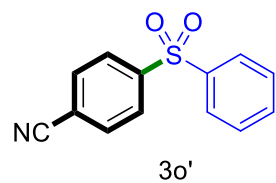
30'

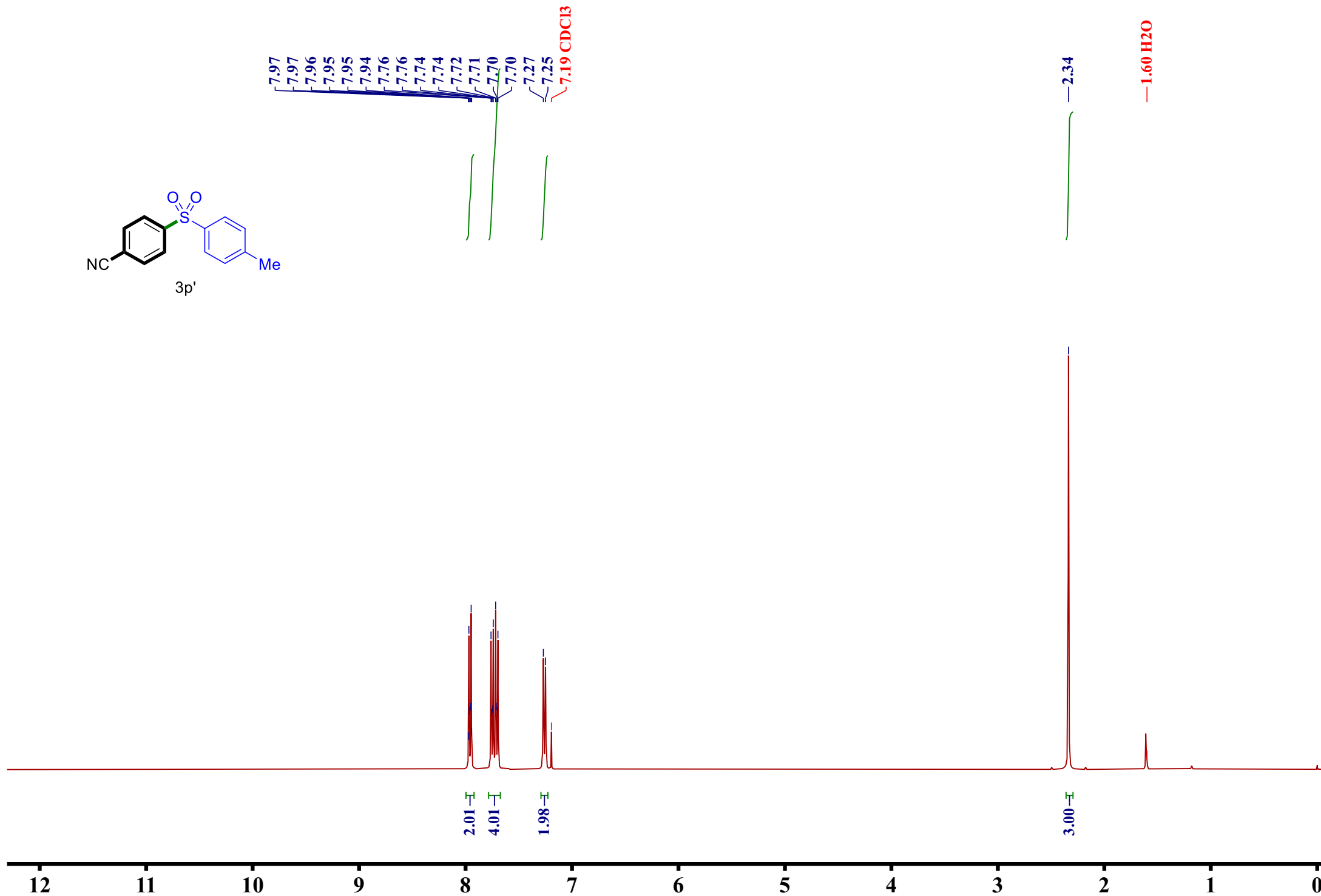
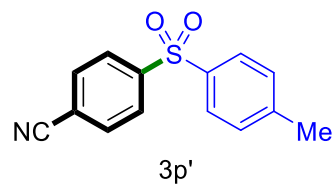
7.99
7.98
7.97
7.97
7.89
7.88
7.88
7.88
7.87
7.86
7.86
7.73
7.73
7.71
7.71
7.71
7.57
7.56
7.56
7.55
7.55
7.54
7.53
7.53
7.52
7.48
7.48
7.47
7.46
7.45
7.45
7.44
7.19 CDCl₃

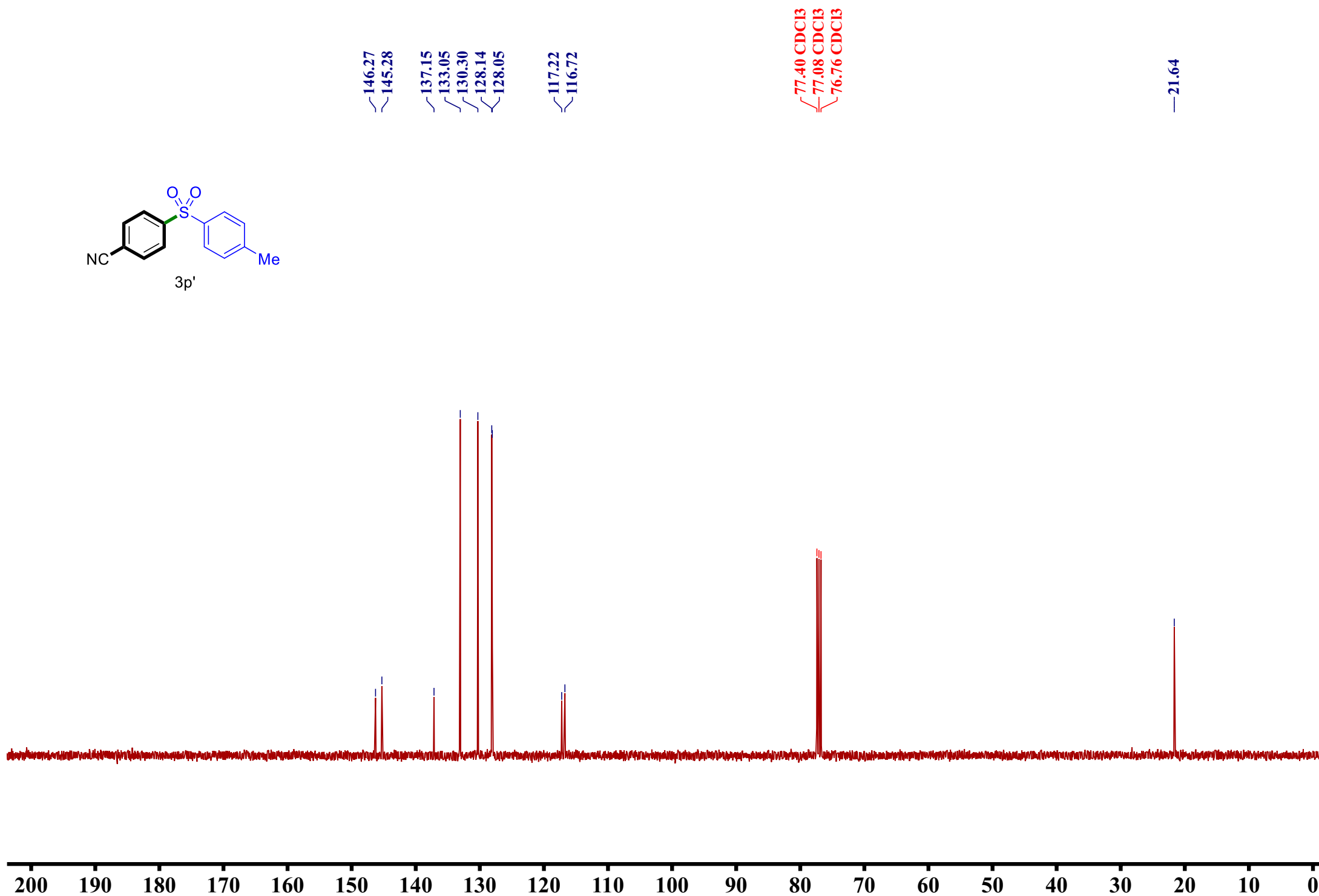
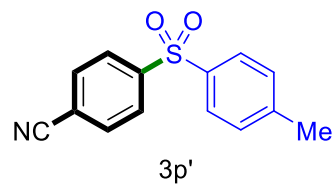
—1.63 H₂O

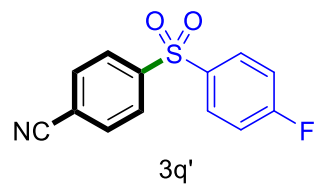
1.98
2.00
2.02
3.02

12 11 10 9 8 7 6 5 4 3 2 1 0



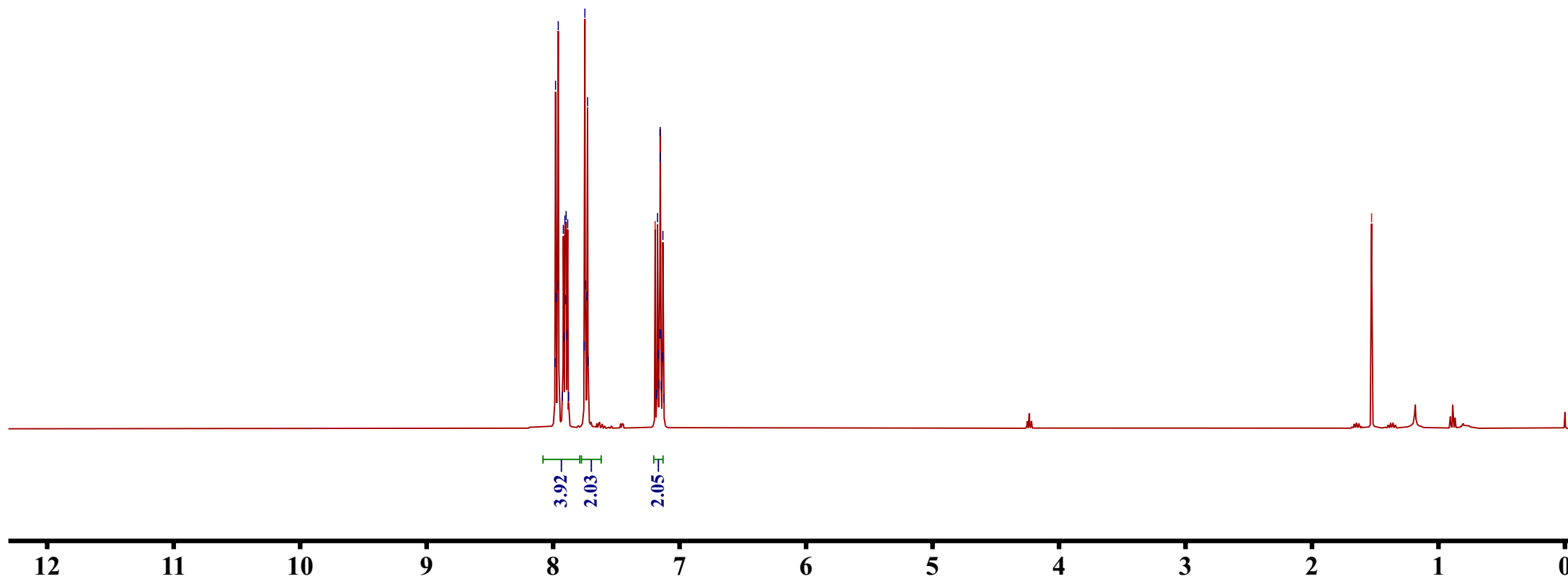


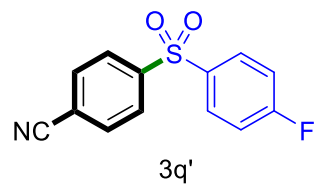




7.99
7.98
7.98
7.96
7.96
7.93
7.92
7.91
7.91
7.90
7.90
7.89
7.88
7.88
7.75
7.75
7.74
7.73
7.73
7.72
7.19 CDCl₃
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.15
7.14
7.14
7.13
7.12

— 1.53 H₂O





— 167.23
— 164.67

— 145.72

136.25
136.21

133.18

130.97

130.87

128.22

117.19

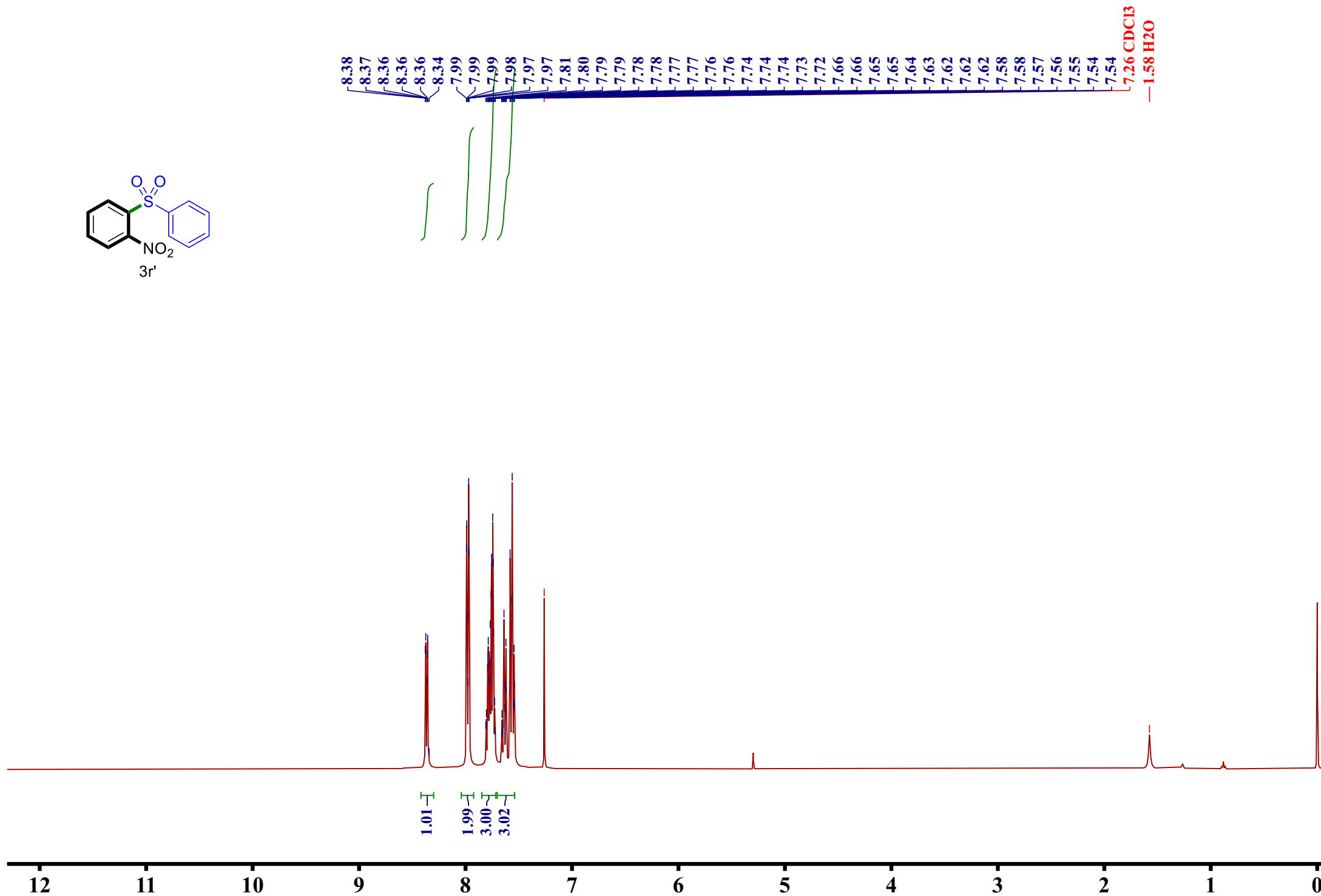
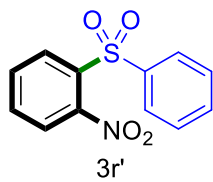
117.11

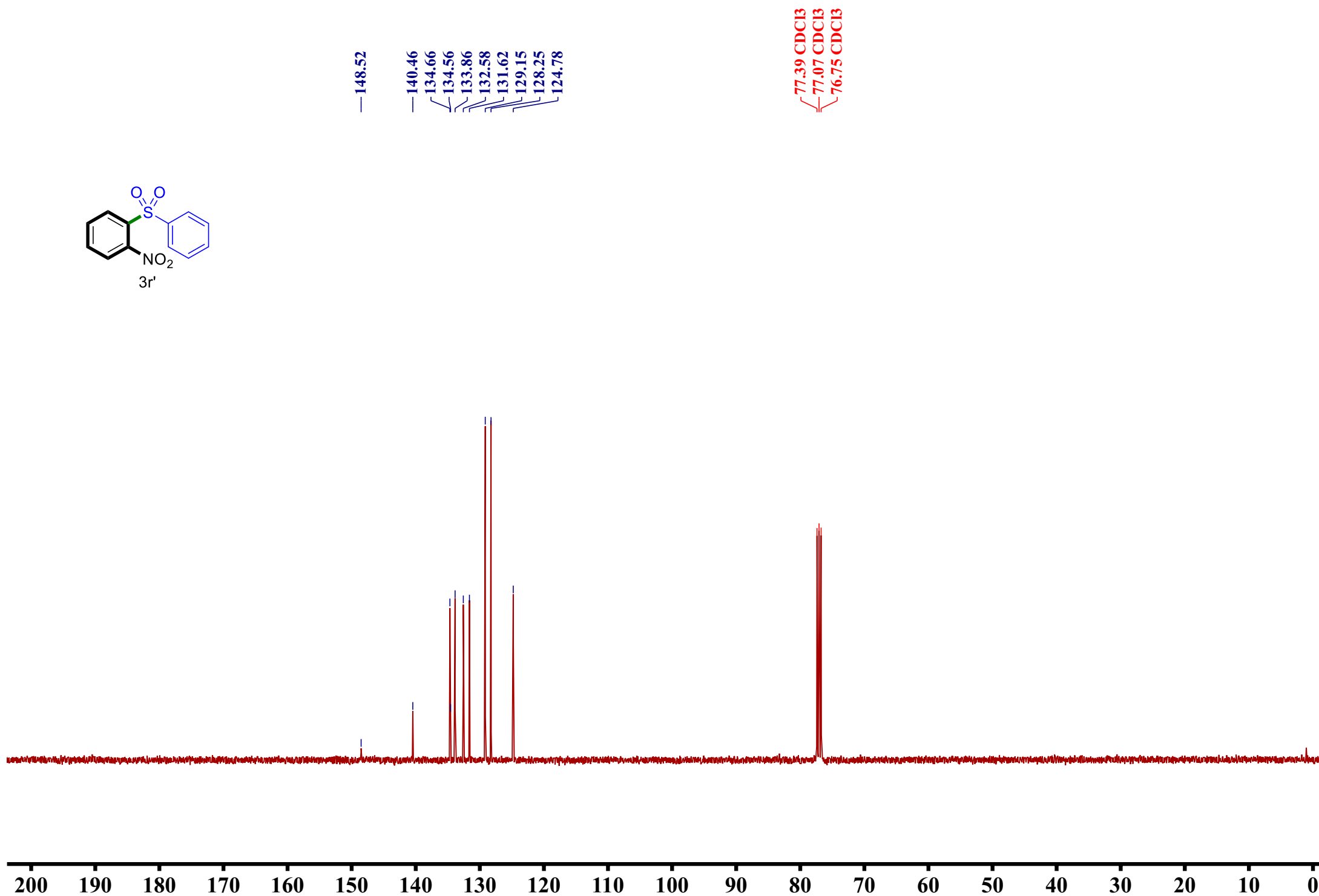
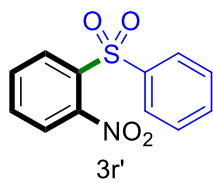
117.07

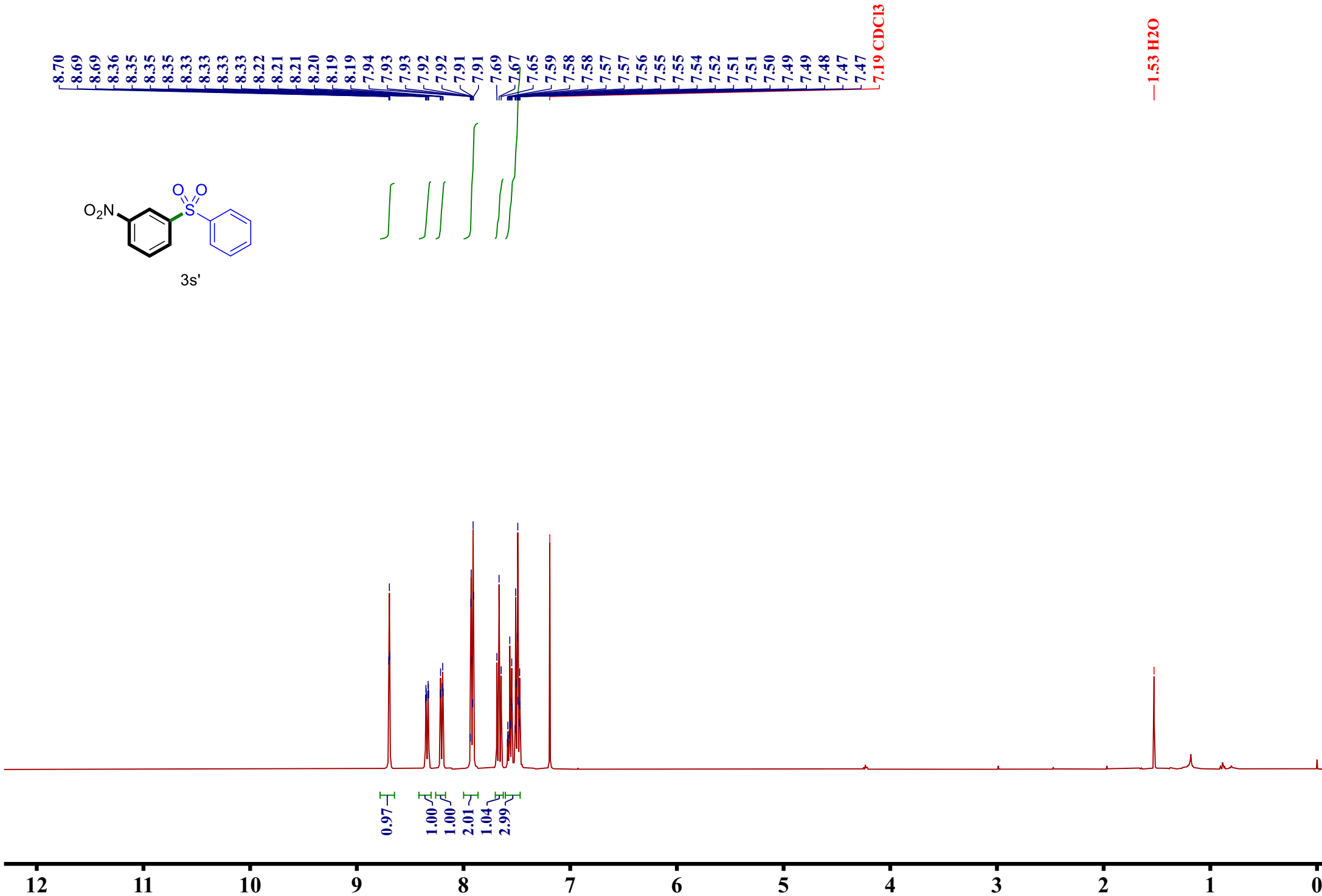
116.96

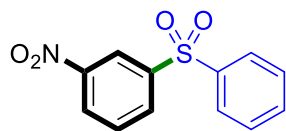
77.37 CDC13
77.25 CDC13
77.05 CDC13
76.73 CDC13

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0





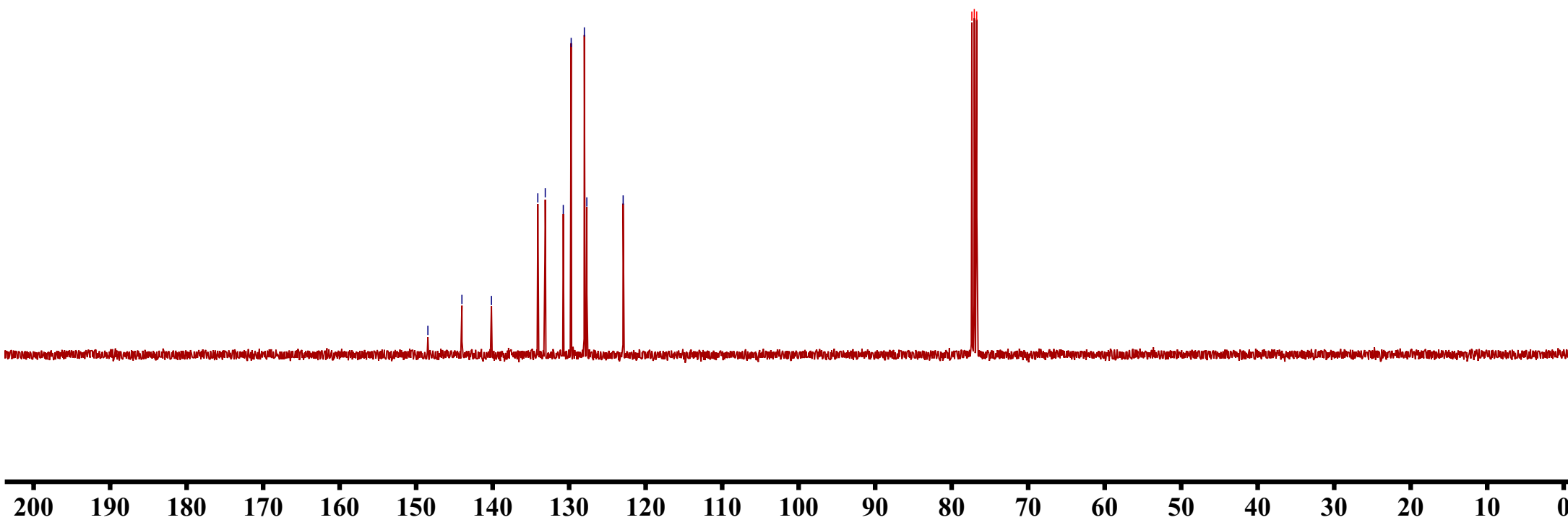


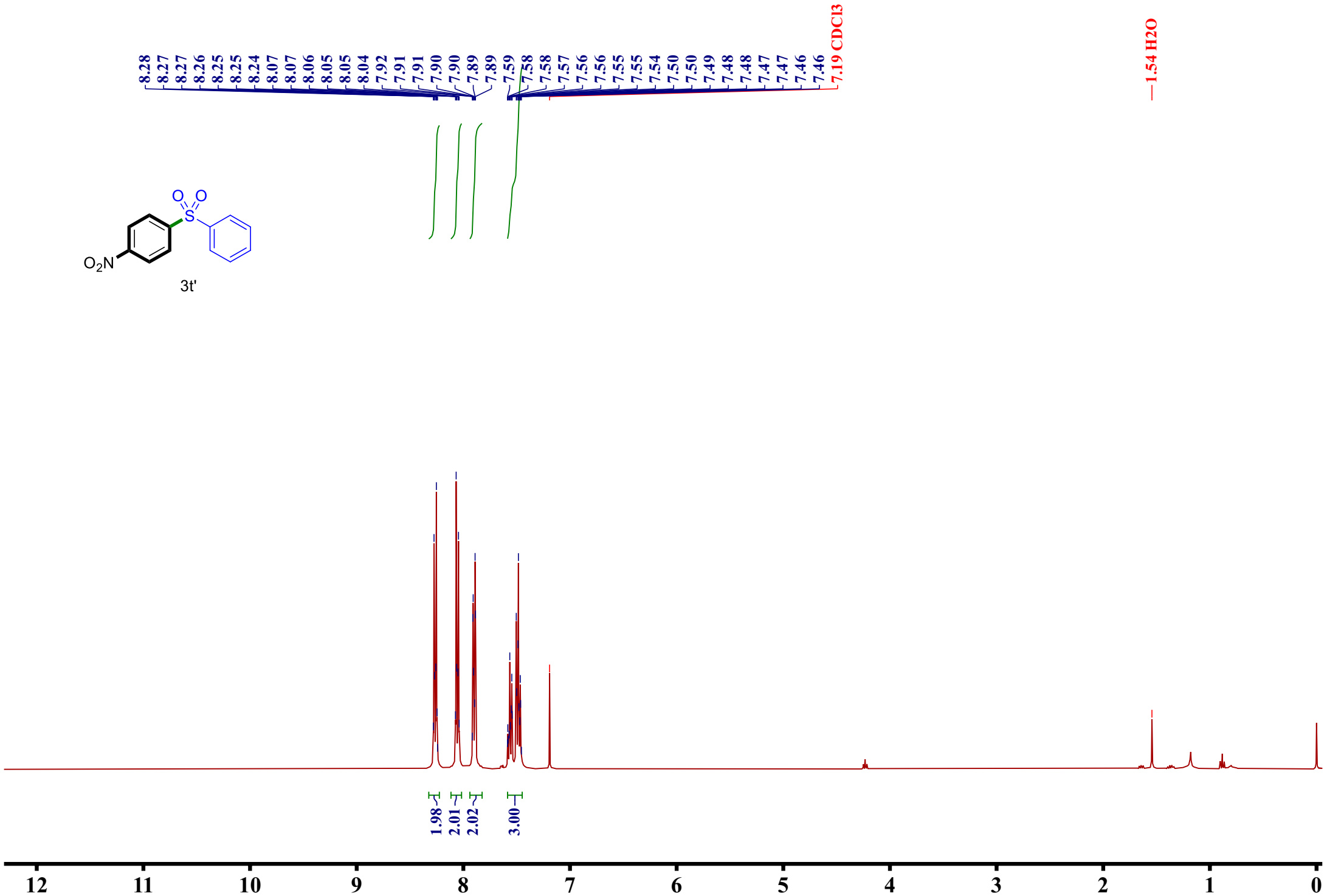


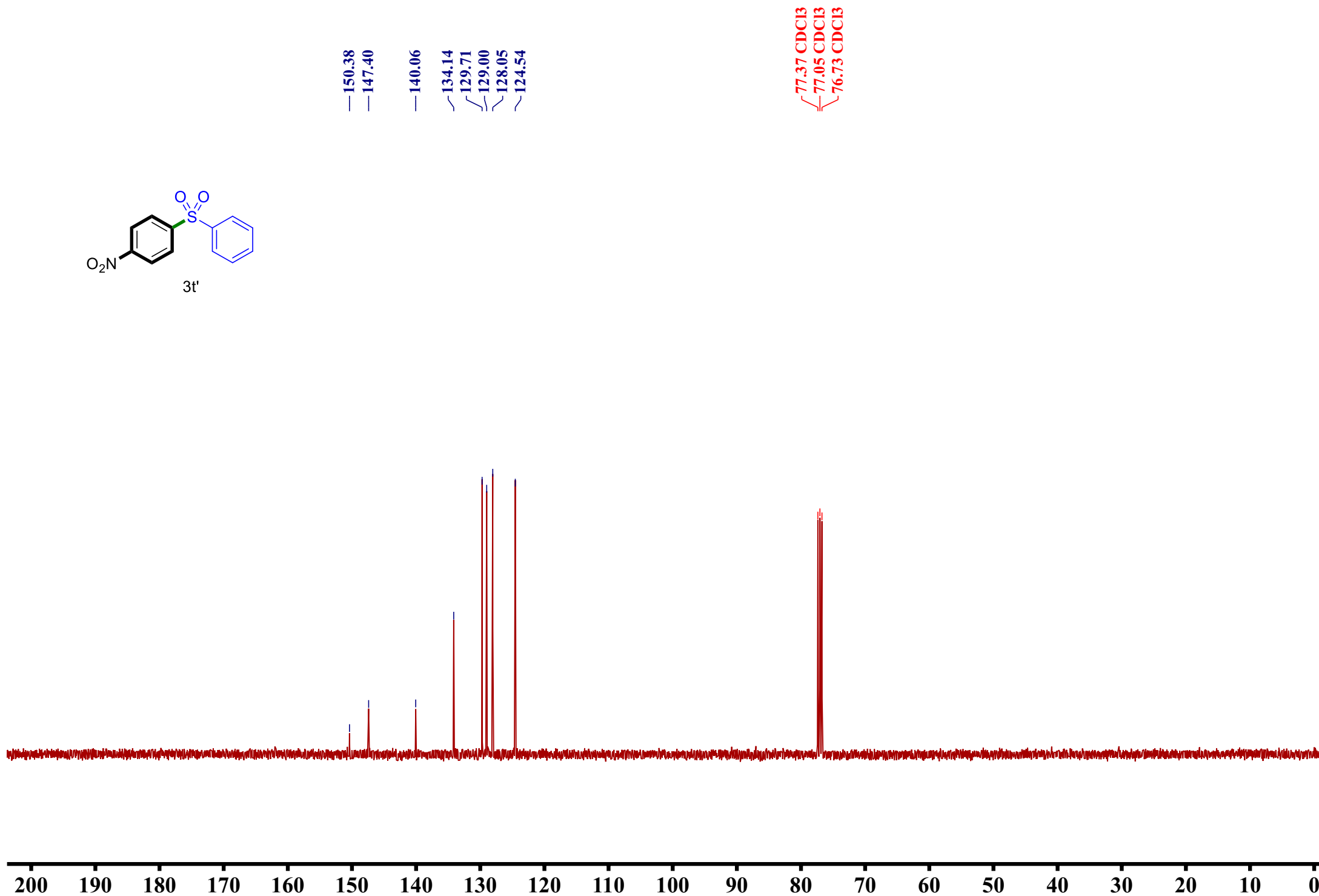
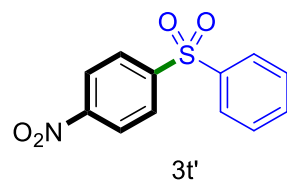
3s'

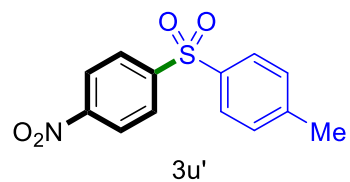
148.47
144.02
140.16
134.10
133.12
130.77
129.73
128.01
127.69
122.94

77.36 CDCl₃
77.04 CDCl₃
76.73 CDCl₃









8.26
8.26
8.25
8.24
8.23
8.23
8.05
8.04
8.04
8.03
8.02
8.01
7.78
7.78
7.76
7.76
7.28
7.26
7.19 CDCl₃

2.34

— 1.56 H₂O

1.99

1.99

2.02

2.00

3.00

12

11

10

9

8

7

6

5

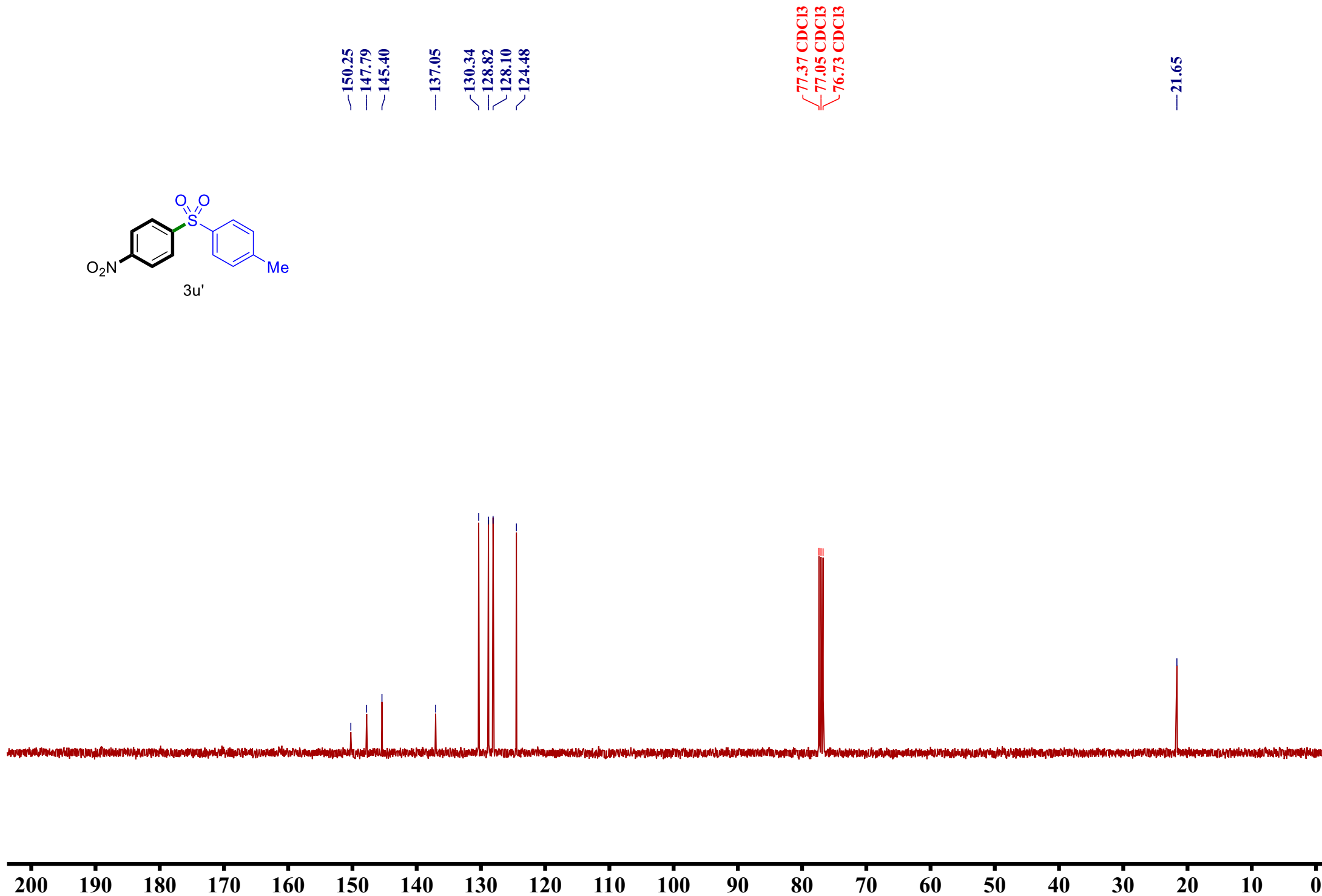
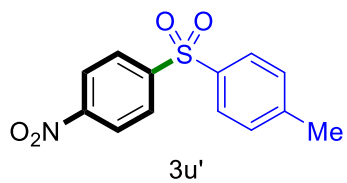
4

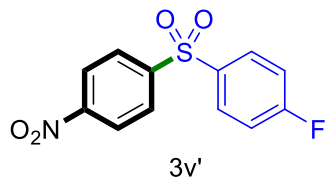
3

2

1

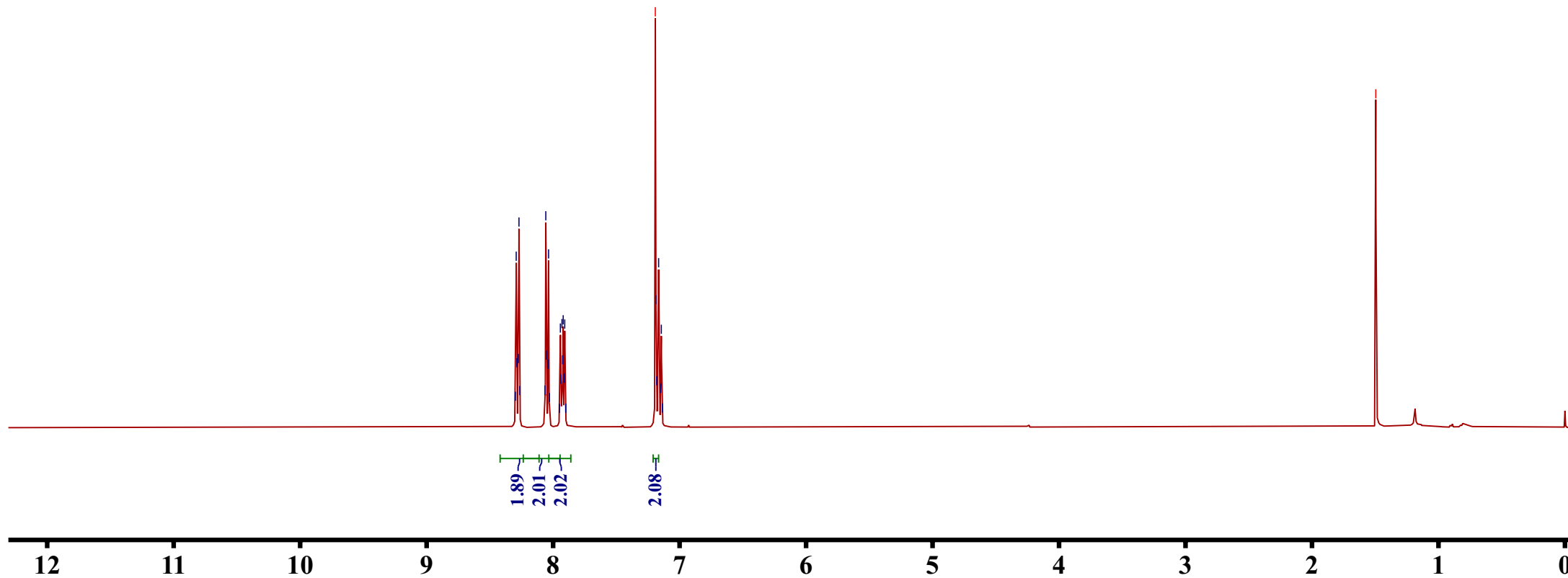
0

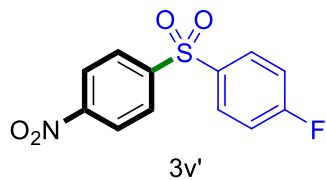




8.30
8.29
8.29
8.28
8.27
8.26
8.06
8.06
8.05
8.04
8.04
8.03
7.95
7.94
7.94
7.93
7.93
7.92
7.91
7.91
7.90
7.19 CDCl3
7.19
7.18
7.17
7.15
7.14
7.14

— 1.50 H2O





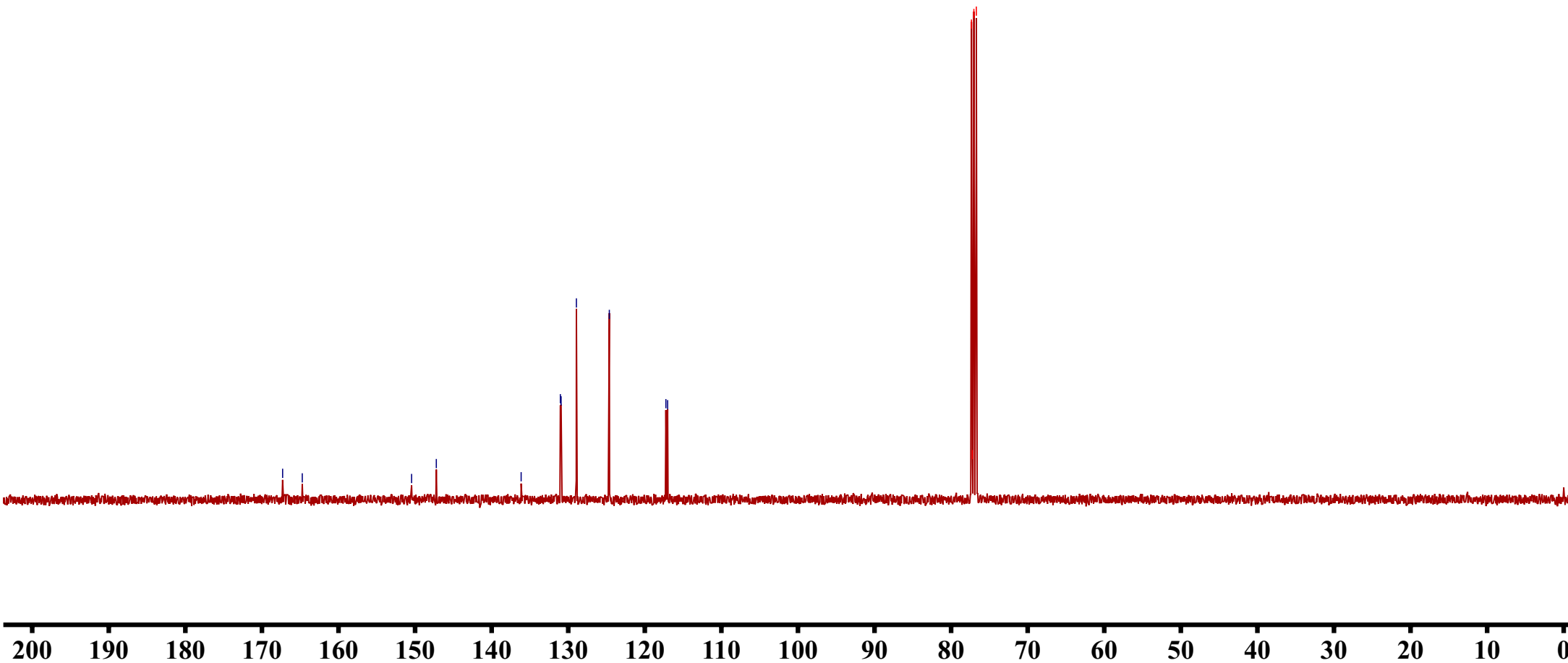
— 167.30
— 164.73

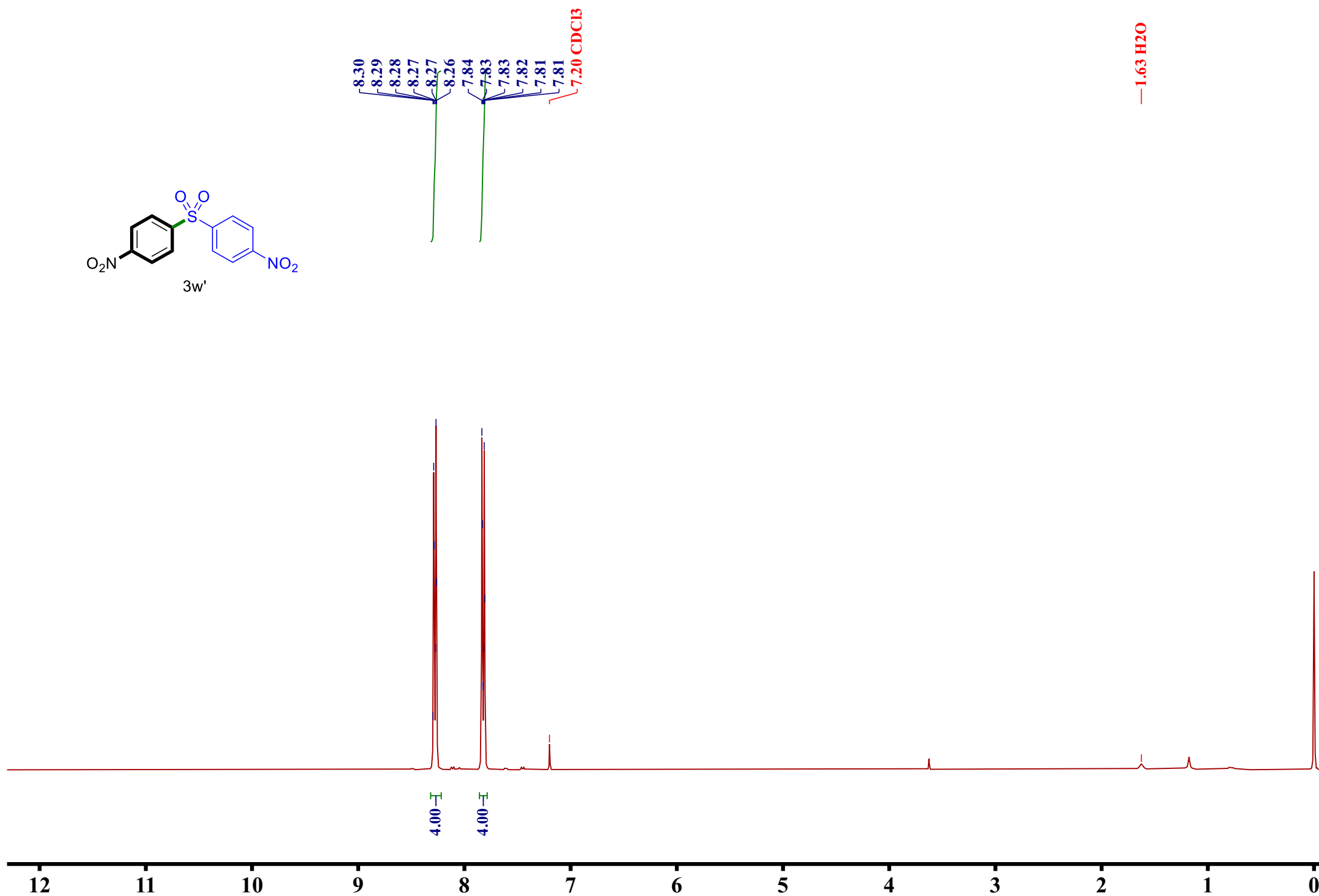
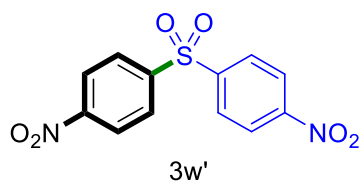
— 150.46
— 147.23

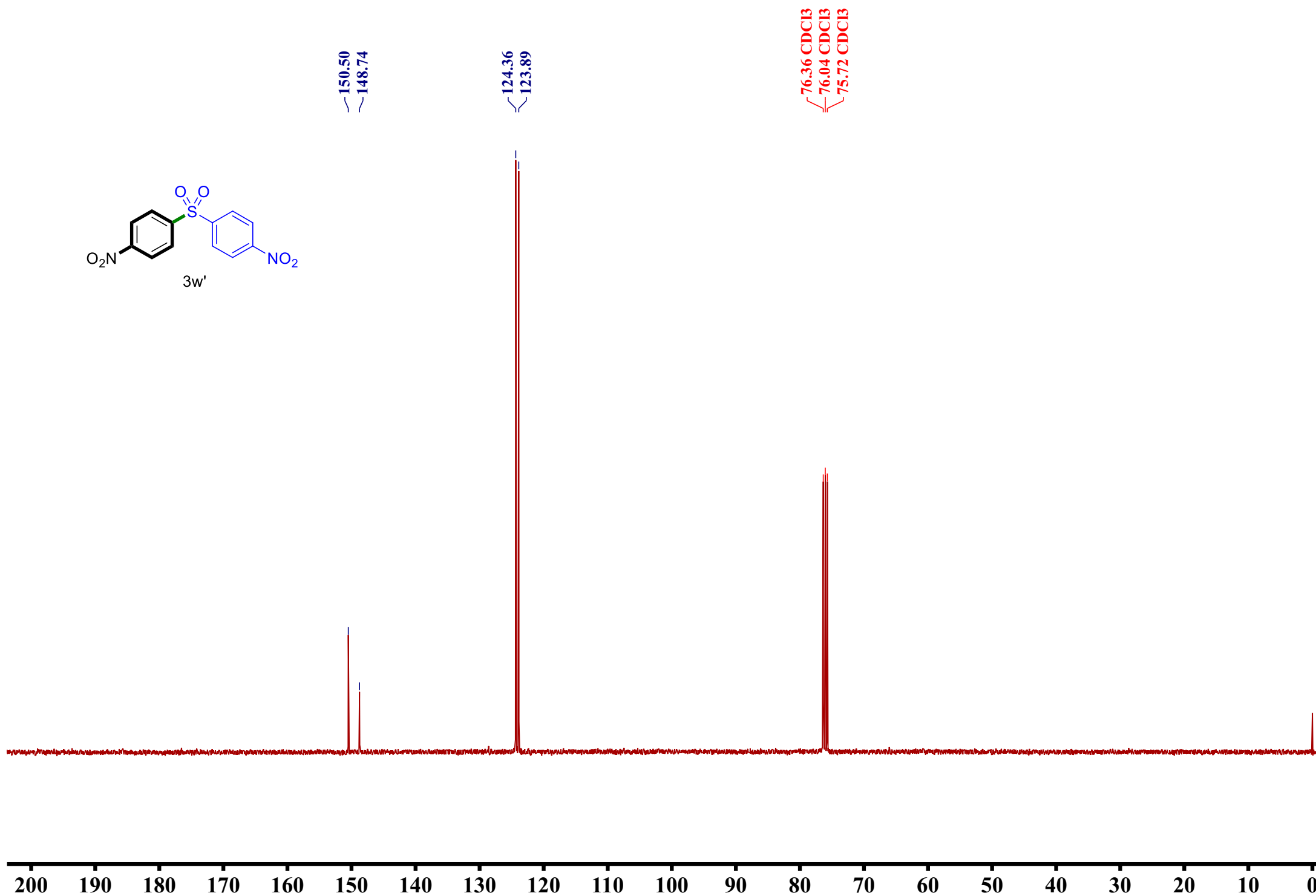
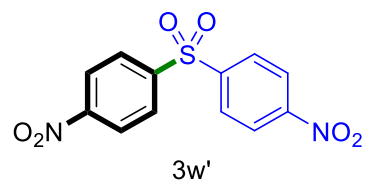
— 136.15
— 131.03
— 130.93
— 128.93
— 124.63

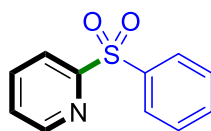
— 117.25
— 117.02

77.34 CDC13
77.23 CDC13
77.02 CDC13
76.71 CDC13

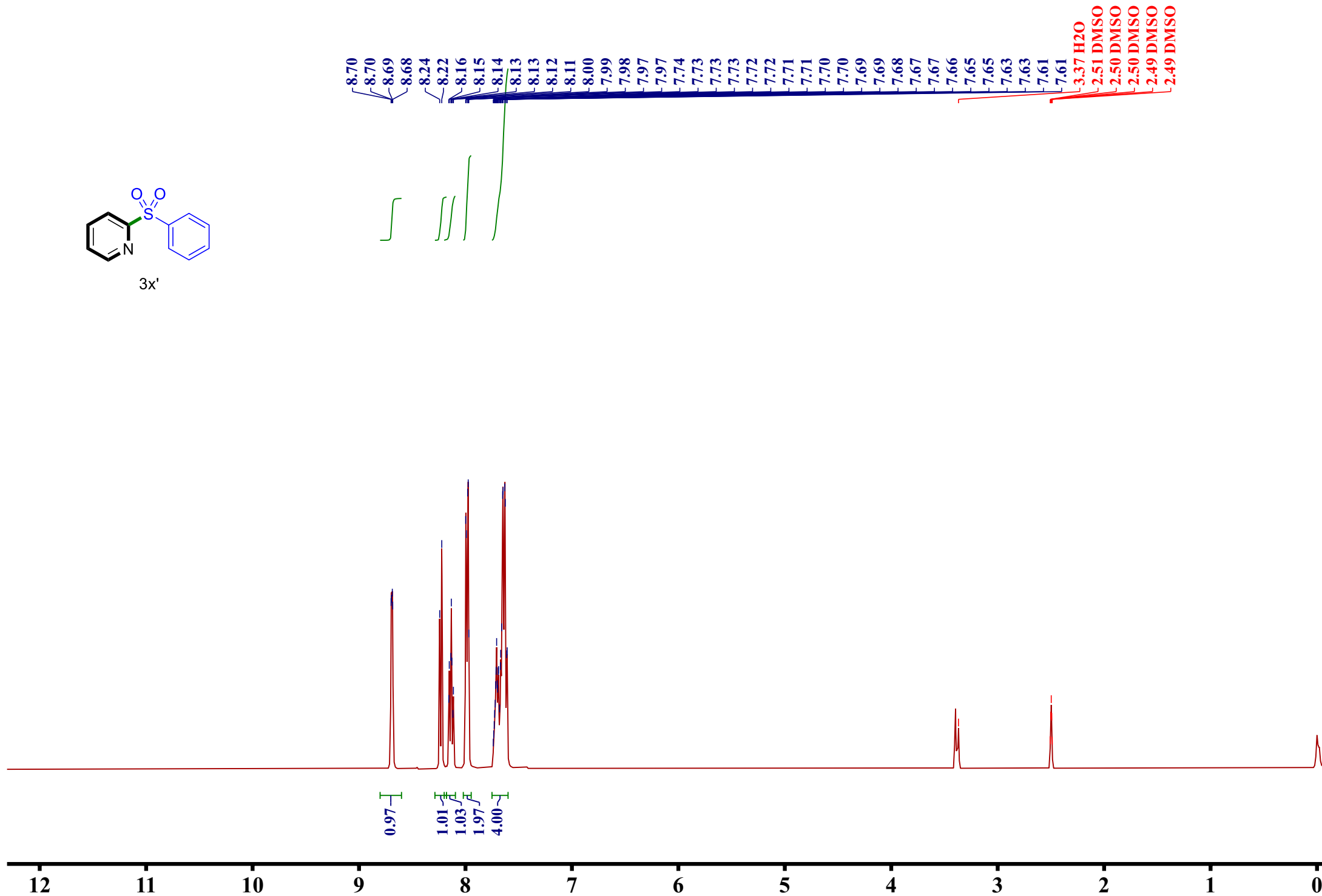


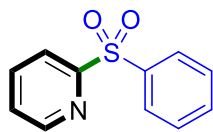






3x'

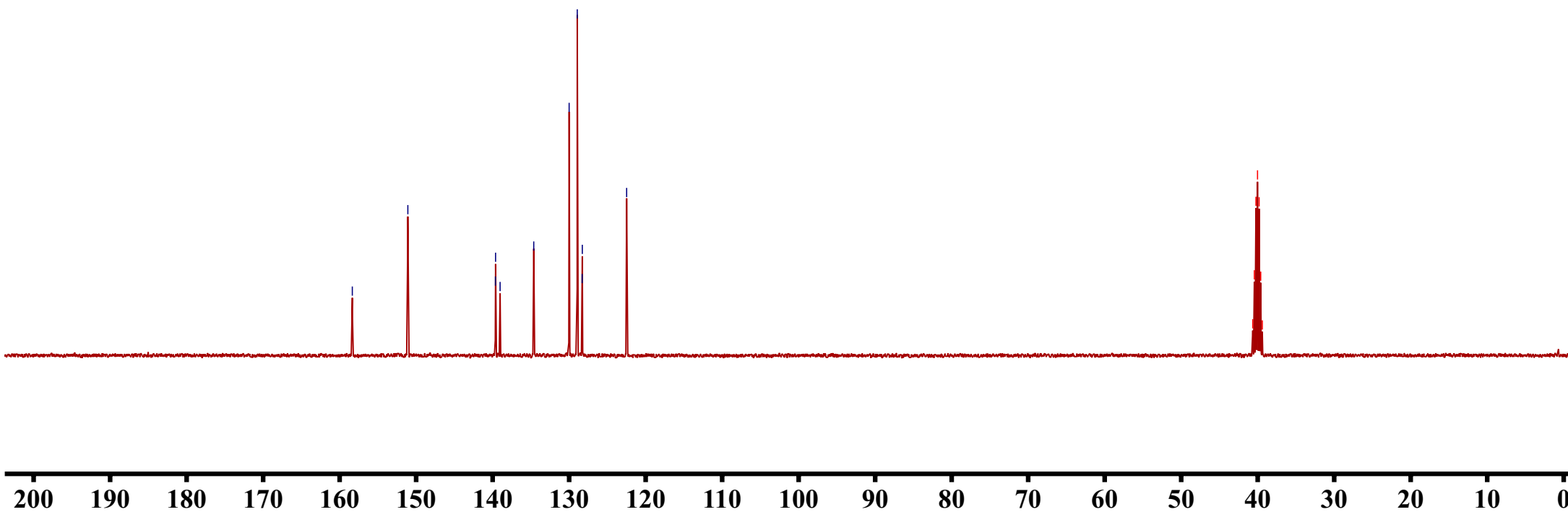


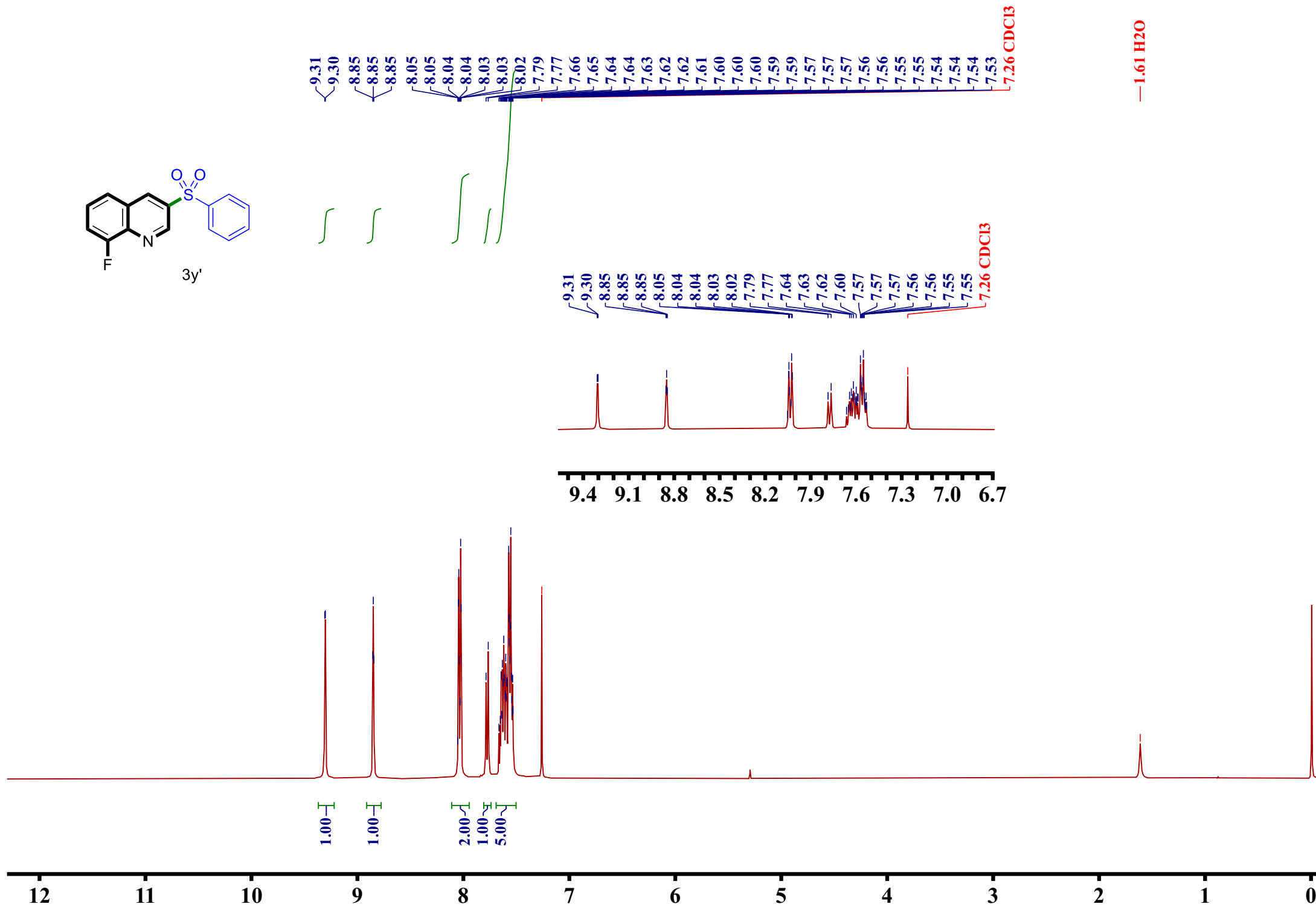
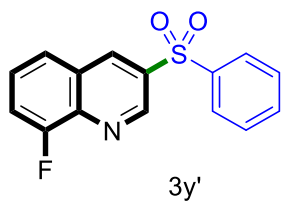


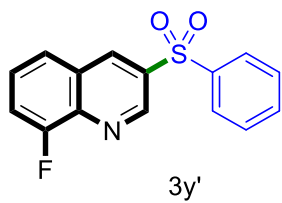
3x'

—158.34
—151.08
139.64
139.62
139.03
134.63
130.00
128.94
128.30
128.28
—122.48

40.65 DMSO
40.44 DMSO
40.23 DMSO
40.02 DMSO
39.81 DMSO
39.60 DMSO
39.39 DMSO

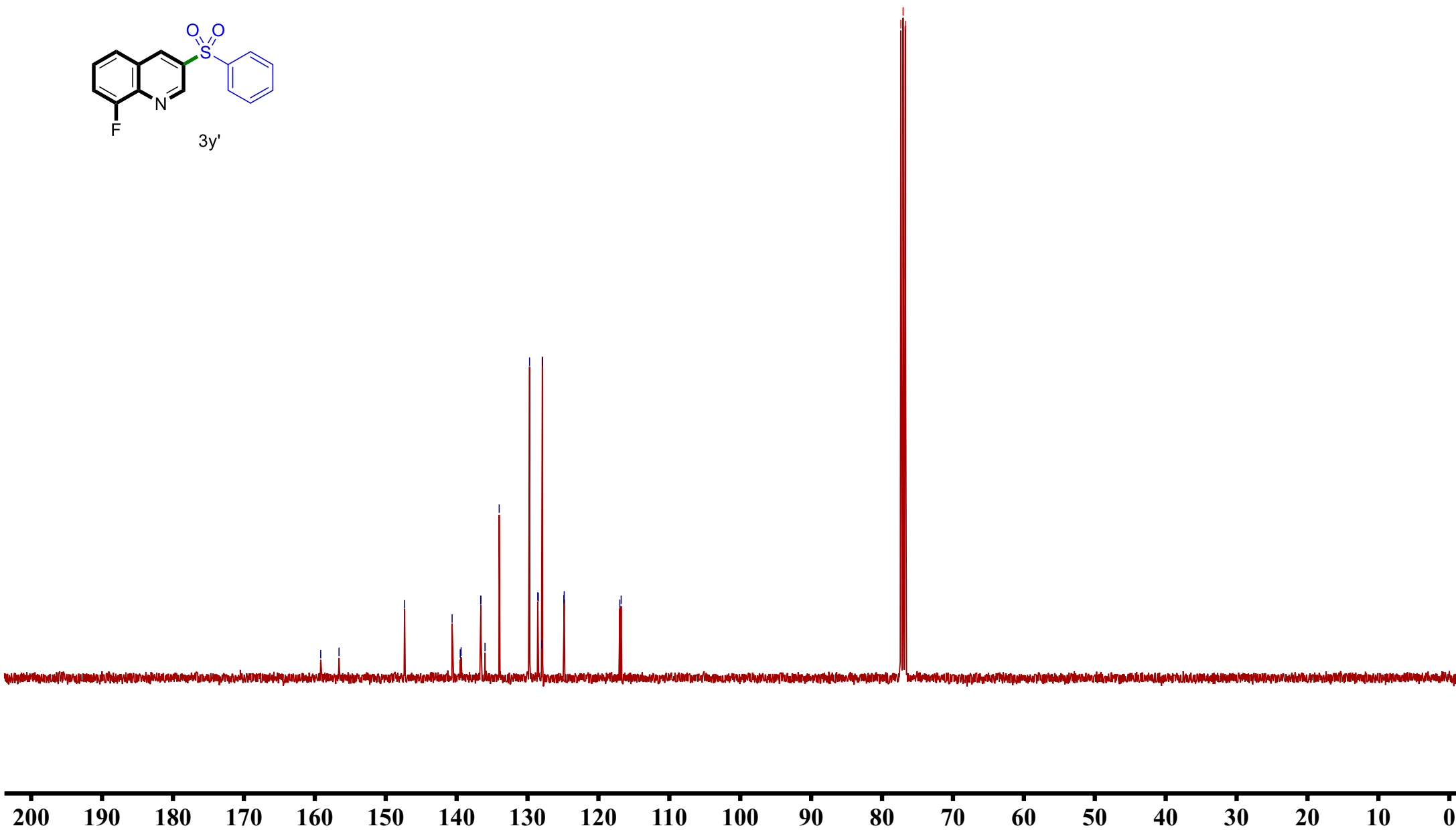


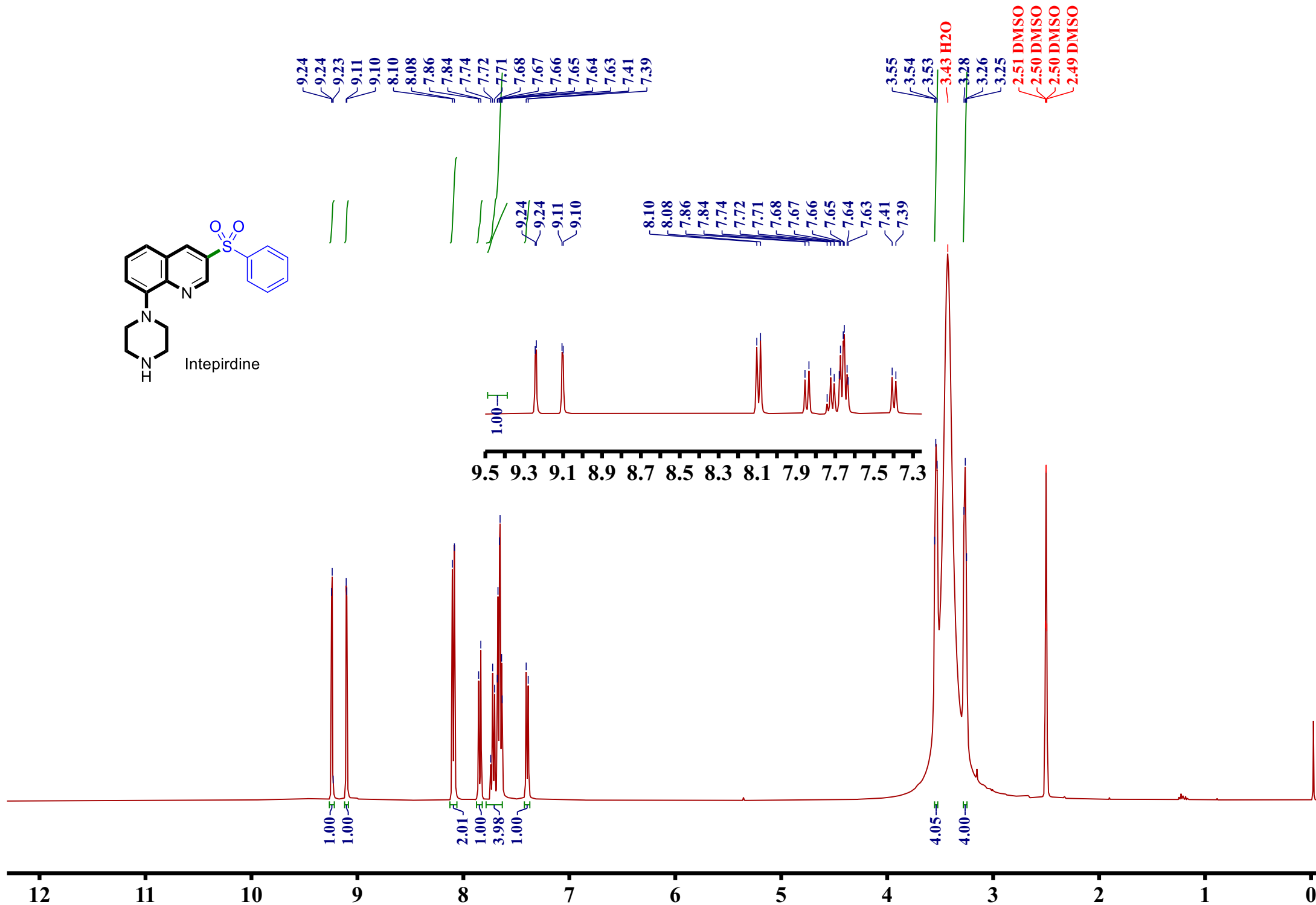
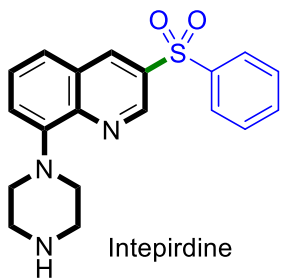


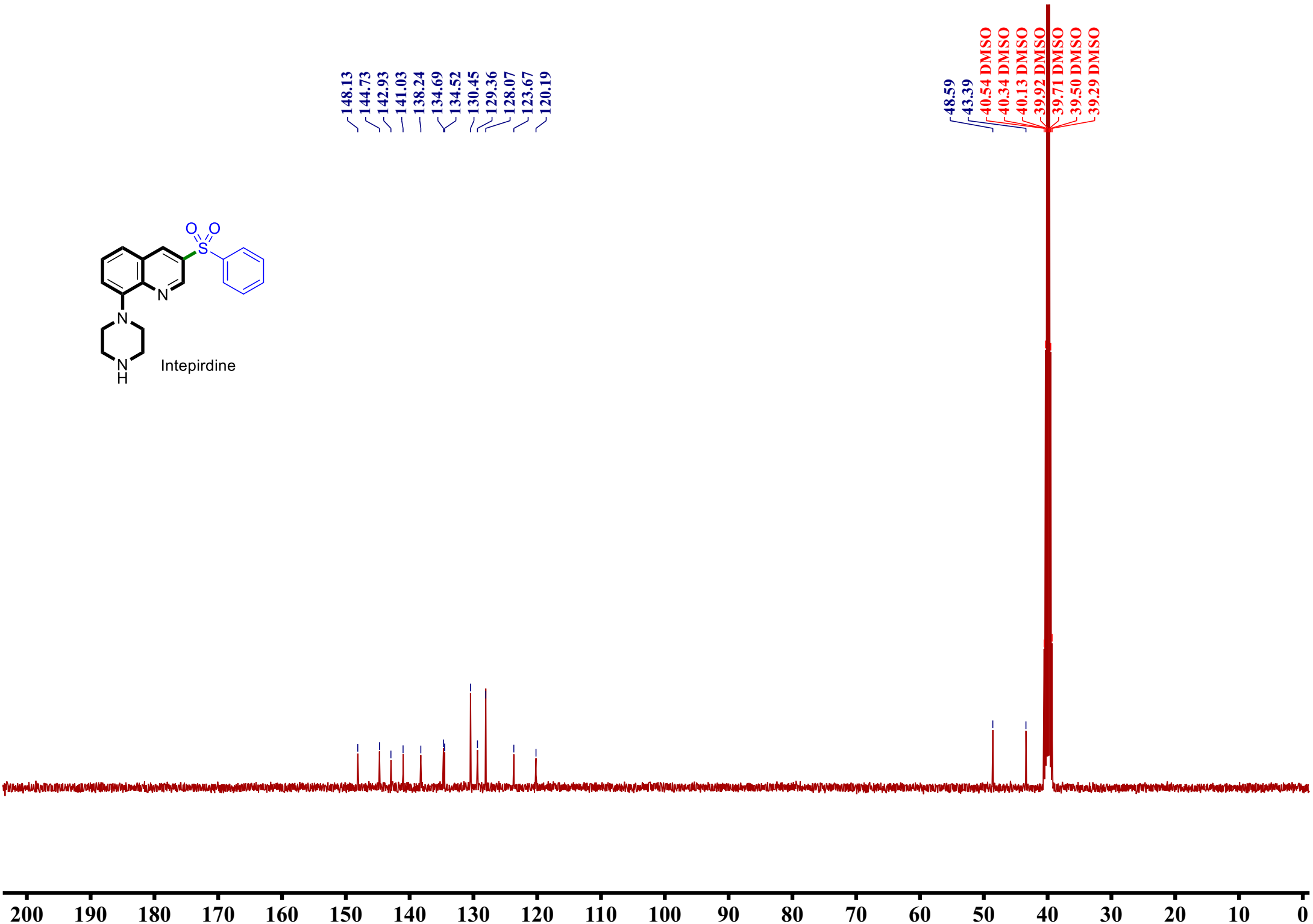
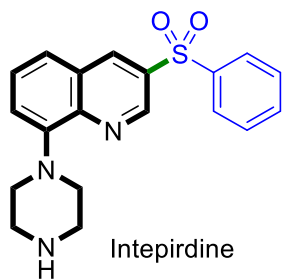


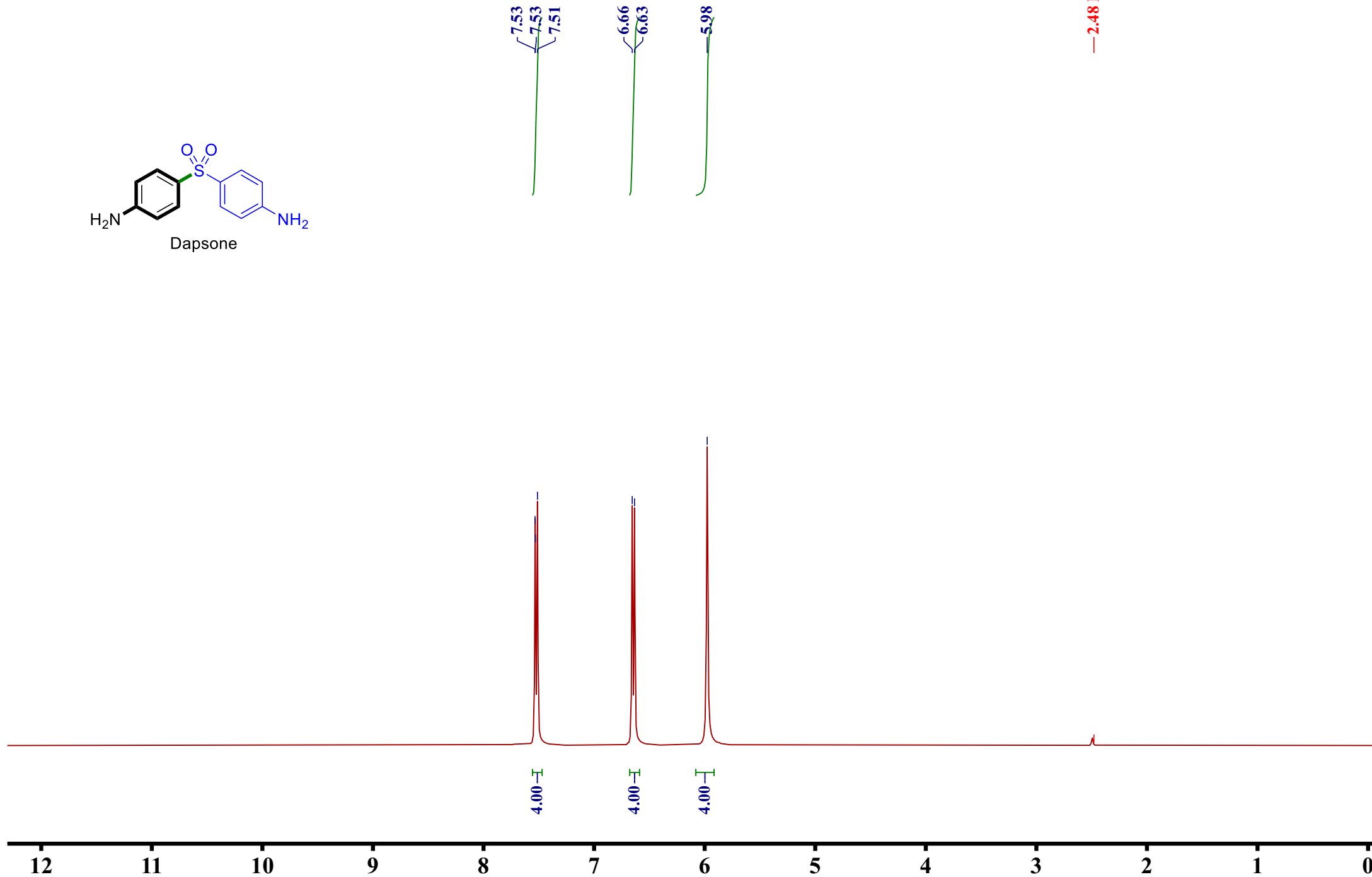
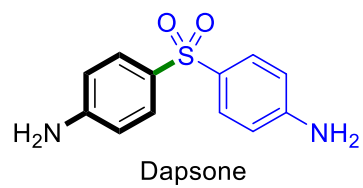
159.16
156.58
147.35
140.64
139.49
139.37
136.61
136.58
136.00
133.99
129.71
128.56
128.48
127.98
127.90
124.87
124.82
116.98
116.79

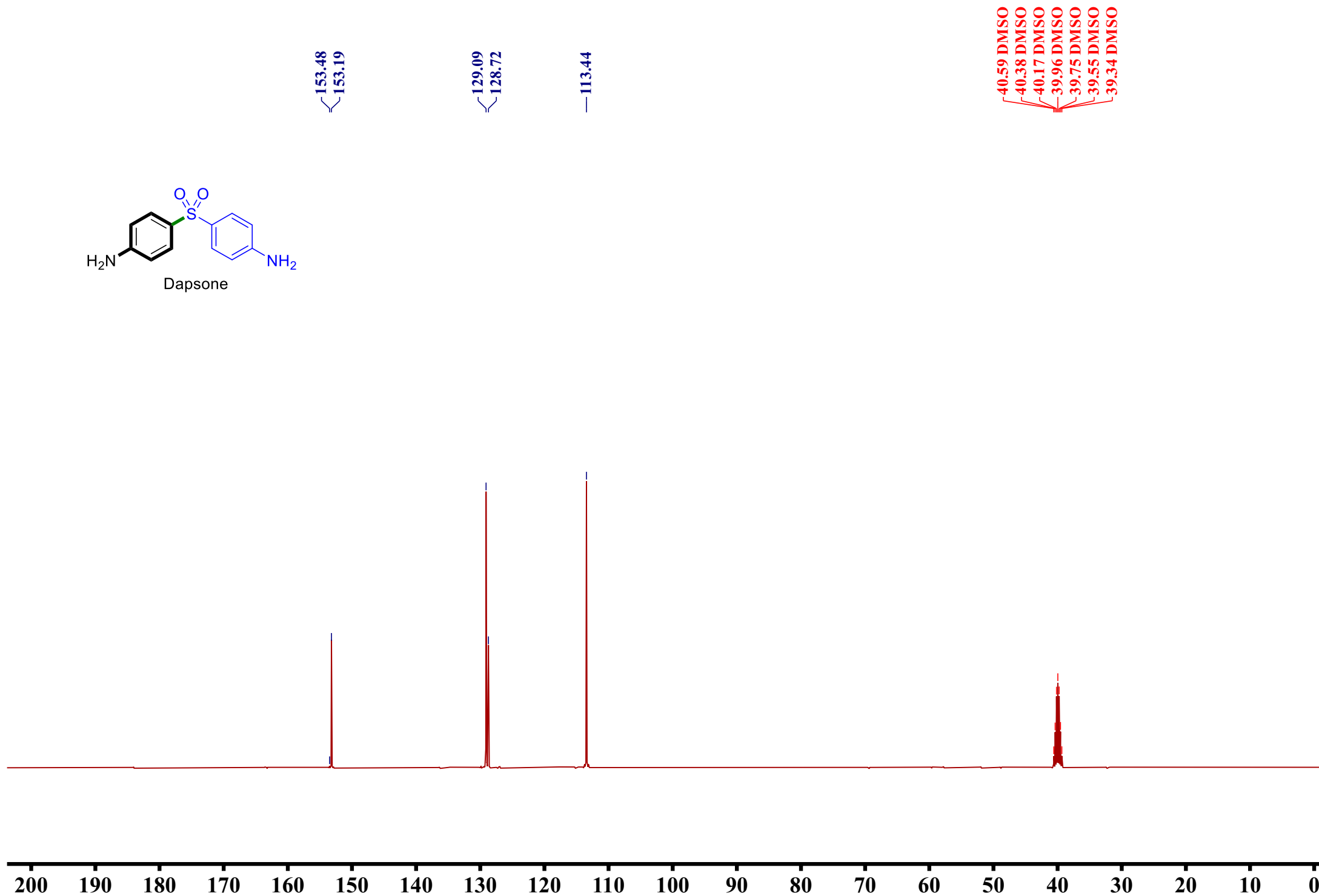
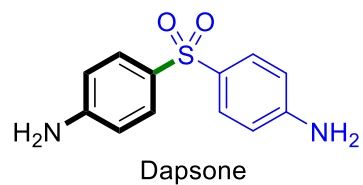
77.35 CDC13
77.04 CDC13
76.72 CDC13

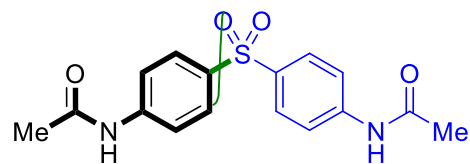












Acedapsone

10.38

7.86
7.86
7.85
7.84
7.83
7.79
7.79
7.78
7.77
7.77
7.76

3.36 H₂O

2.52 DMSO
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO

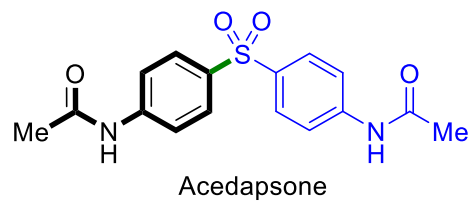
2.08

1.99

4.03
4.04

6.00

12 11 10 9 8 7 6 5 4 3 2 1 0



—169.58

—144.09

—135.52

—128.87

—119.37

40.59 DMSO
40.38 DMSO
40.17 DMSO
39.96 DMSO
39.75 DMSO
39.54 DMSO
39.33 DMSO

—24.61

