

Photoinduced synthesis of α -keto thioamides via thiocarbamoyl 1,4-transposition

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S1. Reagents and methods.

NMR spectra were recorded on a Bruker Fourier 300 at 303°K. Chemical shifts are reported relative to residue peaks of CDCl₃ (7.26 ppm for ¹H and 77.0 ppm for ¹³C), DMSO-*d*₆ (2.50 ppm for ¹H and 39.5 ppm for ¹³C). High-resolution mass spectra (HRMS) spectra were recorded on mass spectrometer Orbitrap LTQ XL with an ESI ion source; needle voltage 3.5 kV/5 kV for negative/positive ions; capillary temperature 350 °C; gas flows — Sheath: 50, Aux: 10; mass range: 100-2000. Samples were introduced *via* an Agilent 1100 chromatograph without a column. The eluent was water/acetonitrile (1/1 v/v) with 0.1% formic acid additive, flow rate 0.35 mL/min, injection volume 1-10 μ L. Macherey-Nagel Silicagel 60 was used for flash chromatography. Thin layer chromatography (TLC) was performed on silica gel 60 F₂₅₄ aluminium sheets (MERCK). Visualization was effected by UV light (254 nm). IUPAC compound names were generated using ChemDraw Software 16.0. Commercially available reagents were used without additional purification. 2-Hydroxy-5-methylisophthalaldehyde was synthesized according to the literature procedure.^{S1}

S2. Solvent optimization

Compound **1a** (20 mg) was dissolved in freshly distilled solvent (2 ml) in a glass vial. The resulting solution was flushed with argon and then obtained solutions were irradiated with 365 nm LED lamp in EvoluChem™ PhotoRedOx box with stirring for 24 h. Then the reaction mixture was evaporated under vacuum or (for DMSO, DMF, DMAc, NMP solutions) dissolved in EtOAc (10 ml), washed with saturated aqueous KCl solution (5×10 ml), dried over anhydrous Na₂SO₄ and evaporated under vacuum. Finally, all residues were analyzed by ¹H NMR in DMSO-*d*₆. The overall aromatic signal from 6.80 ppm to 8.10 ppm (4H) was used as a standard (400%) as a conditional evaluation method.

The quantity of components was evaluated using the following signals:

- singlet signal on 10.00 ppm (1H) for starting aldehyde **1a**
- singlet signal on 10.83 ppm (1H) for product **2a**

The results are presented in Table S1.

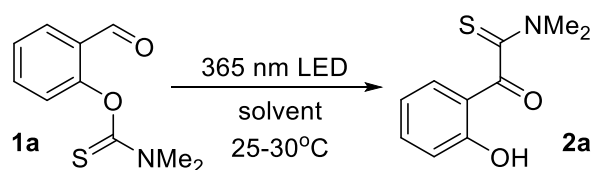


Table S1. Solvents screening results (365 nm, 24h).

Entry	Solvent	2a (%)	1a , (%)
1	DMSO	72	17
2	DMF	52	2
3	DMAc	82	2
4	NMP	63	2
5	Toluene	24	43
6	CHCl ₃	25	46
7	CF ₃ CH ₂ OH	0	51
8	1,4-Dioxane	42	17
9	MeOH	0	37
10	Pyridine	38	0

S3. Experiments with radical quenching reagents

Compound **1a** (30 mg, 0.14 mmol) was dissolved in 3 mL of DMSO- d_6 in a Schlenk vessel. The mixture was degassed under vacuum and filled with argon three times. Next, parts of the solution (0.7 mL) were transferred to three argon-filled NMR tubes and sealed. (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 11 mg, 0.07 mmol) was added to first tube, butylated hydroxytoluene (BHT, 15 mg, 0.07 mmol) was added to the second one, and the last tube was used without additives. NMR tubes with these solutions were sealed and irradiated with 365 nm LED lamp in EvoluchemTM PhotoRedOx box. The mixtures were analyzed by ^1H NMR (see above in Part S2).

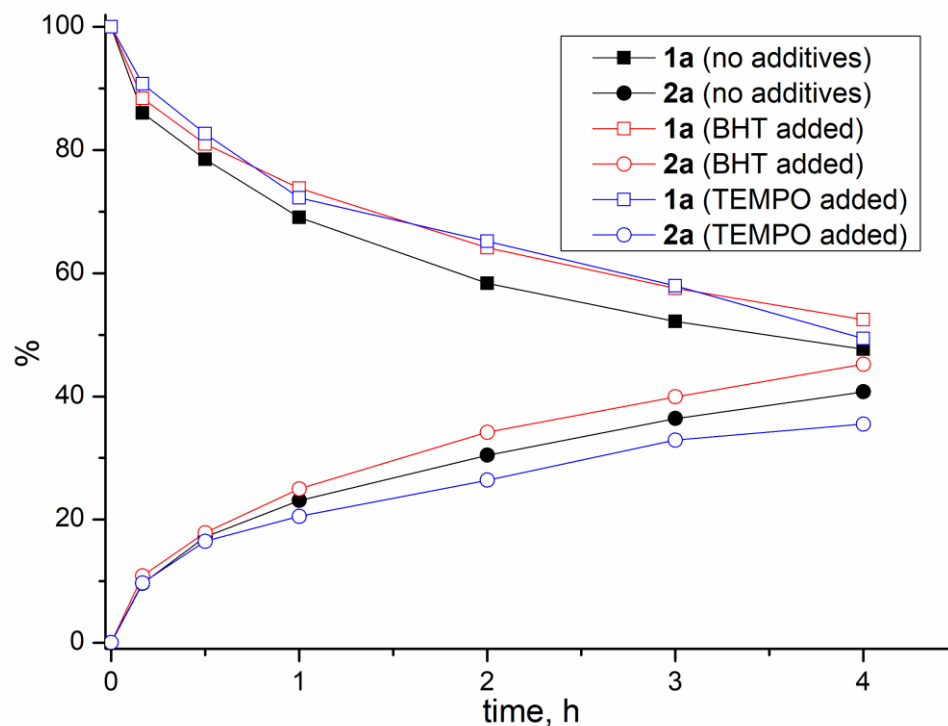
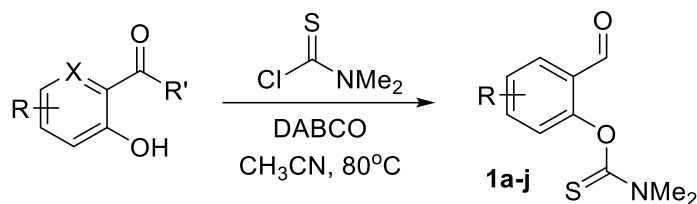


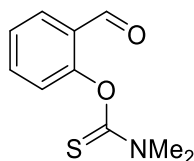
Figure S1. Kinetic study of **1a** phototransformation with BHT and TEMPO.

S4. Synthesis of dimethylcarbamothioates **1**

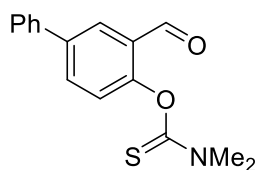


General method

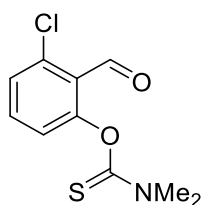
Corresponding 2-hydroxybenzaldehyde (1 equiv.), dimethylcarbamothioic chloride (1.2 equiv.) and DABCO (3 equiv.) were dissolved in CH₃CN (1 mL/ 1 mmol of aldehyde). The resulting mixture was heated at 80 °C for 40 minutes. EtOAc (40 mL) was added, and the resulting mixture was washed with 1M HCl aqueous solution (40 mL), saturated KCl aqueous solution (2×40 mL), and dried over anhydrous Na₂SO₄. All volatiles were removed in vacuo. The product was washed with hexane (2×3 mL) and dried in air.



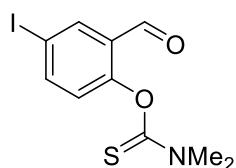
O-(2-formylphenyl) dimethylcarbamothioate **1a**: white solid, Yield 81% (694 mg). ¹H NMR (300 MHz, CDCl₃) δ 10.08 (s, 1H), 7.91 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 3.48 (s, 3H), 3.43 (s, 3H). The spectral properties corresponded to the literature data.^{S2}



O-(3-formyl-[1,1'-biphenyl]-4-yl) dimethylcarbamothioate **1b**: white solid. Yield 87% (267 mg). M.p.142–144 °C. ¹H NMR (300 MHz, CDCl₃) δ 10.13 (s, 1H), 8.12 (d, *J* = 2.4 Hz, 1H), 7.85 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.72 – 7.58 (m, 2H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.42 – 7.34 (m, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 3.50 (s, 3H), 3.45 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 188.5, 187.3, 154.7, 139.7, 139.1, 133.4, 129.4, 129.1, 128.1, 128.1, 127.2, 125.0, 43.6, 39.1. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₆H₁₆NO₂S: 286.0896, found: 286.0899.

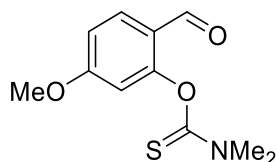


O-(3-chloro-2-formylphenyl) dimethylcarbamothioate **1c**: white solid. Yield 78% (177 mg). M.p.112–114 °C. ¹H NMR (300 MHz, CDCl₃) δ 10.37 (s, 1H), 7.51 (t, *J* = 8.1 Hz, 1H), 7.37 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 3.45 (s, 3H), 3.41 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 188.4, 186.6, 154.1, 138.0, 134.2, 128.5, 126.5, 124.0, 43.5, 39.2. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₀H₁₁ClNO₂S: 244.0194, found: 244.0204.

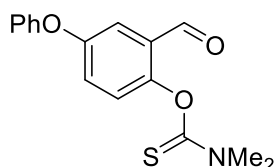


O-(2-formyl-4-iodophenyl) dimethylcarbamothioate **1d**: white solid. Yield 81% (223 mg). M.p.134–136 °C. ¹H NMR (300 MHz, CDCl₃) δ 9.96 (s, 1H), 8.20 (d, *J* = 2.3 Hz, 1H), 7.91 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.90 (d, *J* = 8.5

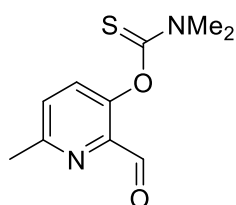
Hz, 1H), 3.47 (s, 3H), 3.42 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 186.9, 186.8, 155.2, 143.6, 138.4, 130.9, 126.7, 90.7, 43.7, 39.2. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{INO}_2\text{S}$: 335.9550, found: 335.9553.



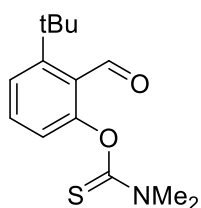
O-(2-formyl-5-methoxyphenyl) dimethylcarbamothioate **1e**: white solid. Yield 58% (538 mg). ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 9.83 (s, 1H), 7.81 (d, J = 8.7 Hz, 1H), 7.01 (dd, J = 8.7, 2.4 Hz, 1H), 6.80 (d, J = 2.4 Hz, 1H), 3.86 (s, 3H), 3.37 (s, 6H). The spectral properties corresponded to the literature data.^{S3}



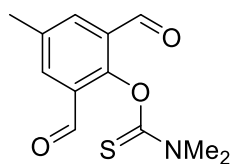
O-(2-formyl-4-phenoxyphenyl) dimethylcarbamothioate **1f**: white solid. Yield 81% (267 mg). M.p. 83–85 °C. ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 9.92 (s, 1H), 7.52 – 7.36 (m, 3H), 7.33 – 7.17 (m, 3H), 7.14 – 7.05 (m, 2H), 3.39 (s, 3H), 3.38 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 187.9, 187.6, 156.3, 155.8, 150.8, 130.2, 130.1, 125.9, 124.8, 124.4, 119.7, 117.7, 43.7, 39.1. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_3\text{S}$: 302.0845, found: 302.0849.



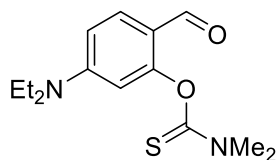
O-(2-formyl-6-methylpyridin-3-yl) dimethylcarbamothioate **1g**: white solid. Yield 79% (557 mg). M.p. 143–145 °C. ^1H NMR (300 MHz, CDCl_3) δ 10.01 (s, 1H), 7.45 – 7.38 (m, 2H), 3.47 (s, 3H), 3.44 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 191.3, 186.7, 156.6, 148.7, 143.9, 133.6, 128.0, 43.6, 39.2, 24.0. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_2\text{S}$: 225.0692, found: 225.0694.



O-(3-(tert-butyl)-2-formylphenyl) dimethylcarbamothioate **1h**: white solid. Yield 90% (191 mg). M.p. 152–154 °C. ^1H NMR (300 MHz, CDCl_3) δ 10.02 (s, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.41 (dd, J = 8.2, 1.8 Hz, 1H), 7.12 (d, J = 1.8 Hz, 1H), 3.48 (s, 3H), 3.42 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 188.3, 187.5, 159.6, 155.3, 129.7, 126.8, 123.7, 121.7, 43.6, 39.1, 35.6, 31.0. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_2\text{S}$: 266.1209, found: 266.1221.

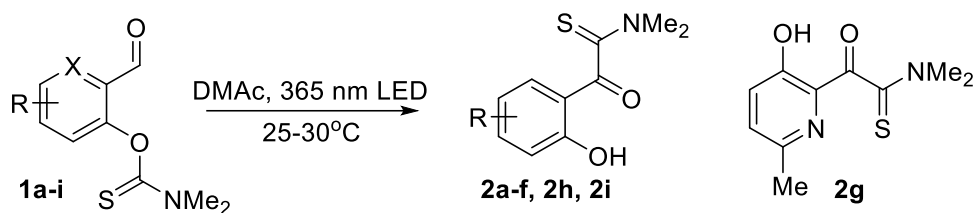


O-(2,6-diformyl-4-methylphenyl) dimethylcarbamothioate **1i**: white solid. Yield 72% (152 mg). M.p. 148–150 °C. ^1H NMR (300 MHz, CDCl_3) δ 10.08 (s, 2H), 7.96 – 7.92 (m, 2H), 3.50 (s, 3H), 3.49 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 187.7, 187.0, 154.5, 137.2, 135.7, 129.9, 43.8, 39.3, 20.9. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{14}\text{NO}_3\text{S}$: 252.0689, found: 252.0689.



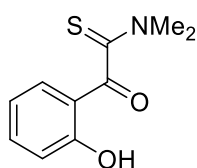
O-(5-(diethylamino)-2-formylphenyl) dimethylcarbamothioate **1j**: white solid. Yield 84% (680 mg). M.p. 120–122 °C. ^1H NMR (300 MHz, CDCl_3) δ 9.74 (s, 1H), 7.70 (d, J = 8.9 Hz, 1H), 6.57 (dd, J = 8.9, 2.5 Hz, 1H), 6.26 (d, J = 2.5 Hz, 1H), 3.47 (s, 3H), 3.45 – 3.36 (m, 7H), 1.21 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 187.3, 186.4, 157.4, 152.9, 132.3, 117.2, 108.8, 105.9, 44.9, 43.4, 39.0, 12.7. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{21}\text{N}_2\text{O}_2\text{S}$: 281.1318, found: 281.1325.

S5. Synthesis of 2-oxoethanethioamides 2

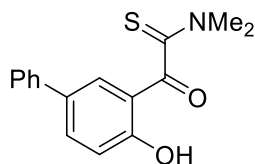


General method

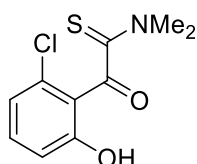
The corresponding starting compound **1** (0.4 mmol) was dissolved in freshly distilled DMAc (8 mL) in a Schlenk vessel. The mixtures were degassed under vacuum and filled with argon three times. The resulting mixture was stirred under 365 nm LED lamp in Evoluchem™ PhotoRedOx box. The progress of the reaction was monitored by TLC and ^1H NMR. After the completion of the reaction, reaction mixtures were dissolved in 100 mL of EtOAc, washed with saturated KCl solution (6×30 mL), and dried over anhydrous Na_2SO_4 . All volatiles were removed in vacuo, and the residue was purified with flash chromatography (eluent: mixture of hexane and EtOAc, v/v 19:1, 6/1).



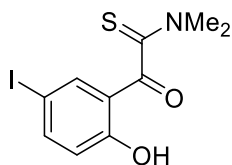
2-(2-hydroxyphenyl)-*N,N*-dimethyl-2-oxoethanethioamide 2a: yellow solid. Yield 64 mg (77% + 10% remained **1a**, 29h of irradiation). M.p. 64–66 °C. ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 10.84 (s, 1H), 7.65 (dd, J = 8.1, 1.8 Hz, 1H), 7.51 (ddd, J = 8.4, 7.2, 1.8 Hz, 1H), 7.01 – 6.76 (m, 2H), 3.42 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 193.8, 193.5, 163.7, 137.6, 132.1, 119.7, 118.8, 116.4, 42.7, 40.5. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{NO}_2\text{S}$: 210.0583, found: 210.0584.



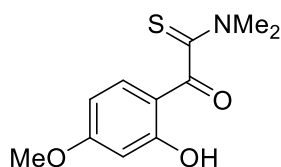
2-(4-hydroxy-[1,1'-biphenyl]-3-yl)-*N,N*-dimethyl-2-oxoethanethioamide 2b: yellow solid. Yield 22 mg (19% + 10% remained **1b**, 48h of irradiation). M.p. 92–94 °C. ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 10.96 (s, 1H), 7.90 (d, J = 2.4 Hz, 1H), 7.83 (dd, J = 8.6, 2.4 Hz, 1H), 7.66 – 7.55 (m, 2H), 7.53 – 7.41 (m, 2H), 7.40 – 7.29 (m, 1H), 7.05 (d, J = 8.6 Hz, 1H), 3.43 (s, 3H), 3.25 (s, 3H). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 195.8, 188.3, 158.8, 138.9, 134.4, 131.5, 129.1, 128.6, 127.2, 126.2, 120.3, 118.3, 42.2, 39.9. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_2\text{S}$: 286.0896, found: 286.0897.



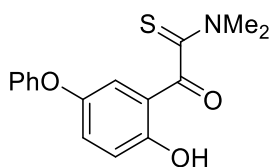
2-(2-chloro-6-hydroxyphenyl)-*N,N*-dimethyl-2-oxoethanethioamide 2c: yellow solid. Yield 81 mg (83%, 24h of irradiation). M.p. 110–112 °C. ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 10.80 (s, 1H), 7.28 (t, J = 8.1 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 6.81 (d, J = 8.3 Hz, 1H), 3.40 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 195.3, 183.8, 157.2, 133.4, 132.7, 124.0, 120.9, 114.9, 42.6, 40.8. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{ClNO}_2\text{S}$: 244.0194, found: 244.0193.



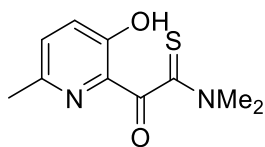
2-(2-hydroxy-5-iodophenyl)-*N,N*-dimethyl-2-oxoethanethioamide **2d**: yellow solid. Yield 98 mg (95%, 24h of irradiation). M.p.164–166 °C. ^1H NMR (300 MHz, DMSO- d_6) δ 11.02 (s, 1H), 7.91 (d, J = 2.4 Hz, 1H), 7.75 (dd, J = 8.6, 2.4 Hz, 1H), 6.78 (d, J = 8.6 Hz, 1H), 3.39 (s, 3H), 3.20 (s, 3H). ^{13}C NMR (75 MHz, DMSO- d_6) δ 195.6, 186.2, 158.3, 143.6, 138.5, 123.2, 120.2, 81.3, 42.1, 39.8. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{INO}_2\text{S}$: 335.9550, found: 335.9554.



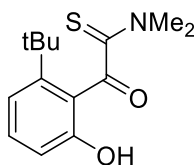
2-(2-hydroxy-4-methoxyphenyl)-*N,N*-dimethyl-2-oxoethanethioamide **2e**: yellow oil. Yield 35 mg (37% + 37% remained **1e**, 154h of irradiation). ^1H NMR (300 MHz, DMSO) δ 11.33 (s, 1H), 7.53 (d, J = 8.8 Hz, 1H), 6.55 (dd, J = 8.8, 2.4 Hz, 1H), 6.50 (d, J = 2.4 Hz, 1H), 3.82 (s, 3H), 3.42 (s, 3H), 3.19 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 194.2, 189.7, 166.2, 163.6, 133.4, 111.5, 108.0, 101.1, 55.9, 42.2, 39.9. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{14}\text{NO}_3\text{S}$: 240.0689, found: 240.0688.



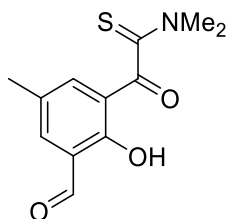
2-(2-hydroxy-5-phenoxyphenyl)-*N,N*-dimethyl-2-oxoethanethioamide **2f**: yellow oil. Yield 36 mg (30%, 24h of irradiation). ^1H NMR (300 MHz, DMSO- d_6) δ 10.72 (s, 1H), 7.46 – 7.33 (m, 2H), 7.31 – 7.20 (m, 2H), 7.17 – 7.05 (m, 1H), 7.05 – 6.89 (m, 3H), 3.38 (s, 3H), 3.20 (s, 3H). ^{13}C NMR (75 MHz, DMSO- d_6) δ 195.8, 187.2, 157.3, 155.4, 148.5, 130.1, 127.7, 123.2, 120.7, 119.9, 119.2, 117.8, 42.1. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_3\text{S}$: 302.0845, found: 302.0847.



2-(3-hydroxy-6-methylpyridin-2-yl)-*N,N*-dimethyl-2-oxoethanethioamide **2g**: yellow solid. Yield 64 mg (71% + 10% remained **1g**, 42h of irradiation). M.p.174–176 °C. ^1H NMR (300 MHz, DMSO- d_6) δ 10.57 (s, 1H), 7.40 (d, J = 8.7 Hz, 1H), 7.36 (d, J = 8.7 Hz, 1H), 3.44 (s, 3H), 3.22 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, DMSO- d_6) δ 195.7, 188.5, 155.4, 149.1, 134.8, 129.8, 126.7, 42.4, 39.6, 23.2. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_2\text{S}$: 225.0692, found: 225.0703.

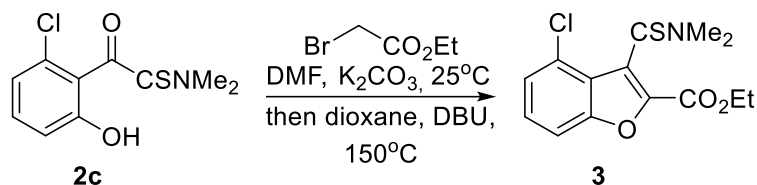


2-(2-(tert-butyl)-6-hydroxyphenyl)-*N,N*-dimethyl-2-oxoethanethioamide **2h**: yellow oil. Yield 40 mg (39%, 48h of irradiation). ^1H NMR (300 MHz, DMSO- d_6) δ 10.82 (s, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.02 (dd, J = 8.4, 1.8 Hz, 1H), 6.95 (d, J = 1.8 Hz, 1H), 3.42 (s, 3H), 3.20 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (75 MHz, DMSO- d_6) δ 195.0, 189.3, 160.2, 160.1, 131.1, 117.2, 116.3, 114.2, 42.2, 35.0, 30.5. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_2\text{S}$: 266.1209, found: 266.1217.

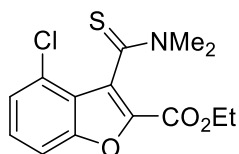


2-(2-formyl-6-hydroxy-4-methylphenyl)-*N,N*-dimethyl-2-oxoethanethioamide **2i**: yellow solid. Yield 80 mg (87%, 21h of irradiation). M.p.160–162 °C. ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 11.60 (s, 1H), 10.19 (s, 1H), 7.85 (d, J = 2.4 Hz, 1H), 7.80 (d, J = 2.4 Hz, 1H), 3.45 (s, 3H), 3.26 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 193.8, 192.6, 188.1, 159.8, 138.1, 137.5, 129.2, 123.2, 120.9, 42.3, 40.0, 19.6. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{14}\text{NO}_3\text{S}$: 252.0689, found: 252.0692.

S6. Synthesis of ethyl 4-chloro-3-(dimethylcarbamothioyl)benzofuran-2-carboxylate **3**

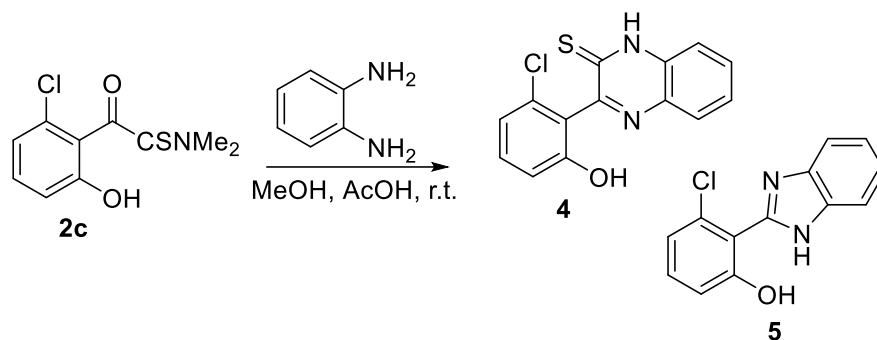


The substance was obtained by the described^{S4} method: A mixture of compound **2c** (16 mg, 0.066 mmol), ethyl bromoacetate (12 mg, 0.069 mmol) and K₂CO₃ (11 mg, 0.08 mmol) in freshly distilled DMF (0.5 mL) was stirred at room temperature for 24 h. EtOAc (20 mL) was added, and the resulting mixture was washed with brine (3×20 mL). Organic layer was dried over anhydrous Na₂SO₄, all volatiles were removed in vacuo. The residue was dissolved in dioxane (1 mL) and DBU (0.06 mmol) was added. The mixture was heated in an autoclave at 150 °C for 6 h. The reaction mixture was evaporated, and the residue was purified with flash chromatography (eluent – mixture of hexane and EtOAc, v/v 100/1, 9/1, 4:1).

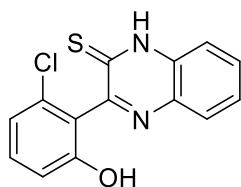


ethyl 4-chloro-3-(dimethylcarbamothioyl)benzofuran-2-carboxylate 3: white solid. Yield 10 mg (58%). M.p. 125–127 °C. ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.78 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.59 (t, *J* = 8.1 Hz, 1H), 7.47 (dd, *J* = 7.8, 0.8 Hz, 1H), 4.31 (qd, *J* = 7.1, 1.3 Hz, 2H), 3.54 (s, 3H), 3.18 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 187.4, 157.7, 154.4, 137.7, 129.5, 128.3, 126.3, 125.0, 122.4, 111.6, 61.6, 43.2, 41.6, 13.9. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₄H₁₅ClNO₃S: 312.0456, found: 312.0460.

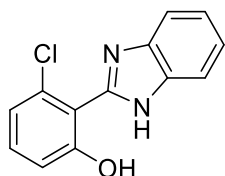
S7. Synthesis of 3-(2-chloro-6-hydroxyphenyl)quinoxaline-2(1H)-thione **4 and 2-(1H-benzo[d]imidazol-2-yl)-3-chlorophenol **5****



The substances were obtained by the described^{S4} method: compound **2c** (17 mg, 0.07 mmol), benzene-1,2-diamine (8 mg, 0.08 mmol) and AcOH (50 μ l) were dissolved in 0.5 mL of MeOH. The resulting mixture was stirred for 48 hours. MeOH was removed in vacuo, and the residue was purified by flash chromatography (eluent - mixture of hexane and EtOAc, v/v 6/1, 3/1, 2/1).

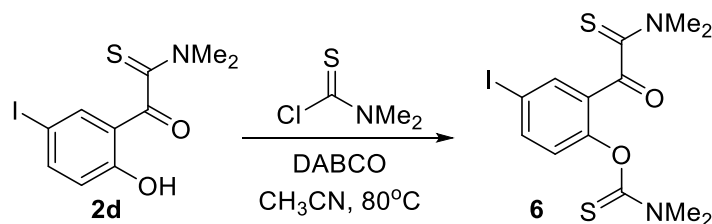


3-(2-chloro-6-hydroxyphenyl)quinoxaline-2(1H)-thione **4**: yellow oil. Yield 8 mg (44%). ¹H NMR (300 MHz, DMSO-*d*₆) δ 14.49 (s, 1H), 9.86 (s, 1H), 7.87 (d, *J* = 6.8 Hz, 1H), 7.73 – 7.65 (m, 1H), 7.60 (d, *J* = 6.9 Hz, 1H), 7.53 – 7.42 (m, 1H), 7.23 (t, *J* = 8.1 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 174.9, 159.6, 156.1, 135.1, 132.2, 132.0, 131.5, 130.0, 128.8, 125.9, 125.7, 119.2, 115.7, 114.3. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₄H₉ClN₂O₂: 289.0197, found: 289.0208.



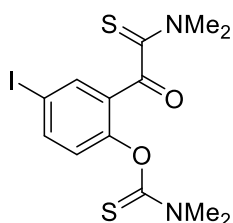
2-(1H-benzo[d]imidazol-2-yl)-3-chlorophenol **5**: yellow oil. Yield 5 mg (31%). ¹H NMR (300 MHz, CDCl₃) δ 8.46 – 8.37 (m, 1H), 8.24 – 8.13 (m, 1H), 7.92 – 7.77 (m, 2H), 7.70 – 7.56 (m, 2H), 7.49 (dd, *J* = 6.8, 2.0 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 158.8, 155.5, 141.7, 139.6, 132.5, 130.6, 130.5, 130.1, 128.7, 128.6, 125.6, 119.6, 111.2. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₃H₁₀ClN₂O: 245.0476, found: 245.0477.

S8. Synthesis of O-(2-(2-(dimethylamino)-2-thioxoacetyl)-4-iodophenyl) dimethylcarbamothioate **6**



General method

2-(2-Hydroxy-5-iodophenyl)-N,N-dimethyl-2-oxoethanethioamide (50 mg, 0.15 mmol, 1 equiv.), dimethylcarbamothioic chloride (22 mg, 0.18 mmol, 1.2 equiv.) and DABCO (34 mg, 0.30 mmol, 3 equiv.) were dissolved in CH₃CN (0.2 mL). The resulting mixture was heated at 80 °C for 40 minutes. EtOAc (40 mL) was added, and the resulting mixture was washed with 1M HCl aqueous solution (40 mL), saturated KCl aqueous solution (2×40 mL), and dried over anhydrous Na₂SO₄. All volatiles were removed in vacuo. The product was washed with hexane (2×3 mL) and dried in air.

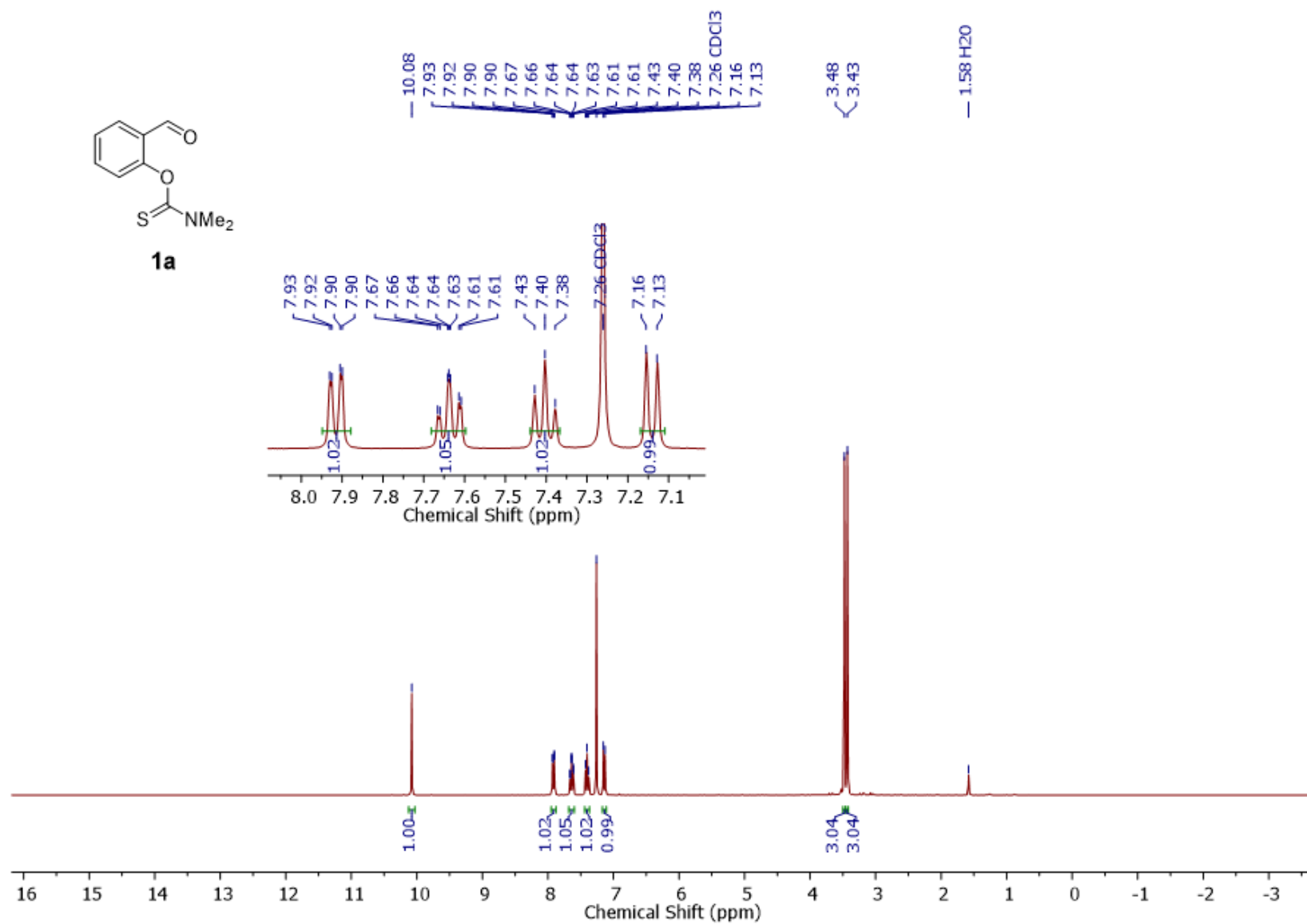


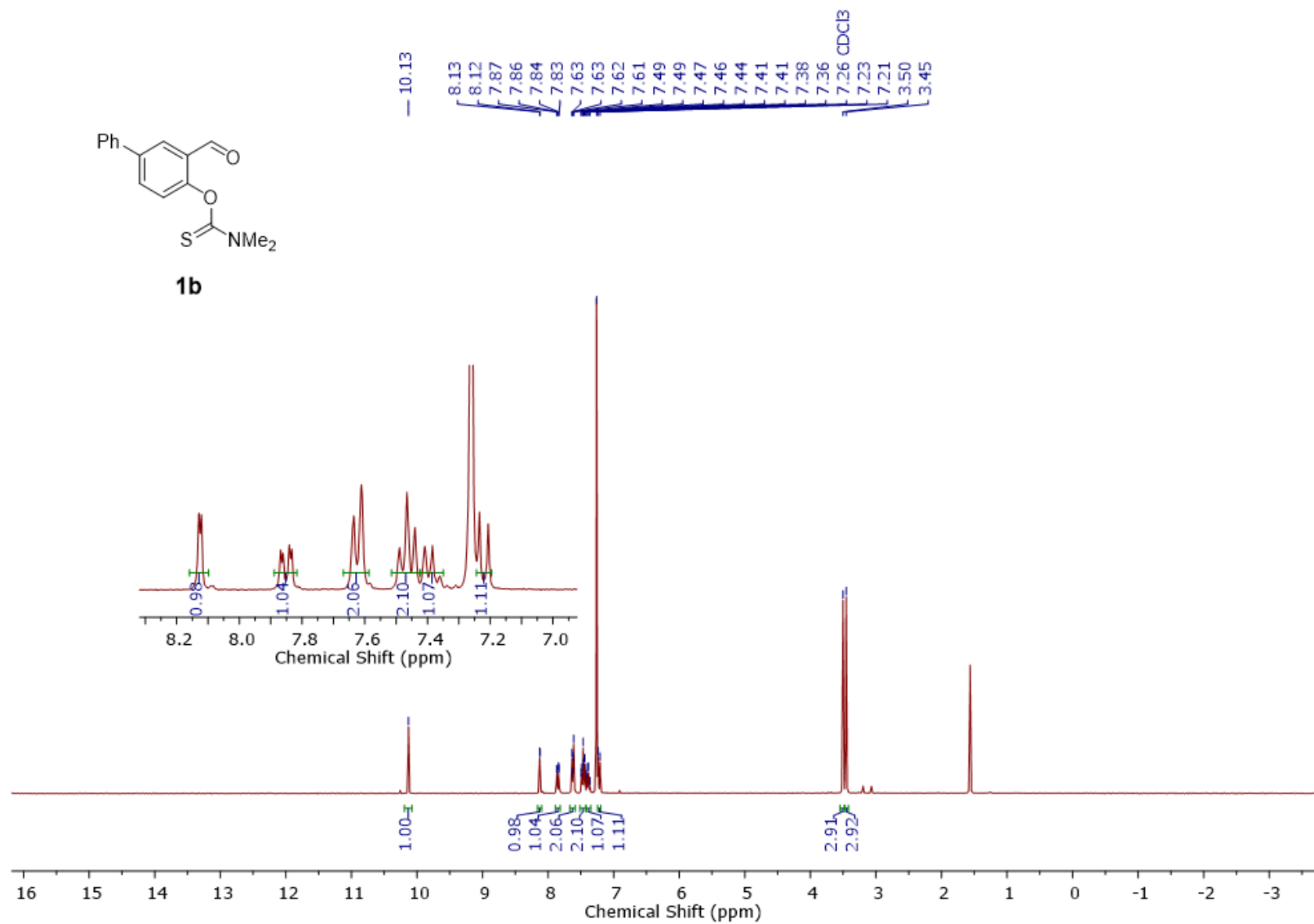
O-(2-(2-(dimethylamino)-2-thioxoacetyl)-4-iodophenyl) dimethylcarbamothioate **6**: yellow solid. Yield 65% (28 mg). M.p. 169–171 °C. ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.11 (d, *J* = 2.2 Hz, 1H), 8.02 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 3.43 (s, 3H), 3.36 (s, 3H), 3.27 (s, 3H), 3.21 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 193.7, 185.1, 182.7, 152.3, 142.9, 138.9, 129.9, 127.7, 91.0, 42.9, 42.9, 40.3, 38.8. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₃H₁₆IN₂O₂S₂: 422.9692, found: 422.9695.

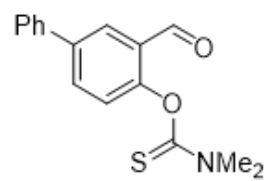
S9. References

- S1. J. Xu, Z. Xu, Z. Wang, C. Liu, B. Zhu, X. Wang, K. Wang, J. Wang and G. Sang, *Luminescence*, 2018, **33**, 219; <https://doi.org/10.1002/bio.3404>.
- S2. Y. Zhao, Y. Xie, C. Xia and H. Huang, *Adv. Synth. Catal.*, 2014, **356**, 2471; <https://doi.org/10.1002/adsc.201400306>.
- S3. S. Chen, X. Liu, Q. Li, S. Fu, H. Zhang, S. Li, L. Wang, C. He, W. Chen and P. Hou, *J. Hazard. Mater.*, 2024, **465**, 133253; <https://doi.org/10.1016/j.jhazmat.2023.133253>.
- S4. V. E. Opryshko, A. Yu. Smirnov, I. N. Myasyanko, A. A. Mikhaylov, M. S. Baranov and D. S. Ivanov, *Org. Biomol. Chem.*, 2025, **23**, 10357; <https://doi.org/10.1039/D5OB01527H>.

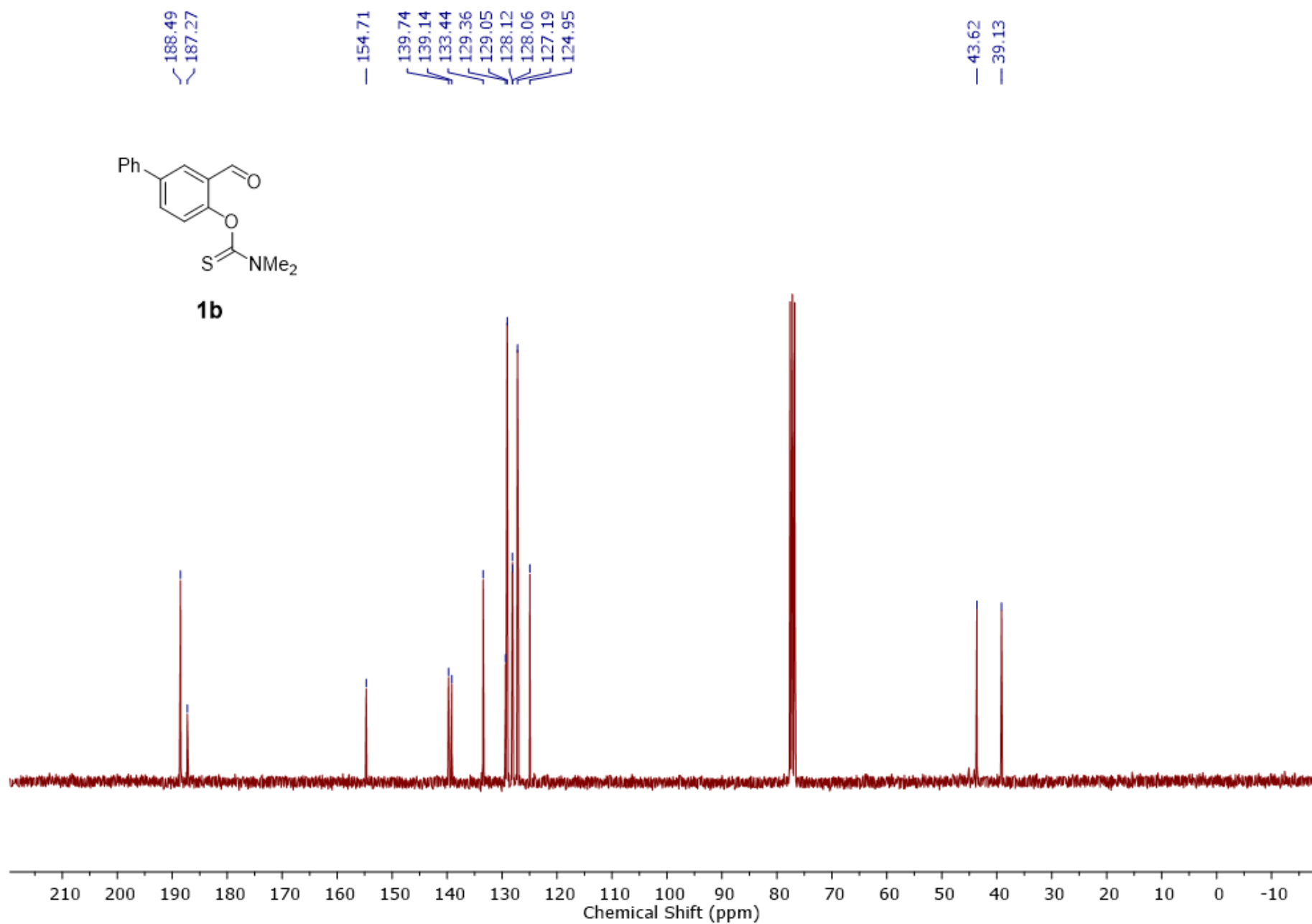
S10. Copies of ^1H and ^{13}C NMR spectra

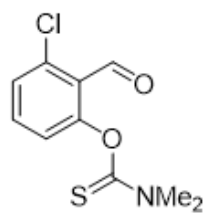




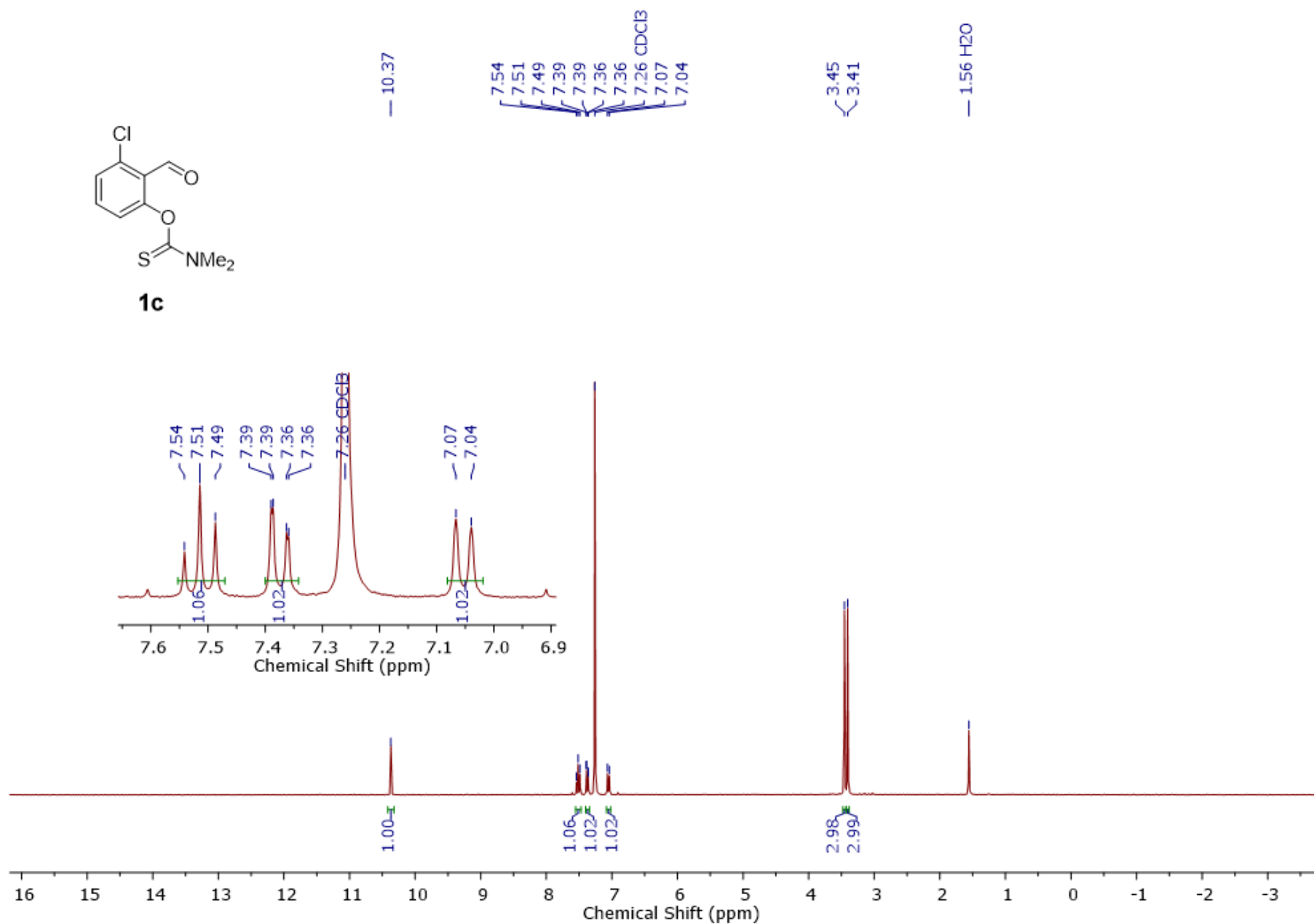


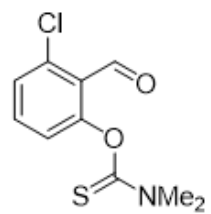
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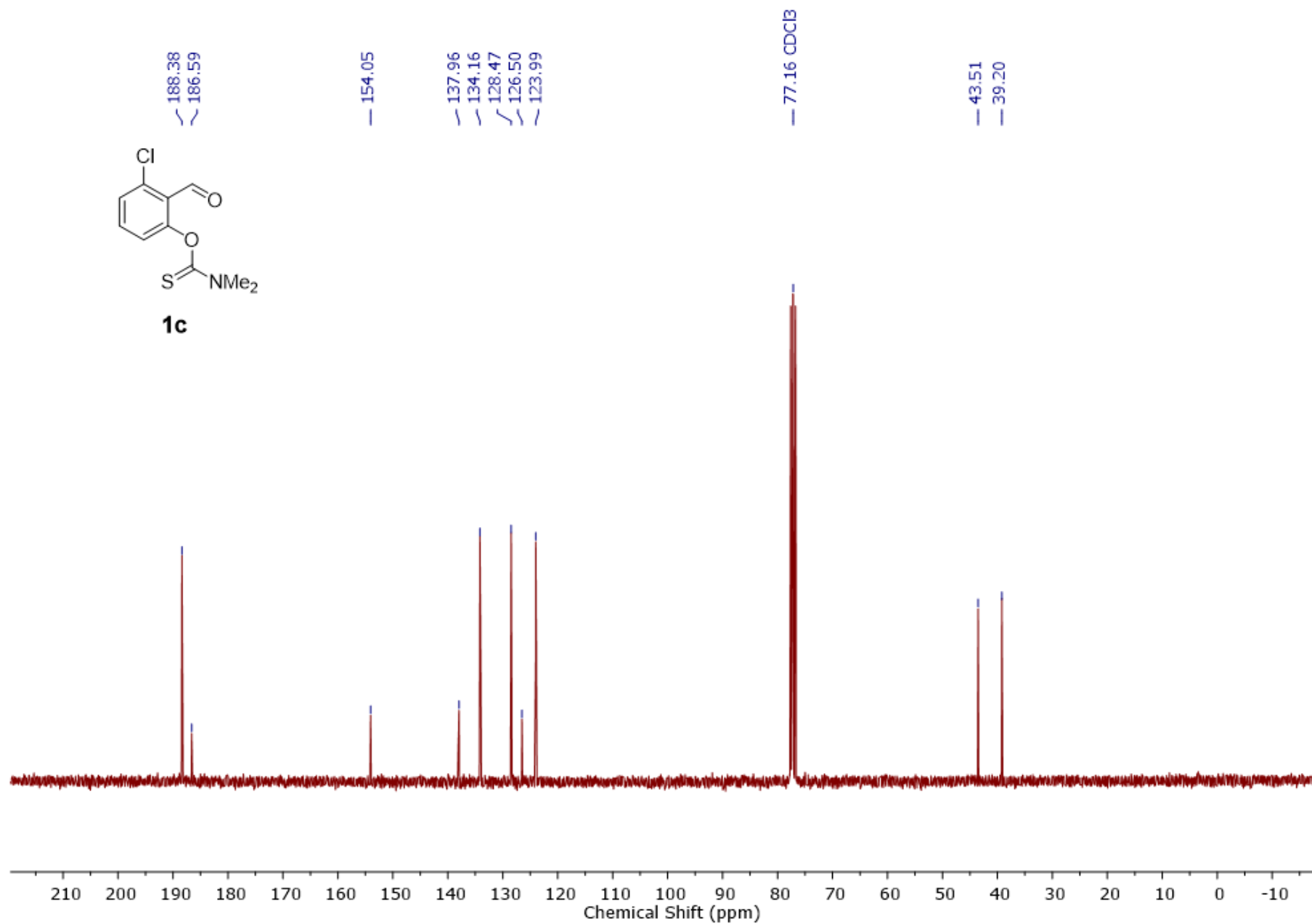


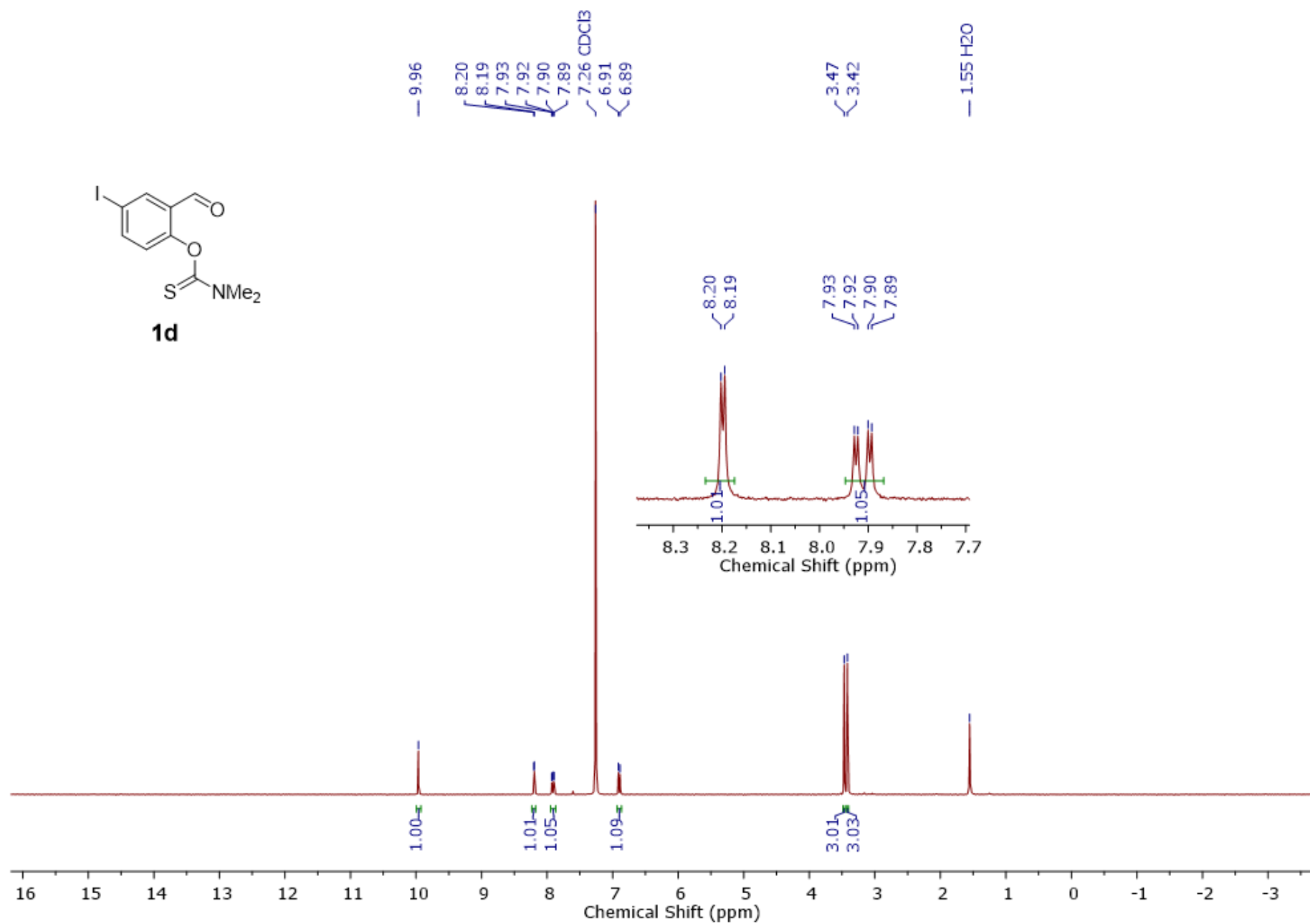
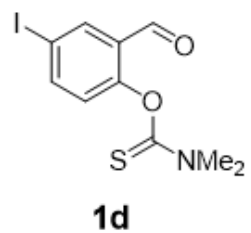
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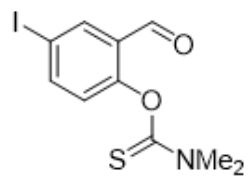




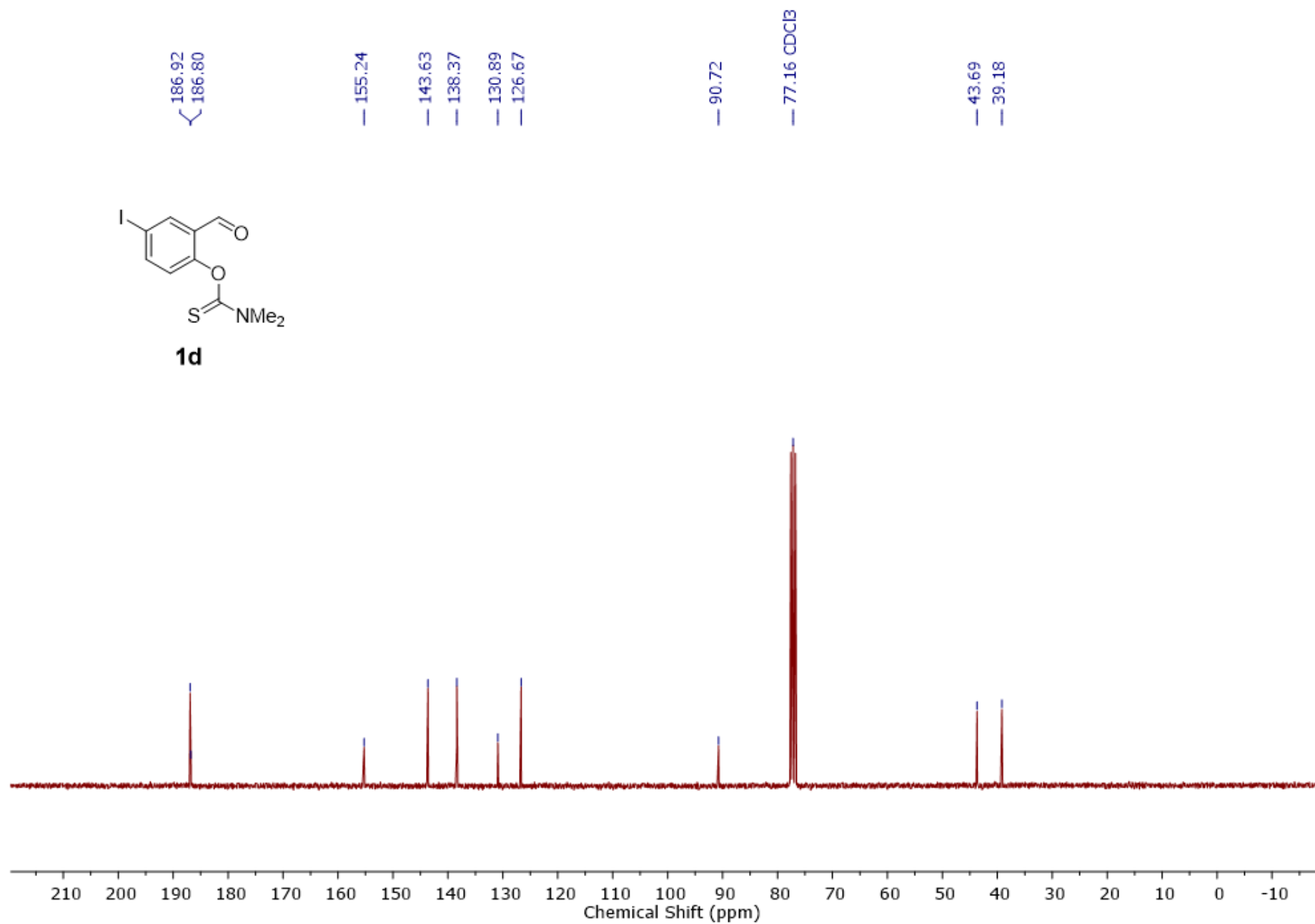
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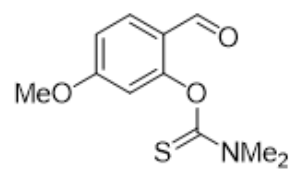




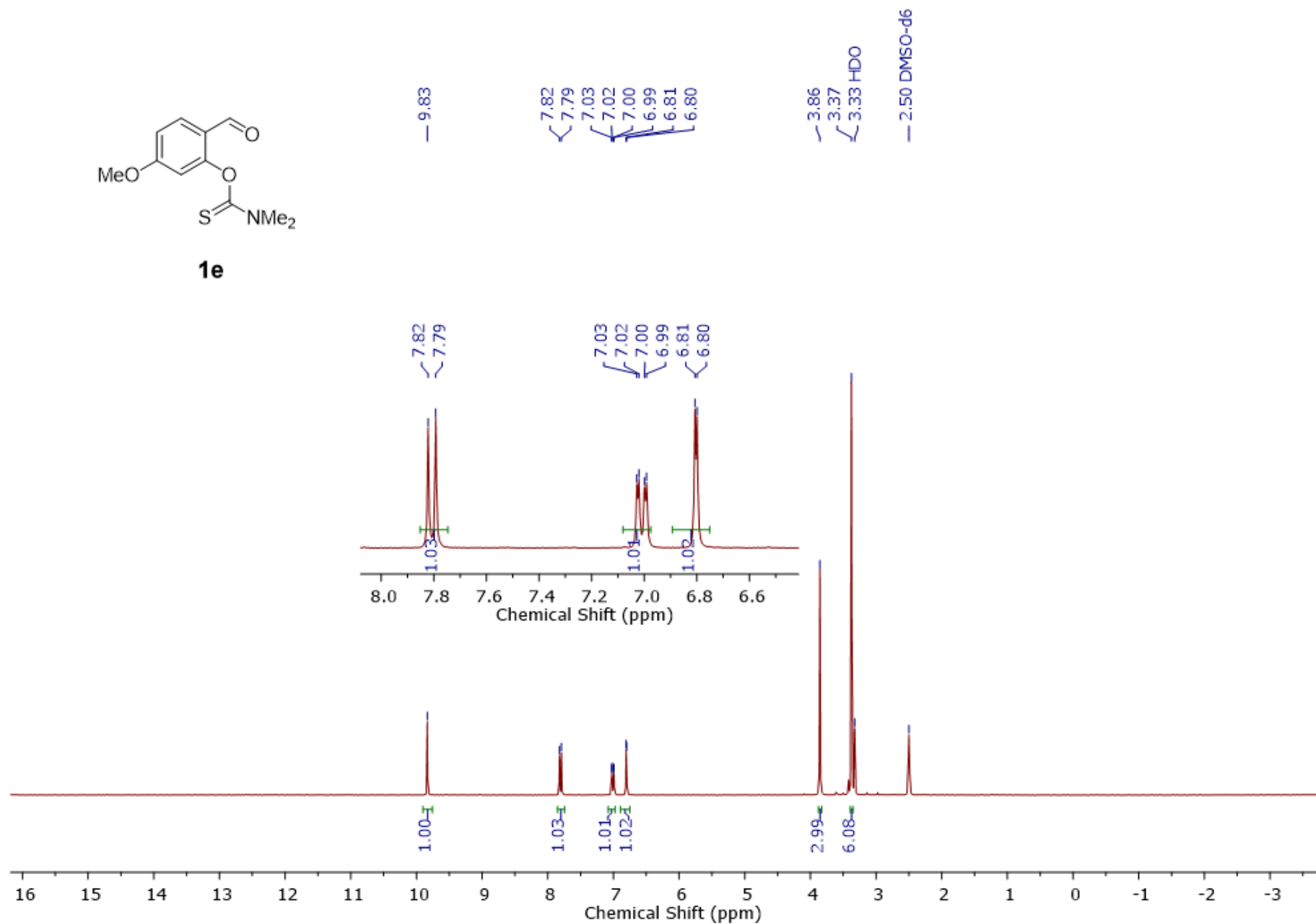


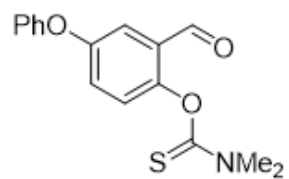
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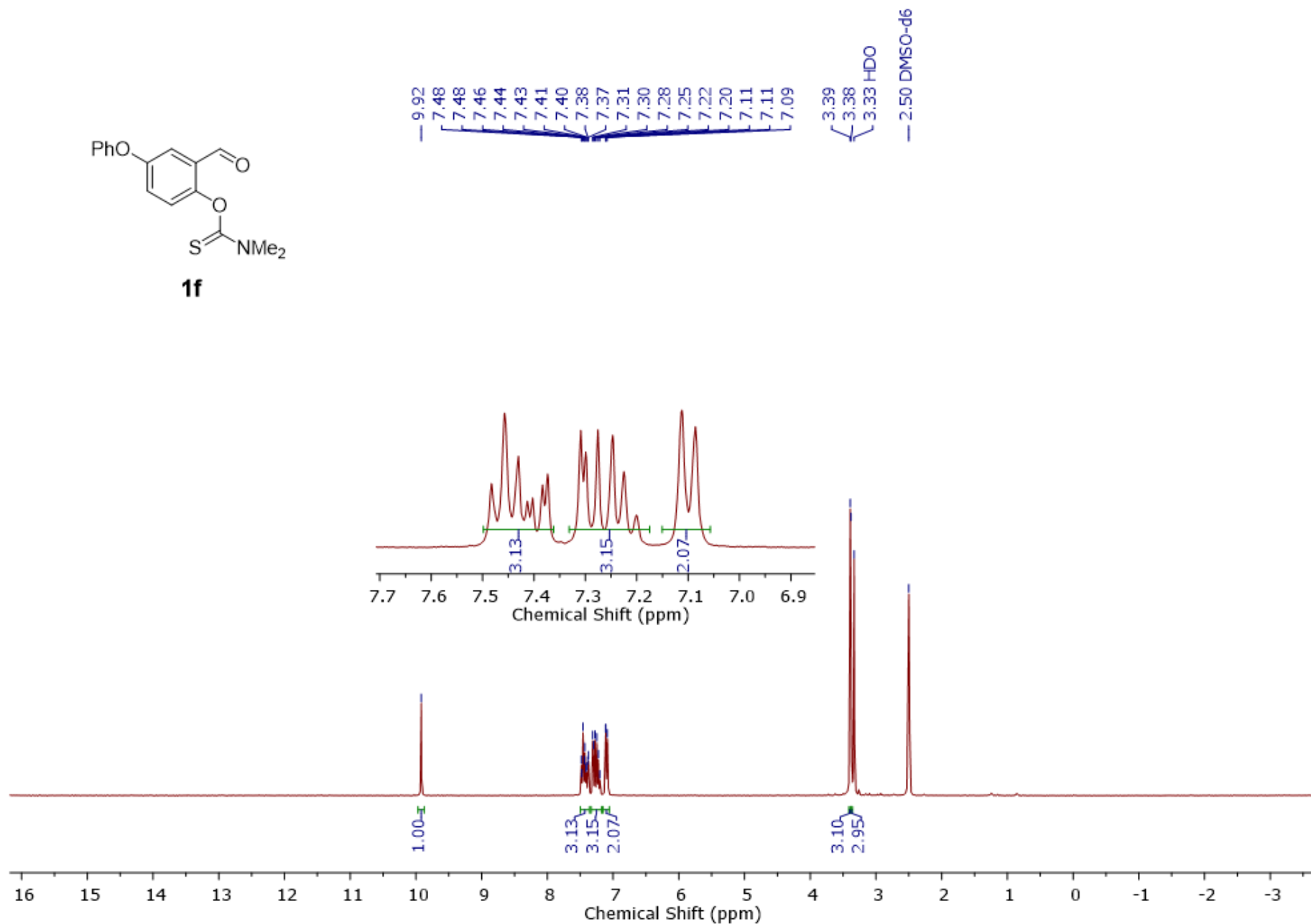


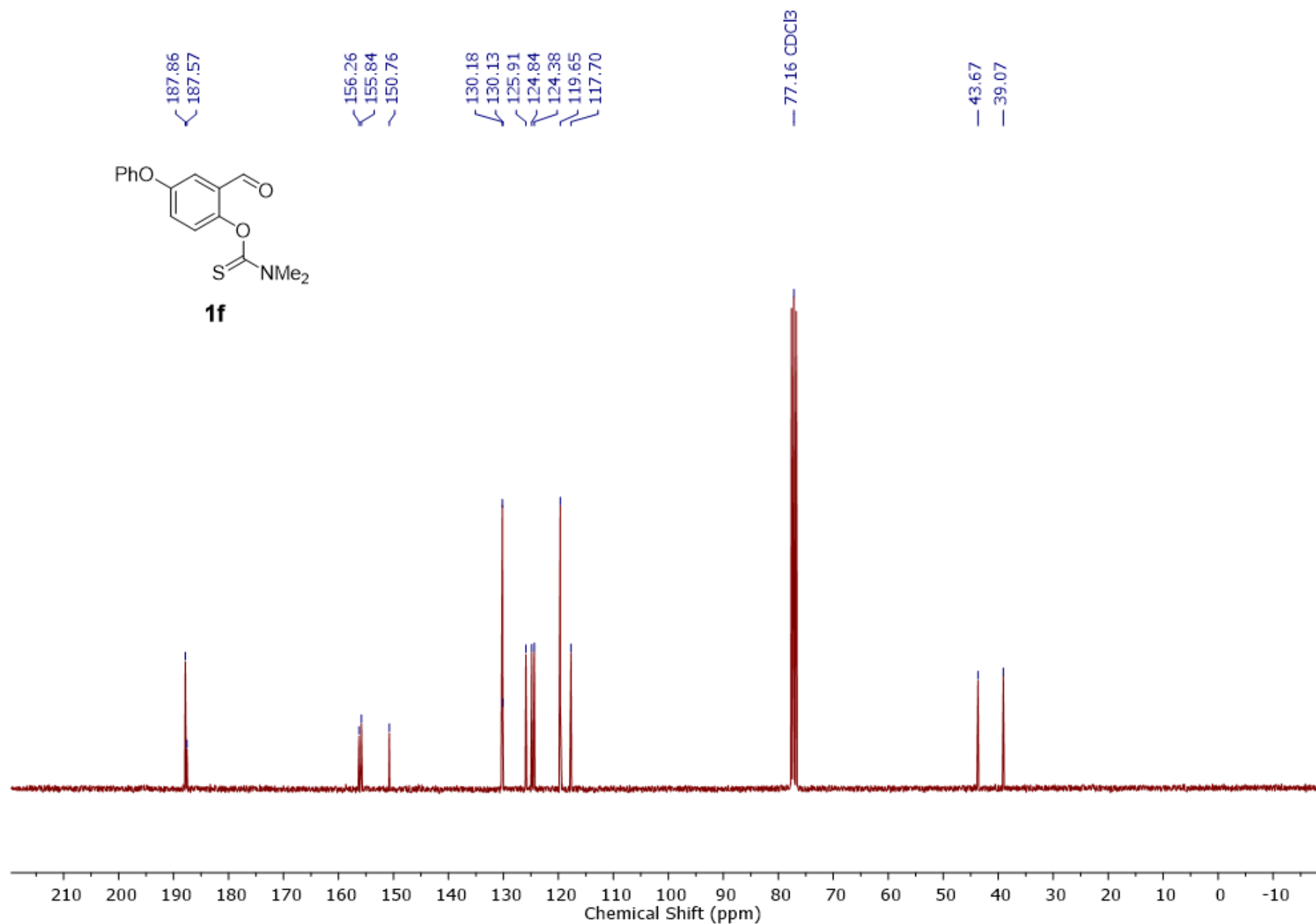
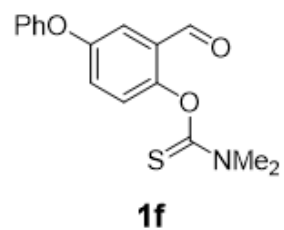
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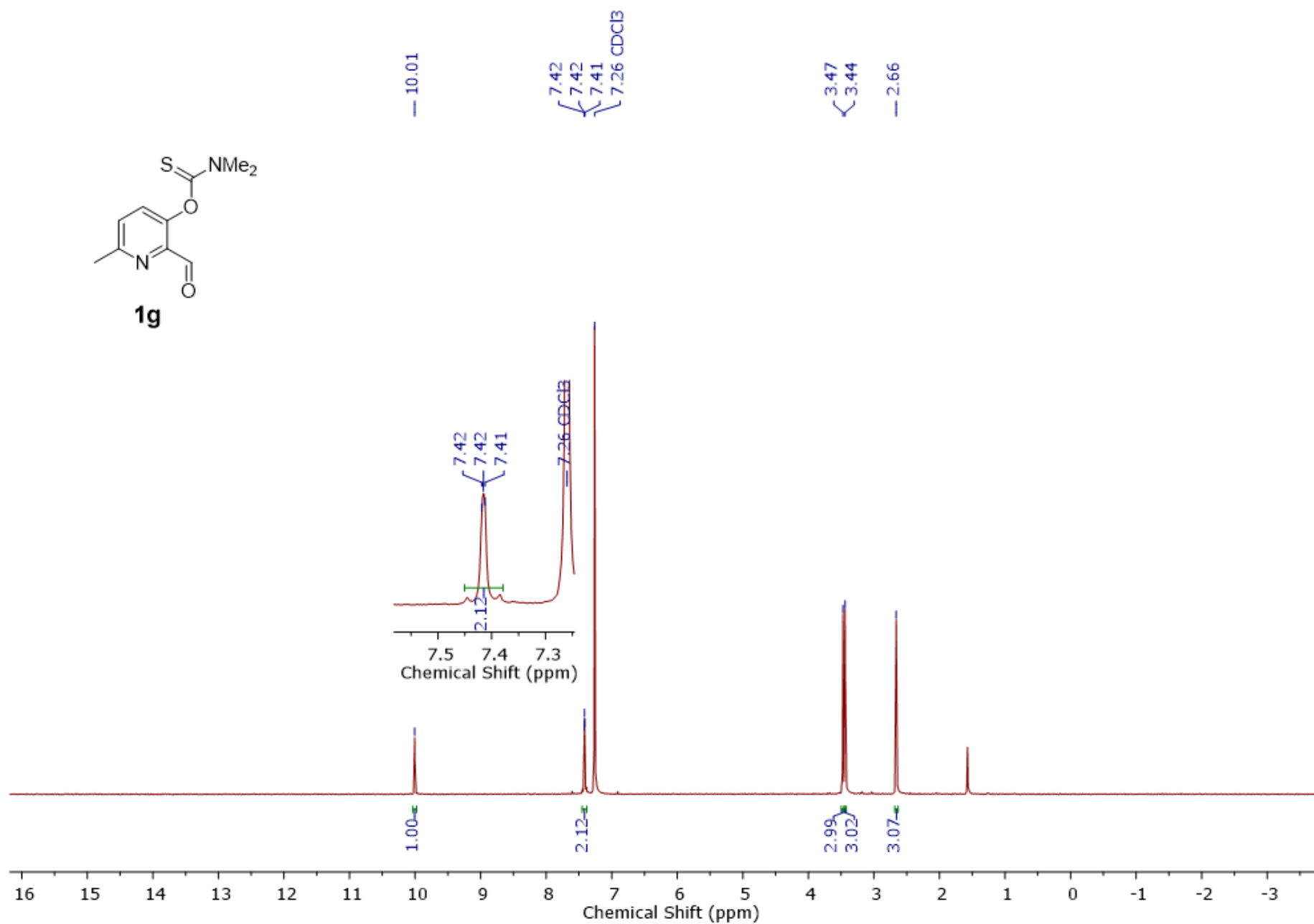
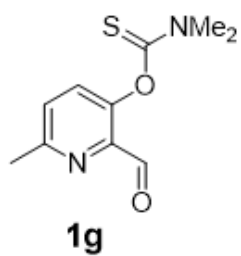


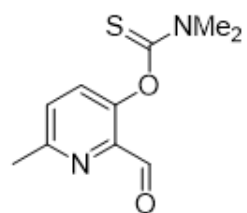


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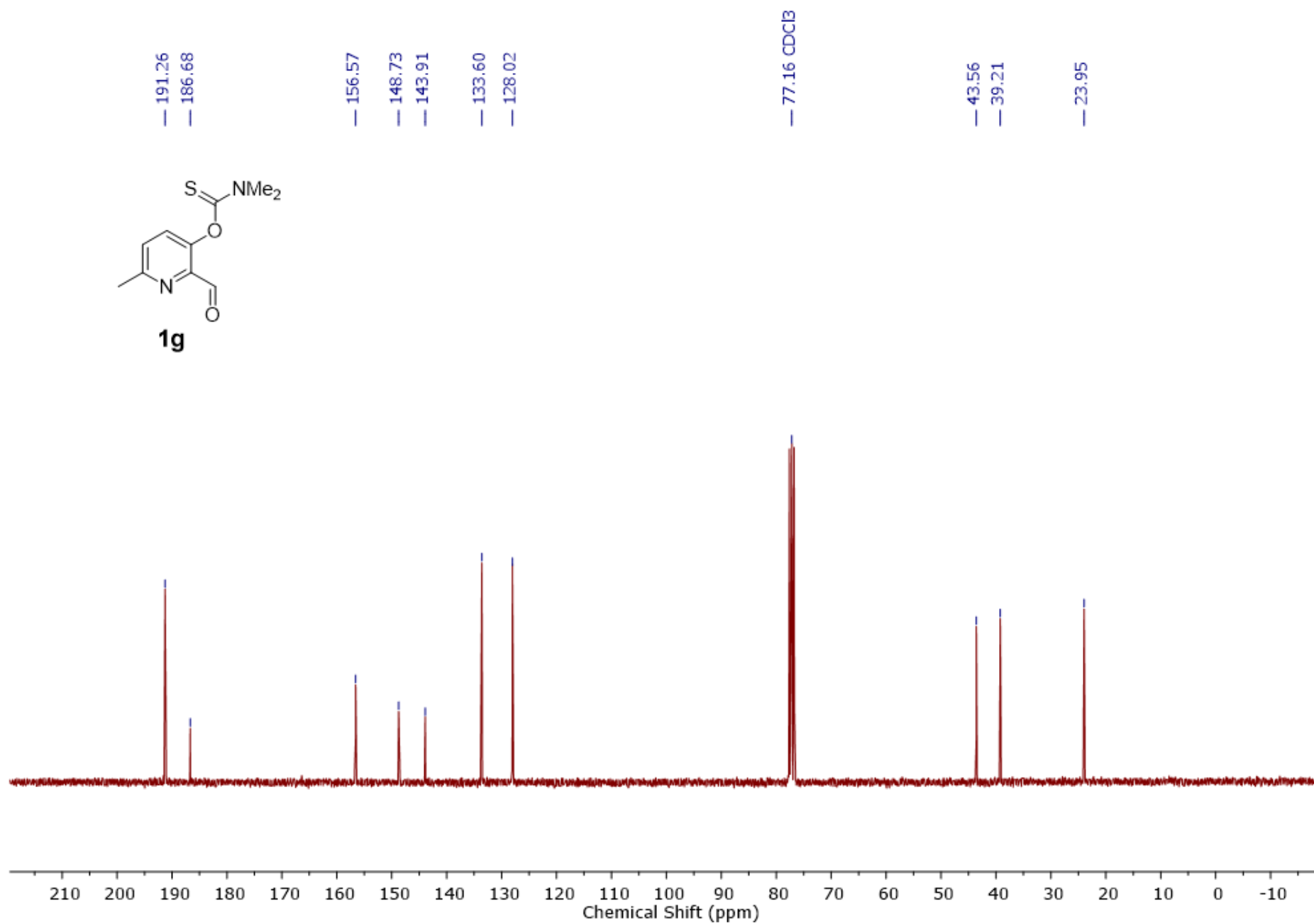


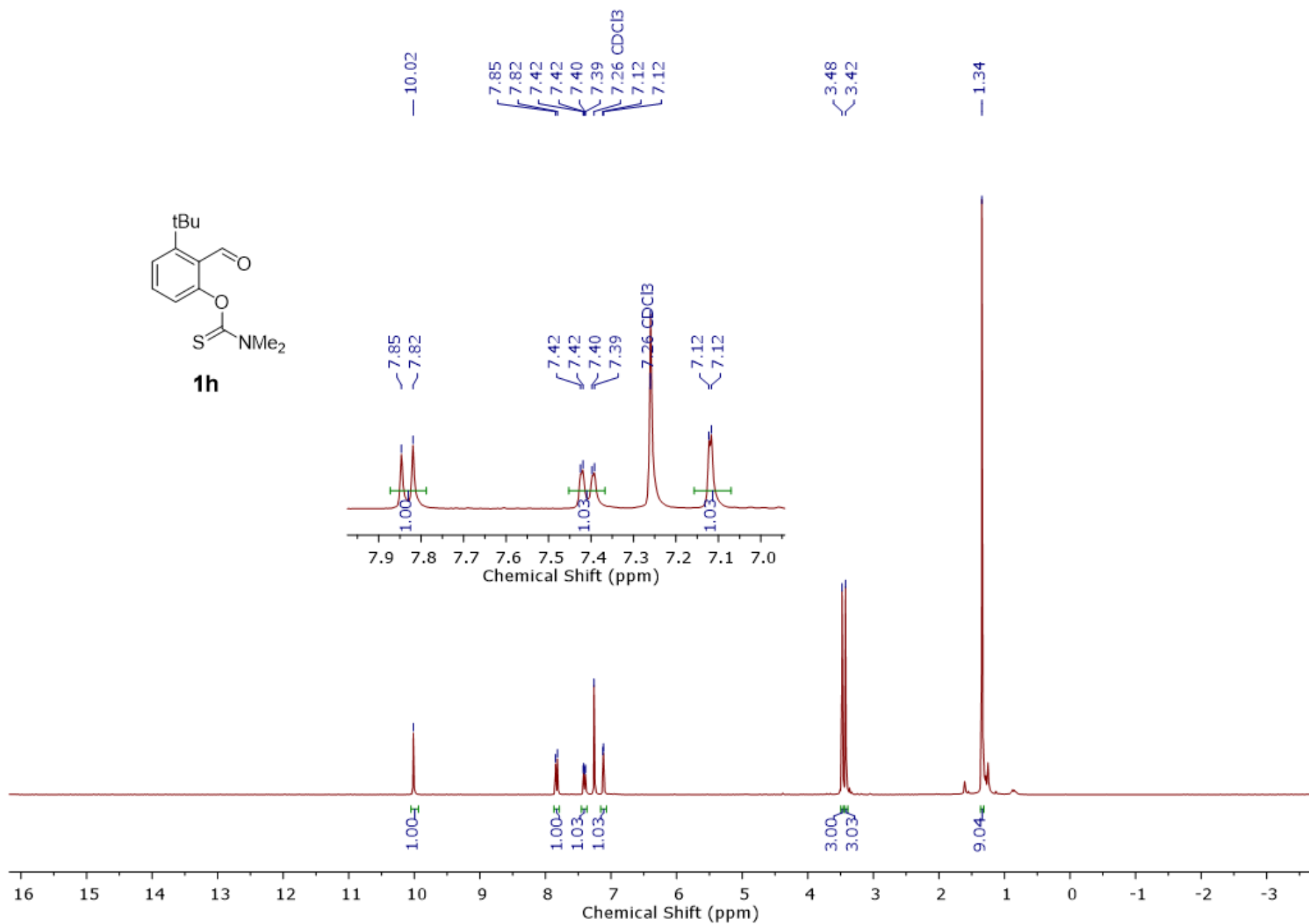


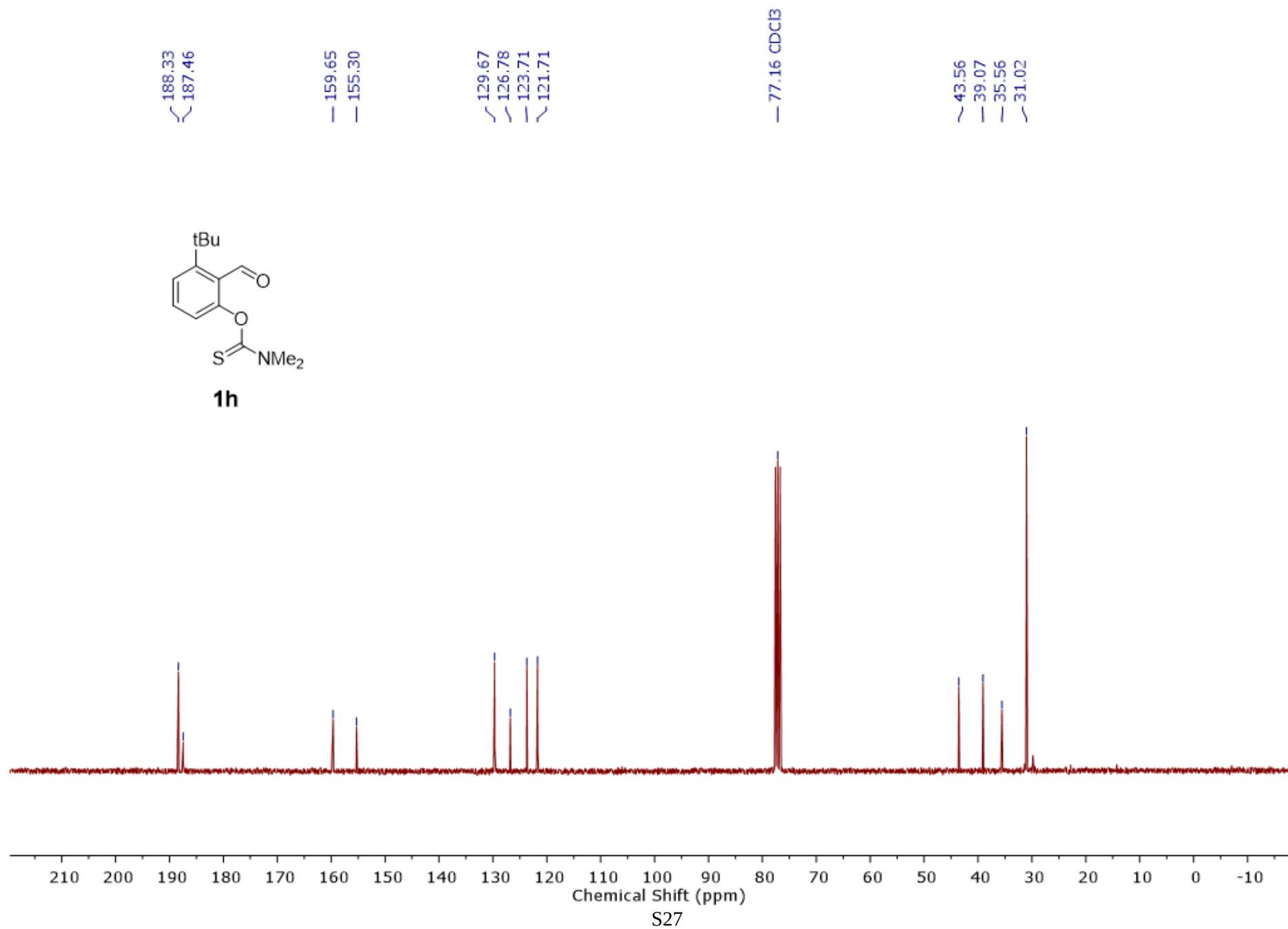
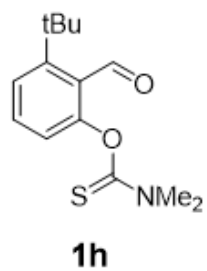


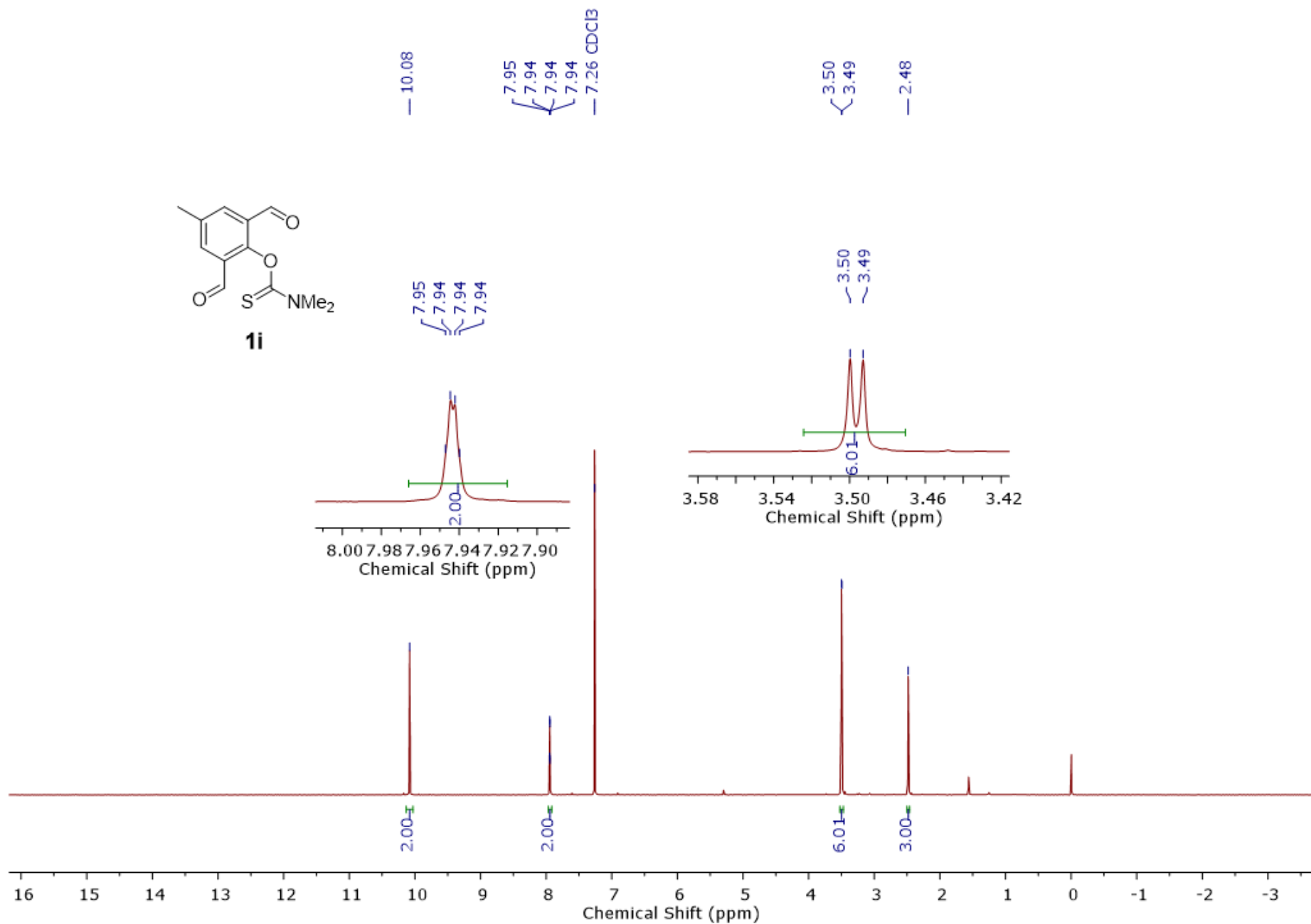


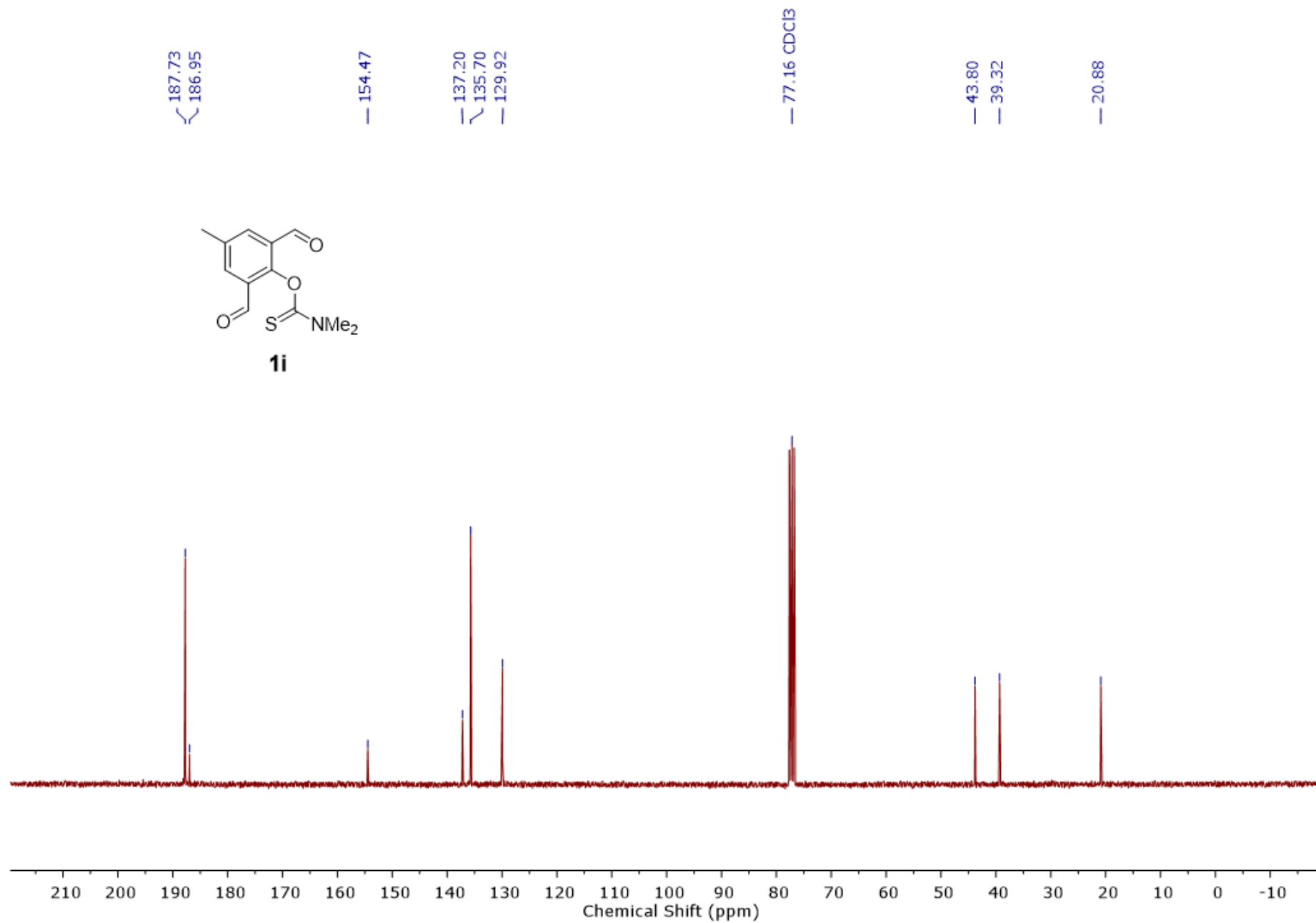
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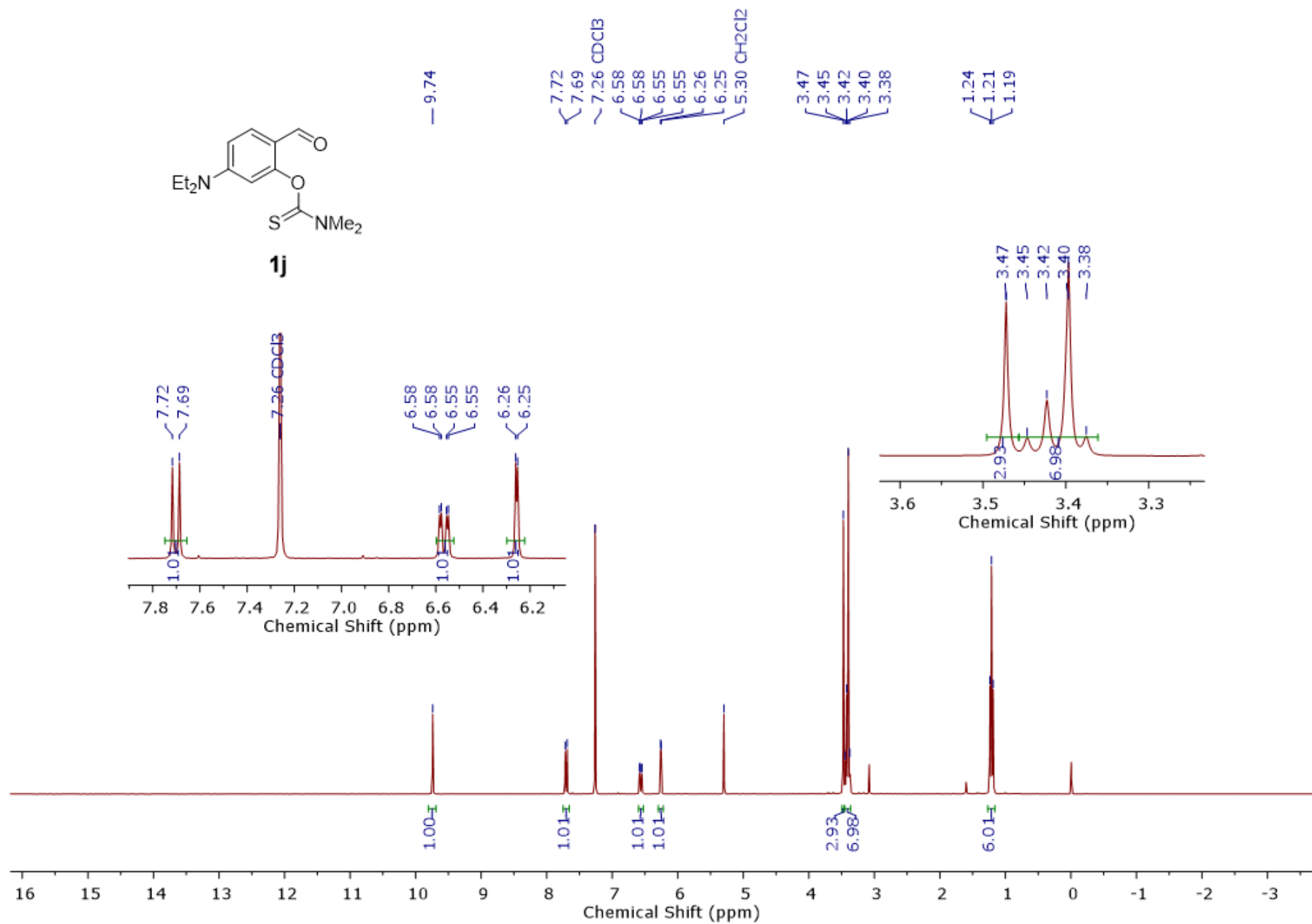


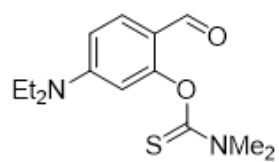




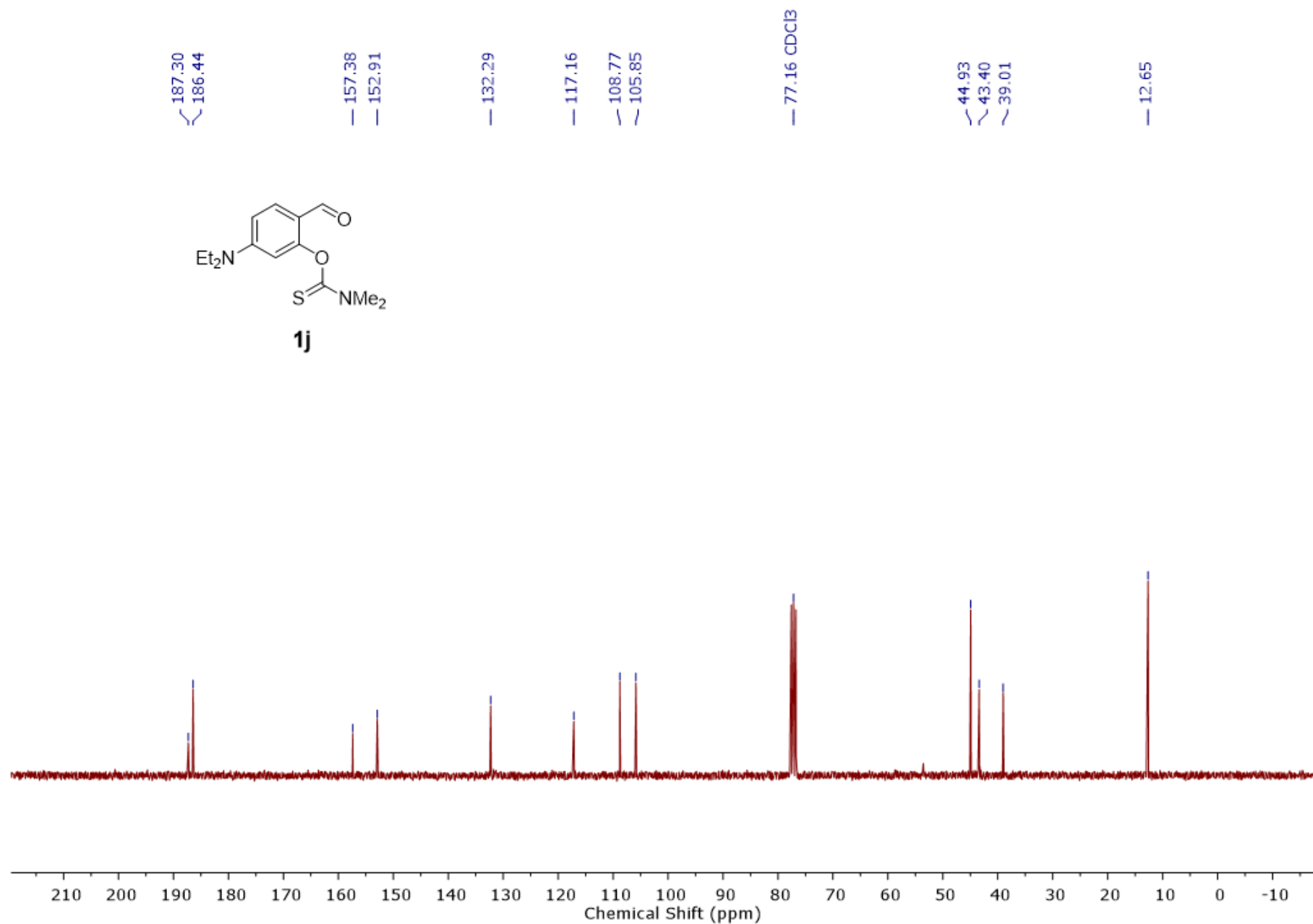


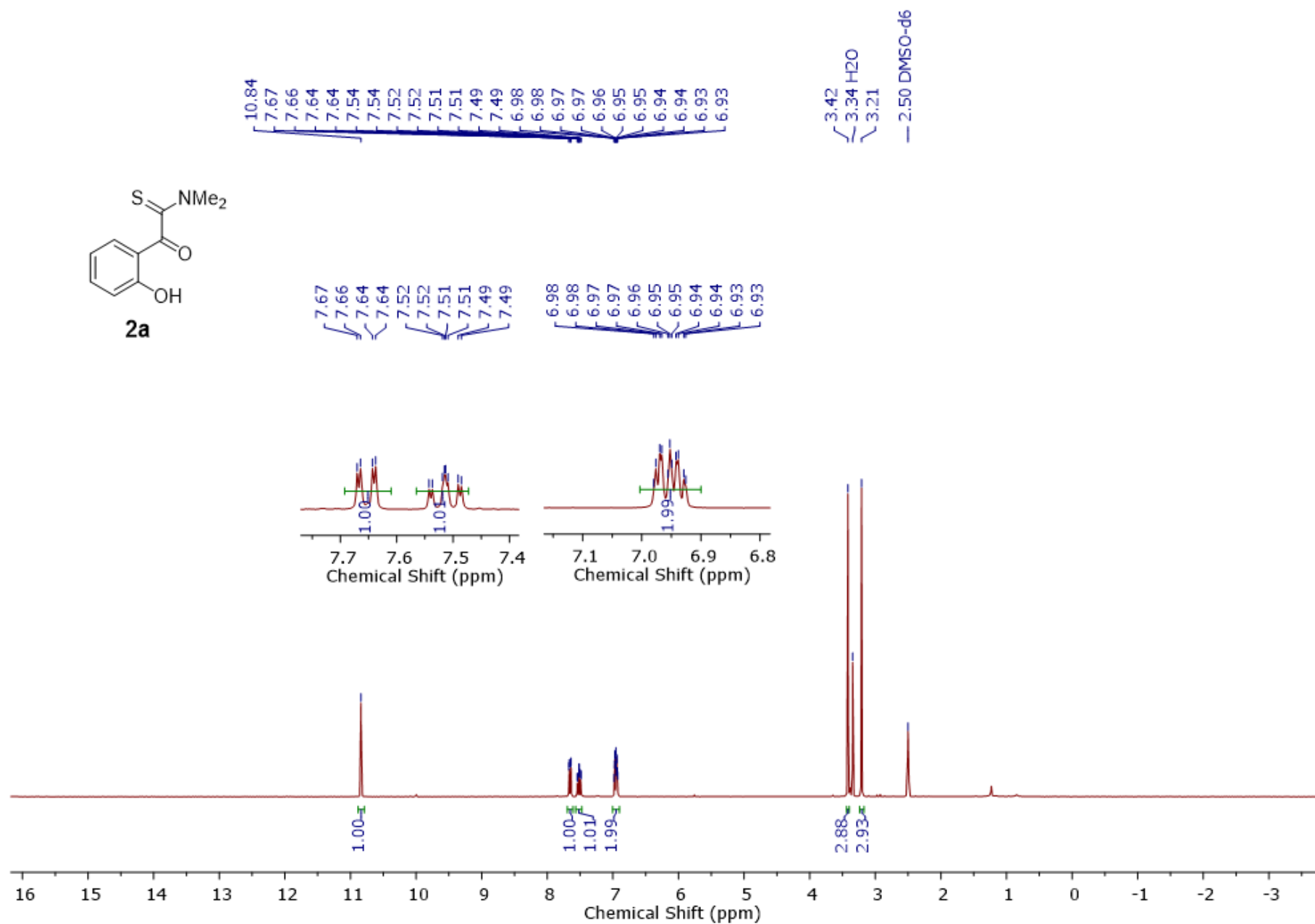
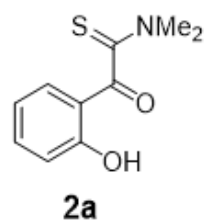


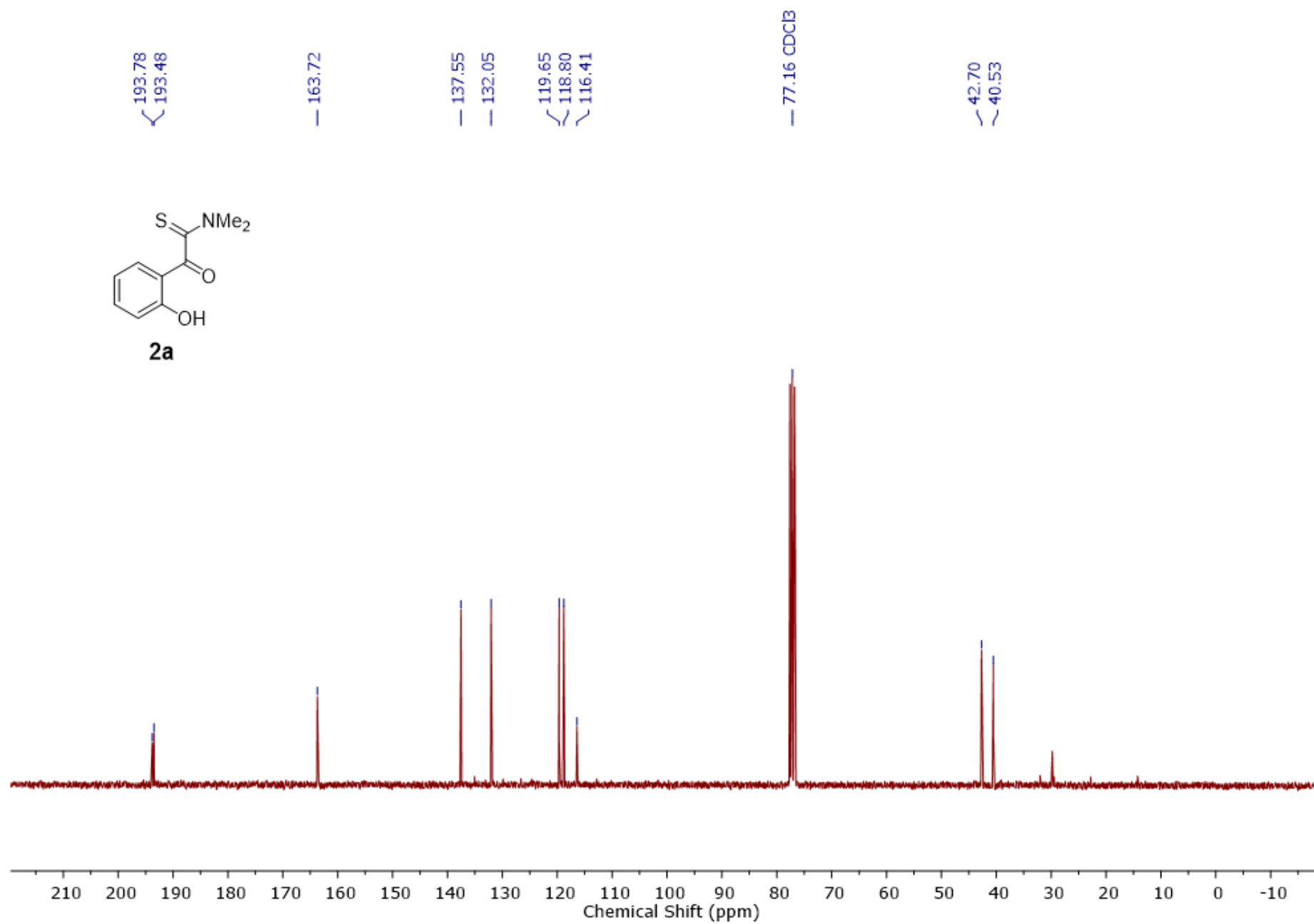
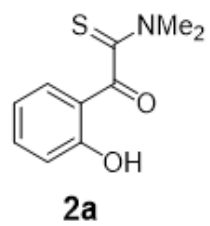


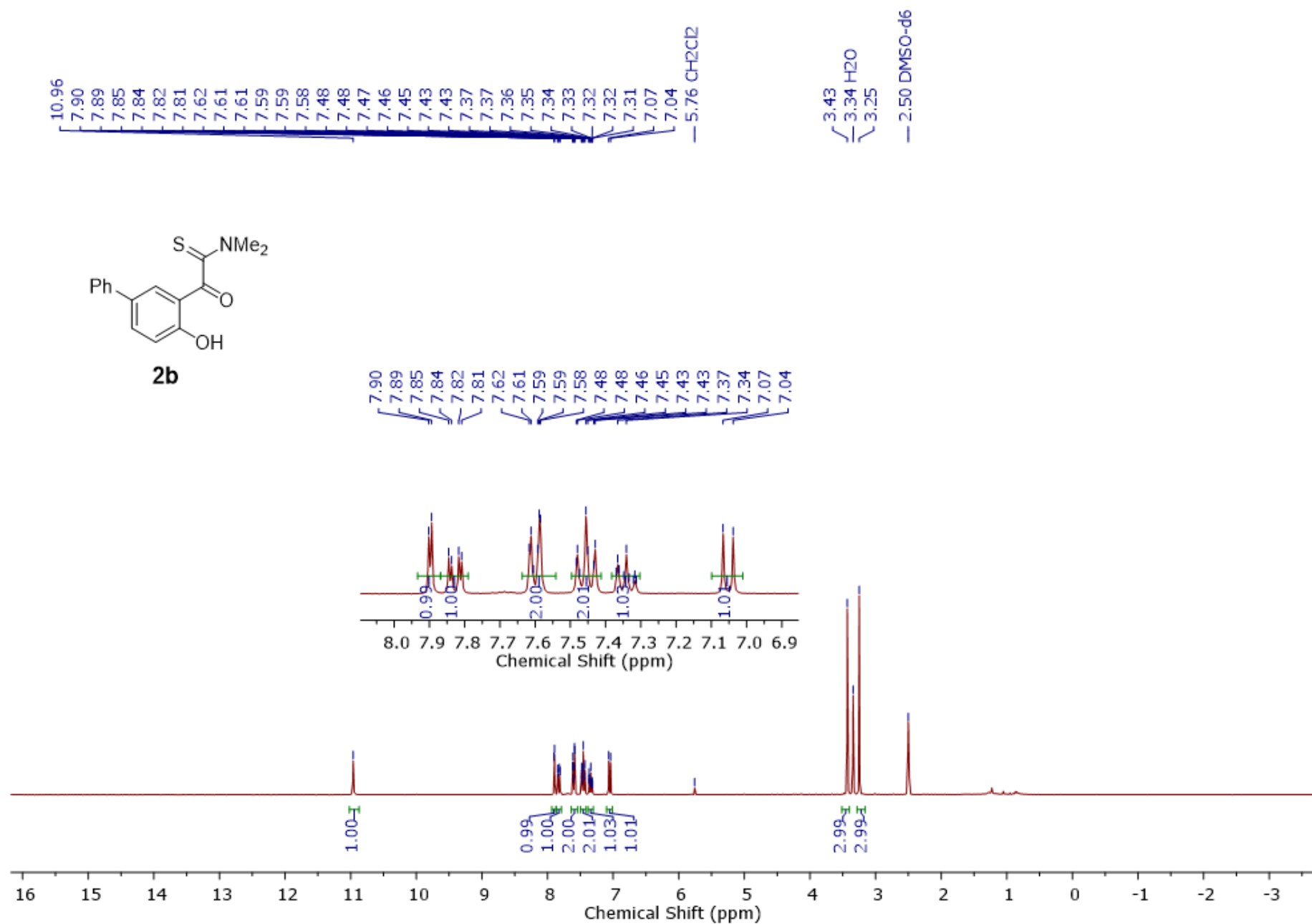


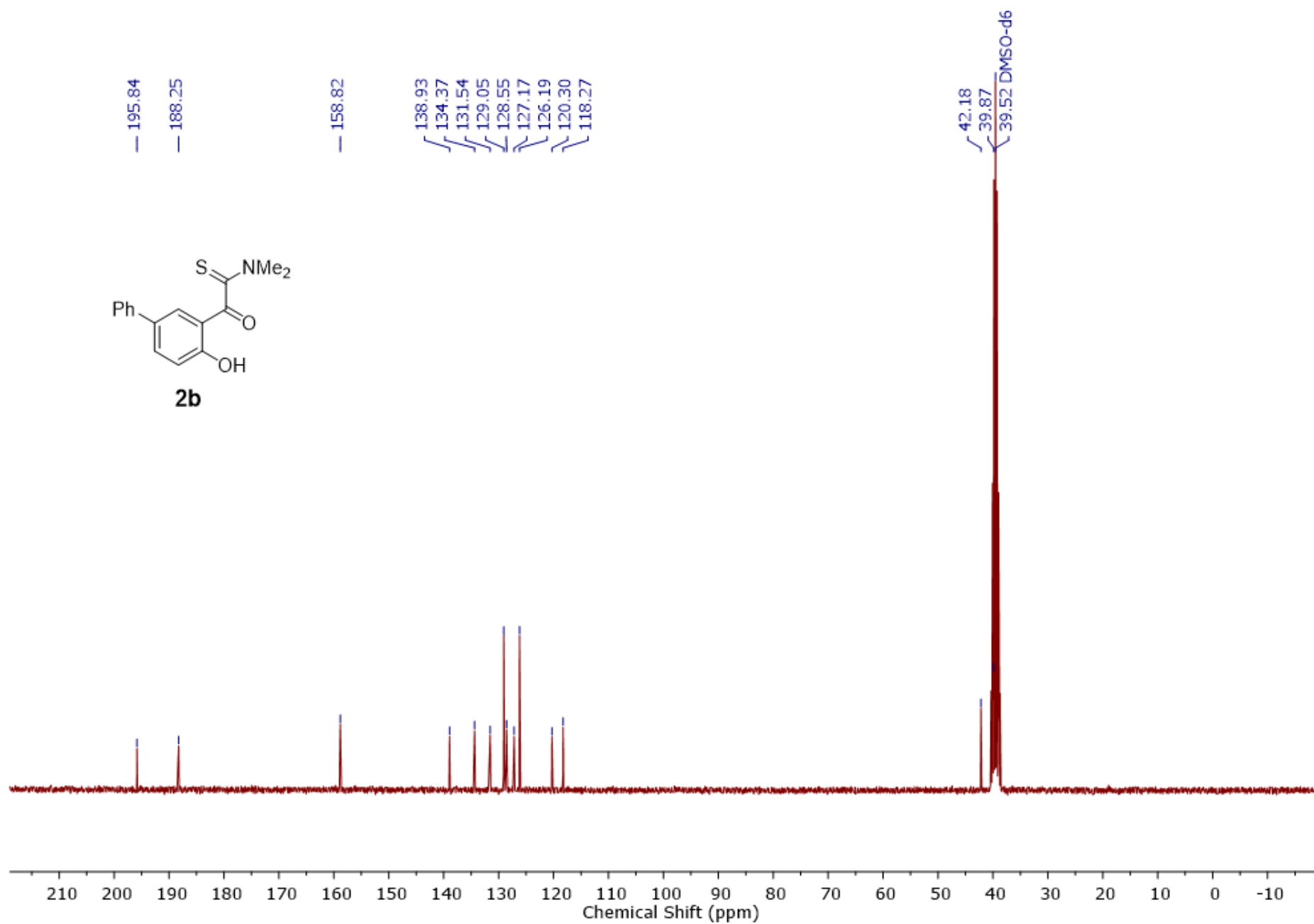
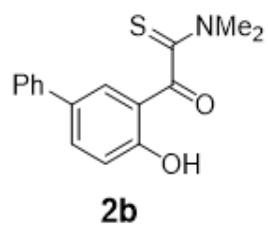
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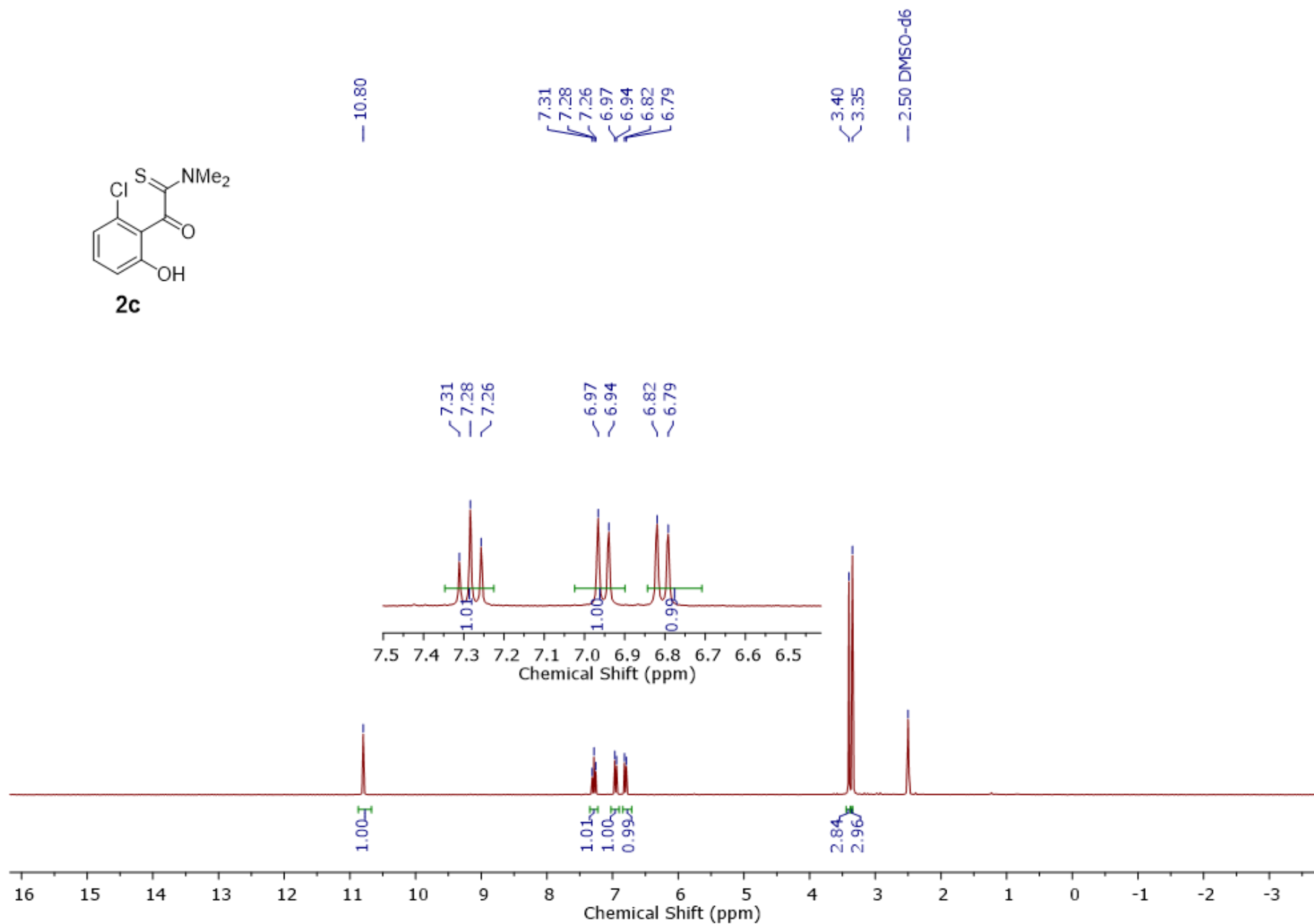
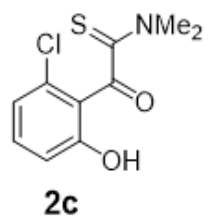


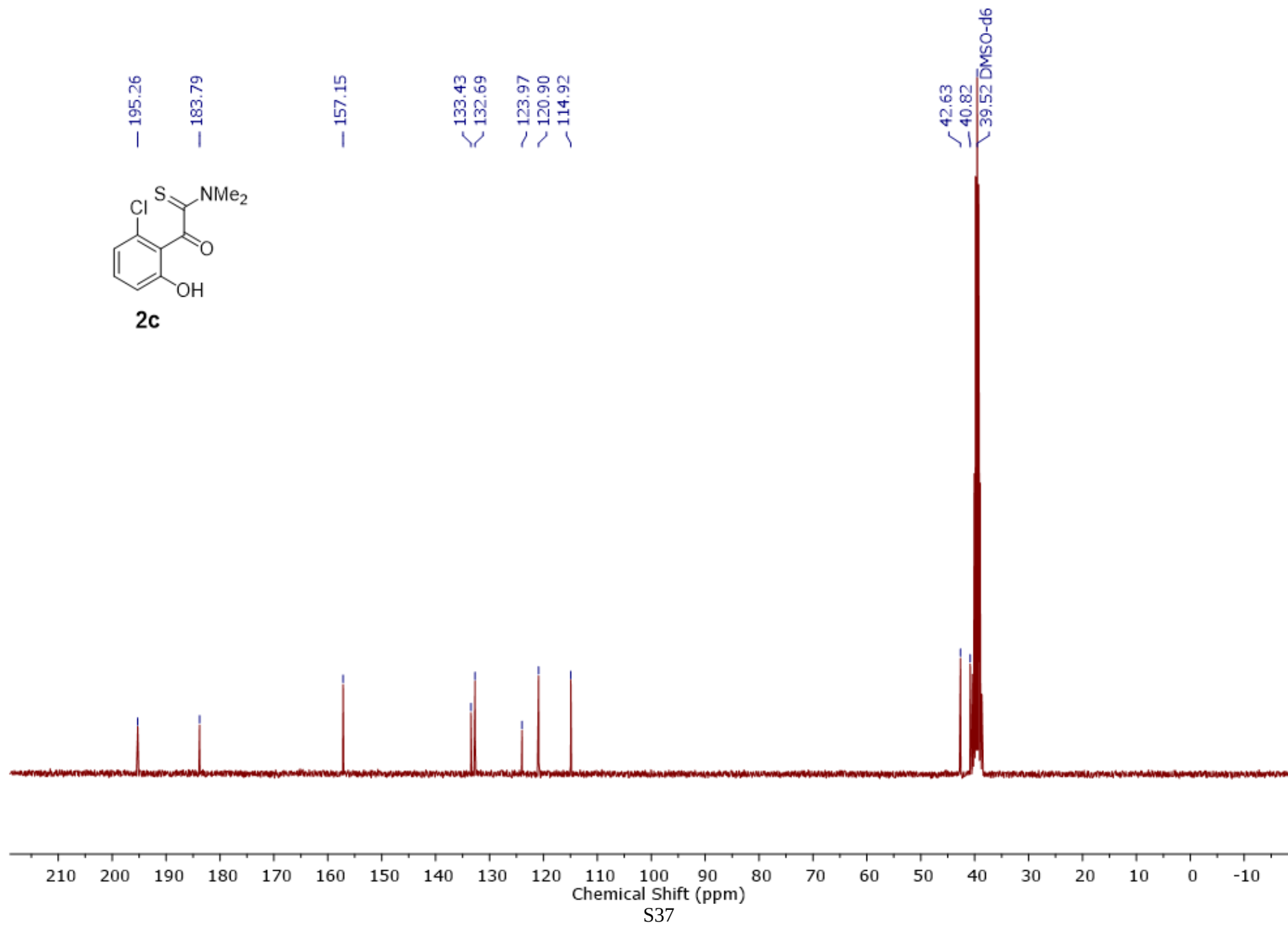
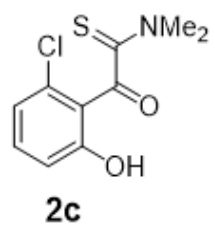


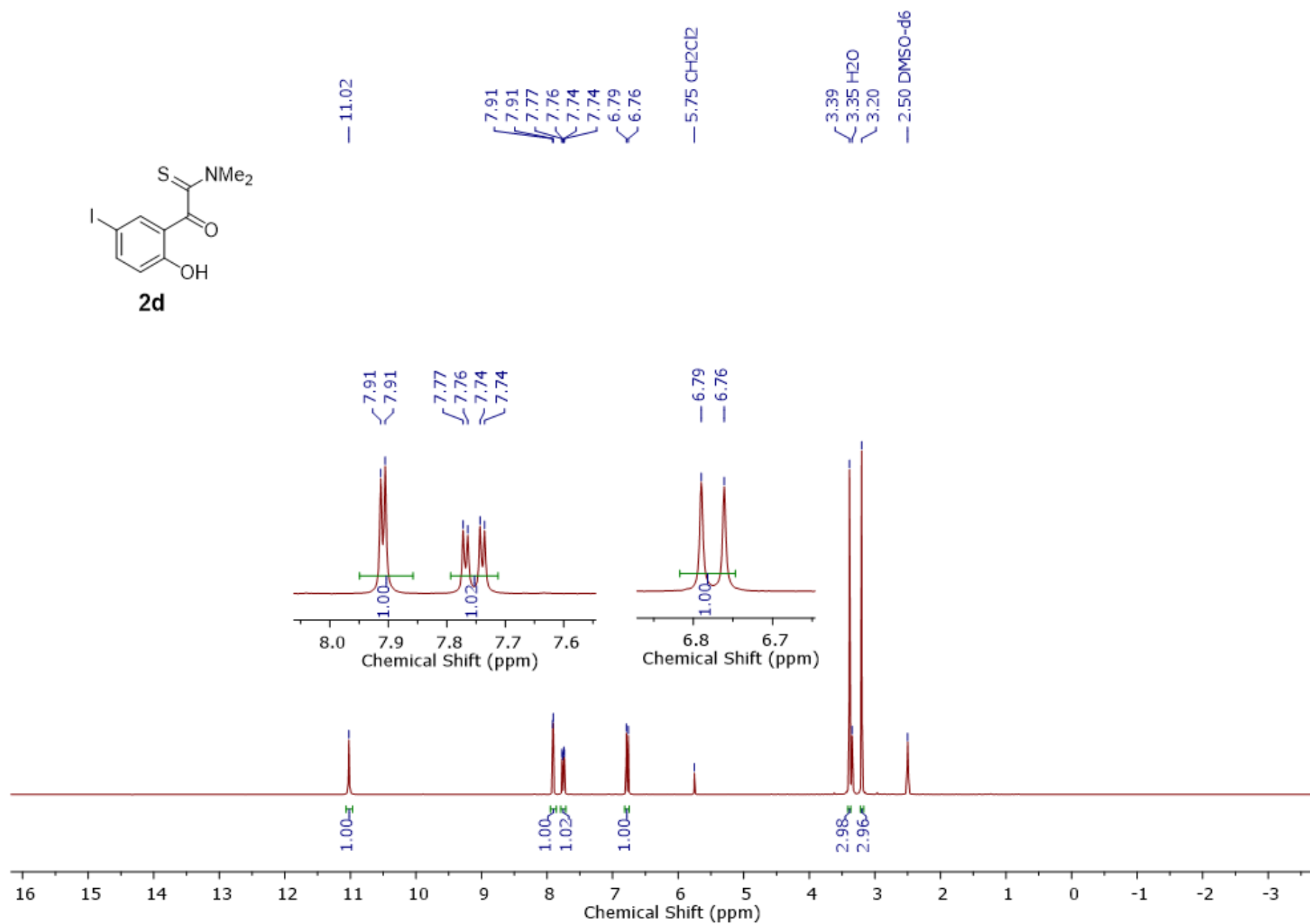
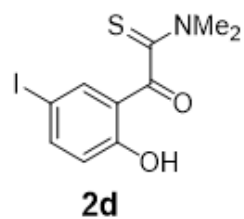


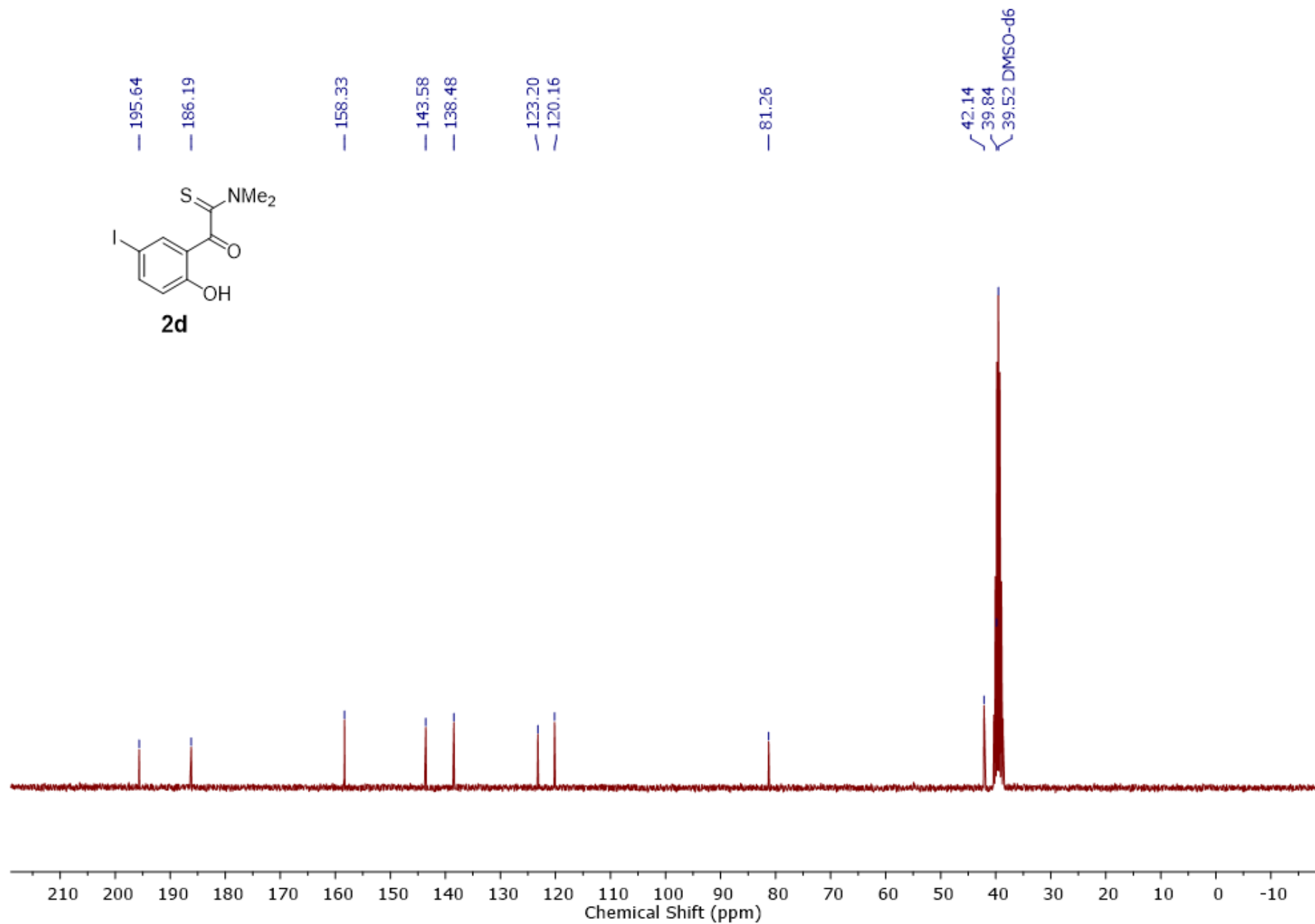
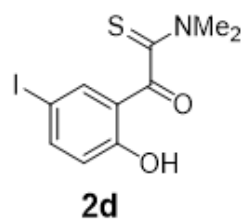


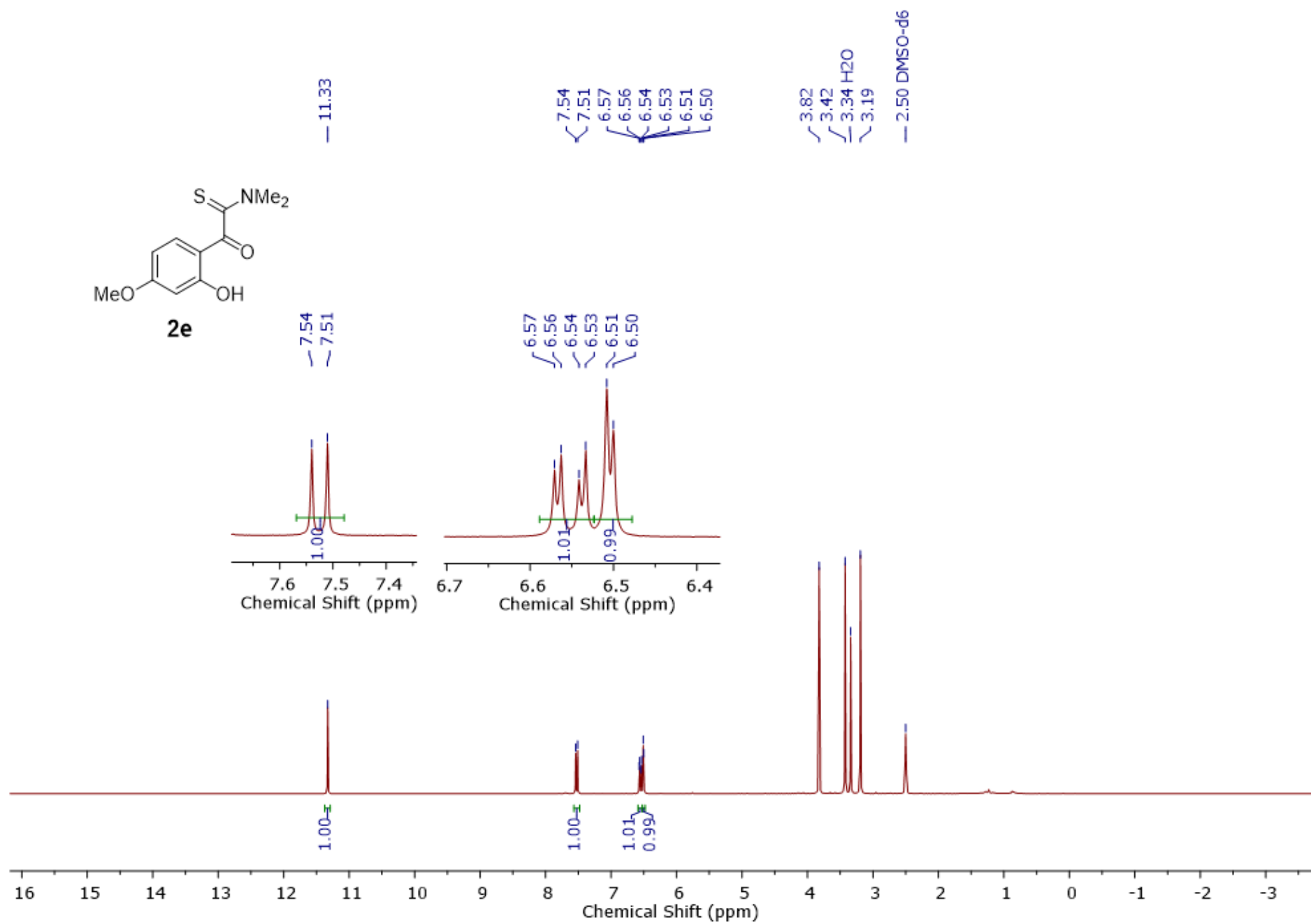


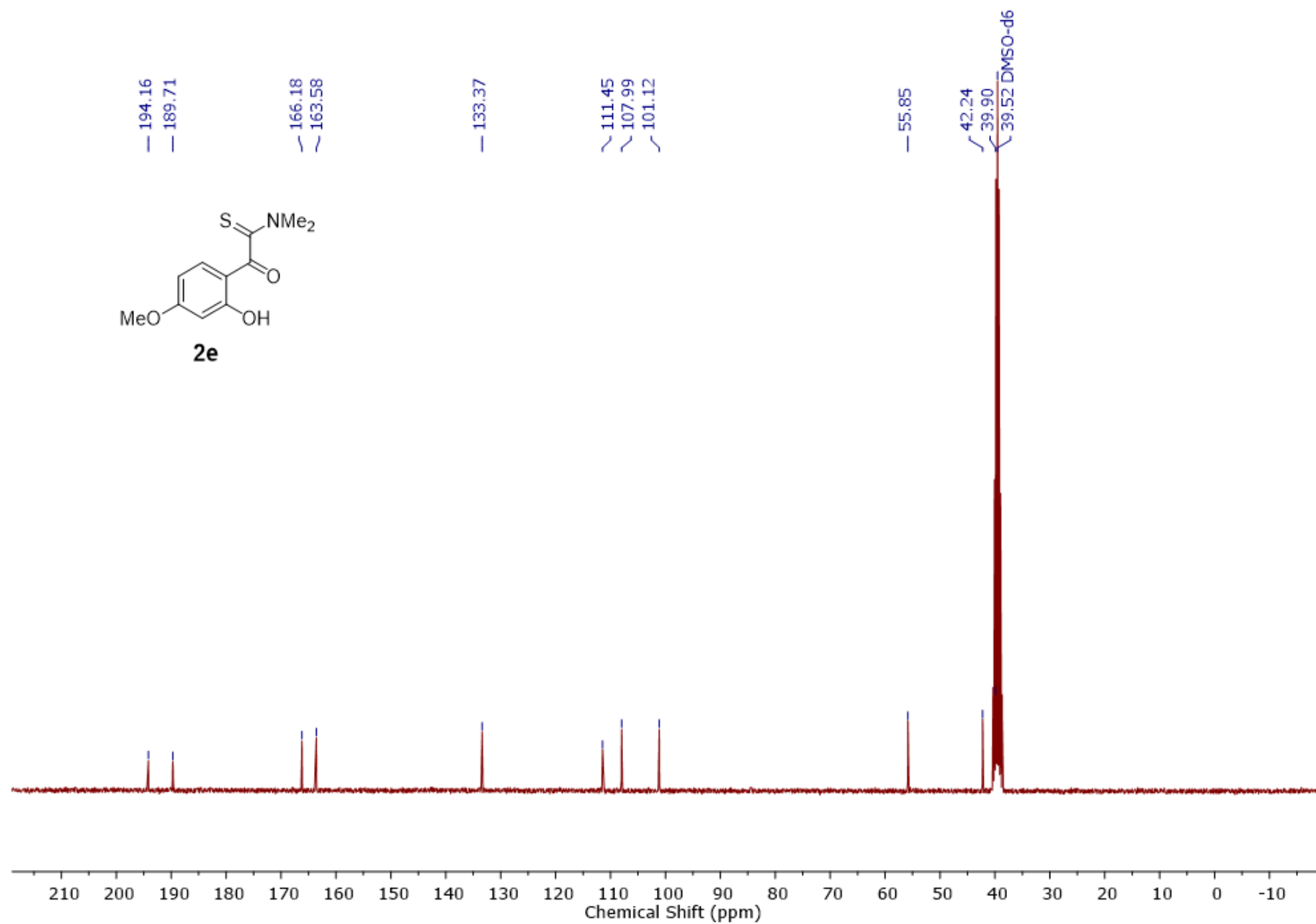


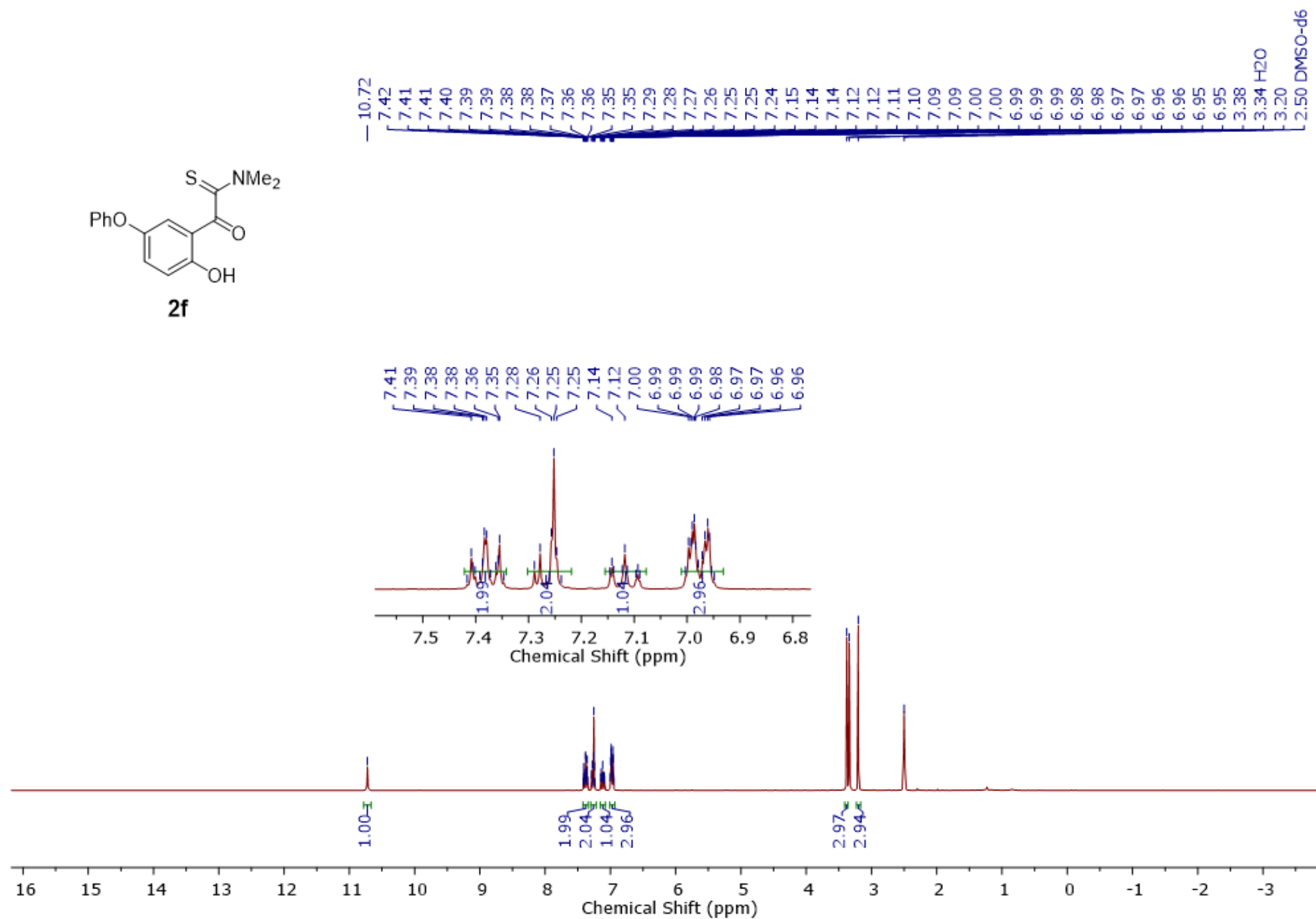
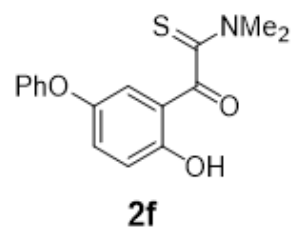


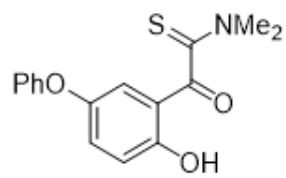












2f

