S-Alkylation of Sulfinamides by Zn-Carbenoids: Expanding Stereoselective Sulfoximine Synthesis Beyond NH Derivatives

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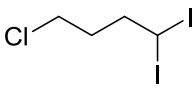
General Information

Unless otherwise noted, all chemicals were used as received from commercial sources and all reactions were performed under argon atmosphere. Anhydrous CH_2Cl_2, Et_2O, THF were obtained by passing commercially available anhydrous solvents through activated alumina columns. Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel F-254 plates. Nuclear magnetic resonance spectra were recorded on NMR spectrometers at 298 K unless otherwise stated at the following frequencies: ^{1}H, 600, 400 or 300 MHz; $^{13}C\{^{1}H\}$, 151 or 101 MHz; ^{19}F, 376 MHz; $^{31}P\{^{1}H\}$ 162 MHz. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent peak as an internal reference. High-resolution mass spectra (HRMS) were recorded on mass spectrometers with a time-of-flight (TOF) mass analyzer using ESI or APCI techniques. X-Ray data was collected on Rigaku, XtaLAB Synergy, Dualflex, HyPix diffractometer.

Synthesis of geminal diiodides 5m, 5o–r



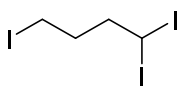
4-Chloro-1,1-diiodobutane (5m).

The title compound was prepared following a modified literature procedure.[1] Accordingly, a solution of diiodomethane (15.8 g, 59.0 mmol, 1.9 equiv) in THF (5 mL) was added dropwise to a solution of LiHMDS (1.0 M solution in THF, 59 mL, 59 mmol, 1.9 equiv) in THF (140 mL) and Et_2O (140 mL) at -78 °C. The orange clear solution was stirred for 30 min at -78 °C whereupon a solution of 3-chloropropyl trifluoromethanesulfonate[2] (7.05 g, 31.1 mmol, 1 equiv) in THF (5 mL) was added dropwise. The resulting solution was warmed to room temperature over 16 h, quenched with 10% aqueous $KHSO_4$ (200 mL) and diluted with Et_2O (100 mL). Layers were separated, the aqueous layer was extracted with Et_2O (100 mL), combined organic layers were dried over Na_2SO_4, filtered and concentrated. Purification of the tarry black residue by silica gel flash column chromatography using gradient elution (20:1 to 10:1 hexane:CH_2Cl_2) afforded the target diiodide **5m** (6.81 g, 64%) as a dark-violet oil. Analytical TLC on silica gel, 20:1 hexane:CH_2Cl_2, R*f* = 0.37.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 (t, *J* = 6.3 Hz, 1H), 3.60 (t, *J* = 6.2 Hz, 2H), 2.58 – 2.51 (m, 2H), 2.00 – 1.91 (m, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 45.3, 42.7, 34.6, -28.5.

HRMS (APCI/TOF) *m/z*: $[M\text{-}Cl]^+$ Calcd. for $C_4H_7I_2$: 308.8632. Found 308.8631.



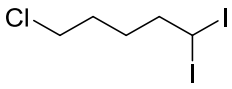
1,1,4-Triiodobutane (5o).

4-Chloro-1,1-diiodobutane **5m** (6.58 g, 19.1 mmol, 1 equiv) and NaI (14.3 g, 95.6 mmol, 5 equiv) were suspended in MeCN (40 mL) and vigorously stirred at 60 °C for 48 h. After cooling to ambient temperature, the orange-brown suspension was diluted with water (200 mL), Et_2O (100 mL) and layers were separated. The aqueous layer was extracted with Et_2O (100 mL), combined organic layers were dried over Na_2SO_4, filtered and concentrated. The obtained dark violet oil (7.50 g, 90%) was used in the next step without further purification. Analytical TLC on silica gel, 20:1 hexane:CH_2Cl_2, R*f* = 0.38.

^1H NMR (400 MHz, $CDCl_3$) δ 5.15 (t, *J* = 6.3 Hz, 1H), 3.22 (t, *J* = 6.7 Hz, 2H), 2.54 – 2.46 (m, 2H), 2.04 – 1.96 (m, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 48.5, 35.2, 3.2, -29.2.

HRMS (APCI/TOF) *m/z*: $[M\text{-}I]^+$ Calcd. for $C_4H_7I_2$: 308.8632. Found 308.8632.



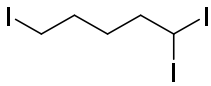
5-Chloro-1,1-diiodopentane (5r).

The title compound was prepared following a modified literature procedure.[1] A solution of diiodomethane (12.7 g, 47.4 mmol, 1.9 equiv) in THF (4 mL) was added dropwise to a solution of LiHMDS (1.0 M solution in THF, 47 mL, 47 mmol, 1.9 equiv) in THF (11 0 mL) and Et_2O (110 mL) at -78 °C. The orange clear solution was stirred for 30 min at -78 °C and a solution of 4-chlorobutyl trifluoromethanesulfonate[3] (6.00 g, 24.9 mmol, 1 equiv) in THF (4 mL) was added dropwise. The resulting orange solution was warmed to room temperature over 16 h, quenched with 10% aqueous $KHSO_4$ (200 mL) and diluted with Et_2O (100 mL). Layers were separated, the aqueous layer was extracted with Et_2O (100 mL), combined organic layers were dried over Na_2SO_4, filtered and concentrated. Purification of the tarry black residue by silica gel flash column chromatography using gradient elution (20:1 to 5:1 hexane:CH_2Cl_2) afforded the target diiodide **5r** (7.00 g, 78%) as a brown oil. Analytical TLC on silica gel, 20:1 hexane:CH_2Cl_2, R*f* = 0.40.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (t, *J* = 6.4 Hz, 1H), 3.55 (t, *J* = 6.6 Hz, 2H), 2.43 – 2.36 (m, 2H), 1.89 – 1.79 (m, 2H), 1.65 – 1.55 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 47.4, 44.5, 30.7, 29.4, -26.7.

LRMS (EI/Q) *m/z*: $[M]^+$ Calcd. for $C_5H_9ClI_2$: 357.8. Found 357.9.



1,1,5-Triiodopentane (5p).

5-Chloro-1,1-diiodopentane **5r** (1.00 g, 2.79 mmol, 1 equiv) and NaI (1.67 g, 11.2 mmol, 4 equiv) were suspended in acetone (3 mL) and vigorously stirred at 50 °C for 48 h. After cooling to ambient temperature, the orange-brown suspension was diluted with water (50 mL), Et_2O (50 mL) and layers were separated. The aqueous layer was extracted with Et_2O (100 mL), combined organic layers were dried over Na_2SO_4, filtered and concentrated. The obtained dark violet oil (1.12 g, 89%) was used in next step without further purification. Analytical TLC on silica gel, 20:1 hexane:CH_2Cl_2, R*f* = 0.42.

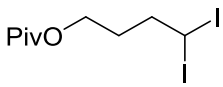
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 (t, *J* = 6.4 Hz, 1H), 3.20 (t, *J* = 6.9 Hz, 2H), 2.42 – 2.35 (m, 2H), 1.94 – 1.85 (m, 2H), 1.61 – 1.52 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 47.1, 32.9, 31.5, 5.8, -26.9.

LRMS (EI/Q) *m/z*: $[M]^+$ Calcd. for $C_5H_9I_3$: 449.8. Found 449.7.

General procedure A for synthesis of functionalized geminal diiodides 5h–k, n, q, s

To a solution of alkyl triiodide **5o** or **5p** (1.15 mmol, 1 equiv) in DMF (11 mL) was added solid nucleophilic reagent (1.15 mmol, 1 equiv) in one portion at room temperature. The yellow solution was stirred for 16 h at room temperature and diluted with water (150 mL) and Et_2O (150 mL). Layers were separated, the organic layer was washed with water (100 mL), dried over Na_2SO_4, filtered, concentrated and purified by silica gel flash column chromatography.



4,4-Diiodobutyl-2,2-dimethylpropanoate (5h).

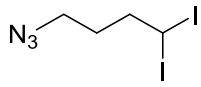
The title compound was prepared from 1,1,4-triiodobutane **5o** (500 mg, 1.15 mmol, 1 equiv), cesium pivalate (269 mg, 1.15 mmol, 1 equiv) and DMF (11 mL) following **general procedure A**. Purification of the brown residue by silica gel flash

column chromatography (20:1 hexane:EtOAc) afforded the target pivalate **5h** (307 mg, 65%) as a yellow oil. Analytical TLC on silica gel, 20:1 hexane:EtOAc, R*f* = 0.26.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 (t, *J* = 6.2 Hz, 1H), 4.12 (t, *J* = 6.2 Hz, 2H), 2.49 – 2.41 (m, 2H), 1.86 – 1.74 (m, 2H), 1.21 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 178.6, 62.2, 45.0, 38.9, 31.0, 27.4, -27.5.

HRMS (APCI/TOF) *m/z*: $[M+NH_4]^+$ Calcd. for $C_9H_{20}I_2NO_2$: 427.9578. Found 427.9584.



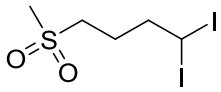
4-Azido-1,1-diiodobutane (5i).

The title compound was prepared from 1,1,4-triiodobutane **5o** (1.09 g, 2.50 mmol, 1 equiv), sodium azide (171 mg, 2.62 mmol, 1.05 equiv) and DMF (25 mL) following **general procedure A**. Purification of the residue by silica gel flash column chromatography using gradient elution (20:1 to 1:1 hexane:CH_2Cl_2) afforded the target azide **5i** (647 mg, 74%) as a yellow oil. Analytical TLC on silica gel, hexane, R*f* = 0.20.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.16 (t, *J* = 6.3 Hz, 1H), 3.38 (t, *J* = 6.6 Hz, 2H), 2.52 – 2.40 (m, 2H), 1.82 – 1.69 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 49.6, 45.3, 31.3, -28.1.

HRMS (APCI/TOF) *m/z*: $[M-N_2+H]^+$ Calcd. for $C_4H_8I_2N$: 323.8741. Found 323.8742.



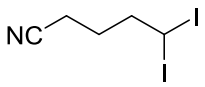
1,1-Diiodo-4-methanesulfonylbutane (5n).

The title compound was prepared from 1,1,4-triiodobutane **5o** (433 mg, 0.994 mmol, 1 equiv), sodium sulfinate (112 mg, 1.09 mmol, 1.1 equiv) and DMF (10 mL) following **general procedure A**. Purification of the residue by silica gel flash column chromatography using gradient elution (3:2 hexane:EtOAc to EtOAc) afforded the target sulfone **5n** (189 mg, 49%) as a white amorphous solid. Analytical TLC on silica gel, 3:2 hexane:EtOAc, R*f* = 0.26.

^{1}H NMR (300 MHz, DMSO-d_6) δ 5.41 (t, *J* = 6.4 Hz, 1H), 3.24 – 3.16 (m, 2H), 2.96 (s, 3H), 2.45 – 2.34 (m, 2H), 1.83 – 1.69 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 51.1, 45.4, 40.2, 24.3, -23.4. Low signal/noise ratio is observed due to low solubility of **5n** in common organic solvents including DMSO.

HRMS (APCI/TOF) *m/z*: $[M+H]^+$ Calcd. for $C_5H_{11}I_2O_2S$: 388.8564. Found 388.8570.



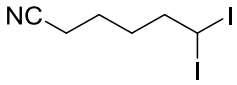
5,5-Diiodopentanenitrile (5q).

The title compound was prepared from 1,1,4-triiodobutane **5o** (433 mg, 0.994 mmol, 1 equiv), sodium cyanide (54 mg, 1.10 mmol, 1.1 equiv) and DMF (10 mL) following **general procedure A**. Purification of the residue by silica gel flash column chromatography (5:1 hexane:EtOAc) afforded the target nitrile **5q** (278 mg, 84%) as a yellow oil. Analytical TLC on silica gel, 5:1 hexane:EtOAc, R*f* = 0.31.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (t, *J* = 6.1 Hz, 1H), 2.55 – 2.48 (m, 2H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.92 – 1.83 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 118.9, 46.3, 27.7, 15.6, -30.4.

LRMS (EI/Q) *m/z*: $[M]^+$ Calcd. for $C_5H_7I_2N$: 334.9. Found 334.9.



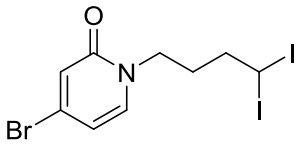
6,6-Diiodohexanenitrile (5s).

The title compound was prepared from 1,1,5-triiodopentane **5p** (225 mg, 0.500 mmol, 1 equiv), sodium cyanide (27 mg, 0.55 mmol, 1.1 equiv) and DMF (5 mL) following **general procedure A**. The crude nitrile (156 mg, 89%) was obtained as a brown oil after extraction and used without further purification. Analytical TLC on silica gel, 5:1 hexane:EtOAc, R*f* = 0.33.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.13 (t, *J* = 6.3 Hz, 1H), 2.48 – 2.33 (m, 4H), 1.80 – 1.56 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 119.3, 47.2, 31.1, 23.7, 17.3, -28.1.

LRMS (EI/Q) *m/z*: $[M\text{-}I]^+$ Calcd. for C_6H_9IN: 222.0. Found 222.0.



4-Bromo-1-(4,4-diiodobutyl)-1,2-dihydropyridin-2-one (5j).

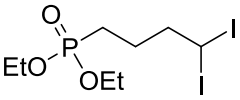
To a suspension of NaH (60% dispersion in mineral oil, 46 mg, 1.15 mmol, 1 equiv) in DMF (5 mL) was added a solution of 4-bromopyridone (200 mg, 1.15 mmol, 1 equiv) in DMF (6 mL) at room temperature. The clear yellow solution was stirred for 30 min at room temperature, and 1,1,4-triiodobutane **5o** (500 mg, 1.15 mmol, 1 equiv) was added as a solution in DMF (1 mL). After 3 h of stirring at room temperature, the brown solution was diluted with water (150 mL) and EtOAc (100 mL). Layers were separated, the organic layer was washed

with water (100 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the residue by silica gel flash column chromatography (2:1 hexane:EtOAc) afforded the target compound **5j** (262 mg, 47%) as a yellow oil which solidified upon standing. Analytical TLC on silica gel, 2:1 hexane:EtOAc, R*f* = 0.25.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 7.2 Hz, 1H), 6.83 – 6.79 (m, 1H), 6.37 – 6.32 (m, 1H), 5.16 (t, *J* = 6.3 Hz, 1H), 3.95 (t, *J* = 7.2 Hz, 2H), 2.43 – 2.35 (m, 2H), 1.89 (p, *J* = 7.5 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.3, 137.0, 135.5, 123.4, 110.7, 47.2, 44.7, 31.7, -28.3.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_9H_{11}NOBrI_2$: 481.8113. Found 481.8130.



Diethyl (4,4-diiodobutyl)phosphonate (5k).

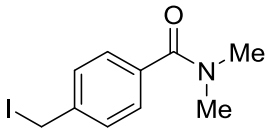
A solution of diethyl phosphite (158 mg, 1.15 mmol, 1 equiv) in DMF (10 mL) was added to NaH (60% dispersion in mineral oil, 46 mg, 1.15 mmol, 1 equiv). The mixture was stirred for 30 min at room temperature and then a solution of 1,1,4-triiodobutane (500 mg, 1.15 mmol, 1 equiv) in DMF (1 mL) was added. After stirring for 1 h, the resulting solution was diluted with water (100 mL) and EtOAc (100 mL). Layers were separated, the organic layer was washed with water (100 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the residue by silica gel flash column chromatography using gradient elution (1:4 hexane:EtOAc to EtOAc) followed by reversed phase C18 flash chromatography using gradient elution (95:5 H_2O:MeCN to 5:95 H_2O:MeCN) afforded the target phosphonate **5k** (135 mg, 26%) as a colorless oil. Analytical TLC on silica gel, 1:4 hexane:EtOAc, R*f* = 0.29.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (t, *J* = 6.4 Hz, 1H), 4.20 – 4.01 (m, 4H), 2.49 – 2.41 (m, 2H), 1.82 – 1.70 (m, 4H), 1.33 (td, *J* = 7.0, 1.1 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 61.8 (d, *J* = 6.5 Hz), 48.3 (d, *J* = 15.3 Hz), 25.2 (d, *J* = 5.0 Hz), 23.8 (d, *J* = 142.3 Hz), 16.7 (d, *J* = 6.1 Hz). Geminal diiodide carbon signal is not observed due to insufficient spectral width.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 28.6.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_8H_{18}O_3I_2P$: 446.9083. Found 446.9095.



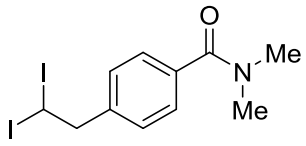
4-(Iodomethyl)-*N*,*N*-dimethylbenzamide (S1).

To a yellow suspension of NaI (5.42 g, 36.2 mmol, 5 equiv) in acetone (25 mL) was added a solution of 4-(chloromethyl)-*N*,*N*-dimethyl-benzamide[4] (1.43 g, 7.23 mmol, 1 equiv) in acetone (5 mL). After 2 h of stirring, the yellow suspension was diluted with CH_2Cl_2 (100 mL), filtered through a pad of *Celite*® and concentrated to afford the target benzylic iodide **S1** (2.00 g, 96%) as a brown amorphous solid. Analytical TLC on silica gel, 1:4 hexane:EtOAc, R*f* = 0.36.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.35 – 7.31 (m, 2H), 4.44 (s, 2H), 3.14 – 2.88 (br s, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.1, 140.9, 135.9, 128.9, 127.8, 39.7, 35.5, 4.6.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{10}H_{13}NOI$: 290.0042. Found 290.0054.



4-(2,2-Diiodoethyl)-*N*,*N*-dimethylbenzamide (4al).

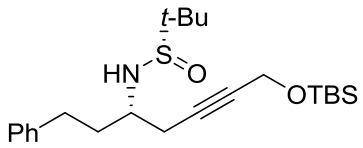
The title compound was prepared following a modified literature procedure.[1] LiHMDS (1.0 M solution in THF, 4.6 mL, 4.6 mmol, 2 equiv) was diluted with THF (14 mL) and Et_2O (18 mL), the mixture was cooled to -78 °C and a solution of diiodomethane (1.22 g, 4.57 mmol, 2 equiv) in THF (1 mL) was added dropwise. The orange solution was stirred for 30 min at -78 °C and a solution of benzyl iodide **S1** (661 mg, 2.29 mmol, 1 equiv) in THF (3 mL) was added dropwise. The resulting solution was warmed to room temperature over 16 h, quenched with water (100 mL) and diluted with Et_2O (100 mL). Layers were separated and the aqueous layer was extracted with Et_2O (2×100 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated. Purification of the residue by reversed phase C18 flash chromatography using gradient elution (95:5 to 5:95 0.1% TFA in H_2O:MeCN) afforded the target gem-diiodide **4al** (375 mg, 38%) as a light-yellow amorphous solid. Analytical TLC on silica gel, 1:4 hexane:EtOAc, R*f* = 0.43.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.28 – 7.24 (m, 2H, overlapped with $CHCl_3$), 5.08 (t, *J* = 7.3 Hz, 1H), 3.78 (d, *J* = 7.3 Hz, 2H), 3.16 –2.93 (br s, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.7, 141.4, 135.2, 129.1, 127.7, 54.1, 39.8, 35.6, -27.4.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{11}H_{14}NOI_2$: 429.9165. Found 429.9179.

Synthesis of *tert*-butyl sulfinamides 3b–d,f,g,l



(*S*)-*N*-[(3*S*)-7-[(*tert*-Butyldimethylsilyl)oxy]-1-phenylhept-5-yn-3-yl]-2-methylpropane-2-sulfinamide (3b).

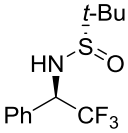
To a solution of (*S*)-*N*-[(3*S*)-7-hydroxy-1-phenylhept--5-yn-3-yl]-2-methylpropane-2-sulfinamide[5] (150 mg, 0.488 mmol, 1 equiv) and 2,6-lutidine (157 mg, 1.46 mmol, 3 equiv) in CH_2Cl_2 (2.5 mL) was added TBSOTf (0.12 mL, 0.13 g, 0.54 mmol, 1.1 equiv) at 0 °C. The brownish clear solution was stirred for 1 h at 0 °C, quenched with water (15 mL) and diluted with CH_2Cl_2 (15 mL). Layers were separated, the aqueous layer was extracted with CH_2Cl_2 (15 mL), combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the residue by silica gel flash column chromatography (65:35 hexane:EtOAc) afforded the target compound **3b** (152 mg, 74%) as a colorless oil. Analytical TLC on silica gel, 3:2 hexane:EtOAc, R*f* = 0.36.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H, overlapped with $CHCl_3$), 7.22 – 7.13 (m, 3H), 4.30 (t, *J* = 2.1 Hz, 2H), 3.50 (d, *J* = 8.5 Hz, 1H), 3.42 – 3.33 (m, 1H), 2.80 – 2.50 (m, 4H), 1.98 – 1.89 (m, 2H), 1.25 (s, 9H), 0.90 (s, 9H), 0.11 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.6, 128.6, 128.5, 126.1, 82.3, 80.6, 56.2, 54.7, 52.0, 36.9, 32.1, 27.2, 26.0, 22.9, 18.4, -5.0.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{23}H_{40}NO_2SSi$: 422.2549. Found 422.2549.

$[\alpha]^{20}_D$ +3 (*c* 1.0, CH_2Cl_2)



(*S*)-2-Methyl-*N*-[(1*R*)-2,2,2-trifluoro-1-phenylethyl]propane-2-sulfinamide (3c).

To a solution of (*S*)-2-methyl-*N*-[(*E*)-phenylmethylidene]propane-2-sulfinamide[6] (200 mg, 0.956 mmol, 1 equiv) and tetrabutylammonium acetate (425 mg, 1.41 mmol, 1.5 equiv) in THF (10 mL) was added (trifluoromethyl)trimethylsilane (0.28 mL, 0.27 g, 1.9 mmol, 2 equiv) at -20 °C. The solution was stirred at -20 °C for 1h, quenched with aqueous saturated NH_4Cl (10 mL) and diluted with EtOAc (20 mL) and water (10 mL). Layers were separated, the aqueous layer was extracted with EtOAc (20 mL), combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated. Purification

of the brownish solid residue by silica gel flash column chromatography (2:1 hexane:EtOAc) afforded the target compound **3c** (160 mg, 60%, 97:3 dr) as a colorless oil. Analytical TLC on silica gel, 2:1 hexane:EtOAc, R*f* = 0.26. Spectral data matches literature known[7] values.

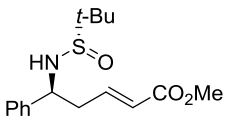
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.33 (m, 5H), 4.83 (qd, *J* = 7.4, 6.0 Hz, 1H), 3.63 (d, *J* = 6.0 Hz, 1H), 1.25 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 133.8, 129.7, 129.3, 128.1, 124.7 (q, *J* =281.5 Hz) , 61.5 (q, *J* = 30.9 Hz), 57.1, 22.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -74.0 (d, *J* = 7.0 Hz).

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{12}H_{16}NOF_3NaS$: 302.0802. Found 302.0789.

[α]$^{20}_D$ +82 (*c* 1.0, CH_2Cl_2)



Methyl (2*E*,5*S*)-5-{[(*S*)-2-methylpropane-2-sulfinyl]amino}-5-phenylpent-2-enoate (3d).

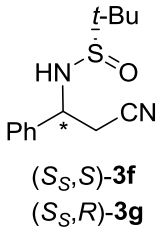
To a solution of (*S*)-2-methyl-*N*-[(1*S*)-1-phenylbut-3-en-1-yl]propane-2-sulfinamide[8] (235 mg, 0.935 mmol, 1 equiv) and Hoveyda-Grubbs 2nd generation Ru metathesis catalyst (18 mg, 30 μmol, 3 mol%) in CH_2Cl_2 (3 mL) was added methyl acrylate (0.42 mL, 0.40 g, 4.7 mmol, 5 equiv). The brown solution was stirred at 45 °C for 4 h and DMSO (0.20 mL, 0.22 g, 2.8 mmol, 3 equiv) was added. The green solution was stirred for 16 h at room temperature and concentrated. Purification of the crude residue by silica gel flash column chromatography (Et_2O) followed by reversed phase C18 flash chromatography using gradient elution (95:5 to 5:95 H_2O:MeCN) afforded the target compound **3d** (163 mg, 56%) as a colorless oil. Analytical TLC on silica gel, Et_2O, R*f* = 0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 6.78 (dt, *J* = 15.7, 7.4 Hz, 1H), 5.79 (dt, *J* = 15.7, 1.5 Hz, 1H), 4.55 (ddd, *J* = 7.4, 5.6, 3.6 Hz, 1H), 3.68 (s, 3H), 3.45 (d, *J* = 3.6 Hz, 1H), 2.91 – 2.81 (m, 1H), 2.74 (dtd, *J* = 14.6, 7.4, 1.5 Hz, 1H), 1.23 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.5, 144.2, 141.1, 129.0, 128.4, 127.2, 124.1, 58.0, 56.2, 51.6, 39.3, 22.8.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{16}H_{23}NO_3NaS$: 332.1296. Found 332.1310.

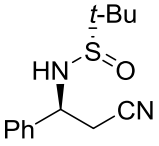
[α]$^{20}_D$ +49 (*c* 1.0, CH_2Cl_2)



(S_S,*S*)-**3f**
(S_S,*R*)-**3g**

_N_-[2-Cyano-1-phenylethyl]-2-methylpropane-2-sulfinamides (*S*,*S*)-3f and (*S*,*R*)-3g.

To a solution of diisopropylamine (531 mg, 5.25 mmol, 1.75 equiv) in THF (12 mL) was added *n*-BuLi (2.7 M solution in hexane, 2.7 mL, 4.5 mmol, 1.5 equiv) dropwise at room temperature. The solution was cooled to -78 °C and acetonitrile (0.24 mL, 0.18 g, 4.5 mmol, 1.5 equiv) was added. After 30 min of stirring at -78 °C the obtained milky suspension was treated dropwise with a solution of (*S*)-2-methyl-*N*-[(*E*)-phenylmethylidene]propane–2-sulfinamide[6] (628 mg, 3.00 mmol, 1 equiv) in THF (3 mL). The yellow solution was stirred for 2 h at -78 °C and quenched with aqueous saturated NH_4Cl solution (10 mL). After slowly warming to room temperature, the mixture was diluted with water (50 mL) and EtOAc (50 mL). Layers were separated and the aqueous layer was extracted with EtOAc (50 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated. Purification of the yellow liquid residue by silica gel flash column chromatography (3:1 hexane:EtOAc) afforded the (*S*,*S*)-diastereomer **3f** (270 mg, 36%) as a yellowish amorphous solid and the (*S,R*)-diastereomer **3g** (152 mg, 20%) as a colorless oil.



(*S*)-*N*-[(1*S*)-2-Cyano-1-phenylethyl]-2-methylpropane-2-sulfinamide (3f).

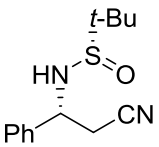
Analytical TLC on silica gel, 1:3 hexane:EtOAc, R*f* = 0.37.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.33 (m, 5H), 4.77 – 4.70 (m, 1H), 3.65 (s, 1H), 3.00 (ddd, *J* = 16.9, 6.3, 1.3 Hz, 1H), 2.85 (dd, *J* = 16.8, 4.8 Hz, 1H), 1.29 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.2, 129.4, 129.3, 126.8, 116.7, 56.6, 54.7, 26.1, 22.7.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{18}N_2OSNa$: 273.1038. Found 273.1039.

$[\alpha]^{20}_D$ +59 (*c* 1.0, CH_2Cl_2)



(*S*)-*N*-[(1*R*)-2-Cyano-1-phenylethyl]-2-methylpropane-2-sulfinamide (3g).

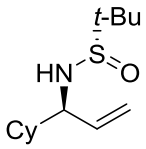
Analytical TLC on silica gel, 1:3 hexane:EtOAc, R*f* = 0.24.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 5H), 4.72 (q, *J* = 5.8 Hz, 1H), 3.78 (d, *J* = 5.4 Hz, 1H), 3.03 – 2.90 (m, 2H), 1.24 (s, 9H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.4, 129.2, 129.1, 127.2, 116.6, 56.5, 55.6, 27.5, 22.7.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{18}N_2OSNa$: 273.1038. Found 273.1046.

$[\alpha]^{20}_D$ +97 (*c* 1.0, CH_2Cl_2)



(*S*)-*N*-[(1*S*)-1-Cyclohexylprop-2-en-1-yl]-2-methylpropane-2-sulfinamide (3l).

Vinylmagnesium bromide (0.7M solution in THF, 10.0 mL, 7.00 mmol, 1.5 equiv) was added to a solution of (*S*)-*N*-[(*E*)-cyclohexylmethylidene]-2-methylpropane-2-sulfinamide[9] (1.00 g, 4.64 mmol, 1 equiv) in CH_2Cl_2 (50 mL) at -78 °C. The mixture was warmed to room temperature over 16 h, quenched with aqueous saturated NH_4Cl solution (50 mL) and extracted with EtOAc (3×50 mL). Combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 and concentrated. Purification of the orange liquid residue by silica gel flash column chromatography (1:3 hexane:MTBE) afforded target compound **3l** (163 mg, 14%, 96:4 dr) as a yellow oil. Analytical TLC on silica gel, 3:1 hexane:MTBE, R*f* = 0.39.

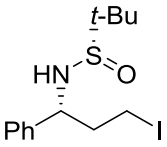
^1H NMR (400 MHz, $CDCl_3$) δ 5.70 – 5.58 (m, 1H), 5.23 – 5.16 (m, 2H), 3.65 – 3.56 (m, 1H), 3.18 (d, *J* = 3.3 Hz, 1H), 1.81 – 1.60 (m, 5H, overlapped with water), 1.50 – 1.40 (m, 1H), 1.31 – 0.75 (m, 14H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 137.3, 118.0, 63.1, 55.6, 43.3, 31.1, 29.6, 28.6, 26.5, 26.3, 22.8.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{26}NOS$: 244.1735. Found 244.1739.

$[\alpha]^{20}_D$ +79 (*c* 1.0, CH_2Cl_2)

Synthesis of cyclic sulfinamides 1v and 1w



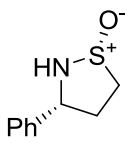
(*S*)-*N*-[(1*R*)-3-Iodo-1-phenylpropyl]-2-methylpropane-2-sulfinamide (S2). To a solution of imidazole (1.40 g, 20.5 mmol, 2 equiv) and PPh_3 (2.83 g, 10.8 mmol, 1.05 equiv) in CH_2Cl_2 (80 mL) was added iodine (2.74 g, 10.8 mmol, 1.05 equiv) in one portion at room temperature. After compete dissolution of iodine, the yellow suspension was cooled to 0 °C and a solution of (*S*)-*N*-[(1*R*)-3-hydroxy-1-phenylpropyl]--2-methylpropane-2-sulfinamide[10] (2.62 g, 10.3 mmol, 1 equiv) in CH_2Cl_2 (20 mL) was added slowly. After 15 min of stirring at 0 °C, the solution was warmed to room temperature and stirred for 2 h. The brown solution was quenched with water (100 mL) and layers were separated. The aqueous layer was extracted with CH_2Cl_2 (100 mL), combined organic layers were dried over Na_2SO_4, filtered and concentrated. Purification of the orange liquid residue by silica gel flash column chromatography (3:1 CH_2Cl_2:EtOAc) afforded the target compound **S2** (3.07 g, 82%) as a slightly off-white amorphous solid. Analytical TLC on silica gel, 3:1 CH_2Cl_2:EtOAc, R*f* = 0.33.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 4.51 (ddd, *J* = 8.2, 5.9, 4.0 Hz, 1H), 3.42 (d, *J* = 4.0 Hz, 1H), 3.10 (ddd, *J* = 9.8, 7.5, 5.9 Hz, 1H), 2.92 (dt, *J* = 9.8, 7.5 Hz, 1H), 2.42 – 2.28 (m, 2H), 1.18 (s, 9H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 140.4, 128.9, 128.2, 127.6, 60.1, 55.9, 42.1, 22.7, 0.9.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{21}NOSI$: 366.0389. Found 366.0394.

$[\alpha]^{20}_D$ +40 (*c* 1.0, CH_2Cl_2)



(1*R*,3*R*)-3-Phenyl-1,2-thiazolidin-1-ium-1-olate (1v). A solution of iodide **S2** (2.68 g, 7.35 mmol, 1 equiv) in toluene (250 mL) was warmed to 110 °C. A solution of AIBN (1.33 g, 8.08 mmol, 1.1 equiv) and *n*-Bu_3SnH (2.56 g, 8.81 mmol, 1.2 equiv) in toluene (50 mL) was added using a syringe pump over 2 h at 110 °C. The clear colorless solution was stirred for 30 min at 110 °C, cooled and concentrated. The residue was partitioned between MeCN (100 mL) and hexane (100 mL). Layers were separated, the MeCN layer was washed with hexane (4×100 mL) and concentrated. Recrystallization of the residue from heptane:EtOAc afforded the cyclic

sulfinamide **1v** (1.01 g, 76%) as white needles. Analytical TLC on silica gel, 50:1 EtOAc:MeOH, R*f* = 0.27.

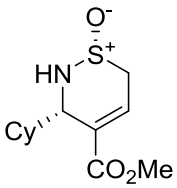
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.39 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 4.72 – 4.67 (m, 1H), 4.65 (s, 1H), 3.09 (dd, *J* = 12.0, 5.7 Hz, 1H), 2.86 (ddd, *J* = 13.6, 12.0, 6.6 Hz, 1H), 2.65 (dt, *J* = 13.6, 6.6 Hz, 1H), 2.61 – 2.51 (m, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 142.2, 128.9, 127.9, 127.4, 67.1, 56.5, 32.7.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_9H_{12}NOS$: 182.0640. Found 182.0648.

[α]$^{20}_D$ -163 (*c* 1.0, CH_2Cl_2)

Melting point 145 – 147 °C



(1*R*,3*S*)-3-Cyclohexyl-4-(methoxycarbonyl)-1,2,3,6-tetrahydro-1,2-thiazin-1-ium-1-olate (S3).

To a solution of (1*S*,3*S*)-1-*tert*-butyl-3-cyclohexyl-4-(methoxycarbonyl)-3,6-dihydro-1$\lambda^{4,2}$-thiazin-1-ium-1-olate[11] (1.68 g, 5.37 mmol, 1 equiv) in THF (50 mL) was added BF_3•Et_2O (1.3 mL, 1.5 g, 11 mmol, 2 equiv) and the clear solution was stirred for 80 min at room temperature followed by 30 min at 50 °C. The mixture was cooled to room temperature, quenched with aqueous saturated $NaHCO_3$ (100 mL) and diluted with EtOAc (100 mL). Layers were separated, the aqueous layer was extracted with EtOAc (100 mL), combined organic layers were washed with brine (100 mL), dried over Na_2SO_4 and concentrated. Recrystallization from EtOAc afforded the target sulfinamide **S3** (957 mg, 69%) as a shiny yellowish solid. Analytical TLC on silica gel, MTBE, R*f* = 0.27.

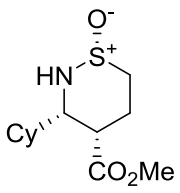
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.91 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.67 (d, *J* = 4.4 Hz, 1H), 4.14 – 4.09 (m, 1H), 4.04 (ddd, *J* = 17.9, 5.9, 1.9 Hz, 1H), 3.78 (s, 3H), 3.18 (ddd, *J* = 17.9, 3.8, 1.3 Hz, 1H), 2.14 – 2.06 (m, 1H), 2.05 – 1.96 (m, 1H), 1.79 – 1.66 (m, 2H), 1.66 – 1.58 (m, 1H), 1.50 – 1.43 (m, 1H), 1.28 – 0.99 (m, 5H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.2, 136.1, 129.8, 57.8, 52.3, 50.9, 42.3, 30.9, 29.9, 26.3, 26.2, 26.0.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{12}H_{20}NO_3S$: 258.1164. Found 258.1166.

[α]$^{20}_D$ -84 (*c* 1.0, CH_2Cl_2)

Melting point 171 – 173 °C (decomposition)



(1*R*,3*S*,4*S*)-3-Cyclohexyl-4-(methoxycarbonyl)-1,2-thiazinan-1-ium-1-olate (1w).

To a suspension of **S3** (950 mg, 3.69 mmol, 1 equiv) in THF (40 mL) was added L-selectride® (1 M solution in THF, 9.2 mL, 9.2 mmol, 2.5 equiv) dropwise at -78 °C. The clear orange solution was warmed to -30 °C and stirred for 3 h at that temperature. After cooling back to -78 °C, the reaction solution was quenched with aqueous saturated NH_4Cl (20 mL), warmed to room temperature and diluted with EtOAc (150 mL) and water (150 mL). Layers were separated, the aqueous layer was extracted with EtOAc (100 mL), combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the residue by silica gel flash column chromatography (MTBE) followed by recrystallization from EtOAc afforded the title compound **1w** (214 mg, 22%) as shiny white crystals. Analytical TLC on silica gel, MTBE, R*f* = 0.24.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 4.02 (d, *J* = 10.0 Hz, 1H), 3.70 (s, 3H), 3.00 (td, *J* = 9.8, 3.3 Hz, 1H), 2.96 – 2.89 (m, 1H), 2.77 (dt, *J* = 5.8, 3.6 Hz, 1H), 2.61 (ddd, *J* = 12.7, 11.2, 3.6 Hz, 1H), 2.52 – 2.40 (m, 1H), 2.22 – 2.08 (m, 2H), 1.81 – 1.56 (m, 5H, overlapped with water), 1.33 – 1.05 (m, 3H), 0.99 – 0.80 (m, 2H).

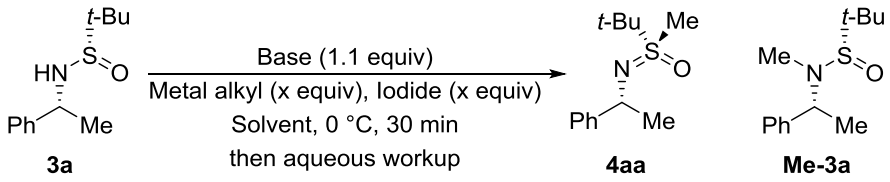
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 174.0, 60.9, 52.1, 50.4, 41.1, 39.5, 30.9, 30.5, 26.6, 26.4, 26.2, 22.3.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{12}H_{22}NO_3S$: 260.1320. Found 260.1322.

[α]$^{20}_D$ -2 (*c* 1.0, CH_2Cl_2)

Melting point 184 – 187 °C

Table S1. Optimization of reaction conditions for *S*-methylation of **3a**[a]



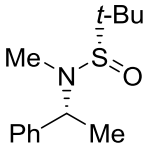
Entry	Base	Solvent	Conc., M	Metal alkyl	Halide	x	Yield, %[b]		
							3a	4aa	Me-3a
1[c]	–	Toluene	0.1	$Zn(CH_2I)_2$		2.5	31	25	-
2[c]	–	THF	0.1	$Zn(CH_2I)_2$		2.5	100	0	-
3[c]	LiHMDS	THF	0.1	$Zn(CH_2I)_2$		2.5	27	68	-
4[c]	LiHMDS	THF	0.1	$IZnCH_2I$		2.5	43	52	-
5[c]	LiHMDS	THF	0.1	$EtZnCH_2I$		2.5	20	70	-
6[d]	LiHMDS	THF	0.1	$EtZnCH_2I$		2.5	99	0	-
7	LiHMDS	THF	0.1	$ZnEt_2$	CH_2I_2	2.5	3	86	-
8	*n*-BuLi	THF	0.1	$ZnEt_2$	CH_2I_2	2.5	4	82	-
9	NaHMDS	THF	0.1	$ZnEt_2$	CH_2I_2	2.5	15	74	-
10	KHMDS	THF	0.1	$ZnEt_2$	CH_2I_2	2.5	8	75	-
11	LiHMDS	DME	0.1	$ZnEt_2$	CH_2I_2	2.5	11	80	-
12	LiHMDS	CH_2Cl_2	0.1	$ZnEt_2$	CH_2I_2	2.5	27	60	-
13	LiHMDS	Et_2O	0.1	$ZnEt_2$	CH_2I_2	2.5	30	60	-
14	LiHMDS	DMF	0.1	$ZnEt_2$	CH_2I_2	2.5	4	50	-
15	LiHMDS	THF	0.04	$ZnEt_2$	CH_2I_2	2.5	2	95	-
16	LiHMDS	THF	0.25	$ZnEt_2$	CH_2I_2	2.5	5	89	-
17	**LiHMDS**	**THF**	**0.1**	**$ZnEt_2$**	**CH_2I_2**	**1.2**	**0**	**95**	-
18	LiHMDS	THF	0.1	$(PhO)_2PO_2ZnCH_2I$		1.2	31	42	-
19	LiHMDS	THF	0.1	$ZnMe_2$	CH_2I_2	2.5	6	83	5
20	LiHMDS	THF	0.1	$ZnMe_2$	MeI	2.5	5	-	89
21	LiHMDS	THF	0.1	Bu_2Mg	CH_2I_2	2.5	85	4	-
22	LiHMDS	THF	0.1	Me_3Al	CH_2I_2	2.5	94	0	-
23	LiHMDS	THF	0.1	$ZnEt_2$	CH_2ClI	2.5	2	87	-
24	LiHMDS	THF	0.1	$ZnEt_2$	CHI_3	2.5	37	59	-
25	LiHMDS	THF	0.1	$ZnEt_2$	CH_2Br_2	2.5	77	0	-

[a] **3a** (0.1 mmol) was deprotonated by base (0.11 mmol) in solvent (1 mL) for 15 min and then sequentially treated with alkyl metal and halide;

[b] ^{1}H NMR yield measured against mesitylene as internal standard;

[c] carbenoid was preformed in solvent (0.5 mL) over 5 min and treated with a solution of (deprotonated) **3a** in solvent (0.5 mL);

[d] carbenoid was preformed in THF (0.5 mL) over 1.5 h.



(*S*)-*N*,2-Dimethyl-*N*-[(1*R*)-1-phenylethyl]propane-2-sulfinamide (Me-3a). To a solution of (*S*)-2-methyl-*N*-[(1*R*)-1-phenylethyl]propane-2-sulfinamide **3a**[12] (45 mg, 0.20 mmol, 1 equiv) in THF (2 mL) was added LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv.) at 0 °C. The yellow solution was stirred for 15 min at 0 °C and MeI (15 µL, 34 mg, 0.24 mmol, 1.2 equiv) was added. After 30 min of stirring at 0 °C the solution was diluted with water (20 mL), EtOAc (20 mL) and layers were separated. The aqueous layer was extracted with EtOAc (20 mL), combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the crude residue by silica gel flash column chromatography (2:1 hexane:EtOAc) afforded the title compound **Me-3a** (38 mg, 79%) as a colorless oil. Analytical TLC on silica gel, 2:1 hexane:EtOAc, R*f* = 0.26.

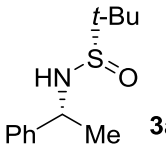
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 4H), 7.30 – 7.24 (m, 1H, overlapped with $CHCl_3$), 4.57 (q, *J* = 7.0 Hz, 1H), 2.39 (s, 3H), 1.60 (d, *J* = 7.0 Hz, 3H), 1.24 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.4, 128.5, 127.7, 127.5, 62.0, 58.7, 26.6, 24.0, 17.7.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{21}NOSNa$: 262.1242. Found 262.1248.

$[\alpha]^{20}_D$ -19 (*c* 1.0, CH_2Cl_2)

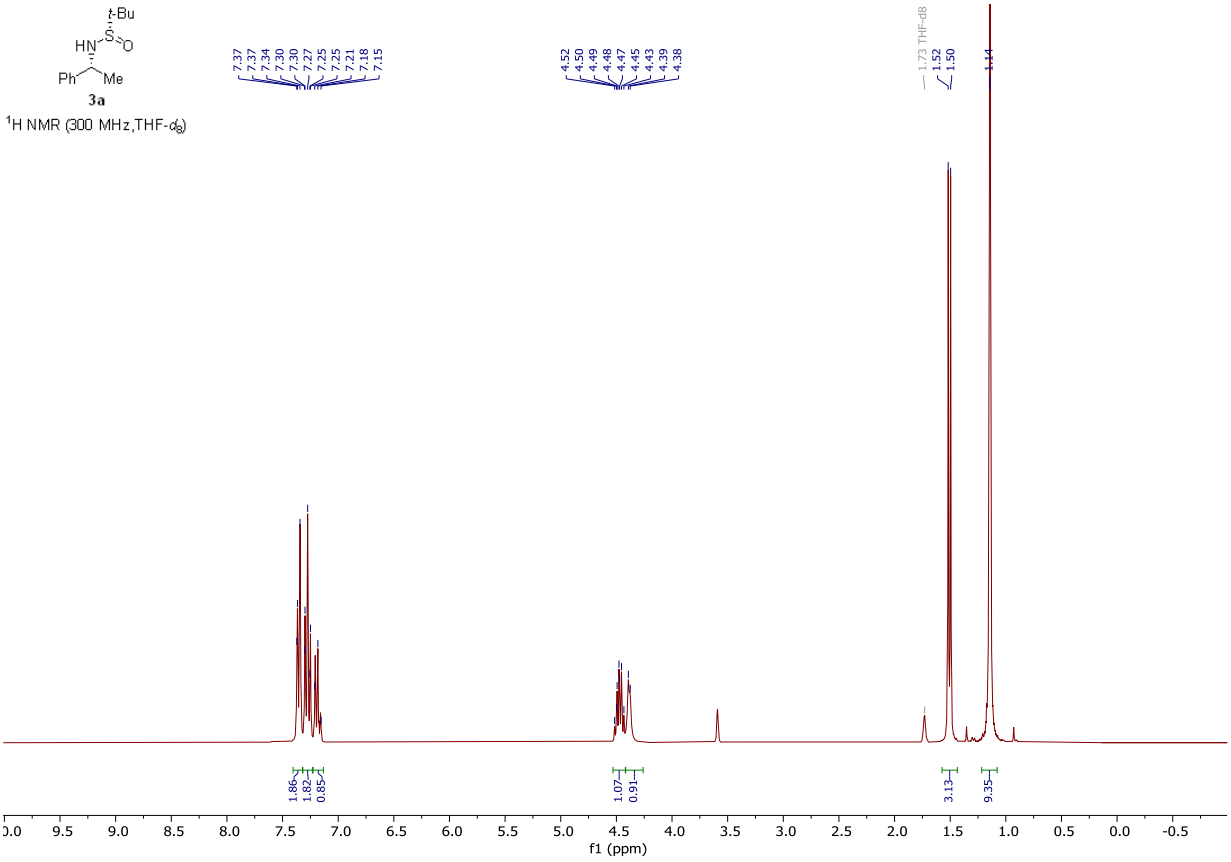
NMR investigation of key dialkylzinc intermediate 4aa-Zn formation

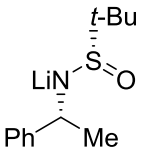


3a

(*S*)-2-Methyl-*N*-[(1*R*)-1-phenylethyl]propane-2-sulfinamide[12] **(3a).**

^{1}H NMR (300 MHz, THF-d_8) δ 7.39 – 7.31 (m, 2H), 7.30 – 7.22 (m, 2H), 7.22 – 7.13 (m, 1H), 4.52 – 4.41 (m, 1H), 4.37 (d, *J* = 5.0 Hz, 1H), 1.50 (d, *J* = 6.7 Hz, 3H), 1.13 (s, 9H).





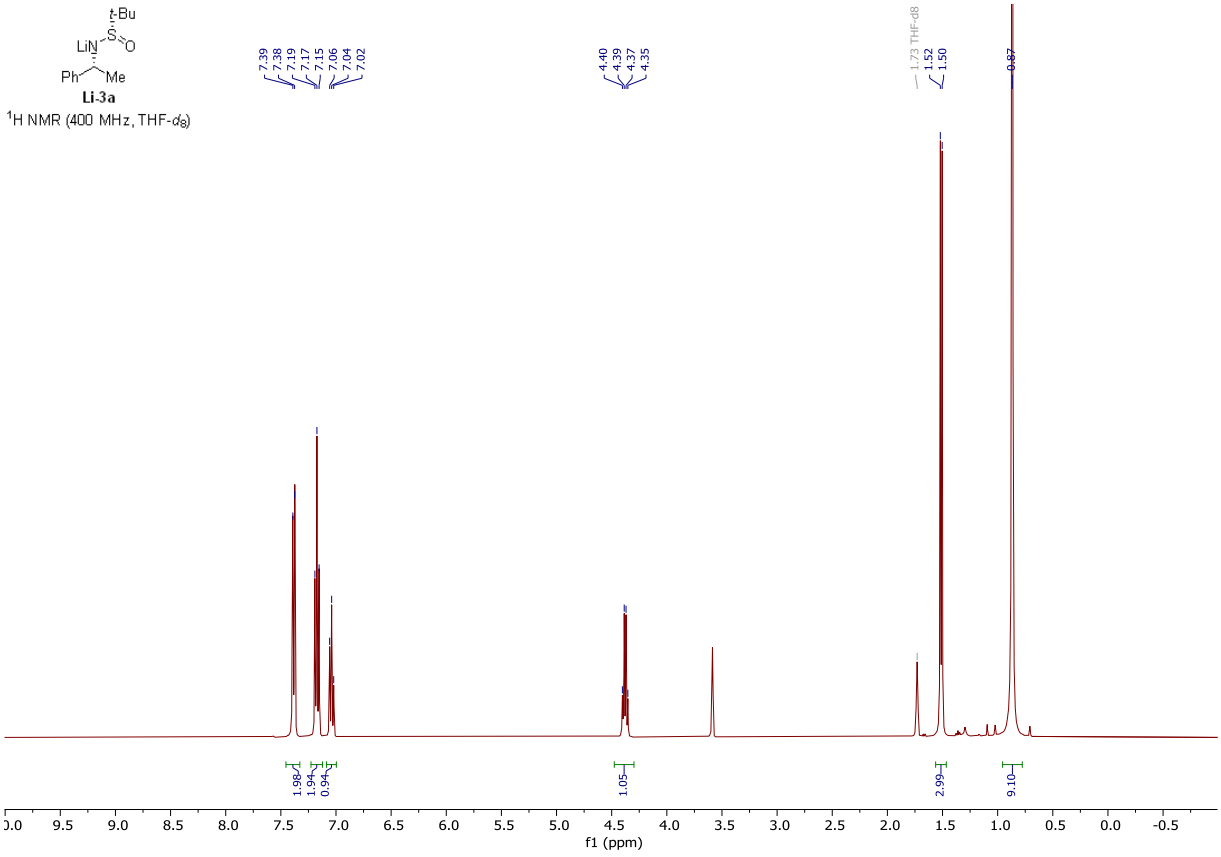
(*S*)-*N*-Lithio-2-methyl-*N*-[(1*R*)-1-phenylethyl]propane-2-sulfinamide (Li-3a).

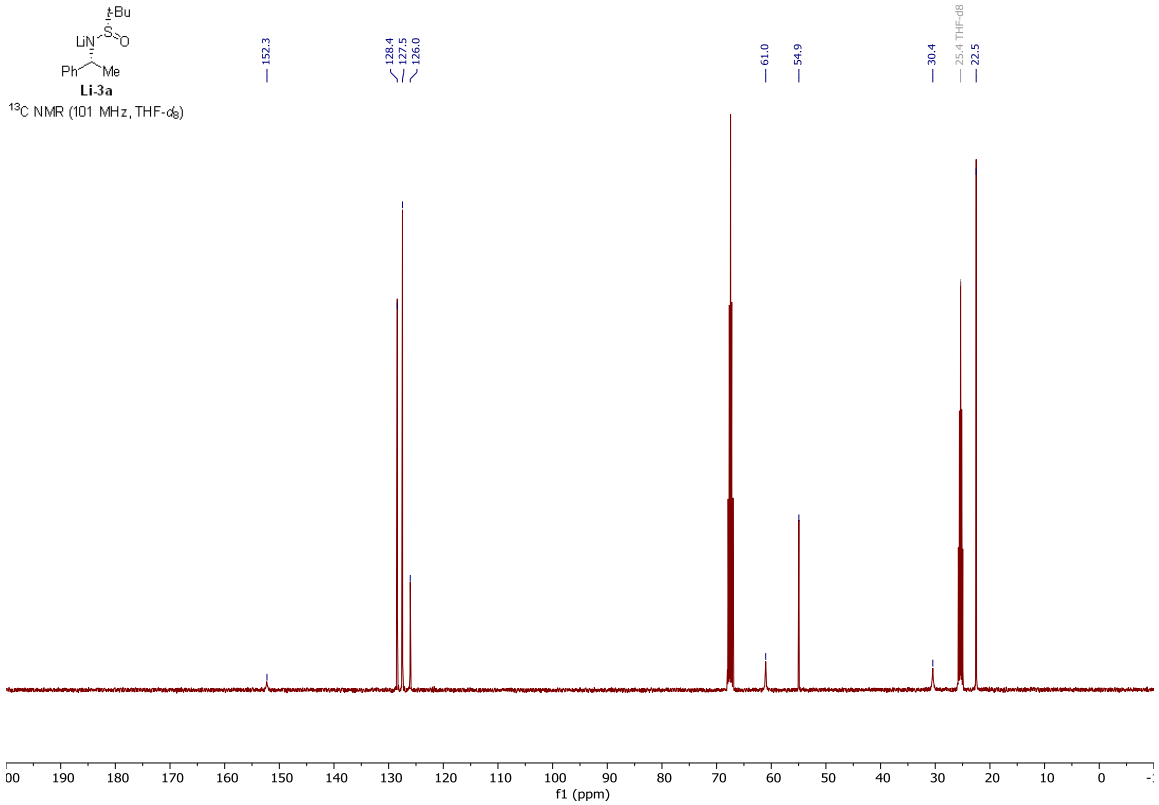
A solution of **3a** (225 mg, 1.00 mmol) in heptane:THF (3:1, 4 mL) was treated dropwise with *n*-BuLi (2.5 M solution in hexane, 0.44 mL, 1.1 mmol, 1.1 equiv) at 0 °C. After 10 min the resulting yellowish solution was concentrated under high vacuum. The obtained solid was suspended in heptane (1.5 mL) in a N_2 filled glovebox, filtered off on a P3 frit, washed with additional heptane (2×0.7 mL) and dried at 50 °C under 30 µbar for 1 h to afford **Li-3a** (207 mg, 90%) as white solid.

Li-3a was stored and manipulated with in a glovebox.

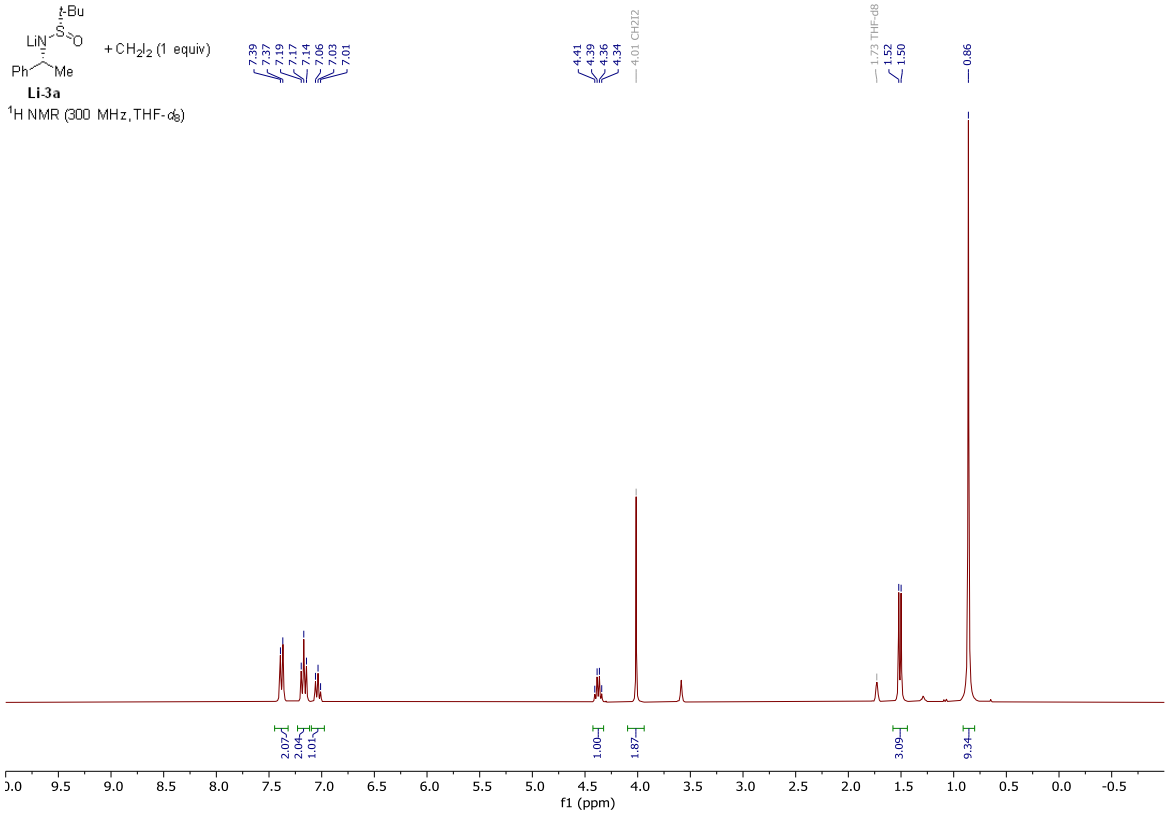
^{1}H NMR (400 MHz, THF-d_8) δ 7.43 – 7.34 (m, 2H), 7.21 – 7.13 (m, 2H), 7.08 – 7.00 (m, 1H), 4.38 (q, J = 6.6 Hz, 1H), 1.51 (d, J = 6.6 Hz, 3H), 0.87 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, THF-d_8) δ 152.3, 128.4, 127.5, 126.0, 61.0, 54.9, 30.4, 22.5.



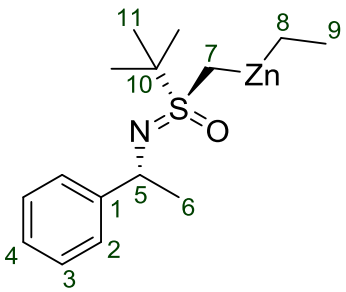


^{1}H NMR chemical shifts in THF-d_8 remained unchanged upon addition of CH_2I_2 (1 equiv).



NMR experiment.

Yellow solution of **Li-3a** (46 mg, 0.20 mmol, 1 equiv) in THF-d_8 (0.7 mL) was treated with $ZnEt_2$ (23 µL, 28 mg, 0.22 mmol, 1.1 equiv,) at 25 °C in a glovebox in a 5 mL microwave reaction vial. The resulting faintly yellow solution was taken out of the glove box, cooled to 0 °C and treated dropwise with CH_2I_2 (18 µL, 60 mg, 0.22 mmol, 1.1 equiv). After 30 min at 0 °C the obtained still faintly yellow solution was taken to the glovebox and transferred into an NMR tube.

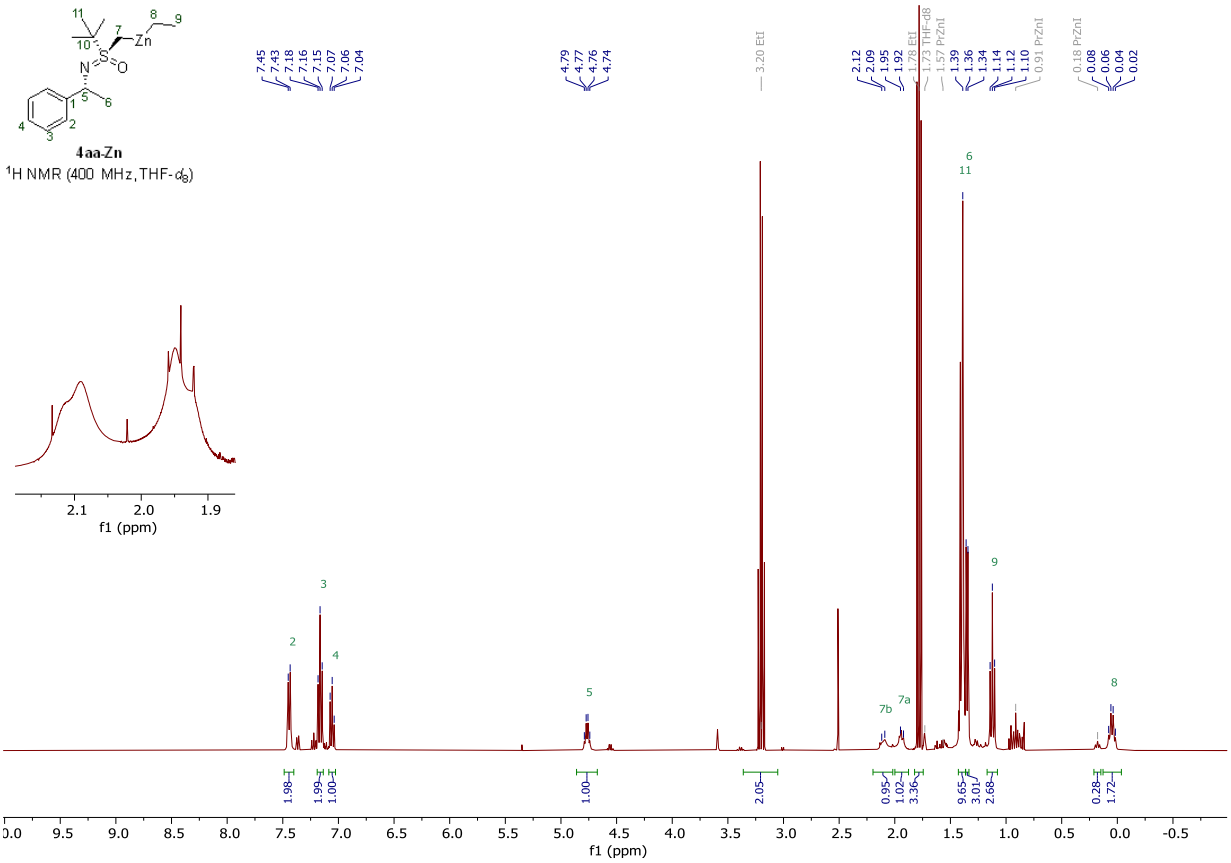


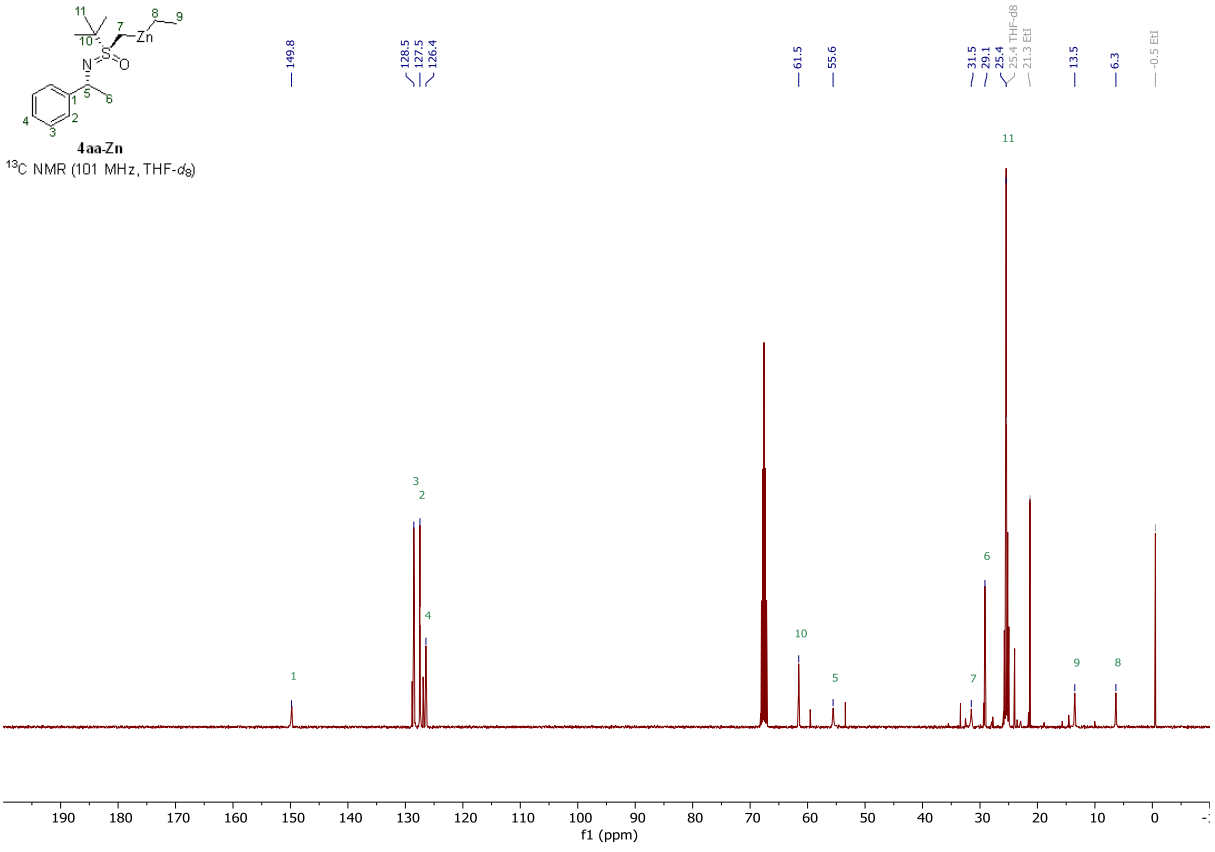
(*R*)-*tert*-Butyl[(ethylzincio)methyl]{[(1*R*)-1-phenylethyl] imino}-λ^6-sulfanone (4aa-Zn).

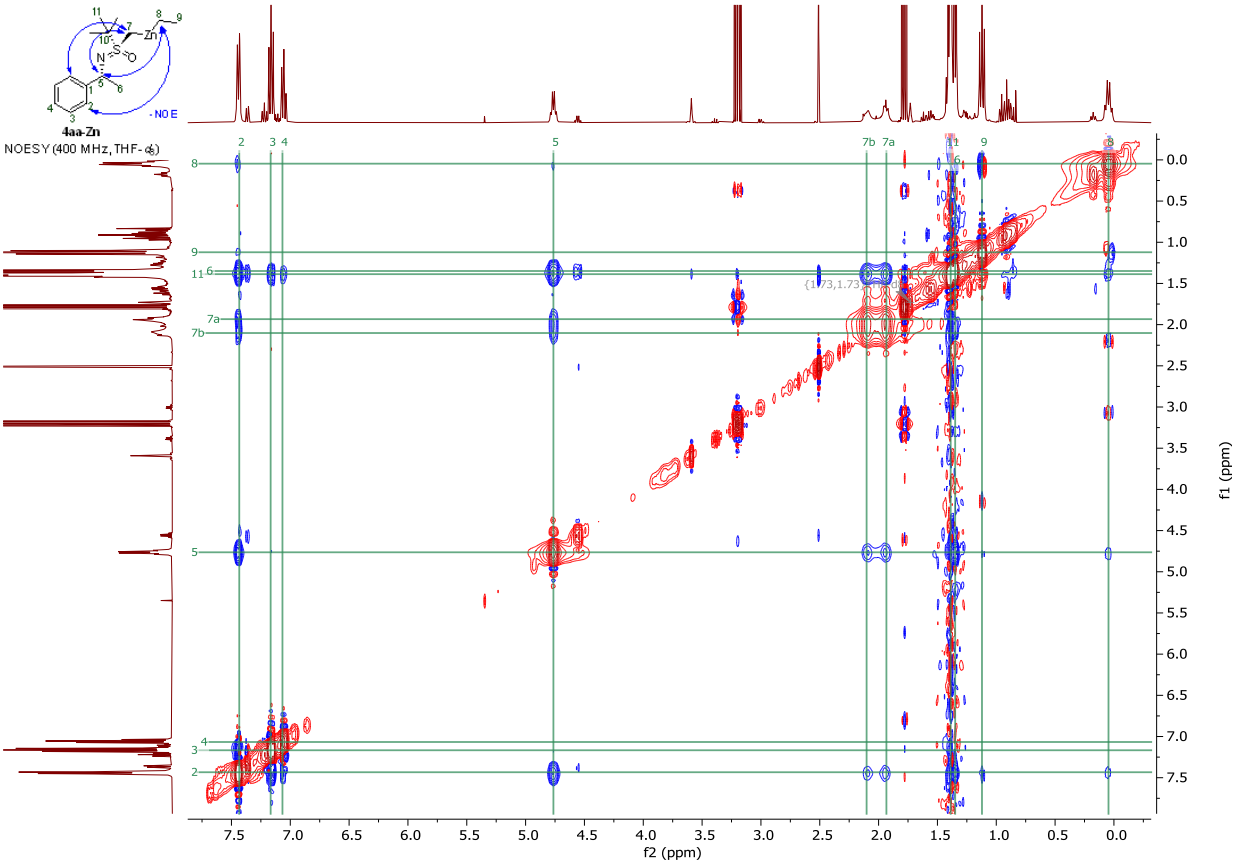
^{1}H NMR (400 MHz, THF-d_8) δ 7.48 – 7.41 (m, 2H, C^2*H*), 7.19 – 7.13 (m, 2H, C^3*H*), 7.08 – 7.03 (m, 1H, C^4*H*), 4.76 (q, *J* = 6.6 Hz, 1H, C^5*H*), 2.10 (d, *J* = 11.0 Hz, 1H, C$^7H_2$), 1.93 (d, *J* = 11.0 Hz, 1H, C$^7H_2$), 1.39 (s, 9H, C$^{11}H_3$), 1.34 (d, *J* = 6.6 Hz, 3H, C$^6H_3$), 1.12 (t, *J* = 8.1 Hz, 3H, C$^9H_3$), 0.05 (q, *J* = 8.1 Hz, 2H, C$^8H_2$).

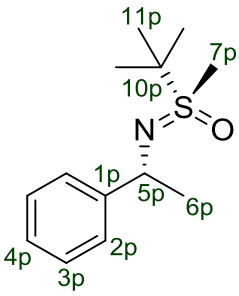
^{13}C{^{1}H} NMR (101 MHz, THF-d_8) δ 149.8 (*C*^{1}), 128.5 (*C*^{3}), 127.5 (*C*^{2}), 126.4 (*C*^{4}), 61.5 (*C*^{10}), 55.6 (*C*^{5}), 31.5 (*C*^{7}), 29.1 (*C*^{6}), 25.5 (*C*^{11}), 13.5 (*C*^{9}), 6.3 (*C*^{8}).

The presence of a minor amount of **4aa** was ascribed to quenching of **4aa-Zn** by inadvertently introduced moisture.


4aa-Zn
^{1}H NMR (400 MHz, THF-d_8)
f1 (ppm)


4aa-Zn
^{13}C NMR (101 MHz, THF-d_8)
f1 (ppm)



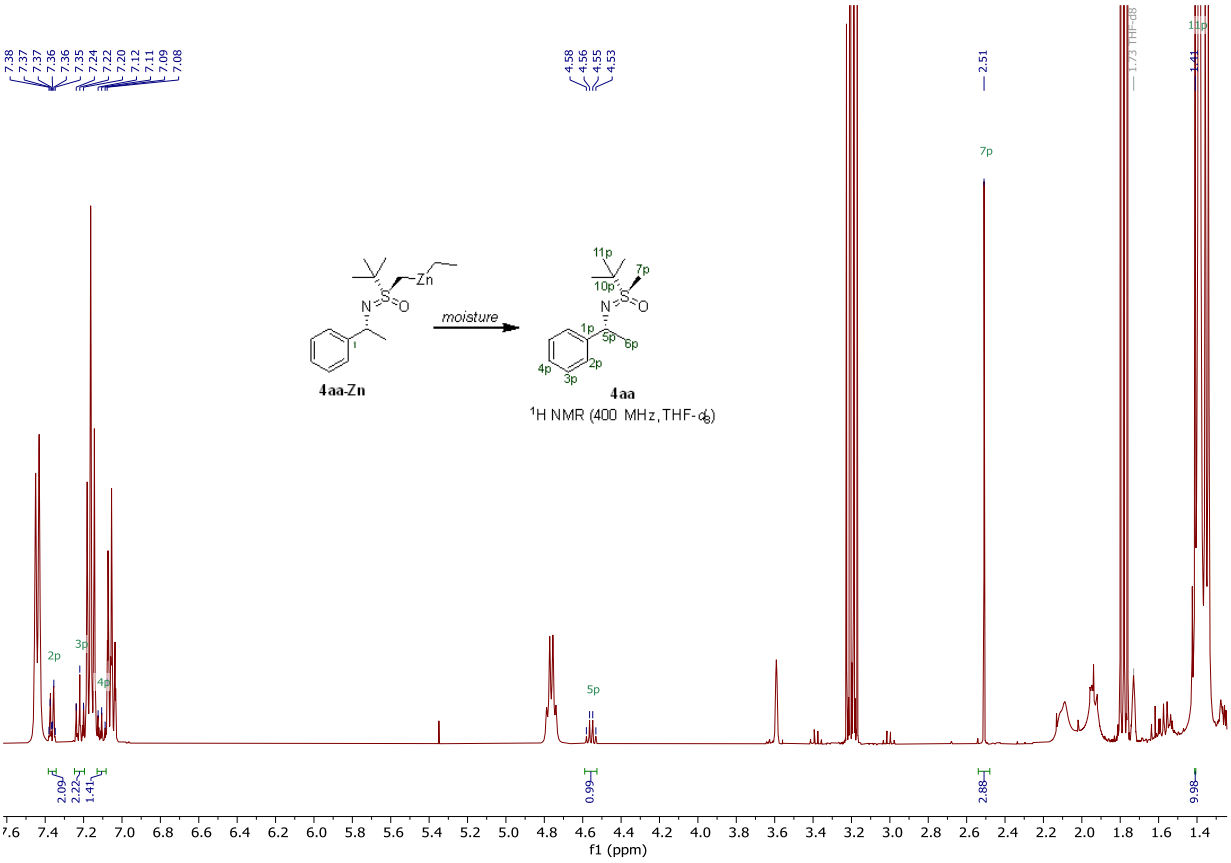


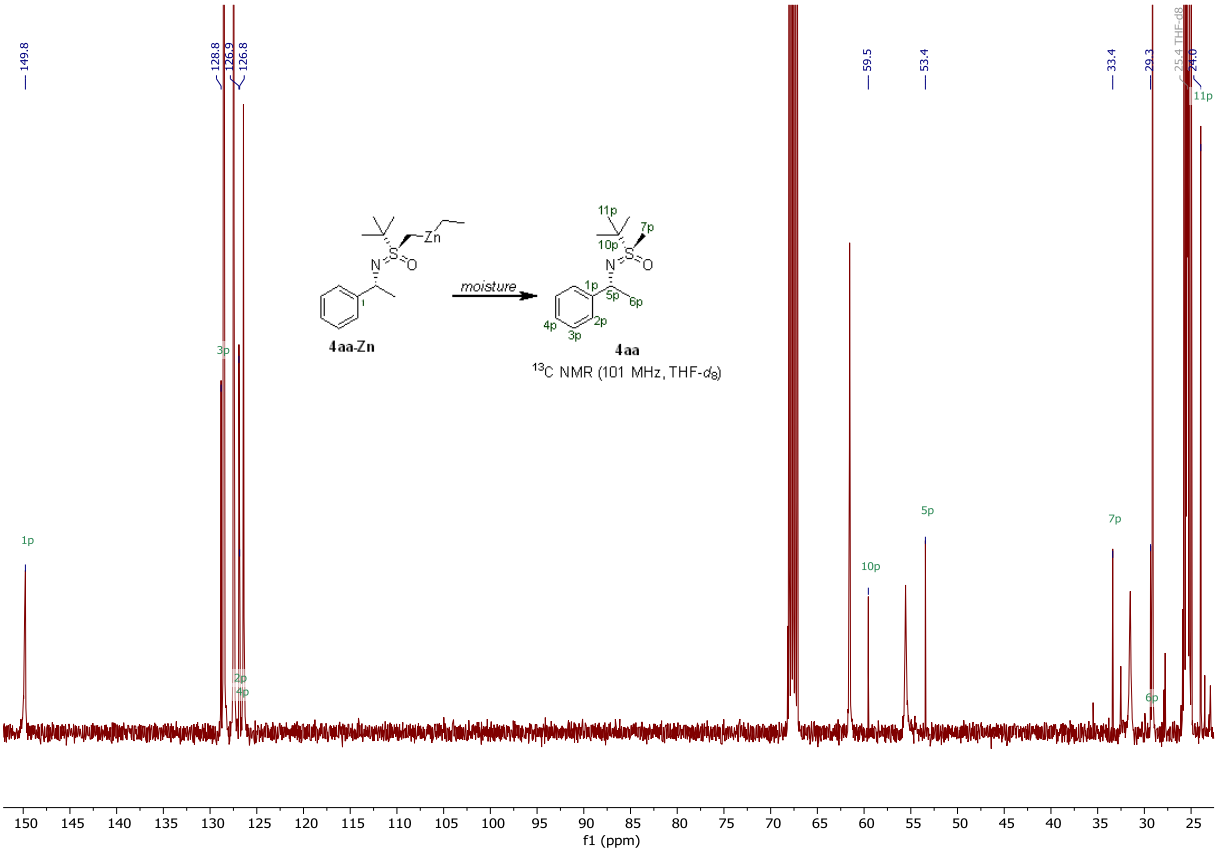
(*S*)-*tert*-Butyl(methyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (4aa).

Chemical shifts for **4aa** present as an impurity in the NMR experiment described above.

^{1}H NMR (400 MHz, THF-d_8) δ 7.39 – 7.34 (m, 2H, C^{2p}H), 7.25 – 7.20 (m, 2H, C^{3p}H), 7.13 – 7.08 (m, 1H, C^{4p}H), 4.56 (q, J = 6.6 Hz, 1H, C^{5p}H), 2.51 (s, 3H, C$^{7p}H_3$), 1.41 (s, 9H, C$^{11p}H_3$), C$^{6p}H_3$CH-signal overlaps with analogous signal in **4aa-Zn**.

^{13}C{^{1}H} NMR (101 MHz, THF-d_8) δ 149.8 (C^{1p}), 128.8 (C^{3p}), 126.9 (C^{2p}), 126.8 (C^{4p}), 59.5 (C^{10p}), 53.4 (C^{5p}), 33.4 (C^{7p}), 29.3 (C^{6p}), 24.0 (C^{11p}).

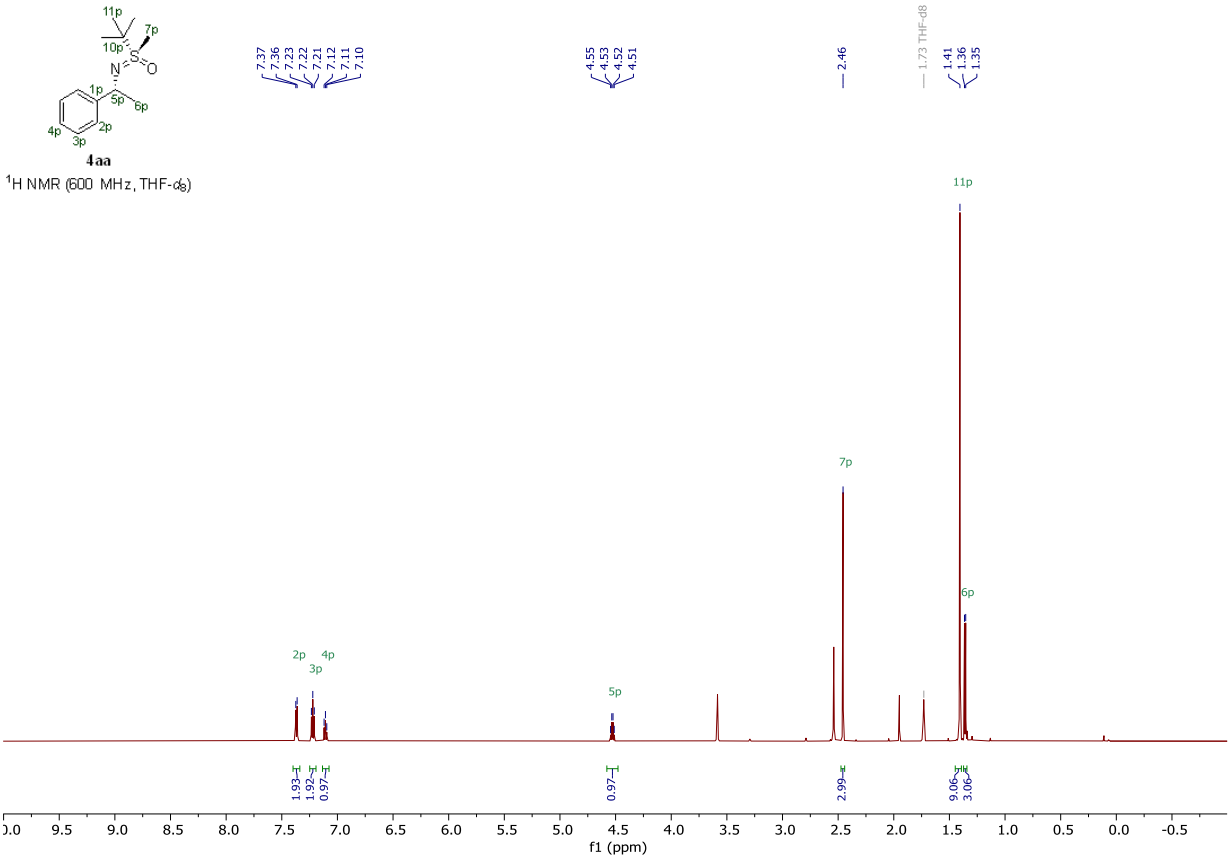

4aa-Zn
moisture
4aa
^{1}H NMR (400 MHz, THF-d_8)
f1 (ppm)

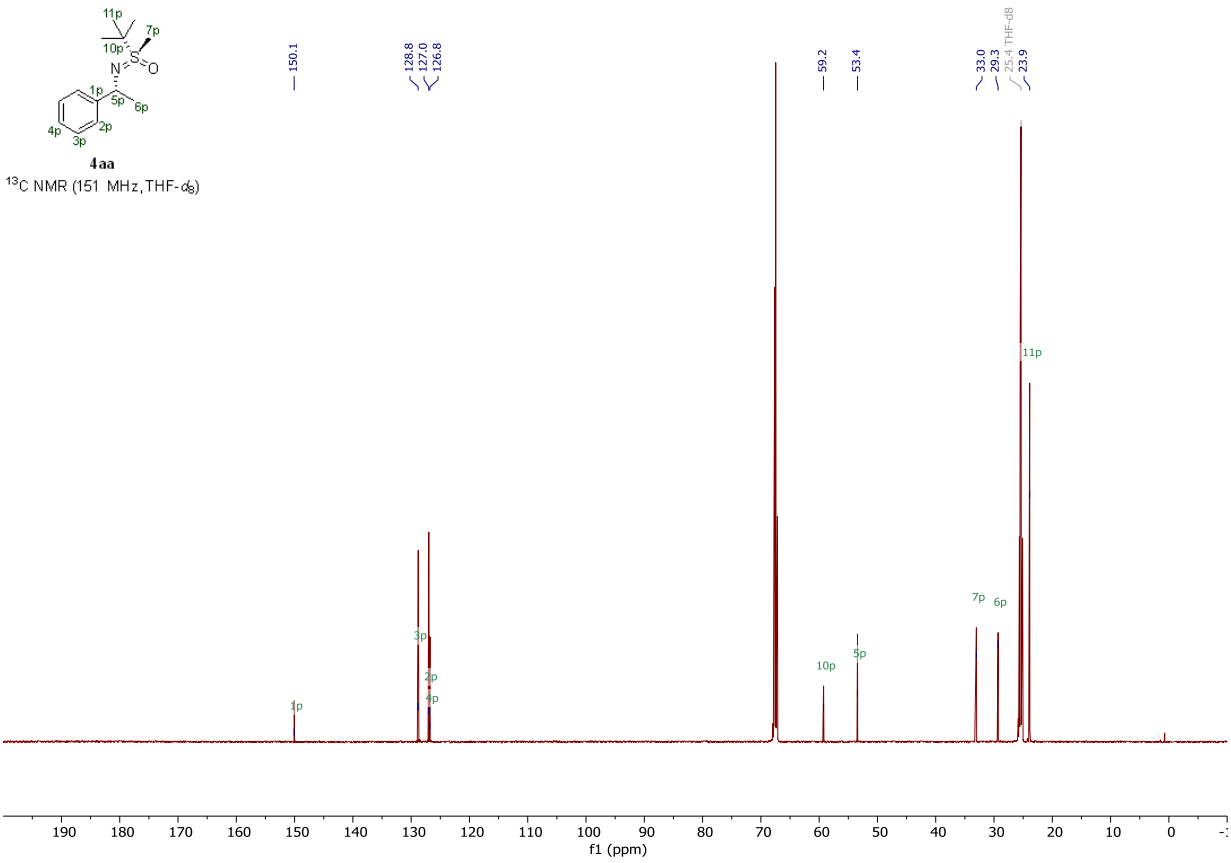

4aa-Zn
moisture
4aa
^{13}C NMR (101 MHz, THF-d_8)
f1 (ppm)

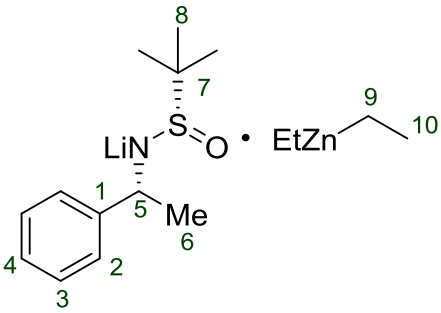
Chemical shifts for pure **4aa** in THF-d_8.

^{1}H NMR (600 MHz, THF) δ 7.39 – 7.33 (m, 2H, C^{2p}*H*), 7.24 – 7.19 (m, 2H, C^{3p}*H*), 7.13 – 7.07 (m, 1H, C^{4p}*H*), 4.52 (q, *J* = 6.6 Hz, 1H, C^{5p}*H*), 2.45 (s, 3H, C^{7p}*H*$_3$), 1.40 (s, 9H, C^{11p}*H*$_3$), 1.36 (d, *J* = 6.6 Hz, 3H, C^{6p}*H*$_3$).

^{13}C{^{1}H} NMR (151 MHz, THF) δ 150.2 (*C*^{1p}), 128.9 (*C*^{3p}), 127.1 (*C*^{2p}), 126.9 (*C*^{4p}), 59.4 (*C*^{10p}), 53.5 (*C*^{5p}), 33.1 (*C*^{7p}), 29.4 (*C*^{6p}), 24.0 (*C*^{11p}).



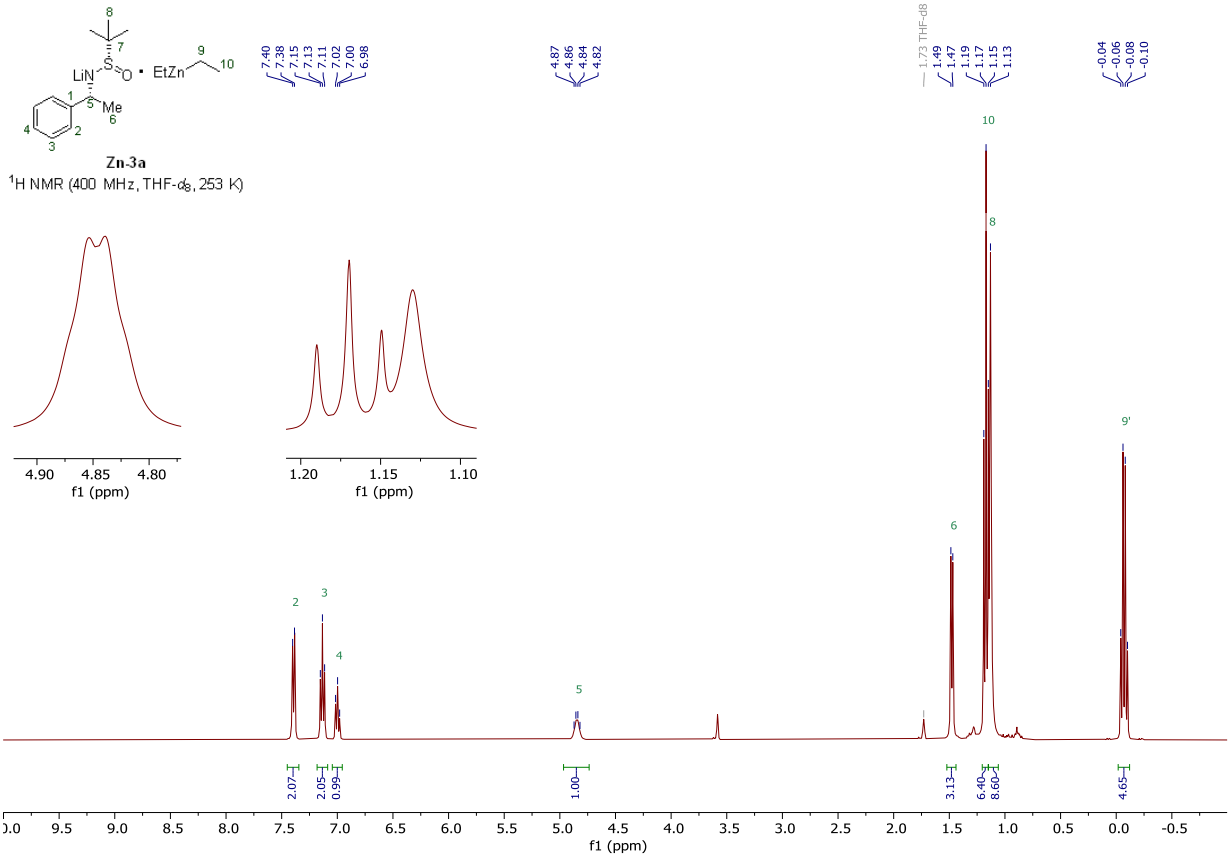


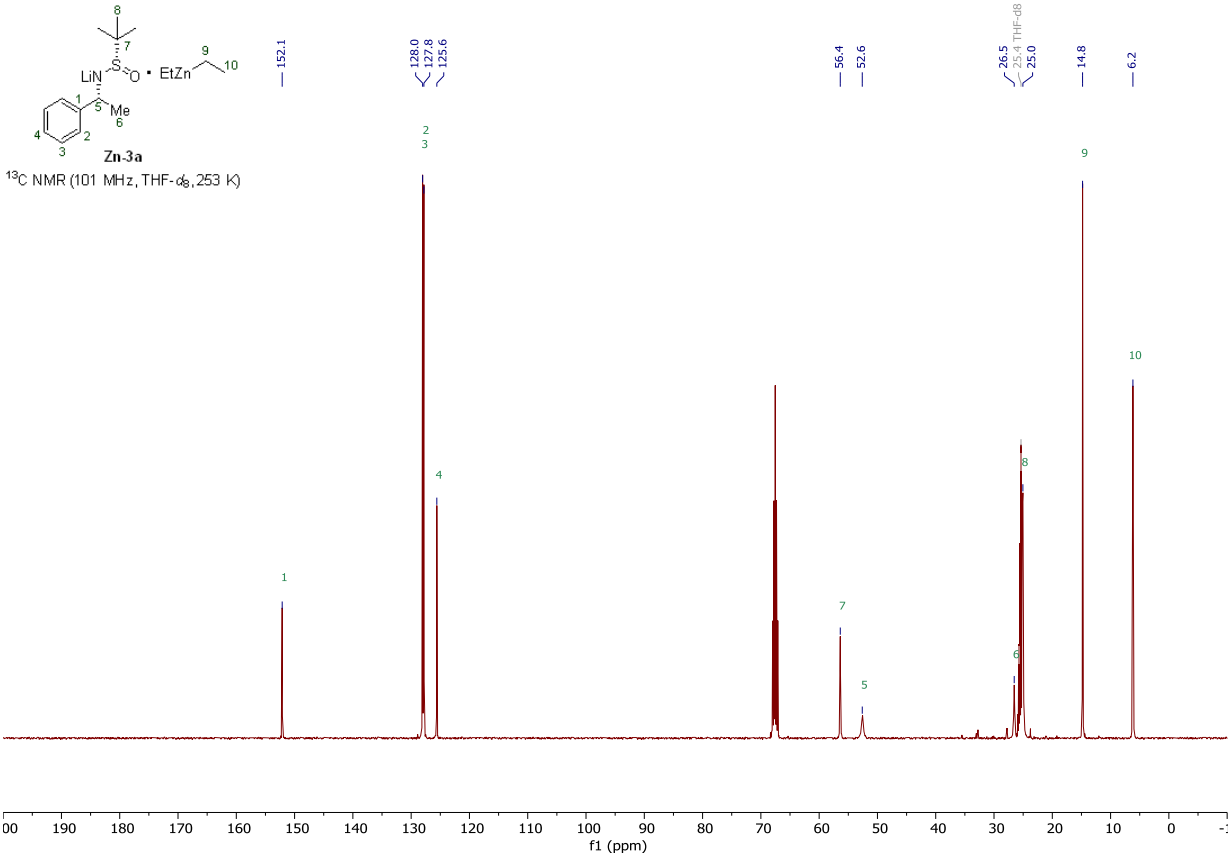


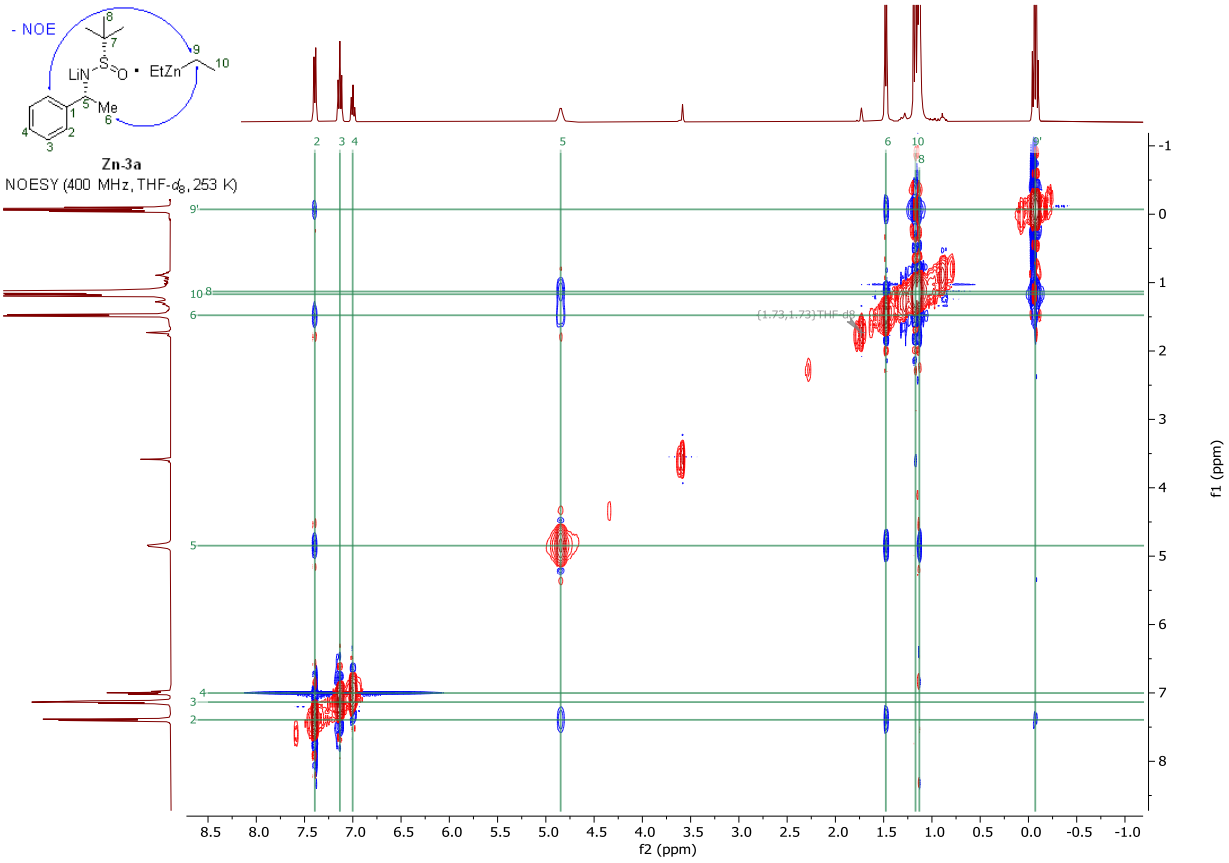
(*S*)-*N*-Lithio-2-methyl-*N*-[(1*R*)-1-phenylethyl]propane-2-sulfinamide complex with diethyl zinc (Zn-3a). Formed *in situ* from **Li-3a** (46 mg, 0.20 mmol, 1 equiv) and $ZnEt_2$ (23 µL, 28 mg, 0.22 mmol, 1.1 equiv) in THF-d_8 (0.6 mL). Slow vapor diffusion of the obtained solution with *n*-heptane afforded crystals of **Li-3a** suitable for X-ray analysis.

^{1}H NMR (400 MHz, THF-d_8, 253K) δ 7.43 – 7.36 (m, 2H, C^2*H*), 7.17 – 7.10 (m, 2H, C^3*H*), 7.04 – 6.95 (m, 1H, C^4*H*), 4.85 (q, *J* = 7.0 Hz, 1H, C^5*H*), 1.48 (d, *J* = 7.0 Hz, 1H, C$^6H_3$), 1.17 (t, *J* = 8.1 Hz, 6H, C$^{10}H_3$), 1.13 (s, 9H, C$^8H_3$), -0.07 (q, *J* = 8.1 Hz, 4H, C$^9H_2$).

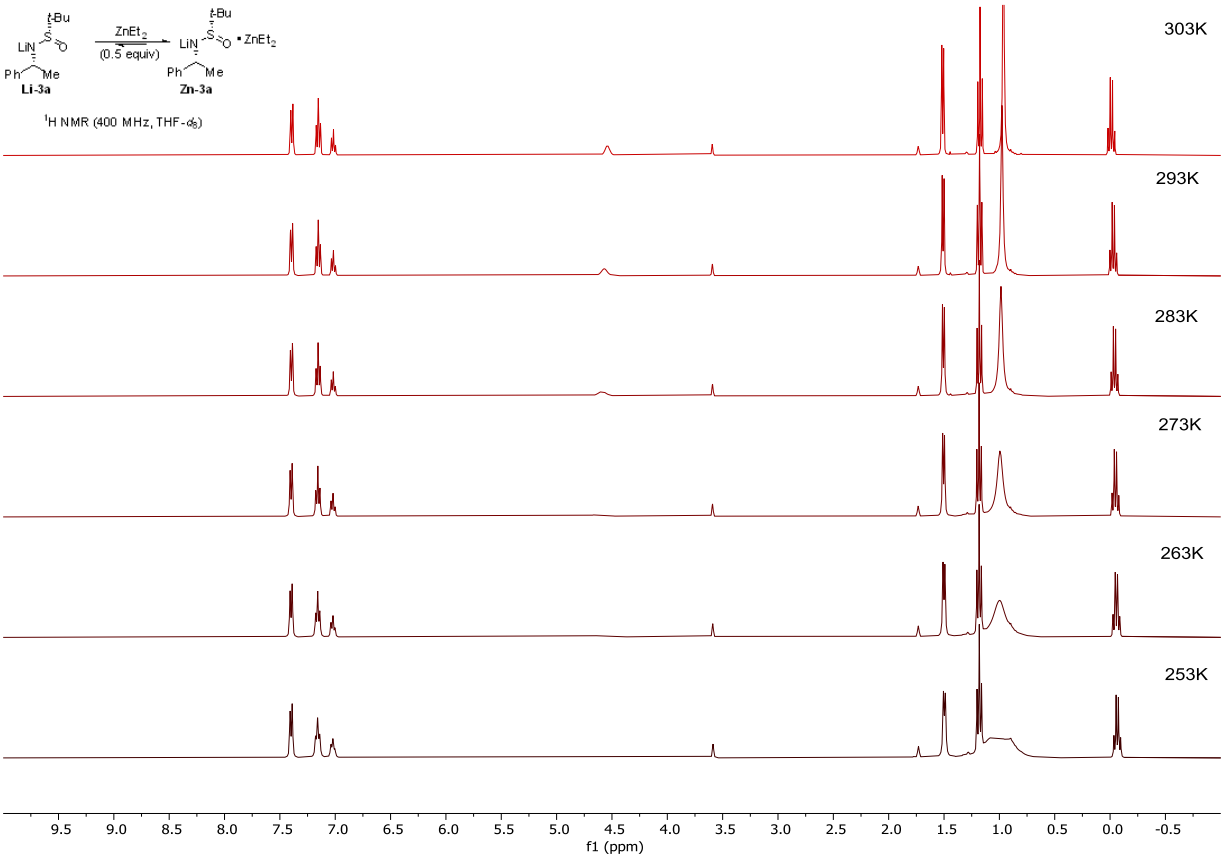
^{13}C{^{1}H} NMR (101 MHz, THF-d_8, 253K) δ 152.1 (*C*^{1}), 128.0 (*C*^{3}), 127.8 (*C*^{2}), 125.6 (*C*^{4}), 56.4 (*C*^{7}), 52.6 (*C*^{5}), 26.5 (*C*^{6}), 25.0 (*C*^{8}), 14.8 (*C*^{9}), 6.2 (*C*^{10}).

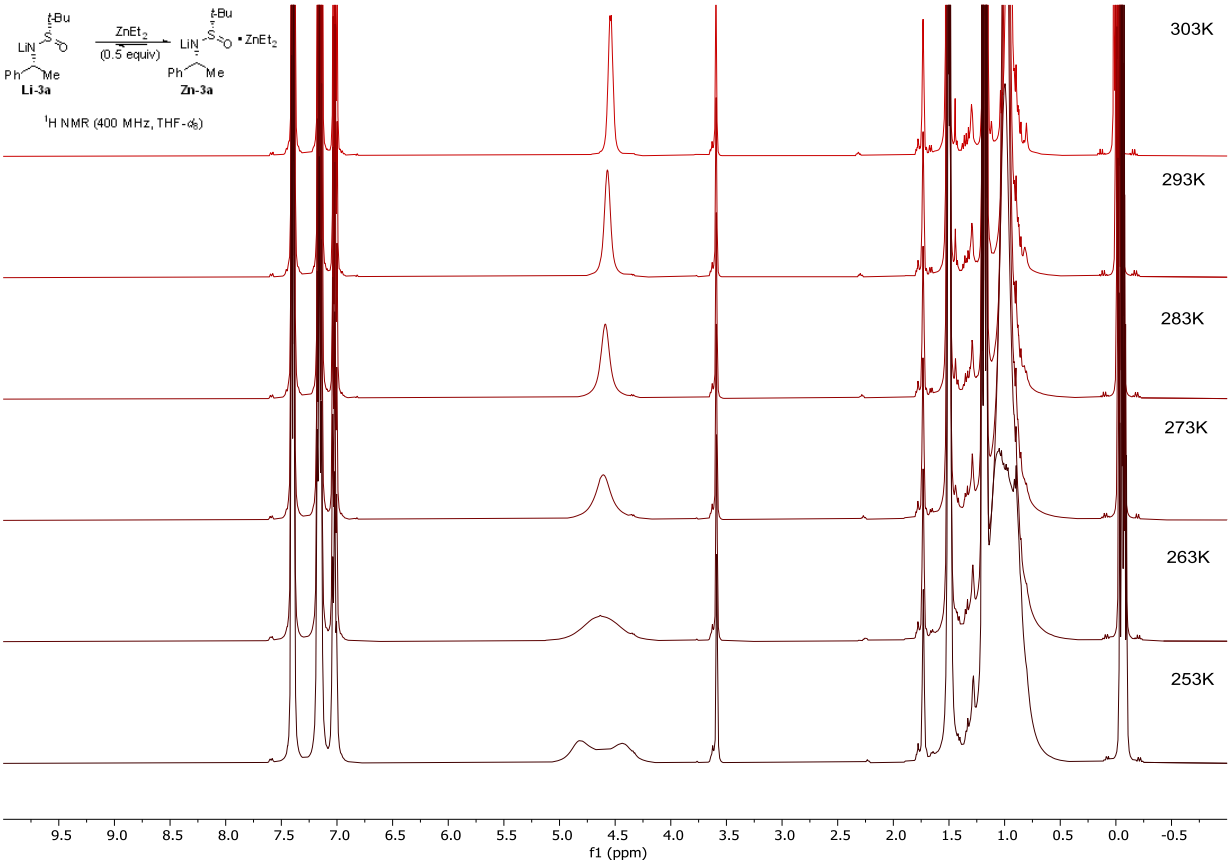

Zn-3a
^{1}H NMR (400 MHz, THF-d_8, 253 K)
f1 (ppm)


Zn-3a
^{13}C NMR (101 MHz, THF-d_8, 253 K)
f1 (ppm)

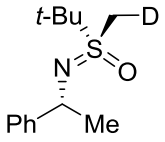


Mixture of **Li-3a** (46 mg, 0.2 mmol) and $ZnEt_2$ (12 µL, 14 mg, 0.10 mmol, 0.5 equiv) in THF-d_8 (0.6 mL) was analyzed by NMR. Coalescence of peaks corresponding to the complex **Zn-3a** and **Li-3a** was observed upon increasing the temperature from -20 °C to 30 °C indicating dynamic complexation.


t-Bu
LiN
Ph
Me
Li-3a
ZnEt2
(0.5 equiv)
Zn-3a
1H NMR (400 MHz, THF-d8)
303K
293K
283K
273K
263K
253K
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


t-Bu
LiN
Ph
Me
Li-3a
ZnEt2
(0.5 equiv)
Zn-3a
1H NMR (400 MHz, THF-d8)
303K
293K
283K
273K
263K
253K
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

Derivatization of 4aa-Zn



(*S*)-*tert*-Butyl(deuteromethyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (4aa-D).

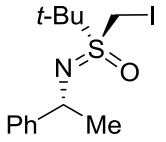
To a solution of sulfinamide **3a**[12] (45 mg, 0.20 mmol, 1 equiv) in THF (2 mL) was added LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv) at 0 °C. The yellow solution was stirred for 30 min at 0 °C and treated with $ZnEt_2$ (1.0 M solution in hexane, 0.24 mL, 0.24 mmol, 1.2 equiv) and diiodomethane (19 µL, 64 mg, 0.24 mmol, 1.2 equiv). The resulting yellowish solution was stirred for 1 h at 0 °C and then D_2O (0.50 mL) was added. The white suspension was warmed to room temperature and vigorously stirred for 16 h whereupon it was quenched with aqueous saturated ammonia (20 mL) and diluted with EtOAc (20 mL). Layers were separated, the aqueous layer was extracted with EtOAc (20 mL), combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the residue by silica gel flash column chromatography (2:1 hexane:EtOAc with 0.5% v/v TEA) afforded the target deuteromethyl sulfoximine **4aa-D** (41 mg, 85%) as a colorless oil. Analytical TLC on silica gel, 2:1 hexane:EtOAc, R*f* = 0.40.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.41 – 7.36 (m, 2H), 7.32 – 7.26 (m, 2H), 7.21 – 7.15 (m, 1H), 4.54 (q, *J* = 6.6 Hz, 1H), 2.47 (t, *J* = 1.9 Hz, 2H), 1.43 (s, 9H), 1.41 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 149.1, 128.5, 126.6, 126.5, 59.5, 53.0, 33.0 (t, *J* = 21.0 Hz), 28.8, 23.9.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_9NOS^1H_{13}{}^2H$: 185.0859. Found 185.0860.

[α]$^{20}_D$ +48 (*c* 1.0, CH_2Cl_2)



(*R*)-*tert*-Butyl(iodomethyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (4aa-I).

To a solution of sulfinamide **3a** (80 mg, 0.36 mmol, 1 equiv) in THF (3.6 mL) was added LiHMDS (1.0 M solution in THF, 0.39 mL, 0.39 mmol, 1.1 equiv) at 0 °C. The yellow solution was stirred for 30 min at 0 °C and $ZnEt_2$ (1.0 M solution in hexane, 0.43 mL, 0.43 mmol, 1.2 equiv) was added followed by diiodomethane (34 µL, 114 mg, 0.43 mmol, 1.2 equiv). After 1 h of stirring at 0 °C the obtained yellow solution was added to a solution

of NIS (240 mg, 1.07 mmol, 3 equiv) in THF (3.6 mL) at 0 °C over 30 min using a syringe pump. After the addition was completed, the resulting dark-brown solution was stirred at 0 °C for 1 h and quenched with 10% aqueous $Na_2S_2O_3$ (5 mL). The mixture was diluted with water (20 mL) and CH_2Cl_2 (20 mL), layers were separated and the aqueous layer was extracted with CH_2Cl_2 (20 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated. Purification of the residue by silica gel flash column chromatography (5:1 hexane:EtOAc) afforded the target iodomethyl sulfoximine **4aa-I** (87 mg, 67%) as a yellowish oil. Analytical TLC on silica gel, 5:1 hexane:EtOAc, R*f* = 0.27.

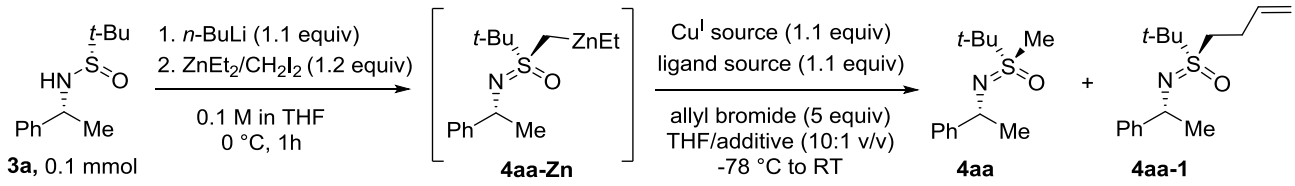
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.44 – 7.38 (m, 2H), 7.33 – 7.26 (m, 2H), 7.23 – 7.16 (m, 1H), 4.77 (q, *J* = 6.6 Hz, 1H), 4.35 (d, *J* = 11.2 Hz, 1H), 4.15 (d, *J* = 11.2 Hz, 1H), 1.53 (s, 9H), 1.40 (d, *J* = 6.6 Hz, 3H).

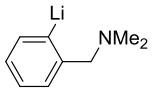
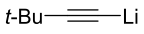
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 148.5, 128.5, 126.7, 126.6, 62.6, 53.3, 28.8, 24.9, 10.5.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_9H_{13}NOSI$: 309.9763. Found 309.9770.

$[\alpha]^{20}_D$ +107 (*c* 1.0, CH_2Cl_2)

Table S2. Optimization of allylation conditions for 4aa-Zn



Entry	Cu^{I} source	"Dummy" ligand source	Additive	Yield, %[a]	
				4aa	4aa-1
1	CuCN•2LiCl	–	-	65	10
2	CuCN•2LiCl	–	HMPA	43	31
3	CuCN•2LiCl	–	TMEDA	25	50
4	CuCN•2LiCl	–	DMSO	43	41
5	CuCN•2LiCl	–	pyridine	41	30
6[b]	CuCN•2LiCl	–	2,2'-bipyridine	62	31
7	CuCl•2LiCl	–	HMPA	59	18
8	CuCl•2LiCl	(TMSM)MgCl	HMPA	11	70
9	CuCN•2LiCl	(TMSM)MgCl	HMPA	60	30
10	CuCl•2LiCl	(TMSM)MgCl	–	20	68
11	CuBr•DMS	(TMSM)MgCl	–	36	42
12	CuI	(TMSM)MgCl	–	33	37
13	**CuBr•LiBr**	**(TMSM)MgCl**	–	**17**	**77**
14[c]	CuBr•LiBr		–	40	50
15[c]	CuBr•LiBr		–	45	38
16[d]	CuBr•LiBr		–	48	38

[a] ^{1}H NMR yield measured against mesitylene as internal standard;

[b] 5 equiv of additive was used;

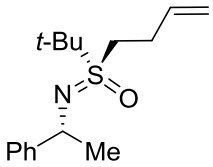
[c] organolithium reagents were prepared following literature[13,14] procedures;

[d] a solution of *tert*-butyl acetylene (14 mg, 0.11 mmol, 1.1 equiv) in THF (0.25 mL) was lithiated with *n*-BuLi (2.4 M solution in hexane, 0.11 mmol, 1.1 equiv) for 5 min at 0 °C.

General procedure B for allylation of diorganozinc intermediate 4aa-Zn

To a solution of sulfinamide **3a** (87 mg, 0.38 mmol, 1 equiv) in THF (3.8 mL) was added LiHMDS (1.0 M solution in THF, 0.42 mL, 0.42 mmol, 1.1 equiv) at 0 °C. The yellow solution was stirred for 30 min at 0 °C and $ZnEt_2$ (1.0 M solution in hexane, 0.46 mL, 0.46 mmol, 1.2 equiv) was added followed by diiodomethane (37 μL, 124 mg, 0.46 mmol, 1.2 equiv). After 1 h of stirring at 0 °C a solution of **4aa-Zn** was obtained.

In parallel, CuBr (61 mg, 0.42 mmol, 1.1 equiv) and LiBr (37 mg, 0.42 mmol, 1.1 equiv) were dissolved in THF (1 mL). The light green solution was cooled to -78 °C and treated with (TMSM)MgCl (1.2 M solution in THF, 0.35 mL, 0.42 mmol, 1.1 equiv). The obtained colorless solution was warmed to 0 °C and the solution of **4aa-Zn** was added. The resulting clear colorless solution was cooled to -78 °C and treated with allylic bromide (1.93 mmol, 5 equiv). The resulting solution was warmed to room temperature over 30 min, stirred for 1 h at room temperature, quenched with aqueous saturated ammonia (20 mL) and diluted with EtOAc (20 mL). Layers were separated, the aqueous layer was extracted with EtOAc (20 mL), combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered, concentrated and purified by silica gel flash column chromatography.



(*S*)-(But-3-en-1-yl)(*tert*-butyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (4aa-1).

The title compound was prepared using sulfinamide **3a** (87 mg, 0.38 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.42 mL, 0.42 mmol, 1.1 equiv), $ZnEt_2$ (1.0 M solution in hexane, 0.46 mL, 0.46 mmol, 1.2 equiv), diiodomethane (37 μL, 124 mg, 0.46 mmol, 1.2 equiv), CuBr (61 mg, 0.42 mmol, 1.1 equiv), LiBr (37 mg, 0.42 mmol, 1.1 equiv), (TMSM)MgCl (1.2 M solution in THF, 0.35 mL, 0.42 mmol, 1.1 equiv), allyl bromide (167 μL, 234 mg, 1.93 mmol, 5 equiv) and THF (4.8 mL).

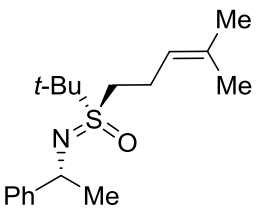
Purification of the brown liquid residue by silica gel flash column chromatography (7:1 hexane:EtOAc + 0.5% v/v TEA) afforded the target homoallyl sulfoximine **4aa-1** (76 mg, 70%) as a colorless oil. Analytical TLC on silica gel, 3:1 hexane:EtOAc, R*f* = 0.42.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.43 – 7.37 (m, 2H), 7.32 – 7.25 (m, 2H), 7.22 – 7.14 (m, 1H), 5.64 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 4.99 – 4.85 (m, 2H), 4.59 (q, *J* = 6.6 Hz, 1H), 2.99 – 2.80 (m, 2H), 2.41 – 2.20 (m, 2H), 1.44 (s, 9H), 1.40 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 149.4, 135.9, 128.5, 126.5, 116.4, 61.5, 52.9, 47.5, 28.8, 27.3, 24.3. Two signals overlap in the aromatic region.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_{12}H_{18}NOS$: 224.1109. Found 224.1118

[α]$^{20}_D$ +61 (*c* 1.0, CH_2Cl_2)



(*S*)-*tert*-Butyl(4-methylpent-3-en-1-yl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (4aa-2).

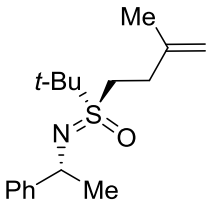
The title compound was prepared using sulfinamide **3a** (80 mg, 0.36 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.39 mL, 0.39 mmol, 1.1 equiv), $ZnEt_2$ (1.0 M solution in hexane, 0.43 mL, 0.43 mmol, 1.2 equiv), diiodomethane (34 μL, 113 mg, 0.43 mmol, 1.2 equiv), CuBr (56 mg, 0.39 mmol, 1.1 equiv), LiBr (34 mg, 0.39 mmol, 1.1 equiv), (TMSM)MgCl (1.2 M solution in THF, 0.33 mL, 1.1 equiv), prenyl bromide (0.21 mL, 0.26 g, 1.8 mmol, 5 equiv) and THF (4.5 mL) following **general procedure B**. Purification of the crude residue by silica gel flash column chromatography (9:1 hexane:EtOAc + 0.5 % v/v TEA) afforded the target sulfoximine **4aa-2** (72 mg, 65%) as a colorless oil. Analytical TLC on silica gel, 9:1 hexane:EtOAc, R*f* = 0.41.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.43 – 7.36 (m, 2H), 7.31 – 7.24 (m, 2H), 7.20 – 7.14 (m, 1H), 4.93 (tdt, *J* = 7.3, 2.9, 1.4 Hz, 1H), 4.60 (q, *J* = 6.6 Hz, 1H), 2.88 (ddd, *J* = 13.3, 10.0, 6.6 Hz, 1H), 2.77 (ddd, *J* = 13.3, 10.0, 7.0 Hz, 1H), 2.33 – 2.18 (m, 2H), 1.64 – 1.61 (m, 3H), 1.47 – 1.42 (m, 12H), 1.39 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 149.5, 134.5, 128.4, 126.5, 126.4, 121.1, 61.4, 52.8, 47.9, 29.0, 25.7, 24.3, 21.8, 17.7.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{18}H_{30}NOS$: 308.2048. Found 308.2043

[α]$^{20}_D$ +51 (*c* 1.0, CH_2Cl_2)



(*S*)-*tert*-Butyl(3-methylbut-3-en-1-yl){[(1*R*)-1-phenylethyl]imino}–λ^6-sulfanone (4aa-3).

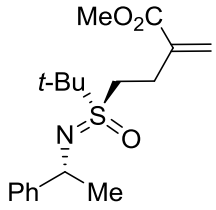
The title compound was prepared using sulfinamide **3a** (80 mg, 0.36 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.39 mL, 0.39 mmol, 1.1 equiv), $ZnEt_2$ (1.0 M solution in hexane, 0.43 mL, 0.43 mmol, 1.2 equiv), diiodomethane (34 µL, 113 mg, 0.43 mmol, 1.2 equiv), CuBr (56 mg, 0.39 mmol, 1.1 equiv), LiBr (34 mg, 0.39 mmol, 1.1 equiv), (TMSM)MgCl (1.2 M solution in THF, 0.33 mL, 1.1 equiv), methallyl bromide (0.18 mL, 0.24 g, 1.8 mmol, 5 equiv) and THF (4.5 mL) following **general procedure B**. Purification of the crude residue by silica gel flash column chromatography (7:1 hexane:EtOAc + 0.5 % v/v TEA) afforded the target sulfoximine **4aa-3** (71 mg, 68%) as a colorless oil. Analytical TLC on silica gel, 5:1 hexane:EtOAc, R*f* = 0.26.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.42 – 7.37 (m, 2H), 7.32 – 7.25 (m, 2H), 7.20 – 7.14 (m, 1H), 4.69 – 4.65 (m, 1H), 4.59 (q, *J* = 6.6 Hz, 1H), 4.53 – 4.49 (m, 1H), 3.01 (ddd, *J* = 13.2, 11.5, 5.5 Hz, 1H), 2.90 (ddd, *J* = 13.2, 11.2, 5.8 Hz, 1H), 2.35 – 2.15 (m, 2H), 1.58 – 1.56 (m, 3H), 1.45 (s, 9H), 1.39 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 149.5, 143.6, 128.5, 126.5, 111.2, 61.5, 52.8, 47.0, 30.8, 29.0, 24.3, 22.4. Two signals overlap in the aromatic region.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_{13}H_{20}NOS$: 238.1266. Found 238.1271

$[\alpha]^{20}_D$ +47 (*c* 1.0, CH_2Cl_2)



Methyl 4-[(*S*)-*tert*-butyl(oxo){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanyl]-2-methylidenebutanoate (4aa-4).

The title compound was prepared using sulfinamide **3a** (100 mg, 0.44 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.49 mL, 0.49 mmol, 1.1 equiv), $ZnEt_2$ (1.0 M solution in hexane, 0.53 mL, 0.53 mmol, 1.2 equiv), diiodomethane (43 µL, 0.14 g, 0.53 mmol, 1.2 equiv), CuBr (70 mg, 0.49 mmol, 1.1 equiv), LiBr (42 mg, 0.49 mmol, 1.1 equiv), (TMSM)MgCl (1.2 M solution in THF, 0.40 mL, 1.1 equiv), methyl 2-(bromomethyl)acrylate (0.27 mL, 0.40 g, 2.1 mmol, 5 equiv) and THF (5.8 mL) following **general procedure B**. Purification of the crude residue by reversed phase C18 flash chromatography using gradient elution (95:5 H_2O:MeCN to 5:95 H_2O:MeCN) afforded the target sulfoximine **4aa-4** (81 mg, 54%) as a colorless oil. Analytical TLC on silica gel, 3:1 hexane:EtOAc, R*f* = 0.26.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.44 – 7.38 (m, 2H), 7.31 – 7.25 (m, 2H), 7.21 – 7.14 (m, 1H), 6.06 – 6.04 (m, 1H), 5.34 – 5.31 (m, 1H, overlapped with $CHDCl_2$), 4.60 (q, *J* = 6.6 Hz, 1H), 3.69 (s, 3H), 3.07 (ddd, *J* = 13.5, 10.0, 6.6 Hz, 1H), 2.94 (ddd, *J* = 13.5, 10.0, 6.6 Hz, 1H), 2.60 – 2.44 (m, 2H), 1.45 (s, 9H), 1.40 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 167.0, 149.4, 138.3, 128.5, 127.0, 126.5, 126.5, 61.6, 52.9, 52.2, 47.3, 28.9, 26.9, 24.3.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_{14}H_{20}NO_3S$: 282.1164. Found 282.1166

$[\alpha]^{20}_D$ +39 (*c* 1.0, CH_2Cl_2)

Alkylation of *tert*-butyl sulfinamides

General procedure C for *S*-alkylation of sulfinamides with $ZnEt_2$ at 0 °C

To a solution of sulfinamide (0.20 mmol, 1 equiv) in THF (2 mL) was added LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv) at 0 °C. The yellow solution was stirred for 30 min at 0 °C, whereupon diethyl zinc (1.0 M solution in hexane, 0.24 mL, 0.24 mmol, 1.2 equiv) was added, followed by geminal diiodide (0.24 mmol, 1.2 equiv.). Diiodomethane and ethylidene iodide were added neat while other geminal diiodides were added as solutions in THF (0.5 mL). After 1 h of stirring at 0 °C the yellowish reaction solution was quenched with aqueous saturated ammonia (20 mL) and diluted with EtOAc (20 mL). Layers were separated and the aqueous layer was extracted with EtOAc (20 mL). Combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered, concentrated and purified by silica gel flash column chromatography.

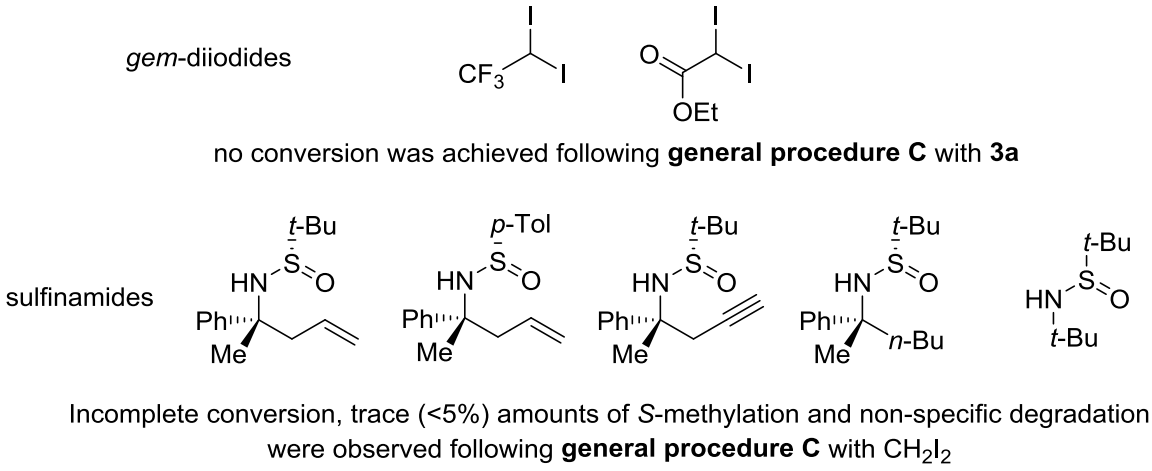
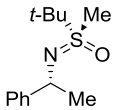


Figure S5. Unsuccessful substrates



(*S*)-*tert*-Butyl(methyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (4aa). The title compound was prepared from sulfinamide **3a** (1.50 g, 6.66 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 7.5 mL, 7.5 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 8.0 mL, 8.0 mmol, 1.2 equiv), diiodomethane (0.64 mL, 2.14 g, 7.99 mmol, 1.2 equiv) and THF (66 mL) following **general procedure C**. The target sulfoximine

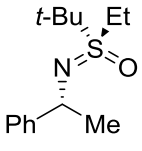
was obtained in pure form as a yellowish oil (1.59 g, 99%) upon evaporation of the extract. Analytical TLC on silica gel, 2:1 hexane:EtOAc, R*f* = 0.40.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.42 – 7.35 (m, 2H), 7.33 – 7.24 (m, 2H), 7.22 – 7.14 (m, 1H), 4.55 (q, *J* = 6.6 Hz, 1H), 2.48 (s, 3H), 1.43 (s, 9H), 1.41 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 149.1, 128.5, 126.6, 126.5, 59.5, 53.0, 33.2, 28.8, 23.9.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{21}NOSNa$: 262.1242. Found 262.1235.

$[\alpha]^{20}_D$ +41 (*c* 1.0, CH_2Cl_2)



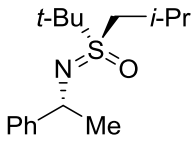
(*S*)-*tert*-Butyl(ethyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (4ab). The title compound was prepared from sulfinamide **3a** (40 mg, 0.18 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.20 mL, 0.20 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.21 mL, 0.21 mmol, 1.2 equiv), ethylidene iodide **5b**[15] (60 mg, 0.21 mmol, 1.2 equiv) and THF (1.8 mL) following **general procedure C**. Purification of the residue by silica gel flash column chromatography (3:1 hexane:EtOAc + 0.5% v/v TEA) afforded the target sulfoximine **4ab** (34 mg, 76%) as a colorless oil. Analytical TLC on silica gel, 3:1 hexane:EtOAc, R*f* = 0.27.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.44 – 7.37 (m, 2H), 7.32 – 7.24 (m, 2H), 7.21 – 7.14 (m, 1H), 4.59 (q, *J* = 6.6 Hz, 1H), 2.99 – 2.79 (m, 2H), 1.44 (s, 9H), 1.39 (d, *J* = 6.6 Hz, 3H), 1.12 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 149.6, 128.4, 126.5, 126.4, 61.3, 52.8, 42.5, 28.9, 24.4, 7.6.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{24}NOS$: 254.1579. Found 254.1578.

$[\alpha]^{20}_D$ +66 (*c* 1.0, CH_2Cl_2)



(*S*)-*tert*-Butyl(2-methylpropyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (4ac). The title compound was prepared from sulfinamide **3a** (338 mg, 1.50 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 1.65 mL, 1.65 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 1.8 mL, 1.8 mmol, 1.2 equiv), 1,1-diiodo-2-methylpropane **5c**[16] (558 mg, 1.8 mmol, 1.2 equiv) and THF (15 mL) following **general procedure C**.

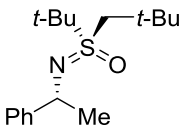
Purification of the residue by silica gel flash column chromatography (5:1 hexane:EtOAc + 0.5% v/v TEA) afforded the target sulfoximine **4ac** (222 mg, 53%) as a light yellow oil. Analytical TLC on silica gel, 5:1 hexane:EtOAc, R*f* = 0.30.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.31 – 7.24 (m, 2H, overlapped with $CHCl_3$), 7.20 – 7.14 (m, 1H), 4.63 (q, *J* = 6.6 Hz, 1H), 2.77 – 2.64 (m, 2H), 2.21 – 2.07 (m, 1H), 1.48 – 1.42 (m, 12H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.0, 128.2, 126.3, 126.2, 62.0, 54.8, 52.7, 28.3, 24.2, 23.9, 23.7, 22.8.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_{12}H_{20}NOS$: 226.1266. Found 226.1267.

[α]$^{20}_D$ +78 (*c* 1.0, CH_2Cl_2)



(*S*)-*tert*-Butyl(2,2-dimethylpropyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (4ad).

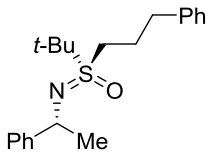
The title compound was prepared following modified **general procedure C**. To a solution of sulfinamide **3a** (68 mg, 0.30 mmol, 1 equiv) in THF (3 mL) was added LiHMDS (1.0 M solution in THF, 0.33 mL, 0.33 mmol, 1.1 equiv) dropwise at room temperature. The resulting yellow clear solution was stirred for 30 min at room temperature and $ZnEt_2$ (1.0 M solution in hexane, 0.36 mL, 0.36 mmol, 1.2 equiv) was added followed by a solution of 1,1-diiodo-2,2-dimethylpropane **4d**[17] (116 mg, 0.36 mmol, 1.2 equiv) in THF (0.5 mL). The yellow solution was stirred for 1.5 h at room temperature, quenched with aqueous saturated ammonia (20 mL) and diluted with EtOAc (20 mL). Layers were separated and the aqueous layer was extracted with EtOAc (20 mL). Combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the liquid residue by silica gel flash column chromatography (10:1 hexane:EtOAc + 0.5% v/v TEA) afforded the target sulfoximine **4ad** (35 mg, 39%) as a colorless oil. Analytical TLC on silica gel, 10:1 hexane:EtOAc, R*f* = 0.18.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.35 (m, 2H), 7.34 – 7.22 (m, 2H), 7.21 – 7.11 (m, 1H), 4.59 (q, *J* = 6.6 Hz, 1H), 2.96 (d, *J* = 14.3 Hz, 1H), 2.71 (d, *J* = 14.3 Hz, 1H), 1.51 – 1.33 (m, 12H), 1.06 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.1, 128.3, 126.7, 126.4, 63.0, 58.1, 53.4, 32.5, 29.9, 28.5, 24.4.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_{13}H_{22}NOS$: 240.1422. Found 240.1431.

[α]$^{20}_D$ +84 (*c* 1.0, CH_2Cl_2)



(*S*)-*tert*-Butyl({[(1*R*)-1-phenylethyl]imino})(3-phenylpropyl)-λ^6-sulfanone (4ae).

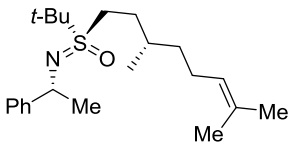
The title compound was prepared from sulfinamide **3a** (338 mg, 1.50 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 1.65 mL, 1.65 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 1.8 mL, 1.8 mmol, 1.2 equiv), (3,3-diiodopropyl)benzene **5e**[18] (670 mg, 1.80 mmol, 1.2 equiv) and THF (15 mL) following **general procedure C**. Purification of the residue by silica gel flash column chromatography using gradient elution (5:1 to 3:1 hexane:EtOAc + 0.5% v/v TEA) afforded the target sulfoximine **4ae** (449 mg, 87%) as a colorless oil. Analytical TLC on silica gel, 5:1 hexane:EtOAc, R*f* = 0.26.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.42 – 7.35 (m, 2H), 7.33 – 7.10 (m, 6H), 7.03 – 6.95 (m, 2H), 4.56 (q, *J* = 6.6 Hz, 1H), 2.94 – 2.77 (m, 2H), 2.56 – 2.43 (m, 2H), 1.98 – 1.80 (m, 2H), 1.42 – 1.36 (m, 12H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 149.5, 141.2, 128.7, 128.7, 128.5, 126.5, 126.5, 126.4, 61.4, 52.9, 47.7, 35.2, 28.9, 24.8, 24.3.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_{17}H_{22}NOS$: 288.1422. Found 288.1426.

[α]$^{20}_D$ +48 (*c* 1.0, CH_2Cl_2)



(*S*)-*tert*-Butyl[(3*S*)-3,7-dimethyloct-6-en-1-yl]{[(1*R*)-1-phenyl ethyl]imino}-λ^6-sulfanone (4af).

The title compound was prepared from sulfinamide **3a** (45 mg, 0.20 mmol, 1.1 equiv), LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.24 mL, 0.24 mmol, 1.2 equiv), (*S*)-8,8-diiodo-2,6-dimethyloct-2-ene **4f**[19] (94 mg, 0.24 mmol, 1.2 equiv) and THF (2 mL) following **general procedure C**. Purification of the residue by silica gel flash column

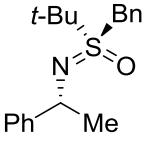
chromatography (9:1 to 3:1 hexane:EtOAc + 0.5% v/v TEA) afforded the target sulfoximine **4af** (40 mg, 55%) as a colorless oil. Analytical TLC on silica gel, 9:1 hexane:EtOAc, R*f* = 0.44.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.31 – 7.24 (m, 2H), 7.20 – 7.14 (m, 1H), 5.03 – 4.97 (m, 1H), 4.60 (q, *J* = 6.6 Hz, 1H), 2.87 – 2.77 (m, 2H), 1.93 – 1.74 (m, 2H), 1.68 – 1.55 (m, 7H), 1.51 – 1.39 (m, 12H), 1.35 – 1.20 (m, 2H), 1.17 – 1.07 (m, 1H), 1.05 – 0.94 (m, 1H), 0.68 (d, *J* = 6.5 Hz, 3H).

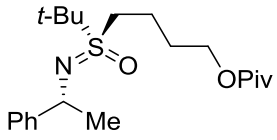
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.1, 131.5, 128.2, 126.3, 126.2, 124.6, 61.2, 52.5, 46.5, 36.8, 32.4, 29.3, 28.7, 25.8, 25.4, 24.4, 19.0, 17.8.

HRMS (ESI/Q-TOF) *m/z*: $[M-C_4H_8+H]^+$ Calcd. for $C_{18}H_{30}NOS$: 308.2048. Found 308.2053.

$[\alpha]^{20}_D$ +54 (*c* 1.0, CH_2Cl_2)



(*S*)-Benzyl(*tert*-butyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (4ag). The title compound was prepared from sulfinamide **3a** following **general procedure C** in 22% yield. See page S74 for improved synthesis and characterization data of **4ag**.



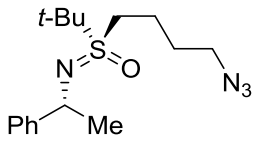
4-[(*S*)-*tert*-Butyl(oxo){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanyl] butyl 2,2-dimethylpropanoate (4ah). The title compound was prepared from sulfinamide **3a** (266 mg, 1.18 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 1.3 mL, 1.3 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 1.4 mL, 1.4 mmol, 1.2 equiv), 4,4-diiodobutyl pivalate **4h** (580 mg, 1.41 mmol, 1.2 equiv) and THF (12 mL) following **general procedure C**. Purification of the residue by silica gel flash column chromatography (3:1 hexane:EtOAc + 0.5% v/v TEA) afforded the target sulfoximine **4ah** (387 mg, 86%) as a light yellow oil. Analytical TLC on silica gel, 2:1 hexane:EtOAc, R*f* = 0.36.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.42 – 7.35 (m, 2H), 7.31 – 7.24 (m, 2H), 7.20 – 7.14 (m, 1H), 4.58 (q, *J* = 6.6 Hz, 1H), 3.92 – 3.84 (m, 2H), 2.95 – 2.78 (m, 2H), 1.71 – 1.62 (m, 2H), 1.56 – 1.47 (m, 2H), 1.43 (s, 9H), 1.39 (d, *J* = 6.6 Hz, 3H), 1.15 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 178.5, 149.4, 128.5, 126.5, 126.5, 63.9, 61.5, 52.9, 47.9, 38.9, 28.8, 28.4, 27.3, 24.3, 20.0.

HRMS (ESI/Q-TOF) *m/z*: [M+Na]$^+$ Calcd. for $C_{21}H_{35}NO_3NaS$: 404.2235. Found 404.2233.

[α]$^{20}_D$ +49 (*c* 1.0, CH_2Cl_2)



(*S*)-(4-Azidobutyl)(*tert*-butyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (4ai).

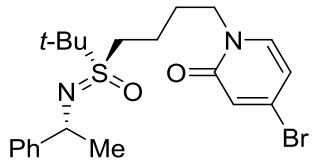
The title compound was prepared from sulfinamide **3a** (338 mg, 1.50 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 1.7 mL, 1.7 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 1.8 mL, 1.8 mmol, 1.2 equiv), 4-azido-1,1-diiodobutane **4i** (532 mg, 1.80 mmol, 1.2 equiv) and THF (15 mL) following **general procedure C**. Purification of the residue by silica gel flash column chromatography (2:1 hexane:EtOAc) afforded the target sulfoximine **4ai** (343 mg, 70%) as a yellow oil. Analytical TLC on silica gel, 2:1 hexane:EtOAc, R*f* = 0.30.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.43 – 7.36 (m, 2H), 7.32 – 7.25 (m, 2H), 7.21 – 7.14 (m, 1H), 4.57 (q, *J* = 6.6 Hz, 1H), 3.16 – 3.03 (m, 2H), 2.95 – 2.67 (m, 2H), 1.69 – 1.55 (m, 2H, overlapped with H_2O), 1.47 – 1.38 (m, 14H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 149.5, 128.5, 126.5, 126.5, 61.5, 52.9, 51.3, 47.8, 28.8, 28.5, 24.3, 20.6.

HRMS (ESI/Q-TOF) *m/z*: [M+Na]$^+$ Calcd. for $C_{16}H_{26}N_4ONaS$: 345.1725. Found 345.1726.

[α]$^{20}_D$ +60 (*c* 1.0, CH_2Cl_2)



4-Bromo-1-{4-[(*S*)-*tert*-butyl(oxo){[(1*R*)-1-phenylethyl] imino}-λ^6-sulfanyl]butyl}-1,2-dihydropyridin-2-one (4aj).

The title compound was prepared from sulfinamide **3a** (60 mg, 0.26 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.29 mL, 0.29 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.32 mL, 0.32 mmol, 1.2 equiv), 4-bromo-1-(4,4-diiodobutyl)pyridin-2(1*H*)-one **5j** (154 mg, 0.320 mmol, 1.2 equiv) and THF (2.6 mL) following **general procedure C**. Purification of the residue by silica gel flash column chromatography (200:1 EtOAc:MeOH) afforded the target sulfoximine **4aj** (48 mg, 40%) as a colorless oil. Analytical TLC on silica gel, EtOAc, R*f* = 0.27.

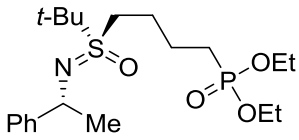
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.42 – 7.33 (m, 2H), 7.32 – 7.24 (m, 2H), 7.22 – 7.13 (m, 1H), 6.91 (d, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 2.2 Hz, 1H), 6.26 (dd, *J* = 7.4, 2.2 Hz, 1H), 4.57 (q, *J* = 6.6

Hz, 1H), 3.73 – 3.53 (m, 2H), 2.97 – 2.74 (m, 2H), 1.62 – 1.50 (m, 4H), 1.41 (s, 9H), 1.38 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 161.3, 149.5, 138.0, 135.4, 128.5, 126.5, 126.5, 123.1, 110.1, 61.7, 52.8, 49.3, 47.6, 28.7, 28.5, 24.2, 20.2.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{21}H_{30}N_2O_2SBr$: 453.1211. Found 453.1213.

[α]$^{20}_{D}$ +40 (*c* 1.0, CH_2Cl_2)



Diethyl {4-[(*S*)-*tert*-butyl(oxo){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanyl]butyl}phosphonate (4ak).

The title compound was prepared from sulfinamide **3a** (51 mg, 0.23 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.25 mL, 0.25 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.27 mL, 0.27 mmol, 1.2 equiv), diethyl (4,4-diiodobutyl)phosphonate **5k** (121 mg, 0.271 mmol, 1.2 equiv) and THF (2.3 mL) following **general procedure C**. Purification of the residue by silica gel flash column chromatography using gradient elution (from EtOAc to 10:1 EtOAc:MeOH) afforded the target sulfoximine **4ak** (72 mg, 76%) as a colorless oil. Analytical TLC on silica gel, 20:1 EtOAc:MeOH, R*f* = 0.26.

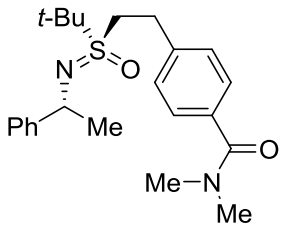
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.44 – 7.32 (m, 2H), 7.32 – 7.22 (m, 2H), 7.22 – 7.11 (m, 1H), 4.57 (q, *J* = 6.6 Hz, 1H), 4.07 – 3.92 (m, 4H), 2.93 – 2.70 (m, 2H), 1.68 – 1.36 (m, 18H), 1.27 (t, *J* = 7.0 Hz, 6H).

^{13}C{^{1}H} NMR (400 MHz, CD_2Cl_2) δ 149.5, 128.5, 126.5, 61.8 (d, *J* = 6.5 Hz), 61.5, 52.9, 47.8 (d, *J* = 1.9 Hz), 28.8, 25.5 (d, *J* = 140.8 Hz), 24.3, 24.0 (d, *J* = 17.9 Hz), 22.4 (d, *J* = 4.6 Hz), 16.7 (d, *J* = 6.1 Hz). Two signals overlap in the aromatic region.

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 30.8.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{20}H_{37}NO_4SP$: 418.2181. Found 418.2189.

[α]$^{20}_{D}$ +43 (*c* 1.0, CH_2Cl_2)



4-{2-[(*S*)-*tert*-Butyl(oxo){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanyl]ethyl}-*N*,*N*-dimethylbenzamide (4al).

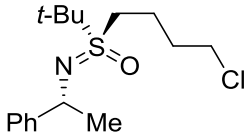
The title compound was prepared from sulfinamide **3a** (23 mg, 0.10 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.11 mL, 0.11 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.12 mL, 0.12 mmol, 1.2 equiv), 4-(2,2-diiodoethyl)-*N*,*N*-dimethylbenzamide **5l** (51 mg, 0.12 mmol, 1.2 equiv) and THF (1 mL) following **general procedure C**. Purification of the residue by silica gel flash column chromatography (9:1 hexane:EtOAc to + 0.5% v/v TEA) afforded the target sulfoximine **4al** (18 mg, 45%) as a colorless oil. Analytical TLC on silica gel, 9:1 hexane:EtOAc, R*f* = 0.23.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.23 (m, 2H, overlapped with $CHCl_3$), 7.23 – 7.18 (m, 1H), 6.90 – 6.84 (m, 2H), 4.68 (q, *J* = 6.6 Hz, 1H), 3.13 – 2.74 (m, 10H), 1.50 – 1.43 (m, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.5, 149.0, 140.9, 134.7, 128.5, 128.5, 127.6, 126.4, 126.3, 61.4, 52.5, 49.7, 39.7, 35.5, 28.8, 28.4, 24.2.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_{19}H_{25}N_2O_2S$: 345.1637. Found 345.1643.

$[\alpha]^{20}_D$ +10 (*c* 0.50, CH_2Cl_2)



(*S*)-*tert*-Butyl(4-chlorobutyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (4am).

The title compound was prepared following modified **general procedure C**. To a solution of sulfinamide **3a** (80 mg, 0.36 mmol, 1 equiv) in THF (3.5 mL) was added LiHMDS (1.0 M solution in THF, 0.39 mL, 0.39 mmol, 1.1 equiv) at 0 °C. After the clear yellowish solution was stirred for 30 min at 0 °C, diethyl zinc (1.0 M solution in hexane, 0.43 mL, 0.43 mmol, 1.2 equiv) was added, followed by a solution of 4-chloro-1,1-diiodobutane **5m** (147 mg, 0.426 mmol, 1.2 equiv) in THF (0.5 mL). After stirring the solution for 30 min at 0 °C, water (2 mL) was added under argon. The resulting white suspension was stirred for 1 h at room temperature, diluted with water (20 mL), EtOAc (20 mL) and filtered through a pad of *Celite*®. Layers were separated and the aqueous layer was extracted with EtOAc (20 mL). Combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the residue by silica gel flash column chromatography using gradient elution (from 4:1 to 1:1 hexane:EtOAc)

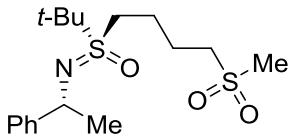
afforded the target sulfoximine **4am** (83 mg, 74%) as a colorless oil. Analytical TLC on silica gel, 3:1 hexane:EtOAc, R*f* = 0.25.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.42 – 7.36 (m, 2H), 7.31 – 7.25 (m, 2H), 7.21 – 7.14 (m, 1H), 4.58 (q, *J* = 6.6 Hz, 1H), 3.41 – 3.30 (m, 2H), 2.93 – 2.75 (m, 2H), 1.75 – 1.58 (m, 4H), 1.43 (s, 9H), 1.40 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 149.4, 128.5, 126.5, 61.5, 52.9, 47.5, 44.7, 32.1, 28.7, 24.3, 20.8. Two signals overlap in the aromatic region.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_{12}H_{19}NOSCl$: 260.0876. Found 260.0877.

[α]$^{20}_D$ +45 (*c* 1.0, EtOAc)



(*S*)-*tert*-Butyl(4-methanesulfonylbutyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (4an).

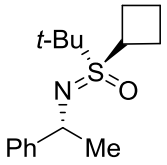
The title compound was prepared from sulfinamide **3a** (45 mg, 0.20 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.24 mL, 0.24 mmol, 1.2 equiv), 1,1-diiodo-4-(methylsulfonyl)butane **5l** (92 mg, 0.24 mmol, 1.2 equiv) and THF (2 mL) following modified **general procedure C**. Accordingly, the geminal diiodide **5n** was added as a solid due to its low solubility in THF. Purification of the crude residue by silica gel flash column chromatography (EtOAc) afforded the target sulfoximine **4an** (63 mg, 89%) as a colorless oil. Analytical TLC on silica gel, EtOAc, R*f* = 0.36.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.42 – 7.36 (m, 2H), 7.33 – 7.26 (m, 2H), 7.23 – 7.15 (m, 1H), 4.57 (q, *J* = 6.6 Hz, 1H), 2.94 – 2.68 (m, 7H), 1.75 – 1.59 (m, 4H), 1.43 (s, 9H), 1.39 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 149.5, 128.6, 126.6, 126.6, 61.7, 54.3, 52.8, 47.5, 40.8, 28.7, 24.2, 22.2, 22.0.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{17}H_{29}NO_3NaS_2$: 382.1487. Found 382.1483.

[α]$^{20}_D$ +54 (*c* 1.0, CH_2Cl_2)



[(*S*)-*tert*-Butyl(cyclobutyl)oxo-λ^6-sulfanylidene][(1*R*)-1-phenylethyl]amine (4ao).

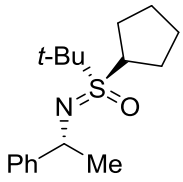
The title compound was prepared following modified **general procedure C**. Accordingly, sulfinamide **3a** (45 mg, 0.20 mmol, 1 equiv) and LiBr (174 mg, 2.00 mmol, 10 equiv) were dissolved in THF (2 mL). LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv) was added at 0 °C and the clear yellowish solution was stirred at 0 °C for 30 min. $ZnEt_2$ (1.0 M solution in hexane, 0.24 mL, 0.24 mmol. 1.2 equiv) was added followed by a solution of 1,1,4-triiodobutane **5o** (105 mg, 0.240 mmol, 1.2 equiv) in THF (0.5 mL). The clear yellowish solution was allowed to warm to room temperature over 16 h, quenched with aqueous saturated ammonia (20 mL) and diluted with EtOAc (20 mL). Layers were separated and the aqueous layer was extracted with EtOAc (20 mL). Combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the crude residue by silica gel flash column chromatography (3:1 hexane:EtOAc) afforded the target sulfoximine **4ao** (27 mg, 48%) as a colorless oil. Analytical TLC on silica gel, 3:1 hexane:EtOAc, R*f* = 0.35.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.44 – 7.38 (m, 2H), 7.31 – 7.24 (m, 2H), 7.20 – 7.13 (m, 1H), 4.68 (q, *J* = 6.6 Hz, 1H), 3.96 – 3.82 (m, 1H), 2.53 – 2.35 (m, 2H), 2.11 – 2.01 (m, 1H), 1.91 – 1.79 (m, 2H), 1.71 – 1.58 (m, 1H, overlapped with water), 1.38 (d, *J* = 6.6 Hz, 3H), 1.36 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 150.2, 128.3, 126.5, 126.2, 61.5, 53.0, 52.5, 29.3, 25.8, 25.0, 24.4, 18.1.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_{12}H_{18}NOS$: 224.1109. Found 224.1117.

$[\alpha]^{20}_D$ +80 (*c* 1.0, CH_2Cl_2)



[(*S*)-*tert*-Butyl(cyclopentyl)oxo-λ^6-sulfanylidene][(1*R*)-1-phenylethyl] amine (4ap).

The title compound was prepared following modified **general procedure C**. Accordingly, sulfinamide **3a** (45 mg, 0.20 mmol, 1 equiv) and LiBr (174 mg, 2.00 mmol, 10 equiv) were dissolved in THF (2 mL). LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv) was added at 0 °C and the clear yellowish solution was stirred at 0 °C for 30 min. $ZnEt_2$ (1.0 M solution in hexane, 0.24 mL, 0.24 mmol. 1.2 equiv) was added, followed by a solution of 1,1,5-triiodopentane **5p** (108 mg, 0.240 mmol, 1.2 equiv) in THF

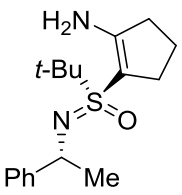
(0.5 mL). The clear yellowish solution was allowed to warm to room temperature over 16 h, quenched with aqueous saturated ammonia (20 mL) and diluted with EtOAc (20 mL). Layers were separated and the aqueous layer was extracted with EtOAc (20 mL). Combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the crude residue by silica gel flash column chromatography (5:1 hexane:EtOAc + 0.5% v/v TEA) afforded the target sulfoximine **4ap** (39 mg, 66%) as a colorless oil. Analytical TLC on silica gel, 4:1 hexane:EtOAc, R*f* = 0.35.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 2H), 7.30 – 7.23 (m, 2H), 7.21 – 7.12 (m, 1H), 4.69 (q, *J* = 6.6 Hz, 1H), 3.55 (p, *J* = 8.7 Hz, 1H), 1.96 – 1.71 (m, 4H), 1.51 – 1.31 (m, 16H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.6, 128.1, 126.4, 126.0, 62.1, 60.4, 52.7, 29.4, 29.3, 28.2, 26.3, 25.4, 24.7.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_{13}H_{20}NOS$: 238.1266. Found 238.1273.

[α]$^{20}_D$ +42 (*c* 0.50, CH_2Cl_2)



2-[(*R*)-*tert*-Butyl(oxo){[(1R)-1-phenylethyl]imino}-λ^6-sulfanyl] cyclopent-1-en-1-amine (4aq).

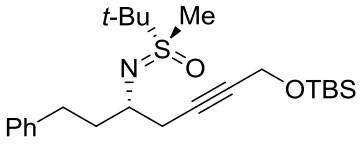
The title compound was prepared from sulfinamide **3a** (50 mg, 0.22 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.24 mL, 0.24 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.27 mL, 0.27 mmol, 1.2 equiv), 5,5-diiodopentanenitrile **5q** (89 mg, 0.27 mmol, 1.2 equiv) and THF (2.2 mL) following **general procedure C**. Purification of the residue by silica gel flash column chromatography (2:1 hexane:EtOAc) afforded the title compound **4aq** (32 mg, 47%) as a thick yellow oil. Analytical TLC on silica gel, 2:1 hexane:EtOAc, R*f* = 0.38.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.47 – 7.41 (m, 2H), 7.29 – 7.22 (m, 2H), 7.18 – 7.12 (m, 1H), 4.38 (q, *J* = 6.5 Hz, 1H), 2.64 – 2.35 (m, 3H), 2.27 – 2.17 (m, 1H), 1.81 – 1.59 (m, 2H, overlapped with water), 1.42 – 1.37 (m, 12H). A broad signal corresponding to the –N*H*$_2$ fragment is observed from 6.7 to 3.0 ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 160.5, 149.5, 128.2, 126.5, 126.2, 93.7, 62.2, 54.1, 36.3, 34.1, 29.4, 24.3, 21.3.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{17}H_{27}N_2OS$: 307.1844. Found 307.1849.

[α]$^{20}_D$ +20 (*c* 1.0, CH_2Cl_2)



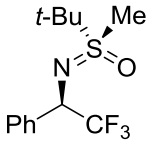
(3*S*,5*S*)-2,2,3,11,11,12,12-Heptamethyl-5-(2-phenylethyl)-10-oxa-λ^6-thia-4-aza-11-silatridec-3-en-7-yn-3-one (4ba). The title compound was prepared from sulfinamide **3b** (60 mg, 0.14 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.16 mL, 0.16 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.17 mL, 0.17 mmol, 1.2 equiv), diiodomethane (14 μL, 46 mg, 0.17 mmol, 1.2 equiv) and THF (1.4 mL) following **general procedure C**. Purification of the crude residue by silica gel flash column chromatography (3:1 hexane:EtOAc) afforded the target sulfoximine **4ba** (46 mg, 74%) as a colorless oil. Analytical TLC on silica gel, 3:1 hexane:EtOAc, R*f* = 0.26.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.30 – 7.13 (m, 5H), 4.30 (t, *J* = 2.2 Hz, 2H), 3.38 (ddd, *J* = 12.9, 8.7, 3.7 Hz, 1H), 2.78 (ddd, *J* = 13.6, 10.7, 5.0 Hz, 1H), 2.70 (s, 3H), 2.63 – 2.46 (m, 2H), 2.32 (ddt, *J* = 16.6, 8.7, 2.2 Hz, 1H), 2.14 – 2.02 (m, 1H), 1.78 – 1.68 (m, 1H), 1.43 (s, 9H), 0.90 (s, 9H), 0.11 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 143.2, 128.8, 128.6, 125.9, 83.6, 80.5, 59.9, 53.6, 52.3, 39.0, 33.1, 32.6, 29.5, 26.0, 24.0, 18.6, -5.0.

HRMS (ESI/Q-TOF) *m/z*: [M-C_4H_8+H]$^+$ Calcd. for $C_{20}H_{34}NO_2SSi$: 380.2080. Found 380.2090.

[α]$^{20}_D$ -35 (*c* 1.0, CH_2Cl_2)



(*S*)-*tert*-Butyl(methyl){[(1*R*)-2,2,2-trifluoro-1-phenylethyl]imino}-λ^6-sulfanone (4ca). The title compound was prepared from sulfinamide **3c** (60 mg, 0.21 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.24 mL, 0.24 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.26 mL, 0.26 mmol, 1.2 equiv), diiodomethane (21 μL, 69 mg, 0.26 mmol, 1.2 equiv) and THF (2.1 mL) following **general procedure C**. Target sulfoximine **4ca** (58 mg, 92%) was obtained as a yellow oil after evaporation of the extract and required no additional purification. Analytical TLC on silica gel, 5:1 hexane:EtOAc, R*f* = 0.21.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.56 – 7.51 (m, 2H), 7.40 – 7.31 (m, 3H), 4.85 (q, *J* = 7.6 Hz, 1H), 2.88 (s, 3H), 1.37 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 137.9, 129.0, 128.7, 128.5, 126.1 (q, *J* = 281.1 Hz), 61.2, 58.6 (q, *J* = 29.8 Hz), 34.9, 23.8.

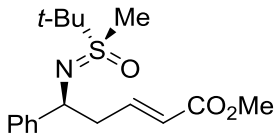
^{19}F NMR (376 MHz, CD_2Cl_2) δ -75.7 (d, *J* = 8.0 Hz).

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_9H_{11}NOF_3S$: 238.0513. Found 238.0516.

$[\alpha]^{20}_D$ -74 (*c* 1.0, CH_2Cl_2)

General procedure D for *S*-alkylation of sulfinamides with $ZnEt_2$ at -30 °C

To a solution of sulfinamide (0.26 mmol, 1 equiv) in THF (2.6 mL) was added LiHMDS (1.0 M solution in THF, 0.29 mL, 1.1 equiv) at -78 °C. The yellow solution was stirred at -78 °C for 30 min and then $ZnEt_2$ (1.0 M solution in hexane, 0.32 mL, 0.32 mmol, 1.2 equiv) was added, followed by geminal diiodide (0.32 mmol, 1.2 equiv). Diiodomethane was added neat while other geminal diiodides were added as solutions in THF (0.5 mL). The resulting clear homogeneous reaction solution was left at -30 °C for 16 h without stirring, cooled to -78 °C and quenched by dropwise addition of aqueous saturated ammonia (2 mL). The mixture was warmed to room temperature over 30 min and diluted with aqueous saturated ammonia (20 mL) and EtOAc (20 mL). Layers were separated and the aqueous layer was extracted with EtOAc (20 mL). Combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered, concentrated and purified by silica gel flash column chromatography.



Methyl (2*E*,5*S*)-5-{[(*S*)-*tert*-butyl(methyl)oxo-λ^6-sulfanylidene]amino}-5-phenylpent-2-enoate (4da).

The title compound was prepared from sulfinamide **3d** (50 mg, 0.16 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.18 mL, 0.18 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.19 mL, 0.19 mmol, 1.2 equiv), diiodomethane (16 µL, 52 mg, 0.19 mmol, 1.2 equiv) and THF (1.6 mL) following modified **general procedure D**. After 16 h at -30 °C the reaction mixture was cooled to -78 °C and quenched by dropwise addition of 1:1 THF:water (1 mL). The white suspension was warmed to room temperature over 30 min and diluted with EtOAc (30 mL) and water (30 mL). The biphasic mixture was filtered through a pad of *Celite*® and layers were separated. The aqueous layer was extracted with EtOAc (20 mL), combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the crude residue by silica gel

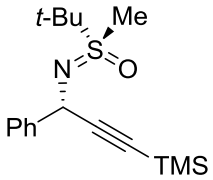
flash column chromatography (15:1 CH_2Cl_2:acetone) afforded the target sulfoximine **4da** (38 mg, 72%) as a colorless oil. Analytical TLC on silica gel, 15:1 CH_2Cl_2:acetone, R*f* = 0.26.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.42 – 7.37 (m, 2H), 7.33 – 7.27 (m, 2H), 7.23 – 7.17 (m, 1H), 6.96 (dt, *J* = 15.7, 7.4 Hz, 1H), 5.81 (dt, *J* = 15.7, 1.4 Hz, 1H), 4.50 (dd, *J* = 7.7, 5.2 Hz, 1H), 3.68 (s, 3H), 2.77 (s, 3H), 2.64 – 2.42 (m, 2H), 1.37 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 167.1, 147.8, 146.8, 128.4, 126.9, 126.9, 122.8, 60.7, 57.4, 51.6, 44.9, 33.8, 24.1.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{17}H_{25}NO_3SNa$: 346.1453. Found 346.1454.

[α]$^{20}_D$ -67 (*c* 1.0, CH_2Cl_2)



(*S*)-*tert*-Butyl(methyl){[(1*S*)-1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl]imino}-λ^6-sulfanone (4ea).

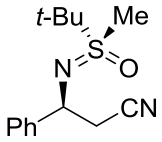
The title compound was prepared from sulfinamide **3e**[20] (50 mg, 0.16 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.18 mL, 0.18 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.19 mL, 0.19 mmol, 1.2 equiv), diiodomethane (16 μL, 52 mg, 0.19 mmol, 1.2 equiv) and THF (1.6 mL) following modified **general procedure D**. After 16 h at -30 °C, the reaction solution was cooled to -78 °C and quenched by dropwise addition of 1:1 THF:water (1 mL). The white suspension was warmed to room temperature over 30 min and diluted with EtOAc (30 mL) and water (30 mL). The biphasic mixture was filtered through a pad of *Celite*® and layers were separated. The aqueous layer was extracted with EtOAc (20 mL), combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the crude residue by silica gel flash column chromatography (3:1 hexane:EtOAc + 0.5% v/v TEA) afforded the target sulfoximine **4ea** (42 mg, 80%) as a yellowish oil. Analytical TLC on silica gel, 3:1 hexane:EtOAc, R*f* = 0.24.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.55 – 7.50 (m, 2H), 7.36 – 7.29 (m, 2H), 7.27 – 7.21 (m, 1H), 5.30 (s, 1H), 2.75 (s, 3H), 1.51 (s, 9H), 0.18 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 143.5, 128.6, 127.4, 127.4, 108.5, 88.1, 62.5, 48.6, 35.9, 24.5, -0.0.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{17}H_{27}NONaSiS$: 344.1480. Found 344.1484.

[α]$^{20}_D$ -57 (*c* 1.0, CH_2Cl_2)



(3*S*)-3-{[(*S*)-*tert*-Butyl(methyl)oxo-λ^6-sulfanylidene]amino}-3-phenyl propanenitrile (4fa).

The title compound was prepared from sulfinamide **3f** (66 mg, 0.26 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.29 mL, 1.1 equiv), $ZnEt_2$ (1.0 M solution in hexane, 0.32 mL, 0.32 mmol, 1.2 equiv), diiodomethane (26 µL, 85 mg, 0.32 mmol, 1.2 equiv) and THF (2.6 mL) following **general procedure D**. The target sulfoximine **4fa** was obtained as a white solid (70 mg, 99%) upon evaporation of the extract. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.30. Crystals suitable for X-ray analysis were obtained by slow evaporation of a toluene solution.

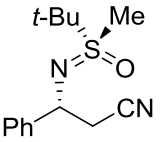
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.48 – 7.40 (m, 2H), 7.37 – 7.30 (m, 2H), 7.30 – 7.21 (m, 1H), 4.73 (dd, *J* = 7.5, 5.5 Hz, 1H), 2.90 (s, 3H), 2.69 – 2.61 (m, 2H), 1.40 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 144.6, 128.7, 127.8, 126.8, 119.2, 60.9, 54.8, 33.9, 31.1, 24.0.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{20}N_2ONaS$: 287.1194. Found 287.1194.

$[\alpha]^{20}_D$ -89 (*c* 1.0, CH_2Cl_2)

Melting point 102 – 104 °C (recrystallized from toluene)



(3*R*)-3-{[(*S*)-*tert*-Butyl(methyl)oxo-λ^6-sulfanylidene]amino}-3-phenyl propanenitrile (4ga).

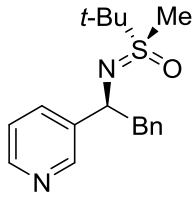
The title compound was prepared from sulfinamide **3g** (66 mg, 0.26 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.29 mL, 0.29 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.32 mL, 0.32 mmol, 1.2 equiv), diiodomethane (26 µL, 85 mg, 0.32 mmol, 1.2 equiv) and THF (1.6 mL) following **general procedure D**. Purification of the crude residue by silica gel flash column chromatography (3:2 hexane:EtOAc + 0.5% v/v TEA) afforded the target sulfoximine **4ga** (51 mg, 73%) as a yellow oil. Analytical TLC on silica gel, 3:2 hexane:EtOAc, R*f* = 0.22.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.47 – 7.41 (m, 2H), 7.39 – 7.32 (m, 2H), 7.32 – 7.25 (m, 1H), 4.71 (t, *J* = 6.2 Hz, 1H), 2.72 (d, *J* = 6.2 Hz, 2H), 2.45 (s, 3H), 1.46 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 144.2, 129.0, 128.0, 126.9, 118.6, 59.9, 53.8, 34.0, 31.0, 23.7.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{20}N_2ONaS$: 287.1194. Found 287.1197.

[α]$^{20}_D$ +31 (*c* 1.0, CH_2Cl_2)



(*S*)-*tert*-Butyl(methyl){[(1*S*)-2-phenyl-1-(pyridin-3-yl)ethyl]imino}-λ^6-sulfanone (4ha).

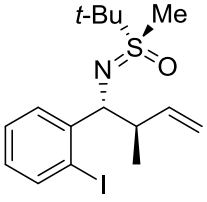
The title compound was prepared from sulfinamide **3h**[21] (70 mg, 0.23 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.25 mL, 0.25 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.28 mL, 0.28 mmol, 1.2 equiv), diiodomethane (22 μL, 74 mg, 0.28 mmol, 1.2 equiv) and THF (2.3 mL) following **general procedure C** and required no additional purification. The target sulfoximine **4ha** (63 mg, 86%) was obtained as an orange oil. Analytical TLC on silica gel, EtOAc, R*f* = 0.32.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 – 8.65 (m, 1H), 8.44 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.30 – 7.17 (m, 6H), 4.53 (dd, *J* = 9.9, 4.0 Hz, 1H), 3.02 (dd, *J* = 12.9, 4.0 Hz, 1H), 2.83 (dd, *J* = 12.9, 9.9 Hz, 1H), 2.08 (s, 3H), 1.32 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.6, 147.9, 142.4, 140.1, 134.5, 130.3, 128.2, 126.4, 123.2, 60.1, 57.7, 48.1, 32.5, 24.0.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{18}H_{25}N_2OS$: 317.1688. Found 317.1691.

[α]$^{20}_D$ -53 (*c* 1.0, CH_2Cl_2)



(*S*)-*tert*-Butyl({[(1*R*,2*R*)-1-(2-iodophenyl)-2-methylbut-3-en-1-yl] imino})methyl-λ^6-sulfanone (4ia).

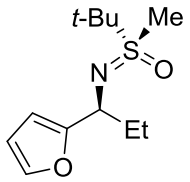
The title compound was prepared from sulfinamide **3i**[22] (81 mg, 0.21 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.23 mL, 0.23 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.25 mL, 0.25 mmol, 1.2 equiv), diiodomethane (20 μL, 67 mg, 0.25 mmol, 1.2 equiv) and THF (2.1 mL) following **general procedure C**. Purification of the crude residue by silica gel flash column chromatography (100:1 CH_2Cl_2:EtOAc) afforded the target sulfoximine **4ia** (51 mg, 61%) as a colorless oil. Analytical TLC on silica gel, 3:1 hexane:EtOAc, R*f* = 0.36.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.79 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.43 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.30 – 7.25 (m, 1H), 6.90 (ddd, *J* = 7.8, 7.2, 1.8 Hz, 1H), 5.98 (ddd, *J* = 17.3, 10.4, 7.8 Hz, 1H), 4.87 (ddd, *J* = 10.4, 2.3, 1.0 Hz, 1H), 4.76 – 4.68 (m, 1H), 4.48 (d, *J* = 4.5 Hz, 1H), 2.52 – 2.40 (m, 1H), 2.31 (s, 3H), 1.43 (s, 9H), 1.08 (d, *J* = 6.8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 148.2, 141.3, 139.4, 130.3, 128.6, 128.1, 114.3, 99.5, 64.6, 59.5, 45.5, 34.0, 23.9, 18.6.

HRMS (ESI/Q-TOF) *m/z*: $[M-C_4H_8+H]^+$ Calcd. for $C_{12}H_{17}NOSI$: 350.0076. Found 350.0076.

$[\alpha]^{20}_D$ -23 (*c* 1.0, CH_2Cl_2)



(*S*)-*tert*-Butyl({[(1*S*)-1-(furan-2-yl)propyl]imino})methyl-λ^6-sulfanone (4ja).

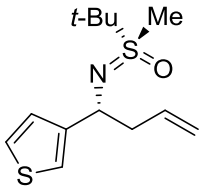
The title compound was prepared from sulfinamide **3j**[23] (80 mg, 0.35 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.39 mL, 0.39 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.42 mL, 0.42 mmol, 1.2 equiv), diiodomethane (34 μL, 112 mg, 0.42 mmol, 1.2 equiv) and THF (3.5 mL) following **general procedure C** and required no additional purification. The target sulfoximine **4ja** (81 mg, 95%) was obtained as a yellow oil. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.38.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.27 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.19 – 6.13 (m, 1H), 4.34 (dd, *J* = 7.7, 5.7 Hz, 1H), 2.77 (s, 3H), 1.95 – 1.65 (m, 2H), 1.39 (s, 9H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.1, 140.8, 110.1, 105.1, 61.4, 53.2, 34.8, 31.4, 24.3, 11.0.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{12}H_{21}NO_2SNa$: 266.1191. Found 266.1191.

$[\alpha]^{20}_D$ -98 (*c* 1.0, CH_2Cl_2)



(*S*)-*tert*-Butyl(methyl){[(1*R*)-1-(thiophen-3-yl)but-3-en-1-yl]imino}-λ^6-sulfanone (4ka).

The title compound was prepared from sulfinamide **3k**[5] (90 mg, 0.35 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.39 mL, 0.39 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.42 mL, 0.42 mmol, 1.2 equiv),

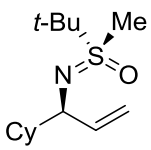
diiodomethane (34 μL, 112 mg, 0.42 mmol, 1.2 equiv) and THF (3.5 mL) following **general procedure C**. Purification of the crude residue by silica gel flash column chromatography (3:1 hexane:EtOAc + 0.5% v/v TEA) afforded the target sulfoximine **4ka** (75 mg, 79%) as a colorless oil. Analytical TLC on silica gel, 3:1 hexane:EtOAc, R*f* = 0.30.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.09 – 7.05 (m, 2H), 5.84 (ddt, *J* = 17.2, 10.2, 6.9 Hz, 1H), 5.03 – 4.94 (m, 2H), 4.55 (t, *J* = 6.6 Hz, 1H), 2.56 – 2.43 (m, 2H), 2.42 (s, 3H), 1.44 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.1, 136.5, 126.7, 125.5, 120.0, 116.2, 59.4, 53.0, 45.5, 33.4, 23.8.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_9H_{14}NOS_2$: 216.0517. Found 216.0517.

[α]$^{20}_D$ +32 (*c* 1.0, CH_2Cl_2)



(*S*)-*tert*-Butyl({[(1*S*)-1-cyclohexylprop-2-en-1-yl]imino})methyl-λ^6-sulfanone (4la).

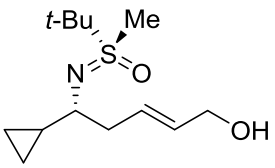
The title compound was prepared from sulfinamide **3l** (61 mg, 0.25 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.28 mL, 0.28 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.30 mL, 0.30 mmol, 1.2 equiv), diiodomethane (24 μL, 80 mg, 0.30 mmol, 1.2 equiv) and THF (3.5 mL) following **general procedure C**. Purification of the crude residue by silica gel flash column chromatography (5:1 hexane:EtOAc + 0.5% v/v TEA) afforded the target sulfoximine **4la** (60 mg, 93%) as a colorless oil. Analytical TLC on silica gel, 5:1 hexane:EtOAc, R*f* = 0.25.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddd, *J* = 17.3, 10.1, 7.2 Hz, 1H), 5.08 (ddd, *J* = 17.3, 2.2, 1.1 Hz, 1H), 4.99 (ddd, *J* = 10.1, 2.2, 1.1 Hz, 1H), 3.55 – 3.50 (m, 1H), 2.68 (s, 3H), 1.92 – 1.79 (m, 1H), 1.75 – 1.57 (m, 3H, overlapped with water), 1.43 (s, 9H), 1.38 – 0.91 (m, 7H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.7, 113.7, 61.0, 59.5, 44.6, 33.6, 30.1, 29.3, 26.9, 26.6, 26.5, 24.0.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_{10}H_{20}NOS$: 202.1266. Found 202.1271.

[α]$^{20}_D$ -49 (*c* 1.0, CH_2Cl_2)



(*S*)-*tert*-Butyl({[(1*R*,3*E*)-1-cyclopropyl-5-hydroxypent-3-en-1-yl] imino})methyl-λ^6-sulfanone (4ma).

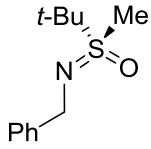
The title compound was prepared from sulfinamide **3m**[5] (50 mg, 0.20 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.44 mL, 0.44 mmol, 2.2 equiv), diethyl zinc (1.0 M solution in hexane, 0.50 mL, 0.50 mmol, 2.5 equiv), diiodomethane (41 µL, 136 mg, 0.50 mmol, 2.5 equiv) and THF (2.0 mL) following modified **general procedure D**. Purification of the crude residue by silica gel flash column chromatography (1:9 hexane:EtOAc + 0.5% v/v TEA) afforded the target sulfoximine **4ma** (30 mg, 57%) as a colorless oil. Analytical TLC on silica gel, 1:9 hexane:EtOAc, R*f* = 0.32.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 – 5.74 (m, 1H), 5.71 – 5.62 (m, 1H), 4.05 (t, *J* = 5.1 Hz, 2H), 2.88 – 2.81 (m, 1H), 2.74 (s, 3H), 2.40 – 2.32 (m, 1H), 2.29 – 2.20 (m, 1H), 1.90 - 1.83 (br s, 1H), 1.41 (s, 9H), 0.92 – 0.84 (m, 1H), 0.46 – 0.28 (m, 3H), 0.22 – 0.08 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 132.3, 130.6, 64.0, 59.9, 57.4, 41.9, 34.2, 24.0, 18.2, 3.0, 3.0.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{25}NO_2SNa$: 282.1504. Found 282.1508.

[α]$^{20}_D$ -70 (*c* 1.0, CH_2Cl_2)



(*S*)-(Benzylimino)(*tert*-butyl)methyl-λ^6-Sulfanone (4na).

The title compound was prepared from sulfinamide **3n**[24] (53 mg, 0.25 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.28 mL, 0.28 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.30 mL, 0.30 mmol, 1.2 equiv), diiodomethane (24 µL, 80 mg, 0.30 mmol, 1.2 equiv) and THF (2.0 mL) following **general procedure C**. Purification of the crude residue by silica gel flash column chromatography (20:1 CH_2Cl_2:acetone) afforded the target sulfoximine **4na** (31 mg, 55%) as a colorless oil. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.29.

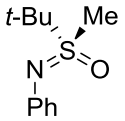
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 – 7.35 (m, 2H), 7.32 – 7.27 (m, 2H), 7.23 – 7.17 (m, 1H), 4.36 – 4.23 (m, 2H), 2.75 (s, 3H), 1.46 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 143.2, 128.4, 127.5, 126.6, 60.3, 46.9, 33.3, 24.2.

HRMS (ESI/Q-TOF) *m/z*: $[M-C_4H_8+H]^+$ Calcd. for $C_8H_{12}NOS$: 170.0640. Found 170.0641.

[α]$^{20}_D$ -3 (*c* 1.0, CH_2Cl_2)

HPLC/csp: >99% ee, HPLC/csp assay: Daicel CHIRALPAK IC, 25 cm × 4.6 mm i.d., mobile phase 20% IPA:80%Heptane, flow rate 1 mL/min, detector UV 220 nm, retention time **(*S*)-4na**, 10.7 min, and **(*R*)-4na**, 12.5 min.



(*S*)-*tert*-Butyl(methyl)(phenylimino)-λ^6-sulfanone (4oa).

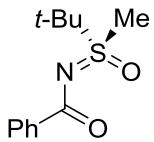
The title compound was prepared from sulfinamide **3m**[25] (81 mg, 0.41 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.45 mL, 0.45 mmol, 1.1 equiv), diethyl zinc (1.0 M solution in hexane, 0.49 mL, 0.49 mmol, 1.2 equiv), diiodomethane (39 µL, 132 mg, 0.49 mmol, 1.2 equiv) and THF (4.1 mL) following **general procedure D**. Purification of the crude residue by silica gel flash column chromatography (50:1 CH_2Cl_2:acetone) afforded the target sulfoximine **4oa** (35 mg, 40%) as a yellow oil. Analytical TLC on silica gel, 50:1 CH_2Cl_2:acetone, R*f* = 0.45.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 2H), 7.12 – 7.07 (m, 2H), 6.96 – 6.91 (m, 1H), 2.88 (s, 3H), 1.52 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.4, 129.2, 123.6, 121.7, 61.2, 32.5, 24.1.

HRMS (ESI/Q-TOF) *m/z*: $[M\text{-}C_4H_8+H]^+$ Calcd. for $C_7H_{10}NOS$: 156.0483. Found 156.0480.

$[\alpha]^{20}_D$ -9 (*c* 1.0, EtOAc)



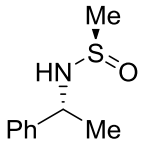
***N*-[(*S*)-*tert*-Butyl(methyl)oxo-λ^6-sulfanylidene]benzamide (4pa).**

The title compound was prepared from (*S*)-*N*-(*tert*-butylsulfinyl)benzamide **3p**[26] following **general procedure C** in 44% yield. For improved synthesis of **4pa** and characterization data see page S79.

Synthesis of alkylsulfinamides 1a–e,h,i

General procedure E for de-*tert*-butylation of *S*-*tert*-butylsulfoximines

To a solution of *tert*-butyl sulfoximine (6.63 mmol, 1 equiv) in THF (50 mL) was added BF_3•Et_2O (1.6 mL, 1.9 g, 13 mmol, 2 equiv). The colorless clear solution was stirred for 1 h at 50 °C, cooled to room temperature and quenched with aqueous saturated $NaHCO_3$ (100 mL). The mixture was extracted with EtOAc (3×100 mL), combined organic extracts were washed with brine (100 mL), dried over Na_2SO_4, concentrated and purified by silica gel flash column chromatography.



(*R*)-*N*-[(1*R*)-1-Phenylethyl]methanesulfinamide (1a). The title compound was prepared from *tert*-butyl sulfoximine **4aa** (1.59 g, 6.63 mmol, 1 equiv), BF_3•Et_2O (1.6 mL, 1.9 g, 13 mmol, 2 equiv) and THF (50 mL). Purification of the crude residue by silica gel flash column chromatography (1:9 hexane:EtOAc) afforded the target sulfinamide **1a** (950 mg, 78%) as a yellowish solid. Analytical TLC on silica gel, 1:9 hexane:EtOAc, R*f* = 0.20. Crystals suitable for X-ray analysis were prepared by slow evaporation of a toluene solution.

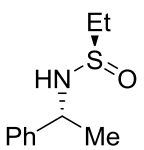
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 5H, overlapped with $CHCl_3$), 4.69 (qd, *J* = 6.6, 3.2 Hz, 1H), 4.03 (s, 1H), 2.53 (s, 3H), 1.53 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 145.0, 129.0, 127.9, 126.8, 51.9, 42.8, 24.0.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_9H_{14}NOS$: 184.0796. Found 184.0799.

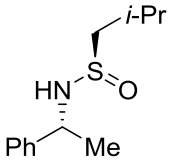
$[\alpha]^{20}_D$ +15 (*c* 1.0, CH_2Cl_2)

Melting point 73 – 75 °C (recrystallized from toluene)

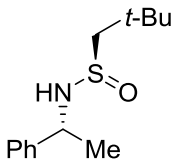


(*R*)-*N*-[(1*R*)-1-Phenylethyl]ethane-1-sulfinamide (1b). The title compound was prepared from *tert*-butyl sulfoximine **4ab** (417 mg, 1.65 mmol, 1 equiv), BF_3•Et_2O (0.40 mL, 0.47 g, 3.3 mmol, 2 equiv) and THF (16 mL) following **general procedure E**. Purification of the crude residue by silica gel flash column chromatography (3:7 hexane:EtOAc) afforded the target sulfinamide **1b** (264 mg, 81%) as a colorless oil. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.21.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 5H, overlapped with $CHCl_3$), 4.66 (qd, *J* = 6.6, 3.2 Hz, 1H), 3.89 (s, 1H), 2.76 – 2.60 (m, 2H), 1.53 (d, *J* = 6.6 Hz, 3H), 1.20 (t, *J* = 7.5 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.3, 128.9, 127.9, 126.6, 51.9, 49.5, 23.6, 7.6.
HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{10}H_{16}NOS$: 198.0953. Found 198.0953.
[α]$^{20}_D$ +19 (*c* 1.0, EtOAc)



(*R*)-2-methyl-*N*-[(1*R*)-1-Phenylethyl]propane-1-sulfinamide (1c).
The title compound was prepared from *tert*-butyl sulfoximine **4ac** (202 mg, 0.718 mmol, 1 equiv), BF_3•Et_2O (0.18 mL, 0.20 g, 1.4 mmol, 2 equiv) and THF (7 mL) following **general procedure E**. Purification of the crude residue by silica gel flash column chromatography (1:1 hexane:EtOAc) afforded the target sulfinamide **1c** (145 mg, 90%) as a colorless oil. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.29.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 5H), 4.66 (qd, *J* = 6.6, 3.2 Hz, 1H), 3.92 (s, 1H), 2.57 – 2.53 (m, 2H), 2.13 – 1.95 (m, 1H), 1.52 (d, *J* = 6.6 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.3, 128.9, 127.9, 126.6, 65.0, 51.9, 24.6, 23.5, 22.5, 22.0.
HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{12}H_{20}NOS$: 226.1266. Found 226.1266.
[α]$^{20}_D$ +13 (*c* 1.0, EtOAc)



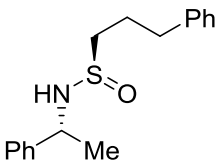
(*R*)-2,2-Dimethyl-*N*-[(1*R*)-1-phenylethyl]propane-1-sulfinamide (1d).
The title compound was prepared from *tert*-butyl sulfoximine **4ad** (207 mg, 0.700 mmol, 1 equiv), BF_3•Et_2O (0.17 mL, 0.20 g, 1.4 mmol, 2 equiv) and THF (7 mL) following **general procedure E**. Purification of the crude residue by silica gel flash column chromatography (1:1 hexane:EtOAc) afforded the target sulfinamide **1d** (140 mg, 84%) as a colorless oil. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.42.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.22 (m, 5H, overlapped with $CHCl_3$), 4.62 (qd, *J* = 6.6, 3.0 Hz, 1H), 3.95 (s, 1H), 2.73 (d, *J* = 13.0 Hz, 1H), 2.59 (d, *J* = 13.0 Hz, 1H), 1.53 (d, *J* = 6.6 Hz, 3H), 1.10 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.2, 128.9, 127.9, 126.7, 71.0, 52.6, 31.0, 29.9, 23.1.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{22}NOS$: 240.1422. Found 240.1427.

[α]$^{20}_D$ +15 (*c* 1.0, CH_2Cl_2)



(*R*)-3-Phenyl-*N*-[(1*R*)-1-phenylethyl]propane-1-sulfinamide (1e).

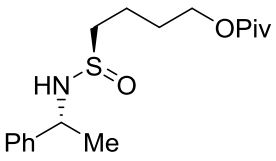
The title compound was prepared from *tert*-butyl sulfoximine **4ae** (385 mg, 1.12 mmol, 1 equiv), BF_3•Et_2O (0.28 mL, 0.32 g, 2.2 mmol, 2 equiv) and THF (11 mL) following **general procedure E**. Purification of the crude residue by silica gel flash column chromatography (3:1 CH_2Cl_2:EtOAc) afforded the target sulfinamide **1e** (198 mg, 61%) as a colorless oil which solidified upon prolonged storage. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.33.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 7H, overlapped with $CHCl_3$), 7.23 – 7.17 (m, 1H), 7.14 – 7.09 (m, 2H), 4.66 (qd, *J* = 6.6, 3.2 Hz, 1H), 3.92 (d, *J* = 3.2 Hz, 1H), 2.73 – 2.59 (m, 4H), 2.05 – 1.87 (m, 2H), 1.52 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.3, 140.7, 128.9, 128.6, 128.6, 127.9, 126.6, 126.4, 55.1, 51.7, 34.7, 25.0, 23.7.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{17}H_{22}NOS$: 288.1422. Found 288.1432.

[α]$^{20}_D$ -13 (*c* 1.0, CH_2Cl_2)



4-[(*R*)-{[(1*R*)-1-Phenylethyl]amino}sulfinyl]butyl-2,2-dimethyl propanoate (1h).

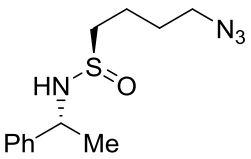
The title compound was prepared from *tert*-butyl sulfoximine **4ah** (383 mg, 1.00 mmol, 1 equiv), BF_3•Et_2O (0.25 mL, 0.28 g, 2.0 mmol, 2 equiv) and THF (10 mL) following **general procedure E**. Purification of the crude residue by silica gel flash column chromatography (2:1 CH_2Cl_2:EtOAc) afforded the target sulfinamide **1h** (272 mg, 83%) as a colorless oil. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.32.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 5H, overlapped with $CHCl_3$), 4.66 (qd, *J* = 6.6, 3.3 Hz, 1H), 4.06 – 3.99 (m, 2H), 3.95 (d, *J* = 3.3 Hz, 1H), 2.77 – 2.61 (m, 2H), 1.76 – 1.63 (m, 4H, overlapped with water), 1.52 (d, *J* = 6.6 Hz, 3H), 1.18 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 178.6, 144.2, 128.9, 127.9, 126.6, 63.6, 55.3, 51.8, 38.9, 27.8, 27.3, 23.7, 20.2.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{17}H_{27}NO_3SNa$: 348.1609. Found 348.1618.

[α]$^{20}_{D}$ -9 (*c* 1.0, CH_2Cl_2)



(*R*)-4-Azido-*N*-[(1*R*)-1-phenylethyl]butane-1-sulfinamide (1i). The title compound was prepared from *tert*-butyl sulfoximine **4ai** (303 mg, 0.940 mmol, 1 equiv), BF_3•Et_2O (0.23 mL, 0.27 g, 1.9 mmol, 2 equiv) and THF (10 mL) following **general procedure E**. Purification of the crude residue by silica gel flash column chromatography (2:1 CH_2Cl_2:EtOAc) afforded the target sulfinamide **1i** (207 mg, 83%) as a light-yellow cloudy oil. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.26.

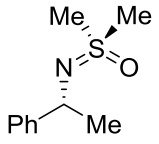
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.16 (m, 5H, overlapped with $CHCl_3$), 4.59 (qd, *J* = 6.6, 3.3 Hz, 1H), 3.89 (d, *J* = 3.3 Hz, 1H), 3.24 – 3.09 (m, 2H), 2.68 – 2.49 (m, 2H), 1.71 – 1.48 (m, 4H, overlapped with water), 1.44 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.3, 128.9, 127.9, 126.6, 55.1, 51.6, 51.0, 28.0, 23.8, 20.8.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{12}H_{18}N_4ONaS$: 289.1099. Found 289.1109.

[α]$^{20}_{D}$ -7 (*c* 1.0, CH_2Cl_2)

Methylation of alkylsulfinamides using $ZnEt_2$



Dimethyl({[(1*R*)-1-phenylethyl]imino})-λ^6-sulfanone (2aa).

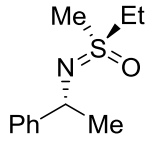
The title compound was prepared from sulfinamide **1a** (55 mg, 0.30 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.33 mL, 0.33 mmol, 1.1 equiv), $ZnEt_2$ (1.0 M solution in hexane, 0.36 mL, 0.36 mmol, 1.2 equiv), diiodomethane (29 µL, 96 mg, 0.36 mmol, 1.2 equiv) and THF (3.6 mL) following **general procedure D**. Purification of the crude residue by silica gel flash column chromatography using gradient elution (100:1 to 25:1 EtOAc:MeOH) afforded the target sulfoximine **2aa** (42 mg, 70%) as a colorless oil. Analytical TLC on silica gel, 20:1 EtOAc:MeOH, R*f* = 0.32.

^{1}H NMR (400 MHz, C_6D_6) δ 7.50 – 7.40 (m, 2H), 7.25 – 7.17 (m, 2H), 7.12 – 7.04 (m, 1H), 4.63 (q, *J* = 6.6 Hz, 1H), 2.24 – 2.22 (m, 3H), 2.02 – 1.97 (m, 3H), 1.60 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 148.6, 128.6, 126.8, 126.7, 53.5, 43.2, 41.6, 28.4.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{10}H_{15}NOSNa$: 220.0772. Found 220.0778.

$[\alpha]^{20}_D$ +94 (*c* 1.0, CH_2Cl_2)



(*R*)-Ethyl(methyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (2ba).

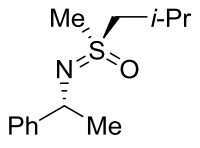
The title compound was prepared from sulfinamide **1b** (61 mg, 0.31 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.34 mL, 0.34 mmol, 1.1 equiv), $ZnEt_2$ (1.0 M solution in hexane, 0.37 mL, 0.37 mmol, 1.2 equiv), diiodomethane (30 µL, 100 mg, 0.37 mmol, 1.2 equiv) and THF (3 mL) following **general procedure D**. Purification of the crude residue by silica gel flash column chromatography using gradient elution (3:1 MTBE:EtOAc to EtOAc) afforded the target sulfoximine **2ba** (40 mg, 61%) as a yellowish oil. Analytical TLC on silica gel, 3:1 MTBE:EtOAc, R*f* = 0.30.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.32 – 7.24 (m, 2H), 7.23 – 7.14 (m, 1H), 4.53 (q, *J* = 6.6 Hz, 1H), 3.01 – 2.70 (m, 5H), 1.48 (d, *J* = 6.6 Hz, 3H), 1.16 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.6, 128.4, 126.7, 126.4, 52.8, 49.1, 40.0, 27.8, 8.8.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{11}H_{17}NOSNa$: 234.0929. Found 234.0927.

$[\alpha]^{20}_D$ +86 (*c* 1.0, CH_2Cl_2)



(*R*)-Methyl(2-methylpropyl){[(1*R*)-1-phenylethyl]imino}-λ⁶-sulfanone (2ca).

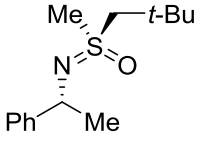
The title compound was prepared from sulfinamide **1c** (56 mg, 0.25 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.28 mL, 0.28 mmol, 1.1 equiv), $ZnEt_2$ (1.0 M solution in hexane, 0.30 mL, 0.30 mmol, 1.2 equiv), diiodomethane (24 μL, 80 mg, 0.30 mmol, 1.2 equiv) and THF (2.5 mL) following **general procedure D**. Purification of the crude residue by silica gel flash column chromatography (20:1 CH_2Cl_2:acetone) afforded the target sulfoximine **2ca** (38 mg, 63%) as a yellowish oil. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.31.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.33 – 7.27 (m, 2H), 7.23 – 7.16 (m, 1H), 4.56 (q, *J* = 6.7 Hz, 1H), 2.95 (s, 3H), 2.89 (dd, *J* = 14.4, 6.7 Hz, 1H), 2.74 (dd, *J* = 14.6, 6.0 Hz, 1H), 2.23 – 2.08 (m, 1H), 1.48 (d, *J* = 6.7 Hz, 3H, overlapped with water), 1.01 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.6, 128.4, 126.7, 126.4, 62.9, 52.9, 42.5, 27.8, 25.0, 22.9, 22.9.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{22}NOS$: 240.1422. Found 240.1415.

$[\alpha]^{20}_D$ +66 (*c* 1.0, CH_2Cl_2)



(*R*)-(2,2-Dimethylpropyl)(methyl){[(1*R*)-1-phenylethyl]imino}-λ⁶-sulfanone (2da).

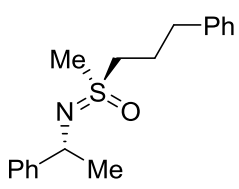
The title compound was prepared from sulfinamide **1d** (60 mg, 0.25 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.28 mL, 0.28 mmol, 1.1 equiv), $ZnEt_2$ (1.0 M solution in hexane, 0.30 mL, 0.30 mmol, 1.2 equiv), diiodomethane (24 μL, 80 mg, 0.30 mmol, 1.2 equiv) and THF (2.5 mL) following **general procedure D**. Purification of the crude residue by silica gel flash column chromatography (20:1 CH_2Cl_2:acetone) afforded the target sulfoximine **2da** (38 mg, 60%) as a colorless oil. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.39.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.33 – 7.27 (m, 2H), 7.23 – 7.16 (m, 1H), 4.54 (q, *J* = 6.6 Hz, 1H), 3.03 – 2.91 (m, 4H), 2.71 (d, *J* = 15.0 Hz, 1H), 1.47 (d, *J* = 6.6 Hz, 3H), 1.11 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.7, 128.4, 126.6, 126.5, 66.1, 53.1, 44.6, 32.2, 29.7, 27.9.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{24}NOS$: 254.1579. Found 254.1570.

$[\alpha]^{20}_D$ +89 (*c* 1.0, CH_2Cl_2)



(*R*)-Methyl({[(1*R*)-1-phenylethyl]imino})(3-phenylpropyl)-λ^6-sulfanone (2ea).

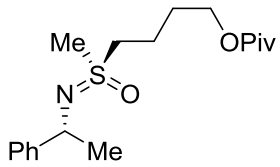
The title compound was prepared from sulfinamide **1e** (57 mg, 0.20 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv), $ZnEt_2$ (1.0 M solution in hexane, 0.24 mL, 0.24 mmol, 1.2 equiv), diiodomethane (19 µL, 64 mg, 0.24 mmol, 1.2 equiv) and THF (2 mL) following **general procedure D**. Purification of the crude residue by silica gel flash column chromatography (MTBE + 0.5% v/v TEA) afforded the target sulfoximine **2ea** (31 mg, 51%) as a yellowish oil. Analytical TLC on silica gel, MTBE, R*f* = 0.40.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.35 – 7.16 (m, 6H, overlapped with $CHCl_3$), 7.03 – 6.97 (m, 2H), 4.51 (q, *J* = 6.7 Hz, 1H), 2.95 – 2.85 (m, 4H), 2.79 – 2.69 (m, 1H), 2.52 – 2.40 (m, 2H), 1.98 – 1.79 (m, 2H), 1.47 (d, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.7, 140.2, 128.7, 128.5, 128.5, 126.8, 126.5, 54.2, 52.9, 40.9, 34.5, 27.8, 25.8. Two signals in the aromatic region overlap.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{18}H_{24}NOS$: 302.1579. Found 302.1591.

$[\alpha]^{20}_D$ +34 (*c* 1.0, CH_2Cl_2)



4-[(*R*)-Methyl(oxo){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanyl] butyl 2,2-dimethylpropanoate (2ha).

The title compound was prepared from sulfinamide **1h** (67 mg, 0.20 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv), $ZnEt_2$ (1.0 M solution in hexane, 0.24 mL, 0.24 mmol, 1.2 equiv), diiodomethane (19 µL, 64 mg, 0.24

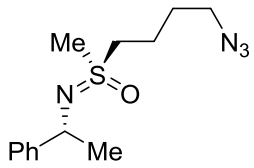
mmol, 1.2 equiv) and THF (2 mL) following **general procedure D**. Purification of the crude residue by silica gel flash column chromatography (MTBE) afforded the target sulfoximine **2ha** (44 mg, 63%) as a yellow oil. Analytical TLC on silica gel, MTBE, R*f* = 0.30.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.31 – 7.25 (m, 2H, overlapped with $CHCl_3$), 7.22 – 7.15 (m, 1H), 4.52 (q, *J* = 6.7 Hz, 1H), 3.91 (t, *J* = 6.2 Hz, 2H), 2.99 – 2.86 (m, 4H), 2.78 – 2.69 (m, 1H), 1.73 – 1.42 (m, 7H), 1.16 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 178.5, 147.5, 128.4, 126.8, 126.4, 63.3, 54.4, 52.9, 40.9, 38.8, 27.7, 27.5, 27.3, 20.8.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{18}H_{30}NO_3S$: 340.1946. Found 340.1952.

[α]$^{20}_D$ +42 (*c* 1.0, CH_2Cl_2)



(*R*)-(4-Azidobutyl)(methyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (2ia).

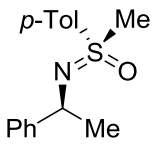
The title compound was prepared from sulfinamide **1i** (53 mg, 0.20 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv), $ZnEt_2$ (1.0 M solution in hexane, 0.24 mL, 0.24 mmol, 1.2 equiv), diiodomethane (19 μL, 64 mg, 0.24 mmol, 1.2 equiv) and THF (2 mL) following **general procedure D**. Purification of the crude residue by silica gel flash column chromatography (MTBE + 0.5% v/v TEA) afforded the target sulfoximine **2ia** (42 mg, 75%) as a yellow oil. Analytical TLC on silica gel, MTBE, R*f* = 0.28.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.34 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 4.53 (q, *J* = 6.7 Hz, 1H), 3.20 – 3.06 (m, 2H), 2.98 – 2.86 (m, 4H), 2.78 – 2.67 (m, 1H), 1.70 – 1.52 (m, 2H, overlapped with water), 1.50 – 1.30 (m, 5H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.6, 128.5, 126.9, 126.5, 54.3, 52.9, 50.8, 41.0, 27.8, 27.7, 21.6.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{21}N_4OS$: 281.1436. Found 281.1439.

[α]$^{20}_D$ +49 (*c* 1.0, CH_2Cl_2)



[(*S*)-Methyl(4-methylphenyl)oxo-λ^6-sulfanylidene][(1*S*)-1-phenylethyl] amine (2ta).

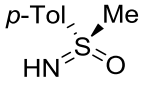
The title compound was prepared from sulfinamide **1t**[27] (53 mg, 0.20 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv), $ZnEt_2$ (1.0 M solution in hexane, 0.24 mL, 0.24 mmol, 1.2 equiv), diiodomethane (19 µL, 64 mg, 0.24 mmol, 1.2 equiv) and THF (2 mL) following **general procedure D**. Purification of the crude residue by reversed phase C18 flash chromatography using gradient elution (90:10 H_2O:MeCN to 5:95 H_2O:MeCN) afforded the target sulfoximine **2ta** (35 mg, 63%) as a colorless oil. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.49.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.30 – 7.12 (m, 7H, overlapped with $CHCl_3$), 4.22 (q, *J* = 6.6 Hz, 1H), 3.09 (s, 3H), 2.39 (s, 3H), 1.49 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.1, 143.6, 136.8, 129.9, 129.0, 128.2, 126.4, 126.4, 54.3, 46.1, 27.9, 21.6.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{16}H_{20}NOS$: 274.1266. Found 274.1271.

$[\alpha]^{20}_D$ +6 (*c* 1.0, EtOAc)

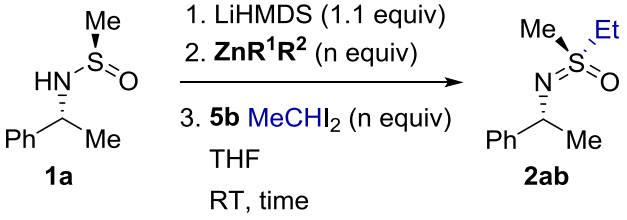


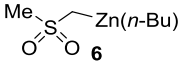
(*S*)-Imino(methyl)(4-methylphenyl)-λ^6-sulfanone (2ua).

The title compound was prepared from (*S*)-*p*-toluenesulfinamide **1u** in 29% yield following **general procedure D.** For improved synthesis using **general procedure G** and characterization data for **2ua**, see page S79.

Synthesis of sulfoximines using ZnPh(*n*-Bu)

Table S3. Optimization of *S*-ethylation conditions for 1a[a]



Entry	ZnR^1R^2	n	Time, h	Yield, %[b]	
				1a	2ab
1[c]	$ZnEt_2$	1.2	16	42	55
2	$ZnEt_2$	1.2	1	40	50
3	$ZnEt_2$	2.5	1	38	51
4[d]	$Zn(t\text{-Bu})_2$	2.5	1	22	55
5[e]	$ZnPh_2$	2.5	1	66	25
6	$ZnPh_2$	2.5	16	33	62
7[f]	$Zn(TMSM)_2$	2.5	16	95	5
8[g]	Zn(TMSM)Et	2.5	16	10	66
9[h]	ZnPh(*n*-Bu)	2.5	16	16	69
10	ZnPh(*n*-Bu)	2.5	48	7	80
11	ZnPh(*n*-Bu)	1.2	48	34	50
12[i]	ZnPh(*t*-Bu)	2.5	48	-	68
13[j]		2.5	48	12	54

[a]**1a** (0.1 mmol) was deprotonated by LiHMDS (0.11 mmol) in THF (1 mL) at room temperature for 15 min followed by sequential addition of ZnR^1R^2 and ethylidene iodide.

The resulting solutions were stirred at room temperature for indicated time before aqueous work-up;

[b] ^{1}H NMR yield measured against mesitylene as internal standard;

[c] Performed at -30 °C following **general procedure D**;

[d] Preparation of Zn(*t*-Bu)$_2$: a solution of $ZnCl_2$ (34 mg, 0.25 mmol, 2.5 equiv) in THF (1.8 mL) was treated with *t*-BuLi (1.8 M solution in pentane, 0.27 mL, 0.50 mmol, 2.5 equiv) at 0 °C following literature procedure.[28] The solution was used after 30 min of stirring at 0 °C;

[e] Preparation of $ZnPh_2$: phenyllithium was prepared from bromobenzene (79 mg, 0.50 mmol, 5 equiv) and *t*-BuLi (1.8 M solution in pentane, 0.55 mL, 1.0 mmol, 10 equiv) in THF (1.5 mL) following literature procedure.[29] Then a solution of $ZnCl_2$ (34 mg, 0.25 mmol, 2.5 equiv) in THF (0.5 mL) was added at 0 °C. The solution was used after 30 min of stirring at 0 °C;

[f] Preparation of Zn(TMSM)$_2$: to a solution of $ZnCl_2$ (34 mg, 0.25 mmol, 2.5 equiv) in THF (1.5 mL) was added (TMSM)MgCl (1.2 M solution in THF, 0.42 mL, 0.50 mmol, 5 equiv) dropwise at 0 °C following modified literature procedure.[30] The solution was used after 30 min of stirring at 0 °C;

[g] Preparation of Zn(TMSM)$_2$: $ZnEt_2$ (1.0 M solution in hexane, 125 µL, 0.125 mmol, 1.25 equiv) was added to a solution of Zn(TMSM)$_2$ (0.125 mmol) obtained as described above at 0 °C and the mixture was diluted with THF (1 mL). The solution was used after 30 min of stirring at 0 °C;

[h] For preparation of ZnPh(*n*-Bu) see **general procedure F**;

[i] Preparation of ZnPh(*t*-Bu): Phenyllithium was prepared from bromobenzene (40 mg, 0.25 mmol, 2.5 equiv) and *t*-BuLi (1.8 M solution in pentane, 0.27 mL, 0.50 mmol, 5 equiv) in THF (1.0 mL) following literature procedure.[29] To the solution was added $ZnCl_2$ (0.25 mL) as a solution in THF (0.75 mL) followed by *t*-BuLi (1.8 M solution in pentane, 0.25 mmol).

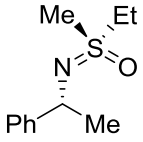
[j] For preparation of diorganozinc **6** see **general procedure G**.

General procedure F for *S*-alkylation of sulfinamides using ZnPh(*n*-Bu).

Preparation of ZnPh(n-Bu).

To a solution of bromobenzene (314 mg, 2.00 mmol, 1 equiv) in THF (8 mL) was added *t*-BuLi (1.9 M solution in pentane, 2.1 mL, 4.0 mmol, 2 equiv) at -78 °C dropwise. The resulting yellow clear solution was stirred for 30 min at -78 °C and then for 30 min at 0 °C. A solution of $ZnCl_2$ (273 mg, 2.00 mmol, 1 equiv) in THF (4 mL) was added, the resulting clear colorless solution was stirred for 5 min at 0 °C and treated with *n*-BuLi (2.5M solution in hexane, 0.80 mL, 2.0 mmol, 1 equiv). Concentration of ZnPh(n-Bu) was determined to be 0.14 M by titration with iodine. The solution was found to retain its reactivity several days after preparation if kept under an inert atmosphere at room temperature.

To a solution of sulfinamide (0.30 mmol, 1 equiv) in THF (3 mL) was added LiHMDS (1.0 M solution in THF, 0.33 mL, 0.33 mmol, 1.1 equiv) at 0 °C. The yellow solution was stirred for 30 min at 0 °C whereupon a solution of ZnPh(*n*-Bu) (0.14 M, 5.4 mL, 0.75 mmol, 2.5 equiv) was added, followed by geminal diiodide (0.75 mmol, 2.5 equiv). Ethylidene iodide was added neat while other diiodides were added as solutions in THF (0.5 mL). The colorless reaction solution was gradually warmed to room temperature, stirred for 48 h at that temperature, quenched with aqueous saturated ammonia (30 mL) and diluted with EtOAc (30 mL). Layers were separated and the aqueous layer was extracted with EtOAc (3×30 mL). Combined organic extracts were washed with brine (30 mL), dried over Na_2SO_4, filtered, concentrated and purified by silica gel flash column chromatography.



(*S*)-Ethyl(methyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (2ab).

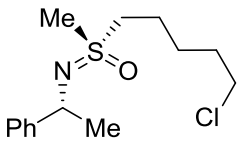
The title compound was prepared from sulfinamide **1a** (55 mg, 0.30 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.33 mL, 0.33 mmol, 1.1 equiv), ZnPh(*n*-Bu) (0.14 M, 5.4 mL, 0.75 mmol, 2.5 equiv), ethylidene iodide **5b** (74 µL, 0.21 g, 0.75 mmol, 2.5 equiv) and THF (3 mL) following **general procedure F**. Purification of the crude residue by silica gel flash column chromatography (10:1 CH_2Cl_2:acetone) afforded the target sulfoximine **2ab** (56 mg, 88%) as a yellow oil. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.18.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.34 – 7.27 (m, 2H), 7.24 – 7.17 (m, 1H), 4.57 (q, *J* = 6.6 Hz, 1H), 3.16 – 3.03 (m, 2H), 2.55 (s, 3H), 1.49 (d, *J* = 6.6 Hz, 3H), 1.42 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 147.8, 128.5, 126.8, 126.4, 53.0, 50.1, 39.1, 28.1, 8.0.

HRMS (APCI/TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{11}H_{18}NOS$: 212.1104. Found 212.1104.

[α]$^{20}_D$ +83 (*c* 1.0, CH_2Cl_2)



(*S*)-(5-Chloropentyl)(methyl){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanone (2ar).

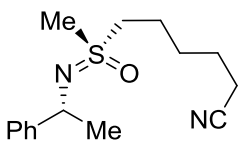
The title compound was prepared from sulfinamide **1a** (55 mg, 0.30 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.33 mL, 0.33 mmol, 1.1 equiv), ZnPh(*n*-Bu) (0.14 M, 5.3 mL, 0.75 mmol, 2.5 equiv), 5-chloro-1,1-diiodopentane **5r** (269 mg, 0.75 mmol, 2.5 equiv) and THF (3 mL) following modified **general procedure F**. After 48 h of stirring at room temperature the reaction mixture was quenched with water (30 mL), diluted with EtOAc (30 mL) and filtered through a pad of *Celite*®**.** Layers were separated and the aqueous layer was extracted with EtOAc (30 mL). Combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the crude residue by silica gel flash column chromatography (1:1 hexane:EtOAc) afforded the target sulfoximine **2ar** (70 mg, 81%) as a yellowish oil. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.18.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 1H), 4.56 (q, *J* = 6.6 Hz, 1H), 3.55 (t, *J* = 6.5 Hz, 2H), 3.15 – 2.98 (m, 2H), 2.56 (s, 3H), 1.95 – 1.78 (m, 4H), 1.66 – 1.55 (m, 2H), 1.48 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.6, 128.5, 126.8, 126.4, 55.7, 53.0, 44.6, 40.1, 32.1, 28.0, 25.8, 22.4.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{23}NOSCl$: 288.1189. Found 288.1192.

[α]$^{20}_D$ +50 (*c* 1.0, CH_2Cl_2)



6-[(*S*)-Methyl(oxo){[(1*R*)-1-phenylethyl]imino}-λ^6-sulfanyl] hexanenitrile (2as).

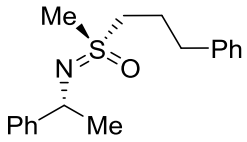
The title compound was prepared from sulfinamide **1a** (44 mg, 0.24 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.26 mL, 0.26 mmol, 1.1 equiv), ZnPh(*n*-Bu) (0.14 M, 4.3 mL, 0.60 mmol, 2.5 equiv), 6,6-diiodohexanenitrile **5s** (209 mg, 0.600 mmol, 2.5 equiv) and THF (2.4 mL) following **general procedure F**. Purification of the crude residue by silica gel flash column chromatography (7:1 acetone: CH_2Cl_2) afforded the target sulfoximine **2as** (47 mg, 70%) as a yellow oil. Analytical TLC on silica gel, 7:1 CH_2Cl_2:acetone, R*f* = 0.30.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 1H), 4.55 (q, *J* = 6.6 Hz, 1H), 3.16 – 2.96 (m, 2H), 2.56 (s, 3H), 2.38 (t, *J* = 6.9 Hz, 2H), 1.98 – 1.86 (m, 2H), 1.78 – 1.69 (m, 2H), 1.67 – 1.57 (m, 2H), 1.48 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.5, 128.6, 126.8, 126.4, 119.4, 55.4, 53.1, 40.3, 28.0, 27.5, 25.1, 22.3, 17.1.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{23}N_2OS$: 279.1531. Found 279.1544.

$[\alpha]^{20}_D$ +48 (*c* 1.0, CH_2Cl_2)



(*S*)-Methyl({[(1*R*)-1-phenylethyl]imino})(3-phenylpropyl)-λ^6-sulfanone (2ae).

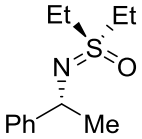
The title compound was prepared from sulfinamide **1a** (55 mg, 0.30 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.33 mL, 0.33 mmol, 1.1 equiv), ZnPh(*n*-Bu) (0.14 M, 5.4 mL, 0.75 mmol, 2.5 equiv), **5e** (3,3-diiodopropyl)benzene (279 mg, 0.750 mmol, 2.5 equiv) and THF (3 mL) following **general procedure F**. Purification of the crude residue by silica gel flash column chromatography (1:1 hexane:EtOAc) afforded the target sulfoximine **2ae** (74 mg, 82%) as a brownish oil. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.33.

^{1}H NMR (400 MHz, C_6D_6) δ 7.48 – 7.41 (m, 2H), 7.24 – 7.03 (m, 6H, overlapped with residual solvent signal), 6.98 – 6.91 (m, 2H), 4.68 (q, *J* = 6.6 Hz, 1H), 2.61 (dt, *J* = 13.7, 7.7 Hz, 1H), 2.49 (dt, *J* = 13.7, 7.4 Hz, 1H), 2.35 (t, *J* = 7.4 Hz, 2H), 2.01 – 1.89 (m, 5H), 1.64 (d, *J* = 6.6 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 148.8, 140.9, 128.8, 128.7, 128.6, 126.8, 126.7, 126.6, 55.0, 53.3, 39.6, 34.4, 28.7, 24.7.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{18}H_{24}NOS$: 302.1579. Found 302.1584.

$[\alpha]^{20}_D$ +51 (*c* 1.0, CH_2Cl_2)



Diethyl({[(1*R*)-1-phenylethyl]imino})-λ^6-sulfanone (2bb).

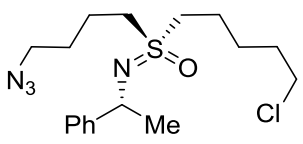
The title compound was prepared from sulfinamide **1b** (49 mg, 0.25 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.28 mL, 0.28 mmol, 1.1 equiv), ZnPh(*n*-Bu) (0.14 M, 4.5 mL, 0.62 mmol, 2.5 equiv), ethylidene iodide **5b** (62 µL, 0.18 g, 0.62 mmol, 2.5 equiv) and THF (2.5 mL) following **general procedure F**. Purification of the crude residue by silica gel flash column chromatography (15:1 CH_2Cl_2:acetone) afforded the target sulfoximine **2bb** (35 mg, 62%) as a colorless oil. Analytical TLC on silica gel, 2:1 hexane:EtOAc, R*f* = 0.29.

^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.33 – 7.24 (m, 2H, overlapped with $CHCl_3$), 7.23 – 7.15 (m, 1H), 4.54 (q, *J* = 6.6 Hz, 1H), 3.10 – 2.92 (m, 2H), 2.86 (dq, *J* = 14.8, 7.4 Hz, 1H), 2.71 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.48 (d, *J* = 6.6 Hz, 3H), 1.38 (t, *J* = 7.4 Hz, 3H), 1.10 (t, *J* = 7.4 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.0, 128.4, 126.6, 126.4, 52.5, 46.1, 46.0, 28.1, 8.3, 7.4.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{12}H_{20}NOS$: 226.1266. Found 226.1267.

$[\alpha]^{20}_D$ +74 (*c* 1.0, CH_2Cl_2)



(*R*)-(4-Azidobutyl)(5-chloropentyl){[(1*R*)-1-phenylethyl] imino}-λ^6-sulfanone (2ir).

The title compound was prepared from sulfinamide **1i** (53 mg, 0.20 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv), ZnPh(*n*-Bu) (0.14 M, 4.4 mL, 0.62 mmol, 2.5 equiv), 5-chloro-1,1-diiodopentane **5r** (179 mg, 0.500 mmol, 2.5 equiv) and THF (2.5 mL) following modified **general procedure F**. After 48 h at room temperature the reaction mixture was quenched with water (30 mL), diluted with EtOAc (30 mL) and filtered through a pad of *Celite*®. Layers were separated and the aqueous layer was extracted with EtOAc (30 mL). Combined organic layers were washed

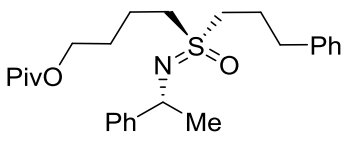
with brine (30 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the crude residue by silica gel flash column chromatography (3:2 hexane:EtOAc) afforded the target sulfoximine **2ir** (52 mg, 70%) as a colorless oil. Analytical TLC on silica gel, 3:2 hexane:EtOAc, R*f* = 0.28.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.34 – 7.28 (m, 2H), 7.24 – 7.18 (m, 1H), 4.52 (q, *J* = 6.6 Hz, 1H), 3.56 (t, *J* = 6.4 Hz, 2H), 3.16 – 2.97 (m, 3H), 2.96 – 2.77 (m, 2H), 2.63 (ddd, *J* = 14.1, 10.6, 5.1 Hz, 1H), 1.94 – 1.79 (m, 4H), 1.65 – 1.50 (m, 4H), 1.47 (d, *J* = 6.6 Hz, 3H), 1.44 – 1.27 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.9, 128.5, 126.8, 126.5, 52.7, 52.5, 50.8, 44.6, 32.2, 27.9, 27.8, 25.9, 21.7, 21.2. Two signals overlap in the aliphatic region.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{17}H_{28}N_4OSCl$: 371.1672. Found 371.1674.

[α]$^{20}_D$ +29 (*c* 1.0, CH_2Cl_2)



4-[(*R*)-Oxo({[(1*R*)-1-phenylethyl]imino})(3-phenylpropyl)-λ^6-sulfanyl]butyl 2,2-dimethylpropanoate (2he).

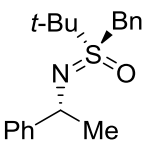
The title compound was prepared from sulfinamide **1h** (65 mg, 0.20 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv), ZnPh(*n*-Bu) (0.14 M, 3.6 mL, 0.50 mmol, 2.5 equiv), (3,3-diiodopropyl)benzene **5e** (186 mg, 0.500 mmol, 2.5 equiv) and THF (2.5 mL) following **general procedure F**. Purification of the crude residue by silica gel flash column chromatography (2:1 hexane:EtOAc) afforded the target sulfoximine **2he** (66 mg, 74%) as a colorless oil. Analytical TLC on silica gel, 2:1 hexane:EtOAc, R*f* = 0.30.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.33 – 7.17 (m, 8H, overlapped with $CHCl_3$), 4.50 (q, *J* = 6.6 Hz, 1H), 3.87 (t, *J* = 6.1 Hz, 2H), 3.05 – 2.69 (m, 5H), 2.62 (ddd, *J* = 14.2, 10.4, 5.2 Hz, 1H), 2.26 – 2.06 (m, 2H), 1.59 – 1.31 (m, 7H), 1.16 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 178.5, 147.9, 140.3, 128.8, 128.6, 128.5, 126.7, 126.6, 126.4, 63.4, 52.7, 52.4, 52.0, 38.8, 34.5, 27.9, 27.7, 27.3, 24.3, 20.4.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{26}H_{38}NO_3S$: 444.2572. Found 444.2581.

[α]$^{20}_D$ +28 (*c* 1.0, CH_2Cl_2)



(*S*)-Benzyl(*tert*-butyl){[(1*R*)-1-phenylethyl]imino}-λ⁶-sulfanone (4ag). The title compound was prepared from sulfinamide **3a** (45 mg, 0.20 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv), ZnPh(*n*-Bu) (0.14 M, 3.6 mL, 0.50 mmol, 2.5 equiv), benzal iodide **5g**[17] (172 mg, 0.500 mmol, 2.5 equiv) and THF (2.0 mL) following **general procedure F**. Purification of the crude residue by silica gel flash column chromatography (8:1 hexane:EtOAc + 0.1 % v/v TEA) afforded the target sulfoximine (33 mg, 52%) as a colorless oil. Analytical TLC on silica gel, 4:1 hexane:EtOAc, R*f* = 0.38.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.10 (m, 10H, overlapped with $CHCl_3$), 4.29 – 4.15 (m, 2H), 4.02 (d, *J* = 12.8 Hz, 1H), 1.47 (s, 9H), 1.30 (d, *J* = 6.6 Hz, 3H).

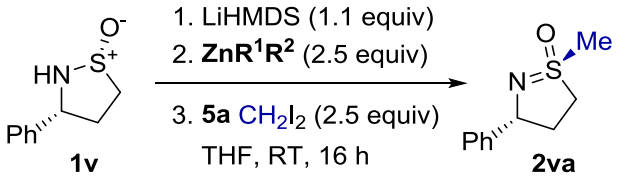
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.7, 131.3, 129.7, 128.4, 128.0, 128.0, 126.3, 126.0, 61.8, 55.1, 52.7, 29.2, 24.4.

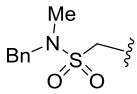
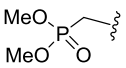
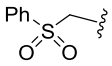
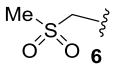
HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{19}H_{26}NOS$: 316.1735. Found 316.1737.

$[\alpha]^{20}_D$ +58 (*c* 1.0, CH_2Cl_2)

Synthesis of sulfoximines using diorganozinc 6

Table S4. Optimization of conditions for *S*-methylation of 1v[a]



Entry	R^1	R^2	Yield, %[b] 1v	Yield, %[b] 2va
1[c]	Et	Et	94	3
2[d]	Ph	*n*-Bu	89	5
3	Tr	*n*-Bu	23	56
4[e]		*n*-Bu	11	53
5[e]		*n*-Bu	10	67
6[e]		*n*-Bu	5	70
7[e]	 6	*n*-Bu	5	74
8[e,f]			8	78

[a] **1a** (0.1 mmol) was deprotonated by LiHMDS (0.11 mmol) in THF (1 mL) at room temperature for 15 min followed by sequential addition of **ZnR^{1}R^2** and diiodomethane;

[b] ^{1}H NMR yield measured against mesitylene as internal standard;

[c] performed at -30 °C following **general procedure D**;

[d] performed for 48 h following **general procedure F**;

[e] mixed diorganozincs in entries 4-8 were prepared following **general procedure G** using *N*-benzyl-*N*-methylmethanesulfonamide, dimethyl methyl phosphonate, methyl phenyl sulfone or dimethyl sulfone as starting materials;

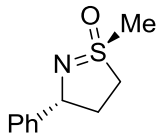
[f] performed using DME instead of THF.

General procedure G for *S*-alkylation of sulfinamides using diorganozinc 6

Preparation of ***6***

To a suspension of $ZnCl_2$ (102 mg, 0.75 mmol, 2.5 equiv) in DME (3 mL) was added *n*-BuLi (2.5 M solution in hexane, 0.30 mL, 0.75 mmol, 2.5 equiv) at 0 °C. After 30 min of stirring at 0 °C a homogeneous yellowish solution of *n*-BuZnCl was obtained. In parallel, *n*-BuLi (2.5 M solution in hexane, 0.30 mL, 0.75 mmol, 2.5 equiv) was added at 0 °C to a solution of dimethyl sulfone (71 mg, 0.75 mmol, 2.5 equiv) in DME (4.5 mL). The immediately formed white suspension was stirred for 30 min at 0 °C and treated with *n*-BuZnCl solution. Stirring for 5 min at 0 °C afforded a suspension of **6**.

A solution of sulfinamide (0.30 mmol, 1 equiv) in DME (3 mL) was treated with LiHMDS (1.0 M solution in THF, 0.33 mL, 0.33 mmol, 1.1 equiv) at 0 °C, stirred for 30 min at that temperature and added to the suspension of **6**. After 5 min at 0 °C, geminal diiodide (0.75 mmol, 2.5 equiv) was added and the slightly opalescent solution was warmed to room temperature over 16 h. Diiodomethane was added neat while **1r** was added as a solution in THF (0.5 mL). The mixture was quenched with aqueous saturated ammonia (2 mL), diluted with brine (30 mL) and extracted with EtOAc (4×30 mL). Combined organic extracts were dried over Na_2SO_4, filtered, concentrated and purified by silica gel flash column chromatography.



(1*R*,3*R*)-1-Methyl-3-phenyl-4,5-dihydro-3*H*-1$\lambda^{4,2}$-thiazol-1-ium-1-olate (2va).

The title compound was prepared from sulfinamide **1v** (54 mg, 0.30 mmol, 1 equiv), $ZnCl_2$ (102 mg, 0.75 mmol, 2.5 equiv), *n*-BuLi (2.5 M solution in hexane, 0.60 mL, 1.5 mmol, 5 equiv), dimethyl sulfone (71 mg, 0.75 mmol, 2.5 equiv), diiodomethane (60 µL, 0.20 g, 0.75 mmol, 2.5 equiv) and DME (7.5 mL). Purification of the crude residue by silica gel flash column chromatography (20:1 EtOAc:MeOH) afforded the target sulfoximine **2va** (44 mg, 75%) as a white solid. Analytical TLC on silica gel, 5:1 EtOAc:MeOH, R*f* = 0.30. Crystals suitable for X-ray analysis were prepared by slow evaporation of *i*-Pr_2O/CH_2Cl_2 solution.

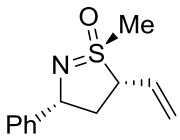
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.38 – 7.28 (m, 2H), 7.27 – 7.20 (m, 1H, overlapped with $CHCl_3$), 4.89 (dd, *J* = 8.2, 6.3 Hz, 1H), 3.47 (ddd, *J* = 12.1, 7.6, 3.0 Hz, 1H), 3.37 – 3.21 (m, 4H), 2.74 – 2.64 (m, 1H), 2.17 (ddt, *J* = 13.1, 12.1, 7.6 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.6, 128.5, 127.2, 126.2, 71.4, 54.4, 43.0, 34.4.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{10}H_{14}NOS$: 196.0796. Found 196.0797.

$[\alpha]^{20}_D$ +18 (*c* 1.0, EtOAc)

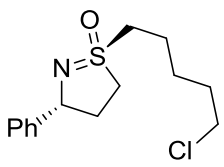
Melting point 91 – 93 °C (recrystallized from *i*-Pr_2O/CH_2Cl_2)



(1*R*,3*R*,5*S*)-5-Ethenyl-1-methyl-3-phenyl-4,5-dihydro-3*H*-1$\lambda^{4,2}$-thiazol-1-ium-1-olate (2a').

The title compound was prepared from sulfinamide **1'**[5] (62 mg, 0.30 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.33 mL, 0.33 mmol, 1.1 equiv), $ZnCl_2$ (102 mg, 0.75 mmol, 2.5 equiv), dimethyl sulfone (71 mg, 0.75 mmol, 2.5 equiv), *n*-BuLi (2.5 M solution in hexane, 0.60 mL, 1.5 mmol, 5 equiv), diiodomethane (60 μL, 0.20 g, 0.75 mmol, 2.5 equiv) and DME (10.5 mL) following modified **general procedure G**. After addition of diiodomethane, the reaction mixture was stirred at 0 °C for 2 h. Purification of the crude residue by silica gel flash column chromatography (2:1 CH_2Cl_2:acetone) afforded the target sulfoximine **2a'** (46 mg, 70%) as a colorless oil. Spectroscopic data matches the previously reported.[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 2H), 7.37 – 7.29 (m, 2H), 7.27 – 7.19 (m, 1H, overlapped with $CHCl_3$), 6.01 – 5.84 (m, 1H), 5.54 – 5.36 (m, 2H), 4.81 (dd, *J* = 9.6, 5.8 Hz, 1H), 3.96 (ddd, *J* = 13.3, 8.9, 7.3 Hz, 1H), 3.16 (s, 3H), 2.75 (ddd, *J* = 13.3, 7.3, 5.8 Hz, 1H), 2.09 – 1.95 (m, 1H).



(1*R*,3*R*)-1-(5-Chloropentyl)-3-phenyl-4,5-dihydro-3*H*-1$\lambda^{4,2}$-thiazol-1-ium-1-olate (2vr).

The title compound was prepared from sulfinamide **1v** (54 mg, 0.30 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.33 mL, 0.33 mmol, 1.1 equiv), $ZnCl_2$ (102 mg, 0.75 mmol, 2.5 equiv), dimethyl sulfone (71 mg, 0.75 mmol, 2.5 equiv), *n*-BuLi (2.5 M solution in hexane, 0.60 mL, 1.5 mmol, 5 equiv), 5-chloro-1,1-

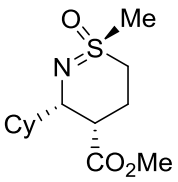
diiodopentane **1r** (269 mg, 0.75 mmol, 2.5 equiv) and DME (10.5 mL) following modified **general procedure G**. After 16 h at room temperature the reaction mixture was quenched with water (30 mL), diluted with EtOAc (30 mL) and filtered through a pad of *Celite*®. Layers were separated and the aqueous layer was extracted with EtOAc (30 mL). Combined organic extracts were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the crude residue by silica gel flash column chromatography (10:1 CH_2Cl_2:acetone) afforded the target sulfoximine **2vr** (30 mg, 35%) as a colorless oil. Analytical TLC on silica gel, 5:1 CH_2Cl_2:acetone, R*f* = 0.40.

^{1}H NMR (400 MHz, C_6D_6) δ 7.70 – 7.60 (m, 2H), 7.31 – 7.20 (m, 2H), 7.15 – 7.07 (m, 1H, overlapped with residual solvent signal), 4.72 (t, *J* = 7.0 Hz, 1H), 3.01 (t, *J* = 6.5 Hz, 2H), 2.74 (ddd, *J* = 13.9, 10.0, 5.6 Hz, 1H), 2.65 – 2.55 (m, 2H), 2.25 (ddd, *J* = 12.4, 11.3, 8.6 Hz, 1H), 2.03 – 1.93 (m, 1H), 1.77 (ddt, *J* = 12.4, 11.3, 7.7 Hz, 1H), 1.55 – 1.31 (m, 2H), 1.31 – 1.14 (m, 2H), 1.14 – 0.87 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 146.2, 128.6, 127.2, 126.7, 71.7, 54.7, 51.9, 44.5, 34.6, 32.1, 25.7, 23.5.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{21}NOSCl$: 286.1032. Found 286.1040.

$[\alpha]^{20}_D$ +29 (*c* 1.0, CH_2Cl_2)



Methyl (1*R*,3*S*,4*S*)-3-cyclohexyl-1-methyl-1-oxo-3,4,5,6-tetrahydro -1$\lambda^{6,2}$-thiazine-4-carboxylate (2wa).

The title compound was prepared from sulfinamide **1w** (52 mg, 0.20 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.22 mL, 0.22 mmol, 1.1 equiv), $ZnCl_2$ (68 mg, 0.50 mmol, 2.5 equiv), dimethyl sulfone (47 mg, 0.50 mmol, 2.5 equiv), *n*-BuLi (2.5 M solution in hexane, 0.40 mL, 1.0 mmol, 5 equiv), diiodomethane (40 µL, 0.13 g, 0.50 mmol, 2.5 equiv) and THF (7 mL) following modified **general procedure G**. Thus, DME was replaced with THF at each stage of the reaction. Purification of the crude residue by silica gel flash column chromatography (20:1 EtOAc:MeOH) afforded the target sulfoximine **2wa** (44 mg, 80%) as a yellow solid. Analytical TLC on silica gel, 20:1 EtOAc:MeOH, R*f* = 0.24. Crystals suitable for X-ray analysis were prepared by slow evaporation of *i*-Pr_2O/CH_2Cl_2 solution.

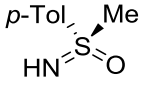
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 3H), 3.37 – 3.27 (m, 2H), 2.99 (ddd, *J* = 13.1, 8.4, 5.0 Hz, 1H), 2.91 (s, 3H), 2.85 (dt, *J* = 8.4, 3.4 Hz, 1H), 2.63 (dtd, *J* = 14.9, 8.4, 4.7 Hz, 1H), 2.36 – 2.28 (m, 1H), 2.28 – 2.18 (m, 1H), 1.83 – 1.57 (m, 5H), 1.30 – 1.04 (m, 3H), 0.96 – 0.80 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.1, 64.5, 51.8, 48.2, 42.2, 40.5, 40.1, 31.1, 30.2, 26.6, 26.4, 26.2, 22.2.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{24}NO_3S$: 274.1477. Found 274.1482.

$[\alpha]^{20}_D$ -93 (*c* 1.0, CH_2Cl_2)

Melting point 156 – 157 °C (recrystallized from *i*-Pr_2O/CH_2Cl_2)

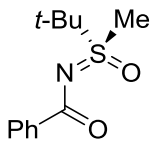


(*S*)-Imino(methyl)(4-methylphenyl)-λ^6-sulfanone (2ua).

The title compound was prepared from (*S*)-*p*-toluenesulfinamide **1u** (47 mg, 0.30 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.33 mL, 0.33 mmol, 1.1 equiv), $ZnCl_2$ (102 mg, 0.75 mmol, 2.5 equiv), dimethyl sulfone (71 mg, 0.75 mmol, 2.5 equiv), *n*-BuLi (2.5 M solution in hexane, 0.60 mL, 1.5 mmol, 5 equiv), diiodomethane (60 μL, 0.20 g, 0.75 mmol, 2.5 equiv) and THF (10.5 mL) following modified **general procedure G**. Thus, DME was replaced with THF at each stage of the reaction and after addition of diiodomethane, the reaction mixture was stirred at 0 °C for 2 h. Purification of the crude residue by silica gel flash column chromatography (EtOAc) afforded the target sulfoximine **2ua** (37 mg, 73%) as a yellow oil. Spectroscopic data matches the previously reported.[31]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.83 (m, 2H), 7.37 – 7.29 (m, 2H), 3.08 (s, 3H), 2.50 – 2.28 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.0, 140.7, 130.0, 127.8, 46.4, 21.6.



***N*-[(*S*)-*tert*-Butyl(methyl)oxo-λ^6-sulfanylidene]benzamide (4pa).**

The title compound was prepared from (*S*)-*N*-(*tert*-butylsulfinyl)benzamide **3p**[26] (68 mg, 0.30 mmol, 1 equiv), LiHMDS (1.0 M solution in THF, 0.33 mL, 0.33 mmol, 1.1 equiv), $ZnCl_2$ (102 mg, 0.75 mmol, 2.5 equiv), dimethyl sulfone (71 mg, 0.75 mmol, 2.5 equiv), *n*-BuLi (2.5 M solution in hexane, 0.60 mL, 1.5 mmol, 5 equiv), diiodomethane (60 μL, 0.20 g, 0.75 mmol, 2.5 equiv) and THF (10.5 mL) following modified **general procedure G**. Thus, DME was replaced with THF at each stage of the reaction and

after addition of diiodomethane, the reaction mixture was stirred at 0 °C for 2 h. Purification of the crude residue by silica gel flash column chromatography (CH_2Cl_2:acetone 20:1) afforded the target sulfoximine **4pa** (68 mg, 95%) as a white amorphous solid. Analytical TLC on silica gel, 1:1 hexane:EtOAc, R*f* = 0.25.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.07 (m, 2H), 7.52 – 7.45 (m, 1H), 7.44 – 7.35 (m, 2H), 3.40 (s, 3H), 1.58 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.7, 136.4, 132.0, 129.4, 128.1, 60.6, 32.5, 23.2.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{12}H_{17}NO_2NaS$: 262.0878. Found 262.0888.

$[\alpha]^{20}_D$ -91 (*c* 1.0, CH_2Cl_2)

Carbenoid decomposition experiments under respective *S*-alkylation conditions

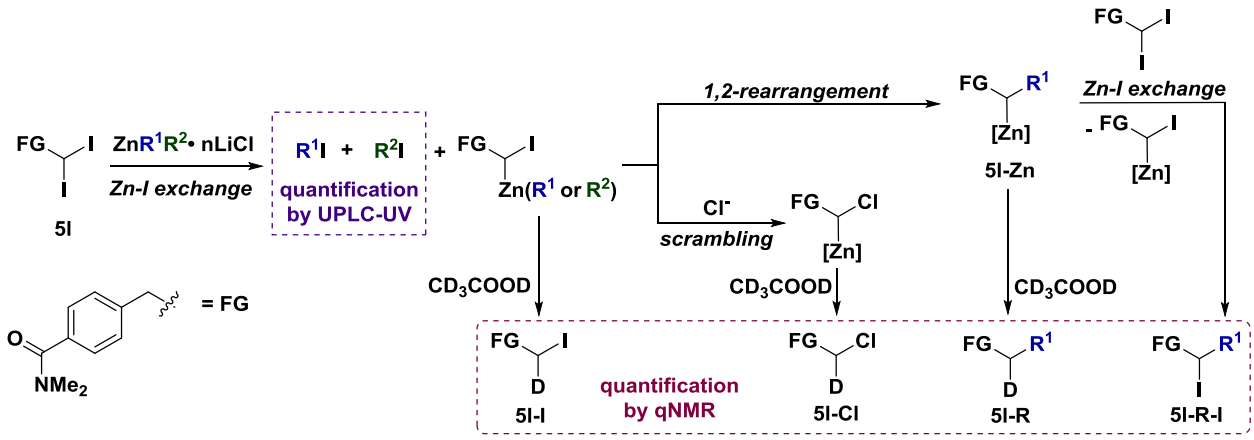


Table S5. Distribution of carbenoid decomposition products

R^1	R^2	n	5l	5l-I	5l-Cl	5l-R	5l-R-I	R^1I	R^2I
Et	Et	0	0	5	-	39	20	58	-
n-Bu	Ph	2	15	31	16	<5	<5	52	28
n-Bu		2	27	37	18	<5	9	65	0

We investigated decomposition of carbenoids arising from diiodide **5l** upon action of $ZnEt_2$, ZnPh(*n*-Bu) and **6** under experimental conditions of the respective *S*-alkylation reactions. The $ZnEt_2$-derived carbenoid was formed and almost fully decomposed in 2 h at 0 °C. The main decomposition pathway corresponded to a 1,2-rearrangement leading to secondary organozinc **5l-Zn**. The latter partially engaged in iodination with the starting **5l** as evidenced by the presence of **5l-R-I**. However, the major product **5l-R** originated via the expected quenching of **5l-Zn**.

In the case of ZnPh(*n*-Bu), zinc-halogen exchange became slower and produced a 52:28 mixture of *n*-BuI and PhI. Carbenoid decomposition also decelerated as evidenced by increased quantity of recovered **5l-I** and metallate rearrangement became less prominent. The iodine containing carbenoid underwent reported[32] scrambling with chloride ions leading to **5l-Cl**.

In the case of **6** complete selectivity for *n*-Bu group in Zn-I exchange was observed. No trace of iodination at the methylsulfone fragment was detected by UPLC-MS and ^{1}H NMR. Stability of the obtained carbenoid was comparable to the ZnPh(*n*-Bu) system since the quantity of recovered **5l-I** remained similar. Minor amount of **5l-R-I** was observed presumably due to Schlenk equilibrium[33,34] between **6** and Zn(*n*-Bu)$_2$. As before, scrambling with choride produced **5l-Cl**.

General procedure for determination and quantification of carbenoid decomposition products

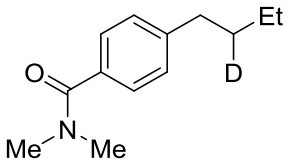
To a solution of 4-(2,2-diiodoethyl)-*N*,*N*-dimethylbenzamide **5l** (86 mg, 0.20 mmol, 1 equiv) in THF (2 mL) was added diethyl zinc (1.0 M solution in hexane, 200 µL, 0.200 mmol, 1 equiv) at 0 °C. The yellow solution was stirred at 0 °C for 2 h, quenched with CD_3COOD (48 µL, 52 mg, 0.80 mmol, 4 equiv) and stirred for 30 min at room temperature. The mixture was partitioned between H_2O (20 mL) and EtOAc (20 mL), layers were separated and the aqueous layer was extracted with EtOAc (2×20 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated. Mesitylene (48.0 mg, 0.40 mmol, 2 equiv) was added and the mixture was analyzed by qNMR in $CDCl_3$.

For UPLC-UV analysis the same reaction was performed in the presence of *tert*-butyl benzene (26.8 mg, 0.200 mmol, 1 equiv), quenched with CD_3COOD (24 µL, 26 mg, 4 equiv) and stirred for 30 min at room temperature. An aliquot of the solution was dissolved in 1:1 MeCN:H_2O and analyzed by UPLC-UV. The amount of EtI was determined against *tert*-butyl benzene standard using a calibration curve at 251 nm.

For qNMR analysis of ZnPh(*n*-Bu) and **6** identical experiments were performed using ZnPh(*n*-Bu) (0.14 M, 1.4 mL, 0.20 mmol, 1 equiv, prepared as described in **general procedure F**) or **6** (0.10 M, 2.0 mL, 0.20 mmol, 1 equiv, prepared as described in **general procedure G** using THF as solvent) and analyzed by qNMR in $CDCl_3$ using mesitylene as standard. The amount of *n*-BuI and PhI was determined by UPLC-UV analysis against *tert*-butyl benzene standard using calibration curves at 251 nm and at 220 nm respectively.

After the ^{1}H qNMR analysis, the crude mixture of carbenoid decomposition products from the $ZnEt_2$ experiment was concentrated and separated by reversed phase preparative

HPLC (Atlantis® T3 - 30×100mm, 5µm – flow 20 mL / min) using gradient elution from 95:5 to 5:95 water:MeCN to obtain **S4** (6 mg, 14%) and **S5** (4 mg, 6%) as colorless oils.

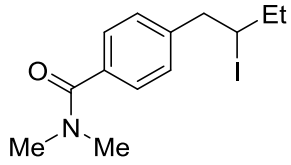


4-(2-Deuterobutyl)-*N*,*N*-dimethylbenzamide (S4).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.22 – 7.16 (m, 2H), 3.19 – 2.93 (br s, 6H), 2.61 (d, *J* = 7.7 Hz, 2H), 1.65 – 1.50 (m, 1H), 1.34 (p, *J* = 6.9 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.0, 144.8, 133.6, 128.4, 127.3, 39.8, 35.6, 35.5, 33.1 (t, *J* = 19.5), 22.3, 14.0.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}NO^1H_{19}{}^2H$: 207.1608. Found 207.1608.



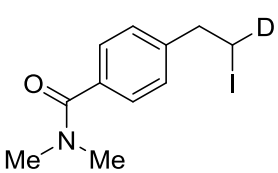
4-(2-Iodobutyl)-*N*,*N*-dimethylbenzamide (S5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.25 – 7.19 (m, 2H), 4.23 (p, *J* = 6.7 Hz, 1H), 3.30 (dd, *J* = 14.3, 7.7 Hz, 1H), 3.19 (dd, *J* = 14.3, 7.1 Hz, 1H), 3.14 – 2.91 (br s, 6H), 1.76 (p, *J* = 7.0 Hz, 2H), 1.05 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.7, 141.5, 134.8, 129.1, 127.5, 47.0, 40.1, 39.8, 35.5, 32.8, 14.4.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{19}NOI$: 332.0511. Found 332.0526.

After the ^{1}H qNMR analysis, the crude mixture of carbenoid decomposition products from the diorganozinc **6** experiment was concentrated and separated by reversed phase preparative HPLC (Atlantis® T3 - 30×100mm, 5µm – flow 20 mL / min) using gradient elution from 95:5 to 5:95 water:MeCN to obtain **S6** (9 mg, 15%), **S7** (4 mg, 9%) and **S8** (2 mg, 3%) as colorless oils.



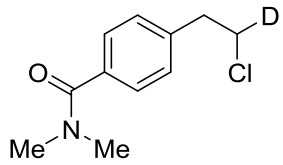
4-[2-Iodo(2-deutero)ethyl]-*N*,*N*-dimethylbenzamide (S6).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.25 – 7.19 (m, 2H), 3.38 – 3.29 (m, 1H), 3.24 – 3.16 (m, 2H), 3.15 – 2.87 (br s, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.7, 142.3, 134.8, 128.5, 127.7,

40.0, 39.8, 35.6, 4.8 (t, *J* = 23.3 Hz).

HRMS (ESI/Q-TOF) *m/z*: [M+H]$^+$ Calcd. for $C_{11}{}^1H_{14}{}^2HNOI$: 305.0261. Found 305.0275.

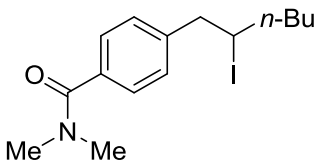


4-[2-Chloro(2-deutero)ethyl]-*N*,*N*-dimethylbenzamide (S7).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.29 – 7.22 (m, 2H, overlapped with $CHCl_3$), 3.75 – 3.66 (m, 1H), 3.18 – 2.95 (m, 8H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.7, 139.9, 134.8, 129.0, 127.6, 44.4 (t, *J* = 22.9 Hz), 39.8, 38.9, 35.6.

HRMS (ESI/Q-TOF) *m/z*: [M+H]$^+$ Calcd. for $C_{11}NOCl^1H_{14}{}^2H$: 213.0905. Found 213.0911.



4-(2-Iodohexyl)-*N*,*N*-dimethylbenzamide (S8).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.24 – 7.19 (m, 2H), 4.29 – 4.21 (m, 1H), 3.29 (dd, *J* = 14.3, 7.8 Hz, 1H), 3.19 (dd, *J* = 14.3, 6.9 Hz, 1H), 3.15 – 2.85 (br s, 6H), 1.87 – 1.75 (m, 1H), 1.75 – 1.63 (m, 1H), 1.62 – 1.50 (m, 1H, overlapped with water), 1.46 – 1.20 (m, 3H), 0.90 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.7, 141.5, 134.9, 129.1, 127.5, 47.4, 39.8, 39.4, 38.1, 35.5, 31.9, 22.0, 14.1.

HRMS (ESI/Q-TOF) *m/z*: [M+H]$^+$ Calcd. for $C_{15}H_{23}NOI$: 360.0824. Found 360.0819.

DFT calculations

Computational method

All calculations were performed using the Gaussian 09 software package.[35] All geometry optimizations were performed without restrictions using the M06-2X method and Def2SVP[36] basis set for all atoms. The stationary points were verified to be real minima (zero imaginary frequency) transition states (TS) (one imaginary frequency) by performing frequency calculations at the same level of theory. Intrinsic reaction coordinates (IRC) were calculated for all TS to confirm that the first-order saddle points connect the correct stationary points of a starting material and a product on the potential energy surface. Single-point energy (SPE) calculations were performed on the stationary points using the Def2TZVP[36] basis set for all atoms with a superfine integral grid (integral=grid=superfine).[37] SPE calculations were carried out in THF (ε=7.4257) using implicit solvent modeling with the PCM method.

Results of the DFT calculations

Initially, Zn coordination sites were investigated by performing optimization of four distinct geometries (Figure S1) – **SM-1** where Zn is coordinated to the N atom, **SM-2** where Zn is coordinated to the O atom, **SM-3** where Zn is coordinated to the S atom and **SM-4** where Zn is coordinated to both O and N atoms. It was found that thermodynamically the most stable isomer is **SM-4** where both O and N coordinate with Zn. The energy difference between both diastereomers of **SM-4** (**SM4** and **SM4'**) is minimal (<0.5 kcal/mol) as a result only one diastereomer is depicted in the figures. The second energetically favored isomer contains Zn–N coordination (**SM-1**) which is 1.9 kcal/mol higher in energy compared to **SM-4**. Both isomers where Zn is coordinated to O (**SM-2**) and S (**SM-3**) are located significantly higher on the potential energy surface (PES) at 8.0 kcal/mol and 15.2 kcal/mol respectively. Therefore, the population of **SM-3** and **SM-2** is unlikely. Then, the transitions between coordination modes were investigated. The transition from **SM-1** to **SM-3** is separated by 18.3 kcal/mol high transition state **TS-5**. Meanwhile, 23.3 kcal/mol high transition state **TS-4** separates isomers **SM-2** and **SM-3**. Unfortunately, we were unable to locate distinct transition states from **SM-1** to **SM-4** and from **SM-2** to **SM-4**.

Forced coordinate scans of the PES starting from both **SM-1** and **SM-2** showed a smooth downhill transition to **SM-4**. This suggests that if there are any transition states between transitions from **SM-1** to **SM-4** and from **SM-2** to **SM-4**, they are very small early transition states, therefore these transitions can be considered barrierless.

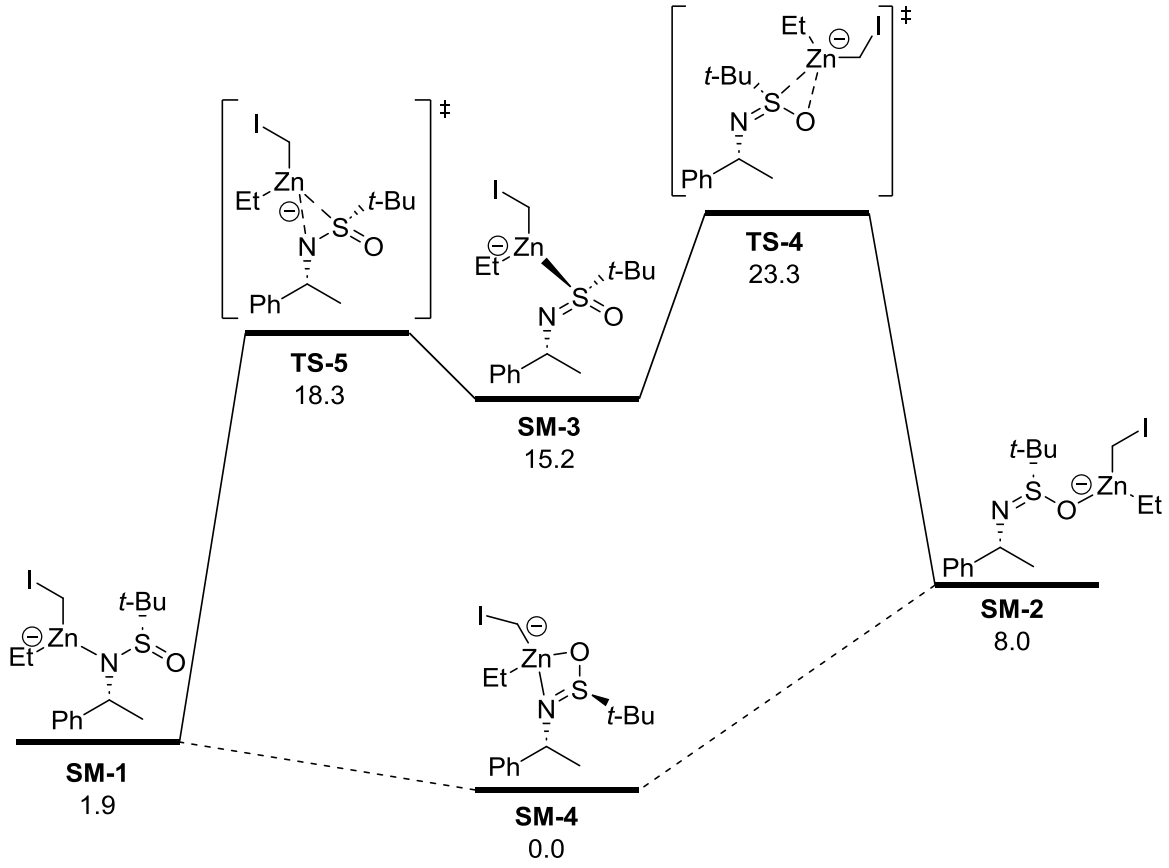


Figure S1. Energy profile of Zn coordination sites

Next, methylene transfer from Zn in **SM-1** was investigated (Figure S2). The formation of S functionalized product **PDT-1A** is kinetically most favorable and is facilitated by the four-membered transition state **TS-1A** (13.2 kcal/mol). Meanwhile, the formation of other possible products **PDT-1B**, **PDT-1C,** and **PDT-1D** is less likely under Curtin-Hammett conditions as respective transition state energies are significantly higher (**TS-1B** – 19.8 kcal/mol, **TS-1C** – 25.9 kcal/mol and **TS-1D** – 24.3 kcal/mol) compared to that of **TS-1A** (13.2 kcal/mol). A similar PES analysis of methylene transfer from Zn in **SM-2** where Zn is coordinated to the O atom was carried out (Figure S3). In this case, the

most likely transformation is methylene transfer to the N atom through the five-membered transition state **TS-2C** (16.5 kcal/mol) forming product **PDT-2C**. Transition state **TS-2A** (20.8 kcal/mol) for methylene transfer to S atom is higher in energy compared to **TS-2C** (16.5 kcal/mol). Similarly, the other transition states **TS-2B** (34.9 kcal/mol) and **TS-2D** (30.9 kcal/mol) are significantly higher on the PES and are unlikely to occur. It must be noted, that the search for a direct path from **SM-4** to **PDT-1A** was fruitless, in all cases Zn lost coordination with either the O atom, leading to **TS-1A** (13.2 kcal/mol, Figure S2), or N atom, leading to **TS-2A** (20.8 kcal/mol, Figure S3).

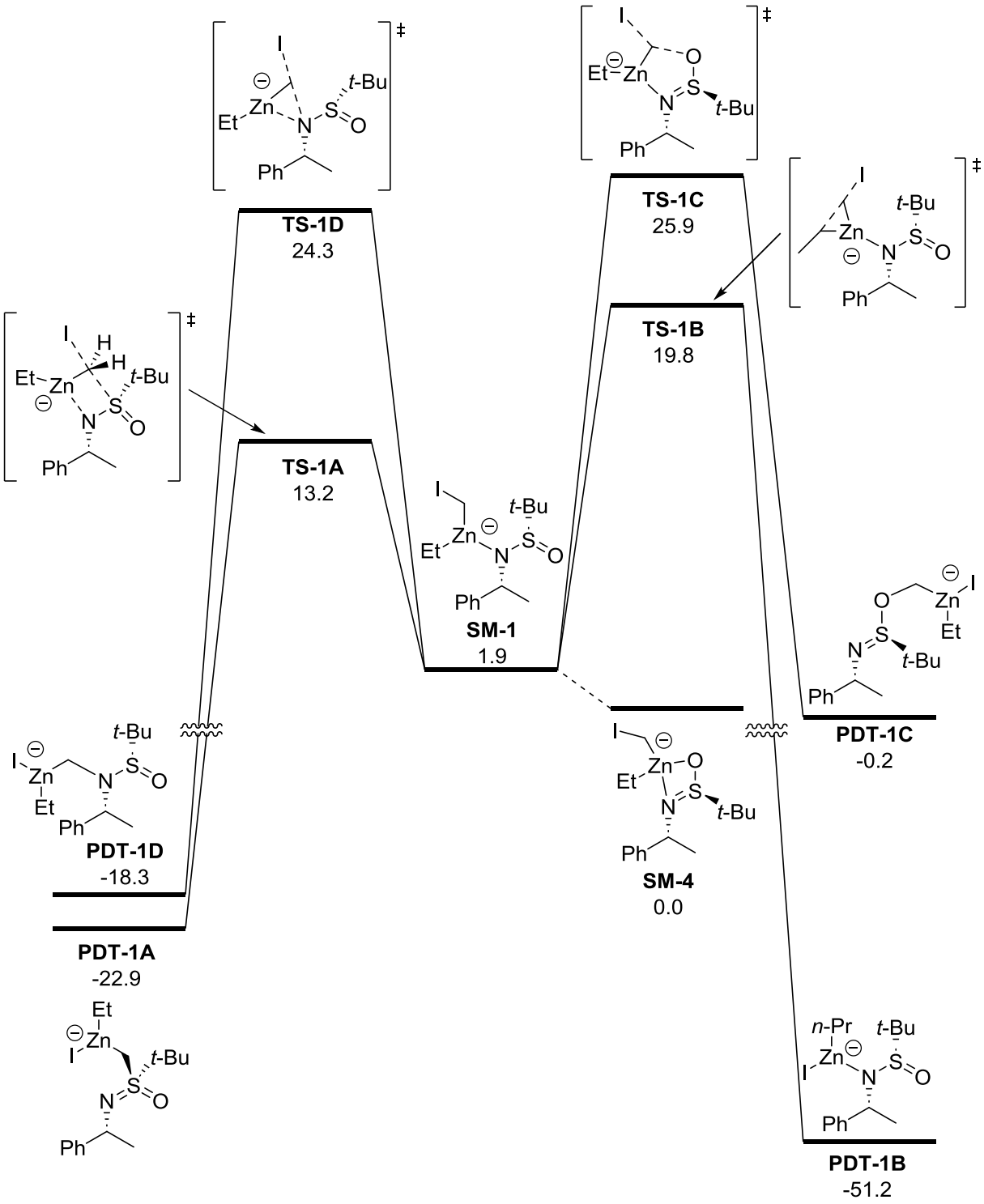


Figure S2. PES of methylene transfer starting from **SM-1**

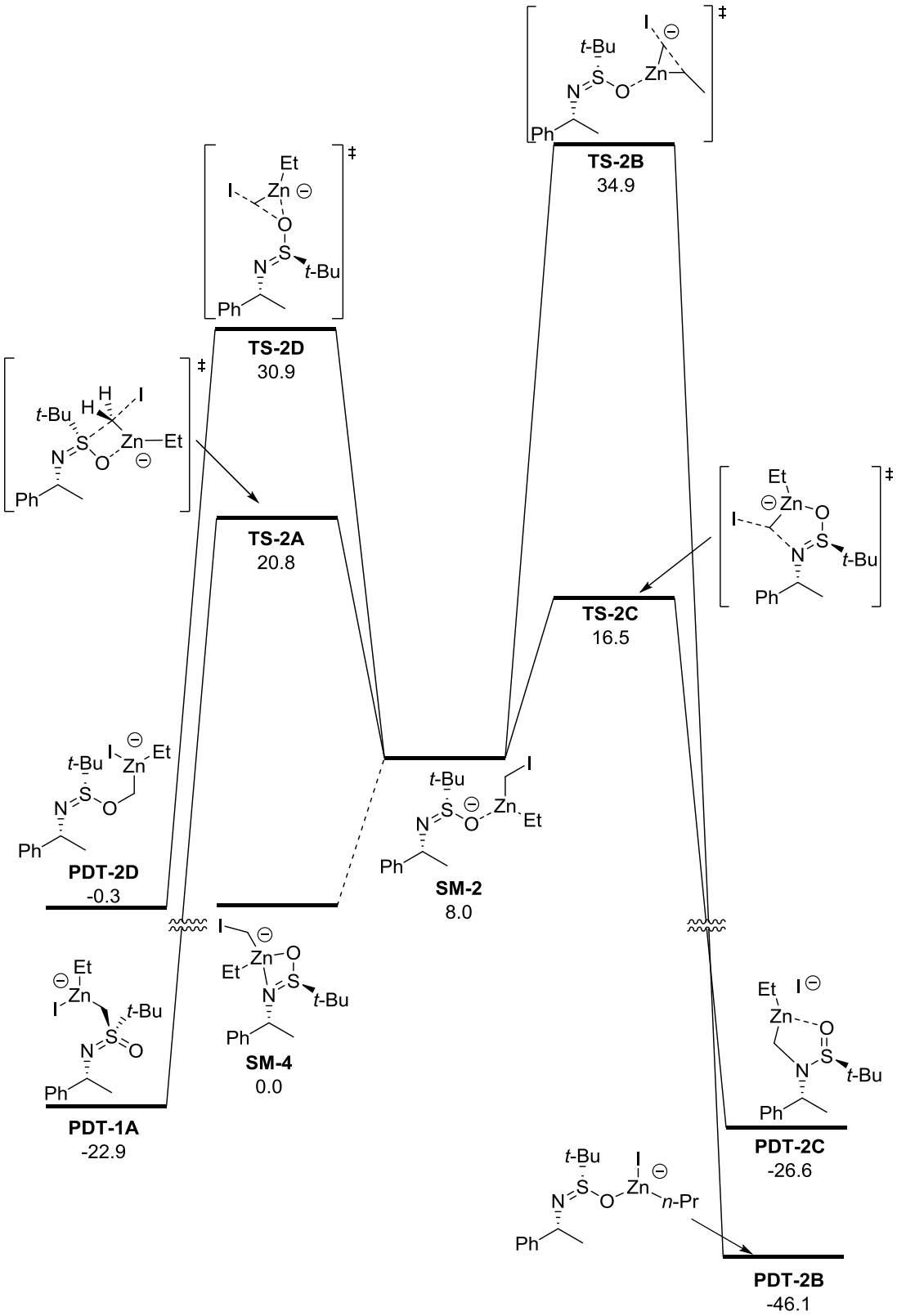


Figure S3. PES of methylene transfer starting from **SM-2**

In order to account for the possible THF coordination to the Zn, calculations of **TS-1A** with explicit THF molecule were conducted. To this end, full reaction paths for both diastereomeric transition states **TS-1A$_{THF}$** and **TS-1A'$_{THF}$** were constructed (Figure S4). The energy difference between THF coordination diastereomers **SM-1$_{THF}$** and **SM-1'$_{THF}$** was found to be less than 0.1 kcal/mol. Similarly, both diastereomeric transition states **SM-1A$_{THF}$** and **SM-1A'$_{THF}$** were close in energy 10.5 kcal/mol and 9.9 kcal/mol respectively. Importantly, the transition states with THF coordination **TS-1A$_{THF}$** (10.5 kcal/mol) and **TS-1A'$_{THF}$** (9.9 kcal/mol) and transition state **TS-1A** (11.3 kcal/mol relative to **SM-1**) without explicit THF coordination are similar in energy. Therefore, we can assume that the omission of the explicit THF coordination in the reaction calculations (Figure S1, Figure S2, and Figure S3) will not influence the calculated PES profile.

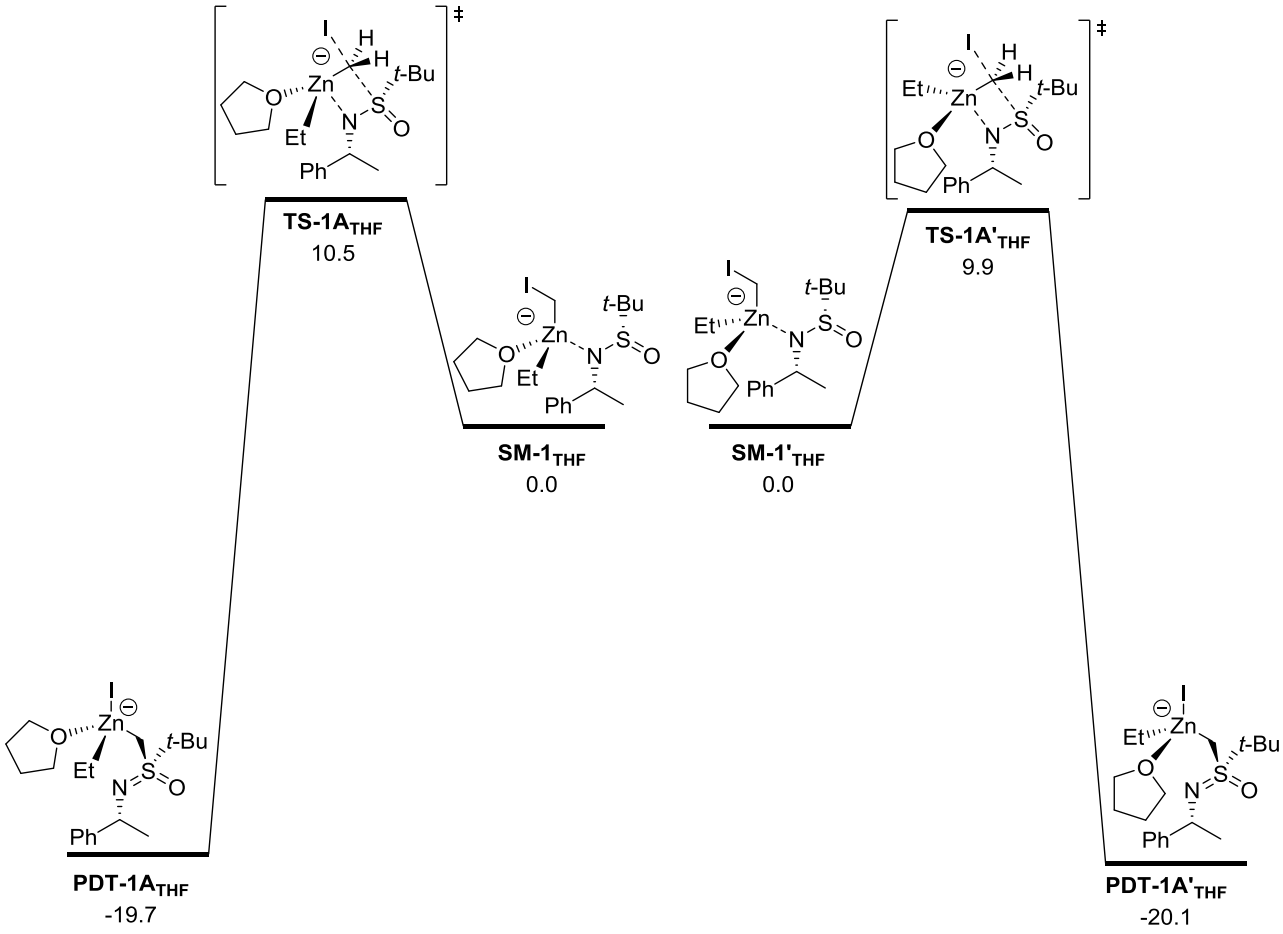
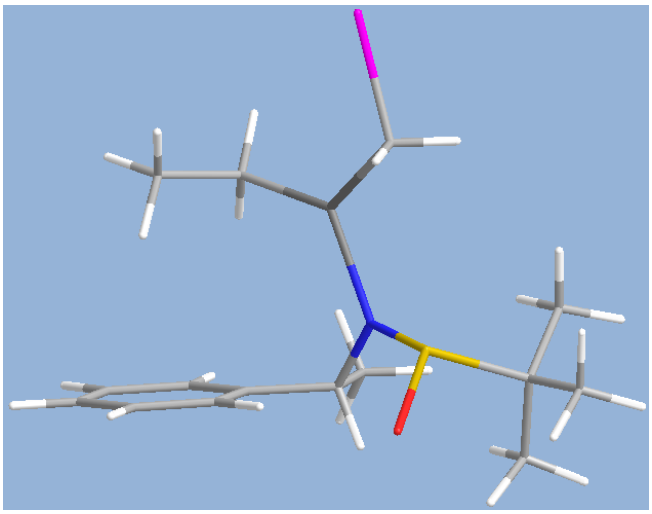


Figure S4. Influence of THF coordination on the energy profile of formation of **PDT-1A**

Optimized geometries

SM-1



Zero-point correction= 0.370889
(Hartree/Particle)
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Thermal correction to Enthalpy= 0.397432
Thermal correction to Gibbs Free Energy= 0.312124
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Sum of electronic and thermal Energies= -3190.196741
Sum of electronic and thermal Enthalpies= -3190.195797
Sum of electronic and thermal Free Energies= -3190.281104

E(RM062X) = -3191.81420637
E(RM062X) = -3191.87372132 (THF)

-1 1

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C	2.52600000	-1.57450000	1.32960000
C	2.59970000	-1.45120000	-0.06640000
C	2.82190000	-2.60310000	-0.82440000
C	2.96860000	-3.84940000	-0.20900000
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H	2.61980000	-2.88820000	3.03160000
H	2.36180000	-0.66520000	1.91500000
H	2.86740000	-2.54390000	-1.91240000
H	3.12680000	-4.73880000	-0.82260000
C	2.43880000	-0.05450000	-0.66950000
H	3.29070000	0.52640000	-0.27250000
C	2.50150000	-0.05630000	-2.19580000
H	2.39740000	0.96930000	-2.57550000
H	3.44940000	-0.47010000	-2.57360000
H	1.66820000	-0.65040000	-2.60160000
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H	-1.60260000	-3.23410000	0.30770000
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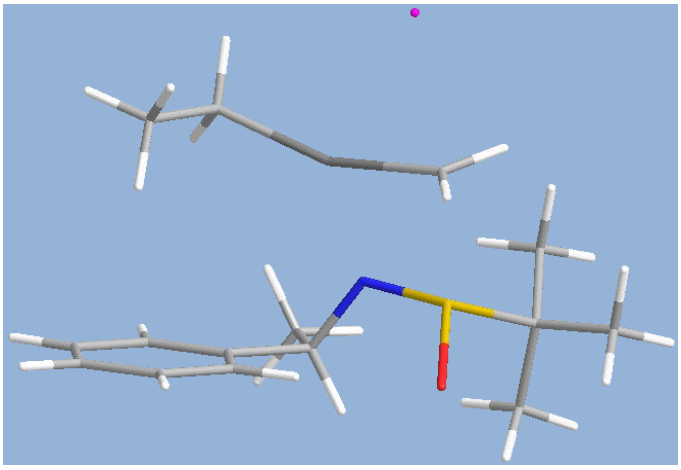
TS-1A



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Sum of electronic and thermal Energies= -3190.167003
Sum of electronic and thermal Enthalpies= -3190.166059
Sum of electronic and thermal Free Energies= -3190.250534

E(RM062X) = -3191.78550077
E(RM062X) = -3191.85565314 (THF)

-1 1

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C	2.87010000	-0.97460000	0.13510000
C	3.45410000	-2.03040000	-0.56740000
C	3.64820000	-3.27400000	0.04180000
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H	2.35490000	-2.57700000	3.10610000
H	2.00660000	-0.36540000	2.00660000
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H	4.09570000	-4.09020000	-0.52910000
C	2.61410000	0.40960000	-0.46540000
H	3.17920000	1.11820000	0.16940000
C	3.09790000	0.53530000	-1.90740000
H	2.91890000	1.55590000	-2.27310000
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H	2.44700000	4.89760000	-0.44610000
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H	-0.85030000	3.19460000	-1.49010000
H	0.31000000	4.44600000	-2.01000000
H	0.73070000	2.70820000	-2.14420000
C	0.05740000	4.44250000	0.79710000
H	0.13240000	5.48120000	0.43640000
H	-1.00800000	4.16800000	0.84200000
H	0.47370000	4.38320000	1.81260000
Zn	-0.46310000	-0.57050000	-0.66870000
C	-0.24560000	-2.29900000	-1.68110000
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H	0.66340000	-2.24580000	-2.30870000
C	-0.14840000	-3.50680000	-0.74130000
H	-1.05860000	-3.60300000	-0.12780000
H	-0.01570000	-4.46700000	-1.27530000
H	0.70200000	-3.41190000	-0.04480000
C	-1.45300000	0.84470000	0.48020000
H	-1.57410000	0.77050000	1.56960000
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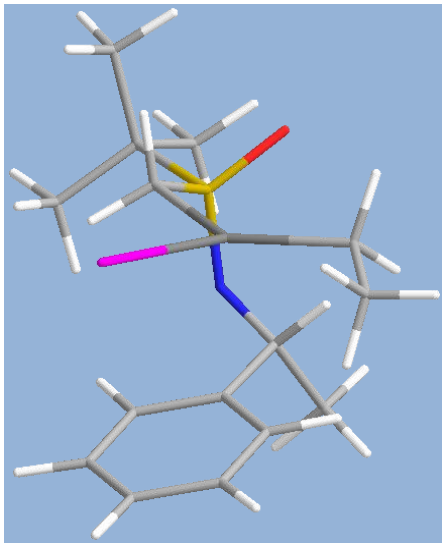
PDT-1A



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Sum of electronic and thermal Enthalpies=	-3190.220440
Sum of electronic and thermal Free Energies=	-3190.303709

E(RM062X) = -3191.85254846
E(RM062X) = -3191.91682847 (THF)

-1 1

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C	1.00810000	1.77210000	-2.53620000
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O	-2.67990000	-0.61030000	1.83490000
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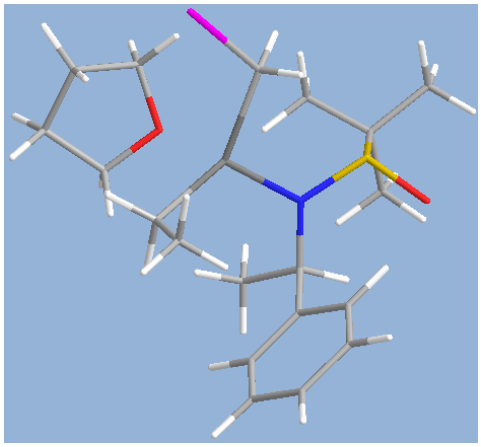
H	-4.52440000	-1.31050000	-2.54380000
H	-3.66280000	0.23170000	-2.21900000
C	-3.87520000	-2.56720000	-0.16700000
H	-4.80900000	-3.00900000	-0.54830000
H	-3.03000000	-3.10360000	-0.62160000
H	-3.83610000	-2.69980000	0.92350000
Zn	0.78580000	-0.42640000	0.92030000
C	1.29990000	0.35460000	2.72950000
H	0.63890000	1.20160000	2.99120000
H	1.09280000	-0.41320000	3.49690000
C	2.76690000	0.77830000	2.81720000
H	3.06440000	1.15670000	3.81400000
H	3.43650000	-0.06020000	2.56750000
H	3.00410000	1.57250000	2.08860000
C	-0.93940000	-1.18910000	-0.01090000
H	-1.03000000	-2.22960000	0.33200000
H	-0.77050000	-1.13770000	-1.09480000
I	2.78300000	-1.45230000	-0.57330000

SM-1_{THF}



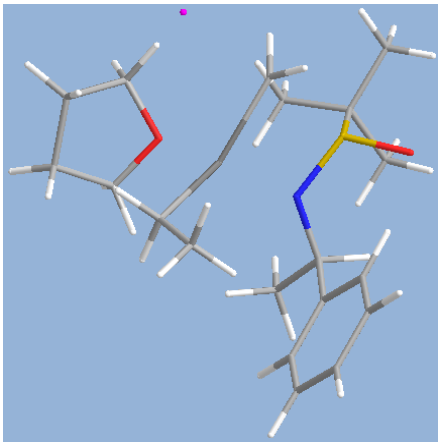
Zero-point correction=	0.490154
(Hartree/Particle)	
Thermal correction to Energy=	0.521701
Thermal correction to Enthalpy=	0.522645
Thermal correction to Gibbs Free Energy=	0.425523
Sum of electronic and zero-point Energies=	-3422.285327
Sum of electronic and thermal Energies=	-3422.253780
Sum of electronic and thermal Enthalpies=	-3422.252836
Sum of electronic and thermal Free Energies=	-3422.349958

E(RM062X) = -3424.25968736
E(RM062X) = -3424.31756548 (THF)

-1 1

C	-3.84490000	-3.71520000	-0.96290000
C	-3.68390000	-2.59830000	-1.78760000
C	-3.30560000	-1.37320000	-1.24810000
C	-3.08920000	-1.23250000	0.13150000
C	-3.25970000	-2.35280000	0.94760000
C	-3.62950000	-3.58700000	0.40530000
H	-4.12820000	-4.68020000	-1.38830000
H	-3.84940000	-2.68620000	-2.86360000
H	-3.17490000	-0.48870000	-1.87820000
H	-3.08660000	-2.28040000	2.02190000
H	-3.73740000	-4.45340000	1.06140000
C	-2.66690000	0.14400000	0.65100000
H	-3.50440000	0.81900000	0.39820000
C	-2.44610000	0.16060000	2.16230000
H	-2.11690000	1.15910000	2.48160000
H	-3.35510000	-0.10970000	2.72250000
H	-1.64740000	-0.54950000	2.42490000
N	-1.46380000	0.58600000	-0.04530000
S	-1.56690000	1.79770000	-1.13500000
O	-2.93870000	1.81760000	-1.79340000
C	-1.62040000	3.41360000	-0.14580000
C	-2.93050000	3.50490000	0.61830000
H	-2.95670000	2.79760000	1.45860000
H	-3.06600000	4.52170000	1.02580000
H	-3.76310000	3.27580000	-0.06390000
C	-0.39850000	3.42930000	0.75840000
H	0.52730000	3.36660000	0.16210000
H	-0.36340000	4.36380000	1.34430000
H	-0.40340000	2.56890000	1.44350000
C	-1.55180000	4.49940000	-1.21520000
H	-1.57360000	5.50060000	-0.75250000
H	-0.62430000	4.41170000	-1.80330000
H	-2.40570000	4.40140000	-1.90110000
Zn	0.30290000	-0.40770000	0.12770000
C	0.32950000	-2.33150000	0.87030000
H	1.30000000	-2.55260000	1.36010000
H	-0.43740000	-2.48260000	1.65560000
C	0.08250000	-3.35400000	-0.24600000
H	0.84240000	-3.26750000	-1.04120000
H	0.09380000	-4.40830000	0.09390000
H	-0.89870000	-3.18770000	-0.72320000
C	1.53480000	0.46630000	-1.32380000
H	1.13630000	0.29150000	-2.33490000
H	1.75610000	1.54360000	-1.27170000
I	3.56090000	-0.40600000	-1.49800000
C	1.03140000	-0.13570000	3.26860000
C	2.44570000	1.11800000	1.93740000
C	2.47750000	-0.54990000	3.61040000
H	0.39920000	-0.99990000	3.02960000
H	0.56210000	0.44030000	4.08380000
C	3.27010000	-0.07890000	2.38620000
H	2.63100000	2.00270000	2.57770000
H	2.59250000	1.39270000	0.88530000
H	2.82500000	-0.03510000	4.51910000
H	2.56340000	-1.63140000	3.77860000
H	4.31820000	0.16800000	2.60320000
H	3.24400000	-0.83440000	1.58690000
O	1.10600000	0.67540000	2.09830000

TS-1A$_{THF}$



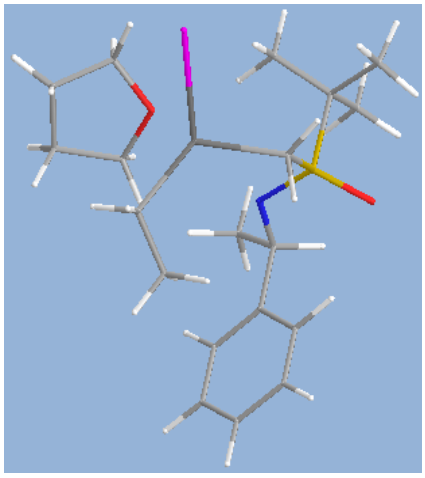
Zero-point correction= 0.490066
(Hartree/Particle)
Thermal correction to Energy= 0.521144
Thermal correction to Enthalpy= 0.522089
Thermal correction to Gibbs Free Energy= 0.426066
Sum of electronic and zero-point Energies= -3422.260728
Sum of electronic and thermal Energies= -3422.229649
Sum of electronic and thermal Enthalpies= -3422.228705
Sum of electronic and thermal Free Energies= -3422.324728

E(RM062X) = -3424.23602564
E(RM062X) = -3424.30141252 (THF)

-1 1

C	-4.38920000	-3.06360000	-1.25500000
C	-3.86050000	-2.02750000	-2.02980000
C	-3.35640000	-0.88260000	-1.42240000
C	-3.37940000	-0.74230000	-0.02630000
C	-3.90960000	-1.78240000	0.73930000
C	-4.40880000	-2.93750000	0.12980000
H	-4.77360000	-3.96780000	-1.73080000
H	-3.83290000	-2.11840000	-3.11740000
H	-2.93160000	-0.06790000	-2.01610000
H	-3.93040000	-1.70920000	1.82730000
H	-4.80570000	-3.74520000	0.74820000
C	-2.80310000	0.54240000	0.57070000
H	-3.40900000	1.36270000	0.14260000
C	-2.90920000	0.59270000	2.09270000
H	-2.48640000	1.53630000	2.46460000
H	-3.95030000	0.51110000	2.44110000
H	-2.32610000	-0.22970000	2.53570000
N	-1.41520000	0.68990000	0.15960000
S	-0.98870000	1.81960000	-0.91040000
O	-2.06210000	2.10450000	-1.93290000
C	-0.84310000	3.47460000	-0.02160000
C	-2.23760000	3.92580000	0.38830000
H	-2.64640000	3.28680000	1.18420000
H	-2.19930000	4.96040000	0.76900000
H	-2.91180000	3.88600000	-0.47950000
C	0.08090000	3.28530000	1.17020000
H	1.08100000	2.95240000	0.85230000
H	0.19020000	4.23940000	1.71280000
H	-0.30930000	2.51760000	1.85260000
C	-0.25380000	4.42030000	-1.06380000
H	-0.13980000	5.43070000	-0.63790000
H	0.73690000	4.07270000	-1.39580000
H	-0.91470000	4.47150000	-1.94050000
Zn	0.25300000	-0.55650000	0.25080000
C	0.17410000	-2.52190000	0.78630000
H	1.20490000	-2.88580000	0.95290000
H	-0.35840000	-2.66480000	1.74780000
C	-0.49160000	-3.39140000	-0.28730000
H	0.04910000	-3.31590000	-1.24480000
H	-0.53090000	-4.46670000	-0.02690000
H	-1.52910000	-3.07320000	-0.48310000
C	1.07180000	0.73970000	-1.19450000
H	0.89260000	0.59180000	-2.26940000
H	1.68750000	1.64220000	-1.06590000
I	3.43290000	-0.63040000	-1.51080000
C	0.91810000	-0.31340000	3.29070000
C	2.58950000	0.57630000	2.02980000
C	2.08070000	-1.31320000	3.43910000
H	-0.06460000	-0.79070000	3.18490000
H	0.88670000	0.39410000	4.13950000
C	3.14150000	-0.78510000	2.44790000
H	2.89160000	1.37810000	2.73070000
H	2.85630000	0.85200000	1.00050000
H	2.44750000	-1.33680000	4.47510000
H	1.75780000	-2.32540000	3.16540000
H	4.14680000	-0.71050000	2.88350000
H	3.20020000	-1.42090000	1.55240000
O	1.17800000	0.41160000	2.09990000

PDT-1A$_{THF}$



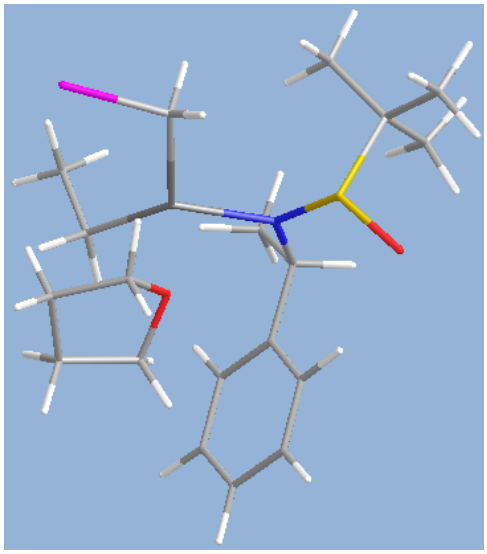
Zero-point correction= 0.492580
(Hartree/Particle)
Thermal correction to Energy= 0.523708
Thermal correction to Enthalpy= 0.524653
Thermal correction to Gibbs Free Energy= 0.426698
Sum of electronic and zero-point Energies= -3422.303908
Sum of electronic and thermal Energies= -3422.272780
Sum of electronic and thermal Enthalpies= -3422.271835
Sum of electronic and thermal Free Energies= -3422.369790

E(RM062X) = -3424.28937305
E(RM062X) = -3424.35014517 (THF)

-1 1

C	-5.19650000	-2.00440000	-1.56480000
C	-4.58420000	-0.87650000	-2.11860000
C	-3.91130000	0.02740000	-1.30510000
C	-3.83960000	-0.16780000	0.08250000
C	-4.46650000	-1.28990000	0.62750000
C	-5.13610000	-2.20560000	-0.19020000
H	-5.71270000	-2.72240000	-2.20500000
H	-4.62320000	-0.70870000	-3.19690000
H	-3.41570000	0.90430000	-1.73100000
H	-4.42890000	-1.47100000	1.70260000
H	-5.60620000	-3.08470000	0.25580000
C	-3.01590000	0.82780000	0.90270000
H	-3.42340000	1.82760000	0.65860000
C	-3.15310000	0.60920000	2.40660000
H	-2.57070000	1.36700000	2.94860000
H	-4.20270000	0.66850000	2.73390000
H	-2.75300000	-0.37600000	2.68640000
N	-1.61750000	0.71530000	0.50720000
S	-1.01520000	1.83280000	-0.40670000
O	-1.99950000	2.68910000	-1.13600000
C	-0.04730000	3.08680000	0.58620000
C	-1.10450000	3.81260000	1.41450000
H	-1.65250000	3.10380000	2.05250000
H	-0.61040000	4.54880000	2.06760000
H	-1.82230000	4.32760000	0.76240000
C	0.95390000	2.36910000	1.47770000
H	1.72440000	1.84910000	0.88720000
H	1.45360000	3.10970000	2.12370000
H	0.44430000	1.62230000	2.10190000
C	0.63290000	4.05600000	-0.37680000
H	1.01460000	4.91940000	0.19240000
H	1.48810000	3.58640000	-0.88270000
H	-0.08450000	4.41800000	-1.12710000
Zn	1.07260000	-0.67550000	-0.65480000
C	0.35320000	-2.55510000	-1.06680000
H	0.95330000	-3.00480000	-1.87810000
H	0.48960000	-3.23690000	-0.20560000
C	-1.12530000	-2.53170000	-1.47560000
H	-1.27630000	-1.93140000	-2.38950000
H	-1.55720000	-3.53020000	-1.68350000
H	-1.76610000	-2.05770000	-0.71110000
C	0.14670000	1.05090000	-1.42650000
H	-0.49580000	0.64450000	-2.22560000
H	0.79730000	1.82440000	-1.85270000
I	3.79500000	-0.18020000	-0.87730000
C	-0.00710000	-1.53680000	2.08100000
C	2.17210000	-0.93230000	2.37050000
C	0.71590000	-2.80920000	2.57810000
H	-0.72630000	-1.69750000	1.26950000
H	-0.52250000	-1.01570000	2.90590000
C	2.20900000	-2.45370000	2.43960000
H	2.03380000	-0.48230000	3.37340000
H	3.03450000	-0.47640000	1.86960000
H	0.45040000	-3.02280000	3.62390000
H	0.44870000	-3.68690000	1.97560000
H	2.83150000	-2.83800000	3.25900000
H	2.60890000	-2.82580000	1.48410000
O	1.01850000	-0.68030000	1.58630000

SM-1′ THF



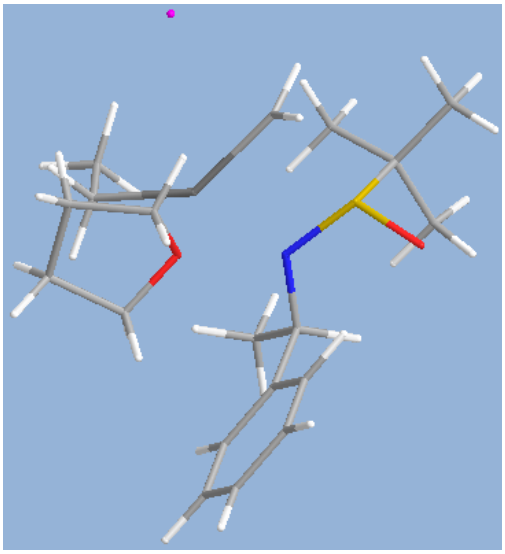
Zero-point correction=	0.490879
(Hartree/Particle)	
Thermal correction to Energy=	0.522229
Thermal correction to Enthalpy=	0.523174
Thermal correction to Gibbs Free Energy=	0.427143
Sum of electronic and zero-point Energies=	-3422.287466
Sum of electronic and thermal Energies=	-3422.256115
Sum of electronic and thermal Enthalpies=	-3422.255171
Sum of electronic and thermal Free Energies=	-3422.351202

E(RM062X) = -3424.26292443
E(RM062X) = -3424.31914250 (THF)

-1 1

C	-5.19648400	-2.00442700	-1.56483400
C	-4.58423600	-0.87654500	-2.11863500
C	-3.91131200	0.02738300	-1.30506400
C	-3.83963900	-0.16775200	0.08253700
C	-4.46645400	-1.28989000	0.62747400
C	-5.13610500	-2.20558600	-0.19022400
H	-5.71271600	-2.72237400	-2.20500100
H	-4.62323700	-0.70874100	-3.19687900
H	-3.41573000	0.90430900	-1.73096700
H	-4.42889100	-1.47098500	1.70260100
H	-5.60624000	-3.08469400	0.25579600
C	-3.01586300	0.82776500	0.90274400
H	-3.42343100	1.82758200	0.65864800
C	-3.15307600	0.60916900	2.40660200
H	-2.57071000	1.36704300	2.94857100
H	-4.20265400	0.66852400	2.73385100
H	-2.75300600	-0.37602700	2.68643900
N	-1.61745400	0.71528000	0.50715200
S	-1.01521500	1.83278800	-0.40674900
O	-1.99947500	2.68914100	-1.13602900
C	-0.04728200	3.08675100	0.58618400
C	-1.10445800	3.81262500	1.41448700
H	-1.65250300	3.10384100	2.05254300
H	-0.61040000	4.54876900	2.06758000
H	-1.82233900	4.32760900	0.76240300
C	0.95387000	2.36909600	1.47766000
H	1.72443700	1.84905900	0.88722600
H	1.45364200	3.10974300	2.12373300
H	0.44427800	1.62232300	2.10189600
C	0.63292700	4.05604100	-0.37682300
H	1.01459300	4.91935500	0.19237700
H	1.48807100	3.58635500	-0.88265600
H	-0.08449300	4.41803900	-1.12710700
Zn	1.07260200	-0.67554000	-0.65483300
C	0.35317500	-2.55511500	-1.06677600
H	0.95325200	-3.00477700	-1.87813900
H	0.48956800	-3.23688900	-0.20558300
C	-1.12528600	-2.53171800	-1.47561600
H	-1.27634400	-1.93144800	-2.38949800
H	-1.55720900	-3.53017100	-1.68347200
H	-1.76610700	-2.05766800	-0.71106600
C	0.14670000	1.05090400	-1.42651400
H	-0.49582200	0.64447800	-2.22563400
H	0.79729900	1.82437600	-1.85272600
I	3.79497800	-0.18016600	-0.87735000
C	-0.00706200	-1.53679400	2.08095500
C	2.17208200	-0.93227200	2.37053400
C	0.71593900	-2.80920300	2.57808500
H	-0.72628500	-1.69747300	1.26947900
H	-0.52246000	-1.01565700	2.90585600
C	2.20903100	-2.45370800	2.43962300
H	2.03377600	-0.48234600	3.37342300
H	3.03449300	-0.47639600	1.86961800
H	0.45043700	-3.02275300	3.62394200
H	0.44871600	-3.68686800	1.97564200
H	2.83147300	-2.83797000	3.25897200
H	2.60893100	-2.82575600	1.48406400
O	1.01854000	-0.68030600	1.58629700

TS-1A′ THF



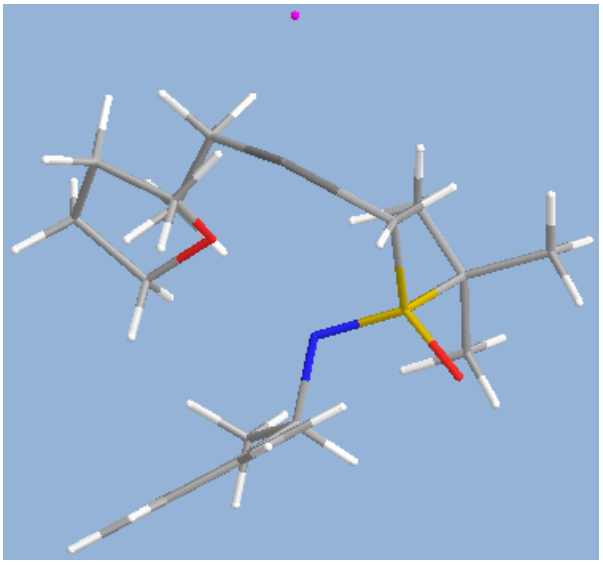
Zero-point correction=	0.490476
(Hartree/Particle)	
Thermal correction to Energy=	0.521492
Thermal correction to Enthalpy=	0.522436
Thermal correction to Gibbs Free Energy=	0.425659
Sum of electronic and zero-point Energies=	-3422.262794
Sum of electronic and thermal Energies=	-3422.231779
Sum of electronic and thermal Enthalpies=	-3422.230835
Sum of electronic and thermal Free Energies=	-3422.327612

E(RM062X) = -3424.23858113
E(RM062X) = -3424.30193393 (THF)

-1 1

C	-4.32340000	-2.78160000	-1.18920000
C	-3.58860000	-1.88130000	-1.96660000
C	-3.07390000	-0.71960000	-1.40120000
C	-3.29250000	-0.42310000	-0.04720000
C	-4.03080000	-1.32700000	0.72080000
C	-4.53960000	-2.50120000	0.15610000
H	-4.72050000	-3.69770000	-1.63150000
H	-3.40870000	-2.09170000	-3.02300000
H	-2.49010000	-0.01260000	-1.99600000
H	-4.20920000	-1.13100000	1.77870000
H	-5.10700000	-3.19760000	0.77740000
C	-2.69820000	0.87260000	0.50910000
H	-3.23380000	1.68650000	-0.01510000
C	-2.90810000	1.02620000	2.01380000
H	-2.47900000	1.97920000	2.35270000
H	-3.97250000	1.00720000	2.29380000
H	-2.38140000	0.21870000	2.54700000
N	-1.27900000	0.93510000	0.19830000
S	-0.72060000	1.97980000	-0.89510000
O	-1.68070000	2.21930000	-2.03510000
C	-0.61870000	3.68290000	-0.09230000
C	-2.03410000	4.20450000	0.11420000
H	-2.55450000	3.64530000	0.90510000
H	-2.00120000	5.26530000	0.41450000
H	-2.60430000	4.11170000	-0.82130000
C	0.14210000	3.54440000	1.21800000
H	1.15710000	3.15030000	1.05910000
H	0.22990000	4.52920000	1.70610000
H	-0.37940000	2.85650000	1.89880000
C	0.12960000	4.54260000	-1.10660000
H	0.23210000	5.57280000	-0.72810000
H	1.13810000	4.14330000	-1.29510000
H	-0.41980000	4.56280000	-2.05860000
Zn	0.40900000	-0.21390000	0.65920000
C	0.66470000	-1.01250000	2.52220000
H	-0.19900000	-1.63750000	2.82350000
H	1.53810000	-1.68950000	2.50790000
C	0.89430000	0.06940000	3.58500000
H	0.03910000	0.76490000	3.64820000
H	1.05370000	-0.32830000	4.60590000
H	1.77860000	0.68110000	3.34110000
C	1.38970000	0.96560000	-0.77500000
H	1.41120000	0.70680000	-1.84490000
H	1.93120000	1.91060000	-0.63530000
I	3.84430000	-0.22000000	-0.43660000
C	0.97460000	-2.61100000	-1.28940000
C	-0.81540000	-2.95190000	0.06810000
C	1.52430000	-3.53470000	-0.20290000
H	1.69370000	-1.85230000	-1.62480000
H	0.59230000	-3.18230000	-2.15630000
C	0.27270000	-3.88420000	0.63460000
H	-1.49180000	-3.48460000	-0.62320000
H	-1.42320000	-2.44970000	0.83170000
H	2.02730000	-4.41590000	-0.62330000
H	2.25700000	-2.97290000	0.39520000
H	-0.02120000	-4.93840000	0.53170000
H	0.44590000	-3.67810000	1.69870000
O	-0.11700000	-1.95140000	-0.66090000

PDT-1A′ $_{THF}$



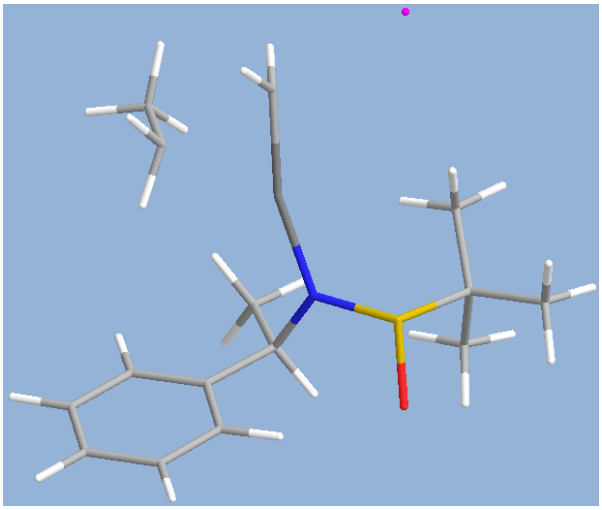
Zero-point correction= 0.492963
(Hartree/Particle)
Thermal correction to Energy= 0.522888
Thermal correction to Enthalpy= 0.523832
Thermal correction to Gibbs Free Energy= 0.431646
Sum of electronic and zero-point Energies= -3422.307878
Sum of electronic and thermal Energies= -3422.277954
Sum of electronic and thermal Enthalpies= -3422.277009
Sum of electronic and thermal Free Energies= -3422.369195

E(RM062X) = -3424.29424632
E(RM062X) = -3424.35567897 (THF)

-1 1

C	-3.64690000	-3.46720000	-1.38960000
C	-3.00280000	-2.43650000	-2.08040000
C	-2.86440000	-1.18060000	-1.49940000
C	-3.36400000	-0.91840000	-0.21530000
C	-4.02150000	-1.95120000	0.45880000
C	-4.16050000	-3.21640000	-0.12130000
H	-3.74770000	-4.45660000	-1.84040000
H	-2.59930000	-2.61520000	-3.07920000
H	-2.36650000	-0.37330000	-2.03970000
H	-4.42050000	-1.78760000	1.46040000
H	-4.66770000	-4.01070000	0.43100000
C	-3.12030000	0.47140000	0.38750000
H	-3.72250000	1.17150000	-0.22450000
C	-3.59150000	0.56420000	1.83710000
H	-3.38770000	1.56750000	2.23320000
H	-4.66970000	0.36560000	1.93380000
H	-3.03840000	-0.15270000	2.46280000
N	-1.70120000	0.78740000	0.30710000
S	-1.21940000	1.80280000	-0.78470000
O	-2.16820000	2.05180000	-1.91030000
C	-0.96760000	3.50640000	-0.06030000
C	-2.34840000	3.91640000	0.44240000
H	-2.68930000	3.23360000	1.23270000
H	-2.29840000	4.93310000	0.86210000
H	-3.07610000	3.90230000	-0.38110000
C	0.03470000	3.42160000	1.08240000
H	1.04960000	3.20980000	0.71650000
H	0.05570000	4.38120000	1.62450000
H	-0.24830000	2.62410000	1.78570000
C	-0.51190000	4.44520000	-1.17330000
H	-0.50130000	5.47980000	-0.79330000
H	0.50390000	4.20620000	-1.51750000
H	-1.20110000	4.38400000	-2.02660000
Zn	1.22700000	0.23810000	0.39630000
C	1.32370000	0.29230000	2.44360000
H	2.06060000	-0.46460000	2.77090000
H	1.82400000	1.25750000	2.65500000
C	0.06090000	0.19270000	3.30290000
H	-0.37840000	-0.81970000	3.26620000
H	0.23270000	0.41300000	4.37420000
H	-0.73290000	0.87110000	2.94850000
C	0.36970000	1.27570000	-1.21830000
H	0.19580000	0.46760000	-1.94480000
H	0.90580000	2.10050000	-1.70280000
I	3.83640000	-0.20050000	-0.55820000
C	1.12020000	-2.76560000	-0.74180000
C	-0.48810000	-2.24770000	0.75460000
C	1.62530000	-3.41060000	0.55370000
H	1.91700000	-2.34820000	-1.36960000
H	0.49900000	-3.46830000	-1.32840000
C	0.50470000	-3.08750000	1.57240000
H	-1.27990000	-2.87860000	0.31100000
H	-0.95560000	-1.40800000	1.28370000
H	1.80420000	-4.48810000	0.43450000
H	2.57010000	-2.92940000	0.84520000
H	0.02620000	-3.98830000	1.98110000
H	0.90110000	-2.49690000	2.40910000
O	0.29390000	-1.69910000	-0.30090000

TS-1B



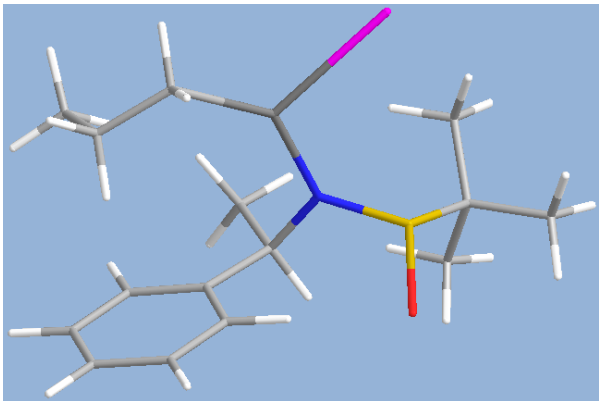
Zero-point correction= 0.370160
(Hartree/Particle)
Thermal correction to Energy= 0.395584
Thermal correction to Enthalpy= 0.396529
Thermal correction to Gibbs Free Energy= 0.310963
Sum of electronic and zero-point Energies= -3190.168201
Sum of electronic and thermal Energies= -3190.142777
Sum of electronic and thermal Enthalpies= -3190.141832
Sum of electronic and thermal Free Energies= -3190.227398

E(RM062X) = -3191.75971263
E(RM062X) = -3191.8362227 (THF)

-1 1

C	-5.23530000	-1.77410000	-1.56390000
C	-4.68170000	-0.58780000	-2.05530000
C	-3.77980000	0.13860000	-1.28550000
C	-3.42050000	-0.29930000	-0.00150000
C	-3.98150000	-1.48290000	0.48300000
C	-4.88000000	-2.21950000	-0.29540000
H	-5.93630000	-2.34870000	-2.17230000
H	-4.95440000	-0.23050000	-3.05040000
H	-3.32860000	1.06360000	-1.65720000
H	-3.71730000	-1.85290000	1.47490000
H	-5.29870000	-3.14820000	0.09760000
C	-2.41020000	0.53830000	0.78120000
H	-2.82400000	1.56090000	0.81010000
C	-2.19700000	0.03960000	2.20780000
H	-1.48670000	0.69230000	2.73330000
H	-3.13660000	0.01180000	2.77990000
H	-1.77340000	-0.97860000	2.20150000
N	-1.14380000	0.58360000	0.05060000
S	-0.67440000	1.99060000	-0.70260000
O	-1.90930000	2.79950000	-1.04130000
C	0.14620000	3.02560000	0.63750000
C	-0.91160000	3.53910000	1.59990000
H	-1.32150000	2.72710000	2.21690000
H	-0.47200000	4.28820000	2.27890000
H	-1.73450000	4.00160000	1.03550000
C	1.20930000	2.16670000	1.30710000
H	1.88980000	1.69350000	0.57690000
H	1.82670000	2.78770000	1.97600000
H	0.74950000	1.37180000	1.91340000
C	0.77270000	4.17790000	-0.14640000
H	1.26570000	4.87970000	0.54500000
H	1.52880000	3.80520000	-0.85400000
H	-0.00270000	4.71890000	-0.70870000
Zn	0.12010000	-0.84350000	0.05560000
C	-0.18240000	-2.98470000	0.66850000
H	-1.25570000	-2.78330000	0.47020000
H	0.08720000	-3.81560000	0.00530000
C	0.02720000	-3.34270000	2.13250000
H	-0.15150000	-2.48540000	2.80420000
H	-0.62970000	-4.16010000	2.48490000
H	1.06440000	-3.66300000	2.31520000
C	1.73610000	-1.86000000	0.01140000
H	2.20770000	-2.14670000	0.95590000
H	1.94480000	-2.58130000	-0.78410000
I	4.20110000	-0.58270000	-0.56190000

PDT-1B



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 Zero-point correction=                           0.374846
(Hartree/Particle)
 Thermal correction to Energy=                    0.399701
 Thermal correction to Enthalpy=                  0.400645
 Thermal correction to Gibbs Free Energy=         0.318539
 Sum of electronic and zero-point Energies=          -3190.307831
 Sum of electronic and thermal Energies=             -3190.282975
 Sum of electronic and thermal Enthalpies=           -3190.282031
 Sum of electronic and thermal Free Energies=        -3190.364137

E(RM062X) =  -3191.89976192
E(RM062X) =  -3191.96467417 (THF)

-1 1
C                 -4.86150000    0.38440000   -1.30400000
 C                -3.69640000    0.65890000   -2.02540000
 C                -2.52630000    1.01690000   -1.36340000
 C                -2.49230000    1.10770000    0.03670000
 C                -3.66520000    0.83930000    0.74740000
 C                -4.84120000    0.47870000    0.08380000
 H                -5.77690000    0.09570000   -1.82430000
 H                -3.70120000    0.59490000   -3.11540000
 H                -1.61560000    1.26220000   -1.91480000
 H                -3.67120000    0.89370000    1.83660000
 H                -5.74150000    0.25840000    0.66160000
 C                -1.18450000    1.53960000    0.70000000
 H                -1.06880000    2.60030000    0.41330000
 C                -1.22650000    1.44670000    2.22450000
 H                -0.25790000    1.75340000    2.63970000
 H                -2.00800000    2.08900000    2.65870000
 H                -1.41170000    0.40980000    2.54630000
 N                -0.04890000    0.79860000    0.15490000
 S                 1.02620000    1.63300000   -0.78610000
 O                 0.28890000    2.72560000   -1.54350000
 C                 2.09870000    2.64440000    0.39560000
 C                 1.30160000    3.80400000    0.97240000
 H                 0.58070000    3.46690000    1.73030000
 H                 1.98430000    4.52500000    1.45340000
 H                 0.75480000    4.31080000    0.16350000
 C                 2.65520000    1.71100000    1.45900000
 H                 3.21060000    0.87570000    1.00520000
 H                 3.33440000    2.26690000    2.12750000
 H                 1.84540000    1.27260000    2.05960000
 C                 3.20470000    3.16910000   -0.51970000
 H                 3.91220000    3.78960000    0.05440000
 H                 3.76160000    2.33530000   -0.97440000
 H                 2.76660000    3.77750000   -1.32470000
 Zn                0.00650000   -1.17790000    0.04970000
 C                -2.76120000   -2.57220000    0.26450000
 H                -3.18380000   -1.74410000   -0.32910000
 H                -3.34280000   -3.47180000   -0.02040000
 C                -3.01450000   -2.29860000    1.74230000
 H                -2.44670000   -1.41190000    2.06550000
 H                -4.07880000   -2.11250000    1.95870000
 H                -2.67930000   -3.14680000    2.36150000
 C                -1.27750000   -2.74810000   -0.05090000
 H                -0.85360000   -3.55440000    0.57590000
 H                -1.15460000   -3.10640000   -1.08960000
 I                 2.56570000   -1.94920000   -0.25560000
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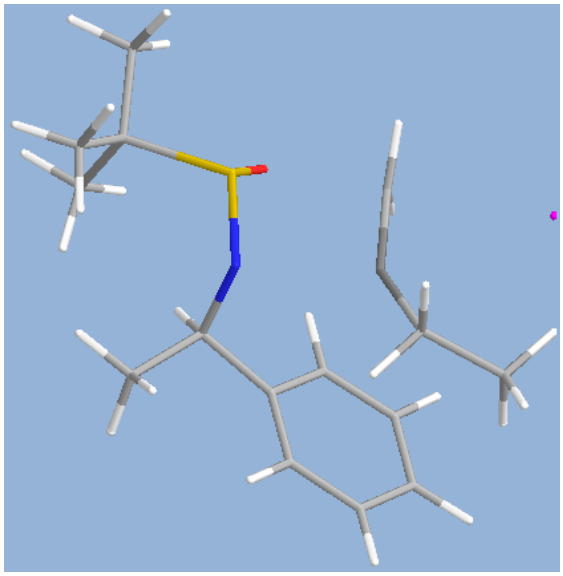
TS-1C

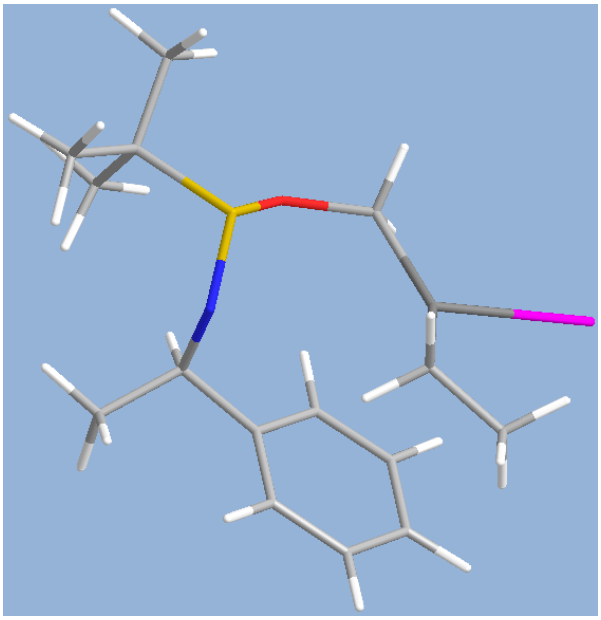


```
 Zero-point correction=                           0.370909
(Hartree/Particle)
 Thermal correction to Energy=                    0.395808
 Thermal correction to Enthalpy=                  0.396752
 Thermal correction to Gibbs Free Energy=         0.314852
 Sum of electronic and zero-point Energies=          -3190.180893
 Sum of electronic and thermal Energies=             -3190.155993
 Sum of electronic and thermal Enthalpies=           -3190.155049
 Sum of electronic and thermal Free Energies=        -3190.236950

E(RM062X) =  -3191.77127465
E(RM062X) =  -3191.83820933 (THF)

-1 1
 C                -1.87212200    3.02479300   -1.35832100
 C                -1.39461900    1.84588900   -1.93122300
 C                -0.09381200    1.42249400   -1.66024700
 C                 0.73483100    2.14264900   -0.78901000
 C                 0.24755300    3.32785900   -0.23004500
 C                -1.04414000    3.76837300   -0.51880600
 H                -2.89588700    3.35018700   -1.54990500
 H                -2.04205100    1.23853300   -2.56580900
 H                 0.29411500    0.49317600   -2.08493800
 H                 0.86905400    3.90146700    0.45926500
 H                -1.41819700    4.68516100   -0.05857100
 C                 2.06542300    1.51291200   -0.39556100
 H                 2.44502300    1.04011600   -1.31769200
 C                 3.08007800    2.54502900    0.09028000
 H                 4.06715800    2.07948700    0.22106500
 H                 3.18036200    3.38423100   -0.61607900
 H                 2.77125300    2.93342900    1.07151500
 N                 1.81434000    0.51163400    0.65573000
 S                 2.16410900   -1.03526600    0.38398400
 O                 1.57181100   -1.50432300   -0.98142300
 C                 3.99311700   -1.29004200    0.03618500
 C                 4.42186900   -0.63811400   -1.27137500
 H                 4.51089100    0.45255300   -1.17706500
 H                 5.40675500   -1.03086100   -1.57626500
 H                 3.68808300   -0.87431600   -2.05636500
 C                 4.74618200   -0.75179300    1.24457500
 H                 4.44001200   -1.28013700    2.16068500
 H                 5.83112800   -0.89410800    1.11025700
 H                 4.53928800    0.31690700    1.39245400
 C                 4.12836300   -2.80865500   -0.07234800
 H                 5.18727000   -3.08305200   -0.20866100
 H                 3.75618600   -3.30231500    0.83864800
 H                 3.54384200   -3.17649500   -0.92674800
 Zn               -0.50067200    0.11132000    0.80482900
 C                -1.26144700    1.25630700    2.28258100
 H                -1.10443800    0.71095700    3.23180500
 H                -0.62036000    2.15325200    2.35689300
 C                -2.73319100    1.65815100    2.16781000
 H                -3.38374500    0.77307400    2.09719200
 H                -3.08556200    2.26670000    3.02338700
 H                -2.92037600    2.24632400    1.25455400
 C                -0.43953200   -1.49172900   -0.49874300
 H                -0.63725900   -1.40333000   -1.56956500
 H                -0.37743200   -2.54716600   -0.21327700
 I                -3.17730000   -1.62076800   -0.24337000
```

PRT-1C



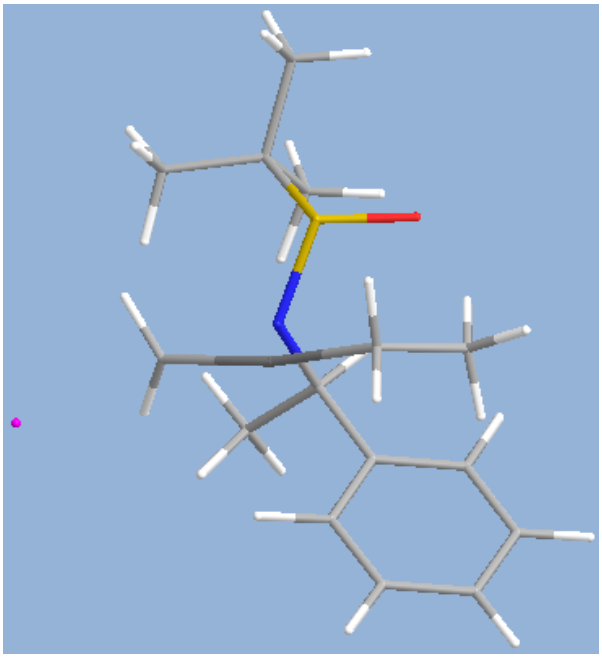
Zero-point correction= 0.372584
(Hartree/Particle)
Thermal correction to Energy= 0.398002
Thermal correction to Enthalpy= 0.398946
Thermal correction to Gibbs Free Energy= 0.315403
Sum of electronic and zero-point Energies= -3190.228077
Sum of electronic and thermal Energies= -3190.202659
Sum of electronic and thermal Enthalpies= -3190.201715
Sum of electronic and thermal Free Energies= -3190.285258

E(RM062X) = -3191.81520538
E(RM062X) = -3191.88040784 (THF)

-1 1

C	-1.83151300	2.76509600	-0.97866100
C	-1.30821100	1.68233400	-1.68572100
C	0.04581700	1.36783400	-1.56782700
C	0.88990900	2.11260400	-0.73727400
C	0.35766800	3.20363800	-0.04660700
C	-0.99268300	3.52984300	-0.16963100
H	-2.89787200	2.98807600	-1.03989100
H	-1.96402900	1.05527600	-2.29136800
H	0.45741800	0.50267600	-2.09397300
H	0.99376700	3.78391800	0.62451300
H	-1.40094400	4.36807800	0.39878100
C	2.31066400	1.61890900	-0.50757400
H	2.57565600	1.04552000	-1.41286600
C	3.32317100	2.74731300	-0.33225900
H	4.34498200	2.33872600	-0.30465300
H	3.25554700	3.48137100	-1.14936100
H	3.15067300	3.25867100	0.62540600
N	2.29207600	0.78623600	0.69516400
S	2.43567000	-0.75929300	0.63893400
O	1.67135400	-1.41948100	-0.67294100
C	4.12664900	-1.31582800	0.00707900
C	4.42060800	-0.82372800	-1.40349900
H	4.55931300	0.26633700	-1.42545000
H	5.35576200	-1.28652700	-1.76316000
H	3.60534100	-1.09899700	-2.08599500
C	5.11426300	-0.73584800	1.01337600
H	4.92202600	-1.12165800	2.02663600
H	6.14383200	-1.00773800	0.72978300
H	5.02946100	0.35988200	1.04861900
C	4.10592200	-2.84029000	0.06313800
H	5.11494900	-3.23575200	-0.14031900
H	3.79562200	-3.19435100	1.05897800
H	3.40587400	-3.24358400	-0.68020900
Zn	-0.96988200	-0.42339800	0.62965000
C	-1.09393700	0.76818600	2.26726700
H	-0.78644900	0.16073900	3.14012100
H	-0.31851600	1.54823500	2.17604600
C	-2.46461300	1.38876500	2.53601600
H	-3.24482200	0.61590400	2.62684000
H	-2.50020100	2.00513500	3.45618300
H	-2.78238400	2.03582700	1.70182900
C	0.24530300	-1.69568000	-0.47587200
H	-0.16999500	-1.68619800	-1.49670200
H	0.16905600	-2.74476300	-0.13272000
I	-3.46410900	-1.19114800	-0.37894100

TS-1D



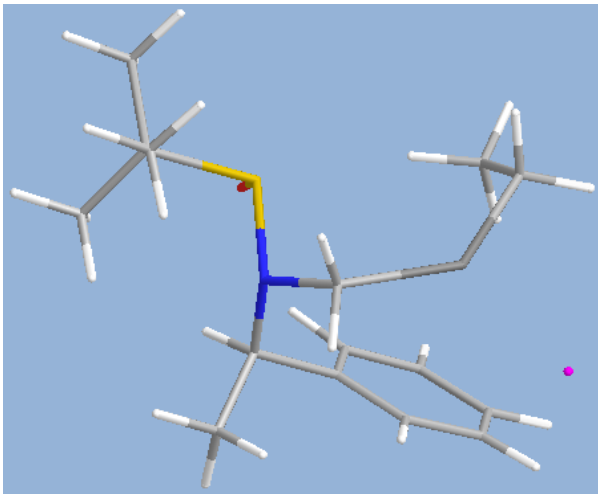
Zero-point correction= 0.371142
(Hartree/Particle)
Thermal correction to Energy= 0.396256
Thermal correction to Enthalpy= 0.397200
Thermal correction to Gibbs Free Energy= 0.313723
Sum of electronic and zero-point Energies= -3190.175985
Sum of electronic and thermal Energies= -3190.150871
Sum of electronic and thermal Enthalpies= -3190.149927
Sum of electronic and thermal Free Energies= -3190.233405

E(RM062X) = -3191.76848397
E(RM062X) = -3191.83964177 (THF)

-1 1

C	1.59505500	-4.38910600	-0.75638700
C	2.79236300	-3.67724400	-0.80689100
C	2.77875600	-2.29629000	-1.00187600
C	1.57552900	-1.60716500	-1.17495400
C	0.37571000	-2.33378000	-1.13162100
C	0.38551800	-3.71120200	-0.91169800
H	1.60183900	-5.46739400	-0.58776200
H	3.74342700	-4.19593400	-0.67113700
H	3.71247900	-1.72947100	-0.99702800
H	-0.58136700	-1.82384700	-1.28235200
H	-0.55908700	-4.25641500	-0.86850800
C	1.57221300	-0.09879700	-1.38476100
H	2.63056700	0.20847000	-1.35794300
C	0.99661100	0.25110900	-2.76007200
H	0.95609400	1.34118600	-2.89688900
H	1.61546800	-0.18572800	-3.55873800
H	-0.02475000	-0.13817400	-2.87791300
N	0.86606600	0.56715700	-0.29016100
S	1.73983600	1.47839200	0.76620300
O	3.13508900	0.90616600	0.93161200
C	2.10320000	3.11600100	-0.10071600
C	3.10760500	2.89412000	-1.22066500
H	2.64928500	2.38872500	-2.08191100
H	3.50349100	3.86264400	-1.56989100
H	3.93927100	2.27900100	-0.84587600
C	0.78412300	3.69158400	-0.58968300
H	0.07201300	3.81323100	0.24200500
H	0.94622700	4.68238900	-1.04548700
H	0.31912900	3.02973300	-1.33424200
C	2.72124800	3.97280800	1.00210300
H	2.99251700	4.96555900	0.60733300
H	2.01374200	4.11408000	1.83401100
H	3.62476300	3.48351700	1.39380100
Zn	-0.47021600	-0.64939700	1.13640700
C	0.25124800	-1.69271000	2.67331300
H	0.16422700	-1.06082300	3.57457200
H	-0.36619700	-2.58396900	2.87406500
C	1.71473600	-2.08863400	2.44513800
H	2.33383600	-1.22612000	2.14682000
H	2.18103400	-2.54015600	3.34034300
H	1.79871100	-2.82744600	1.63252800
C	-1.21980700	0.59502600	-0.19783900
H	-1.31316400	1.67108400	-0.01911400
H	-1.30391000	0.37341600	-1.26368400
I	-3.97600700	0.39012000	-0.20114300

PDT-1D



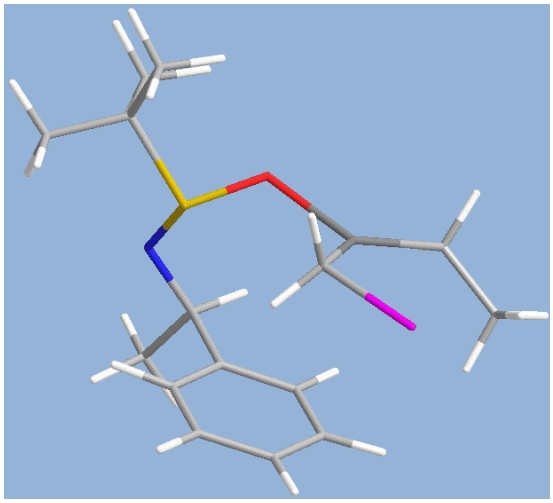
Zero-point correction=	0.373678
(Hartree/Particle)	
Thermal correction to Energy=	0.397883
Thermal correction to Enthalpy=	0.398827
Thermal correction to Gibbs Free Energy=	0.318906
Sum of electronic and zero-point Energies=	-3190.261515
Sum of electronic and thermal Energies=	-3190.237310
Sum of electronic and thermal Enthalpies=	-3190.236366
Sum of electronic and thermal Free Energies=	-3190.316287

E(RM062X) = -3191.84867340
E(RM062X) = -3191.91268280 (THF)

-1 1

C	1.53261600	3.51313800	-0.07282500
C	0.18021400	3.77168400	0.14814500
C	-0.79101800	2.89158900	-0.32659300
C	-0.42915500	1.76149600	-1.06934000
C	0.93217900	1.52497900	-1.30779900
C	1.90829600	2.37873500	-0.79067000
H	2.29380600	4.18393100	0.33013000
H	-0.12114100	4.64716000	0.72724700
H	-1.84576300	3.04880400	-0.09371200
H	1.25405300	0.65068300	-1.87777600
H	2.96041700	2.12938100	-0.94013900
C	-1.50851400	0.80989300	-1.57987000
H	-2.46547300	1.33560000	-1.45722800
C	-1.33105100	0.48610800	-3.06330300
H	-2.15551500	-0.15364900	-3.41016800
H	-1.31954700	1.41374400	-3.65392400
H	-0.38806900	-0.04494500	-3.25157800
N	-1.62567500	-0.43280400	-0.80752900
S	-2.54386000	-0.31848100	0.62568800
O	-3.04174400	1.09551000	0.80857800
C	-4.08544900	-1.21719400	0.06191800
C	-4.68539000	-0.45788400	-1.10939400
H	-4.01870100	-0.51100500	-1.98243400
H	-5.65867200	-0.89620500	-1.38442400
H	-4.83403500	0.59633100	-0.83296900
C	-3.68550300	-2.63622200	-0.31411000
H	-3.19788000	-3.15000800	0.52950100
H	-4.58044900	-3.21478700	-0.59561200
H	-2.98853300	-2.62312000	-1.16432200
C	-5.00989500	-1.18207900	1.27588700
H	-5.96372300	-1.67963600	1.03910400
H	-4.55504800	-1.70077700	2.13444600
H	-5.20980900	-0.14064500	1.56499000
Zn	1.02109100	-0.49416900	0.75991400
C	0.95126800	0.21984500	2.67020400
H	0.61328000	-0.63025100	3.29403500
H	1.97390900	0.44593500	3.01748900
C	0.03766900	1.42432100	2.92479600
H	-0.97167500	1.29667900	2.49667700
H	-0.09676300	1.65482900	4.00000200
H	0.44626700	2.33301400	2.45573900
C	-0.37659000	-1.22709300	-0.58852500
H	-0.70717600	-2.24357700	-0.30606800
H	0.07472100	-1.36900700	-1.58548200
I	3.49823000	-1.19924600	-0.26092500

SM-2



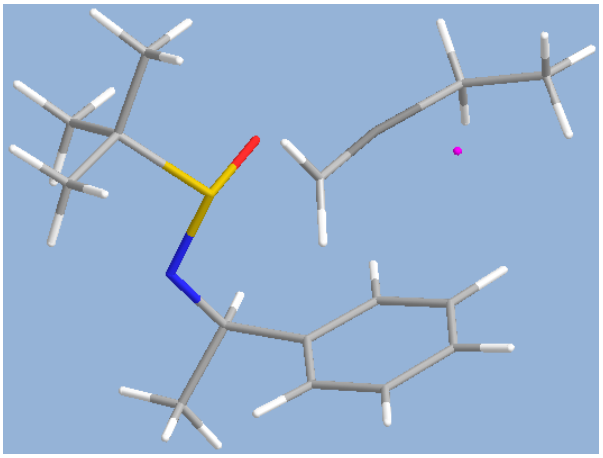
Zero-point correction=	0.369987
(Hartree/Particle)	
Thermal correction to Energy=	0.395837
Thermal correction to Enthalpy=	0.396781
Thermal correction to Gibbs Free Energy=	0.310026
Sum of electronic and zero-point Energies=	-3190.212461
Sum of electronic and thermal Energies=	-3190.186611
Sum of electronic and thermal Enthalpies=	-3190.185667
Sum of electronic and thermal Free Energies=	-3190.272421

E(RM062X) = -3191.80418520
E(RM062X) = -3191.86190481 (THF)

-1 1

C	1.53340000	2.48080000	-1.49320000
C	1.47770000	2.46270000	-0.10170000
C	0.24810000	2.31550000	0.54630000
C	-0.93570000	2.16800000	-0.18470000
C	-0.86470000	2.17780000	-1.58280000
C	0.35590000	2.34370000	-2.23220000
H	2.49650000	2.56630000	-1.99920000
H	2.39800000	2.53090000	0.48200000
H	0.20670000	2.28740000	1.63970000
H	-1.78910000	2.01390000	-2.14270000
H	0.39710000	2.33810000	-3.32370000
C	-2.27820000	1.95000000	0.51560000
H	-2.02210000	1.74460000	1.57850000
C	-3.10340000	3.23680000	0.49070000
H	-4.05870000	3.05890000	1.00460000
H	-2.57120000	4.06800000	0.97810000
H	-3.32300000	3.51600000	-0.55130000
N	-3.09220000	0.88570000	-0.03240000
S	-2.25740000	-0.45230000	-0.33950000
O	-1.56490000	-1.00710000	0.96680000
C	-3.67360000	-1.63720000	-0.51170000
C	-4.44550000	-1.63490000	0.79870000
H	-4.83660000	-0.62670000	0.98940000
H	-5.27530000	-2.35960000	0.74750000
H	-3.77180000	-1.90610000	1.62370000
C	-4.52810000	-1.16250000	-1.68020000
H	-3.93520000	-1.11790000	-2.60800000
H	-5.36290000	-1.86500000	-1.84030000
H	-4.92170000	-0.15970000	-1.46880000
C	-3.03460000	-2.99440000	-0.78610000
H	-3.81480000	-3.76700000	-0.87750000
H	-2.45240000	-2.97460000	-1.72080000
H	-2.35750000	-3.26250000	0.03710000
Zn	0.41220000	-0.61030000	1.14450000
C	0.97320000	-0.19070000	3.05670000
H	0.13880000	0.34600000	3.54470000
H	1.05710000	-1.14410000	3.61050000
C	2.27180000	0.60260000	3.22710000
H	2.53700000	0.80310000	4.28330000
H	3.12900000	0.08150000	2.77110000
H	2.21690000	1.58720000	2.73060000
C	1.21430000	-1.01640000	-0.70530000
H	1.05000000	-2.03290000	-1.09180000
H	0.90440000	-0.30980000	-1.48920000
I	3.40780000	-0.84190000	-0.74460000

TS-2A



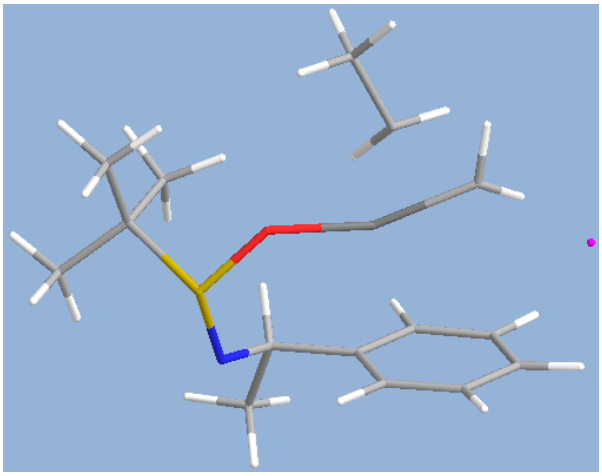
Zero-point correction= 0.369630
(Hartree/Particle)
Thermal correction to Energy= 0.394969
Thermal correction to Enthalpy= 0.395914
Thermal correction to Gibbs Free Energy= 0.311806
Sum of electronic and zero-point Energies= -3190.186049
Sum of electronic and thermal Energies= -3190.160710
Sum of electronic and thermal Enthalpies= -3190.159766
Sum of electronic and thermal Free Energies= -3190.243874

E(RM062X) = -3191.77851201
E(RM062X) = -3191.84331556 (THF)

-1 1

C	1.36690000	2.83860000	-0.63940000
C	0.97690000	2.57590000	0.67270000
C	-0.36830000	2.33710000	0.96550000
C	-1.33780000	2.33790000	-0.04360000
C	-0.93450000	2.61680000	-1.35370000
C	0.40320000	2.87540000	-1.64800000
H	2.42120000	2.97720000	-0.88000000
H	1.72470000	2.52100000	1.46720000
H	-0.67190000	2.09870000	1.98930000
H	-1.67520000	2.58200000	-2.15640000
H	0.70670000	3.06490000	-2.67950000
C	-2.76060000	1.88210000	0.26320000
H	-2.83490000	1.85780000	1.37010000
C	-3.81030000	2.86580000	-0.24440000
H	-4.80970000	2.49570000	0.02380000
H	-3.66290000	3.86700000	0.18770000
H	-3.76620000	2.93940000	-1.34100000
N	-3.07130000	0.57250000	-0.28940000
S	-1.95640000	-0.53610000	-0.06340000
O	-1.53390000	-0.70650000	1.42410000
C	-2.94670000	-2.06560000	-0.41340000
C	-4.10550000	-2.07980000	0.57440000
H	-4.74070000	-1.19900000	0.41650000
H	-4.69690000	-2.99990000	0.43710000
H	-3.71530000	-2.04970000	1.60210000
C	-3.41860000	-1.98310000	-1.85890000
H	-2.56110000	-1.91580000	-2.54690000
H	-3.99360000	-2.88840000	-2.11370000
H	-4.04900000	-1.09500000	-1.99660000
C	-2.01140000	-3.24670000	-0.17930000
H	-2.57480000	-4.18620000	-0.29360000
H	-1.18030000	-3.25730000	-0.89940000
H	-1.59490000	-3.20520000	0.83700000
Zn	0.59910000	-0.42940000	1.26620000
C	1.55690000	-0.23100000	3.02550000
H	1.11210000	0.63290000	3.55470000
H	1.31240000	-1.10340000	3.65750000
C	3.07570000	-0.06440000	2.93700000
H	3.55980000	0.05970000	3.92430000
H	3.54620000	-0.92780000	2.44240000
H	3.35610000	0.80790000	2.32430000
C	0.31240000	-0.63010000	-0.74190000
H	0.22510000	-1.57910000	-1.28700000
H	0.26180000	0.21230000	-1.44140000
I	3.00770000	-0.69390000	-1.14780000

TS-2B



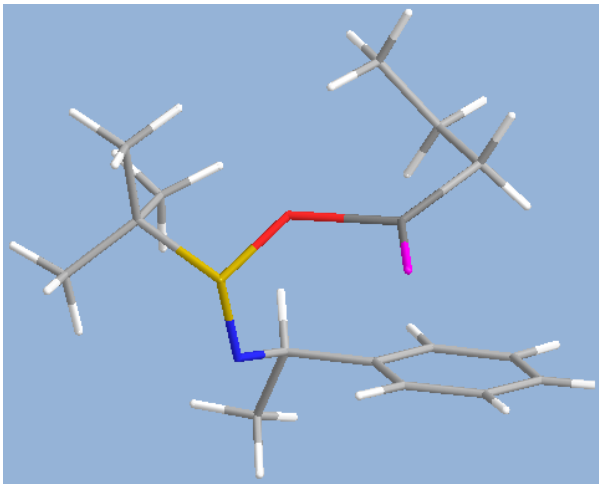
Zero-point correction= 0.369506
(Hartree/Particle)
Thermal correction to Energy= 0.394739
Thermal correction to Enthalpy= 0.395684
Thermal correction to Gibbs Free Energy= 0.312198
Sum of electronic and zero-point Energies= -3190.162276
Sum of electronic and thermal Energies= -3190.137042
Sum of electronic and thermal Enthalpies= -3190.136098
Sum of electronic and thermal Free Energies= -3190.219584

E(RM062X) = -3191.75205568
E(RM062X) = -3191.82115602 (THF)

-1 1

C	2.07990000	2.40660000	0.40490000
C	1.30000000	2.47140000	1.56080000
C	-0.07610000	2.26570000	1.49230000
C	-0.70500000	2.00970000	0.26350000
C	0.08780000	1.95900000	-0.89410000
C	1.47170000	2.14610000	-0.81970000
H	3.16620000	2.48640000	0.45790000
H	1.77410000	2.64220000	2.52940000
H	-0.67690000	2.27980000	2.40660000
H	-0.41290000	1.75410000	-1.84170000
H	2.09200000	2.03430000	-1.71000000
C	-2.22450000	1.80960000	0.20530000
H	-2.45820000	1.12380000	1.04310000
C	-2.92950000	3.13880000	0.48950000
H	-4.01630000	2.97880000	0.54480000
H	-2.58150000	3.59390000	1.42870000
H	-2.72610000	3.83150000	-0.33970000
N	-2.67360000	1.32880000	-1.08520000
S	-2.72550000	-0.21150000	-1.39820000
O	-1.52280000	-1.02440000	-0.74890000
C	-4.11770000	-1.05040000	-0.41840000
C	-3.88670000	-1.00040000	1.08540000
H	-4.10100000	-0.00220000	1.49270000
H	-4.55720000	-1.71740000	1.58940000
H	-2.84890000	-1.27590000	1.32570000
C	-5.38920000	-0.31910000	-0.82430000
H	-5.54910000	-0.37770000	-1.91270000
H	-6.26310000	-0.76650000	-0.32280000
H	-5.32220000	0.74430000	-0.55200000
C	-4.11370000	-2.49390000	-0.91350000
H	-4.96120000	-3.04630000	-0.47510000
H	-4.20590000	-2.53570000	-2.01030000
H	-3.17690000	-2.99200000	-0.62740000
Zn	0.04090000	-0.52620000	0.21530000
C	-0.05050000	-1.25170000	2.32280000
H	0.66000000	-1.07670000	3.13950000
H	-0.91010000	-0.57770000	2.51570000
C	-0.50100000	-2.70480000	2.25590000
H	-1.04470000	-3.04910000	3.15690000
H	-1.16690000	-2.88750000	1.39400000
H	0.36190000	-3.37740000	2.12730000
C	1.80630000	-0.92360000	0.89390000
H	2.26080000	-0.23300000	1.61030000
H	2.09930000	-1.95960000	1.09940000
I	4.17610000	-0.57190000	-0.58860000

PDT-2B



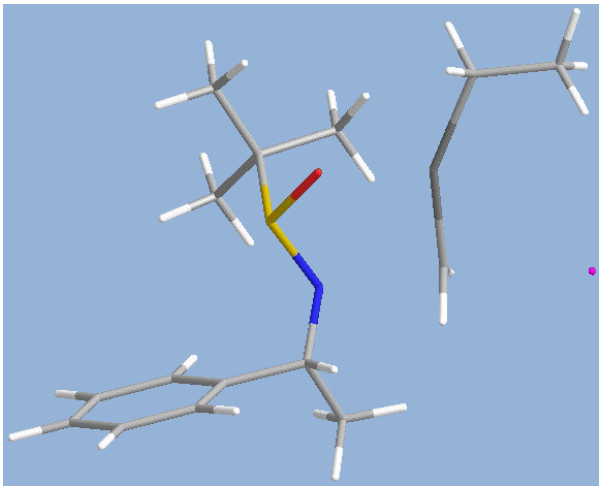
Zero-point correction= 0.373535
(Hartree/Particle)
Thermal correction to Energy= 0.398693
Thermal correction to Enthalpy= 0.399637
Thermal correction to Gibbs Free Energy= 0.316177
Sum of electronic and zero-point Energies= -3190.303718
Sum of electronic and thermal Energies= -3190.278560
Sum of electronic and thermal Enthalpies= -3190.277615
Sum of electronic and thermal Free Energies= -3190.361075

E(RM062X) = -3191.89367538
E(RM062X) = -3191.95427643 (THF)

-1 1

C	2.16280000	3.24980000	-0.69170000
C	1.05840000	3.88470000	-0.11810000
C	-0.21190000	3.33100000	-0.24680000
C	-0.41140000	2.14030000	-0.95950000
C	0.69950000	1.51440000	-1.53220000
C	1.98020000	2.06030000	-1.39120000
H	3.16260000	3.67130000	-0.57200000
H	1.19390000	4.80600000	0.45290000
H	-1.06760000	3.82050000	0.22780000
H	0.53880000	0.58070000	-2.07480000
H	2.83490000	1.53040000	-1.81670000
C	-1.81660000	1.54440000	-1.09400000
H	-2.22190000	1.55580000	-0.06440000
C	-2.68950000	2.45990000	-1.95830000
H	-3.72470000	2.08710000	-1.96280000
H	-2.68260000	3.50130000	-1.60190000
H	-2.31420000	2.43430000	-2.99170000
N	-1.79920000	0.22900000	-1.69880000
S	-1.66390000	-1.03910000	-0.76570000
O	-0.90630000	-0.68040000	0.57750000
C	-3.33760000	-1.42420000	0.04110000
C	-3.82750000	-0.25390000	0.87820000
H	-4.10550000	0.59800000	0.24030000
H	-4.72230000	-0.55080000	1.45330000
H	-3.04360000	0.06210000	1.58250000
C	-4.27780000	-1.71940000	-1.11860000
H	-3.93100000	-2.59040000	-1.69730000
H	-5.29380000	-1.93370000	-0.74730000
H	-4.31440000	-0.85510000	-1.79830000
C	-3.09610000	-2.65490000	0.90640000
H	-4.04960000	-3.02530000	1.32020000
H	-2.63990000	-3.46630000	0.31670000
H	-2.41720000	-2.41130000	1.73520000
Zn	0.97000000	-0.14410000	0.80030000
C	0.04870000	1.54210000	3.05400000
H	0.23780000	2.32280000	3.81870000
H	-0.64880000	1.99770000	2.32800000
C	-0.65490000	0.36540000	3.72680000
H	-1.57130000	0.67400000	4.25570000
H	-0.93130000	-0.38820000	2.97220000
H	0.01140000	-0.11650000	4.46120000
C	1.33680000	1.12790000	2.33730000
H	1.85560000	2.01800000	1.94260000
H	2.03290000	0.67010000	3.06400000
I	2.51700000	-1.79640000	-0.57230000

TS-2C



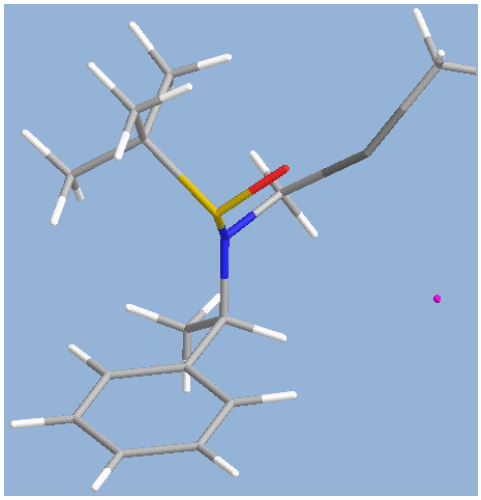
Zero-point correction= 0.370347
(Hartree/Particle)
Thermal correction to Energy= 0.395398
Thermal correction to Enthalpy= 0.396342
Thermal correction to Gibbs Free Energy= 0.312133
Sum of electronic and zero-point Energies= -3190.193731
Sum of electronic and thermal Energies= -3190.168681
Sum of electronic and thermal Enthalpies= -3190.167737
Sum of electronic and thermal Free Energies= -3190.251946

E(RM062X) = -3191.78459104
E(RM062X) = -3191.85042495 (THF)

-1 1

C	6.01968500	-1.13452500	-0.90782200
C	5.12906300	-1.54502800	-1.89608300
C	3.76627400	-1.65392700	-1.60990200
C	3.27177100	-1.35852600	-0.33857000
C	4.17791300	-0.94479500	0.64699700
C	5.53685000	-0.83386900	0.36837600
H	7.08505900	-1.04442400	-1.12823500
H	5.49294000	-1.77661000	-2.89922500
H	3.06820200	-1.96675000	-2.39032000
H	3.79698000	-0.69805000	1.64028000
H	6.22666700	-0.50830700	1.15001200
C	1.78826300	-1.49277300	-0.01524700
H	1.29112400	-1.80932300	-0.95723100
C	1.59385700	-2.61926900	1.00348700
H	0.52512400	-2.77342300	1.20163200
H	2.03395100	-3.55942200	0.63840800
H	2.07907600	-2.34340000	1.95193500
N	1.16988700	-0.28601700	0.53213900
S	1.55602700	1.08602300	-0.24719600
O	0.38310600	1.58496500	-1.14171900
C	1.45616900	2.30926700	1.15548300
C	0.05781400	2.28496200	1.75224600
H	-0.20824700	1.26750700	2.07033700
H	0.01842300	2.95370000	2.62764700
H	-0.68559700	2.65001700	1.02594200
C	2.50476600	1.90490500	2.18172500
H	3.50115100	1.82687500	1.71725500
H	2.55484000	2.65972200	2.98310700
H	2.24388400	0.93024800	2.61659000
C	1.76399800	3.66666400	0.53021600
H	1.67694700	4.45828000	1.29168800
H	2.78512200	3.69075000	0.11882100
H	1.05329100	3.87019200	-0.28262200
Zn	-1.53152600	0.97196000	-0.68675900
C	-2.82866400	2.30226700	-1.47906300
H	-2.65323800	3.27836200	-0.98819500
H	-2.52329600	2.46328300	-2.52908000
C	-4.31556900	1.94734100	-1.41522700
H	-4.96879200	2.71386600	-1.87537600
H	-4.52354000	0.99144900	-1.92078100
H	-4.65572300	1.80717400	-0.37726800
C	-1.04306000	-0.68511300	0.38002100
H	-0.74236300	-1.61557800	-0.10961900
H	-1.02568100	-0.79044300	1.46688500
I	-3.52690200	-1.63724400	0.39215600

PDT-2C



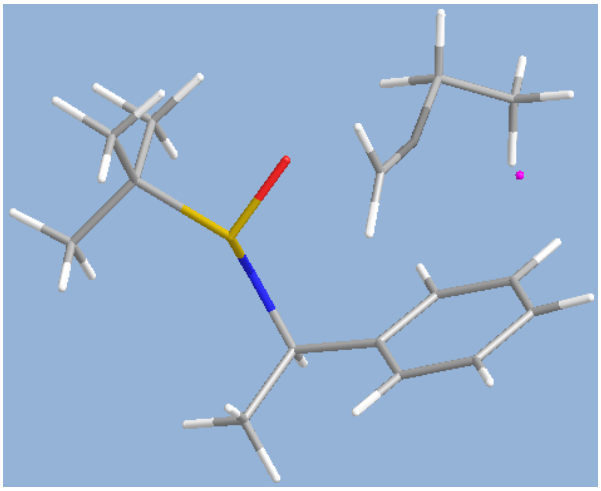
Zero-point correction= 0.372888
(Hartree/Particle)
Thermal correction to Energy= 0.398207
Thermal correction to Enthalpy= 0.399152
Thermal correction to Gibbs Free Energy= 0.314394
Sum of electronic and zero-point Energies= -3190.270060
Sum of electronic and thermal Energies= -3190.244740
Sum of electronic and thermal Enthalpies= -3190.243796
Sum of electronic and thermal Free Energies= -3190.328554

E(RM062X) = -3191.85460006
E(RM062X) = -3191.92144281 (THF)

-1 1

C	4.46360400	-2.10034100	-1.24996300
C	3.15433800	-2.57287200	-1.34237100
C	2.17983300	-2.12481900	-0.45221000
C	2.50107900	-1.19529800	0.54422200
C	3.81776300	-0.73124800	0.63309300
C	4.79366100	-1.17765000	-0.25807000
H	5.22534000	-2.45107400	-1.94928200
H	2.88477100	-3.29127000	-2.11870400
H	1.14329400	-2.46877900	-0.53807200
H	4.08674400	-0.00703600	1.40450500
H	5.81654000	-0.80411300	-0.17521000
C	1.40485600	-0.70433600	1.47386100
H	0.60322000	-1.46367200	1.44163700
C	1.88751000	-0.56722000	2.91551700
H	1.04487500	-0.29090500	3.56214400
H	2.31322300	-1.51718500	3.27047400
H	2.64938700	0.22193700	3.00389000
N	0.80700000	0.58831800	1.05696000
S	0.98113500	0.99969600	-0.58360700
O	-0.39593700	1.18807600	-1.21063100
C	1.56078300	2.76620200	-0.42412600
C	0.53998900	3.58645100	0.34856500
H	0.54618400	3.32290800	1.41358600
H	0.78057400	4.65762400	0.24666500
H	-0.47115900	3.41236600	-0.04910200
C	2.91825000	2.73314400	0.26279200
H	3.63245100	2.10876900	-0.29752200
H	3.32644300	3.75448800	0.32971700
H	2.81932800	2.32487700	1.27922000
C	1.67170200	3.25226600	-1.86842000
H	2.03389800	4.29233700	-1.88197500
H	2.37710400	2.63300400	-2.44443400
H	0.68873600	3.20720000	-2.35714800
Zn	-2.00324800	0.82774700	0.15916400
C	-3.77493900	1.68448900	-0.38746500
H	-3.86773400	2.69929500	0.04343500
H	-3.74872600	1.83269600	-1.48217200
C	-5.00971100	0.85631100	-0.02049700
H	-5.96471900	1.28964000	-0.37900700
H	-4.93864700	-0.16336800	-0.43234900
H	-5.10788100	0.73636200	1.07197500
C	-0.51761800	0.86322600	1.65608900
H	-0.79795400	-0.03240900	2.23299500
H	-0.44442800	1.70303000	2.36815500
I	-1.96716400	-2.02956500	-0.22076200

TS-2D



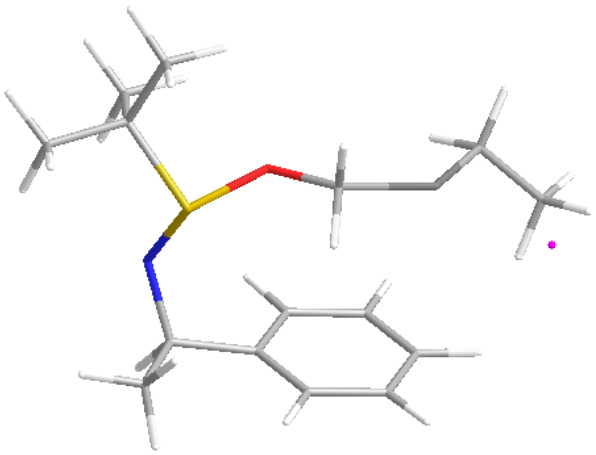
Zero-point correction= 0.370462
(Hartree/Particle)
Thermal correction to Energy= 0.395536
Thermal correction to Enthalpy= 0.396480
Thermal correction to Gibbs Free Energy= 0.312923
Sum of electronic and zero-point Energies= -3190.171704
Sum of electronic and thermal Energies= -3190.146631
Sum of electronic and thermal Enthalpies= -3190.145686
Sum of electronic and thermal Free Energies= -3190.229244

E(RM062X) = -3191.76102300
E(RM062X) = -3191.82823701 (THF)

-1 1

C	2.05678100	1.90707200	-1.27018300
C	1.22164400	2.55948500	-0.36209300
C	-0.16605600	2.47292800	-0.49702800
C	-0.74591600	1.75062600	-1.55033600
C	0.10517900	1.12790500	-2.46856600
C	1.49224700	1.19437400	-2.32376700
H	3.13764700	1.90572100	-1.13141700
H	1.65248100	3.11843400	0.47147600
H	-0.82312700	2.95083900	0.23641900
H	-0.31609300	0.55136100	-3.29442400
H	2.14229100	0.64681100	-3.00795800
C	-2.26335100	1.59522000	-1.56906500
H	-2.67460800	2.60198400	-1.38066000
C	-2.81028600	1.13708300	-2.92341700
H	-3.90882400	1.14380600	-2.88382300
H	-2.47902100	1.79087700	-3.74542800
H	-2.49255900	0.10800500	-3.15010500
N	-2.74418000	0.78815800	-0.44414100
S	-2.26605800	-0.72980400	-0.45963100
O	-1.17065600	-1.00432200	0.67070300
C	-3.70004100	-1.54540300	0.39701300
C	-3.91193000	-0.84558100	1.73244600
H	-4.09222700	0.22498600	1.56524800
H	-4.77726500	-1.29274500	2.24891300
H	-3.01863500	-0.95613900	2.36241400
C	-4.90410200	-1.37767900	-0.52047800
H	-4.71989600	-1.83643800	-1.50555300
H	-5.78386800	-1.86729700	-0.07265800
H	-5.11513500	-0.30962300	-0.66524900
C	-3.32469300	-3.01155600	0.57932300
H	-4.14498900	-3.54466900	1.08658300
H	-3.14554100	-3.49812200	-0.39226900
H	-2.41263800	-3.09475500	1.18476300
Zn	0.34684300	0.45141800	1.38444700
C	-0.00605500	1.60368500	2.99387700
H	-1.10430000	1.70522600	3.05373700
H	0.28301200	1.01765900	3.88391900
C	0.64011500	2.98769400	3.06924700
H	0.39566200	3.52914200	4.00136900
H	1.73961800	2.93219000	3.01347900
H	0.31348400	3.63826900	2.24053700
C	0.73396100	-1.10795700	0.21123400
H	0.83420500	-2.12309600	0.60273800
H	0.62726700	-1.10704900	-0.87921500
I	3.54347600	-1.32586700	-0.25034000

PDT-2D



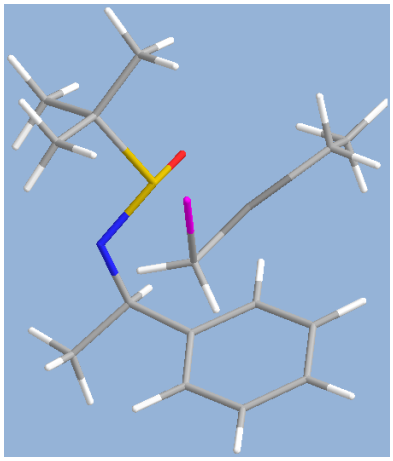
Zero-point correction= 0.372249
(Hartree/Particle)
Thermal correction to Energy= 0.396749
Thermal correction to Enthalpy= 0.397694
Thermal correction to Gibbs Free Energy= 0.316321
Sum of electronic and zero-point Energies= -3190.233269
Sum of electronic and thermal Energies= -3190.208769
Sum of electronic and thermal Enthalpies= -3190.207824
Sum of electronic and thermal Free Energies= -3190.289197

E(RM062X) = -3191.81873595
E(RM062X) = -3191.88148664 (THF)

-1 1

C	1.37754500	2.16877400	0.88833500
C	0.45970700	1.72459600	1.84635600
C	-0.90551300	1.78245900	1.58516600
C	-1.38830000	2.29827800	0.37490800
C	-0.46323700	2.76044300	-0.56575500
C	0.90979600	2.68399000	-0.31729900
H	2.45200200	2.07407400	1.06040600
H	0.81919000	1.29713100	2.78494900
H	-1.62348000	1.37028100	2.29672300
H	-0.80538700	3.15152000	-1.52538800
H	1.62282400	2.99203300	-1.08355100
C	-2.89486200	2.23391200	0.11981200
H	-3.37215200	2.87801300	0.87866400
C	-3.30779200	2.77145200	-1.25101000
H	-4.39931300	2.69189000	-1.35103700
H	-3.01616900	3.82418100	-1.38329900
H	-2.84635800	2.18430300	-2.05993700
N	-3.42933300	0.89270500	0.39393200
S	-2.84093000	-0.24076100	-0.53132800
O	-1.51952200	-0.95868600	0.18086300
C	-4.02353100	-1.61414000	-0.17736200
C	-4.08118900	-1.82909500	1.32960700
H	-4.39551700	-0.90150400	1.82569200
H	-4.80251500	-2.63219000	1.55229900
H	-3.09145500	-2.11476300	1.71012600
C	-5.37479200	-1.17456100	-0.73092700
H	-5.31795400	-0.98262600	-1.81409000
H	-6.11655100	-1.97127700	-0.56205600
H	-5.70398500	-0.25647600	-0.22693600
C	-3.48548800	-2.84240300	-0.90457000
H	-4.17822000	-3.68559000	-0.75648100
H	-3.39363400	-2.65685200	-1.98590000
H	-2.49776800	-3.11858200	-0.51193200
Zn	1.40647400	-0.85438300	0.56906300
C	2.15348500	-1.27207200	2.42057300
H	1.35145500	-1.22554200	3.18065000
H	2.48525800	-2.32695700	2.41096700
C	3.32992300	-0.38867900	2.84209300
H	3.79251400	-0.68661300	3.80283800
H	4.12231700	-0.39580000	2.07632100
H	3.02720900	0.66722700	2.96029400
C	-0.28614900	-0.89821500	-0.59310800
H	-0.29548300	-1.72601200	-1.32806000
H	-0.28215100	0.03453700	-1.18711100
I	3.46735600	-0.33978500	-1.22151200

SM-3



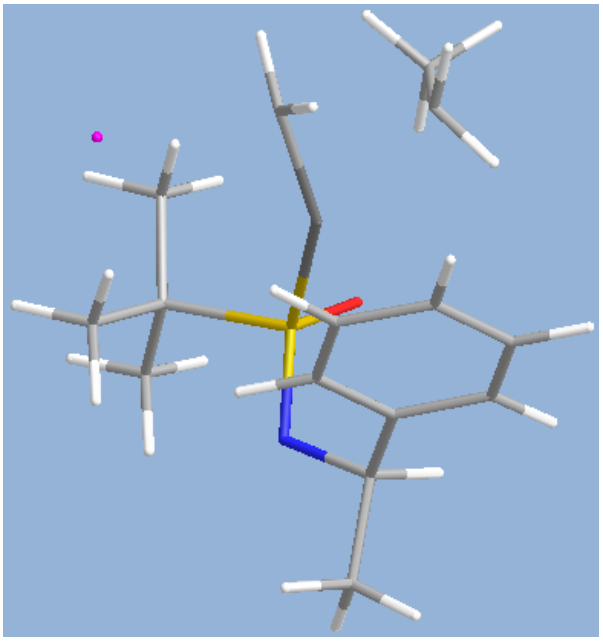
Zero-point correction= 0.370399
(Hartree/Particle)
Thermal correction to Energy= 0.396215
Thermal correction to Enthalpy= 0.397160
Thermal correction to Gibbs Free Energy= 0.312116
Sum of electronic and zero-point Energies= -3190.195697
Sum of electronic and thermal Energies= -3190.169880
Sum of electronic and thermal Enthalpies= -3190.168936
Sum of electronic and thermal Free Energies= -3190.253979

E(RM062X) = -3191.79241014
E(RM062X) = -3191.85251910 (THF)

-1 1

C	0.69180000	-3.75810000	0.30580000
C	1.36300000	-2.87000000	1.14700000
C	2.11080000	-1.81930000	0.60680000
C	2.17730000	-1.61910000	-0.78370000
C	1.48460000	-2.51040000	-1.61040000
C	0.76280000	-3.57700000	-1.07510000
H	0.11000000	-4.58020000	0.72640000
H	1.30600000	-2.98940000	2.23120000
H	2.64210000	-1.12150000	1.26440000
H	1.50840000	-2.36880000	-2.69230000
H	0.23590000	-4.26300000	-1.74210000
C	2.91280000	-0.38870000	-1.31550000
H	3.78570000	-0.25110000	-0.64120000
C	3.45250000	-0.58230000	-2.72710000
H	4.04890000	0.29910000	-2.99800000
H	4.07390000	-1.48780000	-2.81220000
H	2.61920000	-0.64270000	-3.44280000
N	2.07360000	0.79700000	-1.32790000
S	1.52310000	1.19660000	0.12620000
O	2.60280000	1.49780000	1.15200000
C	0.78730000	2.85210000	-0.27930000
C	1.95490000	3.74970000	-0.66420000
H	2.43780000	3.35370000	-1.56770000
H	1.59490000	4.77530000	-0.84940000
H	2.69470000	3.75870000	0.14870000
C	-0.21570000	2.69390000	-1.41190000
H	-1.03180000	2.00920000	-1.13140000
H	-0.66770000	3.67360000	-1.64250000
H	0.28670000	2.29790000	-2.30370000
C	0.12170000	3.31850000	1.01150000
H	-0.27180000	4.33970000	0.88400000
H	-0.72010000	2.66040000	1.28410000
H	0.85000000	3.31190000	1.83540000
Zn	-0.31960000	-0.40720000	1.02110000
C	-0.36020000	-0.28500000	3.04540000
C	-1.32300000	-0.85190000	-0.70000000
H	-0.94820000	0.61670000	3.29820000
H	-0.91920000	-1.12650000	3.49260000
C	1.03260000	-0.17050000	3.67550000
H	-0.89700000	-0.38970000	-1.60160000
H	-1.53280000	-1.90810000	-0.91180000
I	-3.34510000	0.01700000	-0.57080000
H	1.00740000	0.03890000	4.76160000
H	1.60680000	-1.10620000	3.55610000
H	1.63040000	0.61580000	3.18760000

TS-3



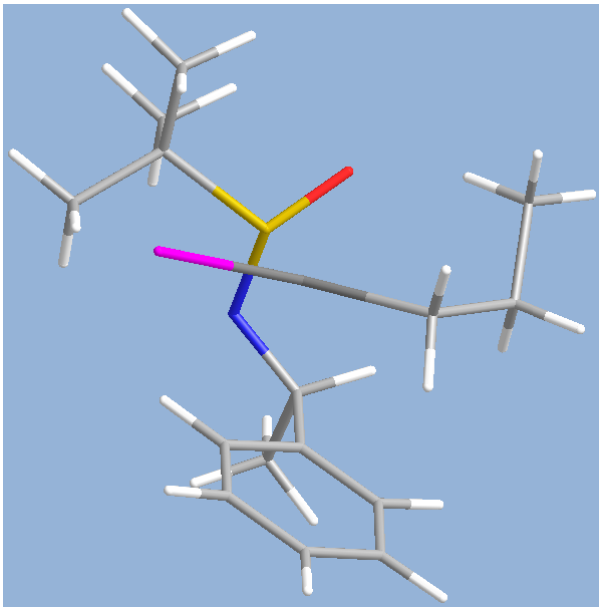
Zero-point correction= 0.369371
(Hartree/Particle)
Thermal correction to Energy= 0.394870
Thermal correction to Enthalpy= 0.395814
Thermal correction to Gibbs Free Energy= 0.311487
Sum of electronic and zero-point Energies= -3190.140038
Sum of electronic and thermal Energies= -3190.114539
Sum of electronic and thermal Enthalpies= -3190.113594
Sum of electronic and thermal Free Energies= -3190.197922

E(RM062X) = -3191.73864877
E(RM062X) = -3191.80971217 (THF)

-1 1

C	0.48655600	3.53540000	-0.11544700
C	-0.80607700	3.87525600	0.28693900
C	-1.88742800	3.06441900	-0.05858300
C	-1.70319100	1.91289600	-0.83246100
C	-0.39842400	1.59064400	-1.24843000
C	0.69294400	2.38948100	-0.88413500
H	1.33697400	4.15010800	0.18368600
H	-0.97062700	4.76439600	0.89906300
H	-2.89417700	3.31531800	0.28542600
H	-0.24129000	0.69210600	-1.85344200
H	1.70072000	2.06924000	-1.16665200
C	-2.88467800	1.02582300	-1.23581500
H	-3.70824200	1.26967700	-0.53244100
C	-3.35098500	1.41051900	-2.64015900
H	-4.21068700	0.78450800	-2.91615700
H	-3.63267700	2.47292200	-2.69590300
H	-2.54107200	1.21788600	-3.35929200
N	-2.58644500	-0.39377100	-1.24604600
S	-2.06868900	-0.95606800	0.14177900
O	-3.07258400	-1.16270000	1.24296600
C	-1.48172100	-2.63613800	-0.34299700
C	-2.71507200	-3.38431700	-0.83413300
H	-3.11400300	-2.89976500	-1.73516400
H	-2.44940000	-4.42892100	-1.06179600
H	-3.49216000	-3.36848900	-0.05611900
C	-0.41057000	-2.49296200	-1.41548600
H	0.45088000	-1.89450000	-1.06723800
H	-0.02148500	-3.49045000	-1.67496500
H	-0.83284500	-2.02458400	-2.31382400
C	-0.92150900	-3.25222100	0.93609000
H	-0.60808700	-4.28856600	0.73786800
H	-0.03501000	-2.69563100	1.28507700
H	-1.68182500	-3.24588400	1.72925900
Zn	-0.14379700	0.21471000	0.85837000
C	0.05682300	1.04741200	2.88011700
C	1.69622500	0.26908200	1.41046500
H	0.92430600	1.50066600	3.37344700
H	-0.65317800	1.87082300	2.67673400
C	-0.57663600	-0.05744200	3.72168800
H	2.20000900	1.24119500	1.36471400
H	2.13599000	-0.37340900	2.18456600
I	3.58277900	-0.46080500	-0.62514900
H	-0.87245300	0.27960800	4.73292100
H	-1.48135000	-0.47283200	3.24436400
H	0.12557300	-0.89610800	3.86188700

PDT-3



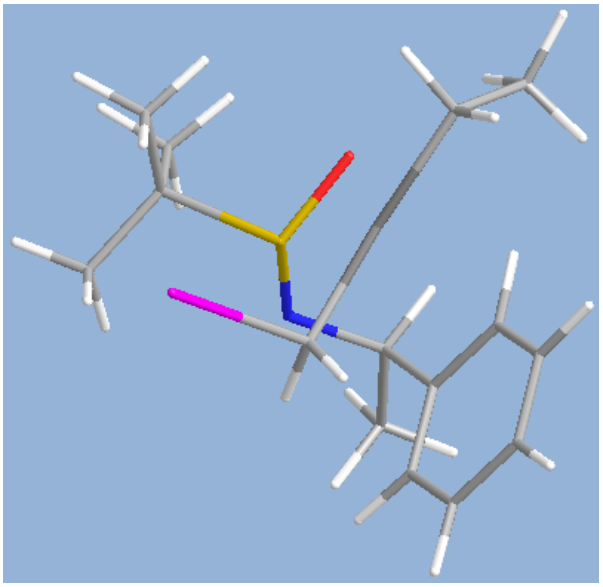
Zero-point correction= 0.374348
(Hartree/Particle)
Thermal correction to Energy= 0.399450
Thermal correction to Enthalpy= 0.400394
Thermal correction to Gibbs Free Energy= 0.317925
Sum of electronic and zero-point Energies= -3190.280958
Sum of electronic and thermal Energies= -3190.255855
Sum of electronic and thermal Enthalpies= -3190.254911
Sum of electronic and thermal Free Energies= -3190.337380

E(RM062X) = -3191.87898235
E(RM062X) = -3191.94097397 (THF)

-1 1

C	2.10344400	-2.93554900	-1.42387100
C	3.20409400	-2.39460800	-0.75626600
C	3.29792200	-1.01912000	-0.56199800
C	2.30626500	-0.15422300	-1.04145500
C	1.21093000	-0.70600500	-1.71804100
C	1.10476300	-2.08873800	-1.89946600
H	2.01511700	-4.01557900	-1.55357700
H	3.98133400	-3.05376500	-0.36379600
H	4.14816400	-0.59970600	-0.01649500
H	0.43568700	-0.02807500	-2.08490800
H	0.22170200	-2.49851300	-2.39322800
C	2.43379800	1.36174500	-0.86100200
H	2.94884600	1.51381300	0.11222000
C	3.35353900	1.91871400	-1.95097800
H	3.47730500	2.99940400	-1.79687300
H	4.33853600	1.42733600	-1.94502900
H	2.88288700	1.76246000	-2.93325500
N	1.18438100	2.08318200	-0.93282900
S	0.20843100	1.79287600	0.29522700
O	0.59903100	2.41327400	1.61624100
C	-1.26854800	2.77175600	-0.25030600
C	-0.81145700	4.22637700	-0.25839100
H	-0.01482700	4.36342600	-1.00152400
H	-1.66684600	4.87702000	-0.50398000
H	-0.41667700	4.49770600	0.73077300
C	-1.71433400	2.31030000	-1.63028100
H	-1.98347800	1.24283000	-1.62815500
H	-2.60794000	2.88292400	-1.93046200
H	-0.91032900	2.47937400	-2.35814300
C	-2.33591000	2.53506300	0.81379500
H	-3.21148500	3.17039100	0.60535600
H	-2.66767800	1.48478700	0.81560600
H	-1.93591800	2.78822400	1.80589600
Zn	-0.20108500	-0.65579700	0.70273600
C	1.91021200	-1.08123600	2.86595000
C	0.84526300	-1.78045500	2.02173500
H	2.47007700	-1.81603700	3.47872700
H	2.66180700	-0.61331600	2.20548400
C	1.33281200	-0.00770000	3.78360200
H	1.29877500	-2.59536600	1.42993200
H	0.11007200	-2.27015600	2.68709400
I	-2.47820400	-1.49894500	-0.38536900
H	2.10352400	0.42874300	4.43904700
H	0.89688600	0.81210000	3.19046800
H	0.54723400	-0.43446400	4.42937500

TS-4



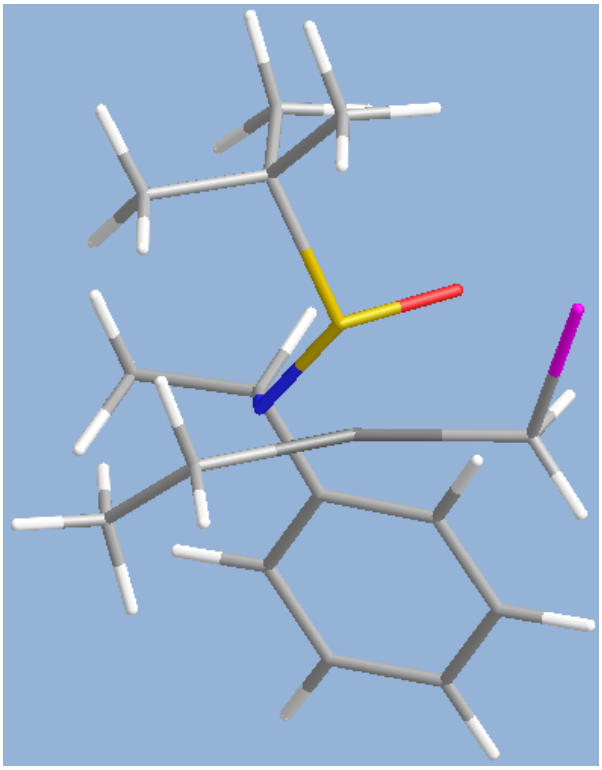
Zero-point correction= 0.369836
(Hartree/Particle)
Thermal correction to Energy= 0.394998
Thermal correction to Enthalpy= 0.395942
Thermal correction to Gibbs Free Energy= 0.312939
Sum of electronic and zero-point Energies= -3190.184427
Sum of electronic and thermal Energies= -3190.159265
Sum of electronic and thermal Enthalpies= -3190.158321
Sum of electronic and thermal Free Energies= -3190.241324

E(RM062X) = -3191.78101704
E(RM062X) = -3191.84036785 (THF)

-1 1

C	-1.47830000	3.37190000	-1.02070000
C	-1.88730000	2.83430000	0.19930000
C	-2.43330000	1.54790000	0.24920000
C	-2.57550000	0.77730000	-0.91380000
C	-2.13570000	1.32070000	-2.12570000
C	-1.60580000	2.60890000	-2.18280000
H	-1.04710000	4.37380000	-1.06500000
H	-1.77120000	3.40710000	1.12310000
H	-2.73210000	1.10940000	1.20580000
H	-2.19740000	0.71650000	-3.03340000
H	-1.26980000	3.01590000	-3.13920000
C	-3.08610000	-0.66040000	-0.80590000
H	-3.62560000	-0.70010000	0.16500000
C	-4.09710000	-0.99540000	-1.89790000
H	-4.47130000	-2.01460000	-1.72880000
H	-4.94260000	-0.28980000	-1.90530000
H	-3.60970000	-0.98680000	-2.88420000
N	-2.03190000	-1.65110000	-0.85320000
S	-0.83400000	-1.33940000	0.17530000
O	-1.29930000	-1.12700000	1.62890000
C	-0.02590000	-3.01380000	0.18980000
C	-1.08320000	-4.00090000	0.66070000
H	-1.89330000	-4.06130000	-0.07720000
H	-0.63180000	-4.99590000	0.81200000
H	-1.50810000	-3.64400000	1.61140000
C	0.47470000	-3.30720000	-1.21680000
H	1.20700000	-2.54680000	-1.53370000
H	0.97050000	-4.29260000	-1.24130000
H	-0.36910000	-3.30100000	-1.91960000
C	1.11340000	-2.90300000	1.19670000
H	1.61480000	-3.87880000	1.30280000
H	1.86160000	-2.16400000	0.86770000
H	0.71800000	-2.59250000	2.17470000
Zn	0.26200000	0.98040000	1.04940000
C	0.16110000	1.43910000	3.01600000
C	1.24000000	1.37320000	-0.70810000
H	0.83450000	0.73050000	3.53030000
H	0.58980000	2.44160000	3.19900000
C	-1.23700000	1.33130000	3.62720000
H	0.74020000	0.96970000	-1.59830000
H	1.55760000	2.40420000	-0.91790000
I	3.14810000	0.27620000	-0.70250000
H	-1.24740000	1.48260000	4.72320000
H	-1.92680000	2.08460000	3.20550000
H	-1.66730000	0.34190000	3.40960000

TS-5



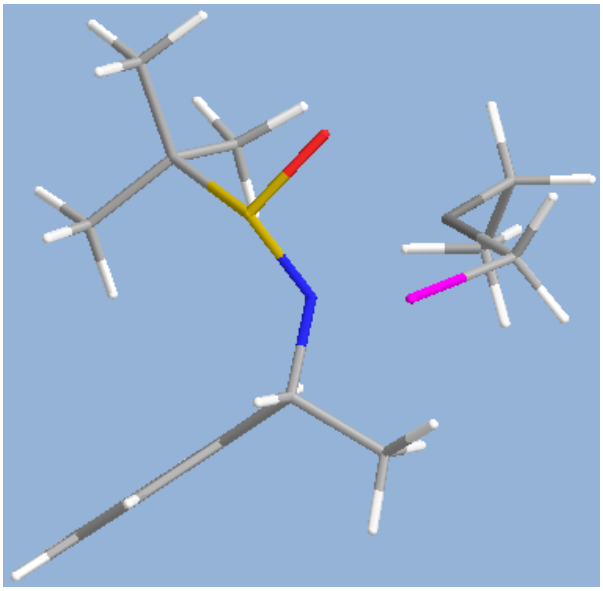
Zero-point correction= 0.370452
(Hartree/Particle)
Thermal correction to Energy= 0.395503
Thermal correction to Enthalpy= 0.396448
Thermal correction to Gibbs Free Energy= 0.311924
Sum of electronic and zero-point Energies= -3190.186701
Sum of electronic and thermal Energies= -3190.161649
Sum of electronic and thermal Enthalpies= -3190.160705
Sum of electronic and thermal Free Energies= -3190.245229

E(RM062X) = -3191.78501019
E(RM062X) = -3191.84731192 (THF)

-1 1

C	5.07602200	3.08025600	-0.05170300
C	3.77824800	2.96837100	-0.56127000
C	3.16397400	1.72478000	-0.65577800
C	3.83523900	0.55861400	-0.25571800
C	5.13171500	0.68062400	0.24928200
C	5.74784000	1.93224100	0.35417100
H	5.55549700	4.05812900	0.03026900
H	3.23966500	3.86238500	-0.88351000
H	2.14856100	1.61889300	-1.04925600
H	5.67795100	-0.20619300	0.57415700
H	6.75986200	2.00484300	0.75953100
C	3.09240400	-0.77099100	-0.40056800
H	2.91181500	-0.86912100	-1.48959300
C	3.92381100	-1.96814800	0.05513200
H	3.36121400	-2.89517700	-0.12317800
H	4.88606300	-2.04016900	-0.47632900
H	4.11493400	-1.89941600	1.13677400
N	1.84116800	-0.71133700	0.34737500
S	0.48485300	-0.68528600	-0.46846900
O	0.50483600	0.12507200	-1.75598600
C	0.03633500	-2.40067900	-1.13243600
C	0.97206400	-2.74773600	-2.27950500
H	1.99614400	-2.92281400	-1.91719800
H	0.63038300	-3.66452700	-2.79062900
H	0.99004600	-1.91672700	-2.99973600
C	0.13937900	-3.37187600	0.03163700
H	-0.49829300	-3.04601800	0.86963400
H	-0.18516100	-4.37998600	-0.27755300
H	1.17195400	-3.42506800	0.40479500
C	-1.40046400	-2.25244300	-1.61862500
H	-1.77660200	-3.20905200	-2.01903400
H	-2.06736300	-1.94758700	-0.79376200
H	-1.45987000	-1.48202200	-2.40033400
Zn	-1.16766700	0.11686600	1.28368600
C	-1.23827300	-1.07748100	2.90860500
H	-1.88053700	-0.63499800	3.68931500
H	-1.74975600	-2.01186700	2.61144000
C	0.14638600	-1.40596400	3.47906500
H	0.61744900	-0.51145100	3.91741700
H	0.11655600	-2.17464700	4.27370400
H	0.83827900	-1.74868900	2.69361600
C	-1.85061900	1.67711000	0.17293400
H	-2.01922700	2.67098700	0.60444600
H	-1.30763300	1.76401500	-0.77838200
I	-3.86888300	1.06950100	-0.46673100

SM-4

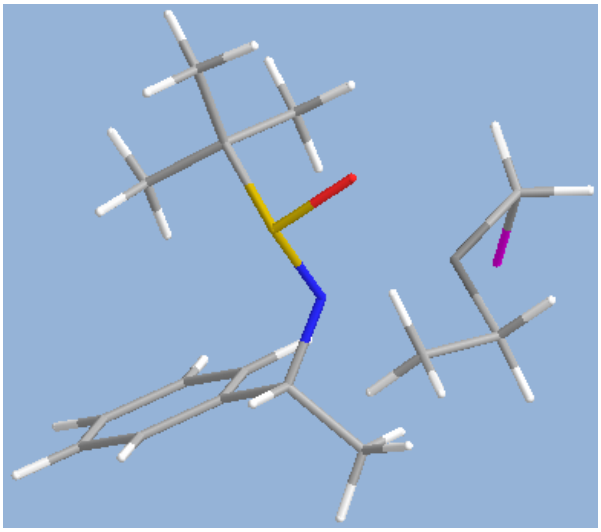


Zero-point correction= 0.369710
(Hartree/Particle)
Thermal correction to Energy= 0.395487
Thermal correction to Enthalpy= 0.396431
Thermal correction to Gibbs Free Energy= 0.311696
Sum of electronic and zero-point Energies= -3190.228404
Sum of electronic and thermal Energies= -3190.202628
Sum of electronic and thermal Enthalpies= -3190.201684
Sum of electronic and thermal Free Energies= -3190.286419

E(RM062X) = -3191.81852021
E(RM062X) = -3191.87634545 (THF)
-1 1

C	-5.08030000	-1.86160000	-0.60060000
C	-4.48620000	-0.79110000	-1.27620000
C	-3.10760000	-0.60910000	-1.22500000
C	-2.29410000	-1.49500000	-0.50480000
C	-2.89590000	-2.56480000	0.15920000
C	-4.28070000	-2.74830000	0.11620000
H	-6.16300000	-1.99890000	-0.63130000
H	-5.10630000	-0.08960000	-1.83840000
H	-2.62990000	0.24110000	-1.71940000
H	-2.26990000	-3.25330000	0.73320000
H	-4.73680000	-3.58390000	0.65170000
C	-0.78870000	-1.25900000	-0.45830000
H	-0.36690000	-1.95160000	0.29920000
C	-0.18220000	-1.62220000	-1.81590000
H	0.91270000	-1.54460000	-1.76470000
H	-0.45910000	-2.64370000	-2.11790000
H	-0.55160000	-0.91820000	-2.57910000
N	-0.46180000	0.12320000	-0.16230000
S	-0.15020000	0.50010000	1.39380000
O	0.97030000	1.55300000	1.23260000
C	-1.56190000	1.61100000	1.93900000
C	-1.84860000	2.59430000	0.81790000
H	-2.27120000	2.06790000	-0.04850000
H	-2.56410000	3.36160000	1.15820000
H	-0.91680000	3.08650000	0.49770000
C	-2.75700000	0.71730000	2.24470000
H	-2.50010000	-0.04520000	2.99800000
H	-3.58690000	1.32450000	2.64300000
H	-3.11520000	0.20410000	1.34060000
C	-1.06050000	2.31560000	3.19520000
H	-1.85200000	2.96610000	3.60360000
H	-0.78260000	1.58590000	3.97340000
H	-0.17530000	2.92030000	2.95810000
Zn	1.20640000	1.31530000	-0.92540000
C	0.63290000	2.87400000	-2.15090000
H	0.55390000	3.81070000	-1.56790000
H	1.40980000	3.07040000	-2.91270000
C	-0.70350000	2.60560000	-2.84980000

SM-4′



Zero-point correction= 0.370277
(Hartree/Particle)
Thermal correction to Energy= 0.395806
Thermal correction to Enthalpy= 0.396750
Thermal correction to Gibbs Free Energy= 0.313025
Sum of electronic and zero-point Energies= -3190.230290
Sum of electronic and thermal Energies= -3190.204761
Sum of electronic and thermal Enthalpies= -3190.203817
Sum of electronic and thermal Free Energies= -3190.287543

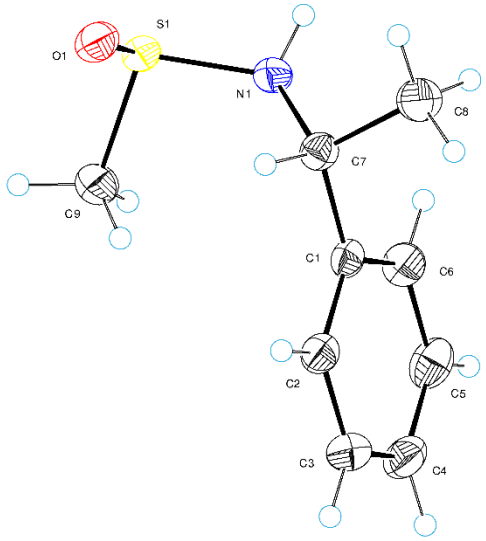
E(RM062X) = -3191.82071536
E(RM062X) = -3191.87698068 (THF)

-1 1

C	4.53364700	-2.19073500	-0.37125000
C	3.21244400	-2.51199200	-0.04410500
C	2.17115100	-1.66763400	-0.41674300
C	2.42930800	-0.48910400	-1.13085300
C	3.74992000	-0.17934600	-1.45777200
C	4.79940600	-1.02138200	-1.07882300
H	5.35134700	-2.84881000	-0.07019900
H	2.99466500	-3.42420600	0.51544400
H	1.13715300	-1.88921900	-0.13527600
H	3.96066700	0.74401700	-2.00446900
H	5.82849900	-0.75759300	-1.33335300
C	1.26875400	0.42005100	-1.51665000
H	1.71410100	1.34550900	-1.94077300
C	0.43976500	-0.25615200	-2.61172100
H	-0.34566400	0.42653700	-2.96524000
H	1.07158700	-0.56040800	-3.46018000
H	-0.04746500	-1.15196300	-2.19369200
N	0.39730900	0.71334600	-0.39034800
S	0.68238200	2.10064800	0.41492800
O	-0.74700300	2.61760800	0.69905700
C	1.19382300	1.57726800	2.13984200
C	0.17955900	0.56178400	2.63603700
H	0.14535300	-0.30812500	1.96183500
H	0.44754800	0.22350800	3.65089100
H	-0.82064000	1.01747500	2.66070500
C	2.59748300	0.99641000	2.04588700
H	3.29301700	1.70735600	1.56970300
H	2.97777400	0.77300100	3.05634800
H	2.60290300	0.06522300	1.46310900
C	1.17030600	2.85427600	2.97401800
H	1.43872100	2.62785900	4.01923500
H	1.89143600	3.59312300	2.58762500
H	0.16637400	3.29941200	2.94499800
Zn	-1.76990000	1.01695000	-0.47907200
C	-2.32960000	2.03448300	-2.18233700
H	-2.47683500	1.37042500	-3.05491800
H	-3.30771800	2.52543500	-2.02451900
C	-1.27863800	3.10111500	-2.50352700
H	-0.28905600	2.64585100	-2.69888600
H	-1.51065700	3.73306800	-3.38418300
H	-1.13219700	3.77180300	-1.64123800
C	-2.76292100	-0.35408900	0.73522000
H	-2.66508500	-0.24773800	1.82529600
H	-3.82573000	-0.52945300	0.51391000
I	-1.91458100	-2.36707400	0.40958100

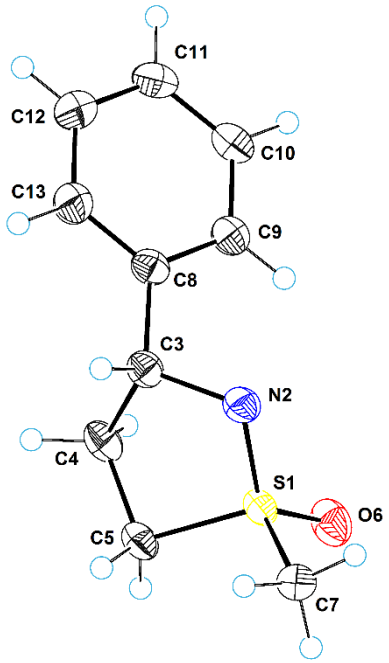
X-Ray Structure, Crystal Data and Structure Refinements for 1a, 2va, 2wa, Li-3a, and 4fa

(*R*)-*N*-[(1*R*)-1-Phenylethyl]methanesulfinamide **(1a)**



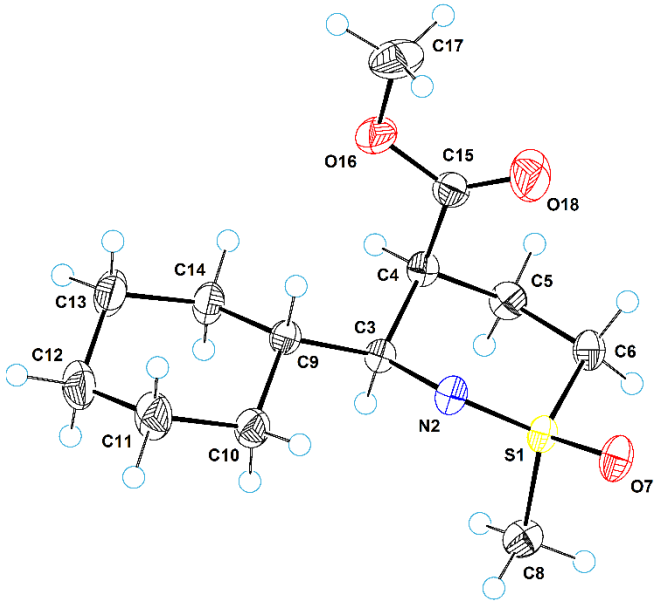
Empirical formula	$C_9H_{13}NOS$
Formula weight	183.28
Temperature/K	140.0(1)
Crystal system, space group	Tetragonal, $P4_12_12$
Unit cell dimensions	a/Å = 7.5986(2), α/° = 90
	b/Å = 7.5986(2), β/° = 90
	c/Å = 34.2923(12), γ/° = 90
Volume/Å^3	1979.99(10)
Z	8
ρ_{calc}g/cm^3	1.2296
μ/mm^{-1}	2.532
F(000)	784
Crystal size/mm^3	0.21 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184 Å)
2Θ max. for data collection/°	165.0
Index ranges	$-9 \le h \le 9$, $-8 \le k \le 9$, $-41 \le l \le 43$
Reflections collected	16795
Independent reflections	2170 [R_{int} = 0.0773, R_{sigma} = 0.0235]
Data/restraints/parameters	2170/0/115
Goodness-of-fit on F^2	1.031
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0349, wR_2 = 0.0763
Final R indexes [all data]	R_1 = 0.0388, wR_2 = 0.0826
Largest diff. peak/hole / e Å^{-3}	0.27/-0.36
Flack's x parameter	0.03(5)

(1*R*,3*R*)-1-Methyl-3-phenyl-4,5-dihydro-3*H*-1$\lambda^{4,2}$-thiazol-1-ium-1-olate (**2va**)



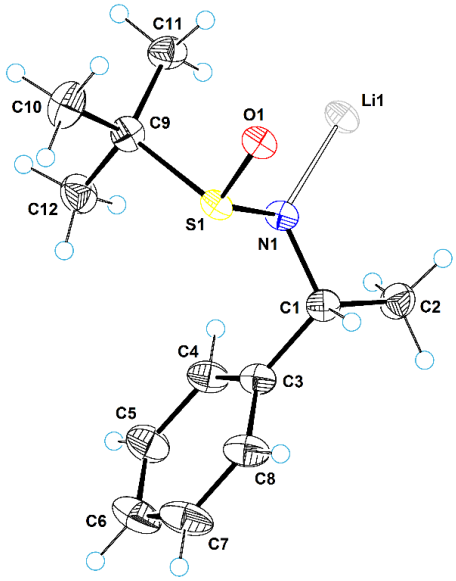
Empirical formula	$C_{10}H_{13}NOS$
Formula weight	195.29
Temperature/K	160.0(3)
Crystal system, space gropu	Monoclinic, $P2_1$
Unit cell dimensions	a/Å = 6.73890(7), α/°= 90
	b/Å = 6.34305(6), β/° = 100.7244(10)
	c/Å = 12.08776(13), γ/° = 90
Volume/Å^3	507.668(9)
Z	2
ρ_{calc}g/cm^3	1.2774
μ/mm^{-1}	2.504
F(000)	208
Crystal size/mm^3	0.22 × 0.13 × 0.04
Radiation	Cu Kα (λ = 1.54184 Å)
2Θ max. for data collection/°	160
Index ranges	-8 ≤ h ≤ 8, -8 ≤ k ≤ 8, -15 ≤ l ≤ 15
Reflections collected	7674
Independent reflections	2179 [R_{int} = 0.0226, R_{sigma} = 0.0169]
Data/restraints/parameters	2179/1/123
Goodness-of-fit on F^2	1.073
Final R indexes [I > 2σ(I)]	R_1 = 0.0311, wR_2 = 0.0866
Final R indexes [all data]	R_1 = 0.0312, wR_2 = 0.0868
Largest diff. peak/hole / e Å^{-3}	0.24/-0.25
Flack's x parameter	0.02(3)

Methyl
(1*R*,3*S*,4*S*)-3-cyclohexyl-1-methyl-1-oxo-3,4,5,6-tetrahydro-1$\lambda^{6,2}$-thiazine-4-carboxylate
(**2wa**)



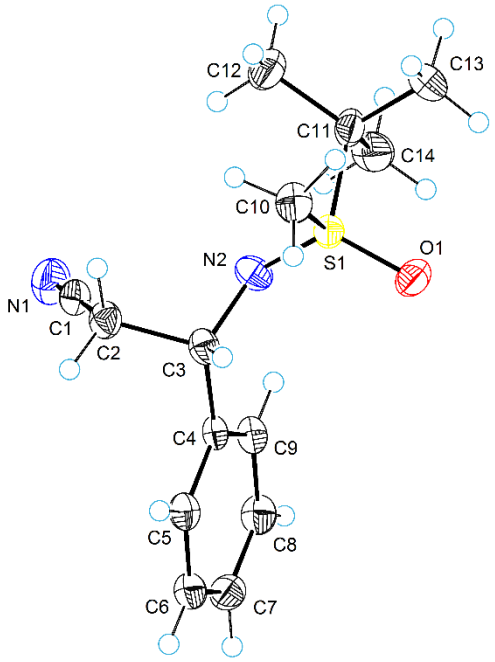
Empirical formula	$C_{13}H_{23}NO_3S$
Formula weight	273.38
Temperature/K	170.0(2)
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	a/Å = 5.48222(4), α/° = 90
	b/Å = 14.93350(11), β/° = 90
	c/Å = 17.88217(13), γ/° = 90
Volume/Å^3	1463.990(18)
Z	4
ρ_{calc}g/cm^3	1.240
μ/mm^{-1}	1.978
F(000)	592.0
Crystal size/mm^3	0.23 × 0.06 × 0.04
Radiation	CuKα (λ = 1.54184 Å)
2Θ max. for data collection/°	160
Index ranges	$-5 \le h \le 6$, $-18 \le k \le 19$, $-22 \le l \le 22$
Reflections collected	14597
Independent reflections	3179 [R_{int} = 0.0214, R_{sigma} = 0.0169]
Data/restraints/parameters	3179/0/174
Goodness-of-fit on F^2	1.029
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0254, wR_2 = 0.0679
Final R indexes [all data]	R_1 = 0.0256, wR_2 = 0.0681
Largest diff. peak/hole / e Å^{-3}	0.29/-0.22
Flack's x parameter	0.002(4)

(*S*)-*N*-Lithio-2-methyl-*N*-[(1*R*)-1-phenylethyl]propane-2-sulfinamide (**Li-3a**)



Empirical formula	$C_{12}H_{18}LiNOS$
Formula weight	231.29
Temperature/K	155.0(1)
Crystal system, space group	Monoclinic, $P2_1$
Unit cell dimensions	a/Å = 8.4381(3), α/° = 90
	b/Å = 5.4756(2), β/° = 103.119(4)
	c/Å = 13.8664(5), γ/° = 90
Volume/Å^3	623.96(4)
Z	2
ρ_{calc}g/cm^3	1.2310
μ/mm^{-1}	2.098
F(000)	248
Crystal size/mm^3	0.11 × 0.08 × 0.01
Radiation	Cu Kα (λ = 1.54184 Å)
2Θ max. for data collection/°	160
Index ranges	$-10 \le h \le 10$, $-6 \le k \le 5$, $-17 \le l \le 17$
Reflections collected	5357
Independent reflections	2142 [R_{int} = 0.0468, R_{sigma} = 0.0541]
Data/restraints/parameters	2142/1/153
Goodness-of-fit on F^2	1.050
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0426, wR_2 = 0.1096
Final R indexes [all data]	R_1 = 0.0456, wR_2 = 0.1131
Largest diff. peak/hole / e Å^{-3}	0.49/-0.20
Flack's x parameter	0.02(3)

(3*S*)-3-{[(*S*)-*tert*-Butyl(methyl)oxo-λ^6-sulfanylidene]amino}-3-phenyl propanenitrile (**4fa**)



Empirical formula	$C_{14}H_{20}N_2OS$
Formula weight	264.38
Temperature/K	140.0(1)
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	a/Å = 6.1844(2), α/° = 90
	b/Å = 8.2409(2), β/° = 90
	c/Å = 28.5035(7), γ/° = 90
Volume/Å^3	1452.68(7)
Z	4
ρ_{calc}g/cm^3	1.209
μ/mm^{-1}	1.898
F(000)	568.0
Crystal size/mm^3	0.22 × 0.09 × 0.07
Radiation	CuKα (λ = 1.54184 Å)
2Θ max. for data collection/°	176.0
Index ranges	$-7 \le h \le 7$, $-10 \le k \le 10$, $-29 \le l \le 36$
Reflections collected	12582
Independent reflections	3152 [R_{int} = 0.0754, R_{sigma} = 0.0296]
Data/restraints/parameters	3152/0/171
Goodness-of-fit on F^2	1.179
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0421, wR_2 = 0.1034
Final R indexes [all data]	R_1 = 0.0461, wR_2 = 0.1095
Largest diff. peak/hole / e Å^{-3}	0.40/-0.81
Flack's x parameter	0.006(8)

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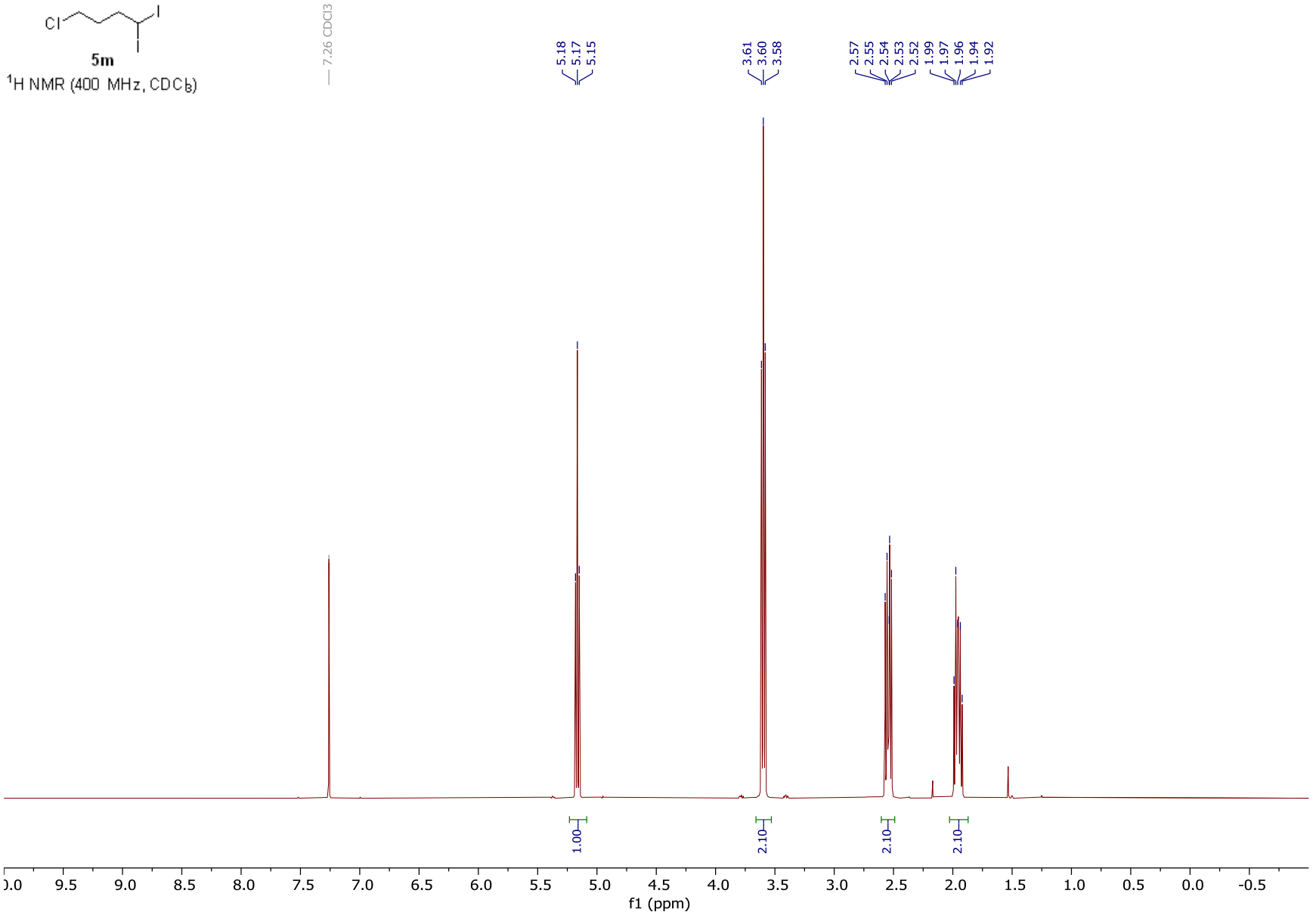
NMR spectra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I
5m
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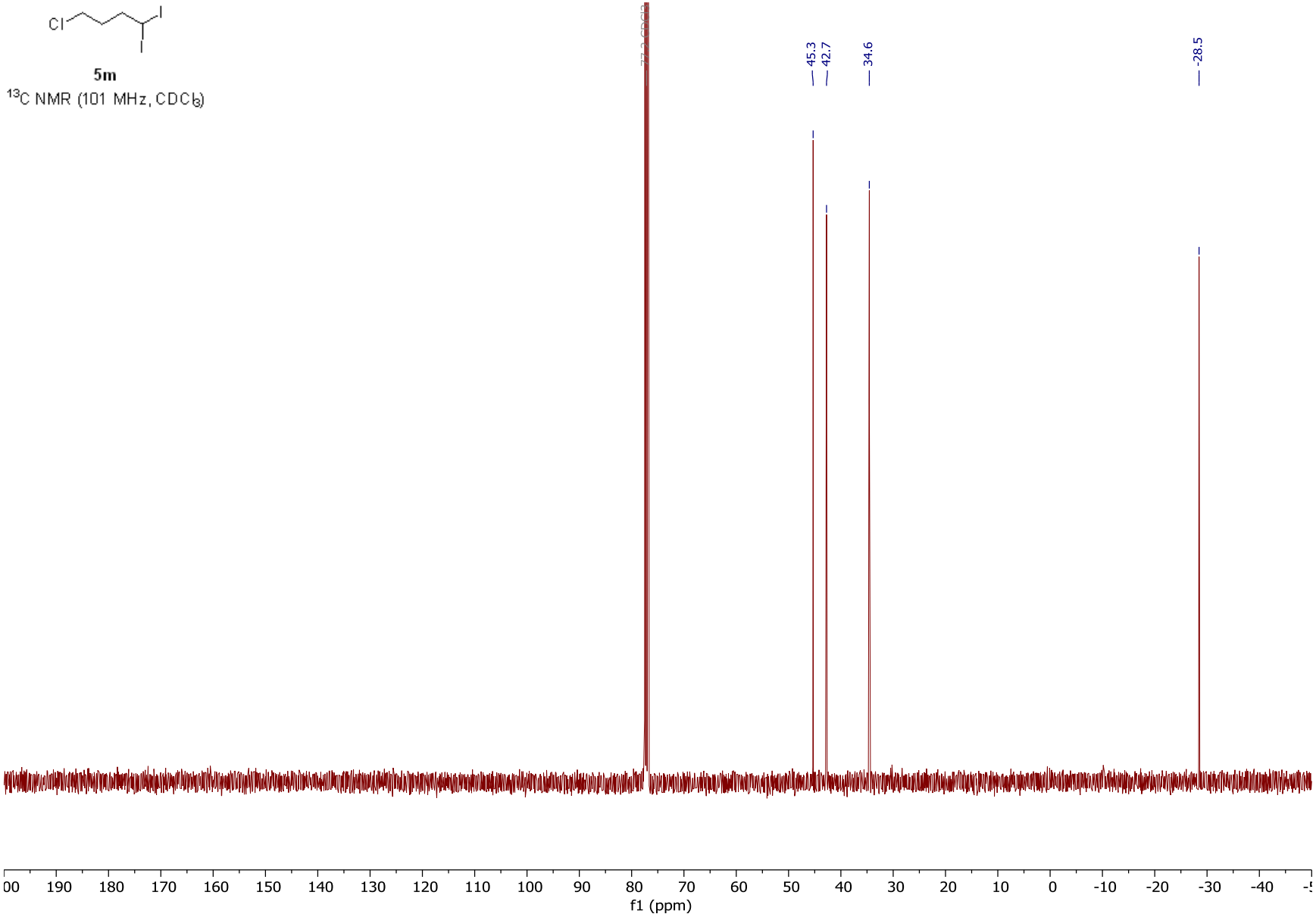
5.18
5.17
5.15
3.61
3.60
3.58
2.57
2.55
2.54
2.53
2.52
1.99
1.97
1.96
1.94
1.92
1.00
2.10
2.10
2.10
f1 (ppm)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I
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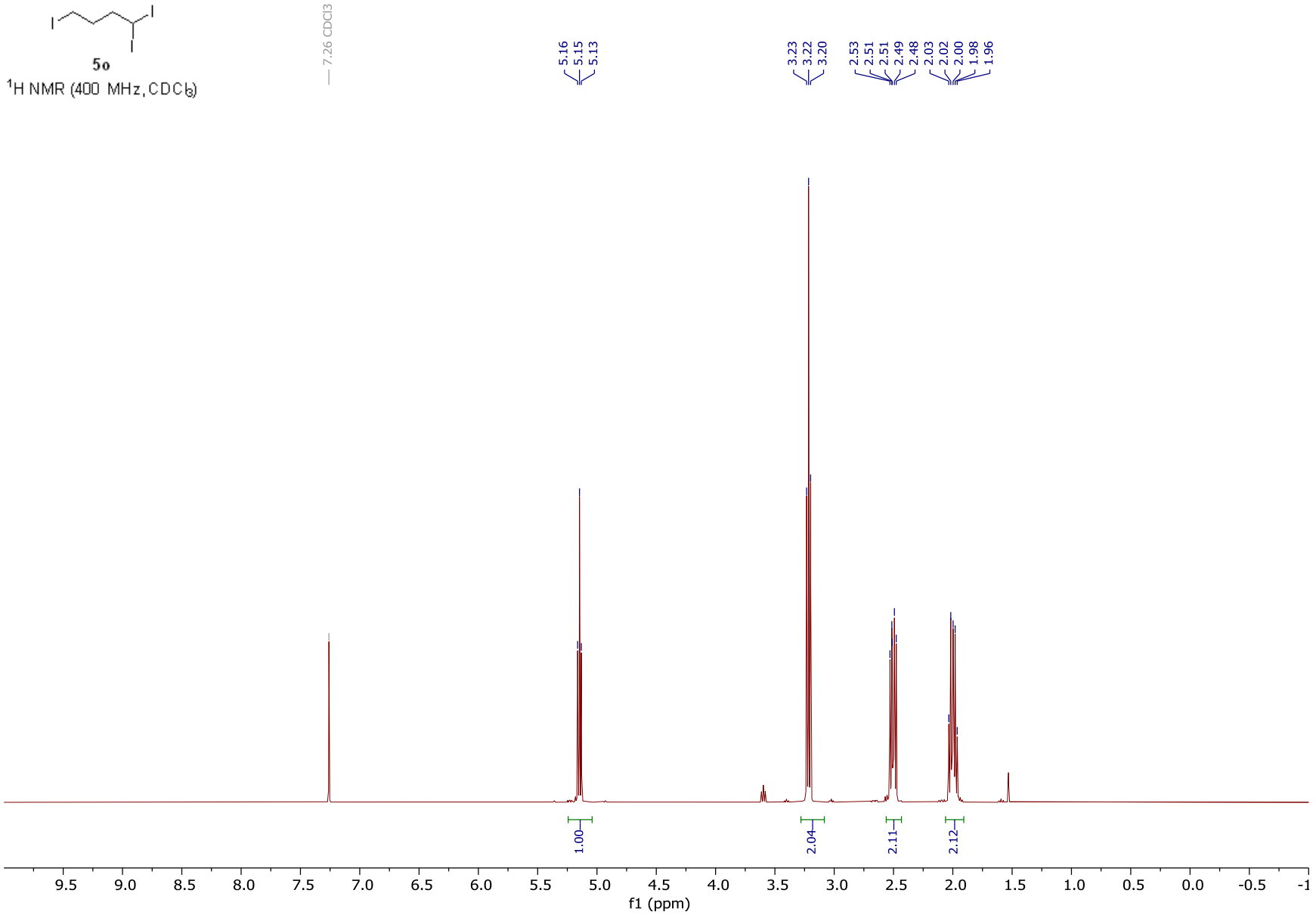
34.6
-28.5
f1 (ppm)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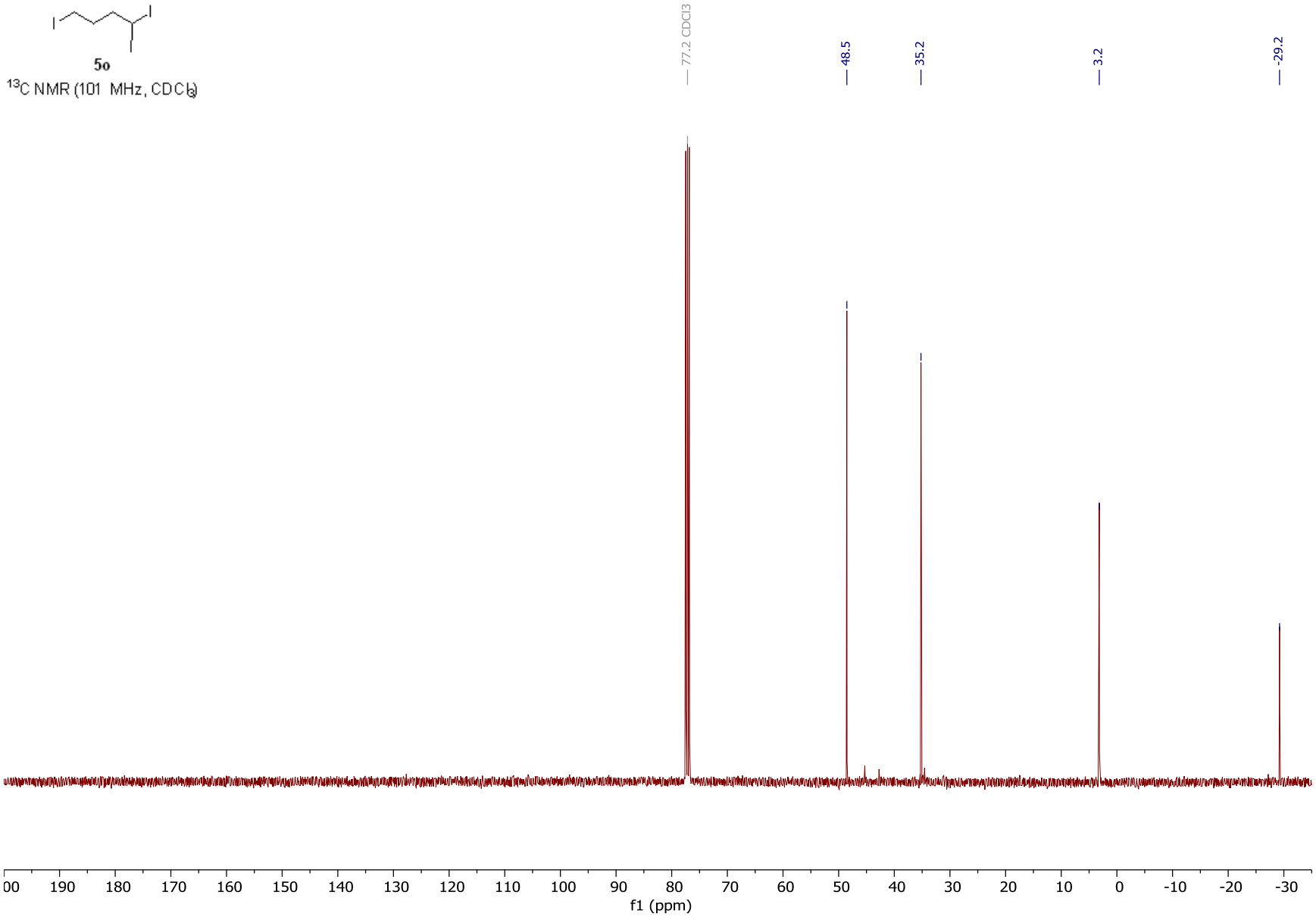
^{1}H NMR (400 MHz, $CDCl_3$)
7.26 CDCl3
5.16
5.15
5.13
3.23
3.22
3.20
2.53
2.51
2.51
2.49
2.48
2.03
2.02
2.00
1.98
1.96
1.00
2.04
2.11
2.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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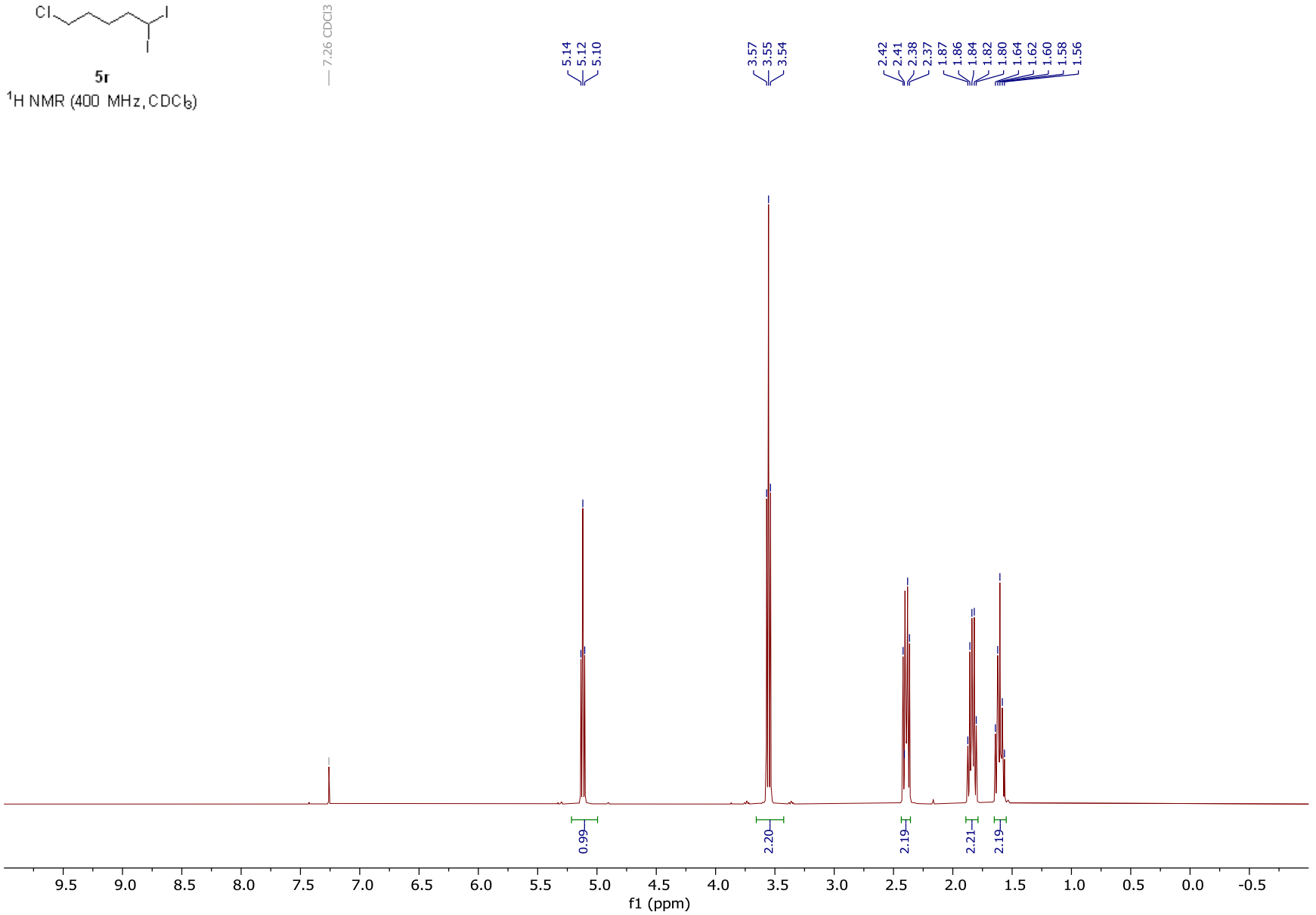
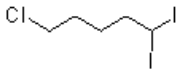
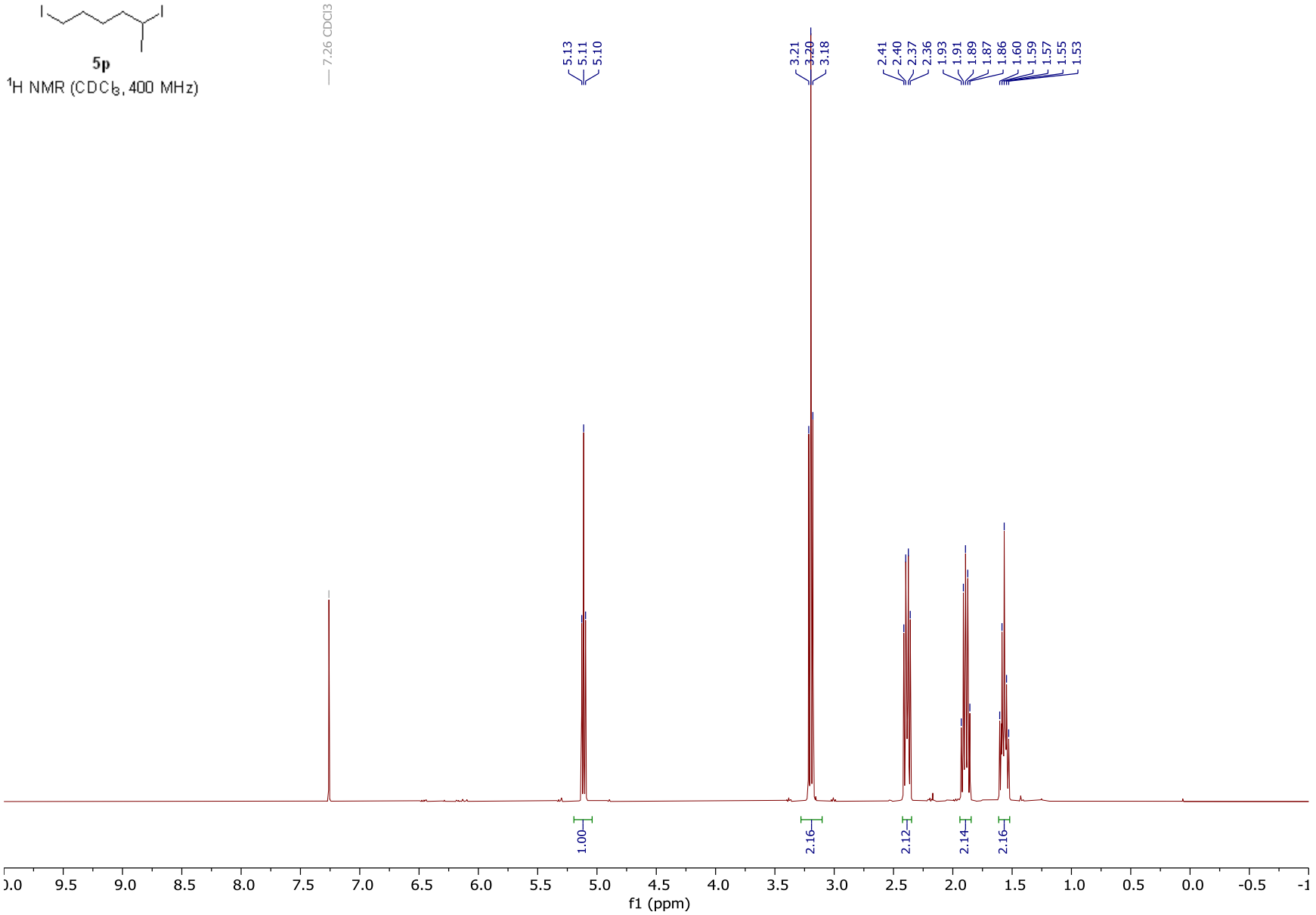
35.2
3.2
-29.2
f1 (ppm)


Cl
I
I
5r
^{1}H NMR (400 MHz, $CDCl_3$)
7.26 CDCl3
5.14
5.12
5.10
3.57
3.55
3.54
2.42
2.41
2.38
2.37
1.87
1.86
1.84
1.82
1.80
1.64
1.62
1.60
1.58
1.56
0.99
2.20
2.19
2.21
2.19
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



5r

^{13}C NMR (101 MHz, $CDCl_3$)


5p
^{1}H NMR (CDCl$_3$, 400 MHz)
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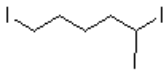
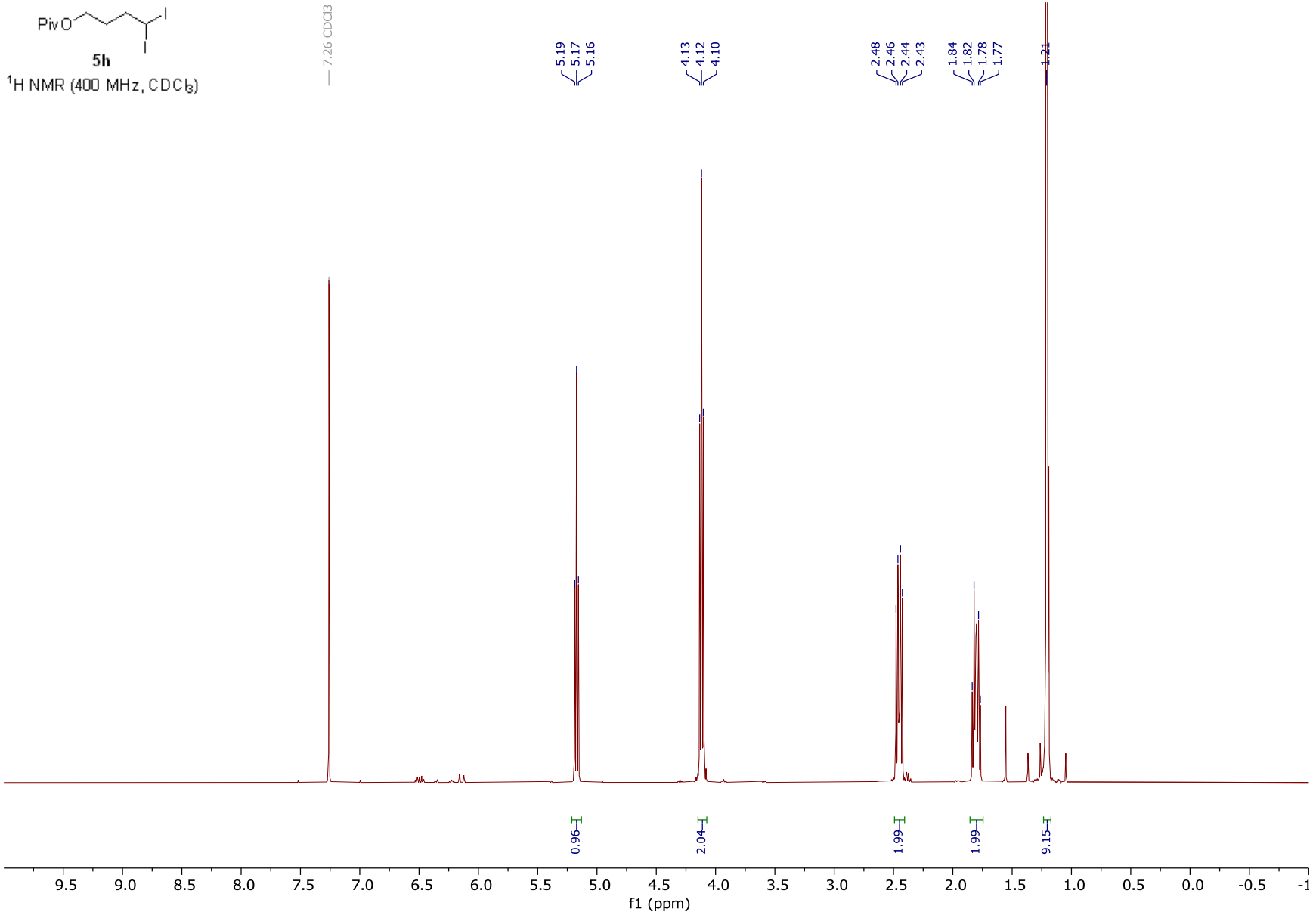
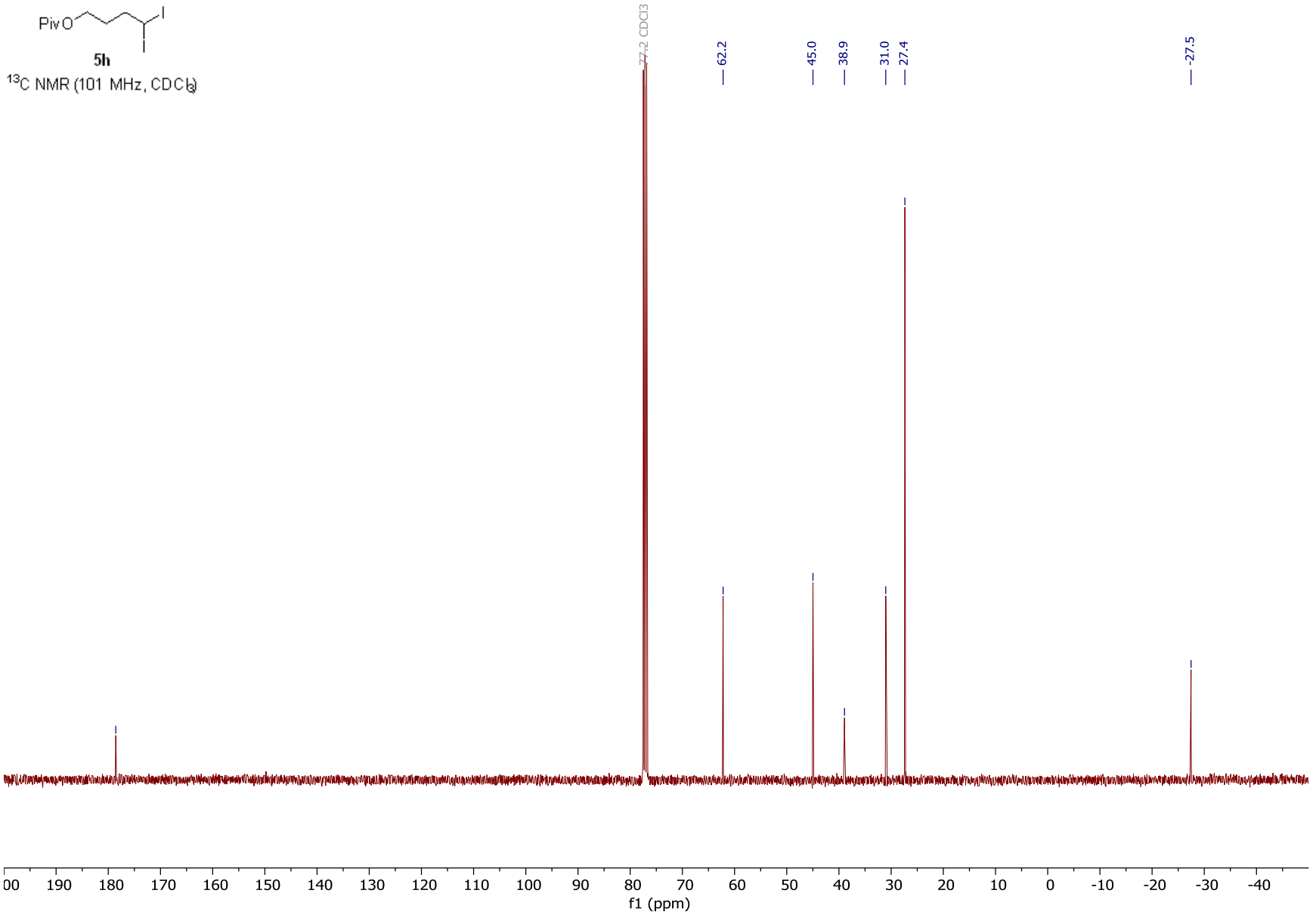
5.13
5.11
5.10
3.21
3.20
3.18
2.41
2.40
2.37
2.36
1.93
1.91
1.89
1.87
1.86
1.60
1.59
1.57
1.55
1.53
1.00
2.16
2.12
2.14
2.16
f1 (ppm)

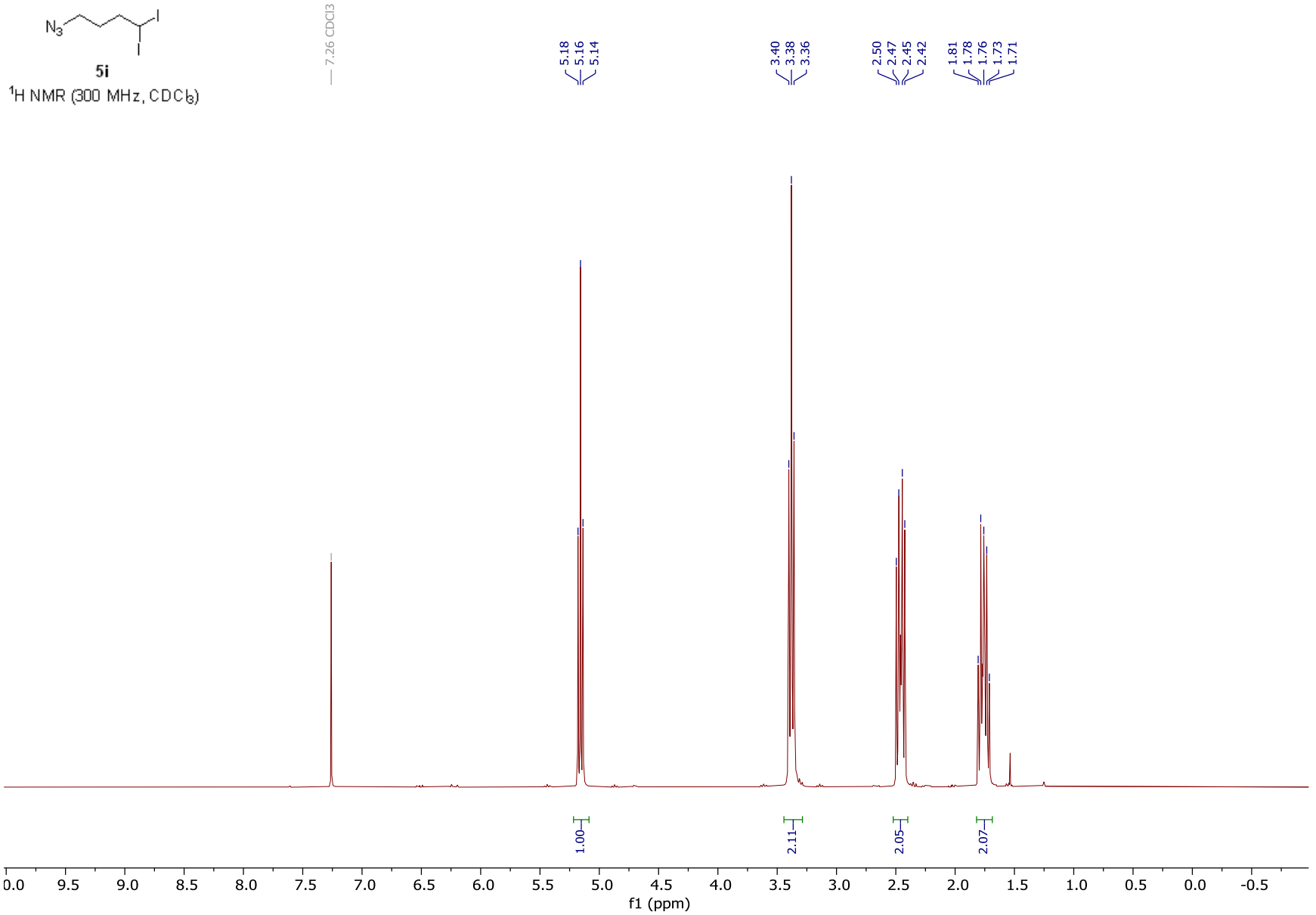


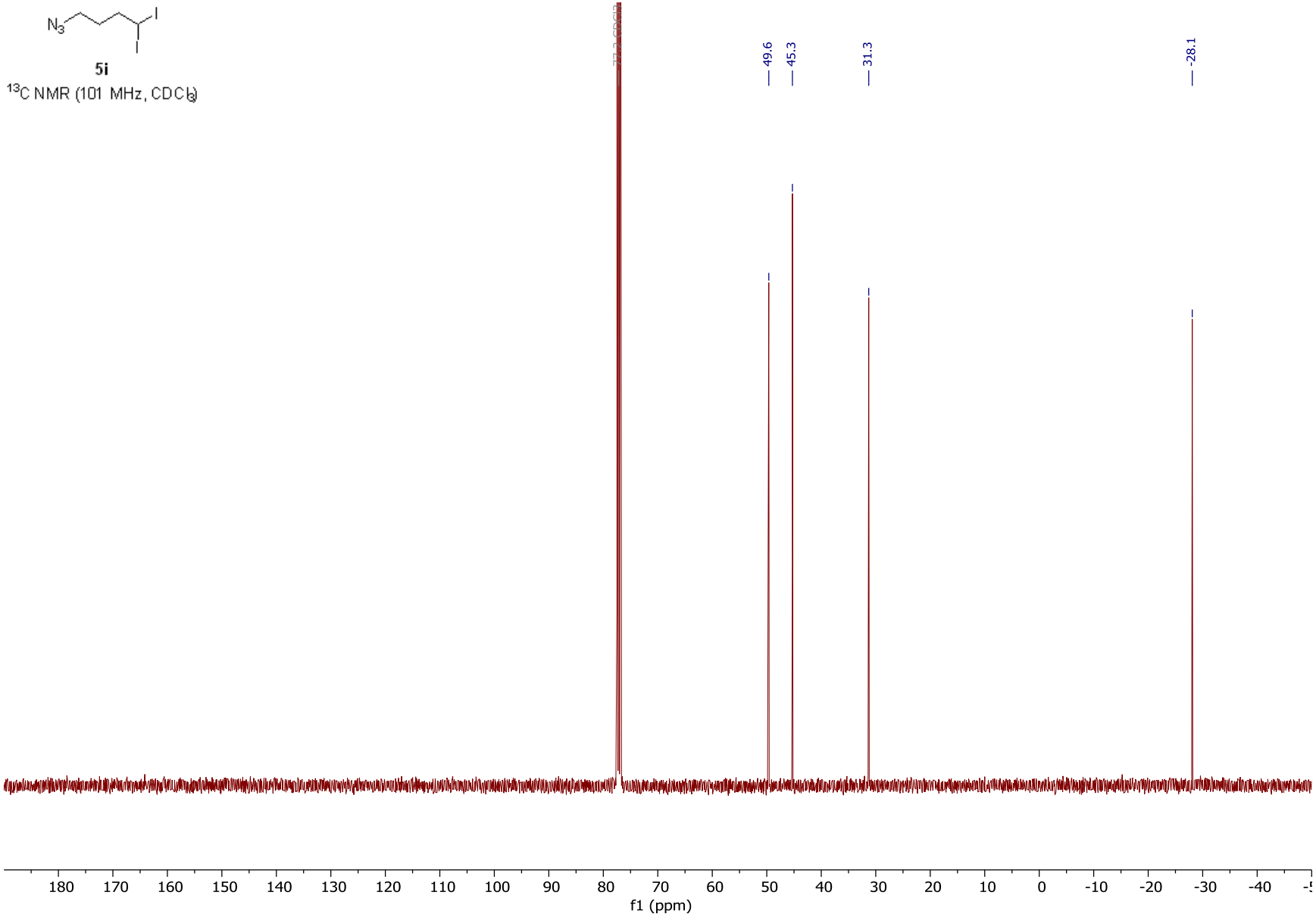
5p

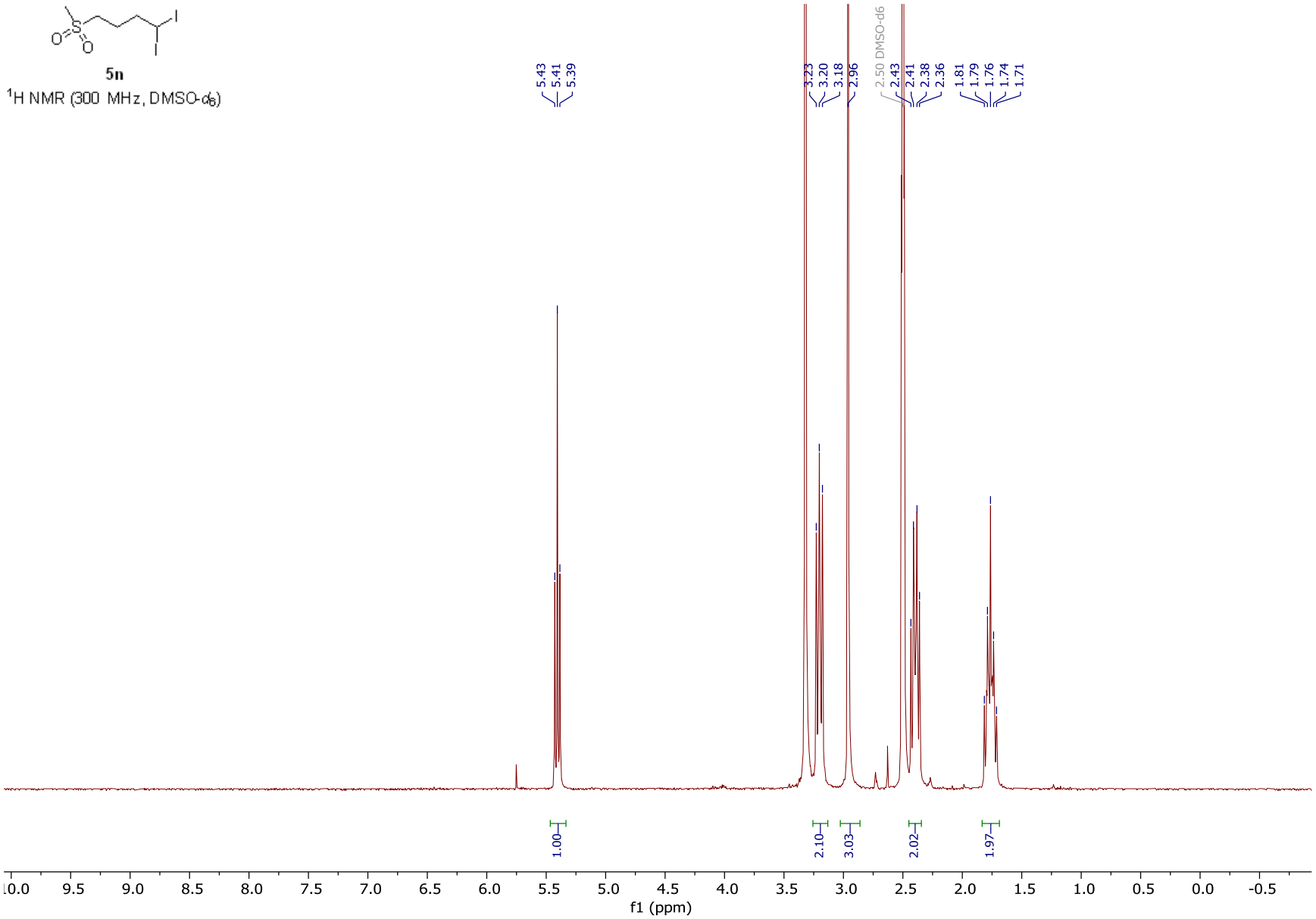
^{13}C NMR ($CDCl_3$, 101 MHz)

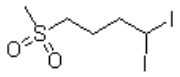

PivO
I
I
5h
^{1}H NMR (400 MHz, $CDCl_3$)
7.26 CDCl3
5.19
5.17
5.16
4.13
4.12
4.10
2.48
2.46
2.44
2.43
1.84
1.82
1.78
1.77
1.21
0.96
2.04
1.99
1.99
9.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


PivO
I
5h
^{13}C NMR (101 MHz, CDCl$_3$)
77.2 CDCl3
62.2
45.0
38.9
31.0
27.4
-27.5
f1 (ppm)


N3
I
I
5i
1H NMR (300 MHz, CDCl3)
7.26 CDCl3
5.18
5.16
5.14
3.40
3.38
3.36
2.50
2.47
2.45
2.42
1.81
1.78
1.76
1.73
1.71
1.00
2.11
2.05
2.07
f1 (ppm)

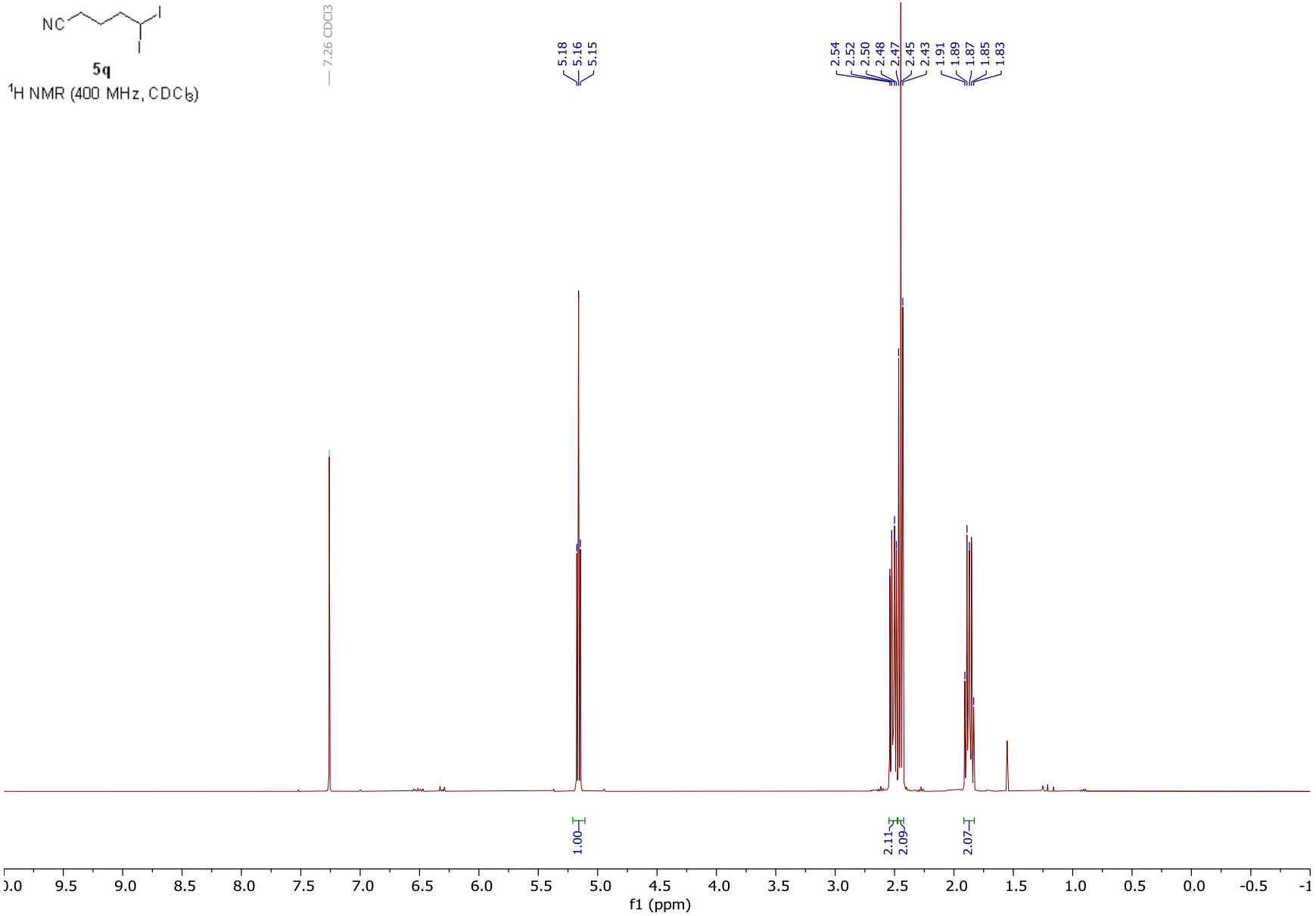

N3
I
I
5i
13C NMR (101 MHz, CDCl3)
49.6
45.3
31.3
28.1
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

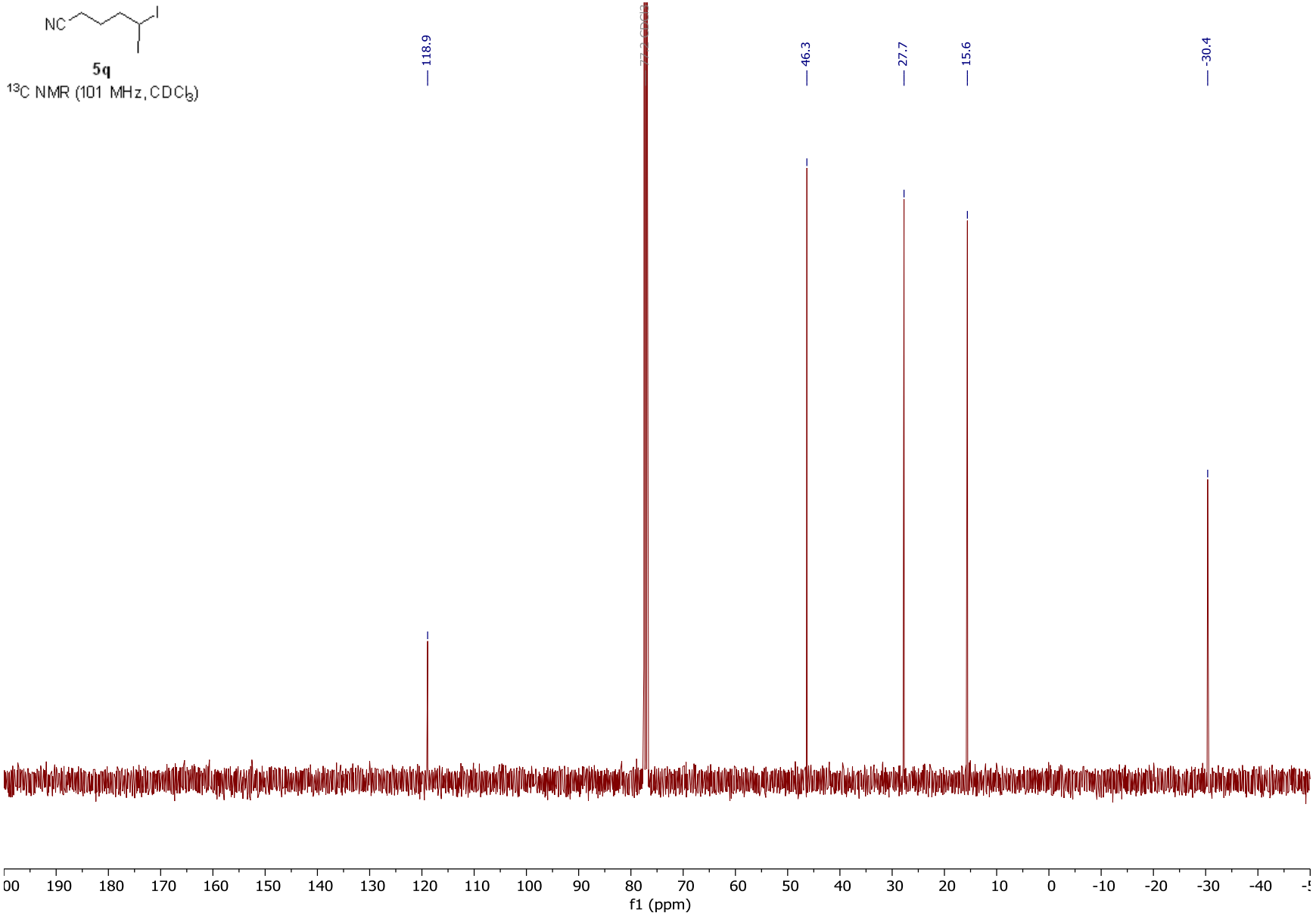

5n
1H NMR (300 MHz, DMSO-d6)
5.43
5.41
5.39
3.23
3.20
3.18
2.96
2.50 DMSO-d6
2.43
2.41
2.38
2.36
1.81
1.79
1.76
1.74
1.71
1.00
2.10
3.03
2.02
1.97
f1 (ppm)

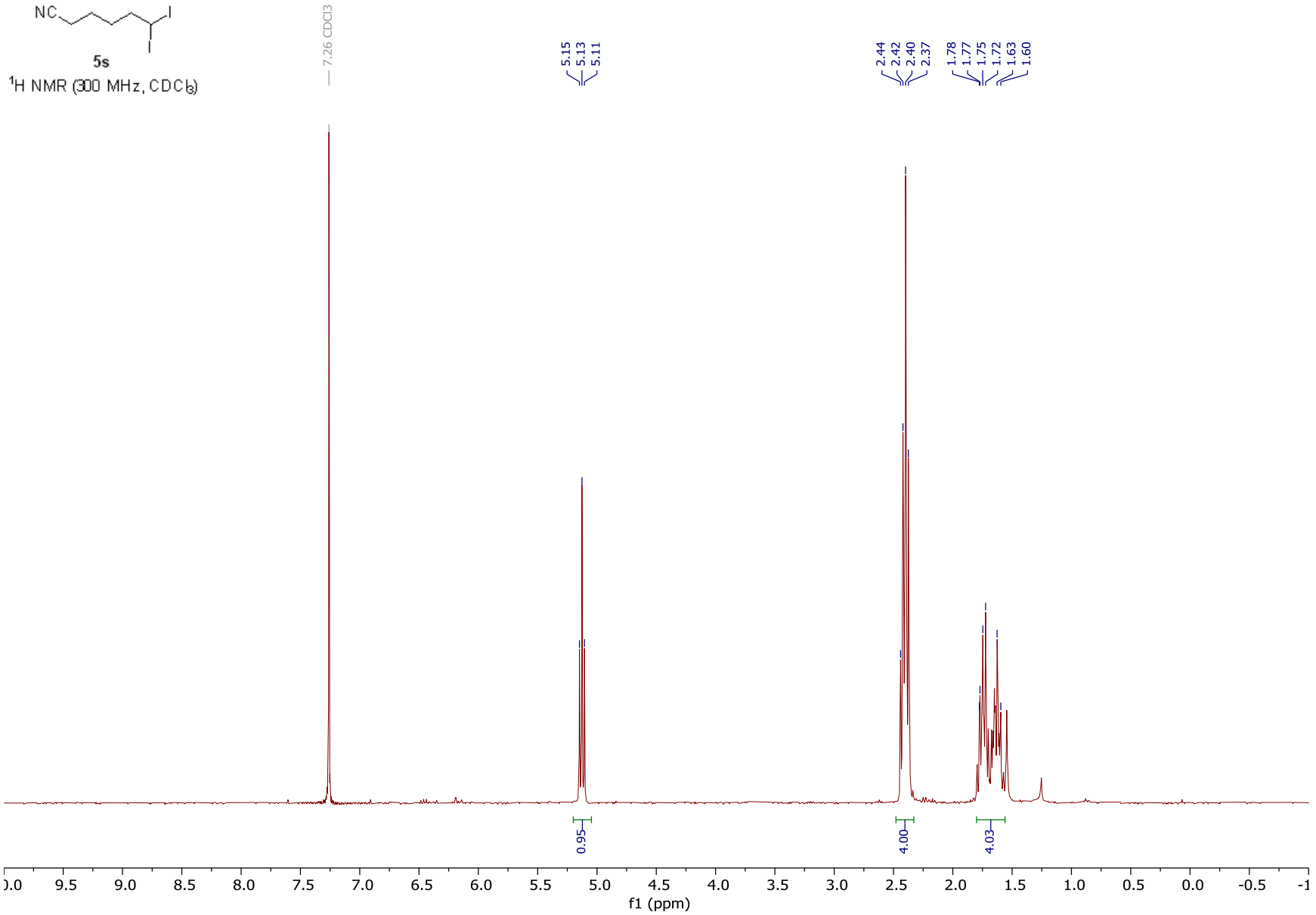


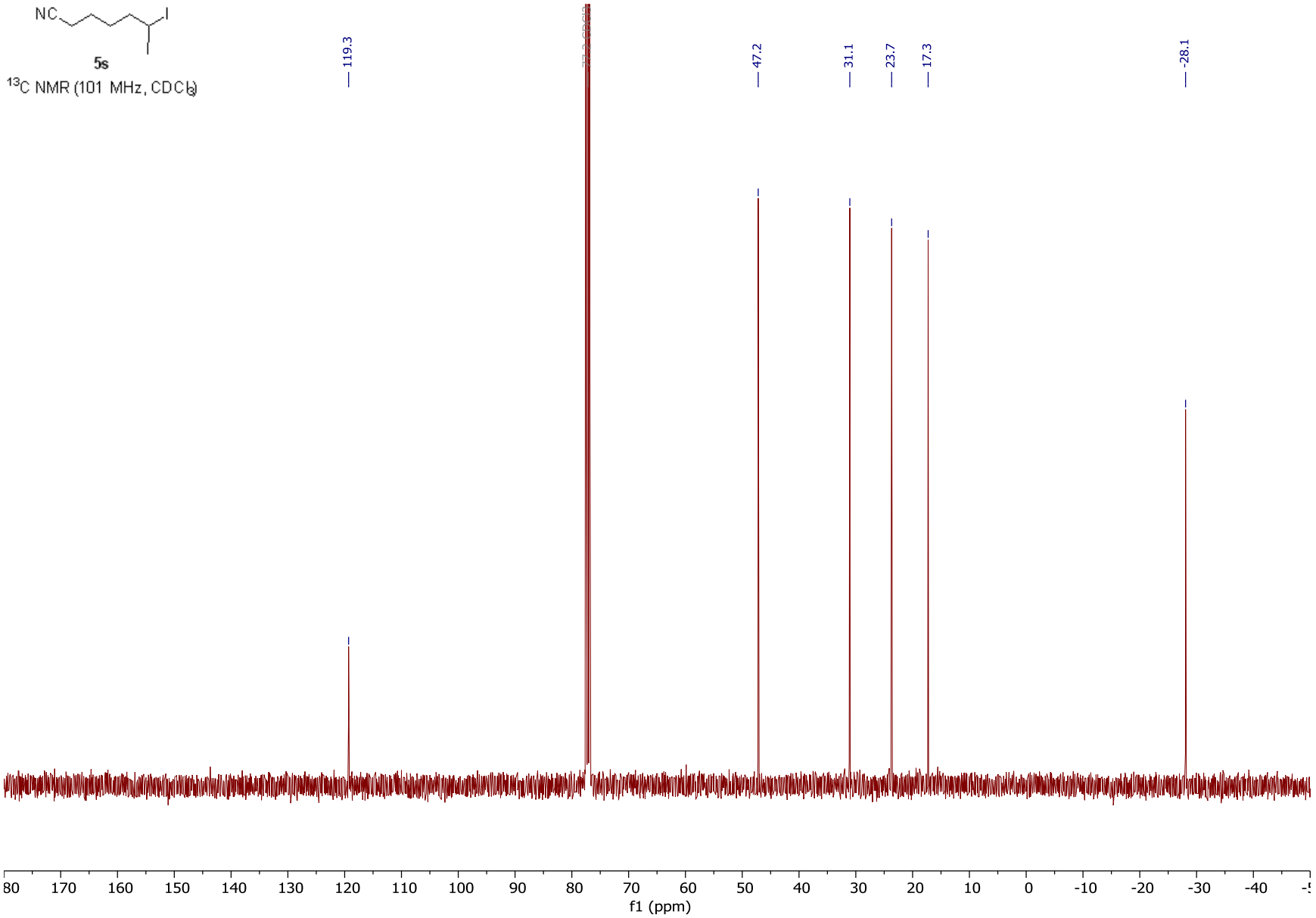
5n

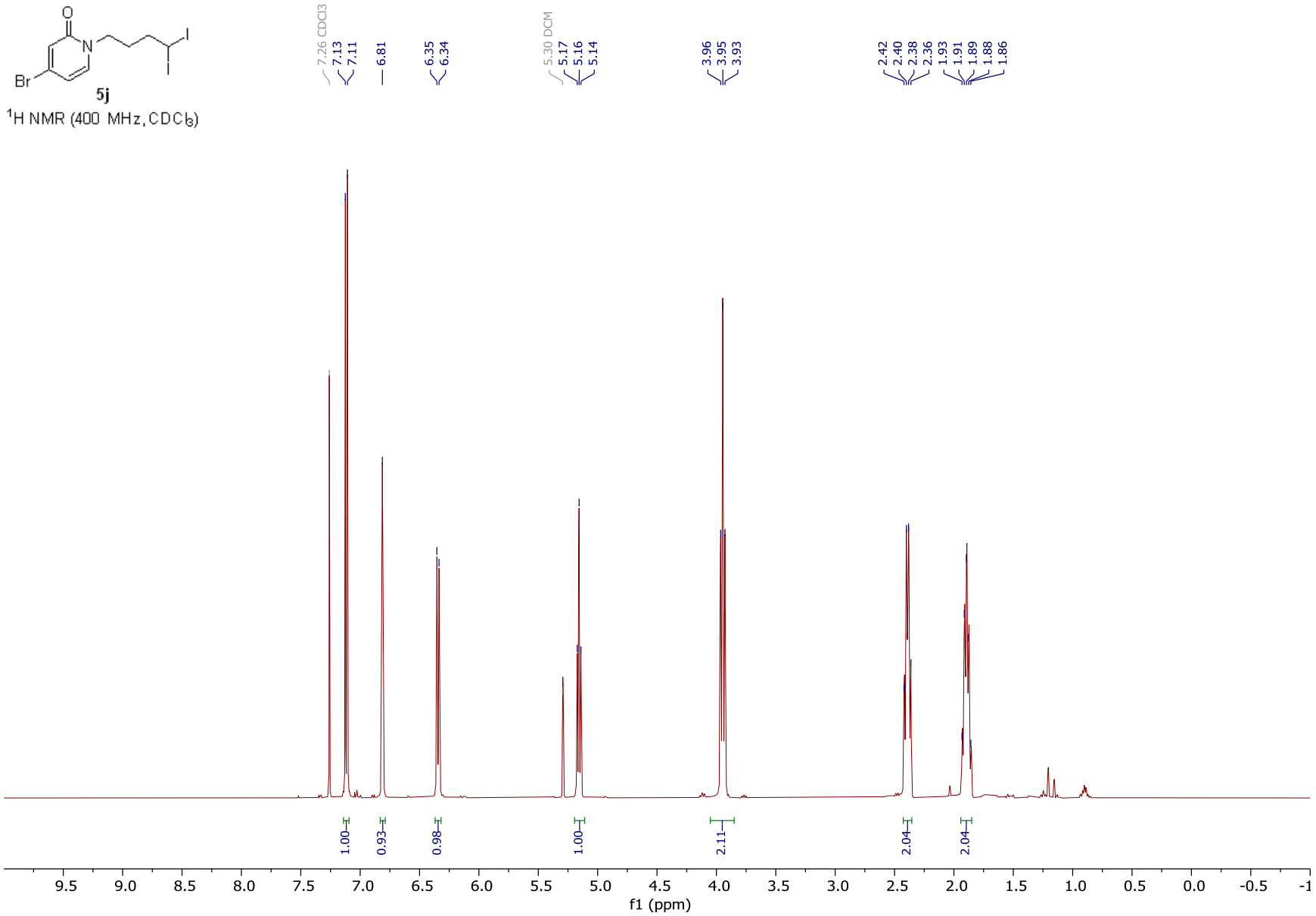
^{13}C NMR (101 MHz, DMSO-d_6)

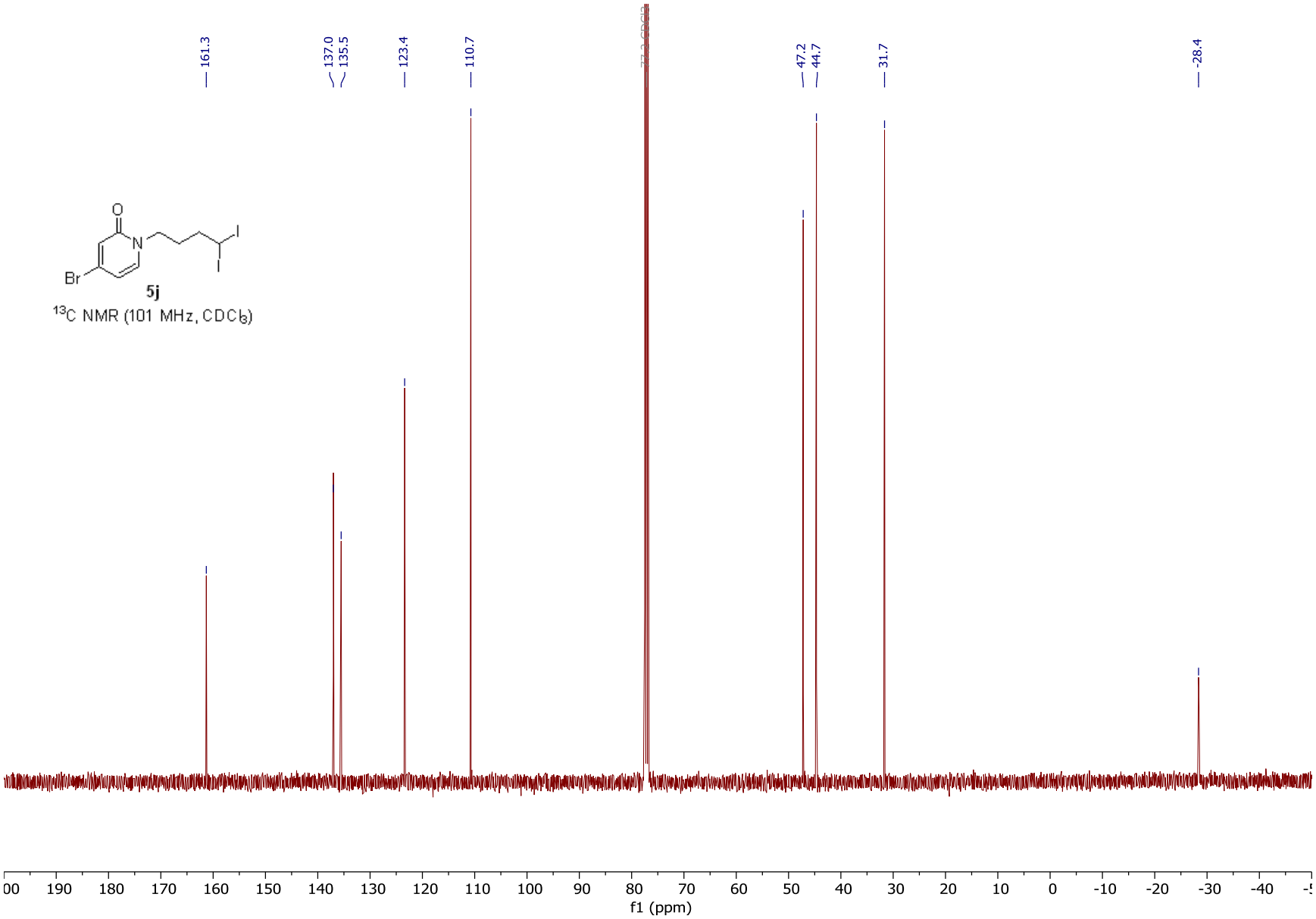

NC
I
I
5q
^{1}H NMR (400 MHz, CDCl$_3$)
7.26 CDCl3
5.18
5.16
5.15
2.54
2.52
2.50
2.48
2.47
2.45
2.43
1.91
1.89
1.87
1.85
1.83
1.00
2.11
2.09
2.07
f1 (ppm)

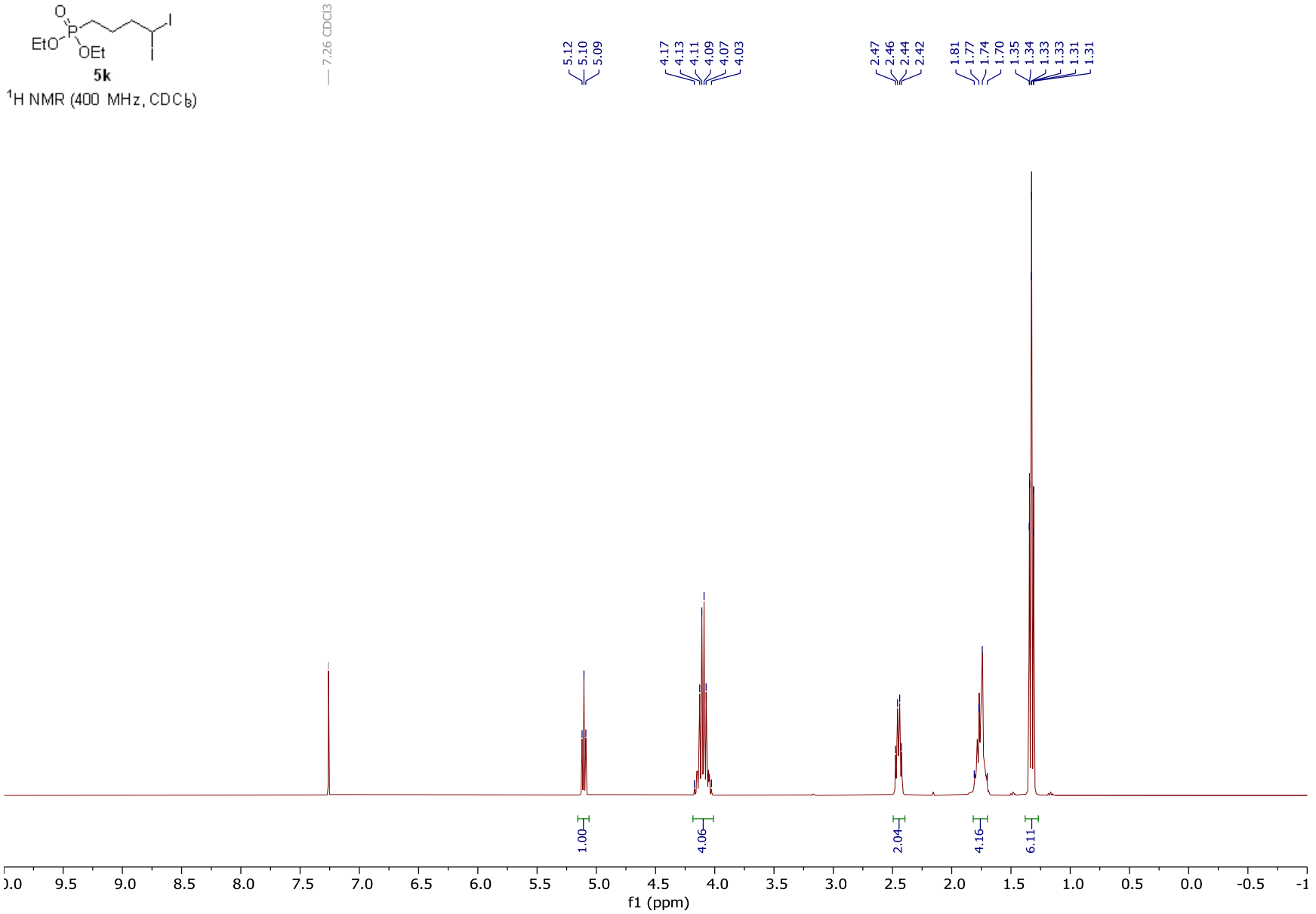

NC
I
5q
^{13}C NMR (101 MHz, $CDCl_3$)
118.9
77.2
46.3
27.7
15.6
-30.4
f1 (ppm)

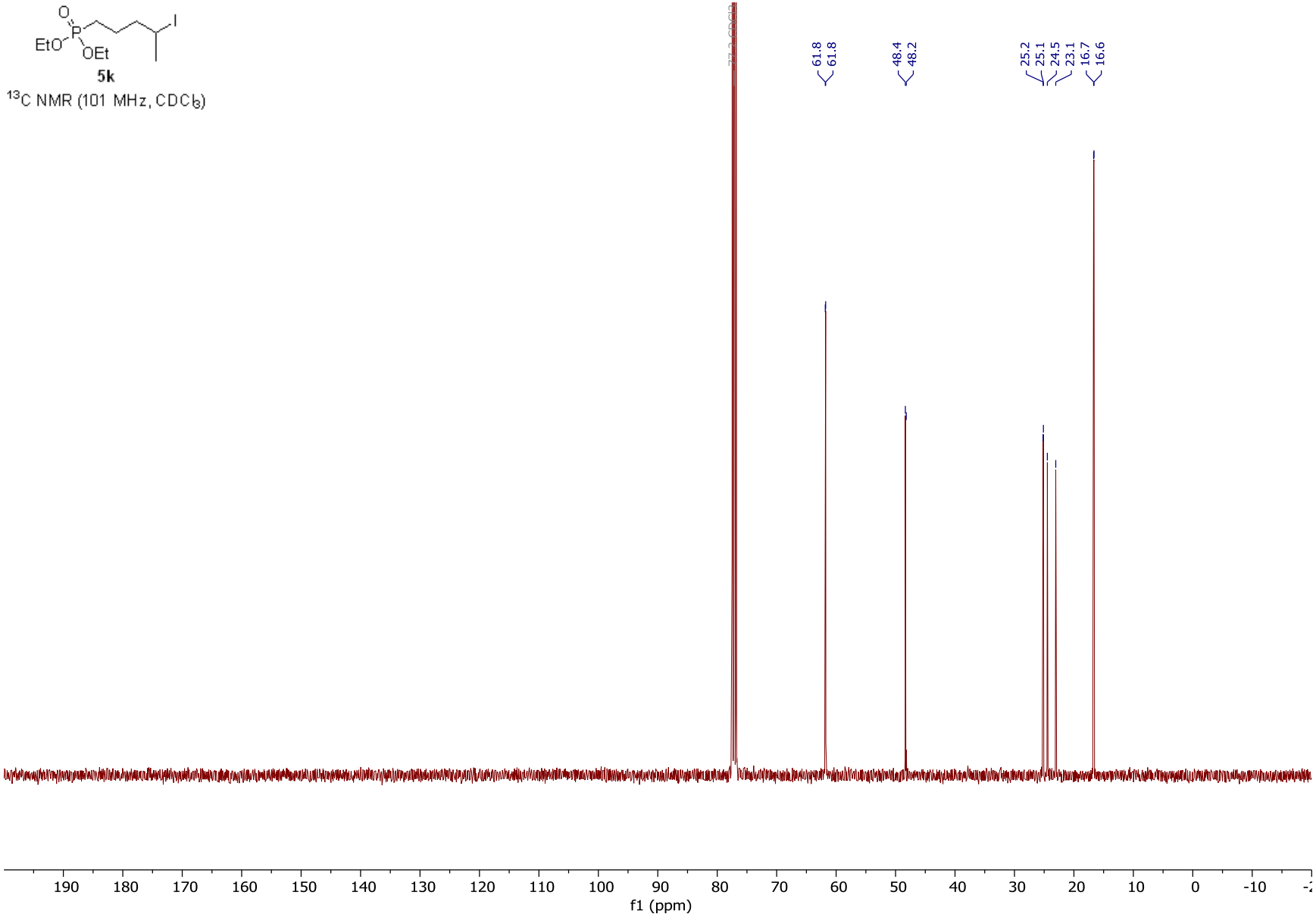

NC
I
I
5s
^{1}H NMR (300 MHz, $CDCl_3$)
7.26 CDCl3
5.15
5.13
5.11
2.44
2.42
2.40
2.37
1.78
1.77
1.75
1.72
1.63
1.60
0.95
4.00
4.03
f1 (ppm)

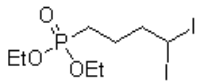

NC
I
5s
^{13}C NMR (101 MHz, $CDCl_3$)
119.3
77.2
47.2
31.1
23.7
17.3
-28.1
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


5j
^{1}H NMR (400 MHz, $CDCl_3$)
7.26 CDCl3
7.13
7.11
6.81
6.35
6.34
5.30 DCM
5.17
5.16
5.14
3.96
3.95
3.93
2.42
2.40
2.38
2.36
1.93
1.91
1.89
1.88
1.86
1.00
0.93
0.98
1.00
2.11
2.04
2.04
f1 (ppm)


161.3
137.0
135.5
123.4
110.7
77.3
47.2
44.7
31.7
-28.4
O
N
Br
I
I
5j
13C NMR (101 MHz, CDCl3)
f1 (ppm)

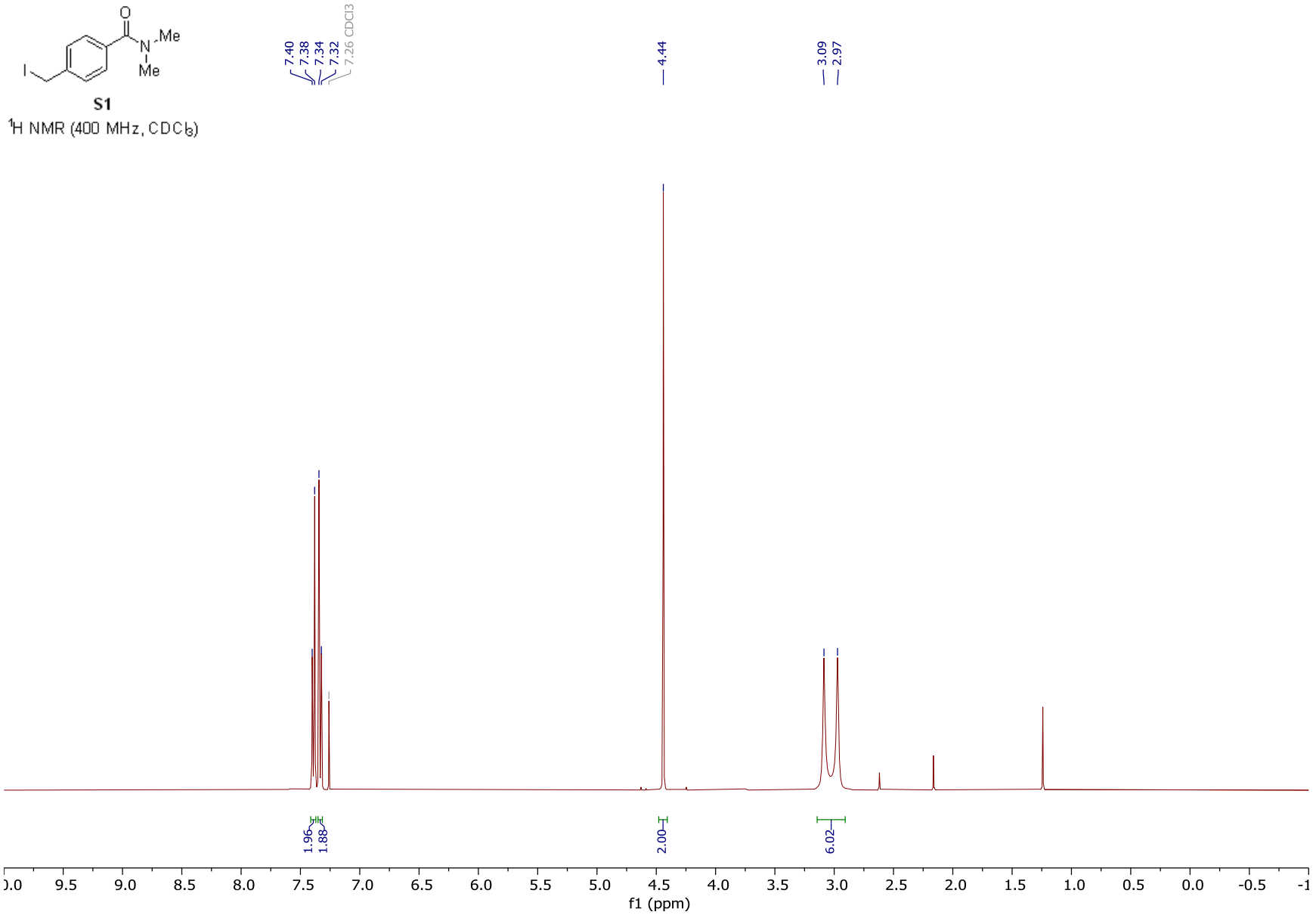

5k
1H NMR (400 MHz, CDCl3)
7.26 CDCl3
5.12
5.10
5.09
4.17
4.13
4.11
4.09
4.07
4.03
2.47
2.46
2.44
2.42
1.81
1.77
1.74
1.70
1.35
1.34
1.33
1.33
1.31
1.31
1.00
4.06
2.04
4.16
6.11
f1 (ppm)

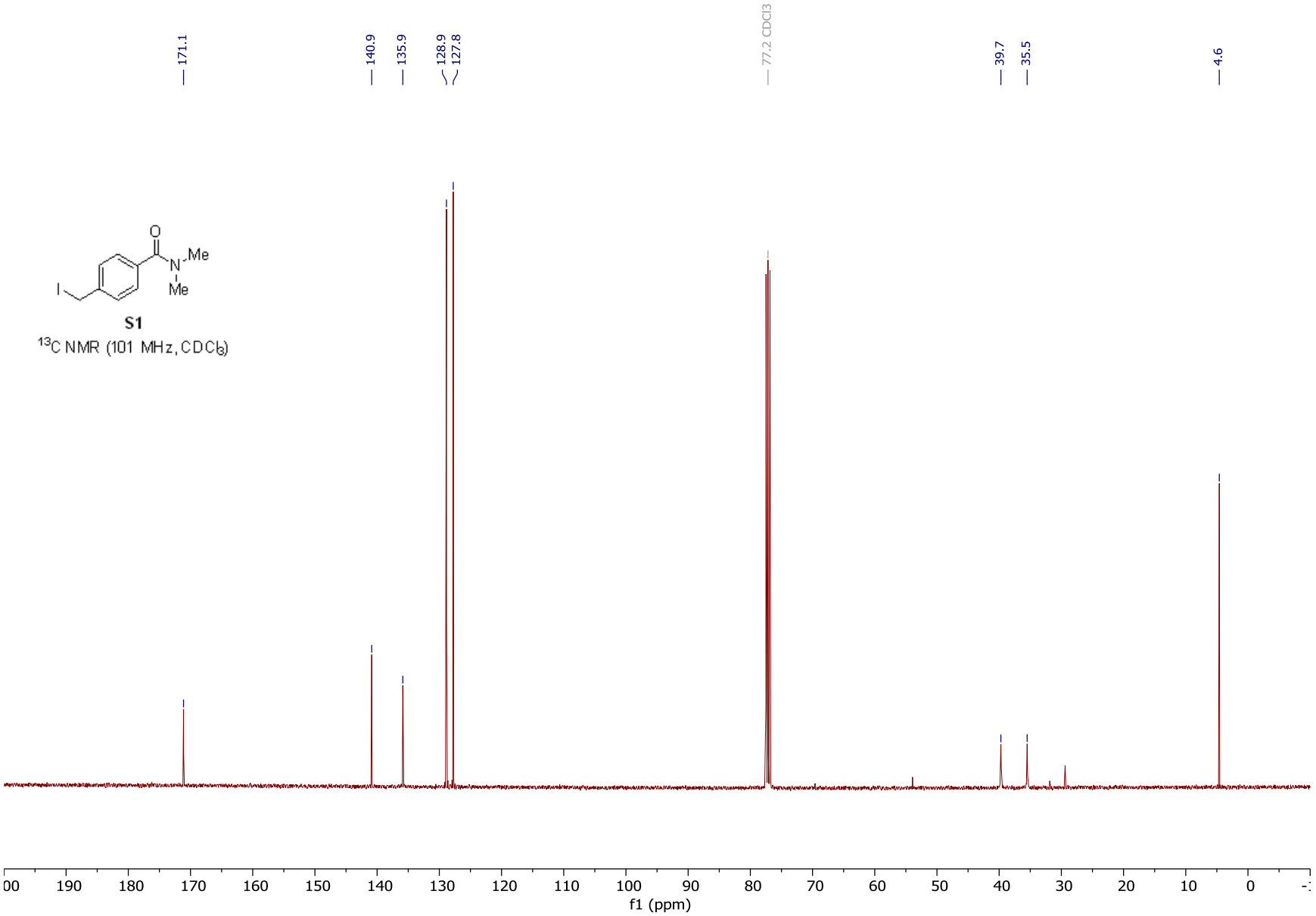

O
EtO
P
OEt
I
5k
^{13}C NMR (101 MHz, $CDCl_3$)
61.8
61.8
48.4
48.2
25.2
25.1
24.5
23.1
16.7
16.6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

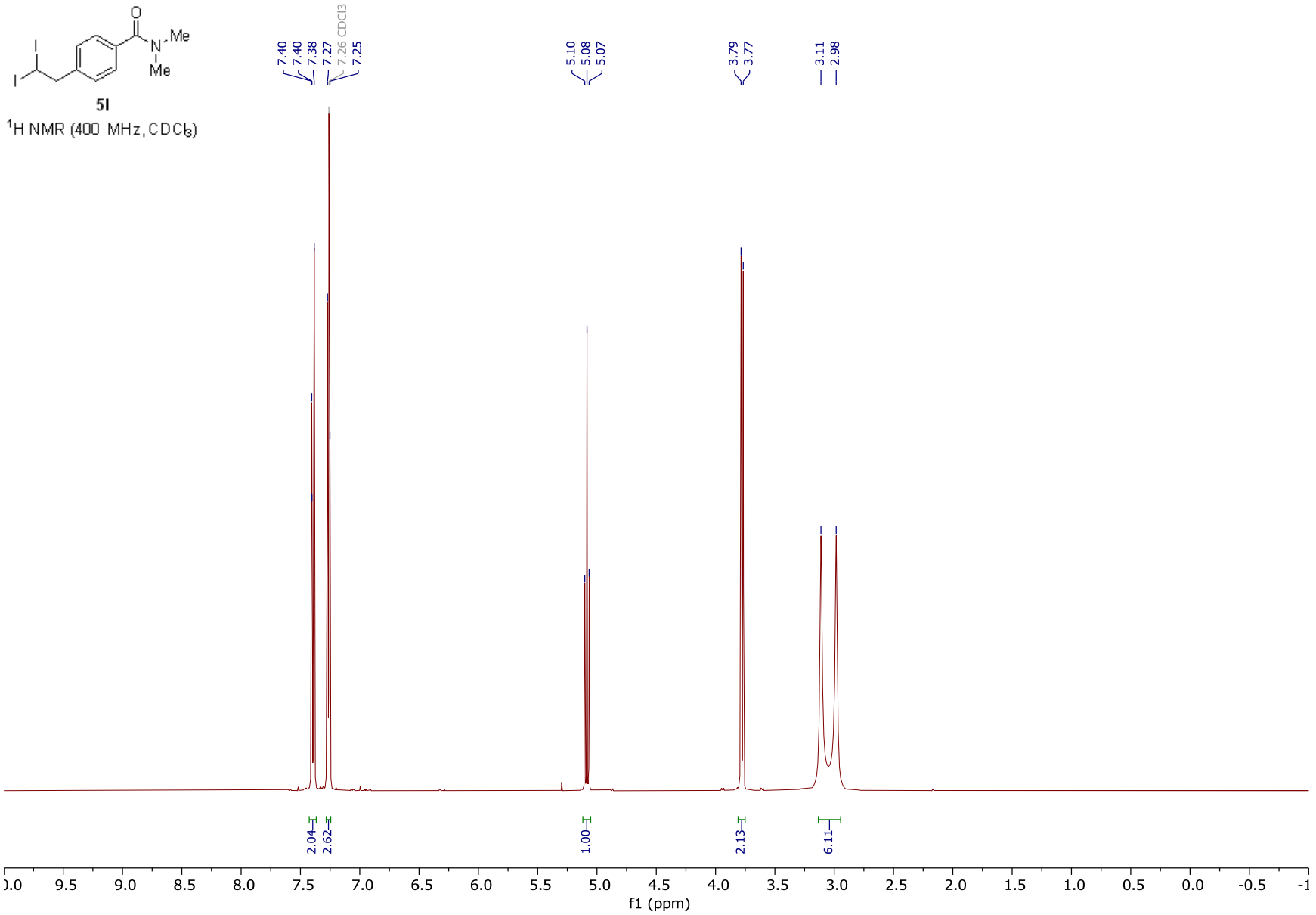


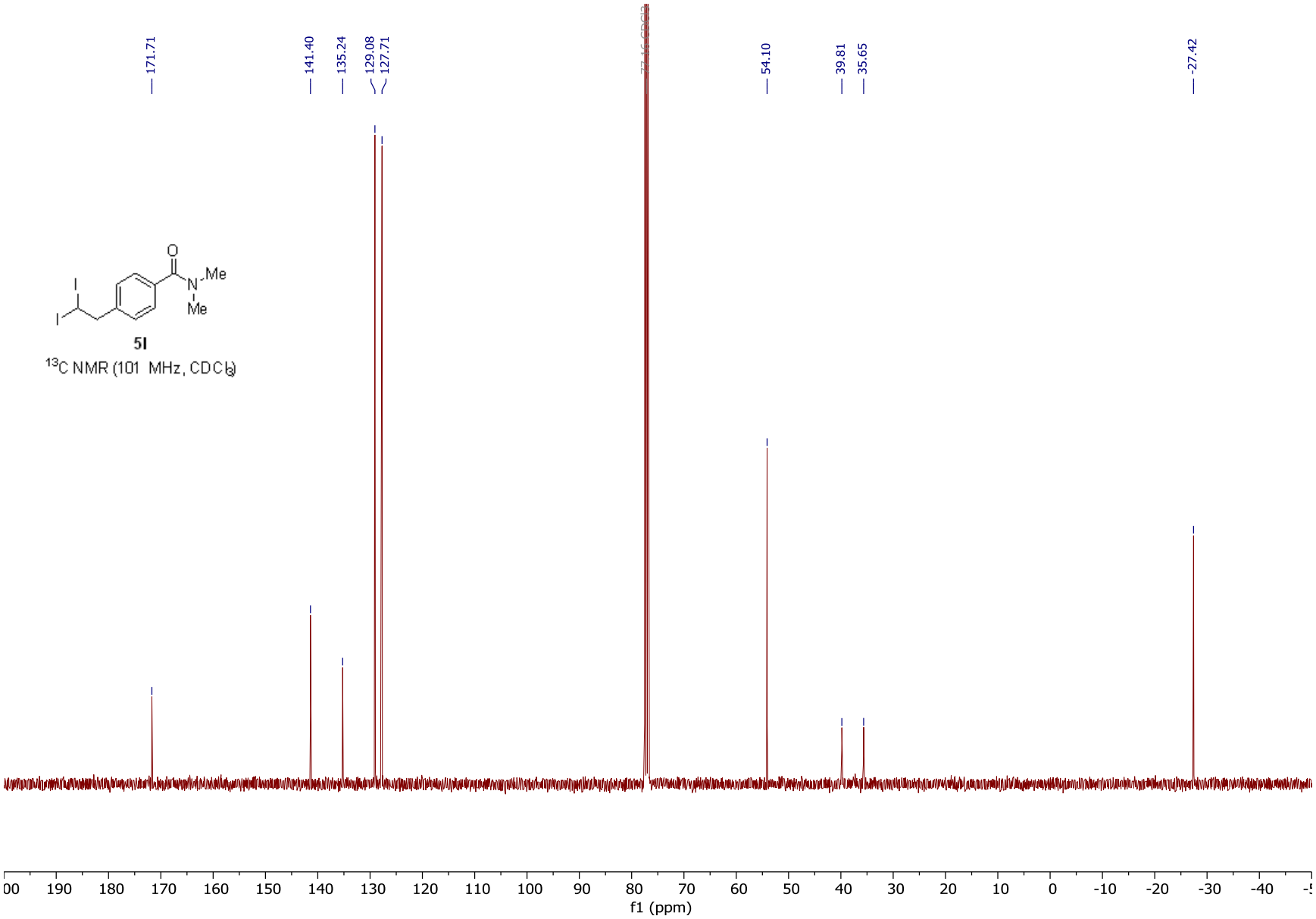
5k

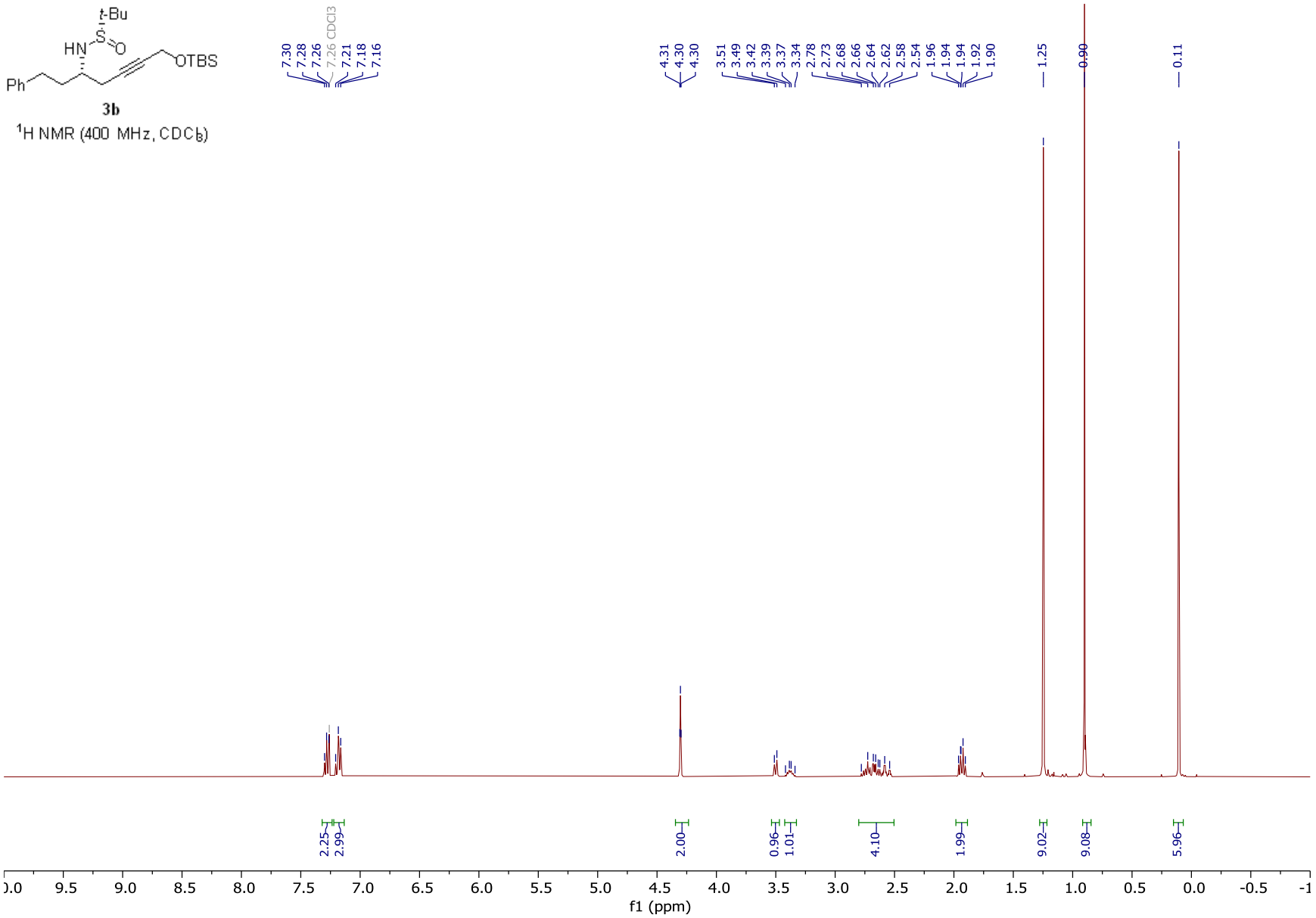
^{31}P NMR (162 MHz, $CDCl_3$)

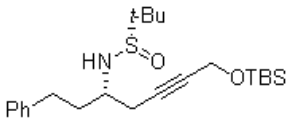

O
N
Me
Me
I
S1
^{1}H NMR (400 MHz, $CDCl_3$)
7.40
7.38
7.34
7.32
7.26 CDCl3
4.44
3.09
2.97
1.96
1.88
2.00
6.02
f1 (ppm)


171.1
140.9
135.9
128.9
127.8
77.2 CDCl3
39.7
35.5
4.6
O
N
Me
Me
I
S1
13C NMR (101 MHz, CDCl3)
f1 (ppm)


5l
^{1}H NMR (400 MHz, CDCl$_3$)
7.40
7.40
7.38
7.27
7.26 CDCl3
7.25
5.10
5.08
5.07
3.79
3.77
3.11
2.98
2.04
2.62
1.00
2.13
6.11
f1 (ppm)

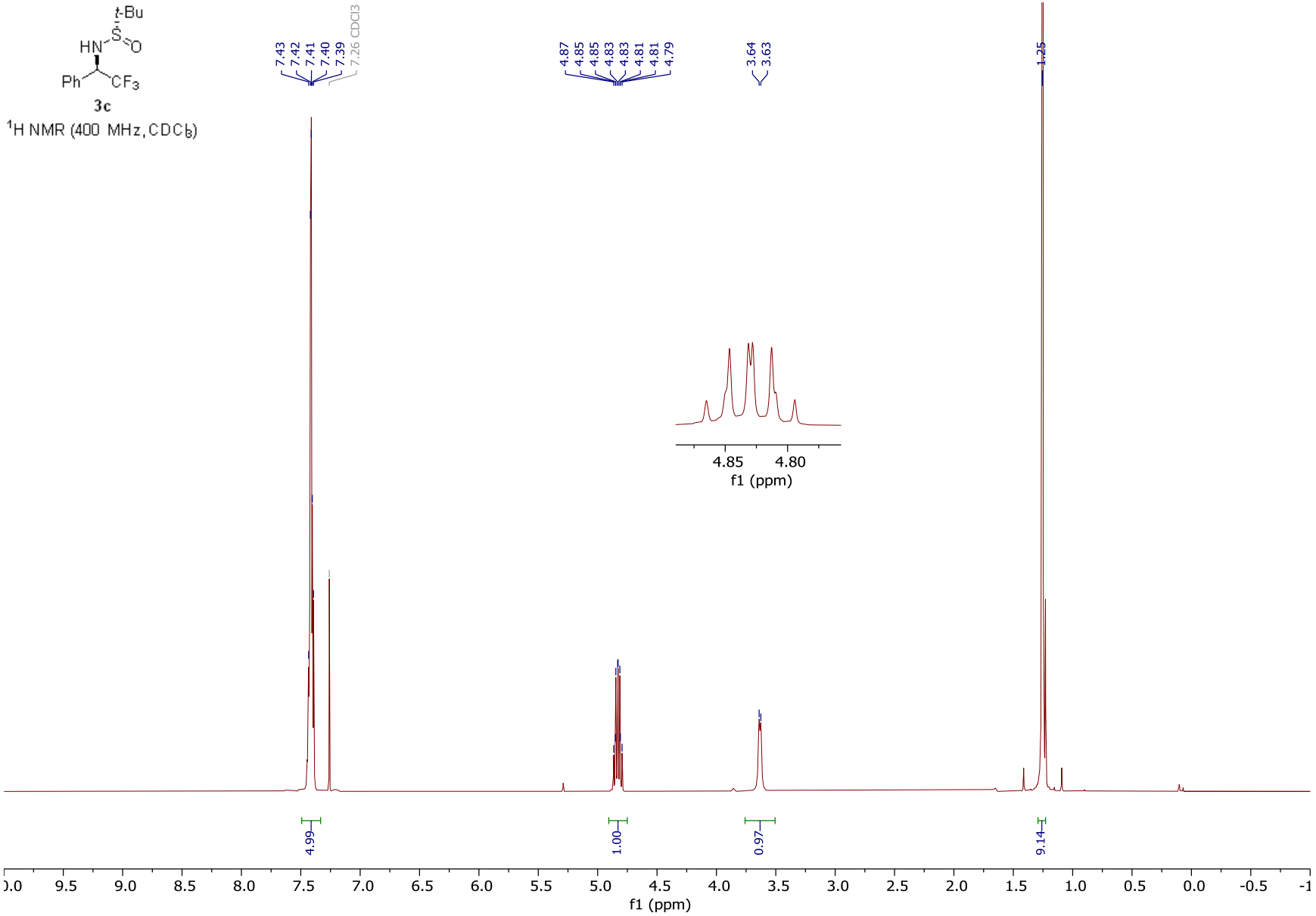

171.71
141.40
135.24
129.08
127.71
77.16
54.10
39.81
35.65
27.42
O
N
Me
Me
I
I
5l
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

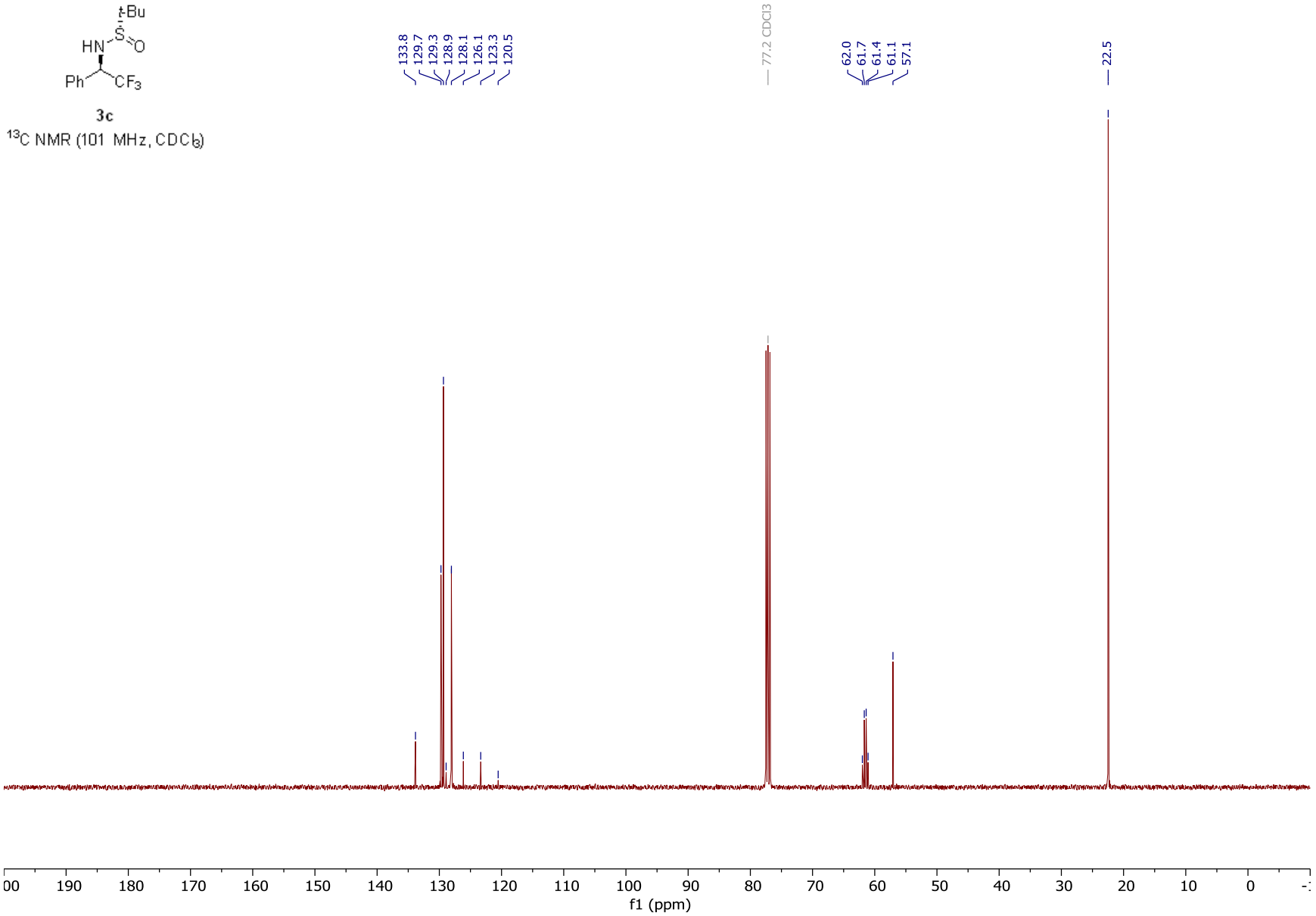

t-Bu
HN
S
O
OTBS
Ph
3b
^{1}H NMR (400 MHz, CDCl$_3$)
7.30
7.28
7.26
7.26 CDCl3
7.21
7.18
7.16
4.31
4.30
4.30
3.51
3.49
3.42
3.39
3.37
3.34
2.78
2.73
2.68
2.66
2.64
2.62
2.58
2.54
1.96
1.94
1.94
1.92
1.90
1.25
0.90
0.11
2.25
2.99
2.00
0.96
1.01
4.10
1.99
9.02
9.08
5.96
f1 (ppm)

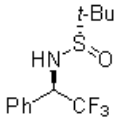


3b

^{13}C NMR (101 MHz, $CDCl_3$)

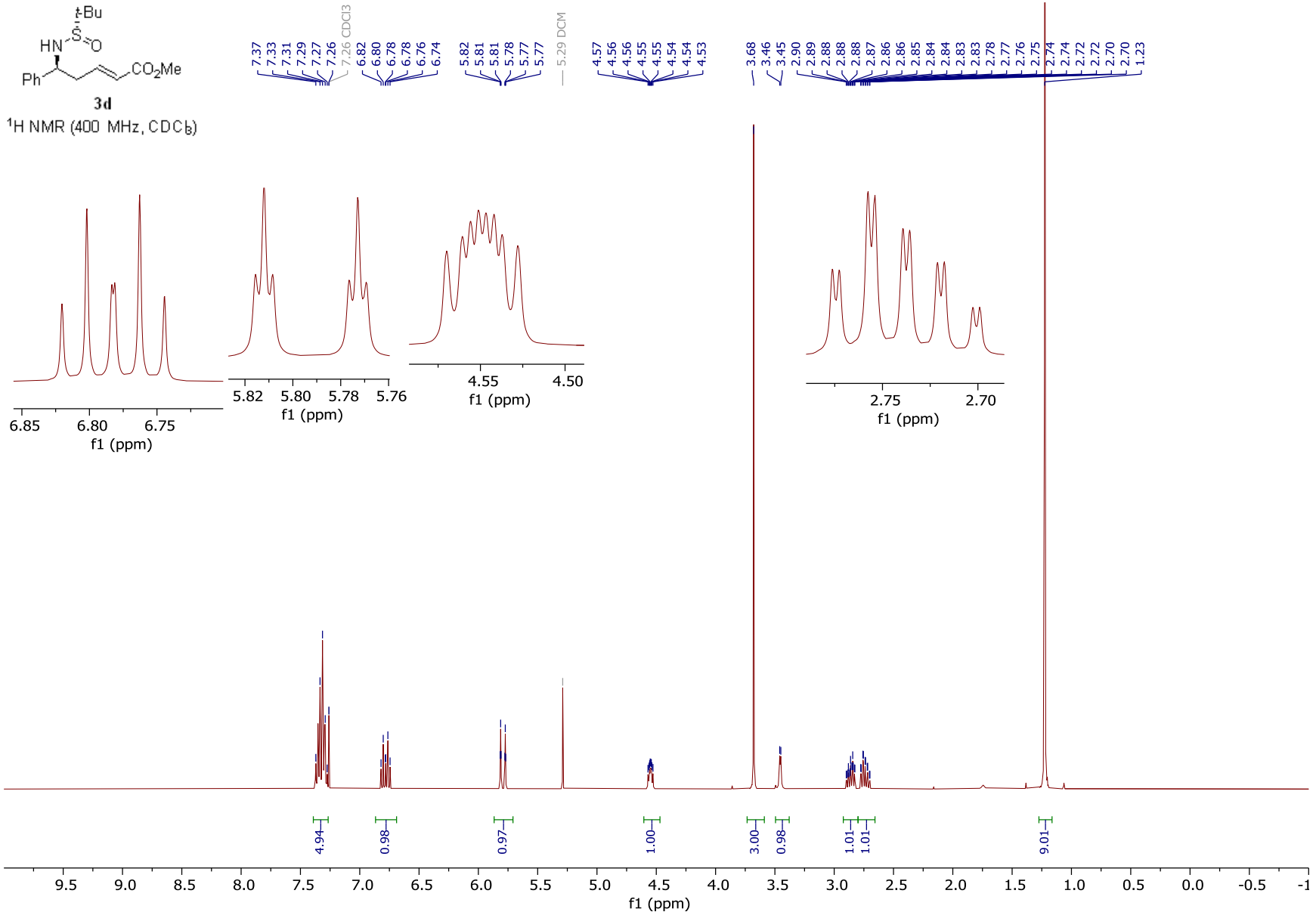

t-Bu
HN
S
O
Ph
CF3
3c
1H NMR (400 MHz, CDCl3)
7.43
7.42
7.41
7.40
7.39
7.26 CDCl3
4.87
4.85
4.85
4.83
4.83
4.81
4.81
4.79
3.64
3.63
1.25
4.85
4.80
f1 (ppm)
4.99
1.00
0.97
9.14
f1 (ppm)

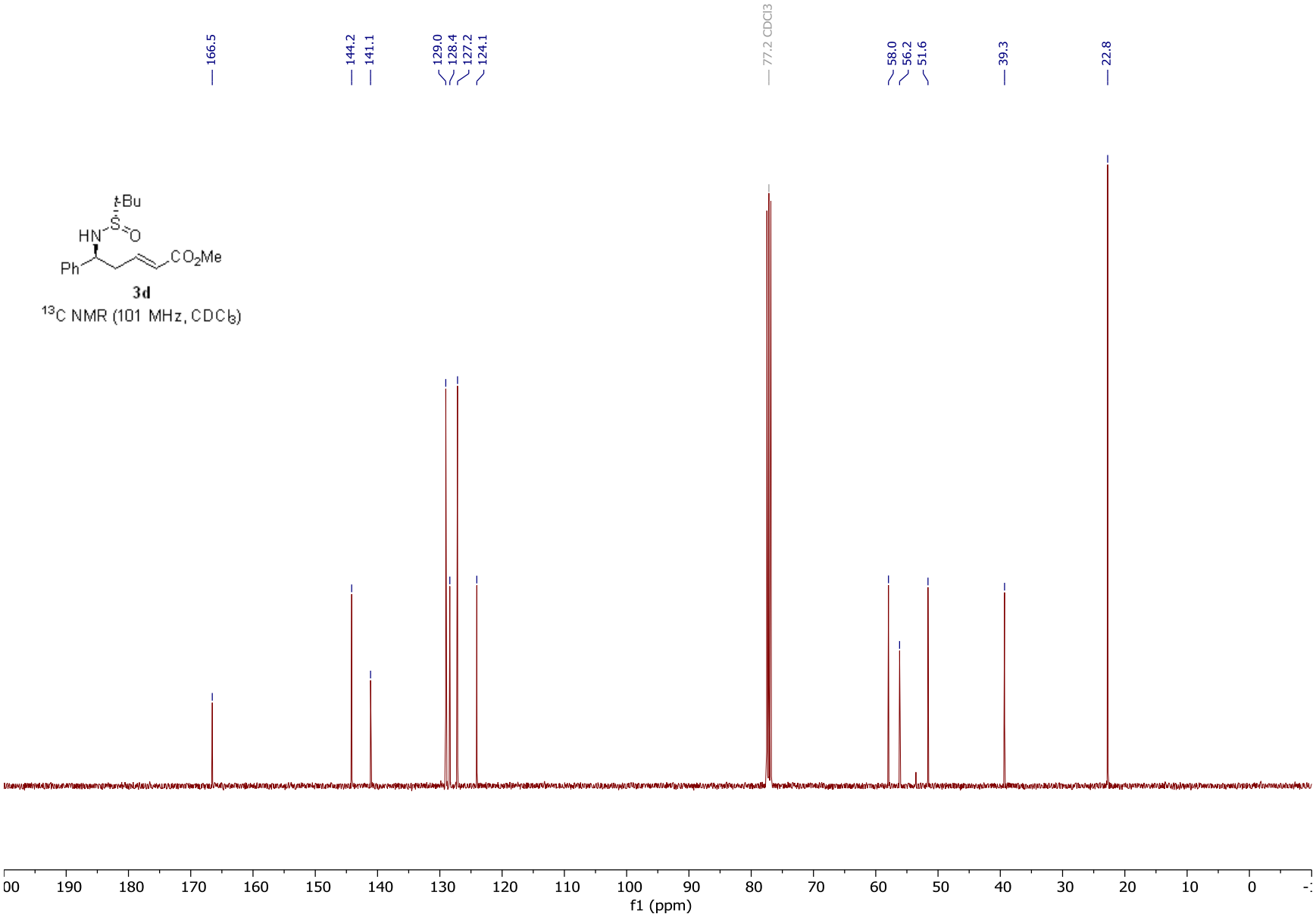

tBu
HN
S
O
Ph
CF3
3c
13C NMR (101 MHz, CDCl3)
133.8
129.7
129.3
128.9
128.1
126.1
123.3
120.5
77.2 CDCl3
62.0
61.7
61.4
61.1
57.1
22.5
f1 (ppm)

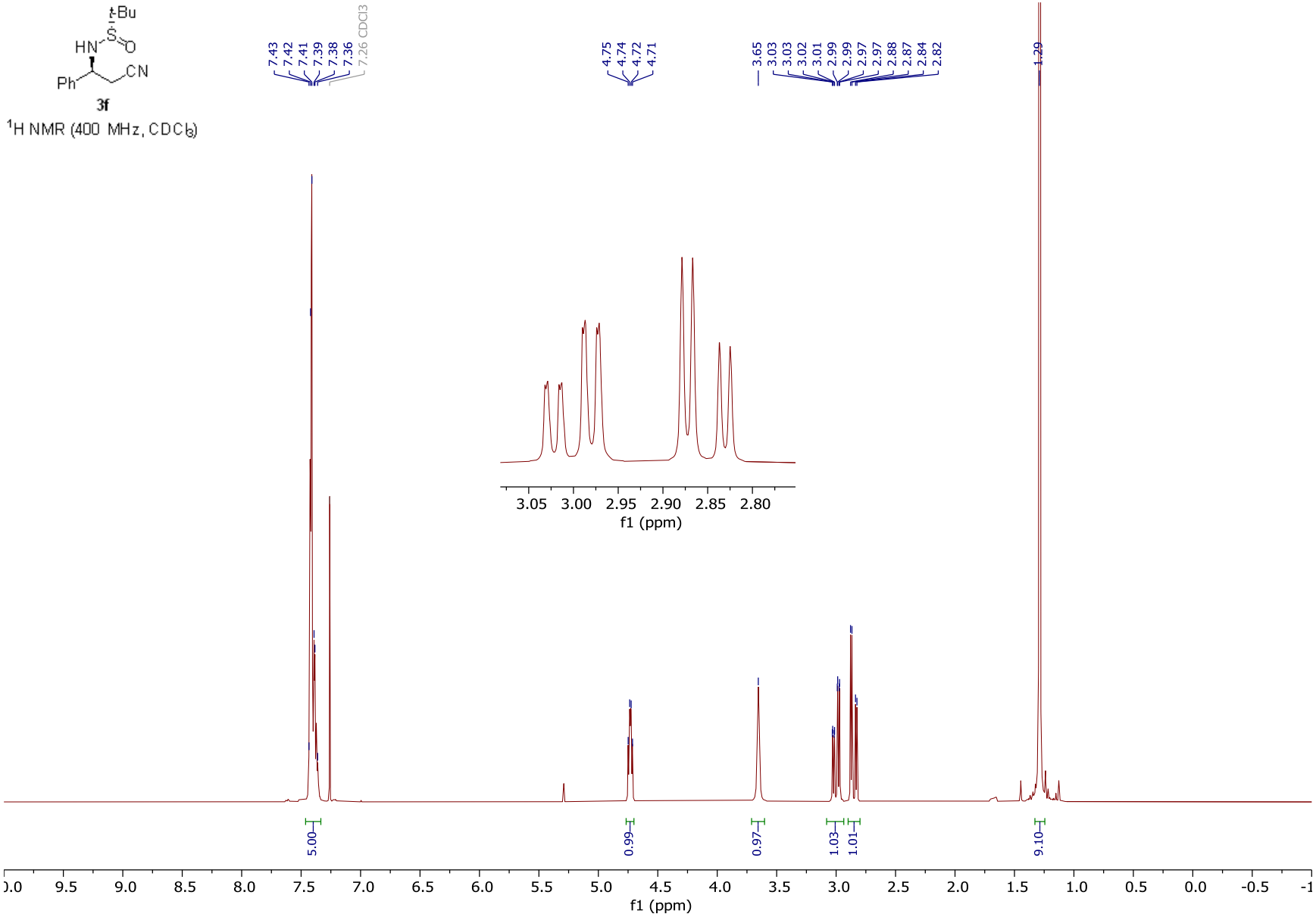


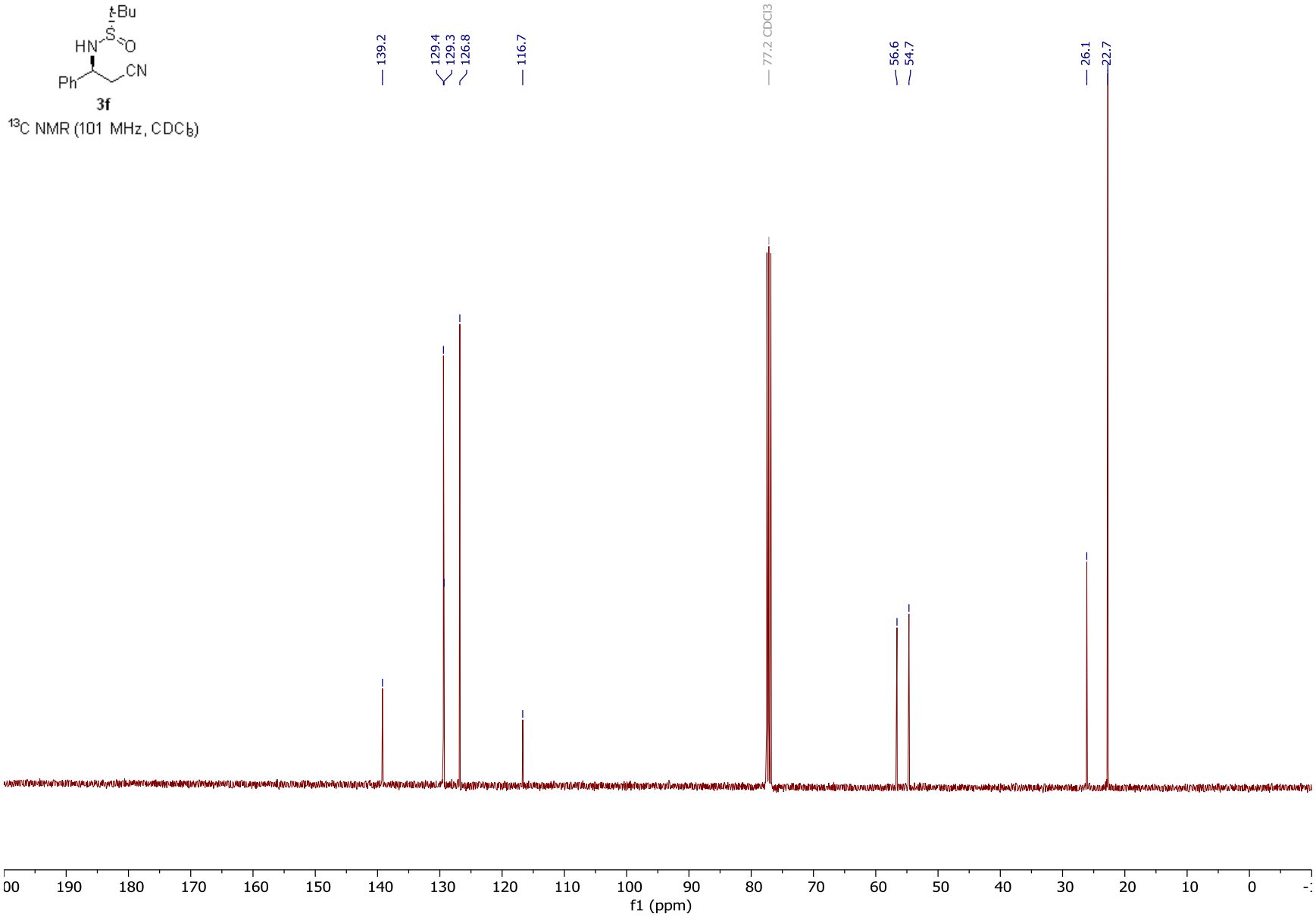
3c

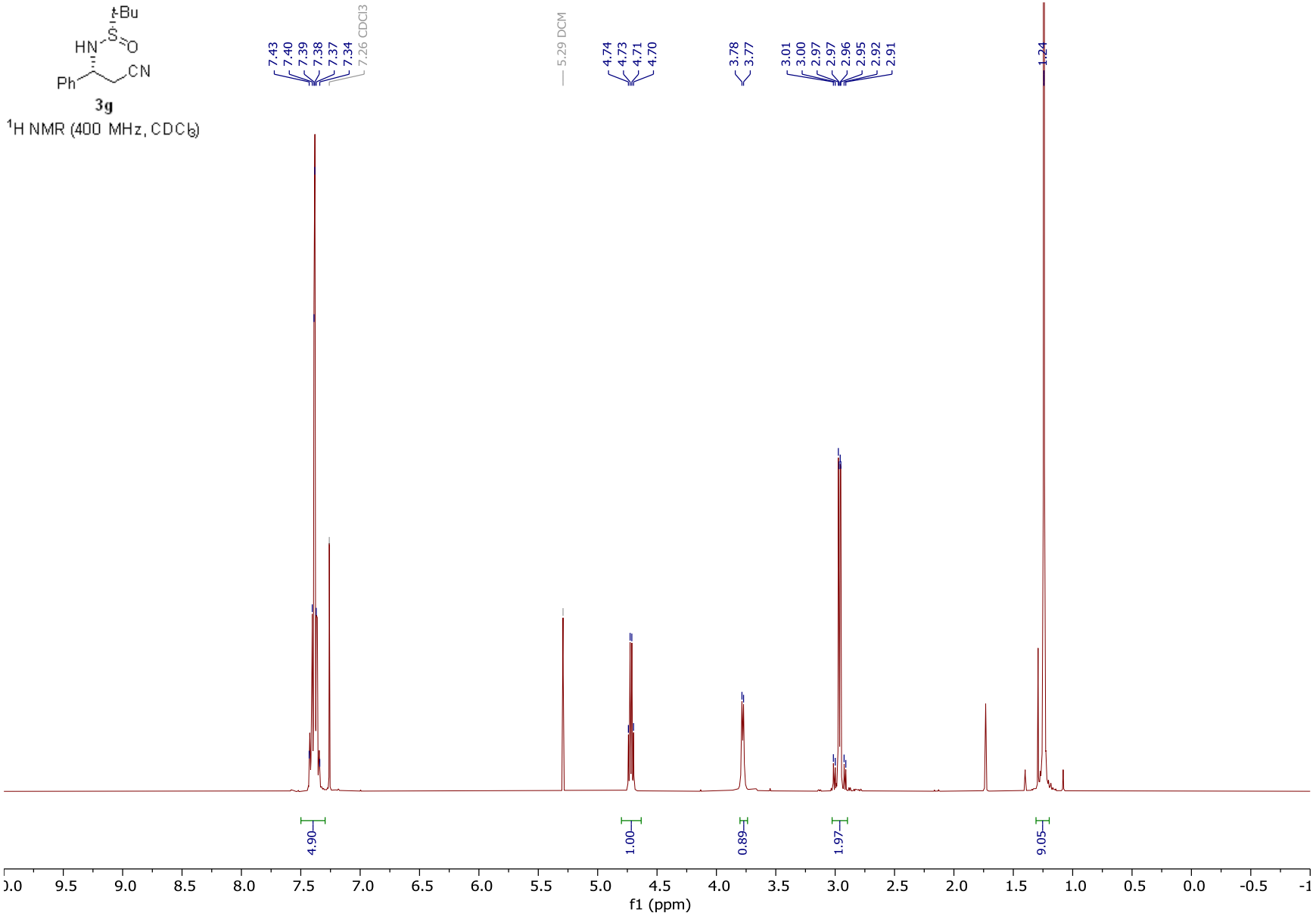
^{19}F NMR (376 MHz, $CDCl_3$)

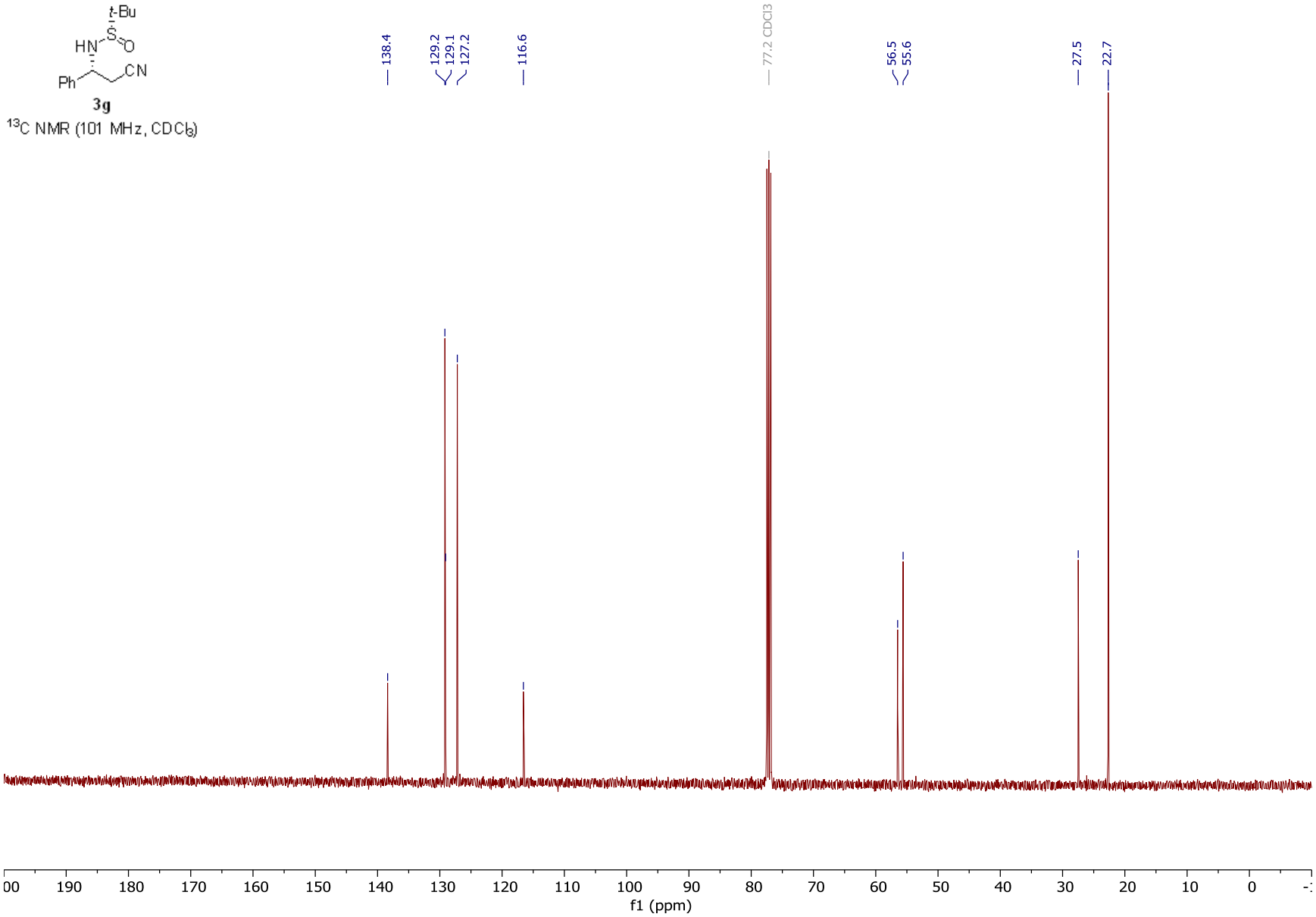

tBu
HN
S
O
Ph
CO2Me
3d
1H NMR (400 MHz, CDCl3)
7.37 7.33 7.31 7.29 7.27 7.26 7.26 CDCl3 6.82 6.80 6.78 6.78 6.76 6.74
5.82 5.81 5.81 5.78 5.77 5.77 5.29 DCM
4.57 4.56 4.56 4.55 4.55 4.54 4.54 4.53
3.68 3.46 3.45 2.90 2.89 2.88 2.88 2.88 2.87 2.86 2.86 2.85 2.84 2.84 2.83 2.78 2.77 2.76 2.75 2.74 2.74 2.72 2.72 2.70 2.70 1.23
6.85 6.80 6.75
f1 (ppm)
5.82 5.80 5.78 5.76
f1 (ppm)
4.55 4.50
f1 (ppm)
2.75 2.70
f1 (ppm)
4.94 0.98 0.97 1.00 3.00 0.98 1.01 1.01 9.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

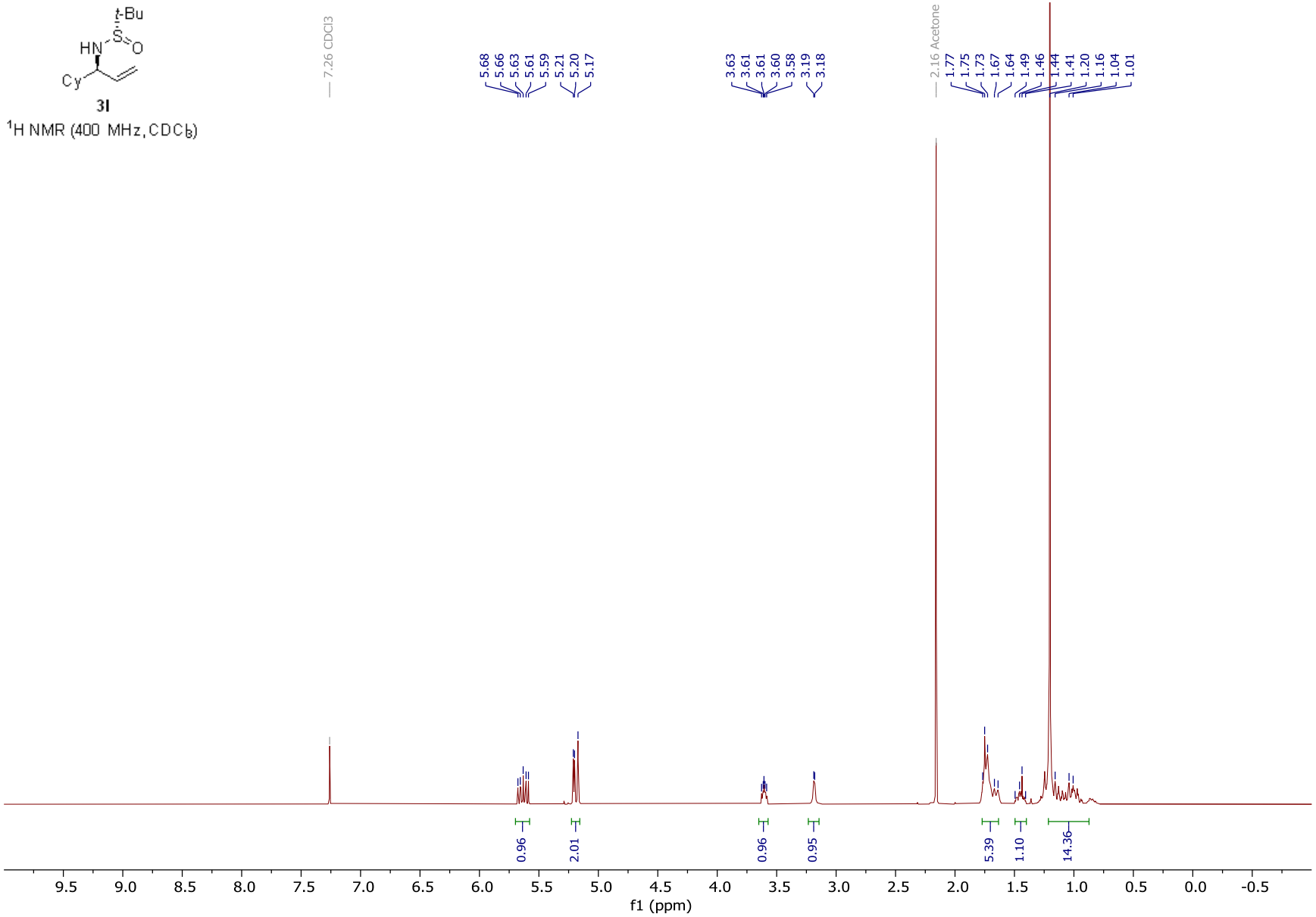

166.5
144.2
141.1
129.0
128.4
127.2
124.1
77.2 CDCl3
58.0
56.2
51.6
39.3
22.8
tBu
HN
S
O
Ph
CO2Me
3d
13C NMR (101 MHz, CDCl3)
f1 (ppm)

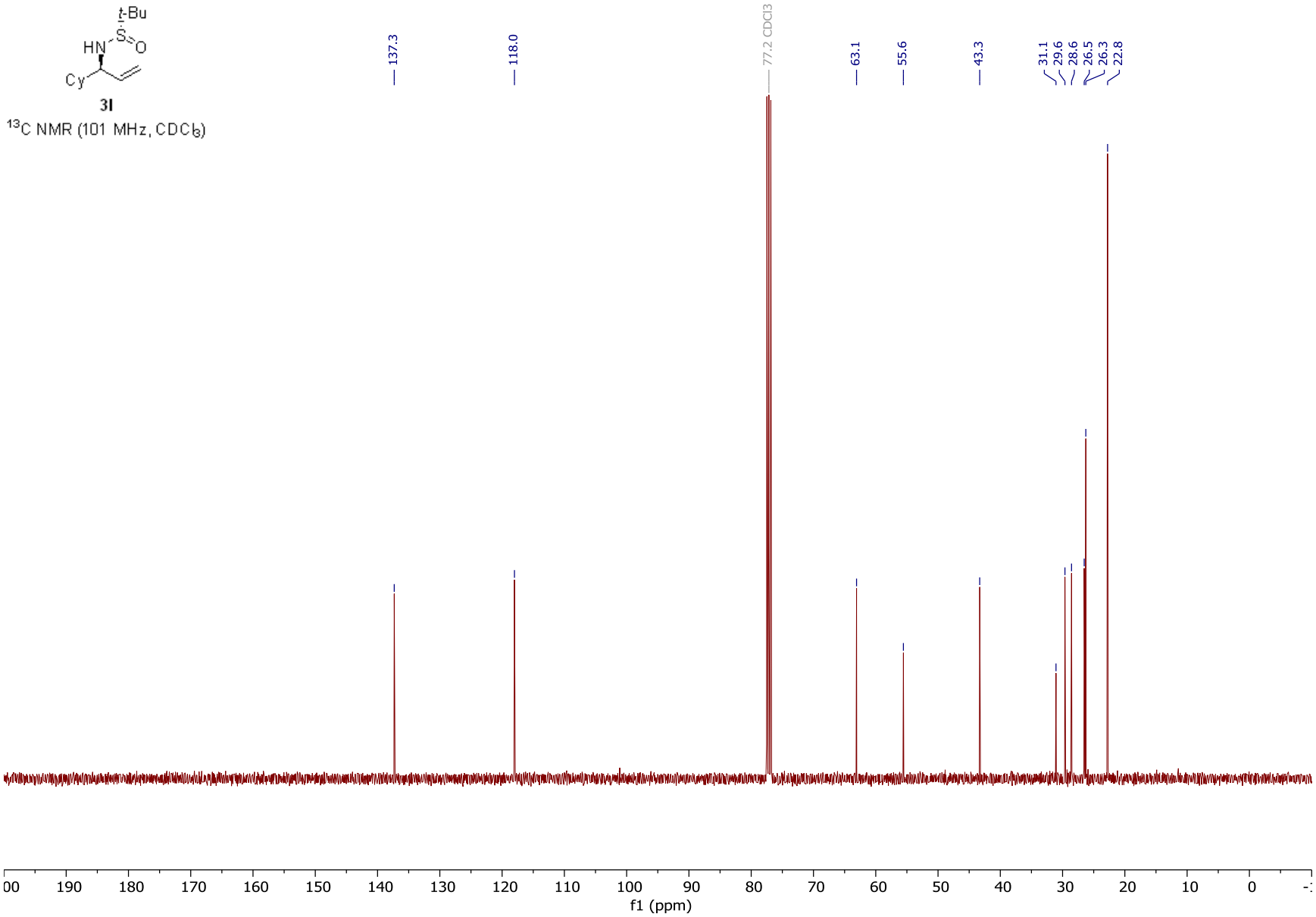

tBu
HN
S
O
Ph
CN
3f
^{1}H NMR (400 MHz, CDCl$_3$)
7.43
7.42
7.41
7.39
7.38
7.36
7.26 CDCl3
4.75
4.74
4.72
4.71
3.65
3.03
3.03
3.02
3.01
2.99
2.99
2.97
2.97
2.88
2.87
2.84
2.82
1.29
3.05 3.00 2.95 2.90 2.85 2.80
f1 (ppm)
5.00
0.99
0.97
1.03
1.01
9.10
f1 (ppm)

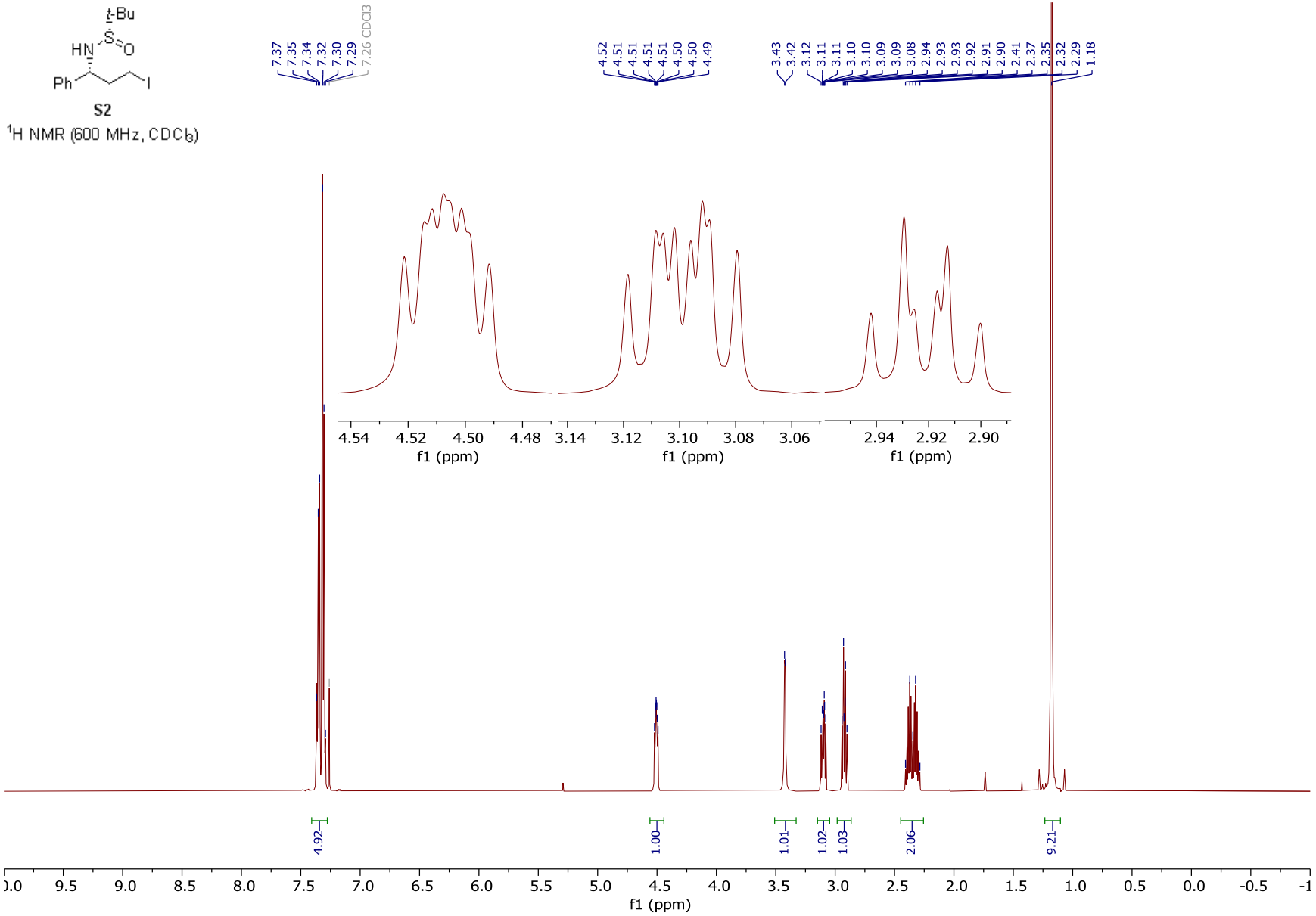

tBu
HN
S
O
Ph
CN
3f
13C NMR (101 MHz, CDCl3)
139.2
129.4
129.3
126.8
116.7
77.2 CDCl3
56.6
54.7
26.1
22.7
f1 (ppm)

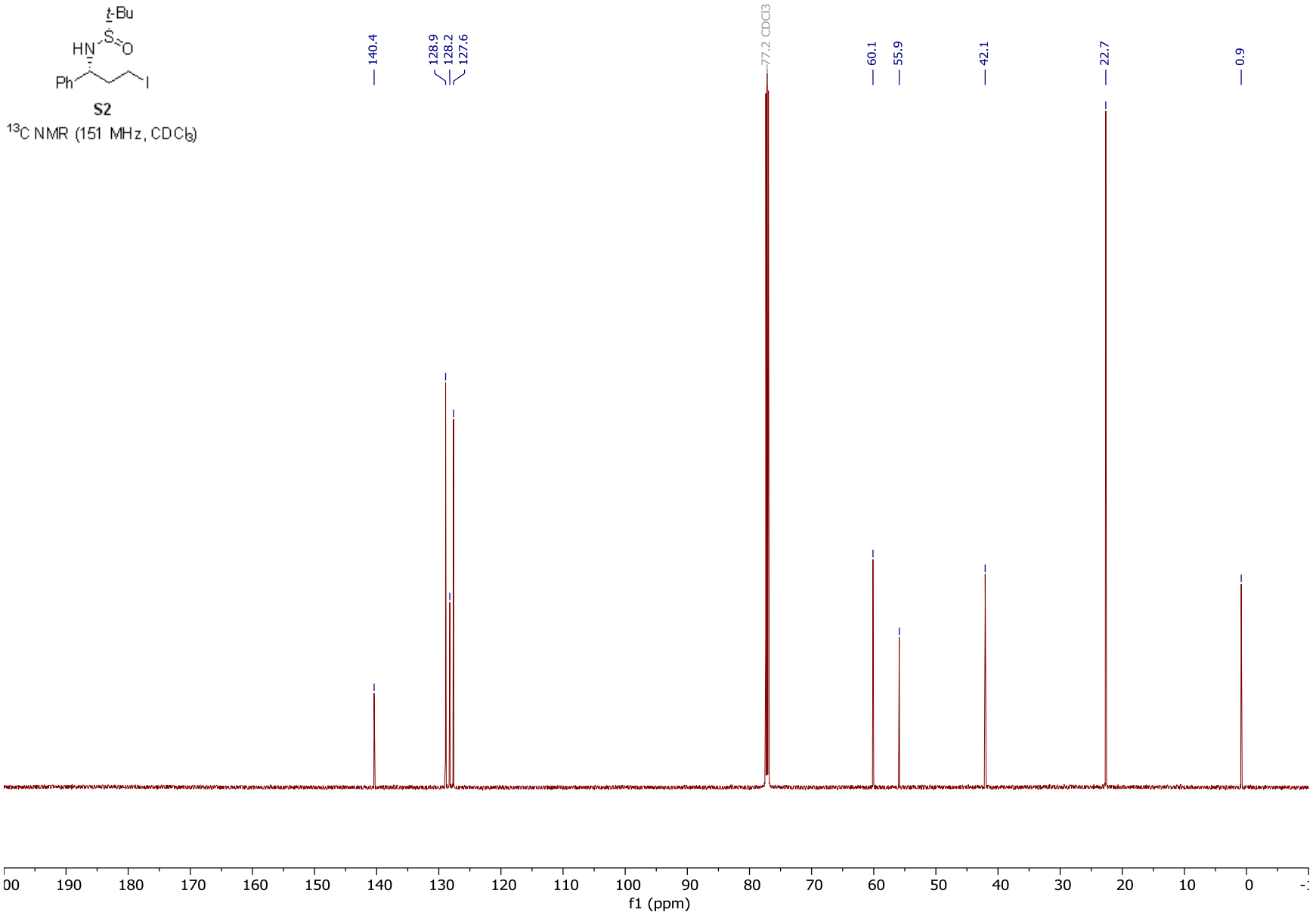

tBu
HN
S
O
Ph
CN
3g
^{1}H NMR (400 MHz, CDCl$_3$)
7.43
7.40
7.39
7.38
7.37
7.34
7.26 CDCl3
5.29 DCM
4.74
4.73
4.71
4.70
3.78
3.77
3.01
3.00
2.97
2.97
2.96
2.95
2.92
2.91
1.24
4.90
1.00
0.89
1.97
9.05
f1 (ppm)

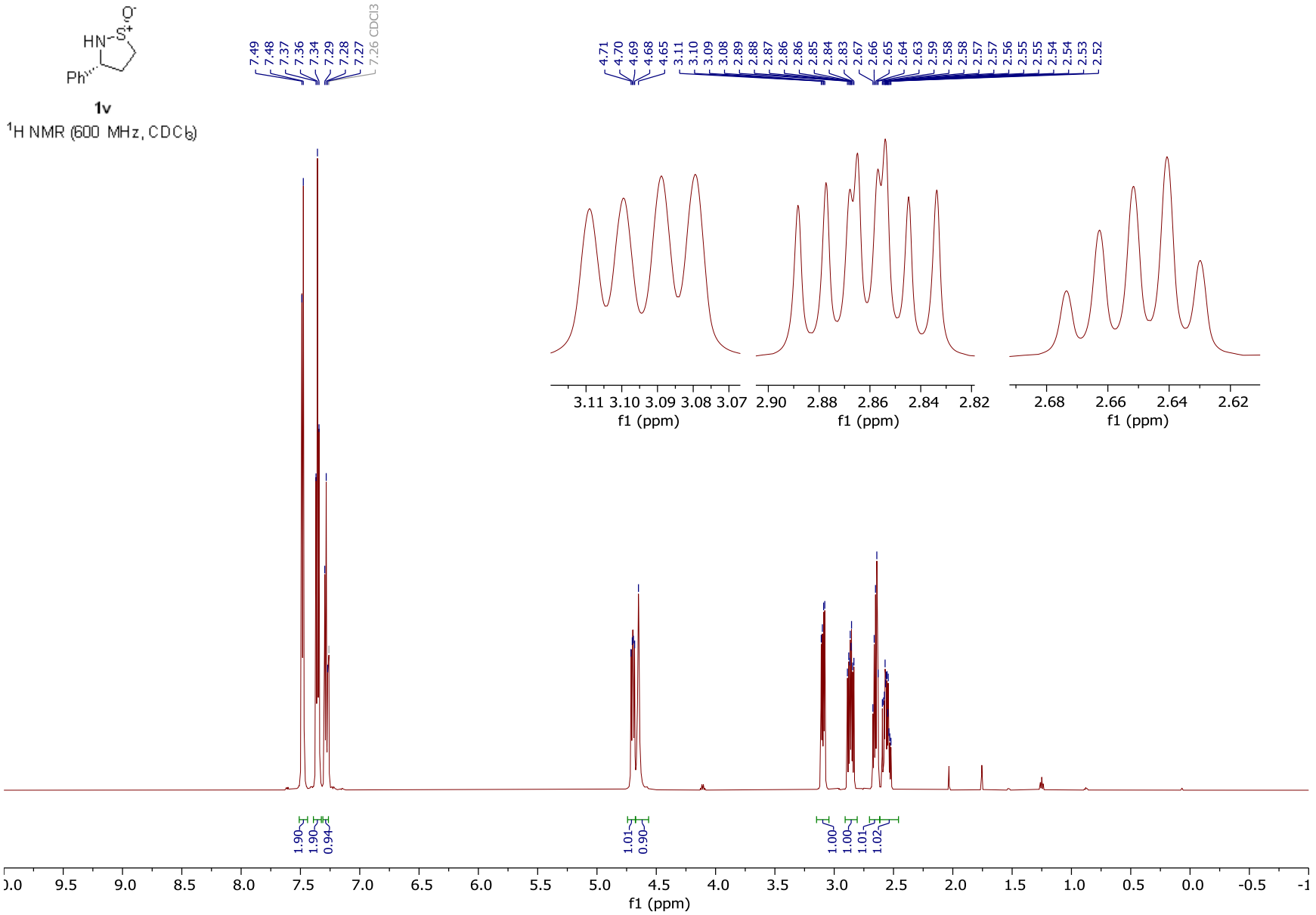

t-Bu
HN
S
O
CN
Ph
3g
^{13}C NMR (101 MHz, $CDCl_3$)
138.4
129.2
129.1
127.2
116.6
77.2 CDCl3
56.5
55.6
27.5
22.7
f1 (ppm)

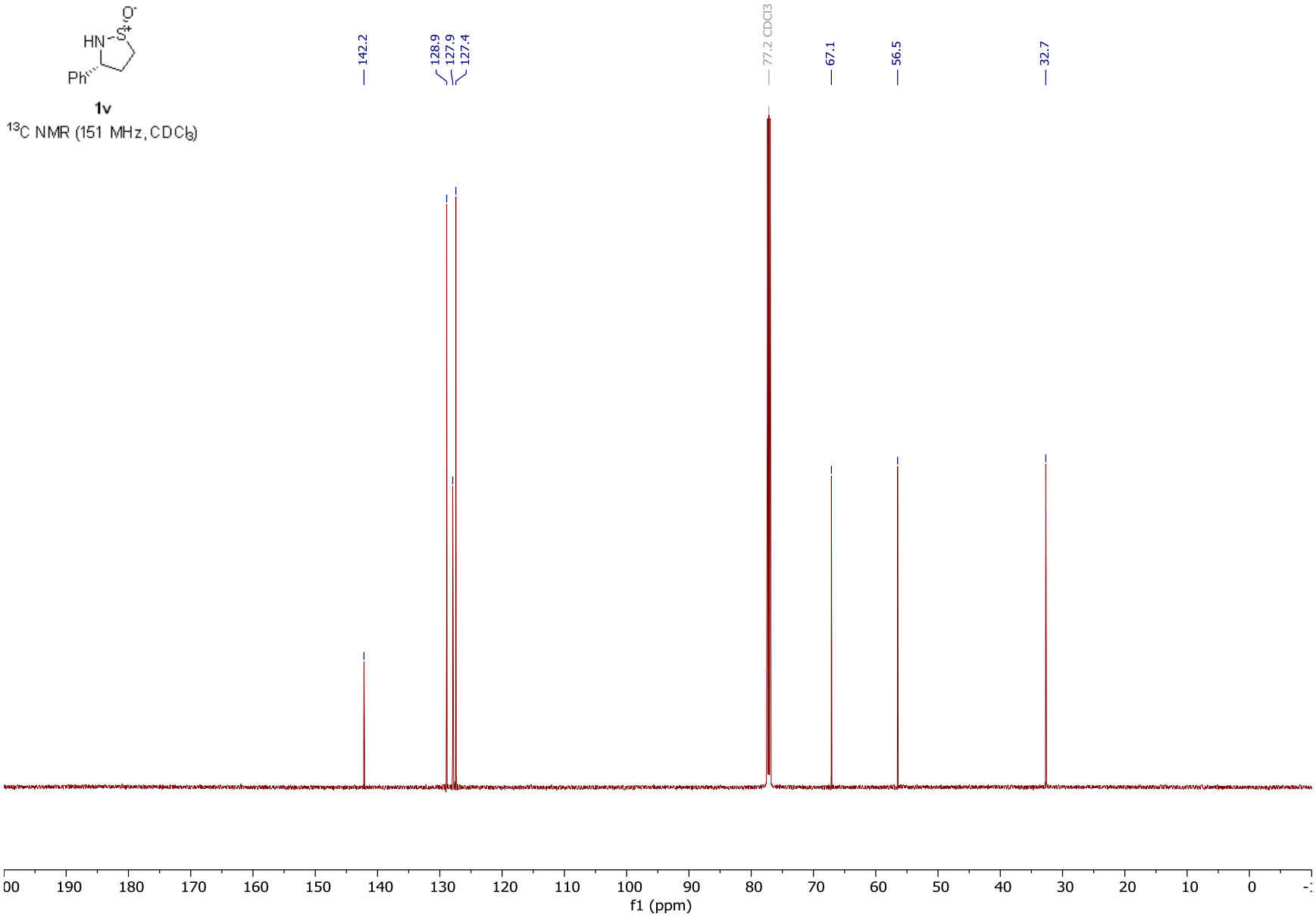

t-Bu
HN
S
O
Cy
3l
^{1}H NMR (400 MHz, $CDCl_3$)
7.26 CDCl3
2.16 Acetone
5.68
5.66
5.63
5.61
5.59
5.21
5.20
5.17
3.63
3.61
3.61
3.60
3.58
3.19
3.18
1.77
1.75
1.73
1.67
1.64
1.49
1.46
1.44
1.41
1.20
1.16
1.04
1.01
0.96
2.01
0.96
0.95
5.39
1.10
14.36
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

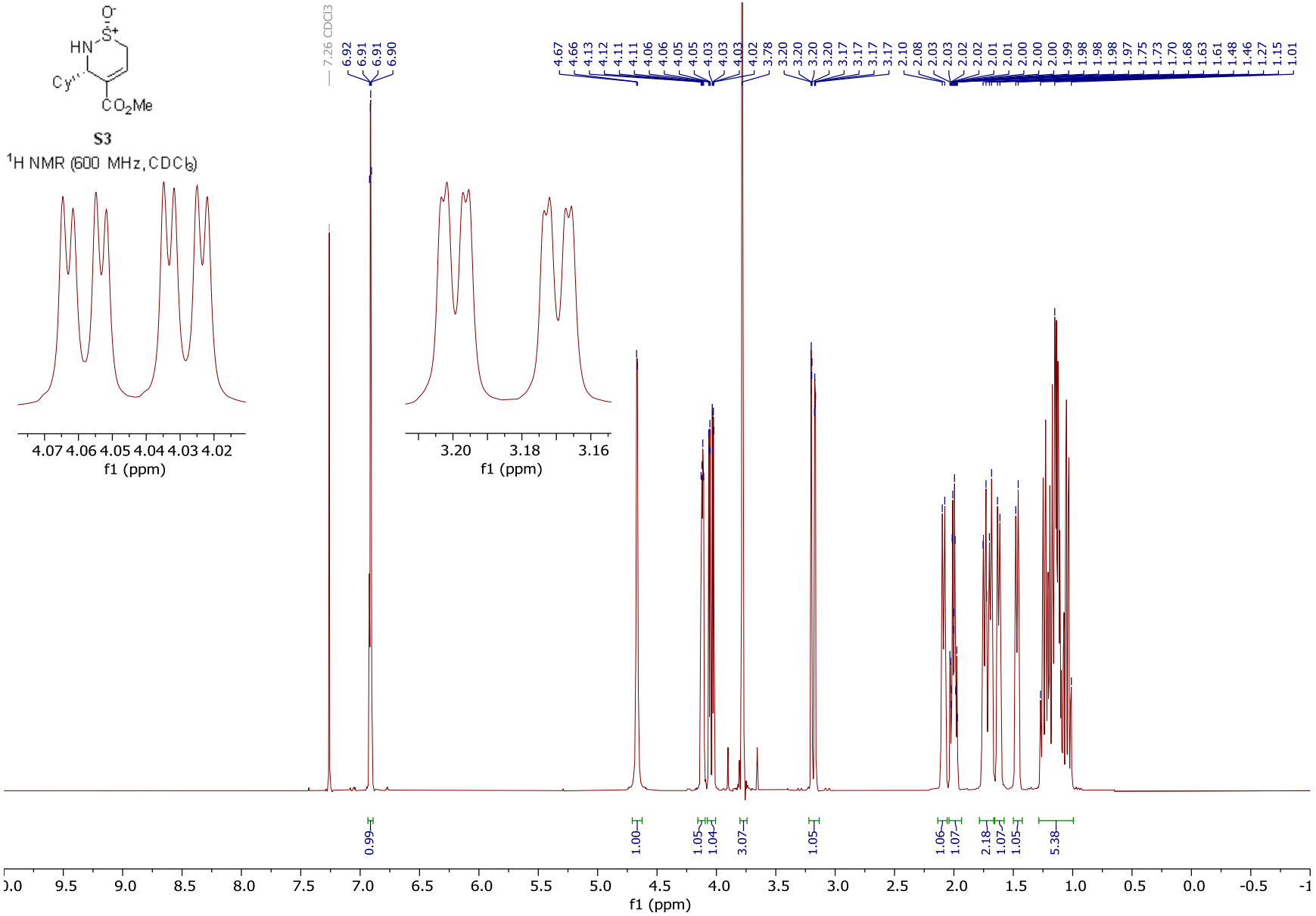

t-Bu
HN
S
O
Cy
3l
13C NMR (101 MHz, CDCl3)
137.3
118.0
77.2 CDCl3
63.1
55.6
43.3
31.1
29.6
28.6
26.5
26.3
22.8
f1 (ppm)

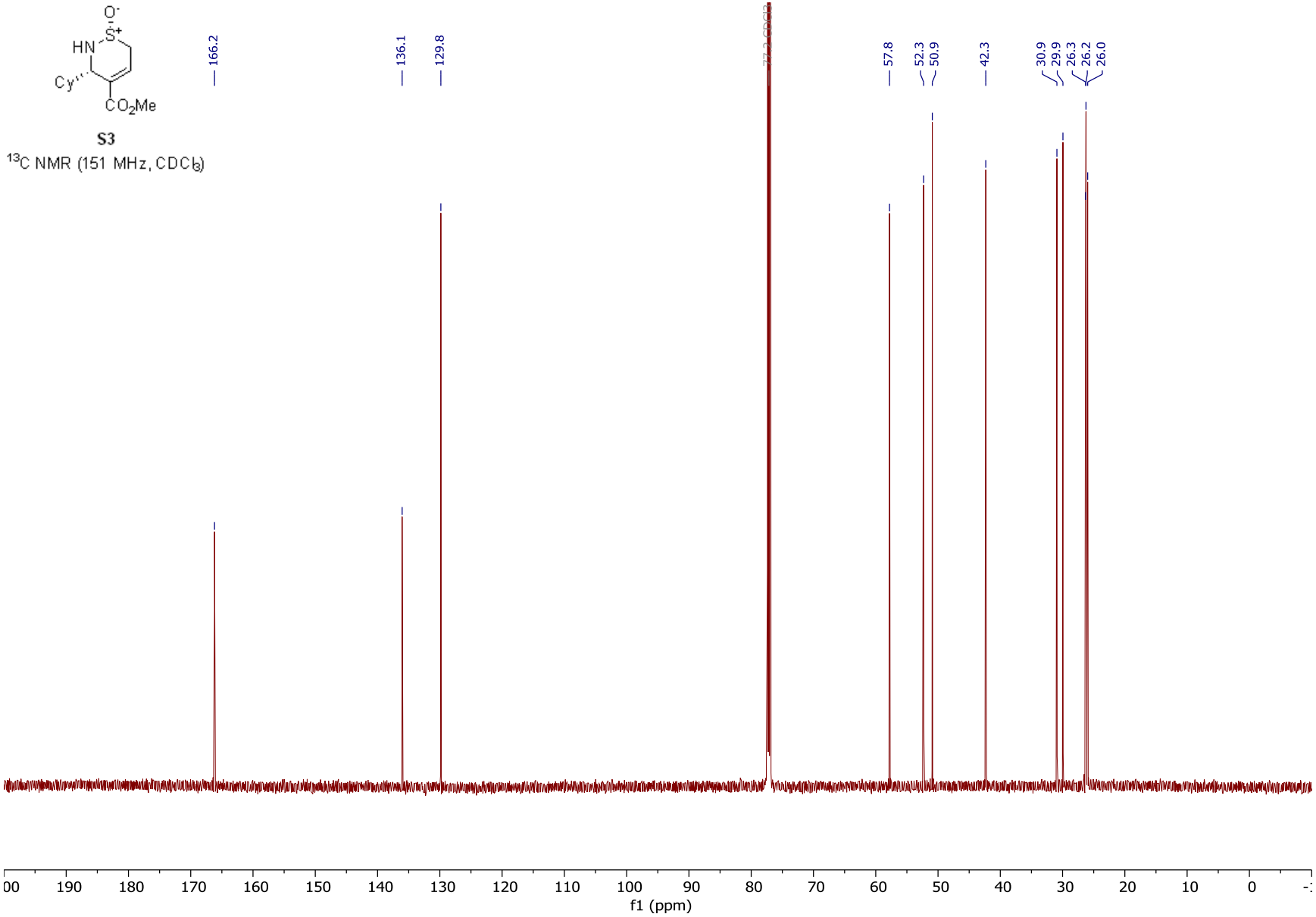

t-Bu
HN
S
O
Ph
I
S2
1H NMR (600 MHz, CDCl3)
7.37
7.35
7.34
7.32
7.30
7.29
7.26 CDCl3
4.52
4.51
4.51
4.51
4.51
4.50
4.50
4.49
3.43
3.42
3.12
3.11
3.11
3.10
3.10
3.09
3.09
3.08
2.94
2.93
2.93
2.92
2.91
2.90
2.41
2.37
2.35
2.32
2.29
1.18
4.54 4.52 4.50 4.48
f1 (ppm)
3.14 3.12 3.10 3.08 3.06
f1 (ppm)
2.94 2.92 2.90
f1 (ppm)
4.92
1.00
1.01
1.02
1.03
2.06
9.21
f1 (ppm)

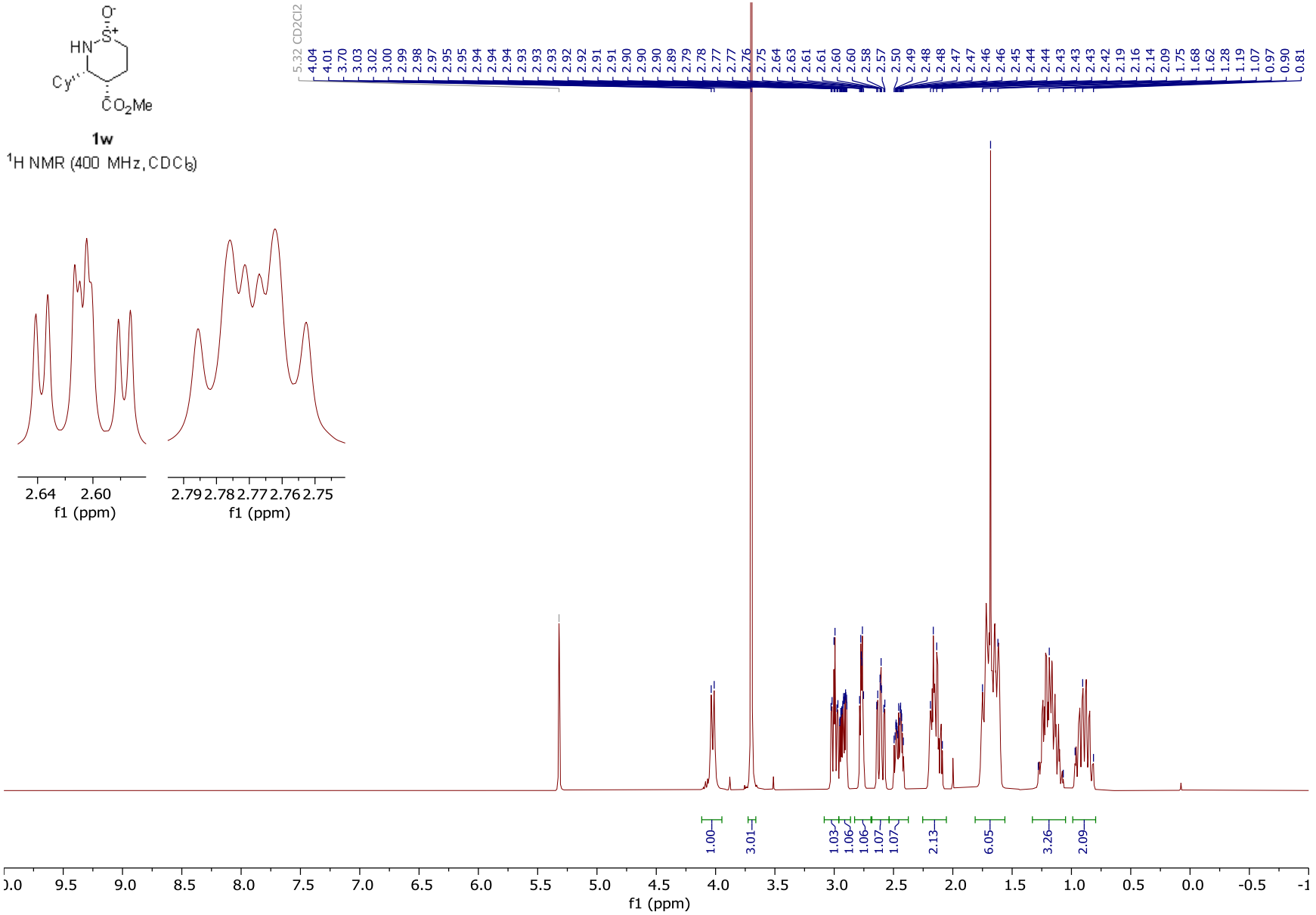

t-Bu
HN
S
O
Ph
I
S2
13C NMR (151 MHz, CDCl3)
140.4
128.9
128.2
127.6
77.2 CDCl3
60.1
55.9
42.1
22.7
0.9
f1 (ppm)

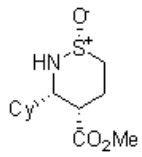

HN
S+
O-
Ph
1v
1H NMR (600 MHz, CDCl3)
7.49 7.48 7.37 7.36 7.34 7.29 7.28 7.27 7.26 CDCl3
4.71 4.70 4.69 4.68 4.65 3.11 3.10 3.09 3.08 3.07 2.89 2.88 2.87 2.86 2.86 2.85 2.84 2.83 2.67 2.66 2.65 2.64 2.63 2.59 2.58 2.58 2.57 2.57 2.56 2.55 2.55 2.54 2.54 2.53 2.52
3.11 3.10 3.09 3.08 3.07
f1 (ppm)
2.90 2.88 2.86 2.84 2.82
f1 (ppm)
2.68 2.66 2.64 2.62
f1 (ppm)
1.90 1.90 0.94 1.01 0.90 1.00 1.00 1.01 1.02
f1 (ppm)


HN
S
O
Ph
1v
^{13}C NMR (151 MHz, CDCl$_3$)
142.2
128.9
127.9
127.4
77.2 CDCl3
67.1
56.5
32.7
f1 (ppm)


S3
1H NMR (600 MHz, CDCl3)
7.26 CDCl3
f1 (ppm)

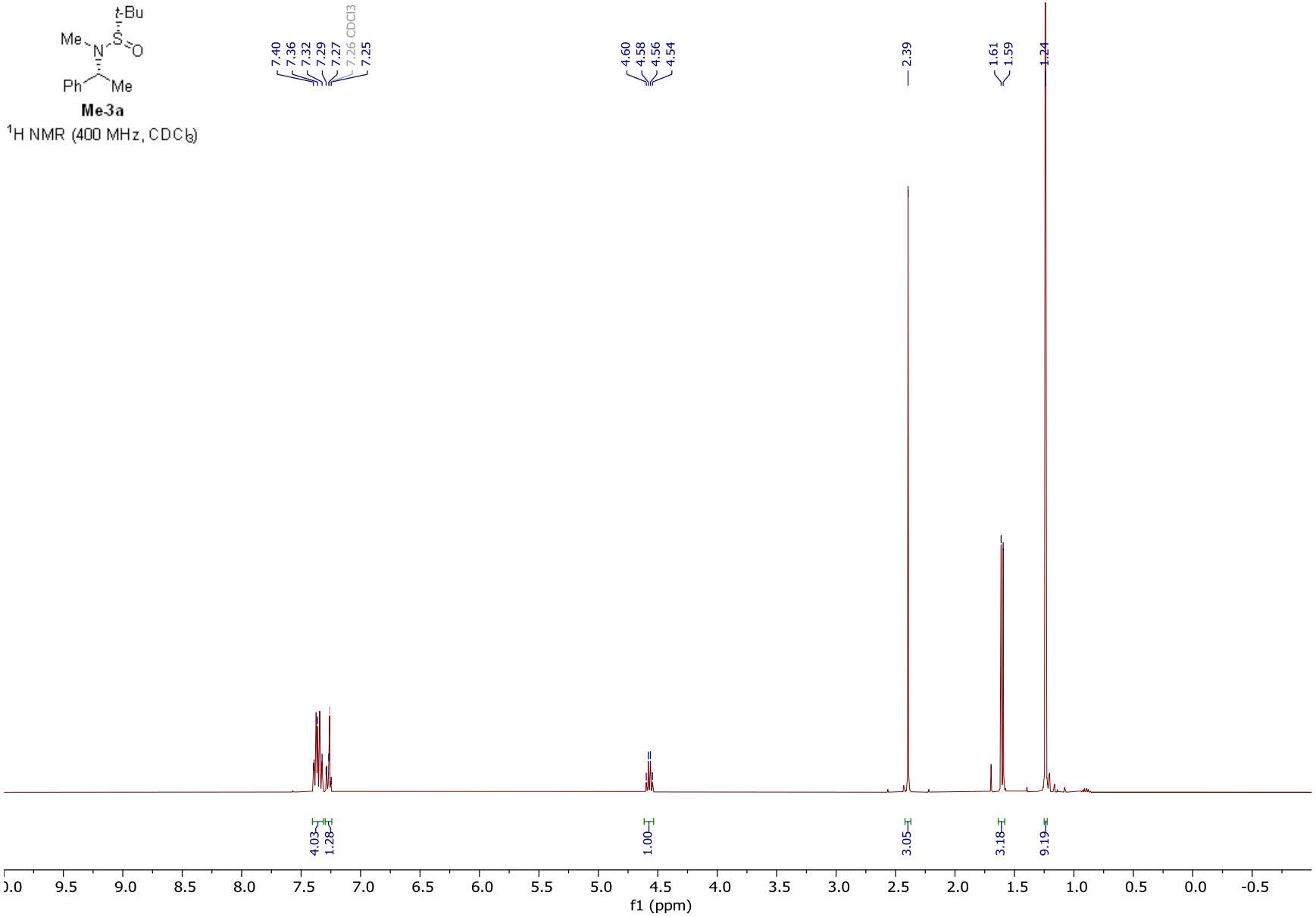

O⁻
S⁺
HN
Cy
CO2Me
S3
13C NMR (151 MHz, CDCl3)
166.2
136.1
129.8
77.2, CDCl3
57.8
52.3
50.9
42.3
30.9
29.9
26.3
26.2
26.0
f1 (ppm)

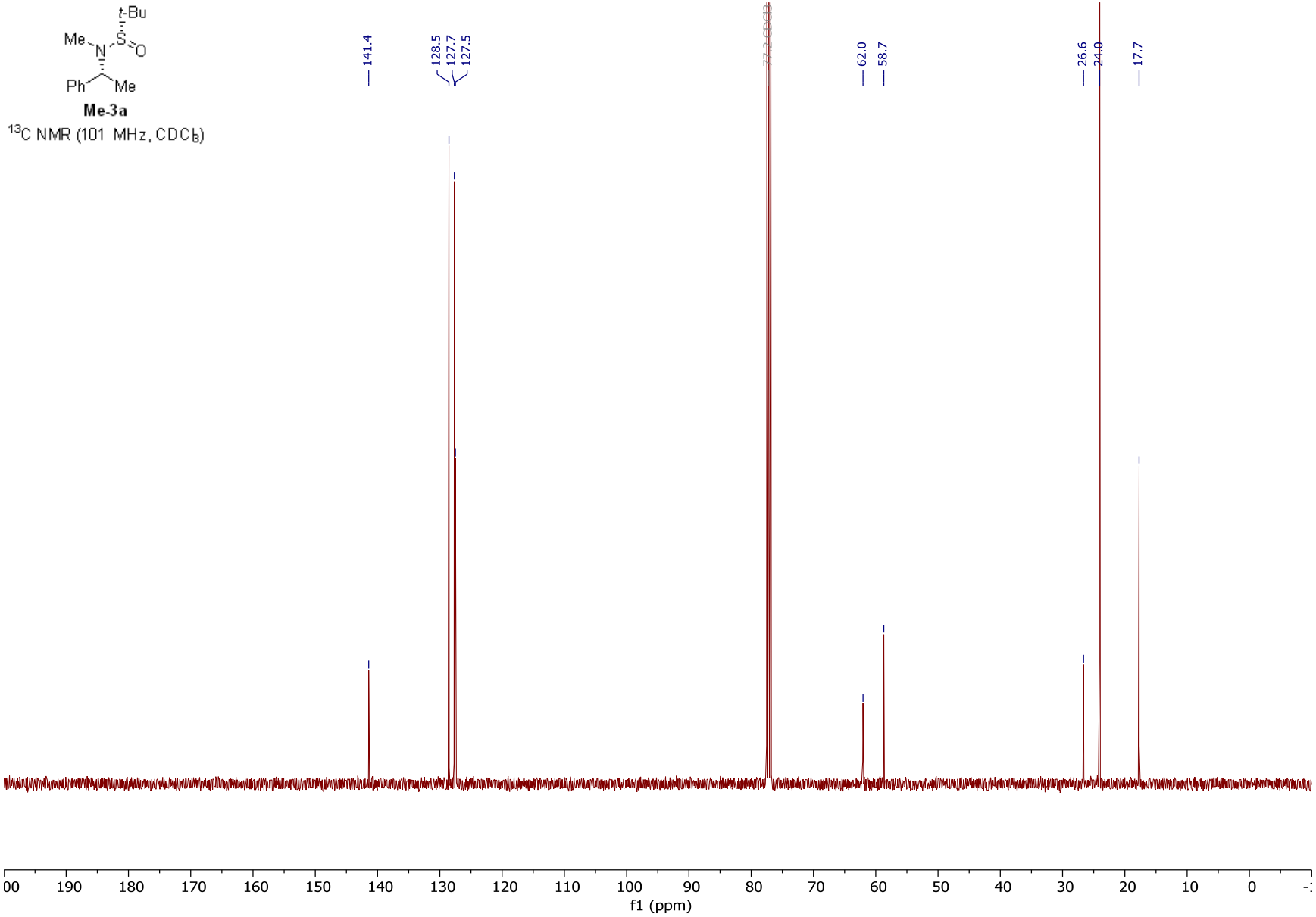

1w
^{1}H NMR (400 MHz, $CDCl_3$)
5.32 CD_2Cl_2
2.64 2.60
f1 (ppm)
2.79 2.78 2.77 2.76 2.75
f1 (ppm)
1.00 3.01 1.03 1.06 1.06 1.07 1.07 2.13 6.05 3.26 2.09
f1 (ppm)

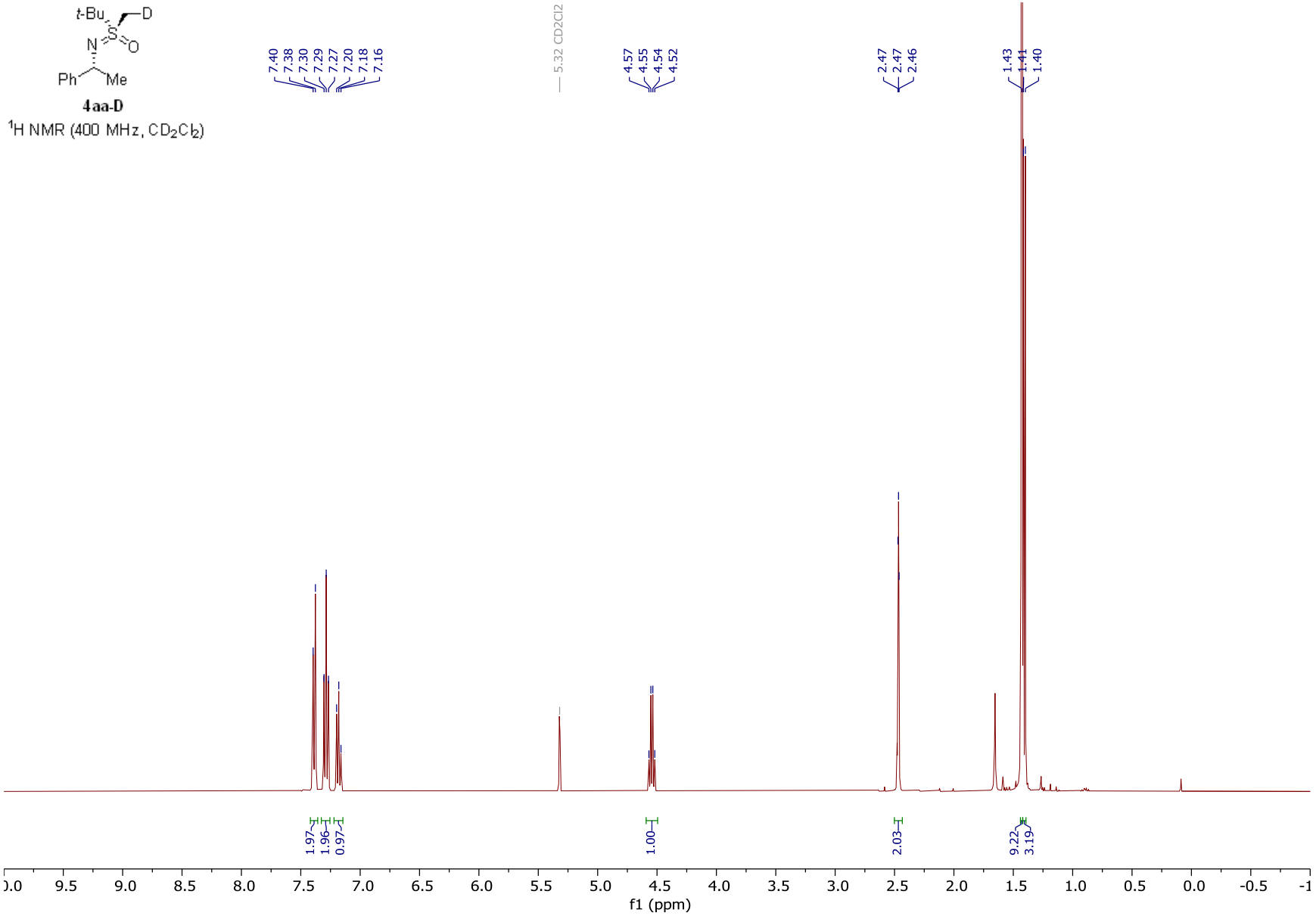


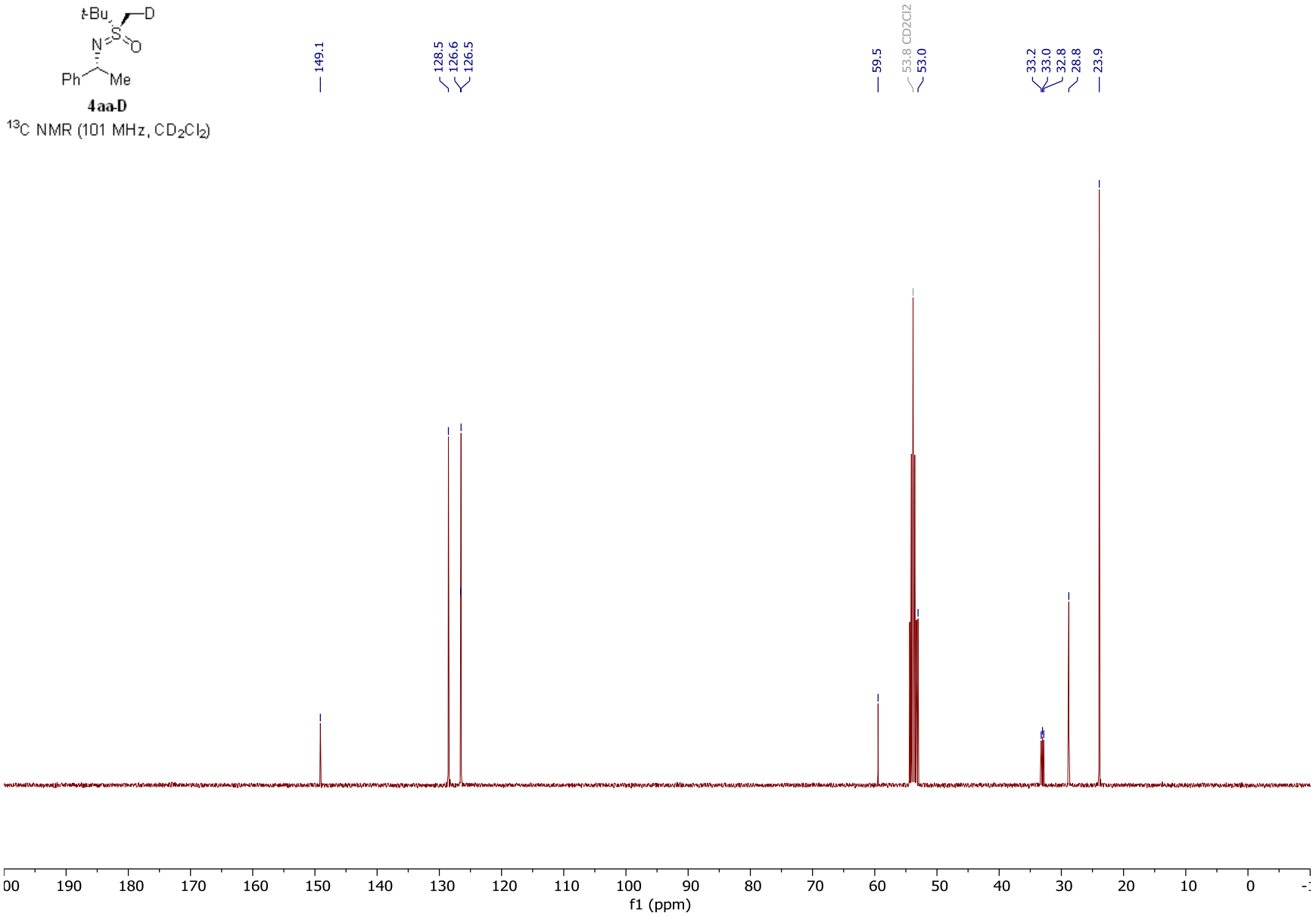
1w

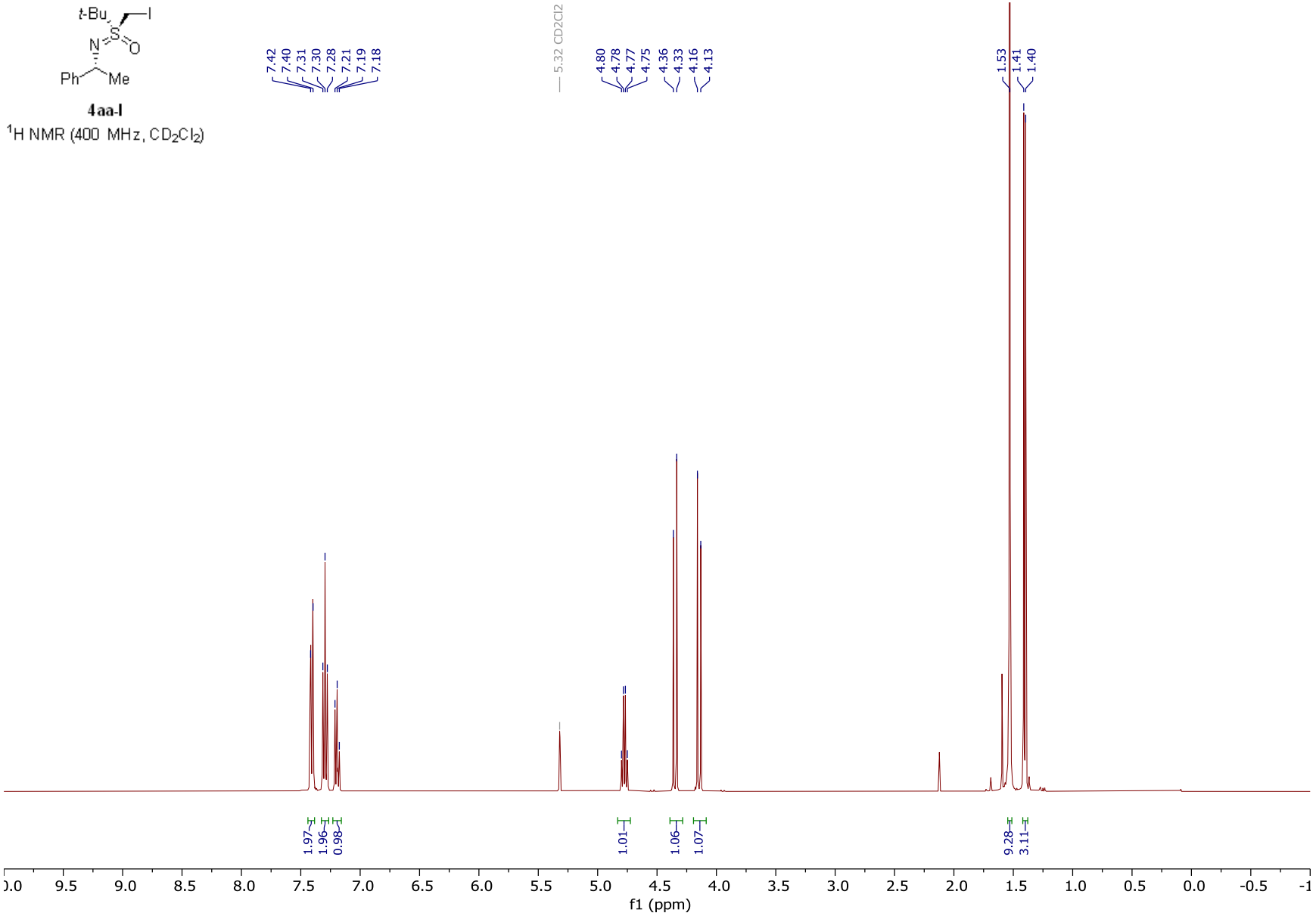
^{13}C NMR (101 MHz, $CDCl_3$)

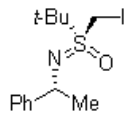

t-Bu
Me
N
S
O
Ph
Me
Me3a
1H NMR (400 MHz, CDCl3)
7.40
7.36
7.32
7.29
7.27
7.26 CDCl3
7.25
4.60
4.58
4.56
4.54
2.39
1.61
1.59
1.24
4.03
1.28
1.00
3.05
3.18
9.19
f1 (ppm)


t-Bu
Me
N
S
O
Ph
Me
Me-3a
13C NMR (101 MHz, CDCl3)
141.4
128.5
127.7
127.5
62.0
58.7
26.6
24.0
17.7
f1 (ppm)


t-Bu
D
N
S
O
Ph
Me
4aa-D
1H NMR (400 MHz, CD2Cl2)
7.40
7.38
7.30
7.29
7.27
7.20
7.18
7.16
5.32 CD2Cl2
4.57
4.55
4.54
4.52
2.47
2.47
2.46
1.43
1.41
1.40
1.97
1.96
0.97
1.00
2.03
9.22
3.19
f1 (ppm)

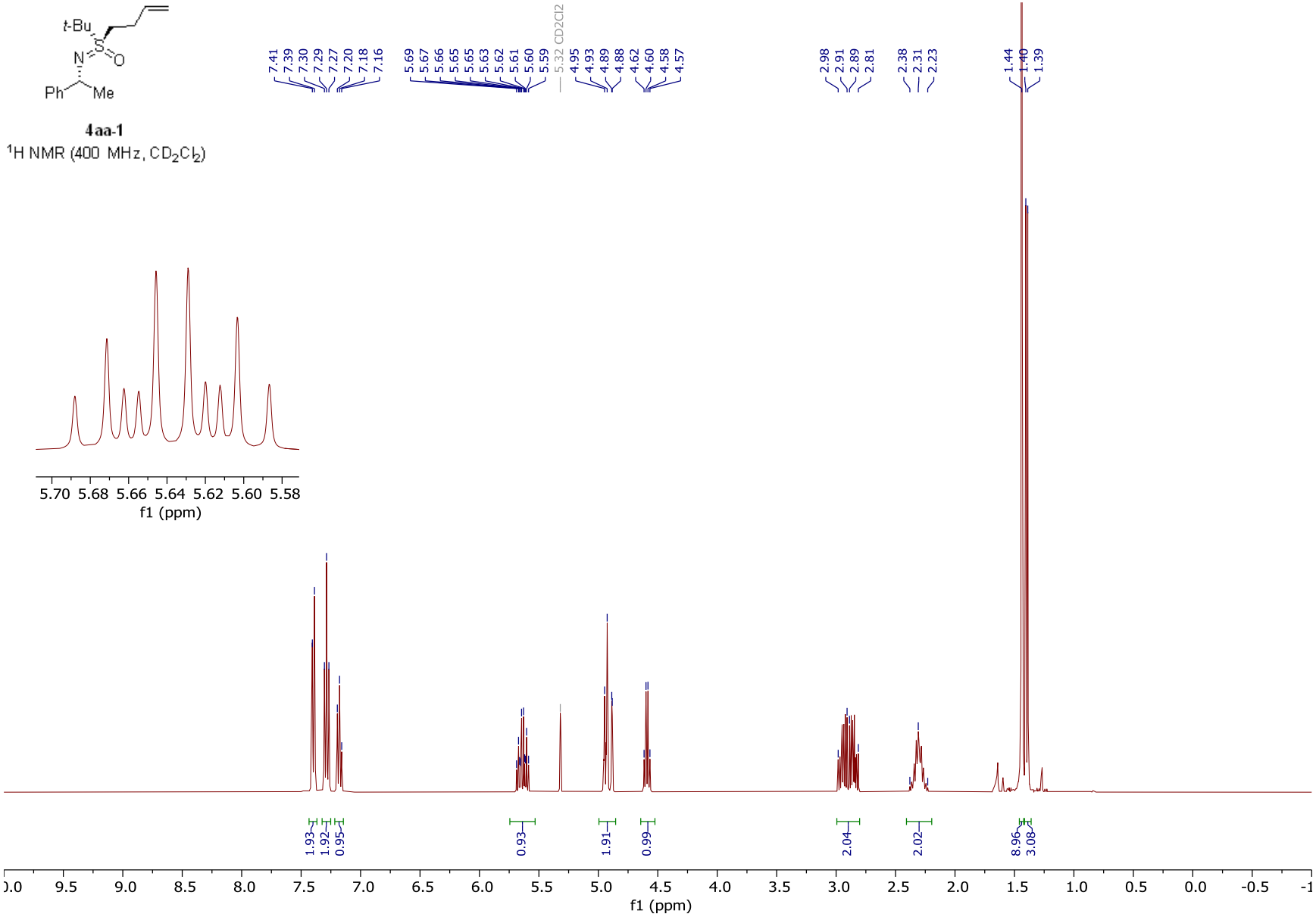

t-Bu
D
N
S
O
Ph
Me
4aa-D
^{13}C NMR (101 MHz, CD_2Cl_2)
149.1
128.5
126.6
126.5
59.5
53.8 CD2Cl2
53.0
33.2
33.0
32.8
28.8
23.9
f1 (ppm)

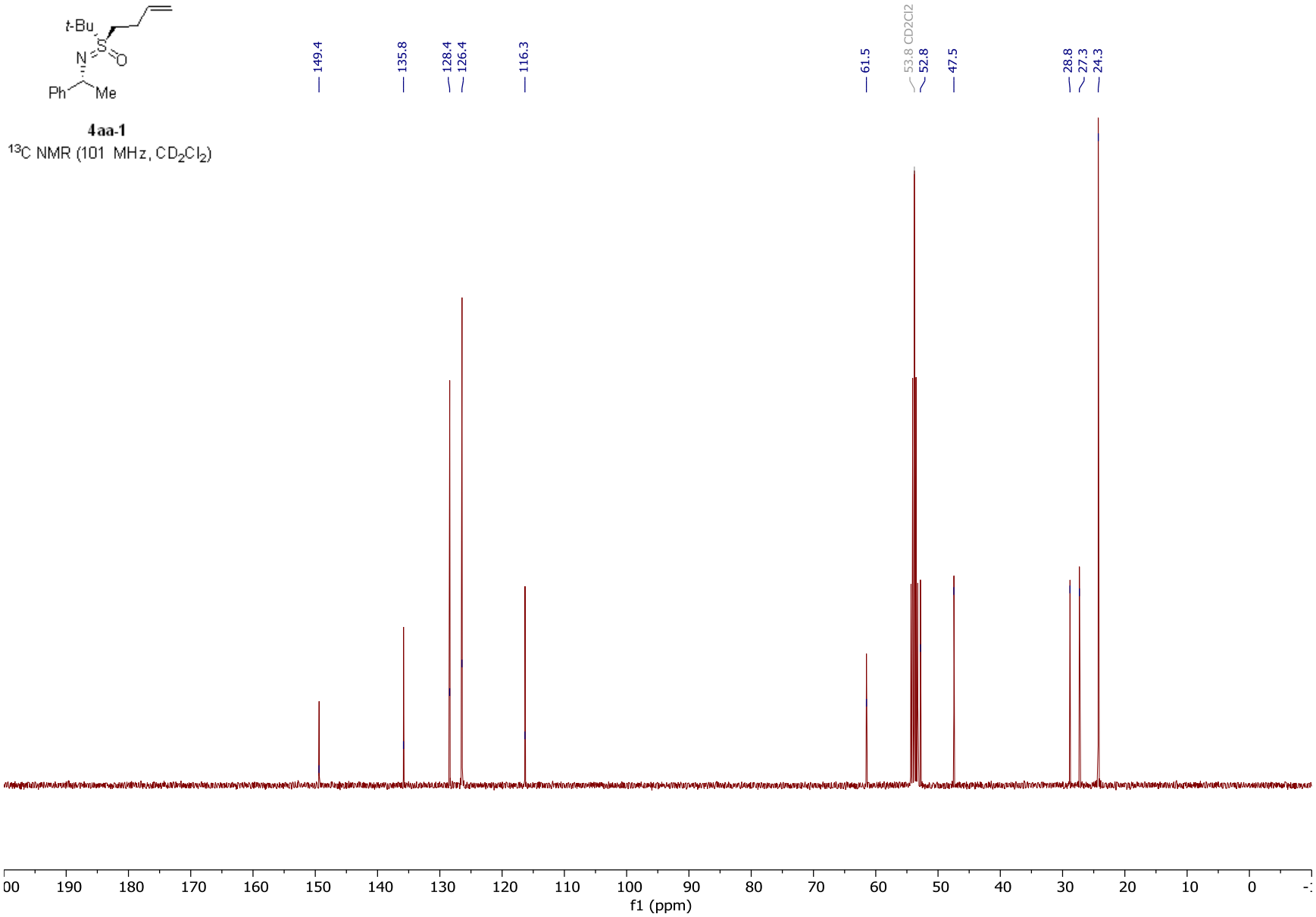

t-Bu
I
N
S
O
Ph
Me
4aa-I
^{1}H NMR (400 MHz, CD_2Cl_2)
7.42
7.40
7.31
7.30
7.28
7.21
7.19
7.18
5.32 CD_2Cl_2
4.80
4.78
4.77
4.75
4.36
4.33
4.16
4.13
1.53
1.41
1.40
1.97
1.96
0.98
1.01
1.06
1.07
9.28
3.11
f1 (ppm)

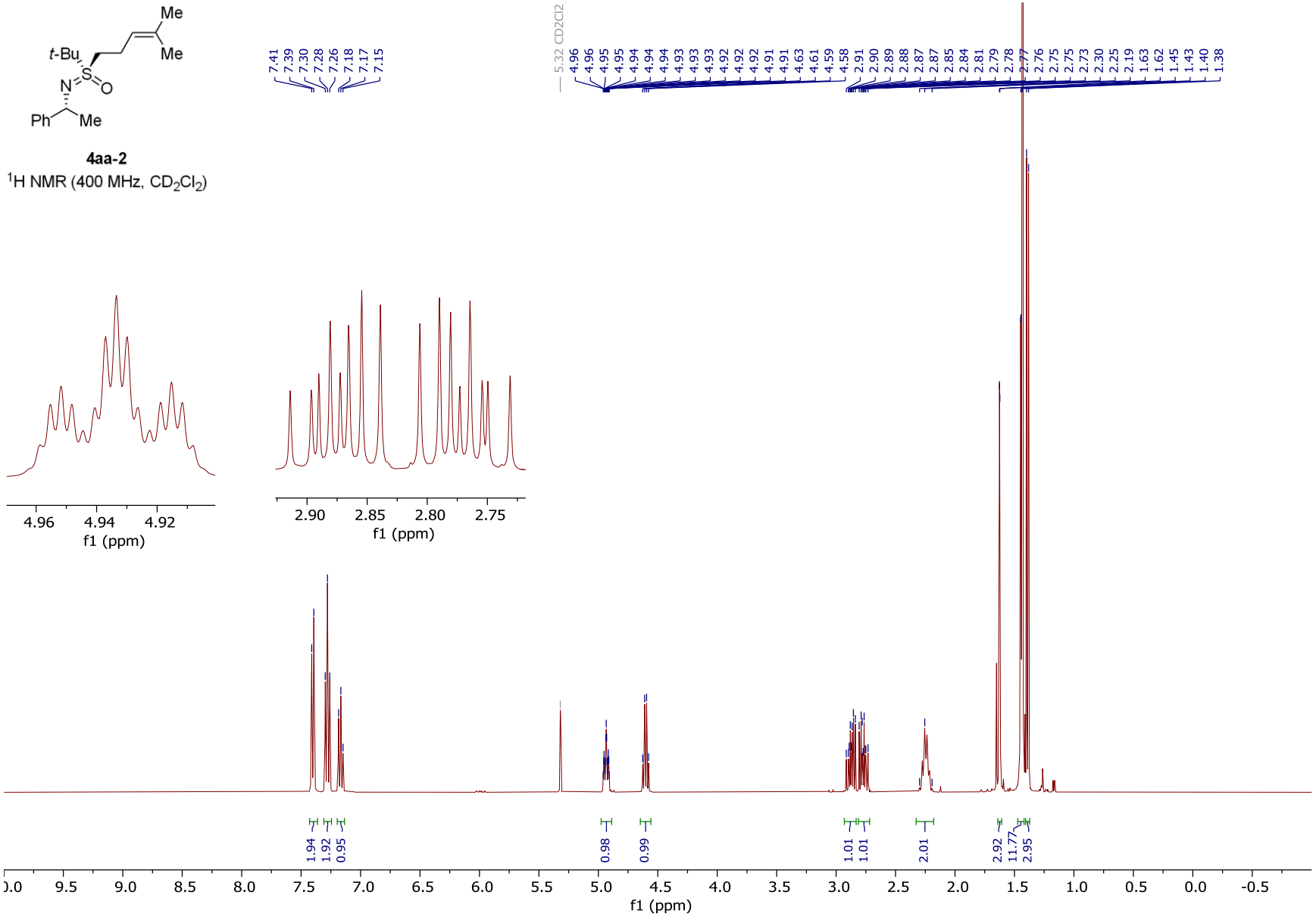


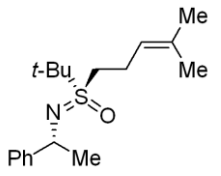
4aa-I

^{13}C NMR (101 MHz, CD_2Cl_2)


t-Bu
N
S
O
Ph
Me
4aa-1
1H NMR (400 MHz, CD2Cl2)
7.41 7.39 7.30 7.29 7.27 7.20 7.18 7.16
5.69 5.67 5.66 5.65 5.65 5.63 5.62 5.61 5.60 5.59
5.32 CD2Cl2
4.95 4.93 4.89 4.88 4.62 4.60 4.58 4.57
2.98 2.91 2.89 2.81
2.38 2.31 2.23
1.44 1.40 1.39
5.70 5.68 5.66 5.64 5.62 5.60 5.58
f1 (ppm)
1.93 1.92 0.95 0.93 1.91 0.99 2.04 2.02 8.96 3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

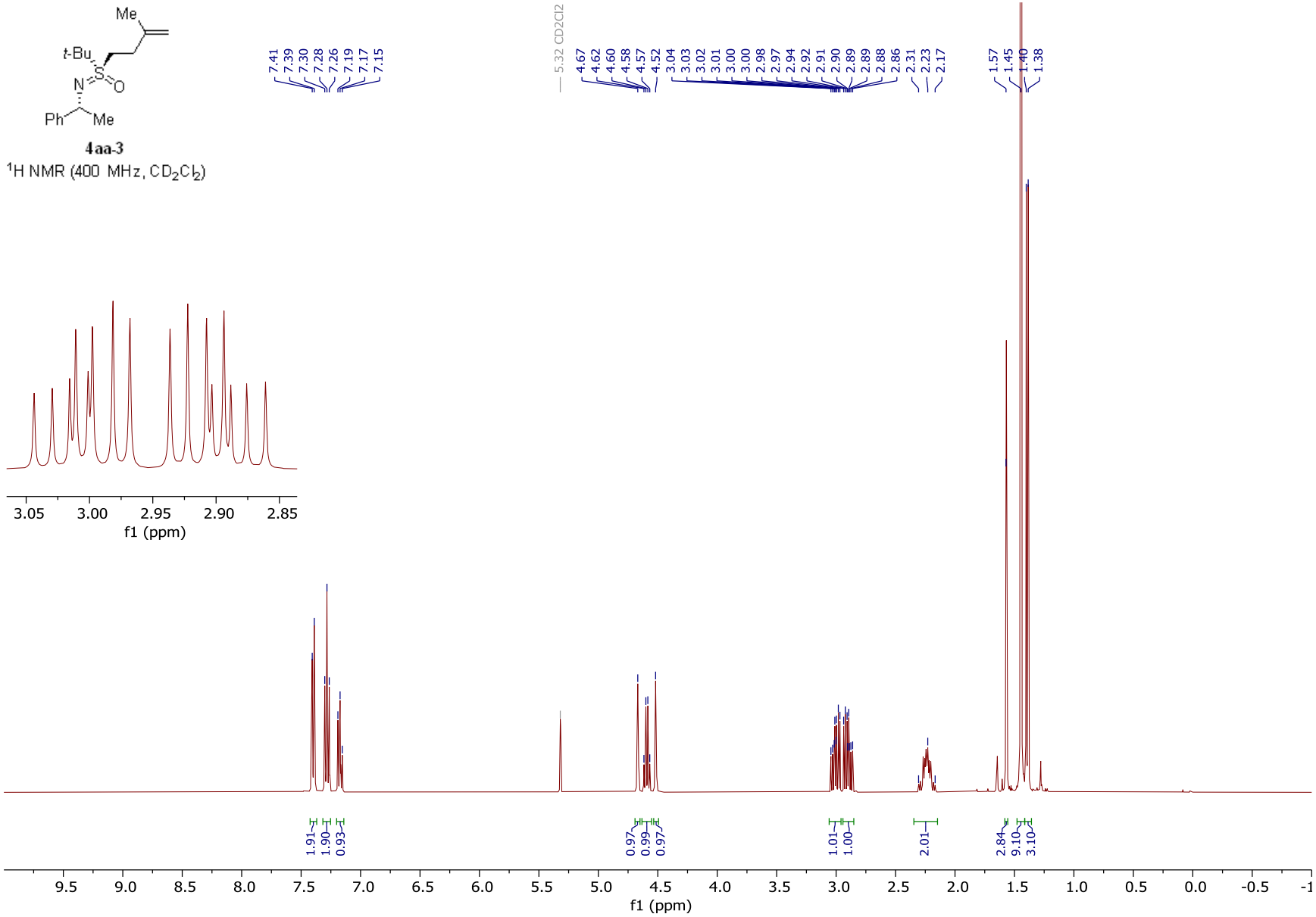

t-Bu
S
N
O
Ph
Me
4aa-1
13C NMR (101 MHz, CD2Cl2)
149.4
135.8
128.4
126.4
116.3
61.5
53.8 CD2Cl2
52.8
47.5
28.8
27.3
24.3
f1 (ppm)

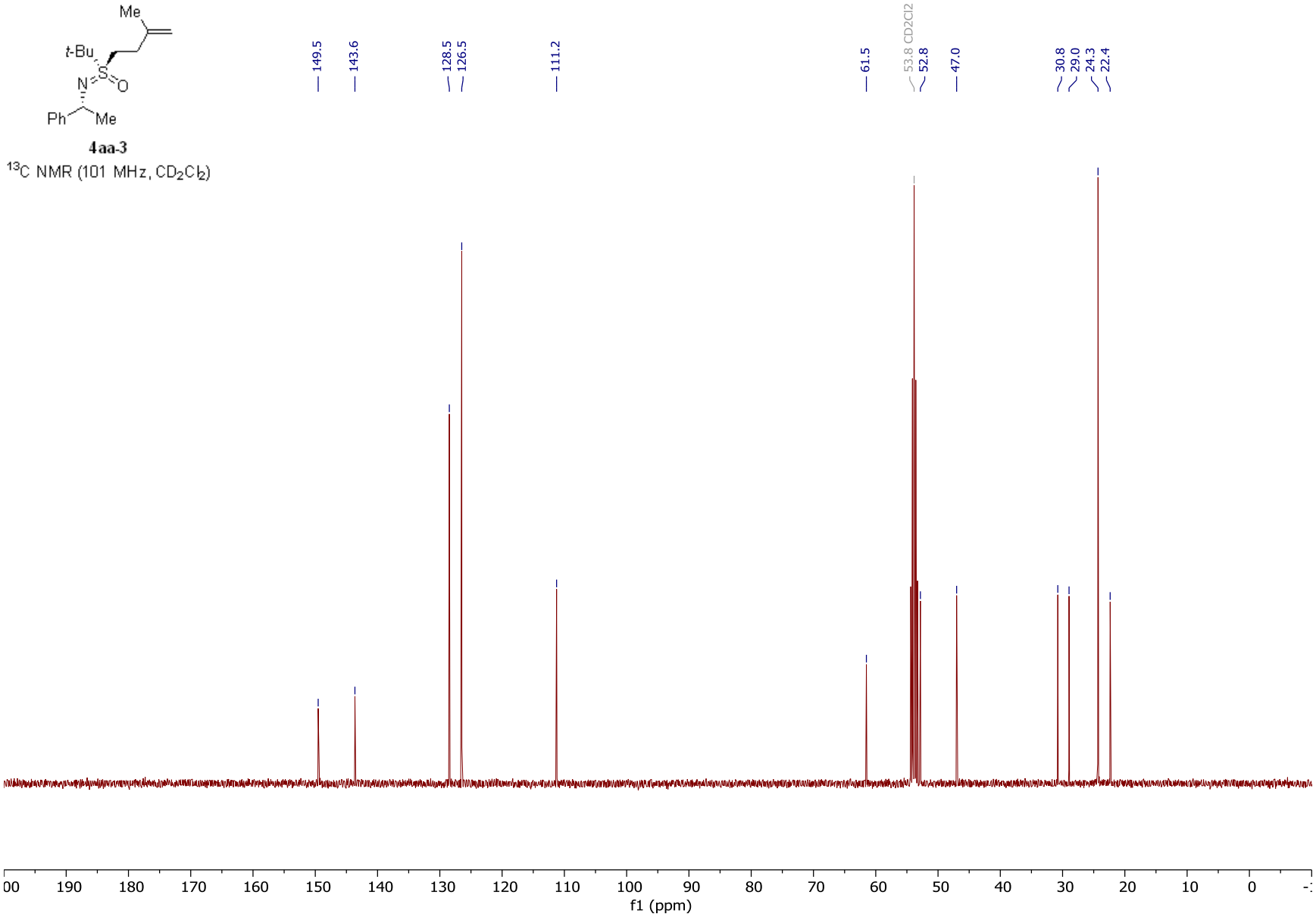

Me
t-Bu
Me
N
S
O
Ph
Me
4aa-2
1H NMR (400 MHz, CD2Cl2)
7.41
7.39
7.30
7.28
7.26
7.18
7.17
7.15
5.32 CD2Cl2
4.96
4.96
4.95
4.95
4.94
4.94
4.94
4.93
4.93
4.92
4.92
4.92
4.91
4.91
4.63
4.61
4.59
4.58
2.91
2.90
2.89
2.88
2.87
2.87
2.85
2.84
2.81
2.79
2.78
2.77
2.76
2.75
2.75
2.73
2.30
2.25
2.19
1.63
1.62
1.45
1.43
1.40
1.38
4.96
4.94
4.92
f1 (ppm)
2.90
2.85
2.80
2.75
f1 (ppm)
1.94
1.92
0.95
0.98
0.99
1.01
1.01
2.01
2.92
11.77
2.95
f1 (ppm)

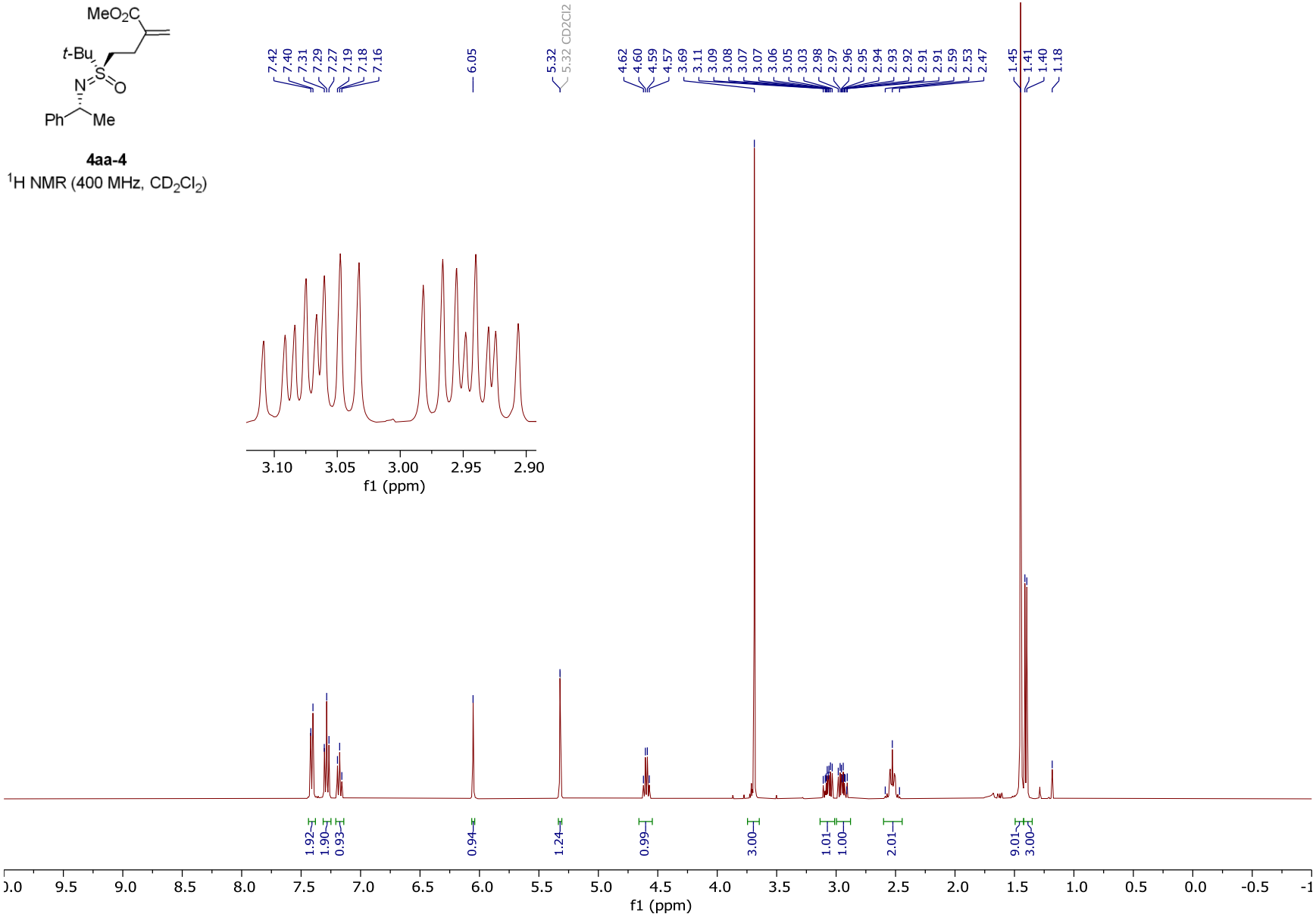


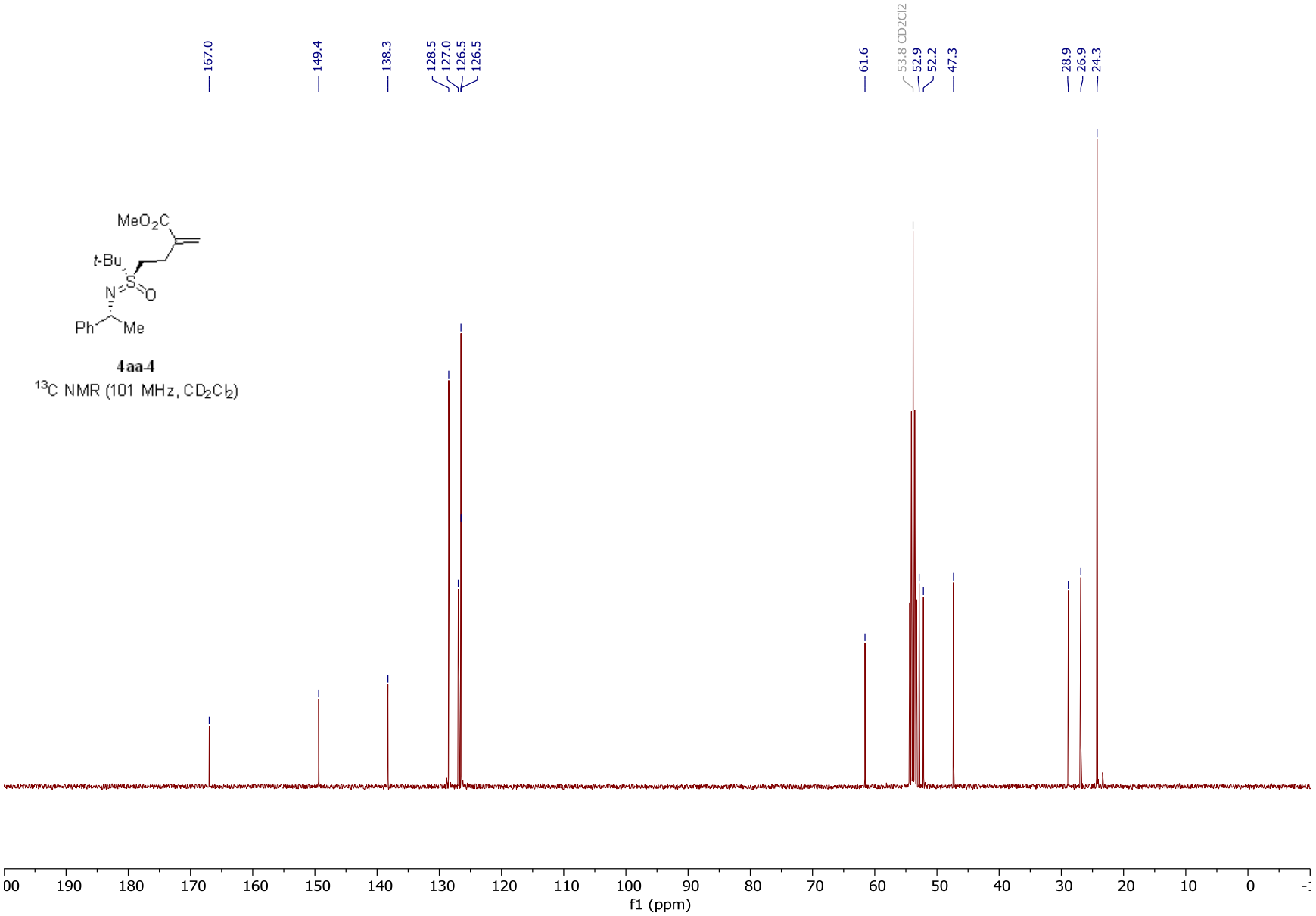
4aa-2

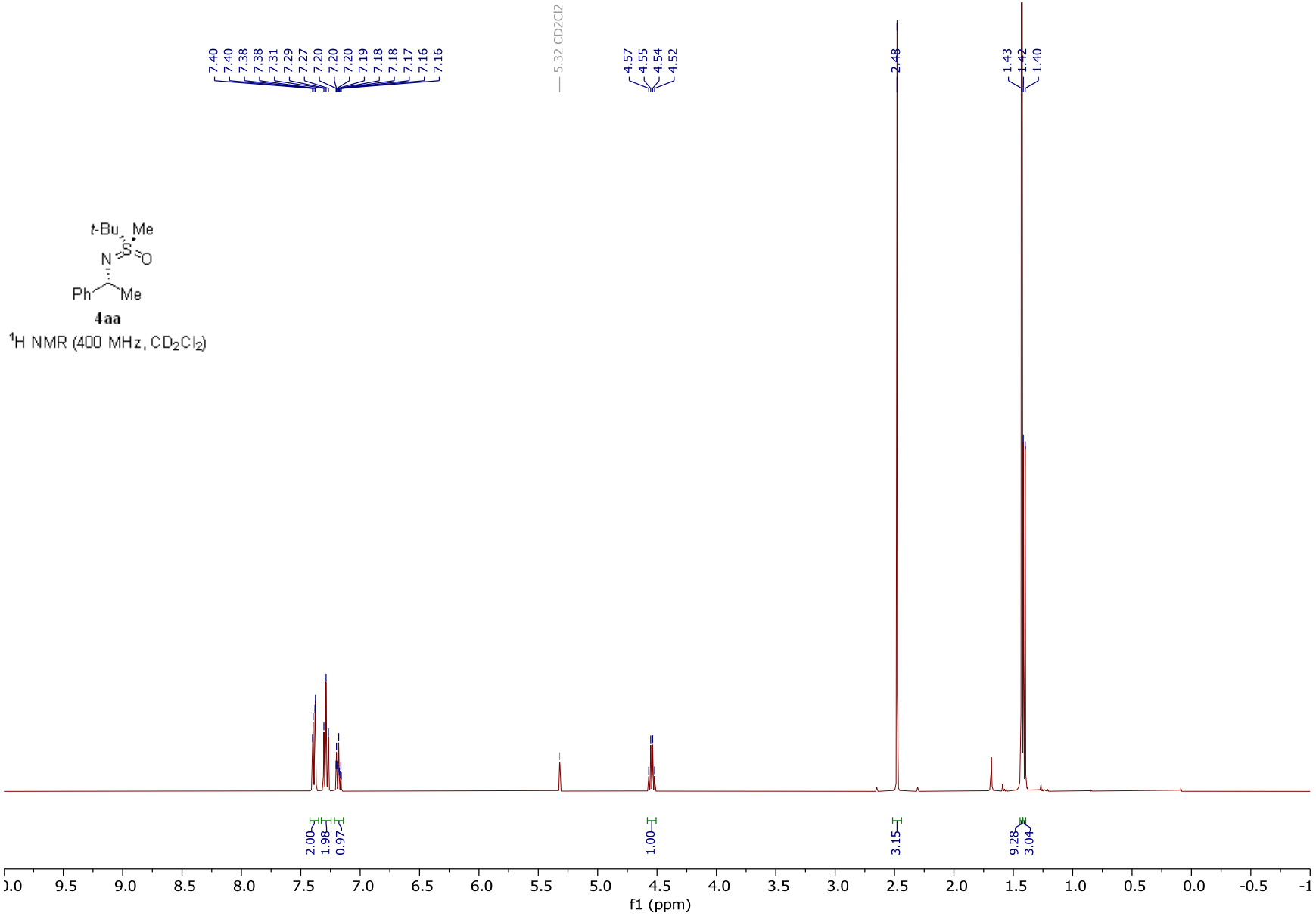
^{13}C NMR (101 MHz, CD_2Cl_2)

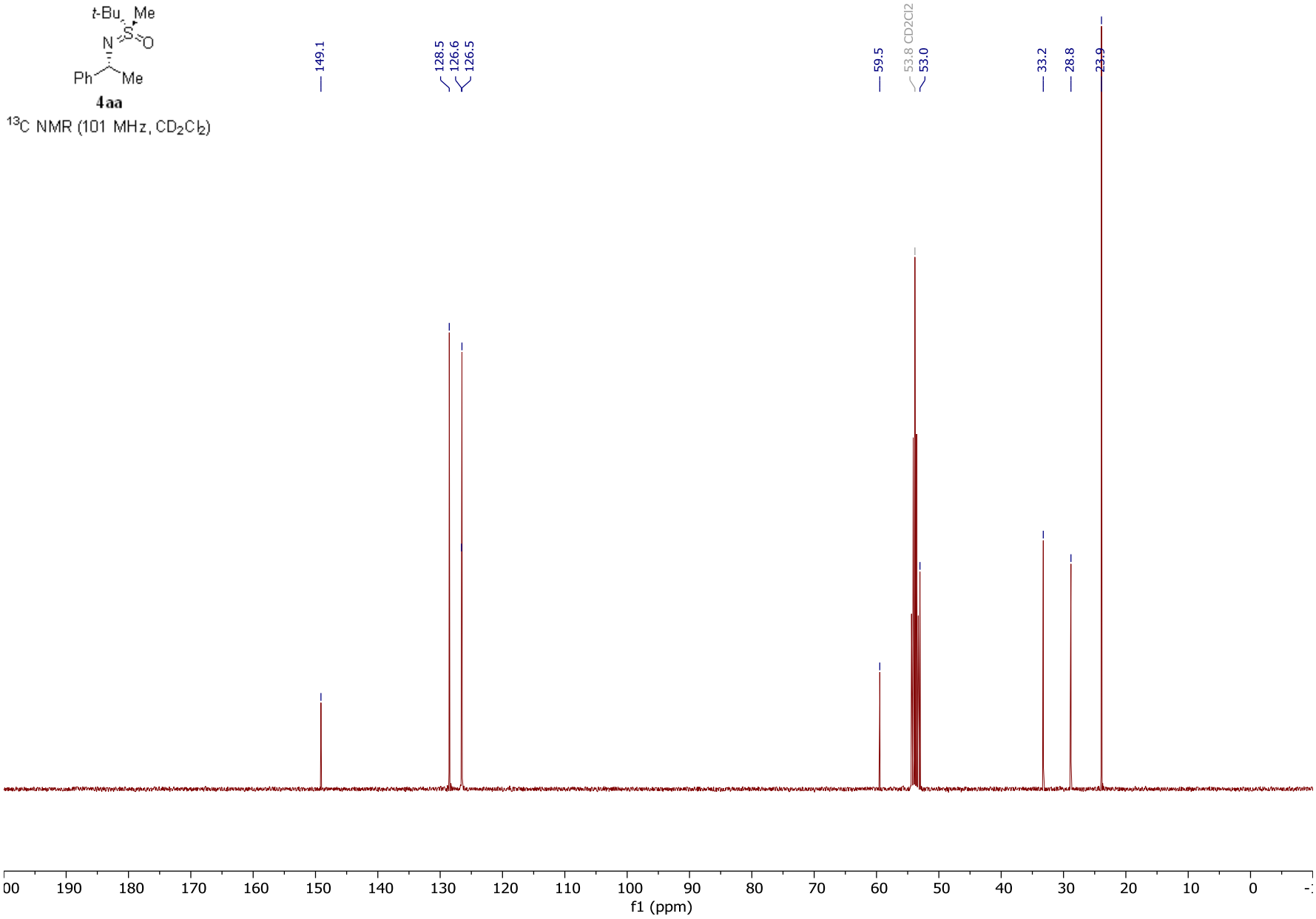

Me
t-Bu
S
N
O
Ph
Me
4aa-3
^{1}H NMR (400 MHz, CD_2Cl_2)
7.41
7.39
7.30
7.28
7.26
7.19
7.17
7.15
5.32 CD_2Cl_2
4.67
4.62
4.60
4.58
4.57
4.52
3.04
3.03
3.02
3.01
3.00
3.00
2.98
2.97
2.94
2.92
2.91
2.90
2.89
2.89
2.88
2.86
2.31
2.23
2.17
1.57
1.45
1.40
1.38
3.05
3.00
2.95
2.90
2.85
f1 (ppm)
1.91
1.90
0.93
0.97
0.99
0.97
1.01
1.00
2.01
2.84
9.10
3.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

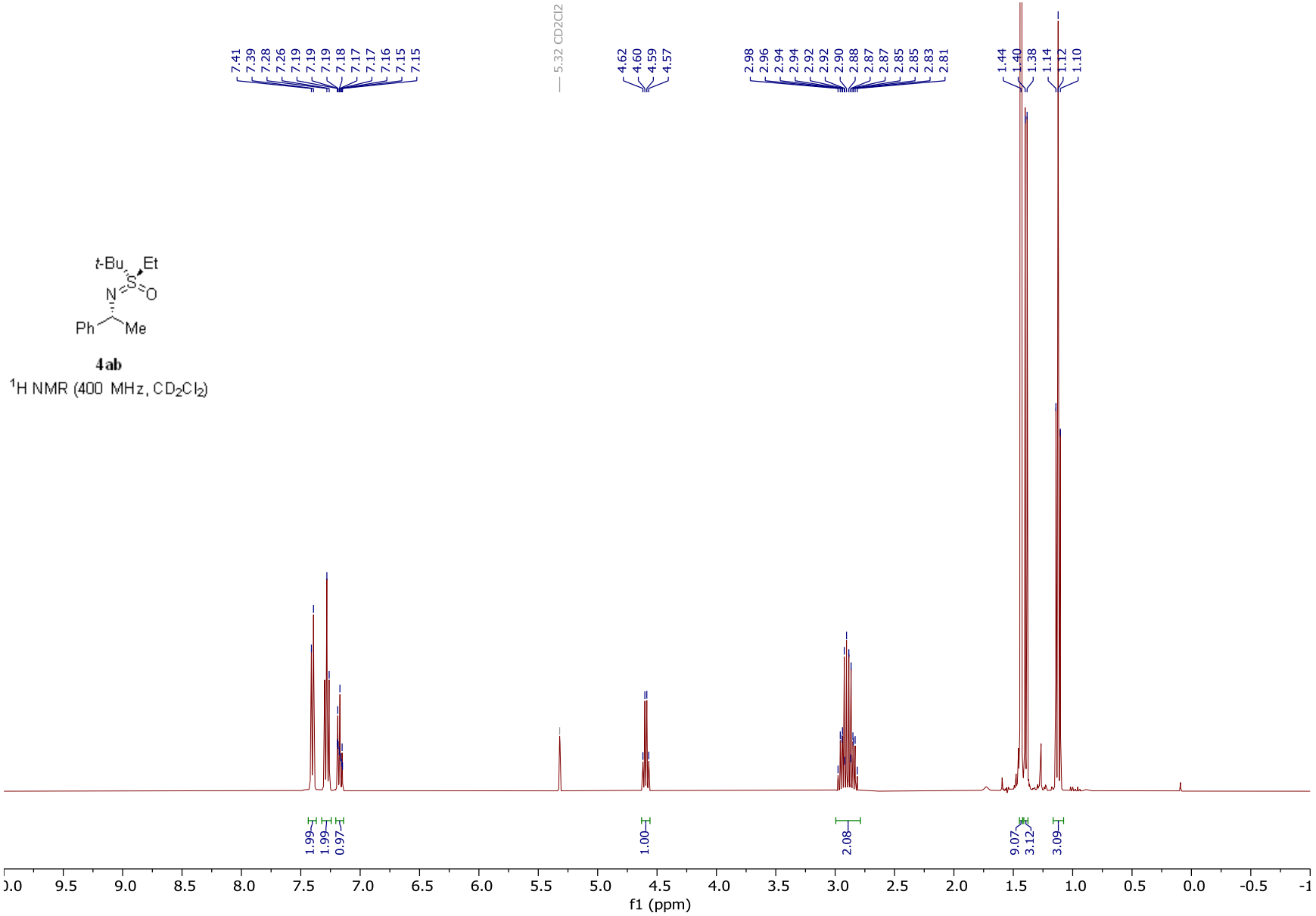

Me
t-Bu
S
N
O
Ph
Me
4aa-3
13C NMR (101 MHz, CD2Cl2)
149.5
143.6
128.5
126.5
111.2
61.5
53.8 CD2Cl2
52.8
47.0
30.8
29.0
24.3
22.4
f1 (ppm)

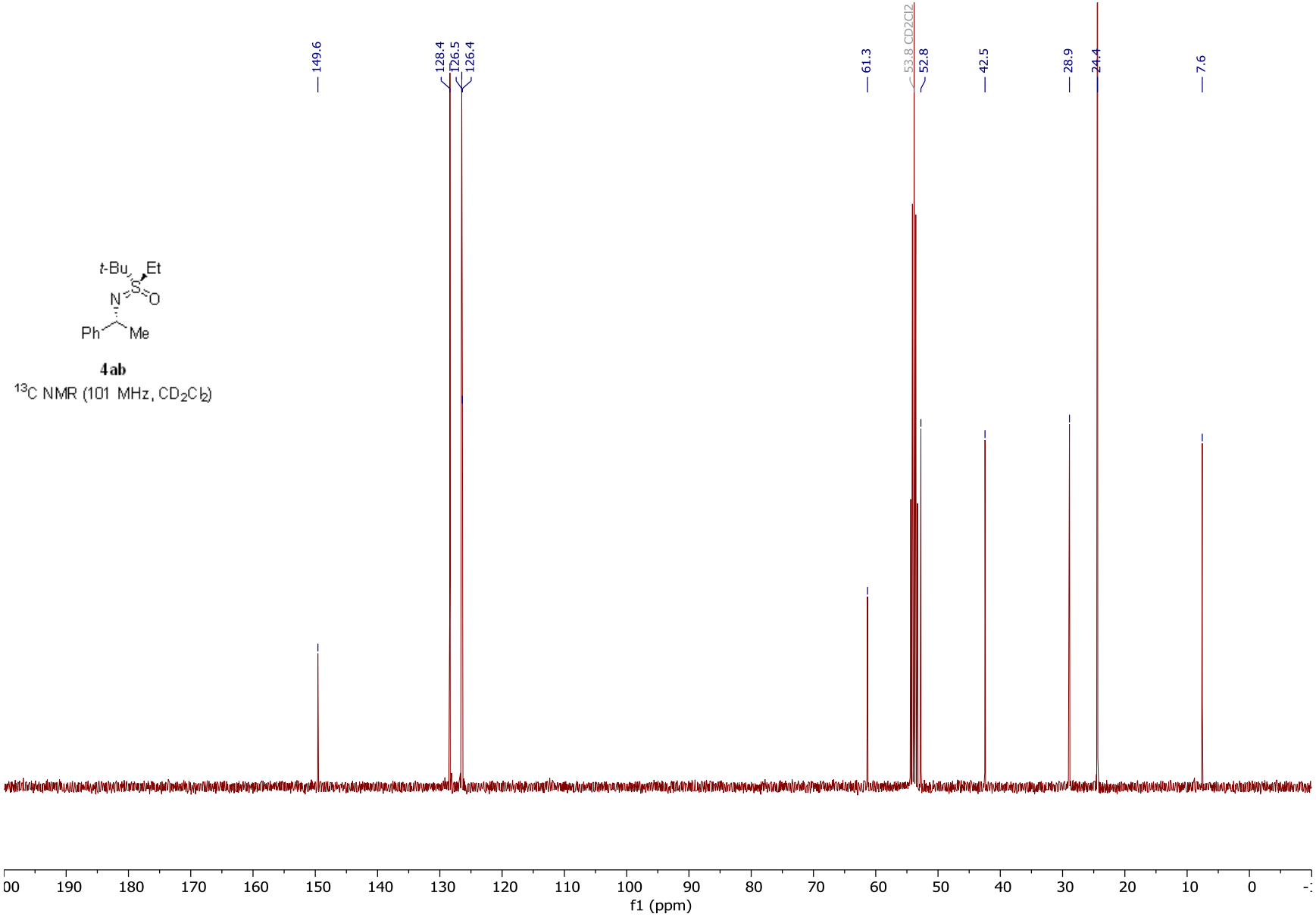

MeO2C
t-Bu
S
N
O
Ph
Me
4aa-4
1H NMR (400 MHz, CD2Cl2)
7.42
7.40
7.31
7.29
7.27
7.19
7.18
7.16
6.05
5.32
5.32 CD2Cl2
4.62
4.60
4.59
4.57
3.69
3.11
3.09
3.08
3.07
3.07
3.06
3.05
3.03
2.98
2.97
2.96
2.95
2.94
2.93
2.92
2.91
2.91
2.59
2.53
2.47
1.45
1.41
1.40
1.18
3.10
3.05
3.00
2.95
2.90
f1 (ppm)
1.92
1.90
0.93
0.94
1.24
0.99
3.00
1.01
1.00
2.01
9.01
3.00
f1 (ppm)

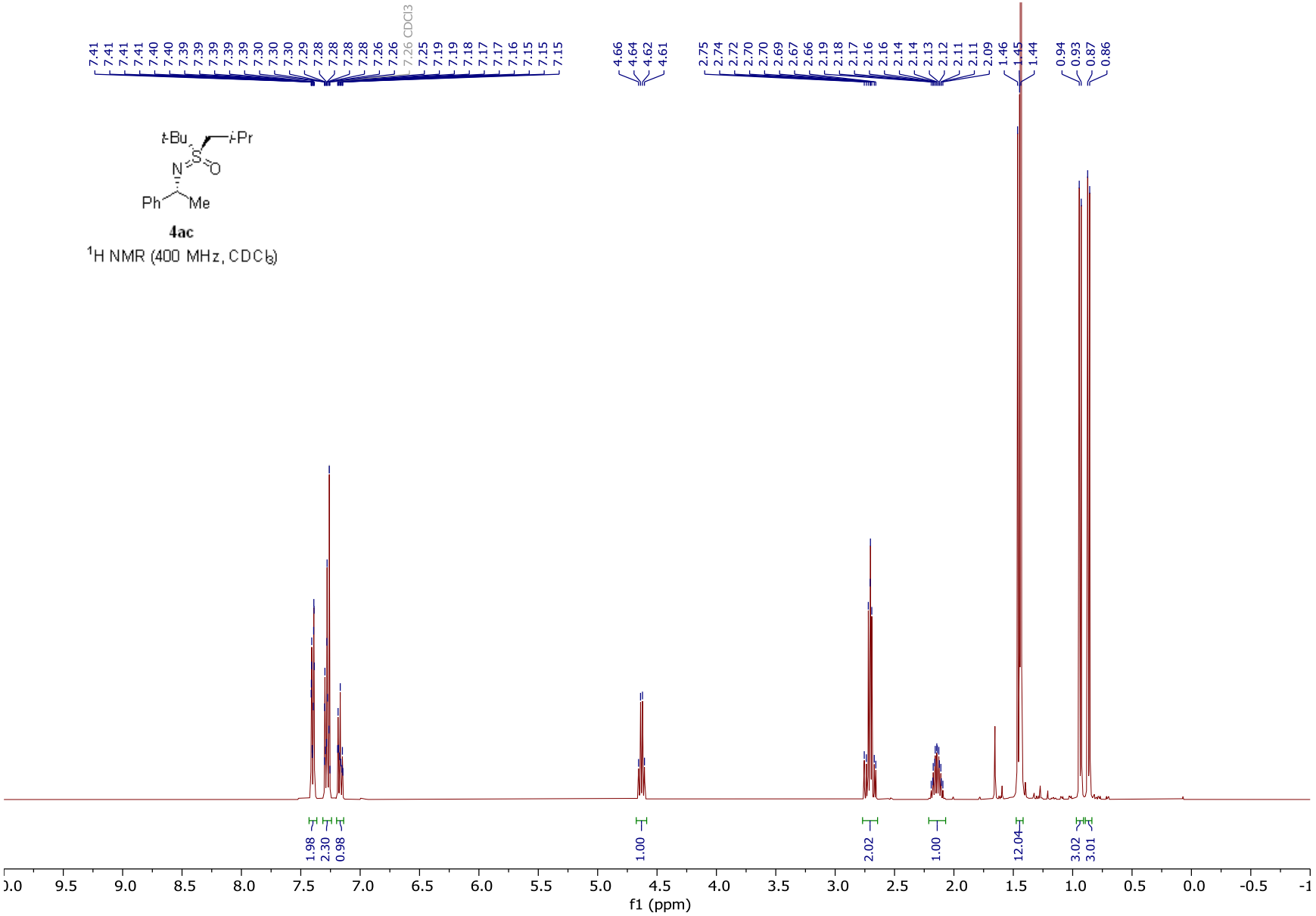

167.0
149.4
138.3
128.5
127.0
126.5
126.5
61.6
53.8 CD2Cl2
52.9
52.2
47.3
28.9
26.9
24.3
MeO2C
t-Bu
N
S
O
Ph
Me
4aa-4
13C NMR (101 MHz, CD2Cl2)
f1 (ppm)

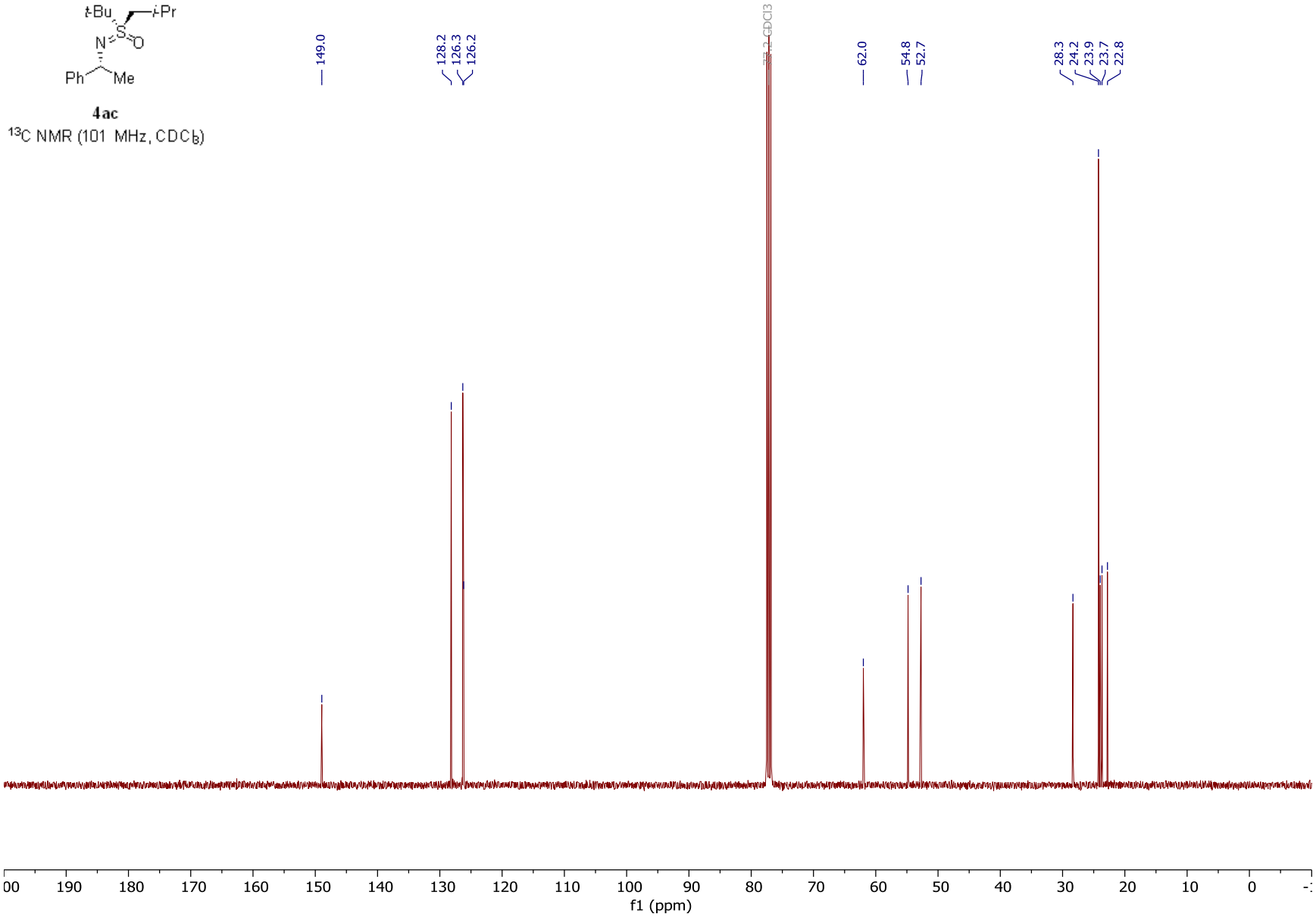

7.40
7.40
7.38
7.38
7.31
7.29
7.27
7.20
7.20
7.20
7.19
7.18
7.18
7.17
7.16
7.16
5.32 CD2Cl2
4.57
4.55
4.54
4.52
2.48
1.43
1.42
1.40
t-Bu
Me
N
S
O
Ph
Me
4aa
1H NMR (400 MHz, CD2Cl2)
2.00
1.98
0.97
1.00
3.15
9.28
3.04
f1 (ppm)

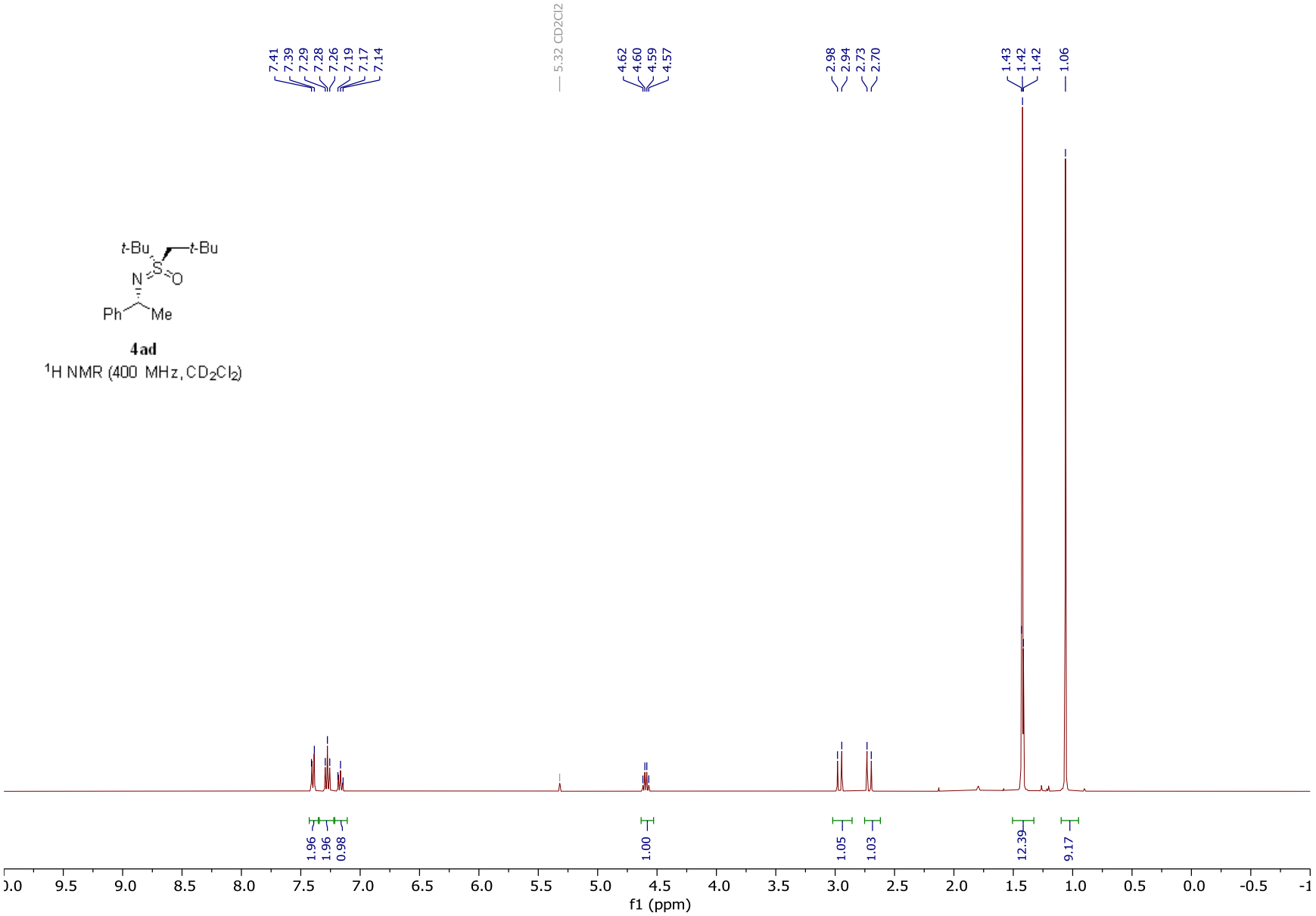

t-Bu
Me
N
S
O
Ph
Me
4aa
13C NMR (101 MHz, CD2Cl2)
149.1
128.5
126.6
126.5
59.5
53.8 CD2Cl2
53.0
33.2
28.8
23.9
f1 (ppm)

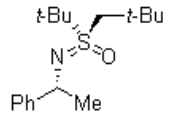

7.41
7.39
7.28
7.26
7.19
7.19
7.19
7.18
7.17
7.17
7.16
7.15
7.15
5.32 CD2Cl2
4.62
4.60
4.59
4.57
2.98
2.96
2.94
2.94
2.92
2.92
2.90
2.88
2.87
2.87
2.85
2.85
2.83
2.81
1.44
1.40
1.38
1.14
1.12
1.10
t-Bu
Et
N
S
O
Ph
Me
4ab
1H NMR (400 MHz, CD2Cl2)
1.99
1.99
0.97
1.00
2.08
9.07
3.12
3.09
f1 (ppm)


149.6
128.4
126.5
126.4
61.3
53.8 CD2Cl2
52.8
42.5
28.9
24.4
7.6
t-Bu
Et
N
S
O
Ph
Me
4ab
13C NMR (101 MHz, CD2Cl2)
f1 (ppm)


7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.30 7.30 7.30 7.29 7.28 7.28 7.28 7.26 7.26 CDCl3 7.25 7.19 7.18 7.17 7.16 7.15 7.15 7.15
4.66 4.64 4.62 4.61
2.75 2.74 2.72 2.70 2.70 2.69 2.67 2.66 2.19 2.18 2.17 2.16 2.16 2.14 2.14 2.13 2.12 2.11 2.11 2.09
1.46 1.45 1.44
0.94 0.93 0.87 0.86
t-Bu
i-Pr
N
S
O
Ph
Me
4ac
1H NMR (400 MHz, CDCl3)
1.98 2.30 0.98 1.00 2.02 1.00 12.04 3.02 3.01
f1 (ppm)

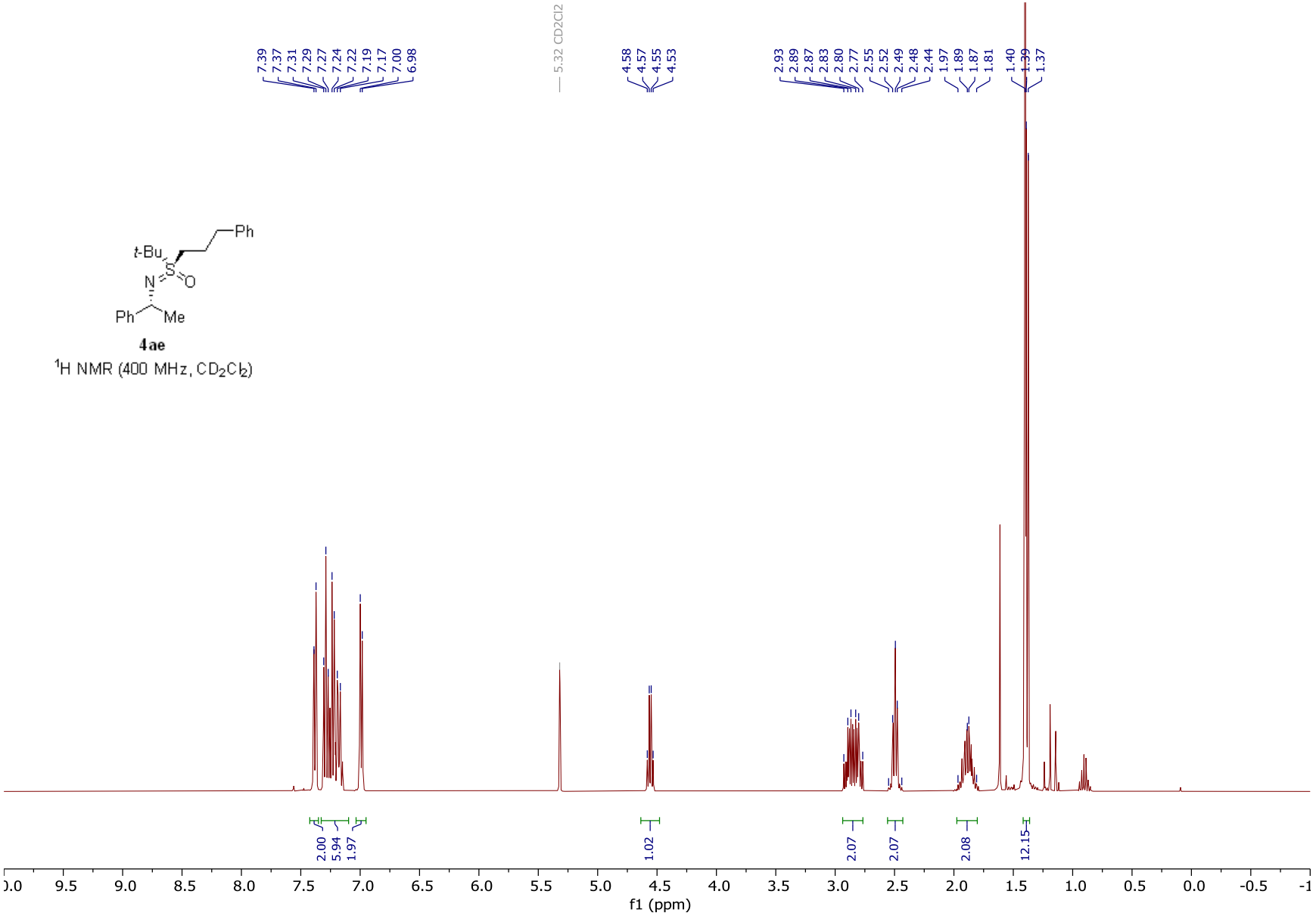

t-Bu
i-Pr
N
S
O
Ph
Me
4ac
13C NMR (101 MHz, CDCl3)
149.0
128.2
126.3
126.2
77.2 CDCl3
62.0
54.8
52.7
28.3
24.2
23.9
23.7
22.8
f1 (ppm)

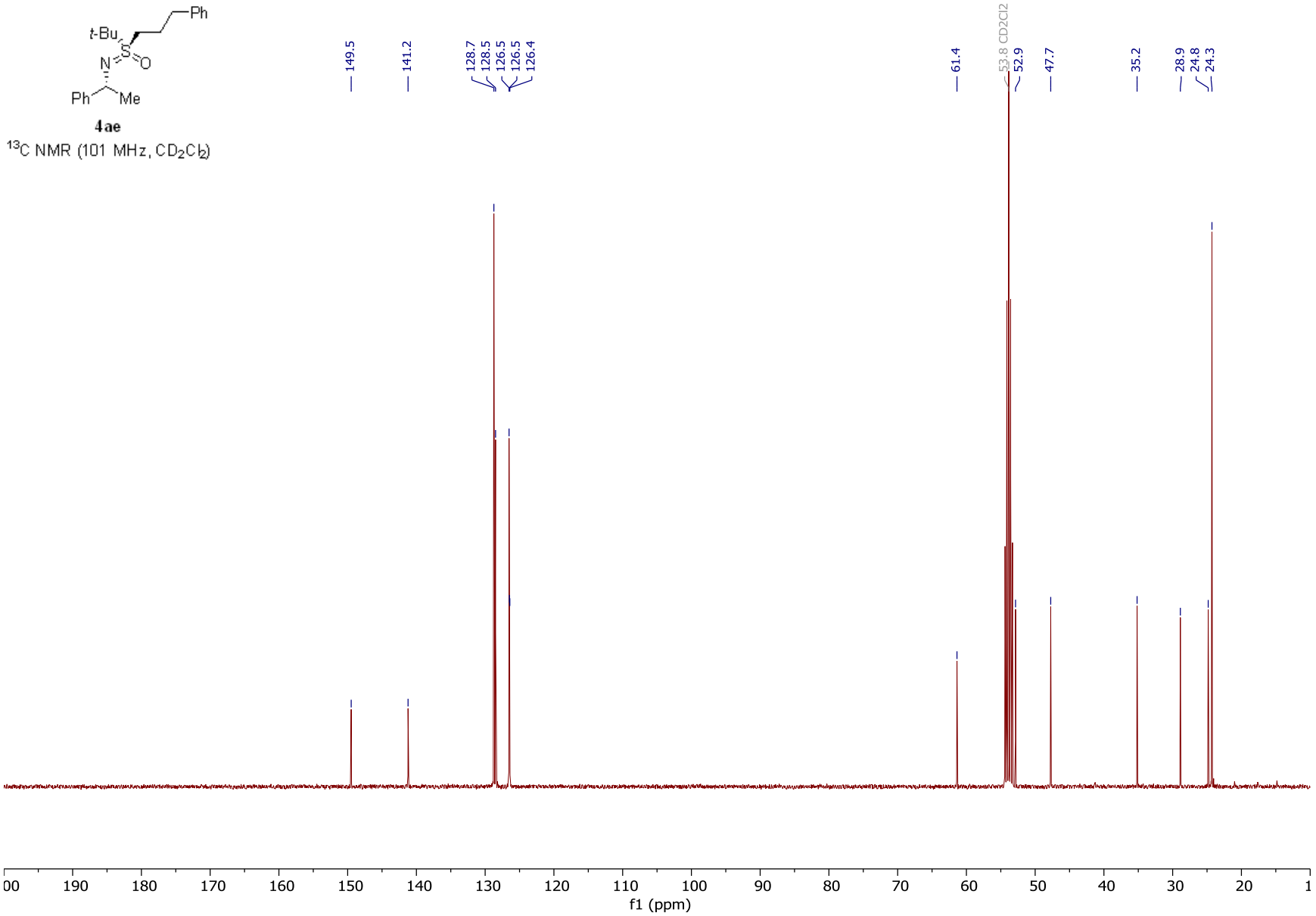

7.41
7.39
7.29
7.28
7.26
7.19
7.17
7.14
5.32 CD2Cl2
4.62
4.60
4.59
4.57
2.98
2.94
2.73
2.70
1.43
1.42
1.42
1.06
t-Bu
t-Bu
N
S
O
Ph
Me
4ad
1H NMR (400 MHz, CD2Cl2)
1.96
1.96
0.98
1.00
1.05
1.03
12.39
9.17
f1 (ppm)

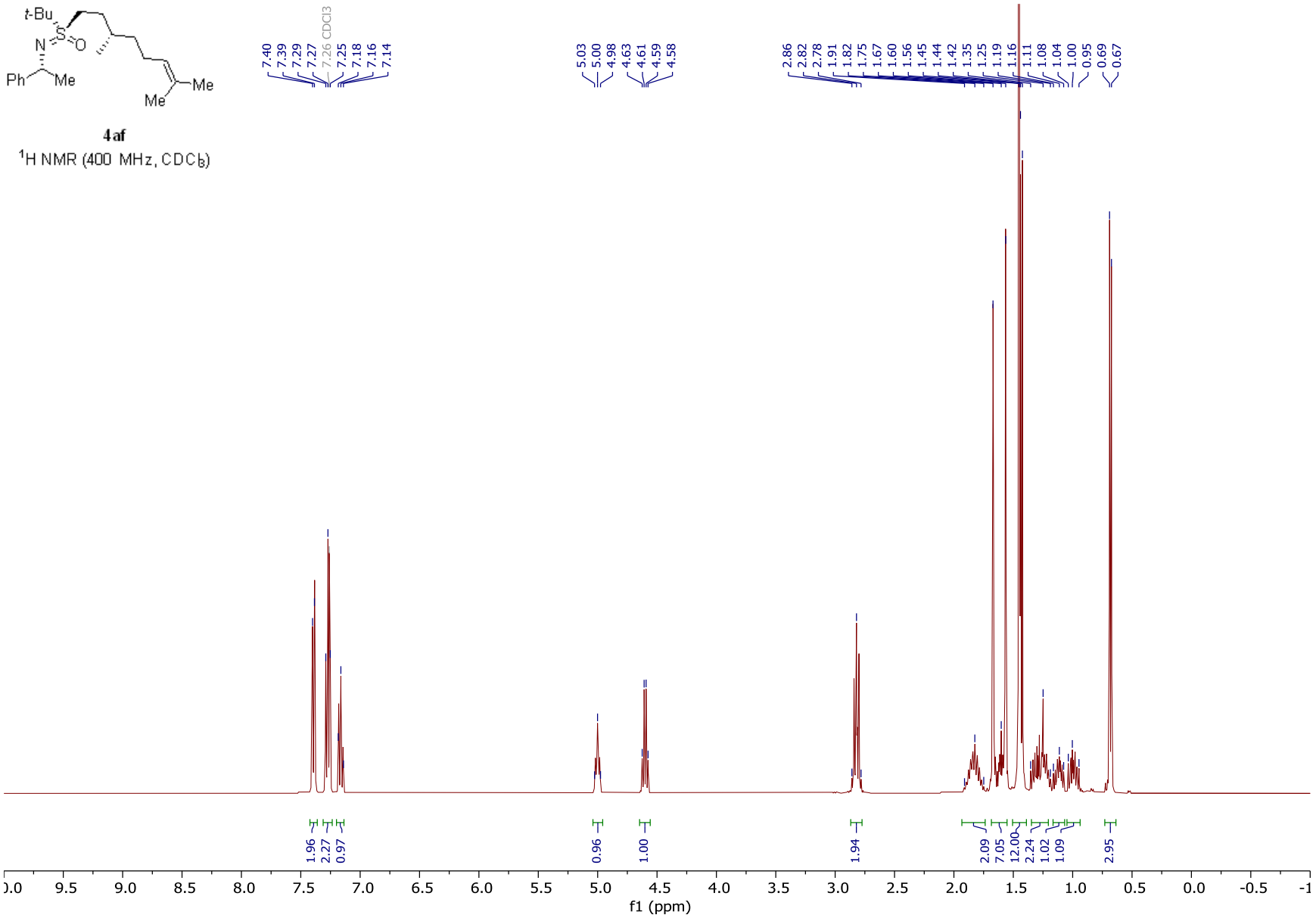


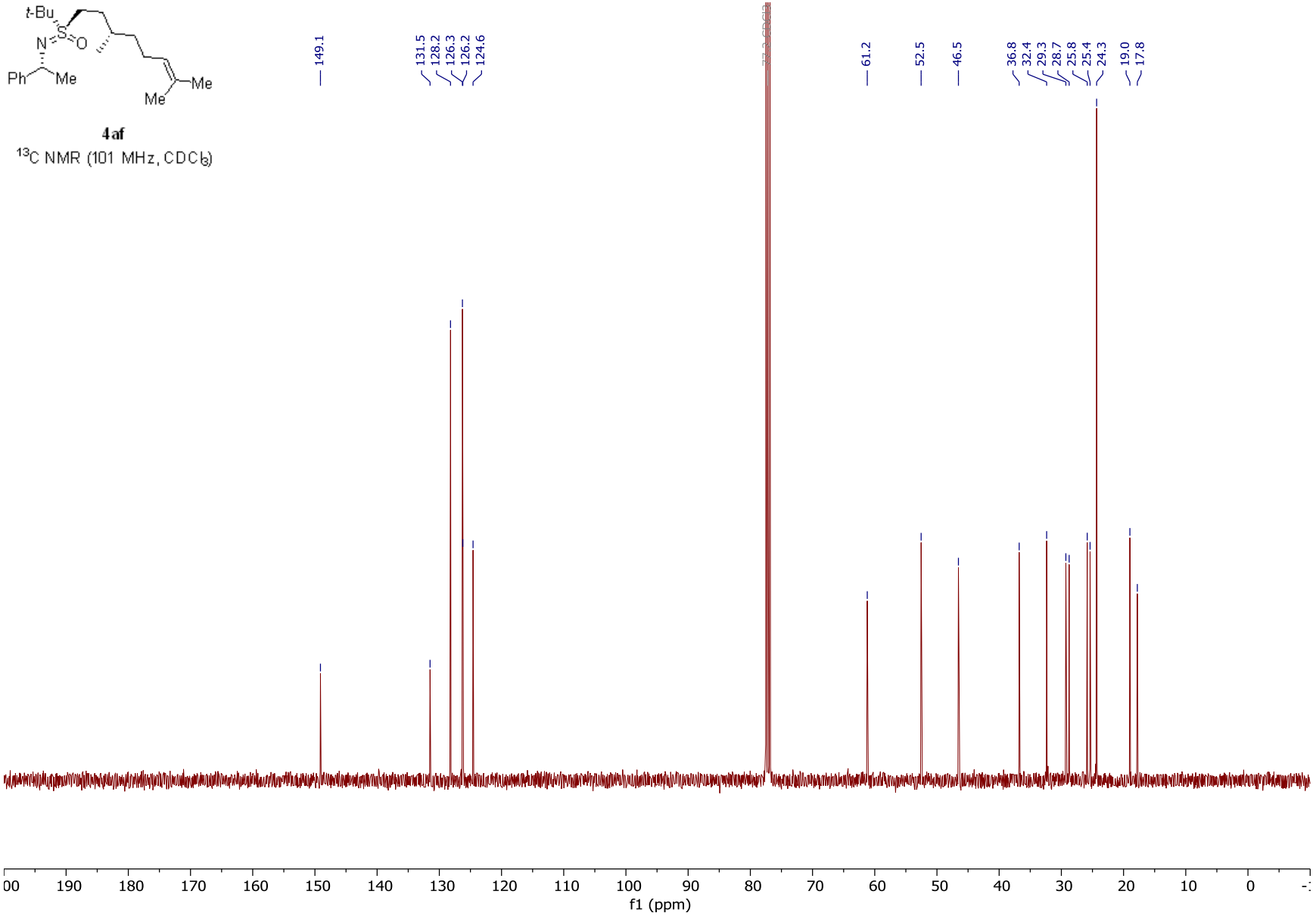
4ad

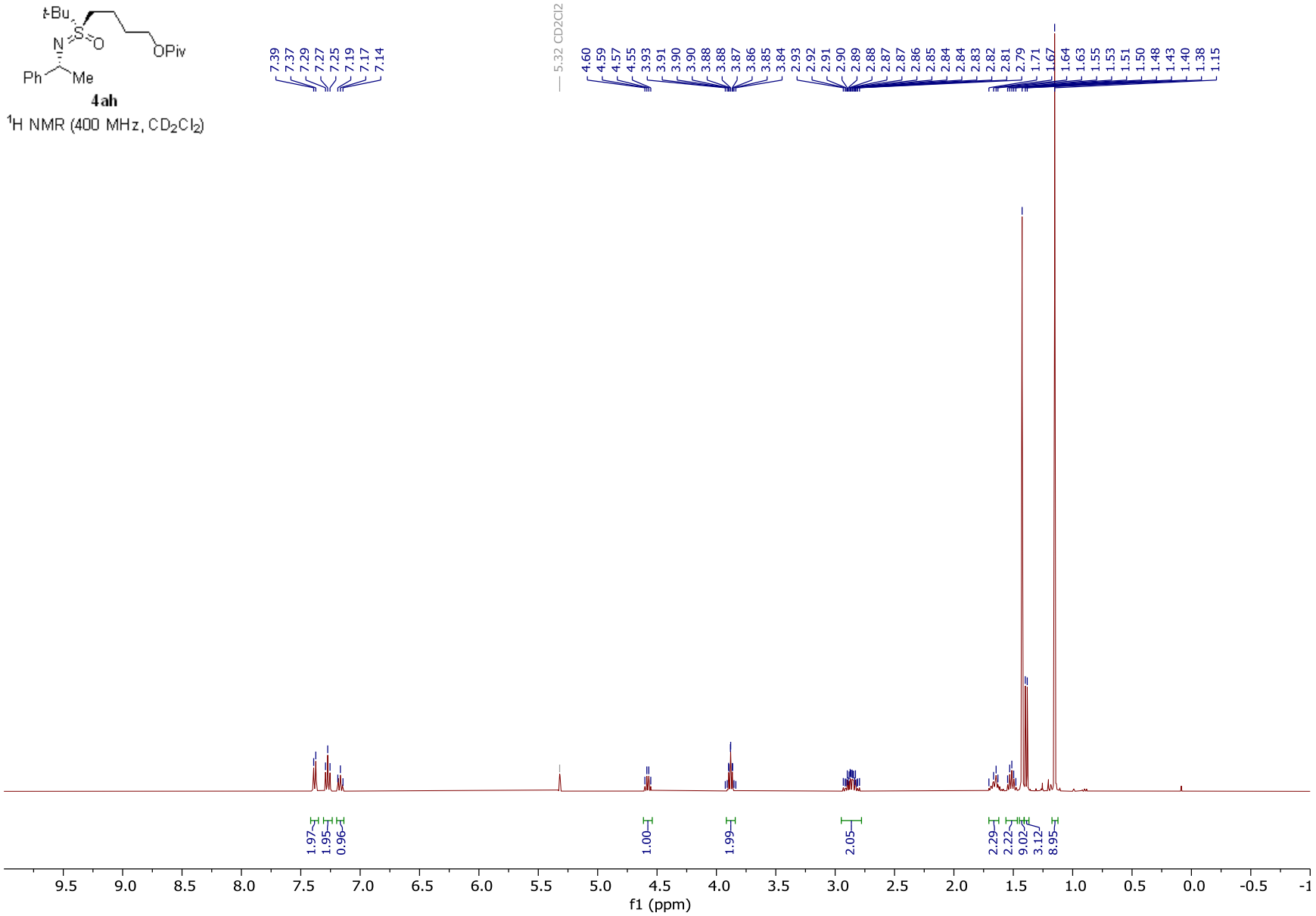
^{13}C NMR (101 MHz, CD_2Cl_2)

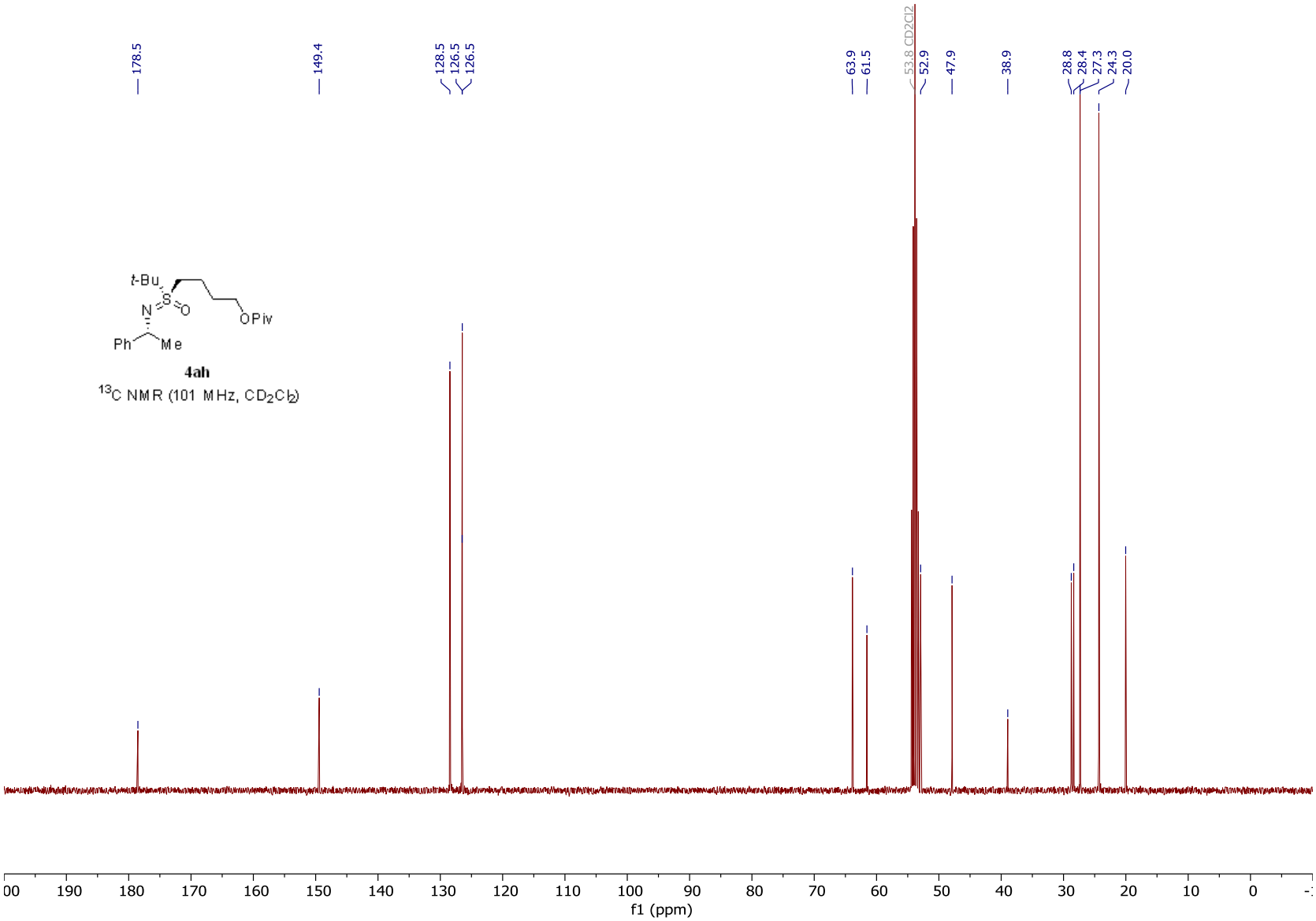

7.39
7.37
7.31
7.29
7.27
7.24
7.22
7.19
7.17
7.00
6.98
5.32 CD2Cl2
4.58
4.57
4.55
4.53
2.93
2.89
2.87
2.83
2.80
2.77
2.55
2.52
2.49
2.48
2.44
1.97
1.89
1.87
1.81
1.40
1.39
1.37
Ph
t-Bu
S
N
O
Ph
Me
4ae
1H NMR (400 MHz, CD2Cl2)
2.00
5.94
1.97
1.02
2.07
2.07
2.08
12.15
f1 (ppm)

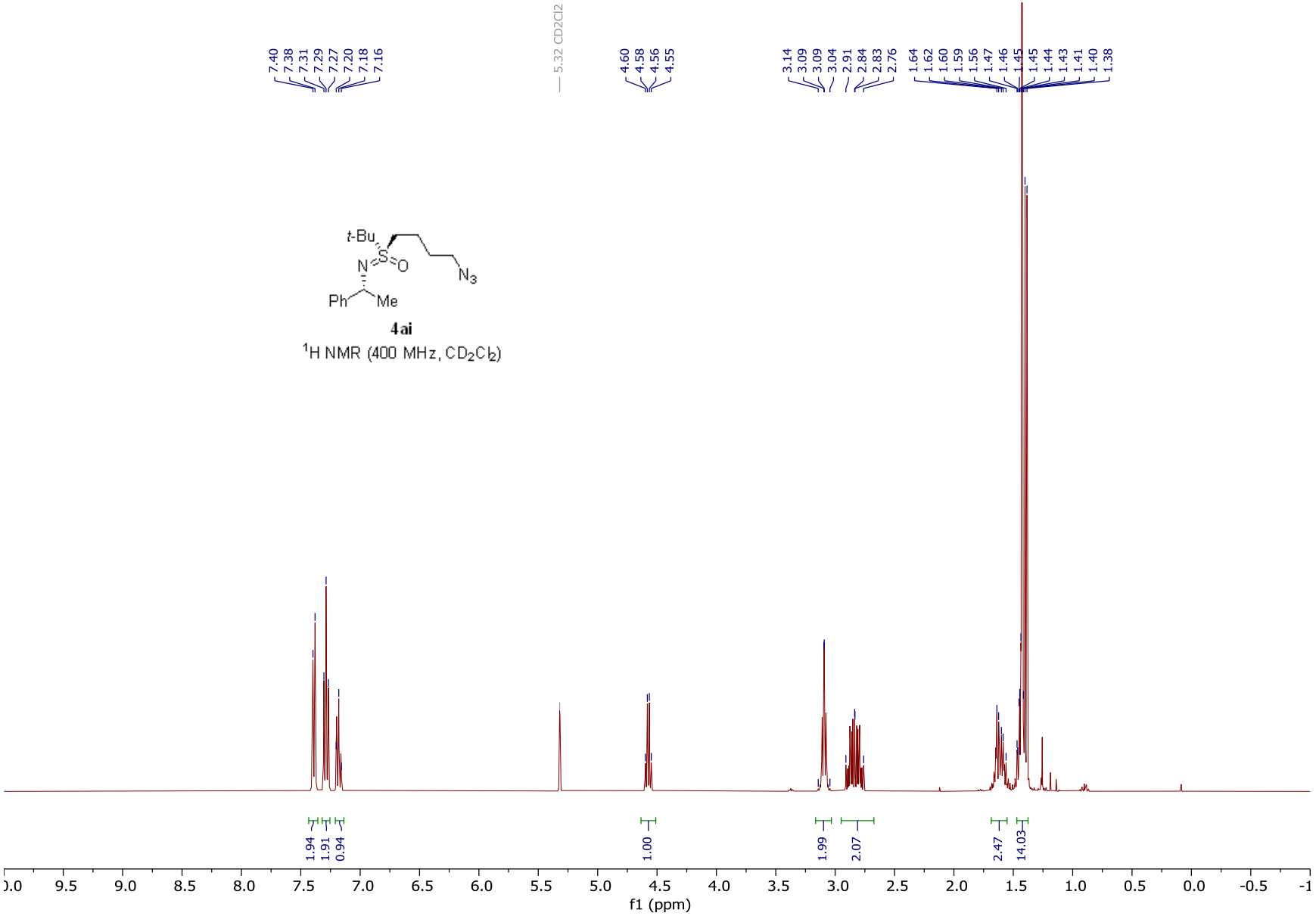

Ph
t-Bu
S
O
N
Ph
Me
4ae
13C NMR (101 MHz, CD2Cl2)
149.5
141.2
128.7
128.5
126.5
126.5
126.4
61.4
53.8 CD2Cl2
52.9
47.7
35.2
28.9
24.8
24.3
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)

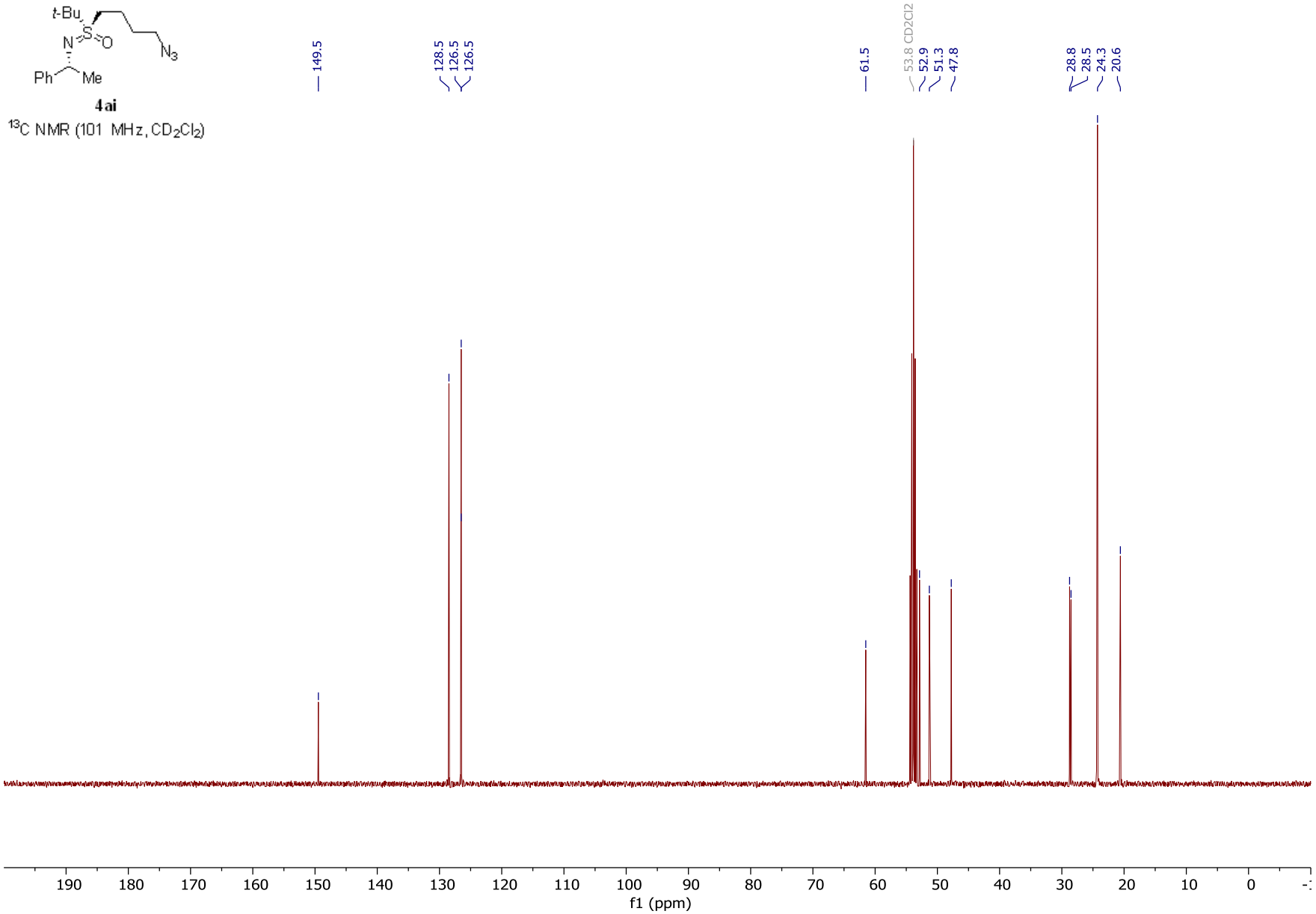

t-Bu
N
S
O
Ph
Me
Me
Me
4af
1H NMR (400 MHz, CDCl3)
7.40
7.39
7.29
7.27
7.26 CDCl3
7.25
7.18
7.16
7.14
5.03
5.00
4.98
4.63
4.61
4.59
4.58
2.86
2.82
2.78
1.91
1.82
1.75
1.67
1.60
1.56
1.45
1.44
1.42
1.35
1.25
1.19
1.16
1.11
1.08
1.04
1.00
0.95
0.69
0.67
1.96
2.27
0.97
0.96
1.00
1.94
2.09
7.05
12.00
2.24
1.02
1.09
2.95
f1 (ppm)

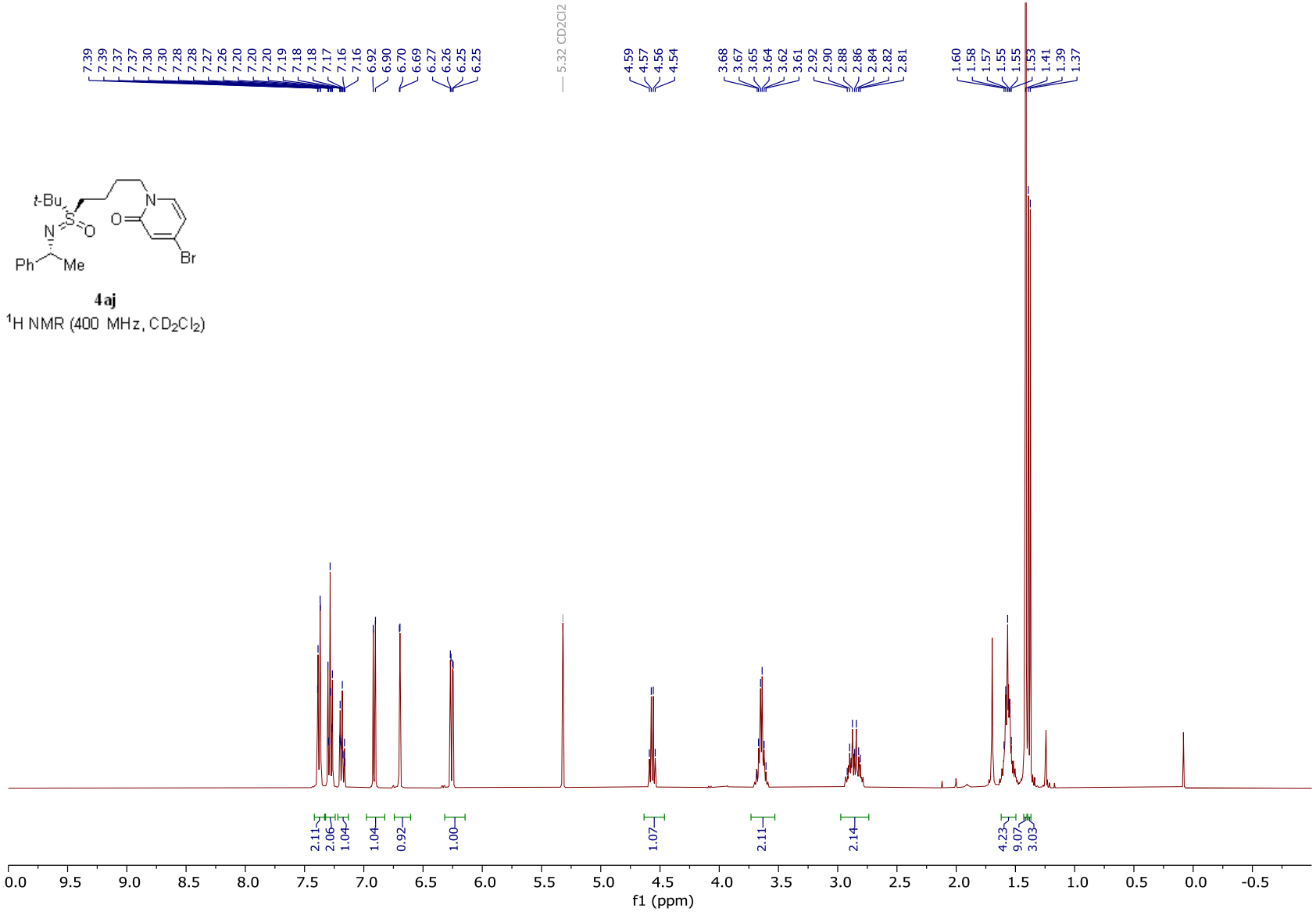

t-Bu
N
S
O
Ph
Me
Me
Me
4af
13C NMR (101 MHz, CDCl3)
149.1
131.5
128.2
126.3
126.2
124.6
77.3 CDCl3
61.2
52.5
46.5
36.8
32.4
29.3
28.7
25.8
25.4
24.3
19.0
17.8
f1 (ppm)


t-Bu
N
S
O
OPiv
Ph
Me
4ah
^{1}H NMR (400 MHz, CD_2Cl_2)
7.39
7.37
7.29
7.27
7.25
7.19
7.17
7.14
5.32 CD_2Cl_2
4.60
4.59
4.57
4.55
3.93
3.91
3.90
3.90
3.88
3.88
3.87
3.86
3.85
3.84
2.93
2.92
2.91
2.90
2.89
2.88
2.87
2.86
2.85
2.84
2.84
2.83
2.82
2.81
2.79
1.71
1.67
1.64
1.63
1.55
1.53
1.51
1.50
1.48
1.43
1.40
1.38
1.15
1.97
1.95
0.96
1.00
1.99
2.05
2.29
2.22
9.02
3.12
8.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


178.5
149.4
128.5
126.5
126.5
63.9
61.5
53.8 CD2Cl2
52.9
47.9
38.9
28.8
28.4
27.3
24.3
20.0
t-Bu
N
S
O
OPiv
Ph
Me
4ah
13C NMR (101 MHz, CD2Cl2)
f1 (ppm)

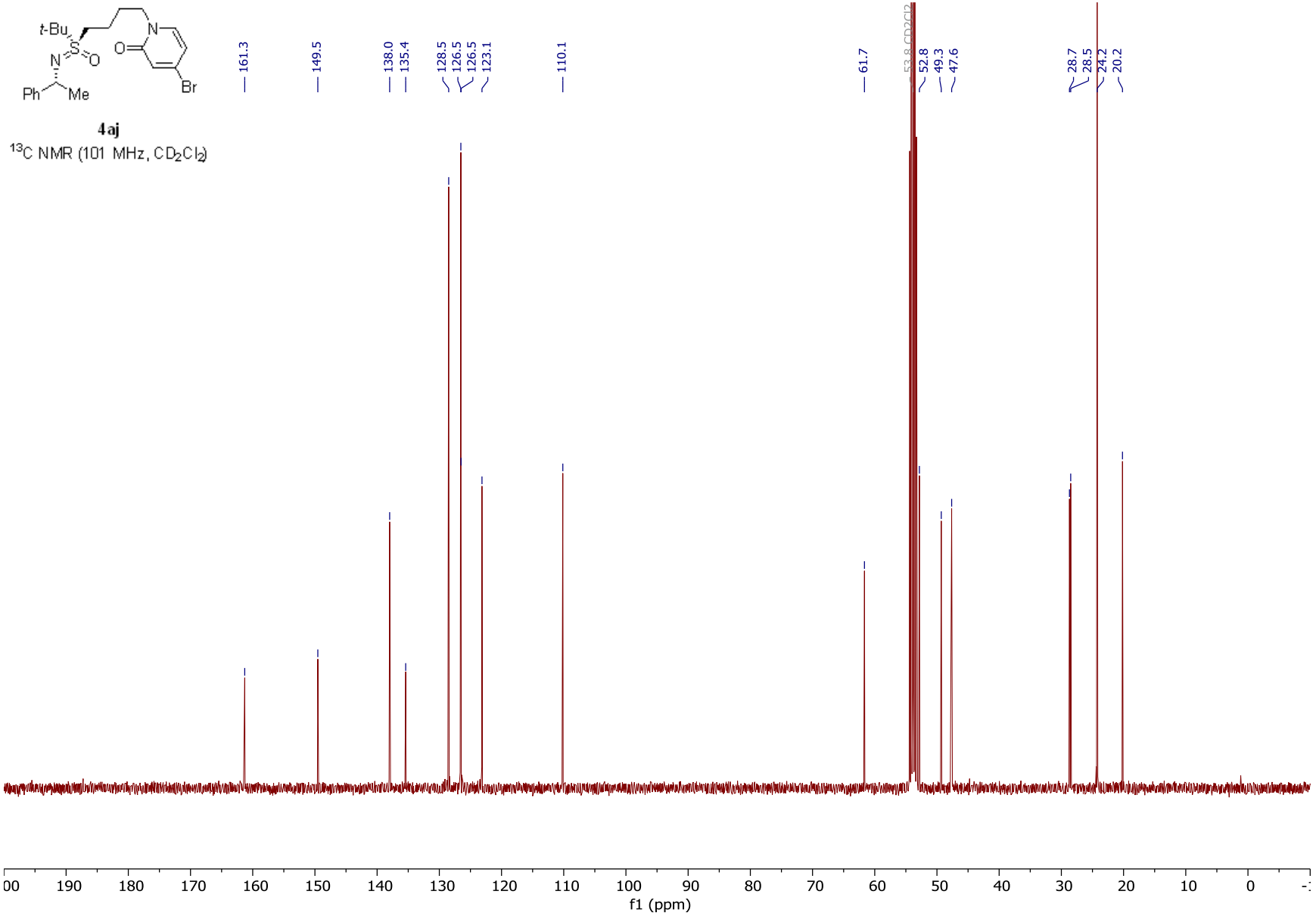

7.40
7.38
7.31
7.29
7.27
7.20
7.18
7.16
5.32 CD2Cl2
4.60
4.58
4.56
4.55
3.14
3.09
3.09
3.04
2.91
2.84
2.83
2.76
1.64
1.62
1.60
1.59
1.56
1.47
1.46
1.45
1.45
1.44
1.43
1.41
1.40
1.38
t-Bu
N
S
O
N3
Ph
Me
4ai
1H NMR (400 MHz, CD2Cl2)
1.94
1.91
0.94
1.00
1.99
2.07
2.47
14.03
f1 (ppm)

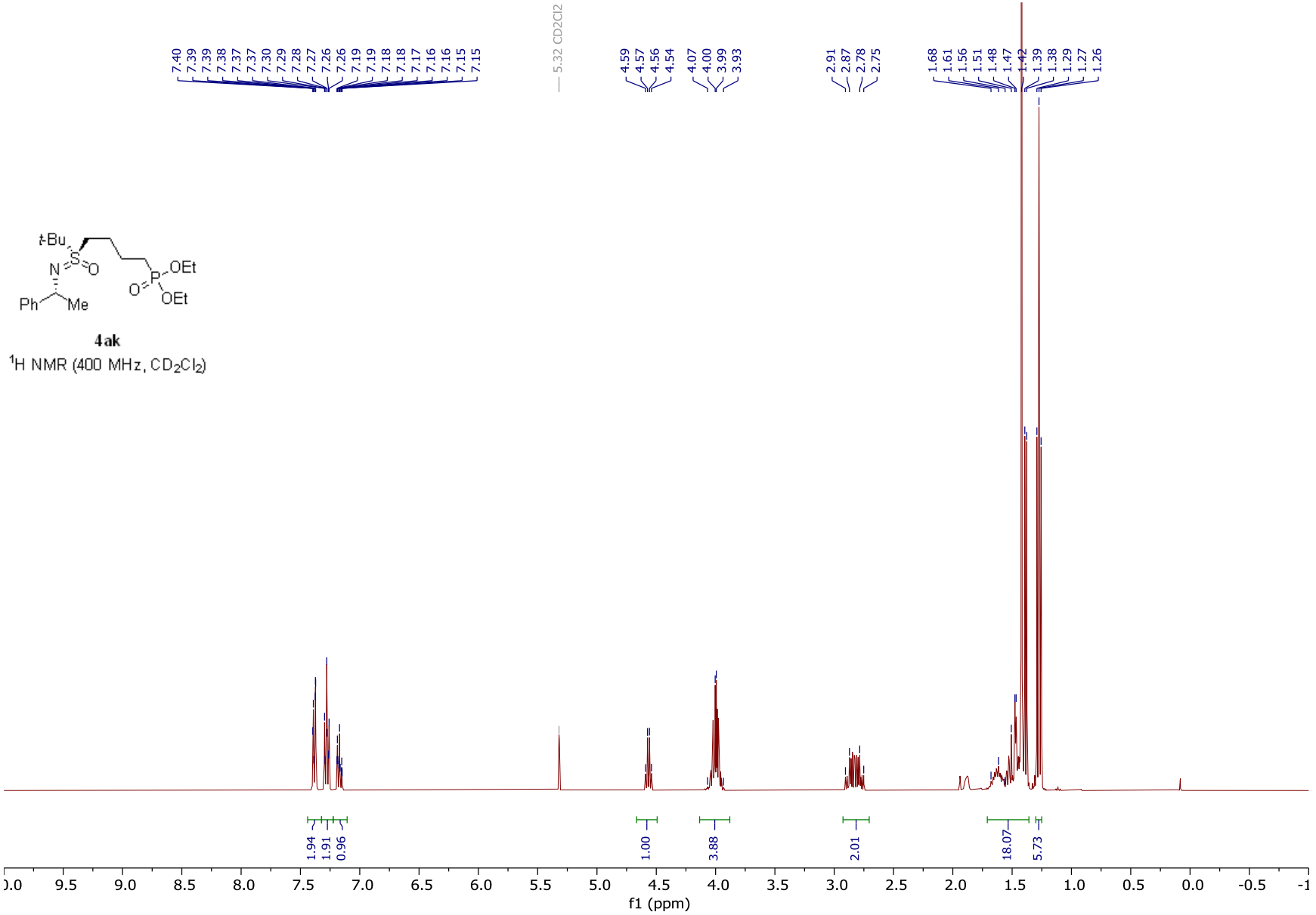

t-Bu
N
S
O
N3
Ph
Me
4ai
13C NMR (101 MHz, CD2Cl2)
149.5
128.5
126.5
126.5
61.5
53.8 CD2Cl2
52.9
51.3
47.8
28.8
28.5
24.3
20.6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



4aj

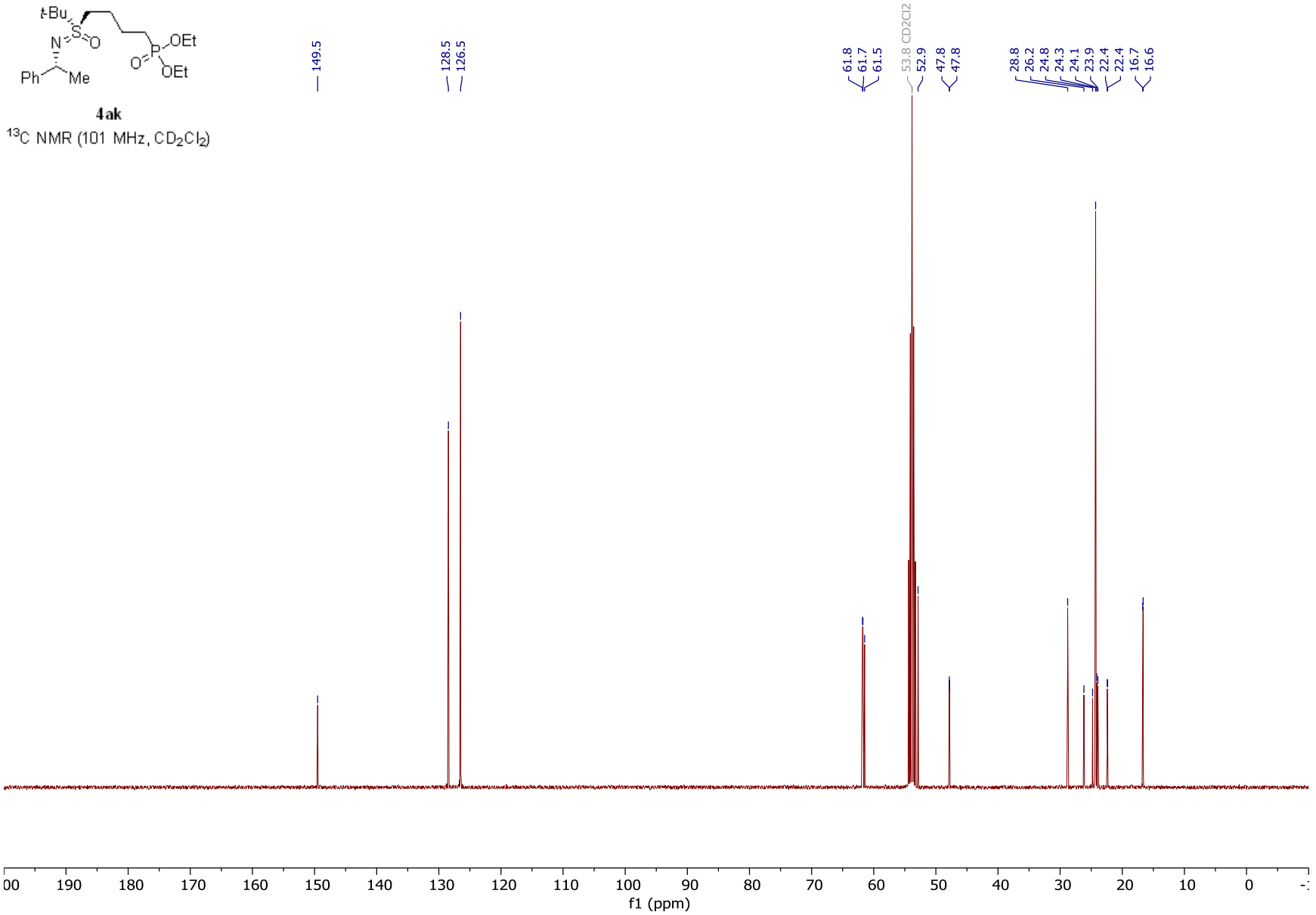
^{1}H NMR (400 MHz, CD_2Cl_2)

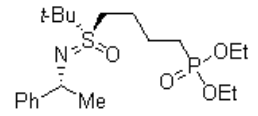

t-Bu
N
S
O
N
O
Ph
Me
Br
4aj
13C NMR (101 MHz, CD2Cl2)
161.3
149.5
138.0
135.4
128.5
126.5
126.5
123.1
110.1
61.7
53.8 CD2Cl2
52.8
49.3
47.6
28.7
28.5
24.2
20.2
f1 (ppm)



4ak

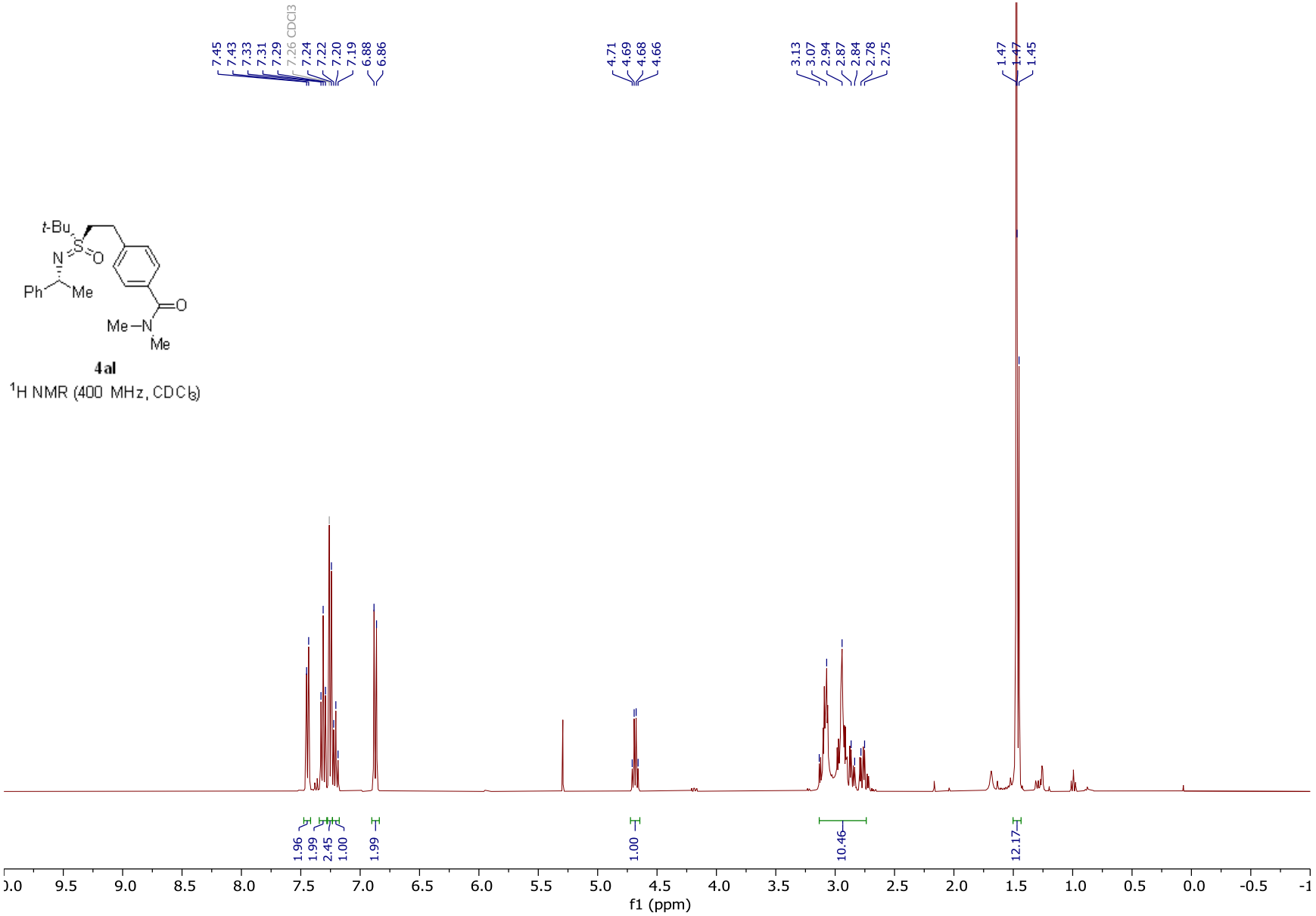
^{1}H NMR (400 MHz, CD_2Cl_2)


t-Bu
N
S
O
OEt
O
P
OEt
Ph
Me
4ak
^{13}C NMR (101 MHz, CD_2Cl_2)
149.5
128.5
126.5
61.8
61.7
61.5
53.8 CD2Cl2
52.9
47.8
47.8
28.8
26.2
24.8
24.3
24.1
23.9
22.4
22.4
16.7
16.6
f1 (ppm)



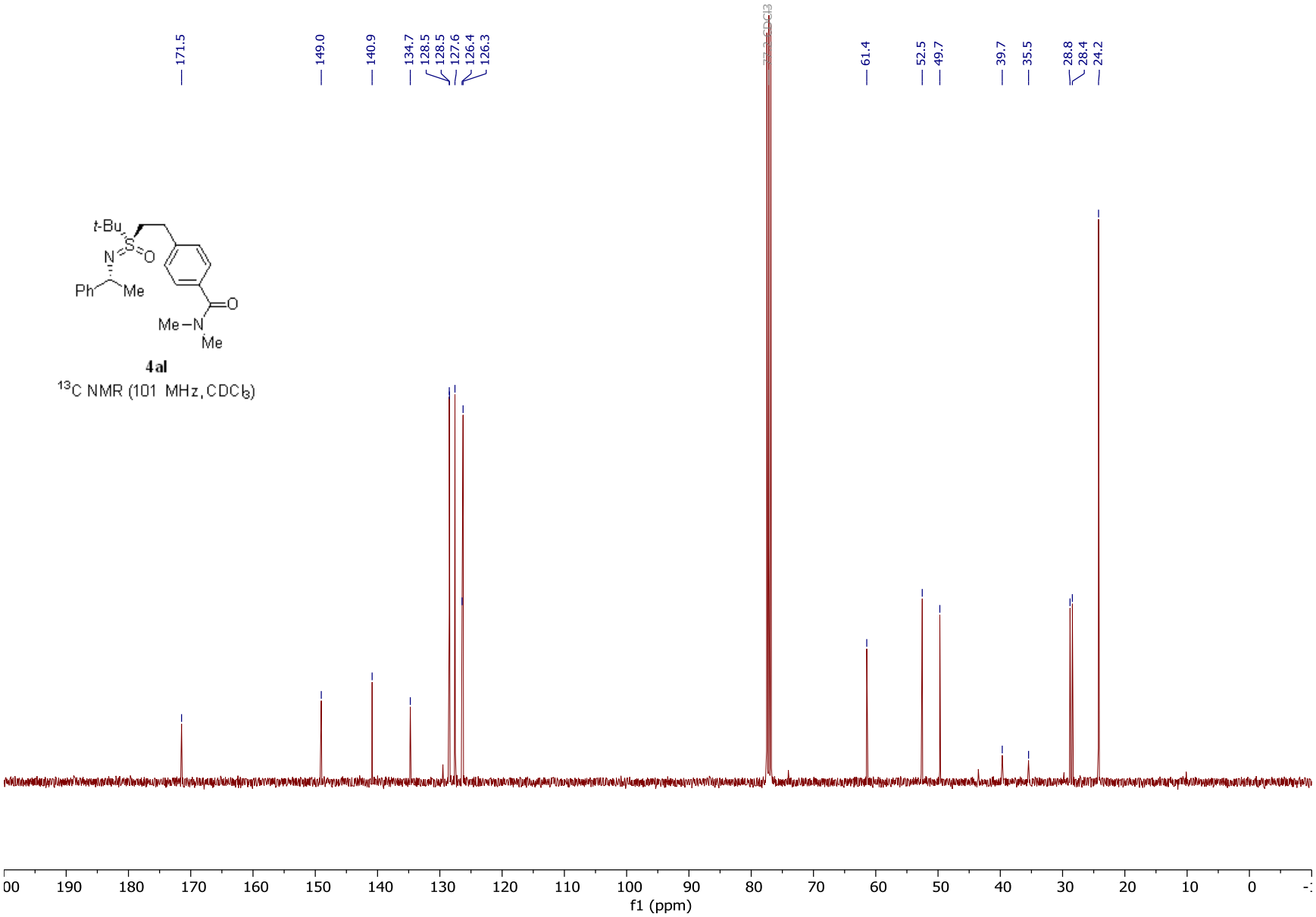
4ak

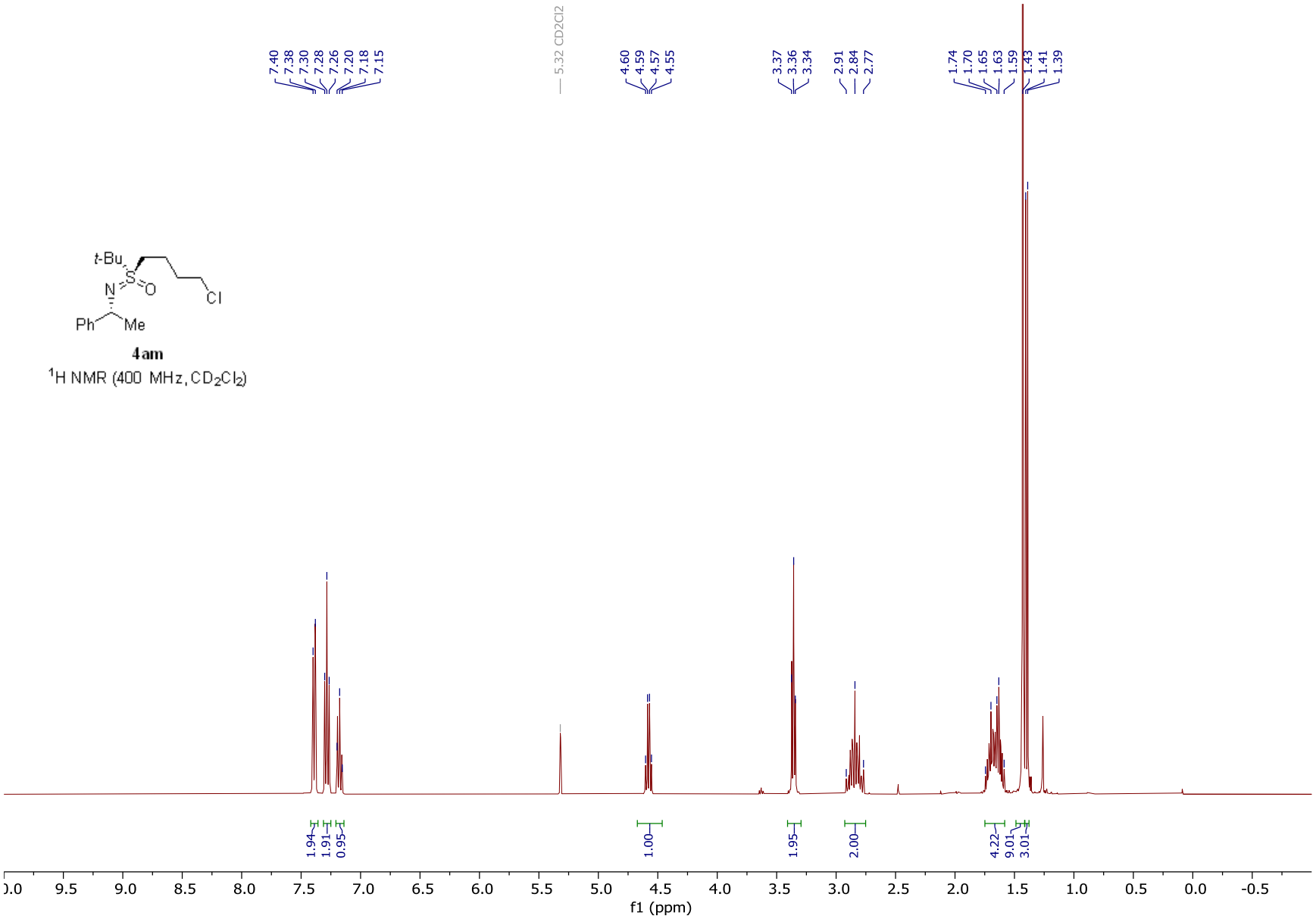
^{31}P NMR (162 MHz, CD_2Cl_2)



4al

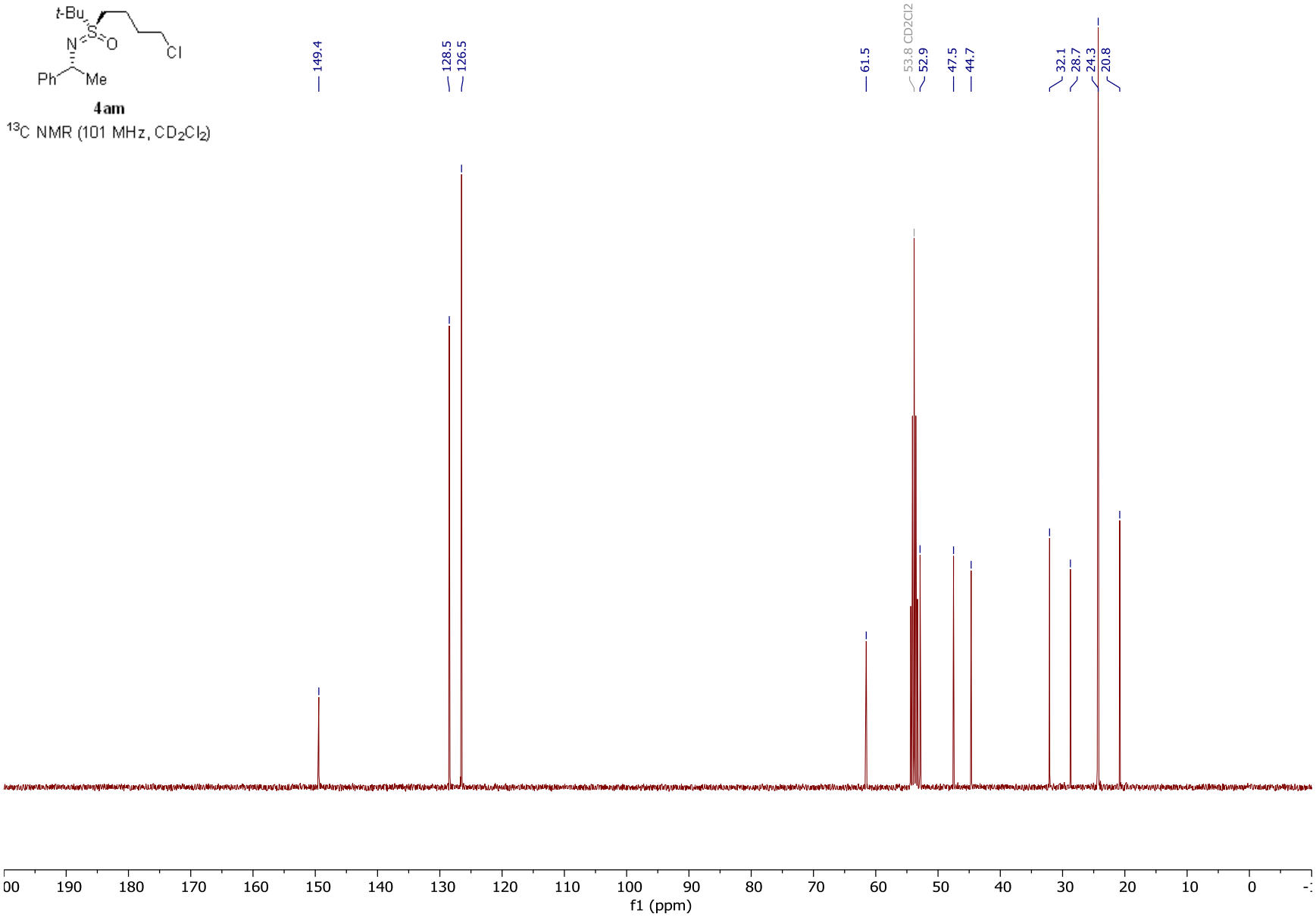
^{1}H NMR (400 MHz, $CDCl_3$)

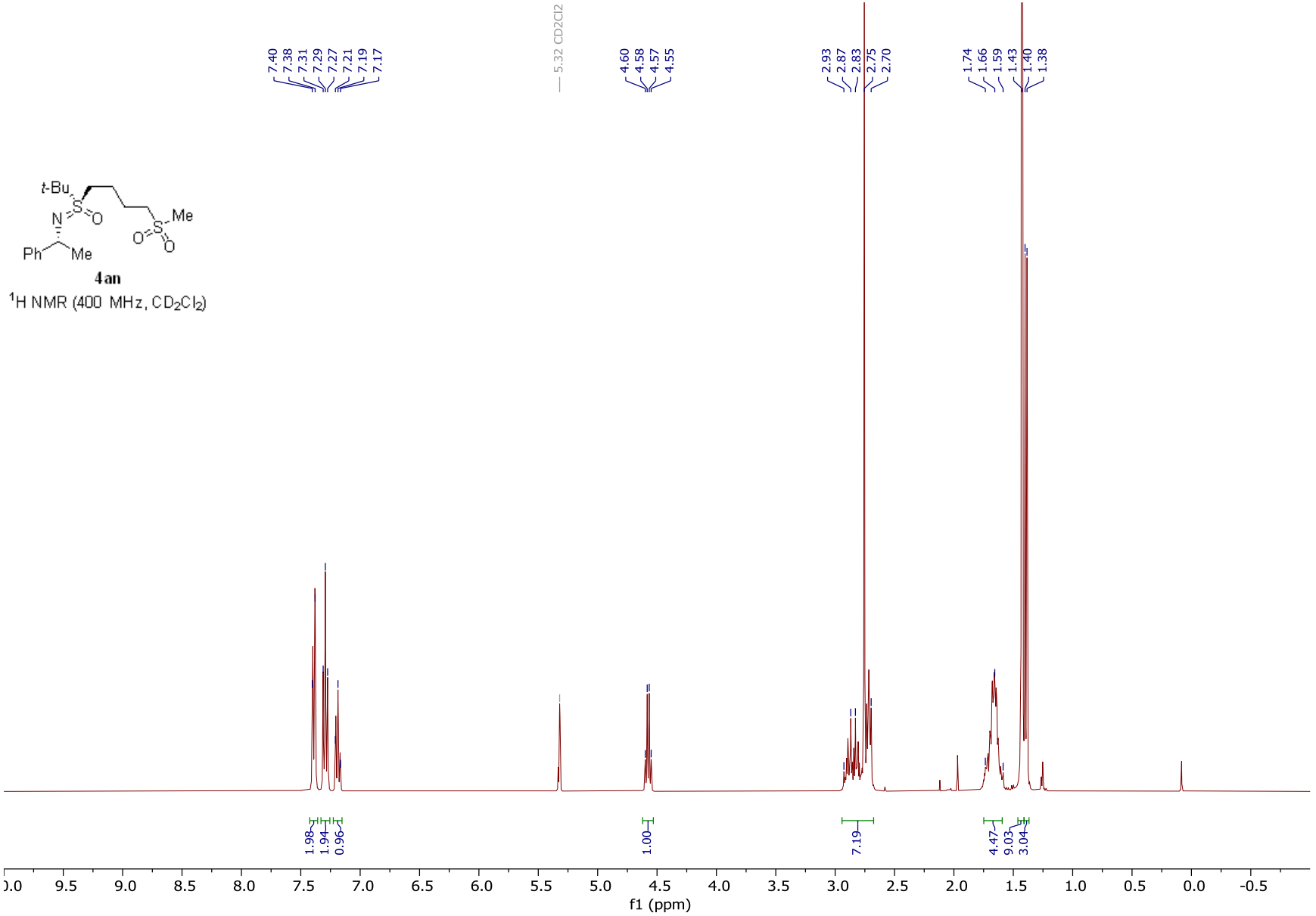

171.5
149.0
140.9
134.7
128.5
128.5
127.6
126.4
126.3
77.3-CDCl3
61.4
52.5
49.7
39.7
35.5
28.8
28.4
24.2
t-Bu
N
S
O
Ph
Me
Me–N
Me
O
4al
13C NMR (101 MHz, CDCl3)
f1 (ppm)

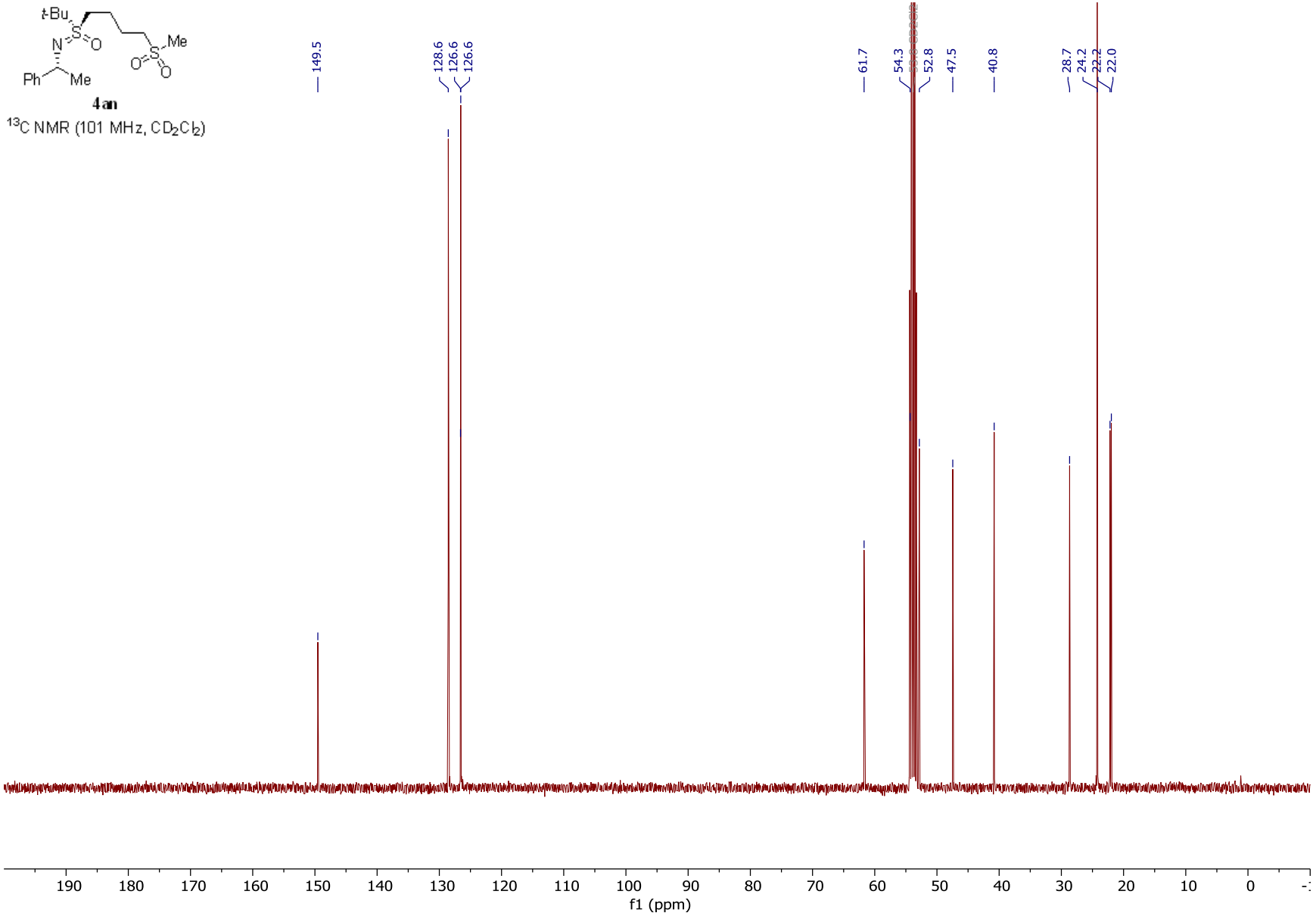


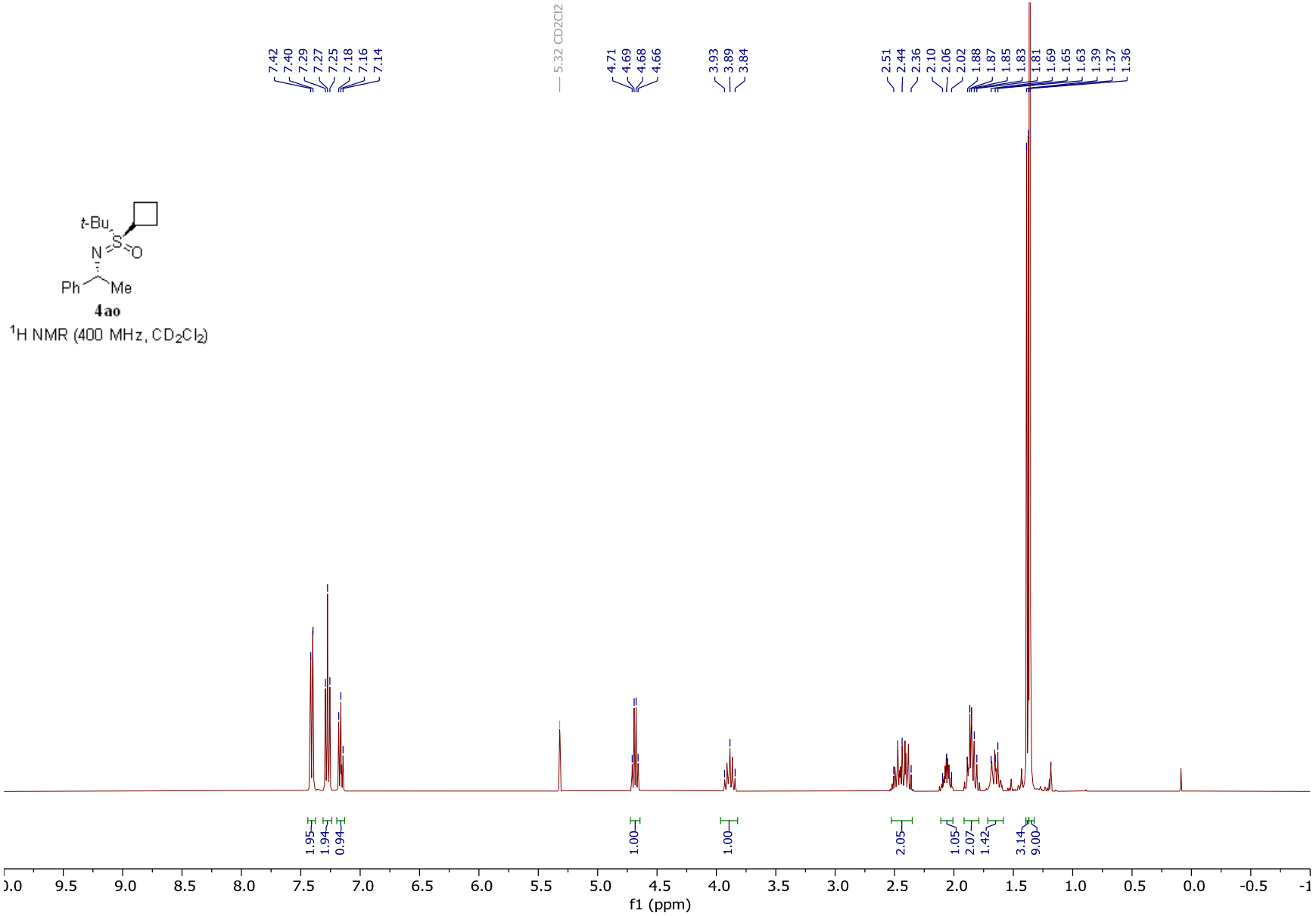
4am

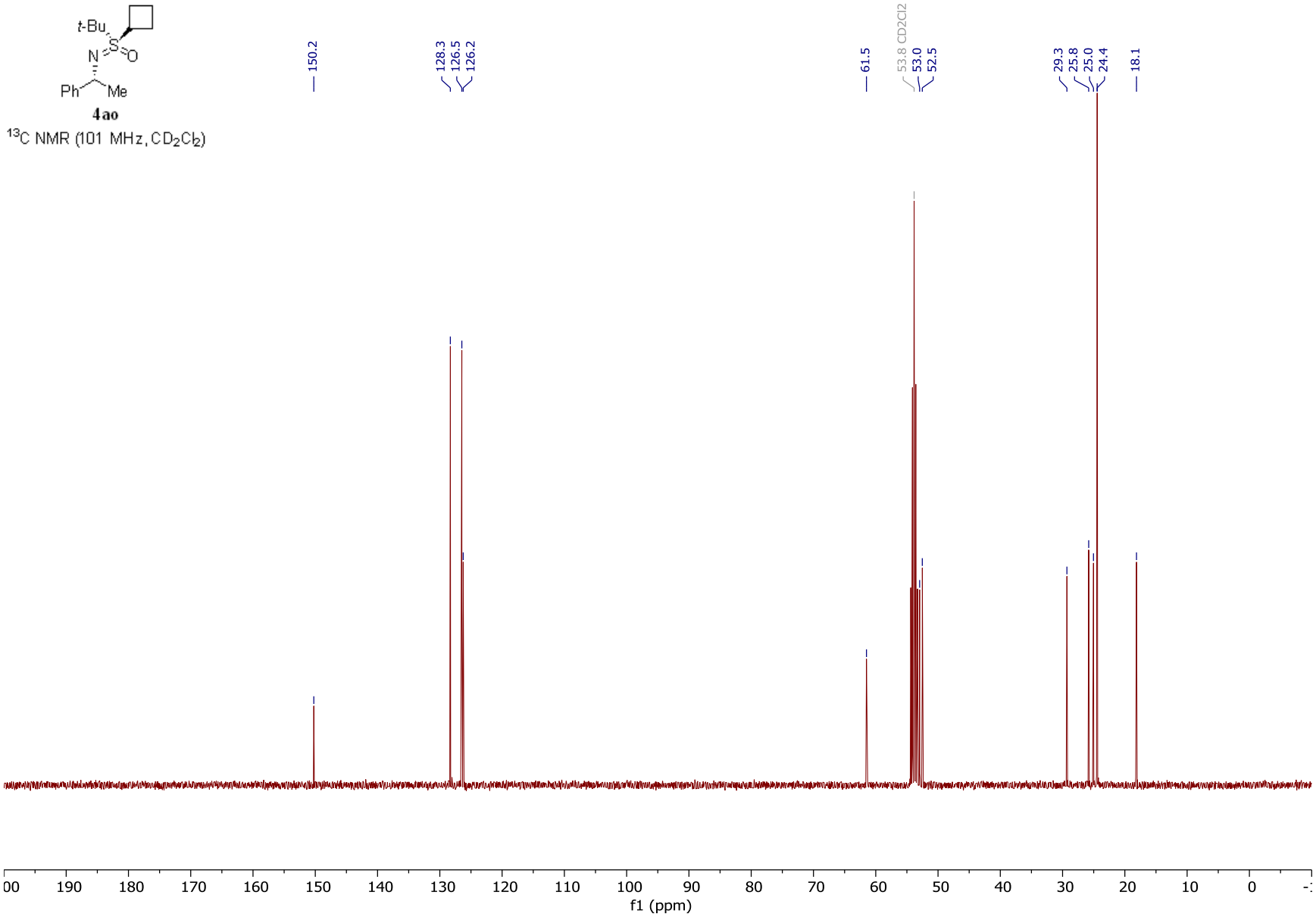
^{1}H NMR (400 MHz, CD_2Cl_2)

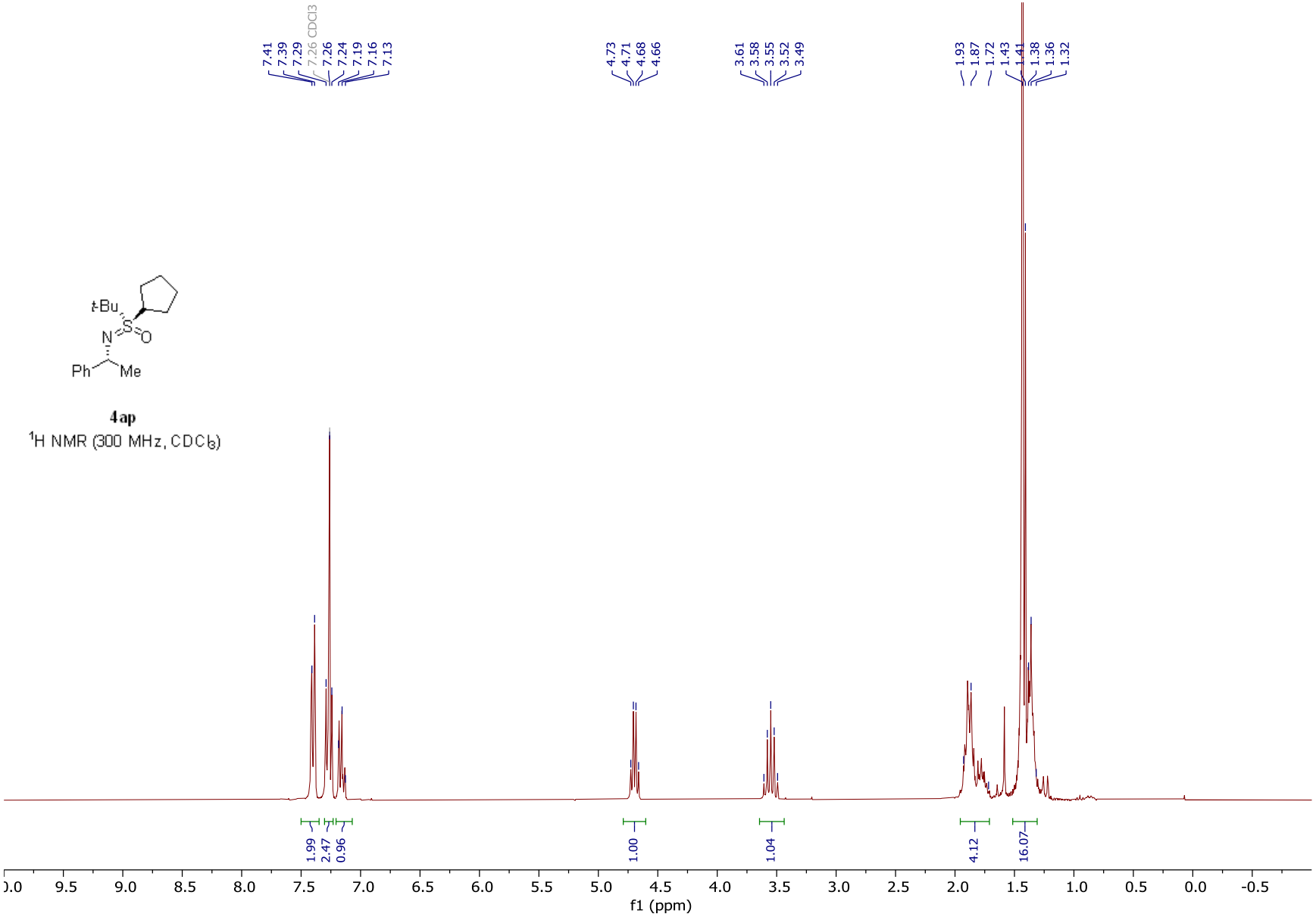

t-Bu
S
N
O
Cl
Ph
Me
4am
^{13}C NMR (101 MHz, CD_2Cl_2)
149.4
128.5
126.5
61.5
53.8 CD2Cl2
52.9
47.5
44.7
32.1
28.7
24.3
20.8
f1 (ppm)

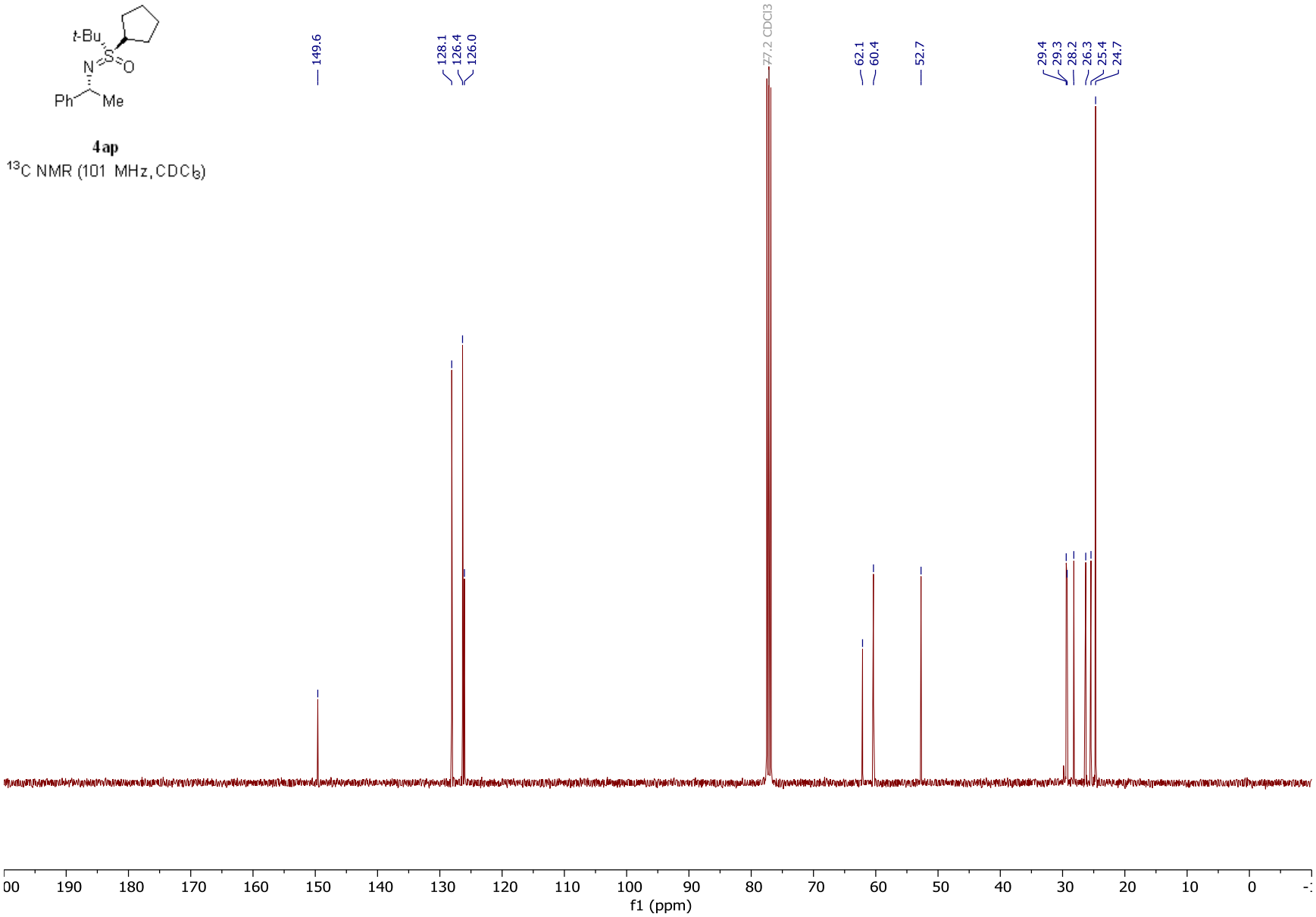

7.40
7.38
7.31
7.29
7.27
7.21
7.19
7.17
5.32 CD2Cl2
4.60
4.58
4.57
4.55
2.93
2.87
2.83
2.75
2.70
1.74
1.66
1.59
1.43
1.40
1.38
t-Bu
N
S
O
Me
O
S
O
Ph
Me
4an
1H NMR (400 MHz, CD2Cl2)
1.98
1.94
0.96
1.00
7.19
4.47
9.03
3.04
f1 (ppm)


t-Bu
N
S
O
Me
O
S
O
Ph
Me
4an
^{13}C NMR (101 MHz, CD_2Cl_2)
149.5
128.6
126.6
126.6
61.7
54.3
52.8
47.5
40.8
28.7
24.2
22.2
22.0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.42
7.40
7.29
7.27
7.25
7.18
7.16
7.14
5.32 CD2Cl2
4.71
4.69
4.68
4.66
3.93
3.89
3.84
2.51
2.44
2.36
2.10
2.06
2.02
1.88
1.87
1.85
1.83
1.81
1.69
1.65
1.63
1.39
1.37
1.36
t-Bu
N
S
O
Ph
Me
4ao
1H NMR (400 MHz, CD2Cl2)
1.95
1.94
0.94
1.00
1.00
2.05
1.05
2.07
1.42
3.14
9.00
f1 (ppm)

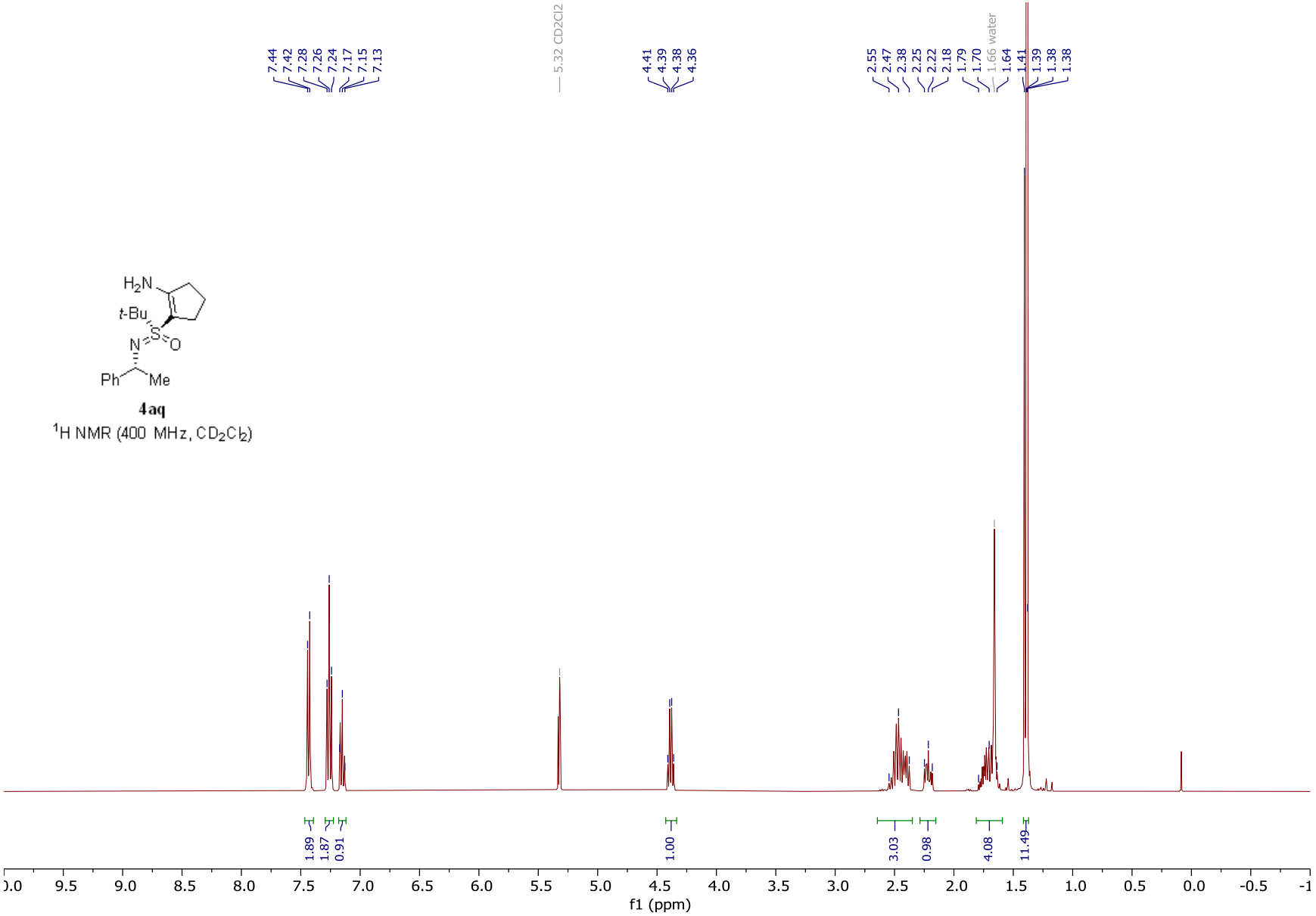

t-Bu
N
S
O
Ph
Me
4ao
13C NMR (101 MHz, CD2Cl2)
150.2
128.3
126.5
126.2
61.5
53.8 CD2Cl2
53.0
52.5
29.3
25.8
25.0
24.4
18.1
f1 (ppm)


7.41
7.39
7.29
7.26 CDCl3
7.26
7.24
7.19
7.16
7.13
4.73
4.71
4.68
4.66
3.61
3.58
3.55
3.52
3.49
1.93
1.87
1.72
1.43
1.41
1.38
1.36
1.32
t-Bu
N
S
O
Ph
Me
4ap
1H NMR (300 MHz, CDCl3)
1.99
2.47
0.96
1.00
1.04
4.12
16.07
f1 (ppm)



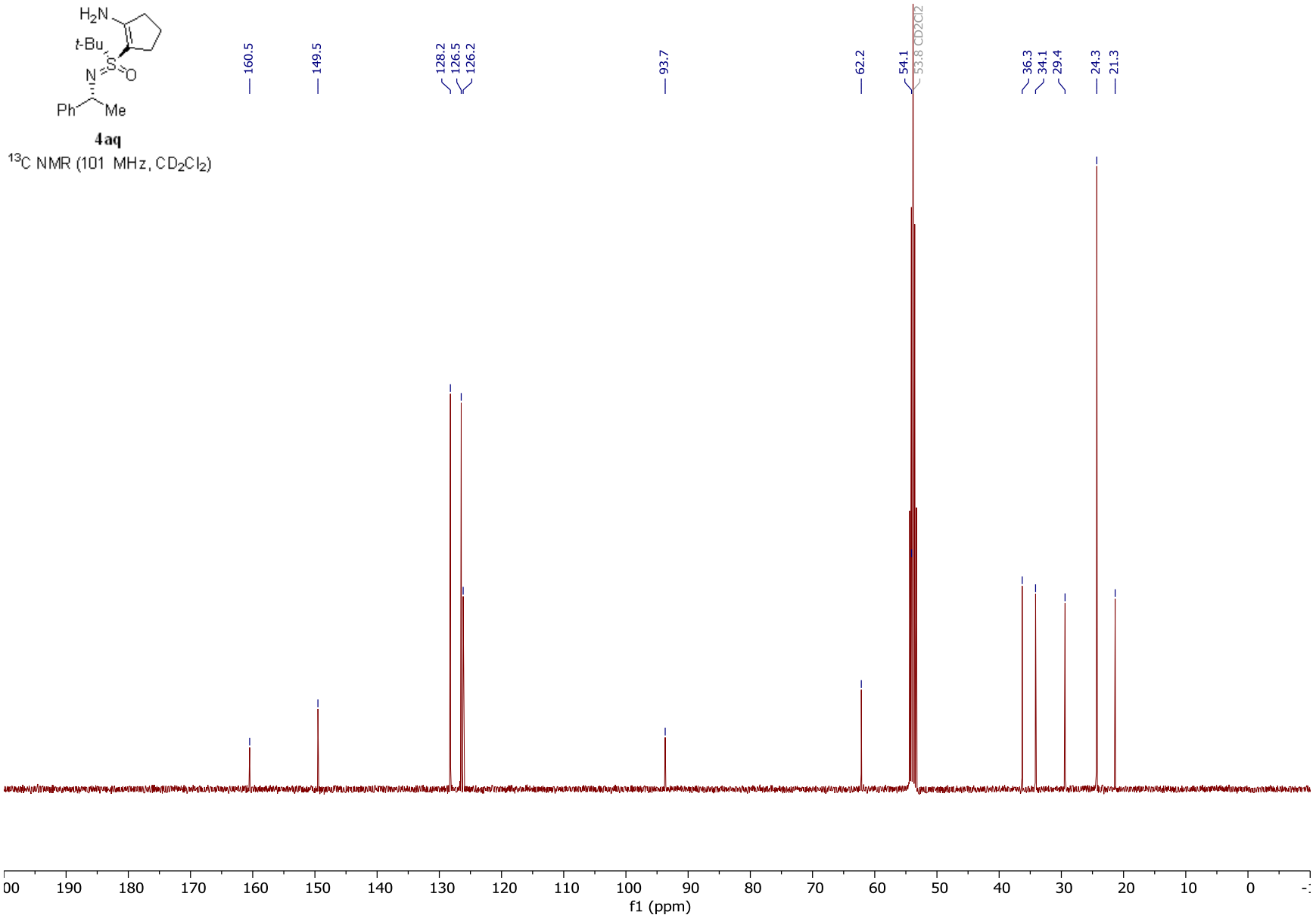
4ap

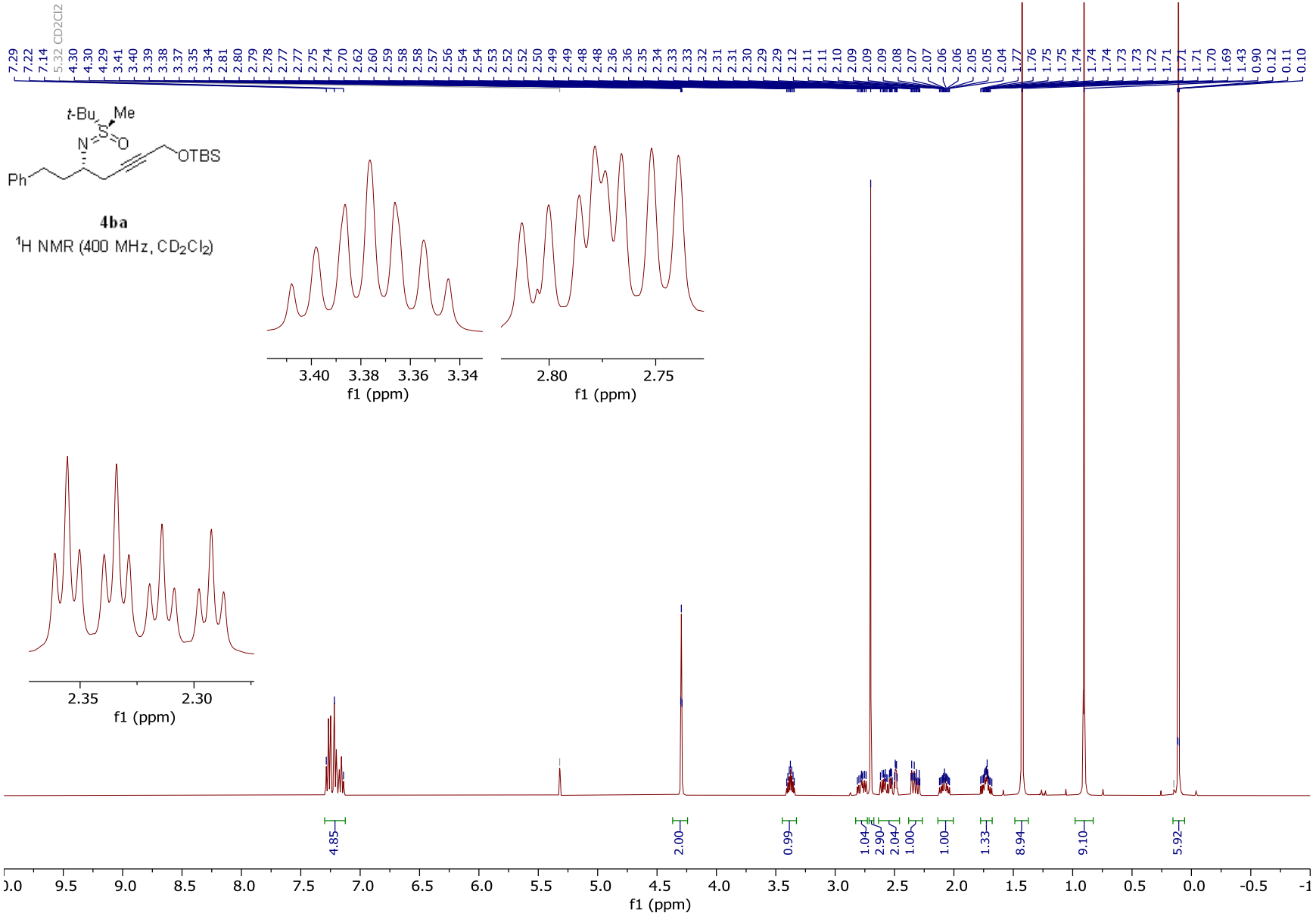
^{13}C NMR (101 MHz, $CDCl_3$)

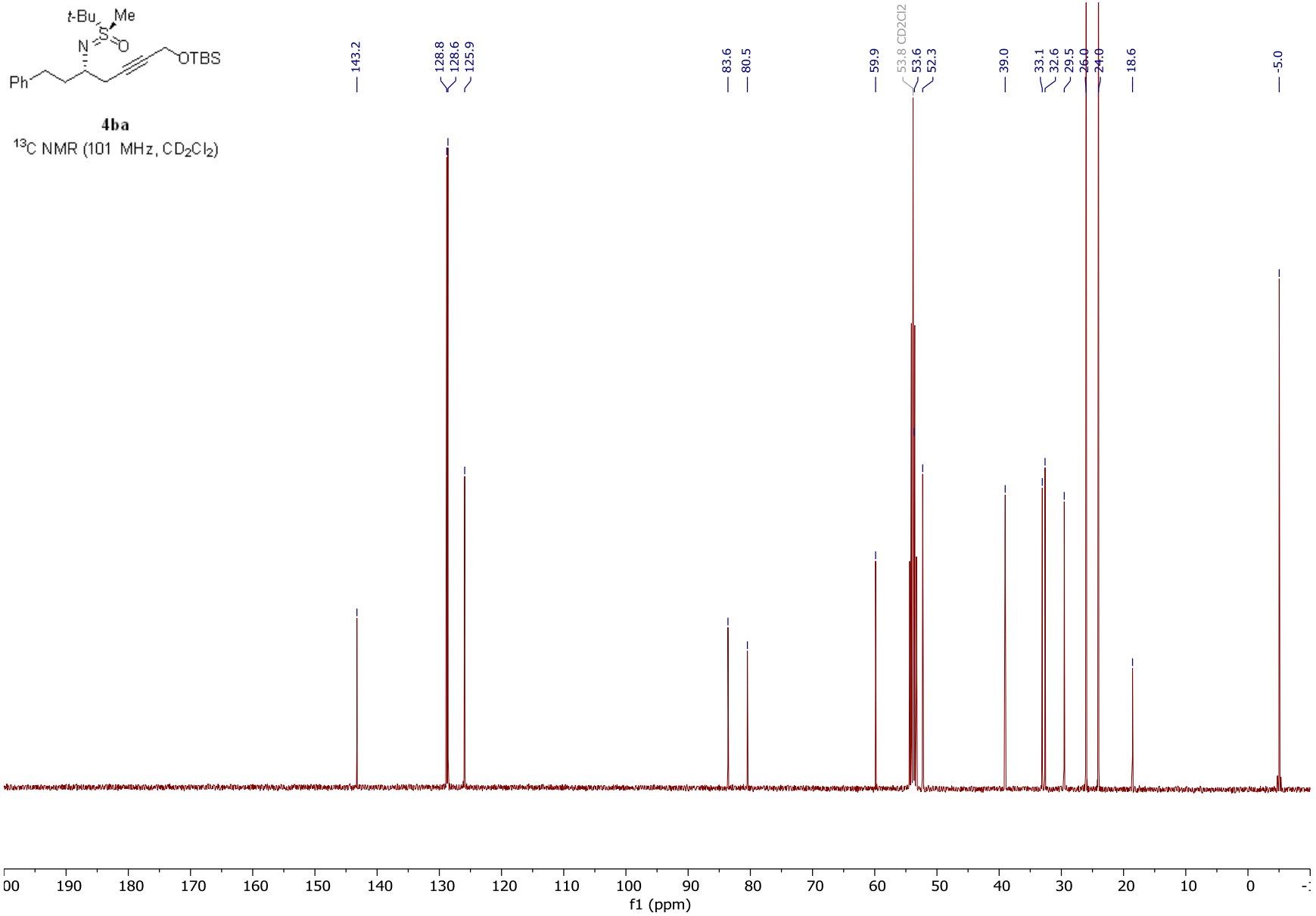


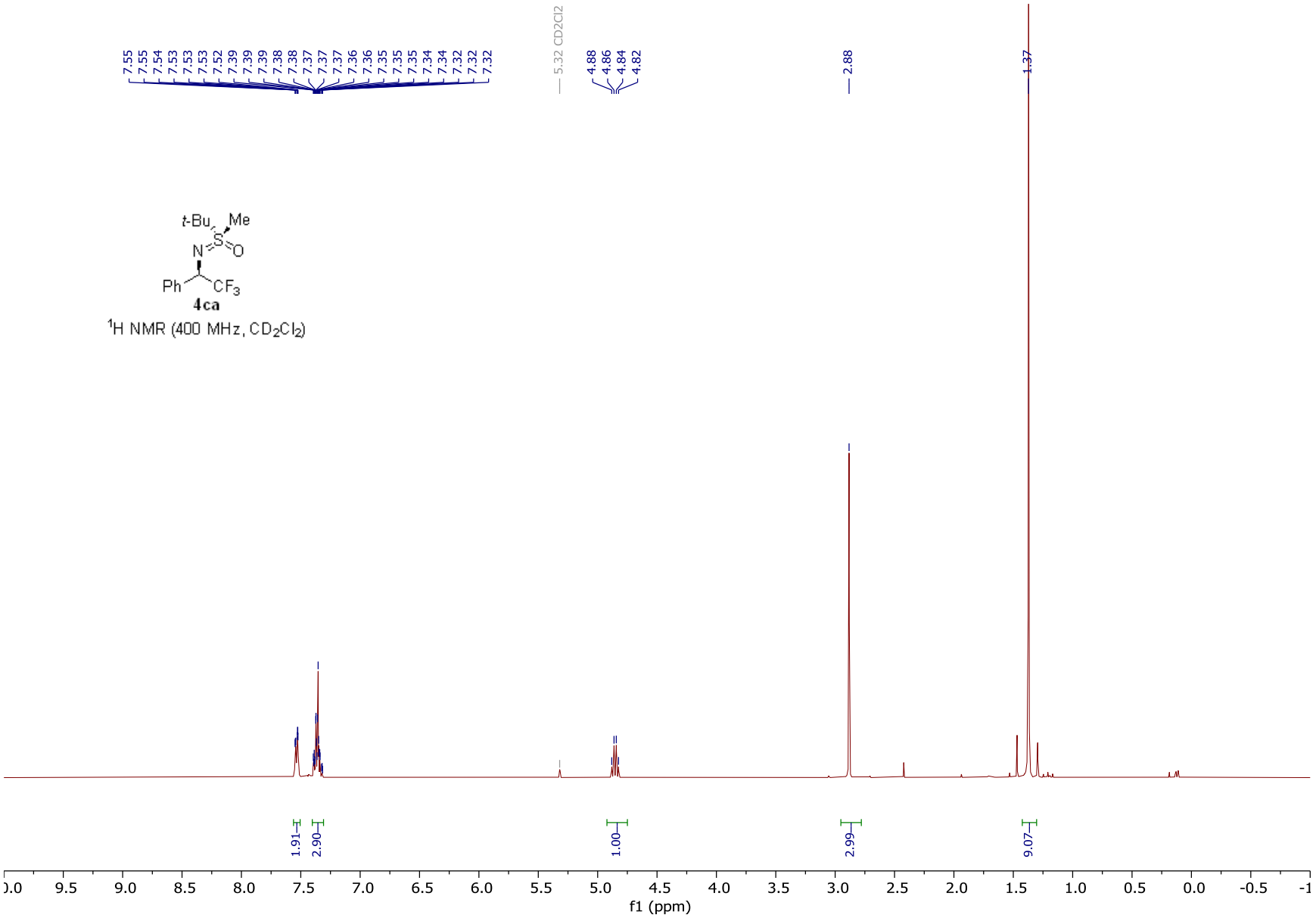
4aq

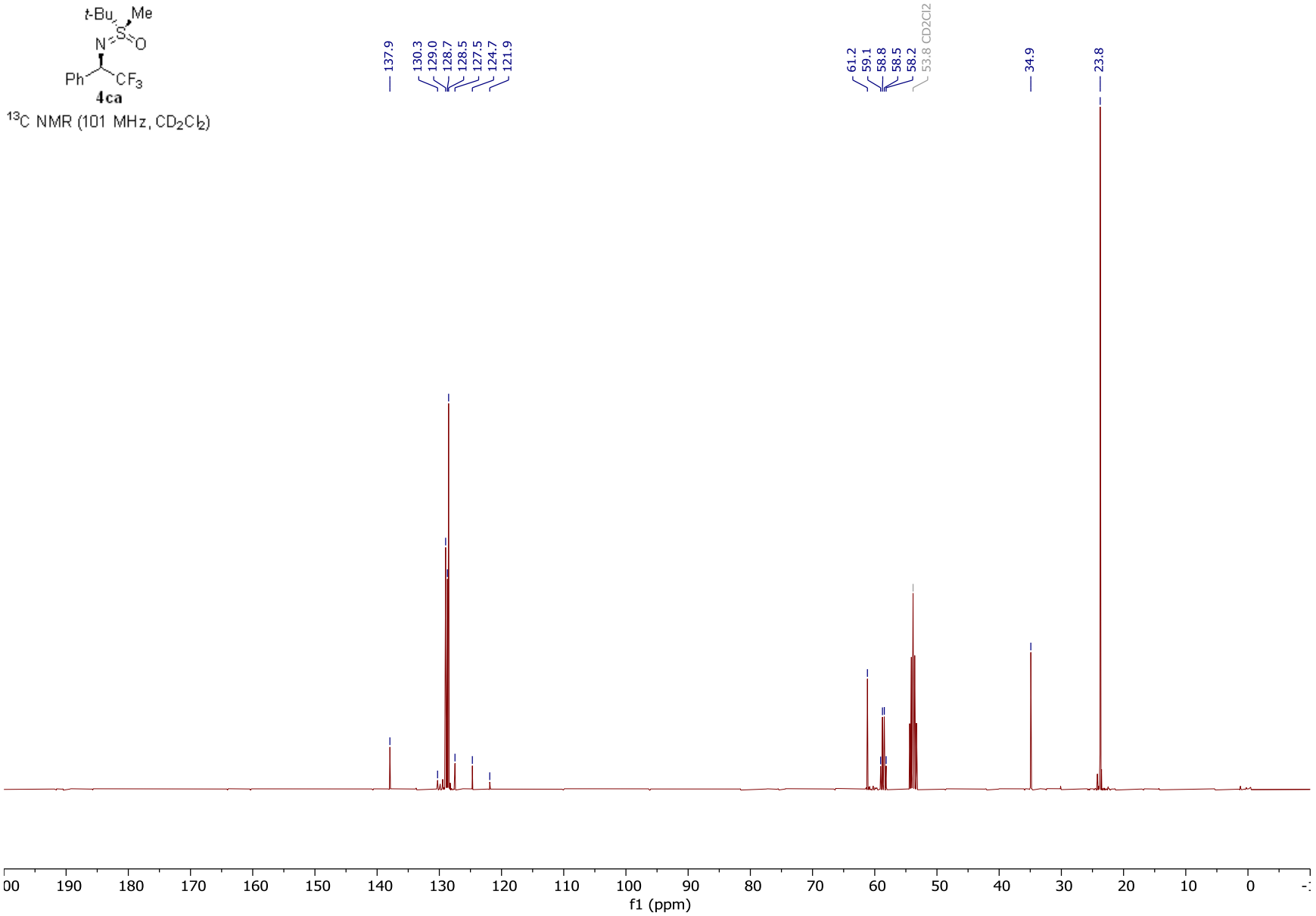
^{1}H NMR (400 MHz, CD_2Cl_2)

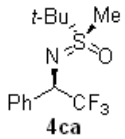

H2N
t-Bu
S
N
O
Ph
Me
4aq
13C NMR (101 MHz, CD2Cl2)
160.5
149.5
128.2
126.5
126.2
93.7
62.2
54.1
53.8 CD2Cl2
36.3
34.1
29.4
24.3
21.3
f1 (ppm)


t-Bu
Me
N
S
O
OTBS
Ph
4ba
1H NMR (400 MHz, CD2Cl2)
CD2Cl2
f1 (ppm)


t-Bu
Me
N
S
O
OTBS
Ph
4ba
13C NMR (101 MHz, CD2Cl2)
143.2
128.8
128.6
125.9
83.6
80.5
59.9
53.8 CD2Cl2
53.6
52.3
39.0
33.1
32.6
29.5
26.0
24.0
18.6
-5.0
f1 (ppm)

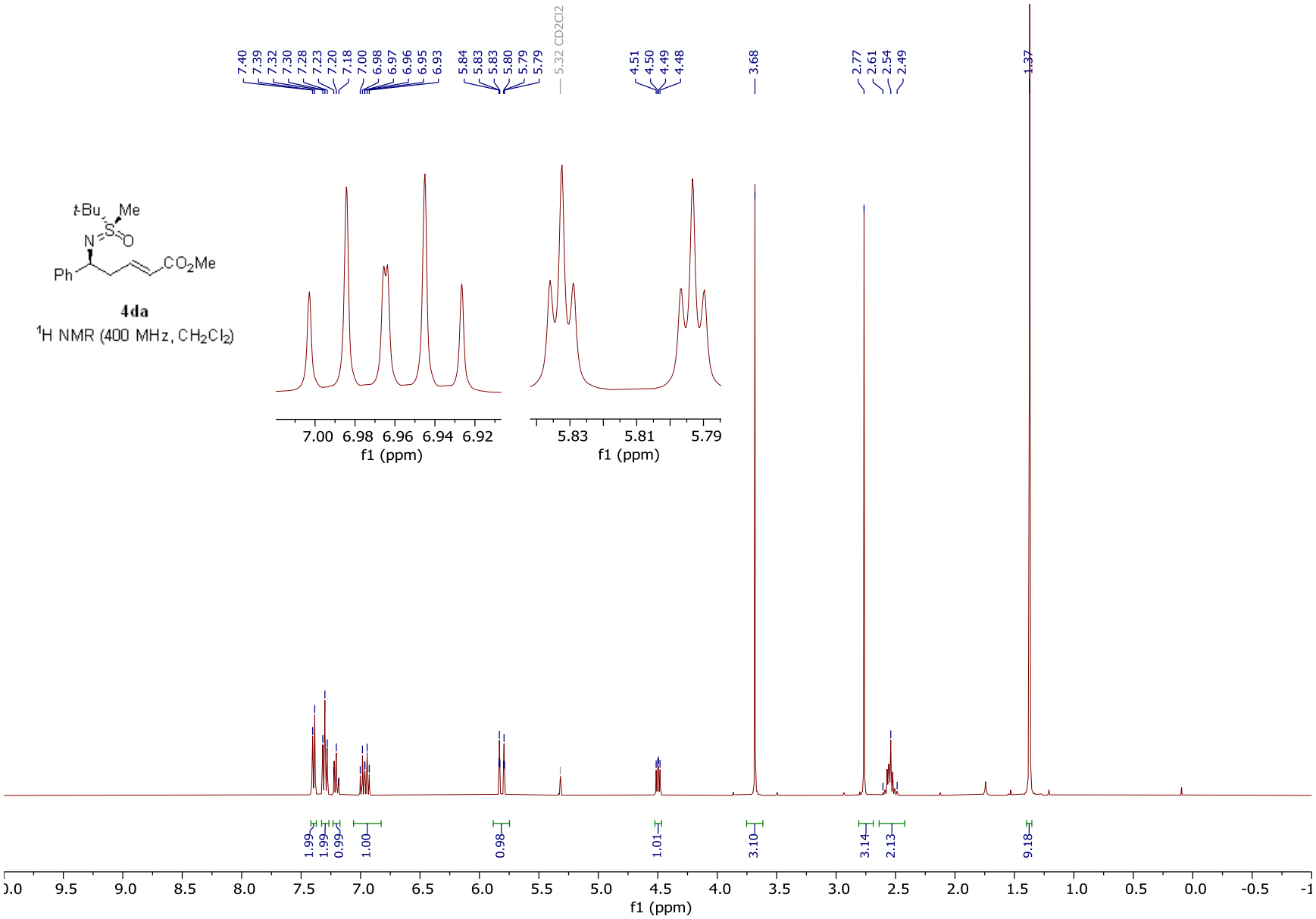

7.55
7.55
7.54
7.53
7.53
7.53
7.52
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.32
7.32
7.32
5.32 CD2Cl2
4.88
4.86
4.84
4.82
2.88
1.37
t-Bu
Me
N
S
O
Ph
CF3
4ca
1H NMR (400 MHz, CD2Cl2)
1.91
2.90
1.00
2.99
9.07
f1 (ppm)

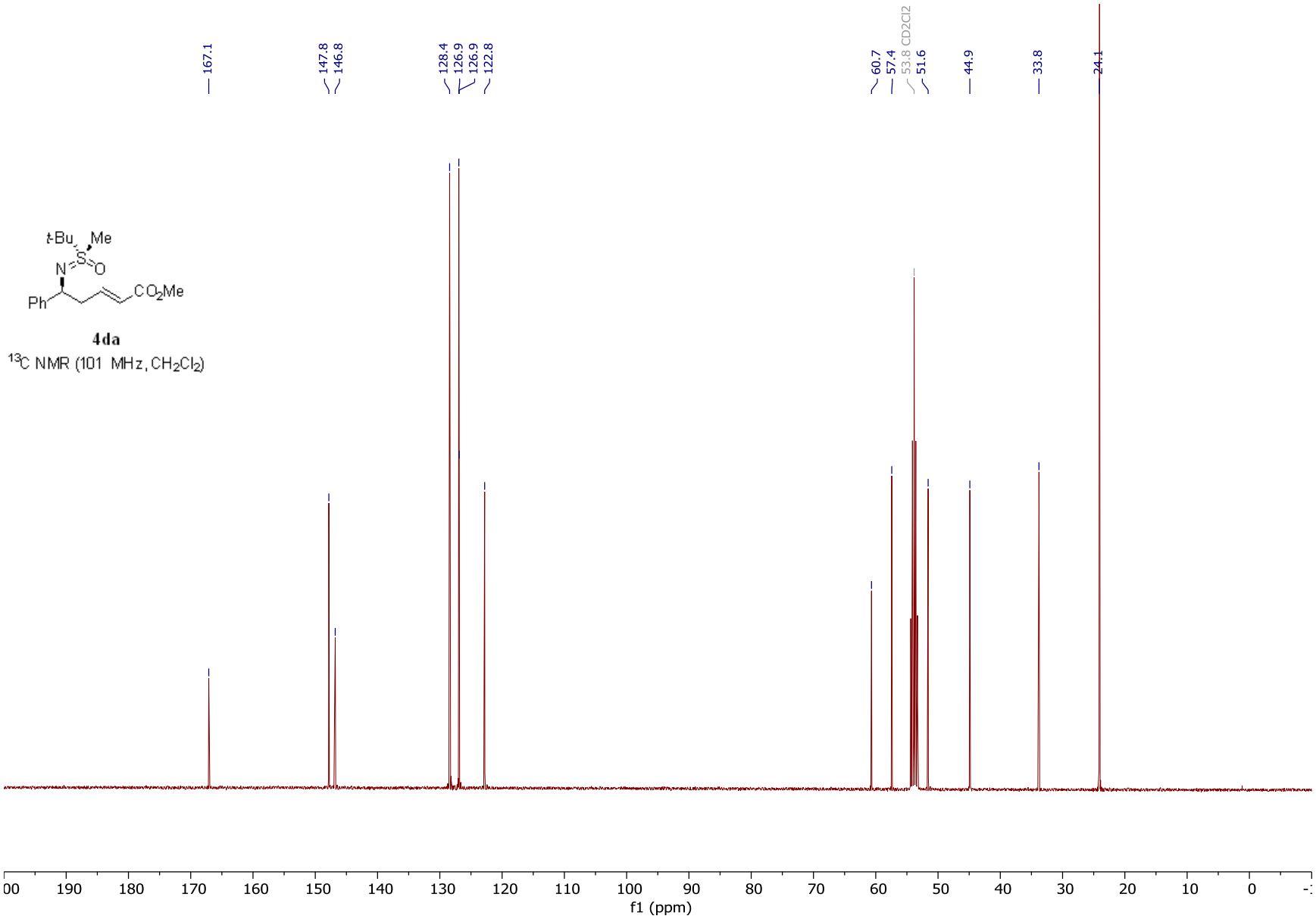

t-Bu
Me
N
S
O
Ph
CF3
4ca
13C NMR (101 MHz, CD2Cl2)
137.9
130.3
129.0
128.7
128.5
127.5
124.7
121.9
61.2
59.1
58.8
58.5
58.2
53.8 CD2Cl2
34.9
23.8
f1 (ppm)

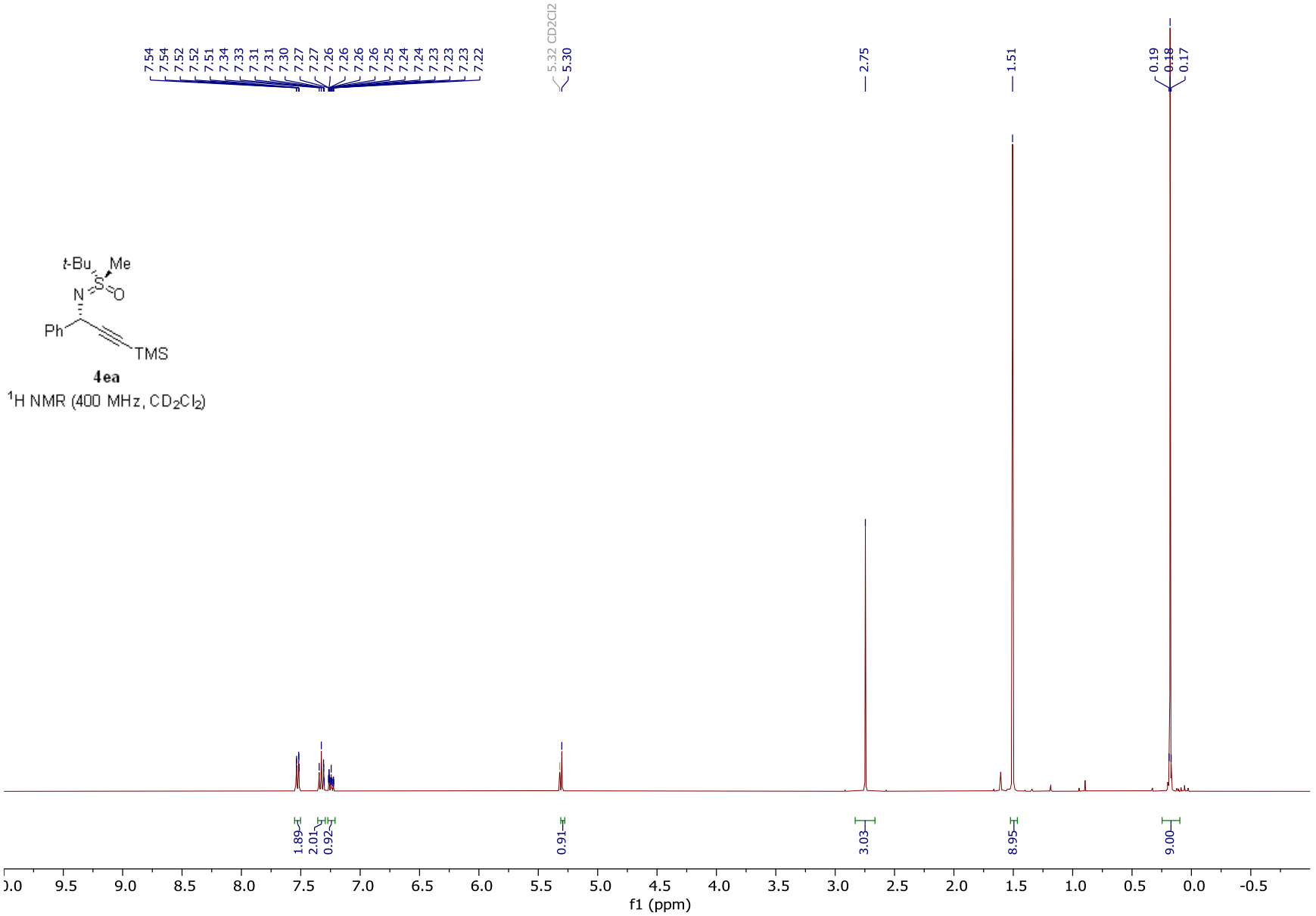


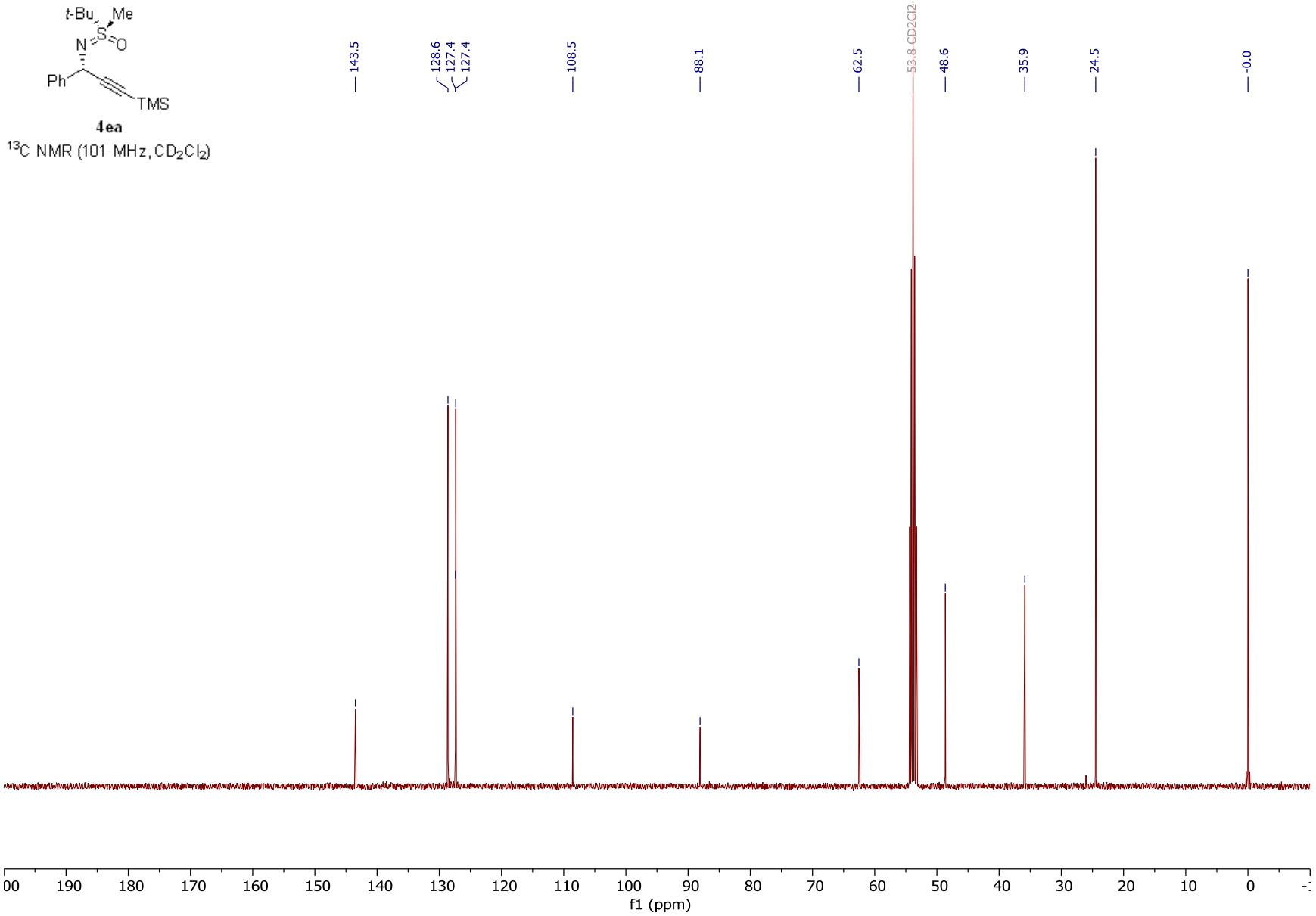
4ca

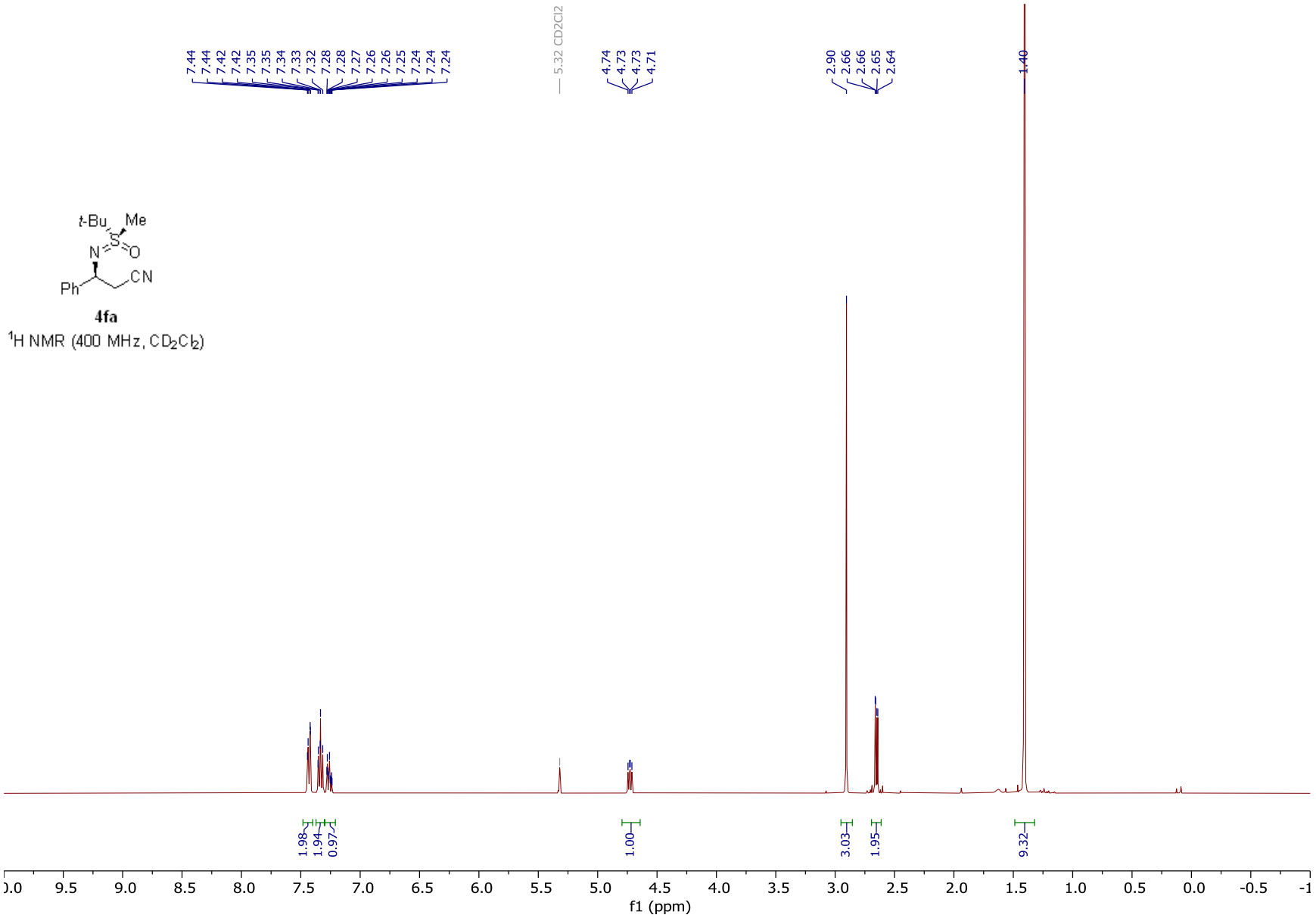
^{19}F NMR (376 MHz, CD_2Cl_2)

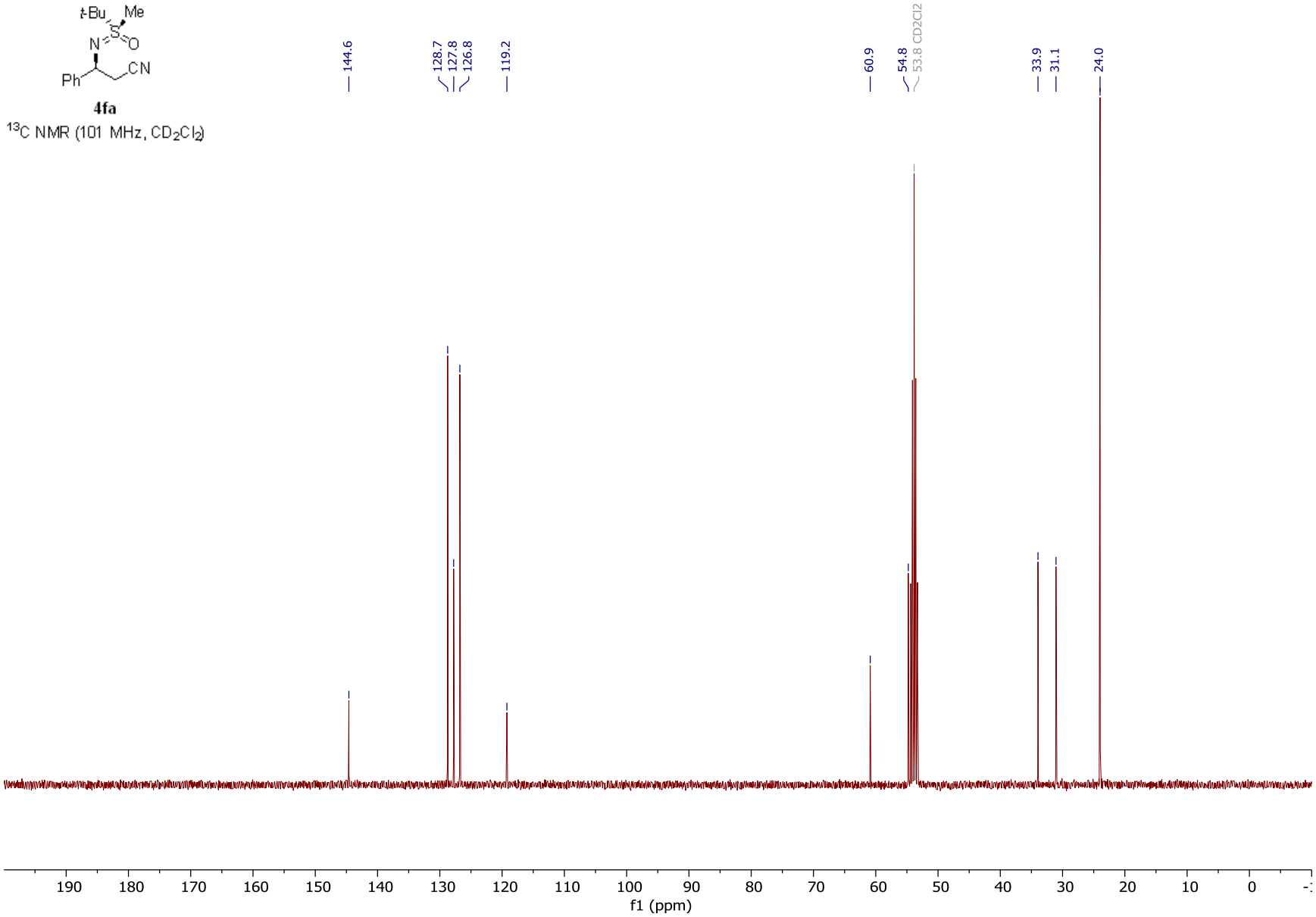

7.40
7.39
7.32
7.30
7.28
7.23
7.20
7.18
7.00
6.98
6.97
6.96
6.95
6.93
5.84
5.83
5.83
5.80
5.79
5.79
5.32 CD2Cl2
4.51
4.50
4.49
4.48
3.68
2.77
2.61
2.54
2.49
1.37
t-Bu
Me
N
S
O
Ph
CO2Me
4da
1H NMR (400 MHz, CH2Cl2)
7.00 6.98 6.96 6.94 6.92
f1 (ppm)
5.83 5.81 5.79
f1 (ppm)
1.99
1.99
0.99
1.00
0.98
1.01
3.10
3.14
2.13
9.18
f1 (ppm)

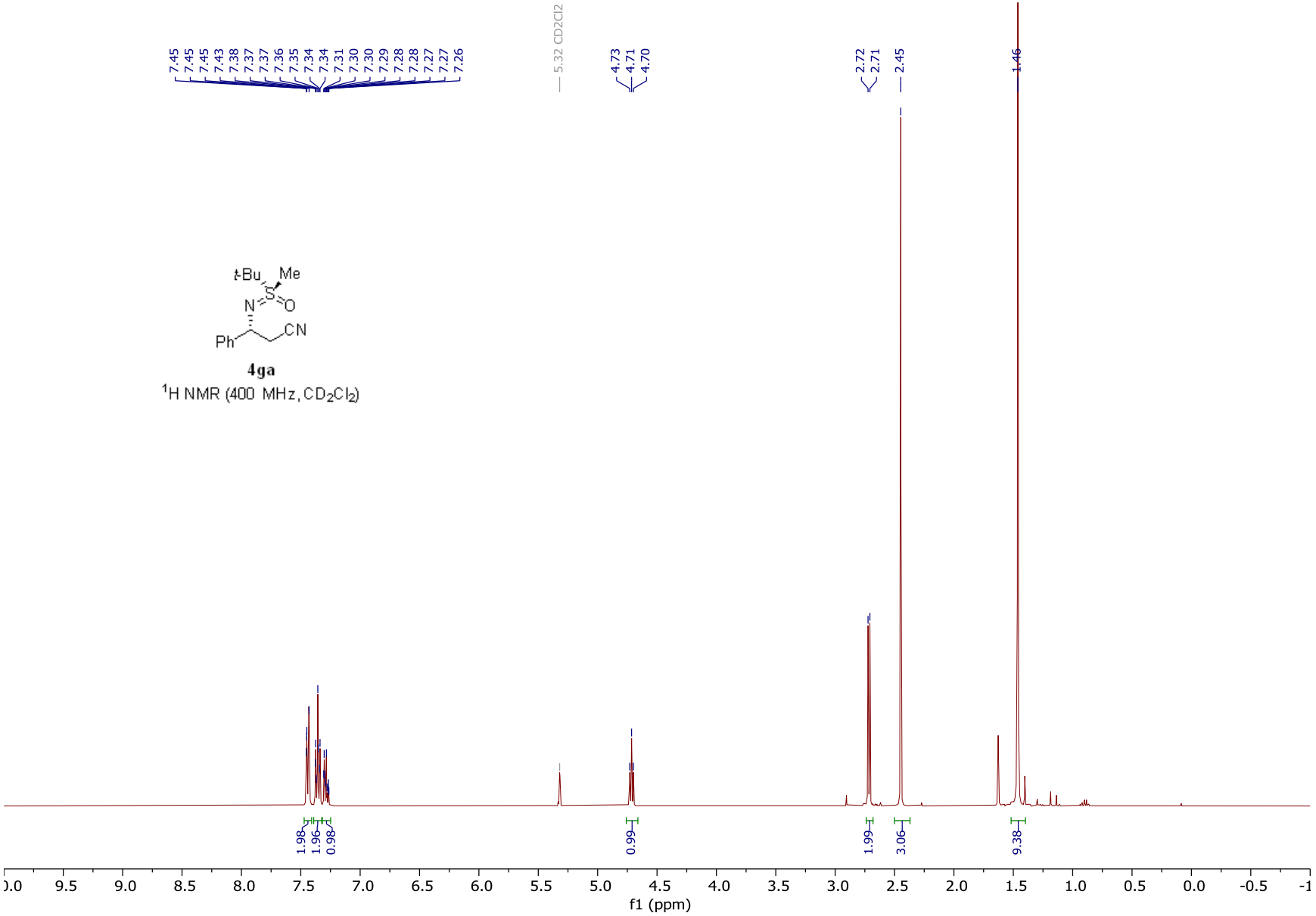

167.1
147.8
146.8
128.4
126.9
126.9
122.8
60.7
57.4
53.8 CD2Cl2
51.6
44.9
33.8
24.1
t-Bu
Me
N
S
O
Ph
CO2Me
4da
13C NMR (101 MHz, CH2Cl2)
f1 (ppm)


7.54
7.54
7.52
7.52
7.51
7.34
7.33
7.31
7.31
7.30
7.27
7.27
7.26
7.26
7.26
7.25
7.24
7.24
7.23
7.23
7.22
5.32 CD2Cl2
5.30
2.75
1.51
0.19
0.18
0.17
t-Bu
Me
N
S
O
Ph
TMS
4ea
1H NMR (400 MHz, CD2Cl2)
1.89
2.01
0.92
0.91
3.03
8.95
9.00
f1 (ppm)


t-Bu
Me
N
S
O
Ph
TMS
4ea
^{13}C NMR (101 MHz, CD_2Cl_2)
143.5
128.6
127.4
127.4
108.5
88.1
62.5
53.8 CD2Cl2
48.6
35.9
24.5
-0.0
f1 (ppm)

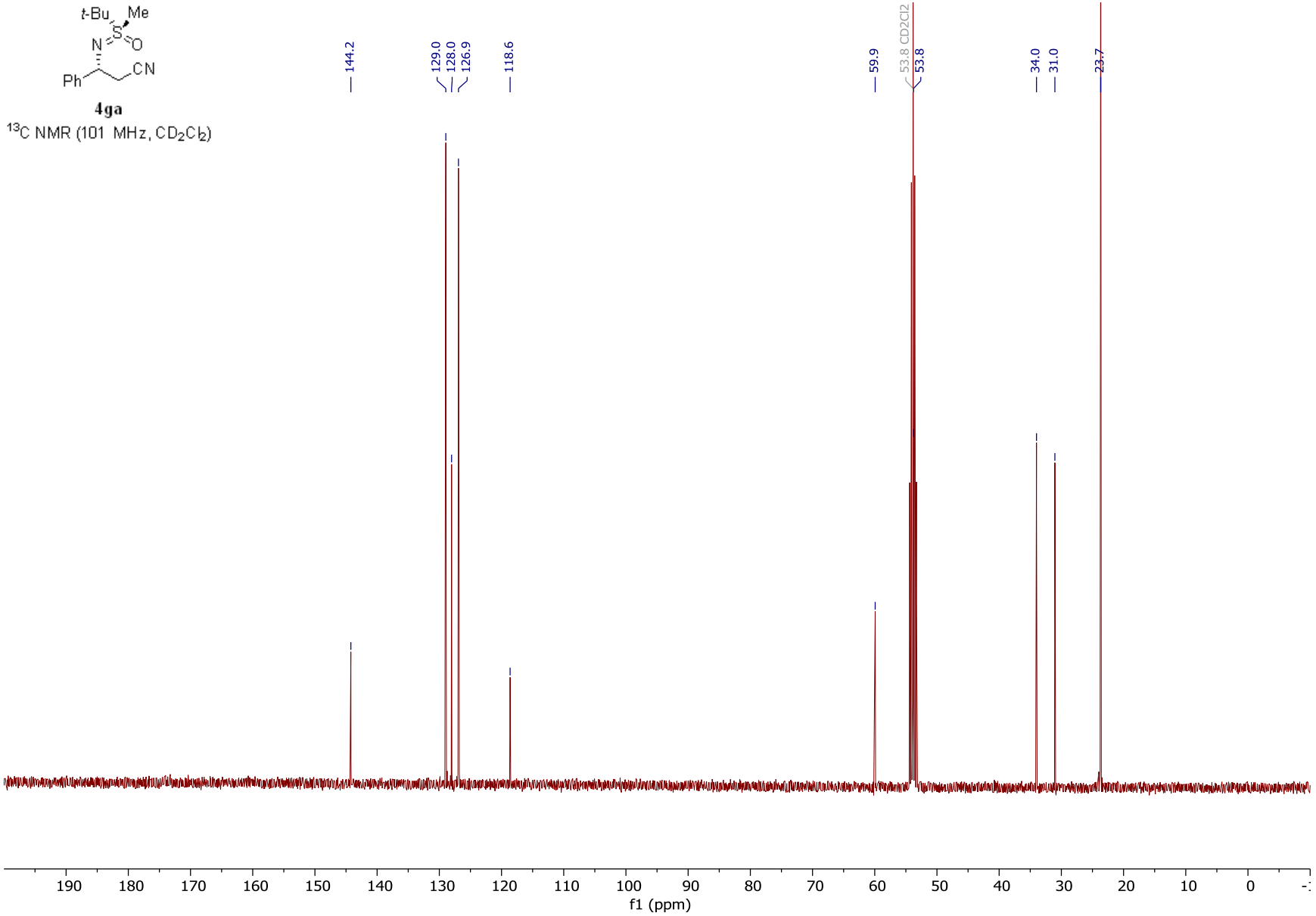

7.44
7.44
7.42
7.42
7.35
7.35
7.34
7.33
7.32
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.24
7.24
5.32 CD2Cl2
4.74
4.73
4.73
4.71
2.90
2.66
2.66
2.65
2.64
1.40
t-Bu
Me
N
S
O
Ph
CN
4fa
1H NMR (400 MHz, CD2Cl2)
1.98
1.94
0.97
1.00
3.03
1.95
9.32
f1 (ppm)

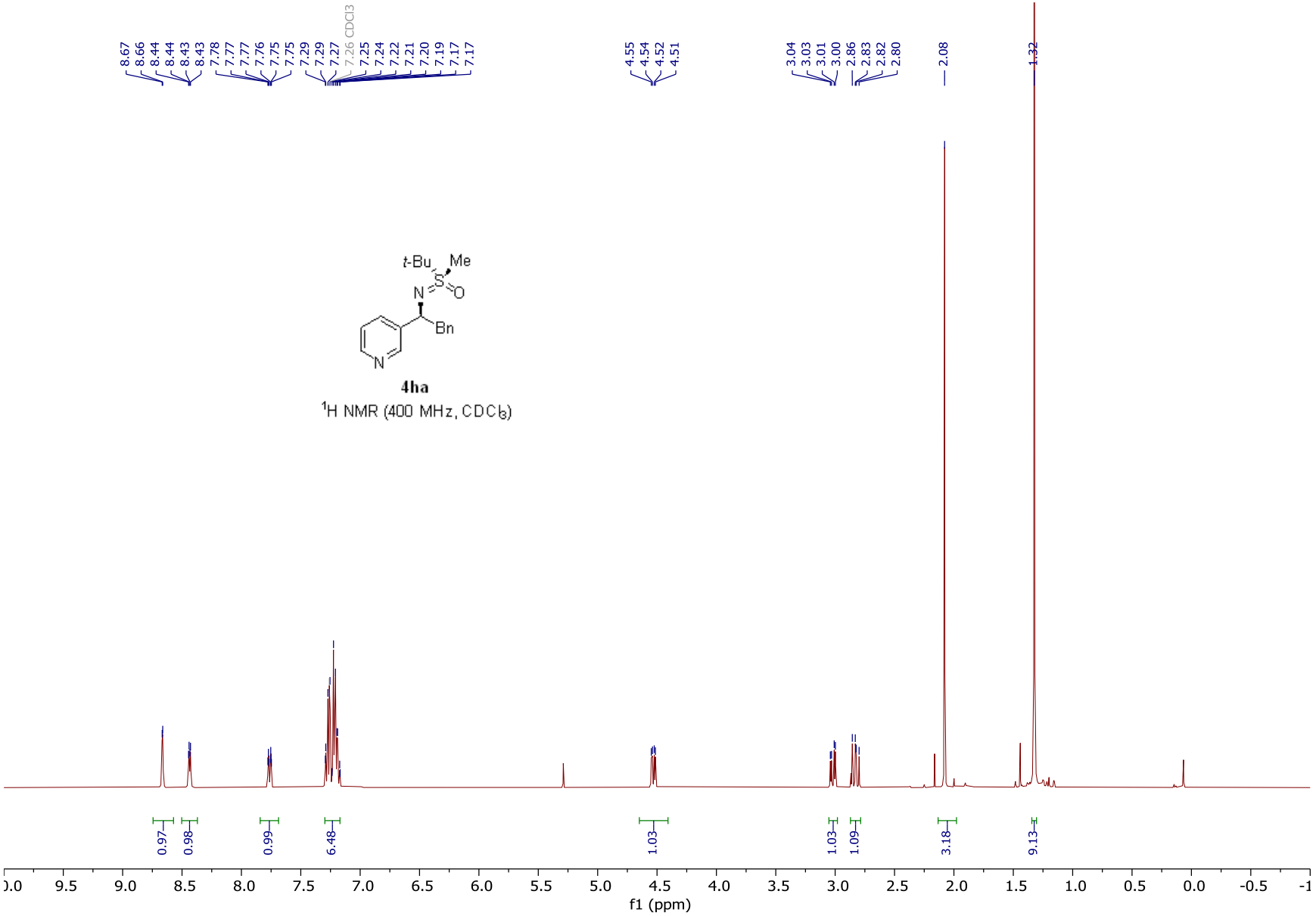

t-Bu
Me
N
S
O
CN
Ph
4fa
^{13}C NMR (101 MHz, CD_2Cl_2)
144.6
128.7
127.8
126.8
119.2
60.9
54.8
53.8 CD2Cl2
33.9
31.1
24.0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

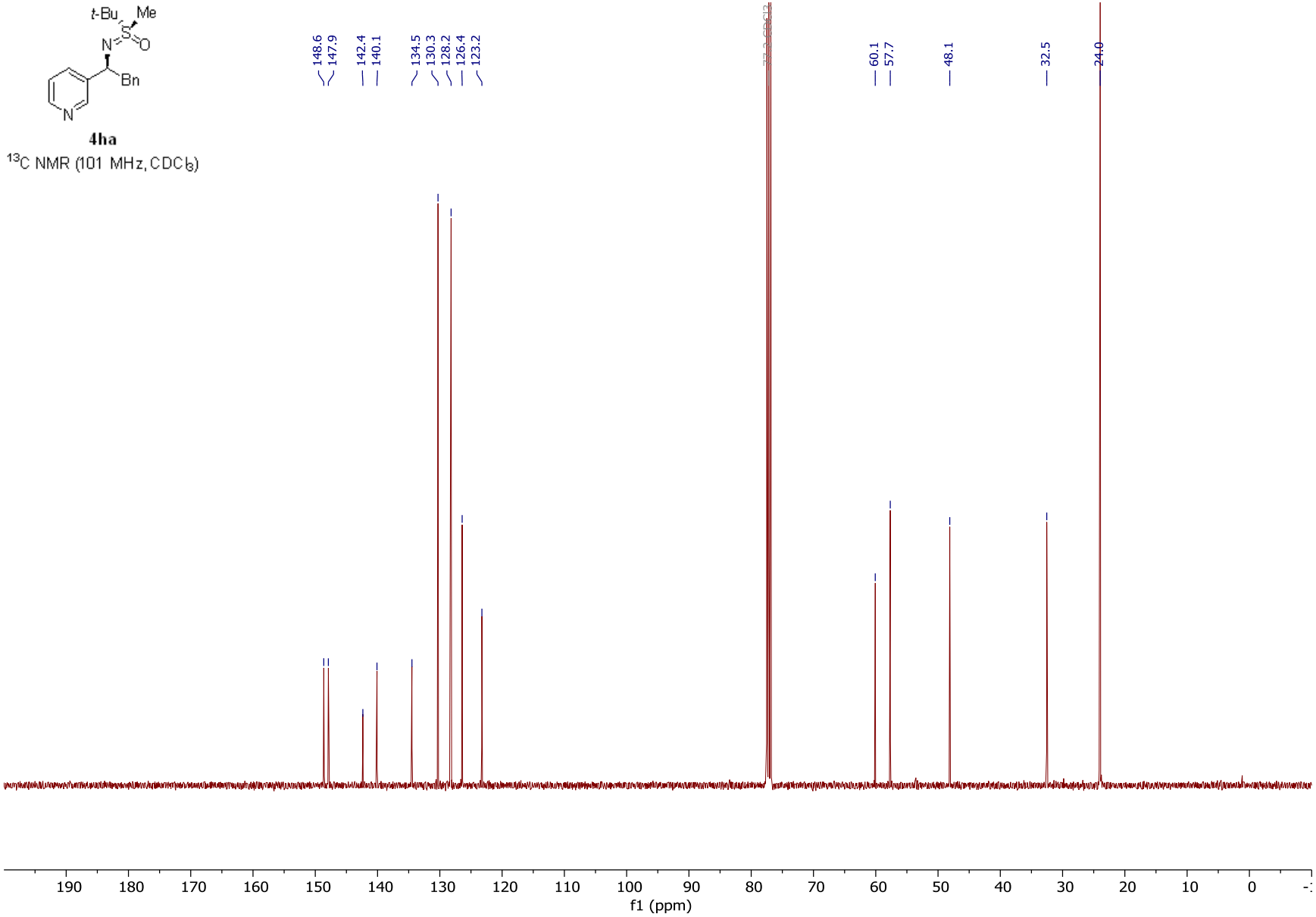


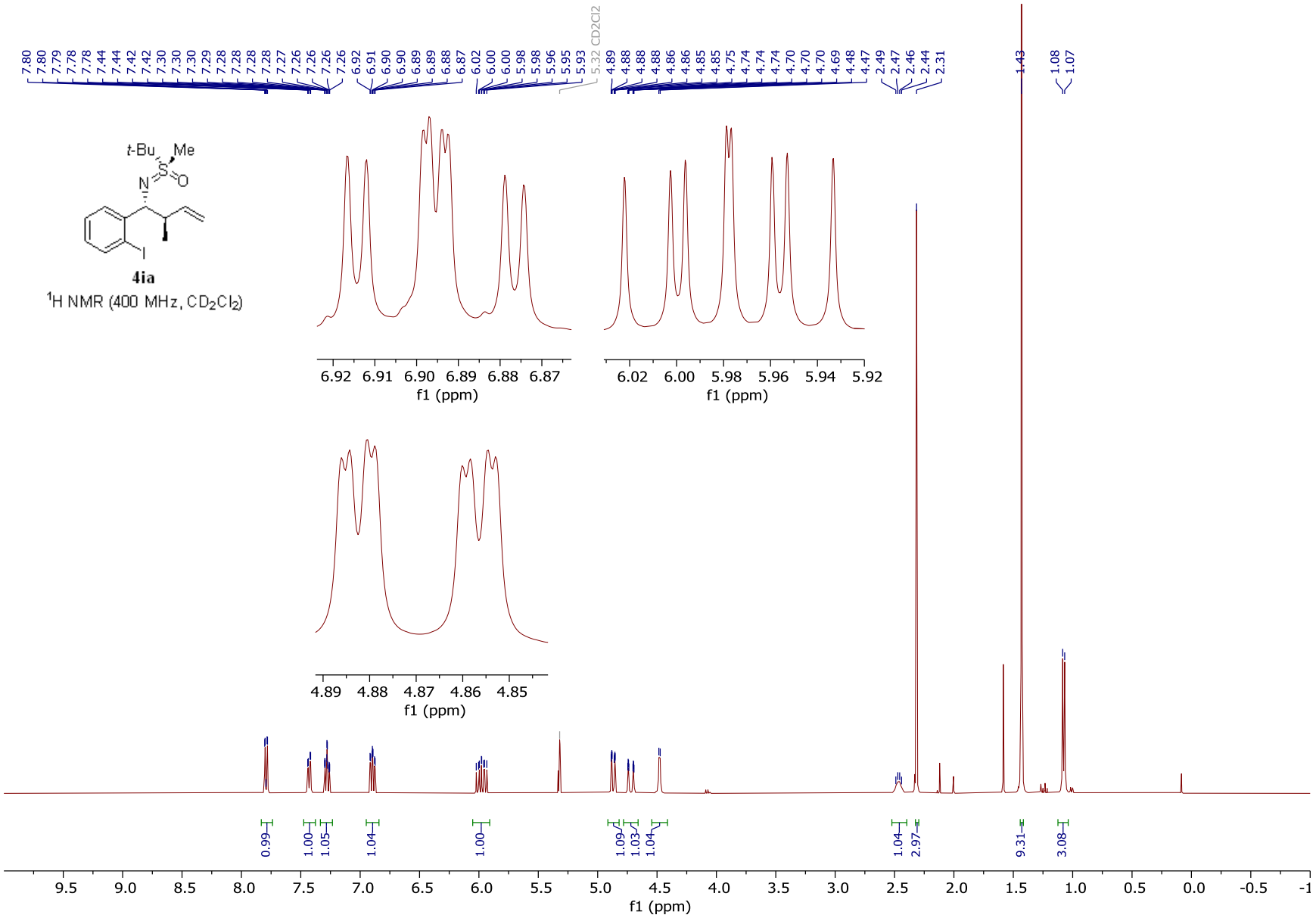
4ga

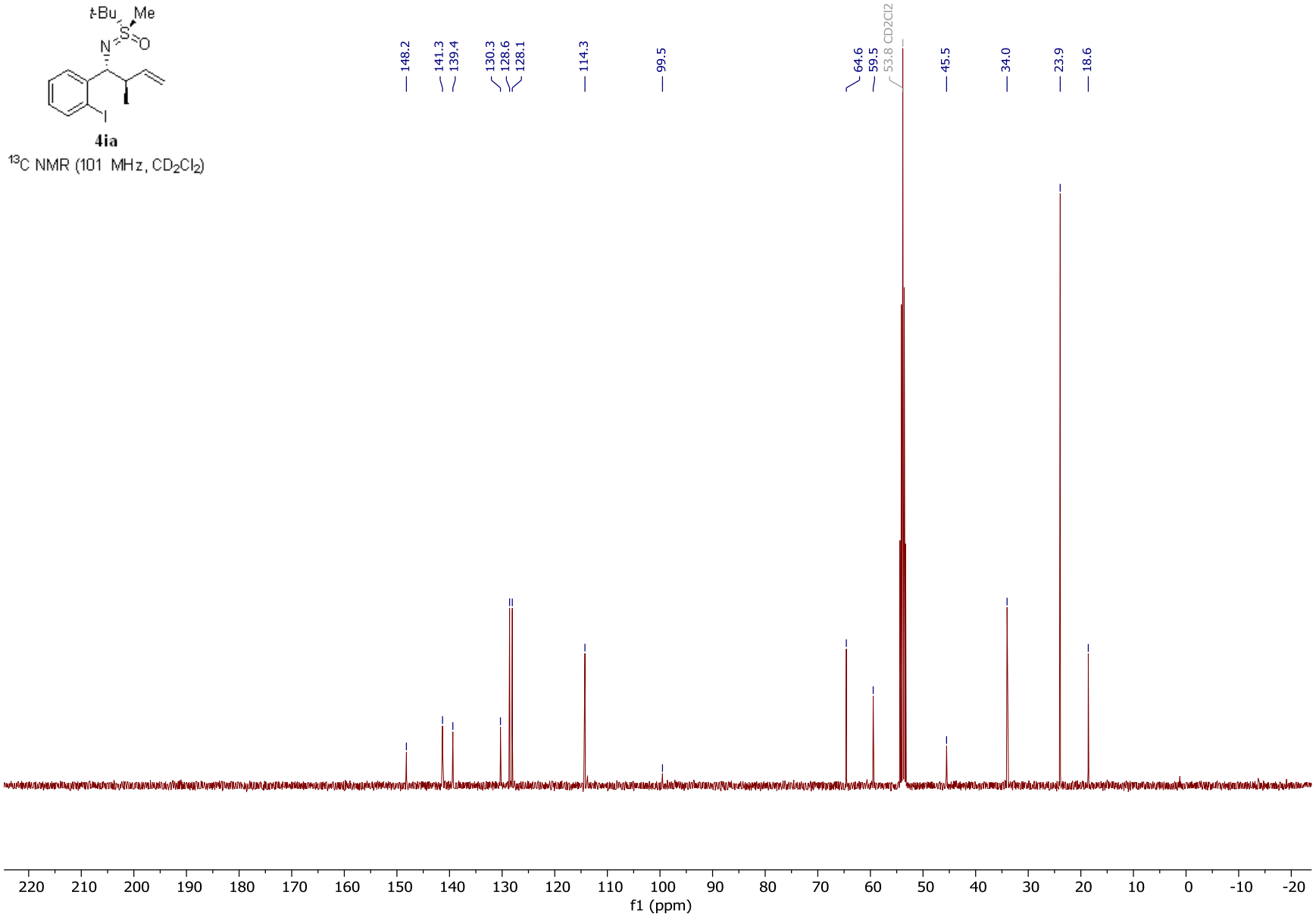
^{1}H NMR (400 MHz, CD_2Cl_2)

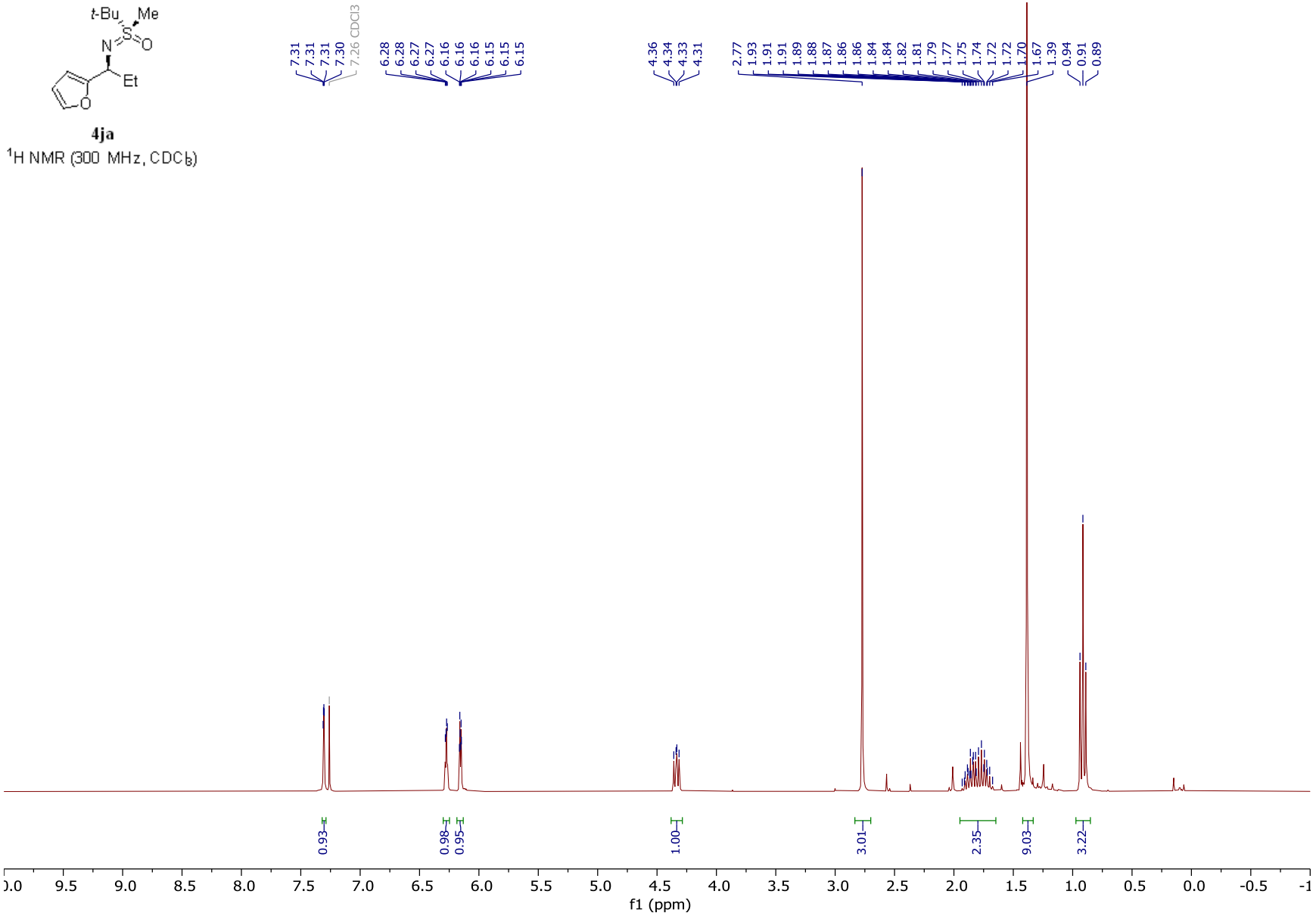

t-Bu
Me
N
S
O
Ph
CN
4ga
^{13}C NMR (101 MHz, CD_2Cl_2)
144.2
129.0
128.0
126.9
118.6
59.9
53.8 CD2Cl2
53.8
34.0
31.0
23.7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.67
8.66
8.44
8.44
8.43
8.43
7.78
7.77
7.77
7.76
7.75
7.75
7.29
7.29
7.27
7.26 CDCl3
7.25
7.24
7.22
7.21
7.20
7.19
7.17
7.17
4.55
4.54
4.52
4.51
3.04
3.03
3.01
3.00
2.86
2.83
2.82
2.80
2.08
1.32
t-Bu
Me
N
S
O
Bn
N
4ha
1H NMR (400 MHz, CDCl3)
0.97
0.98
0.99
6.48
1.03
1.03
1.09
3.18
9.13
f1 (ppm)


t-Bu
Me
N
S
O
Bn
N
4ha
13C NMR (101 MHz, CDCl3)
148.6
147.9
142.4
140.1
134.5
130.3
128.2
126.4
123.2
77.3
77.0
76.8
60.1
57.7
48.1
32.5
24.0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

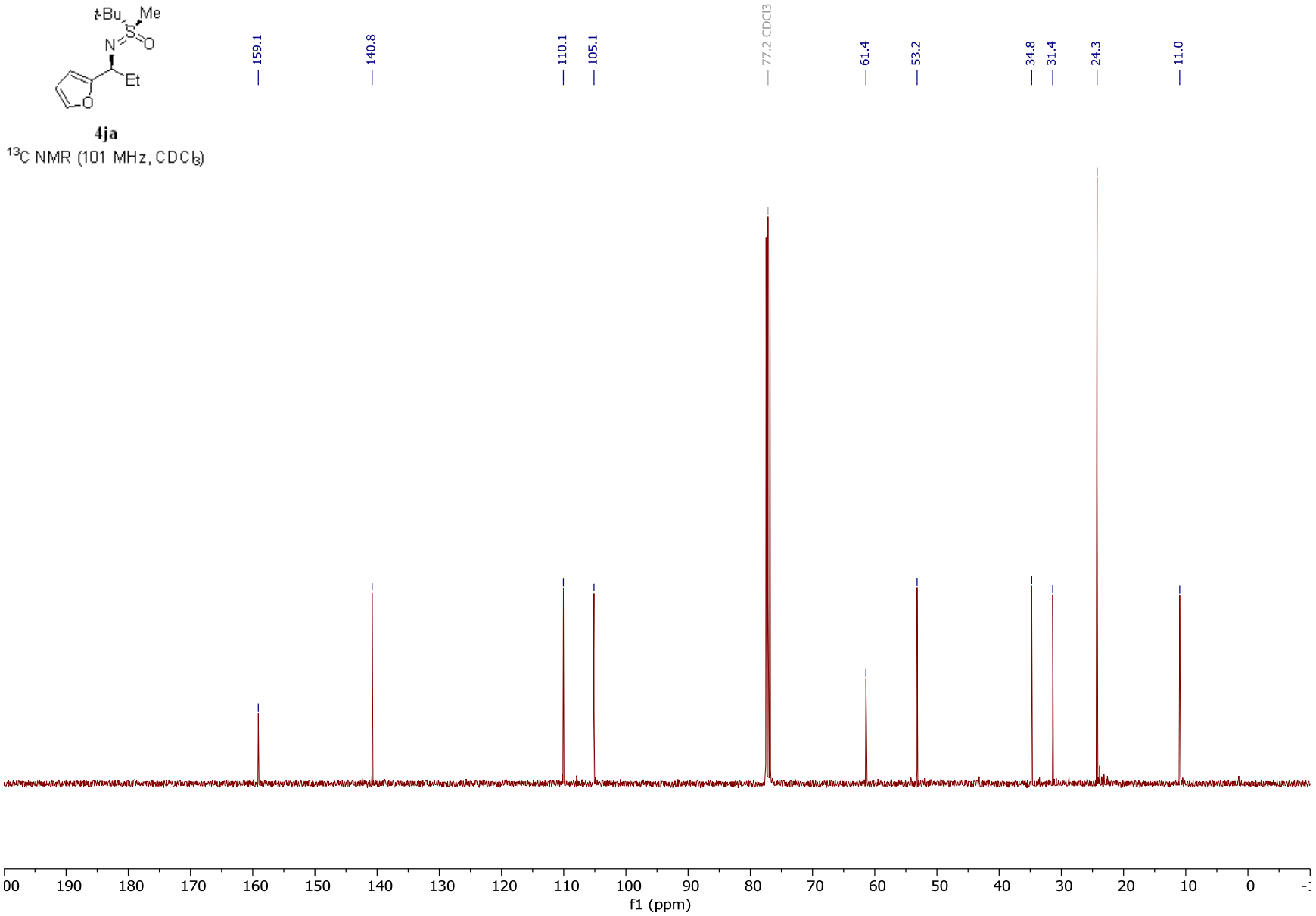

t-Bu
Me
N
S
O
I
4ia
^{1}H NMR (400 MHz, CD_2Cl_2)
CD2Cl2
1.43
1.08
1.07
f1 (ppm)


t-Bu
Me
N
S
O
I
4ia
13C NMR (101 MHz, CD2Cl2)
148.2
141.3
139.4
130.3
128.6
128.1
114.3
99.5
64.6
59.5
53.8 CD2Cl2
45.5
34.0
23.9
18.6
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



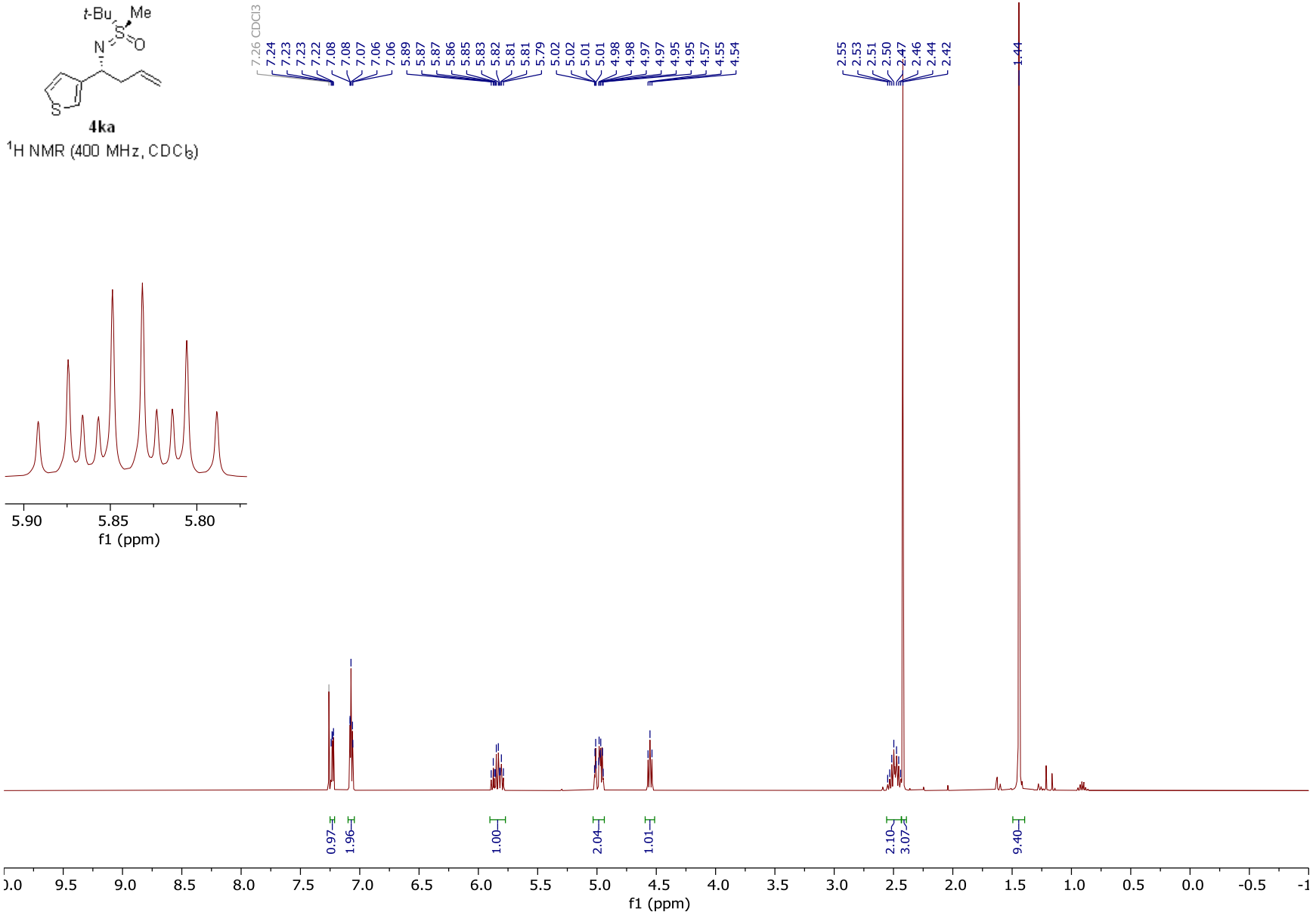
4ja

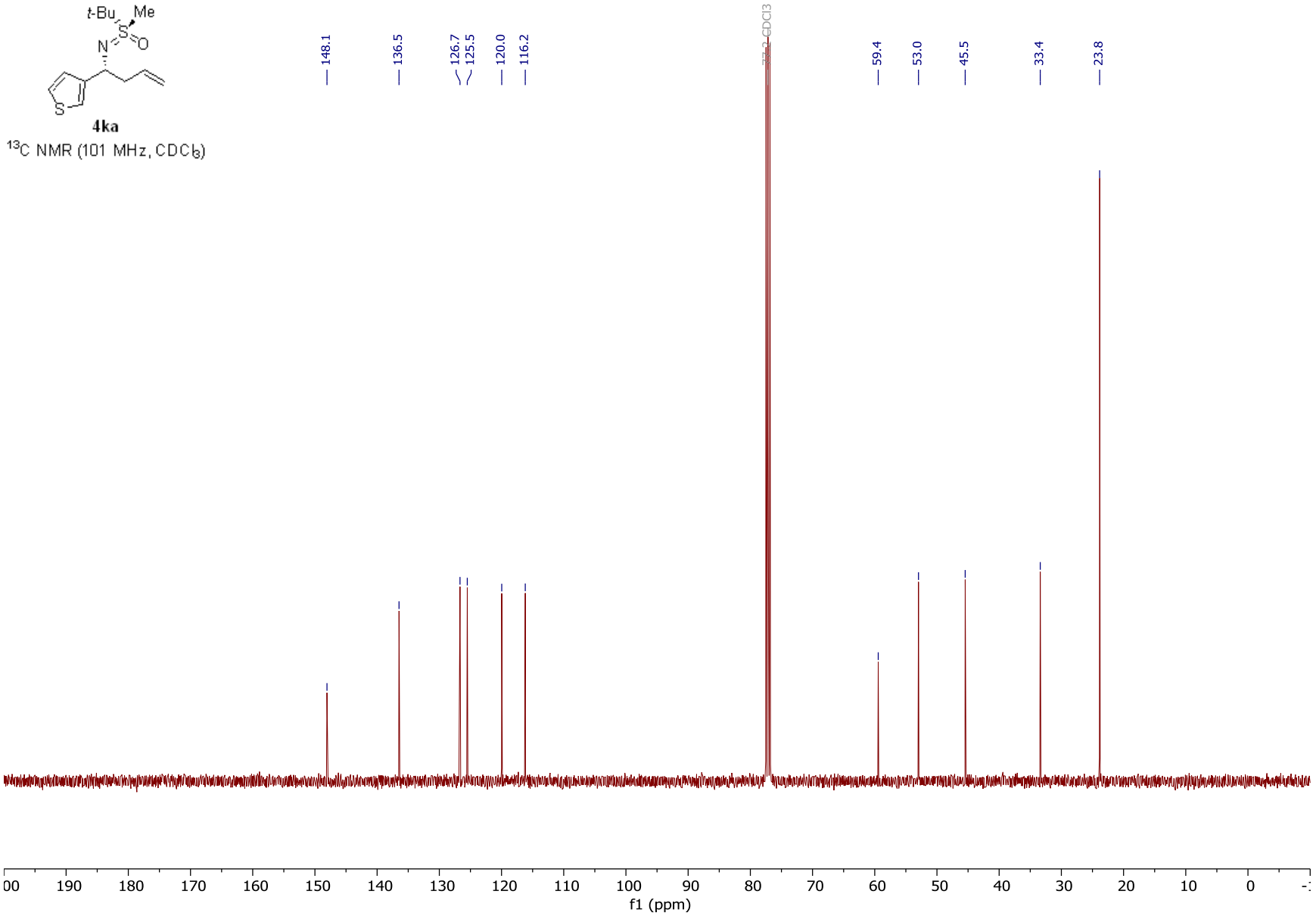
^{1}H NMR (300 MHz, $CDCl_3$)

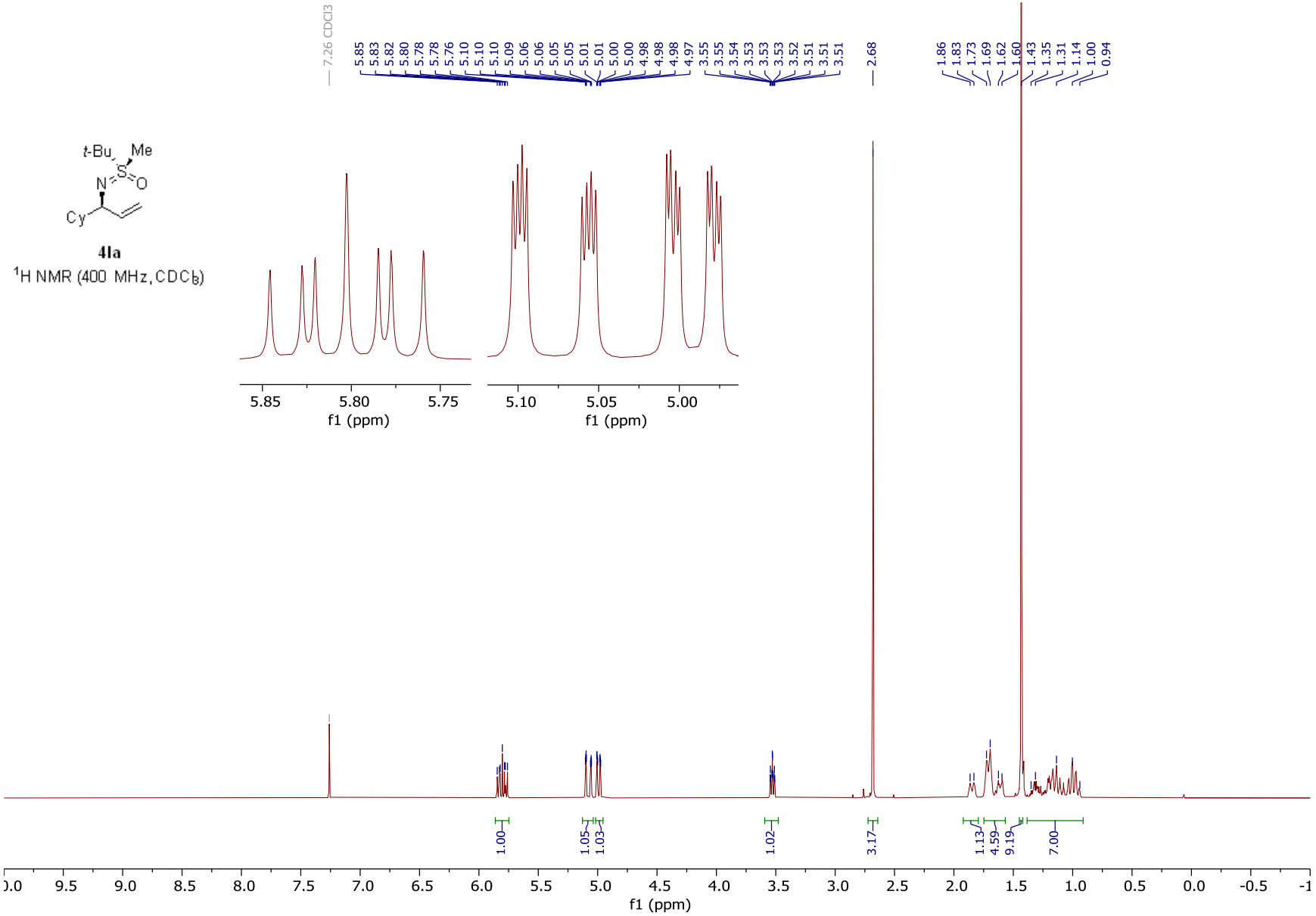


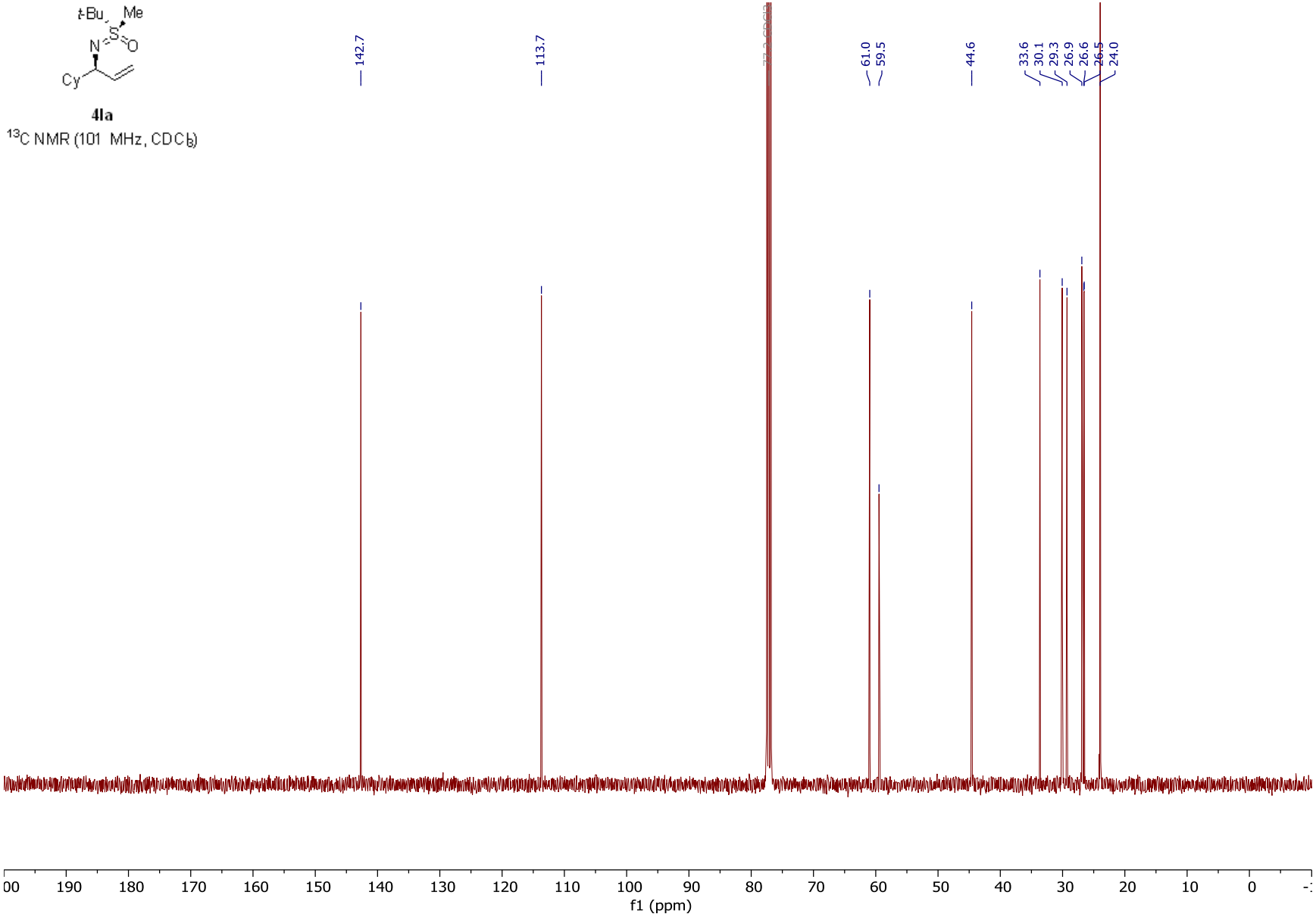
4ja

^{13}C NMR (101 MHz, $CDCl_3$)


t-Bu
Me
S
N
O
S
4ka
1H NMR (400 MHz, CDCl3)
7.26 CDCl3
7.24
7.23
7.23
7.22
7.08
7.08
7.07
7.06
7.06
5.89
5.87
5.87
5.86
5.85
5.83
5.82
5.81
5.81
5.79
5.02
5.02
5.01
5.01
4.98
4.98
4.97
4.97
4.95
4.95
4.57
4.55
4.54
2.55
2.53
2.51
2.50
2.47
2.46
2.44
2.42
1.44
5.90
5.85
5.80
f1 (ppm)
0.97
1.96
1.00
2.04
1.01
2.10
3.07
9.40
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

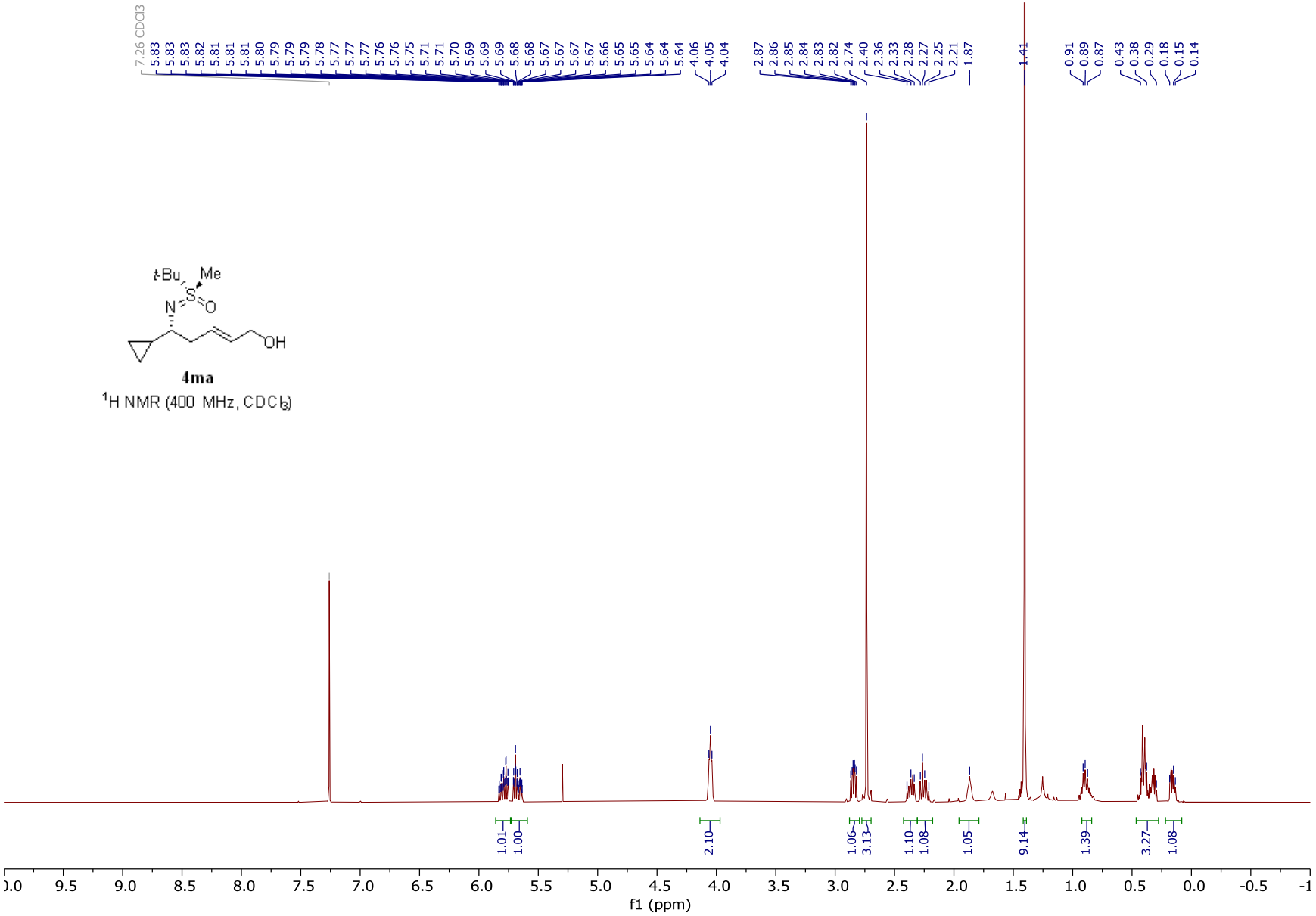

t-Bu
Me
N
S
O
S
4ka
13C NMR (101 MHz, CDCl3)
148.1
136.5
126.7
125.5
120.0
116.2
77.2 CDCl3
59.4
53.0
45.5
33.4
23.8
f1 (ppm)

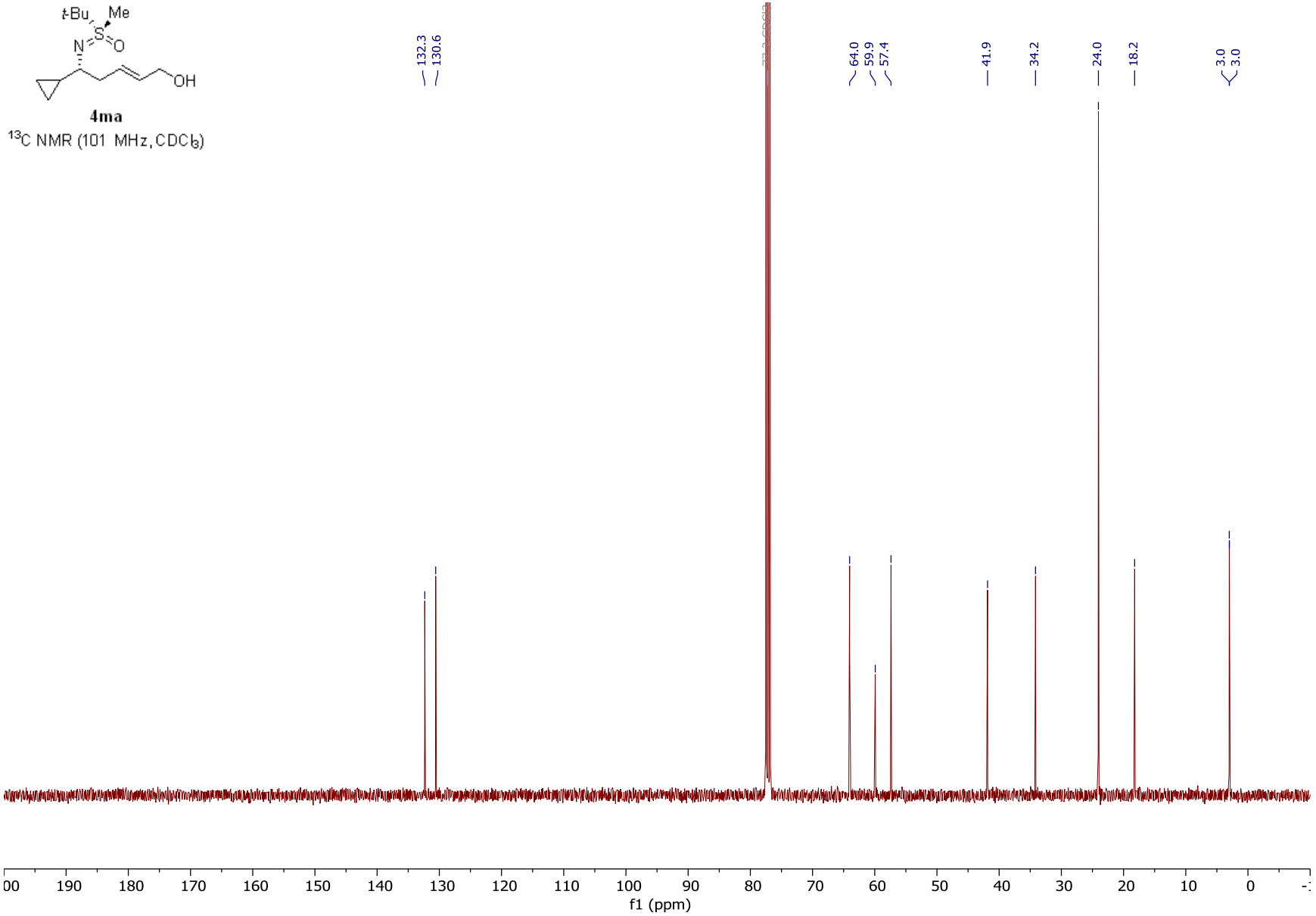

7.26 CDCl3
5.85 5.83 5.82 5.80 5.78 5.78 5.76 5.10 5.10 5.09 5.06 5.06 5.05 5.05 5.01 5.01 5.00 5.00 4.98 4.98 4.98 4.97 3.55 3.55 3.54 3.53 3.53 3.53 3.52 3.51 3.51 3.51
2.68
1.86 1.83 1.73 1.69 1.62 1.60 1.43 1.35 1.31 1.14 1.00 0.94
t-Bu Me
N S O
Cy
4la
^{1}H NMR (400 MHz, $CDCl_3$)
5.85 5.80 5.75
f1 (ppm)
5.10 5.05 5.00
f1 (ppm)
1.00 1.05 1.03 1.02 3.17 1.13 4.59 9.19 7.00
f1 (ppm)

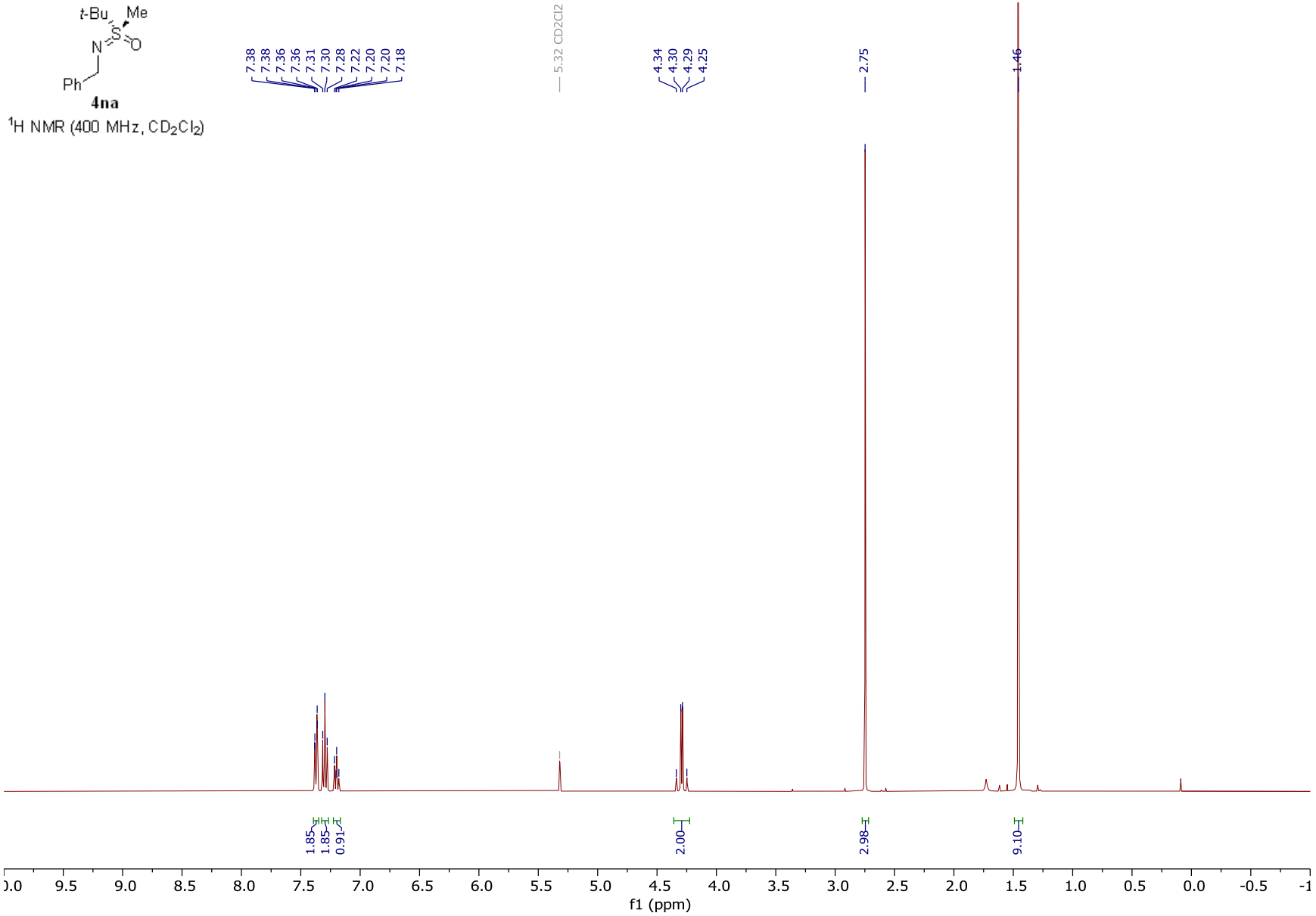


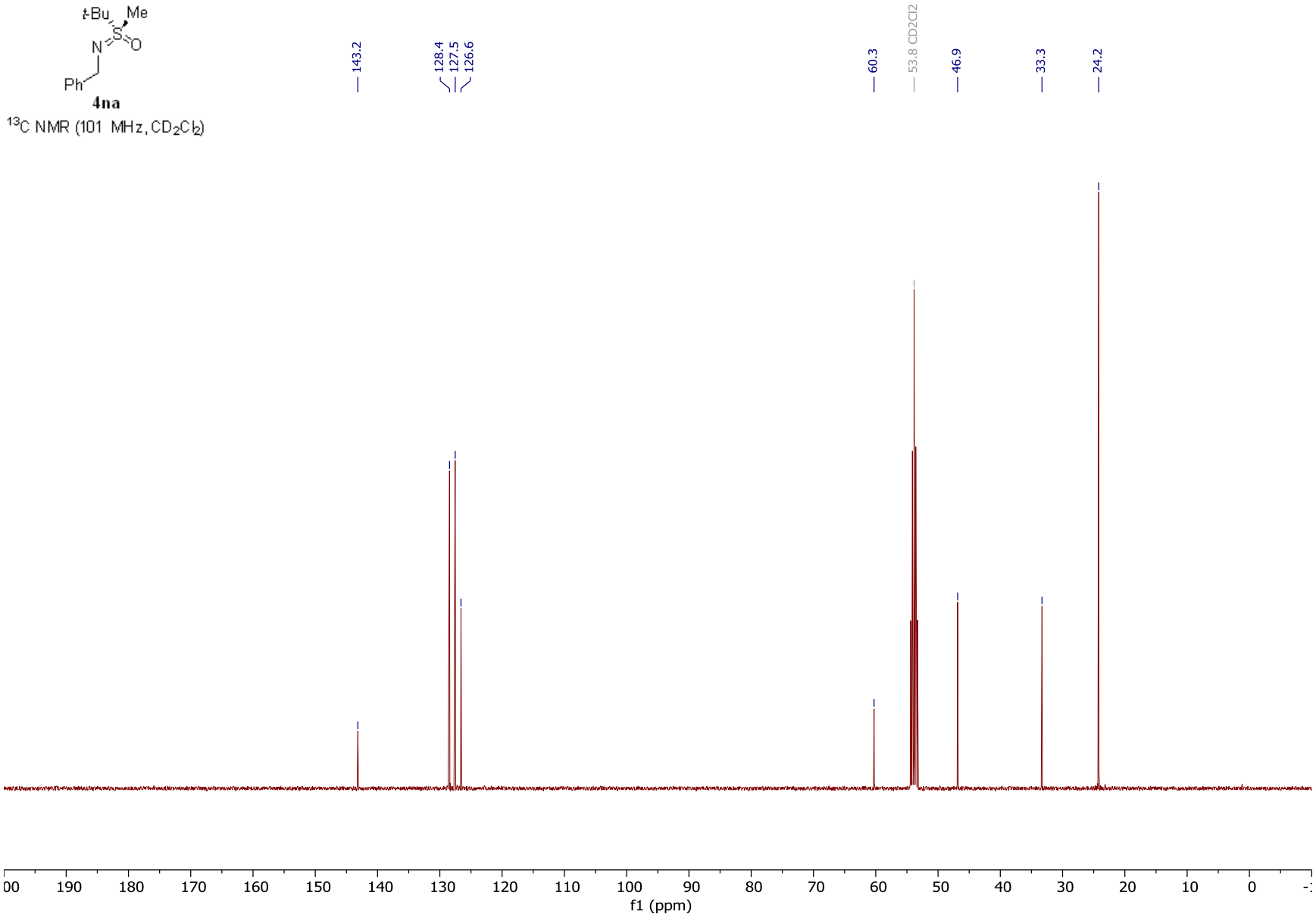
4la

^{13}C NMR (101 MHz, $CDCl_3$)

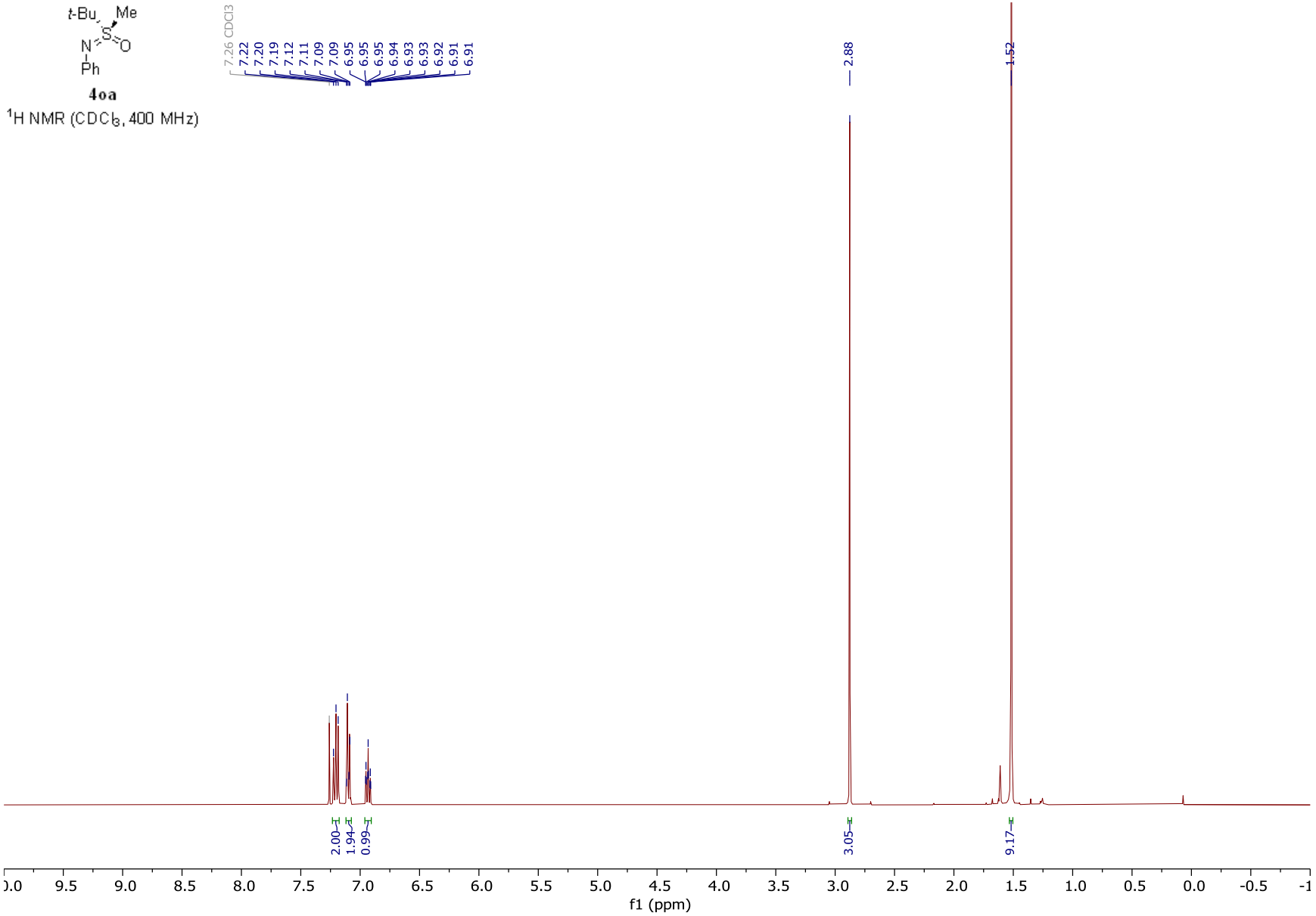

7.26 CDCl3
5.83 5.83 5.83 5.82 5.81 5.81 5.81 5.80 5.79 5.79 5.79 5.78 5.77 5.77 5.77 5.76 5.76 5.75 5.71 5.71 5.70 5.69 5.69 5.69 5.68 5.68 5.67 5.67 5.67 5.66 5.65 5.65 5.64 5.64 5.64
4.06 4.05 4.04
2.87 2.86 2.85 2.84 2.83 2.82 2.74 2.40 2.36 2.33 2.28 2.27 2.25 2.21
1.87
1.41
0.91 0.89 0.87 0.43 0.38 0.29 0.18 0.15 0.14
t-Bu
Me
S
N
O
OH
4ma
1H NMR (400 MHz, CDCl3)
1.01 1.00 2.10 1.06 3.13 1.10 1.08 1.05 9.14 1.39 3.27 1.08
f1 (ppm)

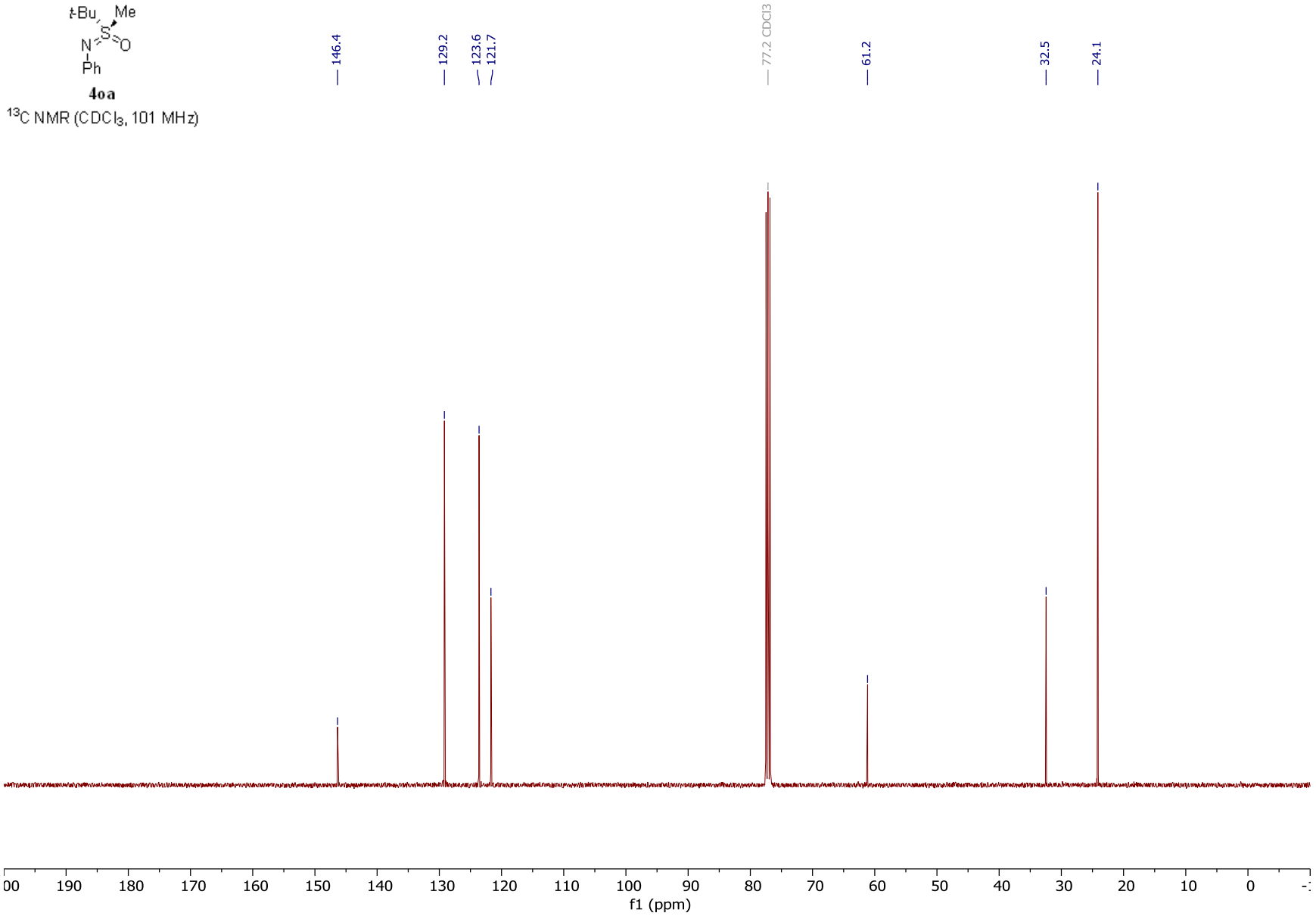

t-Bu
Me
N
S
O
OH
4ma
^{13}C NMR (101 MHz, $CDCl_3$)
132.3
130.6
64.0
59.9
57.4
41.9
34.2
24.0
18.2
3.0
3.0
f1 (ppm)

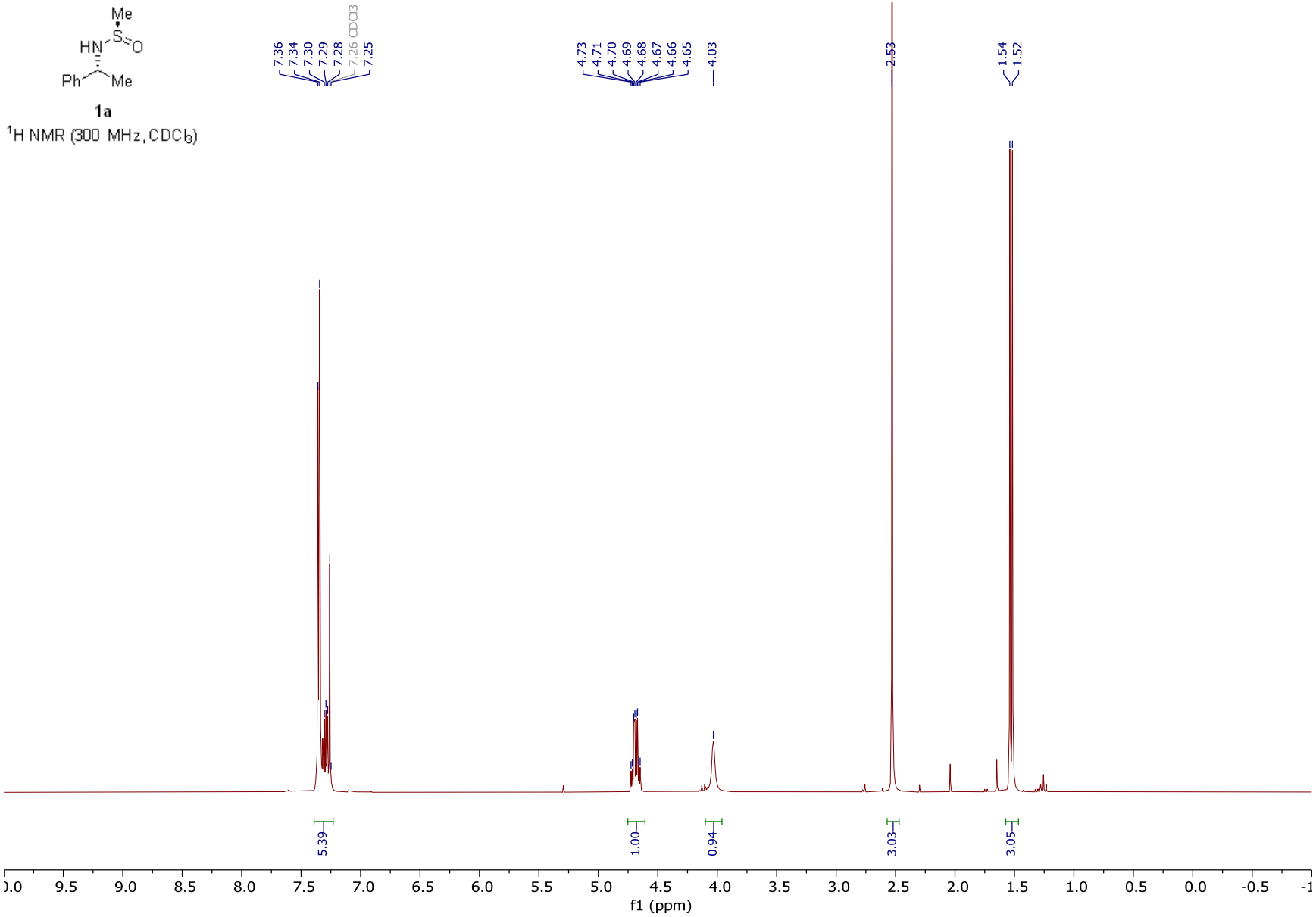

t-Bu
Me
N
S
O
Ph
4na
^{1}H NMR (400 MHz, CD_2Cl_2)
7.38
7.38
7.36
7.36
7.31
7.30
7.28
7.22
7.20
7.20
7.18
5.32 CD_2Cl_2
4.34
4.30
4.29
4.25
2.75
1.46
1.85
1.85
0.91
2.00
2.98
9.10
f1 (ppm)

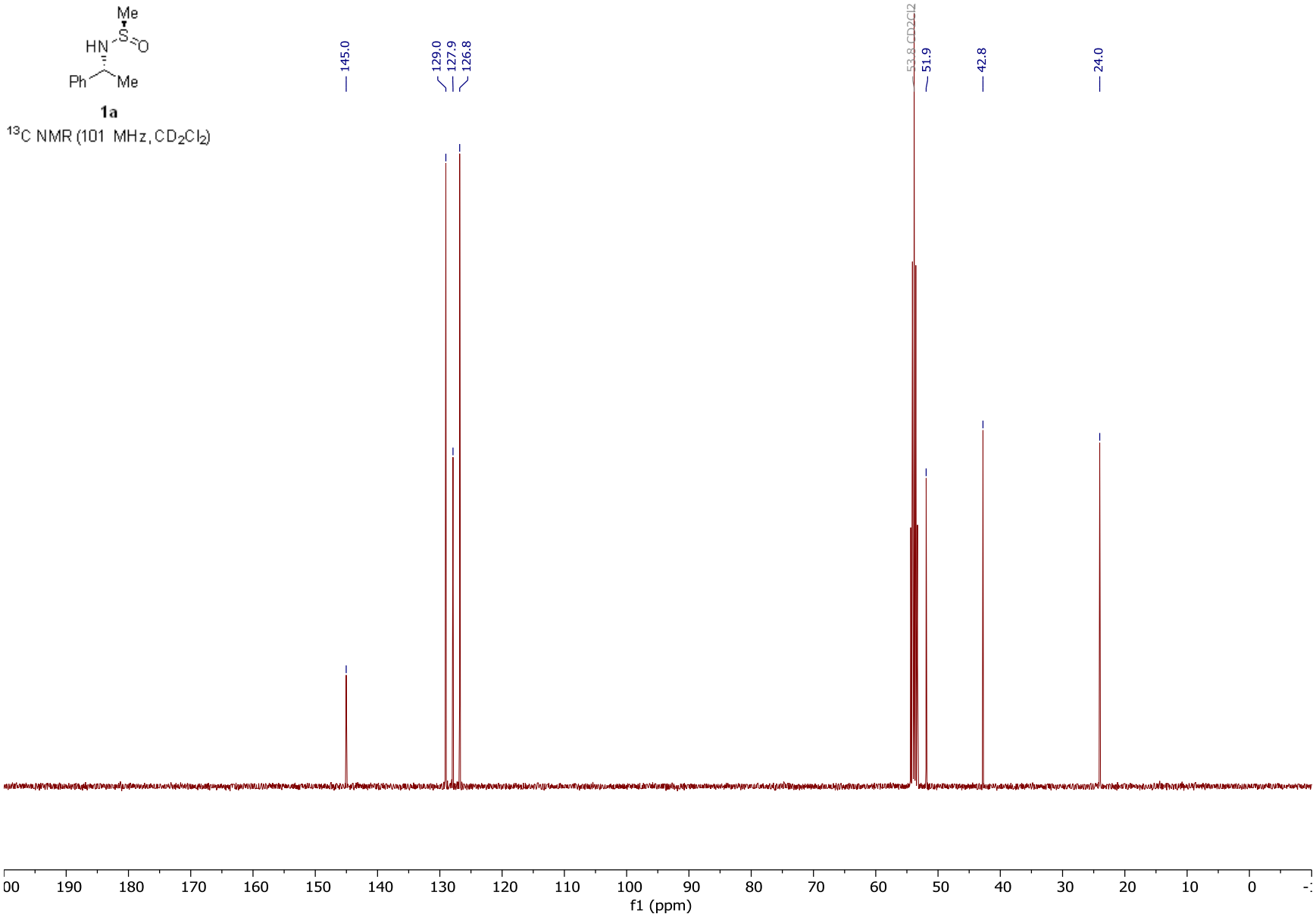


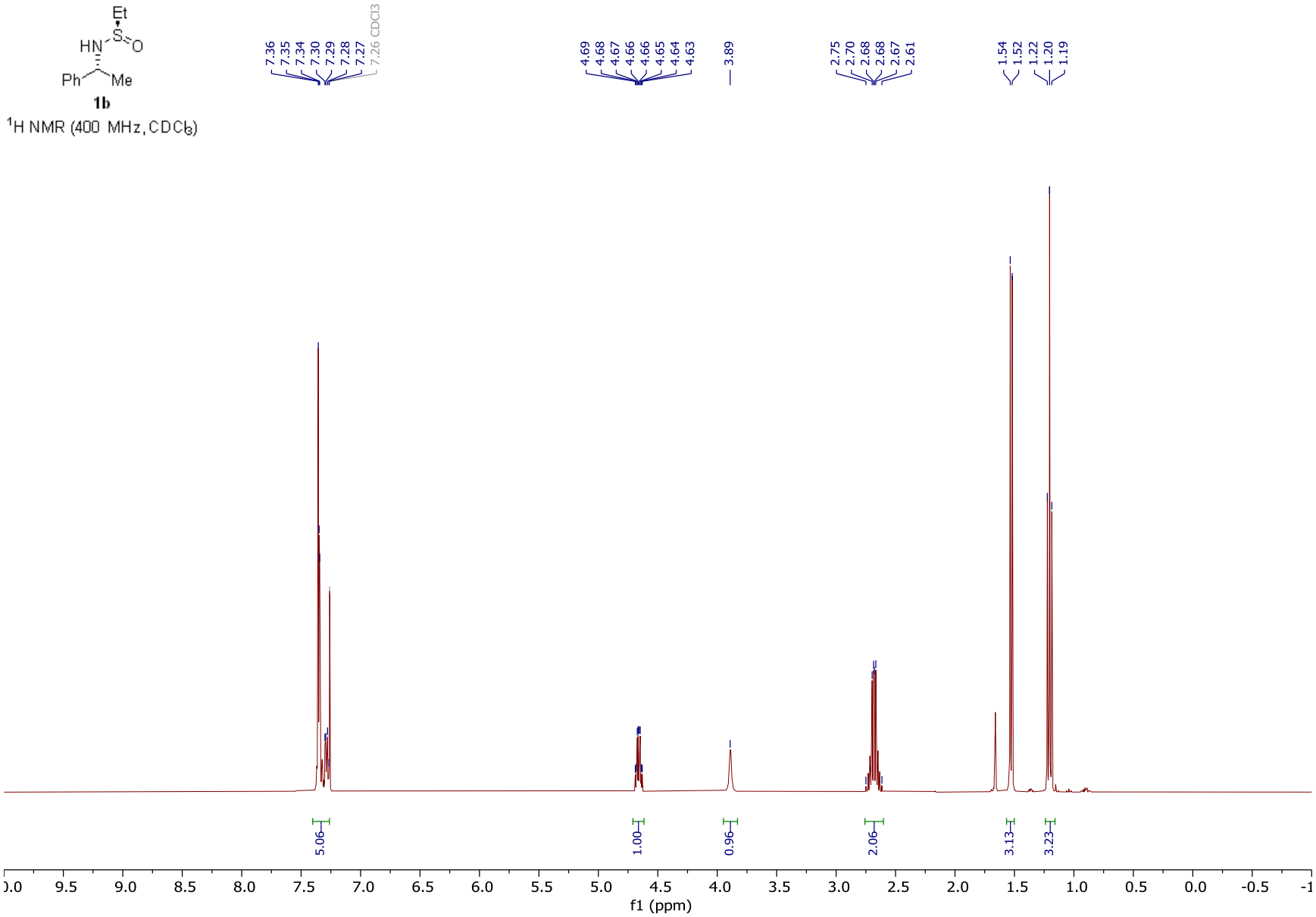
^{13}C NMR (101 MHz, CD_2Cl_2)

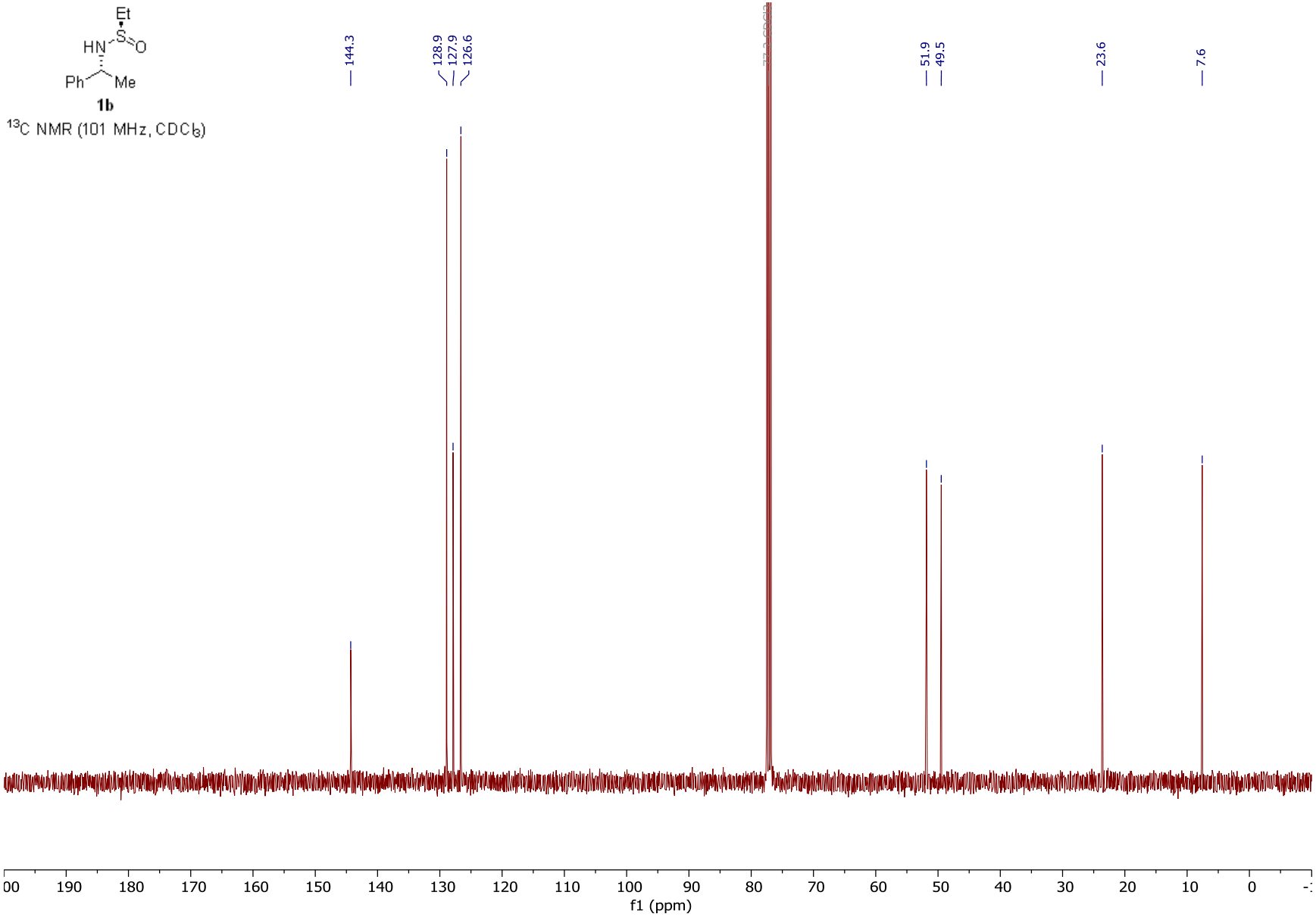

t-Bu
Me
N
S
O
Ph
4oa
^{1}H NMR (CDCl$_3$, 400 MHz)
7.26 CDCl3
7.22
7.20
7.19
7.12
7.11
7.09
7.09
6.95
6.95
6.94
6.93
6.93
6.92
6.91
6.91
2.88
1.52
2.00
1.94
0.99
3.05
9.17
f1 (ppm)

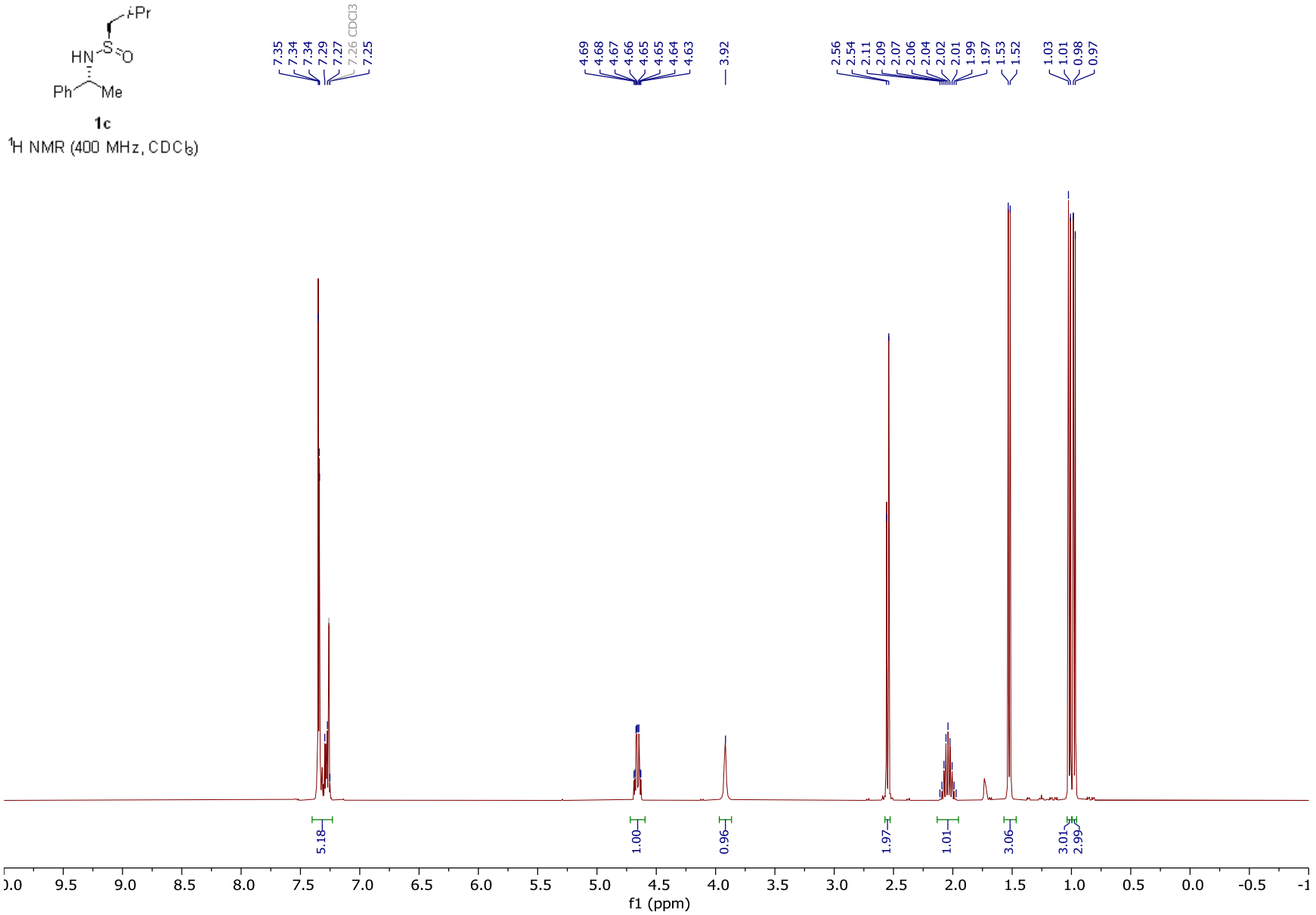

t-Bu
Me
S
O
N
Ph
4oa
13C NMR (CDCl3, 101 MHz)
146.4
129.2
123.6
121.7
77.2 CDCl3
61.2
32.5
24.1
f1 (ppm)

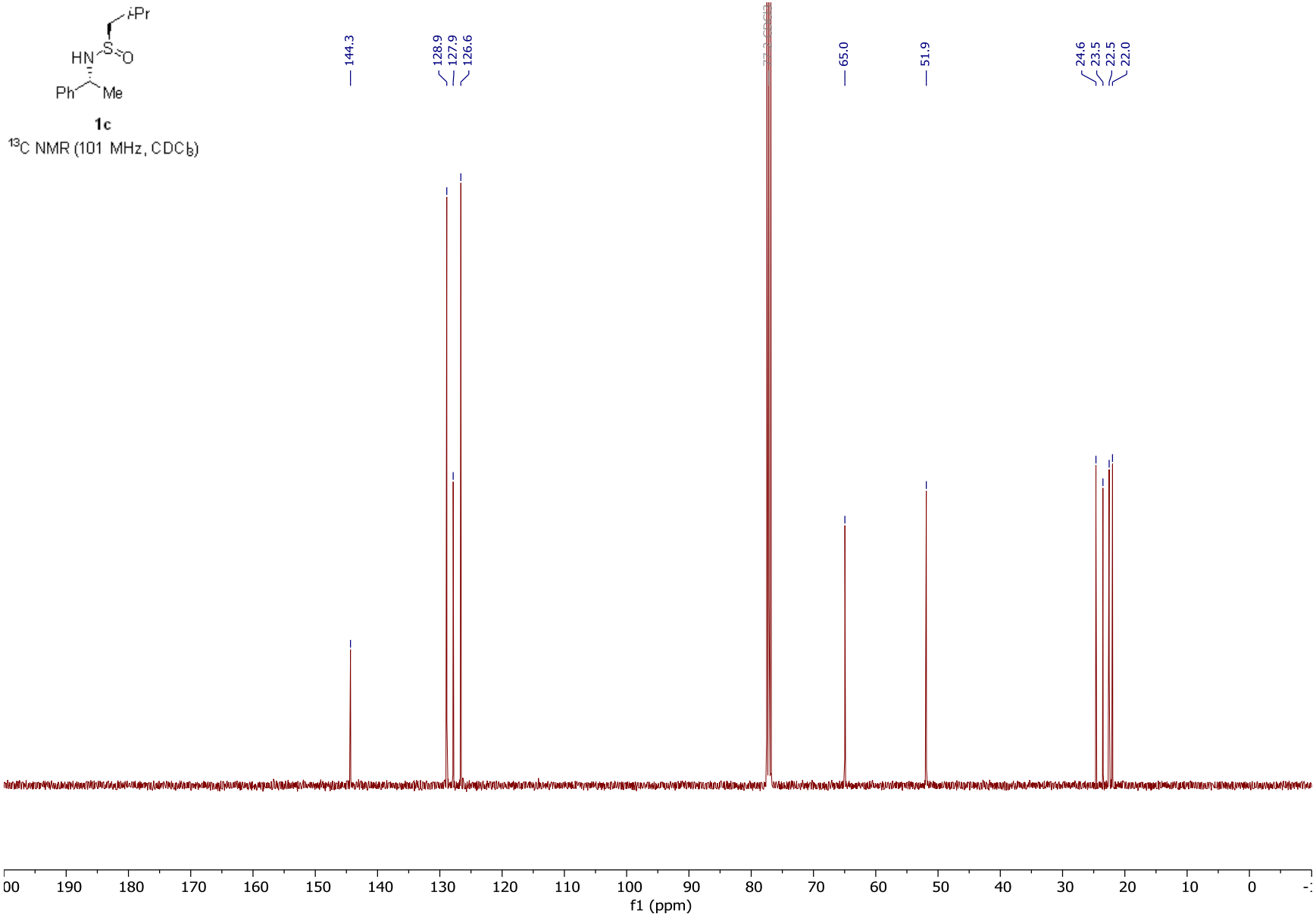

Me
HN
S
O
Ph
Me
1a
^{1}H NMR (300 MHz, CDCl$_3$)
7.36
7.34
7.30
7.29
7.28
7.26 CDCl3
7.25
4.73
4.71
4.70
4.69
4.68
4.67
4.66
4.65
4.03
2.53
1.54
1.52
5.39
1.00
0.94
3.03
3.05
f1 (ppm)

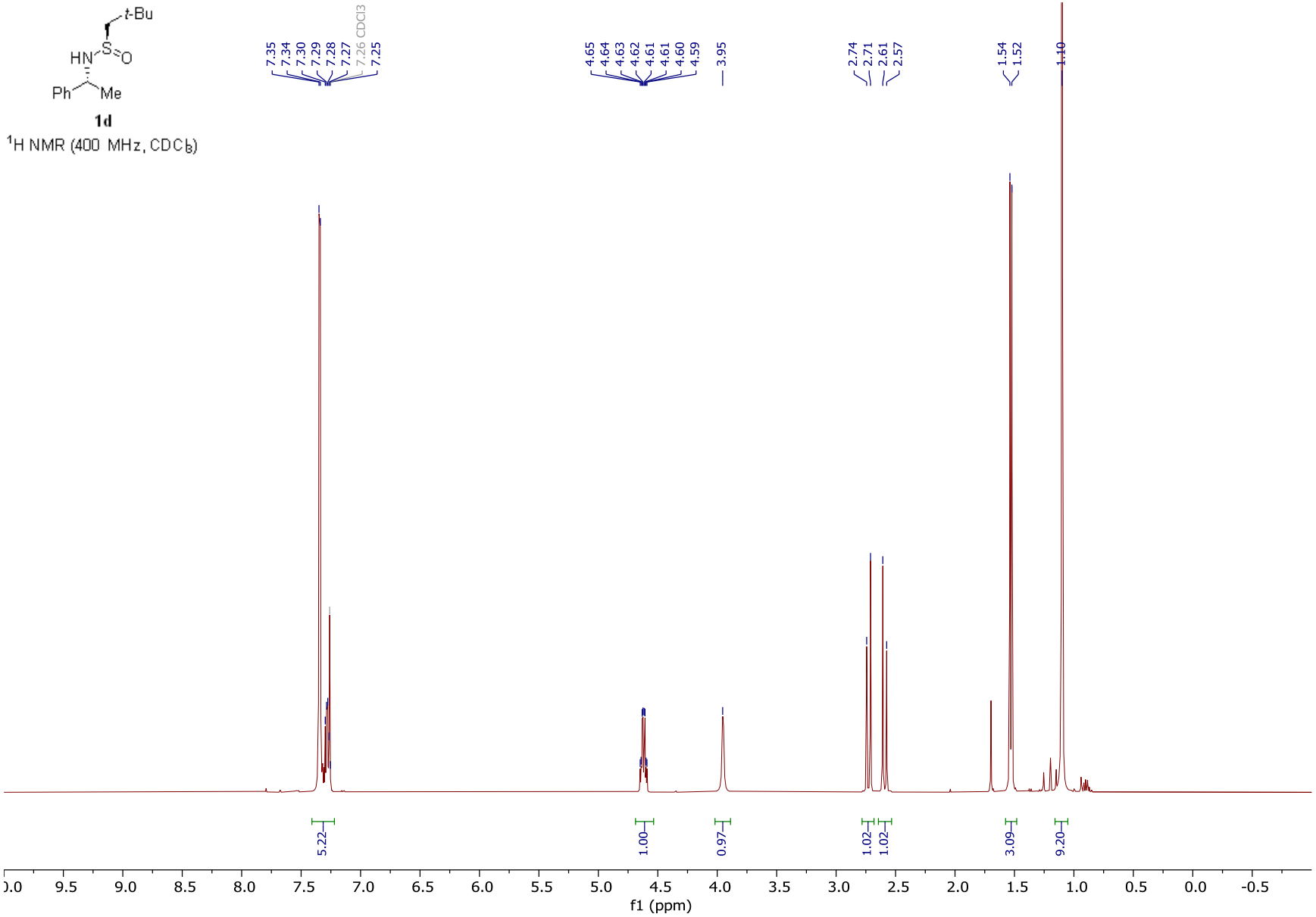

Me
HN
S
O
Ph
Me
1a
^{13}C NMR (101 MHz, CD_2Cl_2)
145.0
129.0
127.9
126.8
53.8 CD2Cl2
51.9
42.8
24.0
f1 (ppm)

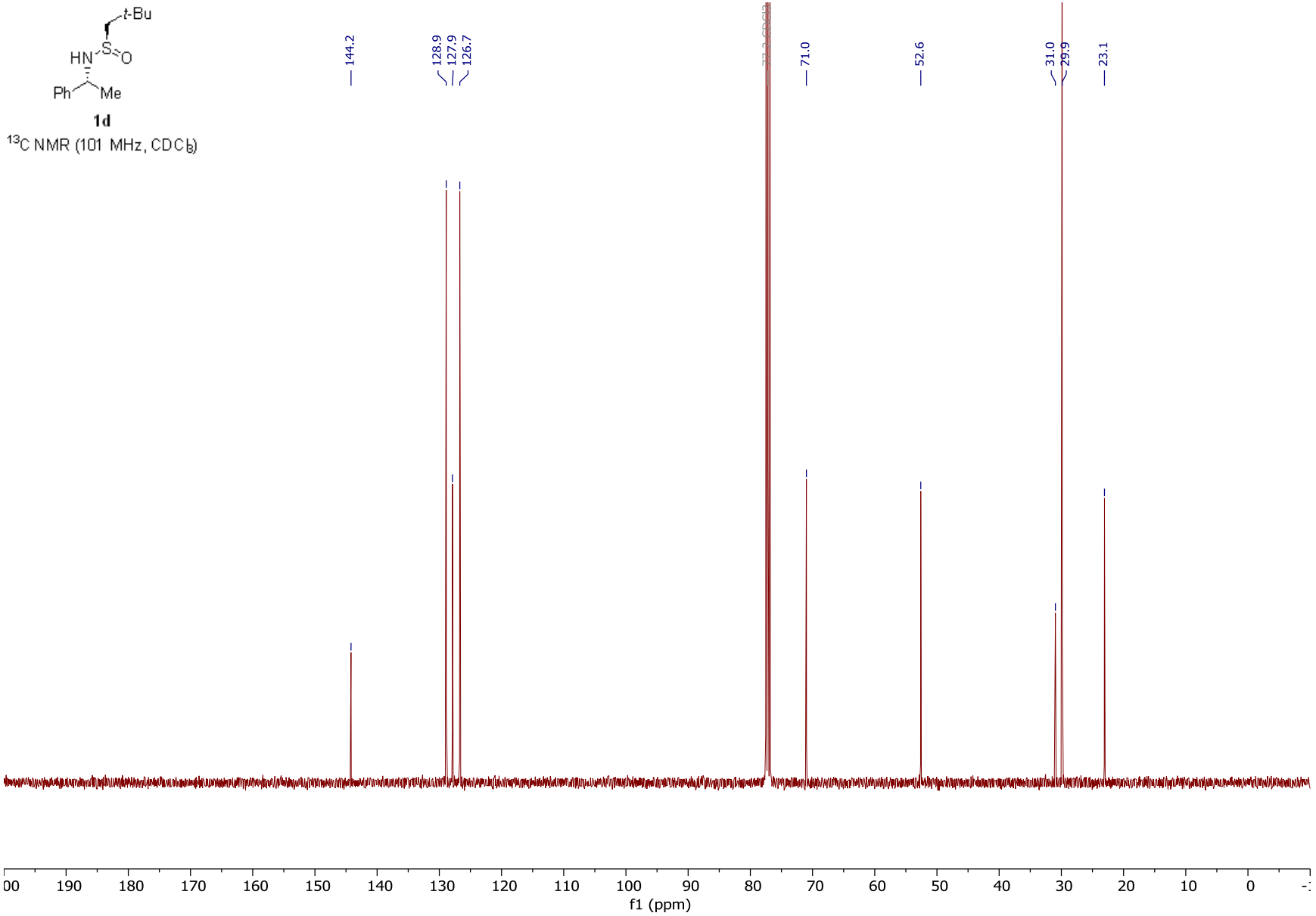

Et
HN
S
O
Ph
Me
1b
^{1}H NMR (400 MHz, $CDCl_3$)
7.36
7.35
7.34
7.30
7.29
7.28
7.27
7.26 CDCl3
4.69
4.68
4.67
4.66
4.66
4.65
4.64
4.63
3.89
2.75
2.70
2.68
2.68
2.67
2.61
1.54
1.52
1.22
1.20
1.19
5.06
1.00
0.96
2.06
3.13
3.23
f1 (ppm)

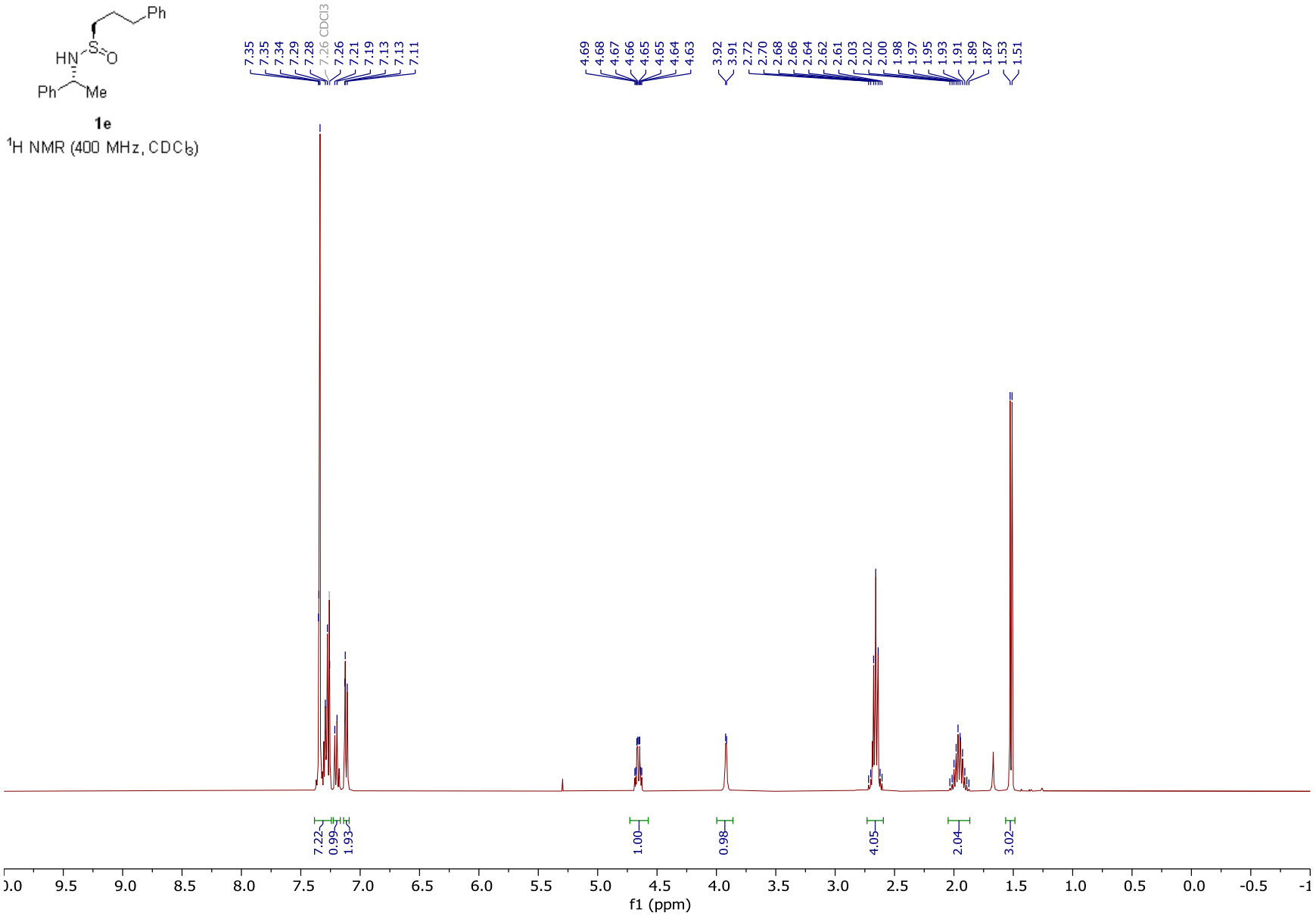

Et
HN
S
O
Ph
Me
1b
^{13}C NMR (101 MHz, $CDCl_3$)
144.3
128.9
127.9
126.6
77.3
51.9
49.5
23.6
7.6
f1 (ppm)

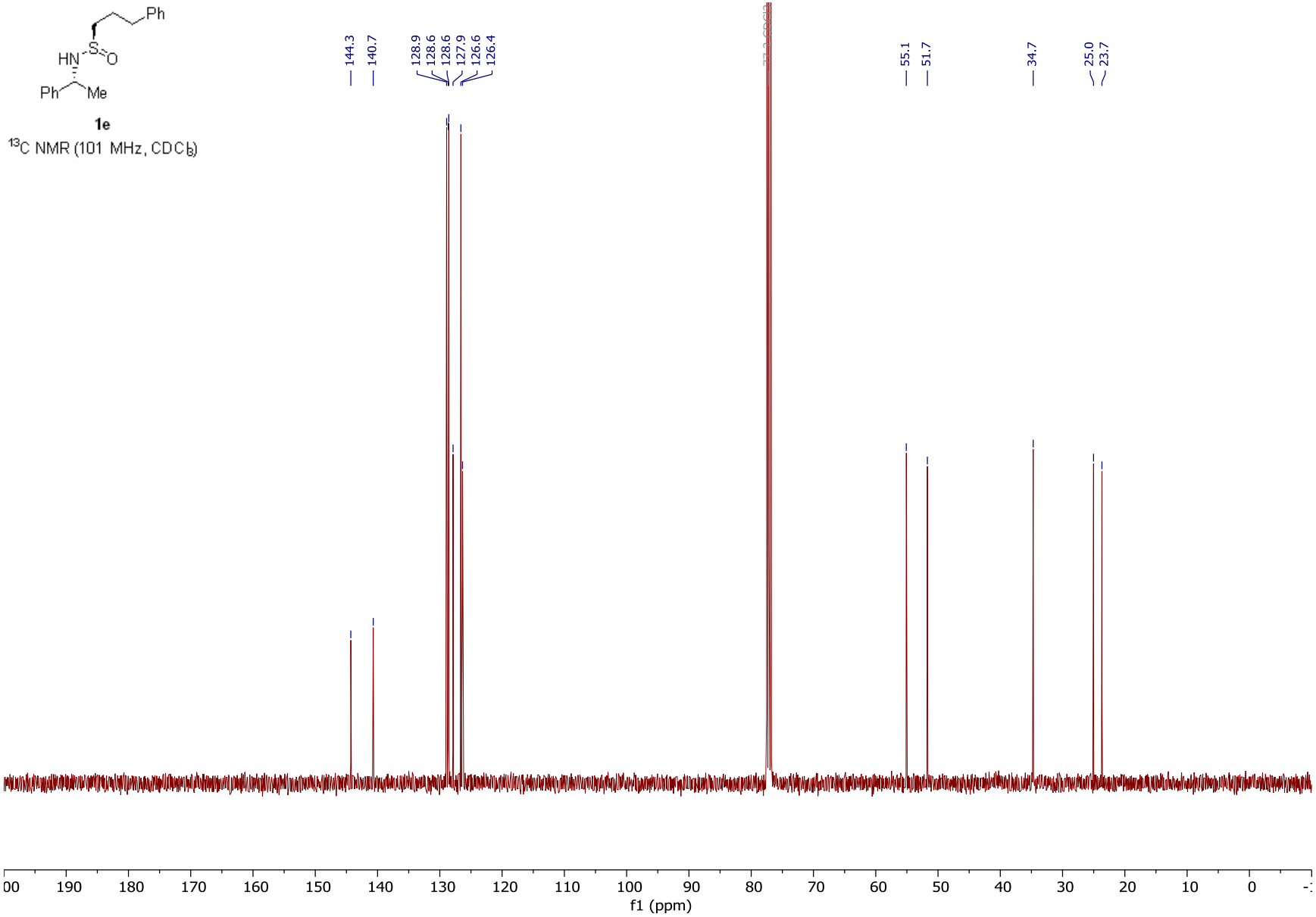

iPr
HN
S
O
Ph
Me
1c
^{1}H NMR (400 MHz, CDCl$_3$)
7.35
7.34
7.34
7.29
7.27
7.26 CDCl3
7.25
4.69
4.68
4.67
4.66
4.65
4.65
4.64
4.63
3.92
2.56
2.54
2.11
2.09
2.07
2.06
2.04
2.02
2.01
1.99
1.97
1.53
1.52
1.03
1.01
0.98
0.97
5.18
1.00
0.96
1.97
1.01
3.06
3.01
2.99
f1 (ppm)

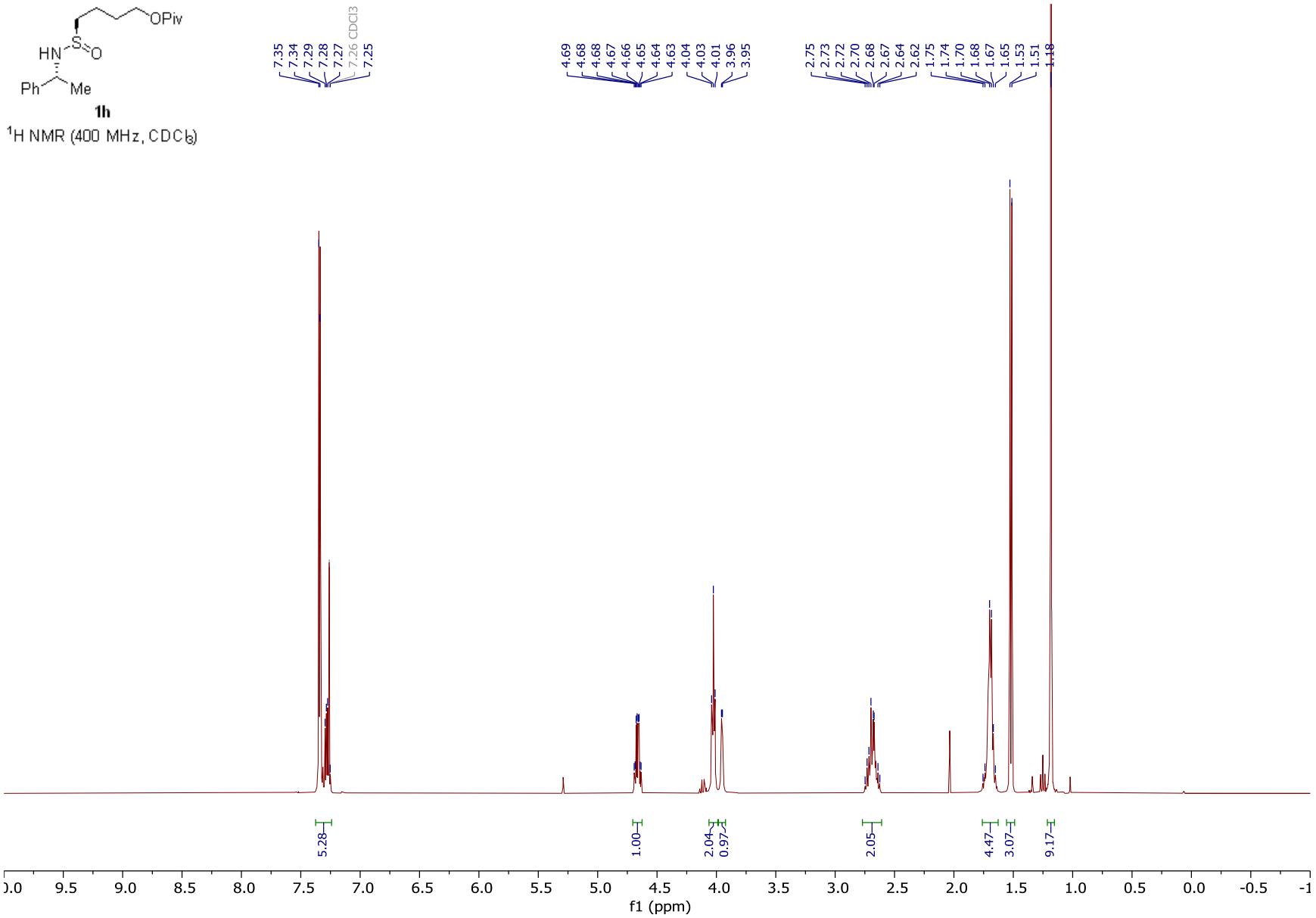

iPr
HN
S
O
Ph
Me
1c
13C NMR (101 MHz, CDCl3)
144.3
128.9
127.9
126.6
77.3 CDCl3
65.0
51.9
24.6
23.5
22.5
22.0
f1 (ppm)

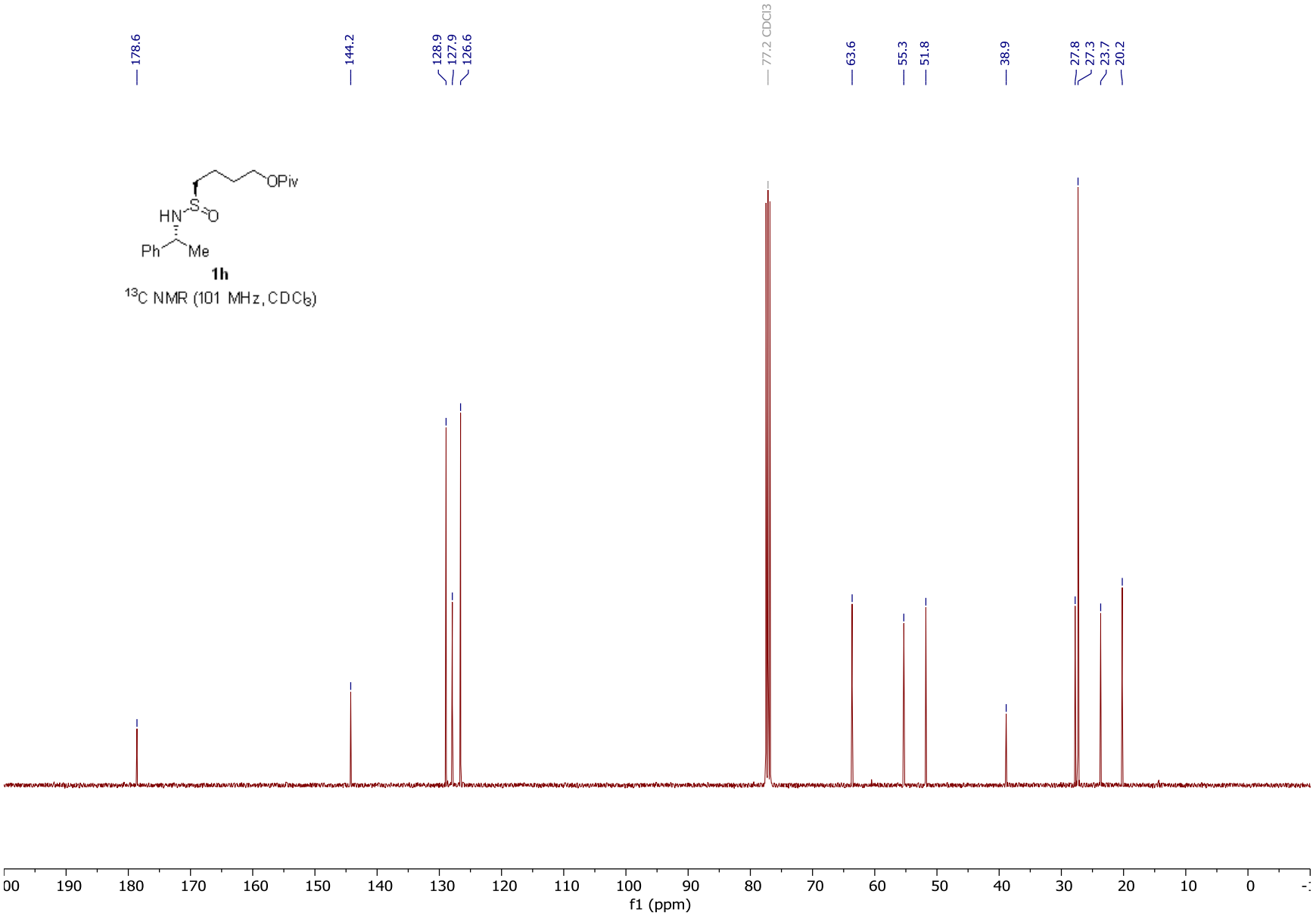

t-Bu
HN
S
O
Ph
Me
1d
1H NMR (400 MHz, CDCl3)
7.35
7.34
7.30
7.29
7.28
7.27
7.26 CDCl3
7.25
4.65
4.64
4.63
4.62
4.61
4.61
4.60
4.59
3.95
2.74
2.71
2.61
2.57
1.54
1.52
1.10
5.22
1.00
0.97
1.02
1.02
3.09
9.20
f1 (ppm)

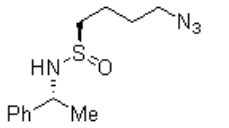

t-Bu
HN
S
O
Ph
Me
1d
13C NMR (101 MHz, CDCl3)
144.2
128.9
127.9
126.7
77.3 CDCl3
71.0
52.6
31.0
29.9
23.1
f1 (ppm)


Ph
HN
S
O
Ph
Me
1e
^{1}H NMR (400 MHz, CDCl$_3$)
7.35
7.35
7.34
7.29
7.28
7.26 CDCl3
7.26
7.21
7.19
7.13
7.13
7.11
4.69
4.68
4.67
4.66
4.65
4.65
4.64
4.63
3.92
3.91
2.72
2.70
2.68
2.66
2.64
2.62
2.61
2.03
2.02
2.00
1.98
1.97
1.95
1.93
1.91
1.89
1.87
1.53
1.51
7.22
0.99
1.93
1.00
0.98
4.05
2.04
3.02
f1 (ppm)


Ph
HN
S
O
Ph
Me
1e
^{13}C NMR (101 MHz, CDCl$_3$)
144.3
140.7
128.9
128.6
128.6
127.9
126.6
126.4
77.3 CDCl3
55.1
51.7
34.7
25.0
23.7
f1 (ppm)

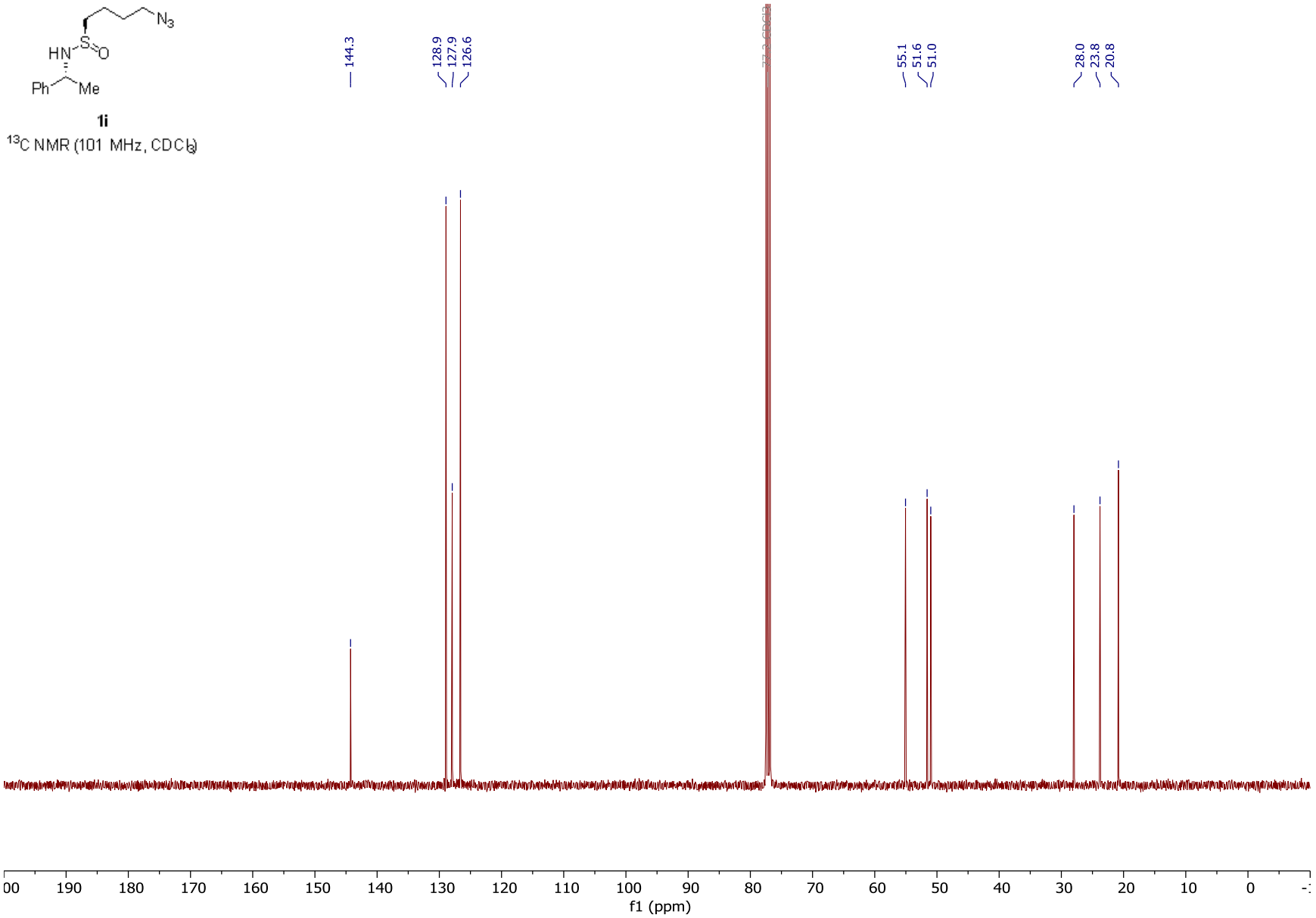

OPiv
HN
S
O
Ph
Me
1h
^{1}H NMR (400 MHz, CDCl$_3$)
7.35
7.34
7.29
7.28
7.27
7.26 CDCl3
7.25
4.69
4.68
4.68
4.67
4.66
4.65
4.64
4.63
4.04
4.03
4.01
3.96
3.95
2.75
2.73
2.72
2.70
2.68
2.67
2.64
2.62
1.75
1.74
1.70
1.68
1.67
1.65
1.53
1.51
1.18
5.28
1.00
2.04
0.97
2.05
4.47
3.07
9.17
f1 (ppm)

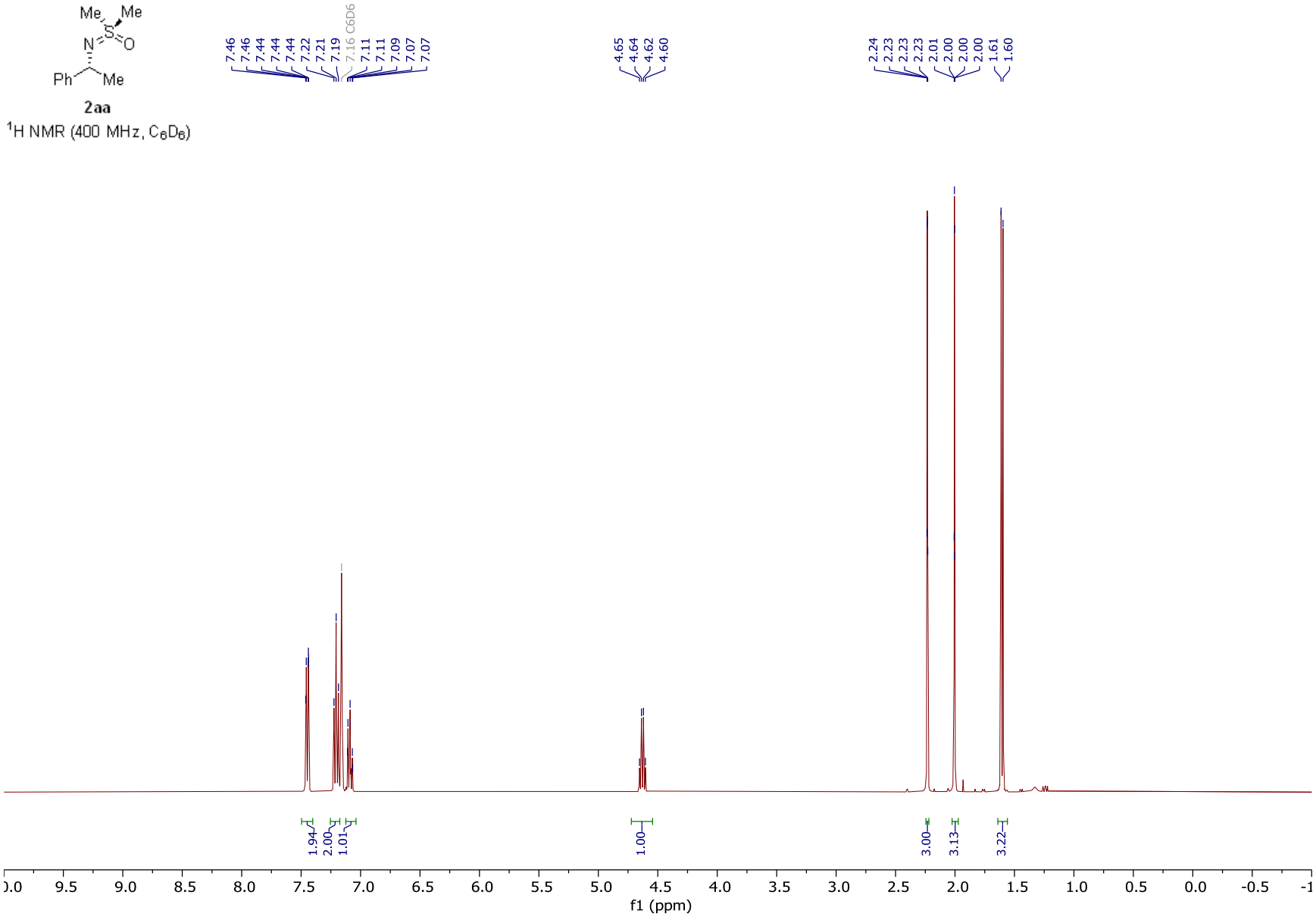

178.6
144.2
128.9
127.9
126.6
77.2 CDCl3
63.6
55.3
51.8
38.9
27.8
27.3
23.7
20.2
OPiv
HN
S
O
Ph
Me
1h
13C NMR (101 MHz, CDCl3)
f1 (ppm)

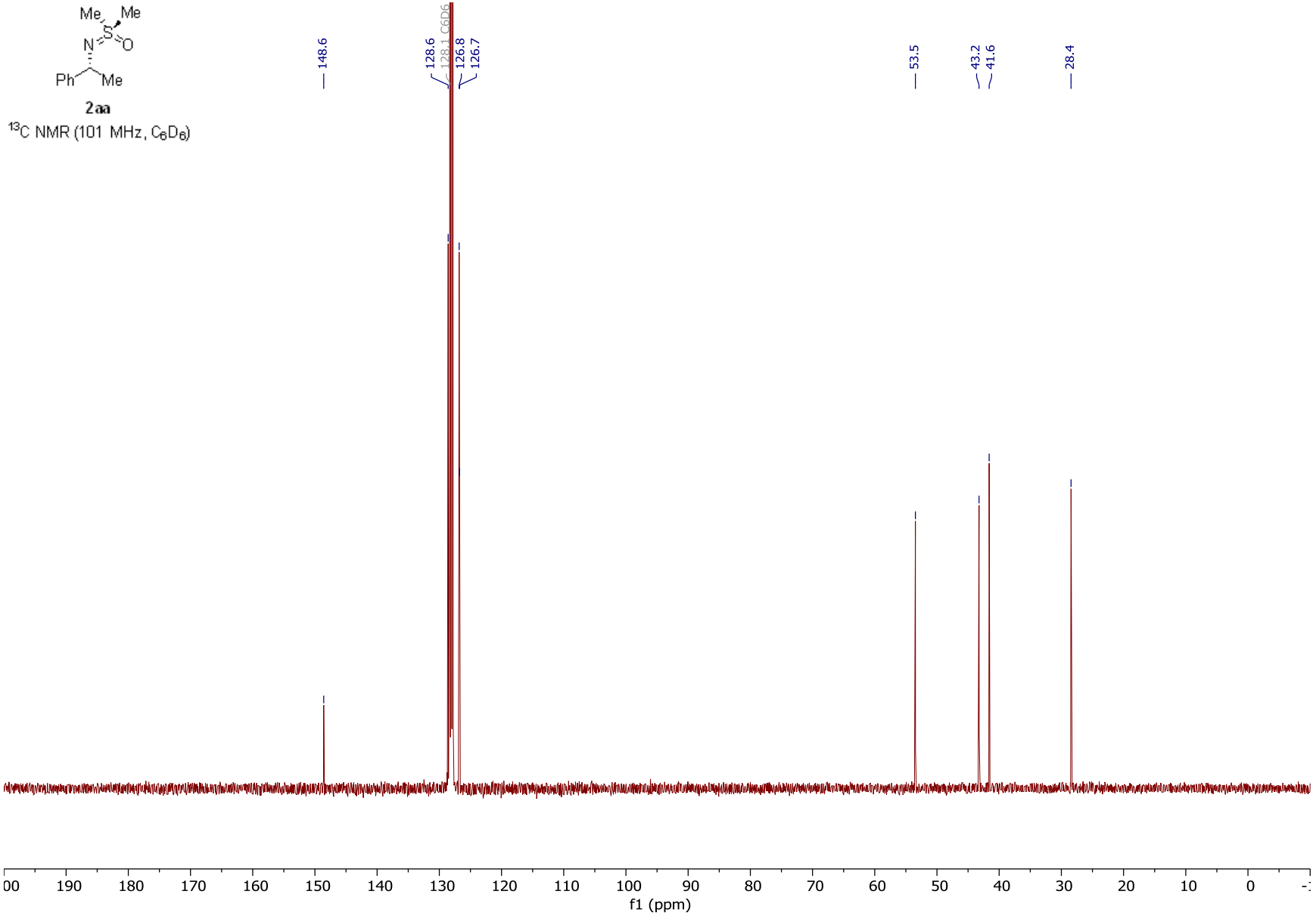


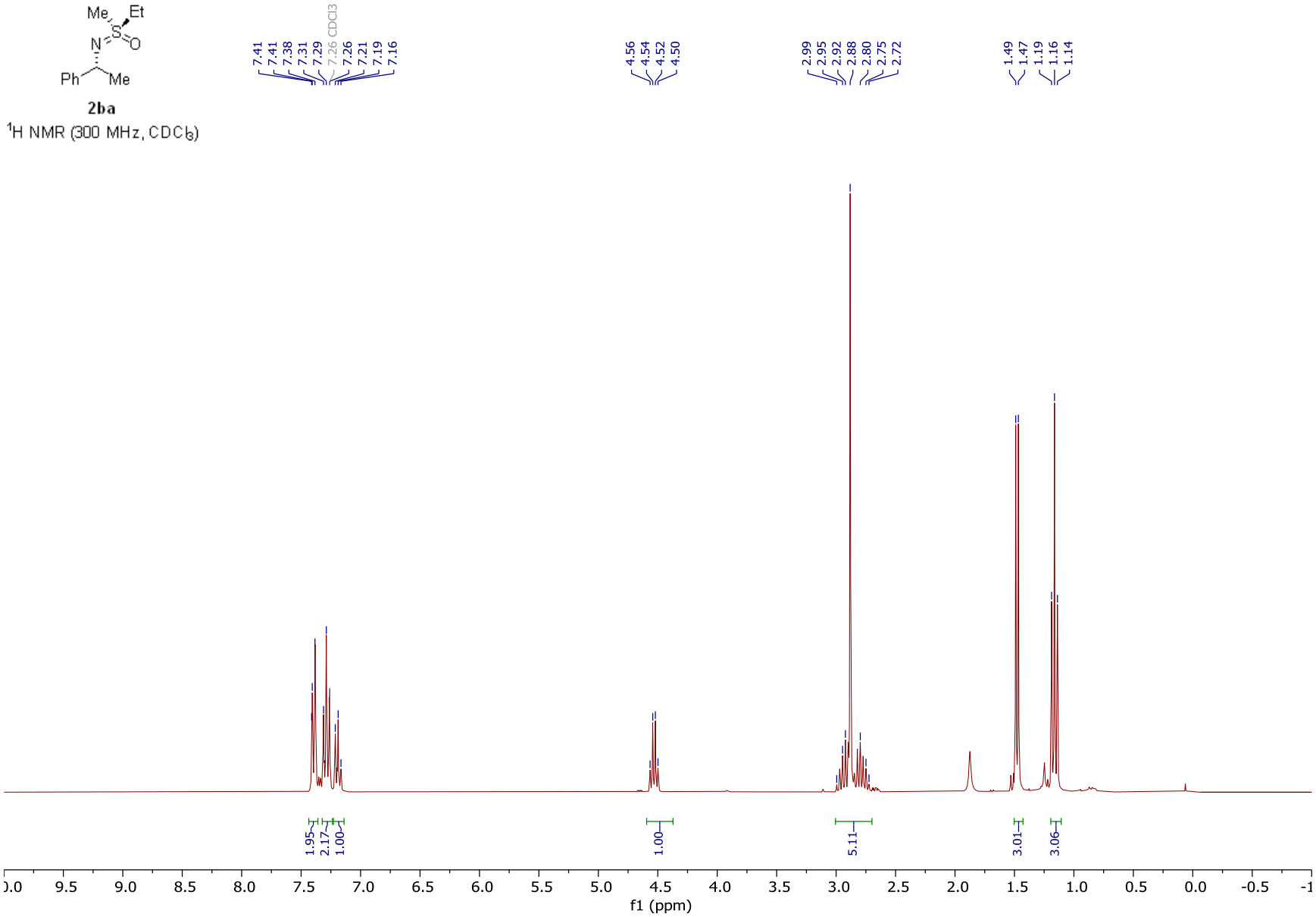
1i

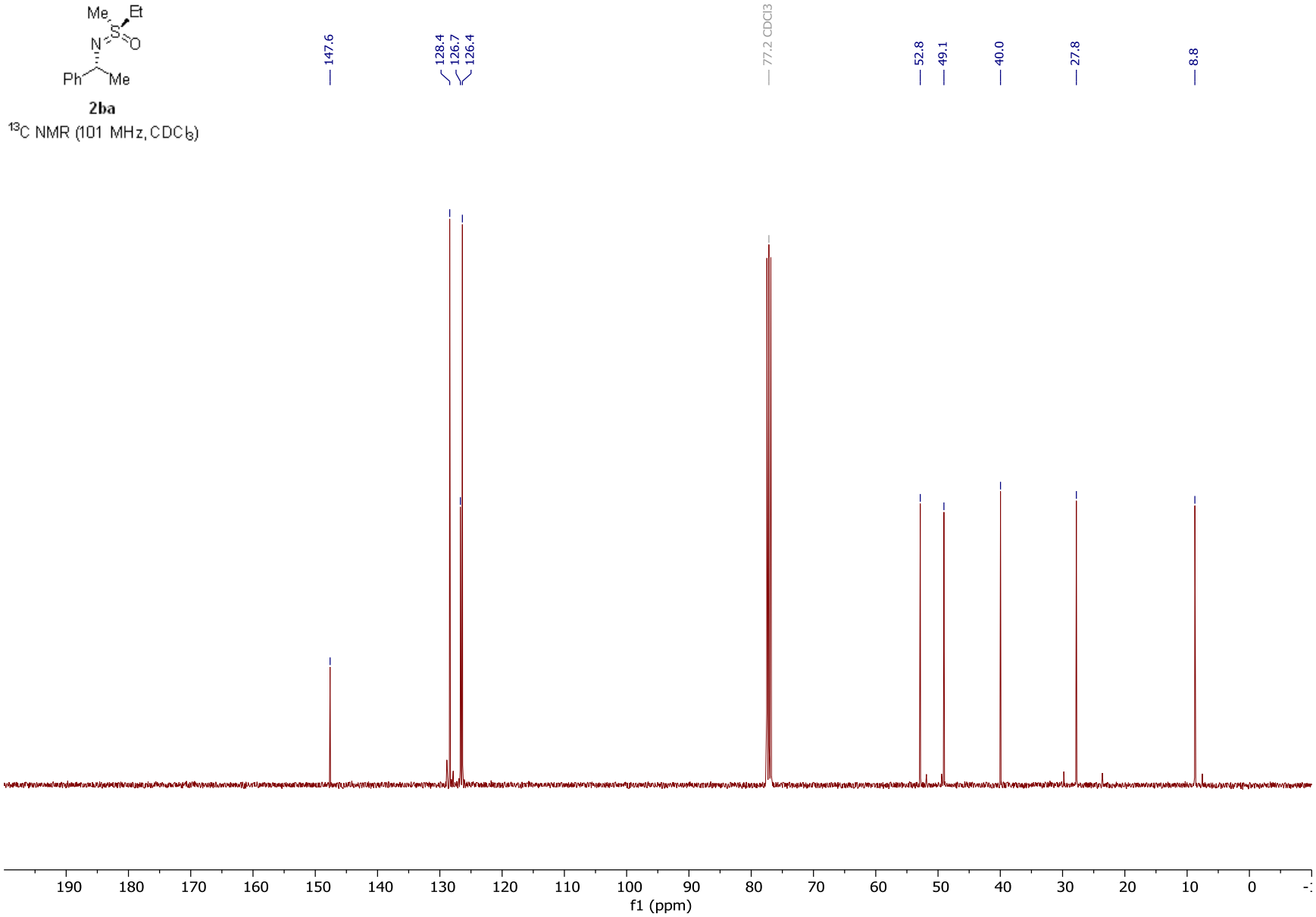
^{1}H NMR (400 MHz, $CDCl_3$)

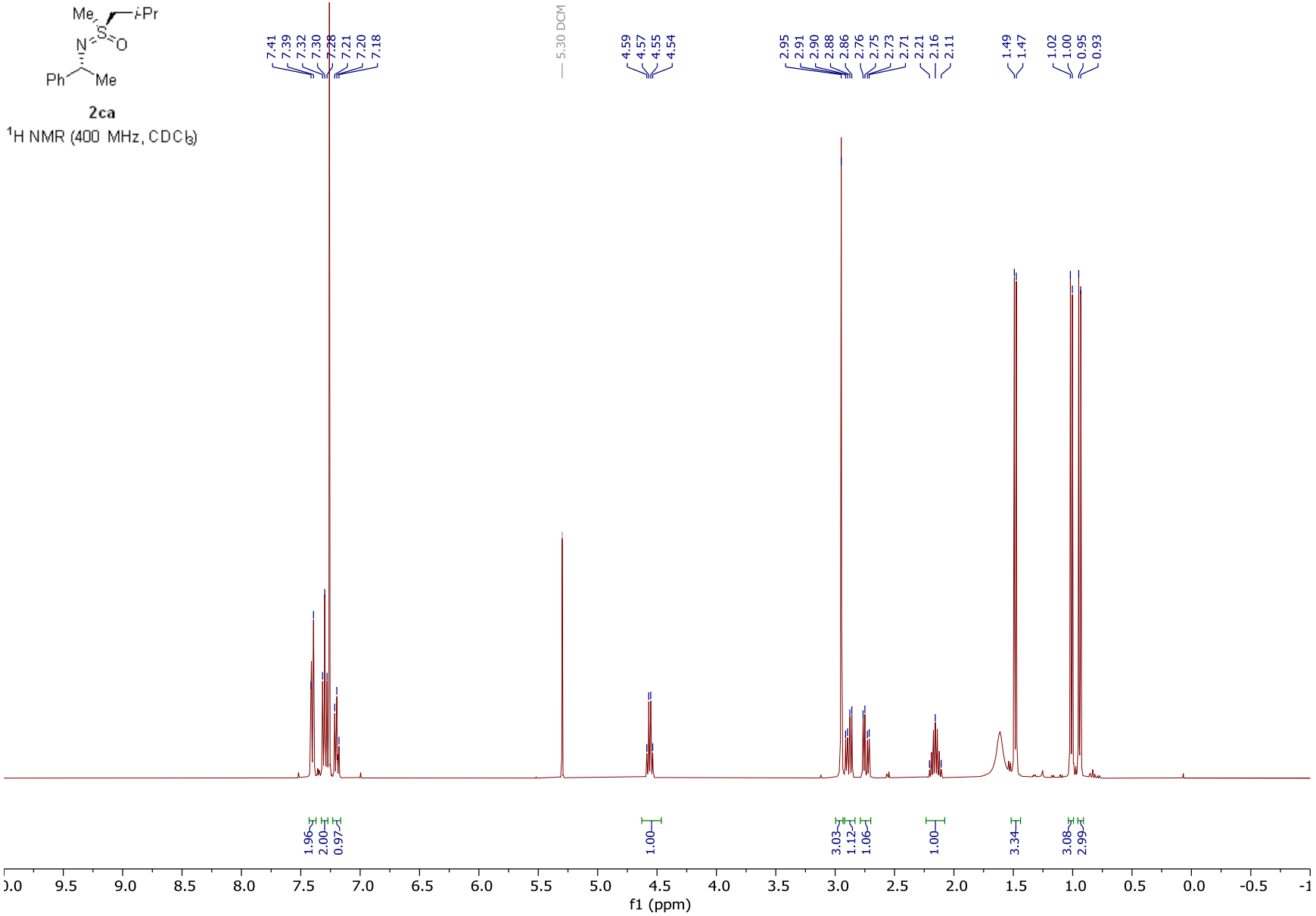

N3
HN
S
O
Ph
Me
1i
13C NMR (101 MHz, CDCl3)
144.3
128.9
127.9
126.6
77.3 CDCl3
55.1
51.6
51.0
28.0
23.8
20.8
f1 (ppm)

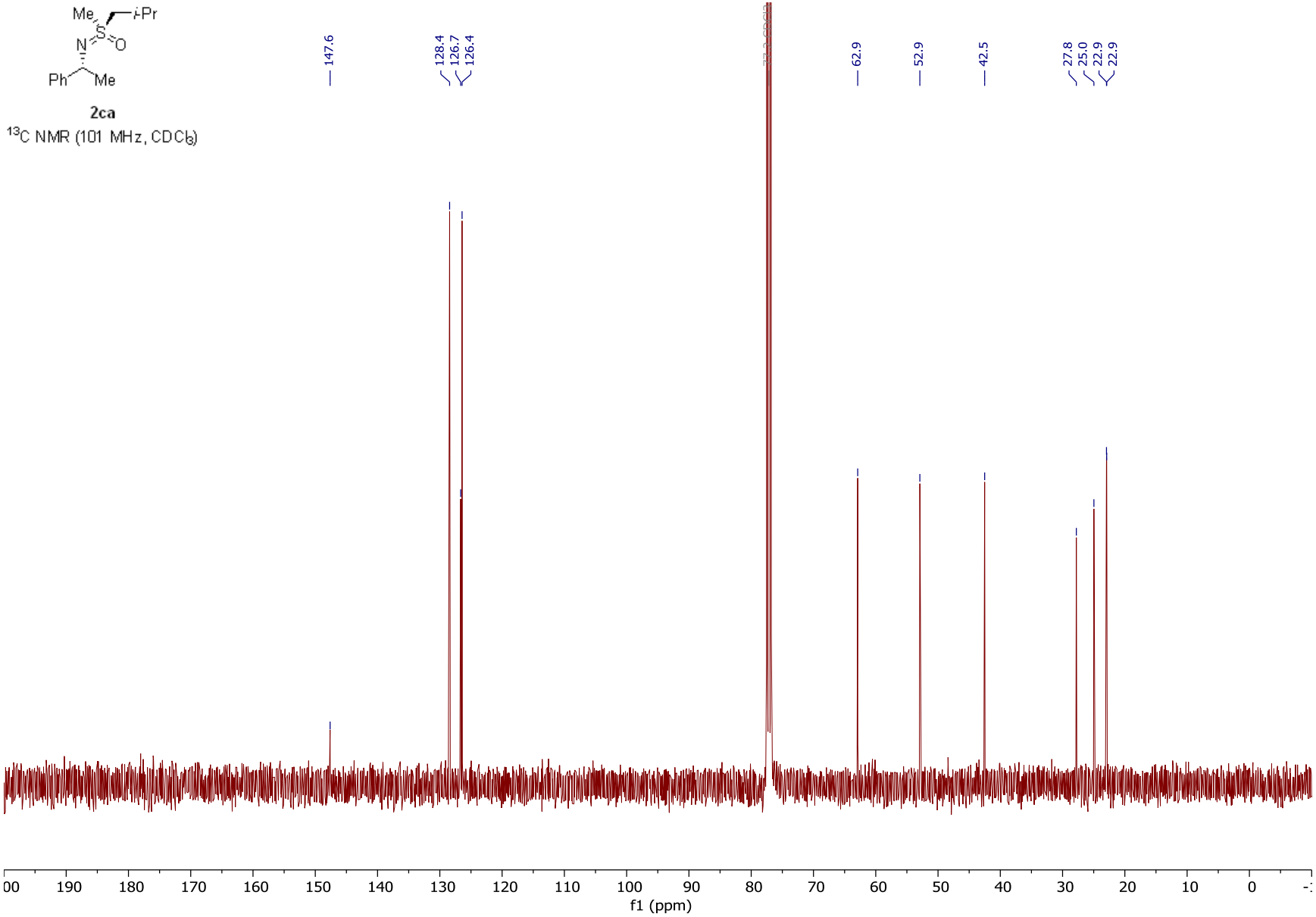

Me
Me
S
N
O
Ph
Me
2aa
^{1}H NMR (400 MHz, C_6D_6)
7.46
7.46
7.44
7.44
7.44
7.22
7.21
7.19
7.16 C6D6
7.11
7.11
7.09
7.07
7.07
4.65
4.64
4.62
4.60
2.24
2.23
2.23
2.23
2.01
2.00
2.00
2.00
1.61
1.60
1.94
2.00
1.01
1.00
3.00
3.13
3.22
f1 (ppm)

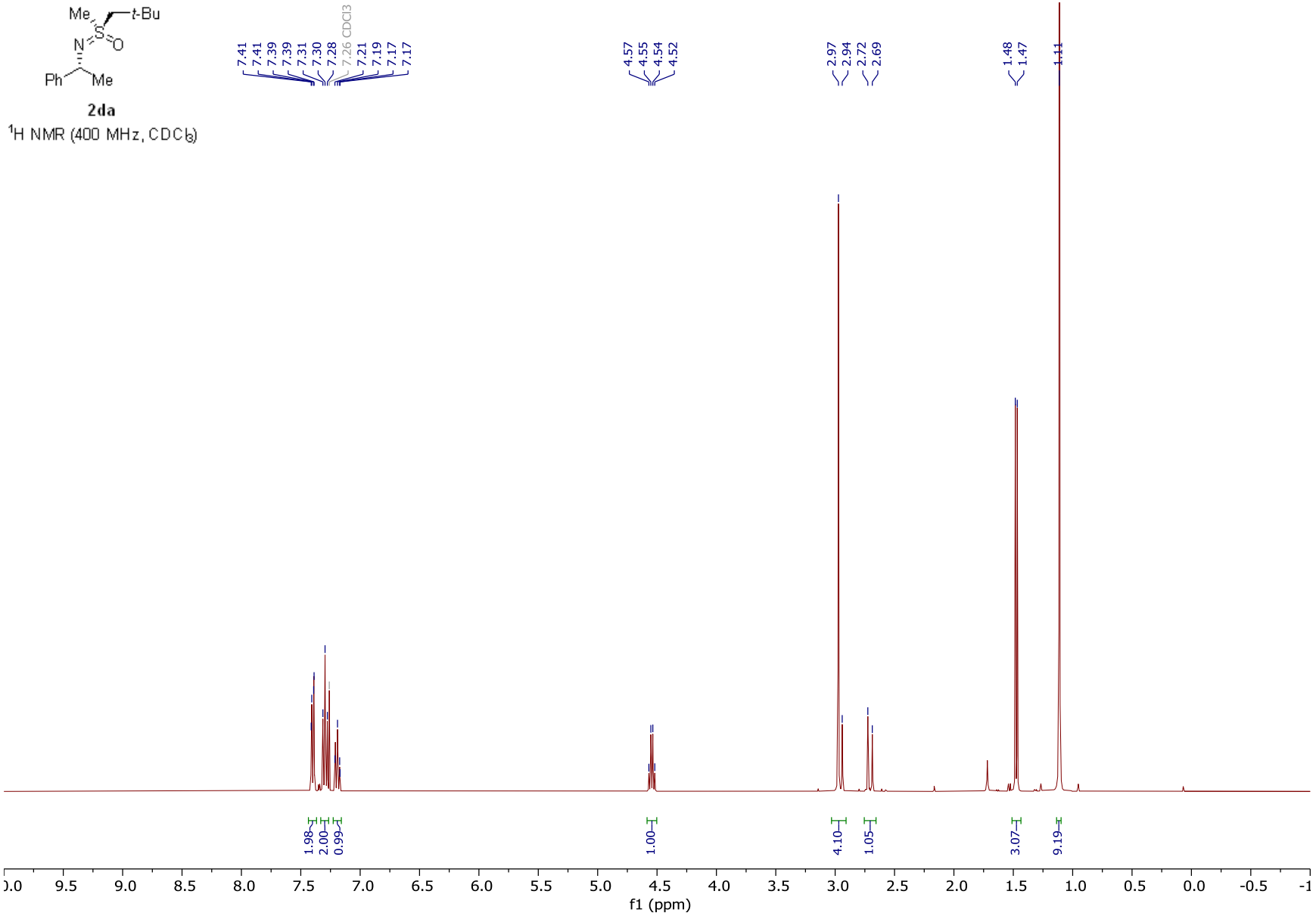

Me
Me
N
S
O
Ph
Me
2aa
13C NMR (101 MHz, C6D6)
148.6
128.6
128.1 C6D6
126.8
126.7
53.5
43.2
41.6
28.4
f1 (ppm)

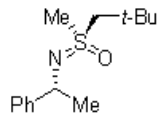

Me
Et
N
S
O
Ph
Me
2ba
^{1}H NMR (300 MHz, $CDCl_3$)
7.41
7.41
7.38
7.31
7.29
7.26 CDCl3
7.26
7.21
7.19
7.16
4.56
4.54
4.52
4.50
2.99
2.95
2.92
2.88
2.80
2.75
2.72
1.49
1.47
1.19
1.16
1.14
1.95
2.17
1.00
1.00
5.11
3.01
3.06
f1 (ppm)


Me
Et
N
S
O
Ph
Me
2ba
13C NMR (101 MHz, CDCl3)
147.6
128.4
126.7
126.4
77.2 CDCl3
52.8
49.1
40.0
27.8
8.8
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
i-Pr
N
S
O
Ph
Me
2ca
^{1}H NMR (400 MHz, $CDCl_3$)
7.41
7.39
7.32
7.30
7.28
7.21
7.20
7.18
5.30 DCM
4.59
4.57
4.55
4.54
2.95
2.91
2.90
2.88
2.86
2.76
2.75
2.73
2.71
2.21
2.16
2.11
1.49
1.47
1.02
1.00
0.95
0.93
1.96
2.00
0.97
1.00
3.03
1.12
1.06
1.00
3.34
3.08
2.99
f1 (ppm)

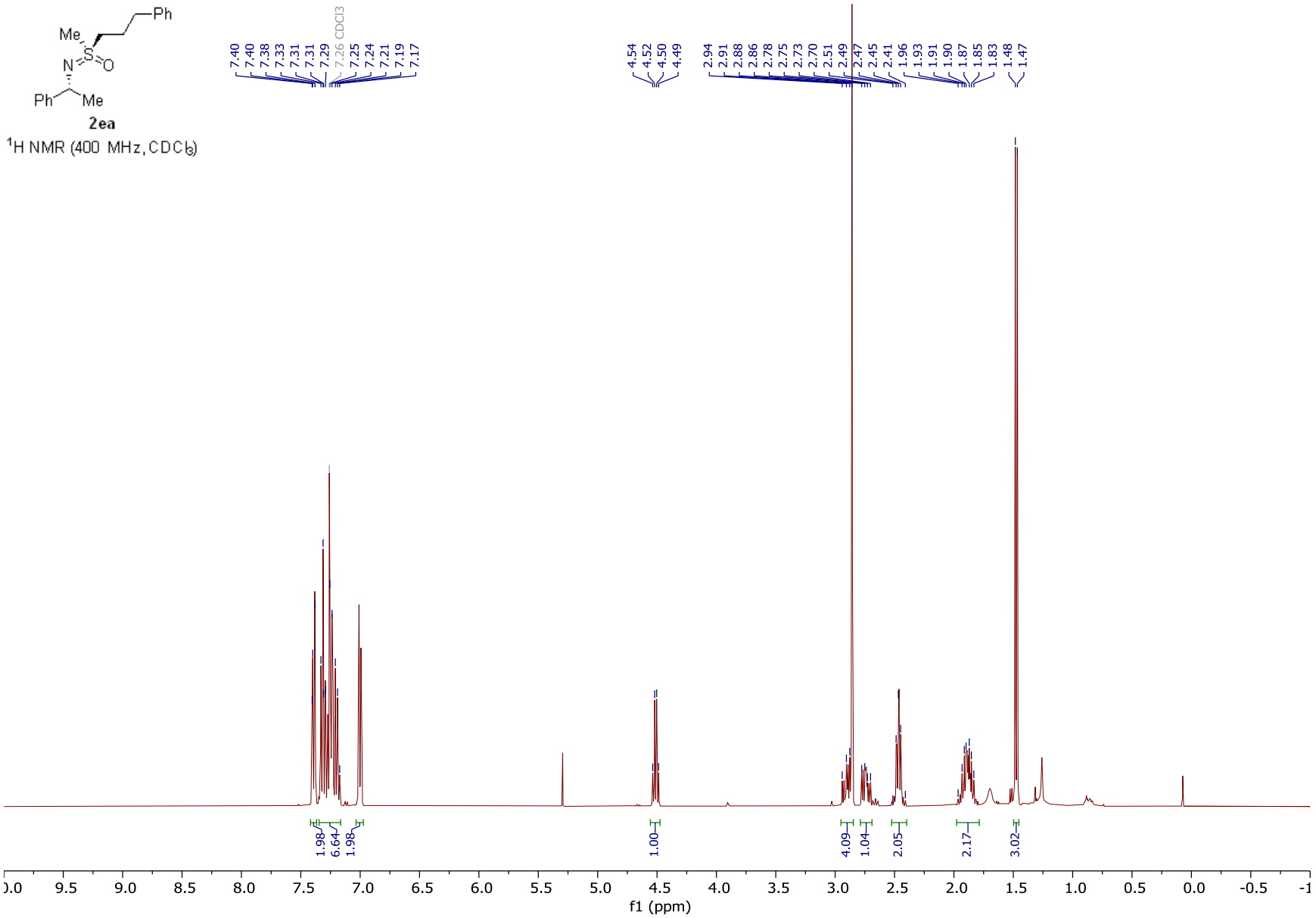

Me
iPr
N
S
O
Ph
Me
2ca
^{13}C NMR (101 MHz, CDCl$_3$)
147.6
128.4
126.7
126.4
77.2
62.9
52.9
42.5
27.8
25.0
22.9
22.9
f1 (ppm)

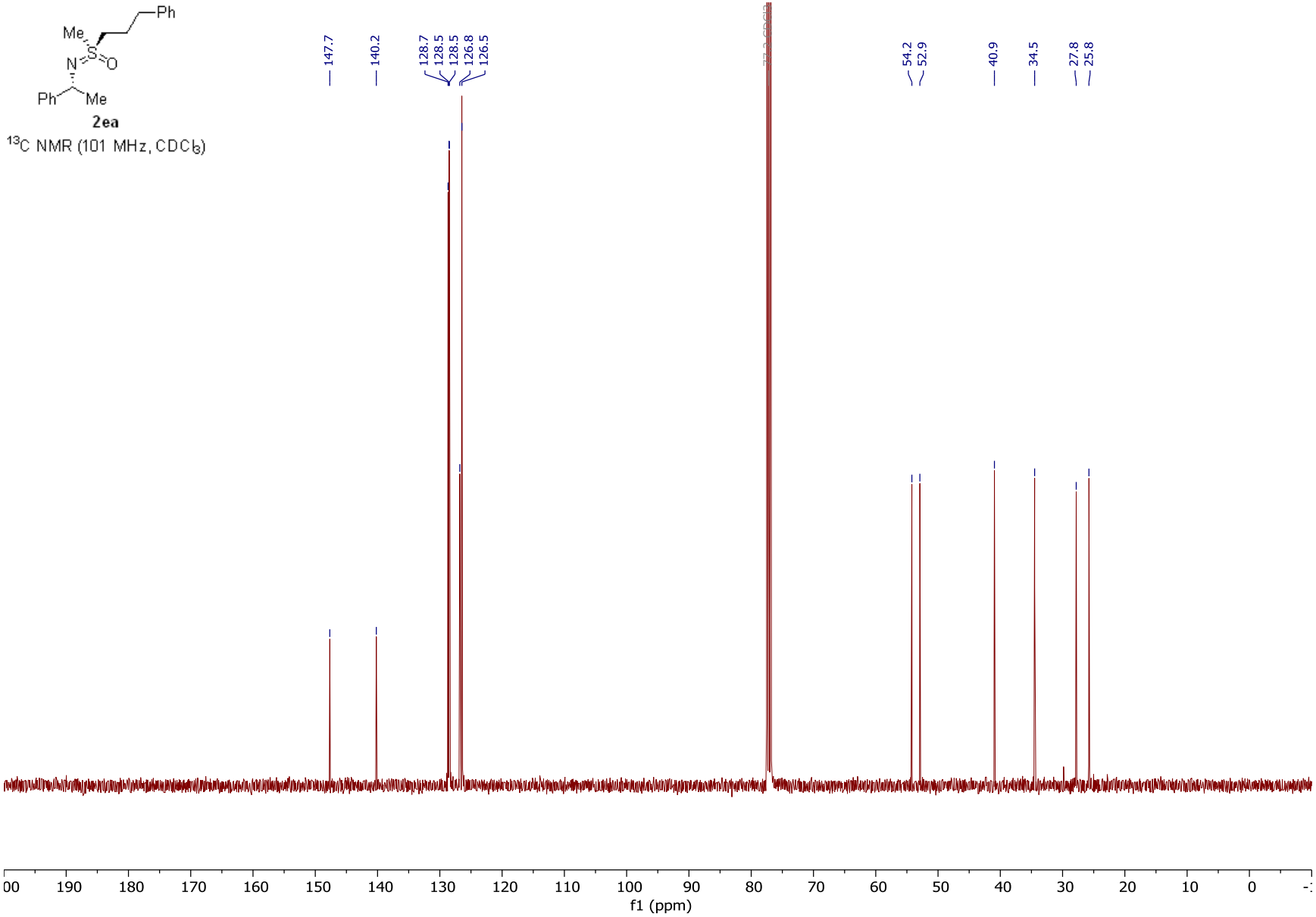

Me
t-Bu
S
N
O
Ph
Me
2da
^{1}H NMR (400 MHz, $CDCl_3$)
7.41
7.41
7.39
7.39
7.31
7.30
7.28
7.26 CDCl3
7.21
7.19
7.17
7.17
4.57
4.55
4.54
4.52
2.97
2.94
2.72
2.69
1.48
1.47
1.11
1.98
2.00
0.99
1.00
4.10
1.05
3.07
9.19
f1 (ppm)

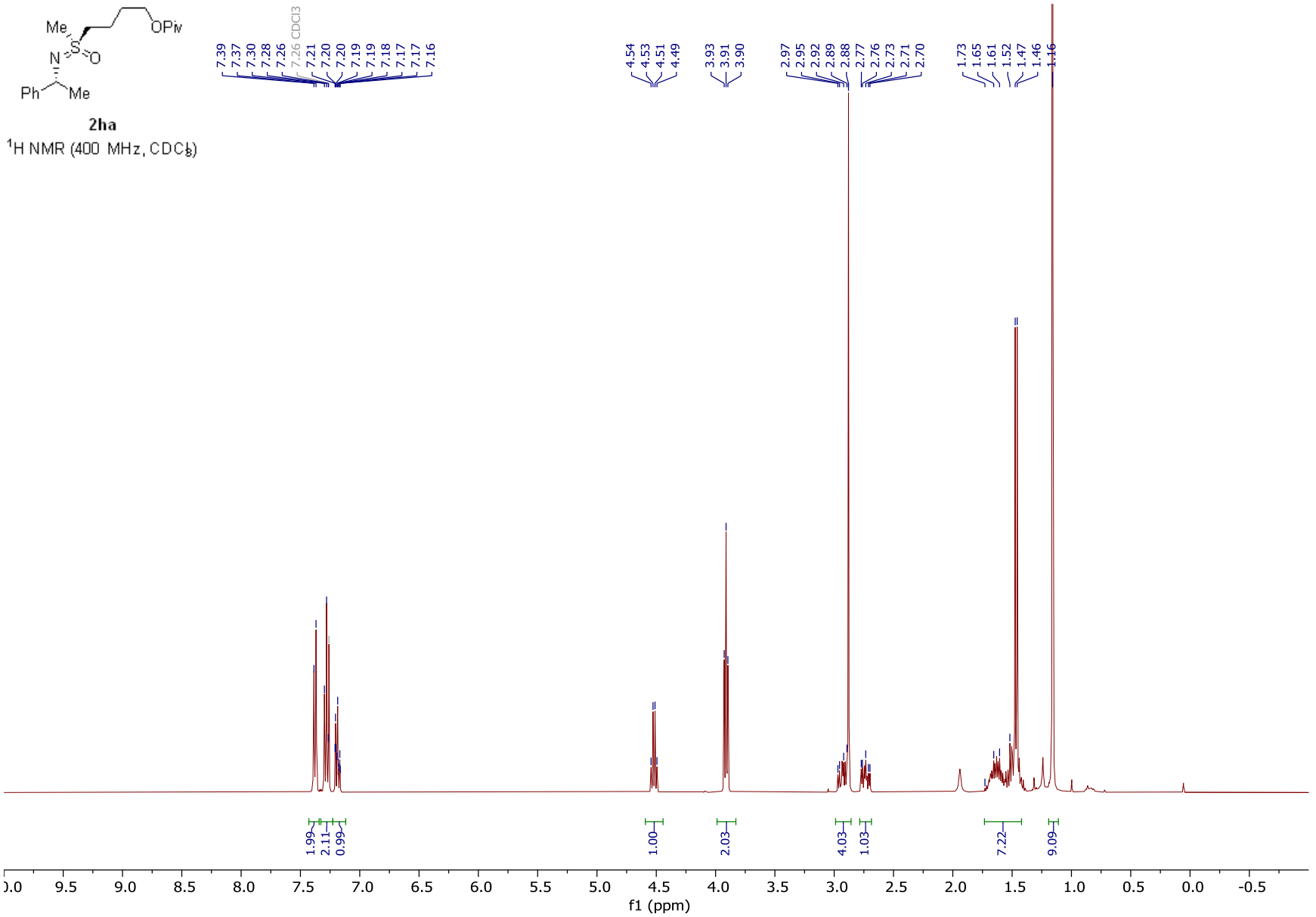


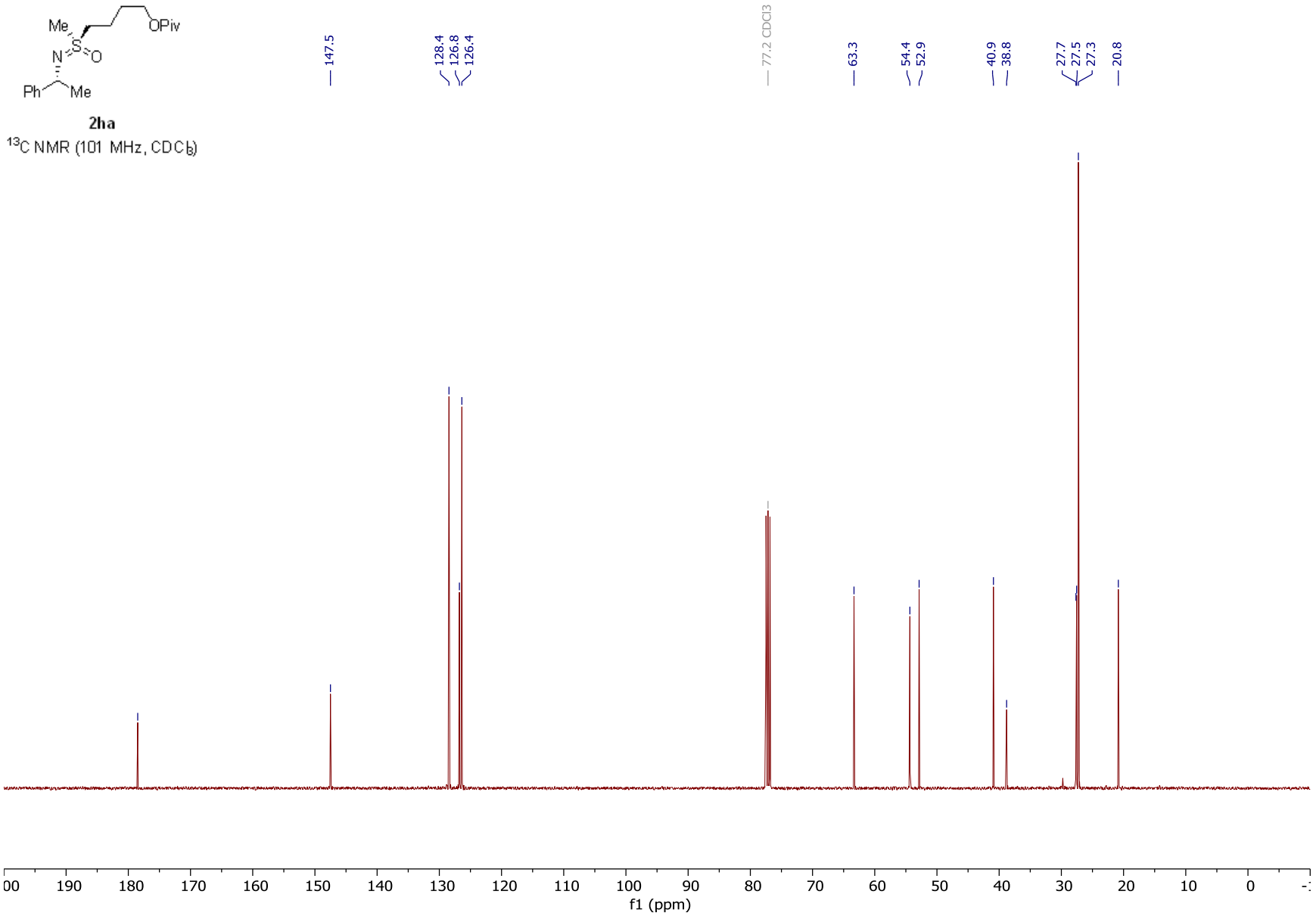
2da

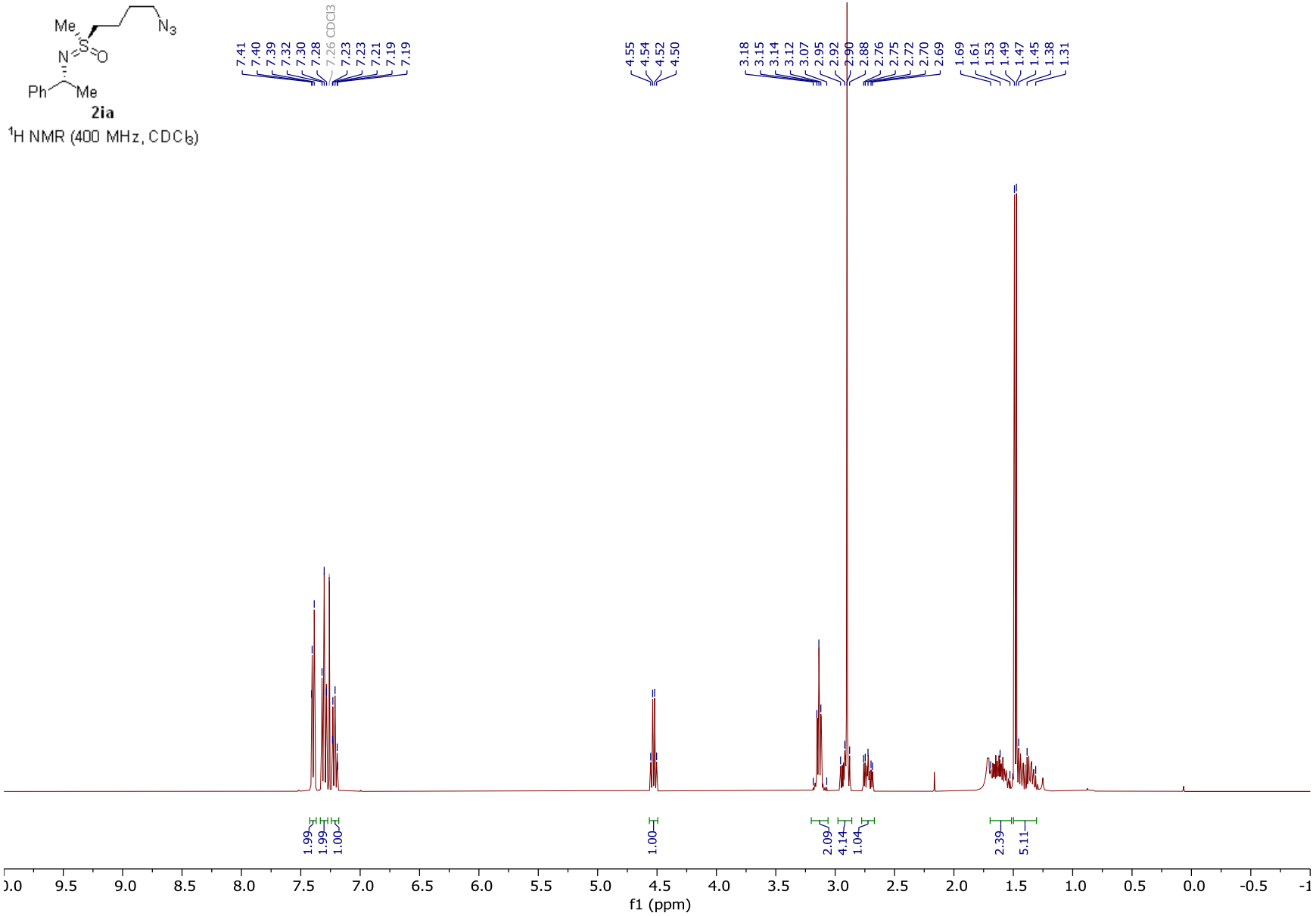
^{13}C NMR (101 MHz, $CDCl_3$)

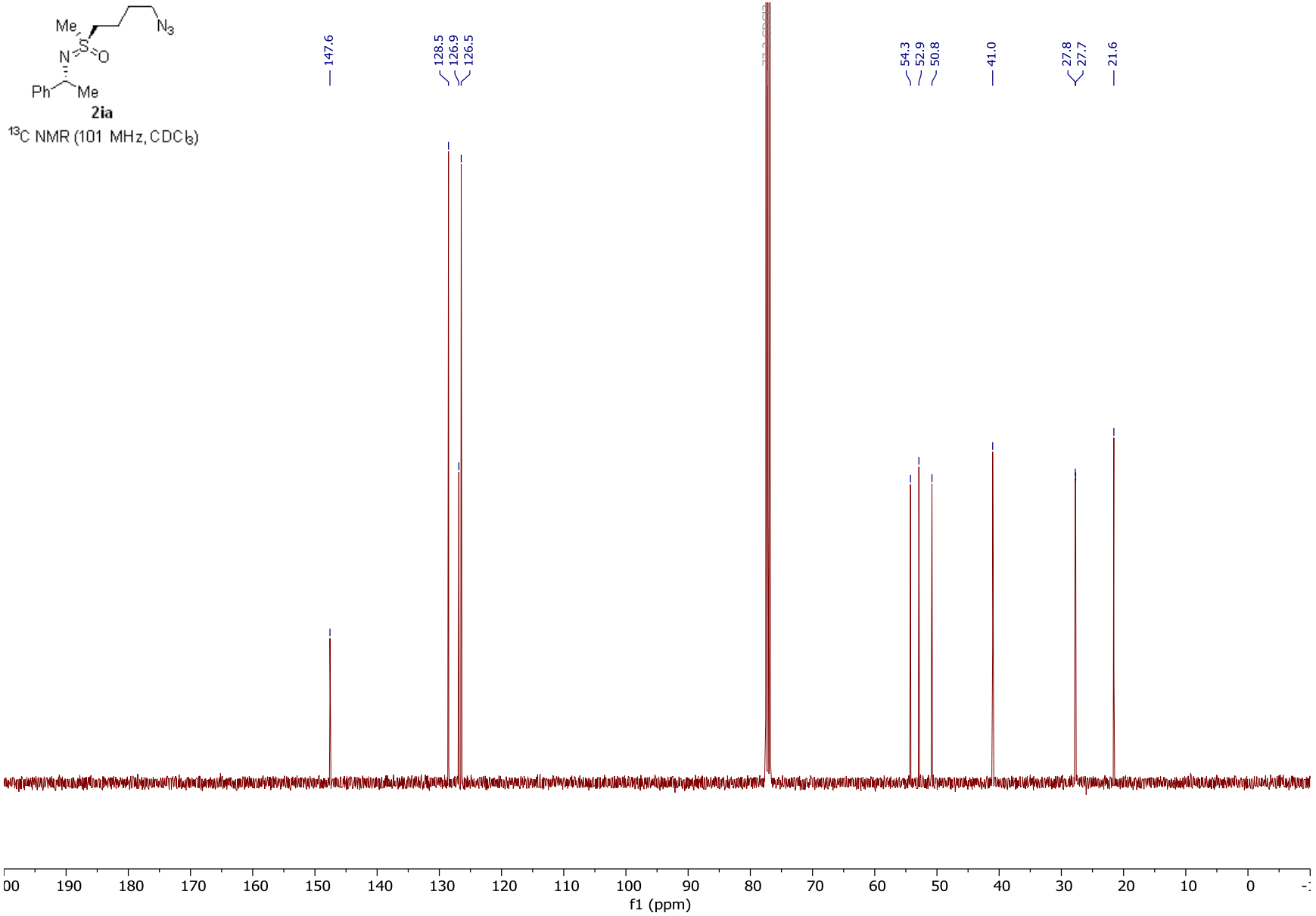

Ph
Me
N
S
O
Ph
Me
2ea
^{1}H NMR (400 MHz, $CDCl_3$)
7.40
7.40
7.38
7.33
7.31
7.31
7.29
7.26 CDCl3
7.25
7.24
7.21
7.19
7.17
4.54
4.52
4.50
4.49
2.94
2.91
2.88
2.86
2.78
2.75
2.73
2.70
2.51
2.49
2.47
2.45
2.41
1.96
1.93
1.91
1.90
1.87
1.85
1.83
1.48
1.47
1.98
6.64
1.98
1.00
4.09
1.04
2.05
2.17
3.02
f1 (ppm)

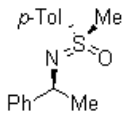

Ph
Me
S
N
O
Ph
Me
2ea
^{13}C NMR (101 MHz, $CDCl_3$)
147.7
140.2
128.7
128.5
128.5
126.8
126.5
77.3
54.2
52.9
40.9
34.5
27.8
25.8
f1 (ppm)


Me
OPiv
N
S
O
Ph
Me
2ha
^{1}H NMR (400 MHz, CDCl$_3$)
7.39
7.37
7.30
7.28
7.26
7.26 CDCl3
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.16
4.54
4.53
4.51
4.49
3.93
3.91
3.90
2.97
2.95
2.92
2.89
2.88
2.77
2.76
2.73
2.71
2.70
1.73
1.65
1.61
1.52
1.47
1.46
1.16
1.99
2.11
0.99
1.00
2.03
4.03
1.03
7.22
9.09
f1 (ppm)


Me
OPiv
N
S
O
Ph
Me
2ha
13C NMR (101 MHz, CDCl3)
147.5
128.4
126.8
126.4
77.2 CDCl3
63.3
54.4
52.9
40.9
38.8
27.7
27.5
27.3
20.8
f1 (ppm)

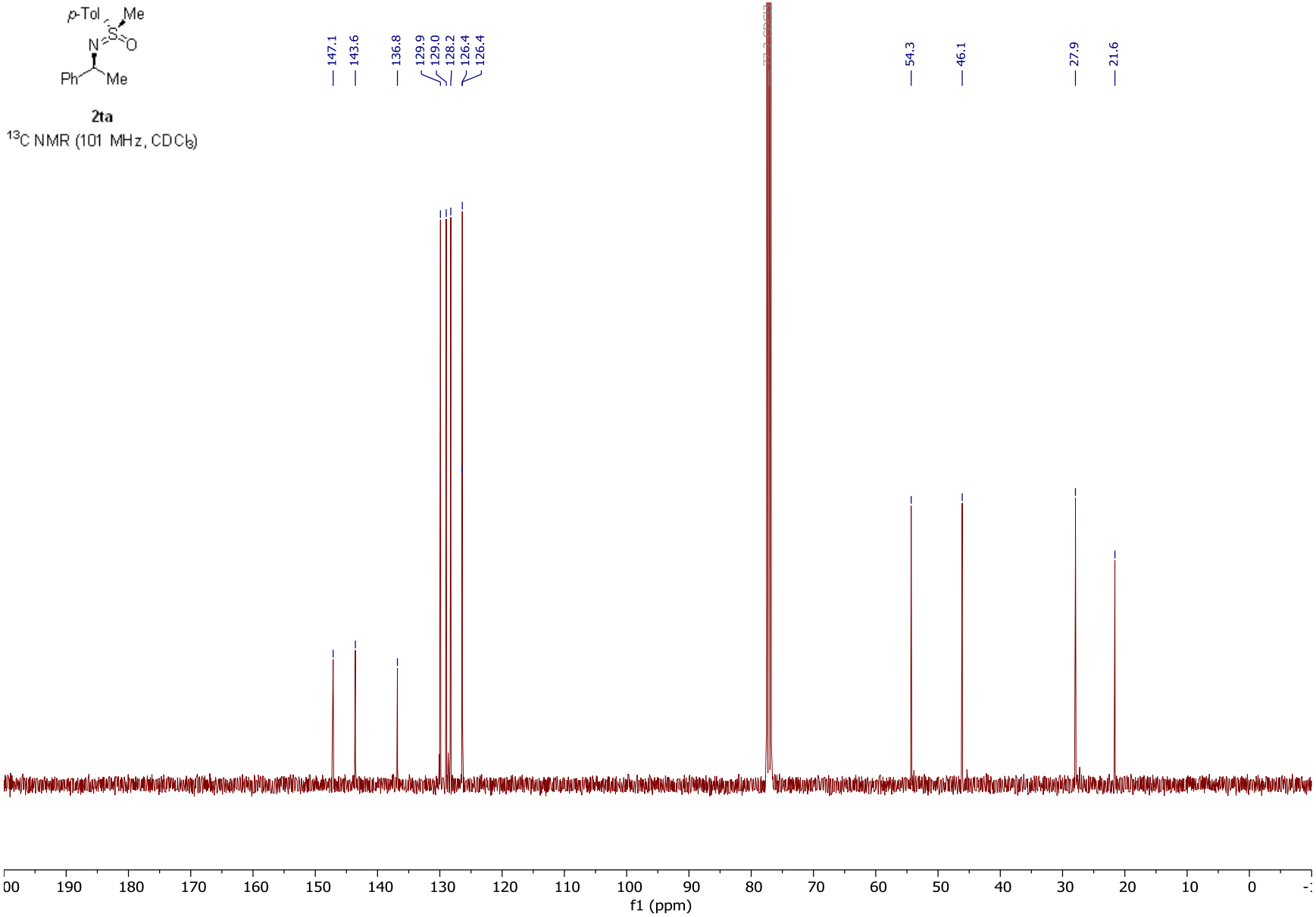

Me
N3
N
S
O
Ph
Me
2ia
1H NMR (400 MHz, CDCl3)
7.41
7.40
7.39
7.32
7.30
7.28
7.26 CDCl3
7.23
7.23
7.21
7.19
7.19
4.55
4.54
4.52
4.50
3.18
3.15
3.14
3.12
3.07
2.95
2.92
2.90
2.88
2.76
2.75
2.72
2.70
2.69
1.69
1.61
1.53
1.49
1.47
1.45
1.38
1.31
1.99
1.99
1.00
1.00
2.09
4.14
1.04
2.39
5.11
f1 (ppm)

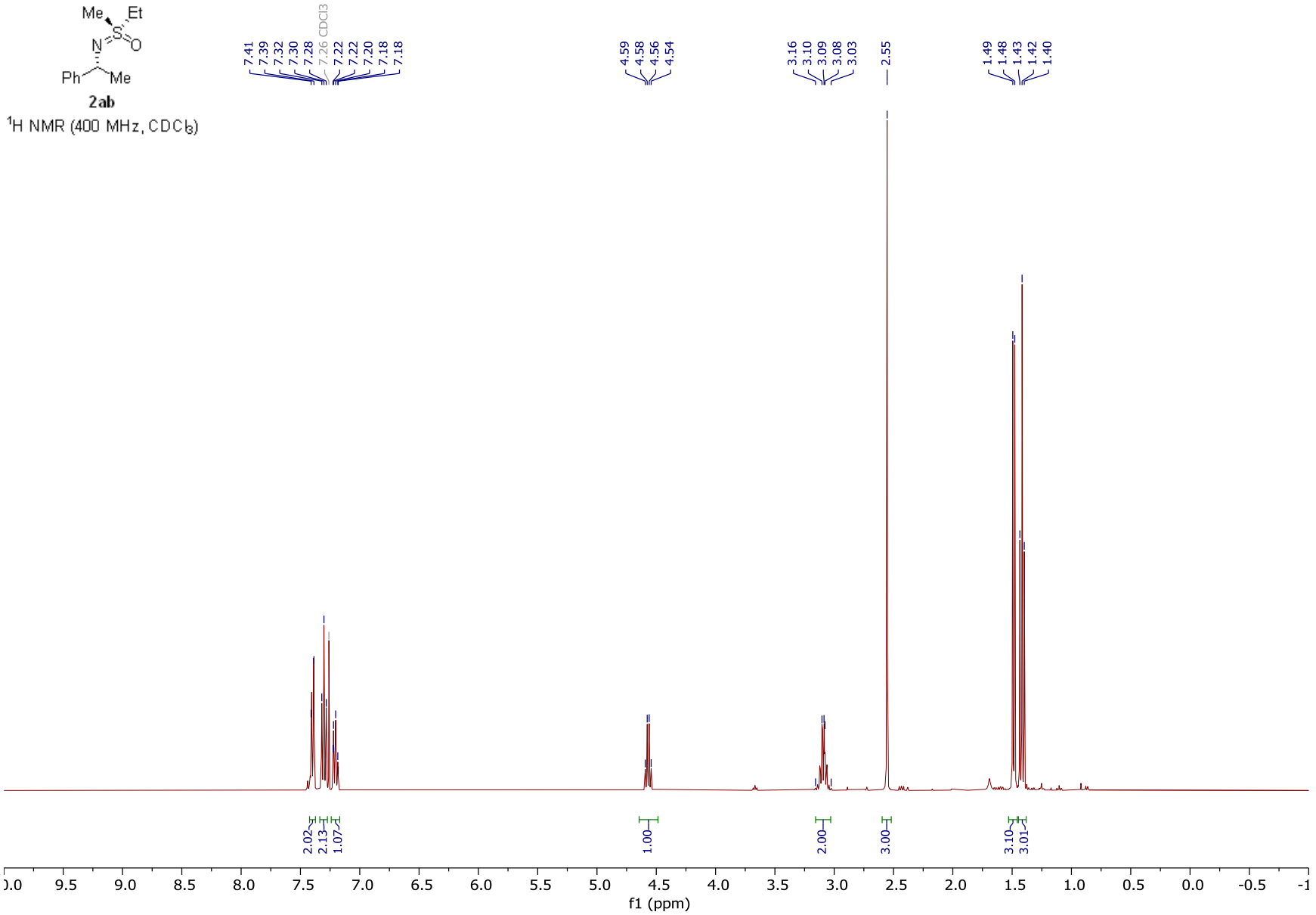

Me
N3
S
N
O
Ph
Me
2ia
13C NMR (101 MHz, CDCl3)
147.6
128.5
126.9
126.5
77.3
54.3
52.9
50.8
41.0
27.8
27.7
21.6
f1 (ppm)

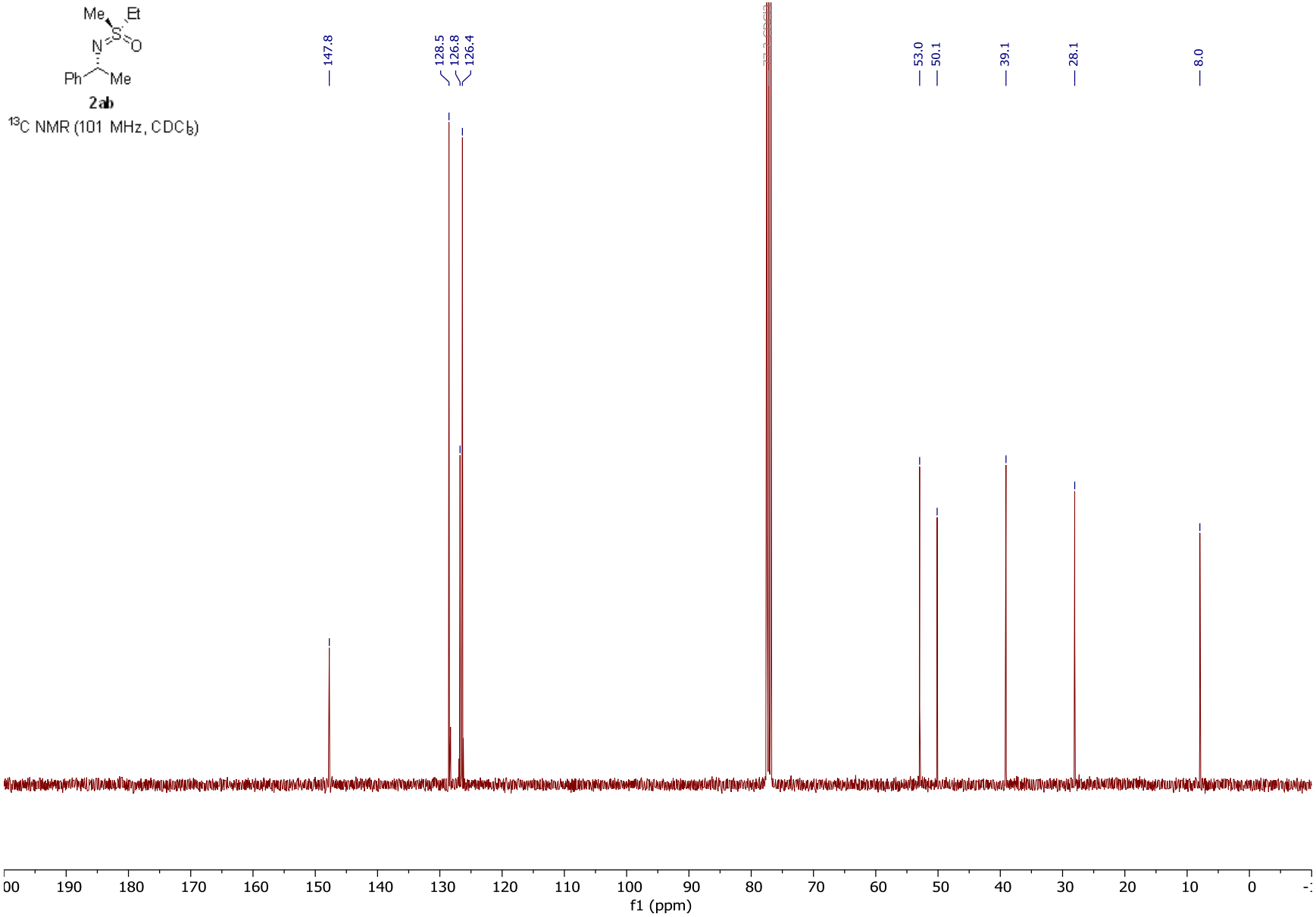


2ta

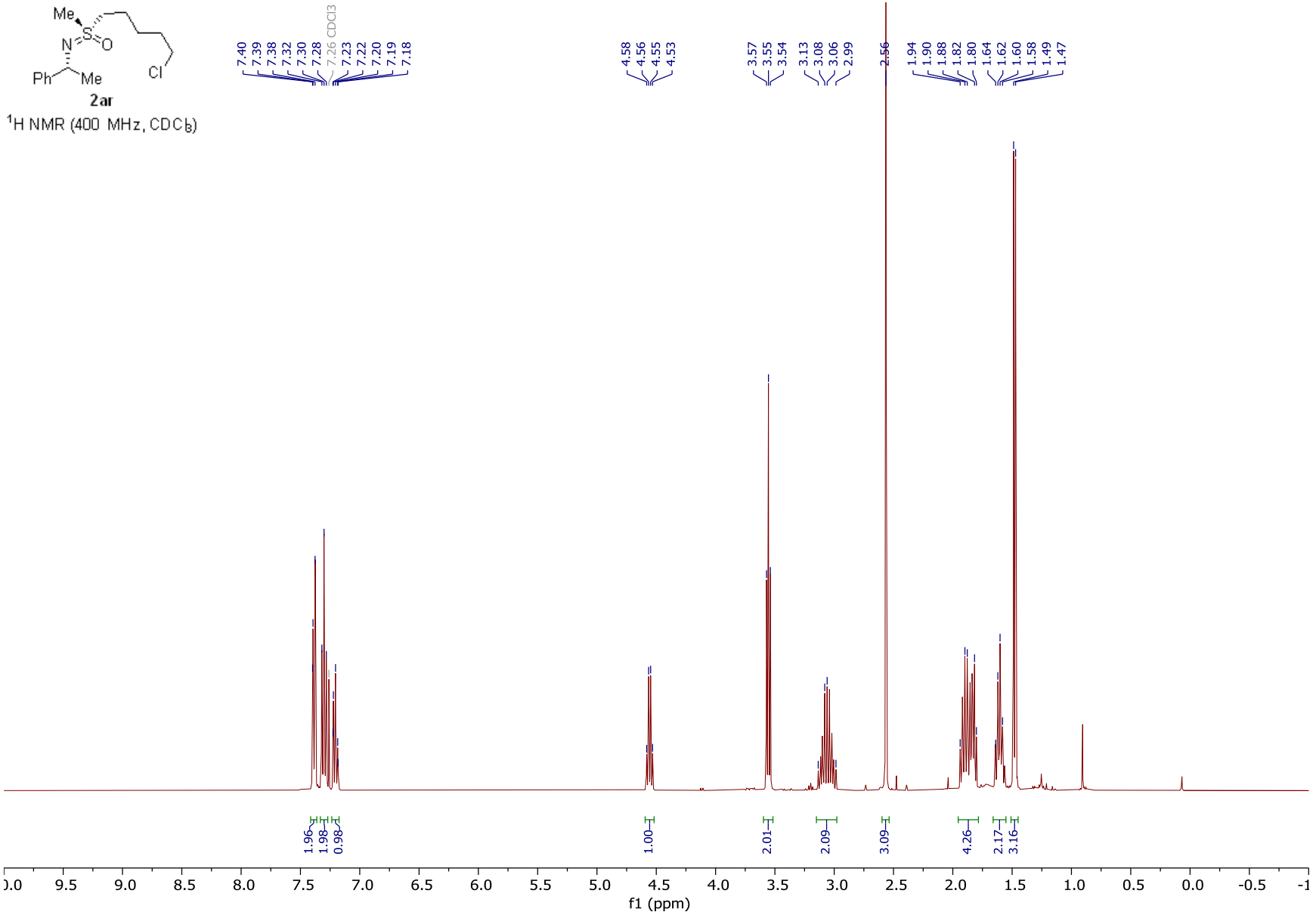
^{1}H NMR (400 MHz, $CDCl_3$)

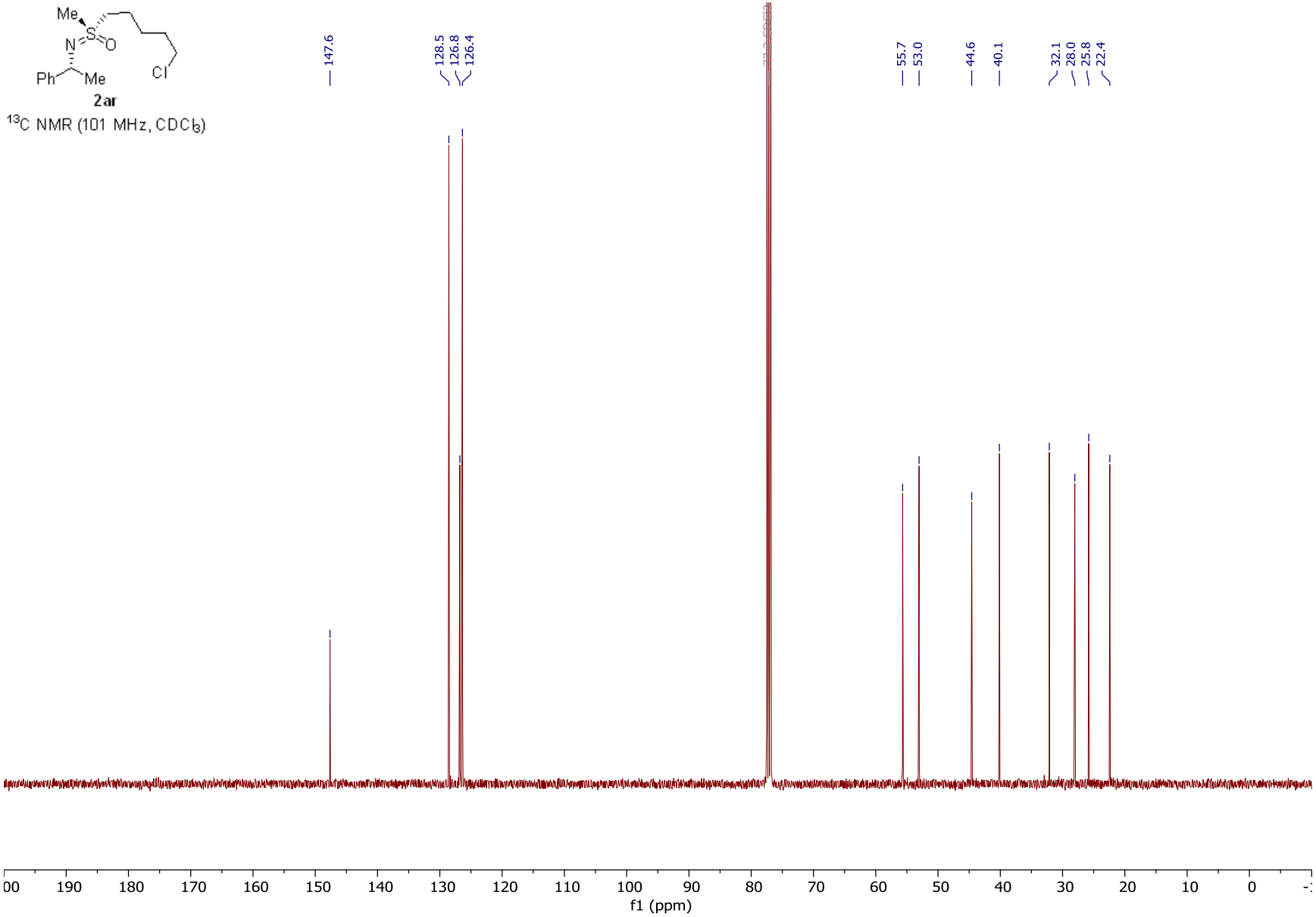

p-Tol
Me
N
S
O
Ph
Me
2ta
13C NMR (101 MHz, CDCl3)
147.1
143.6
136.8
129.9
129.0
128.2
126.4
126.4
54.3
46.1
27.9
21.6
f1 (ppm)

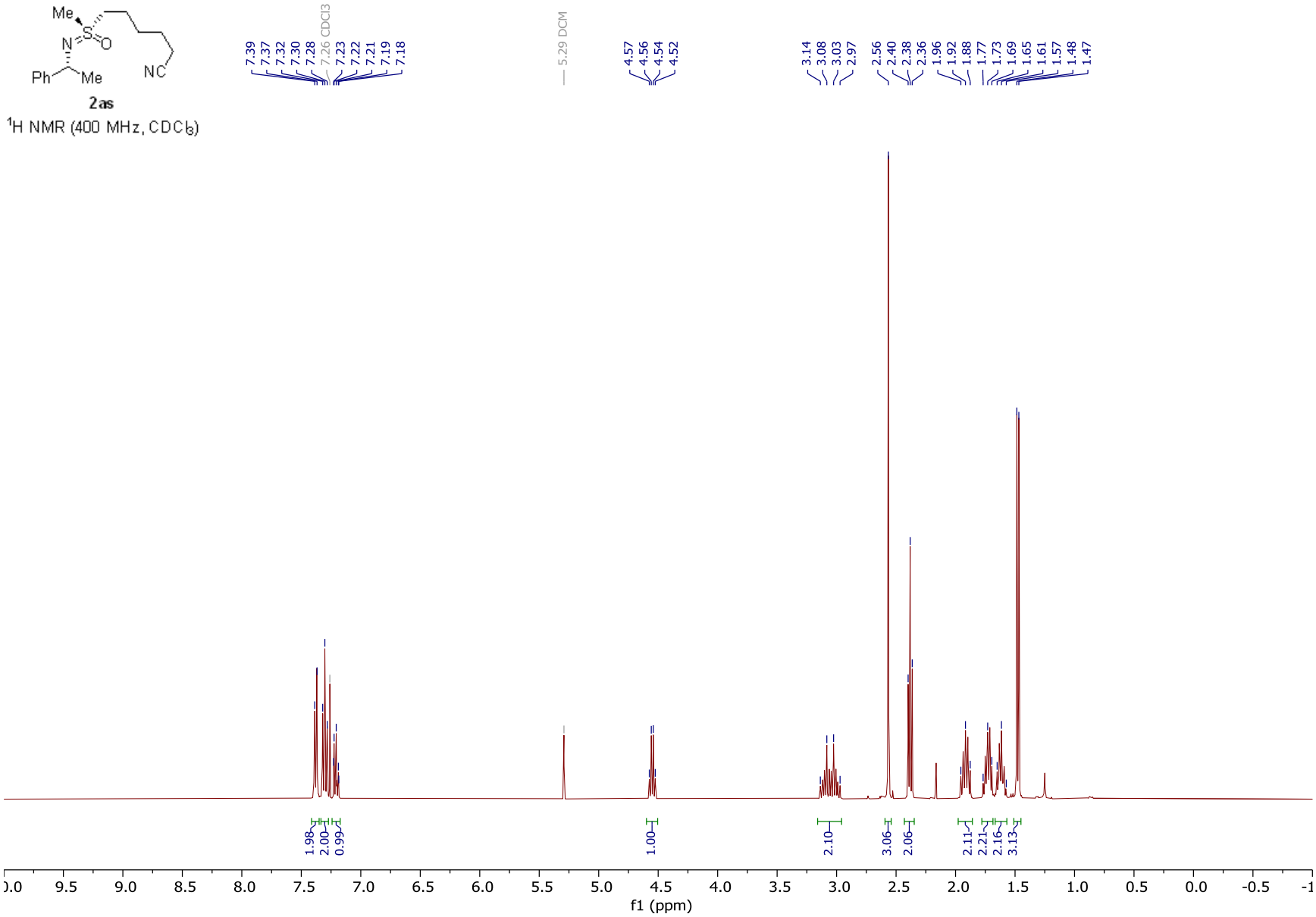

Me
Et
N
S
O
Ph
Me
2ab
^{1}H NMR (400 MHz, CDCl$_3$)
7.41
7.39
7.32
7.30
7.28
7.26 CDCl3
7.22
7.22
7.20
7.18
7.18
4.59
4.58
4.56
4.54
3.16
3.10
3.09
3.08
3.03
2.55
1.49
1.48
1.43
1.42
1.40
2.02
2.13
1.07
1.00
2.00
3.00
3.10
3.01
f1 (ppm)

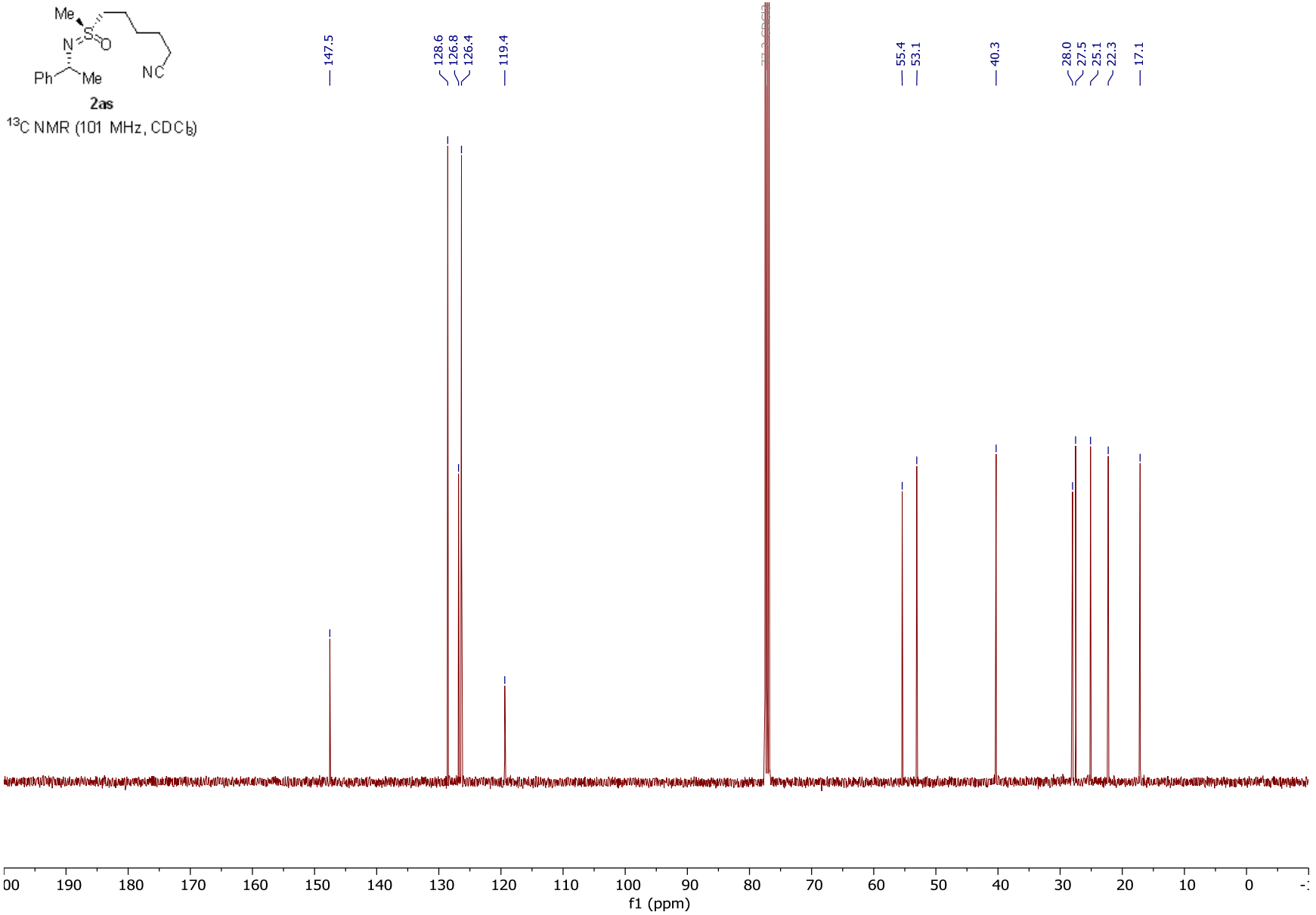


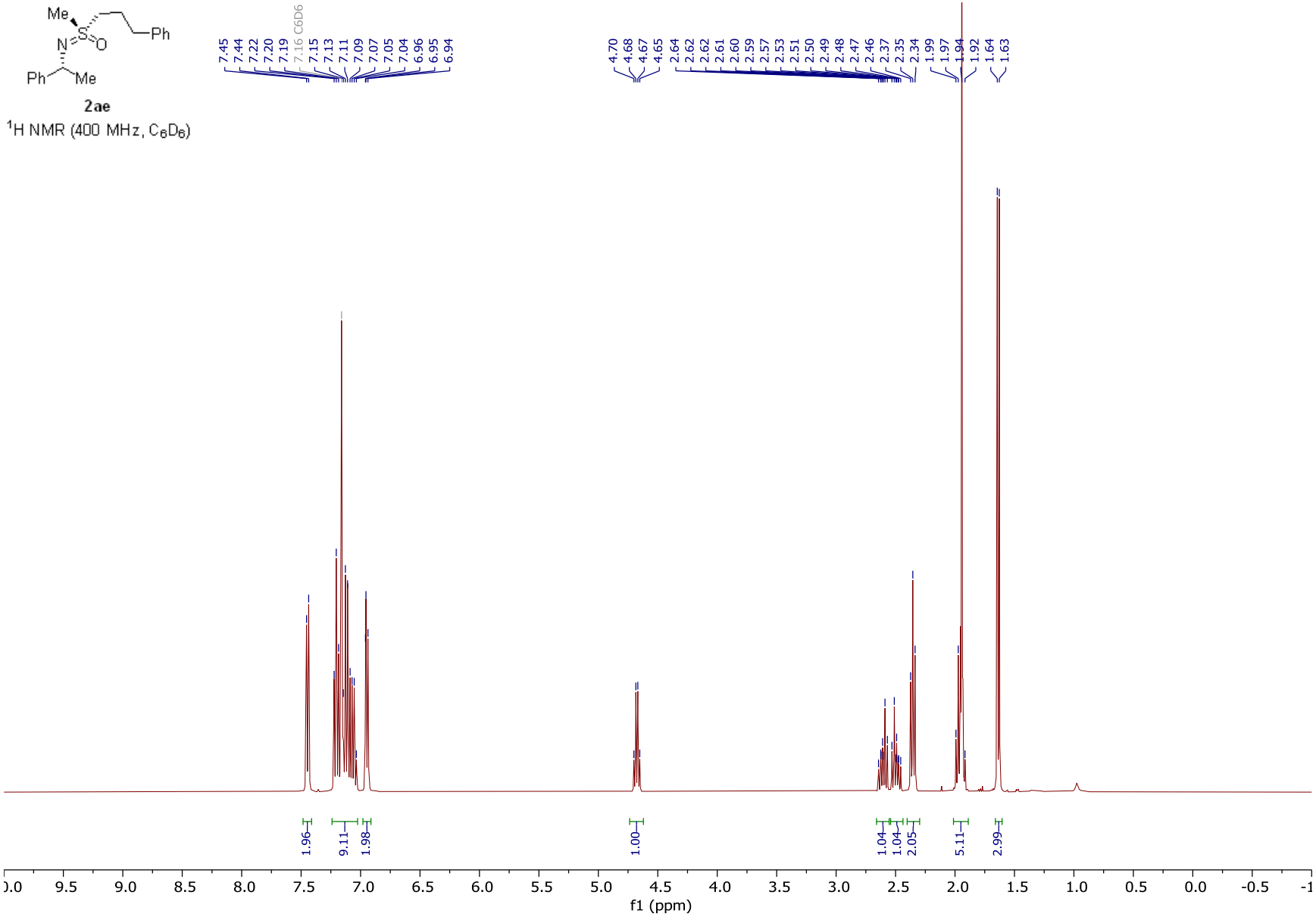
^{13}C NMR (101 MHz, $CDCl_3$)

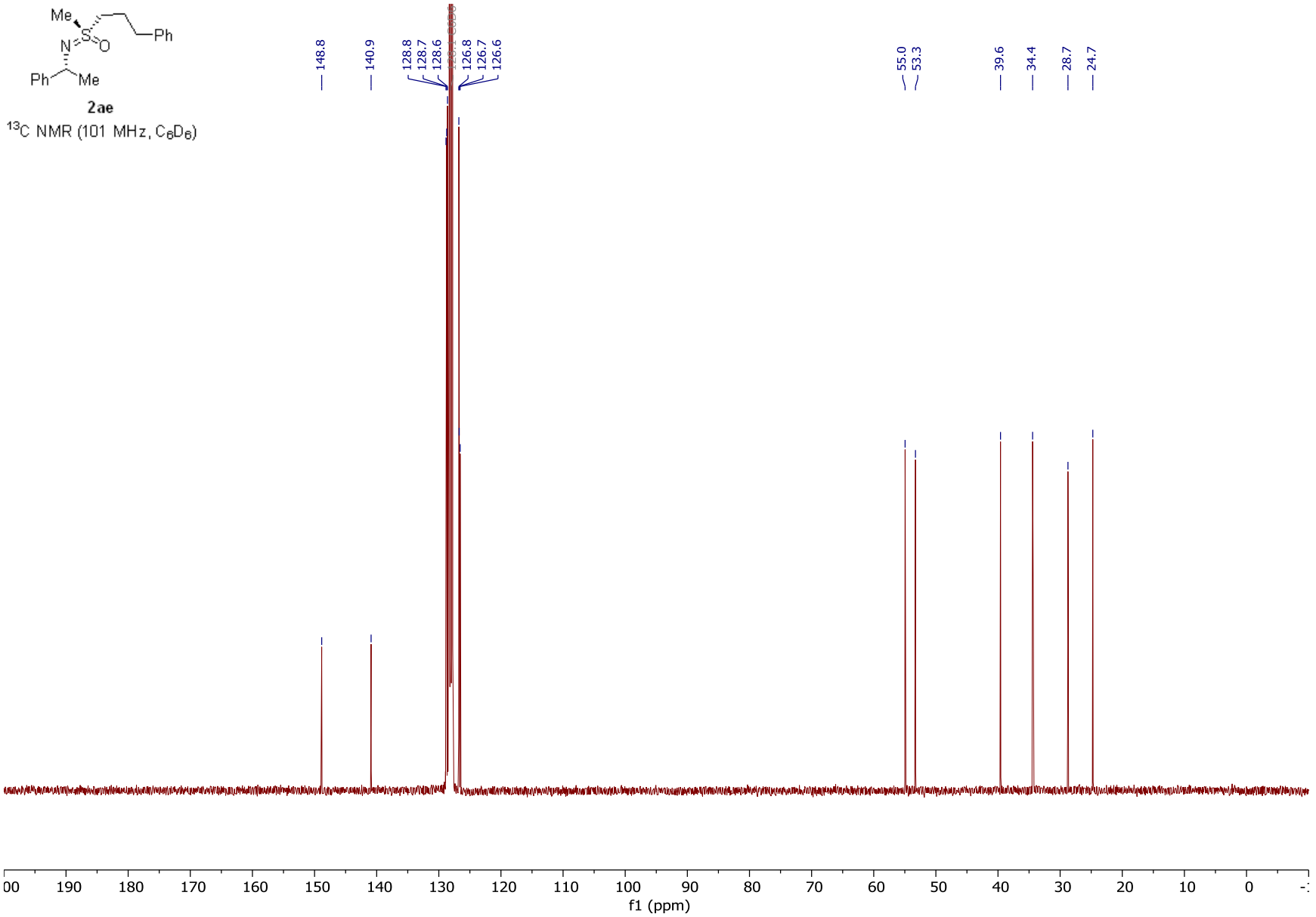

Me
S
N
O
Ph
Me
Cl
2ar
^{1}H NMR (400 MHz, $CDCl_3$)
7.40
7.39
7.38
7.32
7.30
7.28
7.26 CDCl3
7.23
7.22
7.20
7.19
7.18
4.58
4.56
4.55
4.53
3.57
3.55
3.54
3.13
3.08
3.06
2.99
2.56
1.94
1.90
1.88
1.82
1.80
1.64
1.62
1.60
1.58
1.49
1.47
1.96
1.98
0.98
1.00
2.01
2.09
3.09
4.26
2.17
3.16
f1 (ppm)

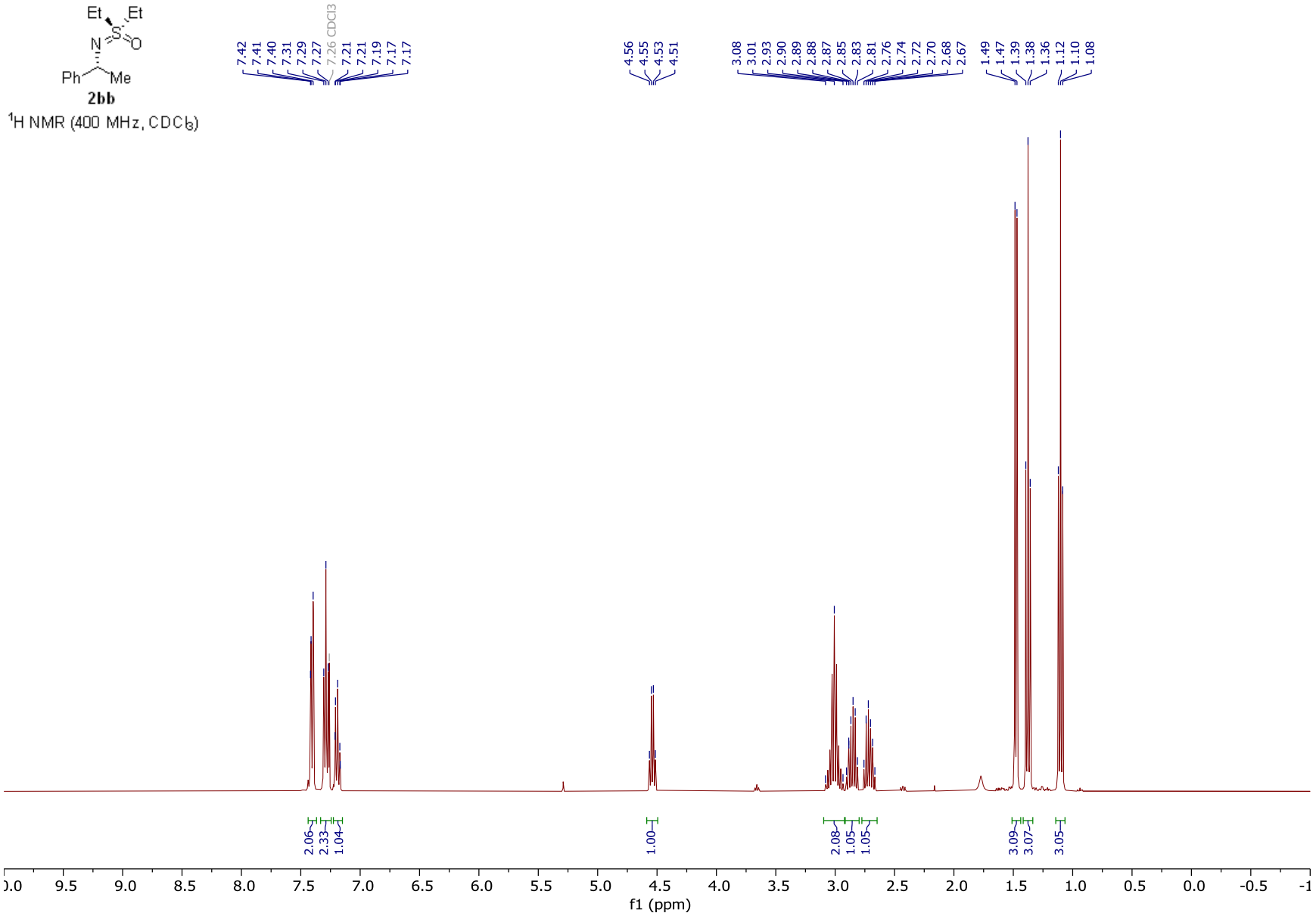

Me
N
S
O
Ph
Me
Cl
2ar
^{13}C NMR (101 MHz, $CDCl_3$)
147.6
128.5
126.8
126.4
77.3
55.7
53.0
44.6
40.1
32.1
28.0
25.8
22.4
f1 (ppm)

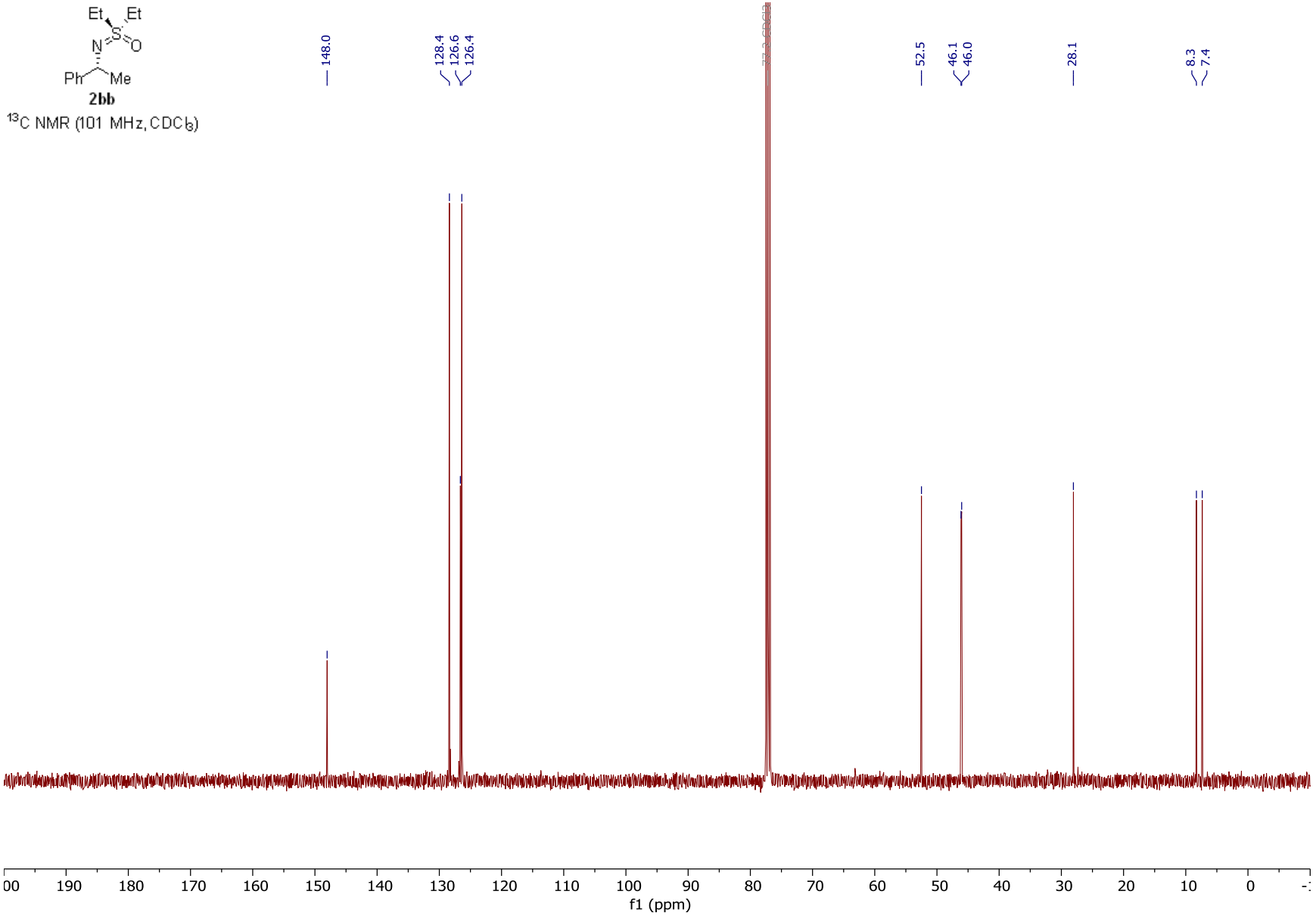

Me
S
N
O
Ph
Me
NC
2as
^{1}H NMR (400 MHz, CDCl$_3$)
7.39
7.37
7.32
7.30
7.28
7.26 CDCl3
7.23
7.22
7.21
7.19
7.18
5.29 DCM
4.57
4.56
4.54
4.52
3.14
3.08
3.03
2.97
2.56
2.40
2.38
2.36
1.96
1.92
1.88
1.77
1.73
1.69
1.65
1.61
1.57
1.48
1.47
1.98
2.00
0.99
1.00
2.10
3.06
2.06
2.11
2.21
2.16
3.13
f1 (ppm)

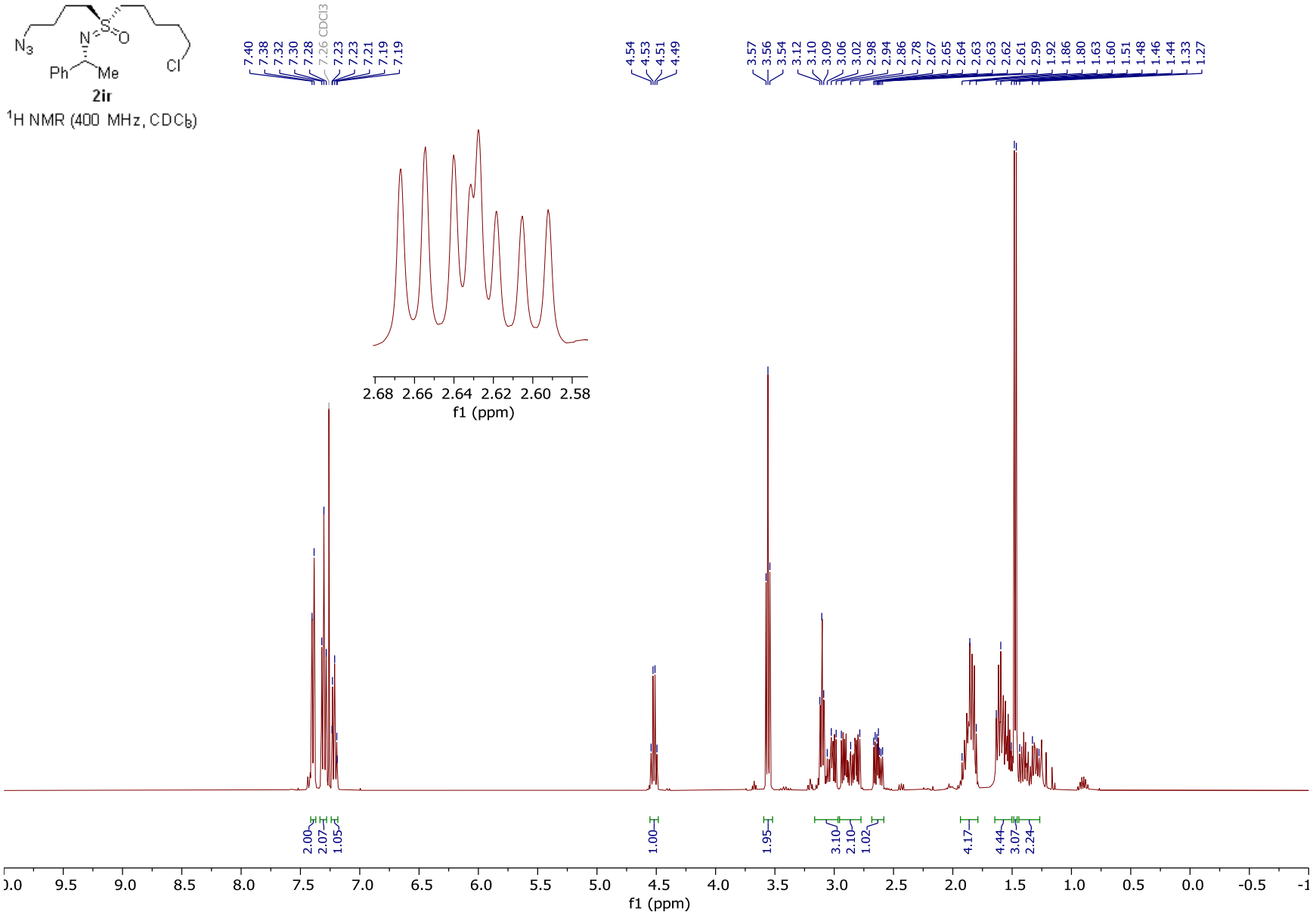

Me
N
S
O
Ph
Me
NC
2as
^{13}C NMR (101 MHz, CDCl$_3$)
147.5
128.6
126.8
126.4
119.4
77.3 CDCl3
55.4
53.1
40.3
28.0
27.5
25.1
22.3
17.1
f1 (ppm)

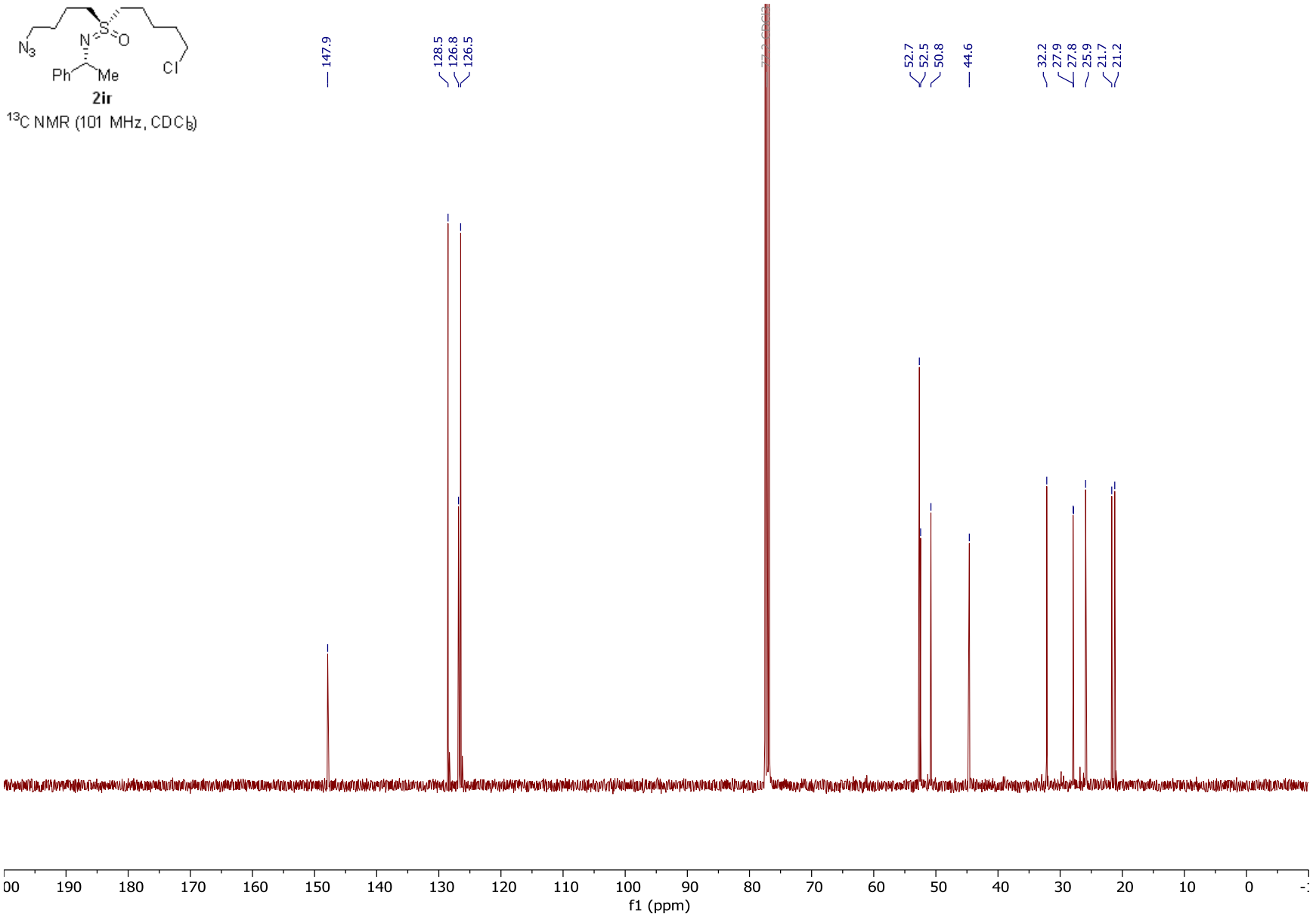

Me
Ph
N
S
O
Ph
Me
2ae
^{1}H NMR (400 MHz, C_6D_6)
7.45
7.44
7.22
7.20
7.19
7.16 C6D6
7.15
7.13
7.11
7.09
7.07
7.05
7.04
6.96
6.95
6.94
4.70
4.68
4.67
4.65
2.64
2.62
2.62
2.61
2.60
2.59
2.57
2.53
2.51
2.50
2.49
2.48
2.47
2.46
2.37
2.35
2.34
1.99
1.97
1.94
1.92
1.64
1.63
1.96
9.11
1.98
1.00
1.04
1.04
2.05
5.11
2.99
f1 (ppm)

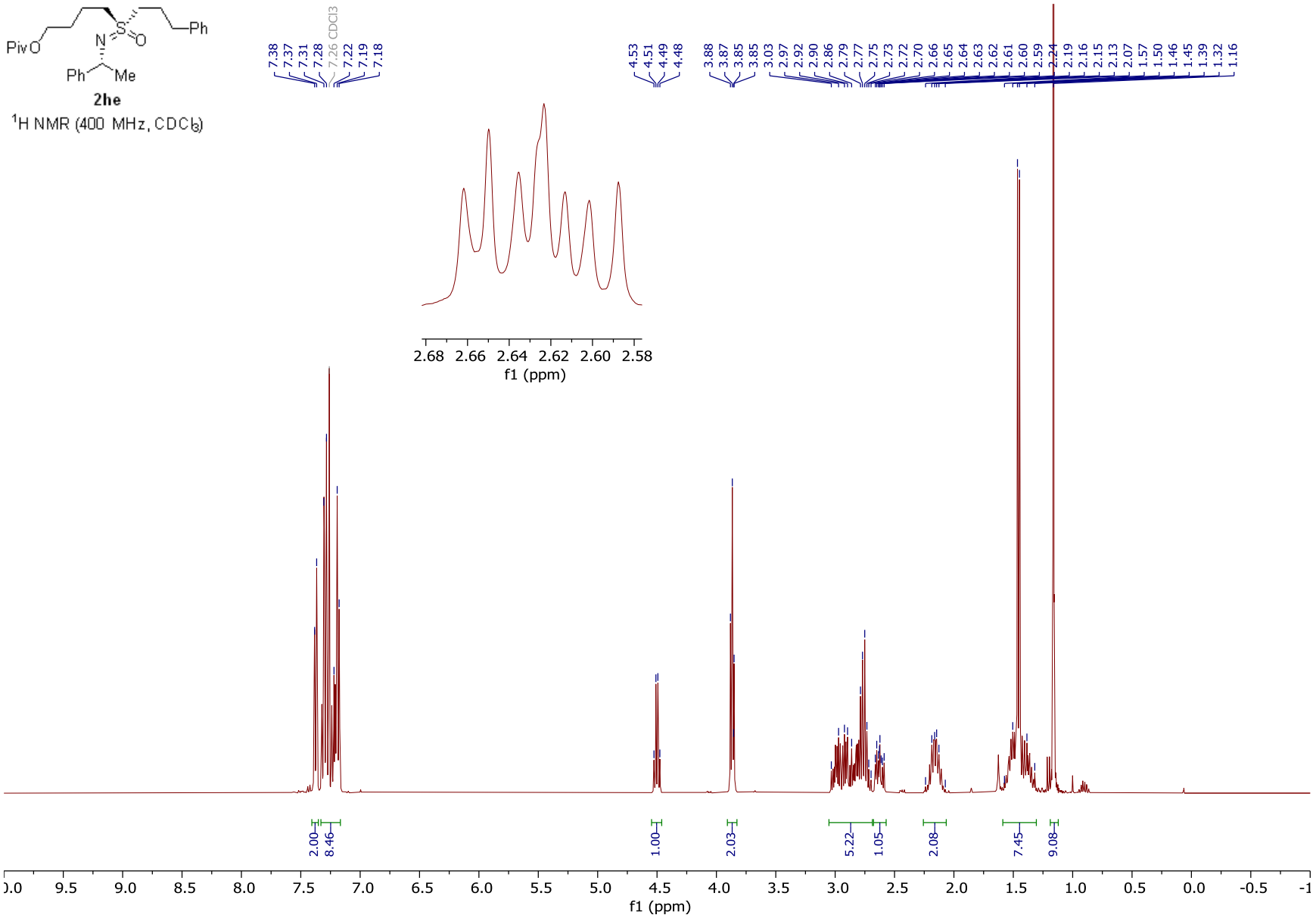

Me
Ph
N
S
O
Ph
Me
2ae
13C NMR (101 MHz, C6D6)
148.8
140.9
128.8
128.7
128.6
126.8
126.7
126.6
55.0
53.3
39.6
34.4
28.7
24.7
f1 (ppm)

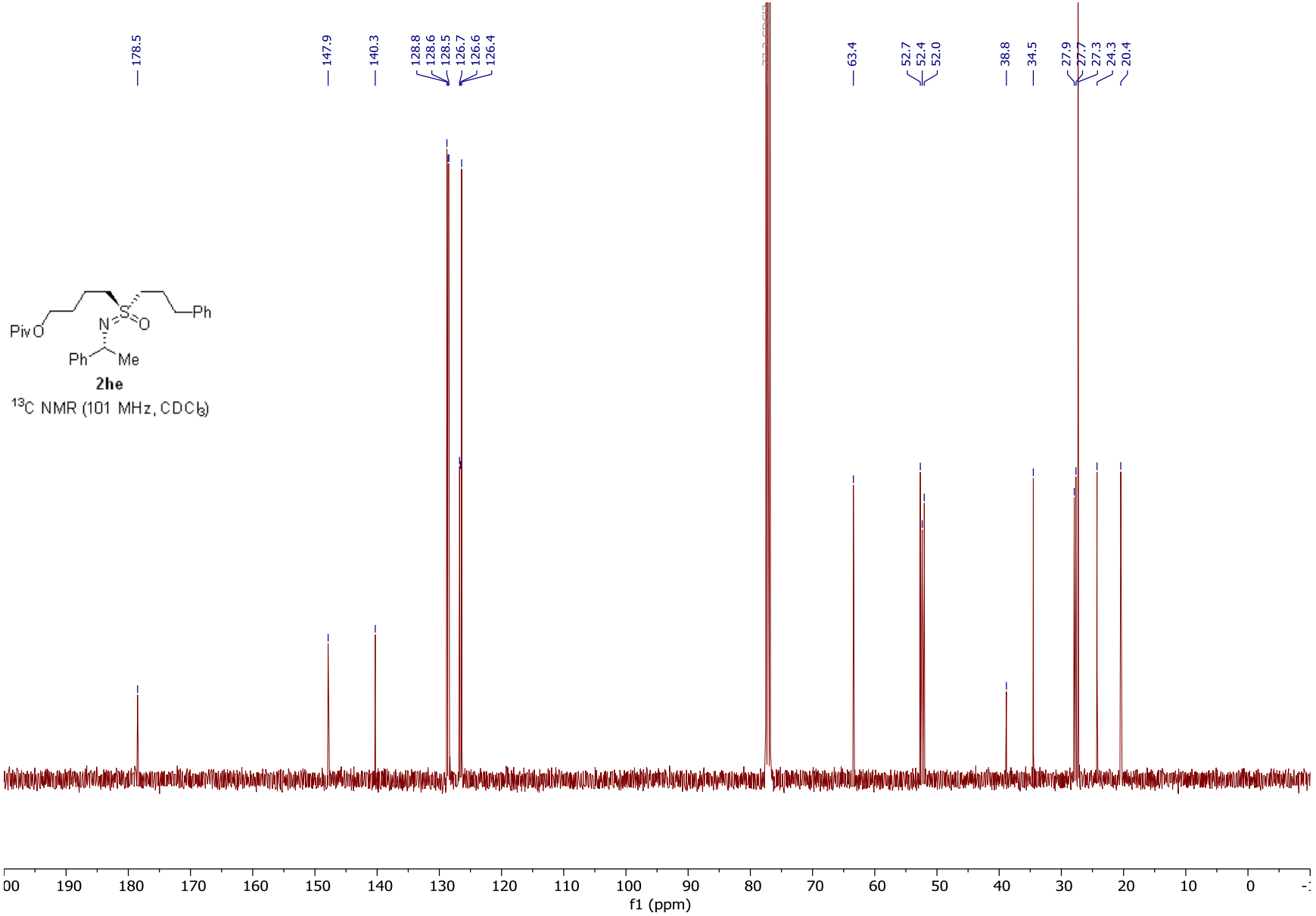

Et
Et
N
S
O
Ph
Me
2bb
^{1}H NMR (400 MHz, CDCl$_3$)
7.42
7.41
7.40
7.31
7.29
7.27
7.26 CDCl3
7.21
7.21
7.19
7.17
7.17
4.56
4.55
4.53
4.51
3.08
3.01
2.93
2.90
2.89
2.88
2.87
2.85
2.83
2.81
2.76
2.74
2.72
2.70
2.68
2.67
1.49
1.47
1.39
1.38
1.36
1.12
1.10
1.08
2.06
2.33
1.04
1.00
2.08
1.05
1.05
3.09
3.07
3.05
f1 (ppm)

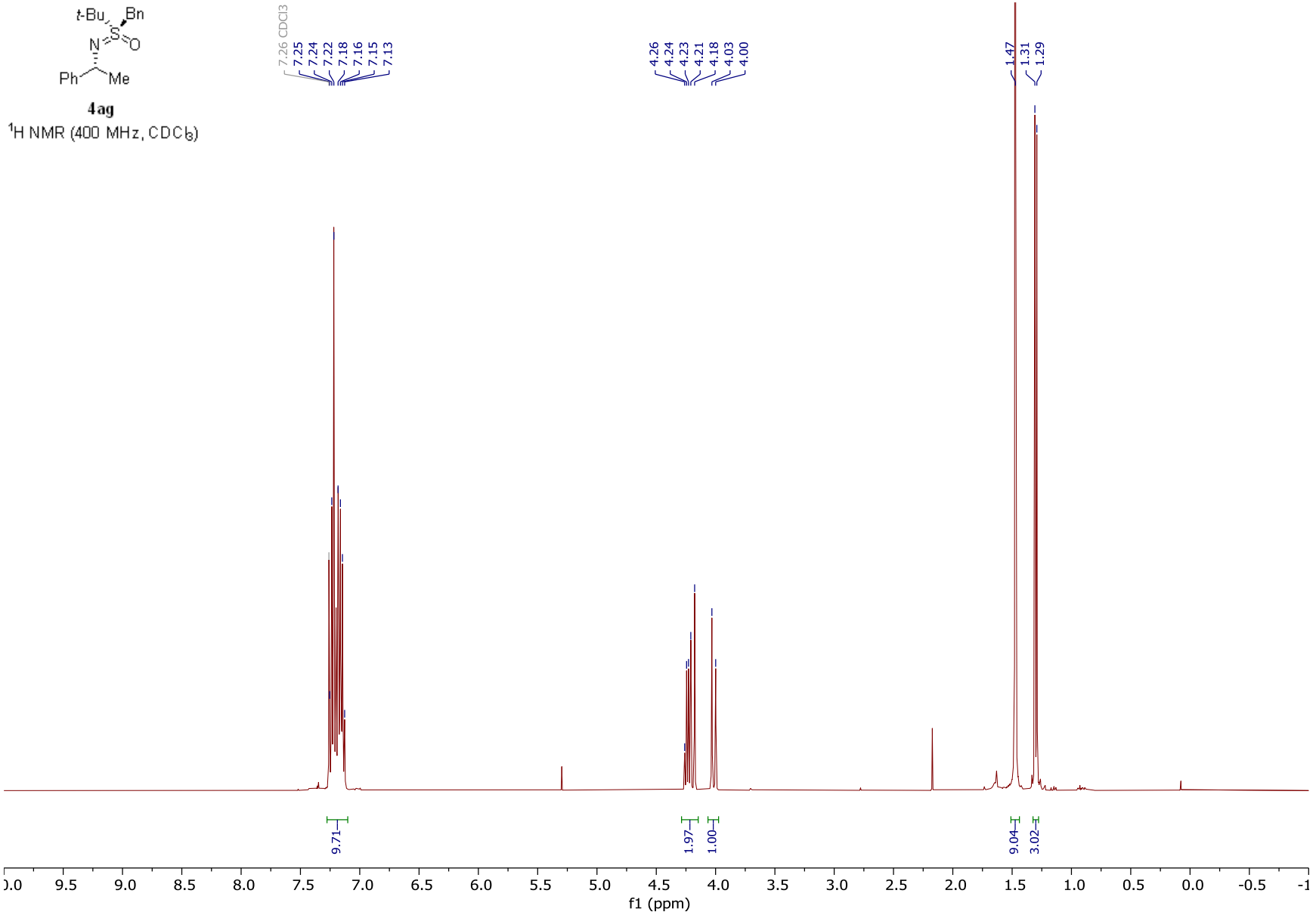

Et
Et
S
N
O
Ph
Me
2bb
^{13}C NMR (101 MHz, $CDCl_3$)
148.0
128.4
126.6
126.4
77.3
52.5
46.1
46.0
28.1
8.3
7.4
f1 (ppm)

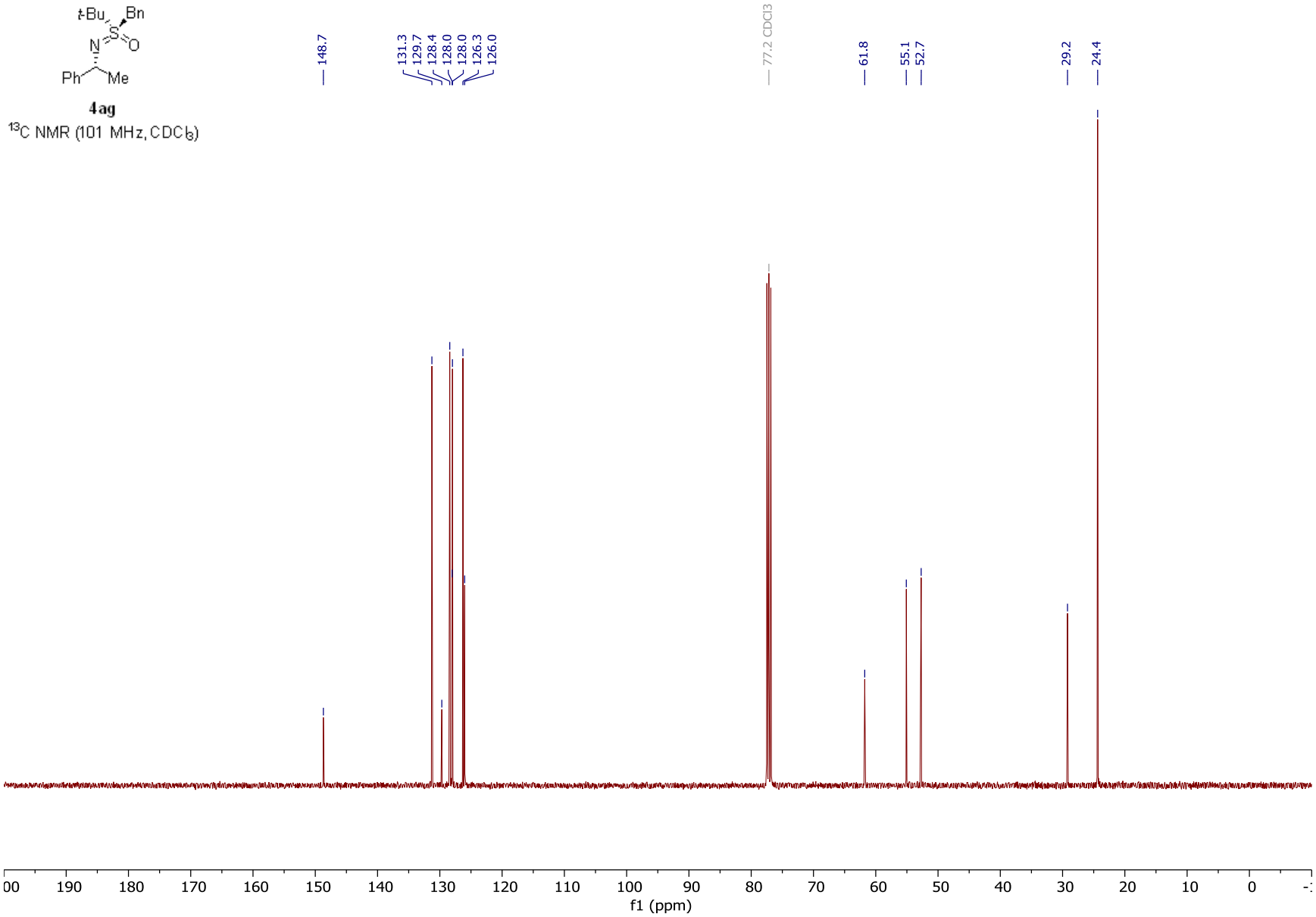

N3
N
S
O
Ph
Me
Cl
2ir
1H NMR (400 MHz, CDCl3)
7.40 7.38 7.32 7.30 7.28 7.26 CDCl3 7.23 7.23 7.21 7.19 7.19
4.54 4.53 4.51 4.49
3.57 3.56 3.54 3.12 3.10 3.09 3.06 3.02 2.98 2.94 2.86 2.78 2.67 2.65 2.64 2.63 2.63 2.62 2.61 2.59 1.92 1.86 1.80 1.63 1.60 1.51 1.48 1.46 1.44 1.33 1.27
2.68 2.66 2.64 2.62 2.60 2.58
f1 (ppm)
2.00 2.07 1.05 1.00 1.95 3.10 2.10 1.02 4.17 4.44 3.07 2.24
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

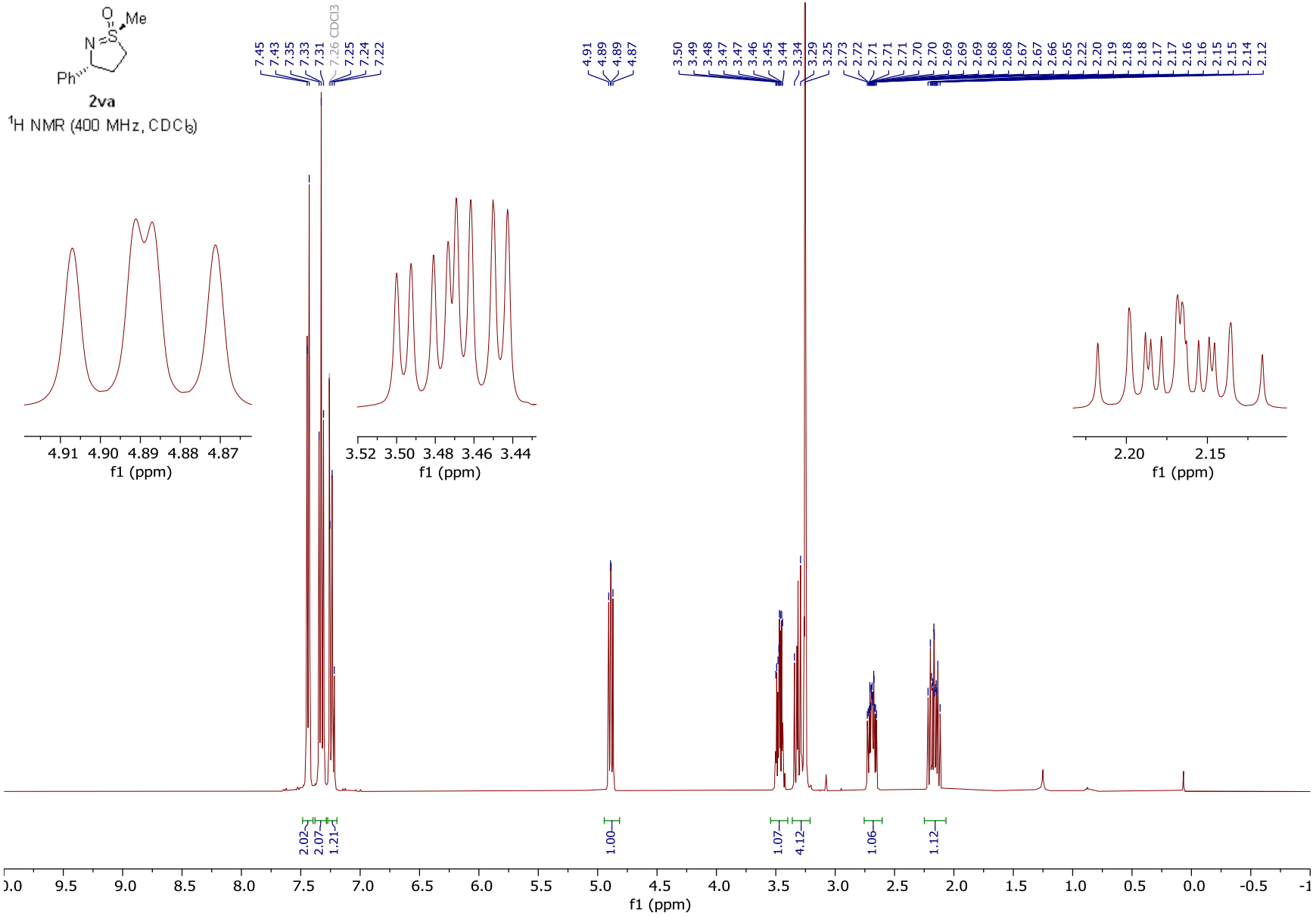

N3
N
S
O
Ph
Me
Cl
2ir
13C NMR (101 MHz, CDCl3)
147.9
128.5
126.8
126.5
77.3
52.7
52.5
50.8
44.6
32.2
27.9
27.8
25.9
21.7
21.2
f1 (ppm)

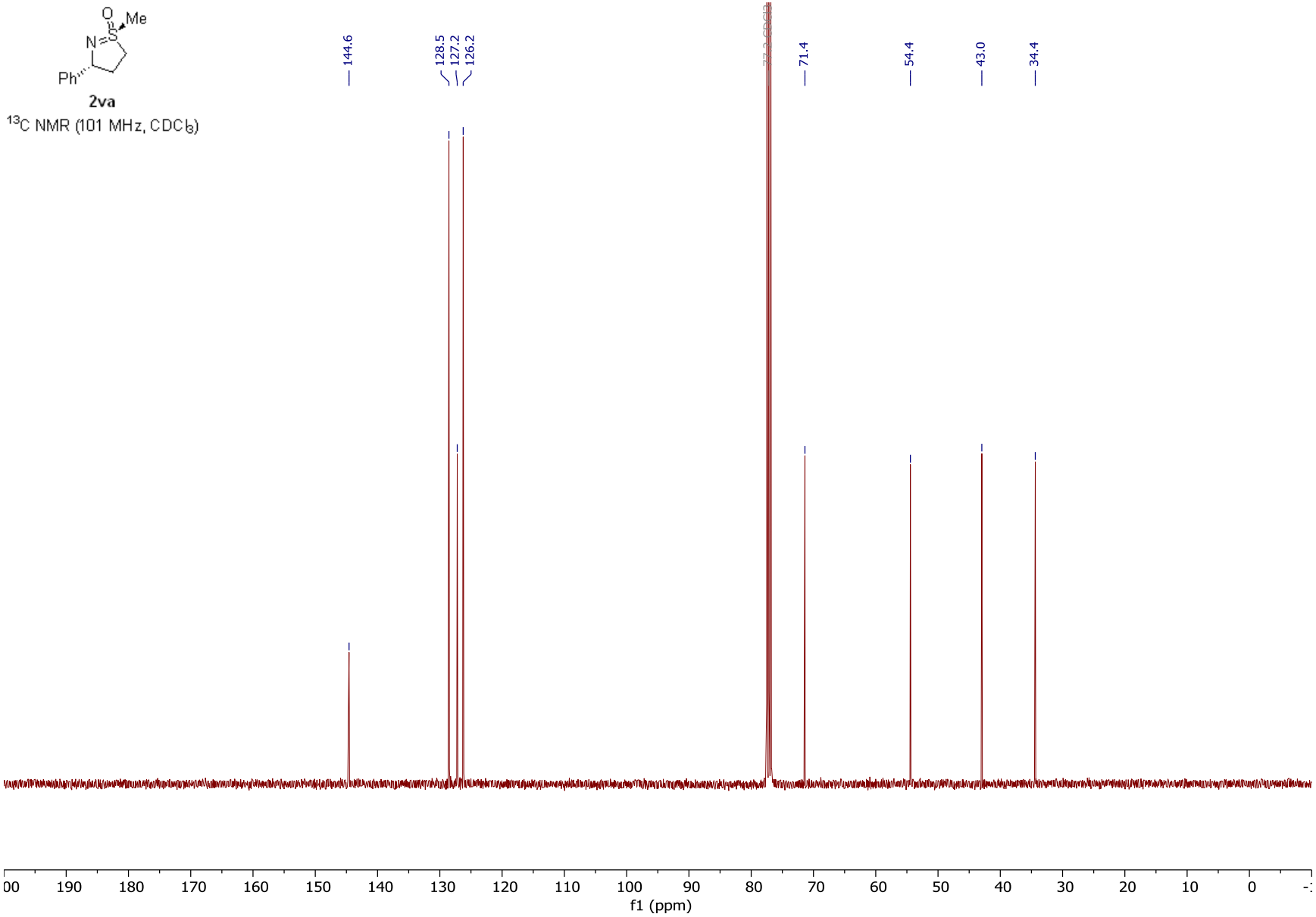

PivO
N
S
O
Ph
Ph
Me
2he
^{1}H NMR (400 MHz, CDCl$_3$)
7.38 7.37 7.31 7.28 7.26 CDCl3 7.22 7.19 7.18
4.53 4.51 4.49 4.48
3.88 3.87 3.85 3.85 3.03 2.97 2.92 2.90 2.86 2.79 2.77 2.75 2.73 2.72 2.70 2.66 2.65 2.64 2.63 2.62 2.61 2.60 2.59 2.24 2.19 2.16 2.15 2.13 2.07 1.57 1.50 1.46 1.45 1.39 1.32 1.16
2.68 2.66 2.64 2.62 2.60 2.58
f1 (ppm)
2.00 8.46 1.00 2.03 5.22 1.05 2.08 7.45 9.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

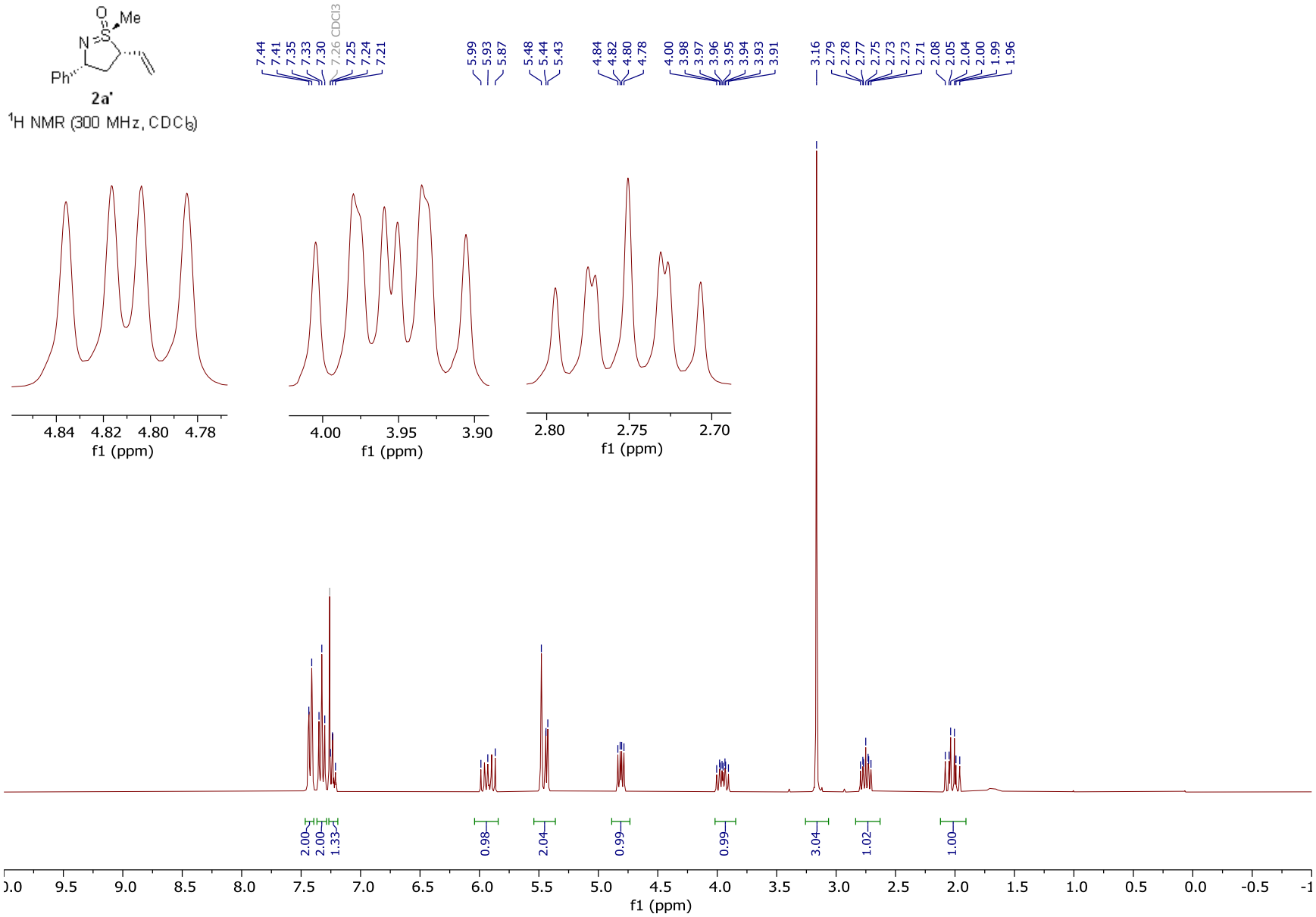

178.5
147.9
140.3
128.8
128.6
128.5
126.7
126.6
126.4
63.4
52.7
52.4
52.0
38.8
34.5
27.9
27.7
27.3
24.3
20.4
PivO
N
S
O
Ph
Ph
Me
2he
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

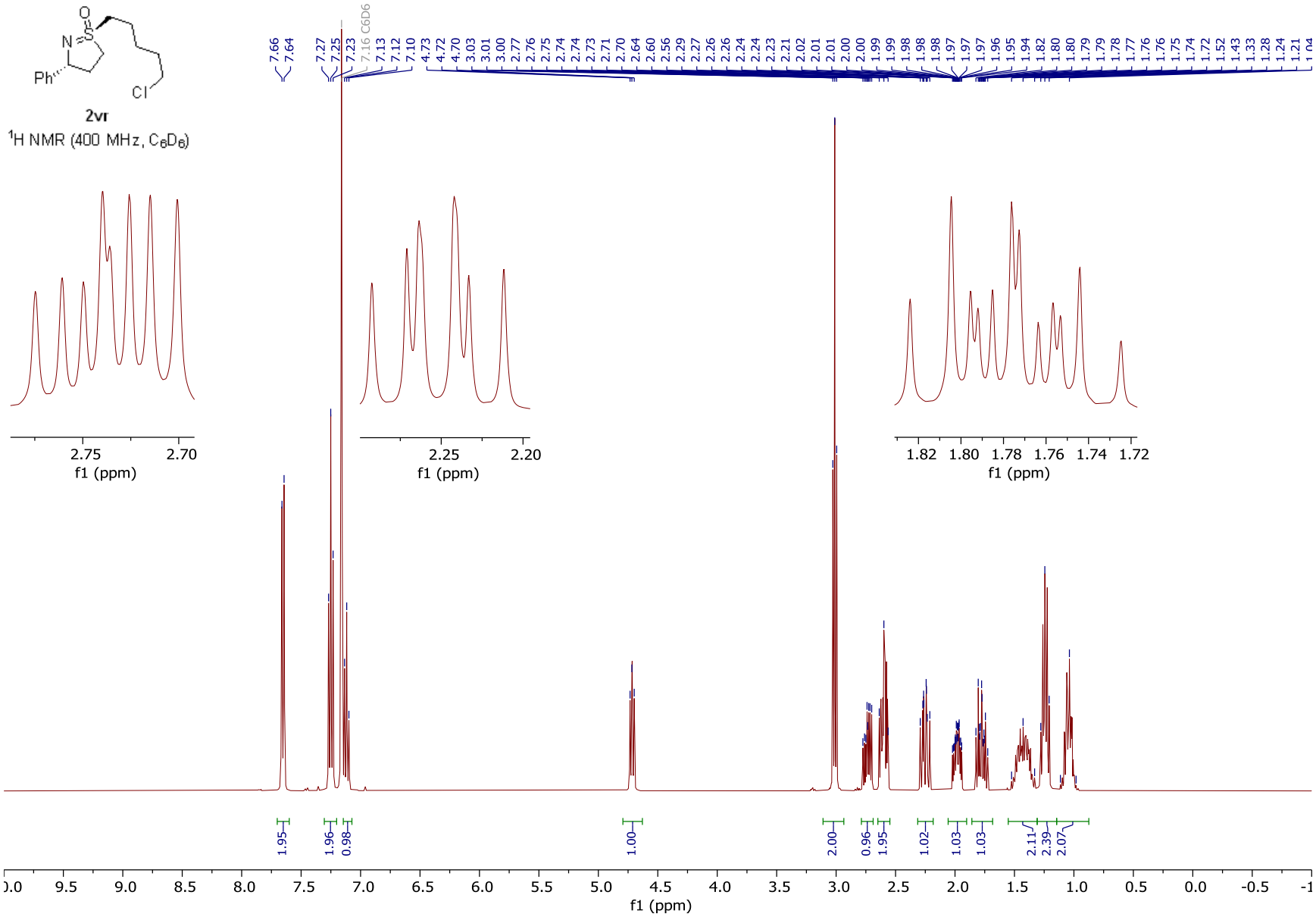

t-Bu
Bn
N
S
O
Ph
Me
4ag
1H NMR (400 MHz, CDCl3)
7.26 CDCl3
7.25
7.24
7.22
7.18
7.16
7.15
7.13
4.26
4.24
4.23
4.21
4.18
4.03
4.00
1.47
1.31
1.29
9.71
1.97
1.00
9.04
3.02
f1 (ppm)

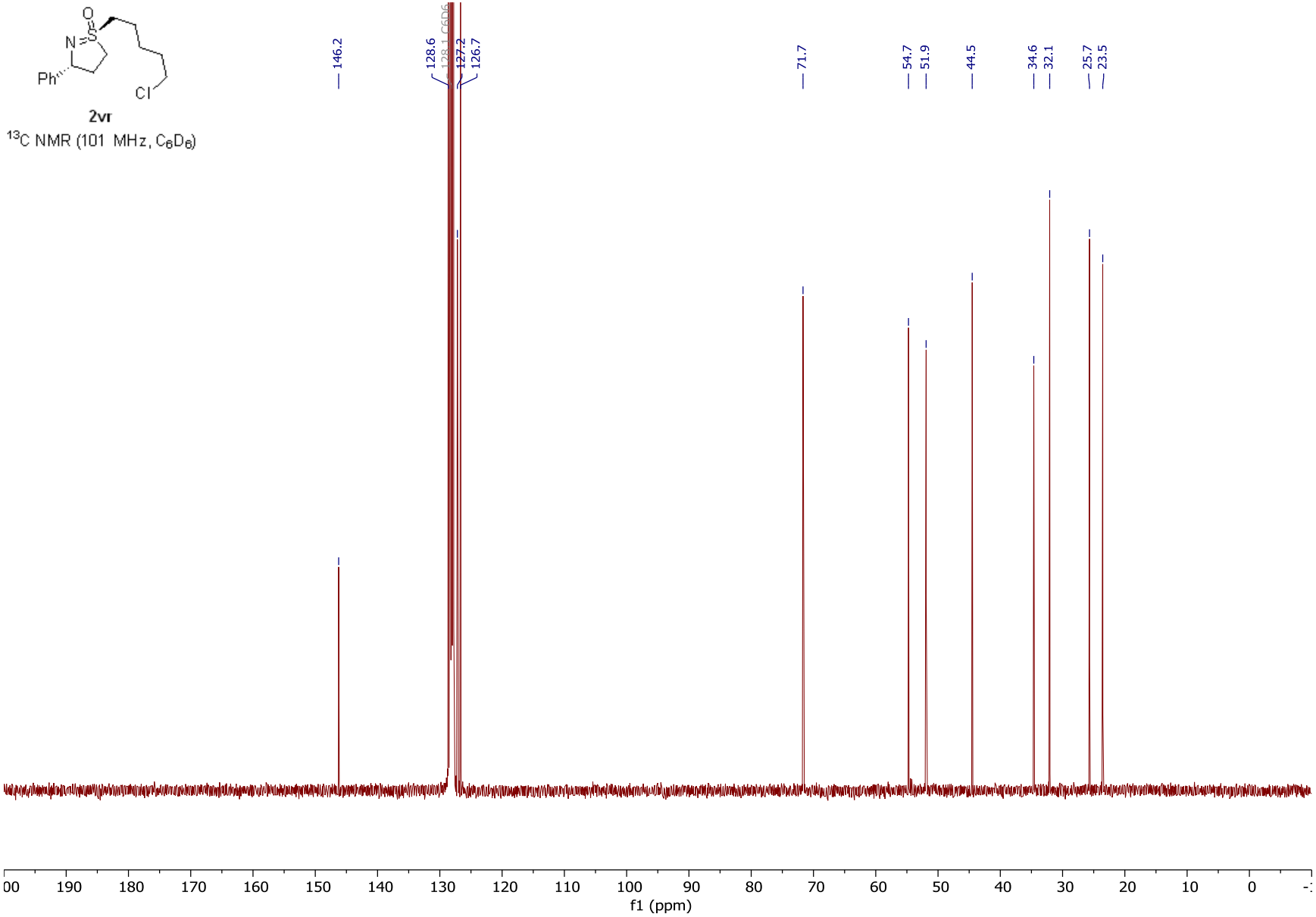

t-Bu
Bn
N
S
O
Ph
Me
4ag
13C NMR (101 MHz, CDCl3)
148.7
131.3
129.7
128.4
128.0
128.0
126.3
126.0
77.2 CDCl3
61.8
55.1
52.7
29.2
24.4
f1 (ppm)

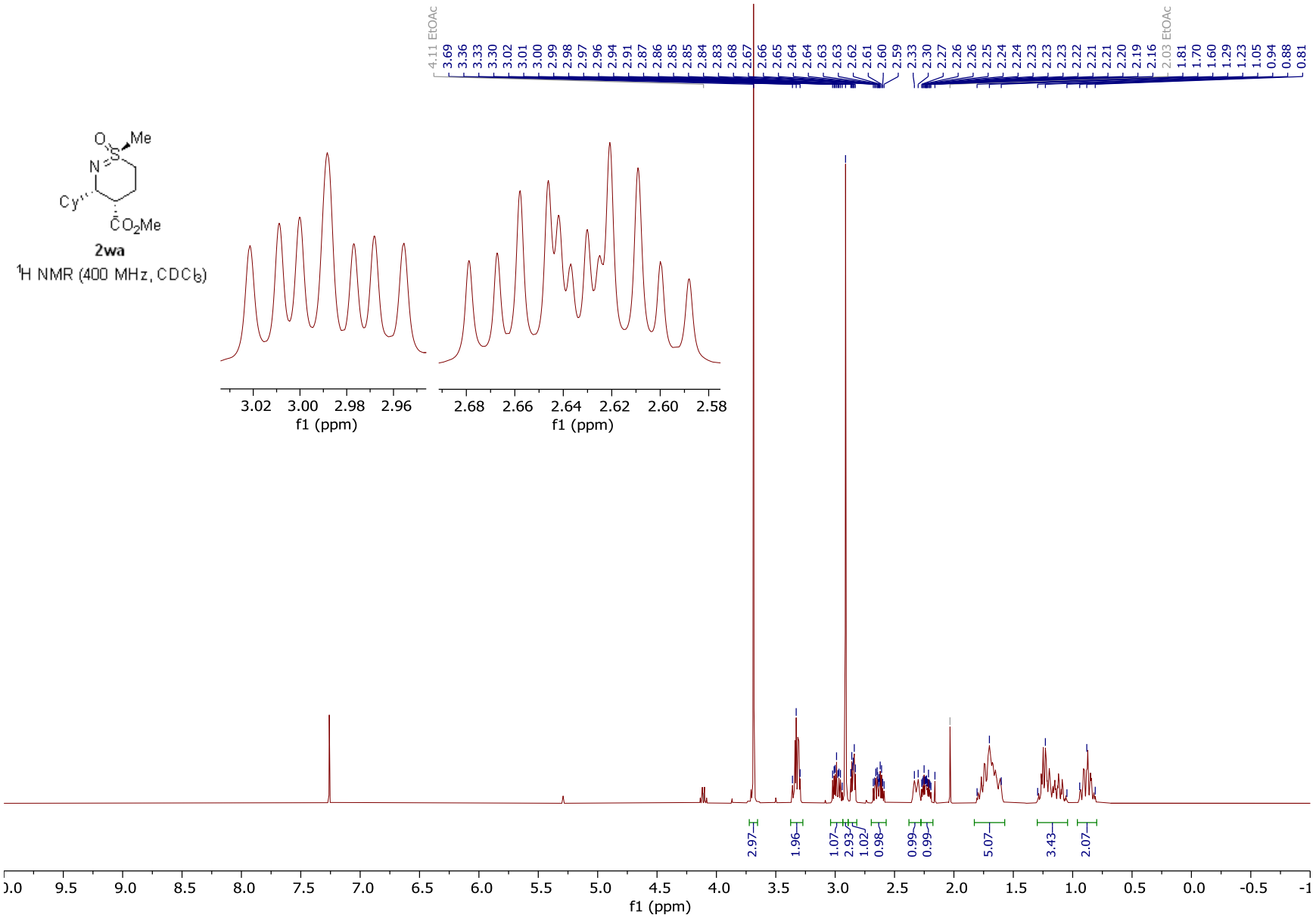

Me
O
N
S
Ph
2va
^{1}H NMR (400 MHz, CDCl$_3$)
7.45 7.43 7.35 7.33 7.31 7.26 CDCl3 7.25 7.24 7.22
4.91 4.89 4.89 4.87
3.50 3.49 3.48 3.47 3.47 3.46 3.45 3.44 3.34 3.29 3.25
2.73 2.72 2.71 2.71 2.71 2.70 2.70 2.69 2.69 2.69 2.68 2.68 2.67 2.67 2.66 2.65 2.22 2.20 2.19 2.18 2.18 2.17 2.17 2.16 2.16 2.15 2.15 2.14 2.12
4.91 4.90 4.89 4.88 4.87
f1 (ppm)
3.52 3.50 3.48 3.46 3.44
f1 (ppm)
2.20 2.15
f1 (ppm)
2.02 2.07 1.21 1.00 1.07 4.12 1.06 1.12
f1 (ppm)

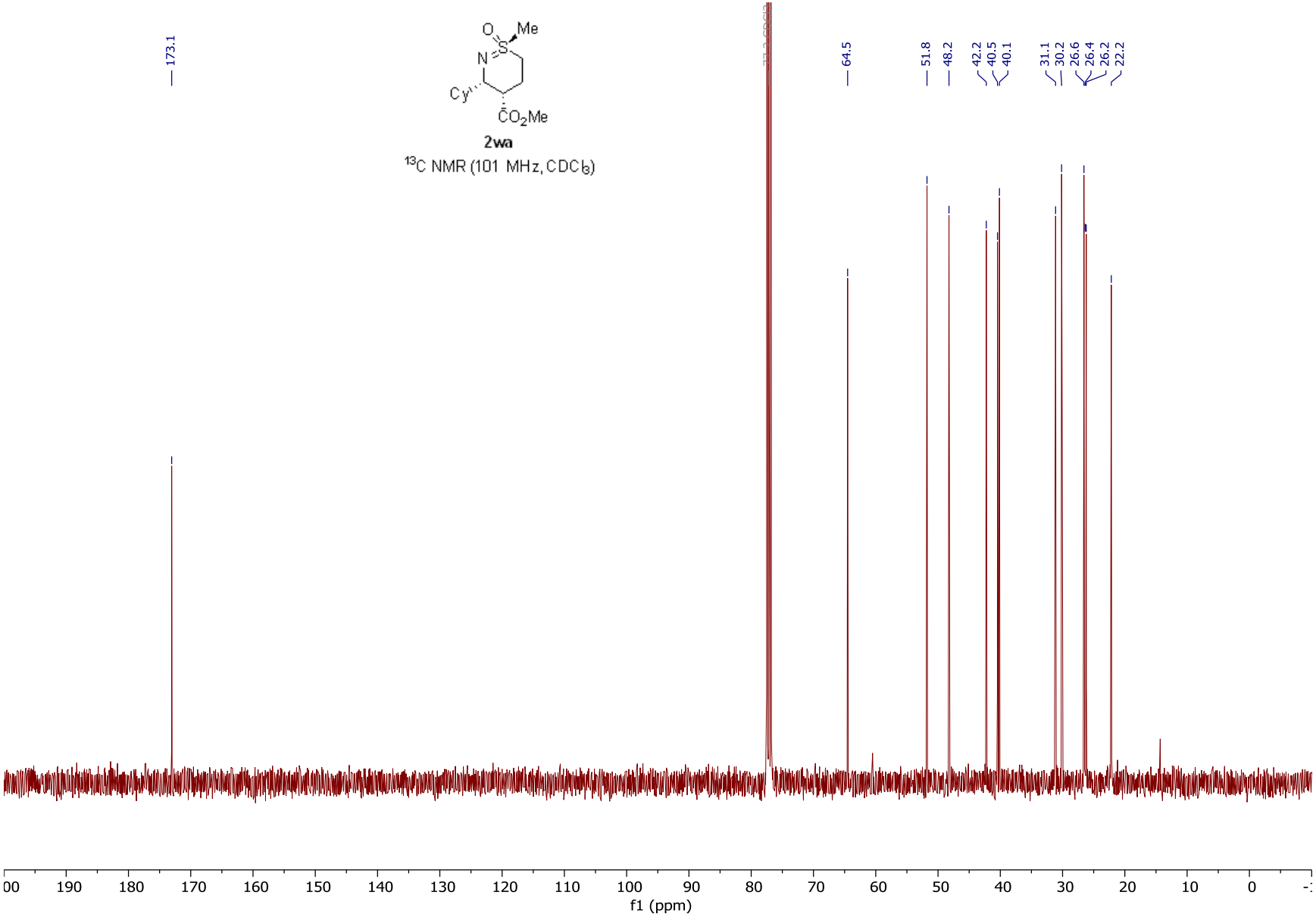

Me
O
N
O
Ph
2va
^{13}C NMR (101 MHz, CDCl$_3$)
144.6
128.5
127.2
126.2
77.3 CDCl3
71.4
54.4
43.0
34.4
f1 (ppm)

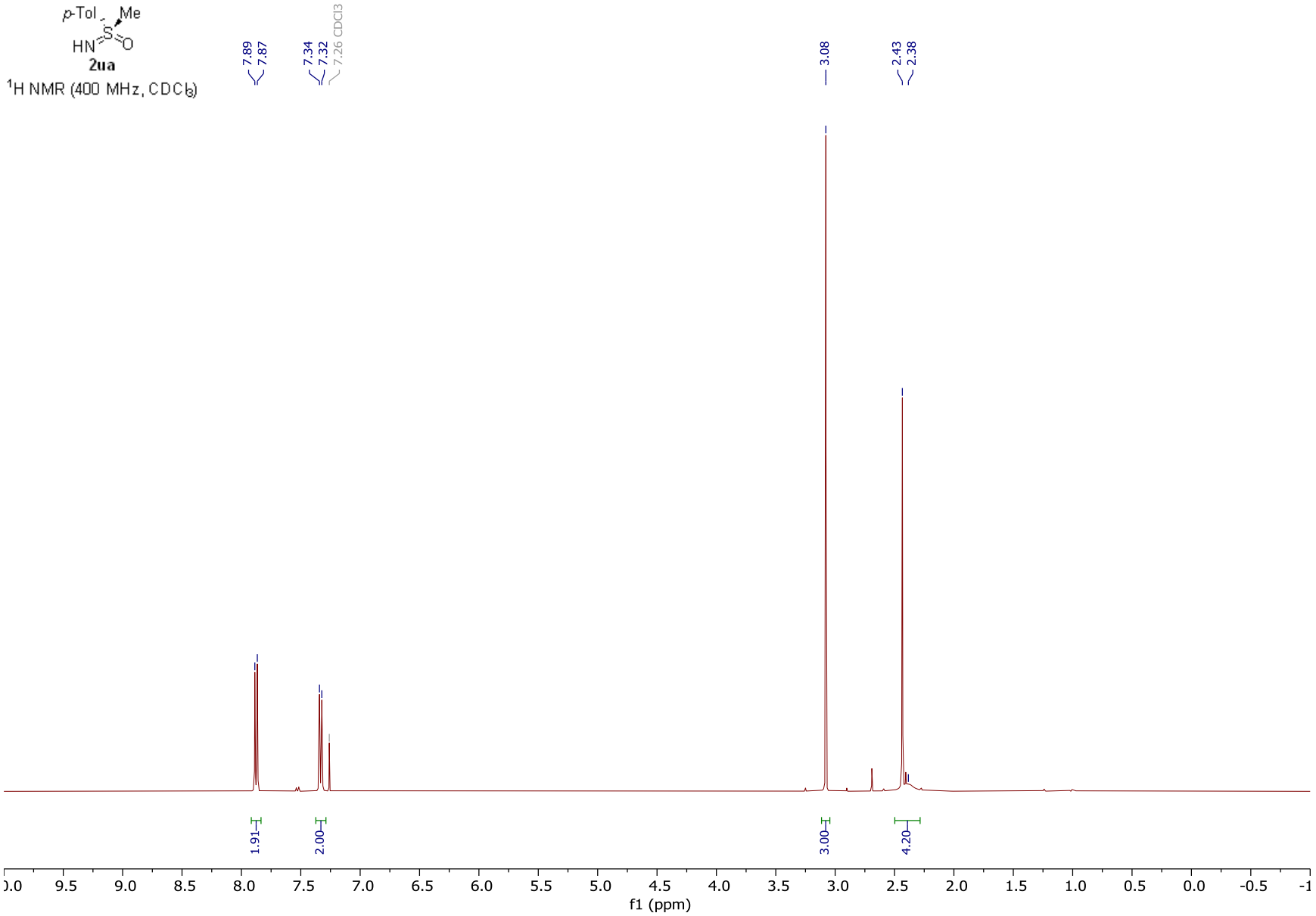

Me
O
N
S
Ph
2a'
1H NMR (300 MHz, CDCl3)
7.44
7.41
7.35
7.33
7.30
7.26 CDCl3
7.25
7.24
7.21
5.99
5.93
5.87
5.48
5.44
5.43
4.84
4.82
4.80
4.78
4.00
3.98
3.97
3.96
3.95
3.94
3.93
3.91
3.16
2.79
2.78
2.77
2.75
2.73
2.73
2.71
2.08
2.05
2.04
2.00
1.99
1.96
4.84 4.82 4.80 4.78
f1 (ppm)
4.00 3.95 3.90
f1 (ppm)
2.80 2.75 2.70
f1 (ppm)
2.00
2.00
1.33
0.98
2.04
0.99
0.99
3.04
1.02
1.00
f1 (ppm)

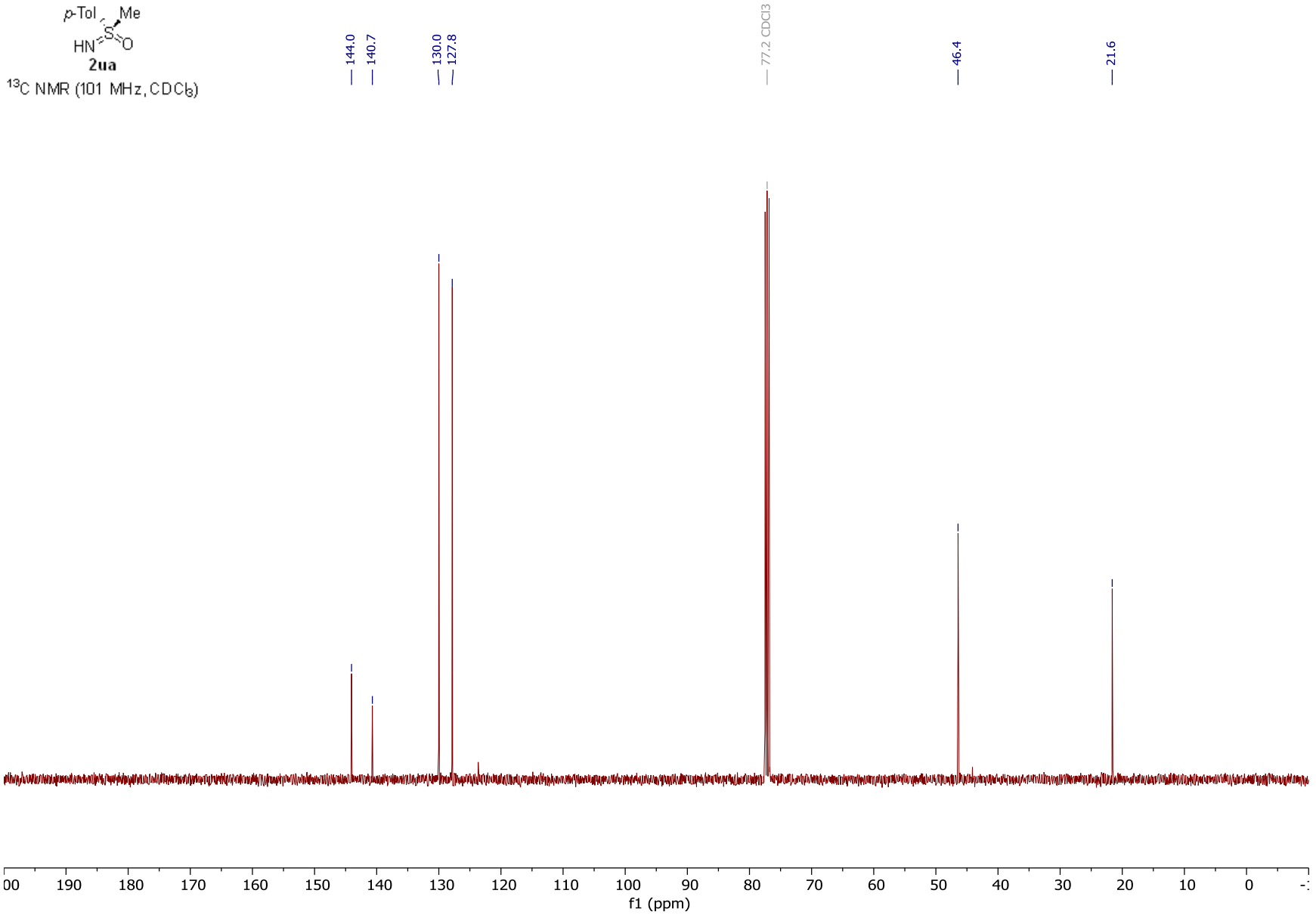

Ph
O
N
Cl
2vr
¹H NMR (400 MHz, C6D6)
7.16 C6D6
f1 (ppm)

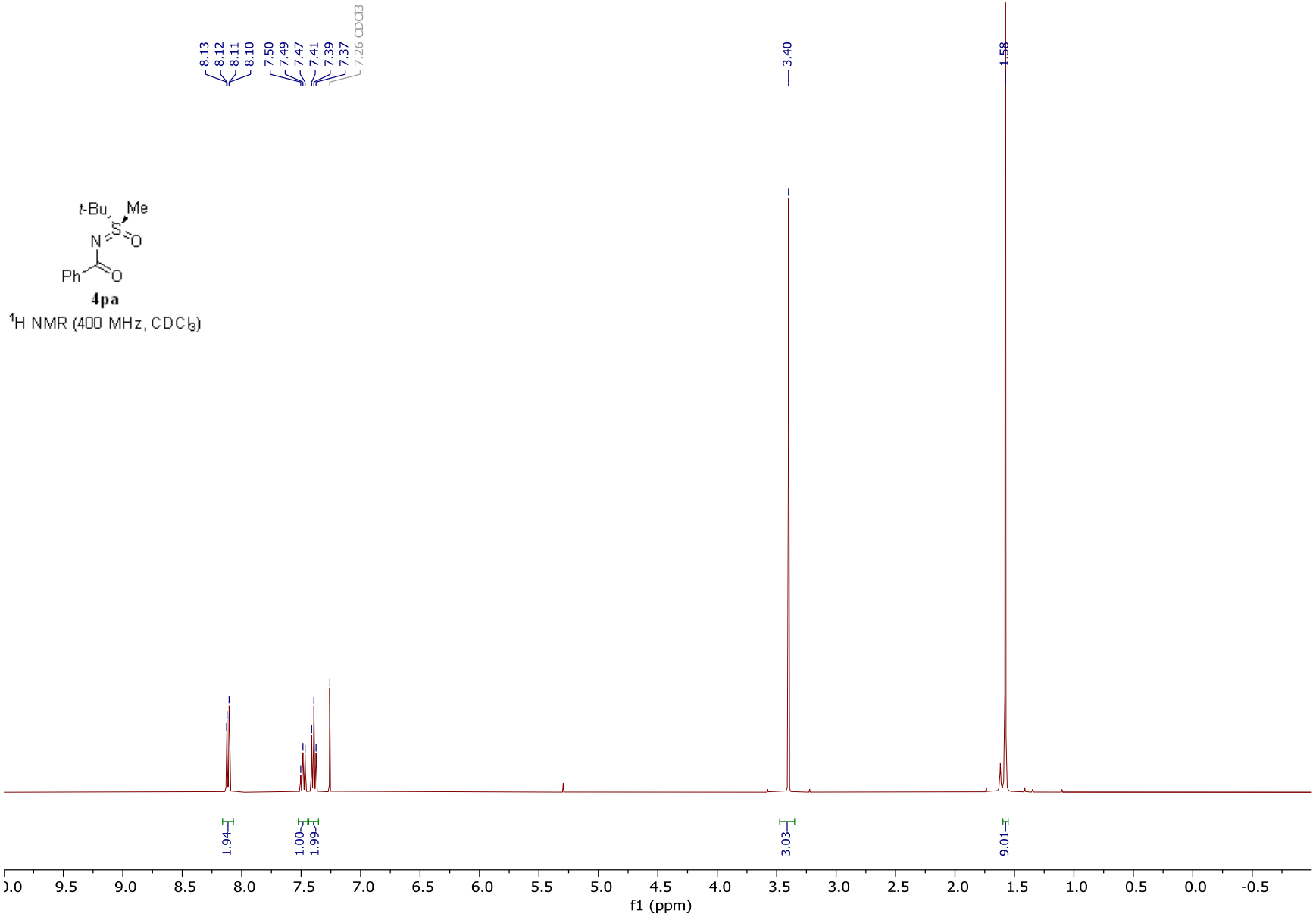

O
N
S
Ph
Cl
2vr
^{13}C NMR (101 MHz, C_6D_6)
146.2
128.6
128.1 C6D6
127.2
126.7
71.7
54.7
51.9
44.5
34.6
32.1
25.7
23.5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

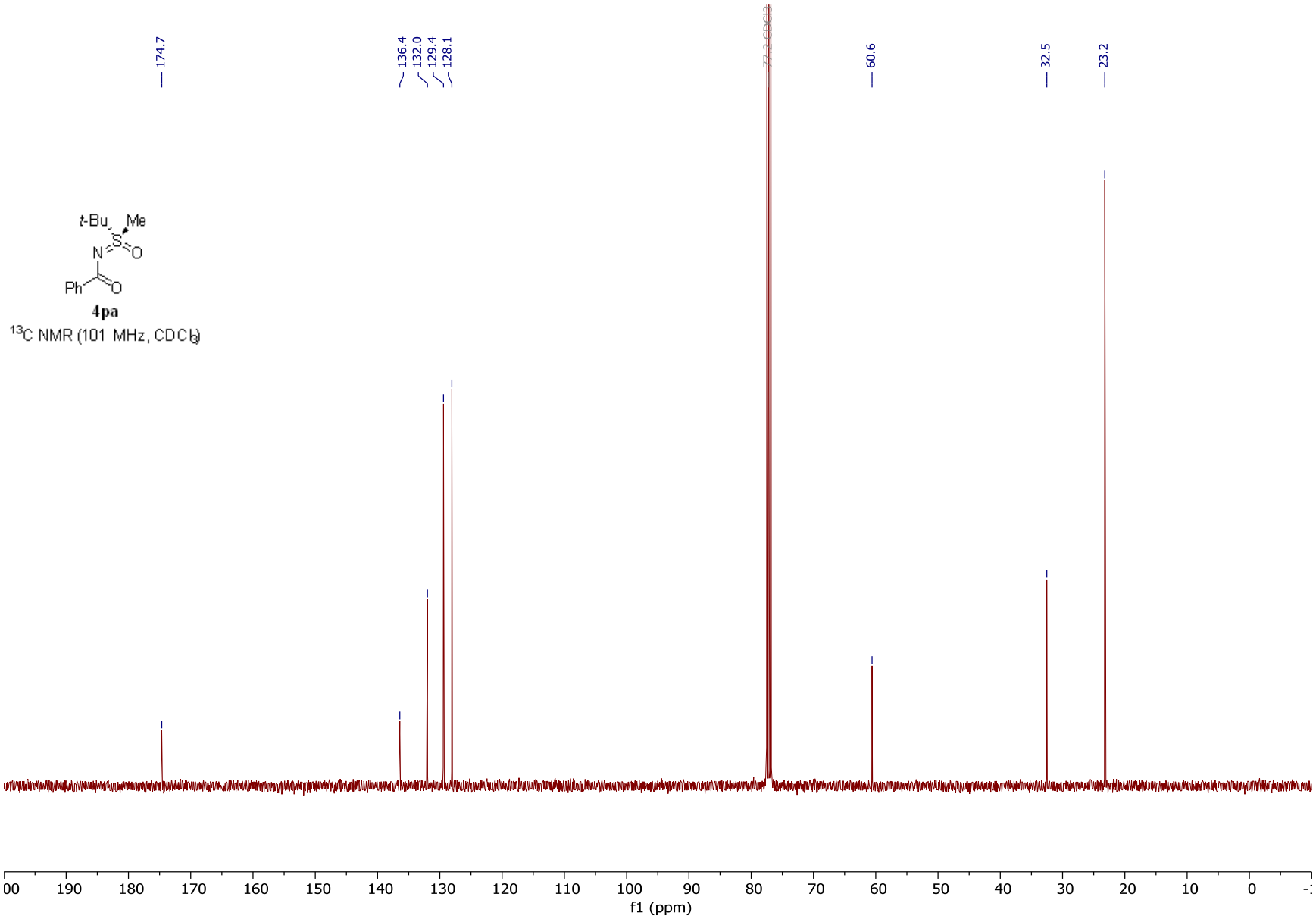

4.11 EtOAc
3.69 3.36 3.33 3.30 3.02 3.01 3.00 2.99 2.98 2.97 2.96 2.94 2.91 2.87 2.86 2.85 2.85 2.84 2.83 2.68 2.67 2.66 2.65 2.64 2.64 2.63 2.63 2.62 2.61 2.60 2.59 2.33 2.30 2.27 2.26 2.26 2.25 2.24 2.24 2.23 2.23 2.23 2.22 2.21 2.21 2.20 2.19 2.16
2.03 EtOAc
1.81 1.70 1.60 1.29 1.23 1.05 0.94 0.88 0.81
Me
O
S
N
Cy
CO2Me
2wa
1H NMR (400 MHz, CDCl3)
3.02 3.00 2.98 2.96
f1 (ppm)
2.68 2.66 2.64 2.62 2.60 2.58
f1 (ppm)
2.97 1.96 1.07 2.93 1.02 0.98 0.99 0.99 5.07 3.43 2.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

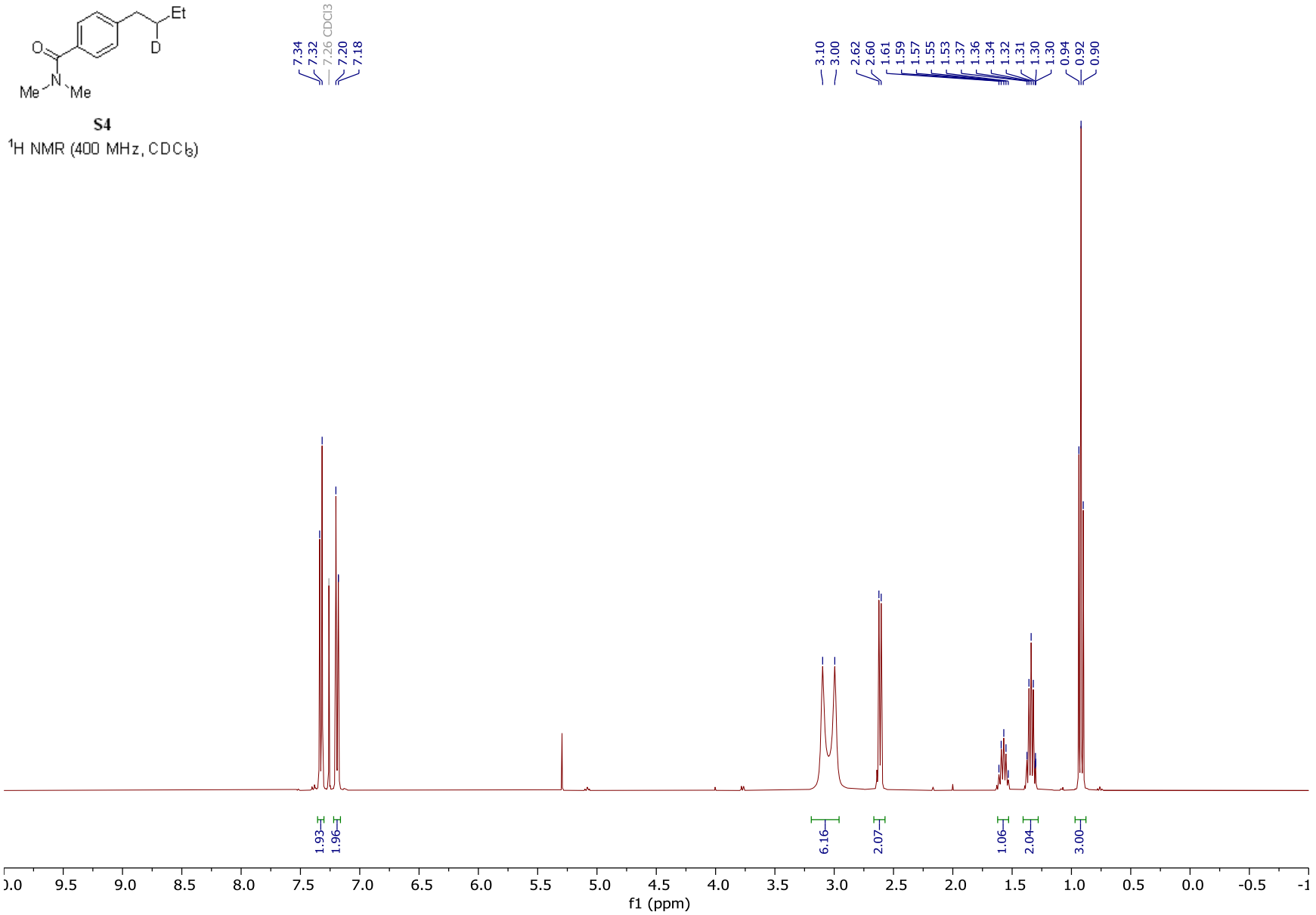

173.1
64.5
51.8
48.2
42.2
40.5
40.1
31.1
30.2
26.6
26.4
26.2
22.2
Me
O
S
N
Cy
CO2Me
2wa
13C NMR (101 MHz, CDCl3)
f1 (ppm)


p-Tol
Me
HN
S
O
2ua
1H NMR (400 MHz, CDCl3)
7.89
7.87
7.34
7.32
7.26 CDCl3
3.08
2.43
2.38
1.91
2.00
3.00
4.20
f1 (ppm)


p-Tol
Me
HN
S
O
2ua
13C NMR (101 MHz, CDCl3)
144.0
140.7
130.0
127.8
77.2 CDCl3
46.4
21.6
f1 (ppm)

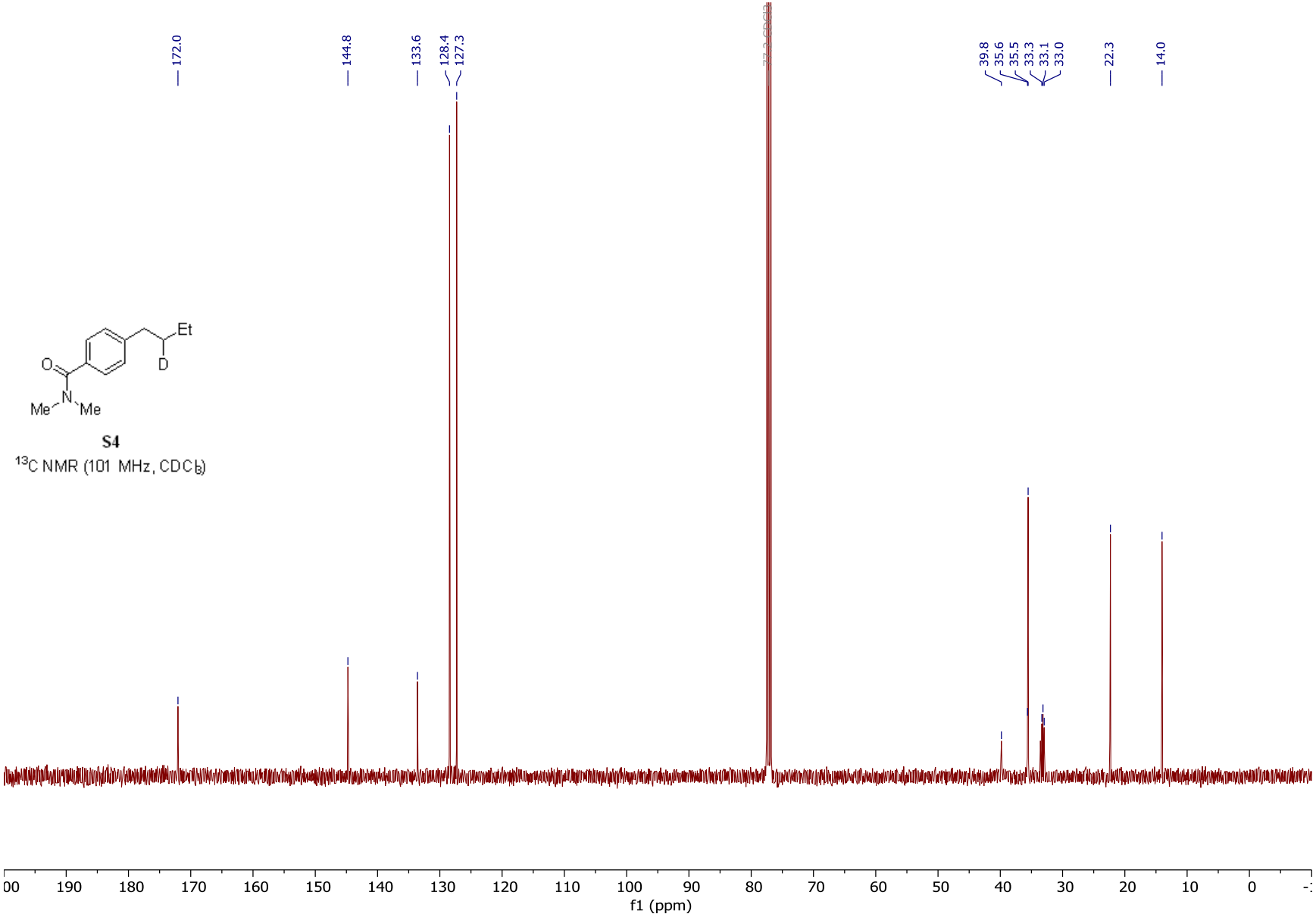

8.13
8.12
8.11
8.10
7.50
7.49
7.47
7.41
7.39
7.37
7.26 CDCl3
3.40
1.58
t-Bu
Me
S
N
O
Ph
O
4pa
1H NMR (400 MHz, CDCl3)
1.94
1.00
1.99
3.03
9.01
f1 (ppm)


174.7
136.4
132.0
129.4
128.1
77.3
60.6
32.5
23.2
t-Bu
Me
N
S
O
Ph
O
4pa
13C NMR (101 MHz, CDCl3)
f1 (ppm)



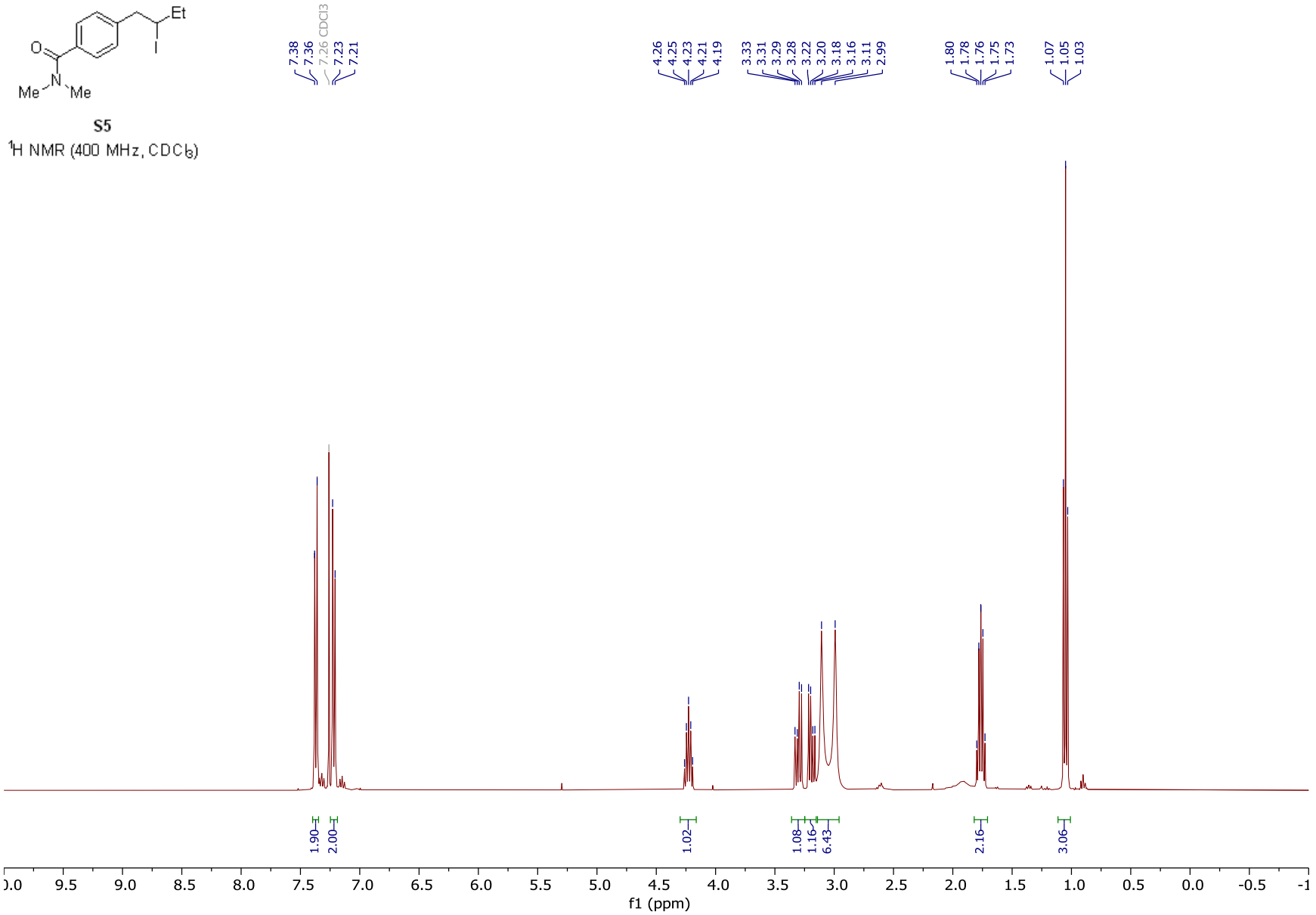
S4

^{1}H NMR (400 MHz, $CDCl_3$)



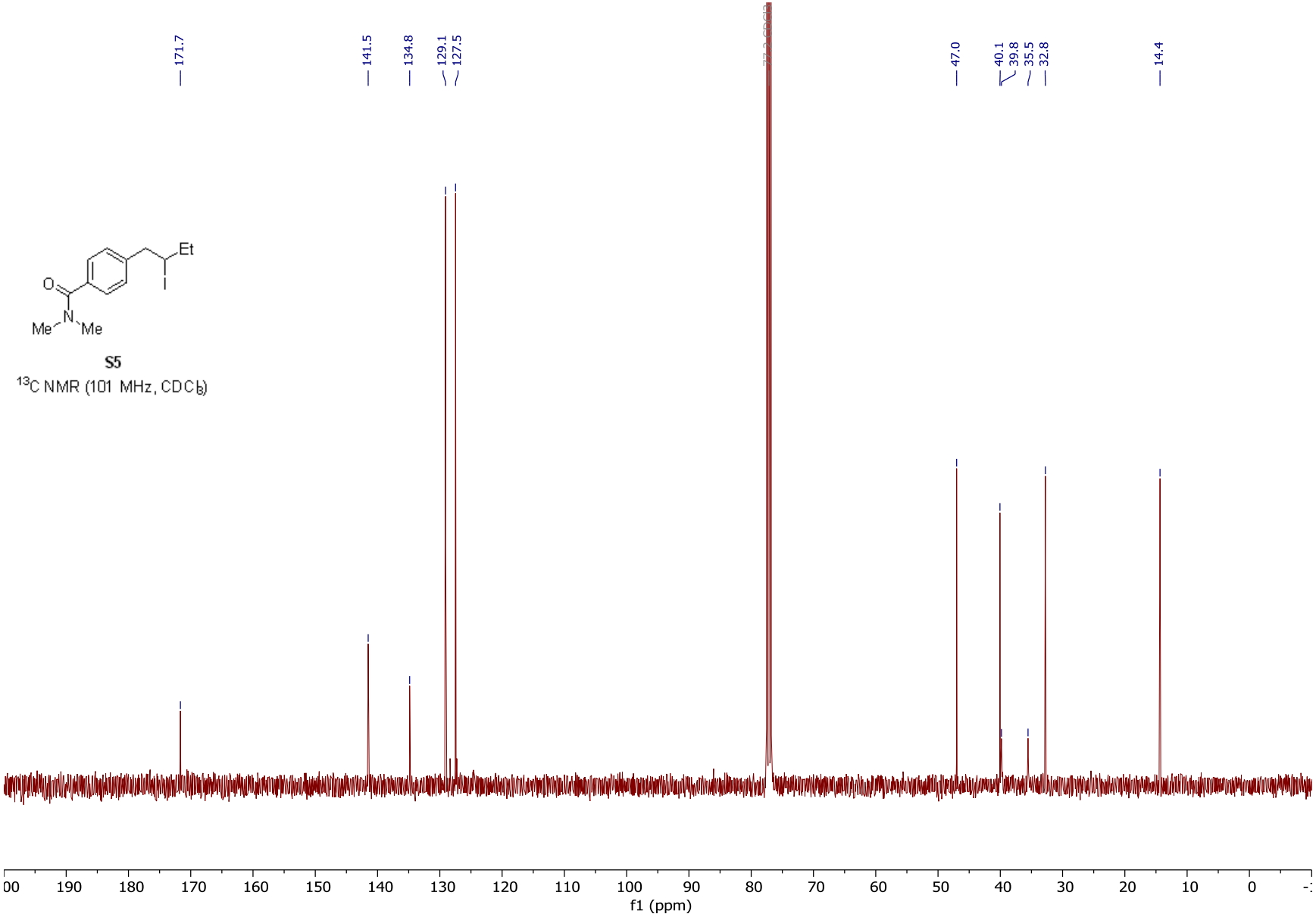
S4

^{13}C NMR (101 MHz, $CDCl_3$)



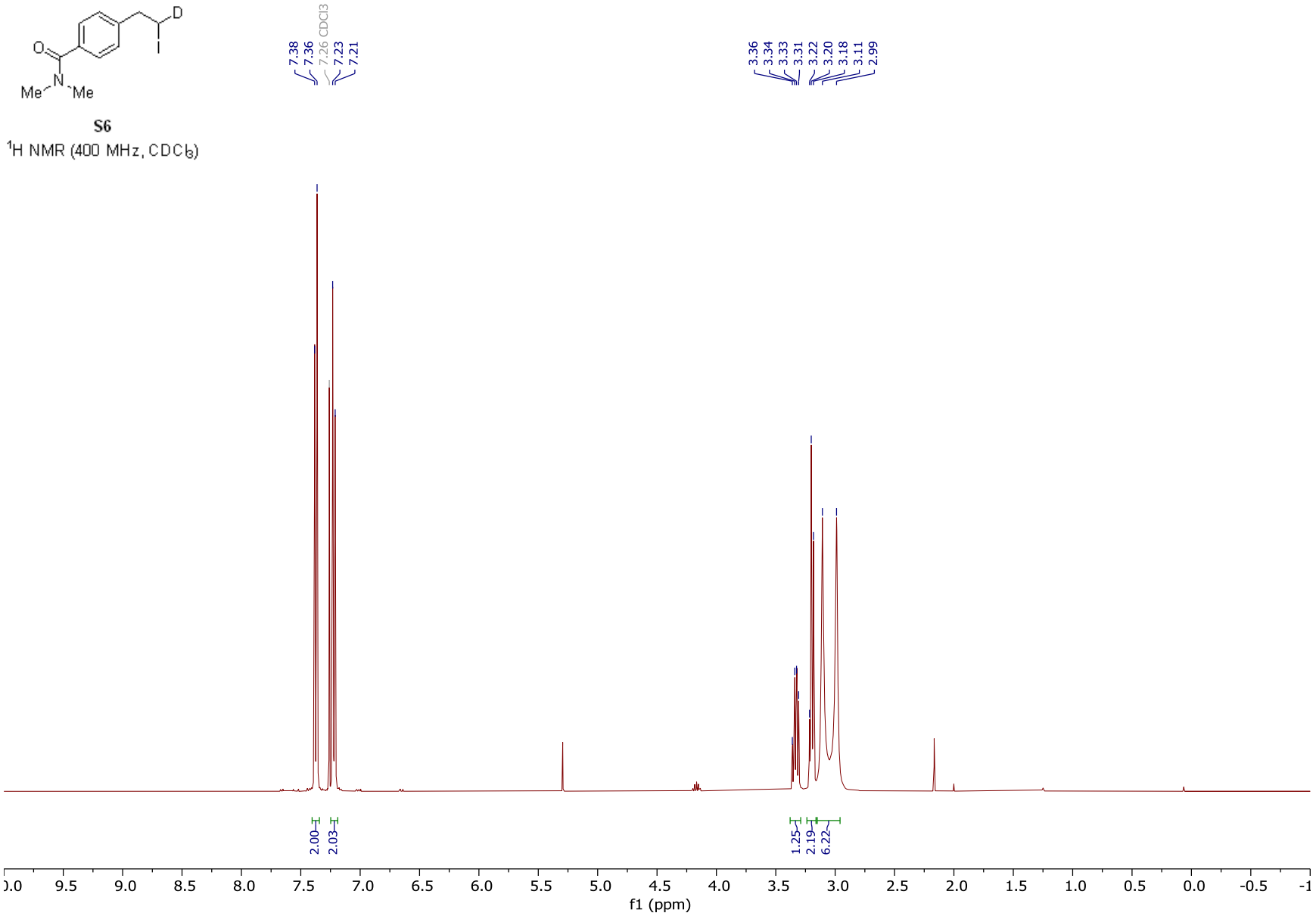
S5

^{1}H NMR (400 MHz, $CDCl_3$)



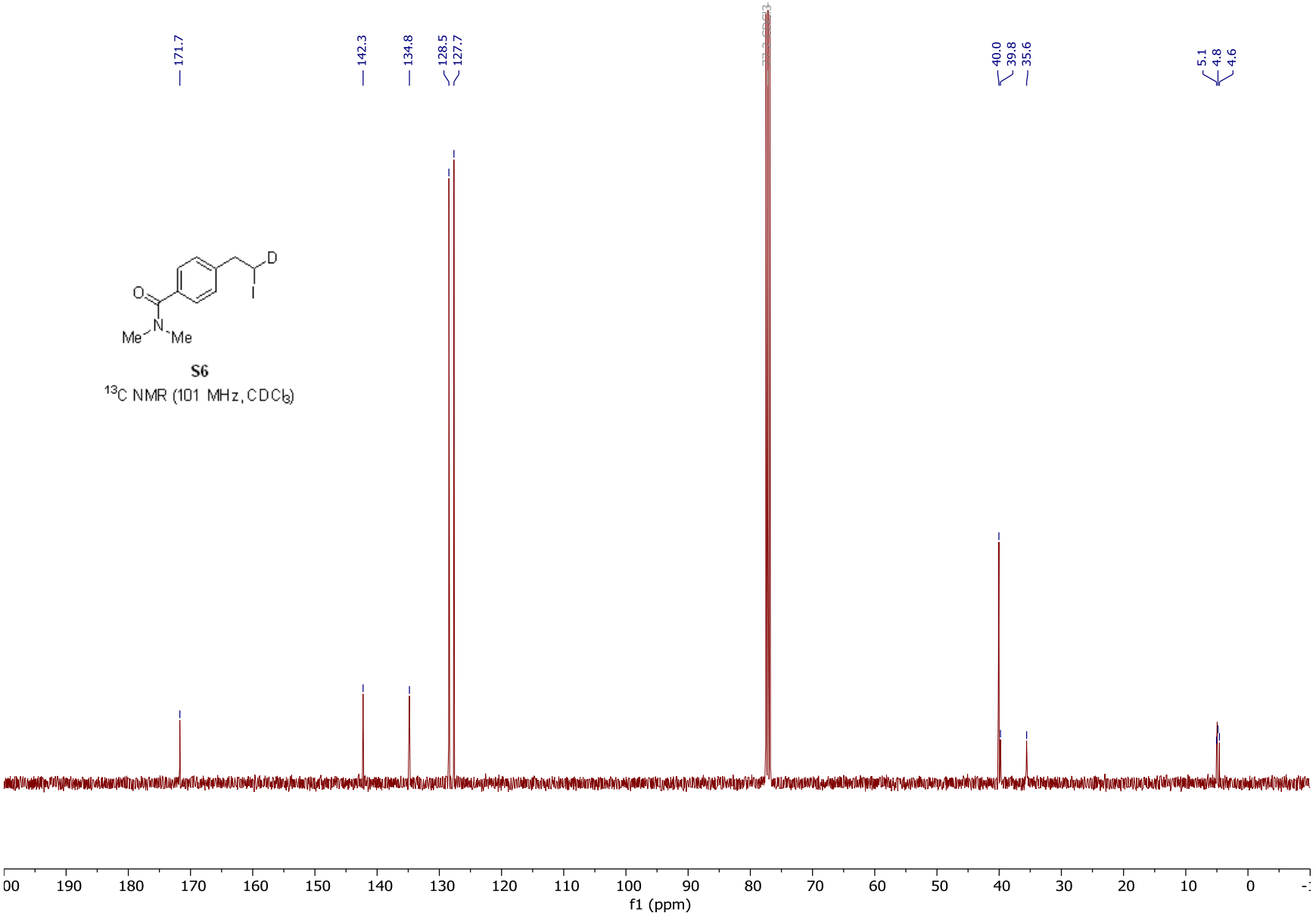
S5

^{13}C NMR (101 MHz, $CDCl_3$)



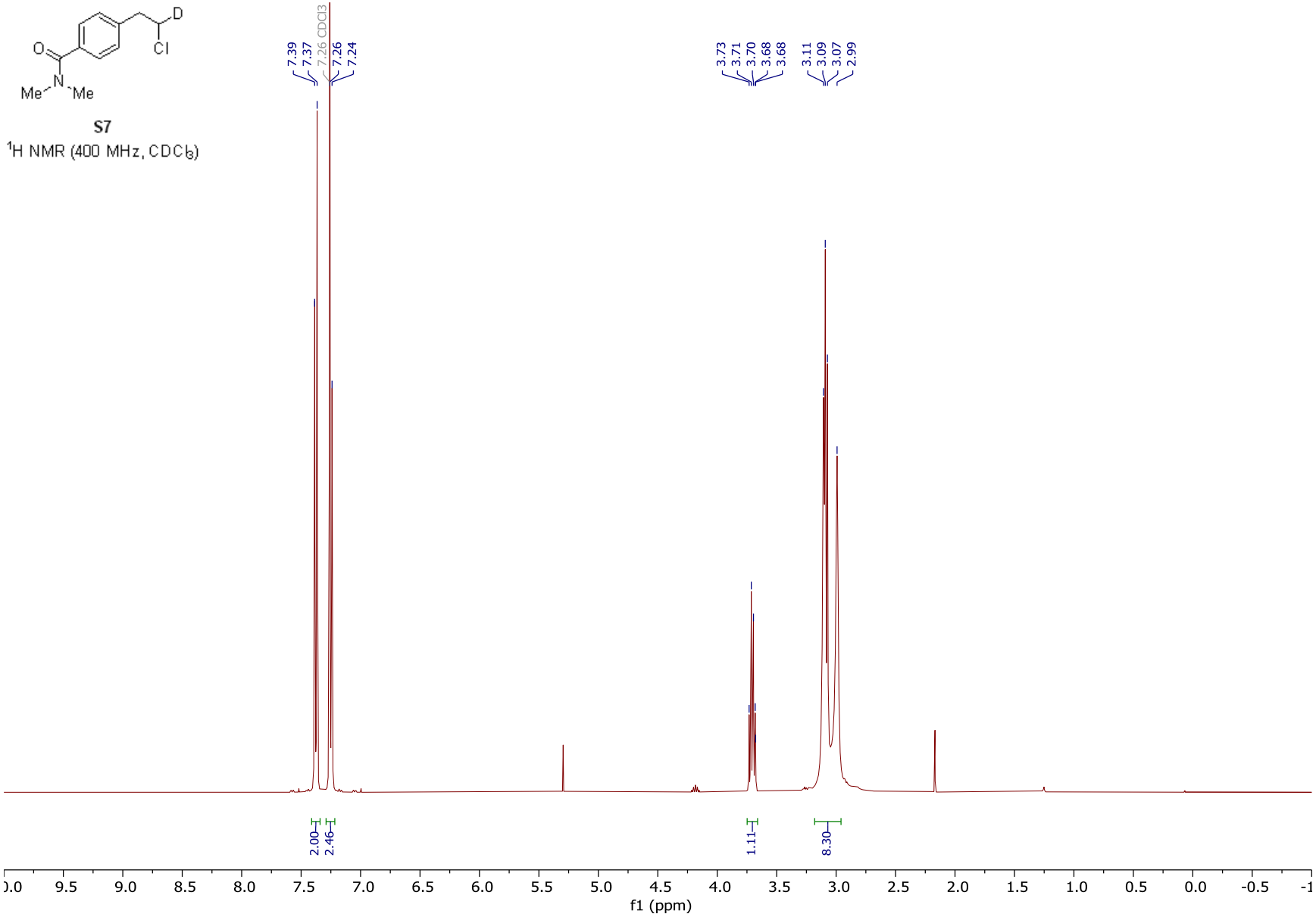
S6

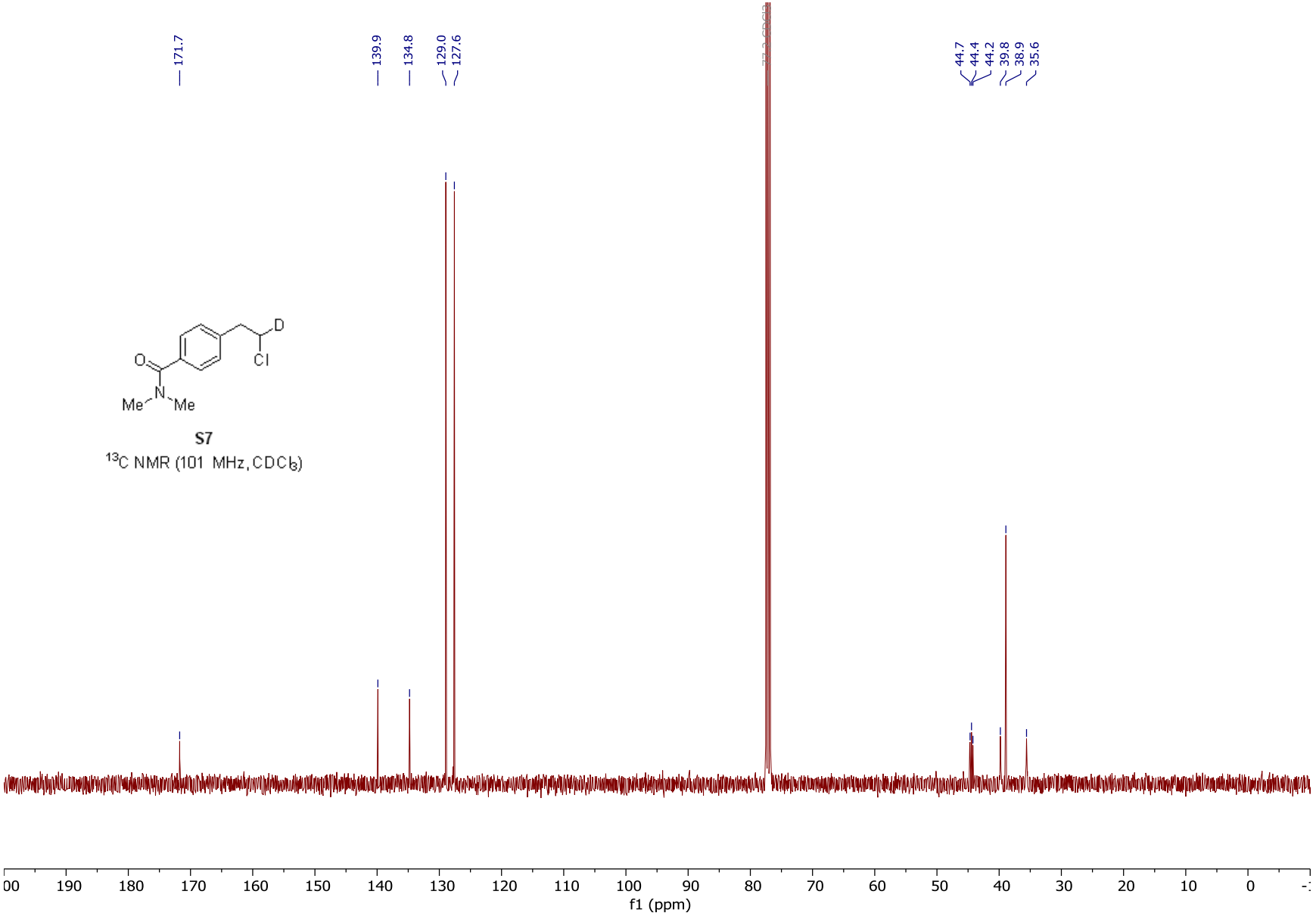
^{1}H NMR (400 MHz, $CDCl_3$)



S6

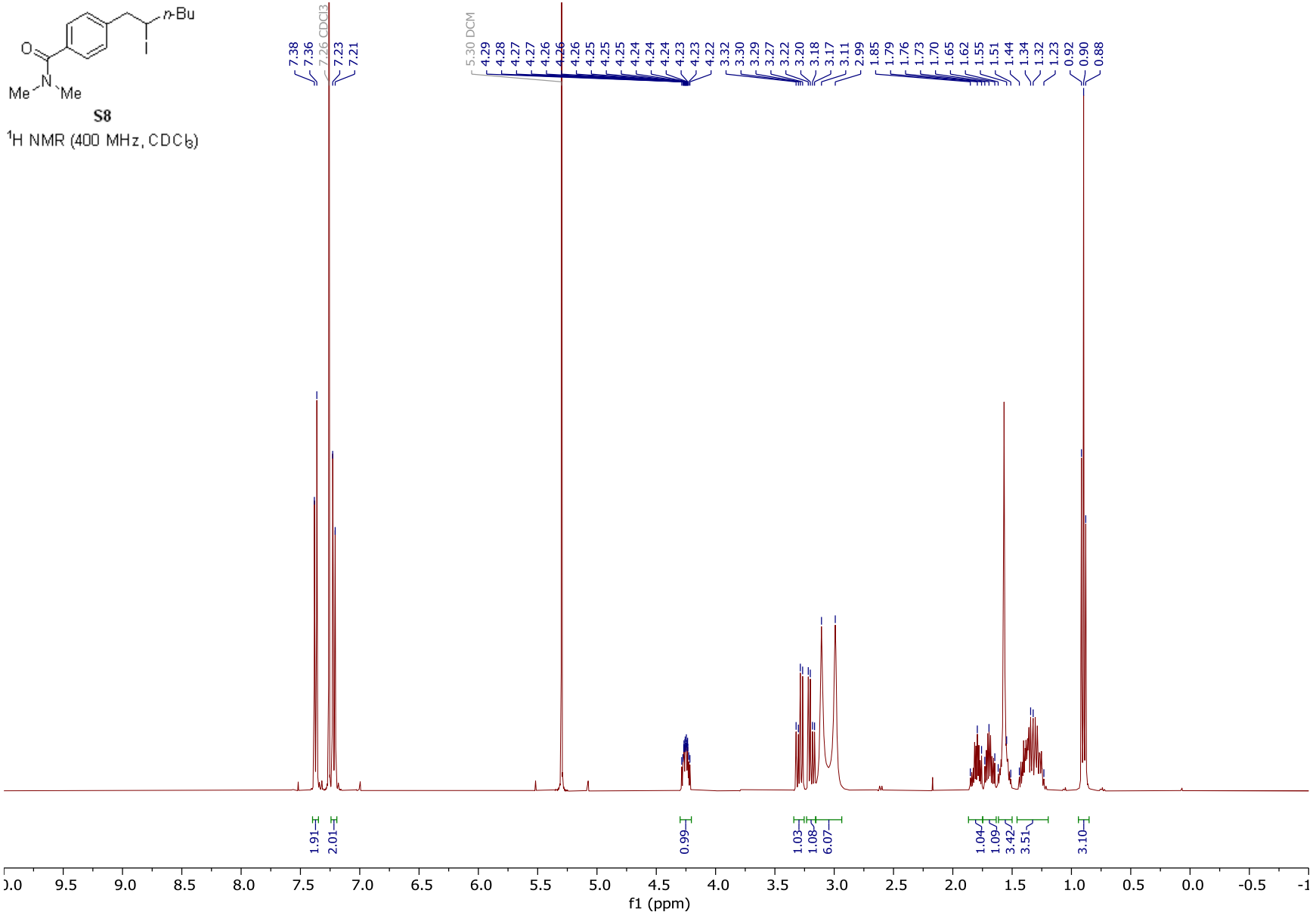
^{13}C NMR (101 MHz, $CDCl_3$)

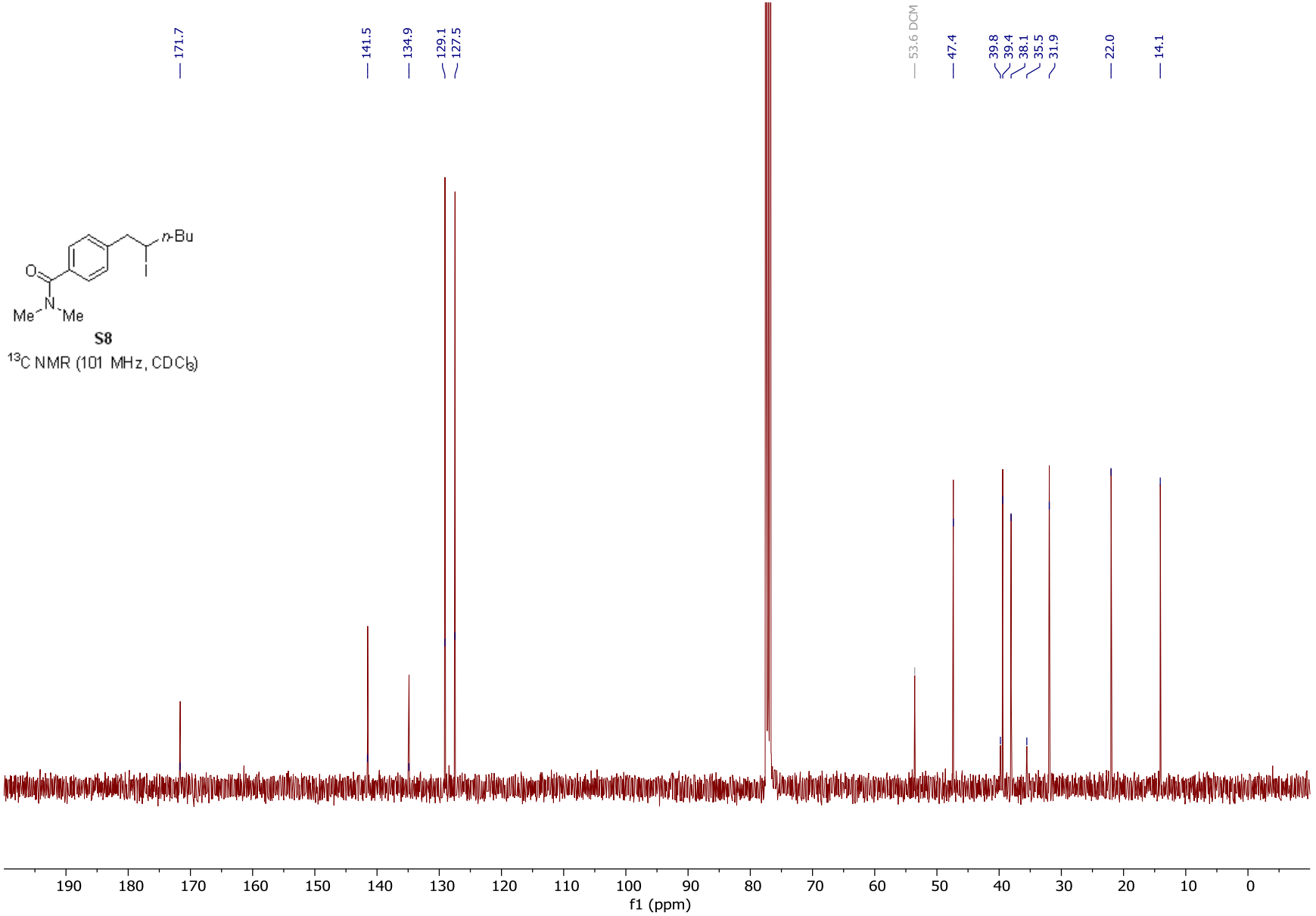

D
O
Cl
N
Me
Me
S7
1H NMR (400 MHz, CDCl3)
7.39
7.37
7.26 CDCl3
7.26
7.24
3.73
3.71
3.70
3.68
3.68
3.11
3.09
3.07
2.99
2.00
2.46
1.11
8.30
f1 (ppm)



S7

^{13}C NMR (101 MHz, $CDCl_3$)


n-Bu
O
N
Me
Me
I
S8
1H NMR (400 MHz, CDCl3)
7.38
7.36
7.26 CDCl3
7.23
7.21
5.30 DCM
4.29
4.28
4.27
4.27
4.26
4.26
4.26
4.25
4.25
4.24
4.24
4.24
4.23
4.23
4.22
3.32
3.30
3.29
3.27
3.22
3.20
3.18
3.17
3.11
2.99
1.85
1.79
1.76
1.73
1.70
1.65
1.62
1.55
1.51
1.44
1.34
1.32
1.23
0.92
0.90
0.88
1.91
2.01
0.99
1.03
1.08
6.07
1.04
1.09
3.42
3.51
3.10
f1 (ppm)


171.7
141.5
134.9
129.1
127.5
53.6 DCM
47.4
39.8
39.4
38.1
35.5
31.9
22.0
14.1
n-Bu
I
O
N
Me
Me
S8
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

HPLC chromatograms for 4na

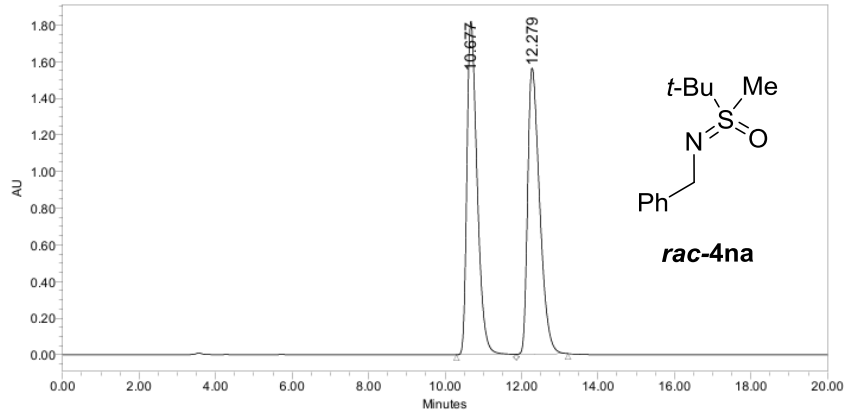
Empower2 software

AK_Report_1

SAMPLE INFORMATION

Sample Name:	rac-4na_IC_20IPA_80Hept	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	007
Vial:	44	Acq. Method Set:	mp3
Injection #:	1	Processing Method:	Glebs
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	2024.11.07. 16:26:53 EET		
Date Processed:	2024.11.07. 17:12:05 EET		

Name: rac-4na
Column: Chiralpak IC 4.6 mm x 250 mm, 5 um
Sample: 1 mg/mL
Flow: 1 mL/min
Eluent: 20% IPA, 80% Hept



	RT	Height	Area	% Area
1	10.677	1821372	33725459	49.91
2	12.279	1561596	33852870	50.09

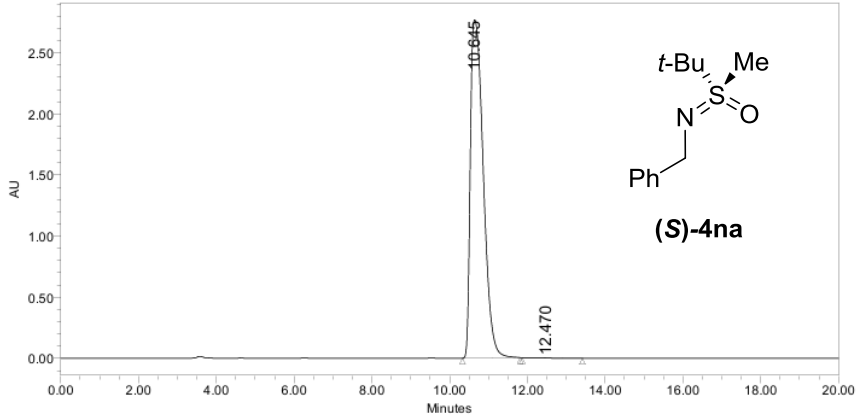
Empower2 software

AK_Report_1

SAMPLE INFORMATION

Sample Name:	S-4na_IC_20IPA_80Hept	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	007
Vial:	45	Acq. Method Set:	mp3
Injection #:	1	Processing Method:	Glebs
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	2024.11.07. 16:47:43 EET		
Date Processed:	2024.11.07. 17:18:55 EET		

Name: S-4na
Column: Chiralpak IC 4.6 mm x 250 mm, 5 um
Sample: 1 mg/mL
Flow: 1 mL/min
Eluent: 20% IPA, 80% Hept



	RT	Height	Area	% Area
1	10.645	2769450	63901907	99.83
2	12.470	233	110785	0.17