Quantitative Modeling of Bis(pyridine)silver (I) Permanganate Oxidation of Hydantoin Derivatives: Guidelines for Predicting the Site of Oxidation in Complex Substrates

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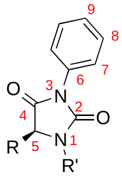
Supporting Information

General Procedures. Unless otherwise stated, all reactions were performed under an argon atmosphere, either in oven-dried or flame-dried round bottom flasks, or modified Schlenk (Kjeldahl shape) flasks. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash column chromatography was performed as described by Still et al. using silica gel (60 Å pore size, 40–63 µm, 4-6% H_2O content).[1] Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or an aqueous solution of ceric ammonium molybdate (CAM) followed by heating (<1 min) on a hot plate (~250 °C). Organic solutions were concentrated on rotary evaporators at ~2 torr (house vacuum) at 25–35 °C, then at ~0.5 torr (vacuum pump) unless otherwise indicated.

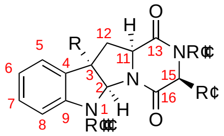
Materials. Commercial reagents and solvents were used as received with the following exceptions: dichloromethane, acetonitrile, tetrahydrofuran, methanol, *N*,*N*-dimethylformamide and triethylamine were purchased from J. T. Baker (Cycletainer TM) and were purified by the method of Grubbs et al. under positive argon pressure.[2] Permanaganate oxidant was stored at 0 °C and remained in good condition for a month. All amino acid derivatives were purchased from Chem-Impex International. All other solvents and chemicals were purchased from either Sigma–Aldrich, Strem Chemicals, or Alfa Aesar–Johnson Matthey.

Instrumentation. Nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were recorded with Varian inverse probe INOVA-500, Varian INOVA-500, and Bruker AVANCE III 400 spectrometers, and are reported in parts per million on the δ scale. ^{1}H NMR are referenced from the residual protium in the NMR solvent (Chloroform-*d*: δ 7.26 ($CHCl_3$), Acetone-d_6: δ 2.05 (Acetone-d_5)). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet), coupling constant(s) in Hertz (Hz), integration, assignment]. ^{13}C NMR are referenced from the carbon resonances of the solvent ($CDCl_3$: δ 77.23, Acetone-d_6: δ 29.92). Data are reported as follows: chemical shift (assignment). Infrared data (IR) were obtained with a Perkin-Elmer 2000 FTIR, and are reported as follows: frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad). Optical rotations were measured on a Jasco-1010 polarimeter. We are grateful to Dr. Li Li for obtaining the mass spectrometric data at the Department of Chemistry's Instrumentation Facility, Massachusetts Institute of Technology. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics APEXIV 4.7 Tesla FTICR-MS using an electrospray (ESI) ionization source.

Positional Numbering System. Numbering of the hydantoin and diketopiperazine substrates is shown below.

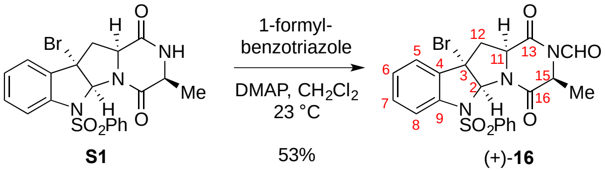


Hydantoin
23- **46**



Tetracyclic Diketopiperazine
(+)-**10**- **17**, **47**- **51**

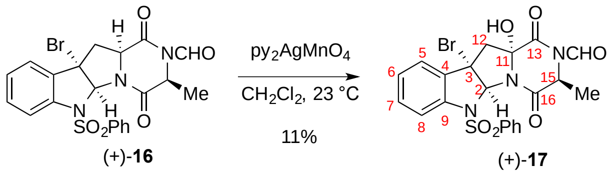
Diketopiperazine Hydroxylation Case Studies



N-formyl Tetracyclic Diketopiperazine (+)-16:

A sample of 1-formylbenzotriazole (242 mg, 1.98 mmol, 3.00 equiv) was added in one portion as a solid to a solution of diketopiperazine **S1**[3] (315 mg, 661 µmol, 1 equiv) and 4-dimethylaminopyridine (242 mg, 1.98 mmol, 3.00 equiv) in dichloromethane (10 mL) under an argon atmosphere. After 24 h, the reaction mixture was diluted in dichloromethane (15 mL) and washed with a saturated aqueous solution of ammonium chloride (1 × 30 mL). The aqueous phase was extracted with dichloromethane (2 × 20 mL) and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude yellow oil was purified via flash column chromatography (eluent: 5% acetone in dichloromethane) to yield *N*-formyl diketopiperazine (+)-**16** (176 mg, 349 µmol, 52.8%) as a white solid.

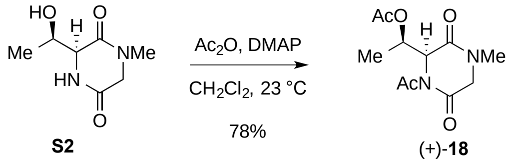
^{1}H NMR (500 MHz, CDCl$_3$, 25 ºC):	δ 9.27 (s, 1H, N$_{14}$C**H**O), 7.88 (d, *J* = 7.9 Hz, 2H, SO$_2$Ph-*o*-**H**), 7.63 (d, *J* = 8.2 Hz, 1H, C$_8$**H**), 7.54 (t, *J* = 7.4 Hz, 1H, SO$_2$Ph-*p*-**H**), 7.42 (t, *J* = 7.8 Hz, 2H, SO$_2$Ph-*m*-**H**), 7.40 – 7.35 (m, 2H, C$_5$**H**, C$_7$**H**), 7.22 (t, *J* = 7.6 Hz, 1H, C$_6$**H**), 6.51 (s, 1H, C$_2$**H**), 4.87 (q, *J* = 7.1 Hz, 1H, C$_{15}$**H**), 4.10 (dd, *J* = 10.6, 6.0 Hz, 1H, C$_{11}$**H**), 3.30 (dd, *J* = 13.2, 6.0 Hz, 1H, C$_{12}$**H$_a$**), 2.99 (dd, *J* = 13.2, 10.7 Hz, 1H, C$_{12}$**H$_b$**), 1.38 (d, *J* = 7.1 Hz, 3H, C$_{15}$**Me**).
^{13}C NMR (125 MHz, CDCl$_3$, 25 ºC):	δ 167.4 (**C$_{13}$**), 164.1 (**C$_{16}$**), 160.0 (N$_{14}$**C**HO), 141.0 (**C$_9$**), 138.1 (SO$_2$Ph-*ipso*-**C**), 133.9 (SO$_2$Ph-*p*-**C**H), 132.5 (**C$_4$**), 131.5 (**C$_5$**), 129.2 (SO$_2$Ph-*m*-**C**H), 128.0 (SO$_2$Ph-*o*-**C**H), 126.6 (**C$_6$**), 124.7 (**C$_7$**), 117.9 (**C$_8$**), 85.7 (**C$_2$**), 58.5 (**C$_{11}$**), 57.7 (**C$_3$**), 52.3 (**C$_{15}$**), 46.3 (**C$_{12}$**), 18.3 (C$_{15}$**Me**).
FTIR (thin film) cm^{-1}:	1731 (m), 1699 (s), 1398 (m), 1367 (m), 1265 (w), 1221 (m), 1205 (m), 1170 (m), 1037 (w), 907(s), 726 (s), 686 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{21}H_{19}N_3O_5S$, [M+H]$^+$: 504.0223, found: 504.0228.
$[\alpha]_D^{23}$:	+176 (c = 0.17, CHCl$_3$).
TLC (5% acetone in dichloromethane), R*f*:	0.52 (UV, CAM).



***N*-formyl Tetracyclic alcohol (+)-17:**

Bis(pyridine)silver(I) permanganate (137 mg, 360 µmol, 3.00 equiv) was added in one portion as a solid to a solution of *N*-formyl diketopiperazine (+)-**16** (50.0 mg, 99.1 µmol, 1 equiv) in dichloromethane (1.2 mL) under an argon atmosphere resulting in a dark purple solution. After 2 h, the brown/purple reaction mixture was diluted in ethyl acetate (20 mL) and washed with a saturated aqueous solution of sodium bisulfite (25 mL) and the aqueous layer was extracted with ethyl acetate (2 × 15 mL). The organic layers were combined and washed with a saturated aqueous solution of ammonium chloride (1 × 20 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to yield a crude white solid. The crude solid was purified via flash column chromatography on silica gel (eluent: 3→5% acetone in dichloromethane) to yield *N*-formyl-tetracyclic alcohol (+)-**17** (5.6 mg, 10.8 µmol, 10.9%) as a white solid, and separately the recovered diketopiperazine (+)-**16** (20.5 mg, 40.6 µmol, 41.1%).

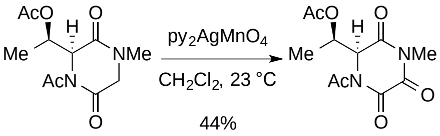
^{1}H NMR (500 MHz, CDCl$_3$, 25 ºC):	δ 9.29 (s, 1H, N$_{14}$C**H**O), 7.94–7.85 (m, 2H, SO$_2$Ph-*o*-**H**), 7.66 (d, *J* = 8.3 Hz, 1H, C$_8$**H**), 7.55 (t, *J* = 7.5 Hz, 1H, SO$_2$Ph-*p*-**H**), 7.50–7.37 (m, 4H, SO$_2$Ph-*m*-**H**, C$_5$**H**, C$_7$**H**), 7.26 (d, *J* = 14.9 Hz, 1H, C$_6$**H**), 6.60 (s, 1H, C$_2$**H**), 4.86 (q, *J* = 7.1 Hz, 1H, C$_{15}$**H**), 3.35 (d, *J* = 14.5 Hz, 1H, C$_{12}$**H$_a$**), 3.28 (d, *J* = 14.5 Hz, 1H, C$_{12}$**H$_b$**), 2.72 (s, 1H, C$_{11}$O**H**), 1.51 (d, *J* = 7.1 Hz, 3H, C$_{15}$**Me**).
^{13}C NMR (125 MHz, CDCl$_3$, 25 ºC):	δ 166.2 (**C$_{13}$**), 165.5 (**C$_{16}$**), 160.4 (N$_{14}$**C**HO), 140.3 (**C$_9$**), 138.6 (SO$_2$Ph-*ipso*-**C**), 134.8 (**C$_4$**), 134.0 (SO$_2$Ph-*p*-**C**H), 131.6 (**C$_5$**), 129.2 (SO$_2$Ph-*m*-**CH)**, 128.1 (SO$_2$Ph-*o*-**C**H), 126.8 (**C$_6$**), 124.4 (**C**$_7$), 118.8 (**C$_8$**), 88.1 (**C$_{11}$**), 87.0 (**C**$_2$), 56.5 (**C**$_3$), 53.4 (**C$_{12}$**), 53.2 (**C$_{15}$**), 19.1 (C$_{15}$**Me**).
FTIR (thin film) cm^{-1}:	3247 (br-w), 1730 (s), 1717 (s), 1675 (s), 1409 (m), 1368 (s), 1242 (m), 1171 (s), 913 (w), 758 (w), 727 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{21}H_{22}BrN_4O_6S$, [M+NH$_4$]$^+$: 537.0438, found: 537.0449.
[α]$_D^{23}$:	+198 (c = 0.11, CHCl$_3$).
TLC (5% acetone in dichloromethane), R*f*:	0.36 (UV, CAM).



<u>Diketopiperzine (+)-18:</u>

Acetic anhydride (343 µL, 4.36 mmol, 3.00 equiv) was added dropwise over 30 seconds to a fine suspension of diketopiperazine **S2** (250 mg, 1.45 mmol, 1 equiv) and 4-dimethylaminopyridine (371 mg, 3.63 mmol, 2.50 equiv) in dichloromethane (15 mL). After 2.5 h, the reaction mixture was diluted in dichloromethane (20 mL) and washed with a saturated aqueous solution of sodium bicarbonate (1 × 50 mL). The aqueous phase was extracted with ethyl acetate (2 × 25 mL) and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude yellow oil was purified via flash column chromatography (eluent: 20% acetone in dichloromethane) to afford diketopiperazine (+)**-18** (289 mg, 1.13 mmol, 77.8%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC):	δ 5.27 (qd, *J* = 6.4, 4.2 Hz, 1H, C**H**OAc), 5.19 (d, *J* = 4.3 Hz, 1H, C**H**C=O), 4.26 (d, *J* = 18.4 Hz, 1H, C**H**$_2$C=O), 3.92 (d, *J* = 18.4 Hz, 1H, COC**H**$_2$), 2.90 (s, 3H, NC**H**$_3$), 2.48 (s, 3H, NCOC**H**$_3$), 1.93 (s, 3H, CHOCOC**H**$_3$), 1.18 (d, *J* = 6.5 Hz, 3H, CHC**H**$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC):	δ 170.8 (N**C**OMe), 169.1 (CHO**C**OMe), 167.4 (AcN**C**=O), 164.9 (MeN**C**=O), 72.1 (**C**HOCOMe), 58.9 (**C**HC=O), 53.5 (**C**H$_2$), 33.4 (N**C**H$_3$), 26.5 (NCO**C**H$_3$), 21.1 (CHOCO**C**H$_3$), 17.4 (H$_3$**C**CHOAc).
FTIR (thin film) cm^{-1}:	2989 (w), 1742 (s), 1713 (s), 1674 (s), 1369 (s), 1218 (s), 1084 (w), 1041 (w), 911 (m), 784 (w), 726 (s).
HRMS (DART) (*m*/*z*):	calc'd for $C_{11}H_{17}N_2O_5$, $[M+H]^+$: 257.1132, found: 257.1114.
$[\alpha]_D^{23}$:	+191 (c = 0.70, $CHCl_3$).
TLC (20% acetone in dichloromethane), R*f*:	0.58 (UV, CAM).



(+)-**18** (+)-**19**

Triketopiperzine (+)-19:

Bis(pyridine)silver(I) permanganate (449 mg, 1.17 mmol, 3.00 equiv) was added in one portion as a solid to a solution of diketopiperazine (+)-**18** (100 mg, 390 µmol, 1 equiv) in dichloromethane (5.0 mL) under an argon atmosphere resulting in a dark purple solution. After 2 h, the brown/purple reaction mixture was diluted in ethyl acetate (20 mL) and washed with a saturated aqueous solution of sodium bisulfite (50 mL). The aqueous layer was extracted with ethyl acetate (2 × 25 mL). The organic layers were combined and washed with a saturated aqueous solution of ammonium chloride (1 × 50 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to yield a crude white solid. The crude solid was purified via flash column chromatography on silica gel (eluent: 5% acetone in dichloromethane) to yield triketopiperazine (+)-**19** (46.4 mg, 172 µmol, 44.0%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 5.58 (d, *J* = 1.7 Hz, 1H, C**H**C=O), 5.31 (qd, *J* = 6.5, 1.8 Hz, 1H, C**H**OAc), 3.21 (s, 3H, NC**H**$_3$), 2.64 (s, 3H, NCOC**H**$_3$), 1.91 (s, 3H, CHOCOC**H**$_3$), 1.23 (d, *J* = 6.6 Hz, 3H, CHC**H**$_3$).

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 171.0 (N**C**OMe), 168.8 (CHO**C**OMe), 166.4 (MeN**C**=O), 157.4 (MeN**C**=O(C=O)), 154.4 (AcN**C**=O(C=O)), 72.0 (**C**HOCOMe), 59.2 (**C**HC=O), 27.8 (N**C**H$_3$), 26.4 (NCO**C**H$_3$), 20.7 (CHOCO**C**H$_3$), 17.8 (H$_3$**C**CHOAc).

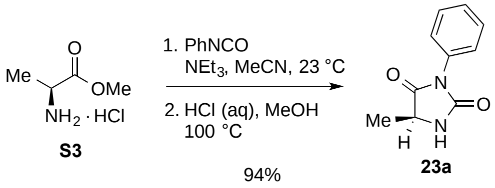
FTIR (thin film) cm^{-1}: 1741 (m), 1693 (s), 1356 (m), 1325 (m), 1211 (s), 1041 (w), 910 (m), 802 (w), 729 (s).

HRMS (DART) (*m*/*z*): calc'd for $C_{11}H_{18}N_3O_6$, $[M+NH_4]^+$: 288.1196, found: 288.1173.

$[\alpha]_D^{23}$: +56 (c = 0.39, $CHCl_3$).

TLC (5% acetone in dichloromethane), R*f*: 0.62 (UV, CAM).

Hydantoin Synthesis



<u>Representative procedure-A for synthesis of hydantoin substrates. Hydantoin 23a:</u>

Triethylamine (5.50 mL, 39.4 mmol, 1.10 equiv) was added to a solution of L-alanine methyl ester hydrogen chloride **S3** (5.00 g, 35.8 mmol, 1 equiv) in acetonitrile (300 mL) under an argon atmosphere. Phenyl isocyanate (4.10 mL, 37.6 mmol, 1.05 equiv) was added dropwise via syringe over 3 min to the resulting solution. After 3 h, saturated aqueous sodium chloride solution (150 mL) was added, the layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting light yellow foam was dissolved in methanol (100 mL) and aqueous hydrogen chloride solution (6 N, 100 mL) and heated to 100 °C. After 3 h, the reaction mixture was allowed to cool to ambient temperature and diluted with deionized water (100 mL). The reaction mixture was extracted with ethyl acetate (4 × 200 mL) and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to yield a white solid. The crude product after workup is of high enough purity for use in the subsequent step. For analytical purposes, the crude solid was purified via flash column chromatography on silica gel (eluent: 10% acetone in dichloromethane) to yield hydantoin **23a** (6.40 g, 33.6 mmol, 94.0% over two steps) as a white solid.

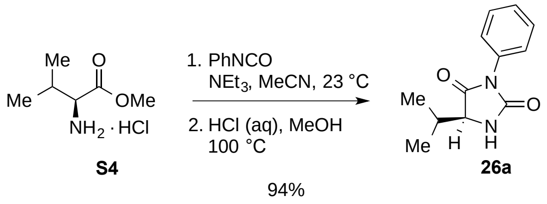
^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC): δ 7.53–7.44 (m, 2H, C$_8$**H**), 7.43–7.35 (m, 3H, C$_7$**H**, C$_9$**H**), 7.01 (s, 1H, N$_1$**H**), 4.19 (qd, *J* = 6.9, 1.3 Hz, 1H, C$_5$**H**), 1.51 (d, *J* = 7.0 Hz, 3H, C$_5$**Me**).

^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC): δ 173.8 (**C$_4$**), 157.0 (**C$_2$**), 131.6 (**C$_6$**), 129.3 (**C$_7$**), 128.5 (**C$_9$**), 126.4 (**C$_8$**), 53.1 (**C$_5$**), 17.9 (C$_5$**Me**).

FTIR (thin film) cm^{-1}: 3212 (br-m), 3108 (w), 1769 (w), 1704 (s), 1501 (m), 1419 (m), 1333 (m), 1182 (m).

HRMS (DART) (*m*/*z*): calc'd for $C_{10}H_{11}N_2O_2$, $[M+H]^+$: 191.0815, found: 191.0817.

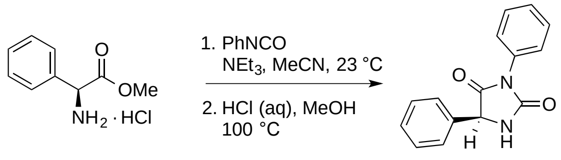
TLC (10% acetone in dichloromethane), R*f*: 0.32 (UV, CAM).



Hydantoin 26a:

The hydantoin **26a** was prepared following the representative procedure-A using L-valine methyl ester hydrogen chloride **S4** (3.00 g, 17.9 mmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 10% acetone in dichloromethane) to yield hydantoin **26a** (3.68 g, 16.9 mmol, 94.2% over two steps) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.53–7.44 (m, 2H, C$_8$**H**), 7.40–7.33 (m, 3H, C$_7$**H**, C$_9$**H**), 6.19 (s, 1H, N$_1$**H**), 4.08 (dd, *J* = 3.7, 1.3 Hz, 1H, C$_5$**H**), 2.33 (hd, *J* = 6.9, 3.7 Hz, 1H, C$_5$C**H**), 1.10 (d, *J* = 7.0 Hz, 3H, C$_5$CH**Me$_a$**), 1.02 (d, *J* = 6.8 Hz, 3H, C$_5$CH**Me$_b$**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 172.5 (**C$_4$**), 157.1 (**C$_2$**), 131.6 (**C$_6$**), 129.3 (**C$_7$**), 128.5 (**C$_9$**), 126.4 (**C$_8$**), 62.3 (**C$_5$**), 30.8 (C$_5$**C**H), 18.9 (C$_5$CH**C$_a$**H$_3$), 16.2 (C$_5$CH**C$_b$**H$_3$).
FTIR (thin film) cm^{-1}:	3295 (br-m), 1776 (w), 1709 (s), 1500 (w), 1412 (m), 1172 (w), 804 (w).
HRMS (DART) (*m*/*z*):	calc'd for $C_{12}H_{15}N_2O_2$, [M+H]$^+$: 219.1128, found: 219.1130.
TLC (5% acetone in dichloromethane), R*f*:	0.41 (UV, CAM).

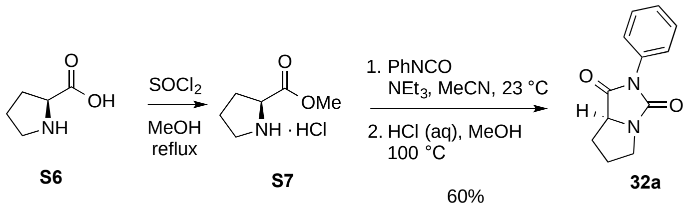


S5 90% **29a**

Hydantoin 29a:

The hydantoin **29a** was prepared following the representative procedure-A using L-phenylglycine methyl ester hydrogen chloride **S5** (2.00 g, 9.92 mmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 10% acetone in dichloromethane) to yield hydantoin **29a** (2.25 g, 8.92 mmol, 89.9% over two steps) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.63–7.32 (m, 10H, **ArH**), 6.53 (s, 1H, N$_1$**H**), 5.19 (d, *J* = 1.3 Hz, 1H, C$_5$**H**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 170.8 (**C**$_4$), 156.6 (**C**$_2$), 134.2, 131.4, 129.3, 129.3, 129.2, 128.4, 126.6, 126.2, 60.6 (**C**$_5$).
FTIR (thin film) cm^{-1}:	3304 (br-w), 1779 (w), 1714 (s), 1496 (w), 1411 (m), 1173 (w), 704 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{15}H_{13}N_2O_2$, $[M+H]^+$: 253.0972, found: 253.0969.
TLC (40% ethyl acetate in hexanes), R*f*:	0.30 (UV, CAM).



Hydantoin 32a:

L-Proline methyl ester hydrogen chloride **S7** was prepared from L-proline **S6** (2.00 g, 17.4 mmol, 1 equiv) following literature procedure.[4] The hydantoin **32a** was prepared following the representative procedure-A using L-proline methyl ester hydrochloride **S7**. The crude product after workup was purified via flash column chromatography on silica gel (eluent: 50% ethyl acetate in hexanes) to yield hydantoin **32a** (2.25 g, 10.4 mmol, 59.8%, over three steps) as a white solid.

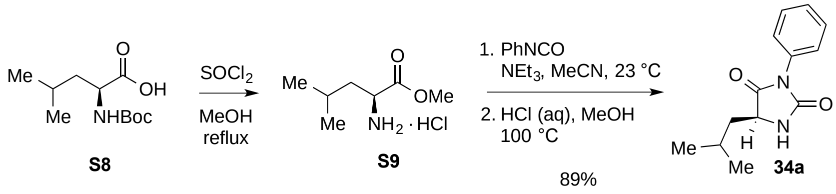
^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC): δ 7.49–7.42 (m, 2H, C$_8$**H**), 7.42–7.37 (m, 3H, C$_7$**H**, C$_9$**H**), 4.24 (dd, *J* = 9.3, 7.5 Hz, 1H, C$_5$**H**), 3.79 (dt, *J* = 11.3, 7.7 Hz, 1H, N$_1$C**H$_a$**), 3.34 (ddd, *J* = 11.3, 8.3, 4.6 Hz, 1H, N$_1$C**H$_b$**), 2.35 (dtd, *J* = 12.4, 7.2, 3.6 Hz, 1H, N$_1$CH$_2$C**H$_a$**), 2.27–2.04 (m, 2H, N$_1$CH$_2$C**H$_b$**, C$_5$C**H$_a$**), 1.85 (dtd, *J* = 12.6, 9.4, 8.3 Hz, 1H, C$_5$C**H$_b$**).

^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC): δ 172.8 (**C$_4$**), 159.5 (**C$_2$**), 132.0 (**C$_6$**), 129.3 (**C$_7$**), 128.3 (**C$_8$**), 126.1 (**C$_9$**), 63.4 (**C$_5$**), 46.0 (N$_1$**C**H$_2$), 28.0 (N$_1$CH$_2$**C**H$_2$), 27.1 (C$_5$**C**H$_2$).

FTIR (thin film) cm^{-1}: 2905 (w), 1775 (w), 1702 (s), 1598 (w), 1495 (w), 1402 (m), 1123 (m), 744 (w).

HRMS (DART) (*m*/*z*): calc'd for $C_{12}H_{13}N_2O_2$, [M+H]$^+$: 217.0972, found: 217.0976.

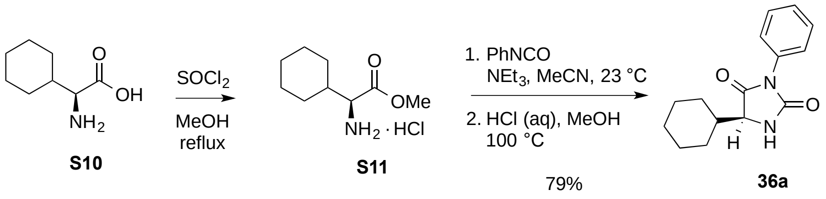
TLC (50% ethyl acetate in hexanes), R*f*: 0.35 (UV, CAM).



Hydantoin 34a:

L-Leucine methyl ester hydrogen chloride **S9** was prepared from *N*-Boc-L-leucine **S8** (8.00 g, 32.1 mmol, 1 equiv) following literature procedure.[4] The hydantoin **34a** was prepared following the representative procedure-A using L-leucine methyl ester hydrogen chloride **S9**. The crude product after workup was purified via flash column chromatography on silica gel (eluent: 35% ethyl acetate in hexanes) to yield hydantoin **34a** (6.61 g, 28.5 mmol, 88.7%, over three steps) as a white solid.

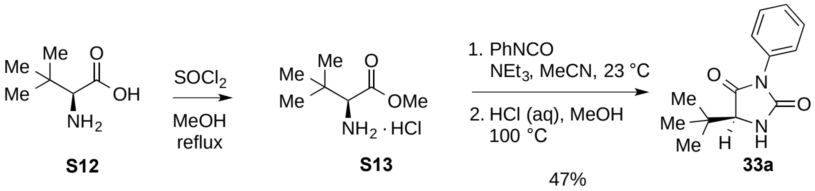
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):	δ 7.53–7.44 (m, 2H, C_8**H**), 7.42–7.32 (m, 3H, C_7**H**, C_9**H**), 6.47 (s, 1H, N_1**H**), 4.19 (ddd, *J* = 9.3, 4.0, 1.4 Hz, 1H, C_5**H**), 2.04–1.77 (m, 2H, C_5C**H_2**), 1.77–1.54 (m, 1H, C_5CH_2C**H**), 1.00 (d, *J* = 6.4 Hz, 3H, C_5CH_2CH**Me_a**), 0.98 (d, *J* = 6.3 Hz, 3H, C_5CH_2CH**Me_b**).
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC):	δ 173.5 (**C_4**), 156.8 (**C_2**), 131.7 (**C_6**), 129.3 (**C_8**), 128.4 (**C_9**), 126.3 (**C_7**), 55.9 (**C_5**), 41.2 (C_5**C**H_2), 25.3 (C_5CH_2**C**H), 23.2 (C_5CH_2CH**C_a**H_3), 21.9 (C_5CH_2CH**C_b**H_3).
FTIR (thin film) cm^{-1}:	3263 (br-w), 3112 (w), 1774 (w), 1727 (s), 1494 (w), 1430 (m), 1397 (m), 765 (w), 749 (w).
HRMS (DART) (*m*/*z*):	calc'd for $C_{13}H_{17}N_2O_2$, $[M+H]^+$: 233.1285, found: 233.1286.
TLC (35% ethyl acetate in hexanes), R*f*:	0.34 (UV, CAM).



Hydantoin 36a:

L-Cyclohexylglycine methyl ester hydrogen chloride **S11** was prepared from L-cyclohexylglycine **S10** (4.00 g, 25.4 mmol, 1 equiv) following literature procedure.[4] The hydantoin **36a** was prepared following the representative procedure-A using L-cyclohexylglycine methyl ester hydrogen chloride **S11**. The crude product after workup was purified via flash column chromatography on silica gel (eluent: 35% ethyl acetate in hexanes) to yield hydantoin **36a** (5.21 g, 20.2 mmol, 79.4% over three steps) as a white solid.

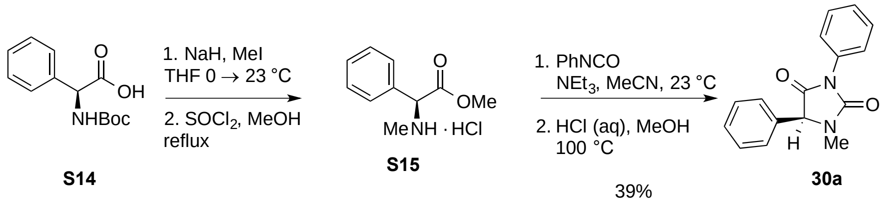
^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.55–7.41 (m, 2H, C$_8$**H**), 7.41–7.33 (m, 3H, C$_7$**H**, C$_9$**H**), 6.59 (s, 1H, N$_1$**H**), 4.03 (dd, *J* = 3.7, 1.3 Hz, 1H, C$_5$**H**), 1.99 (ddt, *J* = 11.9, 8.4, 3.4 Hz, 1H, C$_5$C**H**), 1.92–1.76 (m, 3H), 1.73–1.65 (m, 1H), 1.65–1.56 (m, 1H), 1.40–1.22 (m, 3H), 1.14 (tdt, *J* = 13.4, 10.7, 3.7 Hz, 2H).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 172.7 (**C$_4$**), 157.3 (**C$_2$**), 131.7 (**C$_6$**), 129.3 (**C$_8$**), 128.4 (**C$_9$**), 126.4 (**C$_7$**), 62.1 (**C$_5$**), 40.4 (C$_5$**C**H), 29.4, 26.5, 26.2, 26.0, 25.8.
FTIR (thin film) cm^{-1}:	3294 (br-w), 2924 (w), 2852 (w), 1776 (w), 1709 (s), 1501 (m), 1411 (m), 1169 (w), 693 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{15}H_{19}N_2O_2$, $[M+H]^+$: 259.1441, found: 259.1436.
TLC (35% ethyl acetate in hexanes), R*f*:	0.29 (UV, CAM).



Hydantoin 33a:

L-*tert*-Butylglycine methyl ester hydrogen chloride **S13** was prepared from L-*tert*-butylglycine **S12** (1.00 g, 7.62 mmol, 1 equiv) following literature procedure.[4] The hydantoin **33a** was prepared following the representative procedure-A using L-*tert*-butylglycine methyl ester hydrogen chloride **S11**. The crude product after workup was purified via flash column chromatography on silica gel (eluent: 35% ethyl acetate in hexanes) to yield hydantoin **33a** (833 mg, 3.59 mmol, 47.1% over three steps) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):	δ 7.63–7.41 (m, 2H, C_8**H**), 7.41–7.31 (m, 3H, C_7**H**, C_9**H**), 6.53 (s, 1H, N_1**H**), 3.84 (d, *J* = 1.5 Hz, 1H, C_5**H**), 1.11 (s, 9H, $C_5C($**C**$H_3)_3$).
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC):	δ 171.8 (**C**$_4$), 157.0 (**C**$_2$), 131.7 (**C**$_6$), 129.3 (**C**$_8$), 128.4 (**C**$_9$), 126.5 (**C**$_7$), 65.6 (**C**$_5$), 35.3 (C_5**C**), 25.7 ($C_5C($**C**$H_3)_3$).
FTIR (thin film) cm^{-1}:	3278 (br-w), 1775 (w), 1712 (s), 1501 (w), 1412 (m), 1327 (w), 1170 (w), 763 (w), 704 (w).
HRMS (DART) (*m*/*z*):	calc'd for $C_{13}H_{17}N_2O_2$, $[M+H]^+$: 233.1285, found: 233.1279.
TLC (35% ethyl acetate in hexanes), R*f*:	0.40 (UV, CAM).

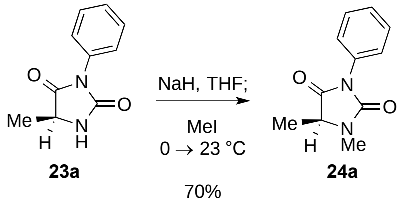


Hydantoin 30a:

Sodium hydride (60% dispersion in mineral oil, 573 mg, 14.3 mmol, 2.40 equiv) was added in one portion as a solid to a solution of *N*-Boc-L-phenylglycine **S14** (1.50 g, 5.97 mmol, 1 equiv) in tetrahydrofuran at 0 °C followed by dropwise addition over 2 min of iodomethane (1.69 g, 741 µL, 11.9 mmol, 2.00 equiv) and the solution was allowed to warm to 23 °C. After 3 h, deionized water (20 mL) was added and the mixture was concentrated under reduced pressure to remove the organic solvent. The solution was diluted in deionized water (30 mL) and washed with ethyl acetate (1 × 50 mL). The aqueous layer was acidified (pH~4) and extracted with ethyl acetate (3 × 50 mL). The organic layers were combined, were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to give the *N*-methylated product. The crude product after workup was converted to the *N*-Me-L-phenylglycine methyl ester hydrogen chloride **S15** following literature procedure.[4] The hydantoin **30a** was prepared following the representative procedure-A using *N*-Me-L-phenylglycine methyl ester hydrogen chloride **S15**. The crude product after workup was purified via flash column chromatography on silica gel (eluent: 30% ethyl acetate in hexanes) to yield hydantoin **30a** (618 mg, 2.31 mmol, 38.8% over four steps) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):	δ 7.50–7.40 (m, 7H, **ArH**), 7.36 (ddt, *J* = 7.7, 5.8, 1.7 Hz, 3H, **ArH**), 4.96 (s, 1H, C_5**H**), 2.98 (s, 3H, N_1**Me**).
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC):	δ 170.2 (**C_4**), 155.8 (**C_2**), 132.9, 132.1, 129.7, 129.6, 129.3, 128.3, 127.5, 126.3, 65.9 (**C_5**), 28.5 (N_1**C**H_3).
FTIR (thin film) cm^{-1}:	3060 (w), 1776 (w), 1718 (s), 1431 (m), 1377 (w), 1197 (m), 1139 (w), 754 (m), 696 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{16}H_{15}N_2O_2$, $[M+H]^+$: 267.1128, found: 267.1113
TLC (30% ethyl acetate in hexanes), R*f*:	0.22 (UV, CAM).

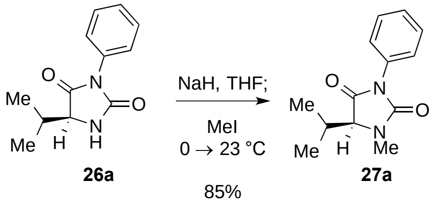
Hydantoin N-Alkylation



Representative Procedure-B for N1-derivatization of hydantoins. Hydantoin 24a:

A sample of sodium hydride (60% dispersion in mineral oil, 21.0 mg, 526 µmol, 1.00 equiv) was added as a solid in one portion to a solution of hydantoin **23a** (100 mg, 526 µmol, 1 equiv) in tetrahydrofuran (5 mL) at 0 °C under an argon atmosphere. After 30 min, iodomethane (373 mg, 164 µL, 2.63 mmol, 5.00 equiv) was added in a single portion via syringe and the reaction mixture was allowed to warm to 23 °C. After 1.5 h, the reaction mixture was diluted by addition of deionized water (15 mL) followed by ethyl acetate (15 mL) and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (2 × 15 mL), and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting oil was purified via flash column chromatography on silica gel (eluent: 50% ethyl acetate in hexanes) to provide *N*-methyl hydantoin **24a** as a white solid (75.0 mg, 367 µmol, 69.8%).

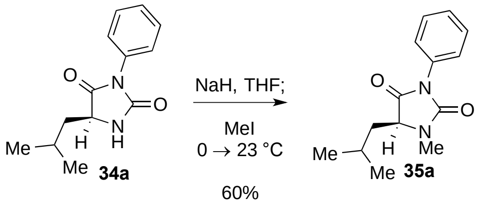
^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.49–7.42 (m, 2H, C$_8$**H**), 7.42–7.38 (m, 2H, C$_7$**H**), 7.37–7.32 (m, 1H, C$_9$**H**), 4.03 (q, *J* = 6.9 Hz, 1H, C$_5$**H**), 3.03 (s, 3H, N$_1$**Me**), 1.54 (d, *J* = 7.0 Hz, 3H, C$_5$**Me**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 172.6 (**C$_4$**), 155.2 (**C$_2$**), 132.0 (**C$_6$**), 129.2 (**C$_8$**), 128.2 (**C$_9$**), 126.2 (**C$_7$**), 57.2 (**C$_5$**), 27.9 (N$_1$**C**H$_3$), 15.4 (C$_5$**C**H$_3$).
FTIR (thin film) cm^{-1}:	1775 (w), 1709 (s), 1502 (w), 1432 (m), 1404 (m), 1381 (m), 1194 (w), 1134 (w), 766 (w), 690 (w).
HRMS (DART) (*m*/*z*):	calc'd for C$_{11}$H$_{13}$N$_2$O$_2$, [M+H]$^{+}$: 205.0972, found: 205.0960.
TLC (50% ethyl acetate in hexanes), R*f*:	0.39 (UV, CAM).



Hydantoin 27a:

The hydantoin **27a** was prepared following the representative procedure-B using hydantoin **26a** (1.50 g, 6.87 mmol, 1 equiv) and iodomethane (2.92 g, 1.28 mL, 20.6 mmol, 3.00 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 30% ethyl acetate in hexanes) to yield hydantoin **27a** (1.35 g, 5.81 mmol, 84.5%) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.52–7.43 (m, 2H, C$_8$**H**), 7.42–7.34 (m, 3H, C$_7$**H**, C$_9$**H**), 3.91 (d, *J* = 3.1 Hz, 1H, C$_5$**H**), 3.07 (s, 3H, N$_1$**Me**), 2.39 (pd, *J* = 7.0, 3.1 Hz, 1H, C$_5$C**H**), 1.22 (d, *J* = 7.0 Hz, 3H, C$_5$CH**Me$_a$**), 1.06 (d, *J* = 7.0 Hz, 3H, C$_5$CH**Me$_b$**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 171.2 (**C$_4$**), 156.0 (**C$_2$**), 132.0 (**C$_6$**), 129.2 (**C$_8$**), 128.2 (**C$_9$**), 126.3 (**C$_7$**), 66.1 (**C$_5$**), 29.3 (C$_5$**C**H), 28.8 (N$_1$**Me**), 17.4 (C$_5$CH**Me$_a$**), 16.9 (C$_5$CH**Me$_b$**).
FTIR (thin film) cm^{-1}:	1770 (w), 1712 (s), 1501 (w), 1431 (m), 1404 (m), 1391 (m), 1138 (w), 959 (w), 757 (w), 690 (w).
HRMS (DART) (*m*/*z*):	calc'd for $C_{13}H_{17}N_2O_2$, [M+H]$^+$: 233.1285, found: 233.1265.
TLC (30% ethyl acetate in hexanes), R*f*:	0.22 (UV, CAM).



Hydantoin 35a:

The hydantoin **35a** was prepared following the representative procedure-B hydantoin **34a** (2.00 g, 8.61 mmol, 1 equiv) and iodomethane (2.44 g, 1.07 mL, 17.2 mmol, 2.00 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 100% dichloromethane → 2% acetone in dichloromethane) to provide hydantoin **35a** (1.28 g, 5.20 mmol, 60.3%) as a white solid.

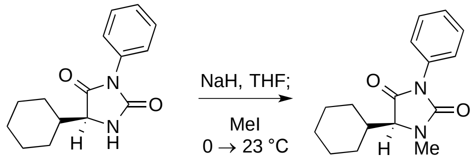
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.47–7.42 (m, 2H, $C_8\mathbf{H}$), 7.41–7.37 (m, 2H, $C_7\mathbf{H}$), 7.37–7.31 (m, 1H, $C_9\mathbf{H}$), 4.01 (dd, *J* = 6.0, 5.1 Hz, 1H, $C_5\mathbf{H}$), 3.02 (s, 3H, $N_1\mathbf{H}$), 1.95 (dq, *J* = 13.3, 6.7 Hz, 1H, $C_5CH_2C\mathbf{H}$), 1.83 (ddd, *J* = 7.0, 5.5, 1.3 Hz, 2H, $C_5C\mathbf{H_2}$), 0.99 (app-dd, *J* = 8.9, 6.5 Hz, 6H, $C_5CH_2CH\mathbf{(Me)_2}$).

^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 172.2 ($\mathbf{C_4}$), 155.6 ($\mathbf{C_2}$), 132.1 ($\mathbf{C_6}$), 129.2 ($\mathbf{C_8}$), 128.1 ($\mathbf{C_9}$), 126.1 ($\mathbf{C_7}$), 60.0 ($\mathbf{C_5}$), 38.3 ($C_5\mathbf{C}H_2$), 28.5 ($N_1\mathbf{Me}$), 24.5 ($C_5CH_2\mathbf{C}H$), 23.3 ($C_5CH_2CH\mathbf{Me_a}$), 22.8 ($C_5CH_2CH\mathbf{Me_b}$).

FTIR (thin film) cm^{-1}: 1775 (w), 1711 (s), 1598 (w), 1502 (m), 1429 (m), 1402 (m), 1383 (m), 1192 (w), 1129 (w), 761 (m), 690 (m).

HRMS (DART) (*m*/*z*): calc'd for $C_{14}H_{19}N_2O_2$, $[M+H]^+$: 247.1441,
found: 247.1429.

TLC (2% acetone in dichloromethane), R*f*: 0.38 (UV, CAM).

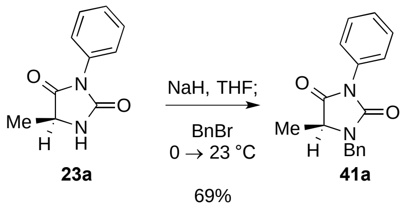


36a 79% **37a**

Hydantoin 37a:

The hydantoin **37a** was prepared following the representative procedure-B using hydantoin **36a** (1.45 g, 5.61 mmol, 1 equiv) and iodomethane (1.59 g, 699 µL, 11.2 mmol, 2.00 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 25% ethyl acetate in hexanes) to provide hydantoin **37a** (1.20 g, 4.41 mmol, 78.6%) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.49–7.41 (m, 2H, C$_8$**H**), 7.40–7.31 (m, 3H, C$_7$**H**, C$_9$**H**), 3.84 (d, *J* = 2.9 Hz, 1H, C$_5$**H**), 3.05 (s, 3H, N$_1$**H**), 2.01 (ddq, *J* = 9.2, 6.4, 3.0 Hz, 1H, C$_5$C**H**), 1.83 (tdd, *J* = 11.0, 9.4, 5.0, 2.5 Hz, 2H), 1.72 (dt, *J* = 11.7, 3.8 Hz, 2H), 1.66 (td, *J* = 9.4, 8.9, 3.4 Hz, 2H), 1.36–1.09 (m, 4H).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 171.4 (**C$_4$**), 156.0 (**C$_2$**), 132.1 (**C$_6$**), 129.2 (**C$_7$**), 128.2 (**C$_9$**), 126.3 (**C$_7$**), 66.1 (**C$_5$**), 39.3 (C$_5$**C**H), 29.0 (N$_1$**Me**), 27.8, 27.7, 26.5, 26.4, 26.2.
FTIR (thin film) cm^{-1}:	2925 (w), 2852 (w), 1772 (w), 1711 (s), 1502 (m), 1431 (m), 1403 (m), 1195 (w), 1134 (w), 963 (w).
HRMS (DART) (*m*/*z*):	calc'd for $C_{16}H_{21}N_2O_2$, [M+H]$^+$: 273.1598, found: 273.1594.
TLC (25% ethyl acetate in hexanes), R*f*:	0.25 (UV, CAM).



Hydantoin 41a:

The hydantoin **41a** was prepared following the representative procedure-B using hydantoin **23a** (250 mg, 1.31 mmol, 1 equiv) and benzyl bromide (448 mg, 311 µL, 2.62 mmol, 2.00 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 25% ethyl acetate in hexanes) to provide hydantoin **41a** (253 mg, 904 µmol, 69.0%) as a white solid.

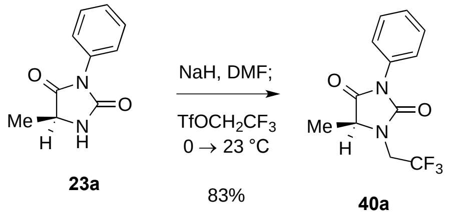
^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC): δ 7.52–7.42 (m, 4H, **ArH**), 7.42–7.30 (m, 6H, **ArH**), 5.07 (d, *J* = 15.2 Hz, 1H, N$_1$C**H$_a$**), 4.24 (d, *J* = 15.2 Hz, 1H, N$_1$C**H$_b$**), 3.95 (q, *J* = 6.9 Hz, 1H, C$_5$**H**), 1.48 (d, *J* = 6.9 Hz, 3H, C$_5$**Me**).

^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC): δ 172.4 (**C$_4$**), 155.2 (**C$_2$**), 135.7, 131.9, 129.1, 129.0, 128.3, 128.2, 128.0, 126.0, 54.7 (**C$_5$**), 44.8, (N$_1$**C**H$_2$), 15.4 (C$_5$**Me**).

FTIR (thin film) cm^{-1}: 1774 (w), 1712 (s), 1502 (w), 1495 (w), 1418 (m), 1241 (w), 1191 (w), 1130 (w), 700 (w).

HRMS (DART) (*m*/*z*): calc’d for $C_{17}H_{17}N_2O_2$, [M+H]$^+$: 281.1285, found: 281.1280.

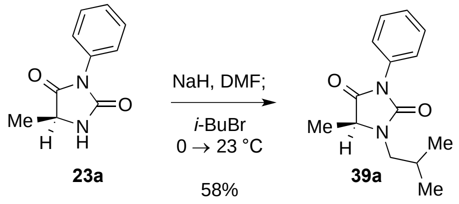
TLC (25% ethyl acetate in hexanes), R*f*: 0.26 (UV, CAM).



Hydantoin 40a:

The hydantoin **40a** was prepared following the representative procedure-B using hydantoin **23a** (250 mg, 1.31 mmol, 1 equiv) and 2,2,2-trifluoroethyl trifluoromethylsulfonate (764 mg, 474 µL, 3.29 mmol, 2.50 equiv) in *N*,*N*-dimethylformamide. The crude product after workup was purified via flash column chromatography on silica gel (eluent: 25% ethyl acetate in hexanes) to provide hydantoin **40a** (294 mg, 1.08 mmol, 82.7%) as a white solid.

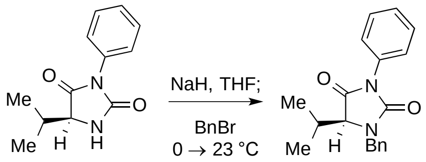
^{1}H NMR (400 MHz, CDCl$_3$, 25 °C):	δ 7.51–7.44 (m, 2H, C$_8$**H**), 7.44–7.34 (m, 3H, C$_7$**H**, C$_9$**H**), 4.42 (dq, *J* = 15.6, 9.3 Hz, 1H, N$_1$C**H$_a$**), 4.27 (q, *J* = 6.9 Hz, 1H, C$_5$**H**), 3.70 (dq, *J* = 15.5, 8.3 Hz, 1H, N$_1$C**H$_b$**), 1.58 (d, *J* = 6.9 Hz, 3H, C$_5$**Me**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 °C):	δ 171.8 (**C$_4$**), 155.3 (**C$_2$**), 131.5 (**C$_6$**), 129.3 (**C$_8$**), 128.6 (**C$_9$**), 126.1 (**C$_7$**), 123.9 (q, *J* = 280.3 Hz, N$_1$CH$_2$**C**F$_3$) 56.0 (**C$_5$**), 42.2 (q, *J* = 35.4 Hz, N$_1$**C**H$_2$) 15.1 (C$_5$**Me**).
^{19}F NMR (282 MHz, CDCl$_3$, 25 °C):	δ –71.03 (t, *J* = 9.1 Hz).
FTIR (thin film) cm^{-1}:	1784 (w), 1717 (s), 1503 (w), 1429 (m), 1256 (m), 1146 (m), 1108 (m), 960 (w), 829 (w), 766 (w), 746 (w).
HRMS (DART) (*m*/*z*):	calc’d for $C_{12}H_{12}F_3N_2O_2$, [M+H]$^+$: 273.0845, found: 273.0835.
TLC (25% ethyl acetate in hexanes), R*f*:	0.25 (UV, CAM).



Hydantoin 39a:

The hydantoin **39a** was prepared following the representative procedure-B using hydantoin **23a** (250 mg, 1.31 mmol, 1 equiv) and 1-bromo-2-methyl propane (540 mg, 429 µL, 3.94 mmol, 3.00 equiv) in *N*,*N*-dimethylformamide. The crude product after workup was purified via flash column chromatography on silica gel (eluent: 20% ethyl acetate in hexanes) to provide hydantoin **39a** (186 mg, 754 µmol, 57.6%) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.52–7.39 (m, 4H, C$_8$**H**, C$_7$**H**), 7.38–7.31 (m, 1H, C$_9$**H**), 4.10 (q, *J* = 7.0 Hz, 1H, C$_5$**H**), 3.50 (dd, *J* = 14.1, 9.2 Hz, 1H, N$_1$C**H$_a$**), 3.04 (dd, *J* = 14.1, 6.0 Hz, 1H, N$_1$C**H$_b$**), 1.98 (dh, *J* = 9.1, 6.6 Hz, 1H, N$_1$CH$_2$C**H**), 1.53 (d, *J* = 7.0 Hz, 3H, N$_1$CH$_2$CH**Me$_a$**), 1.00 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H, N$_1$CH$_2$CH**Me$_b$**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 172.8 (**C$_4$**), 155.4 (**C$_2$**), 132.0 (**C$_6$**), 129.1 (**C$_8$**), 128.1 (**C$_9$**), 126.2 (**C$_7$**), 55.6 (**C$_5$**), 48.4 (N$_1$**C**H$_2$), 27.4 (N$_1$CH$_2$**C**H), 20.4(N$_1$CH$_2$CH**Me$_a$**), 20.1(N$_1$CH$_2$CH**Me$_b$**), 15.7(C$_5$**Me**).
FTIR (thin film) cm^{-1}:	2960 (w), 2871 (w), 1775 (w), 1712 (s), 1502 (w), 1419 (m), 1387 (w), 1193 (w), 1139 (w), 765 (w), 747 (w).
HRMS (DART) (*m*/*z*):	calc'd for $C_{14}H_{19}N_2O_2$, [M+H]$^+$: 247.1441, found: 247.1437.
TLC (20% ethyl acetate in hexanes), R*f*:	0.26 (UV, CAM).

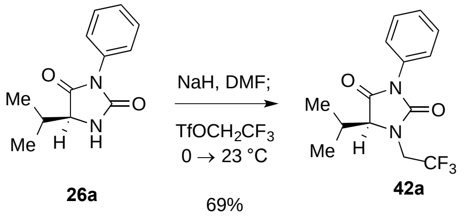


26a 81% **43a**

Hydantoin 43a:

The hydantoin **43a** was prepared following the representative procedure-B using hydantoin **26a** (300 mg, 1.37 mmol, 1 equiv) and benzyl bromide (470 mg, 327 µL, 2.75 mmol, 2.00 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 20% ethyl acetate in hexanes) to provide hydantoin **43a** (343 mg, 1.11 mmol, 81.2%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):	δ 7.52–7.29 (m, 10H, **ArH**), 5.17 (d, *J* = 15.2 Hz, 1H, $N_1C\mathbf{H_a}$), 4.17 (d, *J* = 15.2 Hz, 1H, $N_1C\mathbf{H_b}$), 3.81 (d, *J* = 3.1 Hz, 1H, $C_5\mathbf{H}$), 2.32 (pd, *J* = 7.0, 3.1 Hz, 1H, $C_5C\mathbf{H}$), 1.17 (d, *J* = 7.0 Hz, 3H, $C_5CH\mathbf{Me_a}$), 0.99 (d, *J* = 6.9 Hz, 3H, $C_5CH\mathbf{Me_b}$).
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC):	δ 171.2 ($\mathbf{C_4}$), 156.2 ($\mathbf{C_2}$), 135.8, 132.0, 129.2, 129.2, 128.5, 128.4, 128.3, 126.3, 63.2 ($\mathbf{C_5}$), 45.3 ($N_1\mathbf{C}H_2$), 28.9 ($C_5\mathbf{C}H$), 17.8 ($C_5CH\mathbf{Me_a}$), 16.4 ($C_5CH\mathbf{Me_b}$).
FTIR (thin film) cm^{-1}:	1770 (w), 1710 (s), 1501 (w), 1419 (m), 1382 (w), 1191 (w), 1132 (w), 758 (w), 700 (m), 690 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{19}H_{21}N_2O_2$, $[M+H]^+$: 309.1598, found: 309.1600.
TLC (25% ethyl acetate in hexanes), R*f*:	0.33 (UV, CAM).

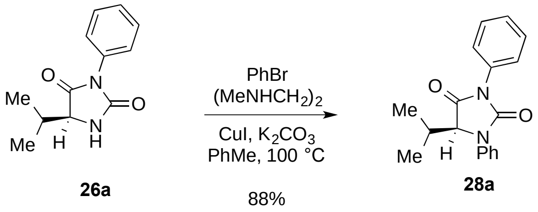


Hydantoin 42a:

The hydantoin **42a** was prepared following the representative procedure-B using hydantoin **26a** (250 mg, 1.31 mmol, 1 equiv) and 2,2,2-trifluoroethyl trifluoromethylsulfonate (638 mg, 396 µL, 2.75 mmol, 2.00 equiv) in *N*,*N*-dimethylformamide. The crude product after workup was purified via flash column chromatography on silica gel (eluent: 20% ethyl acetate in hexanes) to provide hydantoin **42a** (283 mg, 942 µmol, 68.7%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):	δ 7.51–7.43 (m, 2H, C_8**H**), 7.41–7.33 (m, 3H, C_7**H**, C_9**H**), 4.57 (dq, *J* = 15.6, 9.4 Hz, 1H, N_1C**H**$_{\mathbf{a}}$), 4.16 (d, *J* = 3.1 Hz, 1H, C_5**H**), 3.63 (dq, *J* = 16.1, 8.1 Hz, 1H, N_1C**H**$_{\mathbf{b}}$), 2.38 (pd, *J* = 7.0, 3.2 Hz, 1H, C_5C**H**), 1.27 (d, *J* = 7.0 Hz, 3H, C_5CH**Me**$_{\mathbf{a}}$), 0.99 (d, *J* = 6.9 Hz, 3H, C_5CH**Me**$_{\mathbf{a}}$).
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC):	δ 170.1 (**C**$_{\mathbf{4}}$), 155.8 (**C**$_{\mathbf{2}}$), 131.3 (**C**$_{\mathbf{6}}$), 129.1 (**C**$_{\mathbf{8}}$), 128.5 (**C**$_{\mathbf{9}}$), 126.1 (**C**$_{\mathbf{7}}$), 123.9 (q, *J* = 280.9 Hz, N_1CH_2**C**F_3), 63.9 (**C**$_{\mathbf{5}}$), 41.8 (q, *J* = 35.2 Hz, N_1**C**H_2) 28.2 (C_5**C**H), 17.6 (C_5CH**Me**$_{\mathbf{a}}$), 15.6 (C_5CH**Me**$_{\mathbf{b}}$).
^{19}F NMR (282 MHz, $CDCl_3$, 25 ºC):	δ –70.70 (t, *J* = 8.9 Hz).
FTIR (thin film) cm^{-1}:	1780 (w), 1717 (s), 1503 (w), 1429 (m), 1383 (w), 1270 (m), 1248 (m), 1149 (m), 1103 (w), 766 (w), 693 (w).
HRMS (DART) (*m*/*z*):	calc’d for $C_{14}H_{16}F_3N_2O_2$, $[M+H]^+$: 301.1158, found: 301.1164.
TLC (20% ethyl acetate in hexanes), R*f*:	0.34 (UV, CAM).

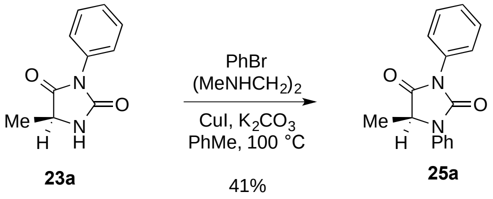
Hydantoin Arylation



Representative Procedure-C for N1 Derivatization of Hydantoins. Hydantoin 28a:

A flame-dried round bottom flask was charged with hydantoin **26a** (655 mg, 3.00 mmol, 1 equiv), potassium carbonate (622 mg, 4.50 mmol, 1.50 equiv), and copper(I) iodide (571 mg, 3.00 mmol, 1.00 equiv) and the flask was evacuated and refilled with argon (2 cycles). The mixture was suspended in toluene (25 mL) and *N*,*N'*-dimethylethylenediamine (0.65 mL, 6.00 mmol, 2.00 equiv) resulting in a pale blue suspension. Bromobenzene (0.38 mL, 3.60 mmol, 1.20 equiv) was added and the flask was sealed with a glass stopper and heated to 100 °C. After 18 h, the blue reaction mixture was allowed to cool to 23 °C, was diluted with deionized water (100 mL), and was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were washed with saturated aqueous sodium chloride solution (1 × 100 mL), were dried over anhydrous sodium sulfate, were filtered, and were dried under reduced pressure to give a yellow oil. The crude residue was purified via flash column chromatography on silica gel (eluent: 15% ethyl acetate in hexanes) to afford hydantoin **28a** (772 mg, 2.62 mmol 87.5%) as a colorless oil.

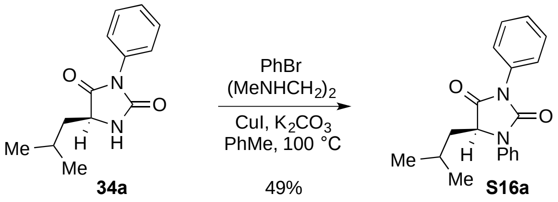
^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.53–7.35 (m, 9H, **ArH**), 7.30–7.22 (m, 1H, **ArH**), 4.63 (d, *J* = 3.1 Hz, 1H, C$_5$**H**), 2.32 (heptd, *J* = 7.0, 3.1 Hz, 1H, C$_5$C**H**), 1.26 (d, *J* = 7.1 Hz, 3H, C$_5$CH**Me$_a$**), 0.93 (d, *J* = 6.9 Hz, 3H, C$_5$CH**Me$_b$**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 170.4 (**C$_4$**), 153.9 (**C$_2$**), 135.8, 131.7, 129.5, 129.3, 128.5, 126.5, 126.1, 123.1, 64.7 (**C$_5$**), 29.3 (C$_5$CH), 17.9 (C$_5$CH**Me$_a$**), 16.1 (C$_5$CH**Me$_b$**).
FTIR (thin film) cm^{-1}:	1771 (w), 1713 (s), 1597 (w), 1498 (m), 1401 (s), 1383 (m), 1153 (m), 844 (w), 757 (m), 690 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{18}H_{19}N_2O_2$, [M+H]$^+$: 295.1441, found: 295.1454.
TLC (15% ethyl acetate in hexanes), R*f*:	0.27 (UV, CAM).



Hydantoin 25a:

The hydantoin **25a** was prepared following the representative procedure-C using hydantoin **23a** (500 mg, 2.63 mmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 20% ethyl acetate in hexanes) to afford hydantoin **25a** (325 mg, 1.22 mmol, 40.6%) as a white solid.

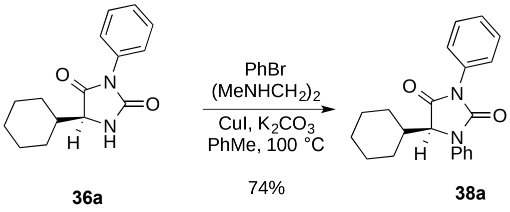
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):	δ 7.61–7.34 (m, 9H, **ArH**), 7.31–7.19 (m, 1H, **ArH**), 4.75 (q, *J* = 6.9 Hz, 1H, C_5**H**), 1.59 (d, *J* = 6.9 Hz, 3H, C_5**Me**).
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC):	δ 171.8 (**C_4**), 153.3 (**C_2**), 135.7, 129.3, 128.6, 126.4, 125.8, 122.2, 56.2 (**C_5**), 16.1 (C_5**Me**).
FTIR (thin film) cm^{-1}:	1771 (w), 1710 (s), 1596 (w), 1494 (m), 1401 (s), 1374 (m), 1155 (m), 758 (m), 736 (m), 689 (s).
HRMS (DART) (*m*/*z*):	calc'd for $C_{16}H_{15}N_2O_2$, $[M+H]^+$: 267.1128, found: 267.1116.
TLC (20% ethyl acetate in hexanes), R*f*:	0.28 (UV, CAM).



Hydantoin S16a:

The hydantoin **S16a** was prepared following the representative procedure-C using hydantoin **34a** (2.50 g, 10.8 mmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 20% ethyl acetate in hexanes) to afford hydantoin **S16a** (1.63 g, 5.29 mmol, 49.1%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):	δ 7.60–7.34 (m, 9H, **ArH**), 7.26 (app-t, *J* = 7.4 Hz, 1H, **ArH**), 4.78 (dd, *J* = 7.1, 4.3 Hz, 1H, C_5**H**), 1.99–1.92 (m, 1H, C_5CH_2C**H**), 1.88 (dt, *J* = 8.5, 5.3 Hz, 2H, C_5C**H$_2$**), 1.00 (d, *J* = 6.4 Hz, 3H, C_5CH_2CH**Me$_a$**), 0.88 (d, *J* = 6.4 Hz, 3H, C_5CH_2CH**Me$_a$**).
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC):	δ 171.4 (**C$_4$**), 153.5 (**C$_2$**), 135.7, 131.7, 129.4, 129.2, 128.4, 126.4, 125.8, 122.3, 58.5 (**C$_5$**), 38.1 (C_5**C**H_2), 24.0 (C_5CH_2**C**H), 23.5 (C_5CH_2CH**Me$_a$**), 22.3 (C_5CH_2CH**Me$_b$**).
FTIR (thin film) cm^{-1}:	1772 (w), 1716 (s), 1597 (w), 1495 (m), 1403 (s), 1155 (m), 758 (m), 690 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{19}H_{21}N_2O_2$, $[M+H]^+$: 309.1598, found: 309.1587.
TLC (20% ethyl acetate in hexanes), R*f*:	0.28 (UV, CAM).



Hydantoin 38a:

The hydantoin **38a** was prepared following the representative procedure-C using hydantoin **36a** (2.00 g, 7.74 mmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 15% ethyl acetate in hexanes) to afford hydantoin **38a** (1.91 g, 5.71 mmol, 73.8%) as a white solid.

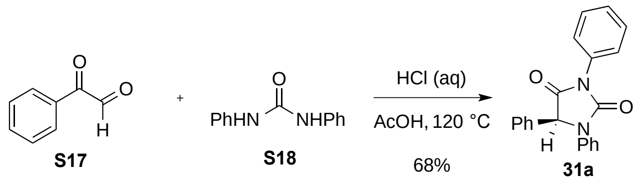
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.64–7.33 (m, 9H, **ArH**), 7.33–7.12 (m, 1H, **ArH**), 4.59 (d, *J* = 2.9 Hz, 1H, C_5**H**), 2.14–1.89 (m, 1H, C_5C**H**), 1.86–1.59 (m, 6H), 1.34 – 0.80 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 170.6 (**C_4**), 153.9 (**C_2**), 136.0, 131.7, 129.6, 129.3, 128.5, 126.6, 126.1, 123.1, 64.7 (**C_5**), 39.3 (C_5**C**H), 28.2, 27.0, 26.5, 26.1, 26.1.

FTIR (thin film) cm^{-1}: 2925 (w), 1772 (w), 1713 (s), 1597 (w), 1495 (m), 1403 (s), 1154 (m), 757 (m), 739 (m), 690 (m).

HRMS (DART) (*m*/*z*): calc’d for $C_{21}H_{23}N_2O_2$, $[M+H]^+$: 335.1754, found: 335.1746.

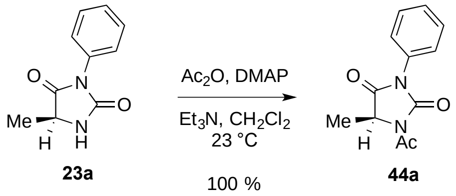
TLC (15% ethyl acetate in hexanes), R*f*: 0.27 (UV, CAM).



Hydantoin 31a:

Aqueous hydrogen chloride solution (12 N, 0.6 mL) was added to a solution of phenylglyoxal hydrate **S17** (1.40 g, 6.57 mmol, 1.00 equiv) and 1,3-diphenylurea **S18** (1.00 g, 6.57 mmol, 1 equiv) in acetic acid (25 mL), and the resulting mixture was heated to 120 °C. After 6 hours, the reaction mixture was allowed to cool to 23 °C, was poured into deionized water (40 mL), and the resulting light yellow precipitate was isolated via vacuum filtration.[5] The isolated solid was purified via flash column chromatography on silica gel (20% ethyl acetate in hexanes) to afford hydantoin **31a** (1.47 g, 4.48 mmol, 68.1%) as a light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):	δ 7.57 (app-dt, *J* = 8.0, 1.1 Hz, 2H, **ArH**), 7.53–7.46 (m, 4H, **ArH**), 7.46–7.35 (m, 6H, **ArH**), 7.32 (app-dd, *J* = 8.7, 7.4 Hz, 2H, **ArH**), 7.13 (app-t, *J* = 7.4 Hz, 1H, **ArH**), 5.62 (s, 1H, C_5**H**).
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC):	δ 169.0 (**C$_4$**), 153.7 (**C$_2$**), 136.5, 133.0, 131.5, 129.4, 129.3, 129.2, 129.3, 128.5, 126.9, 126.4, 125.0, 120.7, 64.1 (**C$_5$**).
FTIR (thin film) cm^{-1}:	1775 (m), 1714 (s), 1597 (w), 1494 (m), 1456 (w), 1395 (s), 1364 (m), 1177 (m), 1149 (m), 841 (w), 751 (m), 643 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{21}H_{17}N_2O_2$, $[M+H]^+$: 329.1285, found: 329.1276.
TLC (20% ethyl acetate in hexanes), R*f*:	0.30 (UV, CAM).

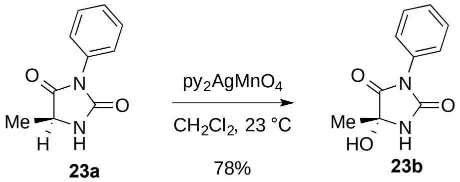


Hydantoin 44a:

Triethylamine (0.147 mL, 1.05 mmol, 2.00 equiv) was added in one portion via syringe to a solution of hydantoin **23a** (100 mg, 526 µmol, 1 equiv) and 4-dimethylaminopyridine (16.1 mg, 132 µmol, 0.250 equiv) in dichloromethane (5 mL) and acetic anhydride (75.2 µL, 0789 mmol, 1.50 equiv) was added dropwise over 1 min to the resulting solution. After 3 h, the reaction mixture was diluted with dichloromethane (15 mL) and washed with saturated aqueous ammonium chloride solution (1 × 25 mL). The organic layer was separated and the aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic layers were washed with saturated aqueous sodium bicarbonate (1 × 50 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude yellow oil was purified via flash column chromatography on silica gel (25% ethyl acetate in hexanes) to afford hydantoin **44a** (122 mg, 525 µmol, 99.8%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC):	δ 7.49 (app-t, *J* = 7.7 Hz, 2H, C_8**H**), 7.42 (app-t, *J* = 7.4 Hz, 1H, C_9**H**), 7.36 (d, *J* = 7.7 Hz, 2H, C_7**H**), 4.69 (q, *J* = 6.8 Hz, 1H, C_5**H)**, 2.61 (s, 3H, N_1CO**C**H_3), 1.69 (d, *J* = 6.9 Hz, 3H,C_5**Me**).
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC):	δ 171.0 (**C_4**), 169.4 (N_1**C**OMe), 152.9 (**C_2**), 130.7 (**C_6**), 129.5(**C_8**), 129.2 (**C_9**), 126.5 (**C_7**), 55.1 (**C_5**), 25.5 (N_1CO**C**H_3), 16.8 (C_5**Me**).
FTIR (thin film) cm^{-1}:	1795 (w), 1727 (s), 1699 (s), 1500 (w), 1398 (m), 1371 (m), 1337 (s), 1278 (s), 1177 (m), 922 (w), 764 (m), 690 (w).
HRMS (DART) (*m*/*z*):	calc'd for $C_{12}H_{13}N_2O_3$, $[M+H]^+$: 233.0921, found: 233.0918.
TLC (25% ethyl acetate in hexanes), R*f*:	0.27 (UV, CAM).

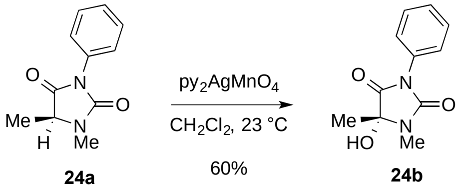
Hydantoin Oxidation



Representative Procedure-D for Hydantoin Oxidation. Alcohol 23b:

Bis(pyridine)silver(I) permanganate (76.8 mg, 200 µmol, 2.00 equiv) was added as a solid in one portion to a solution of hydantoin **23a** (19.0 mg, 100 µmol, 1 equiv) in dichloromethane (1.0 mL) under an argon atmosphere, yielding a dark purple solution. After 1 h, the brown/purple reaction mixture was diluted with ethyl acetate (15 mL), was washed with a saturated aqueous sodium bisulfite solution (25 mL), and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with a saturated aqueous solution of ammonium chloride (1 × 50 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to afford a crude white solid. The crude solid was purified via flash column chromatography on silica gel (eluent: 20% acetone in dichloromethane) to provide alcohol **23b** (16.0 mg, 77.6 µmol, 77.6%) as a white solid.

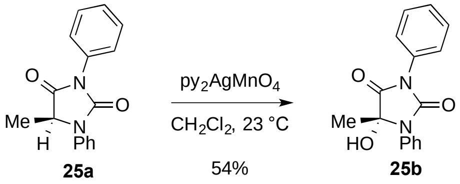
^{1}H NMR (500 MHz, Acetone-*d*$_6$, 25 ºC):	δ 7.95 (s, 1H, N$_1$**H**), 7.68–7.15 (m, 5H, **ArH**), 5.83 (s, 1H, C$_5$O**H**), 1.66 (s, 3H, C$_5$**Me**).
^{13}C NMR (125 MHz, Acetone-*d*$_6$, 25 ºC):	δ 173.7 (**C$_4$**), 154.9 (**C$_2$**), 133.5 (**C$_6$**), 129.5 (**C$_8$**), 128.4 (**C$_9$**), 127.3 (**C$_7$**), 82.9 (**C$_5$**), 23.8 (C$_5$**Me**).
FTIR (thin film) cm^{-1}:	3494 (br-w), 3305 (br-m), 1787 (w), 1716 (s), 1504 (w), 1414 (m), 1298 (w), 1162 (w), 873 (w), 706 (w).
HRMS (DART) (*m*/*z*):	calc'd for $C_{10}H_{14}N_3O_3$, $[M+NH_4]^+$: 224.1030, found: 224.1024.
TLC (20% acetone in dichloromethane), R*f*:	0.25 (UV, CAM).



Alcohol 24b:

The alcohol **24b** was prepared following the representative procedure-D using hydantoin **24a** (20.4 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 5% acetone in dichloromethane) to yield alcohol **24b** (13.1 mg, 59.5 µmol, 59.5%) as a white solid, and separately the recovered hydantoin **24a** (2.3 mg, 11.3 µmol, 11.3%).

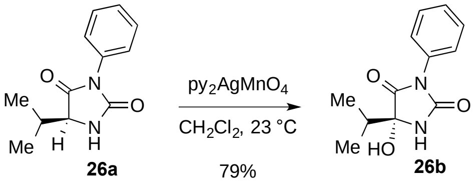
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):	δ 7.50–7.41 (m, 2H, C_8**H**), 7.40–7.32 (m, 3H, C_7**H**, C_9**H**), 3.62 (s, 1H, C_5O**H**), 2.99 (s, 3H, N_1**Me**), 1.67 (s, 3H, C_5**Me**).
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC):	δ 172.7 (**C_4**), 154.0 (**C_2**), 131.4 (**C_6**), 129.3 (**C_8**), 128.5 (**C_9**), 126.1 (**C_7**), 83.9 (**C_5**), 24.4 (N_1**Me**), 21.5 (C_5**Me**).
FTIR (thin film) cm^{-1}:	3300 (br-m), 1780 (w), 1705 (s), 1693 (s), 1496 (w), 1457 (m), 1409 (m), 1381 (m), 1167 (s), 1157 (s), 917 (w), 766 (s), 699 (s).
HRMS (DART) (*m*/*z*):	calc'd for $C_{11}H_{16}N_3O_3$, $[M+NH_4]^+$: 238.1186, found: 238.1180.
TLC (5% acetone in dichloromethane), R*f*:	0.35 (UV, CAM).



Alcohol 25b:

The alcohol **25b** was prepared following the representative procedure-D using hydantoin **25a** (26.6 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 30% ethyl acetate in hexanes) to yield alcohol **25b** (15.3 mg, 54.2 µmol, 54.2%) as a white solid, and separately the recovered hydantoin **25a** (4.80 mg, 18.0 µmol, 18.0%).

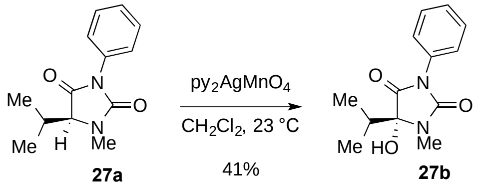
^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.60–7.32 (m, 10H, **ArH**), 3.74 (s, 1H, C$_5$O**H**), 1.65 (s, 3H, C$_5$**Me**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 171.9 (**C$_4$**), 153.1 (**C$_2$**), 133.8, 131.3, 129.5, 129.3, 128.6, 128.1, 127.2, 126.3, 85.6 (**C$_5$**), 22.5 (C$_5$**Me**).
FTIR (thin film) cm^{-1}:	3394 (br-w), 3053 (w), 1774 (w), 1716 (m), 1596 (w), 1496 (m), 1410 (m), 1265 (s), 1171 (w), 889 (w), 733 (s).
HRMS (DART) (*m*/*z*):	calc'd for $C_{16}H_{18}N_3O_3$, $[M+NH_4]^+$: 300.1343, found: 300.1352.
TLC (30% ethyl acetate in hexanes), R*f*:	0.39 (UV, CAM).



Alcohol 26b:

The alcohol **26b** was prepared following the representative procedure-D using hydantoin **26a** (21.8 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 10% acetone in dichloromethane) to afford alcohol **26b** (18.4 mg, 78.5 µmol, 78.5%) as a white solid.

^{1}H NMR (400 MHz, Acetone-*d*$_6$, 25 ºC):	δ 7.85 (s, 1H, N$_1$**H**), 7.55–7.42 (m, 2H, C$_8$**H**), 7.41–7.31 (m, 3H, C$_7$**H**, C$_9$**H**), 5.83 (s, 1H, C$_5$O**H**), 2.31 (p, *J* = 6.9 Hz, 1H, C$_5$C**H**), 1.13 (d, *J* = 6.9 Hz, 3H, C$_5$CH**Me$_a$**), 0.98 (d, *J* = 6.8 Hz, 3H, C$_5$CH**Me$_b$**).
^{13}C NMR (100 MHz, Acetone-*d*$_6$, 25 ºC):	δ 173.7 (**C$_4$**), 155.6 (**C$_2$**), 133.4 (**C$_6$**), 129.6 (**C$_8$**), 128.6 (**C$_9$**), 127.3 (**C$_7$**), 87.9 (**C$_5$**), 34.8 (C$_5$**C**H), 17.1 (C$_5$CH**Me$_a$**), 15.7 (C$_5$CH**Me$_b$**).
FTIR (thin film) cm^{-1}:	3307 (br-m), 1787 (w), 1715 (s), 1502 (w), 1412 (m), 1282 (w), 1143 (w), 1081 (w), 849 (w), 769 (w), 704 (w).
HRMS (DART) (*m*/*z*):	calc'd for $C_{12}H_{18}N_3O_3$, $[M+NH_4]^+$: 252.1343, found: 252.1351.
TLC (10% acetone in dichloromethane), R*f*:	0.17 (UV, CAM).

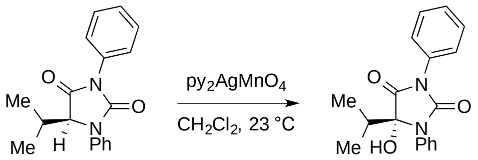


27a **27b**

Alcohol 27b:

The alcohol **27b** was prepared following the representative procedure-D using hydantoin **27a** (23.2 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 3% acetone in dichloromethane) to provide alcohol **27b** (10.1 mg, 40.6 µmol, 40.6%) as a white solid, and separately the recovered hydantoin **27a** (6.10 mg, 26.3 µmol, 26.3%).

^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.49–7.40 (m, 2H, C$_8$**H**), 7.39–7.31 (m, 3H, C$_7$**H**, C$_9$**H**), 3.46 (s, 1H, C$_5$O**H**), 2.97 (s, 3H, N$_1$**Me**), 2.33 (p, *J* = 7.0 Hz, 1H, C$_5$C**H**), 1.18 (d, *J* = 6.9 Hz, 3H, C$_5$CH**Me$_a$**), 1.02 (d, *J* = 7.1 Hz, 3H, C$_5$CH**Me$_b$**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 172.0 (**C$_4$**), 154.7 (**C$_2$**), 131.4 (**C$_6$**), 129.3 (**C$_8$**), 128.5 (**C$_9$**), 126.2 (**C$_7$**), 88.2 (**C$_5$**), 33.9 (C$_5$**C**H), 25.0 (N$_1$**Me**), 16.5 (C$_5$CH**Me$_a$**), 16.0 (C$_5$CH**Me$_b$**).
FTIR (thin film) cm^{-1}:	3382 (br-m), 2971 (w), 1780 (w), 1709 (s), 1503 (m), 1436 (m), 1404 (m), 1151 (m), 1091 (w), 763 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{13}H_{20}N_3O_3$, $[M+NH_4]^+$: 266.1499, found: 266.1503.
TLC (3% acetone in dichloromethane), R*f*:	0.16 (UV, CAM).

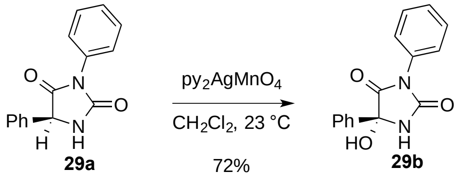


28a **28b**

Alcohol 28b:

The alcohol **28b** was prepared following the representative procedure-D using hydantoin **28a** (29.4 mg, 100 µmol, 1 equiv). The crude mixture was purified via flash column chromatography on silica gel (eluent: 20% ethyl acetate in hexanes) to afford alcohol **28b** (4.0 mg, 12.9 µmol, 12.9%) as a white solid, and separately the recovered hydantoin **28a** (20.8 mg, 70.7 µmol, 70.7%).

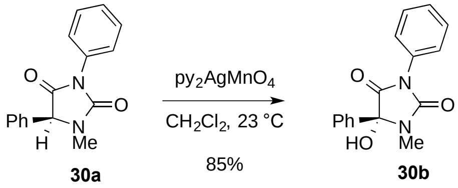
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):	δ 7.66–7.54 (m, 2H, **ArH**), 7.53–7.31 (m, 8H, **ArH**), 3.63 (s, 1H, C$_5$O**H**), 2.24 (p, *J* = 6.9 Hz, 1H, C$_5$C**H**), 1.21 (d, *J* = 6.9 Hz, 3H, C$_5$CH**Me$_a$**), 0.92 (d, *J* = 7.0 Hz, 3H, C$_5$CH**Me$_b$**).
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC):	δ 171.2 (**C$_4$**), 153.7 (**C$_2$**), 134.3, 131.3, 129.4, 129.3, 128.7, 127.8, 127.1, 126.4, 90.2 (**C$_5$**), 34.0 (C$_5$**C**H), 16.5 (C$_5$CH**Me$_a$**), 16.0 (C$_5$CH**Me$_b$**).
FTIR (thin film) cm^{-1}:	3376 (br-m), 2972 (w), 1776 (w), 1704 (s), 1700 (s), 1596 (w), 1496 (m), 1408 (s), 1383 (m), 1166 (m), 1074 (w), 904 (w), 867 (w), 762 (m), 738 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{18}H_{22}N_3O_3$, $[M+NH_4]^+$: 328.1656, found: 328.1664.
TLC (20% ethyl acetate in hexanes), R*f*:	0.22 (UV, CAM).



Alcohol 29b:

The alcohol **29b** was prepared following the representative procedure-D using hydantoin **29a** (25.2 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 10% acetone in dichloromethane) to yield alcohol **29b** (19.2 mg, 71.6 µmol, 71.6%) as a white solid.

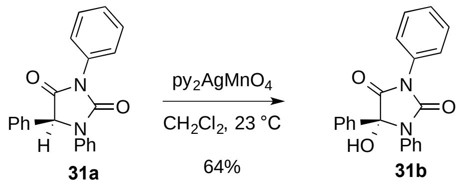
^{1}H NMR (400 MHz, Acetone-*d*$_6$, 25 ºC):	δ 8.36 (s, 1H, N$_1$**H**), 7.91–7.59 (m, 2H, **ArH**), 7.57–7.20 (m, 8H, **ArH**), 6.54 (s, 1H, C$_5$O**H**).
^{13}C NMR (100 MHz, Acetone-*d*$_6$, 25 ºC):	δ 172.6 (**C$_4$**), 155.4 (**C$_2$**), 139.1, 133.4, 129.9, 129.6, 129.3, 128.7, 127.4, 127.2, 85.6 (**C$_5$**).
FTIR (thin film) cm^{-1}:	3306 (br-m), 1787 (w), 1721 (s), 1500 (w), 1411 (m), 1197 (w), 851 (w), 765 (w), 704 (m), 694 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{15}H_{16}N_3O_3$, $[M+NH_4]^+$: 286.1186, found: 286.1167.
TLC (10% acetone in dichloromethane), R*f*:	0.24 (UV, CAM).



Alcohol 30b:

The alcohol **30b** was prepared following the representative procedure-D using hydantoin **30a** (26.6 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 30% ethyl acetate in hexanes) to yield alcohol **30b** (24.0 mg, 85.0 µmol, 85.0%) as a white solid.

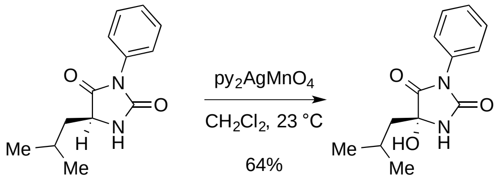
^{1}H NMR (400 MHz, Acetone-*d*$_6$, 25 ºC):	δ 7.68–7.57 (m, 2H, **ArH**), 7.55–7.32 (m, 8H, **ArH**), 6.55 (s, 1H, C_5O**H**), 2.84 (s, 3H, N_1**Me**).
^{13}C NMR (100 MHz, Acetone-*d*$_6$, 25 ºC):	δ 171.9 (**C_4**), 155.2 (**C_2**), 137.0, 133.4, 130.1, 129.7, 129.6, 128.7, 127.3, 127.3, 87.8 (**C_5**), 24.8 (N_1**Me**).
FTIR (thin film) cm^{-1}:	3263 (br-w), 1773 (w), 1702 (s), 1431 (w), 1403 (w), 1362 (m), 1247 (s), 1222 (m), 734 (s), 698 (m).
HRMS (DART) (*m*/*z*):	calc’d for $C_{16}H_{18}N_3O_3$, $[M+NH_4]^+$: 300.1343, found: 300.1330.
TLC (30% ethyl acetate in hexanes), R*f*:	0.16 (UV, CAM).



Alcohol 31b:

The alcohol **31b** was prepared following the representative procedure-D using hydantoin **31a** (32.8 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 20% ethyl acetate in hexanes) to yield alcohol **31b** (22.0 mg, 63.9 µmol, 63.9%) as a white solid.

^{1}H NMR (400 MHz, Acetone-d_6, 25 ºC):	δ 7.75–7.66 (m, 2H, **ArH**), 7.64–7.56 (m, 2H, **ArH**), 7.53 (app-d, *J* = 4.3 Hz, 4H, **ArH**), 7.49–7.31 (m, 4H, **ArH**), 7.31–7.24 (m, 2H, **ArH**), 7.19 (s, 1H, $C_5O\mathbf{H}$), 7.18–7.12 (m, 1H, **ArH**).
^{13}C NMR (100 MHz, Acetone-d_6, 25 ºC):	δ 171.1 ($\mathbf{C_4}$), 154.1 ($\mathbf{C_2}$), 137.3, 136.5, 133.1, 130.0, 129.8, 129.5, 129.4, 129.1, 127.7, 127.5, 126.9, 125.9, 89.4 ($\mathbf{C_5}$).
FTIR (thin film) cm^{-1}:	3342 (br-w), 1783 (w), 1726 (s), 1699 (s), 1597 (w), 1495 (m), 1398 (s), 1354 (m), 1152 (m), 883 (w), 757 (m), 725 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{21}H_{20}N_3O_3$, $[M+NH_4]^+$: 362.1499, found: 362.1508.
TLC (20% ethyl acetate in hexanes), R*f*:	0.21 (UV, CAM).

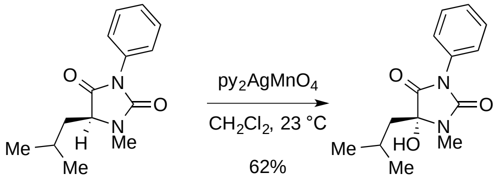


34a **34b**

Alcohol 34b:

The alcohol **34b** was prepared following the representative procedure-D using hydantoin **34a** (23.2 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 35% ethyl acetate in hexanes) to yield alcohol **34b** (16.1 mg, 64.8 µmol, 64.8%) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.61–7.42 (m, 2H, C$_8$**H**), 7.42–7.33 (m, 3H, C$_7$**H**, C$_9$**H**), 6.32 (s, 1H, N$_1$**H**), 3.80 (s, 1H, C$_5$O**H**), 1.95 (d, *J* = 6.5 Hz, 2H, C$_5$C**H$_2$**), 1.82 (dt, *J* = 13.2, 6.6 Hz, 1H, C$_5$CH$_2$C**H**), 1.01 (d, *J* = 6.6 Hz, 3H, C$_5$CH$_2$CH**Me$_a$**), 0.95 (d, *J* = 6.5 Hz, 3H, C$_5$CH$_2$CH**Me$_b$**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 173.0 (**C$_4$**), 155.2 (**C$_2$**), 131.1 (**C$_6$**), 129.7, 129.4, 128.7, 126.2, 125.9, 84.6 (**C$_5$**), 45.0 (C$_5$**C**H$_2$), 24.3 (C$_5$CH$_2$**C**H), 24.1 (C$_5$CH$_2$CH**Me$_a$**), 23.4 (C$_5$CH$_2$CH**Me$_b$**).
FTIR (thin film) cm^{-1}:	3378 (br-m), 3299 (br-m), 2960 (w), 1790 (w), 1795 (s), 1502 (w), 1419 (m), 1265 (w), 1159 (w), 868 (m), 706 (s).
HRMS (DART) (*m*/*z*):	calc'd for $C_{13}H_{20}N_3O_3$, [M+NH$_4$]$^+$: 266.1499, found: 266.1491.
TLC (35% ethyl acetate in hexanes), R*f*:	0.21 (UV, CAM).

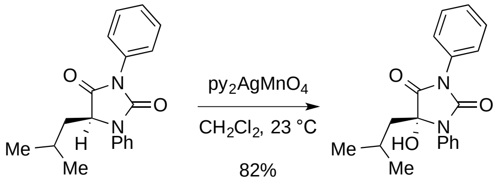


35a **35b**

Alcohol 35b:

The alcohol **35b** was prepared following the representative procedure-D using hydantoin **35a** (24.6 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 30% ethyl acetate in hexanes) to provide alcohol **35b** (16.3 mg, 62.1 µmol, 62.1%) as a white solid, and separately the recovered hydantoin **35a** (2.4 mg, 9.7 µmol, 9.7%).

^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.50–7.40 (m, 2H, C$_8$**H**), 7.40–7.28 (m, 3H, C$_7$**H**, C$_9$**H**), 4.12 (s, 1H, C$_5$O**H**), 2.92 (s, 3H, N$_1$**Me**), 2.01 (dd, *J* = 14.5, 7.8 Hz, 1H, C$_5$C**H$_a$**), 1.88 (dd, *J* = 14.5, 5.2 Hz, 1H, C$_5$C**H$_b$**), 1.56 (dtd, *J* = 7.8, 6.7, 5.2 Hz, 1H, C$_5$CH$_2$C**H**), 0.94 (d, *J* = 6.7 Hz, 3H, C$_5$CH$_2$CH**Me$_a$**), 0.88 (d, *J* = 6.6 Hz, 3H, C$_5$CH$_2$CH**Me$_b$**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 172.9 (**C$_4$**), 154.8 (**C$_2$**), 131.4 (**C$_6$**), 129.3 (**C$_8$**), 128.5 (**C$_9$**), 126.1 (**C$_7$**), 86.2 (**C$_5$**), 42.8 (C$_5$**C**H$_2$), 24.6 (N$_1$**Me**), 24.2 (C$_5$CH$_2$**C**H), 23.8 (C$_5$CH$_2$CH**Me$_a$**), 23.1 (C$_5$CH$_2$CH**Me$_b$**).
FTIR (thin film) cm^{-1}:	3368 (br-w), 2960 (w), 1782 (w), 1711 (s), 1502 (w), 1441 (m), 1403 (m), 1265 (m), 1143 (m), 1063 (w), 733 (s), 703 (m).
HRMS (DART) (*m*/*z*):	calc'd for C$_{14}$H$_{19}$N$_2$O$_3$, [M+H]$^+$: 263.1390, found: 263.1384.
TLC (30% ethyl acetate in hexanes), R*f*:	0.22 (UV, CAM).

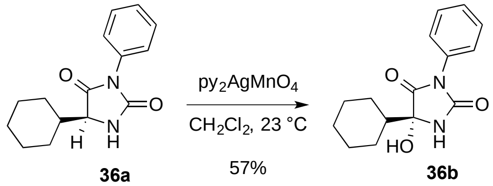


S16a **S16b**

Alcohol S16b:

The alcohol **S16b** was prepared following the representative procedure-D using hydantoin **S16a** (39.0 mg, 126 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 2% acetone in dichloromethane) to yield alcohol **S16b** (33.3 mg, 103 µmol, 81.5 %) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	7.60 (dd, *J* = 7.5, 1.7 Hz, 2H, **ArH**), 7.53–7.39 (m, 7H, **ArH**), 7.31 (d, *J* = 7.3 Hz, 1H, **ArH**), 4.22 (s, 1H, C$_5$O**H**), 2.02–1.87 (m, 2H, C$_5$C**H$_2$**), 1.64 (ddt, *J* = 13.8, 11.9, 6.7 Hz, 1H, C$_5$CH$_2$C**H**), 0.89 (d, *J* = 6.6 Hz, 3H, C$_5$CH$_2$CH**Me$_a$**), 0.74 (d, *J* = 6.7 Hz, 3H, C$_5$CH$_2$CH**Me$_b$**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 172.1 (**C$_4$**), 153.6 (**C$_2$**), 134.3, 131.3, 129.4, 129.3, 128.7, 127.4, 126.3, 126.0, 88.1 (**C$_5$**), 43.2 (C$_5$**C**H$_2$), 24.1 (C$_5$CH$_2$**C**H), 23.8 (C$_5$CH$_2$CH**Me$_a$**), 22.6 (C$_5$CH$_2$CH**Me$_b$**).
FTIR (thin film) cm^{-1}:	3371 (br-w), 2962 (w), 1782 (w), 1713 (s), 1495 (m), 1265 (m), 1166 (m), 734 (s), 693 (s).
HRMS (DART) (*m*/*z*):	calc'd for $C_{19}H_{21}N_2O_3$, [M+H]$^+$: 325.1547, found: 325.1558.
TLC (2% acetone in dichloromethane), R*f*:	0.40 (UV, CAM).

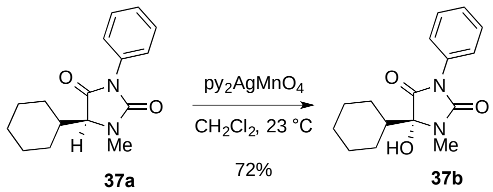


36a **36b**

Alcohol 36b:

The alcohol **36b** was prepared following the representative procedure-D using hydantoin **36a** (25.8 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 35% ethyl acetate in hexanes) to yield alcohol **36b** (15.6 mg, 56.9 µmol, 56.9 %) as a white solid.

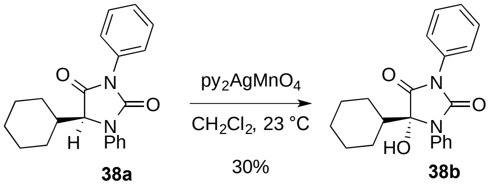
^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC):	δ 7.46–7.39 (m, 2H, C$_8$**H**), 7.37 (app-t, *J* = 7.4 Hz, 1H, C$_9$**H**), 7.32 (dd, *J* = 7.9, 2.6 Hz, 2H, C$_7$**H**), 6.61 (s, 1H, N$_1$**H**), 4.60 (br-s, 1H, C$_5$O**H**), 2.10–1.89 (m, 2H), 1.86–1.55 (m, 5H), 1.29–1.18 (m, 1H), 1.17–1.05 (m, 2H), 0.97 (qd, *J* = 12.4, 3.5 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC):	δ 173.3 (**C**$_4$), 155.6 (**C**$_2$), 131.1 (**C**$_6$), 129.3 (**C**$_8$), 128.7 (**C**$_9$), 126.3 (**C**$_7$), 87.0 (**C**$_5$), 44.0 (C$_5$**C**H), 26.8, 26.1, 25.9, 25.6, 25.4.
FTIR (thin film) cm^{-1}:	3305 (br-w), 2931 (w), 1787 (w), 1717 (s), 1502 (w), 1419 (m), 1264 (s), 733 (s), 703 (s).
HRMS (DART) (*m*/*z*):	calc'd for $C_{15}H_{22}N_3O_3$, $[M+NH_4]^+$: 292.1656, found: 292.1654.
TLC (35% ethyl acetate in hexanes), R*f*:	0.19 (UV, CAM).



Alcohol 37b:

The alcohol **37b** was prepared following the representative procedure-D using hydantoin **37a** (54.5 mg, 200 µmol, 1 equiv) and bis(pyridine)silver(I) permanganate (307.1 mg, 800 µmol, 4.00 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 20% ethyl acetate in hexanes) to yield alcohol **37b** (41.7 mg, 145 µmol, 72.3 %) as a white solid.

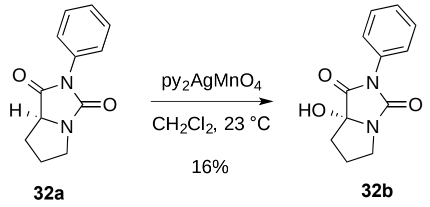
^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.45–7.37 (m, 2H, C$_8$**H**), 7.37–7.32 (m, 1H, C$_9$**H**), 7.32–7.28 (m, 2H, C$_7$**H**), 4.03 (s, 1H, C$_5$O**H**), 2.89 (s, 3H, N$_1$**H**), 1.97–1.88 (m, 1H, C$_5$C**H**), 1.81 (ddd, *J* = 13.0, 6.6, 3.2 Hz, 3H), 1.75–1.62 (m, 2H), 1.46 (td, *J* = 12.4, 9.4 Hz, 1H), 1.28–1.07 (m, 3H), 1.00 (td, *J* = 12.4, 3.2 Hz, 1H).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 172.3 (**C$_4$**), 154.8 (**C$_2$**), 131.4 (**C$_6$**), 129.2 (**C$_8$**), 128.4 (**C$_9$**), 126.2 (**C$_7$**), 88.0 (**C$_5$**), 43.3 (C$_5$**C**H), 26.7, 26.3, 26.1, 25.9, 24.9.
FTIR (thin film) cm^{-1}:	3389 (br-m), 2928 (m), 2852 (w), 1777 (w), 1704 (s), 1502 (m), 1436 (m), 1402 (m), 1148 (m), 1110 (m), 894 (w), 734 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{16}H_{24}N_3O_3$, $[M+NH_4]^+$: 306.1812, found: 306.1817.
TLC (25% ethyl acetate in hexanes), R*f*:	0.28 (UV, CAM).



Alcohol 38b:

The alcohol **38b** was prepared following the representative procedure-D using hydantoin **38a** (33.4 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 20% ethyl acetate in hexanes) to afford alcohol **38b** (10.6 mg, 30.2 µmol, 30.2 %) as a white solid, and separately the recovered hydantoin **38a** (16.3 mg, 49.0 µmol, 49.0%).

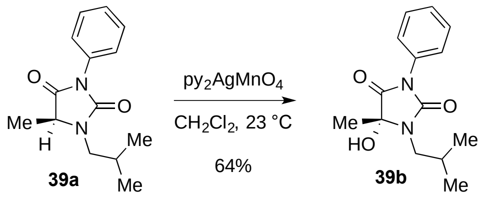
^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.53 (dd, *J* = 7.7, 1.9 Hz, 2H, **ArH**), 7.48–7.30 (m, 8H, **ArH**), 4.06 (s, 1H, C$_5$O**H**), 1.89–1.65 (m, 6H), 1.63–1.51 (m, 2H), 1.16–0.93 (m, 2H), 0.85 (qd, *J* = 11.7, 3.1 Hz, 1H).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 171.6 (**C$_4$**), 153.7 (**C$_2$**), 134.3, 131.3, 129.3, 129.3, 128.6, 127.8, 127.2, 126.4, 90.0 (**C$_5$**), 43.5 (C$_5$**C**H), 26.7, 26.1, 26.0, 25.9, 25.8.
FTIR (thin film) cm^{-1}:	3381 (br-w), 2937 (w), 1780 (w), 1725 (m), 1498 (m), 1409 (m), 1264 (s), 1154 (w), 733 (s), 703 (s).
HRMS (DART) (*m*/*z*):	calc'd for $C_{21}H_{23}N_2O_3$, [M+H]$^+$: 351.1703, found: 351.1699.
TLC (20% ethyl acetate in hexanes), R*f*:	0.23 (UV, CAM).



Alcohol 32b:

The alcohol **32b** was prepared following the representative procedure-D using hydantoin **32a** (21.6 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 25% acetone in hexanes) to yield alcohol **32b** (3.8 mg, 16.4 µmol, 16.4 %) as a white solid, and separately the recovered hydantoin **32a** (15.1 mg, 69.8 µmol, 69.8%).

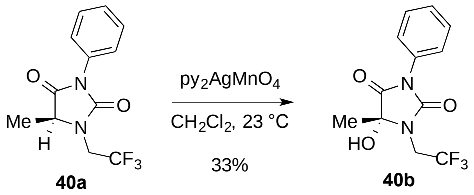
^{1}H NMR (500 MHz, CDCl$_3$, 25 ºC):	δ 7.46 (dd, *J* = 8.5, 7.0 Hz, 2H, C_8**H**), 7.38 (app-dd, *J* = 9.0, 7.5 Hz, 3H, C_7**H**, C_9**H**), 3.76 (dt, *J* = 11.3, 8.3 Hz, 1H, C_5C**H$_a$**), 3.55 (ddd, *J* = 11.7, 8.9, 3.3 Hz, 1H, C_5C**H$_b$**), 3.24 (s, 1H, C_5O**H**), 2.58–2.40 (m, 1H, N_1CH_2C**H$_a$**), 2.35–2.17 (m, 2H, N_1C**H$_a$**, N_1CH_2C**H$_b$**), 1.95 (ddd, *J* = 13.9, 11.2, 8.9 Hz, 1H, N_1C**H$_b$**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 171.7 (**C$_4$**), 157.0 (**C$_2$**), 131.4 (**C$_6$**), 129.3 (**C$_8$**), 128.5 (**C$_9$**), 126.0 (**C$_7$**), 92.8 (**C$_5$**), 45.4 (C_5**C**H_2), 34.4 (N_1**C**H_2), 25.5 (N_1CH_2**C**H_2).
FTIR (thin film) cm^{-1}:	3371 (br-m), 1782 (w), 1709 (s), 1494 (w), 1402 (s), 1195 (m), 1124 (m), 1071 (w), 764 (m), 735 (m), 690 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{12}H_{16}N_3O_3$, $[M+NH_4]^+$: 250.1186, found: 250.1182.
TLC (25% acetone in hexanes), R*f*:	0.16 (UV, CAM).



Alcohol 39b:

The alcohol **39b** was prepared following the representative procedure-D using hydantoin **39a** (18.7 mg, 75.9 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 20% acetone in hexanes) to yield alcohol **39b** (12.7 mg, 48.4 µmol, 63.8 %) as a white solid, and separately the recovered hydantoin **39a** (1.4 mg, 7.5 µmol, 7.5%).

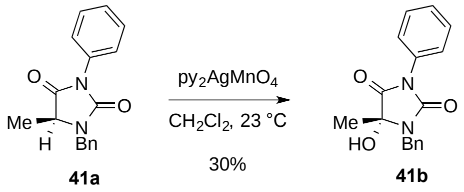
^{1}H NMR (500 MHz, CDCl$_3$, 25 ºC):	δ 7.48–7.41 (m, 2H, C$_8$**H**), 7.41–7.33 (m, 3H, C$_7$**H**, C$_9$**H**), 3.63 (s, 1H, C$_5$O**H**), 3.31 (dd, *J* = 14.2, 8.1 Hz, 1H, N$_1$C**H$_a$**), 3.13 (dd, *J* = 14.2, 7.5 Hz, 1H, N$_1$C**H$_b$**), 2.13 (hept, *J* = 7.1 Hz, 1H, N$_1$CH$_2$C**H**), 1.68 (s, 3H, C$_5$**Me**), 0.96 (d, *J* = 6.7 Hz, 6H, N$_1$CH$_2$CH(**Me**)$_2$).
^{13}C NMR (125 MHz, CDCl$_3$, 25 ºC):	δ 172.7 (**C$_4$**), 154.6 (**C$_2$**), 131.5 (**C$_6$**), 129.2 (**C$_8$**), 128.4 (**C$_9$**), 126.1 (**C$_7$**), 84.5 (**C$_5$**), 47.3 (C$_5$**Me**), 28.4 (N$_1$**C**H$_2$), 22.5 (N$_1$CH$_2$**C**H), 20.5 (N$_1$CH$_2$CH**Me$_a$**) 20.4 (N$_1$CH$_2$CH**Me$_b$**).
FTIR (thin film) cm^{-1}:	3370 (br-m), 2961 (w), 1782 (w), 1706 (s), 1503 (w), 1420 (m), 1374 (m), 1156 (m), 1131 (m), 767 (w).
HRMS (DART) (*m*/*z*):	calc'd for C$_{14}$H$_{22}$N$_3$O$_3$, [M+NH$_4$]$^+$: 280.1656, found: 280.1649.
TLC (25% ethyl acetate in hexanes), R*f*:	0.24 (UV, CAM).



Alcohol 40b:

The alcohol **40b** was prepared following the representative procedure-D using hydantoin **40a** (27.2 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 25% acetone in hexanes) to yield alcohol **40b** (9.6 mg, 33.3 µmol, 33.3%) as a white solid, and separately the recovered hydantoin **40a** (9.5 mg, 34.9 µmol, 34.9%).

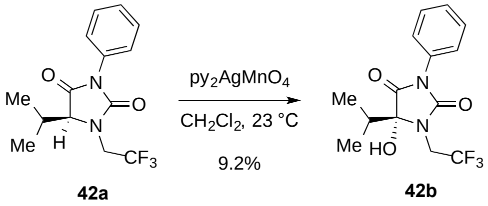
^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.49–7.37 (m, 3H, C$_8$**H**, C$_9$**H**), 7.37–7.31 (m, 2H, C$_7$**H**), 4.47 (s, 1H, C$_5$O**H**), 4.01 (dq, *J* = 15.9, 9.0 Hz, 1H, N$_1$C**H$_a$**), 3.88 (dq, *J* = 15.9, 8.8 Hz, 1H, N$_1$C**H$_b$**), 1.68 (s, 3H, C$_5$**Me**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 172.2 (**C$_4$**), 155.0 (**C$_2$**), 130.9 (**C$_6$**), 129.4 (**C$_8$**), 128.9 (**C$_9$**), 126.2 (**C$_7$**), 125.4 (q, *J* = 280.6 Hz, N$_1$CH**C**F$_3$), 84.3 (**C$_5$**), 40.8 (q, *J* = 36.6 Hz, N$_1$**C**H), 22.6 (C$_5$**Me**).
^{19}F NMR (282 MHz, CDCl$_3$, 25 ºC):	δ –70.55 (t, *J* = 9.1 Hz).
FTIR (thin film) cm^{-1}:	3388 (br-w), 1792 (w), 1733 (m), 1423 (m), 1264 (s), 1155 (m), 1046 (w), 896 (w), 703 (s).
HRMS (DART) (*m*/*z*):	calc'd for $C_{12}H_{15}F_3N_3O_3$, $[M+NH_4]^+$: 306.1060, found: 306.1054.
TLC (25% acetone in hexanes), R*f*:	0.22 (UV, CAM).



Alcohol 41b:

The alcohol **41b** was prepared following the representative procedure-D using hydantoin **41a** (28.0 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 20% acetone in hexanes) to yield alcohol **41b** (9.0 mg, 30.4 µmol, 30.4%) as a white solid, and separately the recovered hydantoin **41a** (1.5 mg, 5.4 µmol, 5.4%).

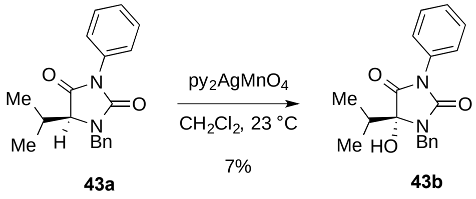
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):	δ 7.56–7.38 (m, 6H, **ArH**), 7.38–7.29 (m, 4H, **ArH**), 4.76 (d, *J* = 15.6 Hz, 1H, N$_1$C**H$_a$**), 4.52 (d, *J* = 15.6 Hz, 1H, N$_1$C**H$_b$**), 3.38 (s, 1H, C$_5$O**H**), 1.54 (s, 3H, C$_5$**Me**).
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC):	δ 172.4 (**C$_4$**), 154.5 (**C$_2$**), 137.6, 131.4, 129.3, 129.0, 128.5, 128.4, 128.0, 126.1, 84.5 (**C$_5$**), 43.1 (N$_1$**C**H$_2$), 22.9 (C$_5$**Me**).
FTIR (thin film) cm^{-1}:	3379 (br-w), 3056 (w), 1783 (w), 1713 (s), 1503 (w), 1417 (m), 1265 (s), 1168 (m), 1136 (m), 733 (s), 701 (s).
HRMS (DART) (*m*/*z*):	calc'd for $C_{17}H_{20}N_3O_3$, $[M+NH_4]^+$: 314.1499, found: 314.1495.
TLC (20% acetone in hexanes), R*f*:	0.15 (UV, CAM).



Alcohol 42b:

The alcohol **42b** was prepared following the representative procedure-D using hydantoin **42a** (30.0 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 20% ethyl acetate in hexanes) to yield alcohol **42b** (2.9 mg, 9.2 µmol, 9.2%) as a white solid, and separately the recovered hydantoin **42a** (21.3 mg, 70.9 µmol, 70.9%).

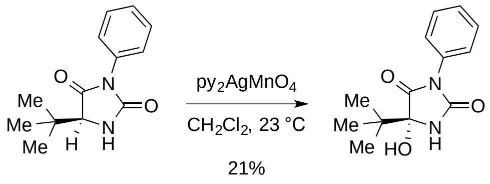
^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.54–7.44 (m, 2H, C$_8$**H**), 7.44–7.32 (m, 3H, C$_7$**H**, C$_9$**H**), 4.10 (dq, *J* = 15.8, 8.9 Hz, 1H, N$_1$C**H$_a$**), 3.94 (dq, *J* = 15.8, 8.8 Hz, 1H, N$_1$C**H$_b$**), 3.44 (s, 1H, C$_5$O**H**), 2.33 (p, *J* = 6.9 Hz, 1H, C$_5$C**H**), 1.29 (d, *J* = 6.9 Hz, 3H, C$_5$CH**Me$_a$**), 1.01 (d, *J* = 7.0 Hz, 3H, C$_5$CH**Me$_b$**).
^{13}C NMR (125 MHz, CDCl$_3$, 25 ºC):	δ 170.7 (**C$_4$**), 155.4 (**C$_2$**), 130.9 (**C$_6$**), 129.4 (**C$_8$**), 128.9 (**C$_9$**), 126.2 (**C$_7$**), 123.7 (q, *J* = 279.7 Hz, N$_1$CH$_2$**CF$_3$**), 88.8 (**C$_5$**), 41.1 (q, *J* = 36.7 Hz, N$_1$**C**H$_2$), 34.3 (C$_5$**C**H), 16.4 (C$_5$CH**Me$_a$**), 15.7 (C$_5$CH**Me$_b$**).
^{19}F NMR (282 MHz, CDCl$_3$, 25 ºC):	δ –70.12 (t, *J* = 8.8 Hz).
FTIR (thin film) cm^{-1}:	3373 (br-w), 1714 (s), 1503 (w), 1425 (m), 1268 (m), 1153 (s), 1080 (m), 831 (w), 695 (w).
HRMS (DART) (*m*/*z*):	calc'd for C$_{14}$H$_{19}$N$_3$O$_3$, [M+NH$_4$]$^+$: 334.1373, found: 334.1365.
TLC (25% ethyl acetate in hexanes), R*f*:	0.21 (UV, CAM).



Alcohol 43b:

The alcohol **43b** was prepared following the representative procedure-D using hydantoin **43a** (30.8 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 20% → 25% ethyl acetate in hexanes) to yield alcohol **43b** (2.3 mg, 7.1 µmol, 7.1%) as a white solid, and separately the recovered hydantoin **43a** (21.5 mg, 69.7 µmol, 69.7%).

^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.43 (app-tt, *J* = 6.9, 1.3 Hz, 4H, **ArH**), 7.38–7.27 (m, 6H, **ArH**), 4.59 (d, *J* = 15.4 Hz, 1H, $N_1C\mathbf{H_a}$), 4.48 (d, *J* = 15.5 Hz, 1H, $N_1C\mathbf{H_b}$), 3.71 (s, 1H, $C_5O\mathbf{H}$), 2.24 (p, *J* = 6.9 Hz, 1H, $C_5C\mathbf{H}$), 1.14 (d, *J* = 6.8 Hz, 3H, $C_5CH\mathbf{Me_a}$), 0.80 (d, *J* = 7.0 Hz, 3H, $C_5CH\mathbf{Me_b}$).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 171.8 ($\mathbf{C_4}$), 155.4 ($\mathbf{C_2}$), 137.6, 131.4, 129.3, 128.8, 128.8, 128.5, 127.9, 126.2, 89.3 ($\mathbf{C_5}$), 43.2 ($N_1\mathbf{C}H_2$), 34.2 ($C_5\mathbf{C}H$), 16.3 ($C_5CH\mathbf{Me_a}$), 15.9 ($C_5CH\mathbf{Me_b}$).
FTIR (thin film) cm^{-1}:	3386 (br-w), 3054 (w), 1774 (w), 1723 (m), 1700 (s), 1497 (m), 1422 (m), 1363 (w), 1264 (s), 1164 (w), 896 (w), 838 (w), 733 (s), 704 (s).
HRMS (DART) (*m*/*z*):	calc'd for $C_{19}H_{24}N_3O_3$, $[M+NH_4]^+$:342.1812, found: 342.1828.
TLC (25% ethyl acetate in hexanes), R*f*:	0.17 (UV, CAM).

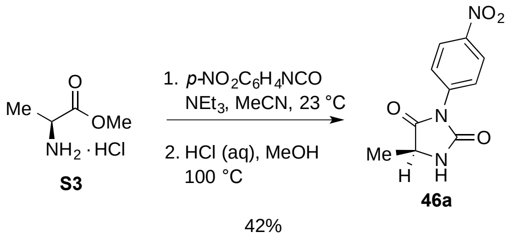


33a **33b**

Alcohol 33b:

The alcohol **33b** was prepared following the representative procedure-D using hydantoin **33a** (23.2 mg, 100 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 35% ethyl acetate in hexanes) to yield alcohol **33b** (5.2 mg, 21.0 µmol, 21.0 %) as a white solid, and separately the recovered hydantoin **33a** (7.0 mg, 30.1 µmol, 30.1%).

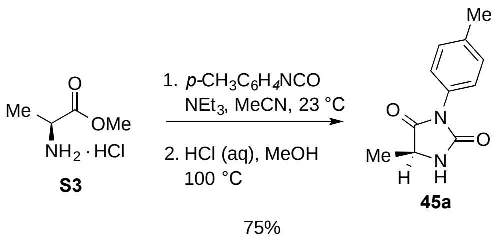
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC):	δ 7.45 (app-t, *J* = 7.6 Hz, 2H, C_8**H**), 7.38 (app-t, *J* = 7.5 Hz, 1H, C_9**H**), 7.34 (app-d, *J* = 7.7 Hz, 2H, C_7**H**), 6.28 (s, 1H, N_1**H**), 3.67 (s, 1H, C_5O**H**), 1.12 (s, 9H, C_5C(**Me**)$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC):	δ 172.5 (**C$_4$**), 155.4 (**C$_2$**), 131.1 (**C$_6$**), 129.4 (**C$_8$**), 128.7 (**C$_9$**), 126.4 (**C$_7$**), 88.4 (**C$_5$**), 38.3 (C_5**C**), 24.0 (C_5C(**Me**)$_3$).
FTIR (thin film) cm^{-1}:	3335 (br-m), 1783 (w), 1711 (s), 1502 (w), 1419 (m), 1200 (w), 1121 (w), 864 (m), 734 (m), 703 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{13}H_{17}N_2O_3$, $[M+H]^+$: 249.1234, found: 249.1234.
TLC (25% ethyl acetate in hexanes), R*f*:	0.21 (UV, CAM).



Hydantoin 46a:

The hydantoin **46a** was prepared following the representative procedure-A using L-alanine methyl ester hydrogen chloride **S3** (500 mg, 3.58 mmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 10% acetone in dichloromethane) to yield hydantoin **46a** (348 mg, 1.49 mmol, 41.6% over two steps) as a yellow solid.

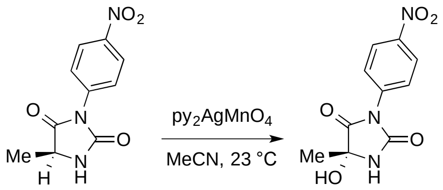
^{1}H NMR (400 MHz, Acetone-d_6, 25 ºC):	δ 8.35 (d, J = 9.1 Hz, 2H, C$_8$**H**), 7.85 (d, J = 9.1 Hz, 2H, C$_7$**H**), 7.62 (s, 1H, N$_1$**H**), 4.38 (q, J = 6.9 Hz, 1H, C$_5$**H**), 1.50 (d, J = 6.9 Hz, 2H, C$_5$**Me**).
^{13}C NMR (100 MHz, Acetone-d_6, 25 ºC):	δ 174.3 (**C$_4$**), 155.5 (**C$_2$**), 147.0 **(C$_9$),** 139.6 **(C$_6$),** 127.1, 124.7, 53.5 (**C$_5$**), 17.7 (C$_5$**Me**).
FTIR (thin film) cm^{-1}:	3241 (br-w), 1779 (w), 1725 (s), 1524 (m), 1411 (m), 1332 (m), 1185 (m), 1115 (w).
HRMS (DART) (m/z):	calc'd for $C_{10}H_{10}N_3O_4$, $[M+H]^+$: 236.0666, found: 236.0669.
TLC (10% acetone in dichloromethane), Rf:	0.39 (UV, CAM).



Hydantoin 45a:

The hydantoin **45a** was prepared following the representative procedure-A using L-alanine methyl ester hydrogen chloride **S3** (500 mg, 3.58 mmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 5% acetone in dichloromethane) to yield hydantoin **45a** (552 mg, 2.70 mmol, 75.4% over two steps) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC):	δ 7.43–7.13 (m, 4H, **ArH**), 6.53 (s, 1H, N$_1$**H**), 4.21 (q, *J* = 6.9 Hz, 1H, C$_5$**H**), 2.37 (s, 3H, C$_9$**Me**) 1.53 (d, *J* = 7.0 Hz, 1H, C$_5$**Me**).
^{13}C NMR (100 MHz, CDCl$_3$, 25 ºC):	δ 174.0 (**C$_4$**), 157.3 (**C$_2$**), 138.6, 130.0, 128.9, 126.3, 53.1 (**C$_5$**), 21.4 (C$_9$**Me**), 17.9 (C$_5$**Me**).
FTIR (thin film) cm^{-1}:	3258 (br-w), 1774 (w), 1712 (s), 1516 (w), 1418 (m), 1177 (w), 893 (w).
HRMS (DART) (*m*/*z*):	calc'd for $C_{11}H_{13}N_2O_2$, [M+H]$^+$: 205.0972, found: 205.0961.
TLC (5% acetone in dichloromethane), R*f*:	0.25 (UV, CAM).

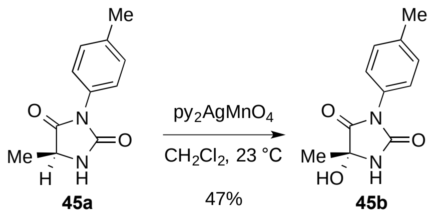


46a 37% **46b**

Alcohol 46b:

The alcohol **46b** was prepared following the representative procedure-D using hydantoin **46a** (47.0 mg, 200 µmol, 1 equiv) in acetonitrile. The crude product after workup was purified via flash column chromatography on silica gel (eluent: 20% acetone in dichloromethane) to yield alcohol **46b** (17.6 mg, 73.0 µmol, 36.5 %) as a white solid.

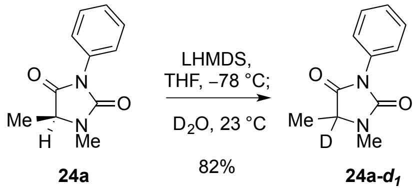
^{1}H NMR (500 MHz, Acetone-*d*$_6$, 25 ºC):	δ 8.38 (d, *J* = 9.2 Hz, 2H, C$_8$**H**), 8.25 (br-s, 1H, N$_1$**H**) 7.84 (d, *J* = 9.0 Hz, 2H, C$_7$**H**), 5.96 (s, 1H, C$_5$O**H**), 1.72 (s, 3H, C$_5$**Me**).
^{13}C NMR (125 MHz, Acetone-*d*$_6$, 25 ºC):	δ 173.3 (**C$_4$**), 154.0 (**C$_2$**), 147.1 (**C$_9$**), 139.2 (**C$_6$**), 127.1, 124.8, 83.0 (**C$_5$**), 23.6 (C$_5$**Me**).
FTIR (thin film) cm^{-1}:	3309 (br-m), 1716 (s), 1596 (w), 1522 (m), 1498 (m), 1343 (s), 1302 (m), 1160 (m), 957 (w).
HRMS (DART) (*m*/*z*):	calc'd for $C_{10}H_{10}N_3O_5$, [M+H]$^+$: 252.0615, found: 252.0621.
TLC (20% acetone in dichloromethane), R*f*:	0.35 (UV, CAM).



Alcohol 45b:

The alcohol **45b** was prepared following the representative procedure-D using hydantoin **45a** (40.8 mg, 200 µmol, 1 equiv). The crude product after workup was purified via flash column chromatography on silica gel (eluent: 20% acetone in dichloromethane) to yield alcohol **45b** (20.7 mg, 94.0 µmol, 47.0 %) as a white solid.

^{1}H NMR (500 MHz, Acetone-d_6, 25 ºC):	δ 7.91 (s, 1H, N$_1$**H**), 7.26 (s, 4H, Ar**H**), 5.81 (s, 1H, C$_5$O**H**), 2.35 (s, 3H, C$_9$**Me**), 1.65 (s, 3H, C$_5$**Me**).
^{13}C NMR (125 MHz, Acetone-d_6, 25 ºC):	δ 173.8 (**C$_4$**), 155.0 (**C$_2$**), 138.3, 130.8, 130.0, 127.2, 82.9 (**C$_5$**), 23.9 (C$_9$**C**H$_3$), 21.1 (C$_5$**Me**).
FTIR (thin film) cm^{-1}:	3307 (br-m), 1713 (s), 1695 (s), 1516 (m), 1410 (m), 1160 (w), 1121 (w), 876 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{11}H_{13}N_2O_3$, $[M+H]^+$: 221.0921, found: 221.0901.
TLC (20% acetone in dichloromethane), R*f*:	0.33 (UV, CAM).

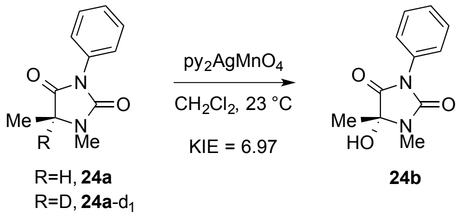


Deuteriohydantoin 24a-*d*$_1$:

An anhydrous solution of hydantoin **24a** (250 mg, 1.22 mmol, 1 equiv) in tetrahydrofuran (30 mL) was cooled to –78 °C and maintained under an argon atmosphere. Anhydrous tetrahydrofuran (30 mL) was charged into a separate flame-dried round bottom flask containing lithium bis(trimethylsilyl)amide (614 mg, 3.66 mmol, 3.00 equiv) and cooled to –78 °C. The hydantoin solution was rapidly transferred into the solution of base at –78 °C via cannula. After 1 h, deuterium oxide (1.00 mL, 49.9 mmol, 40.0 equiv) was added via syringe and the reaction mixture was allowed to warm to 23 °C. The resulting mixture was diluted by addition of ethyl acetate (100 mL) and saturated aqueous solution of ammonium chloride (150 mL). The aqueous layer was extracted with ethyl acetate (2 × 100 mL) and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude oil was purified via flash column chromatography on silica gel (eluent: 25% → 50% ethyl acetate in hexanes) to provide deuteriohydantoin **24a**-*d*$_1$ (206 mg, 1.00 mmol, 82.0%) as a white solid.

^{1}H NMR (500 MHz, CDCl$_3$, 25 ºC):	δ 7.45 (dd, J = 8.3, 7.1 Hz, 2H, C$_8$**H**), 7.41–7.38 (m, 2H, C$_7$**H**), 7.35 (app-t, J = 7.1 Hz, 1H, C$_9$**H**), 3.03 (s, 3H, N$_1$**Me**), 1.53 (s, 3H, C$_5$**Me**).
^{13}C NMR (125 MHz, CDCl$_3$, 25 ºC):	δ 172.6 (**C$_4$**), 155.3 (**C$_2$**), 132.0 (**C$_6$**), 129.2 (**C$_8$**), 128.2 (**C$_9$**), 126.2 (**C$_7$**), 56.83 (t, J = 21.9 Hz, **C$_5$**), 27.8 (N$_1$**Me**), 15.3 (C$_5$**Me**).
FTIR (thin film) cm^{-1}:	1774 (w), 1709 (s), 1501 (w), 1429 (m), 1401 (m), 1144 (m), 886 (w), 760 (w), 695 (w).
HRMS (DART) (*m*/*z*):	calc'd for $C_{11}H_{12}DN_2O_2$, $[M+H]^+$: 206.1034, found: 206.1025.
TLC (50% ethyl acetate in hexanes), R*f*:	0.39 (UV, CAM).

Kinetic Isotope Effect Study



These experiments were conducted following the representative procedure-D and stopped at multiple time points to determine percent conversion. Each time point is a single measurement.

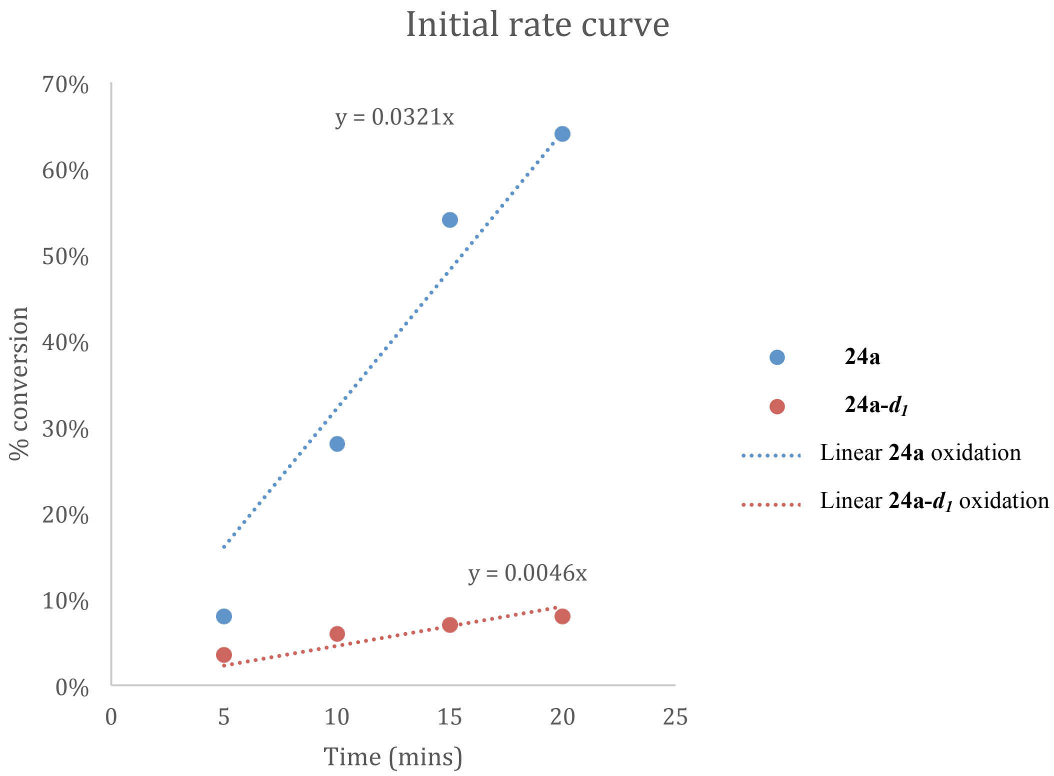
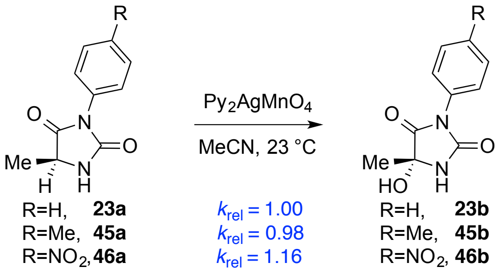


Figure S1. The observed external kinetic isotope effect is consistent with the mechanistic hypothesis that C–H abstraction is the rate-limiting step. The observation of a significant kinetic isotope effect is consistent with the observed and predicted relative rate measurements (internal competition).

Hammett Plot Analysis



These experiments were conducted following representative procedure-D and stopped at multiple time points to obtain rate data and generate the Hammett Plot. This information was not used in the preparation of the mathematical model. The rho value (0.4) is consistent with the mechanistic hypothesis where the radical center in the transition state is better stabilized by greater captodative stabilization. These *para*-substituted hydantoins were not included in the model due to the minimal difference in structure as compared to the variables included in the model.

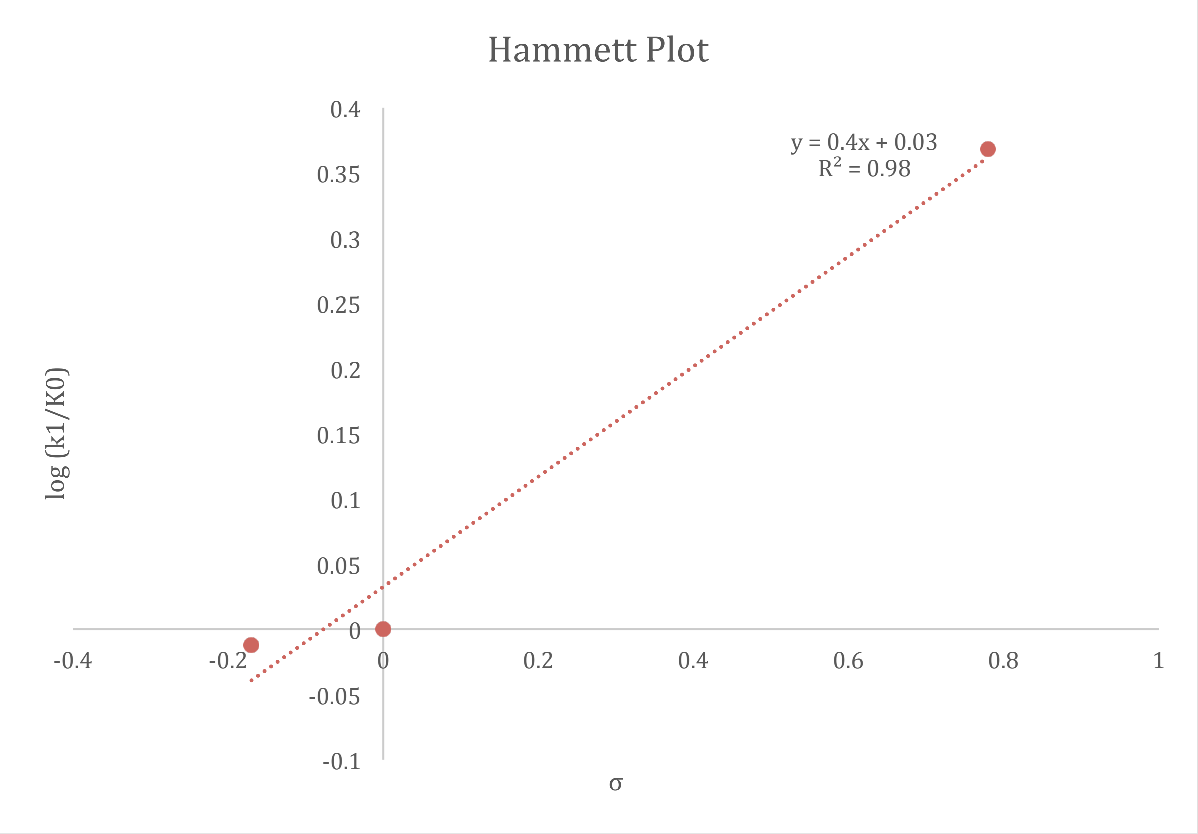
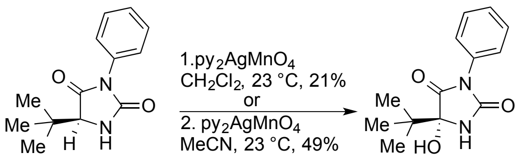


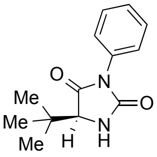
Figure S2. Hammett plot analysis and observed relative rate data.

Stereochemical Studies



33a, 90% ee **33b**, 90% ee

These experiments were conducted following representative procedure-D. The alcohol product is obtained with the same level of enantiomeric excess as the starting material in both dichloromethane and acetonitrile. The hydroxylation is stereospecific and stereoretentive suggesting a rapid oxygen rebound after C–H abstraction. In cases where the resulting alcohol product is particularly prone to ionization or hydantoin-ring opening, or if careful product isolation is not exercised, the product may be isolated with lower levels of enantiomeric enrichment.



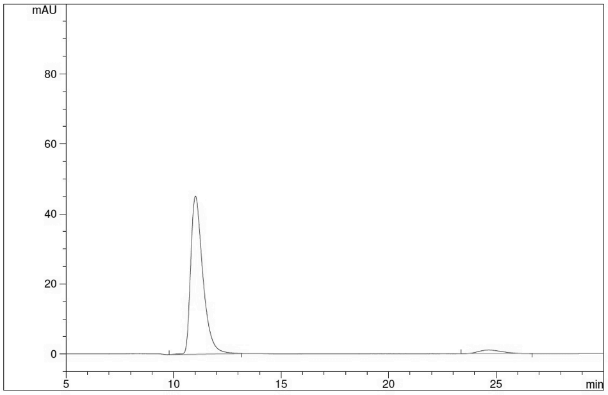
33a

HPLC conditions:
Chiralcel OD-H, column #ODH0CE-KF021

10% isopropanol/ 90% hexanes

1.0 mL/min

254 nm



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-------------------------------------------
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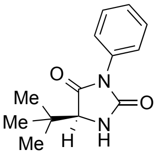


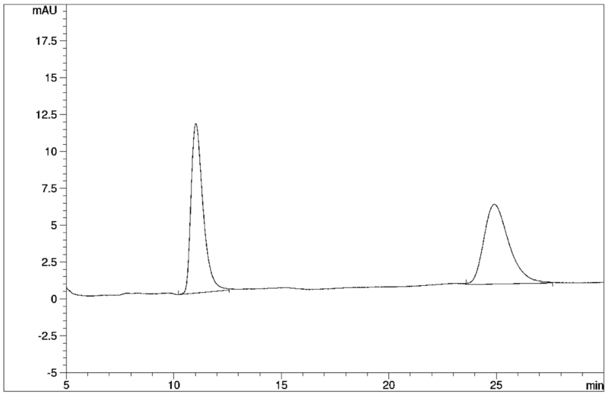
(±)-**33a**

HPLC conditions:
Chiralcel OD-H, column #ODH0CE-KF021

10% isopropanol/ 90% hexanes

1.0 mL/min

254 nm



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-------------------------------------------
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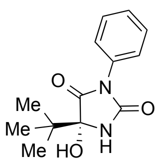


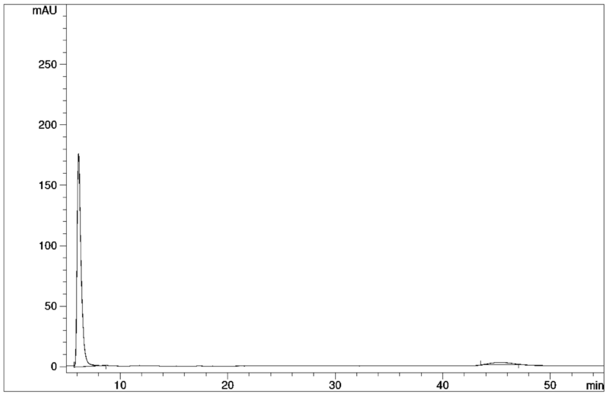
33b

HPLC conditions:
Chiralcel OD-H, column #ODH0CE-KF021

15% isopropanol/ 85%

1.0 mL/min

254 nm



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 2             45.337              5.022
--------------------------------------------
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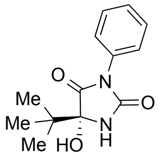


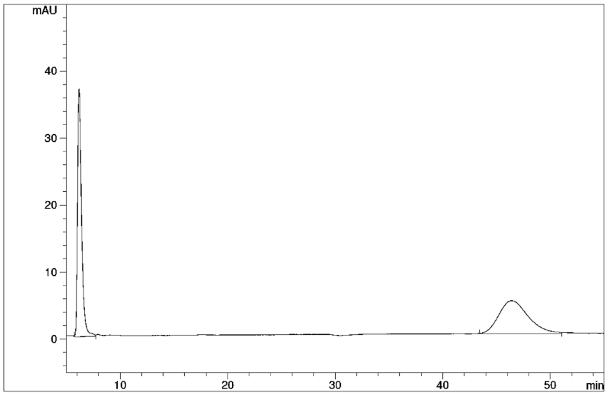
(±)-**33b**

HPLC conditions:
Chiralcel OD-H, column #ODH0CE-KF021

15% isopropanol/ 85%

1.0 mL/min

254 nm



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#    Meas. Ret. Time          Area %
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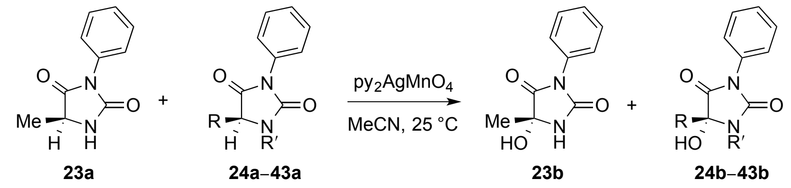
 2             46.403             49.617
--------------------------------------------
```

Relative Rate Measurements and Model Development



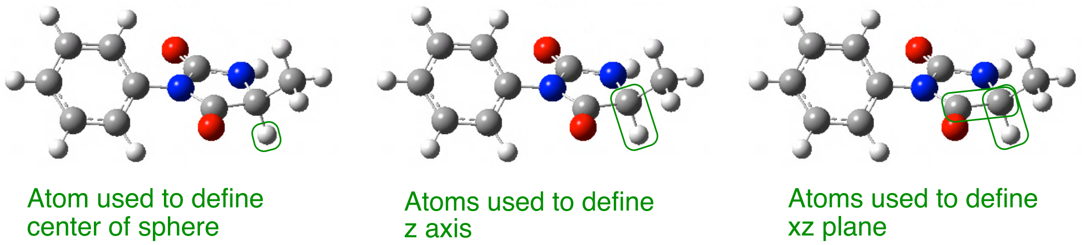
General Procedure for Obtaining Relative Rates:

A sample of bis(pyridine)silver(I) permanganate (15.4 mg, 40.0 μmol, 0.400 equiv) was placed in three vials equipped with stir bars and purged with nitrogen for 10 minutes. Acetonitrile (0.5 mL) was then added to each vial. A solution of hydantoin **23a** (57.0 mg, 0.300 mmol, 3.00 equiv) in acetonitrile (0.75 mL) was combined with a solution of hydantoin substrate **24a–43a** (0.300 mmol, 3.00 equiv) and 1-methylnaphthalene (42.6 μL, 0.300 mmol, 3.00 equiv) in acetonitrile (0.75 mL) under nitrogen. The resulting solution was split into three equal portions (0.5 mL) and added to the stirred solution of oxidant under nitrogen. After 1 h, each reaction mixture passed through a Celite® plug and examined using gas chromatography. Thus, the relative rate data was obtained and converted to $\Delta\Delta G^{\ddagger}$ according to equation 1, in which r_1 and p_1 are the reactant and product of the reference substrate-1 (hydantoin **23a**), and r_i and p_i are the reactant and product of the substrate **24a–43a.**

$$\Delta\Delta G^{\ddagger} = 0.001986 * 298 * \ln\left(\frac{p_i * r_1}{p_1 * r_i}\right) \qquad (1)$$

Model Development:

Gaussian 09 software[6] was used to obtain DFT calculations. The hydantoin and diketopiperazine geometries were optimized at the M06-2X/def2tzvp[7] level of theory with an ultrafine integration grid. These optimized structures were then used as the basis of parameter acquisition. The structural features[8] (bond distances *d*, angles and torsion angles θ[9]) were obtained from the optimized structures in Gaussview. The infrared vibrational frequencies and intensities,[9a,9b,10] as well as ^{13}C[11] and ^{1}H NMR shifts (δ),[10c] are computed using Gaussian 09. The NBO charges[12] are calculated on the Gaussian 09 platform with the external program NBO 6.0. Sterimol[9b,9c,12a,13] (B_1, B_5, L), Hammett (σ)[14], and Taft parameters[15] (σ*) are calculated using Molecular Modeling Pro®[16]. Sambvca 2[17] was employed to determine the percent buried volume ($\%V_{bur}$) at varying spherical radii between 1.75 and 3.5 Å. For these measurements, the hydrogen connected to C5 was used to define the center of the sphere, the Z axis was defined using atoms C5 and the connected hydrogen to define the Z axis, the XZ plane was defined using C5, its connected hydrogen, and C4 (Figure S3), bond radii were scaled by 1.17 Å, the distance of the coordination point from the center of the sphere was 0.0 Å, and the mesh spacing for numerical integration was set at 0.10. All hydrogen atoms were included in these calculations. Several relevant parameters for the hydantoins and diketopiperazines are shown in the Tables S1–S4. Parameters highlighted in red constitute the models. Linear regression plots were created using Prism 7.0b.[18]



Atom used to define center of sphere

Atoms used to define z axis

Atoms used to define xz plane

Figure S3. Atoms used in %V_{bur} calculations.

Table S1. Calculated parameters to describe IR vibrations and the hydrogen that is abstracted from the hydantoins.

Substrate	$\nu_{C\text{-}H}$	$i_{C\text{-}H}$	$\nu_{C=O}$	$i_{C=O}$	δ_H	NBO_H	$\%V_{bur}$
23a	3060.39	8.95	1894.58	93.58	4.57	0.2159	67.0
24a	3038.25	12.71	1881.62	71.64	4.28	0.2131	68.2
25a	3070.16	4.99	1881.72	111.38	5.16	0.2212	72.0
41a	3045.13	12.55	1878.13	88.54	4.43	0.2149	68.1
39a	3036.99	12.38	1878.32	74.23	4.30	0.2138	68.4
26a	3034.78	5.68	1890.25	125.15	3.95	0.2137	70.2
27a	3029.72	7.16	1877.25	76.39	3.59	0.2114	72.6
28a	3037.20	5.19	1877.47	89.40	4.86	0.2198	76.4
42a	3033.03	5.61	1884.16	58.31	3.78	0.2142	71.7
43a	3040.13	15.46	1869.86	65.98	4.37	0.2185	70.7
36a	3034.56	8.39	1889.75	181.78	4.04	0.2144	70.2
37a	3029.70	10.02	1876.34	79.22	3.67	0.2118	73.0
38a	3072.46	8.00	1878.54	99.24	5.30	0.2227	74.1
32a	3086.65	10.14	1885.34	59.07	4.54	0.2222	67.3
31a	3067.03	4.71	1884.19	116.16	6.23	0.2326	73.8
35a	3052.51	12.90	1874.85	84.55	4.46	0.2181	74.5
33a	3051.38	12.94	1889.08	171.74	4.17	0.2200	70.8
34a	3099.02	17.33	1889.34	141.97	4.67	0.2221	73.5
24a-d_1	3038.23	12.949	1880.60	70.92	4.28	0.2131	68.2

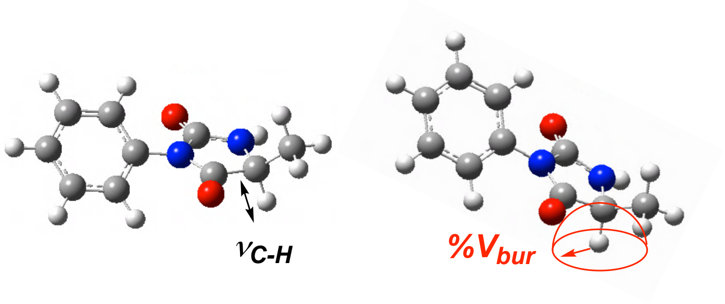


Figure S4. Representative parameters from Table S1.

Table S2. Calculated parameters to describe the C5 position of the hydantoins.

Substrate	$\sigma_{p(C5)}$	L_{C5}	$B1_{C5}$	$B5_{C5}$	δ_{C5}	NBO_{C5}
23a	−0.1200	3.07	1.70	2.20	70.74	−0.13433
24a	−0.1200	3.08	1.70	2.20	75.63	−0.12408
25a	−0.1200	3.08	1.70	2.20	73.15	−0.12297
26a	−0.1760	4.34	2.07	3.34	81.75	−0.12788
27a	−0.1760	4.36	2.08	3.35	89.23	−0.12012
28a	−0.1760	4.40	2.08	3.35	82.40	−0.11791
31a	0.4090	6.37	1.77	3.21	82.45	−0.14009
32a	0.2100	8.83	4.31	4.76	84.19	−0.13765
33a	−0.2040	4.42	2.07	3.37	84.63	−0.1301
34a	−0.1640	5.39	1.74	4.57	71.89	−0.13372
35a	−0.1640	5.39	1.73	4.57	75.43	−0.12306
36a	0.1320	6.41	2.08	3.67	80.13	−0.12404
37a	0.0870	6.43	2.09	3.69	87.21	−0.11777
38a	0.1500	6.51	2.16	3.58	83.07	−0.11274
39a	−0.1200	3.08	1.70	2.20	77.21	−0.12189
41a	−0.1200	3.08	1.70	2.20	77.70	−0.12409
42a	−0.1760	4.36	2.07	3.35	88.00	−0.11433
43a	−0.1760	4.35	2.09	3.34	87.37	−0.11873
24a-d_1	−0.1200	3.07	1.70	2.20	75.62	−0.12408

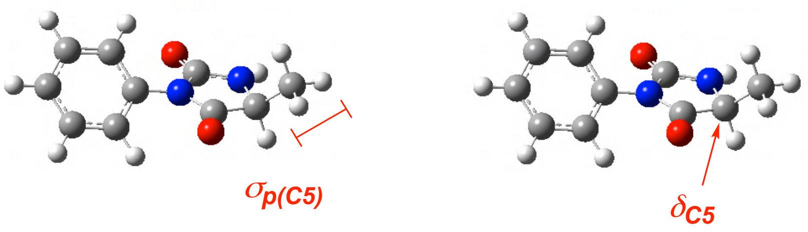


Figure S5. Representative parameters from Table S2.

Table S3. Calculated parameters to describe the N1 position of the hydantoins and bond angles and distances.

Substrate	$\sigma_{p(N1)}$	L_{N1}	$B1_{N1}$	$B5_{N1}$	NBO_{N1}	θ_{COCH}	d_{CH}
23a	0.0000	2.18	1.17	1.17	−0.6272	66.79	1.0947
24a	−0.1200	3.00	1.70	2.20	−0.4378	66.15	1.0969
25a	−0.0930	6.45	1.70	3.37	−0.4338	64.09	1.0939
41a	−0.0880	5.47	1.72	6.16	−0.4292	64.20	1.0960
39a	−0.1640	5.26	1.73	4.58	−0.4407	67.13	1.0970
26a	0.0000	2.18	1.17	1.17	−0.6292	64.61	1.0970
27a	−0.1200	3.03	1.70	2.20	−0.4434	63.40	1.0979
28a	−0.0510	6.46	1.70	3.32	−0.4482	57.96	1.0931
42a	0.2180	4.53	1.70	3.85	−0.4427	61.81	1.0974
43a	−0.0880	5.20	1.73	6.11	−0.4307	62.56	1.0966
36a	0.0000	2.17	1.17	1.17	−0.6285	64.31	1.0966
37a	−0.1200	3.03	1.70	2.21	−0.4426	64.12	1.0977
38a	−0.0510	6.45	1.70	3.33	−0.4483	61.52	1.0939
32a	−0.1580	9.72	3.12	4.23	−0.4298	55.58	1.0924
31a	−0.0090	6.29	1.77	3.22	−0.4255	60.02	1.0942
35a	−0.1200	3.01	1.70	2.21	−0.4351	61.87	1.0955
33a	0.0000	2.17	1.17	1.17	−0.6323	62.65	1.0956
34a	0.0000	2.18	1.17	1.17	−0.6224	57.68	1.0921
24a-*d*$_1$	−0.1200	3.00	1.70	2.20	−0.4378	66.18	1.0969

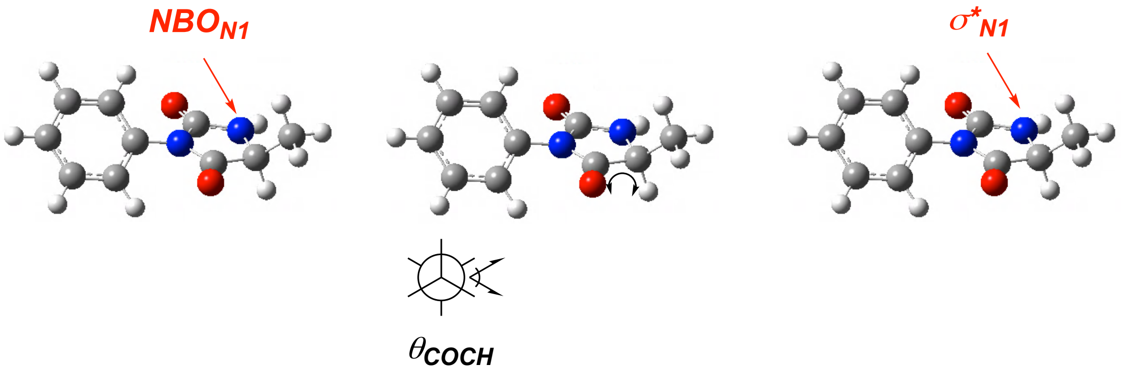


Figure S6. Representative parameters from Table S3.

Table S4. Calculated parameters to describe the diketopiperazines.

Substrate	$\%V_{bur}$	$\sigma_{p(C5)}$	δ_{C5}	NBO_{N1}
Methylene				
(+)-**19**	78.80	0.0000	69.7341	−0.4402
(+)-**19** (2)	71.40	0.0000	69.7341	−0.4402
Threonine Cα				
(+)-**19**	70.30	0.0000	77.2317	−0.4939
C15 – H				
47b	70.30	0.0800	73.4965	−0.4276
48b	72.20	−0.1200	79.5340	−0.4240
50b	66.60	0.0000	71.0492	−0.4286
49b	71.70	0.0250	77.1527	−0.4265
51b	71.90	−0.1200	73.4965	−0.4985
C15 – H (2)				
50b	70.60	0.0000	71.0492	−0.4286
C11 – H				
47b	69.90	0.2990	79.8218	−0.4421
48b	75.40	0.2780	78.6419	−0.4444
50b	77.10	0.4090	88.3891	−0.4388
49b	69.90	0.2990	79.3981	−0.4359
51b	70.10	0.2990	79.9969	−0.4436

Following collection of the relevant parameters, the multidimensional analysis was performed using Matlab® R2015b[19] software, where attempts were made to describe the relative transition state energies $\Delta\Delta G^{\ddagger}$ (determined by relative rate experiments as shown above) using these molecular descriptors. A script previously developed by one of our group members[20] was used to assist this process. First, a correlation matrix was constructed to analyze the intercorrelations between the parameters, as well as the univariate trends in reference to the measured $\Delta\Delta G^{\ddagger}$ (Figure S7). Multivariate linear regression analysis was then performed to correlate the parameters to the measured $\Delta\Delta G^{\ddagger}$, using a forward stepwise search where the criterion for model improvement is set to a combined score of R^2, Q^2 (from leave-one-out cross-validation), $R^2_{\text{K-fold}}$ (from four-fold cross-validation and average of five runs), and the number of parameters in the model. In addition, any models containing collinear parameters (parameters that are correlated with an $R^2 \geq 0.3$) were rejected. The models generated through this process were then studied, and the best was chosen based on its simplicity and interpretability. The most favorable model determined by this method is shown in the paper, with the corresponding data provided in Table S5. For this model, $R^2_{\text{K-fold}} = 0.66$. The leave-one-out analysis was employed to determine the generalizability of the model. This cross validation generates a model leaving one observation out, then determines the ability of the model to predict the point which was left out. A Q^2 that is similar to R^2 implies a robust model. The predicted $\Delta\Delta G^{\ddagger}_{\text{LOO}}$ is shown in Table S5, and the correlation of leave-one-out predictions to experimental values shown in Figure S8.

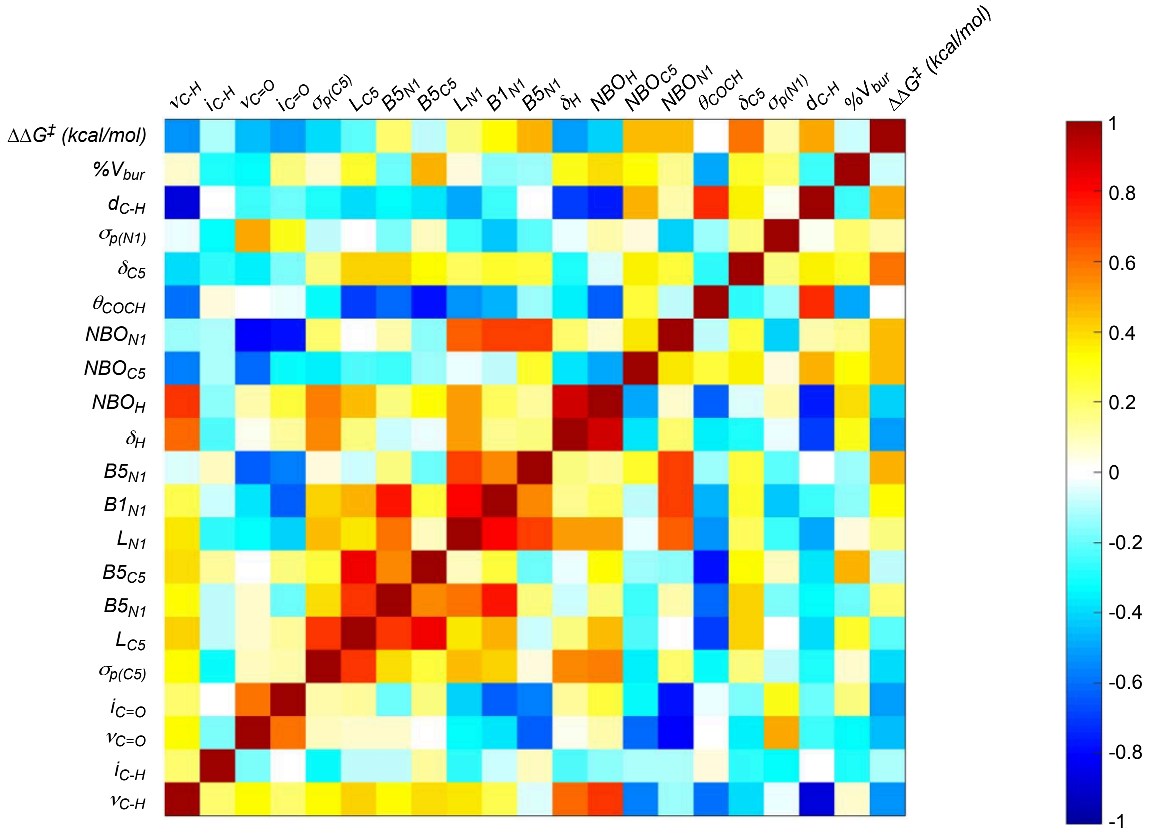


Figure S7. Correlation matrix between relevant parameters.

Table S5. Measured and predicted $\Delta\Delta G^{\ddagger}$ using multivariate correlation and a leave-one-out-analysis.

Substrate	***Measured*** $\Delta\Delta G^{\ddagger}$ ***(kcal/mol)***	***Predicted*** $\Delta\Delta G^{\ddagger}$ ***(kcal/mol)***	***Predicted*** $\Delta\Delta G^{\ddagger}$ ***(LOO) (kcal/mol)***
23a	0.0000	0.2172	0.3342
24a	0.9444	1.1707	1.2213
25a	1.2032	0.7199	0.5821
41a	1.3784	1.3729	1.3717
39a	0.8180	1.2737	1.3557
26a	1.0728	0.9963	0.9831
27a	1.9438	2.0615	2.0992
28a	1.2607	1.2315	1.2187
42a	2.5787	2.0288	1.8861
43a	2.0540	2.0892	2.0986
36a	0.4592	0.1588	0.0161
37a	1.1269	1.2677	1.2954
38a	0.0671	0.6942	0.8456
32a	1.3060	1.1858	1.1174
31a	0.3250	0.1464	−0.0431
35a	0.6906	0.8242	0.8754
33a	1.0847	1.2385	1.3103
34a	0.0614	−0.0290	−0.0833
24a-d_1	1.4793	1.1705	1.1014

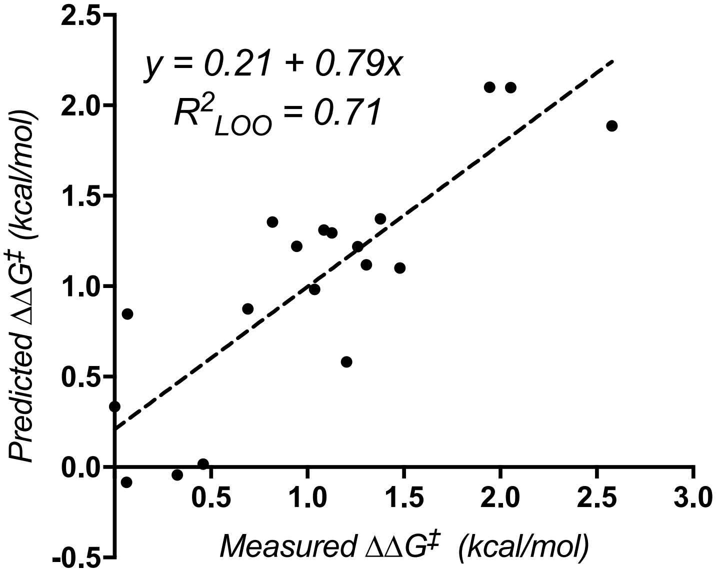


Figure S8. Leave-one-out plot for five-parameter model.

Table S6. Measured and predicted ΔΔG‡ for the model excluding the N1 NBO charge and hydantoins with a N1-H substitution.

Substrate	***Measured ΔΔG‡ (kcal/mol)***	***Predicted ΔΔG‡ (kcal/mol)***	***Predicted ΔΔG‡ (LOO) (kcal/mol)***
24a	0.9444	1.2112	1.2833
25a	1.2032	1.7089	0.5182
41a	1.3784	1.3843	1.3857
39a	0.8180	1.3213	1.4284
27a	1.9438	2.0763	2.1351
28a	1.2607	1.2270	1.2078
42a	2.5787	2.0509	1.8678
43a	2.0540	2.0810	2.0900
37a	1.1269	1.2456	1.2731
38a	0.0671	0.6750	0.8414
32a	1.3060	1.1654	1.0582
31a	0.3250	0.0222	−0.4037
35a	0.6906	0.7961	0.8500
24a-*d*$_1$	1.4793	1.2110	1.1385

As mentioned in the paper, we had the hypothesis that the NBO charge descriptor in the model had only one role, which is to describe how the lack of electron-withdrawing capacity of hydrogen increased the rate of the reaction. To test this theory, a linear regression analysis was also performed excluding both the N1 NBO charge and all hydantoins with an N1-H substitution. The result of this analysis generated a model with a comparable R^2 and Q^2 to the original model, consistent with this theory, and is shown in Table S6 and Figure S9.

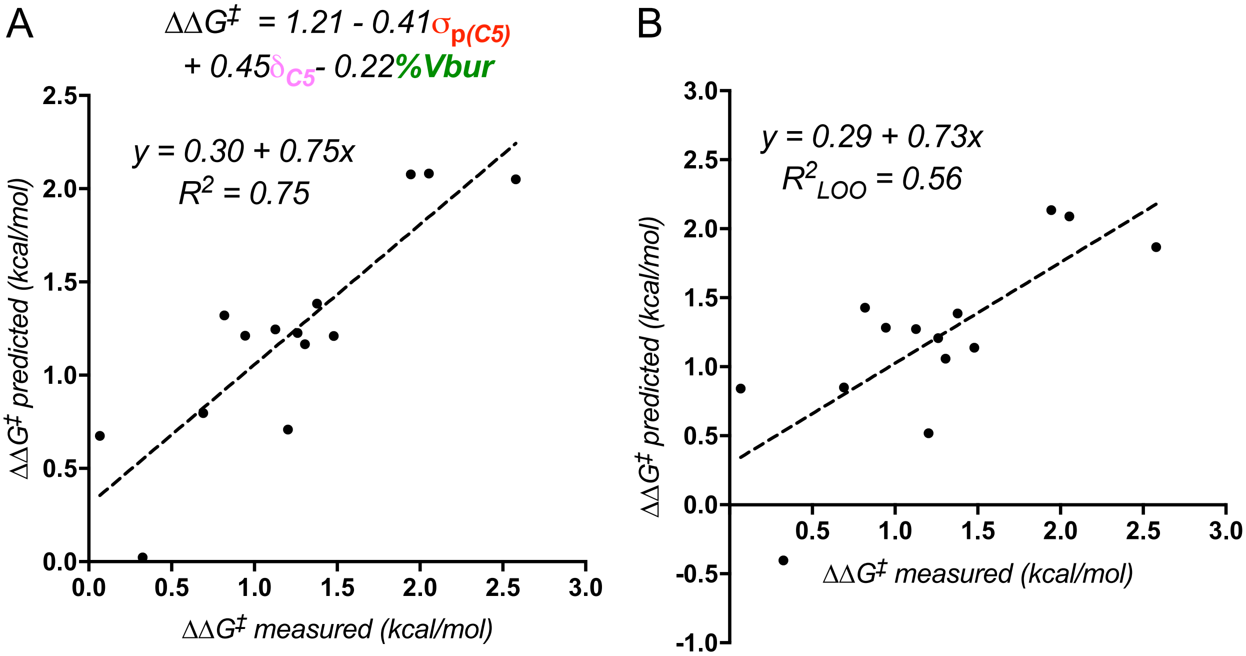


Figure S9. A) Model excluding N1-H substitution and N1 NBO charge and B) leave-one-out plot for this model.

In addition to the ability to gain mechanistic information from the models, each potential model was evaluated for the ability of the model to be extrapolated from explaining the behavior of the hydantoin derivatives to the diketopiperazine derivatives. To do this, the parameters for the hydantoins and diketopiperazines were normalized together, and the model was first used to determine a predicted $\Delta\Delta G^{\ddagger}$ value for each diketopiperazine potential site of oxidation. These $\Delta\Delta G^{\ddagger}$ values were then compared to experimental outcomes to determine whether there was a difference in $\Delta\Delta G^{\ddagger}$ between diketopiperazine sites that were oxidized and those that were not. The results for this analysis for the primary model used in the paper are shown in Table S7. The text in red indicates an inaccurate prediction. The relevant parameters were also evaluated for the ability to serve as classifiers, dividing the oxidized diketopiperazine sites from the unreactive ones.

Two alternative models that were generated but not used in the report are shown in Figures S10-S11. The first model (Figure S10) is similar to the primary model, but it excludes the $\%V_{bur}$ parameter. Although the $\%V_{bur}$ parameter only improves R^2 from 0.75 to 0.82, it is useful in the prediction of the behavior of the oxidation for diketopiperazine derivatives.

The second of these models (Figure S11A) increased the fit slightly by adding the $\sigma_{p(N1)}$ parameter to the primary model. As done for the parameters in the paper, the $\sigma_{p(N1)}$ parameter was examined for subsets of hydantoins, holding either the C5 or N1 substituent constant. Comparison of

$\sigma_{p(N1)}$ among different N1 substituents indicated that this parameter had the same value for all substrates in the N1-H subset, and it also remained consistent for all substrates in the N1-Me subset. However, for the N1-Ph subset, this parameter varied significantly among substrates. Through analysis of the $\sigma_{p(C5)}$ and δ_{C5} parameters in the paper, this subset has already been shown to have more complex behavior than other N1 substituents. Thus, while $\sigma_{p(N1)}$ does improve the model, it does not add valuable mechanistic information or increase the accuracy of the prediction of the oxidation of the diketopiperazine derivatives.

Table S7. Oxidation outcome and predicted $\Delta\Delta G^{\ddagger}$ for diketopiperazine derivatives.

Substrate	***Oxidation outcome***	***Predicted $\Delta\Delta G^{\ddagger}$ (kcal/mol)***
Methylene		
(+)-**19**	Oxidized	0.2667
(+)-**19** (2)	Oxidized	0.1895
Threonine Cα		
(+)-**19**	Not oxidized	0.0943
C15 – H		
47b	Oxidized	0.8877
48b	Oxidized	1.2500
50b	Oxidized	0.6710
49b	Oxidized	0.7517
51b	Oxidized	0.5333
C15 – H (2)		
50b	Oxidized	0.3904
C11 – H		
47b	Oxidized	0.4064
48b	Not oxidized	–0.0334
50b	Oxidized	0.3451
49b	Oxidized	0.3937
51b	Not oxidized	0.4013

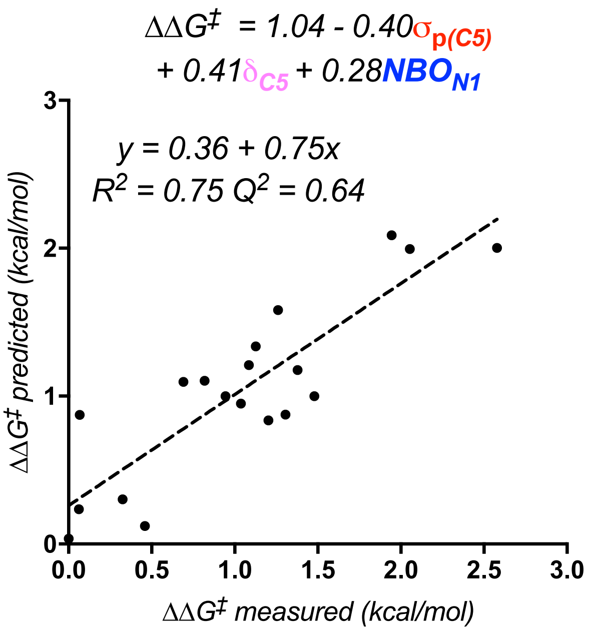


Figure S10. Model lacking %V_{bur}.

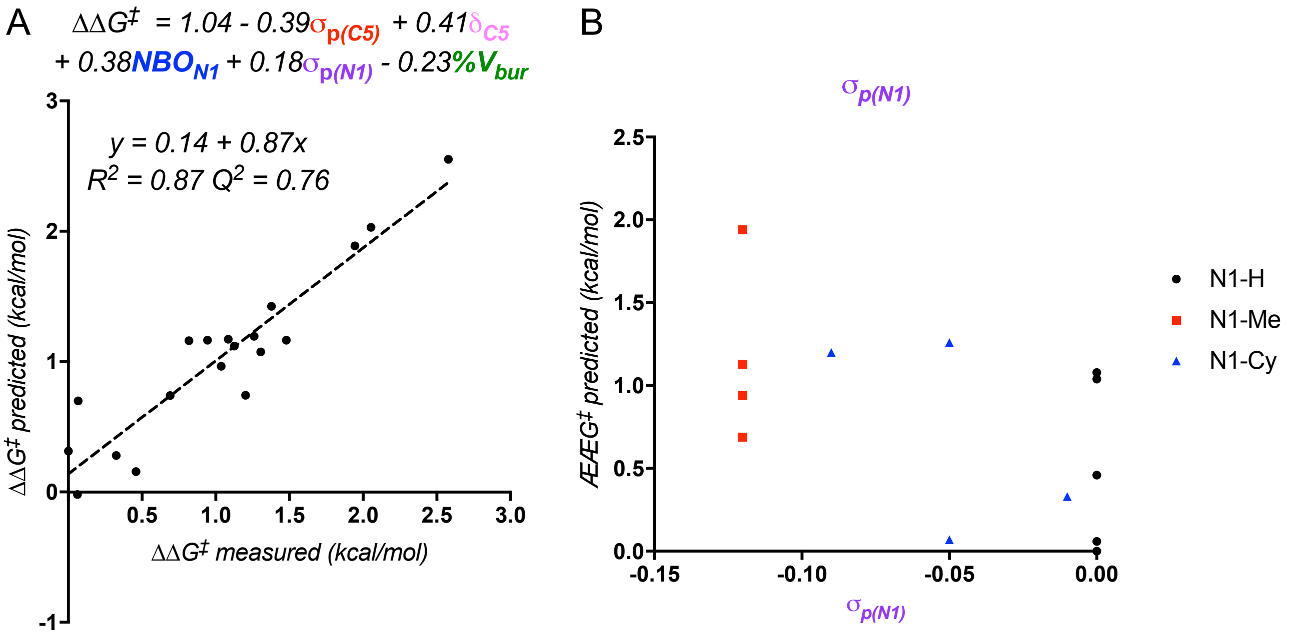


Figure S11. A) Model with the addition of $\sigma_{p(N1)}$. B) Interpretation of $\sigma_{p(N1)}$.

GC Data for Relative Rate Measurement

GC method information: 250 °C inlet, 300 °C detector, flow 1.0 mL/min, oven temperature program: 80 °C for 5 min, 5 °C/min ramp to 150 °C, then 10 °C/min ramp to 300 °C. 1-methylnaphthalene was used as an internal standard. Calibrations and rate measurements were done in triplicate. Agilent Technologies 7890A GC System with a HP-5 (5%-Phenyl)-methylpolysiloxane column and dinitrogen as carrier gas. $\Delta\Delta G^{\ddagger}$ for each run and their averages are presented in Table S8.

Table S8. $\Delta\Delta G^{\ddagger}$ for relative rate measurements.

Substrate	***Run 1*** $\Delta\Delta G^{\ddagger}$	***Run 2*** $\Delta\Delta G^{\ddagger}$	***Run 3*** $\Delta\Delta G^{\ddagger}$	***Average*** $\Delta\Delta G^{\ddagger}$
24a-*d*$_1$	1.825	1.358	1.254	1.479
24a	0.871	1.025	0.937	0.944
25a	1.219	1.179	1.212	1.203
26a	0.977	1.223	0.912	1.038
27a	2.550	x[a]	1.308	1.929
28a	1.050	1.353	1.379	1.261
31a[b]	0.272	0.345	0.358	0.325
32a	1.236	1.550	1.131	1.306
33a	1.038	1.100	1.116	1.085
34a	0.041	0.068	0.075	0.061
35a	0.728	0.678	0.666	0.691
36a	0.282	0.532	0.563	0.459
37a	1.091	1.034	1.256	1.127
38a	–0.262	0.228	0.235	0.067
39a	0.699	0.816	0.939	0.818
41a	1.368	1.411	1.356	1.378
42a	2.101	2.493	3.141	2.579
43a	2.009	2.071	2.082	2.054

[a] Depletion of starting material was minimal and could not be accurately measured. [b] GC spectra show an unidentified peak at 26.3 min, which may be an oxidation or degradation product. Exclusion of this observation does not significantly impact modeling.

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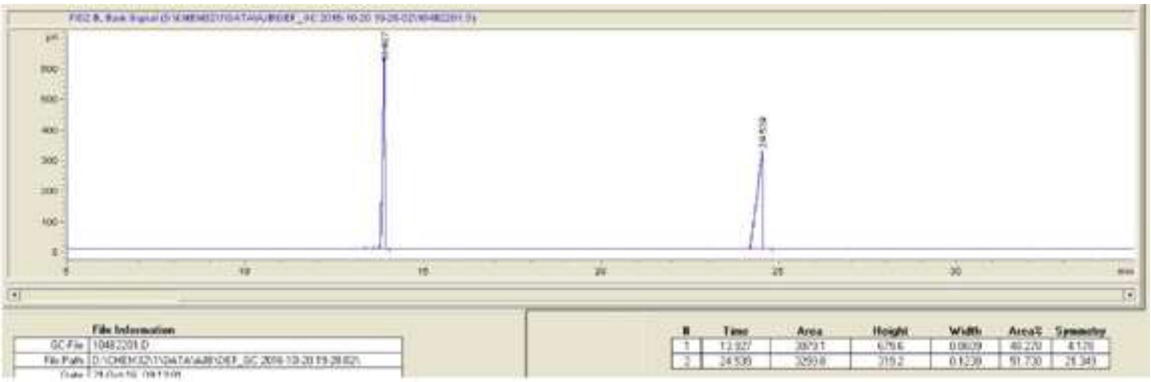
23a calibration back column



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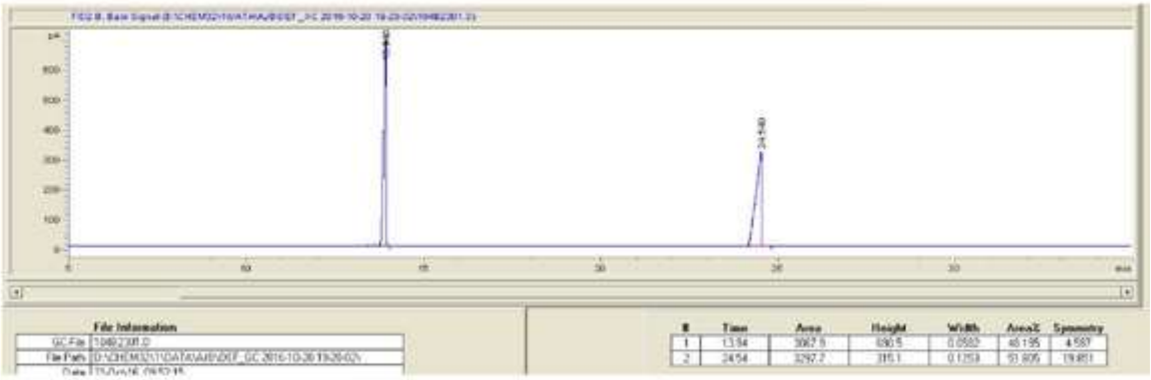

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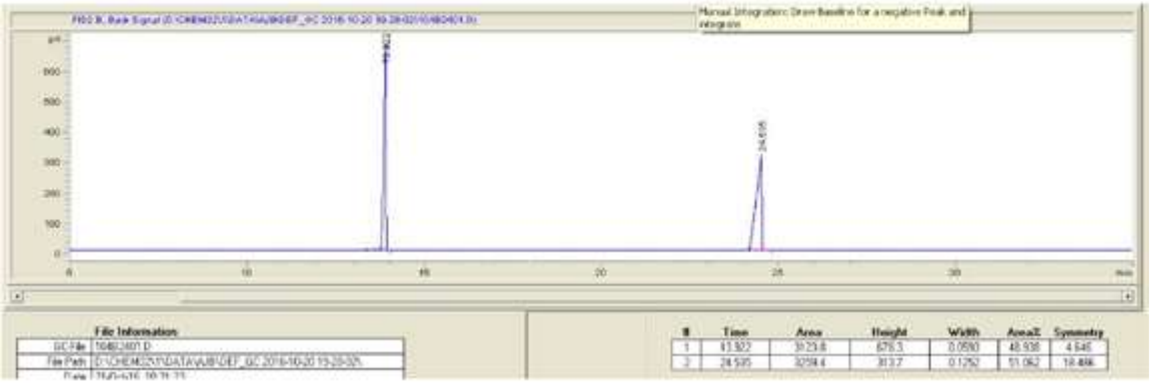

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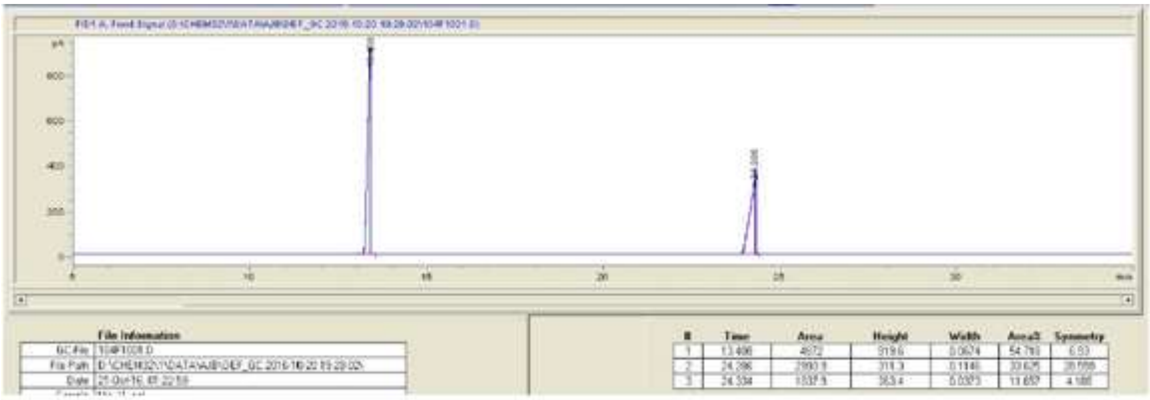
1-methylnaphthalene (internal standard) at 13.9

23a at 24.5

23a calibration front column



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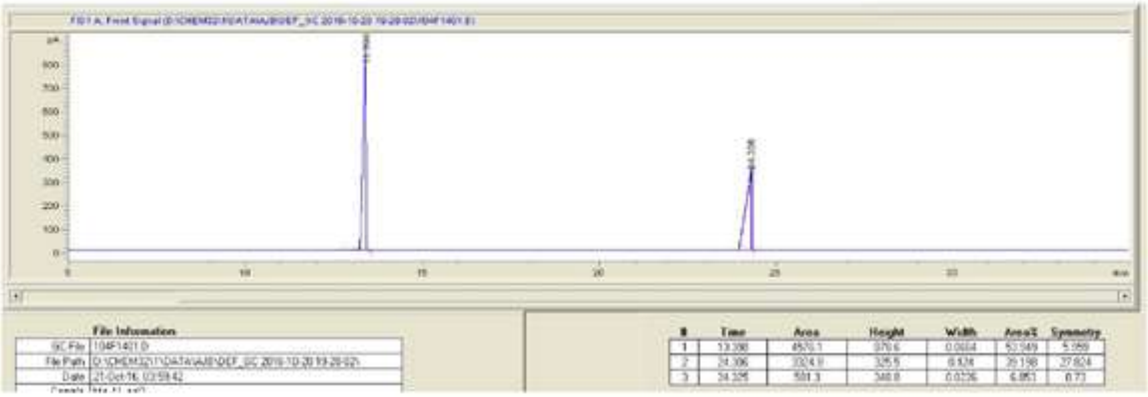

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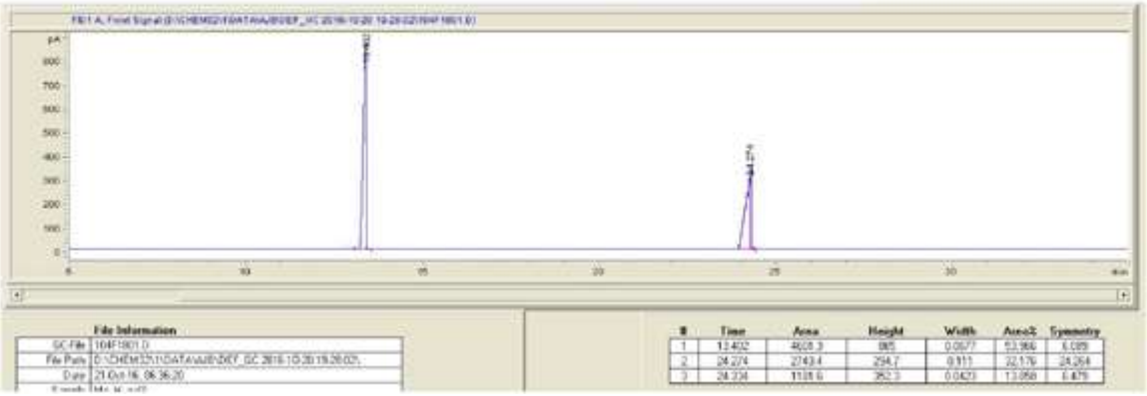

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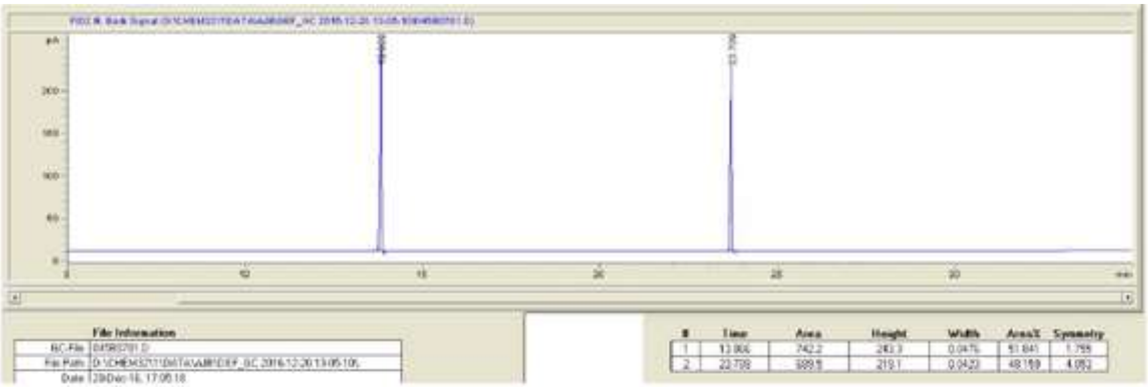
1-methylnaphthalene (internal standard) at 13.4

23a at 24.3

24a-*d*$_1$ calibration



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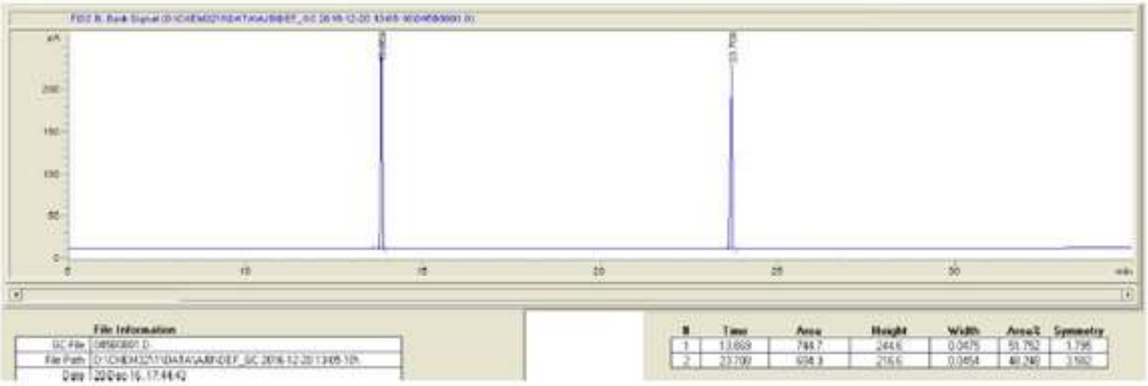

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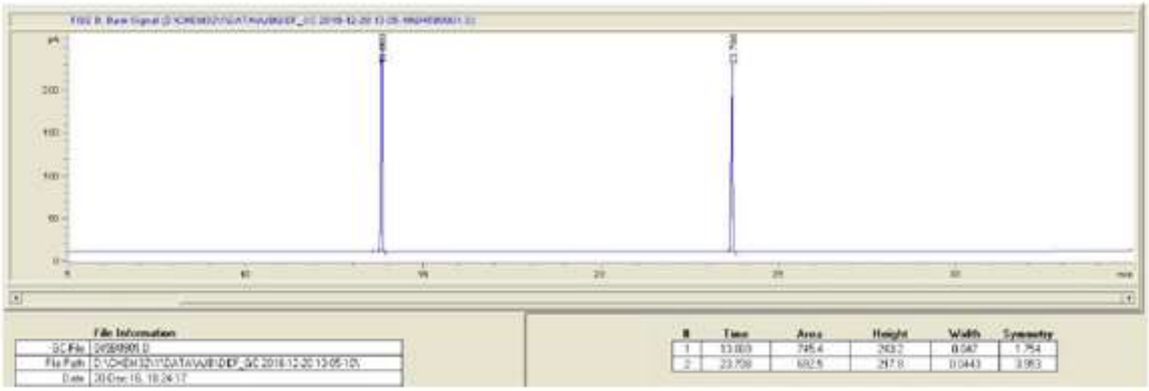

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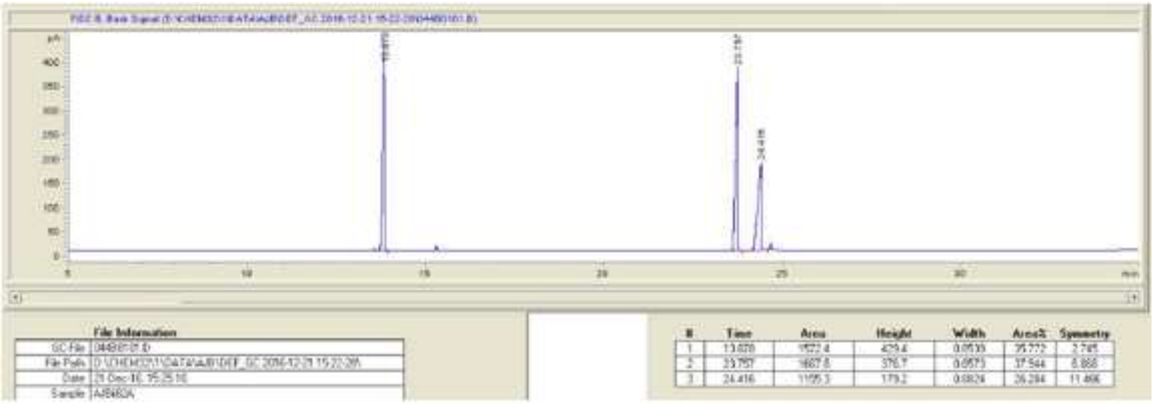
1-methylnaphthalene (internal standard) at 13.9

23a-*d*$_1$ at 23.7

24a-d_1 relative rate measurement



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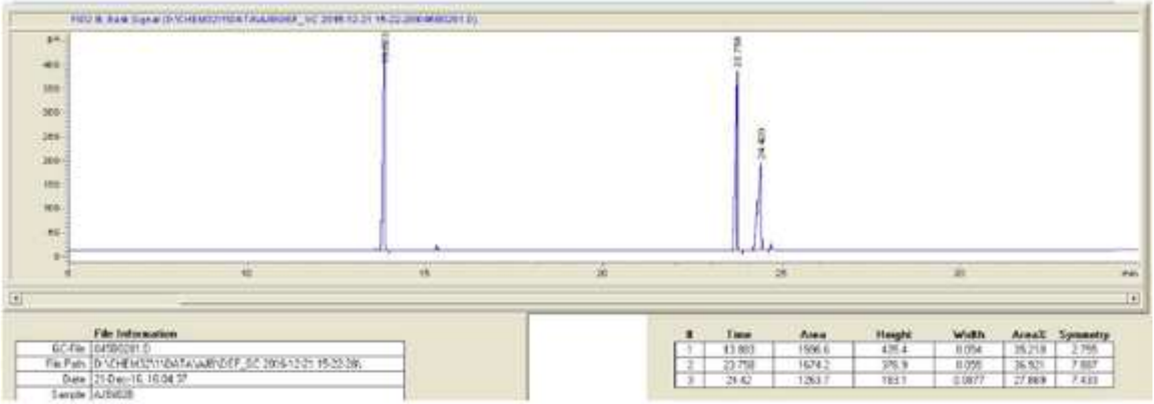

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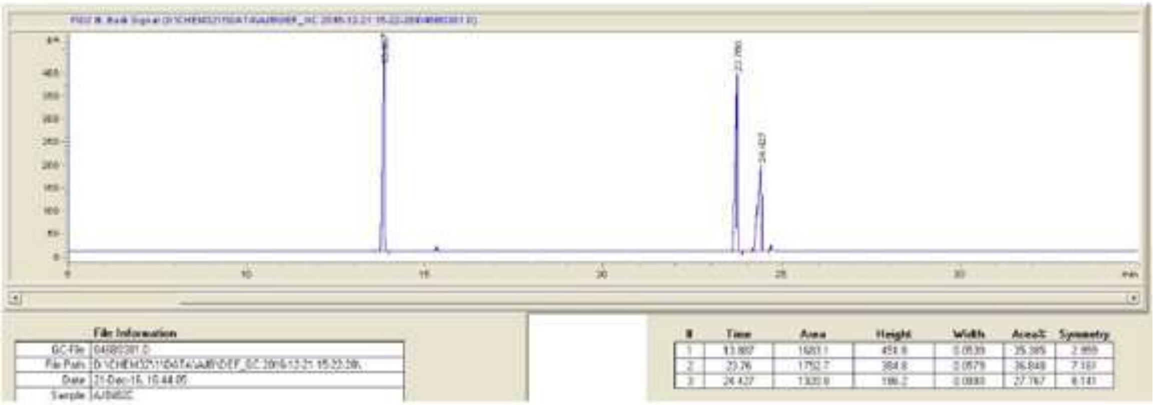

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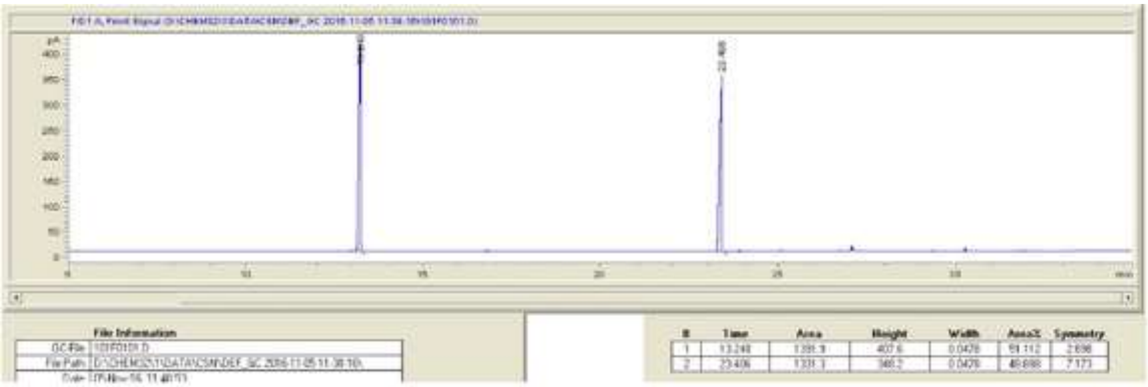
3	24.427	1320.8	186.2	0.0883	27.767	8.141

1-methylnaphthalene (internal standard) at 13.9

23a-d_1 at 23.8

23a at 24.4

24a calibration



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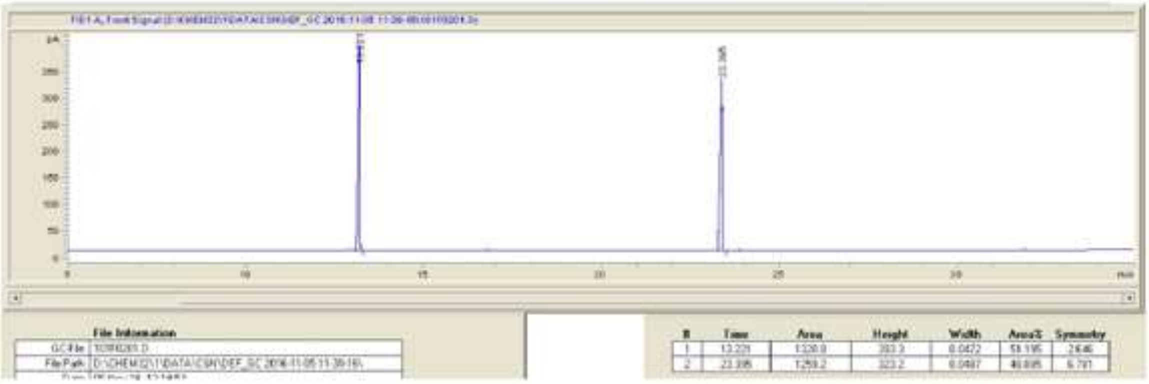

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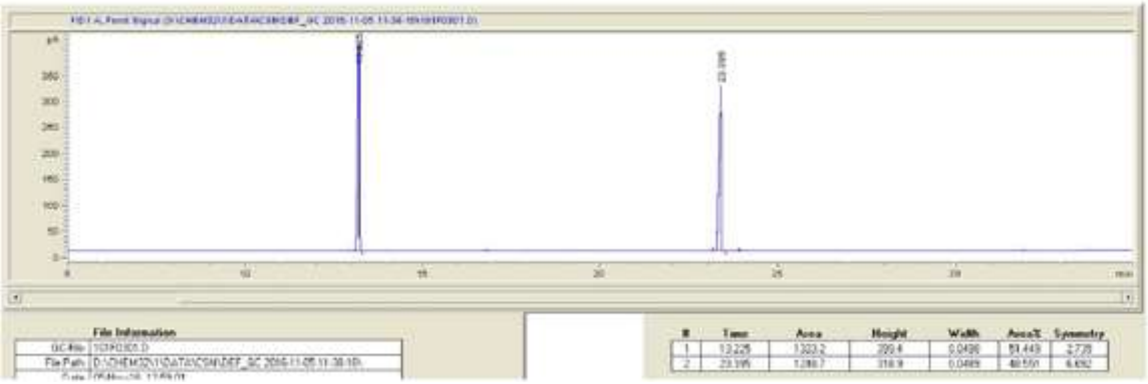

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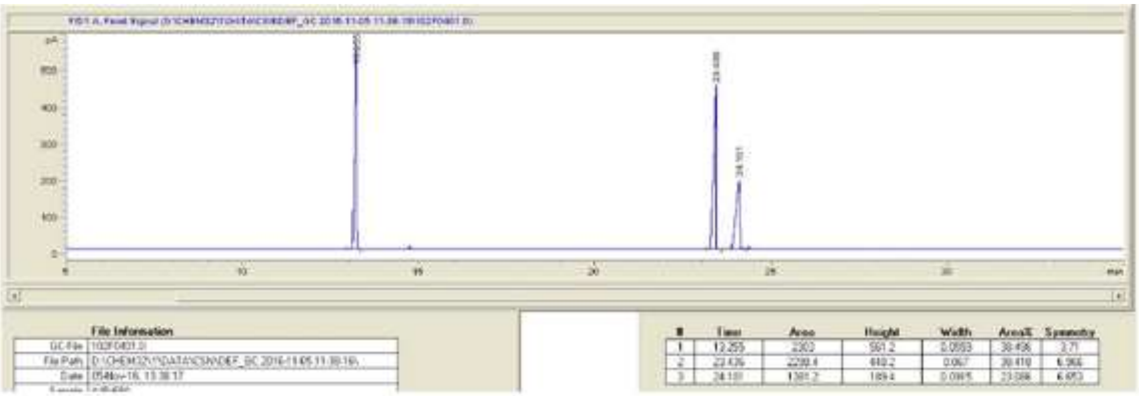
1-methylnaphthalene (internal standard) at 13.2

24a at 23.4

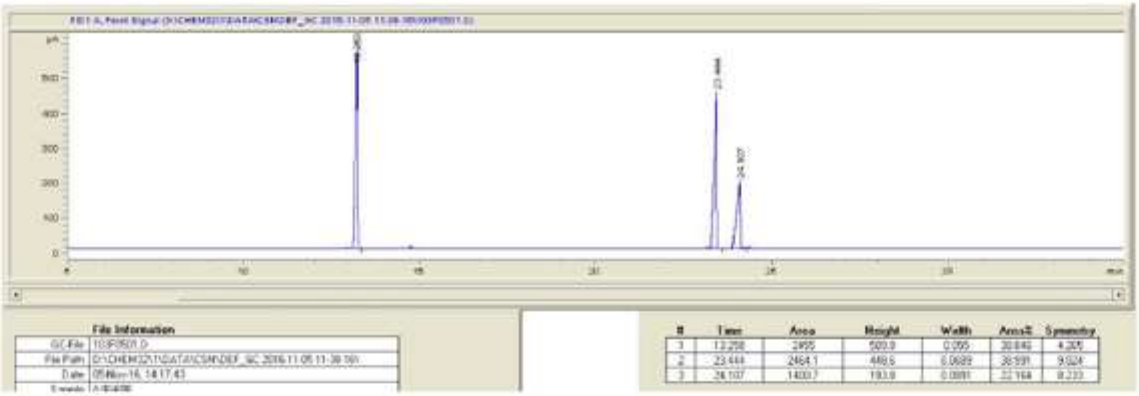
24a relative rate measurement



File Information

GC-File	102F0401.D
File Path	D:\CHEM32\1\DATA\CSM\DEF_GC 2016-11-05 11-38-16\
Date	05-Nov-16, 13:38:17

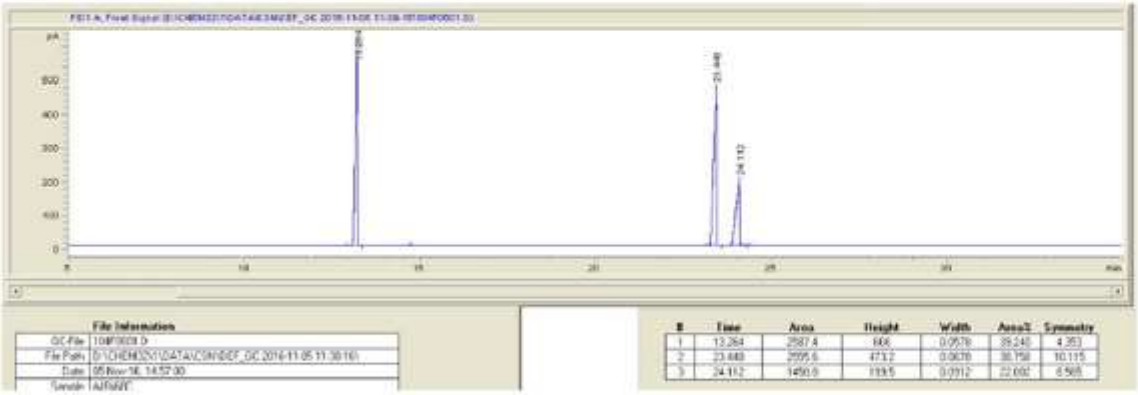
#	Time	Area	Height	Width	Area%	Symmetry
1	13.255	2303	561.2	0.0593	38.456	3.71
2	23.436	2299.4	449.2	0.067	38.410	6.966
3	24.101	1381.2	189.4	0.0915	23.086	6.653



File Information

GC-File	103F0501.D
File Path	D:\CHEM32\1\DATA\CSM\DEF_GC 2016-11-05 11-38-16\
Date	05-Nov-16, 14:17:43

#	Time	Area	Height	Width	Area%	Symmetry
1	13.258	2455	509.9	0.055	38.846	4.205
2	23.444	2464.1	449.6	0.0689	38.991	9.024
3	24.107	1400.7	193.8	0.0881	22.164	8.233



File Information

GC-File	104F0601.D
File Path	D:\CHEM32\1\DATA\CSM\DEF_GC 2016-11-05 11-38-16\
Date	05-Nov-16, 14:57:00

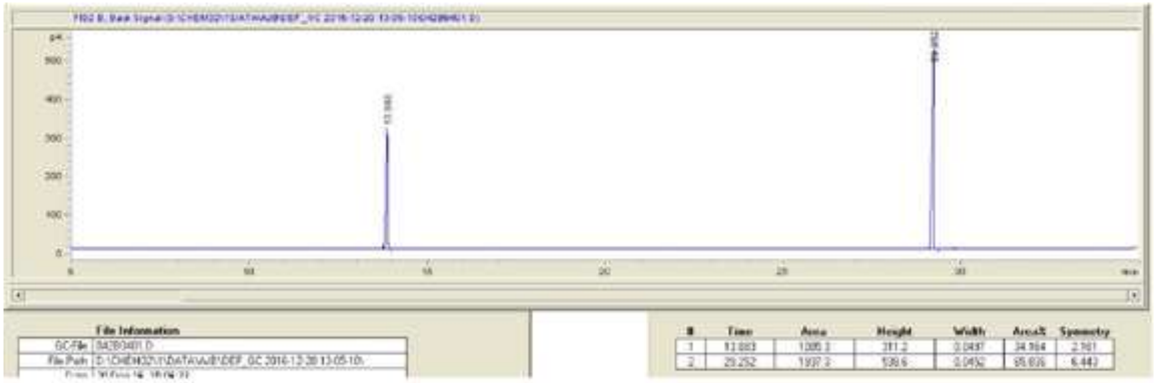
#	Time	Area	Height	Width	Area%	Symmetry
1	13.264	2587.4	606	0.0578	39.240	4.353
2	23.440	2555.6	473.2	0.0678	38.758	10.115
3	24.112	1450.9	193.5	0.0912	22.002	6.565

1-methylnaphthalene (internal standard) at 13.3

24a at 23.4

23a at 24.1

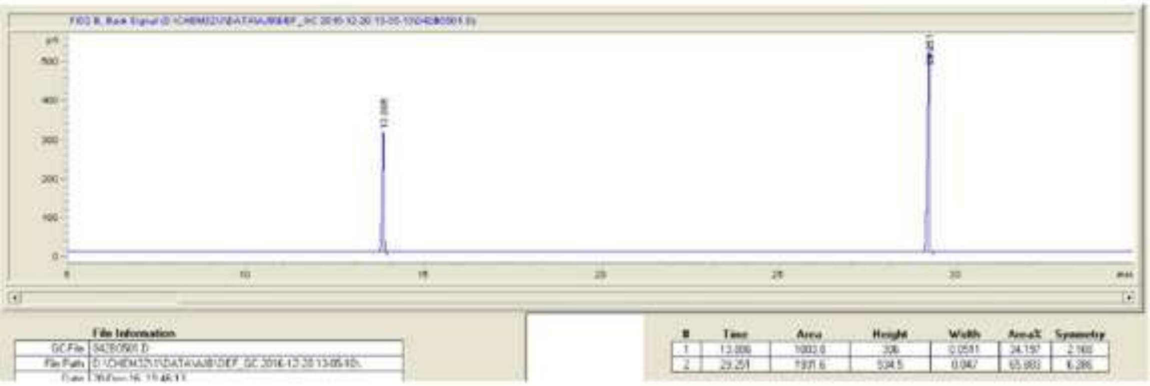
25a calibration



File Information

GC-File	042B0401.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-20 13-05-10\

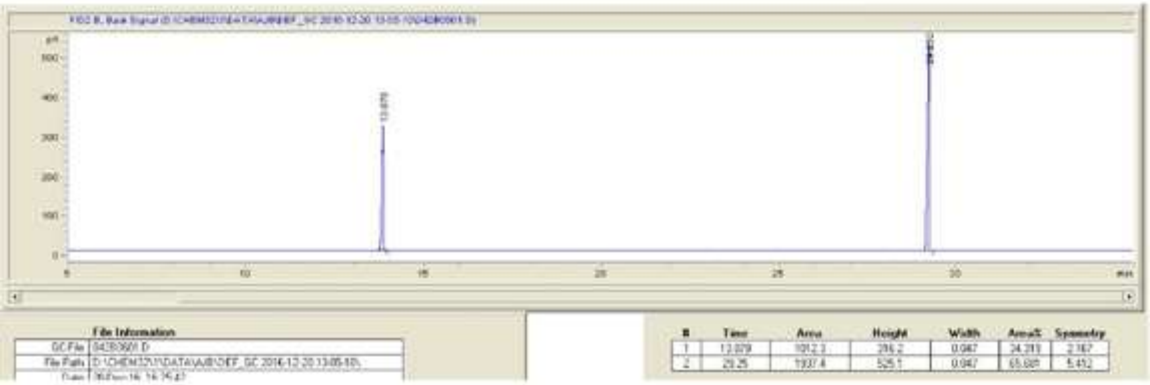
#	Time	Area	Height	Width	Area%	Symmetry
1	13.883	1005.3	311.2	0.0497	34.164	2.161
2	29.252	1937.3	538.6	0.0452	65.836	6.443



File Information

GC-File	042B0501.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-20 13-05-10\

#	Time	Area	Height	Width	Area%	Symmetry
1	13.886	1003.0	306	0.0511	34.157	2.160
2	29.251	1931.6	534.5	0.047	65.843	6.286



File Information

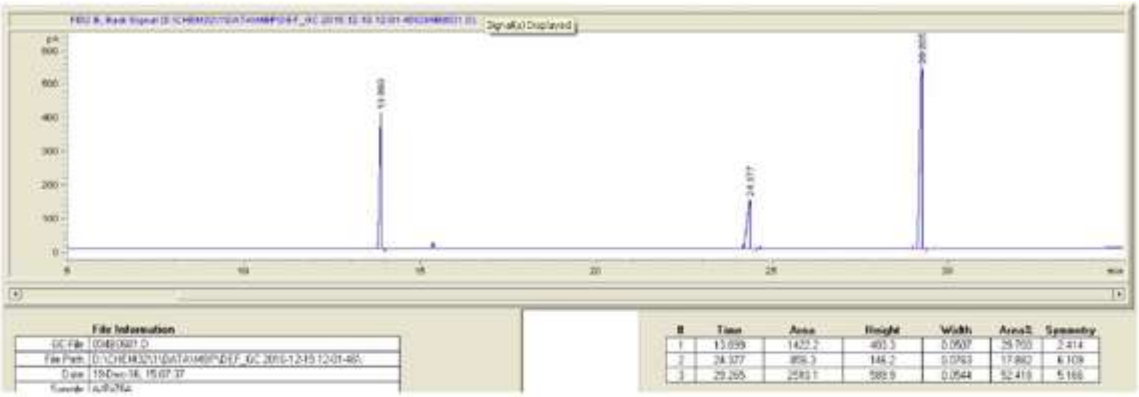
GC-File	042B0601.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-20 13-05-10\

#	Time	Area	Height	Width	Area%	Symmetry
1	13.879	1012.3	296.2	0.047	34.318	2.167
2	29.25	1937.4	525.1	0.047	65.682	5.452

1-methylnaphthalene (internal standard) at 13.9

25a at 29.3

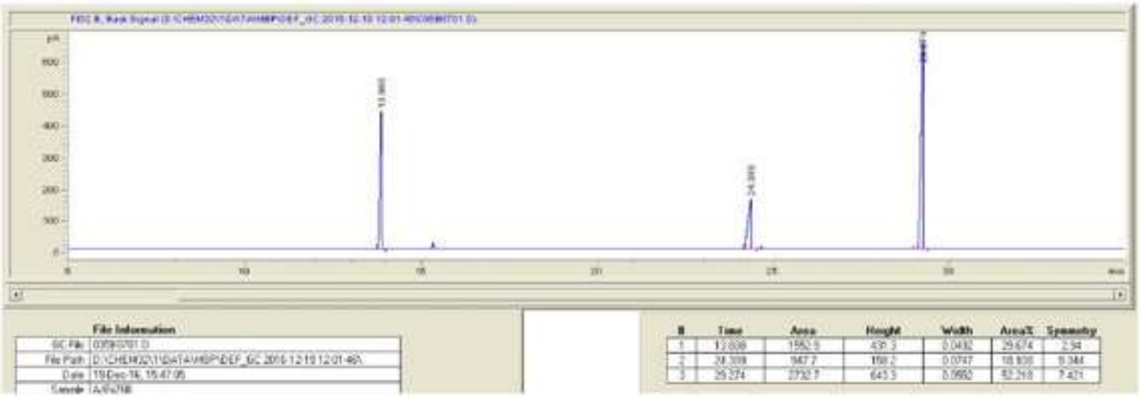
25a relative rate measurement



File Information

GC File	03480601.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-19 12-01-46\
Date	19-Dec-16, 15:07:37
Sample	AJB2764

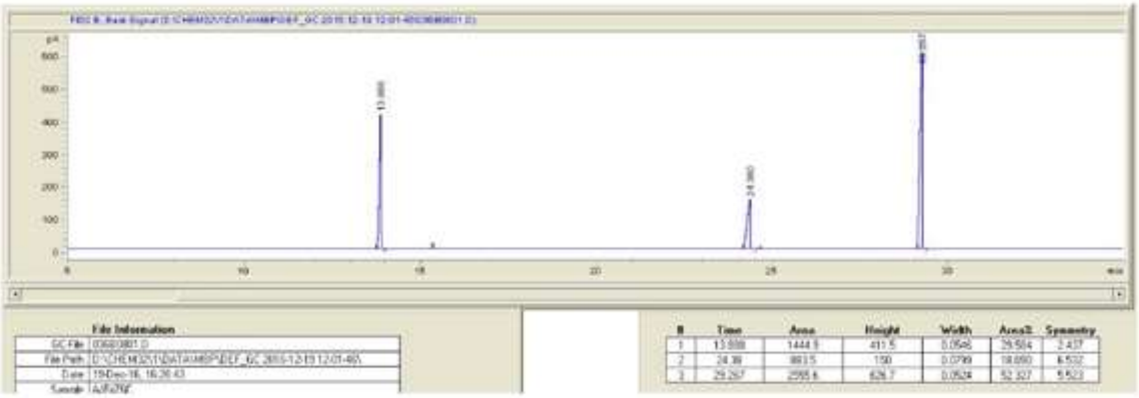
#	Time	Area	Height	Width	Area%	Symmetry
1	13.899	1422.2	403.3	0.0507	29.700	2.414
2	24.377	856.3	146.2	0.0763	17.882	6.109
3	29.265	2503.1	589.9	0.0544	52.418	5.166



File Information

GC File	03590701.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-19 12-01-46\
Date	19-Dec-16, 15:47:05
Sample	AJB2768

#	Time	Area	Height	Width	Area%	Symmetry
1	13.898	1552.5	431.3	0.0492	29.674	2.34
2	24.399	947.7	158.2	0.0747	18.108	8.344
3	29.274	2732.7	643.3	0.0592	52.218	7.421



File Information

GC File	03600801.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-19 12-01-46\
Date	19-Dec-16, 16:26:43
Sample	AJB2769

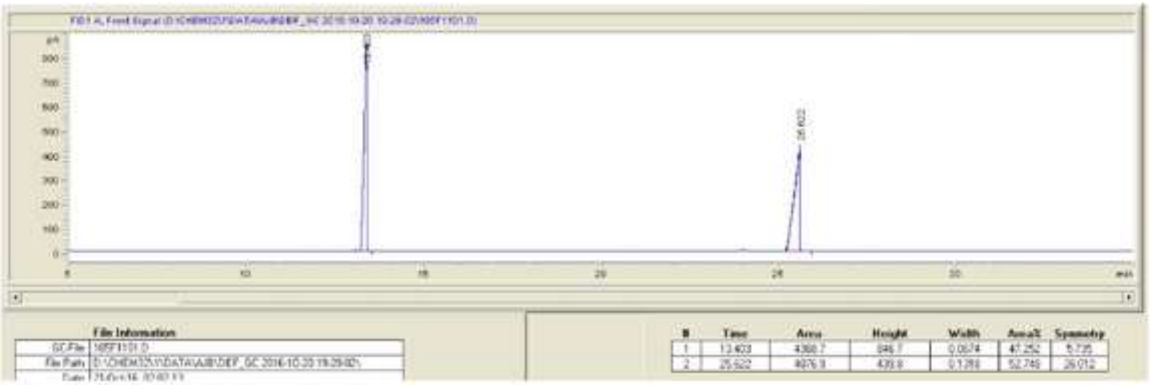
#	Time	Area	Height	Width	Area%	Symmetry
1	13.898	1444.9	411.5	0.0546	29.584	2.437
2	24.39	883.5	150	0.0799	18.090	6.532
3	29.267	2555.6	626.7	0.0524	52.327	5.523

1-methylnaphthalene (internal standard) at 13.9

23a at 24.5

25a at 29.3

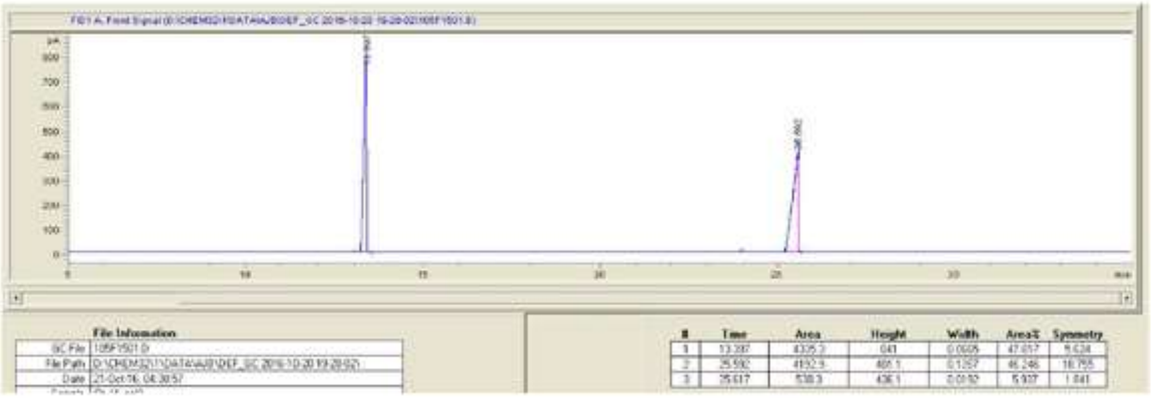
26a calibration



File Information

GC File	105F1101.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-20 19-29-02\
Date	21-Oct-16, 02:02:13

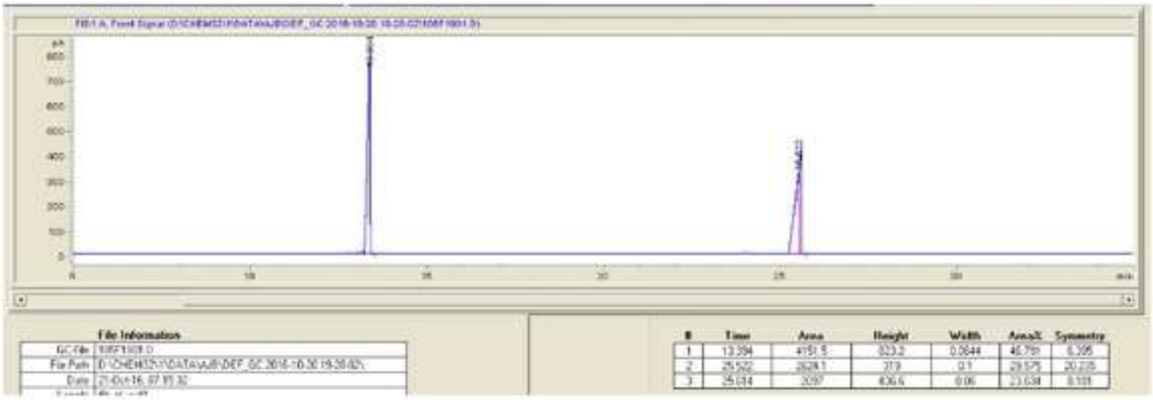
#	Time	Area	Height	Width	Area%	Symmetry
1	13.403	4368.7	846.7	0.0674	47.252	5.735
2	25.622	4876.9	439.8	0.1288	52.748	26.012



File Information

GC File	105F1501.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-20 19-29-02\
Date	21-Oct-16, 04:30:57

#	Time	Area	Height	Width	Area%	Symmetry
1	13.397	4335.2	841	0.0605	47.817	5.624
2	25.592	4192.9	401.1	0.1257	46.246	16.755
3	25.617	538.3	436.1	0.0192	5.937	1.841



File Information

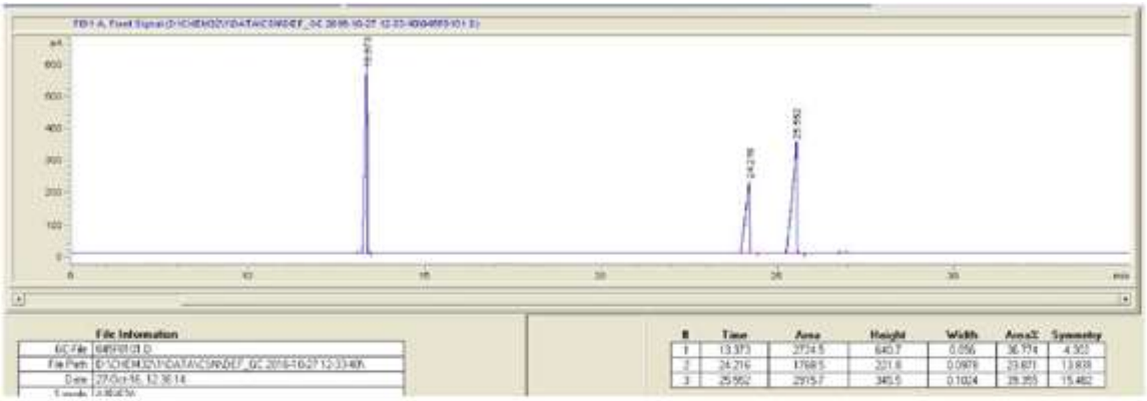
GC File	105F1901.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-20 19-29-02\
Date	21-Oct-16, 07:15:32

#	Time	Area	Height	Width	Area%	Symmetry
1	13.394	4151.5	823.2	0.0844	46.791	6.395
2	25.522	2628.1	379	0.1	29.575	20.235
3	25.614	2097	636.6	0.06	23.638	8.101

1-methylnaphthalene (internal standard) at 13.4

26a at 25.6

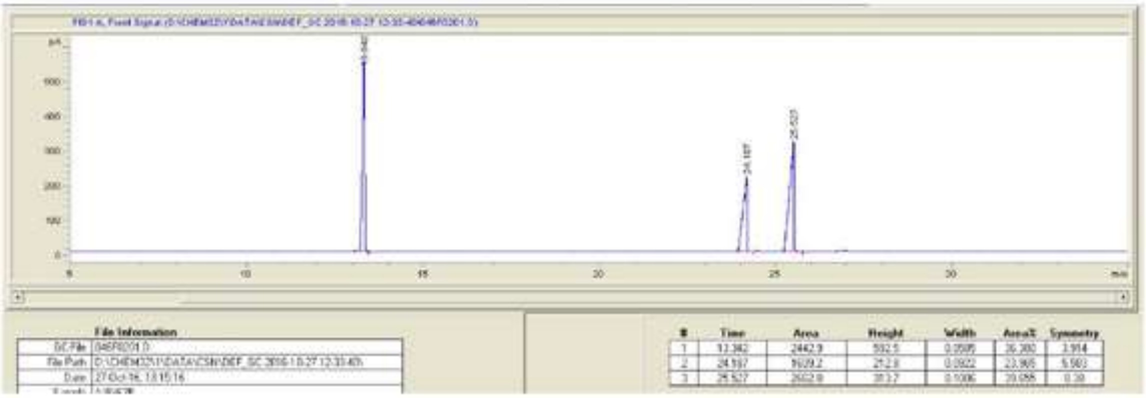
26a relative rate measurement



File Information

GC File	04EF0101.D
File Path	D:\CHEM32\1\DATA\CSM\DEF_GC 2016-10-27 12-33-40\
Date	27-Oct-16, 12:36:14

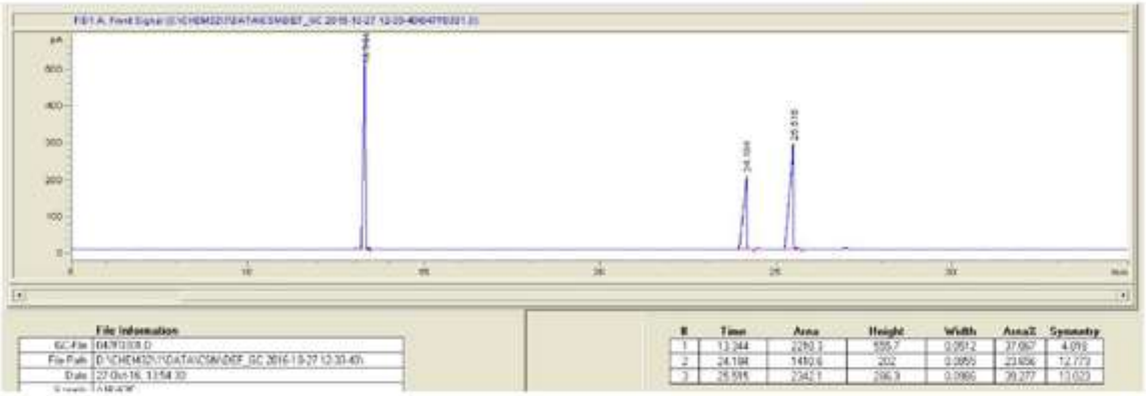
#	Time	Area	Height	Width	Area%	Symmetry
1	13.373	2724.5	640.7	0.056	36.774	4.303
2	24.216	1768.5	221.8	0.0978	23.871	13.838
3	25.552	2915.7	345.5	0.1024	39.355	15.482



File Information

GC File	04EF0201.D
File Path	D:\CHEM32\1\DATA\CSM\DEF_GC 2016-10-27 12-33-40\
Date	27-Oct-16, 13:15:16

#	Time	Area	Height	Width	Area%	Symmetry
1	13.342	2442.9	592.5	0.0585	36.300	3.914
2	24.197	1609.2	212.8	0.0922	23.905	5.583
3	25.527	2602.8	313.7	0.1006	39.795	0.38



File Information

GC File	04EF0301.D
File Path	D:\CHEM32\1\DATA\CSM\DEF_GC 2016-10-27 12-33-40\
Date	27-Oct-16, 13:54:30

#	Time	Area	Height	Width	Area%	Symmetry
1	13.344	2290.3	555.7	0.0512	37.067	4.018
2	24.184	1410.6	202	0.0855	23.656	12.773
3	25.515	2342.1	286.3	0.0986	39.277	13.023

1-methylnaphthalene (internal standard) at 13.3

23a at 24.2

26a at 25.5

27a calibration

#	Time	Area	Height	Width	Area%	Symmetry
1	13.209	1241.6	368.9	0.0505	45.877	2.649
2	24.726	1464.8	428.9	0.0438	54.123	5.928

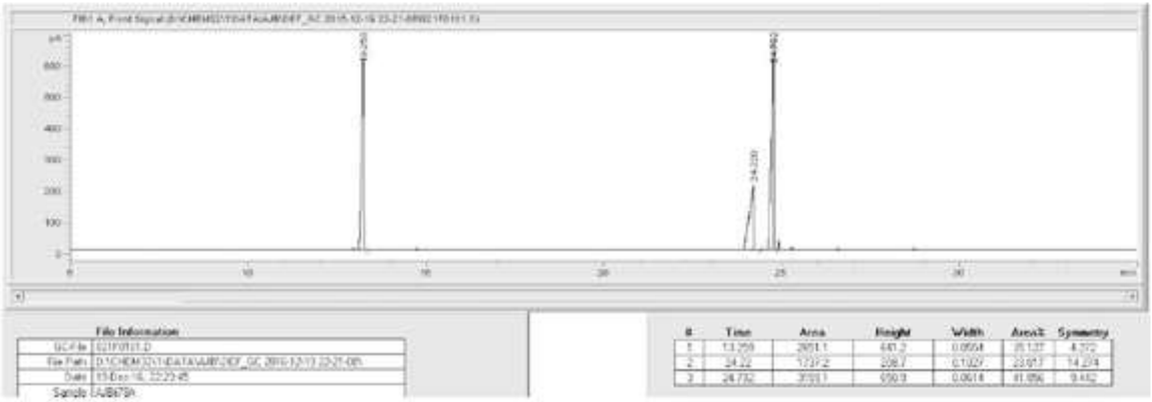
#	Time	Area	Height	Width	Area%	Symmetry
1	13.205	1244.7	372.5	0.0454	45.961	2.503
2	24.725	1463.4	419.2	0.0447	54.039	5.712

#	Time	Area	Height	Width	Area%	Symmetry
1	13.22	1232.4	367.1	0.0472	45.679	2.589
2	24.726	1465.6	420.7	0.0454	54.321	5.897

1-methylnaphthalene (internal standard) at 13.2

27a at 24.7

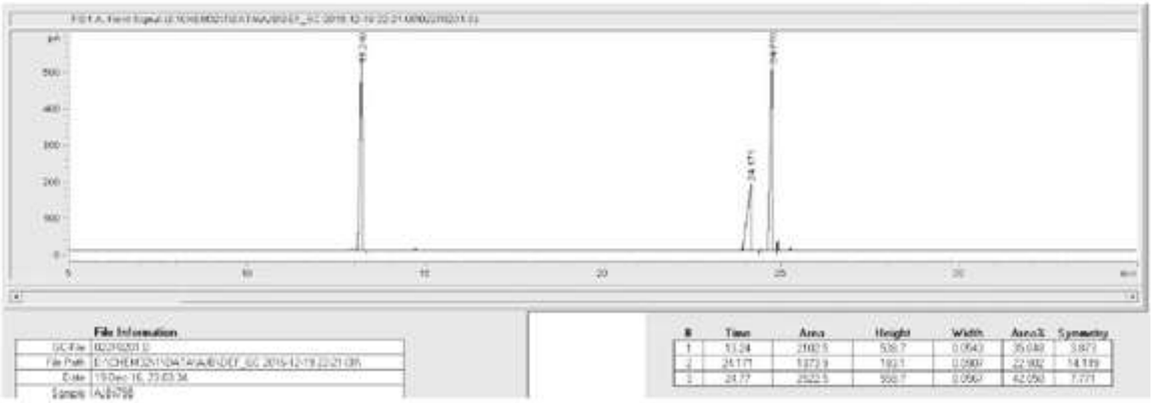
27a relative rate measurement



File Information

GC File	021F0101.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-19 22-21-08\
Date	19-Dec-16, 22:23:45
Sample	AJB679A

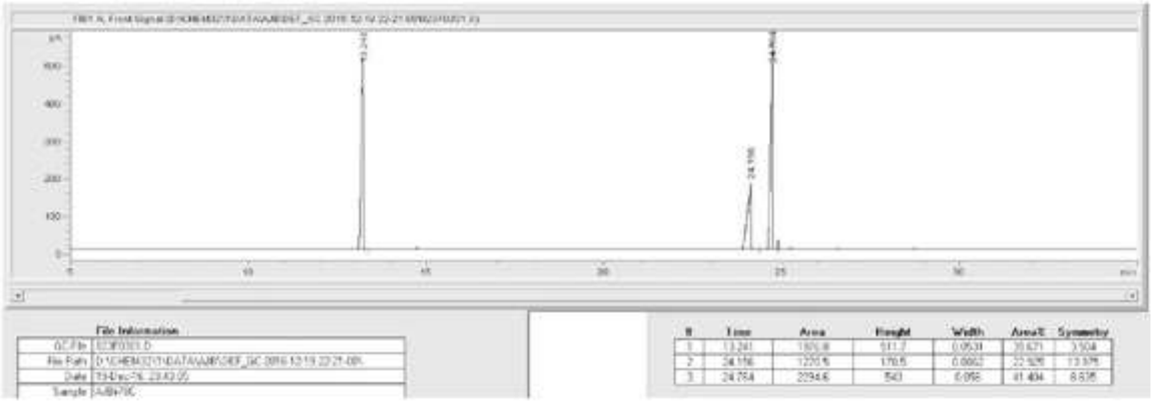
#	Time	Area	Height	Width	Area%	Symmetry
1	13.259	2651.1	641.2	0.0554	35.127	4.272
2	24.22	1737.2	208.7	0.1027	23.017	14.274
3	24.732	3159.1	650.3	0.0618	41.856	9.462



File Information

GC File	022F0201.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-19 22-21-08\
Date	19-Dec-16, 23:03:34
Sample	AJB679B

#	Time	Area	Height	Width	Area%	Symmetry
1	13.24	2102.5	539.7	0.0543	35.049	3.877
2	24.171	1373.9	193.1	0.0907	22.902	14.139
3	24.77	2522.5	550.7	0.0567	42.050	7.771



File Information

GC File	023F0301.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-19 22-21-08\
Date	19-Dec-16, 23:42:05
Sample	AJB679C

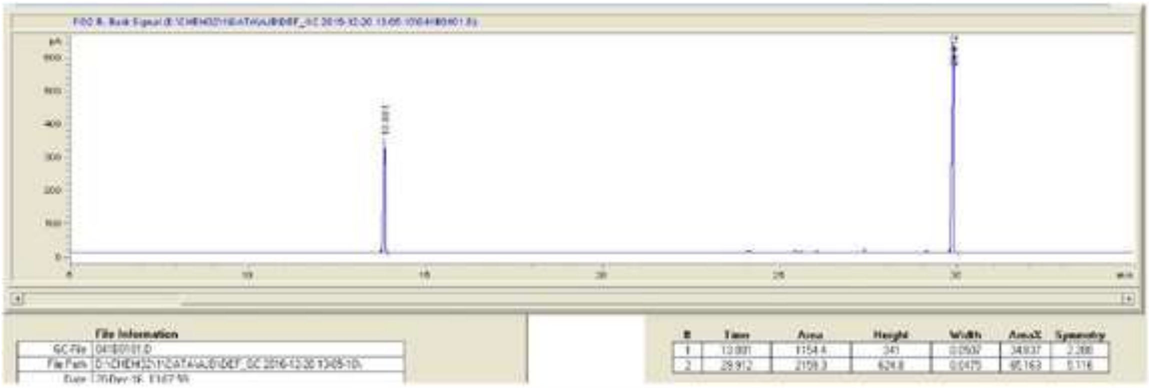
#	Time	Area	Height	Width	Area%	Symmetry
1	13.241	1898.9	511.7	0.0531	35.671	3.504
2	24.156	1220.5	170.5	0.0862	22.925	13.975
3	24.754	2204.6	543	0.056	41.404	8.635

1-methylnaphthalene (internal standard) at 13.4

23a at 24.2

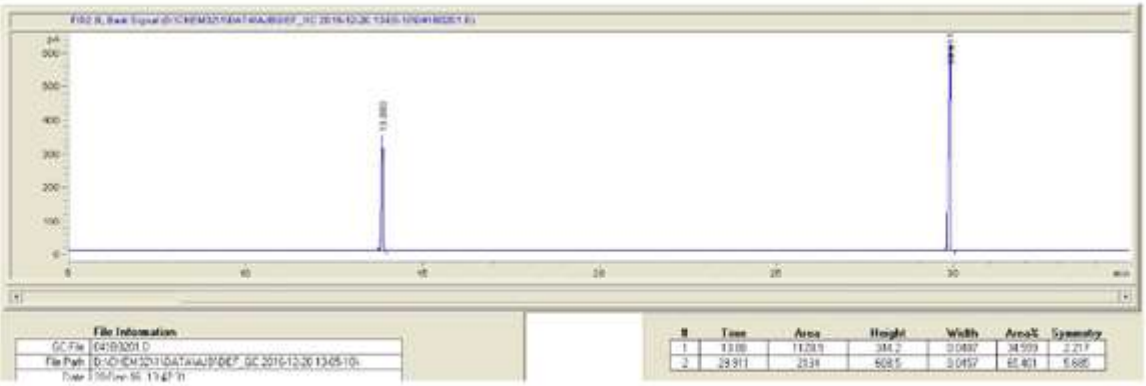
27a at 24.8

28a calibration



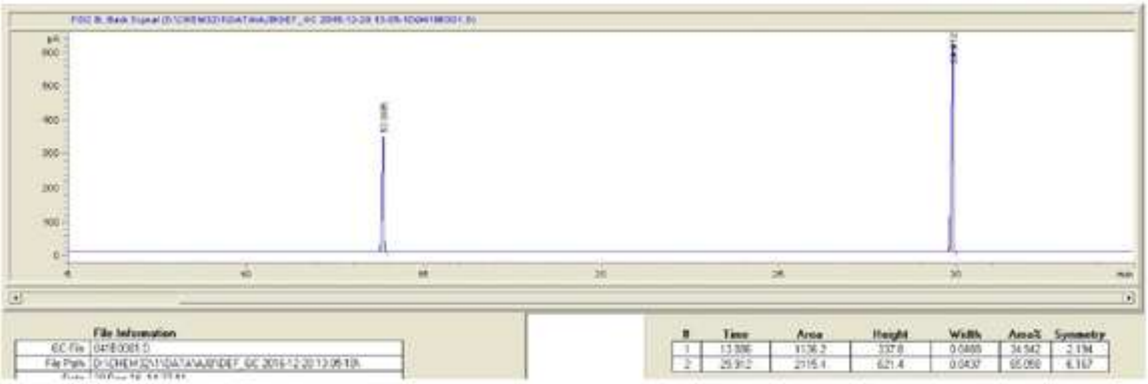
	File Information
GC File	041B0101.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-20 13-05-10\
Date	20-Dec-16, 13:07:59

#	Time	Area	Height	Width	Area%	Symmetry
1	13.881	1154.4	341	0.0507	34.837	2.288
2	29.912	2159.3	624.8	0.0475	65.163	5.116



	File Information
GC File	041B0201.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-20 13-05-10\
Date	20-Dec-16, 13:47:31

#	Time	Area	Height	Width	Area%	Symmetry
1	13.88	1128.9	384.2	0.0487	34.599	2.217
2	29.911	2134	608.5	0.0457	65.401	5.685



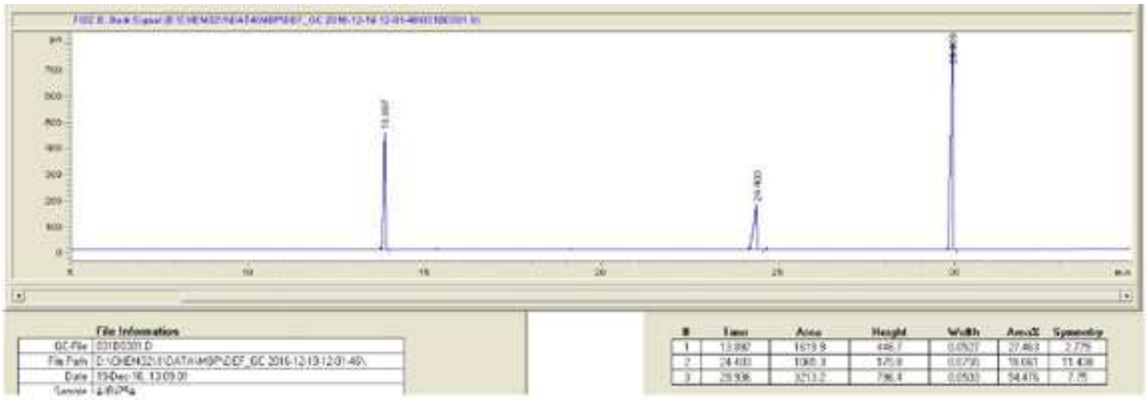
	File Information
GC File	041B0301.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-20 13-05-10\

#	Time	Area	Height	Width	Area%	Symmetry
1	13.886	1136.2	337.8	0.0488	34.942	2.194
2	29.912	2115.4	621.4	0.0437	65.058	6.167

1-methylnaphthalene (internal standard) at 13.9

28a at 29.9

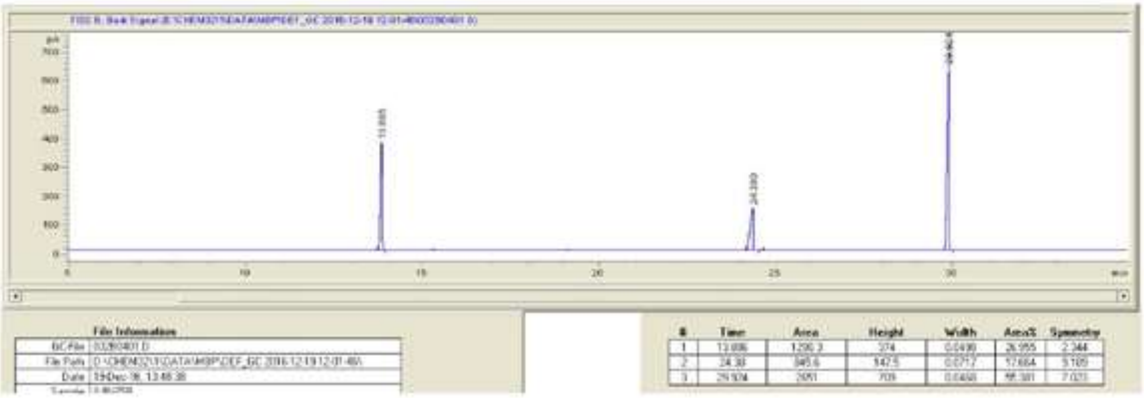
28a relative rate measurement



File Information

GC-File	03180301.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-19 12-01-46\
Date	19-Dec-16, 13:09:01

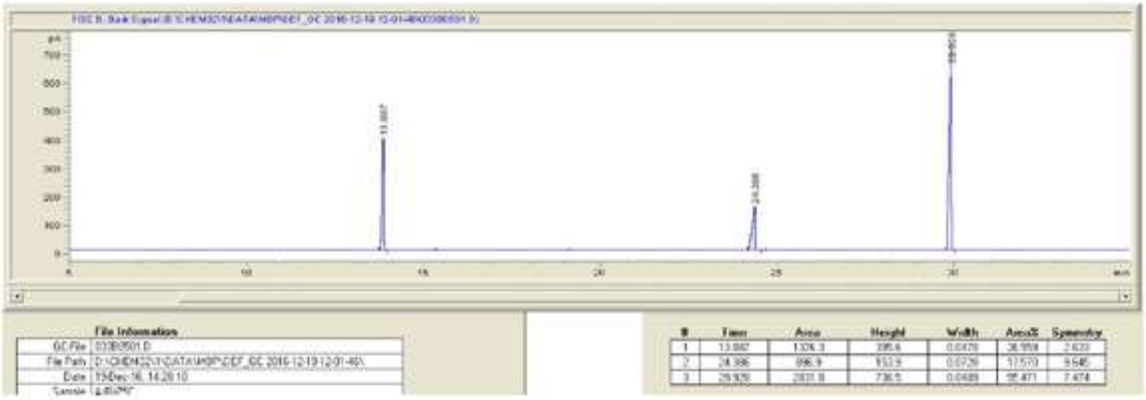
#	Time	Area	Height	Width	Area%	Symmetry
1	13.897	1619.9	446.7	0.0527	27.463	2.779
2	24.400	1065.3	175.0	0.0798	18.061	11.438
3	29.936	3213.2	796.4	0.0503	54.476	7.75



File Information

GC-File	03180401.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-19 12-01-46\
Date	19-Dec-16, 13:48:38

#	Time	Area	Height	Width	Area%	Symmetry
1	13.886	1290.3	374	0.0430	26.955	2.344
2	24.38	845.6	147.5	0.0717	17.664	5.105
3	29.924	2651	709	0.0458	55.381	7.023



File Information

GC-File	03180501.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-19 12-01-46\
Date	19-Dec-16, 14:28:10

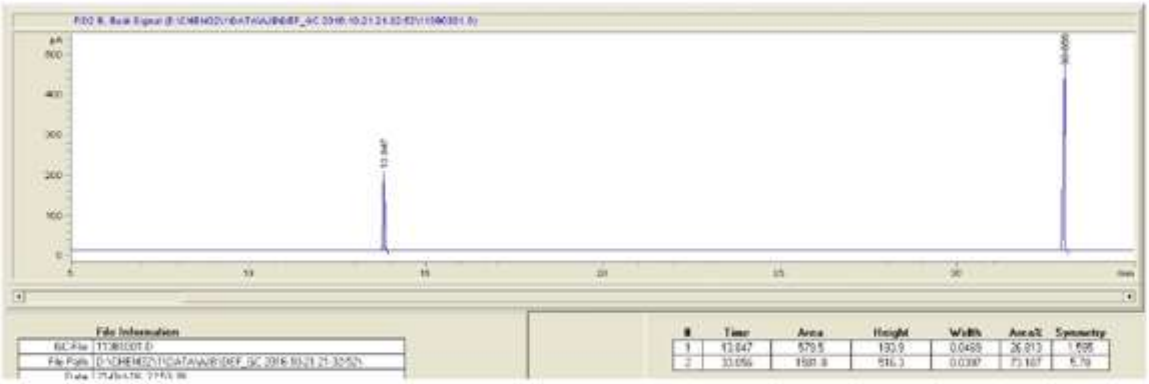
#	Time	Area	Height	Width	Area%	Symmetry
1	13.887	1326.3	395.6	0.0478	26.959	2.633
2	24.386	866.9	153.9	0.0726	17.570	9.545
3	29.925	2731.8	736.5	0.0489	55.471	7.474

1-methylnaphthalene (internal standard) at 13.9

23a at 24.5

28a at 29.9

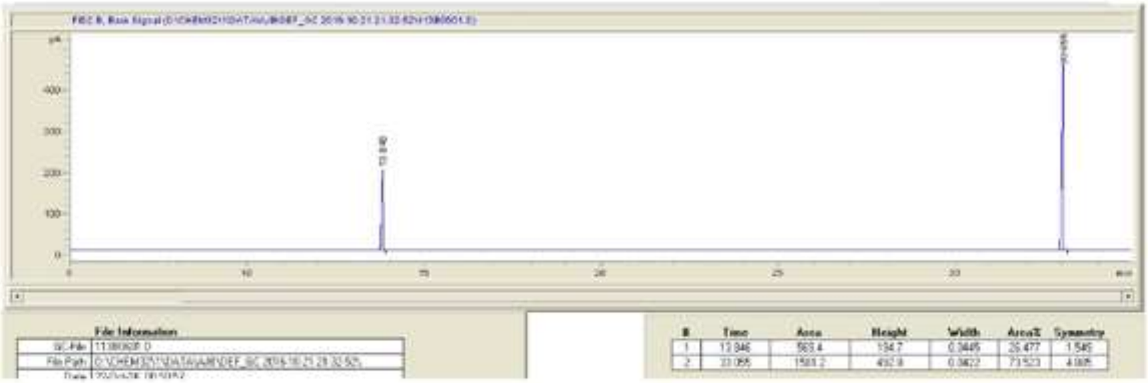
31a calibration



File Information

GC-File	11380107.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-21 21-32-52\

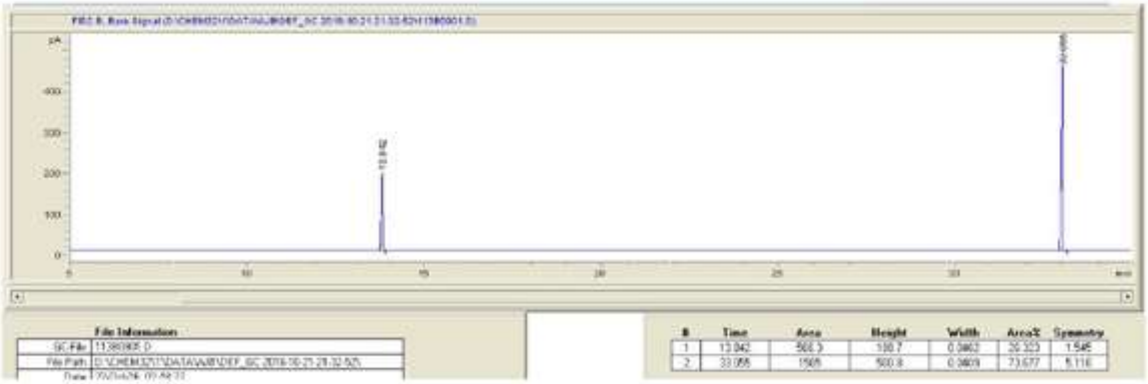
#	Time	Area	Height	Width	Area%	Symmetry
1	13.847	579.5	193.9	0.0469	26.813	1.595
2	33.056	1581.8	516.3	0.0397	73.187	5.79



File Information

GC-File	11380108.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-21 21-32-52\

#	Time	Area	Height	Width	Area%	Symmetry
1	13.846	563.4	194.7	0.0445	26.477	1.545
2	33.055	1564.2	492.8	0.0422	73.523	4.085



File Information

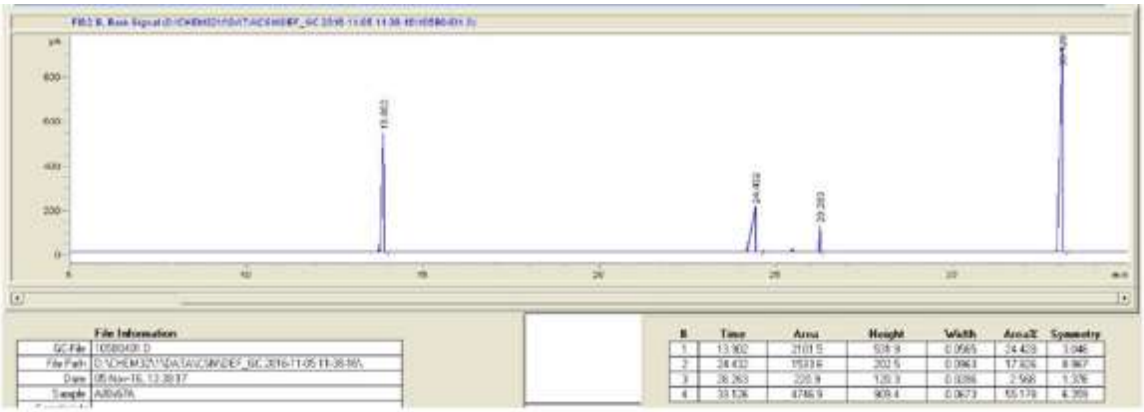
GC-File	11380109.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-21 21-32-52\

#	Time	Area	Height	Width	Area%	Symmetry
1	13.842	566.3	190.7	0.0462	26.323	1.545
2	33.055	1585	500.8	0.0409	73.677	5.116

1-methylnaphthalene (internal standard) at 13.9

31a at 33.1

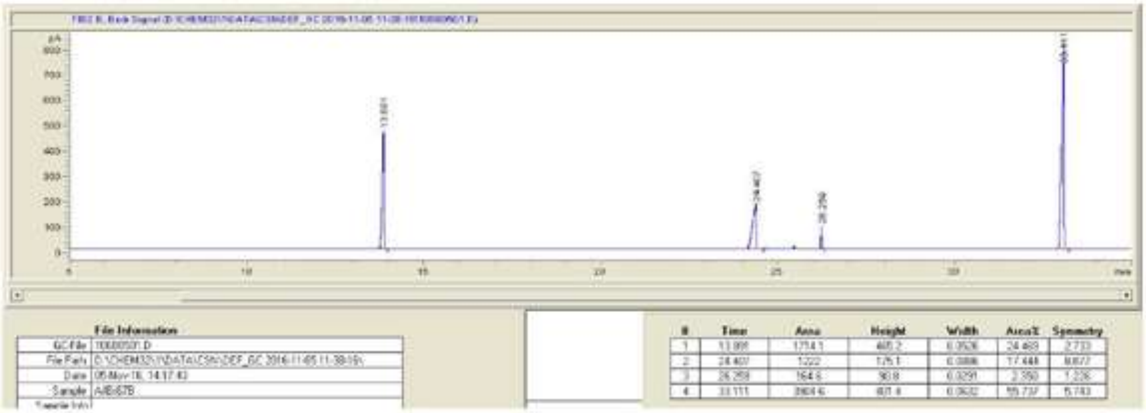
31a relative rate measurement



File Information

GC-File	10580401.D
File Path	C:\CHEM32\1\DATA\CSW\DEF_GC 2016-11-05 11-38-18\
Date	05-Nov-16, 12:38:37
Sample	AJB-67A
Sample Info	

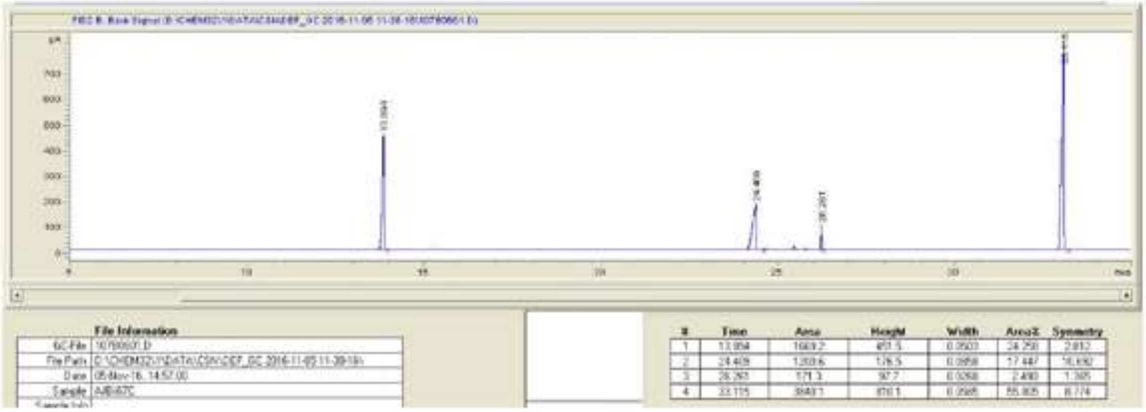
#	Time	Area	Height	Width	Area%	Symmetry
1	13.902	2101.5	538.9	0.0565	24.428	3.046
2	24.432	1533.6	202.5	0.0963	17.826	8.867
3	26.263	220.9	120.3	0.0286	2.568	1.376
4	33.126	4746.9	909.4	0.0673	55.178	4.359



File Information

GC-File	10600501.D
File Path	C:\CHEM32\1\DATA\CSW\DEF_GC 2016-11-05 11-38-18\
Date	05-Nov-16, 14:17:43
Sample	AJB-67B
Sample Info	

#	Time	Area	Height	Width	Area%	Symmetry
1	13.891	1714.1	465.2	0.0526	24.469	2.733
2	24.407	1222	175.1	0.0886	17.444	8.877
3	26.259	164.6	90.8	0.0291	2.350	1.226
4	33.111	3904.6	807.4	0.0632	55.737	5.743



File Information

GC-File	10790601.D
File Path	C:\CHEM32\1\DATA\CSW\DEF_GC 2016-11-05 11-38-18\
Date	05-Nov-16, 14:57:00
Sample	AJB-67C
Sample Info	

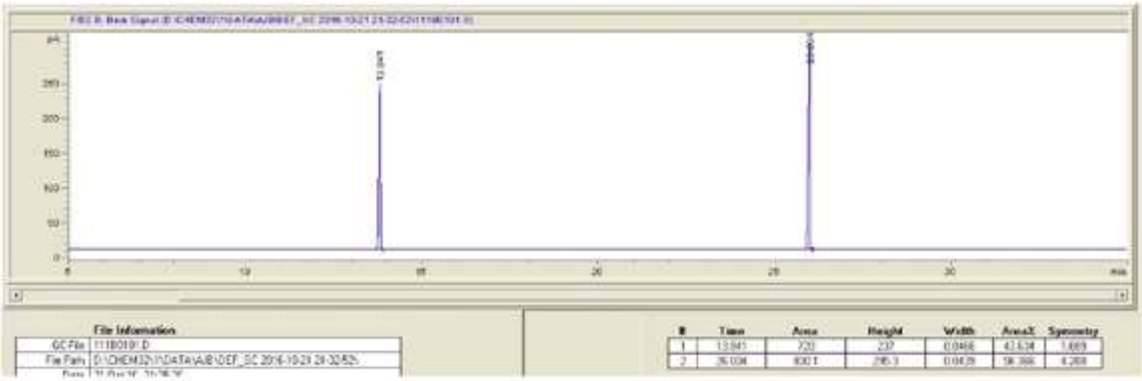
#	Time	Area	Height	Width	Area%	Symmetry
1	13.894	1669.2	491.5	0.0503	24.258	2.812
2	24.409	1200.6	176.5	0.0958	17.447	16.692
3	26.261	171.3	97.7	0.0268	2.490	1.305
4	33.115	3840.1	870.1	0.0665	55.805	8.774

1-methylnaphthalene (internal standard) at 13.9

23a at 24.5

31a at 33.1

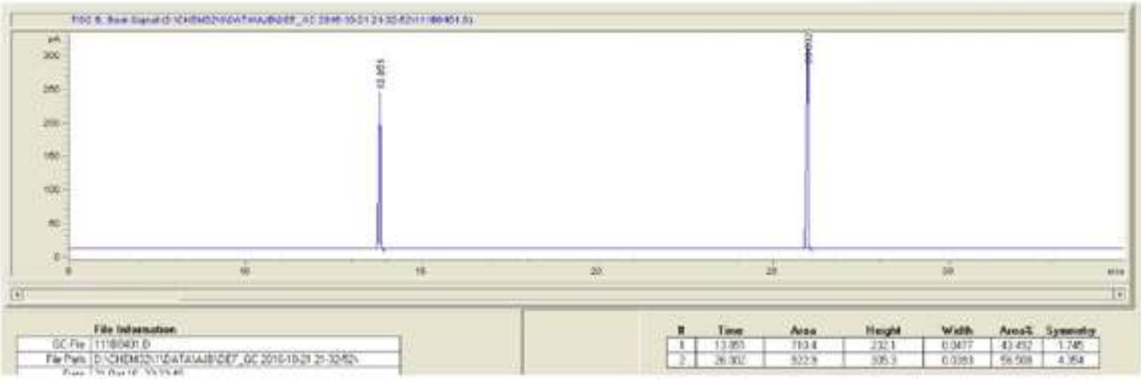
32a calibration



File Information

GC File	11180101.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-21 21-32-52\

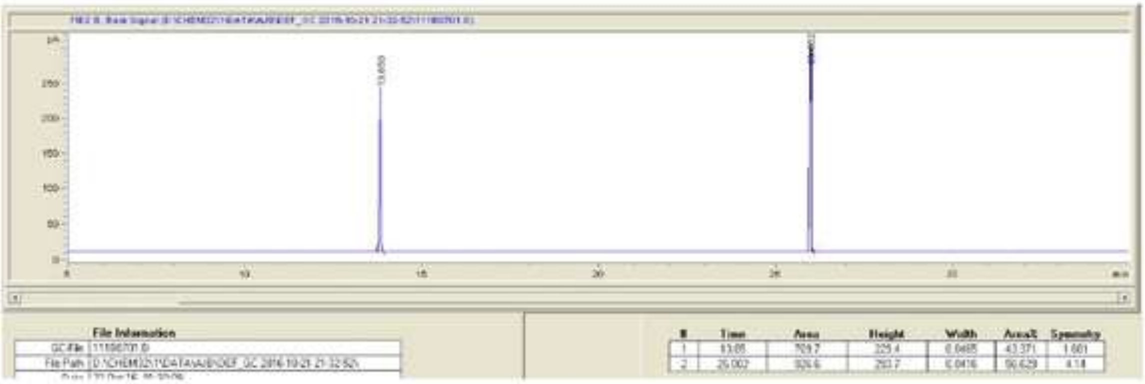
#	Time	Area	Height	Width	Area%	Symmetry
1	13.941	720	237	0.0466	43.634	1.889
2	26.034	930.1	295.3	0.0429	56.366	4.268



File Information

GC File	11180401.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-21 21-32-52\

#	Time	Area	Height	Width	Area%	Symmetry
1	13.855	713.4	232.1	0.0477	43.492	1.745
2	26.002	926.9	305.3	0.0393	56.508	4.354



File Information

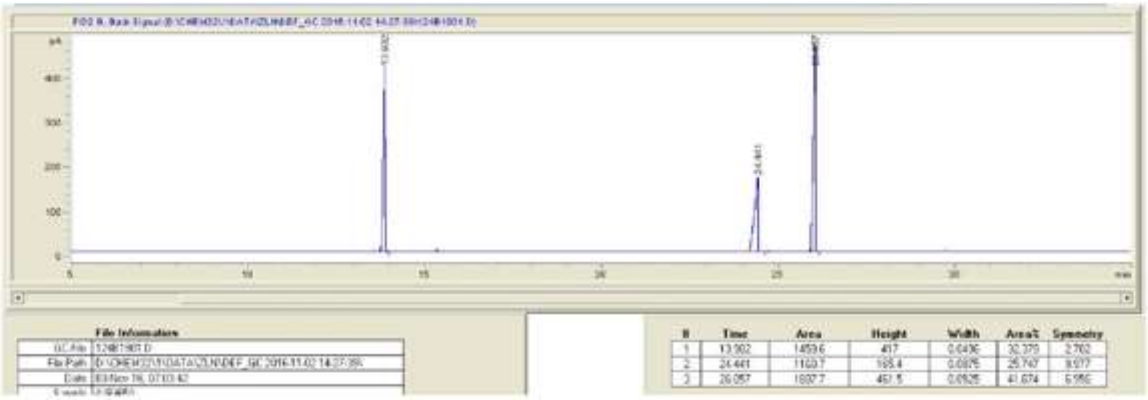
GC File	11180701.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-21 21-32-52\

#	Time	Area	Height	Width	Area%	Symmetry
1	13.85	709.7	225.4	0.0465	43.371	1.601
2	26.002	926.6	293.7	0.0416	56.629	4.18

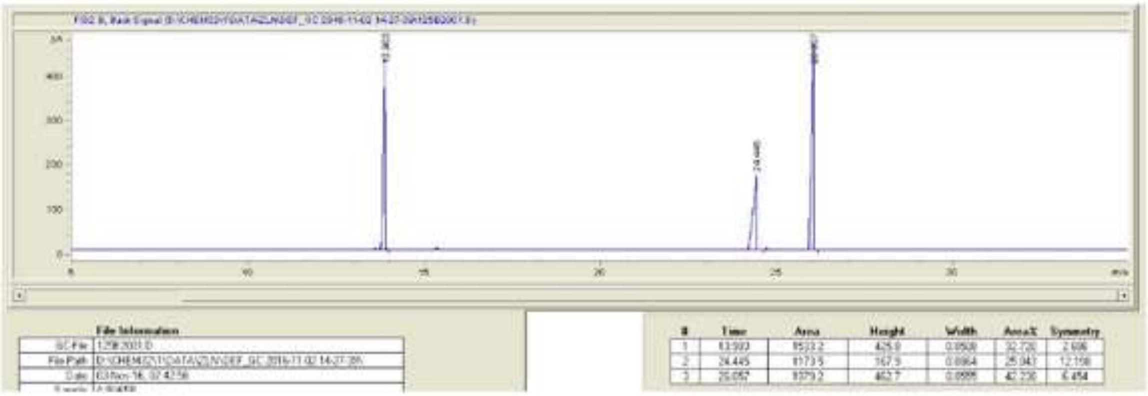
1-methylnaphthalene (internal standard) at 13.9

32a at 26.0

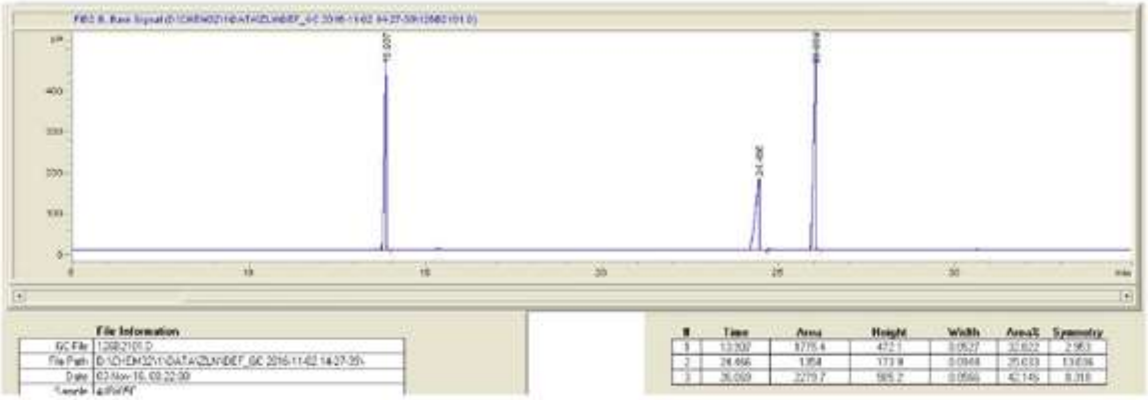
32a relative rate measurement



#	Time	Area	Height	Width	Area%	Symmetry
1	13.902	1459.6	417	0.0436	32.379	2.702
2	24.441	1160.7	165.4	0.0875	25.747	8.977
3	26.057	1887.7	451.5	0.0525	41.874	6.956



#	Time	Area	Height	Width	Area%	Symmetry
1	13.903	1533.2	425.0	0.0508	32.720	2.606
2	24.445	1173.5	167.5	0.0864	25.043	12.158
3	26.057	1979.2	462.7	0.0555	42.236	6.454



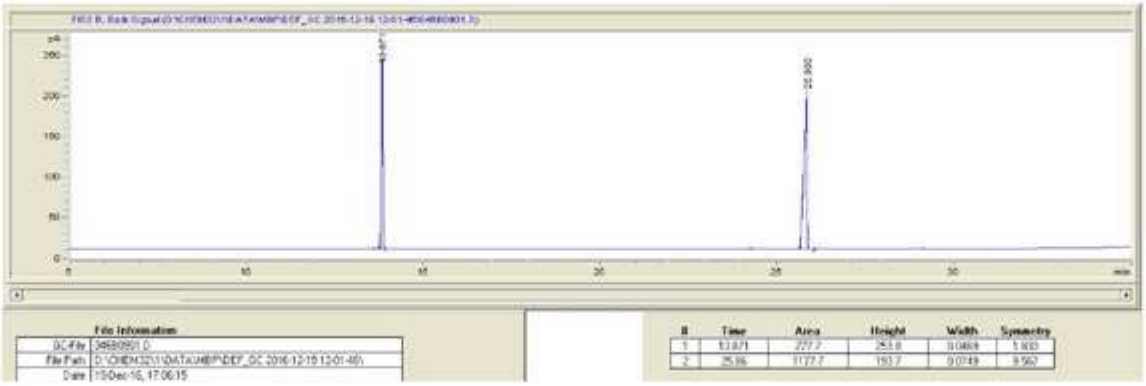
#	Time	Area	Height	Width	Area%	Symmetry
1	13.907	1775.4	472.1	0.0527	32.822	2.953
2	24.466	1354	173.8	0.0968	25.033	13.636
3	26.059	2279.7	565.2	0.0566	42.145	8.318

1-methylnaphthalene (internal standard) at 13.9

23a at 24.5

32a at 26.1

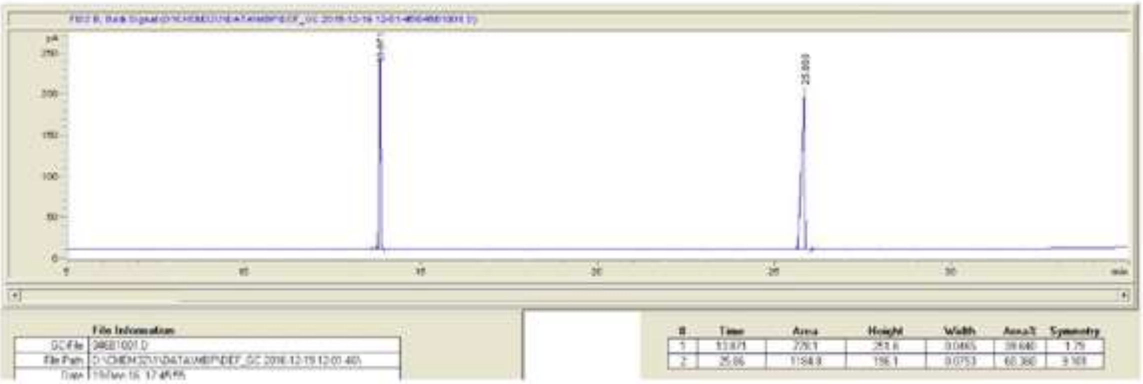
33a calibration



File Information

GC-File	34680901.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-15 12-01-40\
Date	15-Dec-16, 17:06:15

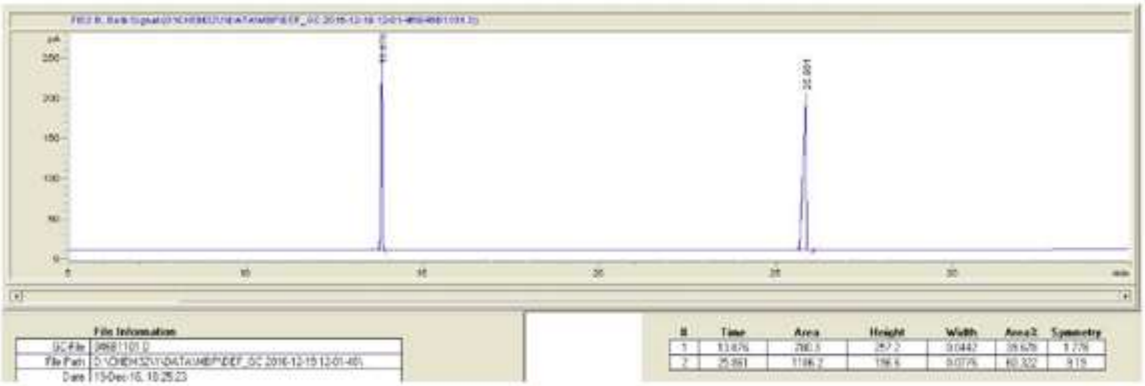
#	Time	Area	Height	Width	Symmetry
1	13.871	777.7	253.8	0.0469	1.803
2	25.86	1177.7	193.7	0.0749	9.562



File Information

GC-File	34681001.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-15 12-01-40\
Date	15-Dec-16, 17:45:55

#	Time	Area	Height	Width	Area%	Symmetry
1	13.871	778.1	251.6	0.0465	39.640	1.79
2	25.86	1184.8	196.1	0.0753	60.360	9.101



File Information

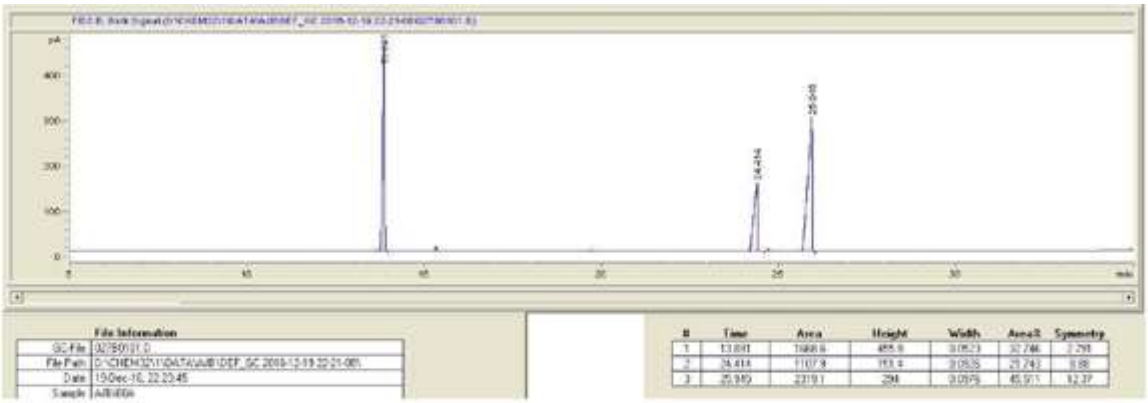
GC-File	34681101.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-15 12-01-40\
Date	15-Dec-16, 18:25:23

#	Time	Area	Height	Width	Area%	Symmetry
1	13.876	780.3	257.2	0.0442	39.678	1.776
2	25.861	1186.2	196.6	0.0776	60.322	9.19

1-methylnaphthalene (internal standard) at 13.9

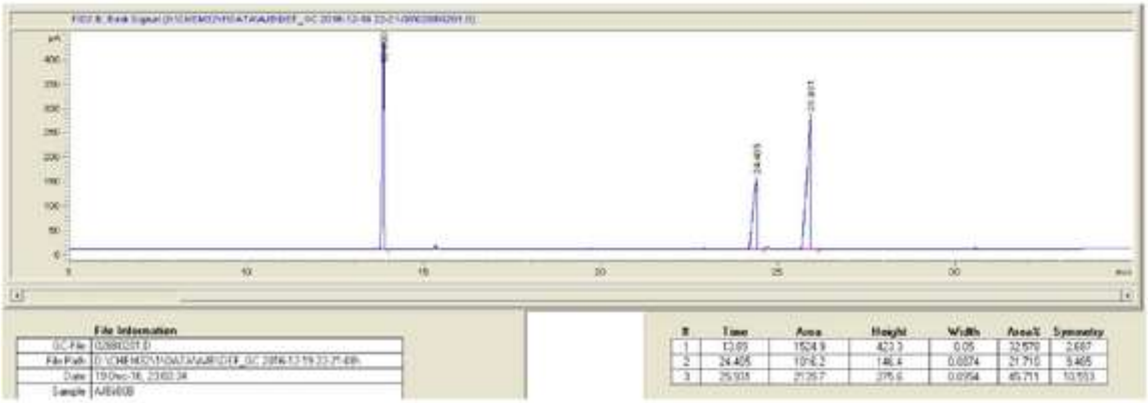
33a at 25.9

33a relative rate measurement



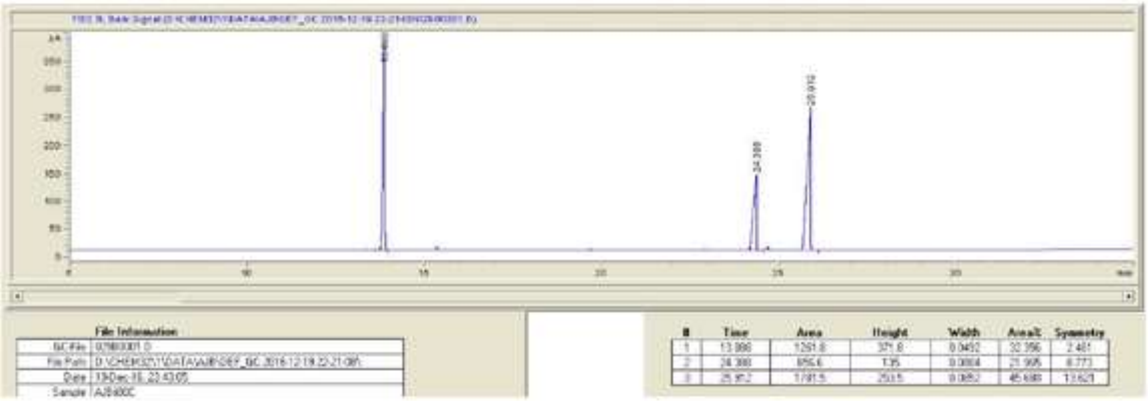
	File Information
GC File	027B0101.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-19 22-21-08\
Date	19-Dec-16, 22:23:45
Sample	AJB400A

#	Time	Area	Height	Width	Area%	Symmetry
1	13.891	1588.6	455.9	0.0523	32.746	2.291
2	24.414	1107.9	153.4	0.0535	21.743	9.88
3	25.949	2219.1	294	0.0576	45.511	12.37



	File Information
GC File	028B0201.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-19 22-21-08\
Date	19-Dec-16, 23:03:34
Sample	AJB400B

#	Time	Area	Height	Width	Area%	Symmetry
1	13.89	1524.9	423.3	0.05	32.570	2.687
2	24.405	1016.2	146.4	0.0874	21.710	9.465
3	25.935	2135.7	375.6	0.0954	45.711	10.553



	File Information
GC File	029B0301.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-19 22-21-08\
Date	19-Dec-16, 23:43:05
Sample	AJB400C

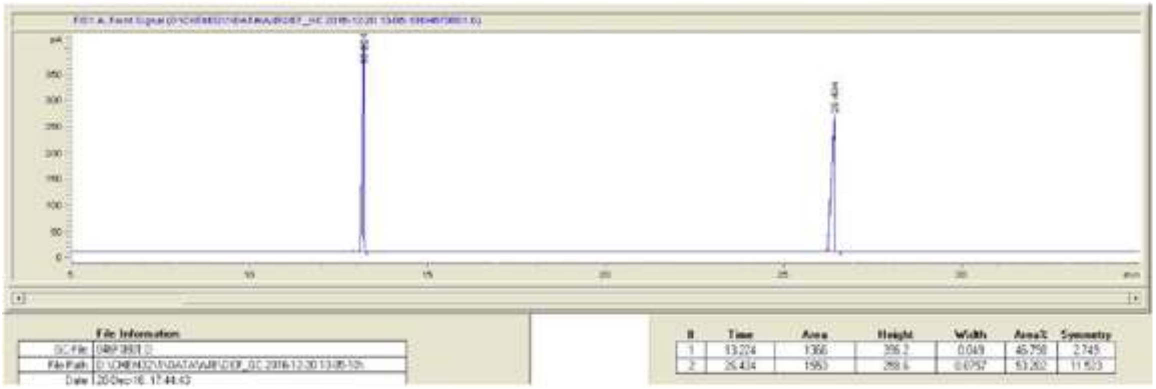
#	Time	Area	Height	Width	Area%	Symmetry
1	13.886	1261.8	371.8	0.0492	32.356	2.481
2	24.388	856.6	135	0.0884	21.965	8.773
3	25.952	1781.5	253.5	0.0852	45.680	13.621

1-methylnaphthalene (internal standard) at 13.9

23a at 24.4

33a at 25.9

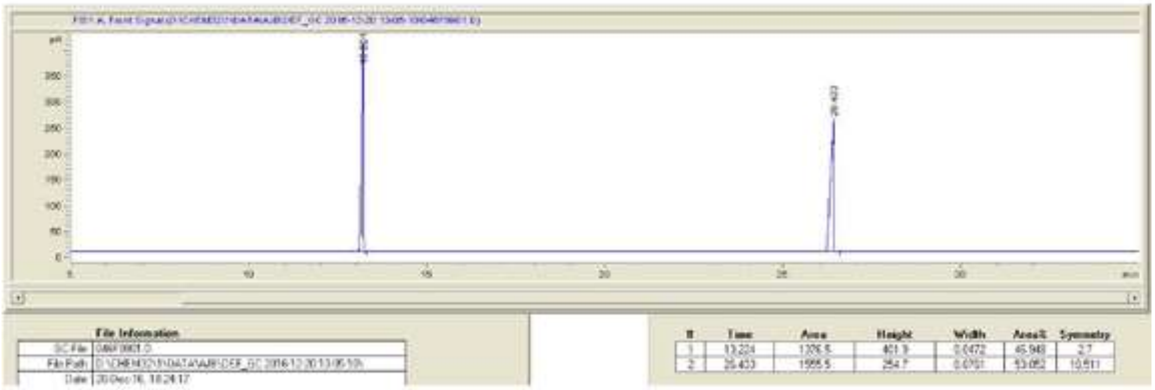
34a calibration



File Information

GC File	08F0801.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-20 13-05-10\
Date	20-Dec-16, 17:44:43

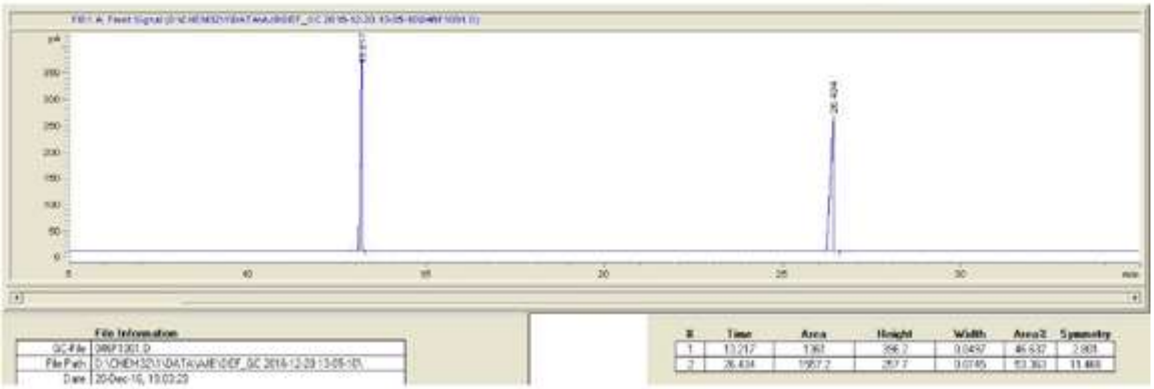
#	Time	Area	Height	Width	Area%	Symmetry
1	13.224	1366	396.2	0.049	46.798	2.745
2	26.434	1553	288.6	0.0757	53.202	11.523



File Information

GC File	08F0901.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-20 13-05-10\
Date	20-Dec-16, 18:24:17

#	Time	Area	Height	Width	Area%	Symmetry
1	13.224	1376.5	401.9	0.0472	46.948	2.7
2	26.433	1555.5	254.7	0.0751	53.052	10.511



File Information

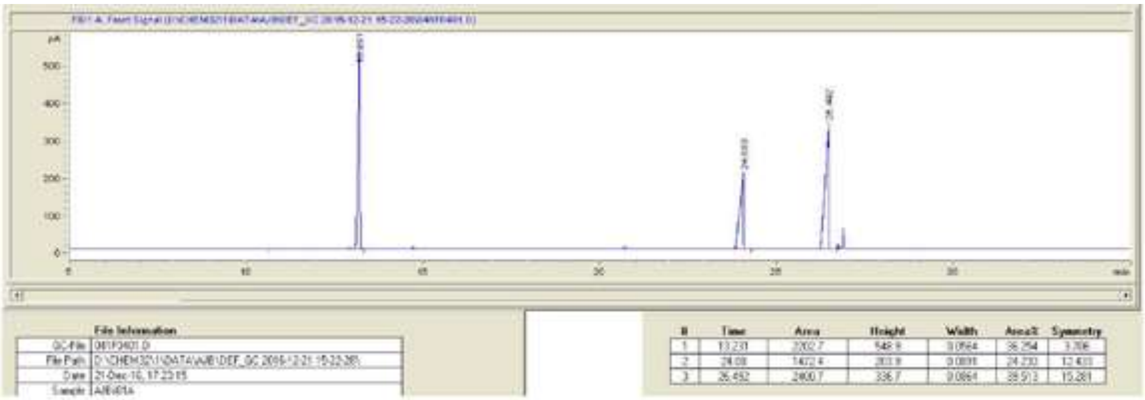
GC File	08F1001.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-20 13-05-10\
Date	20-Dec-16, 19:03:29

#	Time	Area	Height	Width	Area%	Symmetry
1	13.217	1361	396.2	0.0497	46.637	2.901
2	26.434	1557.2	257.7	0.0745	53.363	11.468

1-methylnaphthalene (internal standard) at 13.2

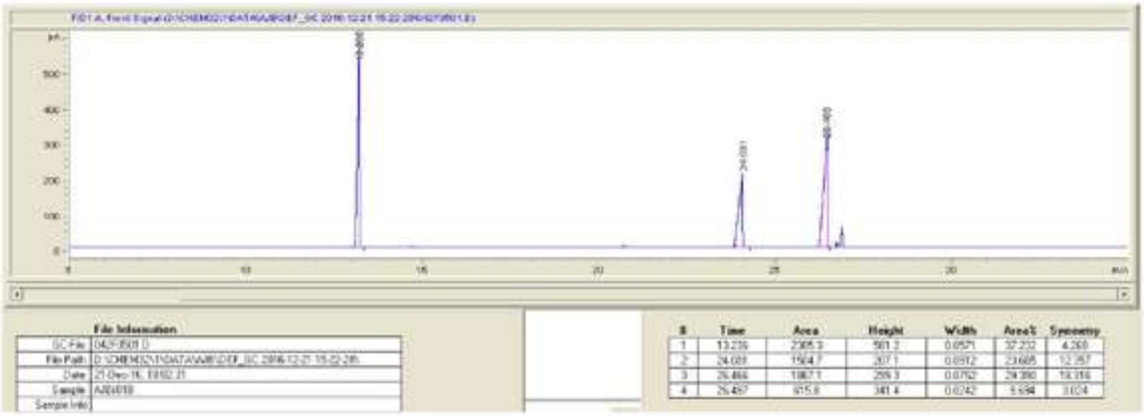
34a at 26.4

34a relative rate measurement



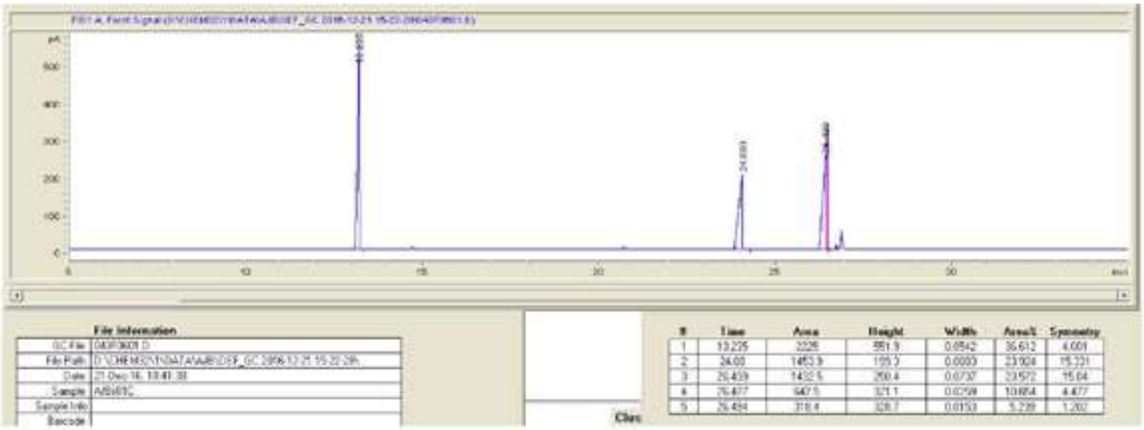
	File Information
GC-File	041F0401.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-21 15-22-28\
Date	21-Dec-16, 17:23:15
Sample	AJB-01A

#	Time	Area	Height	Width	Area%	Symmetry
1	13.231	2202.7	548.9	0.0564	36.254	3.706
2	24.08	1472.4	203.9	0.0891	24.230	12.433
3	26.452	2400.7	336.7	0.0864	39.513	15.281



	File Information
GC-File	042F0501.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-21 15-22-28\
Date	21-Dec-16, 18:02:21
Sample	AJB-01B
Sample Info	

#	Time	Area	Height	Width	Area%	Symmetry
1	13.236	2305.3	591.2	0.0571	37.232	4.268
2	24.081	1504.7	207.1	0.0912	23.685	12.357
3	26.466	1867.1	259.3	0.0762	29.390	18.316
4	26.497	615.8	341.4	0.0242	9.694	3.024



	File Information
GC-File	043F0601.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-21 15-22-28\
Date	21-Dec-16, 18:41:38
Sample	AJB-01C
Sample Info	
Barcode	

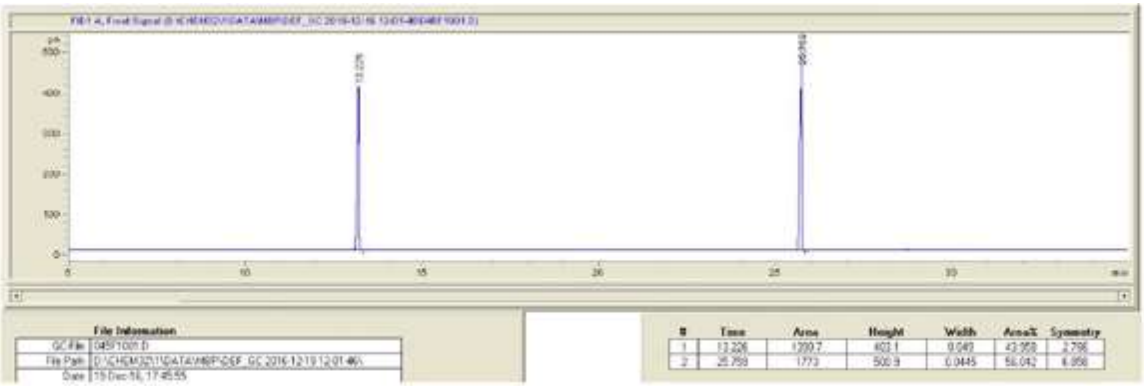
#	Time	Area	Height	Width	Area%	Symmetry
1	13.225	2226	551.9	0.0542	36.612	4.001
2	24.00	1453.9	195.3	0.0893	23.924	15.331
3	26.459	1432.5	250.4	0.0737	23.572	15.04
4	26.477	647.5	321.1	0.0258	10.654	4.477
5	26.494	318.4	328.7	0.0153	5.239	1.202

1-methylnaphthalene (internal standard) at 13.4

23a at 24.1

34a at 26.5

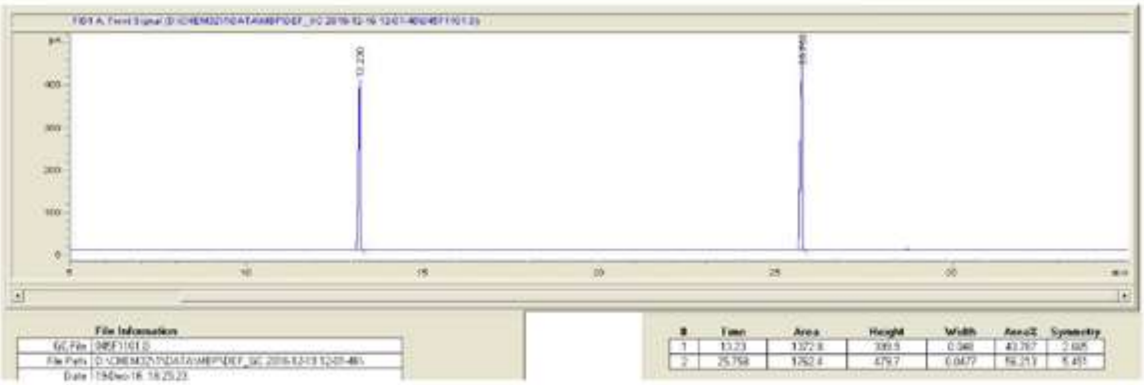
35a calibration



File Information

GC File	045F1001.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-19 12-01-46\
Date	15-Dec-16, 17:45:55

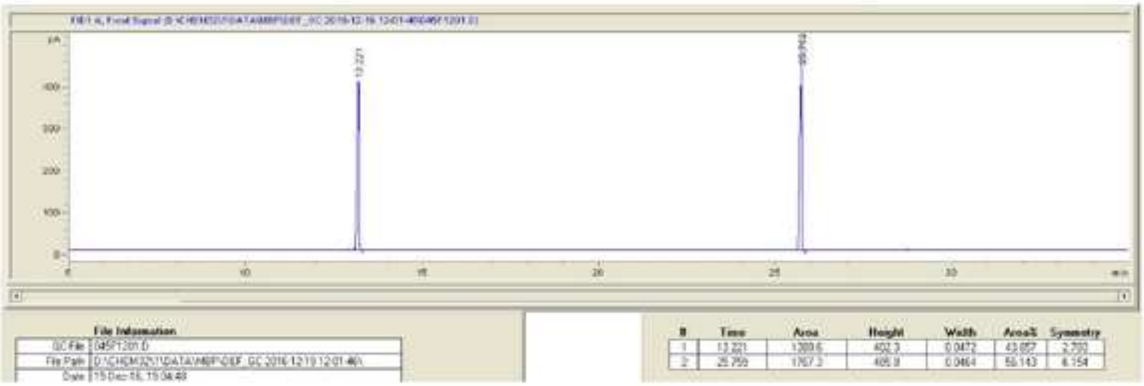
#	Time	Area	Height	Width	Area%	Symmetry
1	13.226	1390.7	403.1	0.049	43.958	2.798
2	25.759	1773	500.9	0.0445	56.042	6.956



File Information

GC File	045F1101.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-19 12-01-46\
Date	19-Dec-16, 18:25:23

#	Time	Area	Height	Width	Area%	Symmetry
1	13.23	1372.8	399.5	0.048	43.787	2.685
2	25.758	1762.4	479.7	0.0477	56.213	5.451



File Information

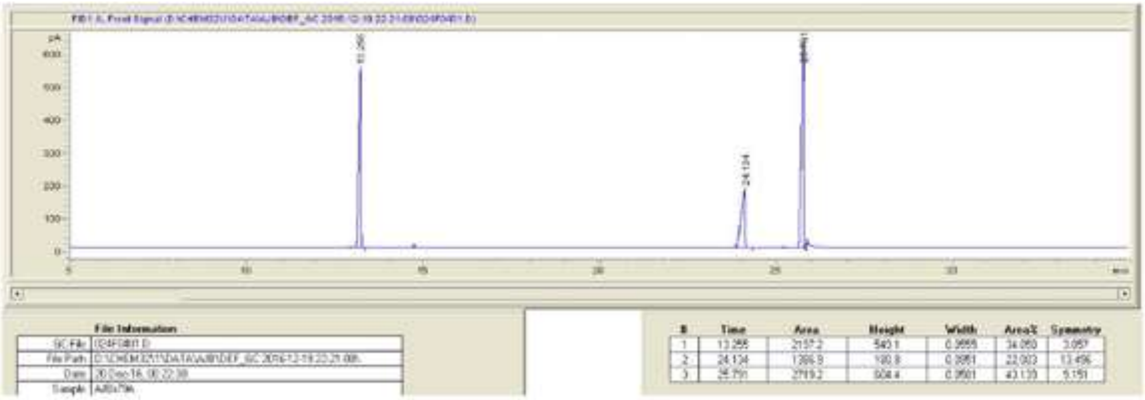
GC File	045F1201.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-19 12-01-46\
Date	15-Dec-16, 15:04:48

#	Time	Area	Height	Width	Area%	Symmetry
1	13.221	1380.6	402.3	0.0472	43.857	2.700
2	25.759	1767.3	485.9	0.0464	56.143	6.154

1-methylnaphthalene (internal standard) at 13.2

35a at 25.8

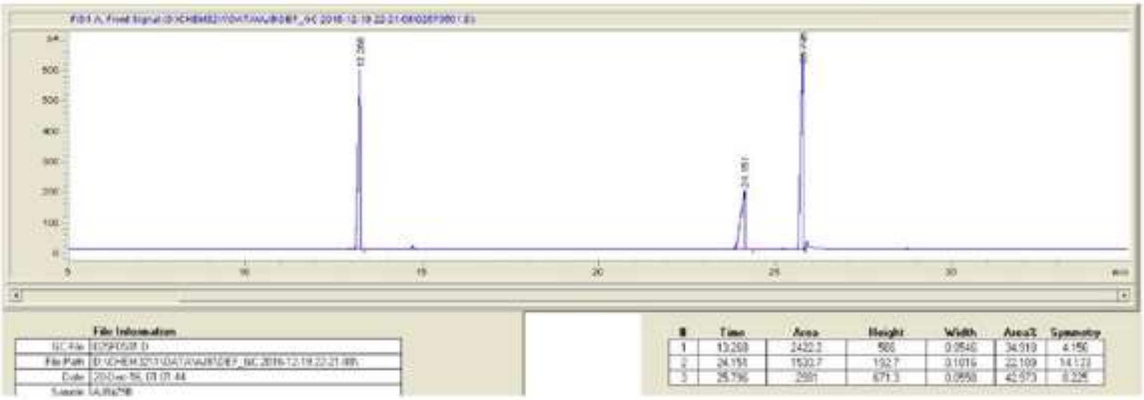
35a relative rate measurement



File Information

GC File	024F0401.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-19 22-21-08\
Date	20-Dec-16, 00:22:38
Sample	AJBii79A

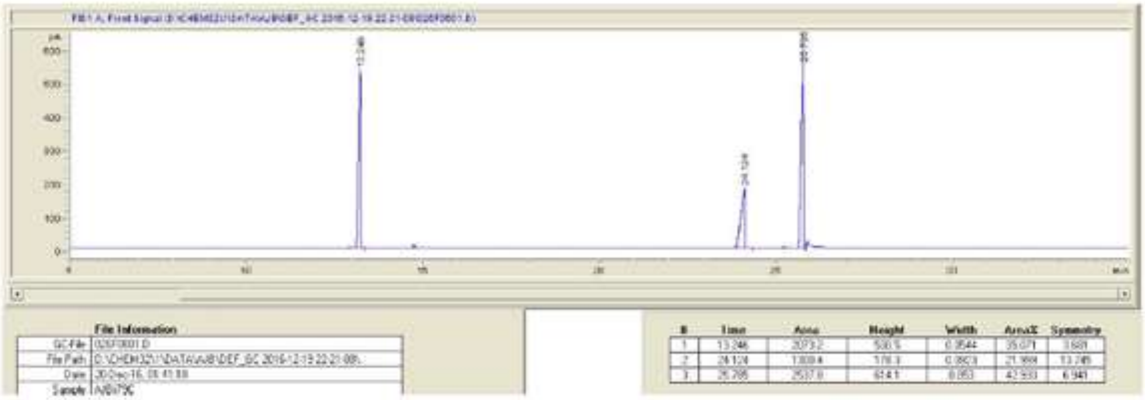
#	Time	Area	Height	Width	Area%	Symmetry
1	13.255	2157.2	540.1	0.0555	34.050	3.057
2	24.134	1396.9	190.8	0.0951	22.003	13.456
3	25.791	2719.2	504.4	0.0501	43.133	5.151



File Information

GC File	025F0501.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-19 22-21-08\
Date	20-Dec-16, 01:01:44
Sample	AJBii79B

#	Time	Area	Height	Width	Area%	Symmetry
1	13.258	2422.2	566	0.0546	34.918	4.156
2	24.151	1530.7	192.7	0.1016	22.109	14.123
3	25.796	2981	671.3	0.0558	42.973	6.225



File Information

GC File	026F0601.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-19 22-21-08\
Date	20-Dec-16, 01:41:58
Sample	AJBii79C

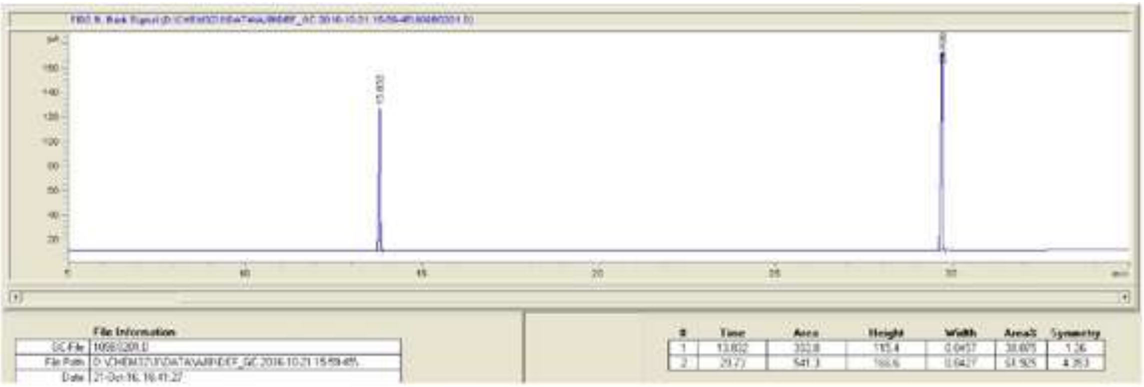
#	Time	Area	Height	Width	Area%	Symmetry
1	13.246	2073.2	536.5	0.0544	35.071	3.681
2	24.124	1300.4	178.3	0.0803	21.996	13.745
3	25.785	2537.8	614.1	0.053	42.933	6.941

1-methylnaphthalene (internal standard) at 13.2

23a at 24.1

35a at 25.8

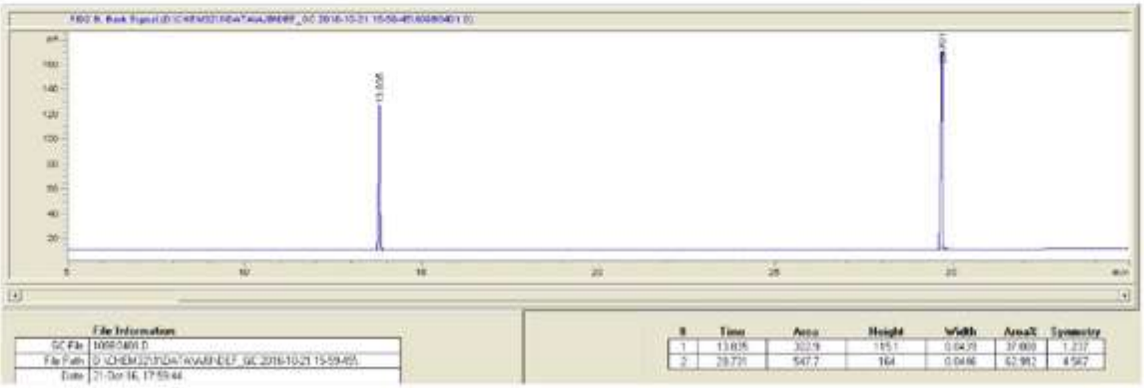
36a calibration



File Information

GC File	10580201.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-21 15-59-45\
Date	21-Oct-16, 16:41:27

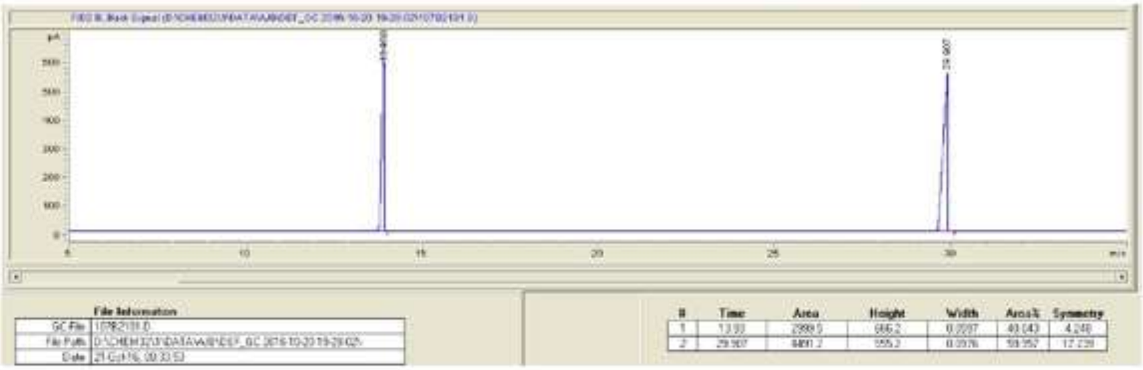
#	Time	Area	Height	Width	Area%	Symmetry
1	13.832	332.8	115.4	0.0457	38.075	1.26
2	29.73	541.3	166.6	0.0427	61.925	4.353



File Information

GC File	10580401.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-21 15-59-45\
Date	21-Oct-16, 17:59:44

#	Time	Area	Height	Width	Area%	Symmetry
1	13.835	322.9	115.1	0.0439	37.088	1.237
2	29.731	547.7	164	0.0466	62.912	4.567



File Information

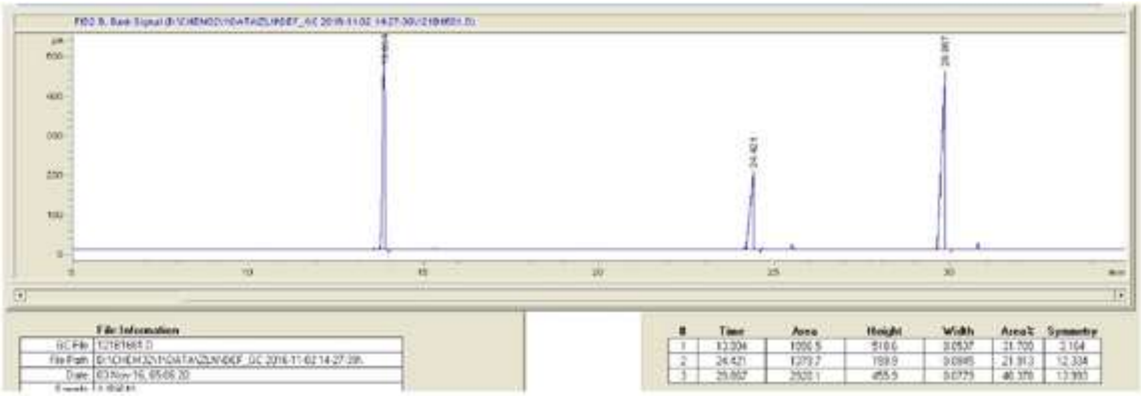
GC File	10782101.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-20 19-29-02\
Date	21-Oct-16, 00:33:53

#	Time	Area	Height	Width	Area%	Symmetry
1	13.93	2999.5	686.2	0.2287	40.043	4.248
2	29.907	4491.2	555.2	0.0976	59.957	17.239

1-methylnaphthalene (internal standard) at 13.9

36a at 29.9

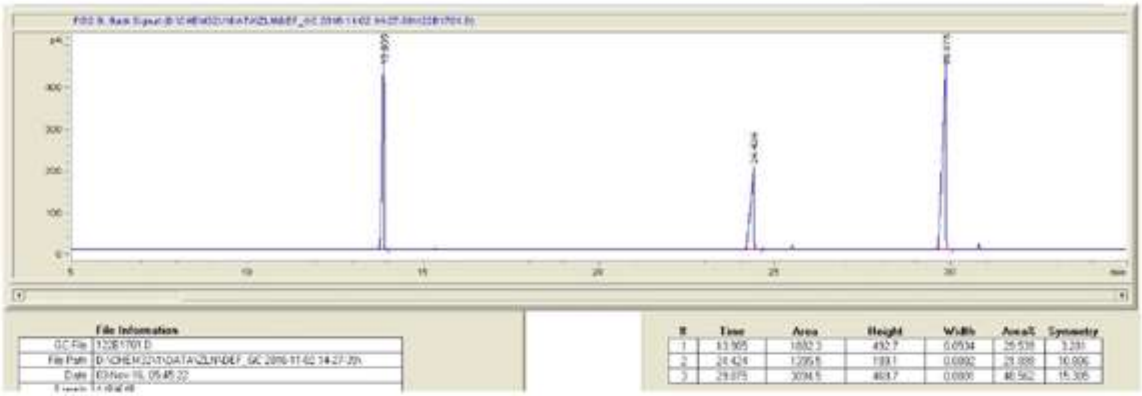
36a relative rate measurement



File Information

GC File	12181681.D
File Path	D:\CHEM32\1\DATA\ZLN\DEF_GC 2016-11-02 14-27-39\
Date	03 Nov 16, 05:06:20

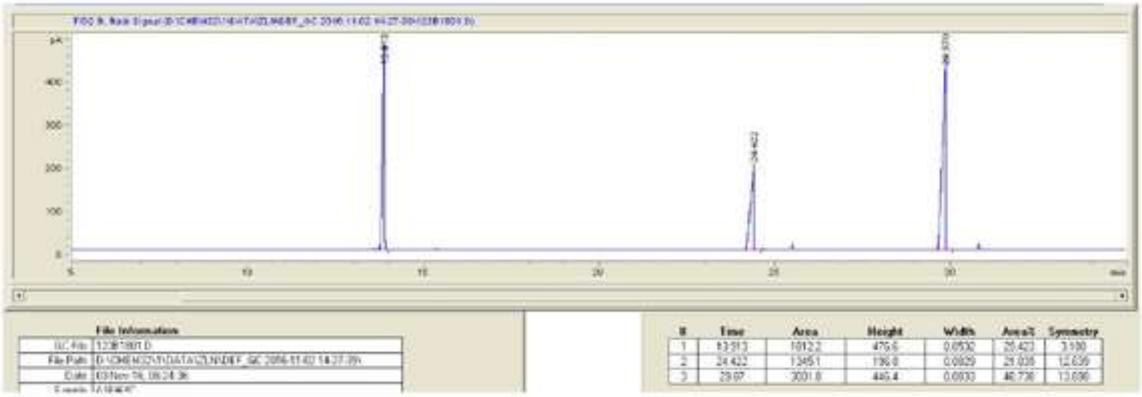
#	Time	Area	Height	Width	Area%	Symmetry
1	13.904	1006.5	510.6	0.0537	31.700	3.164
2	24.421	1279.7	199.9	0.0885	21.913	12.334
3	29.867	2520.1	455.5	0.0779	46.370	13.993



File Information

GC File	12181701.D
File Path	D:\CHEM32\1\DATA\ZLN\DEF_GC 2016-11-02 14-27-39\
Date	03 Nov 16, 05:45:22

#	Time	Area	Height	Width	Area%	Symmetry
1	13.905	1002.3	432.7	0.0534	25.538	3.231
2	24.424	1295.8	193.1	0.0892	23.888	10.906
3	29.875	3094.5	463.7	0.0800	48.562	15.305



File Information

GC File	12181801.D
File Path	D:\CHEM32\1\DATA\ZLN\DEF_GC 2016-11-02 14-27-39\
Date	03 Nov 16, 06:24:36

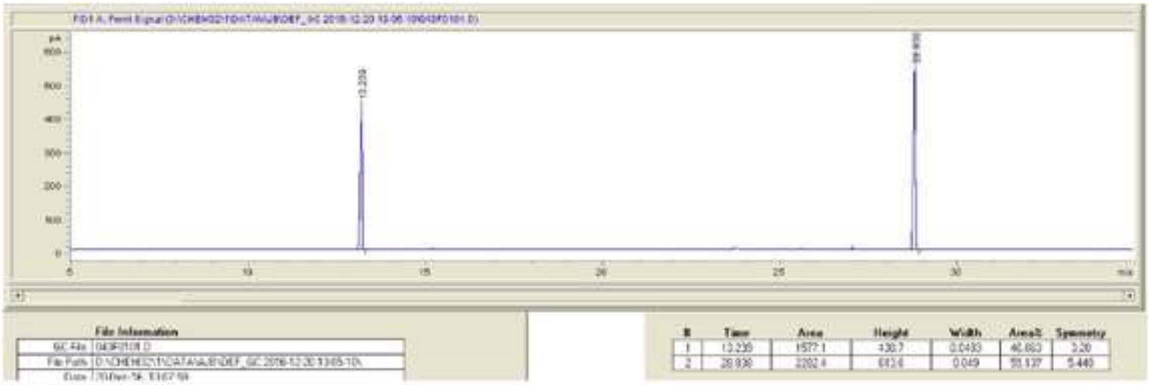
#	Time	Area	Height	Width	Area%	Symmetry
1	13.913	1012.2	476.6	0.0532	25.423	3.130
2	24.422	1345.1	196.8	0.0929	29.036	12.635
3	29.87	3001.8	446.4	0.0930	46.736	13.690

1-methylnaphthalene (internal standard) at 13.9

23a at 24.4

36a at 29.9

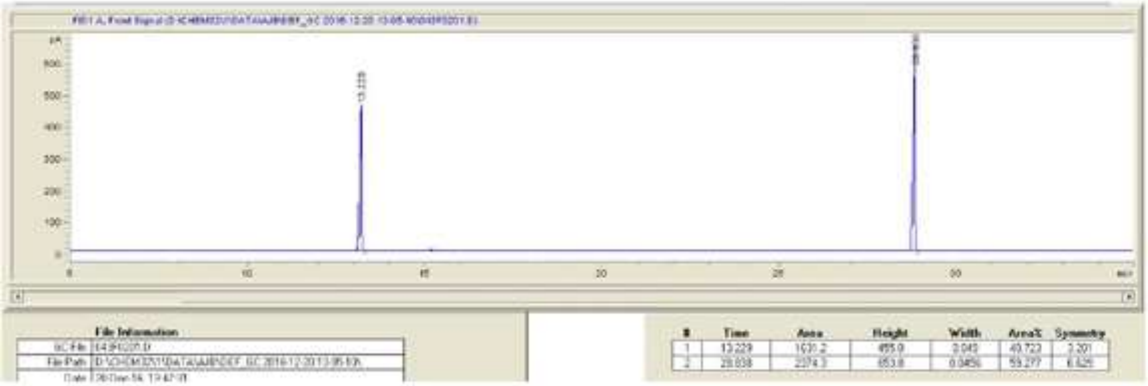
37a calibration



File Information

GC File	043F0101.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-20 13-05-10\
Date	20-Dec-16, 13:57:59

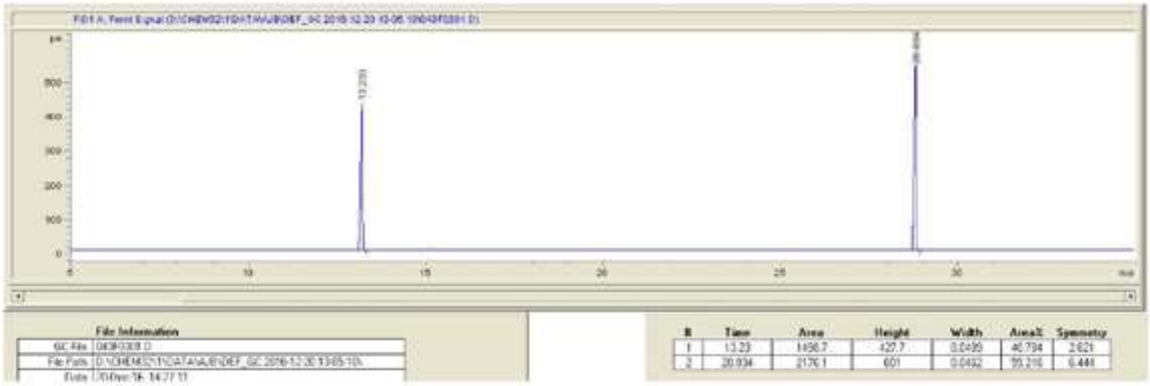
#	Time	Area	Height	Width	Area%	Symmetry
1	13.230	1577.1	430.7	0.0433	40.863	3.20
2	28.836	2282.4	613.6	0.049	59.137	5.440



File Information

GC File	043F0201.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-20 13-05-10\
Date	20-Dec-16, 13:42:13

#	Time	Area	Height	Width	Area%	Symmetry
1	13.229	1631.2	455.0	0.045	40.723	3.201
2	28.838	2374.3	653.8	0.0456	59.277	6.525



File Information

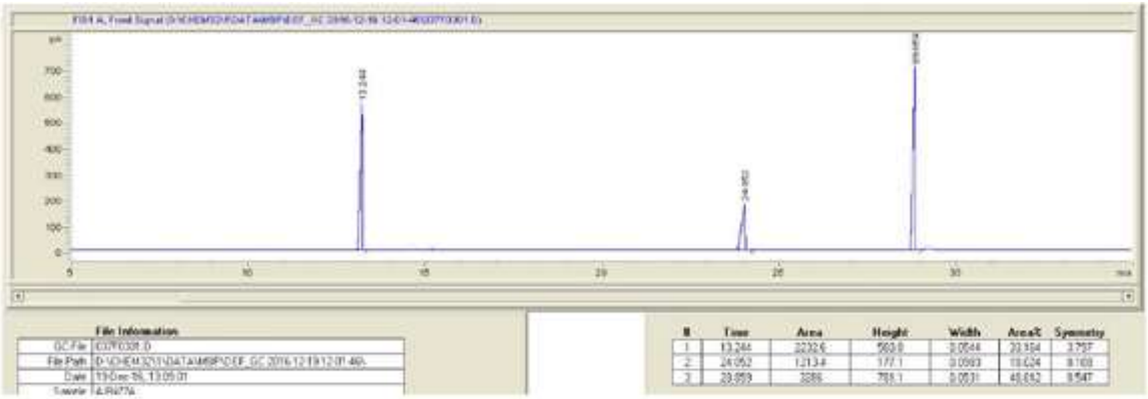
GC File	043F0301.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-12-20 13-05-10\
Date	20-Dec-16, 14:27:11

#	Time	Area	Height	Width	Area%	Symmetry
1	13.23	1496.7	427.7	0.0499	40.794	2.621
2	28.834	2170.1	601	0.0492	59.206	6.444

1-methylnaphthalene (internal standard) at 13.2

37a at 28.8

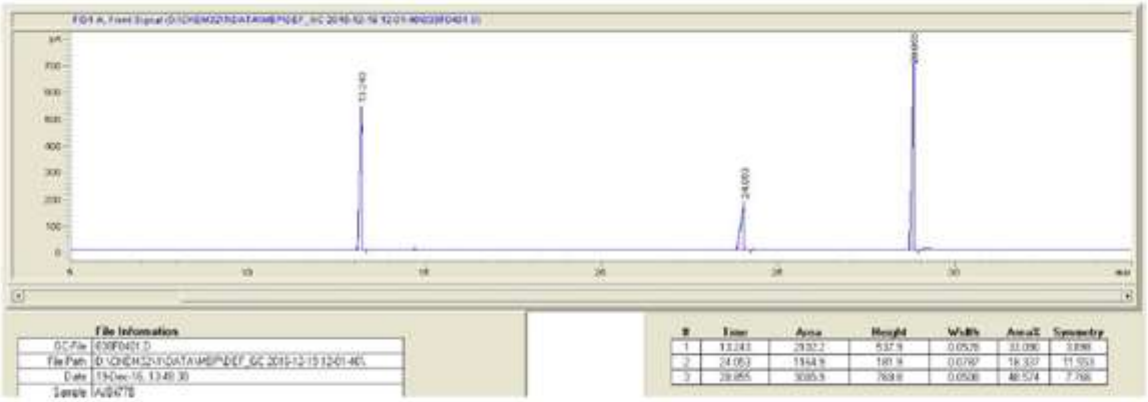
37a relative rate measurement



File Information

GC File	037F0301.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-19 12-01-46\
Date	19-Dec-16, 13:05:01
Sample	AJB477A

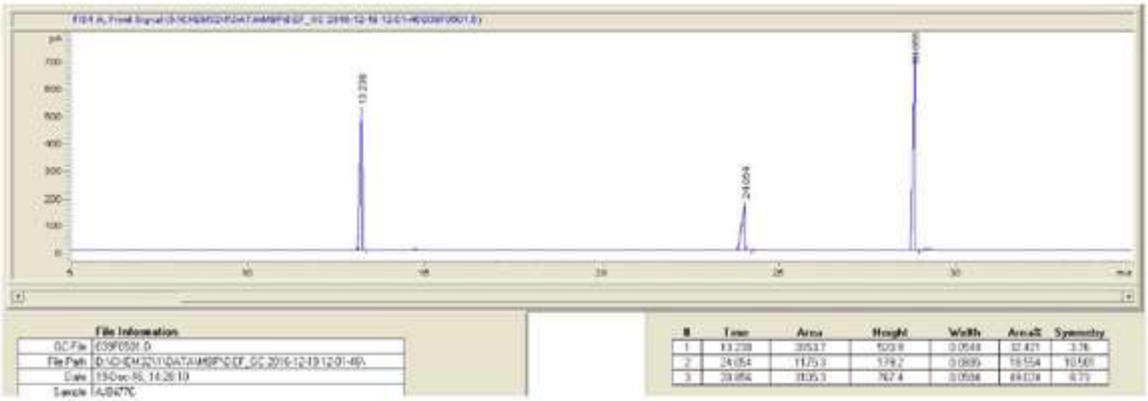
#	Time	Area	Height	Width	Area%	Symmetry
1	13.244	2232.6	583.8	0.0544	33.164	3.757
2	24.052	1213.4	177.1	0.0983	18.024	8.103
3	28.859	3286	755.1	0.0531	48.812	9.547



File Information

GC File	038F0401.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-19 12-01-46\
Date	19-Dec-16, 13:49:30
Sample	AJB477B

#	Time	Area	Height	Width	Area%	Symmetry
1	13.243	2932.2	537.9	0.0578	33.090	3.898
2	24.053	1544.9	181.9	0.0797	18.337	11.553
3	28.855	3085.3	783.8	0.0508	48.574	7.766



File Information

GC File	039F0501.D
File Path	D:\CHEM32\1\DATA\MBP\DEF_GC 2016-12-19 12-01-46\
Date	19-Dec-16, 14:28:10
Sample	AJB477C

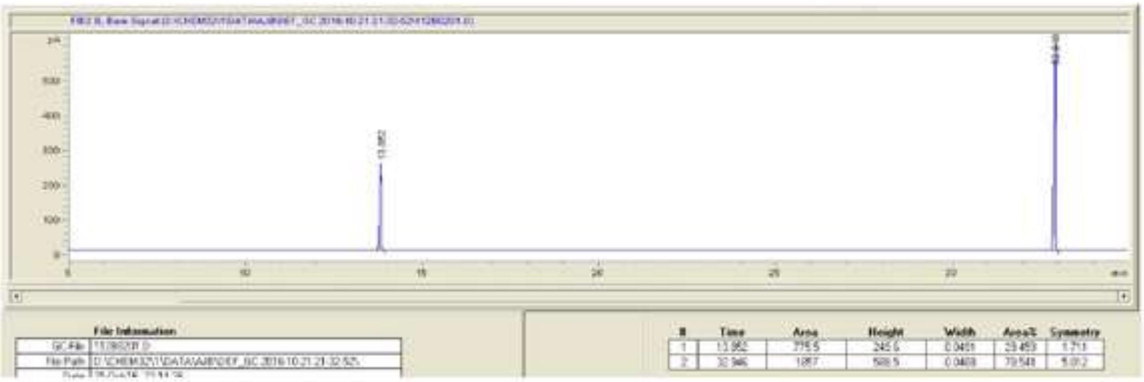
#	Time	Area	Height	Width	Area%	Symmetry
1	13.238	2053.7	503.8	0.0548	32.421	3.76
2	24.054	1175.3	179.2	0.0895	18.554	10.501
3	28.856	3105.3	767.4	0.0508	49.025	6.73

1-methylnaphthalene (internal standard) at 13.2

23a at 24.1

37a at 28.9

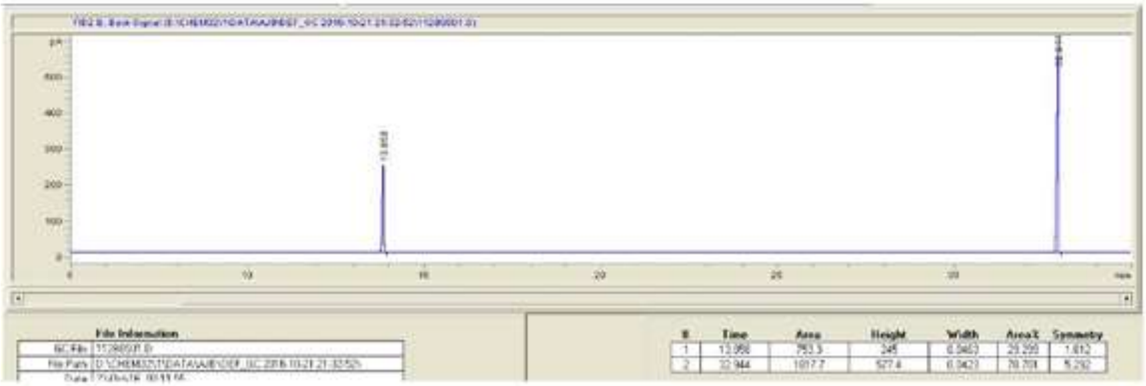
38a calibration



File Information

GC File	11280201.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-21 21-32-52\

#	Time	Area	Height	Width	Area%	Symmetry
1	13.852	775.5	245.6	0.0451	29.459	1.711
2	32.946	1857	588.5	0.0468	70.541	5.012



File Information

GC File	11280501.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-21 21-32-52\

#	Time	Area	Height	Width	Area%	Symmetry
1	13.858	753.3	245	0.0453	29.299	1.812
2	32.944	1817.7	527.4	0.0423	70.701	5.292

File Information

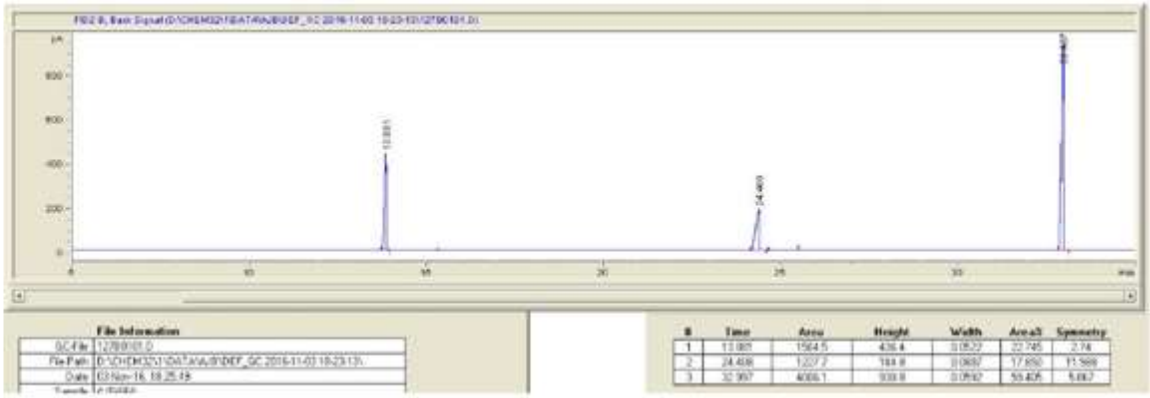
GC File	11280801.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-10-21 21-32-52\

#	Time	Area	Height	Width	Area%	Symmetry
1	13.848	742.8	243.7	0.0476	28.780	1.767
2	32.944	1838.2	595.7	0.0436	71.220	4.724

1-methylnaphthalene (internal standard) at 13.8

38a at 32.9

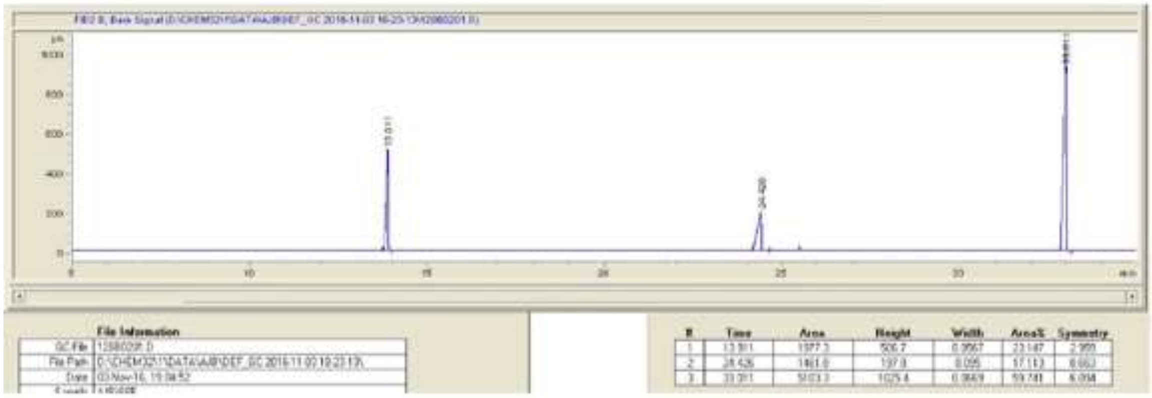
38a relative rate measurement



File Information

GC File	12780101.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-11-03 18-23-13\
Date	03-Nov-16, 18:25:19

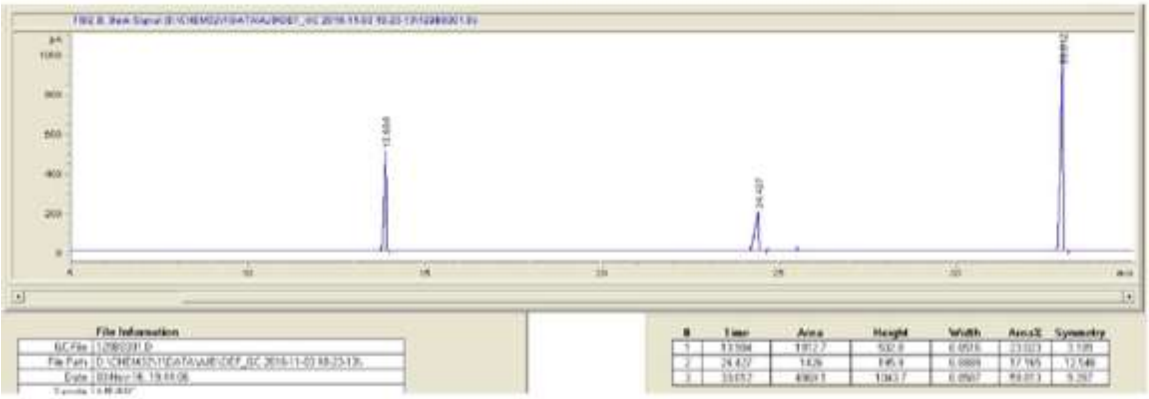
#	Time	Area	Height	Width	Area%	Symmetry
1	13.881	1564.5	436.4	0.0522	22.745	2.74
2	24.408	1227.2	184.8	0.0887	17.850	11.588
3	32.997	4086.1	938.8	0.0592	59.405	5.867



File Information

GC File	12880201.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-11-03 18-23-13\
Date	03-Nov-16, 19:04:52

#	Time	Area	Height	Width	Area%	Symmetry
1	13.911	1977.3	506.7	0.0567	23.147	2.959
2	24.426	1461.8	197.8	0.095	17.113	8.662
3	33.011	5103.3	1025.4	0.0669	59.740	6.094



File Information

GC File	12880301.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2016-11-03 18-23-13\
Date	03-Nov-16, 19:44:06

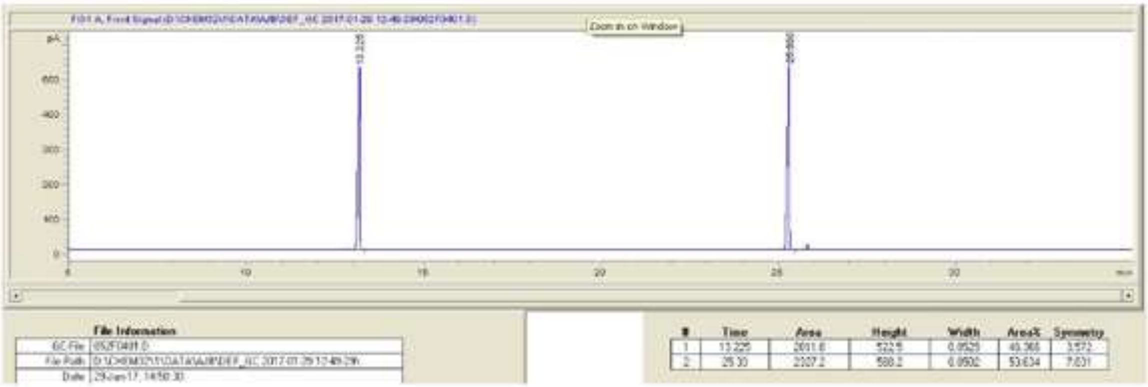
#	Time	Area	Height	Width	Area%	Symmetry
1	13.904	1912.7	502.8	0.0576	23.023	3.109
2	24.427	1476	195.4	0.0889	17.765	12.546
3	33.012	4909.1	1043.7	0.0597	59.013	9.397

1-methylnaphthalene (internal standard) at 13.9

23a at 24.4

38a at 33.0

39a calibration

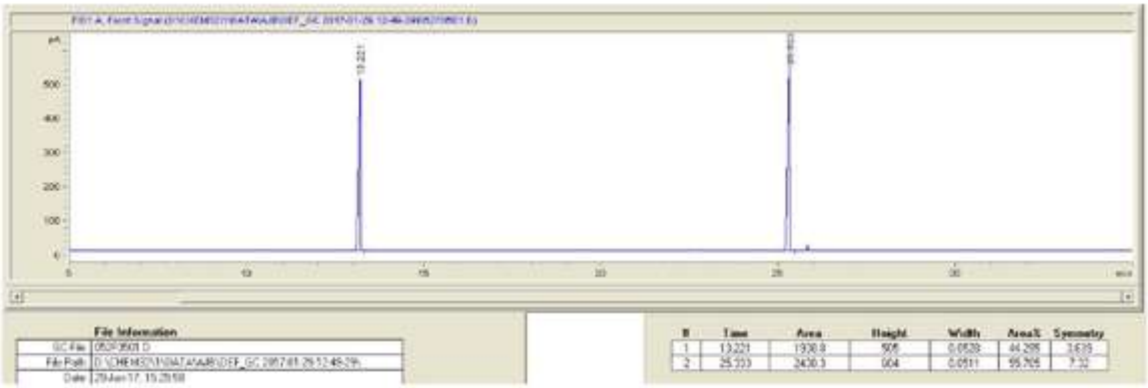


FID1 A, Front Signal (D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\052F0401.D)

File Information

GC File	052F0401.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 14:50:30

#	Time	Area	Height	Width	Area%	Symmetry
1	13.225	2011.8	522.5	0.0525	46.366	3.572
2	25.30	2327.2	588.2	0.0502	53.634	7.031

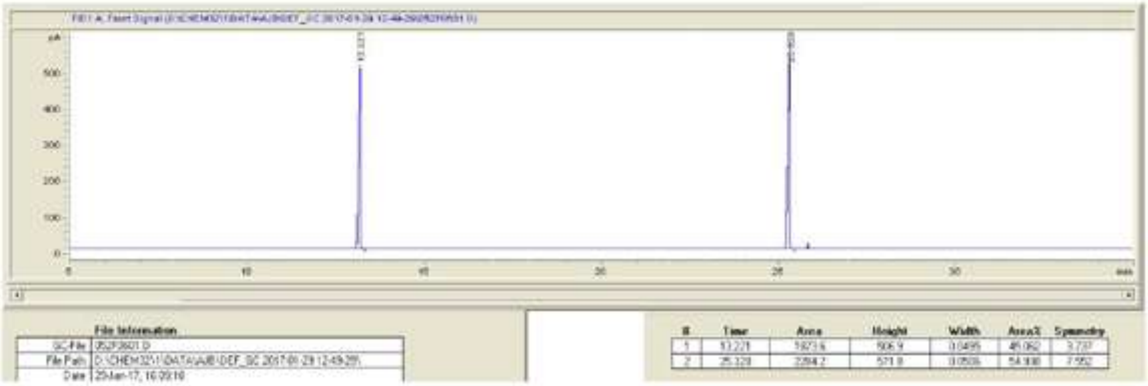


FID1 A, Front Signal (D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\052F0501.D)

File Information

GC File	052F0501.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 15:29:58

#	Time	Area	Height	Width	Area%	Symmetry
1	13.221	1930.8	505	0.0528	44.295	3.639
2	25.333	2430.3	604	0.0511	55.705	7.32



FID1 A, Front Signal (D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\052F0601.D)

File Information

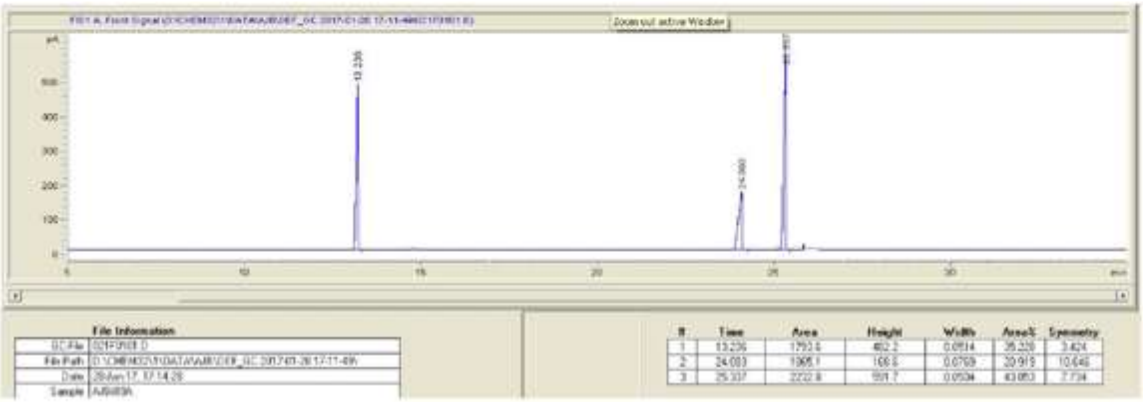
GC File	052F0601.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 16:09:16

#	Time	Area	Height	Width	Area%	Symmetry
1	13.221	1873.6	506.9	0.0495	45.062	3.737
2	25.320	2284.2	571.8	0.0505	54.938	7.552

1-methylnaphthalene (internal standard) at 13.2

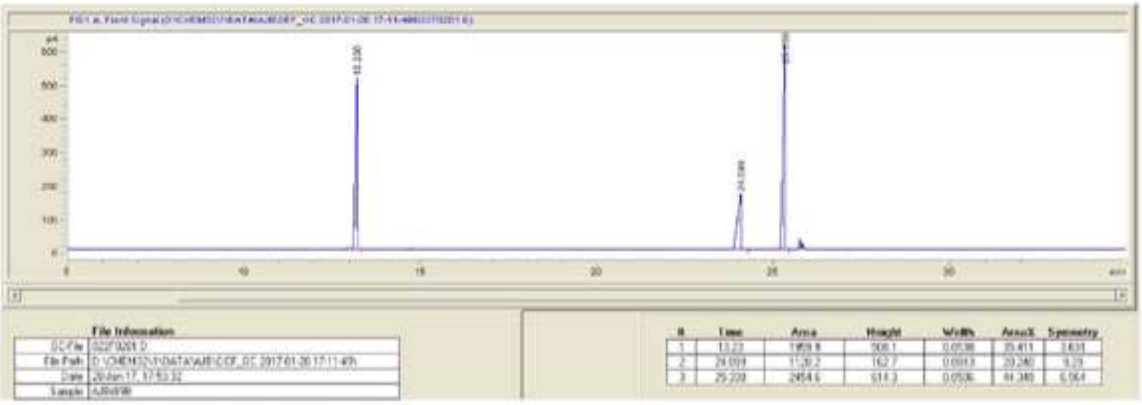
39a at 25.3

39a relative rate measurement



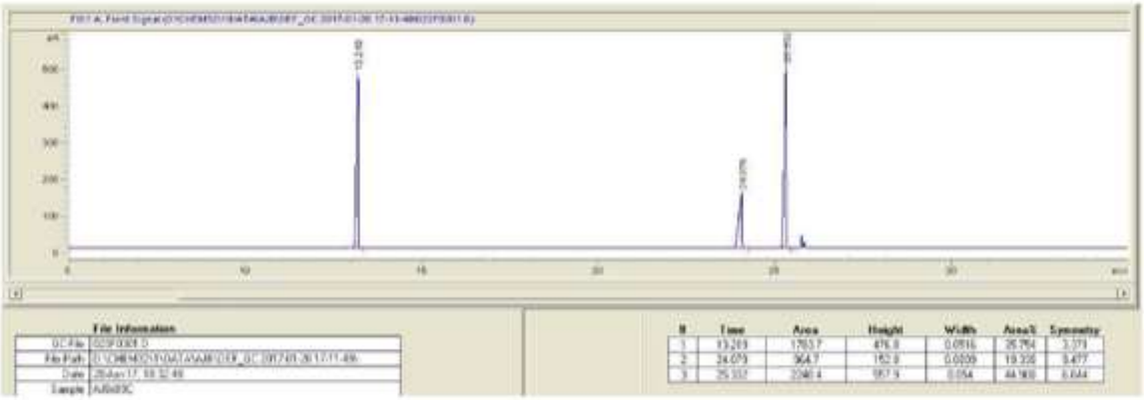
	File Information
GC File	021F0101.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-20 17-11-49\
Date	20-Jan-17, 17:14:28
Sample	AJB493A

#	Time	Area	Height	Width	Area%	Symmetry
1	13.236	1793.6	482.2	0.0514	35.228	3.424
2	24.083	1065.1	166.6	0.0769	20.919	10.646
3	25.337	2232.8	591.7	0.0504	43.853	7.734



	File Information
GC File	022F0201.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-20 17-11-49\
Date	20-Jan-17, 17:53:32
Sample	AJB493B

#	Time	Area	Height	Width	Area%	Symmetry
1	13.23	1959.8	508.1	0.0538	35.411	3.631
2	24.099	1120.2	162.7	0.0913	20.240	9.29
3	25.339	2454.6	614.3	0.0506	44.349	6.564



	File Information
GC File	023F0301.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-20 17-11-49\
Date	20-Jan-17, 18:32:46
Sample	AJB493C

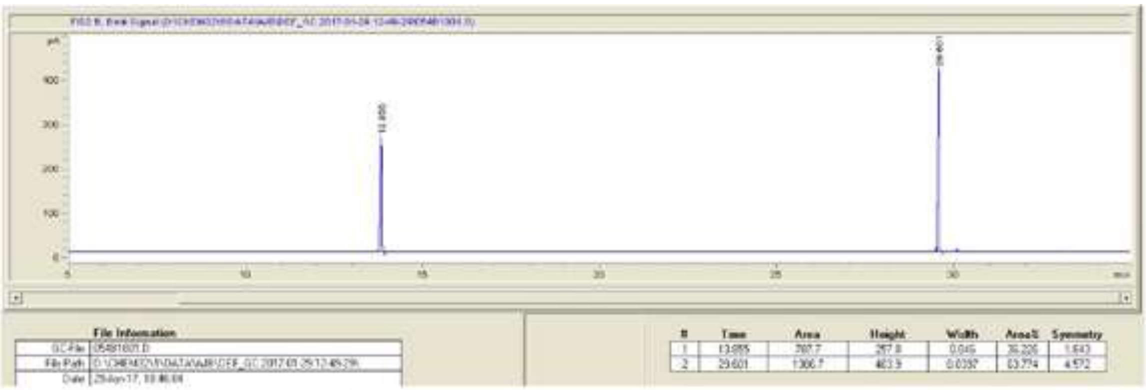
#	Time	Area	Height	Width	Area%	Symmetry
1	13.209	1783.7	476.8	0.0516	35.754	3.379
2	24.079	964.7	152.8	0.0839	19.336	9.477
3	25.332	2240.4	587.9	0.054	44.908	6.644

1-methylnaphthalene (internal standard) at 13.2

23a at 24.1

39a at 25.3

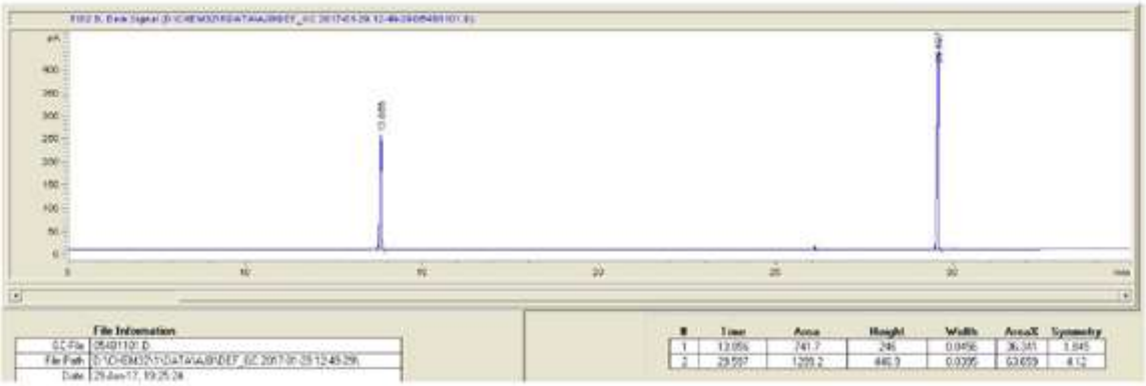
41a calibration



File Information

GC-File	05481001.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 18:46:08

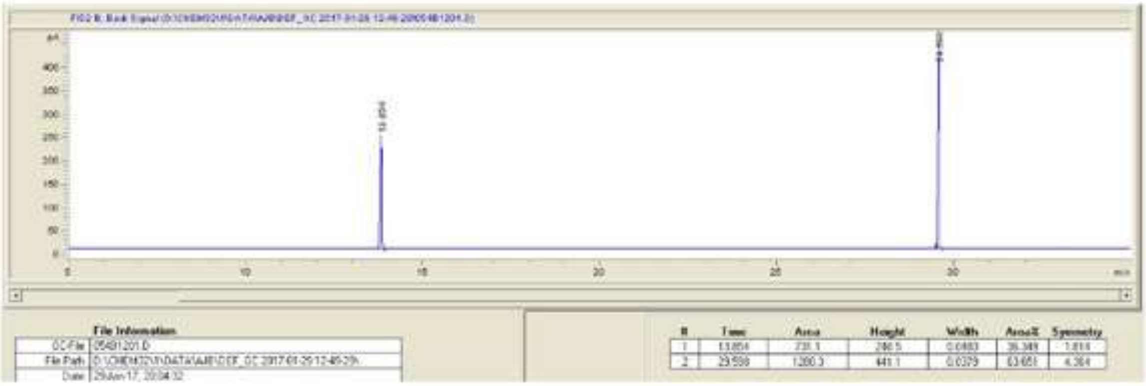
#	Time	Area	Height	Width	Area%	Symmetry
1	13.855	787.7	257.8	0.046	36.226	1.643
2	29.601	1386.7	463.9	0.0397	63.774	4.572



File Information

GC-File	05481101.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 19:25:28

#	Time	Area	Height	Width	Area%	Symmetry
1	13.856	741.7	246	0.0456	36.341	1.845
2	29.597	1299.2	446.3	0.0395	63.659	4.12



File Information

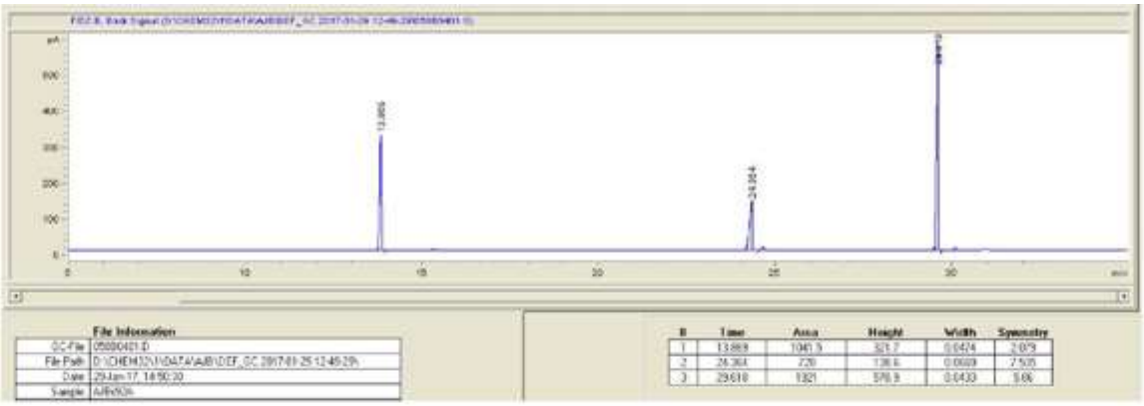
GC-File	05481201.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 20:04:32

#	Time	Area	Height	Width	Area%	Symmetry
1	13.854	731.1	240.5	0.0483	36.349	1.814
2	29.598	1280.3	441.1	0.0379	63.651	4.384

1-methylnaphthalene (internal standard) at 13.9

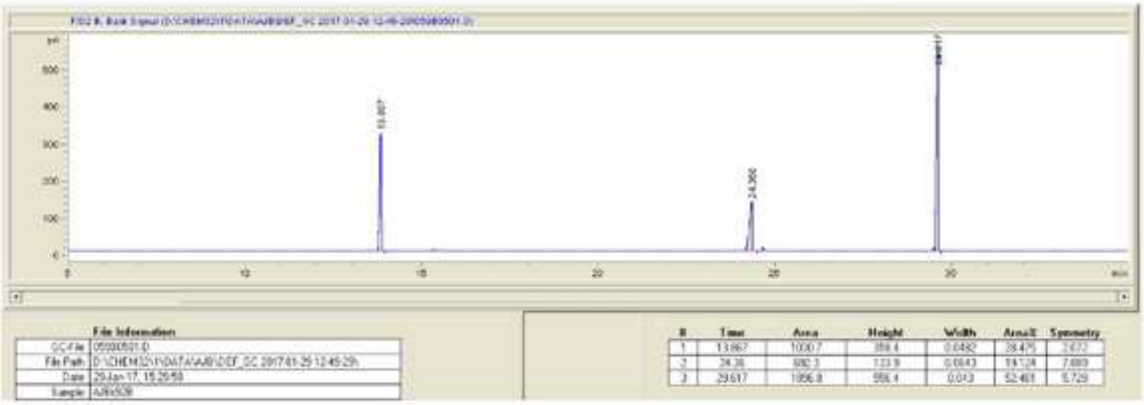
41a at 29.6

41a relative rate measurement



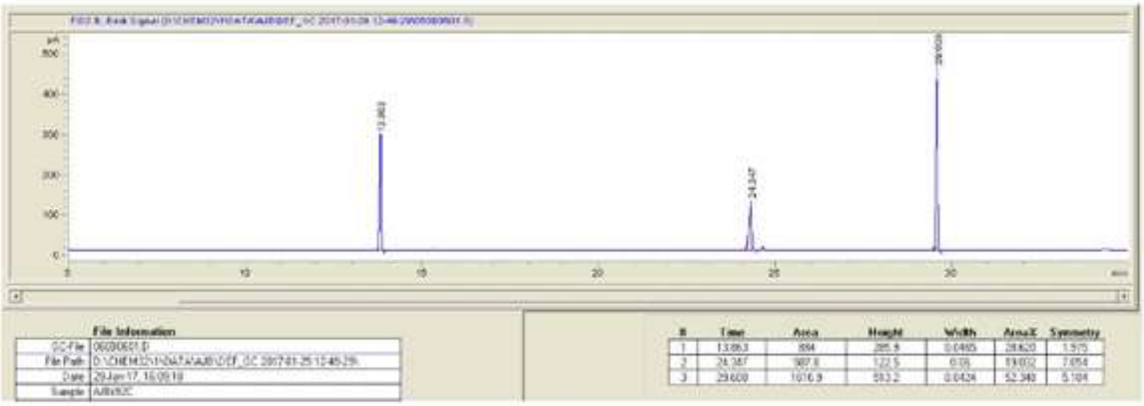
	File Information
GC-File	05000401.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-25 12-45-29\
Date	29-Jan-17, 14:50:30
Sample	AJB692A

#	Time	Area	Height	Width	Symmetry
1	13.869	1041.5	321.7	0.0474	2.079
2	24.364	720	136.6	0.0609	7.505
3	29.610	1321	576.9	0.0433	5.66



	File Information
GC-File	05000501.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-25 12-45-29\
Date	29-Jan-17, 15:29:50
Sample	AJB692B

#	Time	Area	Height	Width	Area%	Symmetry
1	13.867	1030.7	358.4	0.0482	28.475	2.672
2	24.36	692.3	133.9	0.0843	19.124	7.693
3	29.617	1896.8	556.4	0.043	52.401	5.729



	File Information
GC-File	06000601.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-25 12-45-29\
Date	29-Jan-17, 16:09:10
Sample	AJB692C

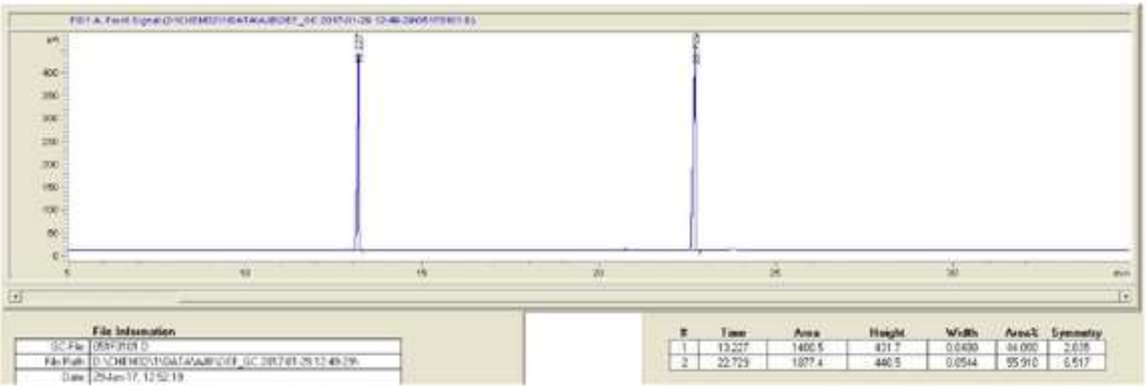
#	Time	Area	Height	Width	Area%	Symmetry
1	13.863	884	285.8	0.0465	28.620	1.975
2	24.347	587.8	122.5	0.05	19.032	7.054
3	29.600	1616.9	583.2	0.0424	52.348	5.104

1-methylnaphthalene (internal standard) at 13.9

23a at 24.3

41a at 29.6

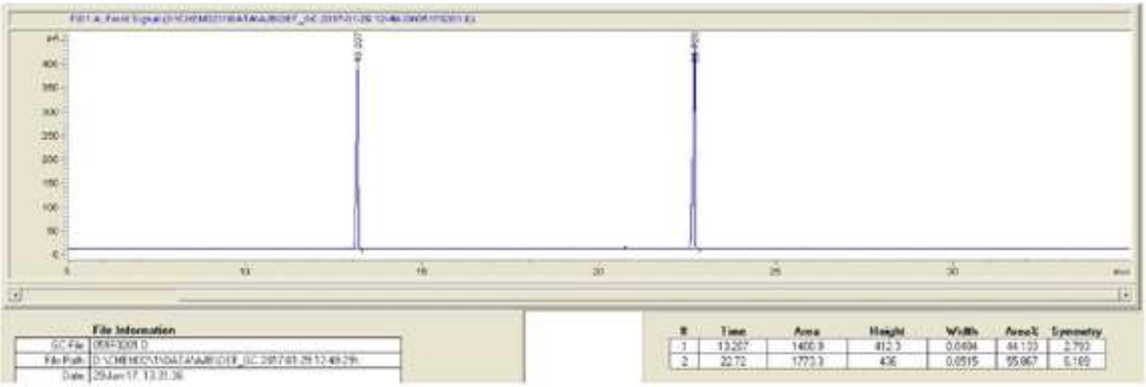
42a calibration



File Information

GC File	059F0101.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 12:52:19

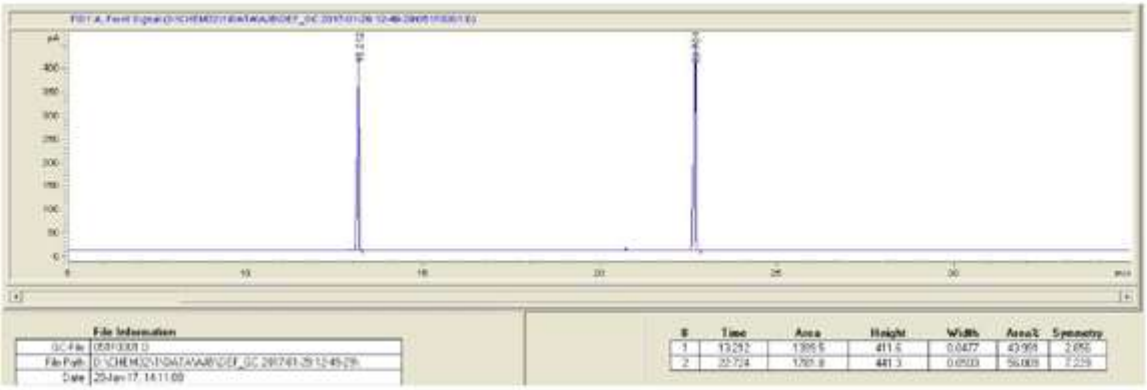
#	Time	Area	Height	Width	Area%	Symmetry
1	13.227	1400.5	431.7	0.0480	44.090	2.035
2	22.729	1777.4	440.5	0.0544	55.910	6.517



File Information

GC File	059F0201.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 13:31:36

#	Time	Area	Height	Width	Area%	Symmetry
1	13.207	1400.9	412.3	0.0494	44.133	2.793
2	22.72	1773.3	436	0.0515	55.867	5.169



File Information

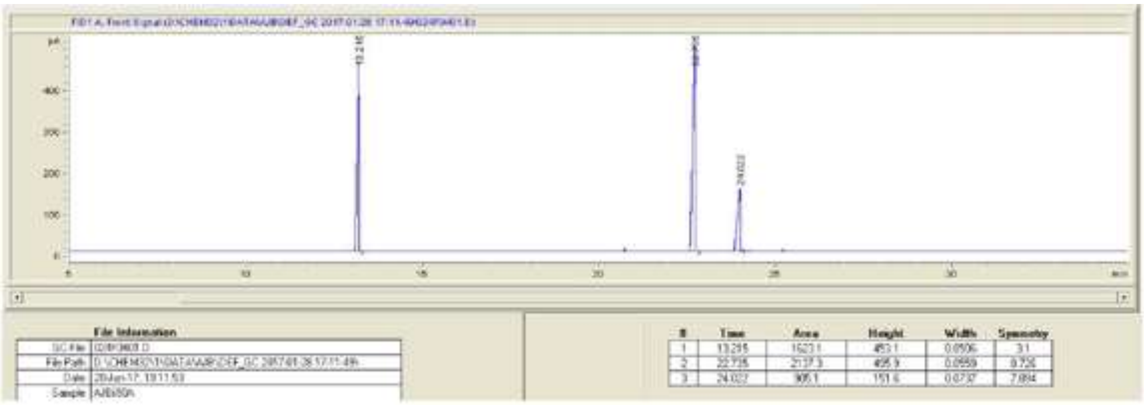
GC File	059F0301.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 14:11:08

#	Time	Area	Height	Width	Area%	Symmetry
1	13.212	1385.5	411.6	0.0477	43.958	2.656
2	22.724	1766.8	441.3	0.0503	56.042	7.229

1-methylnaphthalene (internal standard) at 13.2

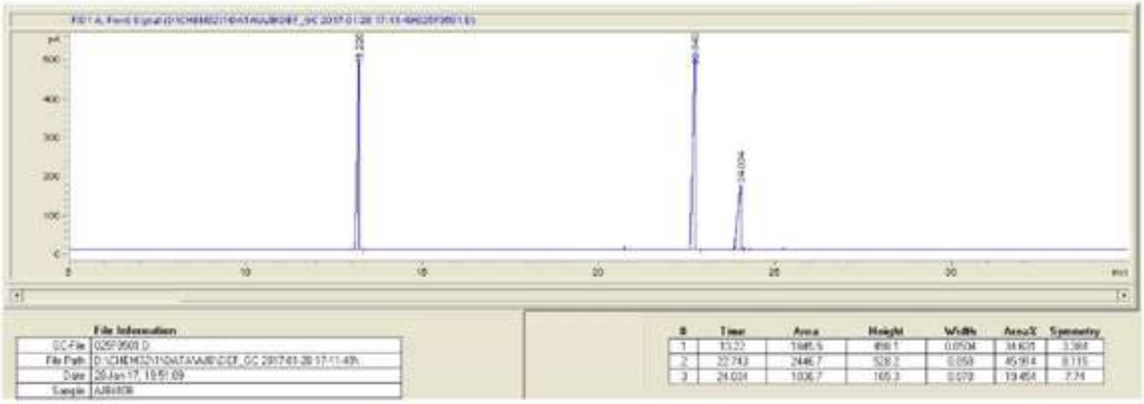
42a at 22.7

42a relative rate measurement



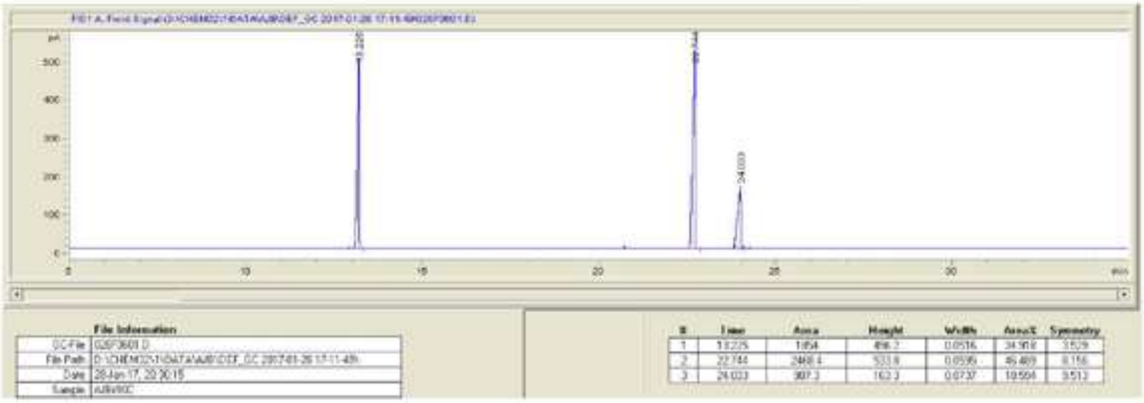
	File Information
GC File	025F0401.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-28 17-11-49\
Date	28-Jan-17, 19:11:53
Sample	AJB450A

#	Time	Area	Height	Width	Symmetry
1	13.215	1623.1	453.1	0.0506	3.1
2	22.735	2137.3	495.9	0.0559	0.726
3	24.027	905.1	151.6	0.0737	7.894



	File Information
GC File	025F0501.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-28 17-11-49\
Date	28-Jan-17, 19:51:09
Sample	AJB450B

#	Time	Area	Height	Width	Area%	Symmetry
1	13.22	1845.5	498.1	0.0504	34.631	3.388
2	22.743	2446.7	528.2	0.058	45.914	0.115
3	24.034	1036.7	165.3	0.079	19.454	7.74



	File Information
GC File	025F0601.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-28 17-11-49\
Date	28-Jan-17, 20:30:15
Sample	AJB450C

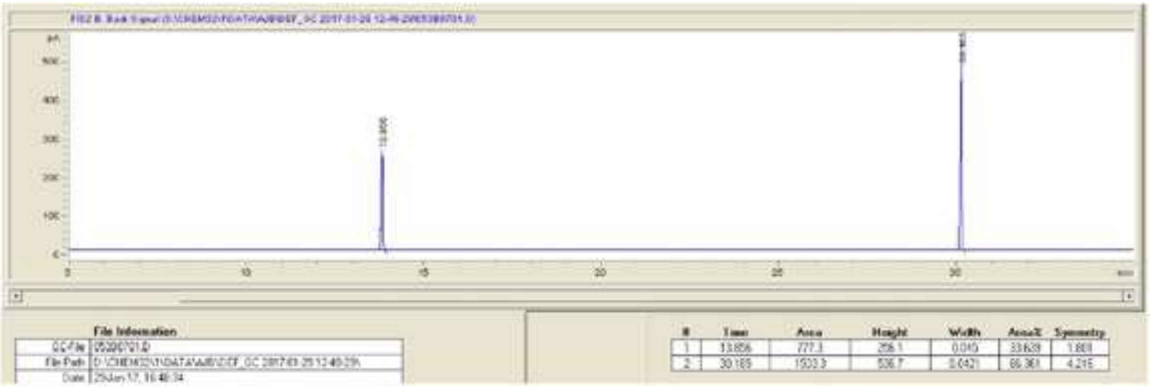
#	Time	Area	Height	Width	Area%	Symmetry
1	13.225	1854	496.2	0.0516	34.918	3.529
2	22.744	2448.4	533.8	0.0595	45.489	0.156
3	24.033	987.3	162.3	0.0737	19.594	3.513

1-methylnaphthalene (internal standard) at 13.4

41a at 22.7

23a at 24.0

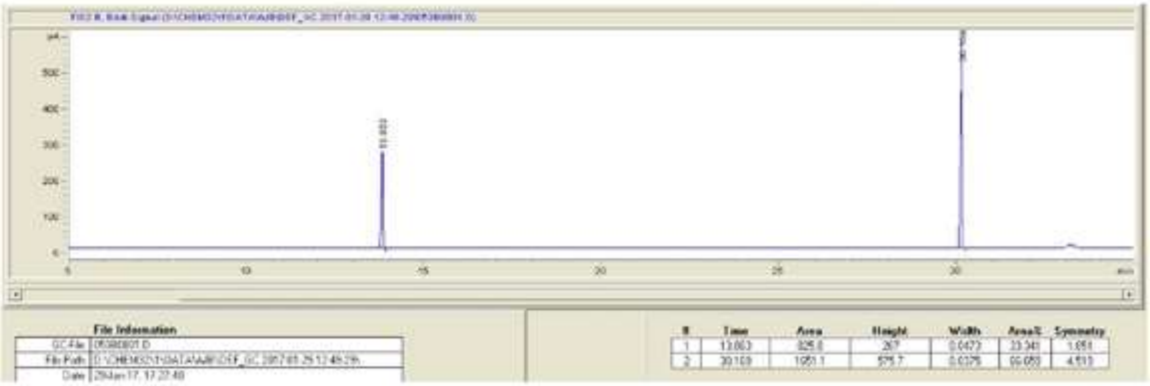
43a calibration



File Information

GC-File	05280701.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 16:48:34

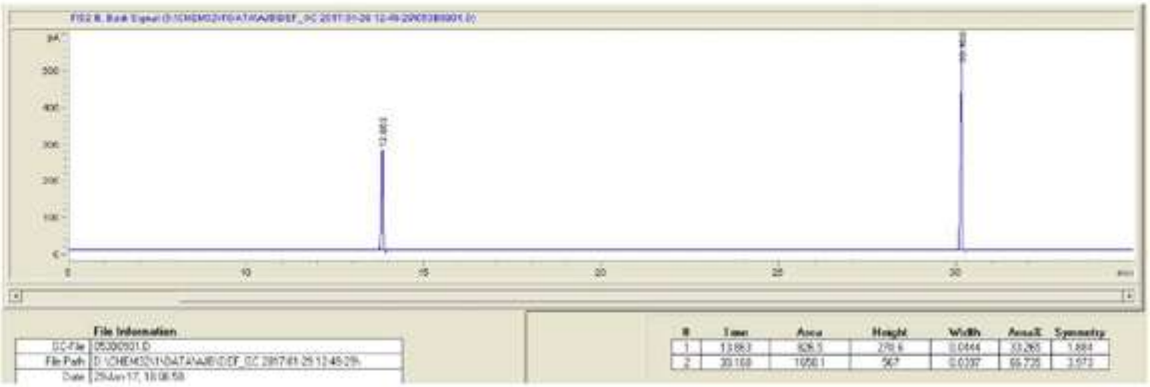
#	Time	Area	Height	Width	Area%	Symmetry
1	13.856	777.3	256.1	0.045	33.639	1.801
2	30.185	1533.3	536.7	0.0421	66.361	4.215



File Information

GC-File	05280801.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 17:27:48

#	Time	Area	Height	Width	Area%	Symmetry
1	13.863	825.8	267	0.0473	33.341	1.851
2	30.169	1651.1	575.7	0.0375	66.659	4.510



File Information

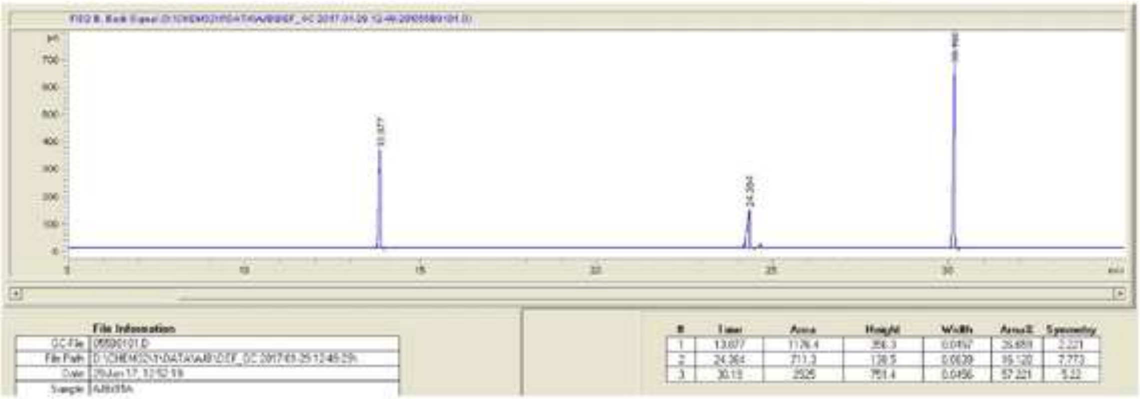
GC-File	05280901.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 18:06:58

#	Time	Area	Height	Width	Area%	Symmetry
1	13.863	826.5	278.6	0.0444	33.265	1.884
2	30.169	1658.1	567	0.0397	66.735	3.573

1-methylnaphthalene (internal standard) at 13.9

43a at 30.2

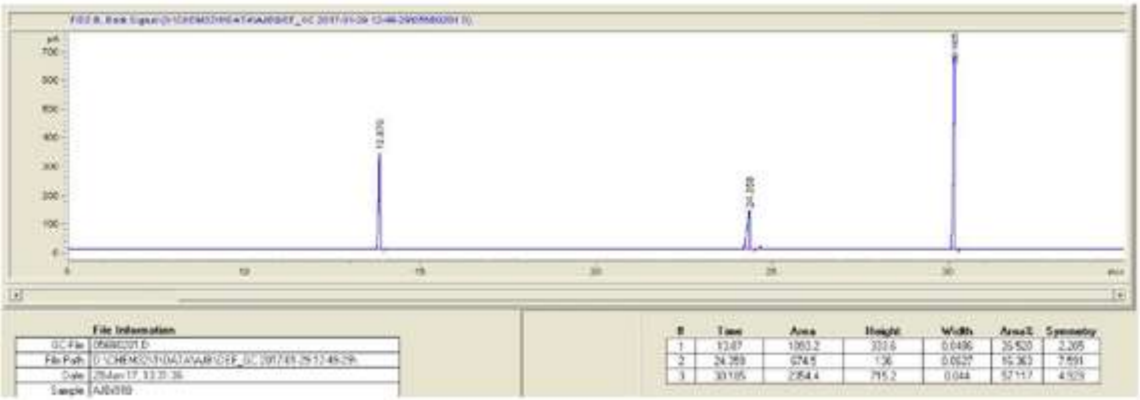
43a relative rate measurement



File Information

GC File	05580101.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 12:52:18
Sample	AJBii59A

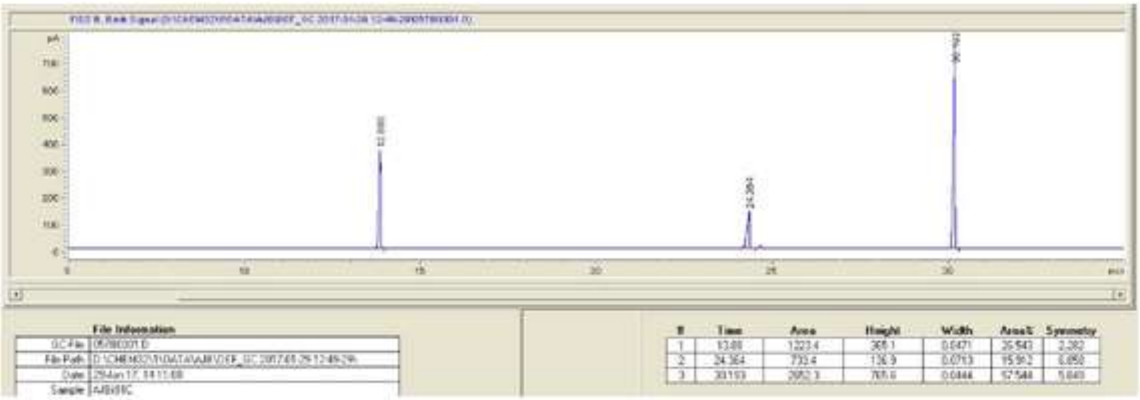
#	Time	Area	Height	Width	Area%	Symmetry
1	13.877	1176.4	356.3	0.0497	26.659	2.221
2	24.364	711.3	138.5	0.0639	16.120	7.773
3	30.15	2525	751.4	0.0496	57.221	5.22



File Information

GC File	05580201.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 13:33:36
Sample	AJBii59B

#	Time	Area	Height	Width	Area%	Symmetry
1	13.87	1093.2	333.6	0.0486	26.520	2.205
2	24.359	674.5	136	0.0627	16.363	7.591
3	30.185	2354.4	715.2	0.044	57.117	4.929



File Information

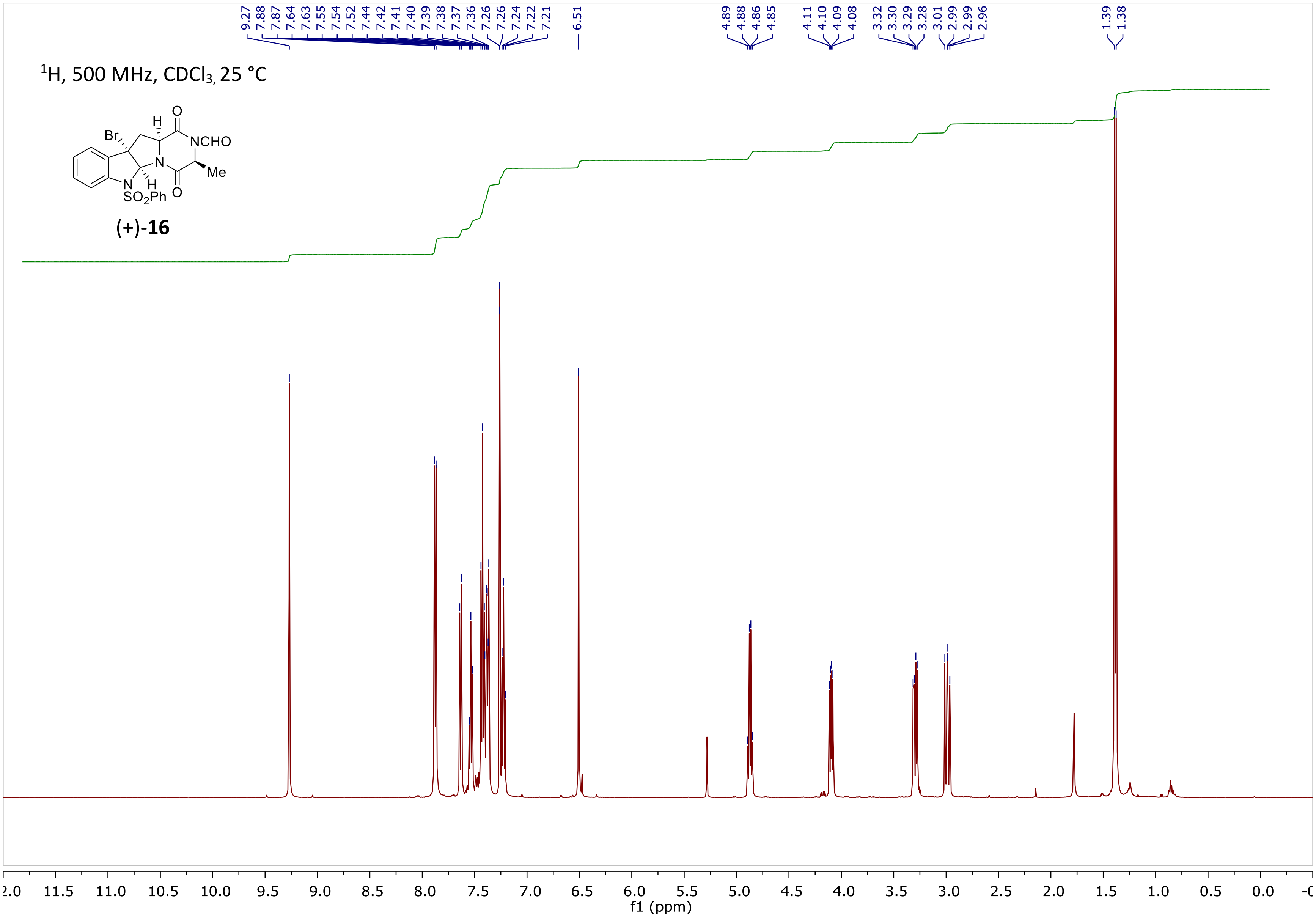
GC File	05780301.D
File Path	D:\CHEM32\1\DATA\AJB\DEF_GC 2017-01-29 12-49-29\
Date	29-Jan-17, 14:11:08
Sample	AJBii59C

#	Time	Area	Height	Width	Area%	Symmetry
1	13.88	1223.4	365.1	0.0471	26.543	2.282
2	24.364	733.4	136.9	0.0713	15.912	6.850
3	30.153	2652.3	765.6	0.0444	57.544	5.640

1-methylnaphthalene (internal standard) at 13.9

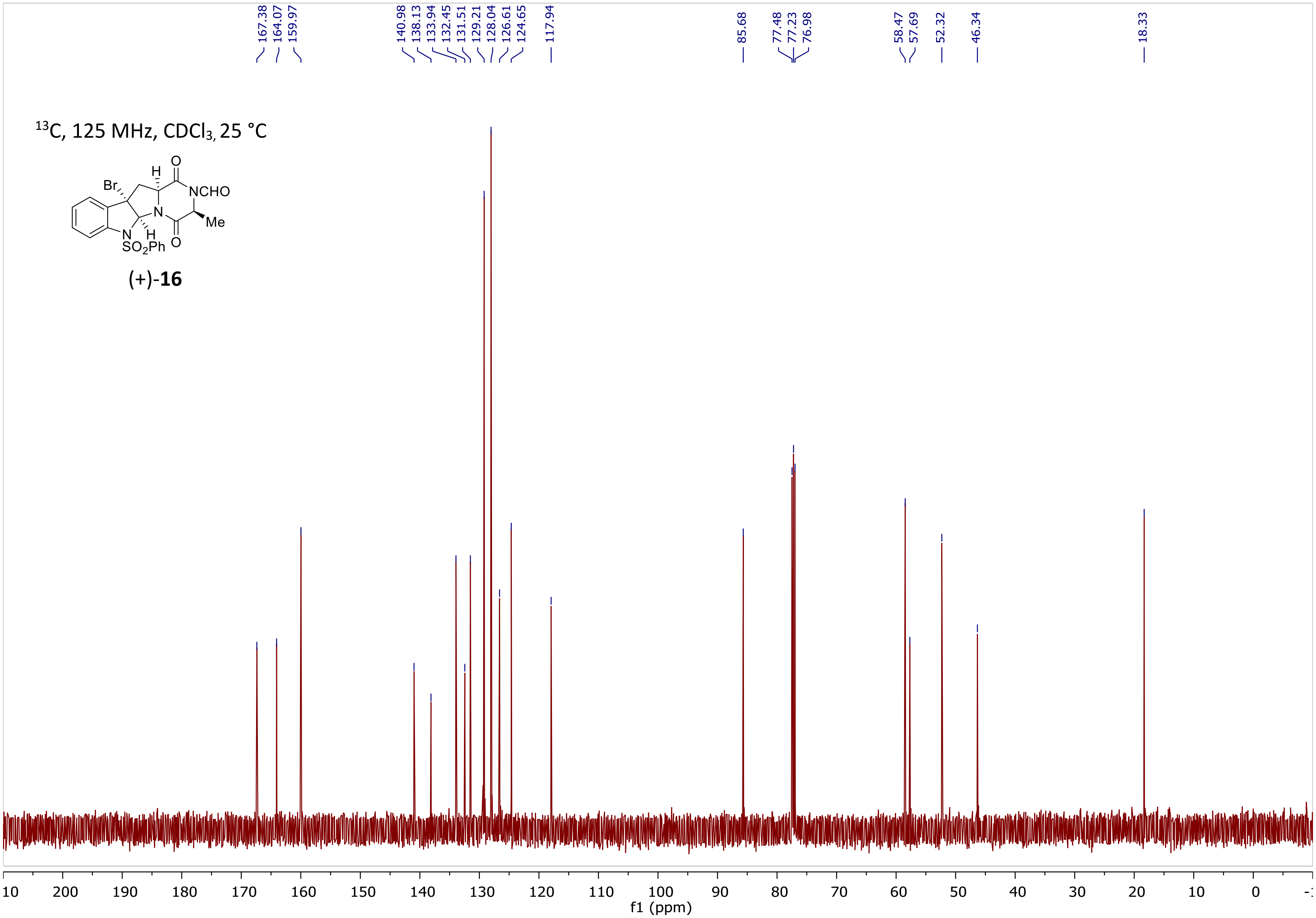
23a at 24.4

43a at 30.2

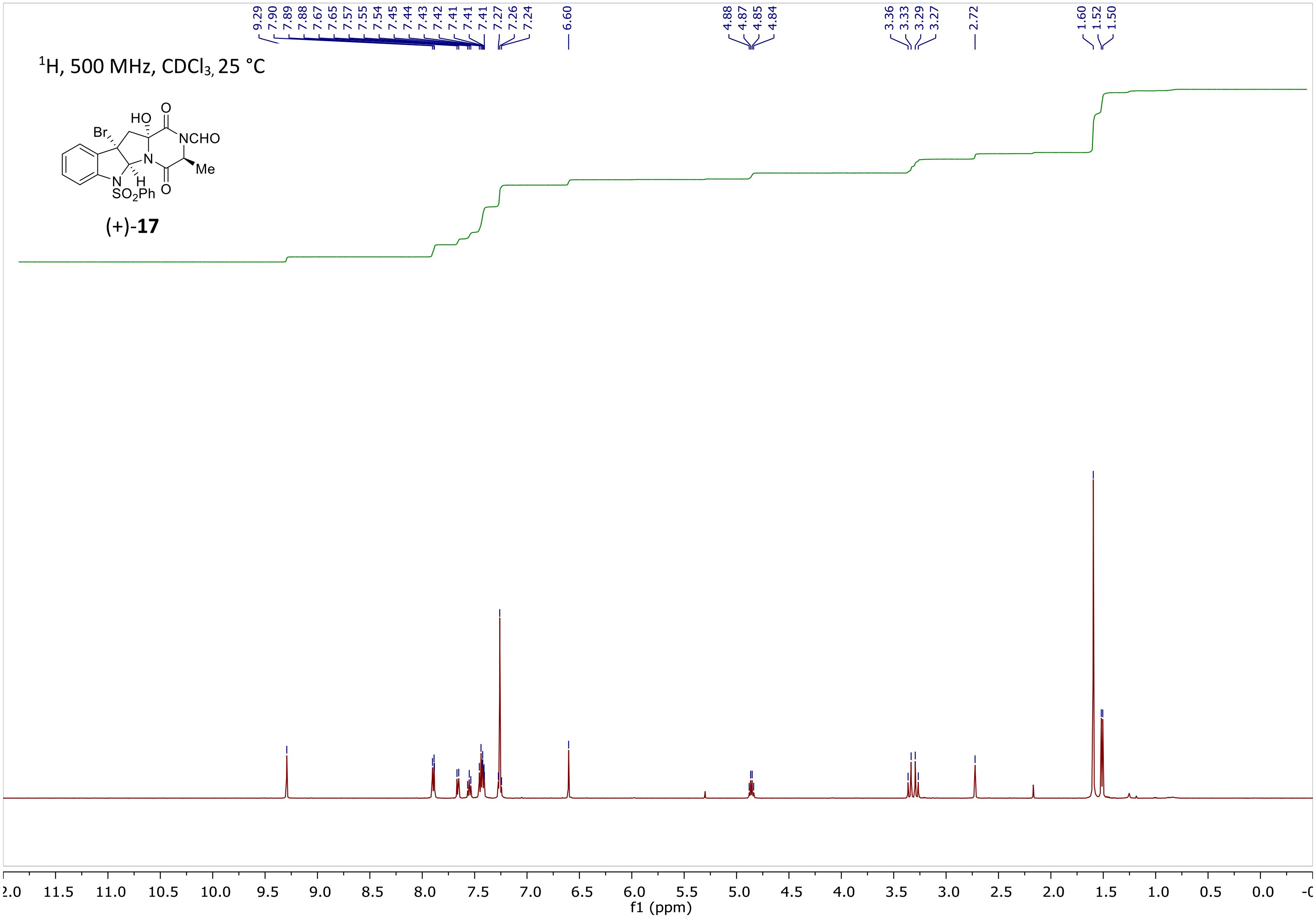


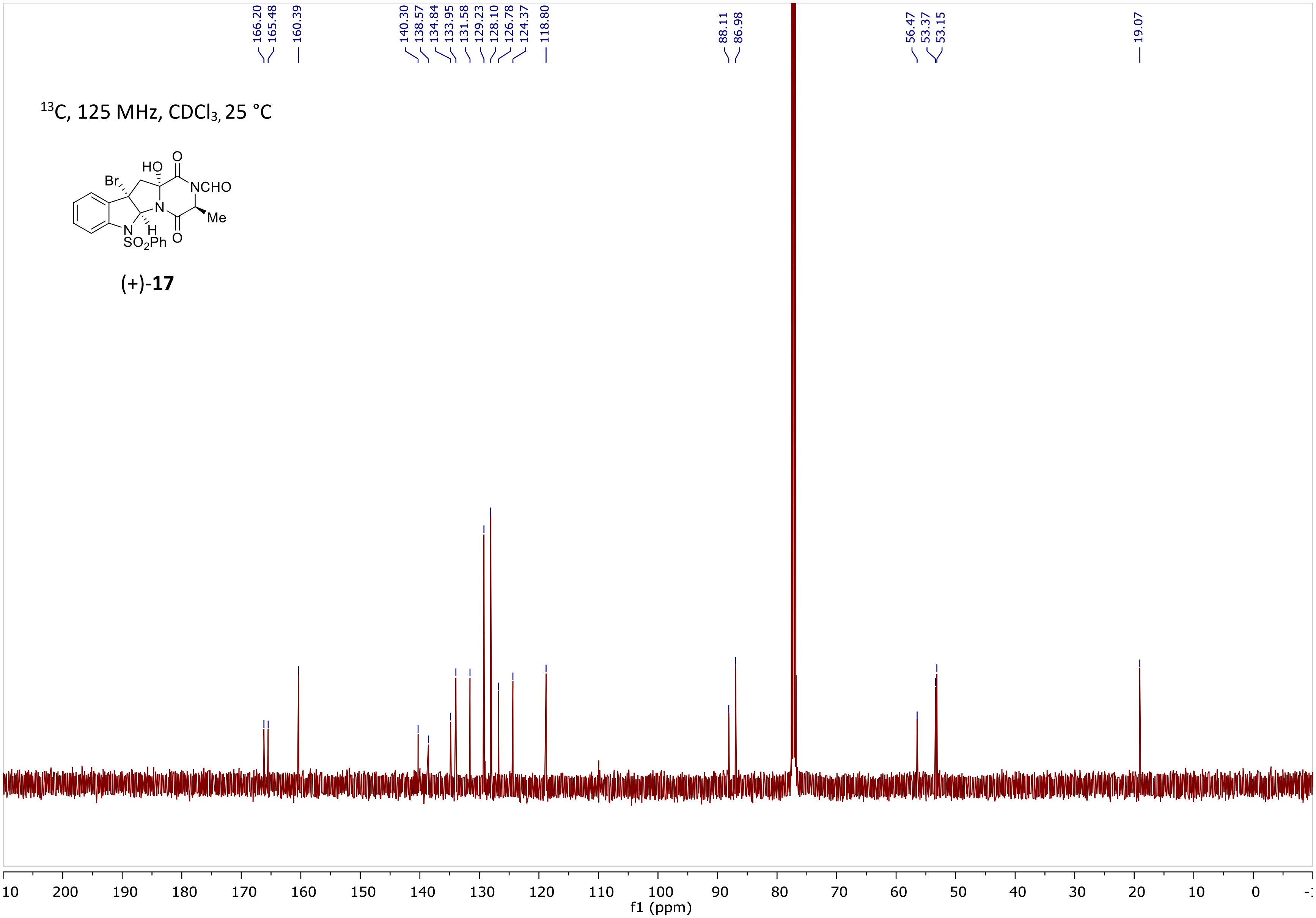
^{1}H, 500 MHz, $CDCl_3$, 25 °C

(+)-**16**

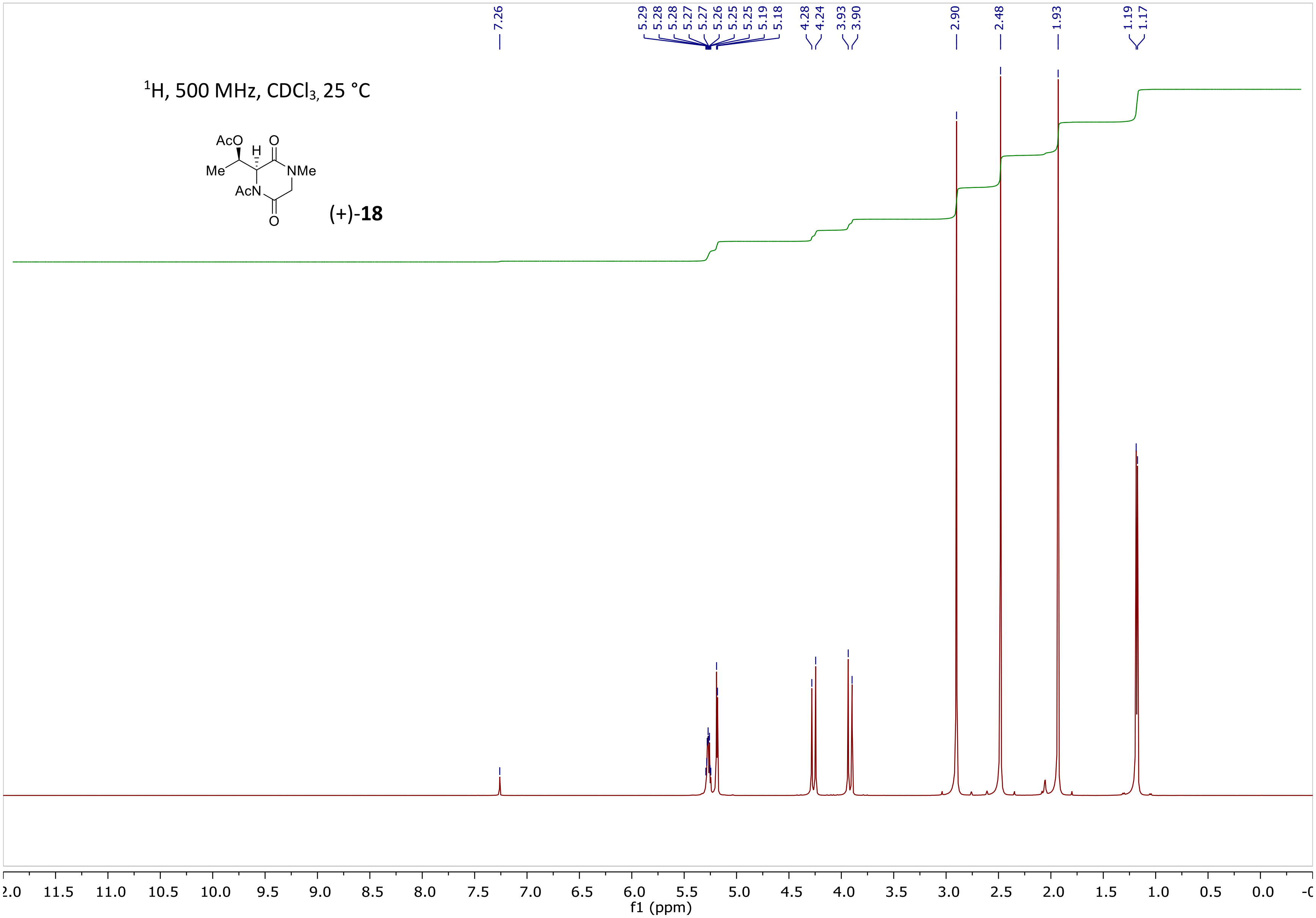

167.38
164.07
159.97
140.98
138.13
133.94
132.45
131.51
129.21
128.04
126.61
124.65
117.94
85.68
77.48
77.23
76.98
58.47
57.69
52.32
46.34
18.33
^{13}C, 125 MHz, CDCl$_3$, 25 °C
Br
H
O
NCHO
N
Me
N
H
SO$_2$Ph
O
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)

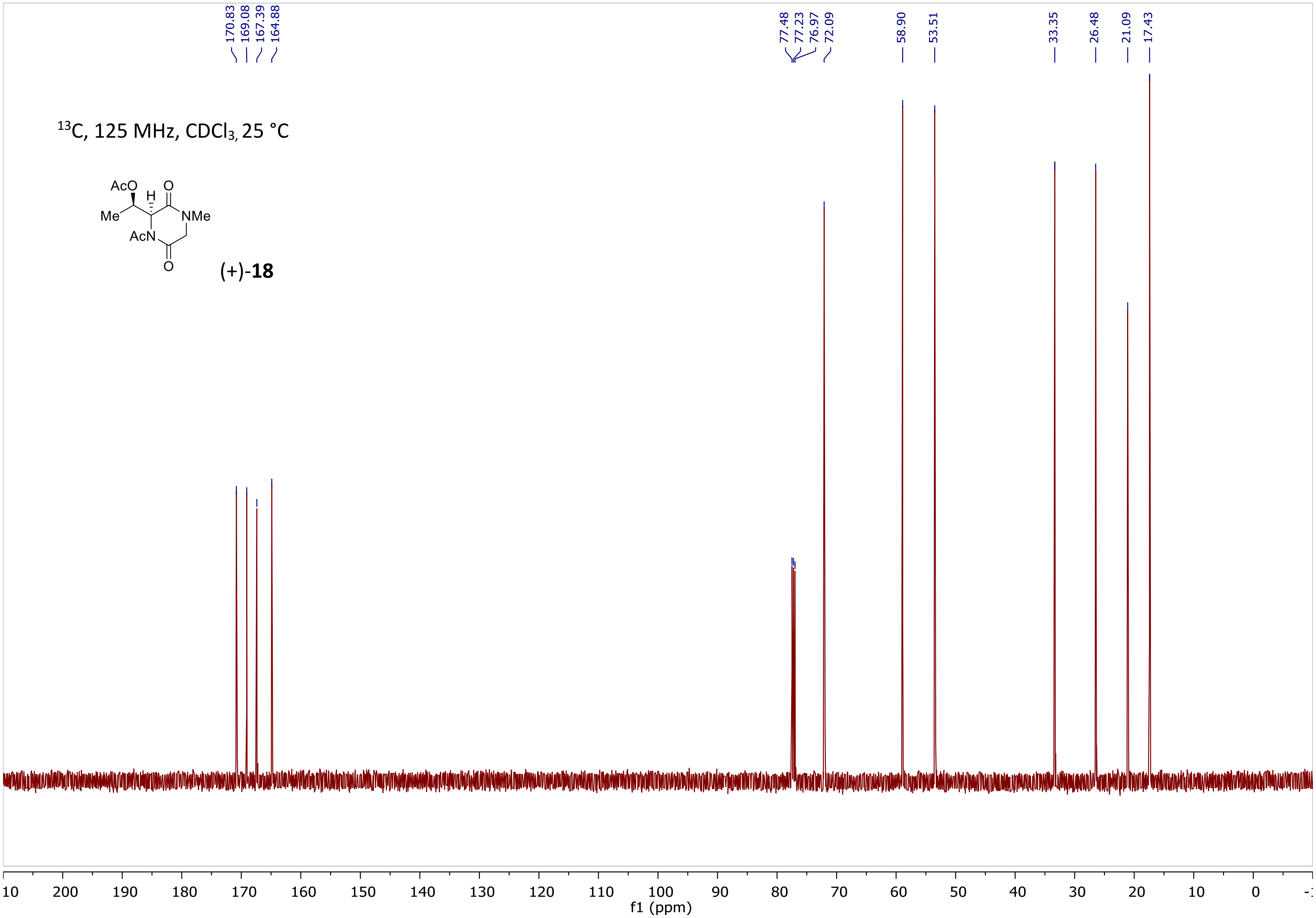
(+)-**16**

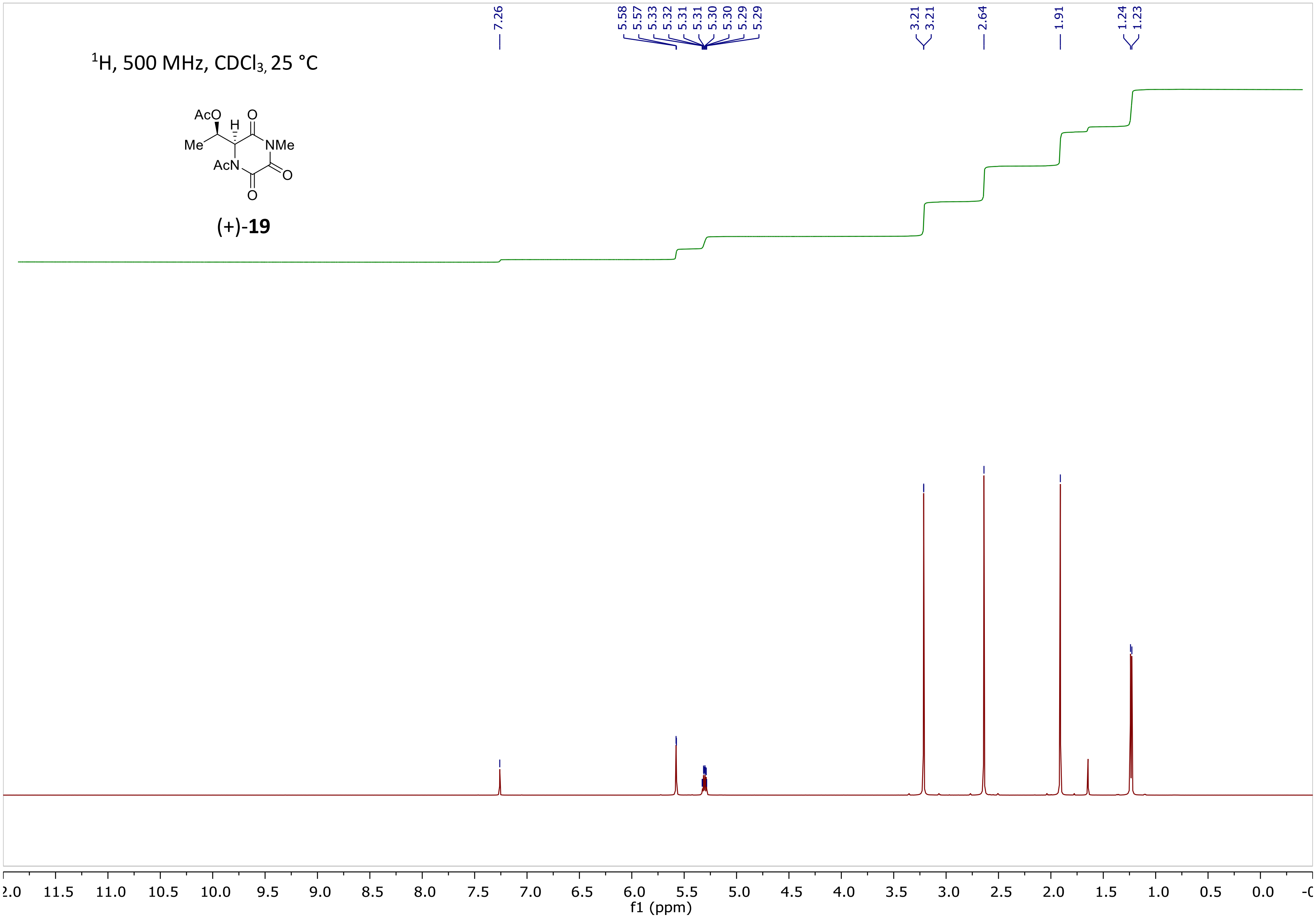

^{1}H, 500 MHz, CDCl$_3$, 25 °C
(+)-**17**
Br
HO
O
NCHO
N
Me
N
H
SO$_2$Ph
O
9.29
7.90
7.89
7.88
7.67
7.65
7.57
7.55
7.54
7.45
7.44
7.43
7.42
7.41
7.41
7.41
7.27
7.26
7.24
6.60
4.88
4.87
4.85
4.84
3.36
3.33
3.29
3.27
2.72
1.60
1.52
1.50
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-
f1 (ppm)

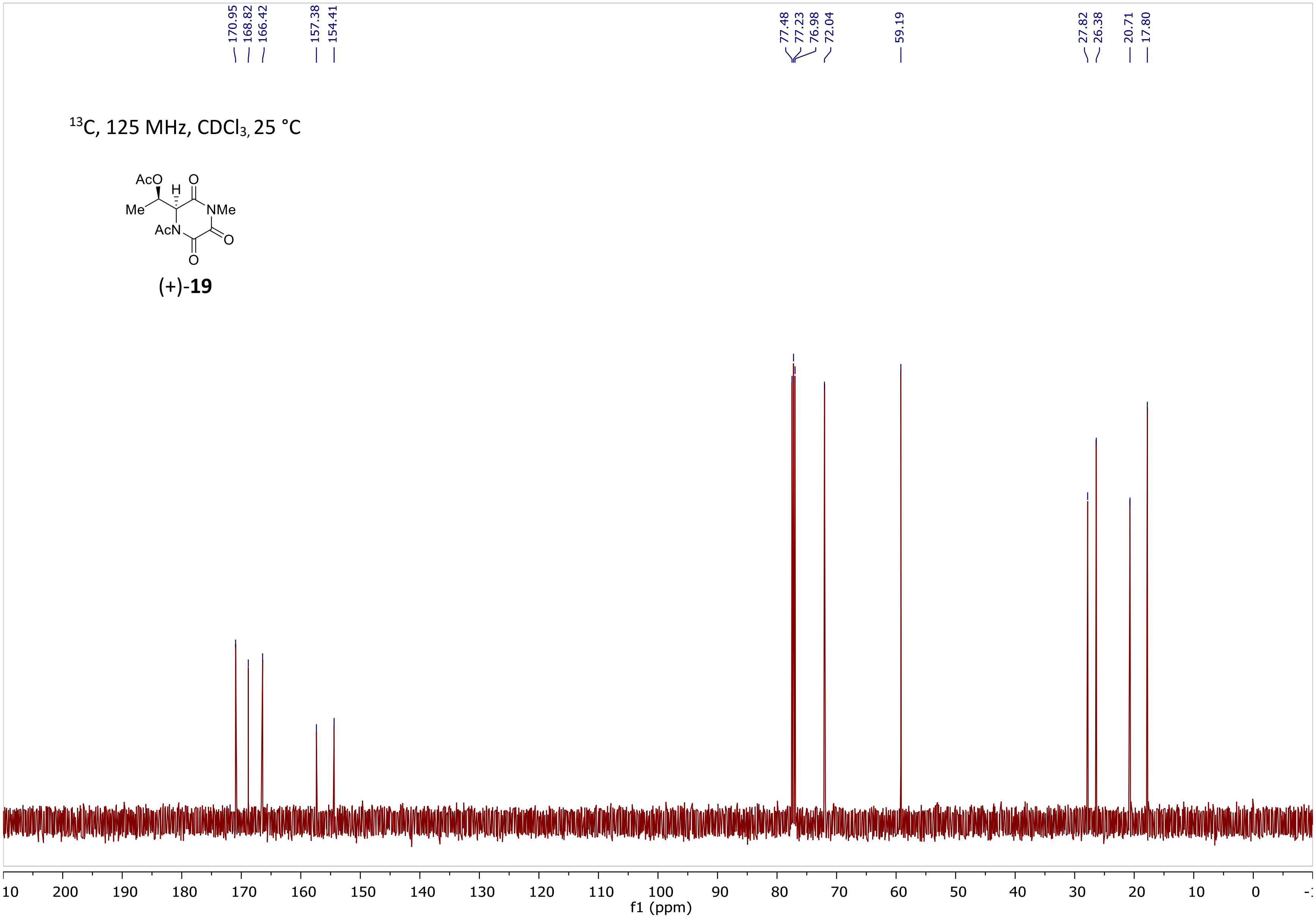

166.20
165.48
160.39
140.30
138.57
134.84
133.95
131.58
129.23
128.10
126.78
124.37
118.80
88.11
86.98
56.47
53.37
53.15
19.07
^{13}C, 125 MHz, CDCl$_3$, 25 °C
Br
HO
O
NCHO
Me
N
H
N
SO$_2$Ph
O
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)

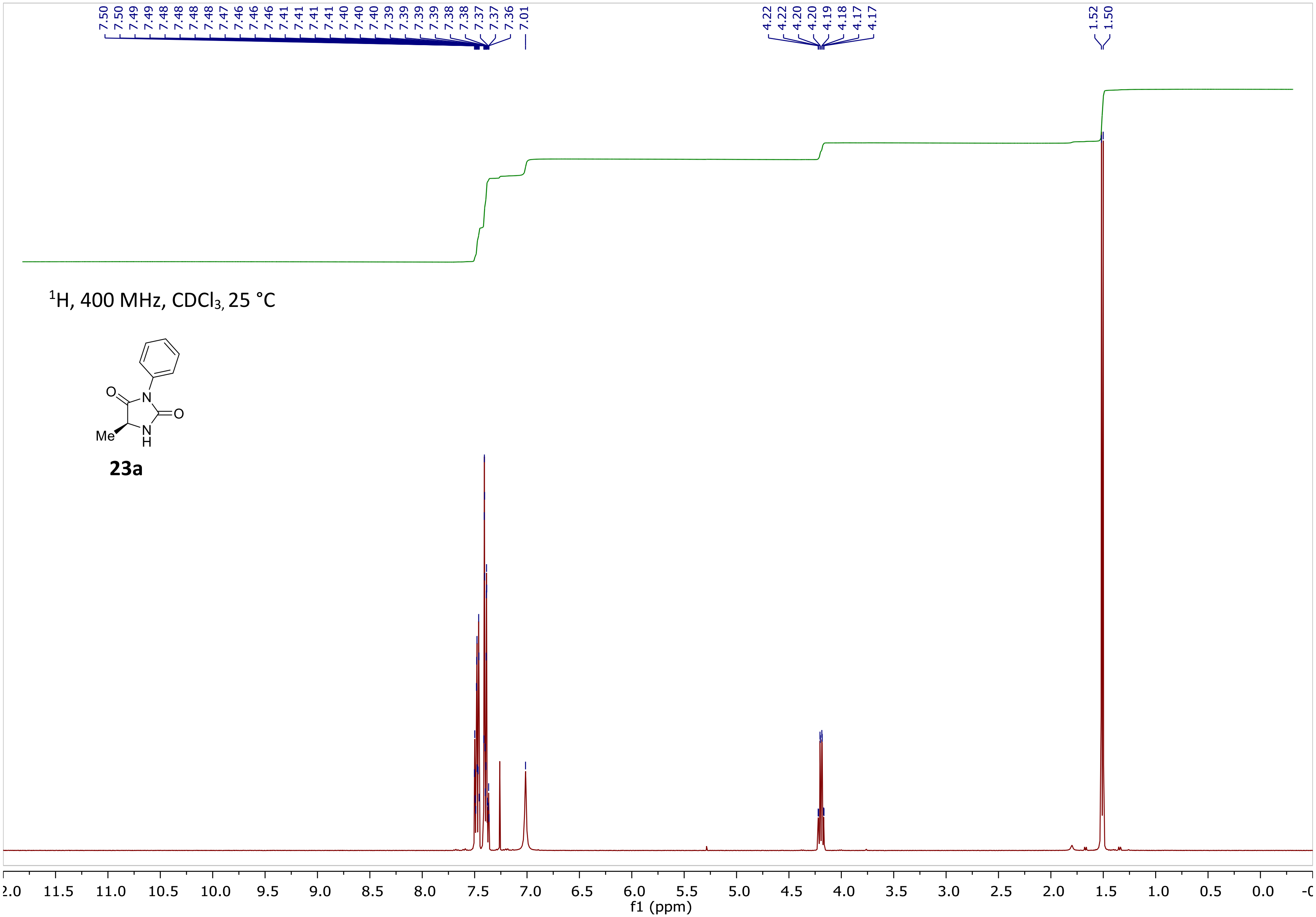
(+)-**17**


7.26
5.29
5.28
5.28
5.27
5.27
5.26
5.25
5.25
5.19
5.18
4.28
4.24
3.93
3.90
2.90
2.48
1.93
1.19
1.17
¹H, 500 MHz, CDCl₃, 25 °C
AcO
H
O
Me
NMe
AcN
O
(+)-18
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


170.83
169.08
167.39
164.88
77.48
77.23
76.97
72.09
58.90
53.51
33.35
26.48
21.09
17.43
^{13}C, 125 MHz, CDCl$_3$, 25 °C
AcO
H
O
Me
NMe
AcN
O
(+)-**18**
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

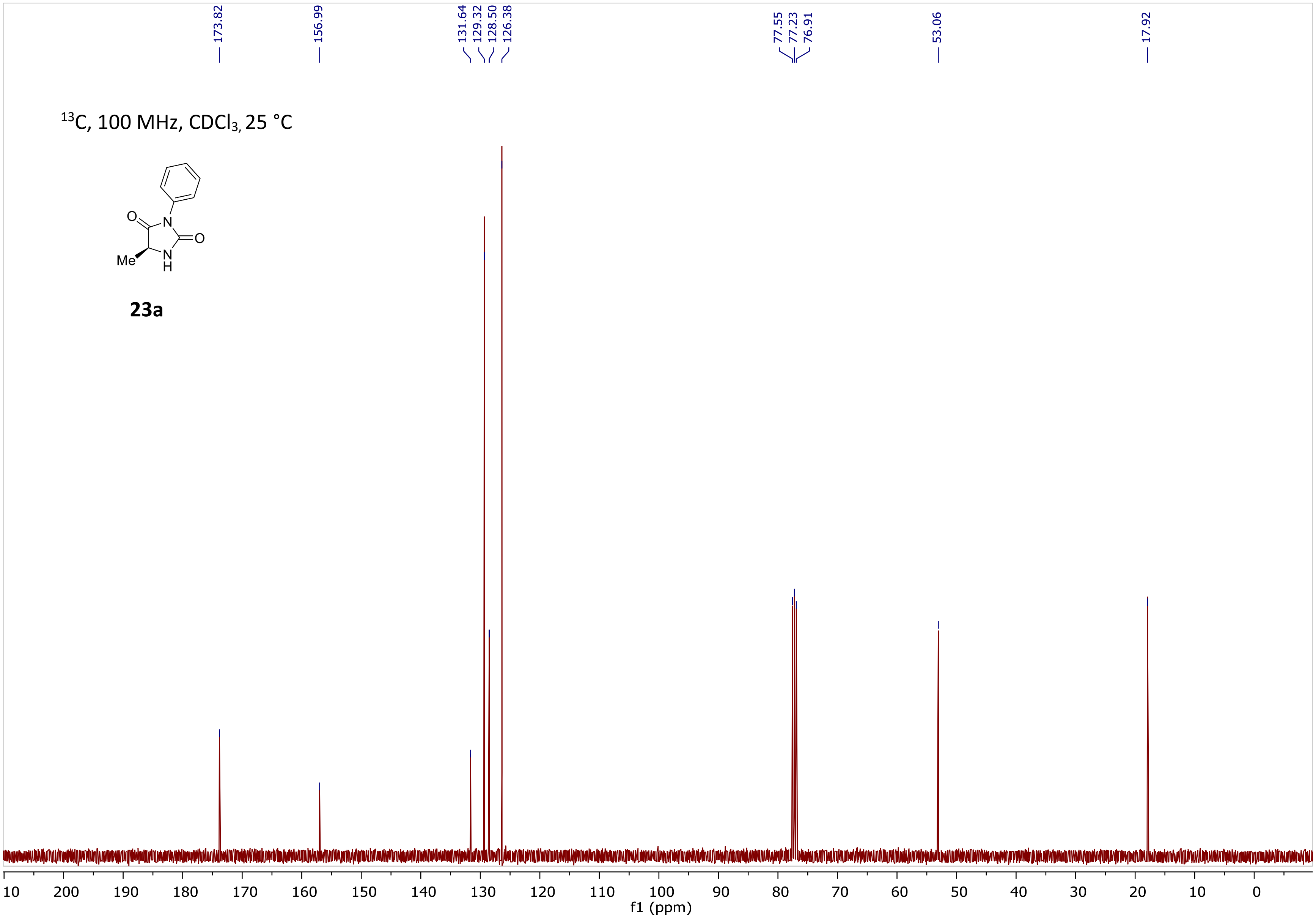

^{1}H, 500 MHz, CDCl$_3$, 25 °C
AcO
H
O
Me
NMe
AcN
O
O
(+)-19
7.26
5.58
5.57
5.33
5.32
5.31
5.31
5.30
5.30
5.29
5.29
3.21
3.21
2.64
1.91
1.24
1.23
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

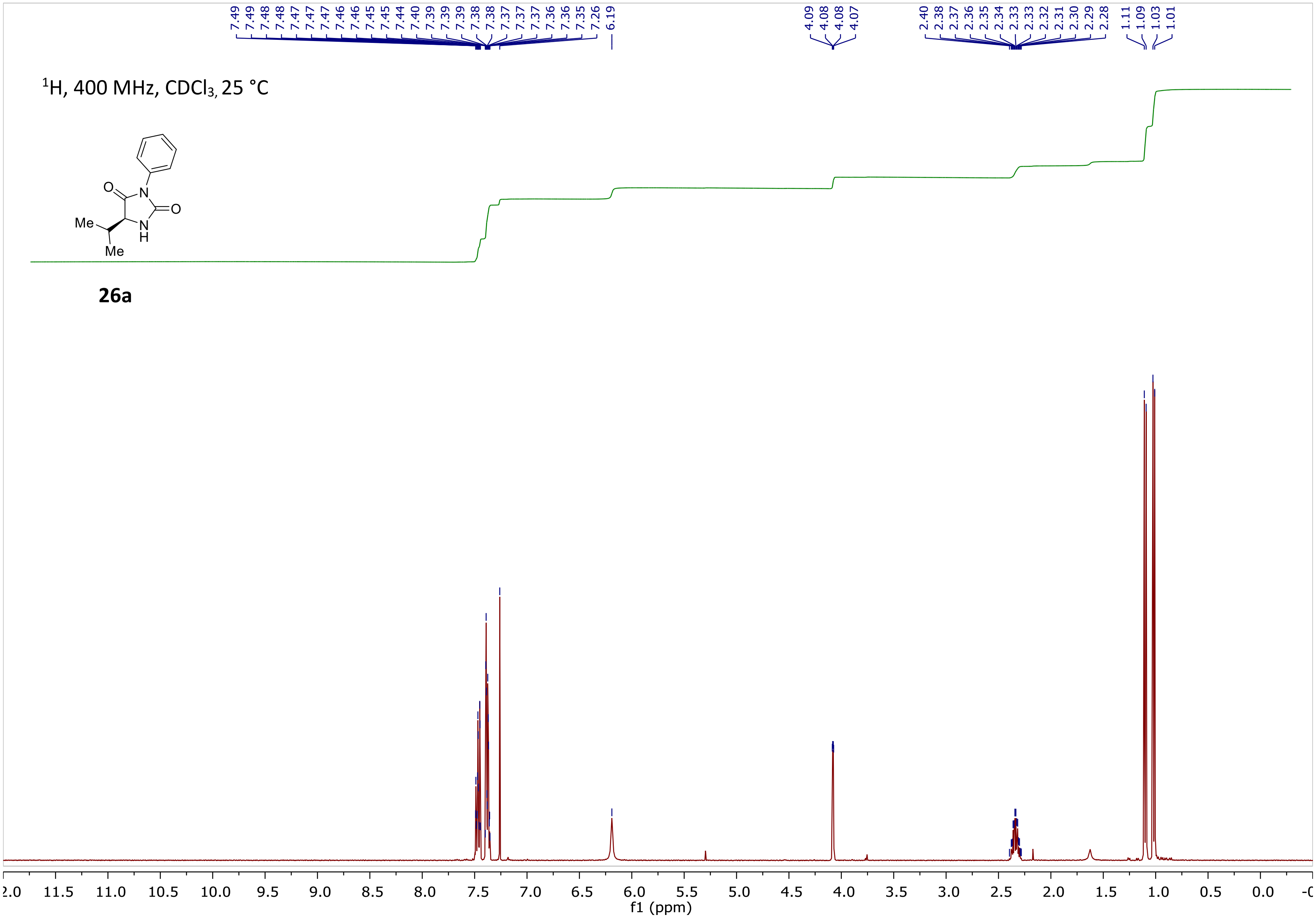

170.95
168.82
166.42
157.38
154.41
77.48
77.23
76.98
72.04
59.19
27.82
26.38
20.71
17.80
^{13}C, 125 MHz, $CDCl_3$, 25 °C
AcO
H
O
Me
NMe
AcN
O
O
(+)-**19**
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



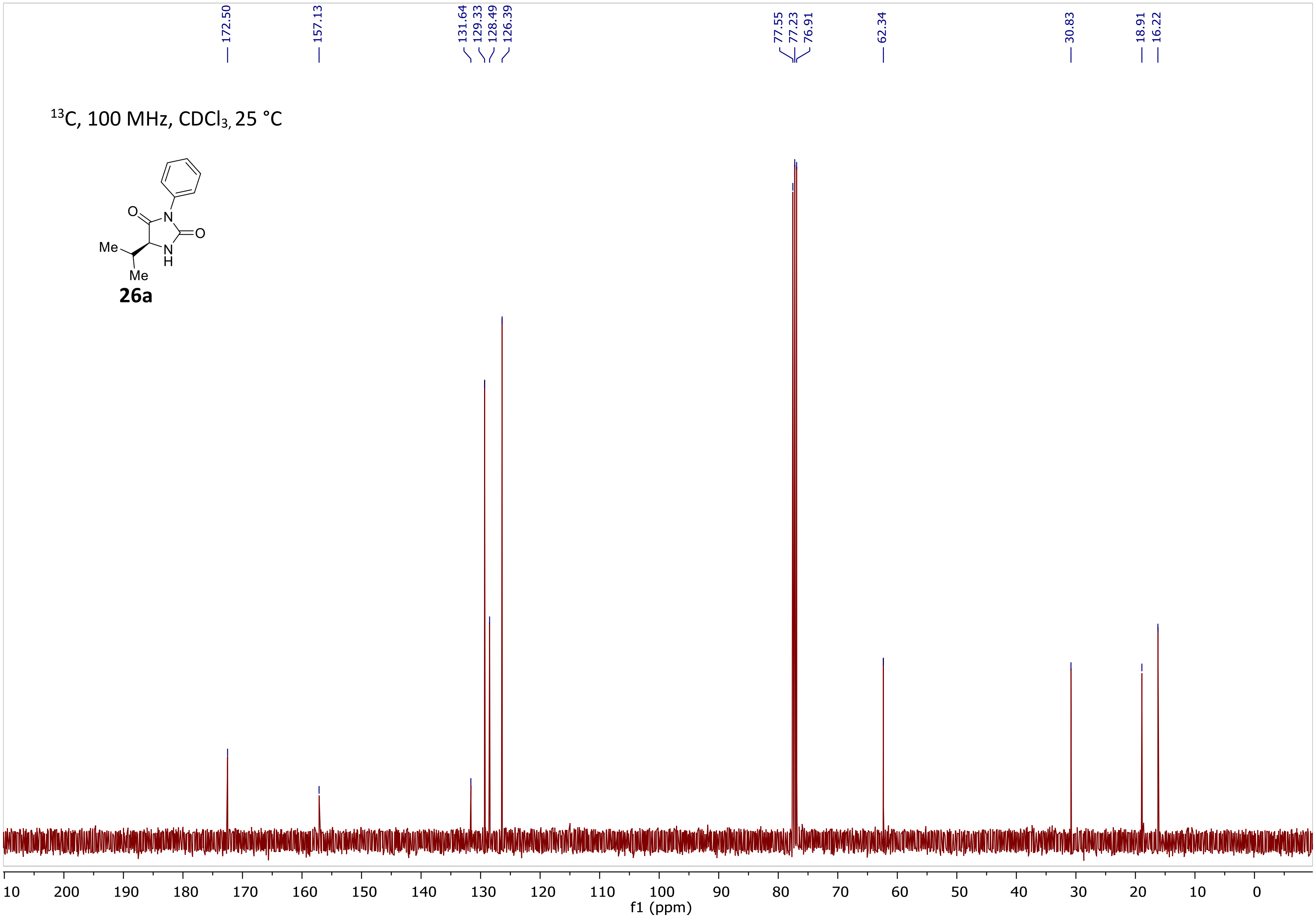
^{1}H, 400 MHz, CDCl$_3$, 25 °C

23a

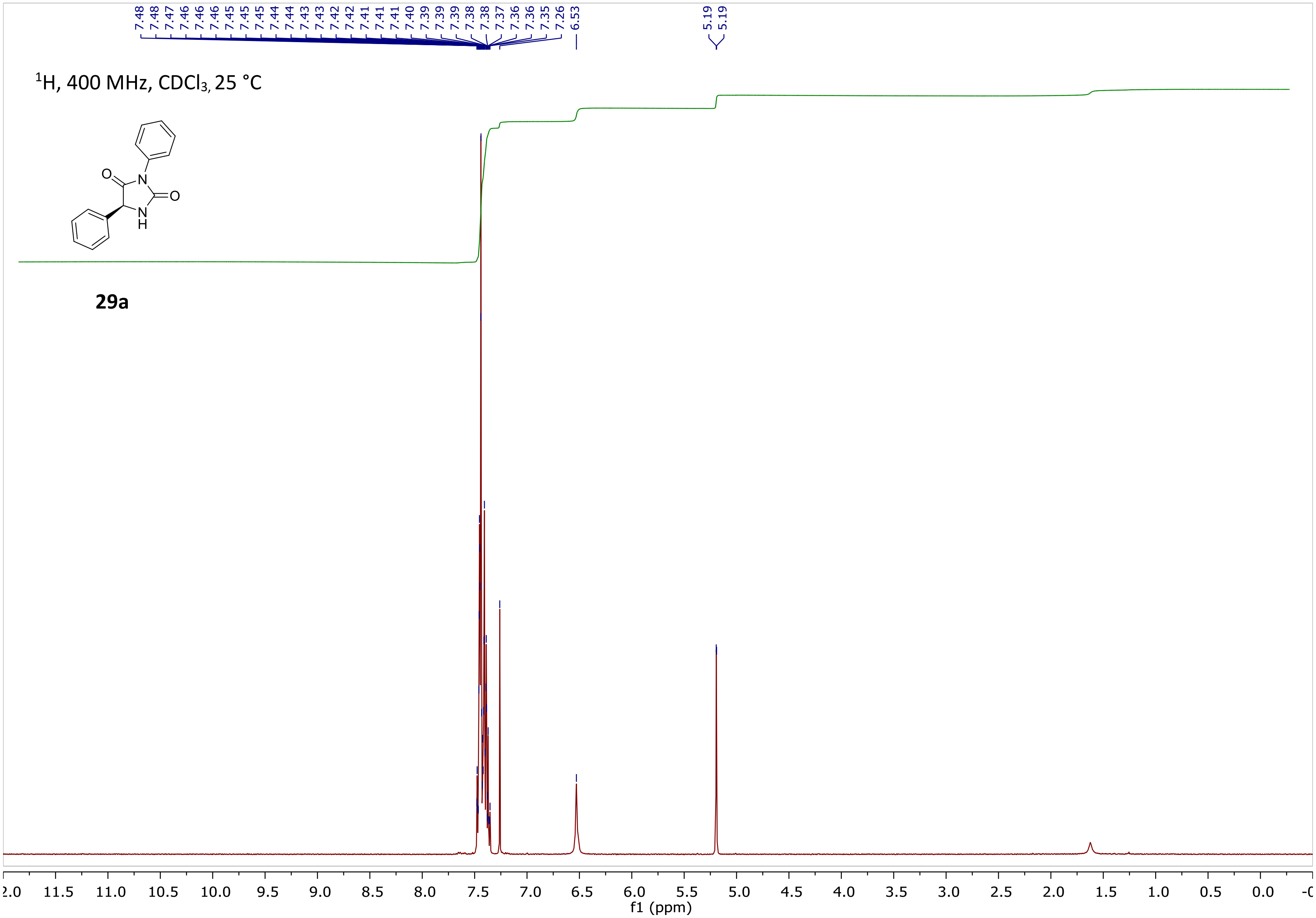

173.82
156.99
131.64
129.32
128.50
126.38
77.55
77.23
76.91
53.06
17.92
^{13}C, 100 MHz, $CDCl_3$, 25 °C
O
N
O
Me
N
H
23a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

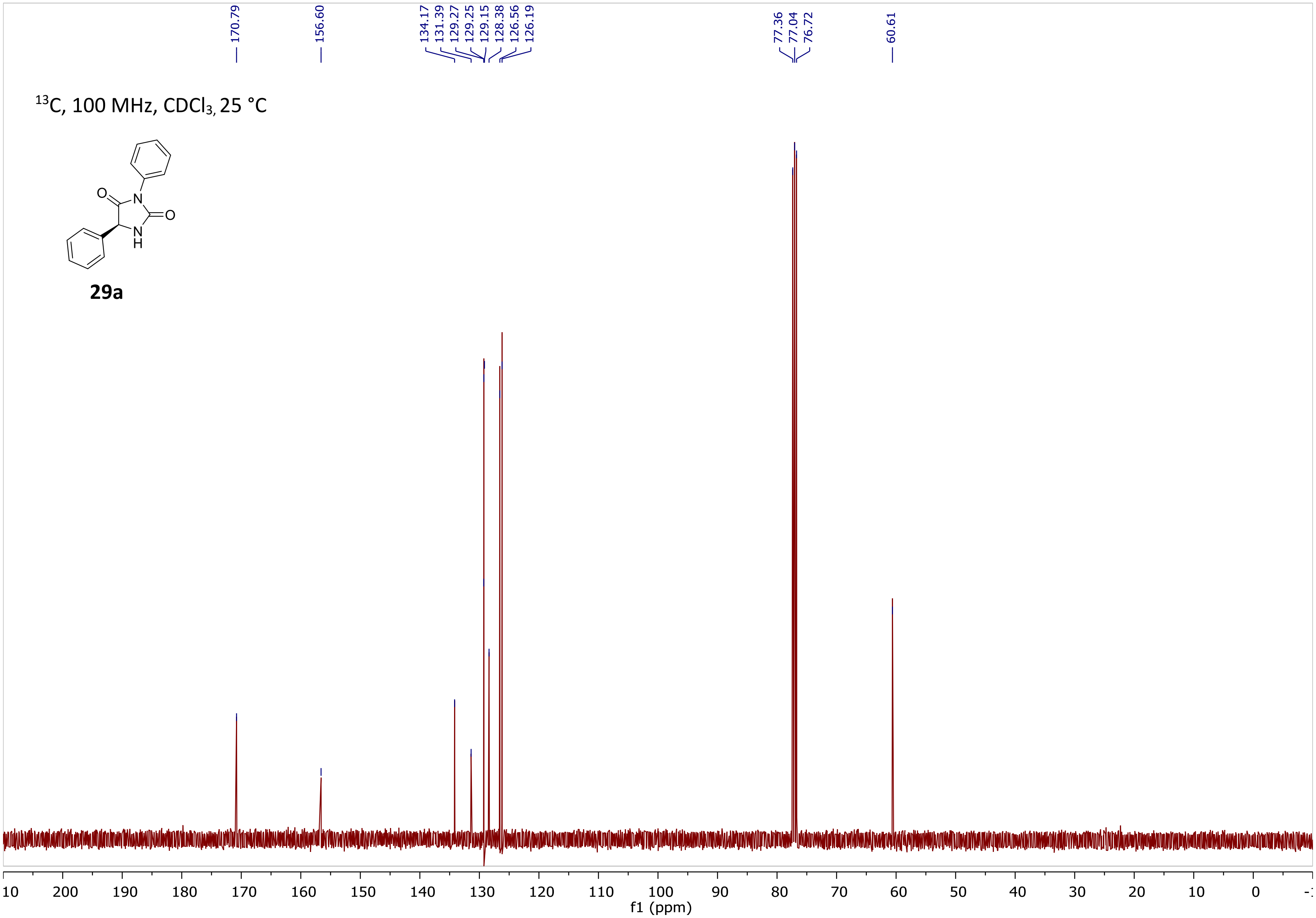

7.49
7.49
7.48
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.26
6.19
4.09
4.08
4.08
4.07
2.40
2.38
2.37
2.36
2.35
2.34
2.33
2.33
2.32
2.31
2.30
2.29
2.28
1.11
1.09
1.03
1.01
¹H, 400 MHz, CDCl₃, 25 °C
O
N
O
NH
Me
Me
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

26a


172.50
157.13
131.64
129.33
128.49
126.39
77.55
77.23
76.91
62.34
30.83
18.91
16.22
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
O
Me
N
H
Me
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

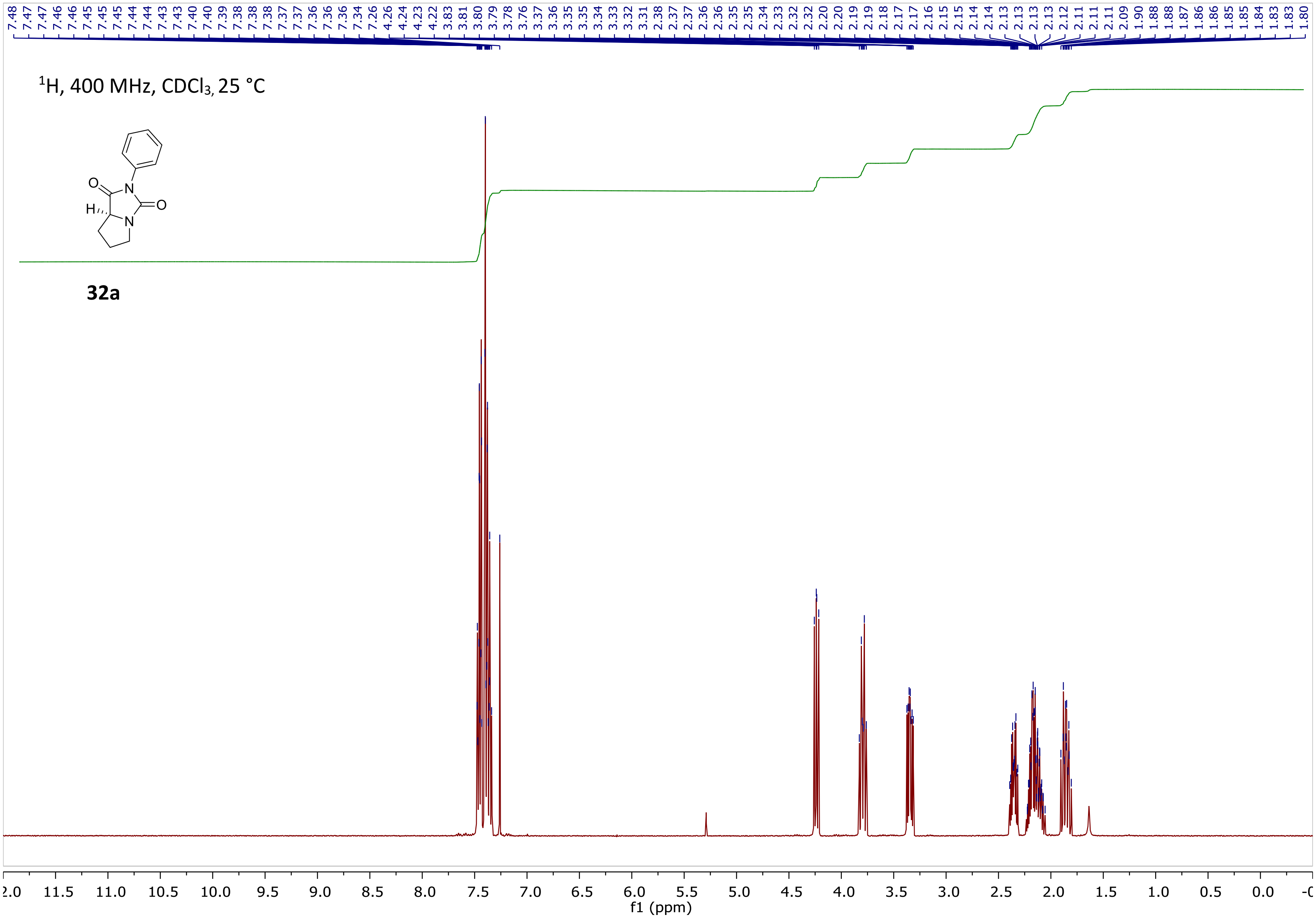
26a


7.48 7.48 7.47 7.46 7.46 7.46 7.45 7.45 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.36 7.36 7.35 7.26 6.53
5.19 5.19
¹H, 400 MHz, CDCl₃, 25 °C
O
N
O
N
H
29a
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

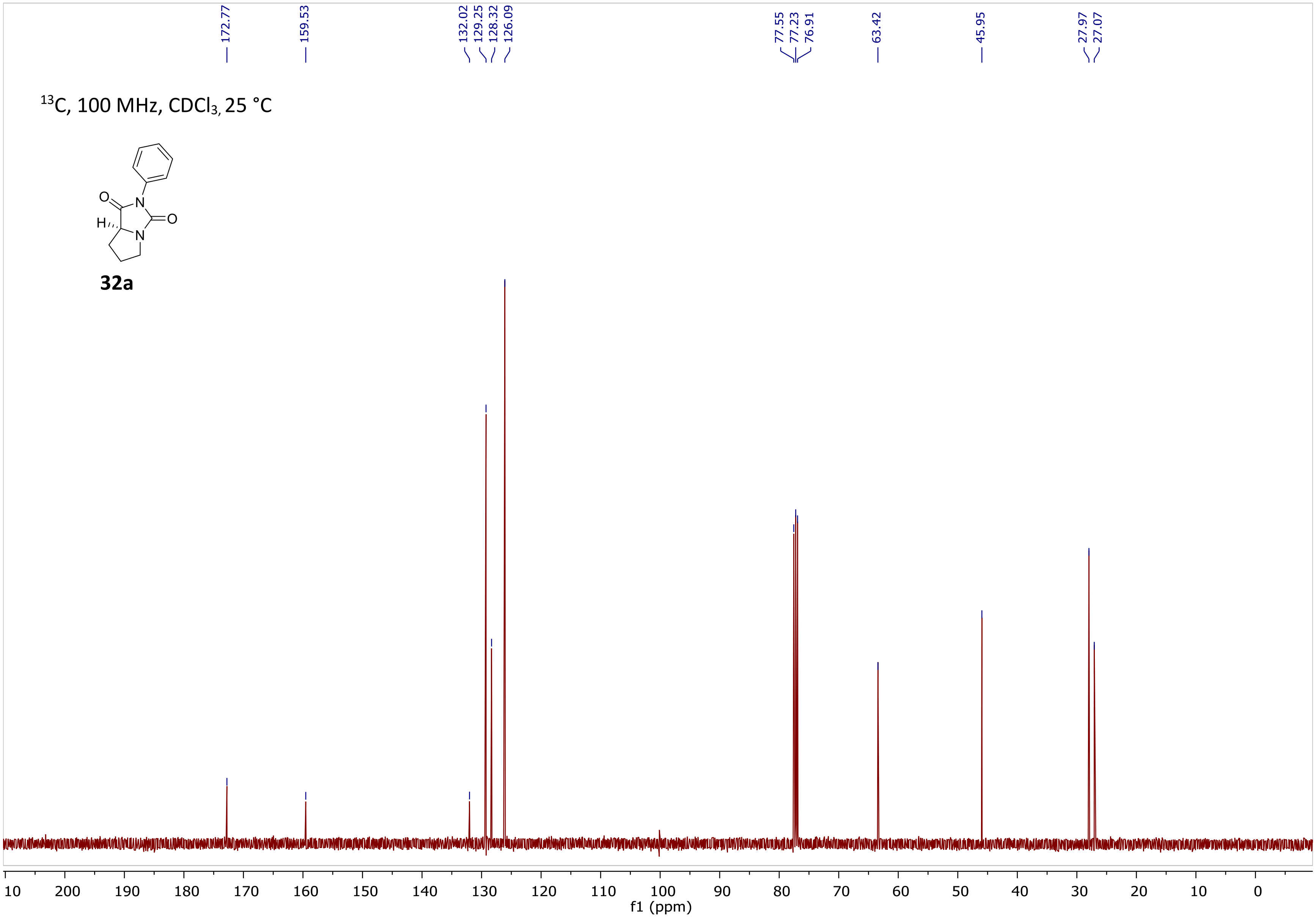


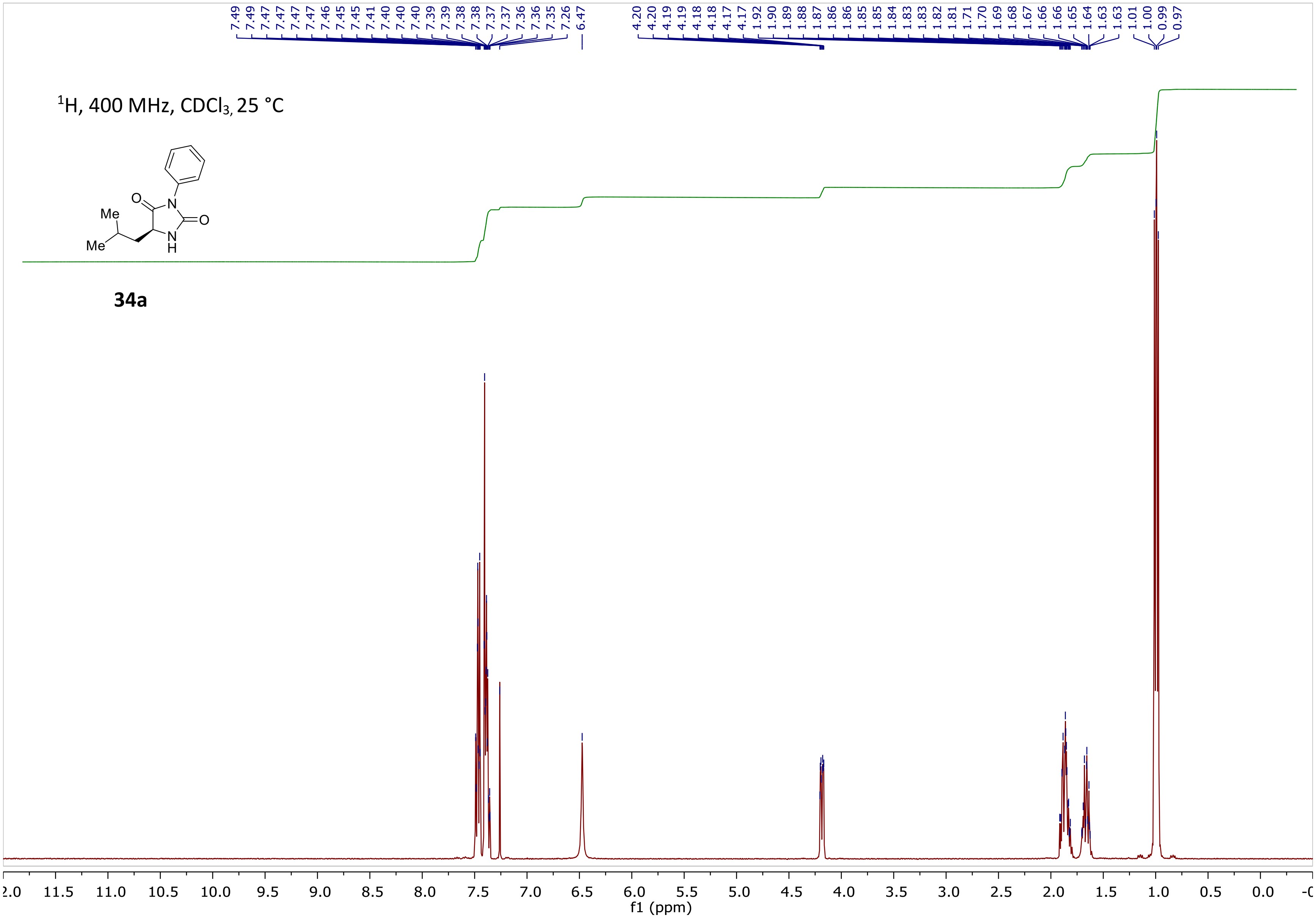
^{13}C, 100 MHz, CDCl$_3$, 25 °C

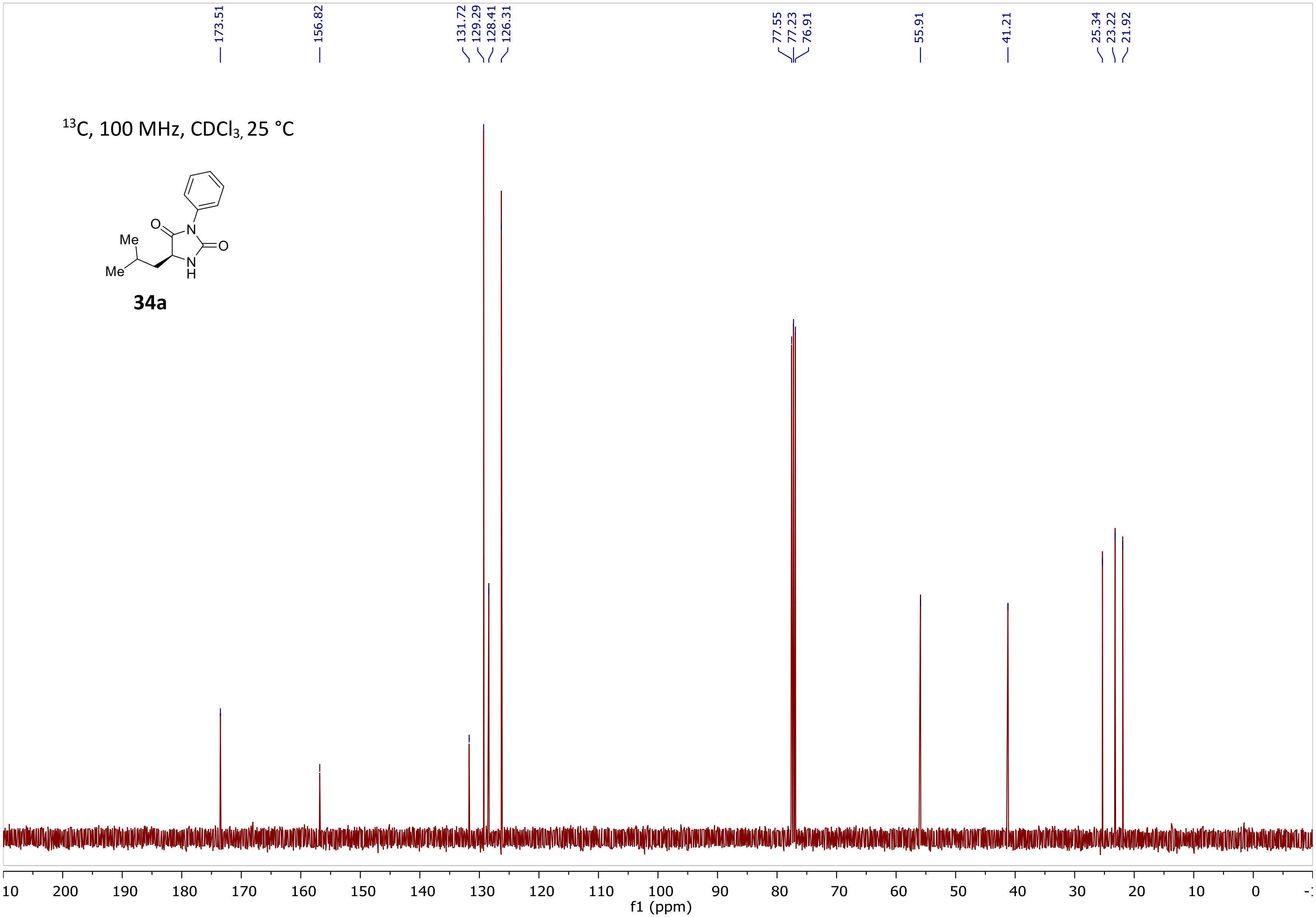
29a

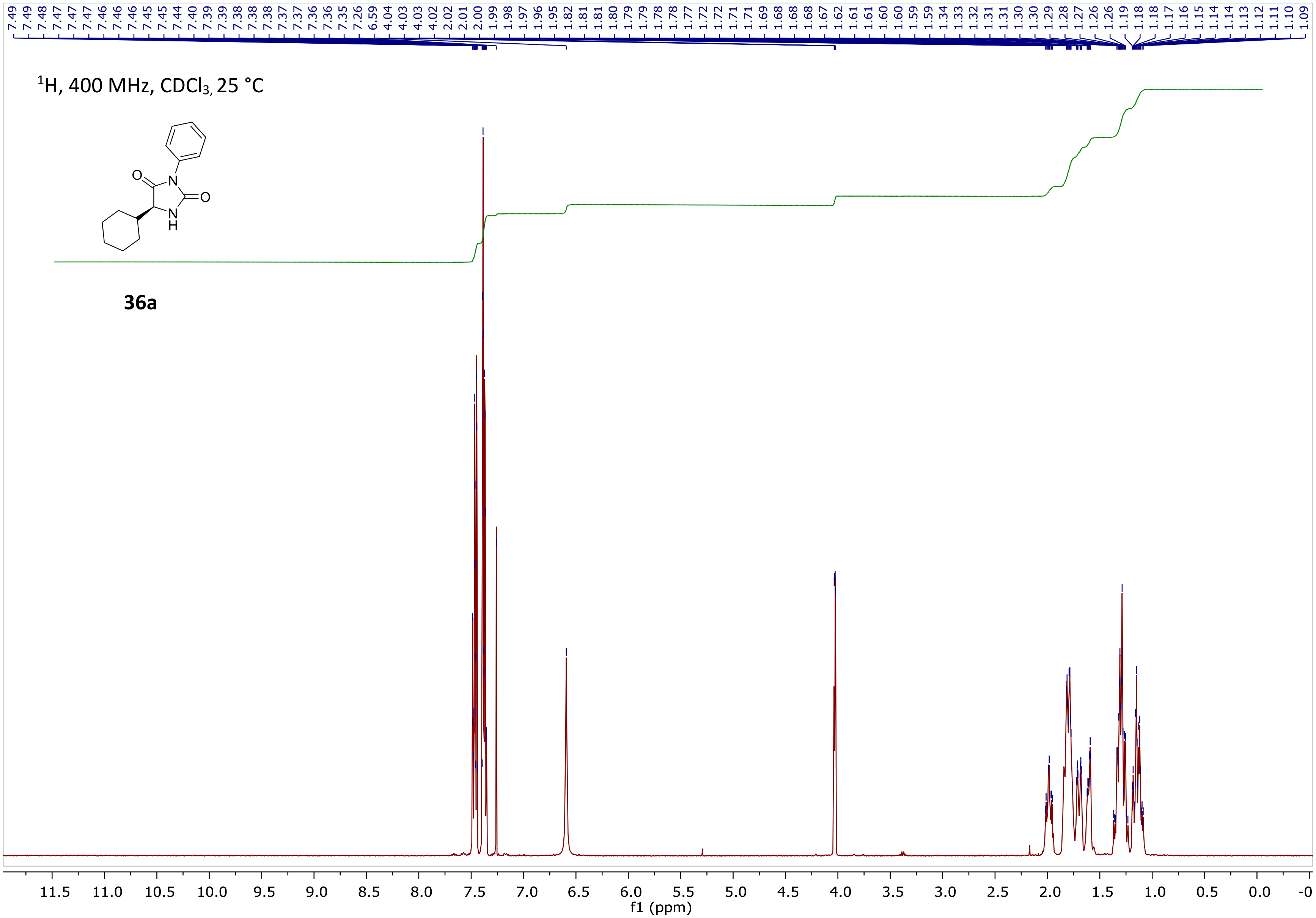

7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.43
7.43
7.40
7.40
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.34
7.26
4.26
4.24
4.23
4.22
3.83
3.81
3.80
3.79
3.78
3.76
3.37
3.36
3.35
3.35
3.34
3.33
3.32
3.31
2.38
2.37
2.37
2.36
2.36
2.35
2.35
2.34
2.33
2.32
2.32
2.20
2.20
2.19
2.19
2.18
2.17
2.17
2.16
2.15
2.15
2.14
2.14
2.13
2.13
2.13
2.13
2.12
2.11
2.11
2.11
2.09
1.90
1.88
1.87
1.86
1.86
1.85
1.85
1.84
1.83
1.80
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
O
H
N
f1 (ppm)
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

32a

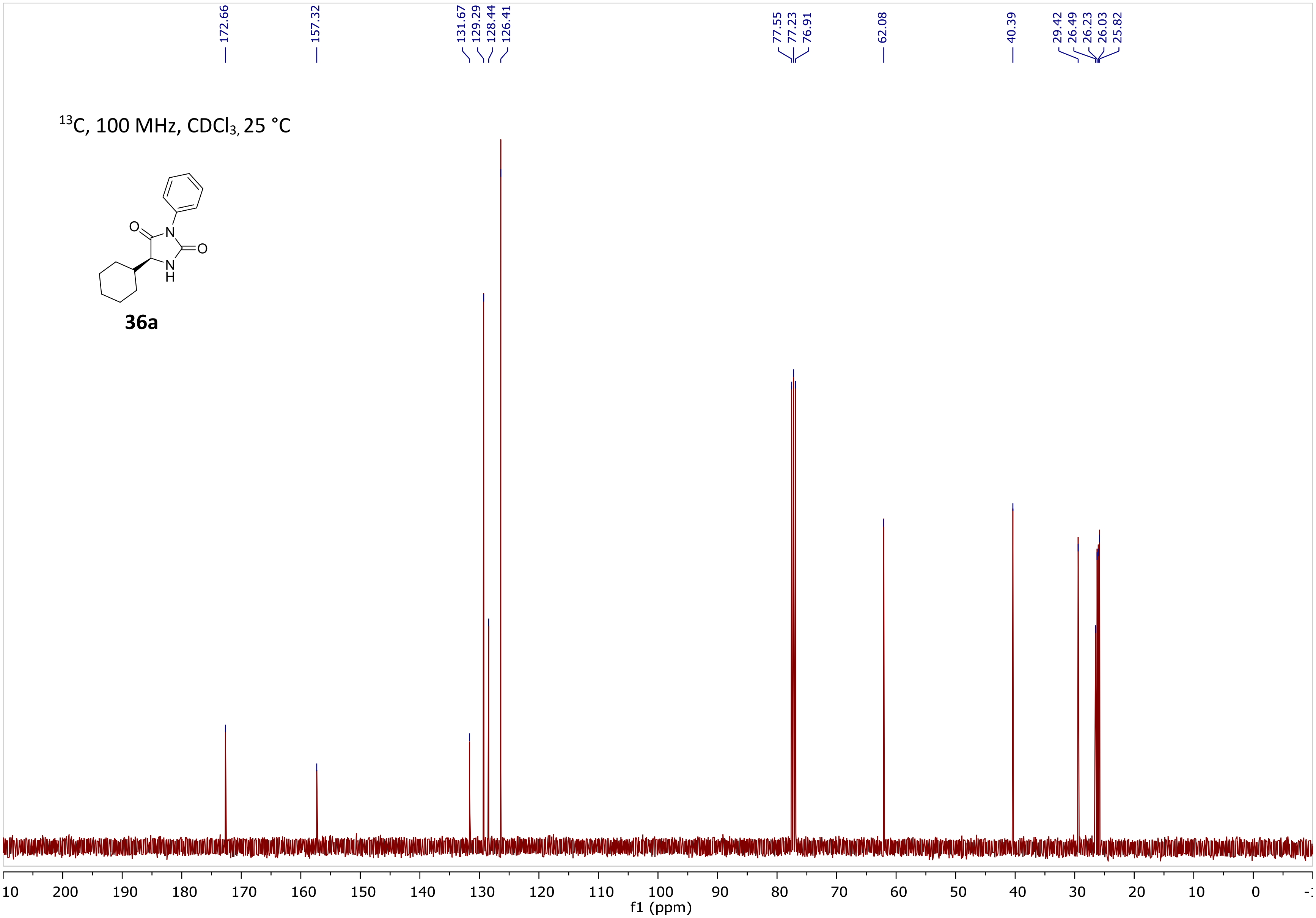

^{13}C, 100 MHz, CDCl$_3$, 25 °C
32a
172.77
159.53
132.02
129.25
128.32
126.09
77.55
77.23
76.91
63.42
45.95
27.97
27.07
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.49 7.49 7.47 7.47 7.47 7.47 7.46 7.45 7.45 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.26 6.47
4.20 4.20 4.19 4.19 4.18 4.18 4.17 4.17 1.92 1.90 1.89 1.88 1.87 1.86 1.86 1.85 1.85 1.84 1.83 1.83 1.82 1.81 1.71 1.70 1.69 1.68 1.67 1.66 1.66 1.65 1.64 1.63 1.63 1.01 1.00 0.99 0.97
¹H, 400 MHz, CDCl₃, 25 °C
O
N
Me
O
N
H
Me
34a
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(
f1 (ppm)

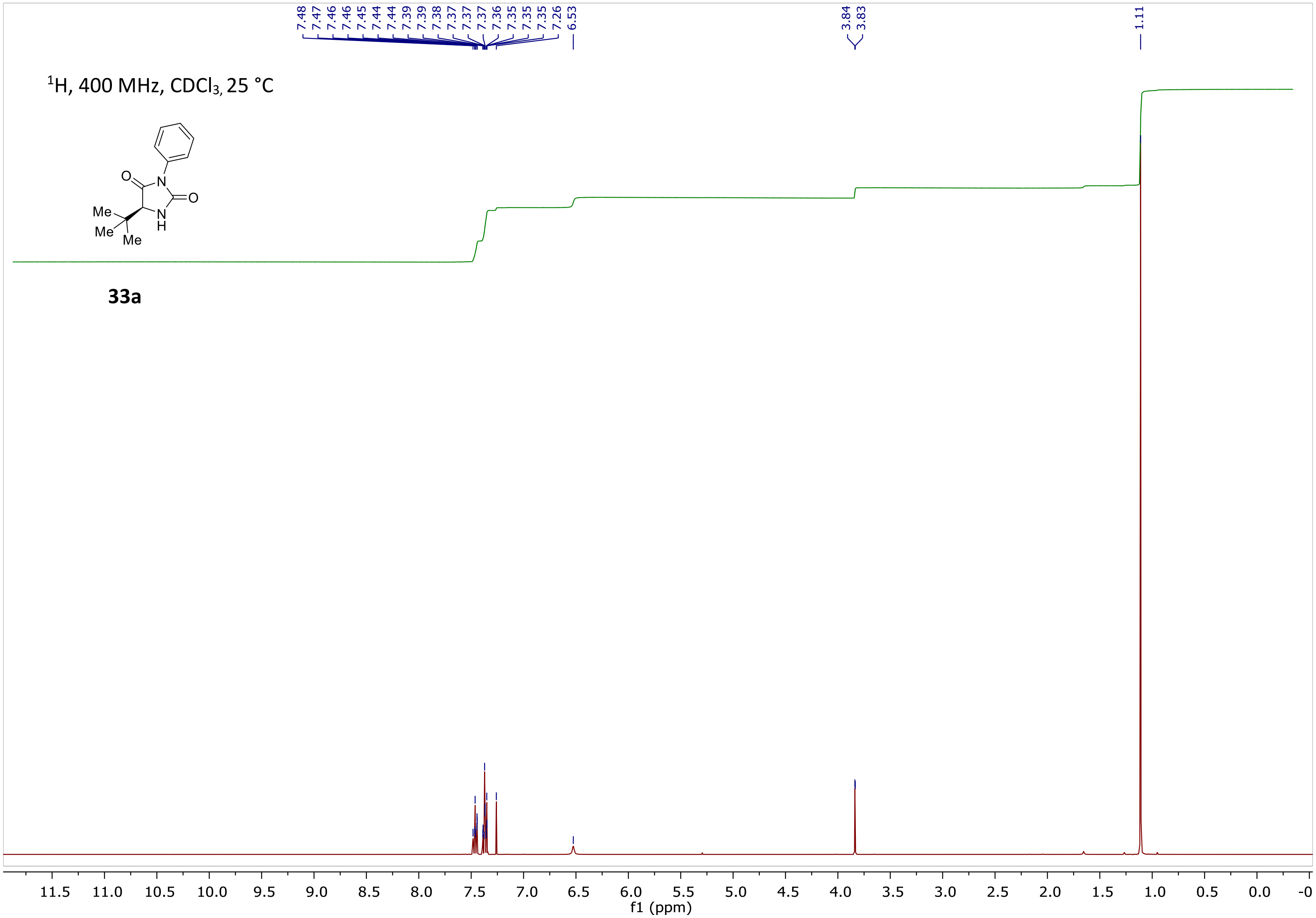

173.51
156.82
131.72
129.29
128.41
126.31
77.55
77.23
76.91
55.91
41.21
25.34
23.22
21.92
^{13}C, 100 MHz, CDCl$_3$, 25 °C
Me
Me
O
N
O
N
H
34a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)

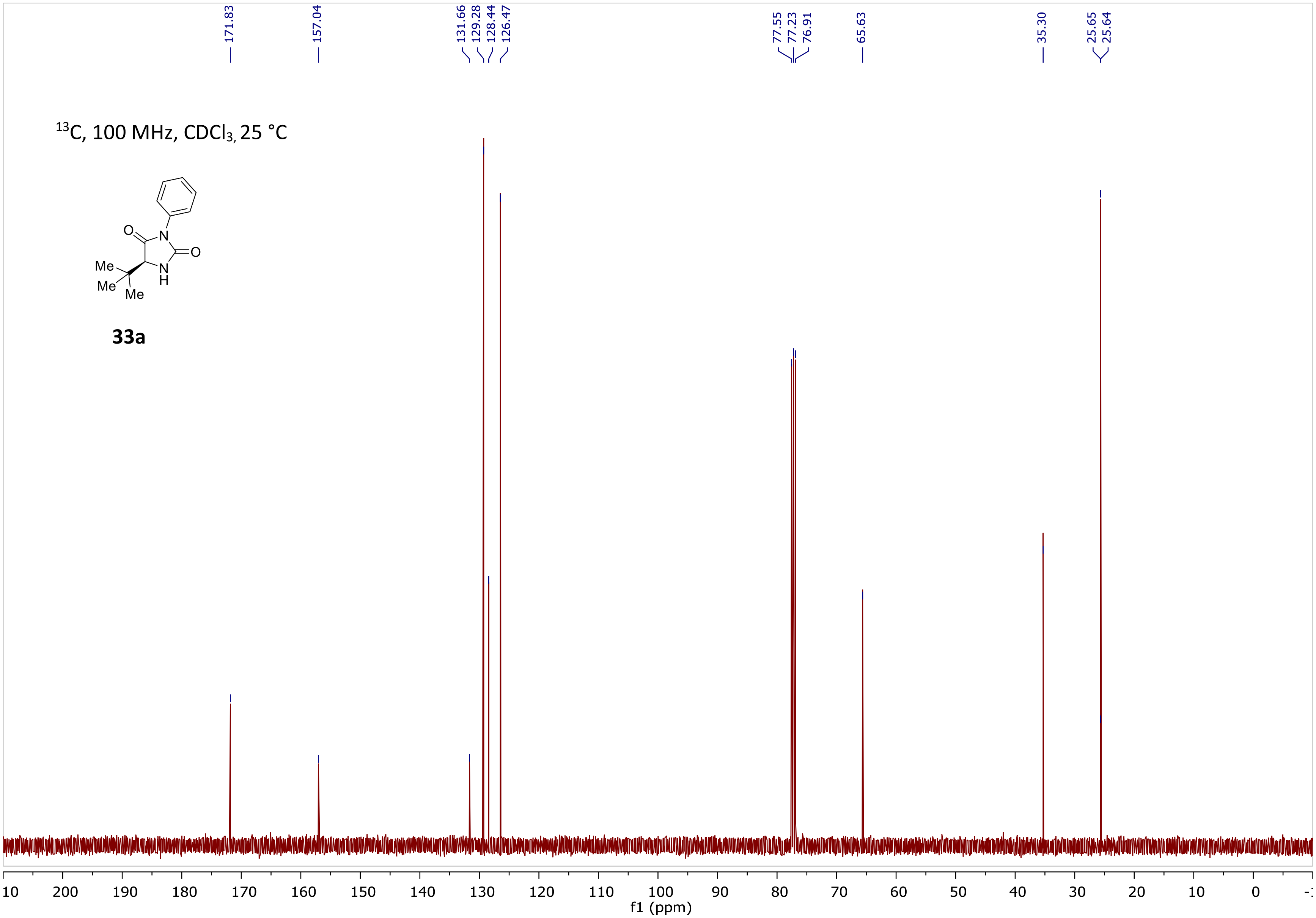

7.49
7.49
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.26
6.59
4.04
4.03
4.03
4.02
2.02
2.01
2.00
1.99
1.98
1.97
1.96
1.95
1.82
1.81
1.81
1.80
1.79
1.79
1.78
1.78
1.77
1.72
1.72
1.71
1.71
1.69
1.68
1.68
1.67
1.62
1.61
1.61
1.60
1.60
1.59
1.59
1.34
1.33
1.32
1.31
1.31
1.30
1.30
1.29
1.28
1.27
1.26
1.26
1.19
1.18
1.18
1.17
1.16
1.15
1.14
1.13
1.12
1.11
1.10
1.09
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
O
N
H
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

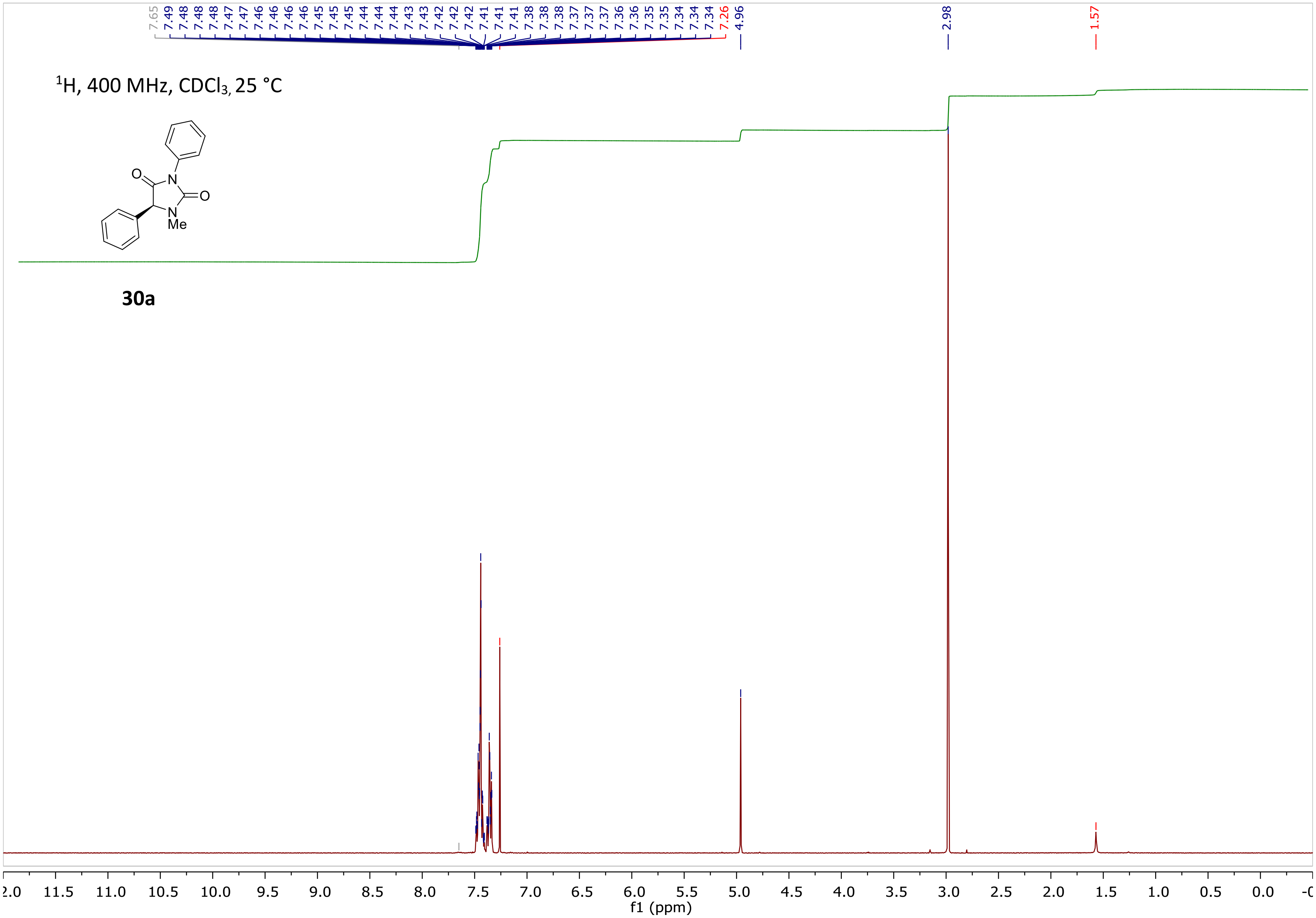
36a

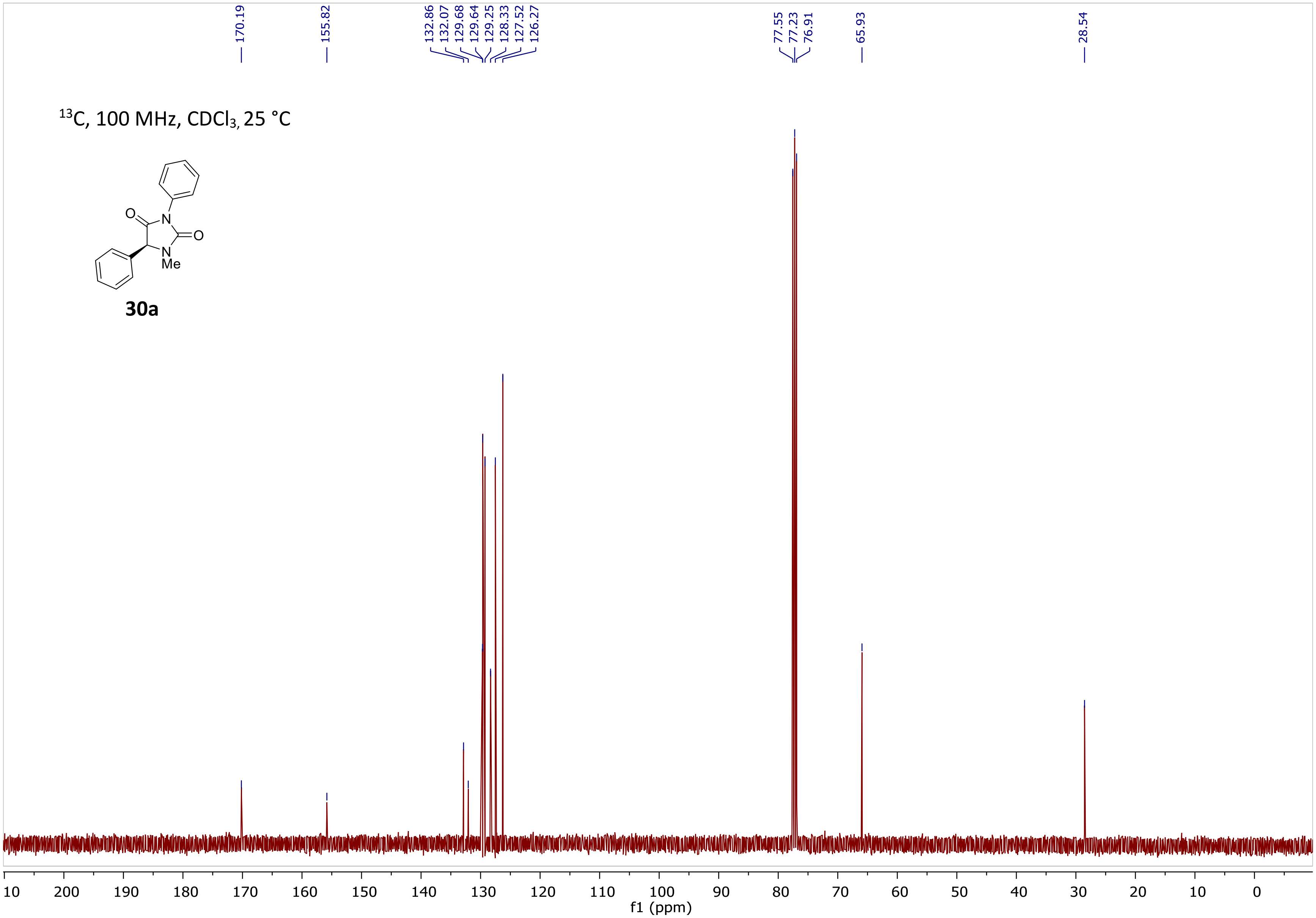

172.66
157.32
131.67
129.29
128.44
126.41
77.55
77.23
76.91
62.08
40.39
29.42
26.49
26.23
26.03
25.82
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
O
N
H
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:
f1 (ppm)

36a

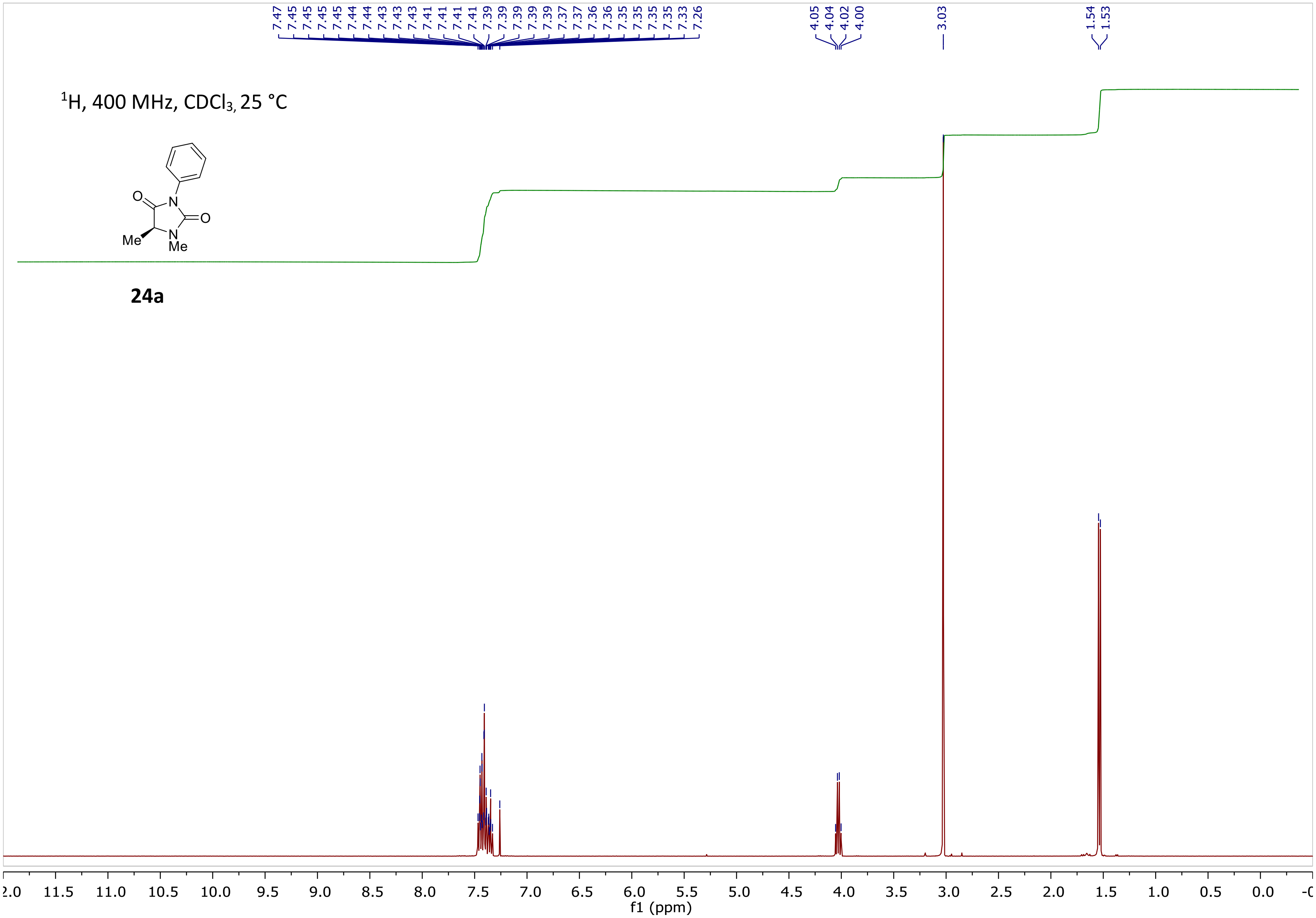

7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.39
7.38
7.37
7.37
7.37
7.36
7.35
7.35
7.35
7.26
6.53
3.84
3.83
1.11
¹H, 400 MHz, CDCl₃, 25 °C
O
N
O
Me
Me
Me
N
H
33a
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


171.83
157.04
131.66
129.28
128.44
126.47
77.55
77.23
76.91
65.63
35.30
25.65
25.64
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
O
Me
Me
Me
N
H
33a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)


7.65
7.49
7.48
7.48
7.48
7.47
7.47
7.46
7.46
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.41
7.38
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.34
7.26
4.96
2.98
1.57
¹H, 400 MHz, CDCl₃, 25 °C
O
N
O
N
Me
30a
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)

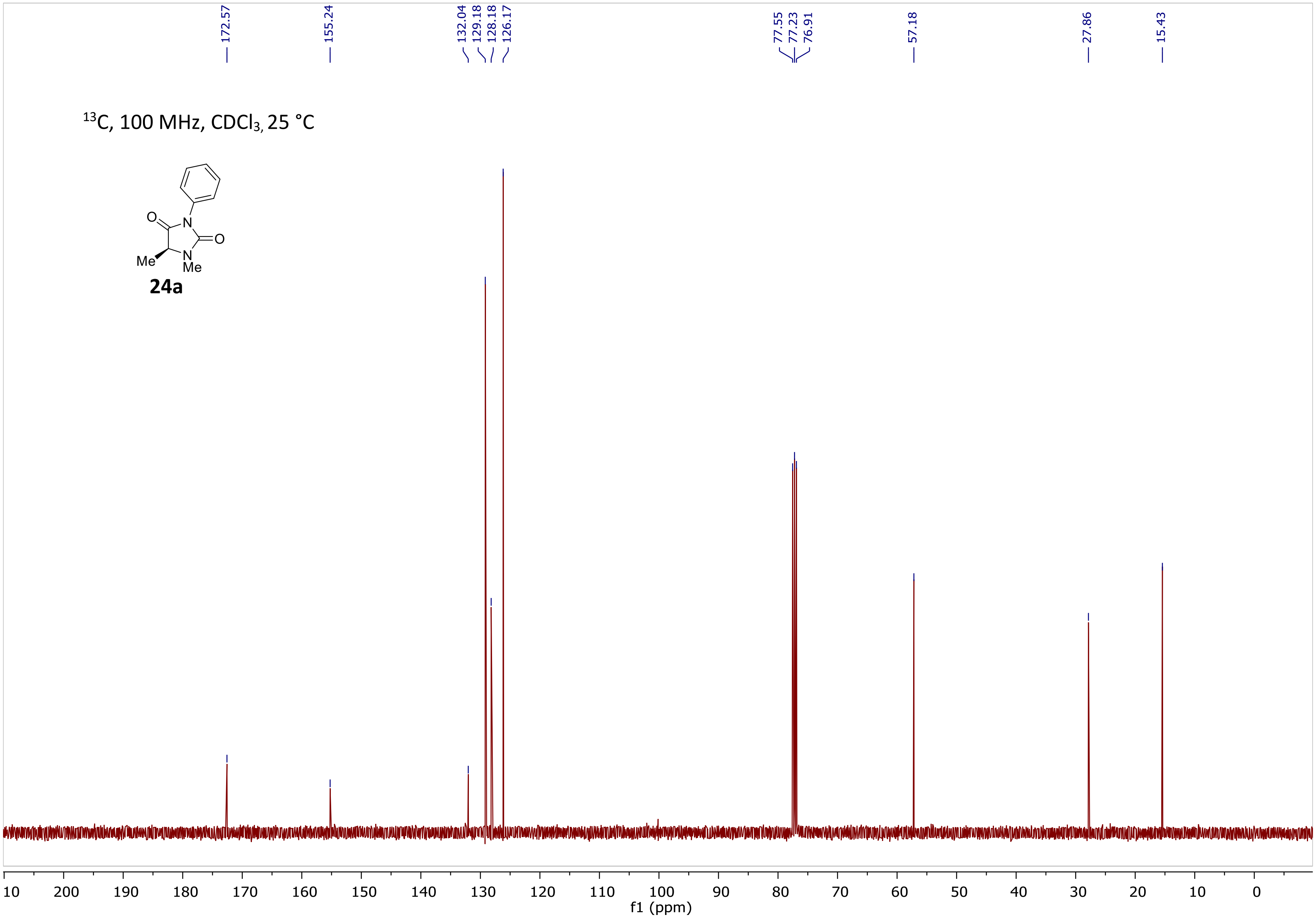

^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
O
N
Me
170.19
155.82
132.86
132.07
129.68
129.64
129.25
128.33
127.52
126.27
77.55
77.23
76.91
65.93
28.54
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

30a

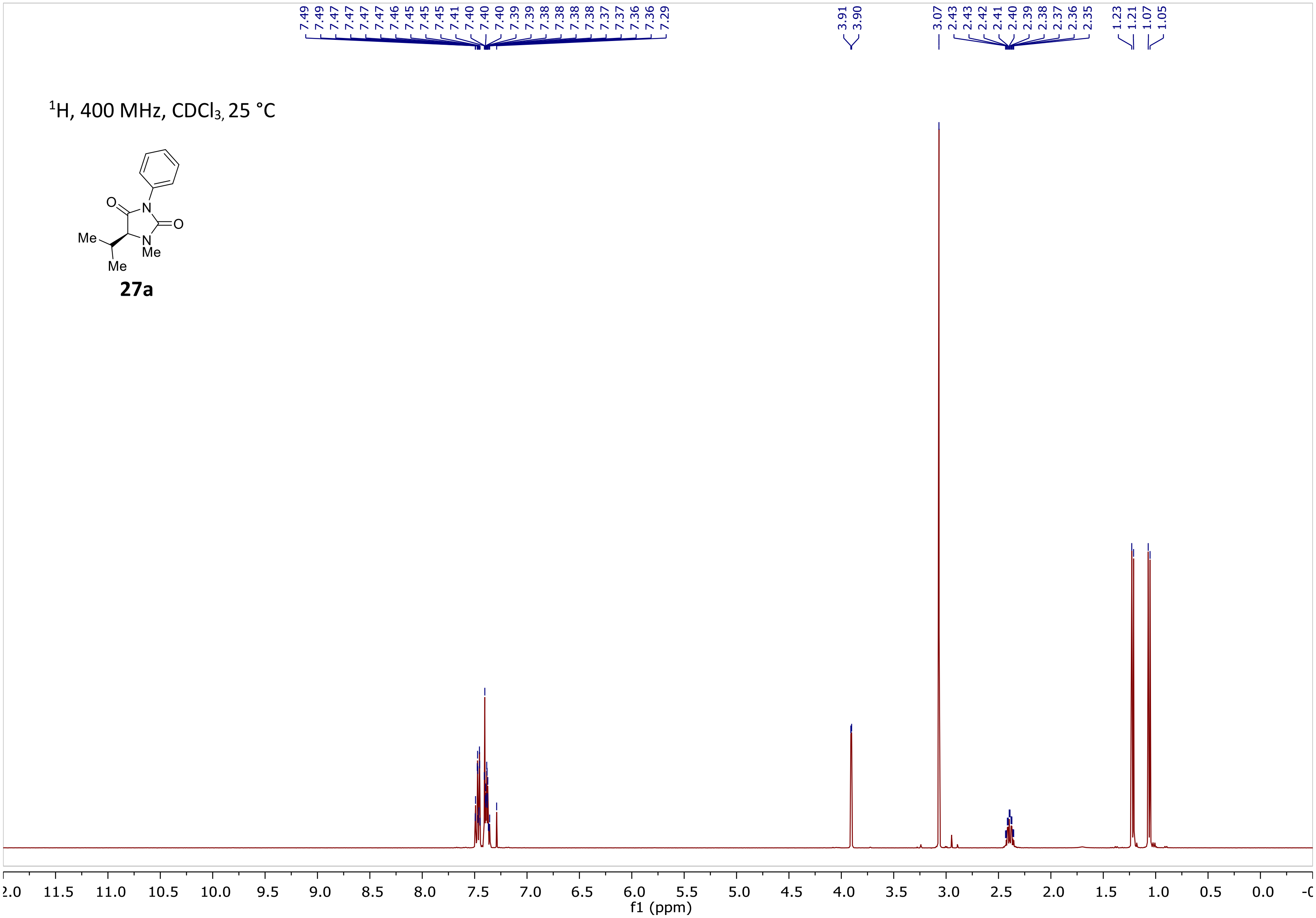


^{1}H, 400 MHz, CDCl$_3$, 25 °C

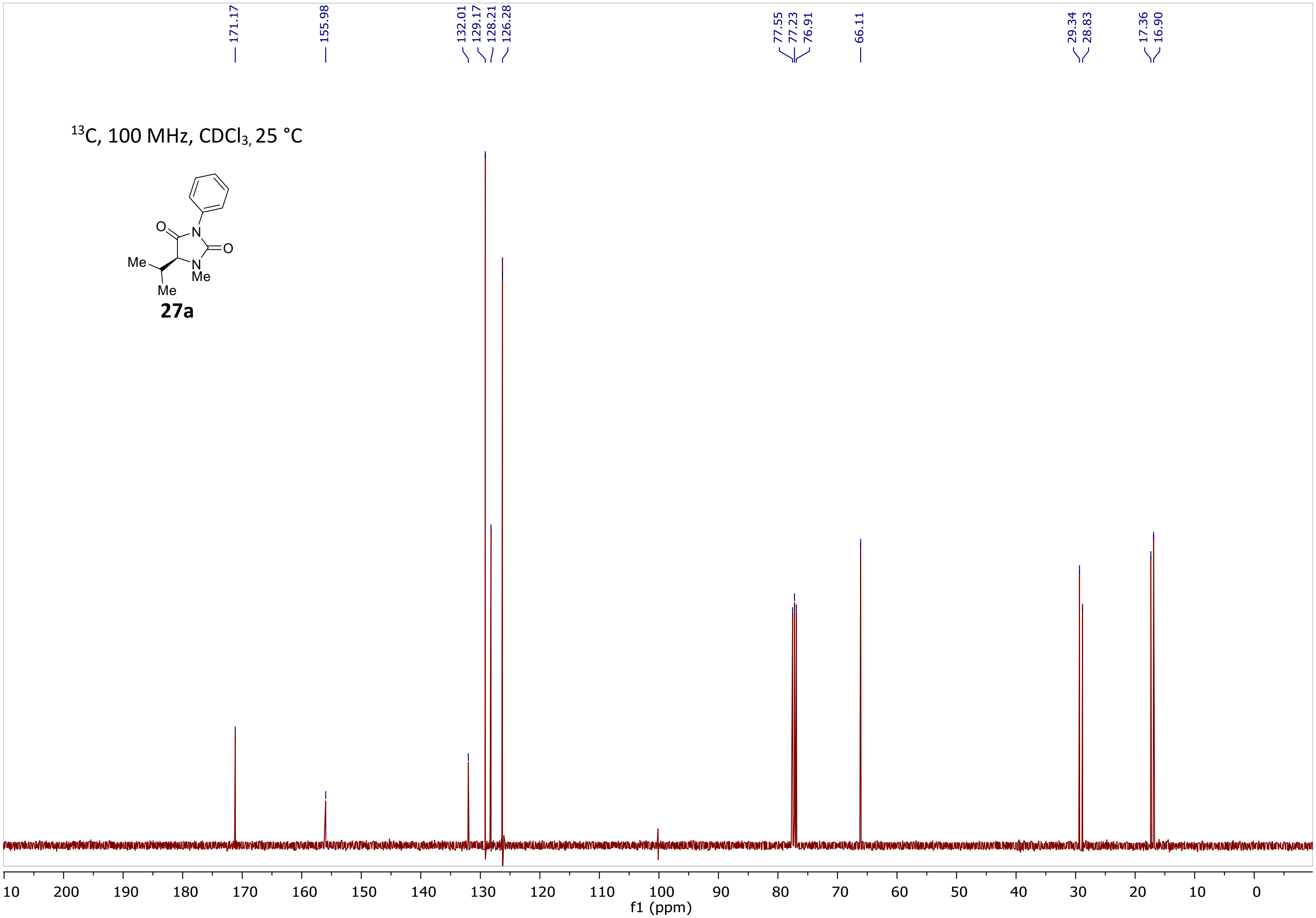
24a

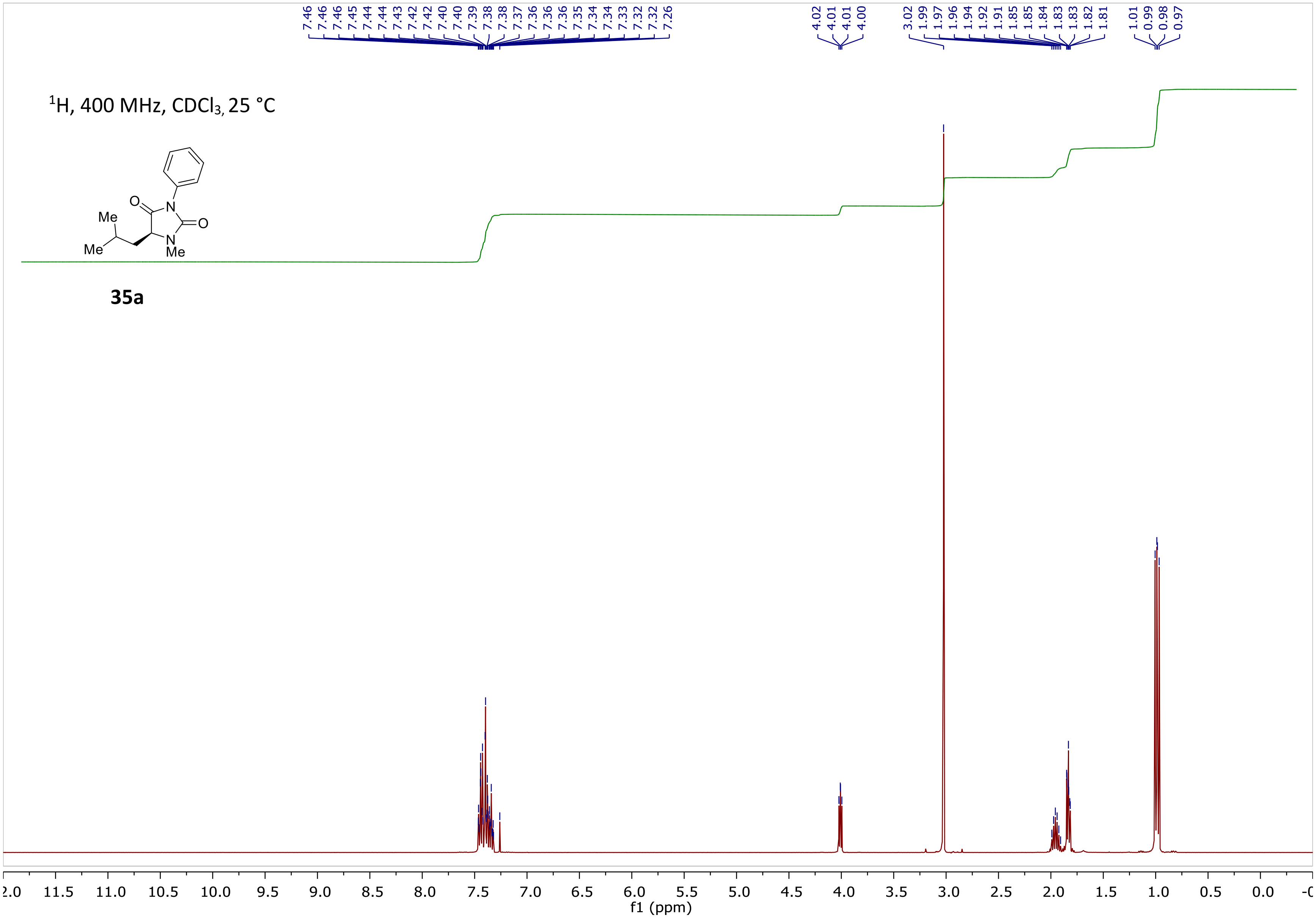

172.57
155.24
132.04
129.18
128.18
126.17
77.55
77.23
76.91
57.18
27.86
15.43
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
O
N
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

24a

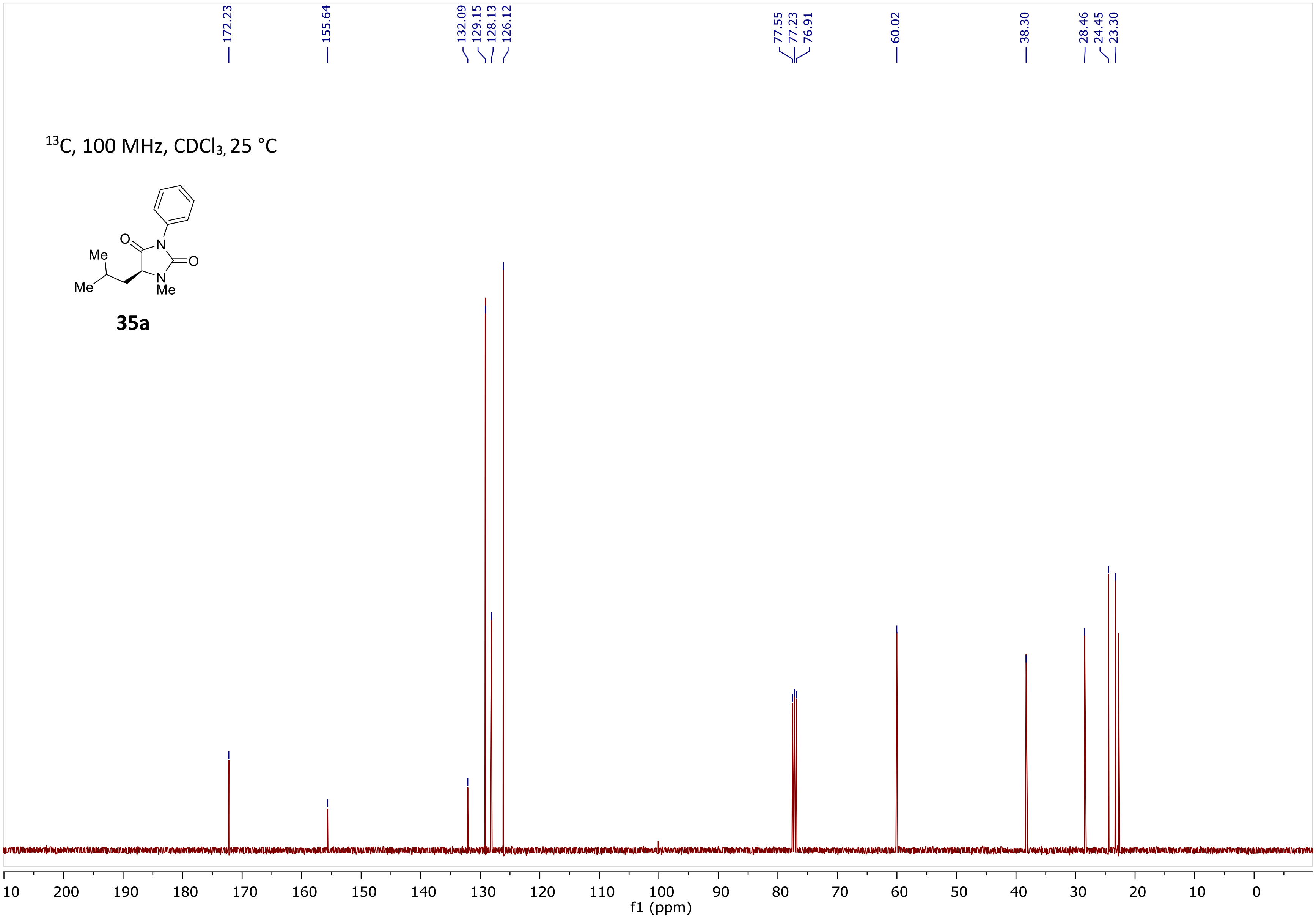

7.49
7.49
7.47
7.47
7.47
7.47
7.46
7.45
7.45
7.45
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.29
3.91
3.90
3.07
2.43
2.43
2.42
2.41
2.40
2.39
2.38
2.37
2.36
2.35
1.23
1.21
1.07
1.05
¹H, 400 MHz, CDCl₃, 25 °C
O
N
O
N
Me
Me
Me
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

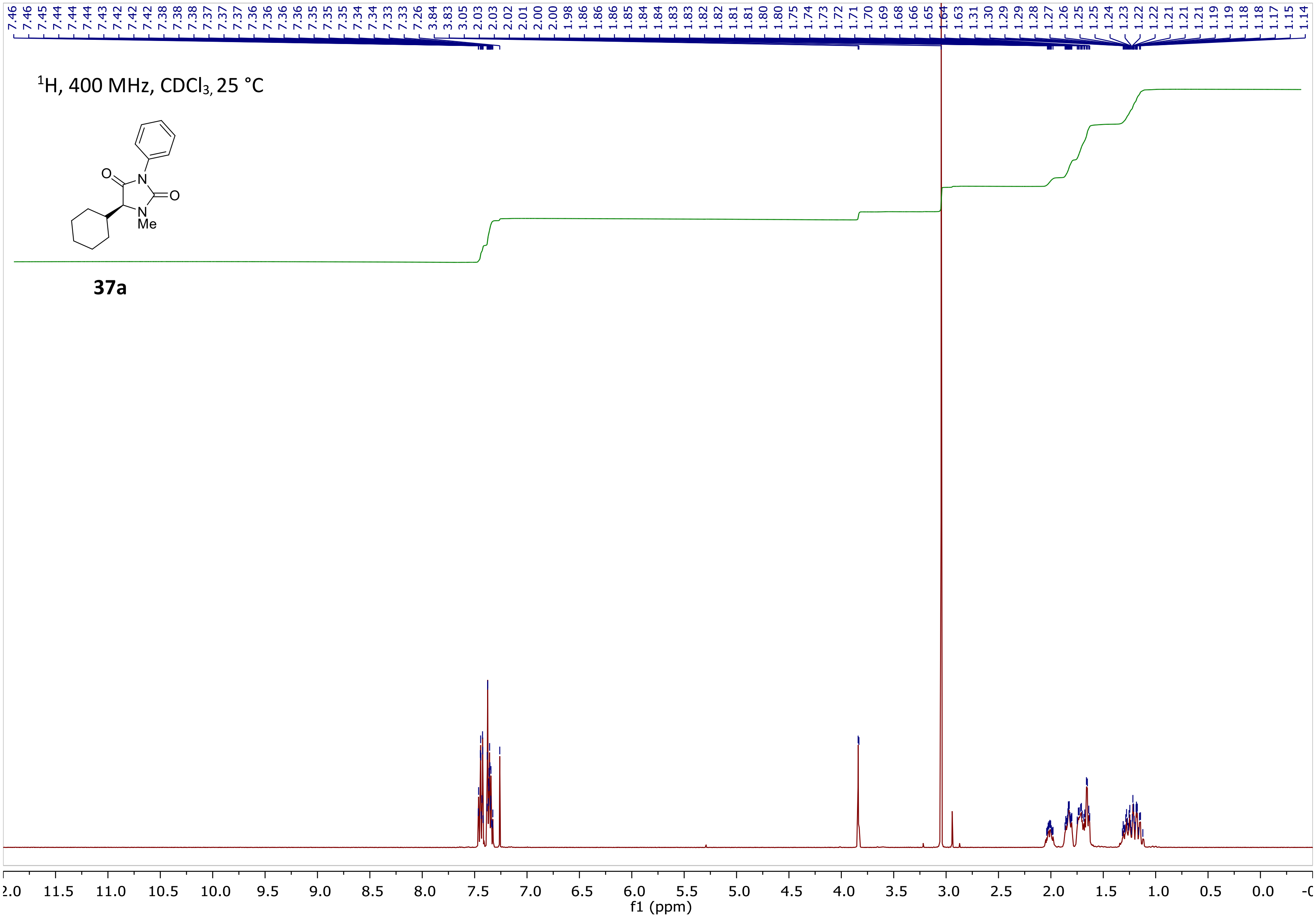
27a


171.17
155.98
132.01
129.17
128.21
126.28
77.55
77.23
76.91
66.11
29.34
28.83
17.36
16.90
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
O
Me
N
Me
Me
27a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

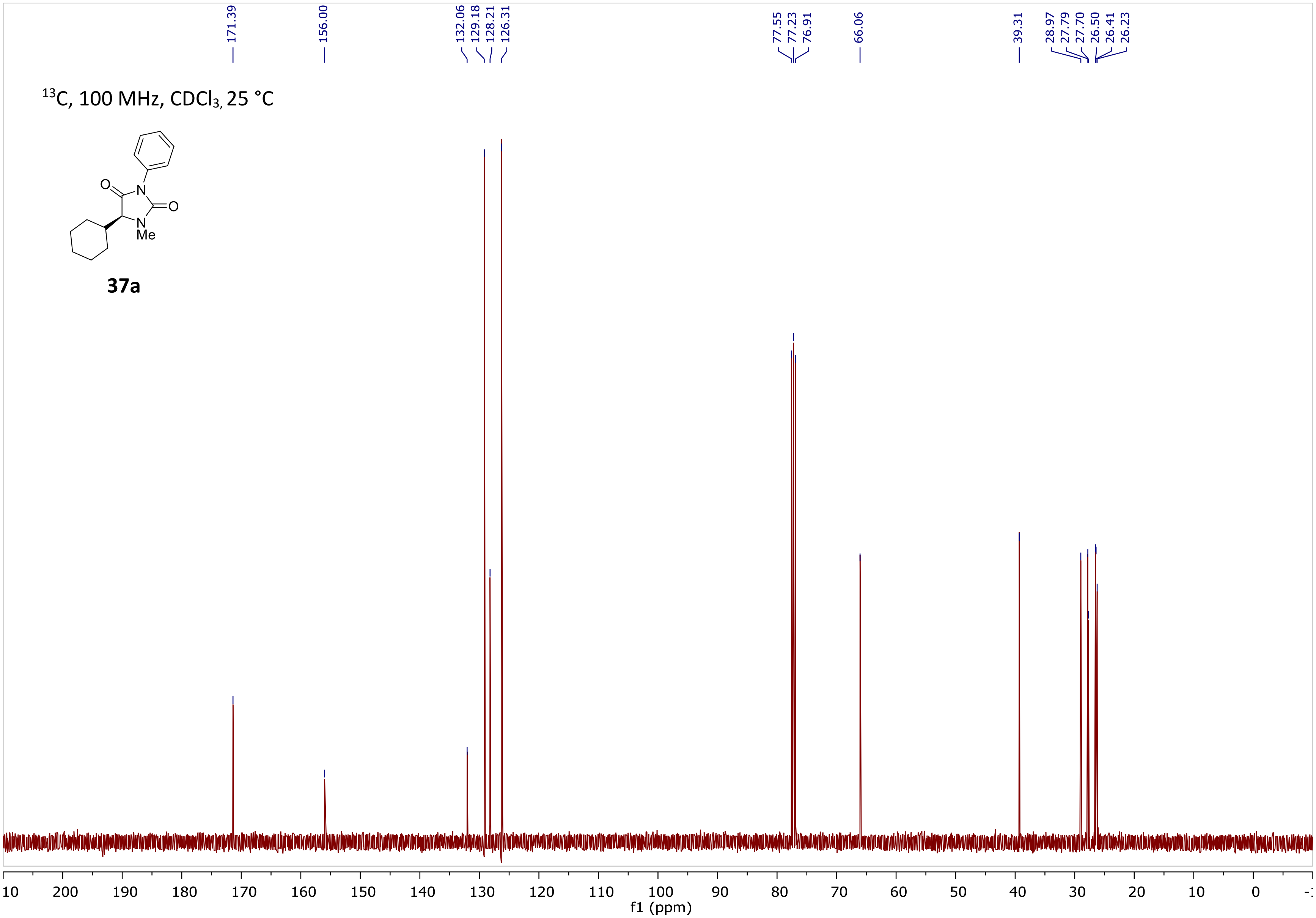

7.46
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.42
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.26
4.02
4.01
4.01
4.00
3.02
1.99
1.97
1.96
1.94
1.92
1.91
1.85
1.85
1.84
1.83
1.83
1.82
1.81
1.01
0.99
0.98
0.97
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
O
N
Me
Me
Me
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

35a


172.23
155.64
132.09
129.15
128.13
126.12
77.55
77.23
76.91
60.02
38.30
28.46
24.45
23.30
^{13}C, 100 MHz, CDCl$_3$, 25 °C
Me
Me
O
N
O
N
Me
35a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

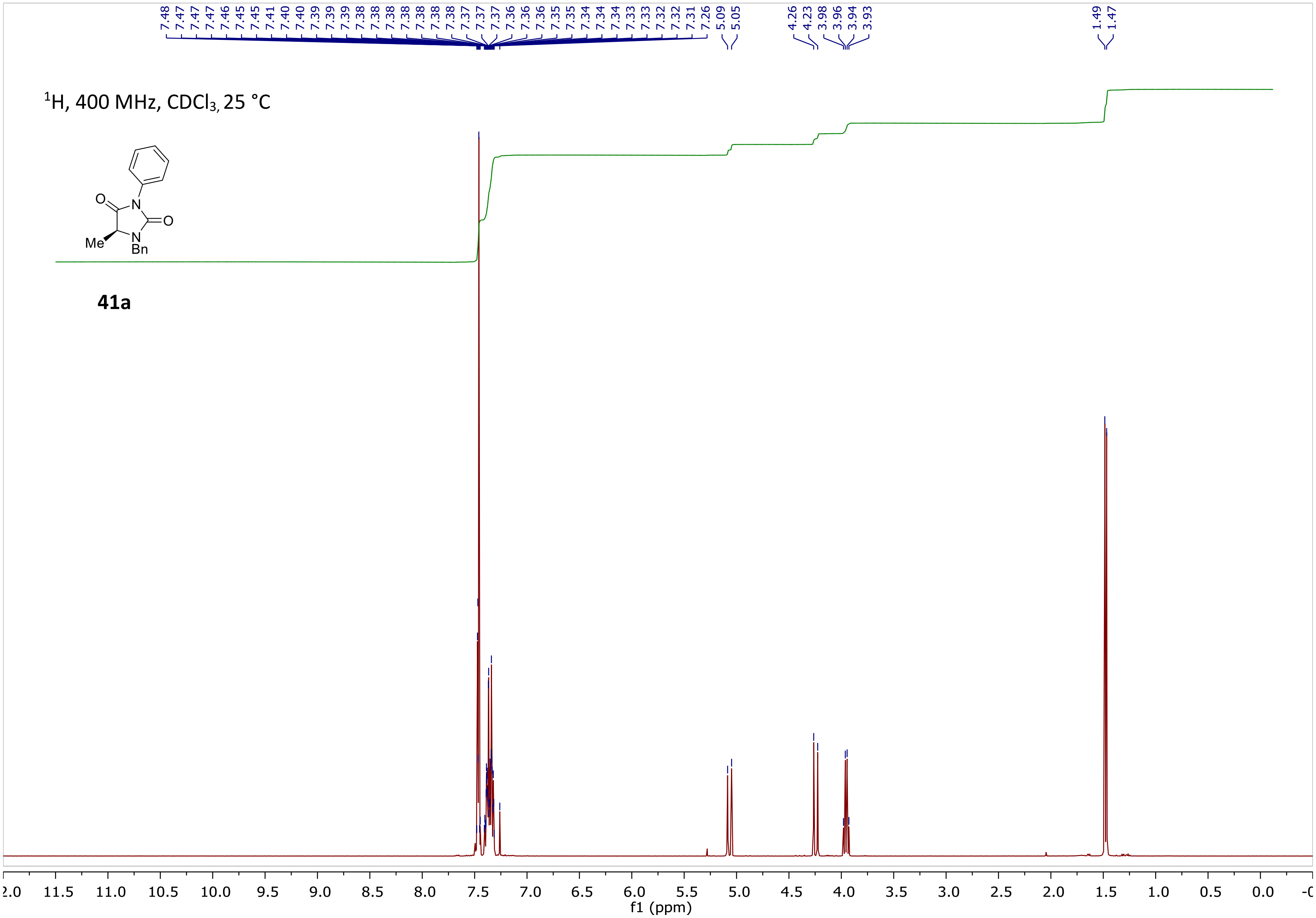

7.46 7.46 7.45 7.44 7.44 7.44 7.43 7.42 7.42 7.42 7.38 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.26 3.84 3.83 3.05 2.03 2.03 2.02 2.01 2.00 2.00 1.98 1.86 1.86 1.85 1.84 1.84 1.83 1.83 1.82 1.81 1.81 1.80 1.75 1.74 1.73 1.72 1.71 1.70 1.69 1.68 1.66 1.65 1.64 1.63 1.31 1.30 1.29 1.29 1.28 1.27 1.26 1.25 1.25 1.24 1.23 1.22 1.22 1.21 1.21 1.21 1.19 1.18 1.18 1.17 1.15 1.14
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
O
N
Me
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(
f1 (ppm)

37a

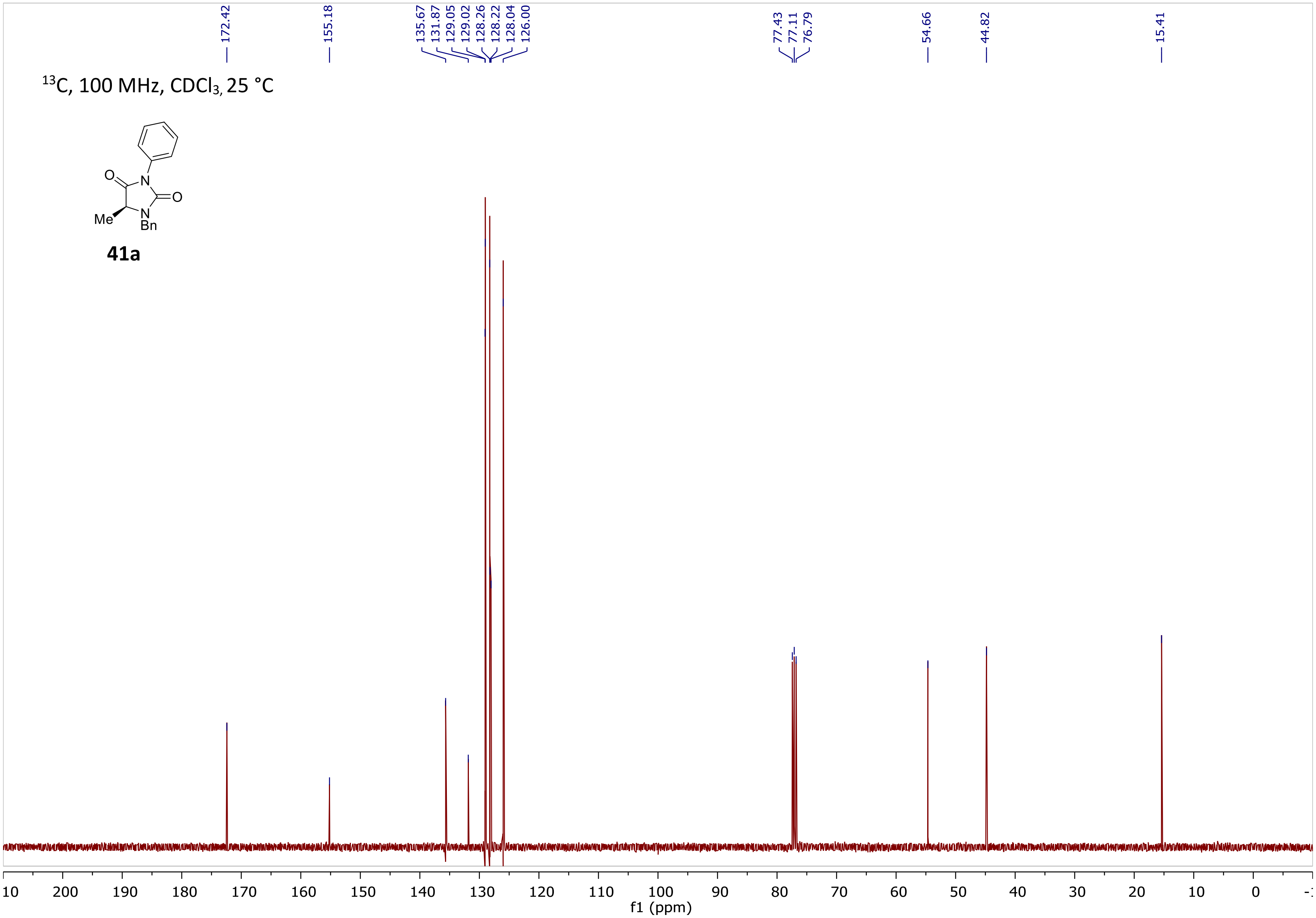


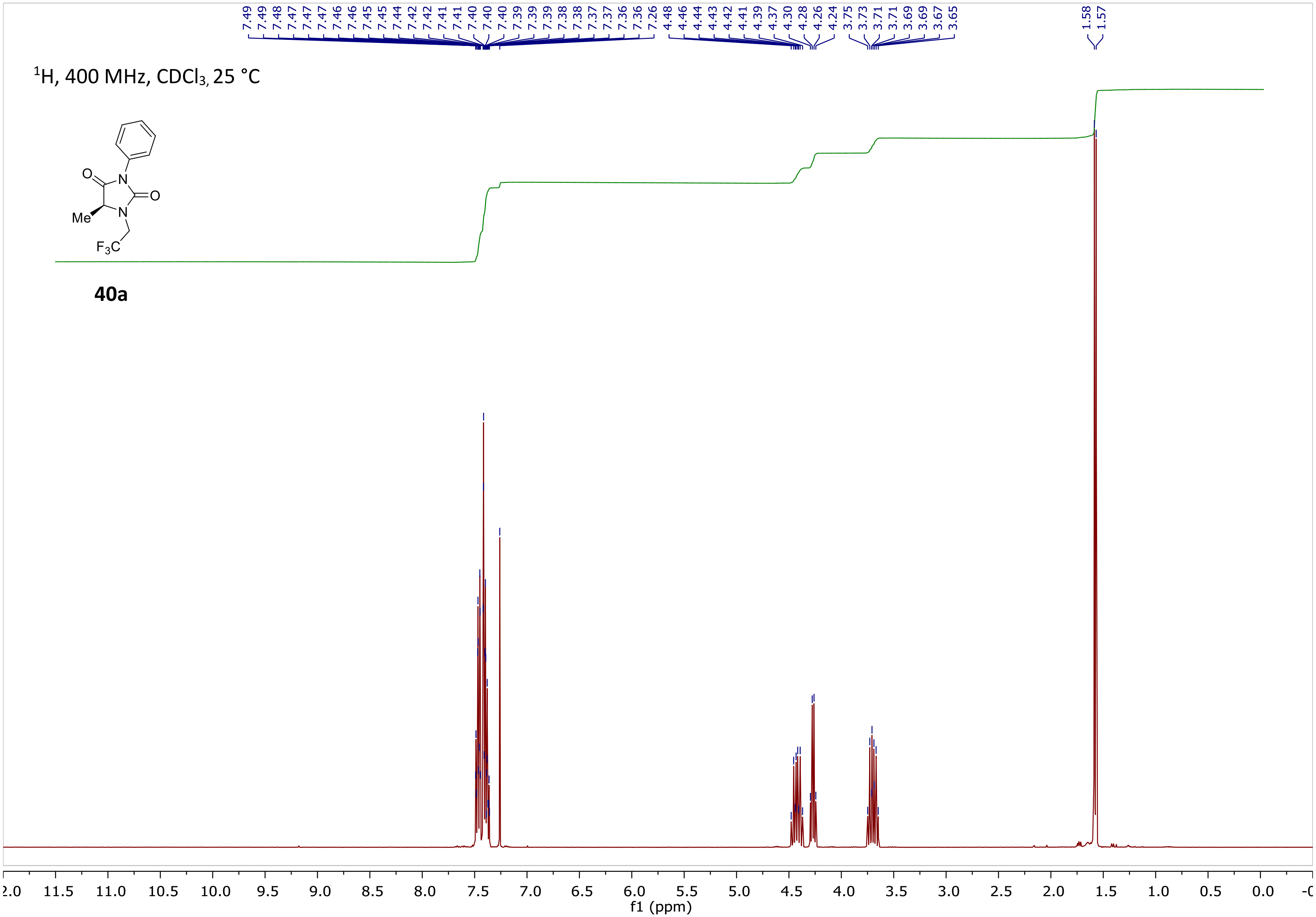
^{13}C, 100 MHz, $CDCl_3$, 25 °C

37a


7.48
7.47
7.47
7.47
7.46
7.45
7.45
7.41
7.40
7.39
7.39
7.39
7.38
7.38
7.38
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.26
5.09
5.05
4.26
4.23
3.98
3.96
3.94
3.93
1.49
1.47
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
O
Me
N
Bn
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)

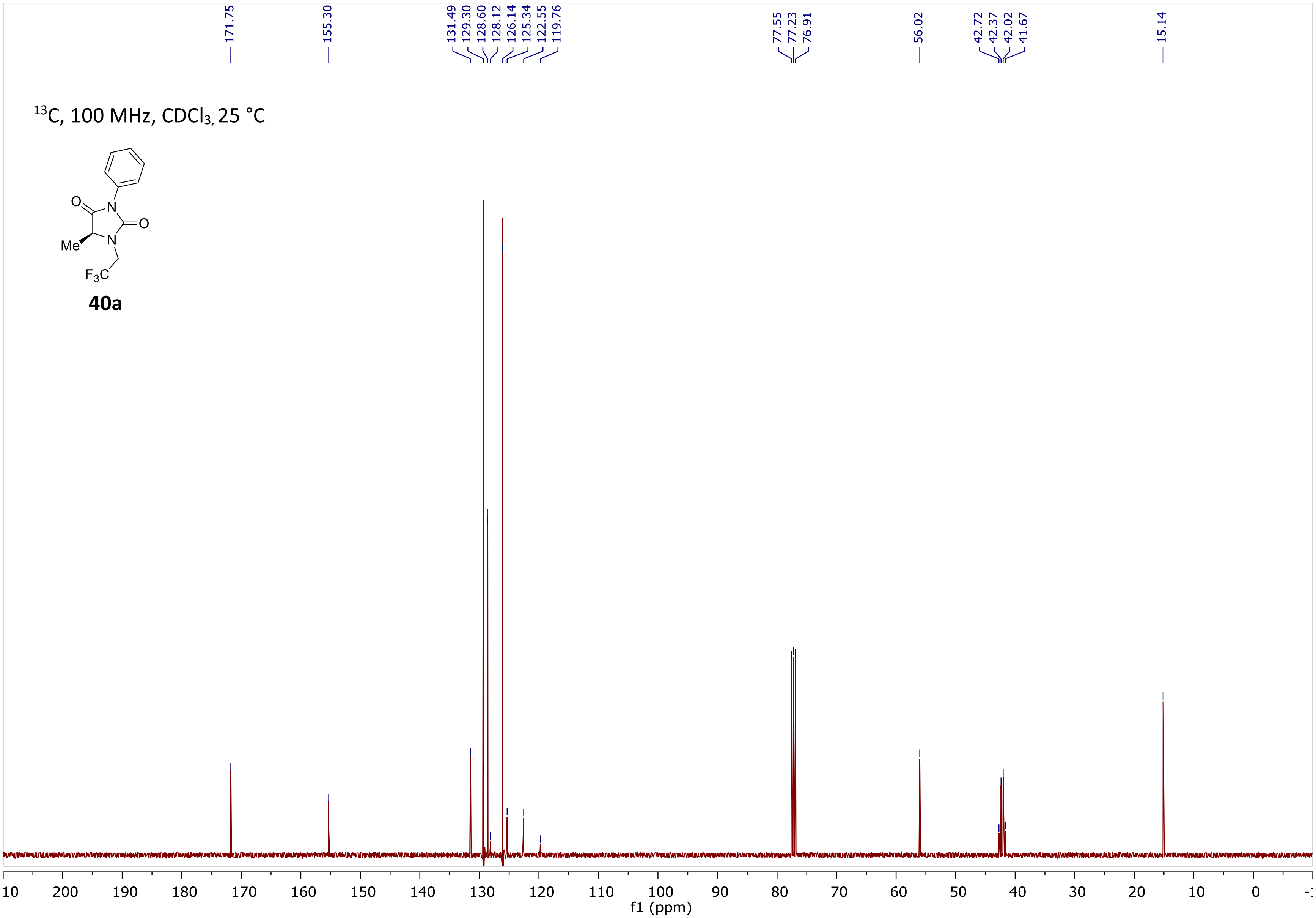
41a

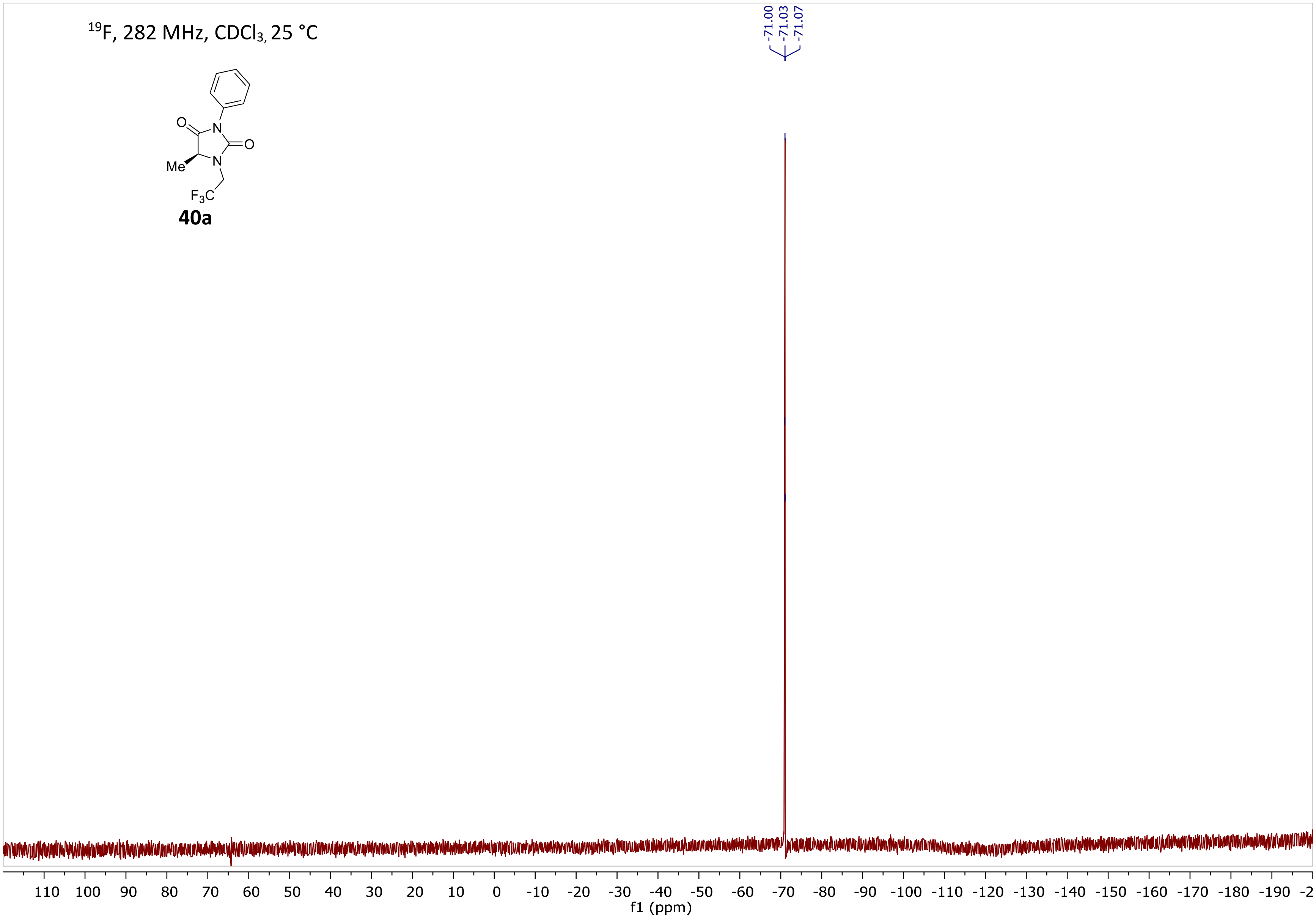

^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
O
Me
N
Bn
41a
172.42
155.18
135.67
131.87
129.05
129.02
128.26
128.22
128.04
126.00
77.43
77.11
76.79
54.66
44.82
15.41
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.49
7.49
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.26
4.48
4.46
4.44
4.43
4.42
4.41
4.39
4.37
4.30
4.28
4.26
4.24
3.75
3.73
3.71
3.71
3.69
3.69
3.67
3.65
1.58
1.57
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
O
Me
N
F$_3$C
40a
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

^{13}C, 100 MHz, $CDCl_3$, 25 °C

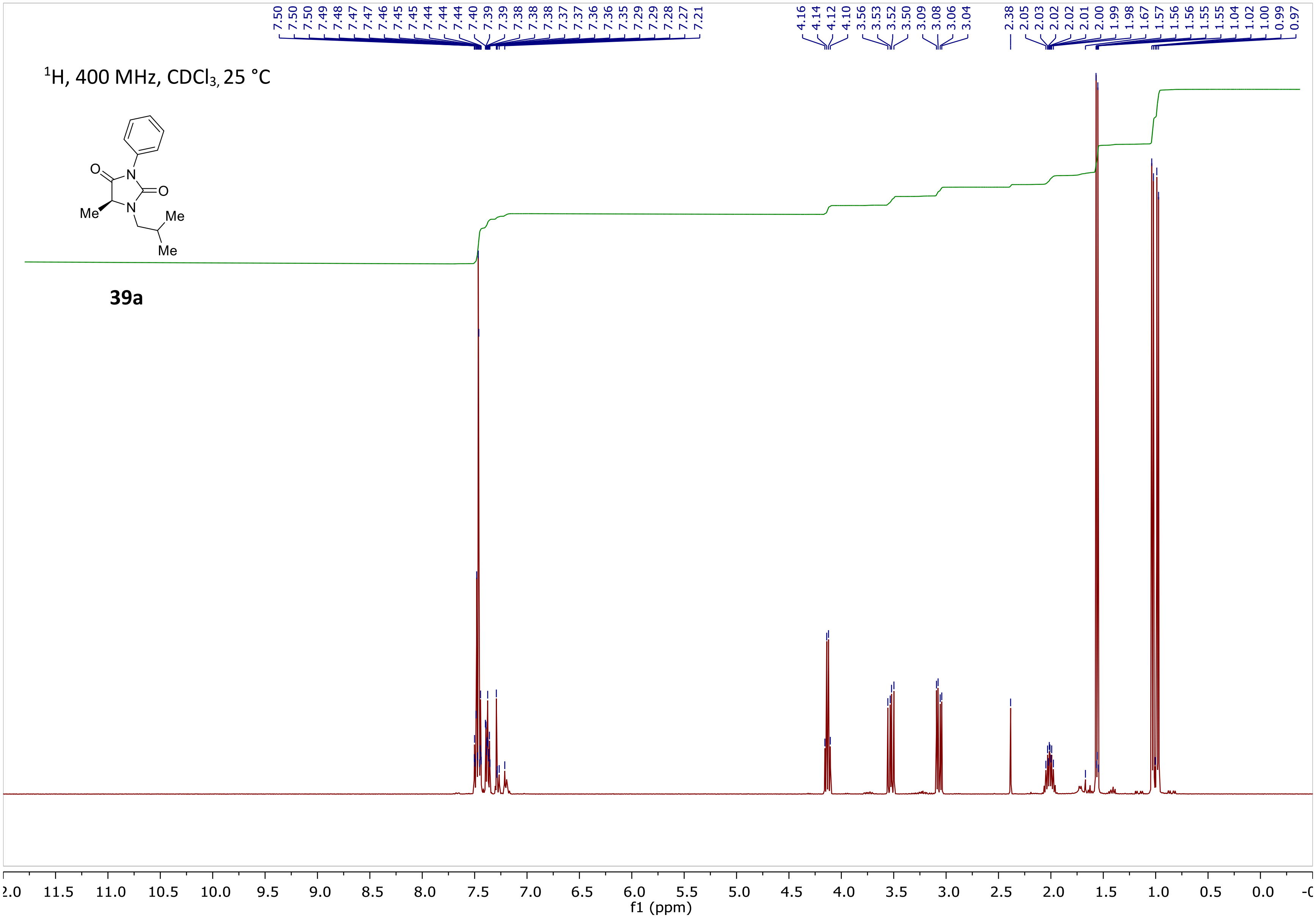
40a



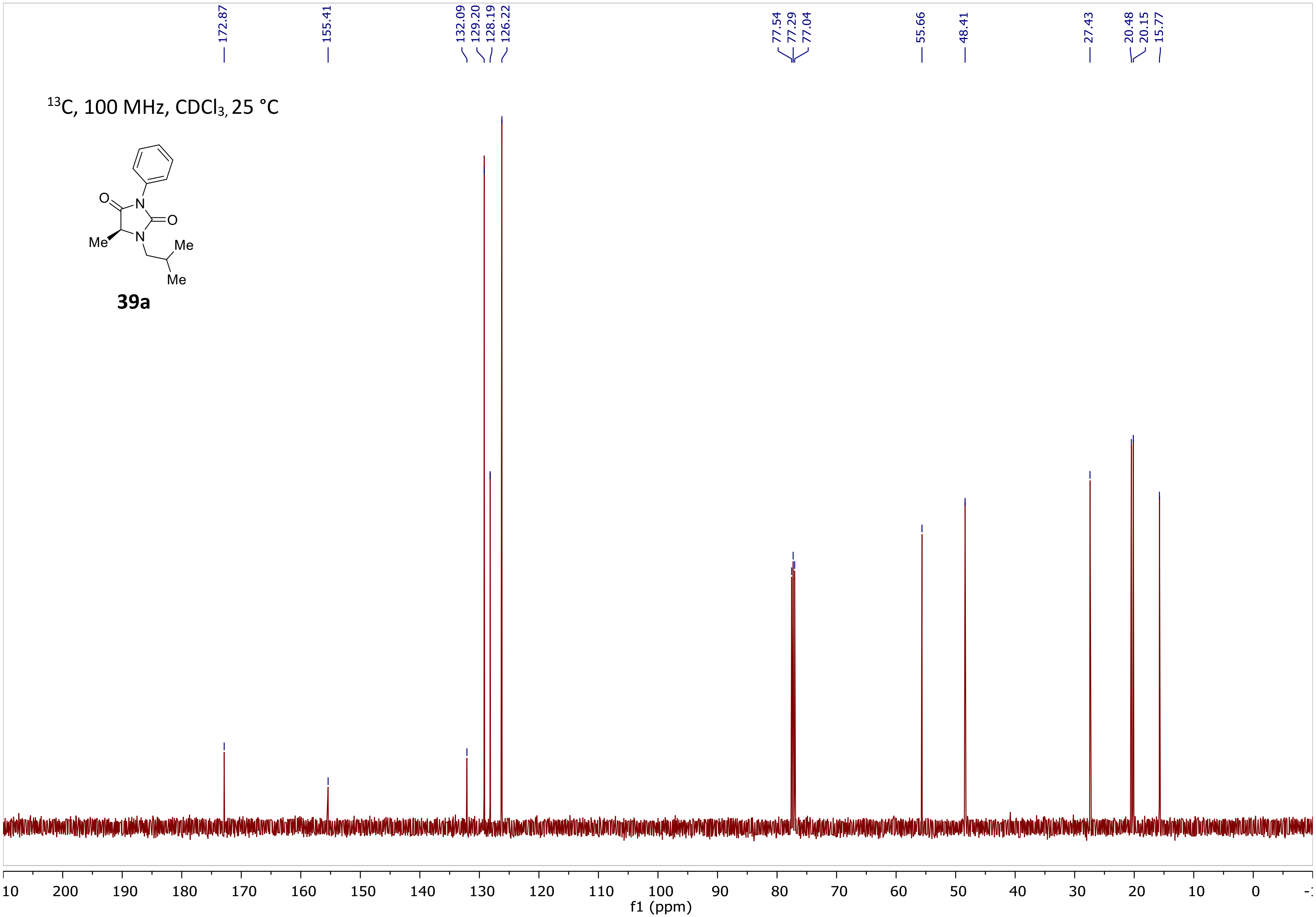


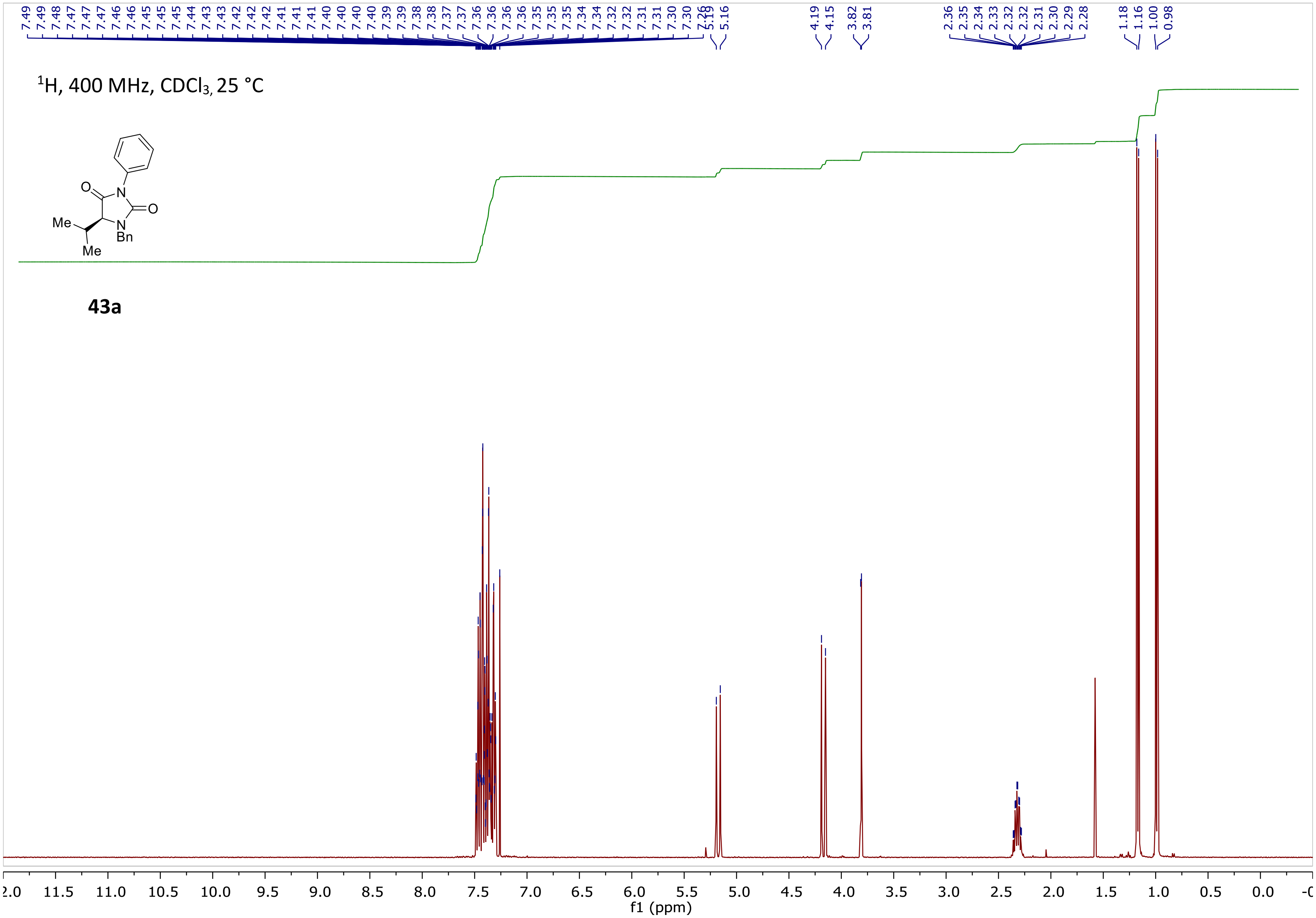
^{19}F, 282 MHz, $CDCl_3$, 25 °C

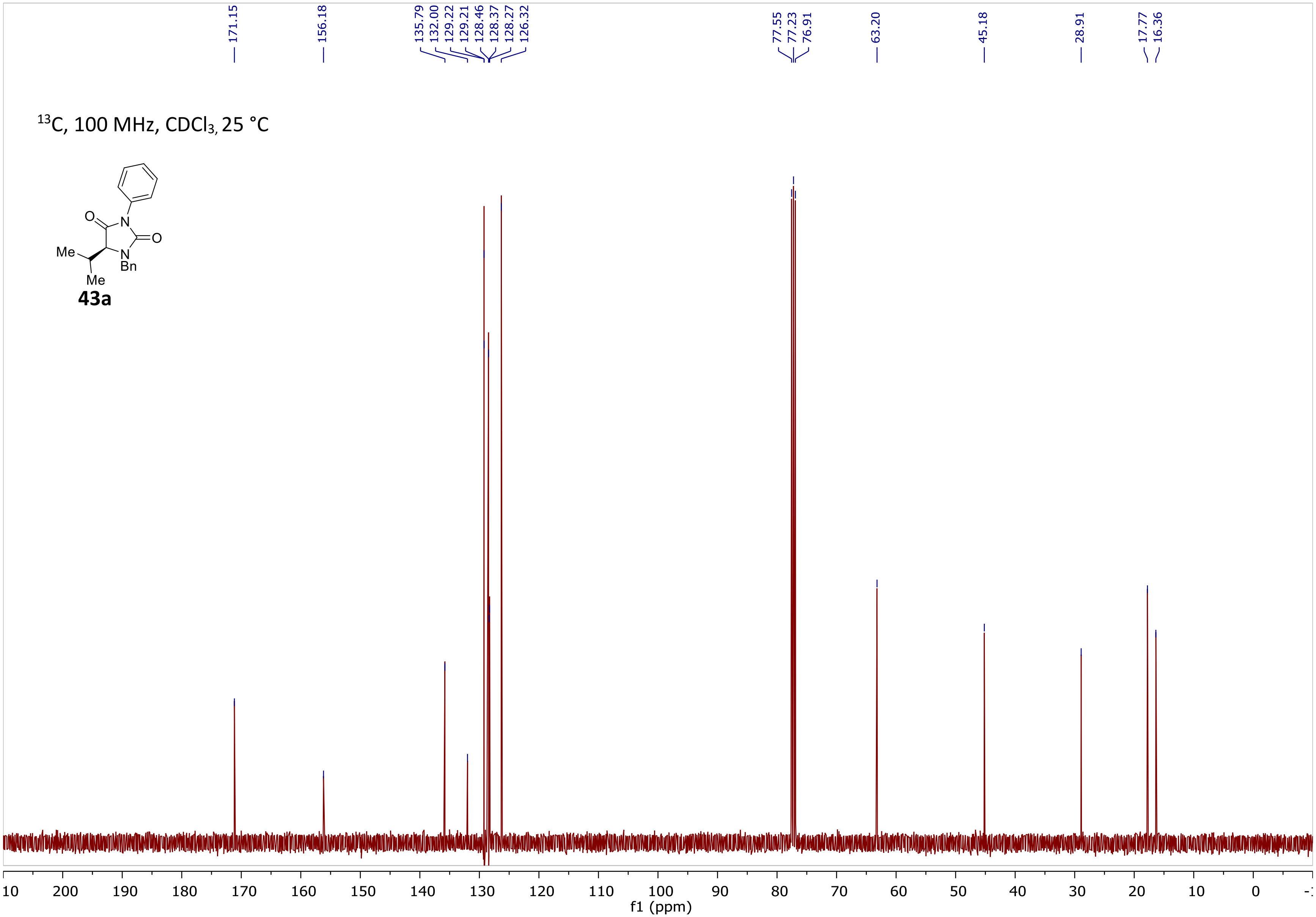
40a

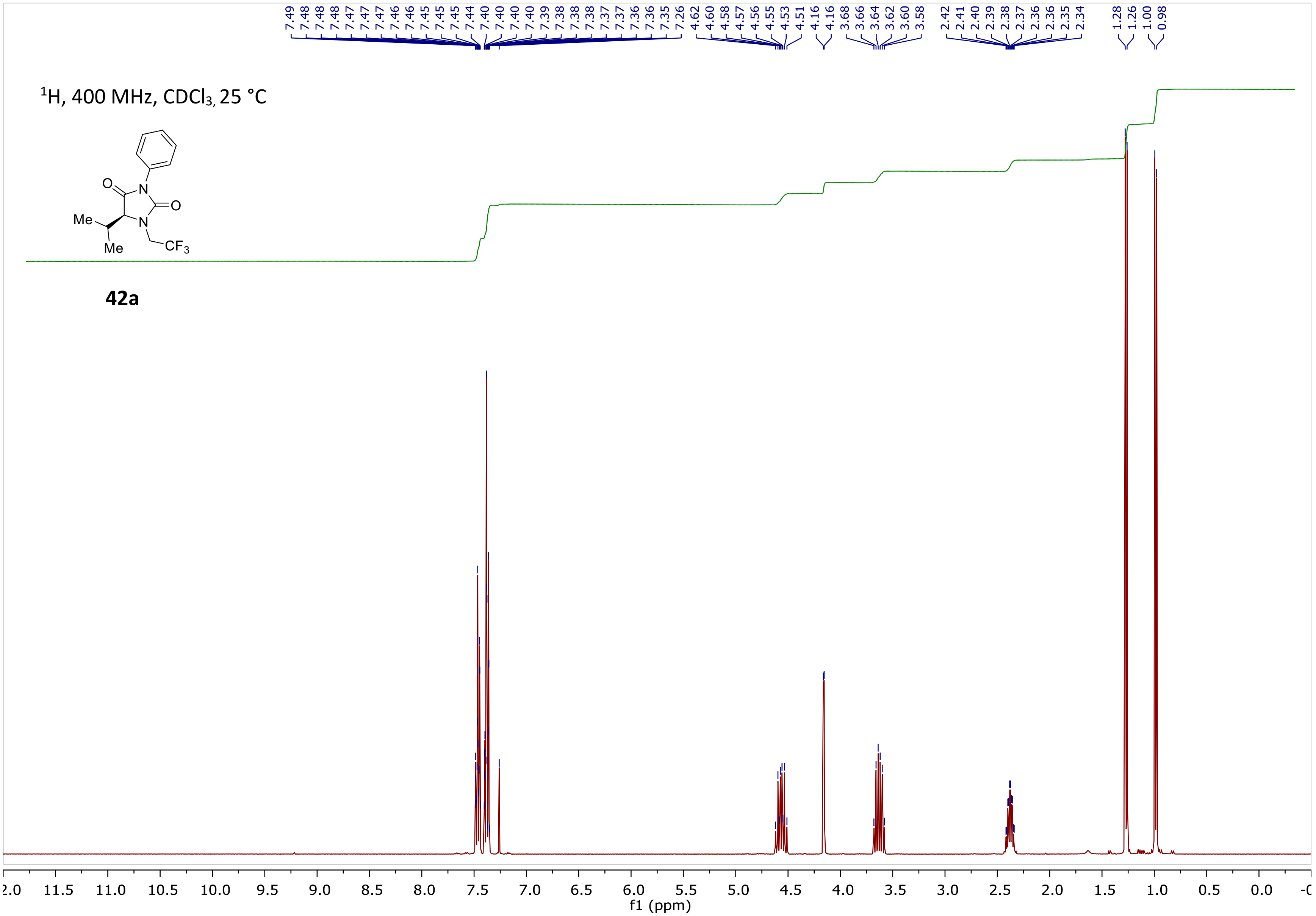

^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
O
Me
N
Me
Me
7.50
7.50
7.50
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.44
7.44
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.29
7.29
7.28
7.27
7.21
4.16
4.14
4.12
4.10
3.56
3.53
3.52
3.50
3.09
3.08
3.06
3.04
2.38
2.05
2.03
2.02
2.02
2.01
2.00
1.99
1.98
1.67
1.57
1.56
1.56
1.55
1.55
1.04
1.02
1.00
0.99
0.97
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)

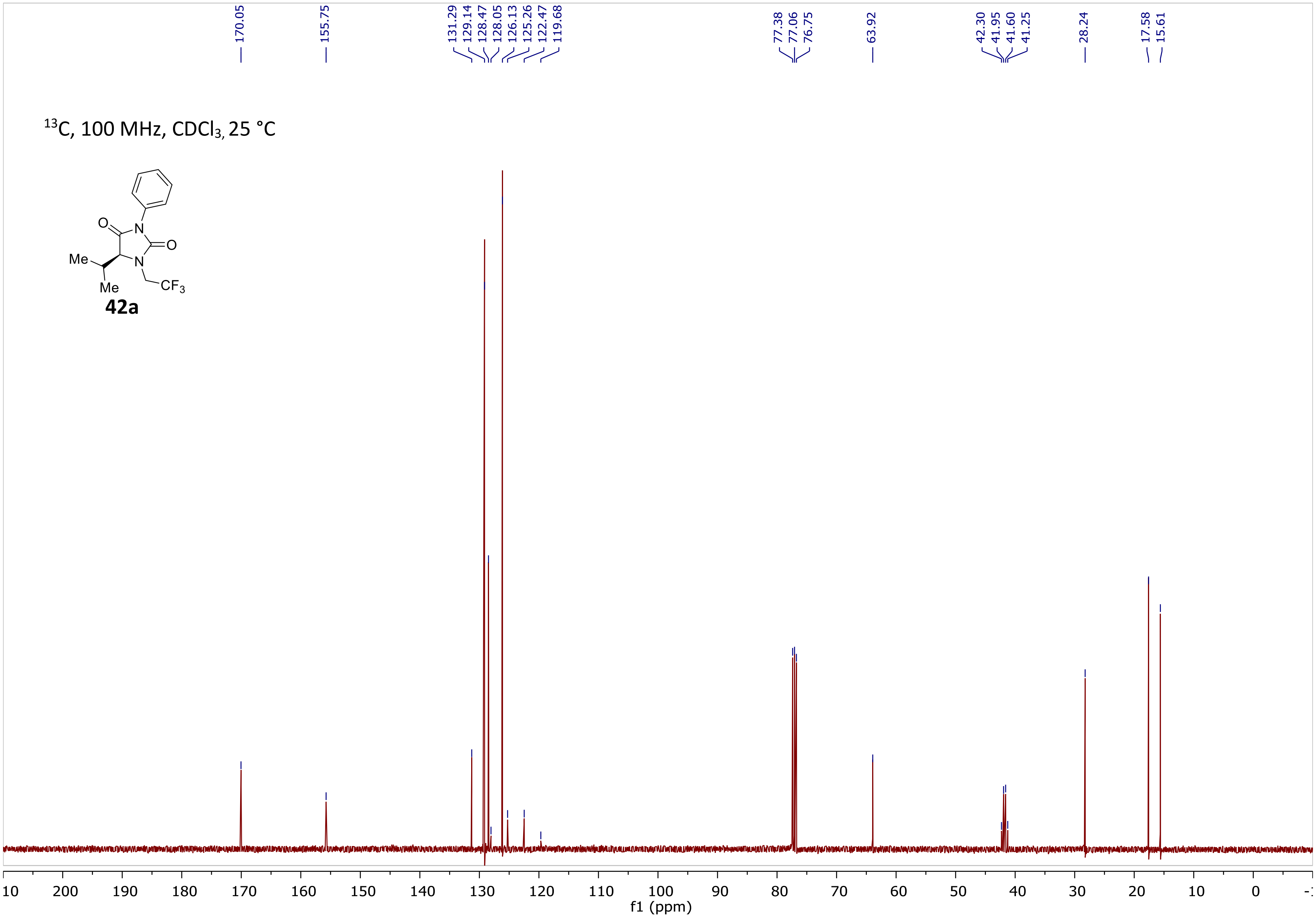
39a

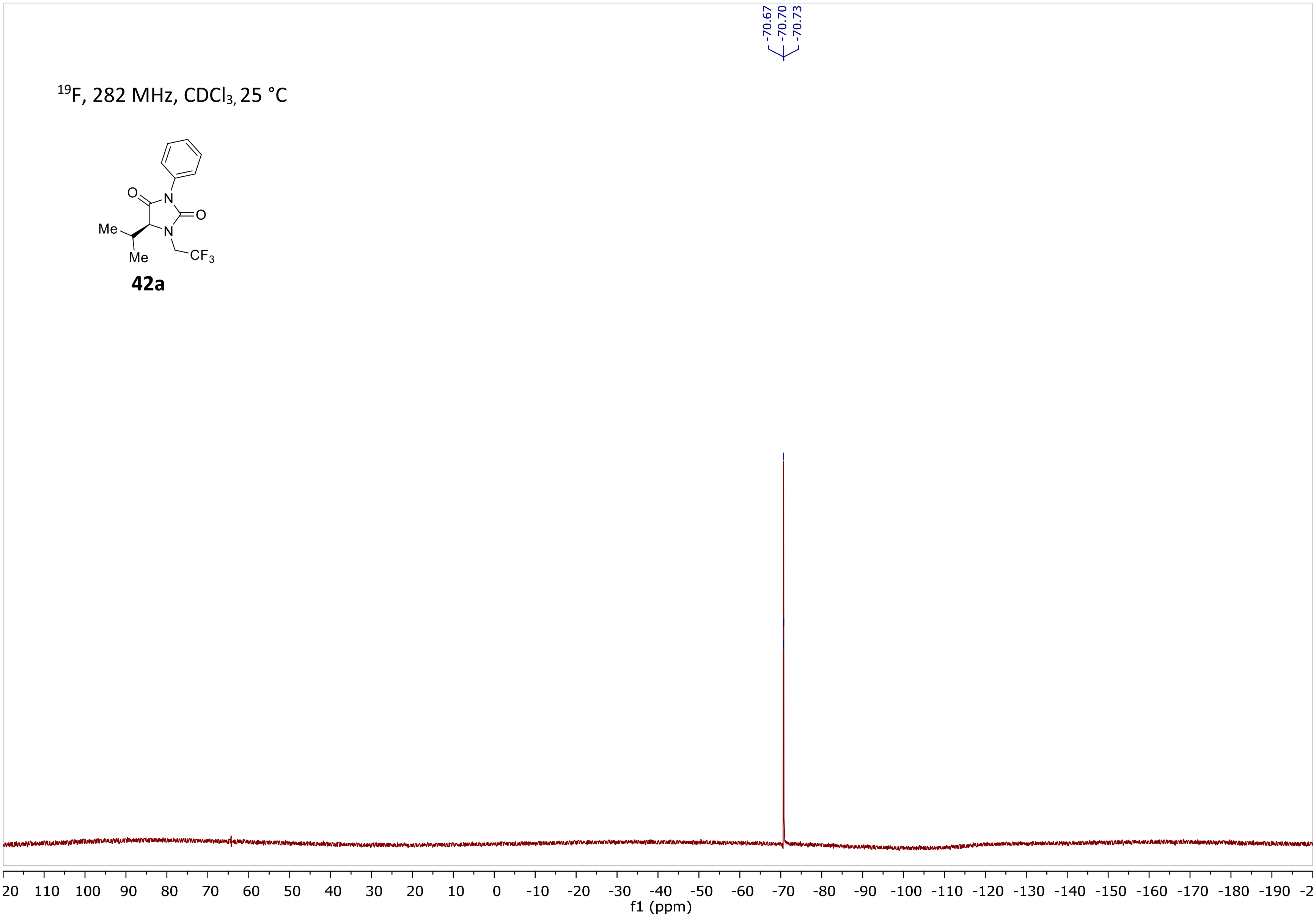

172.87
155.41
132.09
129.20
128.19
126.22
77.54
77.29
77.04
55.66
48.41
27.43
20.48
20.15
15.77
13C, 100 MHz, CDCl3, 25 °C
O
N
O
N
Me
Me
Me
39a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

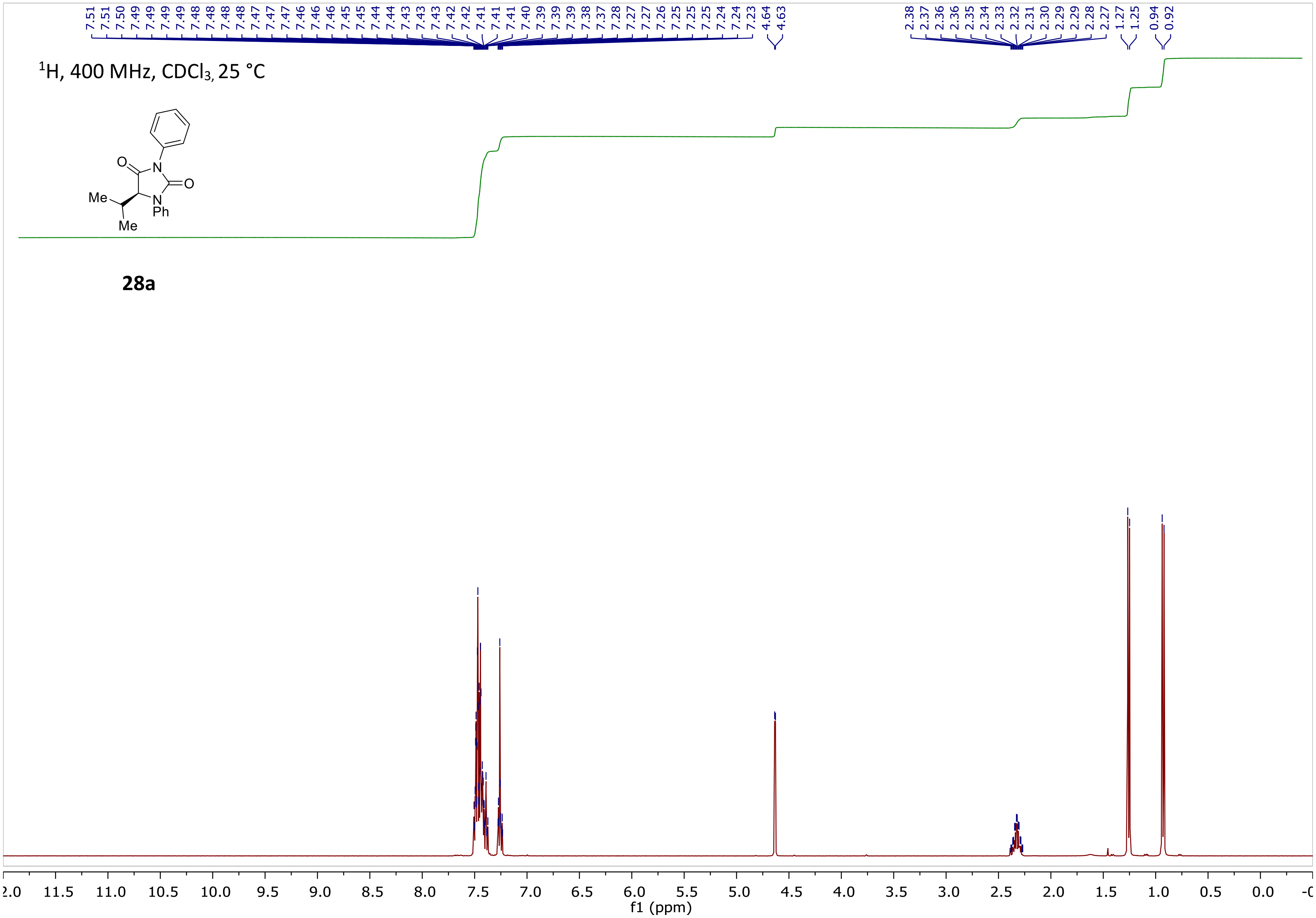

7.49
7.49
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.45
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.32
7.32
7.31
7.31
7.30
7.30
7.26
5.19
5.16
4.19
4.15
3.82
3.81
2.36
2.35
2.34
2.33
2.32
2.32
2.31
2.30
2.29
2.28
1.18
1.16
1.00
0.98
¹H, 400 MHz, CDCl₃, 25 °C
O
N
O
Me
N
Bn
Me
43a
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


171.15
156.18
135.79
132.00
129.22
129.21
128.46
128.37
128.27
126.32
77.55
77.23
76.91
63.20
45.18
28.91
17.77
16.36
13C, 100 MHz, CDCl3, 25 °C
O
N
O
Me
N
Bn
Me
43a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

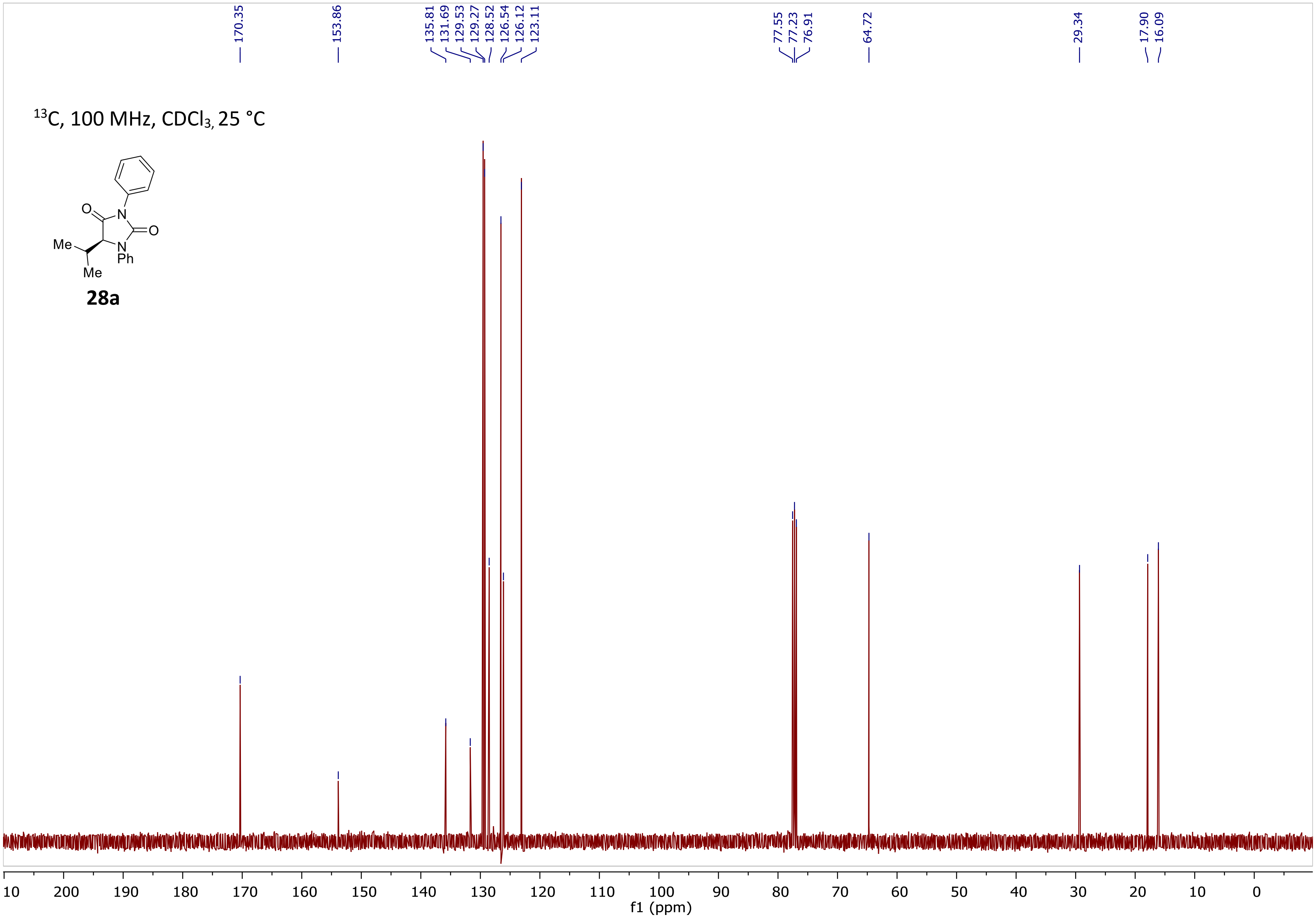

7.49
7.48
7.48
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.45
7.44
7.40
7.40
7.40
7.40
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.26
4.62
4.60
4.58
4.57
4.56
4.55
4.53
4.51
4.16
4.16
3.68
3.66
3.64
3.62
3.60
3.58
2.42
2.41
2.40
2.39
2.38
2.37
2.36
2.36
2.35
2.34
1.28
1.26
1.00
0.98
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
O
Me
N
Me
CF$_3$
42a
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

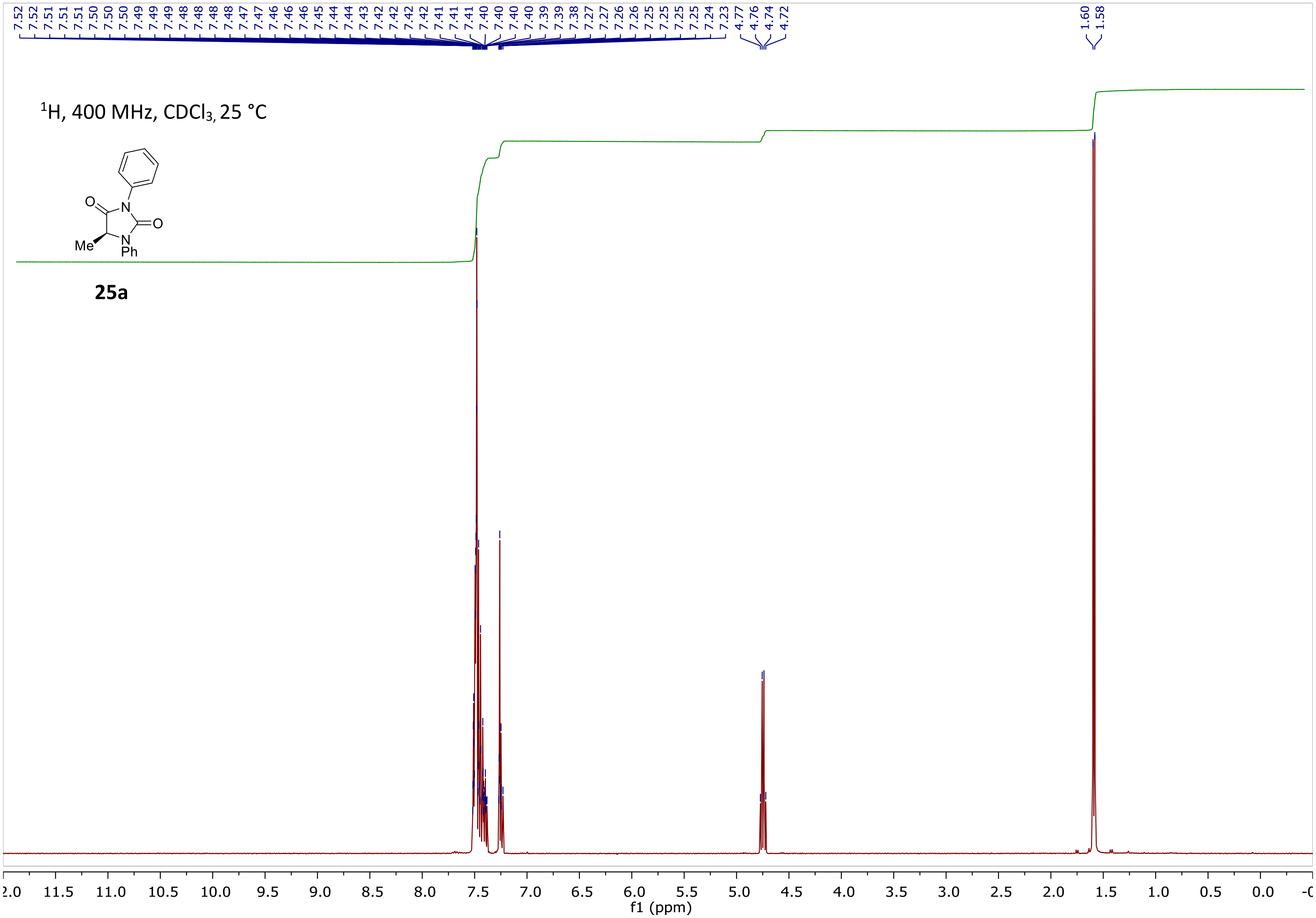

170.05
155.75
131.29
129.14
128.47
128.05
126.13
125.26
122.47
119.68
77.38
77.06
76.75
63.92
42.30
41.95
41.60
41.25
28.24
17.58
15.61
13C, 100 MHz, CDCl3, 25 °C
O
N
O
Me
N
Me
CF3
42a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-70.67
-70.70
-70.73
^{19}F, 282 MHz, CDCl$_3$, 25 °C
O
N
O
Me
N
Me
CF$_3$
42a
20
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

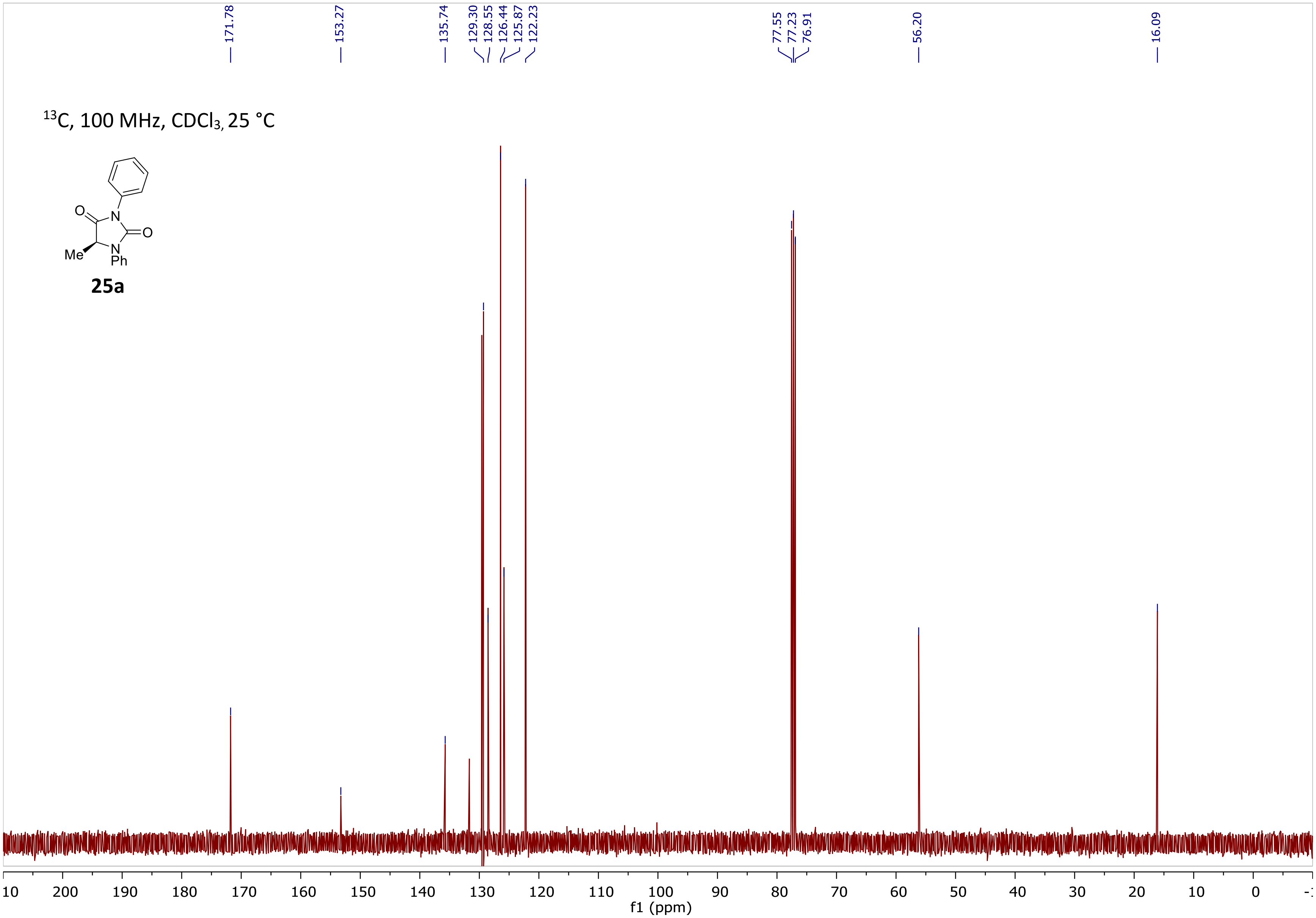

7.51
7.51
7.50
7.49
7.49
7.49
7.48
7.48
7.48
7.48
7.47
7.47
7.46
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.28
7.27
7.27
7.26
7.25
7.25
7.25
7.24
7.24
7.23
4.64
4.63
2.38
2.37
2.36
2.36
2.35
2.34
2.33
2.32
2.31
2.30
2.29
2.29
2.28
2.27
1.27
1.25
0.94
0.92
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
O
Me
N
Ph
Me
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

28a


170.35
153.86
135.81
131.69
129.53
129.27
128.52
126.54
126.12
123.11
77.55
77.23
76.91
64.72
29.34
17.90
16.09
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
O
Me
N
Ph
Me
28a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

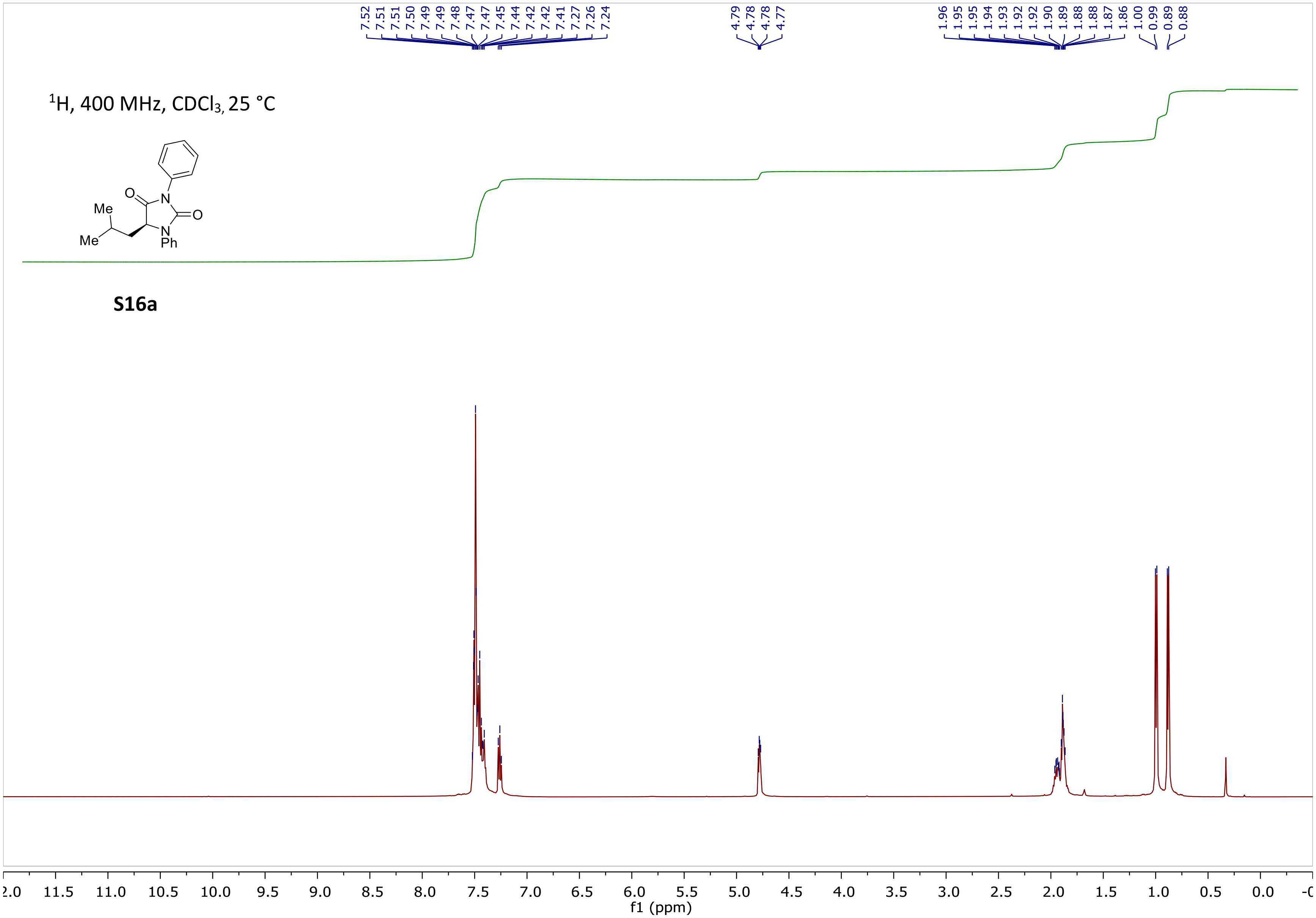

7.52
7.52
7.51
7.51
7.51
7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.40
7.39
7.39
7.38
7.27
7.27
7.26
7.25
7.25
7.25
7.25
7.24
7.23
4.77
4.76
4.74
4.72
1.60
1.58
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
O
N
Me
Ph
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

25a

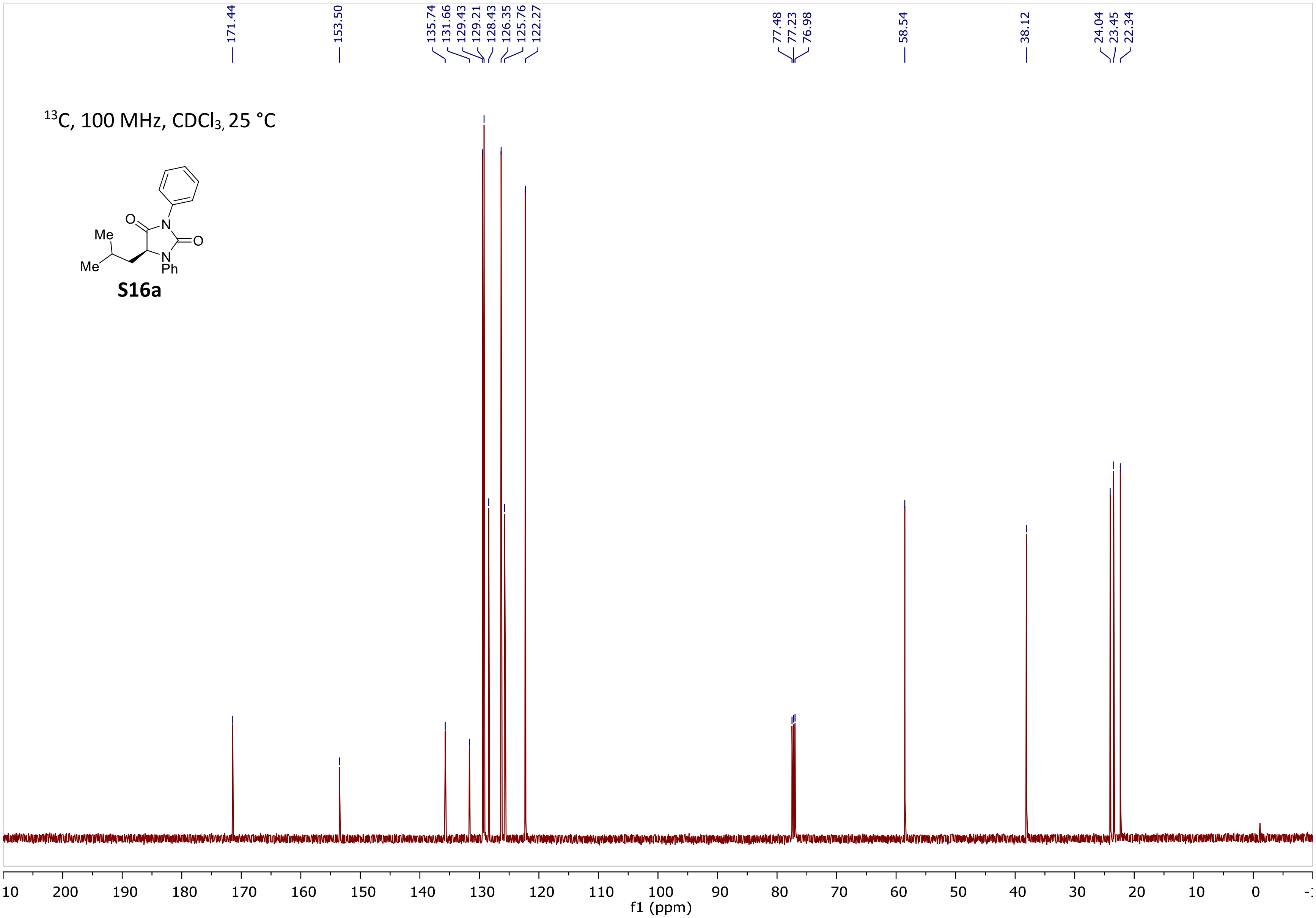


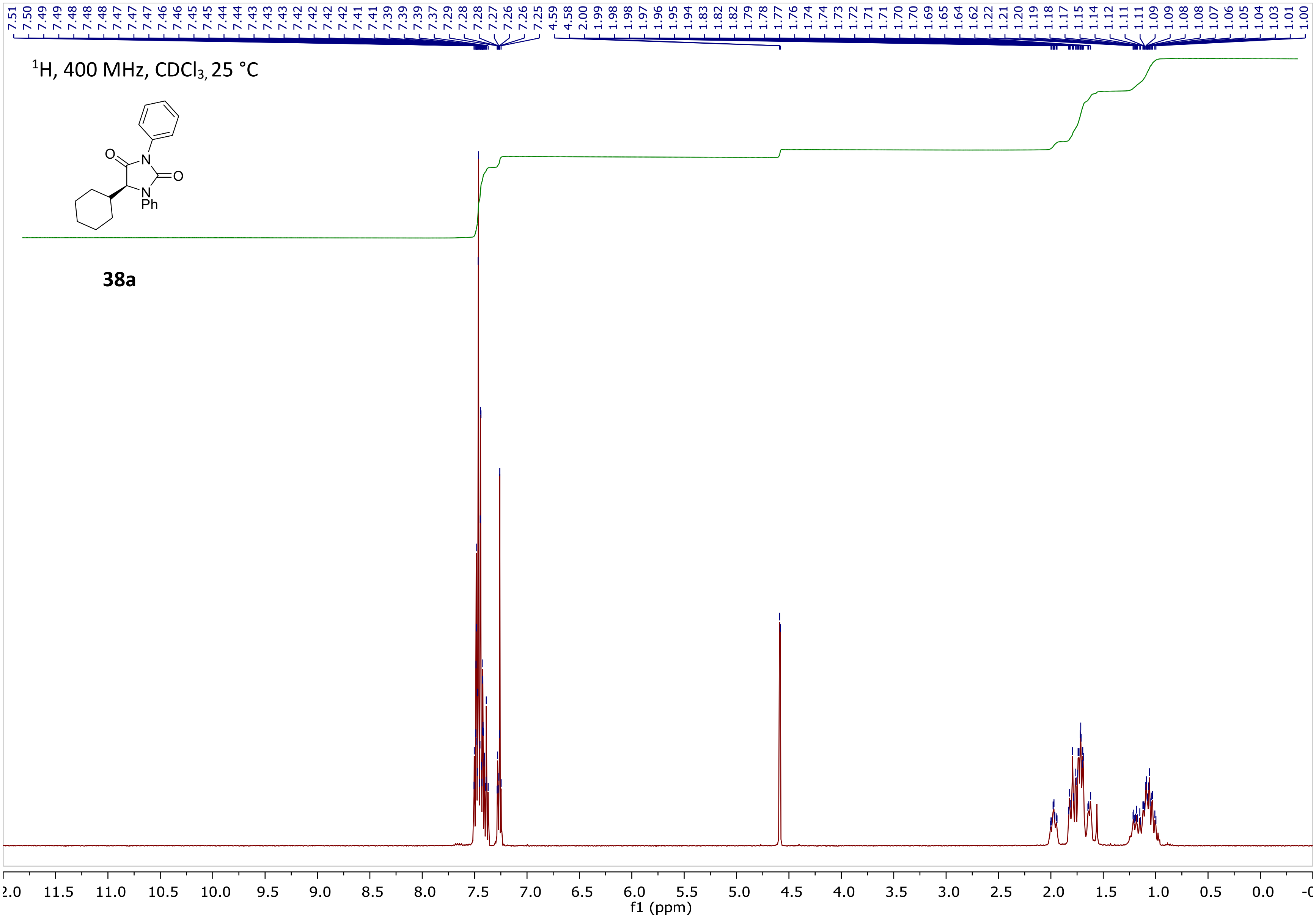
^{13}C, 100 MHz, $CDCl_3$, 25 °C

25a

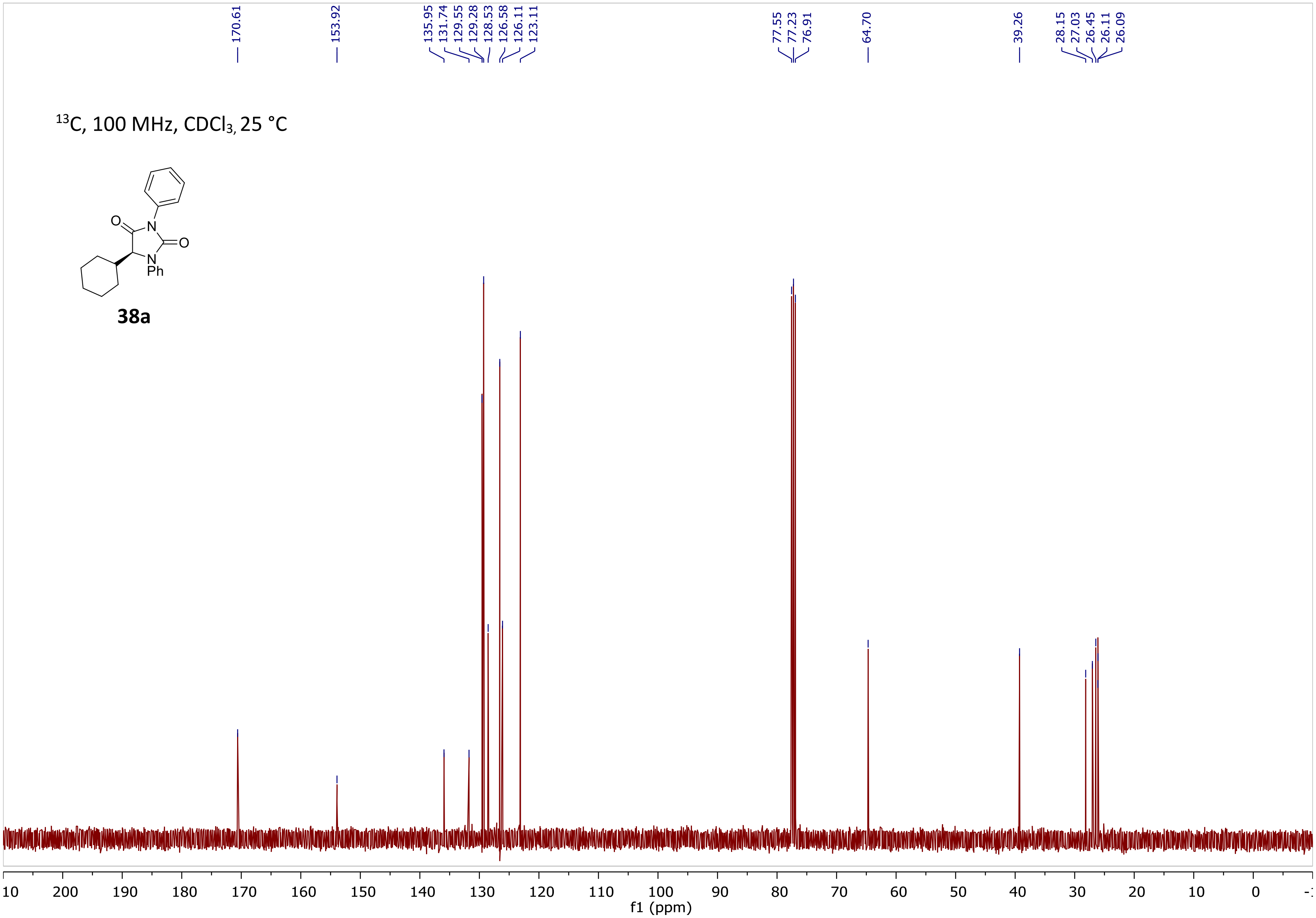

7.52
7.51
7.51
7.50
7.49
7.48
7.47
7.47
7.45
7.44
7.42
7.42
7.41
7.27
7.26
7.24
4.79
4.78
4.78
4.77
1.96
1.95
1.95
1.94
1.93
1.92
1.92
1.90
1.89
1.88
1.88
1.87
1.86
1.00
0.99
0.89
0.88
^{1}H, 400 MHz, CDCl$_3$, 25 °C
Me
Me
O
N
O
N
Ph
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-
f1 (ppm)

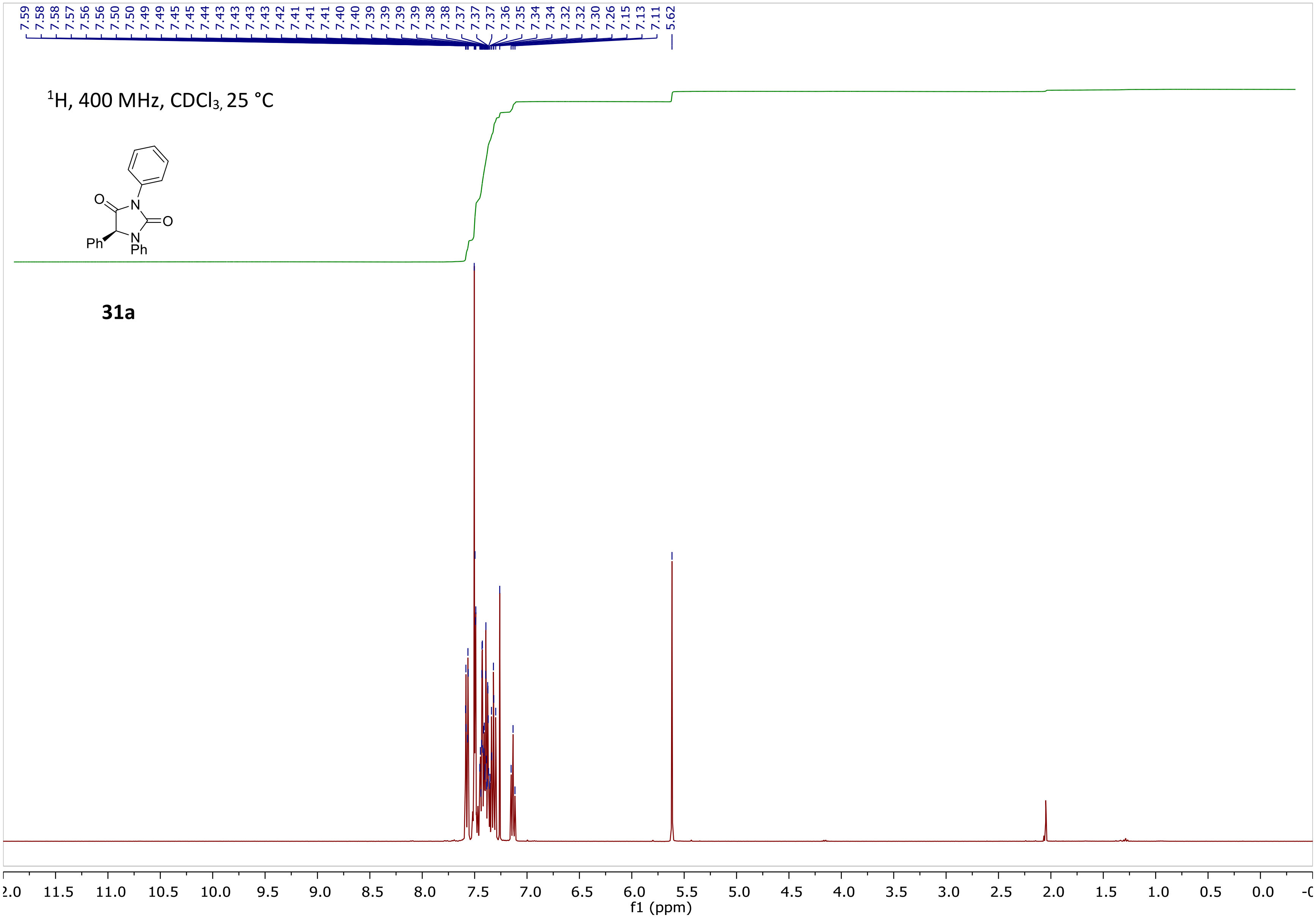
S16a


171.44
153.50
135.74
131.66
129.43
129.21
128.43
126.35
125.76
122.27
77.48
77.23
76.98
58.54
38.12
24.04
23.45
22.34
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
O
Me
Me
N
Ph
S16a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.51 7.50 7.49 7.49 7.48 7.48 7.48 7.47 7.47 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.42 7.42 7.41 7.41 7.41 7.39 7.39 7.37 7.29 7.28 7.28 7.27 7.26 7.26 7.25 4.59 4.58 2.00 1.99 1.98 1.98 1.97 1.96 1.95 1.94 1.83 1.82 1.82 1.79 1.78 1.77 1.76 1.74 1.74 1.73 1.72 1.71 1.71 1.70 1.70 1.69 1.65 1.64 1.62 1.22 1.21 1.20 1.19 1.18 1.17 1.15 1.14 1.12 1.11 1.11 1.09 1.09 1.08 1.08 1.07 1.06 1.05 1.04 1.03 1.01 1.00
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
O
N
Ph
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(
f1 (ppm)

38a

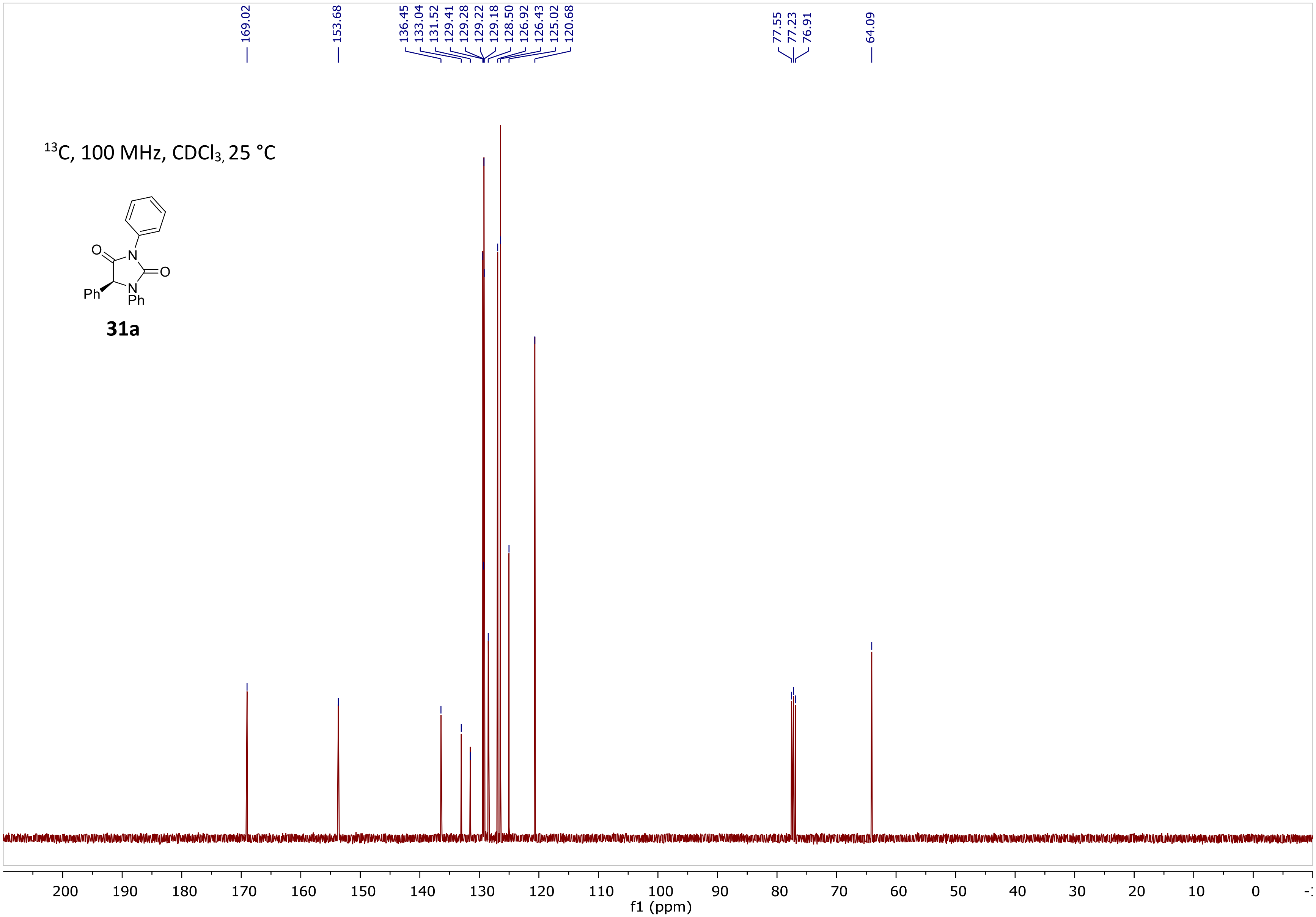

170.61
153.92
135.95
131.74
129.55
129.28
128.53
126.58
126.11
123.11
77.55
77.23
76.91
64.70
39.26
28.15
27.03
26.45
26.11
26.09
13C, 100 MHz, CDCl3, 25 °C
O
N
O
N
Ph
38a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)

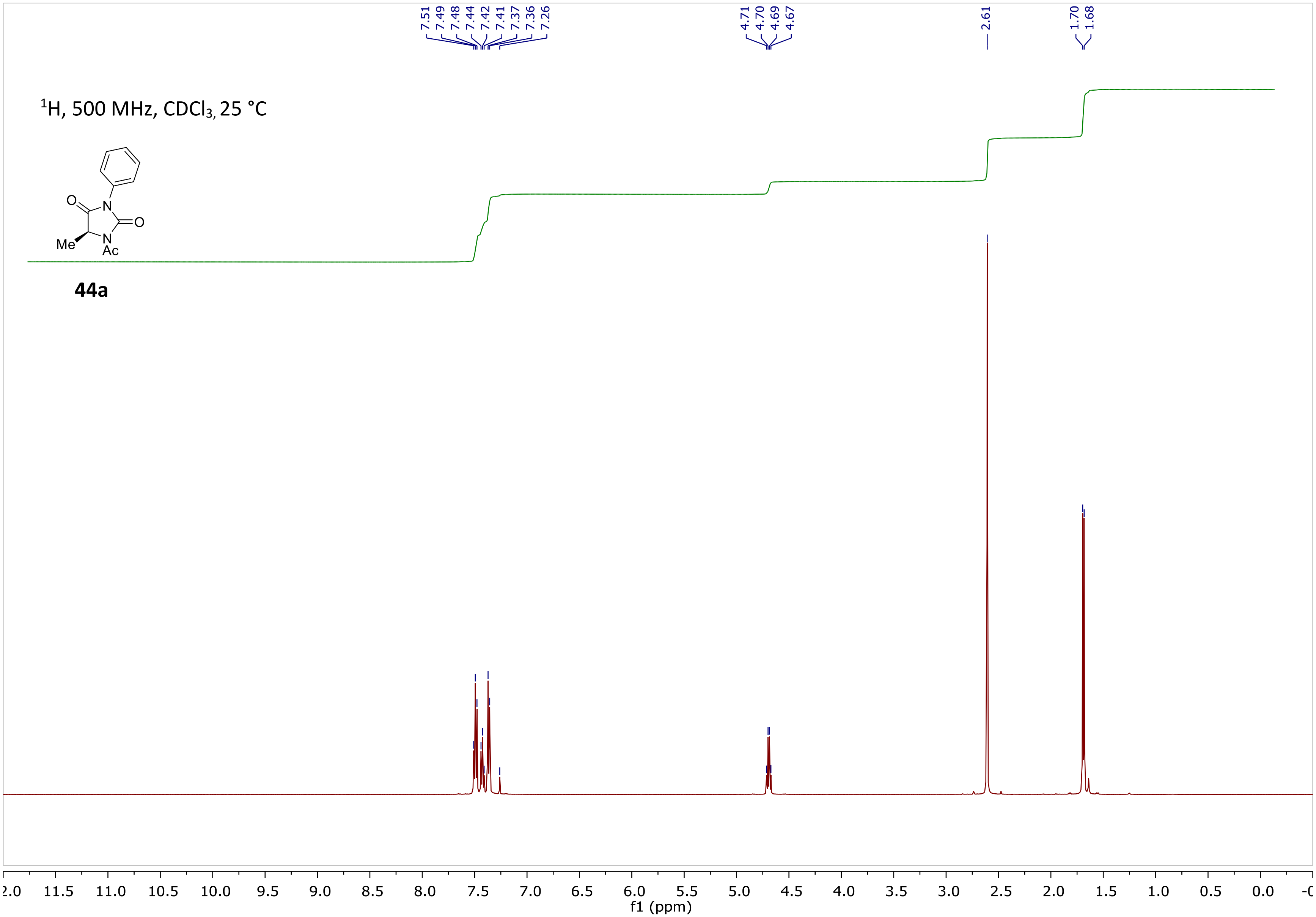

7.59
7.58
7.58
7.57
7.56
7.56
7.50
7.50
7.49
7.49
7.45
7.45
7.44
7.43
7.43
7.43
7.43
7.42
7.41
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.35
7.34
7.34
7.32
7.32
7.30
7.26
7.15
7.13
7.11
5.62
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
O
Ph
N
Ph
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

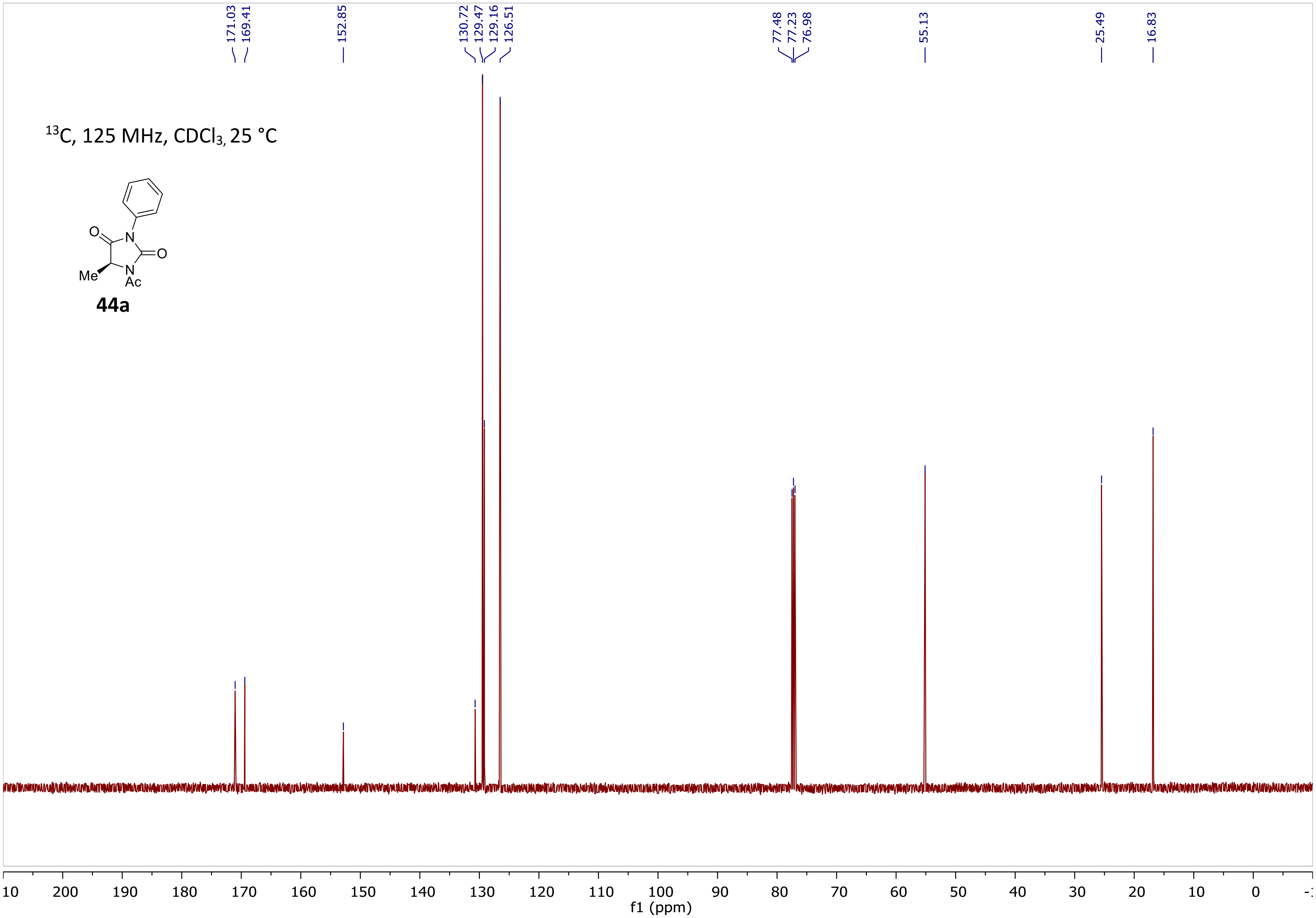
31a

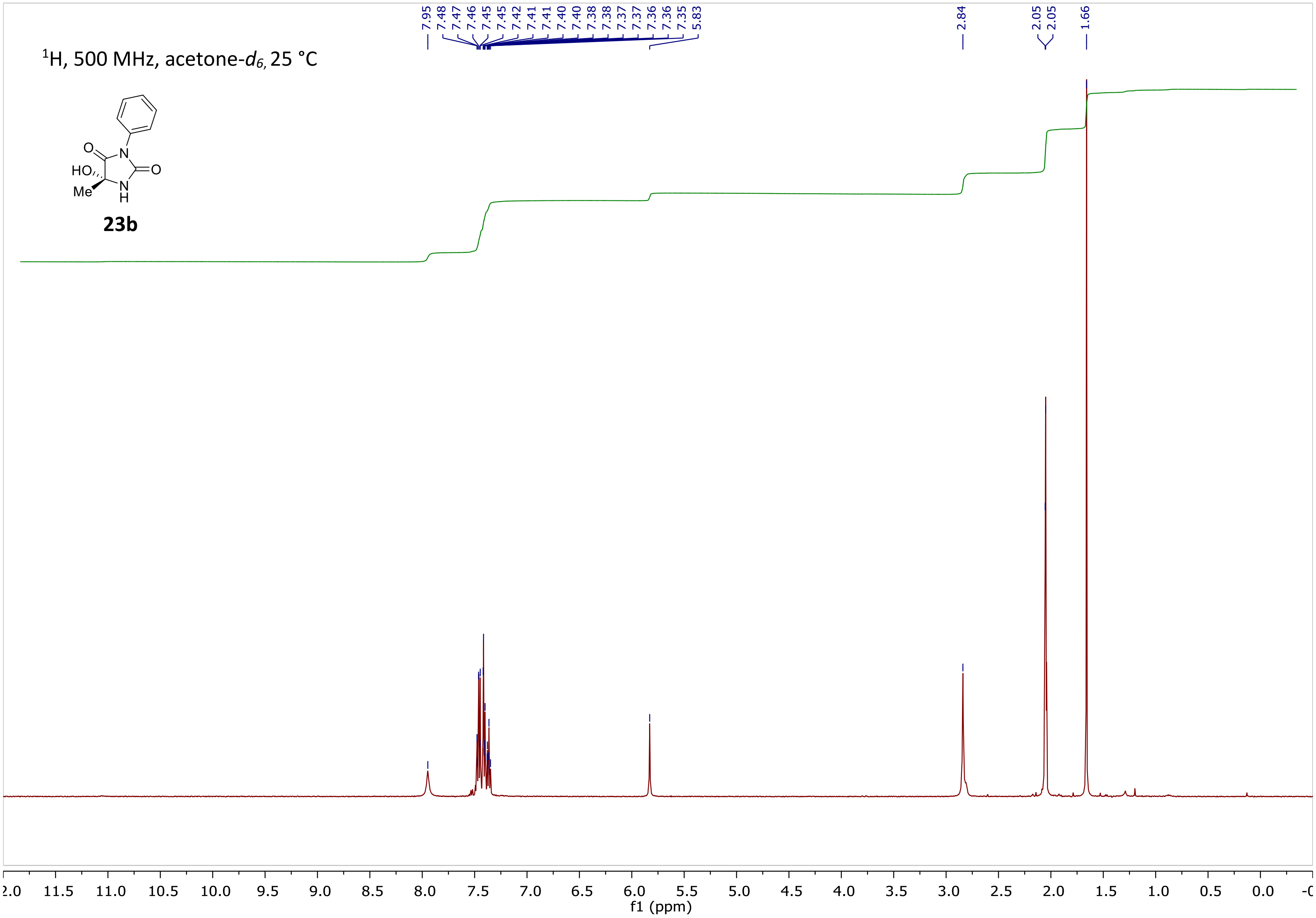
^{13}C, 100 MHz, CDCl$_3$, 25 °C

31a

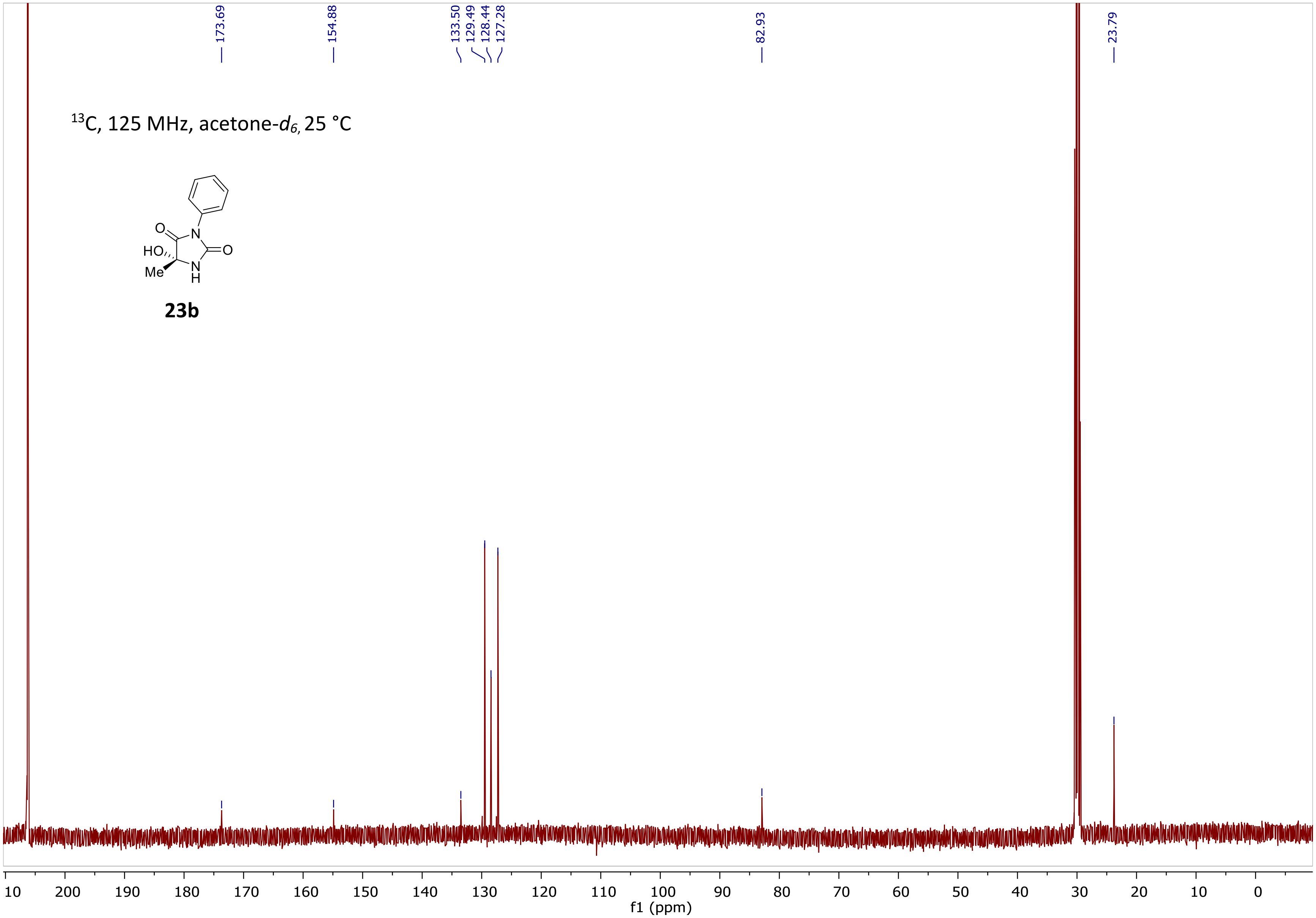


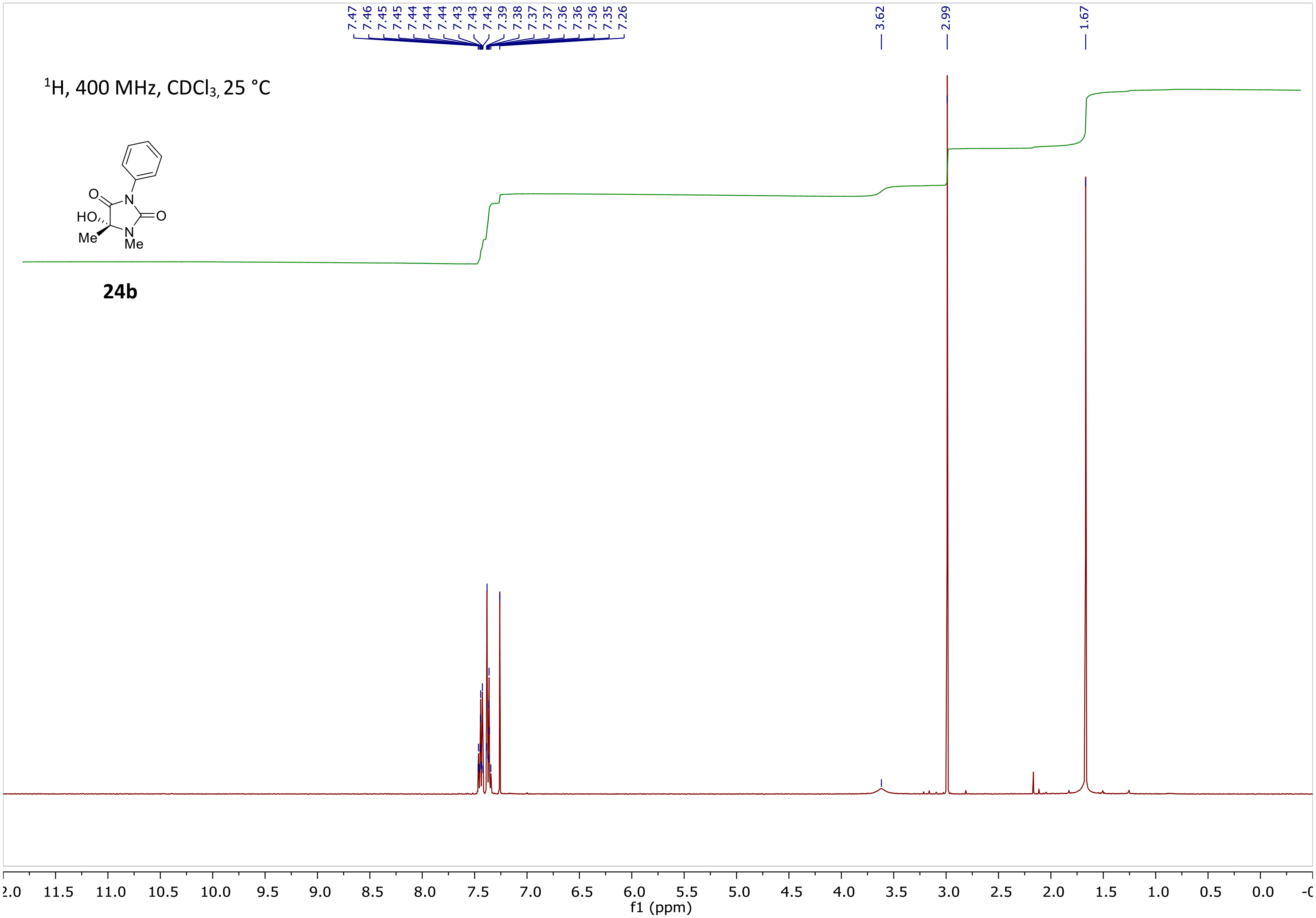

7.51
7.49
7.48
7.44
7.42
7.41
7.37
7.36
7.26
4.71
4.70
4.69
4.67
2.61
1.70
1.68
^{1}H, 500 MHz, CDCl$_3$, 25 °C
O
N
O
Me
N
Ac
44a
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


^{13}C, 125 MHz, CDCl$_3$, 25 °C
O
N
O
Me
N
Ac
44a
171.03
169.41
152.85
130.72
129.47
129.16
126.51
77.48
77.23
76.98
55.13
25.49
16.83
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

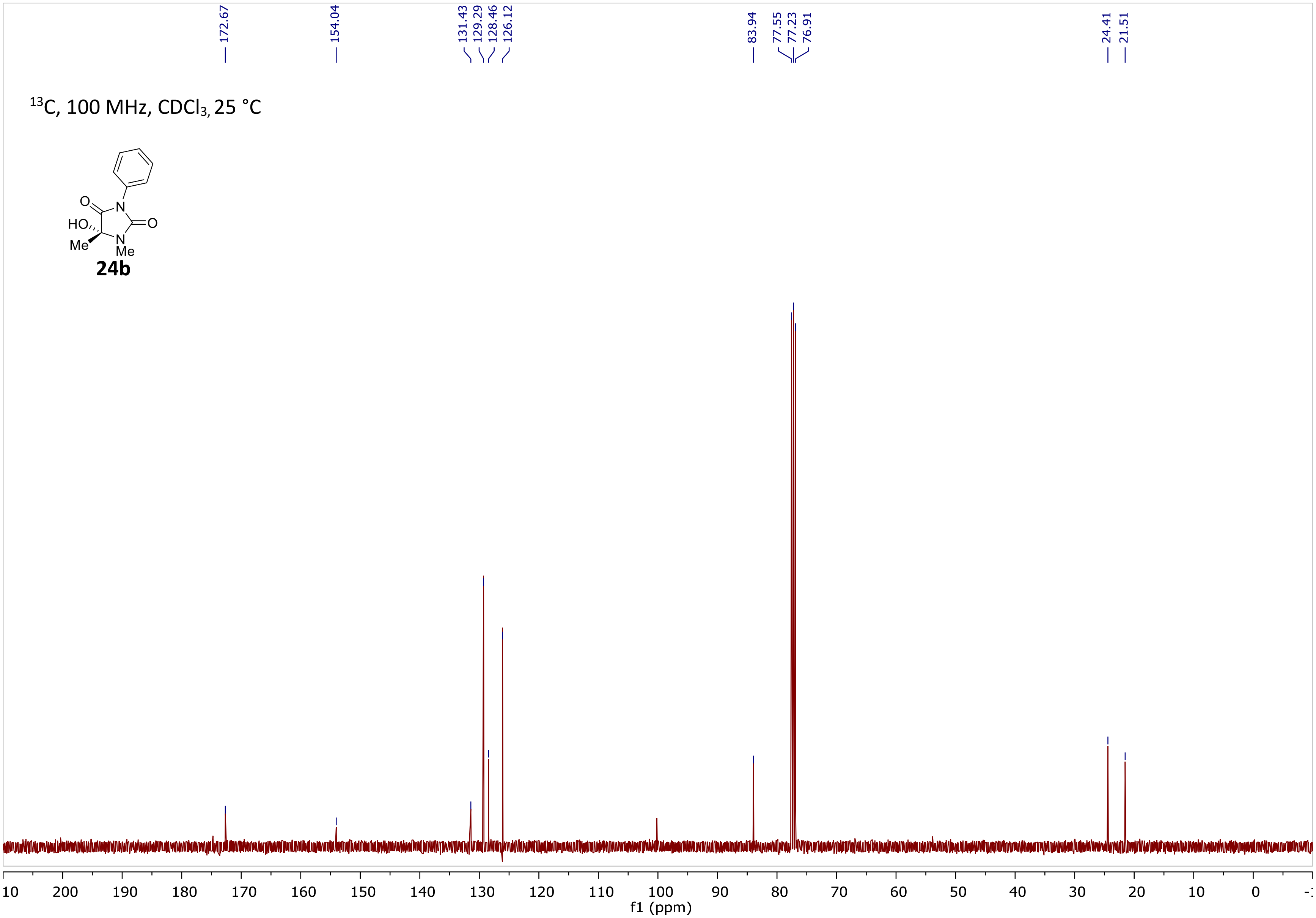

^{1}H, 500 MHz, acetone-d_6, 25 °C
O
N
HO
Me
N
H
O
7.95
7.48
7.47
7.46
7.45
7.45
7.42
7.41
7.41
7.40
7.40
7.38
7.38
7.37
7.37
7.36
7.36
7.35
5.83
2.84
2.05
2.05
1.66
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

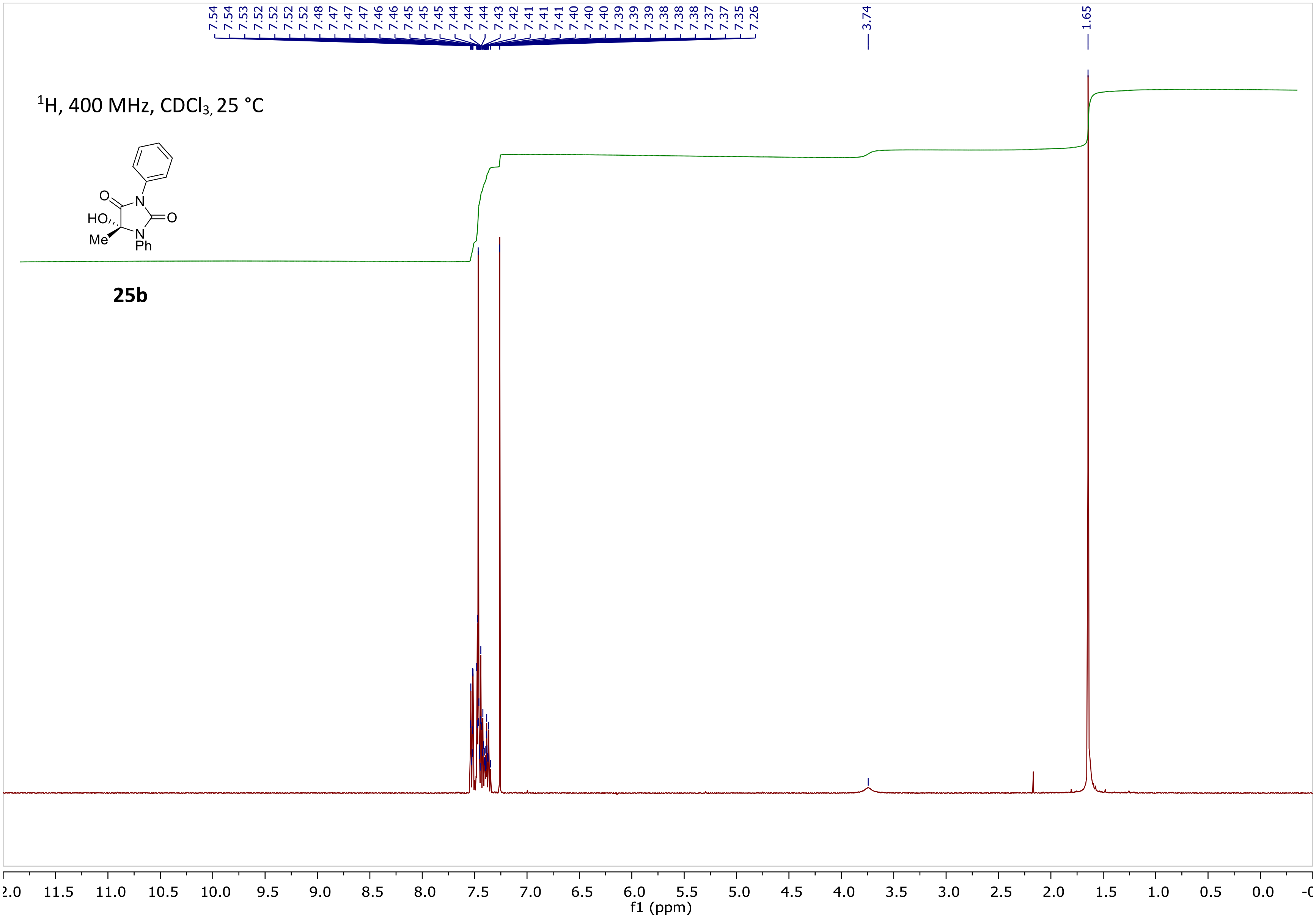
23b

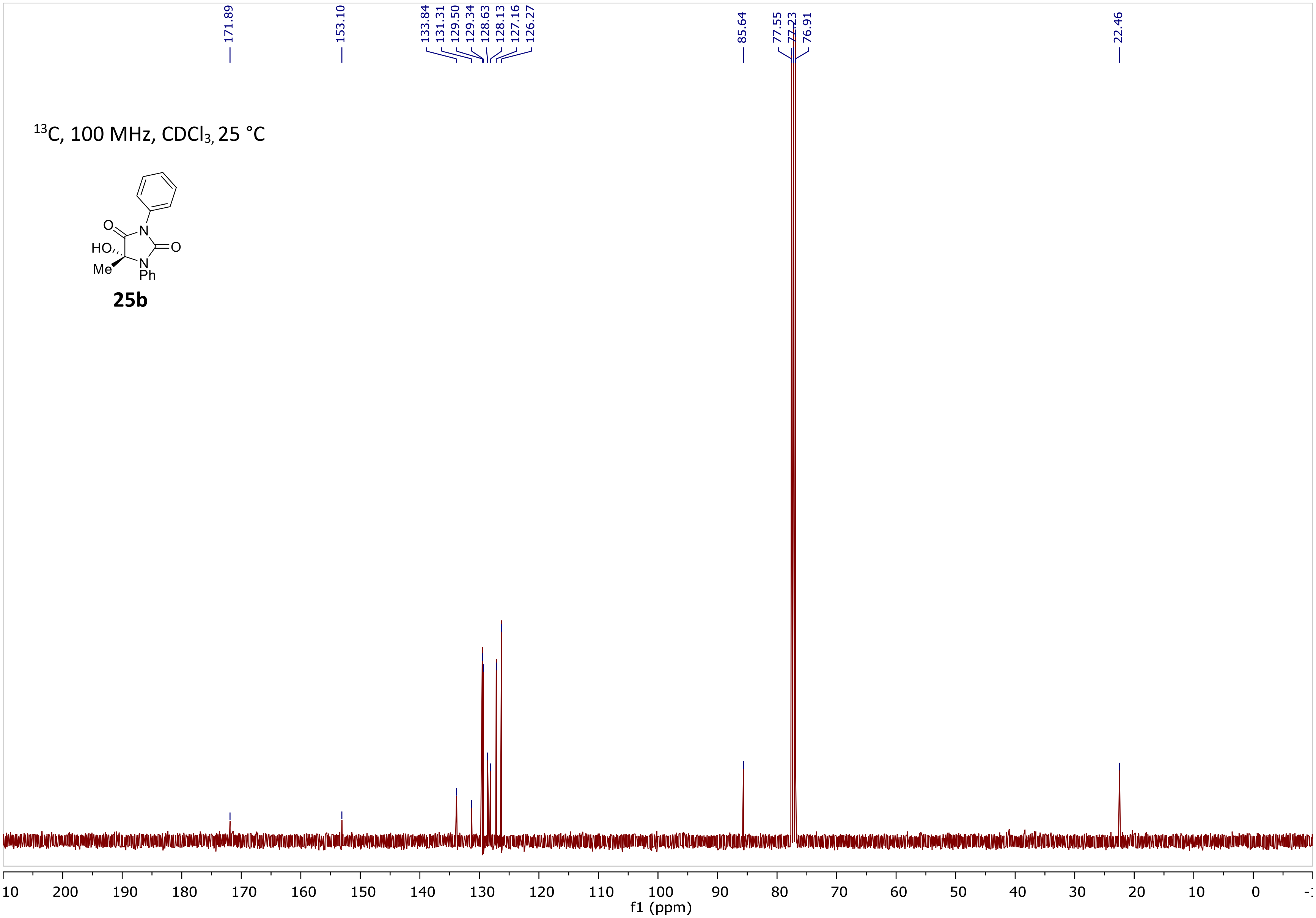

173.69
154.88
133.50
129.49
128.44
127.28
82.93
23.79
13C, 125 MHz, acetone-d6, 25 °C
O
N
HO
O
Me
N
H
23b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

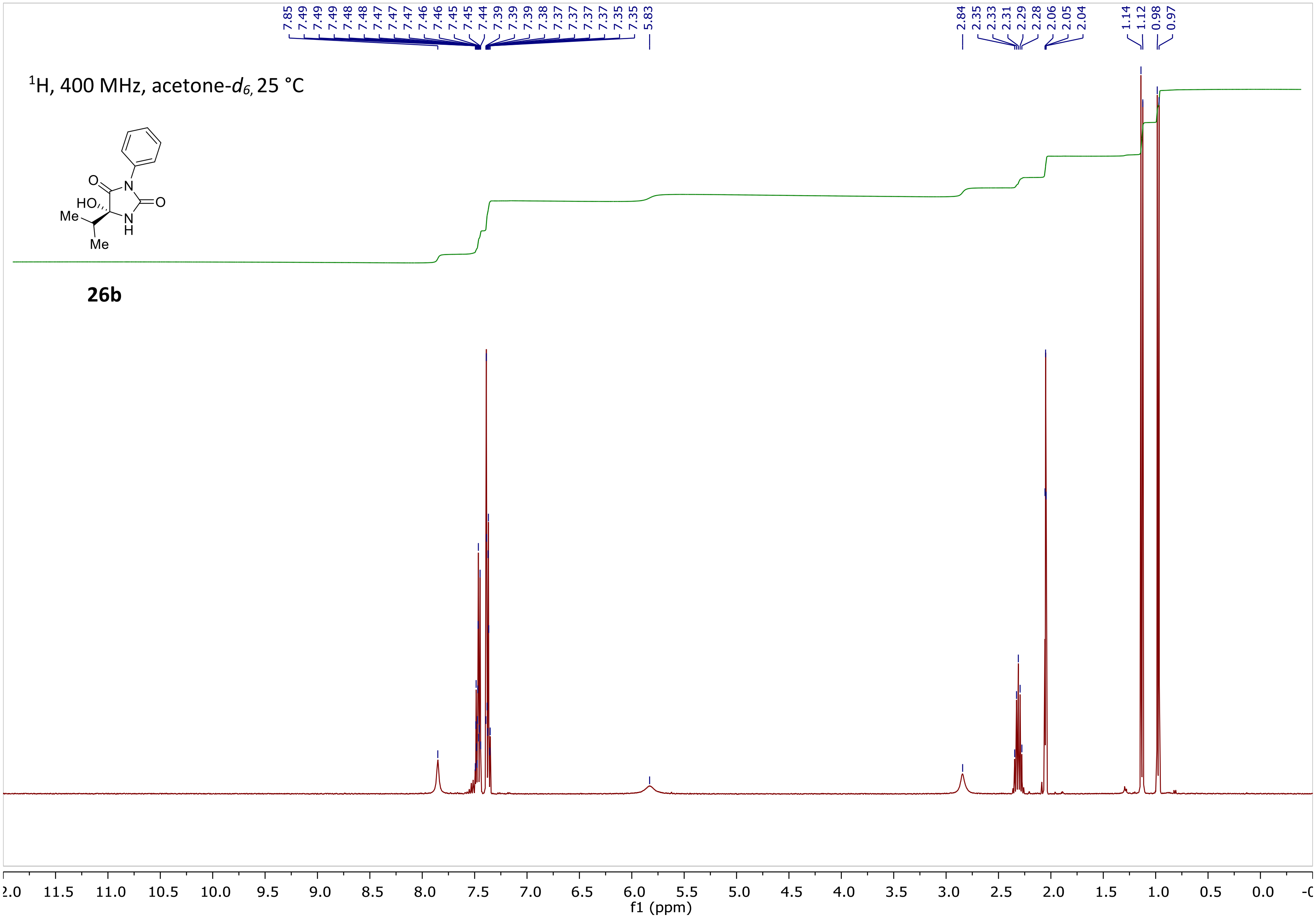

^{1}H, 400 MHz, CDCl$_3$, 25 °C
7.47
7.46
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.39
7.38
7.37
7.37
7.36
7.36
7.36
7.35
7.26
3.62
2.99
1.67
O
N
HO
O
Me
N
Me
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

24b

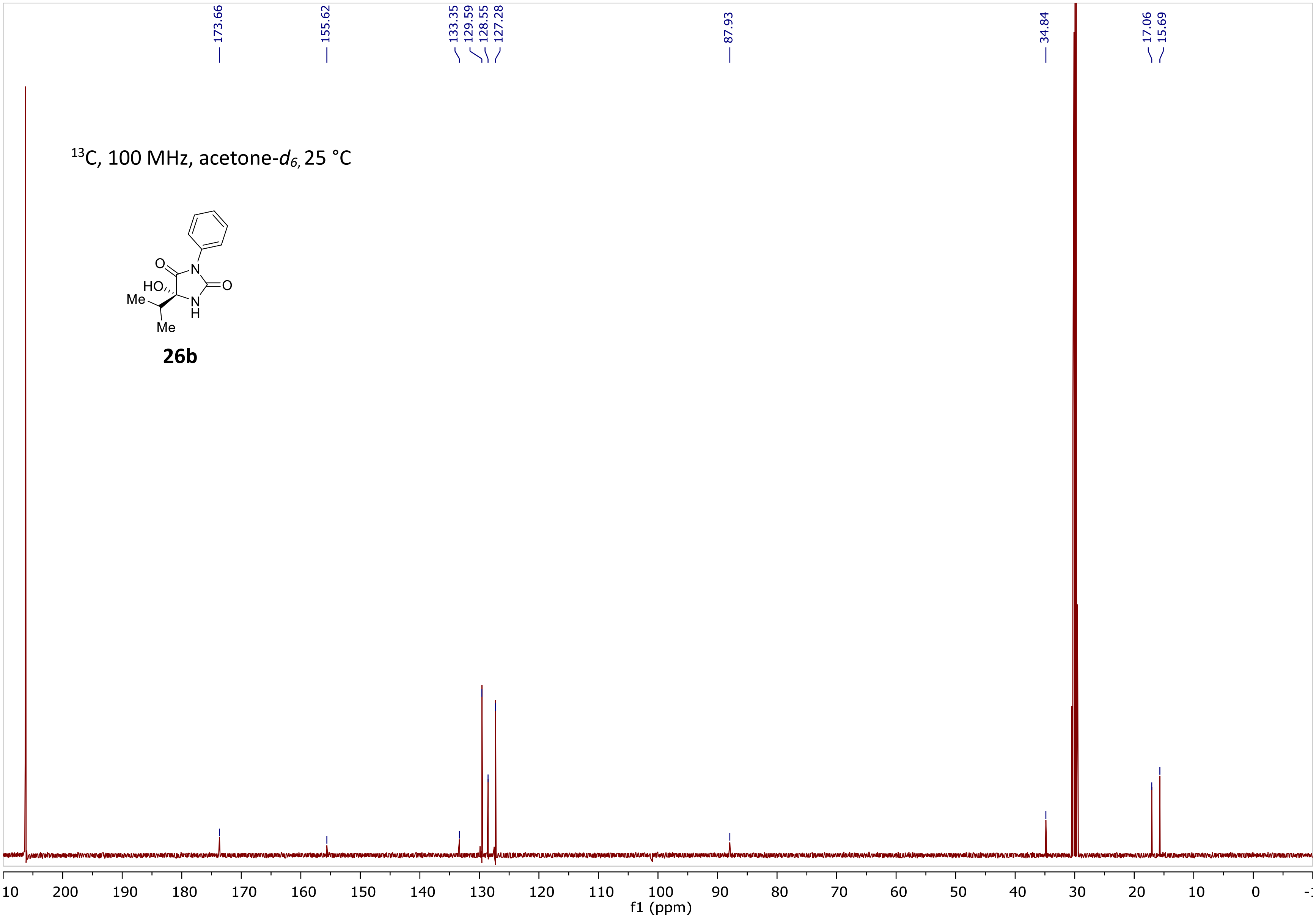

172.67
154.04
131.43
129.29
128.46
126.12
83.94
77.55
77.23
76.91
24.41
21.51
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
HO
Me
N
Me
O
24b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

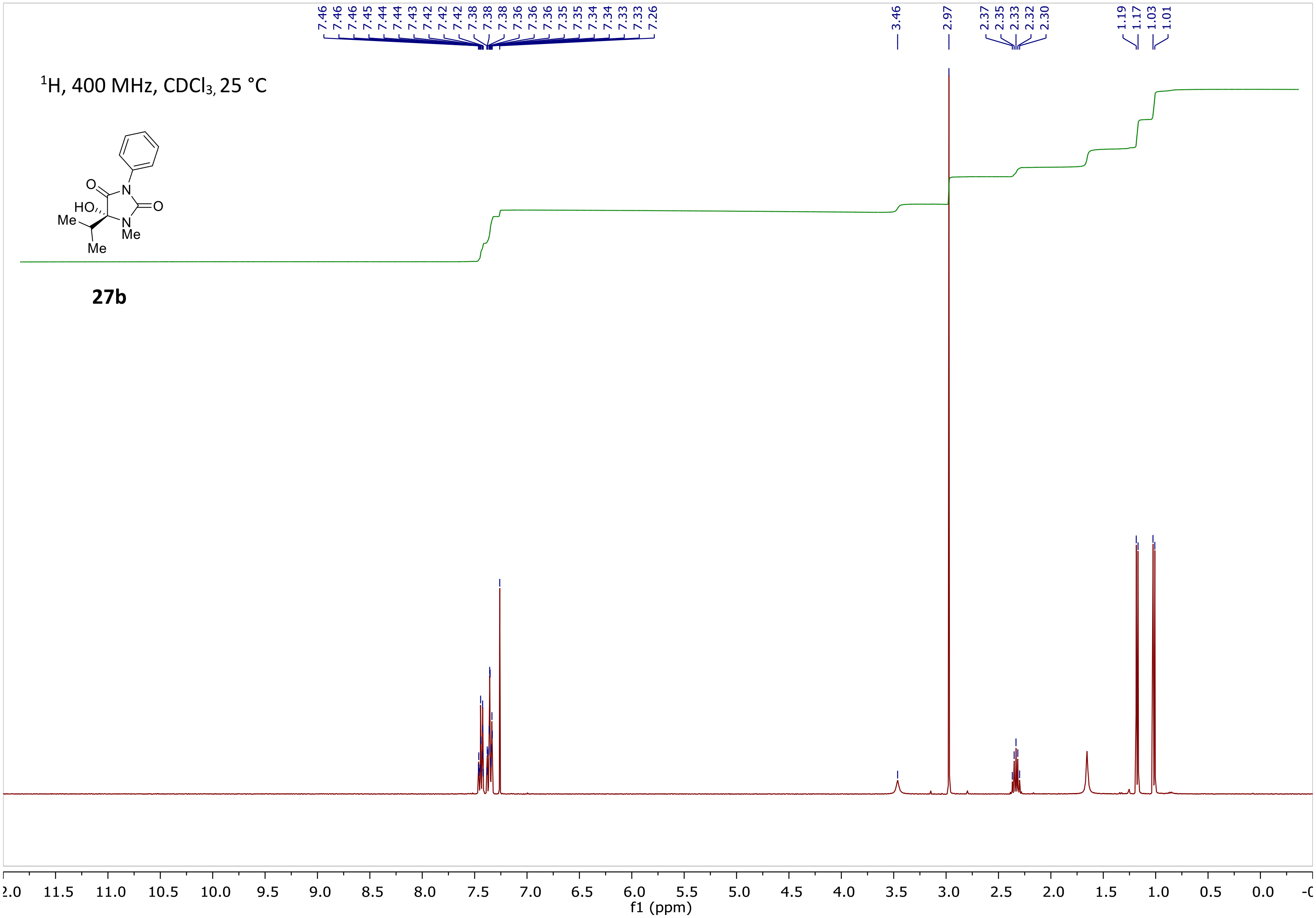

7.54
7.54
7.53
7.52
7.52
7.52
7.52
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.44
7.43
7.42
7.41
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.35
7.26
3.74
1.65
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
HO
O
Me
N
Ph
25b
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


171.89
153.10
133.84
131.31
129.50
129.34
128.63
128.13
127.16
126.27
85.64
77.55
77.23
76.91
22.46
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
HO
O
Me
N
Ph
25b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)

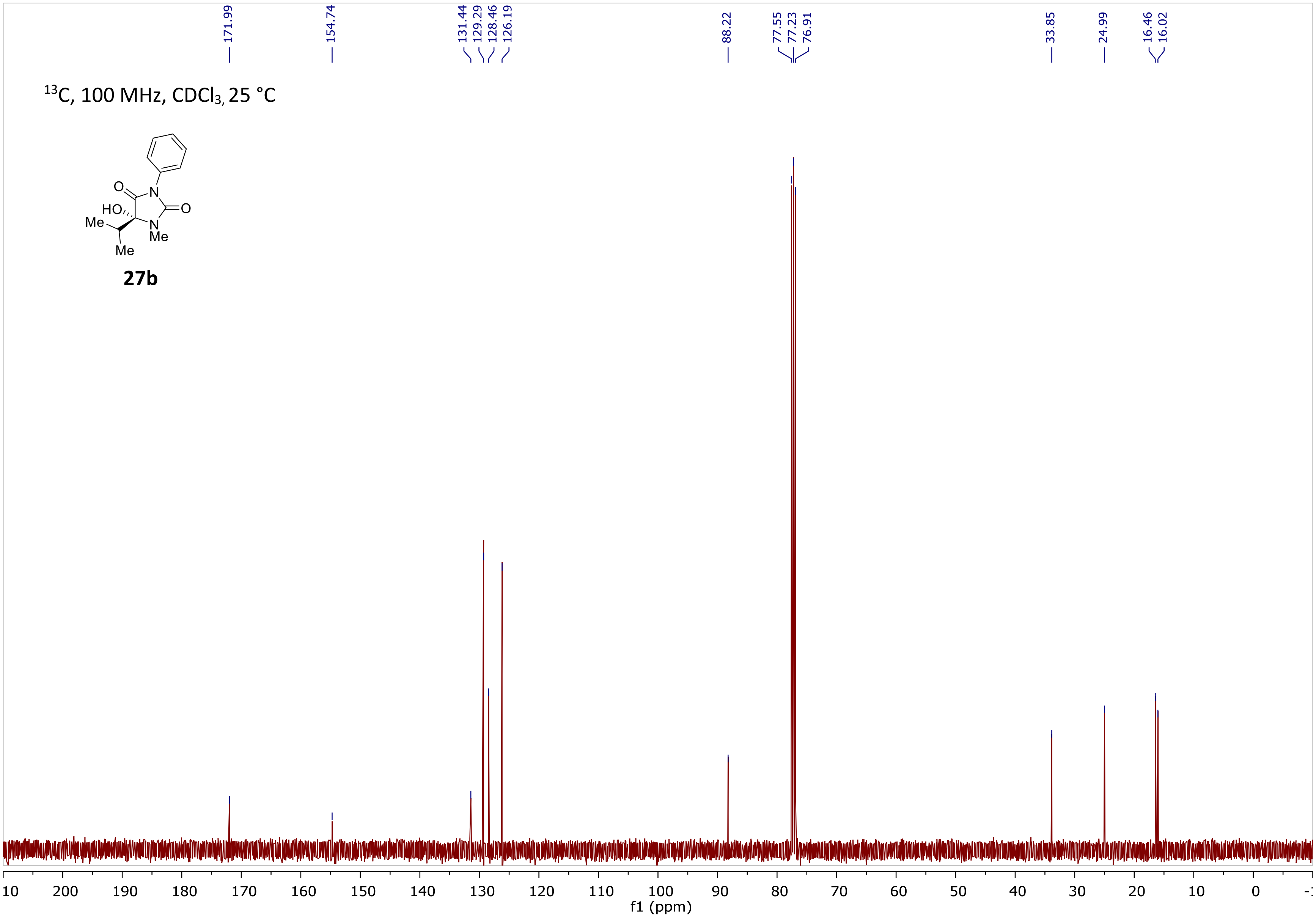

^{1}H, 400 MHz, acetone-d_6, 25 °C

26b

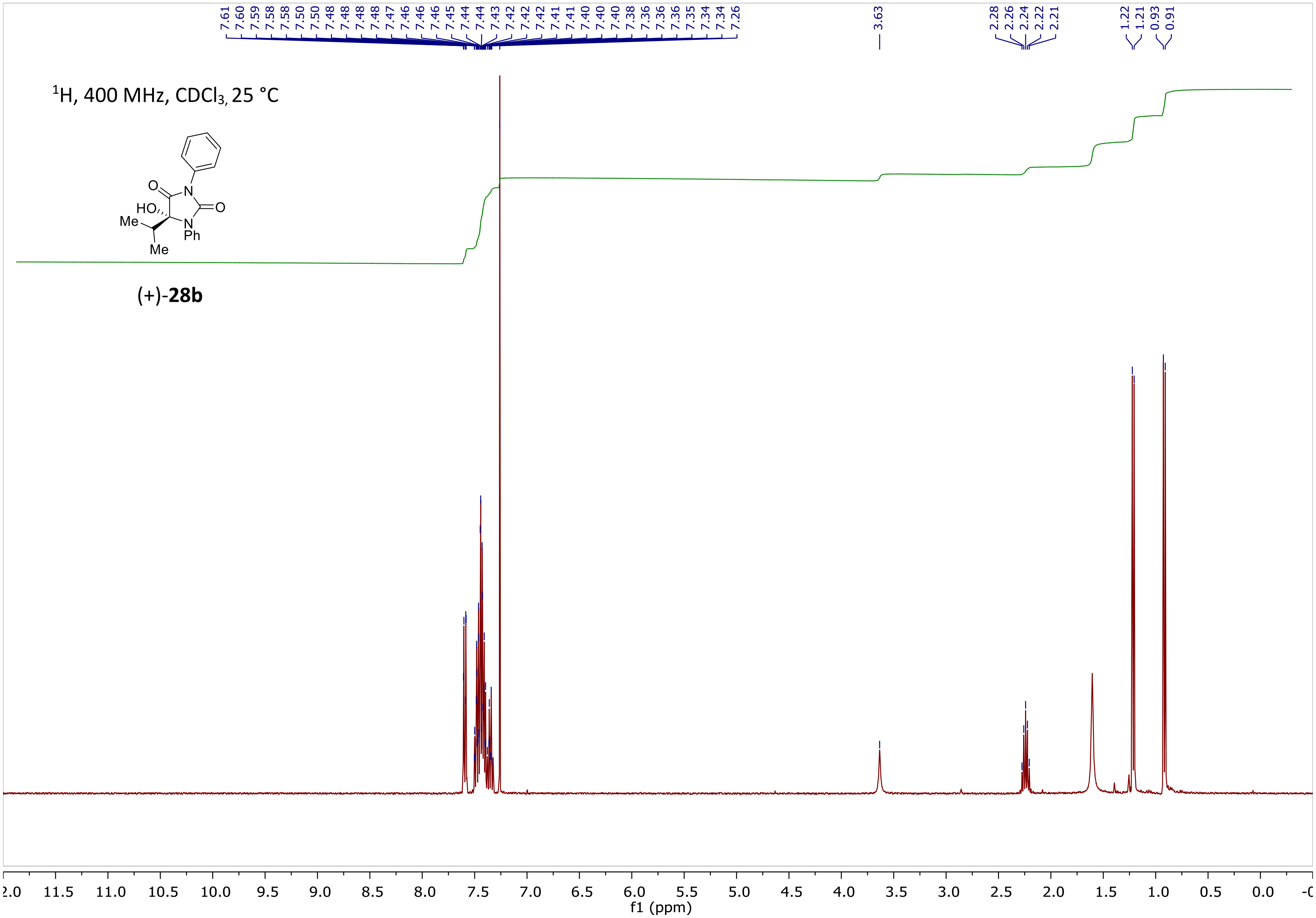

173.66
155.62
133.35
129.59
128.55
127.28
87.93
34.84
17.06
15.69
13C, 100 MHz, acetone-d6, 25 °C
O
N
O
HO
Me
N
H
Me
26b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.46
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.42
7.42
7.38
7.38
7.38
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.26
3.46
2.97
2.37
2.35
2.33
2.33
2.32
2.30
1.19
1.17
1.03
1.01
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
HO
O
Me
N
Me
Me
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-
f1 (ppm)

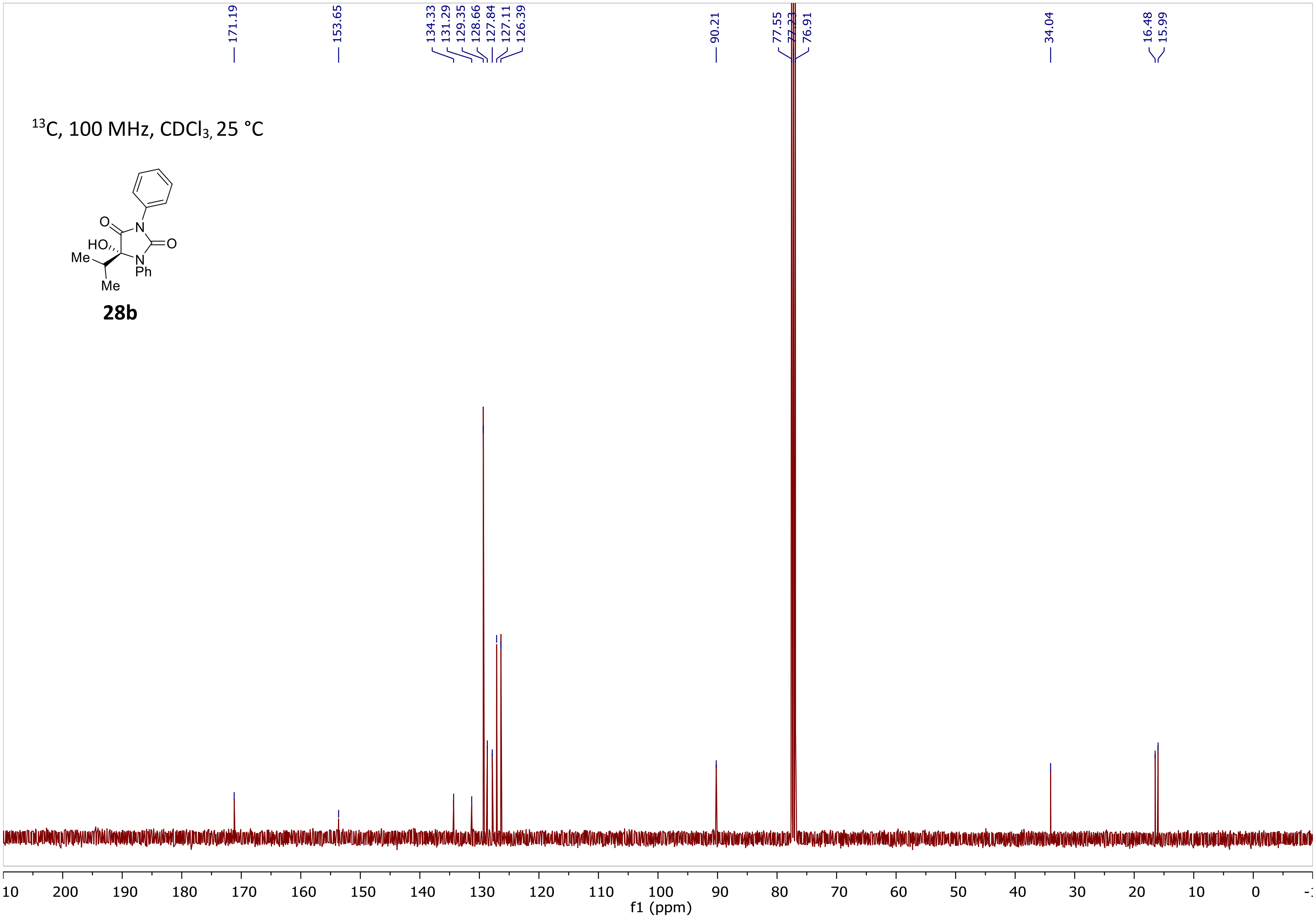
27b

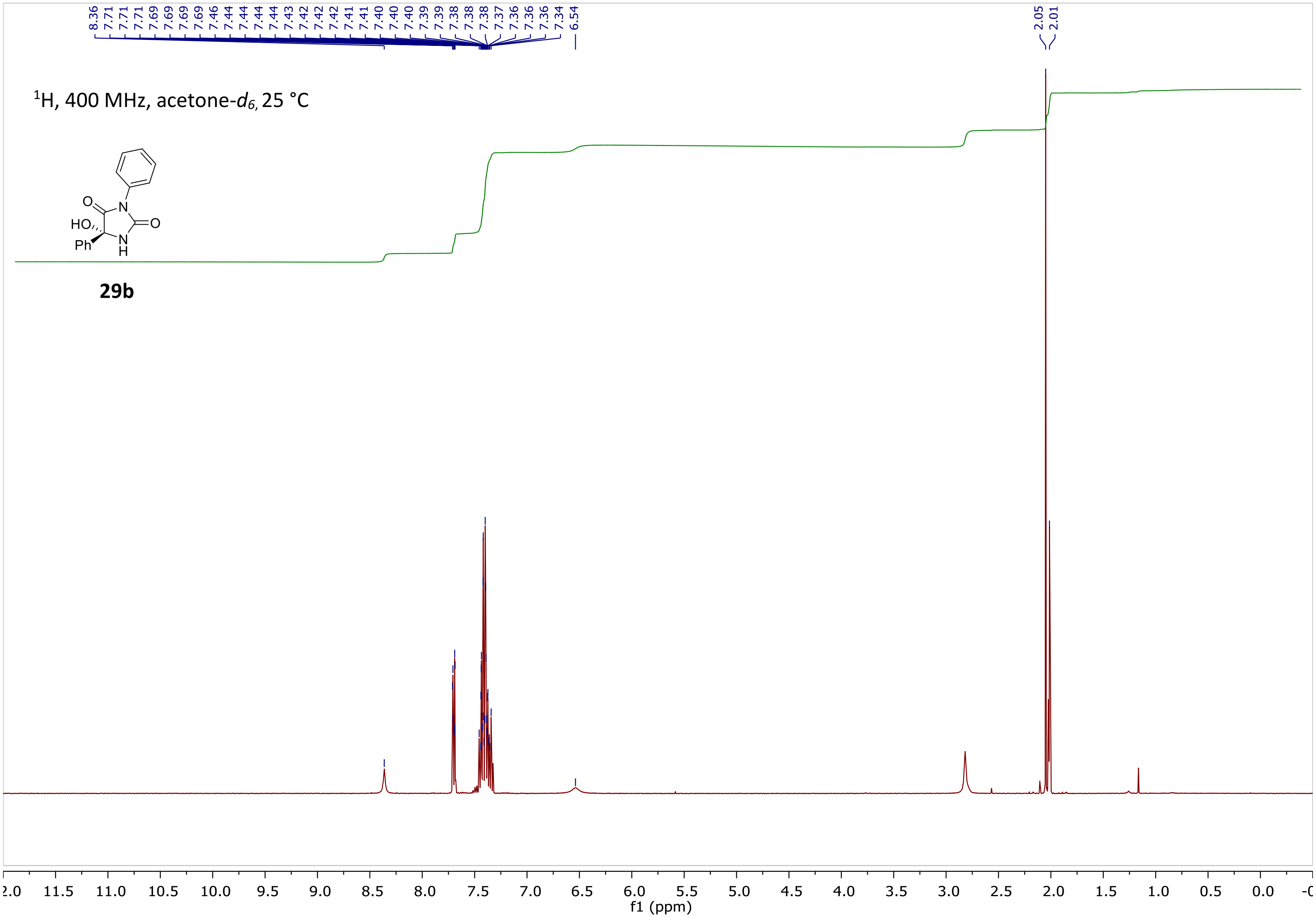

^{13}C, 100 MHz, CDCl$_3$, 25 °C

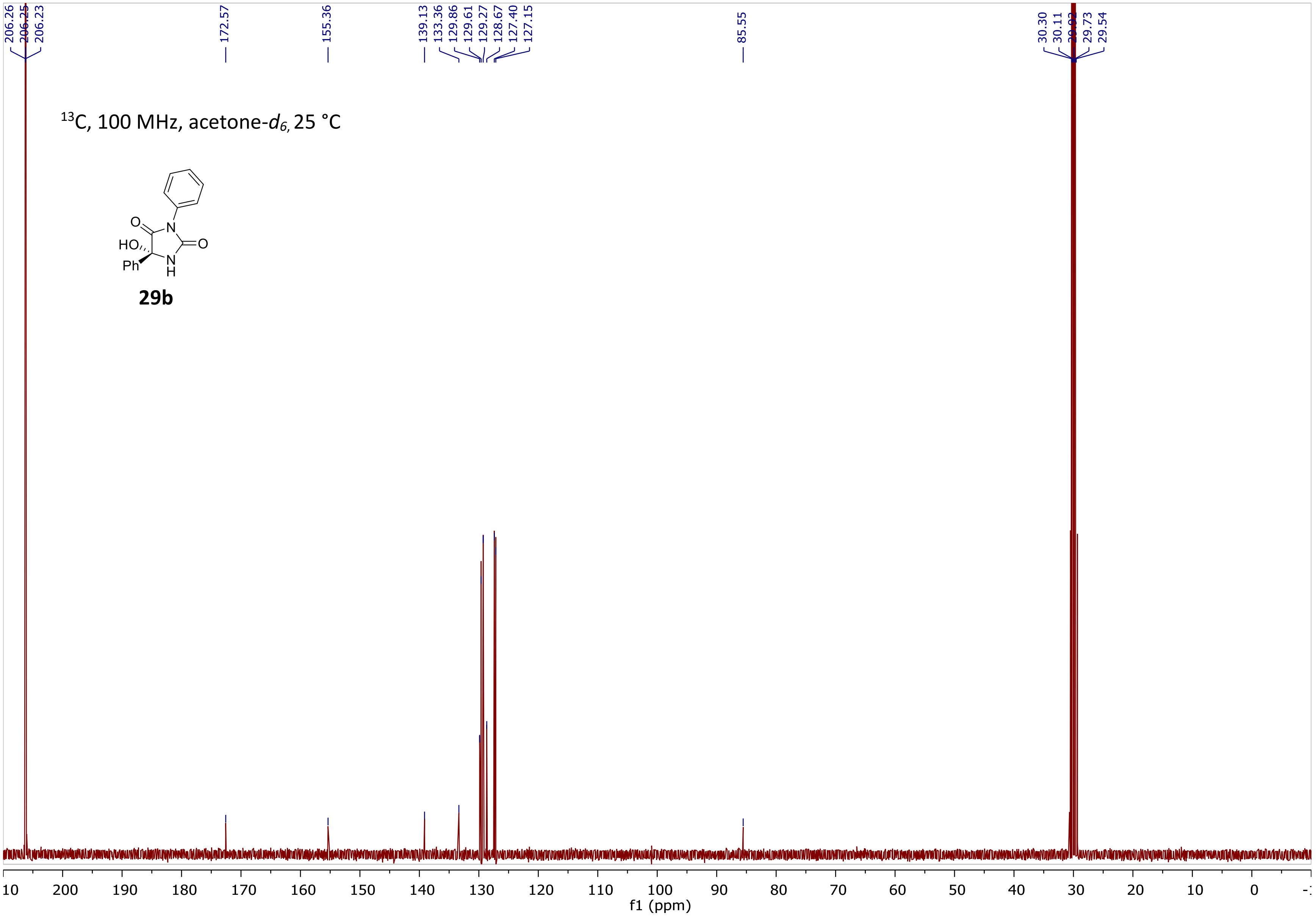
27b

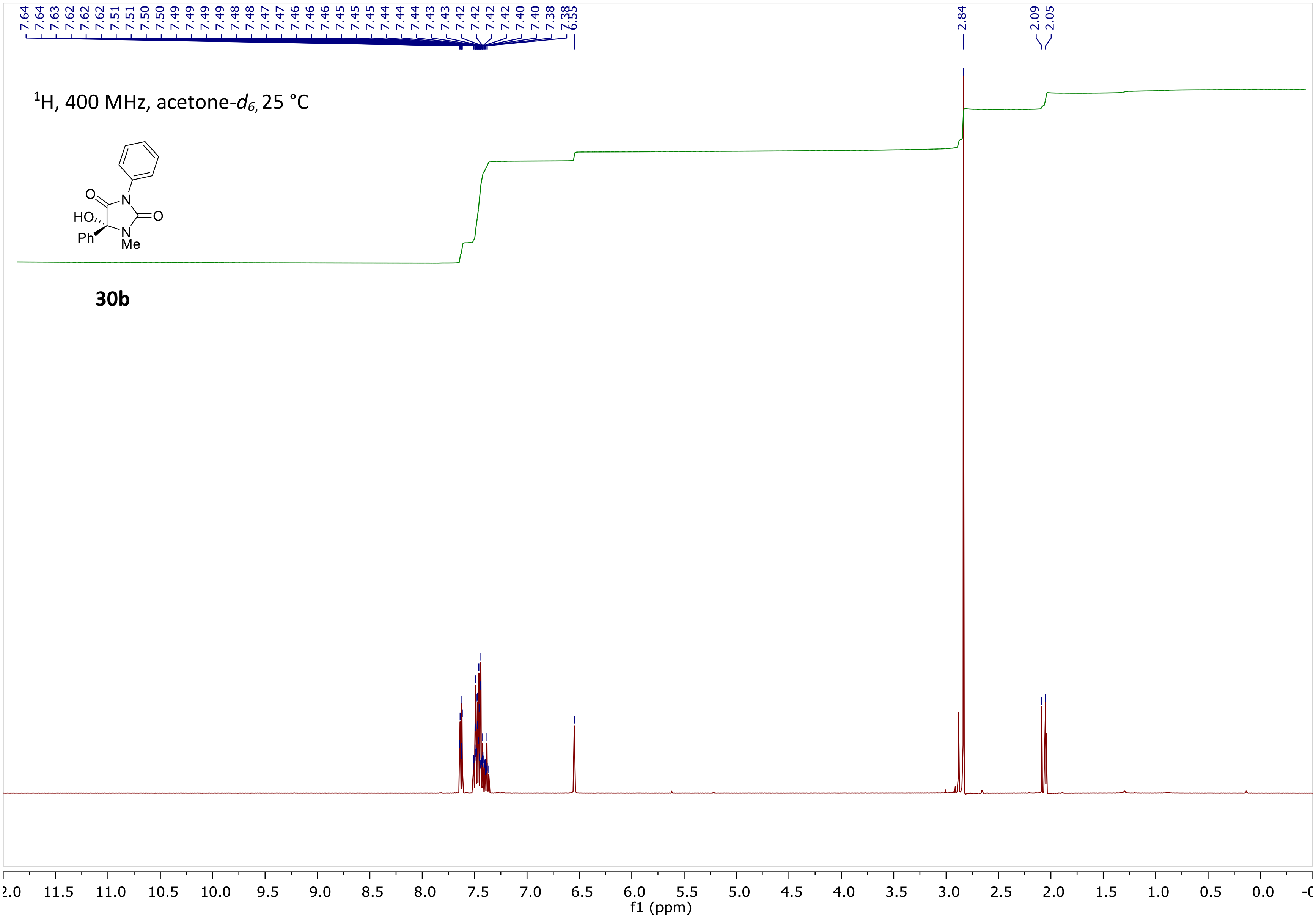

7.61
7.60
7.59
7.58
7.58
7.50
7.50
7.48
7.48
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.42
7.42
7.41
7.40
7.40
7.38
7.36
7.36
7.35
7.34
7.34
7.26
3.63
2.28
2.26
2.24
2.22
2.21
1.22
1.21
0.93
0.91
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
HO
O
Me
N
Ph
Me
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

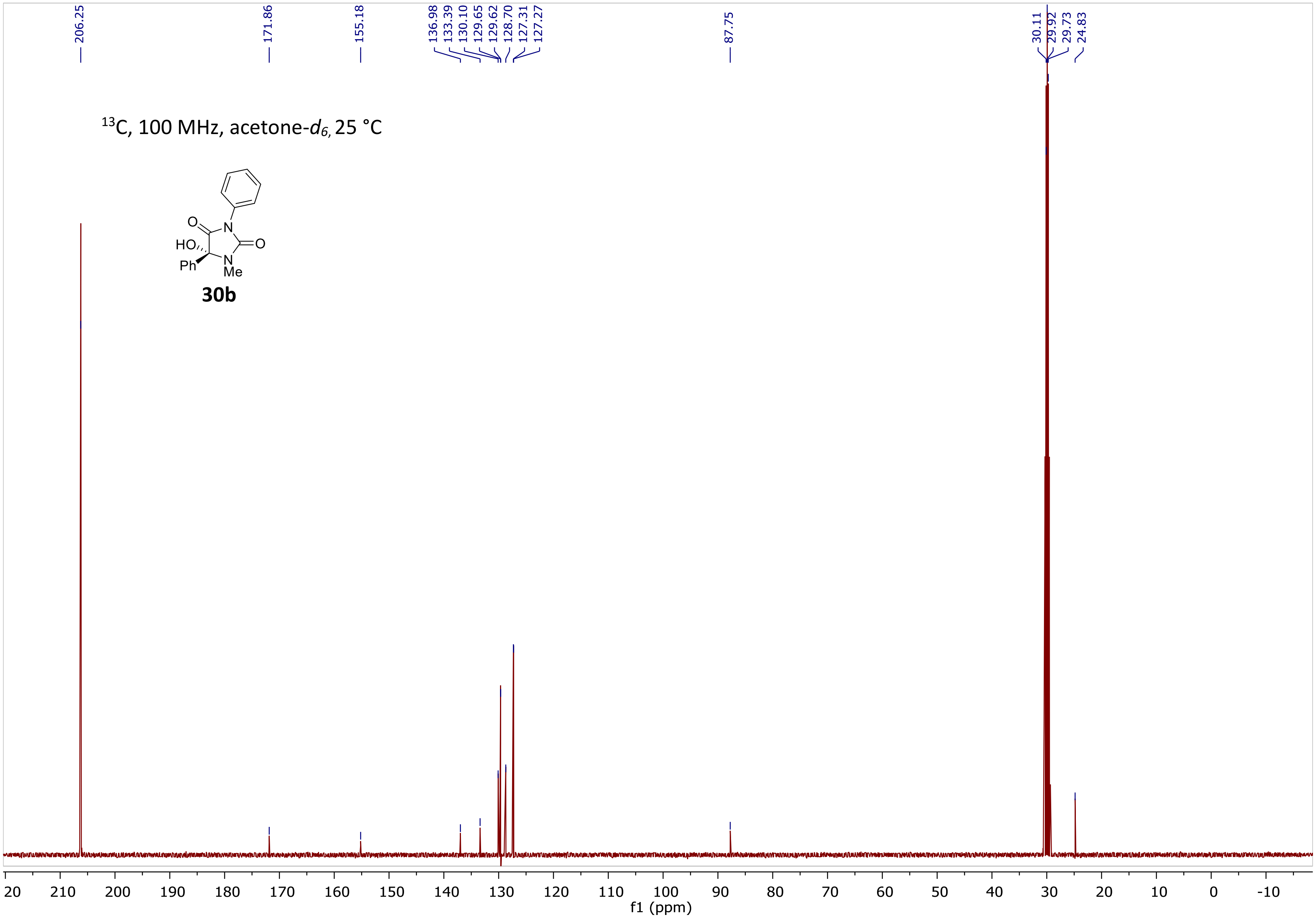
(+)-**28b**


171.19
153.65
134.33
131.29
129.35
128.66
127.84
127.11
126.39
90.21
77.55
77.23
76.91
34.04
16.48
15.99
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
HO
Me
N
Ph
O
Me
28b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

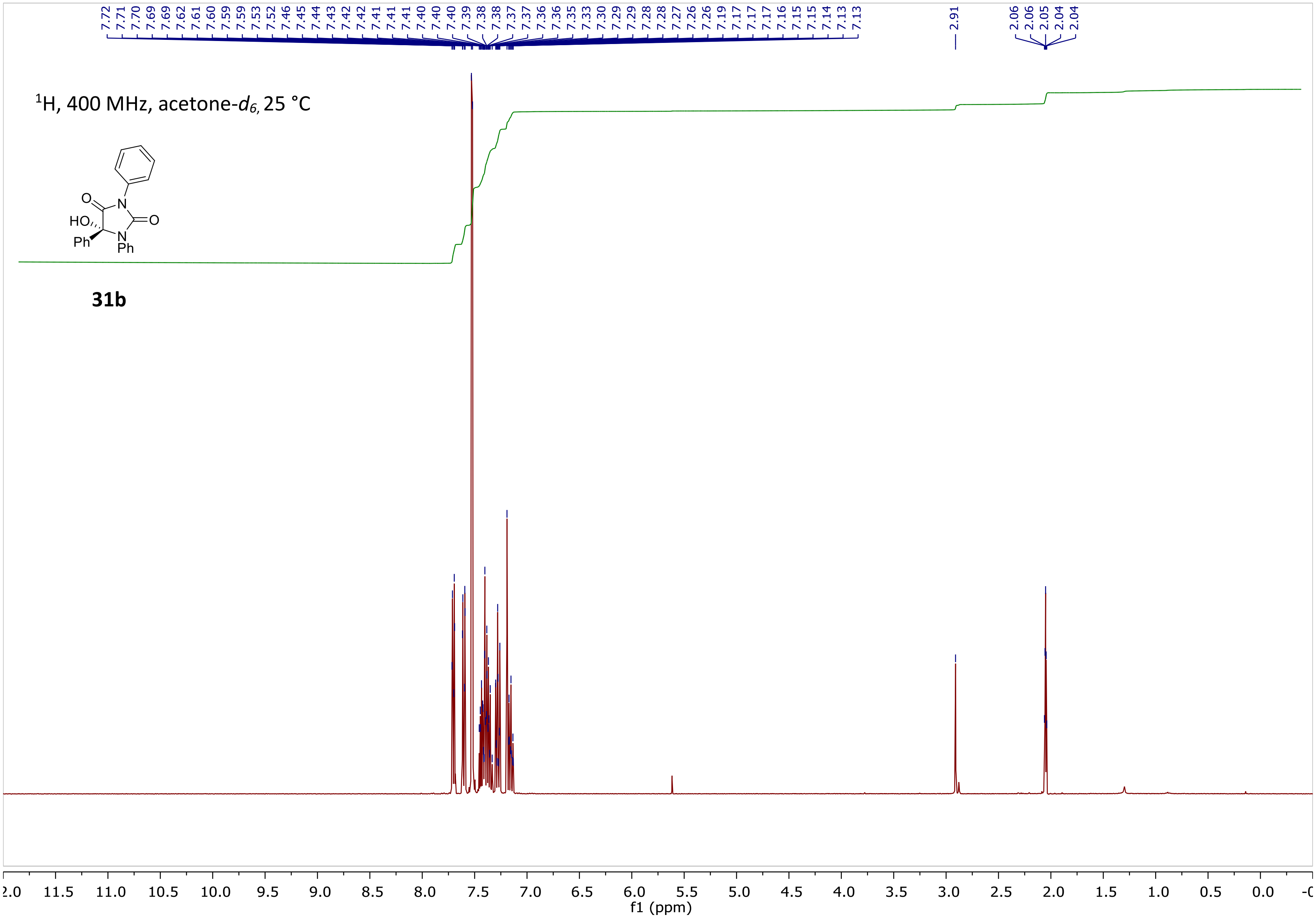

8.36
7.71
7.71
7.71
7.69
7.69
7.69
7.69
7.46
7.44
7.44
7.44
7.44
7.43
7.42
7.42
7.42
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.36
7.36
7.36
7.34
6.54
2.05
2.01
^{1}H, 400 MHz, acetone-d_6, 25 °C
O
N
HO
Ph
N
H
O
29b
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


206.26
206.25
206.23
172.57
155.36
139.13
133.36
129.86
129.61
129.27
128.67
127.40
127.15
85.55
30.30
30.11
29.92
29.73
29.54
13C, 100 MHz, acetone-d6, 25 °C
O
N
HO,,
O
Ph
N
H
29b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

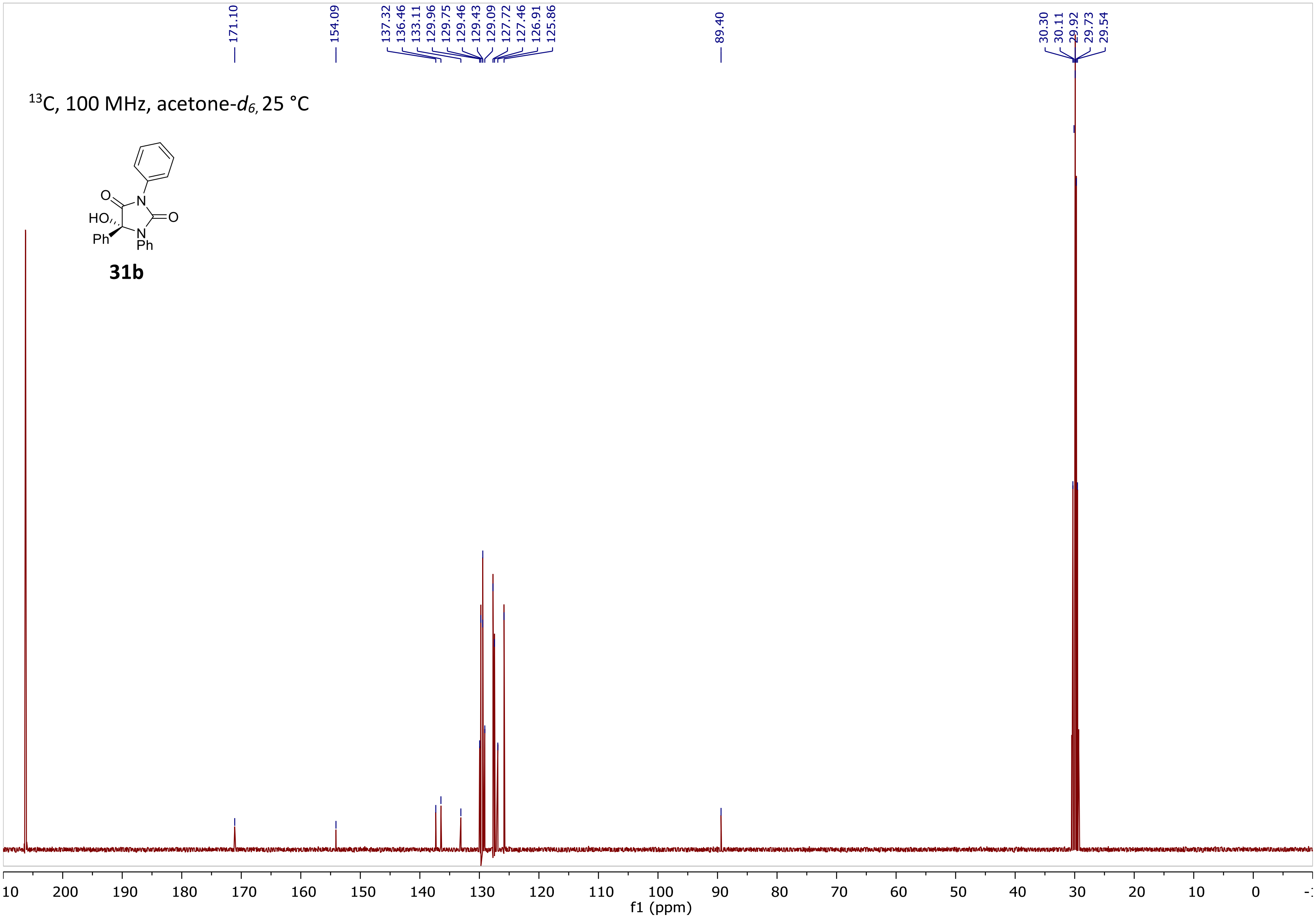

7.64
7.64
7.63
7.62
7.62
7.62
7.51
7.51
7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.42
7.40
7.40
7.38
7.38
6.55
2.84
2.09
2.05
^{1}H, 400 MHz, acetone-d_6, 25 °C
O
N
HO
O
Ph
N
Me
30b
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)


206.25
171.86
155.18
136.98
133.39
130.10
129.65
129.62
128.70
127.31
127.27
87.75
30.11
29.92
29.73
24.83
^{13}C, 100 MHz, acetone-d_6, 25 °C
O
N
HO
O
Ph
N
Me
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

30b

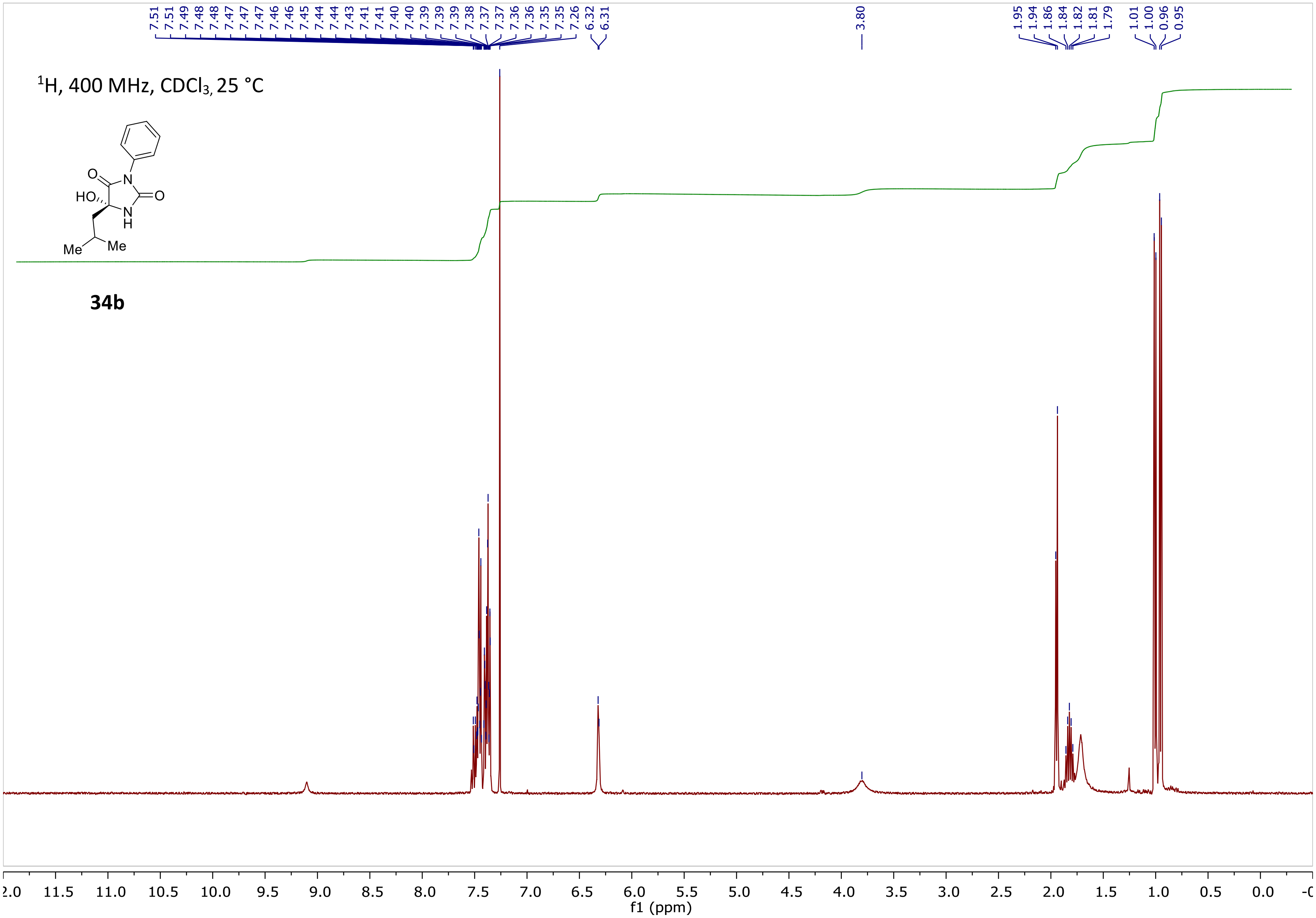

7.72
7.71
7.70
7.69
7.62
7.61
7.60
7.59
7.59
7.53
7.52
7.46
7.45
7.44
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.33
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.19
7.17
7.17
7.17
7.16
7.15
7.15
7.14
7.13
7.13
2.91
2.06
2.06
2.05
2.04
2.04
^{1}H, 400 MHz, acetone-d_6, 25 °C
O
N
HO
O
Ph
N
Ph
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

31b

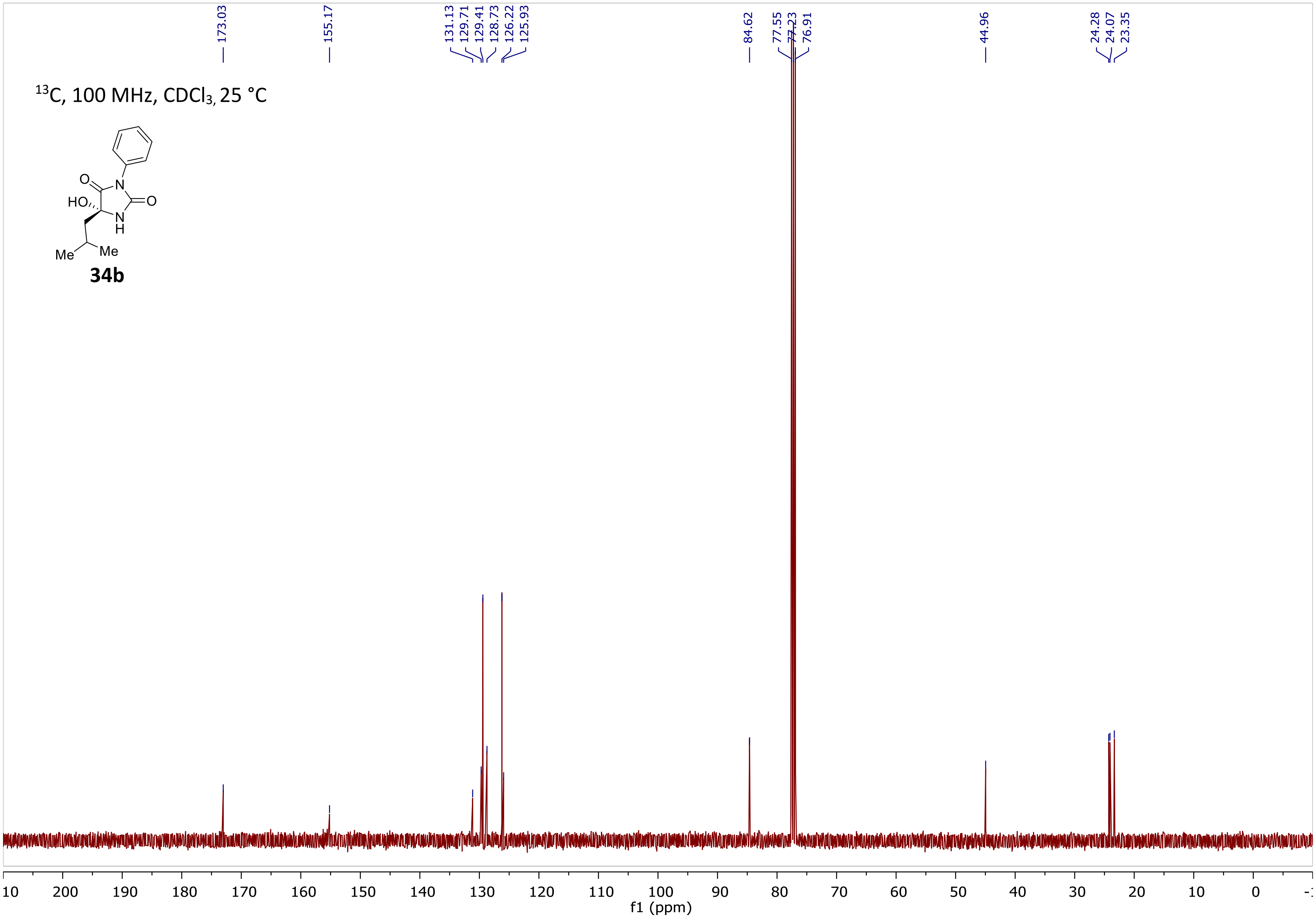


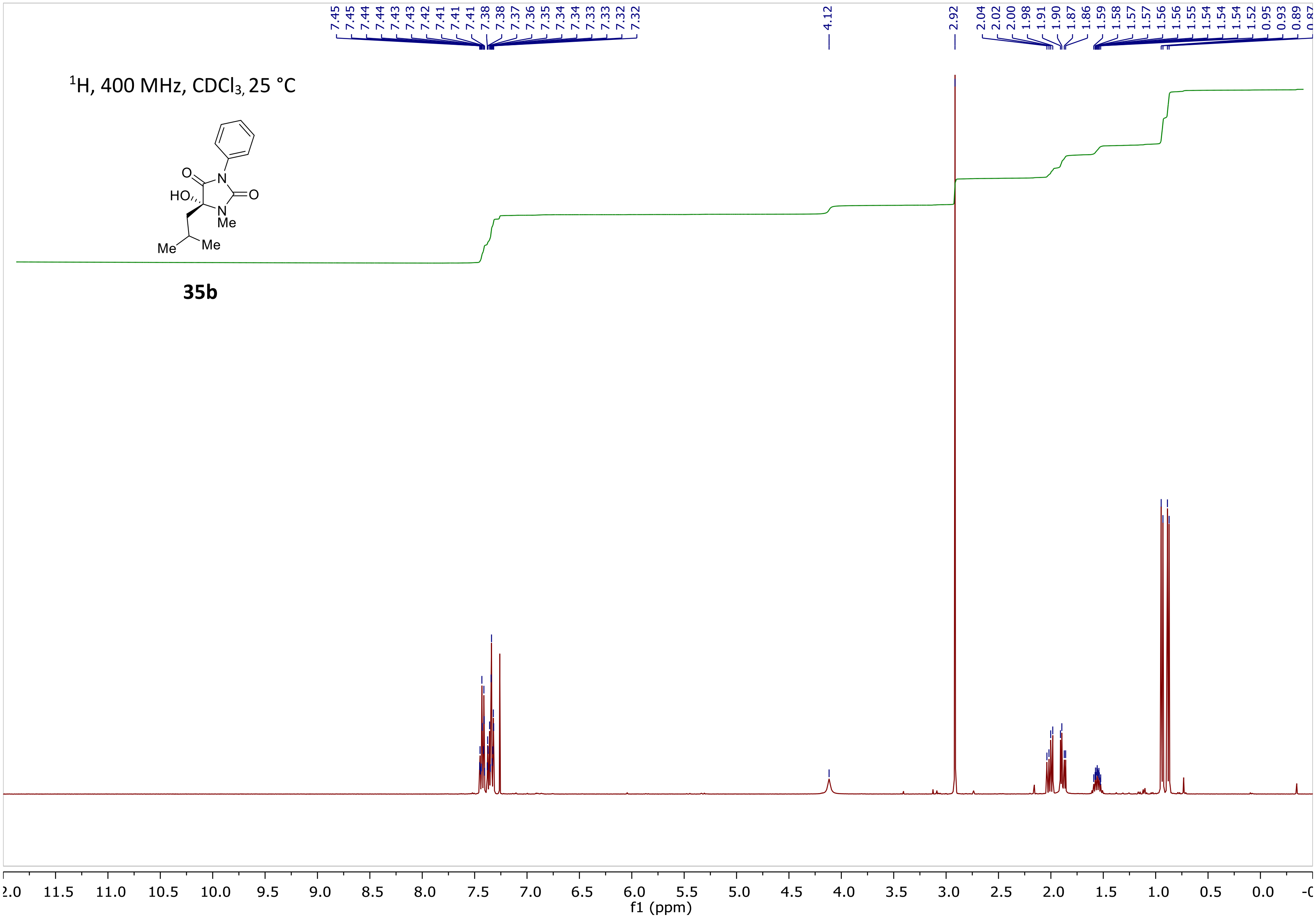
^{13}C, 100 MHz, acetone-$d_{6,}$ 25 °C
O
N
HO
O
Ph
N
Ph
171.10
154.09
137.32
136.46
133.11
129.96
129.75
129.46
129.43
129.09
127.72
127.46
126.91
125.86
89.40
30.30
30.11
29.92
29.73
29.54
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

31b


7.51
7.51
7.49
7.48
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.26
6.32
6.31
3.80
1.95
1.94
1.86
1.84
1.82
1.81
1.79
1.01
1.00
0.96
0.95
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
HO
O
N
H
Me
Me
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

34b

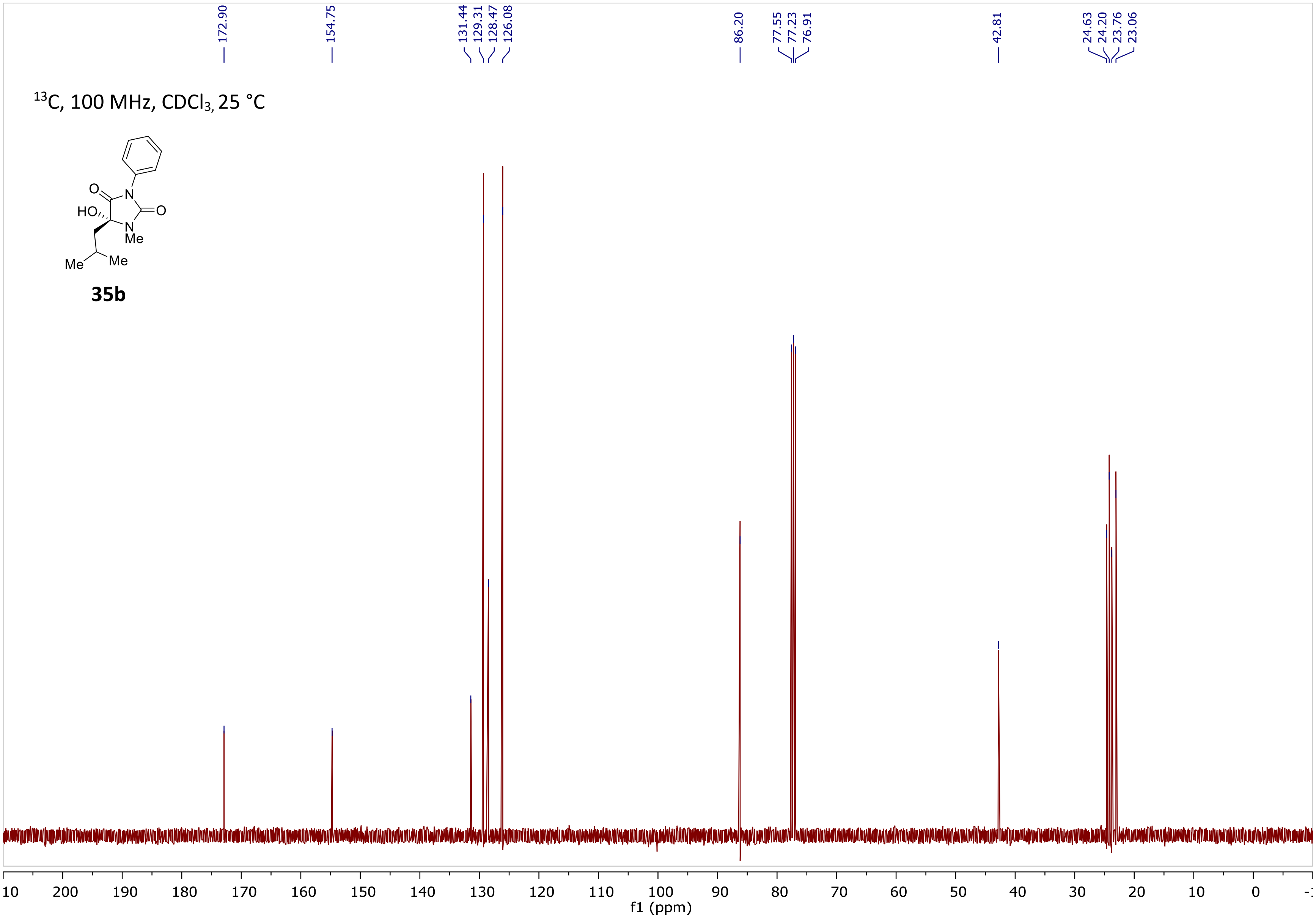

173.03
155.17
131.13
129.71
129.41
128.73
126.22
125.93
84.62
77.55
77.23
76.91
44.96
24.28
24.07
23.35
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
O
HO
N
H
Me
Me
34b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

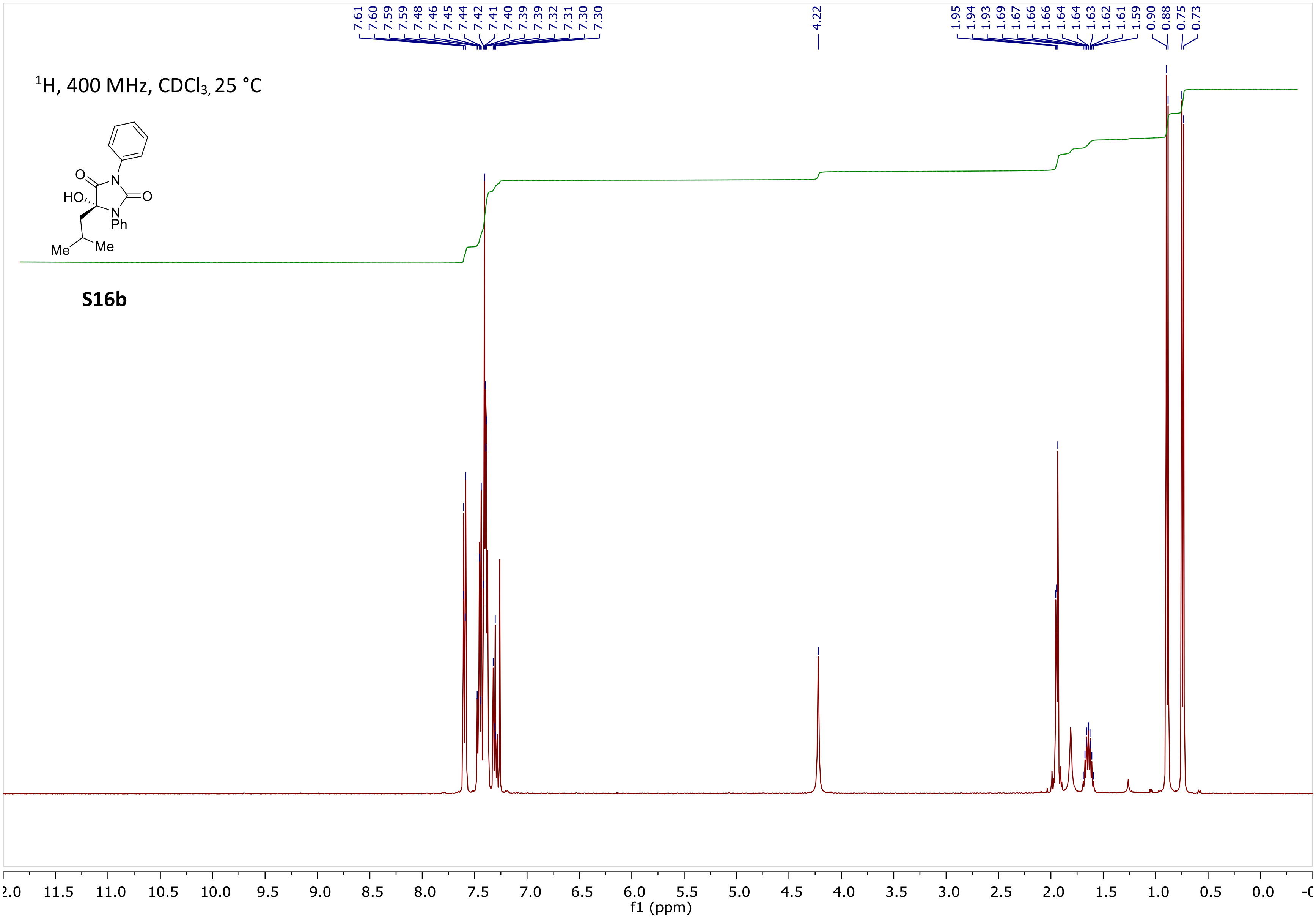

7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.41
7.38
7.38
7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.32
4.12
2.92
2.04
2.02
2.00
1.98
1.91
1.90
1.87
1.86
1.59
1.58
1.57
1.57
1.56
1.56
1.55
1.54
1.54
1.54
1.52
0.95
0.93
0.89
0.8
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
HO
O
N
Me
Me
Me
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-
f1 (ppm)

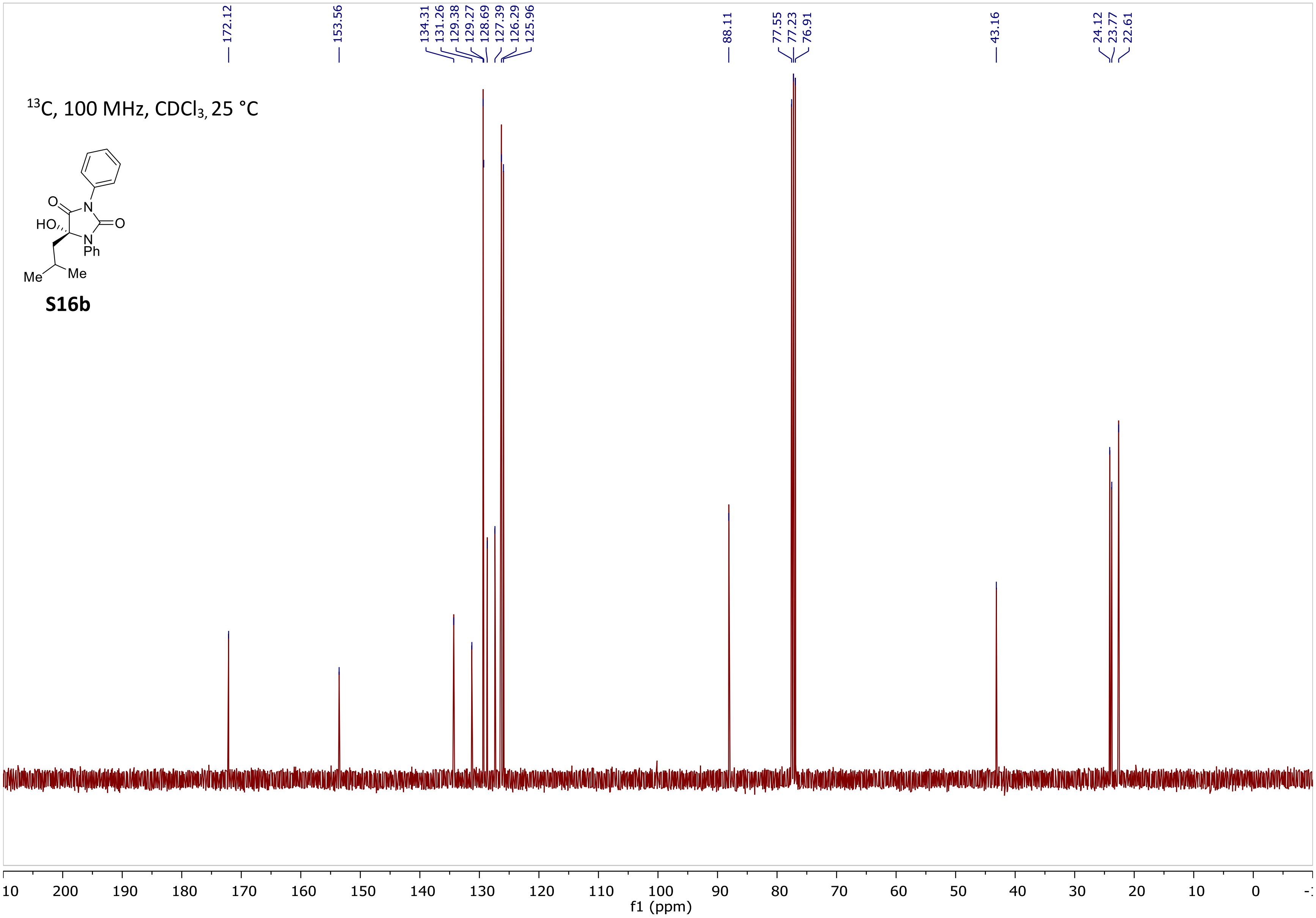
35b

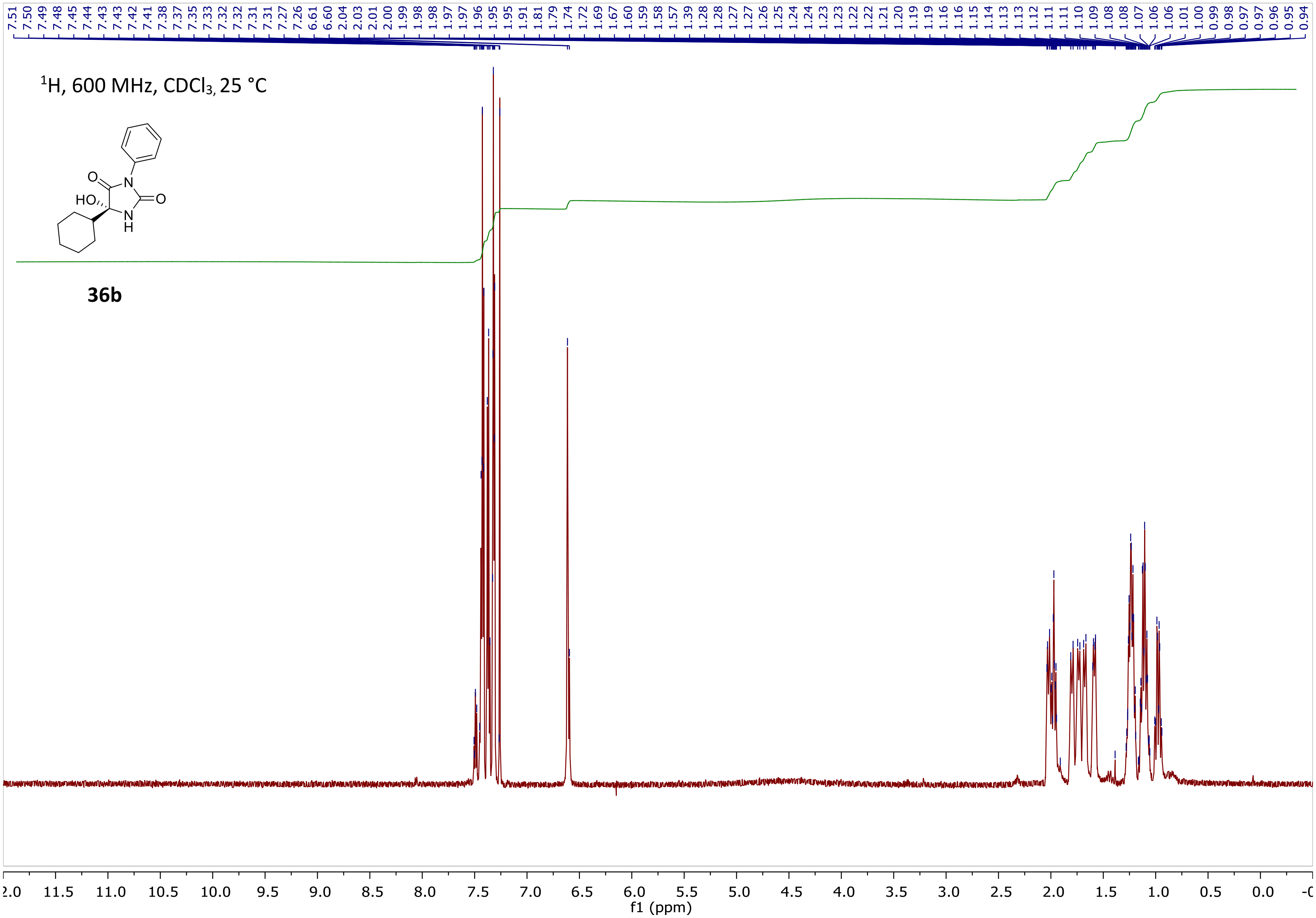
^{13}C, 100 MHz, CDCl$_3$, 25 °C

35b

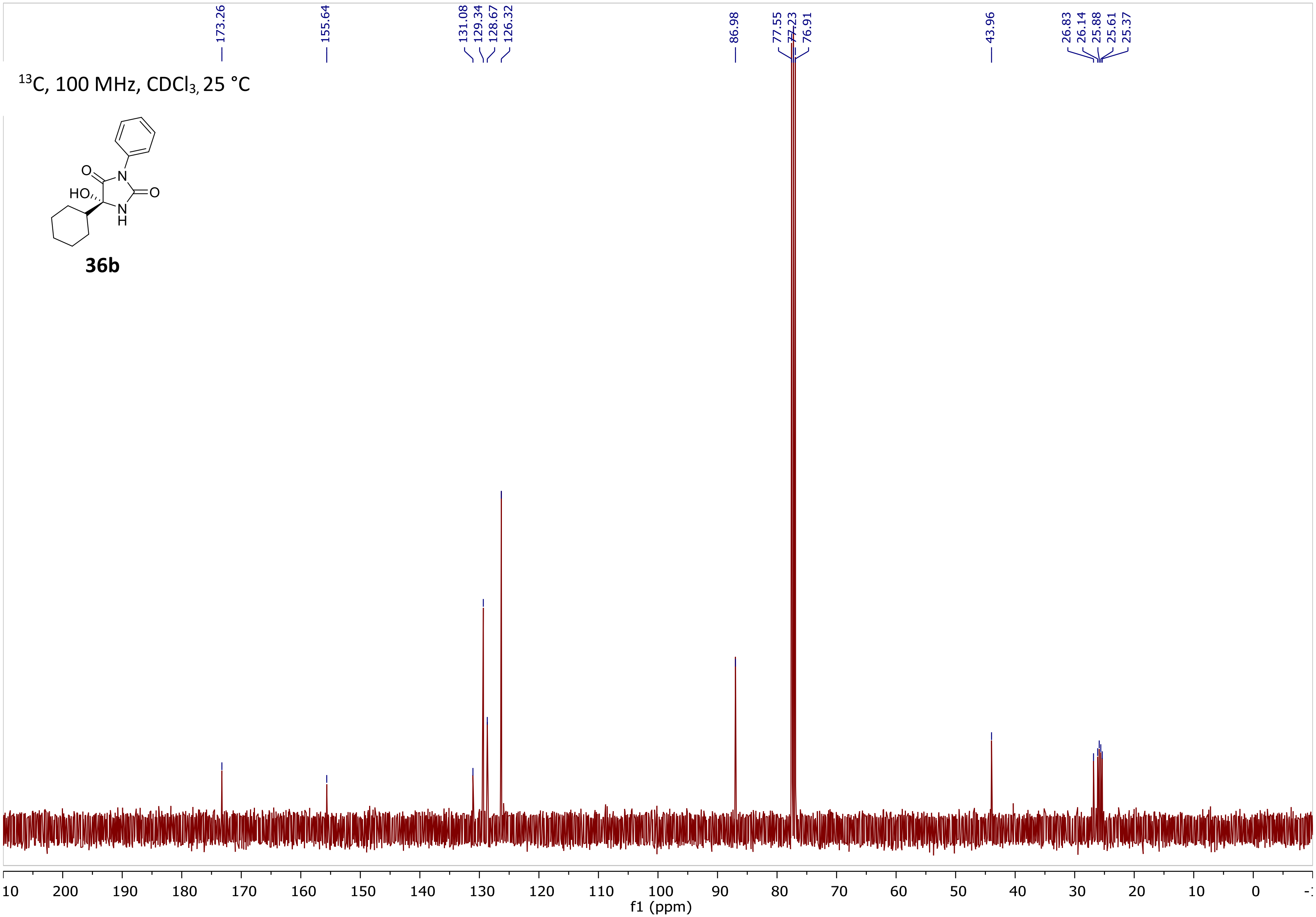


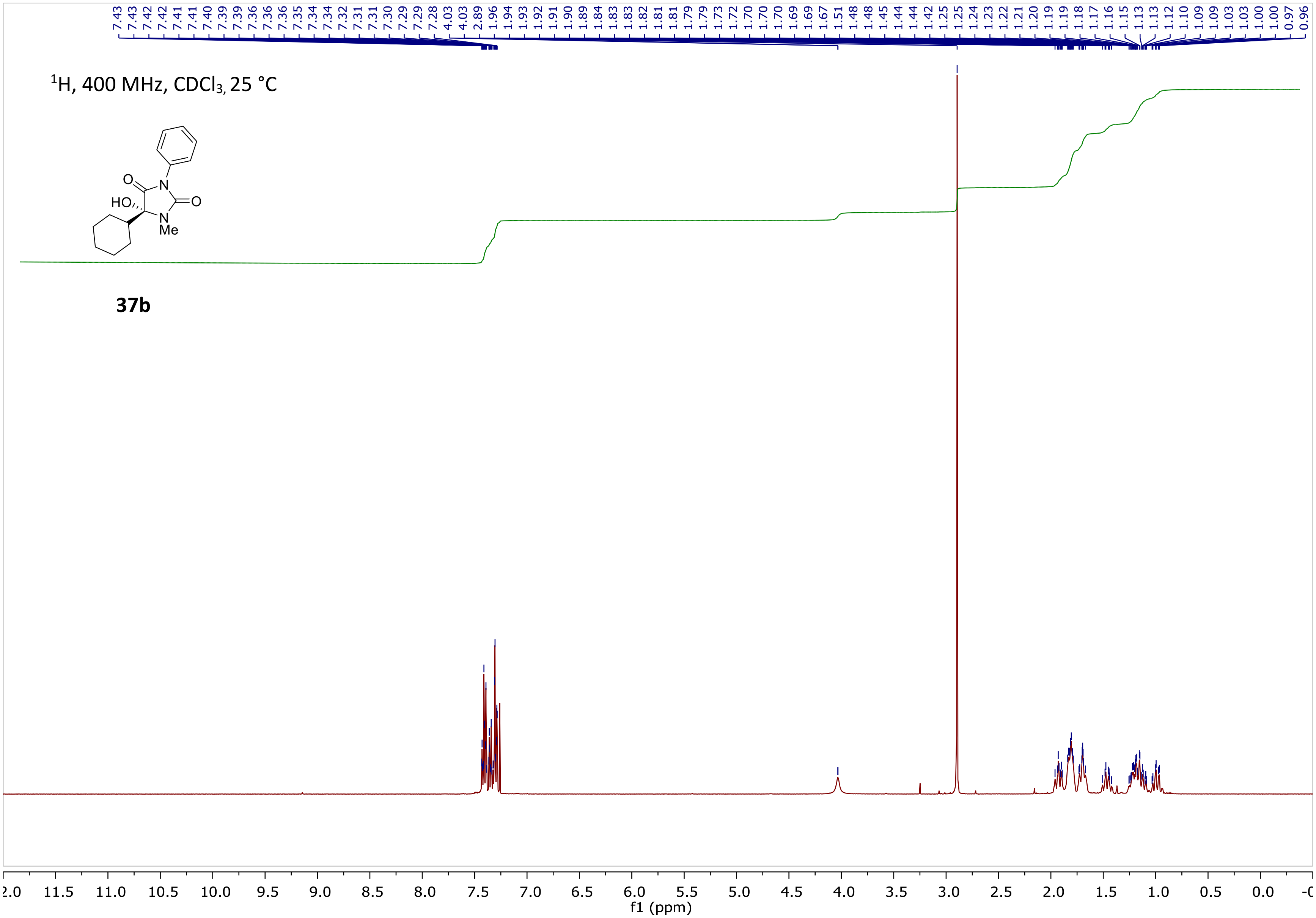

^{1}H, 400 MHz, CDCl$_3$, 25 °C
S16b
7.61 7.60 7.59 7.59 7.48 7.46 7.45 7.44 7.42 7.41 7.40 7.39 7.39 7.32 7.31 7.30 7.30
4.22
1.95 1.94 1.93 1.69 1.67 1.66 1.64 1.64 1.63 1.62 1.61 1.59 0.90 0.88 0.75 0.73
f1 (ppm)
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


172.12
153.56
134.31
131.26
129.38
129.27
128.69
127.39
126.29
125.96
88.11
77.55
77.23
76.91
43.16
24.12
23.77
22.61
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
HO
N
O
Ph
Me
Me
S16b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.51
7.50
7.49
7.48
7.45
7.44
7.43
7.43
7.42
7.41
7.38
7.37
7.35
7.33
7.32
7.32
7.31
7.31
7.27
7.26
6.61
6.60
2.04
2.03
2.01
2.00
1.99
1.98
1.98
1.97
1.97
1.96
1.95
1.95
1.91
1.81
1.79
1.74
1.72
1.69
1.67
1.60
1.59
1.58
1.57
1.39
1.28
1.28
1.27
1.27
1.26
1.25
1.24
1.24
1.23
1.23
1.22
1.22
1.21
1.20
1.19
1.19
1.16
1.16
1.15
1.14
1.13
1.13
1.12
1.11
1.11
1.10
1.09
1.08
1.08
1.07
1.06
1.06
1.01
1.00
0.99
0.98
0.97
0.97
0.96
0.95
0.94
^{1}H, 600 MHz, CDCl$_3$, 25 °C
O
N
HO
O
N
H
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

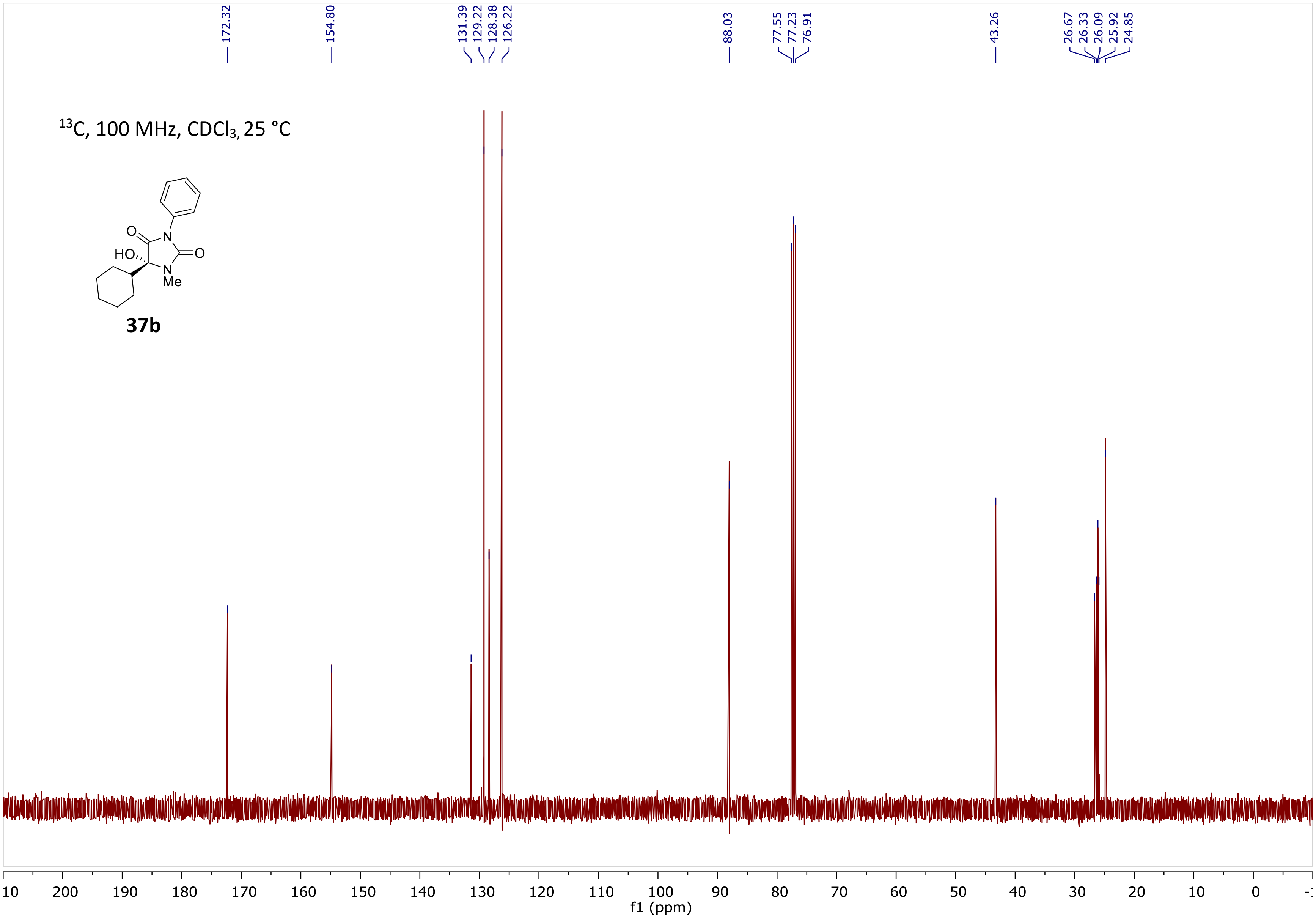
36b

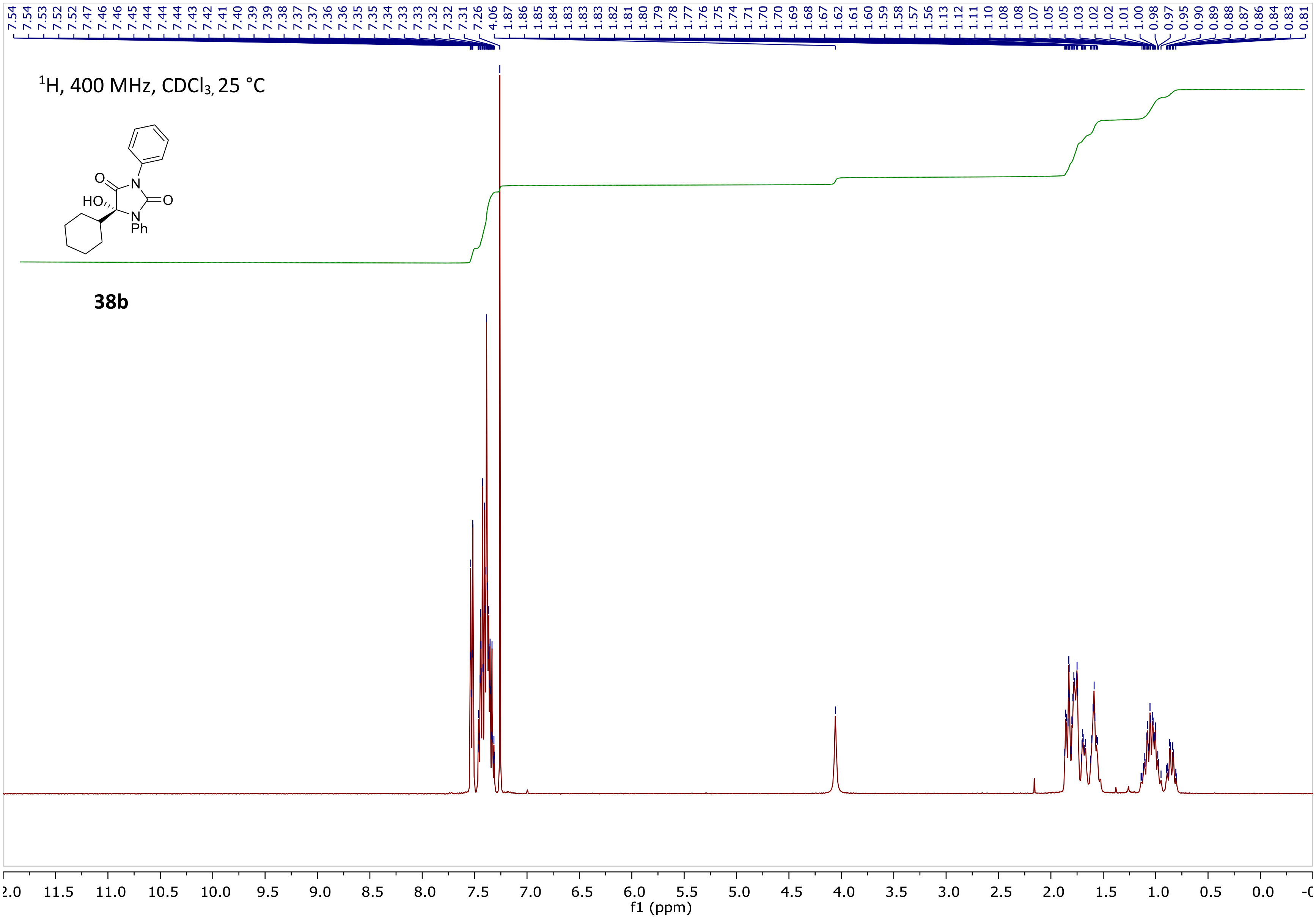

173.26
155.64
131.08
129.34
128.67
126.32
86.98
77.55
77.23
76.91
43.96
26.83
26.14
25.88
25.61
25.37
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
HO
O
N
H
36b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



^{1}H, 400 MHz, CDCl$_3$, 25 °C

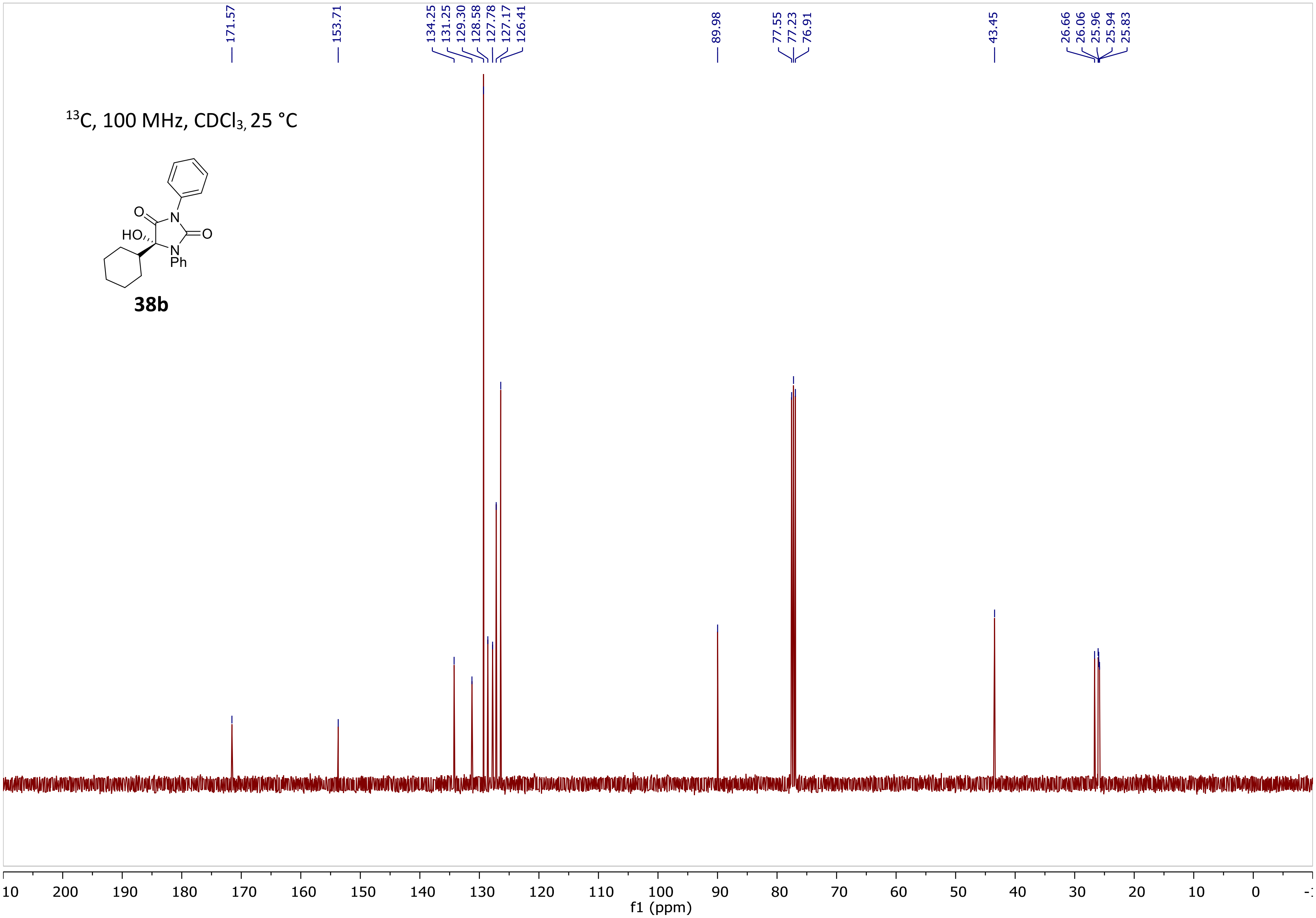
37b

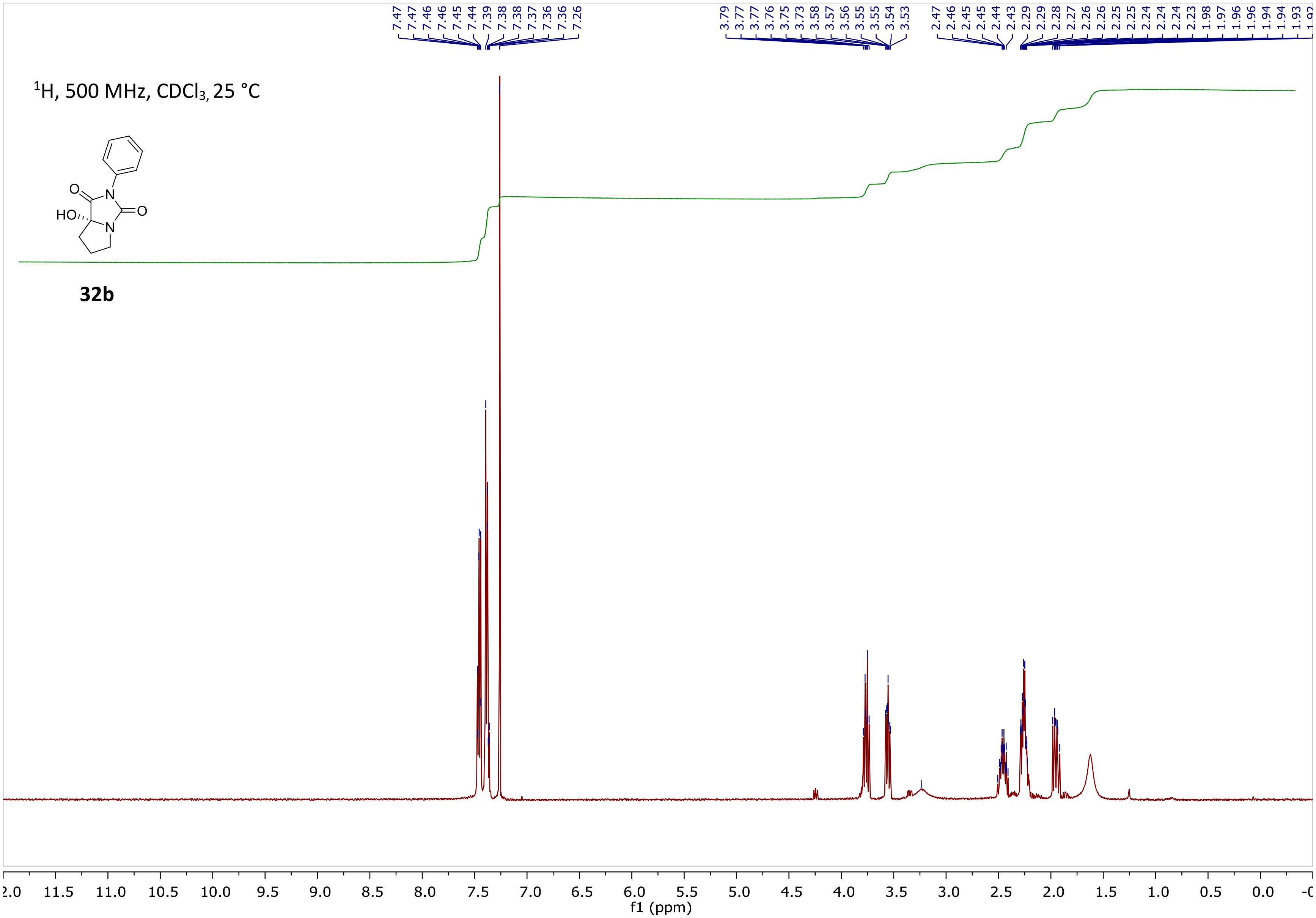

172.32
154.80
131.39
129.22
128.38
126.22
88.03
77.55
77.23
76.91
43.26
26.67
26.33
26.09
25.92
24.85
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
HO
O
N
Me
37b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

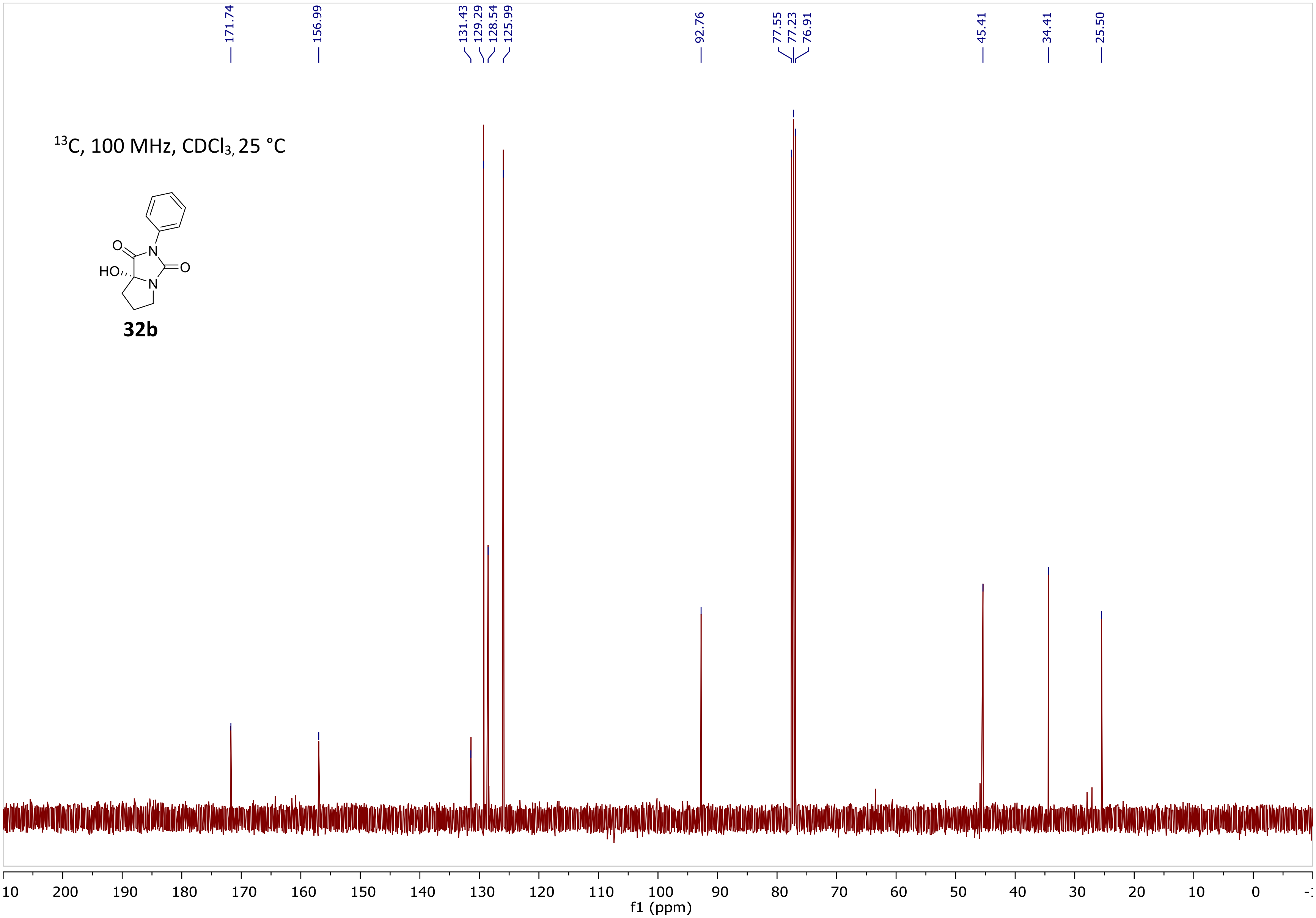

^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
HO
O
N
Ph
38b
7.54
7.54
7.53
7.52
7.52
7.47
7.46
7.46
7.45
7.44
7.44
7.44
7.43
7.42
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.26
4.06
1.87
1.86
1.85
1.84
1.83
1.83
1.83
1.82
1.81
1.80
1.79
1.78
1.77
1.76
1.75
1.74
1.71
1.70
1.70
1.69
1.68
1.67
1.62
1.61
1.60
1.59
1.58
1.57
1.56
1.13
1.12
1.11
1.10
1.08
1.08
1.07
1.05
1.05
1.03
1.02
1.02
1.01
1.00
0.98
0.97
0.95
0.90
0.89
0.88
0.87
0.86
0.84
0.83
0.81
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-
f1 (ppm)

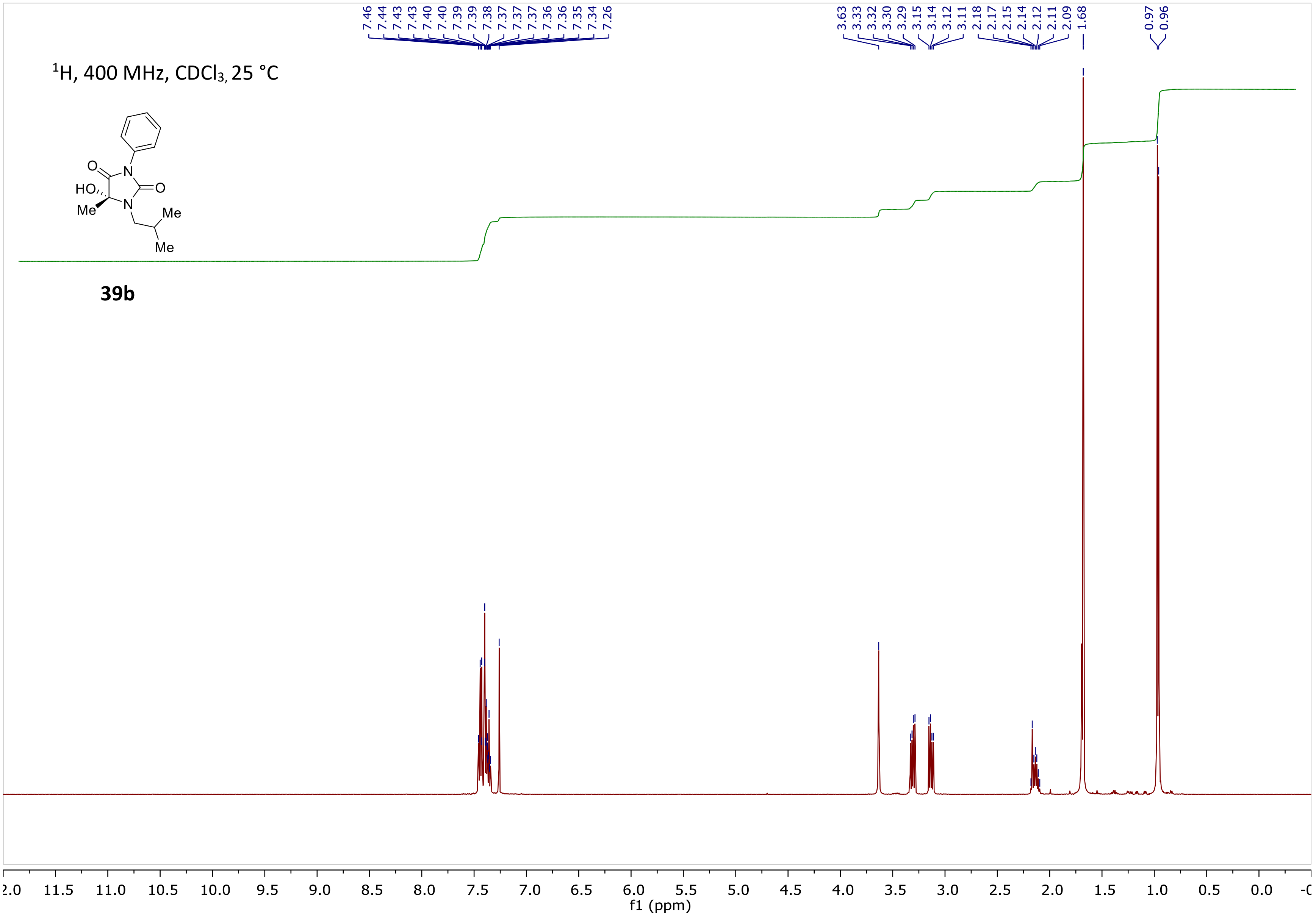
^{13}C, 100 MHz, CDCl$_3$, 25 °C

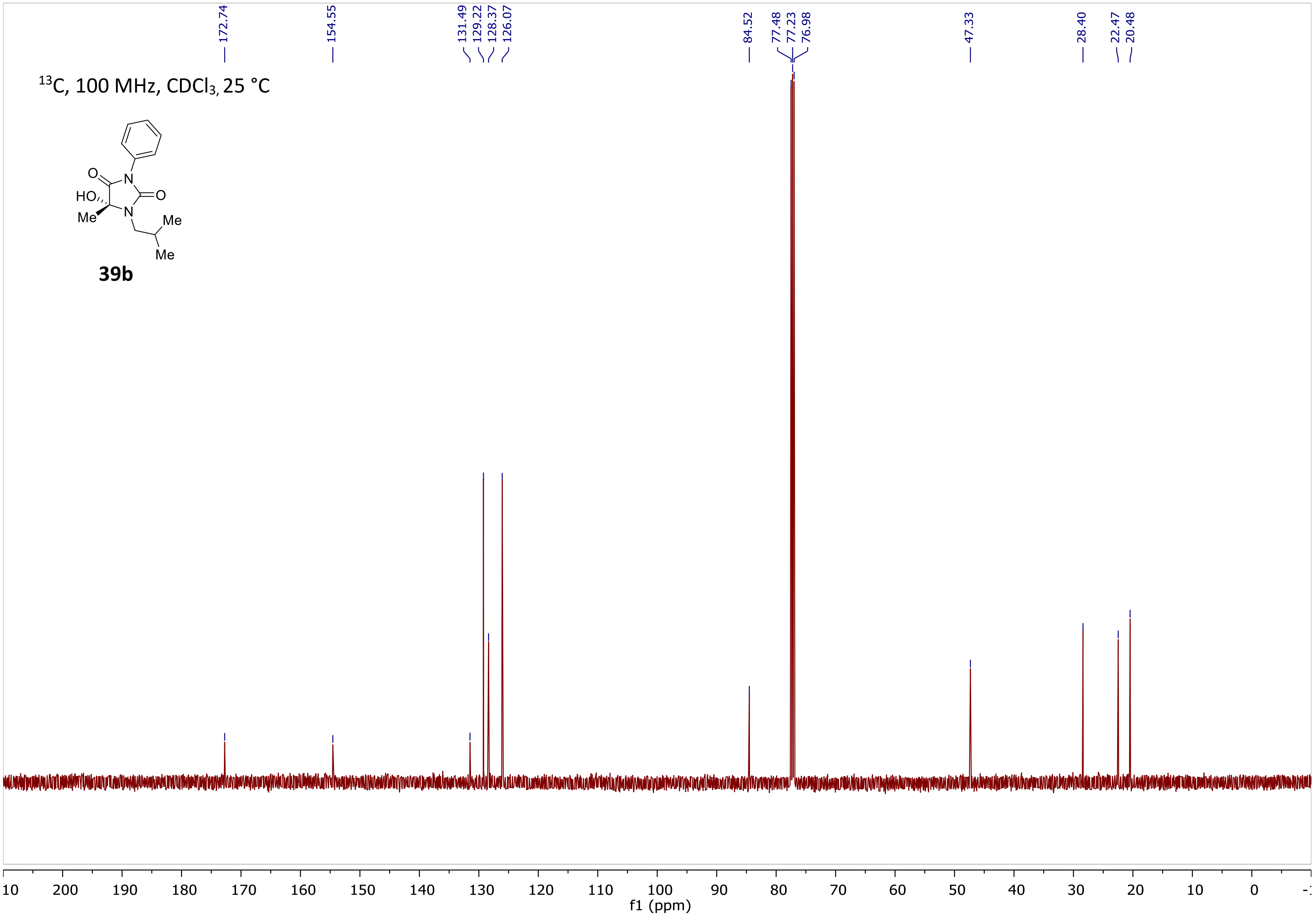
38b

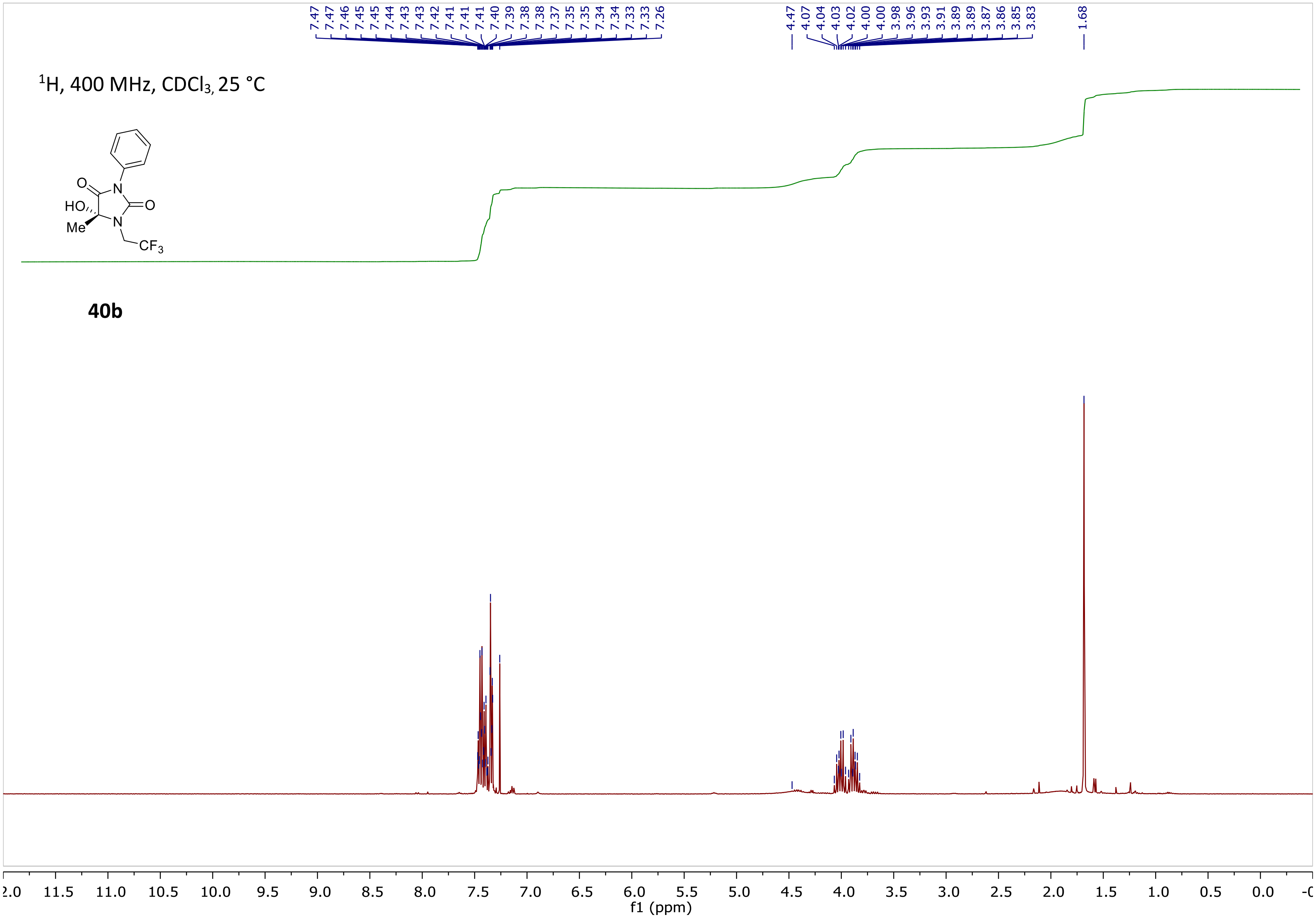


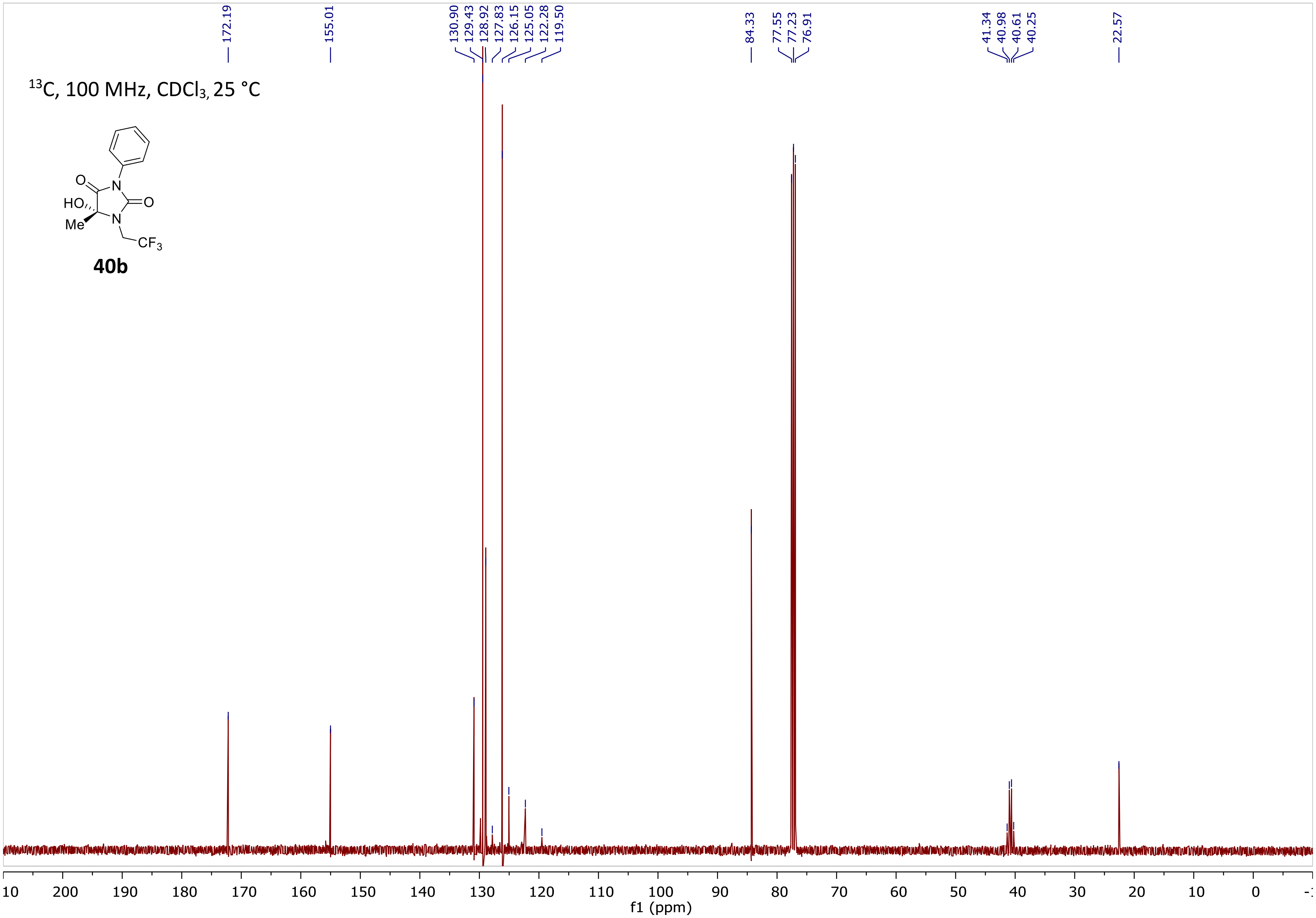

7.47
7.47
7.46
7.46
7.45
7.44
7.39
7.38
7.38
7.37
7.36
7.36
7.26
3.79
3.77
3.77
3.76
3.75
3.73
3.58
3.57
3.56
3.55
3.55
3.54
3.53
2.47
2.46
2.45
2.45
2.44
2.43
2.29
2.29
2.28
2.27
2.26
2.26
2.25
2.25
2.24
2.24
2.24
2.23
1.98
1.97
1.96
1.94
1.94
1.93
^{1}H, 500 MHz, CDCl$_3$, 25 °C
HO
O
N
O
N
32b
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

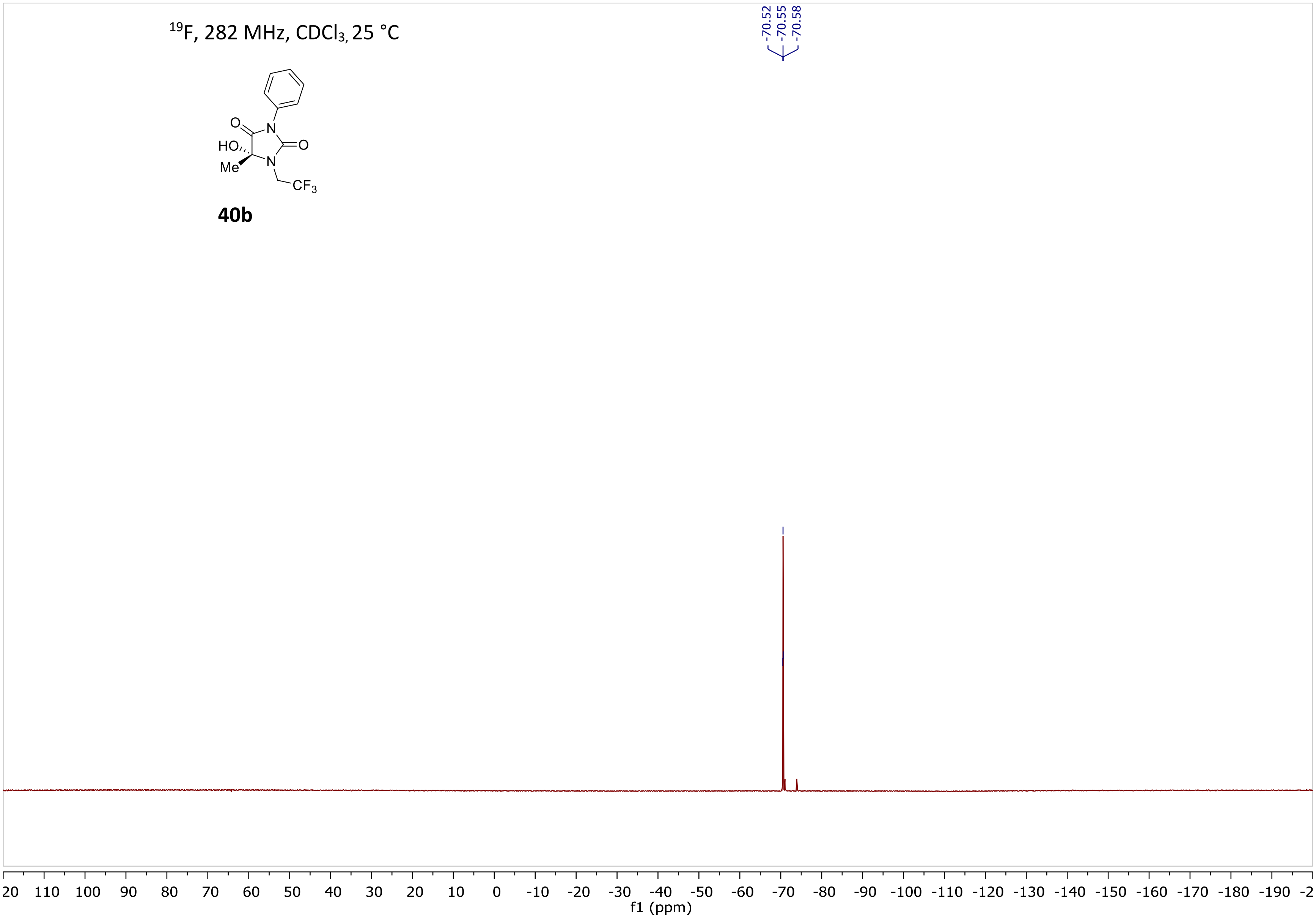

171.74
156.99
131.43
129.29
128.54
125.99
92.76
77.55
77.23
76.91
45.41
34.41
25.50
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
O
HO
N
32b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:
f1 (ppm)


7.46
7.44
7.43
7.43
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.34
7.26
3.63
3.33
3.32
3.30
3.29
3.15
3.14
3.12
3.11
2.18
2.17
2.15
2.14
2.12
2.11
2.09
1.68
0.97
0.96
1H, 400 MHz, CDCl3, 25 °C
O
N
HO
O
Me
N
Me
Me
39b
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

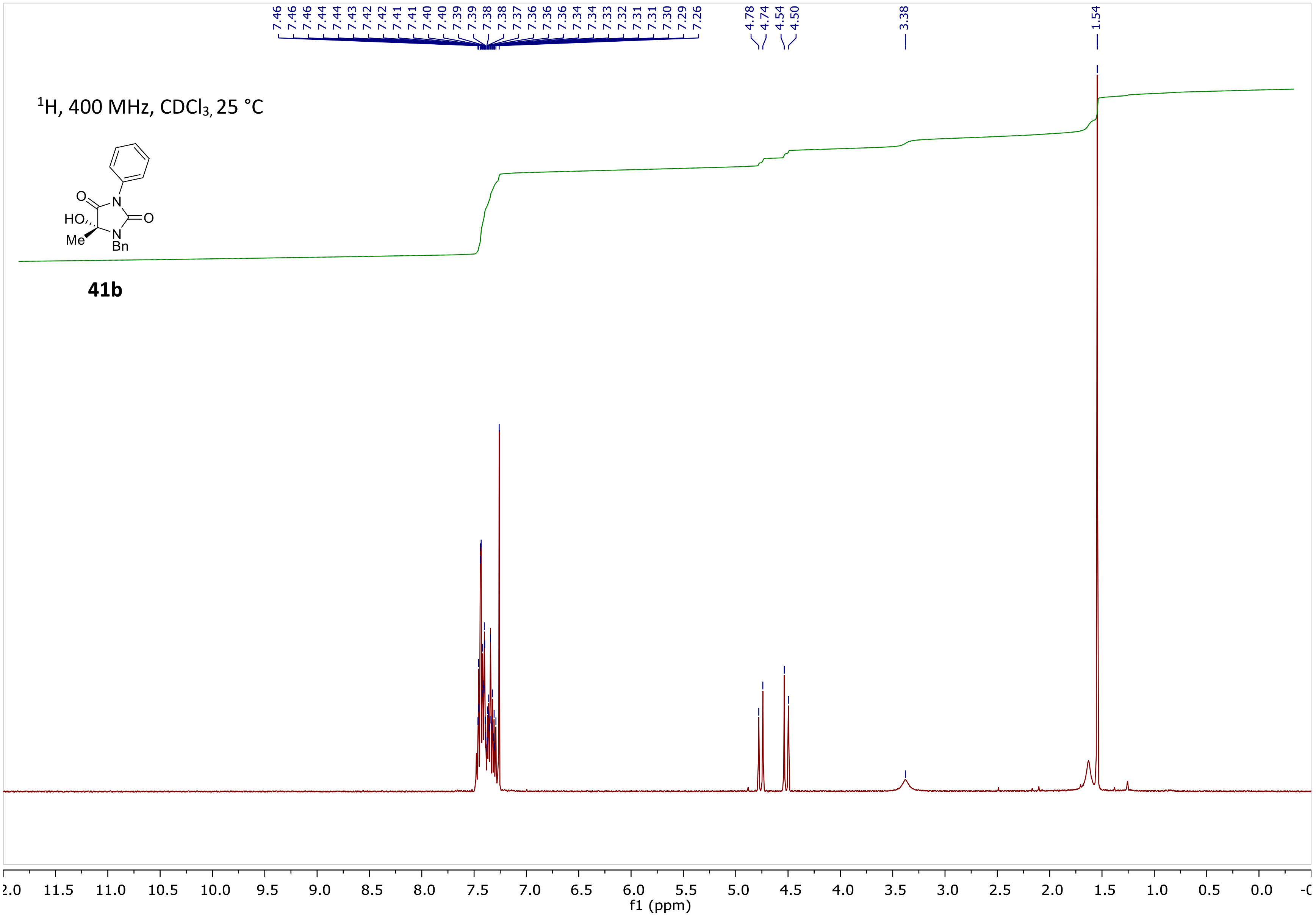

172.74
154.55
131.49
129.22
128.37
126.07
84.52
77.48
77.23
76.98
47.33
28.40
22.47
20.48
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
HO
O
Me
N
Me
Me
39b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.41
7.40
7.39
7.38
7.38
7.37
7.35
7.35
7.34
7.34
7.33
7.33
7.26
4.47
4.07
4.04
4.03
4.02
4.00
4.00
3.98
3.96
3.93
3.91
3.89
3.89
3.87
3.86
3.85
3.83
1.68
^{1}H, 400 MHz, CDCl$_3$, 25 °C
O
N
HO
O
Me
N
CF$_3$
40b
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)


172.19
155.01
130.90
129.43
128.92
127.83
126.15
125.05
122.28
119.50
84.33
77.55
77.23
76.91
41.34
40.98
40.61
40.25
22.57
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
HO
O
Me
N
CF$_3$
40b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

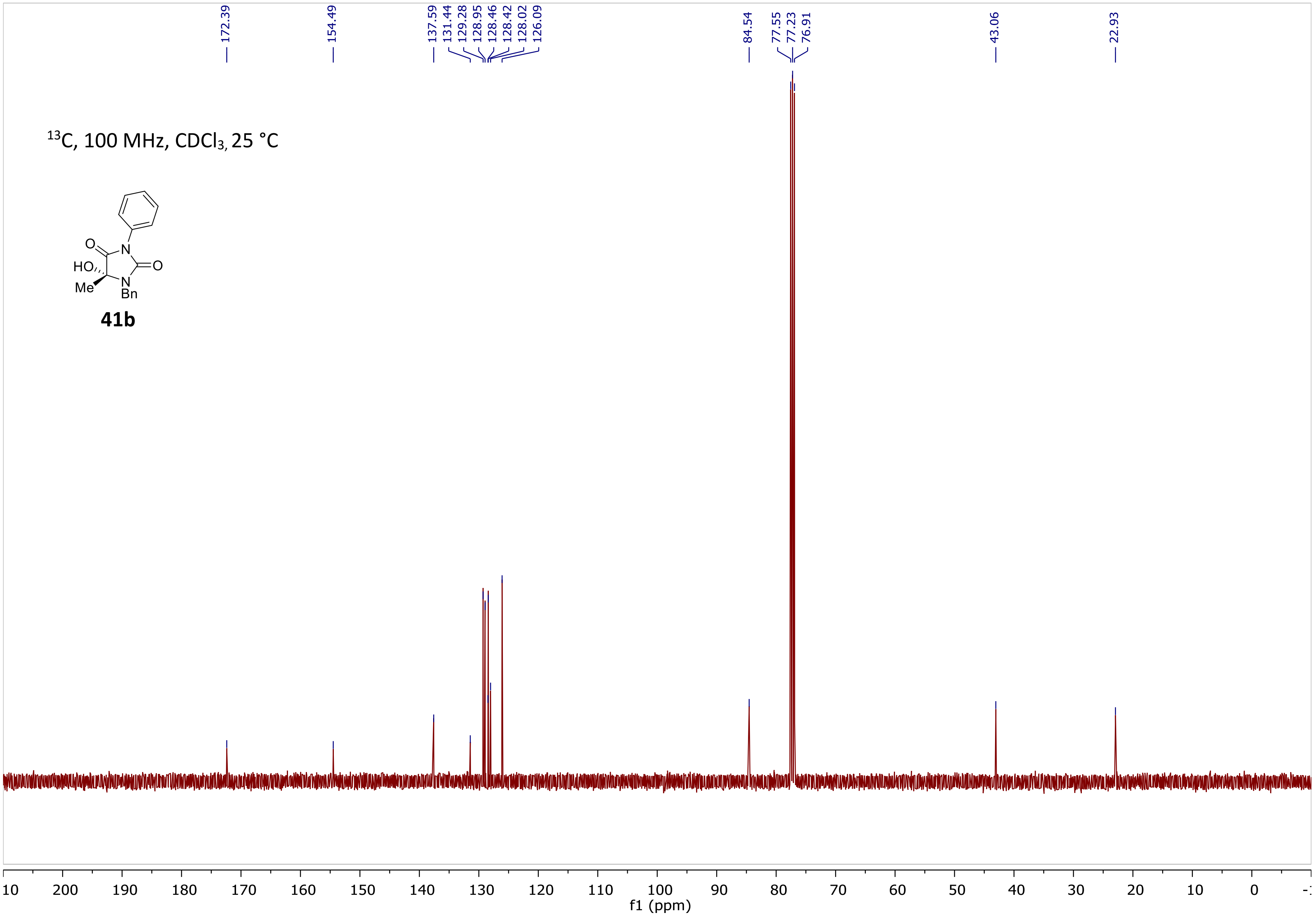

19F, 282 MHz, CDCl3, 25 °C
-70.52
-70.55
-70.58
O
N
O
HO
Me
N
CF3
20
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

40b

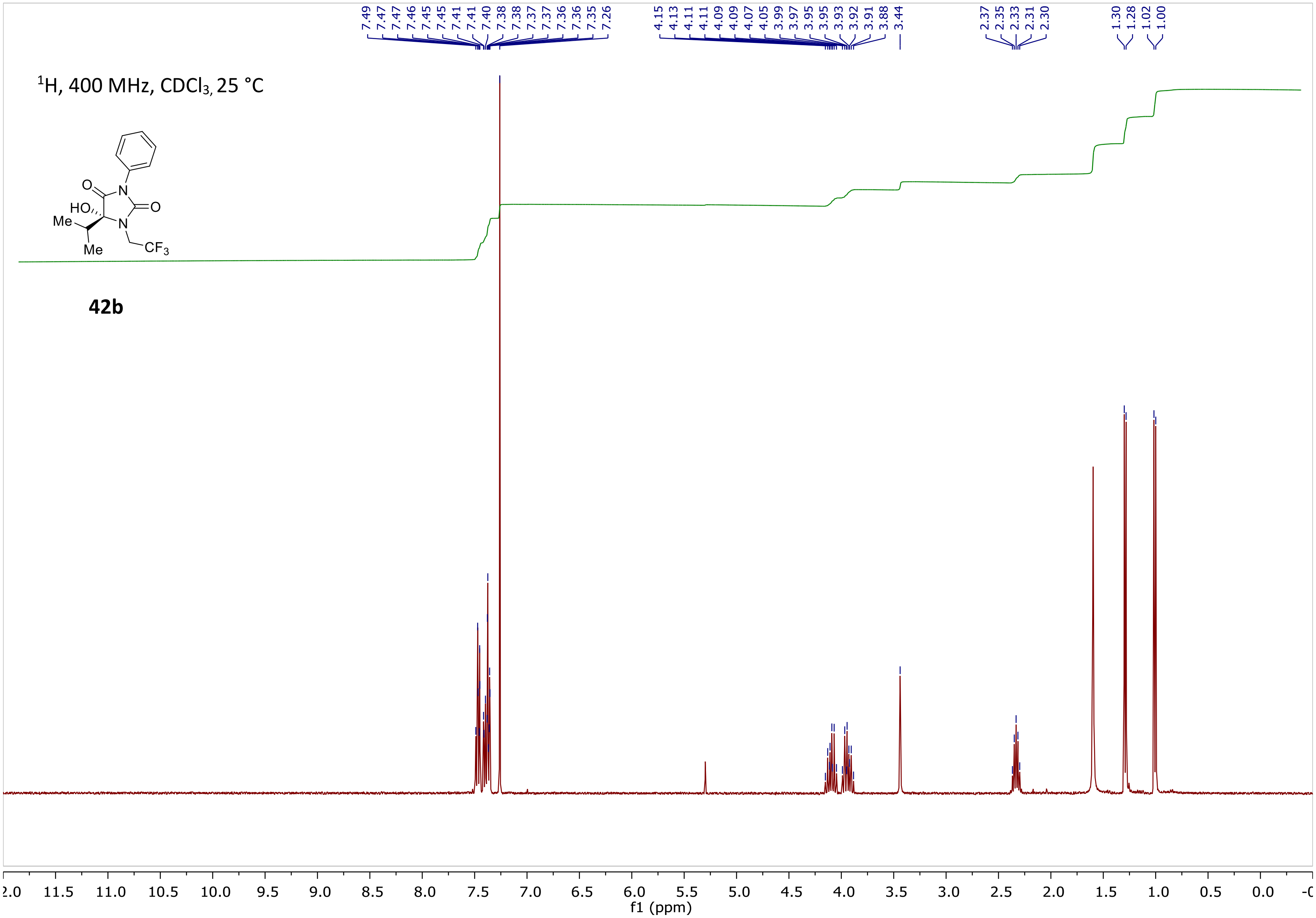


^{1}H, 400 MHz, CDCl$_3$, 25 °C

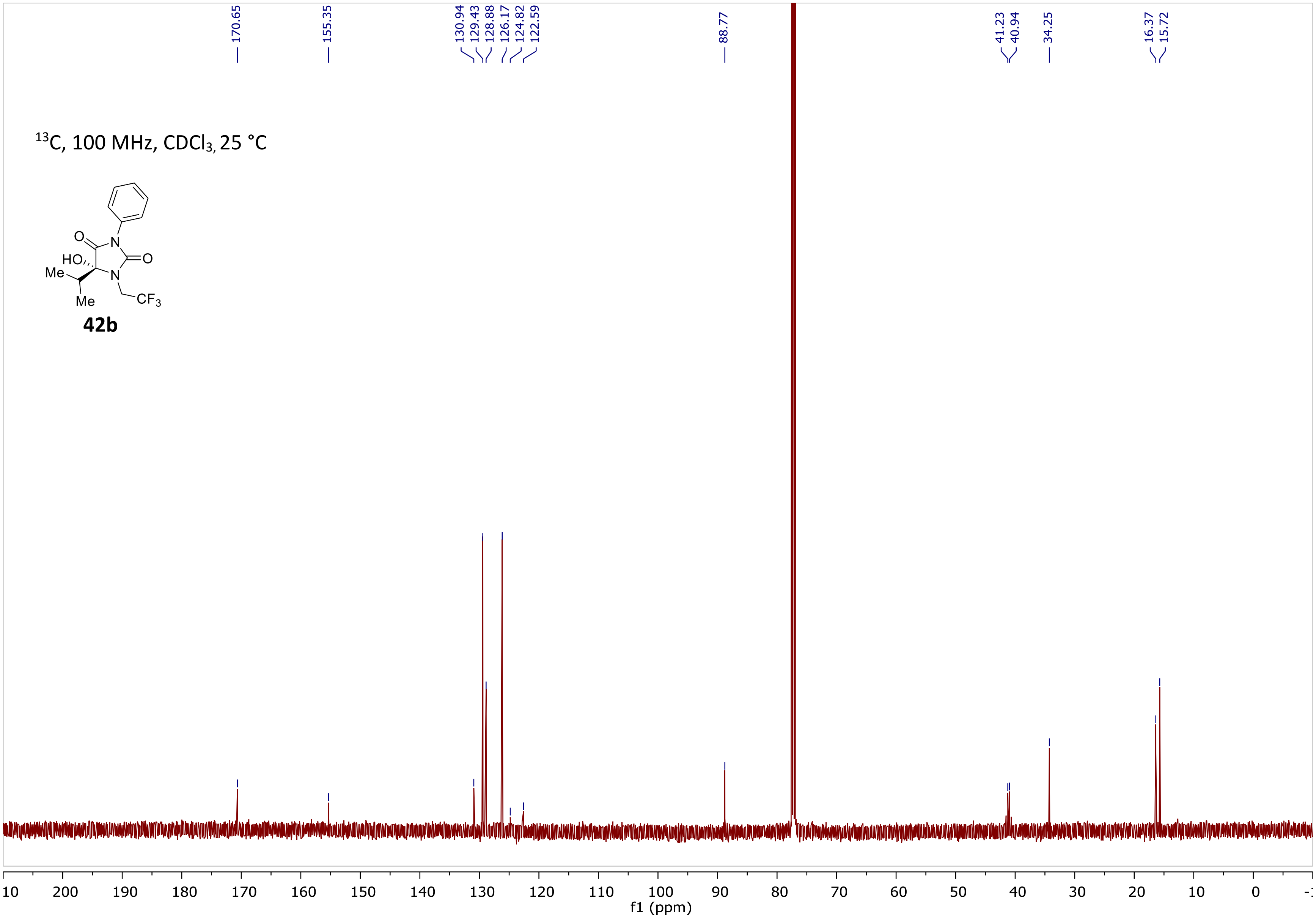
41b

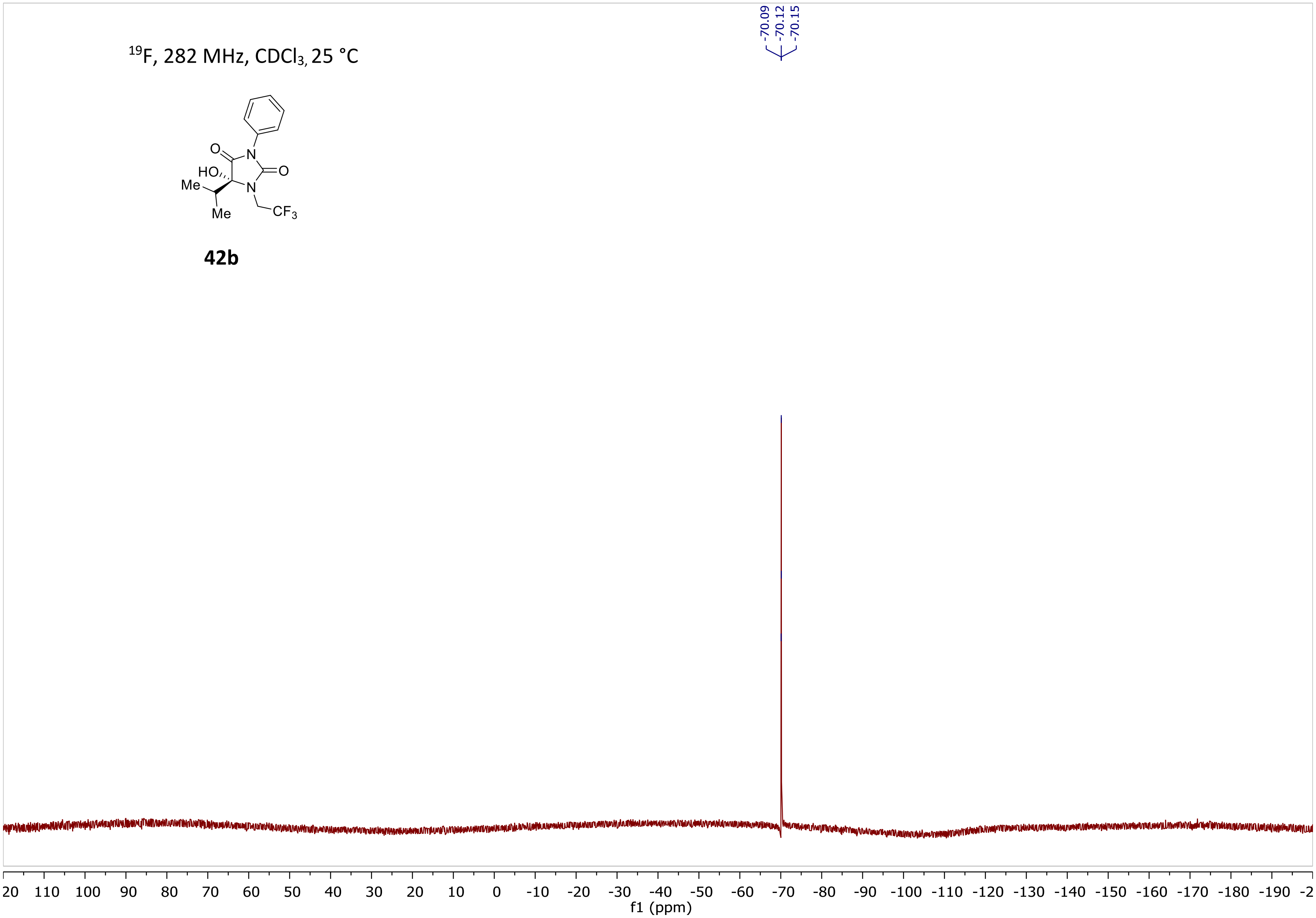

172.39
154.49
137.59
131.44
129.28
128.95
128.46
128.42
128.02
126.09
84.54
77.55
77.23
76.91
43.06
22.93
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
HO
O
Me
N
Bn
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

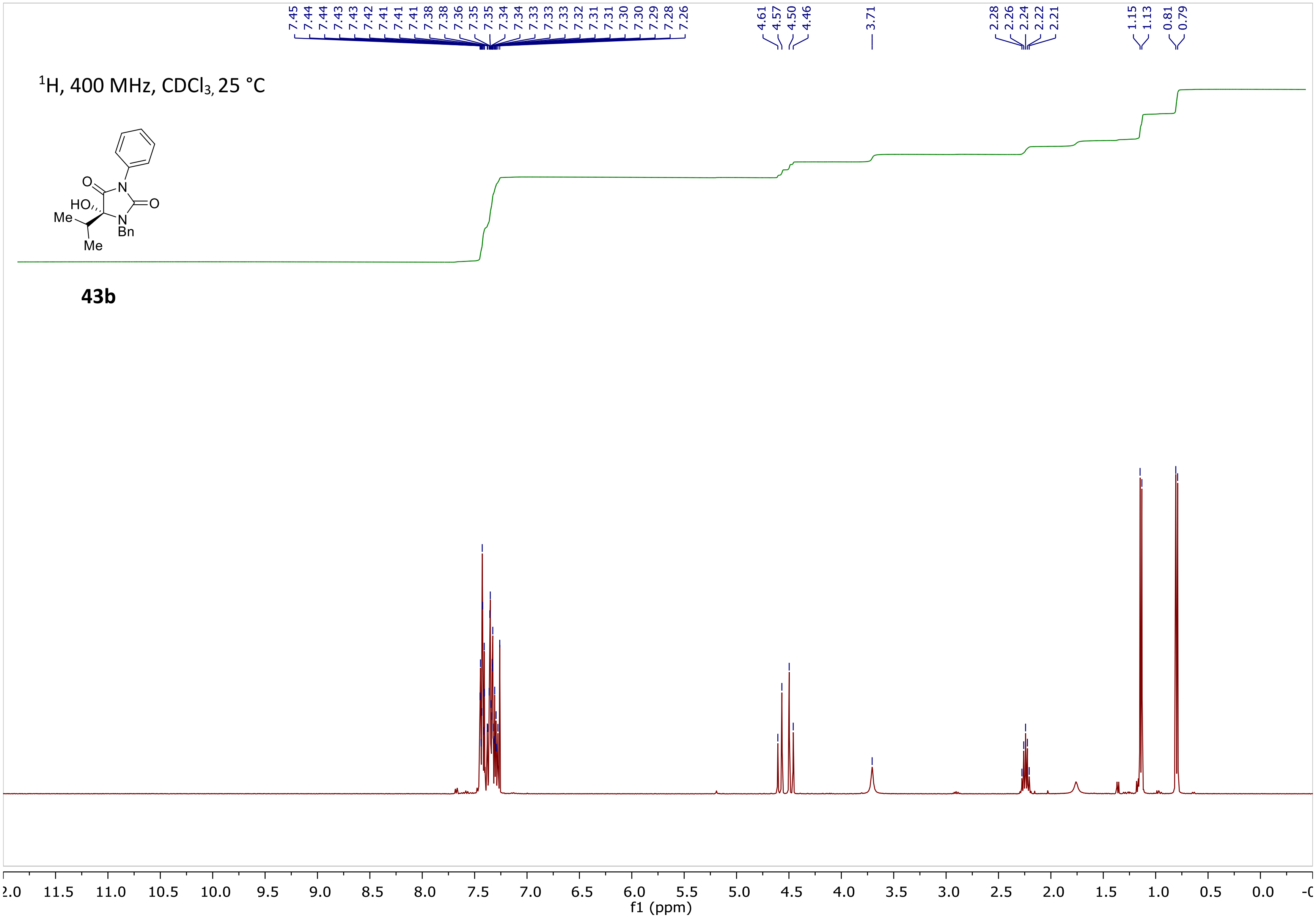
41b

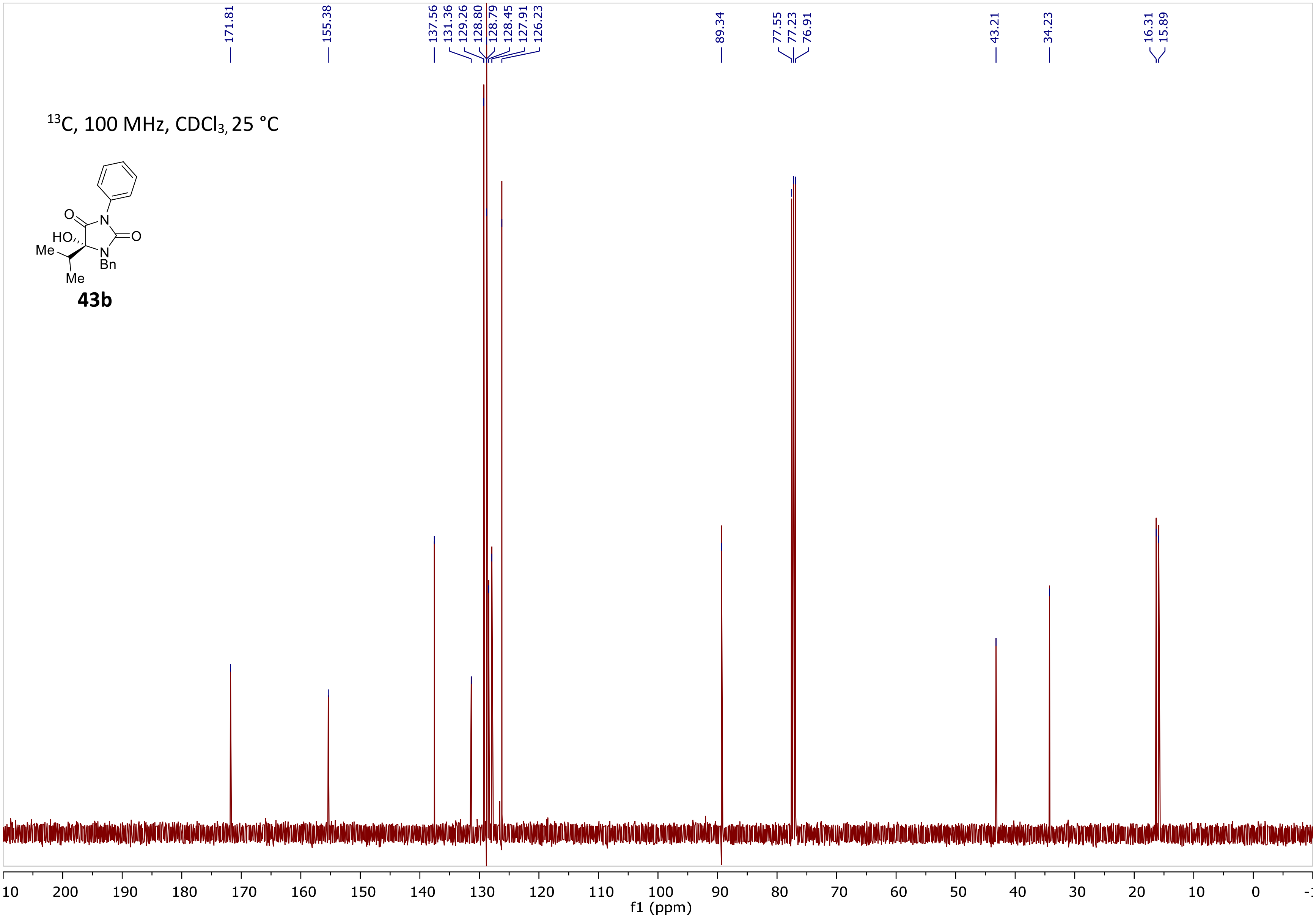

7.49
7.47
7.47
7.46
7.45
7.45
7.41
7.40
7.38
7.38
7.37
7.36
7.35
7.26
4.15
4.13
4.11
4.11
4.09
4.09
4.07
4.05
3.99
3.97
3.95
3.95
3.93
3.92
3.91
3.88
3.44
2.37
2.35
2.33
2.31
2.30
1.30
1.28
1.02
1.00
¹H, 400 MHz, CDCl₃, 25 °C
O
N
HO
O
Me
N
Me
CF₃
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

42b

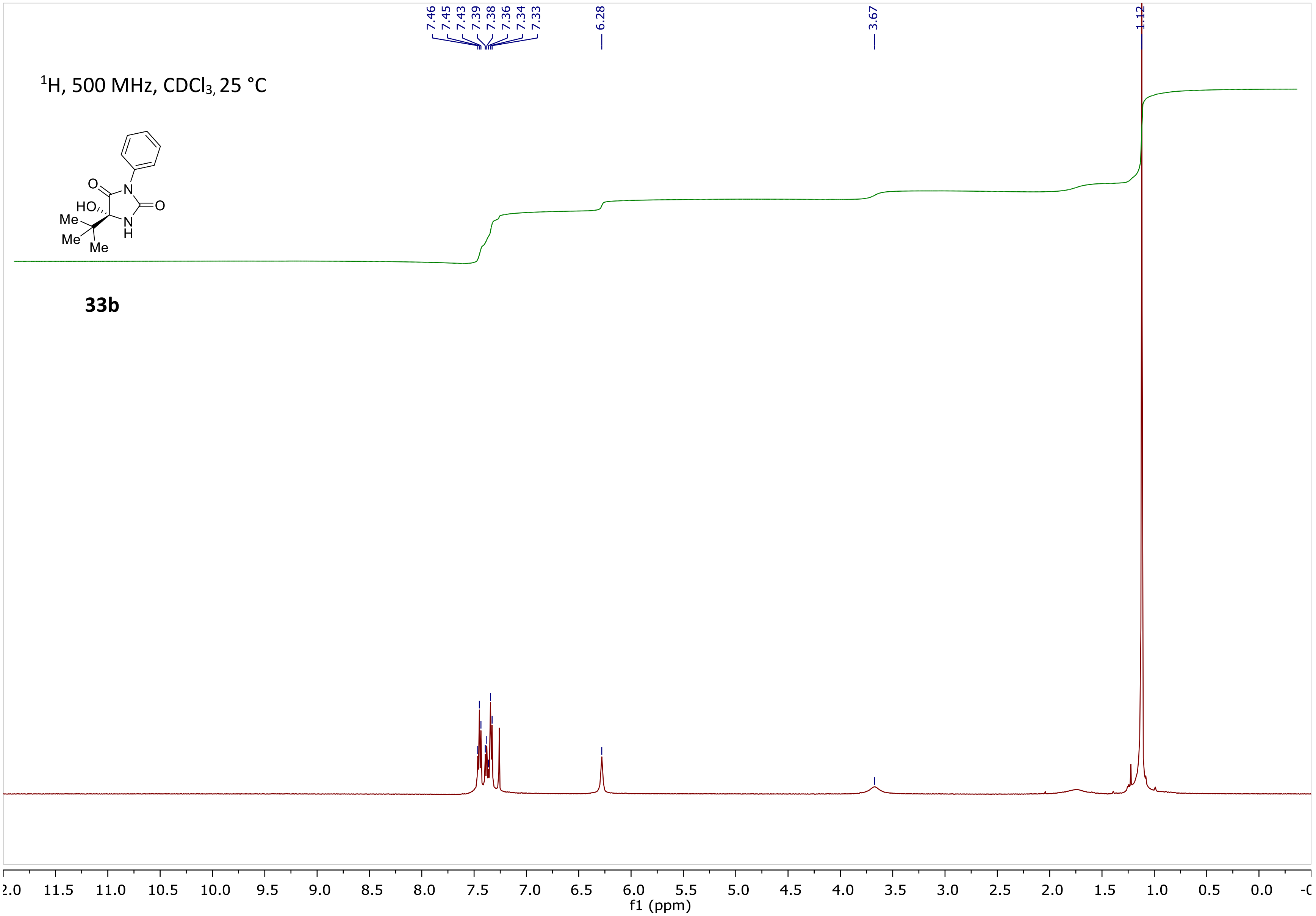

170.65
155.35
130.94
129.43
128.88
126.17
124.82
122.59
88.77
41.23
40.94
34.25
16.37
15.72
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
HO
O
Me
N
Me
CF$_3$
42b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:
f1 (ppm)


^{19}F, 282 MHz, CDCl$_3$, 25 °C
O
N
HO
Me
N
O
Me
CF$_3$
42b
-70.09
-70.12
-70.15
20
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)


7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.41
7.41
7.38
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.26
4.61
4.57
4.50
4.46
3.71
2.28
2.26
2.24
2.22
2.21
1.15
1.13
0.81
0.79
¹H, 400 MHz, CDCl3, 25 °C
O
N
O
HO
Me
N
Bn
Me
43b
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)

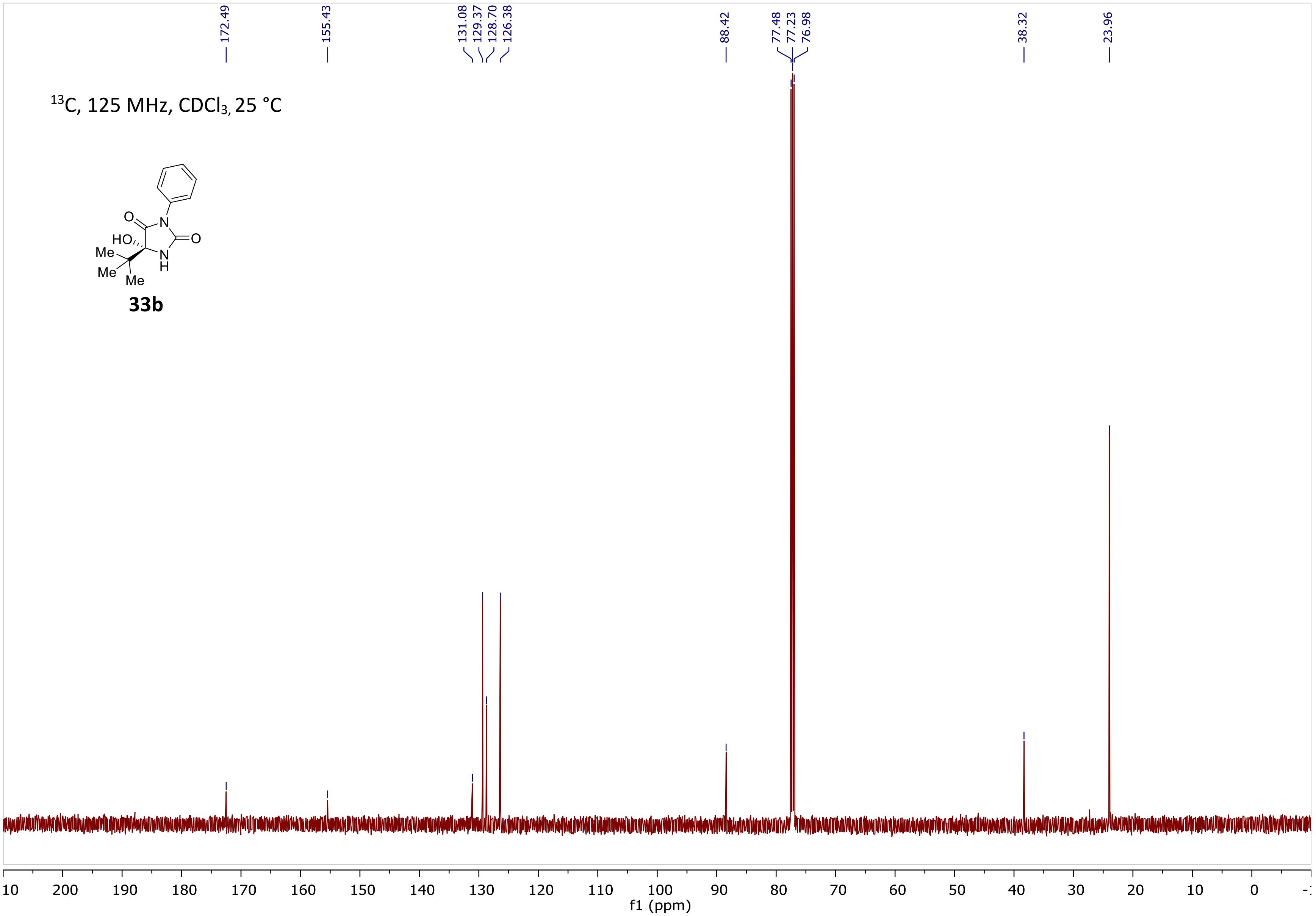

171.81
155.38
137.56
131.36
129.26
128.80
128.79
128.45
127.91
126.23
89.34
77.55
77.23
76.91
43.21
34.23
16.31
15.89
^{13}C, 100 MHz, CDCl$_3$, 25 °C
O
N
HO
O
Me
N
Bn
Me
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

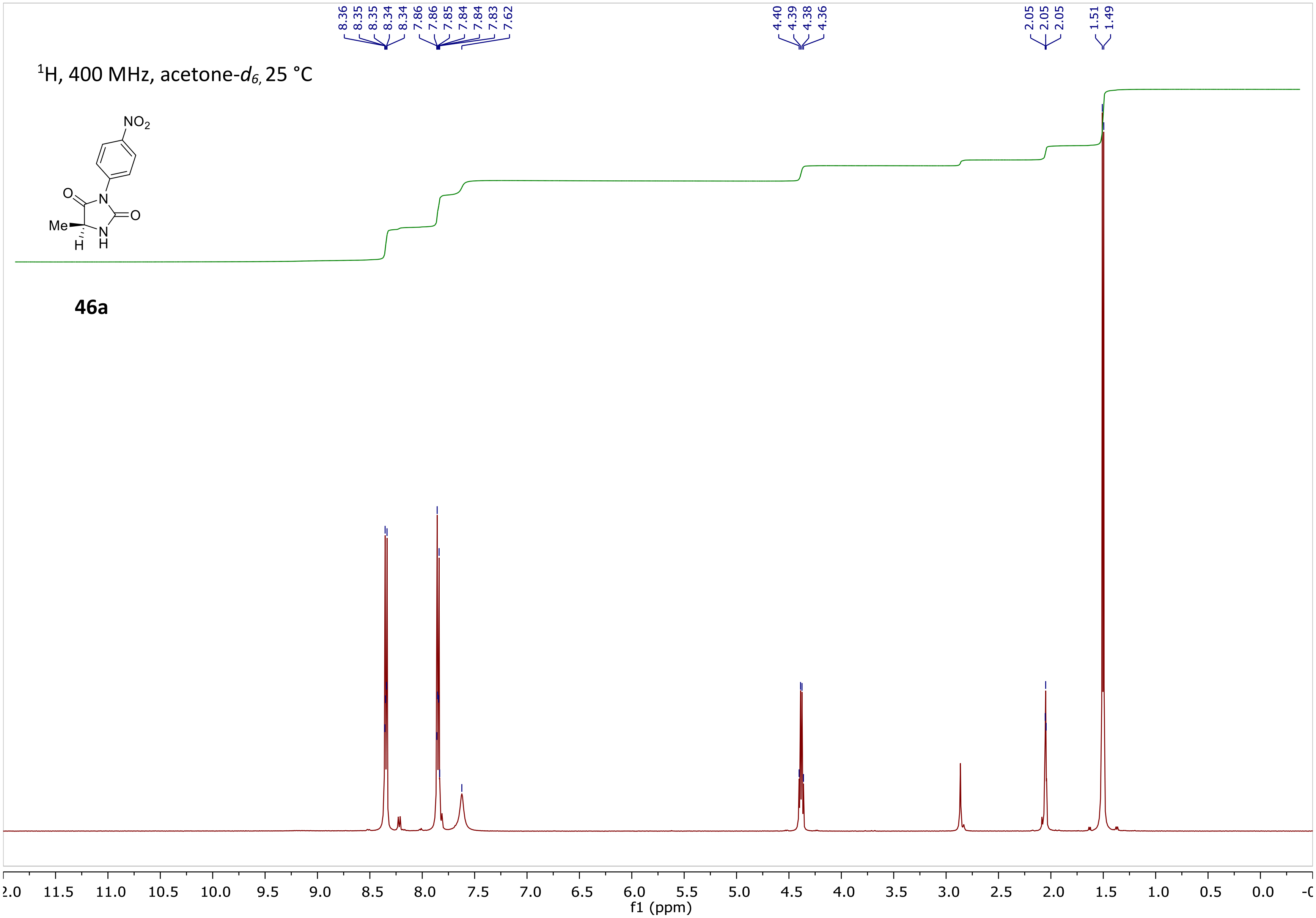
43b

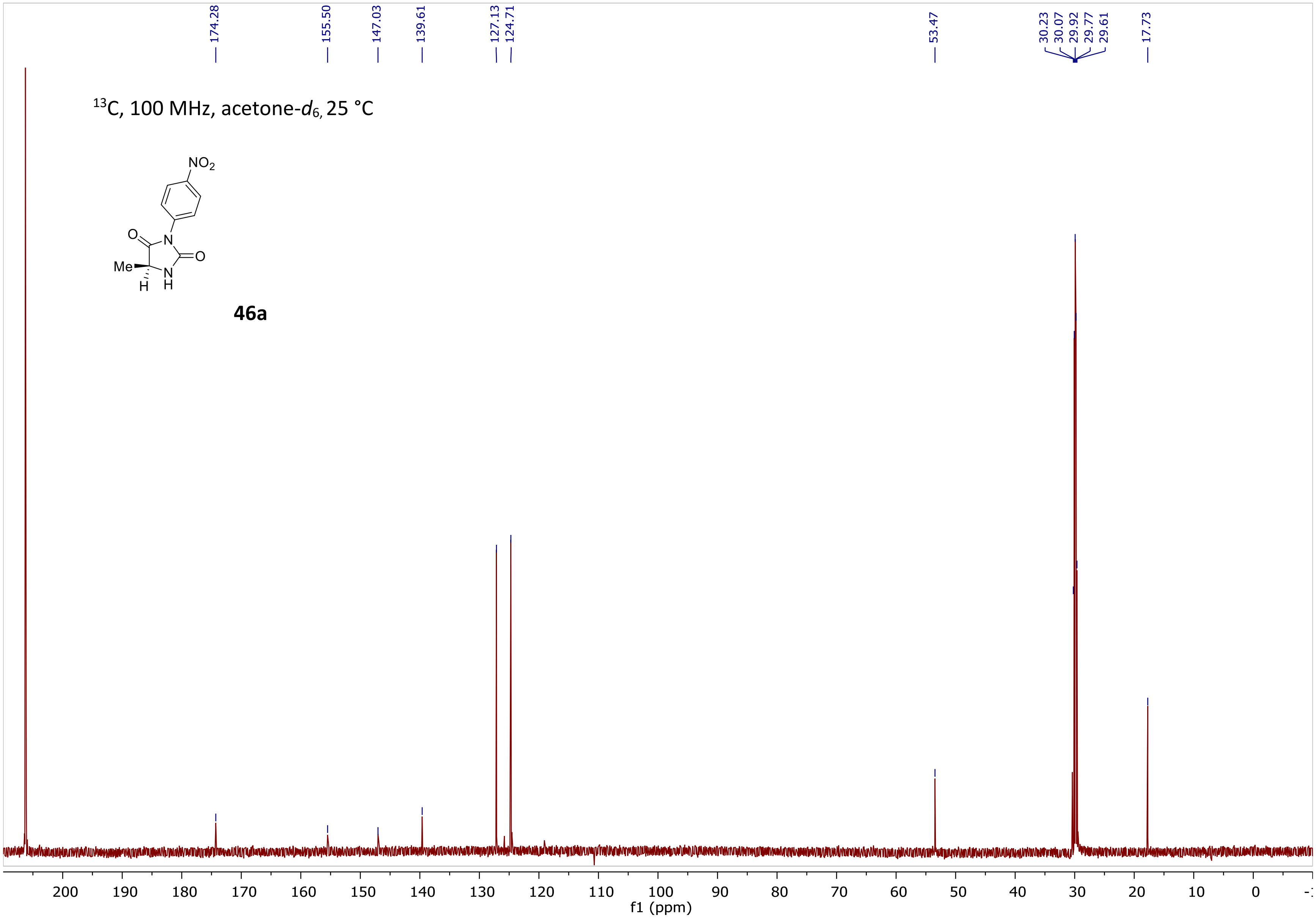


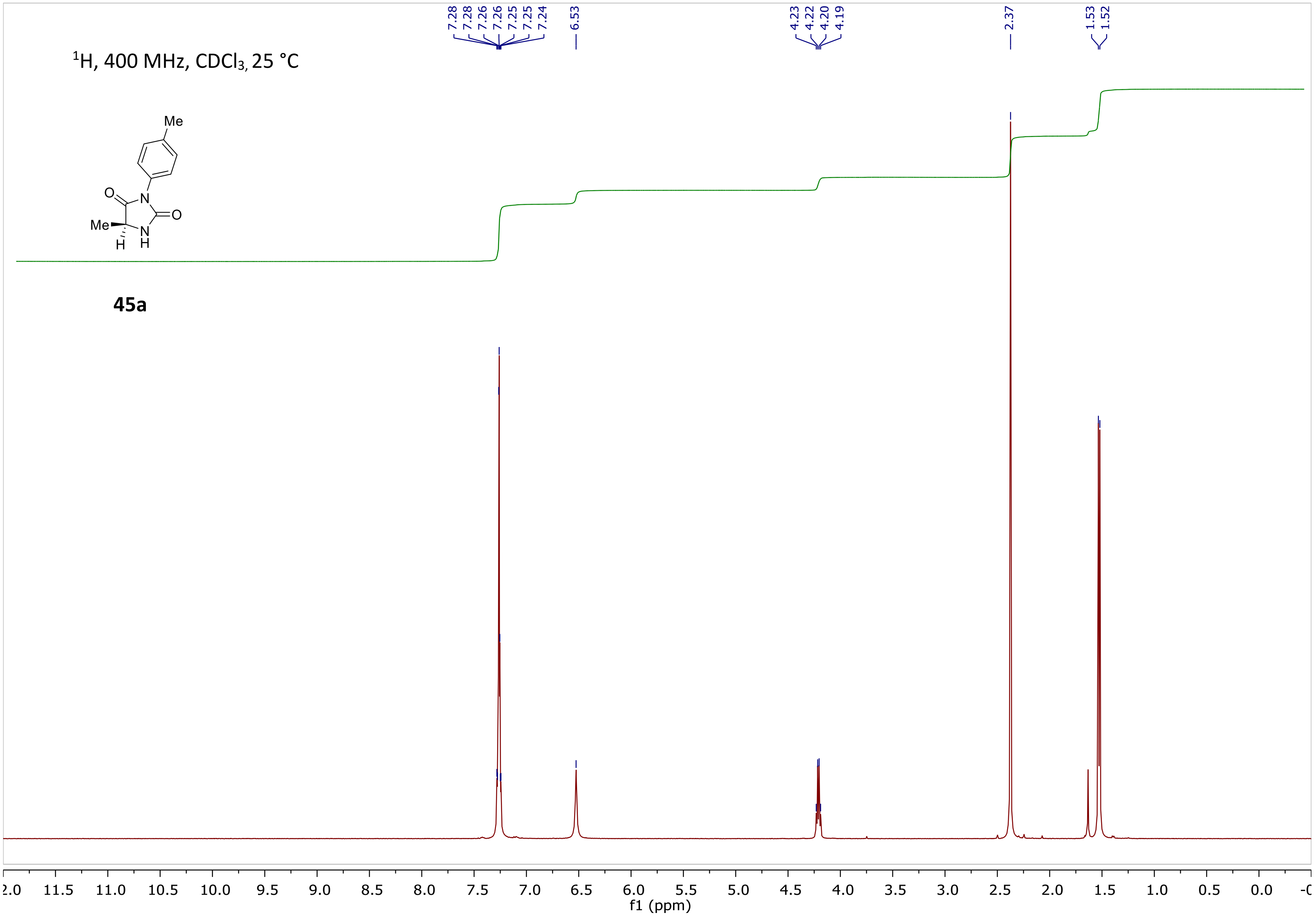
^1H, 500 MHz, $CDCl_3$, 25 °C

33b

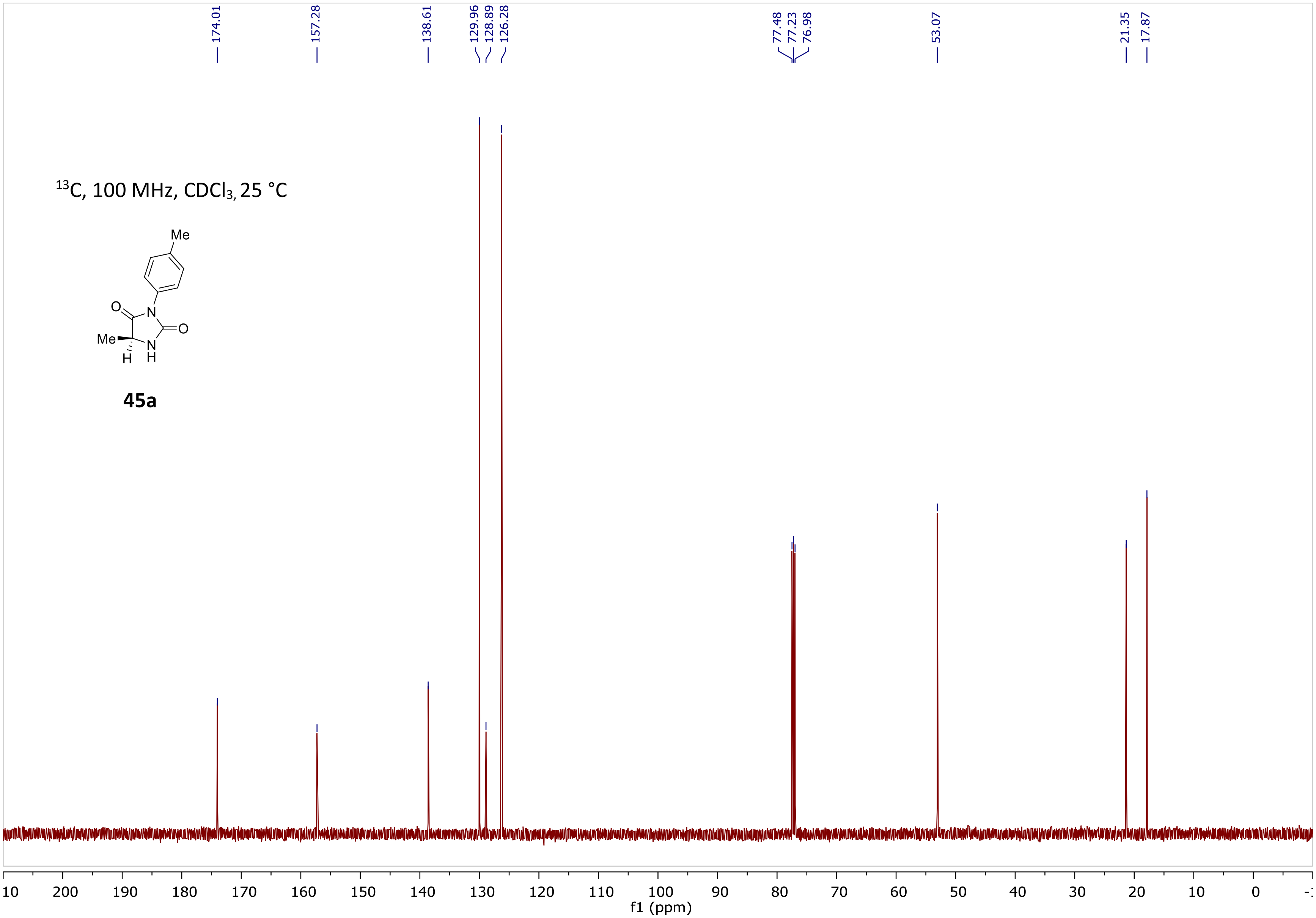

172.49
155.43
131.08
129.37
128.70
126.38
88.42
77.48
77.23
76.98
38.32
23.96
^{13}C, 125 MHz, CDCl$_3$, 25 °C
O
N
HO
O
Me
N
H
Me
Me
33b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

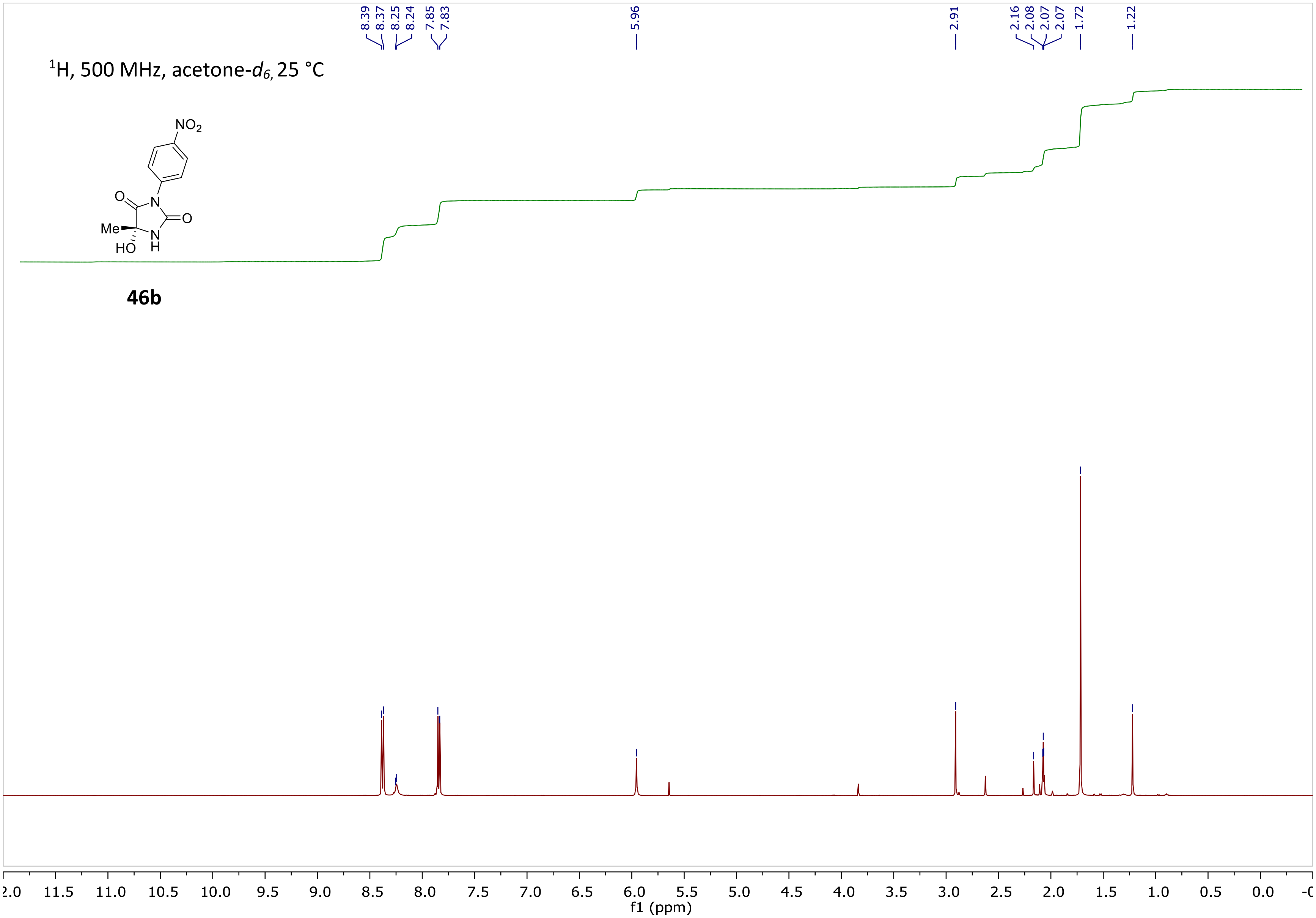

1H, 400 MHz, acetone-d6, 25 °C
NO2
O
N
O
Me
N
H
H
46a
8.36
8.35
8.35
8.34
8.34
7.86
7.86
7.85
7.84
7.84
7.83
7.62
4.40
4.39
4.38
4.36
2.05
2.05
2.05
1.51
1.49
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-
f1 (ppm)

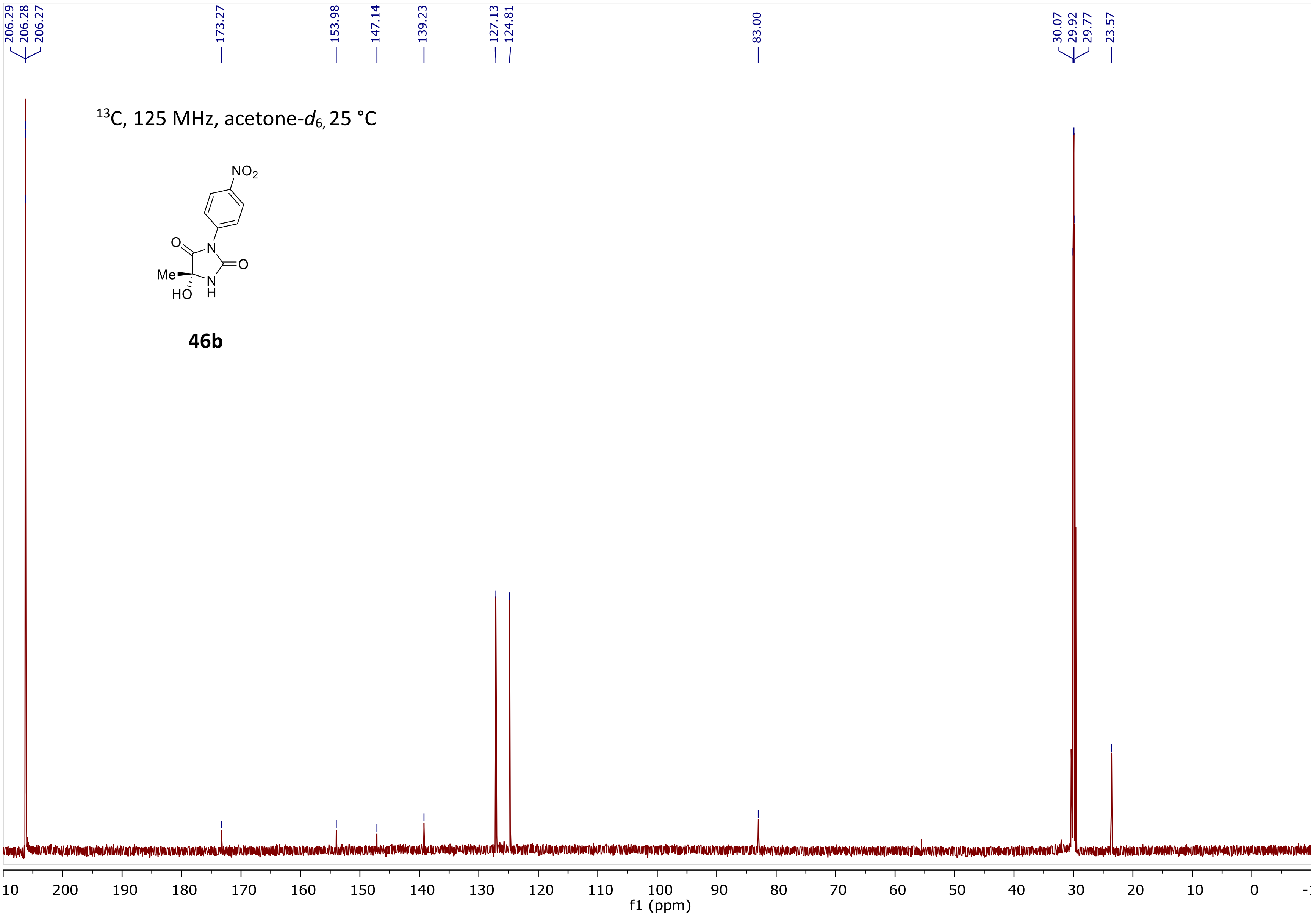

174.28
155.50
147.03
139.61
127.13
124.71
53.47
30.23
30.07
29.92
29.77
29.61
17.73
^{13}C, 100 MHz, acetone-d_6, 25 °C
NO$_2$
O
N
O
Me
N
H
H
46a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


^{1}H, 400 MHz, $CDCl_3$, 25 °C
Me
O
N
O
Me
N
H
H
7.28
7.28
7.26
7.26
7.25
7.25
7.24
6.53
4.23
4.22
4.20
4.19
2.37
1.53
1.52
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

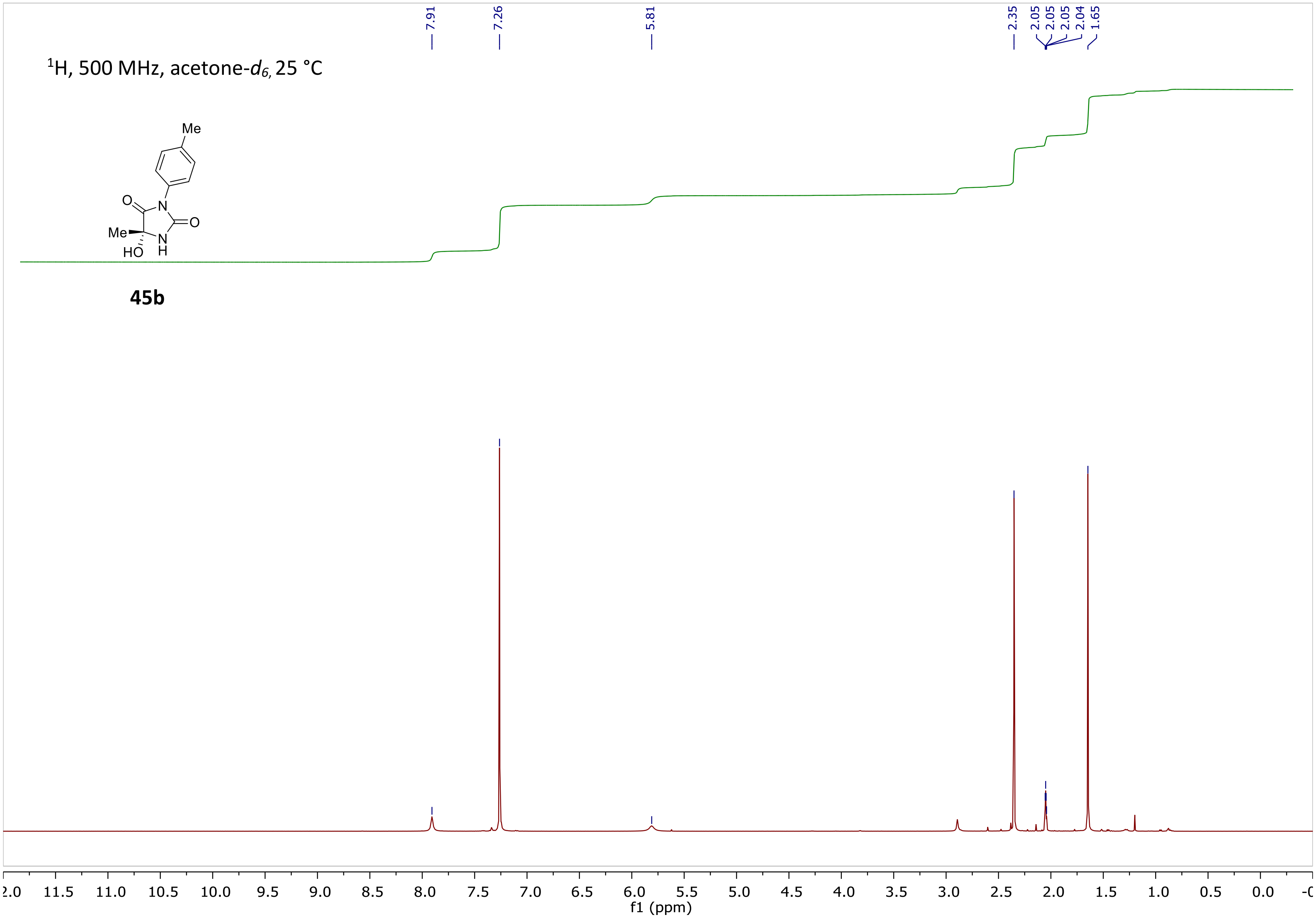
45a


174.01
157.28
138.61
129.96
128.89
126.28
77.48
77.23
76.98
53.07
21.35
17.87
13C, 100 MHz, CDCl3, 25 °C
Me
O
N
O
Me
H
N
H
45a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

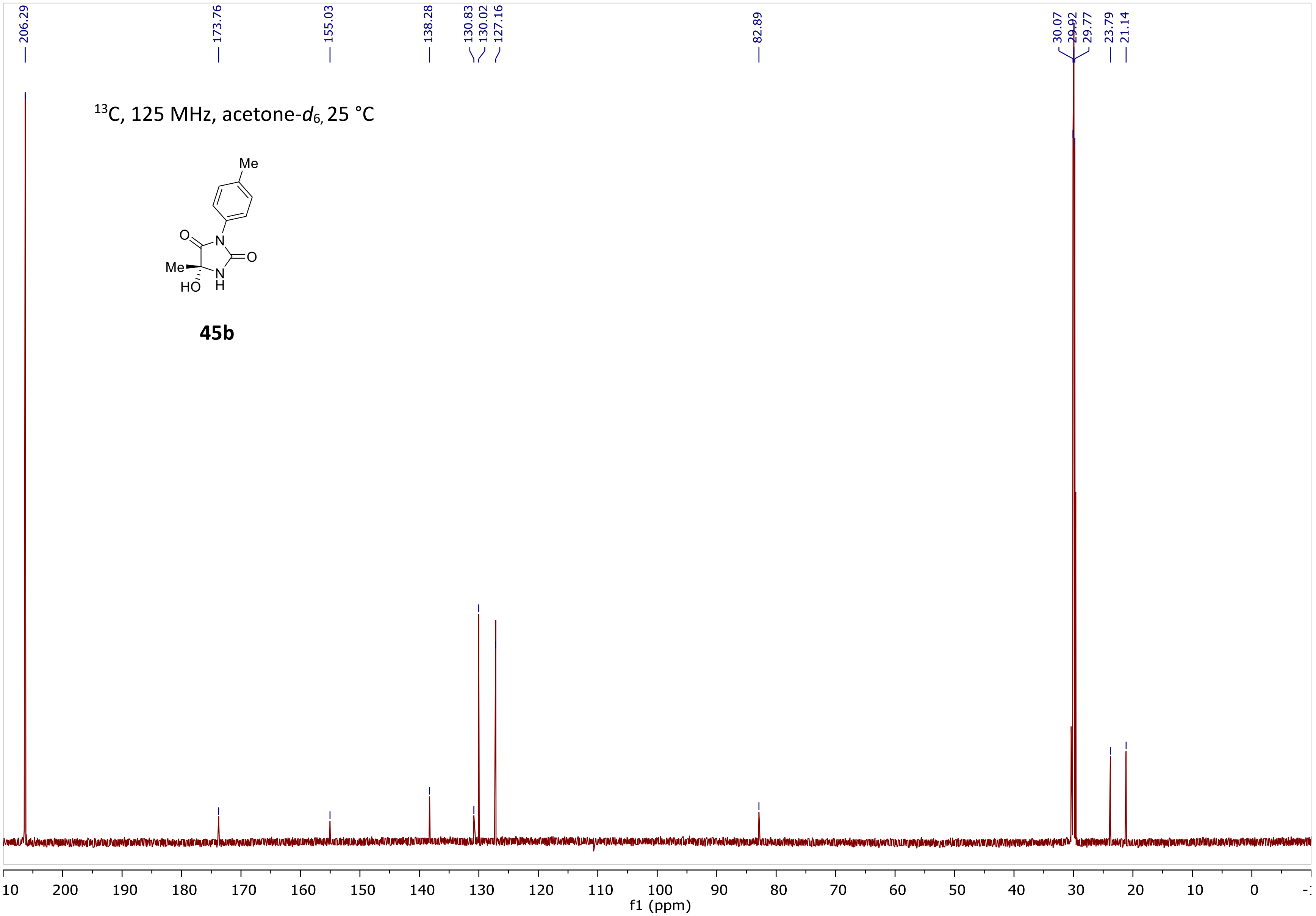

8.39
8.37
8.25
8.24
7.85
7.83
5.96
2.91
2.16
2.08
2.07
2.07
1.72
1.22
1H, 500 MHz, acetone-d6, 25 °C
NO2
O
N
O
Me
N
HO
H
46b
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)

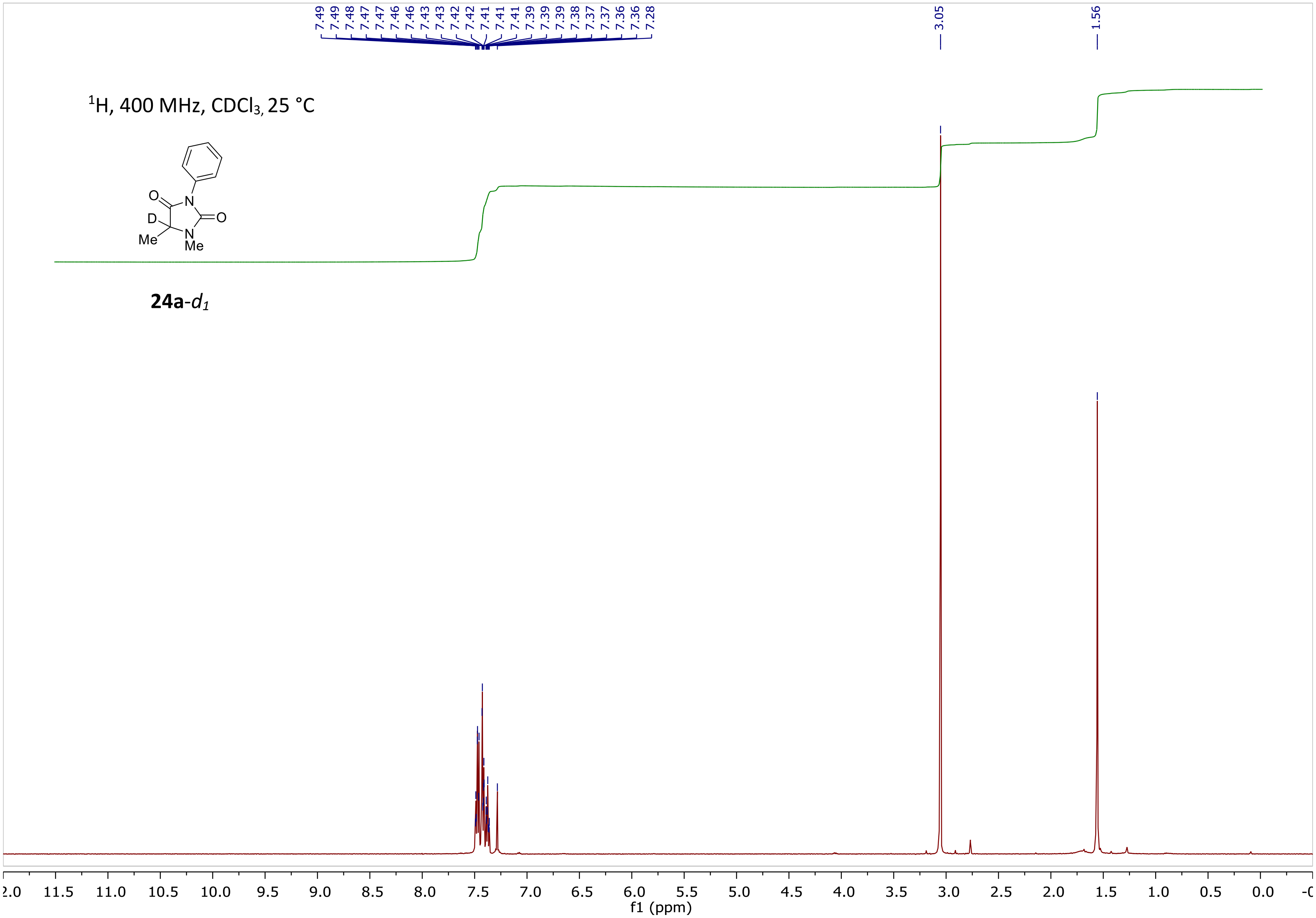

206.29
206.28
206.27
173.27
153.98
147.14
139.23
127.13
124.81
83.00
30.07
29.92
29.77
23.57
^{13}C, 125 MHz, acetone-d_6, 25 °C
NO$_2$
O
N
O
Me
N
HO
H
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

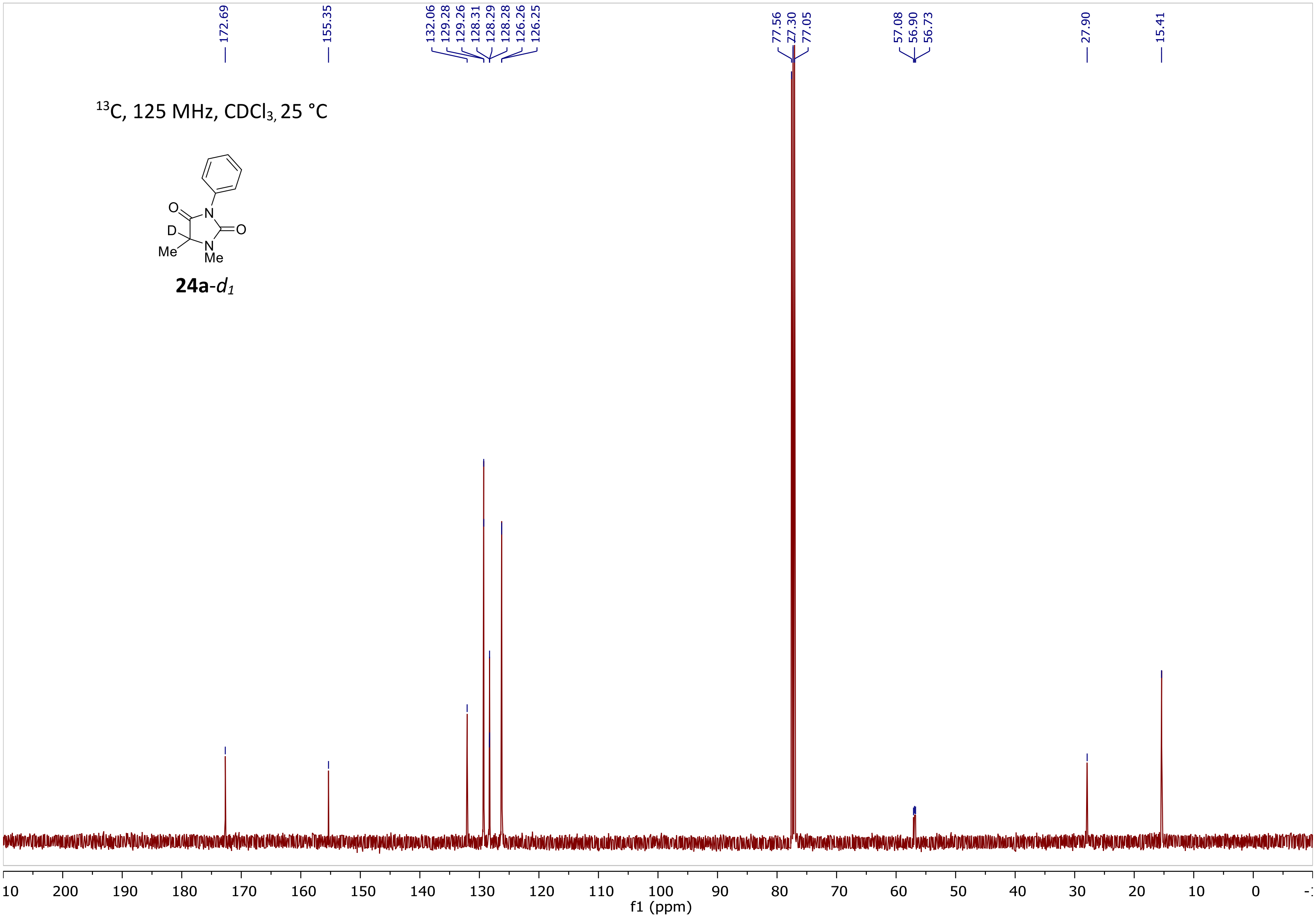
46b


7.91
7.26
5.81
2.35
2.05
2.05
2.05
2.04
1.65
^{1}H, 500 MHz, acetone-d_6, 25 °C
Me
O
N
O
Me
HO
N
H
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-
f1 (ppm)

45b


206.29
173.76
155.03
138.28
130.83
130.02
127.16
82.89
30.07
29.92
29.77
23.79
21.14
^{13}C, 125 MHz, acetone-d_6, 25 °C
Me
O
N
O
Me
N
HO
H
45b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


24a-*d*$_1$
^{1}H, 400 MHz, $CDCl_3$, 25 °C
O
N
D
O
Me
N
Me
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.39
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.28
3.05
1.56
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



^{13}C, 125 MHz, $CDCl_3$, 25 °C

24a-*d*$_1$