An Amine Group Transfer Reaction Driven by Aromaticity

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General Information:

Domino-IEDDA-reactions were set up in a nitrogen filled MBRAUN UNIlab glove box. Other air and/or water sensitive reactions were carried out in a fume hood under Schlenk conditions.

NMR:
NMR spectra were measured on a Bruker Avance II 200 MHz, Avance II 400 MHz, Avance III 400 MHz HD or Avance III 600 MHz spectrometer at 25 °C if not otherwise noted. The ^{1}H (7.26 ppm) or ^{13}C (77.16 ppm) chemical shift of internal residual $CHCl_3$ from $CDCl_3$ was used as reference. Boron trifluoride diethyl etherate was employed for ^{19}F (-153 ppm) as external references.
For 2D NMR experiments, standard Brucker pulse sequences were employed (NOESY mixing time = 1 sec). 20-30 mg of the compound was dissolved in 0.8 mL deuterated solvent.

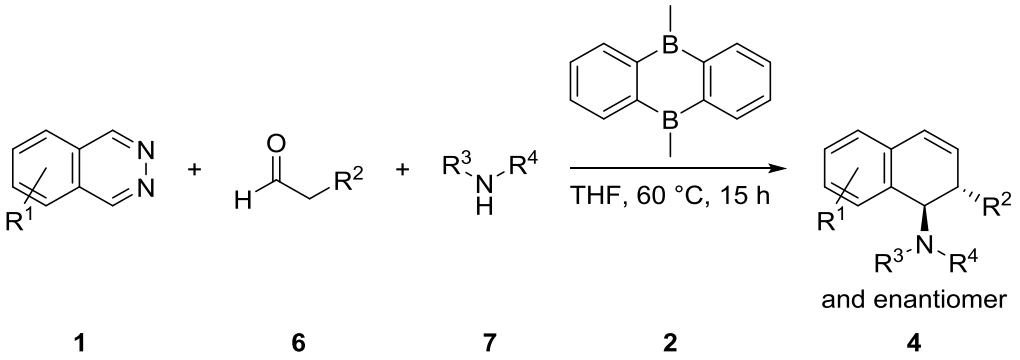
MS:
EI-MS spectra were measured on GC-MS HP 5890 with a HP 5971 mass detector.
ESI-MS spectra were measured on a Bruker Micro TOF.

Chemicals:
The chemicals were purchased from Sigma-Aldrich, Acros Organics, Alfa Aesar and TCI Europe.
Anhydrous solvents were purchased from Acros Organics.
Deuterated solvents were purchased from Euriso - Top GmbH.
Solids were dried over Sicapent® and under high vacuum when necessary.
Technical grade solvents, used during work-up and purification, were distilled prior to use.
Aldehydes **6** were purified by distillation, degassed by freeze-pump-thaw-cycles, and stored in a nitrogen filled glove box.
Amines **7** were degassed by freeze-pump-thaw-cycles, dried either by distillation over CaH_2 or storage over molecular sieve 3 Å, and were stored in a nitrogen filled glove box.
Bidentate Lewis acid **2** was synthesized as described in literature, and was stored in a nitrogen filled glove box.[1,2]
Substituted phthalazines **1b-f**,[3,4] aldehyde **6e**,[5] and amine **7c**[6] were synthesized as described in literature.

Column Chromatography:
Flash column chromatography was carried out with Silica 60 M (0.04 – 0.063 mm) from Macherey-Nagel GmbH & Co. KG.
Thin layer chromatography was carried out on Polygram® SIL G/UV_{254} from Macherey-Nagel GmbH & Co. KG.
In cases when NEt_3 was added to the eluent, the TLC plates were washed with cyclohexane containing 1% NEt_3 and dried prior to use. For a good separation the correct amount of NEt_3 is essential. It depends strongly on the acidity of used Silica.

Synthesis:

General procedure for Domino-IEDDA-reaction catalyzed by BDLA 2:



1 **6** **7** **2** **4**

For small scale reactions (250 µmol) Supelco vials [volume 2 mL, screw top with solid green Melamine cap with PTFE liner, clear glass vial (standard opening, 4.6 mm), O.D. × H × I.D. 12 mm × 32 mm × 4.6 mm, thread 8-425] (Figure S1, a) were used, in order to assure no evaporation of solvent, amine or aldehyde during the reaction. **BEWARE** that a small amount of pressure is build up during the reaction! On this scale the reaction vessel could be opened, after it was cooled to rt, without problems. To heat up the reaction vessel a sand bath proved to be convenient (Figure S1, b).

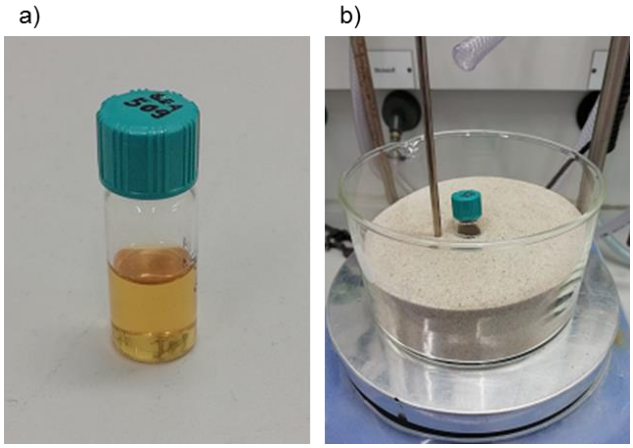
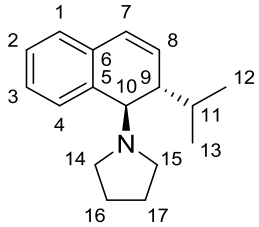


Figure S1. a) Supelco vial (volume 2 mL) used as reaction vessel for small scale reactions (250 µmol); b) sand bath for heating small vials.

The reaction was setup in nitrogen filled glovebox.
Phthalazine **1** and BDLA **2** were suspended in THF (dry, degassed) (1 ml). Then, amine **7** was added, followed by aldehyde **6**. The reaction vessel was sealed and the remaining part of the reaction was carried out in a fume hood. The solution (most cases different shades of orange/yellow; sometimes yellow suspension) was heated to 60 °C (preheated sand bath). Gas evolution was observed after a few minutes. The reaction was kept at this temperature for 15 h. Then the yellow solution was cooled to rt and concentrated under reduced pressure. The remaining oil/solid was purified by flash column chromatography.

1,2-Dihydronaphthalene **4a**



and enantiomer

Starting materials:
Phthalazine (**1a**) (32.9 mg, 250 µmol, 1.00 eq.); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); pyrrolidine (**7a**) (41.5 µL, 500 µmol, 2.00 equiv); 3-methylbutyraldehyde (**6a**) (41.0 µL, 375 µmol, 1.50 equiv).

Purification:
Flash column chromatography (SiO_2: 10 g, cyclohexane/EtOAc + 1% Et_3N, 20:1).

Yield:
53.8 mg (223 µmol, 89%); pale yellow oil.

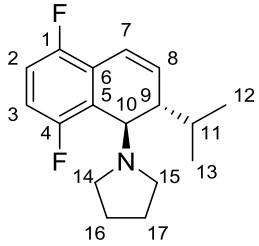
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.21 (ddd, *J* = 7.3, 1.6 Hz, 1H, H2), 7.16 (ddd, *J* = 7.4, 1.6 Hz, 1H, H3), 7.12 – 7.02 (m, 2H, H4, H1), 6.49 (d, *J* = 9.7 Hz, 1H, H7), 6.00 (dd, *J* = 9.7, 5.9 Hz, 1H, H8), 3.63 (s, 1H, H10), 2.48 – 2.39 (m, 4H, H14, H15), 2.36 (dd, *J* = 6.3 Hz, 1H, H9), 1.70 – 1.56 (m, 5H, H11, H16, H17), 0.88 (d, *J* = 6.9 Hz, 3H, H12*, H13*), 0.79 (d, *J* = 6.7 Hz, 3H, H12*, H13*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 134.5 (C6), 131.9 (C5), 130.5 (C4), 130.3 (C8), 127.5 (C2), 126.6 (C7), 126.3 (C3), 125.9 (C1), 61.5 (C10), 49.8 (C14, C15), 45.4 (C9), 32.2 (C11), 23.0 (C16, C17), 20.8 (C12*, C13*), 19.8 (C12*, C13*).

MS (EI) m/z (%) = 241 (5) $[M]^+$, 129 (100).

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{17}H_{24}N^+$: 242.1903; found: 242.1905.

1,2-Dihydronaphthalene **4r**



and enantiomer

Starting materials:
5,8-Difluorophthalazine (**1b**) (42.0 mg, 250 µmol, 1.00 equiv); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); pyrrolidine (**7a**) (24.9 µL, 300 µmol, 1.20 equiv); 3-methylbutyraldehyde (**6a**) (67.0 µL, 625 µmol, 2.50 equiv).

Purification:
Flash column chromatography (SiO_2: 20 g, cyclohexane/EtOAc + 1% Et_3N, 50:1).

Yield:
62.0 mg (224 µmol, 89%); pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 6.94 – 6.80 (m, 2H, H2, H3), 6.72 (dt, *J* = 10.0, 1.0 Hz, 1H, H7), 6.13 (dd, *J* = 9.9, 6.0 Hz, 1H, H8), 4.12 (s, 1H, H10), 2.50 – 2.35 (m, 5H, H9, H14, H15), 1.71 – 1.55 (m, 5H, H11, H16, H17), 0.88 (d, *J* = 6.8 Hz, 3H, H12*, H13*), 0.81 (d, *J* = 6.7 Hz, 3H, H12*, H13*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 156.7 (dd, *J* = 248.4, 2.0 Hz, C4), 154.3 (dd, *J* = 252.8, 2.1 Hz, C1), 132.3 (d, *J* = 2.2 Hz, C8), 123.3 (dd, *J* = 15.9, 5.7 Hz, C6), 120.3 (dd, *J* = 18.9, 3.4

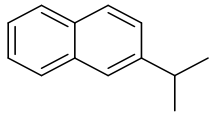
Hz, C5), 118.0 (dd, *J* = 4.7, 2.7 Hz, C7), 114.9 (dd, *J* = 24.3, 9.1 Hz, C2), 114.3 (dd, *J* = 26.8, 8.6 Hz, C3), 52.8 (d, *J* = 1.9 Hz, C10), 49.7 (C14 or C15), 49.7 (C14 or C15), 44.8 (C9), 32.1 (C11), 23.0 (C16, C17), 20.6 (C12*, C13), 19.8 (C12*, C13).

$^{19}F\{^{1}H\}\{^{13}C\}$ NMR (377 MHz, $CDCl_3$ with 0.03% v/v TMS): δ -123.59 (d, J = 18.9 Hz), -129.14 (d, J = 18.7 Hz).

MS (EI) m/z (%) = 277 (7) $[M]^+$, 70 (100).

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{17}H_{22}F_2N^+$: 278.1715; found: 278.1719.

2-(1-Methylethyl)naphthalene (**10a**)



Starting materials:
Phthalazine (**1a**) (32.9 mg, 250 µmol, 1.00 eq.); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); pyrrolidine (**7a**) (24.9 µL, 300 µmol, 1.20 equiv); 3-methylbutyraldehyde (**6a**) (67.0 µL, 625 µmol, 2.50 equiv).

Purification:
Flash column chromatography (SiO_2: 15 g, cyclohexane).

Yield:
14.3 mg (84.0 µmol, 34%); colorless oil.

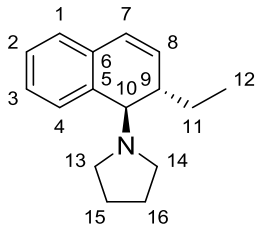
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.83 – 7.75 (m, 3H), 7.64 (d, *J* = 0.6 Hz, 1H), 7.47 – 7.37 (m, 3H), 3.07 (hept, *J* = 6.9 Hz, 1H), 1.34 (d, *J* = 6.9 Hz, 6H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 146.5, 133.8, 132.2, 128.0, 127.71, 127.69, 125.94, 125.89, 125.2, 124.2, 34.4, 24.1.

MS (EI) m/z (%) = 170 (33) $[M]^+$, 155 (100).

Analytical data corresponds to literature.[7]

1,2-Dihydronaphthalene **4b**



and enantiomer

Starting materials:
Phthalazine (**1a**) (32.9 mg, 250 µmol, 1.00 equiv); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); pyrrolidine (**7a**) (41.5 µL, 500 µmol, 2.00 equiv); butyraldehyde (**6b**) (34.5 µL, 375 µmol, 1.50 equiv).

Purification:
Flash column chromatography (SiO_2: 7 g, cyclohexane/EtOAc + 1% Et_3N, 20:1).

Yield:
50.2 mg (221 µmol, 88%); pale yellow oil.

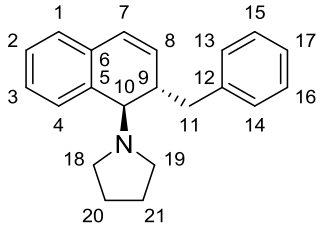
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.22 (td, *J* = 7.3, 1.6 Hz, 1H, H2), 7.16 (td, *J* = 7.3, 1.5 Hz, 1H, H3), 7.10 (dd, *J* = 7.4, 1.5 Hz, 1H, H4), 7.07 (dd, *J* = 7.4, 1.4 Hz, 1H, H1), 6.44 (d, *J* = 9.6 Hz, 1H, H7), 6.07 (ddd, *J* = 9.6, 6.0, 1.1 Hz, 1H, H8), 3.47 (s, 1H, H10), 2.53 – 2.39 (m, 5H, H9, H13, H14), 1.72 – 1.59 (m, 4H, H15, H16), 1.39 – 1.23 (m, 2H, H11), 0.92 (t, *J* = 7.4 Hz, 3H, H12).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 134.1 (C6), 132.1 (C8), 131.4 (C5), 131.0 (C4), 127.7 (C2), 126.2 (C3), 126.0 (C1), 125.7 (C7), 63.7 (C10), 50.4 (C13, C14), 40.7 (C9), 26.4 (C11), 23.0 (C15, C16), 11.9 (C12).

MS (EI) m/z (%) = 227 (4) $[M]^+$, 129 (100).

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{16}H_{22}N^+$: 228.1747; found: 228.1745.

1,2-Dihydronaphthalene **4c**



and enantiomer

Starting materials:
Phthalazine (**1a**) (32.9 mg, 250 µmol, 1.00 equiv); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); pyrrolidine (**7a**) (41.5 µL, 500 µmol, 2.00 equiv); 3-phenylpropionaldehyde (**6c**) (49.9 µL, 375 µmol, 1.50 equiv).

Purification:
Flash column chromatography (2 times) (SiO_2: 7 g, cyclohexane/EtOAc + 1% Et_3N, 15:1).

Yield:
68.8 mg (238 µmol, 95%); pale yellow oil.

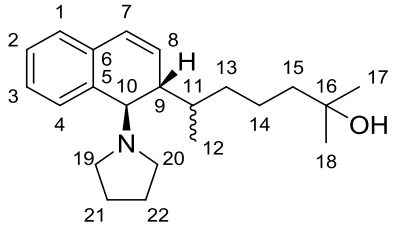
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.33 – 7.24 (m, 3H, H2, H15, H16), 7.26 – 7.16 (m, 2H, H3, H17), 7.19 – 7.10 (m, 4H, H1, H4, H13, H14), 6.50 (d, *J* = 9.5 Hz, 1H, H7), 5.94 (dd, *J* = 9.6, 5.9 Hz, 1H, H8), 3.44 (s, 1H, H10), 2.89 (ddd, *J* = 7.5 Hz, 1H, H9), 2.59 (dd, *J* = 13.3, 7.9 Hz, 1H, H11), 2.48 (dd, *J* = 13.3, 8.1 Hz, 1H, H11), 2.44 – 2.32 (m, 4H, H18, H19), 1.68 – 1.56 (m, 4H, H20, H21).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 140.1 (C12), 133.9 (C6), 131.6 (C8), 131.2 (C4, C5 detected by HMBC $^{3}J_{CH}$ to H7), 129.3 (C13, C14), 128.3 (C15, C16), 127.9 (C2), 126.5 (C3 or C17), 126.2 (C3 or C17), 126.1 (C1), 126.1 (C7), 63.2 (C10), 50.6 (C18, C19), 40.6 (C9), 38.9 (C11), 23.0 (C20, C21).

MS (EI) m/z (%) = 289 (6) $[M]^+$, 91 (100).

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{21}H_{24}N^+$: 290.1903; found: 290.1906.

1,2-Dihydronaphthalene **4d** and **4d'**



and enantiomer

Starting materials:
Phthalazine (**1a**) (32.9 mg, 250 µmol, 1.00 equiv); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); pyrrolidine (**7a**) (41.5 µL, 500 µmol, 2.00 equiv); 3,7-dimethyl-7-hydroxyoctanal (rac) (**6d**) (72.4 µL, 375 µmol, 1.50 equiv).

Purification:
Flash column chromatography (2 times) (SiO_2: 11 g, cyclohexane/EtOAc + 1% Et_3N, 5:1).

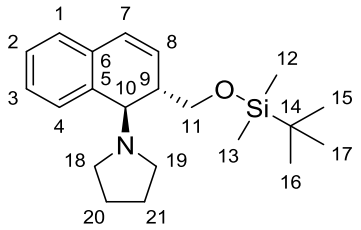
Yield: Two diastereomers and corresponding enantiomers (1:1)
72.5 mg (221 µmol, 89%); pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.20 (td, *J* = 7.3, 1.6 Hz, 2H, H2), 7.15 (tt, *J* = 7.4, 1.6 Hz, 2H, H3), 7.11 – 7.02 (m, 4H, H1, H1), 6.50 (d, *J* = 10.3 Hz, 1H, H7), 6.48 (d, *J* = 10.1 Hz, 1H, H7), 5.98 (ddd, *J* = 9.8, 5.9, 1.1 Hz, 1H, H8), 5.92 (ddd, *J* = 9.8, 5.8, 1.0 Hz, 1H, H8), 3.65 (s, 1H, H10), 3.63 (s, 1H, H10), 2.52 (t, *J* = 5.8 Hz, 1H, H9), 2.50 – 2.34 (m, 9H, H9, H19, H20), 1.67 – 1.59 (m, 8H, H21, H22), 1.59 – 1.06 (m, 10H, H11, H13, H14, H15, H18, H17, H23), 0.79 (d, *J* = 6.8 Hz, 3H, H12), 0.68 (d, *J* = 6.8 Hz, 3H, H12).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 134.60 (C6), 134.50 (C6), 131.89 (C5), 131.73 (C5), 130.73 (C8), 130.48 (C4), 130.46 (C4), 129.50 (C8), 127.53 (C2), 127.51 (C2), 127.12 (C7), 126.49 (C7), 126.43 (C3), 126.41 (3), 125.88 (1), 77.16, 71.10 (16), 61.72 (10), 60.71 (10), 49.71 (19, 20), 49.39 (19, 20), 44.34 (9), 44.25 (15), 44.21 (15), 43.76 (9), 37.95 (11), 36.98 (11), 34.99 (13), 34.22 (13), 29.44 (18), 29.40 (18), 29.36 (17), 29.33 (17), 23.00, 22.98 (21, 22), 22.16 (14), 22.04 (14), 16.98 (12), 16.24 (12).

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{22}H_{34}NO^+$: 328.2635; found: 328.2638.

1,2-Dihydronaphthalene **4e**



and enantiomer

Starting materials:
Phthalazine (**1a**) (32.9 mg, 250 µmol, 1.00 equiv); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); pyrrolidine (**7a**) (41.5 µL, 500 µmol, 2.00 equiv); aldehyde **6e** (71.3 mg, 375 µmol, 1.50 equiv).

Purification:
Consecutive flash column chromatography (SiO_2: 20 g, cyclohexane/EtOAc + 1% Et_3N, 20:1), (SiO_2: 20 g, DCM + 5% MeOH), (SiO_2: 20 g, cyclohexane/EtOAc + 1% Et_3N, 20:1).

Yield:
44.0 mg (128 µmol, 51%); colorless oil.

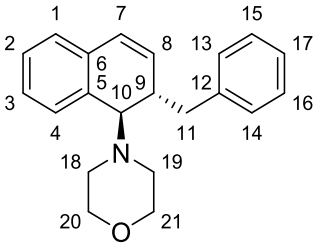
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.25 – 7.13 (m, 3H, H2 – H4), 7.06 (dd, *J* = 7.1, 1.5 Hz, 1H, H1), 6.49 (d, *J* = 9.6 Hz, 1H, H7), 5.93 (ddd, *J* = 9.6, 5.9, 1.0 Hz, 1H, H8), 3.78 (s, 1H, H10), 3.52 (dd, *J* = 9.9, 5.5 Hz, 1H, H11), 3.16 (dd, *J* = 9.9, 8.9 Hz, 1H, H11), 2.85 – 2.76 (m, 1H, H9), 2.51 – 2.48 (s_{br}, 4H, H18, H19), 1.72 – 1.60 (m, 4H, H20, H21), 0.86 (s, 9H, H15 – H17), -0.03 (s, 3H, H12*, H13), -0.04 (s, 3H, H12*, H13).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 133.7 (C6), 131.4 (C5), 131.3 (C4), 128.2 (C8), 127.9 (C7), 127.8 (C2), 126.7 (C3), 126.2 (C1), 63.0 (C11), 59.7 (C10), 50.4 (C18, C19), 41.8 (C9), 26.0 (C15 – C17), 23.2 (C20, C21), 18.4 (C14), -5.2 (C12*, C13), -5.3 (C12*, C13).

MS (EI) m/z (%) = 343 (10) $[M]^+$, 73 (100).

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{21}H_{34}NOSi^+$: 344.2404; found: 344.2408.

1,2-Dihydronaphthalene **4g**



and enantiomer

Starting materials:
Phthalazine (**1a**) (32.9 mg, 250 µmol, 1.00 equiv); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); morpholine (**7b**) (44.4 µL, 500 µmol, 2.00 equiv); 3-phenylpropionaldehyde (**6c**) (49.9 µL, 375 µmol, 1.50 equiv).

Purification:
Flash column chromatography (2 times) (SiO_2: 11 g, cyclohexane/EtOAc + 1% Et_3N, 25:1).

Yield:
61.5 mg (201 µmol, 81%); colorless oil.

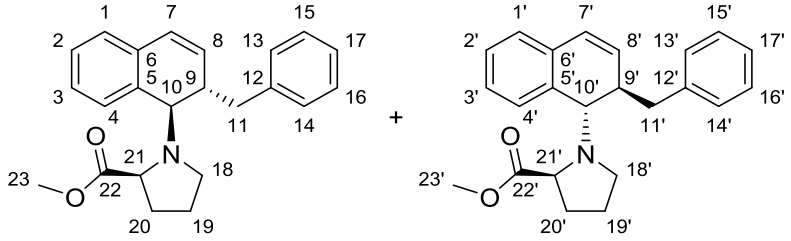
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.32 – 7.25 (m, 3H, H2, H15, H16), 7.25 – 7.18 (m, 3H, H3, H4, H17), 7.18 – 7.14 (m, 2H, H13, H14), 7.10 (dd, *J* = 6.9, 1.8 Hz, 1H, H1), 6.43 (d, *J* = 9.6 Hz, 1H, H7), 5.94 (dd, *J* = 9.6, 5.5 Hz, 1H, H8), 3.60 – 3.50 (m, 4H, H18, H19), 3.47 (s, 1H, H10), 2.87 (ddd, *J* = 7.9, 5.8 Hz, 1H, H9), 2.66 (dd, *J* = 13.3, 7.6 Hz, 1H, H11), 2.45 (dd, *J* = 13.4, 8.4 Hz, 1H, H11), 2.39 – 2.29 (m, 4H, H20, H21).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 139.8 (C12), 134.0 (C6), 131.9 (C8), 131.4 (C4), 130.7 (C5), 129.3 (C13, C14), 128.4 (C15, C16), 128.0 (C2), 127.1 (C3), 126.3 (C17), 126.2 (C7), 126.0 (C1), 67.5 (C18, C19), 64.7 (C10), 49.3 (C20, C21), 39.8 (C11), 37.9 (C9).

MS (EI) m/z (%) = 305 (3) $[M]^+$, 91 (100).

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{21}H_{24}NO^+$: 306.1852; found: 306.1855.

1,2-Dihydronaphthalene **4h** and **4h'**



4h **4h'**

Starting materials:
Phthalazine (**1a**) (32.9 mg, 250 µmol, 1.00 equiv); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); L-proline methyl ester (**7c**) (65.0 mg, 503 µmol, 2.01 equiv); 3-phenylpropionaldehyde (**6c**) (49.9 µL, 375 µmol, 1.50 equiv).

Purification:
Flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc + 1% Et_3N, 15:1).

Yield: Two diastereomers major/minor (1.6:1)
66.5 mg (191 µmol, 77%); yellow oil.

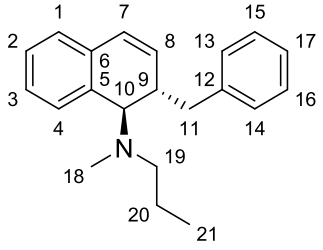
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.33 – 7.22 (m, 8H, H2*, H3*, H4-major*, H15, H16), 7.25 – 7.15 (m, 3H, H2*, H3*, H4-major*, H17), 7.18 – 7.09 (m, 5H, H1-minor, H13, H14), 7.08 (td, *J* = 6.9, 1.7 Hz, 2H, H1-major, H4-minor), 6.48 (d, *J* = 9.6 Hz, 1H, H7-major), 6.45 (d, *J* = 9.6 Hz, 1H, H7-minor), 5.97 (dd, *J* = 9.6, 5.8 Hz, 1H, H8-minor), 5.91 (ddd, *J* = 9.6, 5.8, 1.1 Hz, 1H, H8-major), 3.73 (s, 1H, H10-minor), 3.69 (s, 1H, H10-major), 3.54 (s, 3H, H23-minor), 3.48 (s, 3H, H23-major), 3.31 (t, *J* = 7.5 Hz, 1H, H21-minor), 3.23 (dd, *J* = 9.5, 5.0 Hz, 1H, H21-major), .298 – 2.88 (m, 2H, H18), 2.88 – 2.78 (m, 2H, H9), 2.62 (dt, *J* = 13.6, 6.9 Hz, 2H, H11), 2.48 (td, *J* = 8.6, 7.0 Hz, 1H, H18-major), 2.39 (ddd, *J* = 17.4, 13.4, 8.8 Hz, 2H, H11), 2.08 – 1.99 (m, 1H, H18-minor), 1.98 – 1.47 (m, 8H, H19, H20).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 175.26 (C22-major), 175.09 (C22-minor), 139.88 (C12-major), 139.85 (C12-minor), 134.40 (C6-minor), 133.77 (C6-major), 131.90 (C5-major), 131.80 (C8-minor), 131.26 (C8-major), 131.20 (C2 or C3 or C4 or C17), 130.93 (C2 or C3 or C4 or C17), 129.39 (13-minor, 14-minor), 129.33 (13-major, 14-major), 128.65 (5-minor), 128.42 (15-major, 16-major), 128.37 (15-minor, 16-minor), 128.09 (C2 or C3 or C4 or C17), 128.02 (C2 or C3 or C4 or C17), 127.35 (C2 or C3 or C4 or C17), 126.90 (C2 or C3 or C4 or C17), 126.42 (C2 or C3 or C4 or C17), 126.29 (C2 or C3 or C4 or C17), 126.18 (7-major), 126.15 (1-minor), 125.96 (1-major), 125.94 (7-minor), 62.19 (21-minor), 61.19 (21-major), 60.46 (10-major), 58.32 (10-minor), 52.00 (23-minor), 51.59 (23-major), 50.79 (18-major), 47.90 (18-minor), 41.85 (9-minor), 39.03 (11-minor), 38.89 (11-major), 38.76 (9-major), 30.25 (19-major), 28.68 (19-minor), 23.12 (20-major), 23.01 (20-minor).

MS (EI) m/z (%) = 347 (1) $[M]^+$, 70 (100).

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{23}H_{26}NO_2^+$: 348.1958; found: 348.1959.

1,2-Dihydronaphthalene **4i**



and enantiomer

Starting materials:
Phthalazine (**1a**) (32.9 mg, 250 µmol, 1.00 equiv); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); N-methylpropylamine (**7d**) (53.4 µL, 38.1 mg, 500 µmol, 2.00 equiv); 3-phenylpropionaldehyde (**6c**) (49.9 µL, 375 µmol, 1.50 equiv).
Purification:
Flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc + 0.5% Et_3N, 25:1).

Yield:
44.5 mg (153 µmol, 61%); colorless oil.

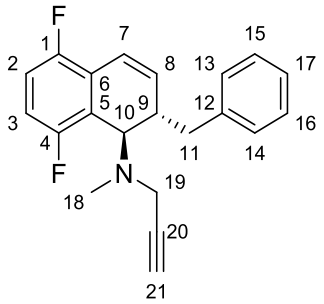
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.34 – 7.27 (m, 2H, H15, H16), 7.26 – 7.19 (m, 4H, H2, H3, H4, H17), 7.19 – 7.15 (m, 2H, H13, H14), 7.11 – 7.07 (m, 1H, H1), 6.42 (d, *J* = 9.5 Hz, 1H, H7), 5.96 (dd, *J* = 9.6, 5.6 Hz, 1H, H8), 3.64 (s, 1H, H10), 2.78 (dd, *J* = 7.4 Hz, 1H, H9), 2.67 (dd, *J* = 13.2, 7.2 Hz, 1H, H11), 2.41 (dd, *J* = 13.2, 8.6 Hz, 1H, H11), 2.24 (t, *J* = 7.4 Hz, 2H, H19), 2.00 (s, 3H, H18), 1.36 – 1.13 (m, 2H, H20), 0.74 (t, *J* = 7.3 Hz, 3H, H21).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 140.0 (C12), 134.1 (C6), 132.5 (C5), 132.0 (C8), 131.1 (C4), 129.4 (C13, C14), 128.4 (C15, C16), 127.6 (C2), 127.3 (C3), 126.2 (C17), 126.0 (C7), 126.0 (C1), 61.5 (C10), 55.8 (C19), 40.3 (C11), 37.7 (C18), 36.9 (C9), 21.2 (C20), 11.9 (C21).

MS (EI) m/z (%) = 291 (3) $[M]^+$, 91 (100).

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{21}H_{26}N$: 292.2060; found: 292.2063.

1,2-Dihydronaphthalene **4k**



and enantiomer

5,8-Difluorophthalazine (**1b**) (42.0 mg, 250 µmol, 1.00 equiv); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); *N*-methylpropargylamine (**7e**) (41.6 µL, 500 µmol, 2.00 equiv); 3-phenylpropionaldehyde (**6c**) (49.9 µL, 375 µmol, 1.50 equiv).

Purification:
Flash column chromatography (SiO_2: 15 g, DCM).

Yield:
49.8 mg (154 µmol, 62%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.34 – 7.26 (m, 2H, H15, H16), 7.24 – 7.19 (m, 1H, H17), 7.17 – 7.13 (m, 2H, H13, H14), 6.95 (ddt, *J* = 14.8, 8.9, 4.5 Hz, 2H, H2, H3), 6.73 (dd, *J* = 9.7, 1.8 Hz, 1H, H7), 6.11 (dd, *J* = 9.8, 5.9 Hz, 1H, H8), 4.07 (s, 1H, H10), 3.26 (d, *J* = 2.4 Hz, 2H, H19), 2.99 (q, *J* = 7.4 Hz, 1H, H9), 2.62 (dd, *J* = 13.3, 7.5 Hz, 1H, H11), 2.42 (dd, *J* = 13.4, 8.2 Hz, 1H, H11), 2.18 (d, *J* = 1.0 Hz, 3H, H18), 2.12 (t, *J* = 2.4 Hz, 1H, H21).

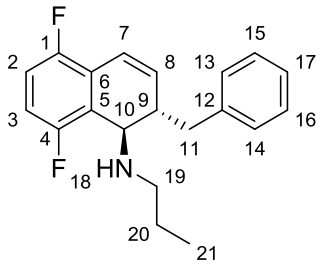
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 157.6 (dd, *J* = 242.4, 2.4 Hz, C4), 154.3 (dd, *J* = 244.9, 2.1 Hz, C1), 139.1 (C12), 133.6 (C8), 129.3 (C13, C14), 128.5 (C15, C16), 126.5 (C17), 122.9 (dd, *J* = 16.2, 5.2 Hz, C6), 119.8 (dd, *J* = 18.7, 3.0 Hz, C5), 117.8 (dd, *J* = 4.9, 2.9 Hz, C7), 115.5 (dd, *J* = 24.3, 9.1 Hz, C2), 114.9 (dd, *J* = 26.1, 8.5 Hz, C3), 80.0 (C20), 72.7 (C21), 55.1 (d, *J* = 1.9 Hz, C10), 43.4 (C19), 39.3 (C11), 38.3 (C18), 37.5 (C9).

^{19}F{^{1}H}{^{13}C} NMR (377 MHz, $CDCl_3$ with 0.03% v/v TMS): δ -122.78 (d, *J* = 18.4 Hz), -128.35 (d, *J* = 18.4 Hz).

MS (EI) m/z (%) = 322 (9) $[M-H]^+$, 91 (100).

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{21}H_{20}F_2N^+$: 324.1558; found: 324.1563.

1,2-Dihydronaphthalene **4m**



and enantiomer

5,8-Difluorophthalazine (**1b**) (42.0 mg, 250 µmol, 1.00 equiv); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); propylamine (**7f**) (41.5 µL, 500 µmol, 2.00 equiv); 3-phenylpropionaldehyde (**6c**) (49.9 µL, 375 µmol, 1.50 equiv).

Purification:
Flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc + 1% Et_3N, 15:1).

Yield:
56.6 mg (181 µmol, 72%); pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.31 – 7.26 (m, 2H, C15, C16), 7.23 – 7.18 (m, 1H, H17), 7.15 – 7.11 (m, 2H, H13, H14), 6.97 – 6.88 (m, 2H, H2, H3), 6.74 (dd, *J* = 9.8, 1.7 Hz, 1H, H7), 6.07 (dd, *J* = 9.7, 6.0 Hz, 1H, H8), 3.90 (s, 1H, H10), 2.96 – 2.85 (m, 1H, H9), 2.60 (dd, *J* = 13.3, 7.5 Hz, 1H, H11), 2.50 – 2.40 (m, 2H, H11, H19), 2.35 – 2.28 (m, 1H, H19), 1.49 – 1.35 (m, 2H, H18, H20), 1.35 – 1.21 (m, 1H, H20), 0.79 (t, *J* = 7.4 Hz, 3H, H21).

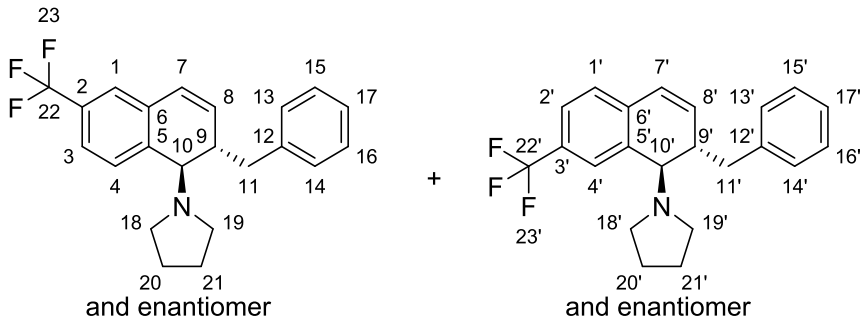
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 157.0 (dd, *J* = 239.9, 1.9 Hz, C4), 154.9 (dd, *J* = 245.1, 1.8 Hz, C1), 139.3 (C12), 133.1 (d, *J* = 2.2 Hz, C8), 129.2 (C13, C14), 128.5 (C15, C16), 126.4 (C17), 123.5 (dd, *J* = 20.2, 3.4 Hz, C5), 121.1 (dd, *J* = 16.2, 5.7 Hz, C6), 118.1 (dd, *J* = 4.5, 2.8 Hz, C7), 115.4 – 114.6 (m, C2, C3), 51.0 (d, *J* = 1.9 Hz, C10), 48.8 (C19), 41.9 (C9), 38.3 (C11), 23.4 (C20), 11.9 (C21).

$^{19}F\{^1H\}\{^{13}C\}$ NMR (377 MHz, $CDCl_3$ with 0.03% v/v TMS): δ -126.42 (d, *J* = 19.0 Hz), -127.62 (d, *J* = 18.9 Hz).

MS (EI) m/z (%) = 313 (5) $[M]^+$, 91 (100).

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{20}H_{22}F_2N^+$: 314.1715; found: 314.1713.

1,2-Dihydronaphthalene **4n** and **4n'**



and enantiomer
4n

and enantiomer
4n'

Starting materials:
6-(Trifluoromethyl)phthalazine (**1c**) (49.6 mg, 250 µmol, 1.00 equiv); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); pyrrolidine (**7a**) (41.5 µL, 500 µmol, 2.00 equiv); 3-phenylpropionaldehyde (**6c**) (49.9 µL, 375 µmol, 1.50 equiv).

Purification:
Flash column chromatography (2 times) (SiO_2: 15 g, cyclohexane/EtOAc + 1% Et_3N, 20:1).

Yield: mixture of regioisomers **4n**/**4n'** (1.3:1)
78.6 mg (220 µmol, 88%); pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.52 (d, *J* = 7.7 Hz, 1H, H2'), 7.46 (d, *J* = 7.8 Hz, 1H, H3), 7.37 (s, 1H, H1), 7.36 (s, 1H, H4'), 7.31 – 7.26 (m, 4H, H15, H16, H15', H16'), 7.25 – 7.18 (m, 4H, H4, H17, H1', H17'), 7.13 (d, *J* = 7.4 Hz, 4H, H13, H14, H13', H14'), 6.52 (d, *J* = 9.6 Hz, 1H, H7'), 6.51 (d, *J* = 9.6 Hz, 1H, H7), 6.10 – 6.02 (m, 2H, H8, H8'), 3.52 (s, 2H, H10, H10'), 2.98 – 2.89 (m, 2H, H9, H9'), 2.59 (ddd, *J* = 12.1, 7.9, 4.0 Hz, 2H, H11, H11'), 2.51 – 2.43 (m, 2H, H11, H11'), 2.43 – 2.30 (m, 8H, H18, H19, H18', 19'), 1.67 – 1.57 (m, 8H, H20, H21, H20', H21').

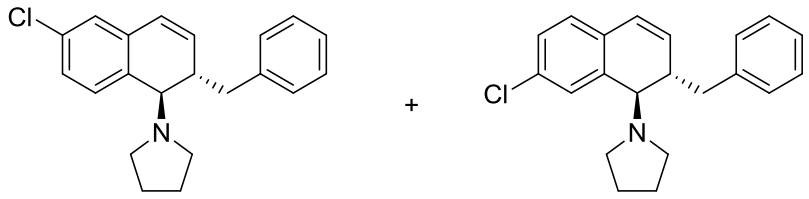
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 139.59 (C12), 139.56 (C12'), 137.14 (C6'), 134.96 (C5), 134.46 (C6), 134.37 (C8'), 133.41 (C8), 131.86 (C5'), 131.31 (C4), 129.23 C13, C14), 129.21 (C13', C14'), 128.47 (C15, C16, C15', C16'), 127.58 (d, *J* = 3.5 Hz, C4'), 126.35 (C17), 126.33 (C17'), 125.24 (C7, C7'), 124.89 (d, *J* = 3.8 Hz, C2'), 123.26 (d, *J* = 3.7 Hz, C3), 122.84 (d, *J* = 3.7 Hz, C1), 62.70 (C10'), 62.40 (C10), 50.48 (C18, C19, C18', C19'), 40.46 (C9'), 40.29 (C9), 38.88 (C11'), 38.84 (C11), 23.09 (C20, C21, C20', C21').

$^{19}F\{^1H\}\{^{13}C\}$ NMR (377 MHz, $CDCl_3$ with 0.03% v/v TMS): δ -62.20 (F23'), -62.57 (F23).

MS (EI) m/z (%) = 357 (10) $[M]^+$, 70 (100).

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{22}H_{23}F_3N^+$: 358.1777; found: 358.1779.

1,2-Dihydronaphthalene **4o** and **4o'**



and enantiomer
4o

and enantiomer
4o'

Starting materials:
6-Chlorophthalazine (**1d**) (41.2 mg, 250 µmol, 1.00 equiv); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); pyrrolidine (**7a**) (41.5 µL, 500 µmol, 2.00 equiv); 3-phenylpropionaldehyde (**6c**) (49.9 µL, 375 µmol, 1.50 equiv).

Purification:
Flash column chromatography (SiO_2: 7 g, cyclohexane/EtOAc + 0.5% Et_3N, 25:1).

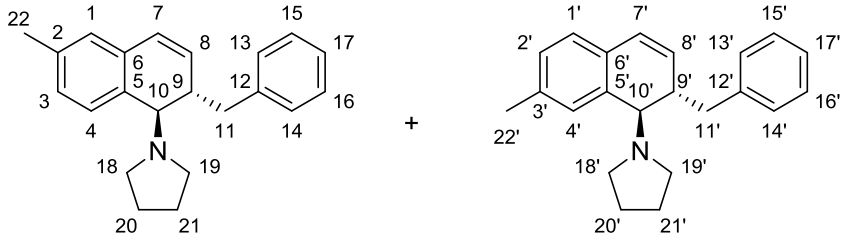
Yield: mixture of regioisomers **4dca**/**4dca'** (~1:1)
71.3 mg (220 µmol, 88%); colorless oil.

NMR spectra could not be assigned unambiguously
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.32 – 7.26 (m, 4H), 7.26 – 7.16 (m, 4H), 7.16 – 7.10 (m, 6H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.44 (t, *J* = 9.7 Hz, 2H), 5.99 (dd, *J* = 9.7, 6.1 Hz, 1H), 5.95 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.42 (s, 2H), 2.89 (p, *J* = 7.9 Hz, 2H), 2.57 (dd, *J* = 13.3, 7.9 Hz, 2H), 2.48 – 2.29 (m, 10H), 1.69 – 1.56 (m, 8H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 139.8, 135.5, 133.45, 133.5, 132.4, 132.3, 132.1, 131.90, 130.85, 129.24, 129.23, 128.4, 127.9, 127.4, 126.4, 126.3, 126.1, 125.19, 125.16, 62.7, 62.4, 50.54, 50.53, 40.5, 40.3, 38.9, 38.8, 23.1.

MS (EI) m/z (%) = 323 (6) $[M]^+$, 70 (100).
HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{21}H_{23}ClN^+$: 324.1514; found: 324.1519.

1,2-Dihydronaphthalene **4p** and **4p'**



and enantiomer **4p** + and enantiomer **4p'**

Starting materials:
6-Methylphthalazine (**1a**) (36.1 mg, 250 µmol, 1.00 equiv); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); pyrrolidine (**7a**) (41.5 µL, 500 µmol, 2.00 equiv); 3-phenylpropionaldehyde (**6c**) (49.9 µL, 375 µmol, 1.50 equiv).

Purification:
Flash column chromatography (2 times) (SiO_2: 15 g, cyclohexane/EtOAc + 1% Et_3N, 20:1).

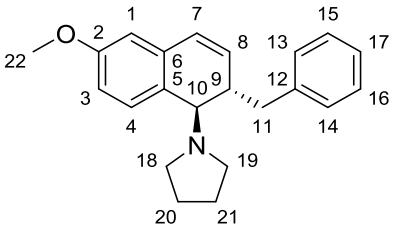
Yield: mixture of regioisomers **4eca**/**4eca'** (1.3:1)
62.2 mg (205 µmol, 82%); pale yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.32 – 7.24 (m, 4H, H15, H16, H15', H16'), 7.23 – 7.18 (m, 2H, H17, H17'), 7.18 – 7.12 (m, 4H, H13, H14, H13', H14'), 7.09 (dd, *J* = 7.6, 1.0 Hz, 1H, H2'), 7.04 – 7.00 (m, 3H, 1', H3, H4), 6.95 (d, *J* = 3.9 Hz, 2H, H1, H4'), 6.46 (d, *J* = 9.6 Hz, 1H, H7'), 6.45 (d, *J* = 9.6 Hz, 1H, H7), 5.91 (ddd, *J* = 9.5, 5.9, 0.8 Hz, 1H, H8), 5.86 (ddd, *J* = 9.4, 5.8, 0.6 Hz, 1H, H8'), 3.42 (s, 2H, H10, H10'), 2.92 – 2.81 (m, 2H, H9, H9'), 2.62 – 2.53 (m, 2H, H11, H11'), 2.53 – 2.44 (m, 2H, H11, H11'), 2.44 – 2.30 (m, 14H, H18, H19, H22, H18', H19', H22'), 1.69 – 1.56 (m, 8H, H20, H21, H20', H21').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 140.3 (C12'), 140.2 (C12), 137.4 (C2), 136.2 (C3'), 133.8 (C6), 132.0 (C4'), 131.6 (C8), 131.4 (C6'), 131.1 (C1'), 131.0 (C5'), 130.6 (C8'), 129.3 (C13, C14, C13', C14'), 128.5 (C2'), 128.3 (C15, C16, C15', C16'), 128.2 (C5), 127.2 (C3), 127.0 (C1), 126.2 (C7), 126.1 (C4, C7'), 125.9 (C17, C17'), 63.2 (C10'), 62.9 (C10), 50.6 (C18, C19), 50.5 (C18', C19'), 40.9 (C9), 40.7 (C9'), 39.0 (C11'), 39.0 (C11), 23.0 (C20, C21, C20', C21'), 21.6 (C22'), 21.3 (C22).

MS (EI) m/z (%) = 303 (4) $[M]^+$, 91 (100).

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{22}H_{26}N^+$: 304.2060; found: 304.2063.

1,2-Dihydronaphthalene **4q**



and enantiomer

Starting materials:
6-Methoxyphthalazine (**1f**) (40.1 mg, 250 µmol, 1.00 equiv); BDLA **2** (2.6 mg, 12.8 µmol, 5.1 mol %); pyrrolidine (**7a**) (41.5 µL, 500 µmol, 2.00 equiv); 3-phenylpropionaldehyde (**6c**) (49.9 µL, 375 µmol, 1.50 equiv).

Purification:
Flash column chromatography (3 times) (SiO_2: 15 g, cyclohexane/EtOAc + 1% Et_3N, 25:1).

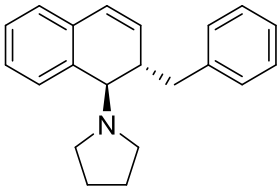
Yield:
24.7 mg (77.3 µmol, 31%); pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.31 – 7.25 (m, 2H, H15, H16), 7.23 – 7.17 (m, 1H, H17), 7.17 – 7.12 (m, 2H, H13, H14), 7.05 (d, *J* = 8.2 Hz, 1H, H3), 6.76 (dd, *J* = 8.2, 2.7 Hz, 1H, H2), 6.69 (d, *J* = 2.6 Hz, 1H, H6), 6.45 (d, *J* = 9.6 Hz, 1H, H7), 5.94 (dd, *J* = 9.5, 5.8 Hz, 1H, H8), 3.83 (s, 3H, H22), 3.39 (s, 1H, H10), 2.87 (q, *J* = 7.4 Hz, 1H, H9), 2.57 (dd, *J* = 13.3, 7.9 Hz, 1H, H11), 2.47 (dd, *J* = 13.3, 8.1 Hz, 1H, H11), 2.43 – 2.28 (m, 4H, H18, H19), 1.67 – 1.57 (m, 4H, H20,H 21).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 159.3 (C1), 140.2 (C12), 135.0 (C5), 132.3 (C8), 132.1 (C3), 129.3 (C13, C14), 128.3 (C15, C16), 126.2 (C7), 126.1 (C17), 123.6 (C4), 111.7 (C2), 111.6 (C6), 62.7 (C10), 55.3 (C22), 50.6 (C18, C19), 40.9 (C9), 39.0 (C11), 23.0 (C20, C21).

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{22}H_{26}NO^+$: 320.2009; found: 320.2012.

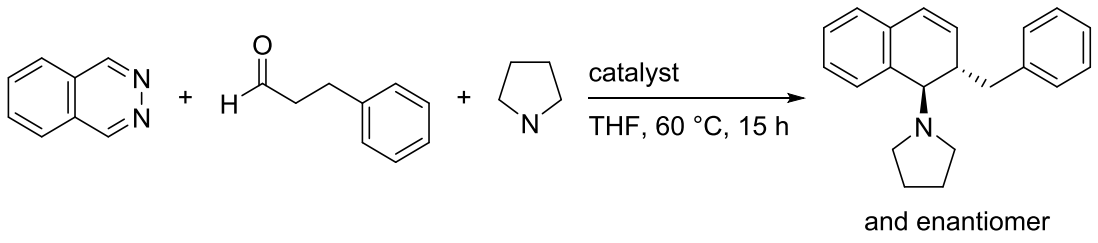
Gram-scale synthesis of 1,2-dihydronaphthalene 4c**:**



and enantiomer

The reaction was setup in nitrogen filled glovebox.
Phthalazine (**1a**) (1.05 g, 8.00 mmol, 1.00 equiv) and BDLA **2** (81.5 mg, 0.40 mmol, 5.00 mol %) were suspended in THF (dry, degassed) (35 mL). Pyrrolidine (**7a**) (1.33 mL, 16.0 mmol, 2.00 equiv) was added to the yellow suspension, which turned into an orange solution. Then, 3-phenylpropionaldehyde (**6c**) (1.58 mL, 12.0 mmol, 1.50 equiv) was added. The reaction vessel was sealed and the rest of the reaction was carried out in a fume hood under Schlenk conditions (connected nitrogen line for pressure compensation).
It was heated to 60 °C (preheated oil bath) and stirred for 15 h. Afterwards, it was cooled to rt and concentrated under reduced pressure.
A brown oil was obtained (some solids) (3.05 g). It was purified by flash column chromatography (SiO_2: 300 g, cyclohexane/EtOAc + 1% NEt_3, 15:1 to 10:1). A yellow oil was obtained (2.21 g, 7.64 mmol, 95%).

Optimization of the catalyst for the domino-IEDDA-reaction:



1a **6c** **7a** **4c**

Table S1. Variation of catalyst for domino-IEDDA-reaction.

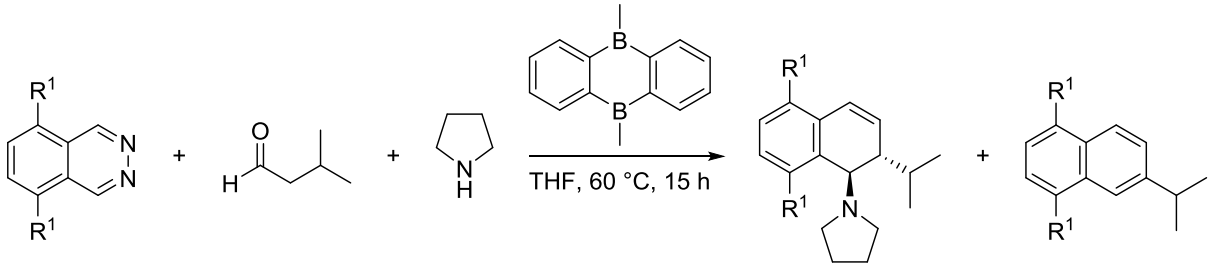
Entry	Catalyst	Yield [%]
1	None	None
2	$BF_3{\cdot}O(CH_2CH_3)_2$ (21.4 mol %)	19
3	$B(C_6F_5)_3$ (5 mol %)	Traces

Domino-IEDDA-reaction without catalyst:
The general procedure for the domino-IEDDA-reaction was followed, but no catalyst was added. Phthalazine (**1a**) (32.9 mg, 250 µmol, 1.00 equiv) dissolved in THF (dry, degassed) (1 ml). Then pyrrolidine (**7a**) (41.5 µL, 500 µmol, 2.00 equiv) was added, followed by 3-phenylpropionaldehyde (**6c**) (49.4 µL, 375 µmol, 1.50 equiv). The reaction vessel was sealed and the remaining part of the reaction was carried out in a fume hood. The orange solution was heated to 60 °C (preheated sand bath) for 15 h (no gas evolution was observed; when the reaction vessel was opened, no build up pressure was detected). Afterwards, it was concentrated under reduced pressure. A yellow oil was obtained. Only phthalazine (**1a**) and generated enamine was detected by ^{1}H-NMR- and mass-spectrometry [gc-MS (EI)].

Domino-IEDDA-reaction with $BF_3{\cdot}O(CH_2CH_3)_2$:
The reaction was setup in nitrogen filled glovebox.
Phthalazine (**1a**) (98.7 mg, 0.75 mmol, 1.00 equiv) was dissolved in THF (dry, degassed) (3 mL). Pyrrolidine (**7a**) (124 µL, 1.50 mmol, 2.00 equiv) and 3-phenylpropionaldehyde (**6c**) (148 µL, 1.13 mmol, 1.50 equiv) were added. The reaction vessel was sealed and the rest of the reaction was carried out in a fume hood under Schlenk conditions (connected nitrogen line for pressure compensation). Then, boron trifluoride diethyl etherate [$BF_3{\cdot}O(C_2H_5)_2$] (20.0 µL, 0.16 mmol, 21.4 mol %) was added. It was heated to 60 °C (preheated oil bath) and stirred for 15 h. Afterwards, the yellow solution was cooled to rt and concentrated under reduced pressure. An orange oil was obtained. It was purified by flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc +1% NEt_3, 15:1). 1-Amino-1,2-dihydronaphthalene **4c** (41.3 mg, 143 µmol, 19%) was isolated as pale yellow oil.

Domino-IEDDA-reaction with $B(C_6F_5)_3$:
General procedure for Domino-IEDDA-reaction was followed
Phthalazine (**1a**) (32.9 mg, 250 µmol, 1.00 equiv) and tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] (6.5 mg, 12.6 µmol, 5 mol %) were dissolved in THF (dry, degassed) (1 ml). Then, pyrrolidine (**7a**) (41.5 µL, 500 µmol, 2.00 equiv) was added, followed by 3-phenylpropionaldehyde (**6c**) (49.4 µL, 375 µmol, 1.50 equiv). The orange solution was heated to 60 °C (preheated sand bath) for 15 h (no gas evolution was observed; when the reaction vessel was opened, no build up pressure was detected). A yellow orange suspension was obtained. Only trace amounts of 1-amino-1,2-dihydronaphthalene **4c** were detected by ^{1}H-NMR- and mass-spectrometry [gc-MS (EI)]. Main components of the crude product were phthalazine (**1a**) and *in situ* formed enamine.

Optimization of the amount of amine for the domino-IEDDA-reaction:



1a: R^1 = H
1b: R^1 = F

6a

7a

2

4a: R^1 = H
4r: R^1 = F

10a: R^1 = H
10b: R^1 = F

Reactions were set up according to the general procedure.
See product section for details.

Table S2. Domino-IEDDA-reaction depending on amount of amine.

Entry	Phthalazine	Aldehyde	Amine	1-Amino-1,2-dihydronaphthalene	Naphthalene (elimination product)
1	**1a**	2.50 equiv	1.20 equiv	**4a** (traces)	**10a** (34%)
2	**1b**	2.50 equiv	1.20 equiv	**4r** (89%)	**10b** (0%)
3	**1a**	1.50 equiv	2.00 equiv	**4a** (89%)	**10a** (0%)

NMR-spectra:

Determination of *cis*- or *trans*-configuration:

The structure of **4a** in *trans*- and *cis*-configuration was computed with B3LYP/6-311++G**(see below for computational details). Proton H10 should give a NOESY signal with protons from the 2-propyl group (H11-H13) only in the *trans*-isomer (Figure S2). Cross peaks for H10 were observed for H4, H9, H11, H12, H13, H14, and H15. Therefore **4a** and all other products **4** were assigned as *trans*-isomer.

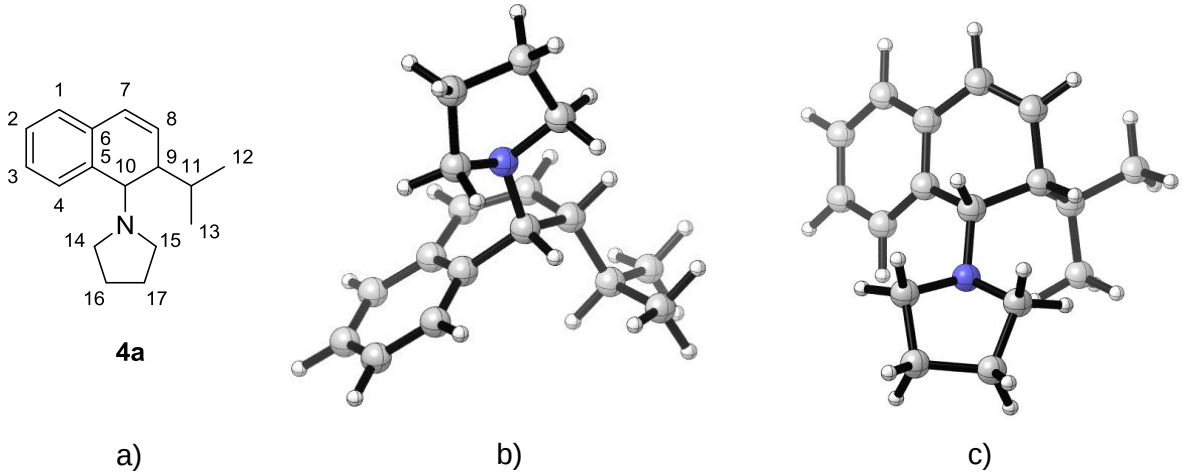
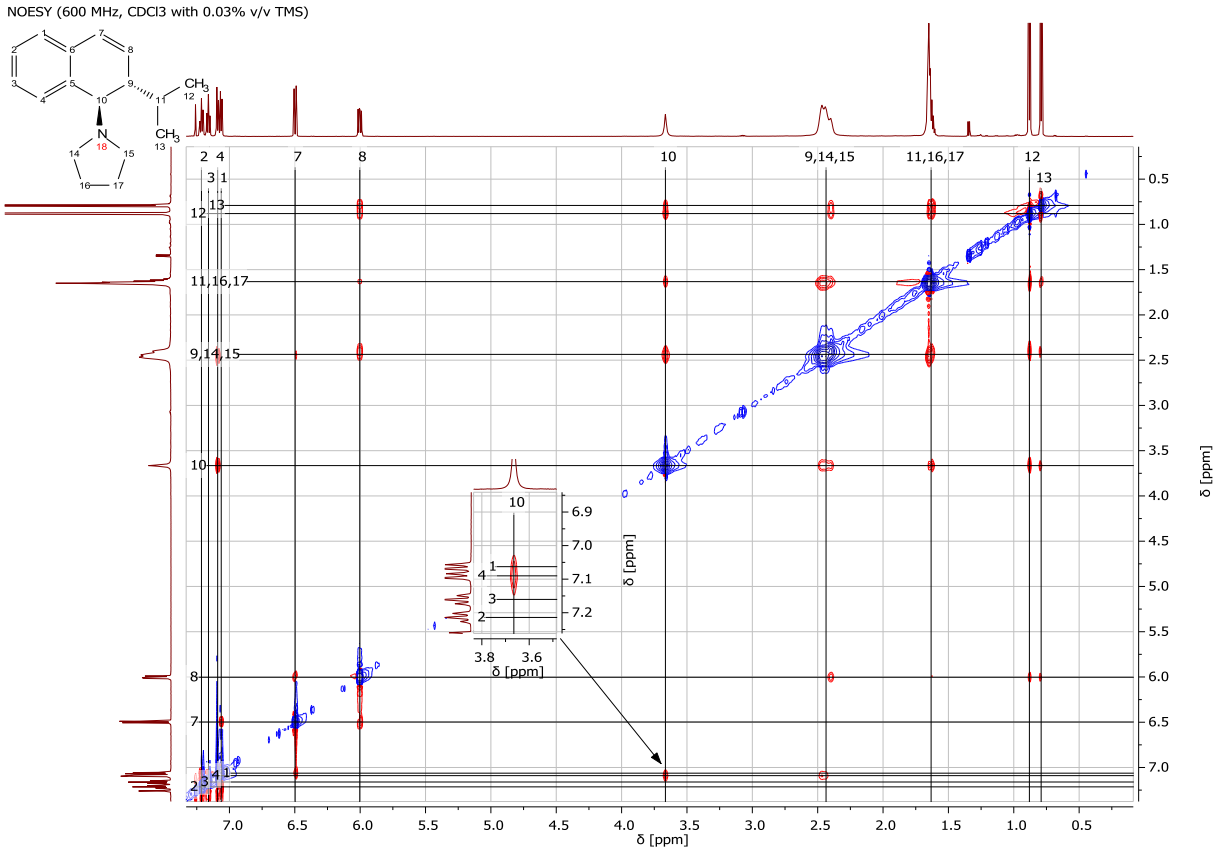
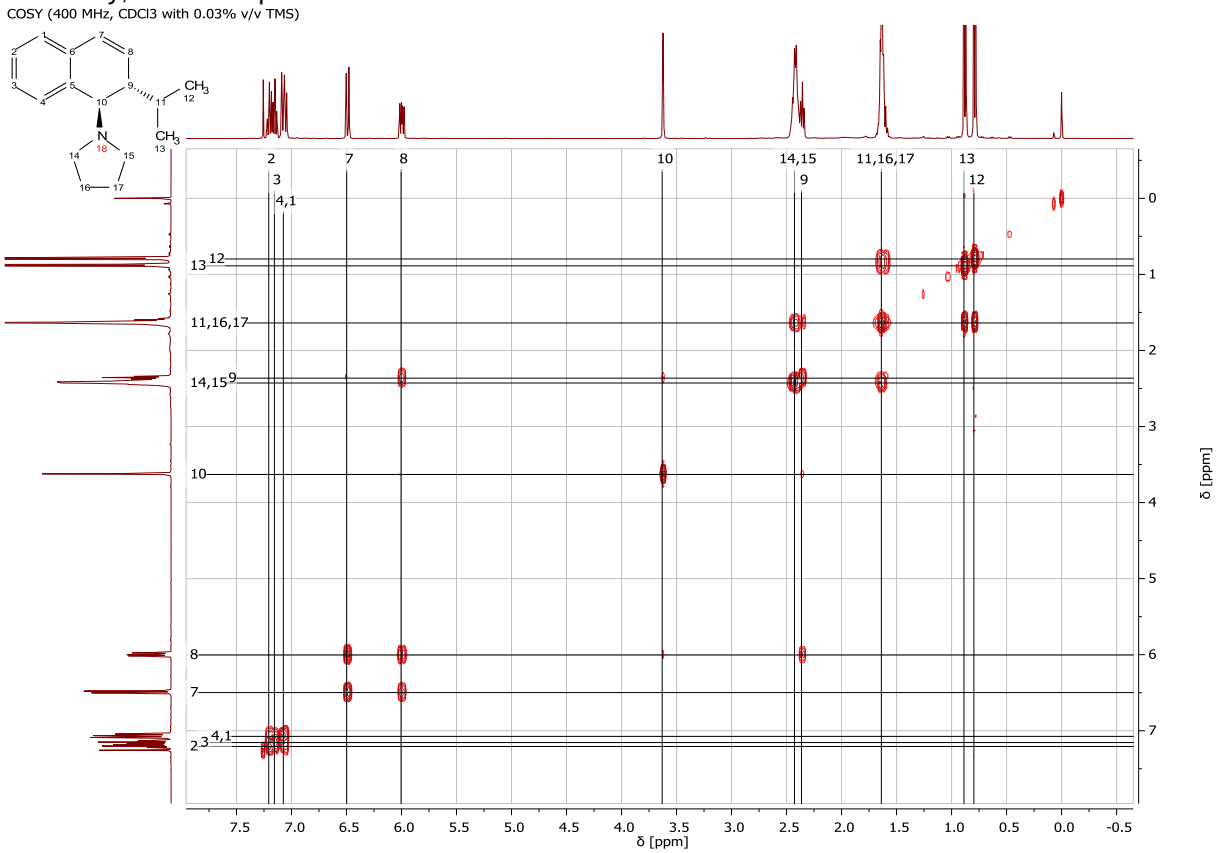


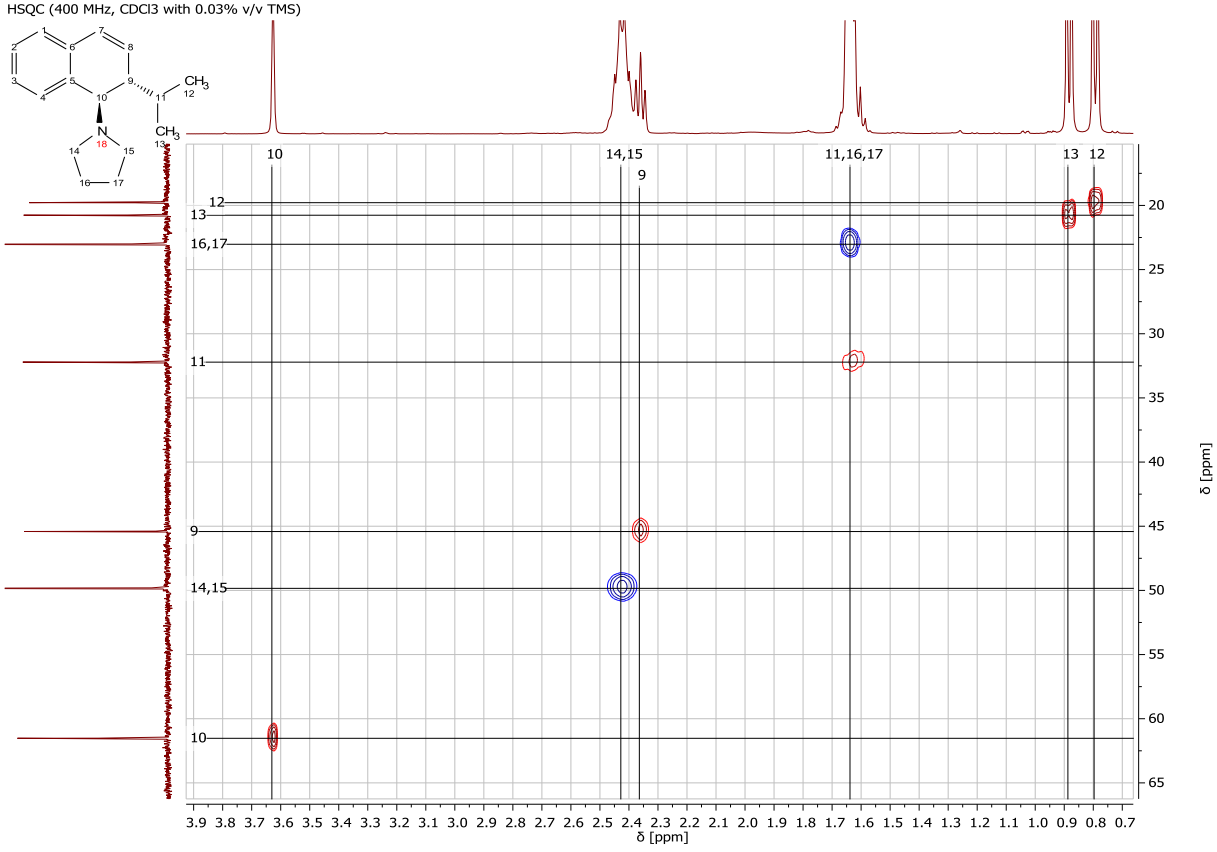
Figure S2. Only one enantiomer is depicted for clarity; a) labeled structure of **4a**; b) computed structure of **4a** in *trans*-configuration; c) computed structure of **4a** in *cis*-configuration.



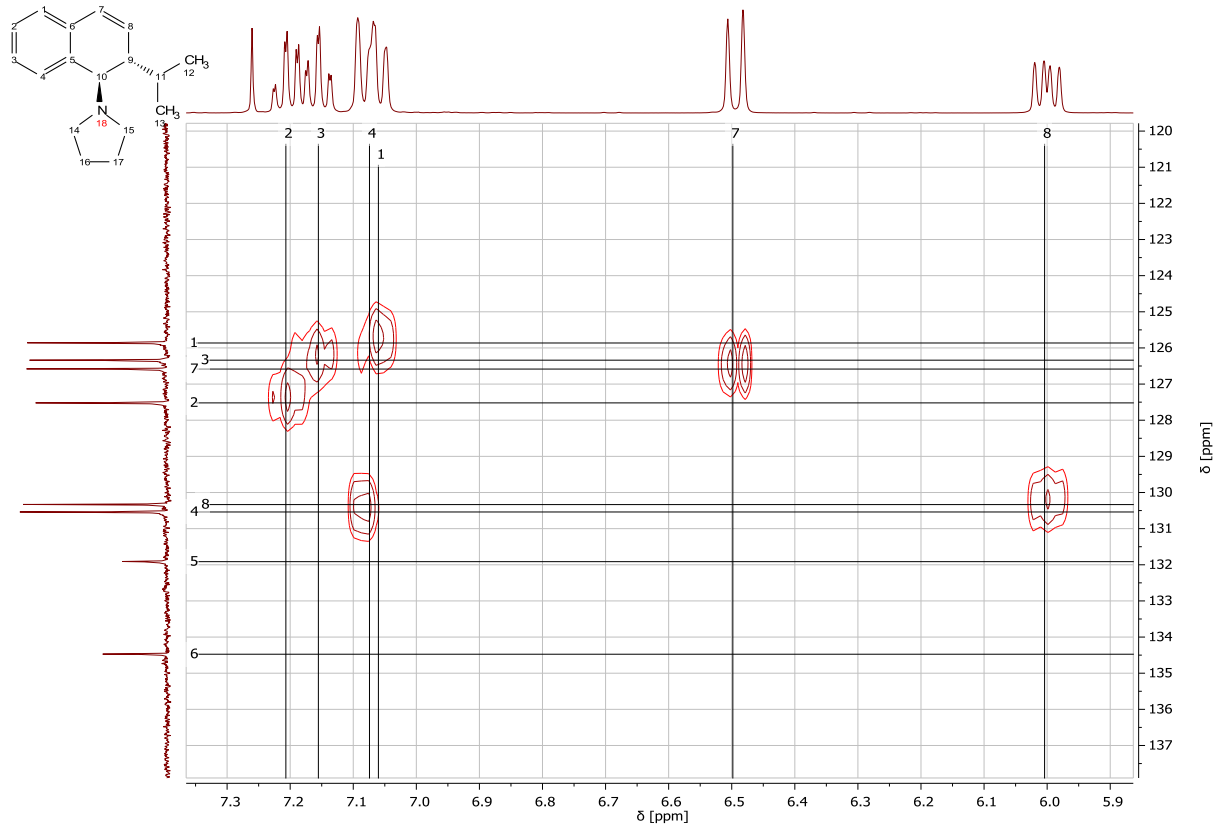
For clarity, other 2D spectra for **4a** are also shown below.



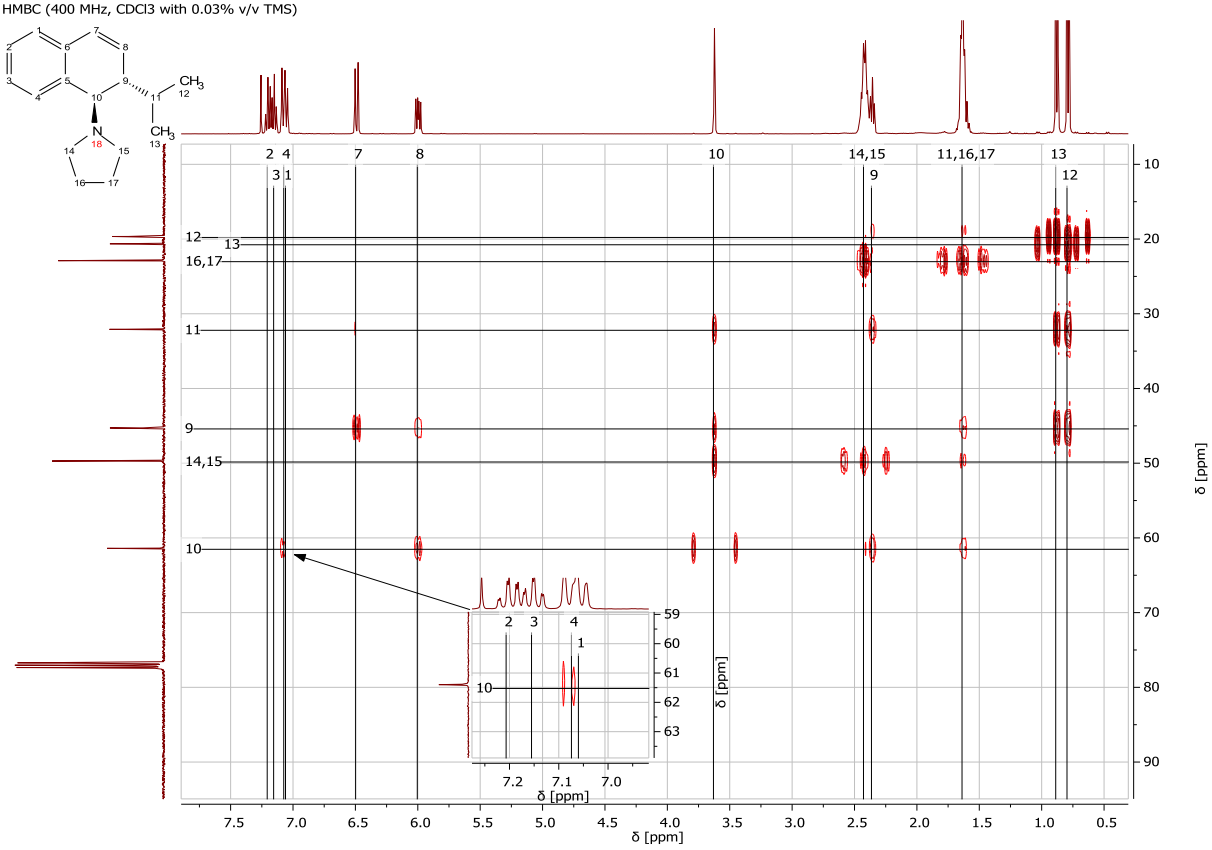
HSQC (400 MHz, CDCl3 with 0.03% v/v TMS)



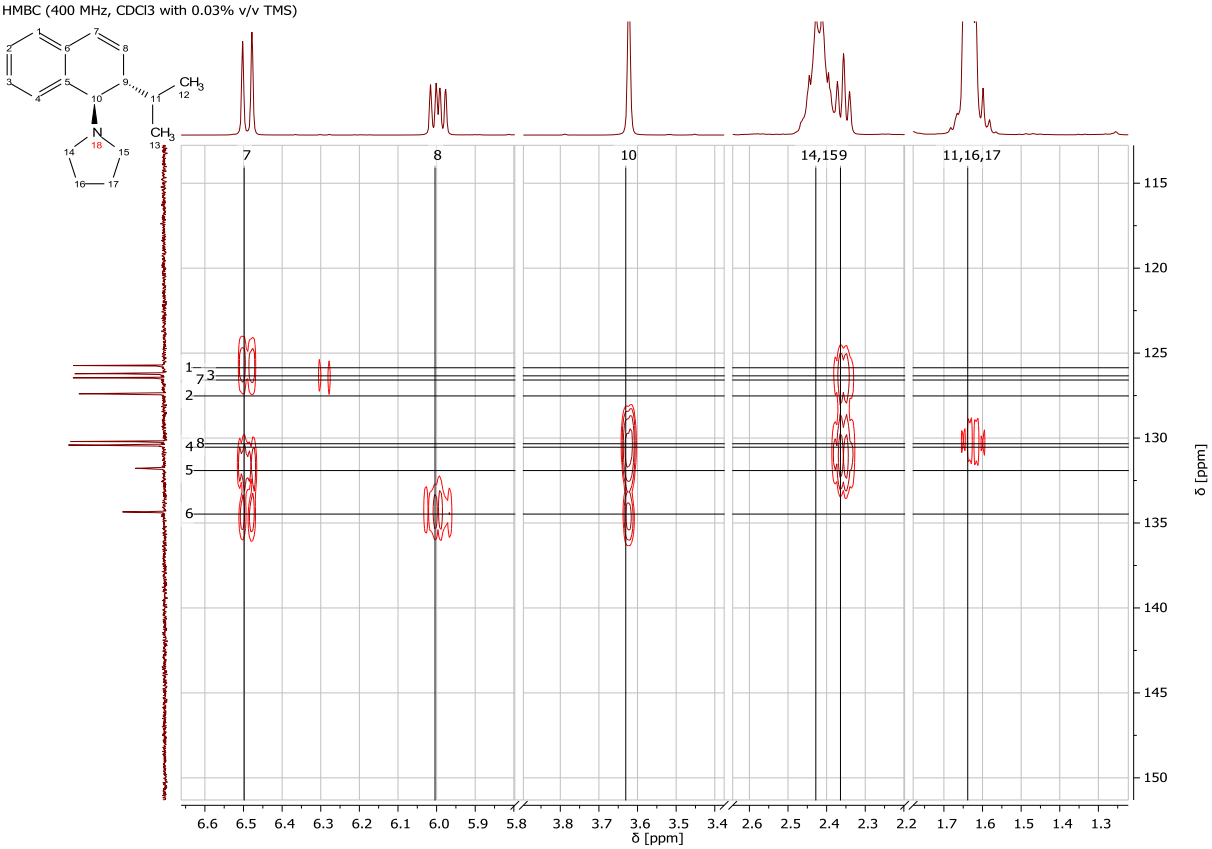
HSQC (400 MHz, CDCl3 with 0.03% v/v TMS)

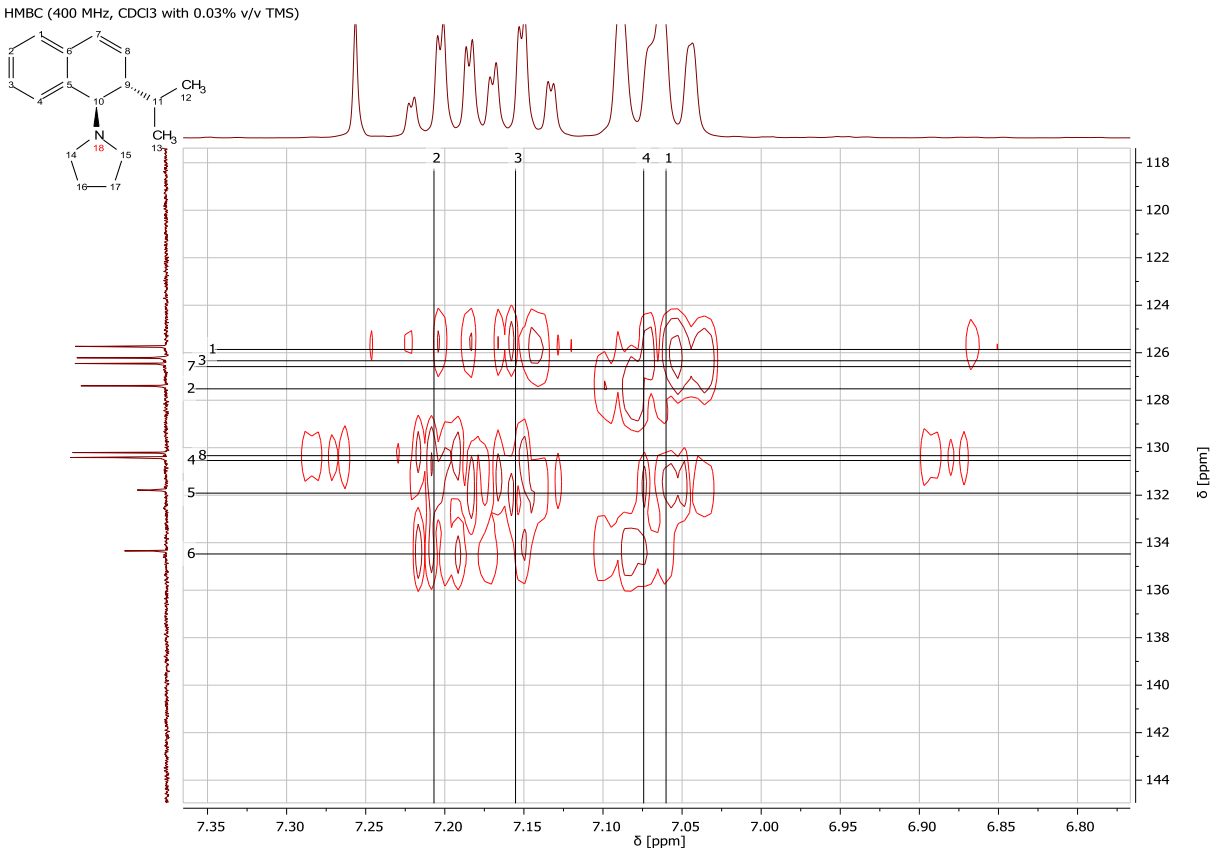


HMBC (400 MHz, CDCl3 with 0.03% v/v TMS)



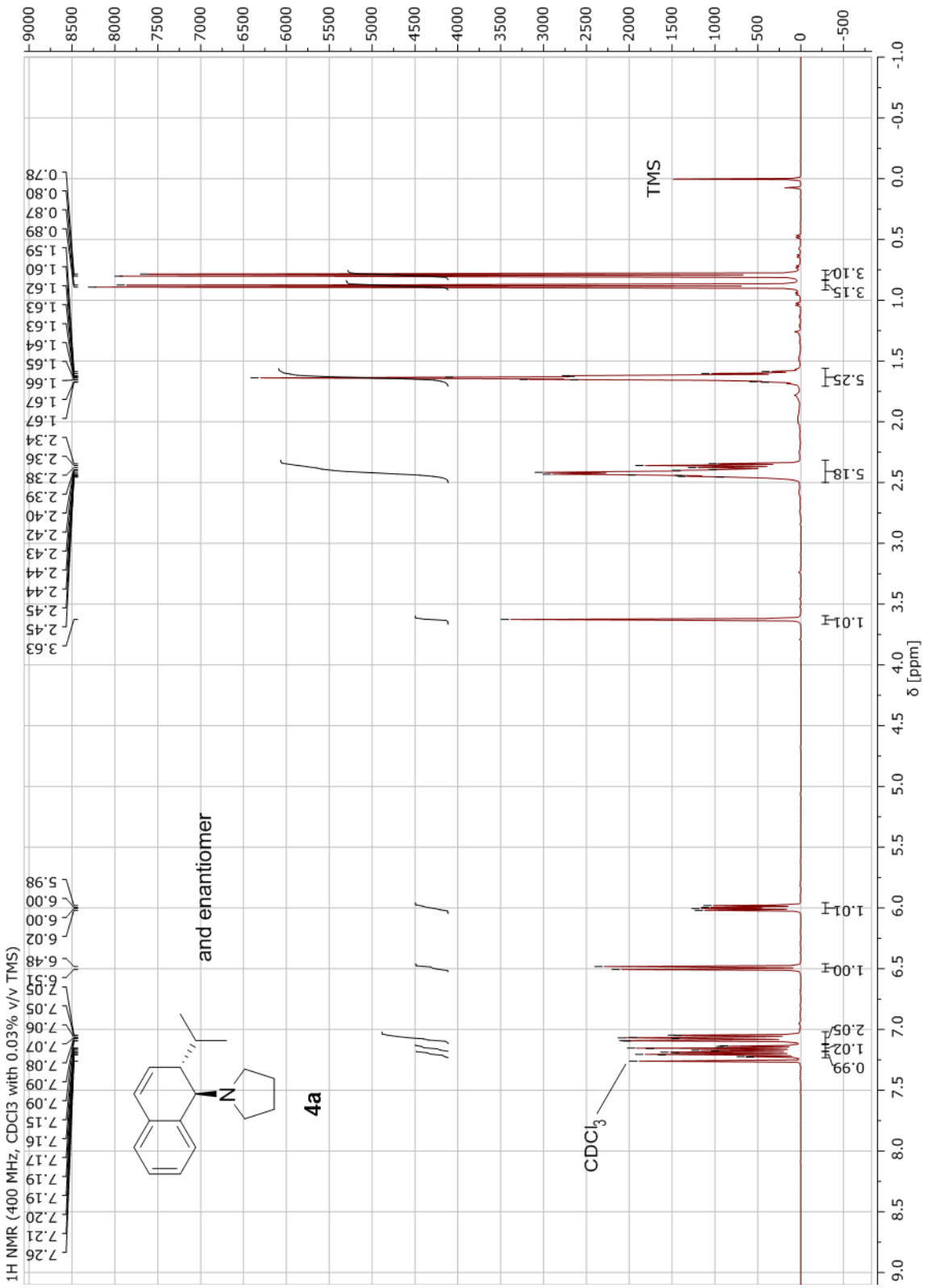
HMBC (400 MHz, CDCl3 with 0.03% v/v TMS)



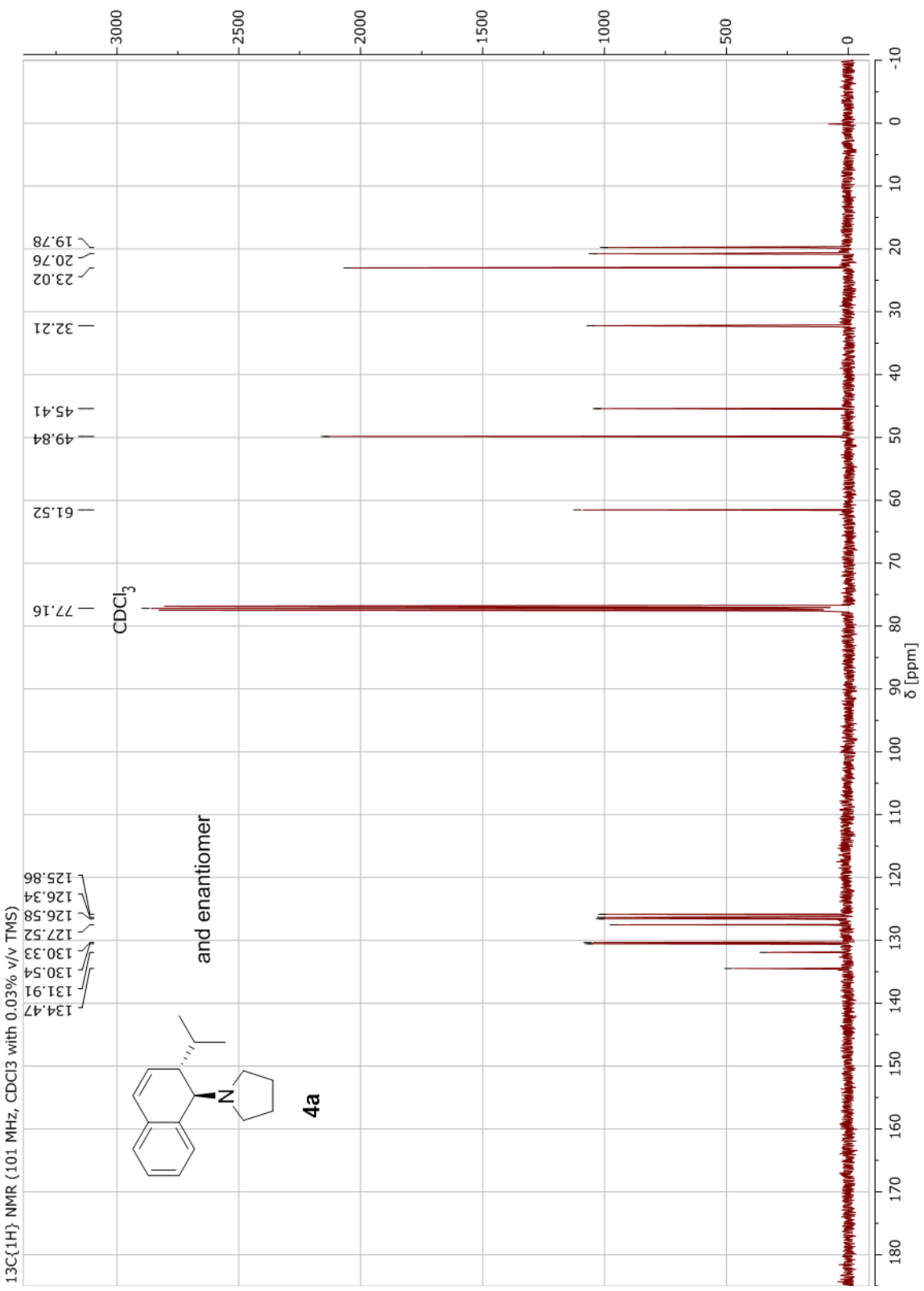

HMBC (400 MHz, CDCl3 with 0.03% v/v TMS)
δ [ppm]
δ [ppm]

^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{19}F{^{1}H}{^{13}C} spectra:

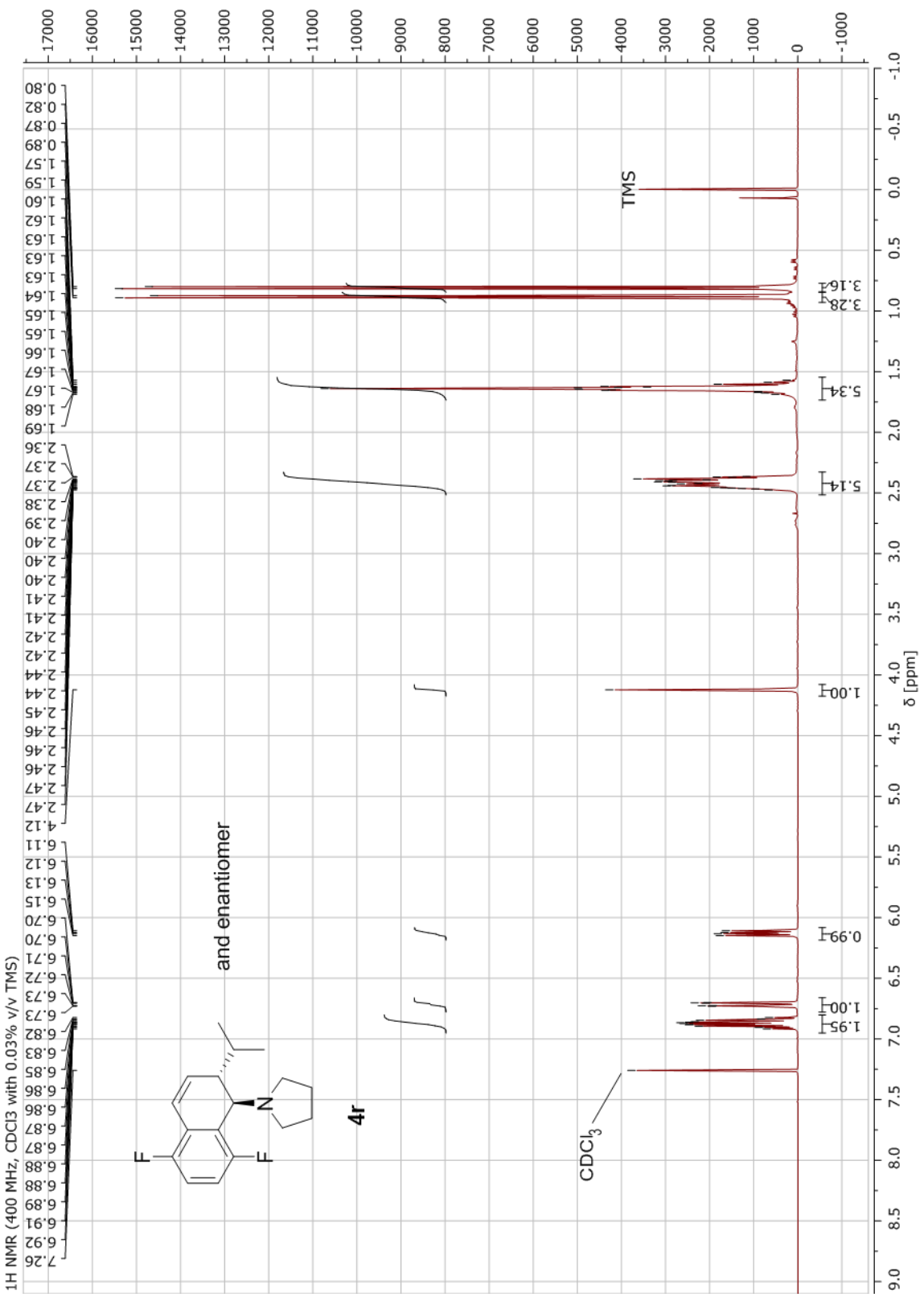
^{1}H NMR spectrum of **4a**



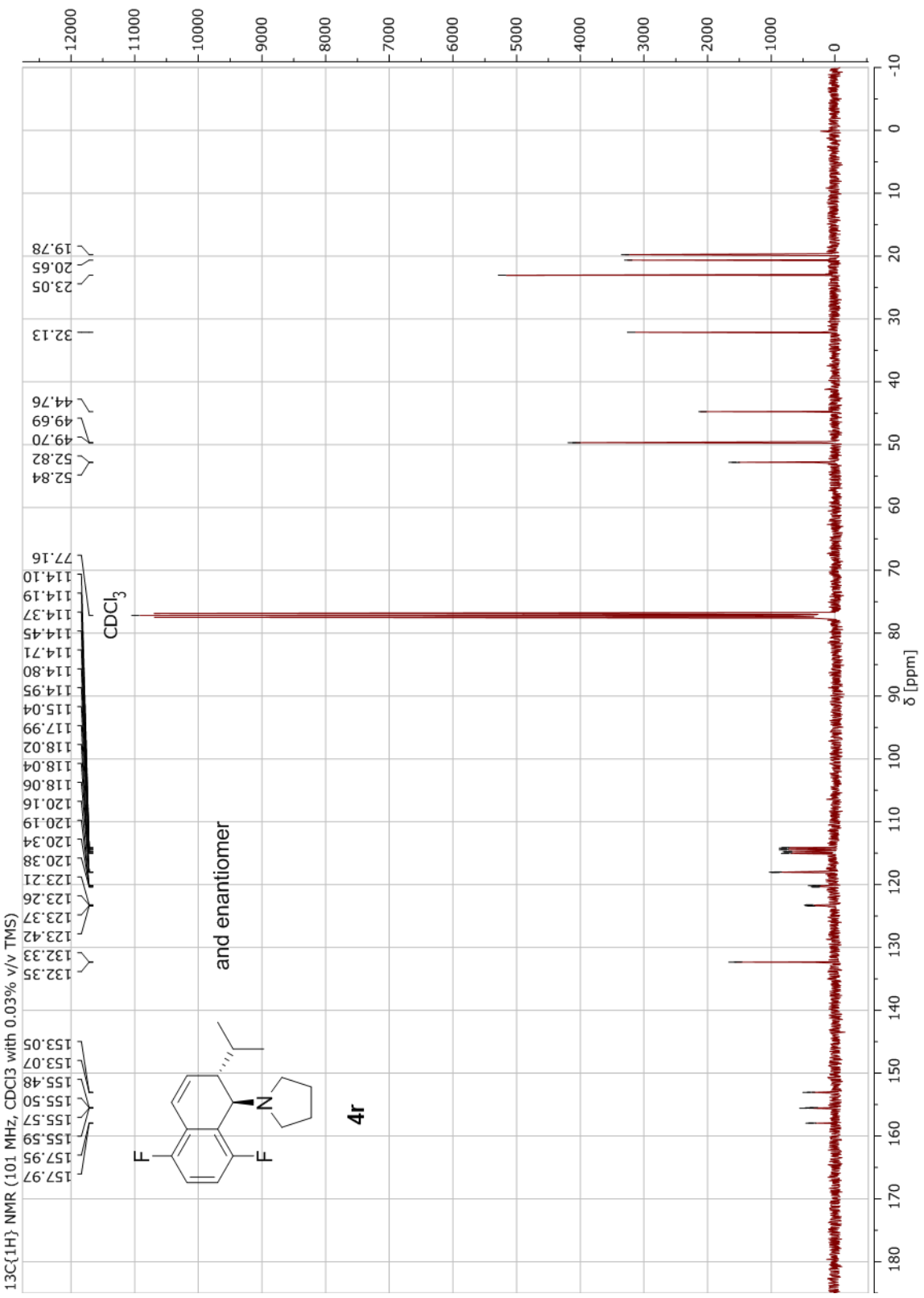
$^{13}C\{^{1}H\}$ NMR spectrum of **4a**



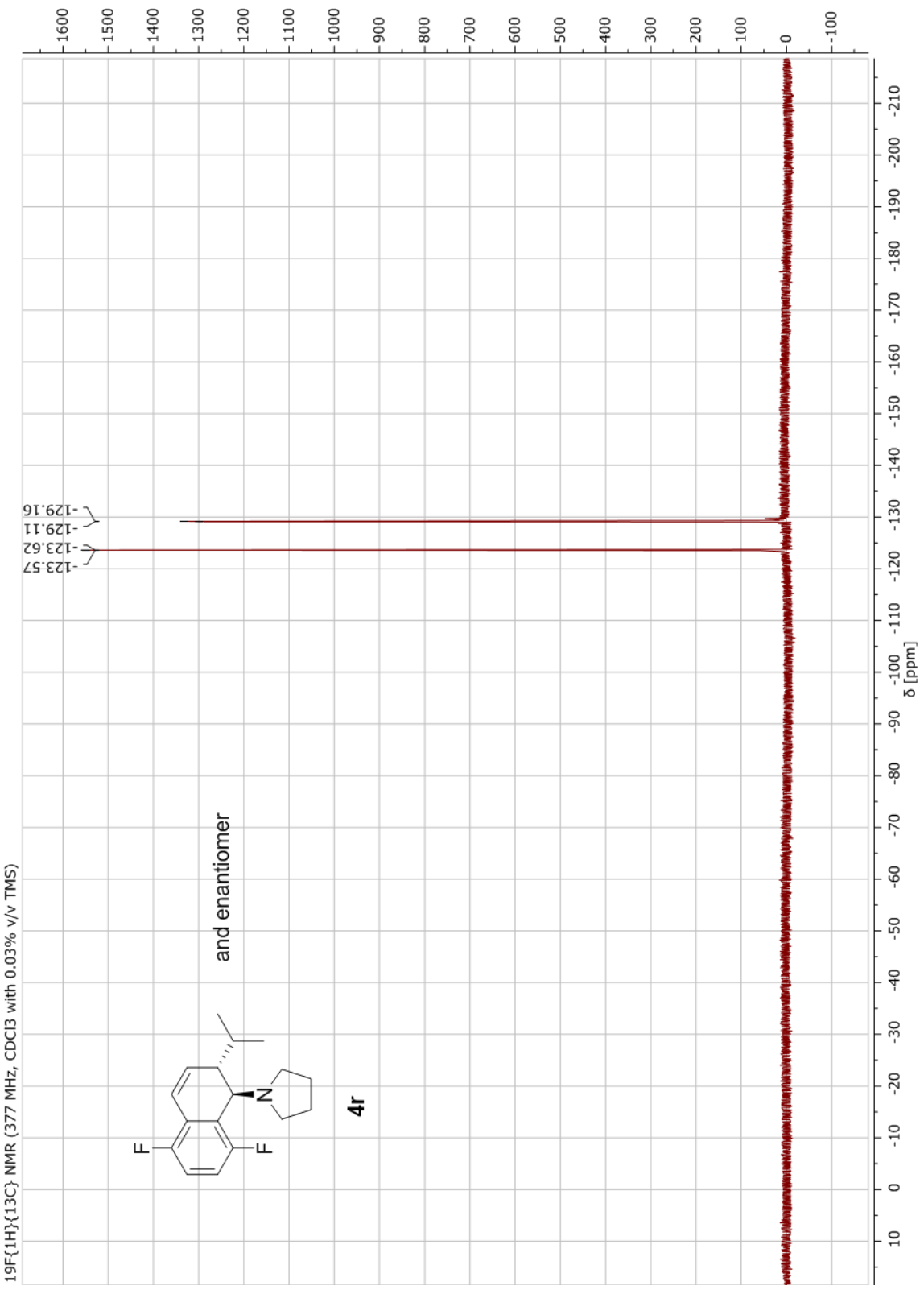
^{1}H NMR spectrum of **4r**



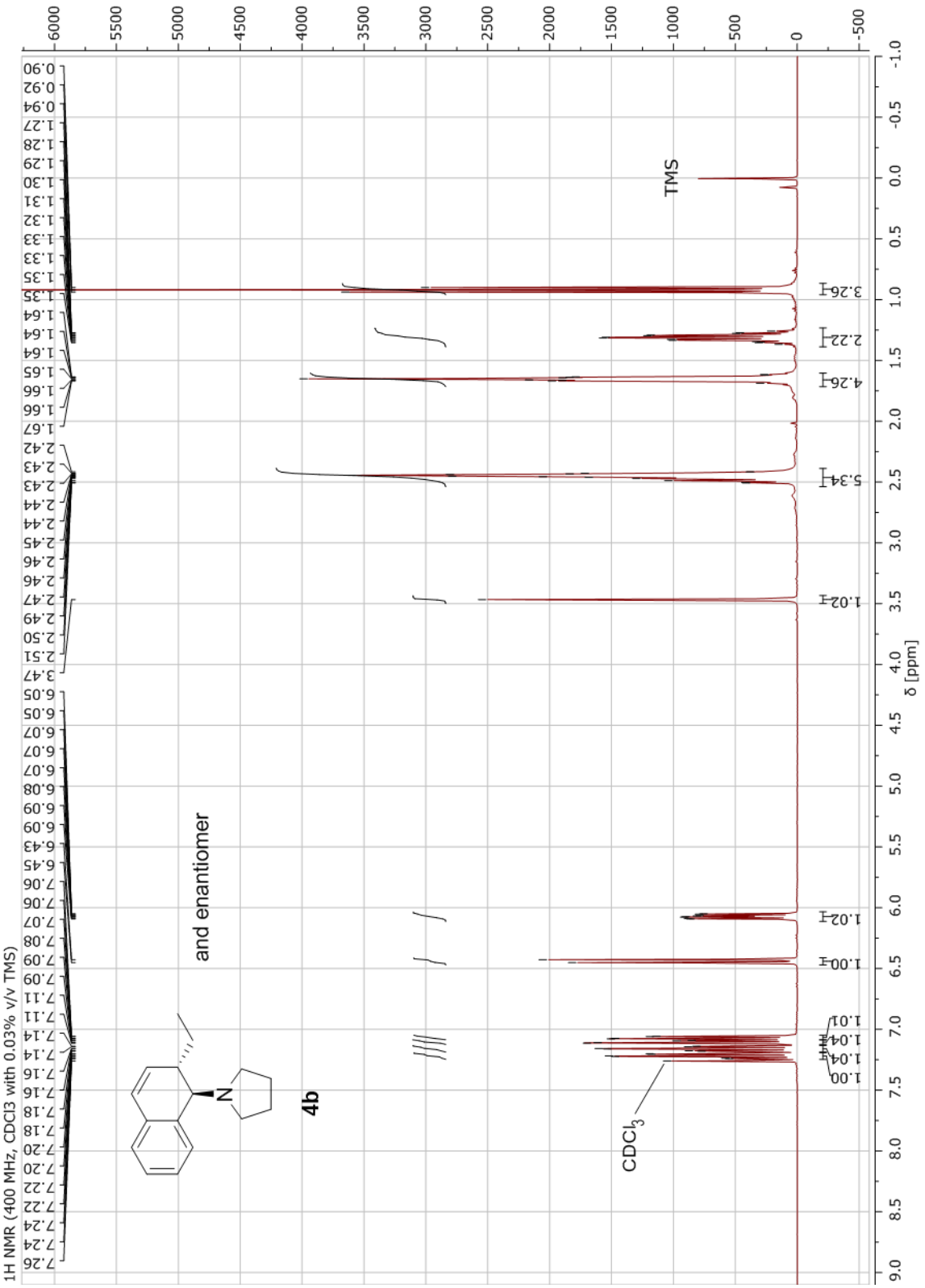
$^{13}C\{^{1}H\}$ NMR spectrum of **4r**



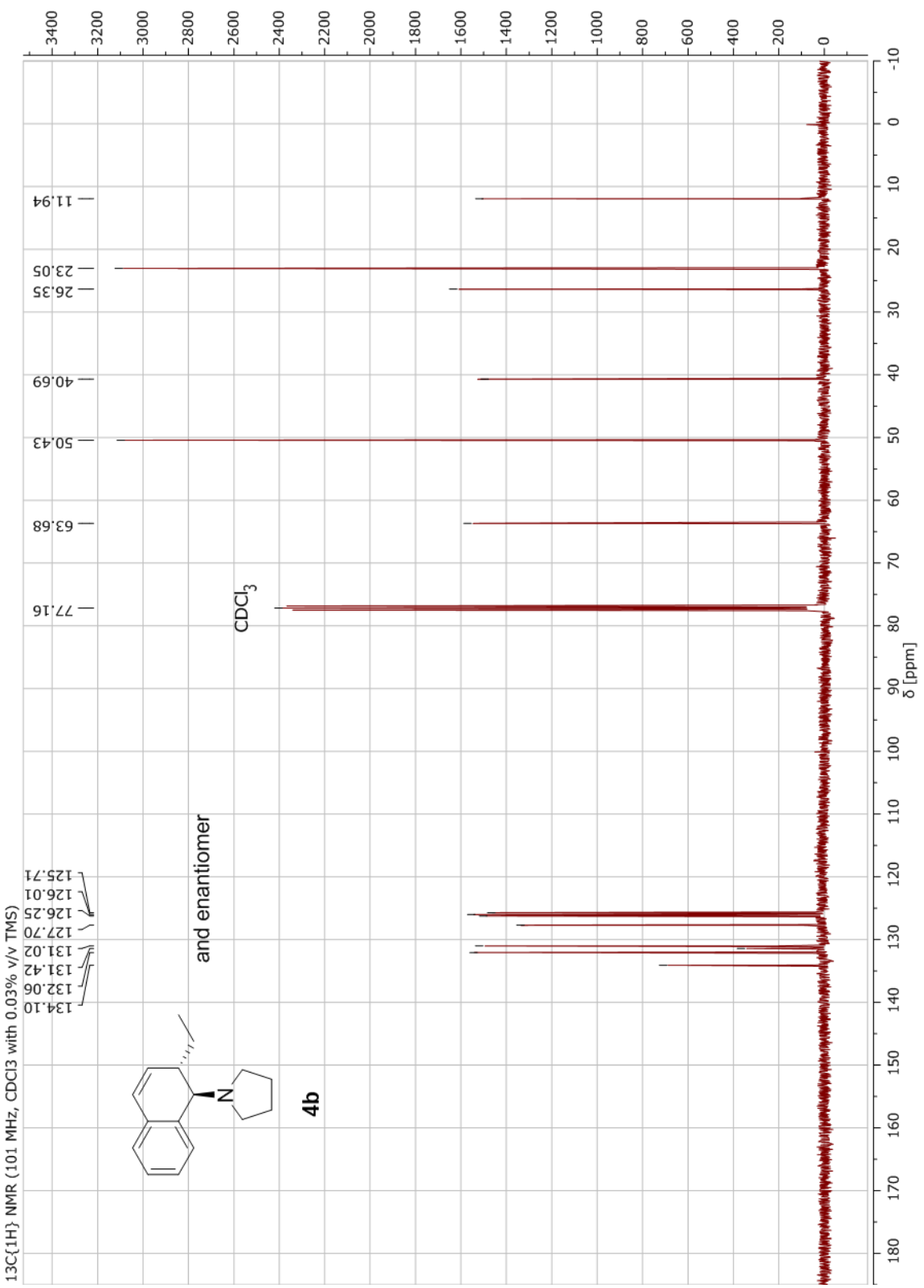
$^{19}F\{^{1}H\}\{^{13}C\}$ NMR spectrum of **4r**



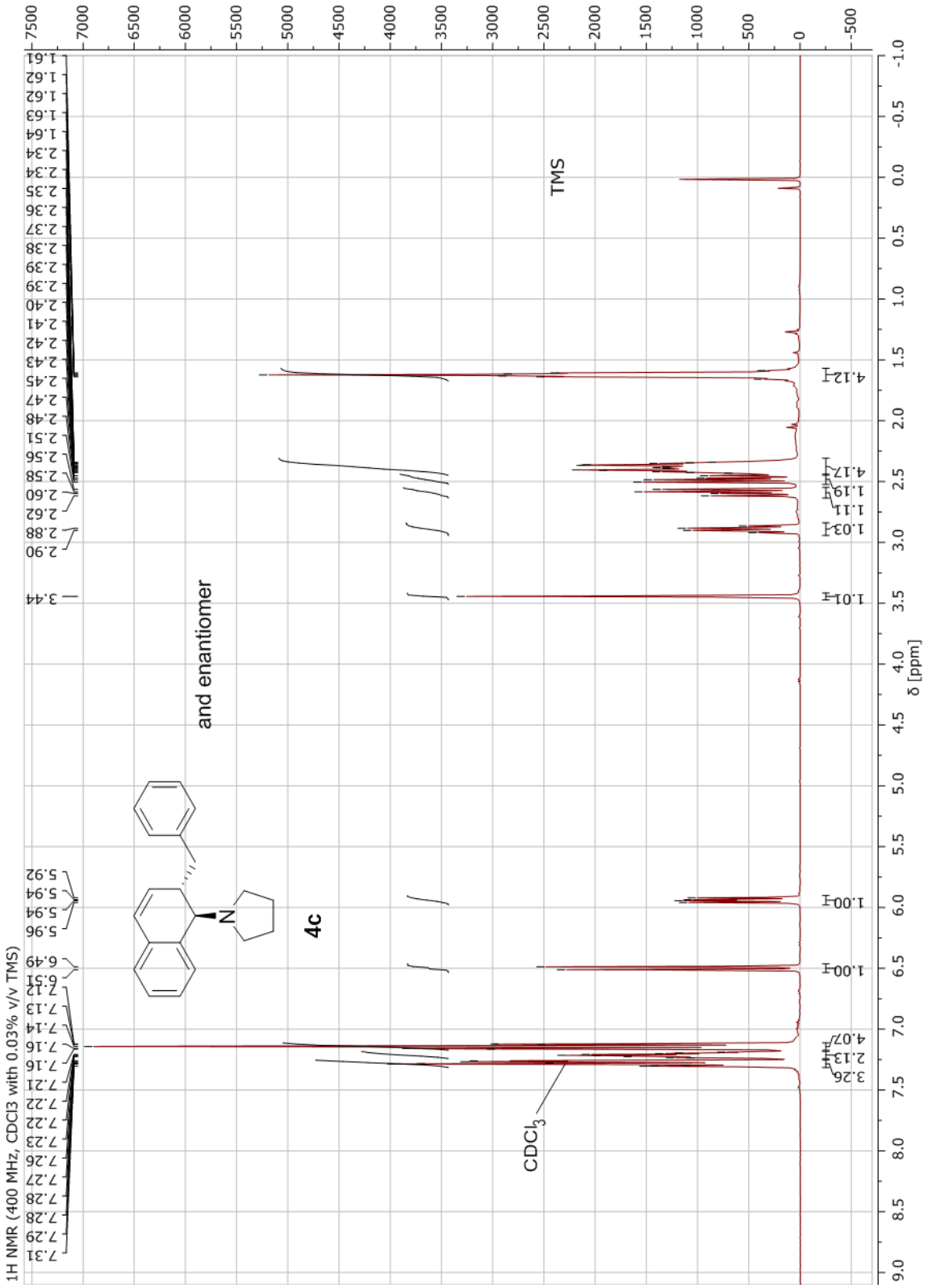
^{1}H NMR spectrum of **4b**



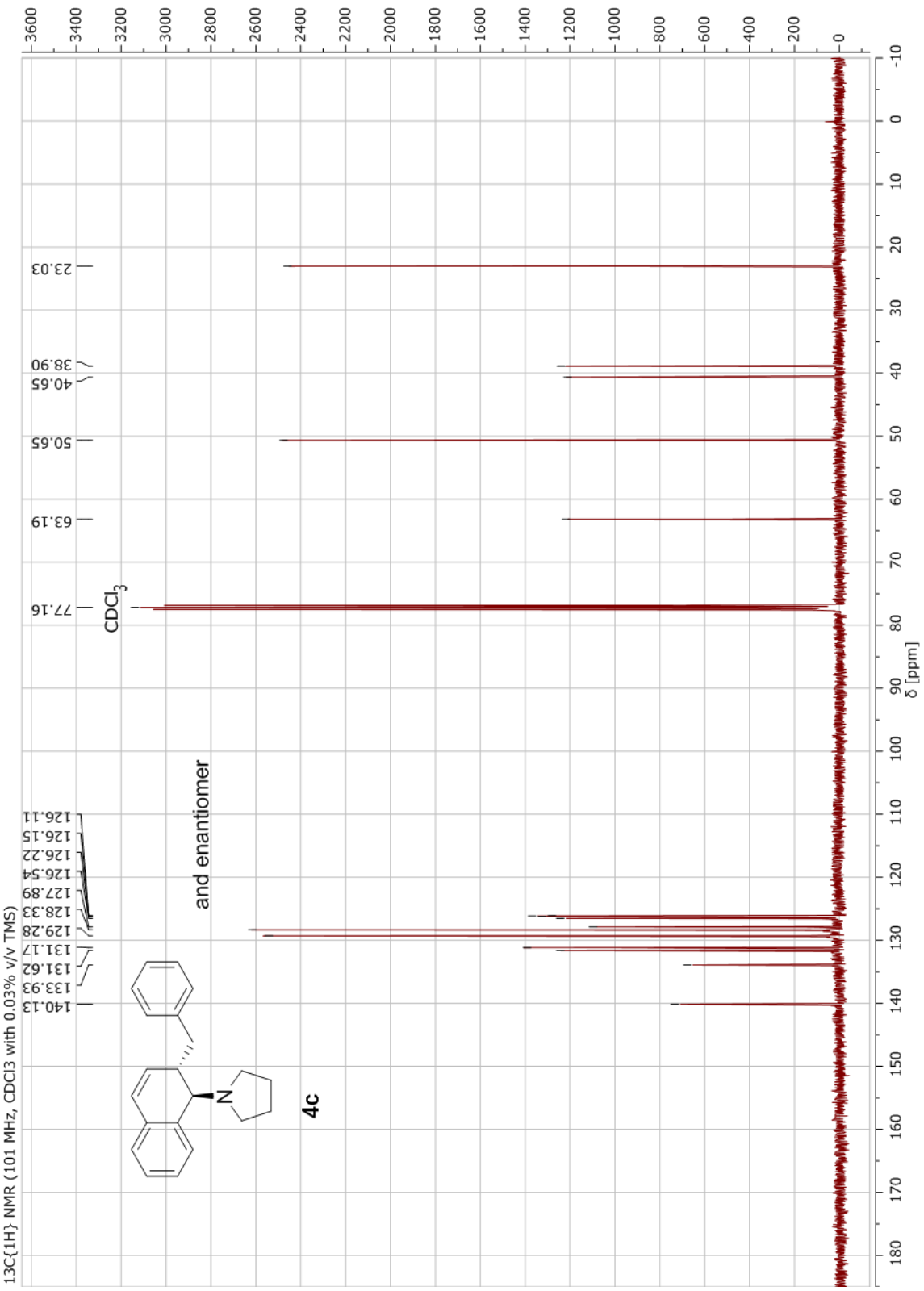
$^{13}C\{^{1}H\}$ NMR spectrum of **4b**



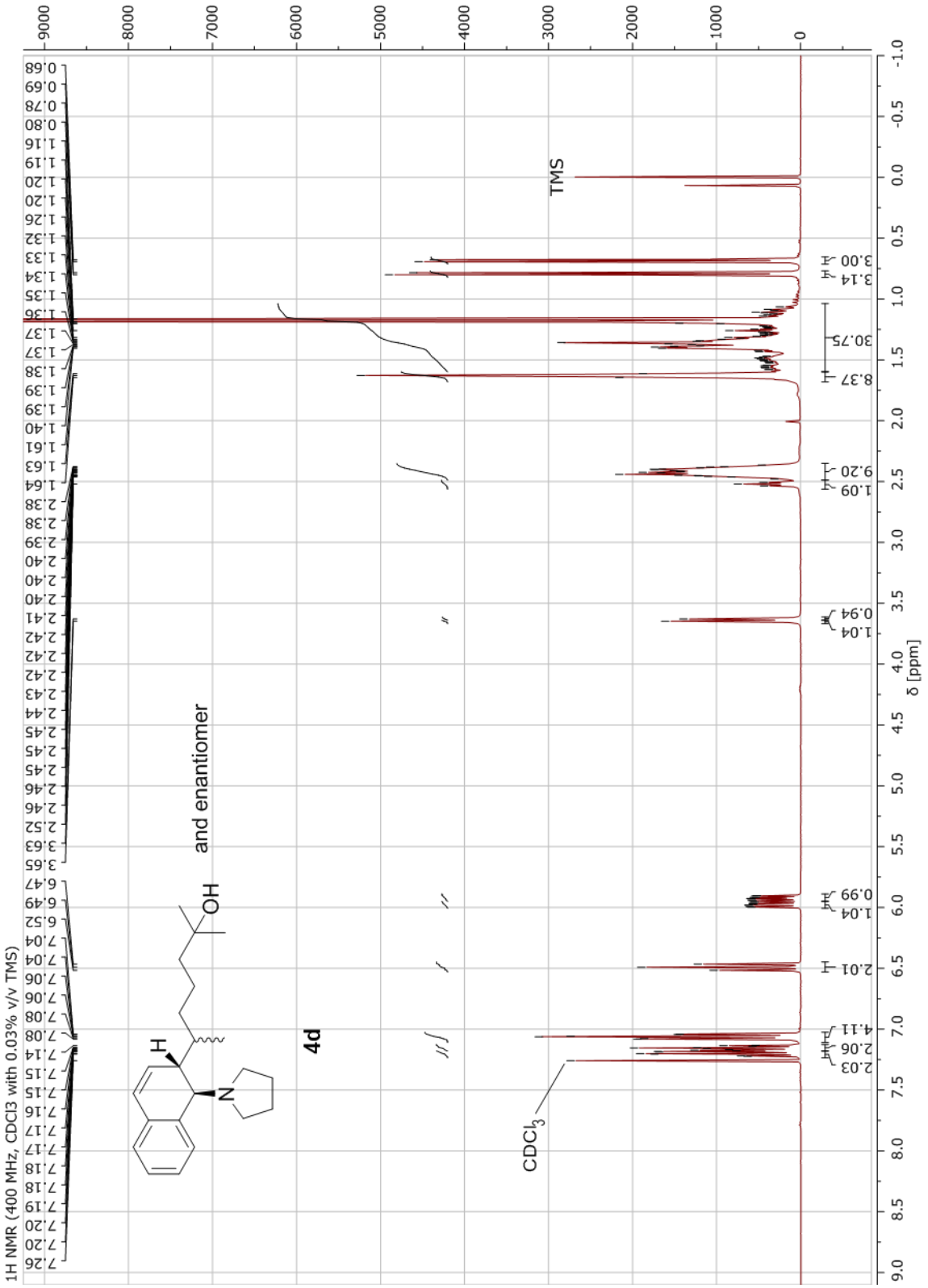
^{1}H NMR spectrum of **4c**



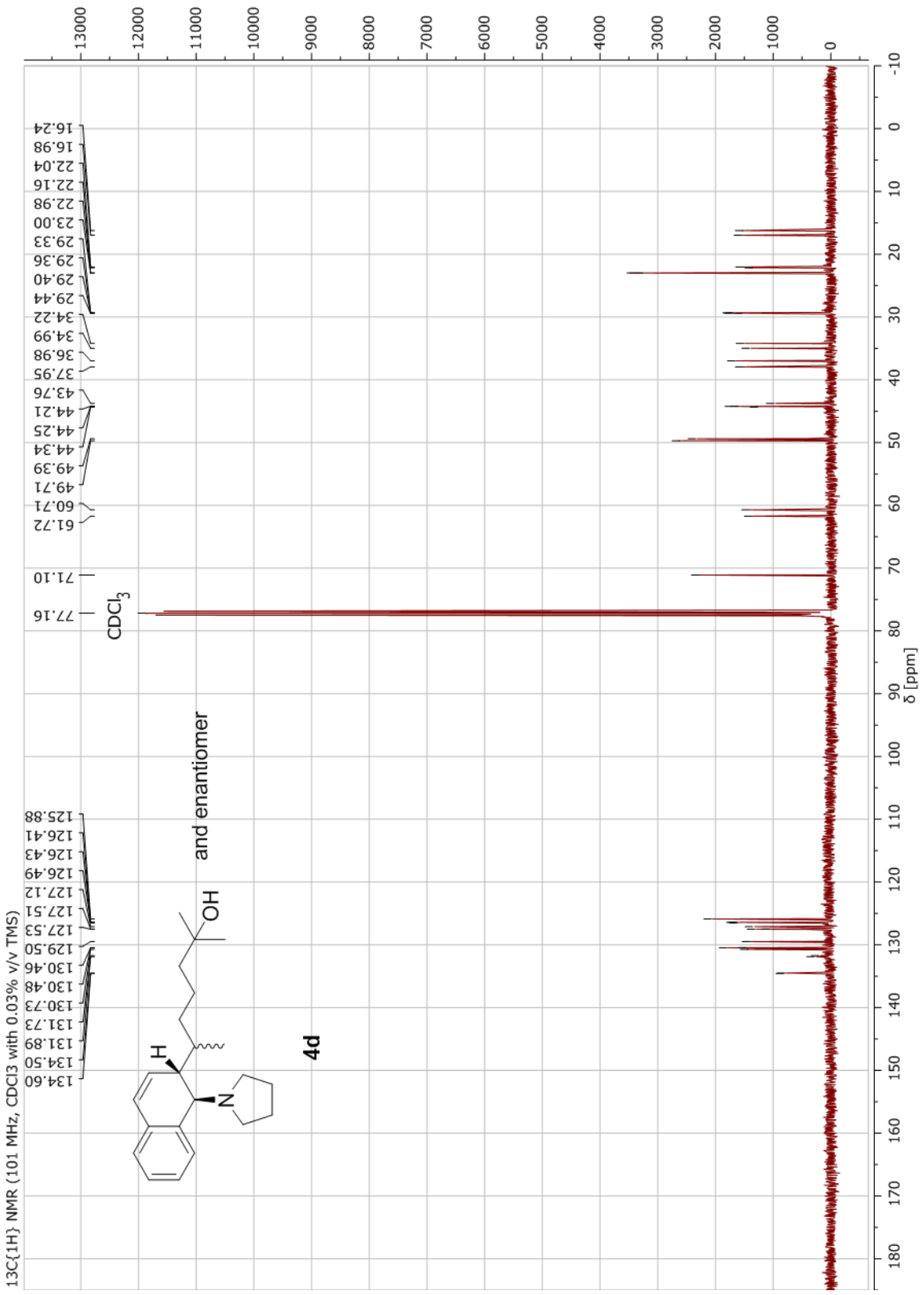
$^{13}C\{^{1}H\}$ NMR spectrum of **4c**



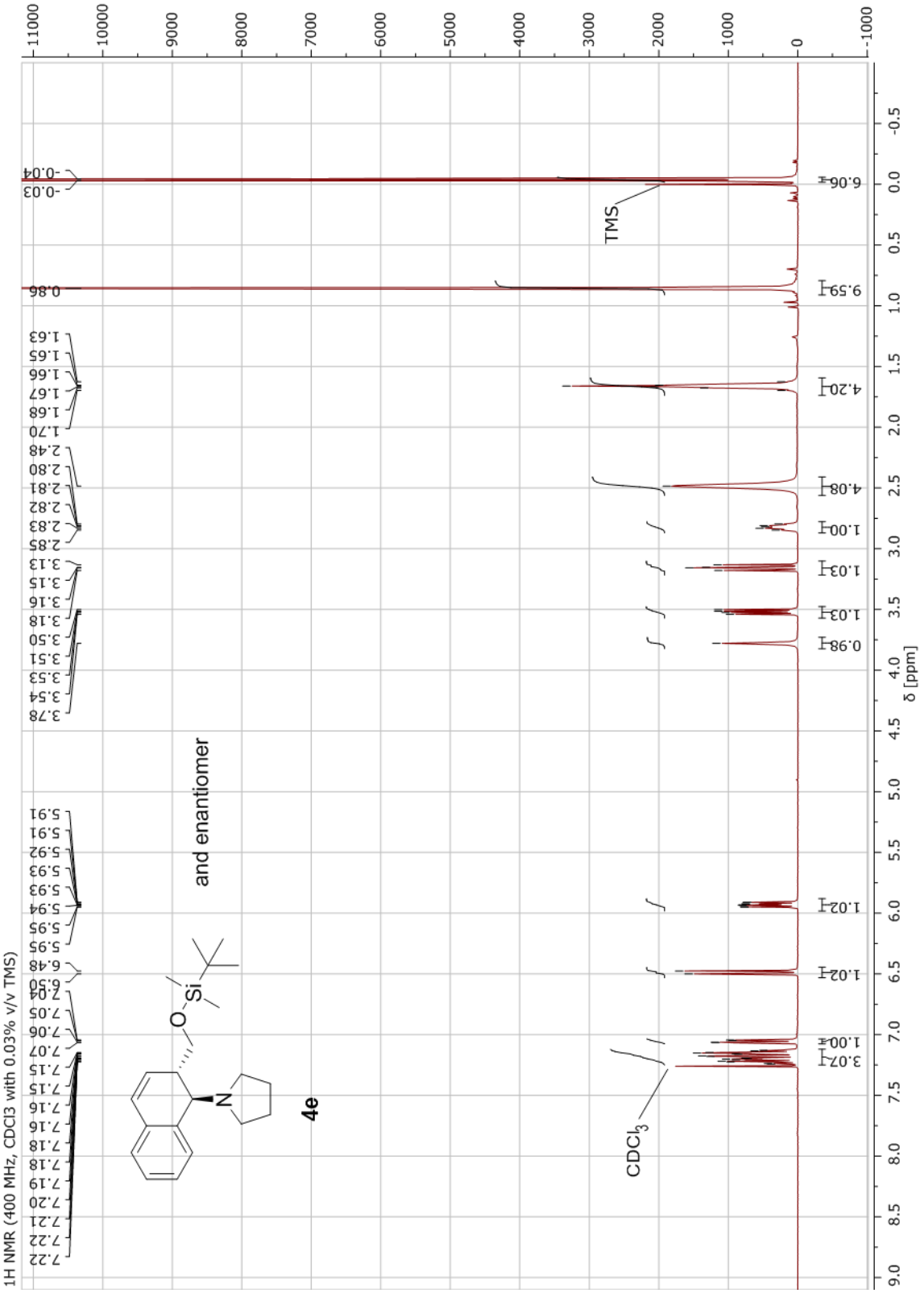
^{1}H NMR spectrum of **4d**



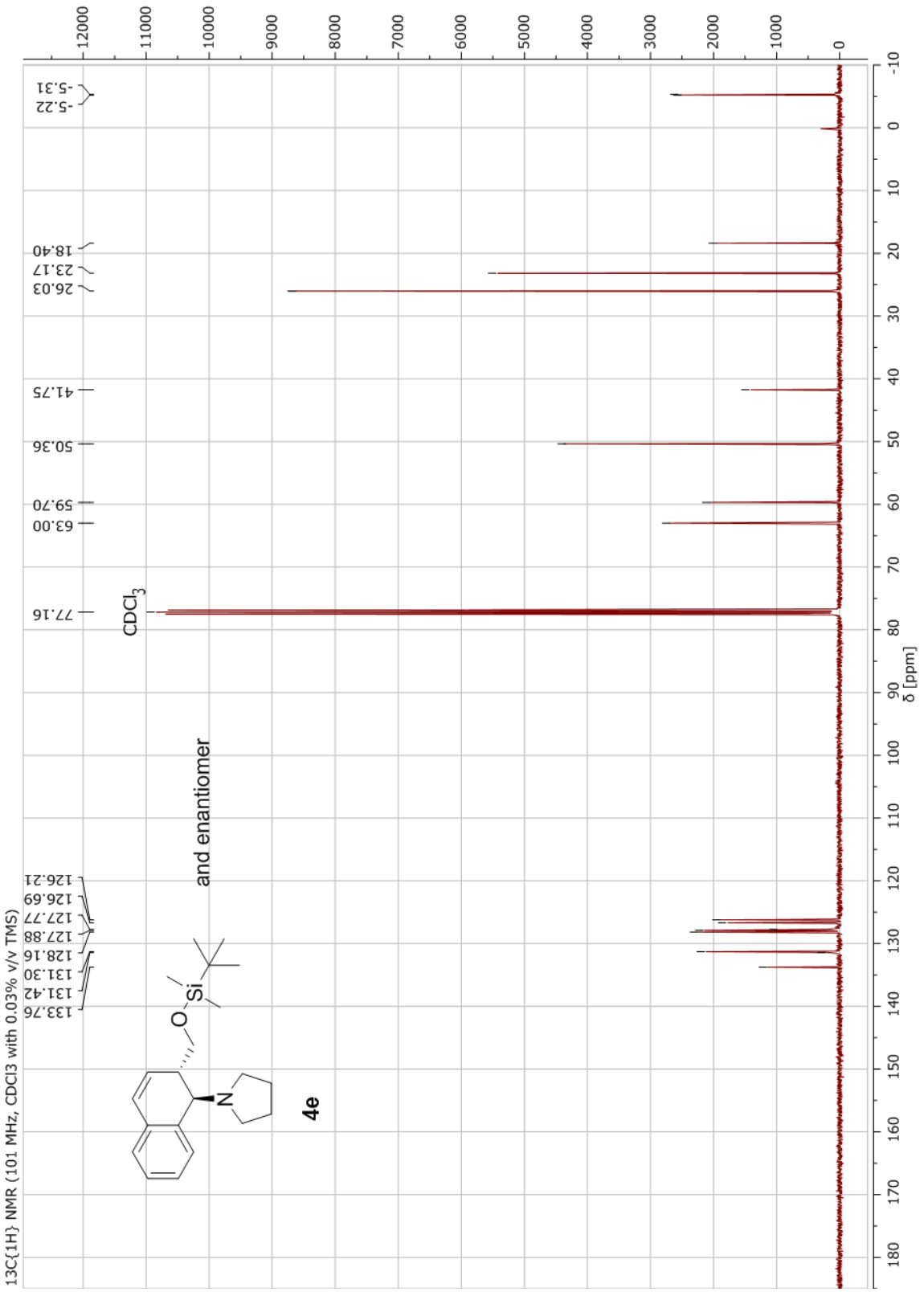
$^{13}C\{^{1}H\}$ NMR spectrum of **4d**



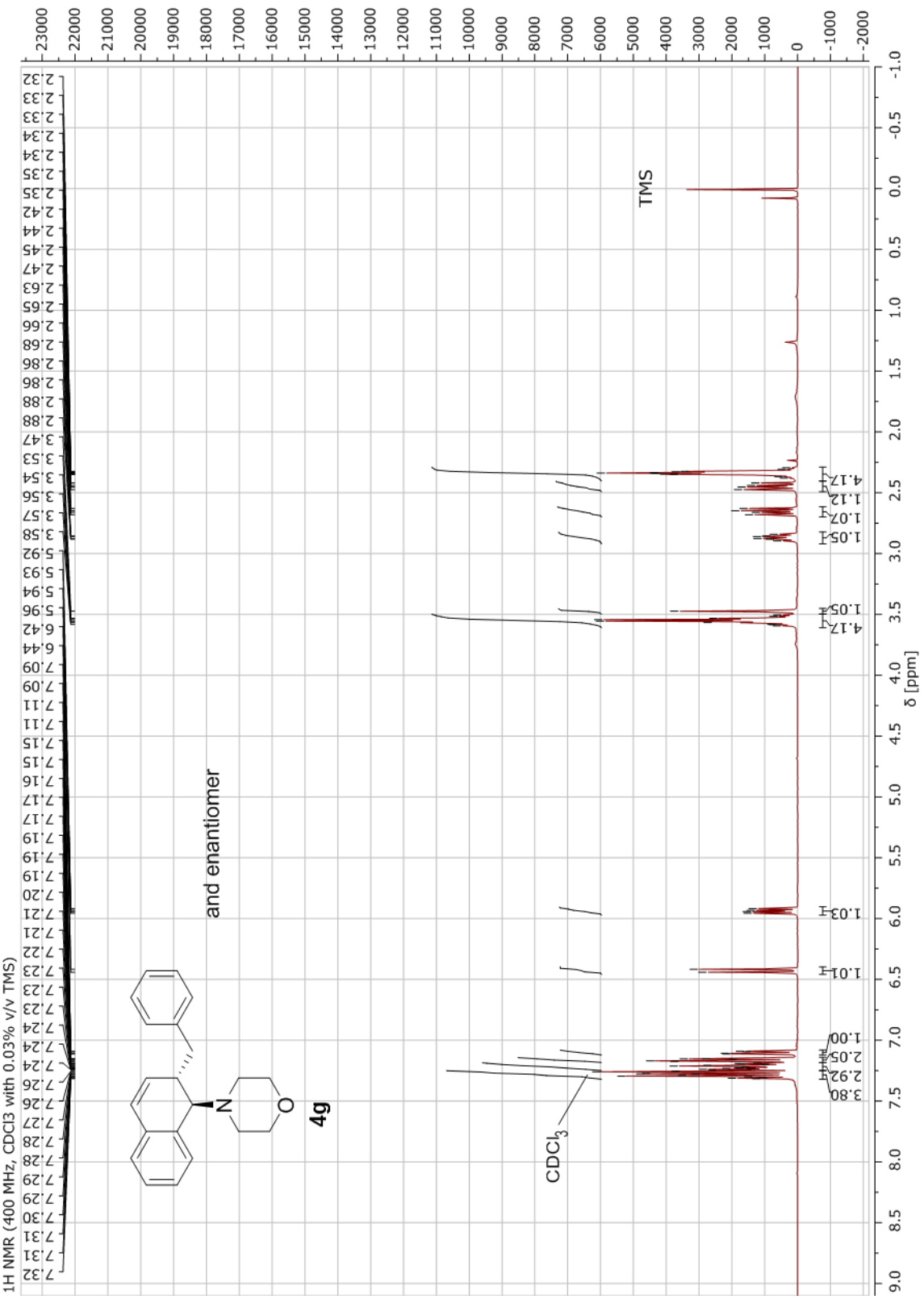
^{1}H NMR spectrum of **4e**



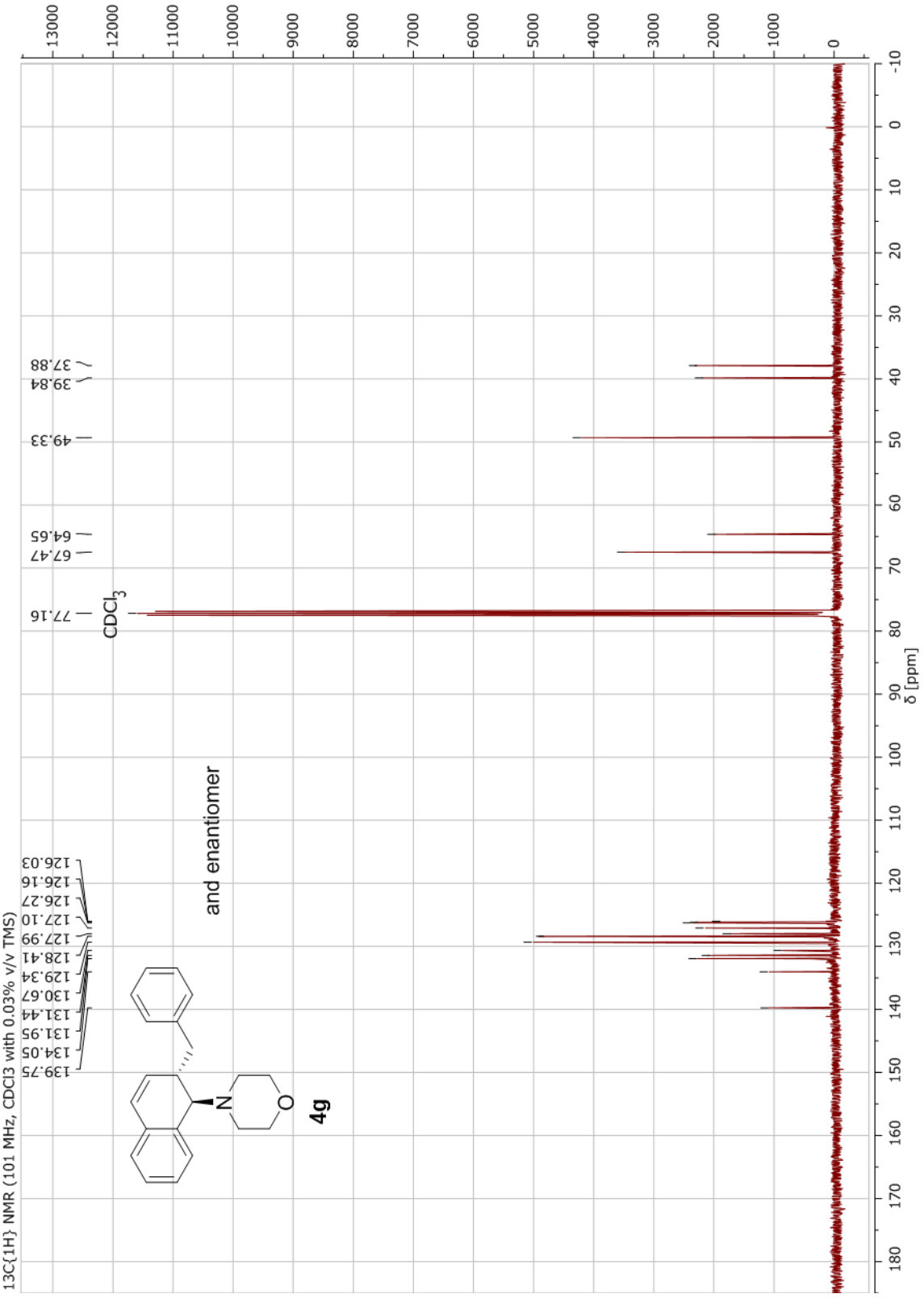
$^{13}C\{^{1}H\}$ NMR spectrum of **4e**



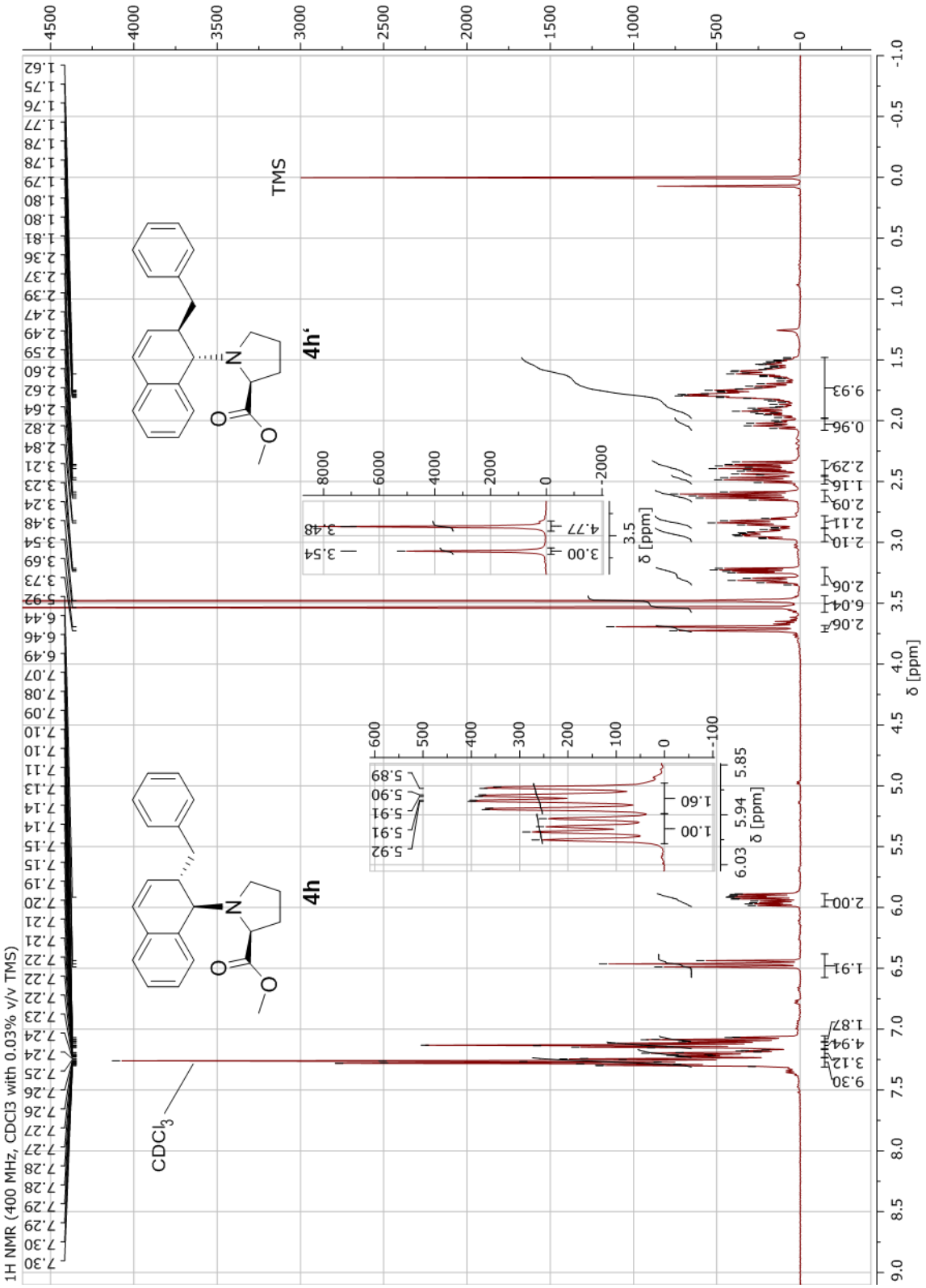
^{1}H NMR spectrum of **4g**



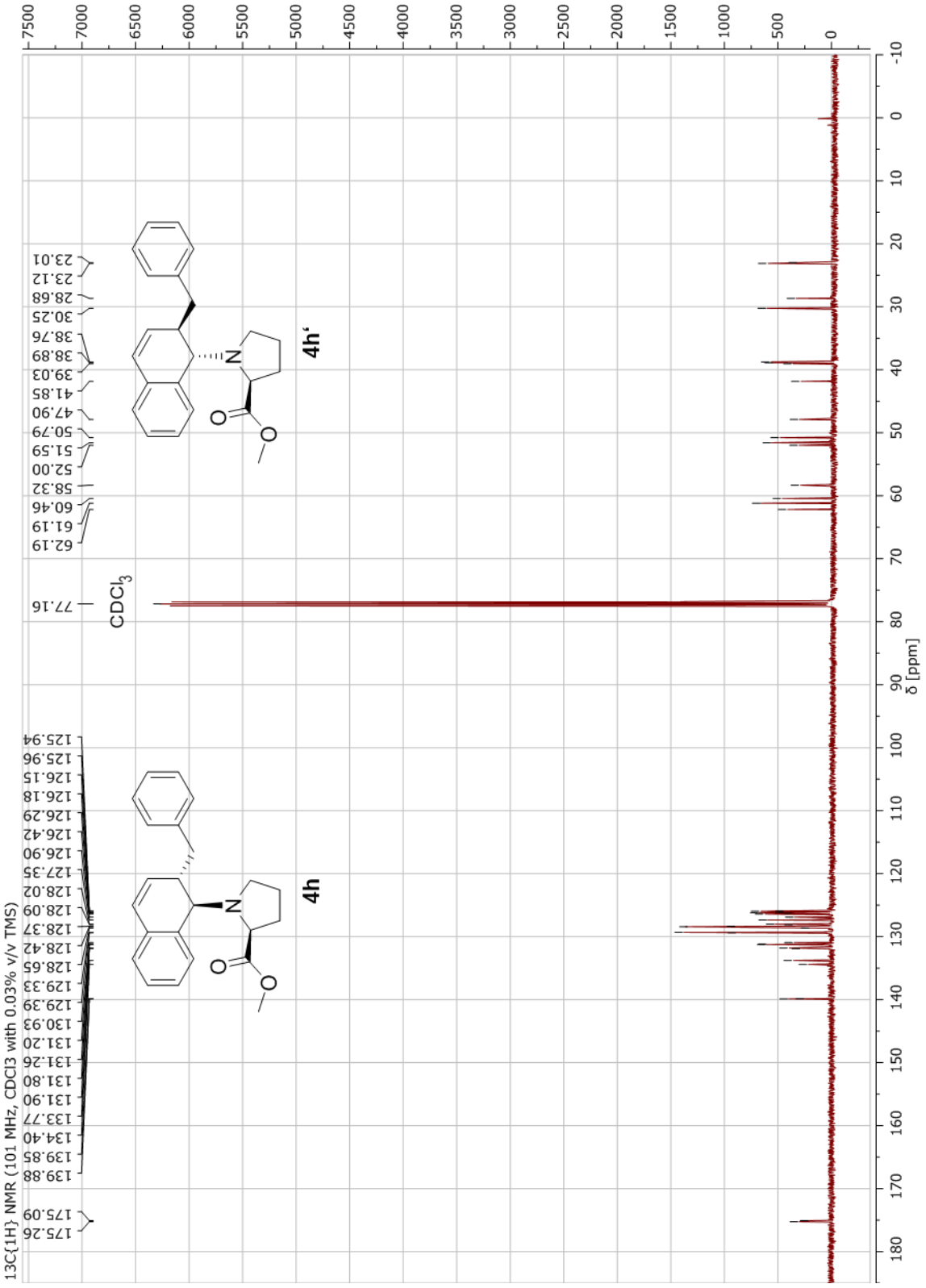
$^{13}C\{^{1}H\}$ NMR spectrum of **4g**



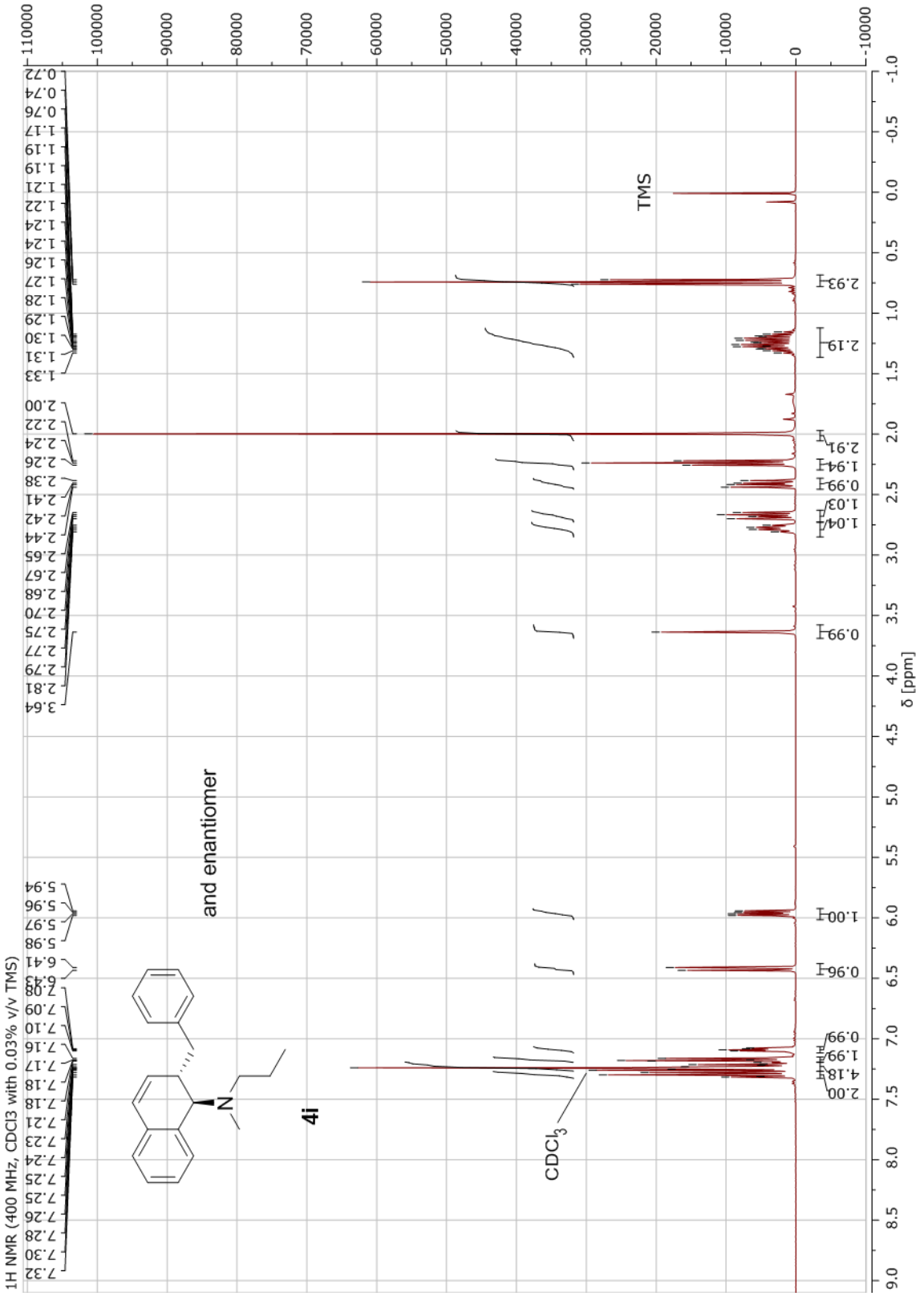
^{1}H NMR spectrum of **4h** and **4h'**



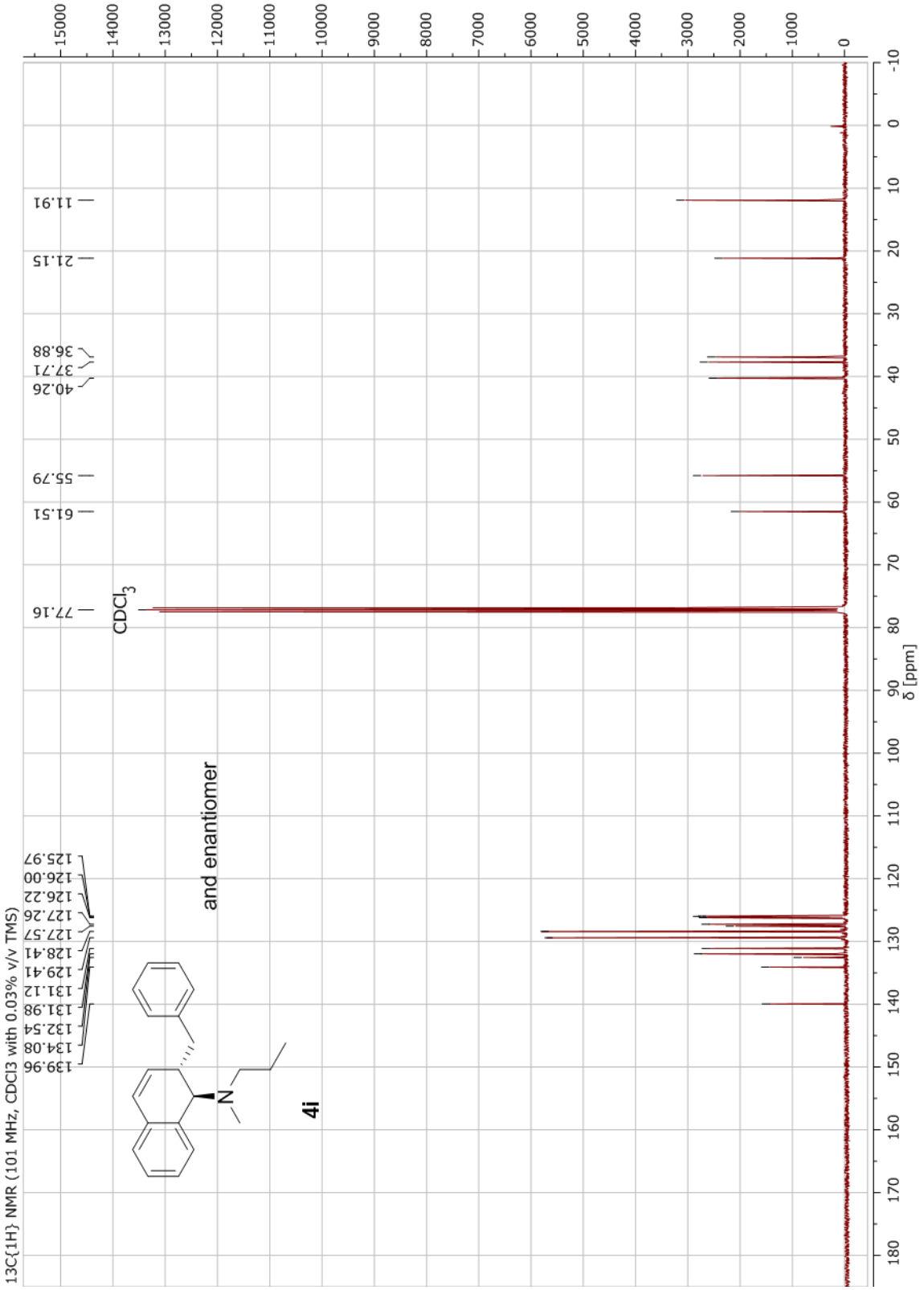
$^{13}C\{^{1}H\}$ NMR spectrum of **4h** and **4h'**



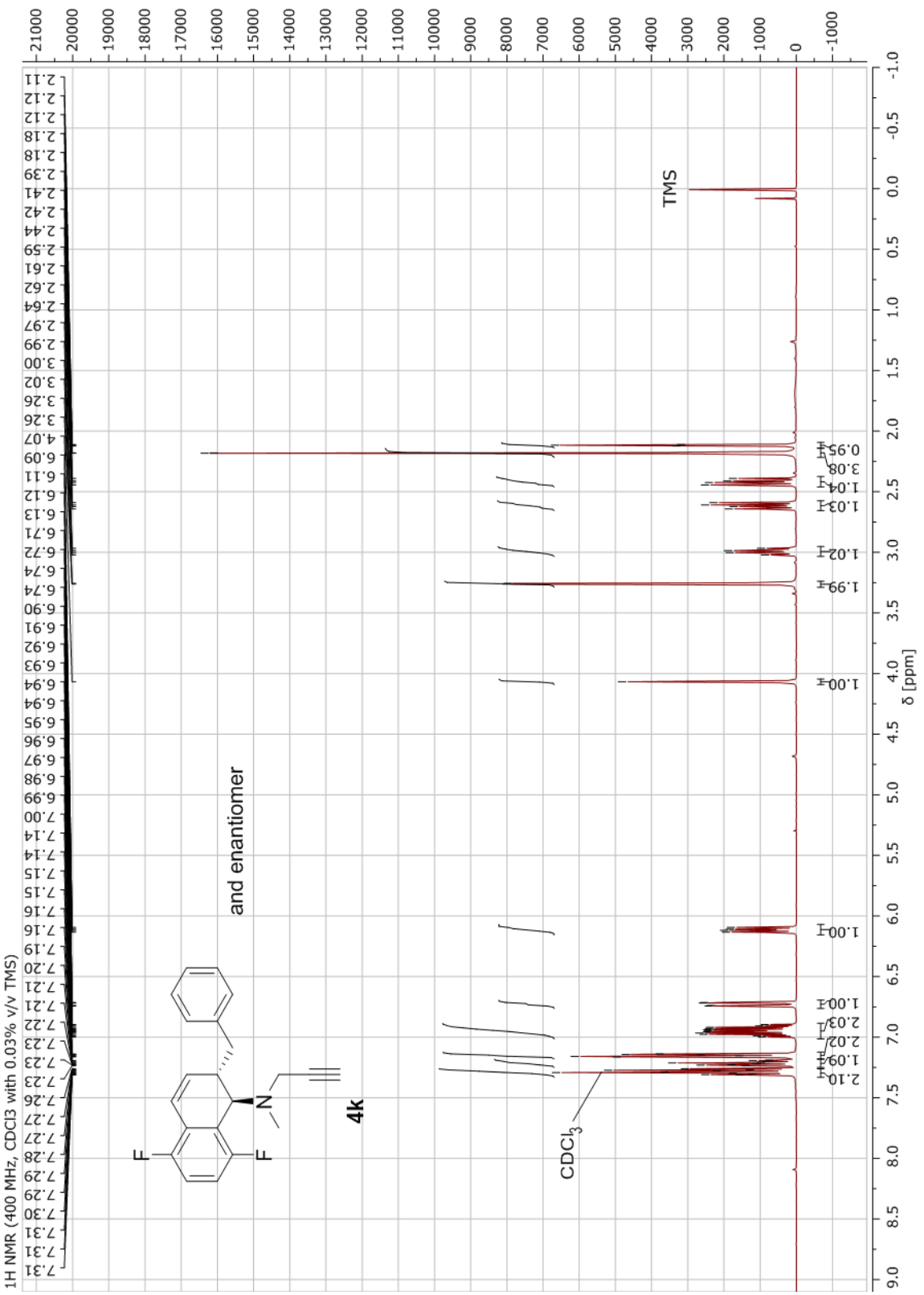
^{1}H NMR spectrum of **4i**



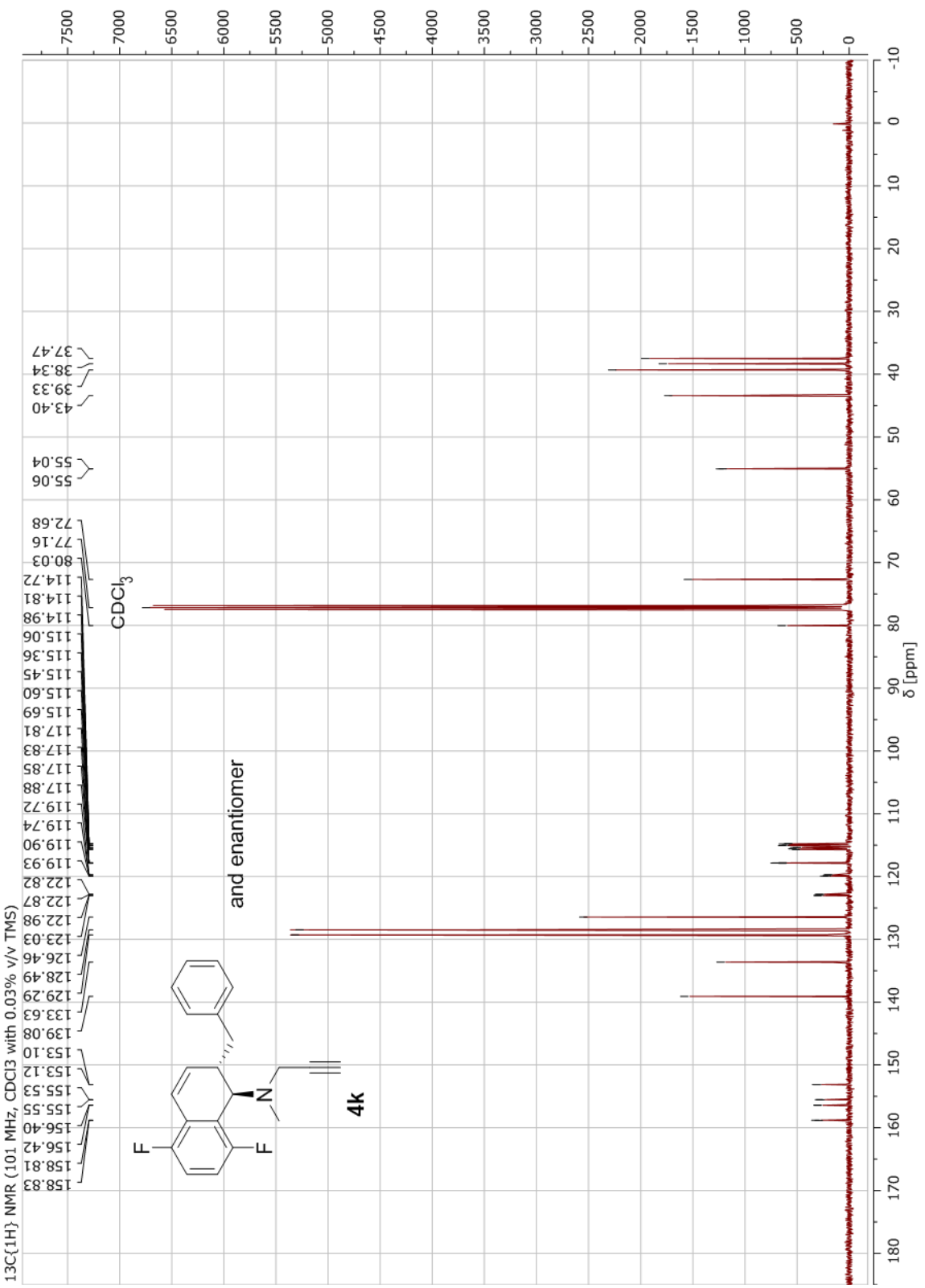
$^{13}C\{^{1}H\}$ NMR spectrum of **4i**



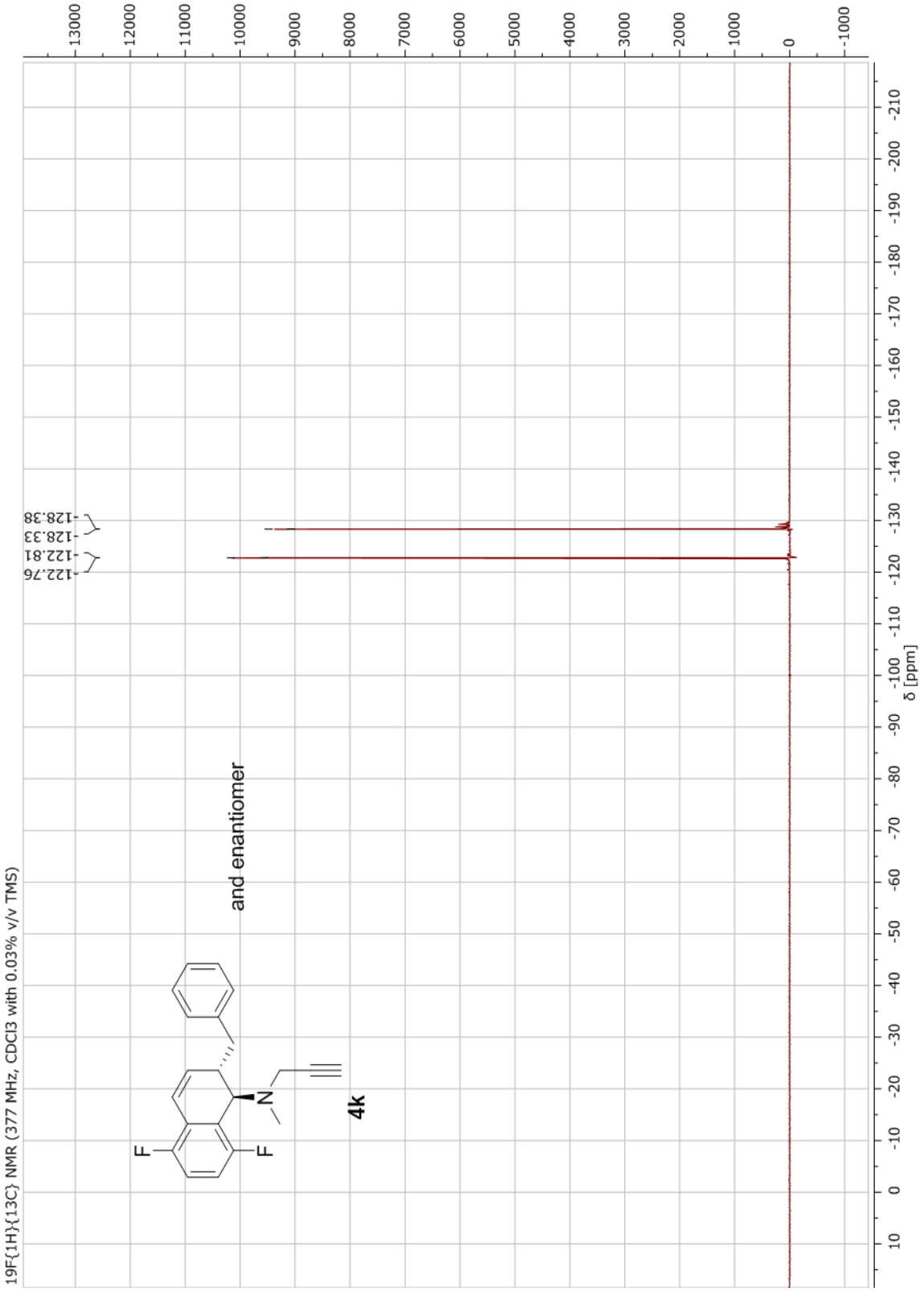
^{1}H NMR spectrum of **4k**



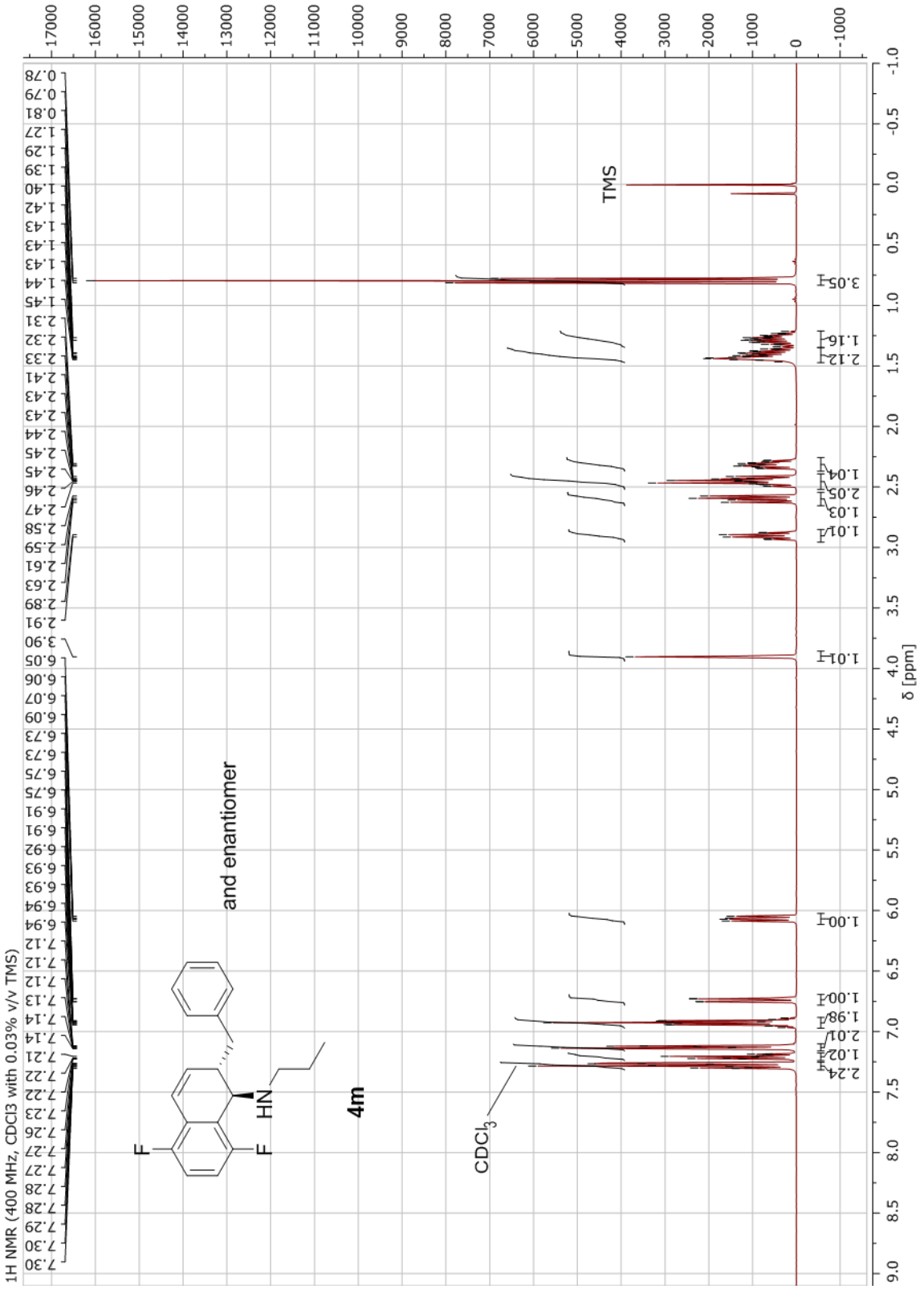
$^{13}C\{^{1}H\}$ NMR spectrum of **4k**



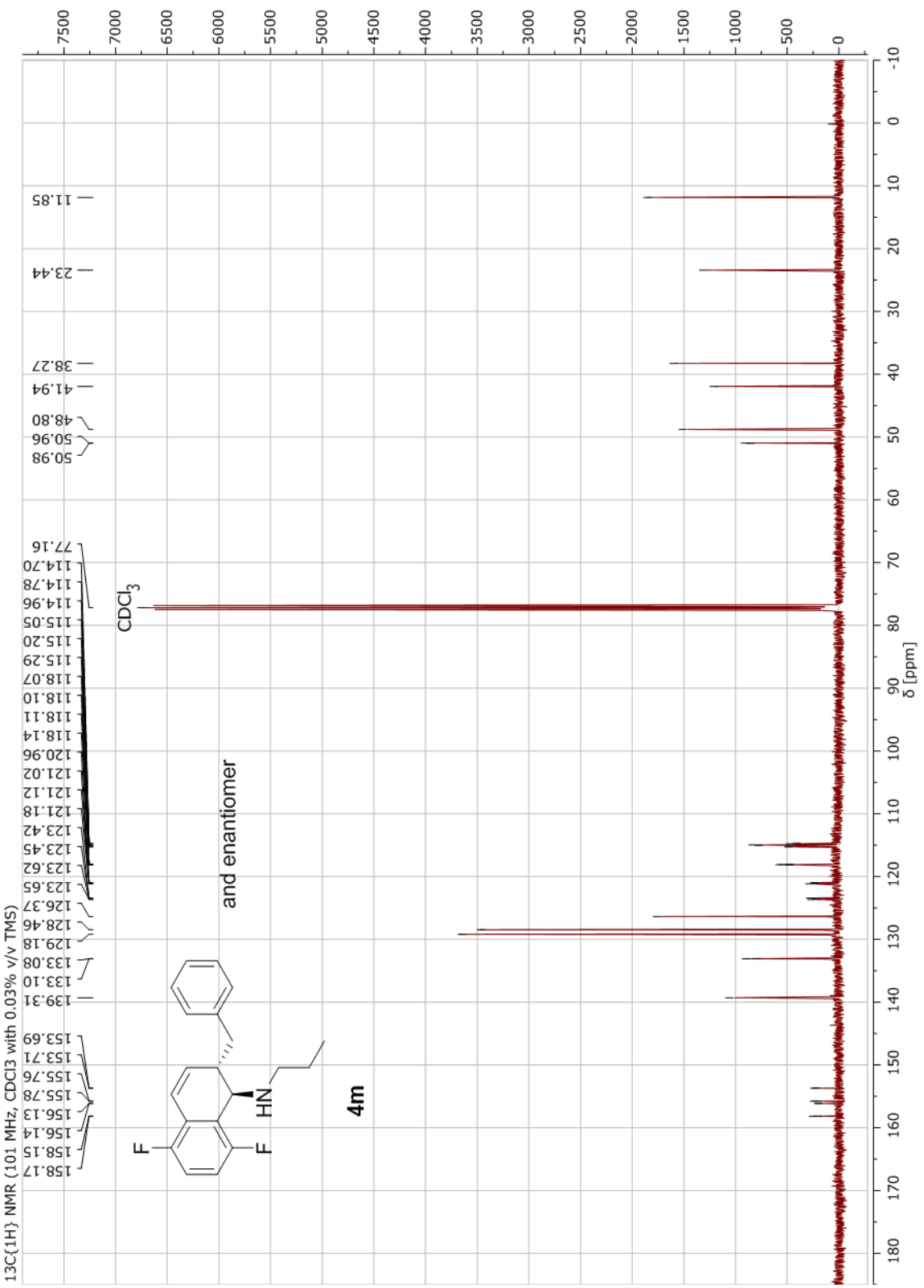
$^{19}F\{^{1}H\}\{^{13}C\}$ NMR spectrum of **4k**



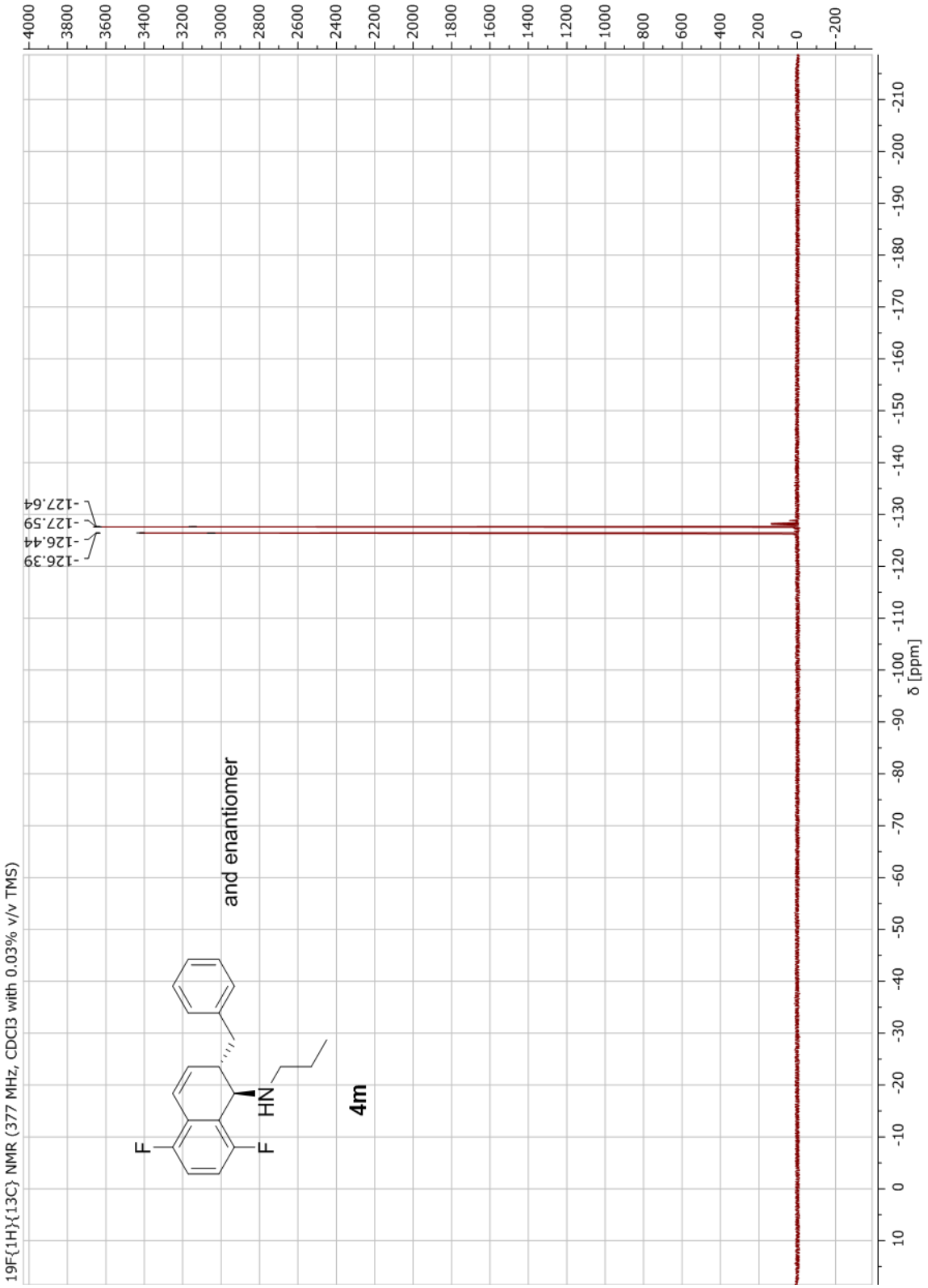
^{1}H NMR spectrum of **4m**



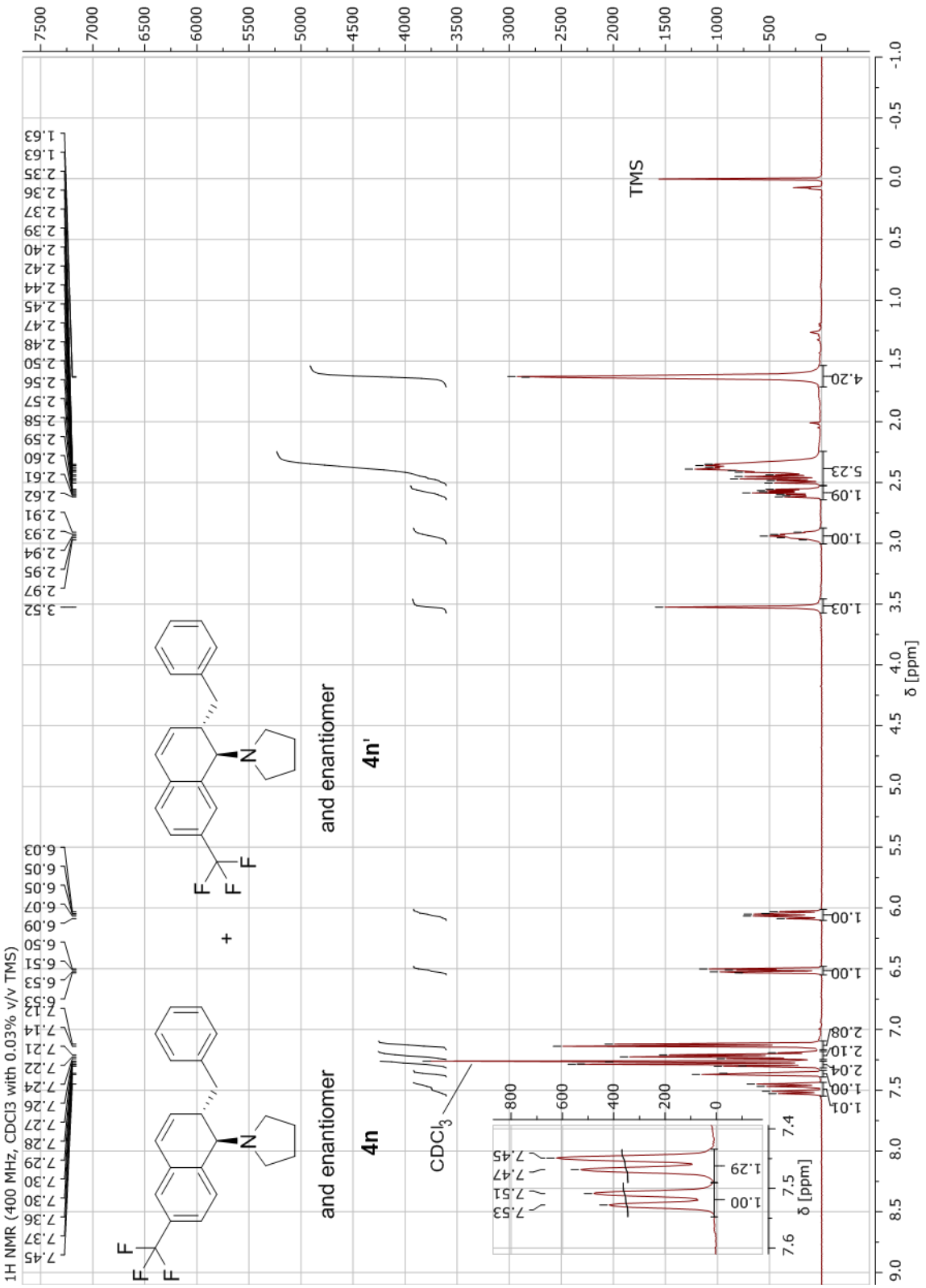
$^{13}C\{^{1}H\}$ NMR spectrum of **4m**



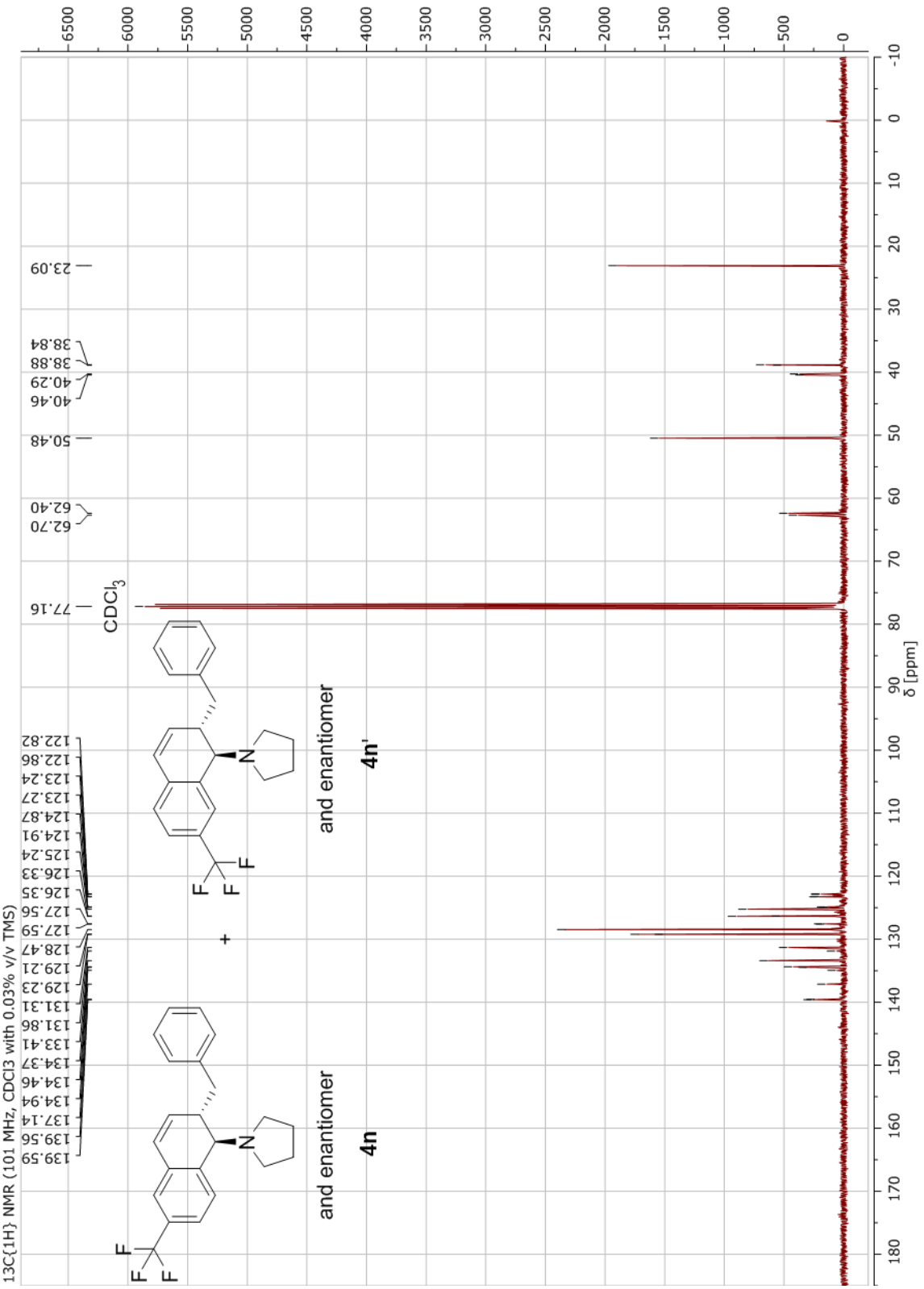
$^{19}F\{^{1}H\}\{^{13}C\}$ NMR spectrum of **4m**



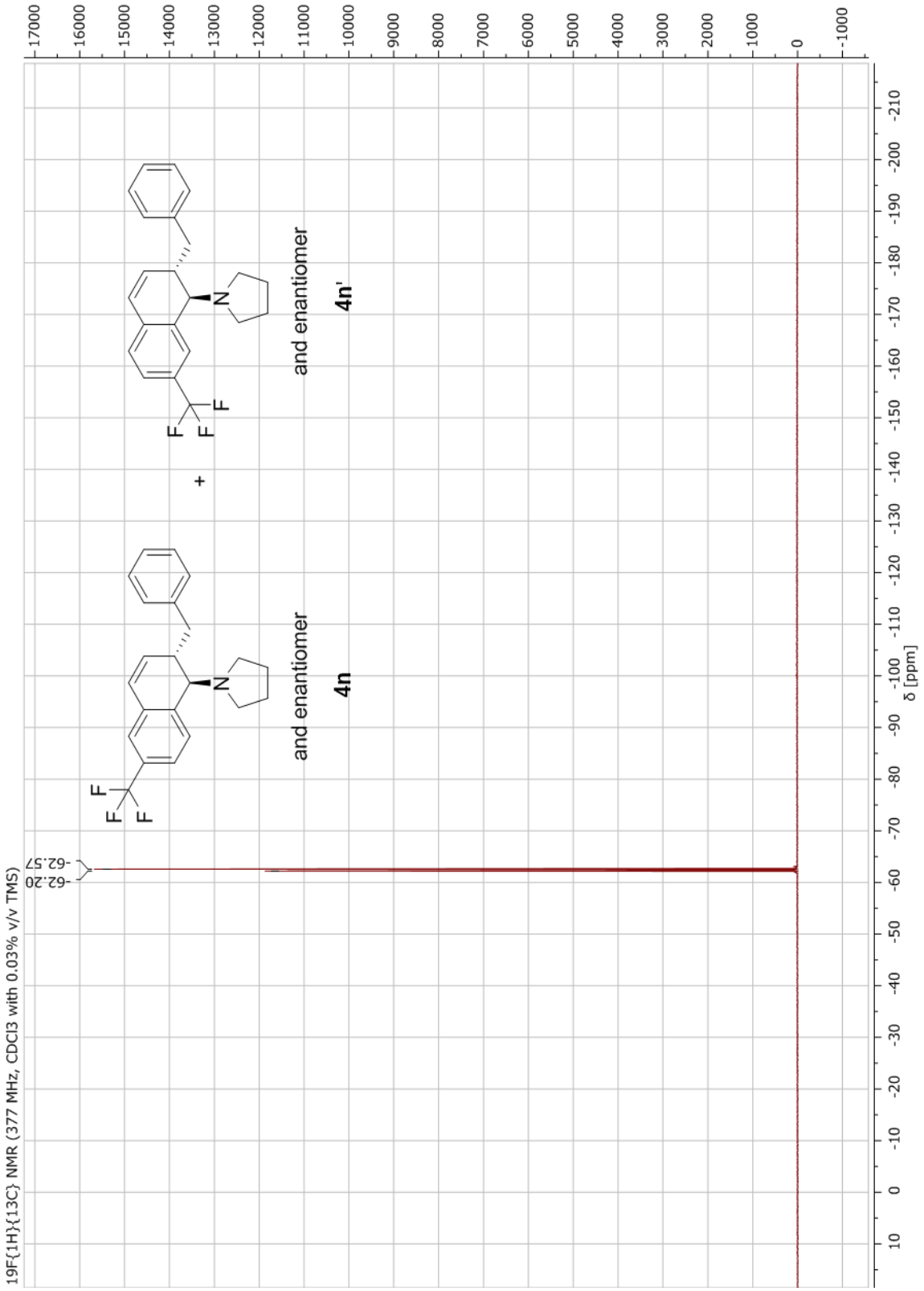
^{1}H NMR spectrum of **4n** and **4n'**



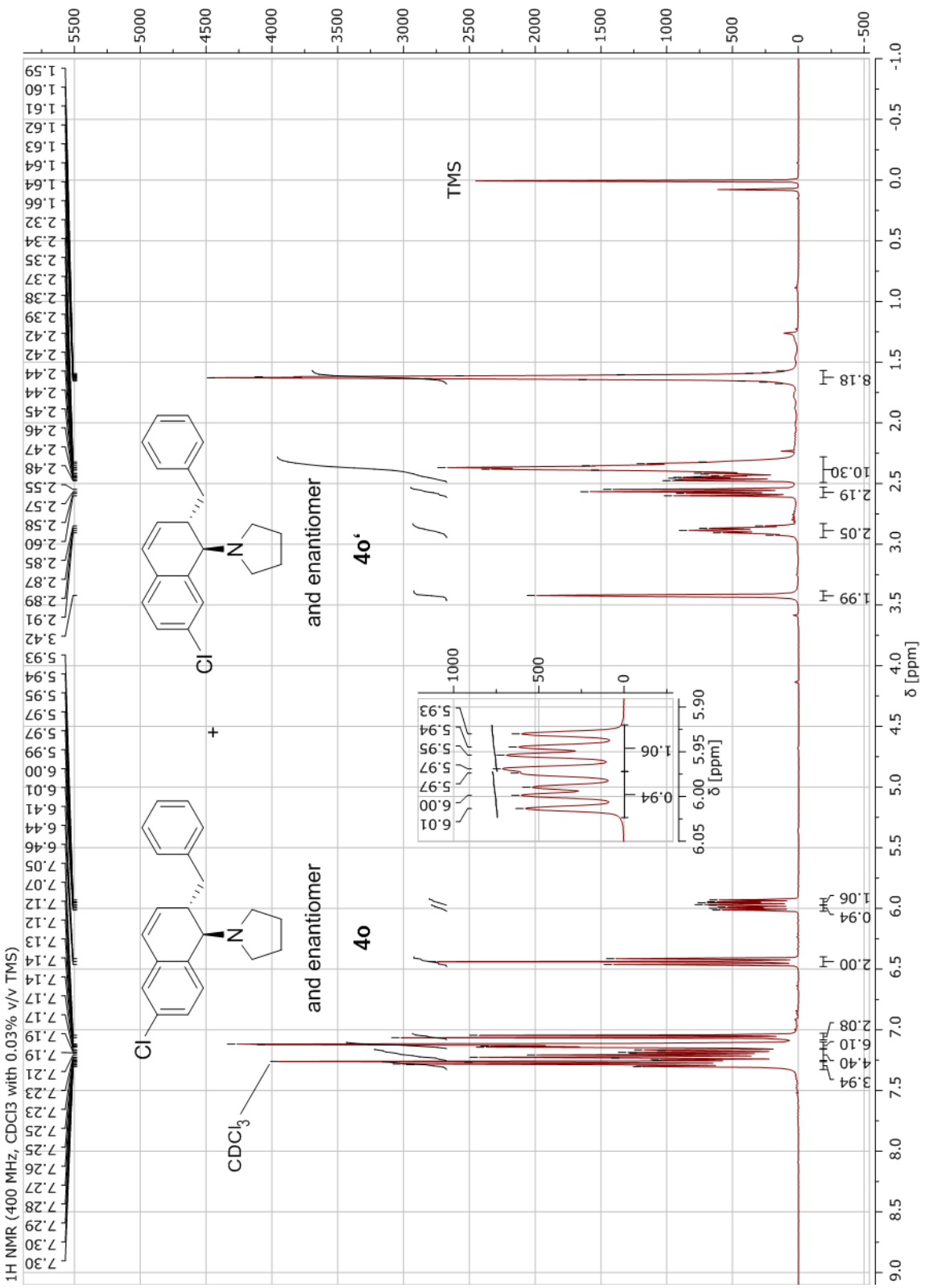
$^{13}C\{^{1}H\}$ NMR spectrum of **4n** and **4n'**



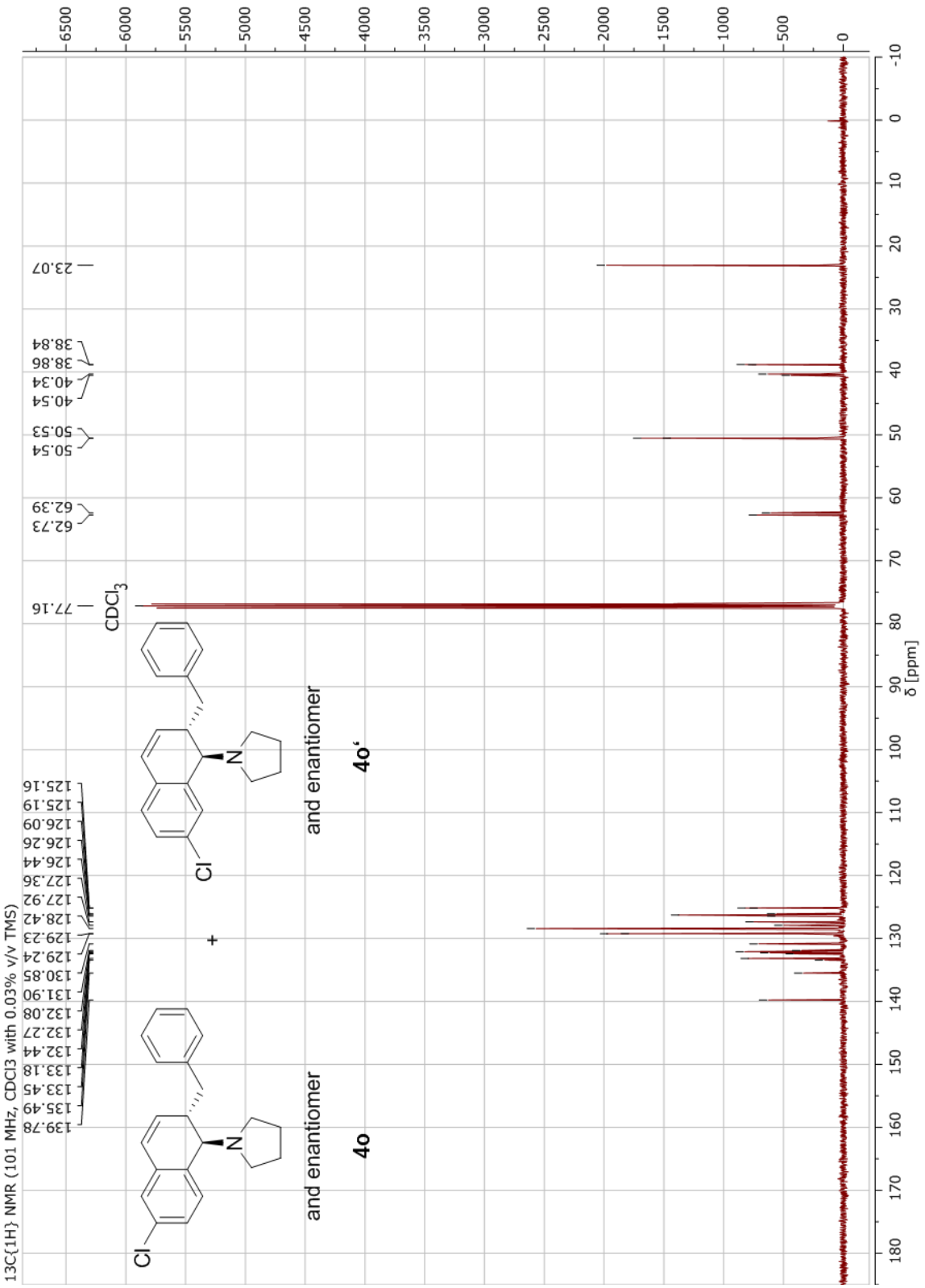
$^{19}F\{^{1}H\}\{^{13}C\}$ NMR spectrum of **4n** and **4n'**



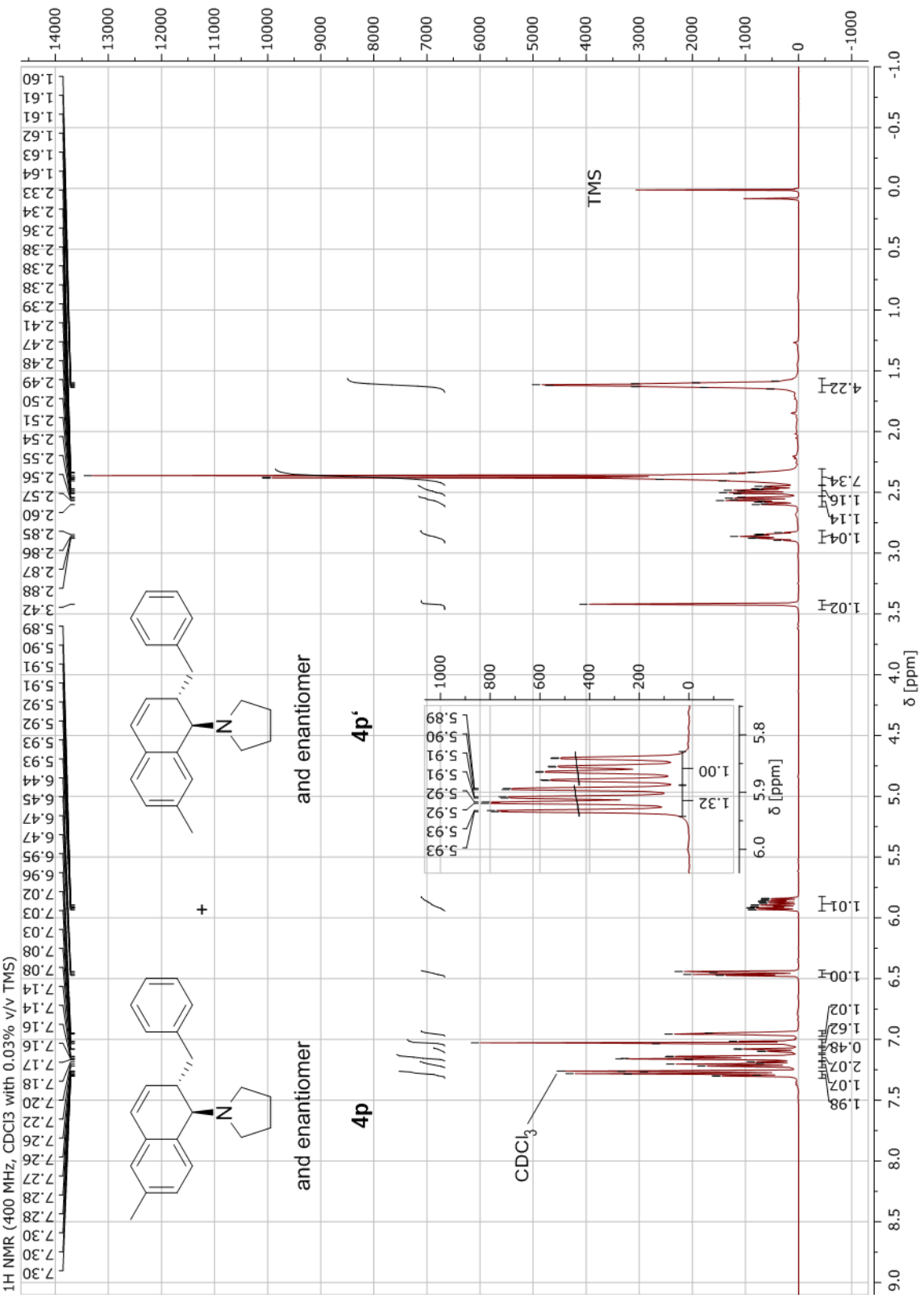
^{1}H NMR spectrum of **4o** and **4o'**



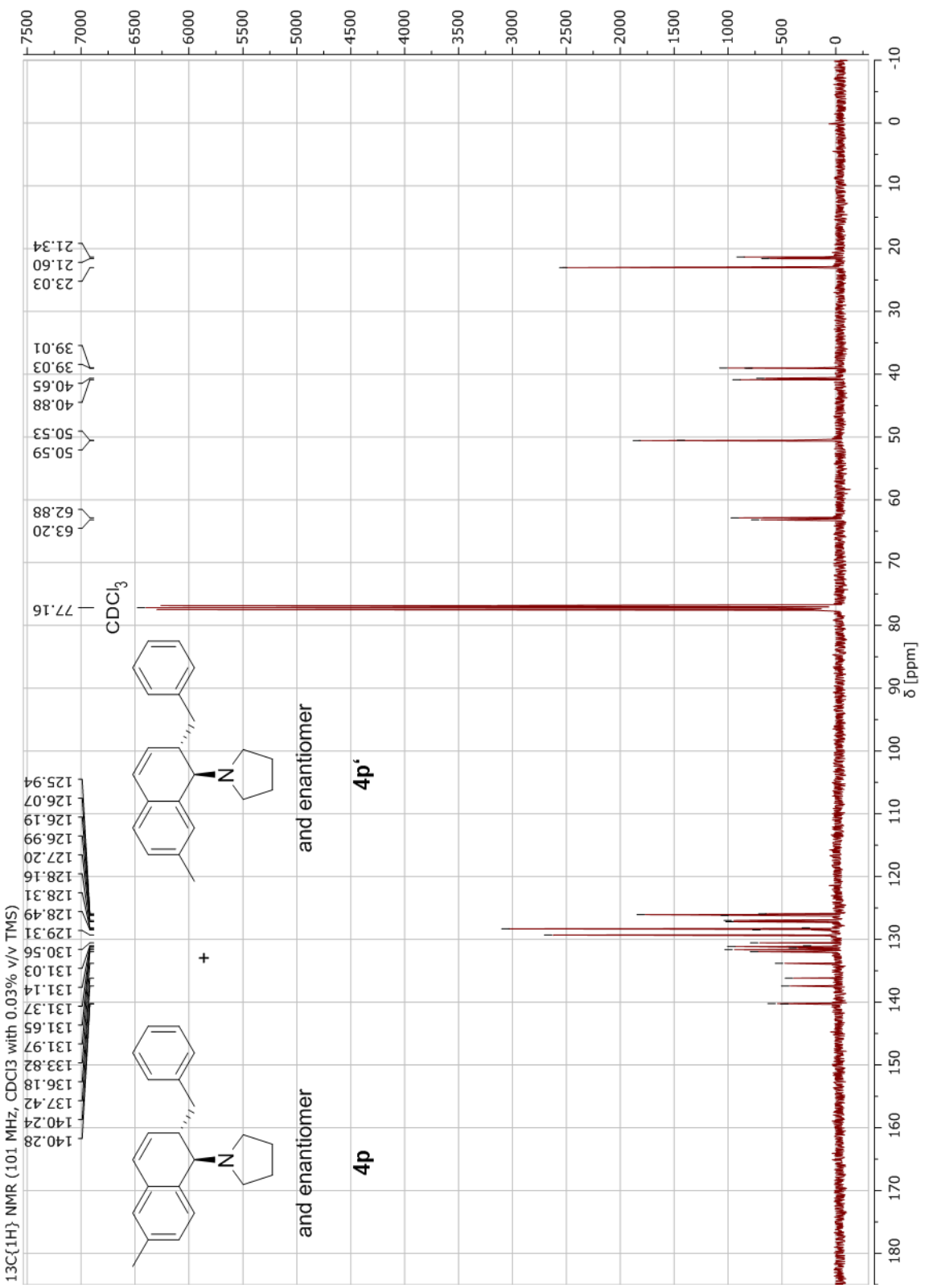
$^{13}C\{^{1}H\}$ NMR spectrum of **4o** and **4o'**



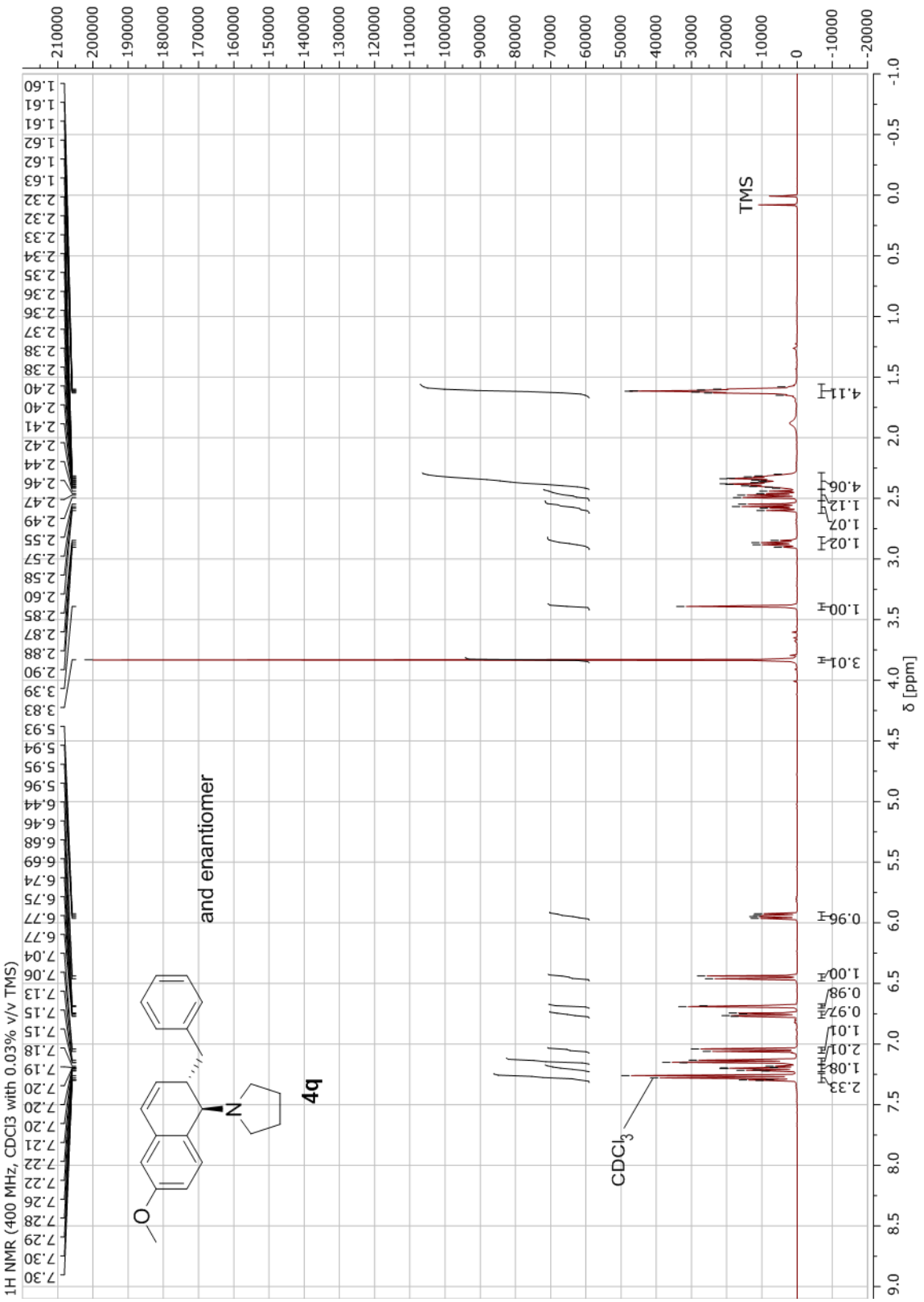
^{1}H NMR spectrum of **4p** and **4p'**



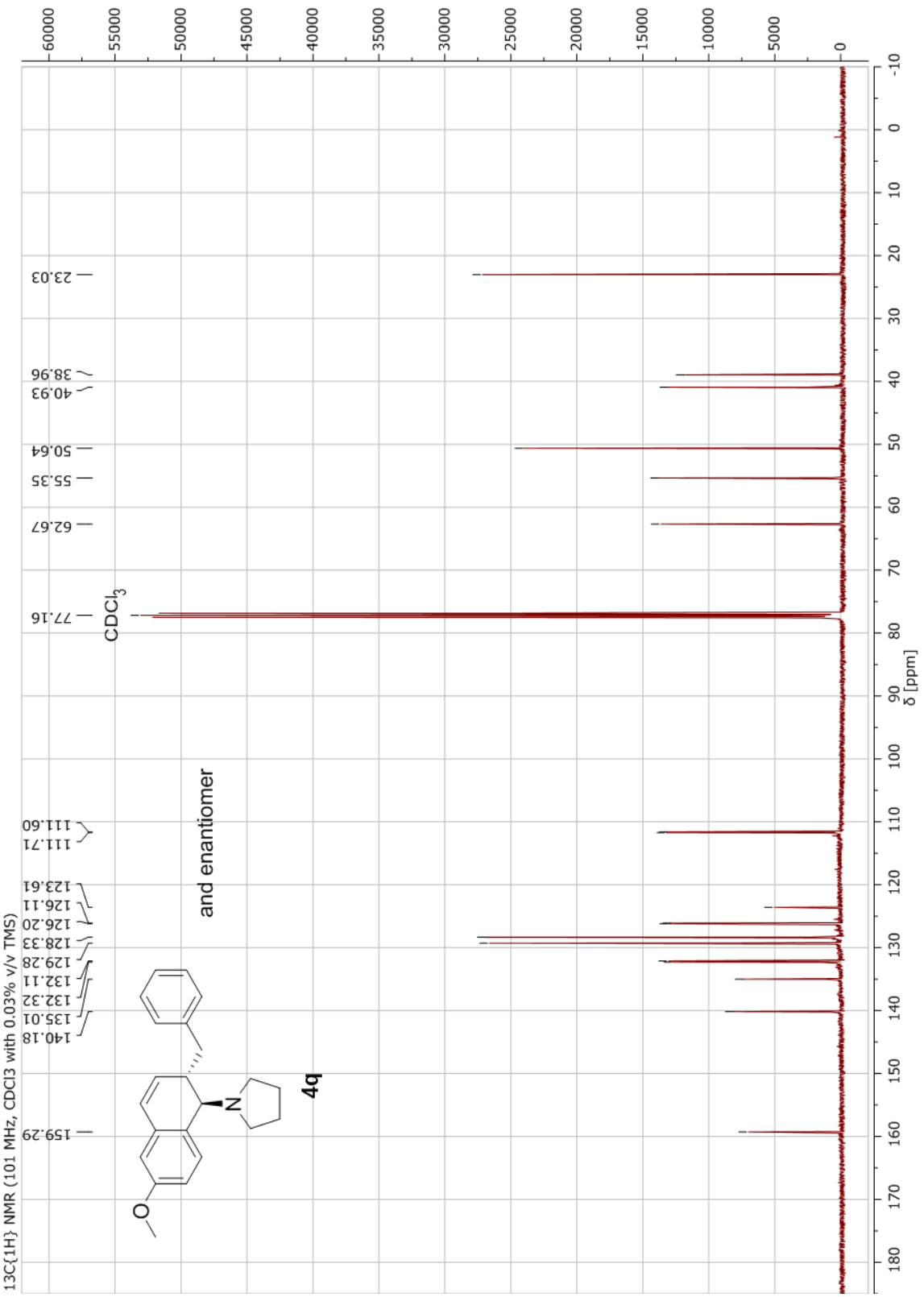
$^{13}C\{^{1}H\}$ NMR spectrum of **4p** and **4p'**



^{1}H NMR spectrum of **4q**



$^{13}C\{^{1}H\}$ NMR spectrum of **4q**



Computational Data:

Geometry optimizations were performed on a B3LYP level using a 6-311++G** basis set.[8–11] In addition, the opt=tight and int=ultrafine keywords and the IEFPCM solvent model (THF) were applied. The absence of imaginary frequencies in ground state and the presence of one imaginary frequency in transition state computations was checked for every optimized geometry. Molecular structures were visualized using CYLview.[12] High accuracy single point energy (SPE) computations on a DLPNO-CCSD(T)/def2-TZVPPD[13,14] level with TightPNO as PNO cutoff threshold were performed using the previously optimized B3LYP structures. All T_1 diagnostic values were below 0.02 (maximum found T_1 = 0.013282050).[17]

DLPNO-CCSD(T) Energies

Table S3: Single point energies (SPE) obtained using DLPNO-CCSD(T)/def2-TZVPPD and the thermal corrections to zero-point vibrational energy (ZPVE), enthalpy and free energy at 298 K calculated at the B3LYP/6-311++G** level of theory.

Compound	SPE (DLPNO-CCSD(T)/def2-TZVPPD) / Hartree	Thermal corrections at 298 K (B3LYP/6-311++G**) / Hartree		
		ZPVE	*H*	*G*
3a	-715.060345764098	0.361418	0.379144	0.316489
TS1a	-927.267997400397	0.492574	0.515399	0.441272
9a	-927.276966734457	0.493999	0.516890	0.442869
TS2a	-927.276263340369	0.490063	0.512821	0.439157
4a	-715.104025481419	0.362263	0.379951	0.317238
7a	-212.212314187221	0.128943	0.134847	0.100850
TS_N[1,9]a	-715.020949293656	0.360165	0.377023	0.317822

Relative Energies of Stepwise Mechanism

Table S4: Relative energies of the stepwise reaction mechanism on a DLPNO-CCSD(T)/def2-TZVPPD//B3LYP/6-311++G** level of theory. All energies are given in kcal/mol.

Reaction step	SPE	SPE+ ZPVE	$\Delta H_{298\ K}$	$\Delta G_{298\ K}$
3a + **7a**	0.00	0.00	0.00	0.00
TS1a	2.93	4.31	3.81	17.94
9a	-2.70	-0.42	-0.88	13.32
TS2a	-2.26	-2.45	-3.00	11.43
4a + **7a**	-27.41	-26.88	-26.90	-26.94

Relative Energies of N[1,9]-Shift Mechanism

Table S5: Relative energies of the N[1,9] shift mechanism on a DLPNO-CCSD(T)/def2-TZVPPD//B3LYP/6-311++G** level of theory. All energies are given in kcal/mol.

Reaction step	SPE	SPE+ ZPVE	$\Delta H_{298\ K}$	$\Delta G_{298\ K}$
3a	0.00	0.00	0.00	0.00
TS_N[1,9]a	24.72	23.94	23.39	25.56
4a	-27.41	-26.88	-26.90	-26.94

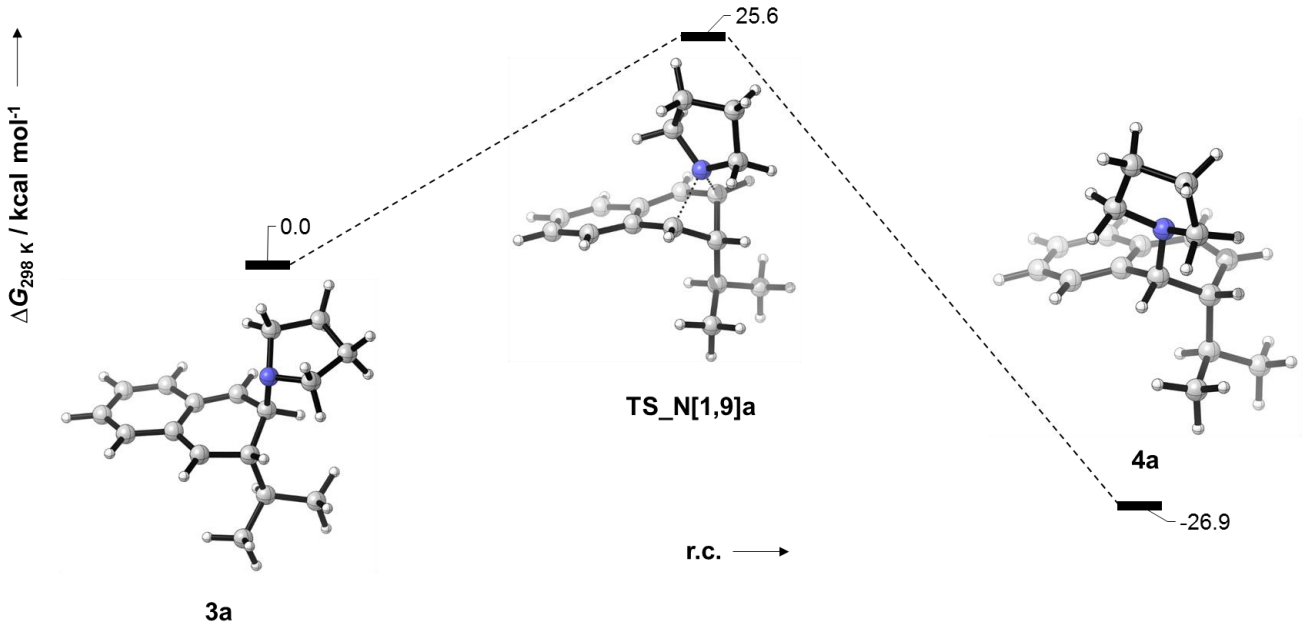


Figure S3: Relative Gibbs energy profile for N[1,9] shift mechanism from intermediate **3a** to product **4a**. Structures were optimized at B3LYP/6-311++G** level of theory and energies were computed at DLPNO-CCSD(T)/def2-TZVPPD using the IEFPCM solvent model for THF.

IRC computations

IRC pathways were computed using the local quadratic approximation algorithm[15,16] on a B3LYP level, using a 6-31+G* basis set and the IEFPCM solvent model for THF. Furthermore, the irc=vtight and int=ultrafine keywords were applied.

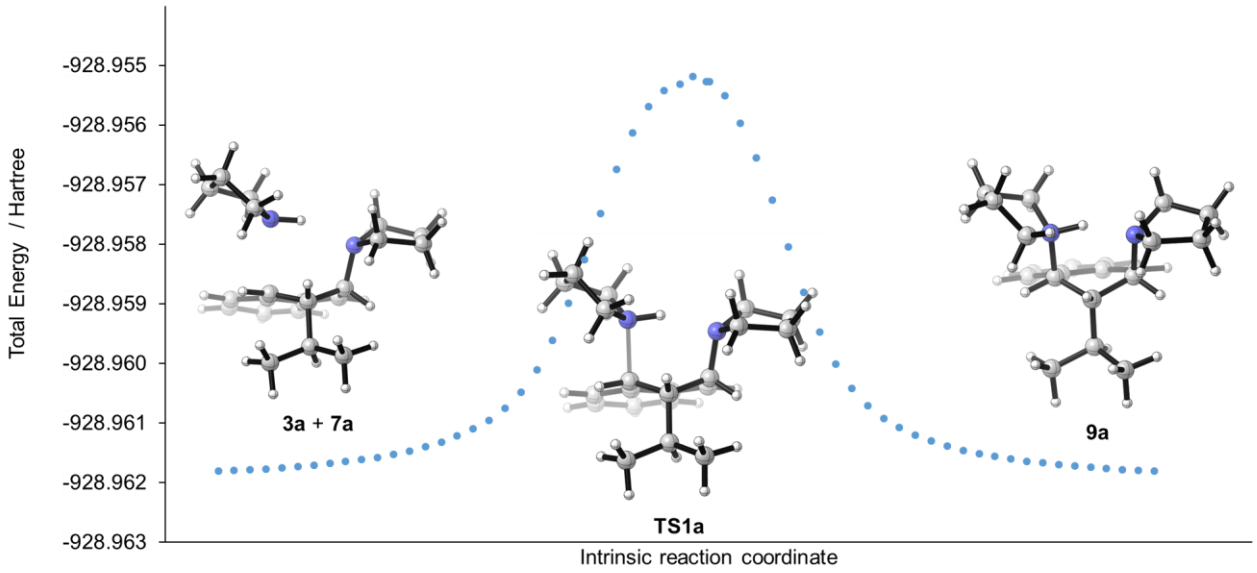


Figure S4: IRC pathway of the attack of pyrrolidine (**7a**) at tetraene **3a** and the formation of zwitterion **9a**.

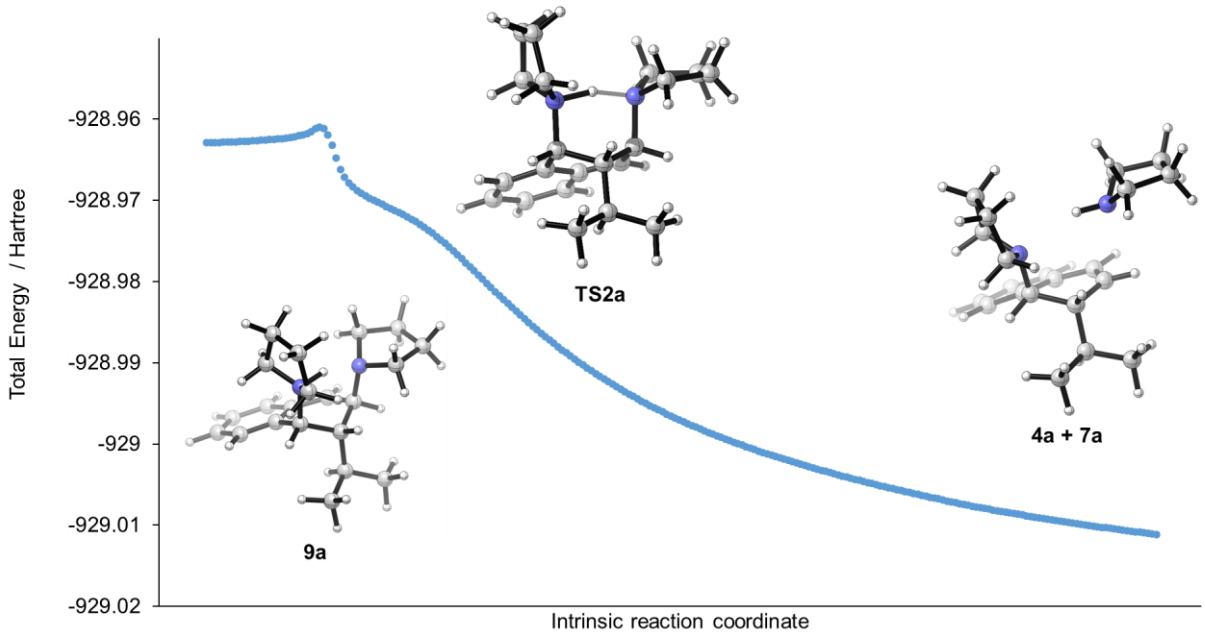


Figure S5: IRC pathway for the rearomatization of zwitterionic intermediate **9a** to product **4a** and pyrrolidine (**7a**).

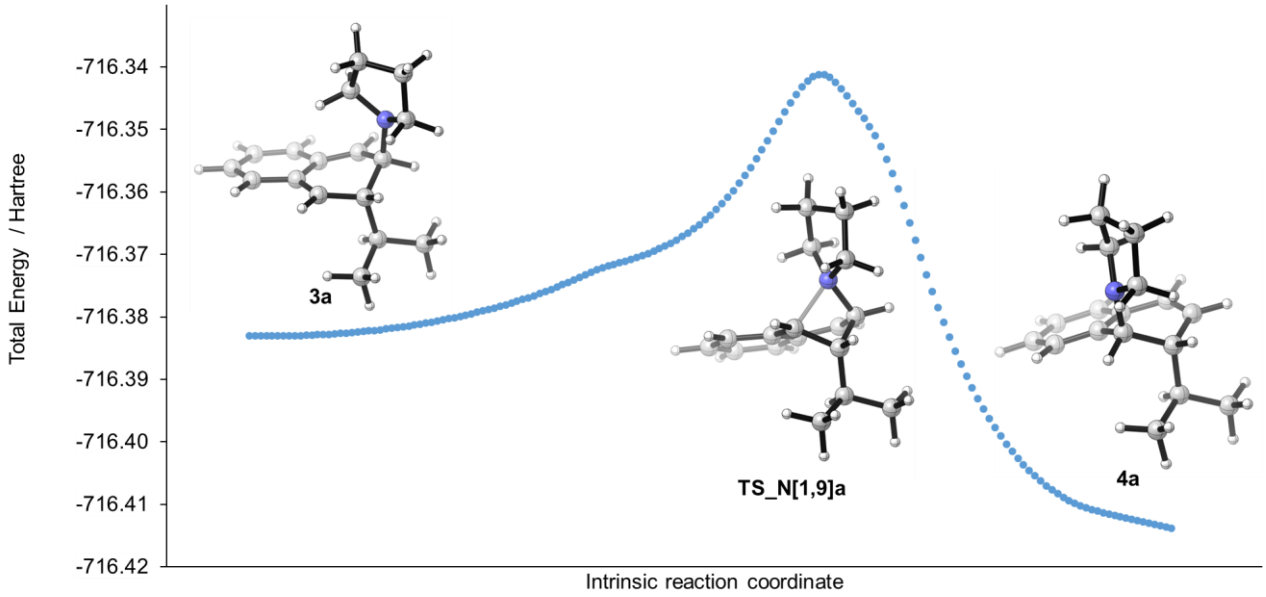


Figure S6: IRC pathway for the N[1,9] rearrangement of tetraene **3a**.

Optimized Geometries

3a:

C	-3.757076	-1.685066	0.680097
C	-2.519529	-1.583374	1.217305
C	-1.490152	-0.771869	0.585701
C	-1.885154	0.047390	-0.584740
C	-3.214744	-0.153895	-1.138623
C	-4.107128	-0.972850	-0.536298
H	0.085526	-1.374239	1.855383
H	-4.505364	-2.314648	1.149075
H	-2.256698	-2.135447	2.114037
C	-0.200468	-0.774672	0.997027
H	-3.482709	0.397708	-2.034162
H	-5.102489	-1.098117	-0.947646
C	0.874193	-0.005994	0.269363
H	1.612044	0.306536	1.019616
C	0.295101	1.270354	-0.400264
H	0.996393	1.576160	-1.184845
C	2.905792	-0.347516	-1.089654
C	1.821915	-2.246387	-0.390115
C	3.884674	-0.994355	-0.066873
H	2.938399	0.742321	-1.079818
H	3.159864	-0.671116	-2.104355
C	3.119857	-2.239116	0.454337
H	1.989016	-2.811370	-1.313912
H	0.966257	-2.693211	0.113654
H	4.830482	-1.258128	-0.545364
H	4.117978	-0.304642	0.747658
H	3.687294	-3.164699	0.333374
H	2.888224	-2.137586	1.518073
C	-1.029925	0.984244	-1.055810
H	-1.327022	1.593833	-1.903303
C	0.184385	2.488052	0.583003
H	-0.402901	2.159488	1.449136
C	-0.547349	3.678626	-0.057709
H	-1.579942	3.438045	-0.317306
H	-0.568160	4.526124	0.633322
H	-0.036174	4.008173	-0.969621
C	1.562581	2.954339	1.078598
H	2.115453	2.175662	1.607601
H	2.180170	3.294772	0.239941
H	1.449034	3.795955	1.768103
N	1.551926	-0.848433	-0.774387

E = -716.540821616 Hartree
ZPVE = 226.79322 kcal/mol
Lowest vibrational frequency = 37.7257 cm^{-1}

Zero-point correction=	0.361418 (Hartree/Particle)
Thermal correction to Energy=	0.378200
Thermal correction to Enthalpy=	0.379144
Thermal correction to Gibbs Free Energy=	0.316489
Sum of electronic and zero-point Energies=	-716.179404
Sum of electronic and thermal Energies=	-716.162622
Sum of electronic and thermal Enthalpies=	-716.161678
Sum of electronic and thermal Free Energies=	-716.224333

***cis*-4a**

C	3.233219	-2.176065	0.624467
C	3.293138	-1.159184	-0.327427
C	2.143369	-0.441752	-0.676100
C	0.898530	-0.787442	-0.099348
C	0.860483	-1.774903	0.881176
C	2.020404	-2.466261	1.245725
H	3.076997	0.872723	-2.175497
H	4.130094	-2.723362	0.892415
H	4.241700	-0.898280	-0.786055
C	2.199624	0.734276	-1.550644
H	-0.074866	-2.003253	1.375303
H	1.970305	-3.233153	2.010859
C	1.230662	1.661496	-1.508940
H	1.314029	2.565485	-2.102476
C	0.031919	1.503334	-0.582703
H	-0.807191	2.055899	-1.015472
C	-0.308673	-0.017059	-0.625069
H	-0.342562	-0.235801	-1.713088
C	-2.739905	0.408478	-0.437052
C	-2.015115	-1.771807	-0.549811
C	-3.970704	-0.419884	-0.037121
H	-2.745402	0.594052	-1.527208
H	-2.704844	1.373358	0.064592
C	-3.483085	-1.890950	-0.116845
H	-1.387787	-2.569026	-0.155512
H	-1.937230	-1.807352	-1.652598
H	-4.283986	-0.170886	0.978996
H	-4.815269	-0.219228	-0.699113
H	-3.559837	-2.378778	0.857178
H	-4.058108	-2.487083	-0.828109
C	0.360869	2.127442	0.812626
H	1.227219	1.582060	1.203756
C	-0.768543	2.005979	1.846057
H	-1.105320	0.975793	1.964766
H	-0.419308	2.371068	2.817009
H	-1.630984	2.618506	1.562248
C	0.763701	3.605381	0.670798
H	1.649322	3.736951	0.045551

H	-0.051499	4.191977	0.231720
H	0.985152	4.033276	1.652841
N	-1.595711	-0.441631	-0.060117

E = -716.575976610 Hartree
ZPVE = 227.74301 kcal/mol
Lowest vibrational frequency = 52.6045 cm^{-1}
Zero-point correction= 0.362932 (Hartree/Particle)
Thermal correction to Energy= 0.379229
Thermal correction to Enthalpy= 0.380173
Thermal correction to Gibbs Free Energy= 0.319840
Sum of electronic and zero-point Energies= -716.213045
Sum of electronic and thermal Energies= -716.196748
Sum of electronic and thermal Enthalpies= -716.195803
Sum of electronic and thermal Free Energies= -716.256137

4a:

C	-2.279061	-3.135975	-0.053842
C	-2.139311	-2.239569	1.004271
C	-1.331219	-1.102221	0.877601
C	-0.625557	-0.884785	-0.324377
C	-0.790334	-1.776398	-1.381657
C	-1.613843	-2.898285	-1.255619
H	-1.614964	-0.358829	2.925534
H	-2.912314	-4.009424	0.055881
H	-2.674949	-2.409255	1.933031
C	-1.245399	-0.095765	1.938811
H	-0.261671	-1.601486	-2.313314
H	-1.728407	-3.582934	-2.088538
C	-0.777763	1.132667	1.683977
H	-0.760006	1.879970	2.470140
C	-0.316969	1.533437	0.298432
H	0.449155	2.307331	0.398081
C	0.317654	0.309579	-0.411991
H	0.469312	0.549909	-1.476657
C	2.285972	-1.199774	-0.420602
C	2.643367	1.034055	0.075155
C	3.705614	-1.167576	0.159158
H	2.323393	-1.106623	-1.523272
H	1.749640	-2.118477	-0.184241
C	3.974434	0.338179	0.418808
H	2.427996	1.862531	0.750327
H	2.676758	1.439384	-0.953754
H	3.744381	-1.731289	1.093776
H	4.429311	-1.614678	-0.525276
H	4.243271	0.510765	1.462746
H	4.788382	0.728065	-0.195757
C	-1.479804	2.190184	-0.516244
H	-2.244352	1.421815	-0.682934
C	-1.015854	2.714639	-1.884517

H	-0.657846	1.922609	-2.544718
H	-1.844193	3.214113	-2.395537
H	-0.208986	3.446912	-1.768244
C	-2.130852	3.338155	0.272624
H	-2.568301	2.996165	1.212658
H	-1.397051	4.118656	0.504725
H	-2.928633	3.799388	-0.316302
N	1.630519	-0.029699	0.183101

E = -716.583909582 Hartree
ZPVE = 227.32322 kcal/mol
Lowest vibrational frequency = 32.9838 cm^{-1}
Zero-point correction= 0.362263 (Hartree/Particle)
Thermal correction to Energy= 0.379006
Thermal correction to Enthalpy= 0.379951
Thermal correction to Gibbs Free Energy= 0.317238
Sum of electronic and zero-point Energies= -716.221647
Sum of electronic and thermal Energies= -716.204903
Sum of electronic and thermal Enthalpies= -716.203959
Sum of electronic and thermal Free Energies= -716.266672

Pyrrolidine (7a):

H	2.075549	-0.735597	-0.360969
H	1.322896	-0.632508	1.243061
C	1.164716	-0.445493	0.167880
H	1.160563	1.383266	-1.015506
C	0.778332	1.029881	-0.055631
H	0.000000	-2.147780	-0.054807
N	0.000000	-1.177444	-0.352471
H	1.195912	1.673455	0.720974
H	-2.075549	-0.735597	-0.360969
C	-1.164716	-0.445493	0.167880
C	-0.778332	1.029881	-0.055631
H	-1.160562	1.383266	-1.015506
H	-1.322896	-0.632507	1.243061
H	-1.195912	1.673455	0.720974

E = -212.649260485 Hartree
ZPVE = 80.91300 kcal/mol
Lowest vibrational frequency = 77.3944 cm^{-1}
Zero-point correction= 0.128943 (Hartree/Particle)
Thermal correction to Energy= 0.133904
Thermal correction to Enthalpy= 0.134848
Thermal correction to Gibbs Free Energy= 0.100851
Sum of electronic and zero-point Energies= -212.520317
Sum of electronic and thermal Energies= -212.515357
Sum of electronic and thermal Enthalpies= -212.514413
Sum of electronic and thermal Free Energies= -212.548410

TS1a:

C	-3.020652	-2.548804	-1.767630
C	-1.655723	-2.549458	-1.791159
C	-0.871274	-1.675405	-0.937694
C	-1.637449	-0.805248	-0.045934

C	-3.058967	-0.841794	-0.065111
C	-3.757832	-1.687510	-0.891920
H	1.032748	-2.341347	-1.609317
H	-3.564164	-3.220945	-2.425834
H	-1.125031	-3.217769	-2.463608
C	0.501947	-1.663878	-0.948156
H	-3.595374	-0.186123	0.617234
H	-4.840983	-1.714743	-0.881515
C	1.309747	-0.789443	-0.035648
H	2.174136	-1.367379	0.310216
C	0.487537	-0.371927	1.221683
H	0.984148	0.481258	1.697223
C	3.099649	0.941607	-0.041539
C	2.287201	0.308022	-2.103252
C	4.280841	0.181018	-0.706125
H	3.049321	0.793102	1.037992
H	3.200220	2.017419	-0.220200
C	3.708895	-0.299513	-2.065456
H	2.322507	1.304475	-2.558158
H	1.563574	-0.289749	-2.654771
H	5.147101	0.835296	-0.826867
H	4.599449	-0.664521	-0.092281
H	4.311442	0.028125	-2.915642
H	3.660025	-1.390829	-2.102921
C	-0.929268	0.041741	0.837223
H	-1.511833	0.490831	1.634794
C	-1.555722	2.177743	-1.029095
C	-0.453664	2.880977	1.006750
C	-2.383662	3.286172	-0.372205
H	-2.139923	1.299166	-1.313814
H	-1.041634	2.546928	-1.922775
C	-1.343219	4.021675	0.485434
H	0.588039	3.176599	1.141451
H	-0.821332	2.510668	1.970867
H	-2.870867	3.929641	-1.106480
H	-3.162504	2.851105	0.261939
H	-0.756809	4.702440	-0.138792
H	-1.782795	4.604755	1.296937
C	0.448939	-1.506260	2.299837
H	0.102608	-2.418147	1.801319
C	-0.518793	-1.198814	3.455400
H	-1.559098	-1.153935	3.129112
H	-0.450068	-1.979535	4.218251
H	-0.269524	-0.246101	3.937216
C	1.844614	-1.775897	2.888612
H	2.576375	-2.078543	2.137689

H	2.231211	-0.884475	3.395693
H	1.789873	-2.578691	3.629568
N	-0.559020	1.795133	-0.004952
N	1.859286	0.472627	-0.700135
H	0.358419	1.536676	-0.413021

E = -929.173124021 Hartree
ZPVE = 309.09472 kcal/mol
Lowest vibrational frequency = −242.4969 cm^{-1}
Zero-point correction= 0.492574 (Hartree/Particle)
Thermal correction to Energy= 0.514455
Thermal correction to Enthalpy= 0.515399
Thermal correction to Gibbs Free Energy= 0.441272
Sum of electronic and zero-point Energies= -928.680550
Sum of electronic and thermal Energies= -928.658669
Sum of electronic and thermal Enthalpies= -928.657725
Sum of electronic and thermal Free Energies= -928.731852
Imaginary frequency= -242.50 cm^{-1}

TS_N[1,9]a:

C	-2.852001	-2.520037	0.404274
C	-2.204167	-1.707788	1.301456
C	-1.178381	-0.793680	0.871433
C	-0.937764	-0.728308	-0.566051
C	-1.588523	-1.619750	-1.445332
C	-2.545732	-2.503537	-0.986891
H	-0.398211	-0.097736	2.770915
H	-3.616669	-3.202027	0.765365
H	-2.449460	-1.760034	2.358207
C	-0.350786	-0.046470	1.690814
H	-1.350667	-1.573019	-2.505224
H	-3.067251	-3.163979	-1.669292
C	0.683576	0.798012	1.021225
H	1.315356	1.356254	1.714874
C	0.095418	1.553777	-0.185662
H	0.863652	2.192954	-0.630325
C	0.022672	0.240683	-0.993613
H	0.285986	0.248371	-2.049858
C	1.876506	-1.456506	0.461700
C	2.791648	0.576306	-0.479517
C	3.210599	-1.772561	-0.216127
H	1.063866	-2.121306	0.158804
H	1.941271	-1.496708	1.555763
C	3.927079	-0.416973	-0.200291
H	2.949039	1.543842	0.000881
H	2.674697	0.748307	-1.554357
H	3.758649	-2.558158	0.306612
H	3.045446	-2.106657	-1.245311
H	4.357589	-0.229773	0.787732
H	4.727995	-0.336177	-0.937207

C	-1.182417	2.385741	-0.039837
H	-1.966382	1.739210	0.364462
C	-1.646079	2.910881	-1.407218
H	-1.836957	2.094571	-2.109394
H	-2.572188	3.484501	-1.307640
H	-0.893040	3.571168	-1.852384
C	-0.961052	3.543123	0.944711
H	-0.682844	3.176770	1.936634
H	-0.166007	4.211419	0.594695
H	-1.871586	4.139861	1.053255
N	1.560591	-0.074161	0.063193

E = -716.503796771 Hartree
ZPVE = 226.00672 kcal/mol
Lowest vibrational frequency = −397.2421 cm^{-1}
Zero-point correction= 0.360165 (Hartree/Particle)
Thermal correction to Energy= 0.376079
Thermal correction to Enthalpy= 0.377023
Thermal correction to Gibbs Free Energy= 0.317822
Sum of electronic and zero-point Energies= -716.143632
Sum of electronic and thermal Energies= -716.127718
Sum of electronic and thermal Enthalpies= -716.126773
Sum of electronic and thermal Free Energies= -716.185975
Imaginary frequency= -397.24 cm^{-1}

TS2a:

C	-3.818014	-0.119781	-2.095976
C	-2.594690	-0.739379	-2.259249
C	-1.550874	-0.648628	-1.273039
C	-1.861064	0.164595	-0.121696
C	-3.114926	0.752145	0.027677
C	-4.113790	0.634677	-0.942380
H	-0.135928	-1.935134	-2.257543
H	-4.571603	-0.227797	-2.872108
H	-2.408420	-1.330273	-3.152486
C	-0.326537	-1.316829	-1.386557
H	-3.315827	1.324703	0.931233
H	-5.081744	1.103290	-0.810110
C	0.690482	-1.262486	-0.317620
H	1.264230	-2.190983	-0.268215
C	0.056335	-0.960478	1.070929
H	0.858326	-0.760488	1.791742
C	3.067347	-0.440533	0.173381
C	2.195655	0.089220	-1.926819
C	3.950546	-1.208828	-0.843988
H	2.875337	-1.009216	1.083941
H	3.545048	0.500237	0.463534
C	3.275245	-0.966484	-2.217659
H	2.610907	1.099662	-2.005817
H	1.318027	0.017725	-2.568603

H	4.975383	-0.833180	-0.819725
H	3.991372	-2.273462	-0.605888
H	3.979127	-0.626998	-2.979876
H	2.810821	-1.884274	-2.586700
C	-0.804145	0.325268	0.935647
H	-1.276418	0.580809	1.886702
C	-0.353097	2.644662	-0.115075
C	0.769301	2.083117	1.876329
C	0.751843	3.697379	0.027713
H	-1.288790	2.979543	0.341879
H	-0.562932	2.353180	-1.142378
C	1.408363	3.403197	1.404693
H	1.479907	1.392548	2.329732
H	-0.035094	2.265502	2.596175
H	1.483736	3.586954	-0.775434
H	0.345875	4.707449	-0.037713
H	2.490803	3.304898	1.308260
H	1.218015	4.196582	2.128735
C	-0.755844	-2.151455	1.647233
H	-1.592826	-2.342505	0.968950
C	-1.329294	-1.832269	3.039365
H	-2.046228	-1.009065	3.022296
H	-1.852154	-2.705355	3.439960
H	-0.531498	-1.573388	3.745408
C	0.085151	-3.436036	1.735140
H	0.397113	-3.798458	0.754161
H	0.983521	-3.280795	2.343948
H	-0.496921	-4.233651	2.205647
N	0.174436	1.480573	0.647624
N	1.789333	-0.130476	-0.520885
H	1.054471	0.884807	0.024822

E = -929.179244439 Hartree
ZPVE = 307.51930 kcal/mol
Lowest vibrational frequency = −965.9474 cm^{-1}
Zero-point correction= 0.490063 (Hartree/Particle)
Thermal correction to Energy= 0.511877
Thermal correction to Enthalpy= 0.512822
Thermal correction to Gibbs Free Energy= 0.439157
Sum of electronic and zero-point Energies= -928.689181
Sum of electronic and thermal Energies= -928.667367
Sum of electronic and thermal Enthalpies= -928.666423
Sum of electronic and thermal Free Energies= -928.740087
Imaginary frequency= -965.95 cm^{-1}

9a:

C	-3.616086	-1.263699	-2.048004
C	-2.283100	-1.604087	-2.130616
C	-1.307050	-1.132119	-1.178213
C	-1.824720	-0.242549	-0.161703

C	-3.185139	0.056984	-0.089390
C	-4.106666	-0.431461	-1.016430
H	0.369038	-2.212062	-1.961716
H	-4.306852	-1.655836	-2.790455
H	-1.946165	-2.263307	-2.926599
C	0.030976	-1.517471	-1.199408
H	-3.533609	0.695844	0.720408
H	-5.159377	-0.185461	-0.945343
C	0.999493	-1.085664	-0.156638
H	1.702885	-1.895967	0.057924
C	0.272259	-0.700369	1.168552
H	0.988863	-0.203129	1.834090
C	3.171476	0.153054	0.169003
C	2.304369	0.139454	-1.975831
C	4.161545	-0.719954	-0.648748
H	3.042142	-0.198042	1.193821
H	3.533357	1.185293	0.216706
C	3.535693	-0.787913	-2.065620
H	2.585101	1.164935	-2.241233
H	1.472358	-0.167054	-2.608472
H	5.158029	-0.272929	-0.655723
H	4.258656	-1.716760	-0.213080
H	4.227460	-0.467014	-2.847506
H	3.225065	-1.808274	-2.303862
C	-0.863354	0.304670	0.843466
H	-1.396463	0.609641	1.744245
C	-0.949651	2.514395	-0.542305
C	0.363852	2.485411	1.499286
C	-0.280478	3.874642	-0.378599
H	-1.984415	2.535818	-0.199433
H	-0.928598	2.106713	-1.551004
C	-0.007283	3.932531	1.132071
H	1.441970	2.338762	1.559698
H	-0.081558	2.157212	2.437851
H	0.654916	3.912252	-0.945003
H	-0.919234	4.686010	-0.729684
H	0.785704	4.631755	1.399023
H	-0.912513	4.235374	1.664088
C	-0.266146	-1.931397	1.950821
H	-0.986572	-2.443854	1.306157
C	-0.988757	-1.523554	3.247319
H	-1.893423	-0.941161	3.062368
H	-1.290760	-2.414675	3.804675
H	-0.331352	-0.935485	3.898538
C	0.852270	-2.928547	2.299999
H	1.311652	-3.372506	1.415452

H	1.641991	-2.446998	2.888325
H	0.447879	-3.748074	2.901032
N	-0.160668	1.620045	0.368379
N	1.880383	0.136067	-0.560821
H	0.704790	1.242061	-0.152279

E = -929.180965749 Hartree
ZPVE = 309.98900 kcal/mol
Lowest vibrational frequency = 32.3544 cm^{-1}
Zero-point correction= 0.493999 (Hartree/Particle)
Thermal correction to Energy= 0.515945
Thermal correction to Enthalpy= 0.516890
Thermal correction to Gibbs Free Energy= 0.442868
Sum of electronic and zero-point Energies= -928.686967
Sum of electronic and thermal Energies= -928.665020
Sum of electronic and thermal Enthalpies= -928.664076
Sum of electronic and thermal Free Energies= -928.738097

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