Combining Bidentate Lewis Acid Catalysis and Photochemistry: Formal Insertion of *o*-Xylene Into an Enamine Double Bond

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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 used for ^{19}F (-153 ppm) as external reference.

UV/Vis:
Spectra were measured with a SPECORD® 200 PLUS UV/Vis spectrophotometer equipped with two automatic eightfold cell changers and a Peltier thermostat system for temperature control manufactured by Analytik Jena. The spectrophotometer system was operated by the software ASpect UV from Analytik Jena. The samples were measured in QS High Precision Cells made of Quartz Suprasil® by Hellma Analytics with a light path of 10 mm.

MS:
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 if 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 **BDLA** was synthesized as described in literature, and was stored in a nitrogen filled glove box.[1,2]
Substituted phthalazines **1b-f**,[3,4] and aldehyde **6d**[5] 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.

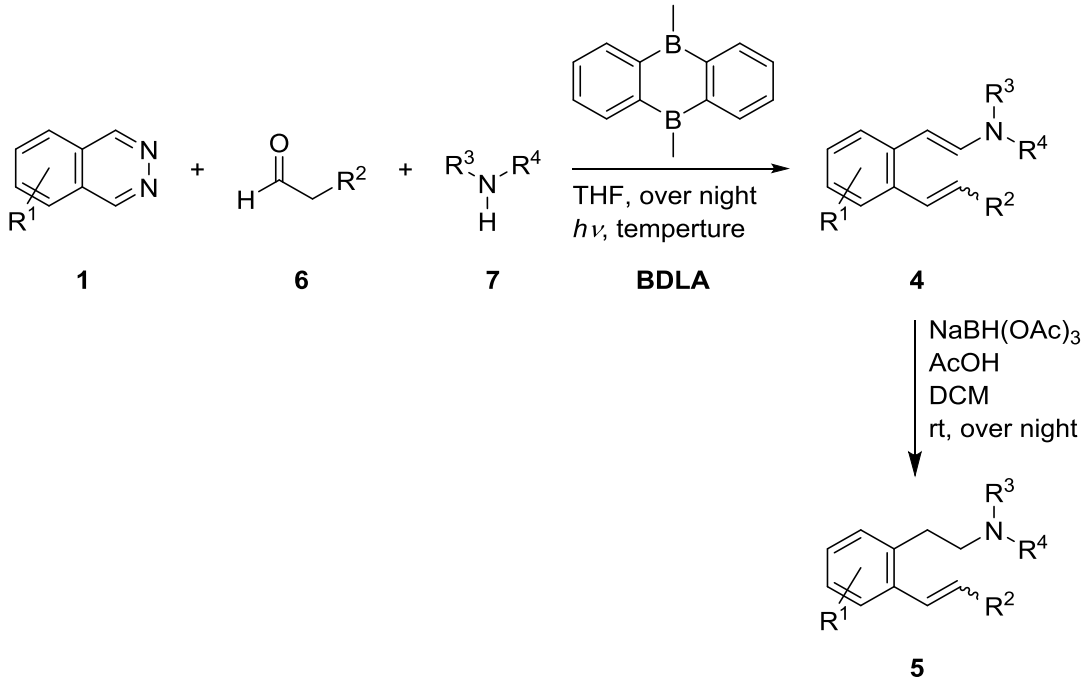
LEDs:

Following LEDs were used for irradiation:

λ_{max} / nm	$\Delta\lambda_{FWHM}$ / nm	Typ
385	10	NCSU276AT-U385
405	12	NCSU276AT-U405
425 – 430	14	LHUV-0425-0650
448	20	LXML-PR01-0500
470	20	LXML-PB01-0030
500	30	NCSE119AT

Synthesis:

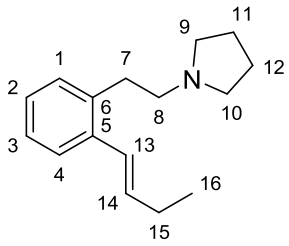
General Procedure for Domino IEDDA/PIRO Reaction Catalyzed by BDLA:

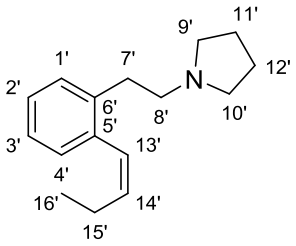


1 **6** **7** **BDLA** **4** **5**

The reaction was set up in a nitrogen filled glovebox.
Phthalazine **1** and **BDLA** were suspended in THF (dry, degassed) (2.00 mL). Then, amine **7** was added, the reaction vessel was sealed and the remaining part of the reaction was carried out in a fume hood. The reaction mixture was heated/cooled to the reported temperature, and irradiated with a LED. Afterwards aldehyde **6** was added. Gas evolution was observed after a few minutes. For electron deficient phthalazines **1**, the reaction mixture was initially cooled, and the temperature was slowly increased until gas evolution started. The reaction was kept irradiated at this temperature overnight. Then, the yellow solution was concentrated under reduced pressure (10^{-1} mbar, volatile compounds were condensed into a cooling trap cooled by liquid nitrogen). The remaining oil (in some cases suspension) was transferred with DCM (dry, degassed) (3 x 2.00 mL) into a Schlenk tube containing $NaBH(OAc)_3$. Then, AcOH was added. The yellow white suspension was stirred at rt overnight. Afterwards it was quenched by the addition of 1 M NaOH solution (15.0 mL). After gas evolution ceased the layers were separated. The aqueous one was extracted with DCM (3 x 10.0 mL). The combined organic fractions were washed with brine (20.0 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography.

Phenethylamine **5a**





Starting materials:
Phthalazine (**1a**) (98.6 mg, 750 µmol, 1.00 equiv); **BDLA** (3.80 mg, 18.6 µmol, 2.49 mol %); pyrrolidine (**7a**) (74.7 µL, 900 µmol, 1.20 equiv); butyraldehyde (**6a**) (100 µL, 1.09 mmol, 1.45 equiv); $NaBH(OAc)_3$ (328 mg, 1.50 mmol, 2.00 equiv); AcOH (90.4 µL, 1.50 mmol, 2.00 equiv).

LED:
425 – 430 nm

Temperature:
30 °C

Purification:
Flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc + 1% NEt_3, 2:1).

Yield: mixture of *E*/*Z*-isomers ***E*-5a**/***Z*-5a** (1.00 : 1.78)
139 mg (604 µmol, 81%); pale yellow oil.

***E*-5a**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.46 – 7.39 (m, 1H, H4), 7.24 – 7.12 (m, 3H, H1, H2, H3), 6.65 (d, *J* = 15.6 Hz, 1H, H13), 6.14 (dt, *J* = 15.7, 6.6 Hz, 1H, H14), 2.95 – 2.86 (m, 2H, H7), 2.66 – 2.53 (m, 6H, H8 – H10), 2.31 – 2.20 (m, 4H, H15), 1.87 – 1.76 (m, 4H, H11, H12), 1.10 (t, *J* = 7.5 Hz, 3H, H16).

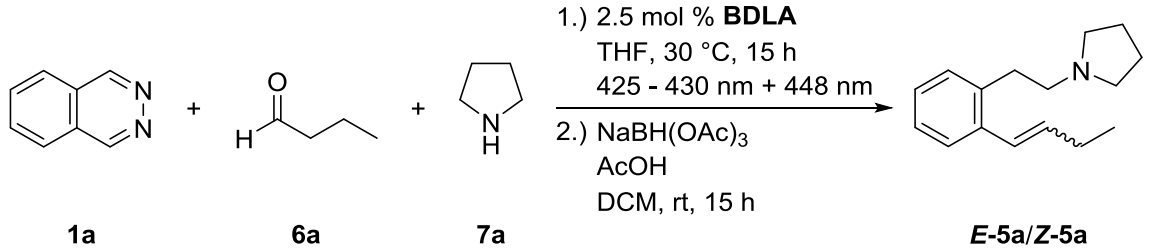
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 137.3 (C6), 137.0 (C5), 134.6 (C14), 129.9 (C1), 127.1 (C3), 126.6 (C4), 126.4 (C13), 126.0 (C2), 57.7 (C8), 54.4 (C9, C10), 33.4 (C7), 26.5 (C15), 23.6 (C11, C12), 14.0 (C16).

***Z*-5a**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.24 – 7.12 (m, 4H, H1' – H4'), 6.50 (d, *J* = 11.4 Hz, 1H, H13'), 5.71 (dt, *J* = 11.5, 7.4 Hz, 1H, H14'), 2.86 – 2.80 (m, 2H, H7'), 2.66 – 2.53 (m, 6H, H8' – H10'), 2.14 (tdd, *J* = 7.5, 7.4, 1.6 Hz, 2H, H15'), 0.99 (t, *J* = 7.5 Hz, 8H, H16').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 138.7 (C6'), 136.8 (C5'), 135.2 (C14'), 129.7 (C4'), 129.4 (C1'), 127.1 (C13'), 127.1 (C3'), 125.9 (C2'), 57.4 (C8'), 54.3 (C9', C10'), 33.5 (C7'), 23.6 (C11', C12'), 21.9 (C15'), 14.5 (C16').

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{16}H_{24}N^+$: 230.1903; found: 230.1904.

Scaled up Synthesis of Phenethylamine **5a**



1a **6a** **7a** ***E*-5a/*Z*-5a**

In case the reaction is scaled up it has to be ensured that the employed light source is strong enough or the reaction vessel is designed for photoreactions, i.e. thin diameter/large surface area. Insufficient irradiation let to the formation of IEDDA/amine group transfer product[6], among others (see 3.00 mmol-Scale below).

1.50 mmol-Scale:

The reaction was set up in a nitrogen filled glovebox.

Phthalazine **1a** (394 mg, 3.00 mmol, 1.00 equiv) and **BDLA** (15.4 mg, 75.5 µmol, 2.52 mol %) were suspended in THF (dry, degassed) (4.00 mL). Then, pyrrolidine (**7a**) (300 µL, 3.62 µmol, 1.21 equiv) was added, the reaction vessel was sealed and the remaining part of the reaction was carried out in a fume hood. The colorless solution was heated to 30 °C, and irradiated with two LEDs (425 – 430 nm + 448 nm). Afterwards butyraldehyde (**6a**) (400 µL, 4.35 mmol, 1.45 equiv) was added. Gas evolution was observed almost immediately. The reaction was kept irradiated at 30 °C overnight. Then, the pale yellow solution was concentrated under reduced pressure (10^{-1} mbar, volatile compounds were condensed into a cooling trap cooled by liquid nitrogen). The remaining yellow suspension was transferred with DCM (dry, degassed) (3 x 4.00 mL) into a Schlenk tube containing $NaBH(OAc)_3$ (670 mg, 1.50 mmol, 2.00 equiv). Then, AcOH (181 µL, 3.00 mmol, 2.00 equiv) was added, and the yellow white suspension was stirred at rt overnight. Afterwards it was quenched by the addition of 1 M NaOH solution (30.0 mL). After gas evolution ceased the layers were separated. The aqueous one was extracted with DCM (3 x 20.0 mL). The combined organic fractions were washed with brine (40.0 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2: 50 g, cyclohexane/EtOAc + 1% NEt_3, 2:1).

Yield:

mixture of *E*/*Z*-isomers ***E*-5a**/***Z*-5a** (1.00 : 1.23)

269 mg (1.17 mmol, 78%); pale yellow oil.

3.00 mmol-Scale:
Starting materials (solvents were scaled up accordingly):
Phthalazine (**1a**) (394 mg, 3.00 mmol, 1.00 equiv); **BDLA** (15.4 mg, 75.5 µmol, 2.52 mol %); pyrrolidine (**7a**) (300 µL, 3.62 µmol, 1.21 equiv); butyraldehyde (**6a**) (400 µL, 4.35 mmol, 1.45 equiv); $NaBH(OAc)_3$ (1.34 g, 6.00 mmol, 2.00 equiv); AcOH (361 µL, 6.00 mmol, 2.00 equiv).

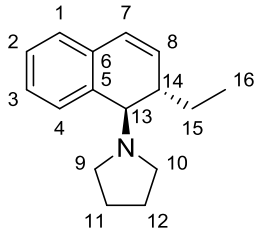
LED (3x):
425 – 430 nm + 2 x 448 nm

Temperature:
30 °C

Purification:
Flash column chromatography (SiO_2: 100 g, cyclohexane/EtOAc + 1% NEt_3, 2:1).

Yield:
IEDDA/PIRO product
mixture of *E*/*Z*-isomers ***E*-5a**/***Z*-5a** (1.10 : 1.00)
447 mg (1.95 mmol, 65%); pale yellow oil.

IEDDA/amine group transfer product[6]
38.3 mg (0.168 mmol, 6%); pale yellow oil.



and enantiomer

^{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, H13), 2.53 – 2.39 (m, 5H, H9, H10, H14), 1.72 – 1.59 (m, 4H, H11, H12), 1.39 – 1.23 (m, 2H, H15), 0.92 (t, *J* = 7.4 Hz, 3H, H16).

Phenethylamine **5b**

Starting materials:
Phthalazine (**1a**) (98.6 mg, 750 µmol, 1.00 equiv); **BDLA** (3.80 mg, 18.6 µmol, 2.49 mol %); pyrrolidine (**7a**) (74.7 µL, 900 µmol, 1.20 equiv); isovaleraldehyde (**6b**) (120 µL, 1.12 mmol, 1.49 equiv); $NaBH(OAc)_3$ (328 mg, 1.50 mmol, 2.00 equiv); AcOH (90.4 µL, 1.50 mmol, 2.00 equiv).

LED:
470 nm

Temperature:
30 °C

Purification:
Flash column chromatography (SiO_2: 20 g, cyclohexane/EtOAc + 1% NEt_3, 5:1).

Yield: mixture of *E*/*Z*-isomers ***E*-5b**/***Z*-5b** (1.16 : 1.00)
132 mg (543 µmol, 72%); pale yellow oil.

***E*-5b**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.45 – 7.39 (m, H4), 7.23 – 7.12 (m, 3H, H1, H2, H3), 6.62 (dd, *J* = 15.7, 0.9 Hz, 1H, H13), 6.06 (dd, *J* = 15.7, 7.0 Hz, 1H, H14), 2.95 – 2.88 (m, 2H, H7), 2.67 – 2.55 (m, 6H, H8 – H10), 2.55 – 2.44 (m, 1H, H15), 1.88 – 1.77 (m, 7H, H11, H12), 1.10 (d, *J* = 6.7 Hz, 4H, H16, H17).

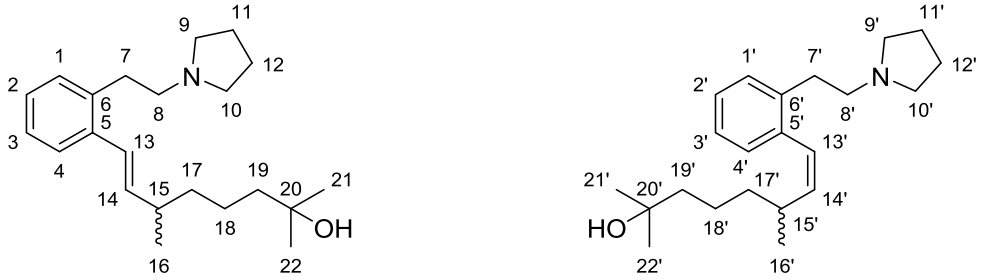
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 140.1 (14), 138.51 (C_{Ar} or C_{Ar}'), 137.27 (C_{Ar} or C_{Ar}'), 137.11 (C_{Ar} or C_{Ar}'), 137.01 (C_{Ar} or C_{Ar}'), 129.87 (C_{Ar} or C_{Ar}'), 129.60 (C_{Ar} or C_{Ar}'), 129.41 (C_{Ar} or C_{Ar}'), 127.08 (C_{Ar} or C_{Ar}'), 127.06 (C_{Ar} or C_{Ar}'), 126.60 (C_{Ar} or C_{Ar}'), 126.04 (C4), 125.95 (C_{Ar} or C_{Ar}'), 124.4 (C13), 57.6 (C8), 54.4 (C9, C10), 33.3 (C7), 31.9 (C15), 23.6 (C11, C12), 22.7 (C16, C17).

***Z*-5b**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.23 – 7.12 (m, 4H, H1' – H4'), 6.41 (d, *J* = 11.4 Hz, 1H, H13'), 5.53 (dd, *J* = 11.3, 10.3 Hz, 1H, H14'), 2.87 – 2.80 (m, 2H, H7'), 2.67 – 2.55 (m, 7H, H8' – H10', H15'), 1.88 – 1.77 (m, 7H, H11', H12'), 0.98 (d, *J* = 6.6 Hz, 4H, H16', H17').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 140.9 (C14'), 138.51 (C_{Ar} or C_{Ar}'), 137.27 (C_{Ar} or C_{Ar}'), 137.11 (C_{Ar} or C_{Ar}'), 137.01 (C_{Ar} or C_{Ar}'), 129.87 (C_{Ar} or C_{Ar}'), 129.60 (C_{Ar} or C_{Ar}'), 129.41 (C_{Ar} or C_{Ar}'), 127.08 (C_{Ar} or C_{Ar}'), 127.06 (C_{Ar} or C_{Ar}'), 126.60 (C_{Ar} or C_{Ar}'), 126.04 (C_{Ar} or C_{Ar}'), 125.95 (C4), 125.4 (C13'), 57.4 (C8'), 54.3 (C9', C10'), 33.4 (C7'), 27.3 (C15'), 23.6 (C11', C12'), 23.25 (C16', C17').

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{17}H_{26}N^+$: 244.2060; found: 244.2057.

Phenethylamine **5c**



Starting materials:
Phthalazine (**1a**) (98.6 mg, 750 µmol, 1.00 equiv); **BDLA** (3.80 mg, 18.6 µmol, 2.49 mol %); pyrrolidine (**7a**) (74.7 µL, 900 µmol, 1.20 equiv); 3,7-dimethyl-7-hydroxyoctanal (**6c**) (200 µL, 1.06 mmol, 1.41 equiv); $NaBH(OAc)_3$ (328 mg, 1.50 mmol, 2.00 equiv); AcOH (90.4 µL, 1.50 mmol, 2.00 equiv).

LED:
470 nm

Temperature:
50 °C

Purification:
Flash column chromatography (SiO_2: 20 g, cyclohexane/EtOAc + 1% NEt_3, 2:1 to 1:1).

Yield: mixture of *E*/*Z*-isomers ***E*-5c**/***Z*-5c** (1.46 : 1.00)
175 mg (531 µmol, 71%); pale yellow oil.

***E*-5c**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.44 – 7.36 (m, 1H, H4), 7.21 – 7.11 (m, 3H, 1, 2, 3), 6.62 (d, *J* = 15.6 Hz, 1H, H13), 5.91 (dd, *J* = 15.6, 8.0 Hz, 1H, H14), 2.94 – 2.86 (m, 2H, H7), 2.67 – 2.54 (m, 6H, H8 , H9, H10), 2.34 (dt, *J* = 13.2, 6.7 Hz, 1H, H15), 1.99 (s, br, -OH), 1.88 – 1.76 (m, 4H, 11, 12), 1.57 – 1.21 (m, 6H, 17, 18, 19), 1.14 (s, 4H, H21, H22), 1.09 (d, *J* = 6.7 Hz, 3H, H16).

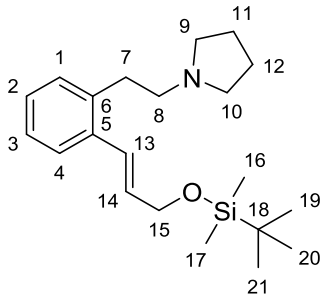
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 138.8 (C14), 137.3 (C6), 137.2 (C5), 129.8 (C1 or C2 or C3), 127.1 (C1 or C2 or C3), 126.6 (C1 or C2 or C3), 126.3 (C4), 126.1 (C13), 125.89, 70.8 (C20), 57.8 (C8), 54.3 (C9, C10), 44.1 (C19), 37.6 (C17), 37.5 (C15), 33.3 (C7), 29.4 (C21, C22), 23.5 (C11, C12), 22.1 (C18), 21.1 (C16).

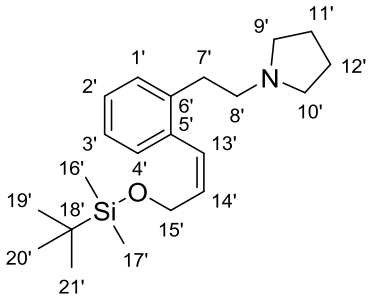
***Z*-5c**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.21 – 7.11 (m, 4H, 1', 2', 3', 4'), 6.47 (d, *J* = 11.5 Hz, 1H, H13'), 5.49 (dd, *J* = 11.4, 10.5 Hz, 1H, H14'), 2.87 – 2.80 (m, 2H, H7'), 2.67 – 2.54 (m, 6H, 8', 9', 10'), 2.48 (dq, *J* = 12.8, 6.4 Hz, 1H, H15'), 1.99 (s, br, -OH), 1.88 – 1.76 (m, 4H, 11', 12'), 1.57 – 1.21 (m, 6H, 17', 18', 19'), 1.20 (s, 6H, 21', 22'), 1.00 (d, *J* = 6.6 Hz, 2H, 16').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 139.7 (C14'), 138.5 (C6'), 137.0 (C5'), 129.5 (C1' or C2' or C3' or C4'), 129.2 (C1' or C2' or C3' or C4'), 127.1 (C1' or C2' or C3' or C4'), 126.5 (C13'), 125.9 (C1' or C2' or C3' or C4'), 70.9 (C20'), 57.2 (C8'), 54.3 (C9', C10'), 44.2 (C19'), 38.2 (C17'), 33.2 (C7'), 32.3 (C15'), 29.5 (C21', C22'), 23.5 (C11', C12'), 22.3 (C18'), 21.3 (C16').

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{22}H_{36}NO^+$: 330.2791; found: 330.2790.

Phenethylamine **5d**





Starting materials:
Phthalazine (**1a**) (98.6 mg, 750 µmol, 1.00 equiv); **BDLA** (3.80 mg, 18.6 µmol, 2.49 mol %); pyrrolidine (**7a**) (74.7 µL, 900 µmol, 1.20 equiv); aldehyde **6d** (207 mg, 1.09 mmol, 1.45 equiv); $NaBH(OAc)_3$ (328 mg, 1.50 mmol, 2.00 equiv); AcOH (90.4 µL, 1.50 mmol, 2.00 equiv).

LED:
425 – 430 nm

Temperature:
30 °C

Purification:
Flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc + 3% NEt_3, 10:1).

Yield: mixture of *E*/*Z*-isomers ***E*-5d**/***Z*-5d** (1.00 : 1.53)
129 mg (374 µmol, 50%); pale yellow oil.

***E*-5d**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.49 – 7.41 (m, 1H, H4), 7.23 – 7.13 (m, 3H, H1, H2, H3), 6.88 (dt, *J* = 15.7, 1.9 Hz, 1H, H13), 6.19 (dt, *J* = 15.6, 5.1 Hz, 1H, H14), 4.37 (dd, *J* = 5.0, 1.8 Hz, 2H, H15), 2.95 – 2.87 (m, 2H, H7), 2.67 – 2.53 (m, 6H, H8 – H10), 1.86 – 1.75 (m, 4H, H11, H12), 0.94 (s, 9H, H19 – H21), 0.12 (s, 6H, H16, H17).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 137.9 (C6), 136.1 (C5), 131.1 (C14), 130.0 (C1), 127.6 (C2 or C3), 126.9 (C13), 126.6 (C2 or C3), 126.2 (C4), 64.2 (15) 57.8 (C8), 54.3 (H9, H10), 33.3 (C7), 26.1 (C19 – C21), 23.6 (C11, C12), 18.6 (C18), -4.95 (C16, C17).

***Z*-5d**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.23 – 7.13 (m, 3H, H1', H2', H3'), 7.07 (d, *J* = 7.1 Hz, 1H, H4'), 6.64 (dt, *J* = 11.5, 1.7 Hz, 1H, H13'), 5.87 (dt, *J* = 11.6, 6.3 Hz, 1H, H14'), 4.29 (dd, *J* = 6.3, 1.6 Hz, 2H, H15'), 2.87 – 2.81 (m, 2H, H7'), 2.67 – 2.53 (m, 6H, H8' – H10'), 1.86 – 1.75 (m, 4H, H11', H12'), 0.87 (s, 9H, H19' – H21'), 0.01 (s, 6H, H16', H17').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 138.7 (C6'), 135.7 (C5'), 132.8 (C14'), 129.6 (C1'), 129.6 (C4'), 128.5 (C13'), 127.6 (C2'), 125.9 (C3'), 60.4 (C15'), 57.4 (C8'), 54.3 (C9', C10'), 33.5 (C7'), 26.1 (C19'–C21'), 23.6 (C11', C12'), 18.4 (C18'), -4.98 (C16', C17').

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{21}H_{36}NOSi^+$: 346.2561; found: 346.2565.

Phenethylamine **5e**

Starting materials:
Phthalazine (**1a**) (98.6 mg, 750 µmol, 1.00 equiv); **BDLA** (3.80 mg, 18.6 µmol, 2.49 mol %); pyrrolidine (**7a**) (74.7 µL, 900 µmol, 1.20 equiv); pent-4-enal (**6e**) (100 µL, 982 µmol, 1.31 equiv); $NaBH(OAc)_3$ (328 mg, 1.50 mmol, 2.00 equiv); AcOH (90.4 µL, 1.50 mmol, 2.00 equiv).

LED:
448 nm

Temperature:
30 °C

Purification:
Flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc + 1% NEt_3, 10:1 to 5:1).

Yield: mixture of *E*/*Z*-isomers ***E*-5e**/***Z*-5e** (1.24 : 1.00)
138 mg (573 µmol, 76%).

***E*-5e**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.46 – 7.40 (m, 1H, H4), 7.24 – 7.13 (m, 3H, H1, H2, H3), 6.69 (dt, *J* = 15.6, 1.7 Hz, 1H, H13), 6.11 (dt, *J* = 15.6, 6.7 Hz, 1H, H14), 5.97 – 5.80 (m, 1H, 16), 5.15 – 4.99 (m, 2H, H17), 3.01 – 2.95 (m, 2H, H15), 2.94 – 2.79 (m, 2H, H7), 2.67 – 2.52 (m, 6H, H8, H9, H10), 1.87 – 1.76 (m, 4H, H11, H12).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 137.4 (C6), 136.7 (C16), 136.3 (C5), 130.21 (C_{Ar} or C_{Ar}'), 129.9 (C14), 129.52 (C_{Ar} or C_{Ar}'), 129.46 (C_{Ar} or C_{Ar}'), 128.6 (C13), 127.33 (C_{Ar} or C_{Ar}'), 127.32 (C_{Ar} or C_{Ar}'), 126.6 (C_{Ar} or C_{Ar}'), 126.1 (C4), 126.0 (C_{Ar} or C_{Ar}'), 115.8 (C17), 57.7 (C8), 54.4 (C9, C10), 37.4 (C15), 33.3 (C7), 23.6 (C11, C12).

***Z*-5e**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.24 – 7.13 (m, 4H, H_{Ar}'), 6.64 (dt, *J* = 11.4, 1.6 Hz, 1H, H13'), 5.97 – 5.80 (m, 1H, H16'), 5.77 (dt, *J* = 11.4, 7.6 Hz, 1H, H14'), 5.15 – 4.99 (m, 2H, H17'), 2.94 – 2.79 (m, 4H, H7', H15'), 2.67 – 2.52 (m, 6H, H8', H9', H10'), 1.87 – 1.76 (m, 4H, H11', H12').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 138.7 (C6'), 136.9 (C16'), 130.2 (C_{Ar} or C_{Ar}'), 130.1 (C14'), 129.52 (C_{Ar} or C_{Ar}'), 129.46 (C_{Ar} or C_{Ar}'), 129.0 (C13'), 127.33 (C_{Ar} or C_{Ar}'), 127.32 (C_{Ar} or C_{Ar}'), 126.6 (C_{Ar} or C_{Ar}'), 126.1 (C_{Ar} or C_{Ar}'), 126.0 (C_{Ar} or C_{Ar}'), 115.2 (C17'), 57.4 (C8'), 54.3 (C9', C10'), 33.5 (C7'), 32.7 (C15'), 23.6 (C11', C12').

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{17}H_{24}N^+$: 242.1903; found: 242.1902.

Phenethylamine **5f**

Starting materials:
Phthalazine (**1a**) (98.6 mg, 750 µmol, 1.00 equiv); **BDLA** (3.80 mg, 18.6 µmol, 2.49 mol %); morpholine (**7b**) (79.6 µL, 900 µmol, 1.20 equiv); butyraldehyde (**6a**) (100 µL, 1.09 mmol, 1.45 equiv); $NaBH(OAc)_3$ (328 mg, 1.50 mmol, 2.00 equiv); AcOH (90.4 µL, 1.50 mmol, 2.00 equiv).

LED:
470 nm

Temperature:
45 °C

Purification:
Flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc + 1% NEt_3, 2:1).

Yield: mixture of *E*/*Z*-isomers ***E*-5f**/***Z*-5f** (1.00 : 1.12)
149 mg, (606 mmol, 81%); pale yellow oil.

***E*-5f**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.44 – 7.40 (m, 1H, H4), 7.22 – 7.12 (m, 3H, H1, H2, H3), 6.62 (dt, *J* = 15.5, 1.7 Hz, 1H, H13), 6.15 (dt, *J* = 15.6, 6.6 Hz, 1H, H14), 3.79 – 3.72 (m, 4H, H11, H12), 2.90 – 2.84 (m, 2H, H7), 2.57 – 2.47 (m, 6H, H8, H9, H10), 2.32 – 2.21 (m, 2H, H15), 1.10 (t, *J* = 7.5 Hz, 3H, H16).

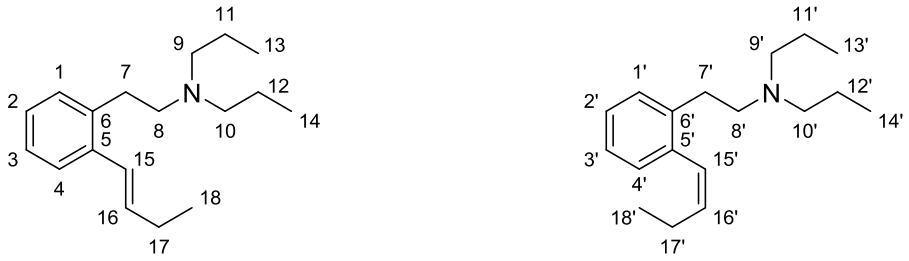
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 136.9 (C5), 136.8 (C6), 134.8 (C14), 129.9 (C1), 129.7 (C_{Ar} or C_{Ar}'), 127.13 (C_{Ar} or C_{Ar}'), 127.10 (C_{Ar} or C_{Ar}'), 126.7 (C_{Ar} or C_{Ar}'), 126.3 (C13), 126.1 (C4), 126.0 (C_{Ar} or C_{Ar}'), 67.1 (C11, C12), 60.2 (C8), 53.8 (C9, C10), 30.7 (C7), 26.5 (C15), 13.9 (C16).

***Z*-5f**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.22 – 7.12 (m, 4H, H_{Ar}'), 6.48 (dt, *J* = 11.4, 1.7 Hz, 1H, H13'), 5.73 (dt, *J* = 11.4, 7.4 Hz, 1H, H14'), 3.79 – 3.72 (m, 4H, H11', H12'), 2.82 – 2.77 (m, 2H, H7'), 2.57 – 2.47 (m, 6H, H8', H9', H10'), 2.19 – 2.09 (m, 3H, H15'), 1.00 (t, *J* = 7.5 Hz, 4H, H16').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 138.3 (C6'), 137.0 (C5'), 135.3 (C14'), 129.7 (C_{Ar} or C_{Ar}'), 129.5 (C1'), 127.13 (C_{Ar} or C_{Ar}'), 127.10 (C_{Ar} or C_{Ar}'), 127.0 (C13'), 126.7 (C_{Ar} or C_{Ar}'), 126.0 (C_{Ar} or C_{Ar}'), 67.1 (C11', C12'), 59.9 (C8'), 53.8 (C9', C10'), 30.9 (C7'), 21.9 (C15'), 14.5 (C16').

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{16}H_{24}NO^+$: 246.1852; found: 246.1849.

Phenethylamine **5g**



Starting materials:
Phthalazine (**1a**) (98.6 mg, 750 µmol, 1.00 equiv); **BDLA** (3.80 mg, 18.6 µmol, 2.49 mol %); dipropylamine (**7c**) (125 µL, 900 µmol, 1.20 equiv); butyraldehyde (**6a**) (100 µL, 1.09 mmol, 1.45 equiv); $NaBH(OAc)_3$ (328 mg, 1.50 mmol, 2.00 equiv); AcOH (90.4 µL, 1.50 mmol, 2.00 equiv).

LED:
470 nm

Temperature:
50 °C

Purification:
Flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc + 1% NEt_3, 30:1).

Yield: mixture of *E*/*Z*-isomers ***E*-5g**/***Z*-5g** (5.83 : 1.00)
161 mg (621 µmol, 83%); pale yellow oil.

***E*-5g**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.44 – 7.39 (m, 1H, H4), 7.19 – 7.09 (m, 3H, H1, H2, H3), 6.64 (d, *J* = 15.6 Hz, 1H, H15), 6.14 (dt, *J* = 15.5, 6.5 Hz, 1H, H16), 2.84 – 2.78 (m, 2H, H7), 2.65 – 2.57 (m, 2H, H8), 2.52 – 2.42 (m, 4H, H9, H10), 2.25 (p, *J* = 7.3 Hz, 2H, H17), 1.57 – 1.43 (m, 4H, H11, H12), 1.11 (td, *J* = 7.4, 1.0 Hz, 3H, H18), 0.95 – 0.86 (m, 6H, H13, H14).

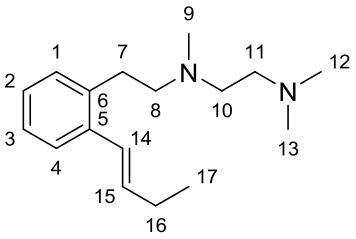
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 137.8 (C_{Ar} or C_{Ar}'), 137.0 (C5), 135.1 (C_{Ar} or C_{Ar}'), 134.6 (C_{Ar} or C_{Ar}'), 134.5 (C_{Ar} or C_{Ar}'), 130.0 (C1), 129.7 (C_{Ar} or C_{Ar}'), 129.6 (C_{Ar} or C_{Ar}'), 127.2 (C_{Ar} or C_{Ar}'), 127.1 (C_{Ar} or C_{Ar}'), 127.0 (C_{Ar} or C_{Ar}'), 126.46 (C_{Ar} or C_{Ar}'), 126.45 (C_{Ar} or C_{Ar}'), 126.1 (C4), 125.7 (C_{Ar} or C_{Ar}'), 56.4 (C9, C10), 55.2 (C8), 31.0 (C7), 26.5 (C17), 20.6 (C11, C12), 13.8 (C18), 12.1 (C13, C14).

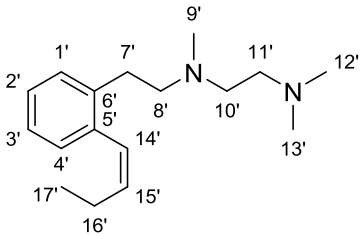
***Z*-5g**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.19 – 7.09 (m, 4H, H1', H2', H3', H4'), 6.50 (d, *J* = 11.4 Hz, 1H, H15'), 5.72 (dt, *J* = 11.4, 7.4 Hz, 1H, H16'), 2.78 – 2.70 (m, 2H, H7'), 2.65 – 2.57 (m, 2H, H8'), 2.52 – 2.42 (m, 4H, H9', H10'), 2.15 (p, *J* = 7.4 Hz, 2H, H17'), 1.57 – 1.43 (m, 4H, H11', H12'), 1.04 – 0.96 (td, *J* = 7.5, 0.9 Hz, 3H, H18'), 0.95 – 0.86 (m, 6H, H13', H14').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 137.8 (C_{Ar} or C_{Ar}'), 135.1 (C_{Ar} or C_{Ar}'), 134.6 (C_{Ar} or C_{Ar}'), 134.5 (C_{Ar} or C_{Ar}'), 129.7 (C_{Ar} or C_{Ar}'), 129.6 (C_{Ar} or C_{Ar}'), 127.2 (C_{Ar} or C_{Ar}'), 127.1 (C_{Ar} or C_{Ar}'), 127.0 (C_{Ar} or C_{Ar}'), 127.0 (C_{Ar} or C_{Ar}'), 126.5 (C_{Ar} or C_{Ar}'), 125.7 (C_{Ar} or C_{Ar}'), 56.3 (C9', C10'), 54.9 (C8'), 31.0 (C7'), 21.9 (C17'), 20.6 (C11', C12'), 14.4 (C18'), 12.1 (C13', C14').

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{18}H_{30}N^+$: 260.2373; found: 260.2374.

Phenethylamine **5h**





Starting materials:
Phthalazine (**1a**) (98.6 mg, 750 µmol, 1.00 equiv); **BDLA** (3.80 mg, 18.6 µmol, 2.49 mol %); N,N,N'-trimethylethylenediamine (**7d**) (121 µL, 900 µmol, 1.20 equiv); butyraldehyde (**6a**) (100 µL, 1.09 mmol, 1.45 equiv); $NaBH(OAc)_3$ (328 mg, 1.50 mmol, 2.00 equiv); AcOH (90.4 µL, 1.50 mmol, 2.00 equiv).

LED:
470 nm

Temperature:
30 °C

Purification:
Flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc/NEt_3, 10:10:1 to 5:5:1).

Yield: mixture of *E*/*Z*-isomers ***E*-5h**/***Z*-5h** (2.09 : 1.00)
134 mg (515 µmol, 69%); pale yellow oil.

***E*-5h**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.44 – 7.39 (m, 1H, H4), 7.20 – 7.10 (m, 3H, H1, H2, H3), 6.62 (d, *J* = 15.6 Hz, 1H, H14) 6.14 (dt, *J* = 15.6, 6.5 Hz, 1H, H15), 2.88 – 2.83 (m, 2H, H7), 2.59 – 2.51 (m, 4H, H8, H10), 2.45 – 2.39 (m, 2H, H11), 2.36 (s, 3H, H9), 2.25 (s, 6H, H12, H13), 2.31 – 2.19 (m, 2H, H16), 1.10 (t, *J* = 7.5 Hz, 3H, H17).

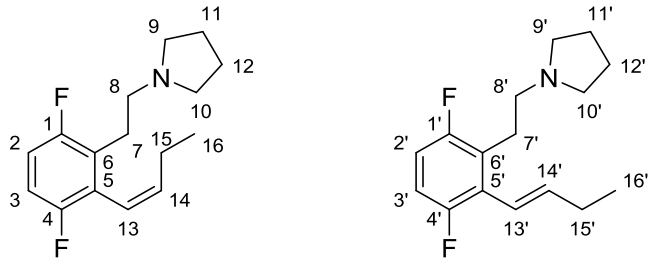
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 137.3 (C6), 137.0 (C5), 134.6 (C15), 129.9 (C1), 127.1 (C2), 126.6 (C3), 126.4 (C14), 126.1 (C4), 59.3 (C8 or C10), 57.60 (C11), 55.6 (C8 or C10), 46.0 (C12, C13), 42.7 (C9), 31.3 (C7), 26.5 (C16), 13.9 (C17).

***Z*-5h**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.20 – 7.10 (m, 4H, H1', H2', H3', H4'), 6.48 (dt, *J* = 11.4, 1.5 Hz, 1H, H14'), 5.72 (dt, *J* = 11.4, 7.4 Hz, 1H, H15'), 2.80 – 2.75 (m, 2H, H7'), 2.59 – 2.51 (m, 4H, H8', H10'), 2.45 – 2.39 (m, 2H, H11'), 2.33 (s, 3H, H9'), 2.25 (s, 6H, H12', H13'), 2.15 (qd, *J* = 7.5, 1.6 Hz, 2H, H16'), 0.99 (t, *J* = 7.5 Hz, 3H, H17').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 138.7 (C6'), 136.8 (C5'), 135.2 (C15'), 129.7 (C1' or C2' or C3' or C4'), 129.5 (C1' or C2' or C3' or C4'), 127.12 (C1' or C2' or C3' or C4' or C14'), 127.09 (C1' or C2' or C3' or C4' or C14'), 125.8 (C1' or C2' or C3' or C4'), 59.0 (C8' or C10'), 57.6 (C11'), 55.4 (C8' or C10'), 46.0 (C12', C13'), 42.6 (C9'), 31.2 (C7'), 21.9 (C16'), 14.5 (C17').

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{17}H_{29}N_2^+$: 261.2325; found: 261.2322.

Phenethylamine **5i**



Starting materials:
5,8-Difluorophthalazine (**1b**) (62.3 mg, 375 µmol, 1.00 equiv); **BDLA** (1.90 mg, 9.30 µmol, 2.49 mol %); pyrrolidine (**7a**) (37.3 µL, 450 µmol, 1.20 equiv); butyraldehyde (50 µL, 544 µmol, 1.45 equiv); $NaBH(OAc)_3$ (164 mg, 735 µmol, 2.00 equiv); AcOH (45.2 µL, 750 µmol, 2.00 equiv).

LED:
448 nm

Temperature:
-15 °C to 10 °C

Purification:
Flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc + 1% NEt_3, 8:1).

Yield: mixture of E/Z-isomers E-5h/Z-5h (1.00 : 5.71)
58.0 mg (219 mmol, 58%); pale yellow oil.

***E*-5i**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 6.93 – 6.78 (m, 2H, H2, H3), 6.30 – 6.25 (m, 2H, H13, H14), 2.97 – 2.88 (m, 2H, H7), 2.64 – 2.47 (m, 6H, H8, H9, H10), 2.32 – 2.22 (m, 2H, H15), 1.86 – 1.73 (m, 4H, H11, H12), 1.10 (t, *J* = 7.5 Hz, 3H, H16).

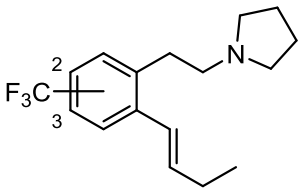
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 157.3 (dd, J = 240.3, 2.5 Hz, C1, detected by hmbc experiment), 155.6 (dd, J = 240.2, 2.2 Hz, C4, detected by hmbc experiment), 140.8 (d, *J* = 8.8 Hz, C14), 126.7 (C5), 119.3 (d, *J* = 2.7 Hz, 13), 114.1 (dd, *J* = 27.1, 9.9 Hz, C2), 113.6 (dd, *J* = 26.0, 9.4 Hz, C3), 55.8 (C8), 54.3 (C9, C10) 27.1 (C15), 25.8 (C7), 23.6 (C11, C12), 13.6 (C16).

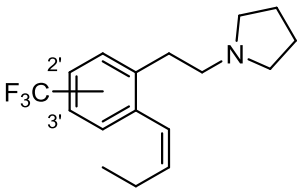
***Z*-5i**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 6.93 – 6.78 (m, 2H, H2', H3'), 6.13 (d, *J* = 11.2 Hz, 1H, H13'), 5.89 (dt, *J* = 11.2, 7.3 Hz, 1H, H14'), 2.86 – 2.79 (m, 2H, H7'), 2.64 – 2.47 (m, 6H, H8', H9', H10'), 1.94 (p, *J* = 7.4 Hz, 2H, H15'), 1.86 – 1.73 (m, 4H, H11', H12'), 0.96 (t, *J* = 7.5 Hz, 1H, H16').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 157.3 (dd, *J* = 240.3, 2.5 Hz, C1'), 155.6 (dd, *J* = 240.2, 2.2 Hz, C4'), 139.14 (d, *J* = 1.4 Hz, C14'), 127.64 (dd, *J* = 17.7, 3.3 Hz, C6'), 126.2 (dd, *J* = 19.1, 4.9 Hz, C5') 118.8 (d, *J* = 2.1 Hz, C13'), 114.5 (dd, *J* = 25.7, 9.0 Hz, C2'), 113.8 (dd, *J* = 26.3, 9.2 Hz, C3'), 55.5 (C8'), 54.2(C9', C10'), 26.3 (C7') 23.6 (C11', C12'), 22.8 (d, *J* = 2.4 Hz, C15'), 13.5 (C16').

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{16}H_{22}F_2N^+$: 266.1715; found: 266.1713.

Phenethylamine **5j**





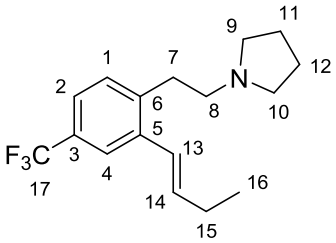
Starting materials:
6-(Trifluoromethyl)phthalazine (**1c**) (149 mg, 750 µmol, 1.00 equiv); **BDLA** (3.80 mg, 18.6 µmol, 2.49 mol %); pyrrolidine (**7a**) (74.7 µL, 900 µmol, 1.20 equiv); butyraldehyde (100 µL, 1.09 mmol, 1.45 equiv); $NaBH(OAc)_3$ (328 mg, 1.50 mmol, 2.00 equiv); AcOH (90.4 µL, 1.50 mmol, 2.00 equiv).

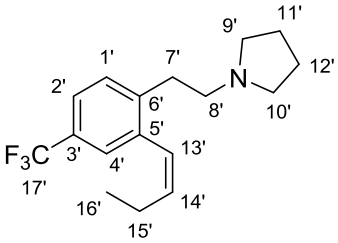
LED:
448 nm

Temperature:
-10 °C to 0 °C

Purification:
Flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc + 1% NEt_3, 8:1).

Yield: mixture of *E*/*Z*-isomers *E*-5j/*Z*-5j (9.00 : 1.00)
67.0 mg (225 µmol, 30%); pale yellow oil.





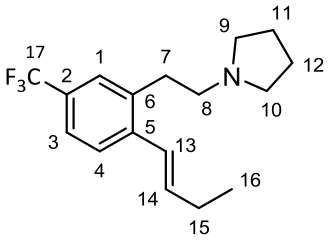
***E*-5j**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.64 (d, *J* = 1.9 Hz, 1H, H4), 7.37 (dd, *J* = 8.1, 1.9 Hz, 1H, H2), 7.25 (d, *J* = 7.8 Hz, 1H, H1), 6.64 (dt, *J* = 15.6, 1.7 Hz, 1H, H13), 6.21 (dt, *J* = 15.6, 6.5 Hz, 1H, H14), 2.97 – 2.90 (m, 2H, H7), 2.66 – 2.54 (m, 6H, H8, H9, H10), 2.31 – 2.22 (m, 2H, H15), 1.87 – 1.78 (m, 4H, H11, H12), 1.11 (t, *J* = 7.5 Hz, 3H, H16).

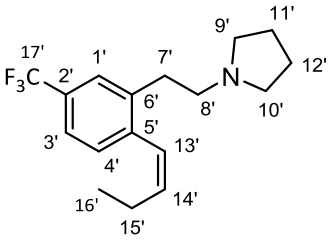
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 141.1 (q, *J* = 1.2 Hz, C6, only visible as doublet due to low intensity), 137.7 (C5), 136.5 (C14), 130.2 (C1), 128.9 (q, *J* = 32.0 Hz, C3), 125.4 (C13), 124.5 (q, *J* = 272.0 Hz, C17), 123.5 (q, *J* = 3.8 Hz, C2), 122.9 (q, *J* = 3.8 Hz, C4), 57.1 (C8), 54.4 (C9, C10), 33.2 (C7), 26.5 (C15), 23.6 (C11, C12), 13.8 (C16).

***Z*-5j**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.42 (dd, *J* = 8.1, 2.0 Hz, 1H, H2'), 7.38 (s, 1H, H4', detected by HMQC experiment), 7.30 (d, *J* = 8.0 Hz, 1H, H1'), 6.47 (d, *J* = 11.5 Hz, 1H, H13'), 5.79 (dt, *J* = 11.4, 7.4 Hz, 1H, H14'), 2.89 – 2.82 (m, 2H, H7'), 2.66 – 2.54 (m, 6H, H8', H9', H10'), 2.11 (pd, *J* = 7.5, 1.7 Hz, 2H, H15'), 1.87 – 1.78 (m, 4H, H11', H12'), 1.00 (t, *J* = 7.5 Hz, 3H, H16').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 142.8 (C6'), 137.4 (C5'), 136.6 (C14'), 129.8 (C1'), 126.4 (q, *J* = 3.6 Hz, C4', only visible as doublet due to low intensity), 126.0 (C13') 123.8 (q, *J* = 3.7 Hz, C2', only visible as doublet due to low intensity), 56.9 (C8'), 54.3 (C9', C10'), 33.3 (C7'), 23.6 (C11', C12'), 21.9 (C15'), 14.3 (C16').

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{17}H_{23}F_3N^+$: 298.1777; found: 298.1780.
Yield: mixture of *E*/*Z*-isomers *E*-5j'/*Z*-5j' (3.12 : 1.00)
54.0 mg (182 µmol, 24%); pale yellow oil.





***E*-5j'**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.50 (d, *J* = 8.5 Hz, 1H, H4), 7.45 – 7.36 (m, 2H, H1, H3), 6.65 (d, *J* = 15.7 Hz, 1H, H13), 6.22 (dt, *J* = 15.6, 6.6 Hz, 1H, H14), 2.98 – 2.91 (m, 2H, H7), 2.68 – 2.55 (m, 6H, H8, H9, H10), 2.32 – 2.21 (m, 2H, H15), 1.88 – 1.78 (m, 4H, H11, H12), 1.11 (t, *J* = 7.4 Hz, 3H, H16).

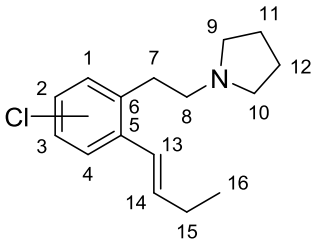
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 140.6 (q, *J* = 1.5 Hz, C5, only visible as doublet due to low intensity), 137.7 (C6), 137.1 (C14), 128.9 (q, *J* = 32.2 Hz, C2), 126.5 (q, *J* = 3.8 Hz, C1), 126.4 (C4), 125.4 (C13), 124.5 (q, *J* = 271.8 Hz, C17), 123.3 (q, *J* = 3.8 Hz, C3), 57.2 (C8), 54.3 (C9, C10), 33.1 (C7), 26.5 (C15), 23.60 (C11, C12), 13.7 (C16).

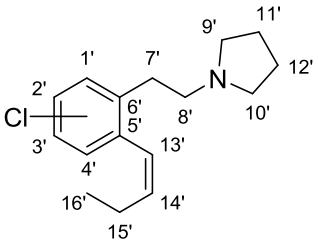
***Z*-5j'**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.45 – 7.36 (m, 2H, H1', H3'), 7.24 (d, *J* = 8.0 Hz, 1H, H4'), 6.48 (d, *J* = 11.4 Hz, 1H, H13'), 5.80 (dt, *J* = 11.5, 7.5 Hz, 1H, H14'), 2.90 – 2.83 (m, 1H, H7'), 2.68 – 2.55 (m, 6H, H8', H9', H10'), 2.11 (pd, *J* = 7.5, 1.7 Hz, 2H, H15'), 1.88 – 1.78 (m, 4H, H11', H12'), 0.99 (t, *J* = 7.5 Hz, 1H, H16').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 140.5 (q, *J* = 1.2 Hz, C5', only visible as doublet due to low intensity), 139.4 (C6'), 136.7 (C14'), 123.0 (C4'), 129.1 (q, *J* = 32.1 Hz, C2', only visible as doublet due to low intensity), 126.1 (q, *J* = 3.9 Hz, C1', only visible as doublet due to low intensity), 126.0 (C13'), 122.7 (q, *J* = 3.9 Hz, C3', only visible as doublet due to low intensity), 56.9 (C8'), 54.3 (C9', C10'), 33.2 (C7'), 23.6 (C11', C12'), 21.9 (C15'), 14.3 (C16').

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{17}H_{23}F_3N^+$: 298.1777; found: 298.1780.

Phenethylamine **5k**





Starting materials:
6-Chlorophthalazine (**1d**) (123 mg, 750 µmol, 1.00 equiv); **BDLA** (3.80 mg, 18.6 µmol, 2.49 mol %); pyrrolidine (**7a**) (74.7 µL, 900 µmol, 1.20 equiv); butyraldehyde (**6a**) (100 µL, 1.09 mmol, 1.45 equiv); $NaBH(OAc)_3$ (328 mg, 1.50 mmol, 2.00 equiv); AcOH (90.4 µL, 1.50 mmol, 2.00 equiv).

LED:
448 nm

Temperature:
-15 °C to 10 °C

Purification:
Flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc + 1% NEt_3, 3:1).

Yield: mixture of *E*/*Z*- ***E*-5k**/***Z*-5k** (5.73 : 1.00)
and the corresponding constitutional isomers (***E*-5k'**/***Z*-5k'**).
142 mg (537 µmol, 72%); pale yellow oil.

NMR spectra could not be assigned unambiguously

***E*-5k** and ***E*-5k'**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.38 (d, *J* = 2.1 Hz, 1H, H4), 7.33 (d, *J* = 8.8 Hz, 1H, H4), 7.15 – 7.03 (m, 6H, H1, H2, H3), 6.56 (dt, *J* = 15.6, 1.7 Hz, 2H, H13), 6.13 (ddt, *J* = 15.6, 13.5, 6.6 Hz, 2H, H14), 2.90 – 2.80 (m, 4H, H7), 2.65 – 2.52 (m, 12H, H8, H9, H10), 2.30 – 2.17 (m, 4H, H15), 1.86 – 1.77 (m, 8H, H11, H12), 1.09 (td, *J* = 7.4, 1.9 Hz, 6H, H16).

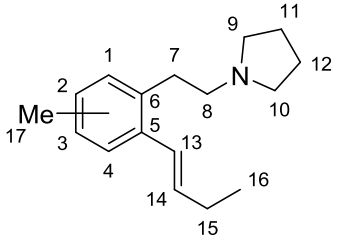
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 139.0 (C_{Ar}), 138.7 (C_{Ar}), 135.91 (C14), 135.7 (C_{Ar}), 135.5 (C_{Ar}), 135.2 (C14), 132.4 (C_{Ar}), 132.2 (C_{Ar}), 131.2 (C_{Ar}), 129.6 (C_{Ar}), 127.35 (C4), 126.9 (C_{Ar}), 126.6 (C_{Ar}), 125.90 (C4), 125.4 (C13), 57.5 (C8), 57.3 (C8), 54.4 (C9, C10), 33.1 (C7), 32.7 (C7), 26.45 (C15), 26.42 (C15), 23.6 (C11, C12), 13.83 (C16), 13.79 (C16).

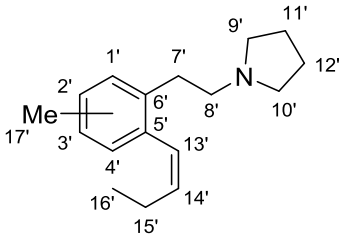
***Z*-5k** and ***Z*-5k'**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.18 (d, *J* = 2.2 Hz, 1H, H_{Ar}'), 7.15 – 7.03 (m, 5H, H_{Ar}'), 6.41 (dd, *J* = 11.4, 1.7 Hz, 2H, H13'), 5.73 (dtd, *J* = 12.2, 7.4, 4.9 Hz, 2H, H14'), 2.82 – 2.73 (m, 4H, H7'), 2.65 – 2.52 (m, 12H, H8', H9', H10'), 2.19 – 2.03 (m, 4H, H15'), 1.86 – 1.77 (m, 8H, H11', H12'), 0.99 (td, *J* = 7.5, 4.9 Hz, 6H, H16').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 140.6 (C_{Ar}'), 138.5 (C_{Ar}'), 137.2 (C_{Ar}'), 136.2 (C14'), 135.87 (C14'), 132.48 (C_{Ar}'), 131.4 (C_{Ar}'), 130.9 (C_{Ar}'), 130.7 (C_{Ar}'), 129.33 (C_{Ar}'), 129.29 (C_{Ar}'), 127.0 (C_z'), 126.03 (C13' or CAr'), 126.00 (C13' or CAr'), 125.93 (C13' or CAr'), 57.2 (C8'), 57.0 (C8'), 54.31 (C9', C10'), 33.25 (C7'), 32.84 (C7'), 23.59 (C11', C12'), 21.9 (C15'), 14.34 (C16'), 14.30 (C16')

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{16}H_{23}ClN^+$: 264.1514; found: 264.1514.

Phenethylamine **5l**





Starting materials:
6-Methylphthalazine (**1e**) (149 mg, 750 µmol, 1.00 equiv); **BDLA** (3.80 mg, 18.6 µmol, 2.49 mol %); pyrrolidine (**7a**) (74.7 µL, 900 µmol, 1.20 equiv); butyraldehyde (**6a**) (100 µL, 1.09 mmol, 1.45 equiv); $NaBH(OAc)_3$ (328 mg, 1.50 mmol, 2.00 equiv); AcOH (90.4 µL, 1.50 mmol, 2.00 equiv).

LED:
448 nm

Temperature:
40 °C

Purification:
Flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc + 5% NEt_3, 20:1).

Yield: mixture of *E*/*Z*-isomers ***E*-5l**/***Z*-5l** (1.71 : 1.00)
and the corresponding constitutional isomers (***E*-5l'**/***Z*-5l'**).
142 mg (584 µmol, 78%); pale yellow oil.

NMR spectra could not be assigned unambiguously

^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.33 (d, *J* = 7.7 Hz, 1H, H_{Ar} or H_{Ar}'), 7.25 (s, 1H, H_{Ar} or H_{Ar}'), 7.12 – 6.93 (m, 10H, H_{Ar} or H_{Ar}'), 6.62 (dd, *J* = 15.7, 5.3 Hz, 2H, H13), 6.47 (d, *J* = 11.4 Hz, 2H, H13'), 6.13 (dt, *J* = 15.5, 6.6 Hz, 2H, H14), 5.69 (dtd, *J* = 11.7, 7.3, 4.7 Hz, 2H, H14'), 2.91 – 2.83 (m, 4H, H7), 2.84 – 2.75 (m, 4H, H7'), 2.66 – 2.53 (m, 24H, H8, H9, H10, H8', H9', H10'), 2.31 (overlapping singlets, look like a t, *J* = 4.1 Hz, 12H, H17, H17'), 2.30 – 2.17 (m, 4H, H15), 2.19 – 2.10 (m, 4H, H15'), 1.88 – 1.75 (m, 16H, H11, H12, H11', H12'), 1.09 (td, *J* = 7.5, 3.0 Hz, 6H, H16), 0.99 (td, *J* = 7.5, 1.8 Hz, 6H, H16').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 138.5, 137.1, 136.7, 136.6, 135.9, 135.6, 135.3, 135.0, 134.9, 134.3, 134.3, 134.1, 133.8, 133.7, 130.6, 130.3, 130.2, 129.8, 129.6, 129.4, 127.9, 127.8, 127.4, 127.2, 126.9, 126.64, 126.59, 126.4, 126.2, 125.9, 57.9, 57.8, 57.6, 57.5, 54.4, 54.3, 33.4, 33.2, 33.0, 32.9, 26.5, 26.5, 23.6, 21.9, 21.24, 21.20, 21.17, 14.49, 14.47, 14.00, 13.99.

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{17}H_{26}N^+$: 244.2060; found 244.2058.

Phenethylamine **5m**

Starting materials:
6-Methoxyphthalazine (**1f**) (120 mg, 750 µmol, 1.00 equiv); **BDLA** (3.80 mg, 18.6 µmol, 2.49 mol %); pyrrolidine (**7a**) (74.7 µL, 900 µmol, 1.20 equiv); butyraldehyde (**6a**) (100 µL, 1.09 mmol, 1.45 equiv); $NaBH(OAc)_3$ (328 mg, 1.50 mmol, 2.00 equiv); AcOH (90.4 µL, 1.50 mmol, 2.00 equiv).

LED:
448 nm

Temperature:
40 °C

Purification:
Flash column chromatography (2 times) (SiO_2: 20 g, cyclohexane/EtOAc + 5% NEt_3, 10:1).

Yield: mixture of *E*/*Z*-isomers ***E*-5m**/***Z*-5m** (2.95 : 1.00)
and the corresponding constitutional isomers (***E*-5m'**/***Z*-5m'**).
142.4 mg (549 µmol, 73%); pale yellow oil.

NMR spectra could not be assigned unambiguously

***E*-5m** and ***E*-5m'**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.35 (d, *J* = 8.2 Hz, 1H, H1 or H2 or H3 or H4), 7.07 (dd, *J* = 10.4, 8.8 Hz, 1H, H1 or H2 or H3 or H4), 6.98 – 6.95 (m, 2H, H1 or H2 or H3 or H4), 6.79 – 6.68 (m, 2H, H1 or H2 or H3 or H4), 6.59 (dd, *J* = 19.4, 15.6 Hz, 2H, H13), 6.14 (dt, *J* = 15.5, 6.6 Hz, 1H, H14), 6.03 (dt, *J* = 15.5, 6.6 Hz, 1H, H14), 3.81 – 3.77 (m, 6H, H17), 2.91 – 2.73 (m, 4H, H7), 2.66 – 2.54 (m, 12H, H8, H9, H10), 2.30 – 2.18 (m, 4H, H15), 1.85 – 1.77 (m, 8H, H11, H12), 1.09 (td, *J* = 7.4, 5.6 Hz, 6H, H16).

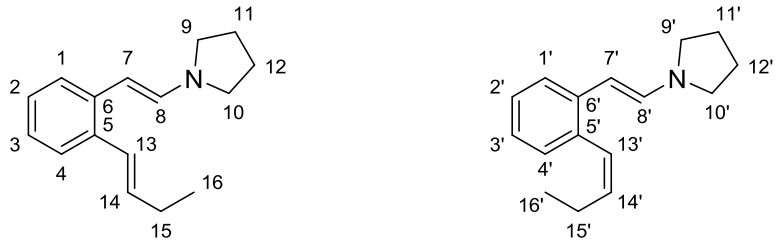
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 158.6 (C_{Ar}-OMe), 158.3 (C_{Ar}-OMe), 140.14, 138.67, 137.94, 137.83, 134.7 (14), 132.8 (14), 130.87, 130.63, 130.33, 129.75, 129.72, 129.27, 127.13 (C4), 126.4 (C13), 125.8 (C13), 115.22, 115.13, 115.05, 112.82, 112.30, 112.06, 111.08, 110.99, 58.0 (C8), 57.6 (C8), 55.4 (C17), 55.3 (C17), 54.4 (C9, C10), 33.5 (C7), 32.5 (C7), 26.5 (C15), 26.4 (C15), 23.6 (C11, C12), 14.1 (C16), 13.9 (C16).

***Z*-5m** and ***Z*-5m'**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.35 (d, *J* = 8.2 Hz, 1H, H1' or H2' or H3' or H4'), 7.07 (dd, *J* = 10.4, 8.8 Hz, 1H, H1' or H2' or H3' or H4'), 6.98 – 6.95 (m, 2H, H1' or H2' or H3' or H4'), 6.79 – 6.68 (m, 2H, H1' or H2' or H3' or H4'), 6.44 (dd, *J* = 17.2, 11.4 Hz, 2H, H13'), 5.74 – 5.60 (m, 2H, H14'), 3.81 – 3.77 (m, 6H, H17'), 2.91 – 2.73 (m, 4H, H7'), 2.66 – 2.54 (m, 12H, H8', H9', H10'), 2.14 (pd, *J* = 7.4, 1.5 Hz, 4H, H15'), 1.85 – 1.77 (m, 8H, H11', H12'), 0.99 (td, *J* = 7.5, 4.4 Hz, 6H, H16').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 158.7 (C'_{Ar}-OMe), 140.14, 138.67, 137.94, 137.83, 135.3 (C14'), 134.6 (C14'), 130.87, 130.63, 130.33, 129.75, 129.72, 129.27, 127.1 (C13'), 126.6 (C13'), 115.22, 115.13, 115.05, 112.82, 112.30, 112.06, 111.08, 110.99, 57.7 (C8'), 57.3 (C8'), 55.33 (C17'), 55.30 (C17'), 54.3 (C9', C10'), 33.7 (C7'), 32.6 (C7'), 23.6 (C11', C12'), 21.9 (C15'), 21.9 (C15'), 14.5 (C16'), 14.4 (C16').

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{17}H_{26}NO^+$: 260.2009; found: 260.2012.

Phenethylenamine **4a**



The reaction was set up in a nitrogen filled glovebox.
Phthalazine (**1a**) (105 mg, 795 µmol, 1.00 equiv) and **BDLA** (4.00 mg, 19.6 µmol, 2.47 mol %) were suspended in THF (dry, degassed) (2.00 mL). Then pyrrolidine (**7a**) (79.6 µL, 960 µmol, 1.21 equiv) was added (yellow suspension turned colorless). The reaction vessel was sealed and the reaming steps of the reaction were carried out in a fume hood. The reaction mixture was irradiated irradiated by a 425 – 430 nm LED and butyraldehyde (**6a**) (110 µL, 1.20 mmol, 1.50 equiv) was added dropwise. Gas evolution started almost immediately. The yellow solution was stirred at rt for 15 h. Afterwards all volatile compounds were removed under vacuum (rt, <1 mbar, recondensed into a liquid N_2 cooling trap). The remaining orange solution was purified by distillation (Kugelrohr-Apperatus). A pale yellow oil was obtained (150 °C at $4x10^{-2}$ mbar).

Yield: mixture of *E*/*Z*-isomers ***E*-4a**/***Z*-4a** (1.00 : 2.60)
95.2 mg (418 µmol, 54%); pale yellow oil.

***E*-4a:**
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.35 – 7.29 (m, 1H, H2), 7.25 (d, *J* = 6.4 Hz, 1H, H1), 7.14 – 7.06 (m, 1H, H4), 7.00 – 6.91 (m, 1H, H3), 6.92 (d, *J* = 13.7 Hz, 1H, H8), 6.67 (d, *J* = 15.7 Hz, 1H, H13), 6.09 (dt, *J* = 15.6, 6.5 Hz, 1H, H14), 5.24 (d, *J* = 13.7 Hz, 1H, H7), 3.29 – 3.19 (m, 4H, H9, H10), 2.31 – 2.22 (m, 2H, H15), 1.96 – 1.90 (m, 4H, H11, H12), 1.12 (t, *J* = 7.5 Hz, 3H, H16).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 137.5 (C6), 137.1 (C8), 133.9 (C5), 133.3 (C14), 127.7 (C13), 127.0 (C4), 126.6 (C2), 123.5 (C1), 123.5 (C3), 95.0 (C7), 49.1 (C9, C10), 26.5 (C15), 25.4 (C11, C12), 14.1 (C16).

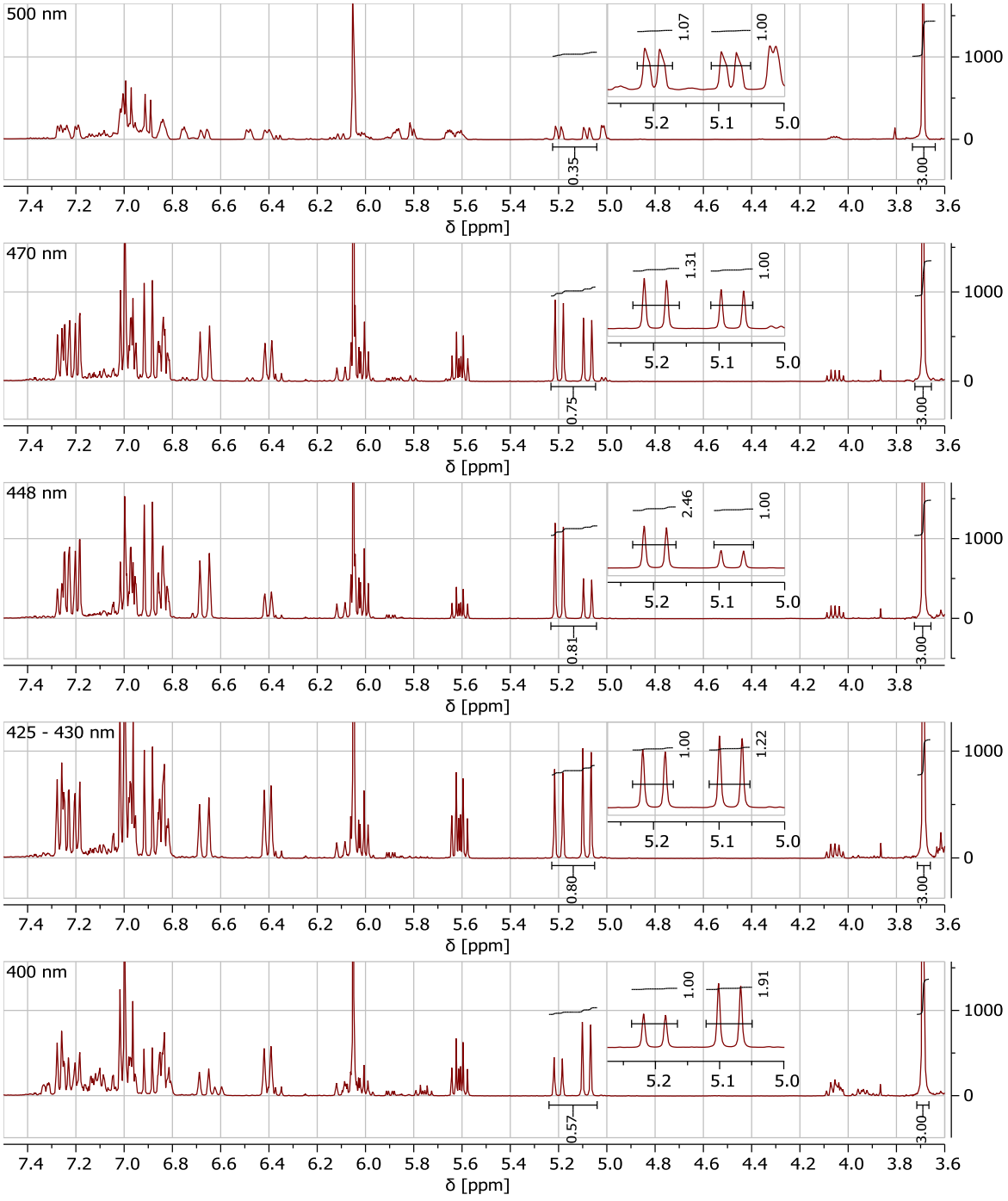
***Z*-4a**:
^{1}H NMR (400 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 7.35 – 7.29 (m, 1H, H1'), 7.14 – 7.06 (m, 2H, H2', H4'), 7.00 (d, *J* = 13.8 Hz, 1H, H8'), 7.00 – 6.91 (m, 1H, H3'), 6.43 (d, *J* = 11.4 Hz, 1H, H13'), 5.67 (dt, *J* = 11.4, 7.4 Hz, 1H, H14'), 5.14 (d, *J* = 13.8 Hz, 1H, H7'), 3.29 – 3.19 (m, 4H, H9', H10'), 2.19 (qd, *J* = 7.4, 1.7 Hz, 2H, H15'), 1.96 – 1.90 (m, 4H, H11', H12'), 1.02 (t, *J* = 7.5 Hz, 3H, H16').

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.03% v/v TMS): δ 138.3 (C6'), 136.6 (C8'), 133.9 (C14'), 133.1 (C5'), 129.7 (C4'), 128.2 (C13'), 127.0 (C2'), 122.5 (C3'), 122.3 (C1'), 95.4 (C7'), 49.1 (C9', C10'), 25.4 (C11', C12'), 22.0 (C15'), 14.6 (C16').

HRMS (ESI) m/z $[M+H]^+$ calc. for $C_{16}H_{22}N^+$: 228.1747; found: 228.1751.

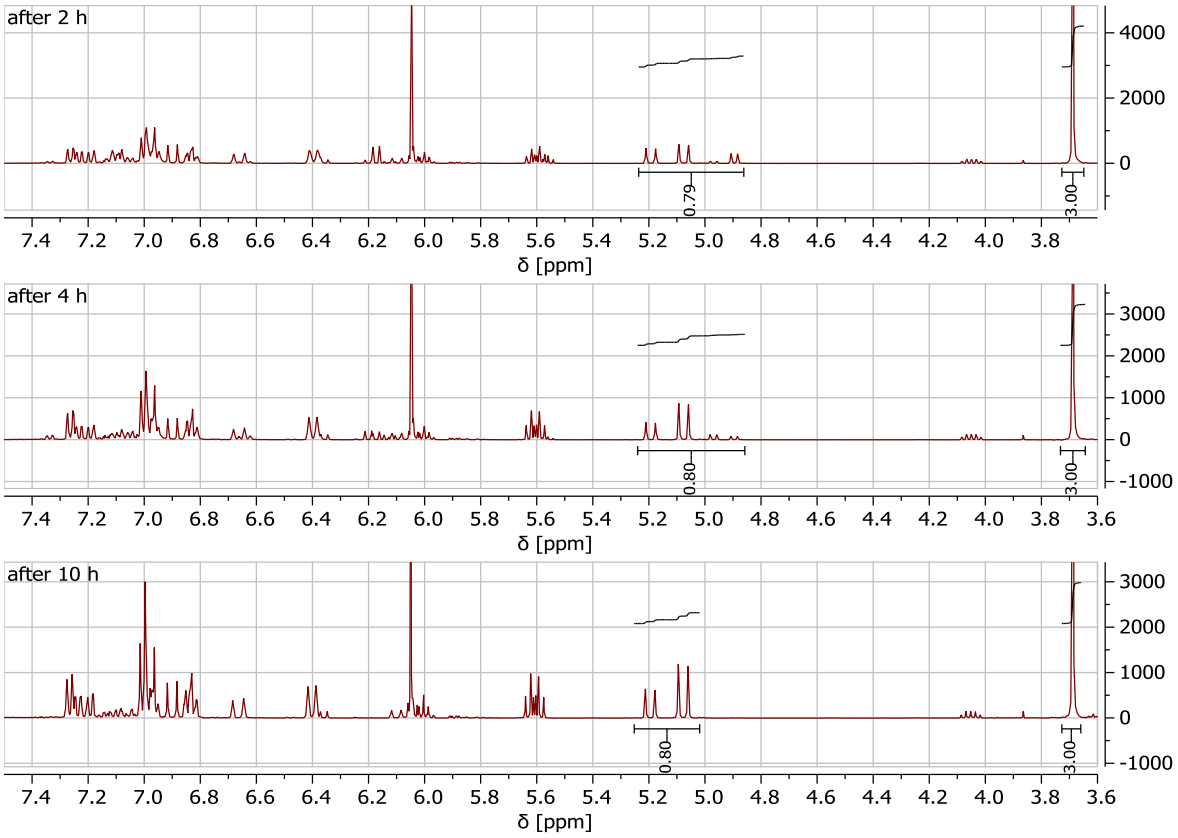
Optimization of Irradiation Wavelength for the Domino IEDDA/PIRO Reaction:

The reaction was set up in a nitrogen filled glovebox.
Phthalazine (**1a**) (49.3 mg, 375 µmol, 1.00 equiv), 1,3,5-trimethoxybenzene (TMB) (21.0 mg, 124 µmol, 0.333 equiv), and **BDLA** (1.90 mg, 9.32 µmol, 2.49 equivl) were suspended in THF-d_8 (dry, degassed) (1.00 mL). Then, pyrrolidine (**7a**) (37.3 µL, 450 µmol, 1.20 equiv) was added, the reaction vessel was sealed and the reaction was continued in a fume hood. The reaction mixture was heated to 30 °C and irradiated with a LED. Then butyraldehyde (**6a**) (50.0 µL, 544 µmol, 1.45 equiv) was added. Gas evolution was observed after a few minutes. The reaction was kept irradiated overnight. Afterwards the vessel was sealed, put back into the glovebox and a NMR sample was prepared.



Isomerization Monitoring of IEDDA/PIRO Product:

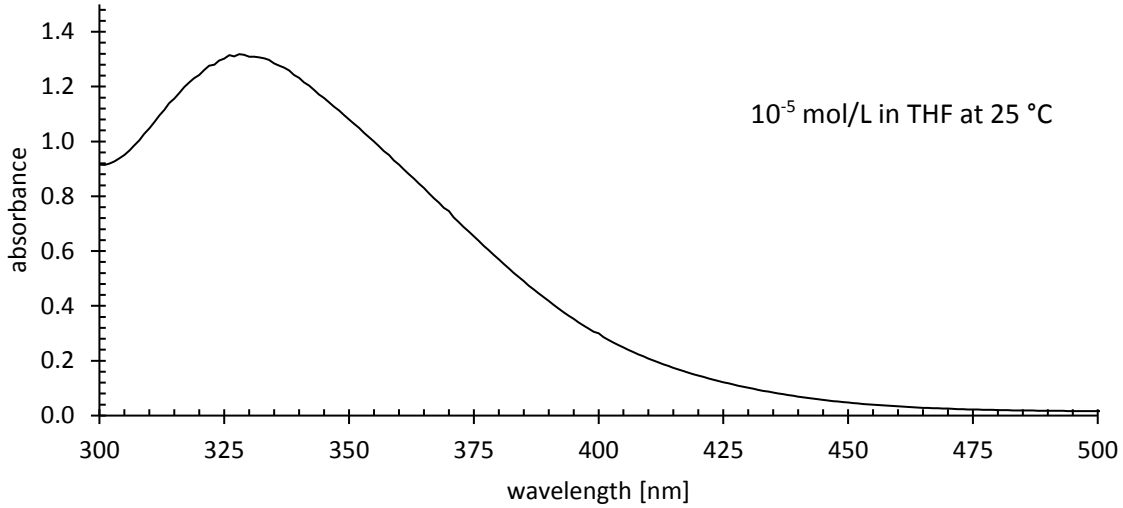
The reaction was set up in a nitrogen filled glovebox.
Phthalazine (**1a**) (148 mg, 1.13 mmol, 1.00 equiv), 1,3,5-trimethoxybenzene (TMB) (63.0 mg, 371 µmol, 0.333 equiv), and **BDLA** (5.70 mg, 28.0 µmol, 2.49 mol %) were suspended in THF-d_8 (dry, degassed) (3.00 mL). Then, pyrrolidine (**7a**) (112 µL, 1.35 mmol, 1.20 equiv) was added, the reaction vessel was sealed and the reaction was continued in a fume hood. The reaction mixture was heated to 30 °C and irradiated with a 425 – 430 nm LED. Then butyraldehyde (**6a**) (150 µL, 1.63 mmol, 1.45 equiv) was added. Gas evolution was observed after a few minutes. Aliquots (0.70 mL) were taken in intervals (2 h, 4 h, 10 h) under Schlenk conditions.



Degradation of BDLA-Phthalazine Complex by Irradiation:

UV/Vis Spectrum of BDLA-Phthalazine Complex

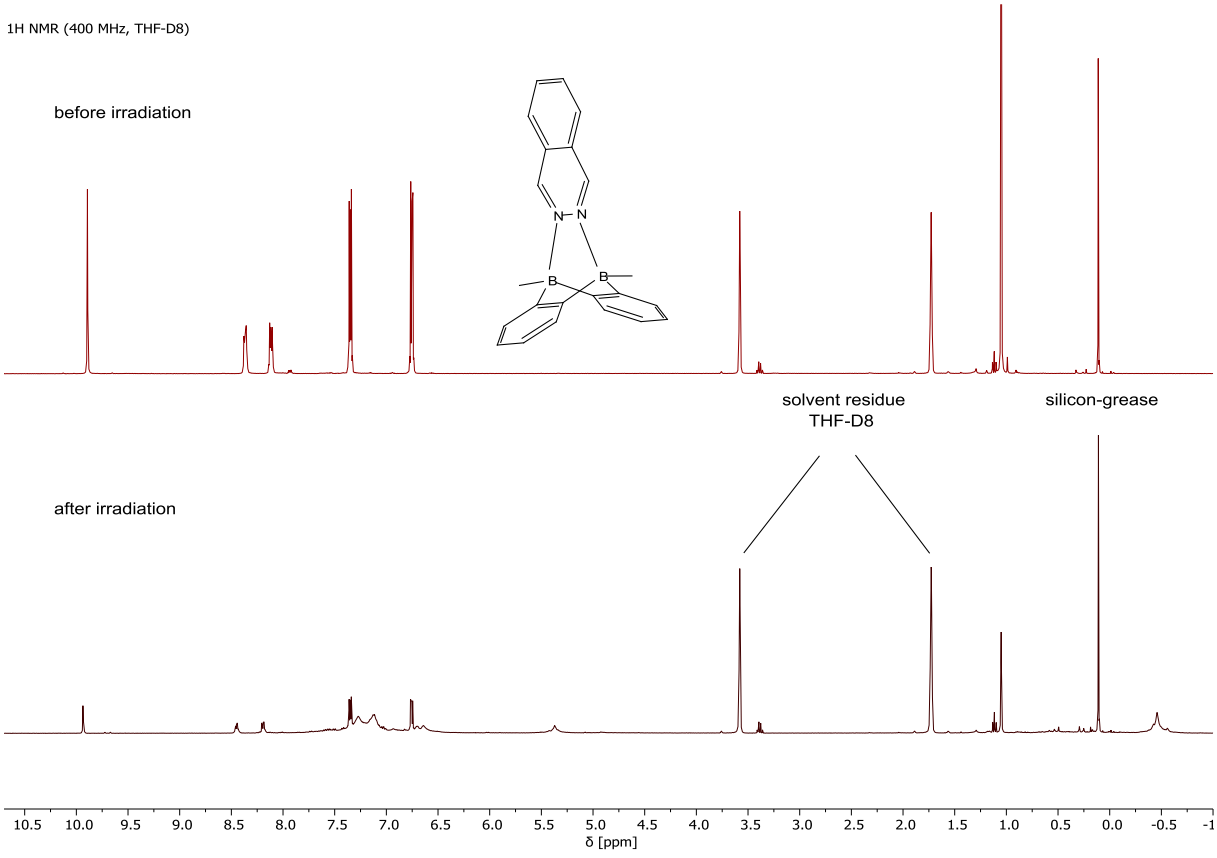
Sample was prepared in a nitrogen filled glovebox.



NMR analysis of BDLA-Phthalazine Complex under irradiation.

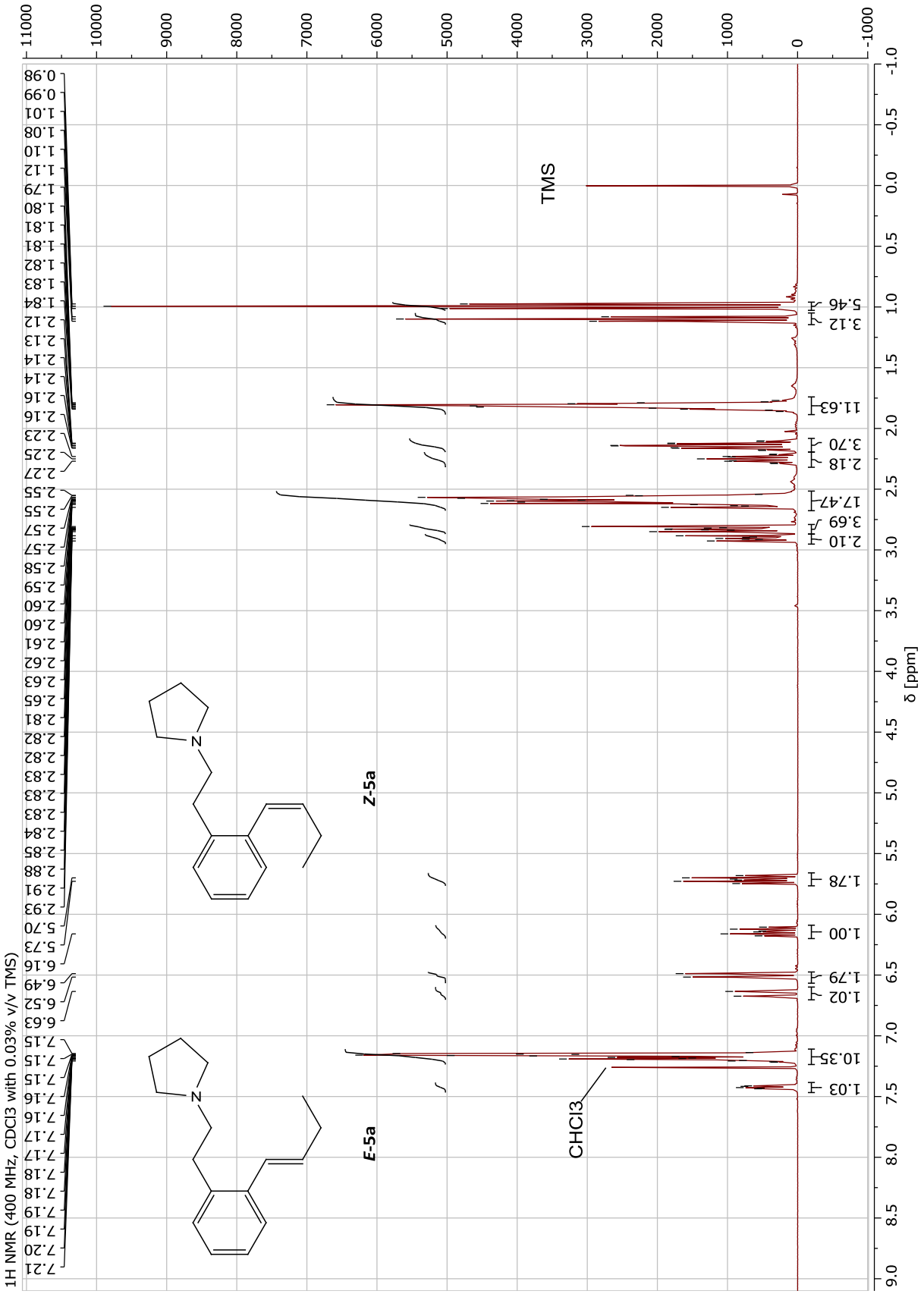
Reaction was set up in a nitrogen filled glovebox.

Phthalazine (**1a**) (3.30 mg, 25.1 µmol, 1.00 equiv) and **BDLA** (5.10 mg, 25.0 µmol, 1.00 equiv) were suspended in THF-d_8 (dry, degassed) (1.00 mL) in a screw cap NMR tube, resulting in a saturated solution. A ^{1}H NMR was measured before it was irradiated by a 425 – 430 nm LED for 15 h at 30 °C. Afterwards a second ^{1}H NMR was measured.

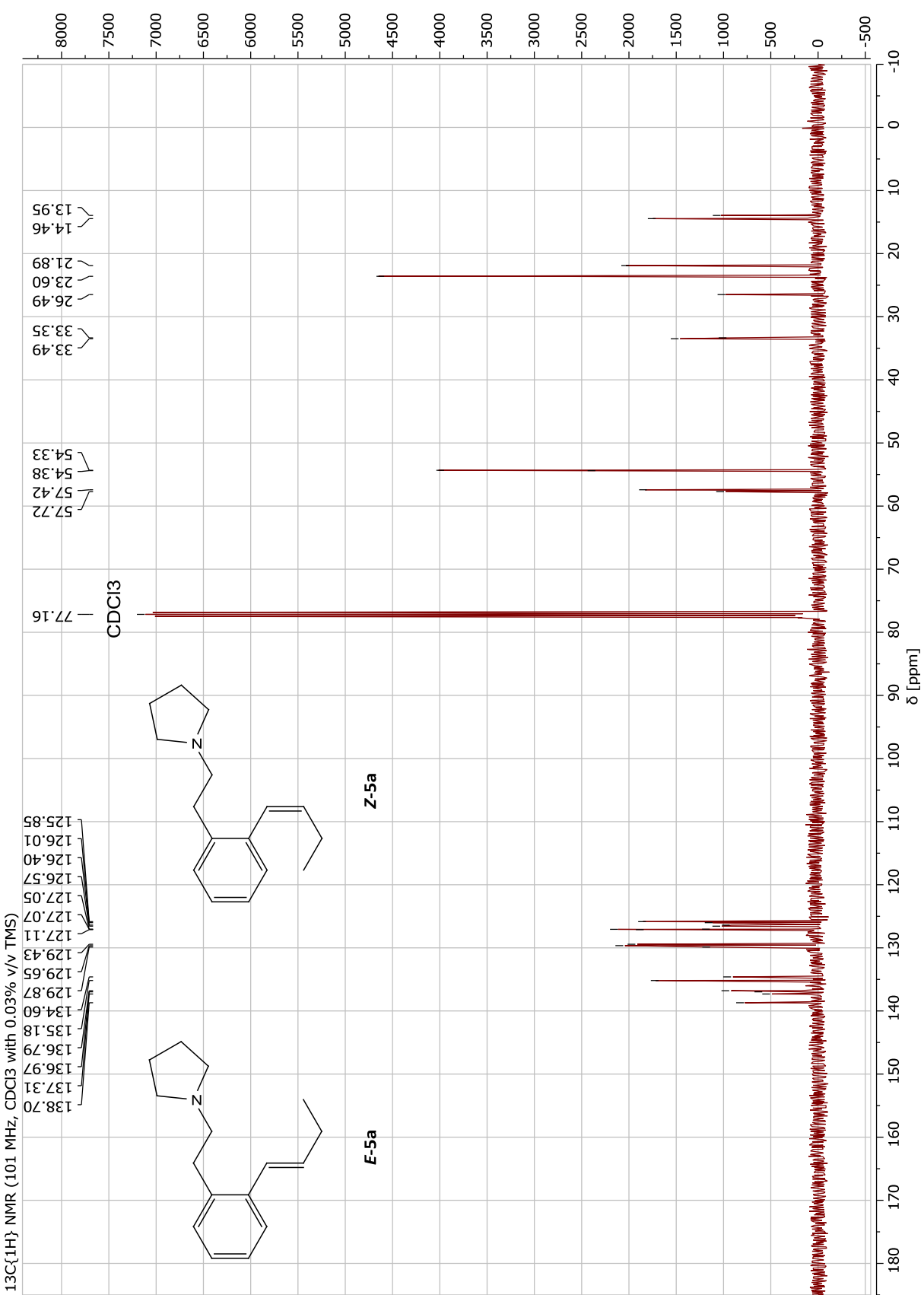


NMR Spectra:

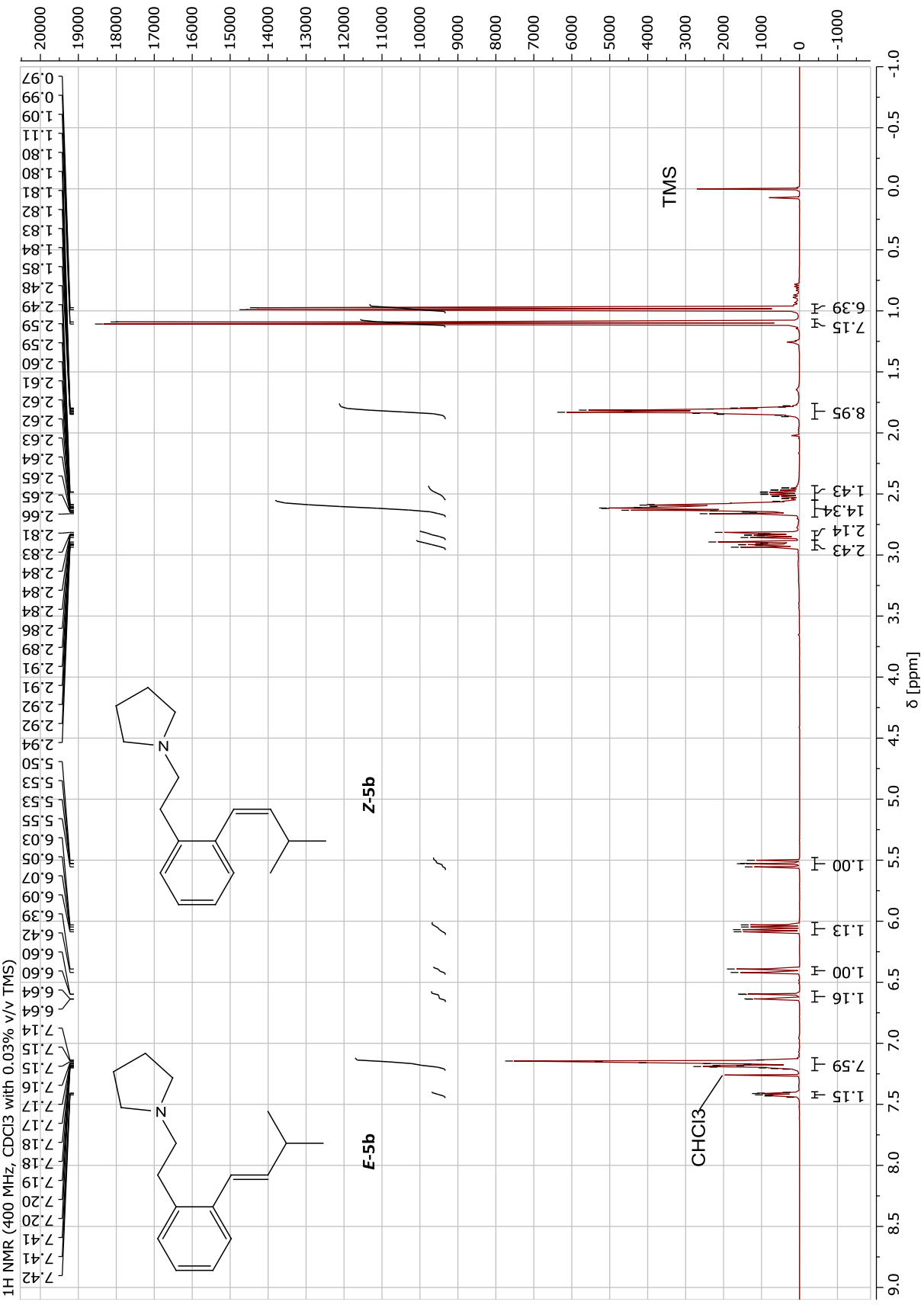
^{1}H NMR of 5a



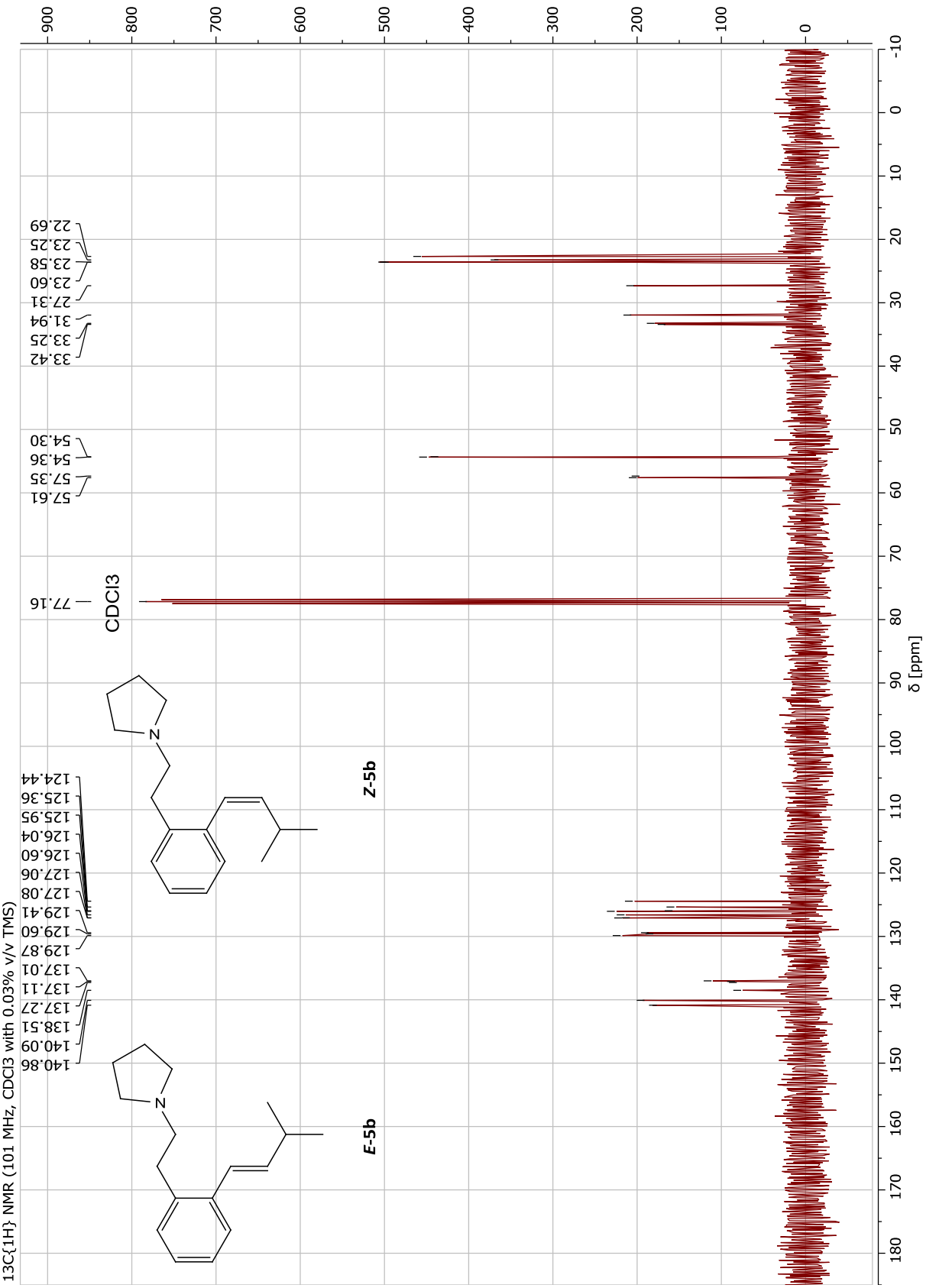
$^{13}C\{^{1}H\}$ NMR of 5a



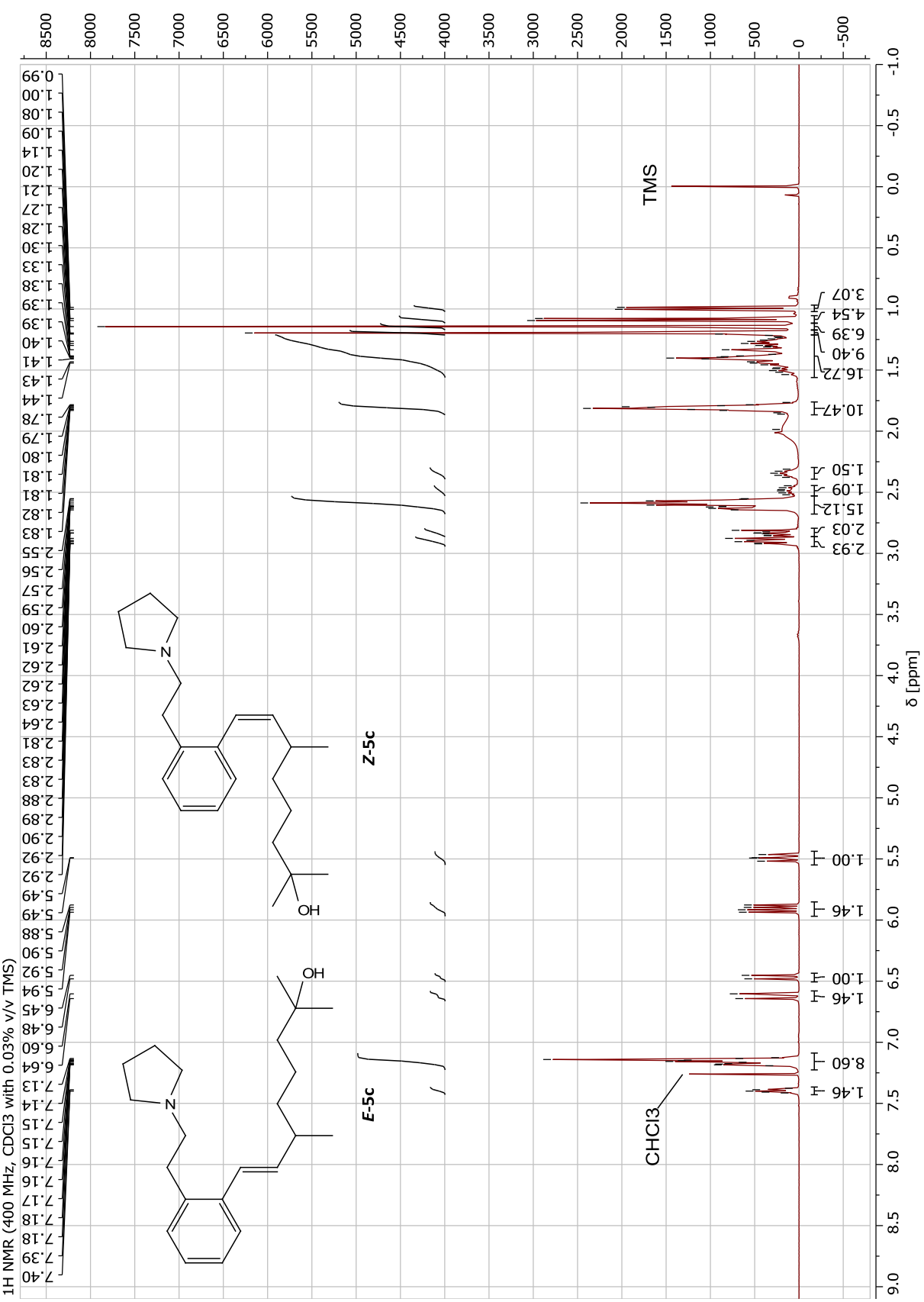
^{1}H NMR of 5b


1H NMR (400 MHz, CDCl3 with 0.03% v/v TMS)
δ [ppm]
TMS
CHCl3
E-5b
Z-5b
N
N
7.42
7.41
7.20
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.15
7.15
7.14
6.64
6.64
6.60
6.60
6.42
6.39
6.09
6.07
6.05
6.03
5.55
5.53
5.53
5.50
2.94
2.92
2.92
2.91
2.91
2.89
2.86
2.84
2.84
2.84
2.83
2.81
2.66
2.65
2.65
2.64
2.63
2.62
2.62
2.61
2.60
2.60
2.59
2.59
2.49
2.48
1.85
1.84
1.83
1.82
1.81
1.80
1.80
1.11
1.09
0.99
0.97
1.15
7.59
1.16
1.00
1.13
1.00
6.39
7.15
8.95
1.43
14.34
2.14
2.43

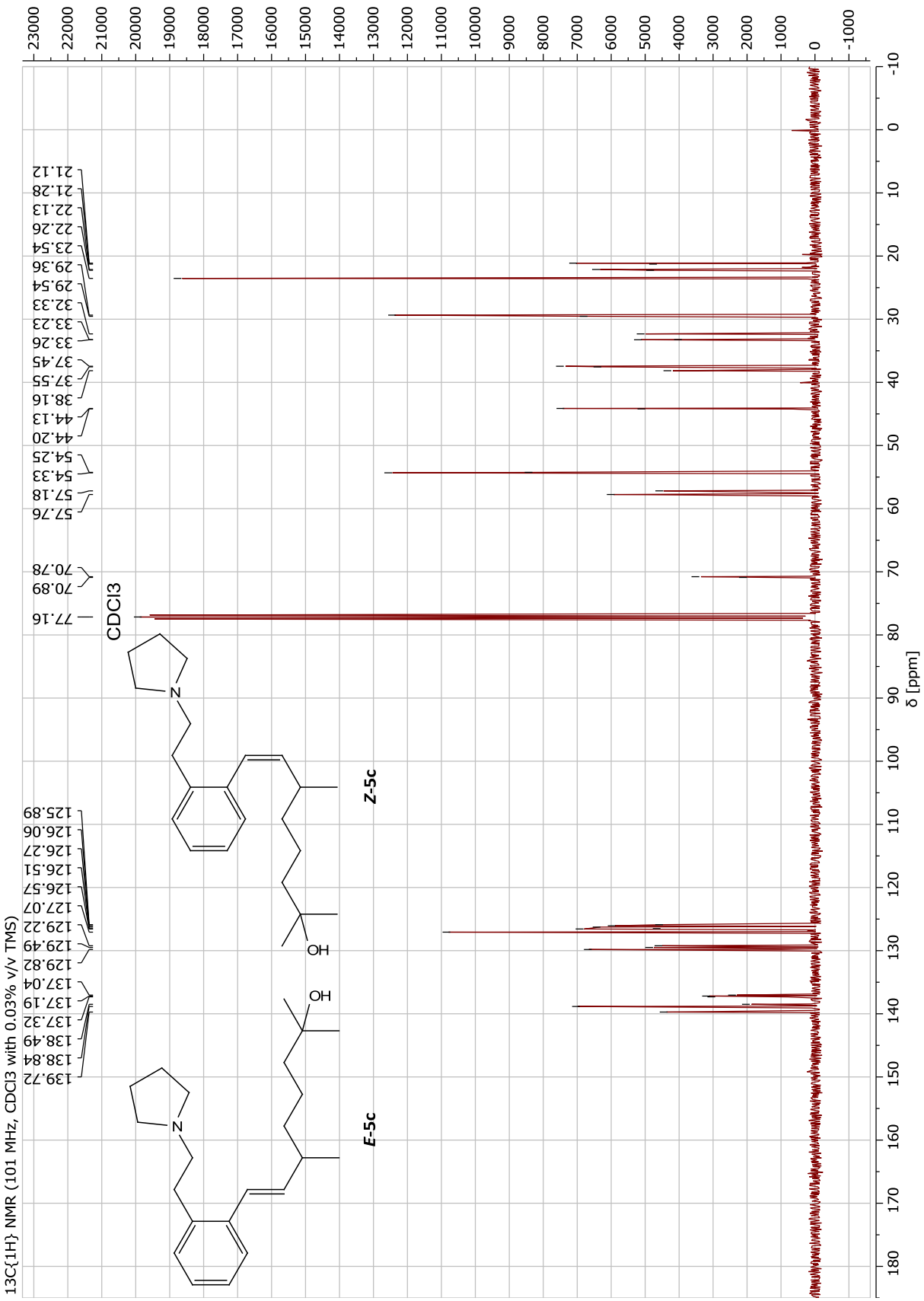
$^{13}C\{^{1}H\}$ NMR of 5b



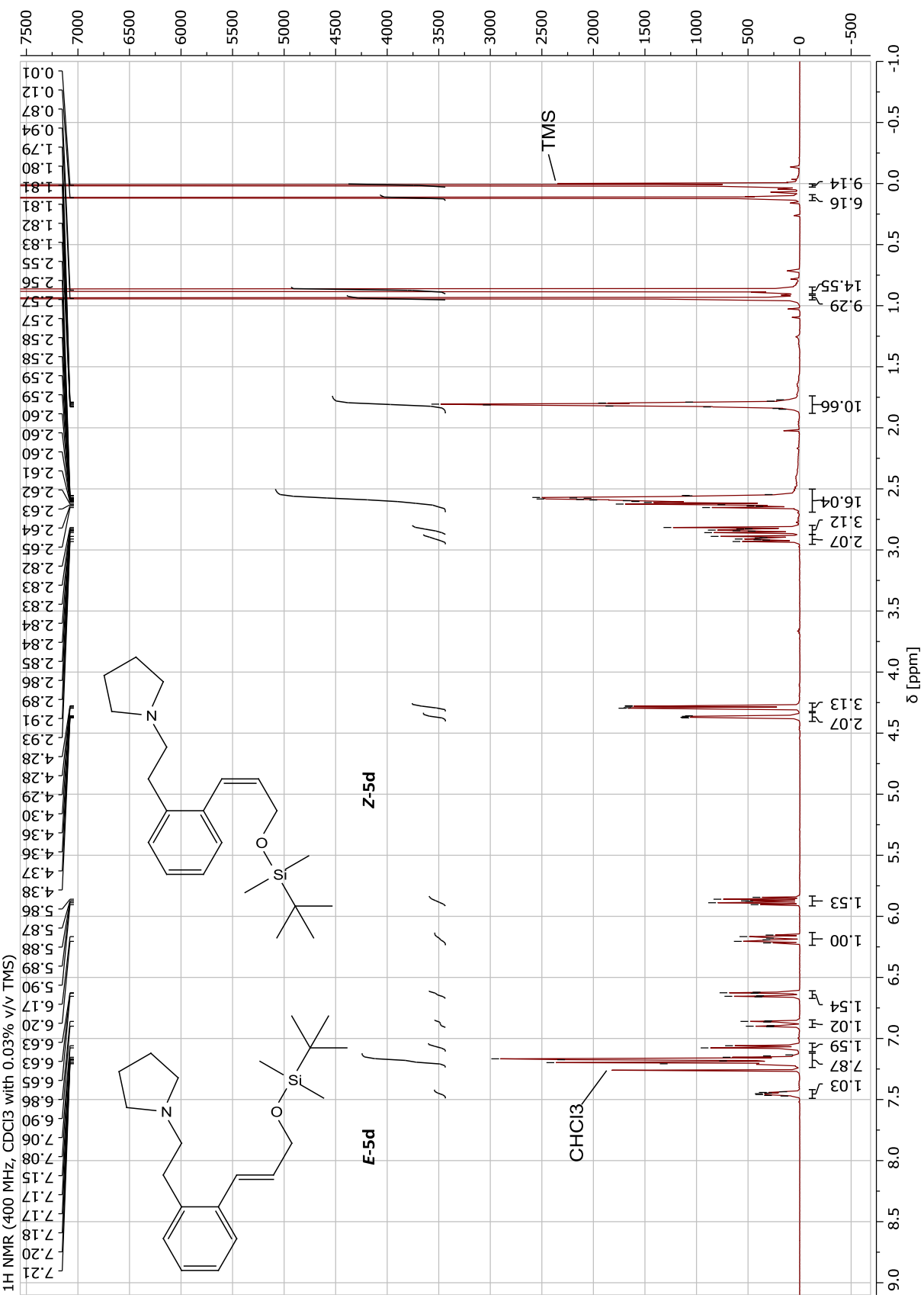
^{1}H NMR of 5c



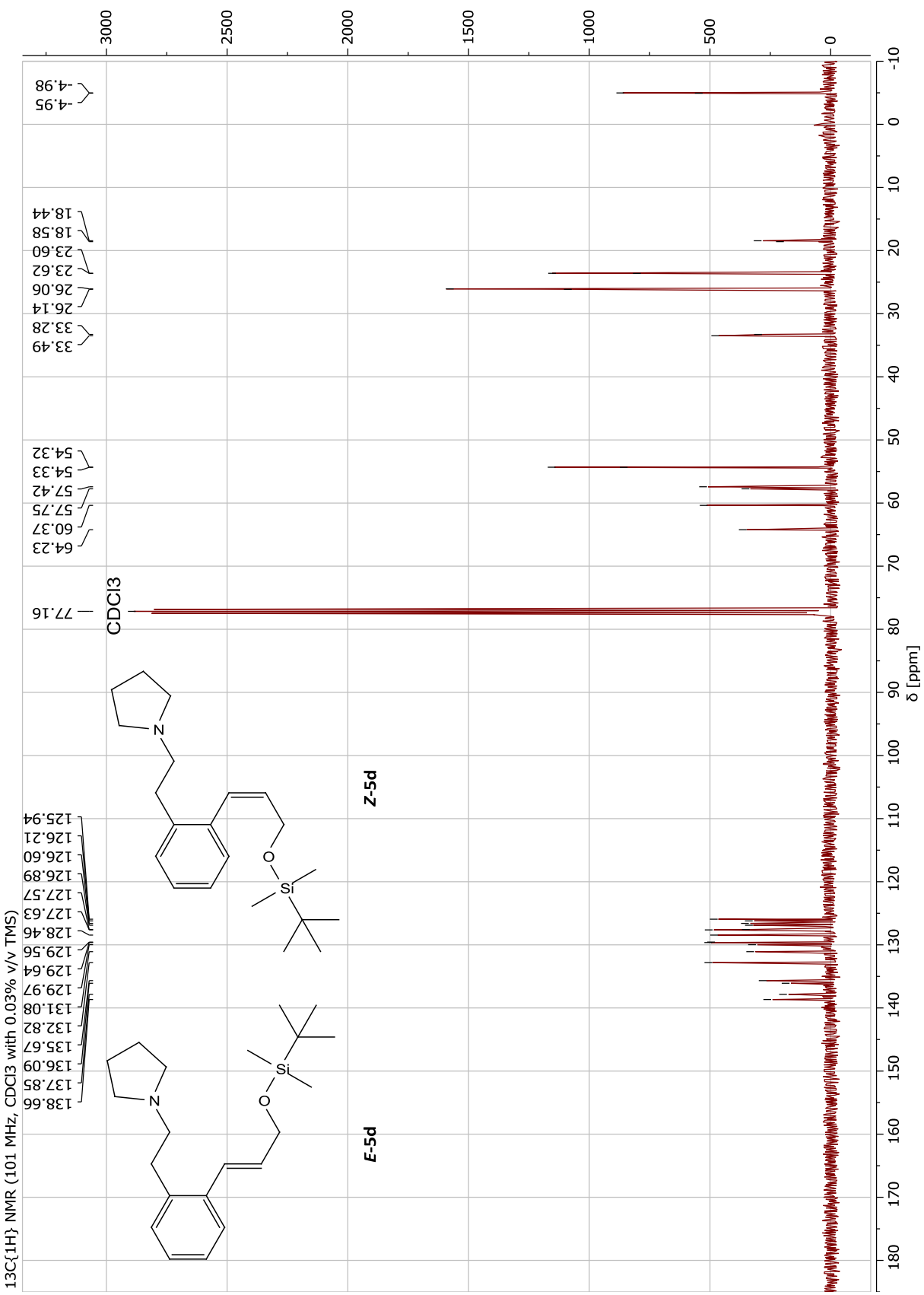
$^{13}C\{^{1}H\}$ NMR of 5c



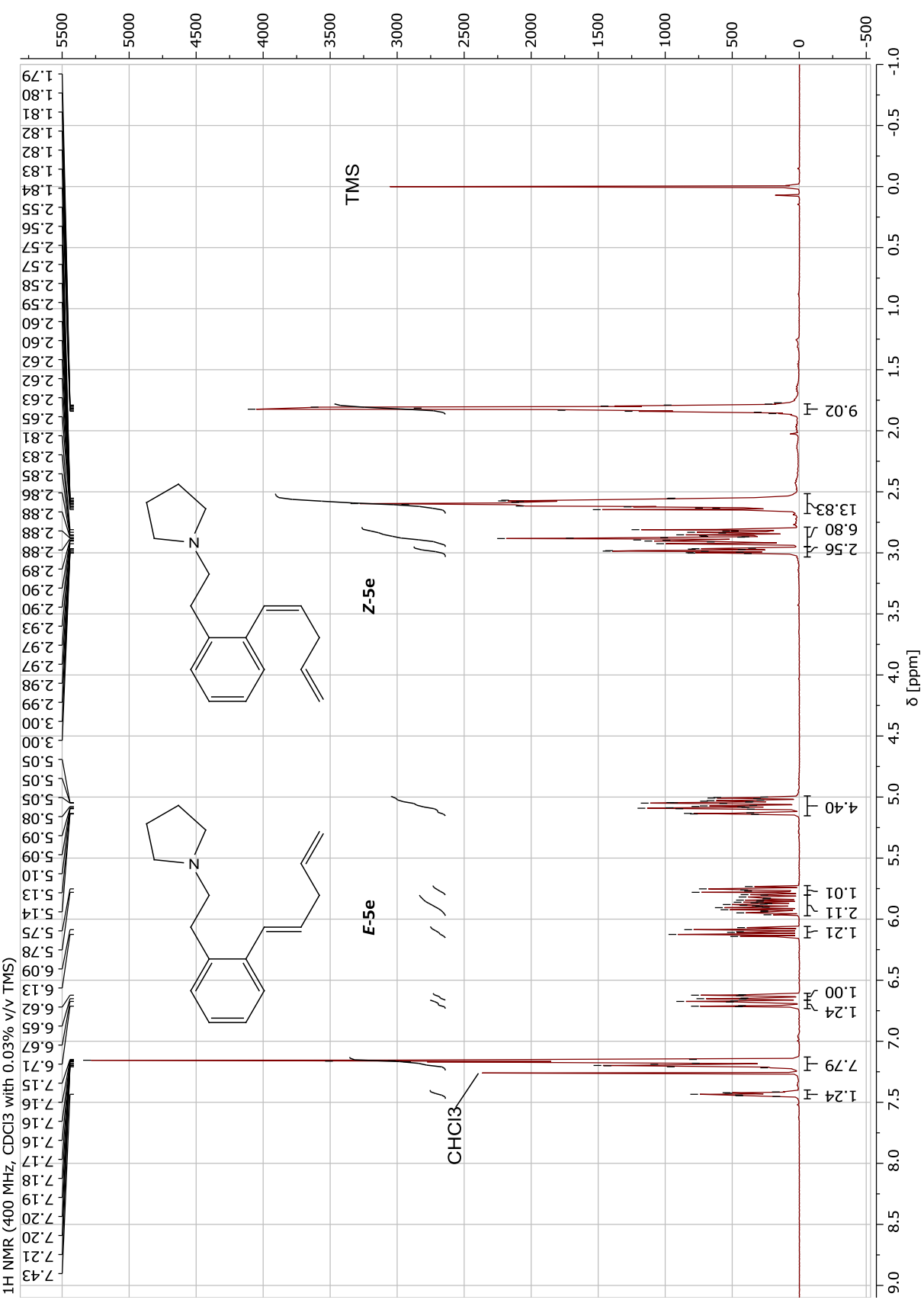
^{1}H NMR of 5d



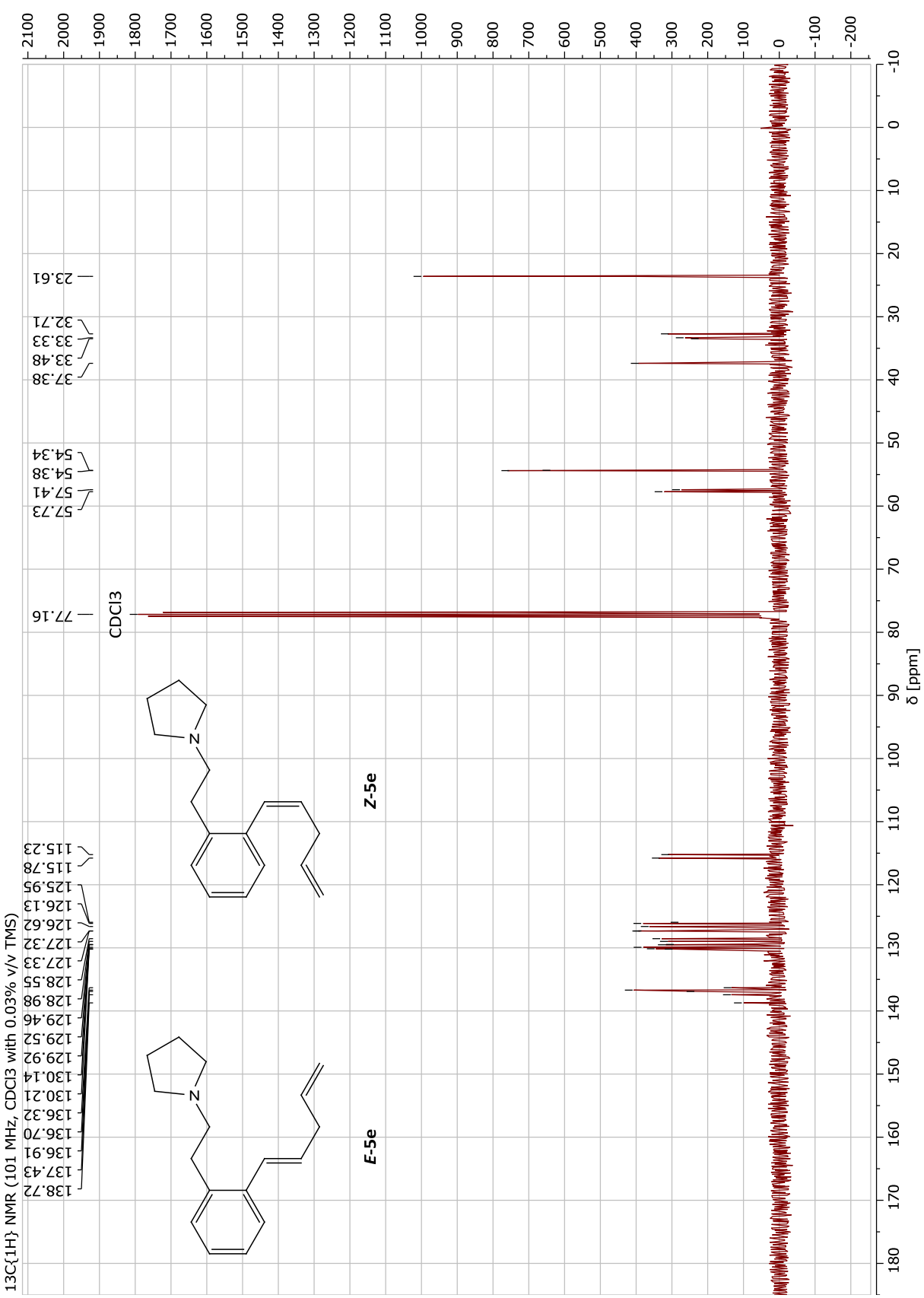
$^{13}C\{^{1}H\}$ NMR of 5d



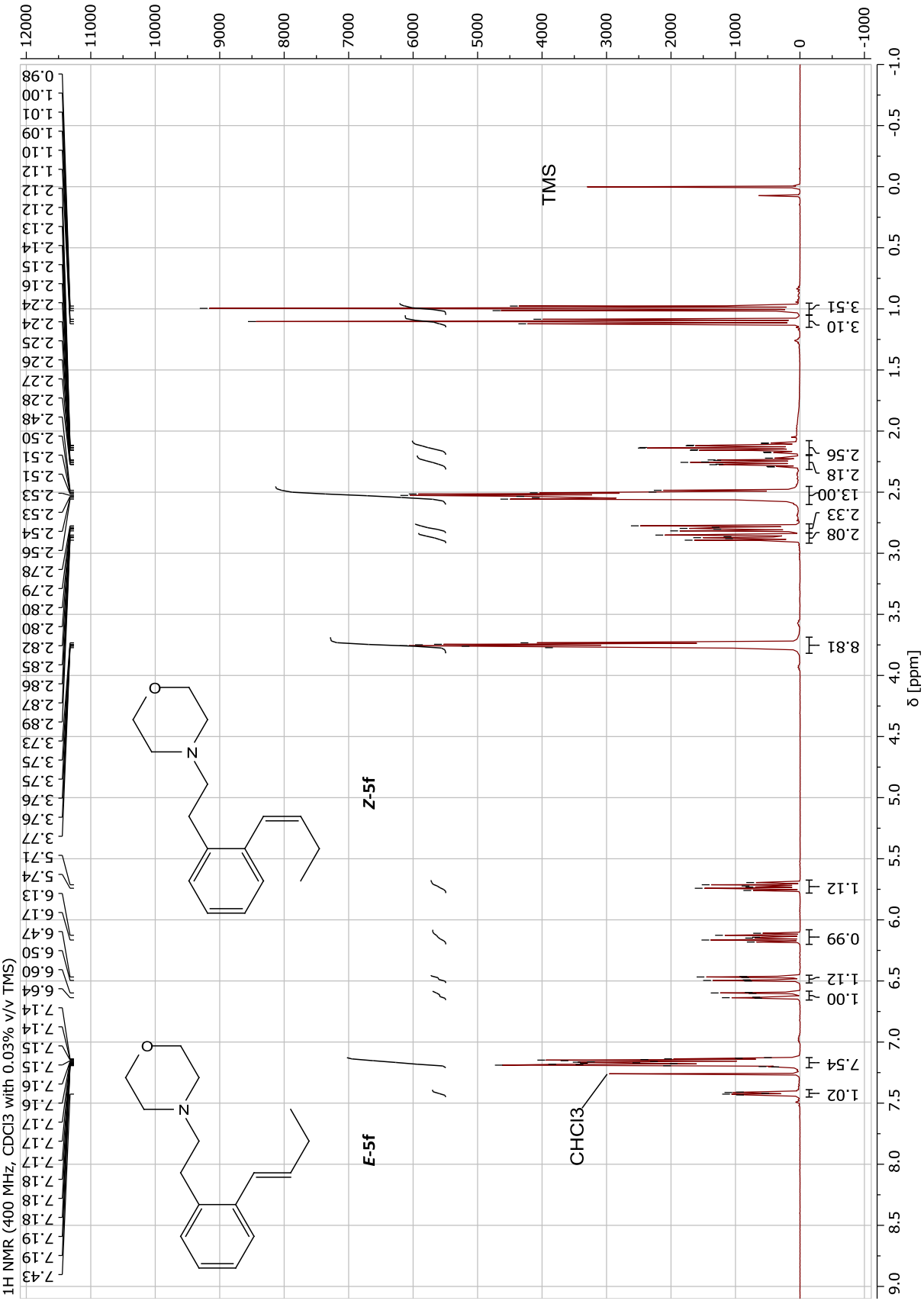
^{1}H NMR of 5e


1H NMR (400 MHz, CDCl3 with 0.03% v/v TMS)
δ [ppm]
TMS
CHCl3
E-5e
Z-5e
N
N
9.02
13.83
6.80
2.56
4.40
1.01
2.11
1.21
1.24
1.00
7.79
1.24

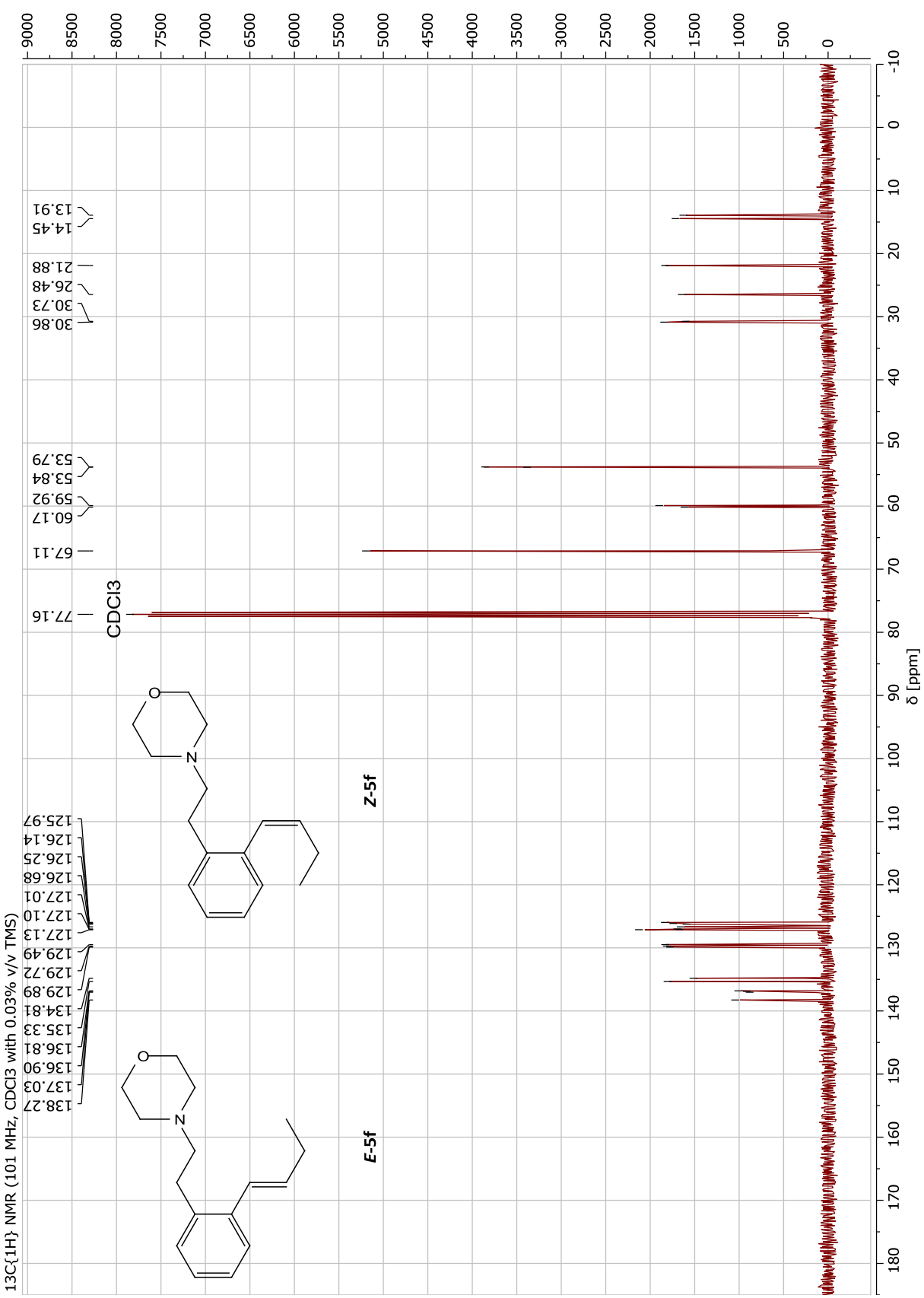
$^{13}C\{^{1}H\}$ NMR of 5e



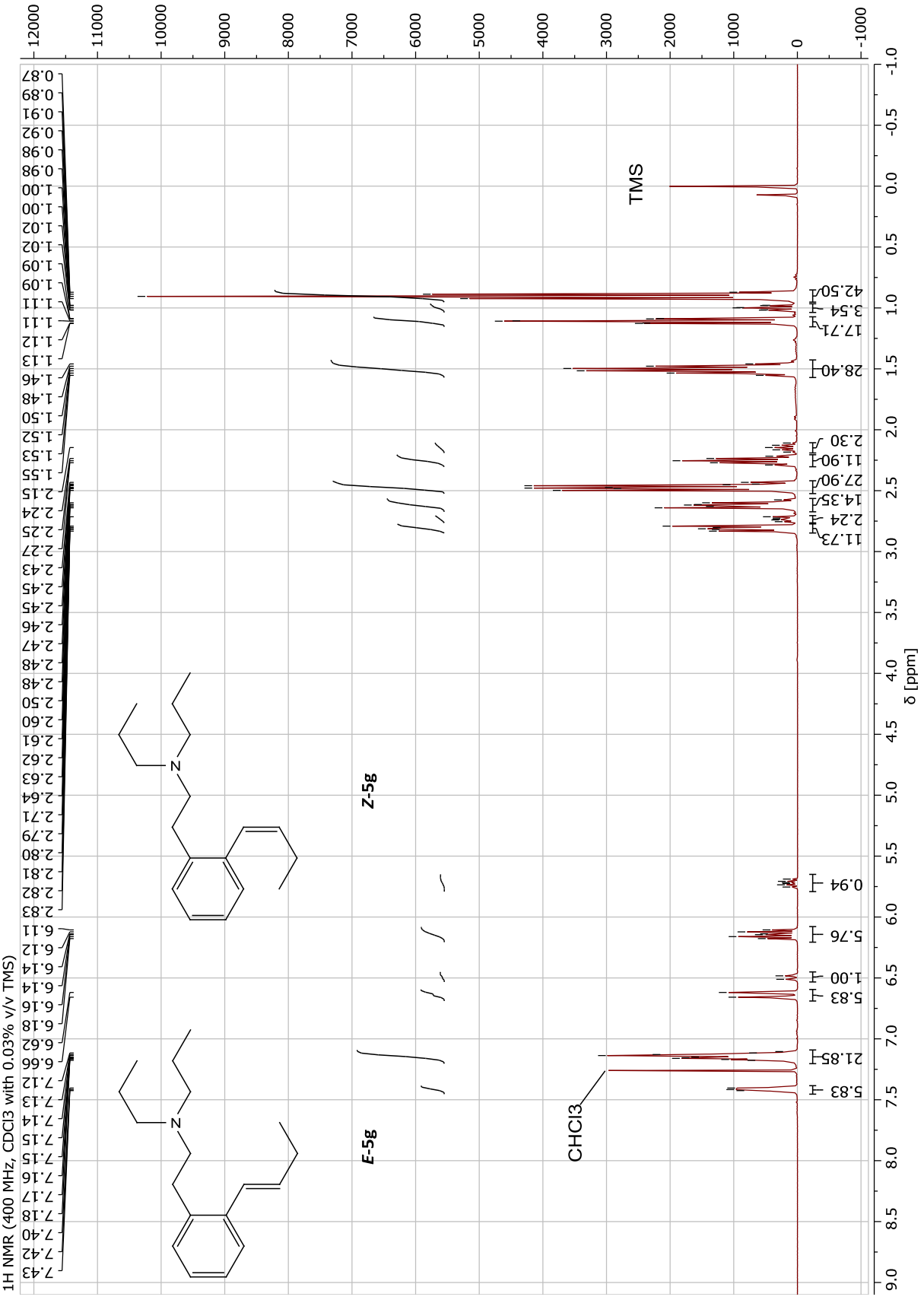
^{1}H NMR of 5f


1H NMR (400 MHz, CDCl3 with 0.03% v/v TMS)
δ [ppm]
TMS
CHCl3
E-5f
Z-5f
8.81
3.51
3.10
2.56
2.18
13.00
2.33
2.08
1.12
0.99
1.12
1.00
7.54
1.02

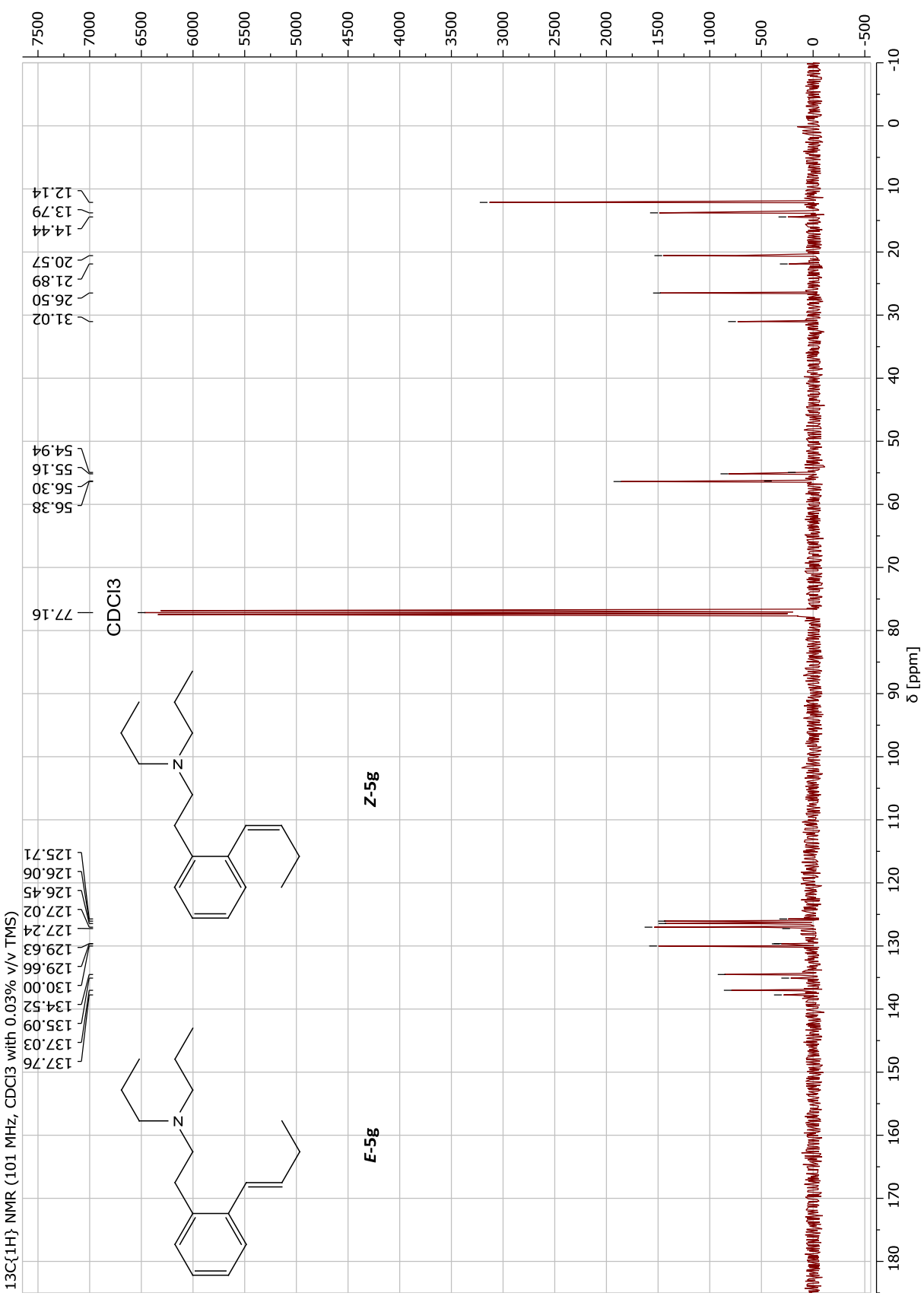
$^{13}C\{^{1}H\}$ NMR of 5f



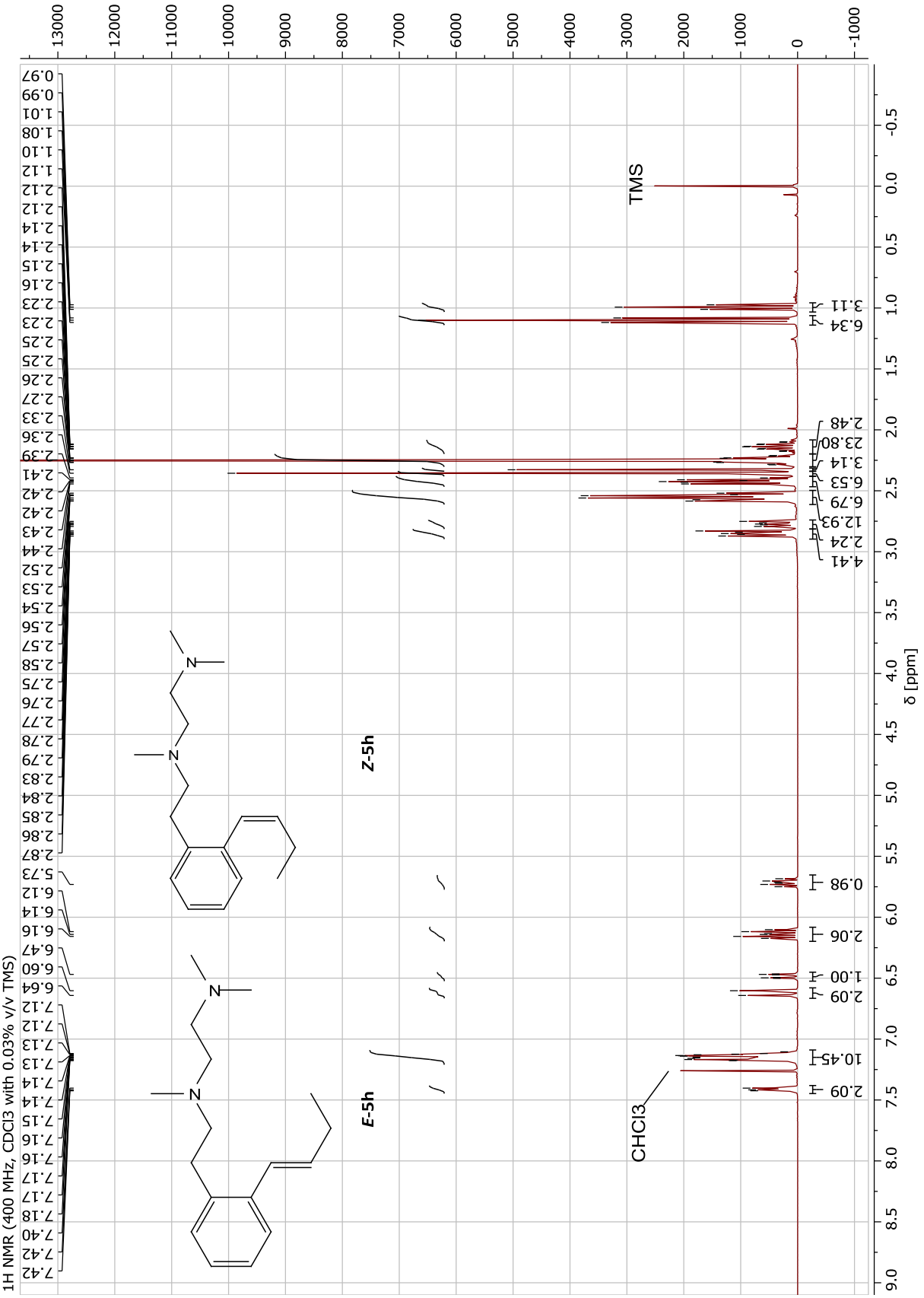
^{1}H NMR of 5g



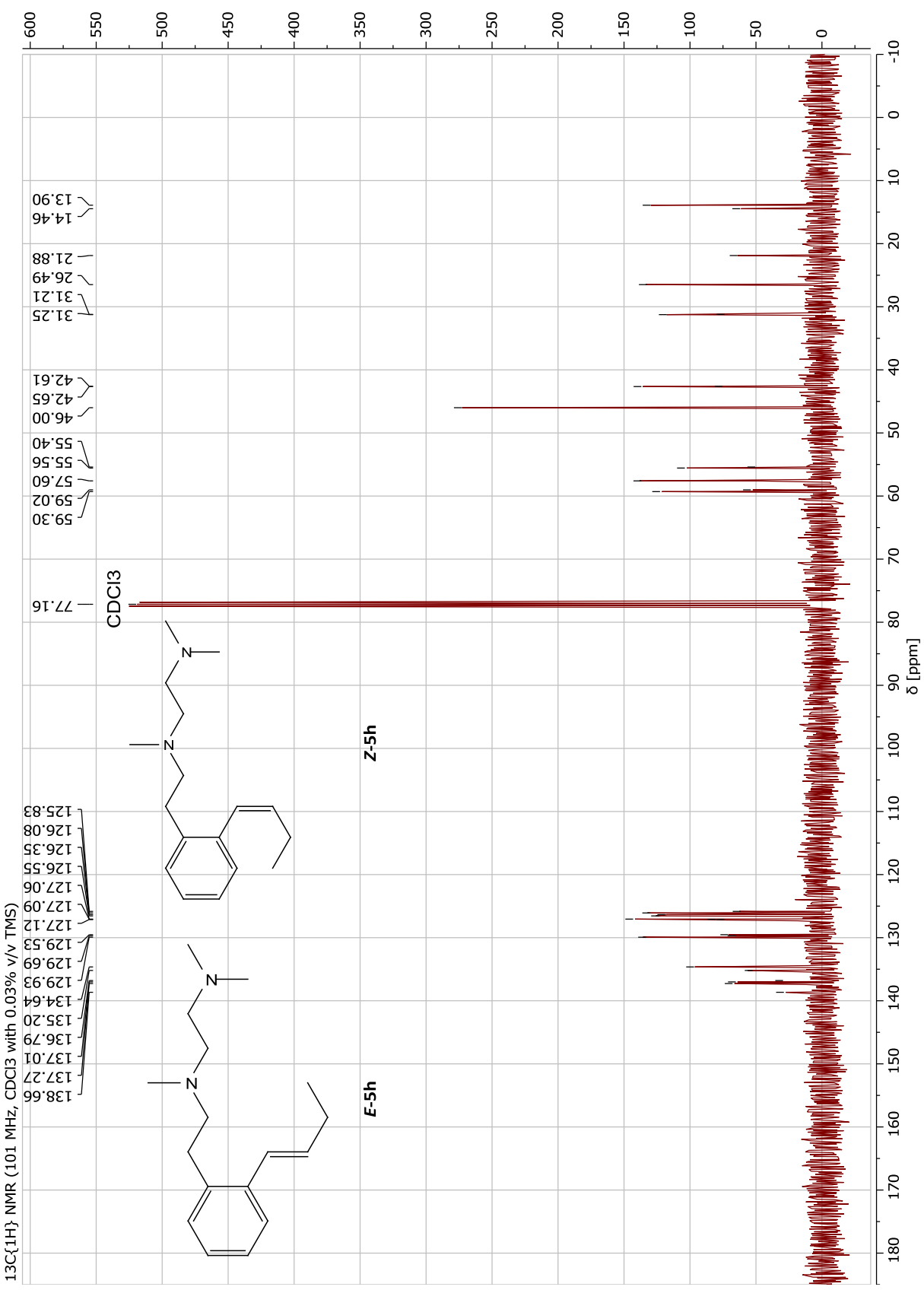
$^{13}C\{^{1}H\}$ NMR of 5g



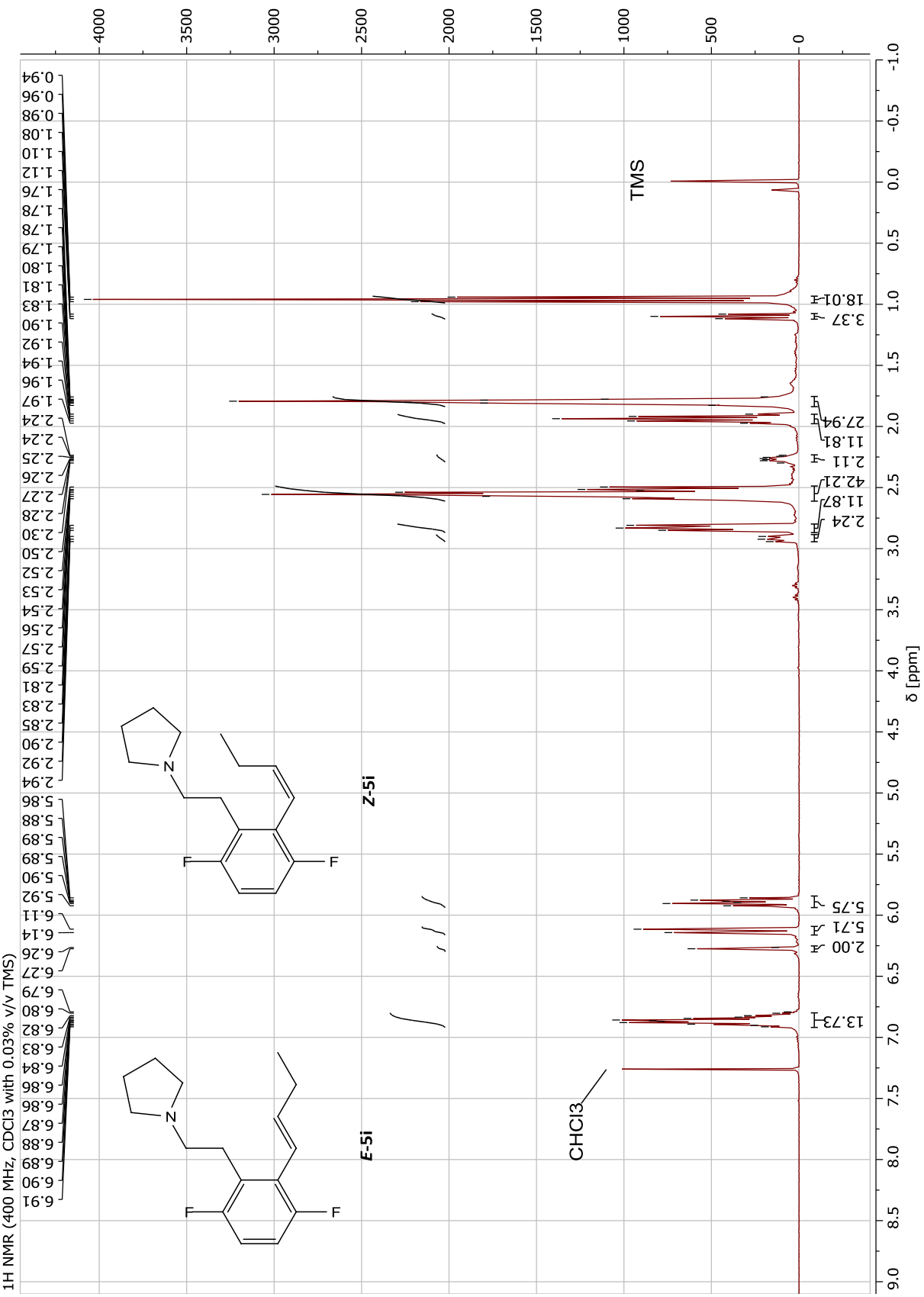
^{1}H NMR of 5h


1H NMR (400 MHz, CDCl3 with 0.03% v/v TMS)
δ [ppm]
TMS
CHCl3
Z-5h
E-5h
6.34
3.11
2.48
23.80
3.14
6.53
6.79
12.93
2.24
4.41
0.98
2.06
1.00
2.09
10.45
2.09

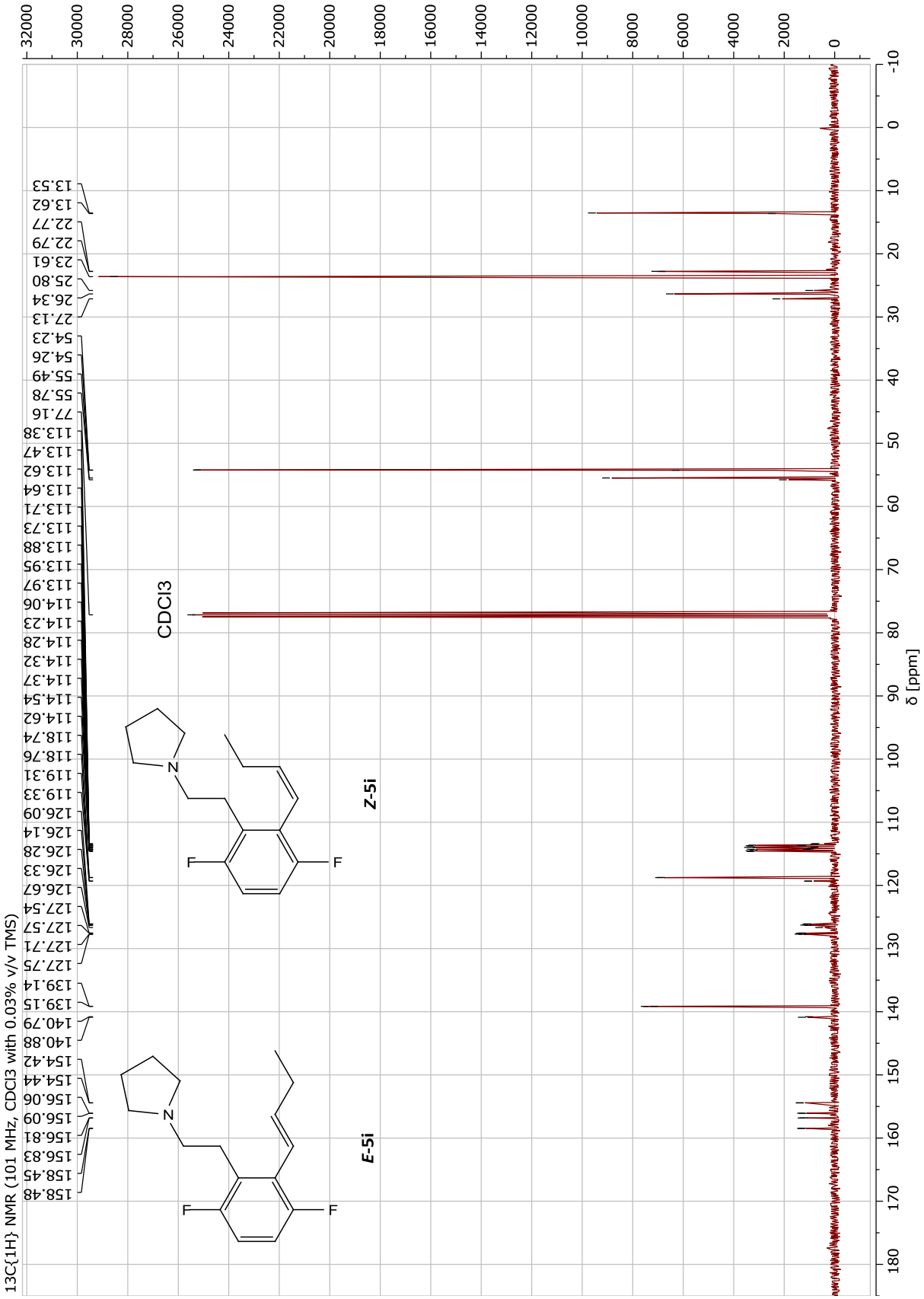
$^{13}C\{^{1}H\}$ NMR of 5h



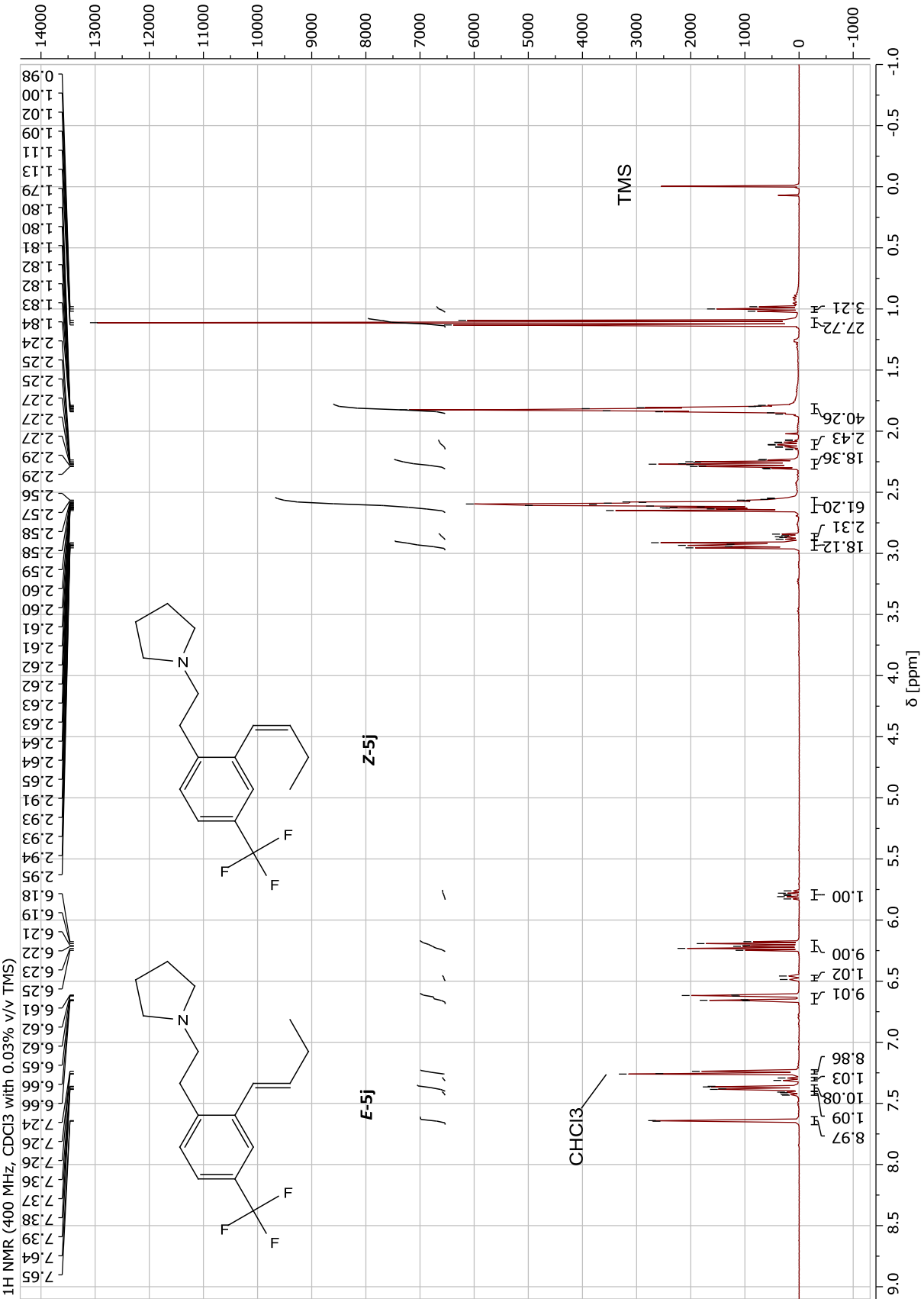
^{1}H NMR of 5i


1H NMR (400 MHz, CDCl3 with 0.03% v/v TMS)
δ [ppm]
TMS
CHCl3
E-5i
Z-5i
F
F
N
13.73
2.00
5.71
5.75
3.37
18.01
2.24
11.87
42.21
2.11
11.81
27.94

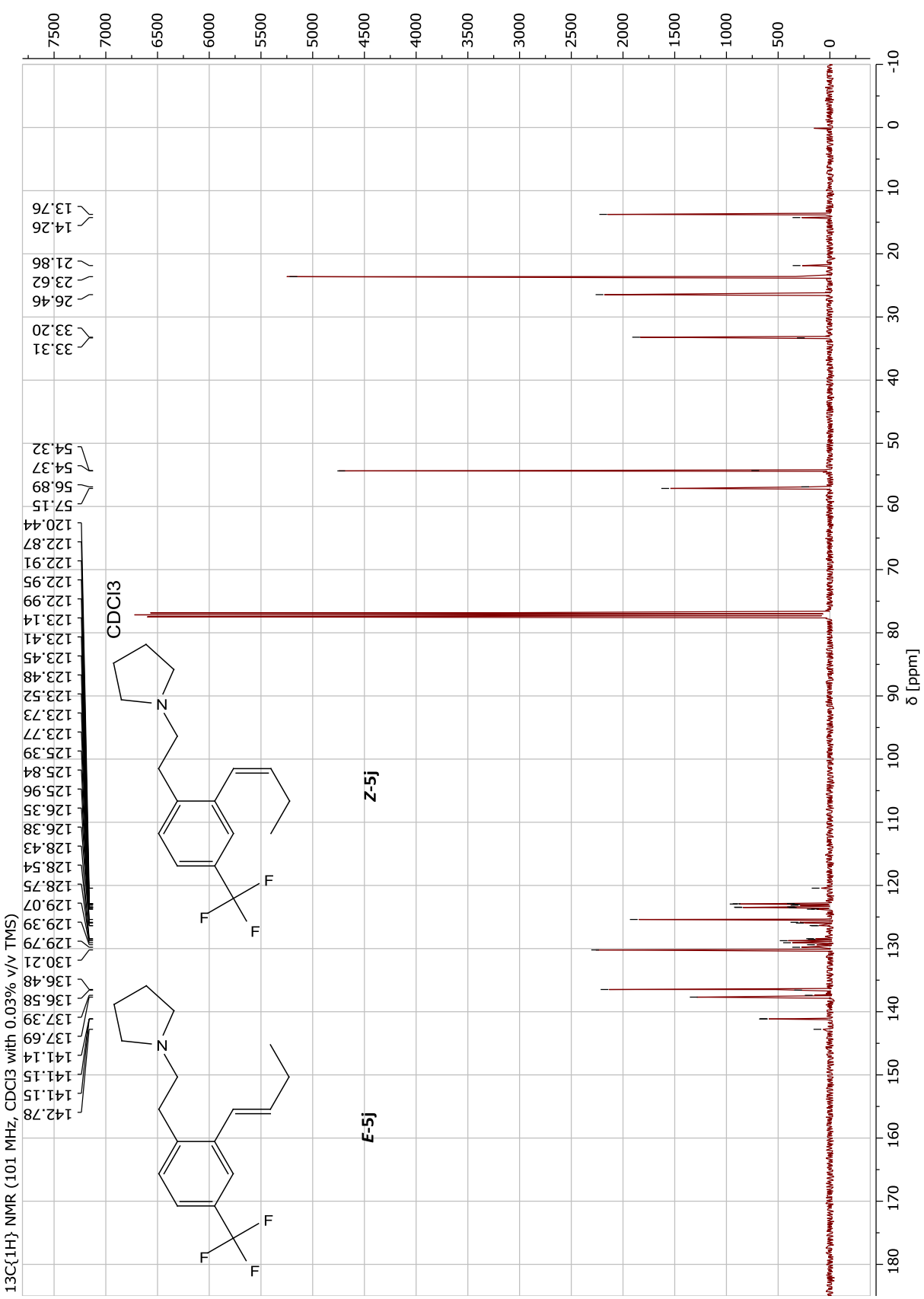
$^{13}C\{^{1}H\}$ NMR of 5i



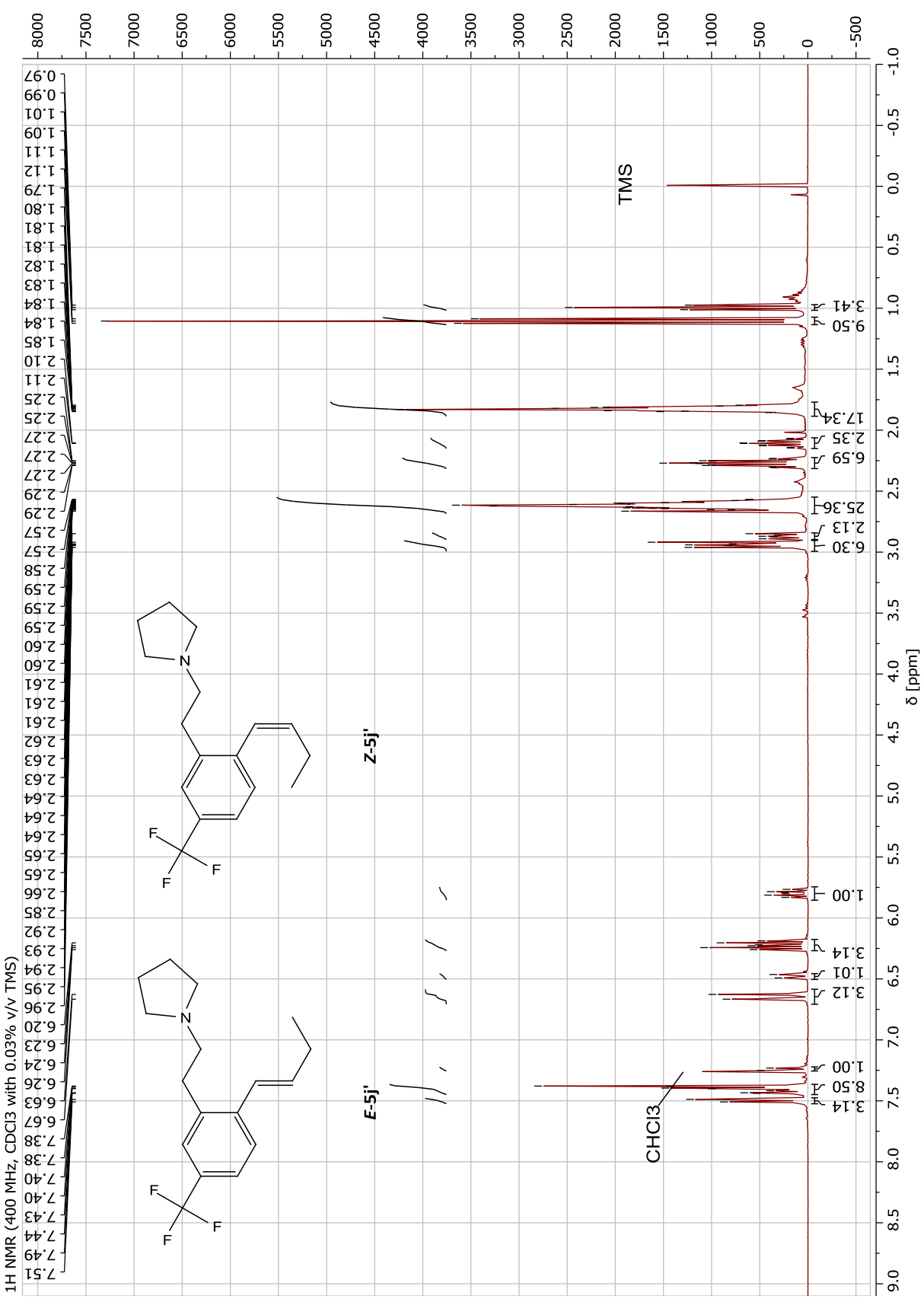
^{1}H NMR of 5j



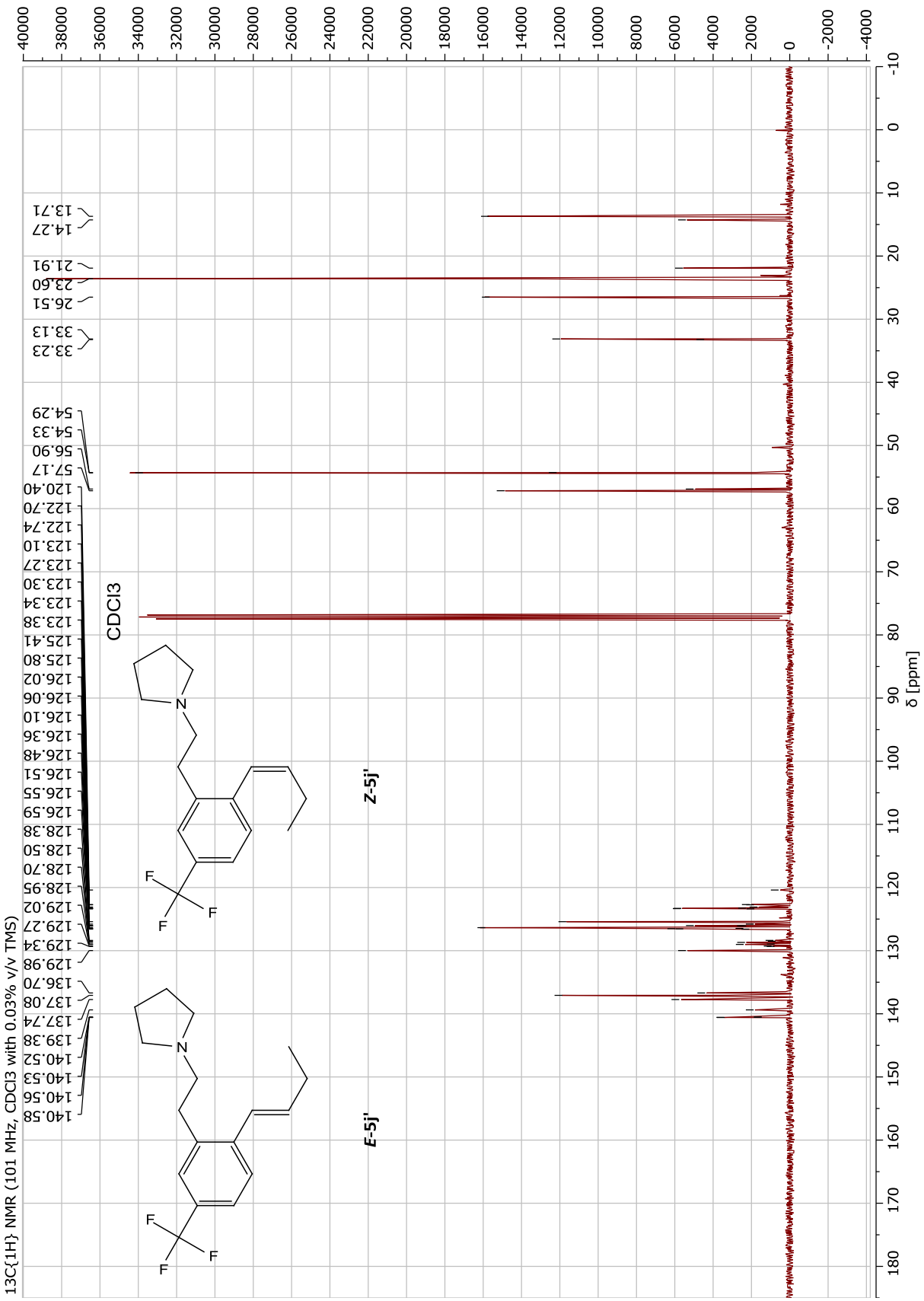
$^{13}C\{^{1}H\}$ NMR of 5j



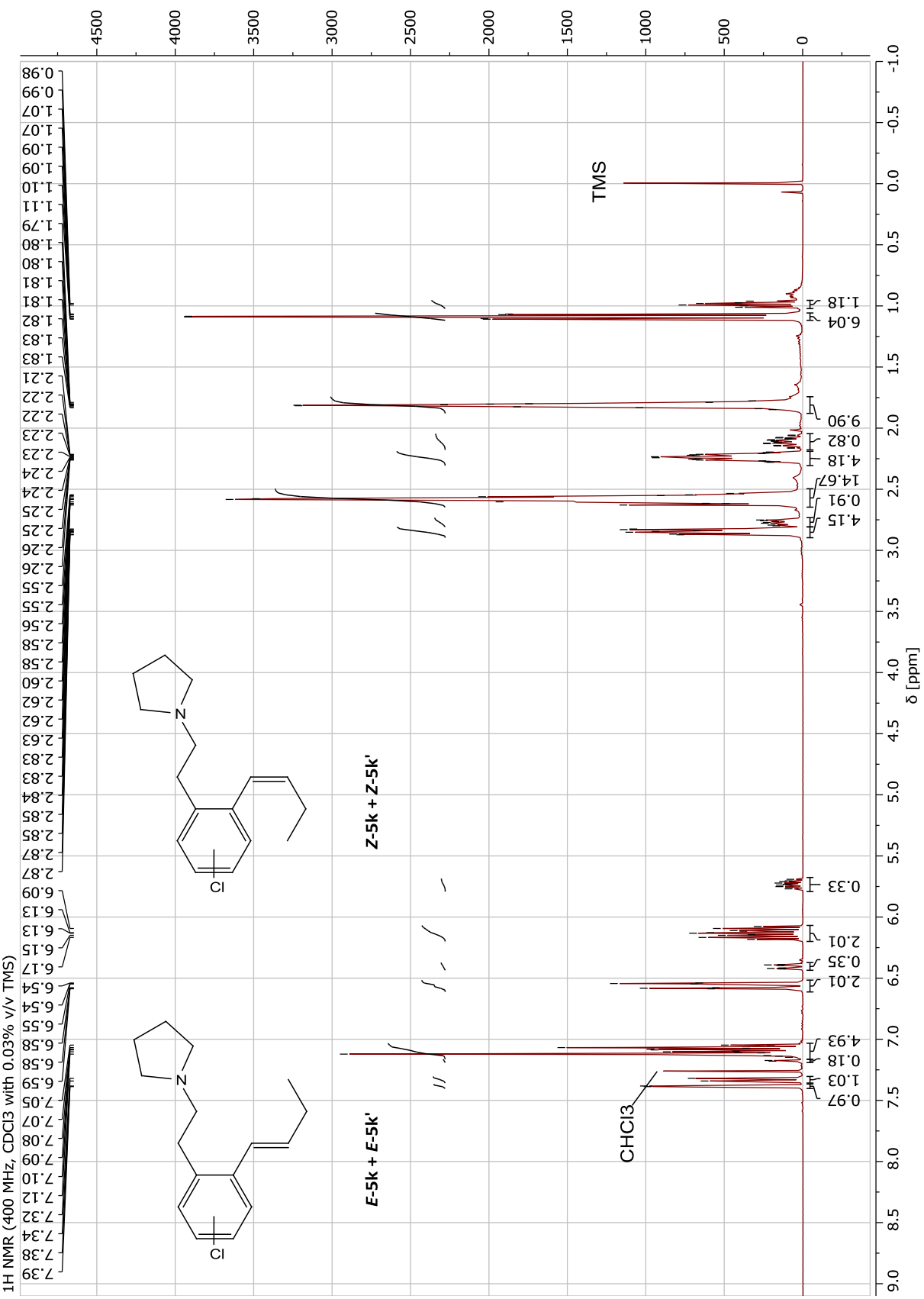
^{1}H NMR of 5j'


1H NMR (400 MHz, CDCl3 with 0.03% v/v TMS)
δ [ppm]
TMS
CHCl3
Z-5j'
E-5j'
N
F
F
F
N
F
F
F

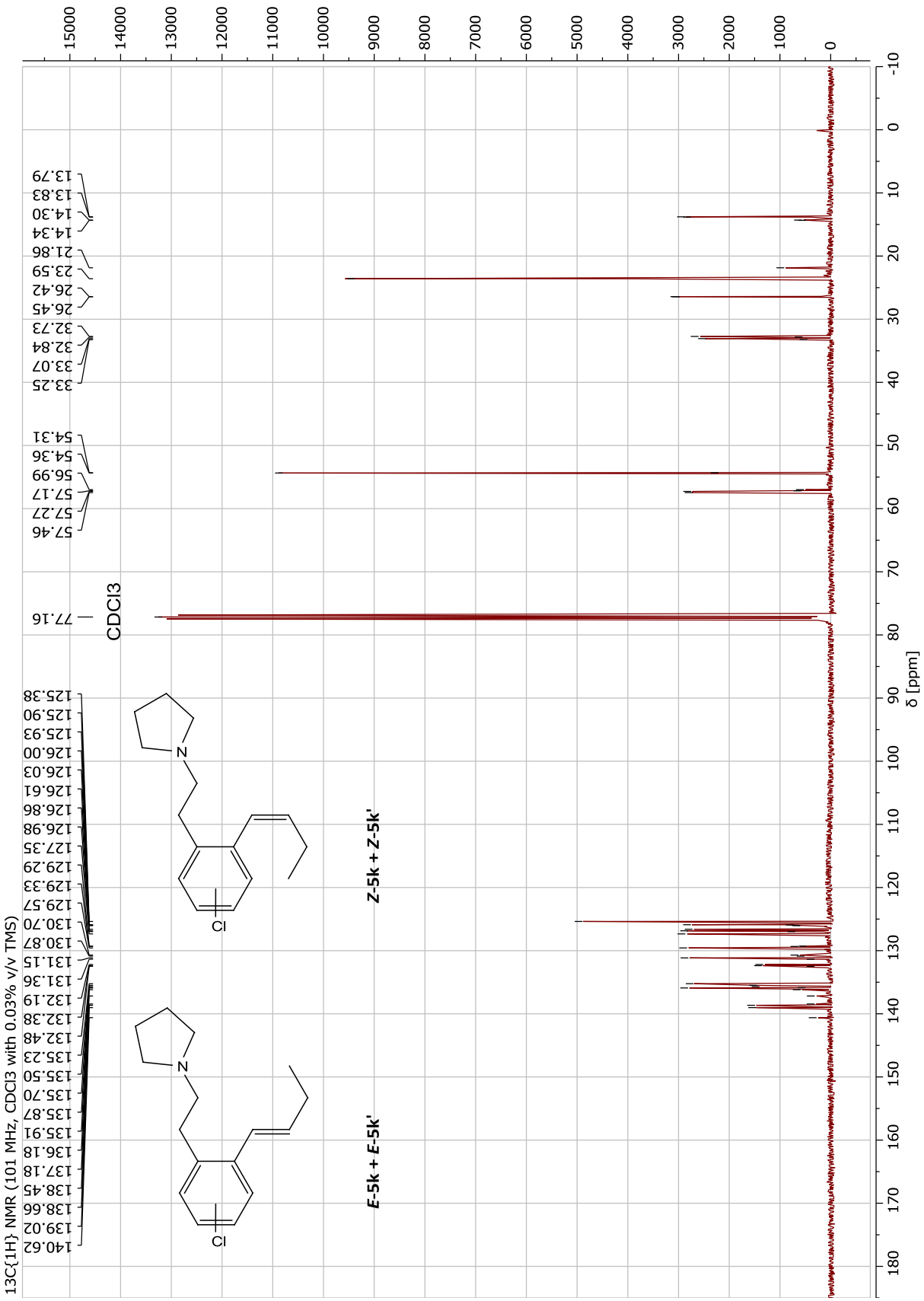
$^{13}C\{^{1}H\}$ NMR of 5j'



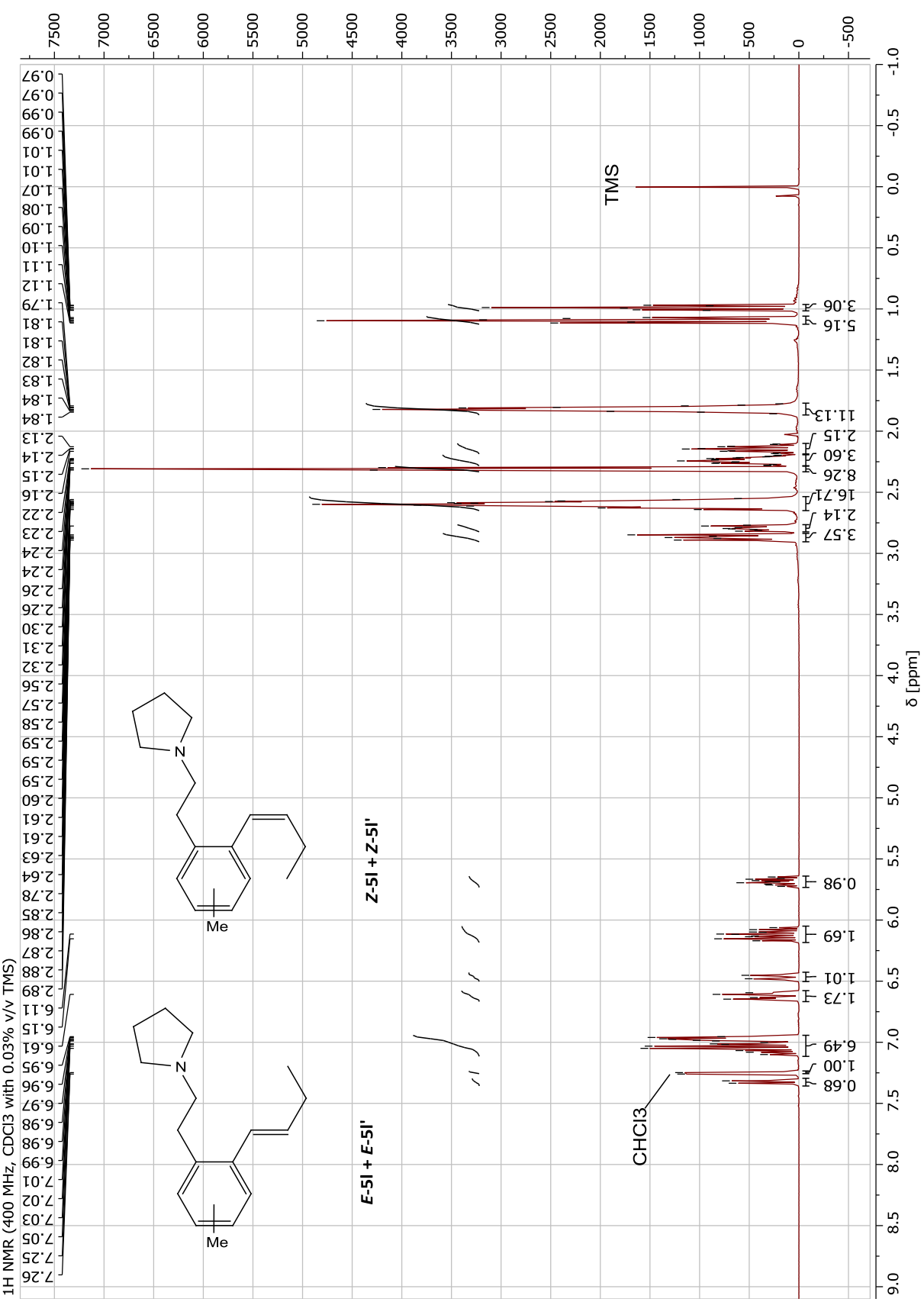
^{1}H NMR of 5k


1H NMR (400 MHz, CDCl3 with 0.03% v/v TMS)
δ [ppm]
TMS
CHCl3
E-5k + E-5k'
Z-5k + Z-5k'
Cl
N
6.04
1.18
9.90
0.82
4.18
14.67
0.91
4.15
0.33
2.01
0.35
2.01
4.93
0.18
1.03
0.97

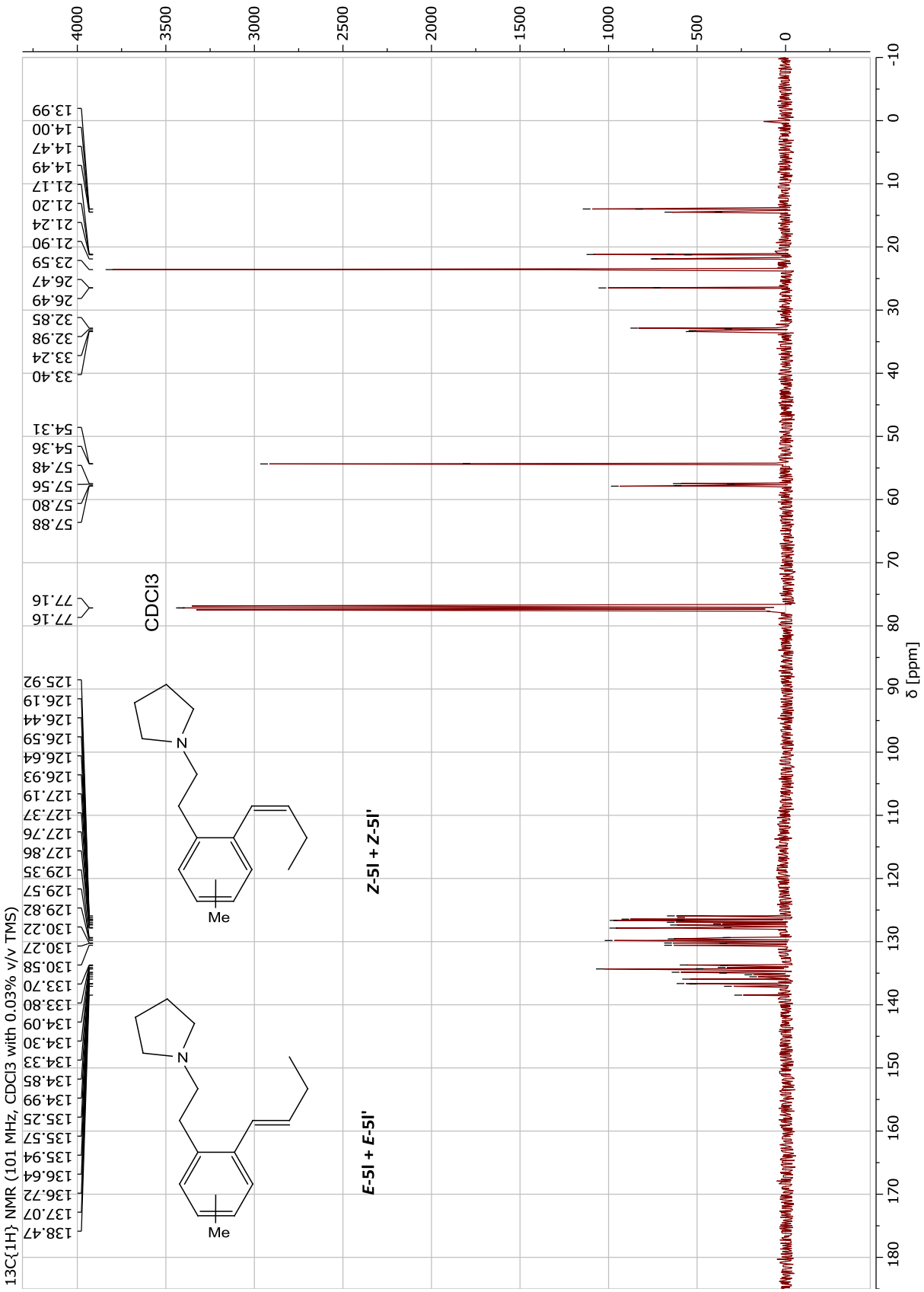
$^{13}C\{^{1}H\}$ NMR 5k


13C{1H} NMR (101 MHz, CDCl3 with 0.03% v/v TMS)
δ [ppm]
CDCl3
77.16
57.46
57.27
57.17
56.99
54.36
54.31
33.25
33.07
32.84
32.73
26.45
26.42
23.59
21.86
14.34
14.30
13.83
13.79
140.62
139.02
138.66
138.45
137.18
136.18
135.91
135.87
135.70
135.50
135.23
132.48
132.38
132.19
131.36
131.15
130.87
130.70
129.57
129.33
129.29
127.35
126.98
126.86
126.61
126.03
126.00
125.93
125.90
125.38
Cl
N
Cl
N
Z-5k + Z-5k'
E-5k + E-5k'

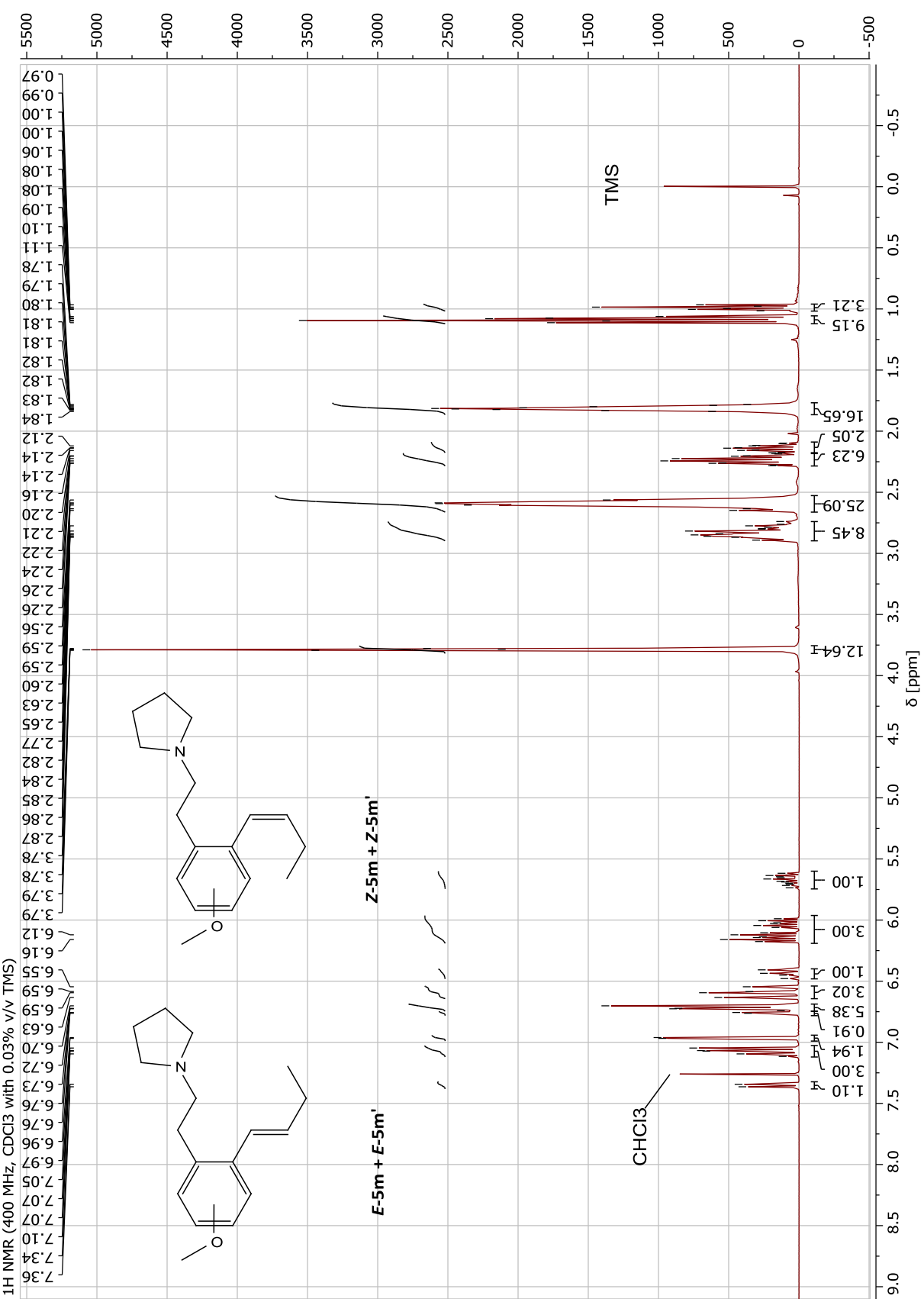
^{1}H NMR of 5l


1H NMR (400 MHz, CDCl3 with 0.03% v/v TMS)
δ [ppm]
TMS
CHCl3
Z-5l + Z-5l'
E-5l + E-5l'
Me
Me
N
N
0.68
1.00
6.49
1.73
1.01
1.69
0.98
3.57
2.14
16.71
8.26
3.60
2.15
11.13
5.16
3.06

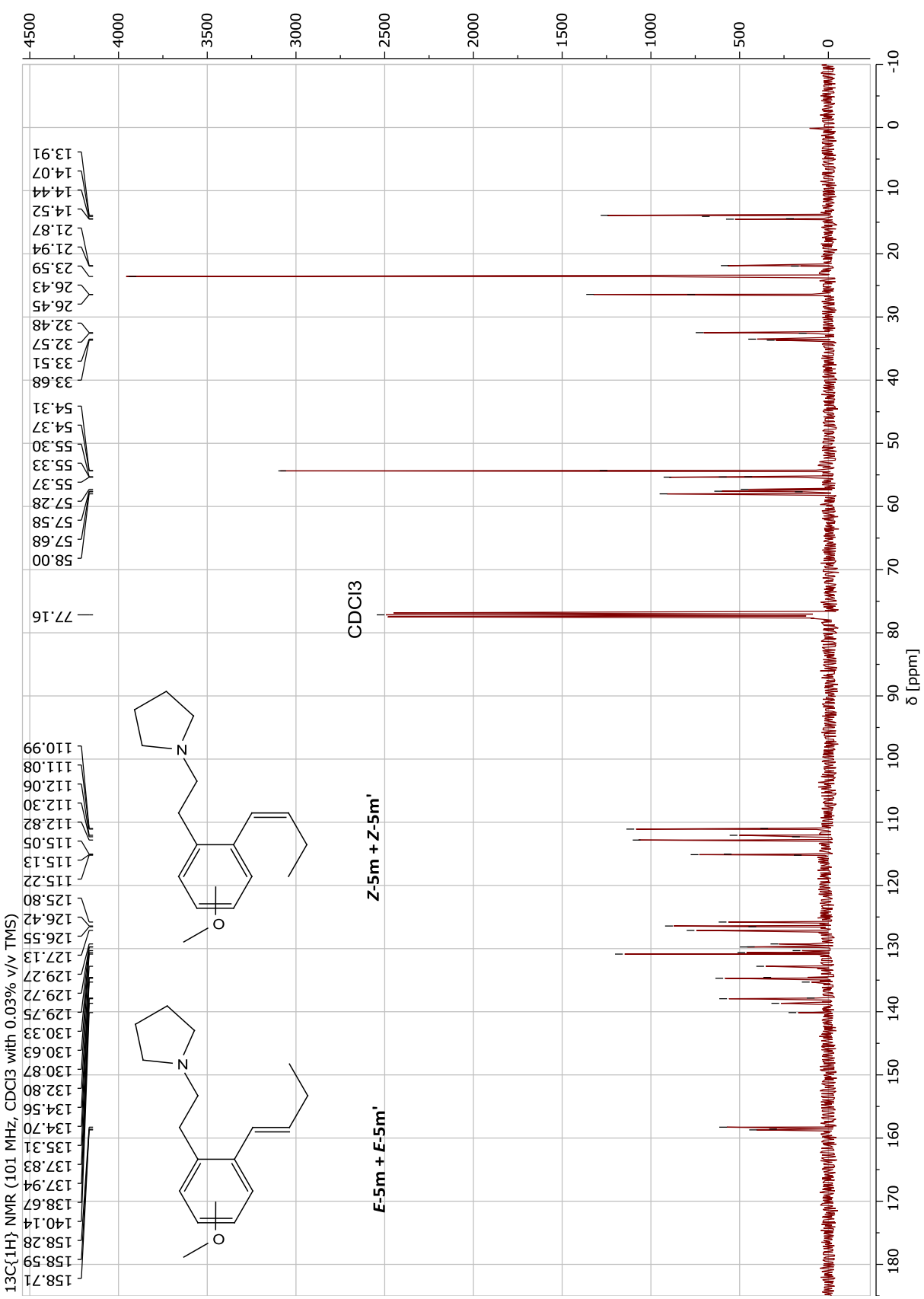
$^{13}C\{^{1}H\}$ NMR of 5l



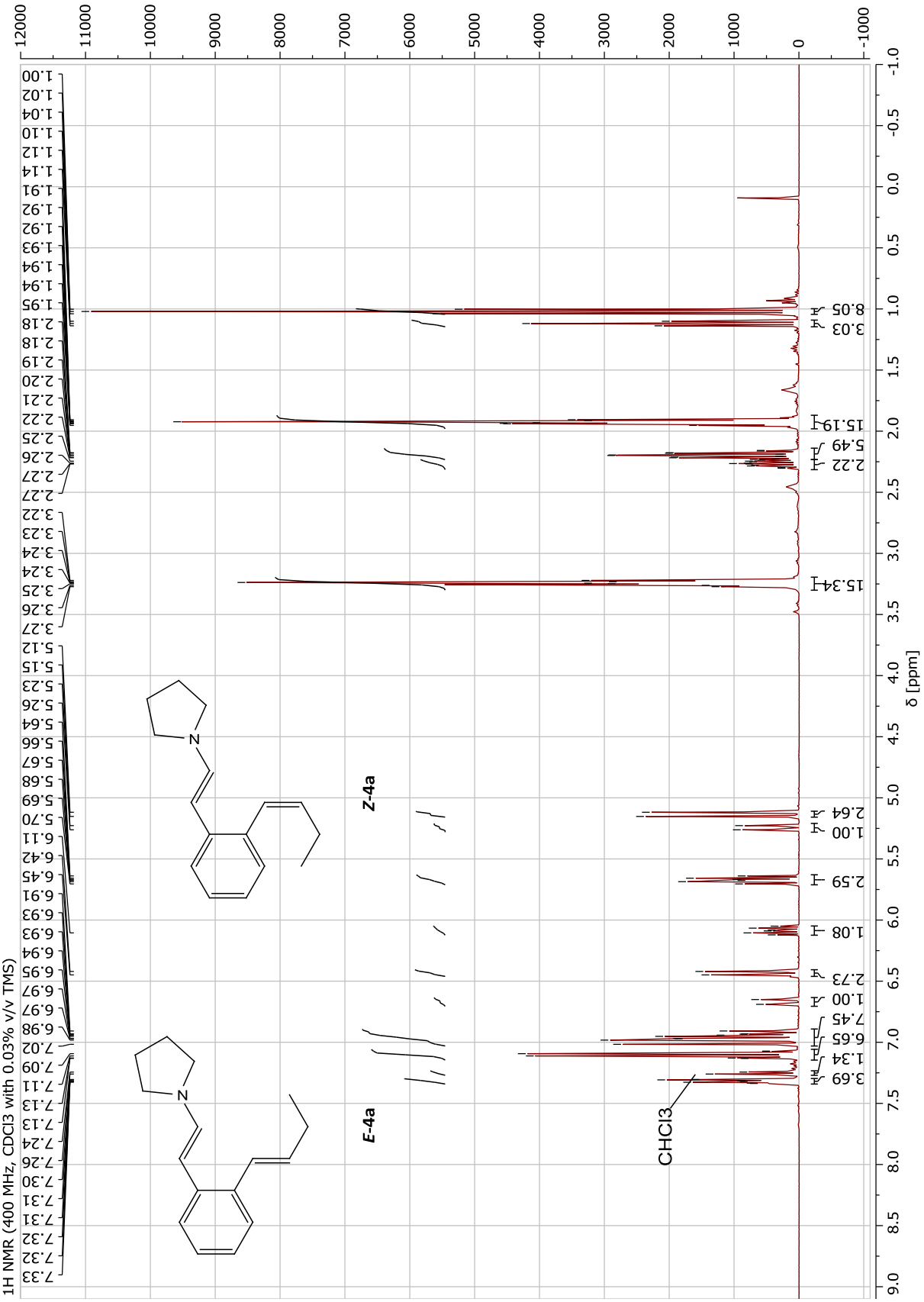
^{1}H NMR of 5m


1H NMR (400 MHz, CDCl3 with 0.03% v/v TMS)
E-5m + E-5m'
Z-5m + Z-5m'
TMS
CHCl3
δ [ppm]

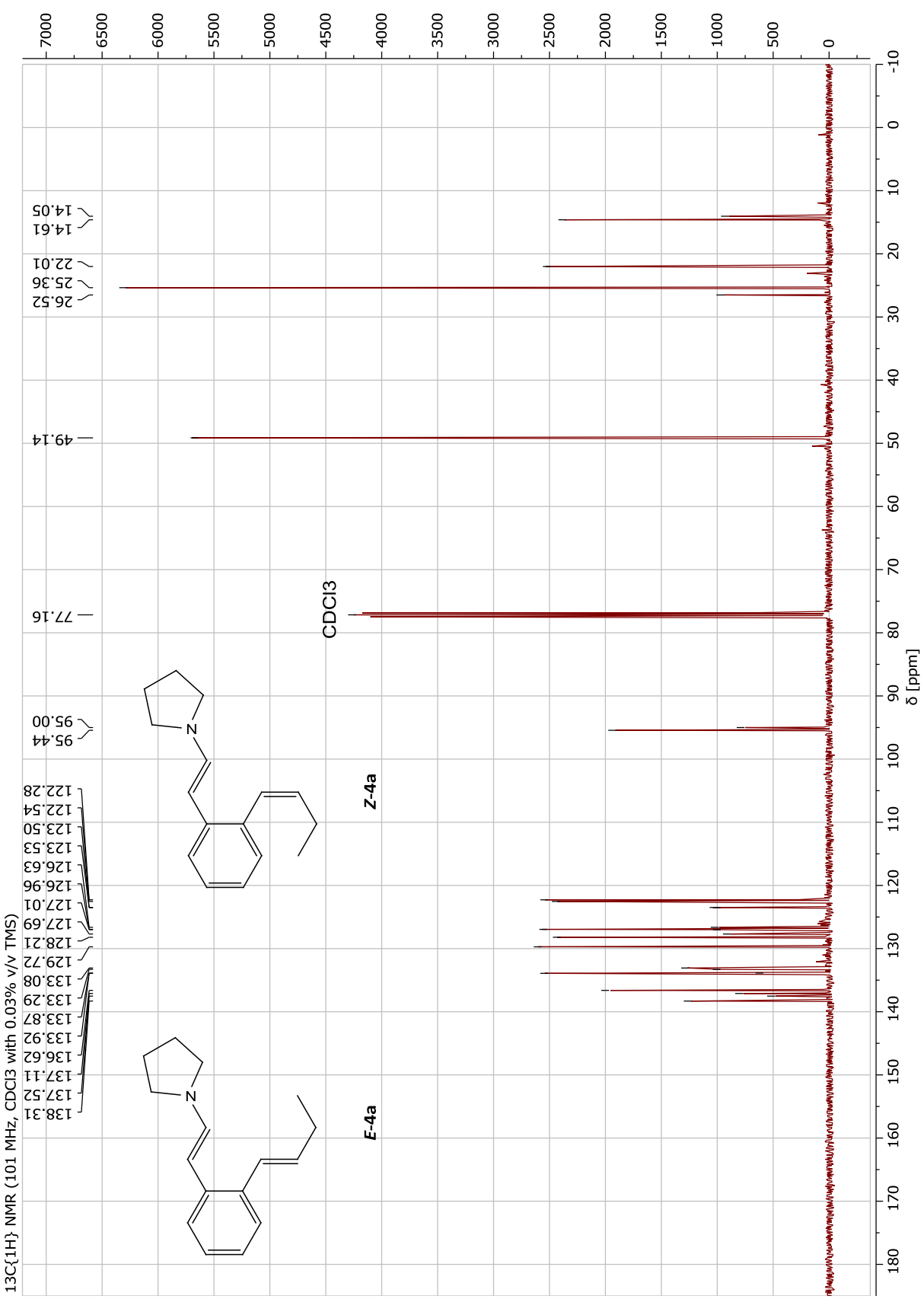
$^{13}C\{^{1}H\}$ NMR of 5m



^{1}H NMR of 4a


1H NMR (400 MHz, CDCl3 with 0.03% v/v TMS)
δ [ppm]
CHCl3
E-4a
Z-4a
3.69
1.34
6.65
7.45
1.00
2.73
1.08
2.59
1.00
2.64
15.34
2.22
5.49
15.19
3.03
8.05

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



Computations:

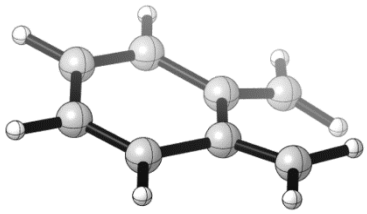
All computations were carried out with the Gaussian 16 software package.[7] Geometry optimizations were performed on a B3LYP-D3 level using the def2-TZVP basis set with the IEFPCM solvent model.[8–11] Additionally, the opt=tight and int=ultrafine keywords were applied. The absence of imaginary frequencies in ground state was checked for every optimized geometry. All possible orientations of the substituents were taken into consideration. For each structure the substituent arrangement with the lowest energy was used. Molecular structures were visualized using the CYLview software.[12] For the time-dependent DFT computations also the previously optimized B3LYP structures were used.[13] Therefore, the Cam-B3LYP method with the cc-pVTZ basis set and the IEFPCM solvent model was applied.[14–16] Using these parameters, the experimentally observed absorption for *o*-quinodimethane in acetonitrile solution by Trahanovsky *et al.* could be reproduced with high accuracy.[17]

Table S1: Computed vertical excitation energies of the low-lying excited state. The values are given in nm.

Compound	*o*-quinodimethane		**3a**	**3i**	**3m-c2**	**3m-c3**
	computed (ACN)	experimental (ACN)	computed (THF)			
HOMO-LUMO transition	378	367	417	419	411	412

Table S2: Coordinates and energy parameters of *o*-quinodimethane (B3LYP-D3/def2-TZVP, IEFPCM=ACN).

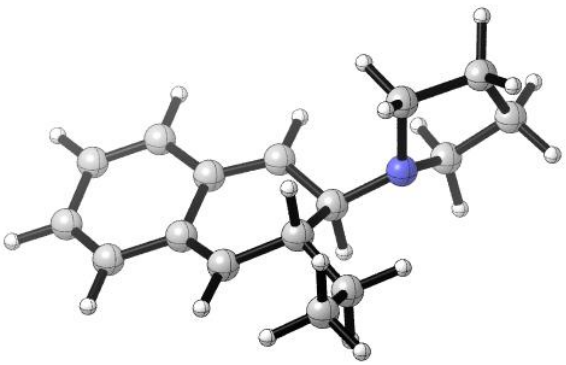
B3LYP-D3/def2-TZVP (SCRF=IEFPCM=ACN)			
XYZ coordinates			
C	1.829131	0.716942	-0.104094
C	0.672225	1.403511	-0.162687
C	-0.620029	0.746388	0.002351
C	-0.620029	-0.746388	-0.002351
C	0.672225	-1.403511	0.162687
C	1.829131	-0.716942	0.104094
H	2.776781	1.233332	-0.191780
H	0.675277	2.480530	-0.281547
H	0.675277	-2.480530	0.281546
H	2.776781	-1.233332	0.191780
C	-1.727914	1.485517	0.207508
H	-2.689366	1.041824	0.426515
H	-1.683172	2.566631	0.174642
C	-1.727914	-1.485517	-0.207508
H	-1.683172	-2.566631	-0.174642
H	-2.689366	-1.041824	-0.426515



E (Hartree/Particle)	-309.736208297
Zero-point correction	0.131937
Thermal correction to Energy	0.138660
Thermal correction to Enthalpy	0.139605
Thermal correction to Gibbs Free Energy	0.101131
Sum of electronic and zero-point Energies	-309.604271
Sum of electronic and thermal Energies	-309.597548
Sum of electronic and thermal Enthalpies	-309.596604
Sum of electronic and thermal Free Energies	-309.635077

Table S3: Coordinates and energy parameters of **3a** (B3LYP-D3/def2-TZVP, IEFPCM=THF).

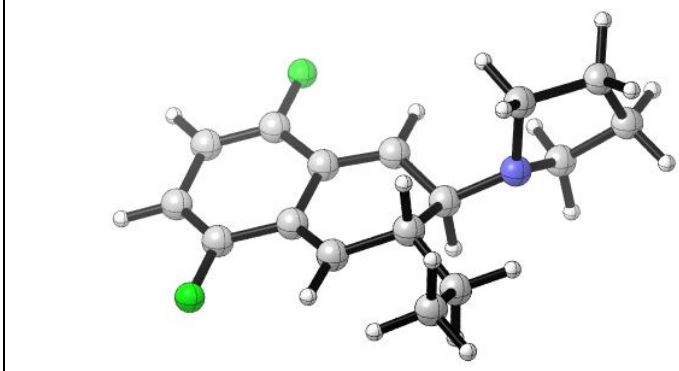
B3LYP-D3/def2-TZVP (SCRF=IEFPCM=THF)			
XYZ coordinates			
C	1.658649	-0.931785	0.039550
C	2.191582	0.443343	-0.098287
C	0.333633	-1.141883	-0.105875
C	1.337362	1.489717	-0.094451
H	-0.060693	-2.149048	-0.041269
H	1.735275	2.497105	-0.137053
C	4.461284	-0.443832	0.013994
H	5.534628	-0.302735	-0.011243
C	3.937926	-1.775127	0.249375
H	4.635200	-2.589827	0.400380
C	3.632157	0.606719	-0.155457
C	2.608734	-2.004722	0.267278
H	2.220088	-3.004781	0.421561
H	4.025835	1.605002	-0.308627
C	-0.963197	2.500154	-0.437346
H	-0.710867	2.653317	-1.491950
H	-2.016935	2.219762	-0.407310
C	-0.600859	-0.023099	-0.512064
C	-0.145342	1.315469	0.096906
H	-0.312923	1.262361	1.186887
N	-2.015064	-0.283696	-0.264142
C	-2.628811	-1.328465	-1.076884
H	-2.114321	-2.299445	-0.975826
H	-2.605332	-1.052929	-2.133106
C	-4.045295	-1.426878	-0.503106
H	-4.465018	-2.425635	-0.622953
H	-4.704533	-0.727048	-1.017447
C	-3.881808	-1.020258	0.984962
H	-4.095033	-1.846807	1.662829
H	-4.562199	-0.207927	1.240014
C	-2.415203	-0.568449	1.112564
H	-2.298835	0.314026	1.742910
H	-1.803853	-1.370356	1.558308
C	-0.757468	3.796776	0.343394
H	-1.028883	3.664370	1.394005
H	0.278389	4.140899	0.311241
H	-1.379155	4.597112	-0.062767
H	-0.505453	0.082374	-1.606900



E (Hartree/Particle)	-677.331485824
Zero-point correction	0.339940
Thermal correction to Energy	0.349593
Thermal correction to Enthalpy	0.350537
Thermal correction to Gibbs Free Energy	0.290135
Sum of electronic and zero-point Energies	-676.997492
Sum of electronic and thermal Energies	-676.981893
Sum of electronic and thermal Enthalpies	-676.980949
Sum of electronic and thermal Free Energies	-677.041351

Table S4: Coordinates and energy parameters of **3i** (B3LYP-D3/def2-TZVP, IEFPCM=THF).

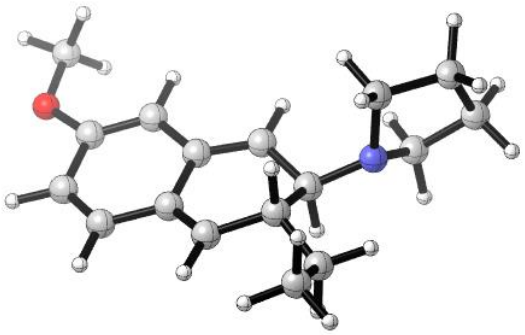
B3LYP-D3/def2-TZVP (SCRF=IEFPCM=THF)			
XYZ coordinates			
C	1.278764	-0.873349	-0.006287
C	1.836254	0.496499	-0.072046
C	-0.045154	-1.060521	-0.166201
C	1.008478	1.559522	-0.025392
H	-0.451345	-2.062411	-0.149242
H	1.429004	2.555902	-0.014181
C	4.105600	-0.441639	0.023227
H	5.176077	-0.292784	0.021649
C	3.557831	-1.773684	0.175306
H	4.218657	-2.622306	0.281927
C	3.278065	0.607140	-0.099427
C	2.228073	-1.950463	0.167866
C	-1.266470	2.620021	-0.364858
H	-0.999823	2.802163	-1.411086
H	-2.324841	2.357406	-0.354140
C	-0.956926	0.094253	-0.521071
C	-0.478113	1.401785	0.138630
H	-0.656403	1.317450	1.224384
N	-2.372933	-0.150243	-0.279722
C	-3.010320	-1.145337	-1.136354
H	-2.515947	-2.130204	-1.080486
H	-2.984512	-0.822966	-2.179082
C	-4.425706	-1.238577	-0.561079
H	-4.872842	-2.217380	-0.733714
H	-5.067118	-0.493231	-1.032186
C	-4.244853	-0.919507	0.945862
H	-4.456240	-1.783453	1.575808
H	-4.917725	-0.120110	1.255441
C	-2.773227	-0.486470	1.086124
H	-2.646928	0.369023	1.750835
H	-2.168255	-1.311075	1.497383
C	-1.044973	3.885580	0.460767
H	-1.329557	3.723770	1.503630
H	-0.003206	4.212625	0.449430
H	-1.648398	4.709271	0.074724
H	-0.858825	0.237434	-1.610816
F	1.707165	-3.195324	0.287110
F	3.782259	1.858775	-0.218513



E (Hartree/Particle)	-875.896715562
Zero-point correction	0.317910
Thermal correction to Energy	0.335271
Thermal correction to Enthalpy	0.336215
Thermal correction to Gibbs Free Energy	0.271258
Sum of electronic and zero-point Energies	-875.578805
Sum of electronic and thermal Energies	-875.561445
Sum of electronic and thermal Enthalpies	-875.560501
Sum of electronic and thermal Free Energies	-875.625457

Table S5: Coordinates and energy parameters of **3m-c2** (B3LYP-D3/def2-TZVP, IEFPCM=THF).

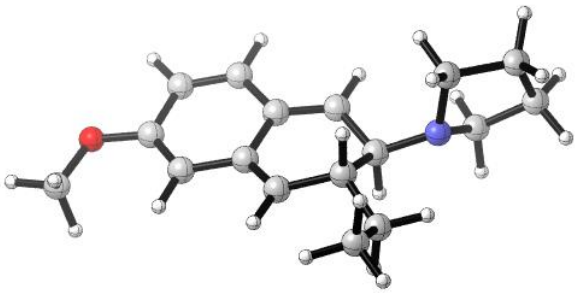
B3LYP-D3/def2-TZVP (SCRF=IEFPCM=THF)			
XYZ coordinates			
C	1.229209	-0.164485	-0.091448
C	1.306504	1.313241	-0.151207
C	0.023958	-0.757254	-0.225467
C	0.177873	2.048870	-0.071141
H	-0.044589	-1.838556	-0.225591
H	0.252500	3.130286	-0.061275
C	3.738711	1.172720	-0.124615
H	4.724833	1.617838	-0.152346
C	3.658881	-0.268984	0.036892
C	2.623277	1.917533	-0.218478
C	2.466012	-0.908867	0.059087
H	2.399510	-1.983526	0.151318
H	2.688551	2.994719	-0.316959
C	-2.327396	2.331427	-0.330567
H	-2.163452	2.602420	-1.378901
H	-3.246448	1.744590	-0.300732
C	-1.223965	0.040076	-0.540017
C	-1.176015	1.425466	0.129654
H	-1.287358	1.275263	1.217496
N	-2.479156	-0.653084	-0.259331
C	-2.787892	-1.793306	-1.115445
H	-1.998263	-2.563927	-1.093554
H	-2.903515	-1.471393	-2.152347
C	-4.076198	-2.349938	-0.502100
H	-4.177063	-3.422299	-0.669573
H	-4.942804	-1.862402	-0.949653
C	-3.968758	-1.985844	1.002062
H	-3.889693	-2.870043	1.634703
H	-4.848490	-1.431284	1.328453
C	-2.701593	-1.117395	1.108599
H	-2.823516	-0.275813	1.791625
H	-1.854621	-1.717782	1.479129
C	-2.500463	3.592246	0.514283
H	-2.688417	3.335836	1.560182
H	-1.618406	4.235441	0.485890
H	-3.346382	4.184338	0.159455
H	-1.225368	0.218945	-1.629166
O	4.881715	-0.853371	0.144606
C	4.936242	-2.266476	0.308091
H	4.494892	-2.779440	-0.551059
H	5.990338	-2.521707	0.382692
H	4.417818	-2.577128	1.219572



E (Hartree/Particle)	-791.910158560
Zero-point correction	0.366465
Thermal correction to Energy	0.384656
Thermal correction to Enthalpy	0.385600
Thermal correction to Gibbs Free Energy	0.319186
Sum of electronic and zero-point Energies	-791.543693
Sum of electronic and thermal Energies	-791.525502
Sum of electronic and thermal Enthalpies	-791.524558
Sum of electronic and thermal Free Energies	-791.590973

Table S6: Coordinates and energy parameters of **3m-c3** (B3LYP-D3/def2-TZVP, IEFPCM=THF).

B3LYP-D3/def2-TZVP (SCRF=IEFPCM=THF)			
XYZ coordinates			
C	0.914047	-0.991869	0.059828
C	1.498044	0.363823	-0.057713
C	-0.413695	-1.161457	-0.102755
C	0.673176	1.433941	-0.055031
H	-0.837849	-2.157127	-0.049252
H	1.099982	2.429963	-0.079446
C	3.728904	-0.606056	0.058682
C	3.154728	-1.922120	0.280142
H	3.840031	-2.747028	0.426152
C	2.943605	0.483981	-0.107333
C	1.822026	-2.100244	0.286264
H	1.399835	-3.087818	0.430195
H	3.363237	1.470412	-0.243884
C	-1.589473	2.517064	-0.426372
H	-1.316344	2.663655	-1.476842
H	-2.652437	2.271966	-0.411954
C	-1.310758	-0.012617	-0.505748
C	-0.818371	1.305711	0.117424
H	-1.010232	1.254457	1.203261
N	-2.734294	-0.235170	-0.271290
C	-3.371662	-1.250709	-1.102617
H	-2.886010	-2.237531	-1.011216
H	-3.332183	-0.961901	-2.154818
C	-4.794883	-1.316336	-0.540704
H	-5.241375	-2.301415	-0.676134
H	-5.430310	-0.592095	-1.051201
C	-4.631742	-0.932677	0.953517
H	-4.876181	-1.760117	1.619684
H	-5.288902	-0.102681	1.212646
C	-3.153170	-0.527651	1.098272
H	-3.014418	0.341348	1.742437
H	-2.570304	-1.354669	1.536388
C	-1.353569	3.805691	0.359221
H	-1.641248	3.679868	1.406375
H	-0.307276	4.117517	0.339906
H	-1.945674	4.625606	-0.052312
H	-1.202341	0.098543	-1.598622
O	5.088748	-0.620232	0.055381
C	5.769926	0.612009	-0.154315
H	6.831446	0.378756	-0.129440
H	5.511597	1.043858	-1.125360
H	5.534233	1.331571	0.634855



E (Hartree/Particle)	-791.909988218
Zero-point correction	0.366506
Thermal correction to Energy	0.384668
Thermal correction to Enthalpy	0.385612
Thermal correction to Gibbs Free Energy	0.319447
Sum of electronic and zero-point Energies	-791.543483
Sum of electronic and thermal Energies	-791.525320
Sum of electronic and thermal Enthalpies	-791.524376
Sum of electronic and thermal Free Energies	-791.590541

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