Supplementary Information

Nickel-Catalyzed Dearomative *trans*-1,2-Carboamination

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1. General experimental

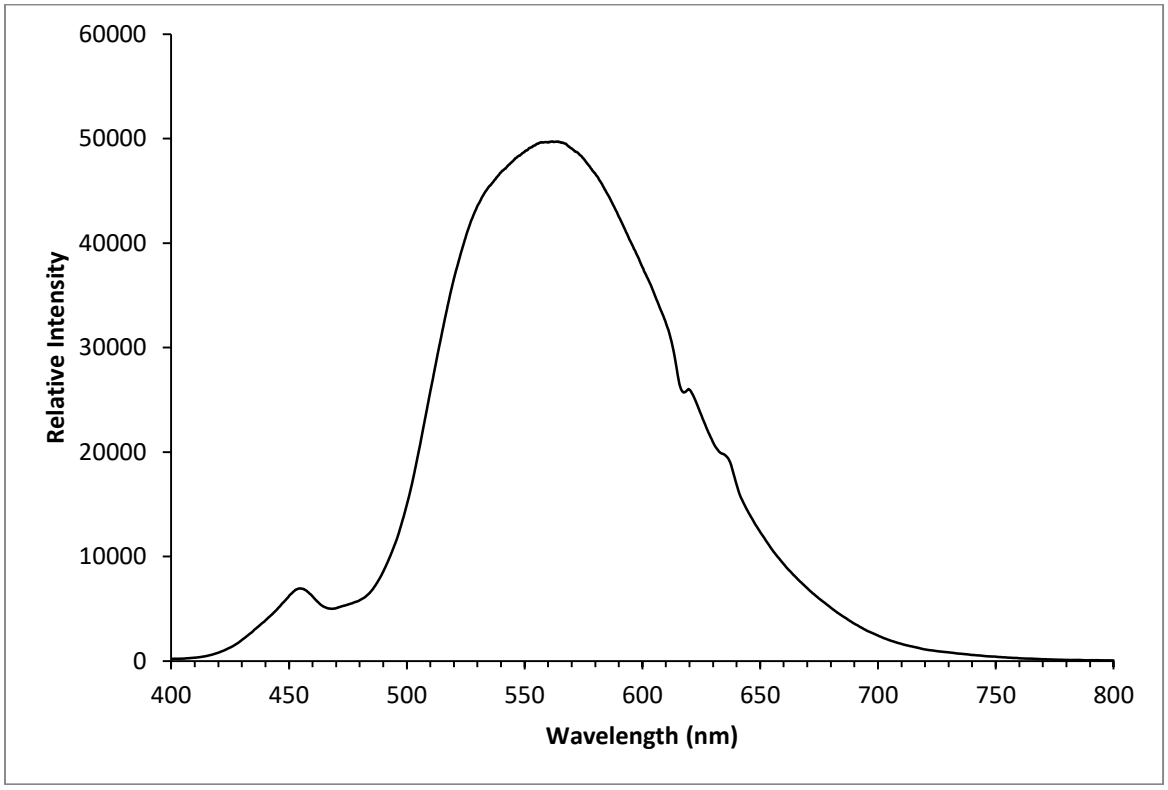
Unless otherwise noted, all reactions were carried out under an inert atmosphere. All chemicals were purchased from commercial suppliers and used as received. *N*-methyl-1,2,4-triazoline-3,5-dione (MTAD) was prepared based on the literature procedures[1,2] and was resublimed before use. Unless otherwise noted, Grignard reagents were prepared as a 3.0 M solution in anhydrous tetrahydrofuran (THF). (*R*,R_p)-*i*Pr-phosferrox was prepared based on the literature procedure[3,4] from D-valinol. C_{18}-derivatized SiO_2 was prepared according to the literature procedure.[5] Dry dichloromethane (CH_2Cl_2), benzene, and THF were obtained by passing commercially available anhydrous, oxygen-free HPLC-grade solvents through activated alumina columns. Analytical thin-layer chromatography was performed on Merck silica gel 60 F_{254} glass plates. Visualization was accomplished with UV light and/or potassium permanganate ($KMnO_4$). Retention factor (R_f) values reported were measured using a 5 × 2 cm TLC plate in a developing chamber containing the solvent system described. Flash column chromatography was performed using Silicycle SiliaFlash® P60 (SiO_2, 40-63 μm particle size, 230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Bruker 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C) or Varian Unity Inova 500 (500 MHz, ^{1}H) MHz spectrometers. Spectra are referenced to residual chloroform (δ = 7.26 ppm, ^{1}H; 77.16 ppm, ^{13}C), residual dimethyl sulfoxide (δ = 2.50 ppm, ^{1}H; 39.5 ppm, ^{13}C), residual methanol (δ = 3.31 ppm, ^{1}H; 49.0 ppm, ^{13}C), or residual benzene (δ = 7.16 ppm, ^{1}H; 128.06 ppm, ^{13}C). Chemical shifts are reported in parts per million (ppm). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Coupling constants *J* are reported in Hertz (Hz). Mass spectrometry (MS) was performed by the University of Illinois Mass Spectrometry Laboratory. Electron Impact (EI^+) spectra were performed at 70 eV using methane as the carrier gas, with time-of-flight (TOF) mass analyzer. Electrospray ionization (ESI^+) spectra were performed using a time-of-flight (TOF) mass analyzer. Data are reported in the form of m/z (intensity relative to the base peak = 100). For several compounds, Waters Q-TOF Ultima ESI and Agilent 6230 ESI TOF LC/MS spectrometers were used to obtain the high resolution mass spectra. Infrared spectra were measured neat on a Perkin-Elmer spectrum BX FT-IR spectrometer. Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 0–33% T); m (medium, 34–66% T), w (weak, 67–100% T), and br (broad). Visible-light spectrum of LED was recorded using an Avantes Sensline Avaspec-ULS TEC Spectrometer. Melting points of solids, compounds that solidified after chromatography, were measured on a Buchi B-540 melting point apparatus and are uncorrected. Optical rotations were recorded on a Jasco P-2000 polarimeter at 589 nm, and are reported in units of 10^{-1} (deg cm^2 g^{-1}). HPLC was performed on a Shimadzu Prominence HPLC system with SPD-M20A UV/VIS Photodiode array detector (220 nm).

2. Experimental Setup

2-1. LED light source

Generic cool white light LED corn bulbs were used for the photochemical experiments. These can be obtained from several manufactures over amazon.com and proved to give consistent results as well as identical visible spectra. Detailed info:

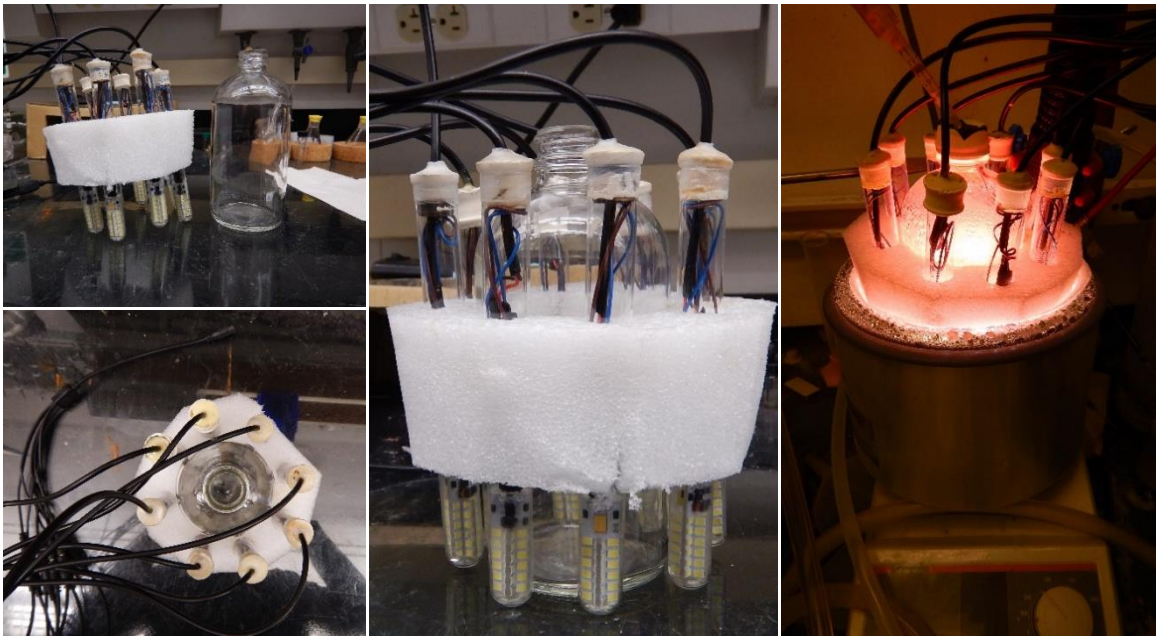
Socket: G4
LED Chip: 48 LEDs SMD 2835
Consume wattage: 4W
Input voltage: AC / DC 12V
Beam degree: 360 degrees
Color temperature: 6500K (Cool White)
Initial lumens (lm): 290



Spectra S1. Spectrum of a LED bulb used.

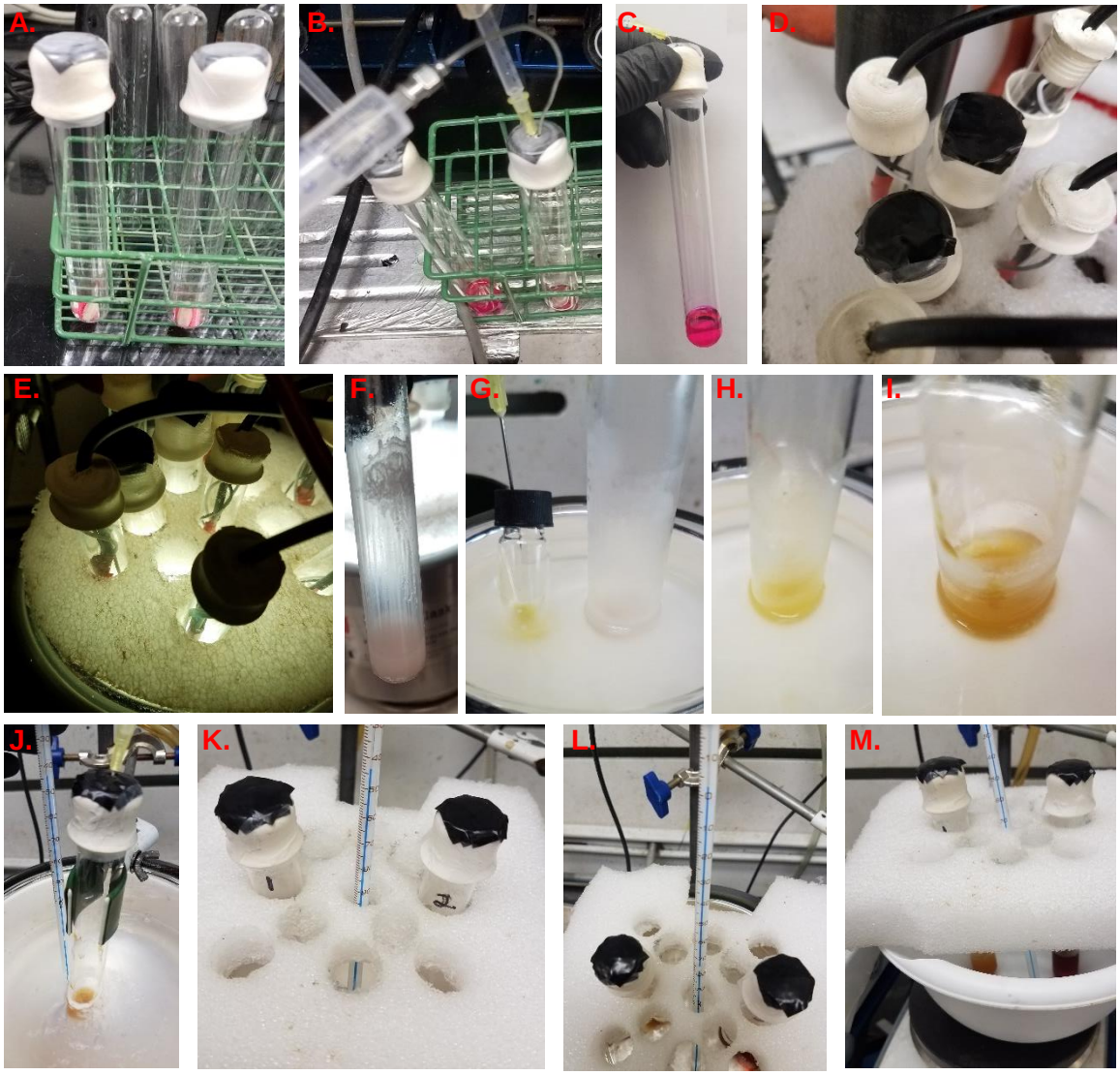
2-2. Photochemical setup for large scale reactions.

Eight 4W LED corn bulbs (12V, cool white light 6500K) were wired to a suitable 12V power supply, then sealed into test tubes and capped with septa (see Picture S1). Lights were arranged in a carousel fashion around a 1 L clear borosilicate glass bottle (Picture S1). A normal reagent or media bottle can be used. The whole setup was kept submerged in a −78 °C bath during the photochemical reaction.



Picture S1. Photochemical set-up for dearomative carboamination.

2-3. Photochemical setup for small scale reactions.



Picture S2. Photochemical set-up for small scale reactions. A. MTAD (1) was weighed into an oven-dried test tube and the atmosphere was exchanged with nitrogen. **B.** Solvent was then added. **C.** Photo of the solution of MTAD in CH_2Cl_2 before the addition of arene. **D.** The reactions were cooled to –78 °C followed by the addition of arene [*note: if the substrate was a solid, it was added at point A. and the solvent was added after cooling*], then sealed with vinyl tape. **E.** Irradiation was then commenced. **F.** Completion of irradiation results in loss of pink color. **G.** The reaction was placed in a small –78 °C bath for ease of visualization during addition of reagents and the catalyst was pre-cooled before transfer. **H.** The reaction after addition of catalyst. **I.** The reaction after dropwise addition of the Grignard reagent. **J.** The reaction was then placed in a –45 °C bath. **K.** The reactions were then sealed with vinyl tape and left to stir for three hours. **L.** Over the three-hour period the bath warmed to 0 °C. **M.** The reactions were then stirred for 15 minutes at room temperature before quenching.

3. Experimental Procedures

3-1. Enantioselective dearomative *trans*-1,2-carboamination

General Procedure A: In an oven-dried test tube, MTAD (**1**, 57.0 mg, 0.50 mmol, 1.0 equiv.) was dissolved in anhydrous CH_2Cl_2 (2.5 mL) under nitrogen atmosphere and cooled to –78 °C. Arene (10 equiv.) was slowly added and the solution was stirred for five minutes. The pink solution was irradiated with LED lights at –78 °C until complete loss of color. Upon decolorization, the LED lights were turned off and a pre-cooled (–78 °C) solution of $[Ni(acac)_2]$ (1.93 mg, 7.50 μmol, 1.5 mol %) and (R,R_p)-*i*Pr-Phosferrox (4.81 mg, 0.01 mmol, 2.0 mol %) in CH_2Cl_2 (0.3 mL) was added, followed by dropwise addition of Grignard reagent (417 μL, 3.0 M in THF, 1.25 mmol, 2.5 equiv.) at the rate to keep the internal temperature below –65 °C. After addition, the cold bath temperature was warmed to –45 °C and allowed to slowly warm to 0 °C over 3 h. Reaction vessel was removed from the cold bath, stirred at room temperature for 15 min, and then quenched with aq. HCl (2 mL, 1M). The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 4 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired compound.

3-2. Racemic dearomative *trans*-1,2-carboamination of mononuclear arenes

General Procedure B: In an oven-dried test tube, MTAD (**1**, 57.0 mg, 0.50 mmol, 1.0 equiv.) was dissolved in anhydrous CH_2Cl_2 (2.5 mL) under nitrogen atmosphere and cooled to –78 °C. Arene (10 equiv.) was slowly added and the solution was stirred for five minutes. The pink solution was irradiated with LED lights at –78 °C until complete loss of color. Upon decolorization, the LED lights were turned off and a pre-cooled (–78 °C) solution of $[Ni(cod)_2]$ (6.88 mg, 0.025 mmol, 10 mol %) and dppf (55 mg, 0.10 mmol, 20 mol %) in CH_2Cl_2 (2.0 mL) was added, followed by dropwise addition of Grignard reagent (417 μL, 3.0 M in THF, 1.25 mmol, 2.5 equiv.) at the rate to keep the internal temperature below –65 °C. After addition, the cold bath temperature was warmed to –45 °C and allowed to slowly warm to 0 °C over 3 h. Reaction vessel was removed from the cold bath, stirred at room temperature for 15 min, and then quenched with aq. HCl (2 mL, 1M). The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 4 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired compound.

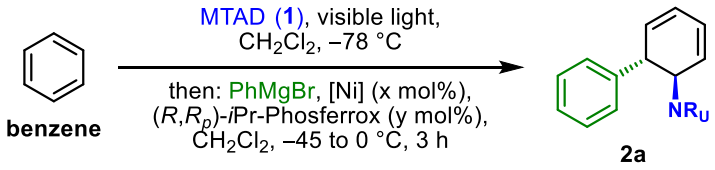
3-3. Racemic dearomative *trans*-1,2-carboamination of polynuclear arenes

General Procedure C: In an oven-dried test tube, MTAD (**1**, 57.0 mg, 0.50 mmol, 1.0 equiv.) was dissolved in anhydrous CH_2Cl_2 (5 mL) under nitrogen atmosphere and cooled to –78 °C. Arene (2.0 equiv.) was slowly added and the solution was stirred for five minutes. The pink solution was irradiated with LED lights at –78 °C until complete loss of color. Upon decolorization, the LED lights were turned off and a pre-cooled (–78 °C) solution of $[Ni(cod)_2]$ (6.88 mg, 0.025 mmol, 10 mol %) and dppf (55 mg, 0.10 mmol, 20 mol %) in CH_2Cl_2 (2.0 mL) was added, followed by dropwise addition of Grignard reagent (417 μL, 3.0 M in THF, 1.25 mmol, 2.5 equiv.) at the rate

to keep the internal temperature below –65 °C. After addition, the cold bath temperature was warmed to –45 °C and allowed to slowly warm to 0 °C over 3 h. Reaction vessel was removed from the cold bath, stirred at room temperature for 15 min, and then quenched with aq. HCl (2 mL, 1M). The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 4 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired compound.

3-4. Optimization of reaction conditions

Table S1: Evaluation of Ni(II) salts and optimization of reaction conditions



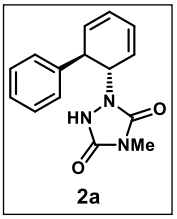
benzene

2a

Entry	Grignard equiv.	[Ni]	x (mol%)	y (mol%)	Yield (%)[a]	e.r.
1	2.5	$Ni(cod)_2$	10	20	70	95:5
2	2.5	$Ni(cod)_2$	5.0	10	67	95:5
3	2.0	$Ni(cod)_2$	5.0	10	62	95:5
4	2.5	$Ni(cod)_2$	5.0	7.0	65	94.5:5.5
5	2.0	$Ni(cod)_2$	5.0	7.0	62	94:6
6	1.5	$Ni(cod)_2$	5.0	7.0	56	93:7
7	2.5	$NiCl_2$	10	20	42	90:10
8	2.5	$Ni(dmg)_2$	10	20	51	90:10
9	2.5	$NiCl_2$•glyme	10	20	55	91:9
10	2.5	$NiBr_2$•glyme	10	20	55	93:7
11	2.5	$Ni(acac)_2$	10	20	59	93:7
12[b]	2.5	$Ni(acac)_2$	10	20	56	90:10
13	2.5	$Ni(acac)_2$	10	12	51	95:5
14	3.0	$Ni(acac)_2$	5.0	7.0	67	95:5
15	2.5	$Ni(acac)_2$	5.0	7.0	65	95:5
16[c]	2.5	$Ni(acac)_2$	5.0	7.0	65	95:5
17[c]	2.5	$Ni(acac)_2$	2.5	3.5	66	97:3
18[c]	2.5	$Ni(acac)_2$	1.5	2.0	70	97:3
19[c]	2.5	$Ni(acac)_2$	1.0	1.4	68	96:4

a) Isolated yield. b) Ni complex formed in THF. c) [Ni] and (*R*,*Rp*)-*i*Pr-Phosferrox weighed out in the air.

4. Characterization of Carboamination Products



2a

Synthesis of (+)-2a: The corresponding compound was prepared following general procedure **A** employing the commercially available 3.0M Grignard reagent in Et_2O. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [94.0 mg, 0.35 mmol, 70%, 97:3 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiracel® OJ-3 column, 50% *i*PrOH in *n*hexane, 0.8 mL/min t_R(minor) = 4.19 min, t_R(major) = 10.9 min).

26.5 mmol scale reaction:

In an oven-dried media bottle, MTAD (**1**, 3.00 g, 26.5 mmol, 1.0 equiv.) was dissolved in anhydrous CH_2Cl_2 (133 mL) under nitrogen atmosphere and cooled to –78 °C. Benzene (23.7 mL, 265 mmol, 10 equiv.) was slowly added and the solution was stirred for five minutes. The pink solution was irradiated with LED lights at –78 °C until complete loss of color. Upon decolorization, the LED lights were turned off and a pre-cooled (–78 °C) solution of [Ni(acac)$_2$] (102 mg, 0.398 mmol, 1.5 mol %) and (*R*,*R*$_p$)-*i*Pr-Phosferrox (255 mg, 0.531 mmol, 2.0 mol %) in CH_2Cl_2 (16 mL) was added, followed by dropwise addition of freshly prepared Grignard reagent (22.1 mL, 3.0 M in Et_2O, 66.3 mmol, 2.5 equiv.) at the rate to keep the internal temperature below –65 °C. After addition, the cold bath temperature was warmed to –45 °C and allowed to slowly warm to 0 °C over 3 h. Reaction vessel was removed from the cold bath, stirred at room temperature for 15 min, and then quenched with aq. HCl (100 mL, 1M). The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered, loaded onto silica and concentrated under reduced pressure. Purification by flash chromatography (CH_2Cl_2, SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [4.63 g, 17.2 mmol, 65%, 97:3 er].

R_f = 0.21 (SiO_2, hexanes:ethyl acetate = 1:1)

$[\alpha]_D^{23}$ = +538.9 (c = 1.00 in $CHCl_3$)

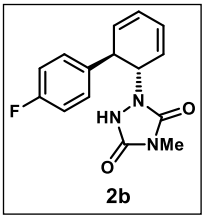
m.p. = 167 – 168 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.35 – 7.26 (m, 5H), 6.35 (ddt, J = 9.6, 5.4, 1.3 Hz, 1H), 6.21 (dddd, J = 9.6, 5.4, 1.9, 0.9 Hz, 1H), 6.00 (ddt, J = 9.6, 4.6, 1.1 Hz, 1H), 5.64 (ddt, J = 9.6, 4.7, 1.1 Hz, 1H), 5.02 (ddd, J = 6.7, 4.7, 1.9 Hz, 1H), 3.78 (ddd, J = 6.7, 4.7, 1.9 Hz, 1H), 3.05 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8, 153.4, 139.8, 130.0, 129.0, 128.9, 128.1, 127.6, 123.3, 120.7, 56.7, 44.9, 25.4.

HRMS (ESI-TOF, m/z) calcd. For $C_{15}H_{16}N_3O_2$ $[M+H]^+$ calc.: 270.1243; Found: 270.1243.

IR (ATR, neat, cm^{-1}): 3100 (w), 1768 (m), 1688 (s), 1479 (m), 753 (m), 719 (s), 702 (s), 686 (s), 617 (w).



2b

Synthesis of (+)-2b: The corresponding compound was prepared following general procedure **A**. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [104 mg, 0.36 mmol, 72%, 96.5:3.5 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiracel® OJ-3 column, 25% *i*PrOH in *n*hexane, 0.8 mL/min t_R(minor) = 6.23 min, t_R(major) = 8.25 min.

$\boldsymbol{R_f}$ = 0.24 (SiO_2, hexanes:ethyl acetate = 1:1)

$\boldsymbol{[\alpha]_D^{22}}$ = +489.0 (c = 1.00 in $CHCl_3$)

m.p. = 128 – 129 ˚C

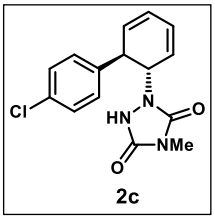
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.29 – 7.23 (m, 2H), 7.05 – 6.97 (m, 2H), 6.37 – 6.32 (m, 1H), 6.21 (dddd, J = 9.6, 5.4, 2.0, 1.0 Hz, 1H), 5.97 (ddt, J = 9.6, 4.6, 1.0 Hz, 1H), 5.64 (ddt, J = 9.6, 4.7, 1.0 Hz, 1H), 4.96 (ddd, J = 7.1, 4.7, 1.7 Hz, 1H), 3.77 (ddd, J = 6.8, 4.6, 2.0 Hz, 1H), 3.06 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 161.3, 154.8 (d, J = 207.2 Hz), 135.6 (d, J = 3.29 Hz), 129.8, 129.7 (d, J = 8.1 Hz), 129.0, 123.6, 120.8, 115.7 (d, J = 21.3 Hz), 57.0, 44.1, 25.4.

^{19}F NMR (471 MHz, $CDCl_3$) δ -115.03 (ddd, *J* = 13.6, 8.3, 5.1 Hz).

HRMS (ESI-TOF, m/z) calcd. For $C_{15}H_{15}N_3O_2F$ $[M+H]^+$ calc.: 288.1148; Found: 288.1156.

IR (ATR, neat, cm^{-1}): 3045 (w), 2251 (w), 1764 (w), 1683 (s), 1507 (m), 1478 (m), 1222 (m), 834 (w).



2c

Synthesis of (+)-2c: The corresponding compound was prepared following general procedure **A**. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [106 mg, 0.35 mmol, 70%, 96.5:3.5 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiracel® OJ-3 column, 15% *i*PrOH in *n*hexane, 0.8 mL/min t_R(minor) = 9.46 min, t_R(major) = 10.9 min.

$\boldsymbol{R_f}$ = 0.24 (SiO_2, hexanes:ethyl acetate = 1:1)

$\boldsymbol{[\alpha]_D^{22}}$ = +531.0 (c = 1.00 in $CHCl_3$)

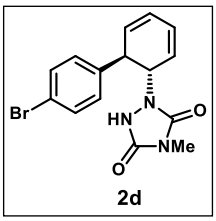
m.p. = 128 – 129 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.23 – 7.18 (m, 2H), 7.18 – 7.11 (m, 2H), 6.24 (ddt, J = 9.6, 5.4, 1.1 Hz, 1H), 6.11 (dddd, J = 9.6, 5.4, 1.8, 1.1 Hz, 1H), 5.85 (ddt, J = 9.6, 4.6, 1.1 Hz, 1H), 5.54 (ddt, J = 9.6, 4.6, 1.1 Hz, 1H), 4.87 (ddd, J = 7.1, 4.6, 1.8 Hz, 1H), 3.67 (ddd, J = 7.1, 4.6, 1.8 Hz, 1H), 2.96 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1, 153.3, 138.5, 133.4, 129.5, 129.4, 129.0, 128.9, 123.7, 120.9, 56.8, 44.2, 25.4.

HRMS (ESI-TOF, m/z) calcd. For $C_{15}H_{15}N_3O_2Cl$ $[M+H]^+$ calc.: 304.0853; Found: 304.0852.

IR (ATR, neat, cm^{-1}): 3045 (w), 1764 (m), 1682 (s), 1478 (s), 1400 (w), 1092 (m), 1015 (m), 828 (m), 728 (m).



2d

Synthesis of (+)-2d: The corresponding compound was prepared following general procedure **A**. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [115 mg, 0.33 mmol, 66%, 96.5:3.5 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiracel® OJ-3 column, 15% *i*PrOH in *n*hexane, 0.8 mL/min t_R(minor) = 10.2 min, t_R(major) = 11.3 min.

***R*$_f$** = 0.24 (SiO_2, hexanes:ethyl acetate = 1:1)

$[\alpha]_D^{21}$ = +420.0 (c = 1.00 in $CHCl_3$)

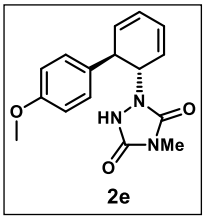
m.p. = 122 – 124 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2H), 7.18 – 7.12 (m, 2H), 6.34 (ddt, J = 9.6, 5.4, 1.3 Hz, 1H), 6.20 (dddd, J = 9.6, 5.4, 1.7, 1.0 Hz, 1H), 5.94 (ddt, J = 9.6, 4.7, 1.3 Hz, 1H), 5.61 (ddt, J = 9.6, 4.8, 1.0 Hz, 1H), 4.91 (ddd, J = 6.3, 4.8, 1.7 Hz, 1H), 3.69 (ddd, J = 6.3, 4.7, 1.7 Hz, 1H), 3.05 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8, 153.4, 138.8, 132.0, 129.9, 129.3, 129.1, 123.7, 121.5, 120.6, 56.4, 44.3, 25.4.

HRMS (ESI-TOF, m/z) calcd. For $C_{15}H_{15}N_3O_2Br$ $[M+H]^+$ calc.: 348.0348; Found: 304.0338.

IR (ATR, neat, cm^{-1}): 3045 (w), 1764 (m), 1682 (s), 1478 (s), 1400 (w), 1011 (w), 905 (w), 822 (w), 728 (m).



Synthesis of (+)-2e: The corresponding compound was prepared following general procedure **A**. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [112 mg, 0.37 mmol, 75%, 95.5:4.5 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiracel® OJ-3 column, 25% *i*PrOH in *n*hexane, 0.8 mL/min t_R(minor) = 8.42 min, t_R(major) = 12.3 min.

$\boldsymbol{R_f}$ = 0.24 (SiO_2, hexanes:ethyl acetate = 1:1)

$[\alpha]_D^{22}$ = +451.0 (c = 1.00 in $CHCl_3$)

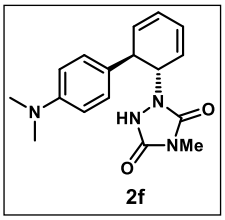
m.p. = 122 – 123 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.21 – 7.14 (m, 2H), 6.87 – 6.79 (m, 2H), 6.31 (ddt, J = 9.6, 5.3, 1.1 Hz, 1H), 6.21 – 6.11 (m, 1H), 5.96 (ddt, J = 9.6, 4.6, 1.1 Hz, 1H), 5.61 (ddd, J = 9.6, 4.6, 1.1 Hz, 1H), 4.95 (ddd, J = 6.7, 4.6, 1.8 Hz, 1H), 3.78 (s, 3H), 3.70 (ddd, J = 6.7, 4.6, 1.8 Hz, 1H), 3.03 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 154.9, 153.3, 131.7, 130.4, 129.1, 128.9, 123.2, 120.8, 114.3, 57.1, 55.4, 44.0, 25.4.

HRMS (ESI-TOF, m/z) calcd. For $C_{16}H_{18}N_3O_3$ $[M+H]^+$ calc.: 300.1348; Found: 300.1337.

IR (ATR, neat, cm^{-1}): 3042 (w), 2955 (w), 2837 (w), 2250 (w), 1764 (w), 1686 (s), 1511 (m), 1477 (m), 1248 (m).



Synthesis of (+)-2f: The corresponding compound was prepared following general procedure **A**, and was quenched by the addition of NH_4Cl (2 mL). Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [63.0 mg, 0.20 mmol, 40%, 96:4 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiracel® OJ-3 column, 25% *i*PrOH in *n*hexane, 0.8 mL/min t_R(minor) = 6.17 min, t_R(major) = 11.8 min.

$\boldsymbol{R_f}$ = 0.17 (SiO_2, hexanes:ethyl acetate = 1:1)

$[\alpha]_D^{23}$ = +669.2 (c = 1.00 in $CHCl_3$)

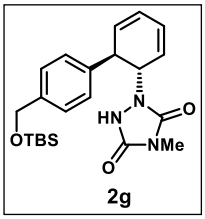
m.p. = 150 – 151 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.16 – 7.07 (m, 2H), 6.73 – 6.61 (m, 2H), 6.29 (ddt, J = 9.6, 5.4, 1.5 Hz, 1H), 6.13 (dddd, J = 9.6, 5.4, 1.9, 1.1 Hz, 1H), 5.96 (ddt, J = 9.6, 4.6, 1.1 Hz, 1H), 5.60 (ddt, J = 9.6, 4.8, 1.1 Hz, 1H), 4.95 (ddd, J = 6.7, 4.8, 1.5 Hz, 1H), 3.66 (ddd, J = 6.7, 4.6, 1.9 Hz, 1H), 3.03 (s, 3H), 2.91 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9, 153.3, 150.1, 130.8, 128.8, 128.7, 127.2, 122.9, 120.9, 112.9, 57.1, 43.9, 40.8, 25.3.

HRMS (ESI-TOF, m/z) calcd. For $C_{17}H_{21}N_4O_2$ $[M+H]^+$ calc.: 313.1665; Found: 313.1662.

IR (ATR, neat, cm^{-1}): 3040 (w), 2885 (w), 2801 (w), 2247 (w), 1763 (m), 1683 (s), 1613 (m), 1519 (m), 1476 (m).



2g

Synthesis of (+)-2g: The corresponding compound was prepared following general procedure **A**. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [139 mg, 0.34 mmol, 67%, 95.5:4.5 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiracel® OJ-3 column, 5% *i*PrOH in *n*hexane, 0.8 mL/min t_R(minor) = 8.76 min, t_R(major) = 12.1 min.

***R*$_f$** = 0.40 (SiO_2, hexanes:ethyl acetate = 1:1)

$[\alpha]_D^{22}$ = +399.9 (c = 1.00 in $CHCl_3$)

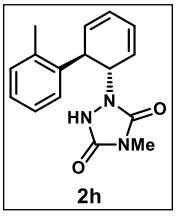
m.p. = 54 – 56 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.33 – 7.16 (m, 4H), 6.30 (ddt, J = 9.6, 5.4, 1.5 Hz, 1H), 6.16 (dddd, J = 9.6, 5.4, 2.0, 1.0 Hz, 1H), 5.95 (ddt, J = 9.5, 4.5, 1.0 Hz, 1H), 5.61 (ddt, J = 9.6, 4.5, 1.0 Hz, 1H), 4.99 (ddd, J = 7.1, 4.5, 1.5 Hz, 1H), 4.71 (s, 2H), 3.76 (ddd, J = 7.1, 4.5, 2.0 Hz, 1H), 3.02 (s, 3H), 0.93 (s, 9H), 0.09 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1, 153.3, 140.8, 138.5, 130.1, 128.8, 127.9, 126.6, 123.3, 121.1, 64.8, 57.0, 44.5, 26.1, 25.3, 18.5, -5.1.

HRMS (ESI-TOF, m/z) calcd. For $C_{22}H_{32}N_3O_3Si$ $[M+H]^+$ calc.: 414.2213; Found: 414.2207.

IR (ATR, neat, cm^{-1}): 3044 (w), 2953 (w), 2929 (w), 2885 (w), 2856 (w), 1765 (w), 1687 (s), 1471 (m), 1087 (m), 835 (s).



2h

Synthesis of (+)-2h: The corresponding compound was prepared following general procedure **A**. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [106 mg, 0.374 mmol, 75%, 92:8 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiralpak® IC-3 column, 15% *i*PrOH in *n*hexane, 0.8 mL/min t_R(major) = 5.86 min, t_R(minor) = 13.7 min.

***R*$_f$** = 0.18 (SiO_2, hexanes:ethyl acetate = 1:1)

[α]$_D^{23}$ = +478.1 (c = 1.54 in $CHCl_3$)

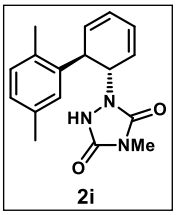
m.p. = 66 – 68 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.22 – 7.18 (m, 1H), 7.18 – 7.09 (m, 3H), 6.36 (ddt, *J* = 9.5, 5.4, 1.2 Hz, 1H), 6.22 (dddd, *J* = 9.6, 5.4, 1.7, 1.0 Hz, 1H), 5.94 (ddt, *J* = 9.5, 5.0, 1.0 Hz, 1H), 5.60 (ddt, *J* = 9.6, 5.4, 1.0 Hz, 1H), 4.91 (td, *J* = 5.0, 1.2 Hz, 1H), 3.91 (td, *J* = 5.0, 1.7 Hz, 1H), 3.05 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7, 152.7, 136.6, 136.2, 131.3, 130.0, 128.9, 127.53, 127.51, 126.2, 123.3, 120.2, 54.1, 41.0, 25.4, 20.0.

HRMS (ESI-TOF, m/z) calcd. For $C_{16}H_{17}N_3O_2Na$ $[M+Na]^+$ calc.: 306.1218; Found: 306.1210.

IR (ATR, neat, cm^{-1}): 3161 (w), 1765 (m), 1686 (s), 1476 (m), 1399 (w), 1026 (w), 748 (w), 724 (w), 601 (w).



2i

Synthesis of (+)-2i: The corresponding compound was prepared following general procedure **A**. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless oil [105 mg, 0.353 mmol, 71%, 94:6 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiralpak® IC-3 column, 15% *i*PrOH in *n*hexane, 0.8 mL/min t_R(major) = 5.03 min, t_R(minor) = 9.77 min.

***R*$_f$** = 0.23 (SiO_2, hexanes:ethyl acetate = 1:1)

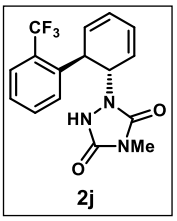
[α]$_D^{23}$ = +211.5 (c = 1.00 in $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 6.97 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.93 (d, *J* = 1.8 Hz, 1H), 6.36 (ddt, *J* = 9.6, 5.5, 1.2 Hz, 1H), 6.22 (dddd, *J* = 9.6, 5.5, 1.8, 1.0 Hz, 1H), 5.93 (ddt, *J* = 9.6, 4.9, 1.2 Hz, 1H), 5.60 (ddt, *J* = 9.6, 4.9, 1.0 Hz, 1H), 4.90 (td, *J* = 4.9, 1.2 Hz, 1H), 3.86 (td, *J* = 4.9, 1.8 Hz, 1H), 3.05 (s, 3H), 2.37 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6, 152.7, 136.5, 135.7, 132.9, 131.2, 130.1, 128.9, 128.2, 128.1, 123.2, 120.1, 54.1, 41.0, 25.4, 21.2, 19.5.

HRMS (ESI-TOF, m/z) calcd. For $C_{17}H_{19}N_3O_2Na$ $[M+Na]^+$ calc.: 320.1375; Found: 320.1367.

IR (ATR, neat, cm^{-1}): 3164 (w), 1766 (m), 1693 (s), 1477 (m), 1399 (w), 1277 (w), 1026 (w), 811 (w), 758 (w).



Synthesis of (+)-2j: The corresponding compound was prepared following general procedure **A**. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [93 mg, 0.28 mmol, 55%, 91:9 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiralpak® IC-3 column, 10% *i*PrOH in *n*hexane, 2.0 mL/min t_R(minor) = 3.46 min, t_R(major) = 7.25 min.

R_f = 0.23 (SiO_2, hexanes:ethyl acetate = 1:1)

$[\alpha]_D^{24}$ = +10.9 (c = 0.50 in $CHCl_3$)

m.p. = 98 – 100 ˚C

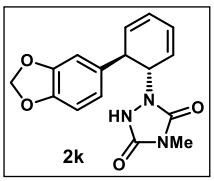
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.58 (m, 1H), 7.50 (d, *J* = 1.2 Hz, 1H), 7.49 (d, *J* = 1.0 Hz, 1H), 7.40 – 7.32 (m, 1H), 7.09 (s, 1H), 6.35 (ddt, *J* = 9.6, 5.6, 1.1 Hz, 1H), 6.13 (dddd, *J* = 9.6, 5.6, 2.0, 0.8 Hz, 1H), 5.86 (ddt, *J* = 9.6, 4.8, 1.1 Hz, 1H), 5.67 (ddt, *J* = 9.6, 4.8, 1.1 Hz, 1H), 5.08 (ddd, *J* = 6.1, 4.8, 1.5 Hz, 1H), 4.09 – 4.01 (m, 1H), 3.05 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 153.5, 139.5, 132.6, 129.5, 129.3, 128.4, 128.1 (q, J = 29.6 Hz) 127.6, 126.3 (q, J = 5.8 Hz), 125.6 (q, J = 274.0 Hz) 122.5, 120.9, 55.4, 39.9 (q, J = 1.6 Hz), 25.4.

^{19}F NMR (471 MHz, $CDCl_3$) δ -58.11 (s).

HRMS (ESI-TOF, m/z) calcd. For $C_{16}H_{14}N_3O_2NaF_3$ $[M+Na]^+$ calc.: 360.0936; Found: 360.0936.

IR (ATR, neat, cm^{-1}): 3148 (w), 1770 (w), 1697 (s), 1478 (m), 1312 (m), 1157 (w), 1115 (m), 765 (m).



Synthesis of (+)-2k: The corresponding compound was prepared following general procedure **A**. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [116 mg, 0.37 mmol, 74%, 97:3 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiracel® OJ-3 column, 25% *i*PrOH in *n*hexane, 0.8 mL/min t_R(minor) = 11.6 min, t_R(major) = 13.3 min.

53.1 mmol scale reaction:

In an oven-dried media bottle, MTAD (**1**, 6.00 g, 53.1 mmol, 1.0 equiv.) was dissolved in anhydrous CH_2Cl_2 (265 mL) under nitrogen atmosphere and cooled to –78 °C. Benzene (47.3 mL, 531 mmol, 10 equiv.) was slowly added and the solution was stirred for five minutes. The pink solution was irradiated with LED lights at –78 °C until complete loss of color. Upon decolorization, the LED lights were turned off and a pre-cooled (–78 °C) solution of $[Ni(acac)_2]$ (204 mg, 0.796 mmol, 1.5 mol %) and (*R*,R_p)-*i*Pr-Phosferrox (510 mg, 1.06 mmol, 2.0 mol %) in CH_2Cl_2 (32 mL) was added, followed by dropwise addition of freshly prepared Grignard reagent (44.2 mL, 3.0 M in Et_2O, 133 mmol, 2.5 equiv.) at the rate to keep the internal temperature below

–65 °C. After addition, the cold bath temperature was warmed to –45 °C and allowed to slowly warm to 0 °C over 3 h. Reaction vessel was removed from the cold bath, stirred at room temperature for 15 min, and then quenched with aq. HCl (200 mL, 1M). The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 200 mL). The combined organic extracts were dried over $MgSO_4$, filtered, loaded onto silica and concentrated under reduced pressure. Purification by flash chromatography (CH_2Cl_2, SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [11.29 g, 36.0 mmol, 68%, 97:3 er].

$\boldsymbol{R_f}$ = 0.2 (SiO_2, hexanes:ethyl acetate = 1:1)

$[\alpha]_D^{23}$ = +475.9 (c = 1.00 in $CHCl_3$)

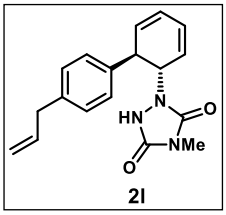
m.p. = 160 – 161 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 6.76 (d, J = 1.2 Hz, 1H), 6.72 (d, J = 1.2 Hz, 2H), 6.28 (ddt, J = 9.6, 5.4, 1.4 Hz, 1H), 6.13 (dddd, J = 9.6, 5.4, 2.0, 1.0 Hz, 1H), 5.96 – 5.88 (m, 3H), 5.60 (ddt, J = 9.6, 4.5, 1.0 Hz, 1H), 4.94 (ddd, J = 7.6, 4.5, 1.7 Hz, 1H), 3.68 (ddd, J = 7.6, 4.5, 2.0 Hz, 1H), 3.03 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1, 153.3, 148.0, 147.0, 133.9, 130.1, 128.7, 123.3, 121.3, 121.1, 108.5, 108.4, 101.2, 57.3, 44.5, 25.3.

HRMS (ESI-TOF, m/z) calcd. For $C_{16}H_{15}N_3O_4$ $[M]^+$ calc.:313.1063; Found: 313.1071

IR (ATR, neat, cm^{-1}): 3452 (w), 3158 (w), 2891 (w), 1765 (w), 1689 (s), 1502 (m), 1483 (m), 1246 (m), 1037 (m).



2l

Synthesis of (+)-2l: The corresponding compound was prepared following general procedure **A**. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless oil [90.0 mg, 0.29 mmol, 58%, 94:6 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiralpak® IC-3 column, 15% *i*PrOH in *n*hexane, 0.8 mL/min t_R(major) = 3.90 min, t_R(minor) = 6.33 min.

$\boldsymbol{R_f}$ = 0.36 (SiO_2, hexanes:ethyl acetate = 1:1)

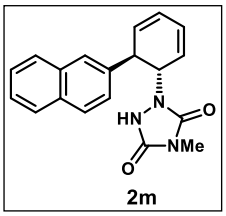
$[\alpha]_D^{23}$ = +362.6 (c = 1.00 in $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (s, 1H), 7.19 (d, J = 8.2 Hz, 1H), 7.13 (d, J = 8.2 Hz, 2H), 6.32 (ddt, J = 9.6, 5.4, 1.5 Hz, 1H), 6.18 (dddd, J = 9.6, 5.4, 1.9, 1.0 Hz, 1H), 6.00 – 5.89 (m, 2H), 5.61 (ddt, J = 9.6, 4.8, 1.0 Hz, 1H), 5.07 (dq, J = 8.0, 1.6 Hz, 1H), 5.05 (t, J = 1.5 Hz, 1H), 4.96 (ddd, J = 6.5, 4.8, 1.6 Hz, 1H), 3.71 (ddd, J = 6.5, 4.8, 1.9 Hz, 1H), 3.39 – 3.32 (m, 2H), 3.03 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8, 153.3, 139.5, 137.4, 137.4, 130.2, 129.1, 129.0, 128.1, 123.2, 120.7, 116.0, 56.7, 44.5, 40.0, 25.4.

HRMS (ESI-TOF, m/z) calcd. For $C_{18}H_{20}N_3O_2$ $[M+H]^+$ calc.: 310.1556; Found: 310.1556.

IR (ATR, neat, cm^{-1}): 3044 (w), 1766 (w), 1682 (s), 1474 (m), 1398 (w), 1023 (w), 753 (m), 606 (w).



Synthesis of (+)-2m: The corresponding compound was prepared following general procedure **A**. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [120 mg, 0.37 mmol, 75%, 94:6 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiralpak® IC-3 column, 25% *i*PrOH in *n*hexane, 0.8 mL/min t_R(minor) = 8.27 min, t_R(major) = 5.09 min.

$\boldsymbol{R_f}$ = 0.33 (SiO_2, hexanes:ethyl acetate = 1:1)

$\boldsymbol{[\alpha]_D^{22}}$ = +409.7 (c = 1.00 in $CHCl_3$)

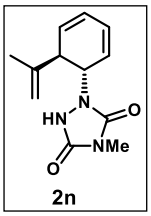
m.p. = 85 – 86 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 3H), 7.70 – 7.64 (m, 1H), 7.59 – 7.53 (m, 1H), 7.47 – 7.41 (m, 3H), 6.37 (ddt, J = 9.6, 5.4, 1.1 Hz, 1H), 6.25 (dddd, J = 9.6, 5.4, 1.9, 1.0 Hz, 1H), 6.06 (ddt, J = 9.6, 4.7, 1.1 Hz, 1H), 5.65 (ddt, J = 9.6, 4.7, 1.0 Hz, 1H), 5.09 (ddd, J = 6.5, 4.7, 1.8 Hz, 1H), 3.92 (ddd, J = 6.5, 4.7, 1.8 Hz, 1H), 3.00 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9, 153.4, 137.1, 133.5, 132.9, 129.9, 129.0, 128.9, 127.9, 127.8, 126.7, 126.3, 126.3, 126.1, 123.6, 120.8, 56.6, 45.0, 25.4.

HRMS (ESI-TOF, m/z) calcd. For $C_{19}H_{18}N_3O_2$ $[M+H]^+$ calc.: 320.1399; Found: 320.1408.

IR (ATR, neat, cm^{-1}): 3048 (w), 2923 (m), 2853 (w), 1765 (w), 1683 (s), 1470 (m), 818 (m), 743 (m), 606 (m), 476 (m).



Synthesis of (+)-2n: The corresponding compound was prepared following general procedure **A**. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless oil [64.0 mg, 0.27 mmol, 55%, 89:11 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiralcel® OJ-3 column, 5% *i*PrOH in *n*hexane, 2.0 mL/min t_R(minor) = 4.9 min, t_R(major) = 6.4 min.

$\boldsymbol{R_f}$ = 0.24 (SiO_2, hexanes:ethyl acetate = 1:1)

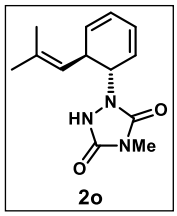
$\boldsymbol{[\alpha]_D^{24}}$ = +188.9 (c = 1.00 in $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 6.24 – 6.12 (m, 1H), 6.02 (dddd, *J* = 9.7, 5.3, 2.2, 0.9 Hz, 1H), 5.74 (ddt, *J* = 9.7, 4.2, 1.1 Hz, 1H), 5.62 (ddt, *J* = 9.7, 4.2, 1.1 Hz, 1H), 4.96 (ddd, *J* = 9.0, 4.2, 1.9 Hz, 1H), 4.86 – 4.76 (m, 2H), 3.25 – 3.16 (m, 1H), 3.06 (s, 3H), 1.79 (dd, *J* = 1.5, 0.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1, 153.5, 143.3, 129.6, 128.2, 123.2, 122.2, 113.9, 53.5, 46.6, 25.4, 20.2.

HRMS (ESI-TOF, m/z) calcd. For $C_{12}H_{15}BrN_3O_2$ $[M+Br]^-$ calc.: 312.0353; Found: 312.0361.

IR (ATR, neat, cm^{-1}): 3167 (w), 1768 (w), 1692 (s), 1476 (m), 1397 (w), 1024 (w), 763 (w), 608 (w).



2o

Synthesis of (+)-2o: The corresponding compound was prepared following general procedure **A**. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless oil [65.0 mg, 0.26 mmol, 53%, 97.5:2.5 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiralpak® IC-3 column, 15% *i*PrOH in *n*hexane, 0.8 mL/min t_R(major) = 5.4 min, t_R(minor) = 9.2 min.

***R*$_f$** = 0.32 (SiO_2, hexanes:ethyl acetate = 1:1)

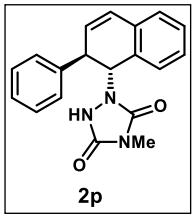
$[\alpha]_D^{23}$ = +555.0 (c = 1.00 in $CHCl_3$)

^{1}H NMR (500 MHz, C_6D_6) δ 8.99 (s, 1H), 5.90 (dddd, *J* = 9.6, 5.3, 2.1, 1.2 Hz, 1H), 5.71 (dddd, *J* = 9.6, 5.3, 2.1, 1.0 Hz, 1H), 5.63 (ddt, *J* = 9.6, 4.1, 1.2 Hz, 1H), 5.55 (ddt, *J* = 9.6, 4.1, 1.0 Hz, 1H), 5.11 (dp, *J* = 9.8, 1.5 Hz, 1H), 4.94 (ddd, *J* = 9.7, 4.1, 2.1 Hz, 1H), 3.54 (tdd, *J* = 9.7, 4.1, 2.1 Hz, 1H), 2.67 (s, 3H), 1.56 (d, *J* = 1.5 Hz, 3H), 1.54 (d, *J* = 1.5 Hz, 3H).

^{13}C NMR (126 MHz, C_6D_6) δ 155.8, 154.1, 135.1, 131.1, 128.4, 124.2, 123.2, 122.7, 56.7, 38.4, 25.8, 24.8, 18.0.

HRMS (ESI-TOF, m/z) calcd. For $C_{13}H_{17}ClN_3O_2$ $[M+Cl]^-$ calc.: 282.1015; Found: 282.1023.

IR (ATR, neat, cm^{-1}): 3157 (w), 1762 (w), 1682 (s), 1476 (m), 1375 (w), 1016 (w), 763 (m), 716 (m).



2p

Synthesis of (+)-2p: The corresponding compound was prepared following general procedure **A** employing the commercially available 3.0M Grignard reagent in Et_2O. Naphthalene was employed in 2.0 equivalents and the cycloaddition was run in 5.0 mL CH_2Cl_2 Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [100 mg, 0.31 mmol, 63%, 94.5:5.5 er]. Enantiomeric excess was determined with HPLC analysis using Diacel Chiracel® OJ-3 column, 25% *i*PrOH in *n*hexane, 0.8 mL/min t_R(minor) = 8.5 min, t_R(major) = 12.3 min.

***R*f** = 0.37 (SiO_2, hexanes:ethyl acetate = 1:1)

[α]D21 = +200.4 (c = 1.00 in $CHCl_3$)

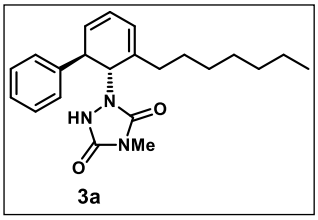
m.p. = 140 – 142 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 1H), 7.36 – 7.18 (m, 9H), 6.69 (dd, J = 9.6, 2.2 Hz, 1H), 6.09 (dd, J = 9.6, 3.8 Hz, 1H), 5.66 – 5.56 (m, 1H), 4.07 (ddd, J = 8.7, 3.8, 2.2 Hz, 1H), 2.90 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8, 154.0, 139.9, 134.1, 130.3, 130.2, 129.2, 128.8, 128.6, 128.4, 127.9, 127.8, 127.1, 126.6, 60.8, 45.4, 25.2.

HRMS (ESI-TOF, m/z) calcd. For $C_{19}H_{18}N_3O_2$ $[M+H]^+$ calc.: 320.1399; Found: 320.1400.

IR (ATR, neat, cm^{-1}): 3063.83 (w), 1763 (w), 1689 (s)1479 (m), 1452 (w), 1279 (w), 1225 (w), 732 (w).



3a

Synthesis of (±)-3a: The corresponding compound was prepared following general procedure **B** employing the commercially available 3.0M Grignard reagent in Et_2O. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless oil [96.0 mg, 0.26 mmol, 52%].

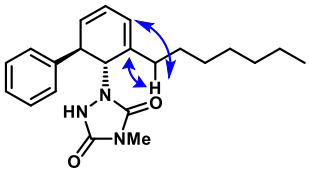
***R*f** = 0.48 (SiO_2, hexanes:ethyl acetate = 1:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.25 – 7.21 (m, 3H), 7.18 (d, *J* = 5.5 Hz, 1H), 6.21 (ddd, *J* = 9.5, 5.5, 1.2 Hz, 1H), 6.10 (dq, *J* = 5.9, 1.2 Hz, 1H), 5.89 (dd, *J* = 9.5, 5.5 Hz, 1H), 4.75 (d, *J* = 2.4 Hz, 1H), 3.77 – 3.51 (m, 1H), 3.10 (s, 3H), 2.06 – 1.79 (m, 2H), 1.40 – 1.00 (m, 10H), 0.84 (t, *J* = 7.3 Hz, 3H).

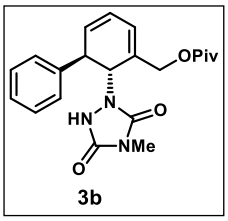
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 152.7, 139.1, 132.5, 128.9, 127.9, 127.5, 126.6, 124.0, 123.8, 57.8, 45.6, 34.4, 31.8, 29.1, 29.0, 27.3, 25.4, 22.7, 14.2.

HRMS (ESI-TOF, m/z) calcd. For $C_{24}H_{29}F_3N_3O_4$ $[M+CF_3COO]^-$ calc.: 480.2116; Found: 480.2115.

IR (ATR, neat, cm^{-1}): 2926 (w), 2855 (w), 1765 (w), 1690 (s), 1468 (m), 1397 (w), 1222 (w), 1026 (w).



HMBC correlations



3b

Synthesis of (±)-3b: The corresponding compound was prepared following general procedure **B** employing the commercially available 3.0M Grignard reagent in Et_2O. ^1H NMR analysis of the crude reaction mixture showed a ratio of constitutional isomers of 9:1. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 4:1 → 2:1) afforded the product as a colorless solid of an inseparable mixture of constitutional isomers [110 mg, 0.29 mmol, 57%].

***R*f** = 0.31 (SiO_2, hexanes:ethyl acetate = 1:1)

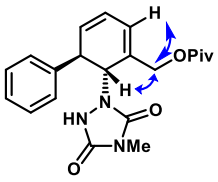
m.p. = 87 – 89 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.26 – 7.21 (m, 3H), 6.35 – 6.31 (m, 1H), 6.21 (ddd, J = 9.6, 5.6, 1.4 Hz, 1H), 5.99 (dd, J = 9.6, 5.2 Hz, 1H), 4.87 (d, J = 4.0 Hz, 1H), 4.59 (d, J = 13.5 Hz, 1H), 4.44 (d, J = 13.5 Hz, 1H), 3.76 – 3.69 (m, 1H), 3.06 (s, 3H), 1.09 (s, 9H).

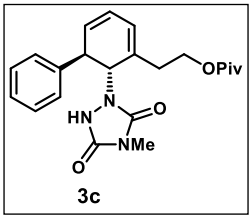
^{13}C NMR (126 MHz, $CDCl_3$) δ 178.6, 154.9, 153.4, 139.1, 129.7, 129.0, 128.0, 127.7, 126.9, 126.8, 122.7, 64.4, 56.8, 45.3, 39.0, 27.2, 25.4.

HRMS (ESI-TOF, m/z) calcd. For $C_{21}H_{29}N_4O_4$ $[M+NH_4]^+$ calc.: 401.2183; Found: 401.2186.

IR (ATR, neat, cm^{-1}): 3061 (w), 2972 (w), 1766 (w), 1688 (s), 1477 (m), 1143 (m), 762 (m), 728 (m).



HMBC correlations



3c

Synthesis of (±)-3c: The corresponding compound was prepared following general procedure **B** employing the commercially available 3.0M Grignard reagent in Et_2O. ^1H NMR analysis of the crude reaction mixture showed a ratio of constitutional isomers of 11:1. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 4:1 → 2:1) afforded the product as a colorless solid of an inseparable mixture of constitutional isomers [111 mg, 0.28 mmol, 56%].

***R*f** = 0.20 (SiO_2, hexanes:ethyl acetate = 1:1)

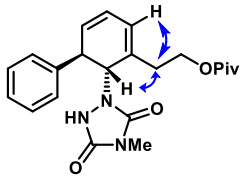
m.p. = 76 – 78 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.42 – 7.09 (m, 5H), 6.21 – 6.06 (m, 2H), 6.00 – 5.86 (m, 1H), 4.85 (d, J = 4.1 Hz, 1H), 4.18 (dtd, J = 12.9, 7.0, 4.1 Hz, 1H), 4.03 – 3.93 (m, 1H), 3.69 – 3.60 (m, 1H), 3.08 (s, 3H), 2.41 – 2.34 (m, 2H), 1.14 (s, 9H).

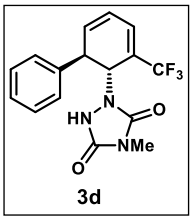
^{13}C NMR (126 MHz, $CDCl_3$) δ 178.8, 154.4, 153.5, 139.4, 129.0, 128.3, 128.1, 127.9, 127.6, 126.4, 122.9, 62.3, 59.1, 45.6, 38.9, 34.3, 27.3, 25.4.

HRMS (ESI-TOF, m/z) calcd. For $C_{24}H_{27}F_3N_3O_6$ $[M+CF_3COO]^-$ calc.: 510.1857; Found: 510.1839.

IR (ATR, neat, cm^{-1}): 2973 (w), 1698 (s), 1590 (w), 1479 (m), 1378 (w), 1284 (w), 1156 (m), 1035 (w).



HMBC correlations



3d

Synthesis of (±)-3d: The corresponding compound was prepared following general procedure **B** employing the commercially available 3.0M Grignard reagent in Et_2O. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 4:1 → 2:1) afforded the product as a colorless solid [66.0 mg, 0.196 mmol, 39%].

***R*f** = 0.26 (SiO_2, hexanes:ethyl acetate = 1:1)

m.p. = 60 – 62 ˚C

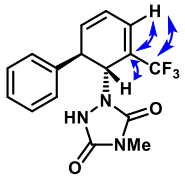
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.37 – 7.27 (m, 3H), 7.22 – 7.18 (m, 2H), 6.98 – 6.93 (m, 1H), 6.36 (ddt, J = 9.6, 5.7, 1.0 Hz, 1H), 6.29 (dd, J = 9.6, 5.3 Hz, 1H), 5.15 (d, J = 2.8 Hz, 1H), 3.85 – 3.75 (m, 1H), 3.08 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1, 153.2, 137.2, 134.3, 131.4 (q, J = 5.9 Hz), 129.3, 128.2, 127.7, 123.1 (q, J = 271.8 Hz), 121.3, 119.5 (q, J = 31.4 Hz), 53.1, 46.0, 25.5.

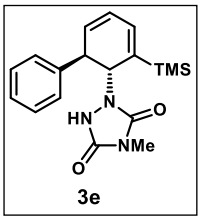
^{19}F NMR (471 MHz, $CDCl_3$) δ -67.0.

HRMS (ESI-TOF, m/z) calcd. For $C_{18}H_{14}F_6N_3O_4$ $[M+CF_3COO]^-$ calc.: 450.0894; Found: 450.0911.

IR (ATR, neat, cm^{-1}): 3617 (w), 1766 (w), 1697 (s), 1479 (m), 1308 (m), 1168 (m), 1116 (m), 728 (m).



HMBC correlations



3e

Synthesis of (±)-3e: The corresponding compound was prepared following general procedure **B** employing the commercially available 3.0M Grignard reagent in Et_2O. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 4:1 → 2:1) afforded the product as a colorless solid [93.0 mg, 0.27 mmol, 54%].

***R*f** = 0.56 (SiO_2, hexanes:ethyl acetate = 1:1)

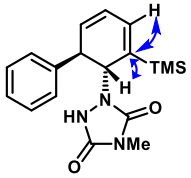
m.p. = 139 – 140 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.15 (m, 5H), 6.65 (dt, J = 5.3, 1.0 Hz, 1H), 6.31 (ddd, J = 9.6, 5.3, 1.3 Hz, 1H), 6.10 (ddt, J = 9.5, 5.4, 1.0 Hz, 1H), 5.01 (dt, J = 2.8, 1.0 Hz, 1H), 3.64 (ddd, J = 5.4, 2.8, 1.3 Hz, 1H), 3.11 (s, 3H), 0.00 (s, 9H).

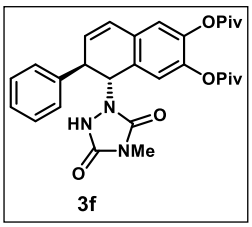
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.1, 152.1, 138.7, 136.7, 132.1, 130.5, 128.8, 127.9, 127.5, 123.8, 56.0, 44.8, 25.4, -2.2.

HRMS (ESI-TOF, m/z) calcd. For $C_{18}H_{24}N_3O_2Si$ $[M+H]^+$ calc.: 342.1638; Found: 342.1649.

IR (ATR, neat, cm^{-1}): 3028 (w), 2954 (w), 1762 (w), 1690 (s), 1478 (m), 1398 (w), 1248 (w), 838 (m).



HMBC correlations



Synthesis of (±)-3f: The corresponding compound was prepared following general procedure **C** employing the commercially available 3.0M Grignard reagent in Et_2O. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 4:1 → 2:1) afforded the product as a colorless solid [114 mg, 0.22 mmol, 44%].

R_f = 0.49 (SiO_2, hexanes:ethyl acetate = 1:1)

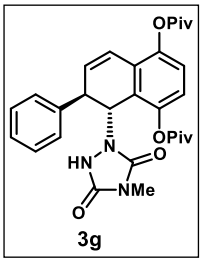
m.p. = 128 – 129 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.34 – 7.22 (m, 5H), 7.04 (s, 1H), 7.00 (s, 1H), 6.59 (dd, J = 9.7, 2.3 Hz, 1H), 6.08 (dd, J = 9.7, 3.5 Hz, 1H), 5.61 (dd, J = 9.7, 1.2 Hz, 1H), 4.09 (dt, J = 9.7, 2.9 Hz, 1H), 2.86 (d, J = 1.2 Hz, 3H), 1.35 (d, J = 1.4 Hz, 9H), 1.33 (d, J = 1.4 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 175.7, 154.8, 154.3, 142.7, 142.0, 139.6, 132.4, 131.2, 128.8, 128.7, 128.3, 127.8, 126.4, 121.63, 121.60, 60.7, 44.8, 39.2, 39.1, 27.2, 27.2, 25.0.

HRMS (ESI-TOF, m/z) calcd. For $C_{29}H_{34}N_3O_6$ $[M+H]^+$ calc.: 520.2448; Found: 520.2456.

IR (ATR, neat, cm^{-1}): 2974 (w), 2873 (w), 1759 (m), 1697 (s), 1479 (m), 1397 (w), 1273 (m), 1108 (s), 731 (m).



Synthesis of (±)-3g: The corresponding compound was prepared following general procedure **C** employing the commercially available 3.0M Grignard reagent in Et_2O. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 4:1 → 2:1) afforded the product as a colorless solid [120 mg, 0.23 mmol, 46%].

R_f = 0.54 (SiO_2, hexanes:ethyl acetate = 1:1)

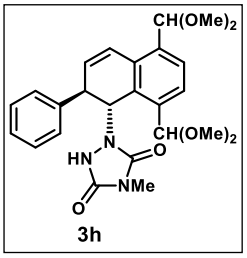
m.p. = 101 – 103 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.17 (m, 5H), 7.09 (d, J = 8.8 Hz, 1H), 6.88 (d, J = 8.8 Hz, 1H), 6.78 (dd, J = 9.9, 1.1 Hz, 1H), 6.23 (ddd, J = 9.9, 6.0, 1.1 Hz, 1H), 5.52 (t, J = 1.1 Hz, 1H), 3.77 (d, J = 6.0 Hz, 1H), 3.10 (s, 3H), 1.46 (s, 9H), 1.29 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.6, 176.6, 154.8, 153.1, 147.3, 144.2, 138.2, 130.1, 129.0, 128.1, 127.8, 127.4, 124.0, 122.9, 120.7, 120.0, 53.3, 44.9, 39.4, 39.3, 27.3, 27.0, 25.3.

HRMS (ESI-TOF, m/z) calcd. For $C_{29}H_{34}N_3O_6$ $[M+H]^+$ calc.: 520.2448; Found: 520.2437.

IR (ATR, neat, cm^{-1}): 3227 (w), 2975 (w), 1750 (m), 1703 (s), 1472 (m), 1221 (w), 1103 (s), 906 (w).



3h

Synthesis of (±)-3h: The corresponding compound was prepared following general procedure **C** employing the commercially available 3.0M Grignard reagent in Et_2O. The reaction was quenched with NH_4Cl (2.0 mL). Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 4:1 → 2:1) afforded the product as a colorless solid [115 mg, 0.25 mmol, 49%].

R_f = 0.11 (SiO_2, hexanes:ethyl acetate = 1:1)

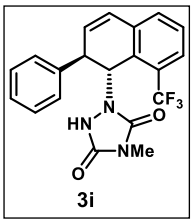
m.p. = 141 – 143 ˚C

^{1}H NMR (500 MHz, C_6D_6) δ 7.72 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.63 (s, 1H), 7.35 (dd, J = 9.9, 0.8 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.02 – 6.96 (m, 2H), 6.95 – 6.89 (m, 1H), 6.35 (t, J = 1.4 Hz, 1H), 5.97 (ddd, J = 9.9, 6.0, 1.4 Hz, 1H), 5.67 (s, 1H), 5.62 (s, 1H), 3.82 – 3.74 (m, 1H), 3.19 (s, 3H), 3.10 (s, 3H), 3.09 (s, 3H), 2.73 (s, 3H), 2.58 (s, 3H).

^{13}C NMR (126 MHz, C_6D_6) δ 154.9, 153.5, 138.2, 134.0, 132.7, 128.8, 128.7, 128.5, 128.4, 128.0, 127.3, 127.01, 126.96, 125.8, 101.3, 100.4, 54.9, 53.7, 52.9, 51.8, 50.7, 45.4, 24.8.

HRMS (ESI-TOF, m/z) calcd. For $C_{25}H_{29}N_3O_6Na$ $[M+Na]^+$ calc.: 490.1954; Found: 490.1945.

IR (ATR, neat, cm^{-1}): 2935 (w), 2829 (w), 1764 (w), 1692 (s), 1475 (m), 1398 (w), 1190 (m), 1111 (m), 1051 (m).



3i

Synthesis of (±)-3i: The corresponding compound was prepared following general procedure **C** employing the commercially available 3.0M Grignard reagent in Et_2O. ^{1}H NMR analysis of the crude reaction mixture showed a ratio of constitutional isomers of 9:1. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [145 mg, 0.37 mmol, 75%]. Complete purging of the constitutional isomer for analysis was achieved by recrystallization from Et_2O:Hexanes.

R_f = 0.30 (SiO_2, hexanes:ethyl acetate = 1:1)

m.p. = 177 – 179 ˚C

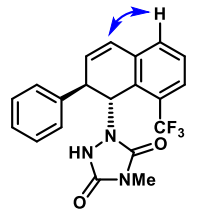
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, J = 7.5, 1.7 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.44 (dd, J = 7.8, 1.8 Hz, 1H), 7.24 – 7.18 (m, 3H), 7.15 (dd, J = 7.8, 1.8 Hz, 2H), 6.87 (dd, J = 9.7, 1.0 Hz, 1H), 6.30 (ddd, J = 9.7, 6.0, 1.0 Hz, 1H), 5.80 (t, J = 1.3 Hz, 1H), 3.98 (dd, J = 6.0, 1.3 Hz, 1H), 3.08 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8, 153.1, 136.7, 135.8, 130.7, 130.5, 129.9, 129.0, 127.8, 127.73, 127.67, 126.1 (q, J = 5.8 Hz), 125.2, 124.7, 122.5, 55.8, 46.1, 25.4.

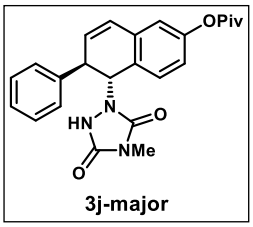
^{19}F NMR (471 MHz, $CDCl_3$) δ -64.3.

HRMS (ESI-TOF, m/z) calcd. For $C_{20}H_{17}N_3O_2F_3$ $[M+H]^+$ calc.: 388.1273; Found: 388.1261.

IR (ATR, neat, cm^{-1}): 3064 (w), 1765 (w), 1691 (s), 1478 (m), 1316 (m), 1164 (w), 1120 (m), 703 (m).



HMBC correlations



3j-major

Synthesis of (±)-3j: The corresponding compound was prepared following general procedure **C** employing the commercially available 3.0M Grignard reagent in Et_2O. ^1H NMR analysis of the crude reaction mixture showed a ratio of constitutional isomers of 1.5:1. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 4:1 → 2:1) afforded the product as a colorless solid [86.0 mg, 0.21 mmol, 41%]. Constitutional isomers were separated by flash chromatography.

R_f = 0.28 (SiO_2, hexanes:ethyl acetate = 1:1)

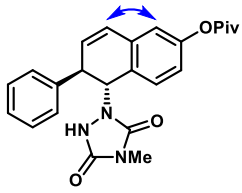
m.p. = 110 – 112 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 1H), 7.35 – 7.16 (m, 6H), 6.91 (d, *J* = 6.8 Hz, 2H), 6.61 (dd, *J* = 9.7, 2.2 Hz, 1H), 6.10 (dd, *J* = 9.7, 3.9 Hz, 1H), 5.57 (dd, *J* = 8.6, 0.9 Hz, 1H), 4.03 (ddd, *J* = 8.6, 3.9, 2.2 Hz, 1H), 2.88 (s, 2H), 1.35 (d, *J* = 0.9 Hz, 9H).

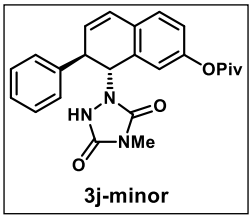
^{13}C NMR (126 MHz, $CDCl_3$) δ 177.2, 154.8, 154.1, 151.7, 139.7, 135.4, 131.37, 131.36, 128.8, 128.3, 127.9, 127.4, 127.3, 121.2, 120.0, 60.5, 45.3, 39.3, 27.2, 25.2.

HRMS (ESI-TOF, m/z) calcd. For $C_{26}H_{28}N_3O_6$ $[M+CH_3COO]^-$ calc.: 478.1984; Found: 478.1962.

IR (ATR, neat, cm^{-1}): 2974 (w), 1751 (m), 1696 (s), 1478 (m), 1244 (m), 1149 (m), 1120 (m), 761 (w).



HMBC correlations



3j-minor

***R*f** = 0.39 (SiO_2, hexanes:ethyl acetate = 1:1)

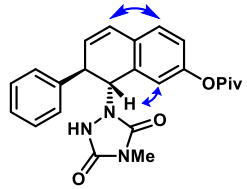
m.p. = 94 – 95 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.21 (m, 5H), 7.18 (d, J = 8.2 Hz, 1H), 6.99 (ddd, J = 8.2, 2.3, 0.7 Hz, 1H), 6.95 (d, J = 2.3 Hz, 1H), 6.62 (dd, J = 9.7, 2.5 Hz, 1H), 6.04 (dd, J = 9.7, 3.4 Hz, 1H), 5.61 (d, J = 10.0 Hz, 1H), 4.08 (ddd, J = 10.0, 3.4, 2.5 Hz, 1H), 2.84 (s, 3H), 1.32 (s, 9H).

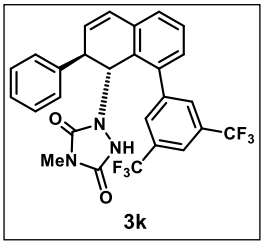
^{13}C NMR (126 MHz, Chloroform-d) δ 177.2, 154.8, 154.5, 151.1, 139.8, 132.2, 131.6, 130.4, 128.8, 128.5, 128.0, 127.9, 127.1, 122.0, 119.6, 61.3, 44.9, 39.2, 27.2, 25.2.

HRMS (ESI-TOF, m/z) calcd. For $C_{24}H_{25}N_3NaO_4$ $[M+Na]^+$ calc.: 442.1737; Found: 442.1736.

IR (ATR, neat, cm^{-1}): 2972 (w), 1750 (w), 1693 (s), 1477 (m), 1395 (w), 1111 (s), 1022 (m), 760 (m).



HMBC correlations



3k

Synthesis of (±)-3k: The corresponding compound was prepared following general procedure **C** employing the commercially available 3.0M Grignard reagent in Et_2O. ^{1}H NMR analysis of the crude reaction mixture showed a ratio of constitutional isomers of 7.7:1. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [115 mg, 0.22 mmol, 43%]. Complete purging of the constitutional isomer for analysis was achieved by recrystallization from Et_2O:Hexanes.

***R*f** = 0.41 (SiO_2, hexanes:ethyl acetate = 1:1)

m.p. = 71 – 72 ˚C

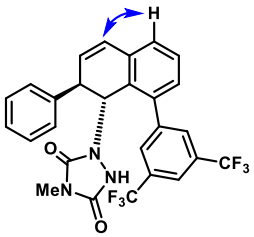
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.33 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.29 – 7.22 (m, 4H), 7.14 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.11 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.95 (d, *J* = 9.6 Hz, 1H), 6.28 (ddd, *J* = 9.6, 5.8, 1.1 Hz, 1H), 5.33 (d, *J* = 1.3 Hz, 1H), 3.89 (d, *J* = 5.8 Hz, 1H), 2.93 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 152.1, 141.3, 140.4, 136.9, 134.6, 131.7 (q, J = 33.2 Hz) 129.9, 129.8, 129.1, 129.0, 128.7, 127.65, 127.57, 127.2, 125.3, 124.2, 122.0, 121.8 – 121.5 (m), 56.0, 45.6, 25.0.

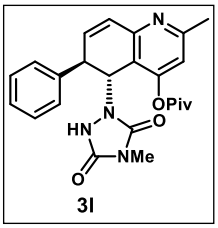
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.9.

HRMS (ESI-TOF, m/z) calcd. For $C_{27}H_{20}N_3O_2F_6$ $[M+H]^+$ calc.: 532.1460; Found: 532.1451.

IR (ATR, neat, cm^{-1}): 3063 (w), 1767 (w), 1697 (s), 1477 (m), 1380 (m), 1278 (s), 1175 (m), 1134 (s).



HMBC correlations



3l

Synthesis of (±)-3l: The corresponding compound was prepared following general procedure **C** employing the commercially available 3.0M Grignard reagent in Et_2O. The reaction was quenched with NH_4Cl (2.0 mL). ^{1}H NMR analysis of the crude reaction mixture showed a ratio of constitutional isomers of 4:1. Purification by flash chromatography (SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) afforded the product as a colorless solid [116 mg, 0.27 mmol, 53%]. Complete purging of the constitutional isomer for analysis was achieved by recrystallization from Et_2O:Hexanes.

***R*$_f$** = 0.17 (SiO_2, hexanes:ethyl acetate = 1:2)

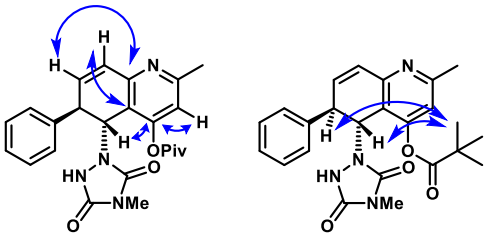
m.p. = 187 – 188 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.28 – 7.15 (m, 6H), 6.95 (dd, *J* = 9.9, 1.1 Hz, 1H), 6.80 (s, 1H), 6.47 (ddd, *J* = 9.9, 5.7, 1.1 Hz, 1H), 5.61 (d, *J* = 1.3 Hz, 1H), 3.75 (d, *J* = 5.7 Hz, 1H), 3.16 (s, 3H), 2.23 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 160.1, 157.2, 155.2, 154.3, 154.2, 138.0, 134.6, 129.0, 127.7, 127.6, 115.9, 113.0, 53.9, 45.0, 39.6, 26.9, 26.3, 25.4, 23.6.

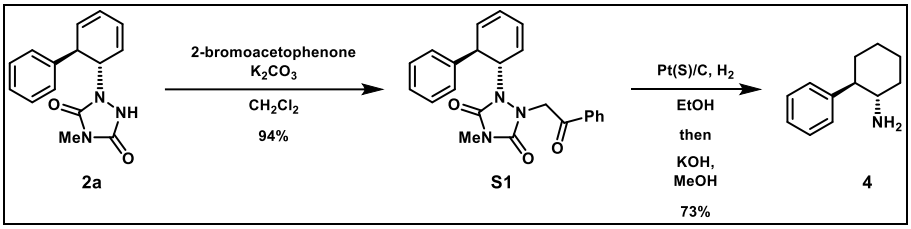
HRMS (ESI-TOF, m/z) calcd. For $C_{26}H_{26}N_4O_6F_3$ $[M+CF_3COO]^-$ calc.: 547.1810; Found: 547.1832.

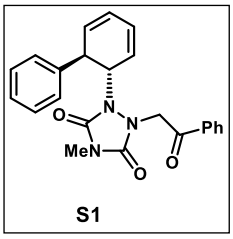
IR (ATR, neat, cm^{-1}): 2975 (w), 1763 (m), 1708 (s), 1474 (m), 1271 (w), 1096 (m), 1023 (w), 767 (w).



4. Derivatization of Carboamination Products

4-1. Synthesis of 4





Synthesis of protected diene S1: To a stirred solution of diene **2a** (1.80 g, 6.68 mmol, 1.0 equiv.) in CH_2Cl_2 (67 mL) under ambient atmosphere was added K_2CO_3 (4.62 g, 33.4 mmol, 5.00 equiv.) and 2-bromoacetophenone (4.00 g, 20.1 mmol, 3.00 equiv.). The resulting suspension was stirred until completion (TLC monitoring). Upon completion, the reaction mixture was quenched with $NaHCO_3$ (sat. aq. 100 mL). The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was loaded onto silica and purified by flash chromatography (CH_2Cl_2, SiO_2, hexanes:ethyl acetate = 5:1 → 3:1) to give the desired compound as an off-white solid [2.43 g, 6.27 mmol, 94%].

***R*f** = 0.44 (SiO_2, hexanes:ethyl acetate = 1:1)

[α]D^{24} = +161.7 (c = 1.00 in $CHCl_3$)

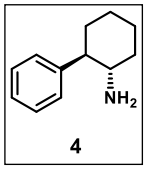
m.p. = 134 – 136 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 2H), 7.68 – 7.59 (m, 1H), 7.53 – 7.47 (m, 2H), 7.24 (s, 2H), 7.23 (s, 2H), 7.20 – 7.12 (m, 1H), 6.16 – 6.03 (m, 2H), 5.99 – 5.87 (m, 1H), 5.50 (dddd, J = 9.6, 3.4, 2.1, 1.0 Hz, 1H), 5.25 – 5.12 (m, 1H), 5.06 (s, 2H), 4.05 – 3.96 (m, 1H), 2.97 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.7, 157.4, 155.4, 141.4, 134.4, 134.3, 131.1, 129.1, 128.7, 128.4, 128.1, 127.7, 127.1, 125.2, 123.3, 60.7, 52.8, 45.2, 25.7.

HRMS (ESI-TOF, m/z) calcd. For $C_{25}H_{24}N_3O_5$ $[M+CH_3COO]^-$ calc.: 446.1721; Found: 446.1732.

IR (ATR, neat, cm^{-1}): 3039 (w), 2939 (w), 1775 (w), 1713 (s), 1695 (s), 1470 (m), 1226 (m), 687 (m).



Synthesis of amine 4: Protected diene **S1** (250 mg, 0.645 mmol, 1.0 equiv.) and Pt(S)/C (30.0 mg, 5% w/w, 1.0 mol%) were suspended in EtOH (6.5 mL) and degassed with H_2. The resulting suspension was stirred under hydrogen atmosphere (1 atm.) overnight. Upon completion, the reaction filtered through celite and concentrated under reduced pressure. The crude residue was then transferred to a pressure tube and was dissolved in MeOH (1 mL) and 50% KOH (aq., 1 mL) and immediately degassed with nitrogen under sonication. The tube was then sealed and stirred at 80 °C for 16 h. The temperature was then raised to 155 °C for 6 h. Upon completion, the reaction was loaded onto silica and purified by flash chromatography (H_2O, SiO_2, CH_2Cl_2:MeOH = 15:1 → 6:1) to give the desired compound as a yellow solid [83.0 mg, 0.471 mmol, 73%].

$\boldsymbol{R_f}$ = 0.27 (SiO_2, CH_2Cl_2:MeOH = 8:1)

$[\alpha]_D^{24}$ = +40.7 (c = 1.00 in $CHCl_3$)

m.p. = 268 – 270 ˚C

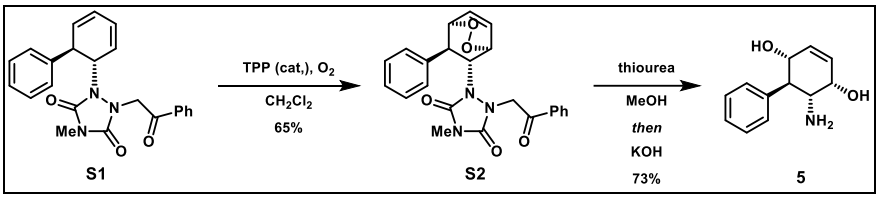
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, J = 7.3 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.23 – 7.20 (m, 2H), 3.09 (td, J = 11.4, 3.9 Hz, 1H), 2.67 (td, J = 11.4, 3.7 Hz, 1H), 2.26 (dd, J = 13.1, 3.7 Hz, 1H), 1.95 – 1.84 (m, 2H), 1.82 – 1.73 (m, 1H), 1.62 – 1.42 (m, 2H), 1.42 – 1.34 (m, 2H).

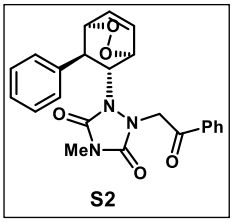
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 129.4, 127.9, 127.8, 55.8, 48.8, 34.1, 31.1, 25.5, 24.8.

HRMS (ESI-TOF, m/z) calcd. For $C_{12}H_{17}NCl$ $[M+Cl]^-$ calc.: 210.1055; Found: 210.1045.

IR (ATR, neat, cm^{-1}): 2939 (s), 2923 (s), 2860 (s), 2222 (w), 1607 (w), 1507 (s), 758 (m), 727 (m), 702 (s).

4-2. Synthesis of 5





S2

Synthesis of endoperoxide S2: Protected diene **S1** (500 mg, 1.290 mmol, 1.0 equiv.) and *meso*-tetraphenylporphyrin (7.93 mg, 0.013 mmol, 1.0 mol%) were dissolved in CH_2Cl_2 (13 mL) and cooled to −78 °C and irradiated with visible light until complete conversion (TLC monitoring). Upon completion, the reaction loaded onto silica and purified by flash chromatography (CH_2Cl_2, SiO_2, hexanes:ethyl acetate = 4:1 → 2:1) to give the desired compound as a colorless solid [351 mg, 0.837 mmol, 65%].

$\boldsymbol{R_f}$ = 0.33 (SiO_2, hexanes:ethyl acetate = 1:1)

$\boldsymbol{[\alpha]_D^{25}}$ = +105.7 (c = 1.00 in $CHCl_3$)

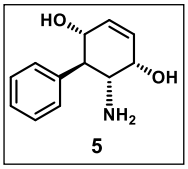
m.p. = 152 – 153 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.91 (m, 2H), 7.69 – 7.57 (m, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.34 – 7.22 (m, 3H), 7.15 – 7.09 (m, 2H), 6.81 (ddd, J = 8.3, 6.5, 1.7 Hz, 1H), 6.65 (ddd, J = 8.3, 6.1, 1.5 Hz, 1H), 5.81 (d, J = 18.3 Hz, 1H), 5.29 (d, J = 18.3 Hz, 1H), 4.76 (ddt, J = 6.1, 3.2, 1.7 Hz, 1H), 4.70 (dq, J = 6.5, 1.5 Hz, 1H), 4.66 (dd, J = 6.1, 1.5 Hz, 1H), 3.89 (dd, J = 6.1, 3.2 Hz, 1H), 3.12 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.1, 157.7, 155.9, 138.3, 134.7, 134.1, 131.7, 131.3, 129.2, 129.1, 128.2, 128.0, 127.7, 76.7, 75.2, 60.7, 54.1, 40.6, 26.2.

HRMS (ESI-TOF, m/z) calcd. For $C_{23}H_{21}N_3O_5Br$ $[M+Br]^-$ calc.: 500.653; Found: 500.0645.

IR (ATR, neat, cm^{-1}): 3063 (w), 2940 (w), 2250 (w), 1775 (w), 1709 (s), 1693 (s), 1472 (m), 1226 (m).



5

Synthesis of diol 5: To a stirred solution of endoperoxide **S2** (200 mg, 0.477 mmol, 1.0 equiv.) in methanol (0.635 mL) in a pressure tube under ambient conditions was added thiourea (72.6 mg, 0.954 mmol, 2.0 equiv.) and the reaction was stirred until complete conversion (TLC monitoring). Upon completion, 50% KOH (aq. 0.635 mL) was added and the reaction was immediately degassed with nitrogen under sonication. The tube was then sealed and stirred at 80 °C for 16 h. The temperature was then raised to 155 °C for 6 h. Upon completion, the reaction was loaded onto silica and purified by flash chromatography (H_2O, SiO_2, CH_2Cl_2:MeOH = 15:1 → 6:1) to give the desired compound as a colorless solid [71.0 mg, 0.346 mmol, 73%].

$\boldsymbol{R_f}$ = 0.12 (SiO_2, CH_2Cl_2:MeOH = 8:1)

$\boldsymbol{[\alpha]_D^{25}}$ = +33.6 (c = 1.00 in MeOH)

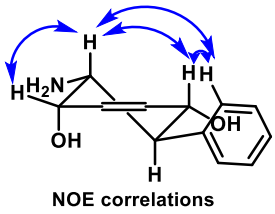
m.p. = 58 – 60 ˚C

^{1}H NMR (500 MHz, MeOD) δ 7.41 – 7.36 (m, 2H), 7.35 – 7.31 (m, 2H), 7.31 – 7.26 (m, 1H), 5.96 – 5.93 (m, 1H), 5.91 (dd, J = 10.0, 1.5 Hz, 1H), 4.27 (dq, J = 9.4, 1.5 Hz, 1H), 4.13 (td, J = 4.0, 1.1 Hz, 1H), 3.05 (dd, J = 11.6, 4.0 Hz, 1H), 2.78 (dd, J = 11.6, 9.4 Hz, 1H).

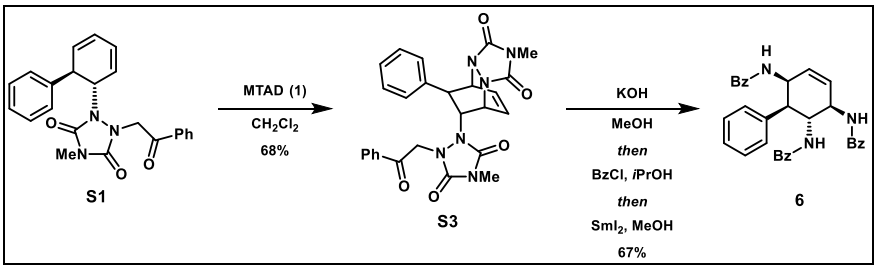
^{13}C NMR (126 MHz, MeOD) δ 141.4, 135.6, 130.2, 129.9, 128.8, 128.2, 73.2, 66.3, 54.3, 52.7.

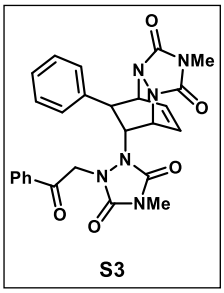
HRMS (ESI-TOF, m/z) calcd. For $C_{14}H_{15}F_3NO_4$ $[M+CF_3COO]^+$ calc.: 318.0959; Found: 318.0971.

IR (ATR, neat, cm^{-1}): 3297 (br), 3028 (w), 2904 (w), 2460 (br), 2066 (w), 1494 (w), 1453 (w), 1058 (m).



4-3. Synthesis of 6





Synthesis of bicycle S3: To a stirred solution of protected diene **S1** (500 mg, 1.290 mmol, 1.0 equiv.) in CH_2Cl_2 (13 mL) at −78 °C was added MTAD (**1**, 146 mg, 1.290 mmol, 1.0 equiv.) as a solution in CH_2Cl_2 (5 mL) and the reaction was allowed to slowly warm to room temperature and stir until complete conversion (TLC monitoring). ^{1}H NMR analysis of the crude reaction mixture showed a d.r. of 3:1. Upon completion, the reaction was loaded onto silica and purified by flash chromatography (CH_2Cl_2, SiO_2, Et_2O:PhMe = 1:1 → 3:1) to give the desired compound as a colorless solid [437 mg, 0.873 mmol, 68%].

***R*$_f$** = 0.51 (SiO_2, CH_2Cl_2:MeOH = 8:1)

[α]$_D^{25}$ = +46.8 (c = 1.00 in $CHCl_3$)

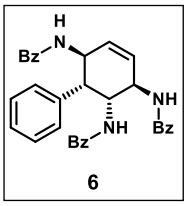
m.p. = 142 – 145 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 2H), 7.60 (ddt, *J* = 8.7, 7.2, 1.3 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.30 – 7.27 (m, 2H), 7.22 – 7.13 (m, 3H), 6.66 (ddd, *J* = 8.1, 5.9, 1.5 Hz, 1H), 6.43 (ddd, *J* = 8.1, 5.5, 1.5 Hz, 1H), 5.18 (ddd, *J* = 5.5, 2.4, 1.5 Hz, 1H), 4.83 (dt, *J* = 5.9, 2.0 Hz, 1H),

4.62 (s, 2H), 4.29 (dd, *J* = 6.3, 2.4 Hz, 1H), 3.51 (dd, *J* = 6.3, 2.0 Hz, 1H), 3.12 (s, 3H), 2.99 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 191.3, 158.5, 157.5, 157.2, 154.6, 138.4, 134.5, 133.9, 130.9, 129.10, 129.09, 128.0, 127.91, 127.90, 127.8, 61.2, 55.9, 52.8, 52.3, 45.8, 25.9, 25.8.

HRMS (ESI-TOF, m/z) calcd. For $C_{26}H_{24}N_6O_5$ $[M]^+$ calc.: 500.1808; Found: 500.1796.

IR (ATR, neat, cm^{-1}): 2948 (w), 1775 (m), 1709 (s), 1456 (m), 1394 (w), 1226 (w), 917 (w), 757 (w).



6

Synthesis of triamide 6: Bicycle **S3** (250 mg, 0.499 mmol, 1.0 equiv.) in a pressure tube was dissolved in MeOH (2 mL) and 50% KOH (aq., 5 mL) and immediately degassed with nitrogen under sonication. The tube was then sealed and stirred at 80 °C for 16 h. The temperature was then raised to 155 °C for 6 h. The reaction was cooled to room temperature and diluted with water (10 mL) and cooled to 0 °C. Then HCl (12N, 4.50 mL) was added dropwise [*note: pH remained basic*]. Then *i*PrOH (5 mL) and benzoyl chloride (0.87 mL, 7.49 mmol, 15 equiv.) were added and the reaction was warmed to ambient temperature and stirred until complete conversion (TLC monitoring). Upon completion, the reaction was carefully quenched with $NaHCO_3$ (sat. aq. 20 mL) and diluted with CH_2Cl_2 (10 mL). The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organics were washed with brine (30 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was passed through a short solumn (SiO_2, hexanes:EtOAc mixture), and used directly for the next step. The product was then dissolved in methanol (3.0 mL), degassed under sonication for 10 minutes, and cooled to 0 °C. SmI_2 (0.10 M THF solution) was then added dropwise to the mixture until the solution turned from colorless to blue, then allowed to warm to room temperature for 30 min. The mixture was diluted with ethyl acetate (10 mL), then NH_4Cl (sat. aq. 10 mL) and water (10 mL) were added and the phases were separated. The aqueous layer was extracted with ethyl acetate (3 × 20 mL), and the combined organics were washed with brine (30 mL), dried over $MgSO_4$, filtered and loaded onto silica and purified by flash chromatography (EtOAc, SiO_2, Et_2O:PhMe = 3:1 → 4:1) to give the desired compound as a colorless solid [173 mg, 0.336 mmol, 67%].

$\boldsymbol{R_f}$ = 0.12 (SiO_2, hexanes:ethyl acetate = 1:2)

$[\alpha]_D^{24}$ = +83.3 (c = 1.00 in $CHCl_3$)

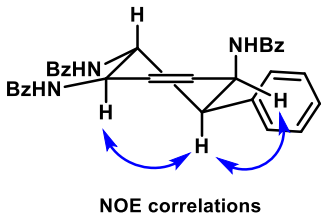
m.p. = 266 – 268 ˚C

^{1}H NMR (500 MHz, MeOD) δ 8.43 (d, J = 9.5, NH), 9.43 (d, J = 9.5, NH), 7.87 (m, NH), 7.79 – 7.72 (m, 2H), 7.67 – 7.59 (m, 2H), 7.18 (ddd, J = 14.7, 8.2, 6.8 Hz, 4H), 7.14 – 7.08 (m, 1H), 5.97 (ddd, J = 9.8, 5.0, 2.4 Hz, 1H), 5.94 – 5.88 (m, 1H), 5.21 – 5.07 (m, 2H), 4.96 (dq, J = 9.3, 1.5 1H), 3.71 (dd, J = 12.8, 5.0 Hz, 1H).

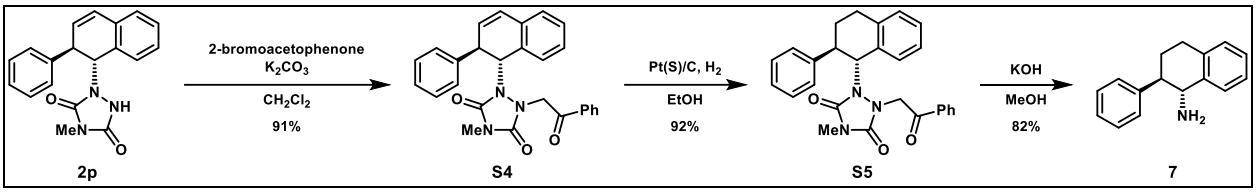
^{13}C NMR (126 MHz, MeOD) δ 171.3, 170.5, 169.6, 139.6, 136.1, 136.0, 135.9, 132.7, 132.5, 132.3, 131.9, 130.3, 129.6, 129.4, 129.3, 129.2, 128.9, 128.6, 128.3, 128.0, 127.8, 54.9, 50.4, 50.3, 50.0.

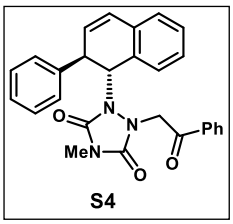
HRMS (ESI-TOF, m/z) calcd. For $C_{33}H_{29}BrN_3O_3$ $[M+Br]^-$ calc.: 596.1383; Found: 596.1392.

IR (ATR, neat, cm^{-1}): 3312 (br), 3061 (w), 3030 (w), 1634 (s), 1578 (m), 1521 (s), 1414 (m), 1328 (m).



4-4. Synthesis of 7





Synthesis of protected naphthalene product S4: To a stirred solution of naphthalene product **2p** (1.28 g, 4.01 mmol, 1.0 equiv.) in CH_2Cl_2 (40 mL) under ambient atmosphere was added K_2CO_3 (2.77 g, 20.0 mmol, 5.00 equiv.) and 2-bromoacetophenone (2.39 g, 12.0 mmol, 3.00 equiv.). The resulting suspension was stirred until completion (TLC monitoring). Upon completion, the reaction mixture was quenched with $NaHCO_3$ (sat. aq. 100 mL). The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was loaded onto silica and purified by flash chromatography (CH_2Cl_2, SiO_2, hexanes:ethyl acetate = 5:1 → 3:1) to give the desired compound as an off-white solid [1.60 g, 3.65 mmol, 91%].

***R*f** = 0.54 (SiO_2, hexanes:ethyl acetate = 1:1)

[*α*]D^{25} = +71.4 (c = 1.00 in $CHCl_3$)

m.p. = 74 – 76 ˚C

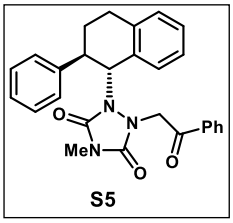
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.42 – 7.36 (m, 2H), 7.34 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 7.11 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.07 (tt, *J* = 7.5, 1.3 Hz, 1H), 6.73 (td, *J* = 7.5, 1.5 Hz, 1H), 6.59 (dd, *J* = 9.7, 2.6 Hz, 1H), 6.00 (dd, *J* = 9.7, 3.0 Hz,

1H), 5.77 (d, *J* = 11.4 Hz, 1H), 4.95 (d, *J* = 18.2 Hz, 1H), 4.63 (d, *J* = 18.2 Hz, 1H), 4.13 (dt, *J* = 11.4, 3.0 Hz, 1H), 2.92 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.2, 157.4, 156.3, 140.8, 134.3, 134.1, 133.4, 131.8, 130.9, 128.8, 128.7, 128.6, 128.5, 128.4, 127.9, 127.8, 127.3, 127.0, 126.0, 62.7, 53.2, 45.2, 25.6.

HRMS (ESI-TOF, m/z) calcd. For $C_{27}H_{23}N_3O_3Cl$ $[M+Cl]^-$ calc.: 472.1433; Found: 472.1438.

IR (ATR, neat, cm^{-1}): 3030 (w), 2939 (w), 1774 (w), 1712 (s), 1694 (s), 1471 (m), 1450 (m) 1226 (m).



S5

Synthesis of protected hydrogenation product S5: Protected naphthalene product **S4** (250 mg, 0.571 mmol, 1.0 equiv.) and Pt(S)/C (20.0 mg, 5% w/w, 1.0 mol%) were suspended in EtOH (5.7 mL) and degassed with H_2. The resulting suspension was stirred under hydrogen atmosphere (1 atm.) overnight. Upon completion, the reaction filtered through celite and concentrated under reduced pressure. The resulting residue was loaded onto silica and purified by flash chromatography (CH_2Cl_2, SiO_2, hexanes:ethyl acetate = 5:1 → 3:1) to give the desired compound as a colorless solid [230 mg, 0.523 mmol, 92%].

***R*$_f$** = 0.27 (SiO_2, hexanes:ethyl acetate = 2:1)

[α]$_D^{23}$ = -26.9 (c = 1.00 in $CHCl_3$)

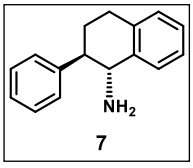
m.p. = 159 – 161 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.46 (m, 1H), 7.44 – 7.40 (m, 2H), 7.36 – 7.31 (m, 2H), 7.27 (d, *J* = 3.0 Hz, 4H), 7.23 – 7.18 (m, 2H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.61 (t, *J* = 7.6 Hz, 1H), 5.62 (d, *J* = 11.1 Hz, 1H), 4.82 (d, *J* = 18.0 Hz, 1H), 4.24 (d, *J* = 18.0 Hz, 1H), 3.41 – 3.25 (m, 1H), 3.10 (tt, *J* = 13.2, 4.8 Hz, 1H), 2.94 (ddd, *J* = 16.8, 4.8, 2.1 Hz, 1H), 2.79 (s, 3H), 2.23 (qd, *J* = 12.8, 4.8 Hz, 1H), 2.18 – 2.11 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 157.2, 156.0, 141.4, 136.9, 135.0, 134.2, 133.9, 129.2, 128.6, 128.5, 128.0, 127.7, 127.6, 127.6, 127.3, 126.8, 62.7, 52.9, 45.4, 30.17, 30.16, 25.4.

HRMS (ESI-TOF, m/z) calcd. For $C_{27}H_{25}N_3NaO_3$ $[M+Na]^+$ calc.: 462.1788; Found: 462.1770.

IR (ATR, neat, cm^{-1}): 3061 (w), 2932 (w), 1771 (w), 1709 (s), 1692 (s), 1470 (m), 1450 (m) 1225 (m).



7

Synthesis of amine 7: Protected hydrogenated naphthalene product **S5** (180 mg, 0.410 mmol, 1.0 equiv.) in a pressure tube was dissolved in MeOH (1 mL) and 50% KOH (aq., 1 mL) and immediately degassed with nitrogen under sonication. The tube was then sealed and stirred at 80 °C for 16 h. The temperature was then raised to 155 °C for 6 h. Upon completion, the reaction was diluted with Et_2O (5

mL) and the phases were separated. The aqueous layer was extracted with Et_2O (5 × 5 mL) and the combined orgaincs were washed with brine, dried over $MgSO_4$, filtered, loaded onto silica and purified by flash chromatography (Et_2O, SiO_2, hexanes:ethyl acetate = 1:2) to give the desired compound as a yellow oil [75.0 mg, 0.336 mmol, 82%].

R_f = 0.15 (SiO_2, hexanes:ethyl acetate = 1:2)

$[\alpha]_D^{23}$ = -9.9 (c = 1.00 in MeOH)

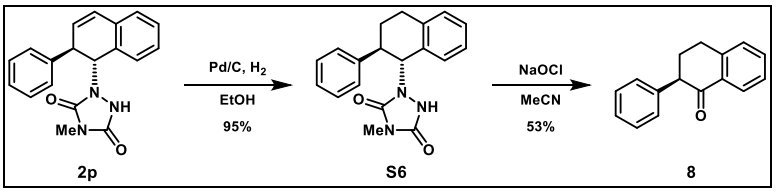
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.38 (dd, *J* = 8.0, 7.0 Hz, 2H), 7.29 (dt, *J* = 8.0, 1.2 Hz, 3H), 7.25 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.21 (td, *J* = 7.7, 1.5 Hz, 1H), 7.15 (dd, *J* = 7.7, 1.5 Hz, 1H), 4.12 (d, *J* = 9.6 Hz, 1H), 3.15 – 2.97 (m, 1H), 2.90 (dt, *J* = 16.8, 4.2 Hz, 1H), 2.77 – 2.54 (m, 1H), 2.10 (tdd, *J* = 9.1, 4.8, 2.6 Hz, 2H), 1.42 (s, 2H).

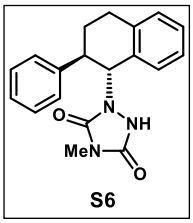
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 140.4, 136.6, 128.8, 128.7, 127.9, 127.3, 126.8, 126.6, 126.3, 56.0, 52.1, 30.02, 30.00.

HRMS (ESI-TOF, m/z) calcd. For $C_{16}H_{17}N$ $[M]^-$ calc.: 223.1361; Found: 223.1352.

IR (ATR, neat, cm^{-1}): 3377 (w), 3060 (w), 3026 (w), 2925 (w), 1601 (w), 1491 (m), 1452 (m) 758 (s).

4-5. Synthesis of ketone 8





Synthesis of hydrogenated naphthalene product S6: Naphthalene product **2p** (100 mg, 0.313 mmol, 1.0 equiv.) and Pd/C (17.0 mg, 10% w/w, 5.0 mol%) were suspended in EtOH (3.0 mL) and degassed with H_2. The resulting suspension was stirred under hydrogen atmosphere (1 atm.) overnight. Upon completion, the reaction filtered through celite and concentrated under reduced pressure. The resulting residue was loaded onto silica and purified by flash chromatography (CH_2Cl_2, SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) to give the desired compound as a colorless solid [96.0 mg, 0.299 mmol, 95%].

R_f = 0.32 (SiO_2, hexanes:ethyl acetate = 1:1)

$[\alpha]_D^{24}$ = +16.9 (c = 1.00 in $CHCl_3$)

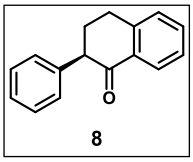
m.p. = 206 – 207 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.27 – 7.23 (m, 4H), 7.22 – 7.14 (m, 3H), 5.56 (d, *J* = 11.0 Hz, 1H), 3.27 (ddd, *J* = 12.4, 11.0, 2.8 Hz, 1H), 3.12 – 3.00 (m, 1H), 2.99 – 2.90 (m, 1H), 2.76 (s, 3H), 2.25 (qd, *J* = 12.6, 5.4 Hz, 1H), 2.16 (ddt, *J* = 13.3, 5.4, 2.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1, 154.5, 141.6, 138.1, 133.6, 129.6, 128.6, 128.1, 127.8, 127.6, 126.8, 126.6, 61.6, 44.8, 29.84, 29.77, 25.0.

HRMS (ESI-TOF, m/z) calcd. For $C_{19}H_{19}BrN_3O_2$ $[M+Br]^-$ calc.: 400.0666; Found: 400.0671.

IR (ATR, neat, cm^{-1}): 3028 (w), 2932 (w), 1767 (w), 1685 (s), 1480 (m), 1454 (m) 751 (m), 727 (m).



Synthesis of (*R*)-(-)-2-phenyl-(1)-tetralone 8: To a stirred solution of hydrogenated naphthalene product **S6** (30.0 mg, 0.093 mmol, 1.0 equiv.) at −20 °C in MeCN (2 mL) was added dropwise NaOCl (0.850 mL). Upon complete addition, the reaction was stirred vigorously at that temperature for 1 min. before quenching with $Na_2S_2O_3$ (10% aq., 5 mL). The reaction was diluted with ethyl acetate and the phases were separated. The aqueous layer was extracted with ethyl acetate (3 × 5 mL). The combined organics were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The resulting residue was loaded onto silica and purified by flash chromatography (ethyl acetate, SiO_2, hexanes:ethyl acetate = 3:1 → 2:1) to give the desired compound as a colorless oil [11.0 mg, 0.050 mmol, 53%]. Characterization data agrees with those reported in the literature.[8]

***R*$_f$** = 0.30 (SiO_2, hexanes:ethyl acetate = 10:1)

$[\alpha]_D^{22}$ = -16.4 (c = 0.85 in $CHCl_3$)

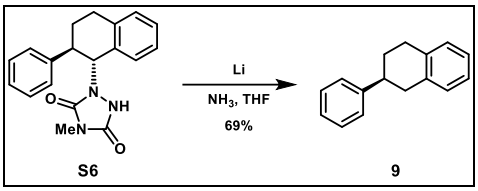
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.31 – 7.27 (m, 2H), 7.21 – 7.17 (m, 2H), 3.94 – 3.68 (m, 1H), 3.17 – 3.09 (m, 1H), 3.05 (dt, *J* = 16.8, 4.8, 1H), 2.54 – 2.32 (m, 2H).

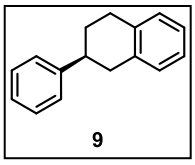
^{13}C NMR (126 MHz, $CDCl_3$) δ 198.3, 144.2, 139.9, 133.6, 133.0, 128.9, 128.7, 128.6, 128.0, 127.1, 126.9, 54.5, 31.3, 28.9.

HRMS (ESI-TOF, m/z) calcd. For $C_{16}H_{15}O$ $[M+H]^+$ calc.: 223.1123; Found: 223.1117.

IR (ATR, neat, cm^{-1}): 3028 (w), 2931 (w), 1730 (w), 1683 (s), 1599 (m), 1453 (m) 1223 (m), 740 (m).

4-6. Synthesis of 9





Synthesis of (*S*)-(-)-2-phenyltetralin 9: To a stirred suspension of hydrogenated naphthalene product **S6** (45.0 mg, 0.140 mmol, 1.0 equiv.) at −78 °C in THF (1 mL) was condensed ammonia (ca. 5 mL), whereupon the substrate became completely soluble. The atmosphere was replaced with nitrogen and lithium (3.90 mg, 0.560 mmol, 4.0 equiv.) was added. The reaction was stirred 30 sec. before the careful addition of solid NH_4Cl (large excess). The reaction was allowed to slowly warm to room temperature with venting and was diluted with water (5 mL) and ethyl acetate (5 mL) and the phases were separated. The aqueous layer was extracted with ethyl acetate (3 × 5 mL). The combined organics were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The resulting residue was loaded onto silica and purified by flash chromatography (ethyl acetate, SiO_2, hexanes) to give the desired compound as a colorless oil [20.0 mg, 0.096 mmol, 69%]. Characterization data for this compound matches with those reported in the literature.[8]

$\boldsymbol{R_f}$ = 0.71 (SiO_2, hexanes:ethyl acetate = 10:1)

$\boldsymbol{[\alpha]_D^{25}}$ = -59.8 (c = 1.0 in $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.31 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 7.17 – 7.08 (m, 4H), 3.11 – 2.88 (m, 5H), 2.21 – 2.10 (m, 1H), 2.02 – 1.90 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8, 136.8, 136.4, 129.2, 129.1, 128.6, 127.0, 126.3, 125.9, 125.8, 40.9, 37.9, 30.5, 29.9.

HRMS (EI-TOF, m/z) calcd. For $C_{16}H_{16}$ $[M]^+$ calc.: 208.1252; Found: 208.1260.

IR (ATR, neat, cm^{-1}): 3025 (w), 3060 (w), 2920 (m), 1493 (m), 1452 (m), 757 (m) 742 (s), 698 (s).

6. HPLC spectra

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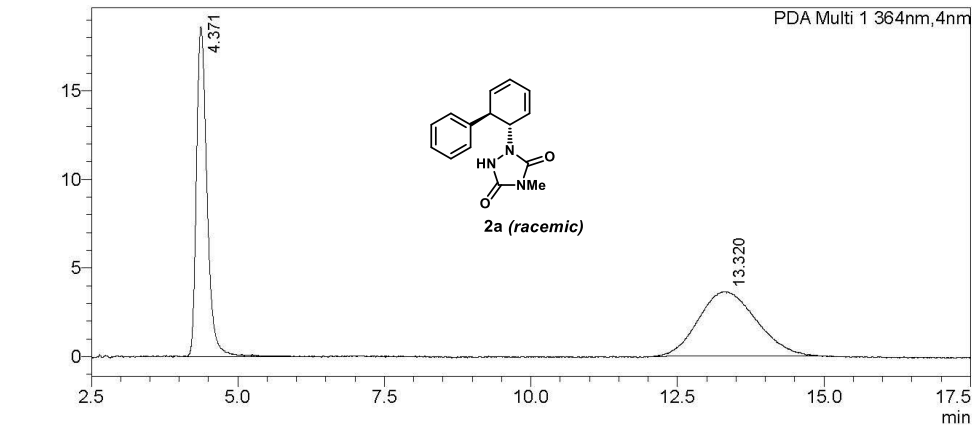

<Peak Table>

PDA Ch1 364nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
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2	13.320	250201	3652	51.576	16.401	8.146
Total		485114	22267	100.000	100.000	

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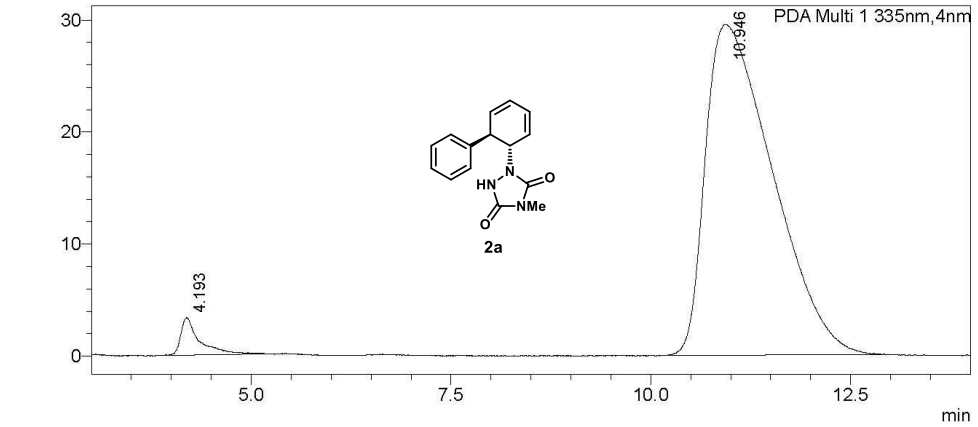

<Peak Table>

PDA Ch1 335nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	4.193	54782	3328	3.070	10.135	--
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Total		1784641	32839	100.000	100.000	

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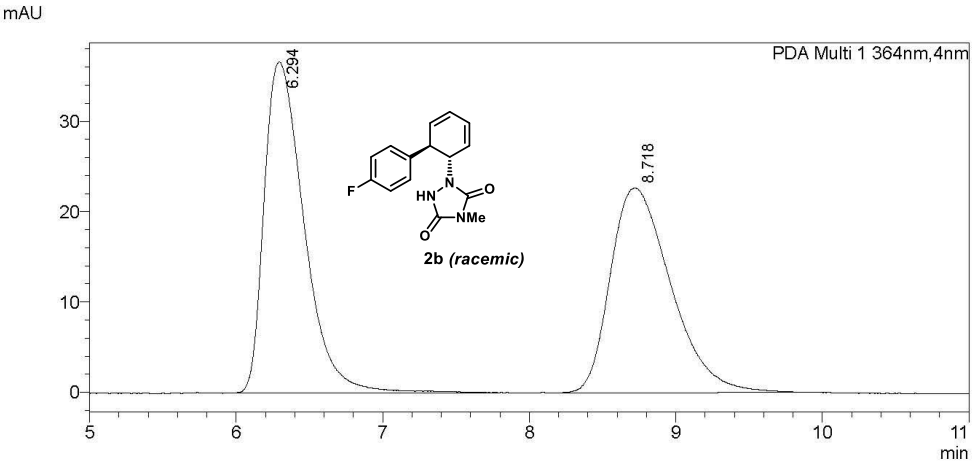

<Peak Table>

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Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	6.294	691424	36632	51.557	61.771	--
2	8.718	649673	22671	48.443	38.229	3.916
Total		1341097	59303	100.000	100.000	

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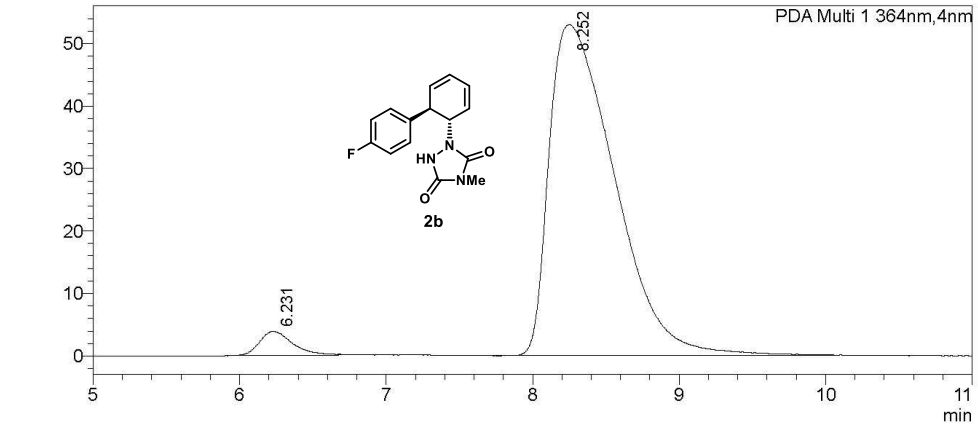

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PDA Ch1 364nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
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Total		1703371	56800	100.000	100.000	

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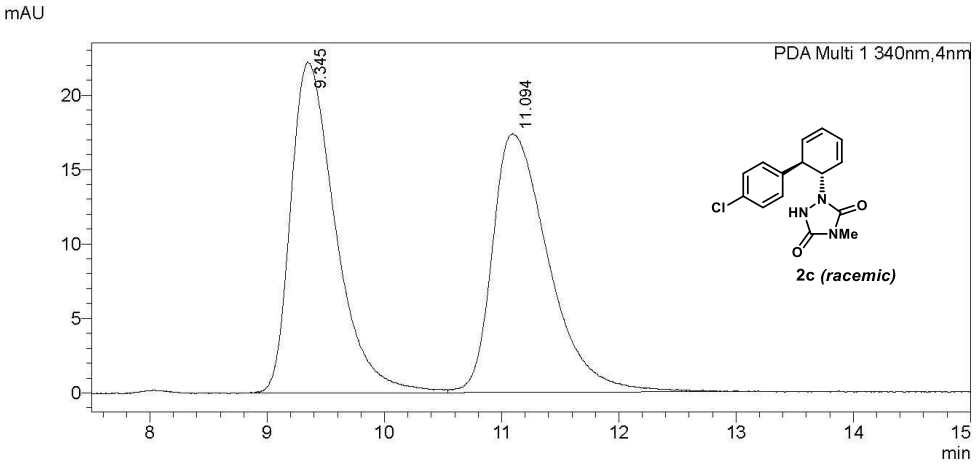

<Peak Table>

PDA Ch1 340nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	9.345	591758	22243	50.540	56.131	--
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Total		1170862	39626	100.000	100.000	

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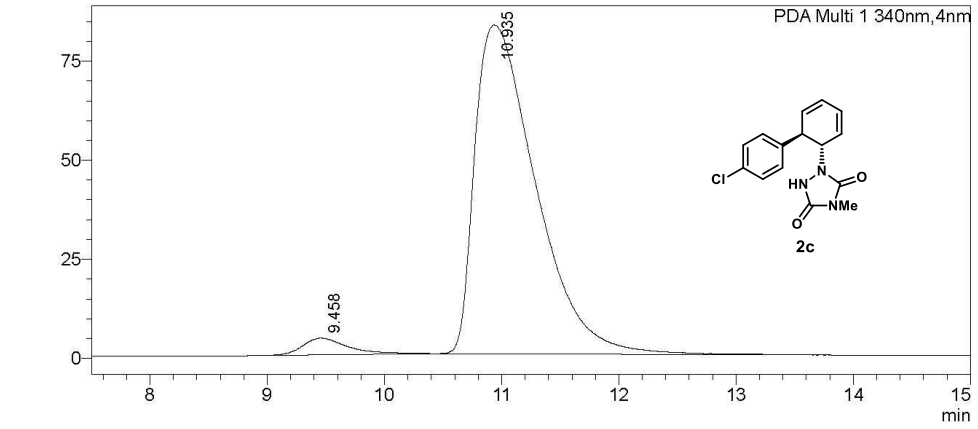

<Peak Table>

PDA Ch1 340nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	9.458	113330	4199	3.636	4.812	--
2	10.935	3003976	83078	96.364	95.188	1.865
Total		3117305	87278	100.000	100.000	

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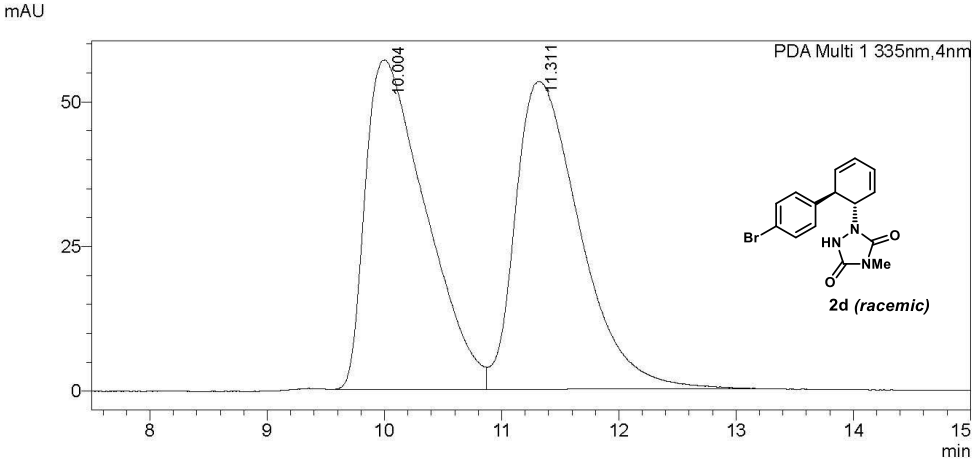

<Peak Table>

PDA Ch1 335nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	10.004	2036925	56958	49.864	51.717	--
2	11.311	2048024	53176	50.136	48.283	1.302
Total		4084949	110134	100.000	100.000	

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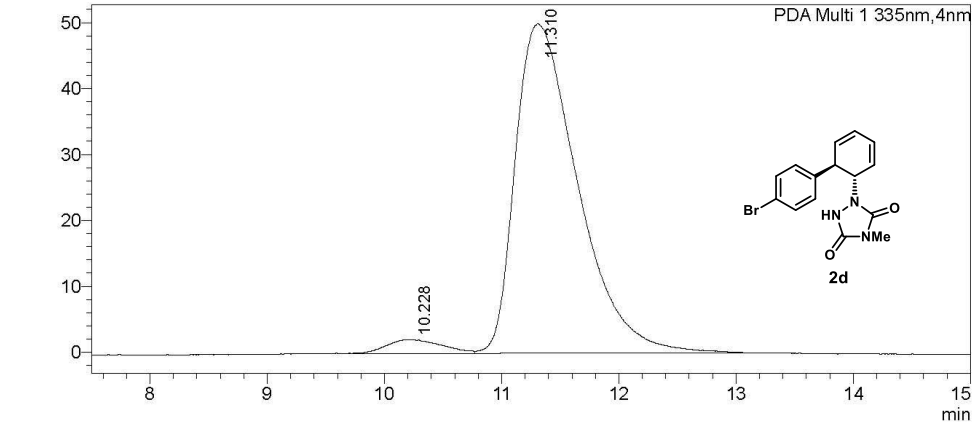

<Peak Table>

PDA Ch1 335nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	10.228	70130	2132	3.648	4.091	--
2	11.310	1852376	49978	96.352	95.909	1.144
Total		1922506	52109	100.000	100.000	

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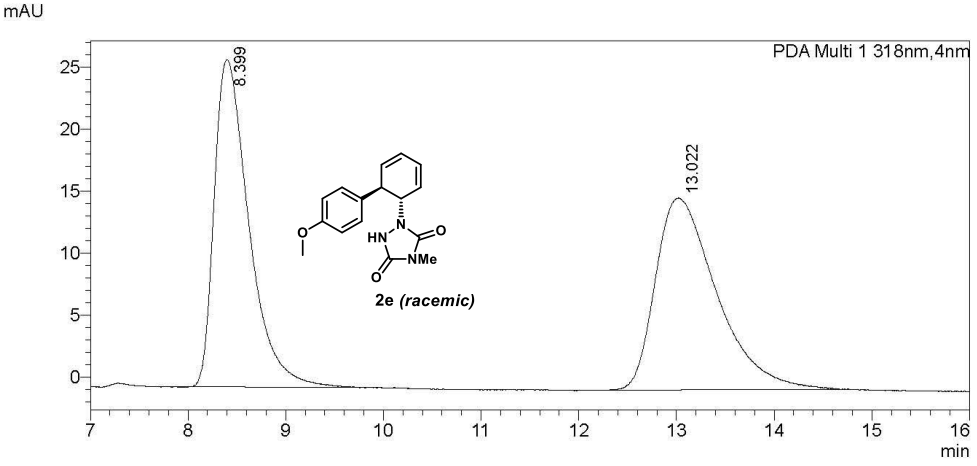

<Peak Table>

PDA Ch1 318nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	8.399	650599	26375	49.220	63.038	--
2	13.022	671221	15465	50.780	36.962	5.277
Total		1321821	41839	100.000	100.000	

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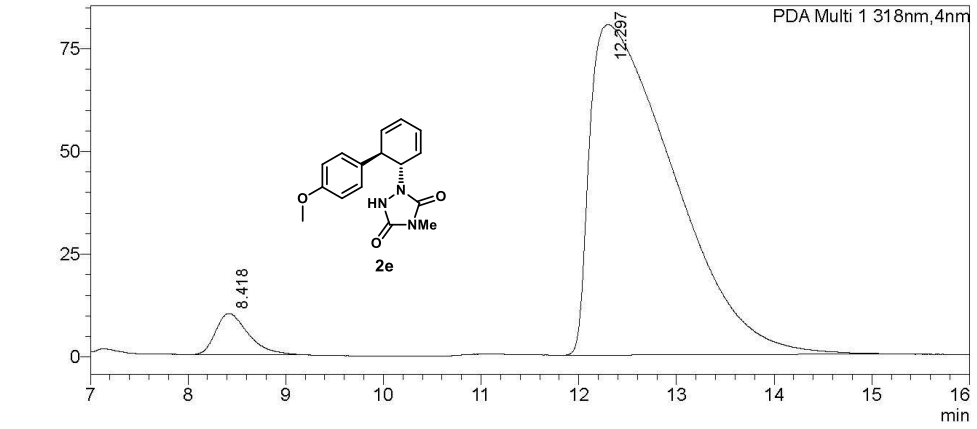

<Peak Table>

PDA Ch1 318nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	8.418	233422	10045	4.634	11.099	--
2	12.297	4803419	80461	95.366	88.901	3.494
Total		5036841	90506	100.000	100.000	

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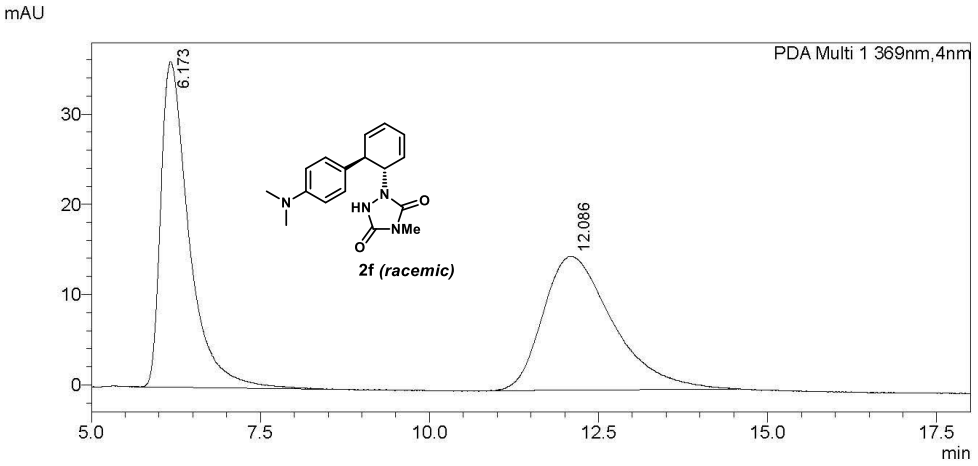

<Peak Table>

PDA Ch1 369nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	6.173	1046796	36035	49.555	70.850	--
2	12.086	1065582	14826	50.445	29.150	4.587
Total		2112379	50860	100.000	100.000	

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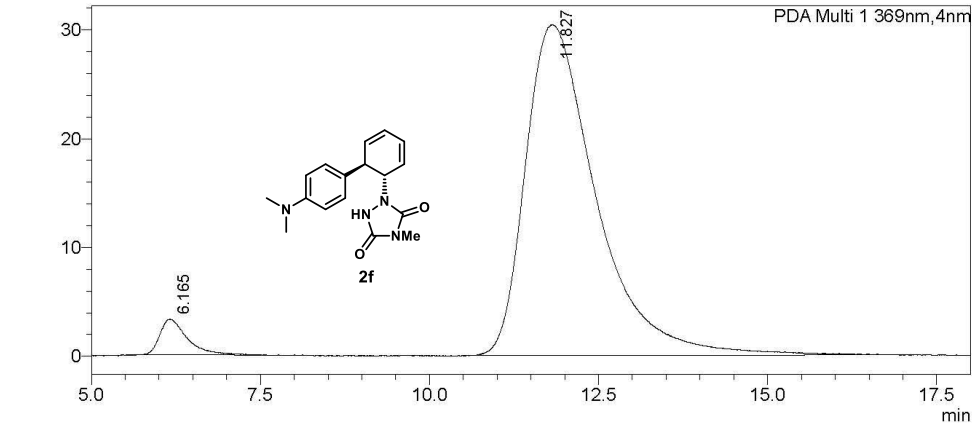

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PDA Ch1 369nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	6.165	93357	3287	4.047	9.756	--
2	11.827	2213611	30409	95.953	90.244	4.520
Total		2306968	33696	100.000	100.000	

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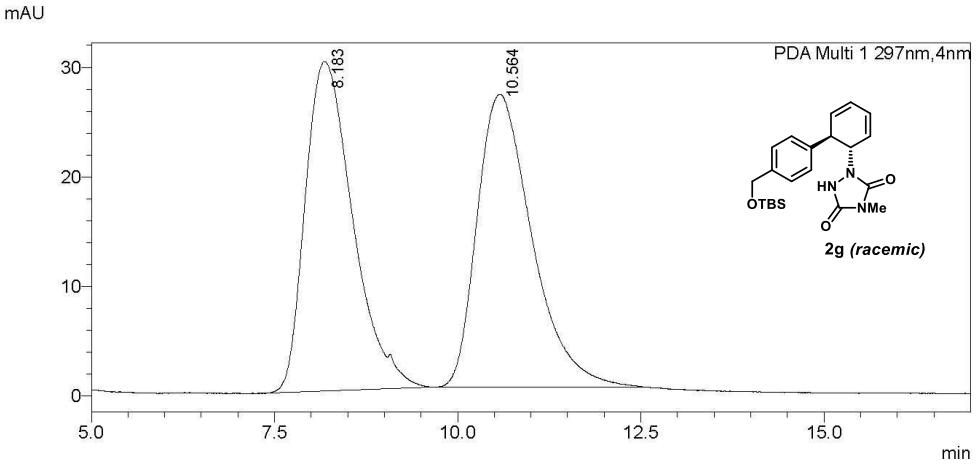

<Peak Table>

PDA Ch1 297nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	8.183	1360917	30057	49.314	52.909	--
2	10.564	1398777	26753	50.686	47.091	1.890
Total		2759694	56810	100.000	100.000	

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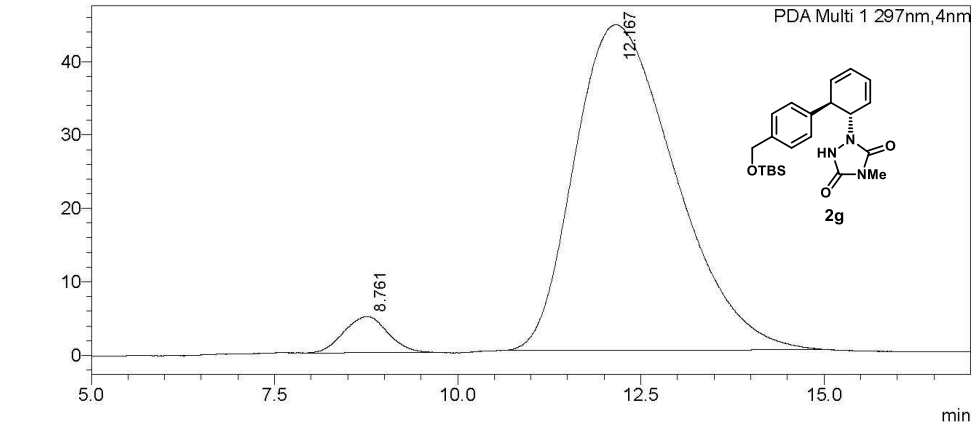

<Peak Table>

PDA Ch1 297nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	8.761	206469	4942	4.634	10.025	--
2	12.167	4248601	44359	95.366	89.975	1.868
Total		4455070	49302	100.000	100.000	

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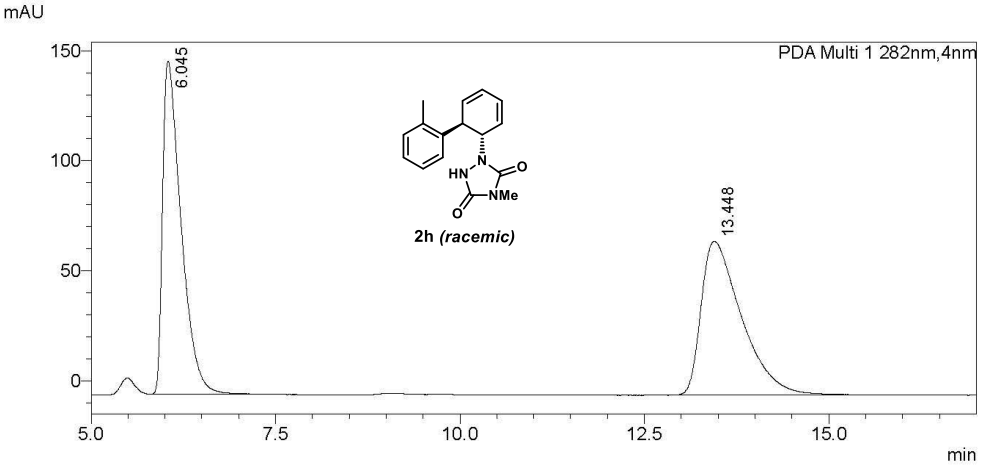

<Peak Table>

PDA Ch1 282nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	6.045	2637066	151254	49.741	68.414	--
2	13.448	2664515	69831	50.259	31.586	10.166
Total		5301580	221084	100.000	100.000	

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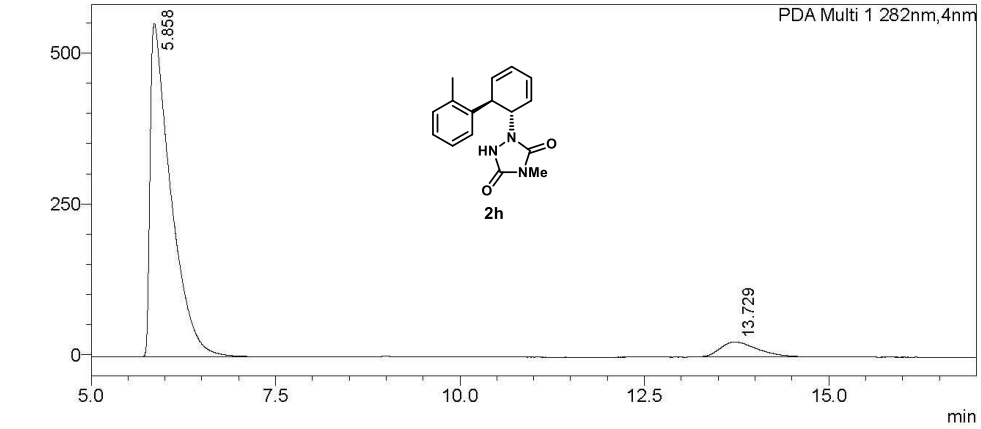

<Peak Table>

PDA Ch1 282nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	5.858	10778992	552993	92.166	95.666	--
2	13.729	916208	25053	7.834	4.334	10.755
Total		11695200	578046	100.000	100.000	

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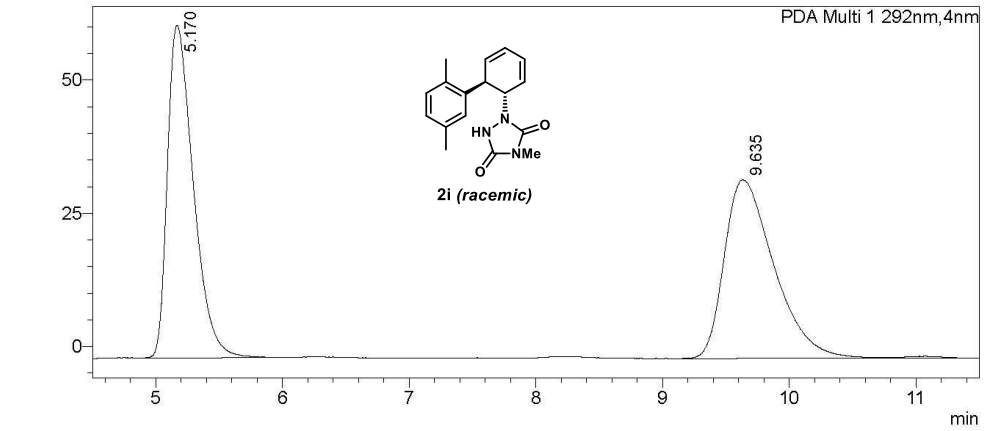

<Peak Table>

PDA Ch1 292nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	5.170	884770	62439	49.136	65.081	--
2	9.635	915883	33502	50.864	34.919	8.166
Total		1800653	95941	100.000	100.000	

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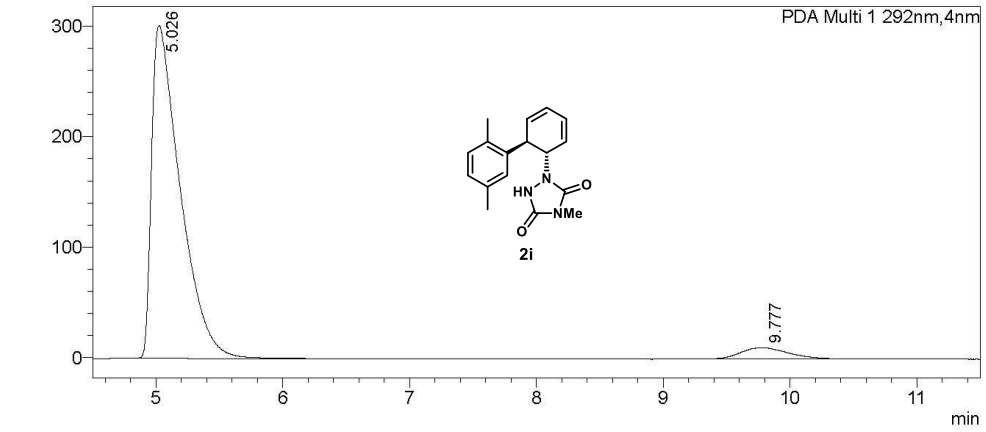

<Peak Table>

PDA Ch1 292nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	5.026	4719060	301296	94.221	96.670	--
2	9.777	289466	10377	5.779	3.330	8.368
Total		5008526	311674	100.000	100.000	

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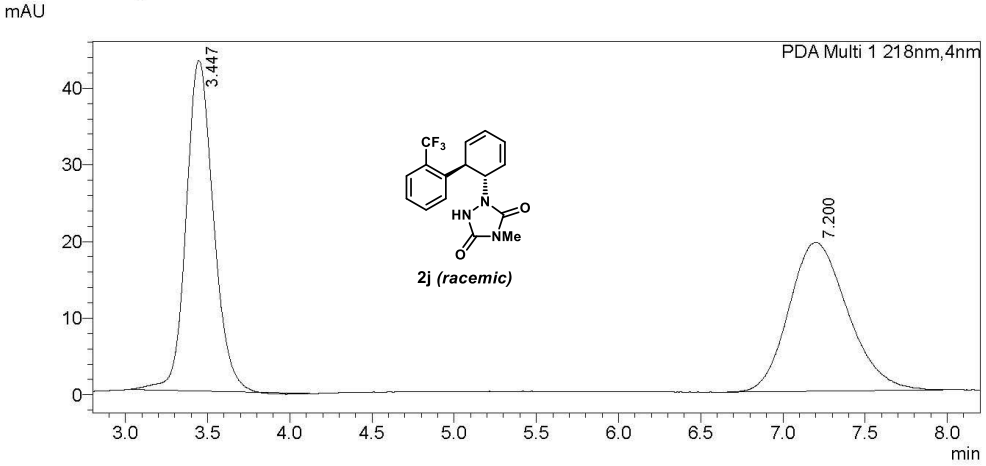

<Peak Table>

PDA Ch1 218nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	3.447	495736	43144	50.728	69.041	--
2	7.200	481515	19346	49.272	30.959	7.757
Total		977251	62490	100.000	100.000	

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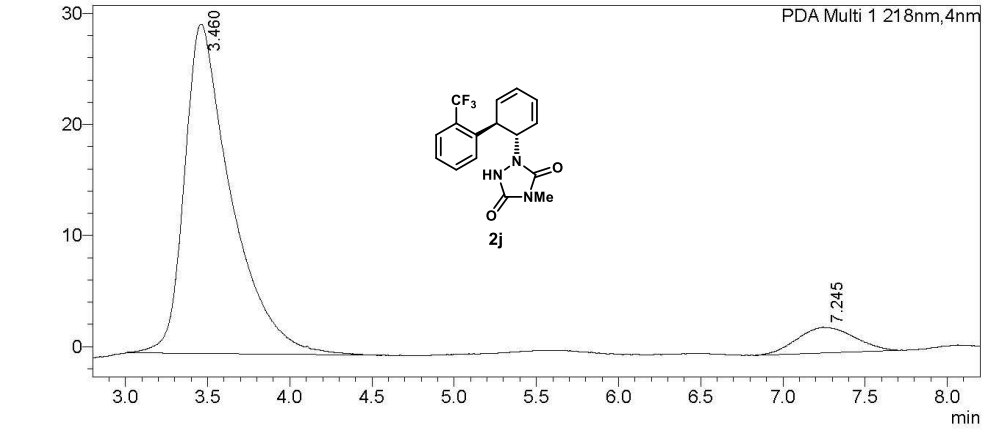

<Peak Table>

PDA Ch1 218nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	3.460	585954	29629	91.279	92.732	--
2	7.245	55986	2322	8.721	7.268	6.539
Total		641939	31951	100.000	100.000	

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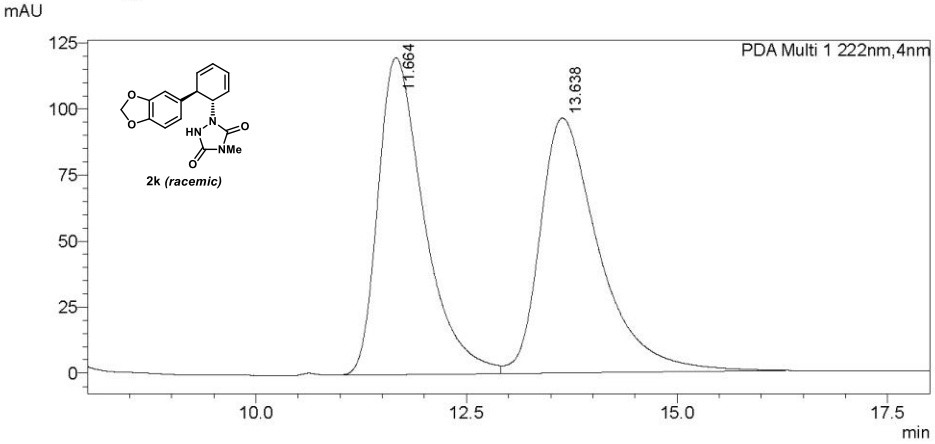

<Peak Table>

PDA Ch1 222nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	11.664	4561233	119984	49.272	55.421	--
2	13.638	4696038	96513	50.728	44.579	1.815
Total		9257271	216498	100.000	100.000	

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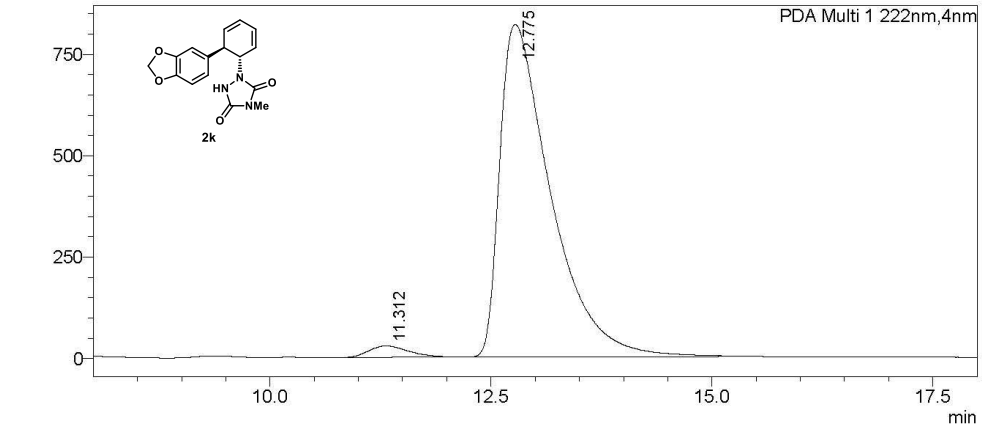

<Peak Table>

PDA Ch1 222nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	11.312	867006	28188	2.560	3.322	--
2	12.775	32997689	820369	97.440	96.678	1.590
Total		33864695	848557	100.000	100.000	

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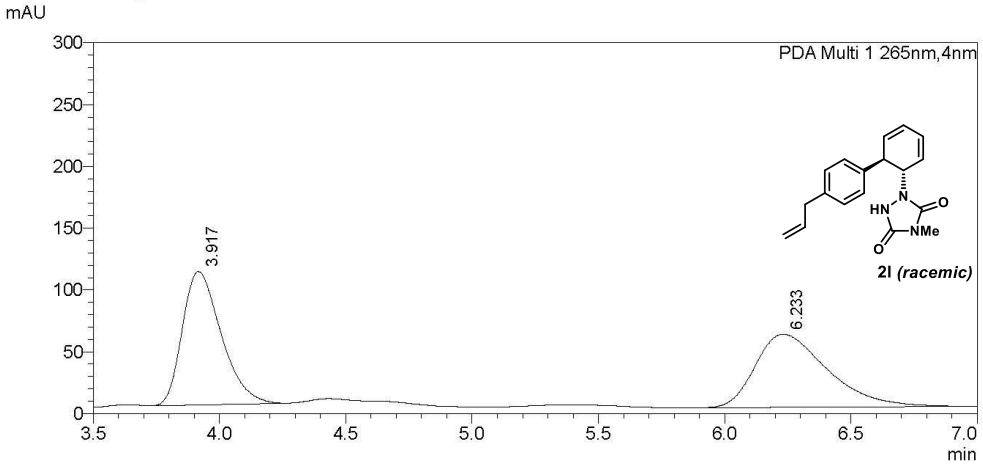

<Peak Table>

PDA Ch1 265nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	3.917	1149421	107972	49.484	64.577	--
2	6.233	1173386	59227	50.516	35.423	5.688
Total		2322807	167199	100.000	100.000	

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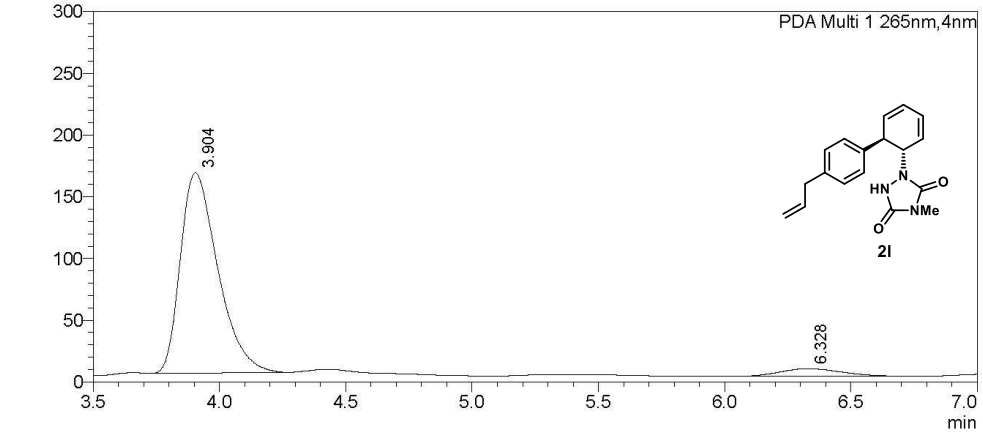

<Peak Table>

PDA Ch1 265nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	3.904	1668851	162573	93.857	96.290	--
2	6.328	109230	6264	6.143	3.710	6.425
Total		1778081	168837	100.000	100.000	

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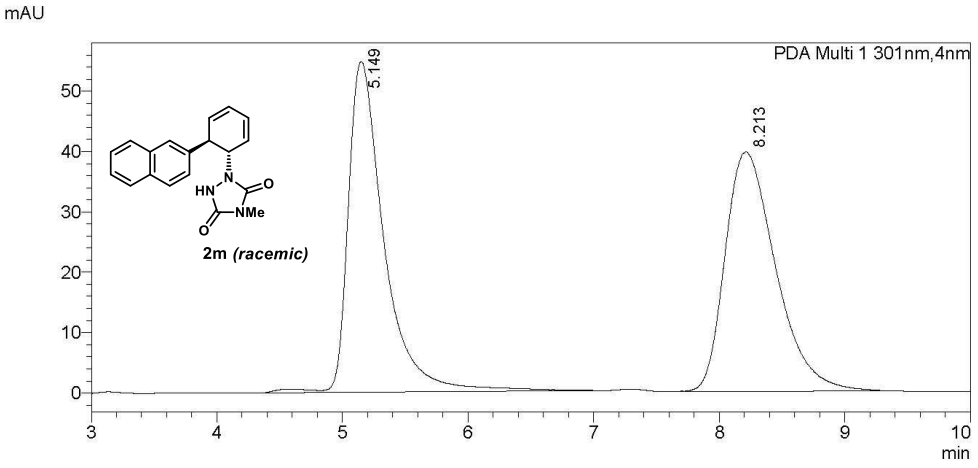

<Peak Table>

PDA Ch1 301nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	5.149	1090245	54750	49.599	57.983	--
2	8.213	1107893	39674	50.401	42.017	5.064
Total		2198138	94424	100.000	100.000	

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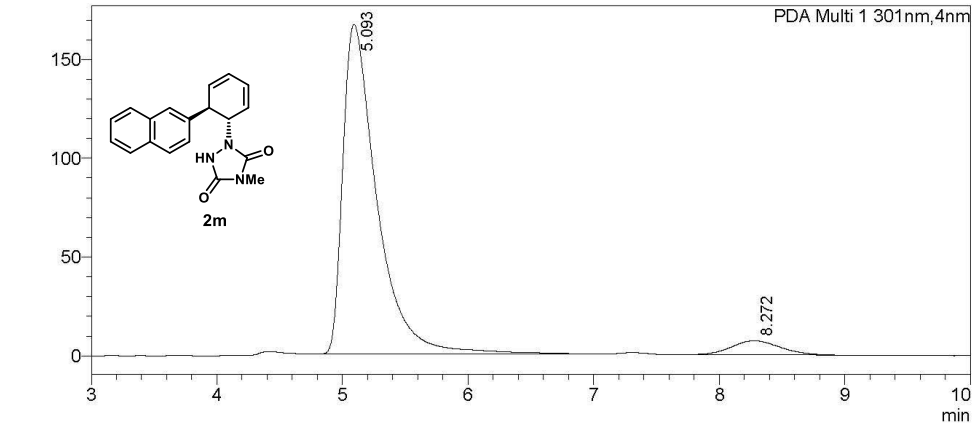

<Peak Table>

PDA Ch1 301nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	5.093	3148132	166680	94.176	95.882	--
2	8.272	194683	7159	5.824	4.118	5.338
Total		3342816	173840	100.000	100.000	

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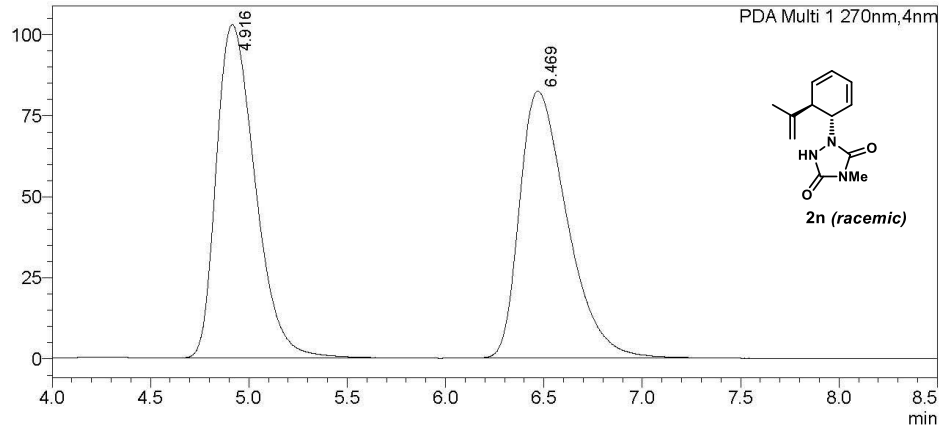
mAU



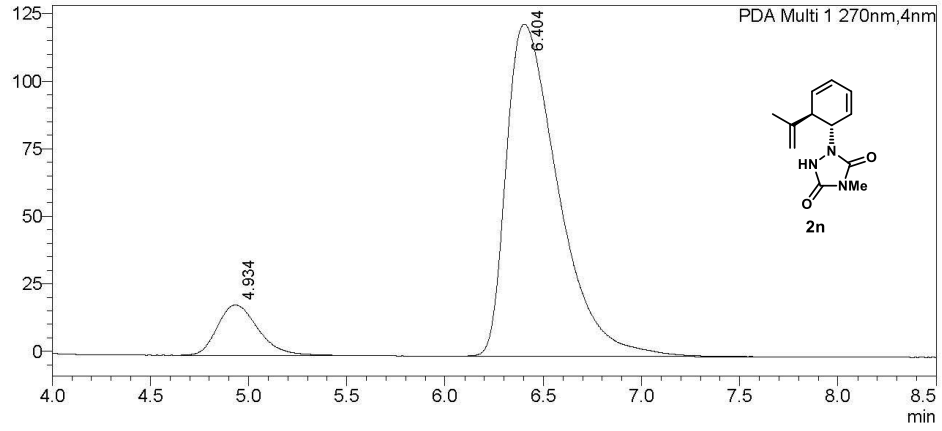
<Peak Table>

PDA Ch1 270nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	4.916	1415480	102986	50.414	55.559	--
2	6.469	1392241	82378	49.586	44.441	3.831
Total		2807721	185364	100.000	100.000	

<Chromatogram>

mAU

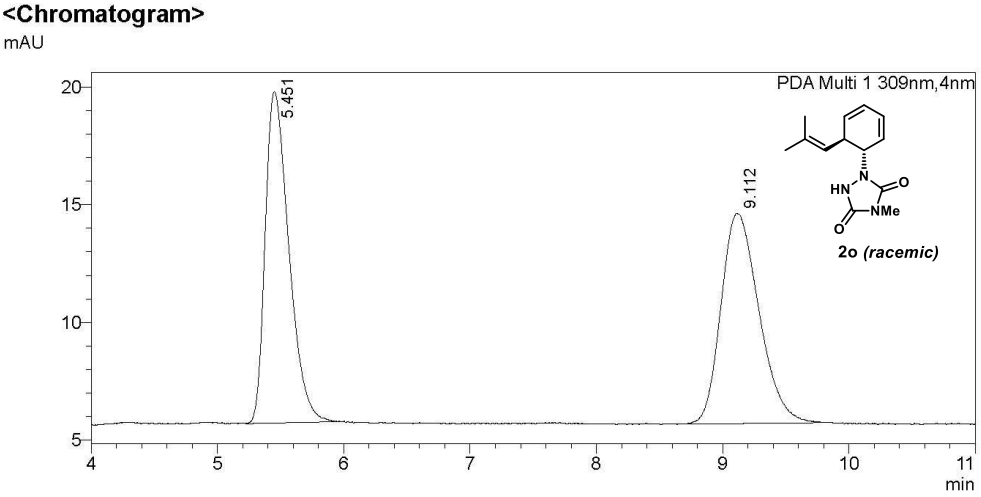


<Peak Table>

PDA Ch1 270nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	4.934	269975	18662	10.696	13.184	--
2	6.404	2254206	122890	89.304	86.816	3.418
Total		2524182	141553	100.000	100.000	

<Chromatogram>

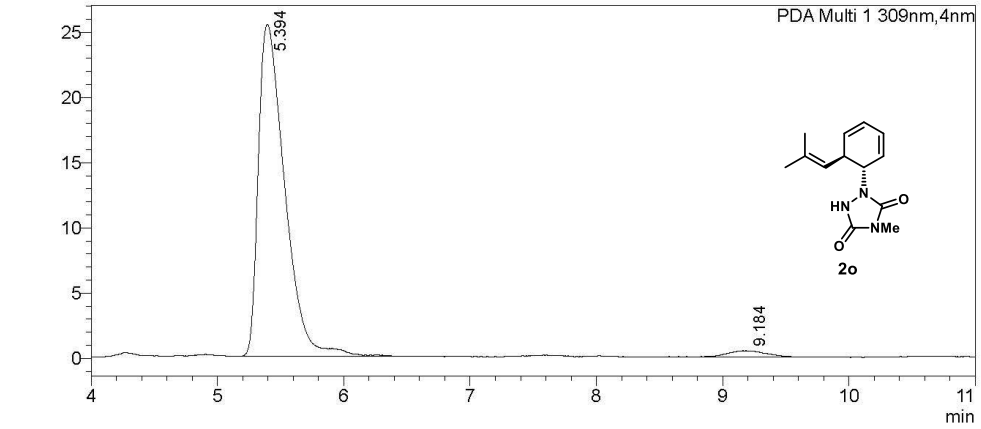


<Peak Table>

PDA Ch1 309nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	5.451	182870	14091	49.512	61.185	--
2	9.112	186475	8939	50.488	38.815	8.058
Total		369344	23030	100.000	100.000	

<Chromatogram>



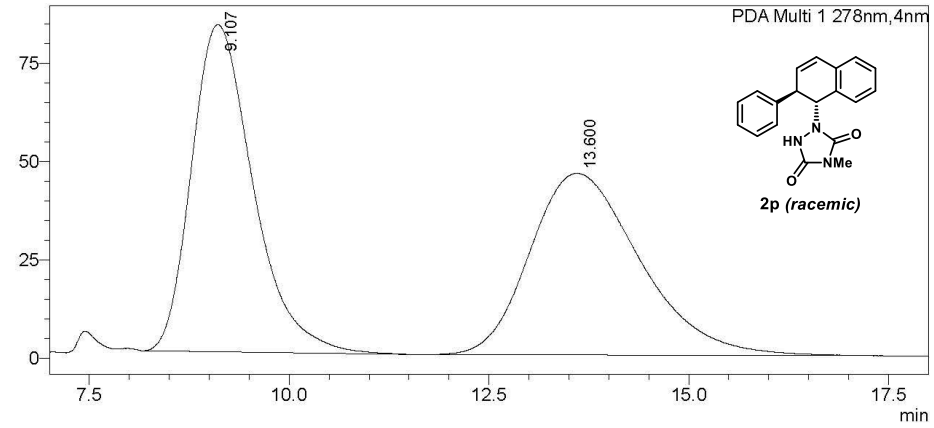
<Peak Table>

PDA Ch1 309nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	5.394	368627	25486	97.454	98.167	--
2	9.184	9631	476	2.546	1.833	8.033
Total		378258	25962	100.000	100.000	

<Chromatogram>

mAU



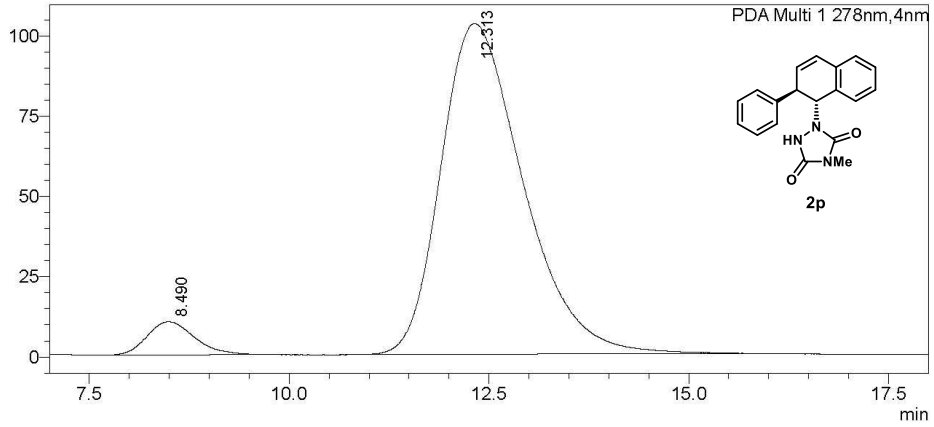
<Peak Table>

PDA Ch1 278nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	9.107	4474139	83244	50.321	64.284	--
2	13.600	4416982	46249	49.679	35.716	2.317
Total		8891120	129494	100.000	100.000	

<Chromatogram>

mAU



<Peak Table>

PDA Ch1 278nm

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	8.490	426497	10372	5.454	9.145	--
2	12.313	7392936	103040	94.546	90.855	2.597
Total		7819433	113412	100.000	100.000	

7. Crystallographic Data

7-1. Crystallographic Data for compound 2p

Single crystals of compound **2p** were obtained by slow crystallization from diethyl ether. A suitable crystal was selected and diffraction data were collected on a Bruker D8 Venture/Photon 100 diffractometer. The crystal was kept at 99.98 K during data collection. The Flack parameter calculated based on the data set is 0, with the error of 6. Thus, the absolute stereochemistry could not be determined.

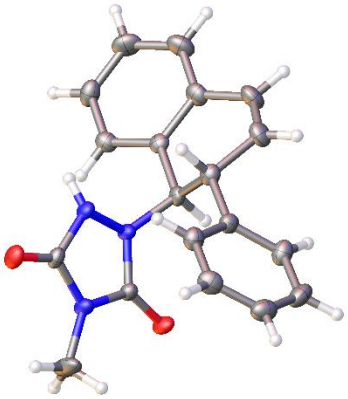


Table 1 Crystal data and structure refinement for compound 2p.

Identification code	CCDC 1822240
Empirical formula	$C_{19}H_{17}N_3O_2$
Formula weight	319.35
Temperature/K	99.98
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.9911(4)
b/Å	14.3103(11)
c/Å	18.8938(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1619.8(2)
Z	4
ρ_{calc}g/cm^3	1.310
μ/mm^{-1}	0.703
F(000)	672.0
Crystal size/mm^3	0.246 × 0.136 × 0.097
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.75 to 136.95
Index ranges	$-7 \le h \le 7$, $-12 \le k \le 17$, $-19 \le l \le 22$
Reflections collected	7574
Independent reflections	2895 [R_{int} = 0.0518, R_{sigma} = 0.0548]
Data/restraints/parameters	2895/0/222
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0618, wR_2 = 0.1469
Final R indexes [all data]	R_1 = 0.0631, wR_2 = 0.1478
Largest diff. peak/hole / e Å^{-3}	0.26/-0.24
Flack parameter	0.0(6)

7-2. Crystallographic Data for compound 3e

Single crystals of compound **3e** were obtained by slow crystallization from diethyl ether. A suitable crystal was selected and diffraction data were collected on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100.15 K during data collection.

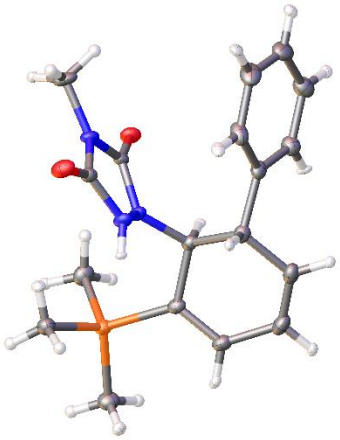
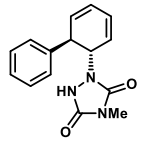


Table 1 Crystal data and structure refinement for compound 3e.

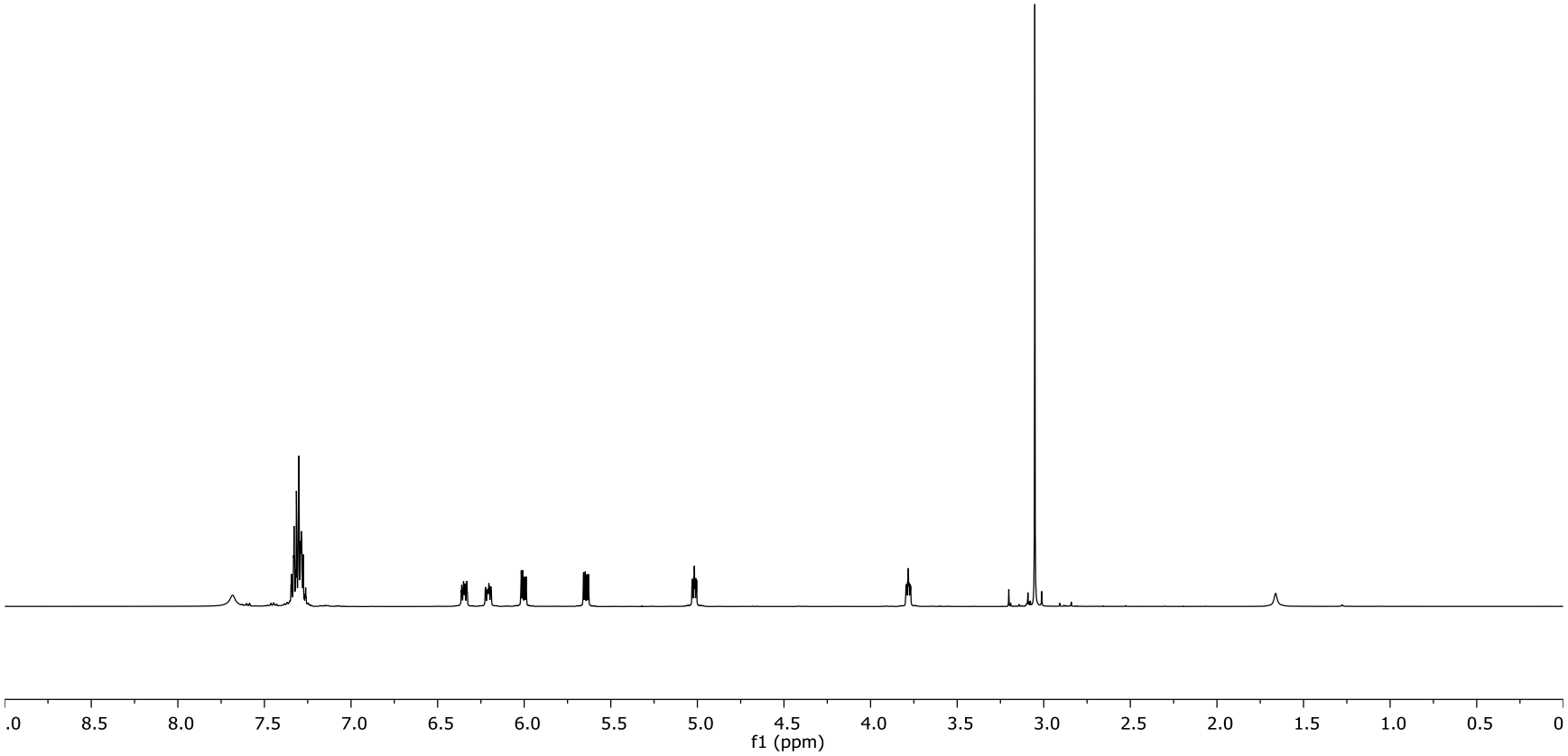
Identification code	CCDC 1822241
Empirical formula	$C_{18}H_{23}N_3O_2Si$
Formula weight	341.48
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.5544(18)
b/Å	6.1514(9)
c/Å	25.784(4)
α/°	90
β/°	93.021(8)
γ/°	90
Volume/Å^3	1830.0(5)
Z	4
ρ_{calc}g/cm^3	1.239
μ/mm^{-1}	0.143
F(000)	728.0
Crystal size/mm^3	0.306 × 0.141 × 0.064
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.33 to 56.876
Index ranges	$-15 \leq h \leq 14$, $-8 \leq k \leq 8$, $-34 \leq l \leq 34$
Reflections collected	48329
Independent reflections	4553 [R_{int} = 0.0692, R_{sigma} = 0.0373]
Data/restraints/parameters	4553/0/238
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0402, wR_2 = 0.0883
Final R indexes [all data]	R_1 = 0.0616, wR_2 = 0.0979
Largest diff. peak/hole / e Å^{-3}	0.31/-0.24

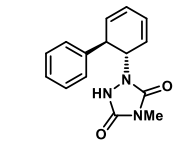
8. NMR Spectra



2a

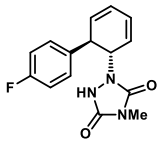
(^{1}H NMR, $CDCl_3$, 500 MHz)





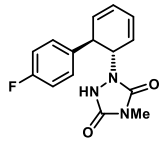
2a

(^{13}C NMR, $CDCl_3$, 126 MHz)



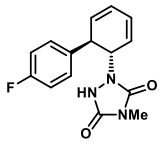
2b

(^{1}H NMR, $CDCl_3$, 500 MHz)



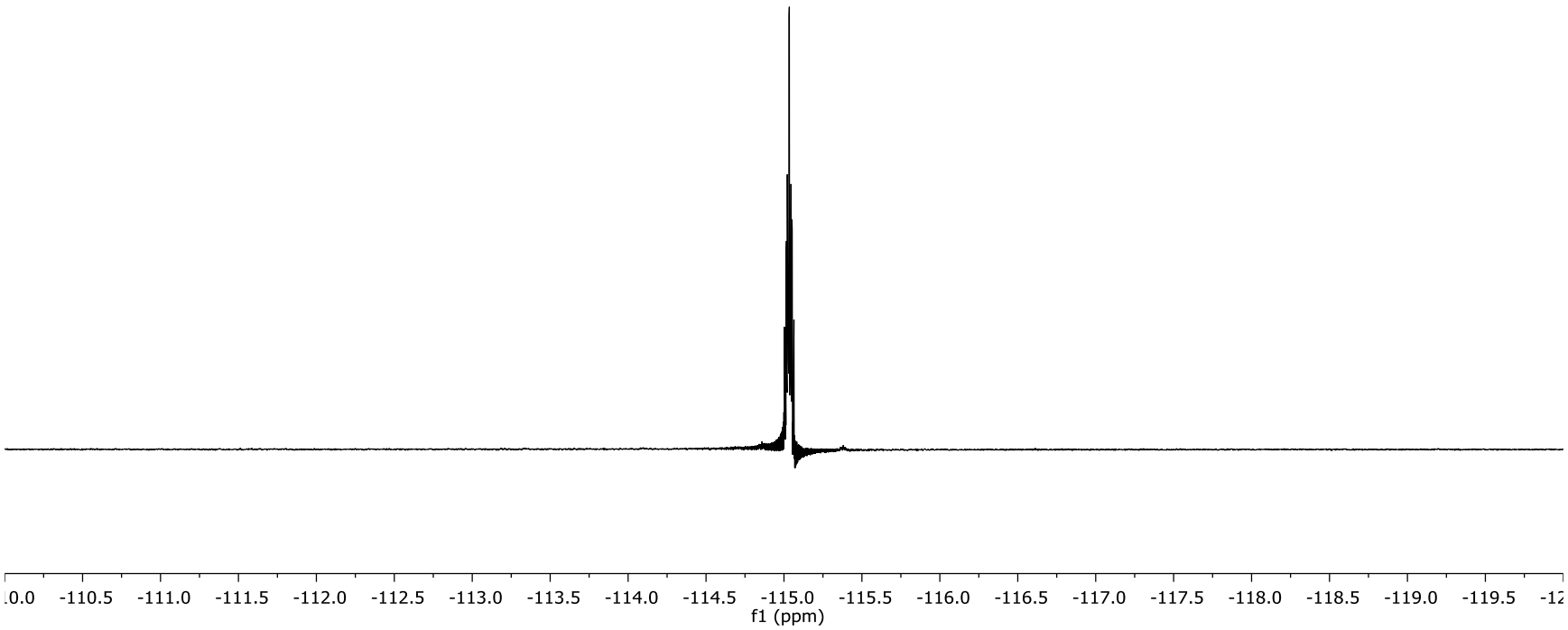
2b

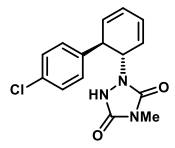
(^{13}C NMR, $CDCl_3$, 126 MHz)



2b

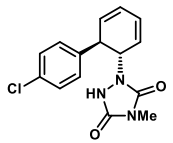
(^{19}F NMR, $CDCl_3$, 471 MHz)





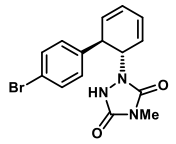
2c

(^{1}H NMR, $CDCl_3$, 500 MHz)



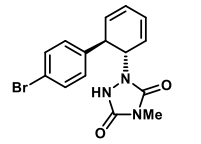
2c

(^{13}C NMR, $CDCl_3$, 126 MHz)



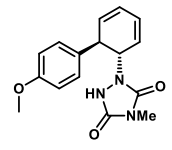
2d

(^{1}H NMR, $CDCl_3$, 500 MHz)



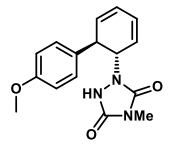
2d

(^{13}C NMR, $CDCl_3$, 126 MHz)



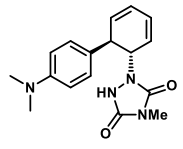
2e

(^{1}H NMR, $CDCl_3$, 500 MHz)



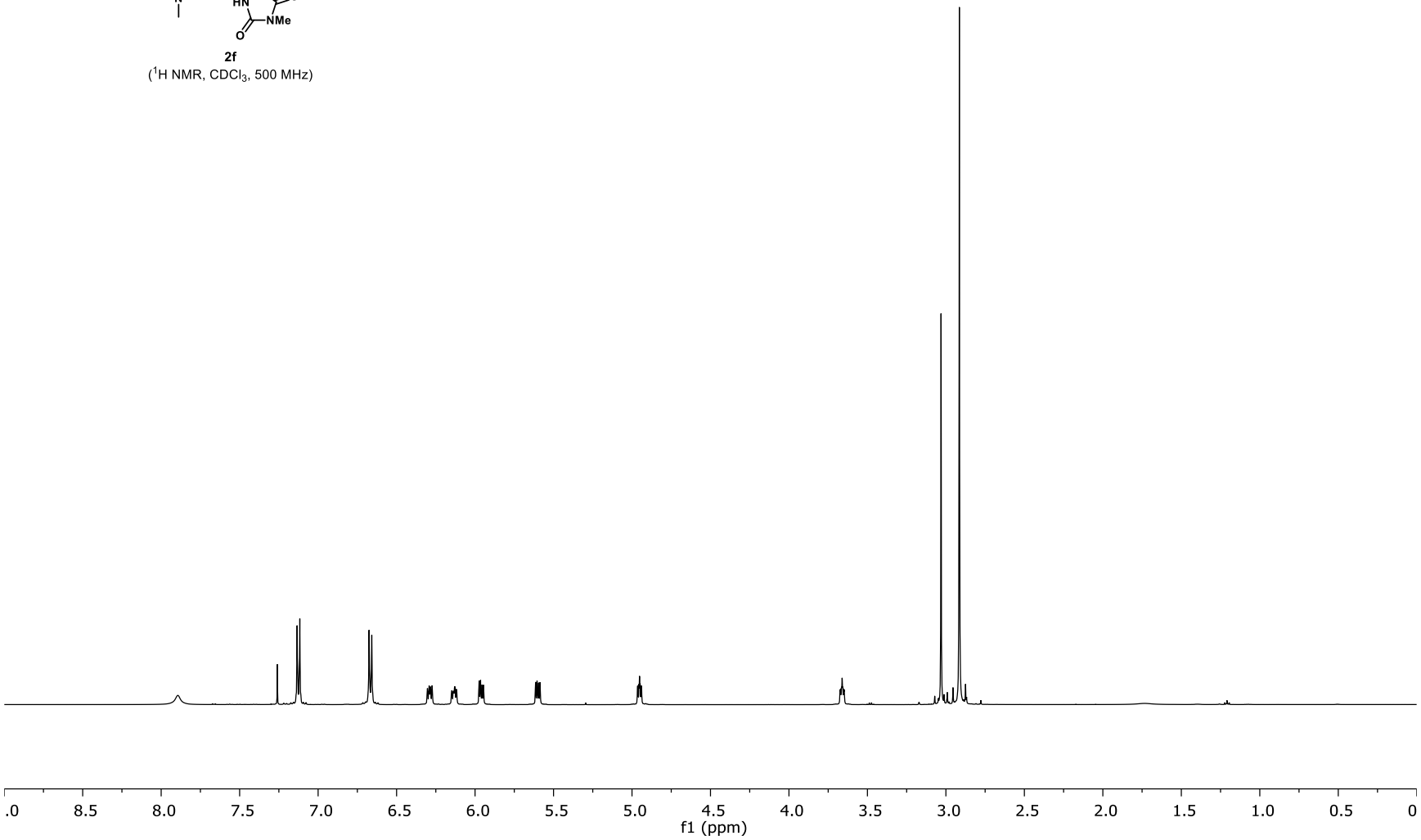
2e

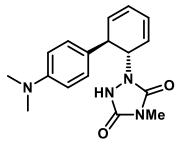
(^{13}C NMR, $CDCl_3$, 126 MHz)



2f

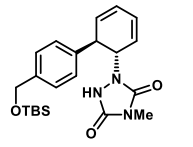
(^{1}H NMR, $CDCl_3$, 500 MHz)





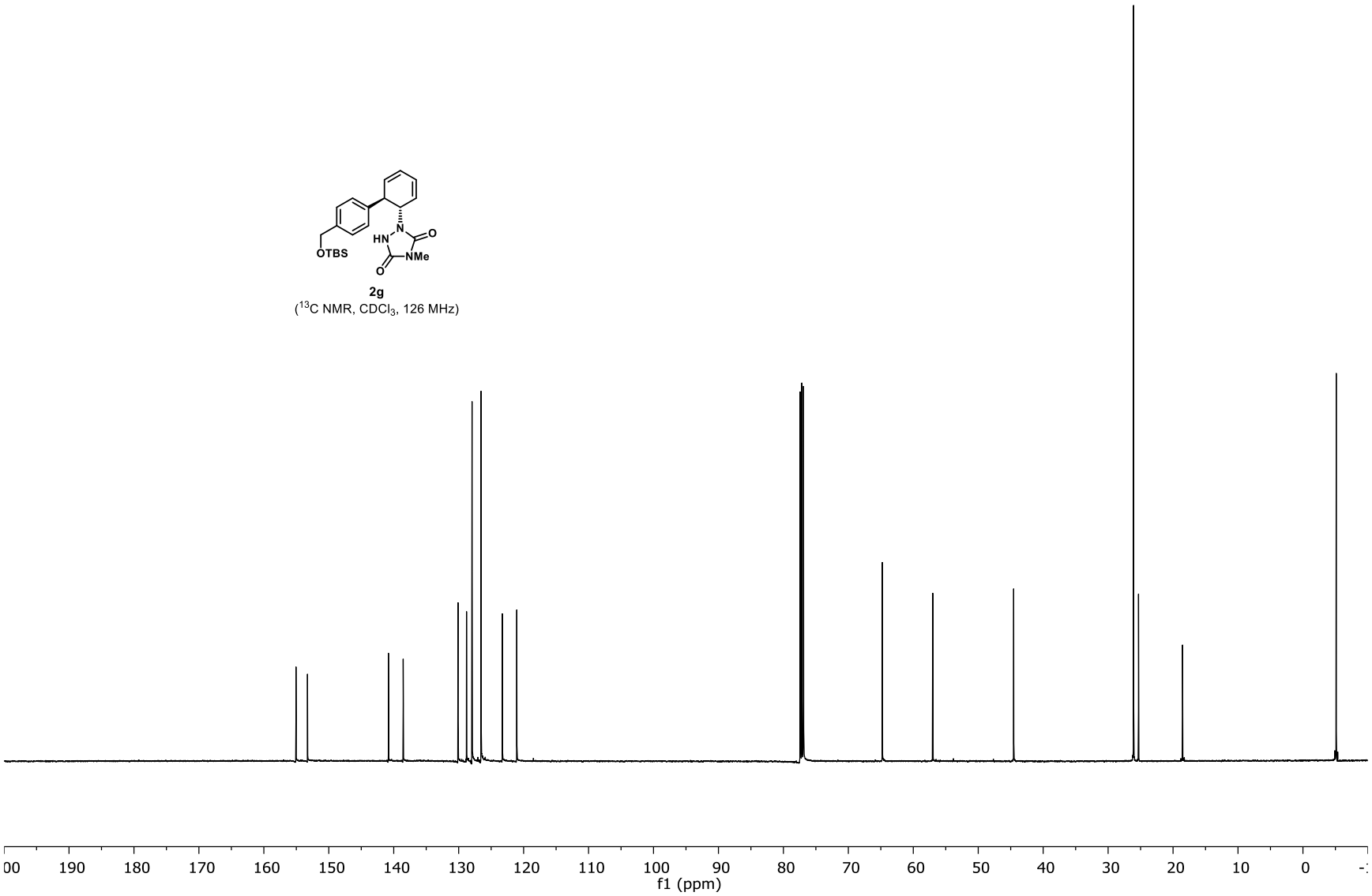
2f

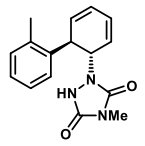
(^{13}C NMR, $CDCl_3$, 126 MHz)



2g

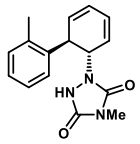
(^{1}H NMR, $CDCl_3$, 500 MHz)


OTBS
HN
N
O
NMe
O
2g
(13C NMR, CDCl3, 126 MHz)
f1 (ppm)



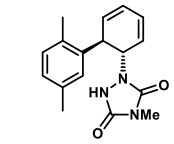
2h

(^{1}H NMR, $CDCl_3$, 500 MHz)



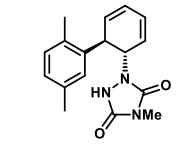
2h

(^{13}C NMR, $CDCl_3$, 126 MHz)



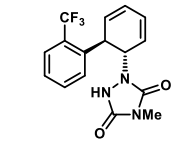
2i

(^{1}H NMR, $CDCl_3$, 500 MHz)



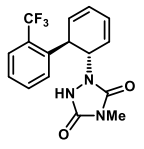
2i

(^{13}C NMR, $CDCl_3$, 126 MHz)

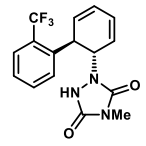


2j

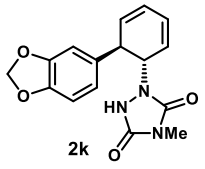
(^{1}H NMR, $CDCl_3$, 500 MHz)



2j
(^{13}C NMR, $CDCl_3$, 126 MHz)

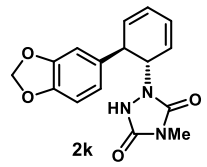


2j
(^{19}F NMR, $CDCl_3$, 471 MHz)



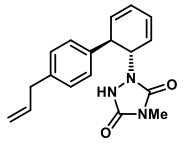
2k

(^{1}H NMR, $CDCl_3$, 500 MHz)



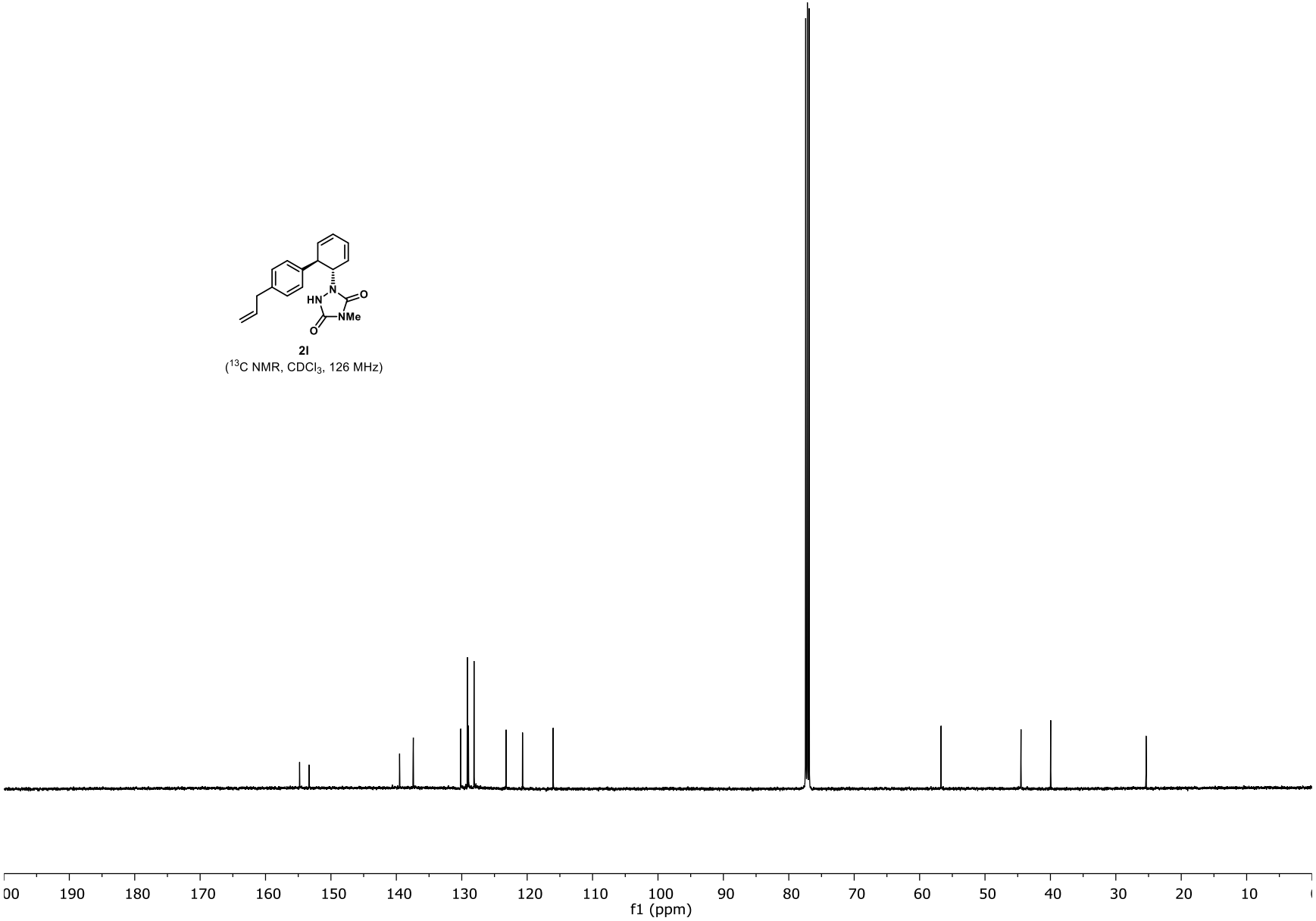
2k

(^{13}C NMR, $CDCl_3$, 126 MHz)



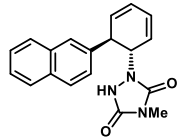
2l

(^{1}H NMR, $CDCl_3$, 500 MHz)



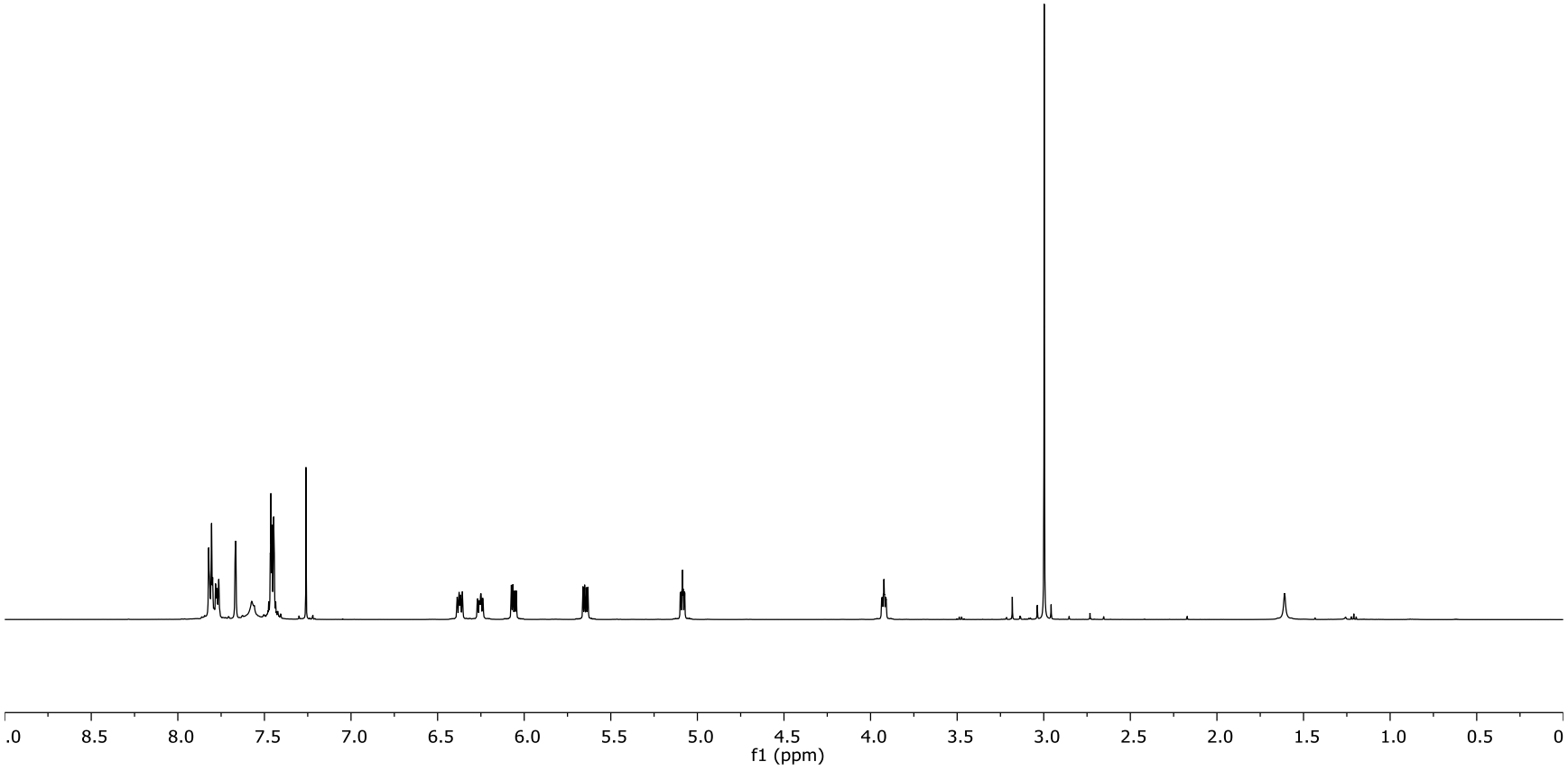
2l

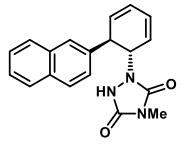
(^{13}C NMR, $CDCl_3$, 126 MHz)



2m

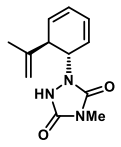
(^{1}H NMR, $CDCl_3$, 500 MHz)





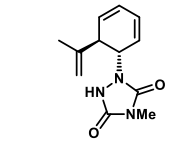
2m

(^{13}C NMR, $CDCl_3$, 126 MHz)



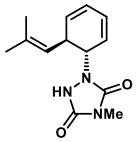
2n

(^{1}H NMR, $CDCl_3$, 500 MHz)



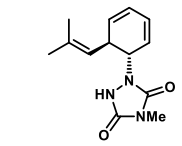
2n

(^{13}C NMR, $CDCl_3$, 126 MHz)



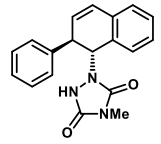
2o

(^{1}H NMR, C_6D_6, 500 MHz)



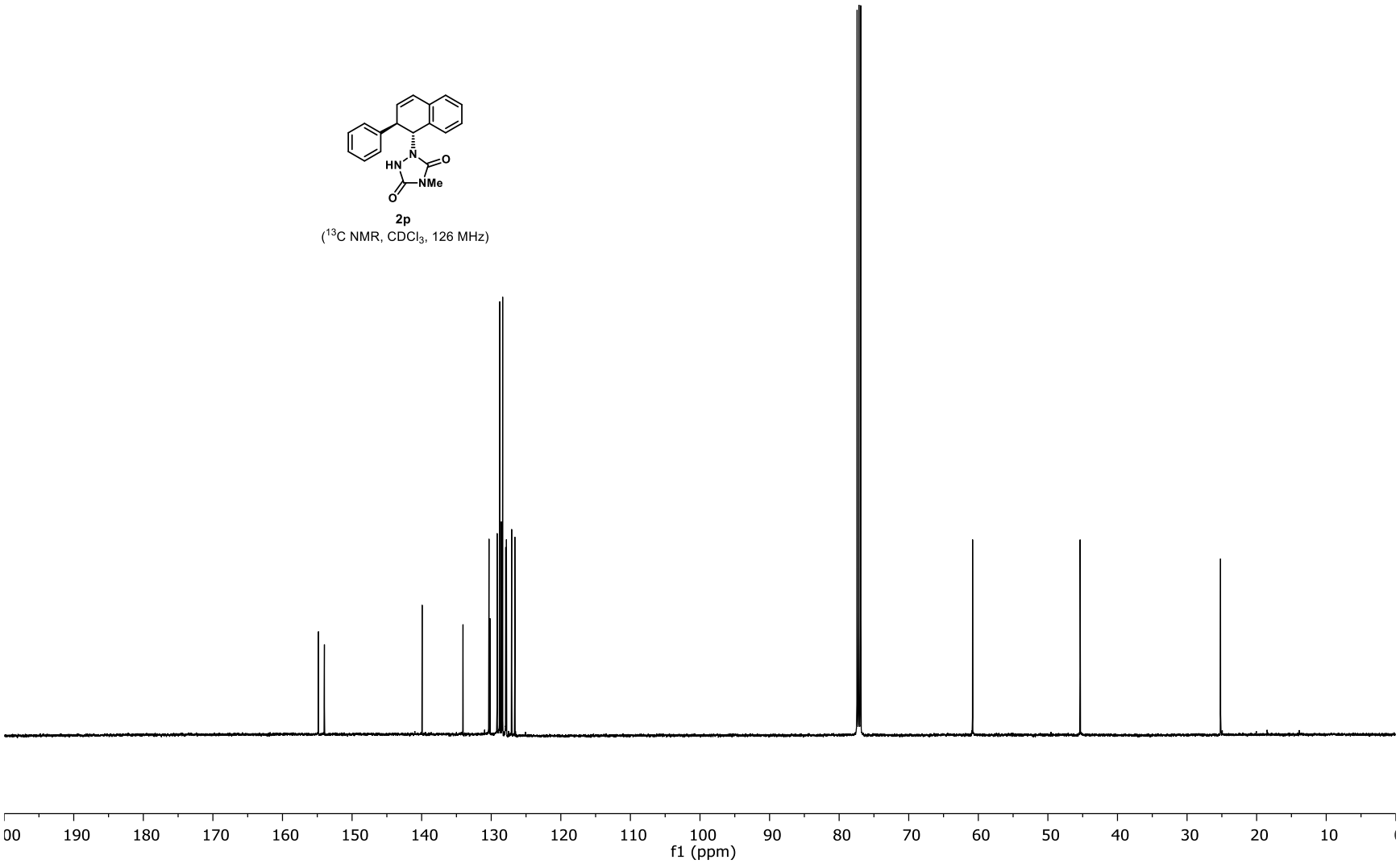
2o

(^{13}C NMR, C_6D_6, 126 MHz)



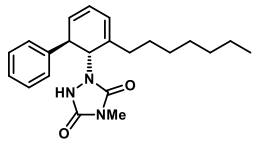
2p

(^{1}H NMR, $CDCl_3$, 500 MHz)

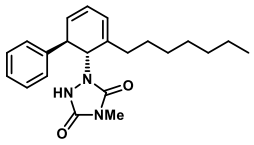


2p

(^{13}C NMR, $CDCl_3$, 126 MHz)

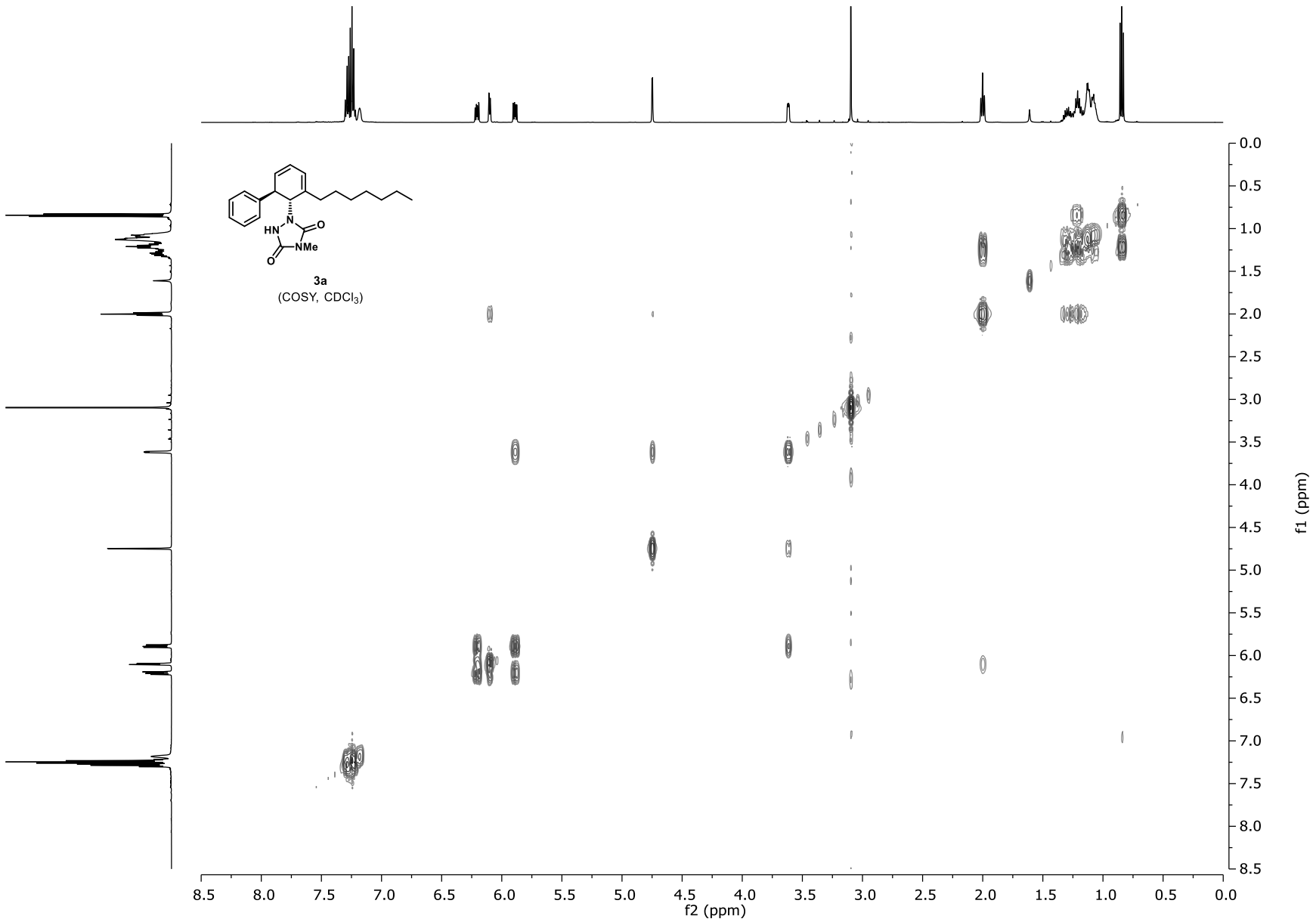


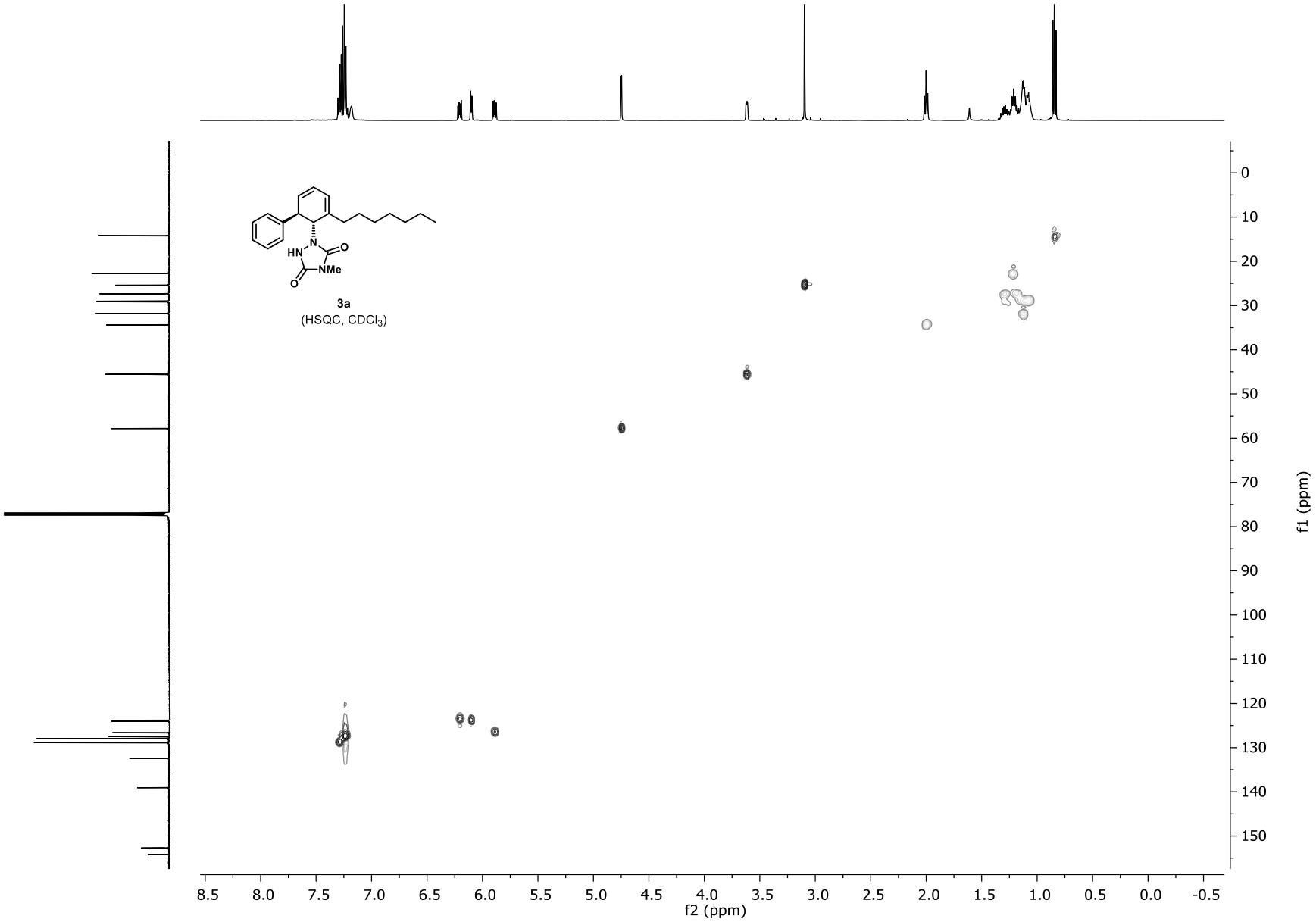
3a
(^{1}H NMR, $CDCl_3$, 500 MHz)

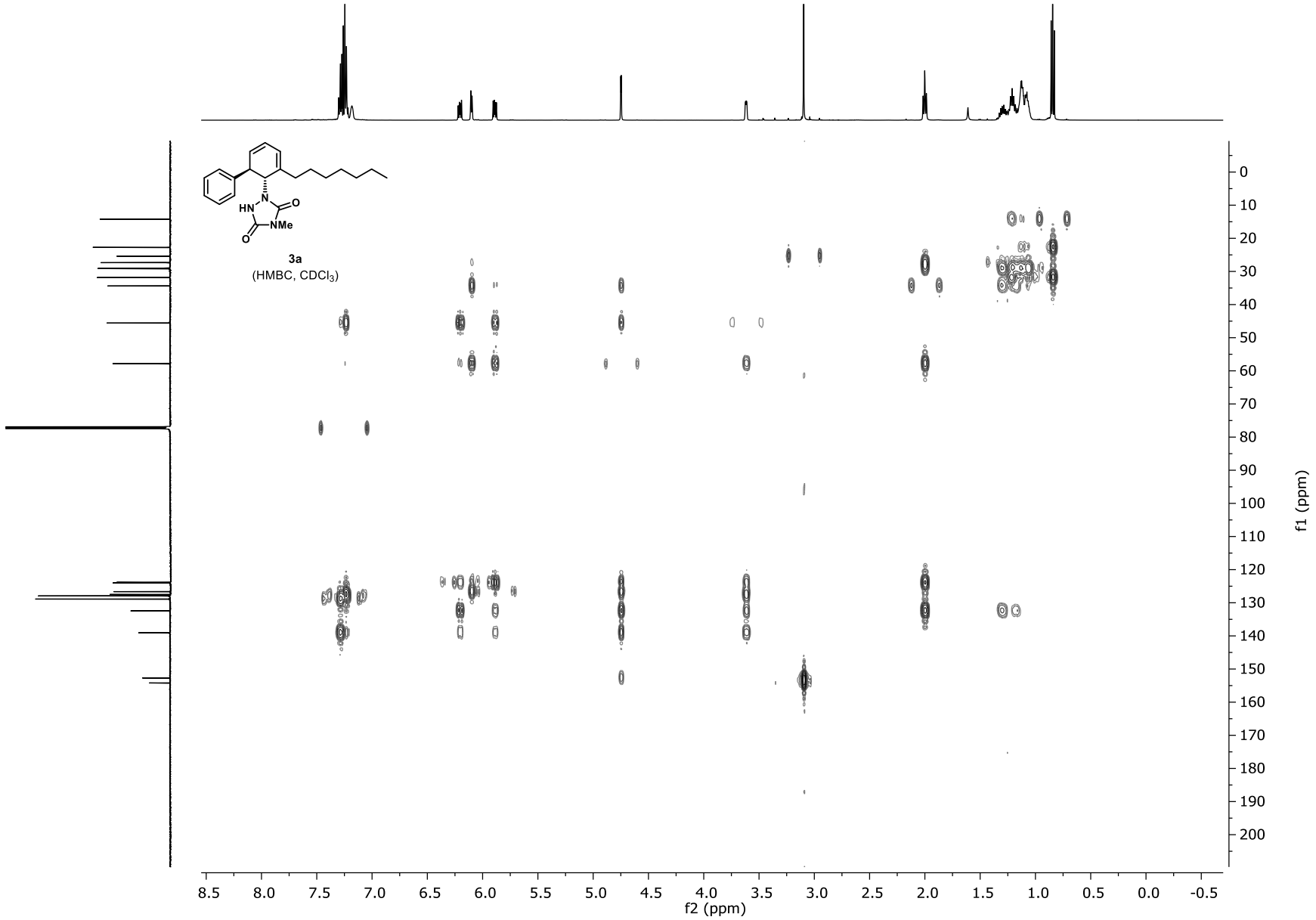


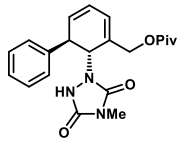
3a

(^{13}C NMR, $CDCl_3$, 126 MHz)

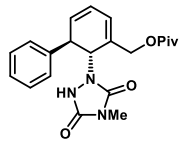

HN
N
O
NMe
O
3a
(COSY, CDCl3)
f2 (ppm)
f1 (ppm)


3a
(HSQC, CDCl3)
f2 (ppm)
f1 (ppm)


3a
(HMBC, CDCl3)
f2 (ppm)
f1 (ppm)

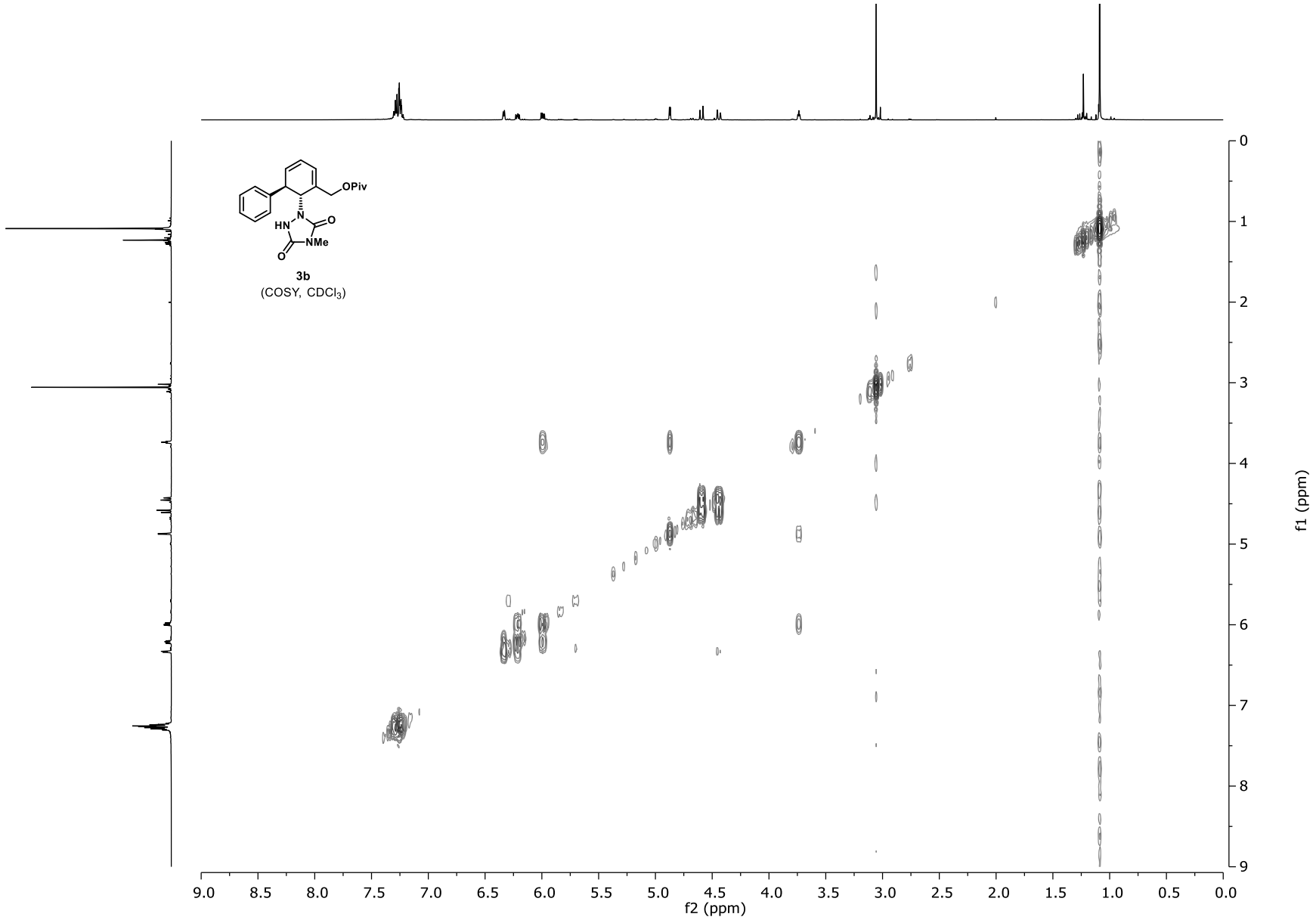


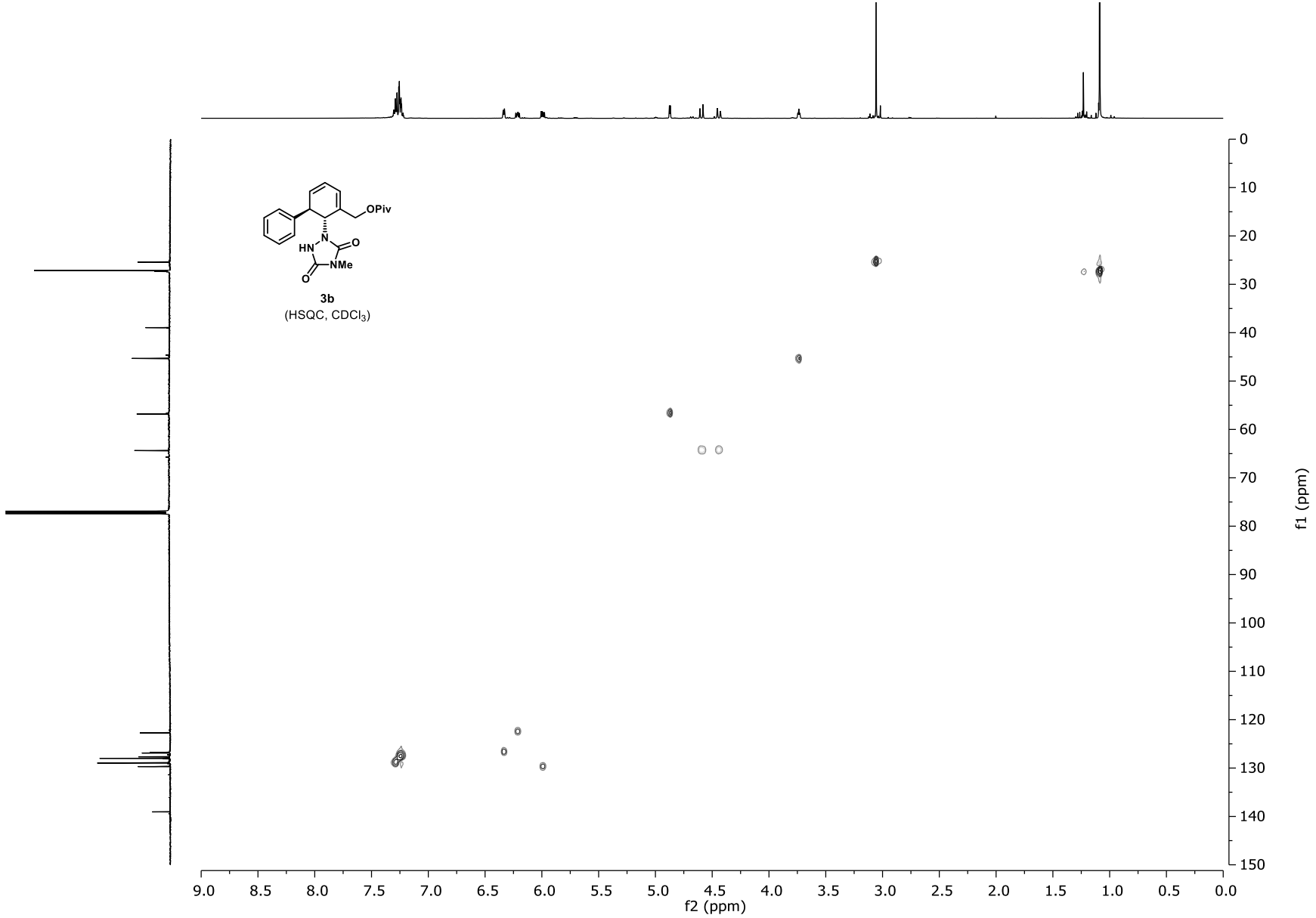
3b
(^{1}H NMR, $CDCl_3$, 500 MHz)

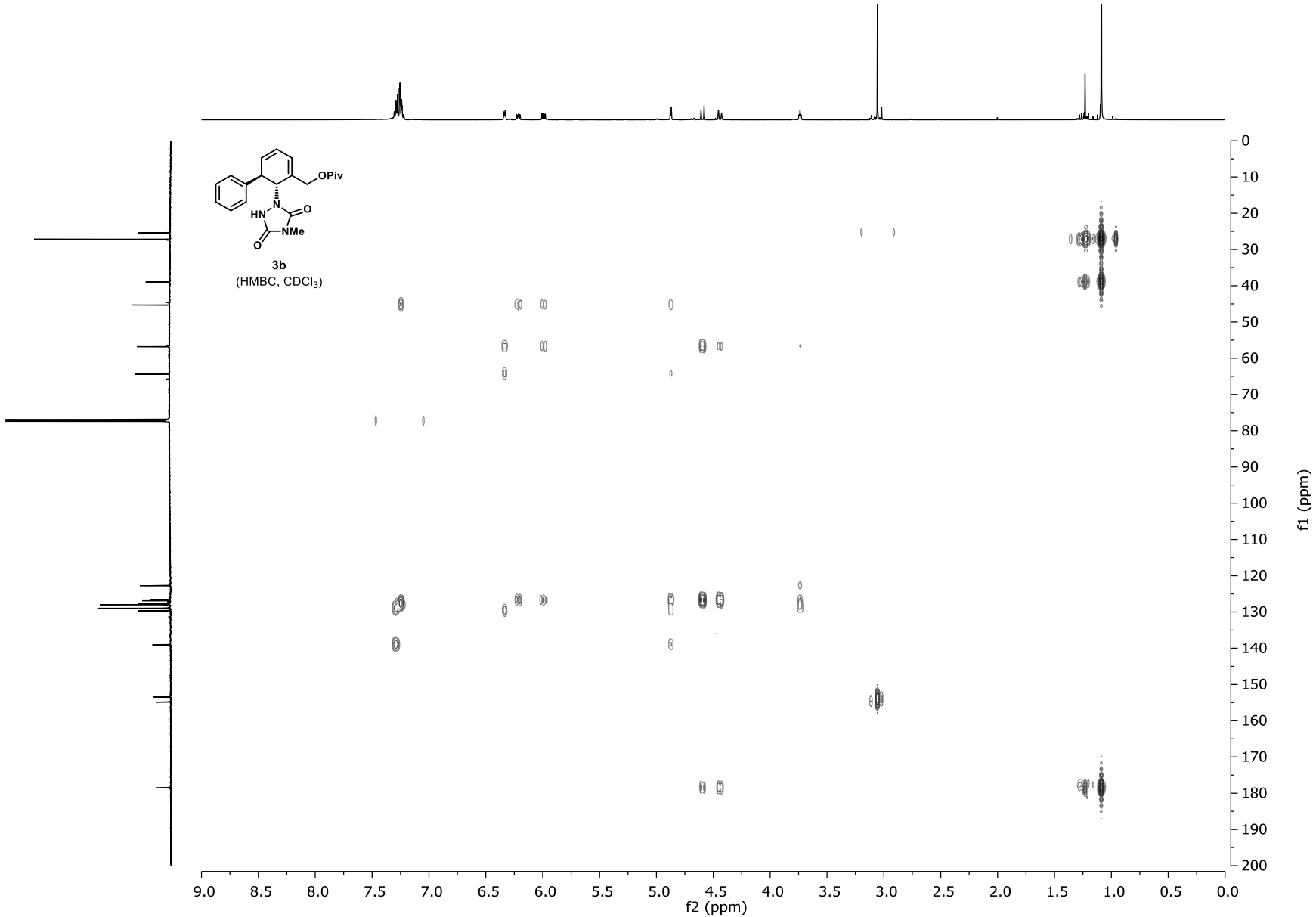


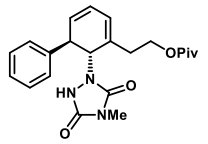
3b

(^{13}C NMR, $CDCl_3$, 126 MHz)


OPiv
HN
N
O
NMe
O
3b
(COSY, CDCl3)
f2 (ppm)
f1 (ppm)

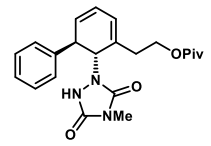

OPiv
HN
N
O
NMe
O
3b
(HSQC, CDCl3)
f2 (ppm)
f1 (ppm)


OPiv
HN
N
O
NMe
O
3b
(HMBC, CDCl3)
f2 (ppm)
f1 (ppm)



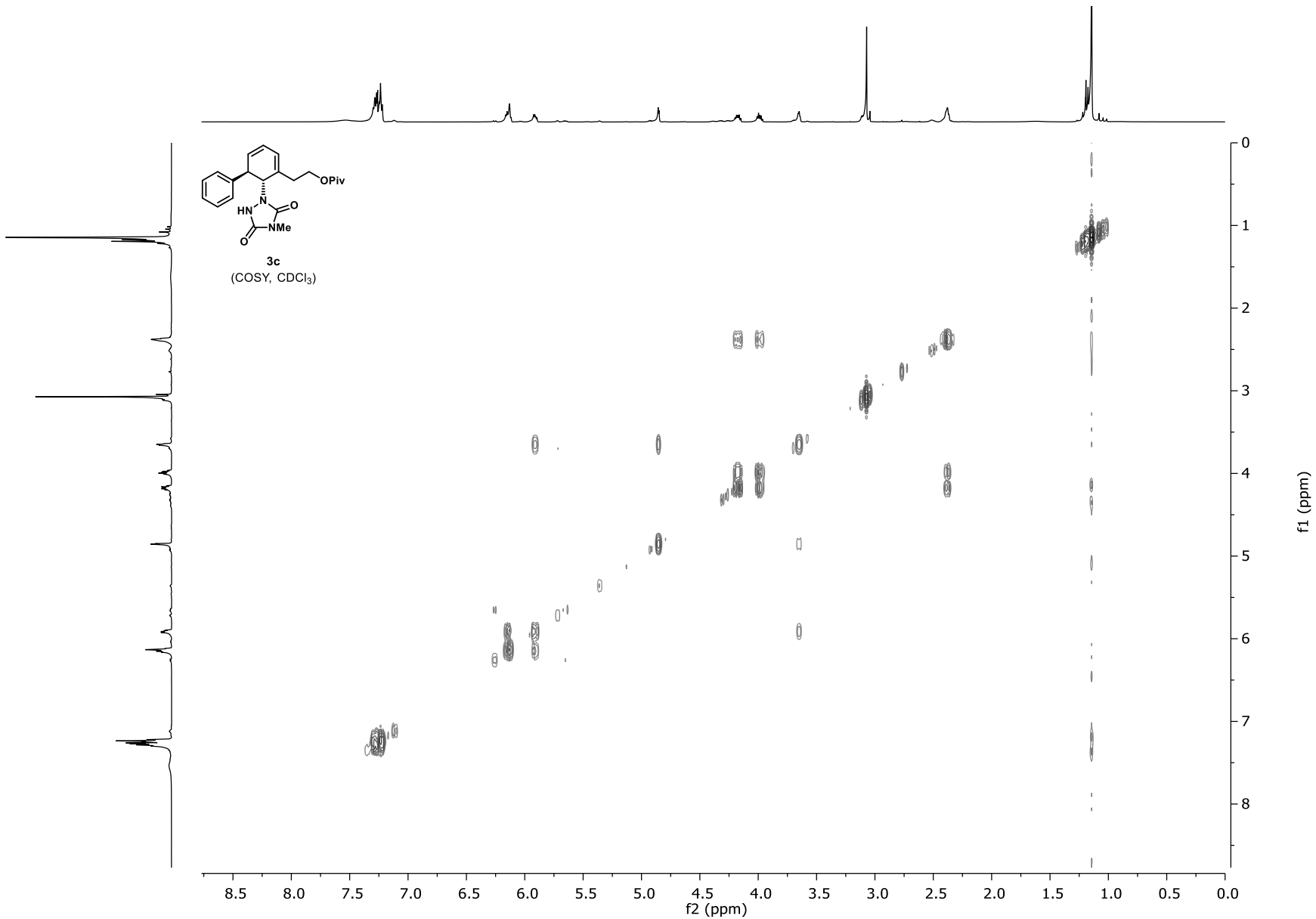
3c

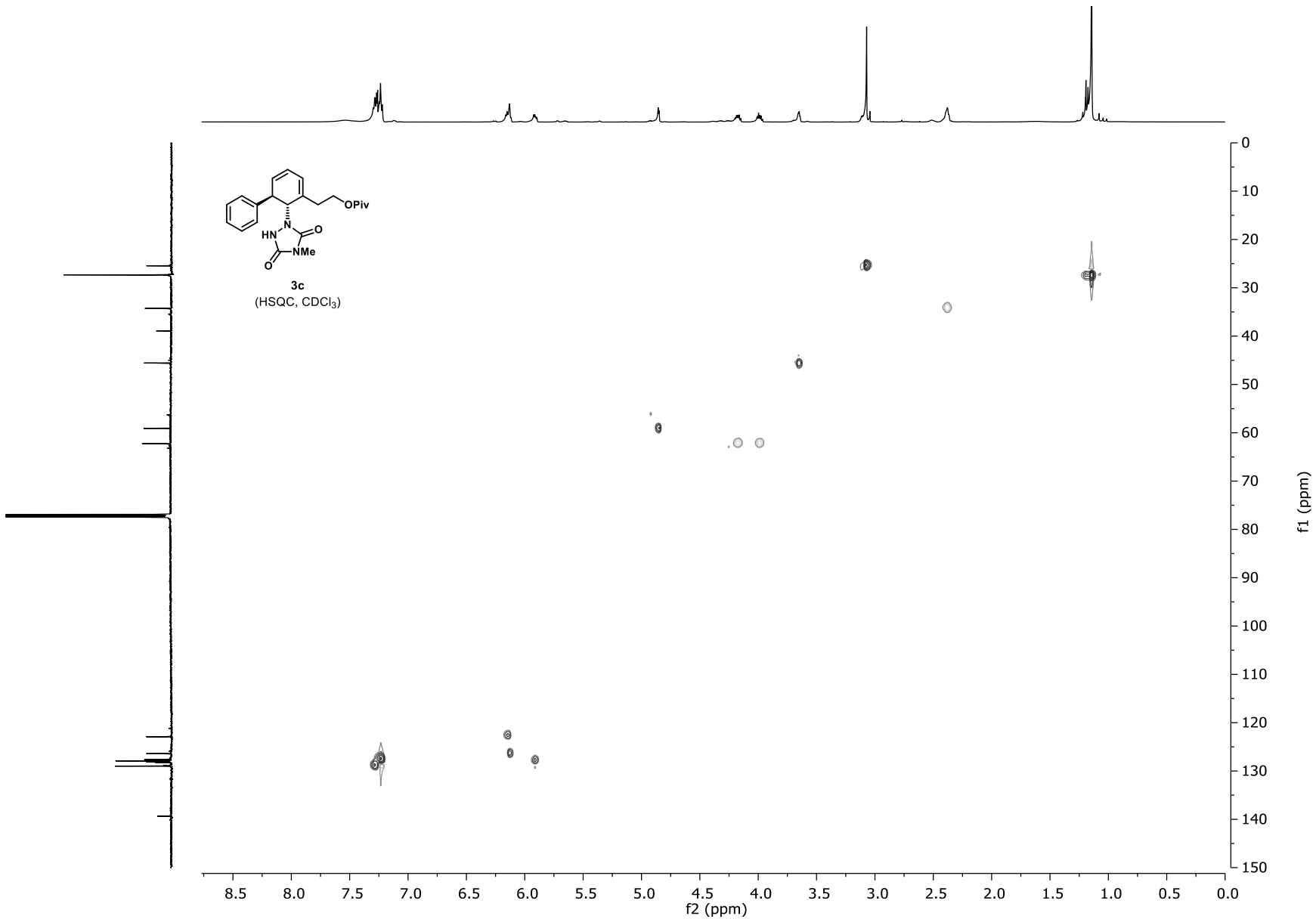
(^{1}H NMR, $CDCl_3$, 500 MHz)

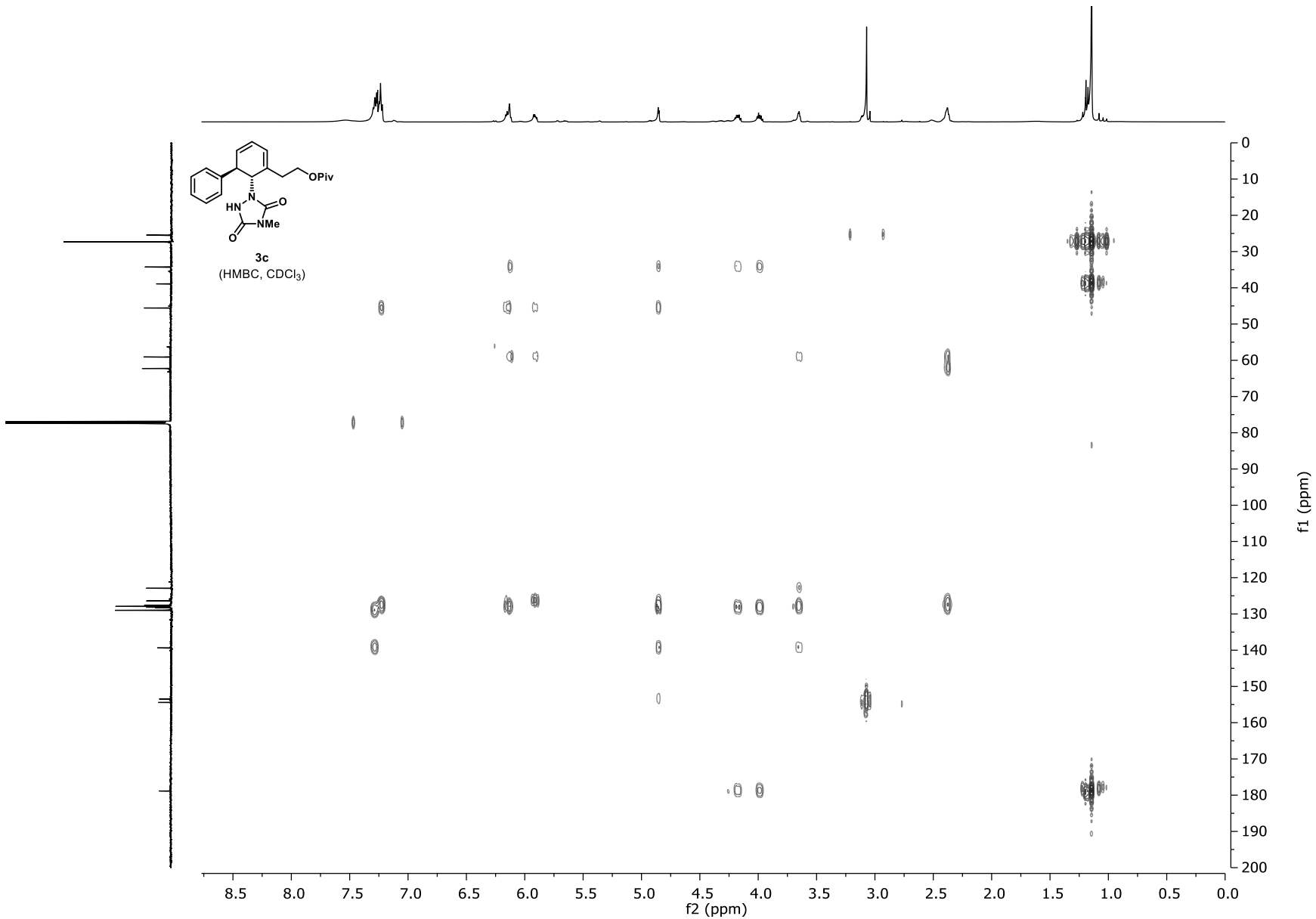


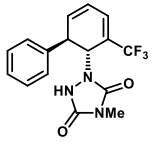
3c

(^{13}C NMR, $CDCl_3$, 126 MHz)


OPiv
HN
N
O
NMe
O
3c
(COSY, CDCl3)
f2 (ppm)
f1 (ppm)

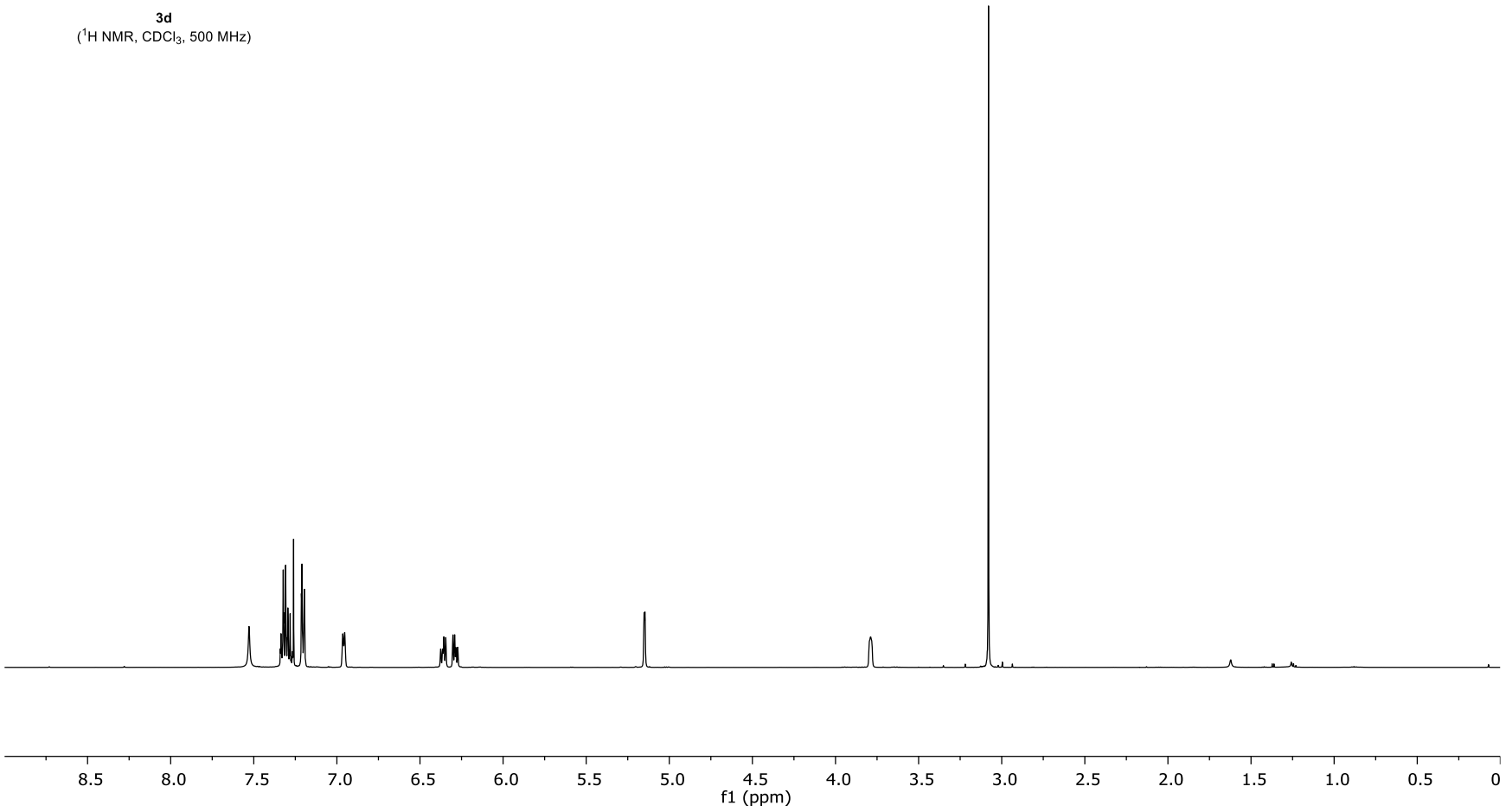

OPiv
HN
N
O
NMe
O
3c
(HSQC, CDCl3)
f2 (ppm)
f1 (ppm)

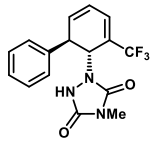

OPiv
HN
N
O
NMe
O
3c
(HMBC, CDCl3)
f2 (ppm)
f1 (ppm)



3d

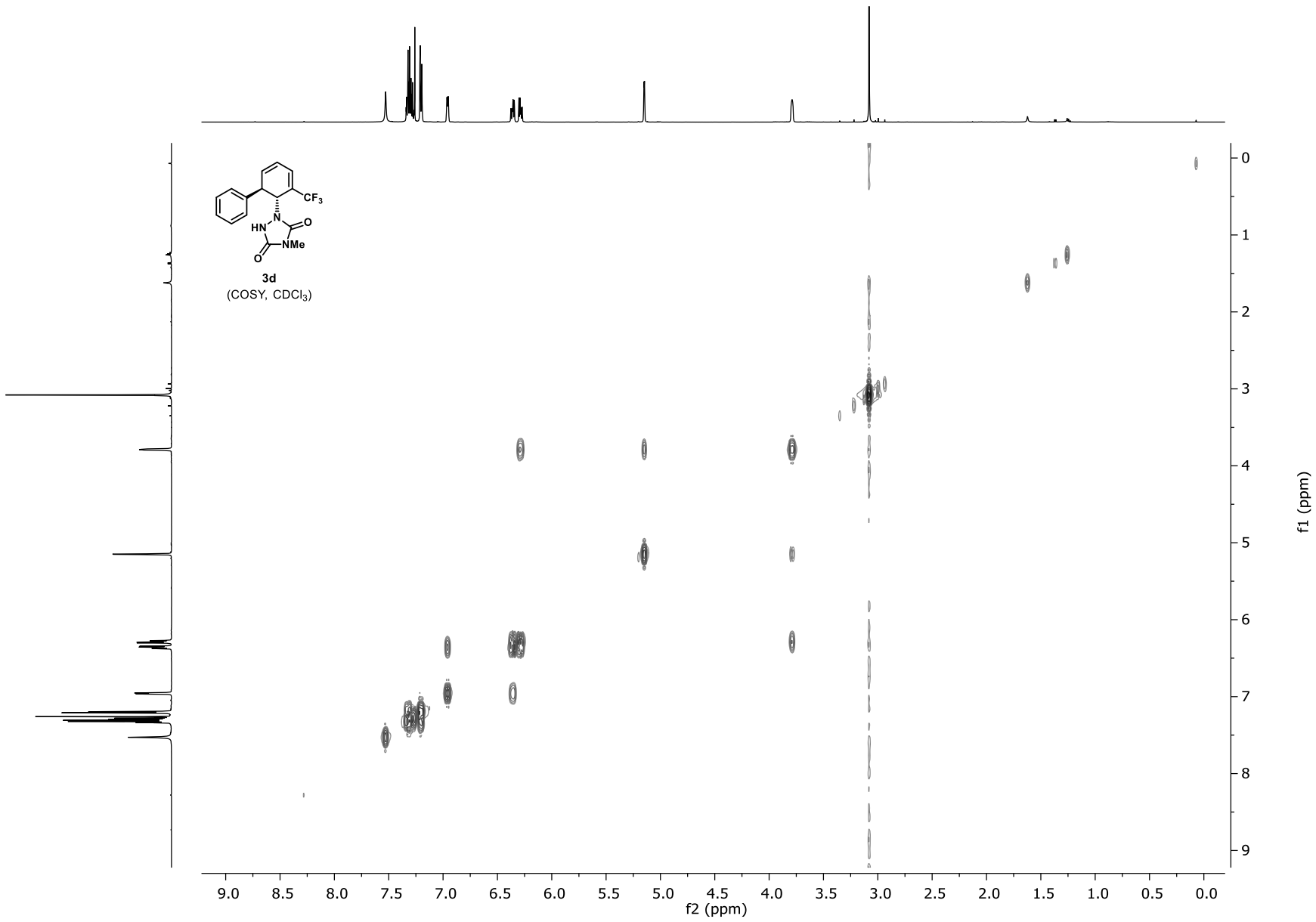
(^{1}H NMR, $CDCl_3$, 500 MHz)

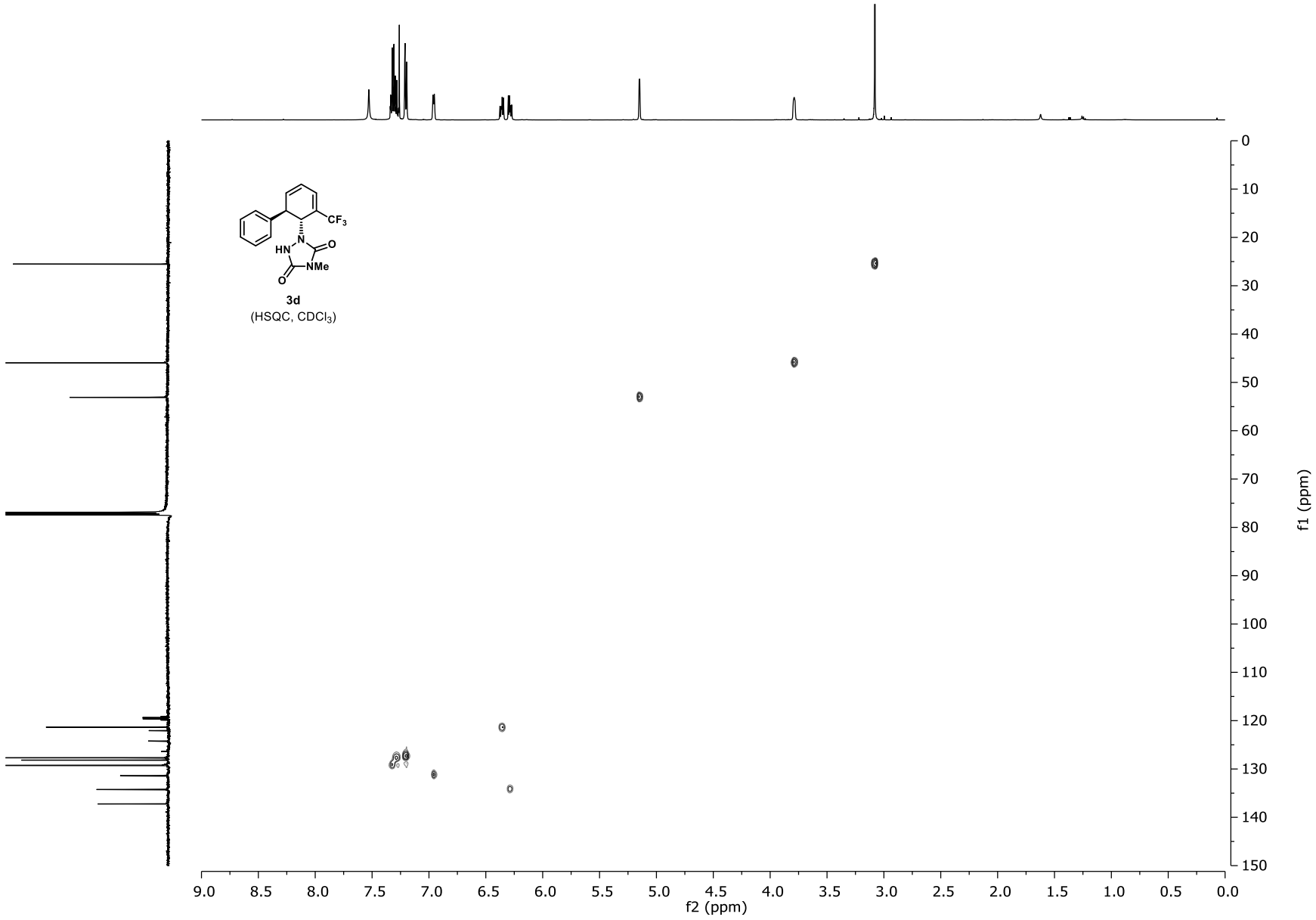


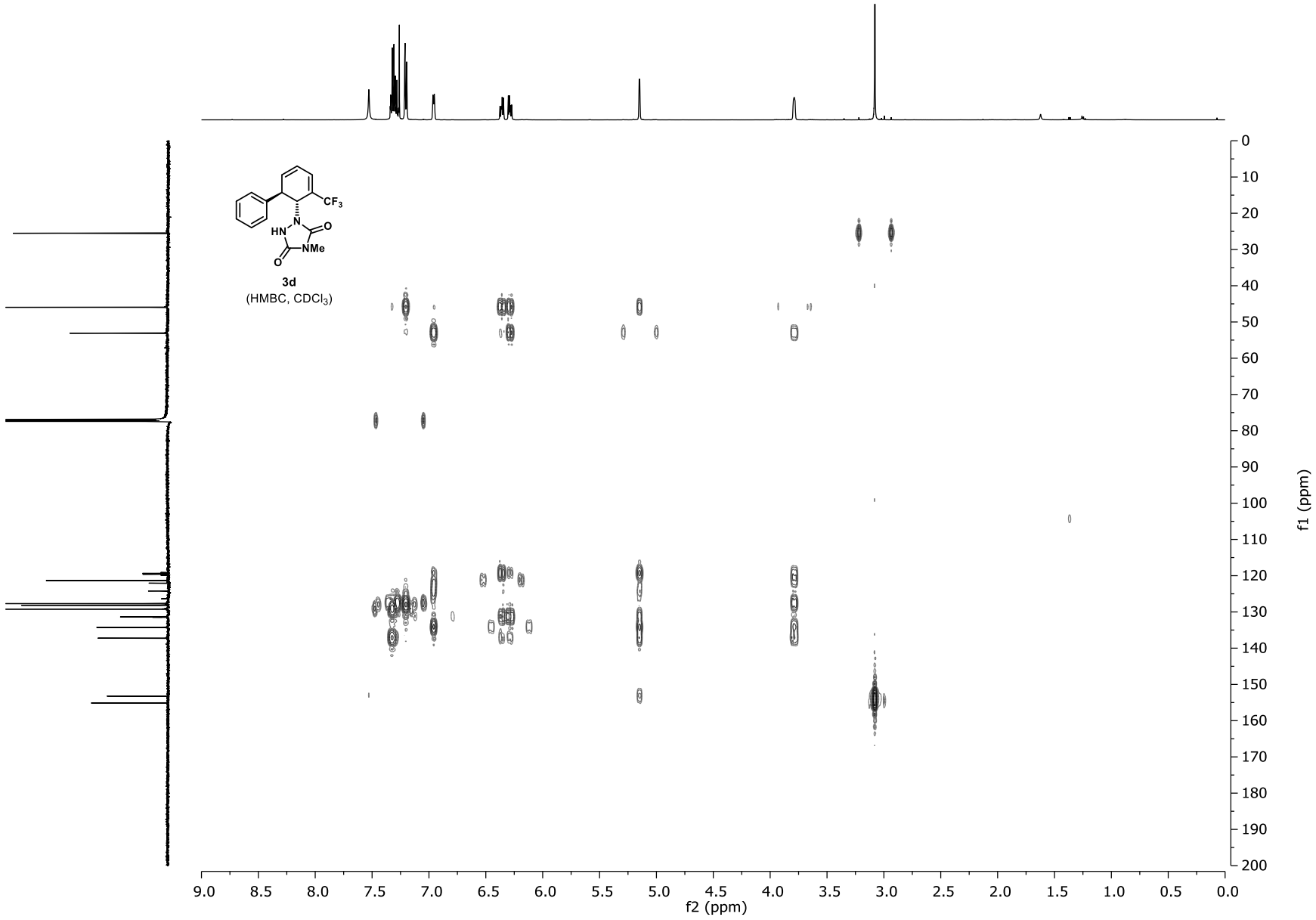


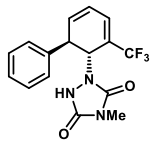
3d

(^{13}C NMR, $CDCl_3$, 126 MHz)


CF3
HN
N
O
NMe
O
3d
(COSY, CDCl3)
f2 (ppm)
f1 (ppm)

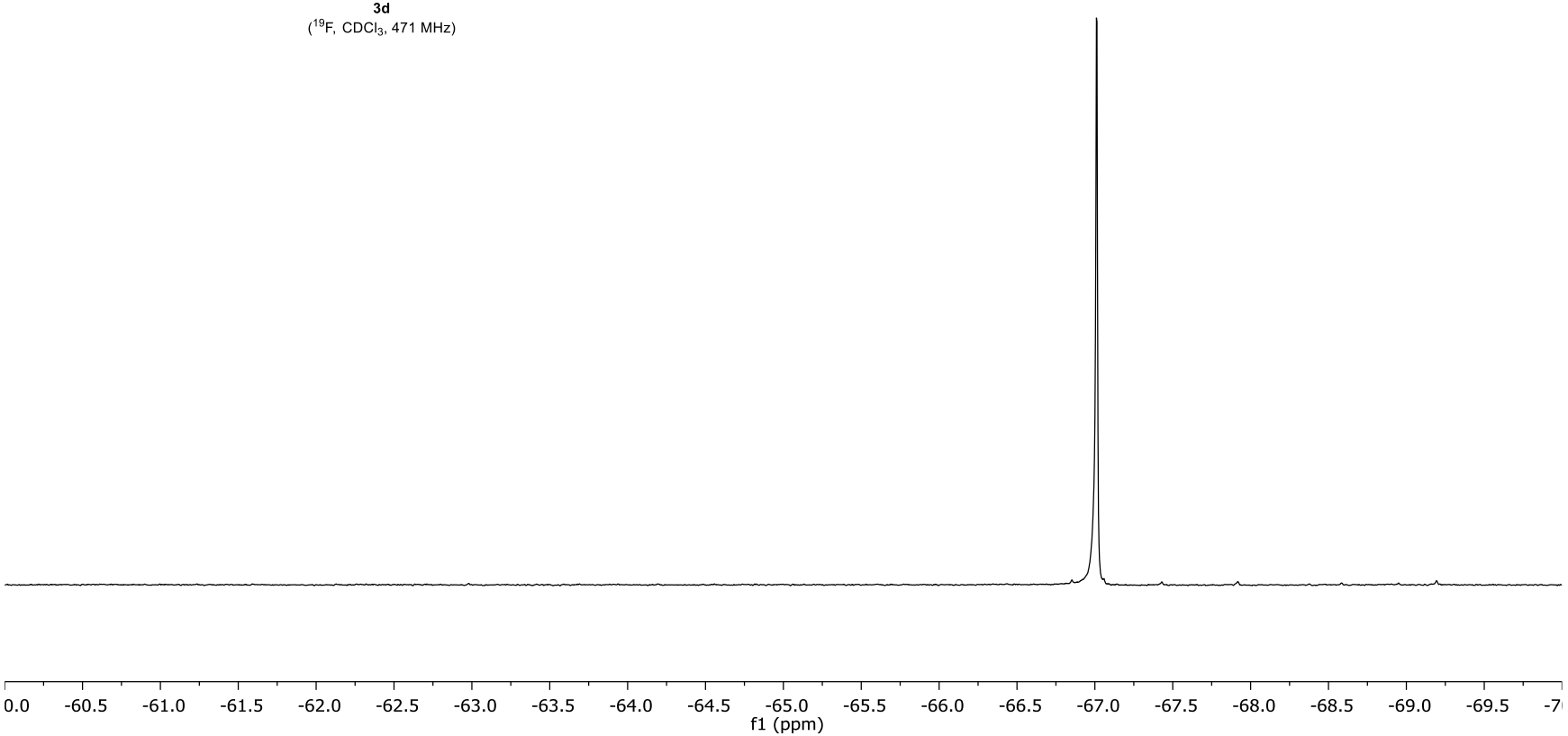

3d
(HSQC, CDCl3)
f2 (ppm)
f1 (ppm)

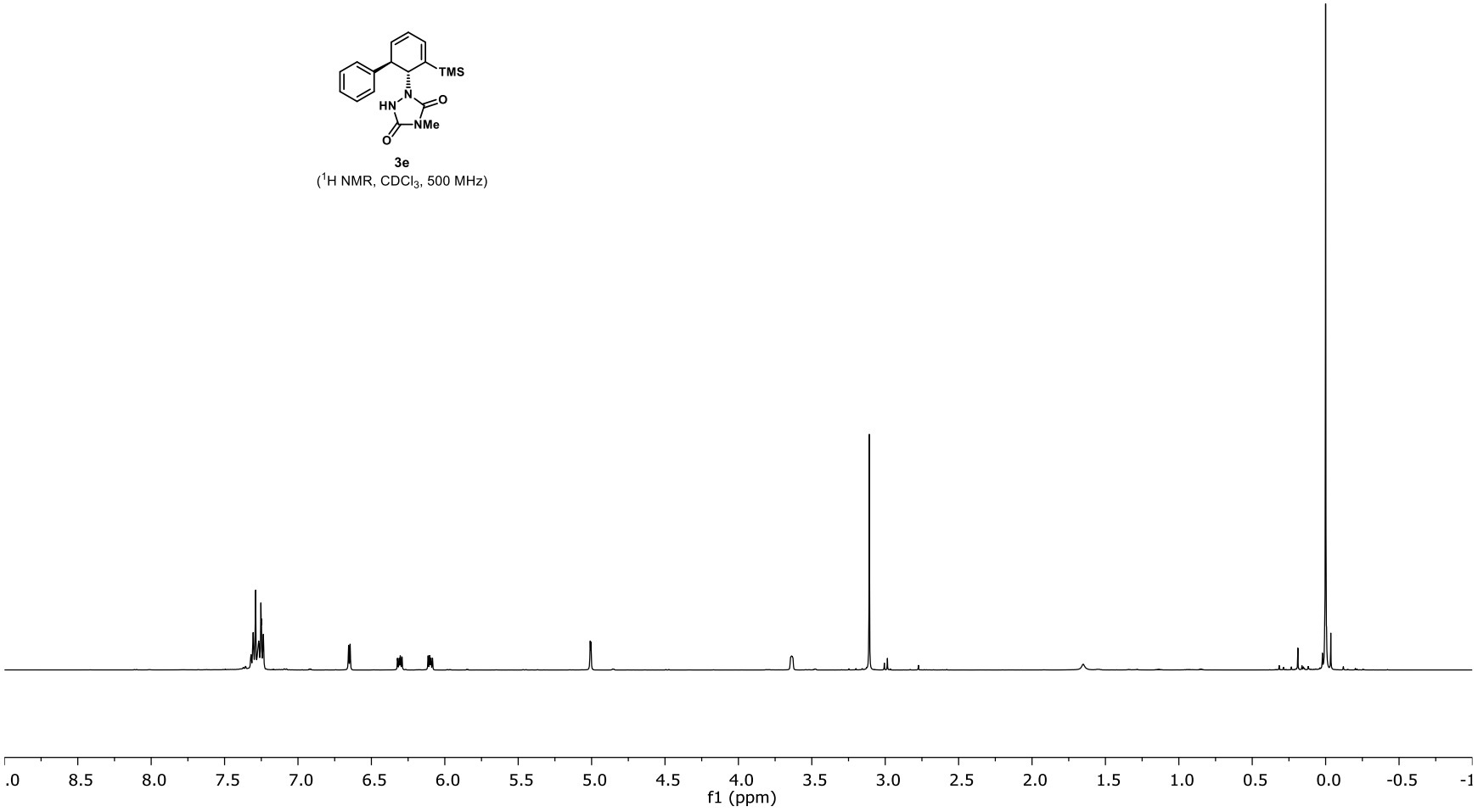

3d
(HMBC, CDCl3)
f2 (ppm)
f1 (ppm)

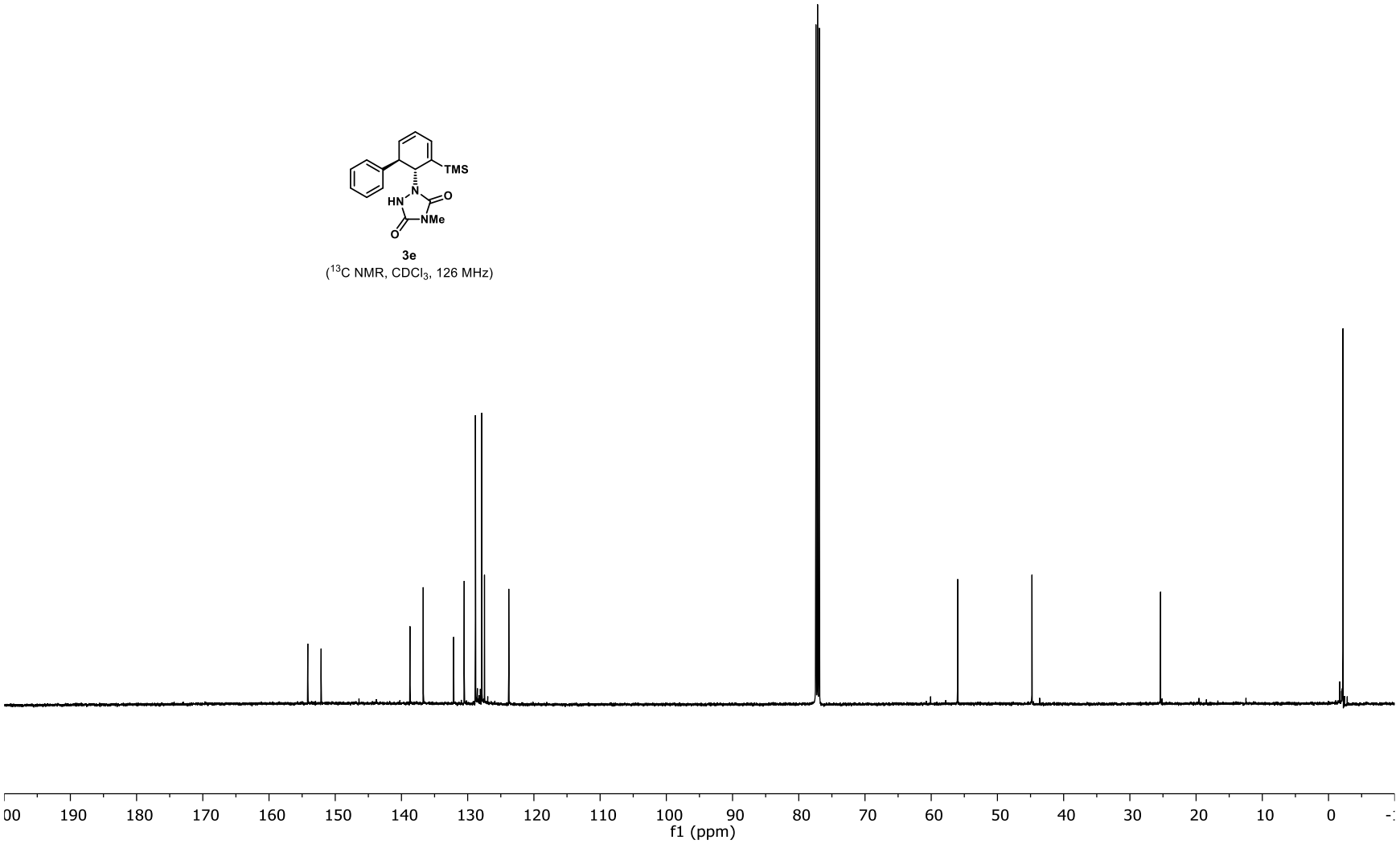


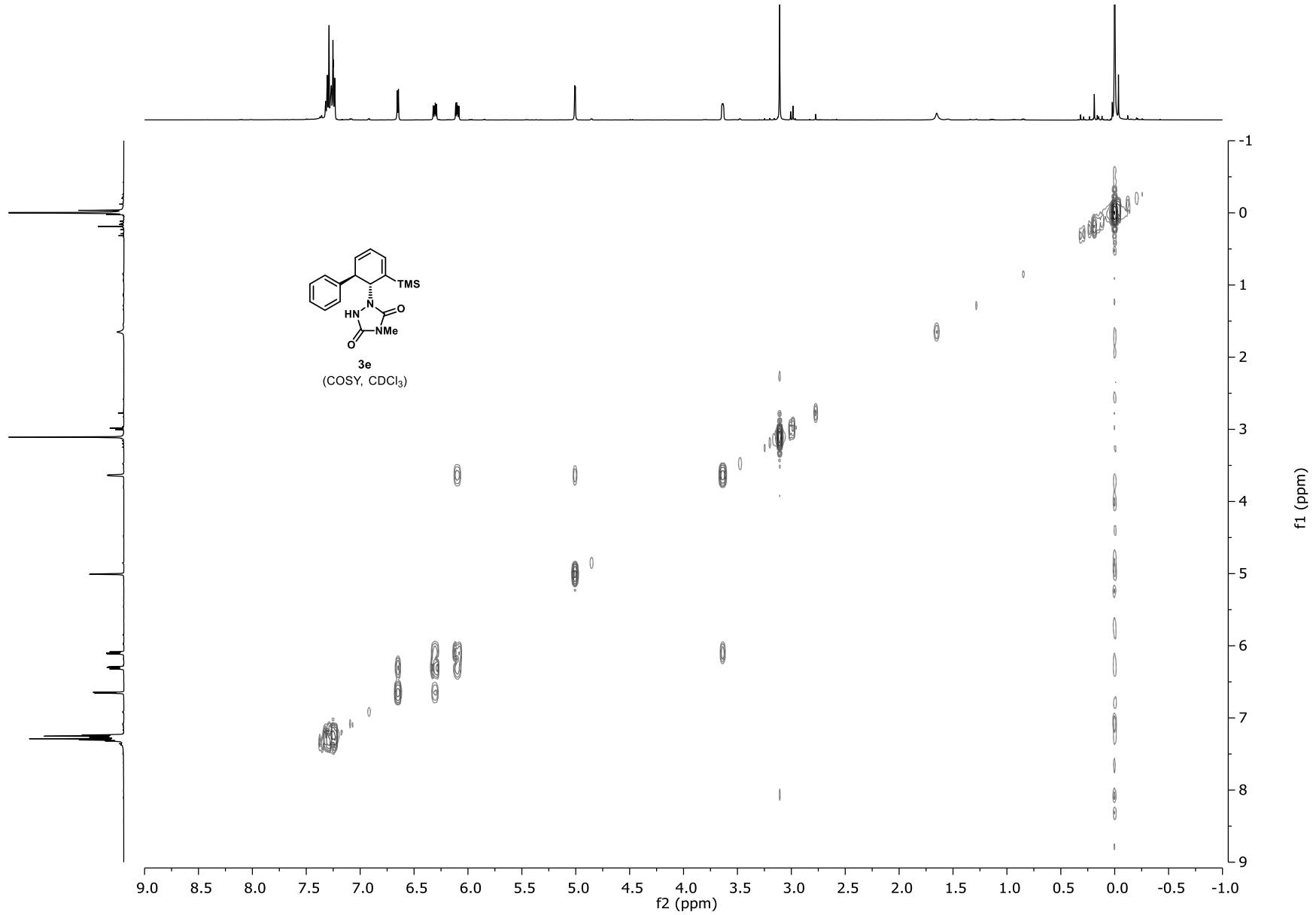
3d

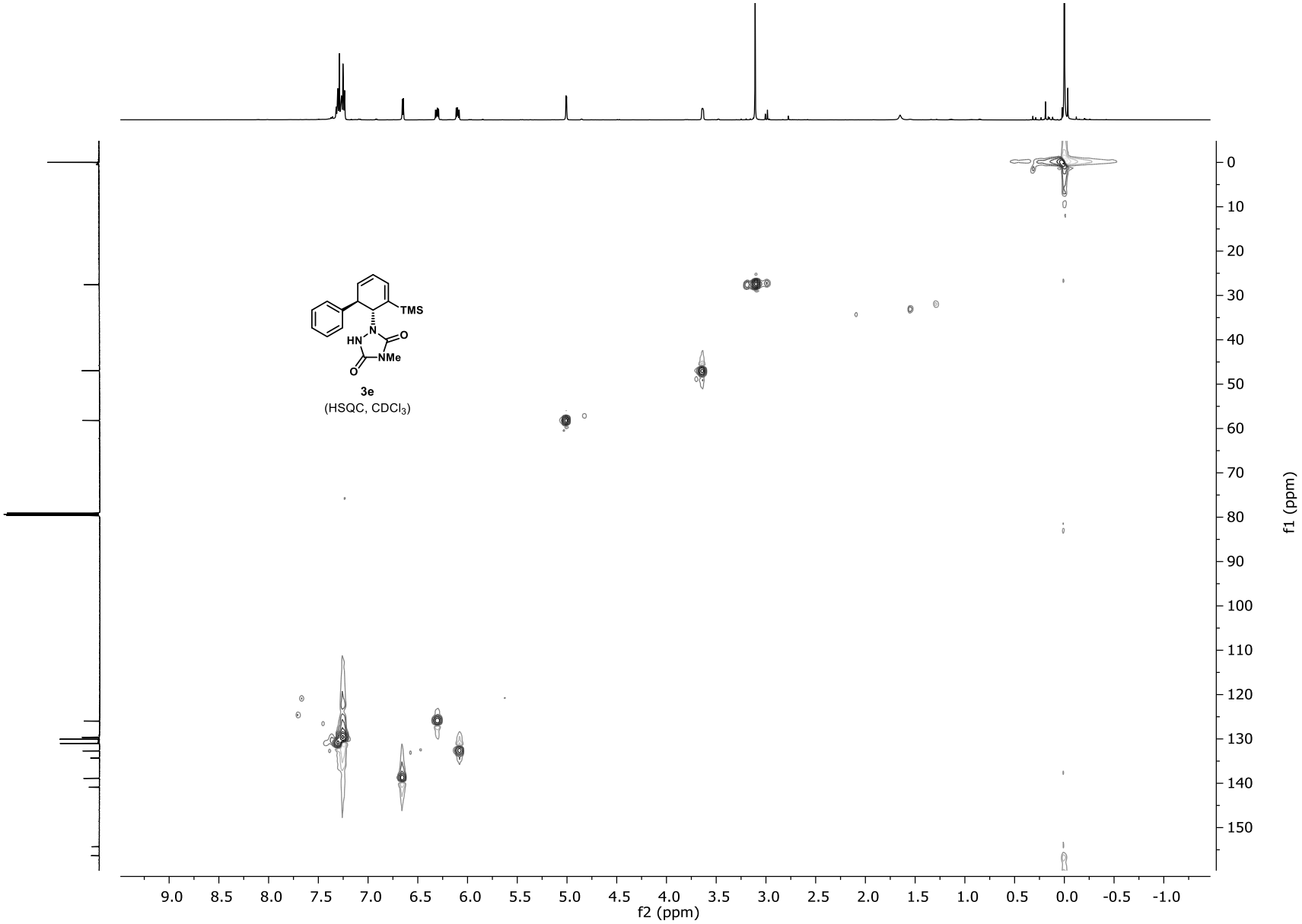
(^{19}F, $CDCl_3$, 471 MHz)

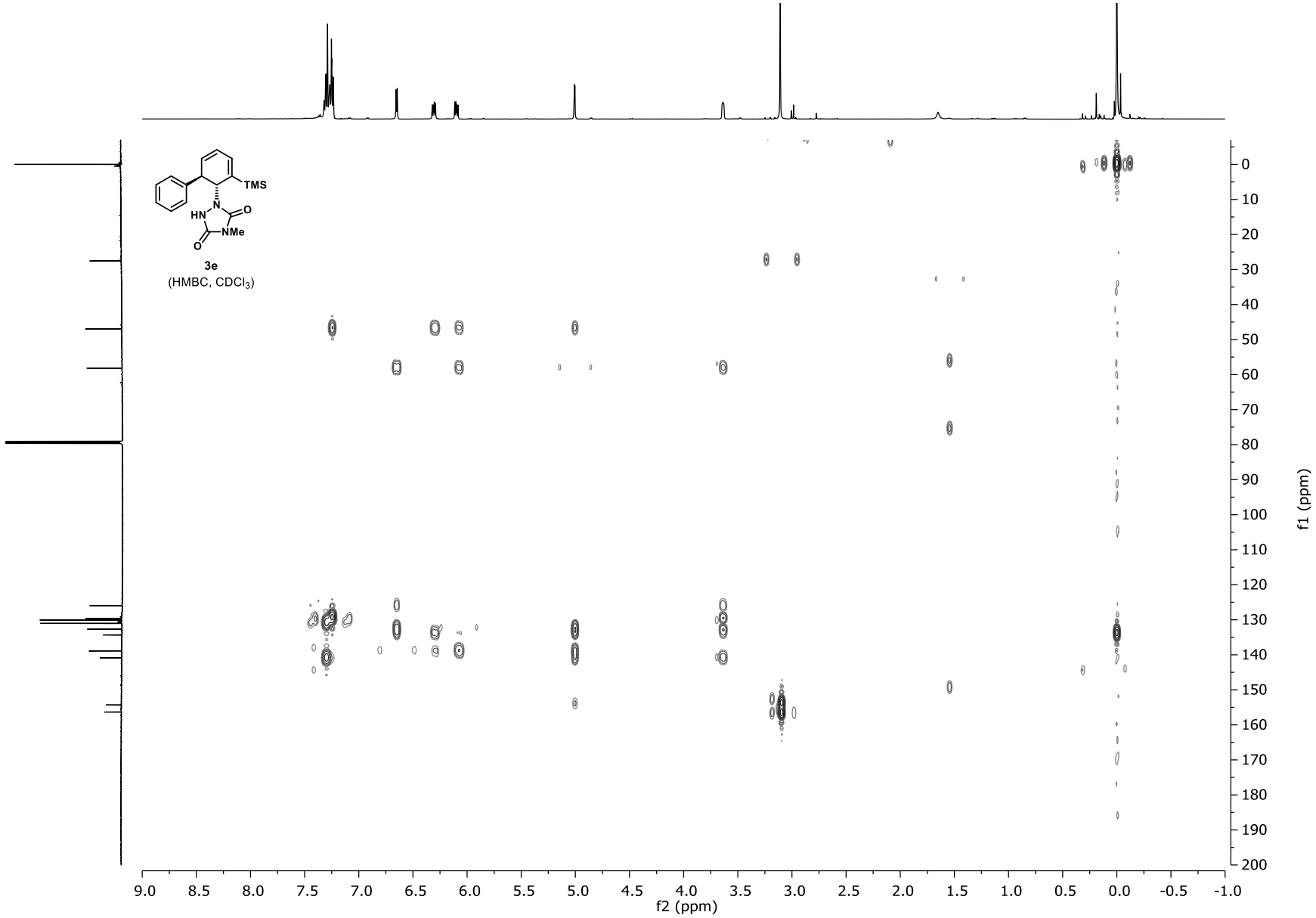


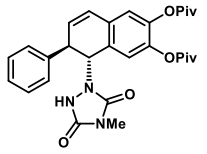

TMS
HN
N
O
NMe
O
3e
(1H NMR, CDCl3, 500 MHz)
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


TMS
HN
N
O
NMe
O
3e
(^{13}C NMR, $CDCl_3$, 126 MHz)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TMS
HN
N
O
NMe
O
3e
(COSY, CDCl3)
f2 (ppm)
f1 (ppm)

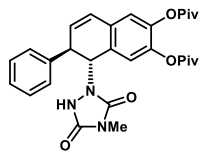

TMS
HN
N
O
NMe
O
3e
(HSQC, CDCl3)
f2 (ppm)
f1 (ppm)


TMS
HN
N
O
NMe
O
3e
(HMBC, CDCl3)
f2 (ppm)
f1 (ppm)



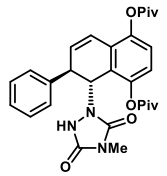
3f

(^{1}H NMR, $CDCl_3$, 500 MHz)



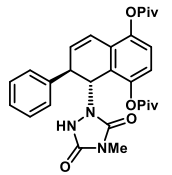
3f

(^{13}C NMR, $CDCl_3$, 126 MHz)



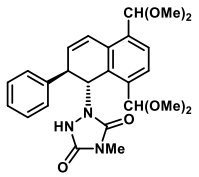
3g

(^{1}H NMR, $CDCl_3$, 500 MHz)



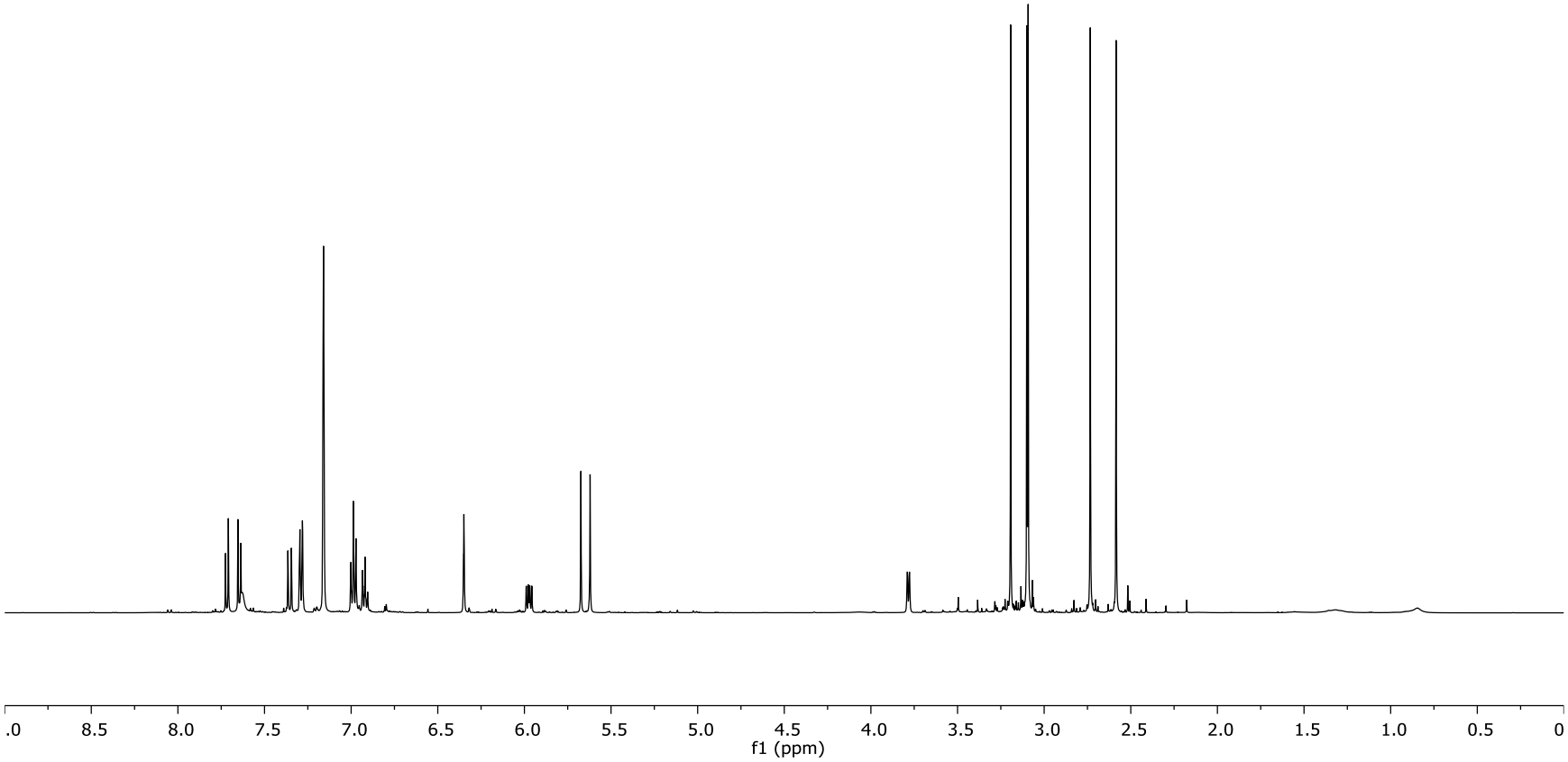
3g

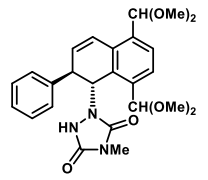
(^{13}C NMR, $CDCl_3$, 126 MHz)



3h

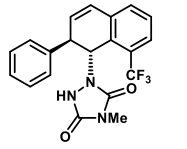
(^{1}H NMR, C_6D_6, 500 MHz)





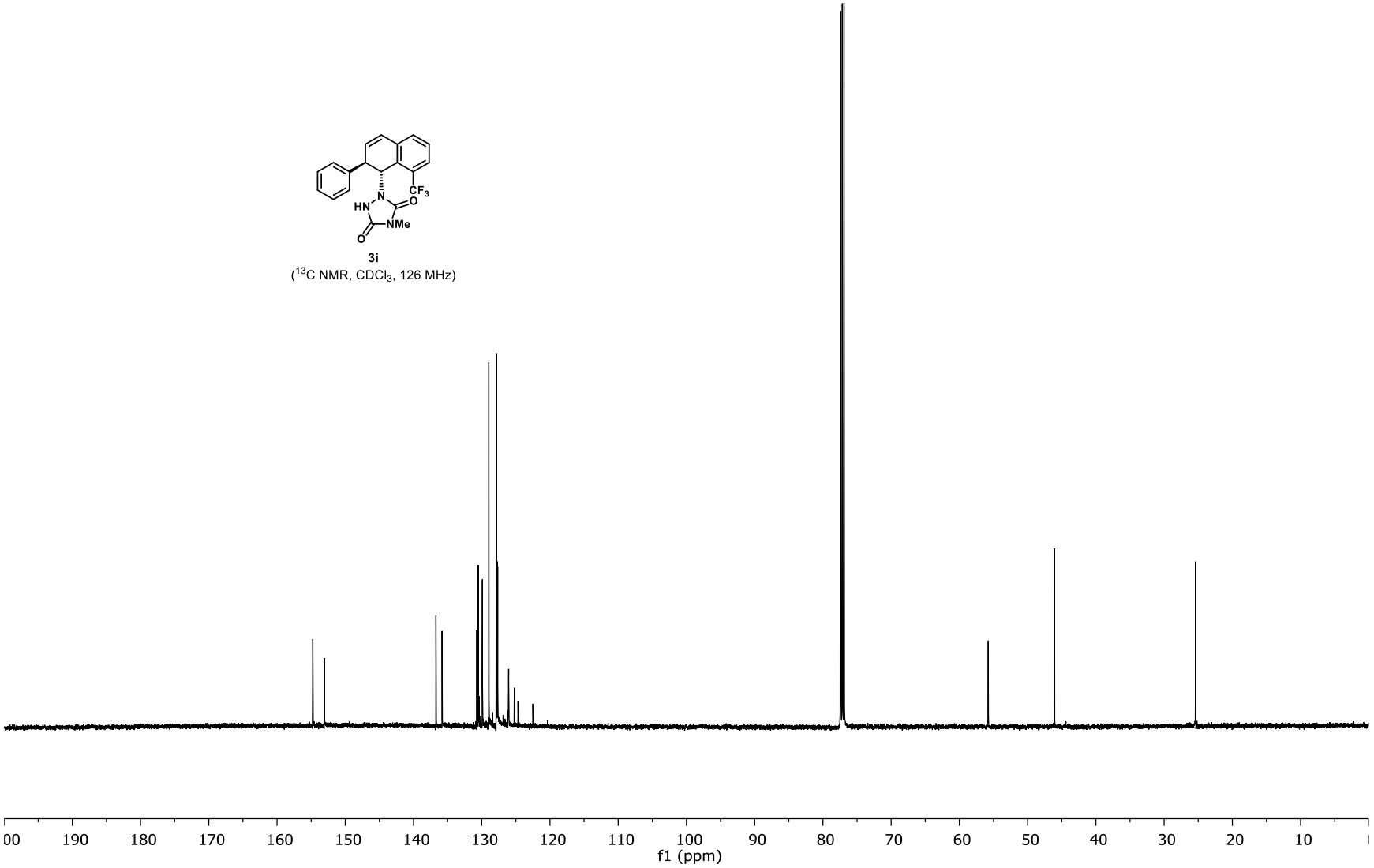
3h

(^{13}C NMR, C_6D_6, 126 MHz)



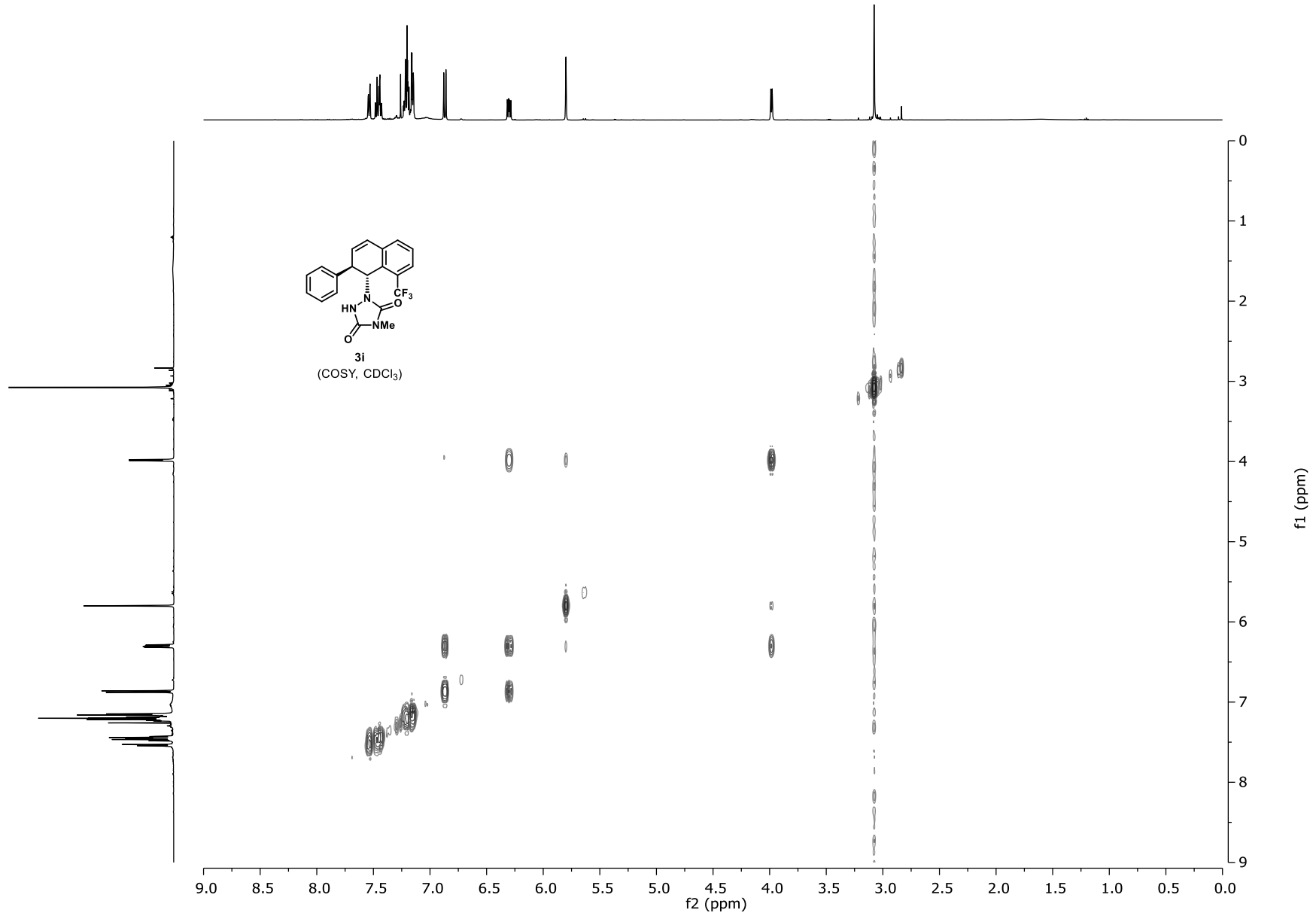
3i

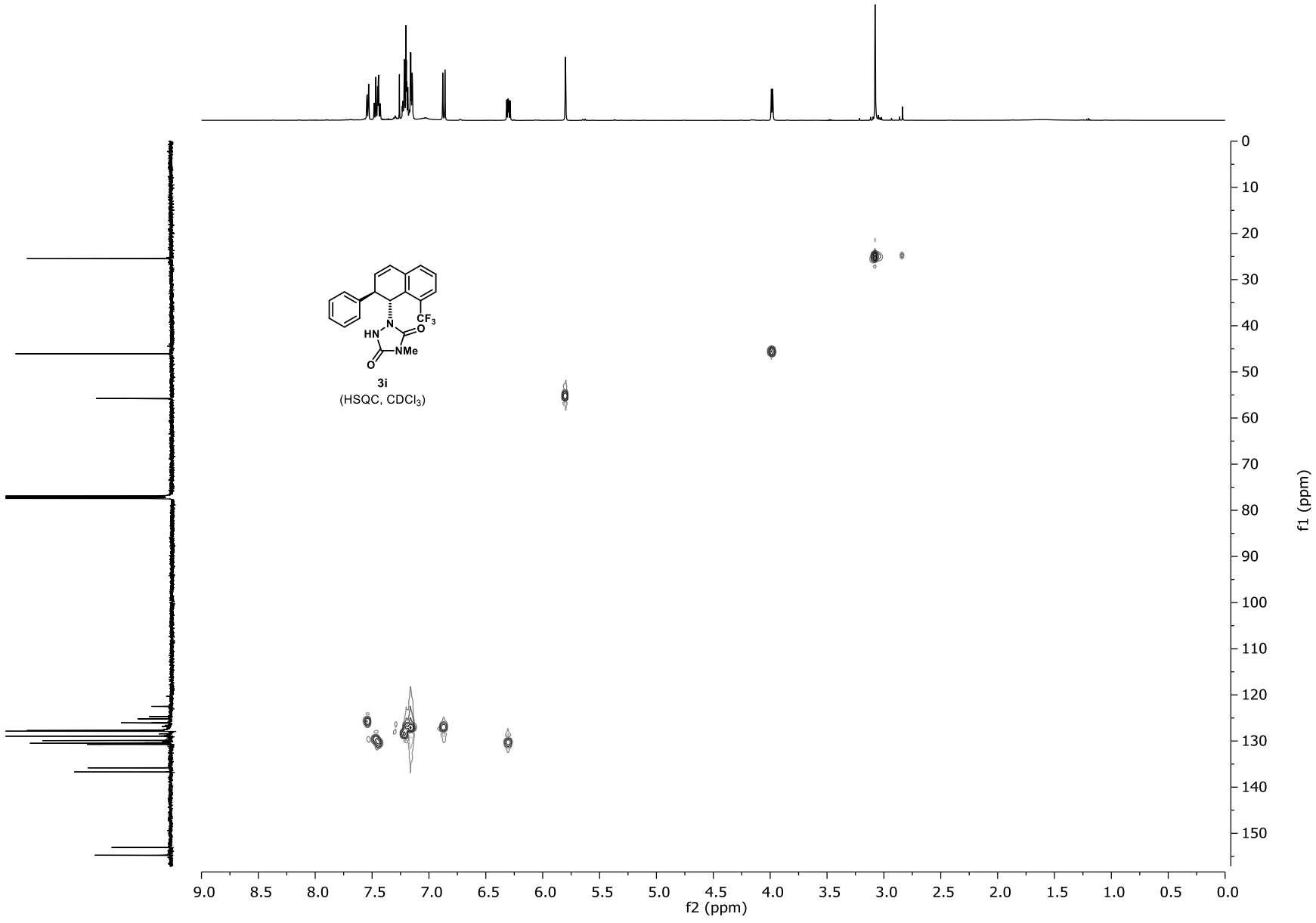
(^{1}H NMR, $CDCl_3$, 500 MHz)

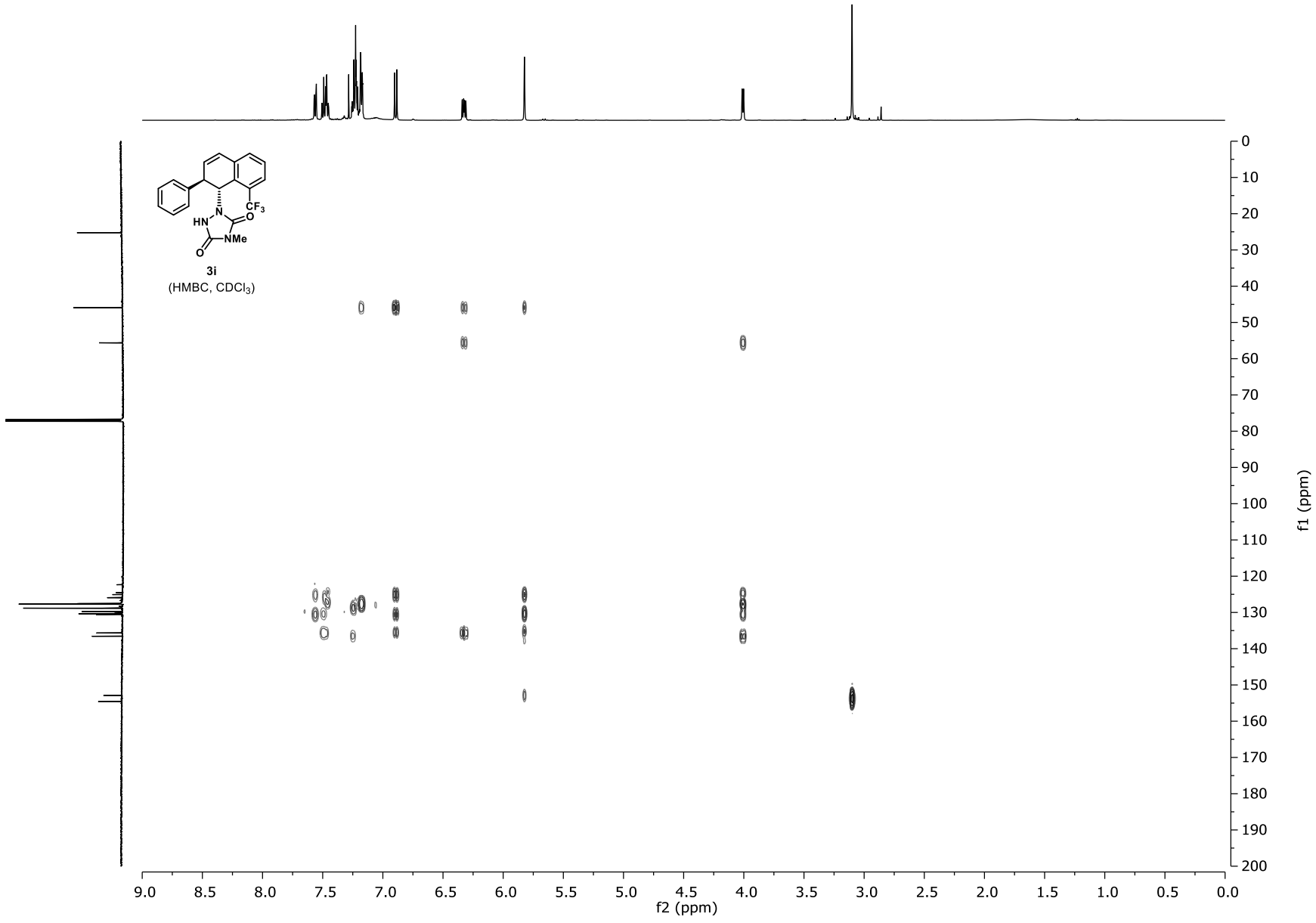


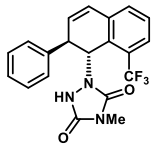
3i

(^{13}C NMR, $CDCl_3$, 126 MHz)


3i
(COSY, CDCl3)
f2 (ppm)
f1 (ppm)

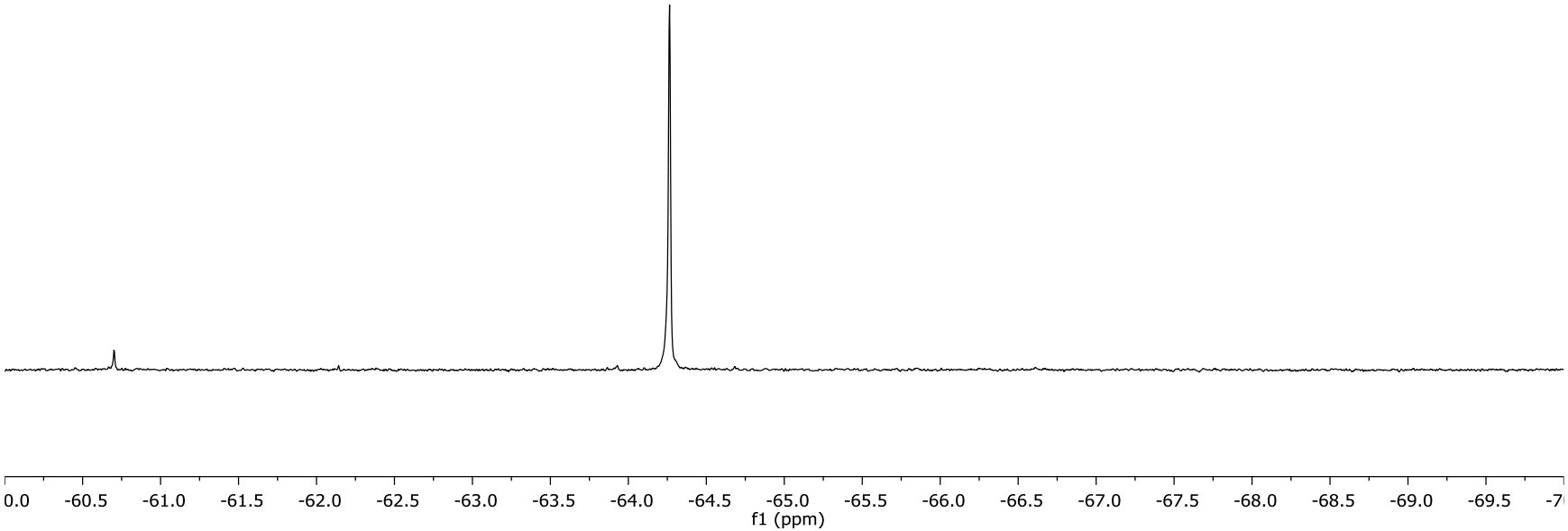

3i
(HSQC, CDCl3)
f2 (ppm)
f1 (ppm)

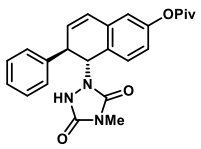

3i
(HMBC, CDCl3)
f2 (ppm)
f1 (ppm)



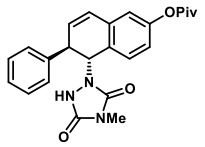
3i

(^{19}F NMR, $CDCl_3$, 471 MHz)



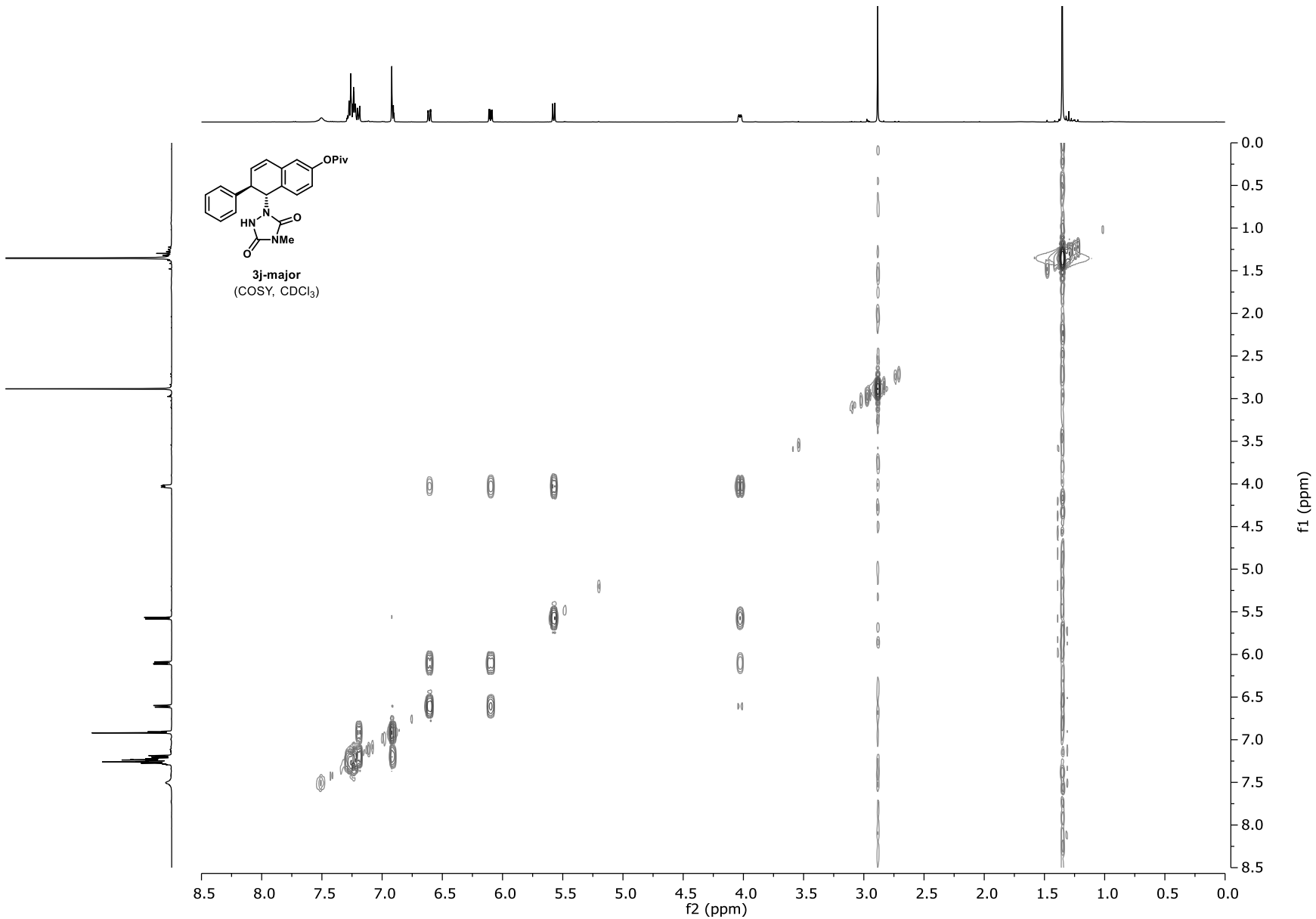


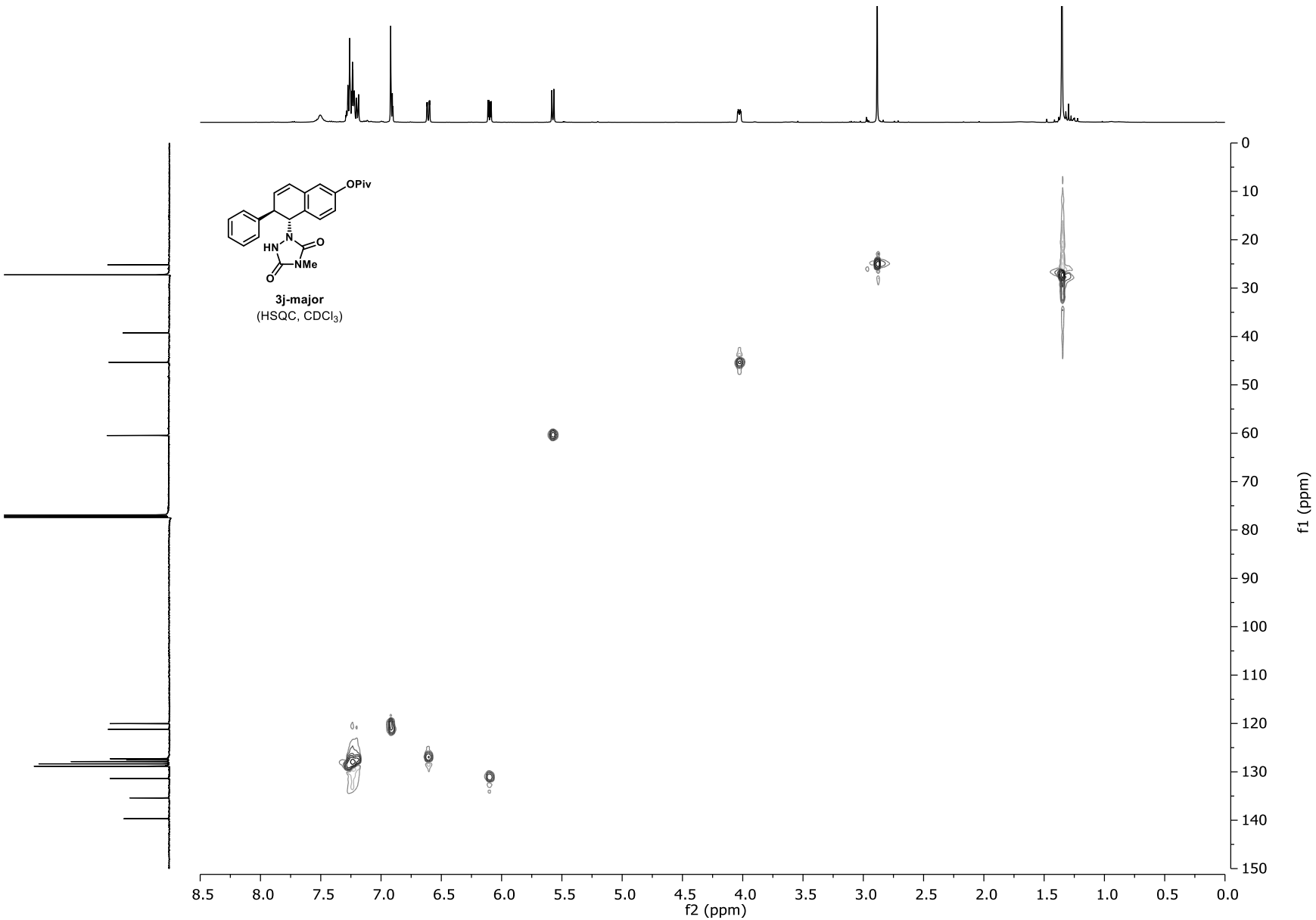
3j-major
(^{1}H NMR, $CDCl_3$, 500 MHz)

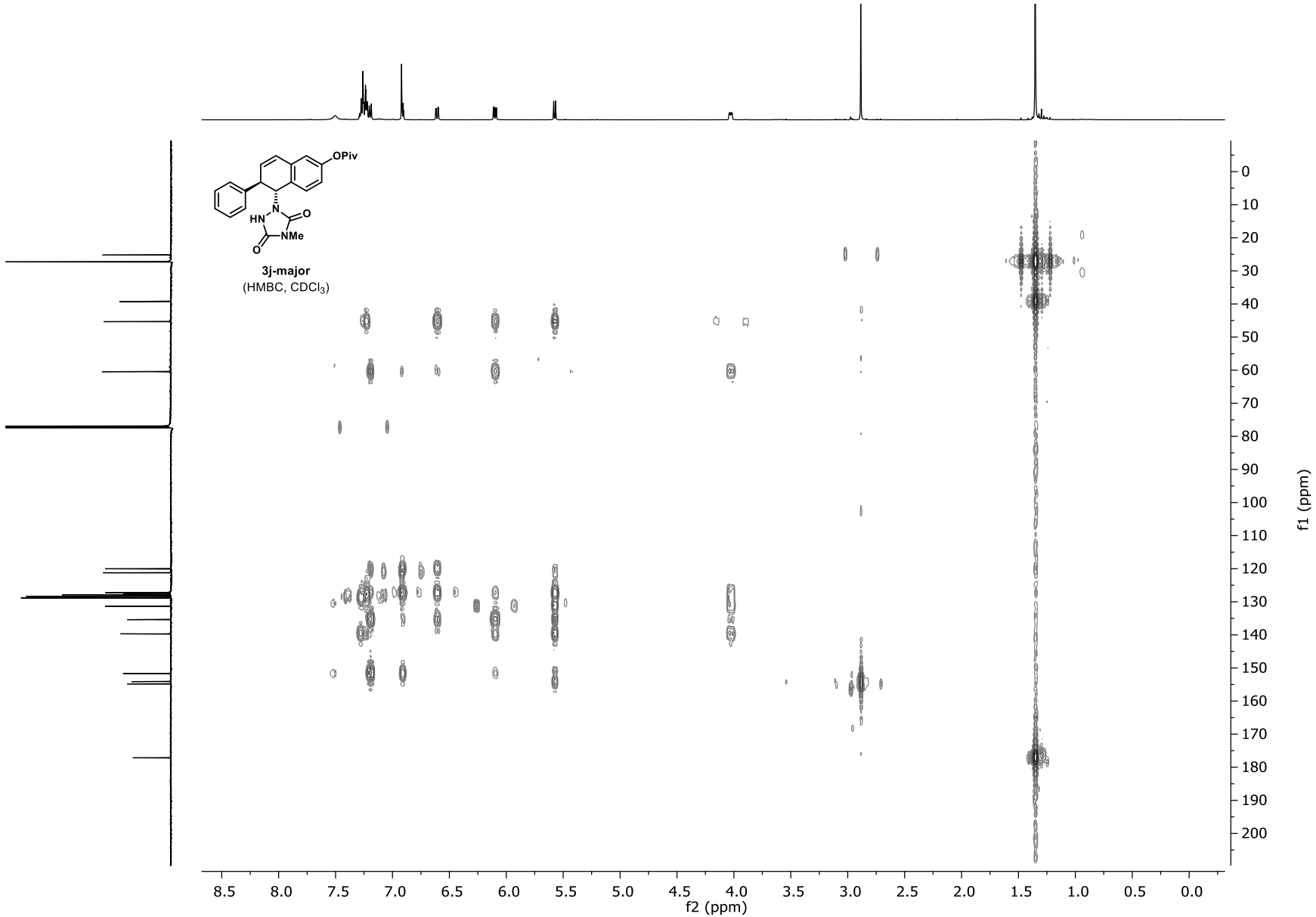


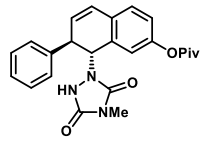
3j-major

(^{13}C NMR, $CDCl_3$, 126 MHz)

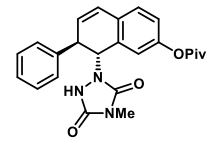

OPiv
HN
N
O
NMe
O
3j-major
(COSY, CDCl3)
f2 (ppm)
f1 (ppm)


OPiv
HN
N
O
NMe
O
3j-major
(HSQC, CDCl3)
f2 (ppm)
f1 (ppm)

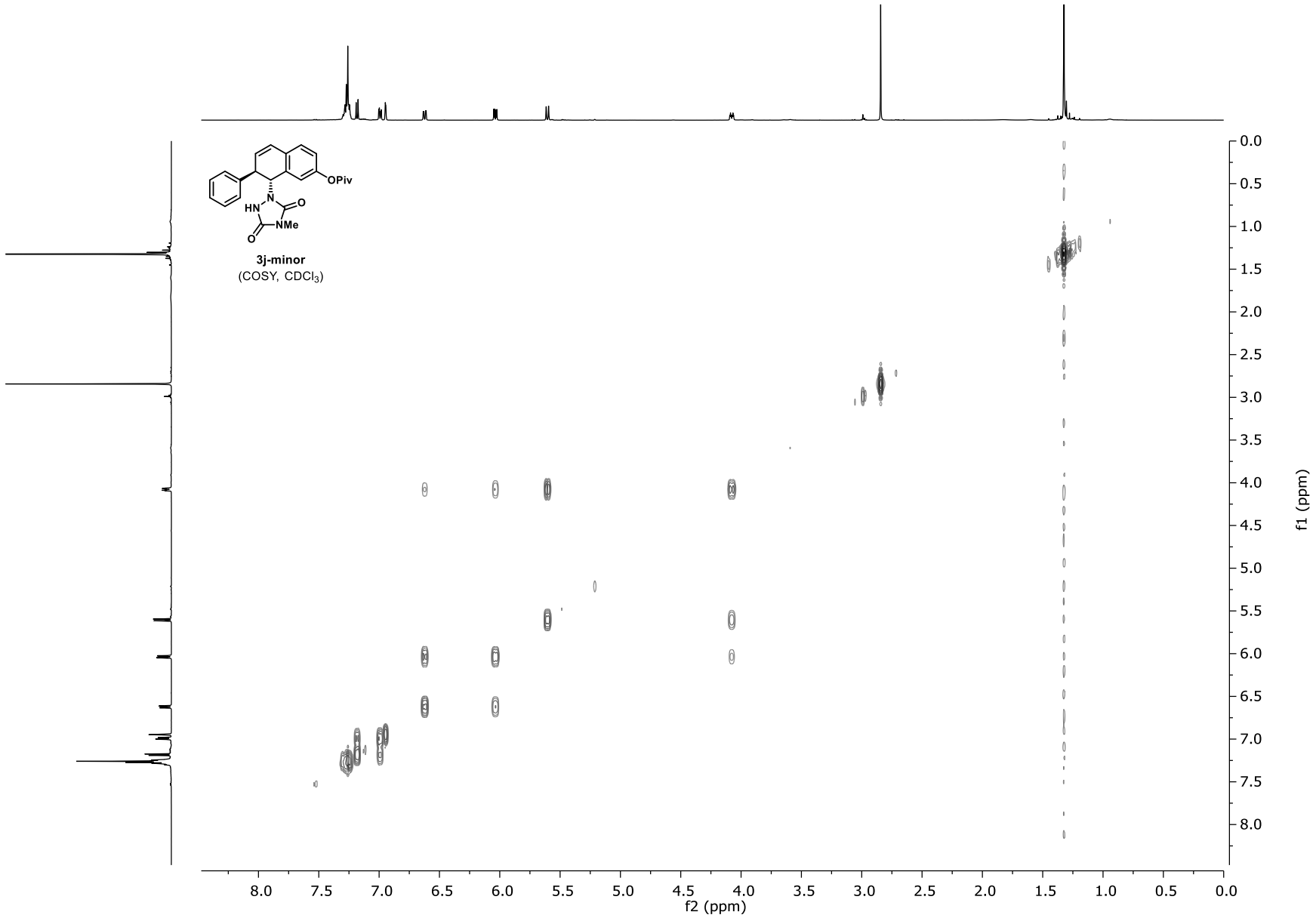

OPiv
HN
N
O
NMe
O
3j-major
(HMBC, CDCl3)
f2 (ppm)
f1 (ppm)

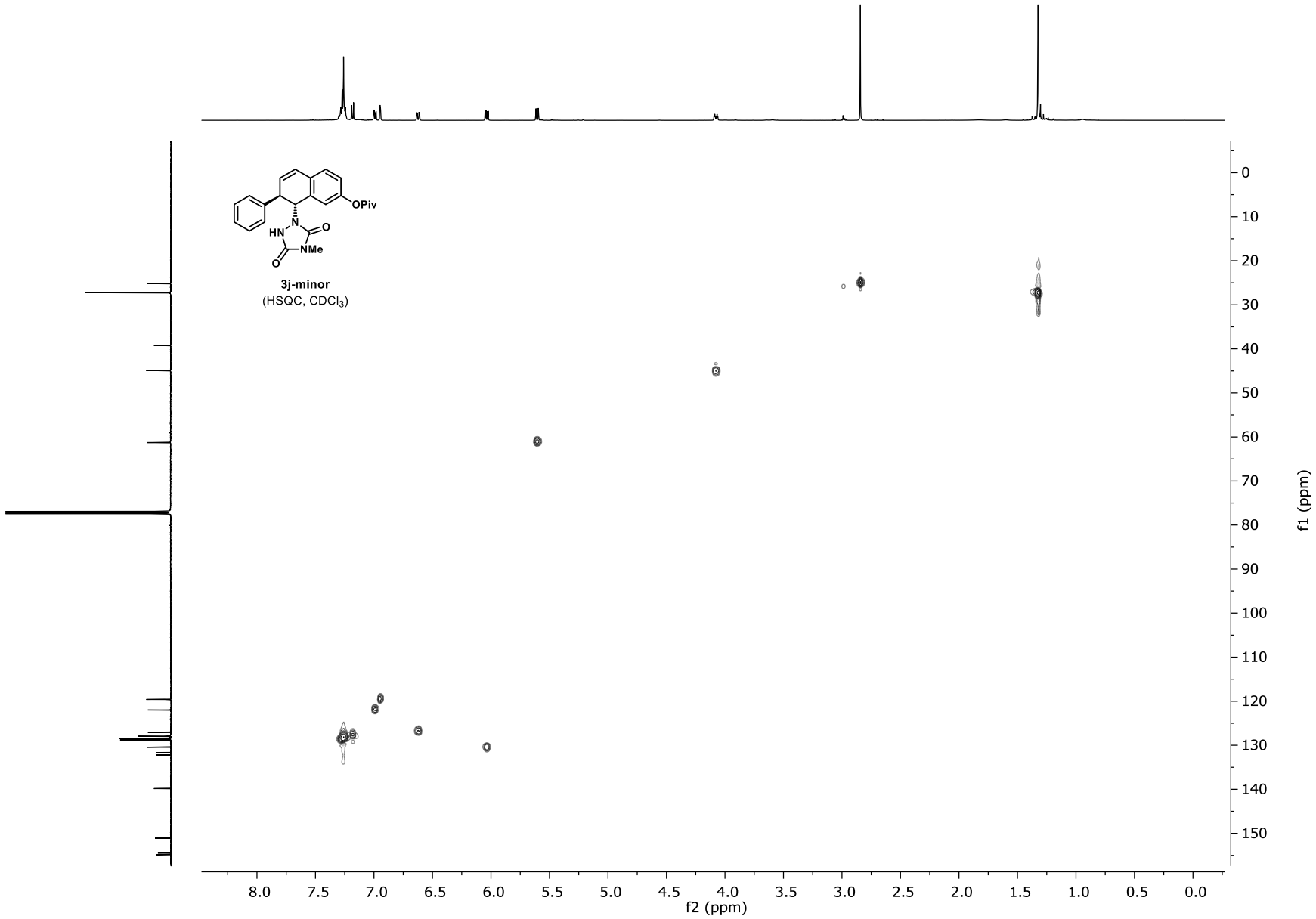


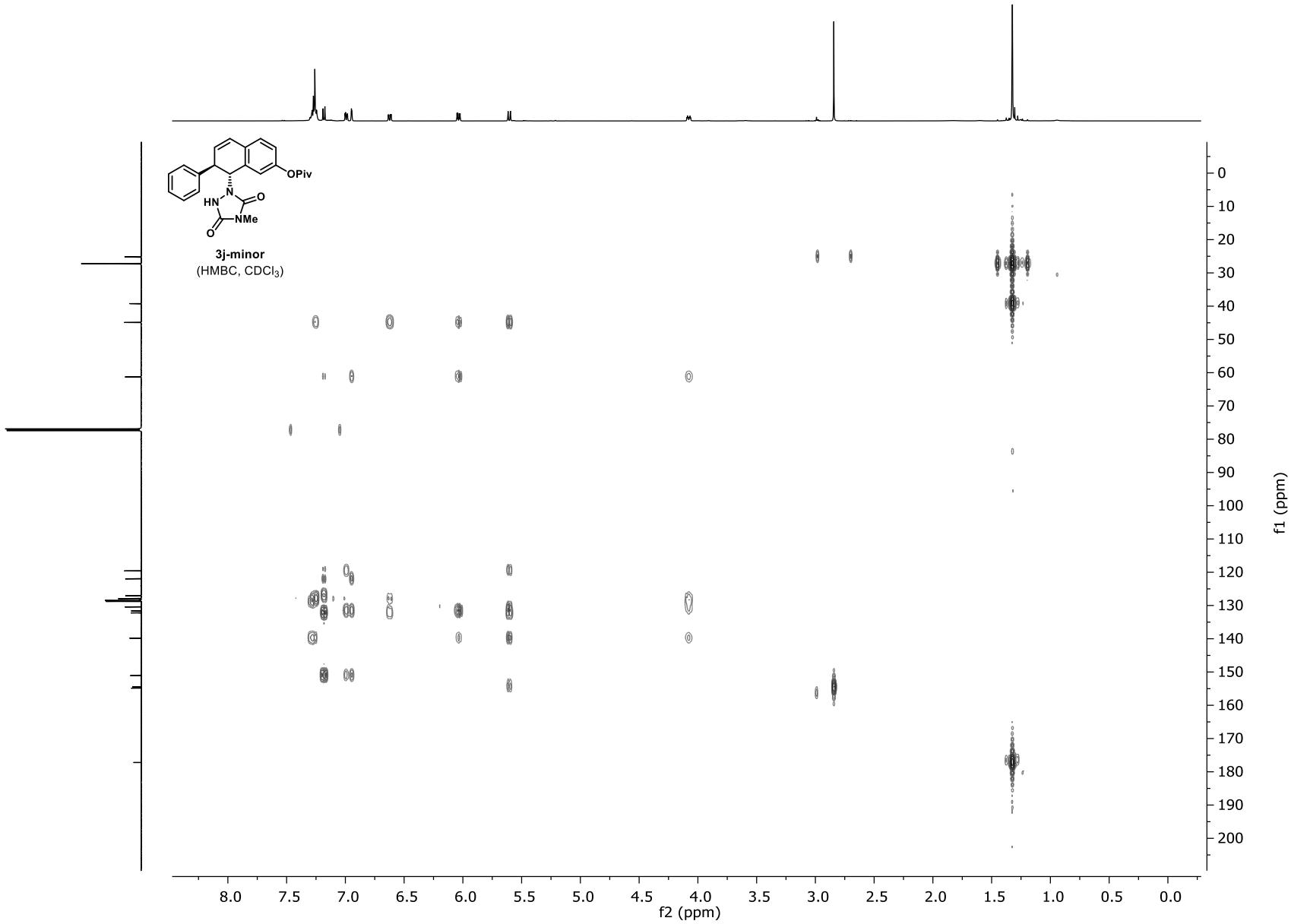
3j-minor
(^{1}H NMR, $CDCl_3$, 500 MHz)

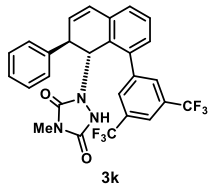


3j-minor
(^{13}C NMR, $CDCl_3$, 126 MHz)


OPiv
HN
N
O
NMe
O
3j-minor
(COSY, CDCl3)
f2 (ppm)
f1 (ppm)

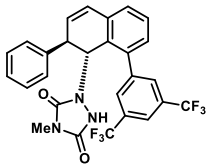

OPiv
HN
N
O
NMe
O
3j-minor
(HSQC, CDCl3)
f2 (ppm)
f1 (ppm)


OPiv
HN
N
O
NMe
O
3j-minor
(HMBC, CDCl3)
f2 (ppm)
f1 (ppm)



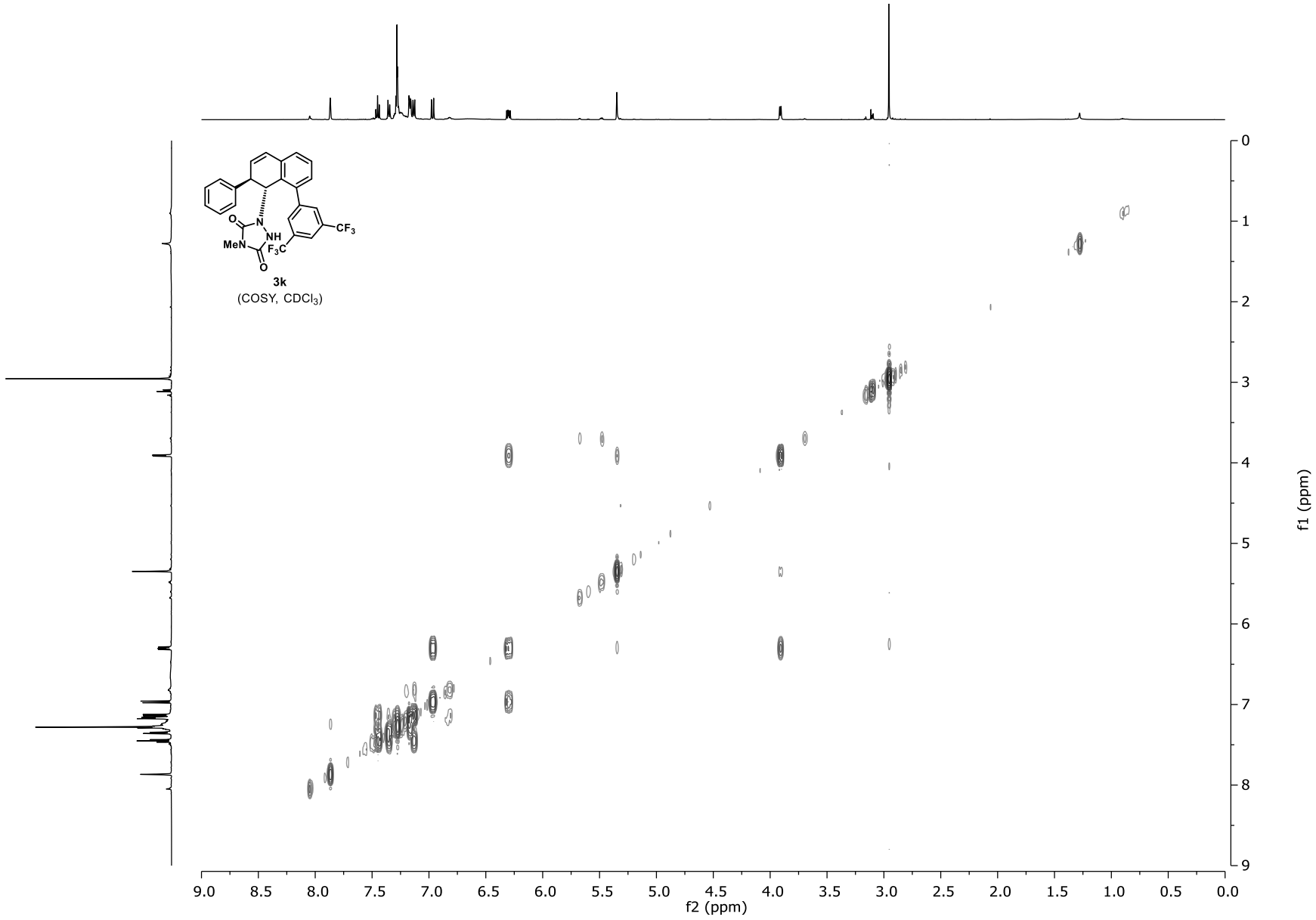
3k

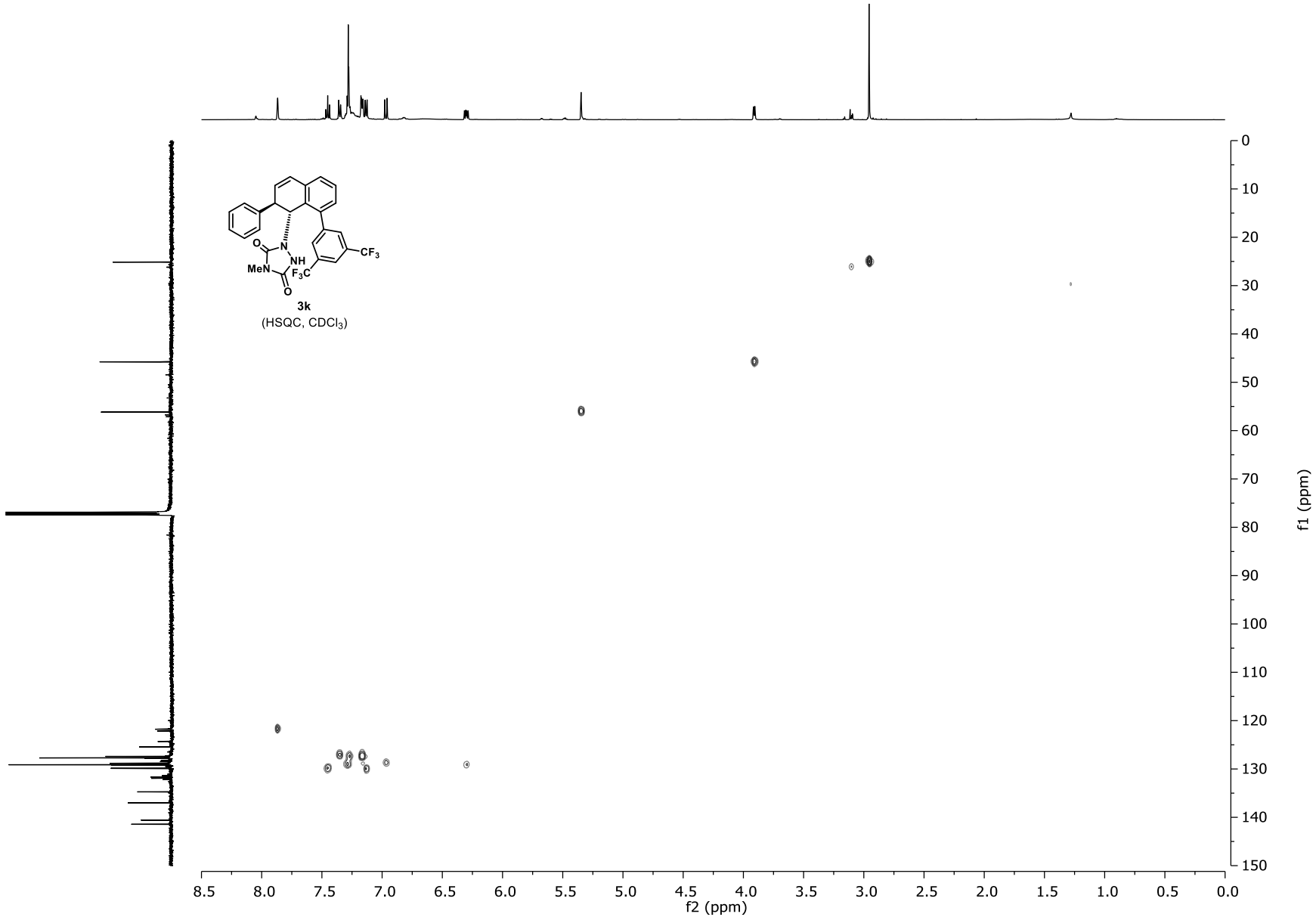
(^{1}H NMR, $CDCl_3$, 500 MHz)

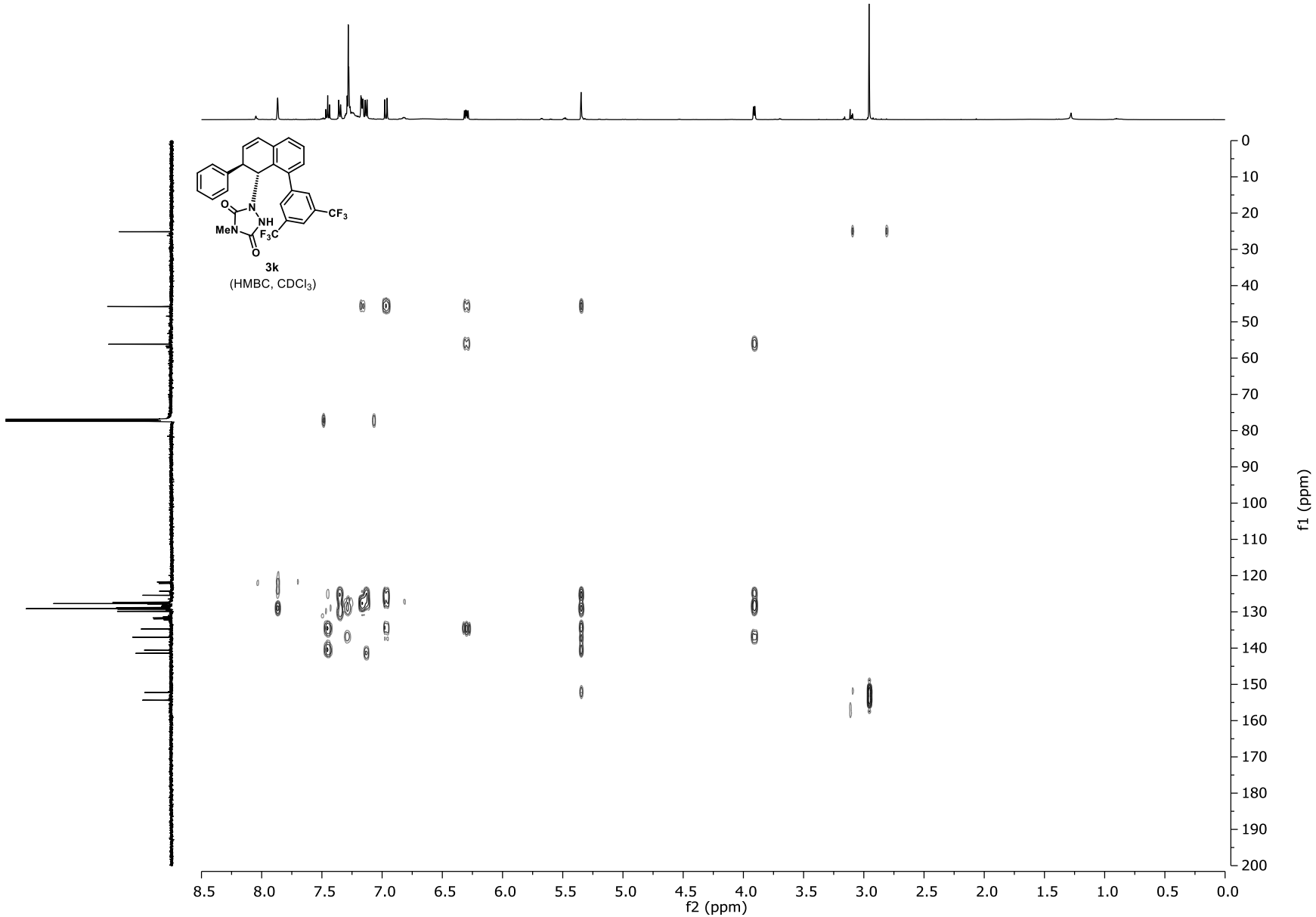


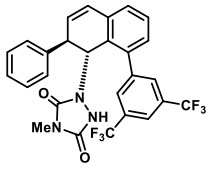
3k

(^{13}C NMR, $CDCl_3$, 126 MHz)


3k
(COSY, CDCl3)
f2 (ppm)
f1 (ppm)

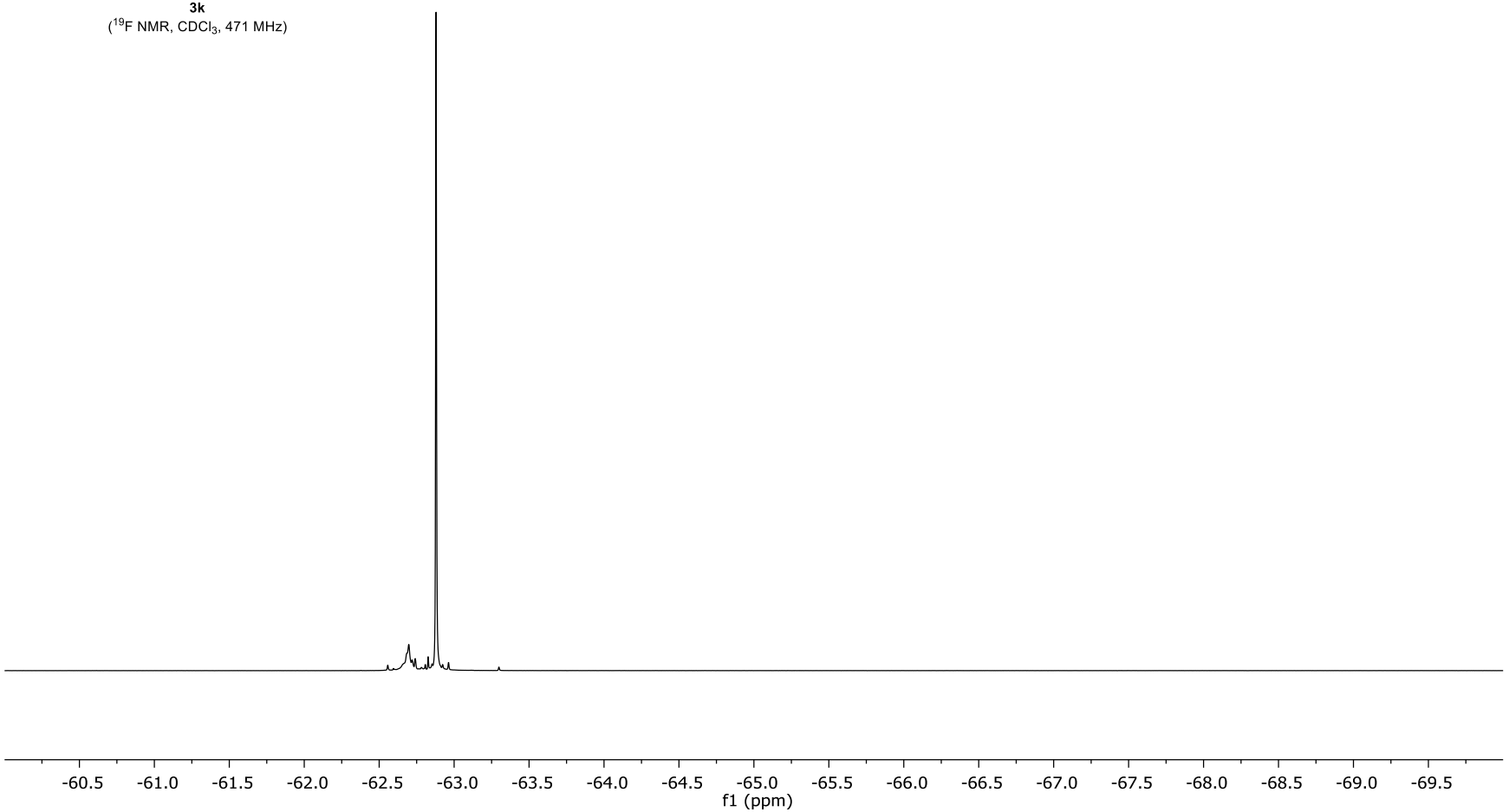

3k
(HSQC, CDCl3)
f2 (ppm)
f1 (ppm)

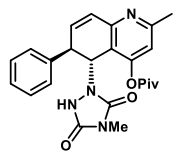

3k
(HMBC, CDCl3)
f2 (ppm)
f1 (ppm)



3k

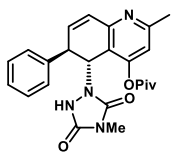
(^{19}F NMR, $CDCl_3$, 471 MHz)





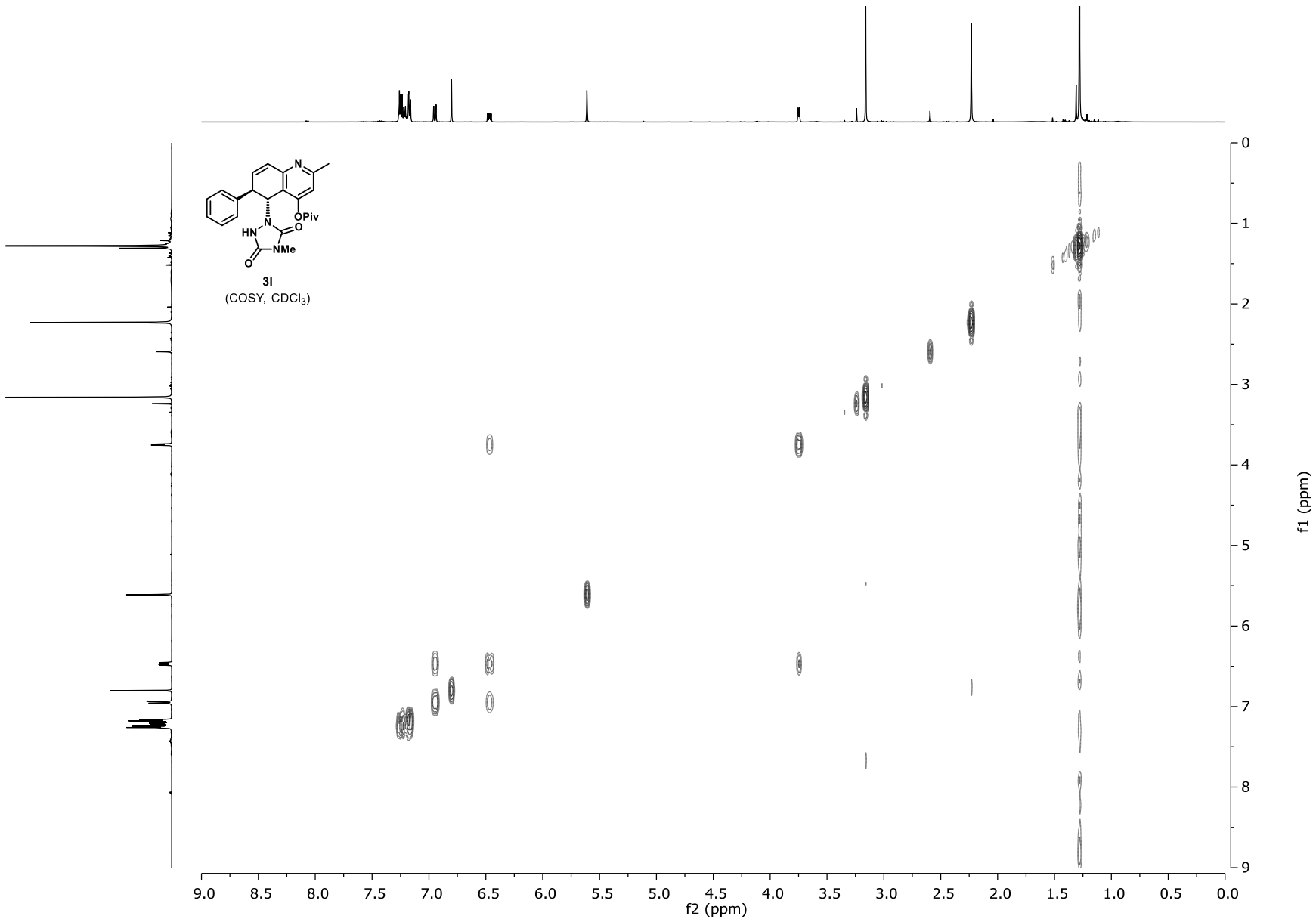
3l

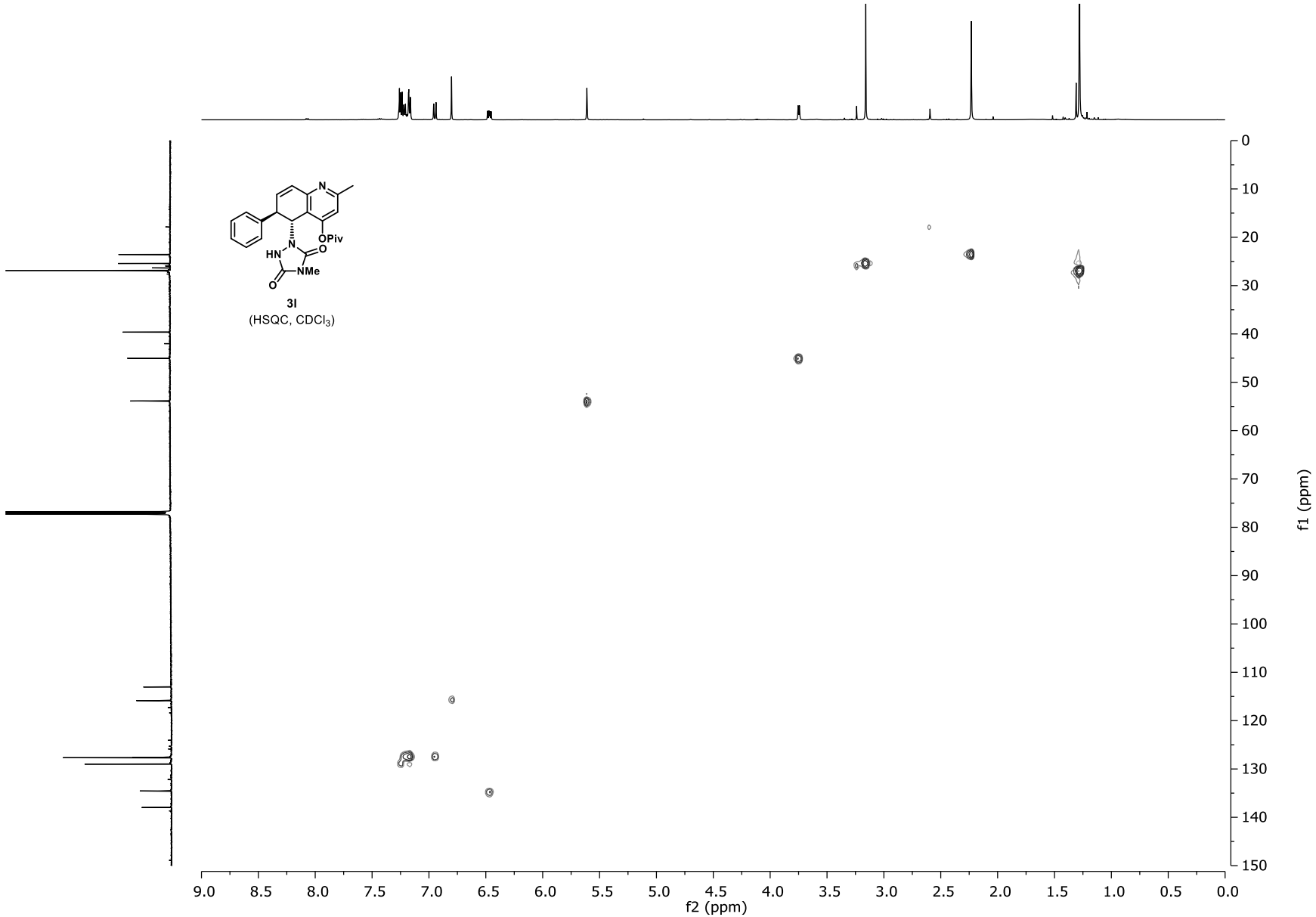
(^{1}H NMR, $CDCl_3$, 500 MHz)

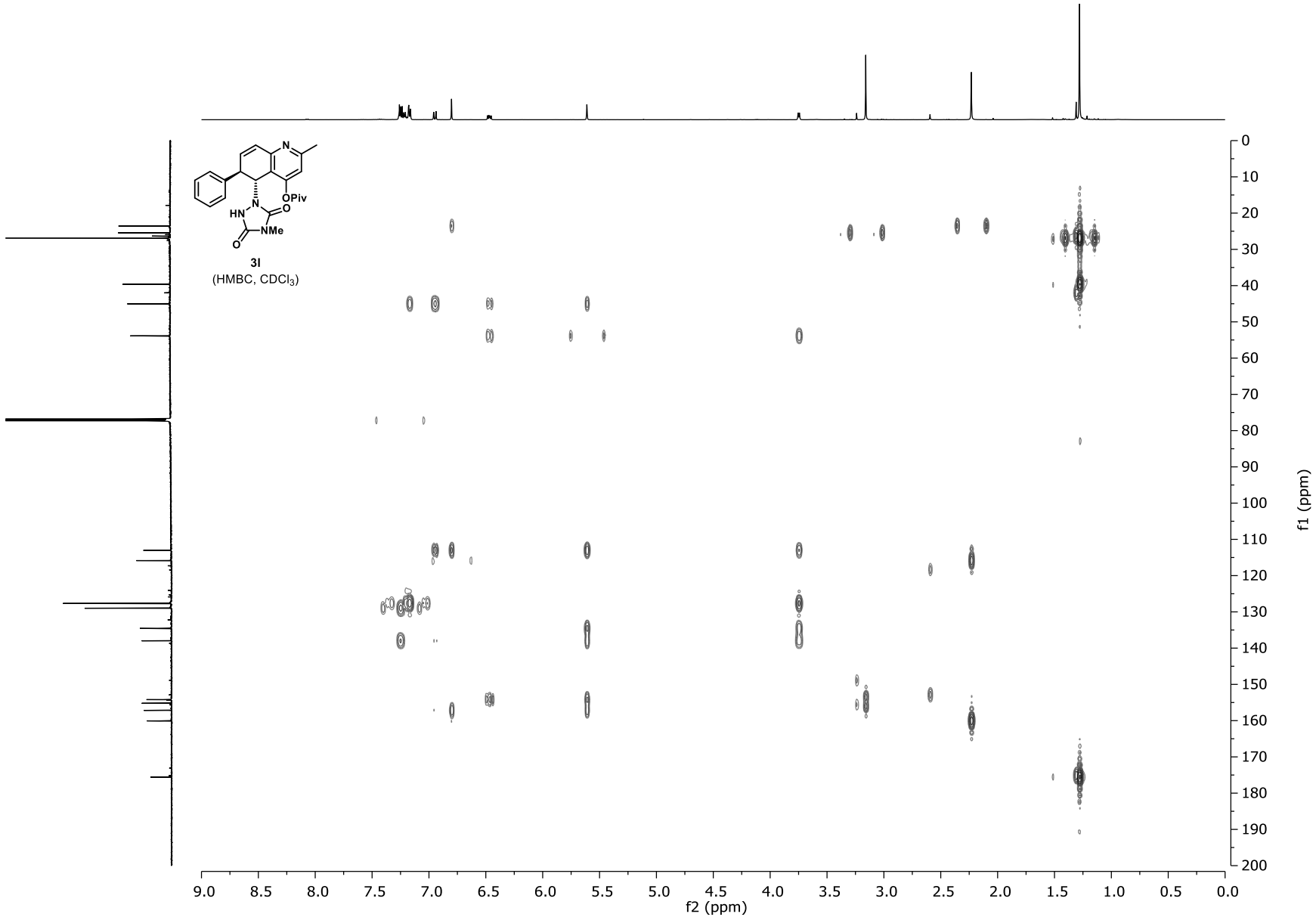


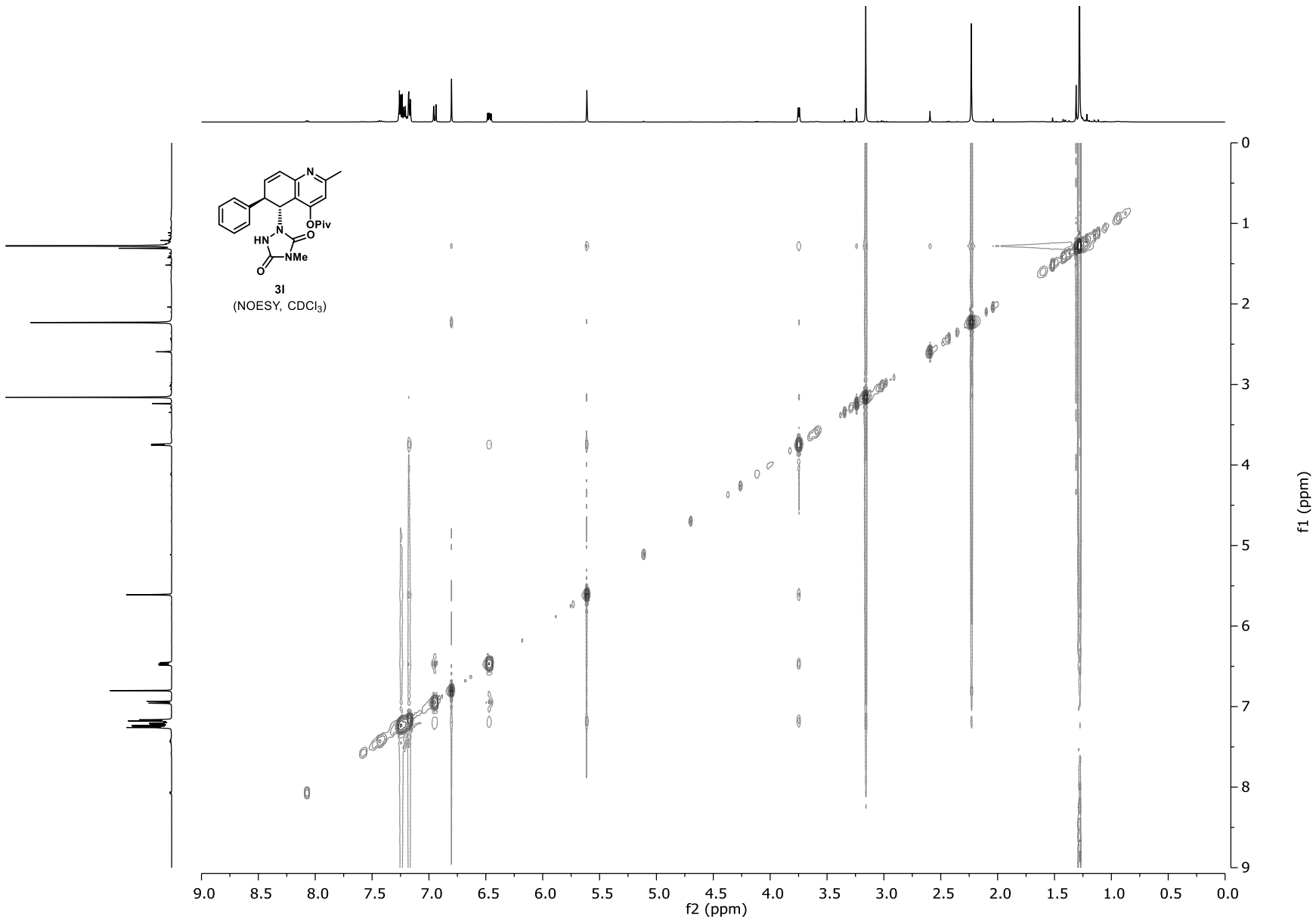
3l

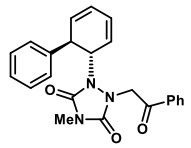
(^{13}C NMR, $CDCl_3$, 126 MHz)


OPiv
HN
N
O
NMe
O
3l
(COSY, CDCl3)
f2 (ppm)
f1 (ppm)


OPiv
HN
N
O
NMe
O
3l
(HSQC, CDCl3)
f2 (ppm)
f1 (ppm)

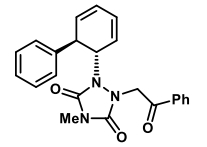

N
OPiv
HN
N
O
O
NMe
O
3l
(HMBC, CDCl3)
f2 (ppm)
f1 (ppm)


OPiv
HN
N
O
NMe
O
3l
(NOESY, CDCl3)
f2 (ppm)
f1 (ppm)



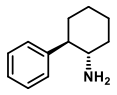
S1

(^{1}H NMR, $CDCl_3$, 500 MHz)



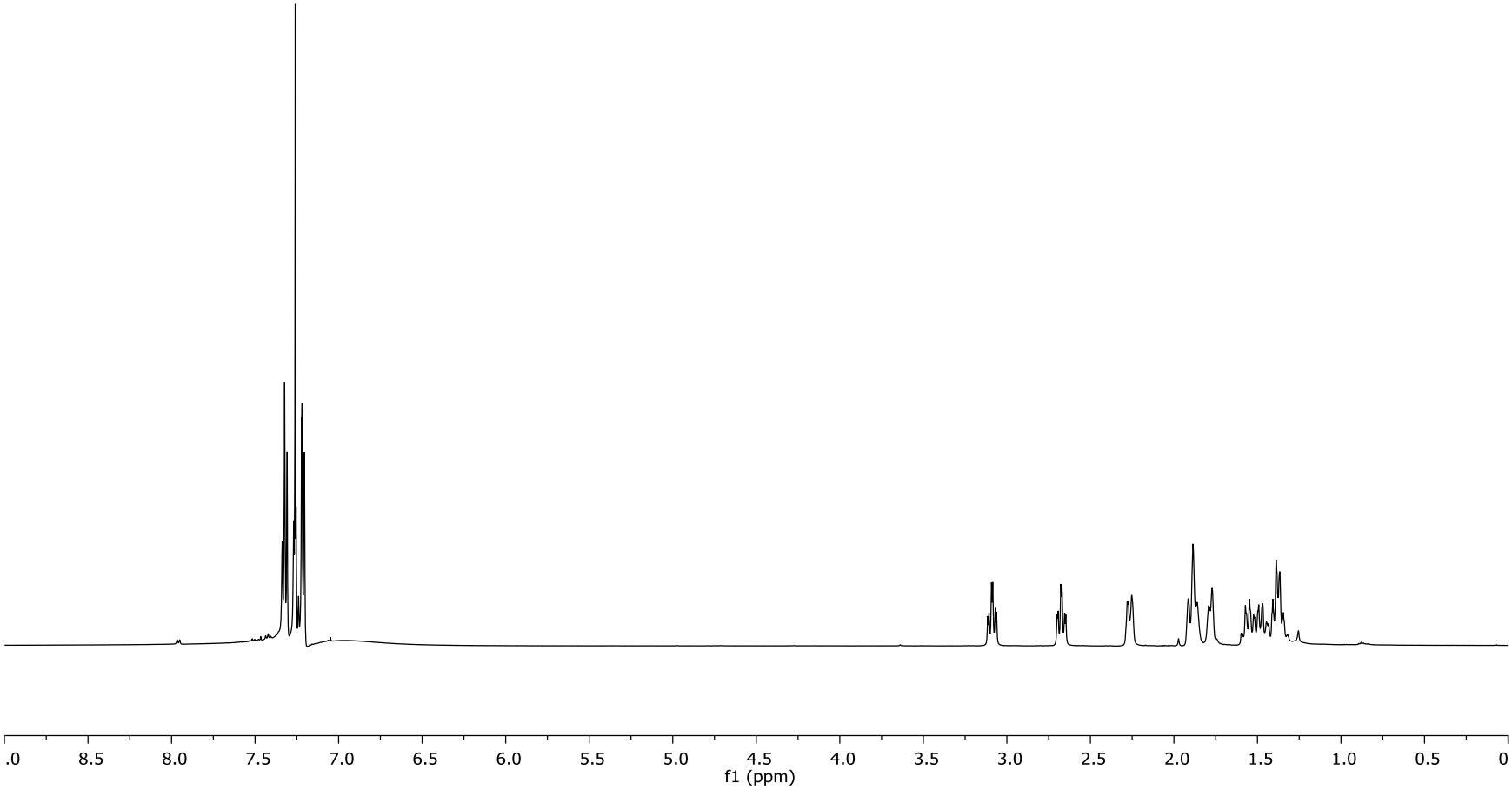
S1

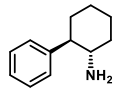
(^{13}C NMR, $CDCl_3$, 126 MHz)



4

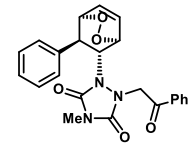
(^{1}H NMR, $CDCl_3$, 500 MHz)





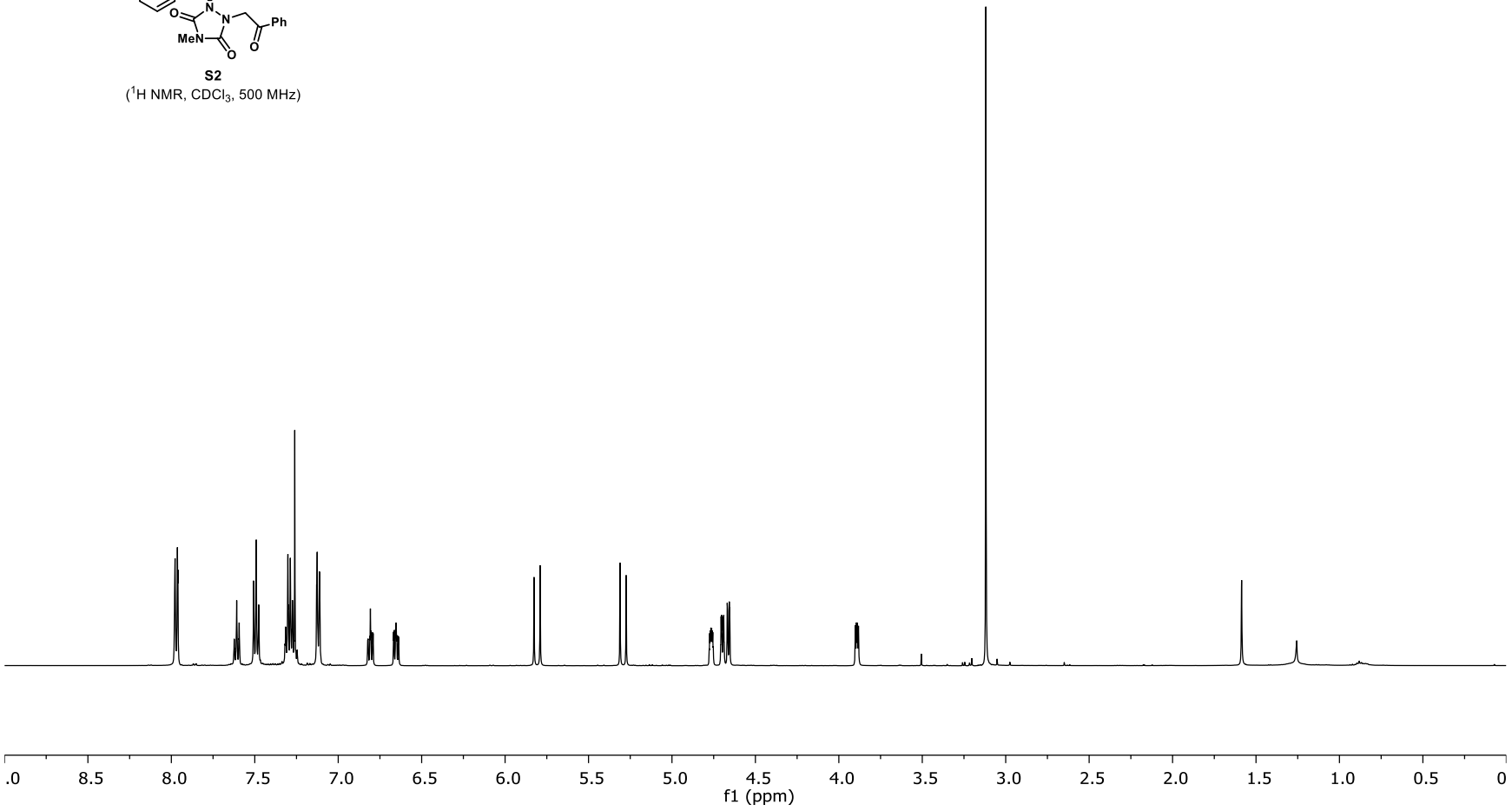
4

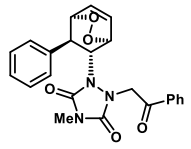
(^{13}C NMR, $CDCl_3$, 126 MHz)



S2

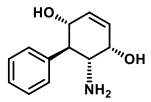
(^{1}H NMR, $CDCl_3$, 500 MHz)





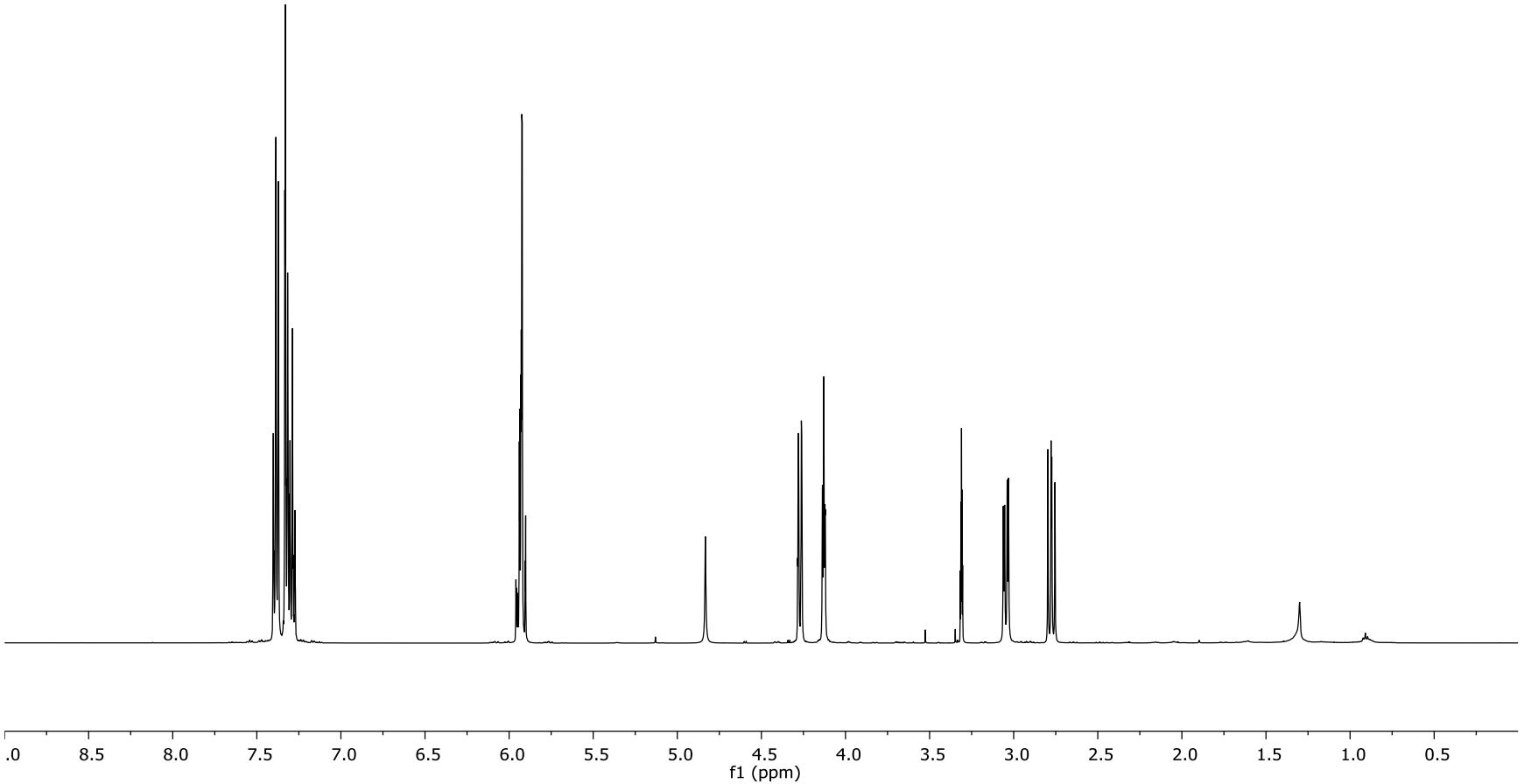
S2

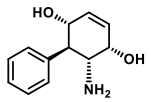
(^{13}C NMR, $CDCl_3$, 126 MHz)



5

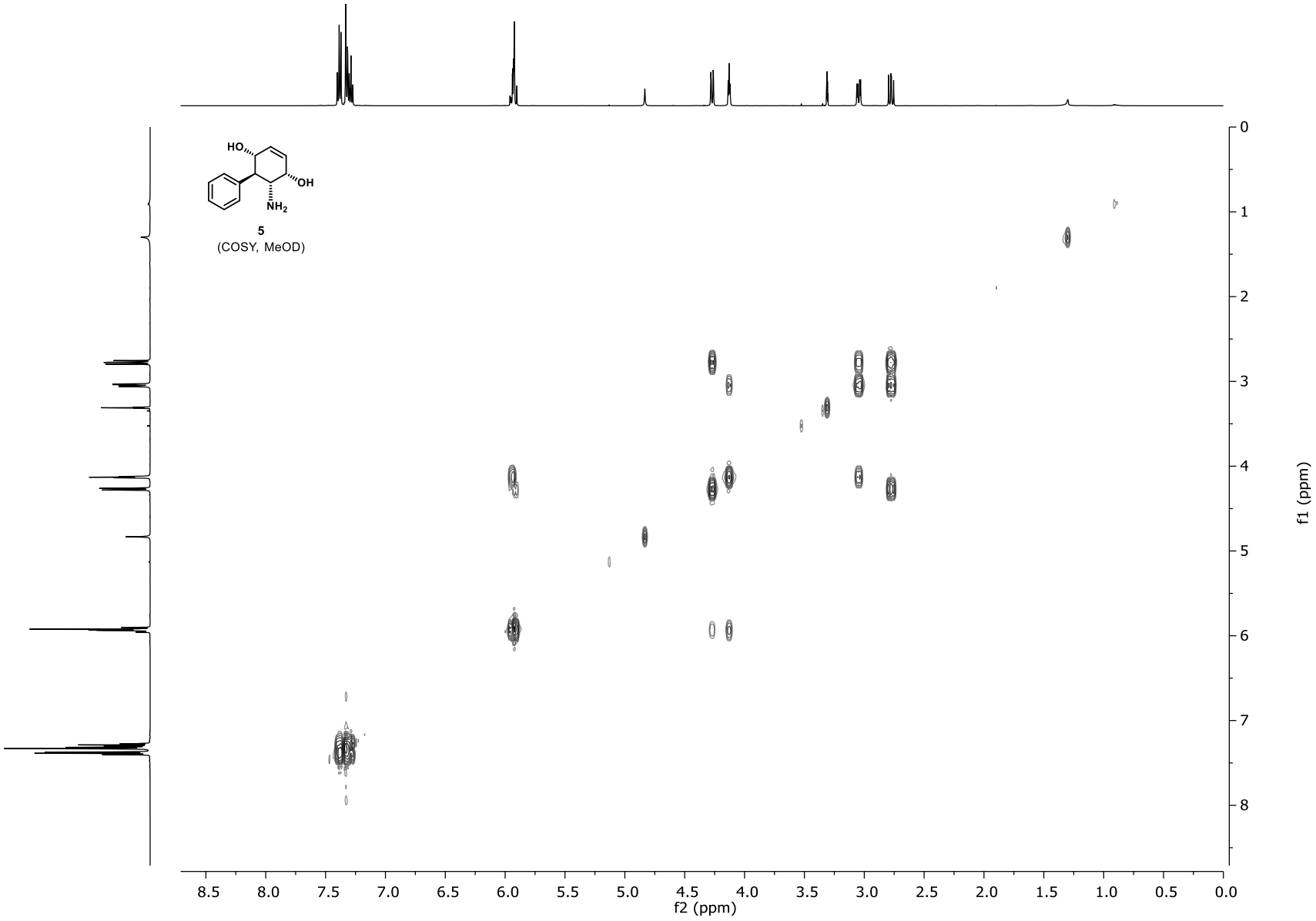
(^{1}H NMR, MeOD, 500 MHz)

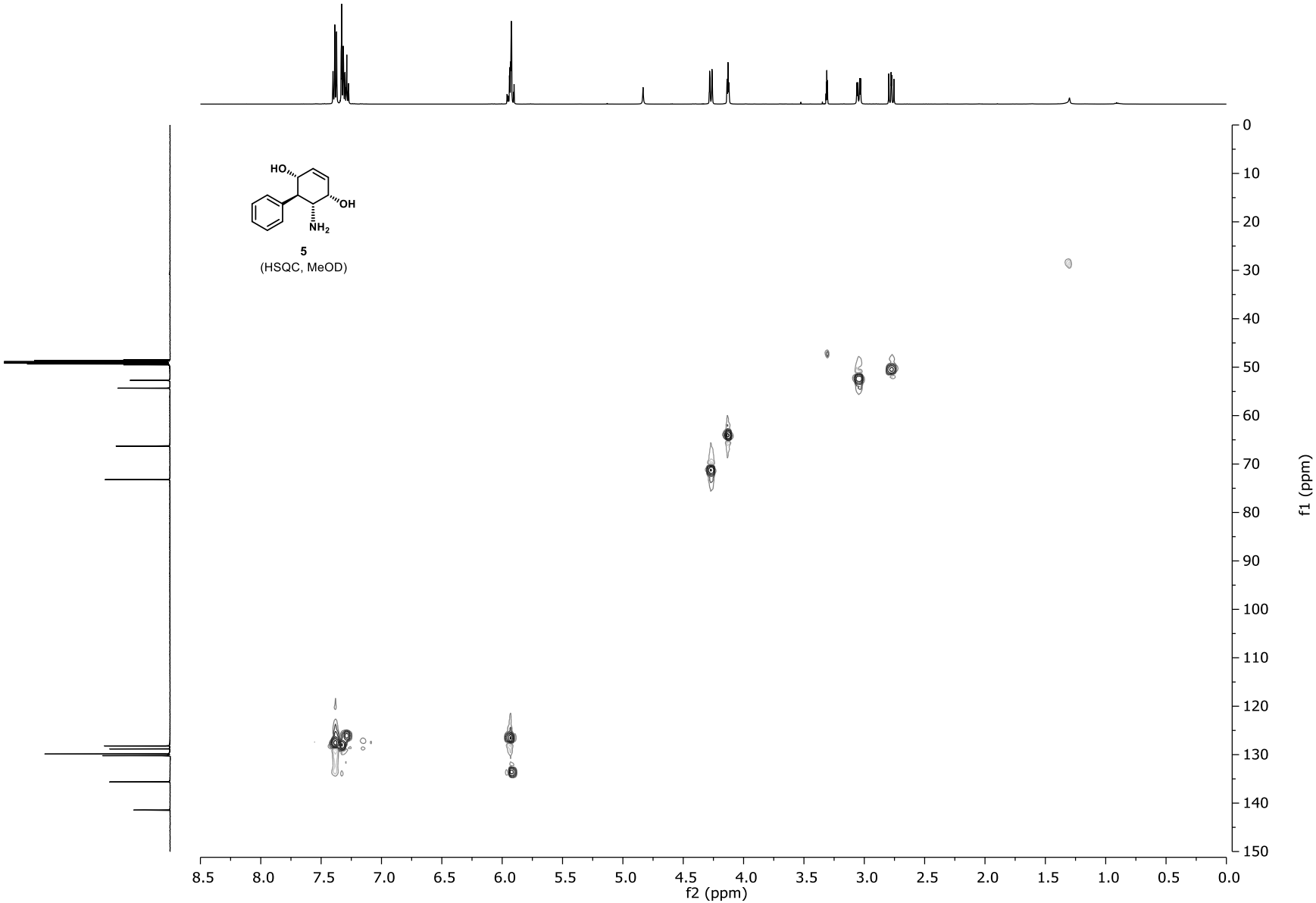


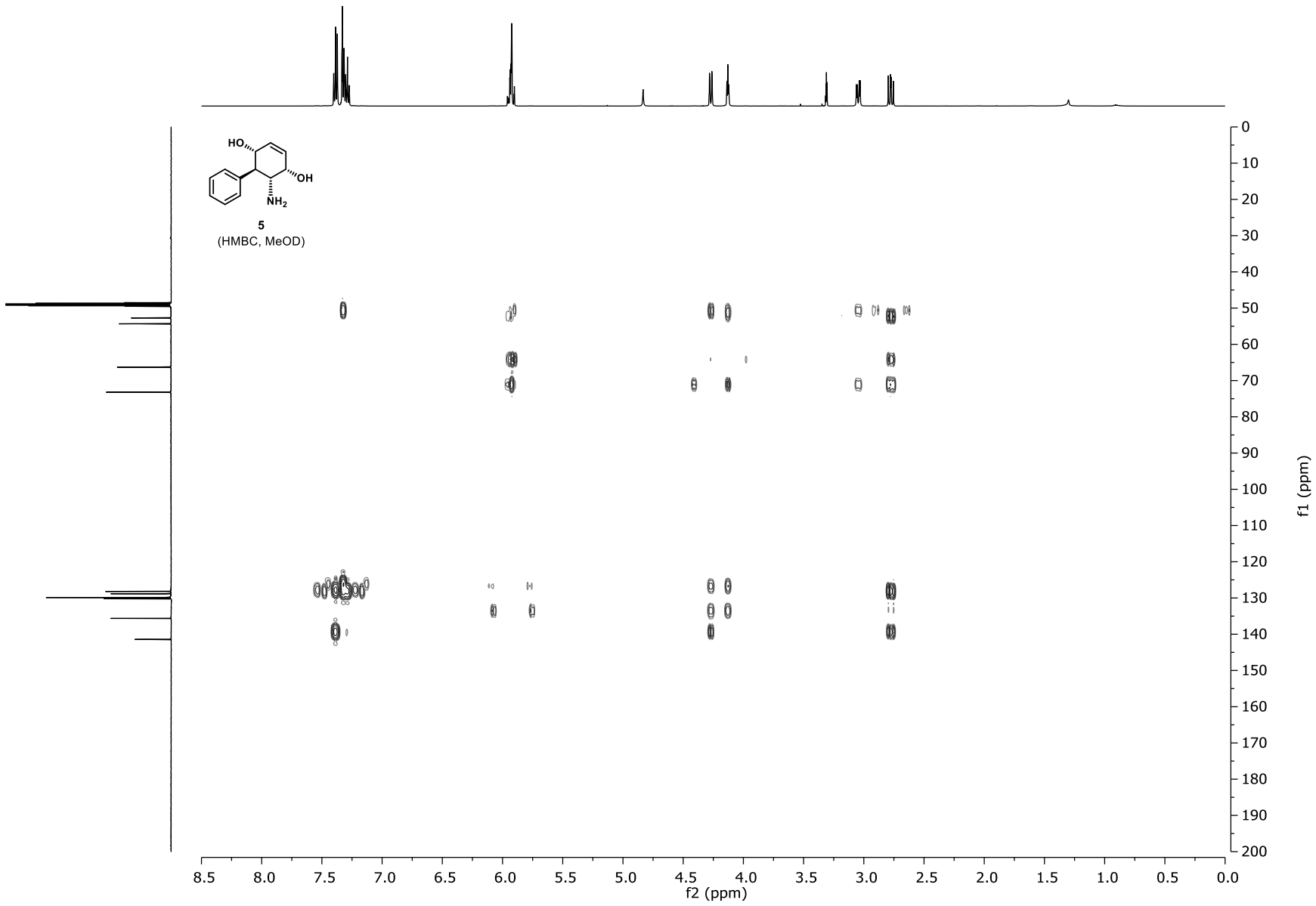


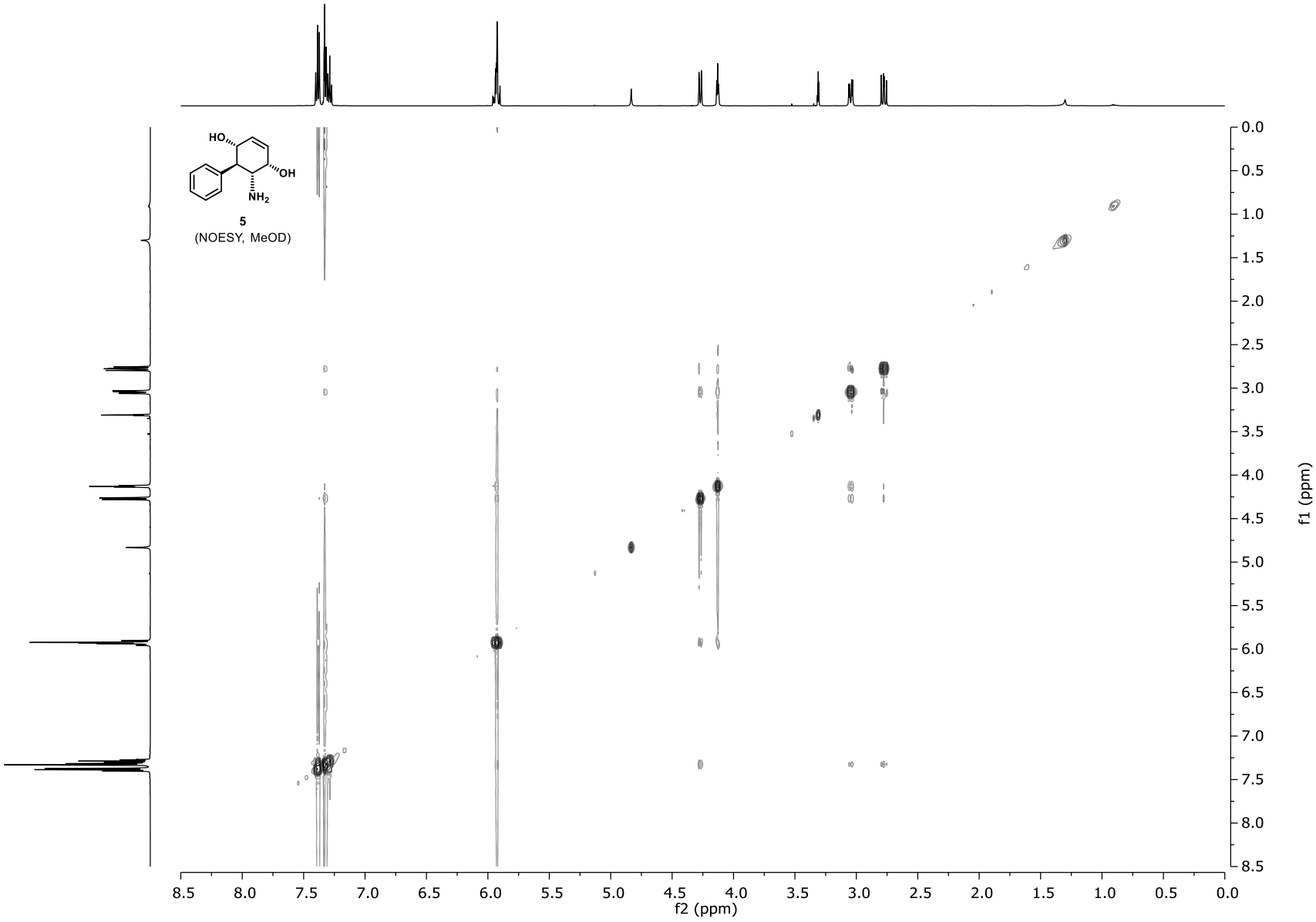
5

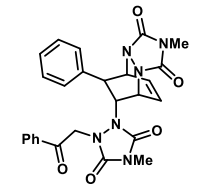
(^{13}C NMR, MeOD, 126 MHz)


HO
OH
NH2
5
(COSY, MeOD)
f2 (ppm)
f1 (ppm)


HO
OH
NH2
5
(HSQC, MeOD)
f2 (ppm)
f1 (ppm)

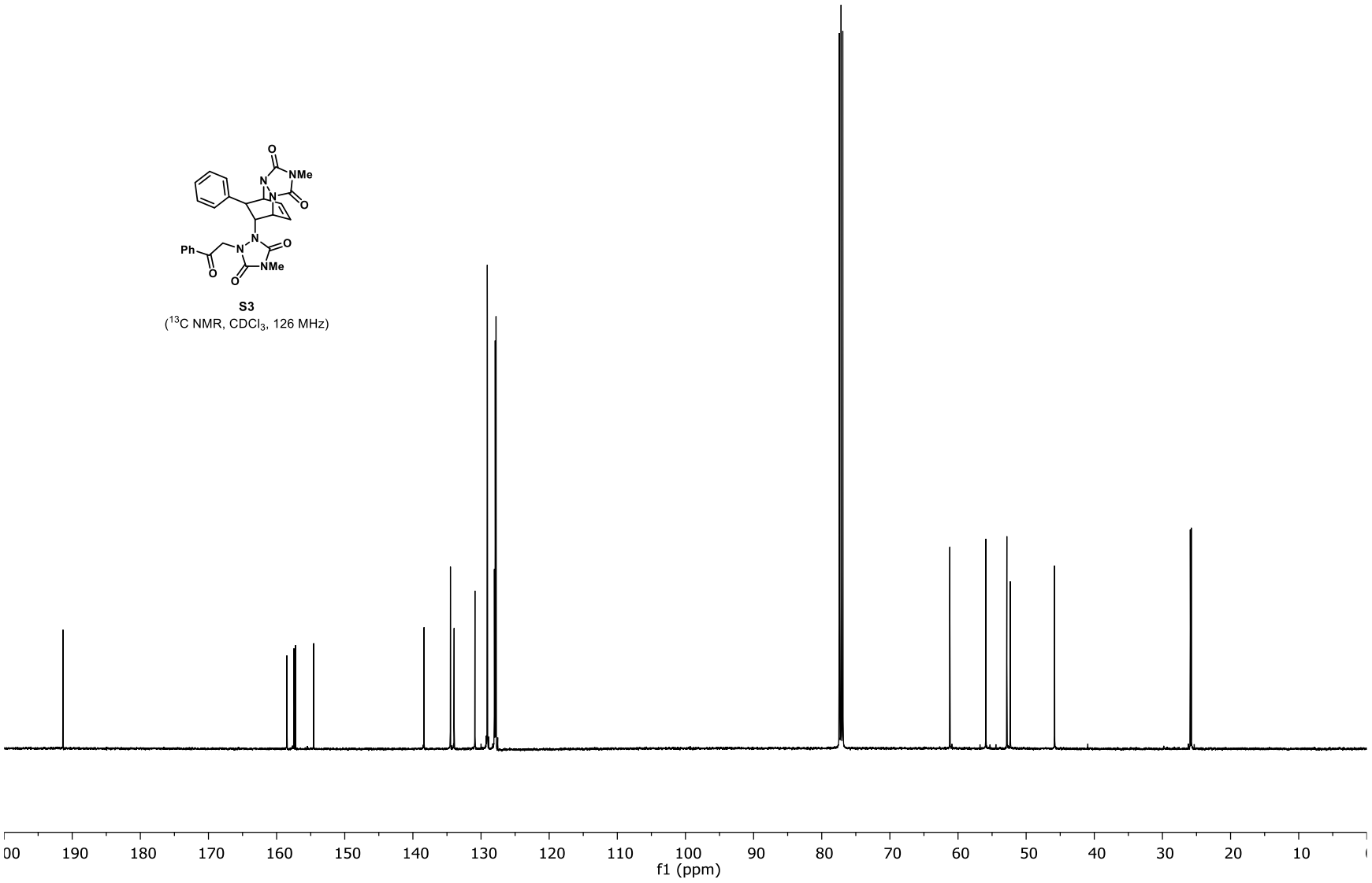

HO
OH
NH2
5
(HMBC, MeOD)
f2 (ppm)
f1 (ppm)


HO
OH
NH2
5
(NOESY, MeOD)
f2 (ppm)
f1 (ppm)



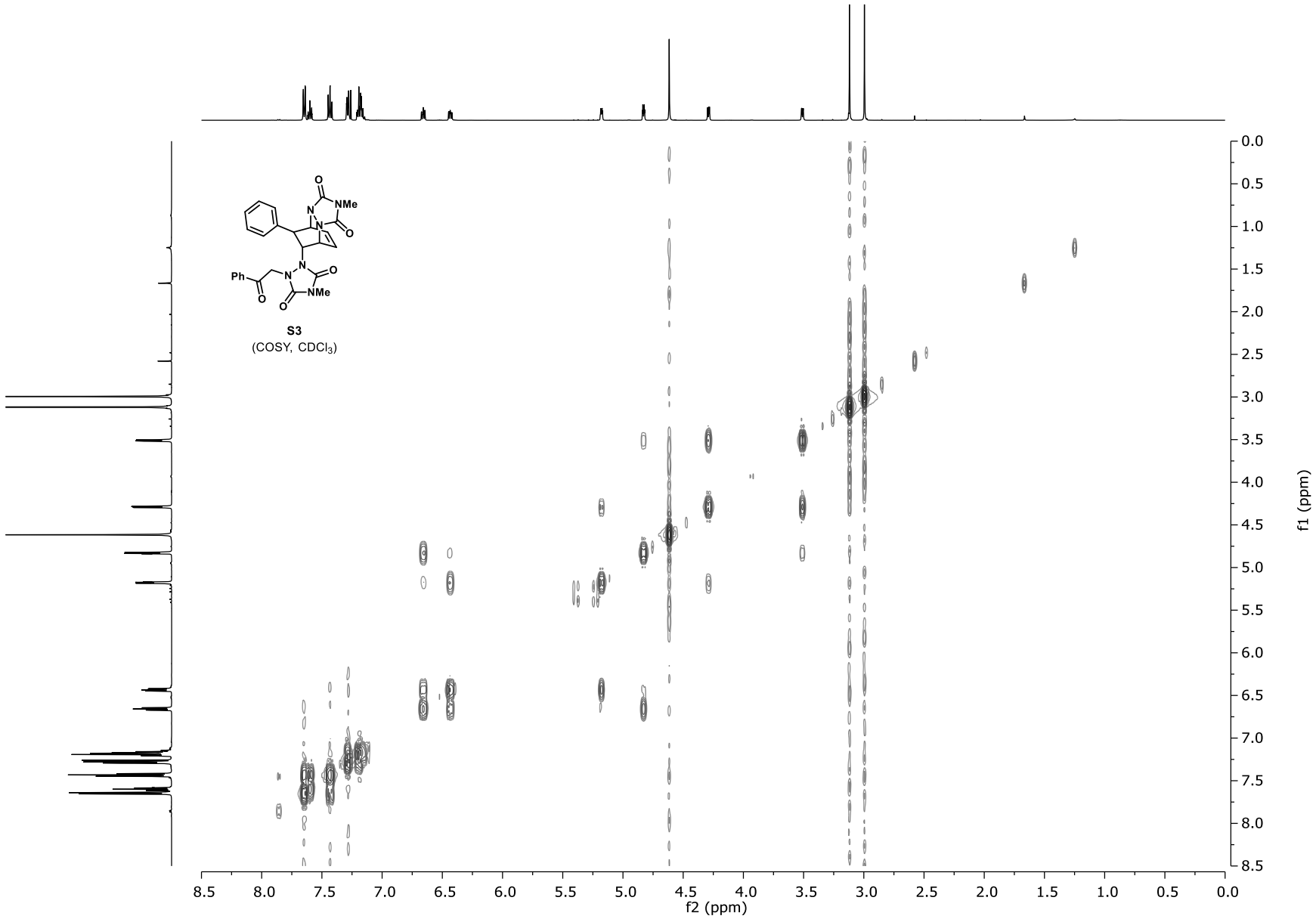
S3

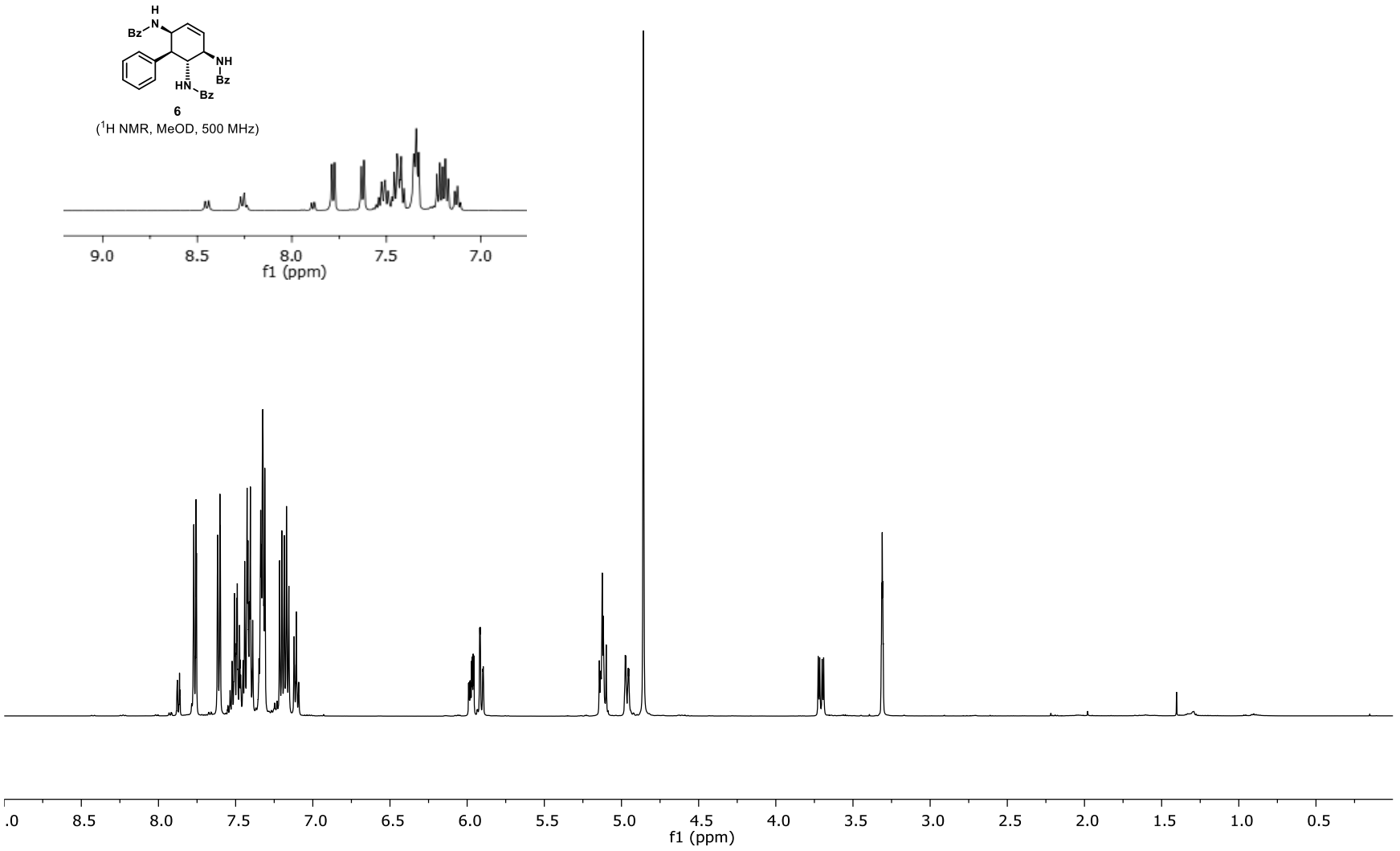
(^{1}H NMR, $CDCl_3$, 500 MHz)

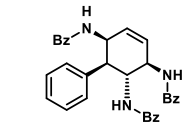


S3

(^{13}C NMR, $CDCl_3$, 126 MHz)

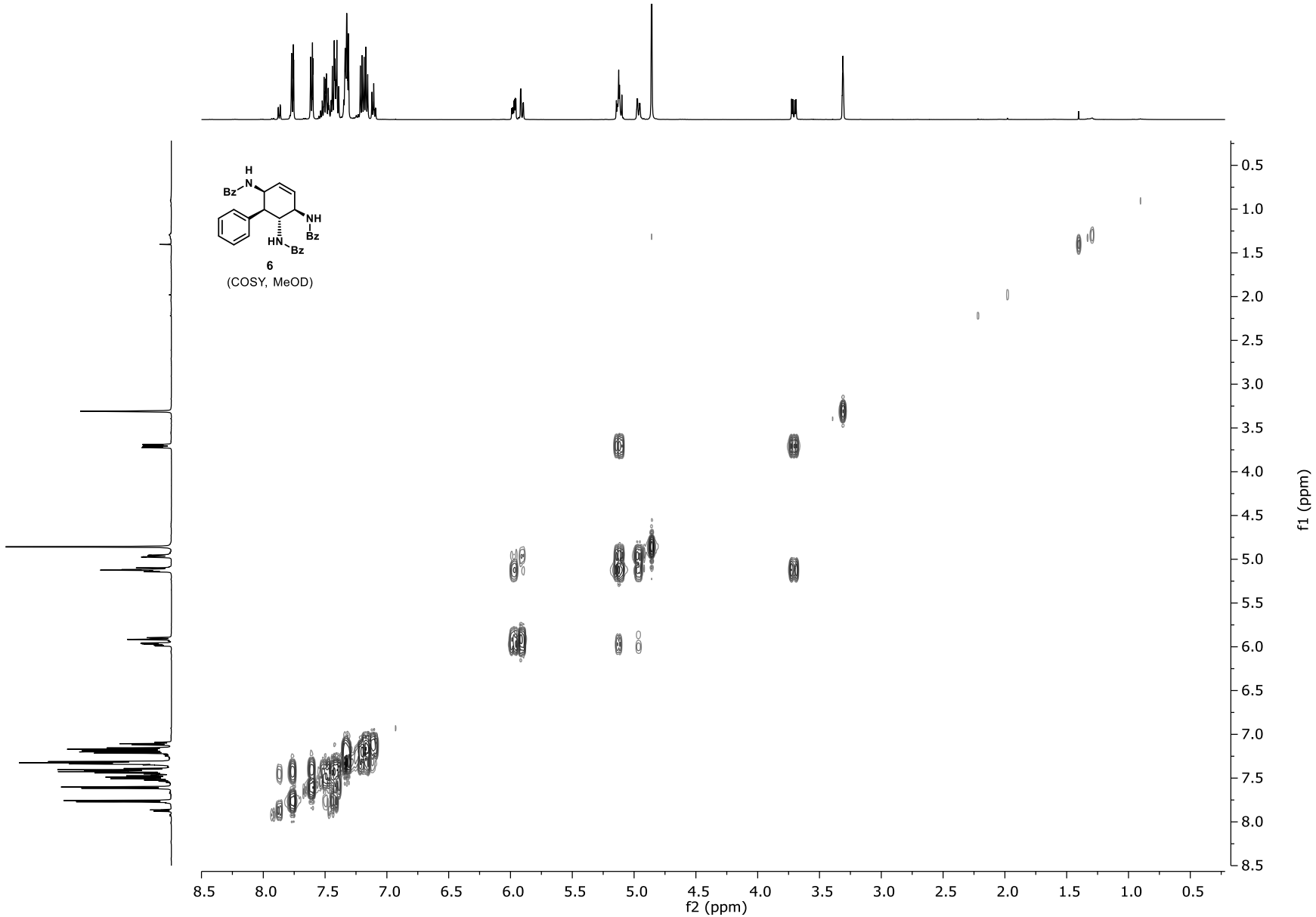

S3
(COSY, CDCl3)
f2 (ppm)
f1 (ppm)

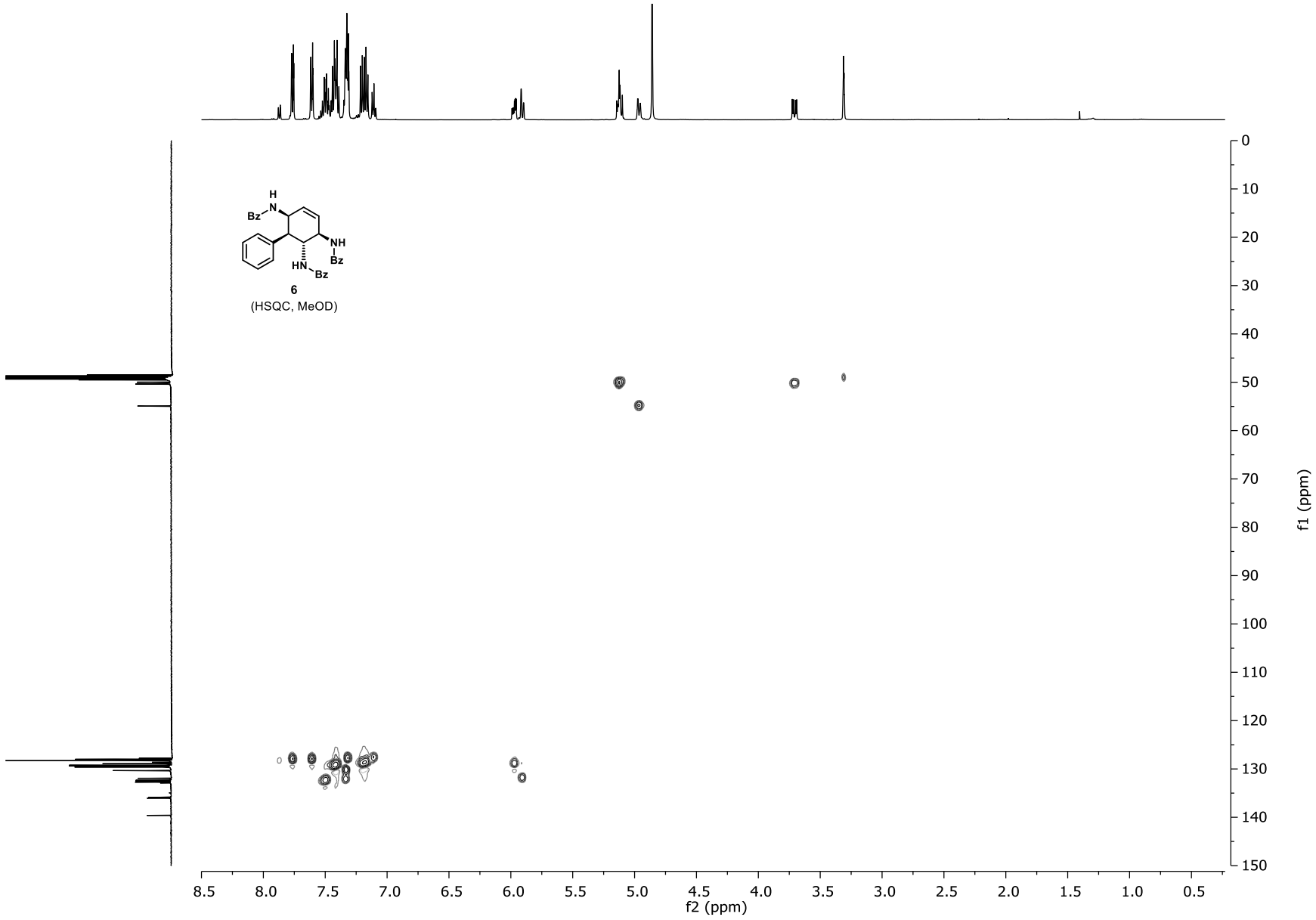

H
N
Bz
NH
Bz
HN
Bz
6
(1H NMR, MeOD, 500 MHz)
9.0
8.5
8.0
7.5
7.0
f1 (ppm)
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

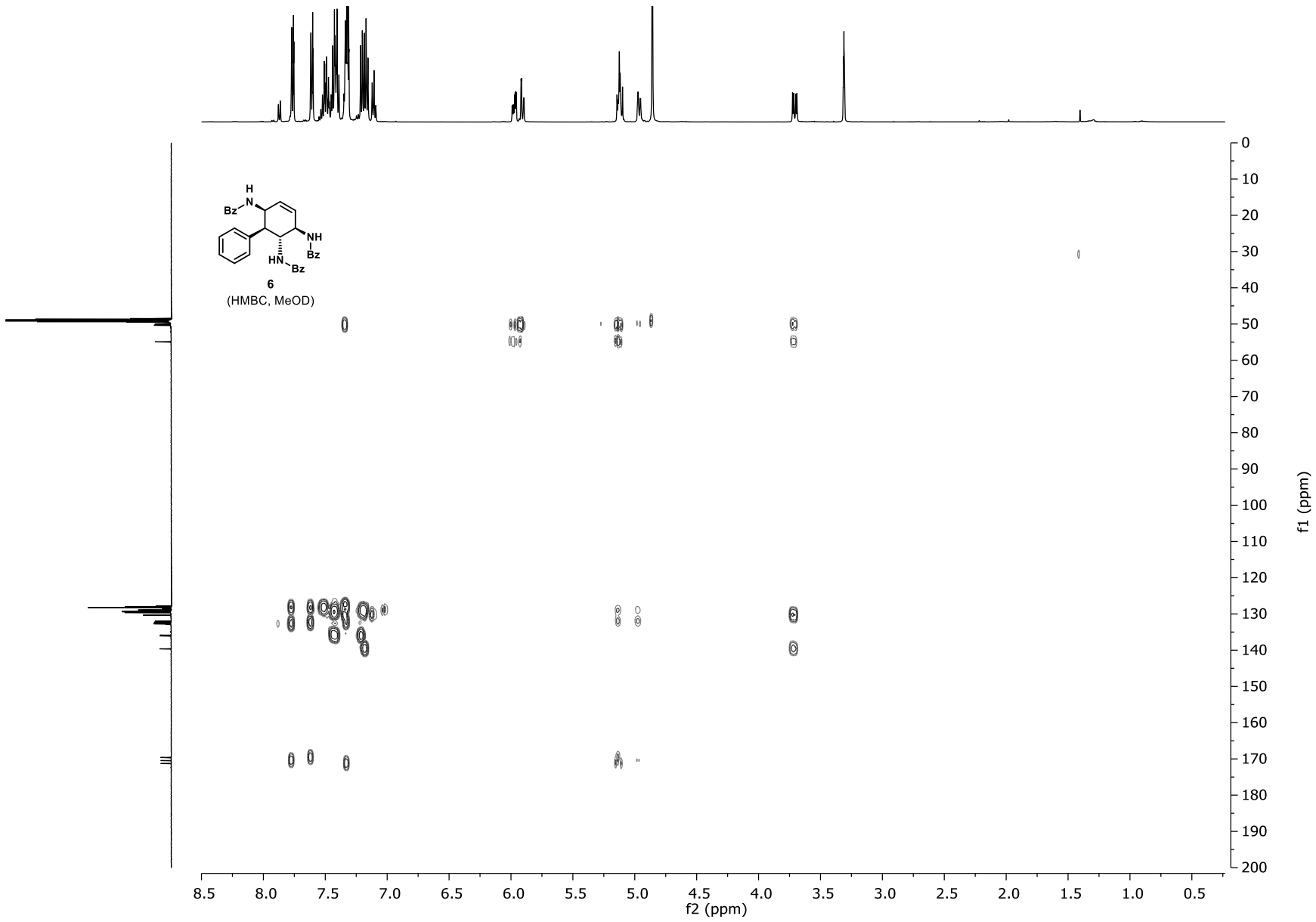


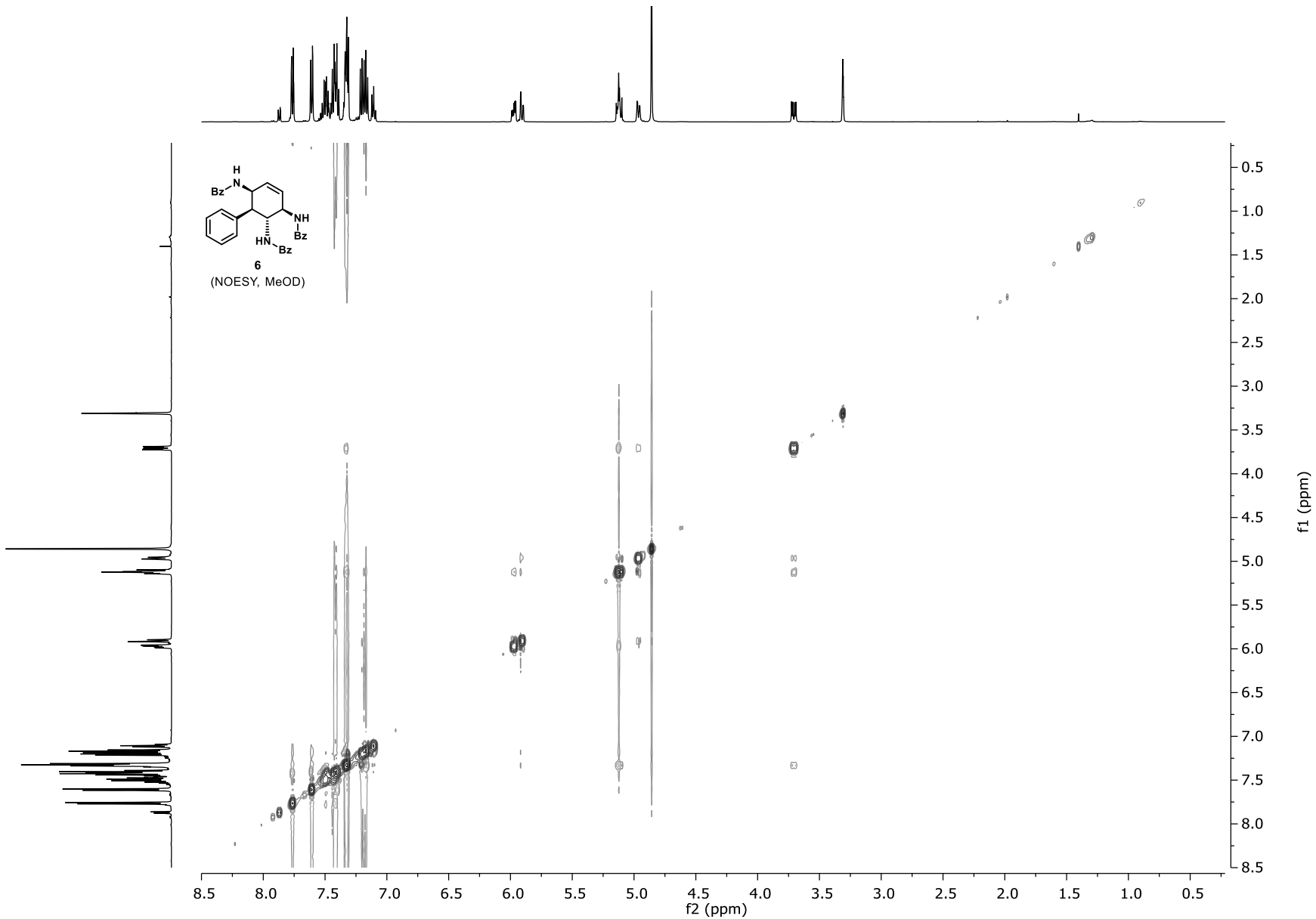
6

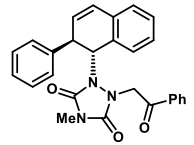
(^{13}C NMR, MeOD, 126 MHz)


6
(COSY, MeOD)
f2 (ppm)
f1 (ppm)


H
N
Bz
NH
Bz
HN
Bz
6
(HSQC, MeOD)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)

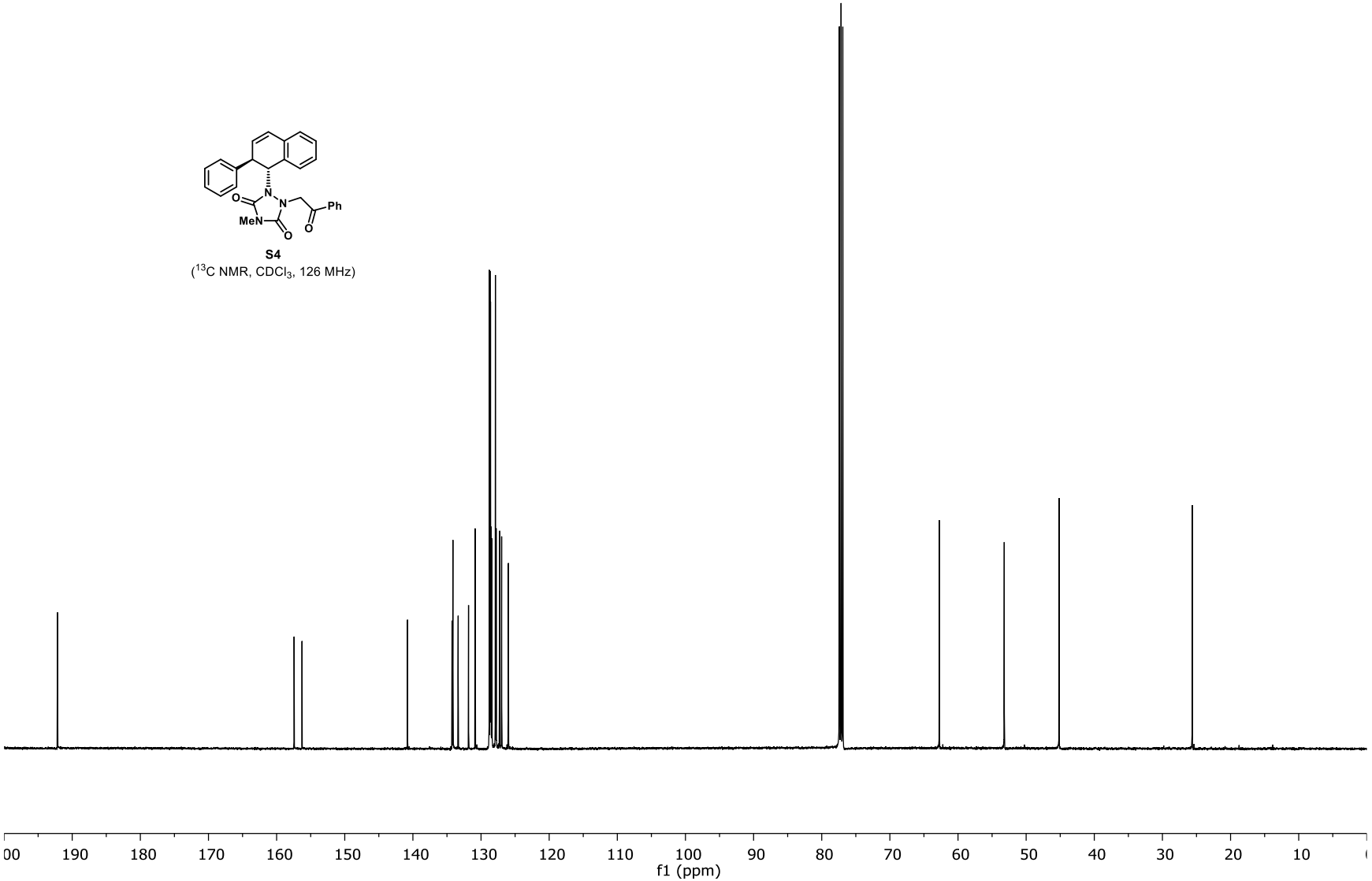

6
(HMBC, MeOD)
f2 (ppm)
f1 (ppm)


6
(NOESY, MeOD)
f2 (ppm)
f1 (ppm)



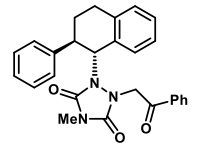
S4

(^{1}H NMR, $CDCl_3$, 500 MHz)



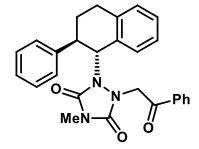
S4

(^{13}C NMR, $CDCl_3$, 126 MHz)



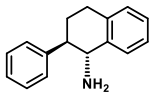
S5

(^{1}H NMR, $CDCl_3$, 500 MHz)



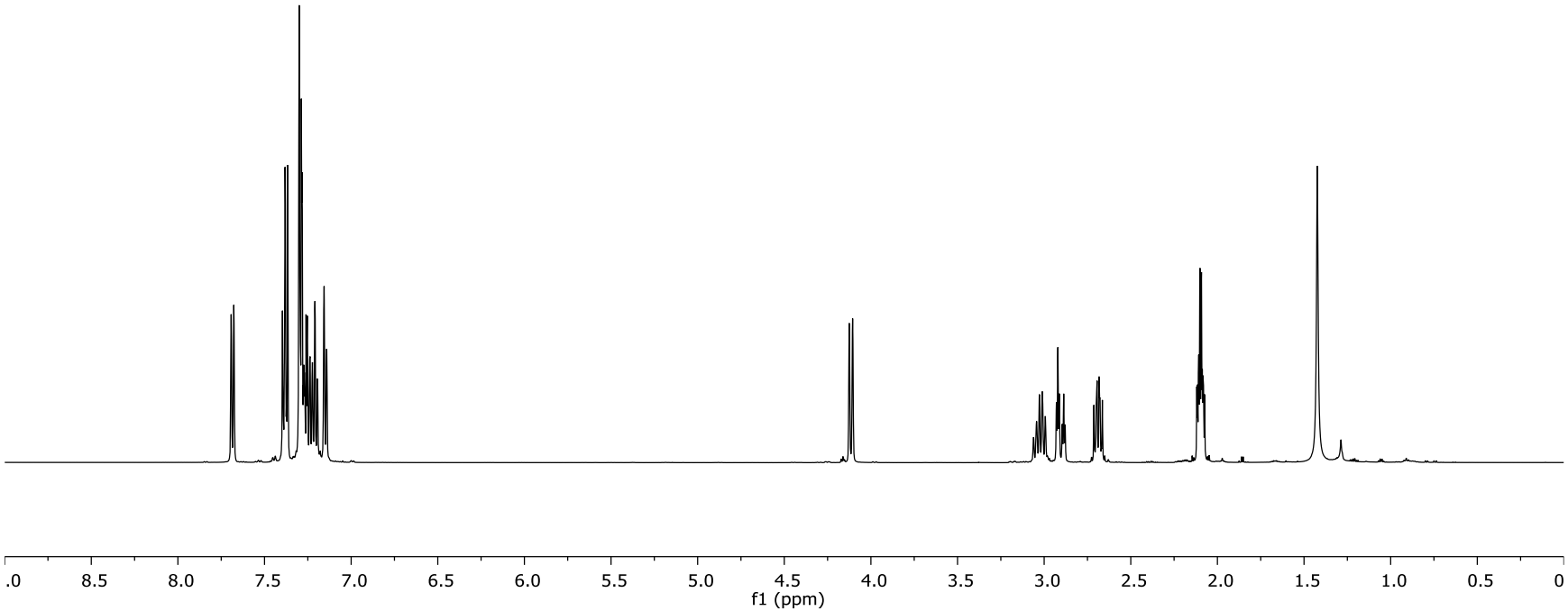
S5

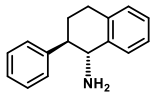
(^{13}C NMR, $CDCl_3$, 126 MHz)



7

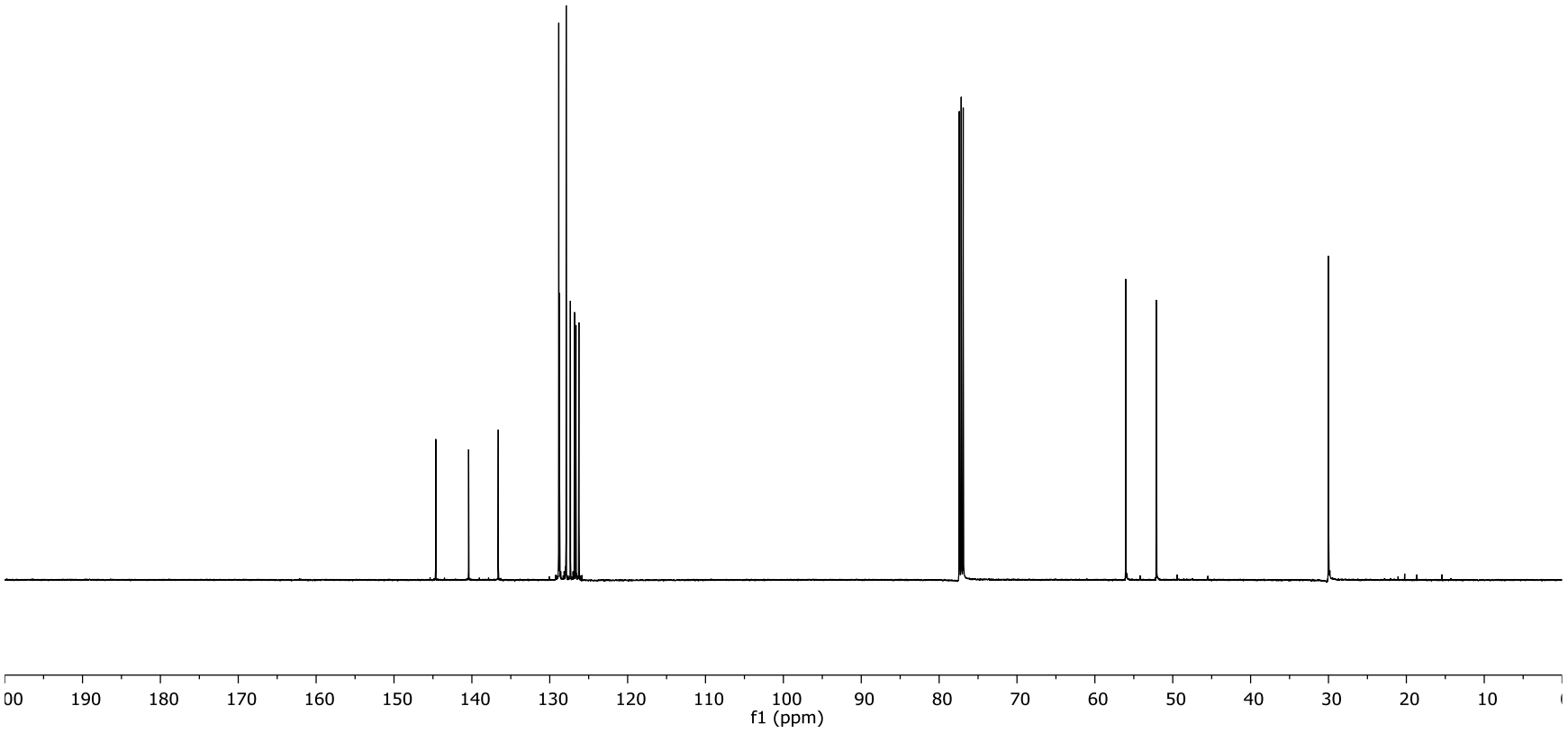
(^{1}H NMR, $CDCl_3$, 500 MHz)

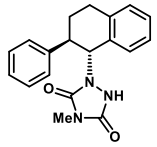




7

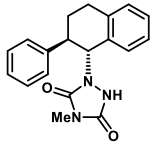
(^{13}C NMR, $CDCl_3$, 126 MHz)





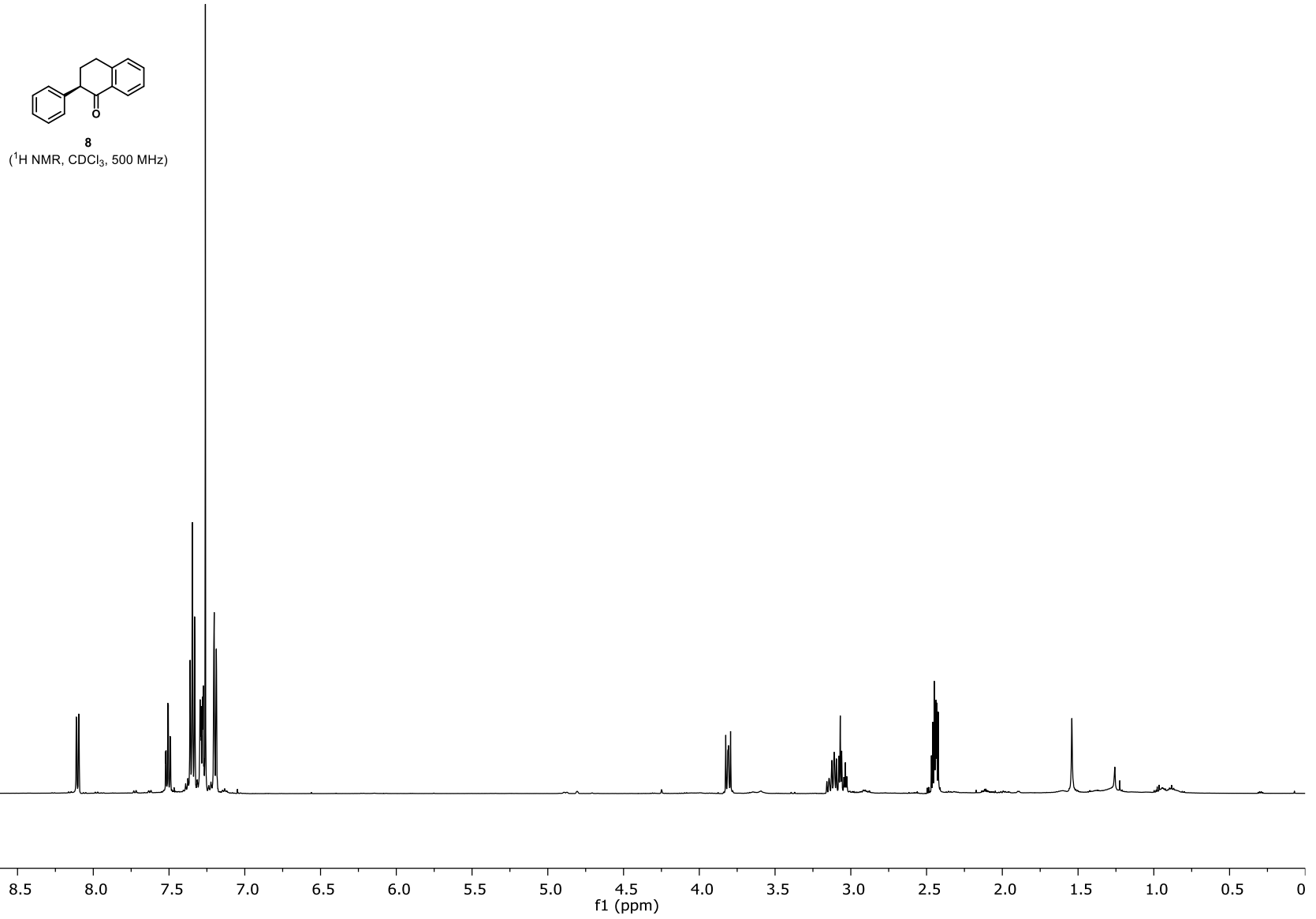
S6

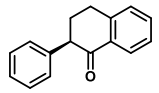
(^{1}H NMR, $CDCl_3$, 500 MHz)



S6

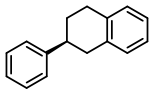
(^{13}C NMR, $CDCl_3$, 126 MHz)


O
8
(1H NMR, CDCl3, 500 MHz)
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)



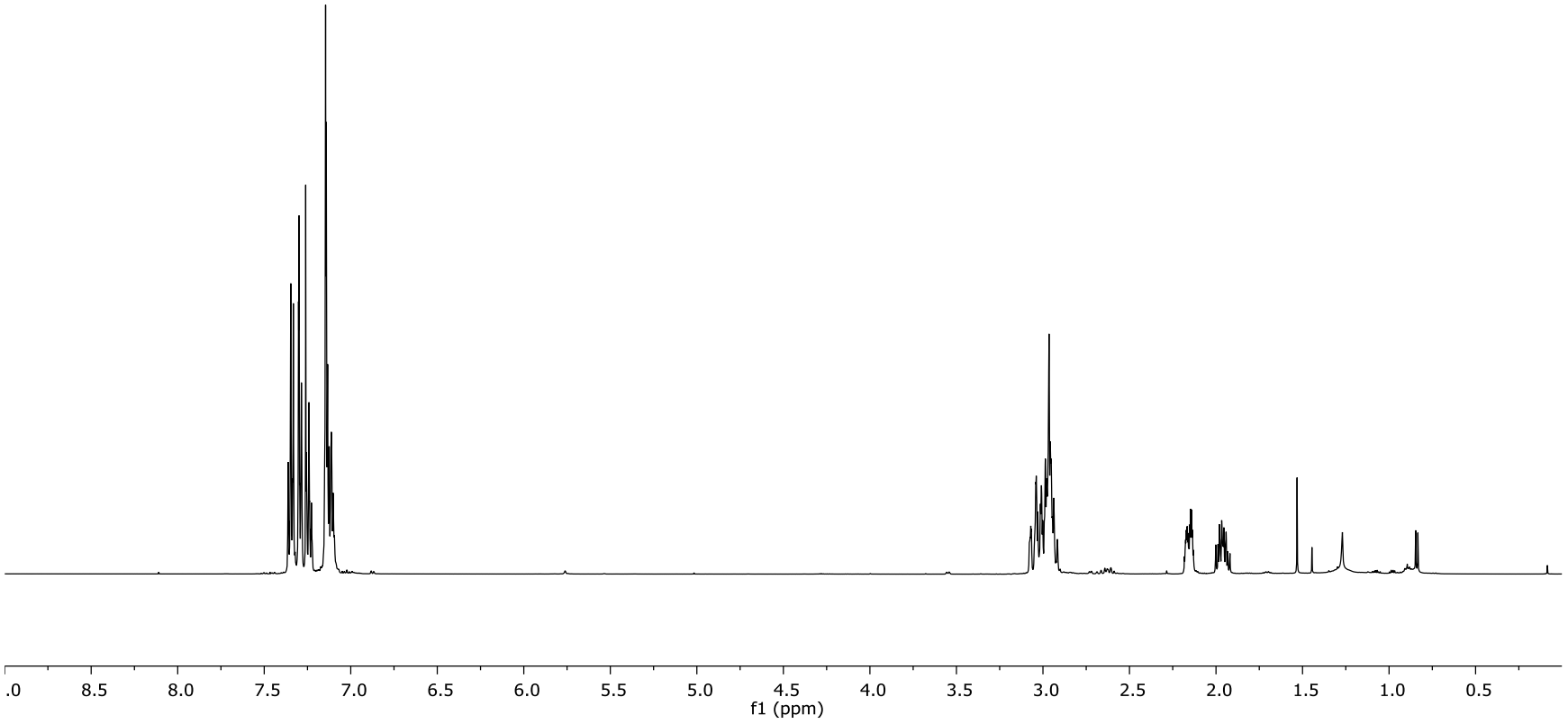
8

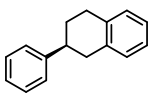
(^{13}C NMR, $CDCl_3$, 126 MHz)



9

(^{1}H NMR, $CDCl_3$, 500 MHz)





9

(^{13}C NMR, $CDCl_3$, 126 MHz)

9. References

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2. Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R.; Watts, C. T. *Org. Synth.* **1971**, *51*, 121.
3. Richards, C. J.; Mulvaney, A. W. *Tetrahedron: Asymmetry* **1996**, *7*, 1419.
4. Krout, M. R.; Mohr, J. T.; Stoltz, B. M. *Org. Synth.* **2009**, *86*, 181.
5. O'Neil, I. A. *Synlett* **1991**, *9*, 661.
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7. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.
8. Huang, Z.; Lim, L. H.; Chen, Z.; Li, Y.; Zhou, F.; Su, H.; Zhou, J. *Angew. Chem. Int. Ed.* **2013**, *52*, 4906.