Supporting Information

Application of pyrrolo-protected amino aldehydes in the stereoselective synthesis of anti 1,2-amino alcohols

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1 General Methods, Materials and Instrumentation

Unless otherwise stated all reactions of air/water sensitive substances were carried out using standard Schlenk techniques under a positive pressure of argon. All reagents and solvents for synthesis were purchased from Acros Organics, Alfa Aesar, Carl Roth, Sigma Aldrich, TCI, Fluorochem, Th. Geyer and VWR and used without further purification. All anhydrous solvents were purchased from Acros Organics.

NMR measurements were performed on a Bruker AVANCE II 300 MHz and a Bruker AVANCE III 500 MHz. The chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak of C_6D_6 (^{1}H: 7.16 ppm, ^{13}C: 128.06 ppm), $CDCl_3$ (^{1}H: 7.26 ppm, singlet; ^{13}C: 77.16 ppm, triplet) and CD_3OD (^{1}H: 3.31 ppm, quintet; ^{13}C: 49.00 ppm, septet).

LC-ESI-HRMS measurements were carried out on an Accela UPLC system (Thermo Scientific) coupled with a Kinetex Phenyl-Hexyl column (50 x 2.1 mm, particle size 1.7 µm) combined with a Q-Exactive mass spectrometer (Thermo Scientific) equipped with an electrospray ion (ESI) source.

Chiral HPLC was performed on a Shimadzu HPLC system using a Lux® 5 µm cellulose-1 (250 x 4.6 mm) column (UV detection at 220 and 254 nm)

Flash chromatography was performed on a Biotage Isolera Prime.

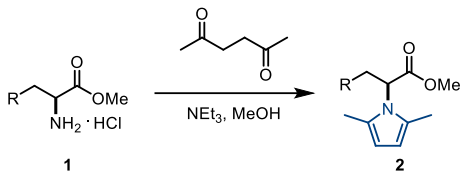
IR spectra were recorded on an FT/IR-4100 ATR spectrometer (JASCO).

Optical rotations were recorded on a P-1020 polarimeter (JASCO) at 589 nm using a 50 mm cell and the solvent and concentration (g/100 mL) indicated.

2 Experimental Procedures and Characterization Data

2.1 General procedures

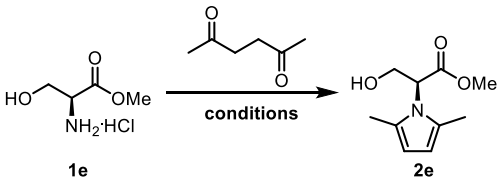
General Procedure 1: Synthesis of pyrroles **2a-f**



1 2

A solution of amino acid methyl ester hydrochloride **1** (2 equiv.) in MeOH (0.5 M) was treated with triethyl amine (2 equiv.) followed by hexane-2,5-dione (1 equiv.) and stirred at room temperature for 16h. The solvent was evaporated and the residue was taken up in water and dichloromethane. The aqueous layer was extracted with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtrated and concentrated. The residue was purified by column chromatography to yield the pyrrole **2**.

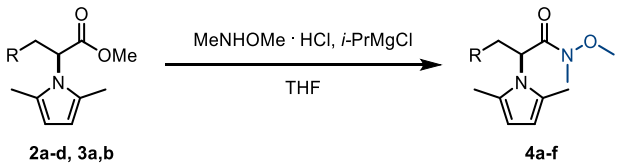
Conditions Paal-Knorr-Synthesis



1e 2e

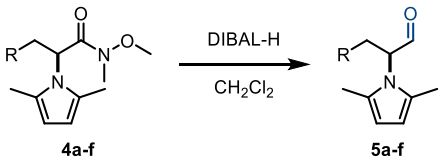
Entry	1e (equiv.)	Ketone (equiv.)	Solvent (M)	NEt_3 (equiv.)	Temp.	Time	Yield
1	1	1	MeOH (0.3)	1	r.t.	2.5h	20%
2	1	1	MeOH (0.5)	1	r.t.	16h	49%
3	1	1	MeOH (0.5)	2	r.t.	16h	62%
4	1	1	MeOH (0.5)	2	r.t.	3d	21%
5	2	1	MeOH (0.5)	2	r.t.	16h	71%
6	2	1	MeOH (0.5)	2	r.t.	3d	64%
7	1	2	MeOH (0.5)	1	r.t.	16h	36%
8	2	1	MeOH (0.5)	4	r.t.	16h	21%
9	2	1	MeOH (0.5)	4	r.t.	3d	24%
10	1	1	MeOH (1)	1	40 °C	16h	47%
11	1	1	MeOH (0.5)	1	40 °C	16h	41%
12	2	1	MeOH (0.5)	2	40 °C	16h	59%
13	1	1	MeOH (0.5)	2	reflux	16h	53%
14	2	1	MeOH (0.5)	4	reflux	16h	28%
15	1	1	AcOH (1)	-	reflux	16h	decomposing
16	1	1	AcOH (1)	-	r.t.	16h	decomposing
17	1	1	ACN (1)	1	r.t	16h	Suspension, no conversion
18	1	1	DMF (1)	1	r.t	16h	Suspension, no conversion

General Procedure 2: Synthesis of Weinreb amides **4a-f**



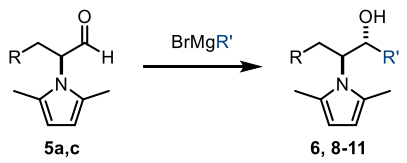
A modified procedure was used:[1] A mixture of methyl ester **2a-d, 3a,b** (1 equiv.) and N,O-dimethyl hydroxylamine hydrochloride (1.55 equiv.) in dry THF (0.5 M) was cooled to –20 °C and treated slowly with *i*-PrMgCl (3 equiv., 2M in THF). The reaction mixture was stirred for additional 30 min, quenched by the addition of saturated ammonium chloride solution and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude residue was purified by column chromatography to yield the Weinreb amide **4a-f**.

General Procedure 3: Synthesis of aldehydes **5a-f**



A solution of Weinreb amide **4a-f** (1 equiv.) in dichloromethane (0.2M) was cooled to –20 °C, treated slowly with DIBAL-H (1.3 equiv., 1 M in hexane) and stirred at –20 °C for 1h. The reaction mixture was quenched by the addition of a small amount methanol followed by saturated K-Na-tartrate solution, warmed to room temperature and extracted with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo* (25 °C). The aldehyde **5a-f** was obtained as slightly yellow oil which was used without further purification in the next step. To obtain analytical pure sample the aldehyde **5a-f** was purified by column chromatography (0 to 40% EtOAc in cyclohexane (R = Ph, Me) or 0 to 15% EtOAc in cyclohexane (R = OTBS), linear gradient).

General Procedure 4: Addition of Grignard reagents



A solution of aldehyde **5a,c** (1 equiv.) in dry THF (0.3 M) was cooled to 0 °C and treated dropwise with a solution of Grignard reagent (1.2 equiv.). The reaction mixture was stirred for 1h, quenched by the addition of saturated ammonium chloride solution and extracted with ethyl

acetate. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude residue was purified by column chromatography (0 to 40% EtOAc in cyclohexane, linear gradient) to yield the alcohol **6,8-11**.

General Procedure 5: Generation and addition of Lithium reagents

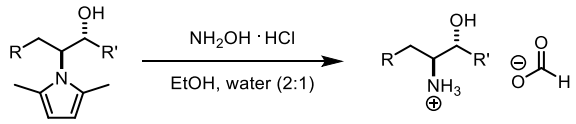
5 **12-29**

5A: Lithium reagent (1 equiv.) was dissolved in dry diethyl ether (0.3 M) and cooled to –78 °C. A solution of aldehyde **5** (1.2 equiv.) in dry diethyl ether (0.3 M) was added dropwise, stirred at -78 °C for 1h, quenched by the addition of saturated ammonium chloride solution and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude residue was purified by column chromatography (0 to 40% EtOAc in cyclohexane (R = Ph, Me) or 0 to 15% EtOAc in cyclohexane (R = OTBS), linear gradient) to yield the alcohol **12-15, 18-21**.

5B: A modified procedure was used:[2] Alkyne (1 equiv.) was dissolved in dry diethyl ether (0.3 M), cooled to –78 °C, treated with *n*-butyl lithium (1 equiv., 2.5 M in pentane) and stirred for 1h. A solution of aldehyde **5** (1.2 equiv.) in dry diethyl ether (0.3 M) was added dropwise, stirred at –78 °C for 1h, quenched by the addition of saturated ammonium chloride solution and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude residue was purified by column chromatography (0 to 40% EtOAc in cyclohexane (R = Ph, Me) or 0 to 15% EtOAc in cyclohexane, linear gradient) to yield the alcohol **23-25, 27-29**.

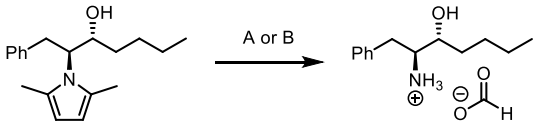
5C: Alkyl iodide (1 equiv.) was dissolved in dry diethyl ether (0.1 M), cooled to 0 °C, treated with *t*-BuLi (2.0 equiv.) and stirred for 20 min. Afterward a solution of aldehyde **5a,b** (1.2 equiv.) in dry diethyl ether was added dropwise, stirred for 1h quenched by the addition of saturated ammonium chloride solution and extracted with ethyl acetate. The residue was purified by column chromatography (0 to 20% EtOAc in cyclohexane, linear gradient) to yield the alcohol **16, 17**.

General Procedure 6: Deprotection



A modified procedure was used:[3] To a solution of alcohol (1 equiv.) in ethanol and water (0.05 M, 2:1) was added hydroxylamine hydrochloride (10 equiv.) and stirred at 140 °C under microwave irradiation for 30 min. After cooling, the reaction mixture was directly injected to column chromatography (C18, 0 – 100% acetonitrile in water + 0.1% formic acid, linear gradient, UV detection at 208 nm) to yield the amino alcohol.

Conditions Deprotection



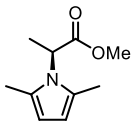
19 **31**

A: $NH_2OH \cdot HCl$ (10 equiv.), ethanol, water (2:1, 0.05M), **B:** 10% conc. HCl in ethanol (0.4M)

Entry	Conditions	Temp. [°C]	Time	Yield
1	A	120	1h (microwave)	95%
2	A	140	30 min (microwave)	95%
3	A	reflux	18h	49%
4	B	120	15 min (microwave)	60%
5	B	120	30 min (microwave)	66%
6	B	120	1h (microwave)	71%

2.2 Synthesis of aldehydes, precursors and alkyl iodides

Methyl (*S*)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)propanoate 2a



According to general procedure 1. *L*-Alanine methyl ester hydrochloride **1a** (400 mg, 2.87 mmol, 2 equiv.), triethyl amine (0.40 mL, 2.87 mmol, 2 equiv.) and hexane-2,5-dione (0.17 mL, 1.43 mmol, 1 equiv.) in MeOH (5.7 mL) were used. After column chromatography (0 to 40% EtOAc in cyclohexane, linear gradient) the pyrrole **2a** (220 mg, 85%) was yield as slightly yellow oil.

$[\alpha]_D^{24} = -41.1$ (c = 1.00, MeOH)

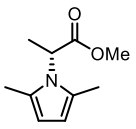
^{1}H-NMR (500 MHz, C_6D_6) δ = 5.96 (s, 2H), 4.43 (q, *J* = 7.3 Hz, 1H), 3.21 (s, 3H), 2.04 (s, 6H), 1.35 (d, *J* = 7.3 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (126 MHz, C_6D_6): δ = 171.69, 127.42, 107.39, 52.56, 51.83, 17.43, 13.20 ppm.

IR (ATR) $\tilde{\nu}$ = 3098 (w), 2991 (w), 2948 (w), 1734 (s), 1520 (w), 1455 (m), 1433 (m), 1398 (s), 1299 (m), 1223 (s), 1111 (s), 1075 (m), 1047 (m), 1002 (w), 968 (m), 955 (m), 858 (m), 763 (s), 745 (s), 728 (m) cm^{-1}.

HR-MS (ESI): Calcd for $C_{10}H_{16}O_2N$ $[M+H]^+$ 182.1176, found 182.1171.

Methyl (*R*)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)propanoate 2b



According to general procedure 1. *D*-Alanine methyl ester hydrochloride **1a** (400 mg, 2.87 mmol, 2 equiv.), triethyl amine (0.40 mL, 2.87 mmol, 2 equiv.) and hexane-2,5-dione (0.17 mL, 1.43 mmol, 1 equiv.) in MeOH (5.7 mL) were used. After column chromatography (0 to 40% EtOAc in cyclohexane, linear gradient) the pyrrole **2b** (207 mg, 80%) was yield as colorless oil.

$[\alpha]_D^{24} = 44.3$ (c = 1.00, MeOH)

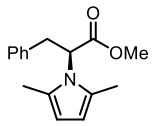
^{1}H-NMR (300 MHz, C_6D_6) δ = 5.93 (s, 2H), 4.44 (q, *J* = 7.2 Hz, 1H), 3.23 (s, 3H), 2.03 (s, 6H), 1.35 (d, *J* = 7.3 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6): δ = 171.71, 127.42, 107.33, 52.54, 51.87, 17.43, 13.19 ppm.

IR (ATR) $\tilde{\nu}$ = 3099 (w), 2991 (w), 2929 (w), 1734 (s), 1521 (w), 1455 (m), 1433 (m), 1398 (s), 1300 (m), 1222 (s), 1111 (s), 1074 (m), 1047 (m), 1002 (w), 968 (m), 955 (m), 858 (m), 763 (s), 745 (s), 728 (m) cm^{-1}.

HR-MS (ESI): Calcd for $C_{10}H_{16}O_2N$ $[M+H]^+$ 182.1176, found 182.1170.

Methyl (*S*)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-3-phenylpropanoate 2c



According to general procedure 1. *L*-Phenylalanine methyl ester hydrochloride **1c** (619 mg, 2.87 mmol, 2 equiv.), triethyl amine (0.40 mL, 2.87 mmol, 2 equiv.) and hexane-2,5-dione (0.17 mL, 1.43 mmol, 1 equiv.) in MeOH (5.7 mL) were used. After column chromatography (0 to 40% EtOAc in cyclohexane, linear gradient) the pyrrole **2c** (302 mg, 82%) was yield as slightly yellow oil.

$[\alpha]_D^{24}$= –129.2 (c = 1.00, MeOH)

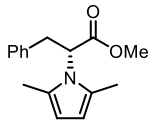
^{1}H-NMR (500 MHz, C_6D_6) δ = 7.05 – 6.96 (m, 3H), 6.82 – 6.72 (m, 2H), 5.91 (s, 2H), 4.55 (dd, *J* = 10.3, 4.6 Hz, 1H), 3.46 (dd, *J* = 13.9, 4.6 Hz, 1H), 3.22 (s, 3H), 3.14 (dd, *J* = 13.9, 10.3 Hz, 1H), 1.88 (s, 6H) ppm.

^{13}C{^{1}H}-NMR (126 MHz, C_6D_6) δ = 171.03, 137.83, 129.68, 128.63, 128.35, 127.01, 107.41, 59.23, 51.93, 38.04, 13.14 ppm.

IR (ATR) $\tilde{\nu}$ = 3029 (w), 2949 (w), 2887 (w), 1738 (s), 1521 (w), 1496 (w), 1436 (m), 1397 (s), 1292 (m), 1277 (m), 1222 (s), 1168 (m), 1083 (w), 1050 (w), 987 (m), 903 (w), 823 (w), 750 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{16}H_{20}O_2N$ $[M+H]^+$ 258.1489, found 258.1478.

Methyl (*R*)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-3-phenylpropanoate 2d



According to general procedure 1. *D*-Phenylalanine methyl ester hydrochloride **1d** (270 mg, 1.25 mmol, 2 equiv.), triethyl amine (0.17 mL, 1.25 mmol, 2 equiv.) and hexane-2,5-dione (0.07 mL, 0.63 mmol, 1 equiv.) in MeOH (2.5 mL) were used. After column chromatography (0 to 40% EtOAc in cyclohexane, linear gradient) the pyrrole **2d** (126 mg, 78%) was yield as slightly yellow oil.

$[\alpha]_D^{20}$= 141.0 (c = 0.54, MeOH)

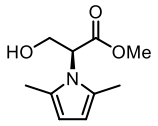
^{1}H-NMR (300 MHz, C_6D_6) δ = 7.06 – 6.92 (m, 3H), 6.81 – 6.73 (m, 2H), 5.92 (s, 2H), 4.54 (dd, *J* = 10.3, 4.6 Hz, 1H), 3.46 (dd, *J* = 13.9, 4.6 Hz, 1H), 3.21 (s, 3H), 3.14 (dd, *J* = 13.8, 10.3 Hz, 1H), 1.88 (s, 6H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6): δ = 171.02, 137.83, 129.69, 128.63, 127.01, 107.41, 59.23, 51.92, 38.05, 13.16 ppm.

IR (ATR) $\tilde{\nu}$ = 2926 (w), 1738 (s), 1522 (w), 1496 (w), 1436 (m), 1398 (s), 1277 (m), 1223 (s), 1169 (m), 1083 (w), 1050 (w), 987 (w), 903 (w), 752 (s), 700 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{16}H_{20}O_2N$ $[M+H]^+$ 258.1489, found 258.1485.

Methyl (*S*)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-3-hydroxypropanoate 2e



According to general procedure 1.: *L*-serine methyl ester hydrochloride **1e** (400 mg, 2.58 mmol, 2 equiv.), hexane-2,5-dione (0.15 mL, 1.29 mmol, 1 equiv.) and triethylamine (0.36 mL, 2.58 mmol, 2 equiv.) in MeOH (5.0 mL) were used. After column chromatography (0 to 50% EtOAc in cyclohexane, linear gradient) the pyrrole **2e** (181 mg, 71%) was obtained as colorless oil.

$[\alpha]_D^{24}$= −53.7 (c = 1.00, MeOH)

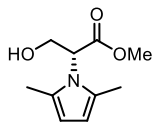
^{1}H-NMR (500 MHz, C_6D_6) δ = 5.91 (s, 2H), 4.60 (t, *J* = 7.0 Hz, 1H), 4.13 (dt, *J* = 12.4, 6.4 Hz, 1H), 3.68 (dt, *J* = 12.2, 6.5 Hz, 1H), 3.15 (s, 3H), 2.29 (t, *J* = 6.3 Hz, 1H), 2.02 (s, 6H) ppm.

^{13}C{^{1}H}-NMR (126 MHz, C_6D_6) δ = 170.74, 128.30, 107.55, 62.33, 59.03, 51.82, 13.13 ppm.

IR (ATR) $\tilde{\nu}$ = 3527 (m), 2942 (w), 2897 (w), 1734 (s), 1718 (s), 1433 (w), 1399 (s), 1314 (m), 1293 (s), 1255 (w), 1200 (s), 1058 (s), 1043 (s), 1024 (w), 984 (s), 903 (w), 805 (w), 760 (s), 741 (m) cm^{-1}.

HR-MS (ESI): Calcd for $C_{10}H_{16}O_3N$ $[M+H]^+$ 198.1125, found 198.1118.

Methyl (*R*)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-3-hydroxypropanoate 2f



According to general procedure 1: *D*-serine methyl ester hydrochloride **1e** (400 mg, 2.58 mmol, 2 equiv.), hexane-2,5-dione (0.15 mL, 1.29 mmol, 1 equiv.) and triethylamine (0.36 mL, 2.58 mmol, 2 equiv.) in MeOH (5.0 mL) were used. After column chromatography (0 to 50% EtOAc in cyclohexane, linear gradient) the pyrrole **2f** (171 mg, 67%) was obtained as colorless oil.

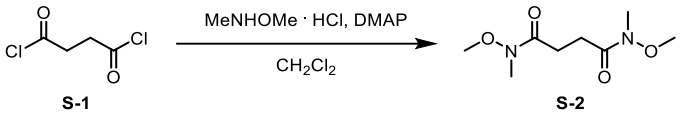
$[\alpha]_D^{24}$= −61.3 (c = 1.00, MeOH)

^{1}H-NMR (500 MHz, C_6D_6) δ = 5.92 (s, 2H), 4.59 (t, J = 7.0 Hz, 1H), 4.12 (dt, *J* = 11.7, 7.0 Hz, 1H), 3.66 (dt, *J* = 11.7, 7.1 Hz, 1H), 3.14 (s, 3H), 2.10 (t, *J* = 7.0 Hz, 1H), 2.01 (s, 6H) ppm.
^{13}C{^{1}H}-NMR (126 MHz, C_6D_6) δ = 170.81, 128.35, 107.61, 62.36, 58.98, 51.80, 13.12 ppm.

IR (ATR) $\tilde{\nu}$ = 3534 (m), 2942 (w), 2897 (w), 1734 (s), 1719 (s), 1433 (w), 1399 (s), 1314 (m), 1293 (s), 1255 (w), 1200 (s), 1058 (s), 1043 (s), 1024 (w), 984 (s), 903 (w), 805 (w), 760 (s), 741 (m) cm^{-1}.

HR-MS (ESI): Calcd for $C_{10}H_{16}O_3N$ $[M+H]^+$ 198.1125, found 198.1117.

N^1,N^4-Dimethoxy-N^1,N^4-dimethylsuccinamide S-2



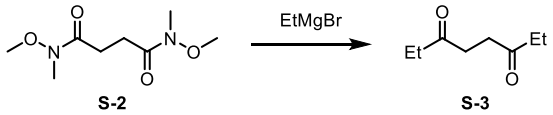
According literature procedure:[4] Succinyl chloride **S-1** (3.6 mL, 32.3 mmol, 1 equiv.) was dissolved in dichloromethane, cooled to –20 °C and treated with *N,O*-dimethyl hydroxylamine hydrochloride (9.45 g, 36.8 96.9 mmol, 3 equiv.), DMAP (395 mg, 3.23 mmol, 0.1 equiv.) and triethyl amine (27 mL, 194 mmol, 6 equiv.). The reaction mixture was quenched by the addition of saturated $NaHCO_3$ solution and extracted with dichloromethane. The combined organic layers were washed with 1 M aq. HCl and brine, dried over magnesium sulfate, filtrated and concentrated *in vacuo* to obtain the Weinreb amide **S-2** (5.60g, 85%), which was used without further purification.

^{1}H-NMR (500 MHz, $CDCl_3$) δ = 3.73 (s, 3H), 3.18 (s, 3H), 2.77 (s, 2H) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$) δ = 173.64, 61.32, 32.32, 26.57 ppm.

The analytical data are in accordance with published data.[4]

Octane-3,6-dione S-3



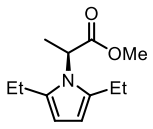
To a solution of Weinreb amide **S-2** (500 mg, 2.45 mmol, 1 equiv.) in diethyl ether (15 mL) was added EtMgBr (3.3 mL, 9.8 mmol, 4 equiv., 3 M) at room temperature. The reaction mixture was stirred for 1h, quenched by the addition of saturated NH_4Cl solution and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over dried over magnesium sulfate, filtrated and concentrated *in vacuo*. The residue was purified by column chromatography (0 to 40% EtOAc in cyclohexane) to yield the diketone **S-3** (195 mg, 56%) as colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$) δ = 2.68 (s, 2H), 2.47 (q, *J* = 7.4 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$) δ = 210.24, 36.07, 35.80, 7.92 ppm.

The analytical data are in accordance with published data.[5]

Methyl (S)-2-(2,5-diethyl-1H-pyrrol-1-yl)propanoate 2g



According to general procedure 1. *L*-Alanine methyl ester hydrochloride **1a** (100 mg, 0.72 mmol, 1 equiv.), triethyl amine (0.20 mL, 1.44 mmol, 2 equiv.) and octane-3,6-dione **S-3** (102 mg, 0.72 mmol, 1 equiv.) in MeOH (1.4 mL) were used. After column chromatography (0 to 40% EtOAc in cyclohexane, linear gradient) the pyrrole **2g** (49.7 mg, 33%) was yield as slightly yellow oil.

^{1}H-NMR (300 MHz, C_6D_6) δ = 6.05 (s, 2H), 4.47 (q, *J* = 7.2 Hz, 1H), 3.22 (s, 3H), 2.38 (ddt, *J* = 17.7, 15.4, 7.7 Hz, 4H), 1.40 (d, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.4 Hz, 6H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 171.92, 133.79, 105.38, 52.21, 51.83, 20.51, 17.74, 13.53 ppm.

Methyl (*S*)-3-((*tert*-butyldimethylsilyl)oxy)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)propanoate 3a

To a stirred solution of alcohol **2e** (3.00 g, 15.2 mmol, 1 equiv.) in dry DMF (20 mL) was added imidazole (1.35 g, 19.8 mmol, 1.3 equiv.) followed by TBSCl (2.98 g, 19.8 mmol, 1.3 equiv.). The reaction mixture was stirred at room temperature for 16h and quenched by the addition of water. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The crude product was purified by column chromatography (0 to 15% EtOAc in cyclohexane, linear gradient) to yield the TBS-protected alcohol **3a** (4.56 g, 96%) as slightly yellow oil.

$[\alpha]_D^{24}$ = −31.1 (c = 1.00, MeOH)

^{1}H-NMR (300 MHz, C_6D_6) δ = 5.97 (s, 2H), 4.69 (dd, *J* = 8.5, 5.3 Hz, 1H), 4.37 (dd, *J* = 10.5, 5.3 Hz, 1H), 3.95 (dd, *J* = 10.5, 8.5 Hz, 1H), 3.18 (s, 3H), 2.13 (s, 6H), 0.88 (s, 9H), -0.05 (s, 3H), -0.10 (s, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 169.93, 128.19, 107.44, 63.27, 59.28, 51.67, 25.94, 18.38, 13.37, -5.63, -5.75 ppm.

IR (ATR) $\tilde{\nu}$ = 2950 (w), 2927 (w), 2891 (w), 2856 (w), 1734 (s), 1402 (m), 1294 (m), 1251 (m), 1212 (m), 1124 (m), 1080 (s), 1046 (w), 1026 (w), 993 (m), 916 (m), 836 (s), 780 (m), 752 (m), 733 (w), 666 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_{16}H_{30}O_3NSi$ $[M+H]^+$ 312.1990 found 312.1979.

Methyl (*R*)-3-((*tert*-butyldimethylsilyl)oxy)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)propanoate 3b

To a stirred solution of alcohol **2f** (729 mg, 3.70 mmol, 1 equiv.) in dry DMF (5 mL) was added imidazole (327 mg, 4.80 mmol, 1.3 equiv.) followed by TBSCl (723 mg, 4.80 mmol, 1.3 equiv.). The reaction mixture was stirred at room temperature for 16h and quenched by the addition of water. The aqueous layer was extracted with ethyl aceteate. The combined organic layers were washed with water and brine, dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The crude product was purified by column chromatography (0 to 15% EtOAc in cyclohexane, linear gradient) to yield the TBS-protected alcohol **3b** (1.06 g, 92%) as colorless oil.

$[\alpha]_D^{24}$= 35.4 (c = 1.00, MeOH)

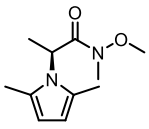
^{1}H-NMR (300 MHz, C_6D_6) δ = 5.97 (s, 2H), 4.69 (dd, *J* = 8.5, 5.3 Hz, 1H), 4.37 (dd, *J* = 10.5, 5.3 Hz, 1H), 3.95 (dd, *J* = 10.5, 8.5 Hz, 1H), 3.18 (s, 3H), 2.13 (s, 6H), 0.88 (s, 9H), -0.05 (s, 3H), -0.10 (s, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 169.93, 128.19, 107.44, 63.27, 59.29, 51.67, 25.94, 18.38, 13.38, -5.63, -5.75 ppm.

IR (ATR) $\tilde{\nu}$ = 2951 (w), 2927 (w), 2892 (w), 2856 (w), 1734 (s), 1402 (m), 1294 (m), 1253 (m), 1212 (m), 1124 (m), 1080 (s), 1046 (w), 1026 (w), 993 (m), 916 (m), 836 (s), 780 (m), 752 (m), 733 (w), 666 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_{16}H_{30}O_3NSi$ $[M+H]^+$ 312.1990 found 312.1980.

(*S*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-*N*-methoxy-*N*-methylpropanamide 4a



According to General Procedure 2. Methyl ester **2a** (4.3 g, 23.7 mmol, 1 equiv.), *N,O*-dimethyl hydroxylamine hydrochloride (3.59 g, 36.8 mmol, 1.55 equiv.) and *i*-PrMgCl (36 mL, 71.1 mmol, 3 equiv., 2 M in THF) in THF (47 mL) were used to yield the Weinreb amide **4a** (4.75 g, 95%) as colorless solid.

$[\alpha]_D^{24}$= −227.5 (c = 1.00, MeOH)

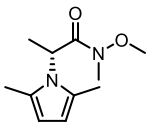
^{1}H-NMR (300 MHz, C_6D_6) δ = 5.90 (s, 2H), 4.73 (q, *J* = 7.1 Hz, 1H), 2.80 (s, 3H), 2.53 (s, 3H), 2.13 (s, 6H), 1.35 (d, *J* = 7.1 Hz, 3H) ppm.

$^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6) δ = 172.55, 127.56, 106.83, 59.89, 51.31, 32.58, 17.45, 13.05 ppm.

IR (ATR) $\tilde{\nu}$ = 2974 (w), 2940 (w), 1656 (s), 1558 (w), 1507 (w), 1457 (m), 1441 (m), 1398 (s), 1296 (m), 1175 (m), 1069 (w), 1020 (w), 981 (s), 790 (m), 746 (s) cm^{-1}.

HR-MS (ESI) Calcd for $C_{11}H_{19}O_2N_2$ $[M+H]^+$ 211.1441, found 211.1431.

(*R*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-*N*-methoxy-*N*-methylpropanamide 4b



According to General Procedure 2. Methyl ester **2b** (1.70 g, 9.36 mmol, 1 equiv), *N,O*-dimethyl hydroxylamine hydrochloride (2.63 g, 14.5 mmol, 1.55 equiv.) and *i*-PrMgCl (14.0 mL, 28.1 mmol, 3 equiv., 2M in THF) in THF (19 mL) were used to yield the Weinreb amide **4b** (1.79 g, 91%) as colorless solid.

$[\alpha]_D^{24}$ = 215.5 (c = 1.00, MeOH)

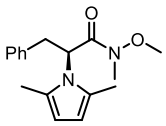
^1H-NMR (300 MHz, C_6D_6) δ = 5.91 (s, 2H), 4.73 (q, *J* = 7.1 Hz, 1H), 2.80 (s, 3H), 2.55 (s, 3H), 2.13 (s, 6H), 1.36 (d, *J* = 7.1 Hz, 3H) ppm.

$^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6) δ = 172.54, 127.58, 106.87, 59.91, 51.34, 32.61, 17.46, 13.06 ppm.

IR (ATR) $\tilde{\nu}$ = 2973 (w), 2940 (w), 1657 (s), 1558 (w), 1507 (w), 1457 (m), 1441 (m), 1398 (s), 1296 (m), 1176 (m), 1069 (w), 1019 (w), 981 (s), 790 (m), 746 (s) cm^{-1}.

HR-MS (ESI) Calcd for $C_{11}H_{19}O_2N_2$ $[M+H]^+$ 211.1441, found 211.1430.

(*S*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-*N*-methoxy-*N*-methyl-3-phenylpropanamide 4c



According to General Procedure 2. Methyl ester **2c** (6.43 g, 25.0 mmol, 1 equiv.), *N,O*-dimethyl hydroxylamine hydrochloride (3.78 g, 38.7 mmol, 1.55 equiv.) and *i*-PrMgCl (37 mL, 75.0 mmol, 3 equiv., 2 M in THF) in THF (50 mL) were used to yield the Weinreb amide **4c** (7.12 g, 99%) as colorless solid.

$[\alpha]_D^{24}$ = −271.2 (c = 1.00, MeOH)

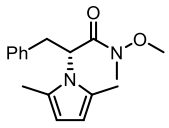
^1H-NMR (500 MHz, C_6D_6) δ = 7.07 – 6.95 (m, 3H), 6.76 (dd, *J* = 7.4, 2.0 Hz, 2H), 5.86 (s, 2H), 4.88 (dd, *J* = 10.5, 4.6 Hz, 1H), 3.42 (dd, *J* = 13.9, 4.6 Hz, 1H), 3.26 (dd, *J* = 13.9, 10.4 Hz, 1H), 2.80 (s, 3H), 2.50 (s, 3H), 1.96 (s, 6H) ppm.

$^{13}C\{^1H\}$-NMR (126 MHz, C_6D_6) δ = 171.87, 138.42, 130.05, 128.47, 128.34, 126.75, 106.88, 59.94, 57.97, 38.13, 32.50, 13.03 ppm.

IR (ATR) $\tilde{\nu}$ = 3034 (w), 2970 (w), 2930 (w), 2891 (w), 1665 (s), 1541 (w), 1456 (w), 1396 (s), 1366 (m), 1295 (m), 1173 (m), 1114 (w), 1080 (w), 1041 (w), 992 (s), 794 (w), 751 (s), 696 (s) cm^{-1}.

HR-MS (ESI) Calcd for $C_{17}H_{23}O_2N_2$ $[M+H]^+$ 287.1754, found 287.1744.

(*R*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-*N*-methoxy-*N*-methyl-3-phenylpropanamide 4d



According to General Procedure 2. Methyl ester **2d** (1.04 g, 4.04 mmol, 1 equiv.), *N,O*-dimethyl hydroxylamine hydrochloride (616 mg, 6,26 mmol, 1.55 equiv.) and *i*-PrMgCl (6.0 mL, 12.1 mmol, 3 equiv., 2 M in THF) in THF (8 mL) were used to yield the Weinreb amide **4d** (1.13 g, 98%) as colorless solid.

$[\alpha]_D^{20}$ = 276.4 (c = 1.00, MeOH)

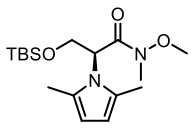
^1H-NMR (300 MHz, C_6D_6) δ = 7.08 – 6.97 (m, 3H), 6.79 – 6.71 (m, 2H), 5.86 (s, 2H), 4.87 (dd, *J* = 10.4, 4.7 Hz, 1H), 3.42 (dd, *J* = 13.9, 4.7 Hz, 1H), 3.27 (dd, *J* = 13.8, 10.4 Hz, 1H), 2.80 (s, 3H), 2.50 (s, 3H), 1.96 (s, 6H) ppm.

$^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6) δ = 171.86, 138.40, 130.05, 128.47, 126.75, 106.87, 59.93, 57.98, 38.12, 32.49, 13.04 ppm.

IR (ATR) $\tilde{\nu}$ = 3034 (w), 2930 (w), 1666 (s), 1455 (w), 1395 (s), 1367 (m), 1294 (m), 1173 (m), 1114 (w), 1079 (w), 1041 (w), 992 (s), 794 (w), 751 (s), 696 (s), 559 (s) cm^{-1}.

HR-MS (ESI) Calcd for $C_{17}H_{23}O_2N_2$ $[M+H]^+$ 287.1754, found 287.1748.

(*S*)-3-((*tert*-Butyldimethylsilyl)oxy)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-*N*-methoxy-*N*-methylpropanamide 4e



According to General Procedure 2. Methyl ester **3a** (6.25 g, 20.1 mmol, 1 equiv.), *N,O*-dimethyl hydroxylamine hydrochloride (3.03 g, 31.1 mmol, 1.55 equiv.) and *i*-PrMgCl (30 mL, 60.3 mmol, 3 equiv., 2 M in THF) in THF (5.8 mL) were used to yield the Weinreb amide **4e** (6.62 g, 97%) as colorless solid.

$[\alpha]_D^{24}$ = –162.6 (c = 1.00, MeOH)

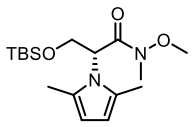
^{1}H-NMR (500 MHz, C_6D_6) δ = 5.89 (s, 2H), 4.95 (dd, *J* = 9.6, 4.9 Hz, 1H), 4.29 (dd, *J* = 10.8, 4.9 Hz, 1H), 4.10 (dd, *J* = 10.8, 9.3 Hz, 1H), 2.76 (s, 3H), 2.55 (s, 3H), 2.24 (s, 6H), 0.88 (s, 10H), -0.05 (s, 3H), -0.09 (s, 3H) ppm.

^{13}C{^{1}H-NMR (126 MHz, C_6D_6) δ = 171.10, 128.61, 106.89, 63.69, 60.03, 57.42, 32.06, 26.04, 18.44, 13.37, -5.60, -5.74 ppm.

IR (ATR) $\tilde{\nu}$ = 2927 (w), 2893 (w), 2855 (w), 1734 (w), 1667 (s), 1541 (w), 1458 (w), 1399 (s), 1386 (m), 1295 (w), 1252 (m), 1136 (m), 1118 (m), 1063 (w), 991 (m), 857 (s), 832 (s), 781 (s), 743 (s), 664 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_{17}H_{33}O_3N_2Si$ $[M+H]^+$ 341.2255 found 341.2244.

(*R*)-3-((*tert*-Butyldimethylsilyl)oxy)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-*N*-methoxy-*N*-methylpropanamide 4f



According to General Procedure 2. Methyl ester **3b** (906 mg, 2.91 mmol, 1 equiv.), *N,O*-dimethyl hydroxylamine hydrochloride (818 mg, 4.51 mmol, 1.55 equiv.) and *i*-PrMgCl (4.4 mL, 8.73 mmol, 3 equiv., 2 M in THF) in THF (5.8 mL) were used to yield the Weinreb amide **4f** (892 mg, 90%) as colorless solid.

$[\alpha]_D^{24}$ = 168.6 (c = 1.00, MeOH)

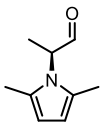
^{1}H-NMR (300 MHz, C_6D_6) δ = 5.91 (s, 2H), 4.96 (dd, *J* = 9.4, 4.9 Hz, 1H), 4.31 (dd, *J* = 10.8, 4.9 Hz, 1H), 4.12 (dd, *J* = 11.0, 9.2 Hz, 1H), 2.75 (s, 3H), 2.53 (s, 3H), 2.25 (s, 6H), 0.89 (s, 10H), -0.04 (s, 3H), -0.08 (s, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 171.10, 128.61, 106.87, 63.68, 60.00, 57.39, 32.03, 26.03, 18.44, 13.39, -5.61, -5.76 ppm.

IR (ATR) $\tilde{\nu}$ = 2927 (w), 2855 (w), 1734 (w), 1667 (s), 1541 (w), 1457 (w), 1399 (s), 1387 (m), 1295 (w), 1252 (m), 1136 (m), 1118 (m), 1064 (w), 991 (m), 857 (s), 833 (s), 780 (s), 744 (s), 663 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_{17}H_{33}O_3N_2Si$ $[M+H]^+$ 341.2255 found 341.2244.

(*S*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)propanal 5a



According to General Procedure 3. Weinreb amide **4a** (1.00 g, 4.76 mmol, 1 equiv.) and DIBAL-H (6.2 mL, 6.19 mmol, 1.3 equiv.,1 M in hexane) in dichloromethane (24 mL) were used to yield the aldehyde **5a** (quant.) as yellow oil.

$[\alpha]^{24}_{D}$ = –18.8 (c = 1.00, MeOH)

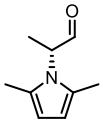
^{1}H-NMR (300 MHz, C_6D_6) δ = 9.16 (s, 1H), 5.96 (s, 2H), 3.85 (q, *J* = 7.0 Hz, 1H), 1.84 (s, 6H), 1.10 (d, *J* = 6.9 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 198.80, 127.34, 107.90, 59.58, 14.55, 13.06 ppm.

IR (ATR) $\tilde{\nu}$ = 2984 (w), 2926 (w), 2812 (w), 1737 (s), 1520 (m), 1444 (m), 1396 (s), 1295 (s), 1200 (w), 1051 (m), 1019 (m), 1003 (m), 853 (m), 754 (s), 714 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_9H_{14}NO$ $[M+H]^+$ 152.1070 found 152.1067.

(*R*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)propanal 5b



According to General Procedure 3. Weinreb amide **4b** (1.40 g, 6.66 mmol, 1 equiv.) and DIBAL-H (8.7 mL, 8.66 mmol, 1.3 equiv.,1 M in hexane) in dichloromethane (33 mL) were used to yield the aldehyde **5b** (quant.) as yellow oil.

$[\alpha]^{24}_{D}$ = 20.8 (c = 1.00, MeOH)

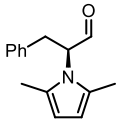
^{1}H-NMR (300 MHz, C_6D_6) δ = 9.18 (s, 1H), 5.96 (s, 2H), 3.87 (q, *J* = 7.1 Hz, 1H), 1.85 (s, 5H), 1.11 (d, *J* = 7.0 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 198.74, 127.35, 107.93, 59.59, 14.55, 13.06 ppm.

IR (ATR) $\tilde{\nu}$ = 2980 (w), 2926 (w), 2812 (w), 1737 (s), 1520 (m), 1444 (m), 1396 (s), 1295 (s), 1200 (w), 1051 (m), 1019 (m), 1003 (m), 853 (m), 753 (s), 714 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_9H_{14}NO$ $[M+H]^+$ 152.1070 found 152.1067.

(*S*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-3-phenylpropanal 5c



According to General Procedure 3. Weinreb amide **4c** (1.12 g, 3.90 mmol, 1 equiv.) and DIBAL-H (5.1 mL, 5.07 mmol, 1 M in hexane, 1.3 equiv.) in dichloromethane (24 mL) were used to yield the aldehyde **5c** (quant.) as yellow oil.

$[\alpha]^{24}_{D}$ = –88.5 (c = 1.00, MeOH)

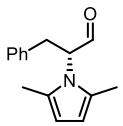
^{1}H-NMR (300 MHz, C_6D_6) δ = 9.20 (s, 1H), 7.04 – 6.92 (m, 3H), 6.68 – 6.59 (m, 2H), 5.91 (s, 2H), 4.02 (dd, *J* = 10.2, 3.9 Hz, 1H), 3.32 (dd, *J* = 13.9, 3.9 Hz, 1H), 2.77 (dd, *J* = 14.0, 10.3 Hz, 1H), 1.65 (s, 6H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 198.07, 137.59, 129.64, 128.63, 126.93, 107.90, 66.28, 35.67, 12.96 ppm.

IR (ATR) $\tilde{\nu}$ = 2930 (w), 2828 (w), 1732 (s), 1601 (w), 1519 (w), 1574 (w), 1454 (m), 1394 (s), 1293 (s), 1248(w), 1071 (w), 1088 (w), 1019 (w), 760 (s), 700 (s), 499 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1383 found 228.1373.

(*R*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-3-phenylpropanal 5d

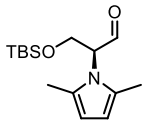


According to General Procedure 3. Weinreb amide **4d** (500 mg, 1.74 mmol, 1 equiv.) and DIBAL-H (2.3 mL, 2.26 mmol, 1 M in hexane, 1.3 equiv.) in dichloromethane (8.7 mL) were used to yield the aldehyde **5d** (quant.) as yellow oil.

^{1}H-NMR (300 MHz, C_6D_6) δ = 9.21 (s, 1H), 7.11 – 6.92 (m, 3H), 6.73 – 6.58 (m, 2H), 5.90 (s, 2H), 4.04 (dd, *J* = 10.2, 3.9 Hz, 1H), 3.32 (dd, *J* = 13.9, 3.9 Hz, 1H), 2.77 (dd, *J* = 13.9, 10.1 Hz, 1H), 1.66 (s, 6H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 198.01, 137.61, 129.64, 128.63, 126.93, 107.93, 66.30, 35.71, 12.96 ppm.

(*S*)-3-((*tert*-Butyldimethylsilyl)oxy)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)propanal 5e



According to General Procedure 3 with slightly modifications. Weinreb amide **4e** (1.13 g, 3.32 mmol, 1 equiv.) and DIBAL-H (4.3 mL, 4.31 mmol, 1.3 equiv., 1 M in hexane) in dichloromethane (17 mL) were used to yield the aldehyde **5e** (quant.) as yellow oil.

$[\alpha]^{24}_{D}$ = −4.2 (c = 1.00, MeOH)

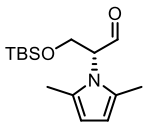
^{1}H-NMR (300 MHz, C_6D_6) δ = 9.17 (s, 1H), 5.96 (s, 2H), 4.30 – 4.16 (m, 2H), 3.82 – 3.68 (m, 1H), 1.96 (s, 6H), 0.85 (s, 10H), -0.11 (s, 3H), -0.16 (s, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 197.79, 107.89, 66.29, 62.09, 25.90, 18.34, 13.27, -5.74, -5.84 ppm.

IR (ATR) $\tilde{\nu}$ = 2955 (w), 2928 (w), 2856 (w), 1735 (m), 1471 (w), 1399 (m), 1295 (w), 1254 (m), 1124 (m), 1101 (m), 938 (w), 835 (s), 777 (s), 754 (s), 688 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_{15}H_{28}NO_2Si$ $[M+H]^+$ 282.1884 found 282.1877.

(*R*)-3-((*tert*-Butyldimethylsilyl)oxy)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)propanal 5f



According to General Procedure 3. Weinreb amide **4f** (1.00 g, 2.94 mmol, 1 equiv.) and DIBAL-H (3.8 mL, 3.82 mmol, 1.3 equiv., 1 M in hexane) in dichloromethane (15 mL) were used to yield the aldehyde **5f** (quant.) as yellow oil.

$[\alpha]^{24}_D$ = 1.3 (c = 1.00, MeOH)

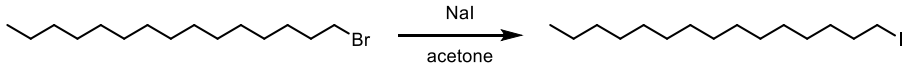
^{1}H-NMR (300 MHz, C_6D_6) δ = 9.18 (s, 1H), 5.95 (s, 1H), 4.35 – 4.16 (m, 2H), 3.83 – 3.69 (m, 1H), 1.96 (s, 6H), 0.84 (s, 8H), -0.13 (d, *J* = 13.9 Hz, 5H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 197.74, 107.92, 66.33, 62.11, 25.91, 18.35, 13.26, -5.73, -5.82 ppm.

IR (ATR) $\tilde{\nu}$ = 2951 (w), 2928 (w), 2856 (w), 1735 (m), 1471 (w), 1399 (m), 1295 (w), 1254 (m), 1124 (m), 938 (w), 835 (s), 777 (s), 753 (s), 668 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_{15}H_{28}NO_2Si$ $[M+H]^+$ 282.1884 found 282.1876.

1-Iodo pentadecane S-4



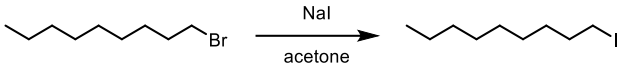
A modified procedure was used:[6] A solution of 1-bromopentadecane (0.5 mL, 500 mg, 1.70 mmol, 1 equiv.) and sodium iodide (765 mg, 5.1 mmol, 3 equiv.) in dry acetone (34 mL, 0.05 M) was stirred at room temperature for 20h. The reaction mixture was quenched by the addition of water and extracted with dichloromethane. The combined organic layers were washed with sat. sodium thiosulfate solution and brine, dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The iodide **S-4** (539 mg, 94%) was obtained as slightly yellow oil and used without further purification.

^{1}H-NMR (500 MHz, $CDCl_3$) δ = 3.19 (t, *J* = 7.0 Hz, 2H), 1.82 (p, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.4 Hz, 2H), 1.26 (s, 22H), 0.88 (t, *J* = 6.9 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$) δ = 33.75, 32.08, 30.68, 29.84, 29.81, 29.77, 29.71, 29.58, 29.51, 28.71, 22.85, 14.27, 7.49 ppm.

The analytical data are in accordance with published data.[7]

1-Iodo nonane S-5



A modified procedure was used:[6] A solution of 1-bromononane (0.32 mL, 352 mg, 1.70 mmol, 1 equiv.) and sodium iodide (765 mg, 5.1 mmol, 3 equiv.) in dry acetone (34 mL, 0.05 M) was stirred at room temperature for 20h. The reaction mixture was quenched by the addition of water and extracted with dichloromethane. The combined organic layers were washed with sat. sodium thiosulfate solution and brine, dried over $MgSO_4$, filtrated and concentrated *in vacuo*. The iodide **S-5** (416 mg, 96%) was obtained as slightly yellow oil and used without further purification.

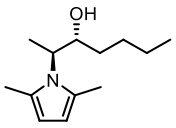
^{1}H-NMR (300 MHz, $CDCl_3$) δ = 3.19 (t, *J* = 7.0 Hz, 2H), 1.82 (p, *J* = 7.1 Hz, 2H), 1.45 – 1.17 (m, 12H), 0.99 – 0.78 (m, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$) δ = 33.72, 31.98, 30.66, 29.53, 29.37, 28.70, 22.81, 14.26, 7.61 ppm.

2.3 Nucleophilic Addition and CBS reduction

2.3.1 Addition of Grignard reagents

(2*S*,3*R*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)octan-3-ol 6



According to General Procedure 4. Aldehyde **5a** (100.0 mg, 0.66 mmol, 1 equiv.) and butyl magnesium bromide (0.8 mL, 0.79 mmol, 1.2 equiv., 1 M in THF) in THF (2.2 mL) were used to yield the *anti*-amino alcohol **6a** (83.0 mg, 60%) and *syn*-amino alcohol **6b** (21.0 mg, 15%) as slightly yellow oils.

<u>*anti*-amino alcohol **6a**</u>

^{1}H-NMR (300 MHz, C_6D_6) δ = 6.00 (s, 2H), 3.77 (dq, *J* = 8.8, 7.0 Hz, 1H), 3.60 (tdd, *J* = 8.6, 5.8, 2.5 Hz, 1H), 2.12 (s, 6H), 1.34 (d, *J* = 7.0 Hz, 3H), 1.31 – 1.02 (m, 6H), 1.00 (d, *J* = 5.9 Hz, 1H), 0.79 (t, *J* = 7.0 Hz, 3H) ppm.

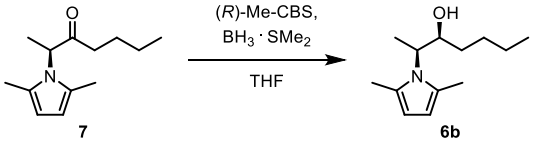
^{13}C{^{1}H}-NMR (126 MHz, C_6D_6) δ = 128.35, 107.68, 74.33, 56.87, 33.98, 28.13, 22.78, 17.26, 14.22 ppm.

<u>*syn*-amino alcohol **6b**</u>

^{1}H-NMR (500 MHz, C_6D_6) δ = 5.98 (s, 2H), 3.82 (dq, *J* = 9.6, 7.1 Hz, 1H), 3.67 (tt, *J* = 9.2, 2.4 Hz, 1H), 2.14 (s, 6H), 1.66 – 1.54 (m, 2H), 1.42 – 1.13 (m, 4H), 1.03 (d, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (126 MHz, C_6D_6) δ = 107.62, 73.63, 57.41, 33.85, 27.85, 23.24, 17.00, 14.39 ppm.

(2*S*,3*S*)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)heptan-3-ol 6b



To a solution of (*R*)-(–)-2-methyl-CBS-oxazaborolidine (66.5 mg, 0.24 mmol, 0.5 equiv.) in THF (2.4 mL) was added $BH_3 \cdot SMe_2$ (0.31 mL, 0.63 mmol, 1.3 equiv., 2 M solution in THF) at 0 °C, and the solution was stirred for 15 min. A solution of ketone **7** (100 mg, 0.48 mmol, 1.0 equiv.) in THF (1.4 mL) was then added dropwise at 0 °C, and the resulting mixture was stirred at this temperature for 1h. The cooling bath was removed and the reaction mixture was stirred additional 2h, quenched by the addition of MeOH and concentrated under reduced pressure. The crude residue was purified by column chromatography (0 to 20% EtOAc in cyclohexane, linear gradient) to yield the *syn*-alcohol **6b** (97 mg, 97%) as single diastereomer.

$[\alpha]_D^{20} = -25.2$ (c = 1.00, MeOH)

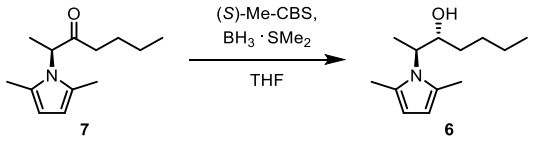
^{1}H-NMR (300 MHz, C_6D_6) δ = 5.98 (d, *J* = 1.5 Hz, 2H), 3.82 (dq, *J* = 9.5, 7.1 Hz, 1H), 3.75 – 3.59 (m, 1H), 2.14 (s, 6H), 1.71 – 1.52 (m, 2H), 1.50 – 1.17 (m, 5H), 1.03 (d, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 107.59, 73.65, 57.41, 33.87, 27.85, 23.23, 17.01, 14.37 ppm.

IR (ATR) $\tilde{\nu}$ = 3455 (br, w), 2953 (m), 2860 (m), 1519 (w), 1443 (m), 1394 (s), 1291 (s), 1198 (w), 1104 (w), 999 (m), 912 (w), 749 (s) cm^{-1}.

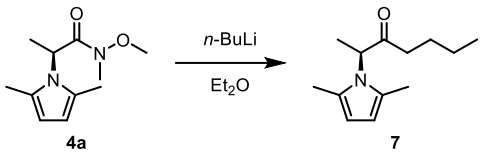
HR-MS (ESI): Calcd for $C_{13}H_{24}NO$ $[M+H]^+$ 210.1852 found 210.1848.

(2*S*,3*R*)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)heptan-3-ol 6



To a solution of (*S*)-(+)-2-methyl-CBS-oxazaborolidine (66.5 mg, 0.24 mmol, 0.5 equiv.) in THF (2.4 mL) was added $BH_3 \cdot SMe_2$ (0.31 mL, 0.63 mmol, 1.3 equiv., 2 M solution in THF) at 0 °C, and the solution was stirred for 15 min. A solution of ketone **8** (100 mg, 0.48 mmol, 1.0 equiv.) in THF (1.4 mL) was then added dropwise at 0 °C, and the resulting mixture was stirred at this temperature for 1h. The cooling bath was removed and the reaction mixture was stirred additional 5h, quenched by the addition of MeOH and concentrated under reduced pressure. The crude residue was purified by column chromatography (0 to 20% EtOAc in cyclohexane, linear gradient) to yield the *anti*-amino alcohol **6a** (76.4 mg, 76%) and *syn*-amino alcohol **6b** (15.7 mg, 16%) as slightly yellow oils.

(*S*)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)heptan-3-one 7



Weinreb amide **4a** (500 mg, 2.38 mmol 1 equiv.) was dissolved in dry diethyl ether (8.0 mL), cooled to –78 °C, treated with *n*-BuLi (1.24 mL, 3.09 mmol, 1.3 equiv., 2.5 M in hexane) and stirred for 1h. The reaction mixture was quenched by the addition of saturated ammonium chloride solution and extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over magnesium sulfate, filtrated and concentrated *in vacuo*. The crude residue was purified by column chromatography (0 to 30% EtOAc in cyclohexane, linear gradient) to yield the ketone **7** (424 mg, 86%) as slightly yellow oil.

$[\alpha]_D^{20}$ = –169.8 (c = 1.00, MeOH)

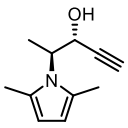
^{1}H-NMR (300 MHz, C_6D_6) δ = 5.98 (s, 2H), 4.06 (q, *J* = 7.0 Hz, 1H), 2.09 – 1.94 (m, 1H), 1.94 (s, 6H), 1.78 (dt, *J* = 17.6, 7.1 Hz, 1H), 1.53 – 1.38 (m, 2H), 1.33 (d, *J* = 7.0 Hz, 3H), 1.15 – 0.98 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 207.36, 127.37, 107.92, 59.10, 38.20, 25.91, 22.50, 15.56, 14.04, 13.25 ppm.

IR (ATR) $\tilde{\upsilon}$ = 2957 (m), 2930 (m), 2871 (m), 1719 (s), 1520 (w), 1443 (m), 1396 (s), 1295 (s), 1065 (m), 1020 (w), 752 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{13}H_{22}NO$ $[M+H]^+$ 208.1696 found 208.1692.

(3*R*,4*S*)-4-(2,5-Dimethyl-1*H*-pyrrol-1-yl)pent-1-yn-3-ol 8



According to General Procedure 4. Aldehyde **5a** (50.0 mg, 0.33 mmol, 1 equiv.) and ethynyl magnesium bromide (0.79 mL, 0.40 mmol, 1.2 equiv. 0.5 M in THF) in THF (1.1 mL) were used to yield the amino alcohol **8** (46.0 mg, 79%, 4:1 dr) as slightly yellow oil (NMR assignment of *anti*-isomer).

$[\alpha]_D^{20}$ = –26.0 (c = 0.33, MeOH)

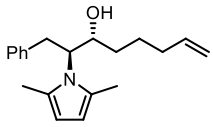
^{1}H-NMR (300 MHz, $CDCl_3$) δ = 5.99 (s, 2H), 4.26 (d, *J* = 8.5 Hz, 1H), 4.07 (dq, *J* = 8.4, 7.0 Hz, 1H), 2.15 (s, 6H), 2.02 (s, 1H), 1.83 (d, *J* = 2.1 Hz, 1H), 1.30 (d, *J* = 7.1 Hz, 3H) ppm.

$^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$) δ = 128.62, 106.79, 82.35, 74.46, 65.32, 56.13, 16.32, 14.53 ppm.

IR (ATR) $\tilde{\nu}$ = 3386 (br, m), 3240 (m), 2923 (m), 1520 (w), 1445 (w), 1393 (s), 1293 (s), 1065 (m), 1015 (s), 755 (s), 656 (m) cm^{-1}.

HR-MS (ESI): Calcd for $C_{11}H_{16}NO$ $[M+H]^+$ 178.1226 found 178.1224.

(2*S*,3*R*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-1-phenyloct-7-en-3-ol 9



According to General Procedure 4. Aldehyde **5c** (50.0 mg, 0.22 mmol, 1 equiv.) and 4-pentenylmagnesium bromide (0.53 mL, 0.26 mmol, 1.2 equiv. 0.5 M in THF) in THF (0.7 mL) were used to yield the amino alcohol **9** (54.0 mg, 83%, 4:1 dr) as slightly yellow oil (NMR assignment of *anti*-isomer).

$[\alpha]_D^{20}$ = –82.1 (c = 1.00, MeOH)

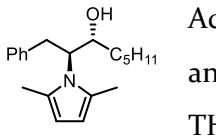
^1H-NMR (500 MHz, $CDCl_3$) δ = 7.23 – 7.12 (m, 4H), 6.94 – 6.86 (m, 3H), 5.82 – 5.71 (m, 3H), 5.57 (d, *J* = 3.2 Hz, 1H), 5.02 – 4.92 (m, 2H), 4.19 (td, *J* = 9.5, 2.9 Hz, 1H), 3.91 (ddd, *J* = 10.7, 9.4, 3.5 Hz, 1H), 3.41 (dd, *J* = 13.6, 3.5 Hz, 1H), 3.11 (dd, *J* = 13.5, 10.9 Hz, 2H), 2.41 (s, 3H), 1.64 (s, 3H), 1.62 – 1.36 (m, 3H), 1.26 – 1.14 (m, 2H) ppm.

$^{13}C\{^1H\}$-NMR (126 MHz, $CDCl_3$) δ = 139.12, 138.54, 130.20, 129.18, 128.37, 126.40, 114.80, 108.35, 105.05, 73.26, 64.14, 37.71, 33.63, 33.47, 24.89, 15.58, 13.13 ppm.

IR (ATR) $\tilde{\nu}$ = 3434 (br, w), 2927 (m), 2859 (w), 1495 (w), 1454 (w), 1394 (s), 1291 (m), 995 (w), 910 (m), 751 (s), 699 (s), 604 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_{20}H_{28}NO$ $[M+H]^+$ 298.2165 found 298.2161.

(2*S*,3*R*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-1-phenyloctan-3-ol 10



According to General Procedure 4. Aldehyde **5c** (200.0 mg, 0.89 mmol, 1 equiv.) and pentyl magnesium bromide (0.54 mL, 1.07 mmol, 1.2 equiv. 2 M in Et_2O) in THF (2.9 mL) were used to yield the amino alcohol **10** (185 mg, 69%, 4:1 dr) as slightly yellow oil (NMR assignment of *anti*-isomer).

$[\alpha]_D^{20}$ = –72.9 (c = 0.82, MeOH)

^1H-NMR (500 MHz, $CDCl_3$) δ = 7.23 – 7.11 (m, 3H), 6.91 – 6.83 (m, 2H), 5.79 (d, *J* = 3.3 Hz, 1H), 5.55 (d, *J* = 3.2 Hz, 1H), 4.22 – 4.10 (m, 1H), 3.89 (ddd, *J* = 10.6, 9.5, 3.5 Hz, 1H), 3.40 (dd, *J* = 13.6,

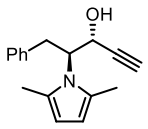
3.5 Hz, 1H), 3.10 (dd, *J* = 13.6, 10.8 Hz, 1H), 2.40 (s, 3H), 1.74 – 1.67 (m, 2H), 1.62 (s, 3H), 1.34 – 1.10 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H) ppm.

$^{13}C\{^1H\}$-NMR (126 MHz, $CDCl_3$) δ = 139.21, 130.25, 129.22, 128.39, 126.41, 108.31, 105.02, 73.46, 64.18, 37.80, 34.10, 31.67, 25.28, 22.77, 15.59, 14.10, 13.16 ppm.

IR (ATR) $\tilde{\nu}$ = 3446 (br, w), 2926 (m), 2856 (m), 1518 (w), 1495 (w), 1455 (w), 1394 (s), 1291 (m), 1028 (m), 927 (w), 750 (s), 699 (s), 550 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_{20}H_{30}NO$ $[M+H]^+$ 300.2322 found 300.2318.

(3*R*,4*S*)-4-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-5-phenylpent-1-yn-3-ol 11



According to General Procedure 4. Aldehyde **5c** (50.0 mg, 0.22 mmol, 1 equiv.) and ethynylmagnesium bromide (0.53 mL, 0.26 mmol, 1.2 equiv. 0.5 M in THF) in THF (0.7 mL) were used to yield the amino alcohol **11** (37.3 mg, 67%, 3:1 dr) as slightly yellow oil (NMR assignment of *anti*-isomer).

$[\alpha]_D^{20}$ = –120.4 (c = 0.13, MeOH)

^1H-NMR (500 MHz, $CDCl_3$) δ = 7.24 – 7.13 (m, 4H), 6.98 – 6.88 (m, 3H), 5.82 (d, *J* = 3.2 Hz, 1H), 5.61 (d, *J* = 3.2 Hz, 1H), 4.86 (dd, *J* = 9.1, 2.1 Hz, 1H), 4.27 (ddd, *J* = 10.5, 9.1, 3.9 Hz, 1H), 3.39 (dd, *J* = 13.8, 3.9 Hz, 1H), 3.18 (dd, *J* = 13.7, 10.6 Hz, 1H), 2.47 (s, 4H), 2.39 (d, *J* = 2.1 Hz, 2H), 1.77 (s, 3H) ppm.

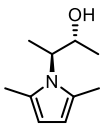
$^{13}C\{^1H\}$-NMR (126 MHz, $CDCl_3$) δ = 138.39, 130.79, 129.14, 128.50, 126.66, 108.55, 105.15, 82.19, 74.84, 64.37, 63.15, 36.86, 15.61, 13.16 ppm.

IR (ATR) $\tilde{\nu}$ = 3391 (br, w), 3282 (w), 2925 (w), 1520 (w), 1495 (w), 1454 (m), 1393 (s), 1291 (s), 1041 (m), 937 (m), 752 (s), 655 (m), 555 (w), 513 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_{17}H_{20}NO$ $[M+H]^+$ 254.1539 found 254.1536.

2.3.2 Addition of lithium reagents

(2*R*,3*S*)-3-(2,5-Dimethyl-1*H*-pyrrol-1-yl)butan-2-ol 12



According to General Procedure 5A. Methyl lithium (0.24 mL, 0.39 mmol, 1.6 M in Et_2O, 1 equiv.) in dry diethyl ether (1.3 mL) and aldehyde **5a** (70 mg, 0.46 mmol, 1.2 equiv.) in dry diethyl ether (1.5 mL) were used to yield the alcohol **12** (54 mg, 83%, >20:1 dr) as colorless oil.

$[\alpha]_D^{24}$= 2.8 (c = 1.00, MeOH)

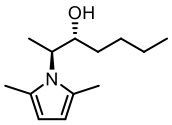
^{1}H-NMR (300 MHz, C_6D_6) δ = 5.96 (s, 2H), 3.83 – 3.64 (m, 2H), 2.09 (s, 6H), 1.33 (d, *J* = 6.7 Hz, 3H), 1.11 (s, br, 1H), 0.77 (d, *J* = 5.8 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 107.63, 70.67, 57.74, 20.86, 17.23, 14.55 ppm.

IR (ATR) $\tilde{\nu}$ = 3445 (br, w), 2971 (m), 2928 (m), 1519 (w), 1456 (w), 1395 (s), 1373 (m), 1293 (s), 1153 (w), 1094 (m), 1014 (m), 1000 (m), 975 (w), 909 (m), 830 (w), 747 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{10}H_{18}NO$ $[M+H]^+$ 168.1383 found 168.1379.

(2*S*,3*R*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)heptan-3-ol 13



According to General Procedure 5A. *n*-Butyl lithium (0.16 mL, 0.39 mmol, 2.5 M in hexane, 1 equiv.) in dry diethyl ether (1.3 mL) and aldehyde **5a** (70 mg, 0.46 mmol, 1.2 equiv.) in dry diethyl ether (1.5 mL) were used to yield the alcohol **13** (72 mg, 88%, >20:1 dr) as slightly yellow oil.

$[\alpha]_D^{24}$= 20.0 (c = 1.00, MeOH)

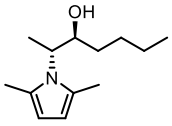
^{1}H-NMR (500 MHz, C_6D_6) δ = 5.98 (s, 2H), 3.76 (p, *J* = 7.1 Hz, 1H), 3.60 (q, *J* = 8.8 Hz, 1H), 2.12 (s, 6H), 1.34 (d, *J* = 7.1 Hz, 3H), 1.29 – 1.20 (m, 1H), 1.18 – 0.99 (m, 6H), 0.79 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (126 MHz, C_6D_6) δ = 128.35, 74.29, 56.86, 33.94, 28.14, 22.78, 17.22, 14.24 ppm.

IR (ATR) $\tilde{\nu}$ = 3446 (br, w), 2931 (m), 2871 (m), 1519 (w), 1457 (m), 1395 (s), 1293 (s), 1200 (w), 1113 (w), 1088 (w), 999 (s), 900 (w), 749 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{13}H_{24}NO$ $[M+H]^+$ 210.1852 found 210.1845.

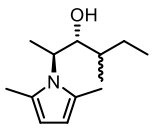
(2*R*,3*S*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)heptan-3-ol S-6



According to General Procedure 5A. *n*-Butyl lithium (0.12 mL, 0.30 mmol, 2.5 M in hexane, 1 equiv.) in dry diethyl ether (1.0 mL) and aldehyde **5b** (54.0 mg, 0.36 mmol, 1.2 equiv.) in dry diethyl ether (1.2 mL) were used to yield the alcohol **S-6** (52.1 mg, 83%, >20:1 dr) as slightly yellow oil.

^{1}H-NMR (300 MHz, C_6D_6) δ = 5.99 (s, 2H), 3.77 (dq, *J* = 8.9, 7.0 Hz, 1H), 3.67 – 3.50 (m, 1H), 2.12 (s, 6H), 1.34 (d, *J* = 7.0 Hz, 3H), 1.26 – 0.88 (m, 6H), 0.79 (t, *J* = 6.8 Hz, 3H) ppm.
^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 107.41, 74.28, 56.85, 33.94, 28.12, 22.77, 17.25, 14.24 ppm.

(2*S*,3*R*,4*rac*)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-4-methylhexan-3-ol 14



According to General Procedure 5A. *sec*-Butyl lithium (0.22 mL, 0.28 mmol, 1.3 M in cyclohexane/hexane, 1 equiv.) in dry diethyl ether (0.9 mL) and aldehyde **5a** (50.0 mg, 0.33 mmol, 1.2 equiv.) in dry diethyl ether (1.1 mL) were used to yield the alcohol **14** (45.7 mg, 78%, >20:1 dr) as slightly yellow oil.

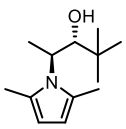
$[\alpha]_D^{20}$ = 7.4 (c = 0.36, MeOH)

^{1}H-NMR (300 MHz, C_6D_6) δ = 6.00 (d, *J* = 1.7 Hz, 4H), 4.07 – 3.95 (m, 1H), 3.95 – 3.85 (m, 1H), 3.72 (ddd, *J* = 9.3, 6.1, 1.9 Hz, 1H), 3.48 (ddd, *J* = 8.0, 6.0, 3.8 Hz, 1H), 2.14 (s, 12H), 1.51 – 1.33 (m, 2H), 1.30 (d, *J* = 1.5 Hz, 3H), 1.27 (d, *J* = 1.4 Hz, 3H), 1.12 (ddd, *J* = 37.9, 12.2, 5.9 Hz, 4H), 0.95 (d, *J* = 6.0 Hz, 1H), 0.83 (d, *J* = 6.1 Hz, 1H), 0.78 – 0.66 (m, 12H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 107.82, 78.59, 75.75, 54.18, 53.99, 36.22, 35.40, 30.24, 27.52, 22.79, 18.00, 16.89, 16.50, 14.59, 12.28, 12.04, 11.83 ppm.

IR (ATR) $\tilde{\nu}$ = 3466 (br, w), 2961 (m), 2927 (m), 1518 (w), 1456 (m), 1394 (s), 1293 (s), 1213 (w), 1111 (w), 988 (s), 749 (s) cm^{-1}.
HR-MS (ESI): Calcd for $C_{13}H_{24}NO$ $[M+H]^+$ 210.1852 found 210.1848.

(3*R*,4*S*)-4-(2,5-dimethyl-1*H*-pyrrol-1-yl)-2,2-dimethylpentan-3-ol 15



According to General Procedure 5A. *tert*-Butyl lithium (0.14 mL, 0.28 mmol, 1.3 M in cyclohexane/hexane, 1 equiv.) in dry diethyl ether (0.9 mL) and aldehyde **5a** (50.0 mg, 0.33 mmol, 1.2 equiv.) in dry diethyl ether (1.1 mL) were used to yield the alcohol **15** (48.7 mg, 78%, >20:1 dr) as slightly yellow oil.

$[\alpha]_D^{20}$ = −25.3 (c = 0.32, MeOH)

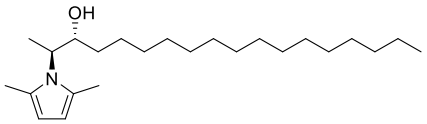
^{1}H-NMR (300 MHz, C_6D_6) δ = 6.01 (s, 2H), 4.10 (qd, *J* = 7.1, 5.4 Hz, 1H), 3.37 (t, *J* = 5.7 Hz, 1H), 2.34 (s, 2H), 2.11 (s, 3H), 1.28 (d, *J* = 7.1 Hz, 3H), 1.07 (d, *J* = 5.9 Hz, 1H), 0.74 (s, 10H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 108.73, 106.77, 80.56, 52.85, 35.63, 26.19, 17.77, 15.68, 13.74 ppm.

IR (ATR) $\tilde{\nu}$ = 3481 (br, w), 2954 (m), 2869 (m), 1517 (w), 1478 (m), 1392 (s), 1294 (s), 994 (s), 749 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{13}H_{24}NO$ $[M+H]^+$ 210.1852 found 210.1849.

(2*S*,3*R*)-2-(2,5-dDimethyl-1*H*-pyrrol-1-yl)octadecan-3-ol 16



According to General Procedure 5C. 1-Iodopentadecane **S-4** (50.0 mg, 0.15 mmol, 1.0 equiv.) and *t*-BuLi (0.16 mL, 0.30 mmol, 2.0 equiv., 1.9M in pentane) in dry diethyl ether (1.5 mL) and aldehyde **5a** (27.2 mg, 0.18 mmol, 1.2 equiv.) in dry diethyl ether (0.6 mL, 0.3 M) were used to yield the alcohol **16** (37.8 mg, 69%, >20:1 dr) as slightly yellow oil.

$[\alpha]_D^{24}$ = −15.7 (c = 0.31, MeOH)

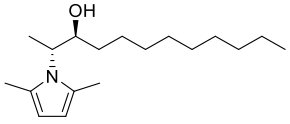
^{1}H-NMR (300 MHz, C_6D_6) δ = 5.99 (s, 2H), 3.78 (dq, *J* = 8.9, 6.9 Hz, 1H), 3.64 (td, *J* = 8.7, 8.3, 4.7 Hz, 1H), 2.13 (s, 6H), 1.41 – 1.01 (m, 31H), 0.91 (t, *J* = 6.6 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 107.68, 74.37, 56.92, 34.35, 32.37, 30.22, 30.17, 30.10, 29.86, 26.06, 23.15, 17.38, 14.39 ppm.

IR (ATR) $\tilde{\nu}$ = 3447 (br, w), 2922 (s), 2852 (s), 1733 (w), 1508 (m), 1457 (m), 1395 (m), 1294 (m), 1213 (w), 1092 (w), 1012 (m), 998 (m), 855 (m), 749 (s), 722 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_{24}H_{46}NO$ $[M+H]^+$ 364.3574 found 364.3558.

(2*S*,3*R*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)dodecan-3-ol 17



According to General Procedure 5C. 1-Iodononane **S-5** (70.0 mg, 0.28 mmol, 1.0 equiv.) and *t*-BuLi (0.29 mL, 0.55 mmol, 2.0 equiv., 1.9M in pentane) in dry diethyl ether (2.8 mL) and aldehyde **5b** (50.0 mg, 0.33 mmol, 1.2 equiv.) in dry diethyl ether (1.1 mL) were used to yield the alcohol **17** (56.0 mg, 72%, >20:1 dr) as slightly yellow oil.

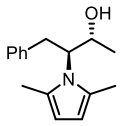
$[\alpha]_D^{24}$ = –15.8 (c = 0.24, MeOH)

^{1}H-NMR (300 MHz, C_6D_6) δ = 5.99 (s, 2H), 3.79 (dq, *J* = 8.9, 7.0 Hz, 1H), 3.65 (t, *J* = 8.7 Hz, 1H), 2.14 (s, 7H), 1.36 (d, *J* = 6.9 Hz, 4H), 1.31 – 0.97 (m, 16H), 0.91 (t, *J* = 7.0, 6.3 Hz, 3H) ppm. ^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 107.69, 74.40, 56.90, 34.32, 32.33, 30.05, 30.00, 29.84, 29.77, 26.05, 23.12, 17.30, 14.39 ppm.

IR (ATR) $\tilde{\nu}$ = 3447 (br, w), 2922 (s), 2852 (s), 1733 (w), 1508 (m), 1457 (m), 1395 (m), 1294 (m), 1213 (w), 1092 (w), 1012 (m), 998 (m), 855 (m), 749 (s), 722 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_{18}H_{34}NO$ $[M+H]^+$ 280.2635 found 280.2632.

(2*R*,3*S*)-3-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-4-phenylbutan-2-ol 18



According to General Procedure 5A. Methyl lithium (0.16 mL, 0.26 mmol, 1.6 M in Et_2O, 1 equiv.) in dry diethyl ether (0.9 mL) and aldehyde **5c** (70 mg, 0.31 mmol, 1.2 equiv.) in dry diethyl ether (1.0 mL) were used to yield the alcohol **18** (53 mg, 84%, >20:1 dr) as slightly yellow oil.

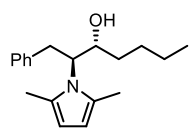
$[\alpha]_D^{24}$ = –98.5 (c = 0.94, MeOH)

^{1}H-NMR (300 MHz, C_6D_6) δ = 7.12 – 6.95 (m, 3H), 6.93 – 6.80 (m, 2H), 6.03 (dd, *J* = 3.3, 1.0 Hz, 1H), 5.81 (dd, *J* = 3.4, 1.0 Hz, 1H), 4.01 – 3.83 (m, 1H), 3.72 (ddd, *J* = 11.0, 9.5, 3.0 Hz, 1H), 3.31 (dd, *J* = 13.4, 3.0 Hz, 1H), 2.93 (dd, *J* = 13.5, 11.2 Hz, 1H), 2.20 (s, 3H), 1.58 (s, 3H), 0.91 (d, *J* = 5.6 Hz, 1H), 0.77 (d, *J* = 6.1 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 139.67, 130.06, 129.49, 128.55, 126.56, 125.62, 109.23, 105.96, 69.31, 65.49, 37.67, 21.09, 15.53, 13.30 ppm.
IR (ATR) $\tilde{\nu}$ = 3446 (br, w), 3027 (w), 2968 (w), 2930 (w), 2370 (w), 2312 (w), 1730 (w), 1507 (w), 1455 (m), 1394 (s), 1293 (s), 1099 (m), 1012 (m), 973 (w), 923 (m), 876 (m), 750 (s), 697 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{16}H_{22}NO$ $[M+H]^+$ 244.1696 found 244.1688.

(2*S*,3*R*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-1-phenylheptan-3-ol 19



According to General Procedure 5A. *n*-Butyl lithium (0.10 mL, 0.26 mmol, 2.5 M in hexane, 1 equiv.) in dry diethyl ether (0.9 mL) and aldehyde **5c** (70 mg, 0.31 mmol, 1.2 equiv.) in dry diethyl ether (1.0 mL) were used to yield the alcohol **19** (61 mg, 82%, >20:1 dr) as slightly yellow oil.

$[\alpha]_D^{24}$= −70.4 (c = 1.00, MeOH)

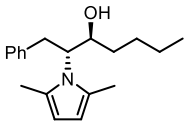
^{1}H-NMR (300 MHz, C_6D_6) δ = 7.11 – 6.99 (m, 3H), 6.94 – 6.87 (m, 2H), 6.05 (d, *J* = 3.1 Hz, 1H), 5.82 (d, *J* = 3.3 Hz, 1H), 3.86 – 3.74 (m, 2H), 3.34 (dd, *J* = 13.5, 2.5 Hz, 1H), 2.96 (dd, *J* = 13.4, 10.5 Hz, 1H), 2.25 (s, 3H), 1.59 (s, 3H), 1.33 – 0.87 (m, 7H), 0.79 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 139.72, 130.08, 129.56, 128.56, 126.58, 125.70, 109.28, 106.03, 72.94, 64.61, 37.90, 33.95, 27.90, 22.73, 15.63, 14.27, 13.29 ppm.

IR (ATR) $\tilde{\nu}$ = 3366 (br, w), 3028 (w), 2955 (w), 2931 (w), 2859 (w), 2373 (w), 2316 (w), 1735 (w), 1519 (m), 1456 (m), 1394 (s), 1291 (m), 1214 (w), 1124 (w), 1028 (m), 998 (w), 968 (w) 928 (w), 901 (w), 750 (s), 699 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{19}H_{28}NO$ $[M+H]^+$ 286.2165 found 286.2155.

(2*R*,3*S*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-1-phenylheptan-3-ol S-7

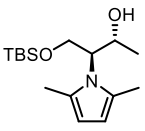


According to General Procedure 5A. *n*-Butyl lithium (0.11 mL, 0.28 mmol, 2.5 M in hexane, 1 equiv.) in dry diethyl ether (0.9 mL) and aldehyde **5d** (76.4 mg, 0.34 mmol, 1.2 equiv.) in dry diethyl ether (1.1 mL) were used to yield the alcohol **S-7** (65 mg, 81%, >20:1 dr) as slightly yellow oil.

^{1}H-NMR (500 MHz, C_6D_6) δ = 7.11 – 6.98 (m, 3H), 6.94 – 6.86 (m, 2H), 6.05 (d, *J* = 2.7 Hz, 1H), 5.82 (d, *J* = 3.3 Hz, 1H), 3.85 – 3.73 (m, 2H), 3.34 (dd, *J* = 13.5, 2.5 Hz, 1H), 2.96 (dd, *J* = 13.4, 10.5 Hz, 1H), 2.25 (s, 3H), 1.59 (s, 3H), 1.35 – 0.88 (m, 7H), 0.79 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (126 MHz, C_6D_6) δ = 139.71, 130.08, 129.56, 128.56, 126.57, 125.67, 109.28, 106.01, 72.89, 64.60, 37.89, 33.93, 27.89, 22.72, 15.64, 14.28, 13.30 ppm.

(2*R*,3*S*)-4-((*tert*-Butyldimethylsilyl)oxy)-3-(2,5-dimethyl-1*H*-pyrrol-1-yl)butan-2-ol 20



According to General Procedure 5A. Methyl lithium (0.09 mL, 0.15 mmol, 1.6 M in Et_2O, 1 equiv.) in dry diethyl ether (0.5 mL) and aldehyde **5e** (50 mg, 0.18 mmol, 1.2 equiv.) in dry diethyl ether (0.6 mL) were used to yield the alcohol **20** (34 mg, 76%, >20:1 dr) as slightly yellow oil.

$[\alpha]_D^{24}$= 4.1 (c = 0.32, MeOH)

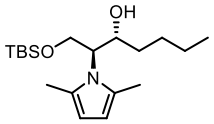
^{1}H-NMR (500 MHz, C_6D_6) δ = 5.94 (s, 2H), 4.23 (dq, *J* = 12.3, 6.1, 6.1 Hz, 1H), 4.16 (dd, *J* = 10.1, 7.1 Hz, 1H), 3.98 (dt, *J* = 9.4, 7.0 Hz, 1H), 3.80 (dd, *J* = 10.1, 6.9 Hz, 1H), 2.63 (s, 1H), 2.13 (s, 3H), 2.09 (s, 3H), 0.93 (d, *J* = 6.2 Hz, 3H), 0.87 (s, 8H), -0.06 (s, 3H), -0.08 (s, 3H) ppm.

$^{13}C\{^1H\}$-NMR (126 MHz, C_6D_6) δ = 128.35, 109.03, 106.63, 68.88, 65.13, 63.74, 30.22, 25.94, 20.79, 18.29, 15.16, 13.75, -5.58, -5.66 ppm.

IR (ATR) $\tilde{\nu}$ = 3443 (br, w), 2955 (m), 2927 (m), 2855 (m), 2374 (w), 2316 (w), 1734 (w), 1520 (w), 1397 (m), 1295 (m), 1254 (m), 1108 (s), 1049 (m), 1014 (m), 987 (w), 937 (w), 880 (w), 834 (s), 776 (s), 749 (s), 666 (m) cm^{-1}.

HR-MS (ESI): Calcd for $C_{16}H_{32}NO_2Si$ $[M+H]^+$ 298.2197 found 298.2189.

(2*S*,3*R*)-1-((*tert*-Butyldimethylsilyl)oxy)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)heptan-3-ol 21



According to General Procedure 5A. *n*-Butyl lithium (0.06 mL, 0.15 mmol, 2.5 M in hexane, 1 equiv.) in dry diethyl ether (0.5 mL) and aldehyde **5e** (50 mg, 0.18 mmol, 1.2 equiv.) in dry diethyl ether (0.6 mL) were used to yield the alcohol **21** (46 mg, 90%, >20:1 dr) as slightly yellow oil.

$[\alpha]_D^{20}$ = 6.1 (c = 0.23, MeOH)

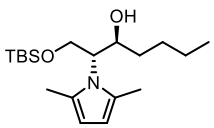
^1H-NMR (500 MHz, C_6D_6) δ = 5.95 (s, 2H), 4.18 (dd, *J* = 10.1, 7.0 Hz, 1H), 4.12 (dq, *J* = 7.5, 4.5, 3.1 Hz, 1H), 4.04 (dt, *J* = 9.3, 6.8 Hz, 1H), 3.81 (dd, *J* = 10.1, 6.7 Hz, 1H), 2.60 (d, *J* = 3.6 Hz, 1H), 2.15 (s, 6H), 1.52 – 1.07 (m, 6H), 0.89 (s, 9H), 0.82 (t, *J* = 7.3 Hz, 3H), -0.04 (s, 3H), -0.07 (s, 3H) ppm.

$^{13}C\{^1H\}$-NMR (126 MHz, C_6D_6) δ = 128.35, 109.05, 106.71, 72.30, 65.31, 62.75, 34.08, 30.22, 27.68, 25.96, 22.84, 18.30, 15.26, 14.30, 13.77, -5.57, -5.64 ppm.

IR (ATR) $\tilde{\nu}$ = 3447 (br, w), 2955 (m), 2927 (m), 2855 (m), 2377 (w), 2320 (w), 1734 (w), 1520 (w), 1396 (m), 1295 (m), 1253 (m), 1114 (m), 1066 (m), 1006 (w), 984 (w), 835 (s), 776 (s), 749 (s), 666 (m) cm^{-1}.

HR-MS (ESI): Calcd for $C_{19}H_{38}NO_2Si$ $[M+H]^+$ 340.2666 found 340.2656.

(2*R*,3*S*)-1-((*tert*-Butyldimethylsilyl)oxy)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)heptan-3-ol S-8

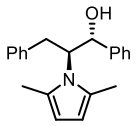


According to General Procedure 5A. *n*-Butyl lithium (0.04 mL, 0.09 mmol, 2.5 M in hexane, 1 equiv.) in dry diethyl ether (0.3 mL) and aldehyde **5f** (30.0 mg, 0.11 mmol, 1.2 equiv.) in dry diethyl ether (0.4 mL) were used to yield the alcohol **S-8** (25.4 mg, 83%, >20:1 dr) as slightly yellow oil.

^{1}H-NMR (500 MHz, C_6D_6) δ = 5.97 (s, 2H), 4.18 (dd, *J* = 10.1, 7.1 Hz, 1H), 4.13 (td, *J* = 8.8, 3.4 Hz, 1H), 4.04 (dt, *J* = 9.4, 6.9 Hz, 1H), 3.81 (dd, *J* = 10.1, 6.7 Hz, 1H), 2.15 (s, 2H), 1.56 – 1.43 (m, 1H), 1.42 – 1.07 (m, 5H), 0.89 (s, 9H), 0.82 (t, *J* = 7.3 Hz, 3H), -0.04 (s, 3H), -0.07 (s, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 128.35, 109.05, 106.71, 72.29, 65.34, 62.75, 34.04, 30.22, 27.66, 25.92, 22.81, 18.30, 15.26, 14.30, 13.77, -5.57, -5.61 ppm.

(1*R*,2*S*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-1,3-diphenylpropan-1-ol 22



A solution of bromobenzene (29 µL, 0.28 mmol, 1 equiv.) in dry diethyl ether (0.9 mL) was treated with *n*-butyl lithium (0.11 mL, 0.28 mmol, 2.5 M in pentane, 1 equiv.) at 0 °C and stirred for 1h. Then the reaction mixture was cooled to –78 °C and a solution of aldehyde **5c** (70 mg, 0.31 mmol, 1.1 equiv.) in dry diethyl ether (1.0 mL) was added. The reaction mixture was stirred at –78 °C for 1h, quenched by the addition of saturated ammonium chloride solution and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The crude residue was purified by column chromatography (0 to 40% EtOAc in cyclohexane, linear gradient) to yield the alcohol **22** (54 mg, 63%, 7:1 dr).

$[\alpha]_D^{24}$ = –44.2 (c = 0.17, MeOH)

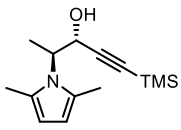
^{1}H-NMR (500 MHz, C_6D_6) δ = 7.08 – 6.88 (m, 10H), 5.99 (d, *J* = 3.2 Hz, 1H), 5.58 (d, *J* = 3.2 Hz, 1H), 4.76 (dd, *J* = 9.7, 3.1 Hz, 1H), 4.24 – 4.15 (m, 1H), 3.55 (dd, *J* = 13.8, 3.3 Hz, 1H), 3.19 (dd, *J* = 13.8, 11.3 Hz, 1H), 2.44 (s, 3H), 1.39 (d, *J* = 3.4 Hz, 1H), 1.29 (s, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 142.76, 139.66, 129.43, 128.58, 128.35, 126.53, 126.24, 109.44, 105.58, 74.93, 65.09, 37.01, 16.22, 12.86 ppm.

IR (ATR) $\tilde{\nu}$ = 3446 (br, w), 3029 (w), 2924 (w), 1716 (w), 1519 (m), 1455 (m), 1229 (w), 1081 (w), 1042 (m), 1002 (w), 974 (w), 926 (w), 845 (w), 749 (s), 697 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{21}H_{24}NO$ $[M+H]^+$ 306.1852 found 306.1843.

(3*R*,4*S*)-4-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-1-(trimethylsilyl)pent-1-yn-3-ol 23



According to General Procedure 5B. TMS-acetylene (56 µL, 0.39 mmol, 1 equiv.) and *n*-butyl lithium (0.16 mL, 0.39 mmol, 2.5 M in hexane, 1 equiv.) in dry diethyl ether (1.3 mL) and aldehyde **5a** (70 mg, 0.46 mmol, 1.2 equiv.) in dry diethyl ether (1.5 mL) were used to yield the alcohol **23** (77 mg, 79%, >20:1 dr) as slightly yellow oil.

$[\alpha]_D^{24}$ = –19.7 (c = 1.00, MeOH)

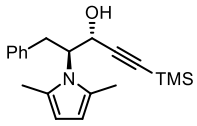
^{1}H-NMR (300 MHz, C_6D_6) δ = 5.95 (s, 2H), 4.36 (d, *J* = 8.2 Hz, 1H), 4.12 (dq, *J* = 8.6, 7.1 Hz, 1H), 2.17 (s, 6H), 1.58 (s, br, 1H), 1.35 (d, *J* = 7.1 Hz, 3H), 0.09 (s, 9H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 107.56, 105.14, 90.53, 66.02, 56.46, 16.65, 14.68, -0.28 ppm.

IR (ATR) $\tilde{\nu}$ = 3446 (br, w), 2959 (w), 2894 (w), 1733 (w), 1395 (m), 1294 (m), 1073 (m), 1015 (m), 840 (s), 757 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{14}H_{24}NOSi$ $[M+H]^+$ 250.1622 found 250.1614.

(3*R*,4*S*)-4-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-5-phenyl-1-(trimethylsilyl)pent-1-yn-3-ol 24



According to General Procedure 5B. TMS-acetylene (56 µL, 0.39 mmol, 1 equiv.) and *n*-butyl lithium (0.16 mL, 0.39 mmol, 2.5 M in hexane, 1 equiv.) in dry diethyl ether (1.3 mL) and aldehyde **5c** (98 mg, 0.43 mmol, 1.1 equiv.) in dry diethyl ether (1.5 mL) were used to yield the alcohol **24** (96 mg, 76%, 9:1 dr) as slightly yellow oil.

$[\alpha]_D^{24}$ = –103.8 (c = 0.31, MeOH)

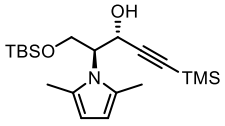
^{1}H-NMR (300 MHz, C_6D_6) δ = 7.07 – 6.92 (m, 3H), 6.94 – 6.82 (m, 2H), 6.00 (d, *J* = 3.3 Hz, 1H), 5.80 (d, *J* = 3.3 Hz, 1H), 4.53 (dd, *J* = 9.6, 6.1 Hz, 1H), 4.22 – 4.07 (m, 1H), 3.23 (dd, *J* = 13.6, 3.3 Hz, 1H), 2.96 (dd, *J* = 13.7, 11.1 Hz, 1H), 2.24 (s, 3H), 1.77 (s, 3H), 1.65 (d, *J* = 1.8 Hz, 1H), 0.06 (s, 9H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 139.09, 129.43, 128.62, 126.71, 109.22, 105.83, 104.72, 90.96, 64.84, 63.92, 36.97, 15.60, 13.37, -0.33 ppm.

IR (ATR) $\tilde{\nu}$ = 3446 (br, w), 3029 (w), 2958 (w), 2898 (w), 2377 (w), 2316 (w), 2174 (w), 1731 (w), 1541 (w), 1454 (w), 1395 (s), 1293 (m), 1250 (s), 1081 (w), 1040 (m), 927 (w), 841 (s), 751 (s), 699 (s), 664 (m) cm^{-1}.

HR-MS (ESI): Calcd for $C_{20}H_{28}NOSi$ $[M+H]^+$ 326.1935 found 326.1924.

(3*R*,4*S*)-5-((*tert*-Butyldimethylsilyl)oxy)-4-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1-(trimethylsilyl)pent-1-yn-3-ol 25



According to General Procedure 5B. TMS-acetylene (21 µL, 0.15 mmol, 1 equiv.) and *n*-butyl lithium (0.06 mL, 0.15 mmol, 2.5 M in hexane, 1 equiv.) in dry diethyl ether (0.5 mL) and aldehyde **5e** (50 mg, 0.18 mmol, 1.2 equiv.) in dry diethyl ether (0.6 mL) were used to yield the alcohol **25** (49 mg, 86%, 19:1 dr) as slightly yellow oil.

$[\alpha]_D^{19}$= −4.2 (c = 0.11, MeOH)

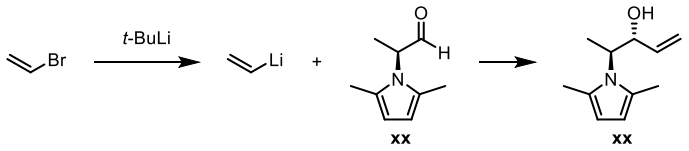
^{1}H-NMR (500 MHz, C_6D_6) δ = 5.94 (s, 2H), 4.74 (dd, *J* = 9.2, 4.4 Hz, 1H), 4.35 (ddd, *J* = 9.3, 7.5, 5.9 Hz, 1H), 4.12 (dd, *J* = 10.4, 5.9 Hz, 1H), 3.84 (dd, *J* = 10.4, 7.5 Hz, 1H), 2.29 (d, *J* = 5.0 Hz, 1H), 2.22 (s, 6H), 0.86 (s, 9H), 0.08 (s, 9H), -0.07 (s, 3H), -0.10 (s, 3H) ppm.

^{13}C{^{1}H}-NMR (126 MHz, C_6D_6) δ = 128.35, 107.61, 104.56, 90.99, 64.03, 63.78, 63.03, 30.23, 25.95, 18.32, 14.40, -0.29, -5.53, -5.59 ppm.

IR (ATR) $\tilde{\nu}$ = 2923 (s), 2853 (m), 1733 (w), 1457 (w), 1249 (m), 1107 (m), 839 (s), 776 (w), 758 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_{19}H_{38}NO_2Si$ $[M+H]^+$ 340.2666 found 340.2656.

(3*R*,4*S*)-4-(2,5-dimethyl-1*H*-pyrrol-1-yl)pent-1-en-3-ol 26



To a solution of vinyl bromide (0.43 mL, 0.43 mmol, 1 equiv., 1M in THF) in THF (1.4 mL) was added *t*-BuLi (0.45 mL, 0.86 mmol, 2 equiv., 1.9 M in pentane) at –78 °C and the reaction mixture was stirred for 1h. A solution of aldehyde **5a** (78.5 mg, 0.52 mmol, 1.2 equiv.) in THF (1.7 mL) was added, stirred at –78 °C for 1h, quenched by the addition of saturated ammonium chloride solution and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo.* The crude residue was purified by column chromatography (0 to 40% EtOAc in cyclohexane) to yield the alcohol **26** (55.3 mg, 72%, 4:1 dr) as slightly yellow oil.

$[\alpha]_D^{20}$= 28.3 (c = 0.58, MeOH)

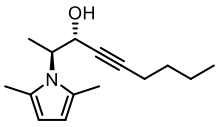
^{1}H-NMR (300 MHz, C_6D_6) δ = 5.98 (s, 2H), 5.45 (ddd, *J* = 17.2, 10.5, 4.9 Hz, 1H), 5.07 (dt, *J* = 17.2, 1.7 Hz, 1H), 4.83 (dt, *J* = 10.6, 1.6 Hz, 1H), 4.12 – 4.00 (m, 1H), 3.86 (tq, *J* = 8.9, 7.0 Hz, 1H), 2.11 (s, 6H), 1.36 (d, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 5.0 Hz, 1H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 138.79, 114.92, 107.70, 74.81, 56.56, 17.24, 14.67 ppm.

IR (ATR) $\tilde{\nu}$ = 3423 (br, w), 2977 (m), 2926 (m), 1519 (w), 1443 (m), 1394 (s), 1293 (s), 1128 (w), 993 (s), 925 (m), 867 (w), 750 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{11}H_{18}NO$ $[M+H]^+$ 180.1383 found 180.1381.

(2*S*,3*R*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)non-4-yn-3-ol 27



According to General Procedure 5B. Hexyne (45 µL, 0.39 mmol, 1 equiv.) and *n*- butyl lithium (0.16 mL, 0.39 mmol, 2.5 M in hexane, 1 equiv.) in dry diethyl ether (1.3 mL) and aldehyde **5a** (70 mg, 0.46 mmol, 1.2 equiv.) in dry diethyl ether (1.5 mL) were used to yield the alcohol **27** (74 mg, 81%, 20:1 dr) as slightly yellow oil.

$[\alpha]_D^{19}$= −71.2 (c = 0.11, MeOH)

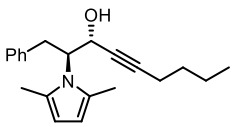
^{1}H-NMR (300 MHz, C_6D_6) δ = 5.98 (s, 2H), 4.44 (d, *J* = 8.7 Hz, 1H), 4.12 (dq, *J* = 8.5, 7.1 Hz, 1H), 2.20 (s, 6H), 1.88 (td, *J* = 6.8, 2.0 Hz, 2H), 1.48 (s, 1H), 1.38 (d, *J* = 7.1 Hz, 3H), 1.27 – 1.08 (m, 4H), 0.76 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) δ = 107.51, 86.48, 79.70, 65.95, 56.95, 30.78, 22.01, 18.53, 16.76, 14.66, 13.71 ppm.

IR (ATR) $\tilde{\nu}$ = 3445 (br, w), 2956 (m), 2929 (m), 2870 (w), 2377 (w), 2312 (w), 2232 (w), 1716 (w), 1519 (w), 1456 (m), 1396 (s), 1294 (s), 1146 (w), 1200 (w), 1012 (s), 747 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{15}H_{24}NO$ $[M+H]^+$ 234.1852 found 234.1845.

(2*S*,3*R*)-2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-1-phenylnon-4-yn-3-ol 28



According to General Procedure 5B. Hexyne (45 µL, 0.39 mmol, 1 equiv.) and *n*- butyl lithium (0.16 mL, 0.39 mmol, 2.5 M in hexane, 1 equiv.) in dry diethyl ether (1.3 mL) and aldehyde **5c** (98 mg, 0.43 mmol, 1.1 equiv.) in dry diethyl ether (1.5 mL) were used to yield the alcohol **28** (103 mg, 85%, 19:1 dr) as slightly yellow oil.

$[\alpha]_D^{24}$= −107.1 (c = 0.39, MeOH)

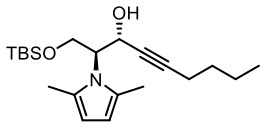
^{1}H-NMR (500 MHz, C_6D_6) δ = 7.07 – 6.95 (m, 3H), 6.91 – 6.84 (m, 2H), 6.01 (d, *J* = 3.2 Hz, 1H), 5.81 (d, *J* = 3.2 Hz, 1H), 4.64 (ddt, *J* = 9.8, 5.9, 2.1 Hz, 1H), 4.15 (ddd, *J* = 11.1, 9.4, 3.3 Hz, 1H), 3.31 (dd, *J* = 13.6, 3.3 Hz, 1H), 2.99 (dd, *J* = 13.6, 11.1 Hz, 1H), 2.29 (s, 3H), 1.84 (td, *J* = 6.7, 2.0 Hz, 2H), 1.76 (s, 3H), 1.46 (d, *J* = 5.9 Hz, 1H), 1.21 – 1.07 (m, 4H), 0.74 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (126 MHz, C_6D_6) δ = 139.23, 129.52, 128.60, 128.35, 126.67, 109.13, 105.77, 86.92, 79.34, 64.82, 64.34, 37.31, 30.73, 21.88, 18.47, 15.59, 13.68, 13.32 ppm.

IR (ATR) $\tilde{\nu}$ = 3446 (br, w), 3029 (w), 2956 (w), 2930 (w), 2870 (w), 2377 (w), 2312 (w), 2233 (w), 1735 (w), 1456 (m), 1395 (s), 1293 (m), 1228 (w), 1146 (w), 1030 (s), 1000 (w), 966 (w), 928 (w), 749 (s), 699 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{21}H_{28}NO$ $[M+H]^+$ 310.2165 found 310.2156.

(2*S*,3*R*)-1-((*tert*-Butyldimethylsilyl)oxy)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)non-4-yn-3-ol 29



According to General Procedure 5B. Hexyne (17 µL , 0.15 mmol, 1.0 equiv.) and *n*-butyl lithium (0.06 mL, 0.15 mmol, 2.5 M in pentane, 1 equiv.) in dry diethyl ether (0.5 mL) and aldehyde **5e** (50.0 mg, 0.18 mmol, 1.2 equiv.) in dry diethyl ether (0.6 mL) were used to yield the alcohol **29** (41.3 mg, 76%, 10:1 dr) as slightly yellow oil.

$[\alpha]_D^{20}$ = −25.9 (c = 0.28, MeOH)

^{1}H-NMR (500 MHz, C_6D_6) δ = 5.97 (s, 2H), 4.82 (ddt, *J* = 9.2, 4.5, 2.1 Hz, 1H), 4.34 (ddd, *J* = 9.3, 7.5, 5.7 Hz, 1H), 4.14 (dd, *J* = 10.4, 5.7 Hz, 1H), 3.86 (dd, *J* = 10.4, 7.5 Hz, 1H), 2.26 (s, 6H), 2.12 (d, *J* = 5.0 Hz, 1H), 1.91 – 1.83 (m, 2H), 1.25 – 1.10 (m, 4H), 0.88 (s, 9H), 0.76 (t, *J* = 7.2 Hz, 3H), -0.05 (s, 3H), -0.08 (s, 3H) ppm.

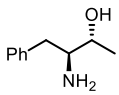
^{13}C{^{1}H}-NMR (126 MHz, C_6D_6) δ = 128.36, 86.84, 79.15, 63.98, 63.80, 63.43, 30.74, 25.96, 21.92, 18.52, 13.73, -5.56, -5.63 ppm.

IR (ATR) $\tilde{\nu}$ = 2922 (s), 2852 (s), 1728 (s), 1516 (w), 1462 (m), 1238 (s), 1070 (w), 822 (w), 721 (w) cm^{-1}.

HR-MS (ESI): Calcd for $C_{21}H_{38}NO_2Si$ $[M+H]^+$ 364.2666 found 364.2658.

2.3 Deprotection

(2*R*,3*S*)-3-Amino-4-phenylbutan-2-ol 30



According to General Procedure 6. Alcohol **18** (30.0 mg, 0.12 mmol, 1 equiv.), hydroxylamine hydrochloride (86.0 mg, 1.23 mmol, 10 equiv.) in ethanol and water (0.8 mL, 2:1) were used to yield the amino alcohol. The residue was redissolved in a small amount of water, washed with diethyl ether, neutralized and extracted with dichloromethane to obtained the free amino alcohol **30** (19.0 mg, 96%, >20:1 dr) as slightly yellow solid.

$[\alpha]_D^{20} = -32.8$ (c = 0.05, MeOH)

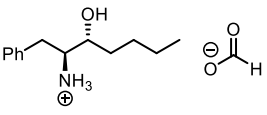
^{1}H-NMR (300 MHz, CD_3OD) δ = 7.43 – 7.24 (m, 5H), 3.97 (qd, *J* = 6.5, 3.3 Hz, 1H), 3.49 (ddd, *J* = 9.1, 6.2, 3.2 Hz, 1H), 3.01 (dd, *J* = 14.3, 6.1 Hz, 1H), 2.86 (dd, *J* = 14.3, 8.7 Hz, 1H), 1.25 (d, *J* = 6.5 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, CD_3OD) δ = 137.33, 130.25, 130.08, 128.36, 66.77, 59.27, 34.88, 17.75 ppm.

IR (ATR) $\tilde{\nu}$ = 3346 (m), 2910 (m), 1604 (m), 1496 (m), 1455 (m), 1106 (w), 1049 (w), 740 (m), 700 (m) cm^{-1}.

HR-MS (ESI): Calcd for $C_{10}H_{16}NO$ $[M+H]^+$ 166.1226 found 166.1225.

(2*S*,3*R*)-3-Hydroxy-1-phenylheptan-2-aminium formate 31



According to General Procedure 6. Alcohol **19** (30.0 mg, 0.11 mmol, 1 equiv.), hydroxylamine hydrochloride (73.0 mg, 1.05 mmol, 10 equiv.) in ethanol and water (2.1 mL, 2:1) were used to yield the amino alcohol **31** (25.2 mg, 95%, >20:1 dr) as slightly yellow solid.

$[\alpha]_D^{23} = -13.38$ (c = 0.10, MeOH)

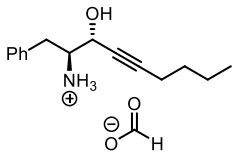
^{1}H-NMR (500 MHz, CD_3OD) δ = 8.44 (s, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 3H), 3.76 (dd, *J* = 9.0, 3.2 Hz, 1H), 3.47 (ddd, *J* = 8.9, 5.5, 3.0 Hz, 1H), 3.04 (dd, *J* = 14.5, 5.7 Hz, 1H), 2.83 (dd, *J* = 14.4, 9.1 Hz, 1H), 1.52 (dp, *J* = 26.8, 8.9 Hz, 3H), 1.35 (ddp, *J* = 21.3, 10.0, 6.3, 5.6 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (126 MHz, CD_3OD) δ = 169.10, 137.52, 130.31, 130.11, 128.39, 71.28, 58.78, 34.33, 32.94, 29.28, 23.57, 14.34 ppm.

IR (ATR) $\tilde{\nu}$ = 3277 (m), 2929 (w), 2856 (w), 2751 (w), 1636 (w), 1578 (m), 1539 (s), 1498 (w), 1393 (s), 1352 (m), 1051 (w), 775 (m), 746 (m), 698 (m), 666 (m) cm^{-1}.

HR-MS (ESI): Calcd for $C_{13}H_{22}NO$ $[M+H]^+$ 208.1696 found 208.1688.

(2*S*,3*R*)-3-Hydroxy-1-phenylnon-4-yn-2-aminium formate 32



According to General Procedure 6. Alcohol **28** (30.0 mg, 0.11 mmol, 1 equiv.), hydroxylamine hydrochloride (67.0 mg, 0.97 mmol, 10 equiv.) in ethanol and water (1.3 mL, 2:1) were used to yield the amino alcohol **32** (22 mg, 82%, 19:1 dr) as yellow oil.

$[\alpha]_D^{23}$= 40.3 (c = 0.22, MeOH)

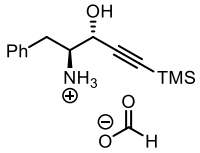
^{1}H-NMR (300 MHz, CD_3OD) δ = 8.49 (s, 1H), 7.43 – 7.21 (m, 6H), 4.44 (dt, *J* = 3.8, 2.0 Hz, 1H), 3.50 (td, *J* = 7.5, 3.5 Hz, 1H), 3.09 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.97 (dd, *J* = 14.0, 7.4 Hz, 1H), 2.33 (td, *J* = 6.9, 2.0 Hz, 2H), 1.64 – 1.41 (m, 4H), 0.96 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (126 MHz, CD_3OD) δ = 169.68, 136.98, 130.25, 130.05, 128.48, 90.07, 76.80, 62.36, 58.53, 36.33, 31.72, 23.06, 19.12, 13.94 ppm.

IR (ATR) $\tilde{\nu}$ = 2962 (w), 2932 (w), 2066 (w), 1576 (s), 1496 (w), 1455 (m), 1346 (m), 1119 (w), 1051 (m), 978 (m), 764 (w), 739 (m), 699 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{15}H_{22}NO$ $[M+H]^+$ 232.1696 found 232.1688.

(2*S*,3*R*)-3-Hydroxy-1-phenyl-5-(trimethylsilyl)pent-4-yn-2-aminium formate 33



According to General Procedure 6. Alcohol **24** (40.0 mg, 0.12 mmol, 1 equiv.), hydroxylamine hydrochloride (85.0 mg, 1.23 mmol, 10 equiv.) in ethanol and water (2.5 mL, 2:1) were used to yield the amino alcohol **33** (32.0 mg, 91%, 9:1 dr) as yellow oil.

$[\alpha]_D^{23}$= 39.1 (c = 0.07, MeOH)

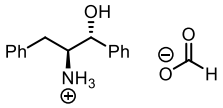
^{1}H-NMR (300 MHz, CD_3OD) δ = 8.50 (s, 1H), 7.42 – 7.23 (m, 6H), 4.49 (dd, *J* = 3.6, 0.8 Hz, 1H), 3.54 (td, *J* = 7.4, 3.6 Hz, 1H), 3.13 (dd, *J* = 14.1, 7.3 Hz, 1H), 2.99 (dd, *J* = 14.4, 7.5 Hz, 1H), 0.23 (s, 9H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, CD_3OD) δ = 169.86, 136.99, 130.26, 130.04, 128.47, 102.71, 93.84, 62.63, 58.03, 36.18, -0.22 ppm.

IR (ATR) $\tilde{\nu}$ = 2956 (w), 2172 (w), 1567 (s), 1496 (w), 1455 (w), 1375 (m), 1344 (m), 1249 (m), 1069 (m), 1032 (m), 975 (w), 841 (s), 760 (m), 741 (m), 698 (s) cm^{-1}.

HR-MS (ESI): Calcd for $C_{14}H_{22}NOSi$ $[M+H]^+$ 248.1465 found 248.1457.

(1*R*,2*S*)-1-Hydroxy-1,3-diphenylpropan-2-aminium formate 34



According to General Procedure 6. Alcohol **22** (30.0 mg, 0.10 mmol, 1 equiv.), hydroxylamine hydrochloride (68.0 mg, 0.98 mmol, 10 equiv.) in ethanol and water (2.0 mL, 2:1) were used to yield the amino alcohol **34** (21.6 mg, 81%, dr = 7:1) as slightly brown solid.

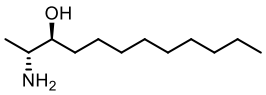
$[\alpha]_D^{23}$= −25.7 (c = 0.08, MeOH)

^{1}H-NMR (300 MHz, CD_3OD) δ = 8.50 (s, 1H), 7.54 – 7.10 (m, 10H), 5.06 (d, *J* = 3.5 Hz, 1H), 3.72 (ddd, *J* = 8.8, 5.1, 3.5 Hz, 1H), 3.31 (dt, *J* = 3.4, 1.6 Hz, 1H), 2.85 – 2.71 (m, 2H) ppm.
^{13}C{^{1}H}-NMR (75 MHz, CD_3OD) δ = 170.10, 141.24, 137.53, 130.23, 130.03, 129.69, 129.17, 128.26, 127.37, 73.32, 59.54, 34.18 ppm.

IR (ATR) $\tilde{\upsilon}$ = 1645 (w), 1578 (m), 1541 (m), 1496 (w), 1393 (m), 1355 (w), 775 (w), 757 (m), 744 (m), 699 (s), 669 (m) cm^{-1}.

HR-MS (ESI): Calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1383 found 228.1375.

(2*R*,3*S*)-2-Aminododecan-3-ol 35



According to General Procedure 6. Alcohol **17** (50.0 mg, 0.18 mmol, 1 equiv.), hydroxylamine hydrochloride (68.0 mg, 0.98 mmol, 10 equiv.) in ethanol and water (3.6 mL, 2:1) were used to yield the amino alcohol. The residue was redissolved in a small amount of water, washed with diethyl ether, neutralized and extracted with dichloromethane to obtained the free amino alcohol **35** (30.0 mg, 83%, >20:1 dr) as slightly yellow solid.

$[\alpha]_D^{23}$= −4.5 (c = 0.09, MeOH)

[Lit:[8] $[\alpha]_D^{23}$= -4.5 (c = 1.5, MeOH) Lit:[9] $[\alpha]_D^{25}$= -4.3 (c = 0.001, MeOH)]

^{1}H-NMR (300 MHz, CD_3OD) δ = 3.48 (dt, *J* = 7.8, 3.8 Hz, 1H), 2.90 (qd, *J* = 6.6, 3.8 Hz, 1H), 1.59 – 1.27 (m, 16H), 1.09 (d, *J* = 6.6 Hz, 3H), 0.92 (t, *J* = 7.0, 6.3 Hz, 2H) ppm.
^{13}C{^{1}H}-NMR (75 MHz, CD_3OD) δ = 75.46, 52.24, 33.98, 33.07, 30.78, 30.76, 30.72, 30.45, 27.20, 23.73, 16.08, 14.42 ppm.

IR (ATR) $\tilde{\upsilon}$ = 3333 (w), 2918 (s), 2850 (s), 1614 (w), 1580 (s), 1550 (w), 1483 (m), 1370 (s), 1310 (w), 1087 (s), 818 (m) cm^{-1}.

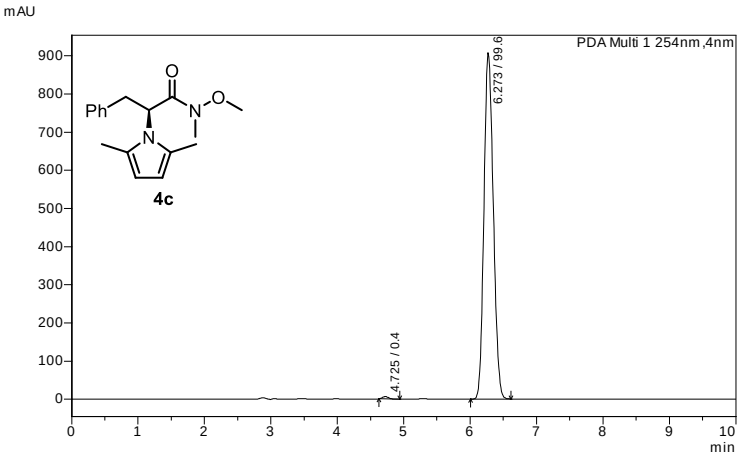
HR-MS (ESI): Calcd for $C_{12}H_{28}NO$ $[M+H]^+$ 202.2165 found 202.2157.

2.5 Determination of Enantiomeric Excess

Method A: eluent: 10% *i*-PrOH in heptane, 1.0 mL/min, column: Lux® 5 µm cellulose-1 (250 x 4.6 mm)

Method B: eluent: 5% *i*-PrOH in heptane, 1.0 mL/min, column: Lux® 5 µm cellulose-1 (250 x 4.6 mm)

Method C: eluent: 3% *i*-PrOH in heptane, 1.0 mL/min, column: Lux® 5 µm cellulose-1 (250 x 4.6 mm)

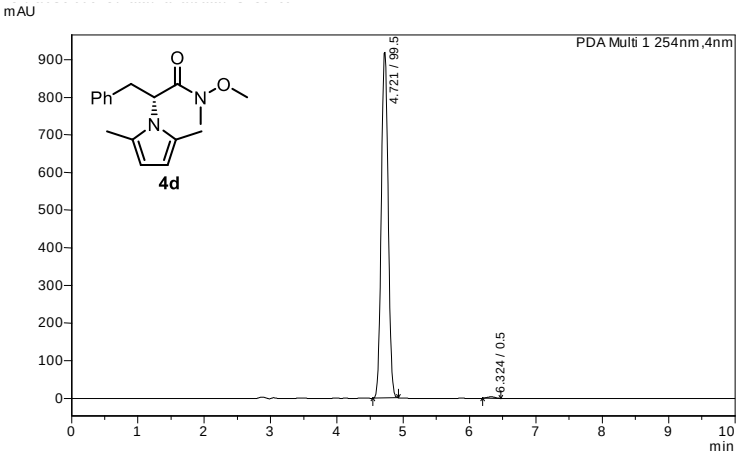


4c

method A

Peak	RT [min]	Area	Area [%]
1	4.7	36075	0.4
2	6.3	8869922	99.6

>99% ee

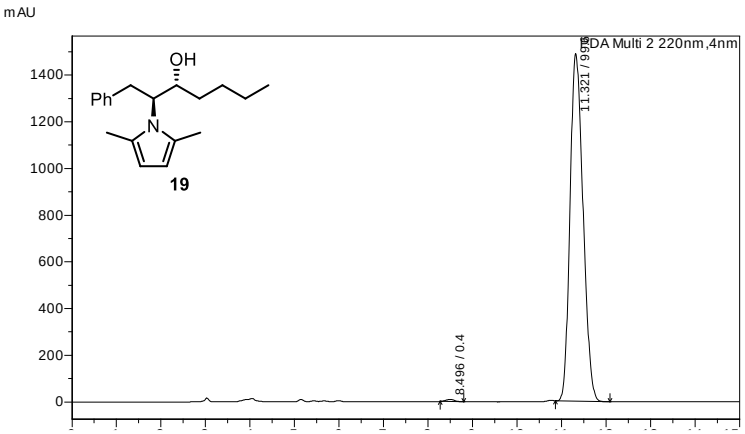


4d

method A

Peak	RT [min]	Area	Area [%]
1	4.7	6589599	99.5
2	6.3	32217	0.5

99% ee

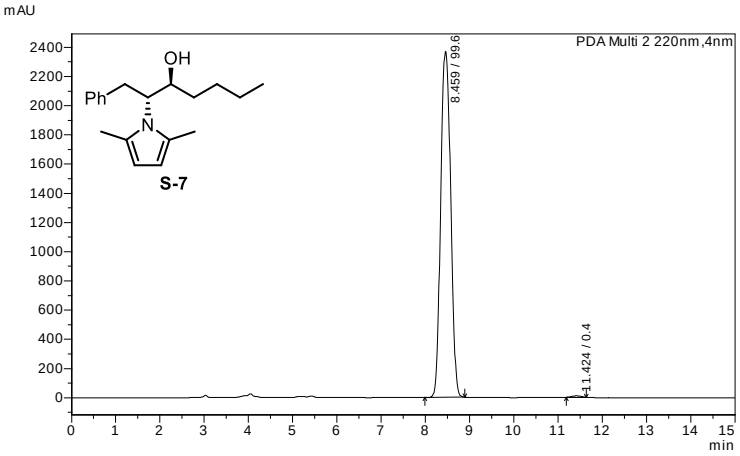


19

method B

Peak	RT [min]	Area	Area [%]
1	8.5	118629	0.4
2	11.3	30255402	99.6

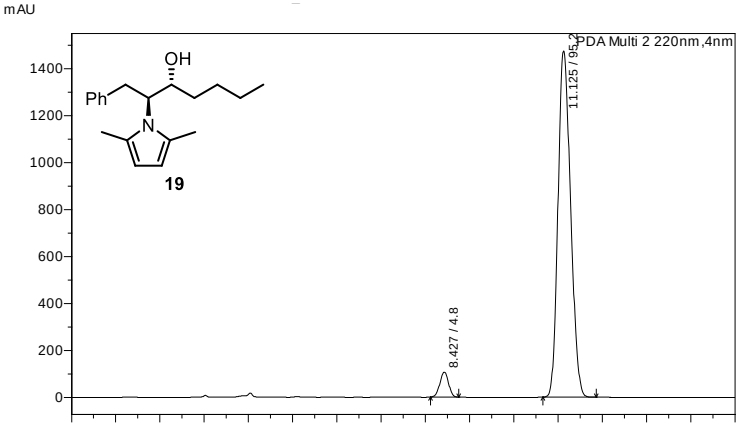
>99% ee



method B

Peak	RT [min]	Area	Area [%]
1	8.5	36998905	99.6
2	11.4	146604	0.4

>99% ee

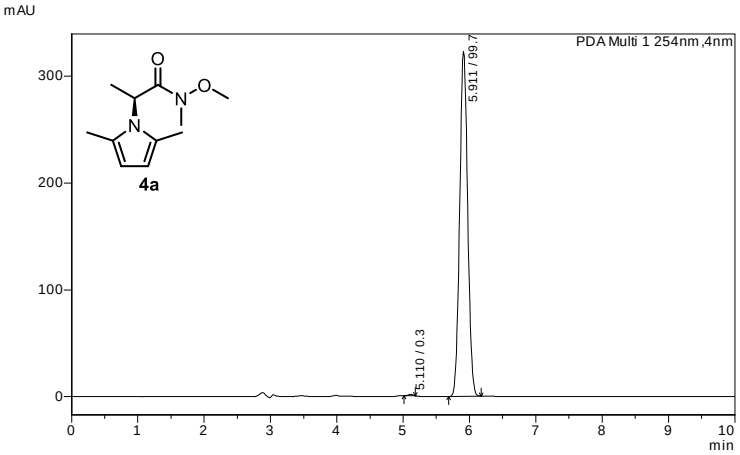


rxn with purified aldehyde

method B

Peak	RT [min]	Area	Area [%]
1	8.4	1460267	4.8
2	11.1	29124427	95.2

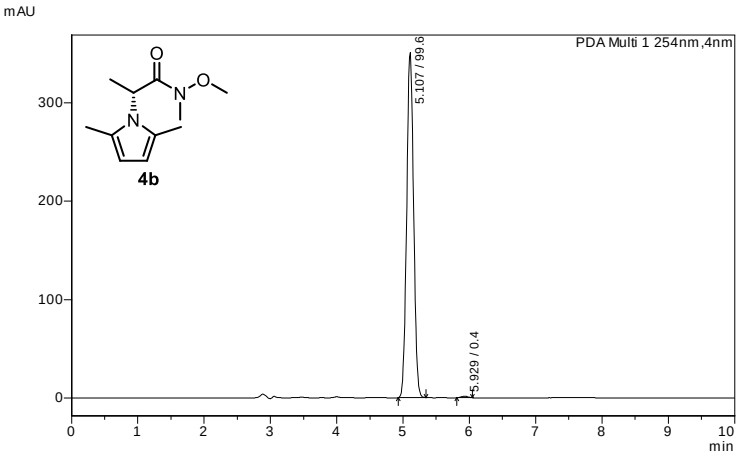
90% ee



method A

Peak	RT [min]	Area	Area [%]
1	5.1	6953	0.3
2	5.9	2705051	99.7

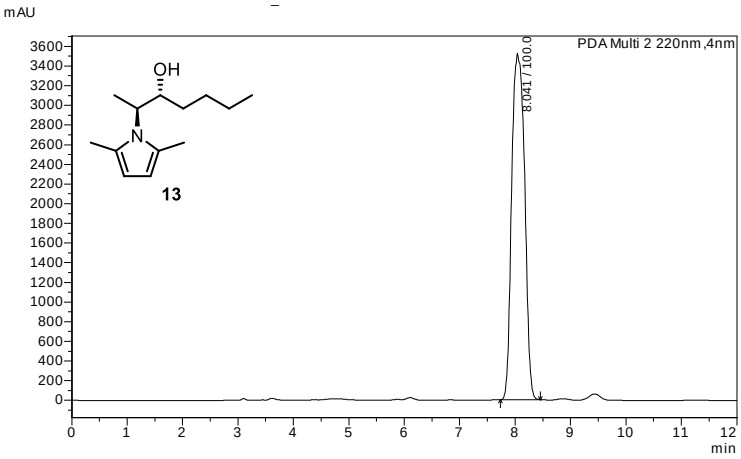
>99% ee



method A

Peak	RT [min]	Area	Area [%]
1	5.1	2533819	99.6
2	5.9	10625	0.4

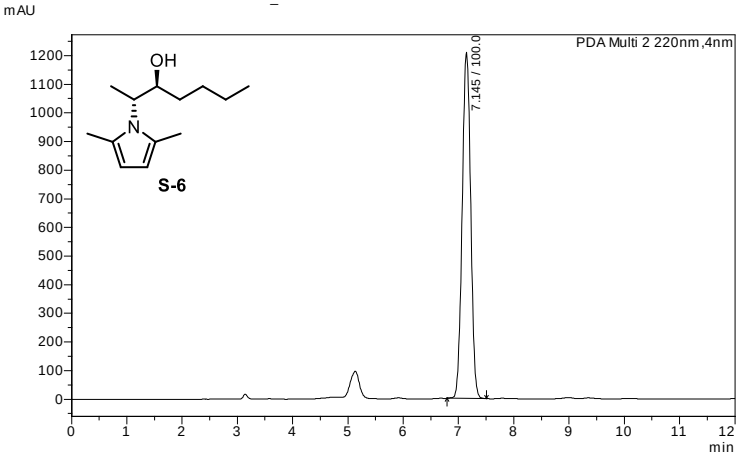
>99% ee



method C

Peak	RT [min]	Area	Area [%]
1	8.0	57135304	100

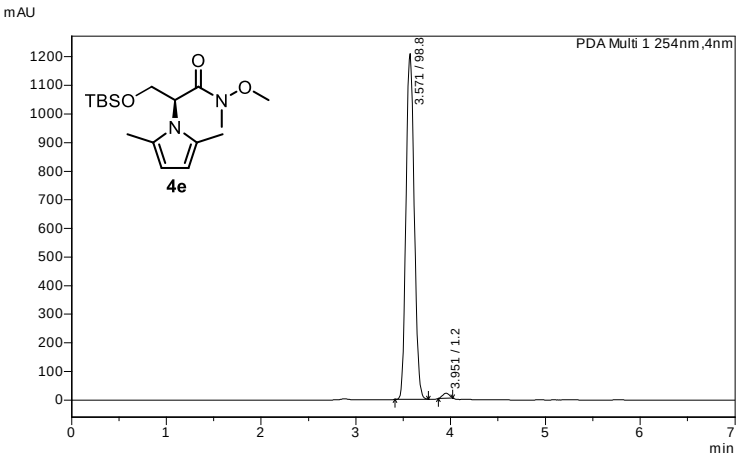
>99% ee



method C

Peak	RT [min]	Area	Area [%]
1	7.1	12922129	100

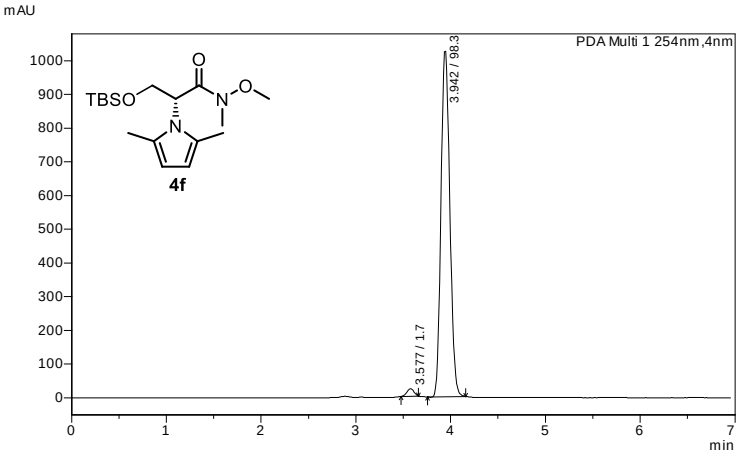
>99% ee



method A

Peak	RT [min]	Area	Area [%]
1	3.6	7294058	98.8
2	4.0	87882	1.2

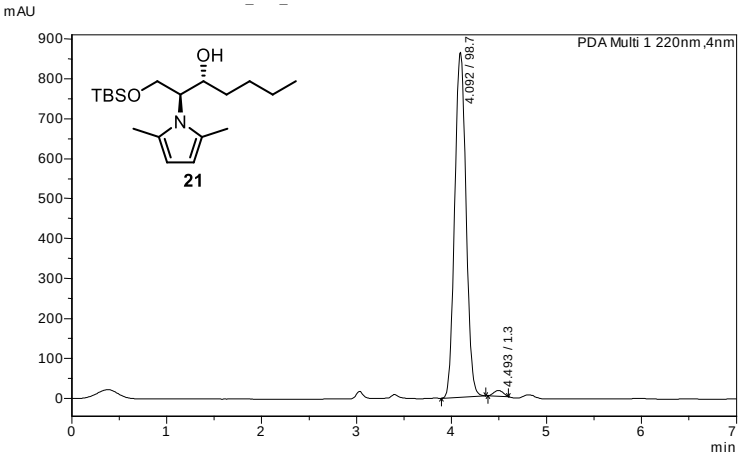
98% ee



method A

Peak	RT [min]	Area	Area [%]
1	3.6	115130	1.7
2	3.9	6658710	98.3

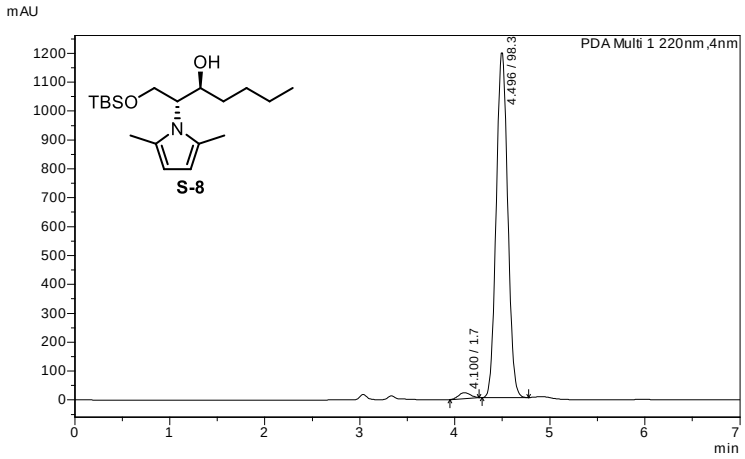
97% ee



method C

Peak	RT [min]	Area	Area [%]
1	4.1	7183352	98.7
2	4.5	96752	1.3

97% ee



method C

Peak	RT [min]	Area	Area [%]
1	4.1	175873	98.3
2	4.5	10033739	1.7

97% ee

3 References

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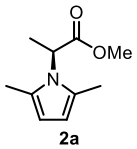
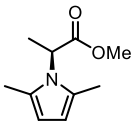
4 NMR Spectra



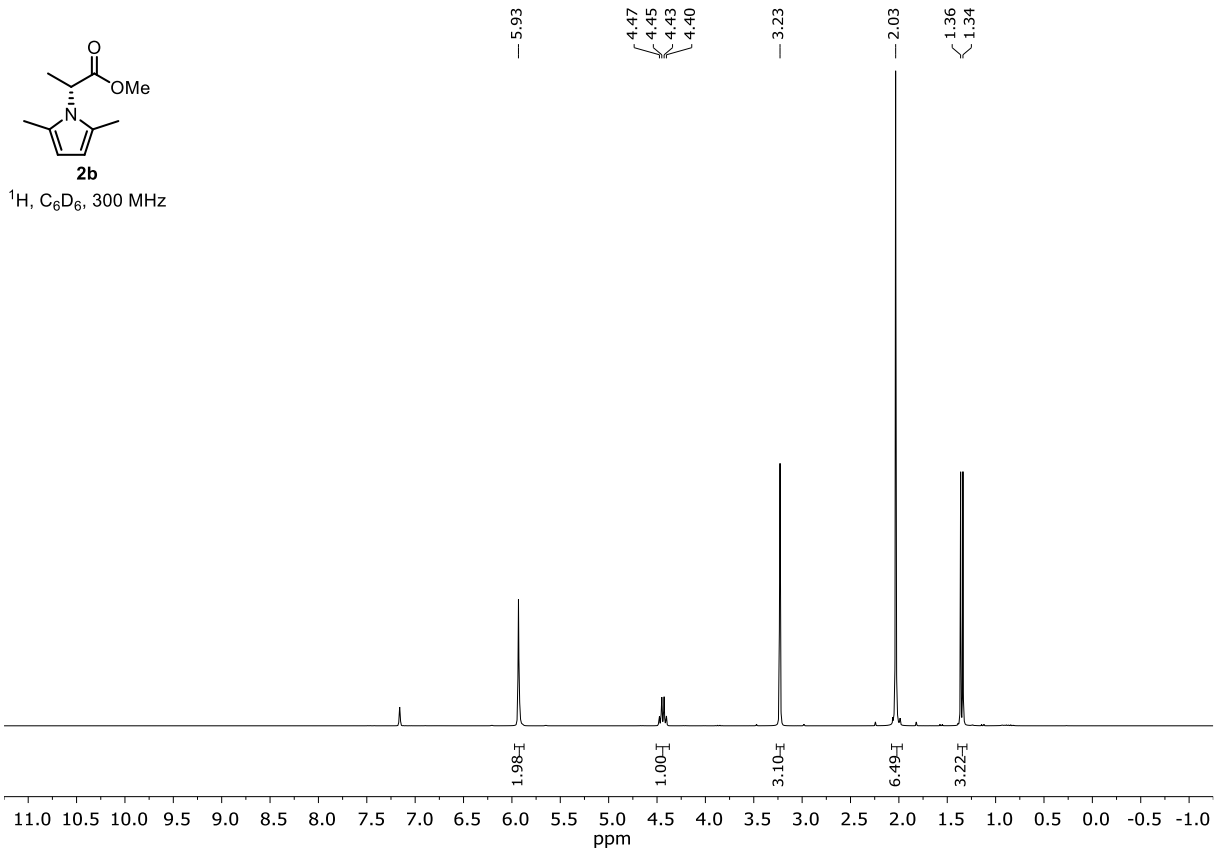
2a

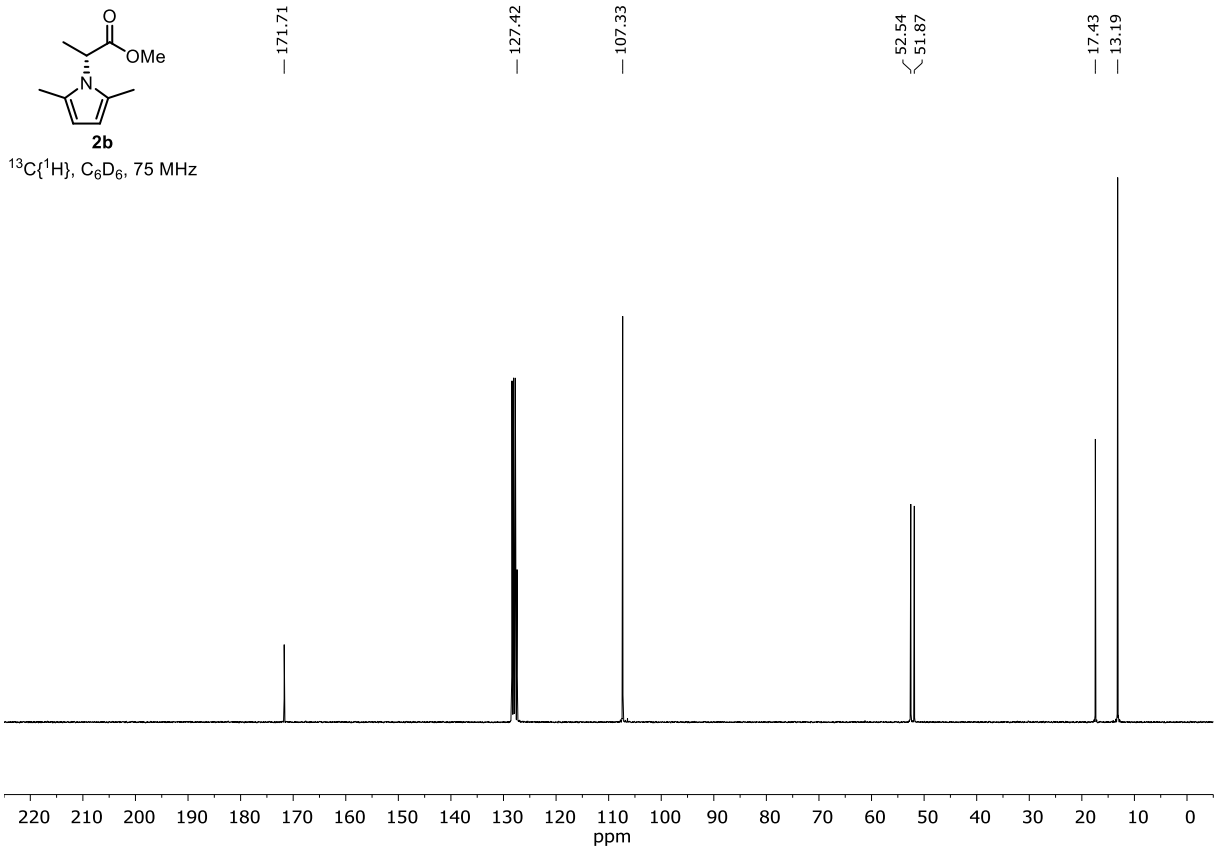
^{1}H, C_6D_6, 500 MHz

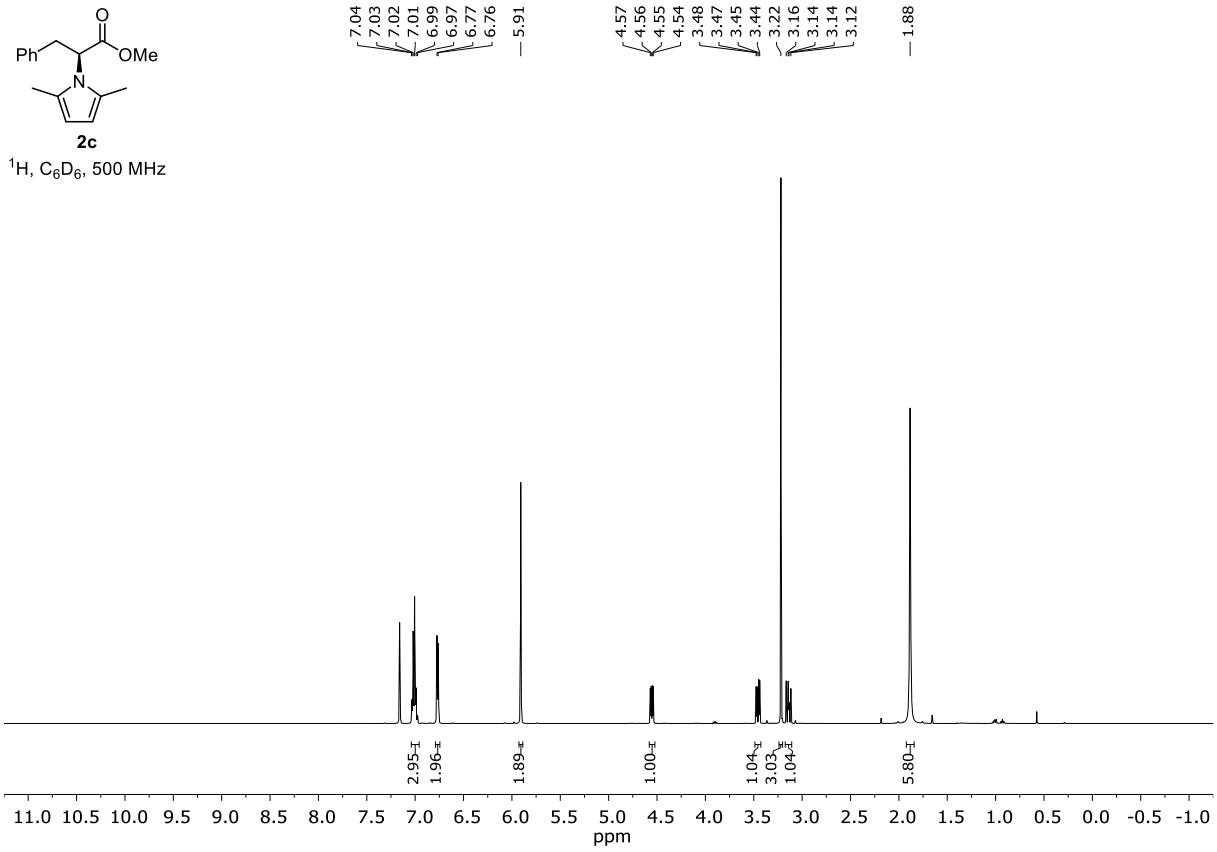


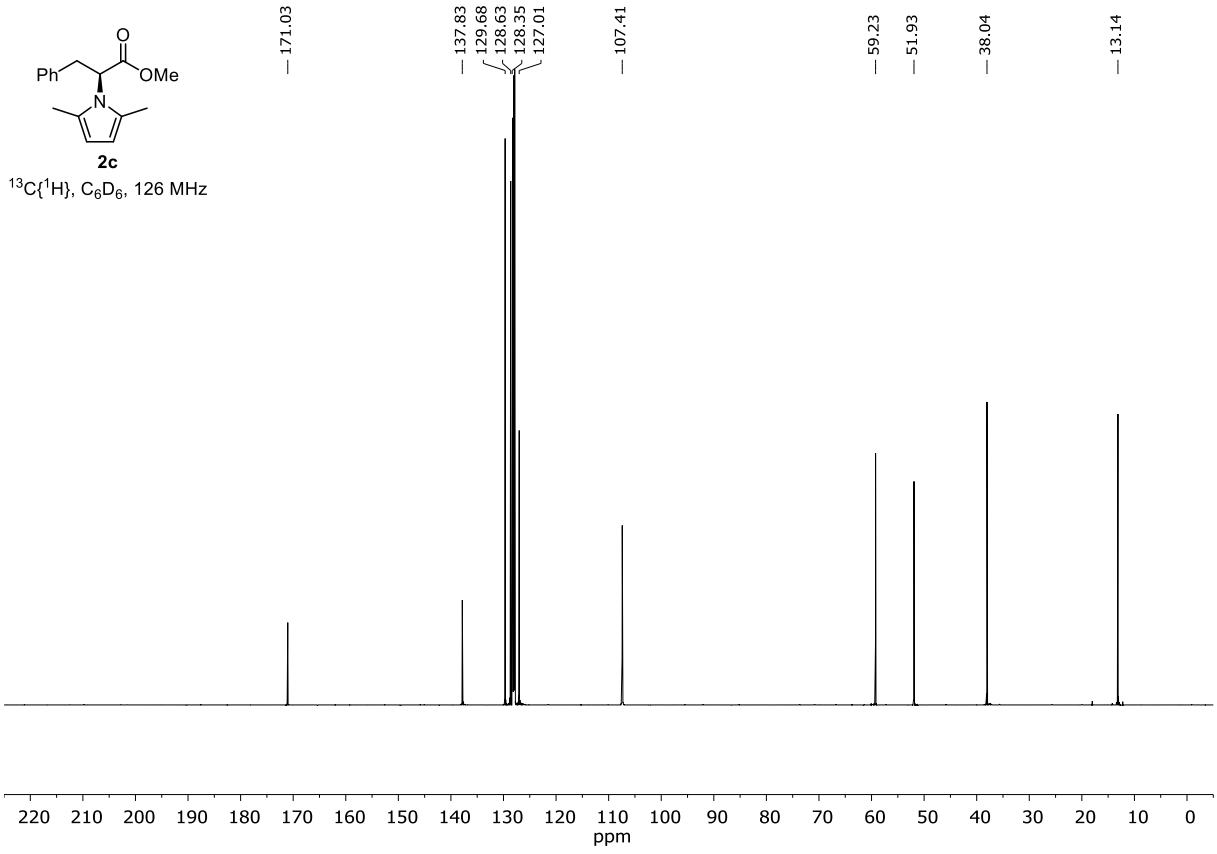
2a

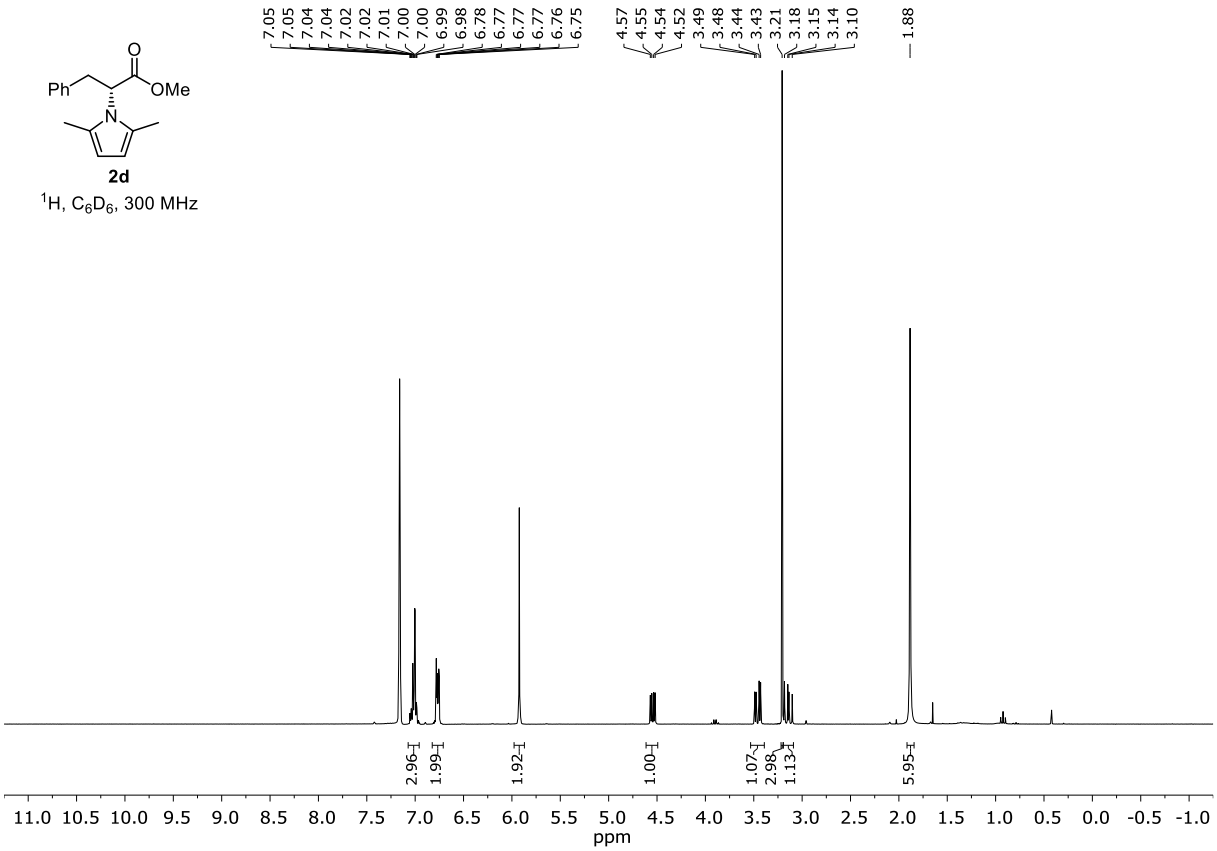
$^{13}C\{^{1}H\}$, C_6D_6, 126 MHz

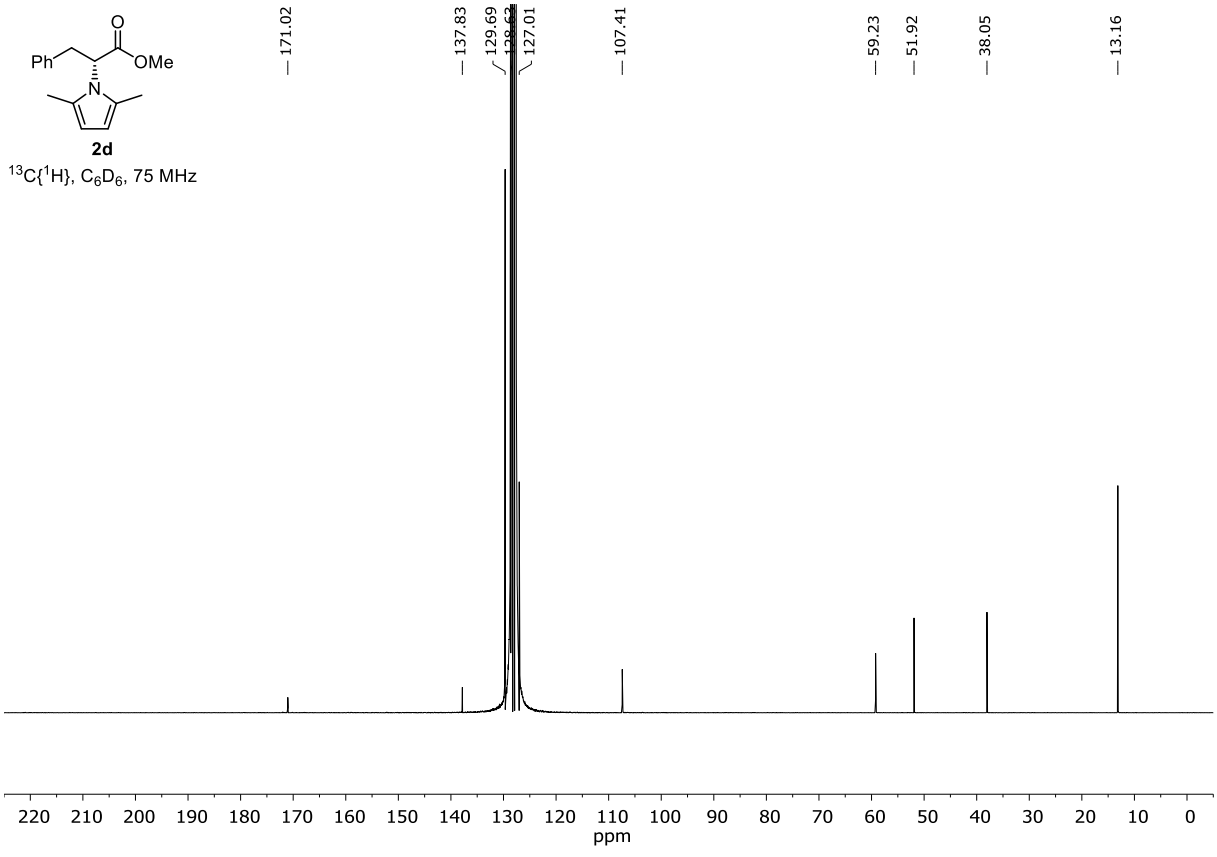

2b
1H, C6D6, 300 MHz
5.93
4.47
4.45
4.43
4.40
3.23
2.03
1.36
1.34
1.98
1.00
3.10
6.49
3.22
ppm

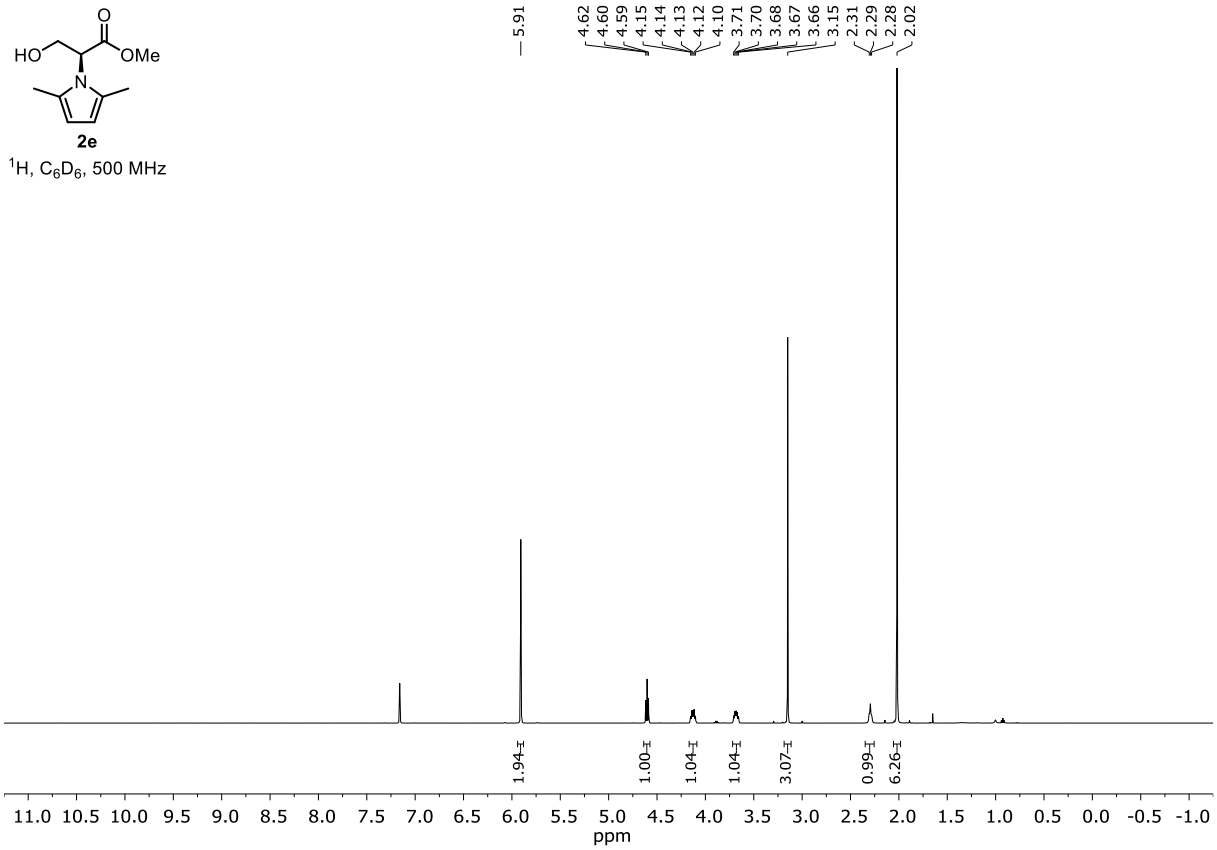

2b
13C{1H}, C6D6, 75 MHz
171.71
127.42
107.33
52.54
51.87
17.43
13.19
ppm

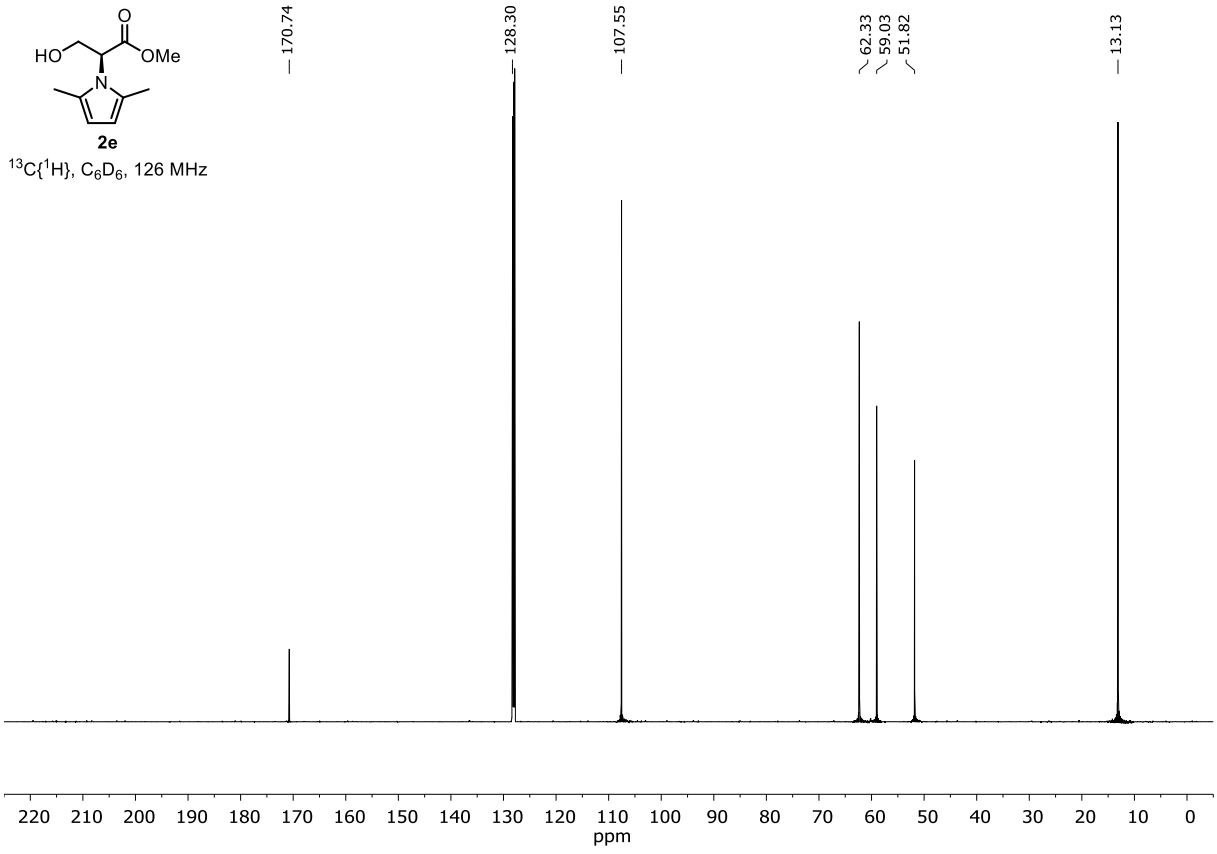

Ph
O
OMe
N
2c
1H, C6D6, 500 MHz
7.04
7.03
7.02
7.01
6.99
6.97
6.77
6.76
5.91
4.57
4.56
4.55
4.54
3.48
3.47
3.45
3.44
3.22
3.16
3.14
3.14
3.12
1.88
2.95
1.96
1.89
1.00
1.04
3.03
1.04
5.80
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

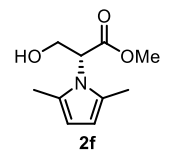

Ph
O
OMe
N
2c
13C{1H}, C6D6, 126 MHz
171.03
137.83
129.68
128.63
128.35
127.01
107.41
59.23
51.93
38.04
13.14
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


Ph
OMe
N
O
2d
^{1}H, C_6D_6, 300 MHz
7.05 7.05 7.04 7.04 7.02 7.02 7.01 7.00 7.00 6.99 6.98 6.78 6.77 6.77 6.76 6.75
4.57 4.55 4.54 4.52
3.49 3.48 3.44 3.43 3.21 3.18 3.15 3.14 3.10
1.88
2.96 1.99 1.92 1.00 1.07 2.98 1.13 5.95
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


Ph
OMe
N
O
2d
^{13}C{^{1}H}, C_6D_6, 75 MHz
171.02
137.83
129.69
128.63
127.01
107.41
59.23
51.92
38.05
13.16
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

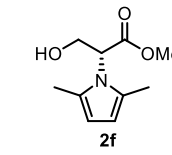

HO
OMe
N
O
2e
1H, C6D6, 500 MHz
5.91
4.62
4.60
4.59
4.15
4.14
4.13
4.12
4.10
3.71
3.70
3.68
3.67
3.66
3.15
2.31
2.29
2.28
2.02
1.94
1.00
1.04
1.04
3.07
0.99
6.26
ppm


HO
OMe
N
O
2e
13C{1H}, C6D6, 126 MHz
170.74
128.30
107.55
62.33
59.03
51.82
13.13
ppm



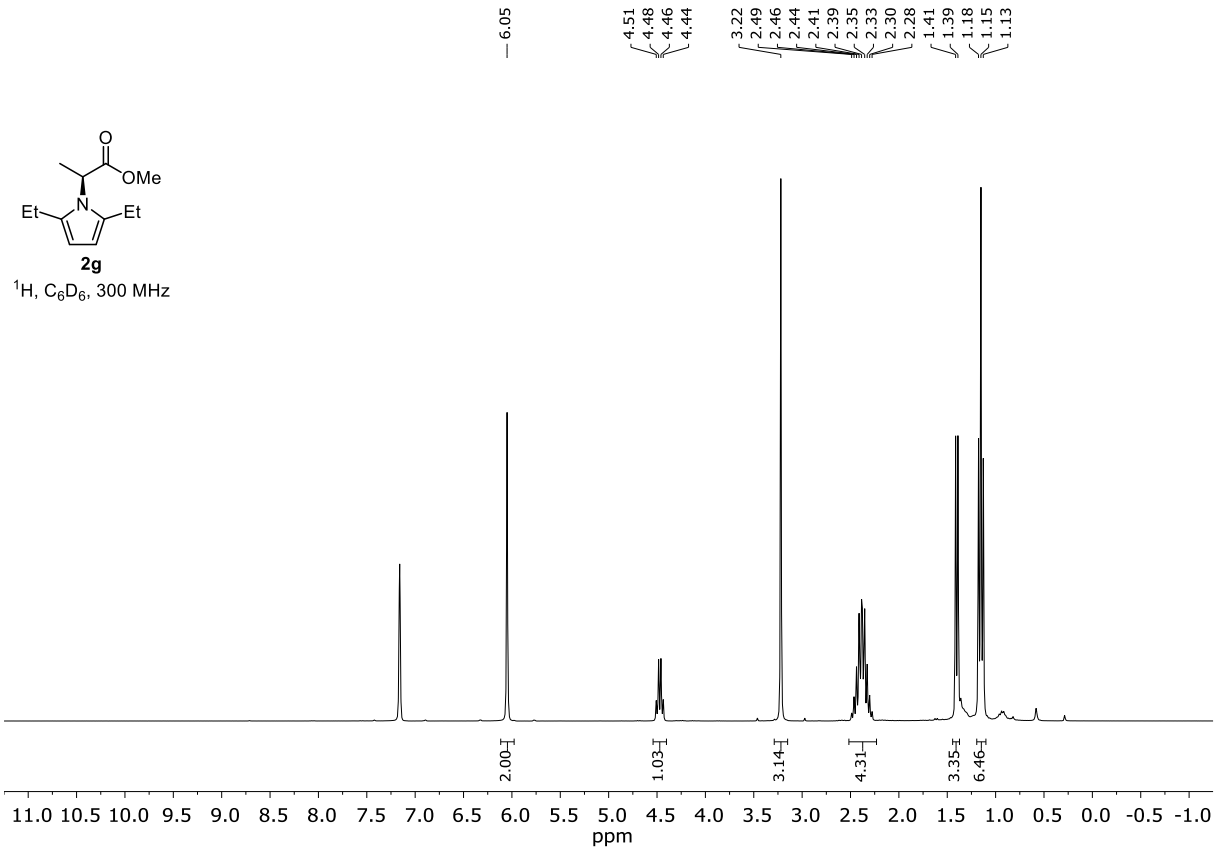
2f

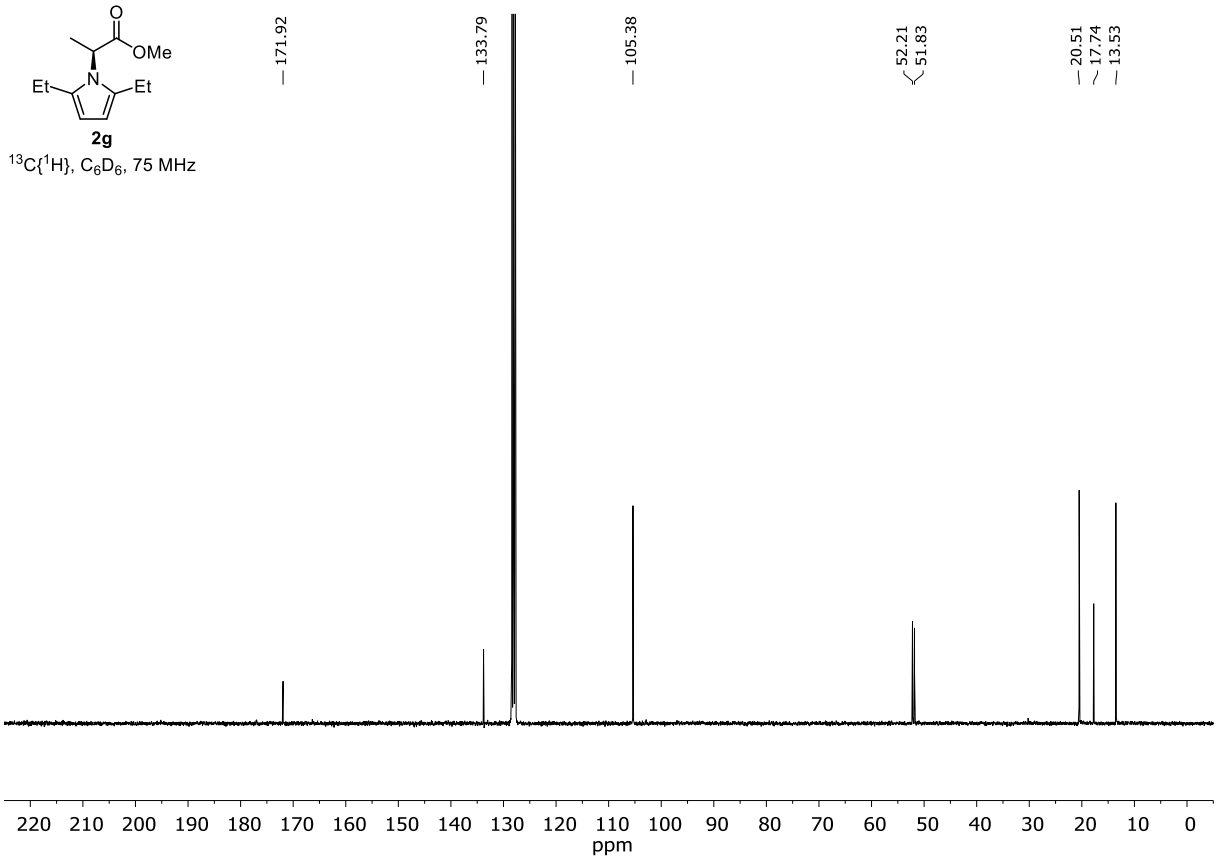
^{1}H, C_6D_6, 500 MHz

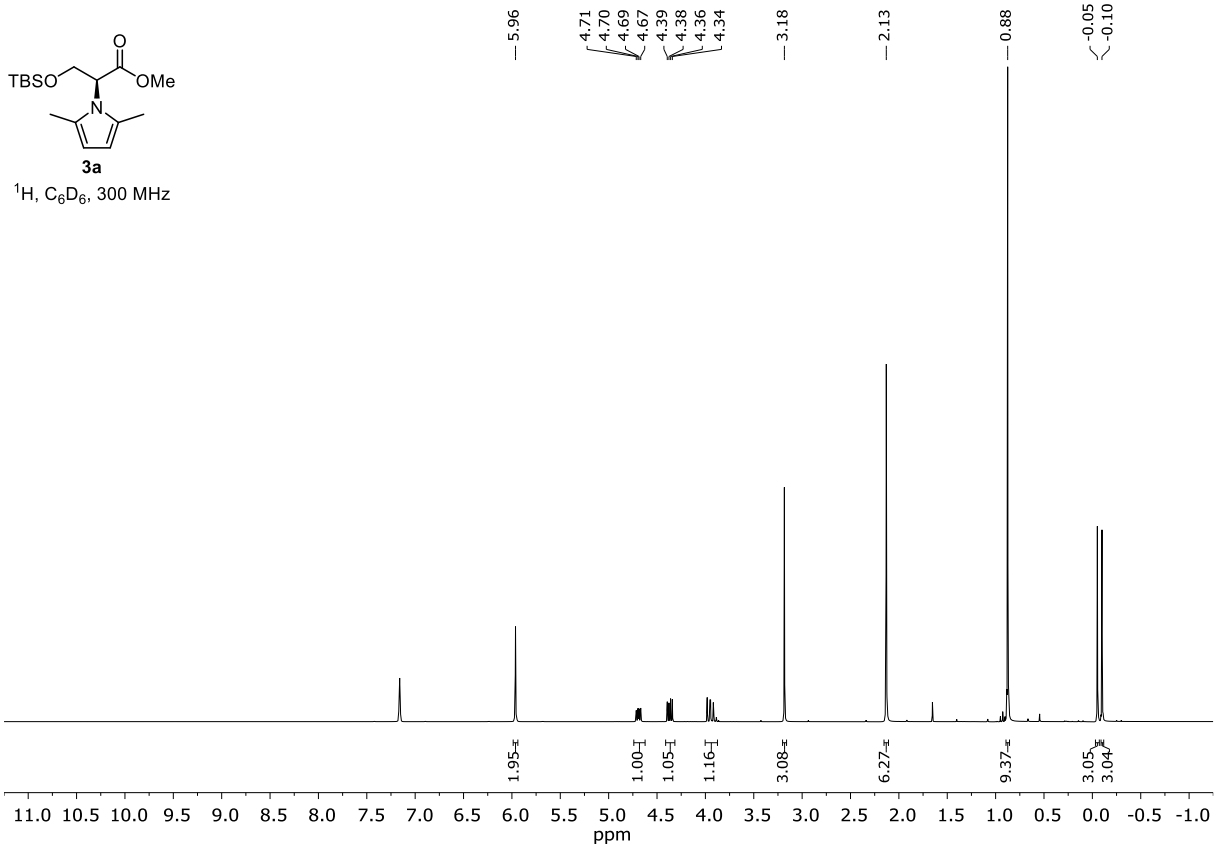


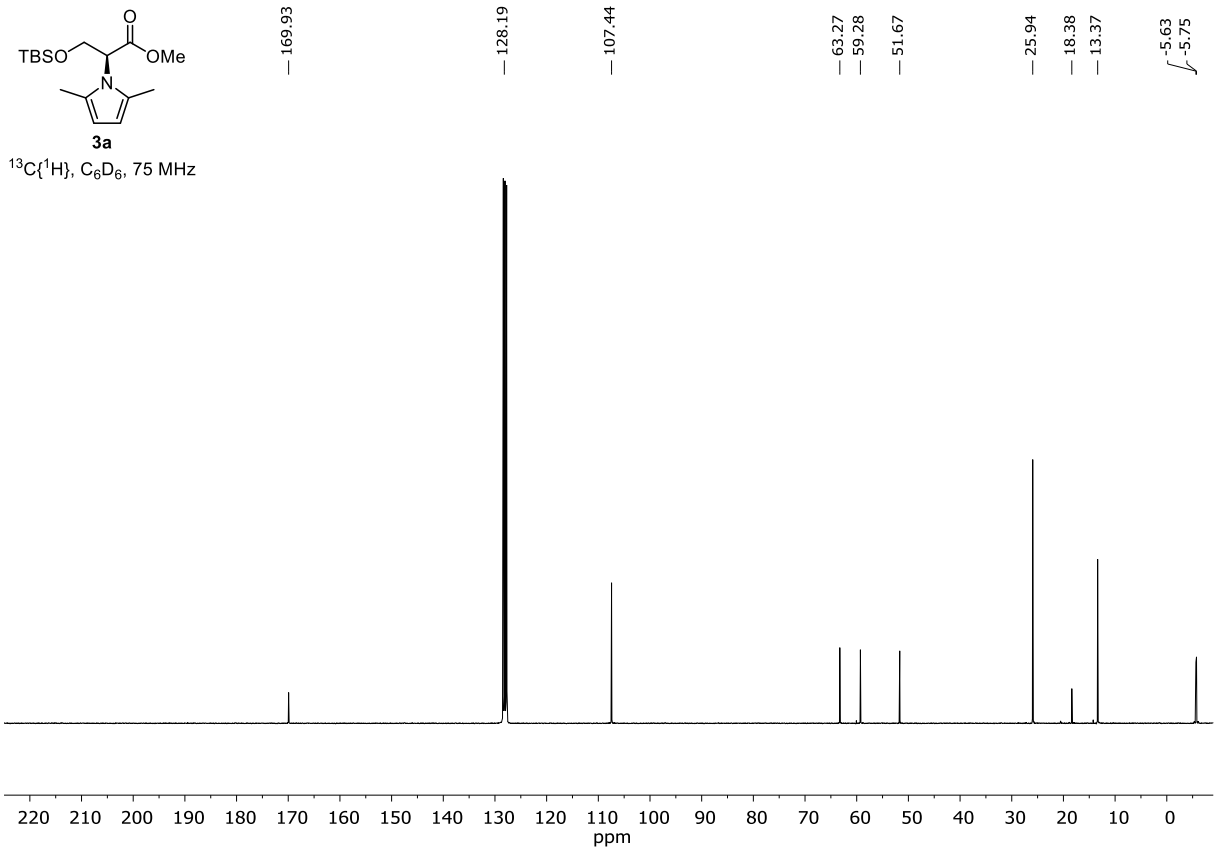
2f

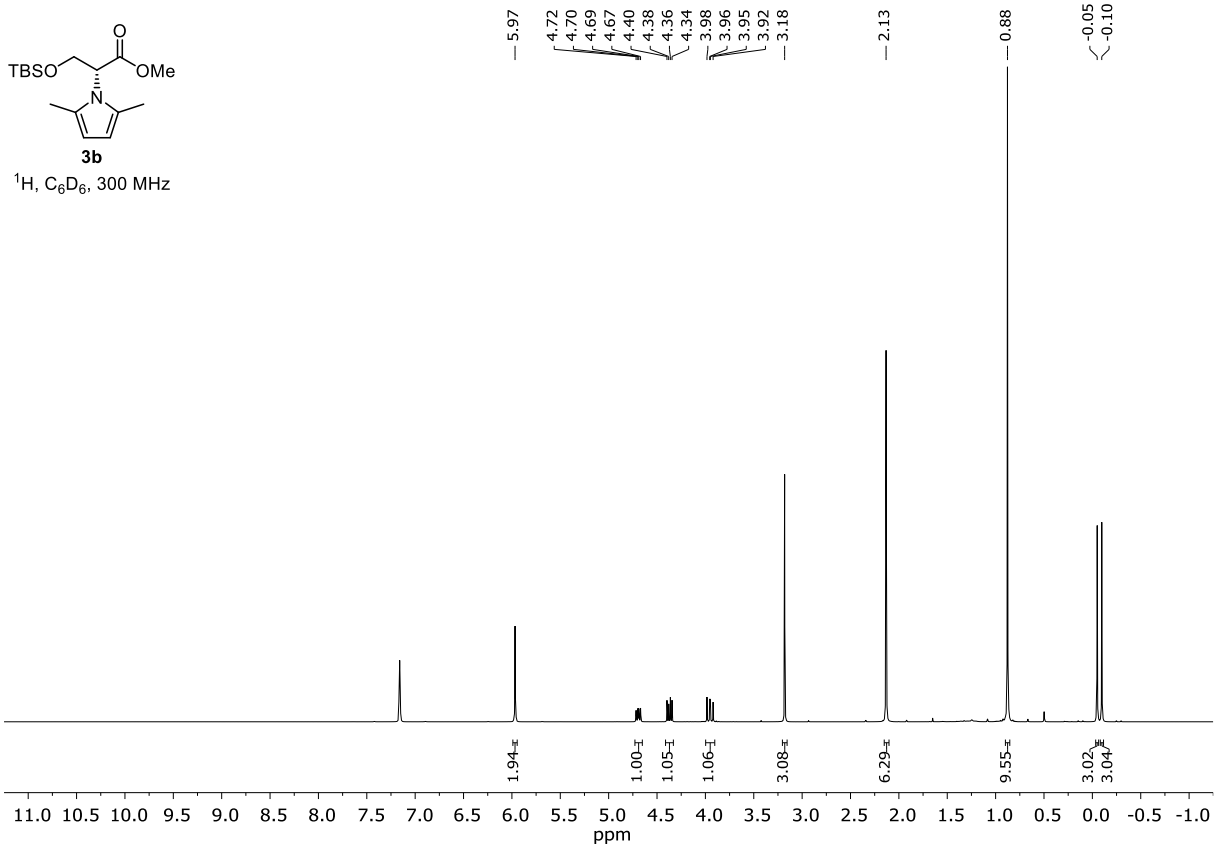
$^{13}C\{^{1}H\}$, C_6D_6, 126 MHz

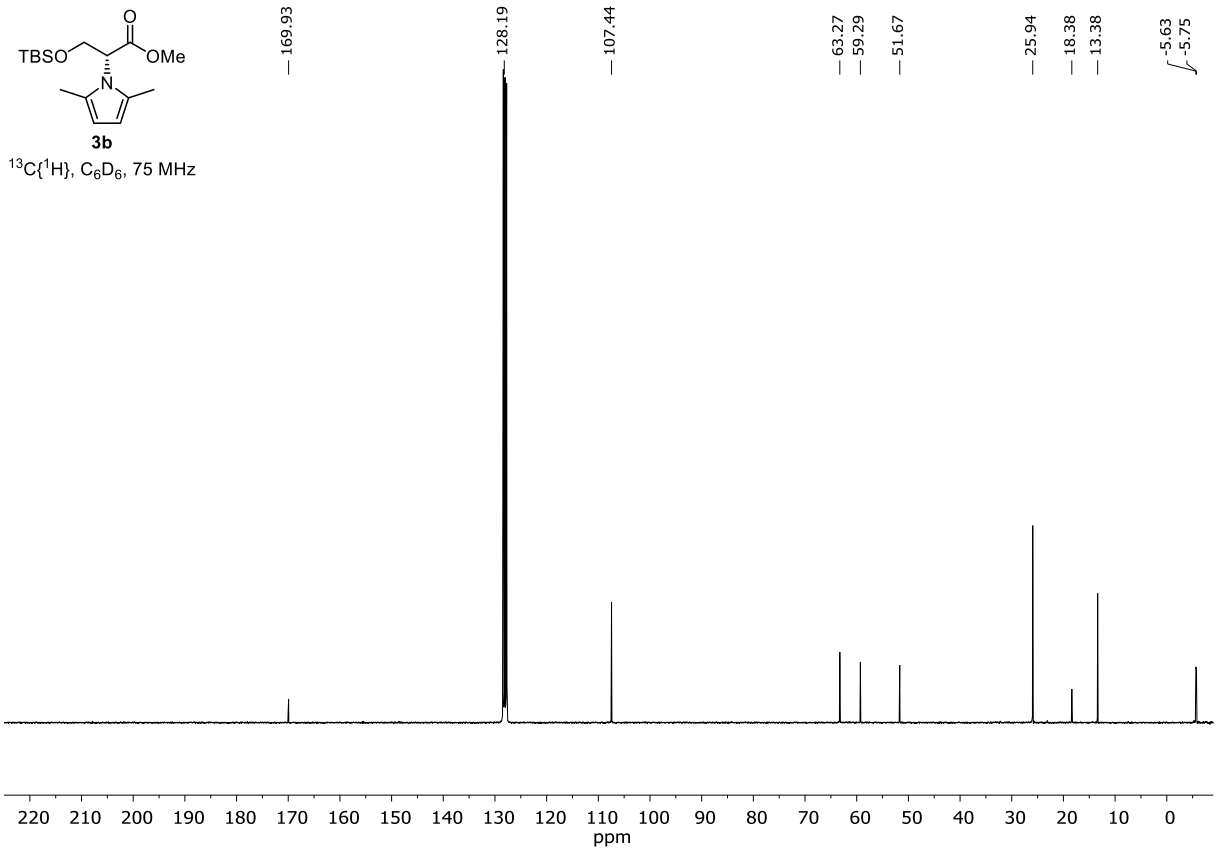

6.05
4.51
4.48
4.46
4.44
3.22
2.49
2.46
2.44
2.41
2.39
2.35
2.33
2.30
2.28
1.41
1.39
1.18
1.15
1.13
O
OMe
N
Et
Et
2g
1H, C6D6, 300 MHz
2.00
1.03
3.14
4.31
3.35
6.46
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

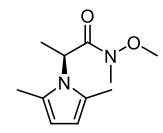

O
OMe
N
Et
Et
2g
13C{1H}, C6D6, 75 MHz
171.92
133.79
105.38
52.21
51.83
20.51
17.74
13.53
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


TBSO
OMe
N
3a
1H, C6D6, 300 MHz
5.96
4.71
4.70
4.69
4.67
4.39
4.38
4.36
4.34
3.18
2.13
0.88
-0.05
-0.10
1.95
1.00
1.05
1.16
3.08
6.27
9.37
3.05
3.04
ppm


TBSO
OMe
N
3a
13C{1H}, C6D6, 75 MHz
169.93
128.19
107.44
63.27
59.28
51.67
25.94
18.38
13.37
-5.63
-5.75
ppm

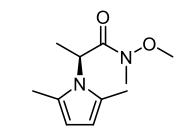

TBSO
OMe
N
3b
1H, C6D6, 300 MHz
5.97
4.72
4.70
4.69
4.67
4.40
4.38
4.36
4.34
3.98
3.96
3.95
3.92
3.18
2.13
0.88
-0.05
-0.10
1.94
1.00
1.05
1.06
3.08
6.29
9.55
3.02
3.04
ppm


TBSO
OMe
N
3b
13C{1H}, C6D6, 75 MHz
169.93
128.19
107.44
63.27
59.29
51.67
25.94
18.38
13.38
-5.63
-5.75
ppm



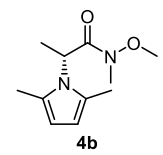
4a

^{1}H, C_6D_6, 300 MHz



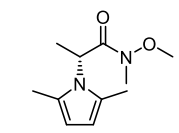
4a

$^{13}C\{^{1}H\}$, C_6D_6, 75 MHz



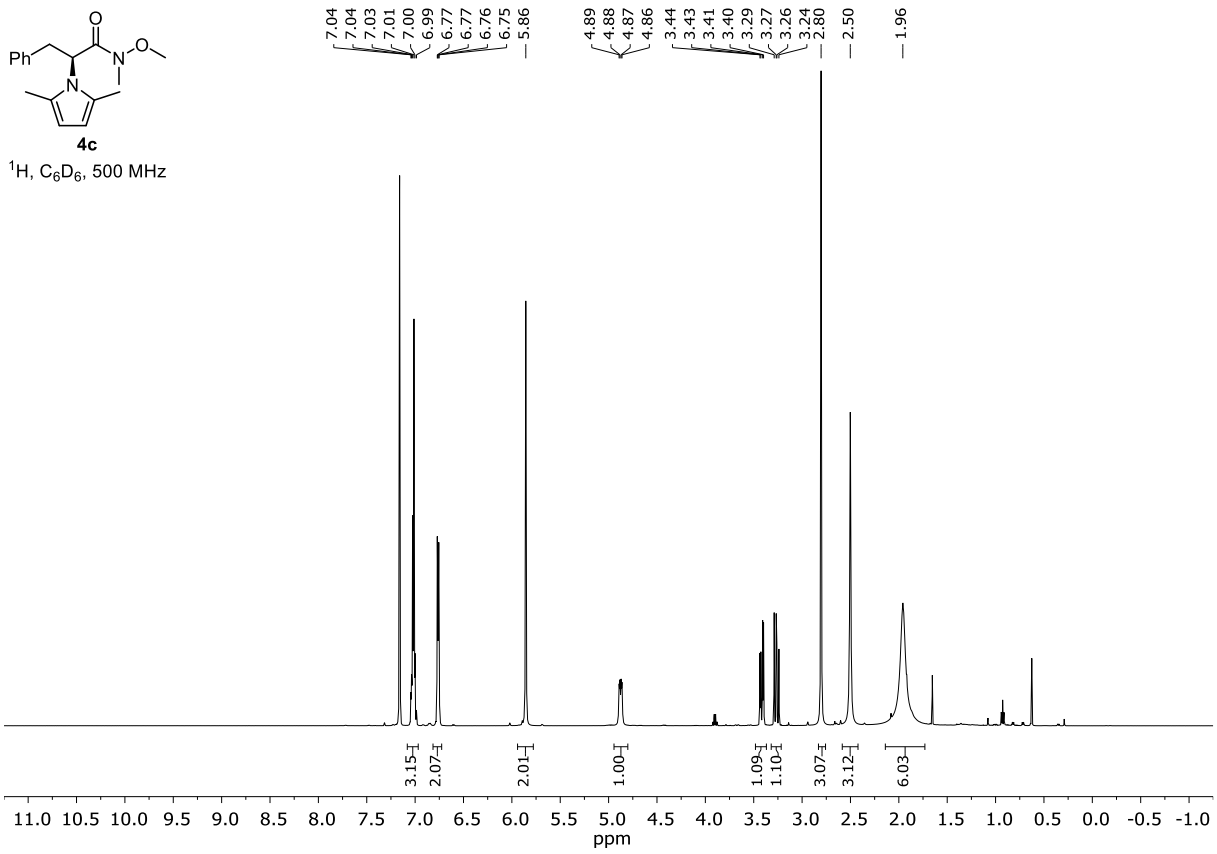
4b

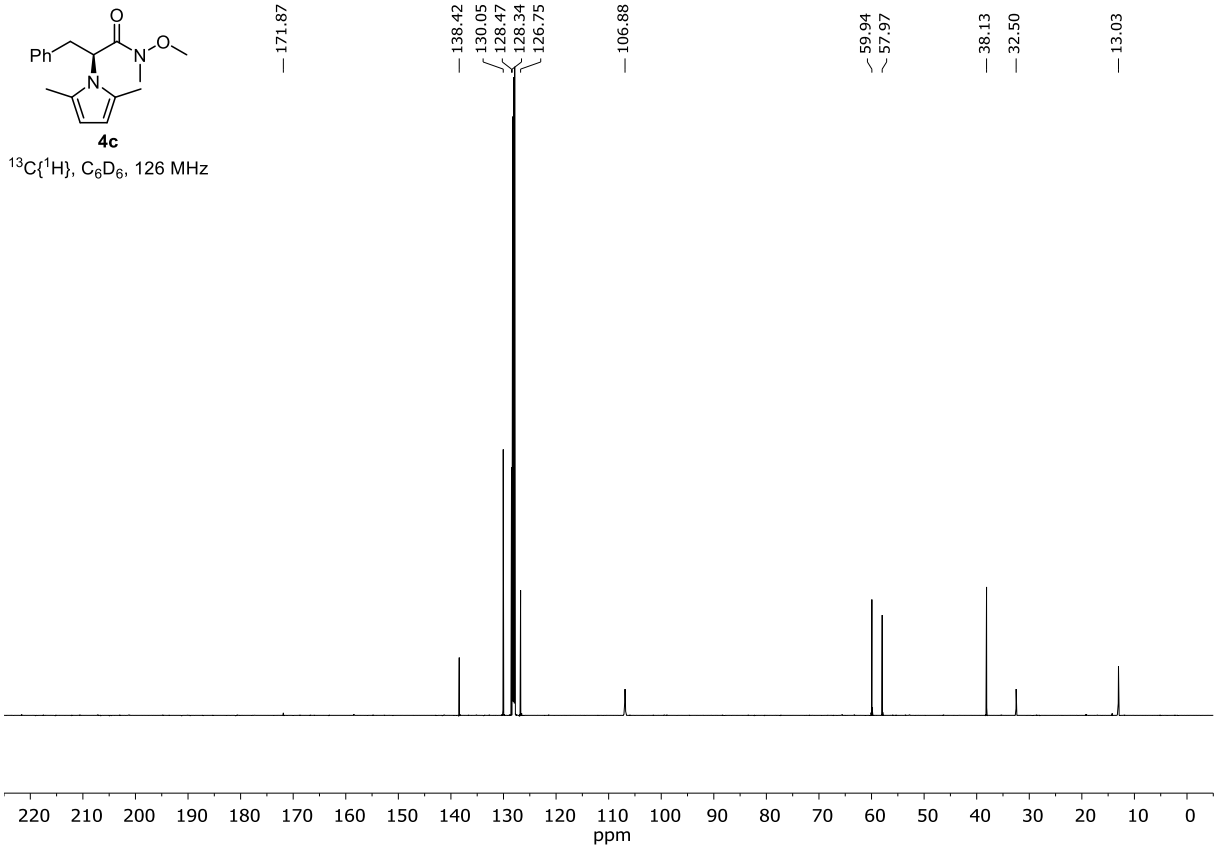
^{1}H, C_6D_6, 300 MHz

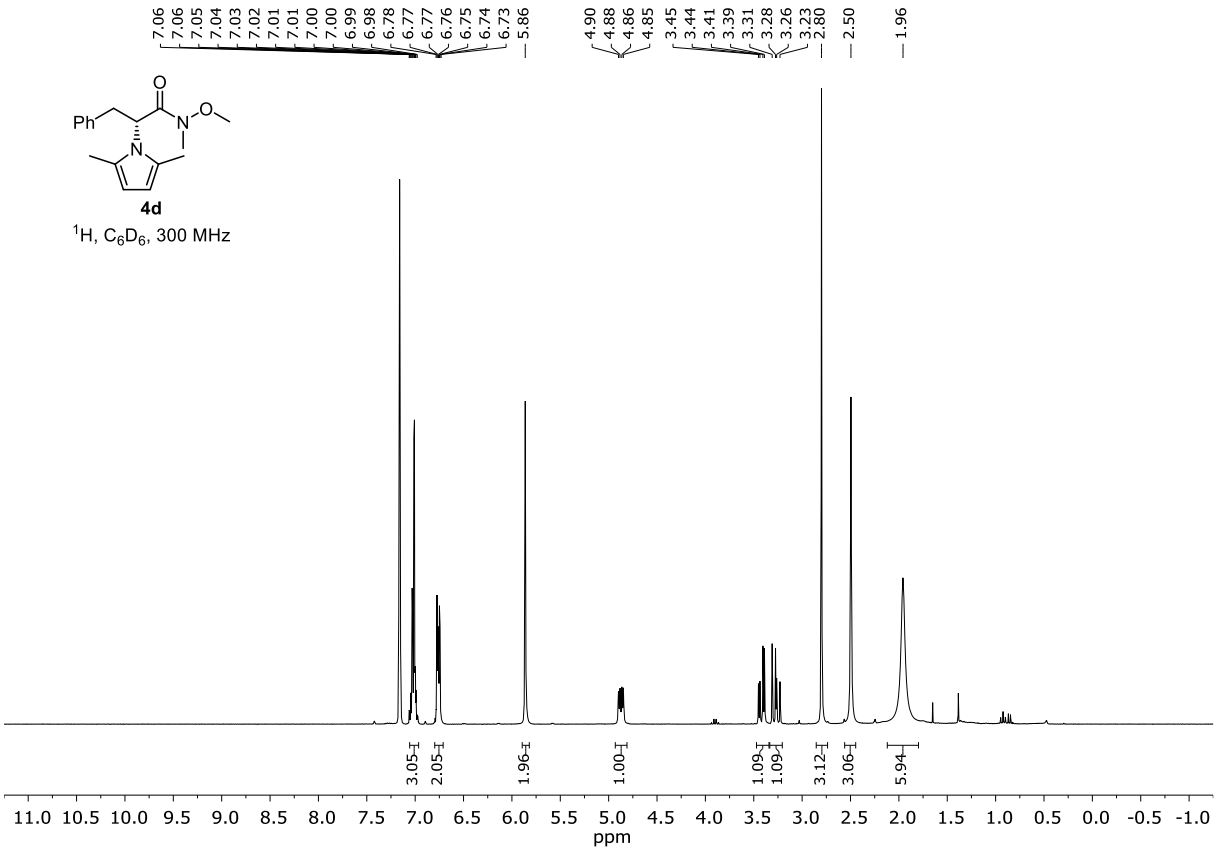


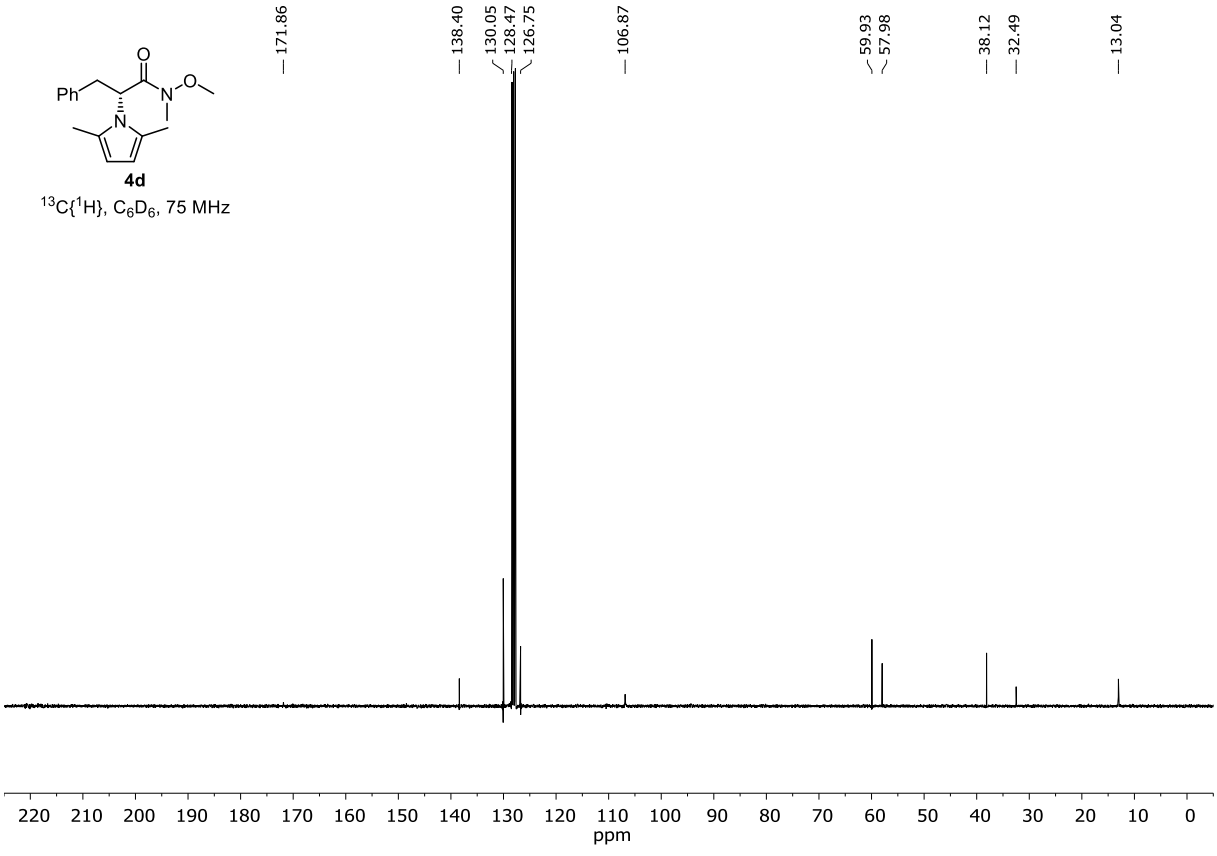
4b

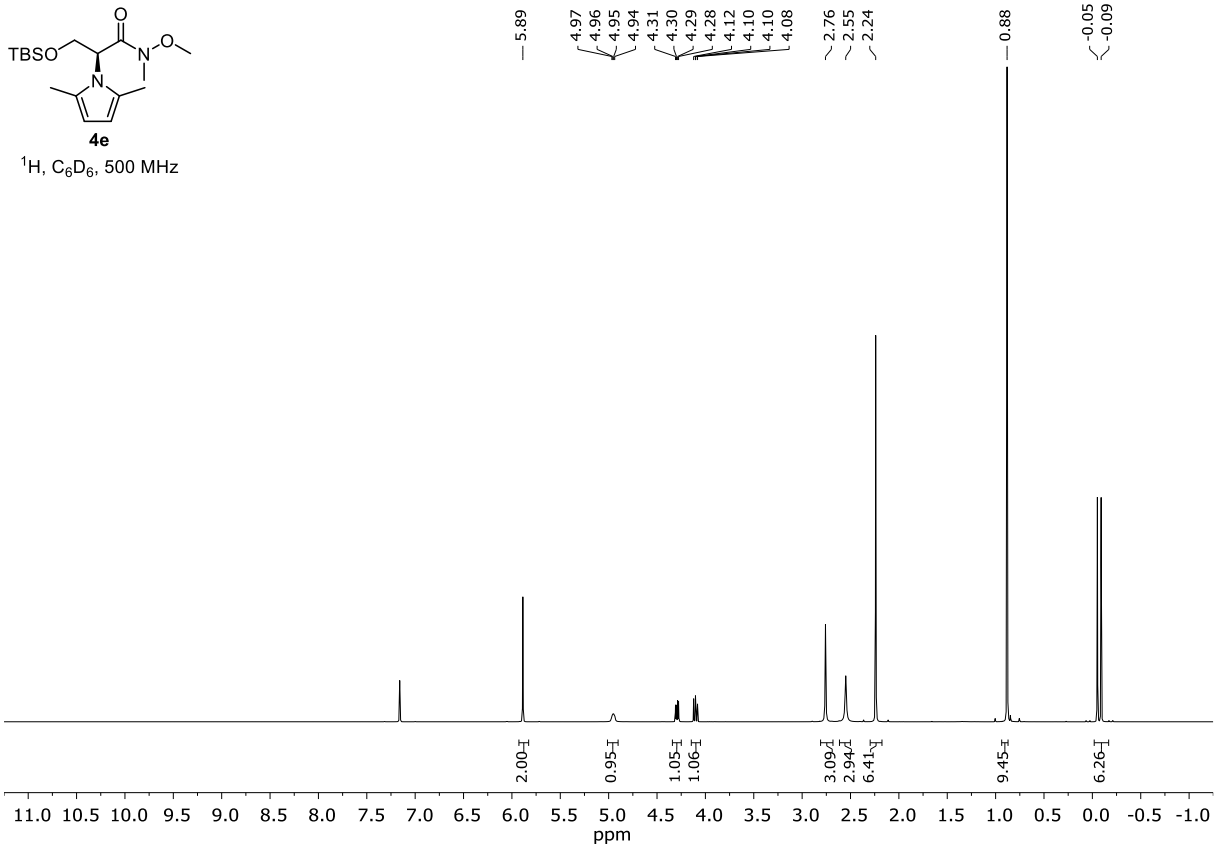
$^{13}C\{^{1}H\}$, C_6D_6, 75 MHz

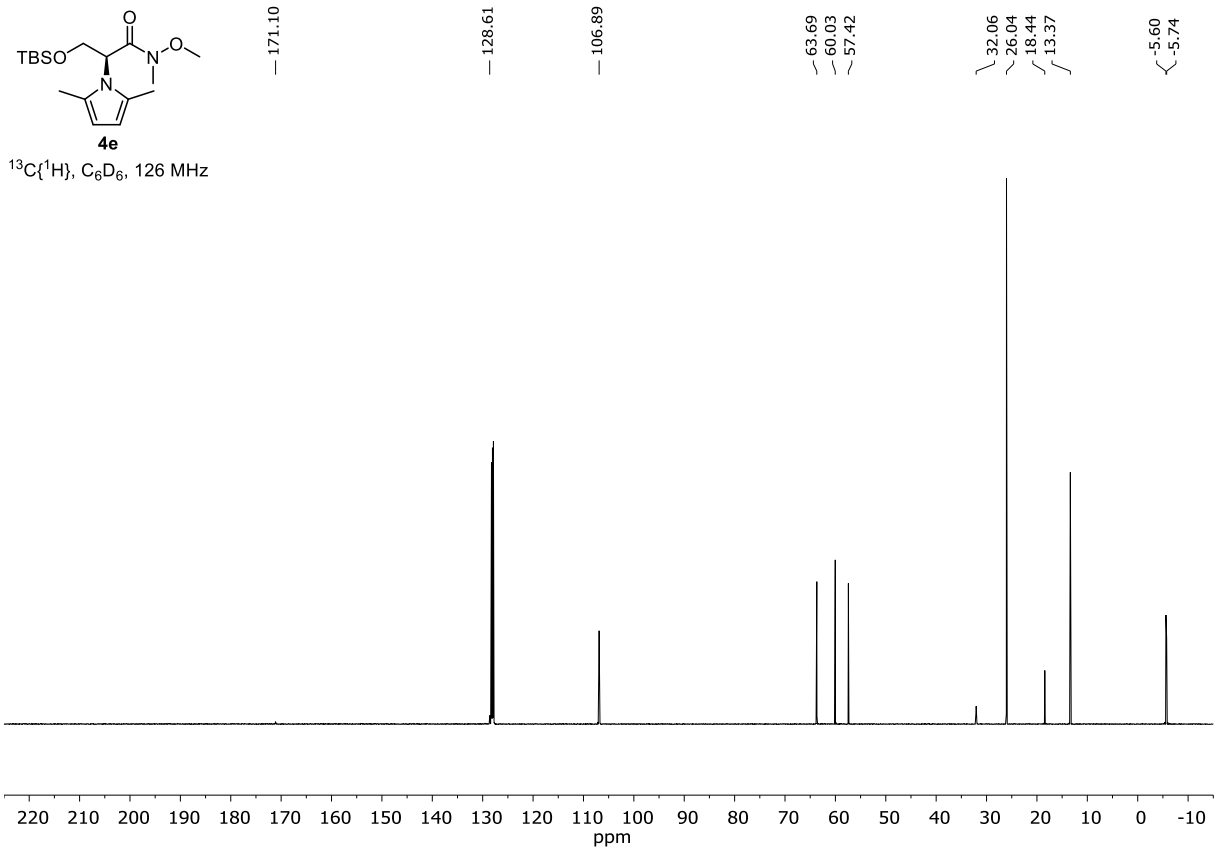

4c
1H, C6D6, 500 MHz
7.04
7.04
7.03
7.01
7.00
6.99
6.77
6.77
6.76
6.75
5.86
4.89
4.88
4.87
4.86
3.44
3.43
3.41
3.40
3.29
3.27
3.26
3.24
2.80
2.50
1.96
3.15
2.07
2.01
1.00
1.09
1.10
3.07
3.12
6.03
ppm

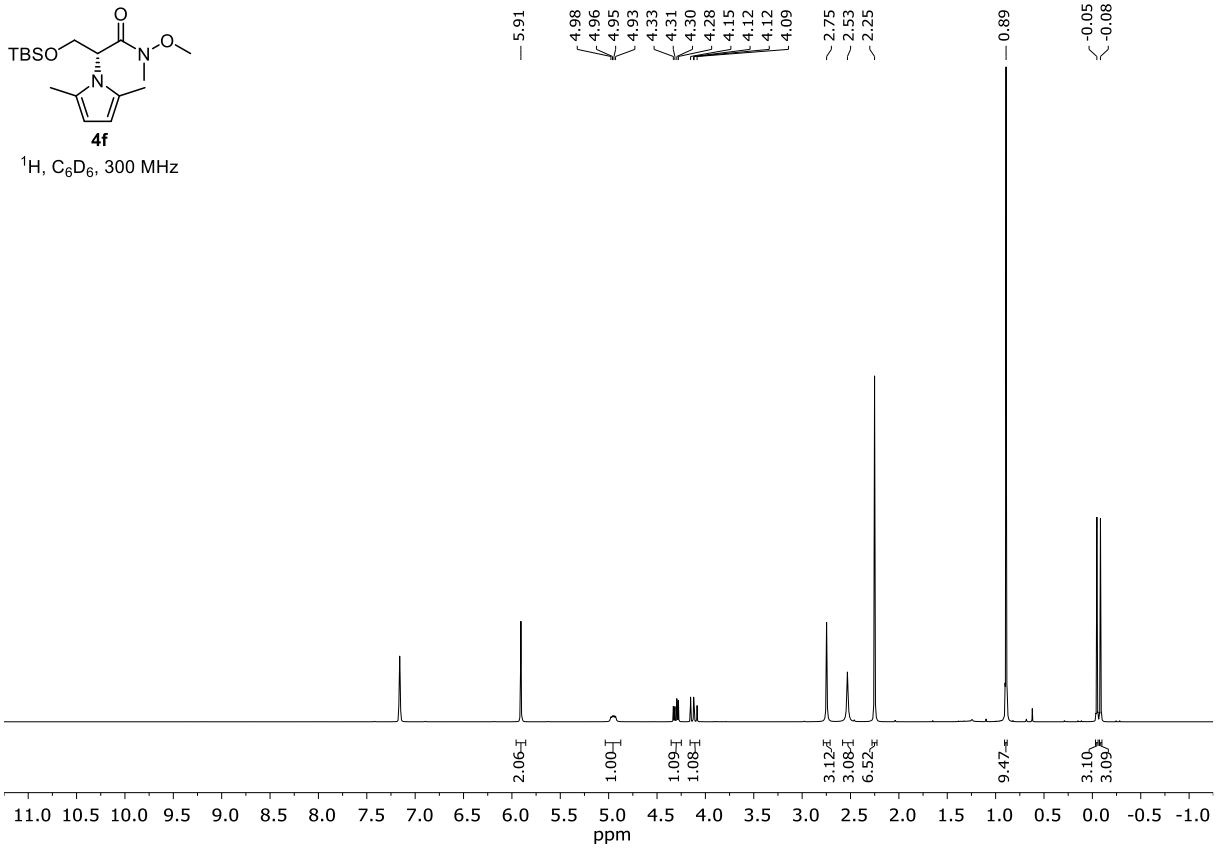

4c
13C{1H}, C6D6, 126 MHz
171.87
138.42
130.05
128.47
128.34
126.75
106.88
59.94
57.97
38.13
32.50
13.03
ppm

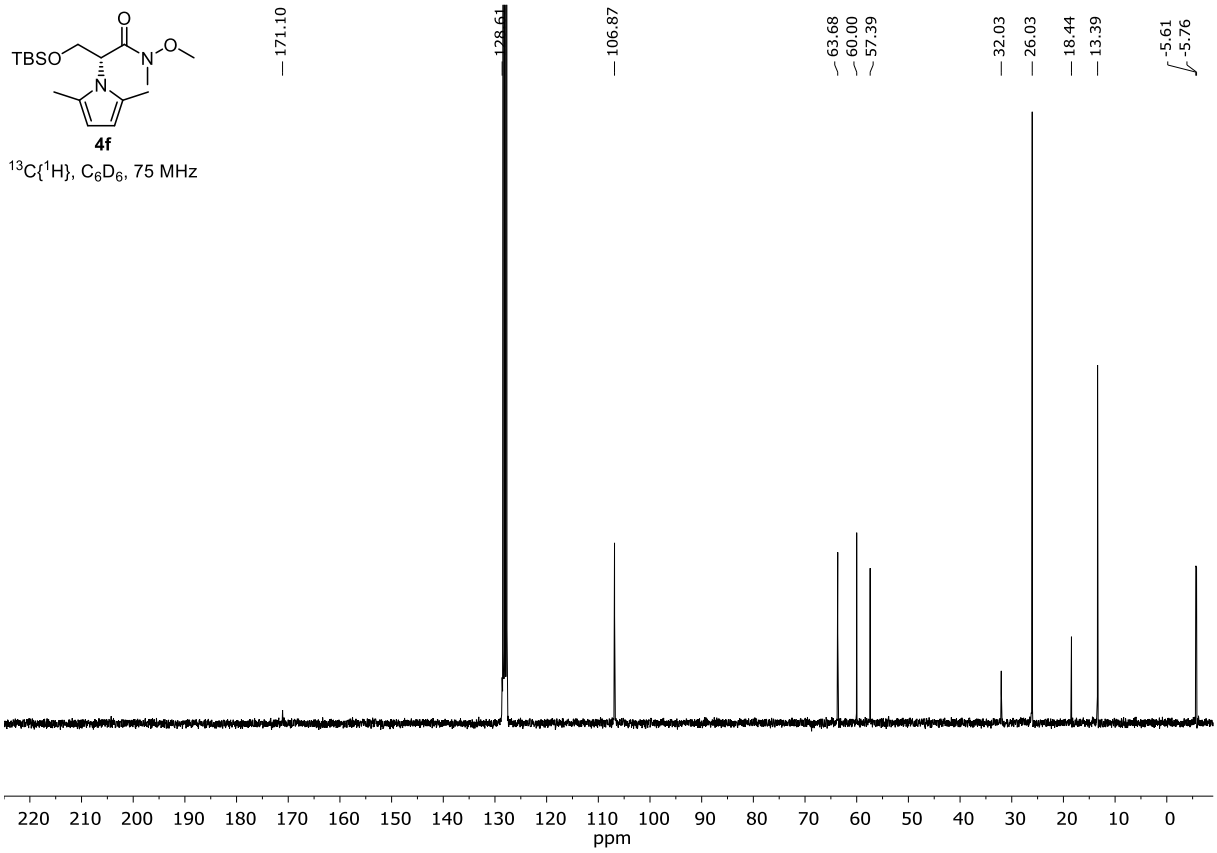

7.06
7.06
7.05
7.04
7.03
7.02
7.01
7.01
7.00
7.00
6.99
6.98
6.78
6.77
6.77
6.76
6.75
6.74
6.73
5.86
4.90
4.88
4.86
4.85
3.45
3.44
3.41
3.39
3.31
3.28
3.26
3.23
2.80
2.50
1.96
Ph
N
O
N
O
4d
1H, C6D6, 300 MHz
3.05
2.05
1.96
1.00
1.09
1.09
3.12
3.06
5.94
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

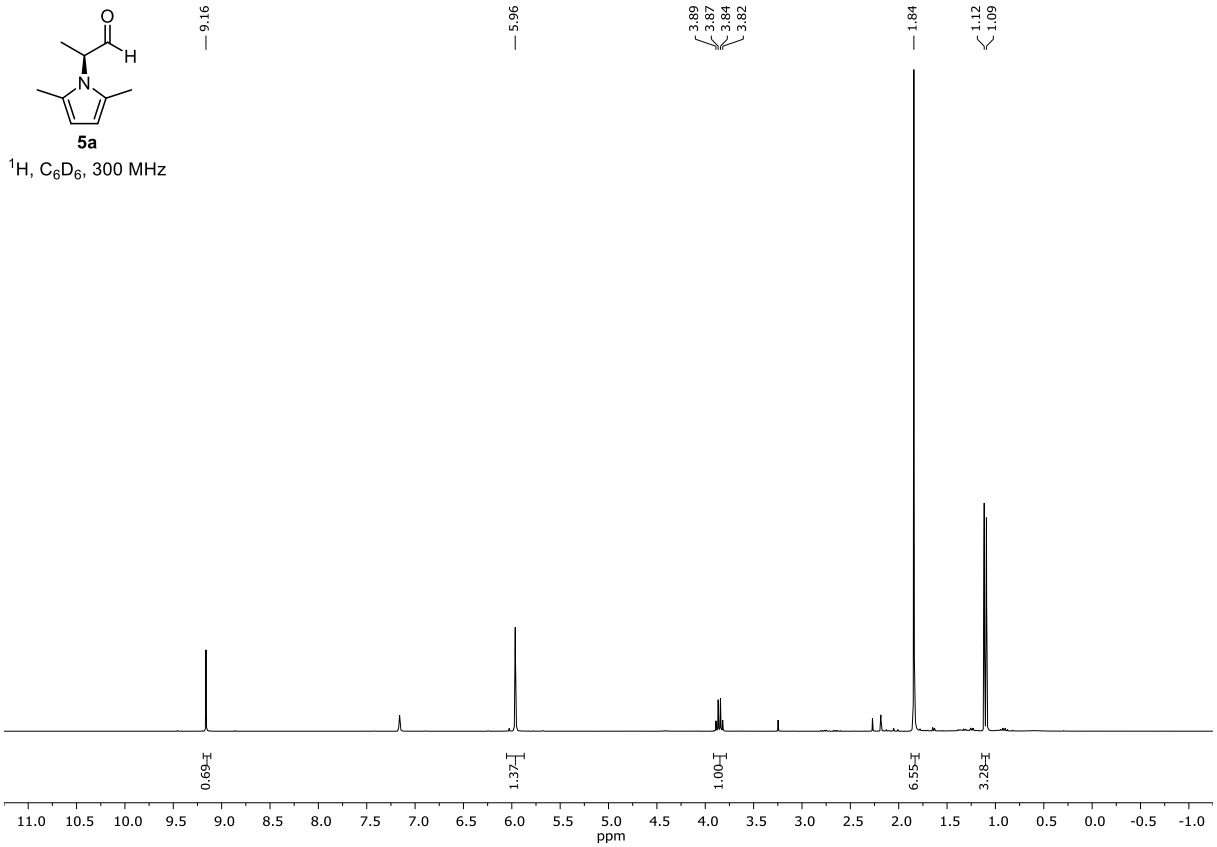

171.86
138.40
130.05
128.47
126.75
106.87
59.93
57.98
38.12
32.49
13.04
Ph
N
O
N
O
4d
13C{1H}, C6D6, 75 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


TBSO
N
O
4e
^{1}H, C_6D_6, 500 MHz
5.89
4.97
4.96
4.95
4.94
4.31
4.30
4.29
4.28
4.12
4.10
4.10
4.08
2.76
2.55
2.24
0.88
-0.05
-0.09
2.00
0.95
1.05
1.06
3.09
2.94
6.41
9.45
6.26
ppm


TBSO
N
O
4e
^{13}C{^{1}H}, C_6D_6, 126 MHz
171.10
128.61
106.89
63.69
60.03
57.42
32.06
26.04
18.44
13.37
-5.60
-5.74
ppm

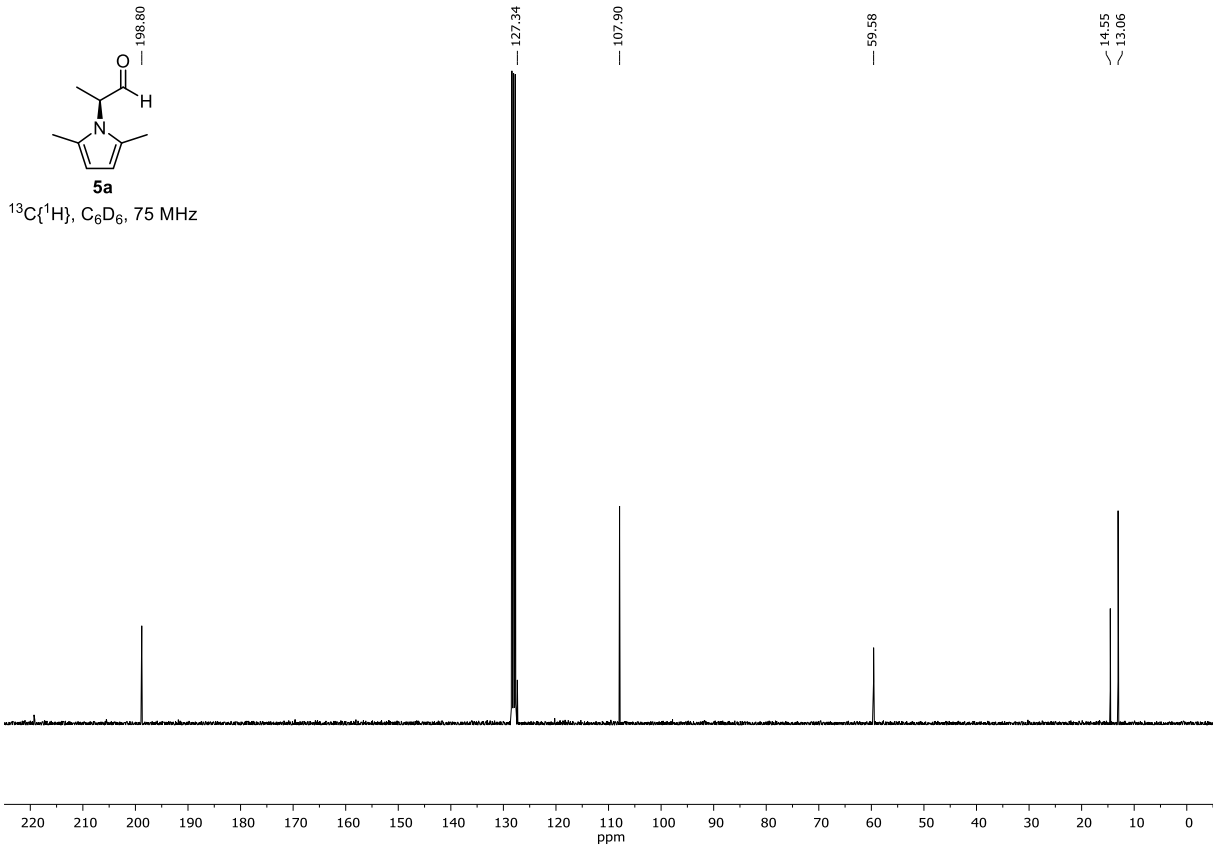

TBSO
O
N
O
N
4f
1H, C6D6, 300 MHz
5.91
4.98
4.96
4.95
4.93
4.33
4.31
4.30
4.28
4.15
4.12
4.12
4.09
2.75
2.53
2.25
0.89
-0.05
-0.08
2.06
1.00
1.09
1.08
3.12
3.08
6.52
9.47
3.10
3.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


TBSO
O
N
O
N
4f
13C{1H}, C6D6, 75 MHz
171.10
128.61
106.87
63.68
60.00
57.39
32.03
26.03
18.44
13.39
-5.61
-5.76
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



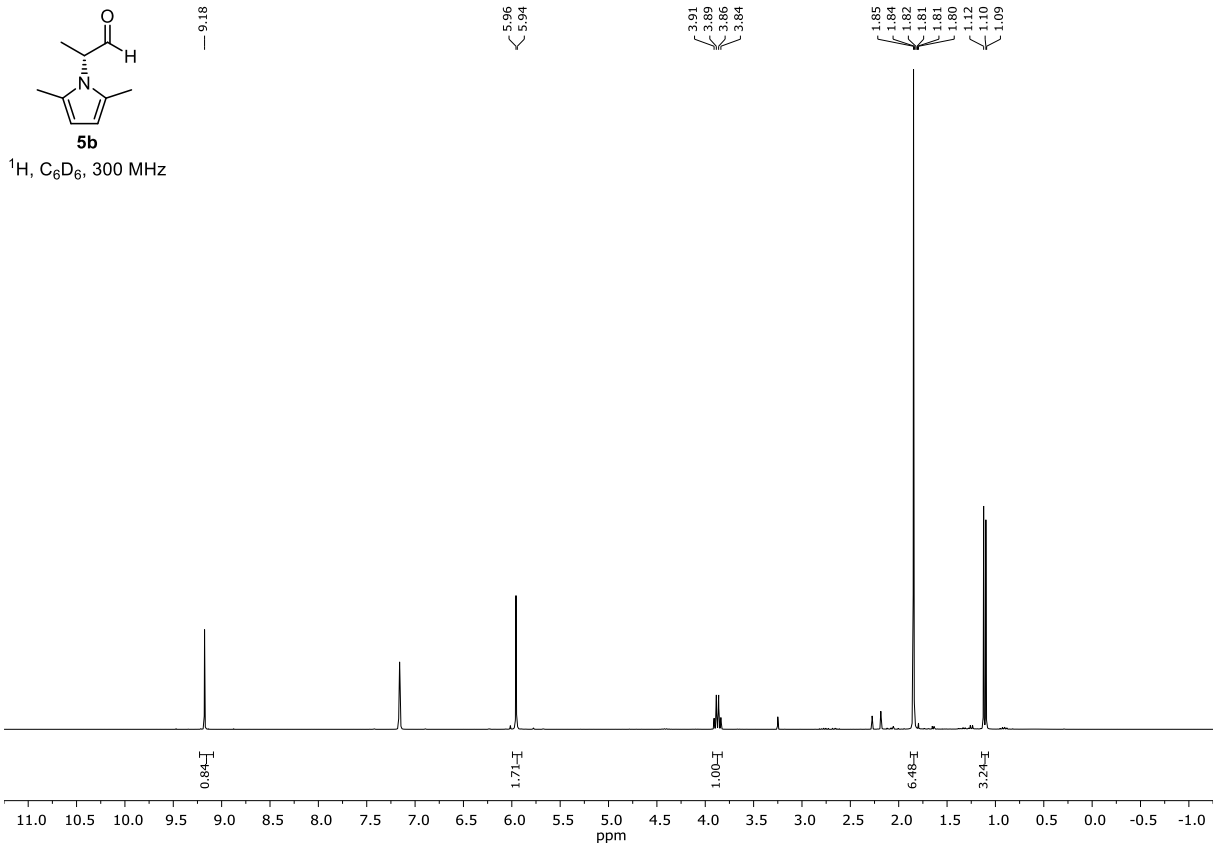
5a

^{1}H, C_6D_6, 300 MHz



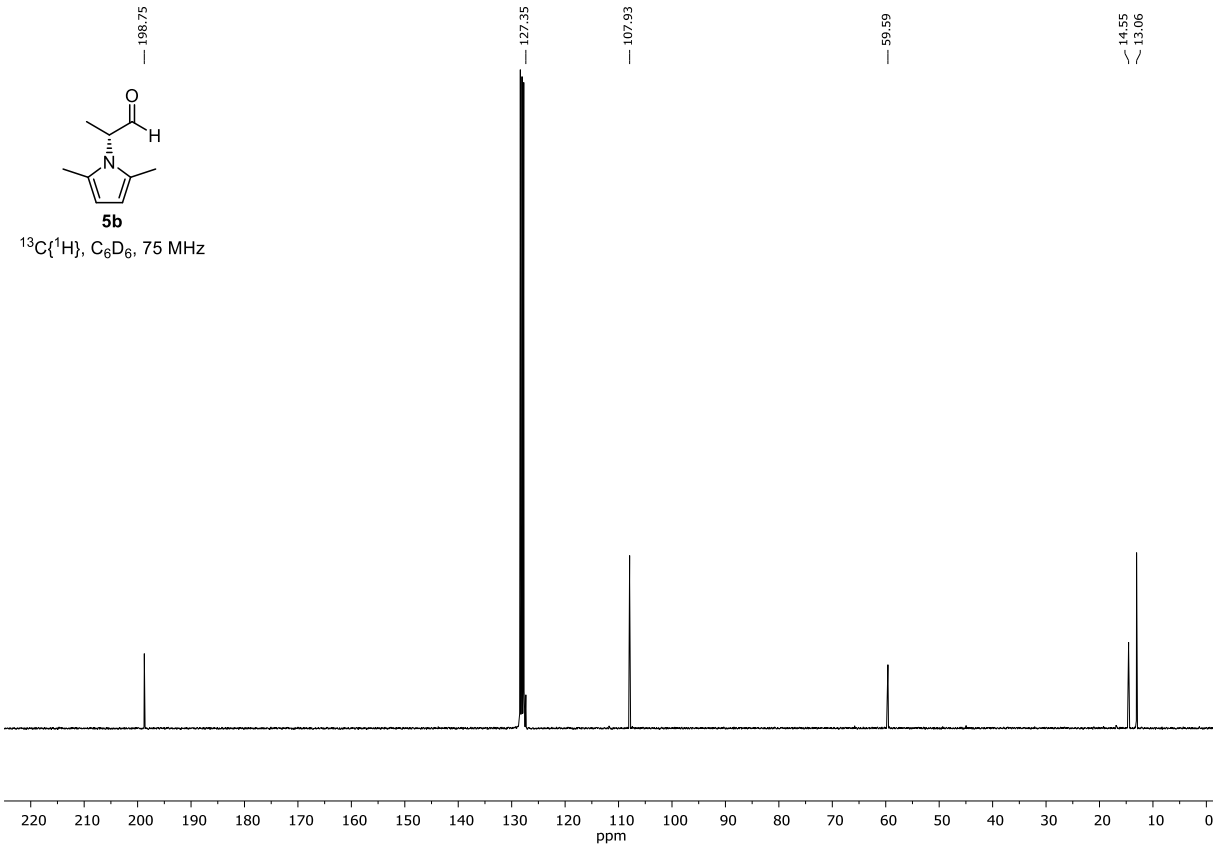
5a

$^{13}C\{^{1}H\}$, C_6D_6, 75 MHz



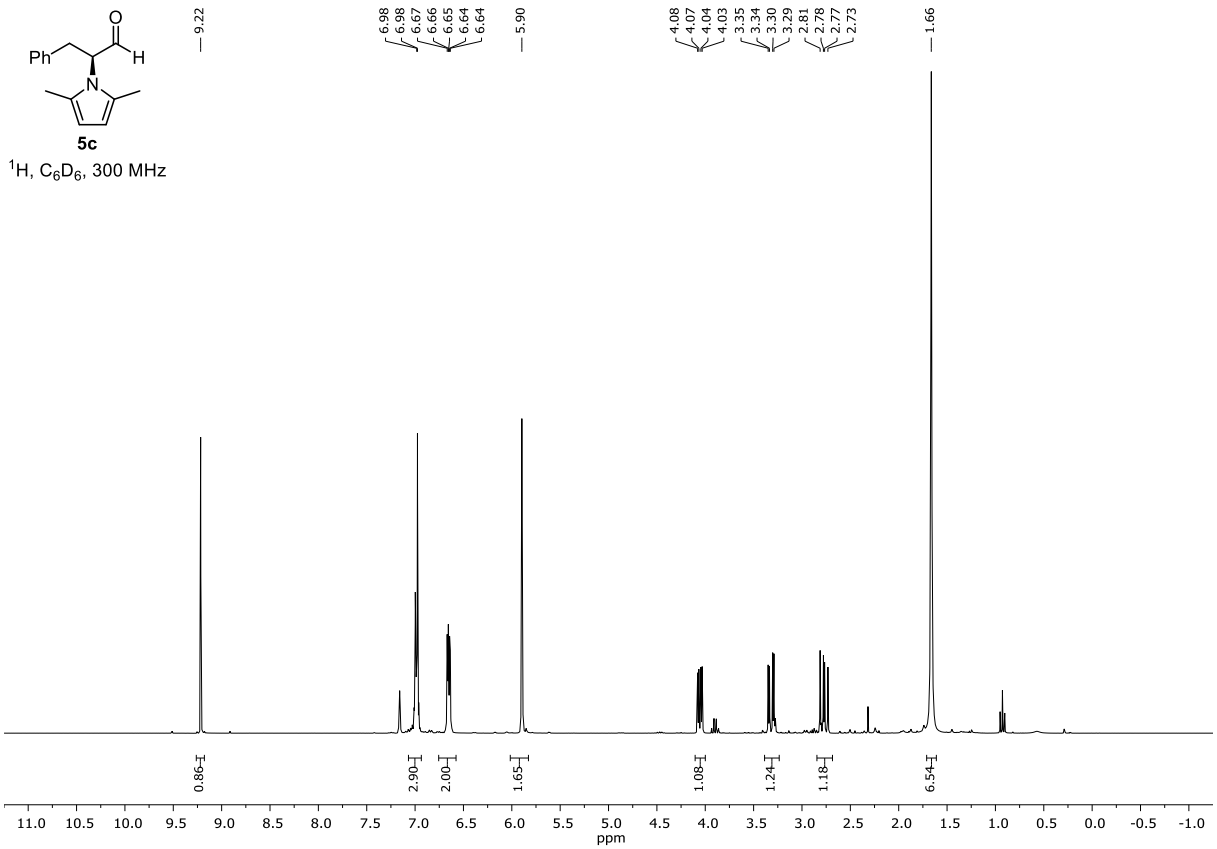
5b

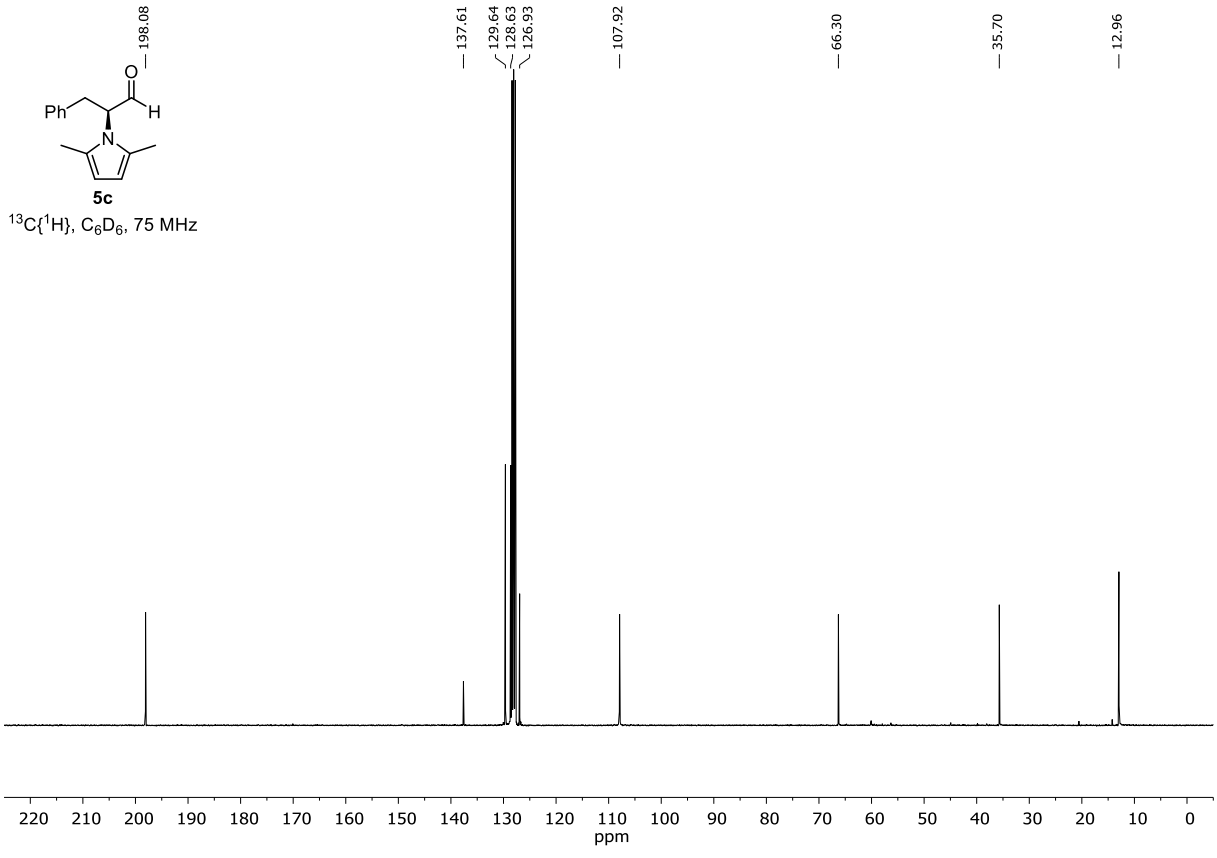
^{1}H, C_6D_6, 300 MHz

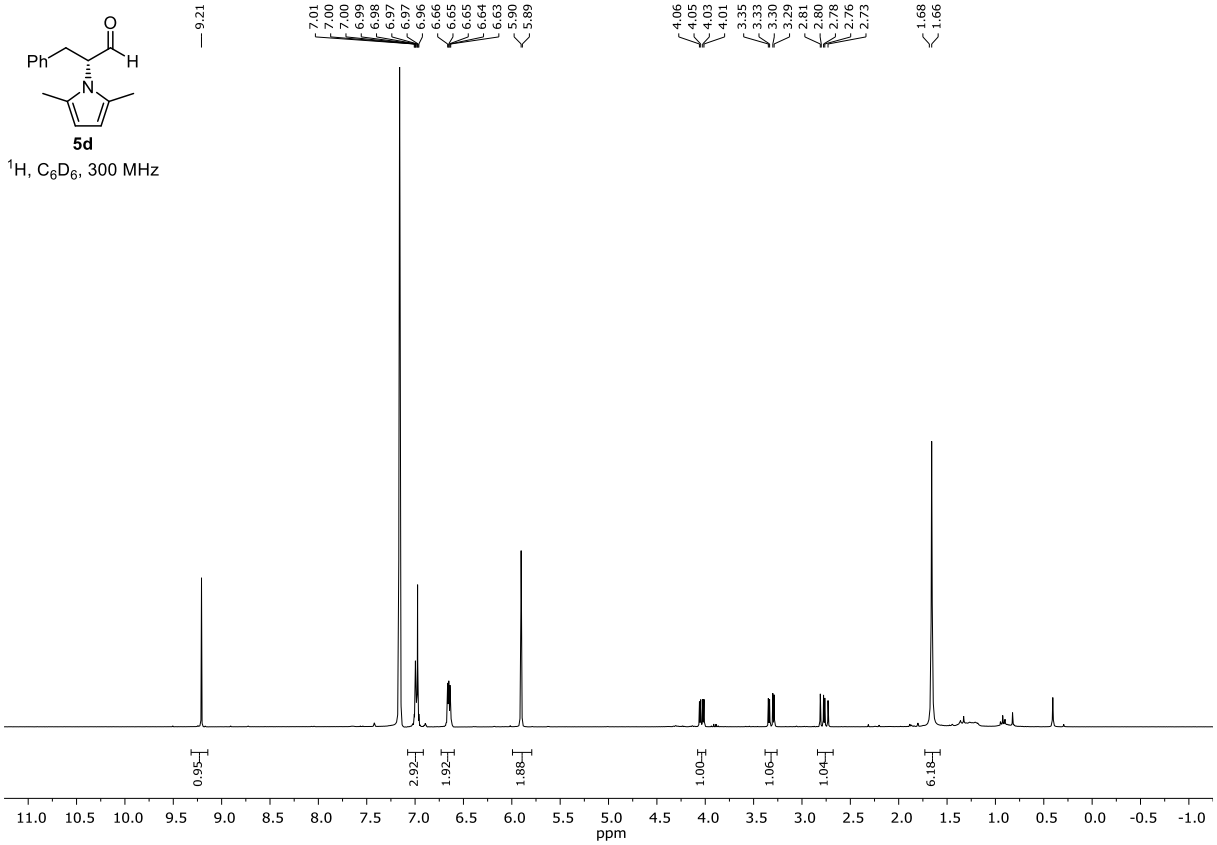


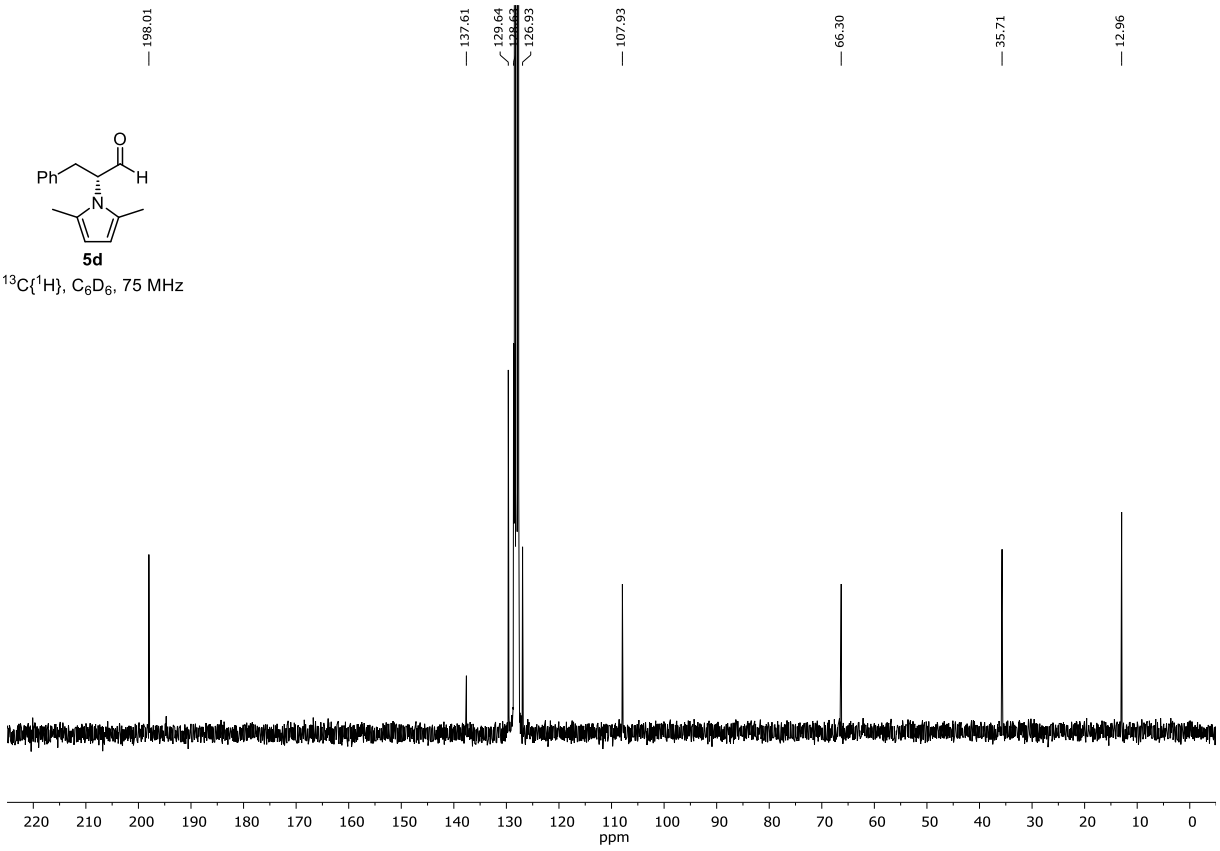
5b

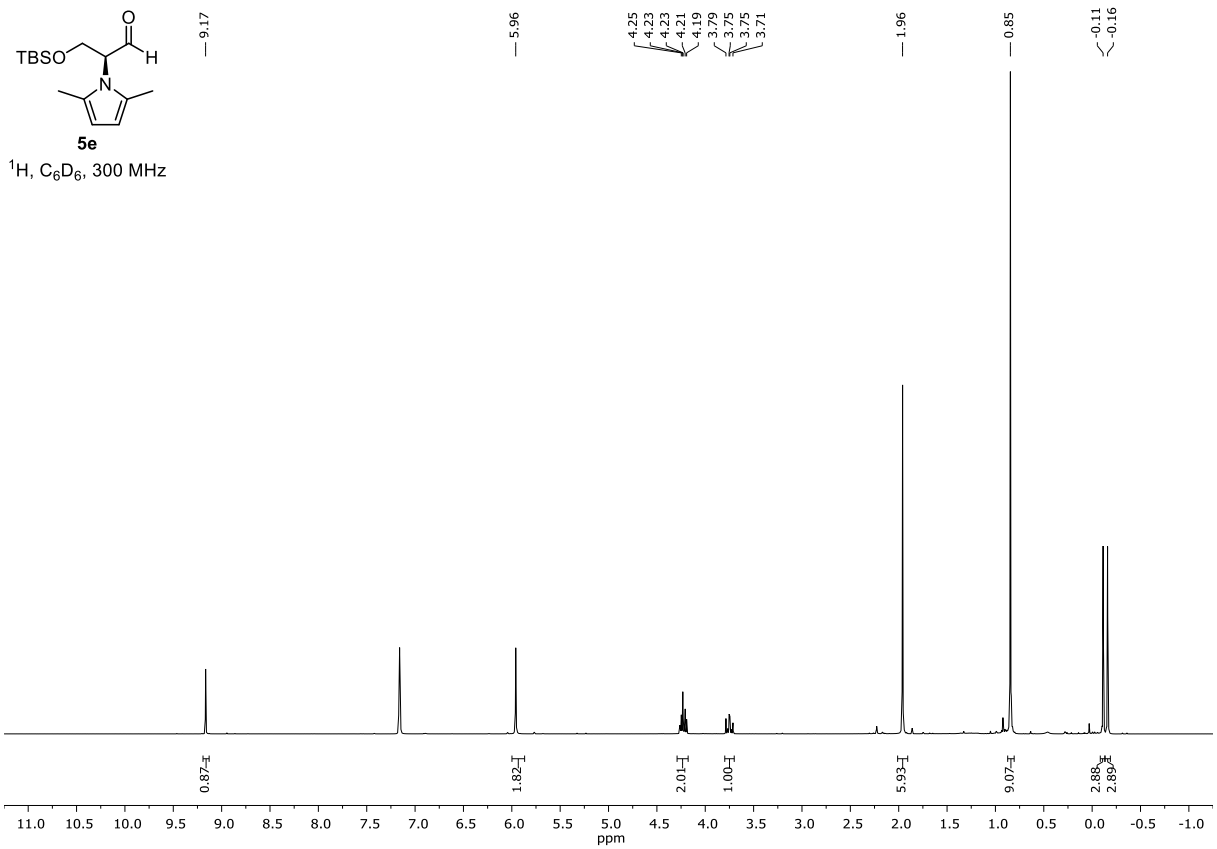
$^{13}C\{^{1}H\}$, C_6D_6, 75 MHz

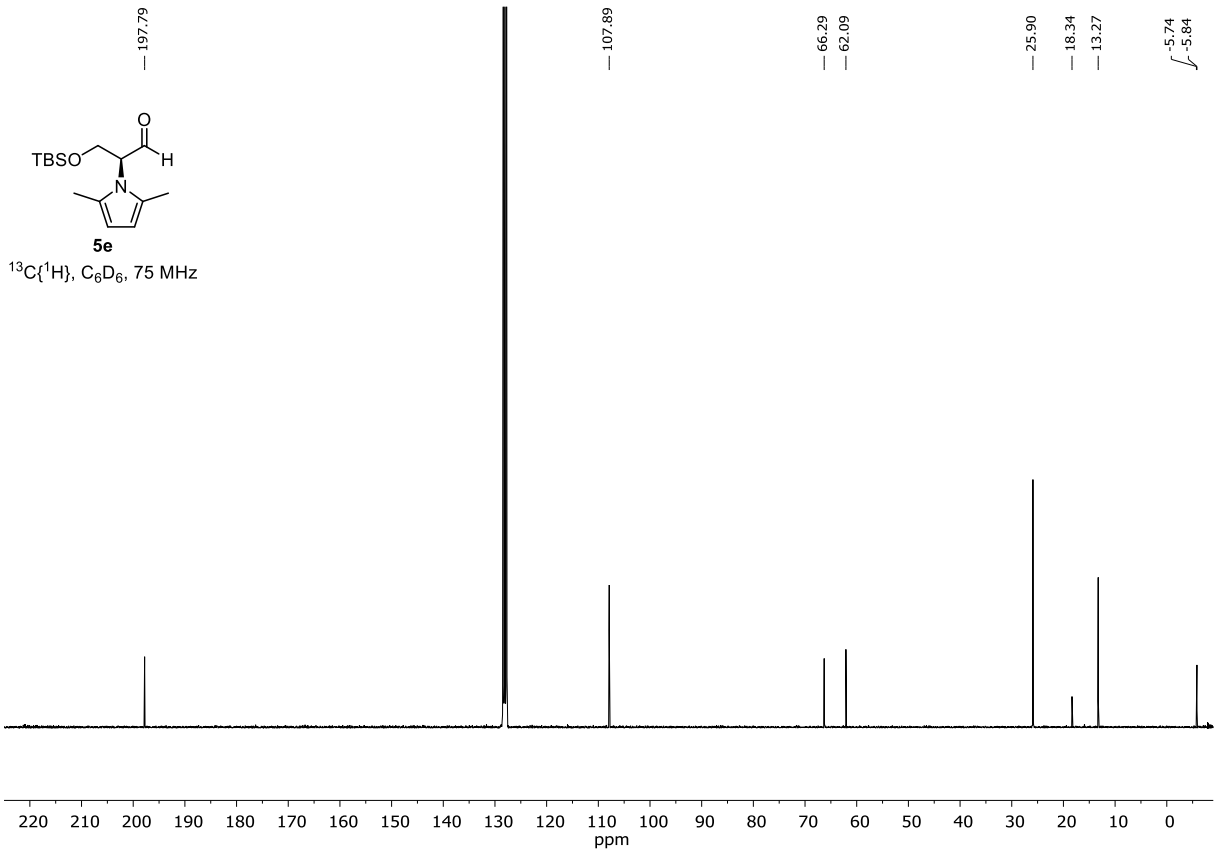

5c
^{1}H, C_6D_6, 300 MHz
9.22
6.98
6.98
6.67
6.66
6.65
6.64
6.64
5.90
4.08
4.07
4.04
4.03
3.35
3.34
3.30
3.29
2.81
2.78
2.77
2.73
1.66
0.86
2.90
2.00
1.65
1.08
1.24
1.18
6.54
ppm

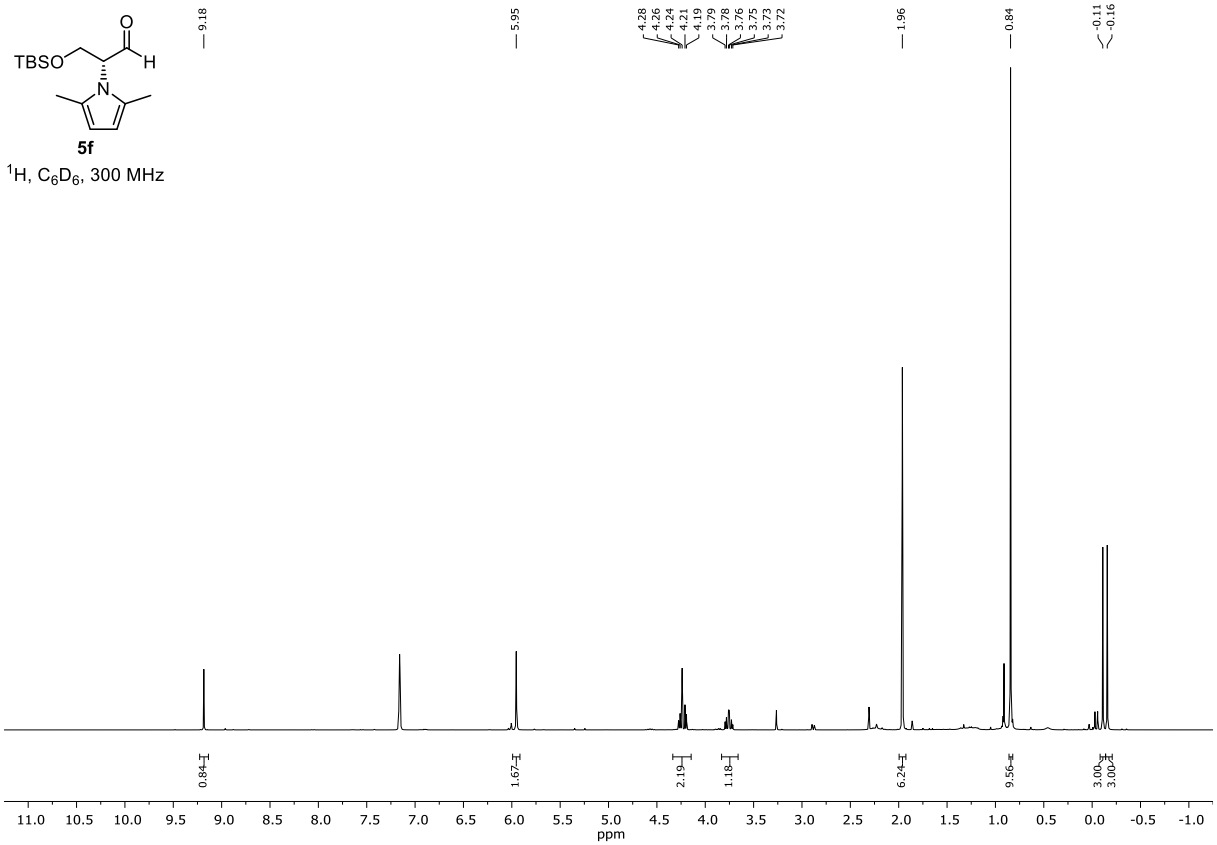

5c
^{13}C{^{1}H}, C_6D_6, 75 MHz
198.08
137.61
129.64
128.63
126.93
107.92
66.30
35.70
12.96
ppm


Ph
O
H
N
5d
^{1}H, C_6D_6, 300 MHz
9.21
7.01
7.00
7.00
6.99
6.98
6.97
6.97
6.96
6.66
6.65
6.65
6.64
6.63
5.90
5.89
4.06
4.05
4.03
4.01
3.35
3.33
3.30
3.29
2.81
2.80
2.78
2.76
2.73
1.68
1.66
0.95
2.92
1.92
1.88
1.00
1.06
1.04
6.18
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


Ph
O
H
N
5d
^{13}C{^{1}H}, C_6D_6, 75 MHz
198.01
137.61
129.64
128.62
126.93
107.93
66.30
35.71
12.96
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

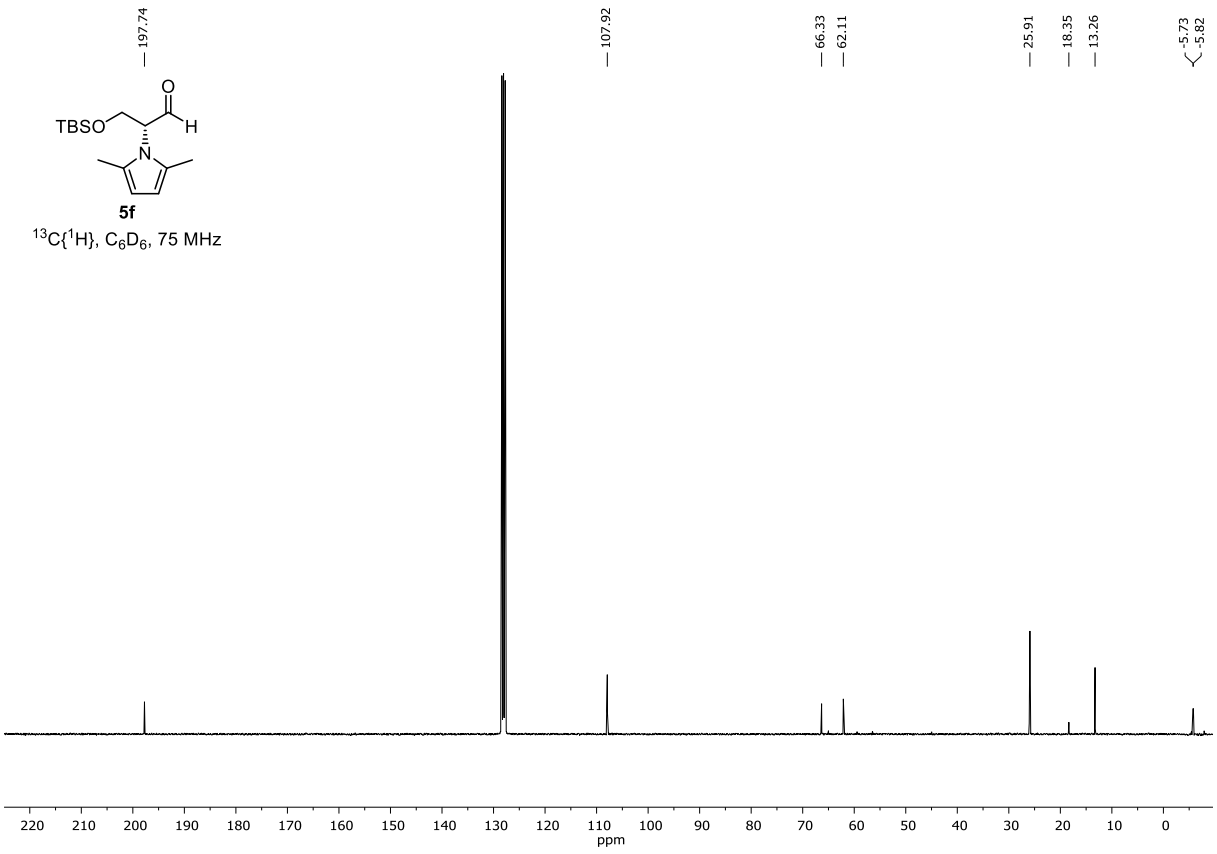

TBSO
O
H
N
5e
1H, C6D6, 300 MHz
9.17
5.96
4.25
4.23
4.23
4.21
4.19
3.79
3.75
3.75
3.71
1.96
0.85
-0.11
-0.16
0.87
1.82
2.01
1.00
5.93
9.07
2.88
2.89
ppm


TBSO
O
H
N
5e
13C{1H}, C6D6, 75 MHz
197.79
107.89
66.29
62.09
25.90
18.34
13.27
-5.74
-5.84
ppm



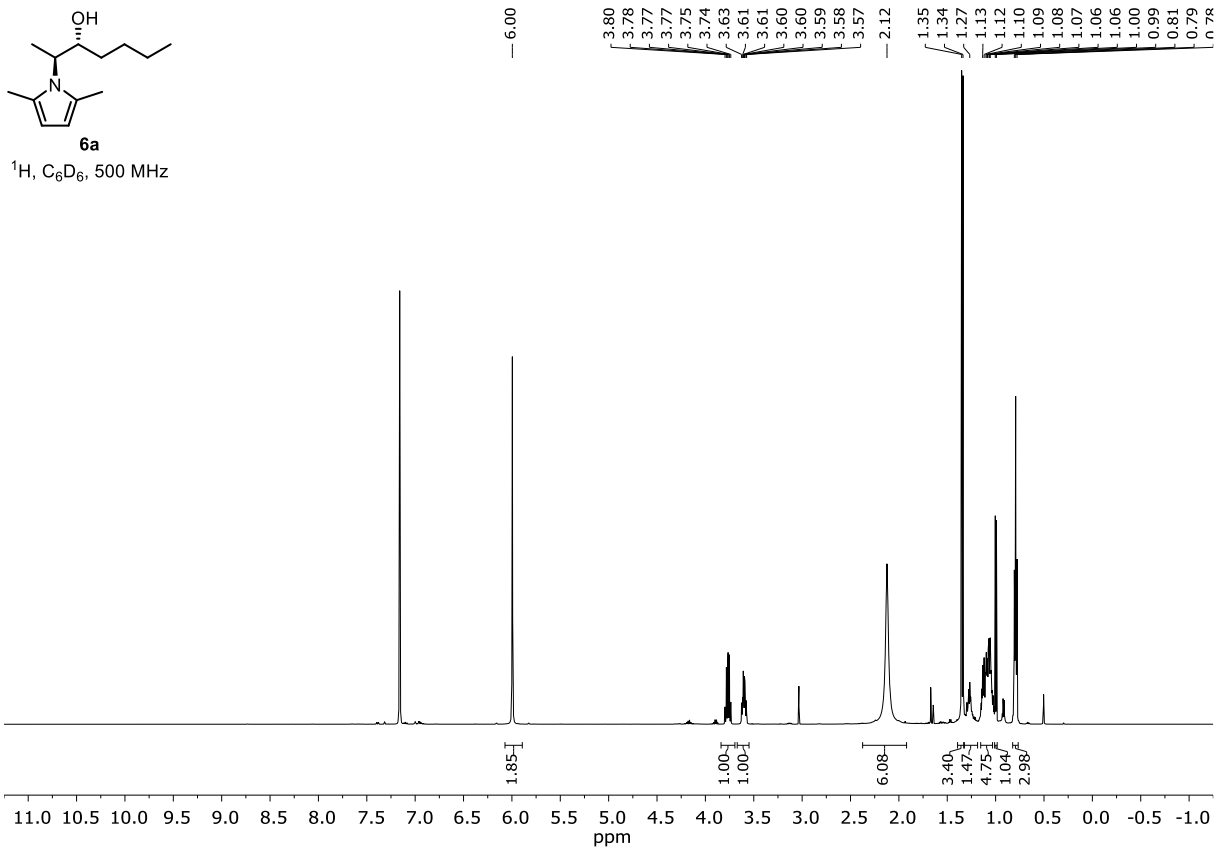
5f

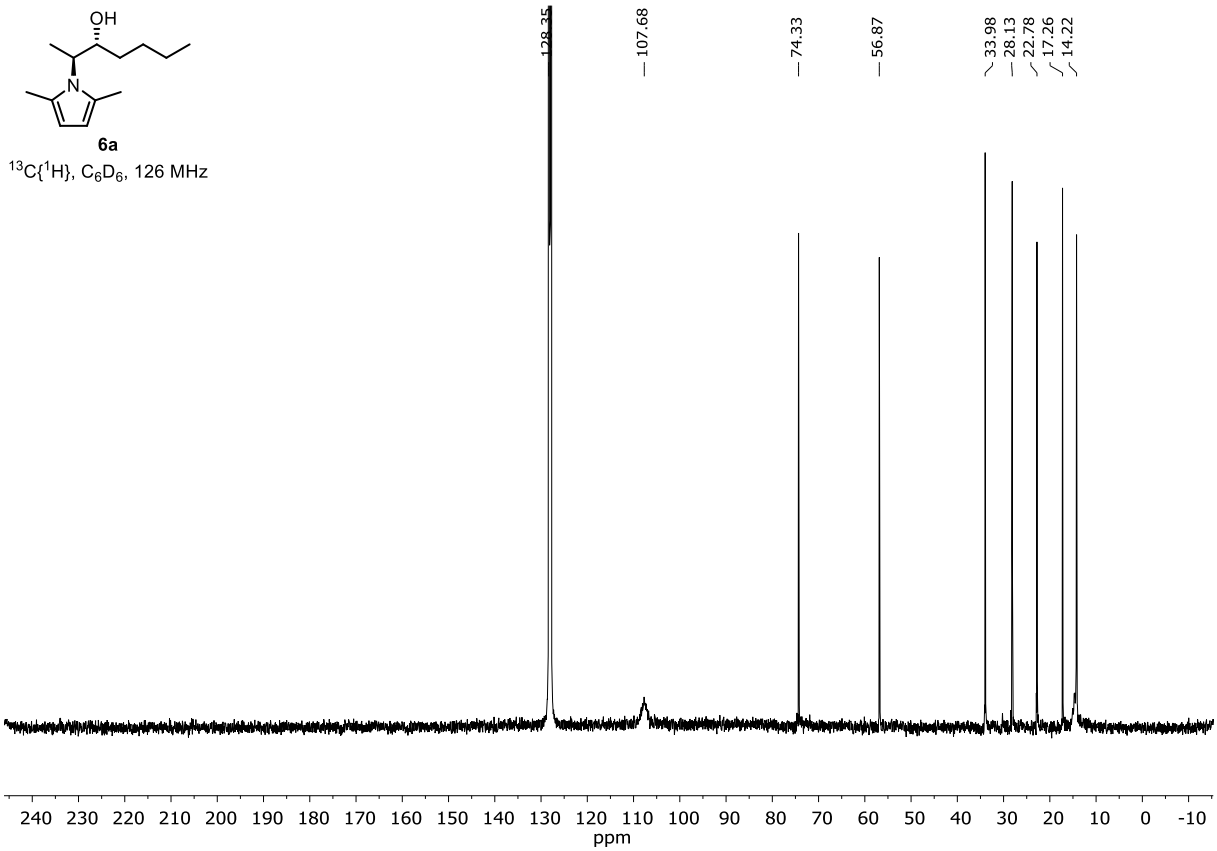
^{1}H, C_6D_6, 300 MHz

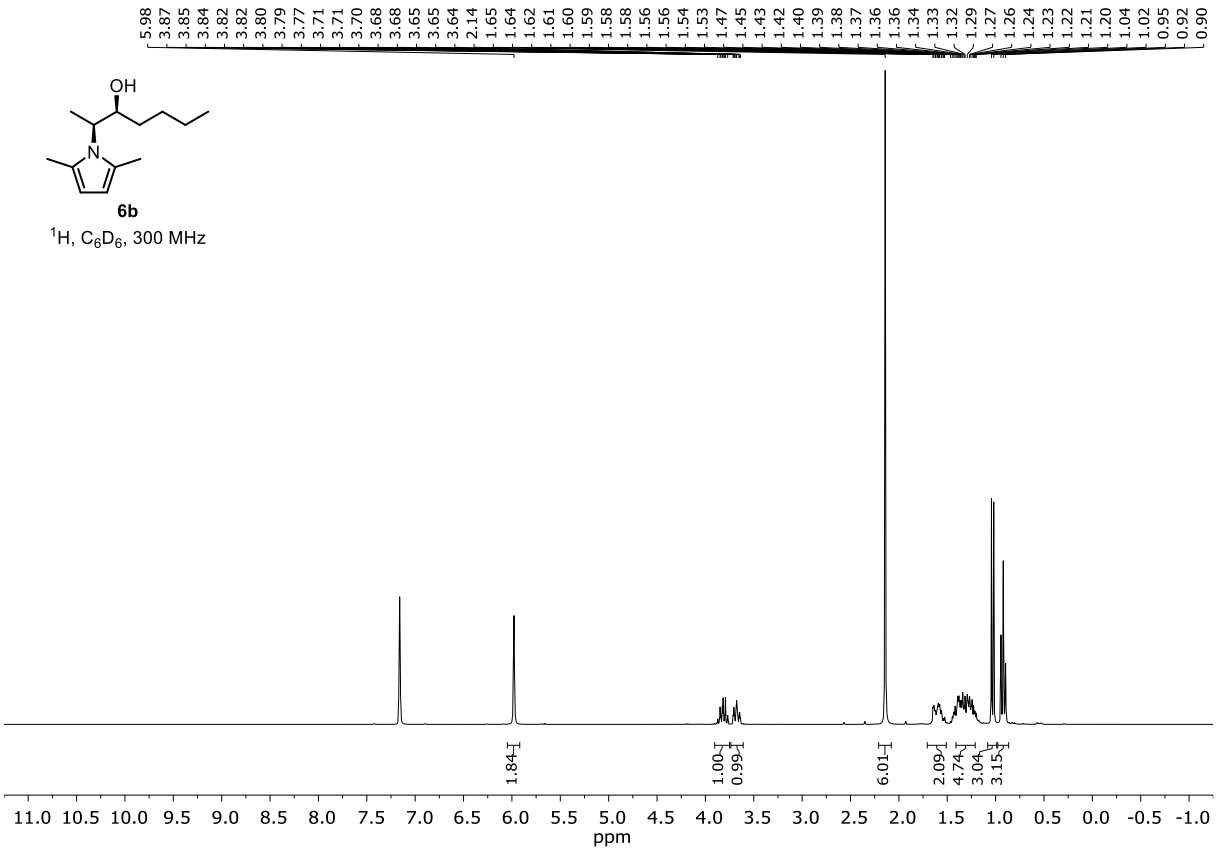


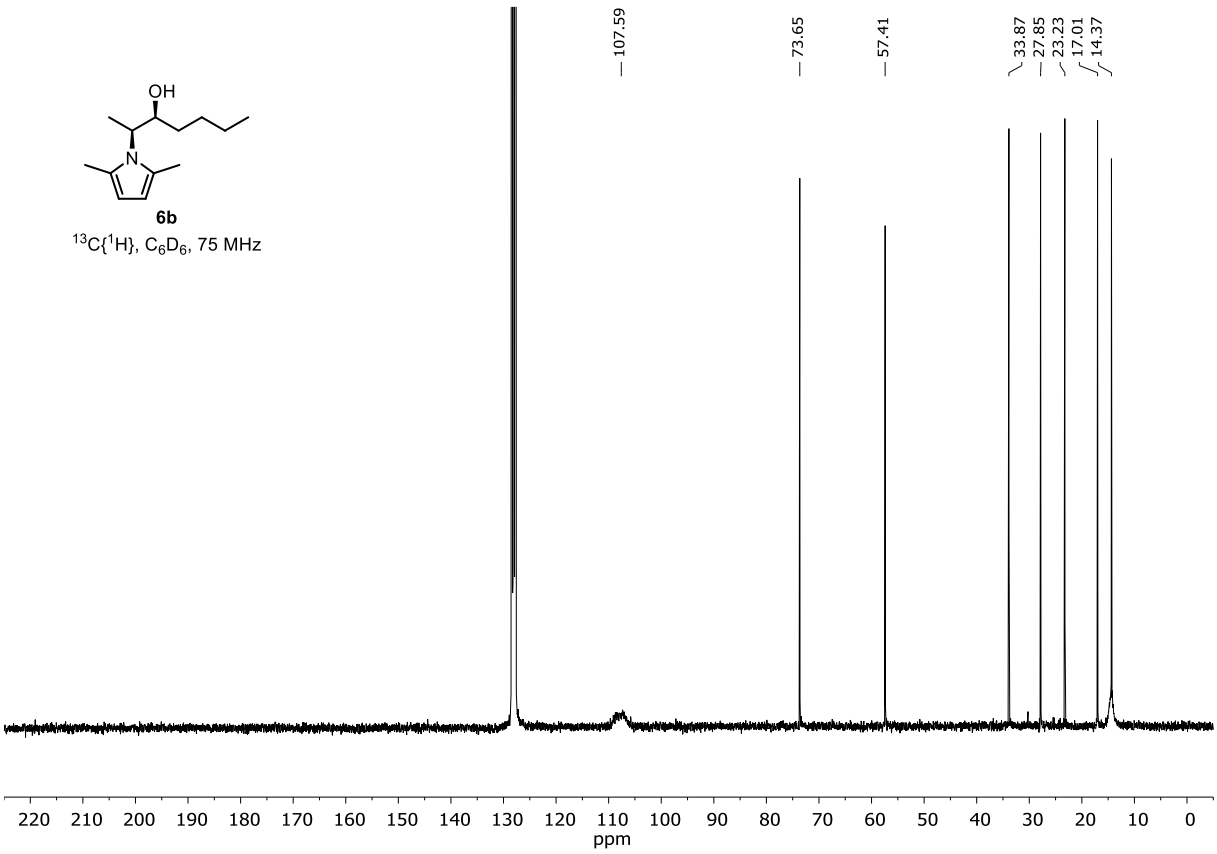
5f

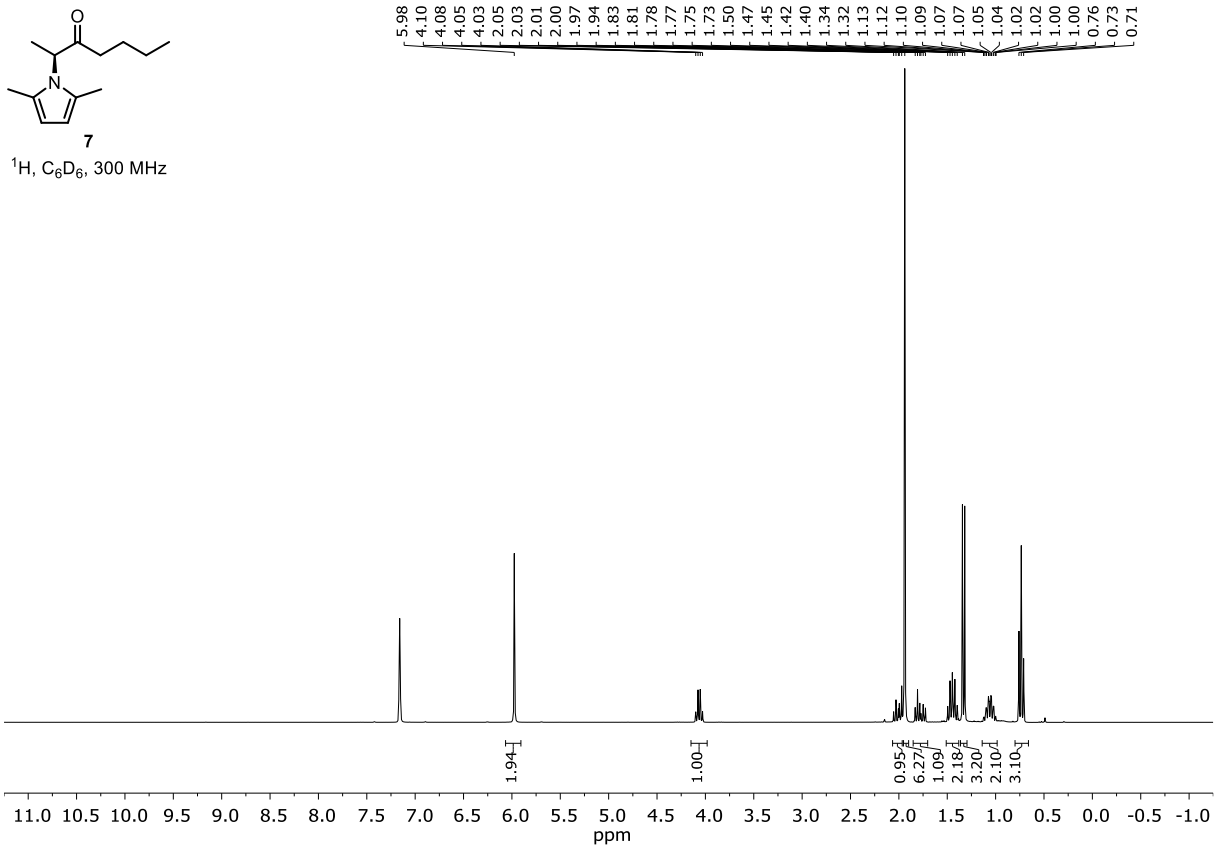
$^{13}C\{^{1}H\}$, C_6D_6, 75 MHz

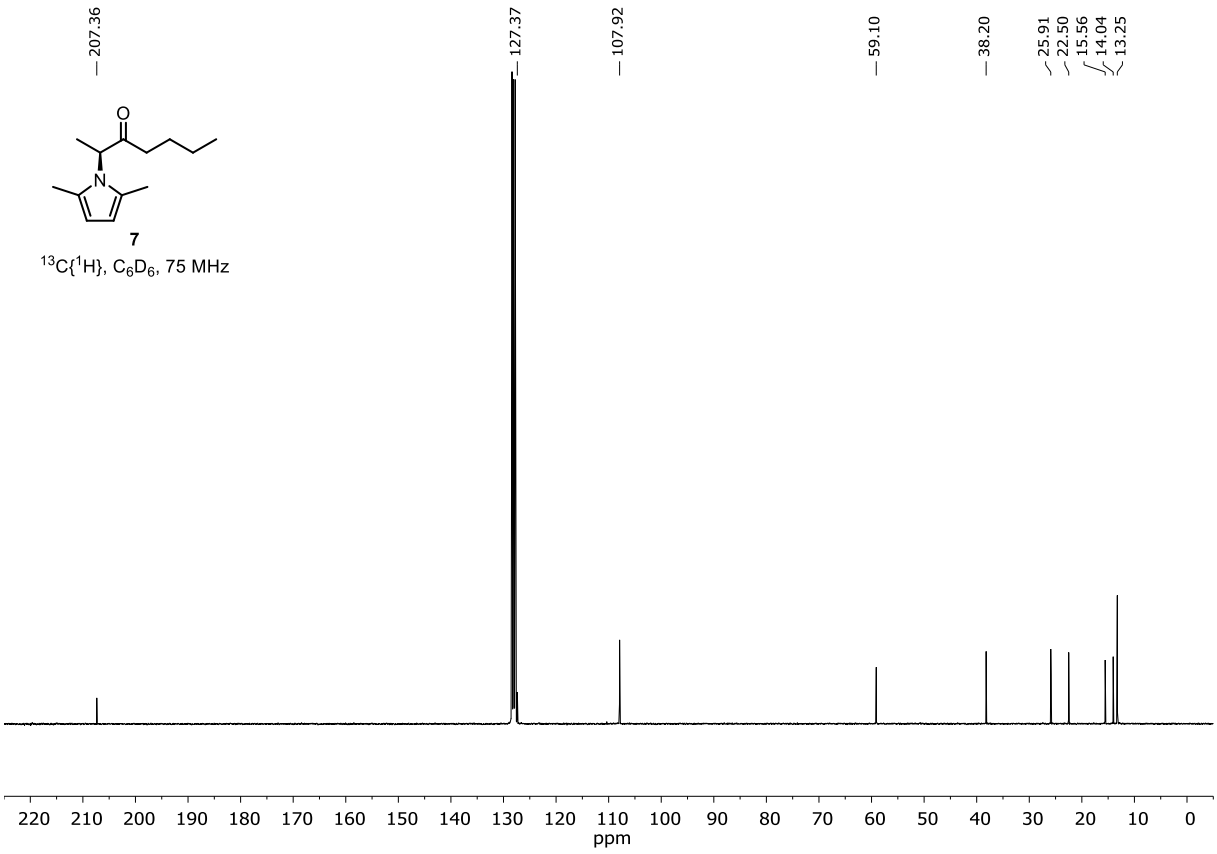

OH
N
6a
1H, C6D6, 500 MHz
6.00
3.80
3.78
3.77
3.77
3.75
3.74
3.63
3.61
3.61
3.60
3.60
3.59
3.58
3.57
2.12
1.35
1.34
1.27
1.13
1.12
1.10
1.09
1.08
1.07
1.06
1.06
1.00
0.99
0.81
0.79
1.85
1.00
1.00
6.08
3.40
1.47
4.75
1.04
2.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

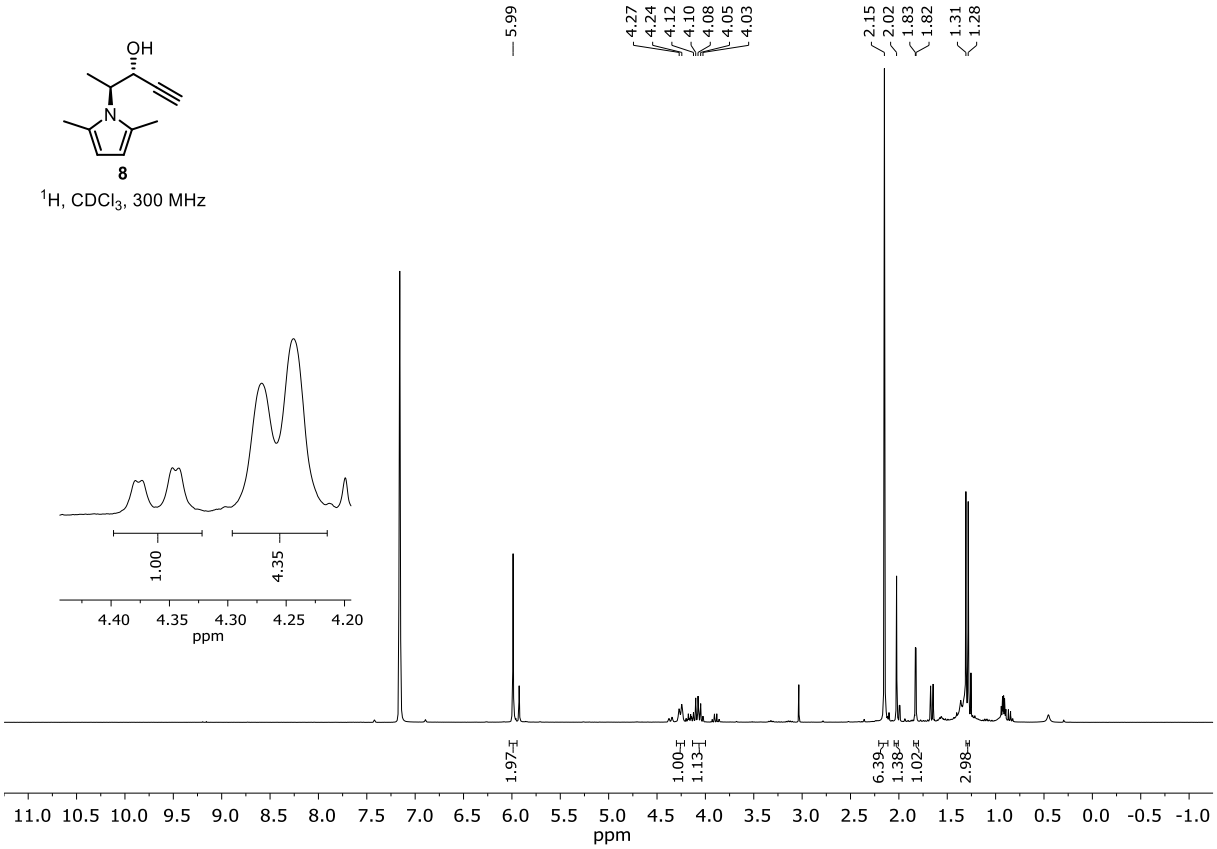

OH
N
6a
13C{1H}, C6D6, 126 MHz
128.35
107.68
74.33
56.87
33.98
28.13
22.78
17.26
14.22
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

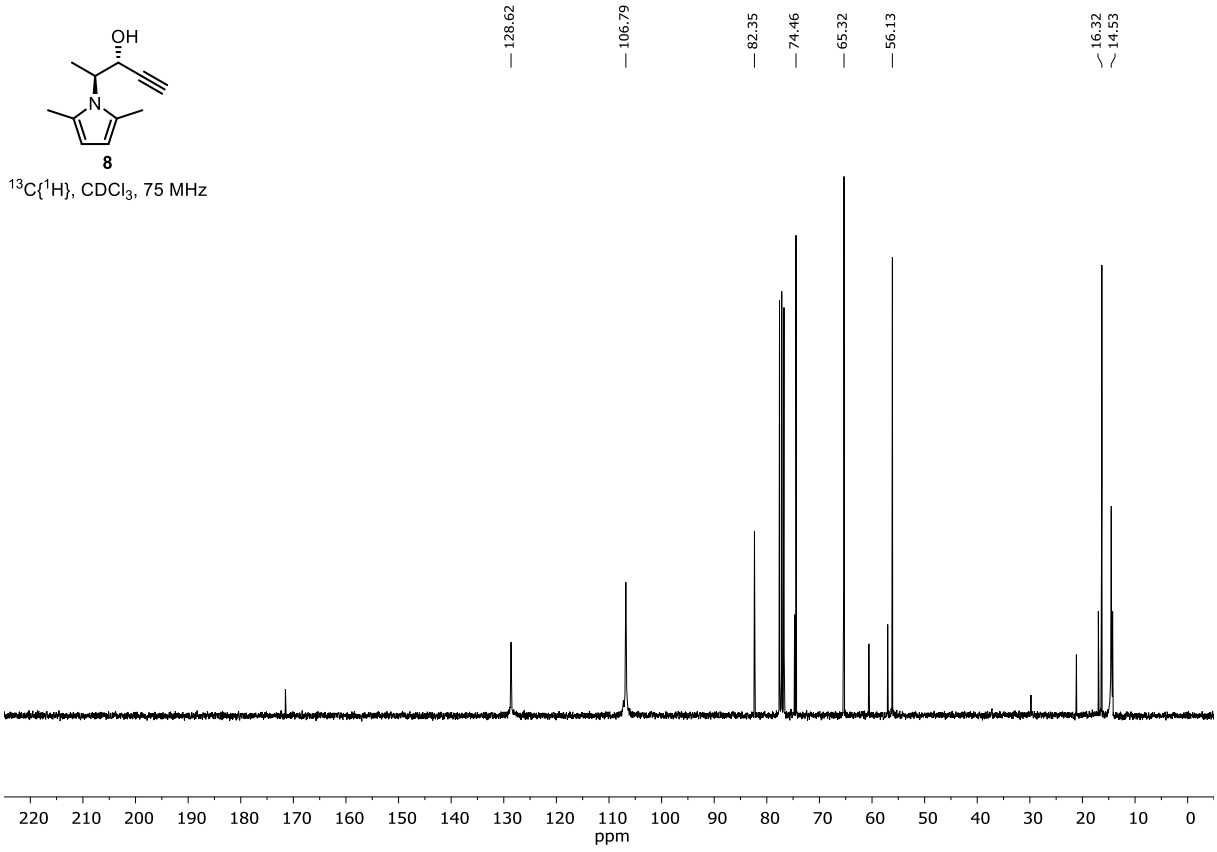

5.98 3.87 3.85 3.84 3.82 3.80 3.79 3.77 3.71 3.71 3.70 3.68 3.68 3.65 3.65 3.64 2.14 1.65 1.64 1.62 1.61 1.60 1.59 1.58 1.58 1.56 1.56 1.54 1.53 1.47 1.45 1.43 1.42 1.40 1.39 1.38 1.37 1.36 1.36 1.34 1.33 1.32 1.29 1.27 1.26 1.24 1.23 1.22 1.21 1.20 1.04 1.02 0.95 0.92 0.90
OH
N
6b
1H, C6D6, 300 MHz
1.84
1.00
0.99
6.01
2.09
4.74
3.04
3.15
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

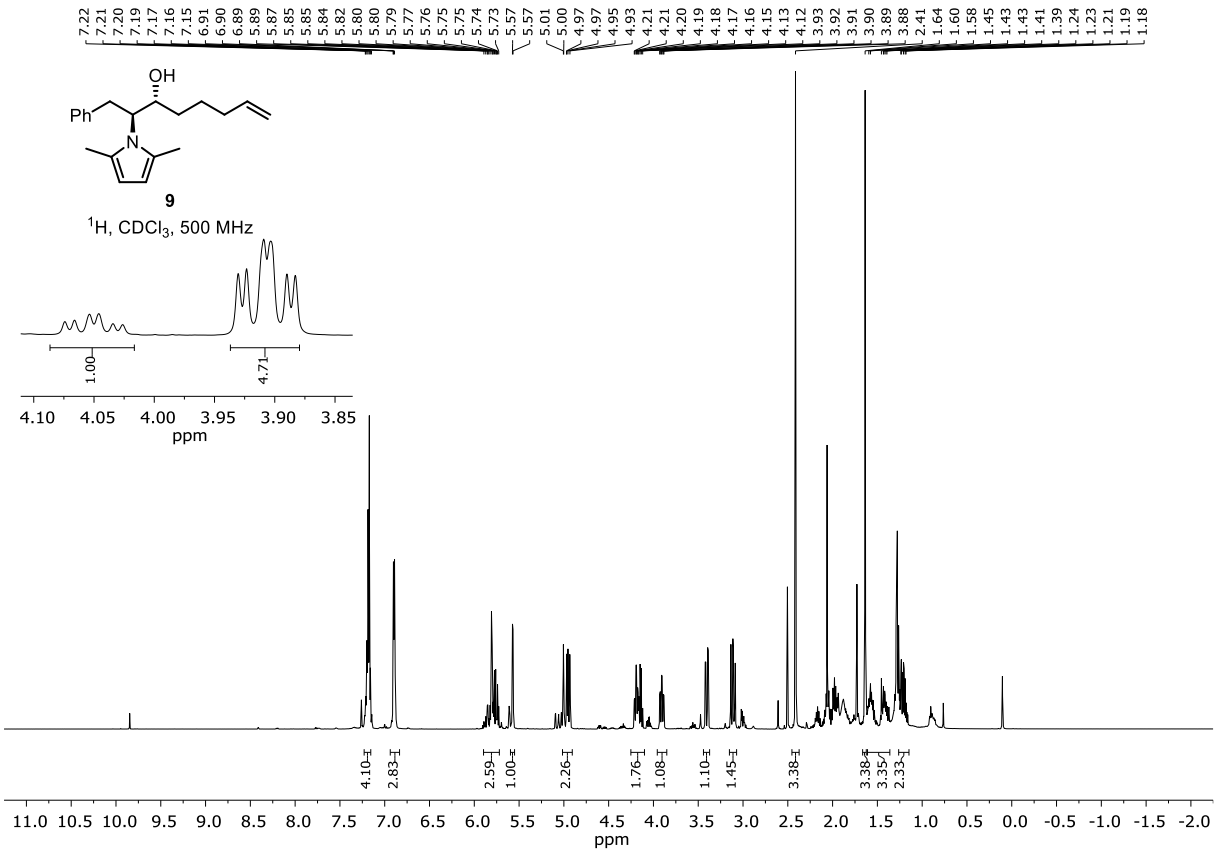

OH
N
6b
13C{1H}, C6D6, 75 MHz
107.59
73.65
57.41
33.87
27.85
23.23
17.01
14.37
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

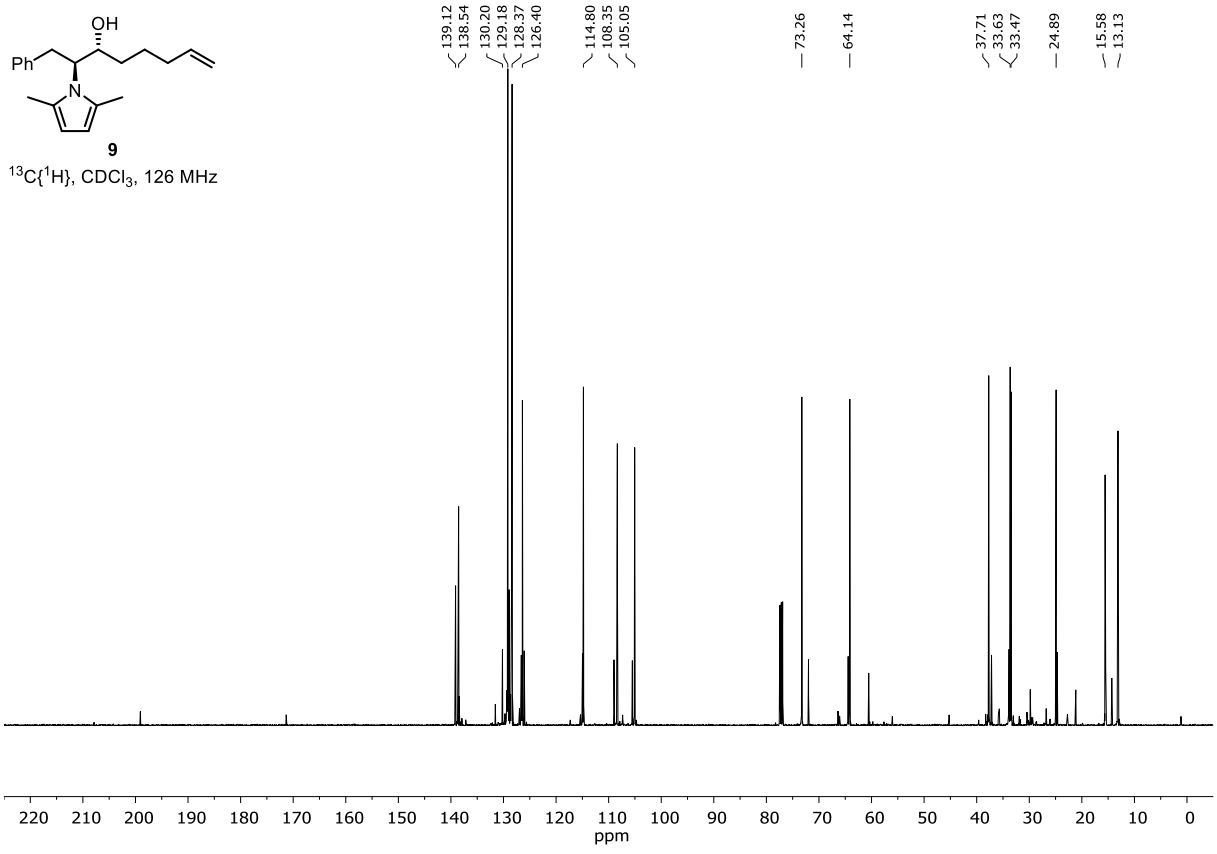

7
^{1}H, C_6D_6, 300 MHz
5.98
4.10
4.08
4.05
4.03
2.05
2.03
2.01
2.00
1.97
1.94
1.83
1.81
1.78
1.77
1.75
1.73
1.50
1.47
1.45
1.42
1.40
1.34
1.32
1.13
1.12
1.10
1.09
1.07
1.07
1.05
1.04
1.02
1.02
1.00
1.00
0.76
0.73
0.71
1.94
1.00
0.95
6.27
1.09
2.18
3.20
2.10
3.10
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

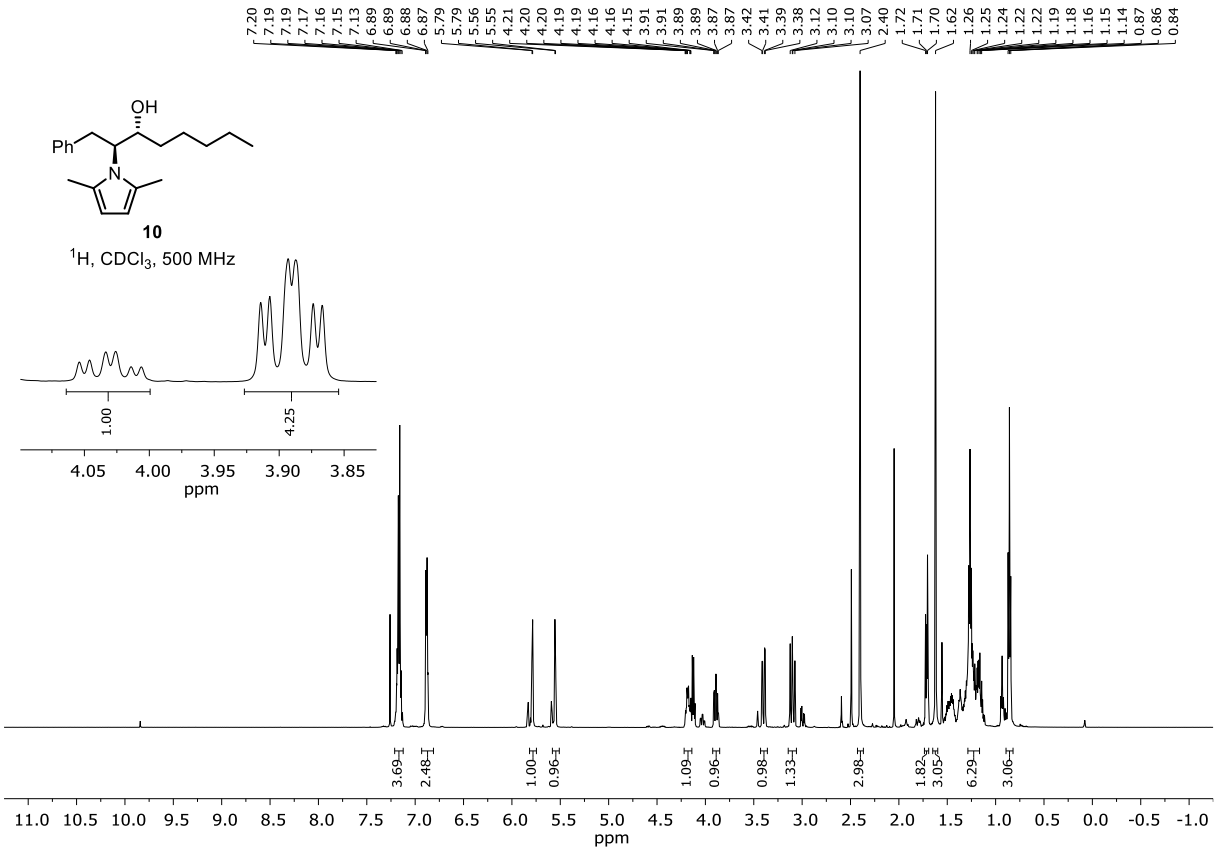

207.36
127.37
107.92
59.10
38.20
25.91
22.50
15.56
14.04
13.25
7
^{13}C{^{1}H}, C_6D_6, 75 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

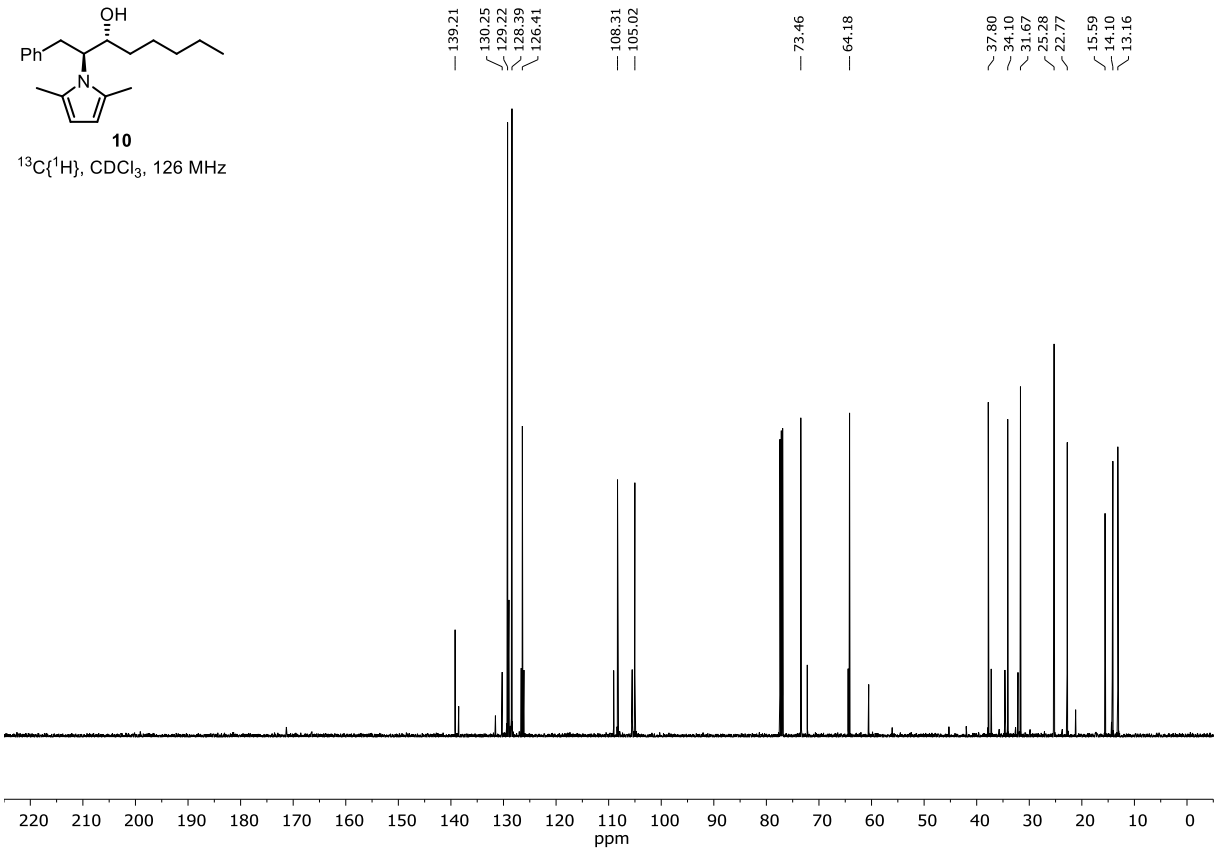

OH
N
8
^{1}H, CDCl$_3$, 300 MHz
5.99
4.27
4.24
4.12
4.10
4.08
4.05
4.03
2.15
2.02
1.83
1.82
1.31
1.28
1.97
1.00
1.13
6.39
1.38
1.02
2.98
1.00
4.35
4.40 4.35 4.30 4.25 4.20
ppm
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

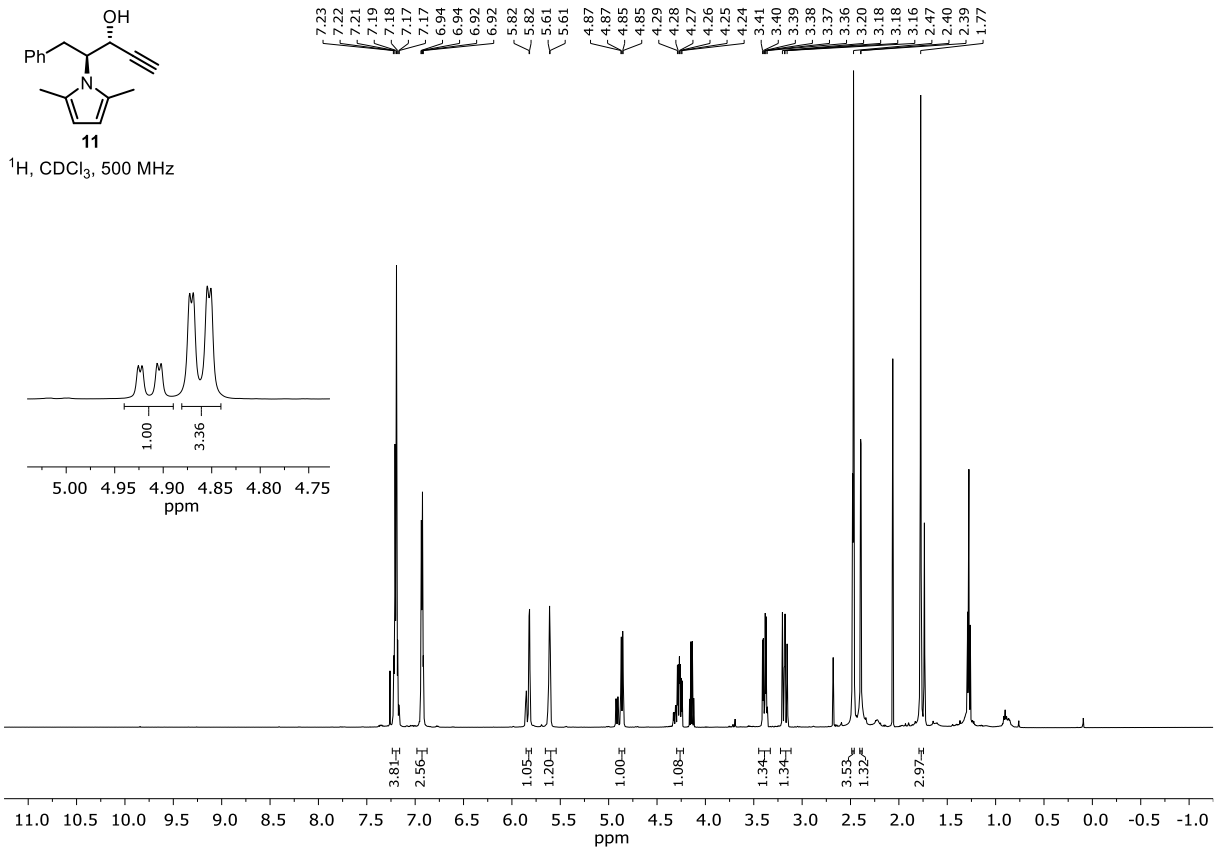

OH
N
8
^{13}C{^{1}H}, CDCl$_3$, 75 MHz
128.62
106.79
82.35
74.46
65.32
56.13
16.32
14.53
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

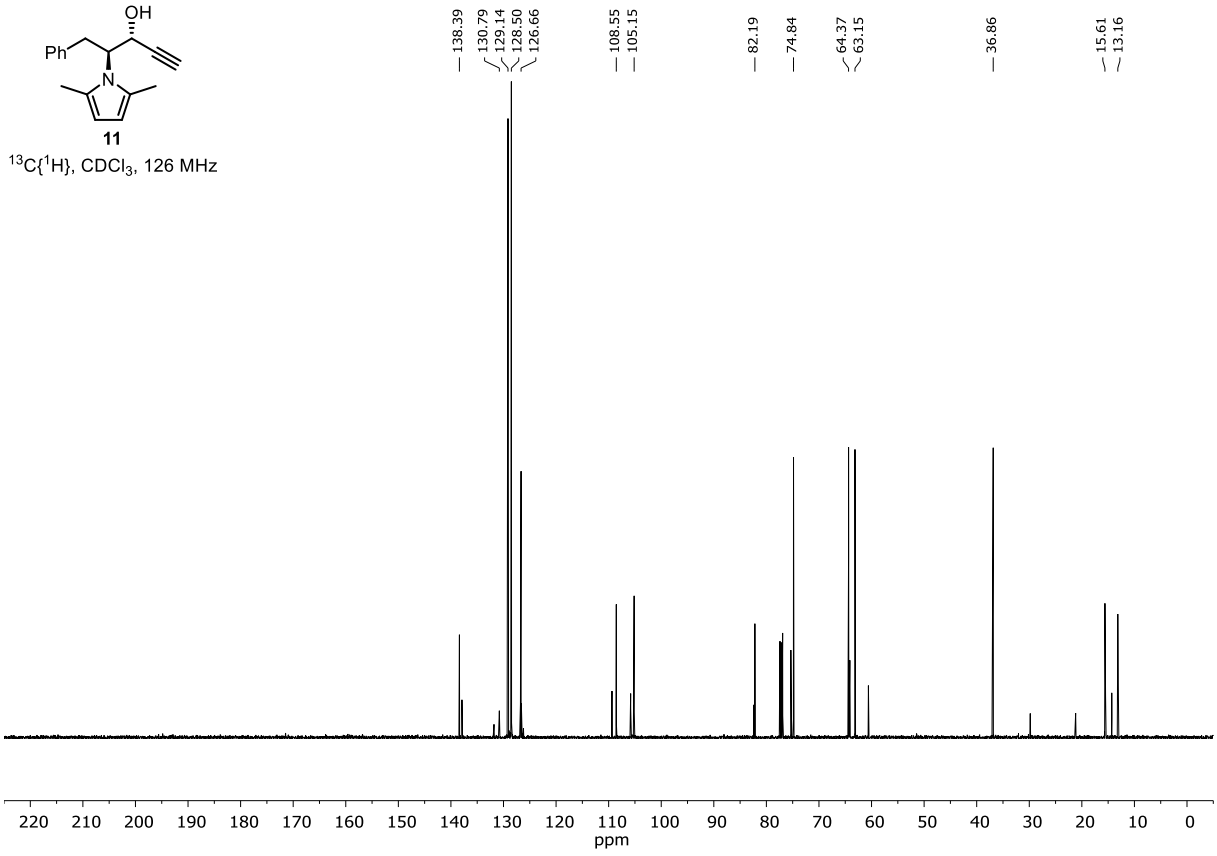

OH
Ph
N
9
1H, CDCl3, 500 MHz
1.00
4.71
4.10 4.05 4.00 3.95 3.90 3.85
ppm
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
ppm

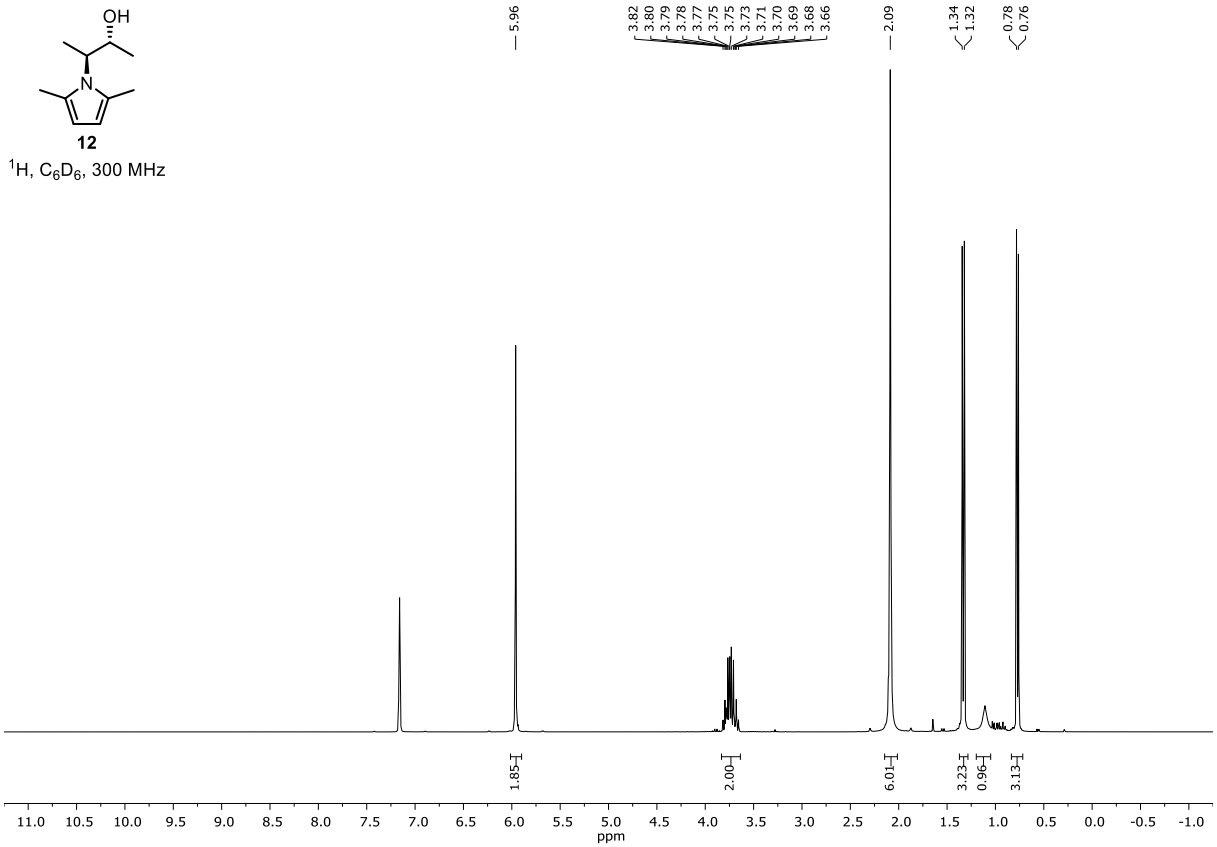

OH
Ph
N
9
13C{1H}, CDCl3, 126 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

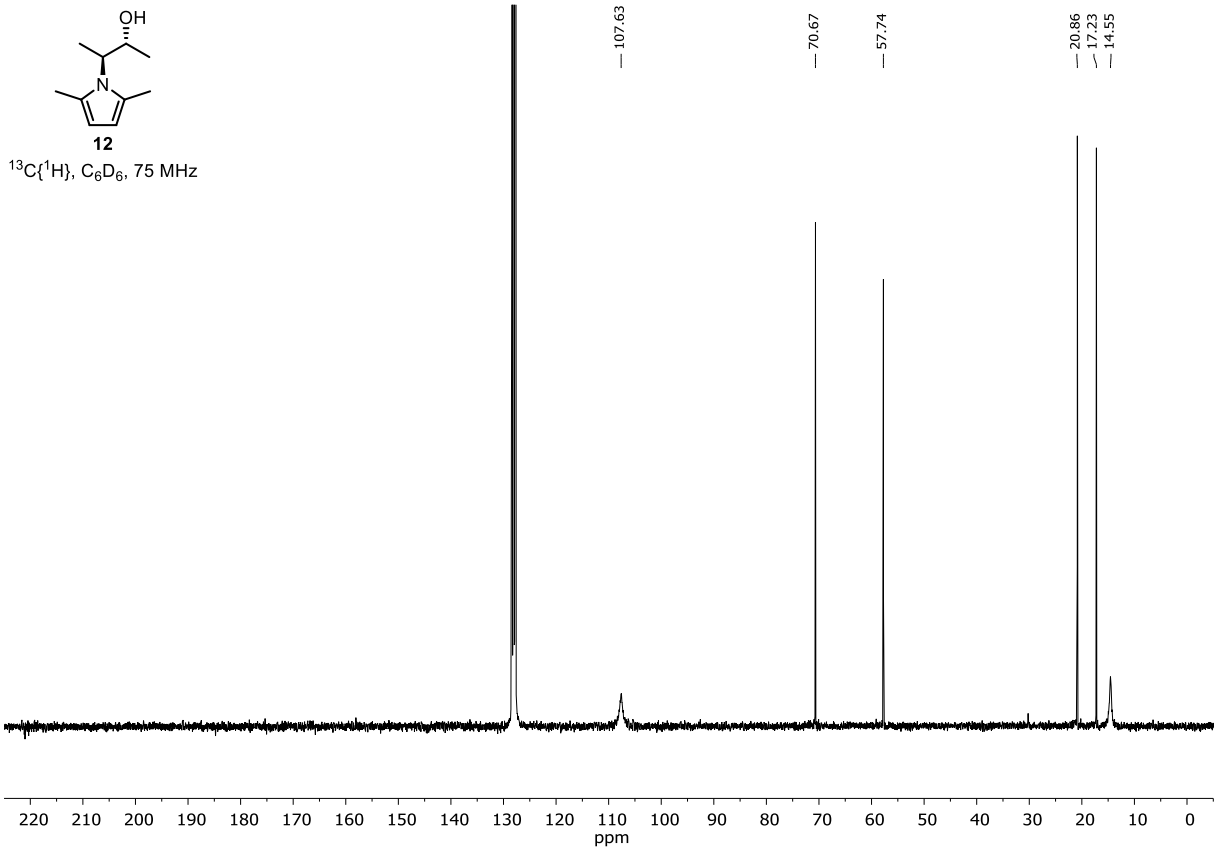

OH
Ph
N
10
1H, CDCl3, 500 MHz
1.00
4.25
4.05 4.00 3.95 3.90 3.85
ppm
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

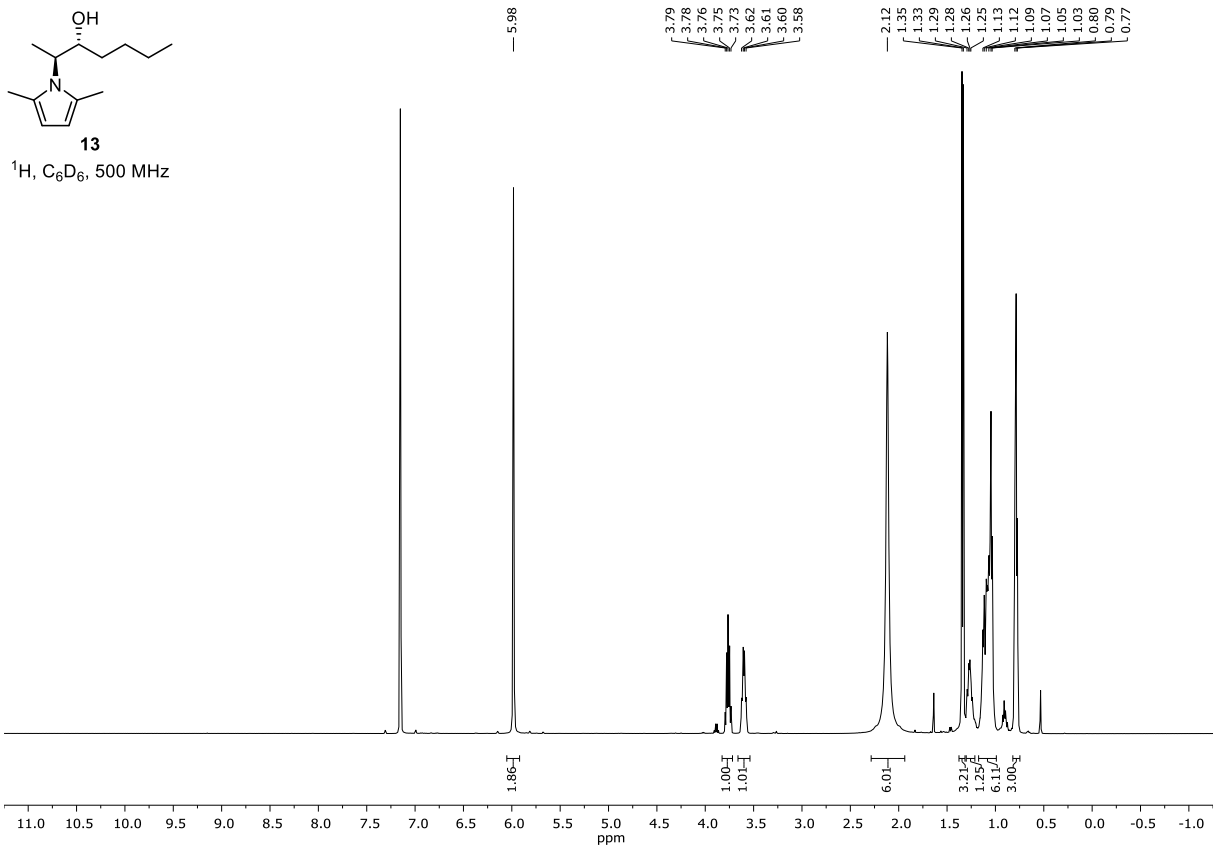

OH
Ph
N
10
13C{1H}, CDCl3, 126 MHz
139.21
130.25
129.22
128.39
126.41
108.31
105.02
73.46
64.18
37.80
34.10
31.67
25.28
22.77
15.59
14.10
13.16
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

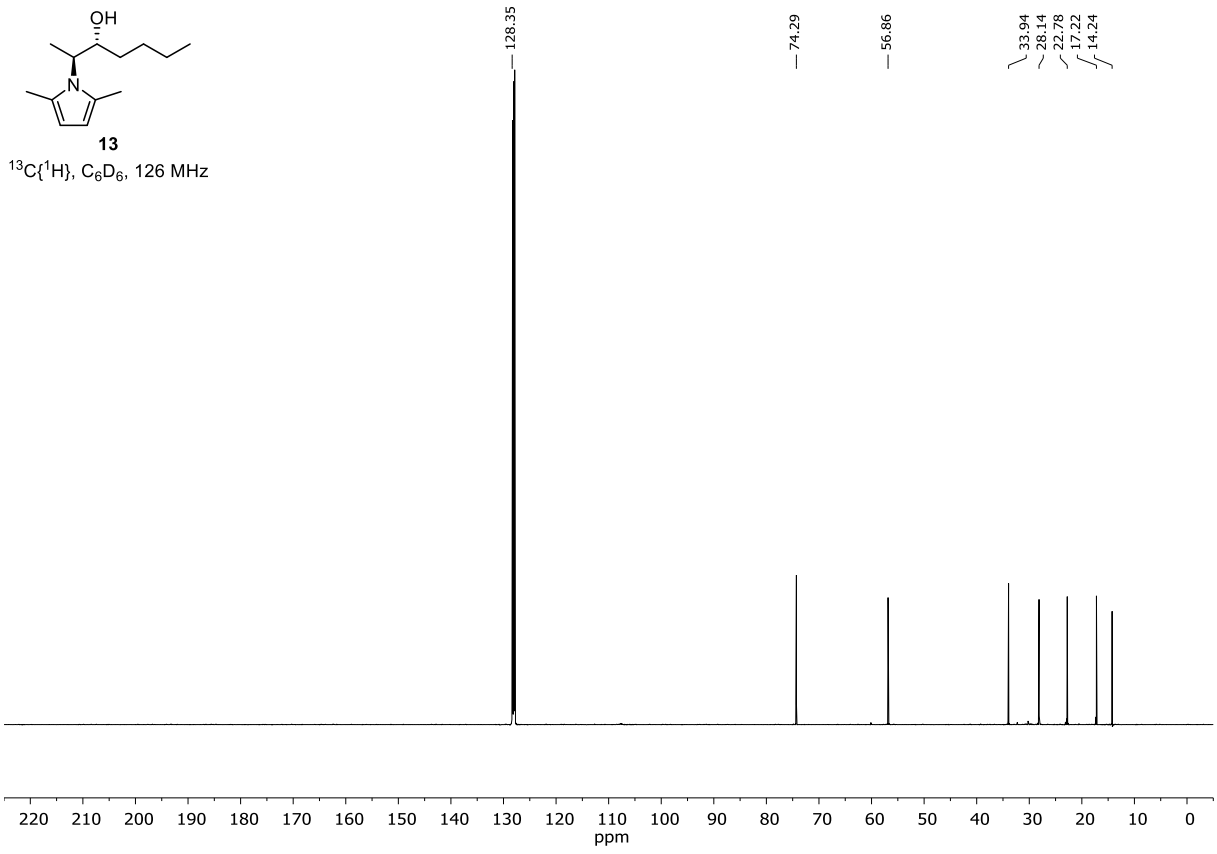

OH
Ph
N
11
1H, CDCl3, 500 MHz
7.23 7.22 7.21 7.19 7.18 7.17 7.17 6.94 6.94 6.92 6.92 5.82 5.82 5.61 5.61 4.87 4.87 4.85 4.85 4.29 4.28 4.27 4.26 4.25 4.24 3.41 3.40 3.39 3.38 3.37 3.36 3.20 3.18 3.18 3.16 2.47 2.40 2.39 1.77
1.00
3.36
5.00 4.95 4.90 4.85 4.80 4.75
ppm
3.81 2.56 1.05 1.20 1.00 1.08 1.34 1.34 3.53 1.32 2.97
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

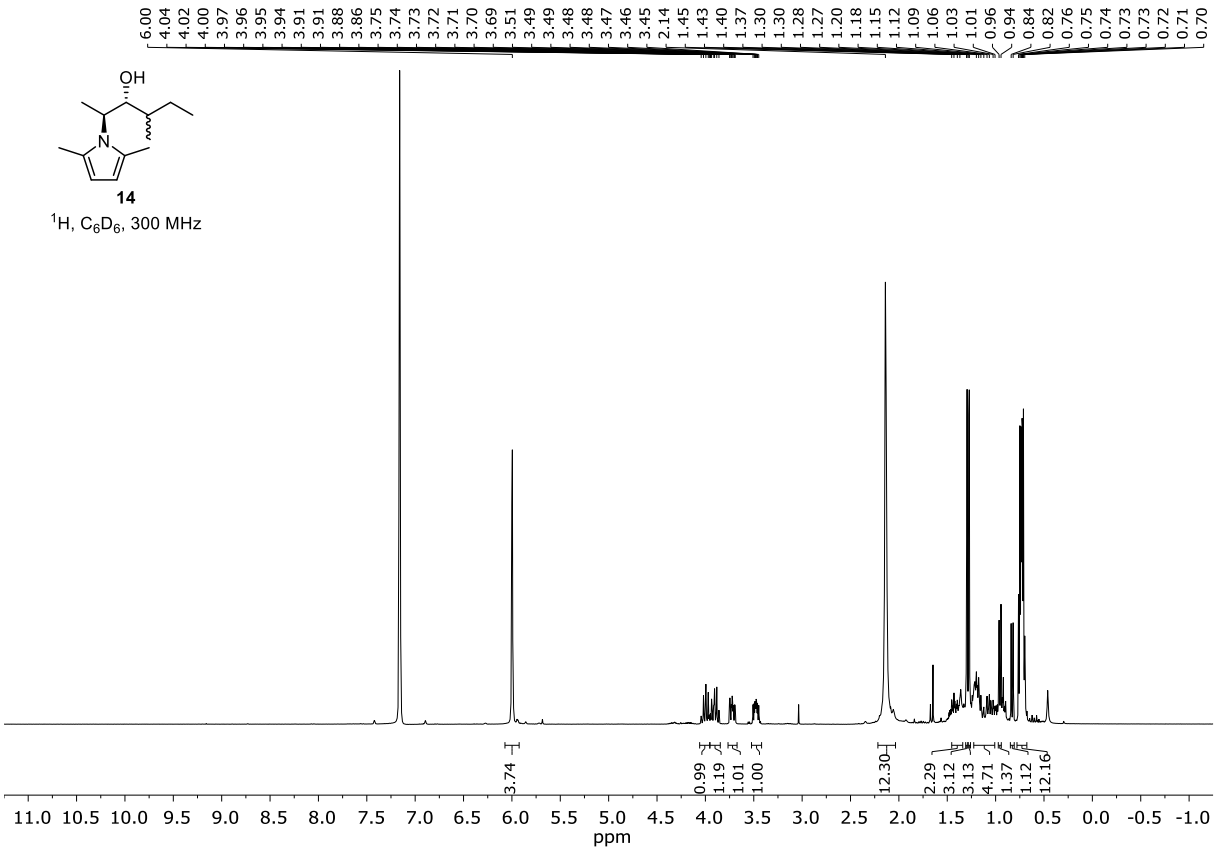

OH
Ph
N
11
13C{1H}, CDCl3, 126 MHz
138.39 130.79 129.14 128.50 126.66 108.55 105.15 82.19 74.84 64.37 63.15 36.86 15.61 13.16
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

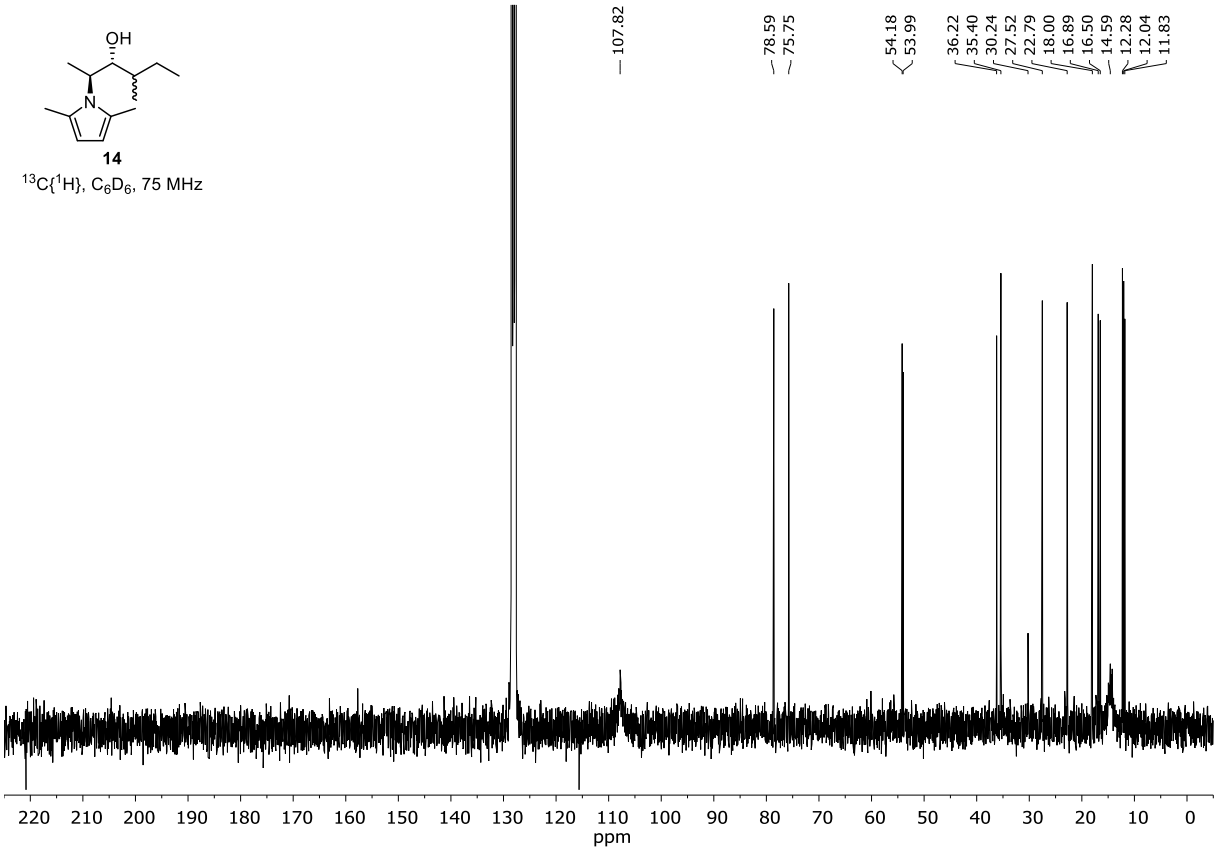

OH
N
12
1H, C6D6, 300 MHz
5.96
3.82
3.80
3.79
3.78
3.77
3.75
3.75
3.73
3.71
3.70
3.69
3.68
3.66
2.09
1.34
1.32
0.78
0.76
1.85
2.00
6.01
3.23
0.96
3.13
ppm

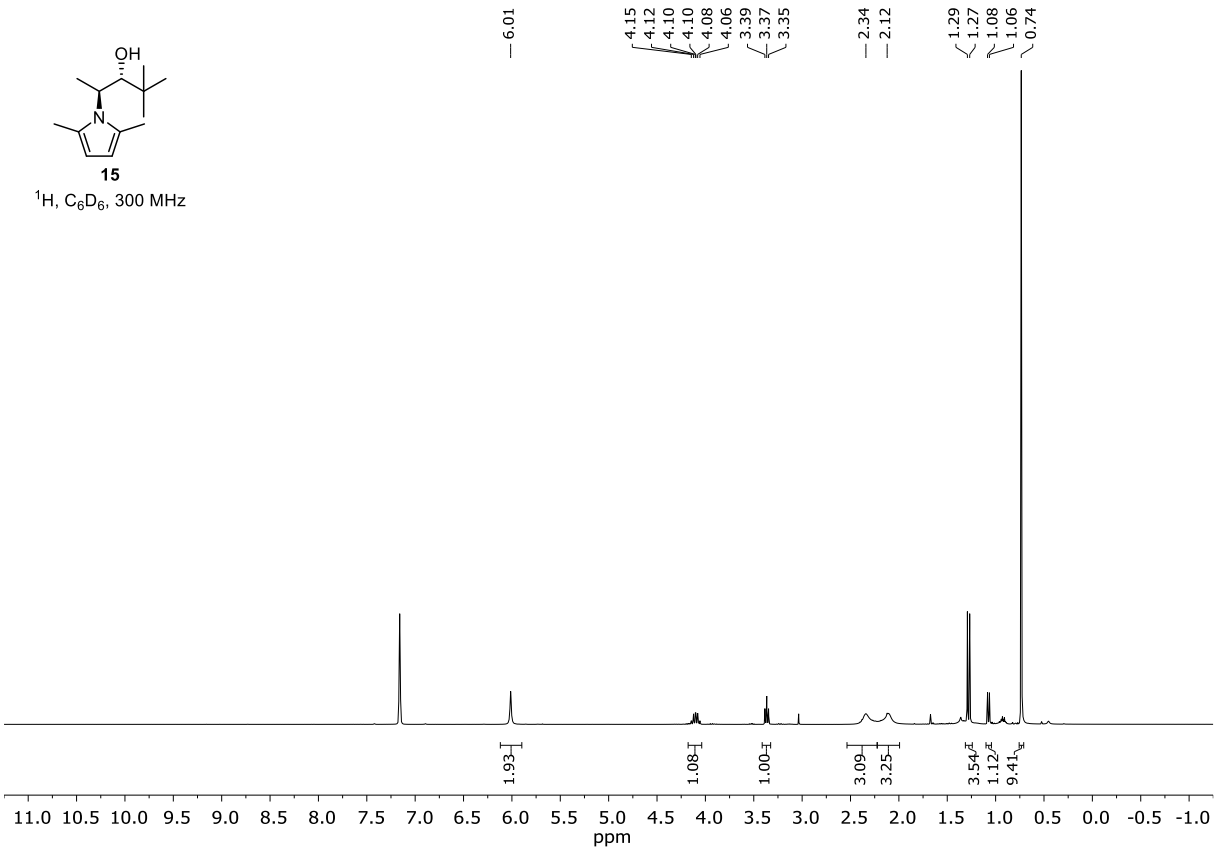

OH
N
12
13C{1H}, C6D6, 75 MHz
107.63
70.67
57.74
20.86
17.23
14.55
ppm

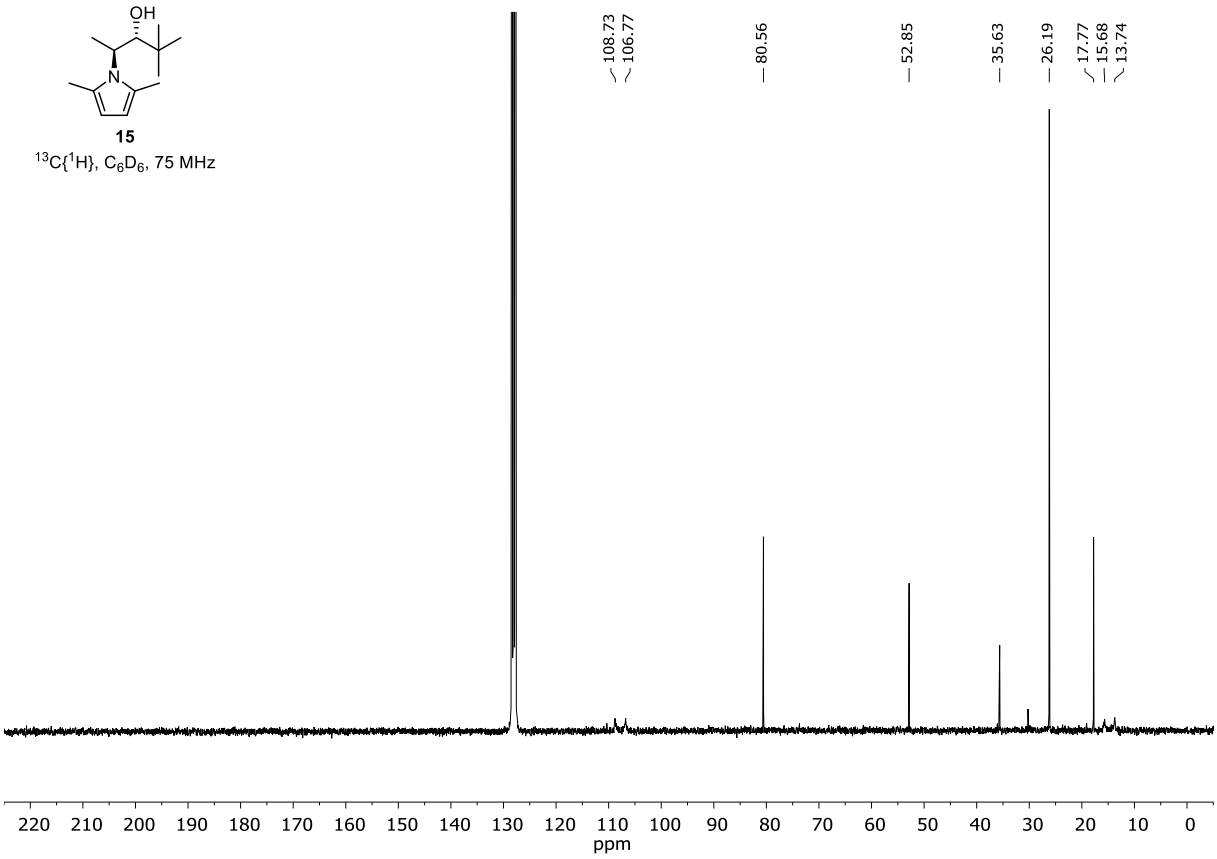

OH
N
13
1H, C6D6, 500 MHz
5.98
3.79
3.78
3.76
3.75
3.73
3.62
3.61
3.60
3.58
2.12
1.35
1.33
1.29
1.28
1.26
1.25
1.13
1.12
1.09
1.07
1.05
1.03
0.80
0.79
0.77
1.86
1.00
1.01
6.01
3.21
1.25
6.11
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

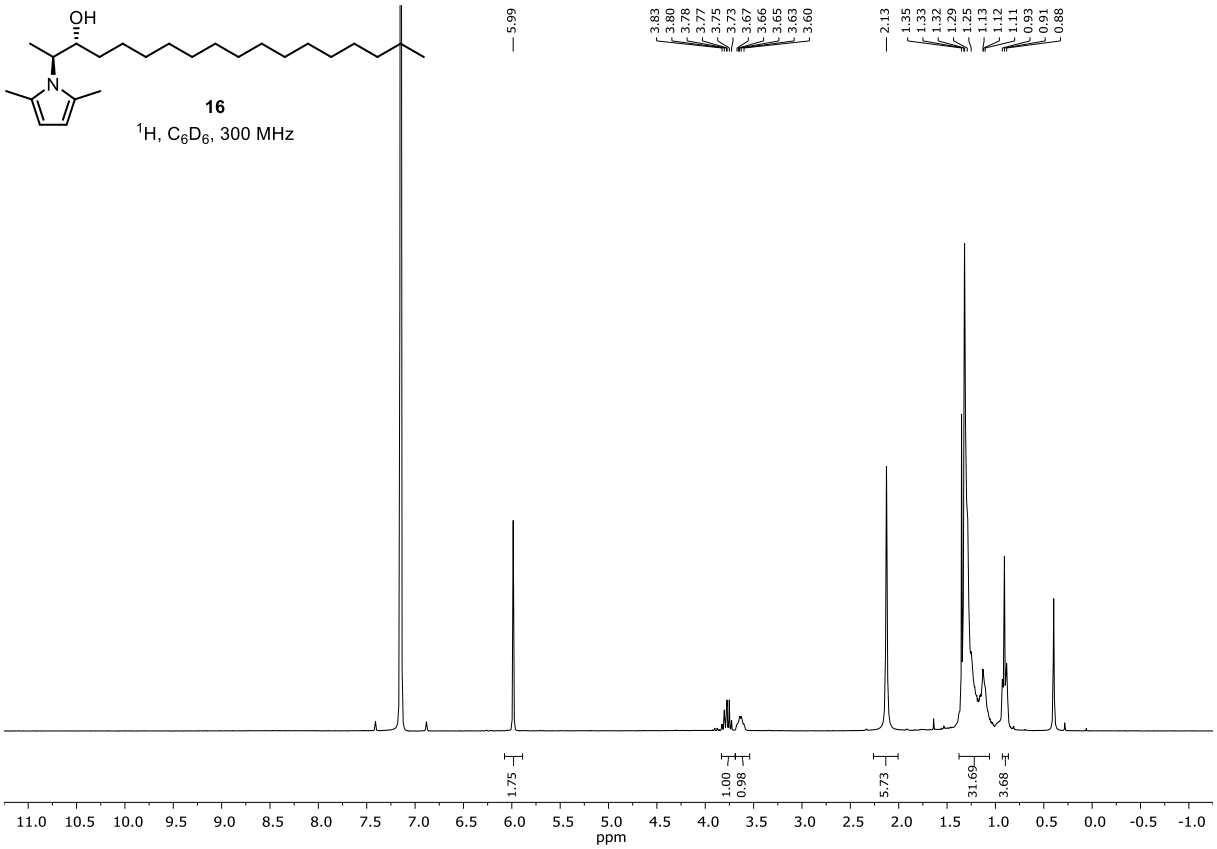

OH
N
13
13C{1H}, C6D6, 126 MHz
128.35
74.29
56.86
33.94
28.14
22.78
17.22
14.24
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

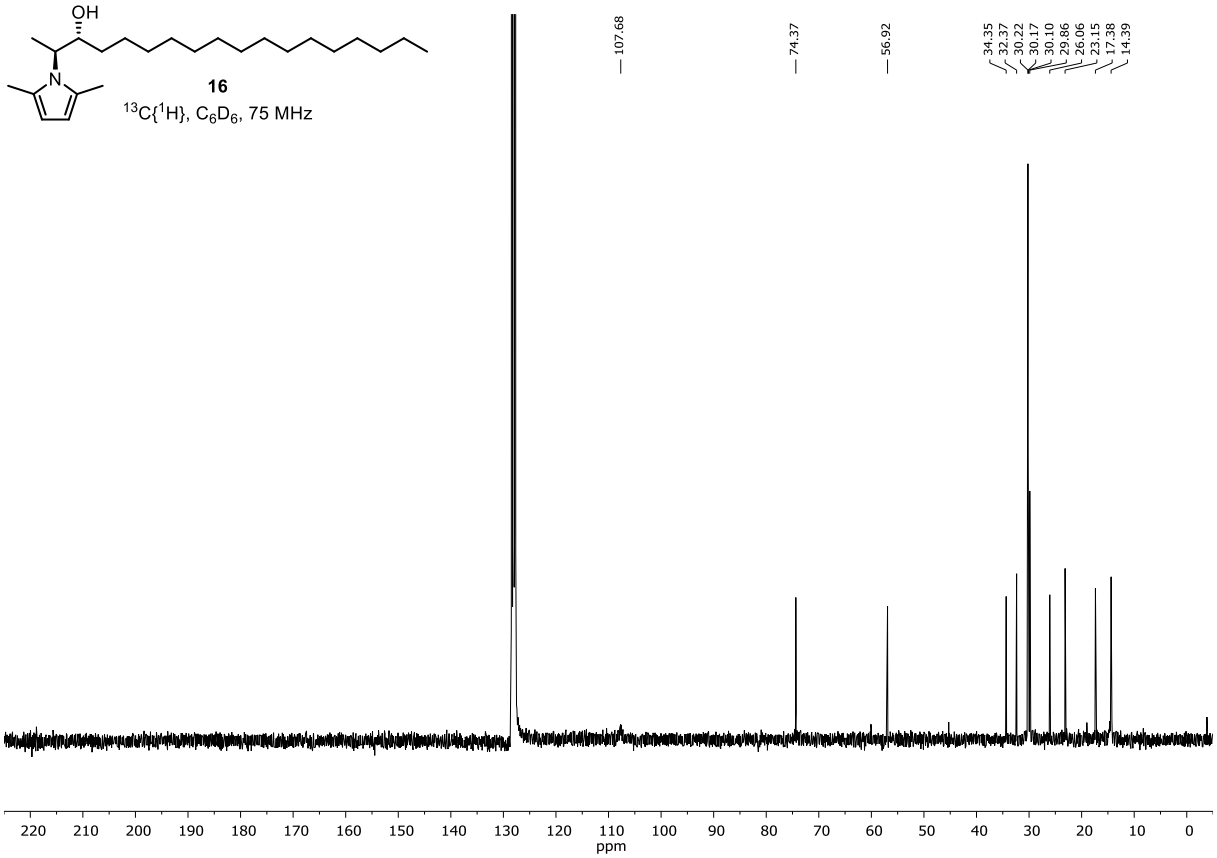

OH
N
14
1H, C6D6, 300 MHz
6.00 4.04 4.02 4.00 3.97 3.96 3.95 3.94 3.91 3.91 3.88 3.86 3.75 3.74 3.73 3.72 3.71 3.70 3.69 3.51 3.49 3.49 3.48 3.48 3.47 3.46 3.45 2.14 1.45 1.43 1.40 1.37 1.30 1.30 1.28 1.27 1.20 1.18 1.15 1.12 1.09 1.06 1.03 1.01 0.96 0.94 0.84 0.82 0.76 0.75 0.74 0.73 0.73 0.72 0.71 0.70
3.74 0.99 1.19 1.01 1.00 12.30 2.29 3.12 3.13 4.71 1.37 1.12 12.16
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

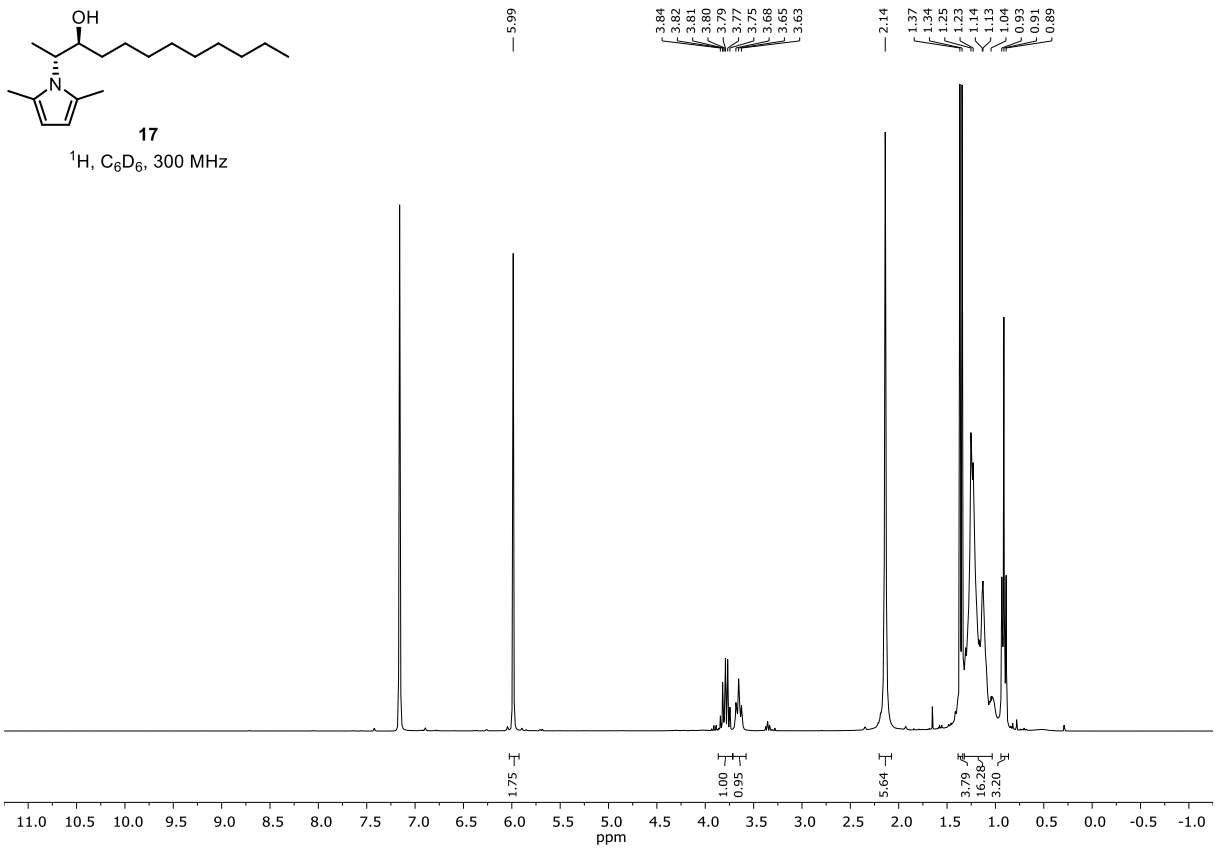

OH
N
14
13C{1H}, C6D6, 75 MHz
107.82
78.59
75.75
54.18
53.99
36.22
35.40
30.24
27.52
22.79
18.00
16.89
16.50
14.59
12.28
12.04
11.83
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

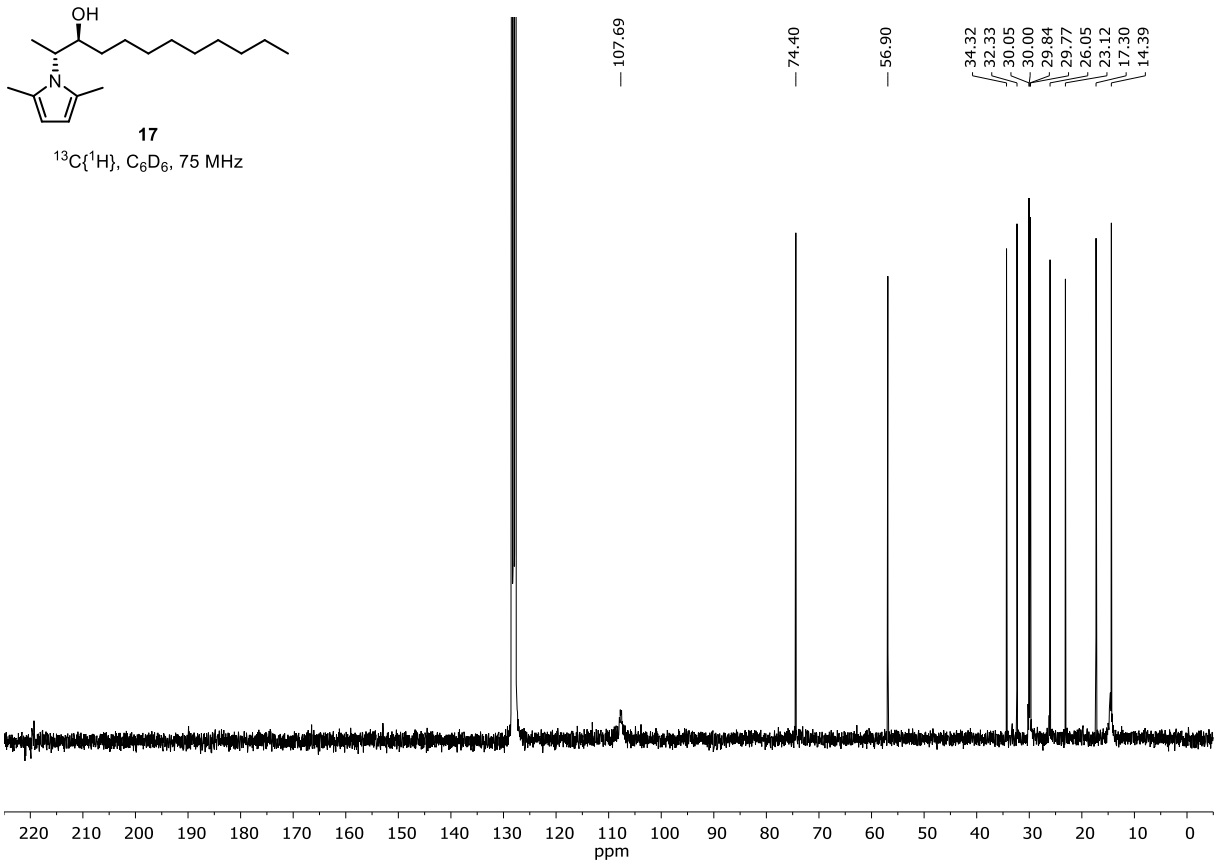

OH
N
15
1H, C6D6, 300 MHz
6.01
4.15
4.12
4.10
4.08
4.06
3.39
3.37
3.35
2.34
2.12
1.29
1.27
1.08
1.06
0.74
1.93
1.08
1.00
3.09
3.25
3.54
1.12
9.41
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

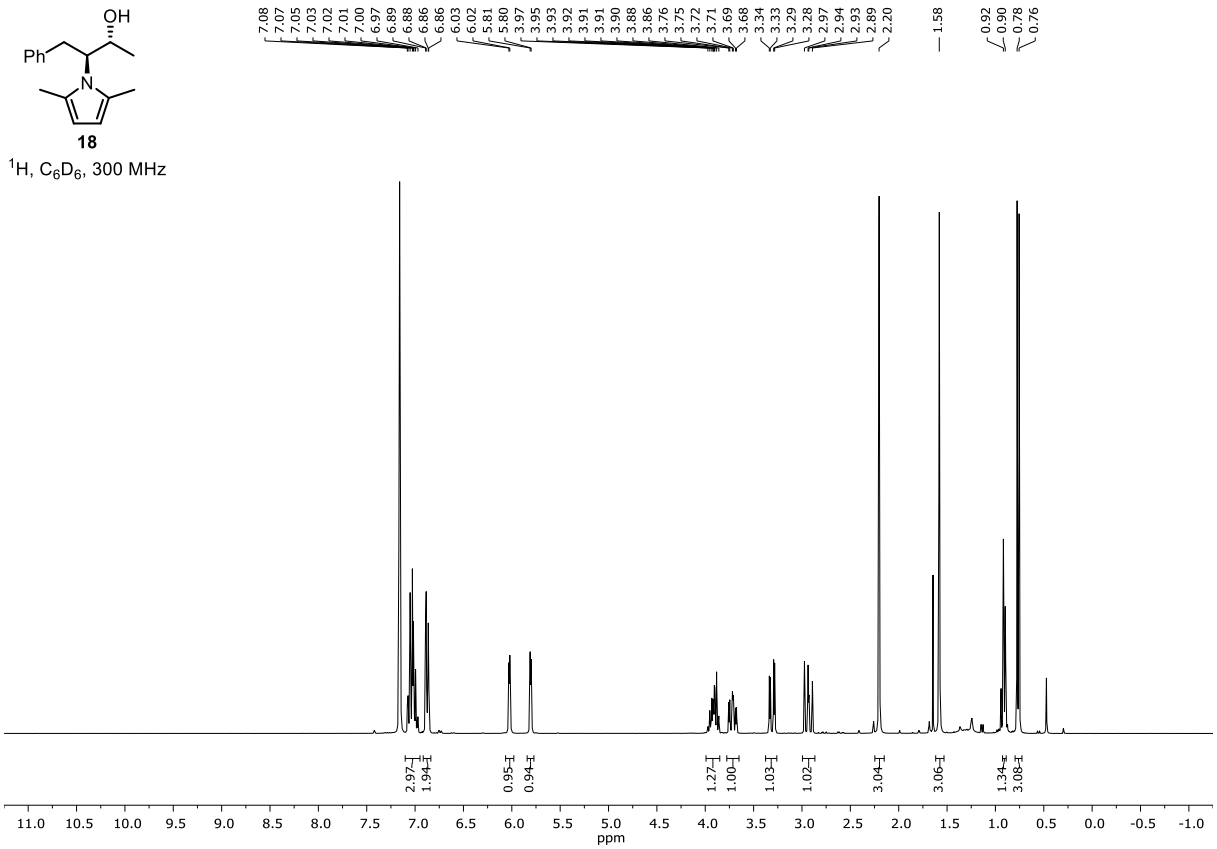

OH
N
15
13C{1H}, C6D6, 75 MHz
108.73
106.77
80.56
52.85
35.63
26.19
17.77
15.68
13.74
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

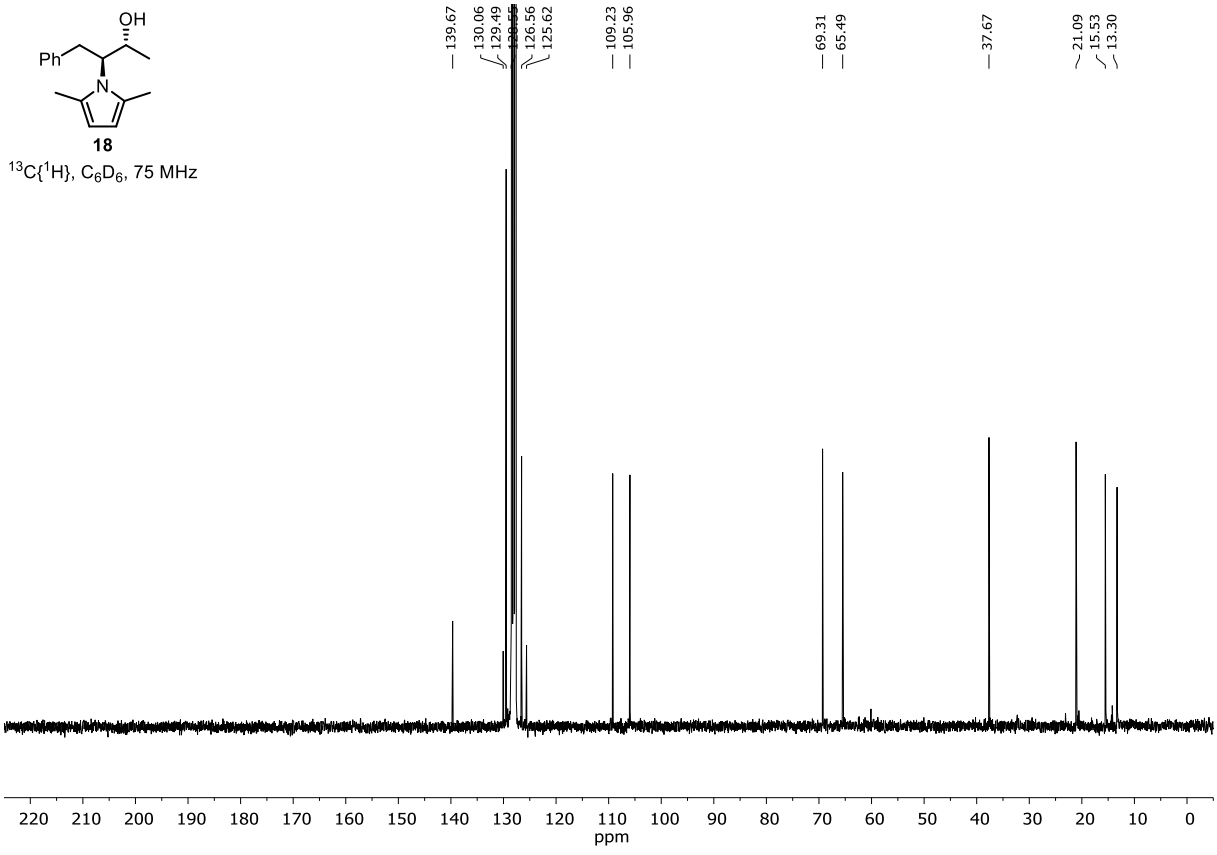

OH
N
16
^{1}H, C_6D_6, 300 MHz
5.99
3.83
3.80
3.78
3.77
3.75
3.73
3.67
3.66
3.65
3.63
3.60
2.13
1.35
1.33
1.32
1.29
1.25
1.13
1.12
1.11
0.93
0.91
0.88
1.75
1.00
0.98
5.73
31.69
3.68
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

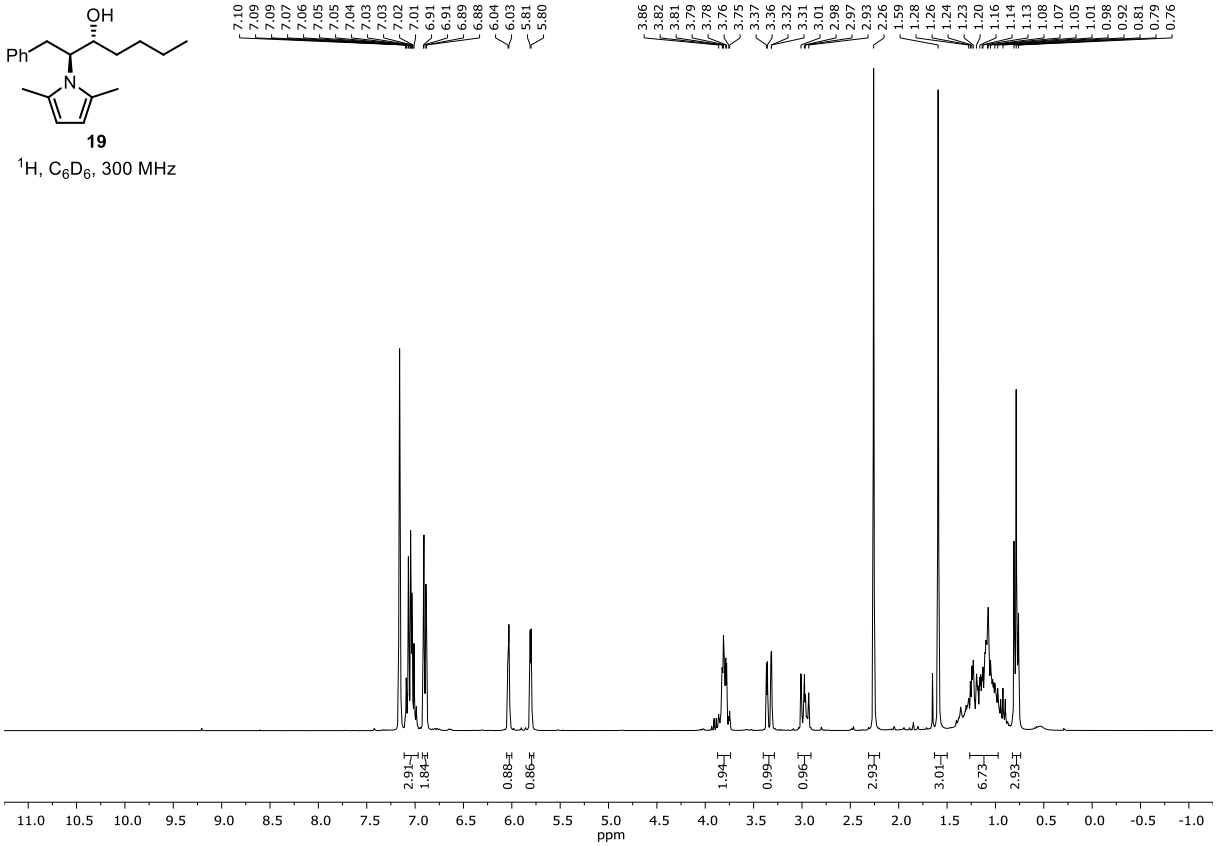

OH
N
16
^{13}C{^{1}H}, C_6D_6, 75 MHz
107.68
74.37
56.92
34.35
32.37
30.22
30.17
30.10
29.86
26.06
23.15
17.38
14.39
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

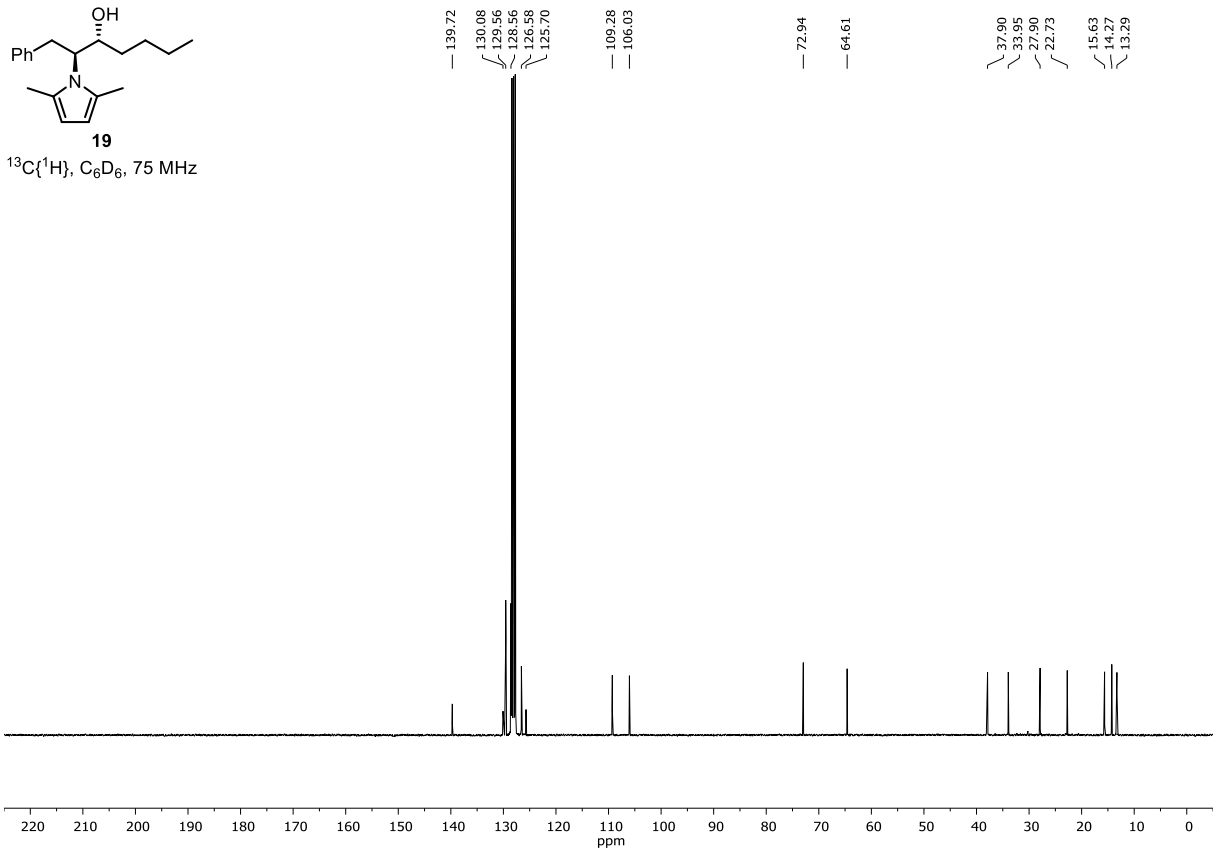

OH
N
17
^{1}H, C_6D_6, 300 MHz
5.99
3.84
3.82
3.81
3.80
3.79
3.77
3.75
3.68
3.65
3.63
2.14
1.37
1.34
1.25
1.23
1.14
1.13
1.04
0.93
0.91
0.89
1.75
1.00
0.95
5.64
3.79
16.28
3.20
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

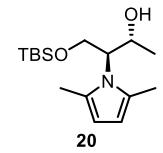

OH
N
17
^{13}C{^{1}H}, C_6D_6, 75 MHz
107.69
74.40
56.90
34.32
32.33
30.05
30.00
29.84
29.77
26.05
23.12
17.30
14.39
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


OH
Ph
N
18
1H, C6D6, 300 MHz
7.08
7.07
7.05
7.03
7.02
7.01
7.00
6.97
6.89
6.88
6.86
6.86
6.03
6.02
5.81
5.80
3.97
3.95
3.93
3.92
3.91
3.91
3.90
3.88
3.86
3.76
3.75
3.72
3.71
3.69
3.68
3.34
3.33
3.29
3.28
2.97
2.94
2.93
2.89
2.20
1.58
0.92
0.90
0.78
0.76
2.97
1.94
0.95
0.94
1.27
1.00
1.03
1.02
3.04
3.06
1.34
3.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


OH
Ph
N
18
13C{1H}, C6D6, 75 MHz
139.67
130.06
129.49
126.56
125.62
109.23
105.96
69.31
65.49
37.67
21.09
15.53
13.30
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

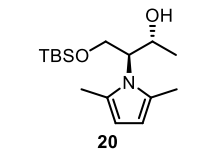

OH
Ph
N
19
1H, C6D6, 300 MHz
7.10 7.09 7.09 7.07 7.06 7.05 7.05 7.04 7.03 7.03 7.02 7.01 6.91 6.91 6.89 6.88 6.04 6.03 5.81 5.80
3.86 3.82 3.81 3.79 3.78 3.76 3.75 3.37 3.36 3.32 3.31 3.01 2.98 2.97 2.93 2.26 1.59 1.28 1.26 1.24 1.23 1.20 1.16 1.14 1.13 1.08 1.07 1.05 1.01 0.98 0.92 0.81 0.79 0.76
2.91 1.84 0.88 0.86 1.94 0.99 0.96 2.93 3.01 6.73 2.93
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


OH
Ph
N
19
13C{1H}, C6D6, 75 MHz
139.72 130.08 129.56 128.56 126.58 125.70 109.28 106.03 72.94 64.61 37.90 33.95 27.90 22.73 15.63 14.27 13.29
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



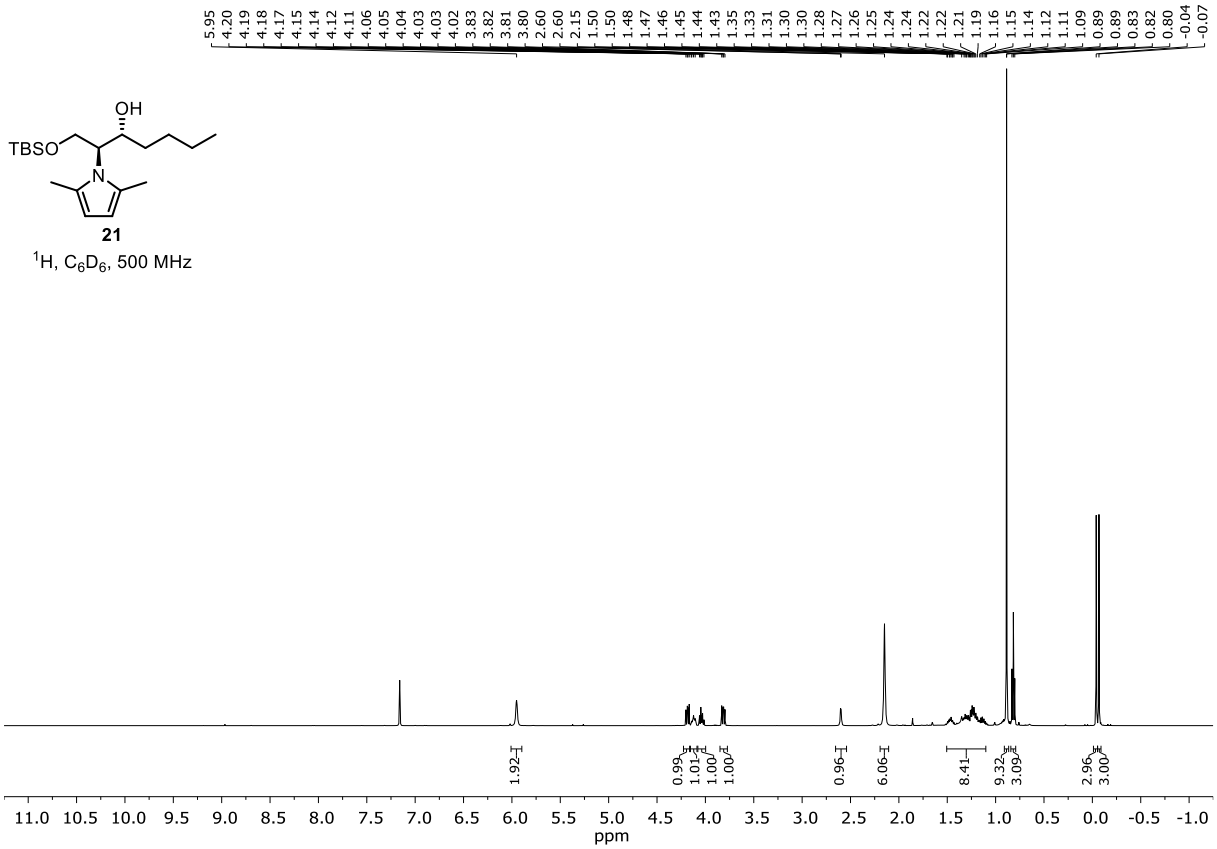
20

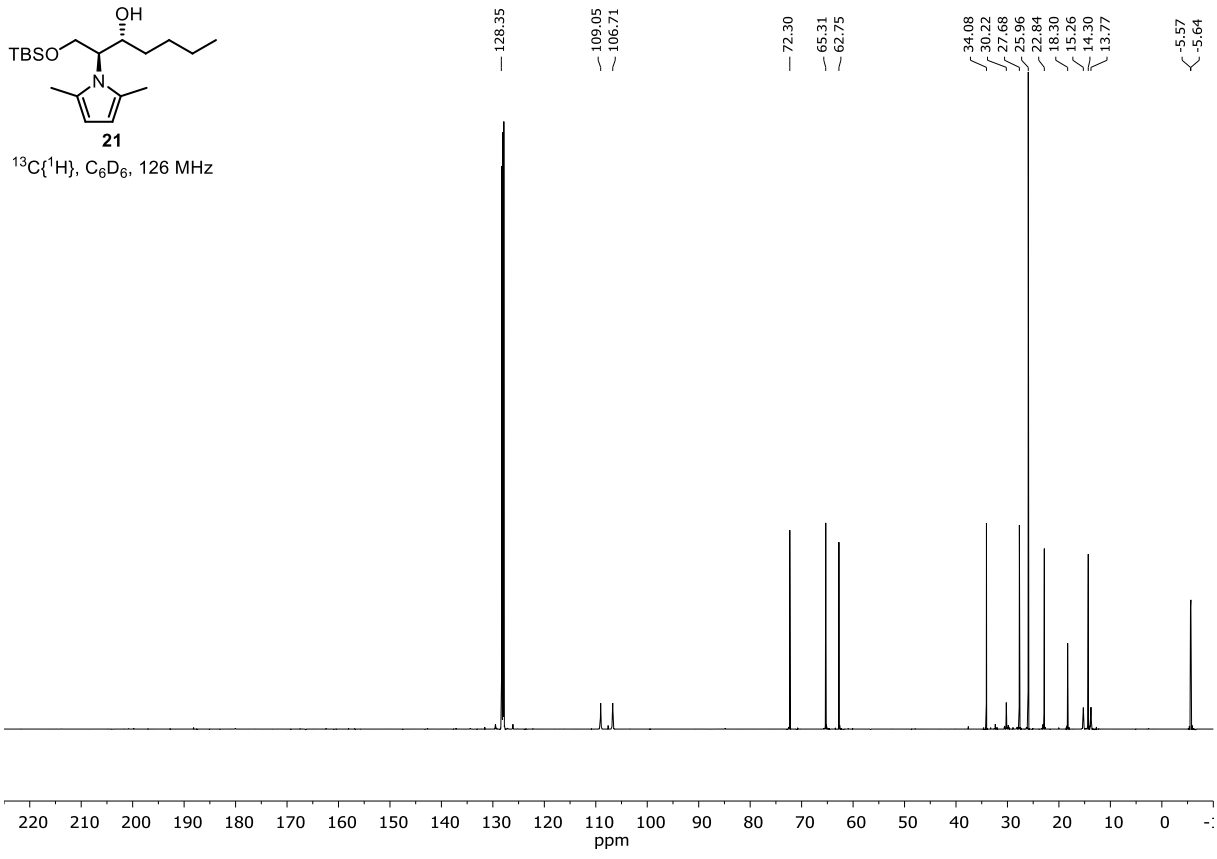
^{1}H, C_6D_6, 500 MHz

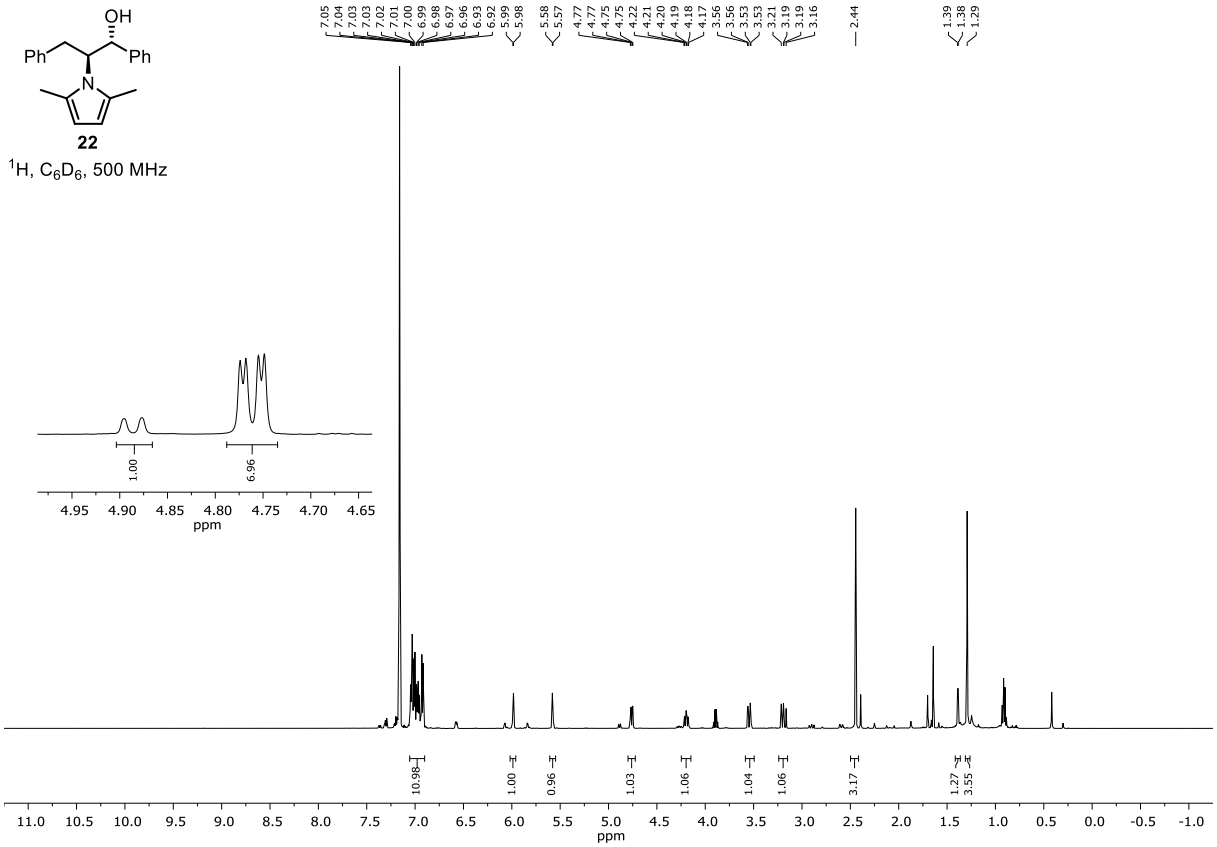


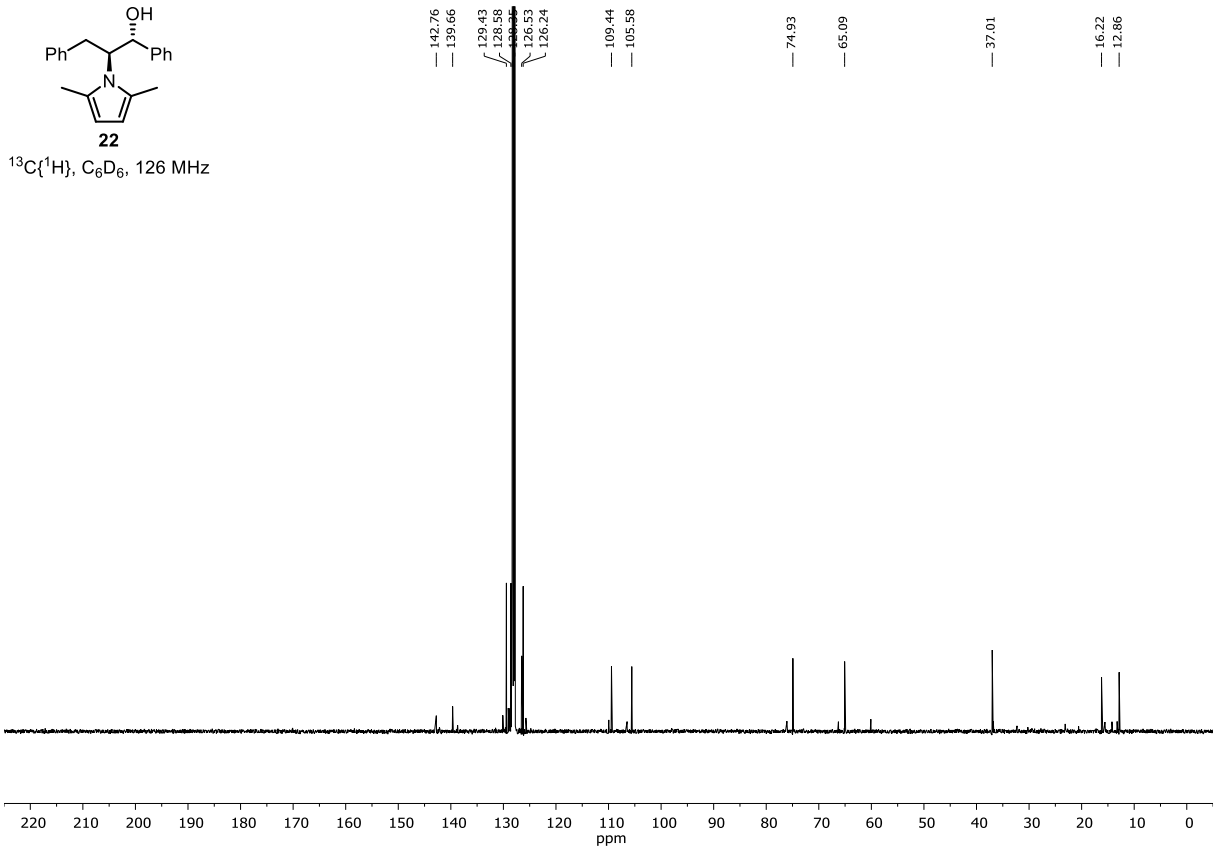
20

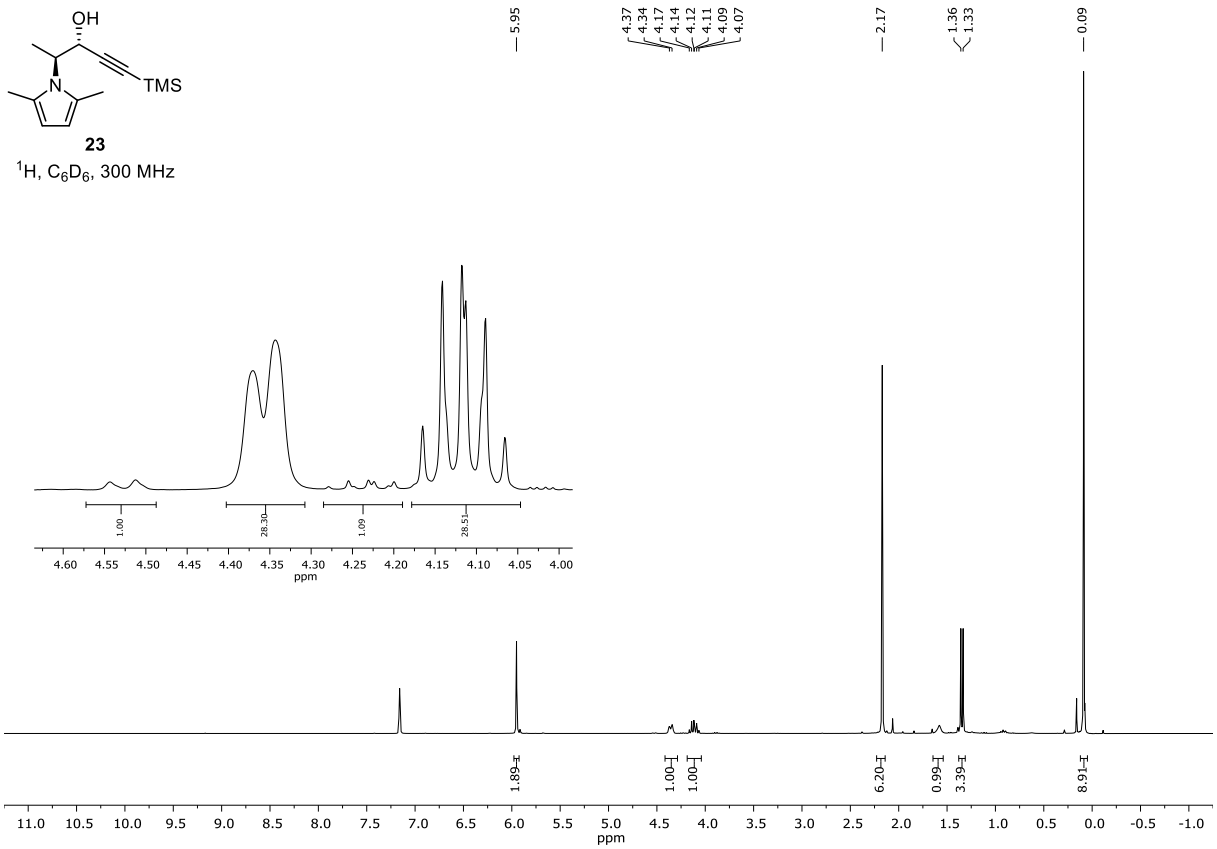
^{13}C{^{1}H}, C_6D_6, 126 MHz

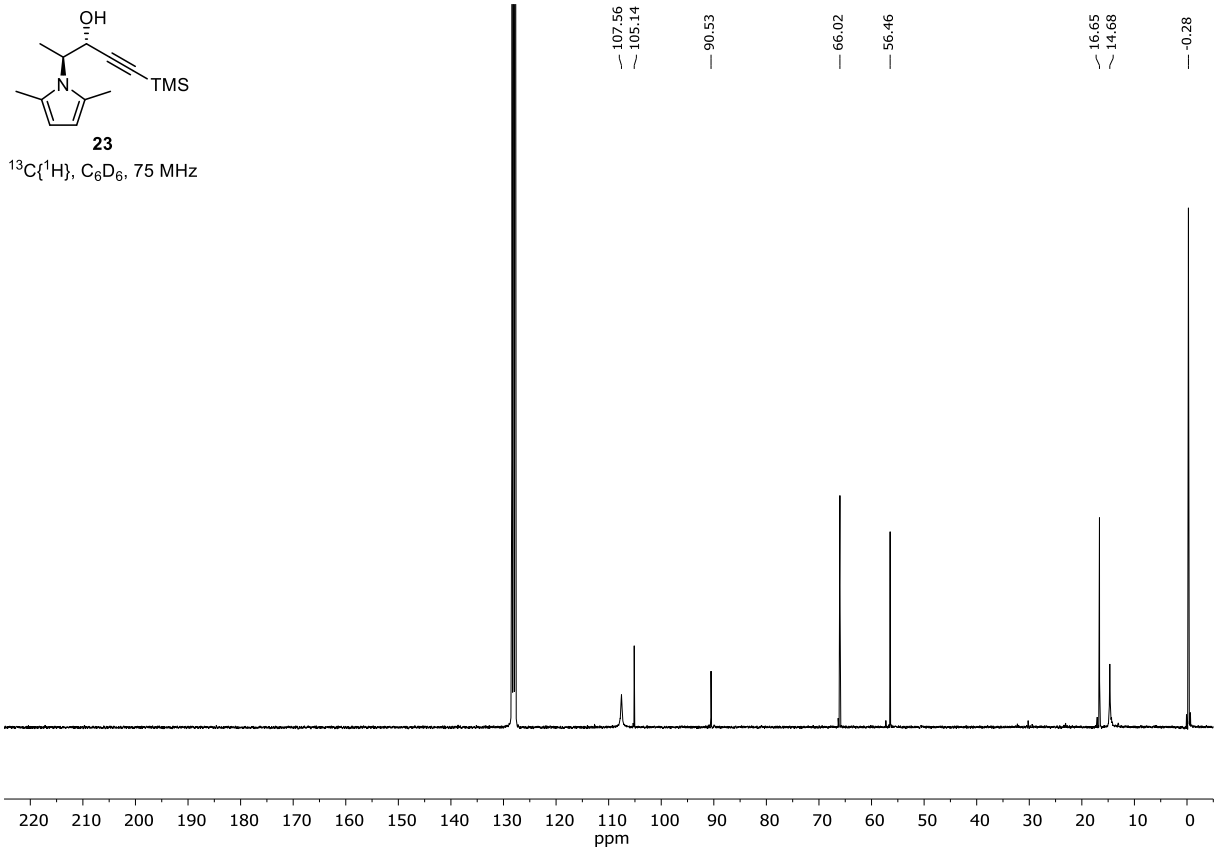

OH
TBSO
N
21
1H, C6D6, 500 MHz
ppm

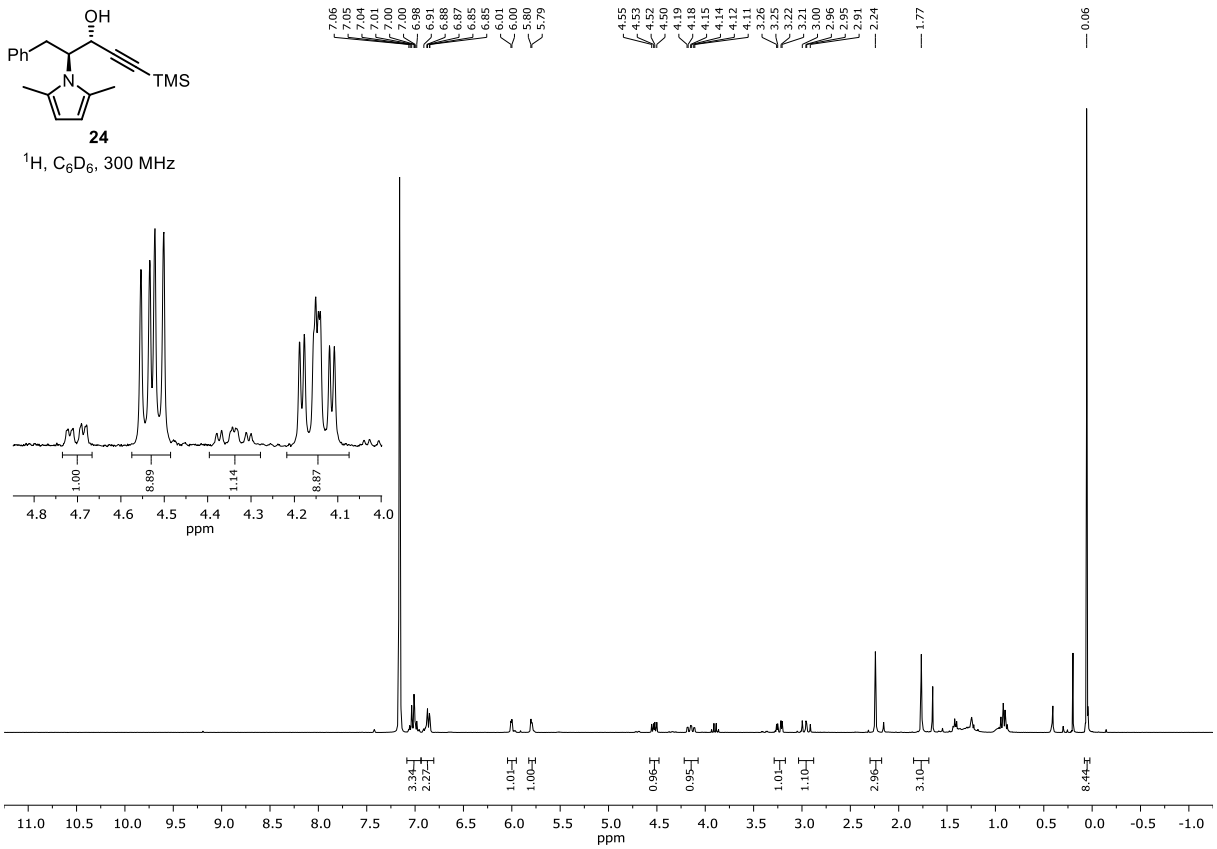

OH
TBSO
N
21
13C{1H}, C6D6, 126 MHz
ppm

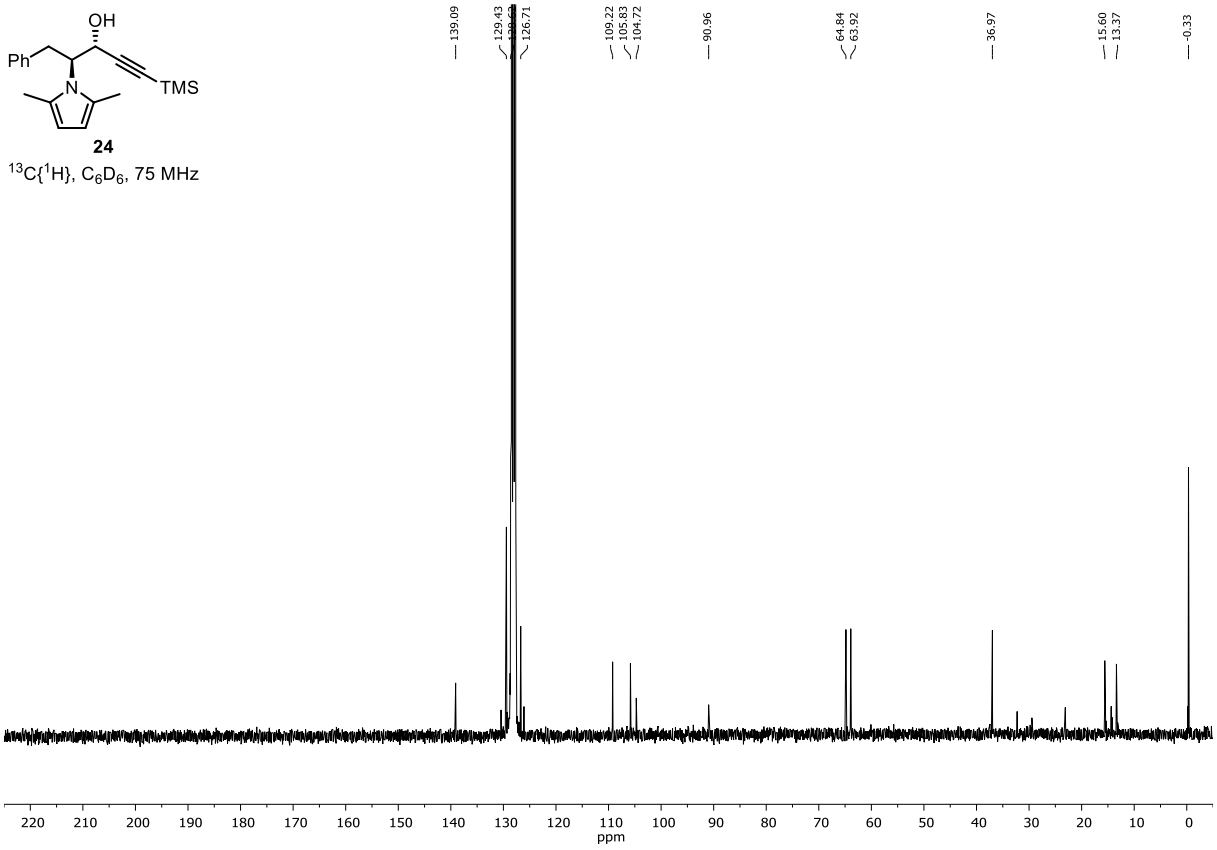

OH
Ph
Ph
N
22
1H, C6D6, 500 MHz
7.05 7.04 7.03 7.03 7.02 7.01 7.00 6.99 6.98 6.97 6.96 6.93 6.92 5.99 5.98 5.58 5.57 4.77 4.77 4.75 4.75 4.22 4.21 4.20 4.19 4.18 4.17 3.56 3.56 3.53 3.53 3.21 3.19 3.19 3.16 2.44 1.39 1.38 1.29
1.00
6.96
4.95 4.90 4.85 4.80 4.75 4.70 4.65
ppm
10.98 1.00 0.96 1.03 1.06 1.04 1.06 3.17 1.27 3.55
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

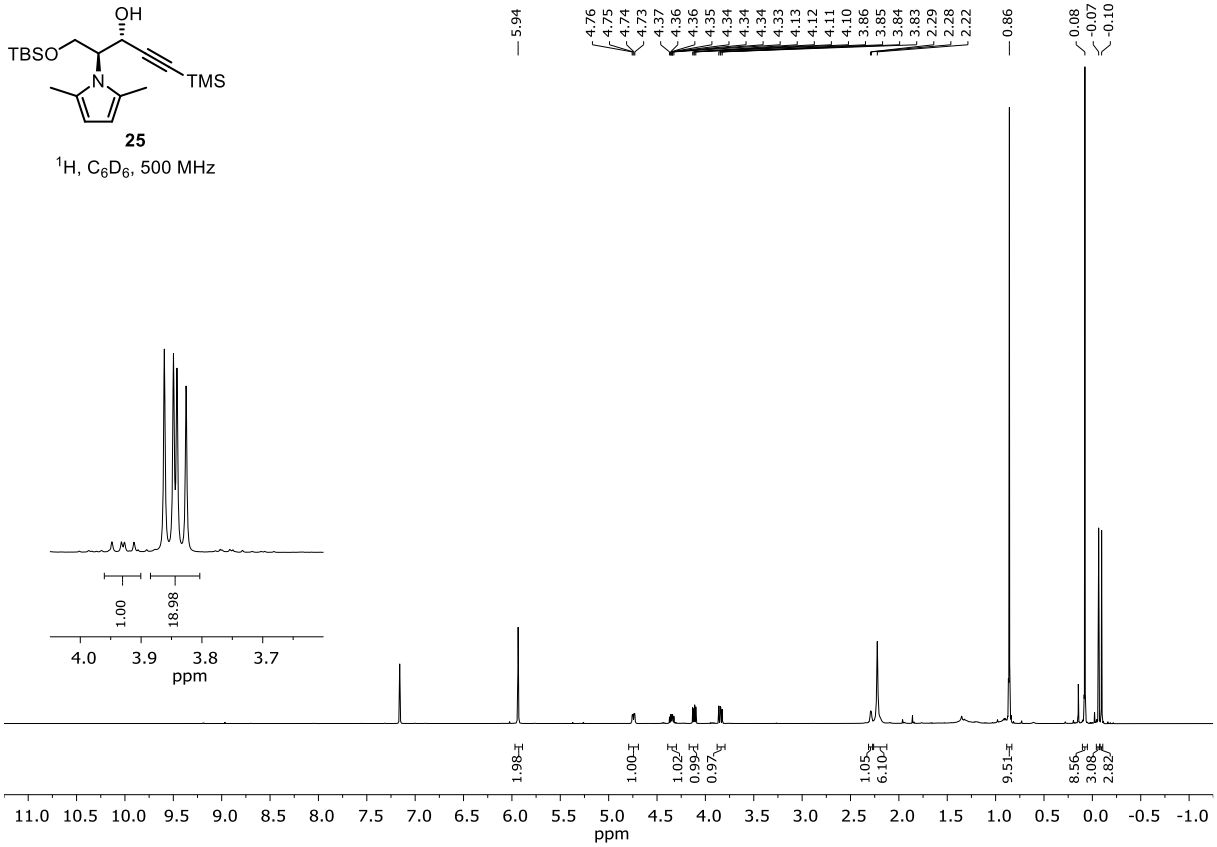

OH
Ph
Ph
N
22
13C{1H}, C6D6, 126 MHz
142.76 139.66 129.43 128.58 126.53 126.24 109.44 105.58 74.93 65.09 37.01 16.22 12.86
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

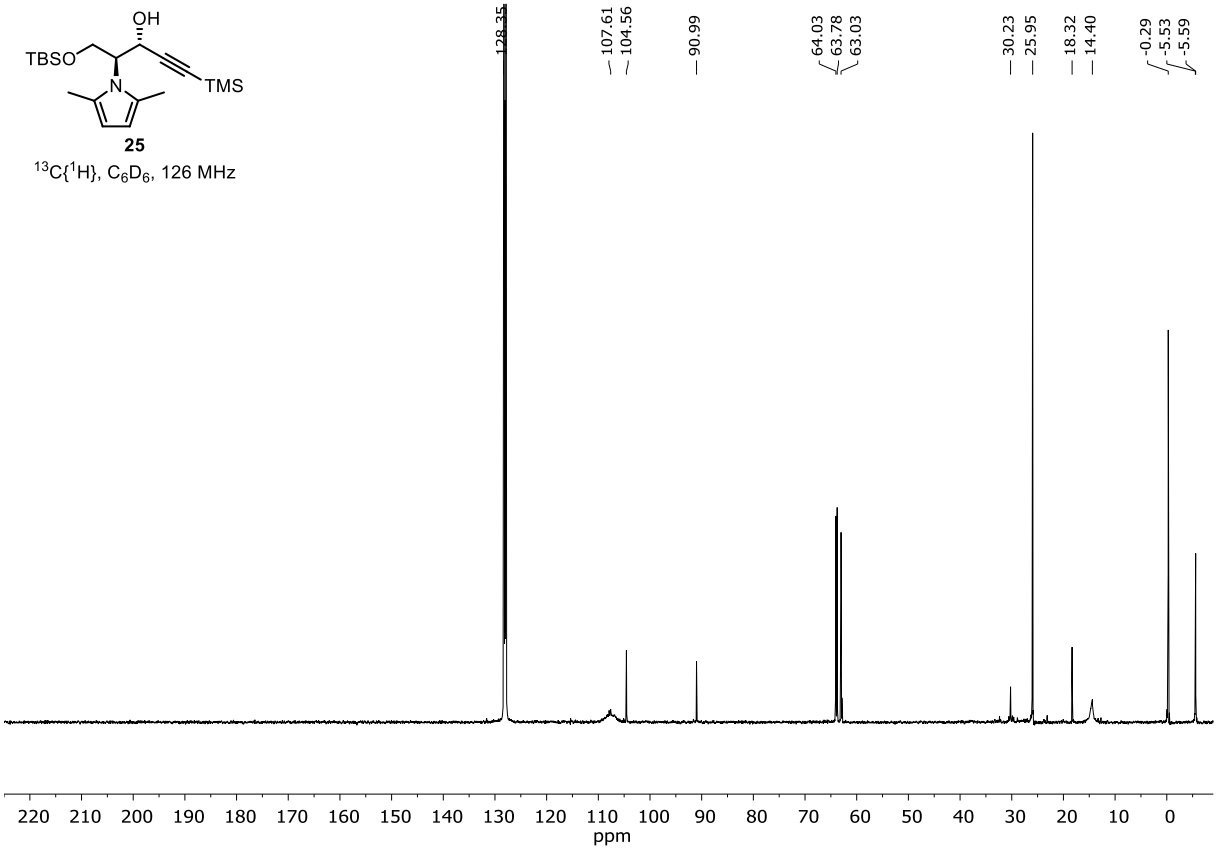

OH
N
TMS
23
1H, C6D6, 300 MHz
5.95
4.37
4.34
4.17
4.14
4.12
4.11
4.09
4.07
2.17
1.36
1.33
0.09
1.00
28.30
1.09
28.51
1.89
1.00
1.00
6.20
0.99
3.39
8.91
ppm

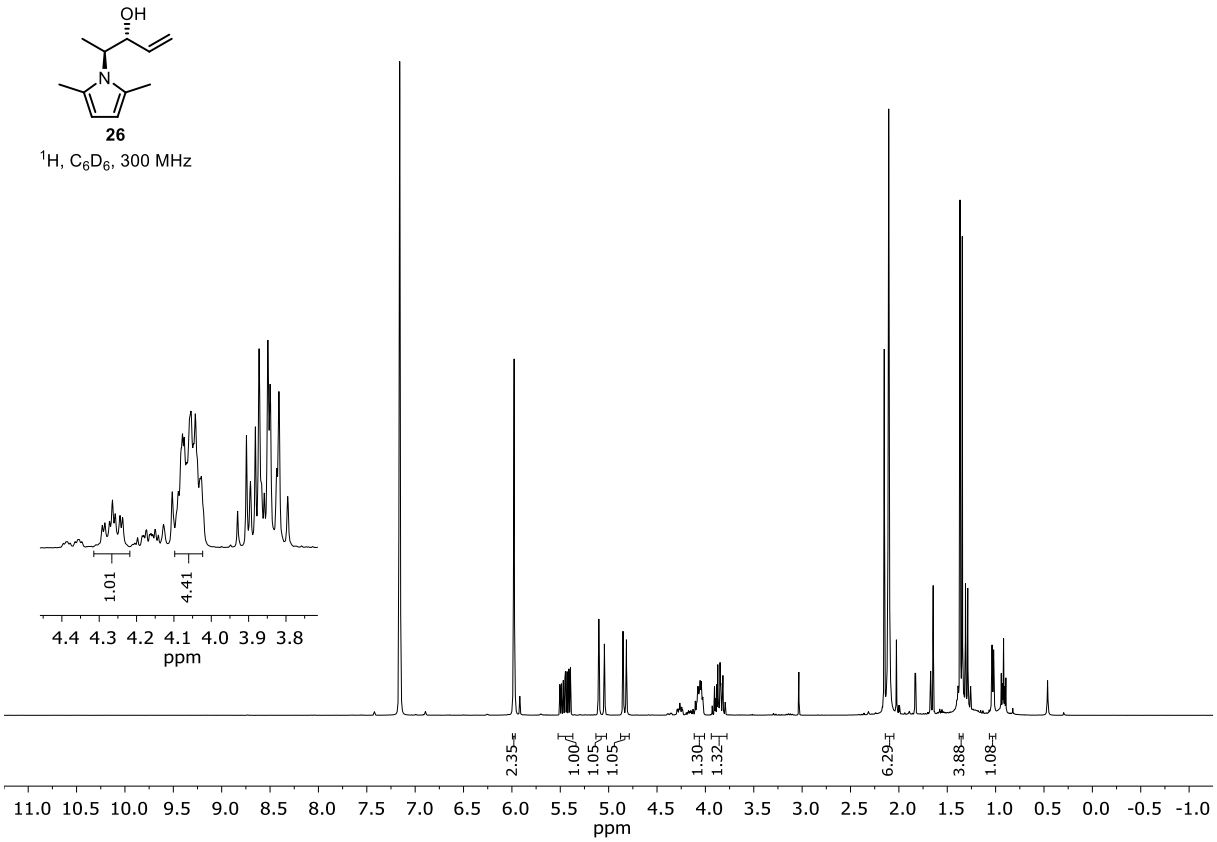

OH
N
TMS
23
13C{1H}, C6D6, 75 MHz
107.56
105.14
90.53
66.02
56.46
16.65
14.68
-0.28
ppm

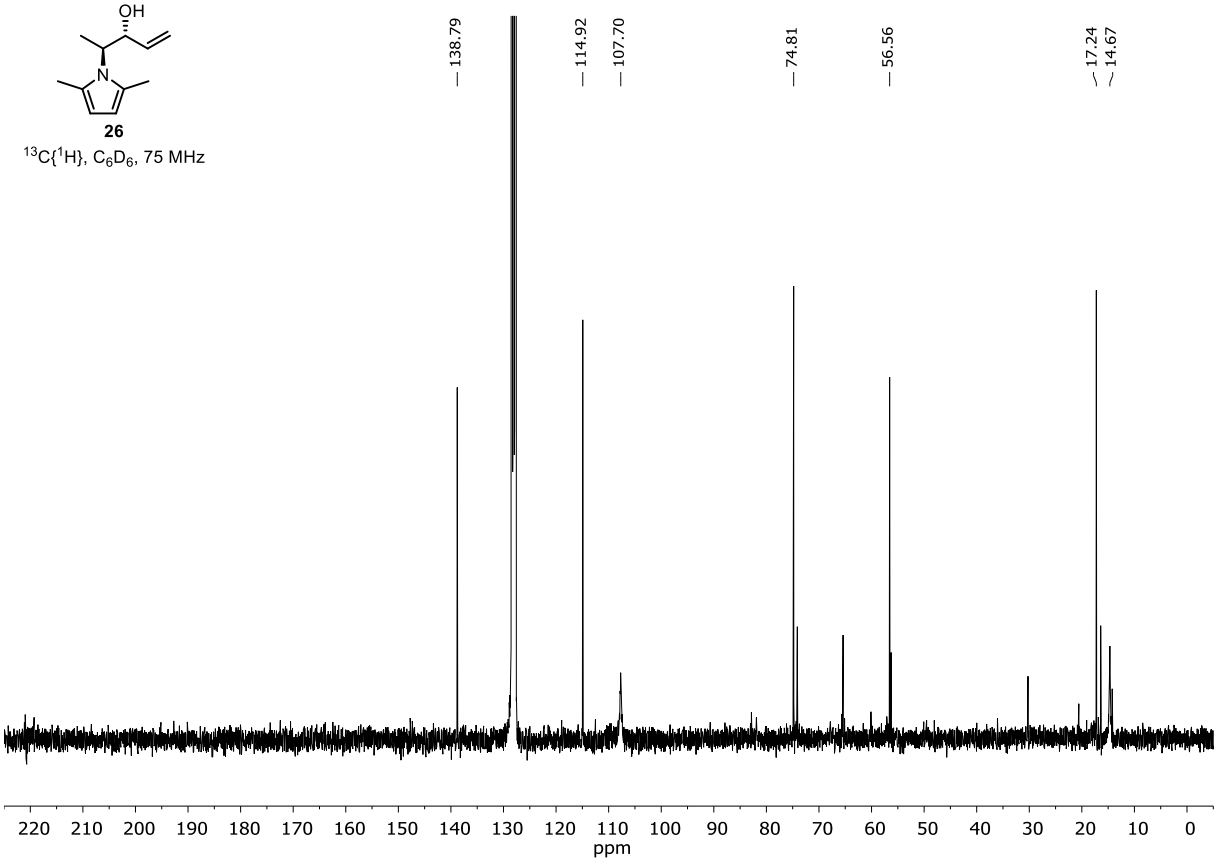

OH
Ph
N
TMS
24
1H, C6D6, 300 MHz
7.06
7.05
7.04
7.01
7.00
6.98
6.91
6.88
6.87
6.85
6.85
6.01
6.00
5.80
5.79
4.55
4.53
4.52
4.50
4.19
4.18
4.15
4.14
4.12
4.11
3.26
3.25
3.22
3.21
3.00
2.96
2.95
2.91
2.24
1.77
0.06
1.00
8.89
1.14
8.87
4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0
ppm
3.34
2.27
1.01
1.00
0.96
0.95
1.01
1.10
2.96
3.10
8.44
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

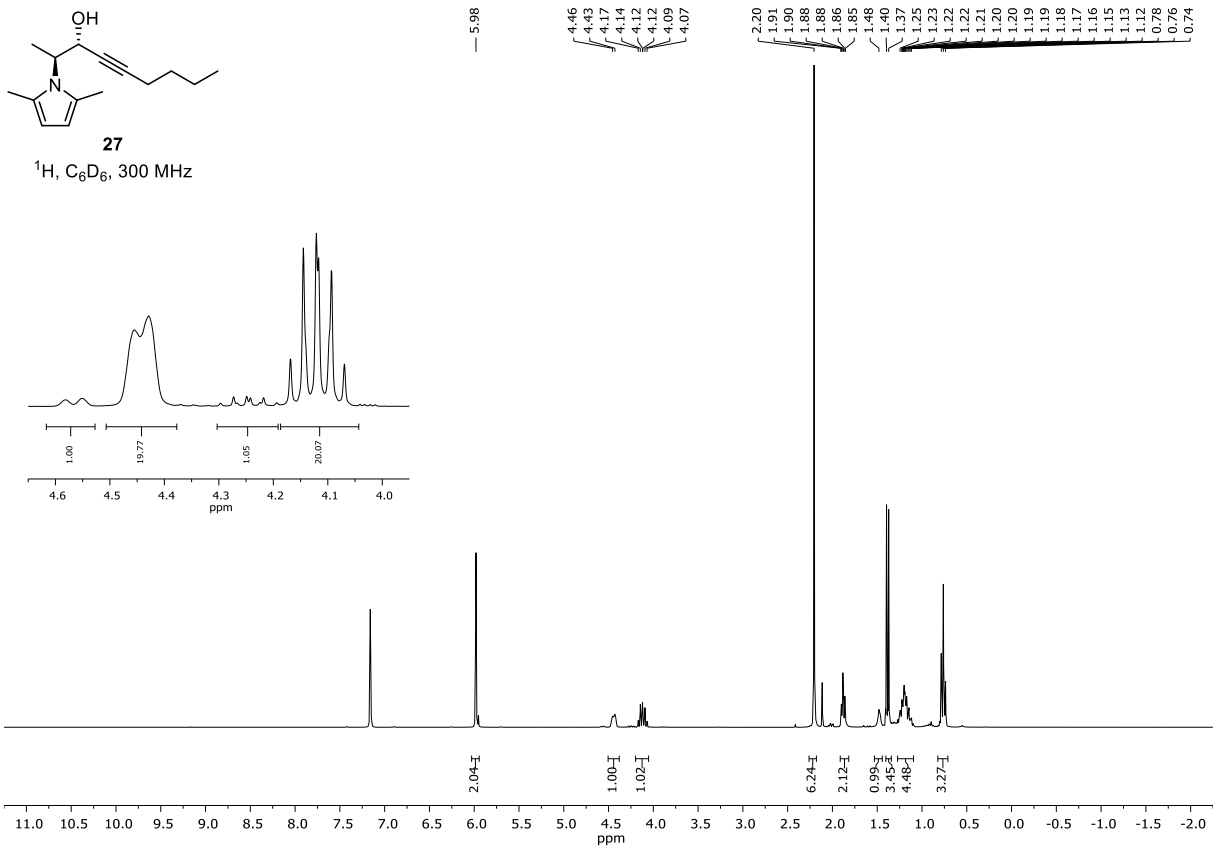

OH
Ph
N
TMS
24
13C{1H}, C6D6, 75 MHz
139.09
129.43
126.71
109.22
105.83
104.72
90.96
64.84
63.92
36.97
15.60
13.37
-0.33
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

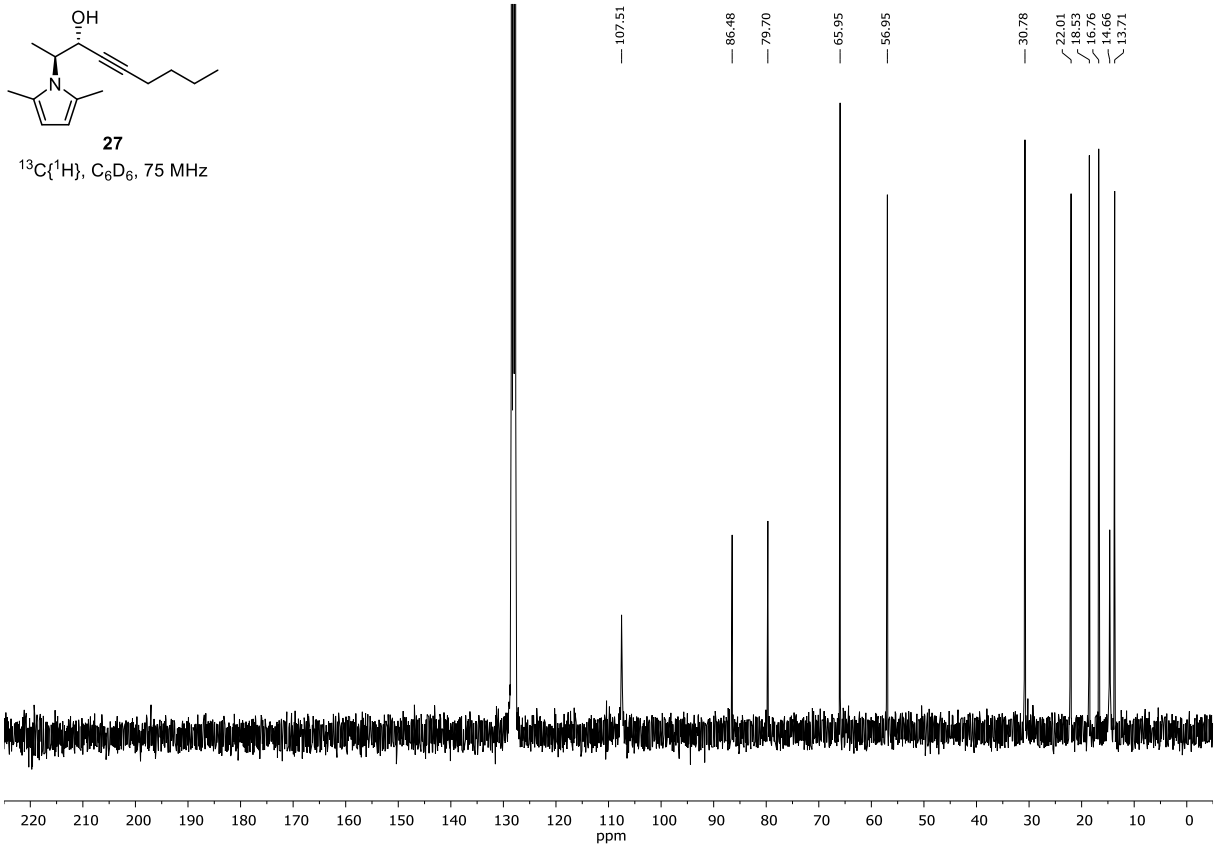

OH
TBSO
TMS
N
25
1H, C6D6, 500 MHz
5.94
4.76
4.75
4.74
4.73
4.37
4.36
4.36
4.35
4.34
4.34
4.34
4.33
4.13
4.12
4.11
4.10
3.86
3.85
3.84
3.83
2.29
2.28
2.22
0.86
0.08
-0.07
-0.10
1.00
18.98
4.0
3.9
3.8
3.7
ppm
1.98
1.00
1.02
0.99
0.97
1.05
6.10
9.51
8.56
3.08
2.82
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

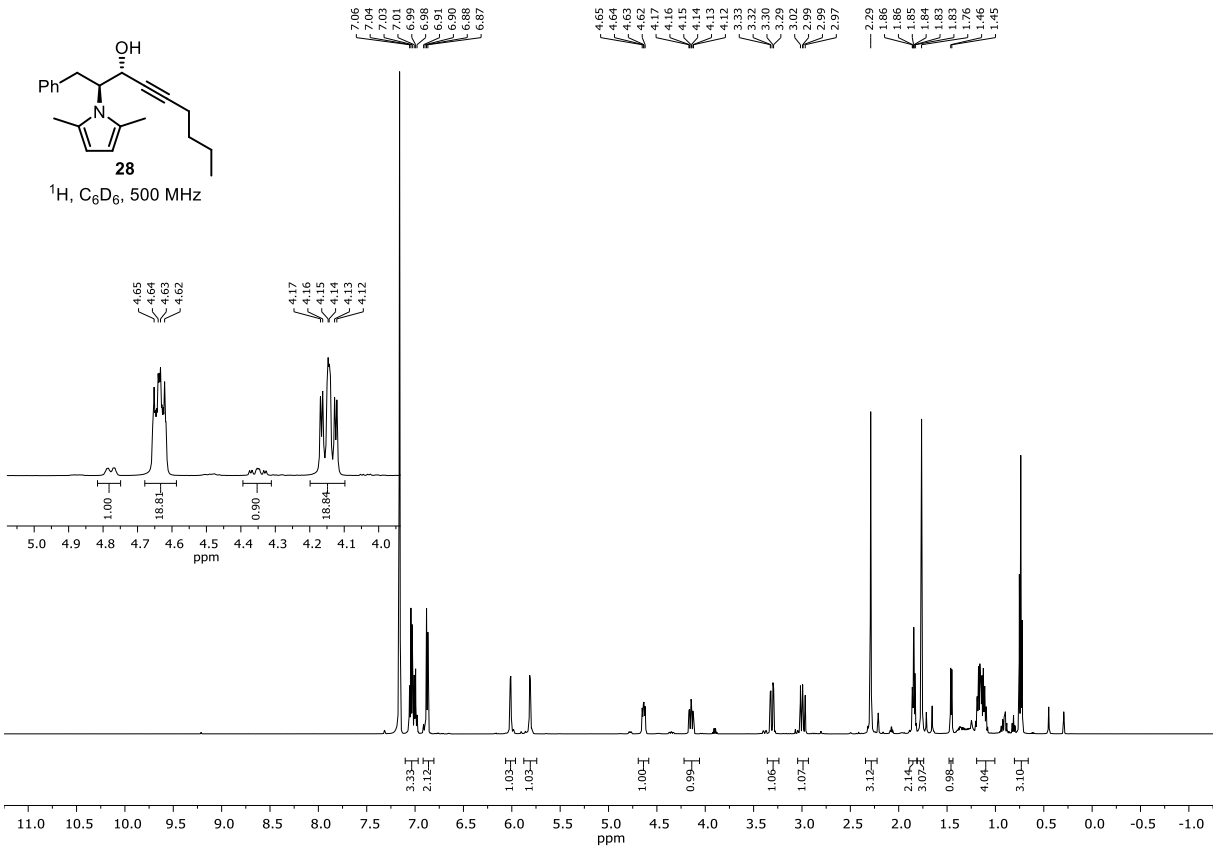

OH
TBSO
TMS
N
25
13C{1H}, C6D6, 126 MHz
128.35
107.61
104.56
90.99
64.03
63.78
63.03
30.23
25.95
18.32
14.40
-0.29
-5.53
-5.59
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

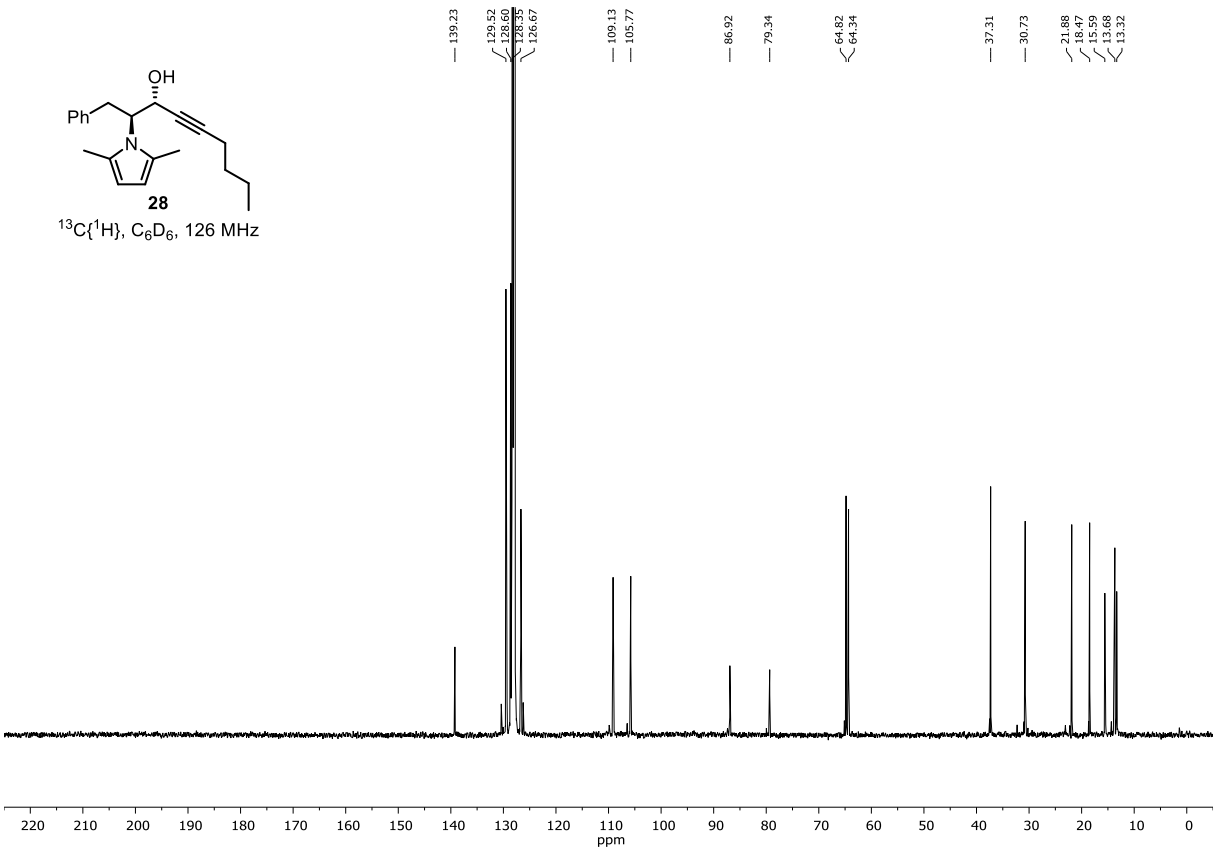

OH
N
26
1H, C6D6, 300 MHz
1.01
4.41
4.4 4.3 4.2 4.1 4.0 3.9 3.8
ppm
2.35
1.00
1.05
1.05
1.30
1.32
6.29
3.88
1.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

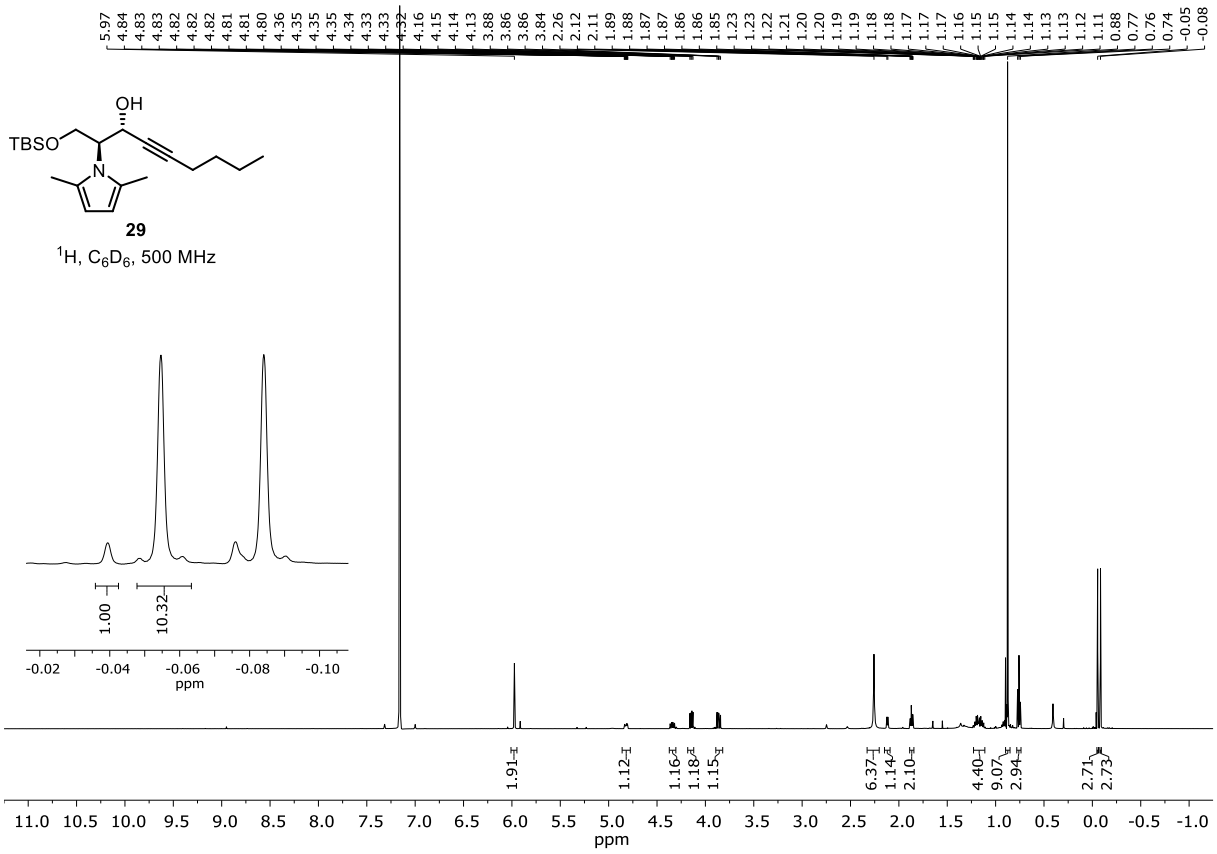

OH
N
26
13C{1H}, C6D6, 75 MHz
138.79
114.92
107.70
74.81
56.56
17.24
14.67
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

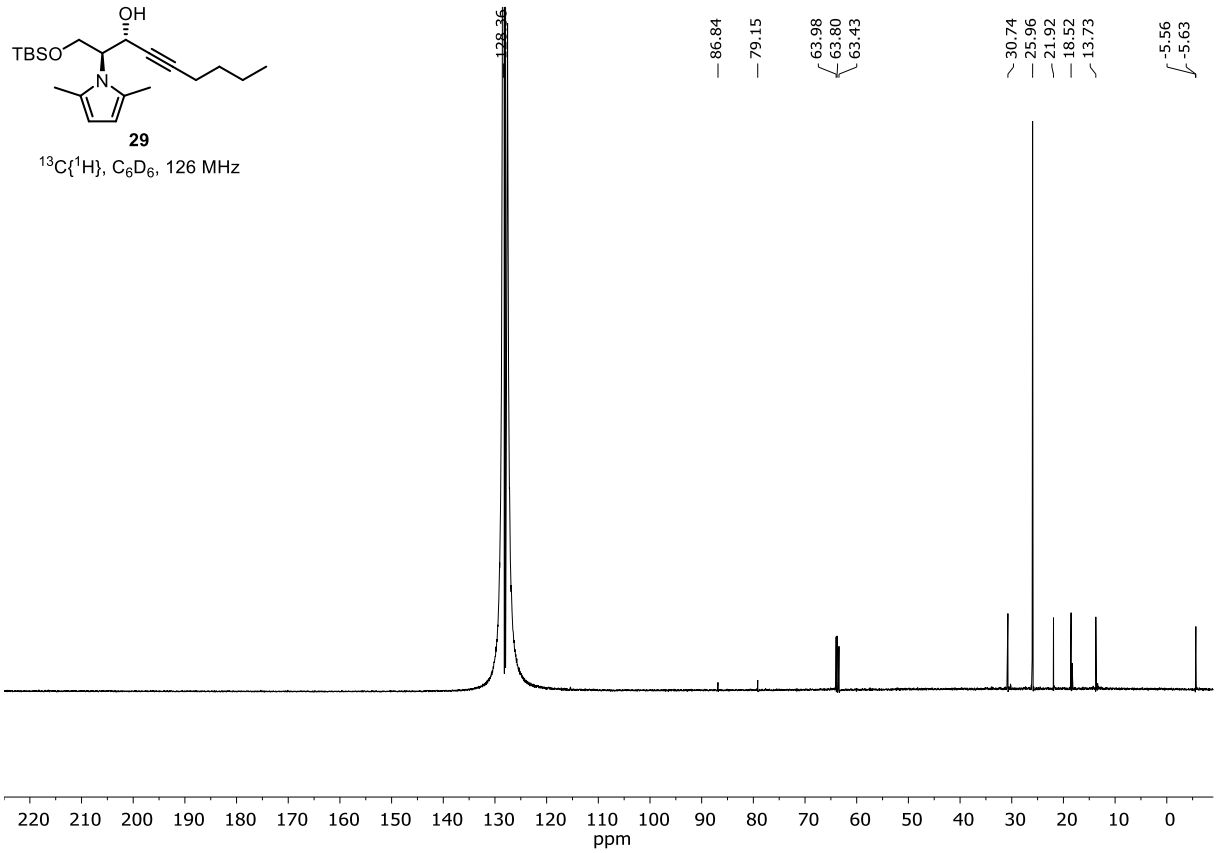

OH
N
27
1H, C6D6, 300 MHz
5.98
4.46
4.43
4.17
4.14
4.12
4.12
4.09
4.07
2.20
1.91
1.90
1.88
1.88
1.86
1.85
1.48
1.40
1.37
1.25
1.23
1.22
1.22
1.21
1.20
1.20
1.19
1.19
1.18
1.17
1.16
1.15
1.13
1.12
0.78
0.76
0.74
1.00
19.77
1.05
20.07
4.6
4.5
4.4
4.3
4.2
4.1
4.0
ppm
2.04
1.00
1.02
6.24
2.12
0.99
3.45
4.48
3.27
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
ppm

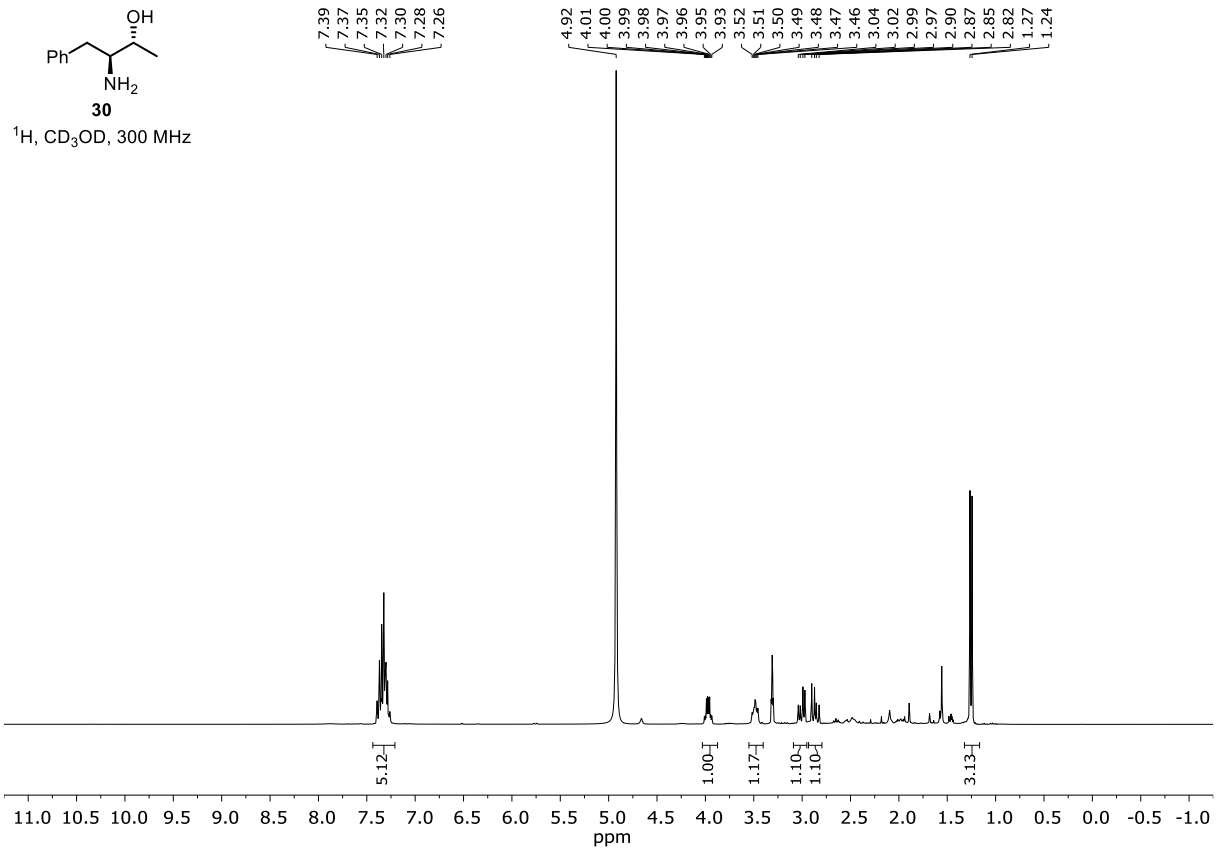

OH
N
27
13C{1H}, C6D6, 75 MHz
107.51
86.48
79.70
65.95
56.95
30.78
22.01
18.53
16.76
14.66
13.71
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

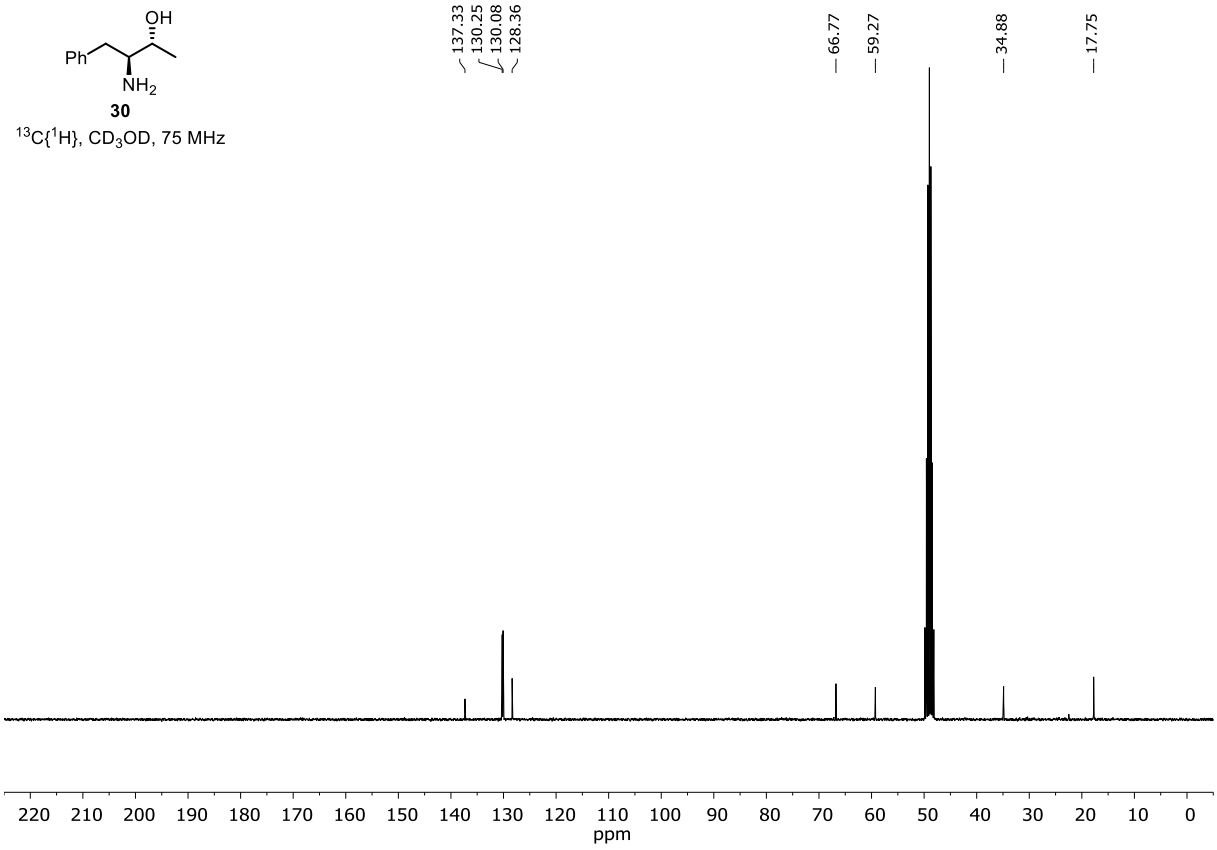

OH
Ph
N
28
1H, C6D6, 500 MHz
ppm

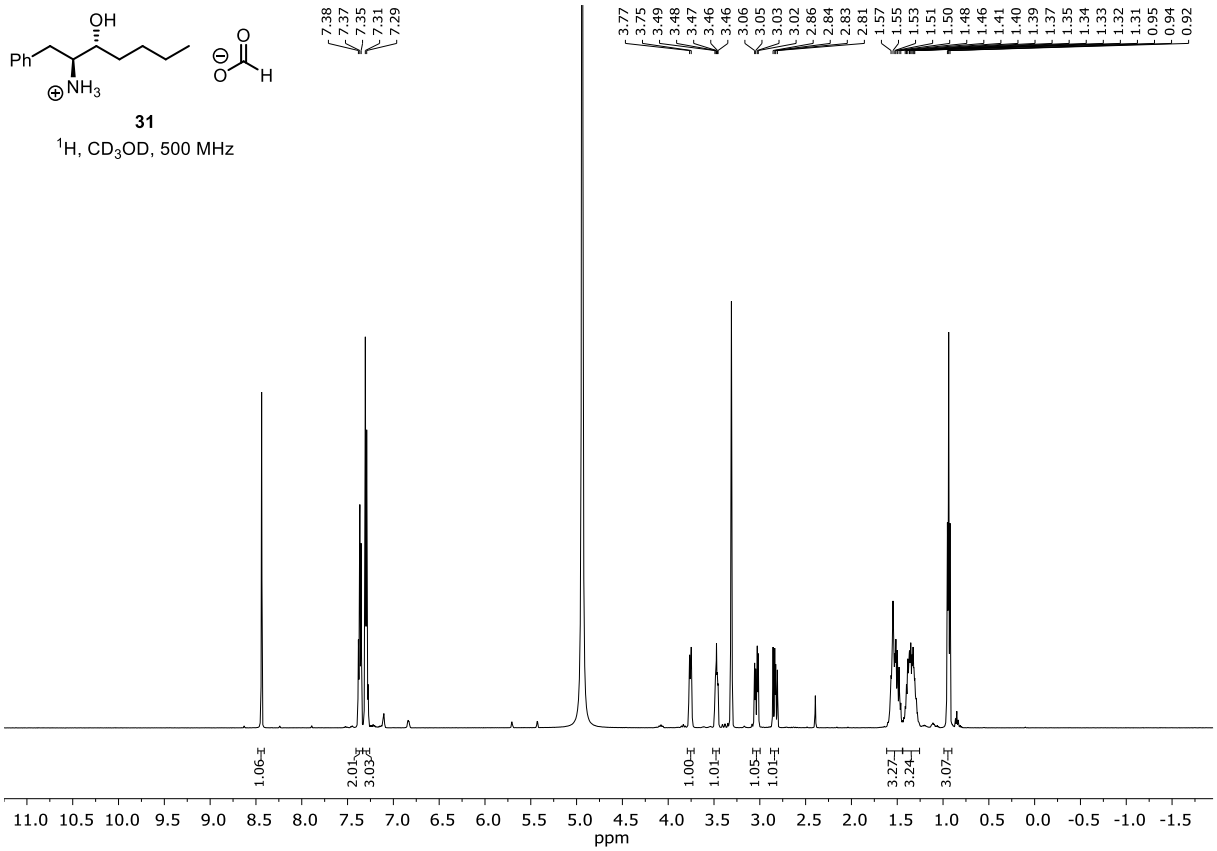

OH
Ph
N
28
13C{1H}, C6D6, 126 MHz
ppm

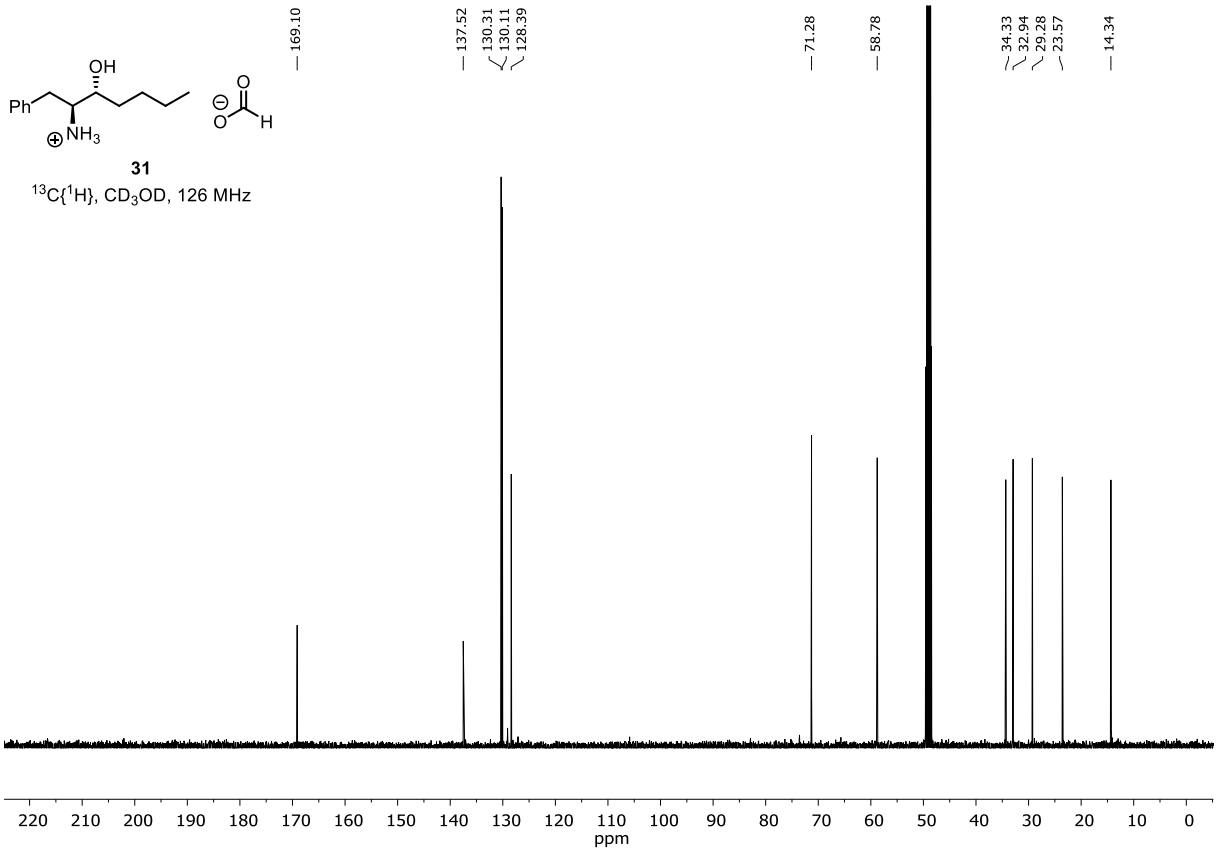

OH
TBSO
N
29
1H, C6D6, 500 MHz
1.00
10.32
-0.02
-0.04
-0.06
-0.08
-0.10
ppm
1.91
1.12
1.16
1.18
1.15
6.37
1.14
2.10
4.40
9.07
2.94
2.71
2.73
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

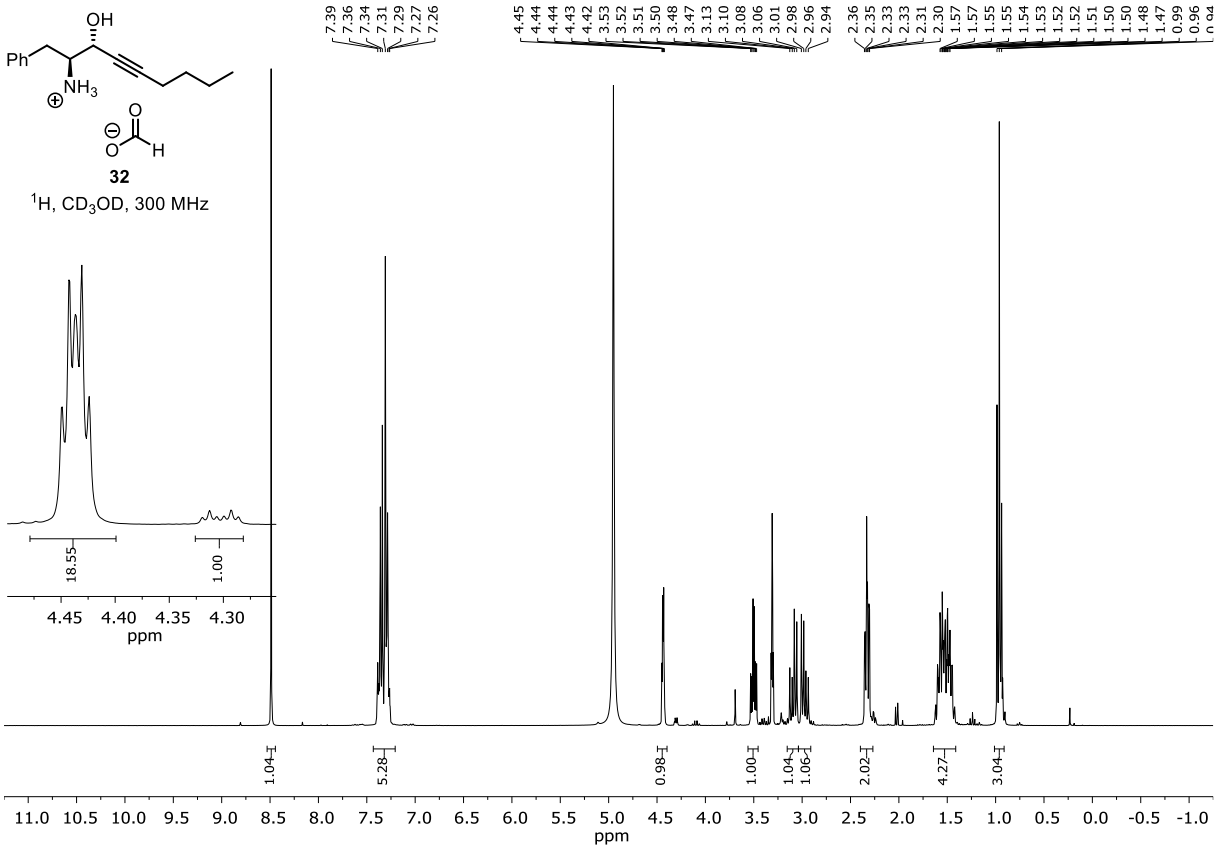

OH
TBSO
N
29
13C{1H}, C6D6, 126 MHz
128.36
86.84
79.15
63.98
63.80
63.43
30.74
25.96
21.92
18.52
13.73
-5.56
-5.63
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

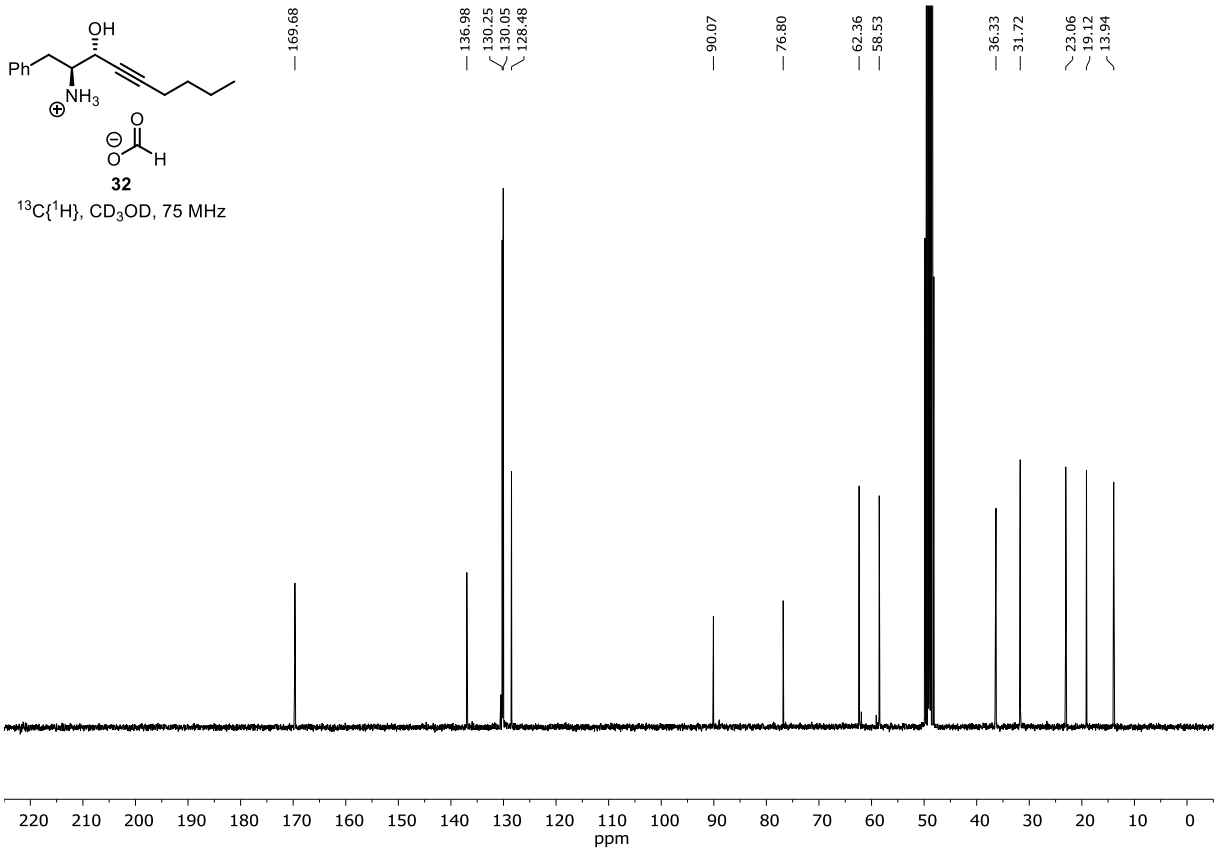

OH
Ph
NH2
30
1H, CD3OD, 300 MHz
7.39
7.37
7.35
7.32
7.30
7.28
7.26
4.92
4.01
4.00
3.99
3.98
3.97
3.96
3.95
3.93
3.52
3.51
3.50
3.49
3.48
3.47
3.46
3.04
3.02
2.99
2.97
2.90
2.87
2.85
2.82
1.27
1.24
5.12
1.00
1.17
1.10
1.10
3.13
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

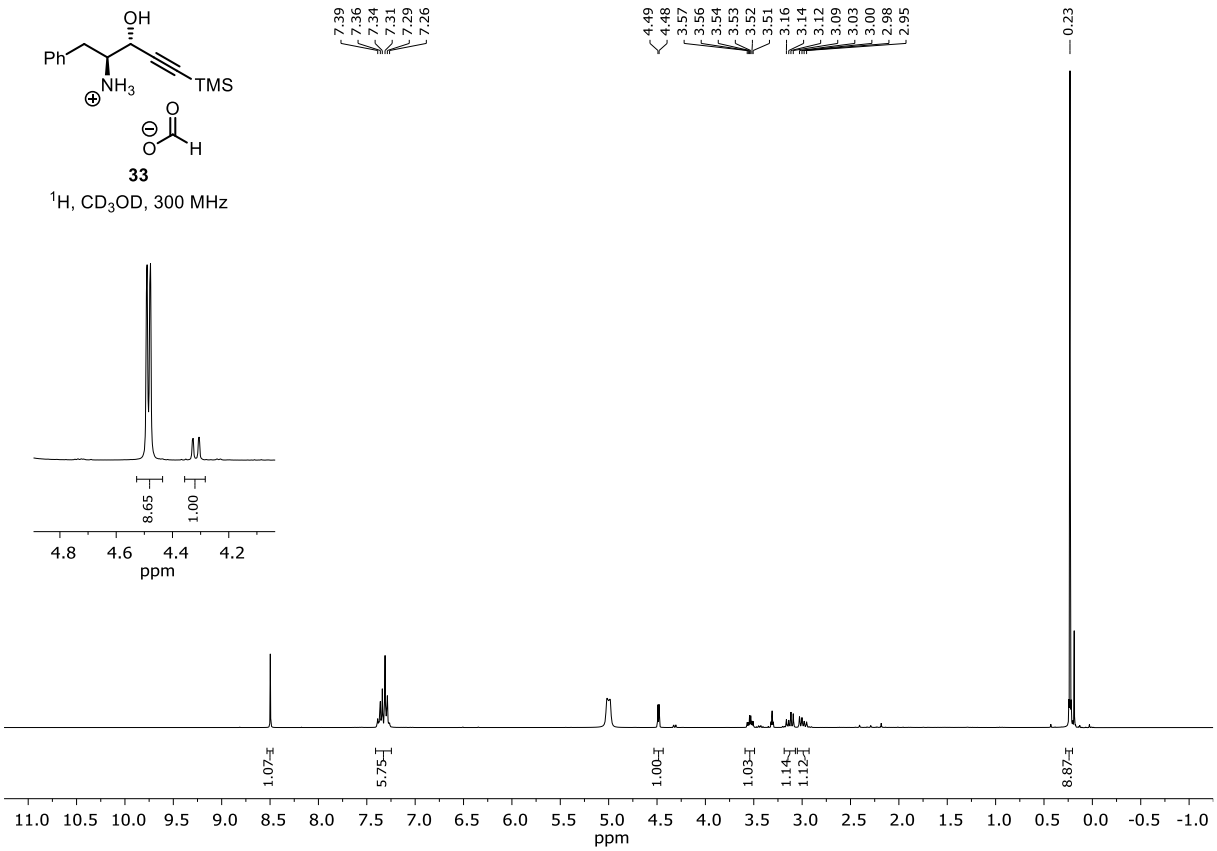

OH
Ph
NH2
30
13C{1H}, CD3OD, 75 MHz
137.33
130.25
130.08
128.36
66.77
59.27
34.88
17.75
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

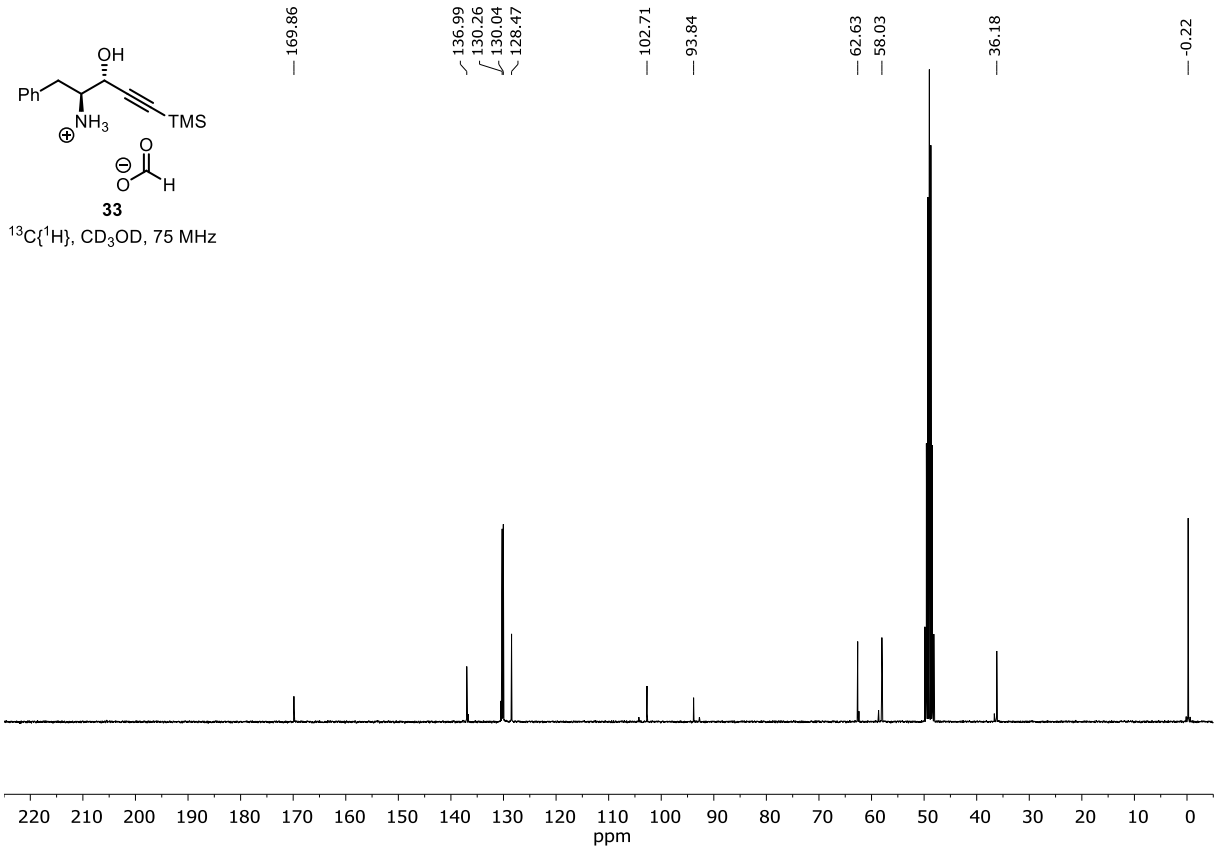

OH
Ph
NH3
O
O
H
31
1H, CD3OD, 500 MHz
7.38
7.37
7.35
7.31
7.29
3.77
3.75
3.49
3.48
3.47
3.46
3.46
3.06
3.05
3.03
3.02
2.86
2.84
2.83
2.81
1.57
1.55
1.53
1.51
1.50
1.48
1.46
1.41
1.40
1.39
1.37
1.35
1.34
1.33
1.32
1.31
0.95
0.94
0.92
1.06
2.01
3.03
1.00
1.01
1.05
1.01
3.27
3.24
3.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
ppm

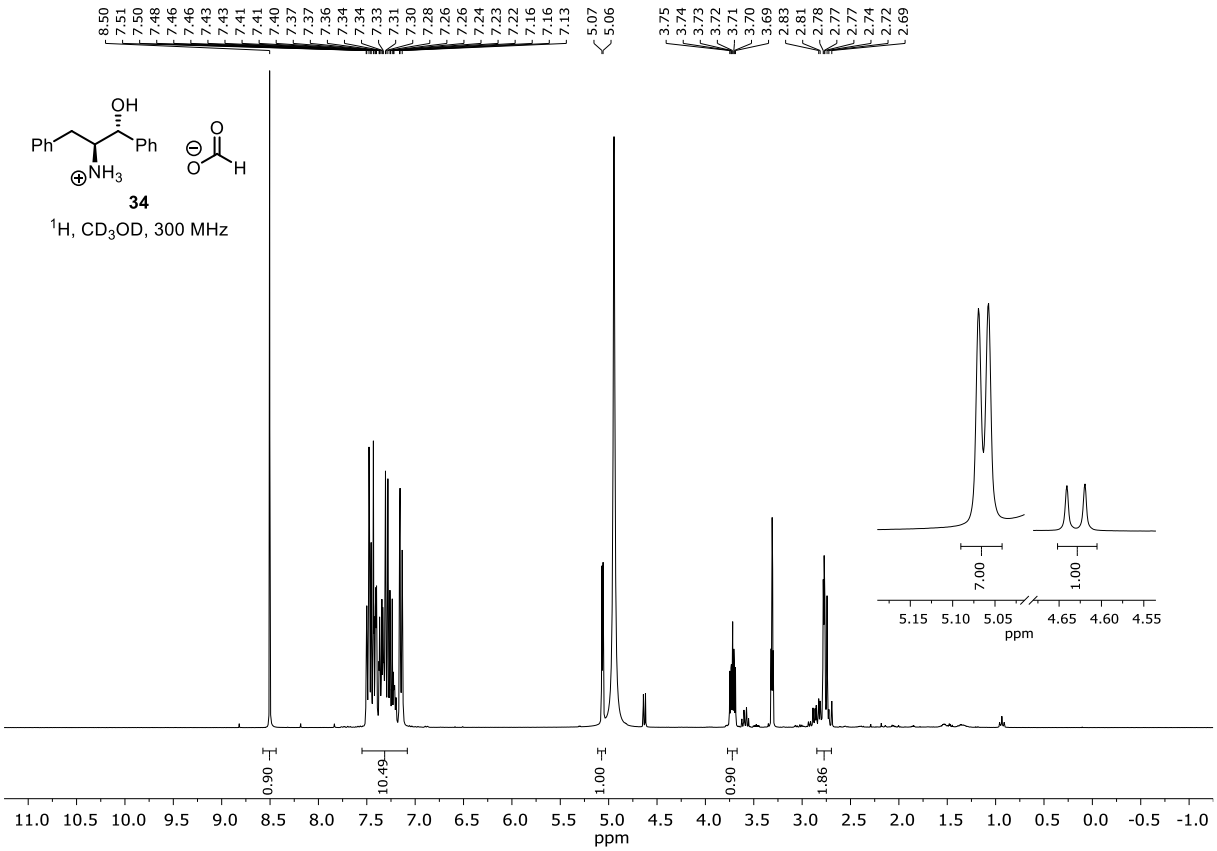

OH
Ph
NH3
O
O
H
31
13C{1H}, CD3OD, 126 MHz
169.10
137.52
130.31
130.11
128.39
71.28
58.78
34.33
32.94
29.28
23.57
14.34
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

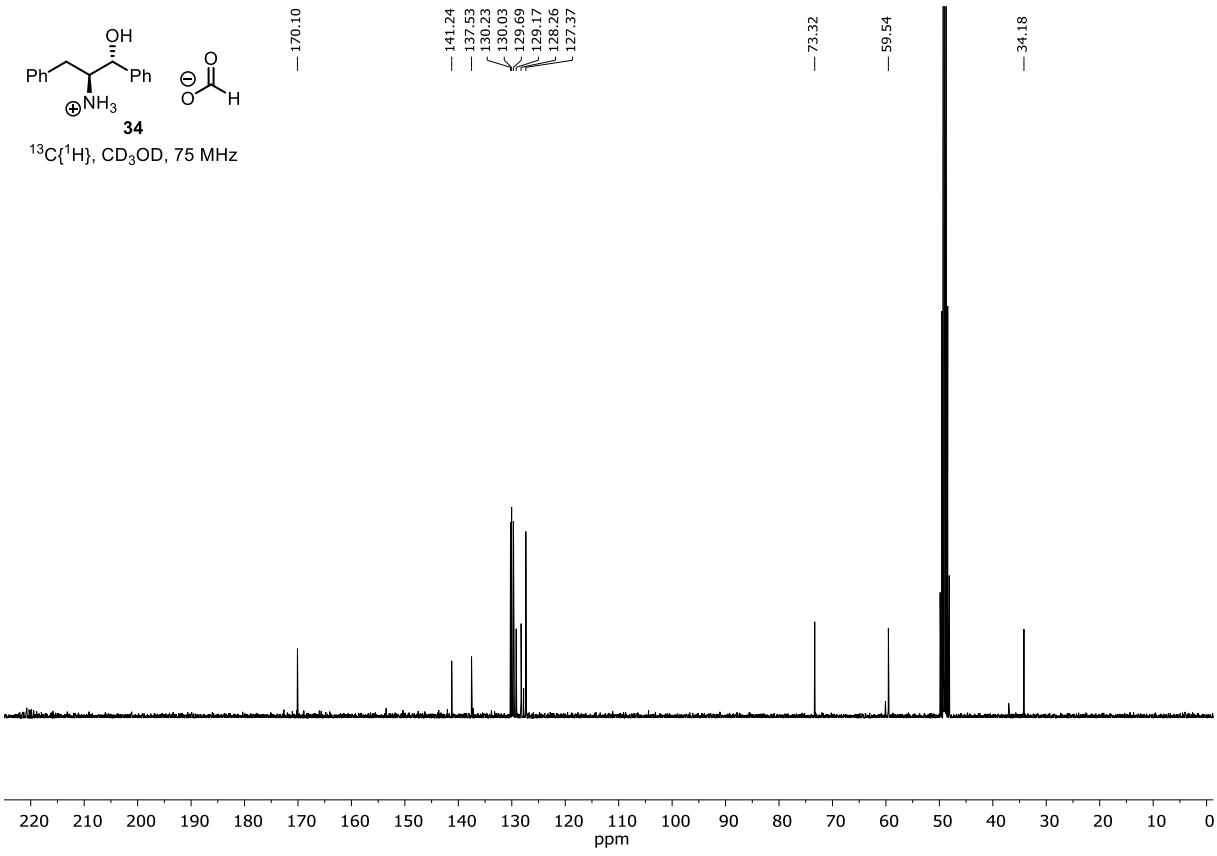

OH
Ph
NH3
O
O
H
32
1H, CD3OD, 300 MHz
7.39
7.36
7.34
7.31
7.29
7.27
7.26
4.45
4.44
4.44
4.43
4.42
3.53
3.52
3.51
3.50
3.48
3.47
3.13
3.10
3.08
3.06
3.01
2.98
2.96
2.94
2.36
2.35
2.33
2.33
2.31
2.30
1.57
1.57
1.55
1.55
1.54
1.53
1.52
1.52
1.51
1.50
1.50
1.48
1.47
0.99
0.96
18.55
1.00
4.45 4.40 4.35 4.30
ppm
1.04
5.28
0.98
1.00
1.04
1.06
2.02
4.27
3.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

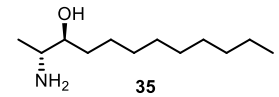

OH
Ph
NH3
O
O
H
32
13C{1H}, CD3OD, 75 MHz
169.68
136.98
130.25
130.05
128.48
90.07
76.80
62.36
58.53
36.33
31.72
23.06
19.12
13.94
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


OH
Ph
NH3
TMS
O
O
H
33
1H, CD3OD, 300 MHz
7.39
7.36
7.34
7.31
7.29
7.26
4.49
4.48
3.57
3.56
3.54
3.53
3.52
3.51
3.16
3.14
3.12
3.09
3.03
3.00
2.98
2.95
0.23
8.65
1.00
4.8
4.6
4.4
4.2
ppm
1.07
5.75
1.00
1.03
1.14
1.12
8.87
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


OH
Ph
NH3
TMS
O
O
H
33
13C{1H}, CD3OD, 75 MHz
169.86
136.99
130.26
130.04
128.47
102.71
93.84
62.63
58.03
36.18
-0.22
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

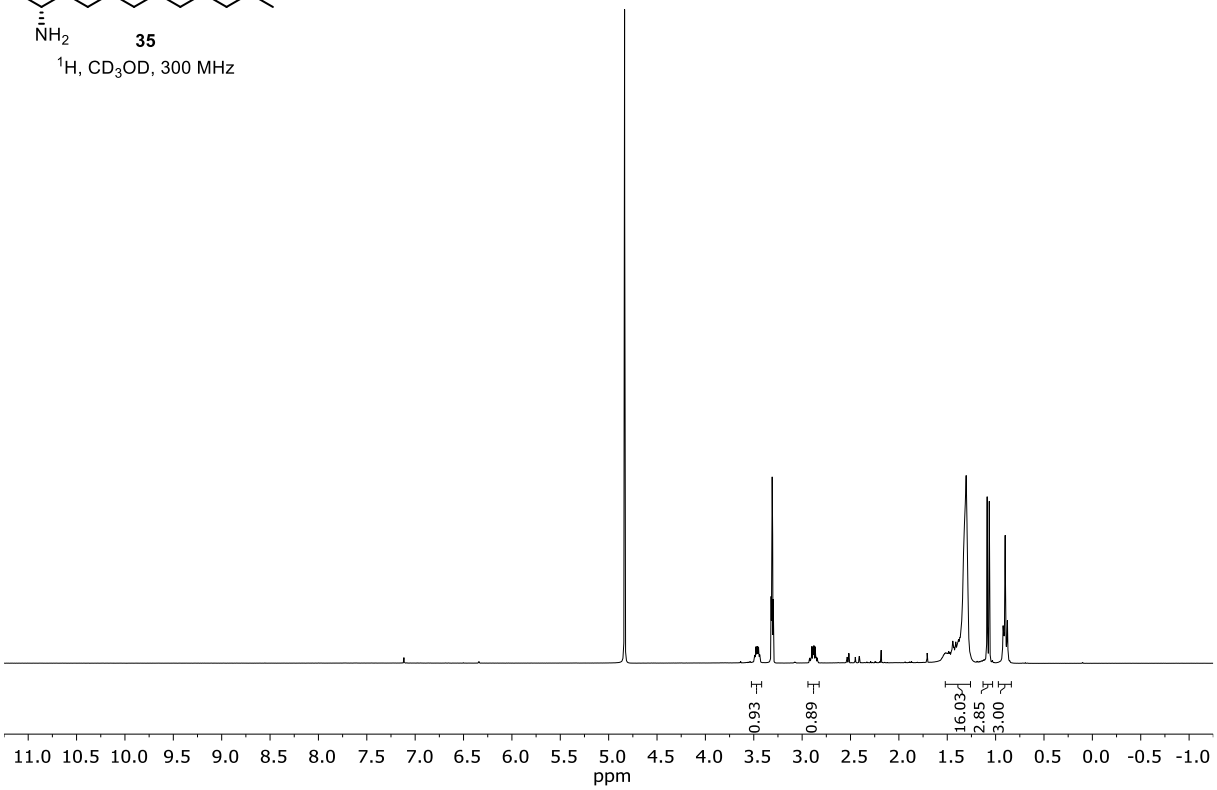

8.50 7.51 7.50 7.48 7.46 7.46 7.43 7.43 7.41 7.41 7.40 7.37 7.37 7.36 7.34 7.34 7.33 7.31 7.30 7.28 7.26 7.26 7.24 7.23 7.22 7.16 7.13
5.07 5.06
3.75 3.74 3.73 3.72 3.71 3.70 3.69
2.83 2.81 2.78 2.77 2.74 2.72 2.69
OH
Ph
Ph
NH3
O
O
H
34
1H, CD3OD, 300 MHz
0.90
10.49
1.00
0.90
1.86
7.00
1.00
5.15 5.10 5.05
4.65 4.60 4.55
ppm
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

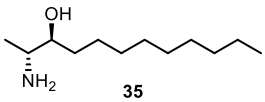

OH
Ph
Ph
NH3
O
O
H
34
13C{1H}, CD3OD, 75 MHz
170.10
141.24
137.53
130.23
130.03
129.69
129.17
128.26
127.37
73.32
59.54
34.18
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



35

^{1}H, CD_3OD, 300 MHz





35

$^{13}C\{^{1}H\}$, CD_3OD, 75 MHz