Supporting Information

General Experimental

NMR Spectroscopy

^{1}H NMR spectra were recorded using either a Bruker AV400 spectrometer at 400 MHz, a Bruker AV600 spectrometer at 600 MHz or a Bruker AV800 spectrometer at 800 MHz. ^{13}C NMR spectra were recorded using either a Bruker AV400 spectrometer at 100 MHz a Bruker AV600 spectrometer at 150 MHz or a Bruker AV800 spectrometer at 200 MHz. Residual solvent peaks were used as an internal reference for ^{1}H NMR spectra ($CDCl_3$ δ 7.26 ppm, C_6D_6 δ 7.16 ppm) and ^{13}C NMR spectra ($CDCl_3$, 1:1:1 triplet at δ 77.16 ppm, C_6D_6 δ 128.06 ppm).

Proton decoupled ^{31}P data were acquired at 162 MHz on a Bruker AV400 spectrometer or at 243 MHz on a Bruker AV600 spectrometer.

Coupling constants (*J*) are quoted to the nearest 0.1 Hz. The following abbreviations (or combinations thereof) were used to describe ^{1}H NMR,: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The abbreviation d = doublet was used to describe ^{13}C or ^{31}P multiplicities.

Samples of the catalysts were measured using Wilmad® low pressure/vacuum NMR tubes prepared in the glovebox.

Infrared Spectroscopy

IR spectra were recorded on an Alpha-P Bruker FT-IR Spectrometer.

Mass Spectrometry

HRMS measurements were performed by an Agilent LC-MS time-of-flight mass spectrometer or on Waters Xevo G2-S QTOF (ESI or APPI). High resolution mass are given in *m/z*. Samples of the catalysts were prepared in the glovebox in dry and degassed MeOH.

Chromatography

Flash chromatography was performed with Silicycle silica gel 60 (0.040-0.063 μm grade). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were either visualized

under UV-light at 254 nm or by dipping the plates in an aqueous potassium permanganate solution followed by heating.

Melting Points

Melting points were measured on a Büchi melting point apparatus, model B-540, and are uncorrected.

Optical Rotations

Optical rotations were measured on a Polartronic M polarimeter using a 0.5 cm cell with a Na 589 nm filter. Samples of the catalysts were prepared in the glovebox and measured in dry and degassed CH_2Cl_2.

X-ray Analysis

X-ray analyses were performed by Dr R. Scopelliti, Dr E. Solari and Dr F. Fadaei Tirani at EPFL.

Experimental procedures and reagents

Most of the commercially available chemicals were used as purchased for the synthesis of substrates. All reactions out of the glovebox were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. Diethyl ether, dichloromethane, toluene and THF were purified by an Innovative Technology Solvent Delivery System.

The synthesis of diazaphospholene derivatives was performed in a MB-200-B MOD Glove Box Workstation (O_2 level <0.6 ppm, H_2O level <0.1 ppm) using oven-dried schlenk flasks. Acetonitrile, toluene, hexane, dichloromethane, diethyl ether, methanol, cyclohexene, chloroform-*d*, benzene-d_6 were distilled and degassed using freeze-pump-thaw cycles prior to use in the glovebox and kept over molecular sieves. Tribromophosphine 99.999% was purchased from Apollo Scientific and used as received in the glovebox. Reduction reactions were set up in the glovebox in test tubes closed with septa and secured with parafilm. Reactions were then run outside of the glovebox, either at room temperature or at 2 °C. Standard NMR tubes capped with septa and wrapped with parafilm were used to measure NMR spectra. All analytical samples of air-sensitive

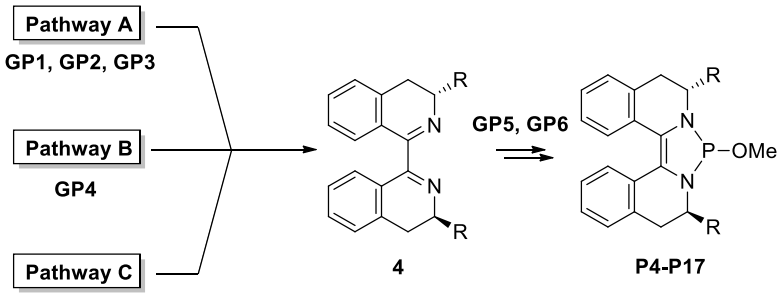
diazaphospholenes were prepared inside the glovebox prior to analysis.

Rhodium and nickel catalysts were prepared in the laboratory following reported procedures.

Experimental Procedures and Characterization Data

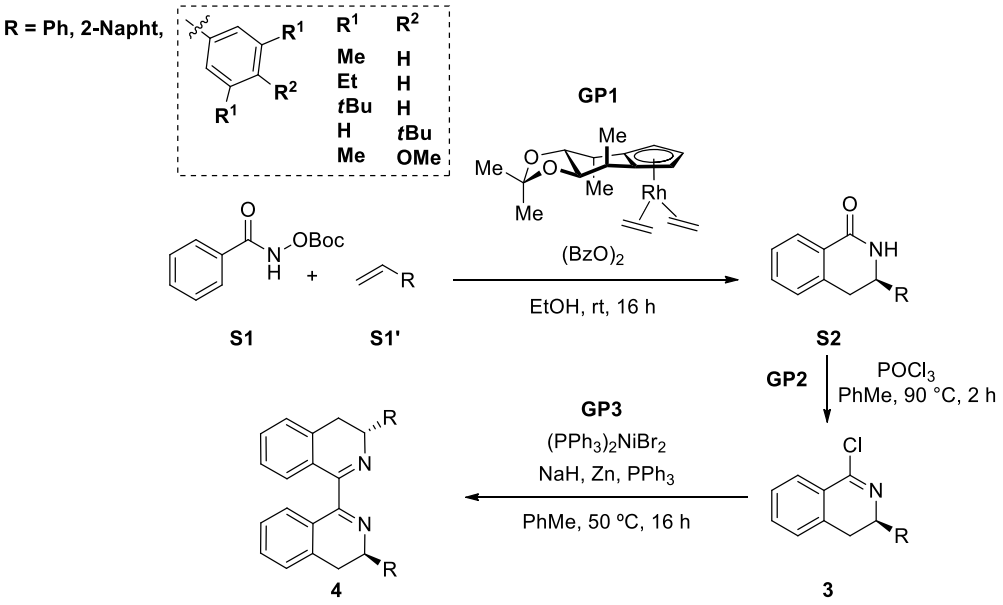
Catalysts and Intermediates

Three different pathways have been used to synthesize various biisoquinoline ligands **4**. All of them have then been converted into methoxydiazaphospholene precatalysts **P4-17** following general procedures **GP5** and **GP6**.



Biisoquinoline 4 Synthetic Routes

Pathway A



The syntheses of *O*-Boc hydroxamates **S1** and dihydroisoquinolinones **S2** have previously been reported in the literature.[1]

[1] Ye, B.; Cramer, N. *Science* **2012**, *338*, 504.

General Procedure 1 for the enantioselective Rh(III)-catalyzed isoquinolinone synthesis (GP1)

Without protection from air and moisture, $Cp^{X}Rh(III)$ catalyst (7.6 mg, 0.02 mmol), dibenzoylperoxide (5 mg, 0.02 mmol) and *O*-Boc hydroxamate **S1** (1.0 mmol) were weighed into a vial equipped with a magnetic stir bar and sealed with a rubber septum. EtOH (1 mL) was added followed by freshly distilled styrene **S1'** (2.00 mmol) and the reaction was stirred for 16 hours at 23 °C. The volatiles were evaporated *in vacuo* and the residue was purified on silica gel column chromatography giving the desired dihydroisoquinolinone **S2**.

General Procedure 2 for the Formation of Imidoyl Chloride Derivatives 3 (GP2)

Dihydroisoquinolinone **S2** (2 mmol) was dissolved in dry toluene (20 mL) before freshly distilled phosphoryl trichloride (1.18 mL, 12.66 mmol) was added dropwise via syringe to the stirred mixture. The mixture was heated at 90 °C for 2 hours, cooled to room temperature and the solvent was removed under vacuum. The resulting residue was cooled to -30 °C in an acetonitrile/LN_2 bath and a mixture of Et_2O/Et_3N 5% was added dropwise to the flask. The mixture was then stirred at room temperature for 10 minutes. Finally, it was filtered over basic alumina, eluting with Et_2O/Et_3N 5%. The filtrate was concentrated under reduced pressure to give the desired imidoyl chloride **3** which was used in the following step without further purification.

General Procedure 3 for the Ullmann-Type Homocoupling Reaction (GP3)

The following procedure was adapted from a previous literature report.[2]

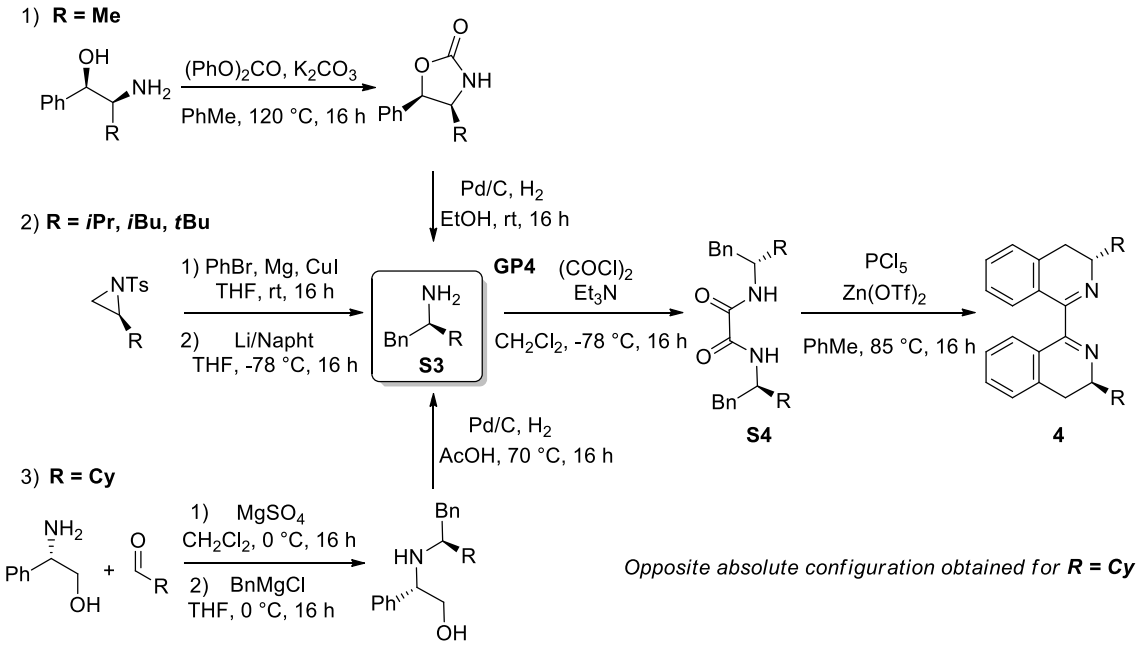
A flame-dried Schlenk flask was charged inside the glovebox with $NiBr_2(PPh_3)_2$ (0.5 equiv), PPh_3 (1 equiv), Zn dust (3 equiv), oil-free and dry NaH (8 equiv) and the desired imidoyl chloride derivative **3** (1 equiv). Dry and degassed toluene (0.15 M) was then added to the mixture. The Schlenk flask was sealed and taken out of the glovebox, and stirred at

[2] Lin, G.; Hong, R. *J. Org. Chem.* **2001**, *66*, 2877.

50 °C for 16 hours. The dark brown reaction mixture was cooled and transferred dropwise to a flask containing a saturated solution of EDTA in ammonia (25%) at 0 °C. The solution was diluted with EtOAc and the resulting dark grey mixture was stirred under air at room temperature until good separation of the biphasic mixture was achieved (minimum 3 hours).

The aqueous layer was separated and extracted with EtOAc (3x). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure to give the crude product. Purification of the crude material by flash chromatography (SiO_2, Pentane:EtOAc) afforded the desired chiral biisoquinoline **4**.

Pathway B



Synthesis of chiral amines S3

1) Methyl substituted amine was synthesized following a previously reported procedure.[3]

2) *Iso*propyl, *iso*butyl and *tert*butyl substituted amines were synthesized following a previously reported procedure.[4]

[3] Evans, D. A.; Mathre,D. J.; Scott, W. L. *J. Org. Chem.* **1985**, *50*, 1830.
[4] Seo, H.; Hirsch-Weil, D.; Abboud, K. A.; Hong, S. *J. Org. Chem.* **2008**, *73*, 1983.

3) Cyclohexyl substituted amine was synthesized following a previously reported procedure.[5]

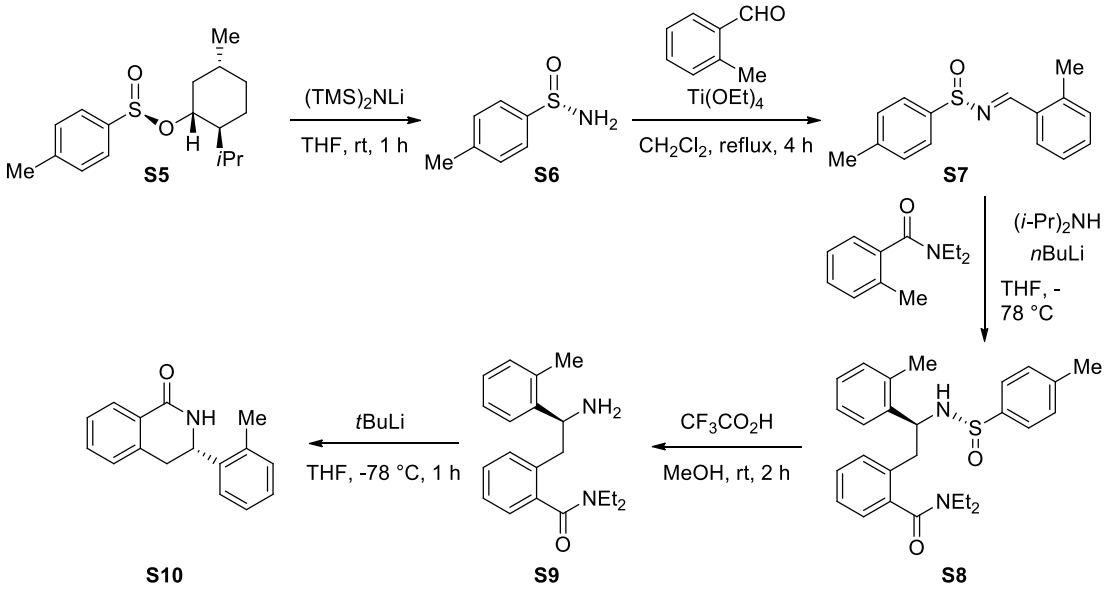
General Procedure 4 to form biisoquinolines 4 from chiral amines S3[6]

Under an argon atmostphere, oxalyl chloride (0.096 mL, 1.1 mmol) was added dropwise to a cooled, magnetically stirred, solution of chiral amine **S3** (2.25 mmol) and triethylamine (0.350 mL, 2.53 mmol) in THF (28 mL) at 0 ˚C. The reaction mixture was allowed to warm to room temperature and then stirred for 12 h. The reaction mixture was cooled to 0 ˚C before quenching with water (10 mL). The mixture was extracted with $CHCl_3$ (3 x 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography to afford the desired diamine **S4**.

To a solution of **S4** (1.38 mmol) in toluene (60 mL) under nitrogen was added $Zn(OTf)_2$ (1.51 g, 4.14 mmol) and PCl_5 (1.72 g, 8.28 mmol). The reaction mixture was heated at 85 ˚C for 12 h and then cooled to room temperature before quenching with a 30% aqueous NH_4OH solution (20 mL). The mixture was extracted with EtOAc (3 x 35 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude product by flash chromatography afforded the target biisoquinoline **4**.

[5] Takahashi, H.; Chida, Y.; Yoshii, T.; Suzuki, T.; Yanaura, S.. *Pharm. Bull.* **1986**, *34*, 2071.
[6] Rodig, M. J.; Seo, H.; Hirsch-Weil, D.; Abboud, K. A.; Hong, S. *Tetrahedron Asymmetry* **2011**, *22*, 1097.

Pathway C



A solution of lithium bis(trimethylsilyl)amide (0.767 g, 4.58 mmol) in THF (5 mL) was added dropwise to a solution of (*S*)-(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-methylbenzenesulfinate **S5** (1.00 g, 3.40 mmol) in THF (8 mL) at -78 °C. The reaction was warmed to room temperature and stirred for 1 h, before being quenched with sat. NH_4Cl (6mL), extracted with EtOAc, washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (DCM/EtOAc 1:1) afforded title compound **S6** in 73 % yield (385 mg).[7]

A mixture of (*S*)-4-methylbenzenesulfinamide **S6** (374 mg, 2.41 mmol), 2-methylbenzaldehyde (0.279 ml, 2.410 mmol) and tetraethoxytitanium (1.05 mL, 5.00 mmol) in CH_2Cl_2 (30 mL) was refluxed for 4 h. The reaction was cooled to 0°C and quenched with H_2O (10 mL). The biphasic mixture was filtered through celite/Na_2SO_4, extracted with CH_2Cl_2, washed with brine, dried over Na_2SO_4 and concentrated under

[7] Davis, F. A.; Zhang, Y.; Andemichael, Y.; Fang, T.; Fanelli, D. L.; Zhang, H. *J. Org. Chem.* **1999,** *64,* 1403.

reduced pressure. The crude product **S7** was obtained in 90% yield (555 mg) and used without further purification in the next step.[8]

N-butyllithium (0.924 mL, 2.31 mmol) was added dropwise to a solution of diisopropylamine (0.338 mL, 2.42 mmol) in THF (8 mL) at 0 °C. *N*,*N*-diethyl-2-methylbenzamide (402 mg, 2.1 mmol) was then added at -78 °C. The mixture was stirred at -78 °C for 30 minutes, after which, a solution of (*S*,*E*)-4-methyl-*N*-(2-methylbenzylidene)benzenesulfinamide **S7** (540 mg, 2.10 mmol) in THF (2 mL) was added dropwise at -78 °C. The resulting mixture was stirred at -78 °C for 30 min. Finally, the reaction was quenched at -78 °C with sat. NH_4Cl (5 mL), warmed up to room temperature, extracted with EtOAc, washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (pentane/EtOAc 1:1) afforded the title compound **S8** in 52% yield (488 mg).[9]

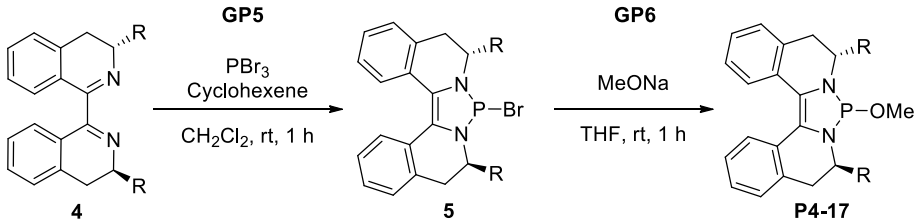
2,2,2-trifluoroacetic acid (0.41 mL, 5.41 mmol) was added dropwise to a solution of *N*,*N*-diethyl-2-((*S*)-2-((*S*)-4-methylphenylsulfinamido)-2-(*o*-tolyl)ethyl)benzamide **S8** (485 mg, 1.08 mmol) in MeOH (8 mL) at 0 °C. The reaction was warmed up to room temperature and stirred for 2 hours. The solvent was evaporated with toluene and the residue dissolved in EtOAc, washed with 1M NaOH, brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude material by flash chromatography (DCM/EtOH/aq.NH_3 300:15:1) afforded the title compound **S9** in 80% yield (269 mg).[10]

Tert-butyllithium (1.368 mL, 2.60 mmol) was added dropwise to a solution of (*S*)-2-(2-amino-2-(*o*-tolyl)ethyl)-*N*,*N*-diethylbenzamide **S9** (269 mg, 0.867 mmol) in THF (10 mL) at -78 °C and the mixture stirred at -78 ºC for 1 h. The reaction was quenched with sat. NH_4Cl at -78 °C, extracted with EtOAc, washed with brine, dried over $MgSO_4$ and

[8] Akindele, T.; Yamamoto, Y.; Maekawa, M.; Umeki, H.; Yamada, K.-I.; Tomioka, K. *Org. Lett.* **2006**, *8*, 5729.
[9] Davis, F. A.; Andemichael, Y. W. *J. Org. Chem.* **1999,** *64*, 8627-8634 & Derdau, V.; Snieckus, V. *J. Org. Chem.* **2001,** *66*, 1992.
[10] Davis, F. A.; Andemichael, Y. W. *J. Org. Chem.* **1999,** *64*, 8627.

concentrated under reduced pressure. Purification by flash chromatography (pentane/EtOAc 2:1) afforded isoquinolinone **S10** in 95% yield (196 mg).

Synthesis Pathway towards Precatalysts P4-17 from biisoquinolines 4



General Procedure 5 for the Cyclization with PBr_3 (GP5)

The following procedure was slightly adapted from a previous literature report.[11]

In a flame-dried Schlenk flask in the glove box was added biisoquinoline **4** (0.113 mmol, 1 equiv), freshly distilled cyclohexene (0.035 mL, 0.340 mmol) and dried and degassed CH_2Cl_2 (1.14 mL). Finally, tribromophosphine (10.67 µl, 0.113 mmol) was added as a pure liquid via hamilton syringe to the solution at room temperature. The mixture was stirred for one hour then concentrated under high vacuum. The resulting solid was suspended in a mixture of hexane:Et_2O 4:1 and sonicated for 10 minutes before being filtered on a sintered funnel. The solid was rinsed with hexane and dried under vacuum.

Given the sensitivity of these intermediates, bromine derivatives **5** were directly engaged in the next step to form the alkoxydiazaphospholenes **P4-17**.

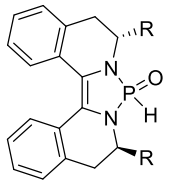
General Procedure 6 for the Formation of Chiral Methoxydiazaphospholenes C (GP6)

A flame-dried Schlenk tube inside the glovebox was charged with bromodiazaphospholene **5** (0.150 mmol) and solid sodium methanolate (0.016 g, 0.300 mmol) followed by THF (0.5 mL). The mixture was stirred for one hour, then evaporated to dryness under high vacuum. The crude compound was suspended in toluene (1 mL) and stirred for several

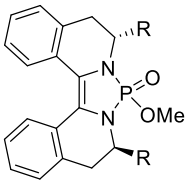
[11] Dube, J. W.; Farrar, G. J.; Norton, E. L.; Szekely, K. L. S.; Cooper, B. F. T.; Macdonald, C. L. B. *Organometallics*, **2009**, *28*, 4377.

minutes. Finally, the suspension was filtered on a small pad of celite, rinsed with toluene (3x0.5 mL) and evaporated to dryness again.

The resultant yellow powder was pure enough to be used directly in catalysis without further purification unless otherwise mentioned. Two products derived from exposure to residual moisture or air have been identified.



Phosphine oxide (SPO)

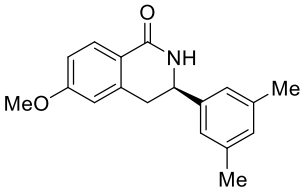


Methyl phosphinate

The small amount of residual phosphine oxide (SPO) resulting from hydrolysis is specified for each compound.

Characterization data of synthetic intermediates towards optimal catalyst P17

(*R*)-3-(3,5-Dimethylphenyl)-6-methoxy-3,4-dihydroisoquinolin-1(2*H*)-one (S2a)



The title compound **S2a** was obtained in 70% yield (0.758 g, 95:5 *er*) from 1.04 g of *N*-((*tert*-butoxycarbonyl)oxy)-4-methoxybenzamide following **GP1**.

Appearance: White solid;

M.p.: 97.8–99.1 °C

R_f: 0.11 (Pentane/EtOAc 20%);

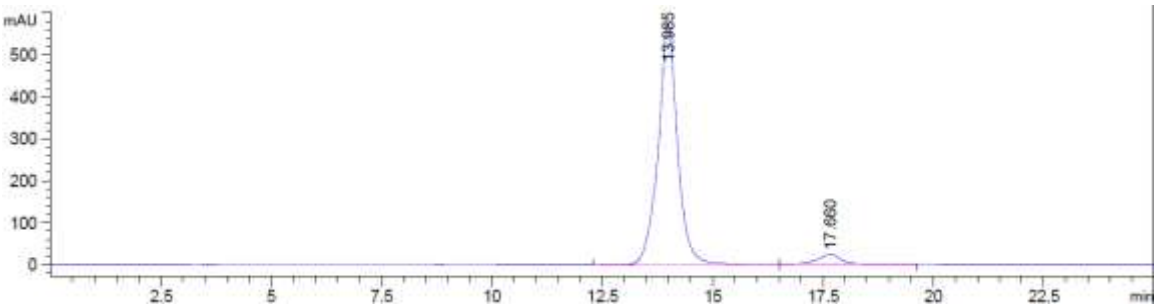
$[\alpha]_D^{20}$: +112.0 (*c* = 1.0, $CHCl_3$);

^{1}H NMR (400 MHz, C_6D_6): δ 8.51 (d, *J* = 8.6 Hz, 1 H), 6.69 (d, *J* = 9.9 Hz, 3 H), 6.60 (dd, *J* = 8.6, 2.6 Hz, 1 H), 6.44 (d, *J* = 2.5 Hz, 1 H), 5.84 (s, 1 H), 4.21 (dd, *J* = 11.1, 4.5 Hz, 1 H), 3.18 (s, 3 H), 2.74 (dd, *J* = 15.6, 11.1 Hz, 1 H), 2.52 (dd, *J* = 15.5, 4.4 Hz, 1 H), 2.09 (s, 6 H).

^{13}C NMR (100 MHz, C_6D_6): δ 165.9, 162.6, 141.7, 139.9, 137.8 (x2), 130.4, 129.4, 124.3 (x2), 122.2, 112.6, 112.1, 55.6, 54.4, 37.5, 21.0 (x2) ppm;

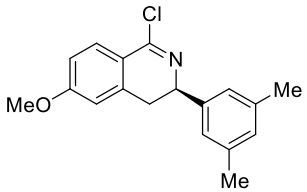
IR (ATR): ν_{max} = 3186, 3070, 2943, 2896, 2866, 1661, 1605, 1578, 1462, 1380, 1331, 1314, 1157, 1033, 861, 834, 819, 794, 756, 742, 704, 640, 534 cm^{-1};

HRMS (ESI): calculated for $[C_{18}H_{19}NO_2+H^+]$: 282.1416, found: 282.1488.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.985	BB	0.4445	1.75508e4	574.43909	95.0640
2	17.660	BB	0.5562	911.28223	23.82792	4.9360

(*R*)-1-Chloro-3-(3,5-dimethylphenyl)-6-methoxy-3,4-dihydroisoquinoline (3a)



The title compound **3a** was obtained in 93% yield from 650 mg of dihydroisoquinolinone **S2a** following **GP2**.

Appearance: Colorless oil;

$[\alpha]_D^{20}$: +63.73 (*c* = 0.17, $CHCl_3$);

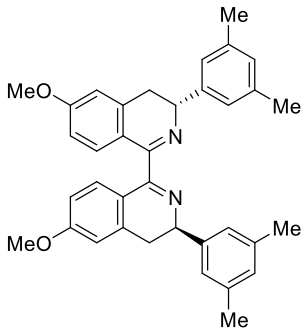
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.6 Hz, 1H), 7.06 (s, 2H), 6.93 (s, 1H), 6.85 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.72 (d, *J* = 2.6 Hz, 1H), 4.73 (dd, *J* = 10.7, 8.8 Hz, 1H), 3.86 (s, 3H), 2.97 (d, *J* = 8.8 Hz, 2H), 2.34 (s, 6H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 154.8, 142.7, 140.2, 138.1, 129.5, 129.0, 124.7, 121.3, 112.9, 112.5, 63.3, 55.6, 35.3, 21.5 ppm;

IR (ATR): ν_{max} = 3007, 2944, 2917, 2841, 1663, 1606, 1566, 1496, 1378, 1320, 1290, 1258, 1241, 1161, 1126, 1113, 1095, 1030, 966, 948, 850, 778, 702 cm^{-1};

HRMS (ESI): calculated for $[C_{18}H_{18}ClNO]^+$: 299.1077, found: 299.1081.

(3*R*,3'*R*)-3,3'-Bis(3,5-dimethylphenyl)-6,6'-dimethoxy-3,3',4,4'-tetrahydro-1,1'-biisoquinoline (**4a**)



The title compound **4a** was obtained in 54% yield (250 mg) from 594 mg of **3a** following **GP3**. The *meso*-(3*R*,3'*S*) corresponding biisoquinoline was isolated in 14% yield (76 mg)

Appearance: White solid;

Rf: 0.32 (Pentane/EtOAc 20 %);

M.p.: 110.1–110.8 °C

$[\alpha]_D^{20}$: -33.33 (c = 0.04, $CHCl_3$);

^{1}H NMR (400 MHz, C_6D_6): δ 7.75 (d, *J* = 8.5 Hz, 2 H), 7.31 (m, 4 H), 6.80 (s, 2 H), 6.61 (d, *J* = 2.5 Hz, 2 H), 6.57 (dd, *J* = 8.5, 2.5 Hz, 2 H), 4.82 (dd, *J* = 14.5, 5.4 Hz, 2 H), 3.25 (s, 6 H), 2.91 (dd, *J* = 15.0, 15.0 Hz, 2 H), 2.79 (dd, *J* = 15.8, 5.4 Hz, 2 H), 2.17 (s, 12 H).ppm;

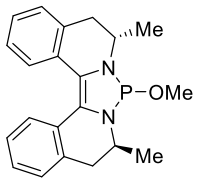
^{13}C NMR (100 MHz, C_6D_6): δ 164.7, 161.9, 144.9, 140.7, 137.7, 130.0, 128.3, 128.1, 127.8, 125.7, 123.3, 113.5, 112.1, 61.9, 54.8, 35.7, 21.5 ppm;

IR (ATR): ν_{max} = 2996, 2913, 2836, 1602, 1561, 1496, 1450, 1292, 1252, 1190, 1147, 1121, 1072, 1031, 945, 929, 904, 880, 867, 815, 786, 761, 702, 679, 616, 587, 494 cm^{-1};

HRMS (ESI): calculated for $[C_{36}H_{36}N_2O_2+H^+]$: 529.2777, found: 529.2933.

Characterization Data of Chiral Methoxydiazaphospholenes P4-P17

(6*S*,10*S*)-8-Methoxy-6,10-dimethyl-5,6,10,11-tetrahydro-8*H* [1,3,2]diazaphospholo[4,3-*a*:5,1-*a'*]diisoquinoline (P4)



Obtained without further purification in 85% yield over 2 steps (113 mg, + 4% SPO) from 110 mg of corresponding biisoquinoline following **Pathway B-1** then **GP5** and **GP6**.

Appearance: Yellow solid

M.p.: 114–116 °C;

$[\alpha]_D^{20}$: −30.91 (c = 0.62, CH_2Cl_2);

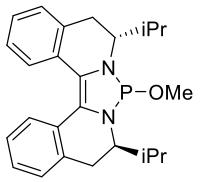
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 7.7, 1.4 Hz, 2 H), 7.18–7.14 (m, 2 H), 7.13–7.05 (m, 2 H), 7.05–6.99 (m, 2 H), 4.08–3.93 (m, 2 H), 3.14 (ddd, *J* = 14.7, 4.4, 1.9 Hz, 1 H), 3.07 (d, *J* = 6.3 Hz, 3 H), 3.02 (dd, *J* = 14.3, 4.1 Hz, 1 H), 2.78 (ddd, *J* = 14.5, 5.7, 2.0 Hz, 1 H), 2.74 (dd, *J* = 14.5, 5.9 Hz, 1 H), 1.34 (d, *J* = 6.5 Hz, 3 H), 1.30 (d, *J* = 6.6 Hz, 3 H) ppm;

^{13}C NMR (200 MHz, $CDCl_3$): δ 134.1, 133.3, 129.7, 129.6, 128.8 (x2), 126.2 (x2), 126.1, 126.0, 125.7, 125.6, 120.9 (d, $J_{C–P}$ = 9.9 Hz), 120.8 (d, $J_{C–P}$ = 10.6 Hz), 50.4 (d, $J_{C–P}$ = 4.4 Hz), 47.7 (d, $J_{C–P}$ = 21.3 Hz), 46.7 (d, $J_{C–P}$ = 17.2 Hz), 39.6 (d, $J_{C–P}$ = 5.5 Hz), 39.1 (d, $J_{C–P}$ = 3.3 Hz), 21.8 (d, $J_{C–P}$ = 13.8 Hz), 21.7 (d, $J_{C–P}$ = 7.4 Hz) ppm;

^{31}P NMR (162 MHz, $CDCl_3$): δ 88.0 ppm;

HRMS (ESI): calculated for $[C_{21}H_{23}N_2OP]^+$: 350.1548, found: 350.1548.

(6*R*,10*R*)-6,10-Diisopropyl-8-methoxy-5,6,10,11-tetrahydro-8*H*-[1,3,2]diazaphospholo[4,3-*a*:5,1-*a*′]diisoquinoline (P5)



Obtained after precipitation in MeCN (0.5 mL) and subsequent filtration in 48% yield over 2 steps (33 mg, + 5% SPO) from 60 mg of corresponding biisoquinoline following **Pathway B-2** then **GP5** and **GP6**.

Appearance: Yellow solid

M.p.: 99–102 °C;

$[\alpha]_D^{20}$: −44.8 (c = 0.45, CH_2Cl_2);

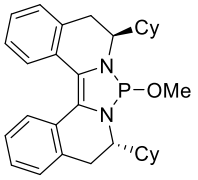
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, *J* = 7.9, 1.3 Hz, 1 H), 7.65 (dd, *J* = 7.7, 1.4 Hz, 1 H), 7.21–7.16 (m, 1 H), 7.16–7.09 (m, 2 H), 7.06 (tt, *J* = 7.4, 1.3 Hz, 2 H), 6.99 (tdd, *J* = 7.3, 1.6, 0.8 Hz, 1 H), 3.78 (tdd, *J* = 5.6, 4.1, 2.7 Hz, 1 H), 3.57 (dddd, *J* = 11.9, 9.0, 4.8, 2.8 Hz, 1 H), 3.23 (dd, *J* = 14.9, 4.8 Hz, 1 H), 3.17 (d, *J* = 6.6 Hz, 3 H), 3.00 (ddd, *J* = 15.6, 12.9, 2.8 Hz, 2 H), 2.93 (dd, *J* = 14.6, 5.5 Hz, 1 H), 1.71 (h, *J* = 6.7 Hz, 1 H), 1.54 (dp, *J* = 8.9, 6.7 Hz, 1 H), 0.99 (d, *J* = 6.7 Hz, 3 H), 0.95 (dd, *J* = 6.7, 2.2 Hz, 3 H), 0.84 (d, *J* = 6.7 Hz, 3 H), 0.68 (d, *J* = 6.7 Hz, 3 H) ppm;

^{13}C NMR (200 MHz, $CDCl_3$): δ 135.5, 133.0, 131.4, 130.0, 128.9, 128.2, 126.5, 126.2, 126.0, 125.8, 125.6, 125.3, 120.7, 120.2, 59.4 (d, $J_{C–P}$ = 26.5 Hz), 56.4 (d, $J_{C–P}$ = 12.5 Hz), 50.6, 34.3, 34.2, 33.4, 31.0, 21.0, 20.7, 19.6, 19.1 ppm;

^{31}P NMR (162 MHz, $CDCl_3$): δ 99.6 ppm;

HRMS (ESI): calculated for $[C_{25}H_{31}N_2OP]^+$: 406.2174, found: 406.2169.

(6*S*,10*S*)-6,10-Dicyclohexyl-8-methoxy-5,6,10,11-tetrahydro-8*H*-[1,3,2]diazaphospholo[4,3-*a*:5,1-*a'*]diisoquinoline (*ent*-P6)



Obtained after precipitation in MeCN (0.5 mL) and subsequent filtration in 74% yield over 2 steps (117 mg, +2% SPO) from 140 mg of corresponding biisoquinoline following **Pathway B-3** then **GP5** and **GP6**.

Appearance: Yellow solid

M.p.: 141–142 °C;

$[\alpha]_D^{20}$: +31.72 (c = 0.62, CH_2Cl_2);

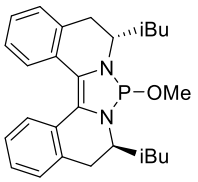
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.7 Hz, 1 H), 7.67 (d, *J* = 7.7 Hz, 1 H), 7.19–7.09 (m, 3 H), 7.05 (dd, *J* = 7.3, 7.3 Hz, 2 H), 6.99 (dd, *J* = 7.6, 7.6 Hz, 1 H), 3.83 (p, *J* = 4.2, 3.3 Hz, 1 H), 3.69–3.57 (m, 1 H), 3.23–3.17 (m, 1 H), 3.17 (d, *J* = 6.6 Hz, 3 H), 3.06–2.98 (m, 2 H), 2.95 (dd, *J* = 14.6, 5.6 Hz, 1 H), 1.89–1.76 (m, 2 H), 1.75–1.60 (m, 4 H), 1.57–1.54 (m, 3 H), 1.50–1.34 (m, 2 H), 1.27–0.82 (m, 10 H), 0.72–0.56 (m, 1 H) ppm;

^{13}C NMR (200 MHz, $CDCl_3$): δ 135.5, 133.1, 131.4, 130.0, 128.8, 128.2, 126.4, 126.1, 125.9, 125.7, 125.5, 125.3, 120.6 (d, $J_{C–P}$ = 6.4 Hz), 120.1 (d, $J_{C–P}$ = 8.9 Hz), 58.5 (d, $J_{C–P}$ = 26.6 Hz), 55.2 (d, *J* = 14.0 Hz), 50.7, 44.9, 40.0, 33.9, 33.2 (d, $J_{C–P}$ = 5.4 Hz), 31.2, 31.0 (d, $J_{C–P}$ = 6.3 Hz), 30.0, 29.2, 26.7 (x2), 26.6, 26.4, 26.2, 26.1 ppm;

^{31}P NMR (162 MHz, $CDCl_3$): δ 100.0 ppm;

HRMS (ESI): calculated for $[C_{31}H_{39}N_2OP]^+$: 486.2800, found: 486.2805.

(6*S*,10*S*)-6,10-Diisobutyl-8-methoxy-5,6,10,11-tetrahydro-8*H*-[1,3,2]diazaphospholo[4,3-*a*:5,1-*a'*]diisoquinoline (P7)



Obtained after precipitation in MeCN (0.5 mL) and subsequent filtration in 42% yield over 2 steps (37 mg, + 6% SPO) from 96 mg of corresponding biisoquinoline following **Pathway B-2** then **GP5** and **GP6**.

Appearance: Pale green solid

M.p.: 112–113 °C (decomp.);

$[\alpha]_D^{20}$: −27.33 (c = 0.50, CH_2Cl_2);

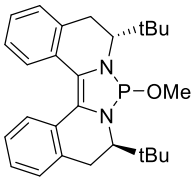
^{1}H NMR (800 MHz, $CDCl_3$): δ 7.75 (ddd, *J* = 11.4, 7.8, 1.2 Hz, 2 H), 7.17 (d, *J* = 7.5 Hz, 1 H), 7.15–7.10 (m, 2 H), 7.07 (tt, *J* = 7.4, 1.6 Hz, 2 H), 7.01 (td, *J* = 7.7, 1.4 Hz, 1 H), 4.11–4.05 (m, 2 H), 3.33–3.27 (m, 1 H), 3.08 (d, *J* = 6.2 Hz, 3 H), 3.02 (dd, *J* = 14.3, 4.9 Hz, 1 H), 2.89 (dt, *J* = 14.3, 3.0 Hz, 1 H), 2.75 (dd, *J* = 14.6, 2.7 Hz, 1 H), 1.74–1.63 (m, 2 H), 1.37 (dt, *J* = 14.2, 7.3 Hz, 1 H), 1.26–1.16 (m, 2 H), 1.13–1.08 (m, 1 H), 0.95 (d, *J* = 6.5 Hz, 3 H), 0.93 (d, *J* = 6.5 Hz, 3 H), 0.86 (d, *J* = 6.6 Hz, 3 H), 0.83 (d, *J* = 6.6 Hz, 3 H) ppm;

^{13}C NMR (200 MHz, $CDCl_3$): δ 133.9, 132.6, 130.5, 129.6, 129.1, 128.9, 126.3, 126.1 (x2), 125.9, 125.6, 125.3, 120.1 (d, $J_{C–P}$ = 8.1 Hz), 120.0 (d, $J_{C–P}$ = 6.8 Hz), 50.6 (d, $J_{C–P}$ = 4.3 Hz), 50.5 (d, $J_{C–P}$ = 15.7 Hz), 47.8 (d, $J_{C–P}$ = 16.1 Hz), 44.2 (d, $J_{C–P}$ = 3.9 Hz), 44.1 (d, $J_{C–P}$ = 4.2 Hz), 36.6, 35.5 (d, $J_{C–P}$ = 8.1 Hz), 25.3, 25.0 (x2), 23.8, 22.9, 21.7 ppm;

^{31}P NMR (162 MHz, $CDCl_3$): δ 91.8 ppm;

HRMS (ESI/QTOF): calculated for $[C_{27}H_{35}N_2OP]^+$: 434.2487, found: 434.2488.

(6*R*,10*R*)-6,10-di-*tert*-Butyl-8-methoxy-5,6,10,11-tetrahydro-8*H*-[1,3,2]diazaphospholo[4,3-*a*:5,1-*a'*]diisoquinoline (P8)



Obtained after precipitation in MeCN (0.5 mL) and subsequent filtration in 15% yield over 2 steps (37 mg, + 10% SPO) from 170 mg of corresponding biisoquinoline following **Pathway B-2** then **GP5** and **GP6**.

Appearance: Yellow solid

M.p.: 152−153 °C;

$[\alpha]_D^{20}$: −45.45 (c = 0.77, CH_2Cl_2);

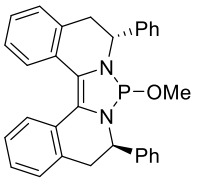
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, *J* = 24.1, 7.8 Hz, 2 H), 7.20 (d, *J* = 7.5 Hz, 1 H), 7.15–7.11 (m, 2 H), 7.10–7.02 (m, 2 H), 6.93 (dd, *J* = 7.6, 7.6 Hz, 1 H), 3.83–3.79 (m, 2 H), 3.35 (dd, *J* = 15.4, 6.3 Hz, 1 H), 3.28 (d, *J* = 6.1 Hz, 3 H), 3.17 (dt, *J* = 14.7, 2.3 Hz, 1 H), 3.10 (dd, *J* = 15.5, 1.6 Hz, 1 H), 2.89 (dd, *J* = 14.7, 6.3 Hz, 1 H), 0.77 (s, 12 H), 0.76 (s, 12 H) ppm;

^{13}C NMR (200 MHz, $CDCl_3$): δ 133.7, 132.8, 130.5, 130.3, 128.2, 127.6, 126.7, 126.5, 126.0, 125.9, 125.8, 125.4, 121.2 (d, $J_{C–P}$ = 10.9 Hz), 120.4 (d, $J_{C–P}$ = 7.5 Hz), 63.3 (d, $J_{C–P}$ = 27.3 Hz), 57.4 (d, $J_{C–P}$ = 11.0 Hz), 51.1 (d, $J_{C–P}$ = 4.4 Hz), 37.2 (d, $J_{C–P}$ = 4.2 Hz), 34.3, 34.2 (d, $J_{C–P}$ = 7.0 Hz), 32.9, 28.3 (x3), 27.1 (x3) ppm;

^{31}P NMR (400 MHz, $CDCl_3$): δ 105.5 ppm;

HRMS (ESI): calculated for $[C_{27}H_{35}N_2OP]^+$: 434.2487, found: 434.2482.

(6*R*,10*R*)-8-Methoxy-6,10-diphenyl-5,6,10,11-tetrahydro-8*H*-[1,3,2]diazaphospholo[4,3-*a*:5,1-*a'*]diisoquinoline (P9)



Obtained after precipitation in MeCN (0.5 mL) and subsequent filtration in 45% yield over 2 steps (74 mg, no SPO) from 130 mg of corresponding biisoquinoline following **Pathway A** then **GP5** and **GP6**.

Appearance: Yellow solid

M.p.: 142–143 °C;

$[\alpha]_D^{20}$: +8.62 (c = 0.58, CH_2Cl_2);

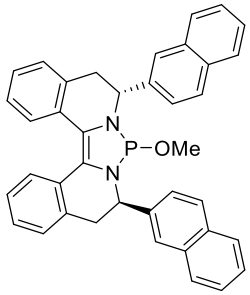
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96–7.89 (m, 2 H), 7.25–7.11 (m, 8 H), 7.15–7.04 (m, 4 H), 7.06–6.99 (m, 4 H), 5.01–4.92 (m, 2 H), 3.43 (dd, *J* = 14.6, 4.7 Hz, 1 H), 3.30 (dd, *J* = 14.6, 4.7 Hz, 1 H), 3.22–3.17 (m, 1 H), 3.17 (dd, *J* = 14.6, 5.6 Hz, 1 H), 2.97 (d, *J* = 7.8 Hz, 3 H) ppm;

^{13}C NMR (200 MHz, $CDCl_3$): δ 142.7 (d, $J_{C–P}$ = 3.7 Hz), 142.4 (d, $J_{C–P}$ = 2.3 Hz), 133.8, 132.7, 130.6, 130.0, 129.0, 128.8, 128.4 (x2), 128.3 (x2), 127.8, 127.5, 127.4, 127.3, 127.1 (x2), 126.5, 126.4, 126.3, 126.2, 125.9, 125.6, 121.7 (d, $J_{C–P}$ = 10.3 Hz), 121.2 (d, $J_{C–P}$ = 8.9 Hz), 56.8 (d, $J_{C–P}$ = 25.4 Hz), 54.5 (d, $J_{C–P}$ = 17.7 Hz), 50.7, 39.7 (x2) ppm;

^{31}P NMR (400 MHz, $CDCl_3$): δ 97.02 ppm;

HRMS (APCI): calculated for $[C_{31}H_{27}N_2OP]^+$: 474.1861, found: 474.1865.

(6*R*,10*R*)-8-Methoxy-6,10-di(naphthalen-2-yl)-5,6,10,11-tetrahydro-8*H*-[1,3,2]diazaphospholo[4,3-*a*:5,1-*a'*]diisoquinoline (P10)



Obtained after being scratched in hexane (0.5 mL) and filtered in 59% yield over 2 steps (71 mg, + 1% SPO) from 107 mg of corresponding biisoquinoline following **Pathway A** then **GP5** and **GP6**.

Appearance: Yellow solid

M.p.: 166–170°C (decomp.);

$[\alpha]_D^{20}$: +90.74 (c = 0.36, CH_2Cl_2);

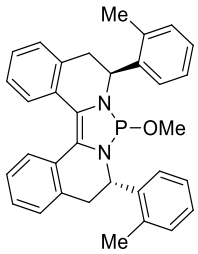
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.9 Hz, 1 H), 7.98 (dd, *J* = 7.9, 1.9 Hz, 1 H), 7.74–7.68 (m, 5 H), 7.66 (d, *J* = 8.6 Hz, 1 H), 7.60 (dd, *J* = 12.5, 1.7 Hz, 2 H), 7.41–7.35 (m, 5 H), 7.20 (dd, *J* = 8.5, 1.9 Hz, 1 H), 7.15 (td, *J* = 7.5, 1.9 Hz, 1 H), 7.11–7.00 (m, 5 H), 5.16 (dd, *J* = 4.9, 4.9 Hz, 1 H), 5.08 (ddd, *J* = 9.9, 5.2, 4.9 Hz, 1 H), 3.47 (dd, *J* = 14.6, 4.5 Hz, 1 H), 3.38–3.26 (m, 3 H), 3.00 (d, *J* = 7.8 Hz, 3 H) ppm;

^{13}C NMR (200 MHz, $CDCl_3$): δ 140.1, 139.8, 133.9, 133.3 (x2), 132.9 (x2), 132.8, 130.6, 130.0, 129.0, 128.8, 128.2, 128.1 (x2), 127.9, 127.7 (x2), 126.9, 126.6, 126.5, 126.4, 126.3 (x2), 126.0 (x3), 125.9, 125.8 (x2), 125.7, 125.2, 121.8 (d, $J_{C–P}$ = 10.6 Hz), 121.4 (d, $J_{C–P}$ = 8.8 Hz), 57.1 (d, $J_{C–P}$ = 25.2 Hz), 54.9 (d, $J_{C–P}$ = 17.6 Hz), 50.8, 39.9 (d, $J_{C–P}$ = 5.0 Hz), 39.7 (d, $J_{C–P}$ = 3.7 Hz) ppm;

^{31}P NMR (162 MHz, $CDCl_3$): δ 97.1 ppm;

HRMS (APCI): calculated for $[C_{39}H_{31}N_2OP]^+$: 574.2174, found: 574.2176.

(6*S*,10*S*)-8-Methoxy-6,10-di-*o*-tolyl-5,6,10,11-tetrahydro-8*H*-[1,3,2]diazaphospholo[4,3-*a*:5,1-*a'*]diisoquinoline (*ent*-P11)



Obtained without further purification in 64% yield over 2 steps (109 mg, +2% SPO) from 114 mg of corresponding biisoquinoline following **Pathway B-3** then **GP5** and **GP6**.

Appearance: Yellow solid

M.p.: 153–157 °C (decomp.);

$[\alpha]_D^{20}$: −89.9 (c = 0.36, CH_2Cl_2);

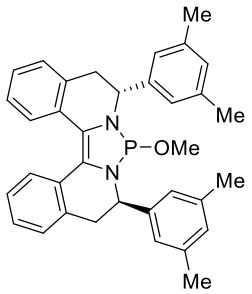
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.96 (m, 2 H), 7.22 (d, *J* = 7.3 Hz, 1 H), 7.17–7.01 (m, 13 H), 5.01 (ddd, *J* = 8.3, 6.1, 3.6 Hz, 1 H), 4.89 (ddd, *J* = 6.6, 6.6, 6.6 Hz, 1 H), 3.37 (dd, *J* = 14.3, 8.4 Hz, 1 H), 3.16 (d, *J* = 6.7 Hz, 2 H), 3.09 (dd, *J* = 14.3, 3.6 Hz, 1 H), 2.96 (d, *J* = 7.7 Hz, 3 H), 2.39 (s, 3 H), 2.35 (s, 3 H) ppm;

^{13}C NMR (200 MHz, $CDCl_3$): δ 140.0, 139.0 (d, $J_{C–P}$ = 3.4 Hz), 136.6, 135.3, 134.8, 133.8, 130.5, 130.4, 130.1, 130.0, 128.7, 128.5, 127.9, 127.8, 127.4 (x2), 126.3 (x4), 126.2, 126.1, 125.9, 125.7, 122.5 (d, $J_{C–P}$ = 11.6 Hz), 122.1 (d, $J_{C–P}$ = 8.9 Hz), 52.4, 52.3, 50.8, 39.3 (d, $J_{C–P}$ = 4.1 Hz), 38.5, 19.7 (d, $J_{C–P}$ = 5.6 Hz), 19.6 ppm;

^{31}P NMR (162 MHz, $CDCl_3$): δ 95.5 ppm;

HRMS (ESI): calculated for $[C_{33}H_{31}N_2OP]^+$: 502.2174, found: 502.2170.

(6*R*,10*R*)-6,10-Bis(3,5-dimethylphenyl)-8-methoxy-5,6,10,11-tetrahydro-8*H*-[1,3,2]diazaphospholo[4,3-*a*:5,1-*a'*]diisoquinoline (P12)



Obtained without further purification in 79% yield over 2 steps (81 mg, + 1% SPO) from 93 mg of corresponding biisoquinoline following **Pathway A** then **GP5** and **GP6**.

Appearance: Yellow solid

M.p.: 125–126 °C (decomp.);

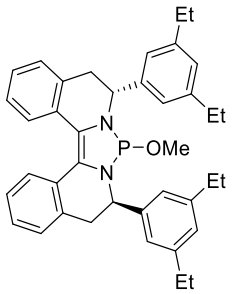
$[\alpha]_D^{20}$: +19.89 (c = 0.31, CH_2Cl_2);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (tq, *J* = 6.4, 3.4, 3.0 Hz, 2 H), 7.14–7.00 (m, 6 H), 6.85 (s, 2 H), 6.83 (d, *J* = 4.2 Hz, 2 H), 6.78 (s, 2 H), 4.75 (dt, *J* = 8.1, 4.3 Hz, 1 H), 4.64 (td, *J* = 7.4, 4.1 Hz, 1 H), 3.26 (dd, *J* = 14.5, 7.5 Hz, 1 H), 3.25–3.20 (m, 1 H), 3.16 (dd, *J* = 14.5, 7.5 Hz, 1 H), 3.11 (dd, *J* = 15.2, 3.3 Hz, 1 H), 3.02 (d, *J* = 7.6 Hz, 3 H), 2.22 (s, 6 H), 2.21 (s, 6 H) ppm;

^{31}P NMR (400 MHz, $CDCl_3$): δ 95.5 ppm;

HRMS (ESI): calculated for $[C_{35}H_{35}N_2OP]^+$: 530.2487, found: 530.2493.

(6*R*,10*R*)-6,10-Bis(3,5-diethylphenyl)-8-methoxy-5,6,10,11-tetrahydro-8*H*-[1,3,2]diazaphospholo[4,3-*a*:5,1-*a'*]diisoquinoline (P13)



Obtained without further purification in 78% yield over 2 steps (52 mg, no SPO) from 60 mg of corresponding biisoquinoline following **Pathway A** then **GP5** and **GP6**.

Appearance: Yellow solid

M.p.: 83–84 °C (decomp.);

$[\alpha]_D^{20}$: +18.10 (c = 0.70, CH_2Cl_2);

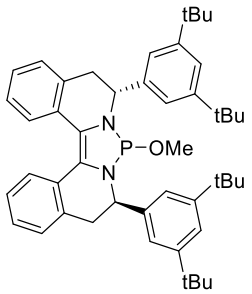
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.91 (m, 2 H), 7.14–7.00 (m, 6 H), 6.84 (d, *J* = 3.2 Hz, 4 H), 6.77 (d, *J* = 1.6 Hz, 2 H), 4.85 (dt, *J* = 6.4, 4.4 Hz, 1 H), 4.77 (td, *J* = 7.2, 4.4 Hz, 1 H), 3.32 (dd, *J* = 14.3, 3.7 Hz, 1 H), 3.25 (dd, *J* = 14.7, 6.4 Hz, 1 H), 3.21–3.15 (m, 1 H), 3.13 (dd, *J* = 14.7, 6.4 Hz, 1 H), 2.97 (d, *J* = 7.5 Hz, 3 H), 2.52 (q, *J* = 7.5 Hz, 4 H), 2.50 (q, *J* = 7.3 Hz, 4 H), 1.13 (t, *J* = 7.5 Hz, 6 H), 1.10 (t, *J* = 7.3 Hz, 6 H) ppm;

^{13}C NMR (200 MHz, $CDCl_3$): δ 144.1 (x2), 143.9 (x2), 142.3, 142.0, 134.4, 133.3, 128.9, 128.6, 126.9, 126.7, 126.2 (x2), 126.1, 125.9, 125.7, 125.0, 124.5, 124.4 (x4), 124.0, 121.9 (d, $J_{C–P}$ = 10.6 Hz), 121.7 (d, $J_{C–P}$ = 9.1 Hz), 57.0 (d, $J_{C–P}$ = 24.1 Hz), 55.3 (d, $J_{C–P}$ = 18.0 Hz), 50.6, 40.3, 39.9 (d, $J_{C–P}$ = 3.7 Hz), 28.9 (x4), 15.6 (x2), 15.4 (x2) ppm;

^{31}P NMR (162 MHz, $CDCl_3$): δ 95.4 ppm;

HRMS (ESI): calculated for $[C_{39}H_{43}N_2OP]^+$: 586.3113, found: 586.3126.

(6*R*,10*R*)-6,10-Bis(3,5-di-tert-butylphenyl)-8-methoxy-5,6,10,11-tetrahydro-8*H*-[1,3,2]diazaphospholo[4,3-*a*:5,1-*a'*]diisoquinoline (P14)



Obtained without further purification in 78% yield over 2 steps (71 mg, no SPO) from 95 mg of corresponding biisoquinoline following **Pathway A** then **GP5** and **GP6**.

Appearance: Yellow solid

M.p.: 130–132 °C (decomp.);

$[\alpha]_D^{20}$: +25.3 (c = 0.54, CH_2Cl_2);

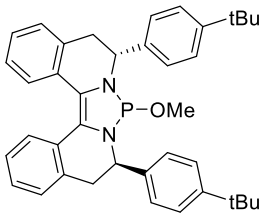
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.95 (m, 1 H), 7.95–7.90 (m, 1 H), 7.17–7.16 (m, 2 H), 7.15–7.07 (m, 3 H), 7.06–6.99 (m, 3 H), 6.96 (d, J = 1.8 Hz, 2 H), 6.86 (d, J = 1.8 Hz, 2 H), 5.00–4.94 (m, 2 H), 3.46 (dd, J = 14.7, 4.8 Hz, 1 H), 3.27 (dd, J = 14.2, 4.8 Hz, 1 H), 3.18 (dd, J = 5.0, 2.0 Hz, 1 H), 3.11 (dd, J = 14.7, 5.0 Hz, 1 H), 2.87 (d, J = 7.3 Hz, 3 H), 1.19 (s, 18 H), 1.16 (s, 18 H) ppm;

^{13}C NMR (200 MHz, $CDCl_3$): δ 150.3 (x2), 150.2 (x2), 141.8, 141.7, 134.3, 132.8, 131.2, 130.3, 129.2, 128.9, 127.2, 126.4, 126.2 (x3), 126.1, 125.9, 125.5, 122.1, 121.7, 121.6 (x2), 121.0, 120.9, 57.4, 57.2, 50.4, 39.8, 39.6 (d, $J_{C–P}$ = 5.8 Hz), 34.9 (x4), 31.6 (x6), 31.5 (x6) ppm;

^{31}P NMR (162 MHz, $CDCl_3$): δ 95.6 ppm;

HRMS (ESI): calculated for $[C_{47}H_{59}N_2OP]^+$: 698.4365, found: 698.4377.

(6*R*,10*R*)-6,10-Bis(4-(tert-butyl)phenyl)-8-methoxy-5,6,10,11-tetrahydro-8*H*-[1,3,2]diazaphospholo[4,3-*a*:5,1-*a'*]diisoquinoline (P15)



Obtained without further purification in 26% yield over 2 steps (15 mg, + 1% SPO) from 52 mg of corresponding biisoquinoline following **Pathway A** then **GP5** and **GP6**.

Appearance: Yellow solid

M.p.: 189−191 °C;

$[\alpha]_D^{20}$: +14.67 (c = 0.50, CH_2Cl_2);

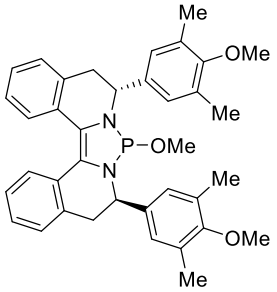
^{1}H NMR (400 MHz, C_6D_6): δ 8.20 (d, *J* = 7.3 Hz, 2 H), 7.13–6.98 (m, 9 H), 6.98–6.80 (m, 5 H), 5.04–4.87 (m, 2 H), 3.29 (d, *J* = 14.5 Hz, 1 H), 3.11 (d, *J* = 14.5 Hz, 1 H), 3.01 (d, *J* = 7.5, 3 H), 3.06–2.91 (m, 2 H), 1.10 (s, 9 H), 1.06 (s, 9 H) ppm;

^{13}C NMR (200 MHz, $CDCl_3$): δ 150.2 149.9, 141.1, 139.7, 139.3, 134.1, 133.0, 131.4, 130.6, 130.0, 129.0, 128.8, 127.6, 127.1, 126.9, 126.4, 126.3, 126.2, 126.1, 125.9, 125.6 (x2), 125.3 (x2), 125.2 (x2), 121.7 (d, $J_{C–P}$ = 10.1 Hz), 121.2 (d, $J_{C–P}$ = 9.2 Hz), 56.6 (d, $J_{C–P}$ = 24.4 Hz), 54.3 (d, $J_{C–P}$ = 16.9 Hz), 50.7, 39.7 (d, $J_{C–P}$ = 9.3 Hz), 34.6 (d, $J_{C–P}$ = 4.4 Hz), 31.5 (x6) ppm;

^{31}P NMR (162 MHz, C_6D_6): δ 96.2 ppm;

HRMS (ESI): calculated for $[C_{39}H_{43}N_2OP]^+$: 586.3108, found: 586.3116.

(6*R*,10*R*)-8-Methoxy-6,10-bis(4-methoxy-3,5-dimethylphenyl)-5,6,10,11-tetrahydro-8*H*-[1,3,2]diazaphospholo[4,3-*a*:5,1-*a'*]diisoquinoline (P16)



Obtained without further purification in 73% yield over 2 steps (92 mg, + 5% SPO) from 113 mg of corresponding biisoquinoline following **Pathway A** then **GP5** and **GP6**.

Appearance: Yellow solid

M.p.: 128–132 °C;

$[\alpha]_D^{20}$: +34.41 (c = 0.62, CH_2Cl_2);

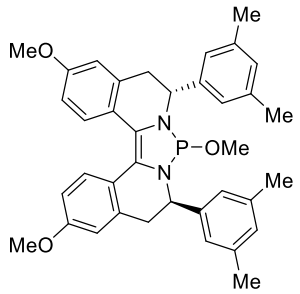
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14–8.09 (m, 2 H), 7.22 (tdd, *J* = 12.3, 5.3, 3.5 Hz, 6 H), 7.04 (d, *J* = 2.0 Hz, 2 H), 6.97 (d, *J* = 1.9 Hz, 2 H), 4.87 (qd, *J* = 5.5, 3.5, 2.7 Hz, 1 H), 4.76 (dd, *J* = 7.6, 4.3 Hz, 1 H), 3.84 (s, 6 H), 3.44–3.34 (m, 2 H), 3.33–3.23 (m, 2 H), 3.17 (dd, *J* = 7.4, 2.0 Hz, 3 H), 2.36 (d, *J* = 2.0 Hz, 6 H), 2.35 (d, *J* = 2.0 Hz, 6 H) ppm;

^{13}C NMR (200 MHz, $CDCl_3$): δ 156.4, 156.2, 137.1 (d, $J_{C–P}$ = 1.7 Hz), 136.9 (d, $J_{C–P}$ = 5.7 Hz), 134.4, 133.6, 130.6 (x2), 130.4 (x2), 130.1, 129.9 (x2), 128.8 (x2), 128.6, 128.4, 127.9 (x2), 126.1 (x3), 126.0, 125.9, 125.7, 122.0 (d, $J_{C–P}$ = 11.4 Hz), 121.9 (d, $J_{C–P}$ = 8.3 Hz), 59.7, 59.6, 56.6 (d, $J_{C–P}$ = 22.6 Hz), 55.2 (d, $J_{C–P}$ = 16.2 Hz), 50.7, 40.4 (d, $J_{C–P}$ = 4.3 Hz), 40.2 (d, $J_{C–P}$ = 2.9 Hz), 16.3 (x2), 16.2 (x2) ppm;

^{31}P NMR (162 MHz, $CDCl_3$): δ 95.3 ppm;

HRMS (ESI): calculated for $[C_{37}H_{39}N_2O_3P]^+$: 590.2693, found: 590.2704.

(6*R*,10*R*)-6,10-Bis(3,5-dimethylphenyl)-3,8,13-trimethoxy-5,6,10,11-tetrahydro-8*H*-[1,3,2]diazaphospholo[4,3-*a*:5,1-*a'*]diisoquinoline (P17)



Obtained without further purification in 69% yield over 2 steps (407 mg, no SPO) from 500 mg of corresponding biisoquinoline following **Pathway A** then **GP5** and **GP6**.

Appearance: Yellow solid

M.p.: 148–149°C;

$[\alpha]_D^{20}$: +105.3 (c = 1.1, CH_2Cl_2);

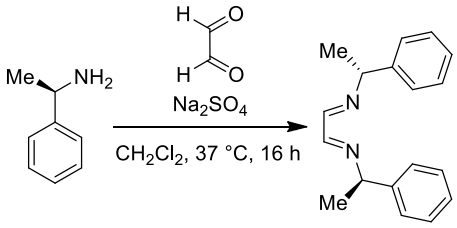
^{1}H NMR (800 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 8.7, 6.4 Hz, 2 H), 6.87 (s, 2 H), 6.84 (d, *J* = 8.9 Hz, 2 H), 6.81 (s, 2 H), 6.70 (dd, *J* = 8.7, 2.8 Hz, 1 H), 6.65–6.63 (m, 2 H), 6.62 (d, *J* = 2.8 Hz, 1 H), 4.74 (dt, *J* = 7.6, 3.9 Hz, 1 H), 4.64 (td, *J* = 7.6, 3.9 Hz, 1 H), 3.80 (d, *J* = 10.4 Hz, 6 H), 3.25 (dd, *J* = 14.5, 7.6 Hz, 1 H), 3.21 (dt, *J* = 14.5, 3.9 Hz, 1 H), 3.14 (dd, *J* = 14.5, 7.6 Hz, 1 H), 3.09 (dd, *J* = 14.5, 3.9 Hz, 1 H), 3.03 (d, *J* = 7.4 Hz, 3 H), 2.24 (s, 6 H), 2.23 (s, 6 H).ppm;

^{13}C NMR (200 MHz, $CDCl_3$): δ 157.9, 157.8, 142.2 (d, $J_{C–P}$ = 1.7 Hz), 141.9 (d, $J_{C–P}$ = 5.7 Hz), 137.8 (x2), 137.6 (x2), 135.9, 135.1, 129.4, 129.3, 127.0, 126.9, 126.3 (x2), 125.5 (x2), 123.3, 123.1, 120.5 (d, $J_{C–P}$ = 10.7 Hz), 120.3 (d, $J_{C–P}$ = 8.7 Hz), 113.5, 113.3, 112.3, 112.2, 57.1 (d, $J_{C–P}$ = 23.2 Hz), 55.5 (d, $J_{C–P}$ = 15.8 Hz), 55.4, 55.3, 50.8, 40.7 (d, $J_{C–P}$ = 4.3 Hz), 40.6 (d, $J_{C–P}$ = 2.9 Hz), 21.5 (x4) ppm;

^{31}P NMR (162 MHz, $CDCl_3$): δ 95.2 ppm;

HRMS (ESI): calculated for $[C_{37}H_{39}N_2O_3P]^+$: 590.2698, found: 590.2699.

Synthesis and Characterization Data of Chiral Diazaphospholene P2

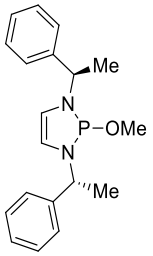


S11

Oxalaldehyde (287 µL, 2.5 mmol) was added dropwise to a mixture of (*R*)-1-phenylethanamine (636 µL, 5.00 mmol) and sodium sulfate (2.84 g, 20.0 mmol) in CH_2Cl_2 (5 mL) at 23 °C, followed by formic acid (9.43 µL, 250 µmol). The reaction mixture was then heated to reflux and stirred overnight before being filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (pentane:EtOAc 9:1) to give bisimine **S11** as a yellow oil (623 mg, 94 %). All spectroscopic data matched that previously reported in the literature.[12]

Chiral catalyst **P2** was then synthesized from the bisimine following general procedures **GP5** and **GP6**.

2-Methoxy-1,3-bis((*R*)-1-phenylethyl)-2,3-dihydro-1*H*-1,3,2-diazaphosphole (P2)



Obtained in 43 % yield (118 mg) over 2 steps.

Appearance: Brown wax

$[\alpha]_D^{20}$: −14.9 (c = 1.1, CH_2Cl_2);

[12] Mastranzo, V. M.; Quintero, L.; de Parrodi, C. A.; Juaristi, E.; Walsh, P. J. *Tetrahedron* **2004**, *60*, 1781-1789

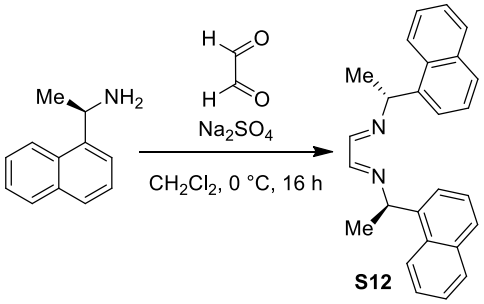
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.23 (m, 10 H), 5.86 (t, *J* = 2.6 Hz, 1 H), 5.78 (t, *J* = 2.5 Hz, 1 H), 4.91–4.71 (m, 2 H), 3.00 (d, *J* = 7.0 Hz, 3 H), 1.75 (dd, *J* = 8.5, 7.0 Hz, 6 H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9 (d, $J_{C–P}$ = 2.9 Hz), 144.5 (d, $J_{C–P}$ = 4.1 Hz), 128.5, 128.4, 127.1, 126.8 (d, $J_{C–P}$ = 1.4 Hz), 126.6 (d, $J_{C–P}$ = 1.9 Hz), 115.2 (d, $J_{C–P}$ = 9.2 Hz), 113.8 (d, $J_{C–P}$ = 9.2 Hz), 57.1 (d, $J_{C–P}$ = 21.8 Hz), 55.9 (d, $J_{C–P}$ = 25.6 Hz), 50.2 (d, $J_{C–P}$ = 2.6 Hz), 23.3 (d, $J_{C–P}$ = 14.3 Hz), 22.1 (d, $J_{C–P}$ = 8.9 Hz) ppm;

^{31}P NMR (162 MHz, $CDCl_3$): δ 99.6 ppm;

HRMS (APCI): calculated for $[C_{19}H_{24}N_2OP]^+$: 327.1621, found: 327.1621.

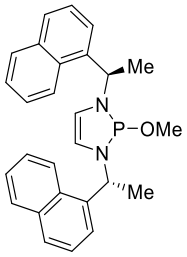
Synthesis and Characterization Data of Chiral Diazaphospholene P3



Oxalaldehyde (0.287 mL, 2.5 mmol) was added dropwise to a mixture of (*R*)-1-(naphthalen-1-yl)ethanamine (856 mg, 5.00 mmol) and sodium sulfate (2,84 g, 20.0 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The reaction mixture was then stirred at room temperature overnight before being filtered and evaporated with hexane. The crude residue was then scratched in hexane forming a precipitate which was filtered off and washed with pentane. Bisimine **S12** was obtained as a white powder in 76% yield (696 mg).

Chiral catalyst **P3** was then synthesized from the bisimine following general procedures **GP5** and **GP6**.

2-Methoxy-1,3-bis((*R*)-1-(naphthalen-1-yl)ethyl)-2,3-dihydro-1*H*-1,3,2-diazaphosphole (P3)



Obtained in 24% yield (48 mg) over 2 steps after sonication and precipitation in hexane.

Appearance: Beige solid

M.p.: 99–102 °C;

$[\alpha]_D^{20}$: −27.5 (c = 0.8, CH_2Cl_2);

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.25–8.18 (m, 1 H), 8.09 (dt, *J* = 6.4, 3.6 Hz, 1 H), 7.90–7.86 (m, 1 H), 7.86–7.82 (m, 1 H), 7.79 (d, *J* = 8.1 Hz, 1 H), 7.70 (d, *J* = 8.2 Hz, 1 H), 7.61 (d, *J* = 7.1 Hz, 1 H), 7.55–7.50 (m, 2 H), 7.48–7.42 (m, 3 H), 7.24 (dd, *J* = 8.2, 7.2 Hz, 1 H), 7.14 (d, *J* = 7.1 Hz, 1 H), 5.83 (t, *J* = 2.6 Hz, 1 H), 5.64 (p, *J* = 6.9 Hz, 1 H), 5.57 (t, *J* = 2.5 Hz, 1 H), 5.54 (p, *J* = 6.8 Hz, 1 H), 3.07 (d, *J* = 7.0 Hz, 3 H), 1.89 (d, *J* = 6.8 Hz, 3 H), 1.84 (d, *J* = 6.9 Hz, 3 H) ppm;

^{13}C NMR (150 MHz, $CDCl_3$): δ 139.5 (d, $J_{C–P}$ = 4.2 Hz), 139.2 (d, $J_{C–P}$ = 8 Hz), 134.0 (x2), 131.4, 131.0, 129.0 (x2), 128.4, 127.8, 126.3, 126.2, 125.7, 125.5 (x2), 125.3, 123.8 (x2), 123.7, 123.6 (x2), 123.1, 115.3 (d, $J_{C–P}$ = 8.9 Hz), 113.7 (d, $J_{C–P}$ = 9.2 Hz), 53.5 (d, $J_{C–P}$ = 21.2 Hz), 51.5 (d, $J_{C–P}$ = 4.5 Hz), 50.4 (d, $J_{C–P}$ = 2.5 Hz), 22.9 (d, $J_{C–P}$ = 14.5 Hz), 22.2 (d, $J_{C–P}$ = 4.5 Hz) ppm;

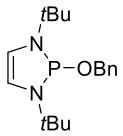
^{31}P NMR (162 MHz, $CDCl_3$): δ 100.8 ppm;

HRMS (APCI): calculated for $[C_{27}H_{27}N_2OP]^+$: 426.1861, found: 426.1859.

Synthesis and Characterization Data of Achiral Diazaphospholene P1

In a flame-dried Schlenk flask in the glovebox, a solution of phenylmethanol (0.167 mL, 1.612 mmol) and triethylamine (0.268 mL, 1.934 mmol) in THF (1.075 mL) was added dropwise at room temperature to a suspension of 2-bromo-1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazaphosphole (0.300 g, 1.075 mmol) in THF (4.30 mL). The mixture was stirred at room temperature for 1 h before being evaporated to dryness. The resulting solid was then suspended in toluene and filtered through celite before being dried under vacuum again. Finally, recrystallization of the so obtained solid from MeCN afforded white crystals of pure compound **P1**.

2-(Benzyloxy)-1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazaphosphole (P1)



Appearance: White solid

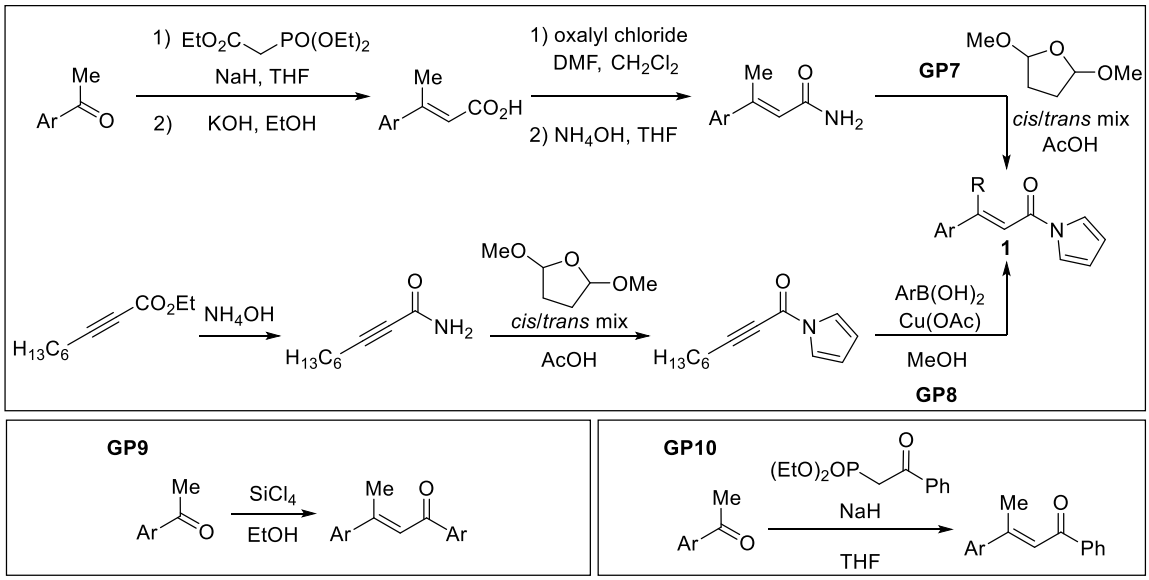
^{1}H NMR (800 MHz, $CDCl_3$): δ 7.28 (dd, *J* = 7.5, 7.5 Hz, 2 H), 7.26 (d, *J* = 7.1 Hz, 2 H), 7.21 (dd, *J* = 7.1, 7.1 Hz, 1 H), 6.08 (d, *J* = 1.7 Hz, 2 H), 4.22 (d, *J* = 4.7 Hz, 2 H), 1.40 (s, 18 H) ppm; matches previous literature report.[13]

^{13}C NMR (201 MHz, $CDCl_3$): δ 140.1, 128.2 (x2), 127.1 (x2), 126.9, 112.3 (x2), 63.6 (d, $J_{c\text{-}p}$ = 3.9 Hz), 53.01 (d, $J_{c\text{-}p}$ = 16.3 Hz) (x2), 31.1 (d, $J_{c\text{-}p}$ = 10.1 Hz) (x6).ppm;

^{31}P NMR (162 MHz, $CDCl_3$): δ 94.2 ppm.

[13] Chong, C. C.; Hirao, H.; Kinjo, R. *Angew. Chem. Int. Ed.* **2015**, *54*, 190-194

Substrates 5a-w and Intermediates



General procedure 7 (GP7)

2,5-dimethoxytetrahydrofuran (mix of *cis*- and *trans*- isomers, 194 µL, 1.5 mmol) was added to a solution of primary amide (1.0 mmol) in AcOH (4.0 mL) and the solution was heated to 100 ºC and stirred for 3 hours. After cooling to room temperature, the reaction mixture was diluted with EtOAc (10 mL) and added dropwise to a saturated aqueous solution of $NaHCO_3$ (20 mL) in an ice-bath. After bubbling had ceased, the mixture was stirred vigourously for 1 hour while allowing it warm to room temperature. The two phases were separated and the aqueous layer further extracted with EtOAc (3 x 10 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography to give the desired *N*-acyl-pyrrole product.

General procedure 8 (GP8)

Inside the glovebox, CuOAc (6.12 mg, 50 µmol) was added to a solution of 1-(1*H*-pyrrol-1-yl)non-2-yn-1-one (204 mg, 1.0 mmol) and arylboronic acid (1.5 mmol) in degassed MeOH (2 mL). The mixture was stirred at 23 ºC for 16 hours before the volatiles were

removed *in vacuo*. The residue was diluted with EtOAc (5 mL), washed with brine (5 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash chromatography to give the desired *N*-acyl-pyrrole product.

General procedure 9 (GP9)

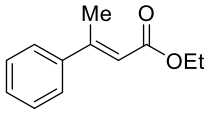
Tetrachlorosilane (229 μL, 2.0 mmol) was added dropwise to a solution of aryl ketone (2.0 mmol) in EtOH (2.0 mL) at 0 ^{o}C. The reaction was allowed to warm to 23 ^{o}C and stirred for 3 hours. The reaction was neutralised by the dropwise addition of a saturated aqueous solution of $NaHCO_3$ (10 mL). The product was extracted with EtOAc (3 x 10 mL) and the combined organic extracts were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography to give the desired enone product.

General procedure 10 (GP10)

A solution of diethyl (2-oxo-2-phenylethyl)phosphonate (438 μL, 2.0 mmol) in THF (2.5 mL) was added dropwise to a suspension of NaH (60 % dispersion, 88 mg, 2.2 mmol) in THF (5 mL) at 23 ^{o}C and the resultant mixture was stirred for 30 minutes. A solution of aryl ketone (2.0 mmol) in THF (2.5 mL) was added dropwise at 23 ^{o}C. The reaction mixture was heated to reflux and stirred for 16 hours. After cooling to room temperature, the reaction was quenched by the dropwise addition of a saturated aqueous solution of NH_4Cl (20 mL). The product was extracted with EtOAc (3 x 15 mL) and the combined organic extracts washed with brine (15 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography to give the desired enone product.

Synthesis and characterization of substrates synthesis intermediates

Ethyl (*E*)-3-phenylbut-2-enoate (S13)

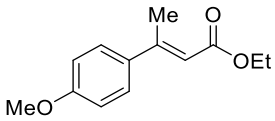


Triethyl phosphonoacetate (7.14 mL, 36.0 mmol) was added dropwise to a suspension of NaH (60 % dispersion, 1.80 g, 45.0 mmol) in THF (43 mL) at 0 ºC. After 1 hour of stirring, acetophenone (3.50 mL, 30 mmol) was added dropwise at 0 ºC. The reaction was allowed to slowly warm to room temperature and stirred for 16 hours. The reaction was quenched by the dropwise addition of a saturated aqueous solution of $NaHCO_3$ (50 mL) and the product extracted with EtOAc, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography (EtOAc:pentane 2:98) to give the desired compound **S13** as a colourless oil (4.33 g, 76 %). All spectroscopic data matched that previously reported in the literature.[14]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.43 (m, 2H), 7.43–7.31 (m, 3H), 6.14 (q, *J* = 1.3 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.58 (d, *J* = 1.3 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 155.6, 142.4, 129.1, 128.6, 126.4, 117.3, 60.0, 18.1, 14.5 ppm.

Ethyl (*E*)-3-(4-methoxyphenyl)but-2-enoate (S14)



Triethyl phosphonoacetate (7.14 mL, 36.0 mmol) was added dropwise to a suspension of NaH (60 % dispersion, 1.80 g, 45.0 mmol) in THF (43 mL) at 0 ºC. After 1 hour of stirring, 1-(4-methoxyphenyl)ethanone (4.12 mL, 30 mmol) was added dropwise at 0 ºC. The

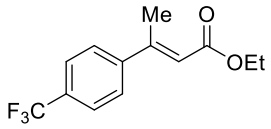
[14] Nguyen, T. N. T.; Thiel, N. O.; Pape, F.; Teichert, J. F. *Org. Lett.* **2016**, *18*, 2455-2458

reaction was allowed to slowly warm to room temperature and stirred for 16 hours. The reaction was quenched by the dropwise addition of a saturated aqueous solution of $NaHCO_3$ (50 mL) and the product extracted with EtOAc, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography (EtOAc:pentane 2:98) to give the desired compound **S14** as a colourless oil (5.49 g, 83 %). All spectroscopic data matched that previously reported in the literature.[14]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.41 (m, 2H), 6.94–6.85 (m, 2H), 6.11 (q, *J* = 1.3 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 2.56 (d, *J* = 1.3 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 160.6, 155.0, 134.5, 127.8, 115.5, 114.0, 59.8, 55.5, 17.8, 14.5 ppm.

Ethyl (*E*)-3-(4-(trifluoromethyl)phenyl)but-2-enoate (S15)



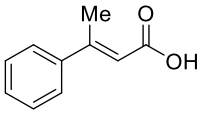
Triethyl phosphonoacetate (7.14 mL, 36.0 mmol) was added dropwise to a suspension of NaH (60 % dispersion, 1.80 g, 45.0 mmol) in THF (30 mL) at 0 °C. After 1 hour of stirring, a solution of 1-(4-(trifluoromethyl)phenyl)ethanone (5.64 g, 30 mmol) in THF (13 mL) was added dropwise at 0 °C. The reaction was allowed to slowly warm to room temperature and stirred for 16 hours. The reaction was quenched by the dropwise addition of a saturated aqueous solution of $NaHCO_3$ (50 mL) and the product extracted with EtOAc, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography (EtOAc:pentane 2:98) to give the desired compound **S15** as a pale yellow oil (4.80 g, 62 %). All spectroscopic data matched that previously reported in the literature.[15]

[15] Youn, S. W.; Kim, B. S.; Jagdale, A. R. *J. Am. Chem. Soc.* **2012**, *134*, 11308-11311

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 6.15 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.58 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 153.8, 145.8, 130.8 (q, *J* = 32.2 Hz), 126.7, 125.5 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 270.6 Hz), 118.9, 60.1, 18.0, 14.3 ppm.

(*E*)-3-Phenylbut-2-enoic acid (**S16**)



Potassium hydroxide (6.17 g, 110 mmol) was added to a solution of ethyl (*E*)-3-phenylbut-2-enoate (4.19 g, 22 mmol) in EtOH (44.0 mL) at 23 ^{o}C. The reaction was stirred for 16 hours after which the volatiles were removed *in vacuo* and the residue slowly acidified with 2 M HCl_{aq}. The product was extracted with EtOAc, dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was recrystallised from boiling hexane to give **S16** as white needles (3.41 g, 96 %). All spectroscopic data matched that previously reported in the literature.[16]

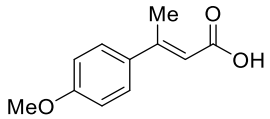
Melting Point:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.47 (m, 2H), 7.42–7.37 (m, 3H), 6.18 (q, *J* = 1.2 Hz, 1H), 2.61 (d, *J* = 1.2 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 158.7, 142.2, 129.5, 128.7, 126.6, 116.6, 18.5 ppm.

[16] Mohite, A. R.; Bhat, R. G. *Org. Lett.* **2013**, *15*, 4564-4567

(*E*)-3-(4-Methoxyphenyl)but-2-enoic acid (**S17**)



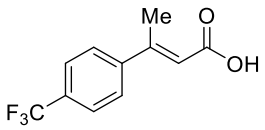
Potassium hydroxide (5.61 g, 100 mmol) was added to a solution of ethyl (*E*)-3-(4-methoxyphenyl)but-2-enoate (4.41 g, 20 mmol) in EtOH (40.0 mL) at 23 ºC. The reaction was stirred for 16 hours after which the volatiles were removed *in vacuo* and the residue slowly acidified with 2 M HCl_{aq}. The product was extracted with EtOAc, dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was recrystallised from boiling ethanol to give **S17** as white needles (3.36 g, 87 %). All spectroscopic data matched that previously reported in the literature.[17]

Melting Point: 154.7–156.1 ºC

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.44 (m, 2H), 6.94–6.87 (m, 2H), 6.15 (s, 1H), 3.84 (s, 3H), 2.59 (s, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 160.7, 157.9, 134.0, 127.8, 114.4, 113.9, 55.3, 17.9 ppm.

(*E*)-3-(4-(Trifluoromethyl)phenyl)but-2-enoic acid (**S18**)



Potassium hydroxide (4.21 g, 75 mmol) was added to a solution of ethyl (*E*)-3-(4-(trifluoromethyl)phenyl)but-2-enoate (3.87 g, 15 mmol) in EtOH (30.0 mL) at 23 ºC. The reaction was stirred for 16 hours after which the volatiles were removed *in vacuo* and the residue slowly acidified with 2 M HCl_{aq}. The product was extracted with EtOAc, dried

[17] Fukuyama, T.; Arai, M.; Matsubara, H.; Ryu, I. *J. Org. Chem.* **2004**, *69*, 8105-8107

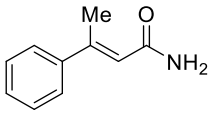
($MgSO_4$) and concentrated *in vacuo* to give **S18** as a white solid (3.39 g, 98 %). All spectroscopic data matched that previously reported in the literature.[18]

Melting Point: 122.4–123.9 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 6.19 (d, *J* = 1.4 Hz, 1H), 2.61 (d, *J* = 1.3 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 157.1, 145.7, 131.3 (q, *J* = 32.6 Hz), 126.9, 125.7 (q, *J* = 3.9 Hz), 124.0 (q, *J* = 272.2 Hz), 118.2, 18.5 ppm.

(*E*)-3-Phenylbut-2-enamide (1v)



Oxalyl chloride (3.43 mL, 40 mmol) was added dropwise to a solution of (*E*)-3-phenylbut-2-enoic acid (3.24 g, 20 mmol) in CH_2Cl_2 (50.0 mL) at 23 °C, followed by a single drop of DMF. The reaction was stirred at 23 °C for 30 minutes, at which point the reaction was concentrated *in vacuo*. The residue was dissolved in THF (50.0 mL) and ammonium hydroxide (25 %, 22.6 mL) was added dropwise. The reaction mixture was stirred at 23 °C for 30 minutes before being concentrated *in vacuo*. The residue was diluted with EtOAc, washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a white solid. The crude product was recrystallised from benzene to give white needles (3.07 g, 95 %). All spectroscopic data matched that previously reported in the literature.[19]

Melting Point: 117.2–118.5 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.41 (m, 2H), 7.37–7.35 (m, 3H), 6.08 (q, *J* = 1.1 Hz, 1H), 5.81 (br, 1H), 5.62 (br, 1H), 2.56 (d, *J* = 1.2 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 152.5, 142.5, 128.7, 128.5, 126.2, 118.7, 17.7 ppm.

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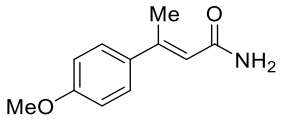
[18] Takimoto, M.; Shimizu, K.; Mori, M. *Org. Lett.* **2001**, *3*, 3345-3347
[19] Wen, J.; Jiang, J.; Zhang, X. *Org. Lett.* **2016**, *18*, 4451-4453

(*E*)-3-(4-Methoxyphenyl)but-2-enamide (**S19**)



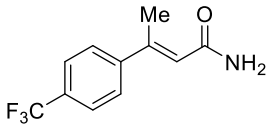
Oxalyl chloride (2.57 mL, 30 mmol) was added dropwise to a solution of (*E*)-3-(4-methoxyphenyl)but-2-enoic acid (2.88 g, 15 mmol) in CH_2Cl_2 (37.5 mL) at 23 ºC, followed by a single drop of DMF. The reaction was stirred at 23 ºC for 30 minutes, at which point the reaction was concentrated *in vacuo*. The residue was dissolved in THF (37.5 mL) and ammonium hydroxide (25 %, 17.0 mL) was added dropwise. The reaction mixture was stirred at 23 ºC for 30 minutes before being concentrated *in vacuo*. The residue was diluted with EtOAc, washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give **S19** as a white solid (1.98 g, 69 %). All spectroscopic data matched that previously reported in the literature.[19]

Melting Point: 133.6–134.5 ºC

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.36 (m, 2H), 6.94–6.84 (m, 3H), 6.04 (s, 1H), 5.59 (br, 2H), 3.82 (s, 3H), 2.54 (s, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 160.2, 152.1, 134.7, 127.5, 116.9, 113.9, 55.3, 17.5 ppm.

(*E*)-3-(4-(Trifluoromethyl)phenyl)but-2-enamide (**S20**)



Oxalyl chloride (1.71 mL, 20 mmol) was added dropwise to a solution of (*E*)-3-(4-(trifluoromethyl)phenyl)but-2-enoic acid (2.30 g, 10 mmol) in CH_2Cl_2 (25.0 mL) at 23 ºC, followed by a single drop of DMF. The reaction was stirred at 23 ºC for 30 minutes, at which point the reaction was concentrated *in vacuo*. The residue was dissolved in THF (25.0 mL) and ammonium hydroxide (25 %, 13.5 mL) was added dropwise. The reaction

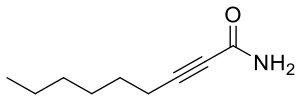
mixture was stirred at 23 °C for 30 minutes before being concentrated *in vacuo*. The residue was diluted with EtOAc, washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give **S20** as an off-white solid (1.37 g, 60 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 6.14 (s, 1H), 5.65 (br, 2H), 2.56 (d, *J* = 1.3 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 151.4, 146.2, 130.8 (q, *J* = 32.6 Hz), 126.7, 125.6 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 271.9 Hz), 121.0, 17.9 ppm;

HRMS (ESI): calculated for $[C_{11}H_{10}F_3NO+H]^+$: 230.0787, found: 230.0794.

Non-2-ynamide (**S21**)



Aqueous ammonium hydroxide (25 %, 15.0 mL) was added to a solution of ethyl non-2-ynoate (10.0 mL, 50.0 mmol) and the resultant suspension was heated to 55 °C and stirred for 24 hours. After cooling to room temperature, the volatiles were removed *in vacuo* and the white slurry filtered. The precipitate was washed with a mixture of hexane:EtOAc (4:1) and then dried under vacuum to give **S21** as a white solid (4.12 g, 54 %). All spectroscopic data matched that previously reported in the literature.[20]

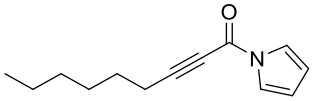
Melting Point: 90.7–91.1 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 (br, 1H), 5.68 (br, 1H), 2.29 (t, *J* = 7.1 Hz, 2H), 1.60–1.51 (m, 2H), 1.45–1.21 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 89.1, 74.9, 31.2, 28.5, 27.6, 22.4, 18.6, 14.0 ppm.

[20] Linstadt, R. T. H.; Peterson, C. A.; Lippincott, D. J.; Jette, C. I.; Lipshutz, B. H. *Angew. Chem. Int. Ed.* **2014**, *53*, 4159-4163

1-(1*H*-Pyrrol-1-yl)non-2-yn-1-one (**S22**)



2,5-dimethoxytetrahydrofuran (mix of *cis*- and *trans*- isomers, 3.88 mL, 30 mmol) was added to a solution of non-2-ynamide (3.06 g, 20 mmol) in AcOH (80.0 mL) and the solution was heated to 100 ^{o}C and stirred for 3 hours. After cooling to room temperature, the reaction mixture was diluted with Et_2O (50 mL) and added dropwise to a saturated aqueous solution of $NaHCO_3$ (200 mL) in an ice-bath. After bubbling had ceased, the mixture was stirred vigourously for 1 hour while allowing it warm to room temperature. The two phases were separated and the aqueous layer further extracted with Et_2O (3 x 50 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography to give **S22** as a pale yellow oil (3.51 g, 86 %).

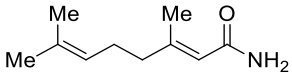
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (br, 2H), 6.30 (t, *J* = 2.4 Hz, 2H), 2.47 (t, *J* = 7.1, 2H), 1.70–1.61 (m, 2H), 1.50–1.41 (m, 2H), 1.39–1.26 (m, 4H), 0.91 (t, *J* = 6.7 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 113.8, 96.1, 74.0, 31.3, 28.7, 27.6, 22.6, 19.2, 14.3 ppm.

IR (ATR): ν_{max} = 2929, 2859, 2244, 2221, 1683, 1467, 1399, 1330, 1300, 1161, 1070, 744 cm^{-1};

HRMS (ESI): calculated for $[C_{13}H_{17}NO+H]^+$: 204.1383, found: 204.1381.

(*E*)-3,7-Dimethylocta-2,6-dienamide (**S23**)



Oxalyl dichloride (344 μL, 4.0 mmol) was added dropwise to a solution of geranic acid (352 μL, 2.0 mmol) in CH_2Cl_2 (5.0 mL) followed by a drop of DMF. The reaction was

stirred for 30 minutes at room temperature at which point the volatiles were removed *in vacuo*. The residue was dissolved in THF (5.0 mL) and aqueous ammonium hydroxide (25 %, 4.62 mL) was added slowly with vigorous stirring. After the addition was complete, the reaction was stirred for another 30 minutes at room temperature after which, the reaction was concentrated *in vacuo*. The resisude was dissolved in EtOAc, washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to give **S23** as a white solid (259 mg, 77 %). All spectroscopic data matched that previously reported in the literature.[21]

Melting Point: 65.2–65.9 ^{o}C

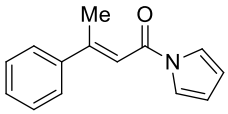
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.61 (q, *J* = 1.3 Hz, 1H), 5.53–5.22 (br, 2H), 5.10–5.04 (m, 1H), 2.15 (s, 3H), 2.16–2.09 (m, 4H), 1.68 (s, 3H), 1.60 (s, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 156.3, 132.8, 123.5, 117.4, 41.2, 26.5, 26.1, 18.8, 18.1 ppm.

[21] Zweifel, T.; Naubron, J.-V.; Grützmacher, H. *Angew. Chem. Int. Ed.* **2009**, *48*, 559-563

Characterization of substrates 1a-w

(*E*)-3-Phenyl-1-(1*H*-pyrrol-1-yl)but-2-en-1-one (1a)



The title compound was obtained in 79 % yield using **GP7**. All spectroscopic data matched that previously reported in the literature.[22]

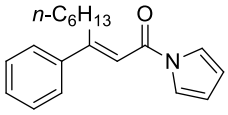
Appearance: Colourless oil;

Rf: 0.18 (Pentane/EtOAc 5 %);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.49 (m, 2H), 7.47–7.39 (m, 5H), 6.75 (q, *J* = 1.4 Hz, 1H), 6.32 (t, *J* = 2.3 Hz, 2H), 2.62 (d, *J* = 1.3 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 158.1, 142.2, 129.6, 128.9, 126.5, 119.4, 116.1, 113.1, 19.2 ppm.

(*E*)-3-Phenyl-1-(1*H*-pyrrol-1-yl)non-2-en-1-one (1b)



The title compound was obtained in 60 % yield using **GP8**.

Appearance: Colourless oil;

Rf: 0.20 (Pentane/EtOAc 5 %);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.47 (m, 2H), 7.47–7.37 (m, 5H), 6.63 (s, 1H), 6.31 (t, *J* = 2.3 Hz, 2H), 3.11–3.03 (m, 2H), 1.51–1.21 (m, 8H), 0.92–0.79 (m, 3H) ppm;

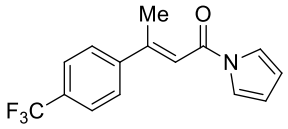
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 163.2, 141.5, 129.4, 128.9, 126.9, 119.4, 116.2, 113.0, 32.2, 31.7, 29.6, 29.1, 22.7, 14.2 ppm;

[22] Tanaka, Y.; Kanai, M.; Shibasake, M. *J. Am. Chem. Soc.* **2010**, *132*, 8862-8863

IR (ATR): ν_{max} = 2956, 2928, 2858, 2221, 1690, 1609, 1467, 1303, 1072, 743 cm^{-1};

HRMS (ESI): calculated for $[C_{19}H_{23}NO+H]^+$: 282.1852, found: 282.1867.

(*E*)-3-(4-(Trifluoromethyl)phenyl-1-(1*H*-pyrrol-1-yl)but-2-en-1-one (1c)



The title compound was obtained in 82 % yield using **GP7**.

Appearance: White solid;

Melting Point: 93.6–93.9 ºC;

Rf: 0.23 (Pentane/EtOAc 5 %);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.39 (t, *J* = 2.3 Hz, 2H), 6.75 (q, *J* = 1.4 Hz, 1H), 6.34 (t, *J* = 2.3 Hz, 2H), 2.61 (d, *J* = 1.4 Hz, 3H) ppm;

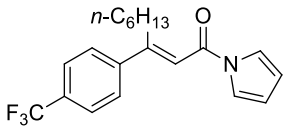
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 156.1, 145.7, 131.4 (q, *J* = 32.8 Hz), 126.9, 125.9 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.1 Hz), 119.3, 117.9, 113.4, 19.2 ppm;

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.7 ppm;

IR (ATR): ν_{max} = 3156, 1683, 1616, 1470, 1323, 1296, 1162, 743 cm^{-1};

HRMS (ESI): calculated for $[C_{15}H_{12}F_3NO+H]^+$: 280.0994, found: 280.0943.

(*E*)-3-(4-(Trifluoromethyl)phenyl)-1-(1*H*-pyrrol-1-yl)non-2-en-1-one (1d)



The title compound was obtained in 78 % yield using **GP8**.

Appearance: Colourless oil;

Rf: 0.15 (Pentane/EtOAc 5 %);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.38(t, *J* = 2.3 Hz, 2H), 6.62 (s, 1H), 6.33 (t, *J* = 2.3 Hz, 2H), 3.09–2.98 (m, 2H), 1.51–1.21 (m, 8H), 0.88–0.80 (m, 3H) ppm;

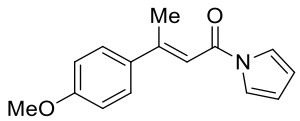
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, 161.3, 145.1, 131.2 (q, *J* = 32.6 Hz), 127.3, 125.9 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.7 Hz), 119.4, 118.0, 113.4, 32.3, 31.6, 29.5, 28.9, 22.7, 14.2 ppm;

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.7 ppm;

IR (ATR): ν_{max} = 2956, 2931, 2859, 1695, 1614, 1467, 1325, 1128, 1069, 743 cm^{-1};

HRMS (ESI): calculated for $[C_{20}H_{22}F_3NO+H]^+$: 350.1726, found: 350.1724.

(*E*)-3-(4-Methoxyphenyl-1-(1*H*-pyrrol-1-yl)but-2-en-1-one (1e)



The title compound was obtained in 82 % yield using **GP7**. All spectroscopic data matched that previously reported in the literature.[23]

Appearance: White solid;

Melting Point: 72.8–73.3 ºC;

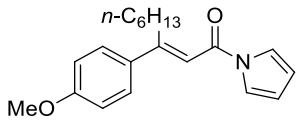
Rf: 0.15 (Pentane/EtOAc 5 %);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.47 (m, 2H), 7.41 (t, *J* = 2.3 Hz, 2H), 6.99–6.90 (m, 2H), 6.73 (q, *J* = 1.3 Hz, 1H), 6.31 (t, *J* = 2.3 Hz, 2H), 3.86 (s, 3H), 2.61 (d, *J* = 1.3 Hz, 3H) ppm;

[23] Zhao, D.; Mao, L.; Wang, L.; Yang, D.; Wang, R. *Chem. Commun.* **2012**, *48*, 889-891

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 161.0, 157.8, 134.3, 128.0, 119.3, 114.2, 112.9, 55.6, 18.9 ppm.

(*E*)-3-(4-Methoxyphenyl)-1-(1*H*-pyrrol-1-yl)non-2-en-1-one (1f)



The title compound was obtained in 56 % yield using **GP8**.

Appearance: Colourless oil;

Rf: 0.21 (Pentane/EtOAc 5 %);

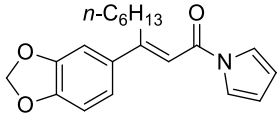
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.43 (m, 2H), 7.40 (t, *J* = 2.4 Hz, 2H), 6.99–6.90 (m, 2H), 6.62 (s, 1H), 6.31 (t, *J* = 2.4 Hz, 2H), 3.86 (s, 3H), 3.11–3.02 (m, 2H), 1.52–1.20 (m, 8H), 0.91–0.80 (m, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.20, 163.16, 160.9, 133.5, 128.3, 119.4, 114.3, 114.2, 112.8, 55.5, 31.9, 31.7, 29.6, 29.4, 22.7, 14.2 ppm;

IR (ATR): ν_{max} = 2955, 2927, 2856, 1687, 1596, 1511, 1464, 1318, 1287, 1239, 1179, 1117, 827, 742 cm^{-1};

HRMS (ESI): calculated for $[C_{20}H_{25}NO_2+H]^+$: 312.1958, found: 312.1966.

(*E*)-3-(Benzo[*d*][1,3]dioxol-5-yl)-1-(1*H*-pyrrol-1-yl)non-2-en-1-one (1g)



The title compound was obtained in 86 % yield using **GP8**.

Appearance: Colourless oil;

Rf: 0.19 (Pentane/EtOAc 5 %);

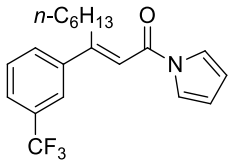
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (t, *J* = 2.3 Hz, 2H), 7.06–6.95 (m, 2H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.58 (s, 1H), 6.30 (t, *J* = 2.3 Hz, 2H), 6.02 (s, 2H), 3.06–2.97 (m, 2H), 1.50–1.22 (m, 8H), 0.89–0.79 (m, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 163.0, 148.9, 148.3, 135.5, 121.1, 119.4, 115.0, 112.9, 108.6, 107.2, 101.7, 32.2, 31.7, 29.6, 29.3, 22.7, 14.2 ppm;

IR (ATR): ν_{max} = 2955, 2927, 2857, 1690, 1595, 1466, 1245, 1121, 1039, 743 cm^{-1};

HRMS (ESI): calculated for $[C_{20}H_{23}NO_3+H]^+$: 326.1751, found: 326.1755.

(*E*)-3-(3-Trifluoromethylphenyl)-1-(1*H*-pyrrol-1-yl)non-2-en-1-one (1h)



The title compound was obtained in 63 % yield using **GP8**.

Appearance: Colourless oil;

Rf: 0.17 (Pentane/EtOAc 5 %);

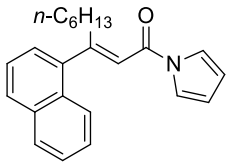
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.61 (m, 3H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 2.3 Hz, 2H), 6.62 (s, 1H), 6.33 (t, *J* = 2.3 Hz, 2H), 3.09–3.01 (m, 2H), 1.51–1.18 (m, 8H), 00.87–0.79 (m, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 161.2, 142.3, 131.4 (q, *J* = 32.6 Hz), 130.2, 129.5, 126.0 (q, *J* = 4.0 Hz), 124.0 (q, 270.9 Hz), 123.6 (q, *J* = 3.9 Hz, 119.4, 117.8, 113.3, 32.2, 31.6, 29.4, 28.9, 22.7, 14.1 ppm;

IR (ATR): ν_{max} = 2957, 2929, 2858, 1693, 1615, 1467, 1332, 1124, 1098, 742 cm^{-1};

HRMS (ESI): calculated for $[C_{20}H_{22}F_3NO+H]^+$: 350.1726, found: 350.1721.

(*E*)-3-(Naphthalen-1-yl)-1-(1*H*-pyrrol-1-yl)non-2-en-1-one (1i)



The title compound was obtained in 92 % yield using **GP8**.

Appearance: Colourless oil;

Rf: 0.26 (Pentane/EtOAc 5 %);

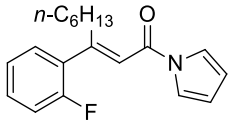
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.83 (m, 3H), 7.58–7.45 (m, 3H), 7.38 (br, 2H), 7.33 (dd, *J* = 7.0, 1.2 Hz, 1H), 6.56 (s, 1H), 6.30 (t, *J* = 2.4 Hz, 2H), 3.16–3.07 (m, 2H), 1.49–1.18 (m, 8H), 0.85–0.77 (m, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 162.8, 140.6, 133.9, 130.8, 128.7, 128.6, 126.6, 126.3, 125.4, 125.2, 124.7, 119.4, 119.3, 113.2, 35.4, 31.7, 29.7, 28.6, 22.7, 14.2 ppm;

IR (ATR): ν_{max} = 2955, 2928, 2856, 1693, 1618, 1466, 1264, 1118, 1072, 778, 743 cm^{-1};

HRMS (ESI): calculated for $[C_{23}H_{25}NO+H]^+$: 332.2009, found: 332.2019.

(*E*)-3-(2-Fluorophenyl)-1-(1*H*-pyrrol-1-yl)non-2-en-1-one (1j)



The title compound was obtained in 72 % yield using **GP8**.

Appearance: Colourless oil;

Rf: 0.12 (Pentane/EtOAc 5 %);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.36 (m, 2H), 7.39–7.28 (m, 2H), 7.19 (td, *J* = 7.5, 1.2 Hz, 1H), 7.13 (ddd, *J* = 10.7, 8.2, 1.2 Hz, 1H), 6.55 (s, 1H), 6.31 (t, *J* = 2.3 Hz, 2H), 3.05–2.96 (m, 2H), 1.44–1.12 (m, 8H), 0.87–0.78 (m, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0, 159.7 (d, *J* = 248.4 Hz), 157.7, 130.4 (d, *J* = 8.4 Hz), 129.7 (d, *J* = 3.3 Hz), 129.6 (d, *J* = 13.6 Hz), 124.4 (d, *J* = 3.6 Hz), 119.8 (d, *J* = 2.9

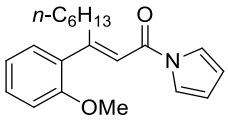
Hz), 119.5, 116.3 (d, *J* = 22.7 Hz), 113.2, 32.9 (d, *J* = 2.3 Hz), 31.7, 29.3, 28.5, 22.7, 14.2 ppm;

^{19}F NMR (376 MHz, $CDCl_3$): δ -115.9 ppm;

IR (ATR): ν_{max} = 2956, 2928, 2858, 1695, 1620, 1467, 1268, 743 cm^{-1};

HRMS (ESI): calculated for $[C_{19}H_{22}FNO+H]^+$: 300.1758, found: 300.1758.

(*E*)-3-(2-Methoxyphenyl)-1-(1*H*-pyrrol-1-yl)non-2-en-1-one (1k)



The title compound was obtained in 58 % yield using **GP8**.

Appearance: Colourless oil;

Rf: 0.22 (Pentane/EtOAc 5 %);

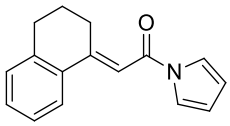
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (t, *J* = 2.3 Hz, 2H), 7.34 (ddd, *J* = 8.2, 7.4, 1.8 Hz, 1H), 7.17 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.98 (td, *J* = 7.4, 1.0 Hz, 1H), 6.94 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.47 (s, 1H), 6.29 (t, *J* = 2.3 Hz, 2H), 3.84 (s, 3H), 3.05–2.96 (m, 2H), 1.44–1.14 (m, 8H), 0.83 (t, *J* = 6.8 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 162.8, 156.6, 131.5, 129.8, 129.4, 120.7, 119.5, 118.4, 112.9, 111.2, 55.6, 33.1, 31.7, 29.5, 28.5, 22.7, 14.2 ppm;

IR (ATR): ν_{max} = 2954, 2925, 2855, 1690, 1613, 1464, 1245, 738 cm^{-1};

HRMS (ESI): calculated for $[C_{20}H_{25}NO_2+H]^+$: 312.1958, found: 312.1967.

(*E*)-2-(3,4-Dihydronaphthalen-1(2*H*)-ylidene)-1-(1*H*-pyrrol-1-yl)ethanone (1l)



The title compound was obtained in 44 % yield using **GP7**.

Appearance: Colourless oil;

Rf: 0.19 (Pentane/EtOAc 3 %);

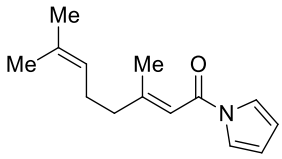
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.43 (t, *J* = 2.3 Hz, 2H), 7.34 (td, *J* = 7.4, 1.3 Hz, 1H), 7.29–7.17 (m, 2H), 6.96 (t, *J* = 2.0 Hz, 1H), 6.33 (t, *J* = 2.3 Hz, 2H), 3.22 (ddd, *J* = 7.3, 6.0, 1.9 Hz, 2H), 2.85 (t, *J* = 6.2 Hz, 2H), 1.90 (p, *J* = 6.3 Hz, 2H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 157.5, 140.9, 134.3, 130.3, 129.5, 126.7, 124.9, 117.3, 112.9, 111.2, 30.2, 29.2, 22.9 ppm;

IR (ATR): ν_{max} = 2935, 1683, 1588, 1465, 1254, 1122, 741 cm^{-1};

HRMS (ESI): calculated for $[C_{16}H_{15}NO+H]^+$: 238.1226, found: 238.1227.

(*E*)-3,7-Dimethyl-1-(1*H*-pyrrol-1-yl)octa-2,6-dien-1-one (1m)



The title compound was obtained in 44 % yield using **GP7**.

Appearance: Colourless oil;

Rf: 0.35 (Pentane/EtOAc 5 %);

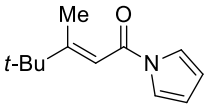
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (t, *J* = 2.4 Hz, 2H), 6.31 (q, *J* = 1.3 Hz, 1H), 6.29 (t, *J* = 2.4 Hz, 2H), 5.10 (tq, *J* = 5.6, 1.5 Hz, 1H), 2.27 (dq, *J* = 12.3, 6.5 Hz, 4H), 2.21 (d, *J* = 1.3 Hz, 3H), 1.71 (d, *J* = 1.5 Hz, 3H), 1.63 (s, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 162.6, 133.0, 122.9, 119.3, 114.8, 112.8, 41.3, 26.1, 25.9, 19.9, 17.9 ppm;

IR (ATR): ν_{max} = 2968, 2916, 2856, 1697, 1466, 1276, 1121, 1068, 742 cm^{-1};

HRMS (ESI): calculated for $[C_{14}H_{19}NO+H]^+$: 218.1539, found: 218.1546.

(*E*)-3,3,4-Trimethyl-1-(1*H*-pyrrol-1-yl)pent-2-en-1-one (1n)



The title compound was obtained in 44 % yield using **GP7**.

Appearance: Colourless oil;

Rf: 0.27 (Pentane/EtOAc 3 %);

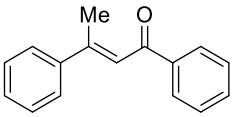
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, *J* = 2.3 Hz, 2H), 6.37 (q, *J* = 1.2 Hz, 1H), 6.29 (t, *J* = 2.3 Hz, 2H), 2.16 (d, *J* = 1.2 Hz, 3H), 1.19 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 164.6, 119.3, 112.8, 112.4, 38.4, 29.9, 28.7, 22.8, 16.2 ppm;

IR (ATR): ν_{max} = 2964, 2872, 1695, 1619, 1464, 1275, 1251, 1117, 1064, 826, 740 cm^{-1};

HRMS (ESI): calculated for $[C_{12}H_{17}NO+H]^+$: 192.1383, found: 192.1384.

(*E*)-1,3-Diphenylbut-2-en-1-one (1o)



The title compound was obtained in 63 % yield using **GP9**. All spectroscopic data matched that previously reported in the literature.[24]

[24] Chen, X.; Zhou, H.; Zhang, K.; Li, J.; Huang, H. *Org. Lett.* **2014**, *16*, 3912-3915

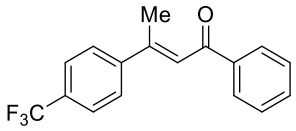
Appearance: Yellow oil;

Rf: 0.21 (Pentane/EtOAc 2 %);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.98 (m, 2H), 7.61–7.53 (m, 3H), 7.51–7.39 (m, 5H), 7.18 (q, *J* = 1.3 Hz, 1H), 2.61 (d, *J* = 1.3 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 155.2, 142.9, 138.5, 132.7, 129.3, 128.7, 128.7, 128.4, 126.6, 122.3, 19.0 ppm;

(*E*)-3-(4-(Trifluoromethyl)phenyl)-1-phenylbut-2-en-1-one (1p)



The title compound was obtained in 66 % yield using **GP10**. All spectroscopic data matched that previously reported in the literature.[25]

Appearance: Yellow oil;

Rf: 0.31 (Pentane/EtOAc 3 %);

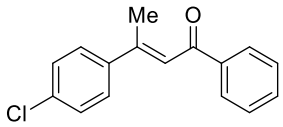
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.96 (m, 2H), 7.72–7.58 (m, 4H), 7.58–7.51 (m, 1H), 7.51–7.45 (m, 2H), 7.16 (q, *J* = 1.4 Hz, 1H), 2.58 (d, *J* = 1.3 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 153.1, 146.4, 139.0, 133.0, 131.0 (q, *J* = 32.6 Hz), 128.8, 128.5, 127.0, 125.7 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 270.5 Hz), 123.9, 19.0 ppm;

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.6 Hz.

[25] Zhang, T.; Jiang, J.; Yao, L.; Geng, H.; Zhang, X. *Chem. Commun.* **2017**, *53*, 9258-9261

(*E*)-3-(4-Chlorophenyl)-1-phenylbut-2-en-1-one (1q)



The title compound was obtained in 71 % yield using **GP10**. All spectroscopic data matched that previously reported in the literature.[26]

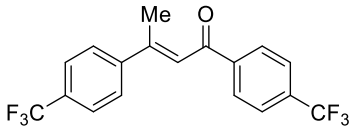
Appearance: Yellow oil;

Rf: 0.31 (Pentane/EtOAc 3 %);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01–7.96 (m, 2H), 7.59–7.53 (m, 1H), 7.52–7.46 (m, 4H), 7.41–7.36 (m, 2H), 7.14 (q, *J* = 1.4 Hz, 1H), 2.56 (d, *J* = 1.3 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 153.6, 141.2, 139.3, 135.2, 132.8, 128.9, 128.7, 128.4, 127.9, 122.5, 18.9 ppm;

(*E*)-1,3-Bis(4-(Trifluoromethyl)phenyl)but-2-en-1-one (1r)



The title compound was obtained in 75 % yield using **GP9**. All spectroscopic data matched that previously reported in the literature.[27]

Appearance: White solid;

Melting Point: 67.3–68.5 ºC

Rf: 0.38 (Pentane/EtOAc 3 %);

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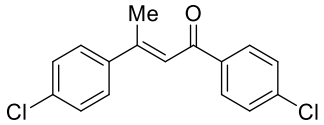
[26] Park, Y.; Min, J.; Eom, D.; Lee, P. H. *Org. Lett.* **2015**, *17*, 3934-3937
[27] Deng, K.; Huai, Q.-Y.; Shen, Z.-L.; Li, H.-J.; Liu, C.; Wu, Y.-C. *Org. Lett.* **2015**, *17*, 1473-1476

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.72–7.63 (m, 4H), 7.14 (q, *J* = 1.6 Hz, 1H), 2.62 (d, *J* = 1.2 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 155.3, 146.2, 141.9, 134.2 (q, *J* = 32.4 Hz), 131.3 (q, *J* = 32.7 Hz), 128.7, 127.0, 125.9–125.7 (m, 2C), 124.0 (q, *J* = 270.6 Hz), 123.8 (q, *J* = 271.0 Hz), 123.0, 19.2 ppm;

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.7, -63.1 ppm

(*E*)-1,3-Bis(4-Chlorophenyl)but-2-en-1-one (1s)



The title compound was obtained in 68 % yield using **GP9**. All spectroscopic data matched that previously reported in the literature.[27]

Appearance: Yellow solid;

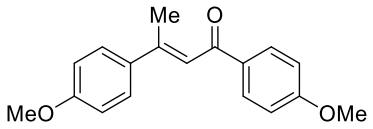
Melting Point: 68.1–69.3 ºC

Rf: 0.34 (Pentane/EtOAc 3 %);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.53–7.36 (m, 6H), 7.08 (q, *J* = 1.4 Hz, 1H), 2.56 (d, *J* = 1.3 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 154.5, 141.1, 139.2, 137.6, 135.4, 129.8, 129.03, 129.00, 127.9, 121.9, 19.0 ppm;

(*E*)-1,3-Bis(4-Chlorophenyl)but-2-en-1-one (1t)



The title compound was obtained in 75 % yield using **GP9**. All spectroscopic data matched that previously reported in the literature.[27]

Appearance: Off-white solid;

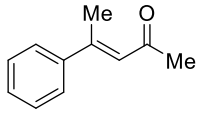
Melting Point: 96.4–97.3 ºC

Rf: 0.38 (Pentane/EtOAc 3 %);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.95 (m, 2H), 7.59–7.50 (m, 2H), 7.12 (q, *J* = 1.3 Hz, 1H), 6.99–6.90 (m, 4H), 3.88 (s, 3H), 3.86 (s, 3H), 2.57 (d, *J* = 1.2 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 163.2, 160.6, 153.7, 135.2, 132.7, 130.6, 128.0, 120.7, 114.1, 113.8, 55.6, 55.5, 18.7 ppm;

(*E*)-4-Phenylpent-3-en-2-one (1u)



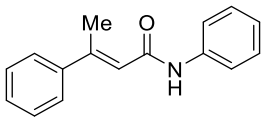
A solution of ethyl (*E*)-3-phenylbut-2-enoate (80 mg, 421 μmol) and *N,O*-dimethylhydroxylamine hydrochloride (82 mg, 841 μmol) in THF (560 μL) was cooled to -5 ºC. To this was added dropwise a solution of isopropylmagnesium chloride in THF (2 M, 904 μL, 1.81 mmol). The reaction was stirred at -5 ºC for 30 minutes before slowly quenching with a saturated aqueous solution of NH_4Cl (2 mL). The product was extracted with EtOAc (3 x 3 mL), washed with brine (5 mL), dried ($MgSO_4$) and concentrated *in vacuo* to give a colourless oil. The crude Weinreb amide was dissolved in THF (560 μL) and cooled to -30 ºC. A solution of methylmagnesium bromide in Et_2O (3 M, 182 μL, 547

μmol) was added dropwise, before allowing the reaction solution to slowly warm to -5 ºC. The reaction was stirred for a further 30 minutes while maintaining the temperature at -5 ºC before being quenched with a saturated aqueous solution of NH_4Cl (2 mL). The product was extracted with Et_2O (3 x 3 mL), washed with brine (5 mL), dried ($MgSO_4$) and concentrated *in vacuo* to give a pale yellow oil. The residue was purified by flash chromatography (10 % Et_2O/pentane) to give a colourless oil (45 mg, 67 %). All spectroscopic data matched that previously reported in the literature.[28]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.46 (m, 2H), 7.41–7.36 (m, 3H), 6.51 (q, *J* = 1.2 Hz, 1H), 2.54 (d, *J* = 1.2 Hz, 3H), 2.30 (s, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 153.7, 142.4, 129.0, 128.4, 126.4, 124.4, 32.3, 18.5 ppm.

(*E*)-*N*,3-Diphenylbut-2-enamide (1w)



Oxalyl chloride (86 μL, 1.0 mmol) was added dropwise to a solution of (*E*)-3-phenylbut-2-enoic acid (81 mg, 0.5 mmol) in CH_2Cl_2 (1.25 mL) at 23 ºC, followed by a single drop of DMF. The reaction was stirred at 23 ºC for 30 minutes, at which point the reaction was concentrated *in vacuo*. The residue was dissolved in THF (50.0 mL) and added dropwise to a mixture of aniline (50 μL, 0.55 mmol) and triethylamine (100 μL, 0.75 mmol). The reaction mixture was stirred at 23 ºC for 30 minutes before being concentrated *in vacuo*. The residue was diluted with EtOAc, washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a white solid (111 mg, 94 %). All spectroscopic data matched that previously reported in the literature.[29]

[28] Chen, X.; Zhou, H.; Zhang, K.; Li, J.; Huang, H. *Org. Lett.* **2014**, *16*, 3912-3915
[29] Cristau, H. J.; Taillefer, M.; Urbani, J. P.; Fruchier, A. *Tetrahedron*, **1996**, *52*, 2005-2020

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.30 (m, 10H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.17 (q, *J* = 1.4 Hz, 1H), 2.62 (d, *J* = 1.3 Hz, 3H) ppm;

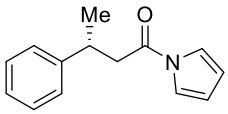
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 153.4, 142.7, 138.2, 129.2, 128.9, 128.7, 126.4, 124.4, 120.1, 119.9, 18.0 ppm.

Synthesis and characterization of products 2a-w

General procedure 11 for the reduction of substrates 1a-w with P17

In an oven-dried vial inside the glovebox, pinacol borane (21.8 μL, 0.15 mmol, 1.5 equiv) was added to a solution of substrate (0.10 mmol, 1 equiv) in toluene (100 μL) at ambient temperature. Catalyst **P17** (2.95 mg, 5.00 μmol, 0.05 equiv) was then added in one portion, the vial sealed and immediately transferred to a refrigerator at 2 ºC. After 12 hours, the reaction was quenched by the dropwise addition of saturated aqueous NH_4Cl (~200 μL). The product was extracted with EtOAc (3 x 200 μL) and the combined organic extracts were filtered through $MgSO_4$/silica then concentrated *in vacuo*. The crude residue was purified by flash chromatography to give the desired compound.

3-Phenyl-1-(1*H*-pyrrol-1-yl)butan-1-one (2a)



The title compound was obtained in 97 % yield. All spectroscopic data was in accordance with that previously reported in the literature.[30]

Appearance: White solid;

Rf: 0.32 (Pentane/EtOAc 3 %);

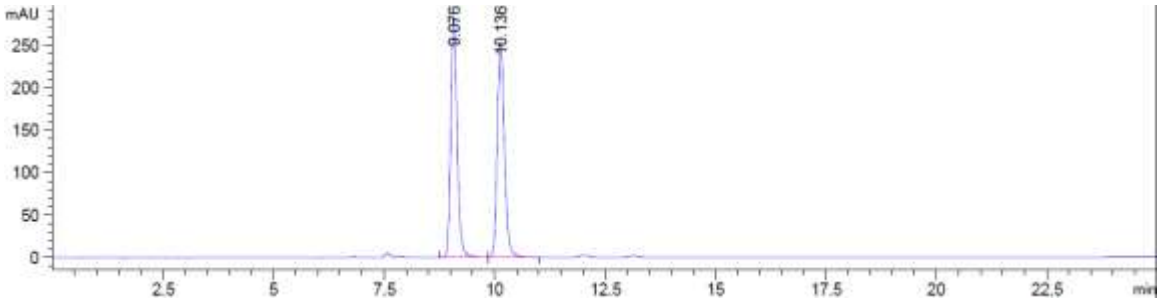
$[\alpha]_D^{20}$: +13.1 (c = 1.0, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.17 (m, 7H), 6.25 (t, *J* = 2.4 Hz, 2H), 3.54–3.40 (m, 1H), 3.12 (dd, *J* = 16.1, 6.0 Hz, 1H), 3.01 (dd, *J* = 16.1, 8.2 Hz, 1H), 1.37 (d, *J* = 7.0 Hz, 3H) ppm;

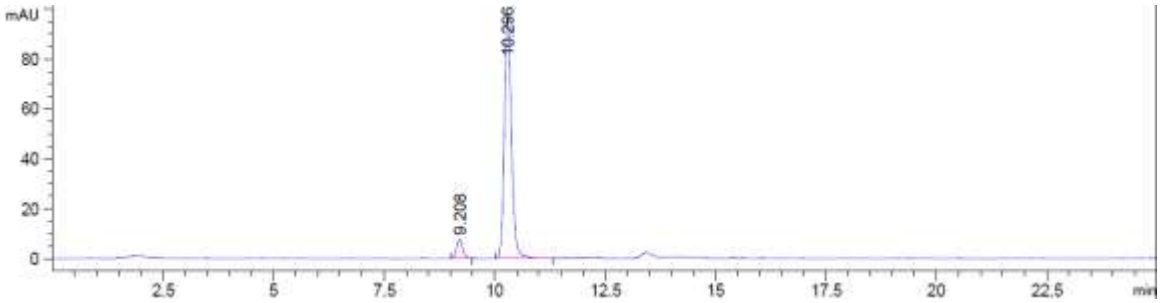
^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 145.68, 128.8, 126.9, 126.8, 119.1, 113.2, 43.2, 36.1, 21.8 ppm;

[30] Shintani, R.; Kimura, T.; Hayashi, T. *Chem. Commun.* **2005**, *25*, 3213-3214

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 9.2 min, t_R (major) 10.3 min, 93.5:6.5 er.

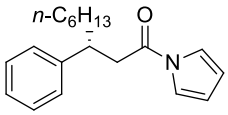


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.076	BB	0.1559	2859.94531	282.93182	49.9657
2	10.136	BB	0.1732	2863.87207	254.62418	50.0343



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.208	BB	0.1513	73.65166	7.58665	6.3542
2	10.296	BB	0.1735	1085.45935	96.27319	93.6458

3-Phenyl-1-(1*H*-pyrrol-1-yl)nonan-1-one (2b)



The title compound was obtained in 96 % yield.

Appearance: Colourless oil;

Rf: 0.21 (Pentane/EtOAc 3 %);

$[\alpha]_D^{20}$: +9.3 (c = 1.0, $CHCl_3$);

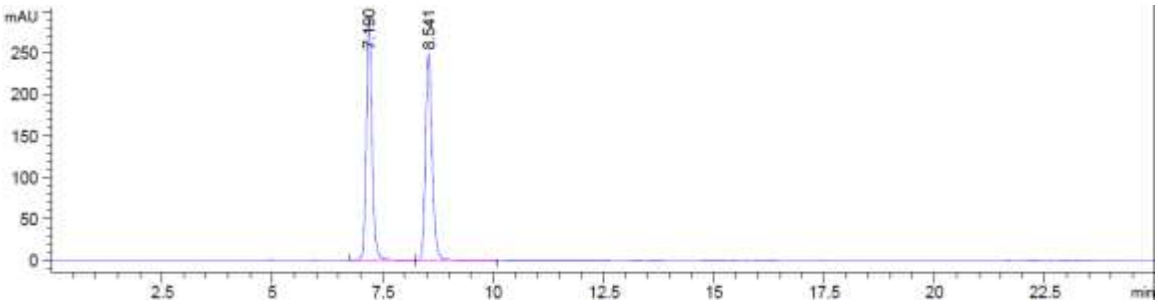
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.16 (m, 7H), 6.26 (t, *J* = 2.5 Hz, 2H), 3.34–3.25 (m, 1H), 3.09 (d, *J* = 7.1 Hz, 2H), 1.82–1.62 (m, 2H), 1.32–1.08 (m, 8H), 0.84 (t, *J* = 6.8 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 144.2, 128.7, 127.6, 126.7, 119.1, 113.1, 42.2, 41.8, 36.3, 31.8, 29.3, 27.5, 22.7, 14.2 ppm;

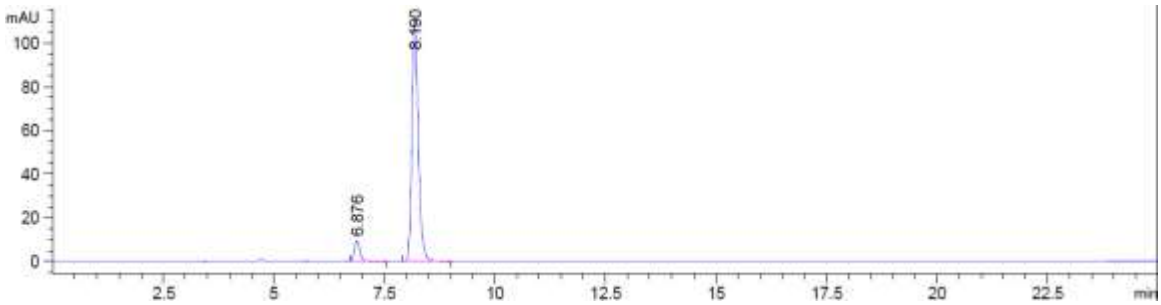
IR (ATR): ν_{max} = 2955, 2926, 2856, 1716, 1467, 1277, 1072, 923, 740, 699 cm^{-1};

HRMS (ESI): calculated for $[C_{19}H_{26}NO+H]^+$: 284.2009, found: 284.2013;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 6.9 min, t_R (major) 8.2 min, 93:7 er.

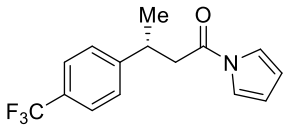


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.190	BB	0.1415	2674.97900	290.28708	50.2225
2	8.541	BB	0.1646	2651.27856	248.28230	49.7775



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.876	VB	0.1347	83.84624	9.52484	6.9894
2	8.190	BB	0.1542	1115.76538	110.12046	93.0106

3-(4-(Trifluoromethyl)phenyl)-1-(1*H*-pyrrol-1-yl)butan-1-one (2c)



The title compound was obtained in 79 % yield.

Appearance: Colourless oil;

Rf: 0.39 (Pentane/EtOAc 3 %);

$[\alpha]_D^{20}$: +3.9 (c = 1.0, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.28 (br, 2H), 6.28 (t, *J* = 2.3 Hz, 2H), 3.57 (m, 1H), 3.15 (dd, *J* = 16.5, 6.6 Hz, 1H), 3.07 (dd, *J* = 16.4, 7.5 Hz, 1H), 1.41 (d, *J* = 7.0 Hz, 3H) ppm;

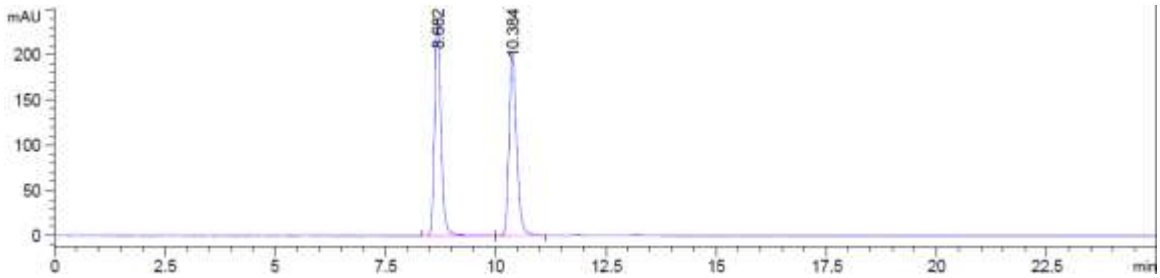
^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 149.7, 129.1 (q, *J* = 32.2 Hz), 127.4, 125.8 (q, *J* = 3.6 Hz), 124.3 (q, *J* = 270.4 Hz) 119.1, 113.5, 42.7, 35.8, 21.9 ppm;

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.4 ppm;

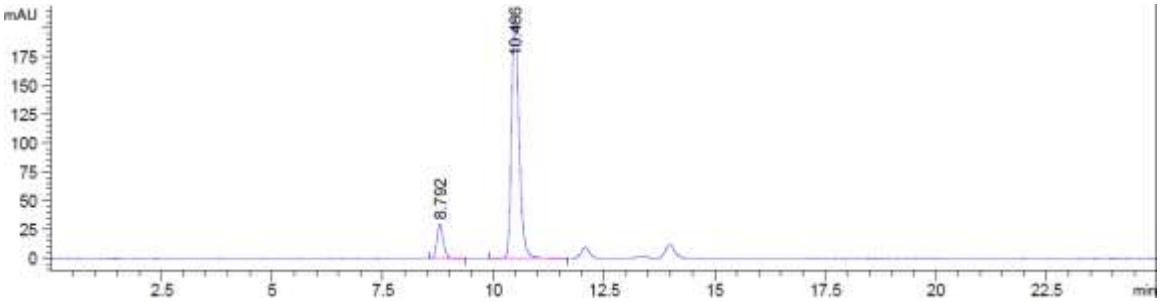
IR (ATR): ν_{max} = 2970, 1717, 1470, 1325, 1114 cm^{-1};

HRMS (ESI): calculated for $[C_{15}H_{14}F_3NO+H]^+$: 282.1100, found: 282.1096;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 8.8 min, t_R (major) 10.5 min, 89.5:10.5 er.

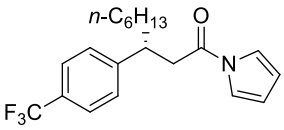


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.682	BB	0.1559	2423.12646	239.82341	50.0575
2	10.384	BV	0.1844	2417.56006	200.93843	49.9425



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.792	BB	0.1517	296.15103	29.85465	10.5856
2	10.486	BV	0.1838	2501.52661	208.76564	89.4144

3-(4-(Trifluoromethyl)phenyl-1-(1*H*-pyrrol-1-yl)nonan-1-one (2d)



The title compound was obtained in 99 % yield.

Appearance: Colourless oil;

Rf: 0.28 (Pentane/EtOAc 3 %);

$[\alpha]_D^{20}$: +4.7 (c = 1.0, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.25 (br, 2H), 6.27 (t, *J* = 2.5 Hz, 2H), 3.43–3.33 (m, 1H), 3.19-3.03 (m, 2H), 1.84–1.63 (m, 2H), 1.37–1.15 (m, 8H), 0.85 (t, *J* = 6.8 Hz, 3H) ppm;

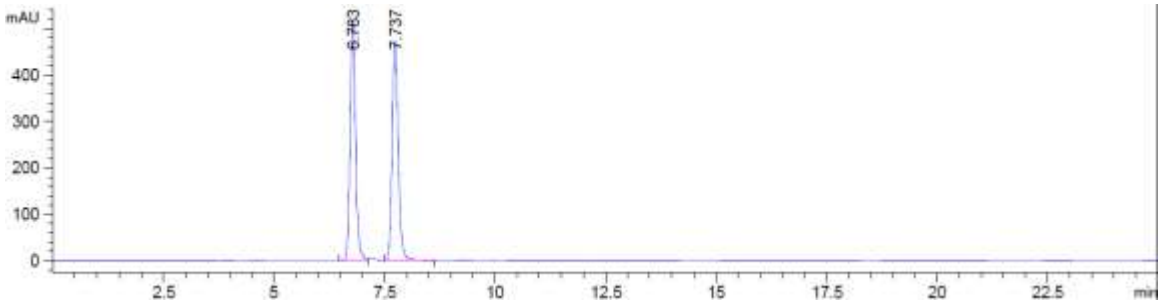
^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 148.3, 129.0 (q, *J* = 32.1 Hz), 128.0, 125.7 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 270.3 Hz), 119.1, 113.4, 41.7, 41.5, 36.2, 31.8, 29.3, 27.4, 22.7, 14.2 ppm;

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.4 ppm;

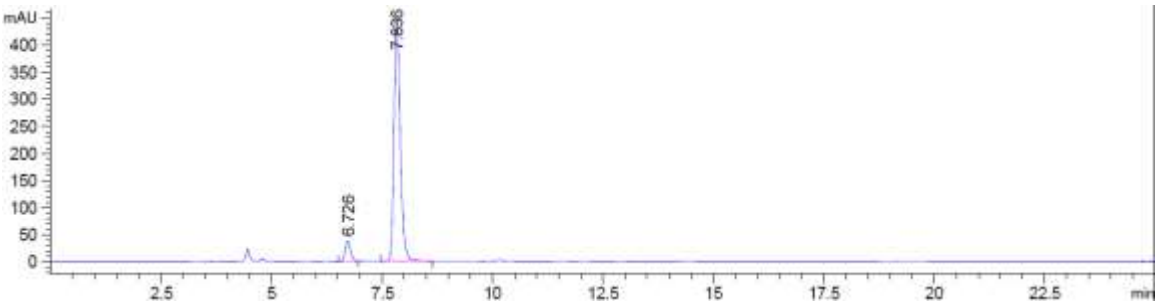
IR (ATR): ν_{max} = 2956, 2928, 2857, 1717, 1468, 1323, 1112, 1068, 741, 610 cm^{-1};

HRMS (ESI): calculated for $[C_{20}H_{24}F_3NO+H]^+$: 352.1883, found: 352.1873;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 6.7 min, t_R (major) 7.8 min, 93:7 er.

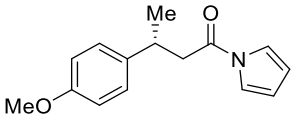


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.783	BV	0.1326	4450.39648	516.29901	49.8040
2	7.737	BB	0.1449	4485.43066	471.69357	50.1960



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.726	BV	0.1284	325.82867	38.61213	6.8451
2	7.836	VV	0.1524	4434.22754	444.46594	93.1549

3-(4-Methoxyphenyl)-1-(1*H*-pyrrol-1-yl)butan-1-one (2e)



The title compound was obtained in 90 % yield.

Appearance: Colourless oil;

Rf: 0.41 (Pentane/EtOAc 5 %);

$[\alpha]_D^{20}$: +15.0 (c = 1.0, $CHCl_3$);

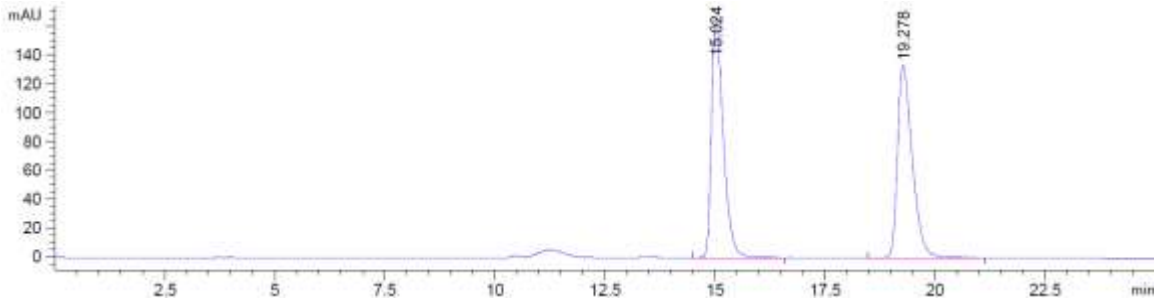
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (br, 2H), 7.22–7.14 (m, 2H), 6.90–6.81 (m, 2H), 6.27 (t, *J* = 2.4 Hz, 2H), 3.79 (s, 3H), 3.45 (m, 1H), 3.10 (dd, *J* = 16.0, 6.2 Hz, 1H), 3.00 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.36 (d, *J* = 7.0 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 158.3, 137.8, 127.8, 119.1, 114.1, 113.2, 55.4, 43.5, 35.3, 29.8, 22.0 ppm;

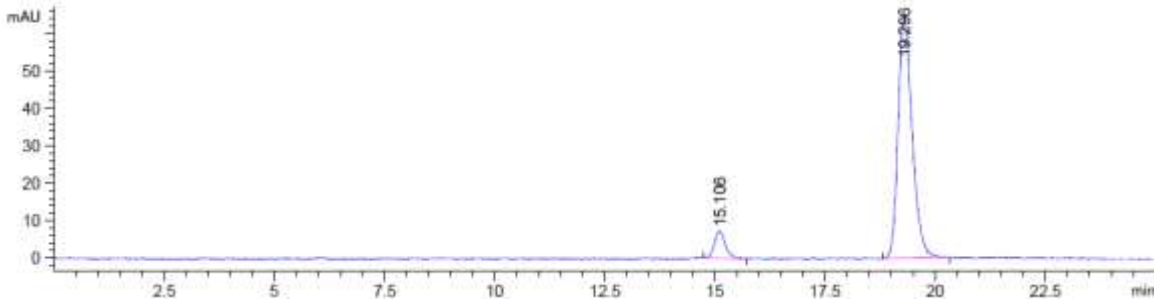
IR (ATR): ν_{max} = 2960, 2927, 1713, 1512, 1467, 1288, 1245, 742 cm^{-1};

HRMS (ESI): calculated for $[C_{15}H_{17}NO_2+H]^+$: 244.1332, found: 244.1335;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 15.1 min, t_R (major) 19.3 min, 92:8 er.

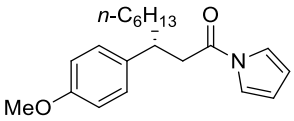


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.024	BB	0.2817	3104.91699	166.42241	49.9329
2	19.278	BB	0.3560	3113.26294	133.54861	50.0671



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.106	BB	0.2651	122.22636	7.16055	7.8810
2	19.296	BB	0.3413	1428.66479	63.77761	92.1190

3-(4-Methoxyphenyl-1-(1*H*-pyrrol-1-yl)nonan-1-one (2f)



The title compound was obtained in 95 % yield.

Appearance: Colourless oil;

Rf: 0.24 (Pentane/EtOAc 3 %);

$[\alpha]_D^{20}$: +12.4 (c = 1.0, $CHCl_3$);

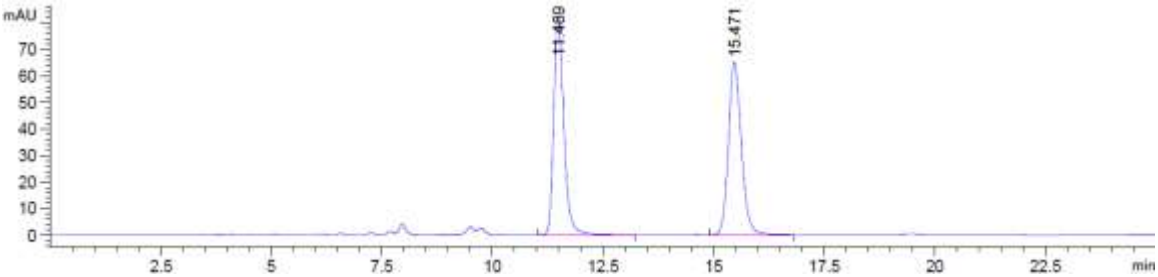
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (br, 2H), 7.18–7.09 (m, 2H), 6.88–6.79 (m, 2H), 6.25 (t, *J* = 2.4 Hz, 2H), 3.78 (s, 3H), 3.24 (dtd, *J* = 9.7, 7.0, 5.2 Hz, 1H), 3.07–3.03 (m, 2H), 1.80–1.57 (m, 2H), 1.30–1.12 (m, 8H), 0.84 (t, *J* = 6.9 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 158.3, 136.2, 128.5, 119.1, 114.1, 113.1, 55.4, 42.4, 41.0, 36.4, 31.8, 29.3, 27.5, 22.8, 14.2 ppm;

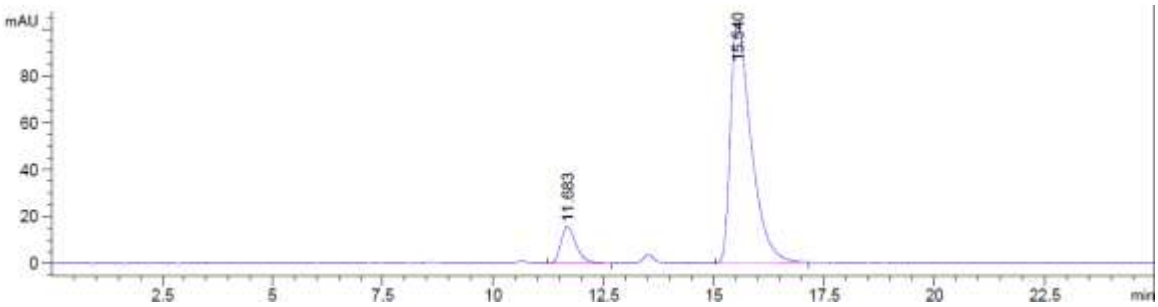
IR (ATR): ν_{max} = 2954, 2927, 2855, 1718, 1513, 1468, 1249, 742 cm^{-1};

HRMS (ESI): calculated for $[C_{20}H_{27}NO_2+H]^+$: 314.2115, found: 314.2109;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 11.7 min, t_R (major) 15.5 min, 90:10 er.

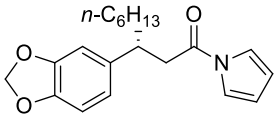


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.489	BB	0.2406	1300.34753	82.18198	49.7633
2	15.471	BB	0.3070	1312.71716	65.16725	50.2367



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.683	BB	0.3530	376.88208	15.64610	10.1387
2	15.540	BB	0.4855	3340.39722	102.14400	89.8613

3-(Benzo[*d*][1,3]dioxol-5-yl)-1-(1*H*-pyrrol-1-yl)nonan-1-one (2g)



The title compound was obtained in 84 % yield.

Appearance: Colourless oil;

Rf: 0.21 (Pentane/EtOAc 3 %);

$[\alpha]_D^{20}$: +2.2 (c = 1.0, $CHCl_3$);

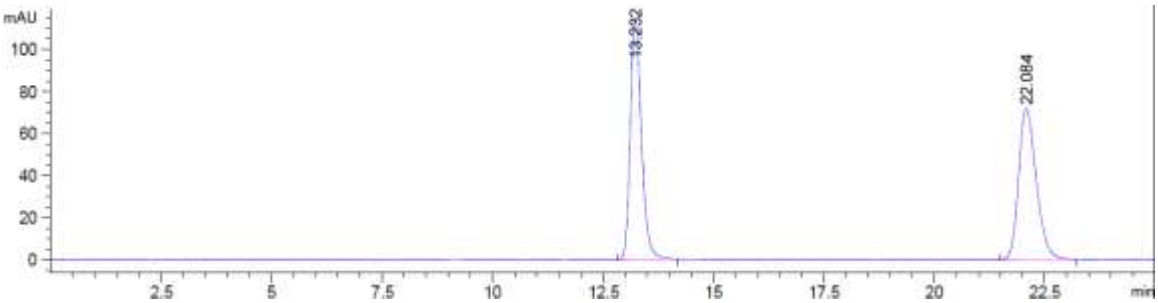
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (br, 2H), 6.76–6.63 (m, 3H), 6.26 (t, *J* = 2.4 Hz, 2H), 5.92 (s, 2H), 3.26–3.17 (m, 1H), 3.03 (d, *J* = 7.0 Hz, 2H), 1.77–1.55 (m, 2H), 1.32–1.12 (m, 8H), 0.85 (t, *J* = 6.8 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 147.9, 146.2, 138.0, 120.8, 119.1, 113.2, 108.4, 107.6, 101.0, 42.4, 41.6, 36.4, 31.8, 29.3, 27.5, 22.7, 14.2 ppm;

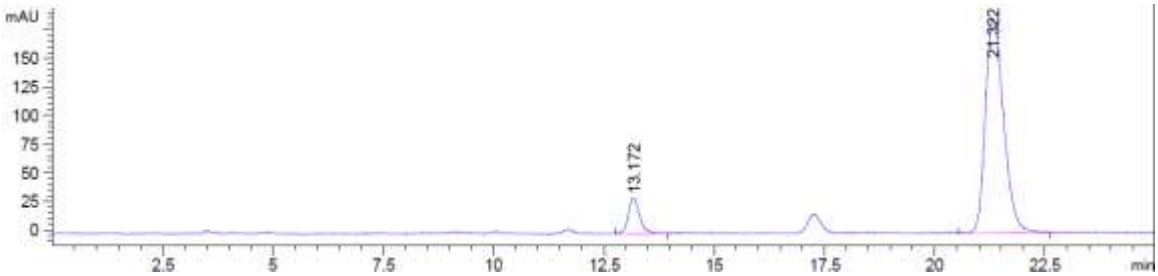
IR (ATR): ν_{max} = 2955, 2927, 2856, 1717, 1487, 1468, 1247, 1040, 743 cm^{-1};

HRMS (ESI): calculated for $[C_{20}H_{25}NO_3+H]^+$: 328.1907, found: 328.1906;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 13.2 min, t_R (major) 21.3 min, 90.5:9.5 er.

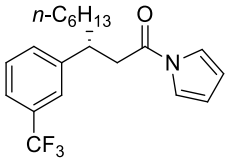


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.232	BB	0.2671	2000.30481	113.77279	50.1240
2	22.084	BB	0.4200	1990.40698	71.68199	49.8760



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.172	BB	0.2634	557.18768	31.04731	9.3797
2	21.322	BB	0.4454	5383.17041	187.24117	90.6203

3-(3-(Trifluoromethyl)phenyl)-1-(1*H*-pyrrol-1-yl)nonan-1-one (2h)



The title compound was obtained in 84 % yield.

Appearance: Colourless oil;

Rf: 0.27 (Pentane/EtOAc 3 %);

$[\alpha]_D^{20}$: +15.6 (c = 1.0, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.37, (m, 4H), 7.25 (br, 2H), 6.27 (t, *J* = 2.4 Hz, 2H), 3.44–3.34 (m, 1H), 3.14 (dd, *J* = 16.4, 6.6 Hz, 1H), 3.08 (dd, *J* = 16.4, 7.4 Hz, 1H), 1.85–1.61 (m, 2H), 1.29–1.09 (m, 8H), 0.85 (t, *J* = 6.8 Hz, 3H) ppm;

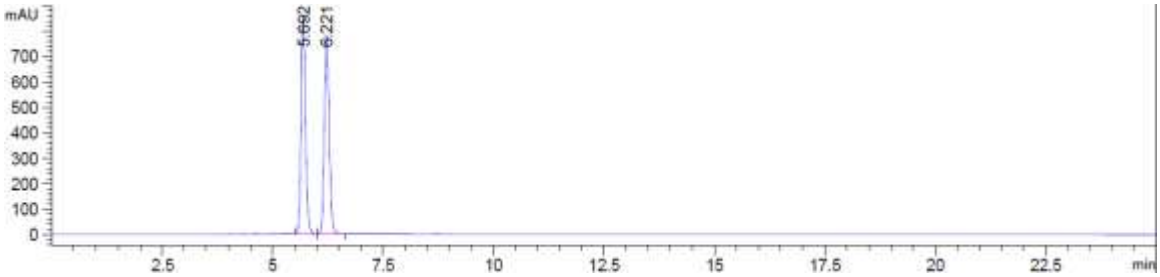
^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 145.2, 131.3, 131.0 (q, *J* = 31.8 Hz), 129.1, 124.3 (q, *J* = 271.0 Hz), 124.2 (q, *J* = 3.5 Hz), 123.7 (q, *J* = 3.7 Hz), 119.1, 113.4, 41.8, 41.5, 36.2, 31.7, 29.2, 27.4, 22.7, 14.2 ppm;

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.5 ppm;

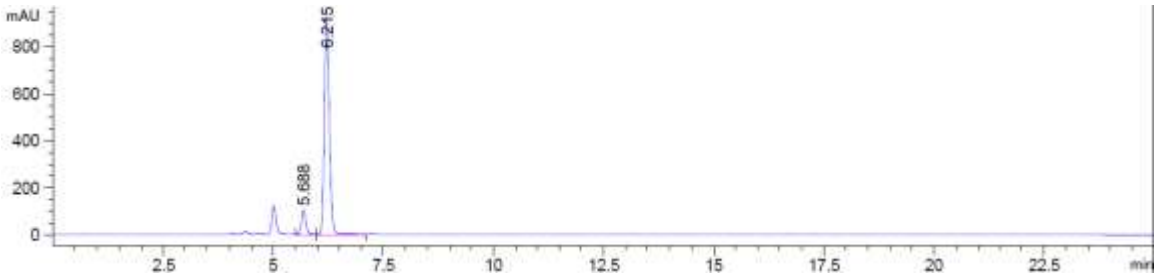
IR (ATR): ν_{max} = 2956, 2929, 2858, 1718, 1469, 1327, 1164, 1125, 1074, 742 cm^{-1};

HRMS (ESI): calculated for $[C_{20}H_{24}F_3NO+H]^+$: 352.1883, found: 352.1880;

Chiral HPLC (Chiralpak IB, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 5.7 min, t_R (major) 6.2 min, 91:9 er.

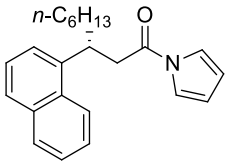


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.692	BB	0.1073	5958.90869	855.34198	49.7817
2	6.221	BB	0.1174	6011.17920	784.34125	50.2183



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.688	BB	0.1067	710.06433	105.22192	8.9683
2	6.215	BV	0.1231	7207.39746	923.00580	91.0317

3-(Naphthalen-1-yl)-1-(1*H*-pyrrol-1-yl)nonan-1-one (2i)



The title compound was obtained in 92 % yield.

Appearance: Colourless oil;

Rf: 0.25 (Pentane/EtOAc 3 %);

$[\alpha]_D^{20}$: +13.3 (c = 1.0, $CHCl_3$);

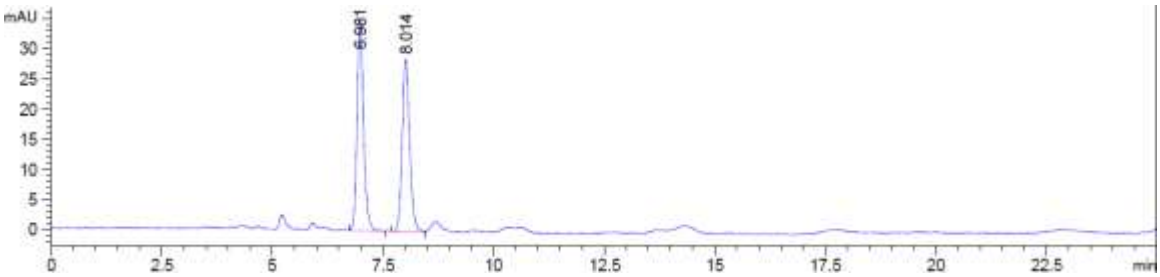
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.59–7.38 (m, 4H), 7.30–7.25 (br, 2H), 6.26 (t, *J* = 2.4 Hz, 2H), 4.29 (br, 1H), 3.22 (d, *J* = 6.8 Hz, 2H), 2.00–1.86 (m, 2H), 1.36–1.09 (m, 8H), 0.82 (t, *J* = 7.0 Hz) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 140.4, 134.1, 131.9, 129.0, 127.0, 126.2, 125.6, 125.4, 123.1, 119.0, 113.1, 41.8, 35.7, 31.7, 29.4, 27.4, 24.6, 22.6, 14.1 ppm;

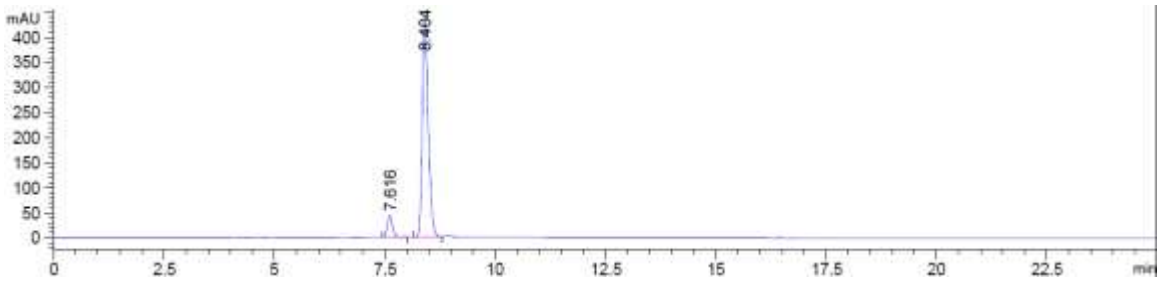
IR (ATR): ν_{max} = 2954, 2927, 2856, 1717, 1468, 779, 742 cm^{-1};

HRMS (ESI): calculated for $[C_{23}H_{27}NO+H]^+$: 334.2165, found: 334.2169;

Chiral HPLC (Chiralpak IB, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 7.6 min, t_R (major) 8.4 min, 92:8 er.

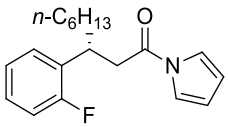


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.981	BB	0.1546	357.82013	35.21249	51.7976
2	8.014	BV	0.1780	332.98447	28.56079	48.2024



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.616	VB	0.1284	365.07010	43.30137	8.1610
2	8.404	BV	0.1406	4108.28223	433.50510	91.8390

3-(2-Fluorophenyl)-1-(1*H*-pyrrol-1-yl)nonan-1-one (2j)



The title compound was obtained in 91 % yield.

Appearance: Colourless oil;

Rf: 0.25 (Pentane/EtOAc 3 %);

$[\alpha]_D^{20}$: +1.9 (c = 1.0, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (br, 2H), 7.25–7.15 (m, 2H), 7.08 (td, *J* = 7.5, 1.3 Hz, 1H), 7.01 (ddd, *J* = 10.9, 8.1, 1.3 Hz, 1H), 6.26 (t, *J* = 2.4 Hz, 2H), 3.62–3.50 (m, 1H), 3.21 (dd, *J* = 16.3, 7.0 Hz, 1H), 3.13 (dd, *J* = 16.4, 7.2 Hz, 1H), 1.83–1.70 (m, 2H), 1.32–1.13 (m, 8H), 0.84 (t, *J* = 6.8 Hz, 3H) ppm;

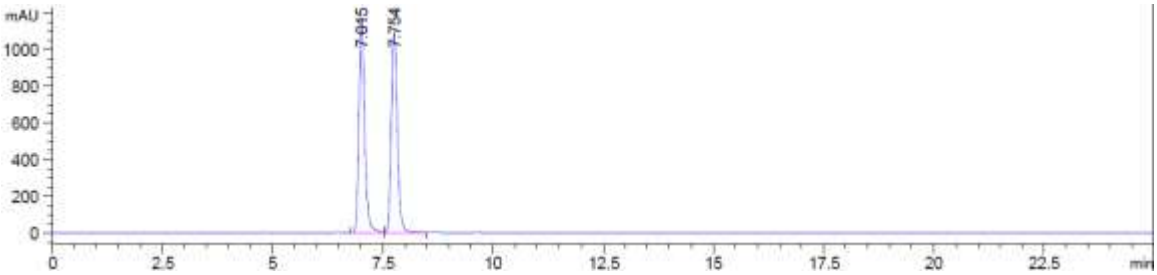
^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 162.5, 160.0, 130.6 (d, *J* = 13.9 Hz), 129.5 (d, *J* = 5.3 Hz), 128.2 (d, *J* = 8.4 Hz), 124.3 (d, *J* = 3.4 Hz), 119.1, 115.9 (d, *J* = 22.7 Hz), 113.2, 40.5, 36.4, 34.8, 31.8, 29.2, 27.6, 22.7, 14.2 ppm;

^{19}F NMR (376 MHz, $CDCl_3$): δ -117.3 (dt, *J* = 11.7, 6.1 Hz) ppm;

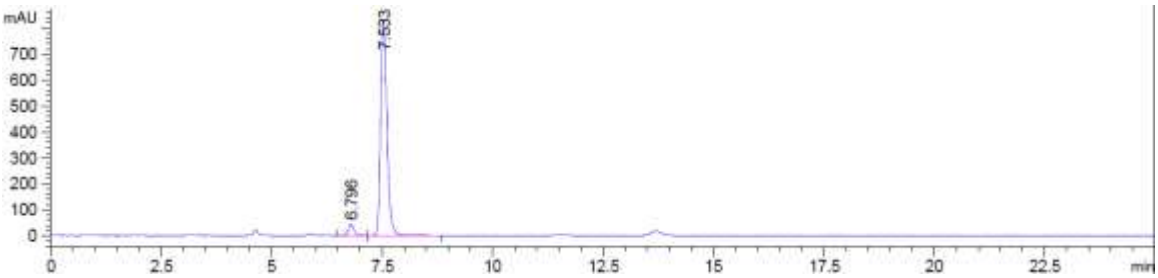
IR (ATR): ν_{max} = 2955, 2926, 2856, 1717, 1491, 741 cm^{-1};

HRMS (ESI): calculated for $[C_{19}H_{24}FNO+H]^+$: 302.1915, found: 302.1913;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 6.8 min, t_R (major) 7.5 min, 95.5:4.5 er.

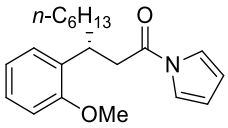


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.015	BV	0.1373	1.05801e4	1172.43689	50.5120
2	7.754	VV	0.1469	1.03657e4	1090.70435	49.4880



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.796	BB	0.1339	375.94644	42.22051	4.3977
2	7.533	BB	0.1505	8172.70361	832.70276	95.6023

3-(2-Methoxyphenyl)-1-(1*H*-pyrrol-1-yl)nonan-1-one (2k)



The title compound was obtained in 87 % yield.

Appearance: Colourless oil;

Rf: 0.24 (Pentane/EtOAc 3 %);

$[\alpha]_D^{20}$: -4.6 (c = 1.0, $CHCl_3$);

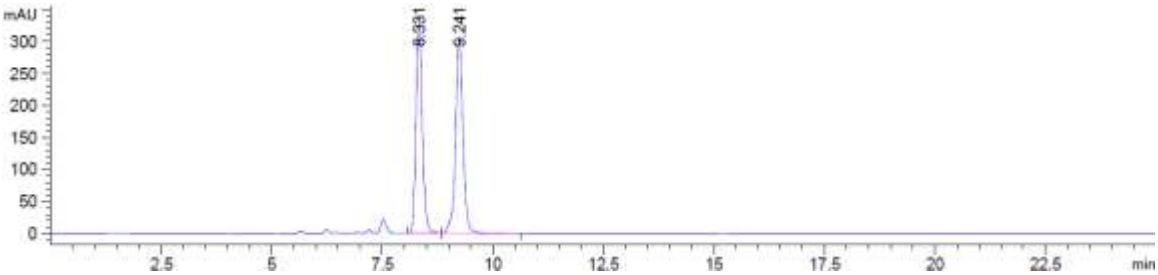
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (br, 2H), 7.28–7.14 (m, 2H), 6.96–6.82 (m, 2H), 6.25 (t, *J* = 2.4 Hz, 2H), 3.80 (s, 3H), 3.72–3.61 (m, 1H), 3.15 (dd, *J* = 15.5, 6.3 Hz, 1H), 3.02 (dd, *J* = 15.5, 7.8 Hz, 1H), 1.87–1.70 (m, 2H), 1.33–1.12 (m, 8H), 0.84 (t, *J* = 6.8 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 157.5, 131.8, 128.2, 127.6, 120.8, 119.3, 112.9, 110.9, 55.4, 41.0, 36.3, 34.0, 31.9, 29.4, 27.6, 22.8, 14.2 ppm;

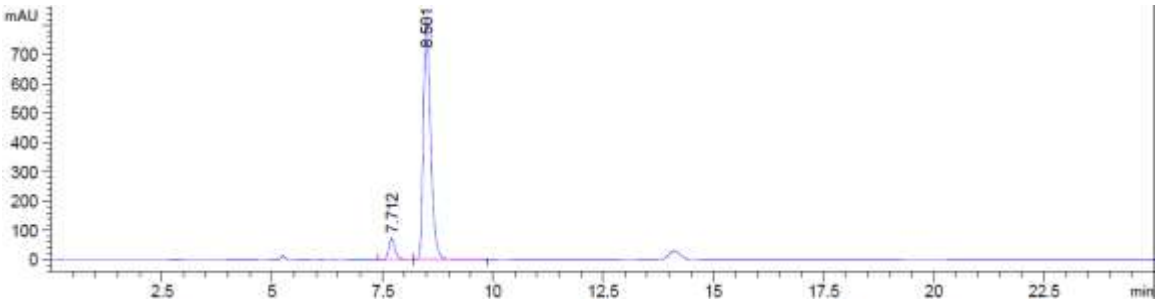
IR (ATR): ν_{max} = 2954, 2927, 2856, 1718, 1467, 1330, 1242, 742 cm^{-1};

HRMS (ESI): calculated for $[C_{20}H_{27}NO_2+H]^+$: 314.2115, found: 314.2106;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 7.7 min, t_R (major) 8.5 min, 93:7 er.

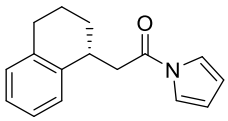


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.331	BV	0.1529	3385.50000	337.88968	48.4715
2	9.241	VB	0.1776	3599.02173	305.25543	51.5285



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.712	BB	0.1552	739.67786	73.63854	7.2880
2	8.501	BB	0.1756	9409.56641	821.52972	92.7120

1-(1*H*-Pyrrol-1-yl)-2-(1,2,3,4-tetrahydronaphthalen-1-yl)ethan-1-one (2l)



The title compound was obtained in 97 % yield.

Appearance: White solid;

Melting Point: 71.9–72.3 °C

Rf: 0.26 (Pentane/EtOAc 3 %);

$[\alpha]_D^{20}$: +32.4 (c = 1.0, $CHCl_3$);

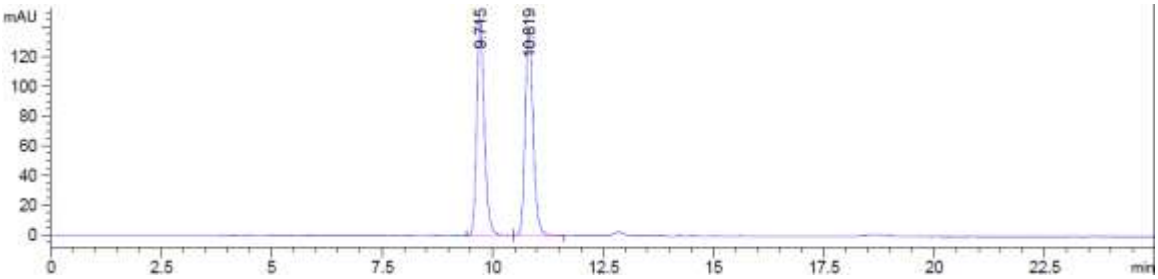
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (br, 2H), 7.22–7.09 (m, 4H), 6.31 (t, *J* = 2.4 Hz, 2H), 3.65–3.58 (m, 1H), 3.18 (dd, *J* = 16.5, 4.8 Hz, 1H), 3.11 (dd, *J* = 16.5, 9.2 Hz, 1H), 2.90–2.72 (m, 2H), 2.08–1.93 (m, 1H), 1.88–1.74 (m, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 139.2, 137.4, 129.6, 128.5, 126.4, 126.2, 119.2, 113.3, 42.2, 34.0, 29.7, 28.1, 19.6 ppm;

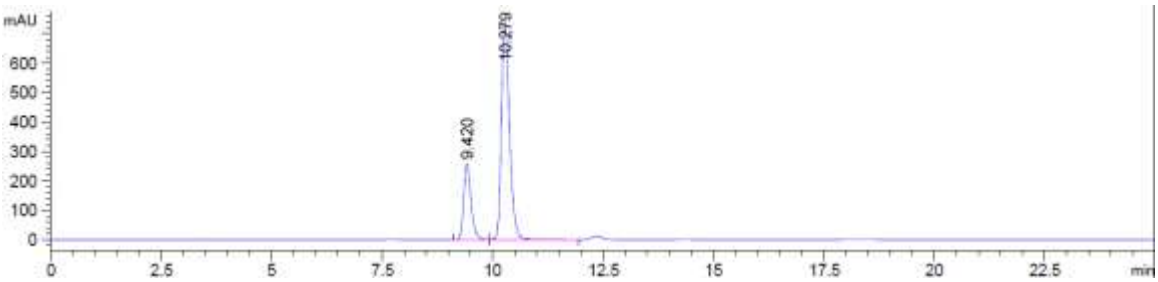
IR (ATR): ν_{max} = 2930, 2863, 1715, 1489, 1304, 743 cm^{-1};

HRMS (ESI): calculated for $[C_{16}H_{17}NO+H]^+$: 240.1383, found: 240.1376;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 9.4 min, t_R (major) 10.3 min, 76:24 er.

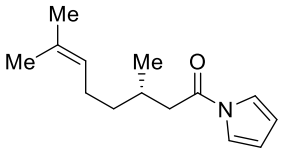


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.715	BB	0.1831	1739.89966	145.93436	49.9907
2	10.819	BB	0.1914	1740.54675	139.67526	50.0093



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.420	VV	0.1773	3004.40332	258.97202	24.2405
2	10.279	VB	0.1943	9389.72656	738.84943	75.7595

3,7-Dimethyl-1-(1*H*-pyrrol-1-yl)oct-6-en-1-one (2m)



The title compound was obtained in 96 % yield.

Appearance: Colourless oil;

Rf: 0.51 (Pentane/EtOAc 2 %);

$[\alpha]_D^{20}$: +4.6 (c = 1.0, $CHCl_3$);

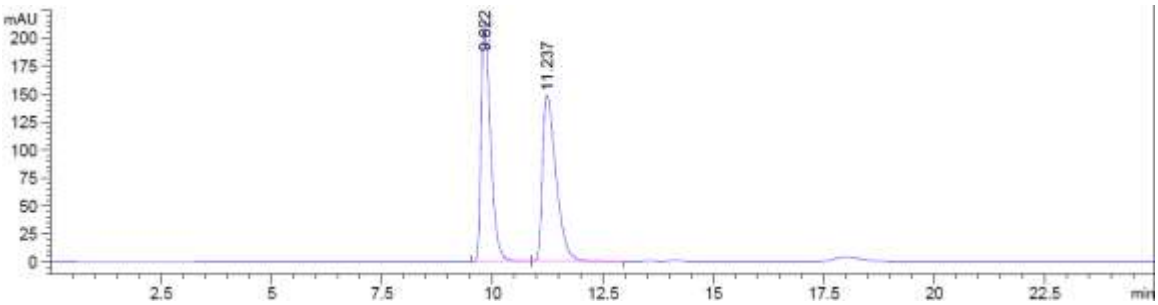
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (br, 2H), 6.29 (br, 2H), 5.10 (t, *J* = 7.3 Hz, 1H), 2.82 (ddd, *J* = 15.6, 5.8, 2.2 Hz, 1H), 2.59 (ddd, *J* = 15.6, 8.4, 2.3 Hz, 1H), 2.23–2.12 (m, 1H), 2.11–1.96 (m, 2H), 1.68 (s, 3H), 1.61 (s, 3H), 1.50–1.39 (m, 1H), 1.37–1.25 (m, 1H), 1.02 (d, *J* = 6.7 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 131.9, 124.2, 119.2, 113.1, 42.0, 37.1, 30.0, 25.9, 25.6, 19.9, 17.8 ppm;

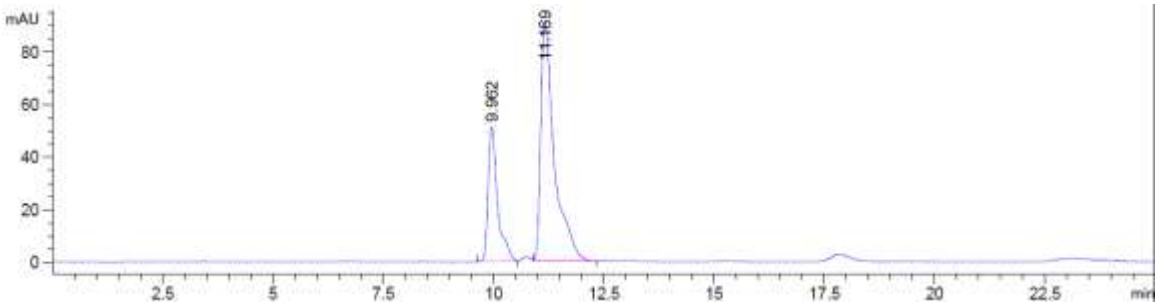
IR (ATR): ν_{max} = 2964, 2916, 2854, 1717, 1468, 1329, 1307, 1266, 1070, 741 cm^{-1};

HRMS (ESI): calculated for $[C_{14}H_{21}NO+H]^+$: 220.1696, found: 220.1693;

Chiral HPLC (Chiralpak ID, 0.2 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 10.0 min, t_R (major) 11.2 min, 72:28 er.

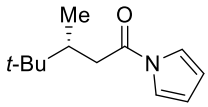


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.822	BB	0.2241	3155.44751	213.95639	49.9881
2	11.237	BB	0.3244	3156.94482	148.27219	50.0119



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.962	BB	0.2209	758.03333	51.16053	28.0998
2	11.169	VB	0.3156	1939.61194	90.64657	71.9002

1-(1*H*-Pyrrol-1-yl)-2-(1,2,3,4-tetrahydronaphthalen-1-yl)ethan-1-one (2n)



The title compound was obtained in 88 % yield.

Appearance: Colourless oil;

Rf: 0.34 (Pentane/EtOAc 3 %);

$[\alpha]_D^{20}$: +1.8 (c = 1.0, $CHCl_3$);

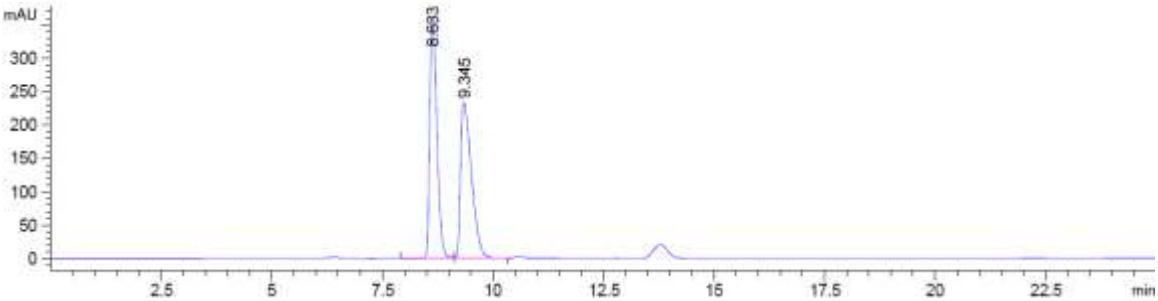
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (br, 2H), 6.29 (t, *J* = 2.5 Hz, 2H), 2.97 (dd, *J* = 15.3, 2.9 Hz, 1H), 2.46 (dd, *J* = 15.3, 10.7 Hz, 1H), 2.00 (tt, *J* = 9.9, 6.8 Hz, 1H), 0.96–0.92 (m, 12H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 119.2, 113.1, 39.9, 37.7, 33.1, 27.3, 15.2 ppm;

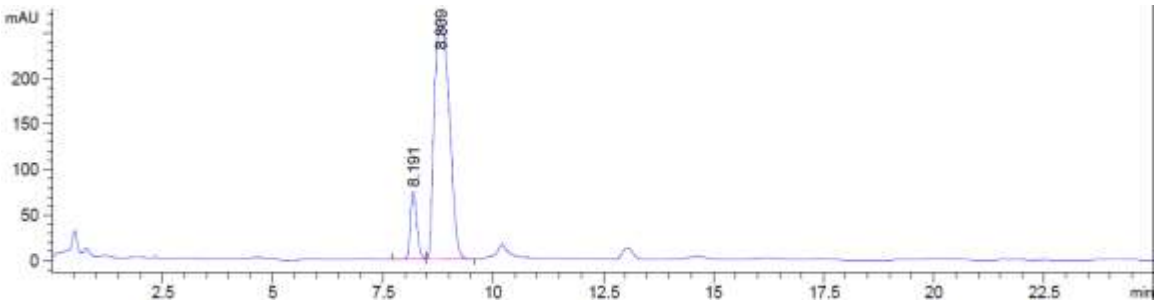
IR (ATR): ν_{max} = 2960, 2927, 2870, 1717, 1468, 1321, 1309, 1266, 741 cm^{-1};

HRMS (ESI): calculated for $[C_{12}H_{19}NO+H]^+$: 194.1539, found: 194.1531;

Chiral HPLC (Chiralpak IG, 0.5 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 8.2 min, t_R (major) 8.8 min, 89:11 er.

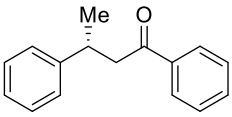


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.633	BV	0.1752	4052.57544	360.27985	50.1610
2	9.345	VV	0.2652	4026.56567	233.48718	49.8390



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.191	BV	0.1648	762.92401	73.70290	10.9527
2	8.809	VB	0.4045	6202.72998	261.71912	89.0473

1,3-Diphenylbutan-1-one (2o)



The title compound was obtained in 95 % yield. All spectroscopic data matched that previously reported in the literature.[31]

Appearance: White solid;

Melting Point: 68.4–69.3 ºC

Rf: 0.16 (Pentane/EtOAc 5 %);

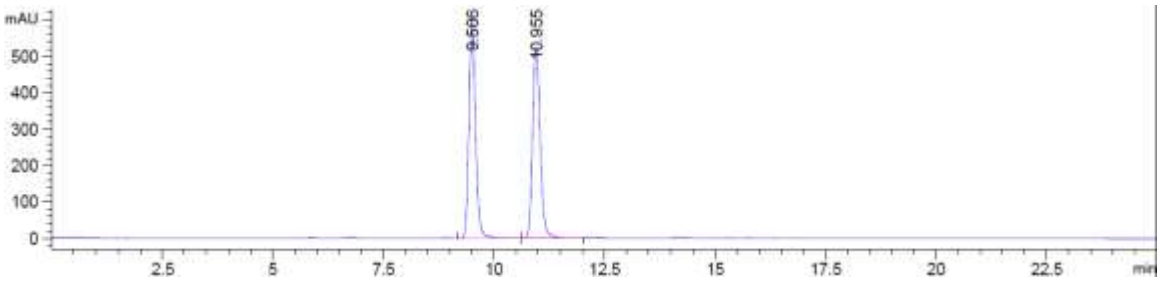
$[\alpha]_D^{20}$: -5.9 (c = 1.0, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–7.89 (m, 2H), 7.59–7.49 (m, 1H), 7.49–7.40 (m, 2H), 7.35–7.15 (m, 5H), 3.58–3.44 (m, 1H), 3.30 (dd, *J* = 16.5, 5.7 Hz, 1H), 3.19 (dd, *J* = 16.5, 8.3 Hz, 1H), 1.34 (d, *J* = 6.9 Hz, 3H) ppm;

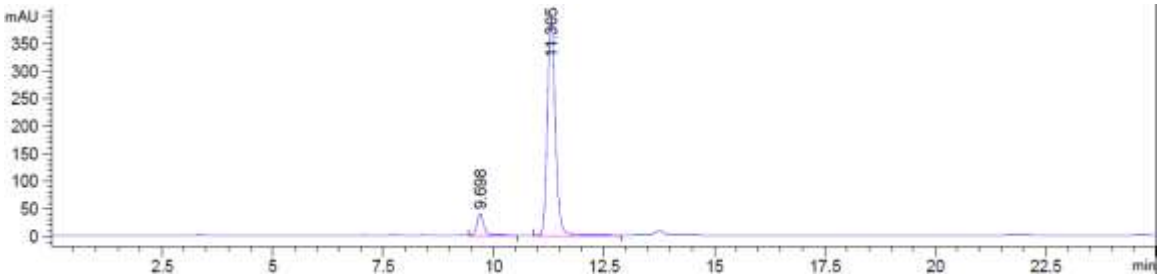
[31] Kalutharage, N.; Yi, C. S. *Angew. Chem. Int. Ed.* **2013**, *52*, 13651-13655

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 146.7, 137.3, 133.1, 128.7, 128.7, 128.2, 127.0, 126.4, 47.2, 35.7, 22.0 ppm;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 9.7 min, t_R (major) 11.3 min, 92:8 er.

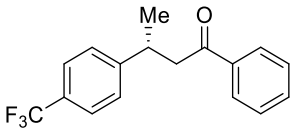


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.506	BB	0.1598	6242.40088	598.17627	49.9166
2	10.955	BB	0.1836	6263.26709	523.28558	50.0834



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.698	VB	0.1660	419.20728	38.82856	7.8903
2	11.305	BB	0.1911	4893.75439	393.52460	92.1097

1-Phenyl-3-(4-(trifluoromethyl)phenyl)butan-1-one (2p)



The title compound was obtained in 96 % yield. All spectroscopic data matched that previously reported in the literature.[32]

Appearance: Pale yellow solid;

Melting Point: 44.7–45.0 ºC

Rf: 0.36 (Pentane/EtOAc 3 %);

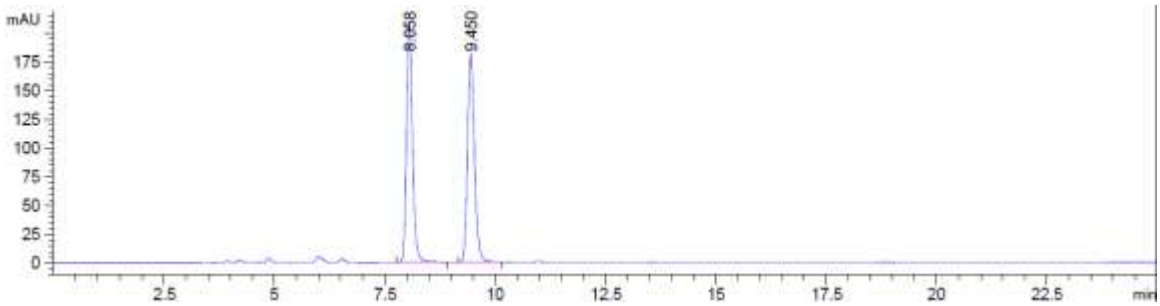
$[\alpha]_D^{20}$: -7.2 (c = 1.0, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–7.89 (m, 2H), 7.61–7.51 (m, 3H), 7.50–7.36 (m, 4H), 3.65–3.55 (m, 1H), 3.33 (dd, *J* = 16.9, 6.4 Hz, 1H), 3.23 (dd, *J* = 16.9, 7.5 Hz, 1H), 1.37 (d, *J* = 7.0 Hz, 3H) ppm;

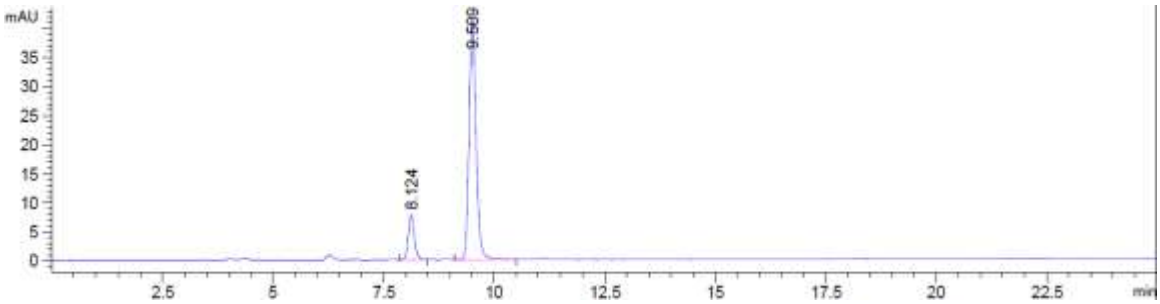
^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 150.7, 137.1, 133.3, 128.8, 128.7 (q, *J* = 32.1 Hz), 128.1, 127.4, 125.6 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 270.1 Hz), 46.7, 35.4, 22.0 ppm;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 8.1 min, t_R (major) 9.5 min, 86:14 er.

[32] Endo, K.; Hamada, D.; Yakeishi, S.; Shibata, T. *Angew. Chem. Int. Ed.* **2013**, *52*, 606-610

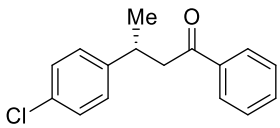


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.058	VB	0.1451	1986.40564	208.68663	50.1159
2	9.450	VB	0.1696	1977.22144	180.81450	49.8841



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.124	BB	0.1435	72.69984	7.74735	13.7687
2	9.509	BB	0.1705	455.30988	41.32847	86.2313

3-(4-Chlorophenyl)-1-phenylbutan-1-one (2q)



The title compound was obtained in 96 % yield. All spectroscopic data matched that previously reported in the literature.[33]

[33] Stopka, T.; Niggeman, M. *Org. Lett.* **2015**, *17*, 1437-1440

Appearance: White solid;

Melting Point: 55.3–56.9 ºC

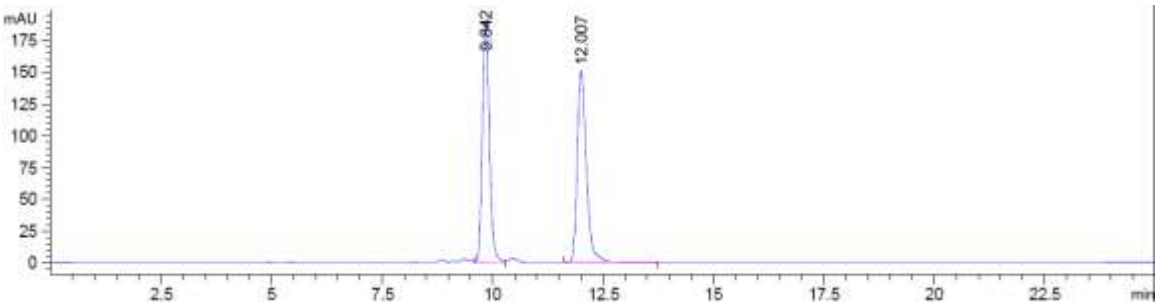
Rf: 0.36 (Pentane/EtOAc 3 %);

$[\alpha]_D^{20}$: +1.9 (c = 1.0, $CHCl_3$);

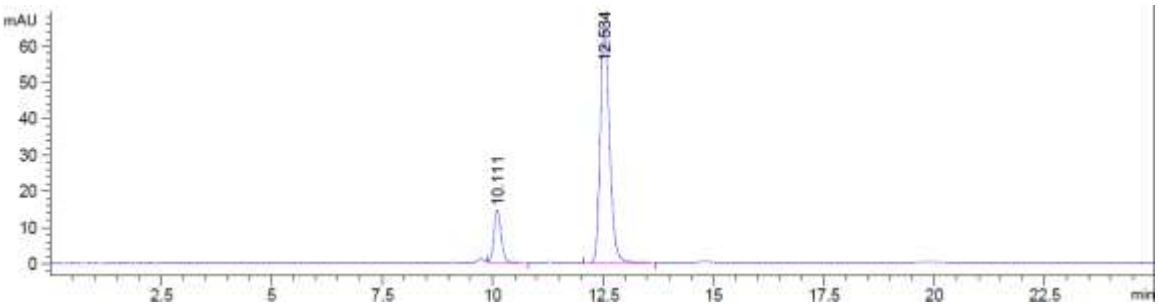
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96–7.88 (m, 2H), 7.60–7.51 (m, 1H), 7.49–7.40 (m, 2H), 7.30–7.16 (m, 4H), 3.54–3.46 (m, 1H), 3.27 (dd, *J* = 16.7, 6.3 Hz, 1H), 3.17 (dd, *J* = 16.6, 7.7 Hz, 1H), 1.32 (d, *J* = 7.0 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 145.1, 137.2, 133.2, 132.0, 128.8, 128.4, 128.2, 47.0, 35.1, 22.1 ppm;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 10.1 min, t_R (major) 12.5 min, 85.5:14.5 er.

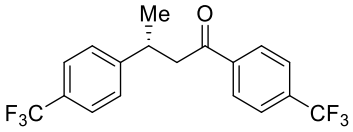


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.842	BV	0.1706	2082.92163	188.93042	49.1366
2	12.007	BB	0.2165	2156.11987	151.04872	50.8634



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.111	VB	0.1783	166.43102	14.45940	14.6872
2	12.534	BB	0.2267	966.74268	66.07794	85.3128

1,3-Bis(4-(trifluoromethyl)phenyl)butan-1-one (2r)



The title compound was obtained in 88 % yield. All spectroscopic data matched that previously reported in the literature.[34]

Appearance: Colourless oil;

Melting Point: 71.4–72.7 ^{o}C

Rf: 0.23 (Pentane/EtOAc 3 %);

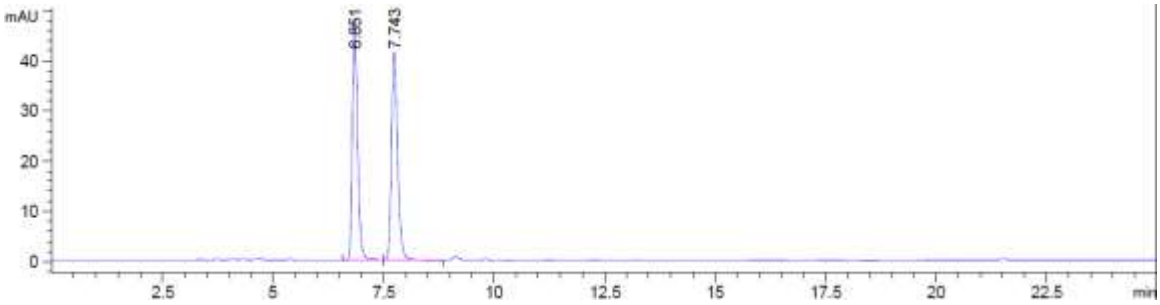
$[\alpha]_D^{20}$: +5.7 (c = 1.0, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–7.97 (m, 2H), 7.75–7.68 (m, 2H), 7.59–7.52 (m, 2H), 7.41–7.34 (m, 2H), 3.64–3.54 (m, 1H), 3.34 (dd, *J* = 17.1, 6.5 Hz, 1H), 3.24 (dd, *J* = 17.1, 7.4 Hz, 1H), 1.38 (d, 7.0 Hz, 3H) ppm;

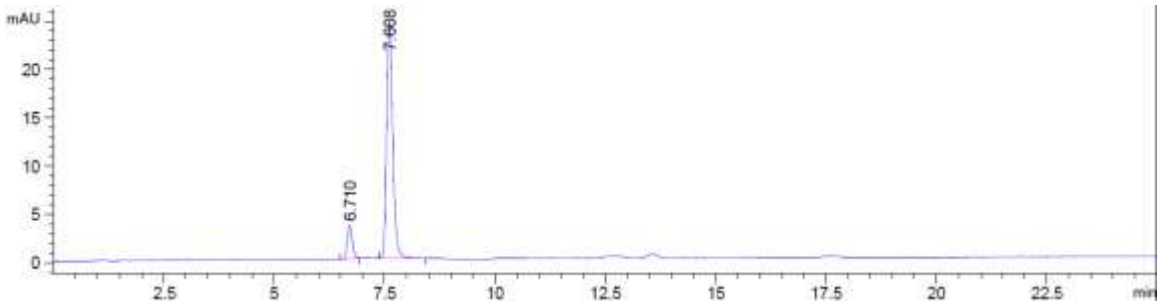
[34] Makarov, I. S.; Madsen, R. *J. Org. Chem.* **2013**, *78*, 6593-6598

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 150.3, 139.7, 134.7 (q, *J* = 32.7 Hz), 128.9 (q, *J* = 32.2 Hz), 128.5, 127.4, 125.9 (q, *J* = 3.7 Hz), 125.7 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 270.9 Hz), 123.7 (q, *J* = 271.0 Hz), 47.0, 35.4, 22.0 ppm;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 6.7 min, t_R (major) 7.6 min, 89.5:10.5 er.

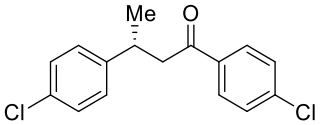


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.851	BV	0.1274	400.36786	47.93473	49.7902
2	7.743	VV	0.1476	403.74216	41.44687	50.2098



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.710	BB	0.1186	26.71501	3.43961	10.2767
2	7.608	BB	0.1468	233.24298	24.54977	89.7233

1,3-Bis(4-chlorophenyl)butan-1-one (2s)



The title compound was obtained in 96 % yield. All spectroscopic data matched that previously reported in the literature.[35]

Appearance: Colourless oil;

Rf: 0.37 (Pentane/EtOAc 3 %);

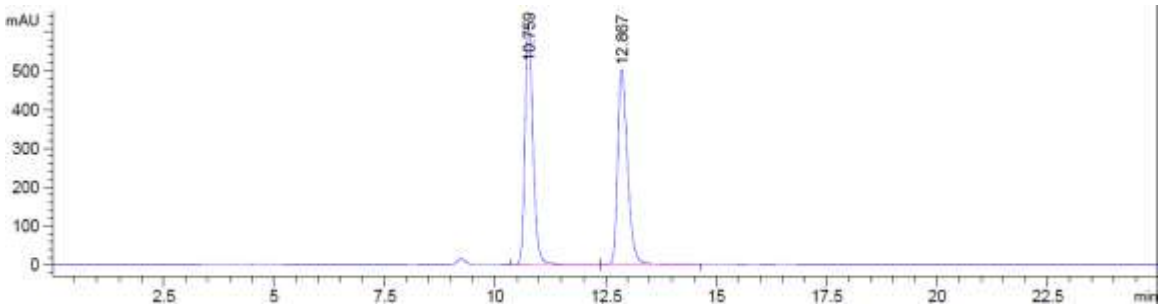
$[\alpha]_D^{20}$: +6.2 (c = 1.0, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.80 (m, 2H), 7.46–7.37 (m, 2H), 7.30–7.23 (m, 2H), 7.23–7.15 (m, 2H), 3.52–3.42 (m, 1H), 3.23 (dd, *J* = 16.8, 6.4 Hz, 1H), 3.14 (dd, *J* = 16.8, 7.6 Hz, 1H), 1.32 (d, *J* = 7.0 Hz, 3H) ppm;

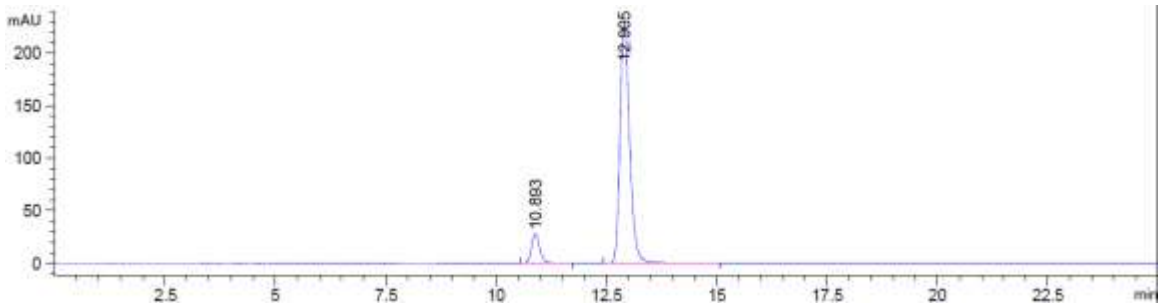
^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 144.7, 139.5, 135.4, 132.0, 129.4, 128.9, 128.6, 128.2, 46.8, 35.0, 21.9 ppm;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 10.9 min, t_R (major) 12.9 min, 91.5:8.5 er.

[35] Musa, S.; Ackermann, L.; Gelman, D. *Adv. Synth. Catal.* **2013**, *355*, 3077-3080

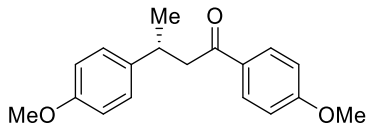


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.759	BB	0.1895	7741.27588	620.67822	49.9856
2	12.867	BB	0.2362	7745.73584	501.45010	50.0144



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.893	BB	0.1886	367.82672	30.52549	8.4964
2	12.905	BV	0.2437	3961.37451	246.23849	91.5036

1,3-Bis(4-methoxyphenyl)butan-1-one (2t)



The title compound was obtained in 79 % yield. All spectroscopic data matched that previously reported in the literature.[34]

Appearance: Off-white solid;

Melting Point: 71.4–72.7 ºC

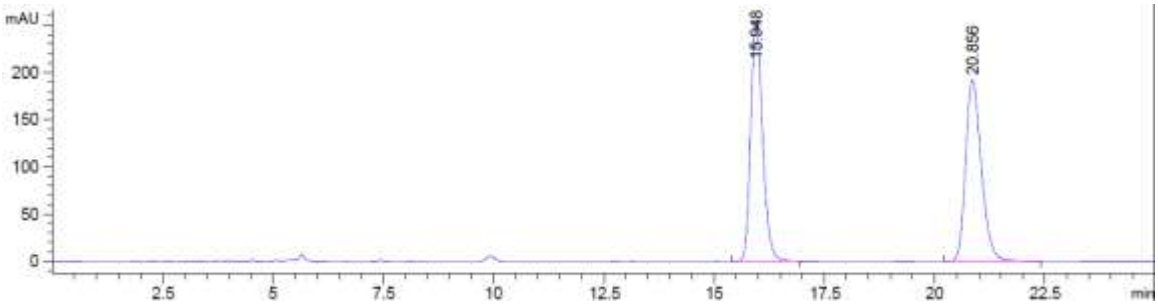
Rf: 0.17 (Pentane/EtOAc 3 %);

$[\alpha]_D^{20}$: +5.6 (c = 1.0, $CHCl_3$);

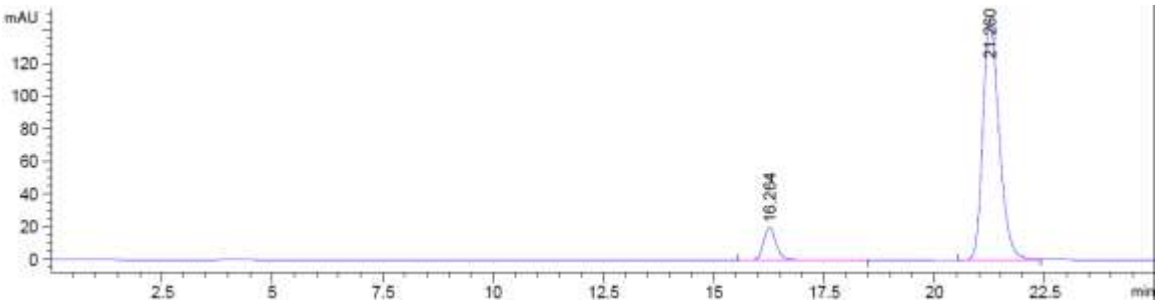
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.87 (m, 2H), 7.23–7.14 (m, 2H), 6.95–6.89 (m, 2H), 6.89–6.79 (m, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 3.49–3.37 (m, 1H), 3.20 (dd, *J* = 16.1, 5.9 Hz, 1H), 3.09 (dd, *J* = 16.1, 8.2 Hz, 1H), 1.30 (d, *J* = 6.9 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 163.5, 158.1, 139.0, 130.51, 130.48, 127.9, 114.0, 113.8, 55.6, 55.4, 47.1, 35.2, 22.2 ppm;

Chiral HPLC (Chiralpak IF, 1 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 16.3 min, t_R (major) 21.3 min, 90.5:9.5 er.

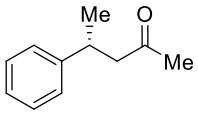


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.948	VV	0.2879	4790.57861	254.16432	49.9694
2	20.856	VB S	0.3823	4796.43701	192.73134	50.0306



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.264	BB	0.3059	406.60001	20.28137	9.7108
2	21.260	BV	0.3971	3780.49902	146.48889	90.2892

4-Phenylpentan-2-one (2u)



The title compound was obtained in 87 % yield. All spectroscopic data was in accordance with that previously reported in the literature.[36]

Appearance: Colourless oil;

Rf: 0.19 (Et_2O/Pentane 10 %);

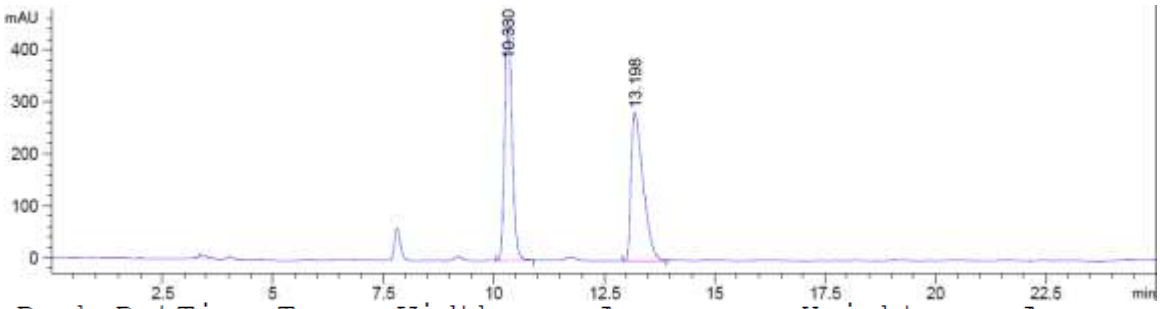
$[\alpha]_D^{20}$: -18.3 (c = 1.0, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.15 (m, 5H), 3.38–3.28 (m, 1H), 2.78 (dd, *J* = 16.3, 6.5 Hz, 1H), 2.68 (dd, *J* = 16.3, 7.9 Hz, 1H), 2.09 (s, 3H), 1.29 (d, *J* = 7.0 Hz, 3H) ppm;

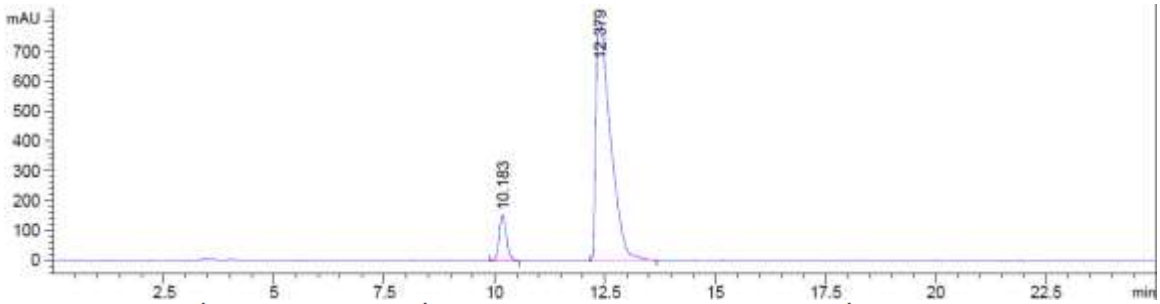
^{13}C NMR (100 MHz, $CDCl_3$): δ 207.8, 146.1, 128.4, 126.7, 126.2, 51.9, 35.4, 30.5, 22.0 ppm;

Chiral HPLC (Chiralpak IG, 1 % *i*-PrOH/hexane, 1.0 mL/min, 210 nm): t_R (minor) 10.2 min, t_R (major) 12.4 min, 91.5:8.5 er.

[36] Chen, W.; Sun, L.; Huang, X.; Wang, J.; Peng, Y.; Song, G. *Adv. Synth. Catal.* **2015**, *357*, 1474-1482

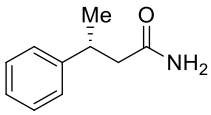


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.330	BV	0.1763	5301.00244	460.58286	49.7124
2	13.198	BV	0.2758	5362.34277	284.61880	50.2876



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.183	BV	0.1726	1724.62683	154.07452	8.5330
2	12.379	BV	0.3282	1.84867e4	804.26141	91.4670

3-Phenylbutanamide (2v)



The title compound was obtained in 49 % yield. All spectroscopic data was in accordance with that previously reported in the literature.[37]

Appearance: White solid;

[37] Wen, J.; Jiang, J.; Zhang, X. *Org. Lett.* **2016**, *18*, 4451.

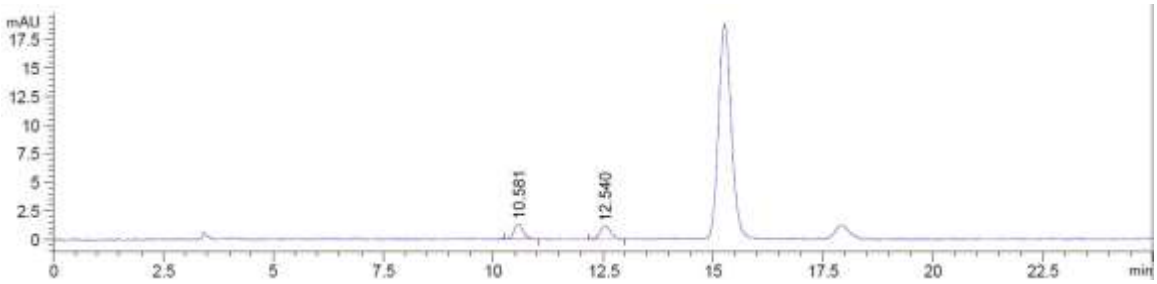
Rf: 0.11 (Pentane/EtOAc 50 %);

$[\alpha]_D^{20}$: -17.8 (c = 0.17, $CHCl_3$);

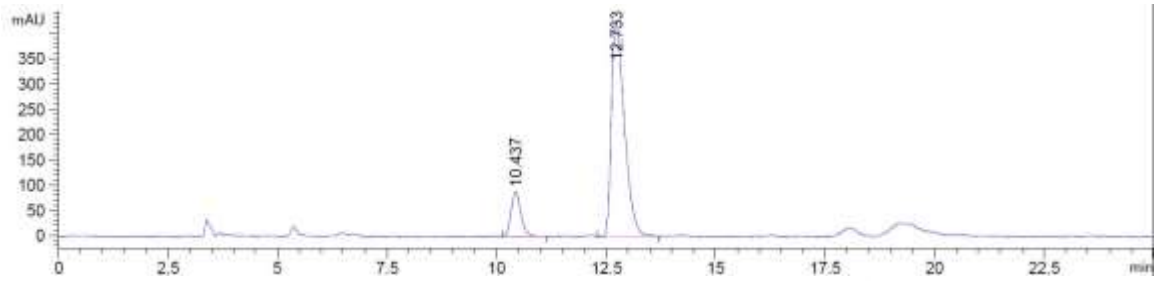
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, *J* = 7.5, 7.5 Hz, 2 H), 7.25–7.17 (m, 3 H), 5.31 (bs, 1 H), 5.22 (bs, 1 H), 3.33–3.24 (m, 1 H), 2.52 (dd, J = 14.3, 7.3 Hz, 1 H), 2.44 (dd, J = 14.3, 7.6 Hz, 1 H), 1.33 (d, *J* = 6.9 Hz, 3 H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 145.9, 128.8, 126.9, 126.7, 45.0, 36.9, 21.9 ppm;

Chiral HPLC (Chiralpak ID, 10 % *i*-PrOH/hexane, 1.0 mL/min, 210 nm): t_R (minor) 10.4 min, t_R (major) 12.3 min, 86:14 er.

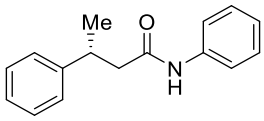


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.575	BB	0.2312	874.47015	58.21982	48.9970
2	12.553	BB	0.2585	910.27222	50.92278	51.0030



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.437	BB	0.2412	1400.80676	89.22672	13.7706
2	12.733	BB	0.3128	8771.66699	424.94998	86.2294

***N*,3-Diphenylbutanamide (2w)**



The title compound was obtained in 63 % yield. All spectroscopic data was in accordance with that previously reported in the literature.[38]

Appearance: White solid;

Melting Point: 136.8–137.4 ºC

Rf: 0.12 (Pentane/EtOAc 10 %);

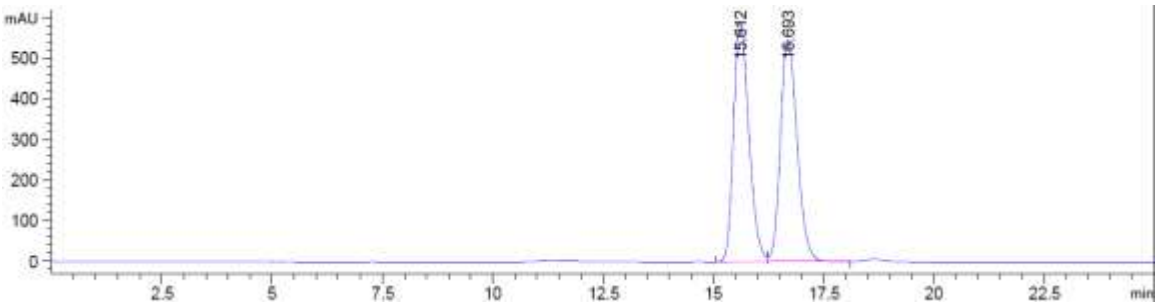
$[\alpha]_D^{20}$: -24.6 (c = 1.0, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.24 (m, 9H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.88 (br, 1H), 3.45–3.35 (m, 1H), 2.66 (dd, *J* = 14.1, 7.5 Hz, 1H), 2.60 (dd, *J* = 14.2, 7.3 Hz, 1H), 1.41 (d, *J* = 6.9 Hz, 3H) ppm;

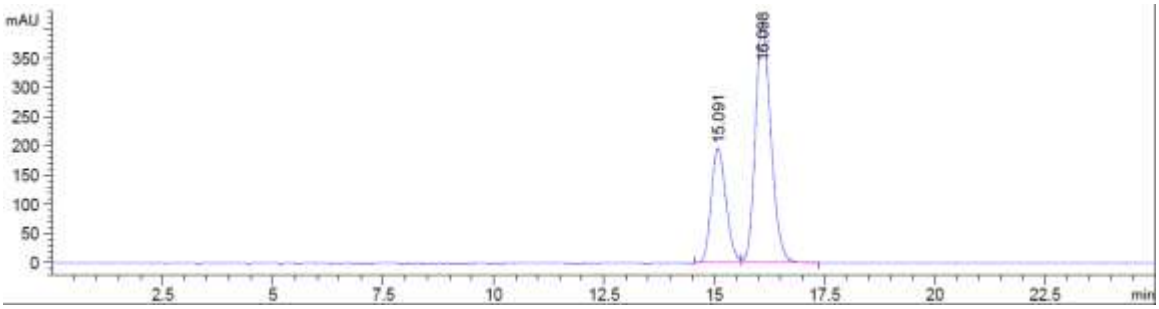
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 145.7, 137.7, 128.9, 128.8, 126.8, 126.7, 124.3, 120.0, 46.8, 37.0, 21.7 ppm;

Chiral HPLC (Chiralpak IG, 10 % *i*-PrOH/hexane, 1.0 mL/min, 254 nm): t_R (minor) 15.1 min, t_R (major) 16.1 min, 69:31 er.

[38] Sakuma, S.; Miyaura, N. *J. Org. Chem.* **2001**, *66*, 8944-8946



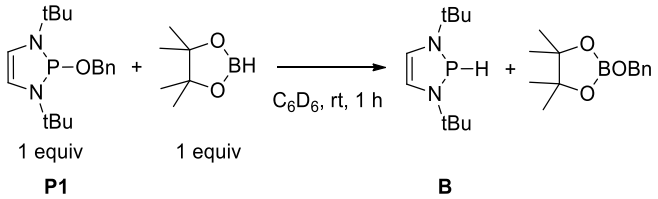
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.612	BV	0.3737	1.42444e4	590.01160	49.7871
2	16.693	VB	0.4111	1.43662e4	545.72601	50.2129



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.091	BV	0.3641	4576.25488	196.21973	31.1578
2	16.098	VB	0.3839	1.01111e4	409.69690	68.8422

Stoichiometric NMR experiments

A)

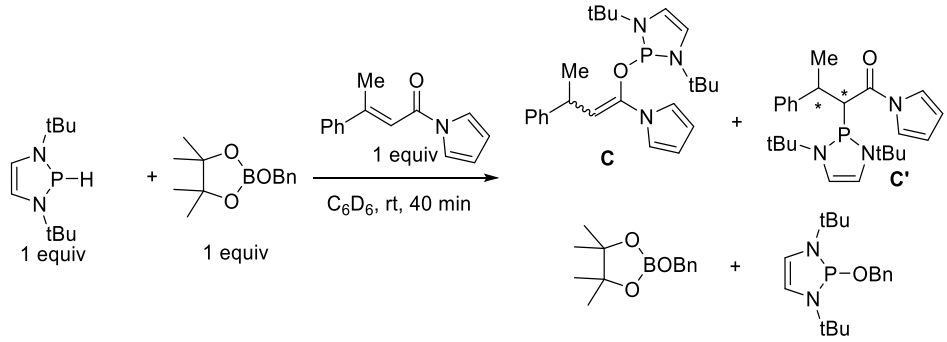


t_1 - A Young's NMR tube was filled with 2-(benzyloxy)-1,3-di-tert-butyl-2,3-dihydro-1*H*-1,3,2-diazaphosphole **P1** (0.030 g, 0.100 mmol) (weighed as a solid in the glovebox), C_6D_6 (0.4 mL) and 2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (added as a pure liquid using a Hamilton syringe).

The formation of active catalyst species **B** (doublet at 57.5 ppm) was monitored by ^{31}P NMR on a 400 MHz spectrometer, along with the disappearance of **P1** (Singlet at 93.03 ppm).

t_2 (= t_1 + 1 h) - The reaction appeared to be complete after 1 hour, so 1 equivalent of (*E*)-3-phenyl-1-(1*H*-pyrrol-1-yl)but-2-en-1-one **1a** (0.021 g, 0.101 mmol) previously dissolved in 0.1 mL of C_6D_6 was added to the tube inside the glovebox.

Monitoring of the reaction by ^{31}P NMR showed appearance of 4 new signals at 96.6, 98.6, 108.3 and 113.2 ppm respectively.



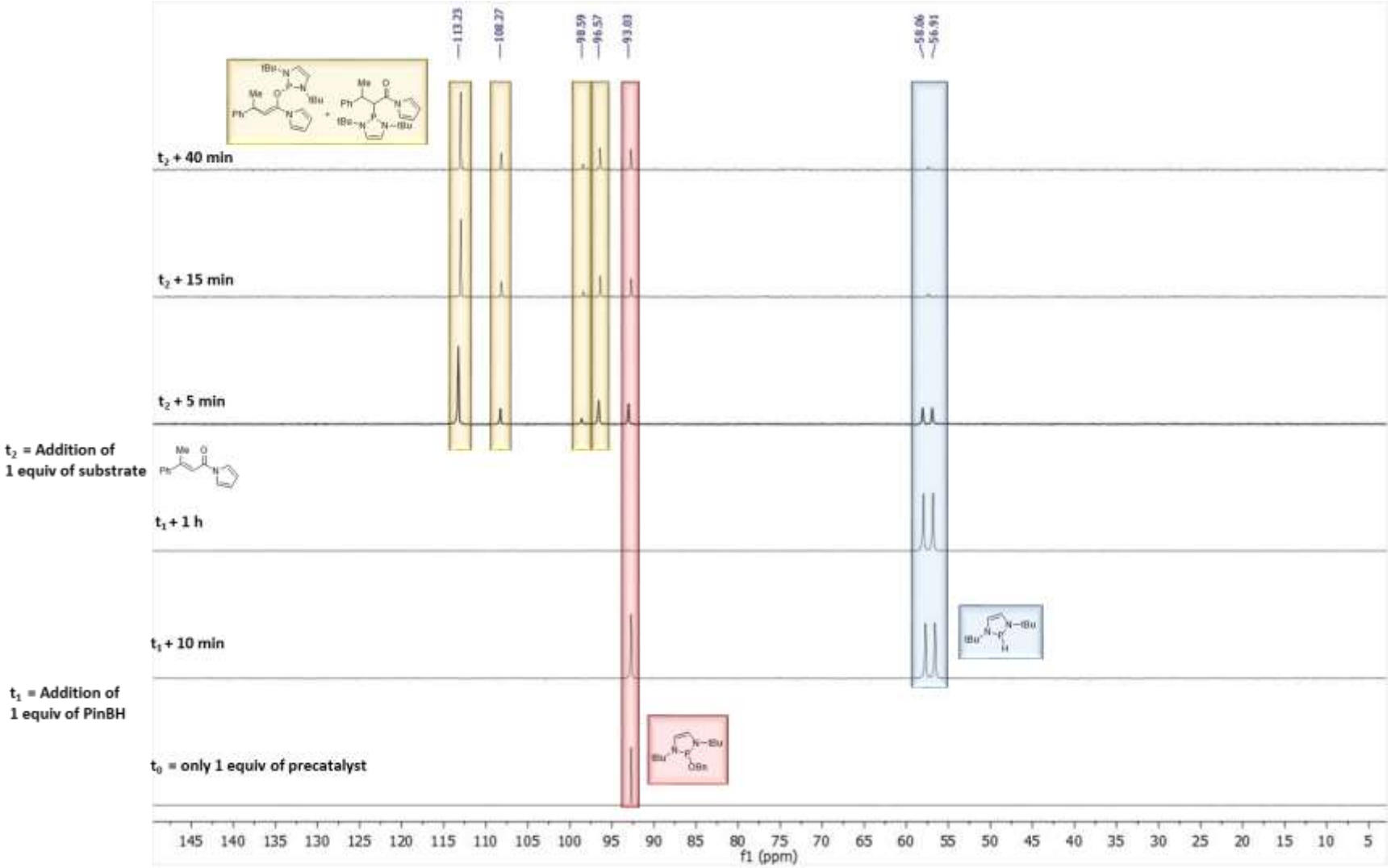
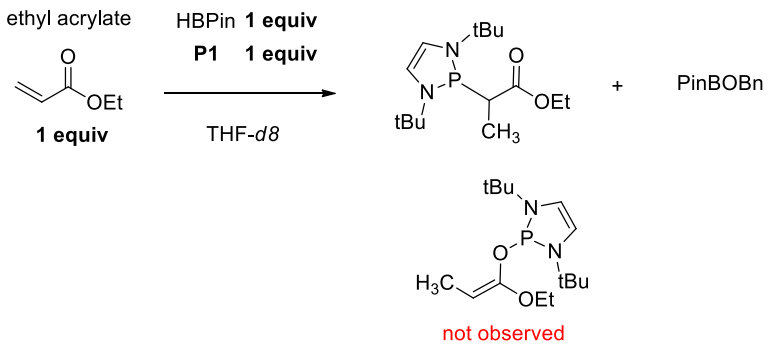
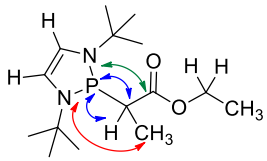


Figure S1 – ^{31}P NMR spectra of a stoichiometric NMR experiment in C_6D_6 between **P1** and PinBH. Addition of model substrate **1a**

B) To support the formation of the proposed intermediate C', a stoichiometric NMR experiment has been performed on the simpler ethyl acrylate substrate.





	^{1}H NMR	^{13}C NMR
J P-**CH** (Hz)	1.5	30.2
J P-**CH**3 (Hz)	14.2	17.9
J P-**C**(O)OEt (Hz)	-	8.2

A Young's NMR tube was filled with 2-(benzyloxy)-1,3-di-tert-butyl-2,3-dihydro-1*H*-1,3,2-diazaphosphole **P1** (0.030 g, 0.100 mmol) (weighed as a solid in the glovebox), THF-*d*8 (0.4 mL) and 2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (added as a pure liquid using a Hamilton syringe). The formation of active catalyst species **B** was monitored by ^{31}P NMR and occurred concurrently with the disappearance of **P1**. After 1 hour, the reaction had reached completion and 1 equivalent of ethyl acrylate was added to the tube. A single new resonance was observed to form in the ^{31}P NMR spectrum at 93.95 ppm as the active catalyst was consumed (Figure S2). This intermediate was further characterized by ^{1}H NMR and ^{13}C NMR (Figure S3 and S4), and the resonances in these spectra were assigned on the basis of a 2-D HSQC experiment (Figure S5). Owing to the P-C and P-H coupling constants (See table above) and the lack of a resonance in the ^{1}H proton spectrum corresponding to an alkenyl proton, we believe that this species is the C-bound phosphorous enolate. Extrapolating this result to the experiment described above led us to the conclusion that the four species observed in the ^{31}P spectrum might correspond to the diastereomeric O- and C-bound phosphorous enolates.

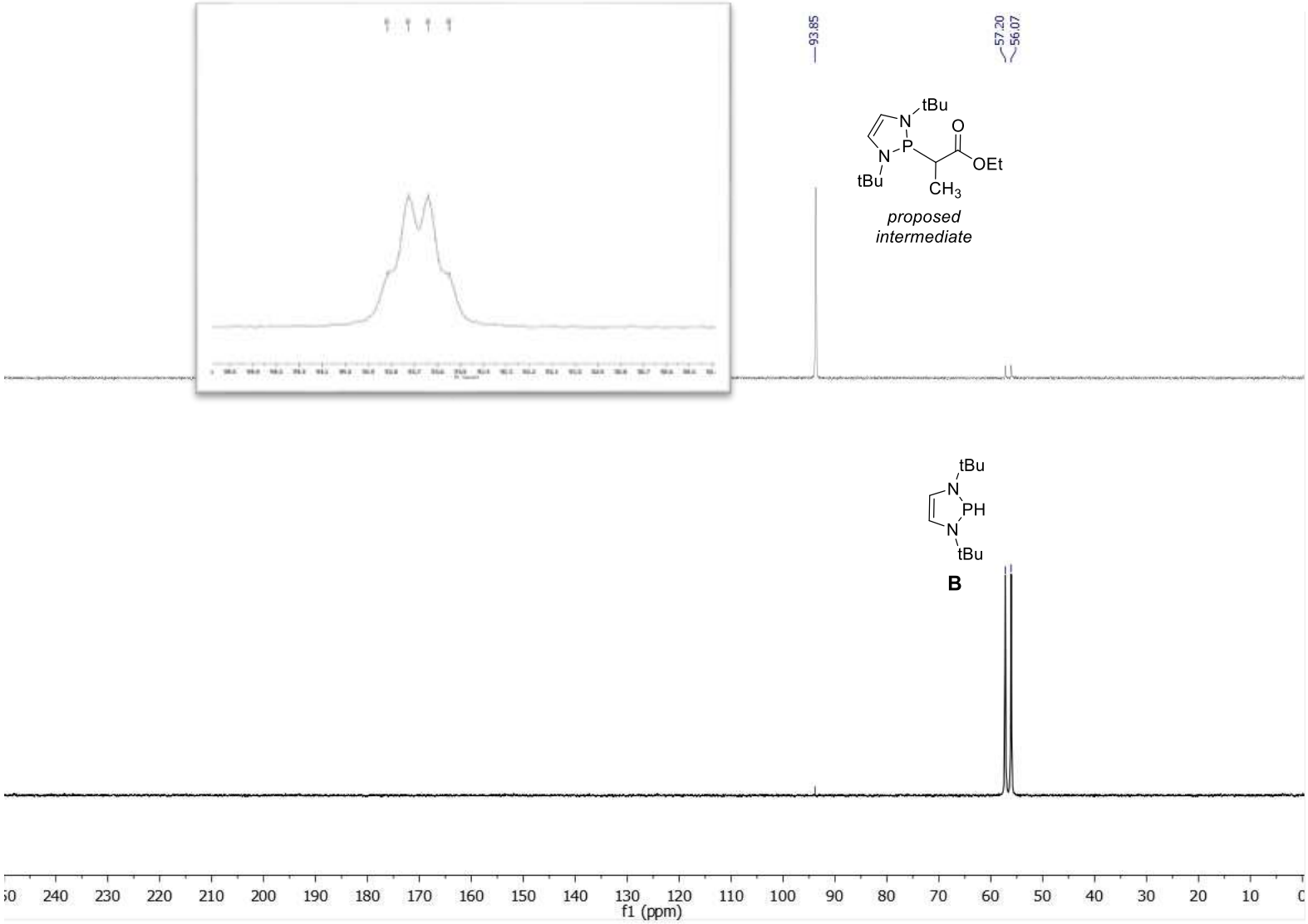


Figure S2 – ^{31}P NMR spectra of stoichiometric NMR experiment between ethyl acrylate and PinBH in THF-*d8*.

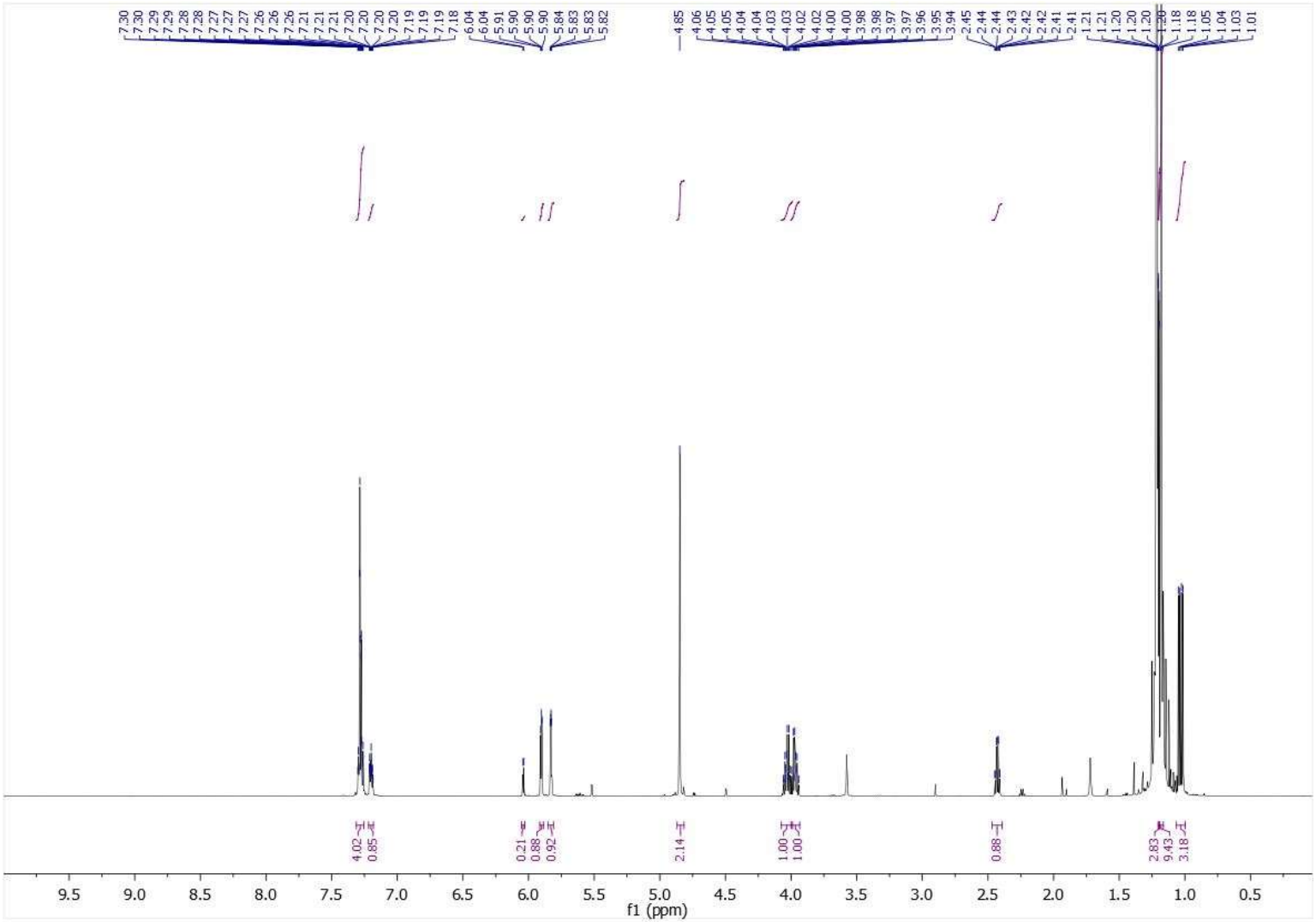


Figure S3 – ^{1}H NMR spectra of stoichiometric NMR experiment between ethyl acrylate and **B** in THF-*d8*.

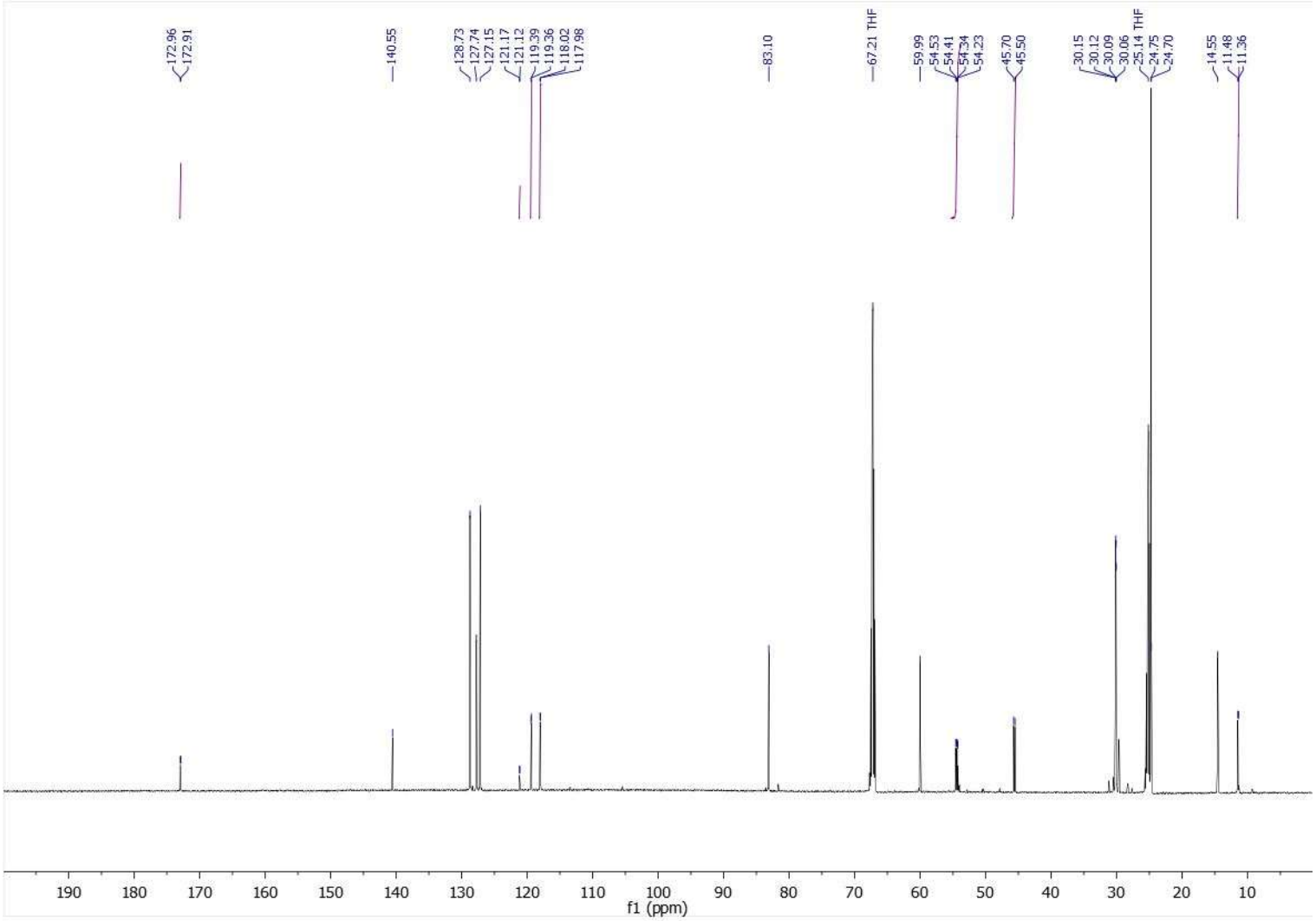


Figure S4 – ^{13}C NMR spectra of stoichiometric NMR experiment between ethyl acrylate and **B** in THF-*d8*.

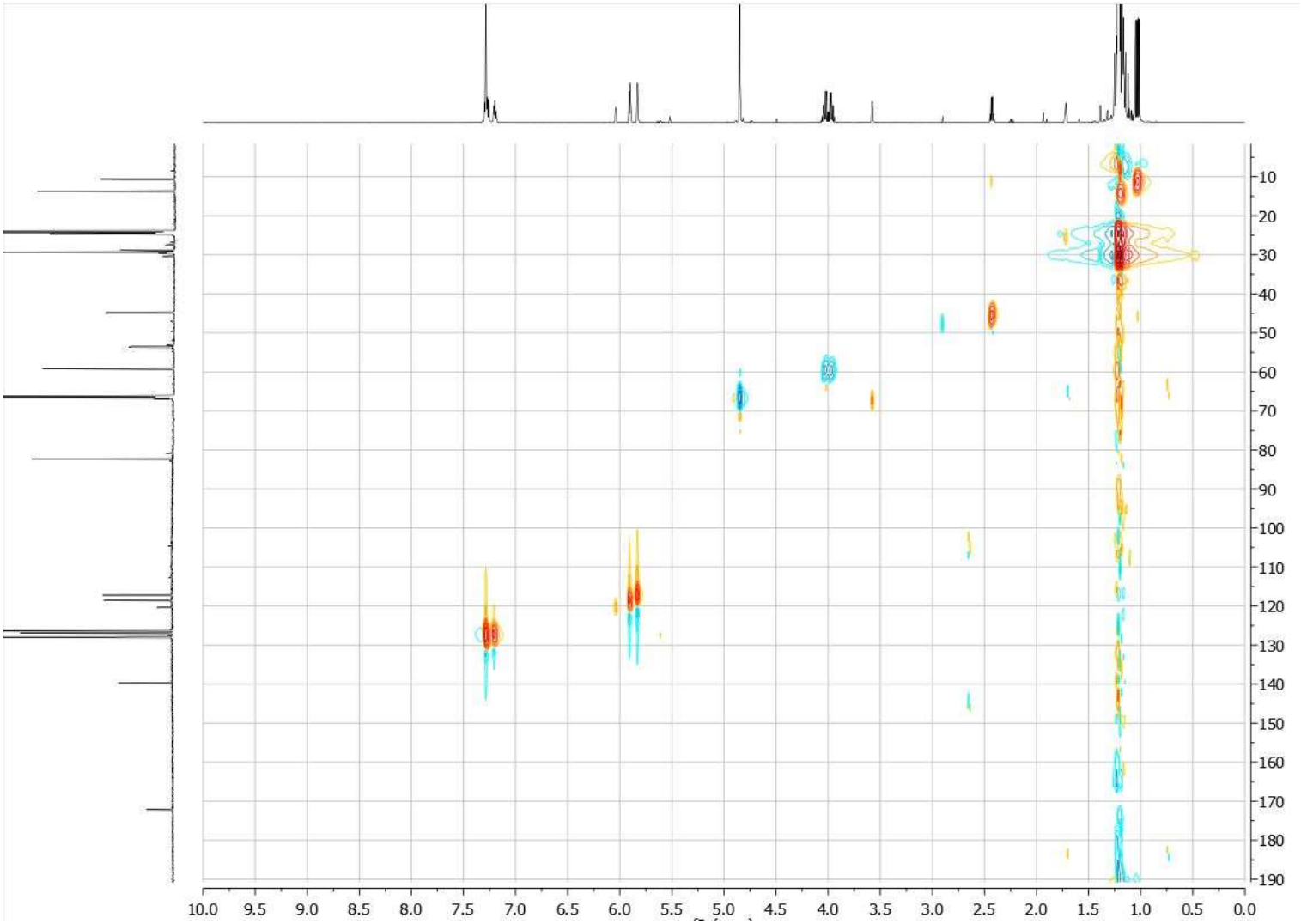
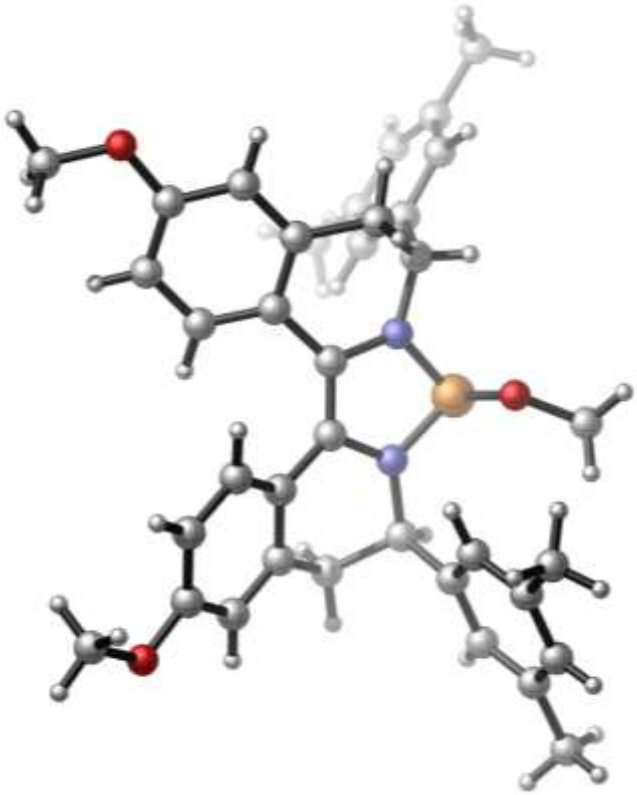


Figure S5 – HSQC spectra of stoichiometric NMR experiment between ethyl acrylate and **B** in THF-*d8*.

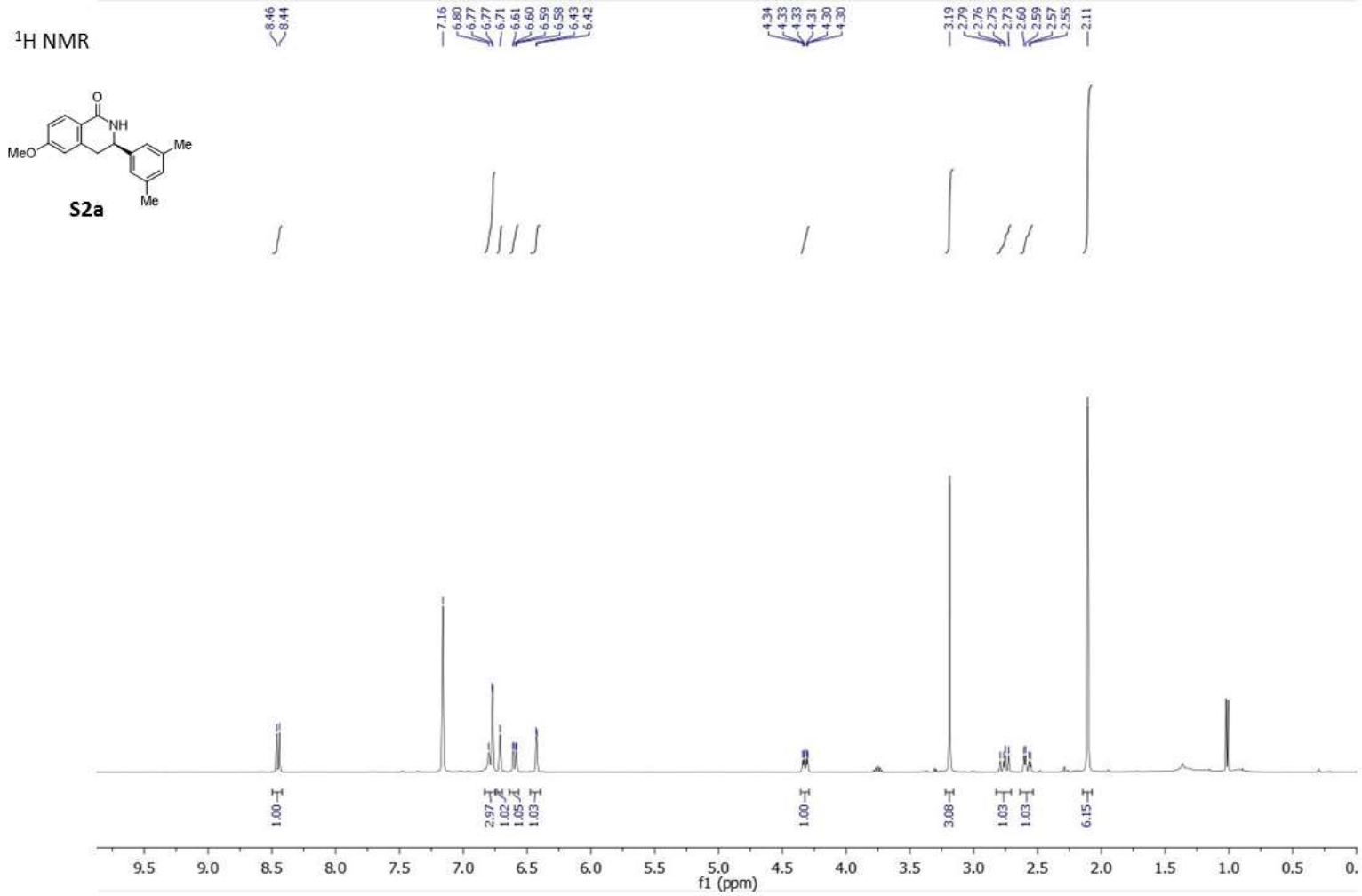
X-ray Crystallographic Data of Catalyst C2-f



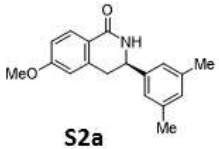
Empirical formula	$C_{37}H_{39}N_2O_3P$	
Formula weight	590.67	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	$P3_12_1$	
Unit cell dimensions	a = 16.71139(14) Å	α = 90°.
	b = 16.71139(14) Å	β= 90°.
	c = 12.95592(12) Å	γ = 120°.
Volume	3133.46(6) $Å^3$	
Z	3	
Density (calculated)	0.939 Mg/m^3	

Absorption coefficient	0.813 mm^{-1}
F(000)	942
Crystal size	0.240 x 0.090 x 0.076 mm^3
θ range for data collection	4.581 to 76.156°.
Index ranges	$-21 \leq h \leq 20$, $-21 \leq k \leq 20$, $-15 \leq l \leq 16$
Reflections collected	55381
Independent reflections	4357 [R_{int} = 0.0352]
Completeness to θ = 67.684°	99.9 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.800
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4357 / 0 / 208
Goodness-of-fit on F^2	1.058
Final R indices [I>2σ(I)]	R_1 = 0.0259, wR_2 = 0.0731
R indices (all data)	R_1 = 0.0277, wR_2 = 0.0740
Absolute structure parameter	0.005(5)
Largest diff. peak and hole	0.148 and -0.145 e.$Å^{-3}$

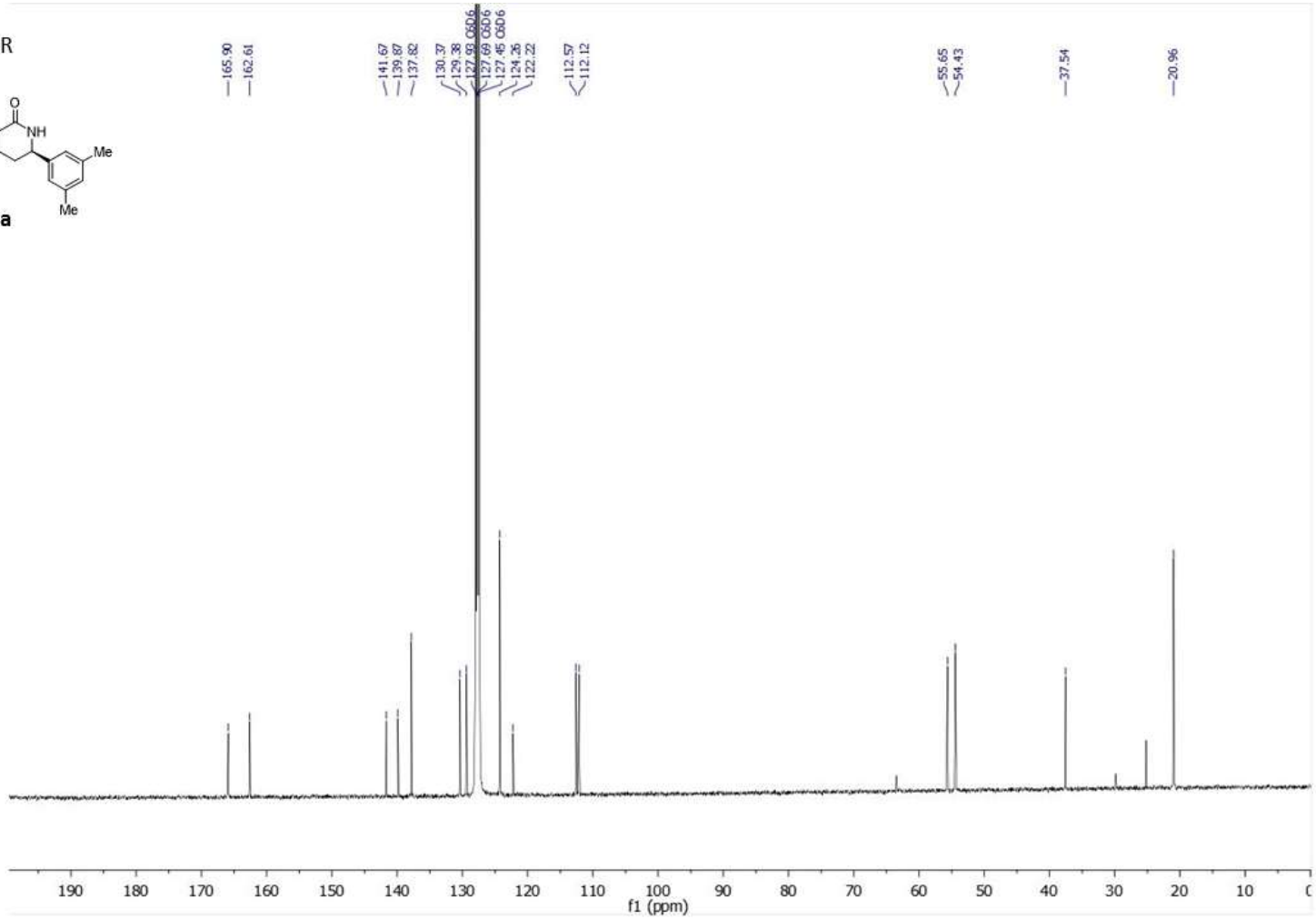
^{1}H, ^{13}C, ^{31}P and ^{19}F NMR Spectra



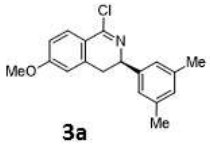
^{13}C NMR


O
NH
MeO
Me
Me

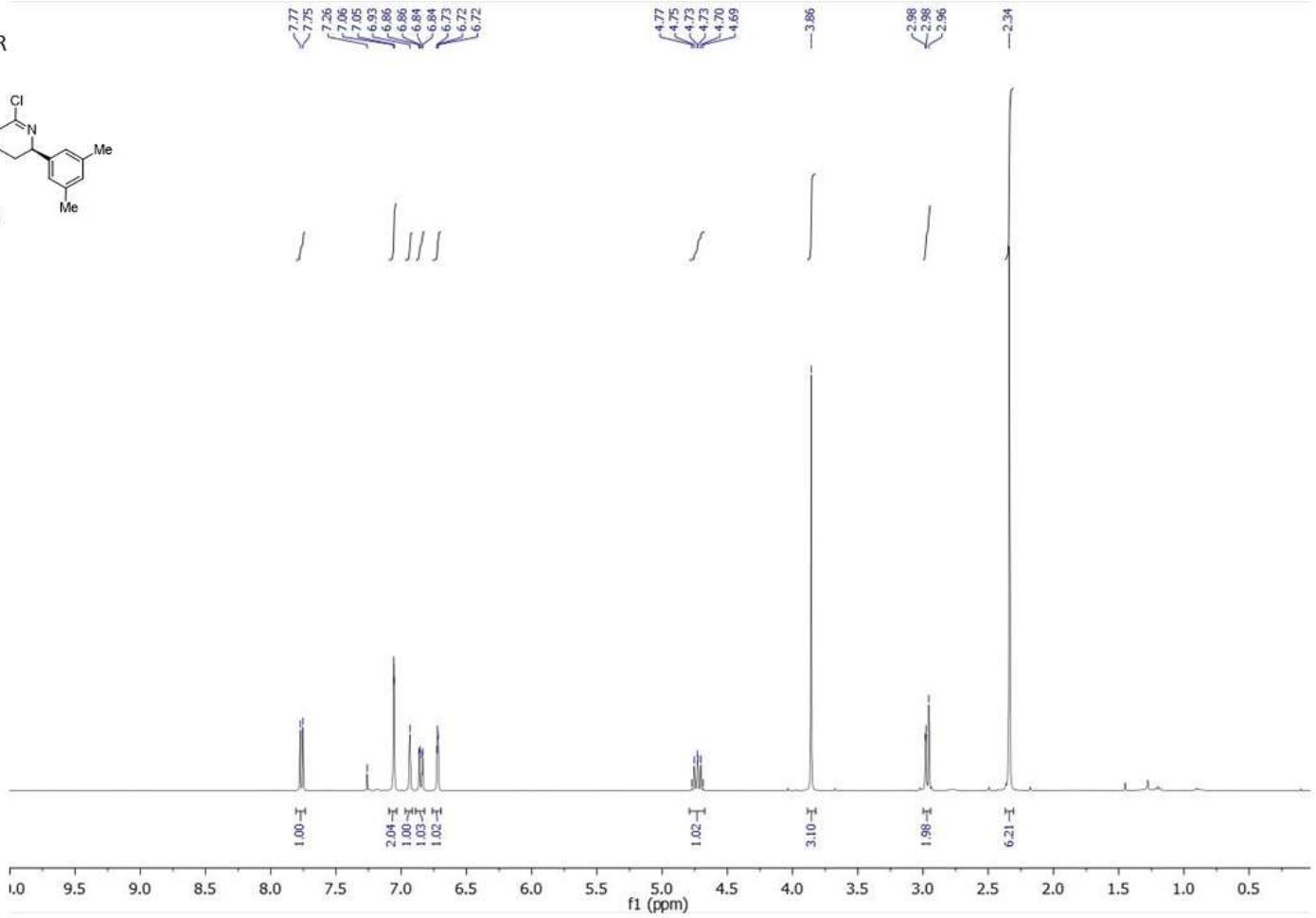
S2a


165.90
162.61
141.67
139.87
137.82
130.37
129.38
127.93 C6D6
127.69 C6D6
127.45 C6D6
124.26
122.22
112.57
112.12
55.65
54.43
37.54
20.96
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

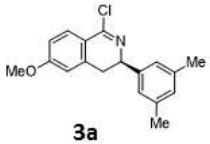
^{1}H NMR


Cl
N
MeO
Me
Me

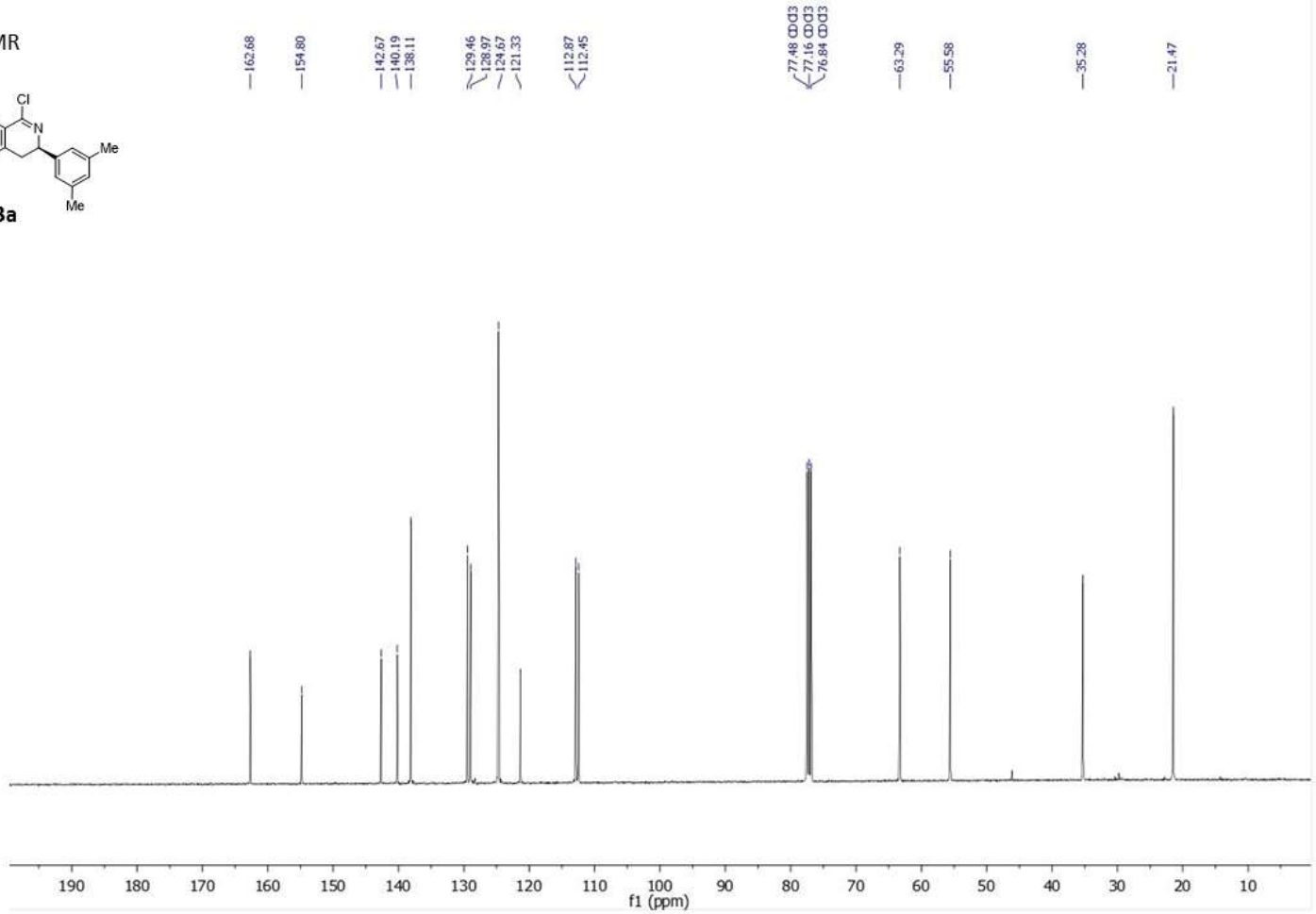
3a


7.77
7.75
7.26
7.06
7.05
6.93
6.86
6.86
6.84
6.84
6.73
6.72
6.72
4.77
4.75
4.73
4.73
4.70
4.69
3.86
2.98
2.98
2.96
2.34
1.00
2.04
1.00
1.03
1.02
1.02
3.10
1.98
6.21
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
f1 (ppm)

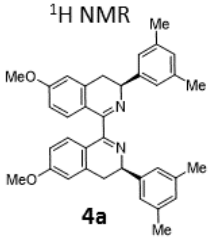
^{13}C NMR


Cl
N
MeO
Me
Me

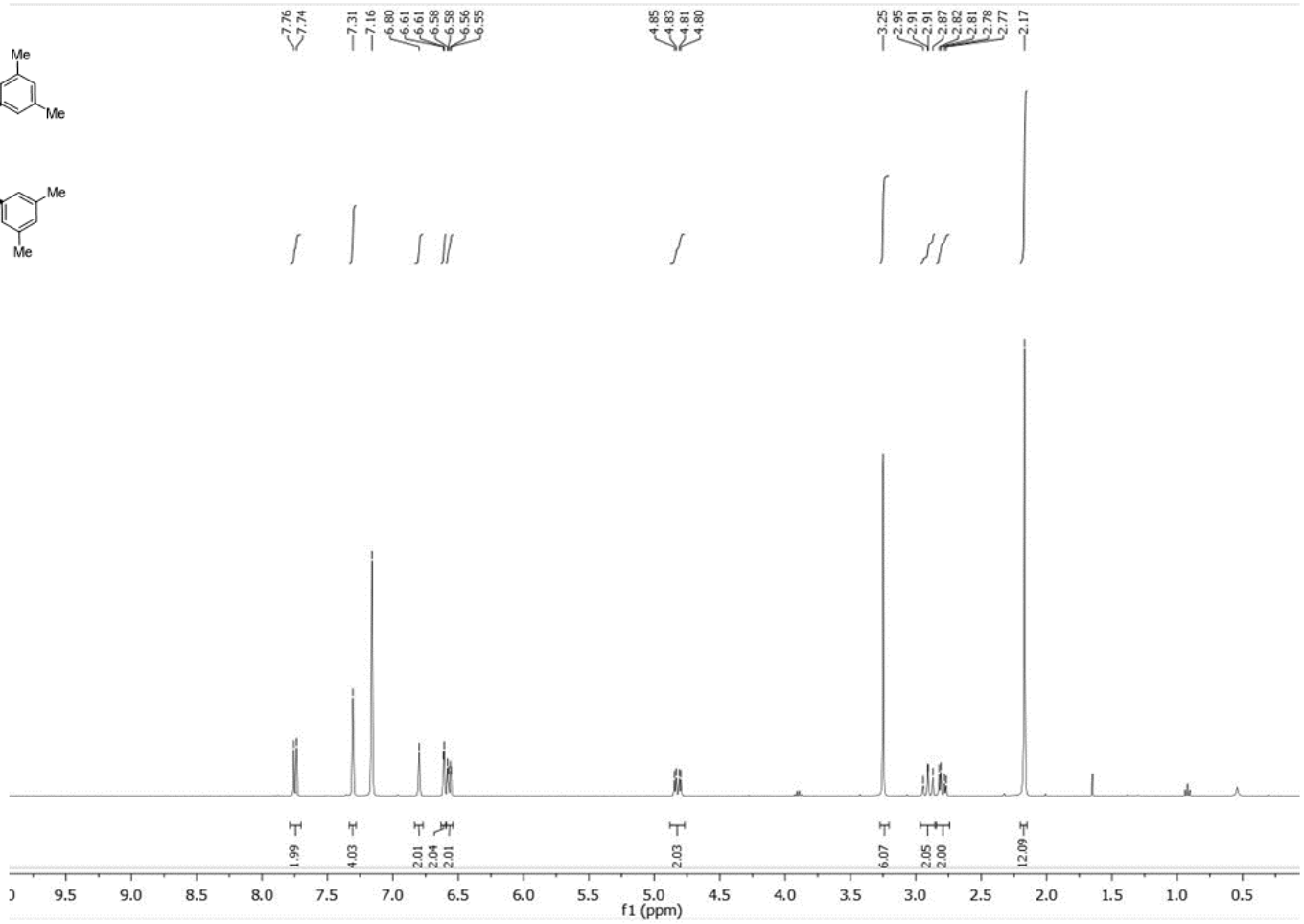
3a

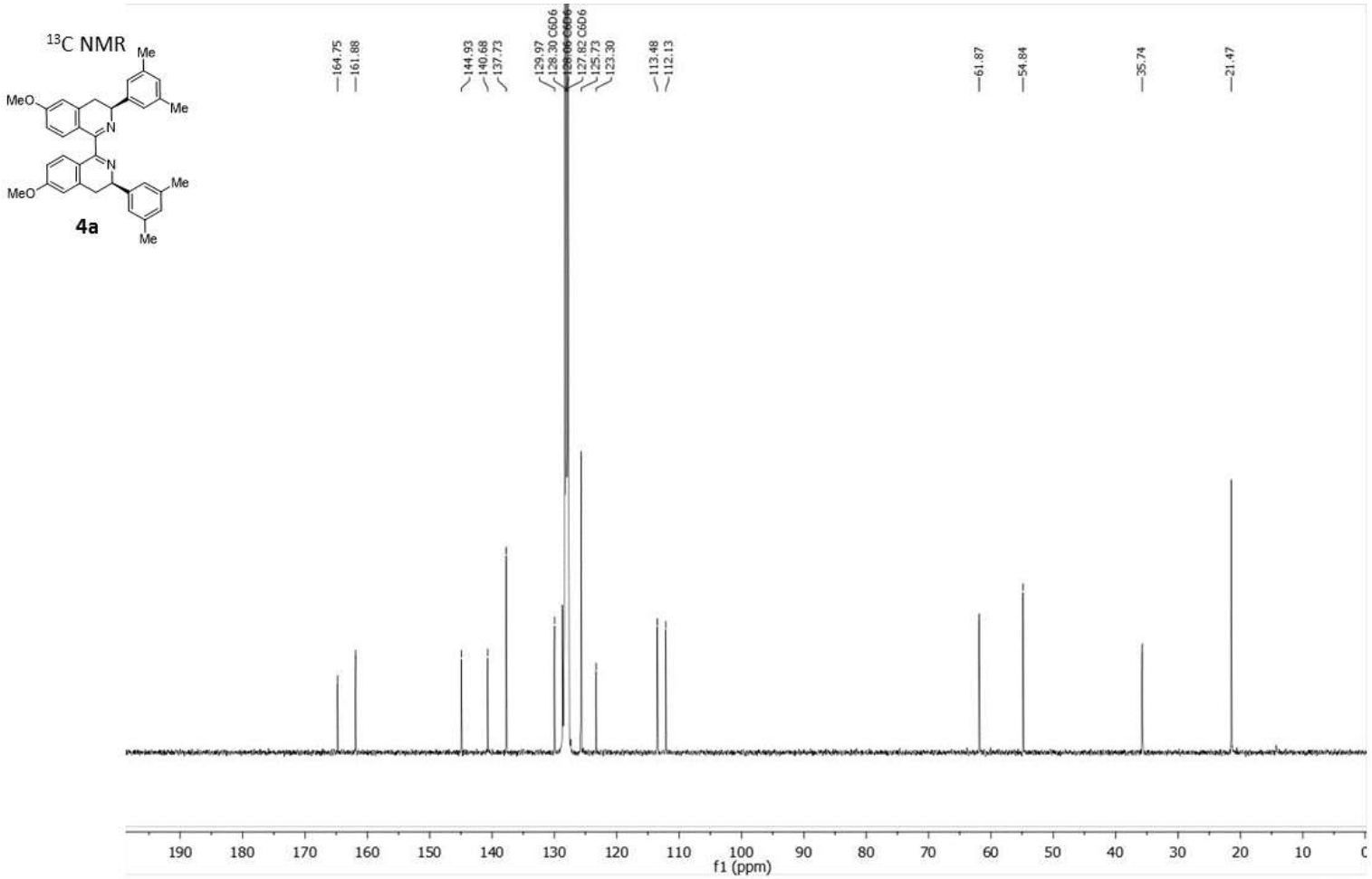

162.68
154.80
142.67
140.19
138.11
129.46
128.97
124.67
121.33
112.87
112.45
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.29
55.58
35.28
21.47
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

^{1}H NMR

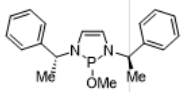

Me
MeO
Me
N
N
MeO
Me
Me

4a

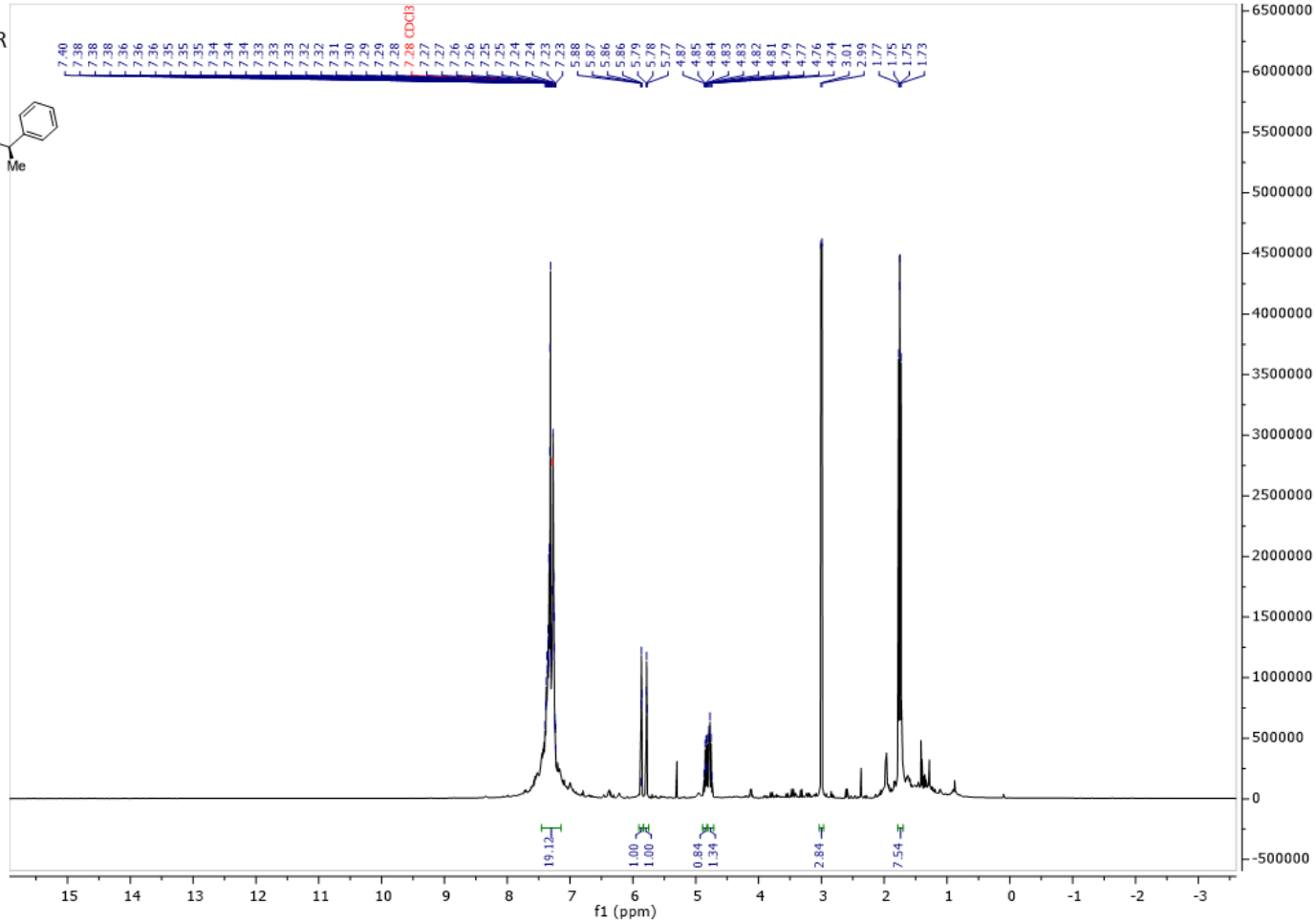

7.76
7.74
7.31
7.16
6.80
6.61
6.61
6.58
6.58
6.56
6.55
4.85
4.83
4.81
4.80
3.25
2.95
2.91
2.91
2.87
2.82
2.81
2.78
2.77
2.17
1.99
4.03
2.01
2.04
2.01
2.03
6.07
2.05
2.00
12.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


13C NMR
4a
MeO
MeO
Me
Me
Me
Me
N
N
164.75
161.88
144.93
140.68
137.73
129.97
128.30 C6D6
128.06 C6D6
127.82 C6D6
125.73
123.30
113.48
112.13
61.87
54.84
35.74
21.47
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

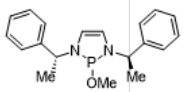
^{1}H NMR



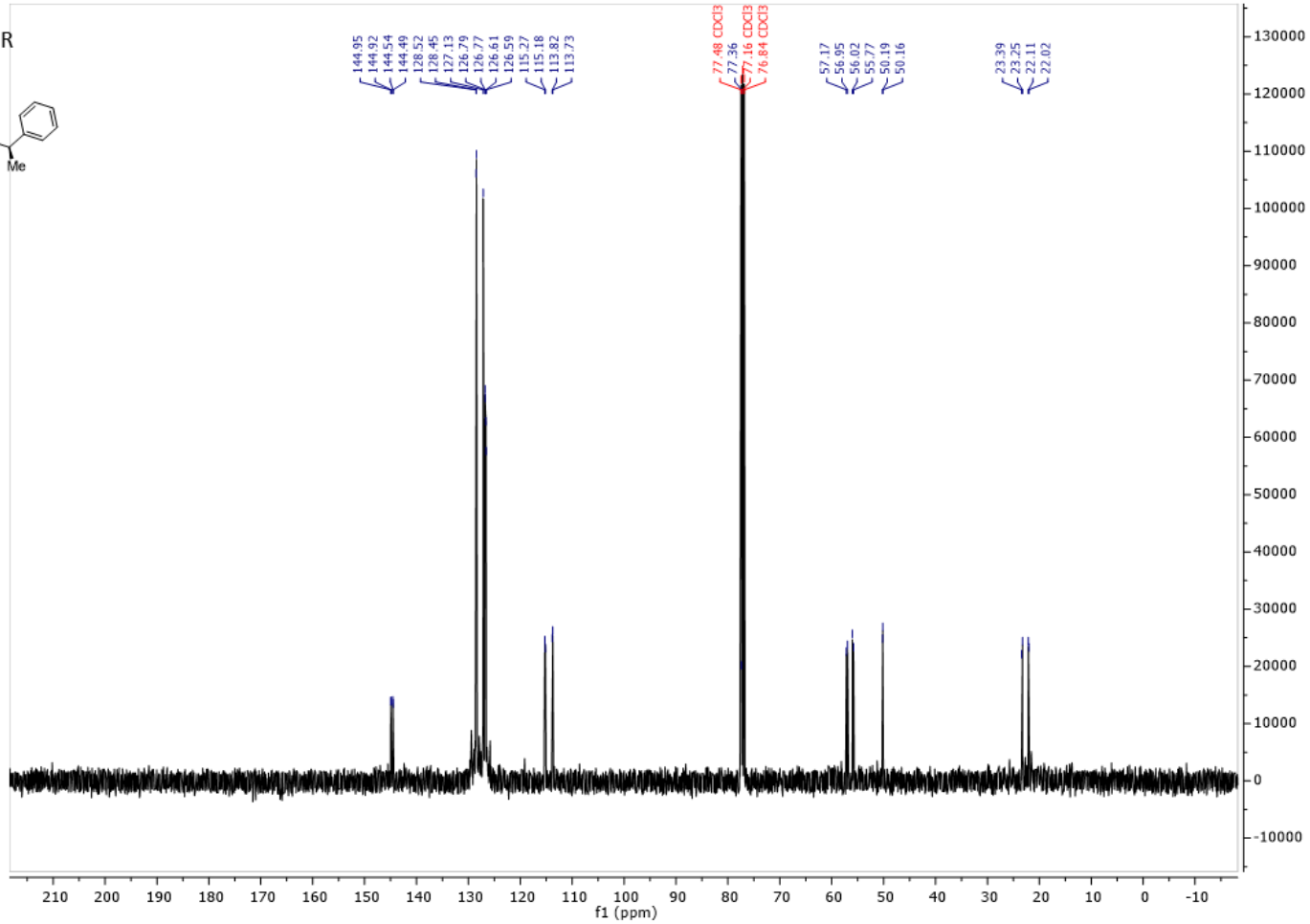
P2



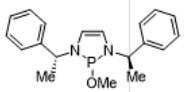
^{13}C NMR


Me
N
P
N
OMe
Me

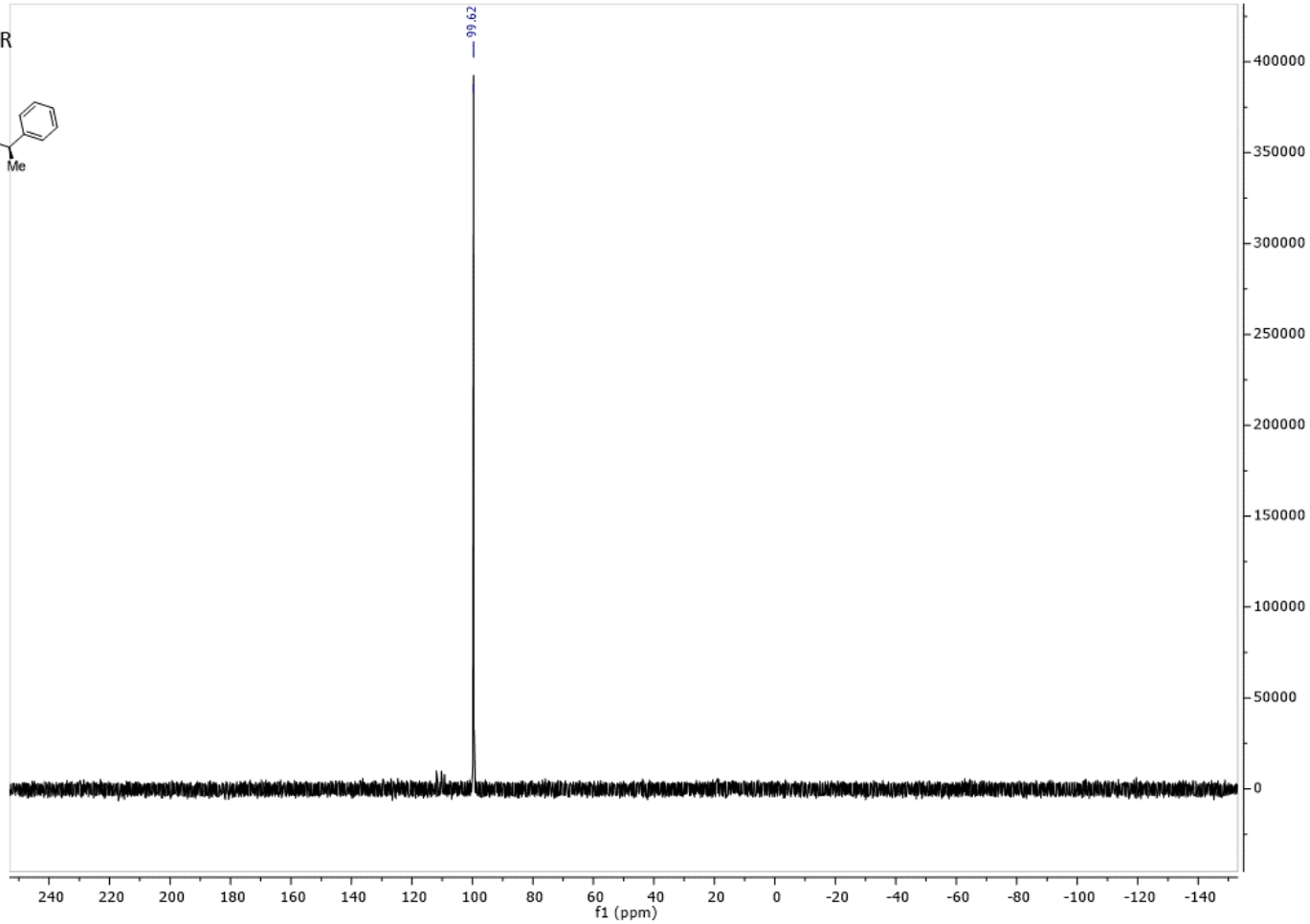
P2


144.95
144.92
144.54
144.49
128.52
128.45
127.13
126.79
126.77
126.61
126.59
115.27
115.18
113.82
113.73
77.48 CDCl3
77.36
77.16 CDCl3
76.84 CDCl3
57.17
56.95
56.02
55.77
50.19
50.16
23.39
23.25
22.11
22.02
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

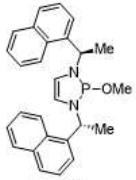
^{31}P NMR


Me
N
P
N
OMe
Me

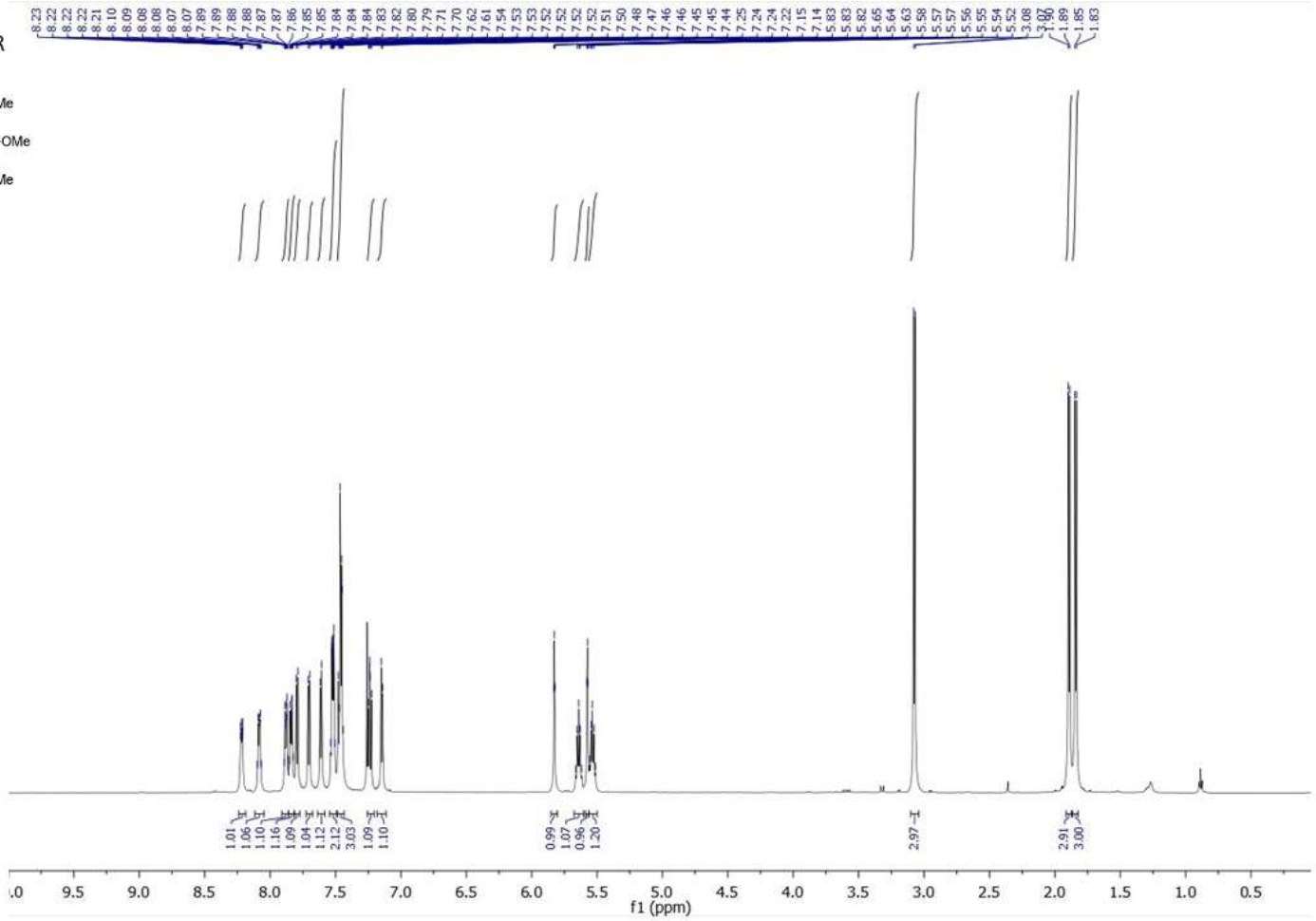
P2


99.62
400000
350000
300000
250000
200000
150000
100000
50000
0
240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140
f1 (ppm)

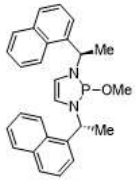
^{1}H NMR



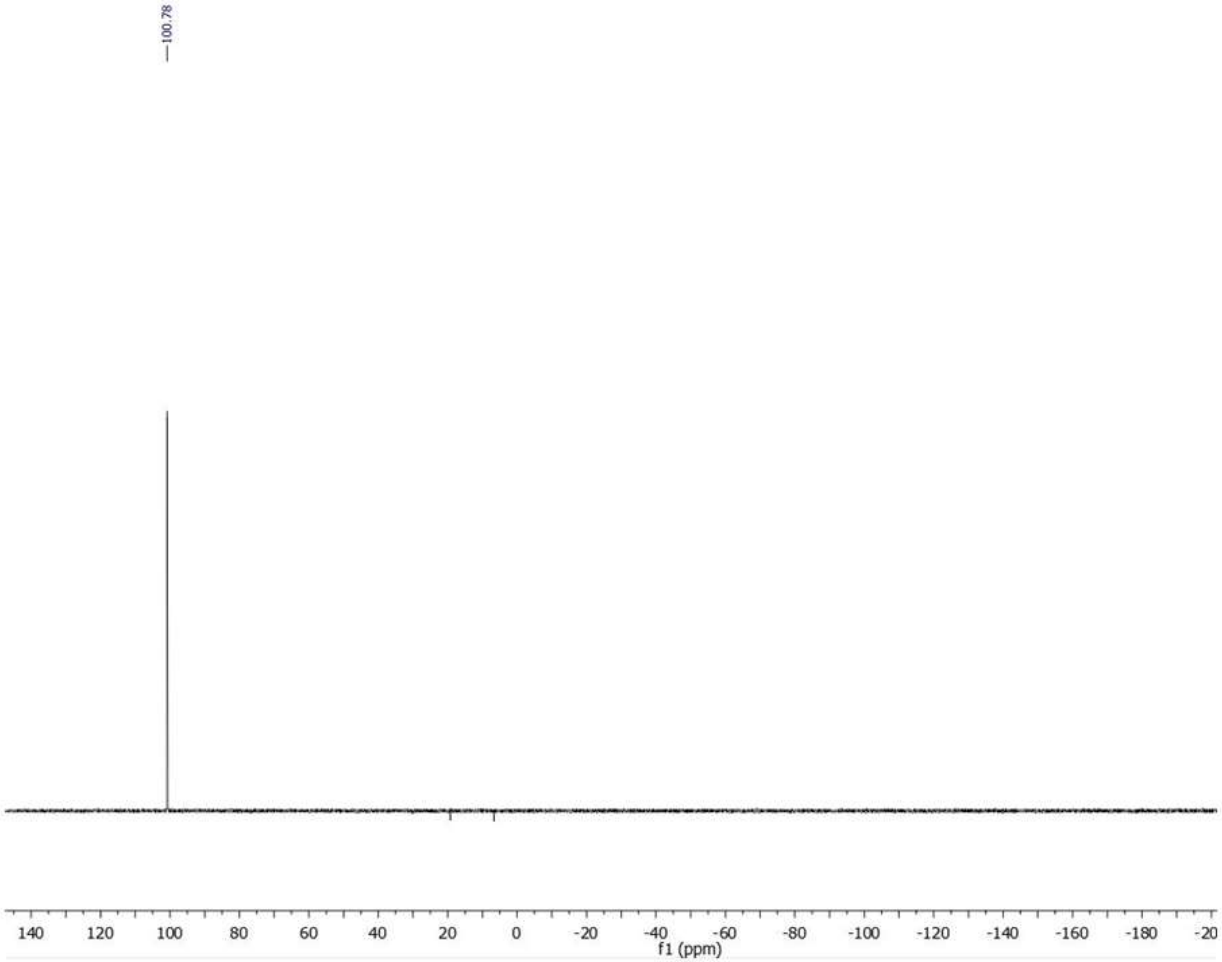
P3



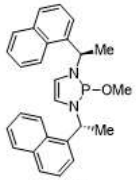
^{31}P NMR


Me
N
P–OMe
N
Me

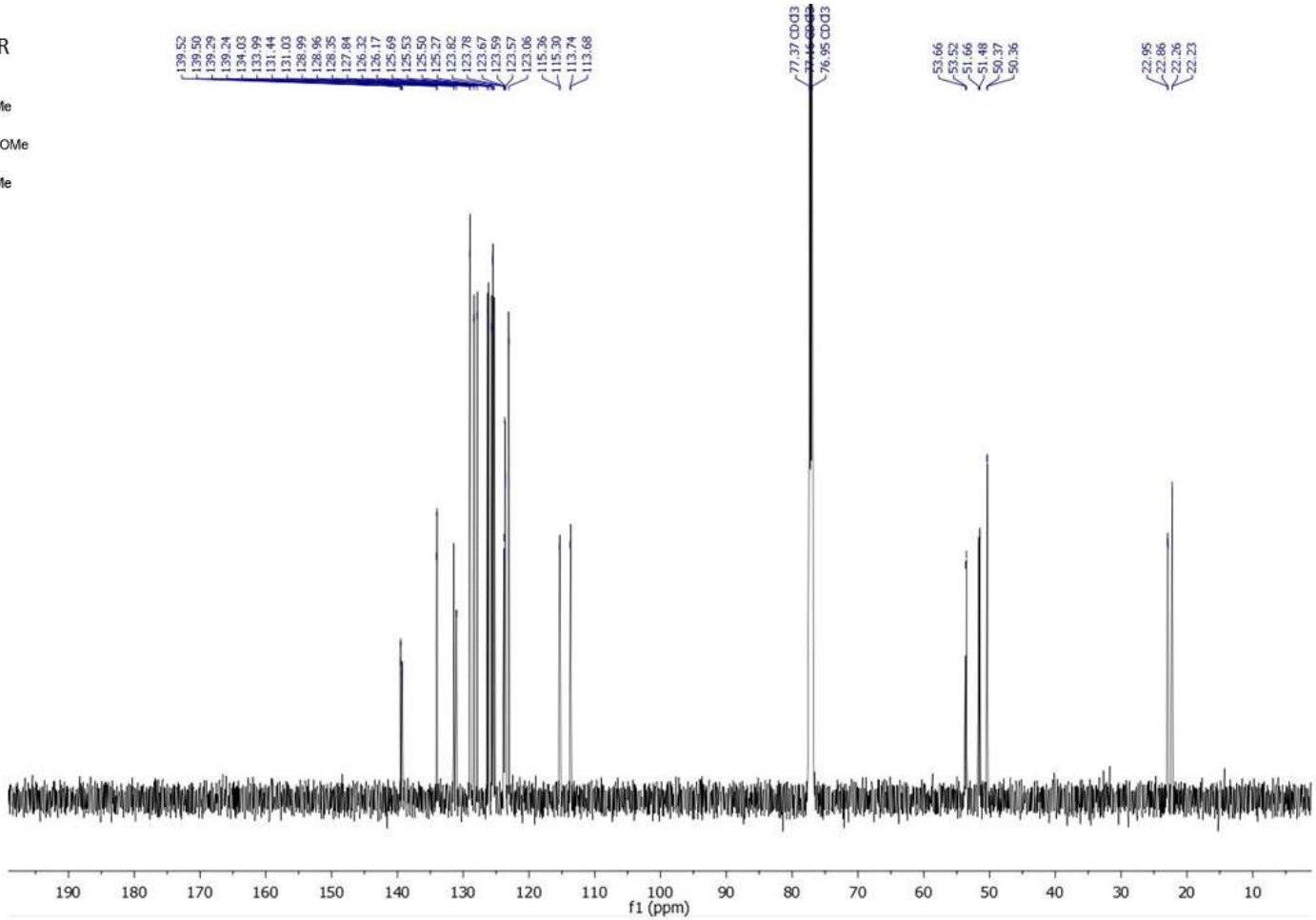
P3


100.78
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-20
f1 (ppm)

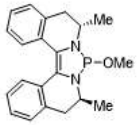
^{13}C NMR


Me
N
P–OMe
N
Me

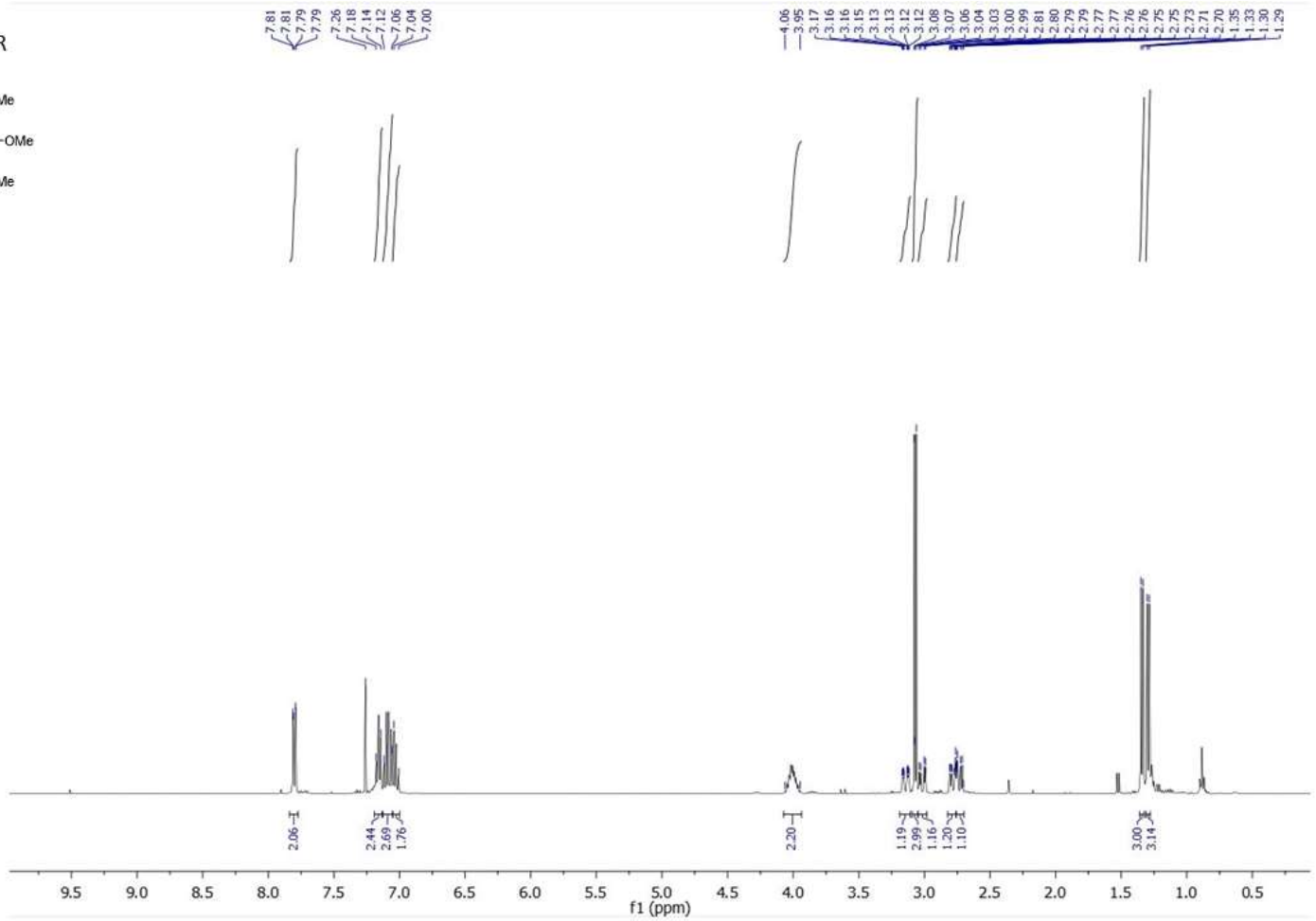
P3


139.52
139.50
139.29
139.24
134.03
133.99
131.44
131.03
128.99
128.96
128.35
127.84
126.32
126.17
125.69
125.53
125.50
125.27
123.82
123.78
123.67
123.59
123.57
123.06
115.36
115.30
113.74
113.68
77.37 CDCl3
76.95 CDCl3
53.66
53.52
51.66
51.48
50.37
50.36
22.95
22.86
22.26
22.23
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

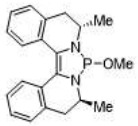
^{1}H NMR


Me
N
P–OMe
N
Me

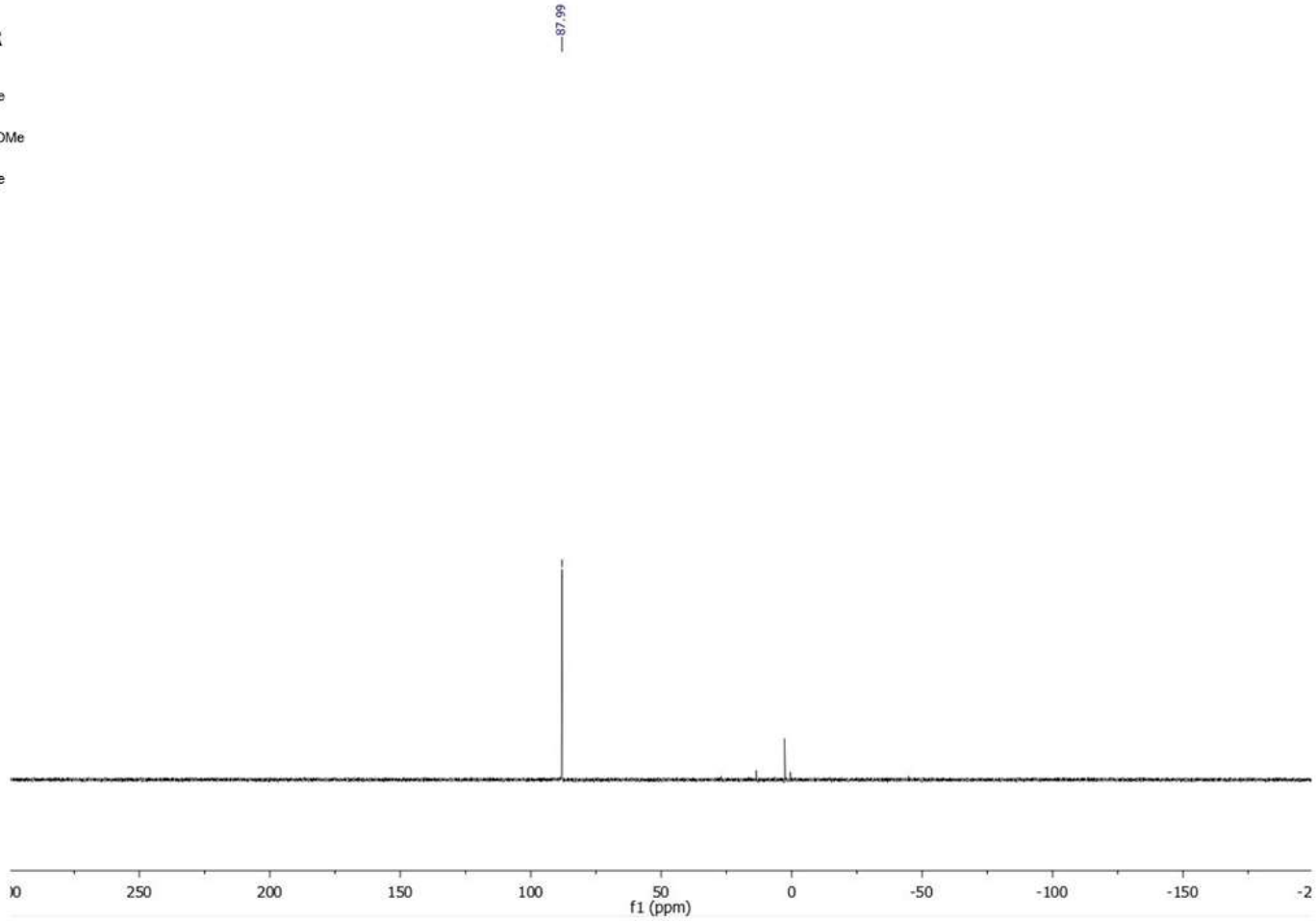
P4


7.81
7.81
7.79
7.79
7.26
7.18
7.14
7.12
7.06
7.04
7.00
4.06
3.95
3.17
3.16
3.16
3.15
3.13
3.13
3.12
3.12
3.08
3.07
3.06
3.04
3.03
3.00
2.99
2.81
2.80
2.79
2.79
2.77
2.77
2.76
2.76
2.75
2.75
2.73
2.71
2.70
1.35
1.33
1.30
1.29
2.06
2.44
2.69
1.76
2.20
1.19
2.99
1.16
1.20
1.10
3.00
3.14
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
f1 (ppm)

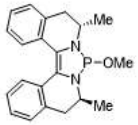
^{31}P NMR



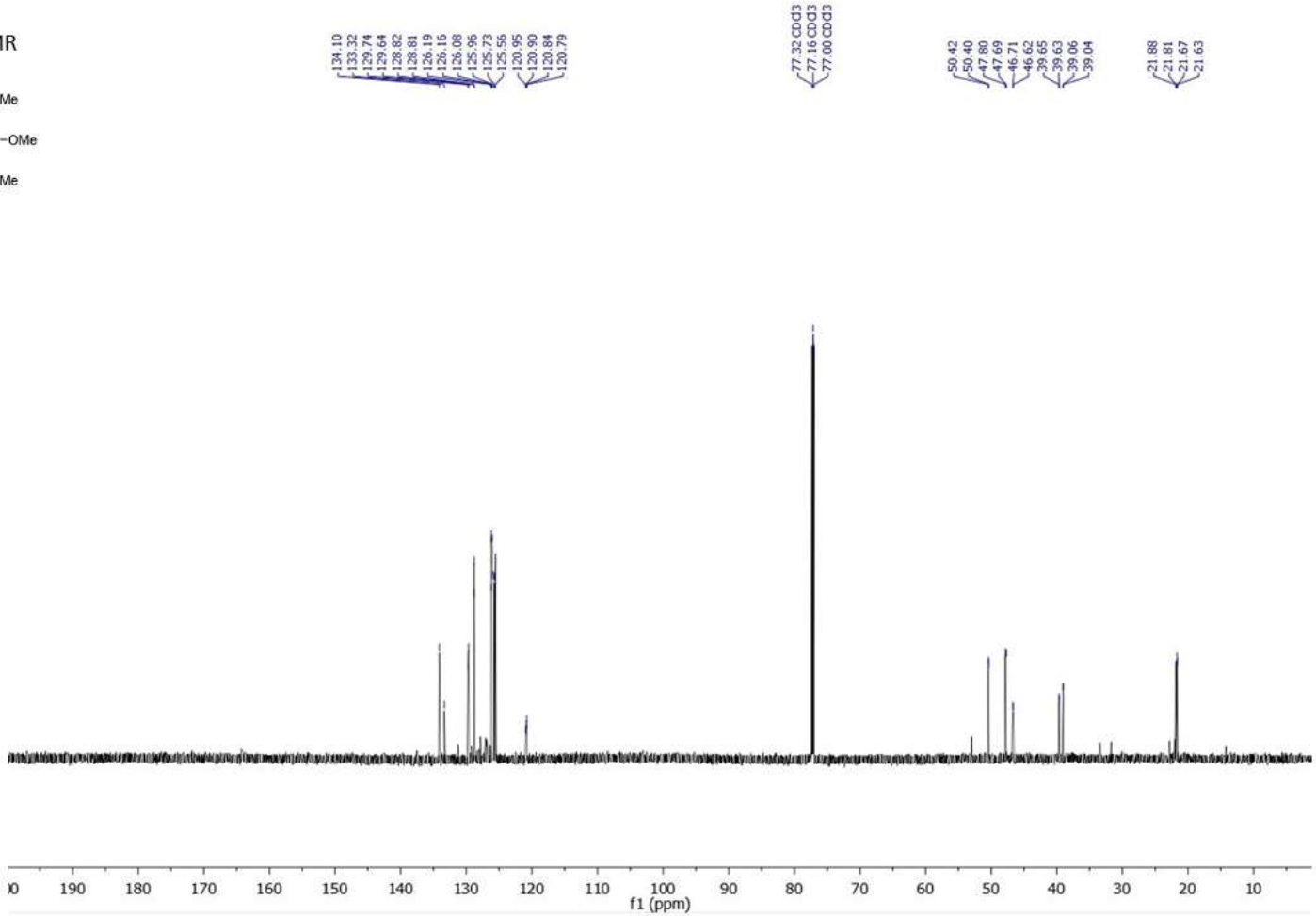
P4



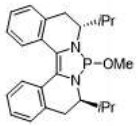
^{13}C NMR


Me
N
P–OMe
N
Me

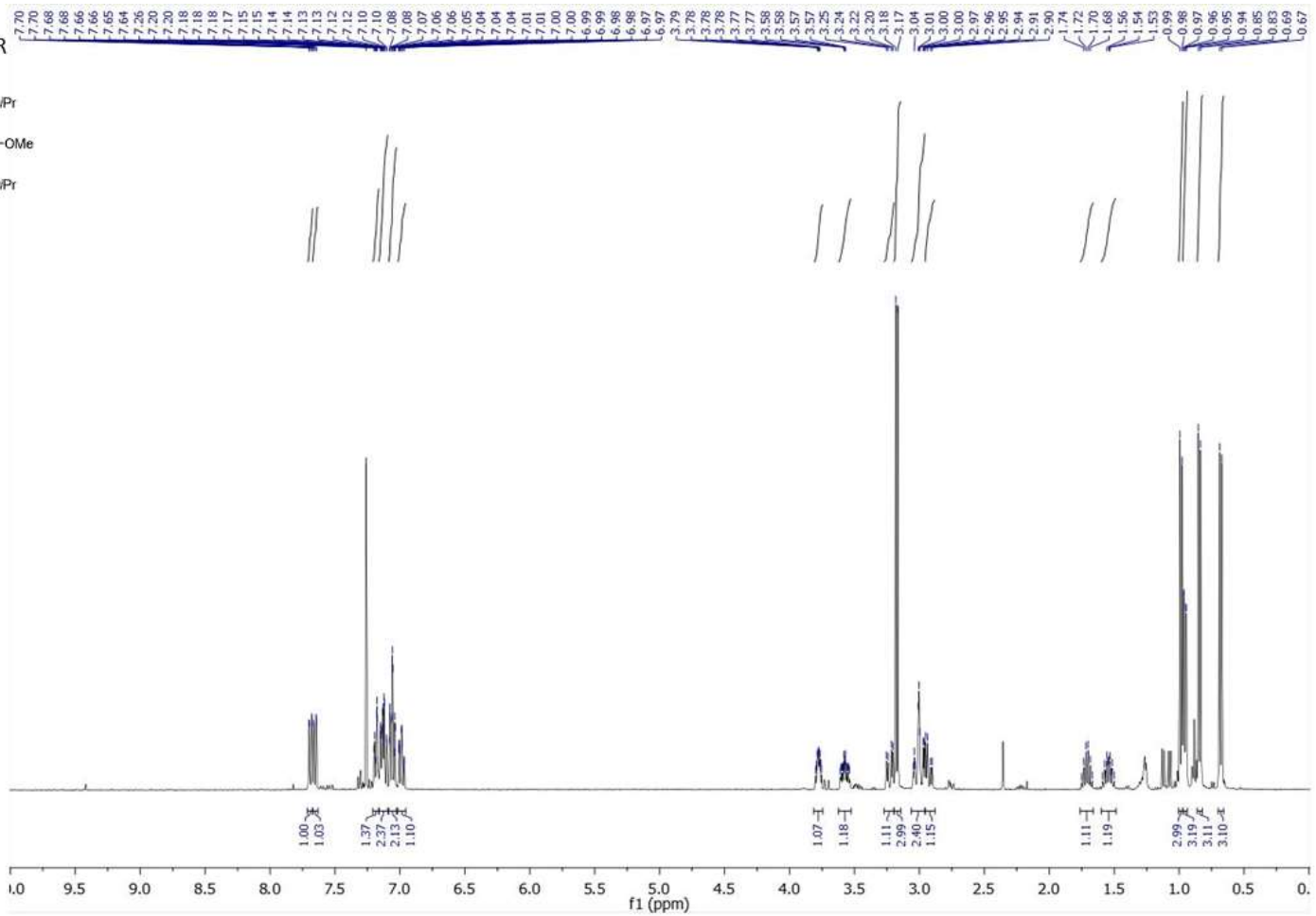
P4


134.10
133.32
129.74
129.64
128.82
128.81
126.19
126.16
126.08
125.96
125.73
125.56
120.95
120.90
120.84
120.79
77.32 CDCl3
77.16 CDCl3
77.00 CDCl3
50.42
50.40
47.80
47.69
46.71
46.62
39.65
39.63
39.06
39.04
21.88
21.81
21.67
21.63
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

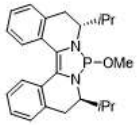
^{1}H NMR



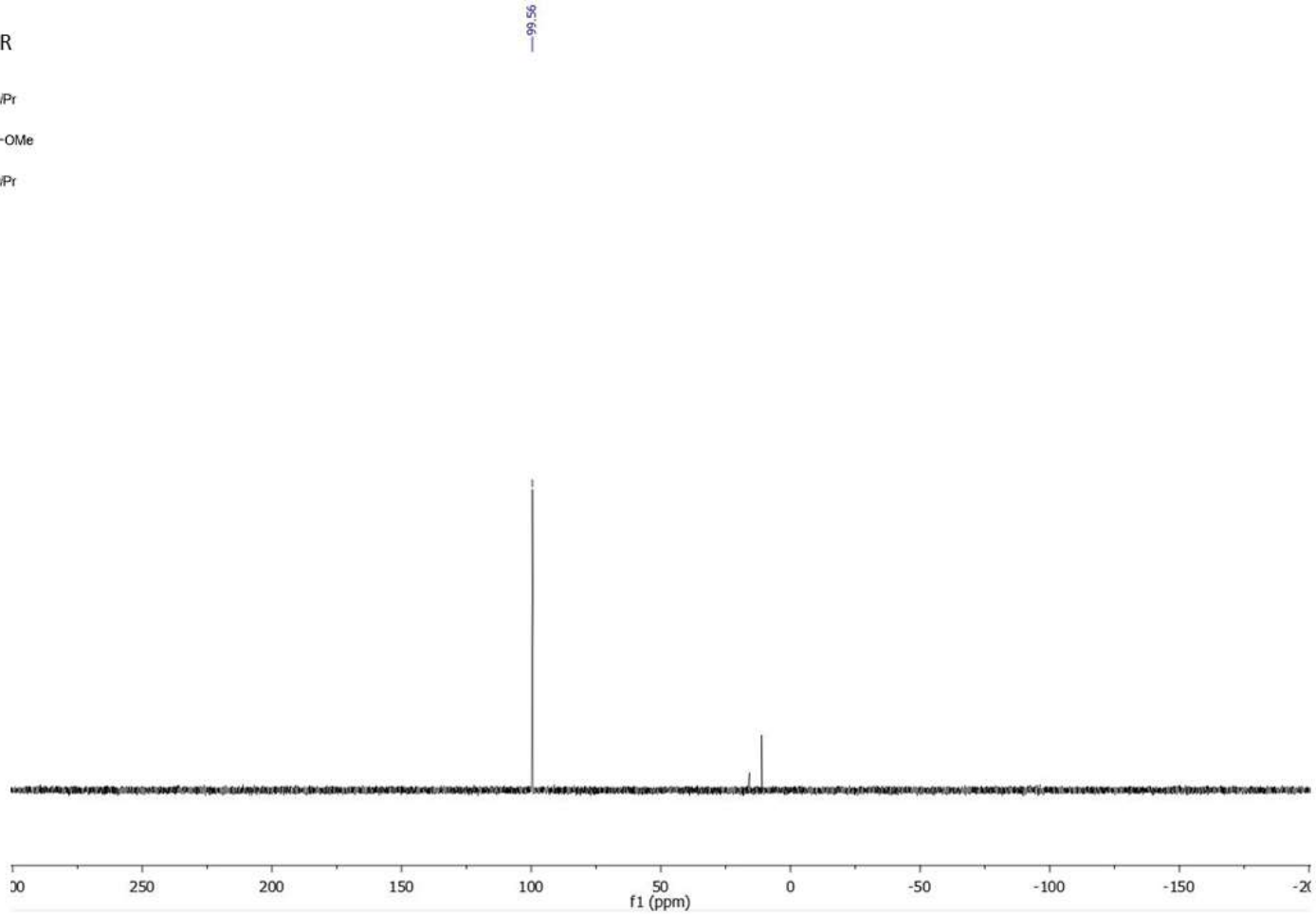
P5



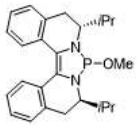
^{31}P NMR



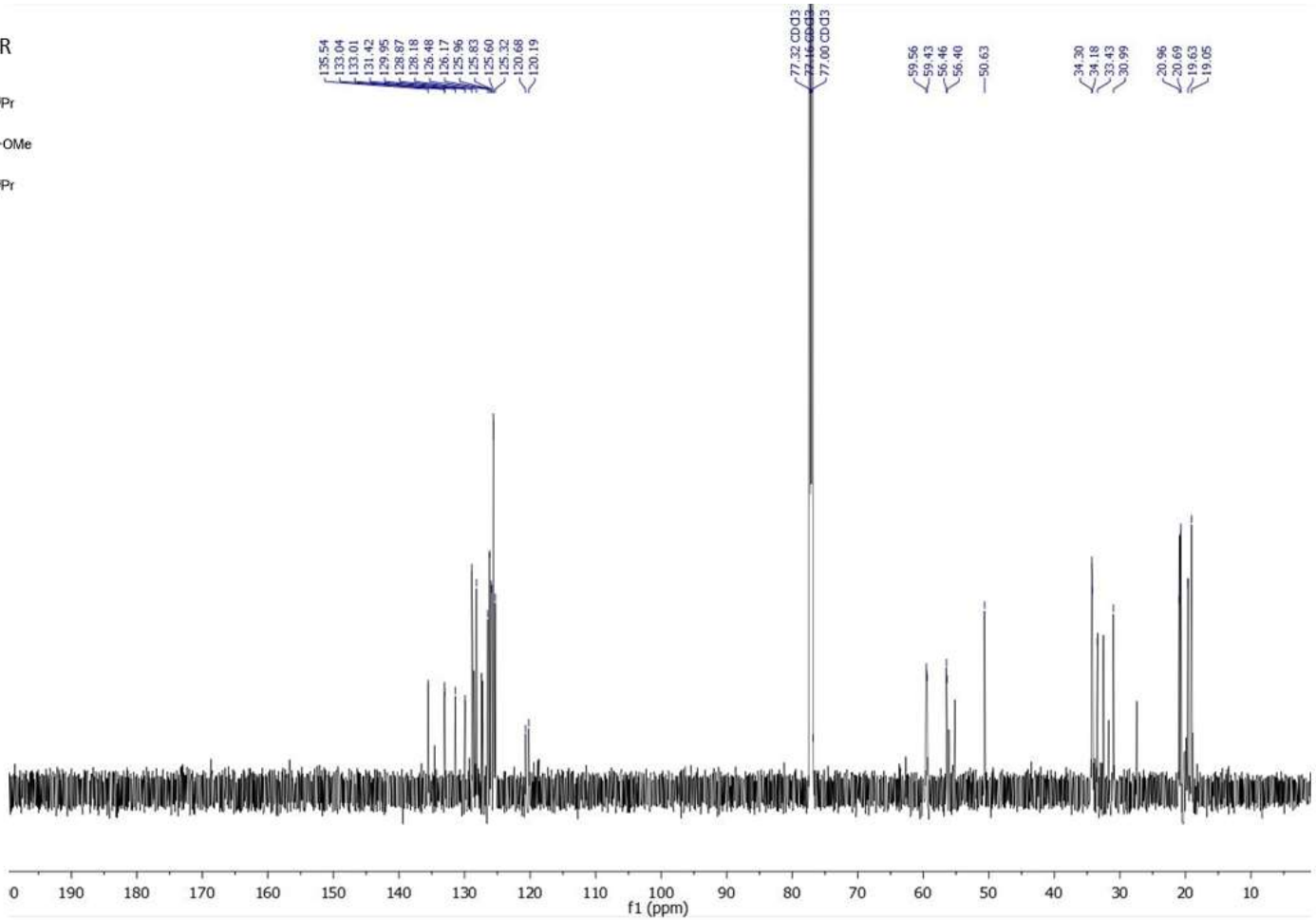
P5



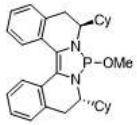
^{13}C NMR


iPr
N
P–OMe
N
iPr

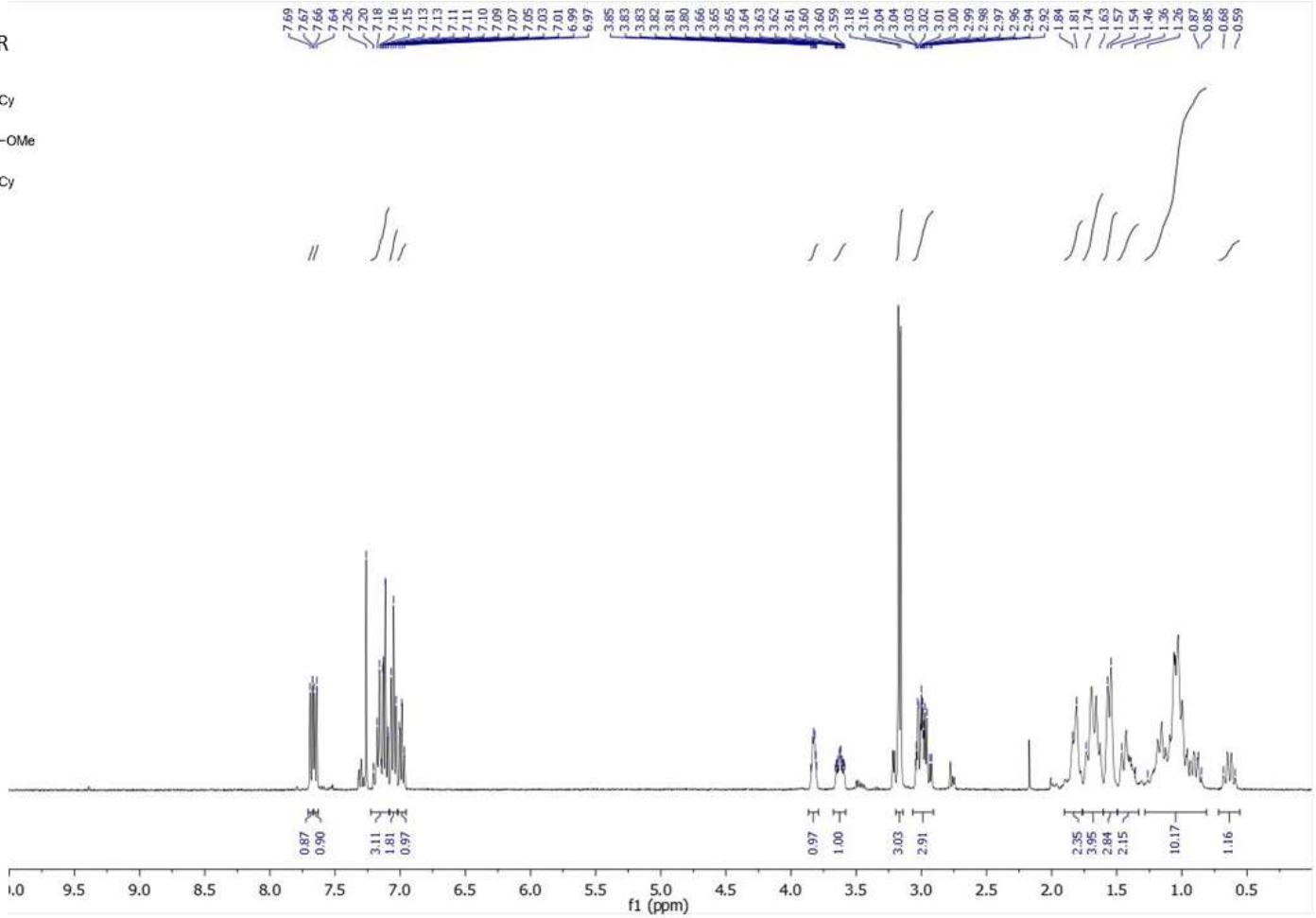
P5


135.54
133.04
133.01
131.42
129.95
128.87
128.18
126.48
126.17
125.96
125.83
125.60
125.32
120.68
120.19
77.32 CDCl3
77.16 CDCl3
77.00 CDCl3
59.56
59.43
56.46
56.40
50.63
34.30
34.18
33.43
30.99
20.96
20.69
19.63
19.05
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

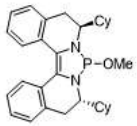
^{1}H NMR


Cy
N
P–OMe
N
Cy

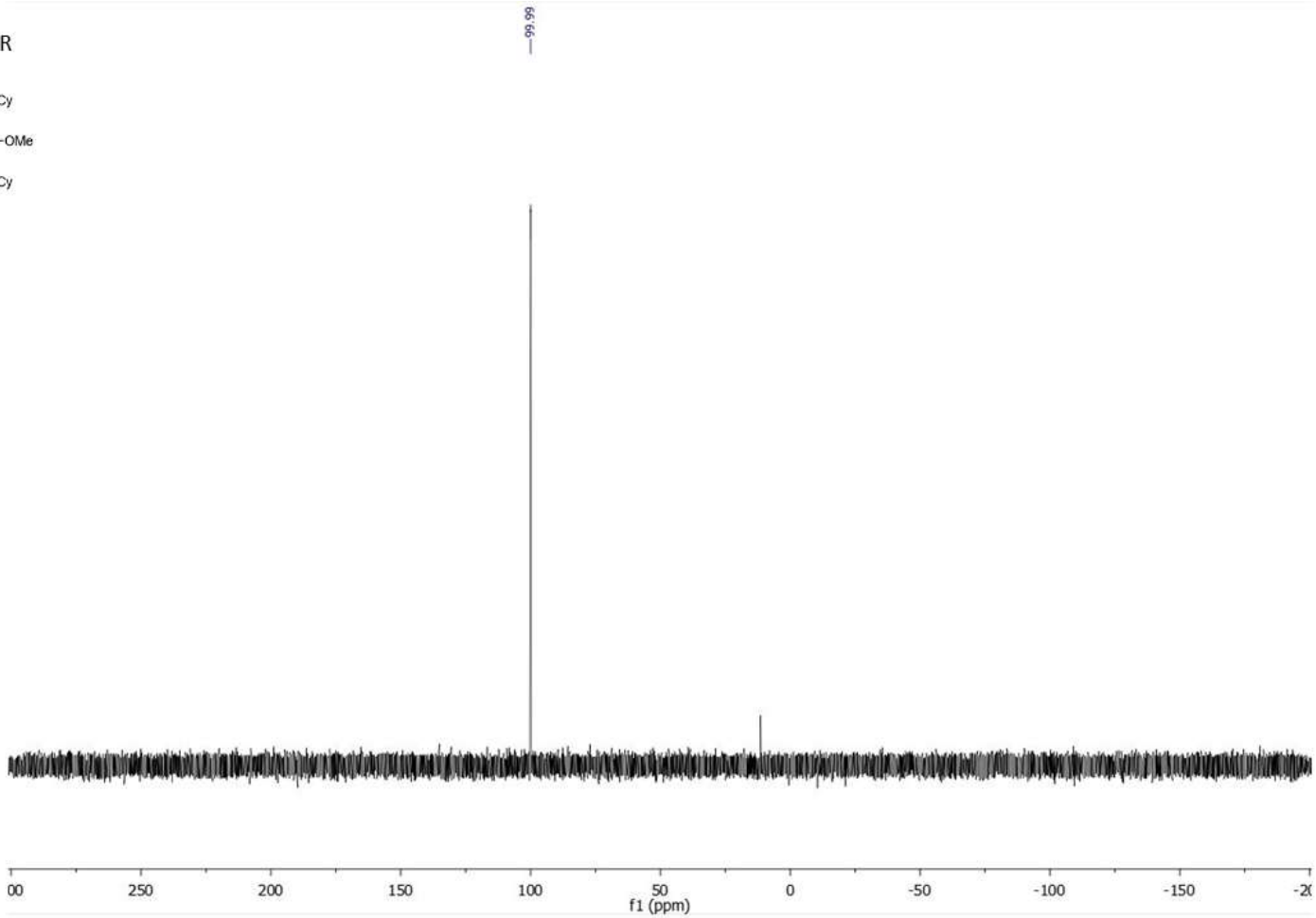
***ent*-P6**


7.69 7.67 7.66 7.64 7.26 7.20 7.18 7.16 7.15 7.13 7.13 7.11 7.11 7.10 7.09 7.07 7.05 7.03 7.01 6.99 6.97
3.85 3.83 3.83 3.82 3.81 3.80 3.66 3.65 3.65 3.64 3.63 3.62 3.61 3.60 3.60 3.59 3.18 3.16 3.04 3.04 3.03 3.02 3.01 3.00 2.99 2.98 2.97 2.96 2.94 2.92
1.84 1.81 1.74 1.63 1.57 1.54 1.46 1.36 1.26 0.87 0.85 0.68 0.59
0.87 0.90 3.11 1.81 0.97 0.97 1.00 3.03 2.91 2.35 3.95 2.84 2.15 10.17 1.16
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
f1 (ppm)

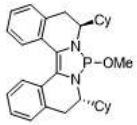
^{31}P NMR



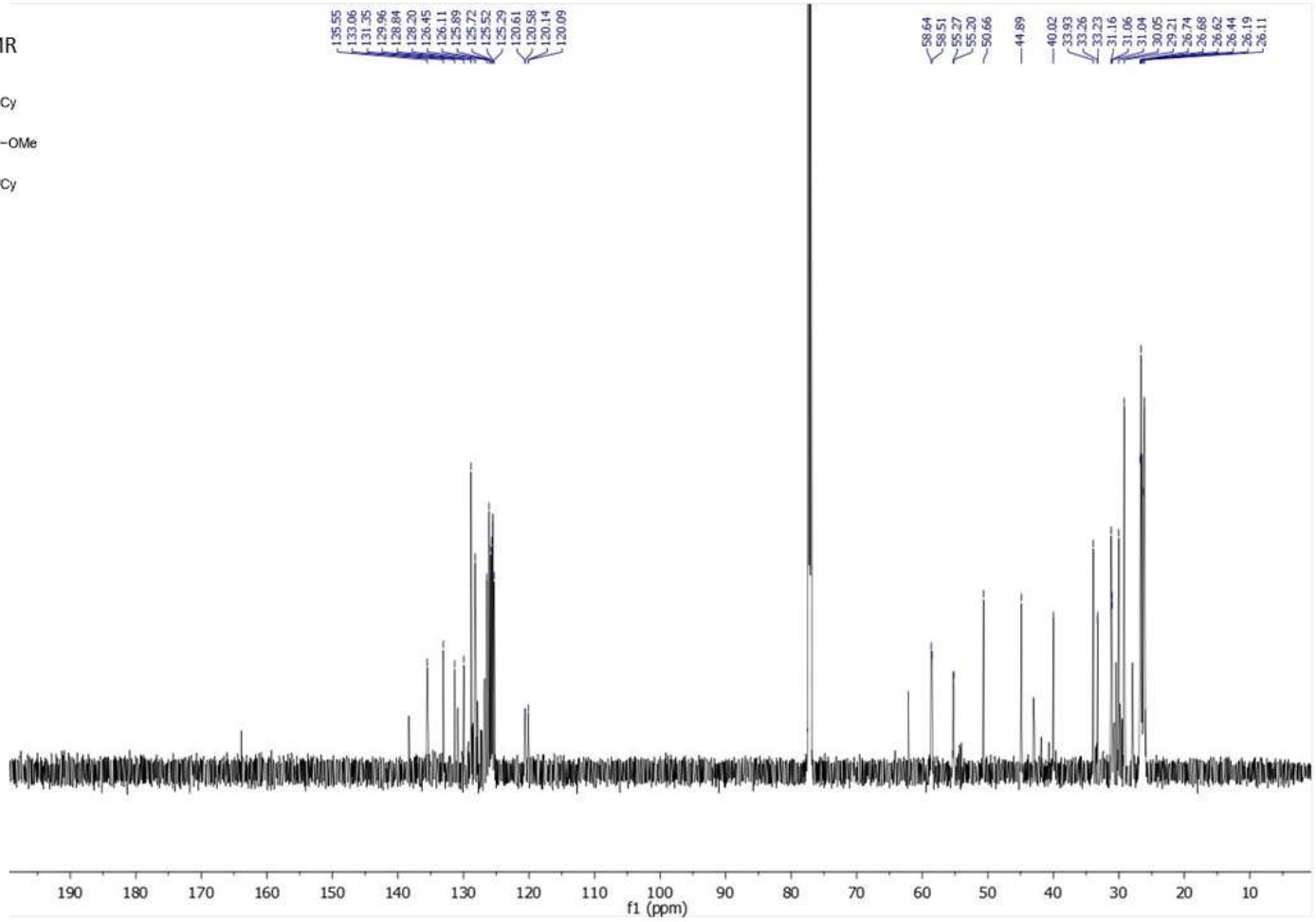
***ent*-P6**



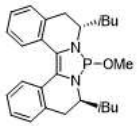
^{13}C NMR



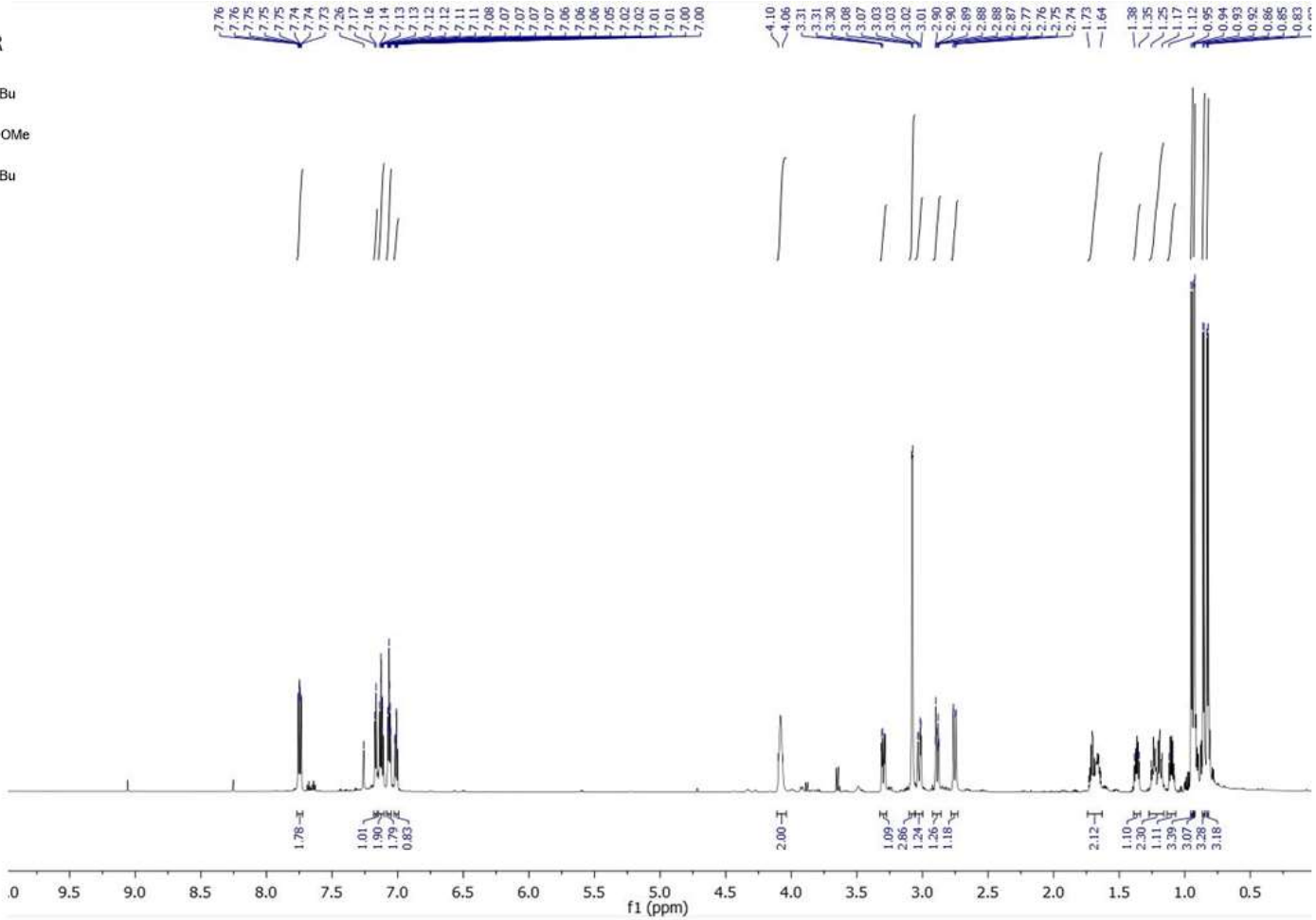
***ent*-P6**



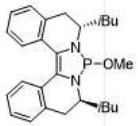
^{1}H NMR



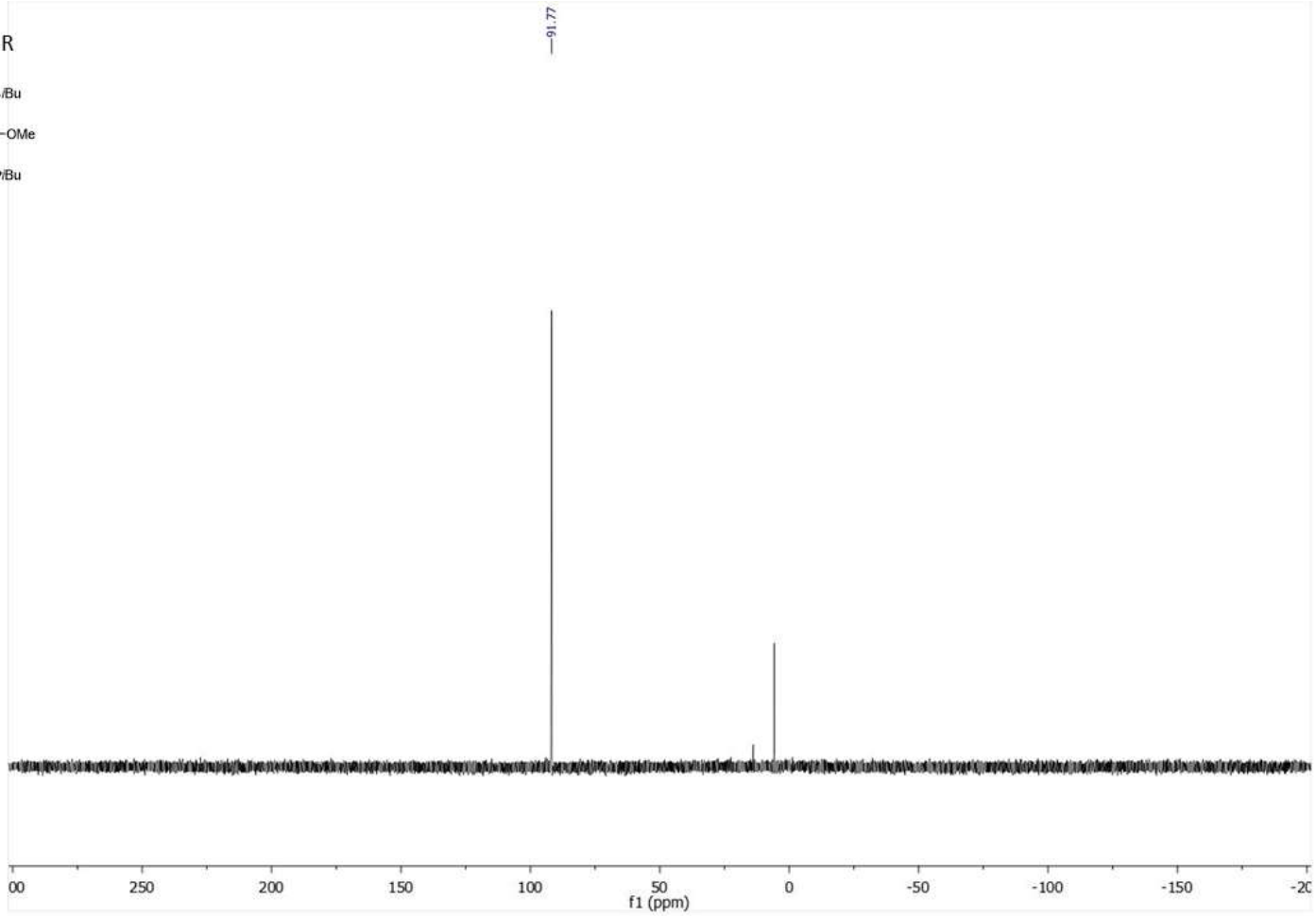
P7



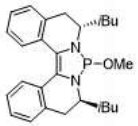
^{31}P NMR



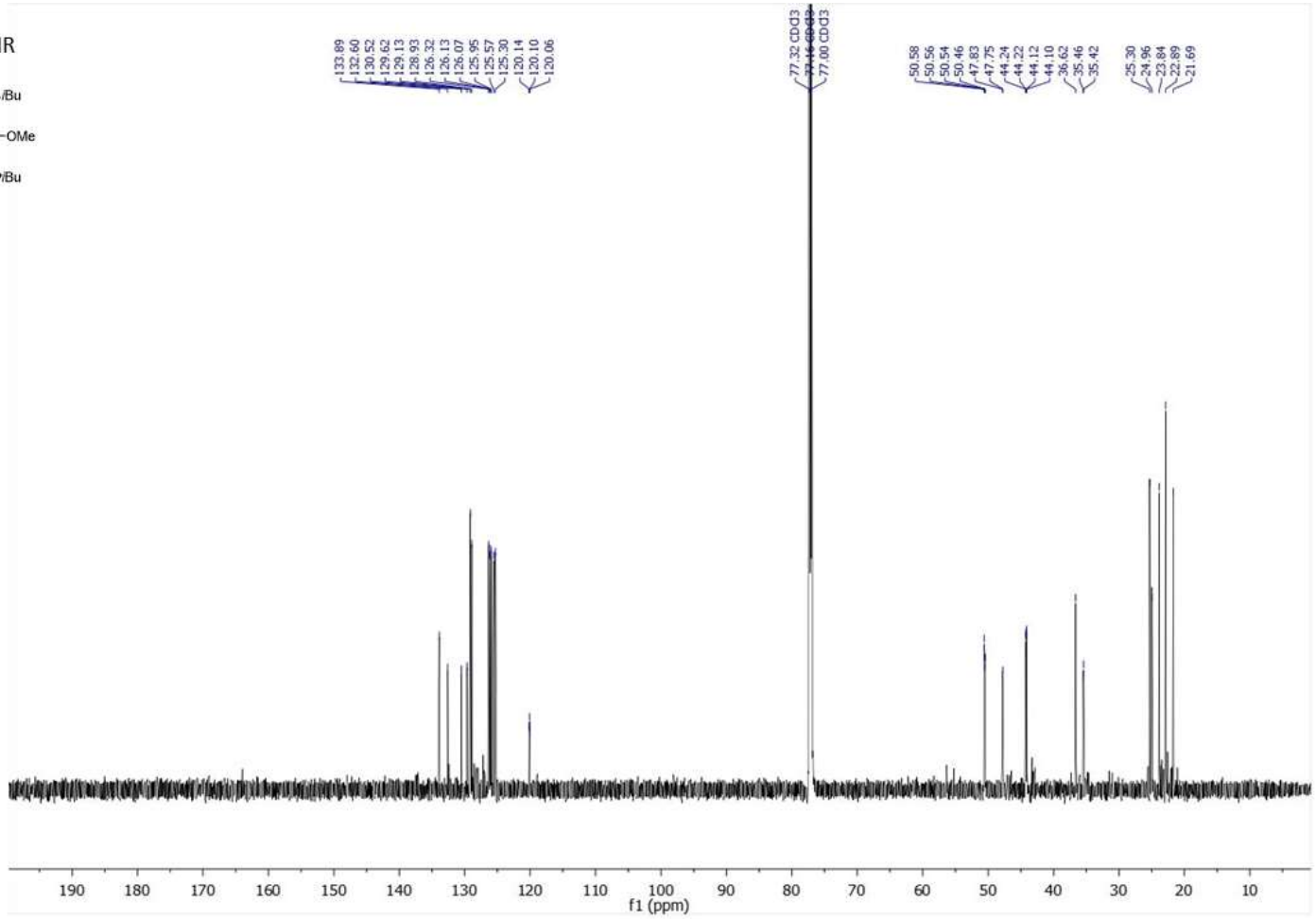
P7



^{13}C NMR


iBu
N
P–OMe
N
iBu

P7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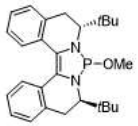
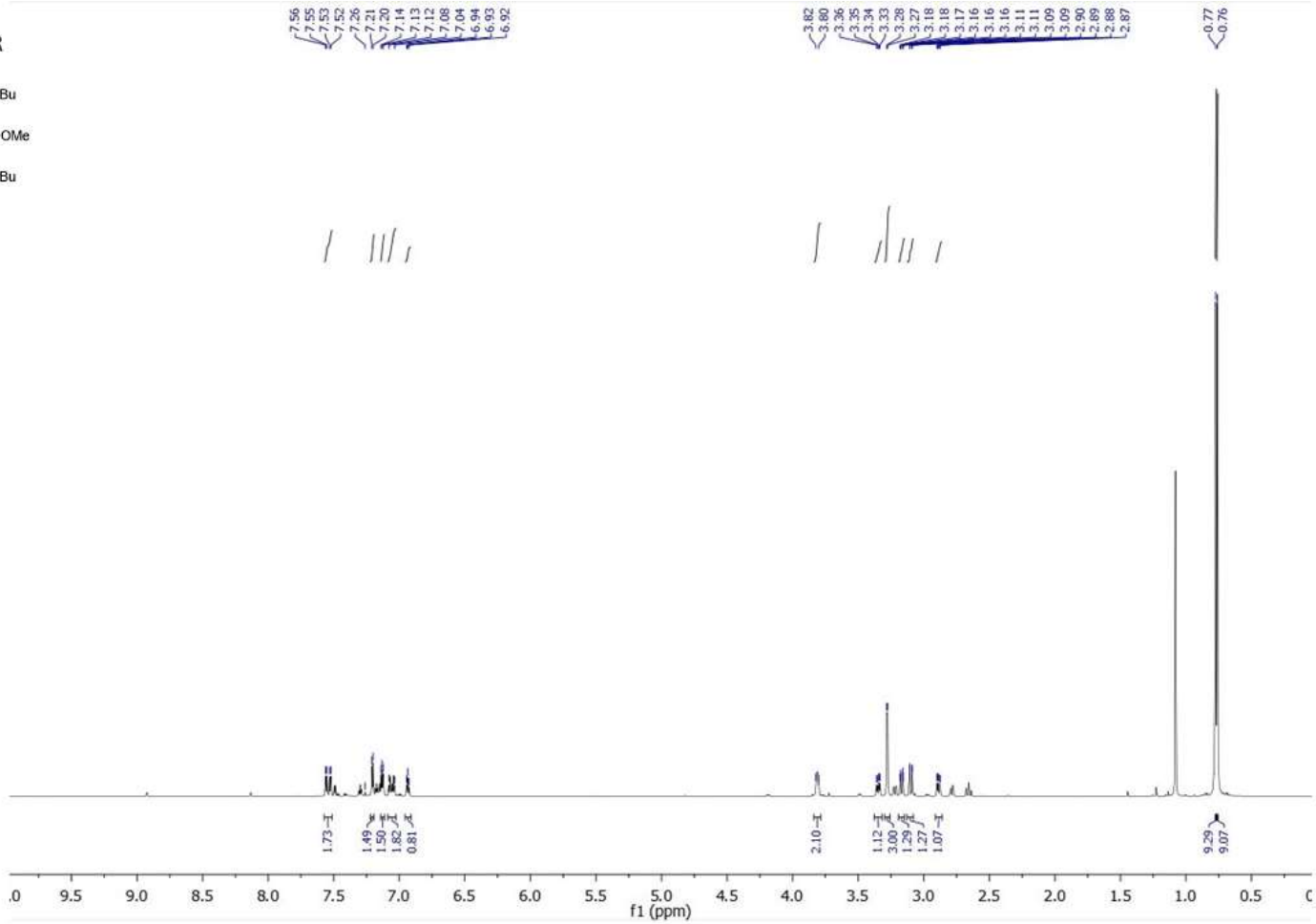
129.62
129.13
128.93
126.32
126.13
126.07
125.95
125.57
125.30
120.14
120.10
120.06
77.32 CDCl3
77.16 CDCl3
77.00 CDCl3
50.58
50.56
50.54
50.46
47.83
47.75
44.24
44.22
44.12
44.10
36.62
35.46
35.42
25.30
24.96
23.84
22.89
21.69
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

^{1}H NMR


tBu
N
P–OMe
N
tBu

P8


7.56
7.55
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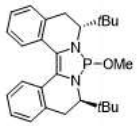
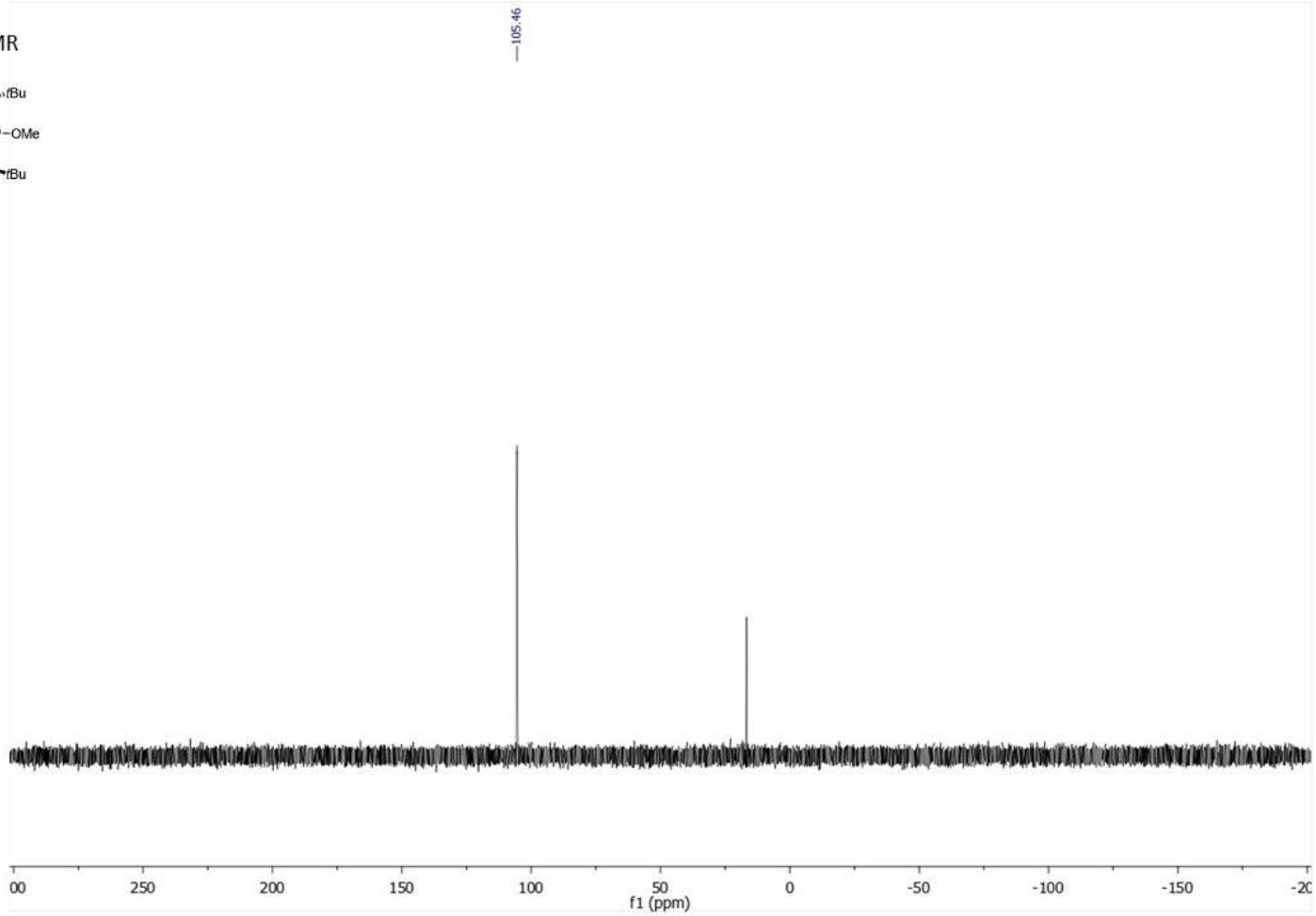
7.52
7.26
7.21
7.20
7.14
7.13
7.12
7.08
7.04
6.94
6.93
6.92
3.82
3.80
3.36
3.35
3.34
3.33
3.28
3.27
3.18
3.18
3.17
3.16
3.16
3.11
3.11
3.09
3.09
2.90
2.89
2.88
2.87
0.77
0.76
1.73
1.49
1.50
1.82
0.81
2.10
1.12
3.00
1.29
1.27
1.07
9.29
9.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

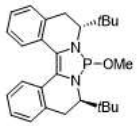
^{31}P NMR



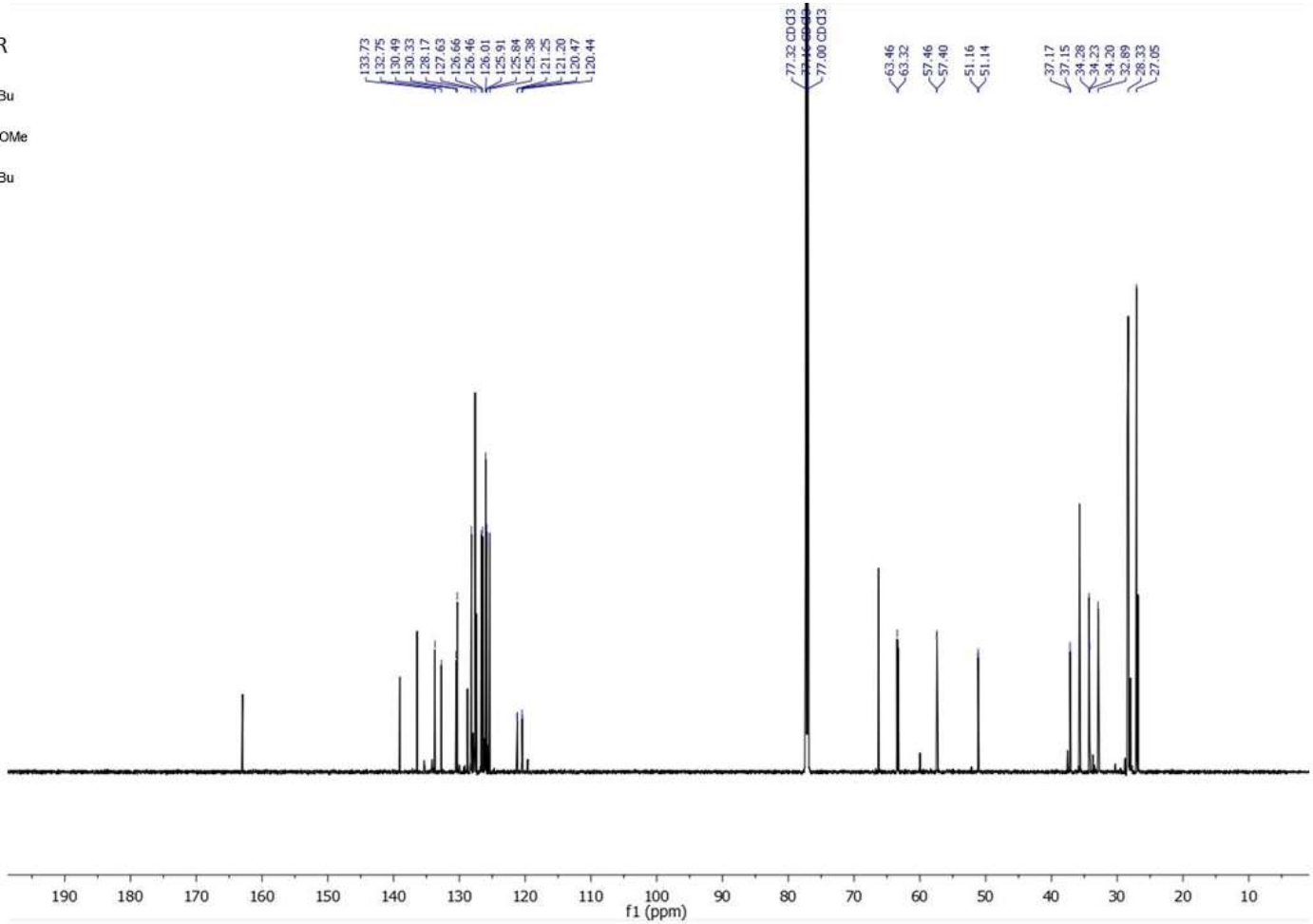
P8



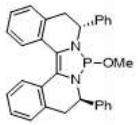
^{13}C NMR


tBu
N
P–OMe
N
tBu

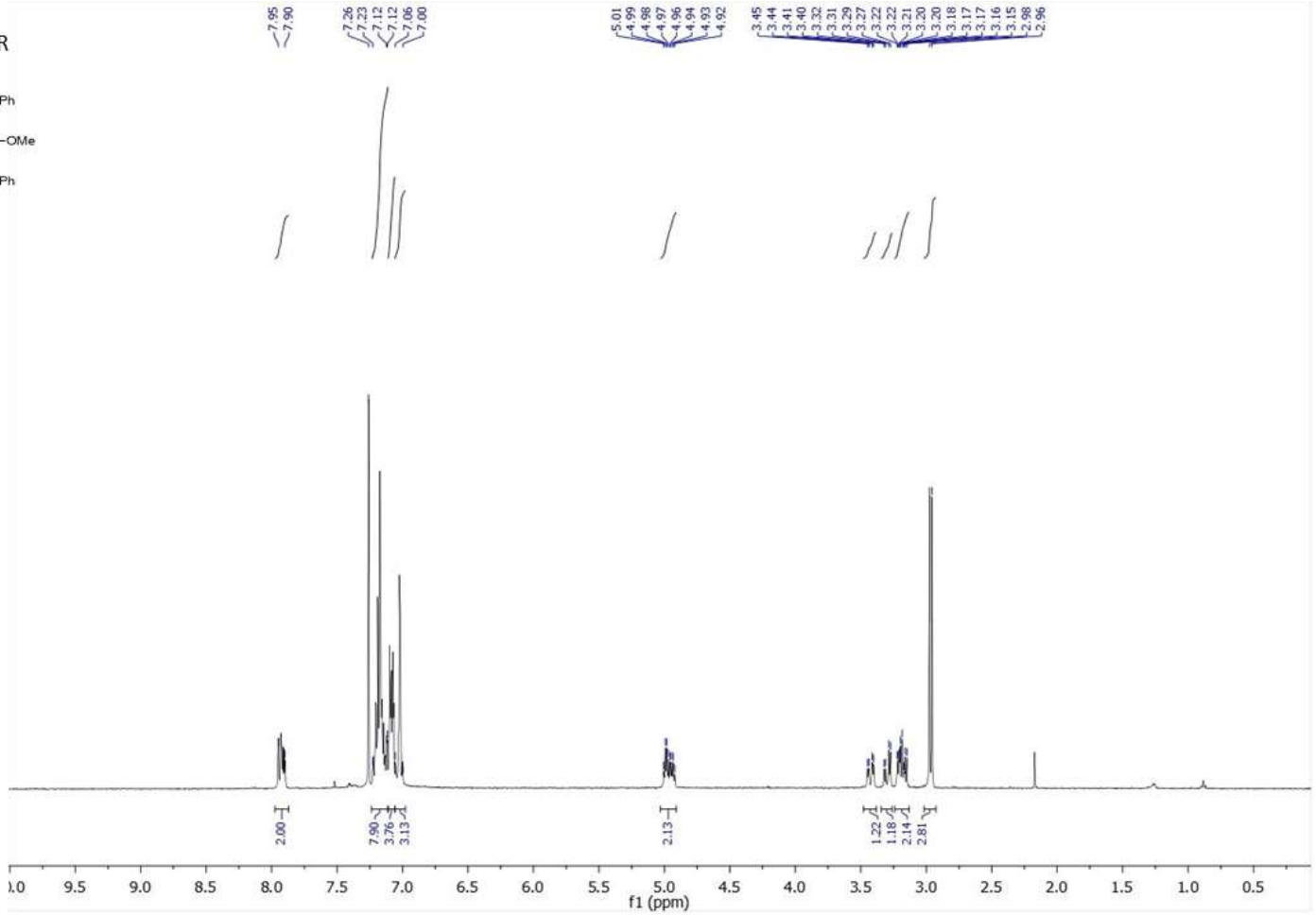
P8


133.73
132.75
130.49
130.33
128.17
127.63
126.66
126.46
126.01
125.91
125.84
125.38
121.25
121.20
120.47
120.44
77.32 CDCl3
77.16 CDCl3
77.00 CDCl3
63.46
63.32
57.46
57.40
51.16
51.14
37.17
37.15
34.28
34.23
34.20
32.89
28.33
27.05
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

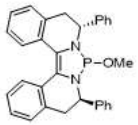
^{1}H NMR


Ph
N
P–OMe
N
Ph

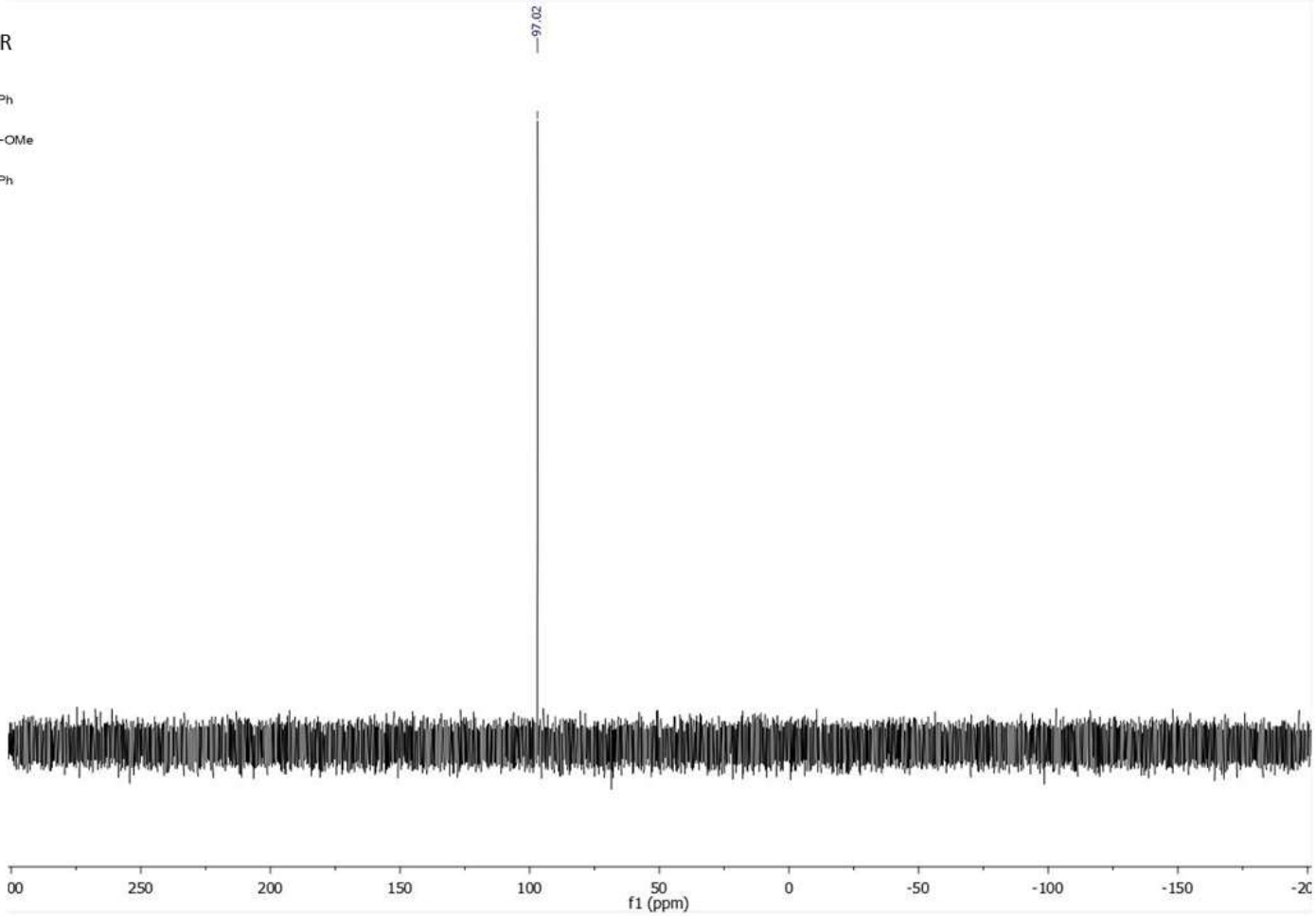
P9


7.95
7.90
7.26
7.23
7.12
7.12
7.06
7.00
5.01
4.99
4.98
4.97
4.96
4.94
4.93
4.92
3.45
3.44
3.41
3.40
3.32
3.31
3.29
3.27
3.22
3.22
3.21
3.20
3.20
3.18
3.17
3.17
3.16
3.15
2.98
2.96
2.00
7.90
3.76
3.13
2.13
1.22
1.18
2.14
2.81
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
f1 (ppm)

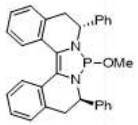
^{31}P NMR



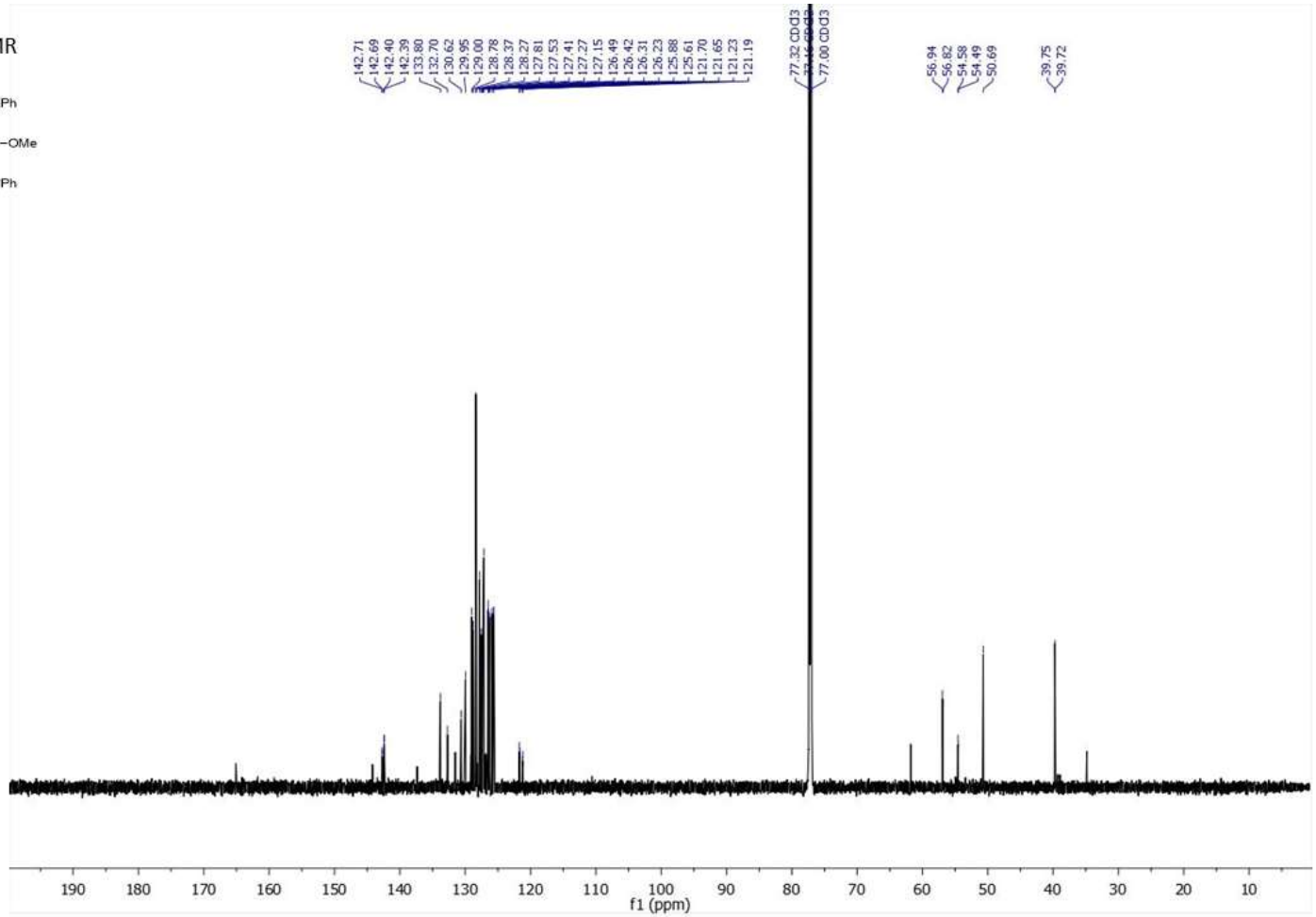
P9



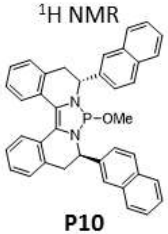
^{13}C NMR


Ph
N
P–OMe
N
Ph

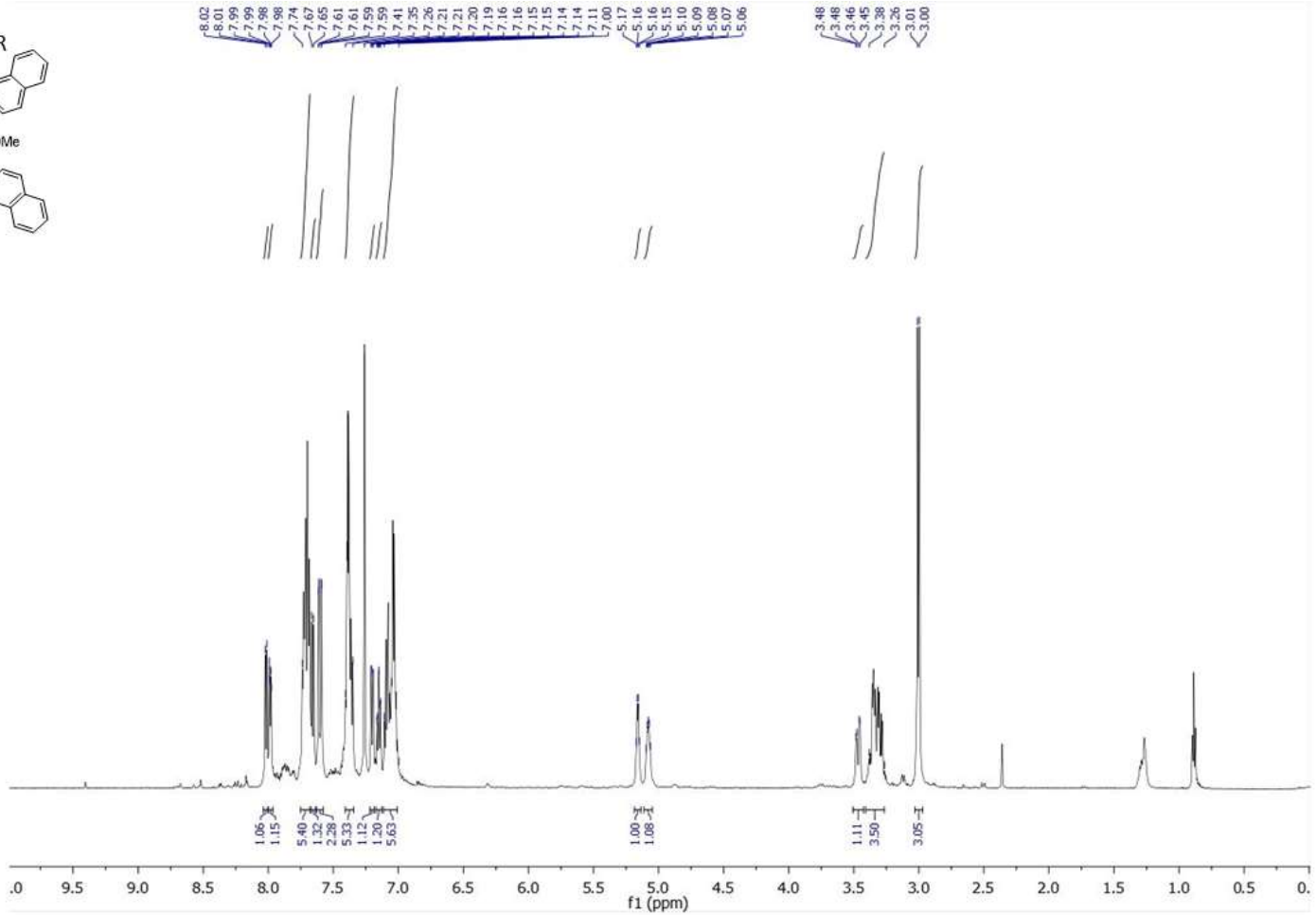
P9


142.71
142.69
142.40
142.39
133.80
132.70
130.62
129.95
129.00
128.78
128.37
128.27
127.81
127.53
127.41
127.27
127.15
126.49
126.42
126.31
126.23
125.88
125.61
121.70
121.65
121.23
121.19
77.32 CDCl3
77.16 CDCl3
77.00 CDCl3
56.94
56.82
54.58
54.49
50.69
39.75
39.72
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

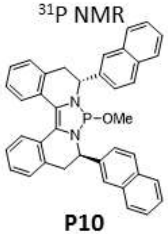
^{1}H NMR


P-OMe

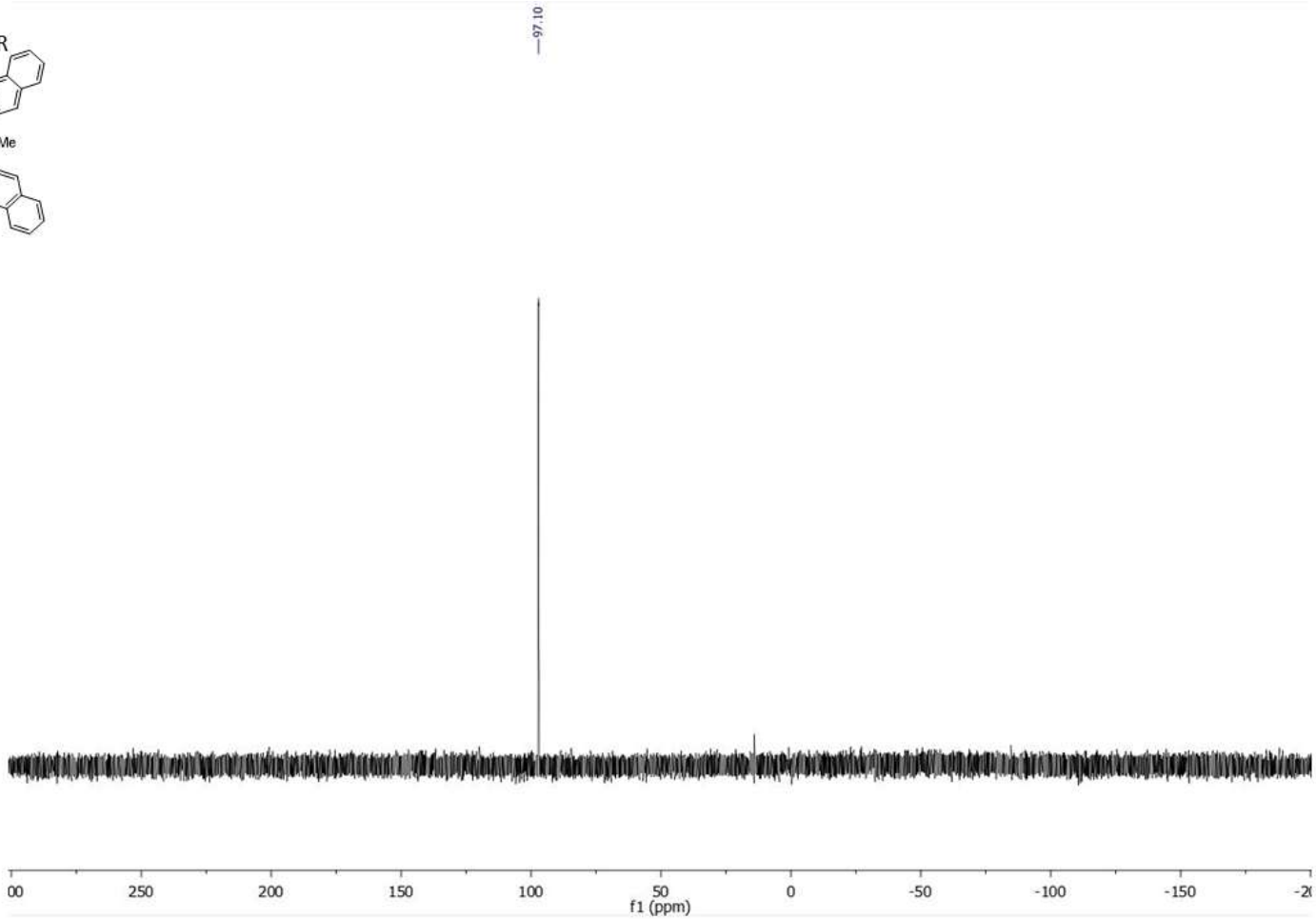
P10


8.02
8.01
7.99
7.99
7.98
7.98
7.74
7.67
7.65
7.61
7.61
7.59
7.59
7.41
7.35
7.26
7.21
7.21
7.20
7.19
7.16
7.16
7.15
7.15
7.14
7.14
7.11
7.00
5.17
5.16
5.16
5.15
5.10
5.09
5.08
5.07
5.06
3.48
3.48
3.46
3.45
3.38
3.26
3.01
3.00
1.06
1.15
5.40
1.32
2.28
5.33
1.12
1.20
5.63
1.00
1.08
1.11
3.50
3.05
.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.
f1 (ppm)

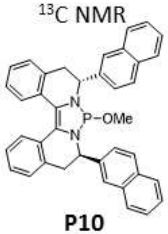
^{31}P NMR



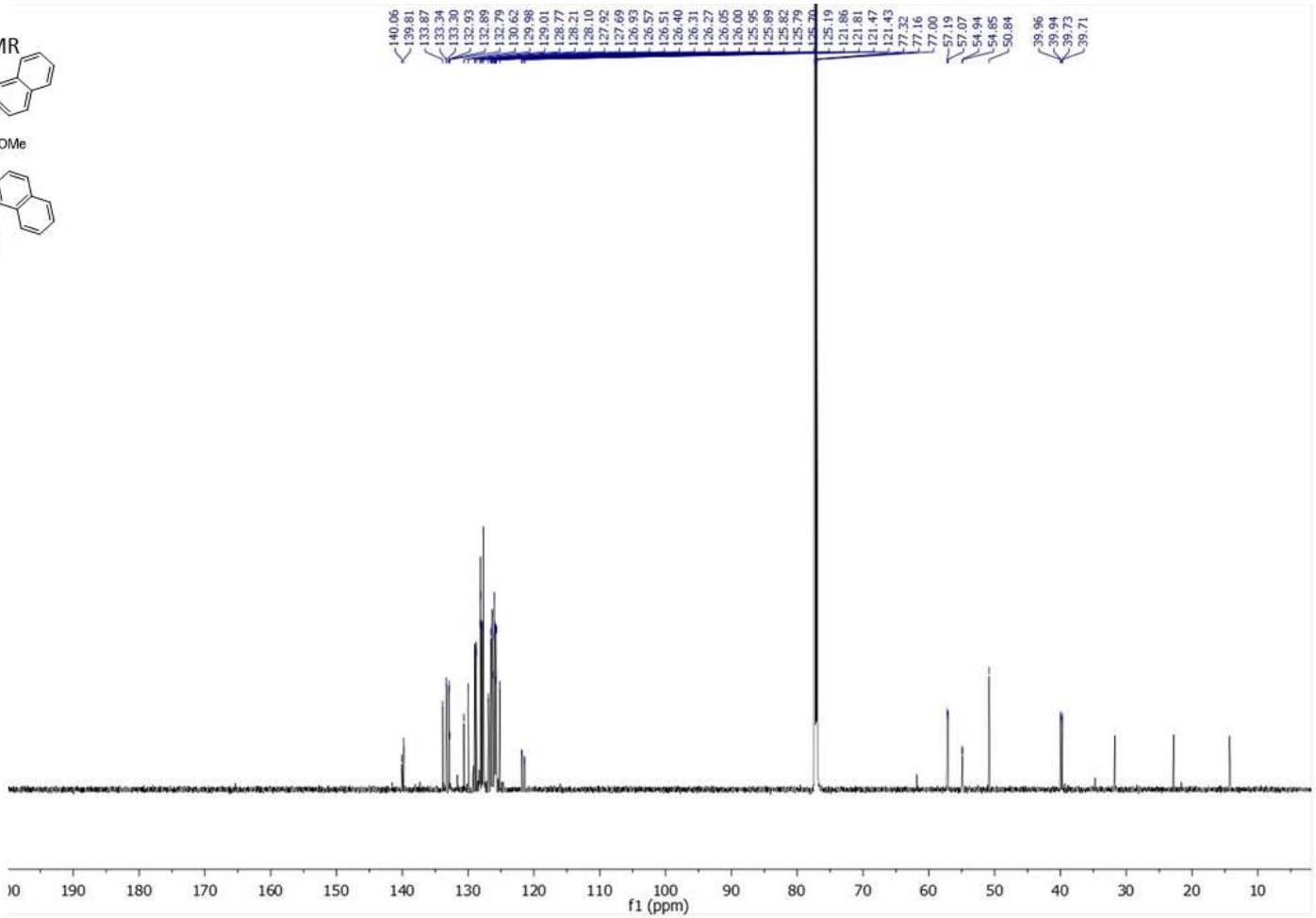
P10



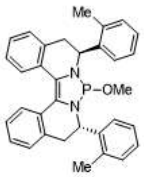
^{13}C NMR


N
P–OMe
N

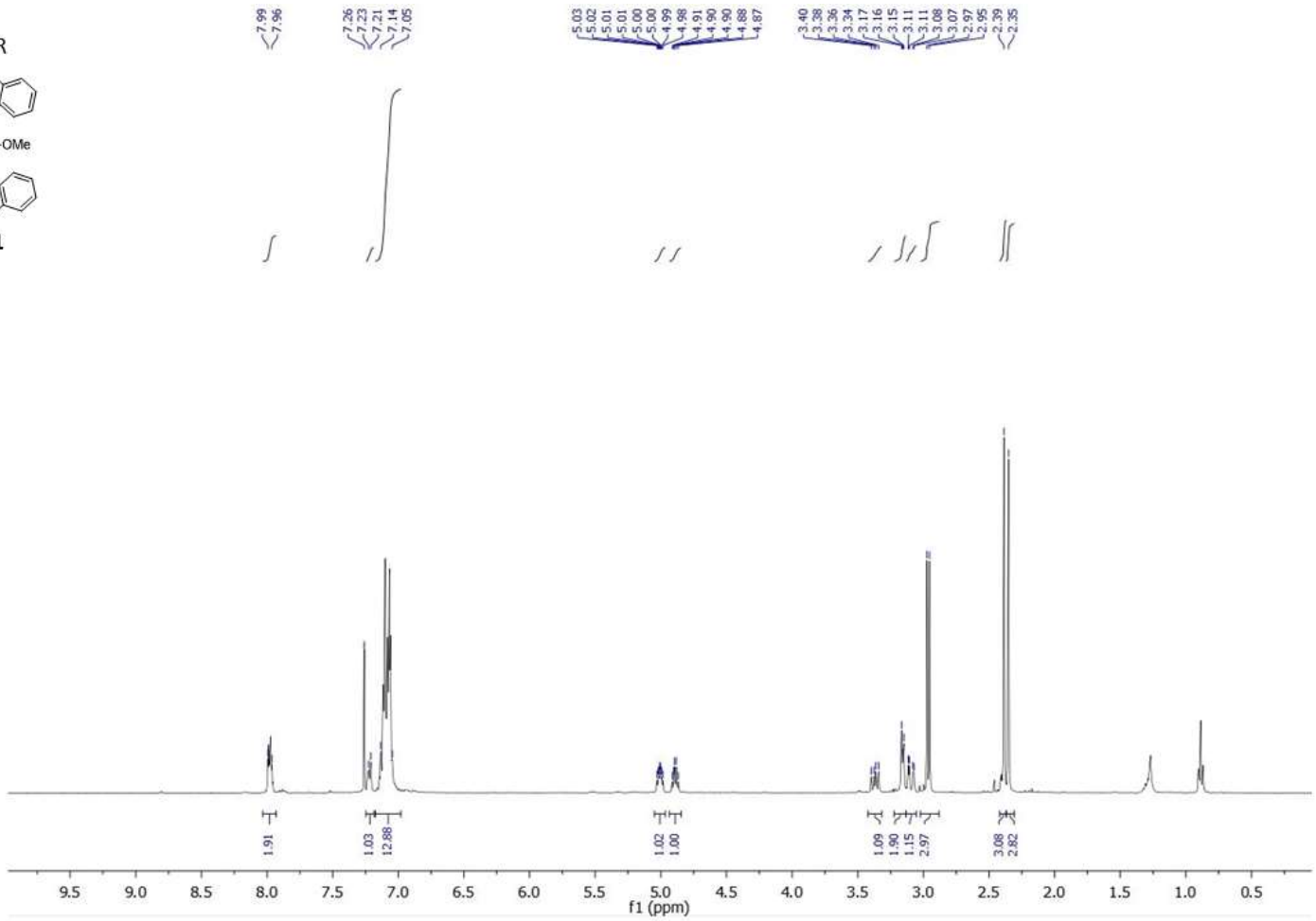
P10


140.06
139.81
133.87
133.34
133.30
132.93
132.89
132.79
130.62
129.98
129.01
128.77
128.21
128.10
127.92
127.69
126.93
126.57
126.51
126.40
126.31
126.27
126.05
126.00
125.95
125.89
125.82
125.79
125.20
125.19
121.86
121.81
121.47
121.43
77.32
77.16
77.00
57.19
57.07
54.94
54.85
50.84
39.96
39.94
39.73
39.71
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

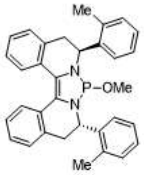
^{1}H NMR



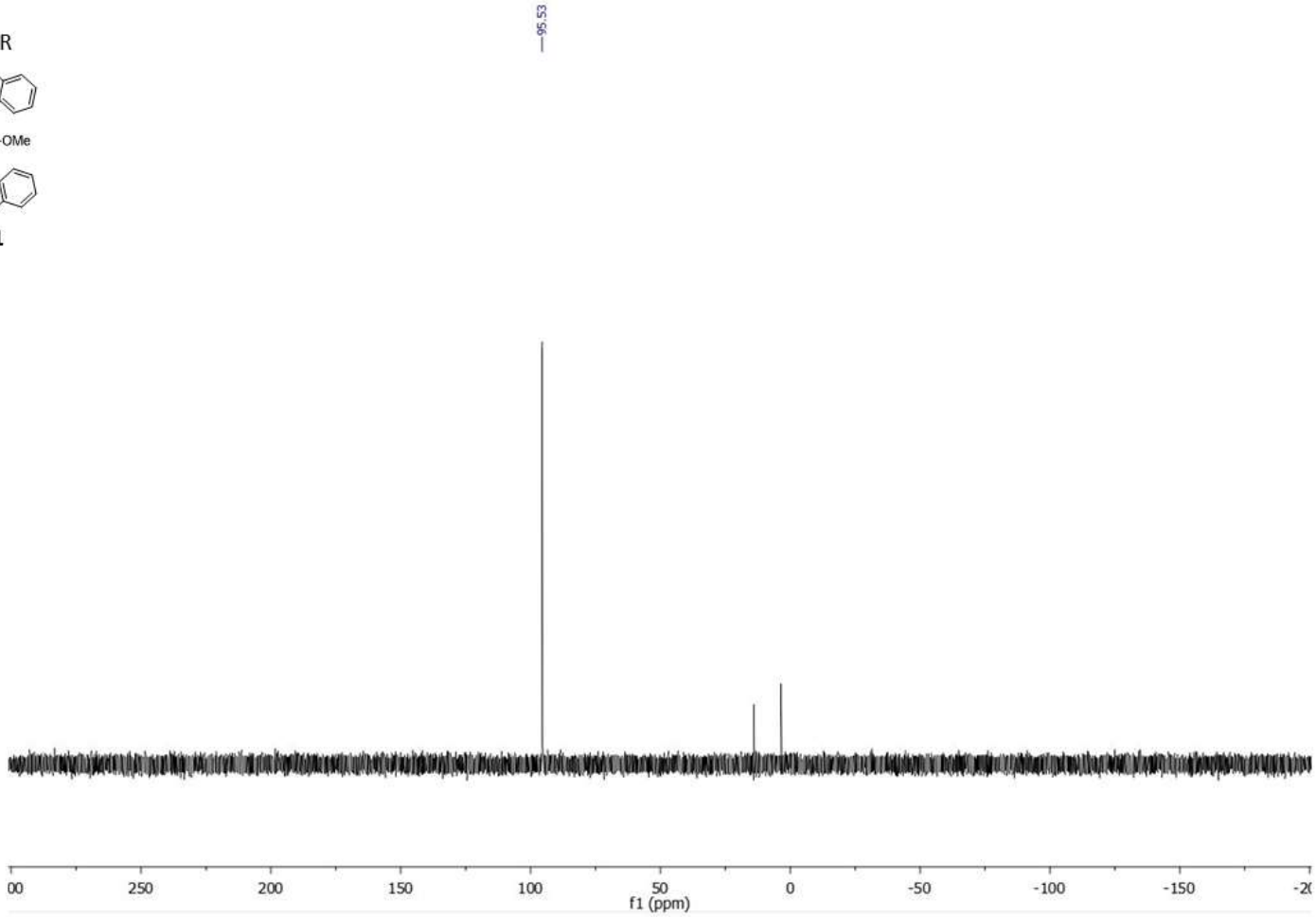
***ent*-P11**



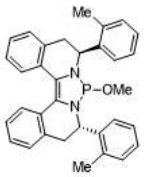
^{31}P NMR



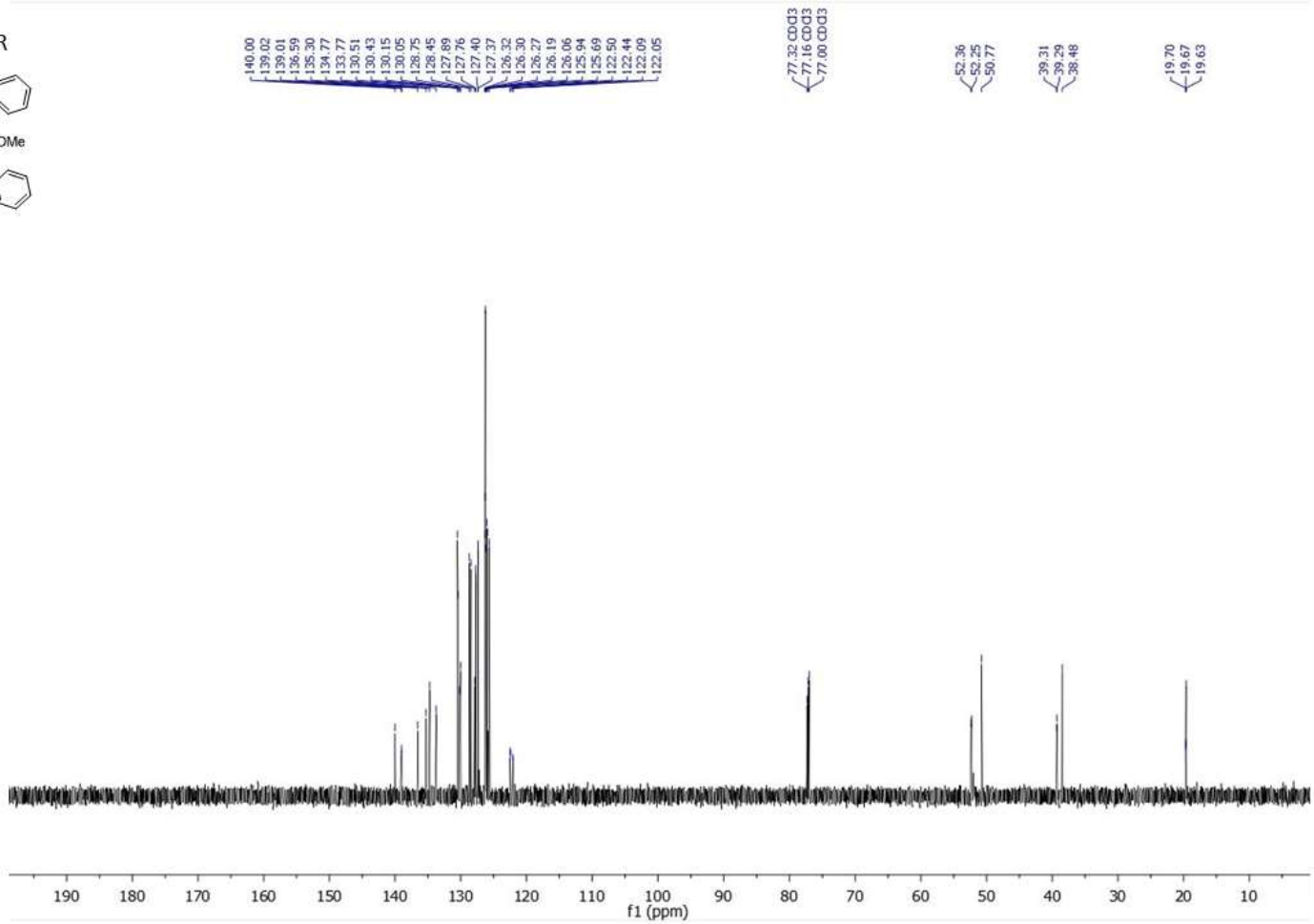
***ent*-P11**



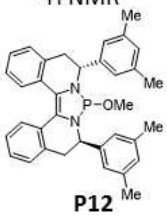
^{13}C NMR



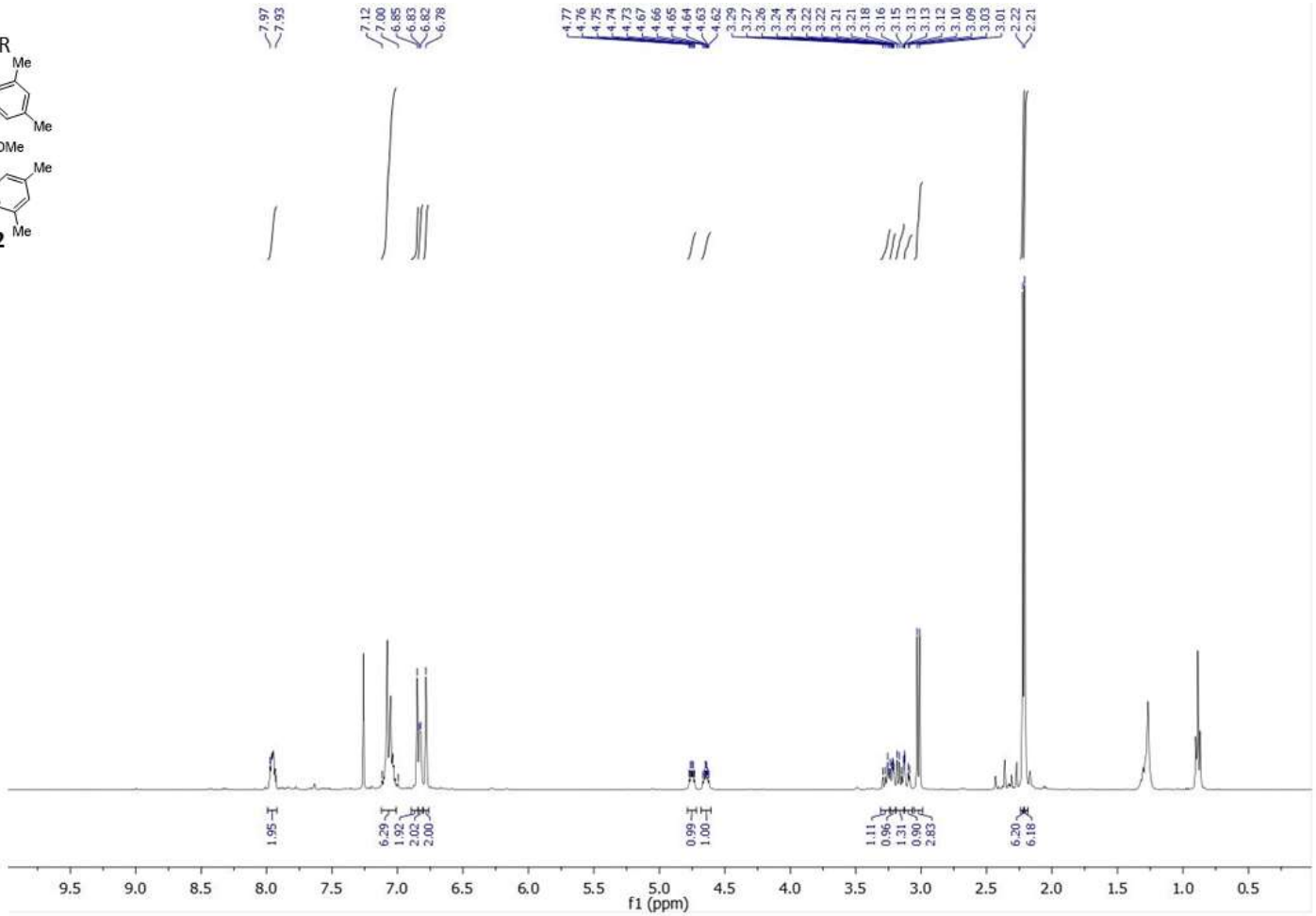
***ent*-P11**



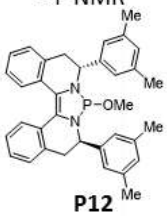
^{1}H NMR


Me
Me
N
P–OMe
N
Me
Me

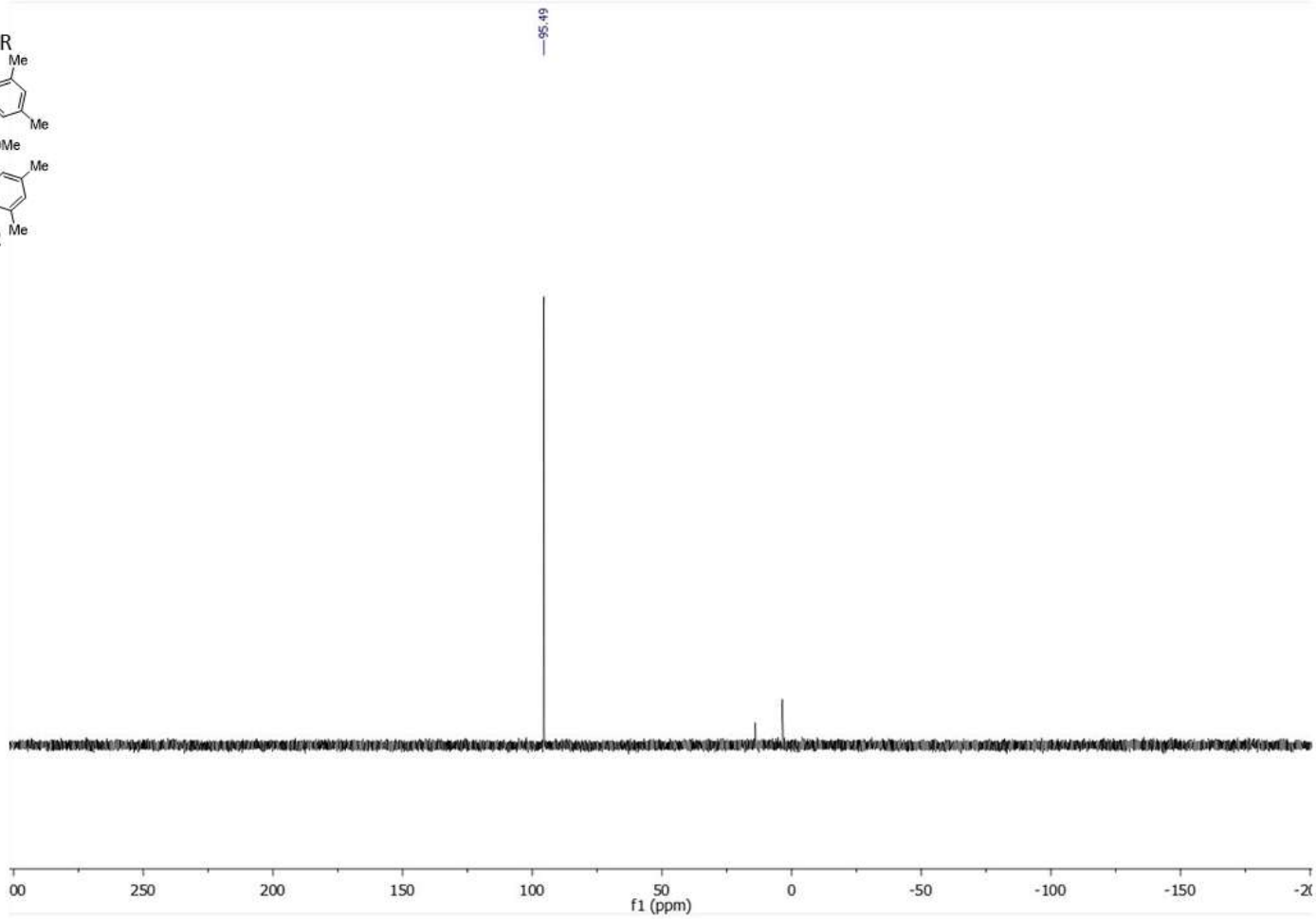
P12


7.97
7.93
7.12
7.00
6.85
6.83
6.82
6.78
4.77
4.76
4.75
4.74
4.73
4.67
4.66
4.65
4.64
4.63
4.62
3.29
3.27
3.26
3.24
3.24
3.22
3.22
3.21
3.21
3.18
3.16
3.15
3.13
3.13
3.12
3.10
3.09
3.03
3.01
2.22
2.21
1.95
6.29
1.92
2.02
2.00
0.99
1.00
1.11
0.96
1.31
0.90
2.83
6.20
6.18
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
f1 (ppm)

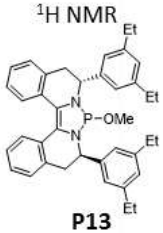
^{31}P NMR



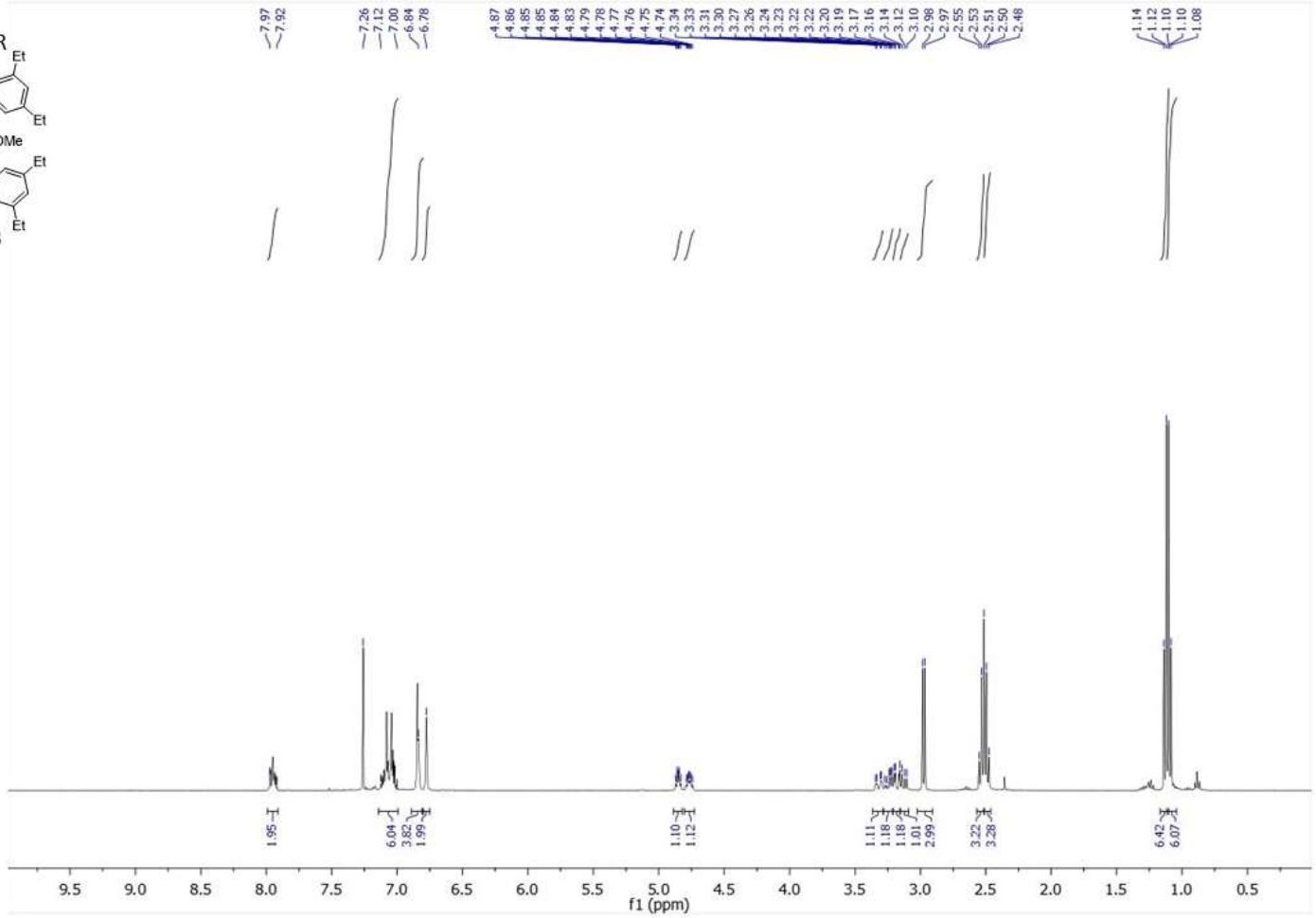
P12



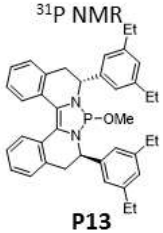
^{1}H NMR


Et
Et
N
P-OMe
N
Et
Et

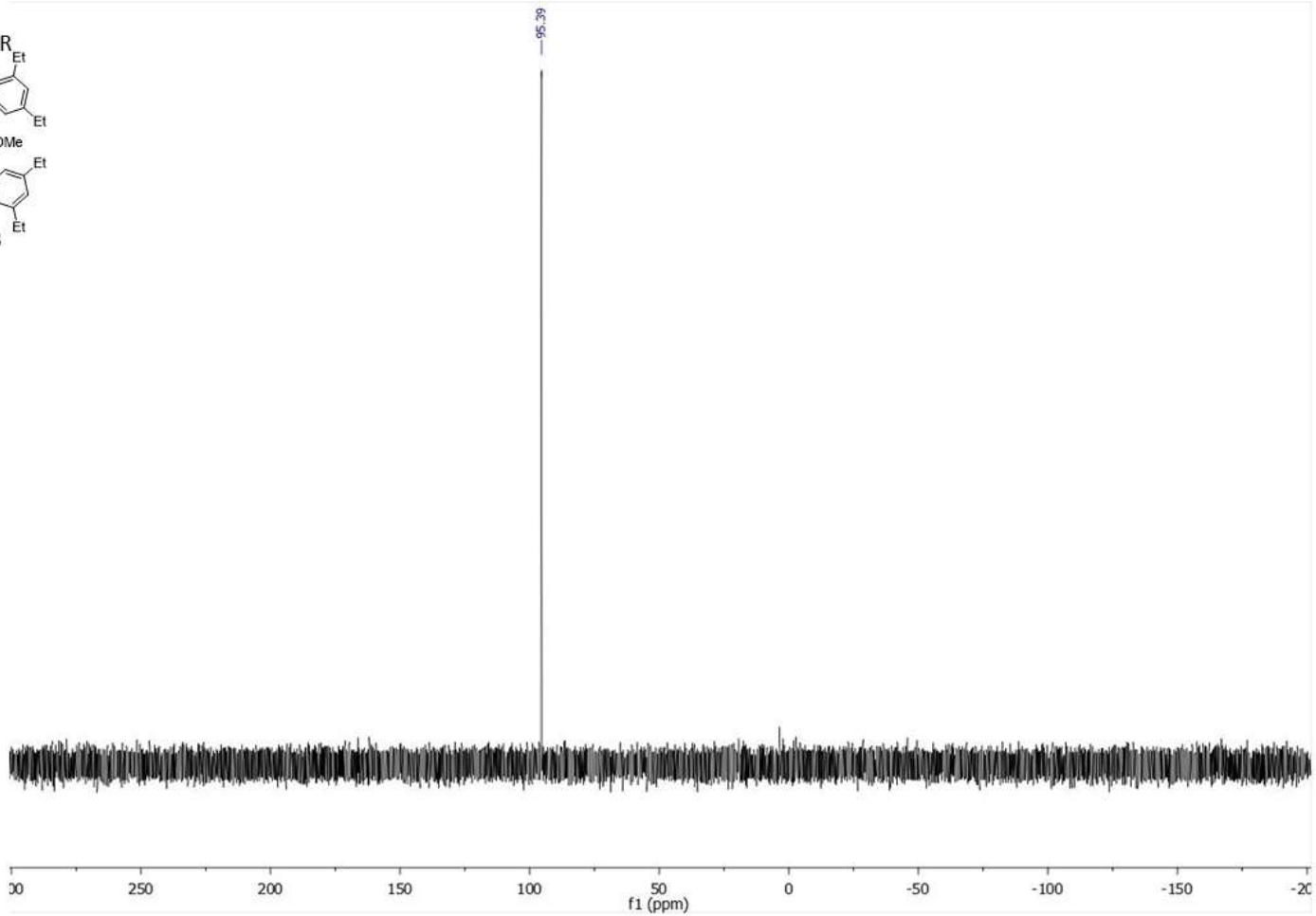
P13


7.97
7.92
7.26
7.12
7.00
6.84
6.78
4.87
4.86
4.85
4.85
4.84
4.83
4.79
4.78
4.77
4.76
4.75
4.74
3.34
3.33
3.31
3.30
3.27
3.26
3.24
3.23
3.22
3.22
3.20
3.19
3.17
3.16
3.14
3.12
3.10
2.98
2.97
2.55
2.53
2.51
2.50
2.48
1.14
1.12
1.10
1.10
1.08
1.95
6.04
3.82
1.99
1.10
1.12
1.11
1.18
1.18
1.01
2.99
3.22
3.28
6.42
6.07
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
f1 (ppm)

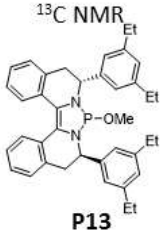
^{31}P NMR



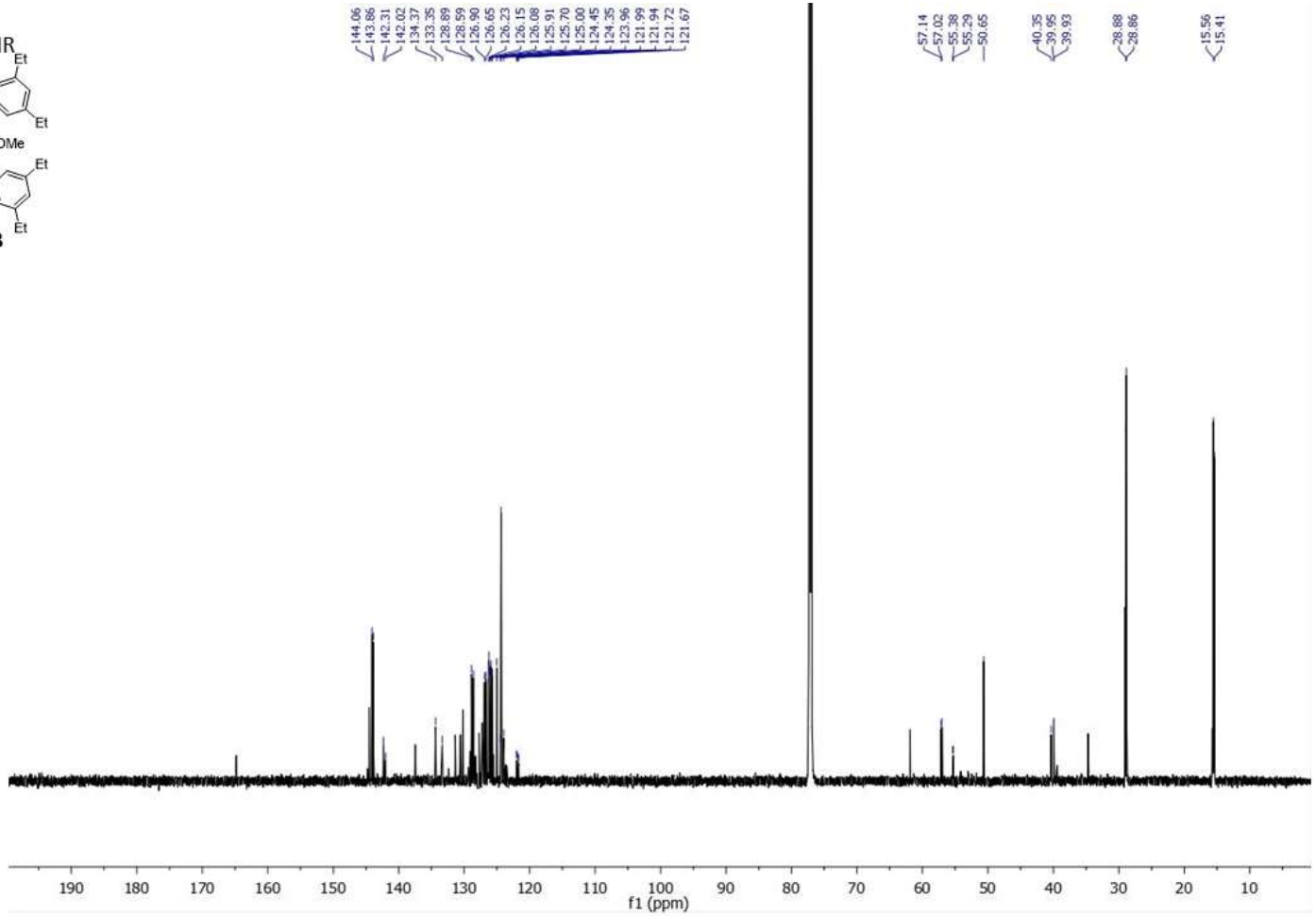
P13



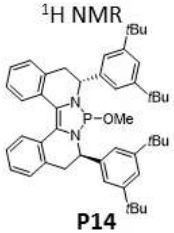
^{13}C NMR


Et
Et
N
P-OMe
N
Et
Et

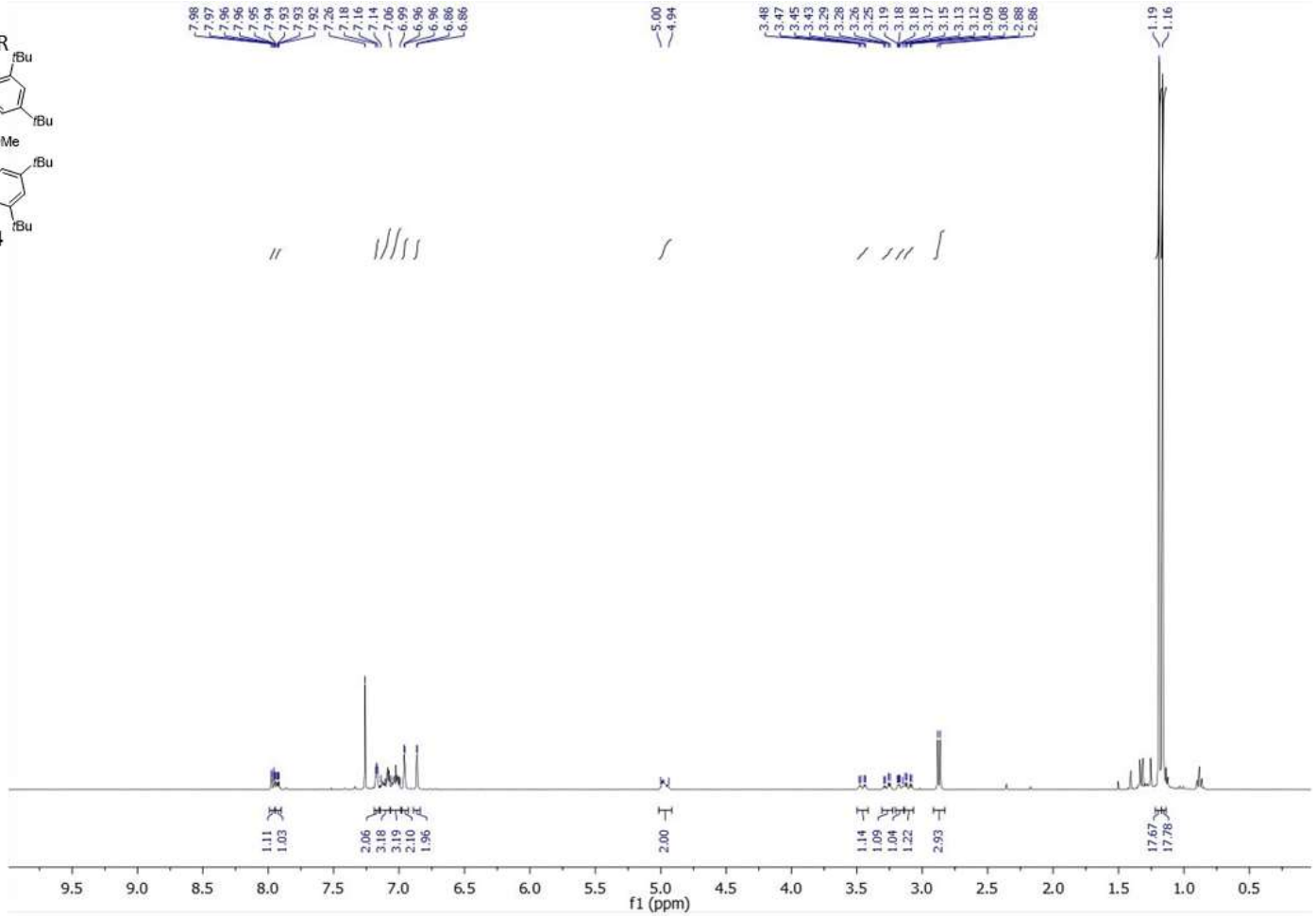
P13


144.06
143.86
142.31
142.02
134.37
133.35
128.89
128.59
126.90
126.65
126.23
126.15
126.08
125.91
125.70
125.00
124.45
124.35
123.96
121.99
121.94
121.72
121.67
57.14
57.02
55.38
55.29
50.65
40.35
39.95
39.93
28.88
28.86
15.56
15.41
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

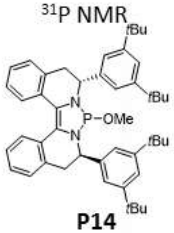
^{1}H NMR


tBu
tBu
N
P−OMe
N
tBu
tBu

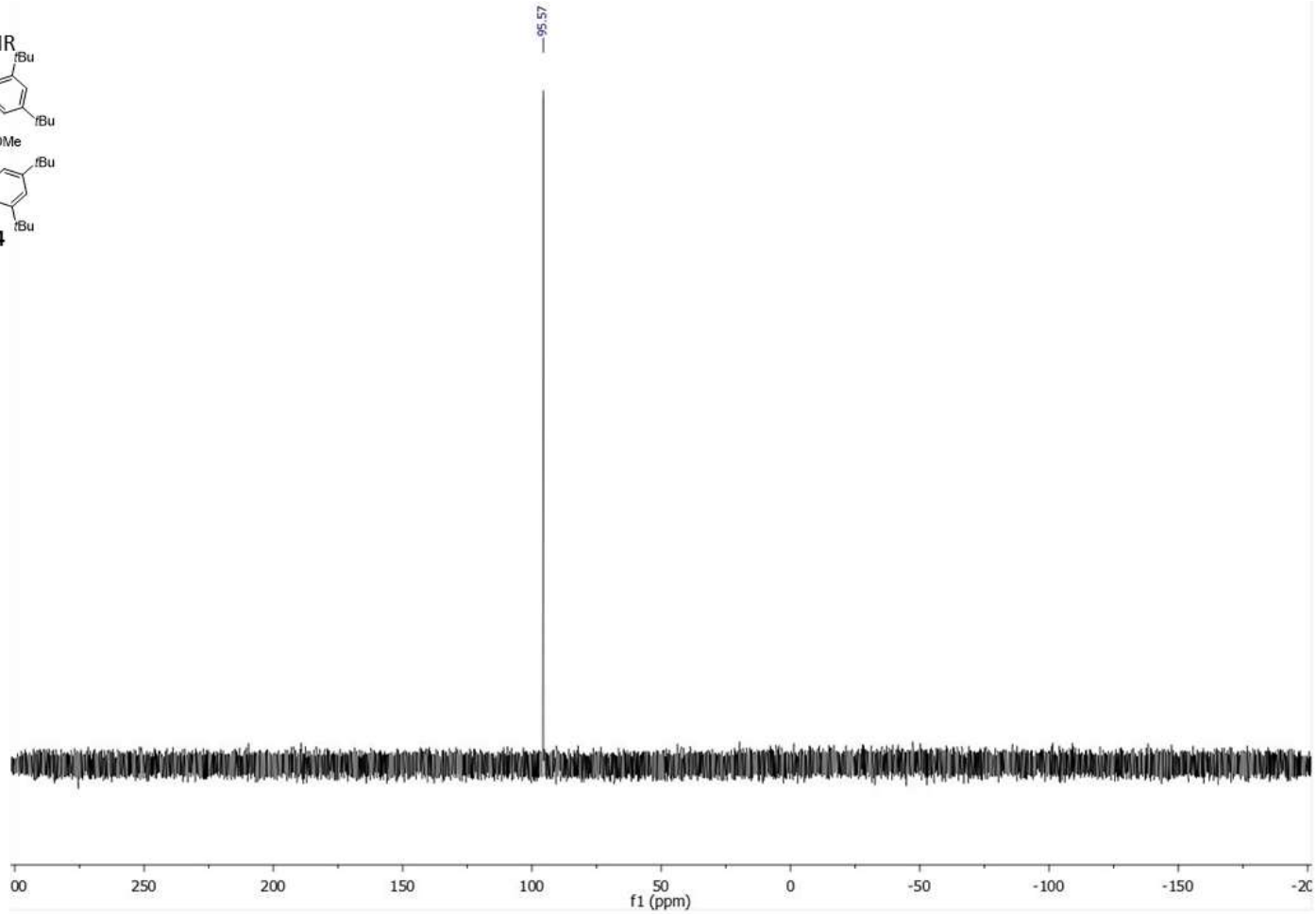
P14


7.98
7.97
7.96
7.96
7.95
7.94
7.93
7.93
7.92
7.26
7.18
7.16
7.14
7.06
6.99
6.96
6.96
6.86
6.86
5.00
4.94
3.48
3.47
3.45
3.43
3.29
3.28
3.26
3.25
3.19
3.18
3.18
3.17
3.15
3.13
3.12
3.09
3.08
2.88
2.86
1.19
1.16
1.11
1.03
2.06
3.18
3.19
2.10
1.96
2.00
1.14
1.09
1.04
1.22
2.93
17.67
17.78
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
f1 (ppm)

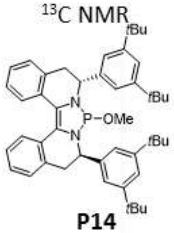
^{31}P NMR


tBu
tBu
N
P−OMe
N
tBu
tBu

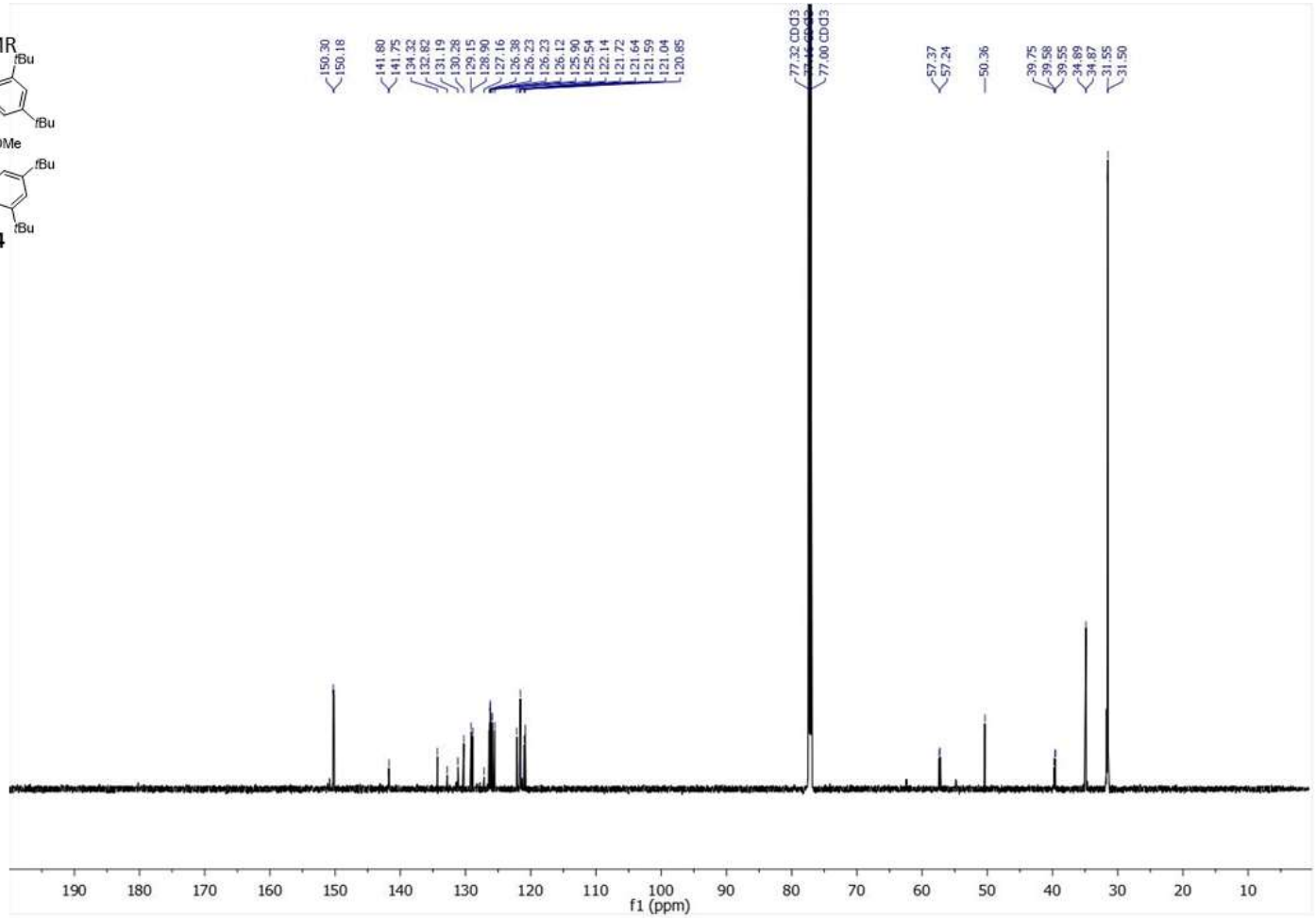
P14


95.57
00
250
200
150
100
50
0
-50
-100
-150
-20
f1 (ppm)

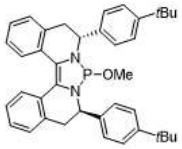
^{13}C NMR


tBu
tBu
N
P−OMe
N
tBu
tBu

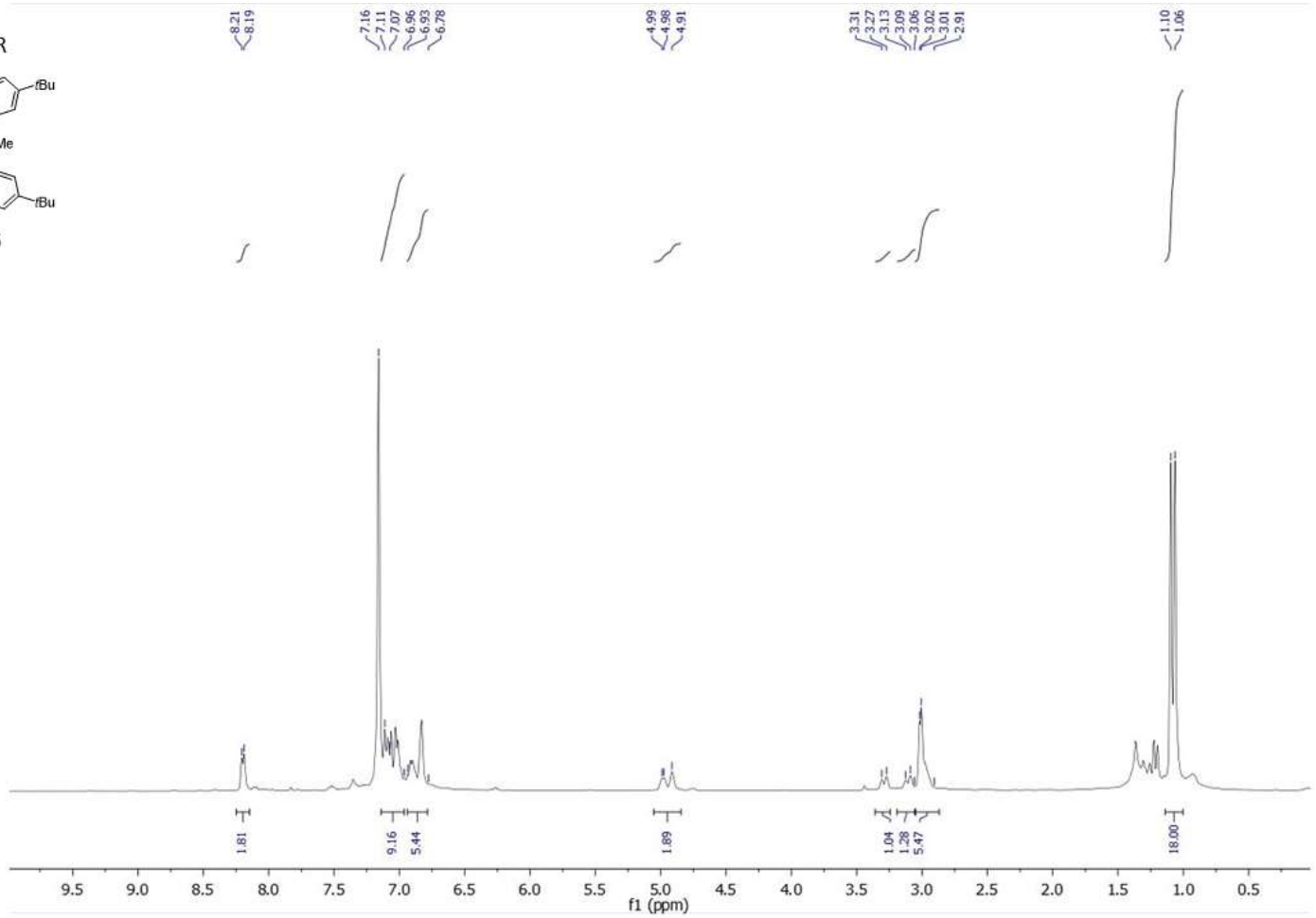
P14


150.30
150.18
141.80
141.75
134.32
132.82
131.19
130.28
129.15
128.90
127.16
126.38
126.23
126.23
126.12
125.90
125.54
122.14
121.72
121.64
121.59
121.04
120.85
77.32 CDCl3
77.16 CDCl3
77.00 CDCl3
57.37
57.24
50.36
39.75
39.58
39.55
34.89
34.87
31.55
31.50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

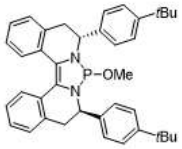
^{1}H NMR


tBu
N
P–OMe
N
tBu

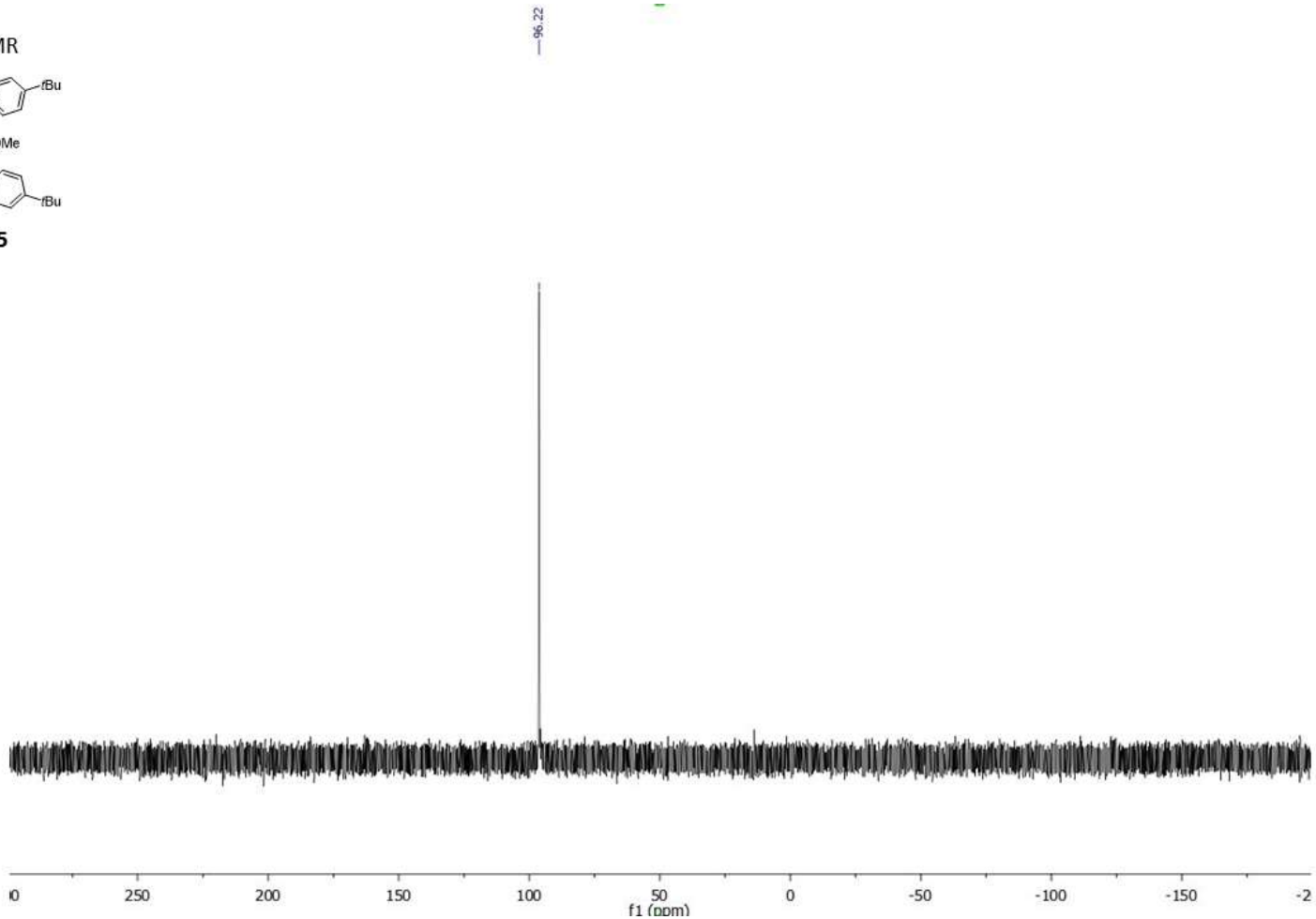
P15


8.21
8.19
7.16
7.11
7.07
6.96
6.93
6.78
4.99
4.98
4.91
3.31
3.27
3.13
3.09
3.06
3.02
3.01
2.91
1.10
1.06
1.81
9.16
5.44
1.89
1.04
1.28
5.47
18.00
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
f1 (ppm)

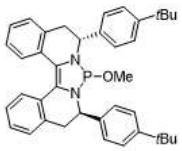
^{31}P NMR



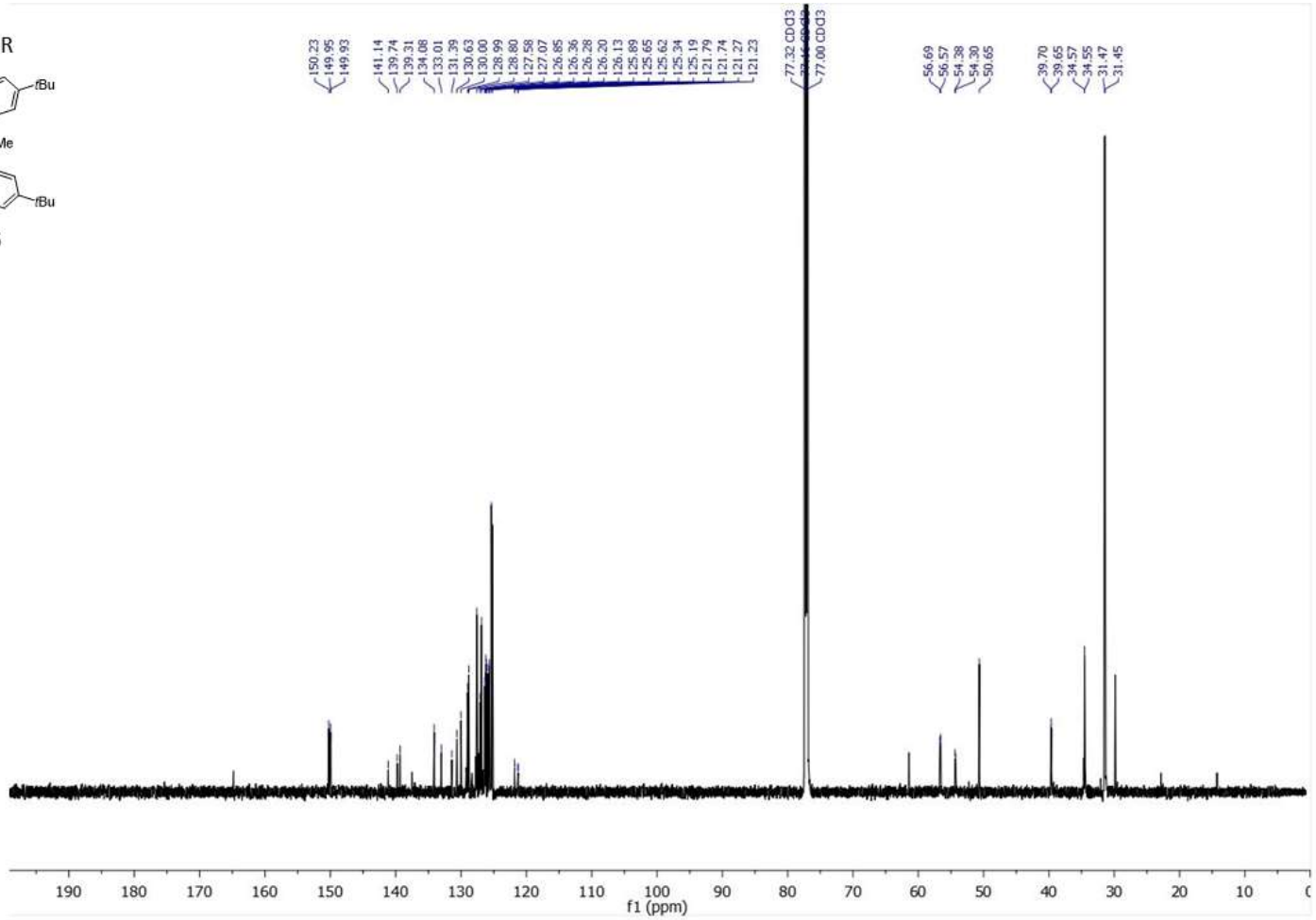
P15



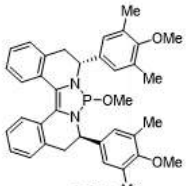
^{13}C NMR


tBu
N
P–OMe
N
tBu

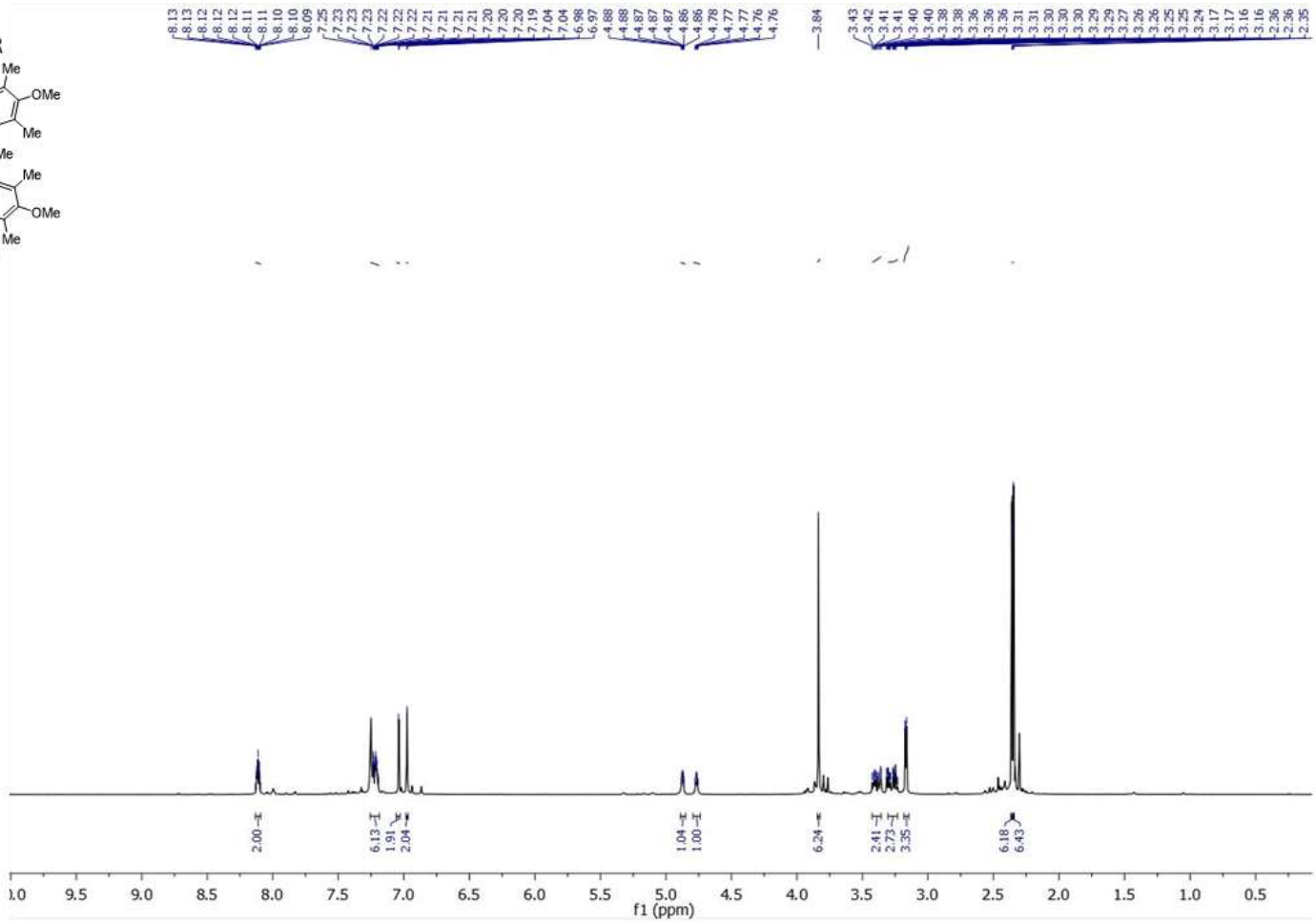
P15


150.23
149.95
149.93
141.14
139.74
139.31
134.08
133.01
131.39
130.63
130.00
128.99
128.80
127.58
127.07
126.85
126.36
126.28
126.20
126.13
125.89
125.65
125.62
125.34
125.19
121.79
121.74
121.27
121.23
77.32 CDCl3
77.00 CDCl3
56.69
56.57
54.38
54.30
50.65
39.70
39.65
34.57
34.55
31.47
31.45
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

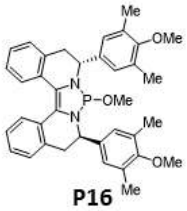
^{1}H NMR


Me
OMe
Me
N
P–OMe
N
Me
OMe
Me

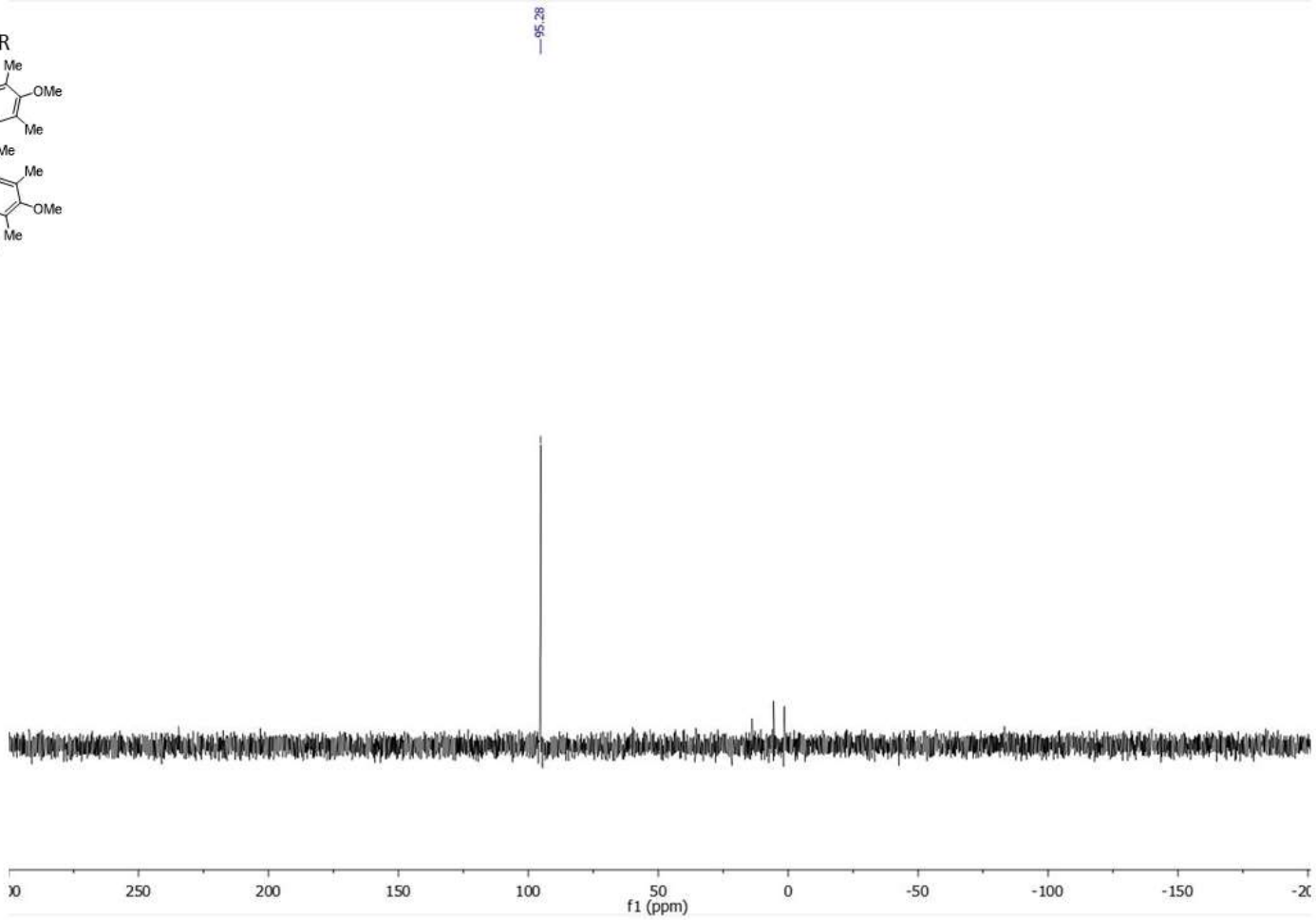
P16


8.13 8.13 8.12 8.12 8.12 8.11 8.11 8.10 8.10 8.09
7.25 7.23 7.23 7.23 7.22 7.22 7.22 7.21 7.21 7.21 7.21 7.20 7.20 7.20 7.19 7.04 7.04 6.98 6.97
4.88 4.87 4.87 4.87 4.86 4.86 4.78 4.77 4.77 4.76 4.76
3.84
3.43 3.42 3.41 3.41 3.40 3.40 3.38 3.38 3.36 3.36 3.36 3.31 3.31 3.30 3.30 3.30 3.29 3.29 3.27 3.26 3.26 3.25 3.24 3.17 3.17 3.16 3.16 2.36 2.36 2.35
2.00
6.13 1.91 2.04
1.04 1.00
6.24
2.41 2.73 3.35
6.18 6.43
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
f1 (ppm)

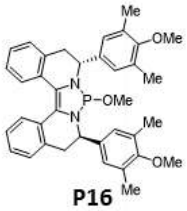
^{31}P NMR


Me
OMe
Me
N
P–OMe
N
Me
OMe
Me
Me

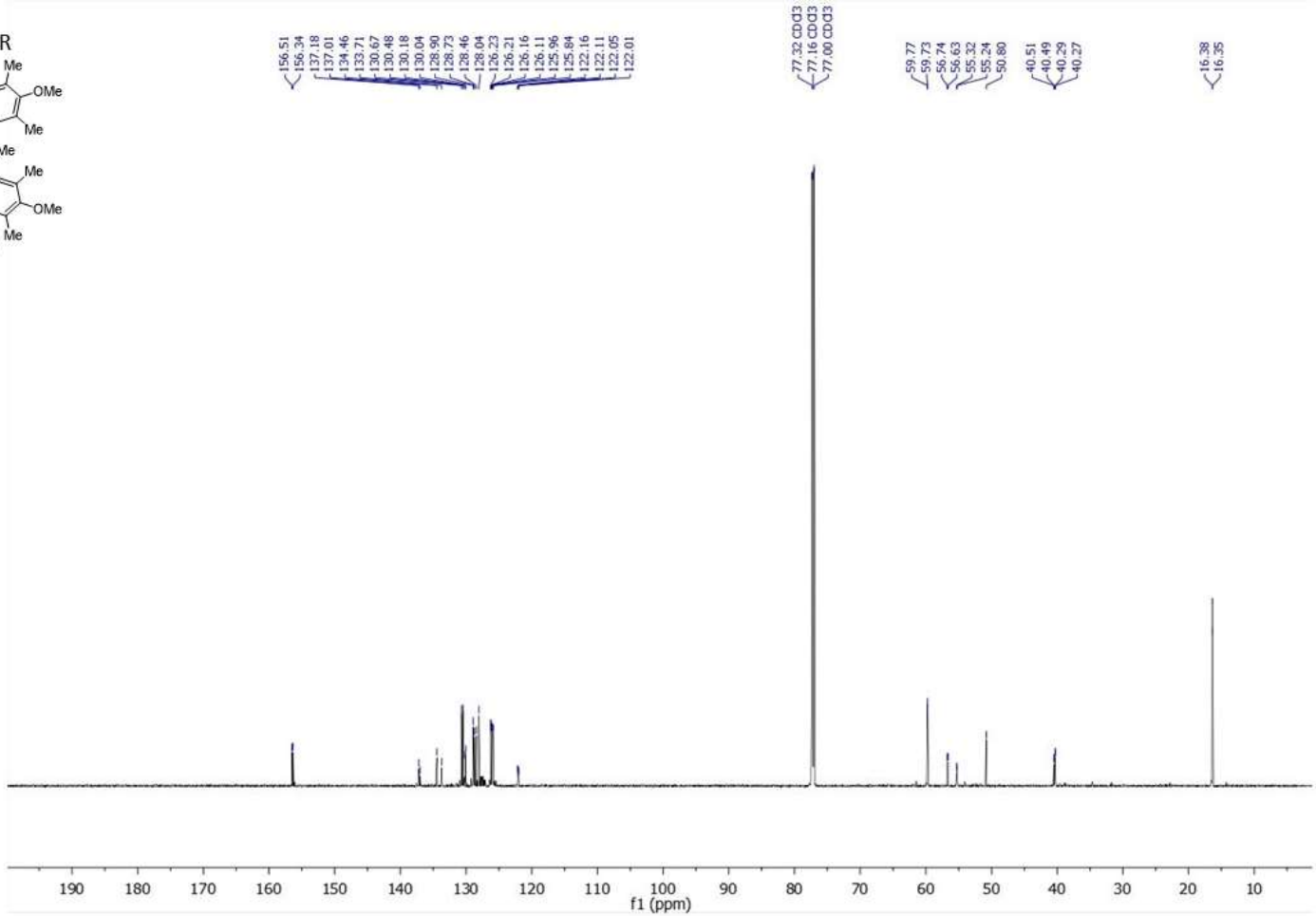
P16


95.28
250
200
150
100
50
0
-50
-100
-150
f1 (ppm)

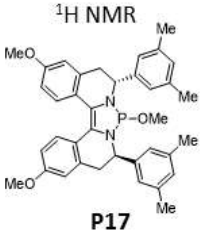
^{13}C NMR


Me
OMe
Me
N
P−OMe
N
Me
OMe
Me
Me

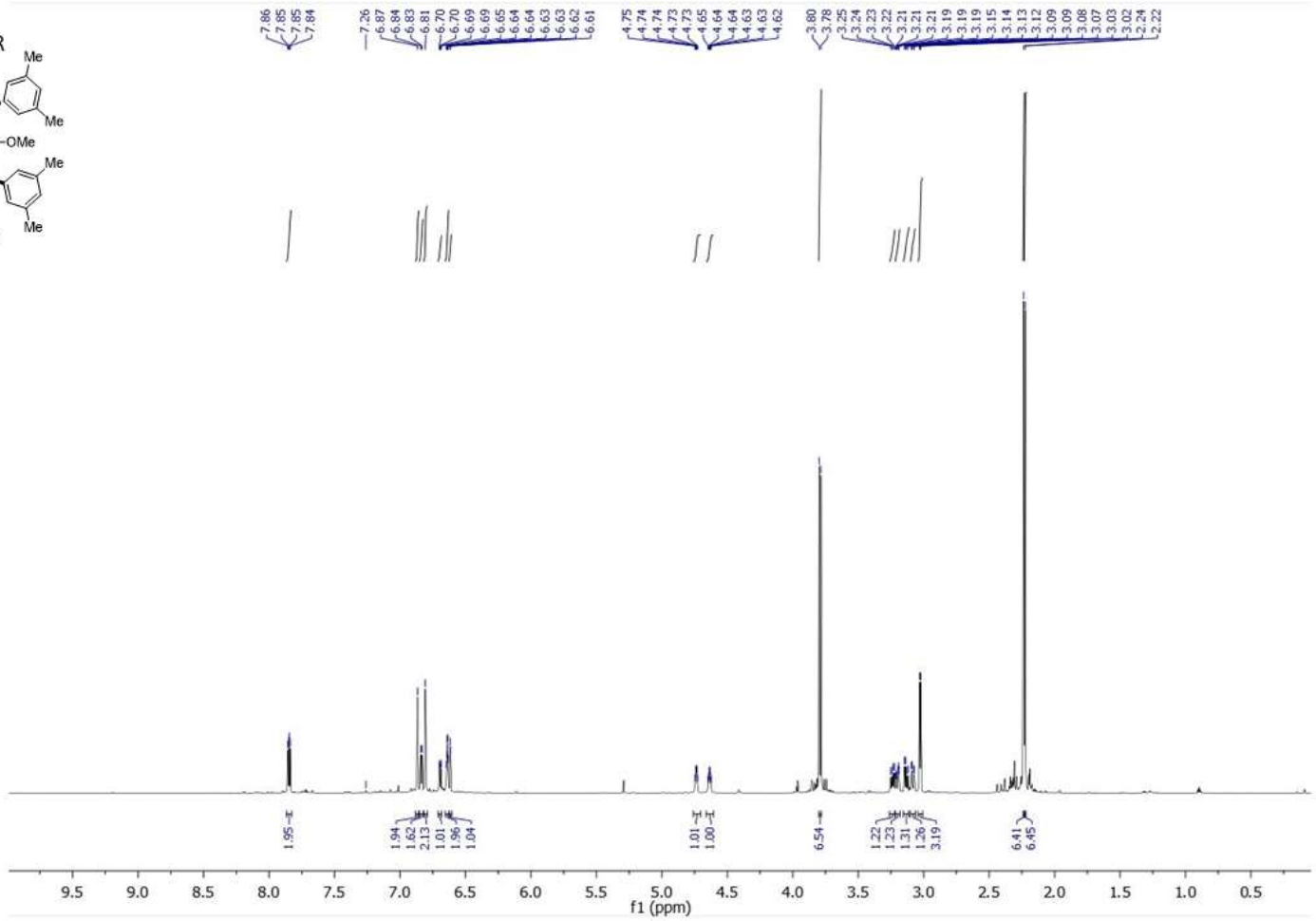
P16


156.51
156.34
137.18
137.01
134.46
133.71
130.67
130.48
130.18
130.04
128.90
128.73
128.46
128.04
126.23
126.21
126.16
126.11
125.96
125.84
122.16
122.11
122.05
122.01
77.32 CDCl3
77.16 CDCl3
77.00 CDCl3
59.77
59.73
56.74
56.63
55.32
55.24
50.80
40.51
40.49
40.29
40.27
16.38
16.35
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

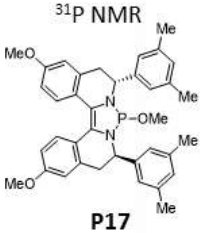
^{1}H NMR


MeO
Me
Me
N
P–OMe
N
Me
Me
MeO

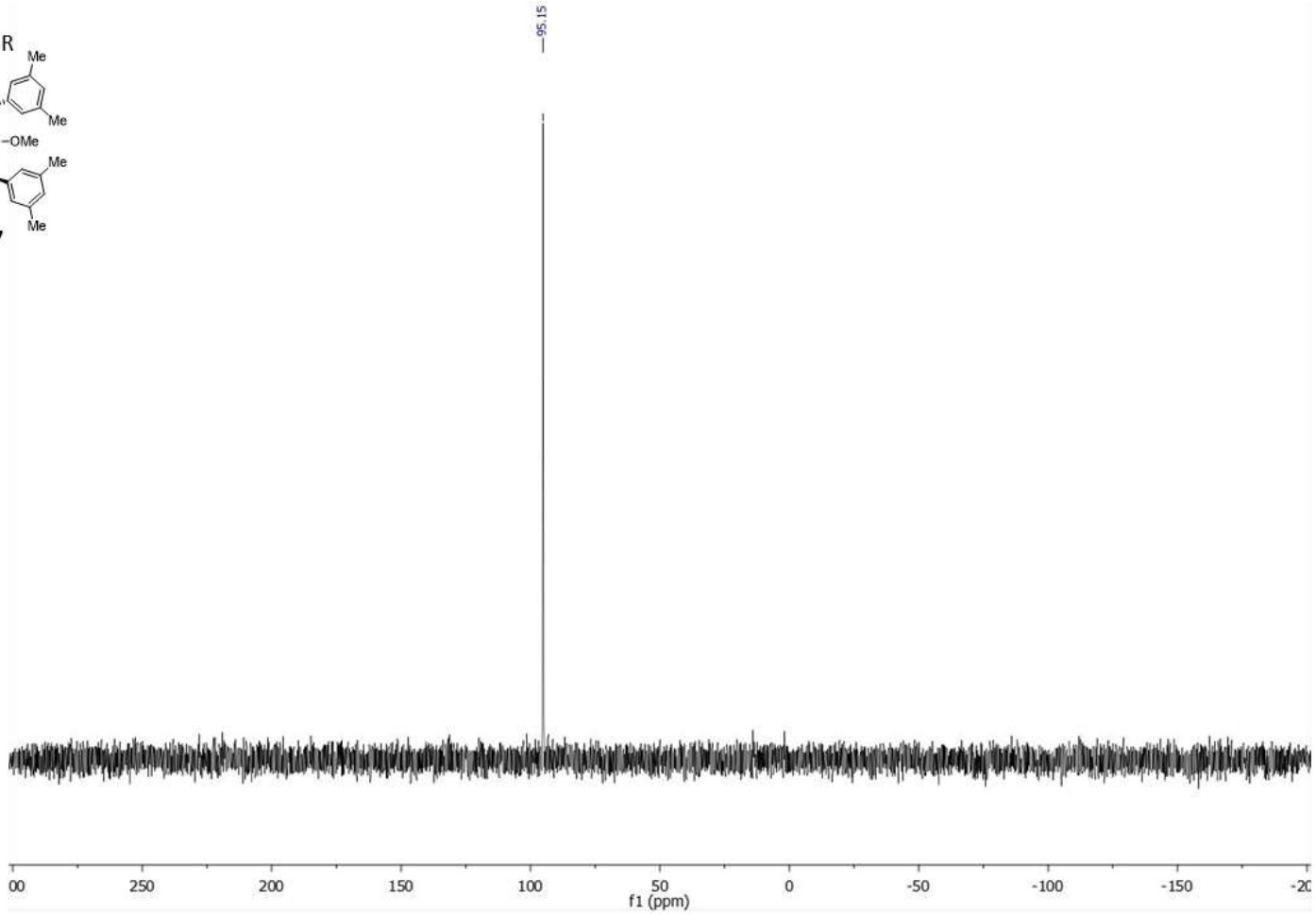
P17


7.86 7.85 7.85 7.84
7.26
6.87 6.84 6.83 6.81 6.70 6.70 6.69 6.69 6.65 6.64 6.64 6.63 6.63 6.62 6.61
4.75 4.74 4.74 4.73 4.73 4.65 4.64 4.64 4.63 4.63 4.62
3.80 3.78
3.25 3.24 3.23 3.22 3.21 3.21 3.21 3.19 3.19 3.19 3.15 3.14 3.13 3.12 3.09 3.09 3.08 3.07 3.03 3.02 2.24 2.22
1.95
1.94 1.62 2.13 1.01 1.96 1.04
1.01 1.00
6.54
1.22 1.23 1.31 1.26 3.19
6.41 6.45
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
f1 (ppm)

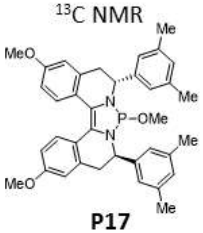
^{31}P NMR


MeO
Me
Me
N
P–OMe
N
Me
Me
MeO

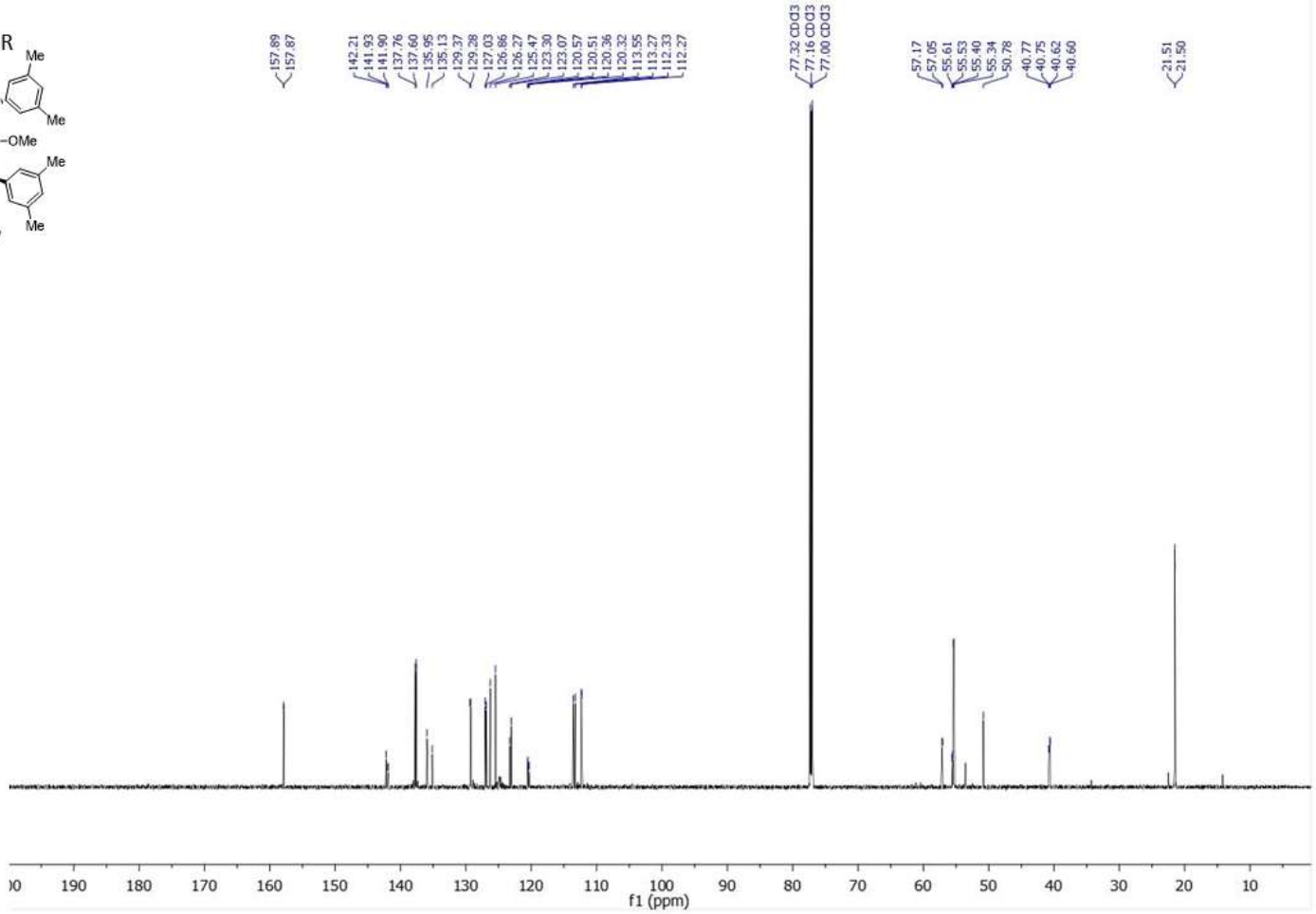
P17


95.15
00
250
200
150
100
50
0
-50
-100
-150
-20
f1 (ppm)

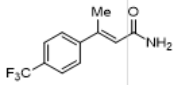
^{13}C NMR


MeO
Me
Me
N
P–OMe
N
Me
MeO
Me

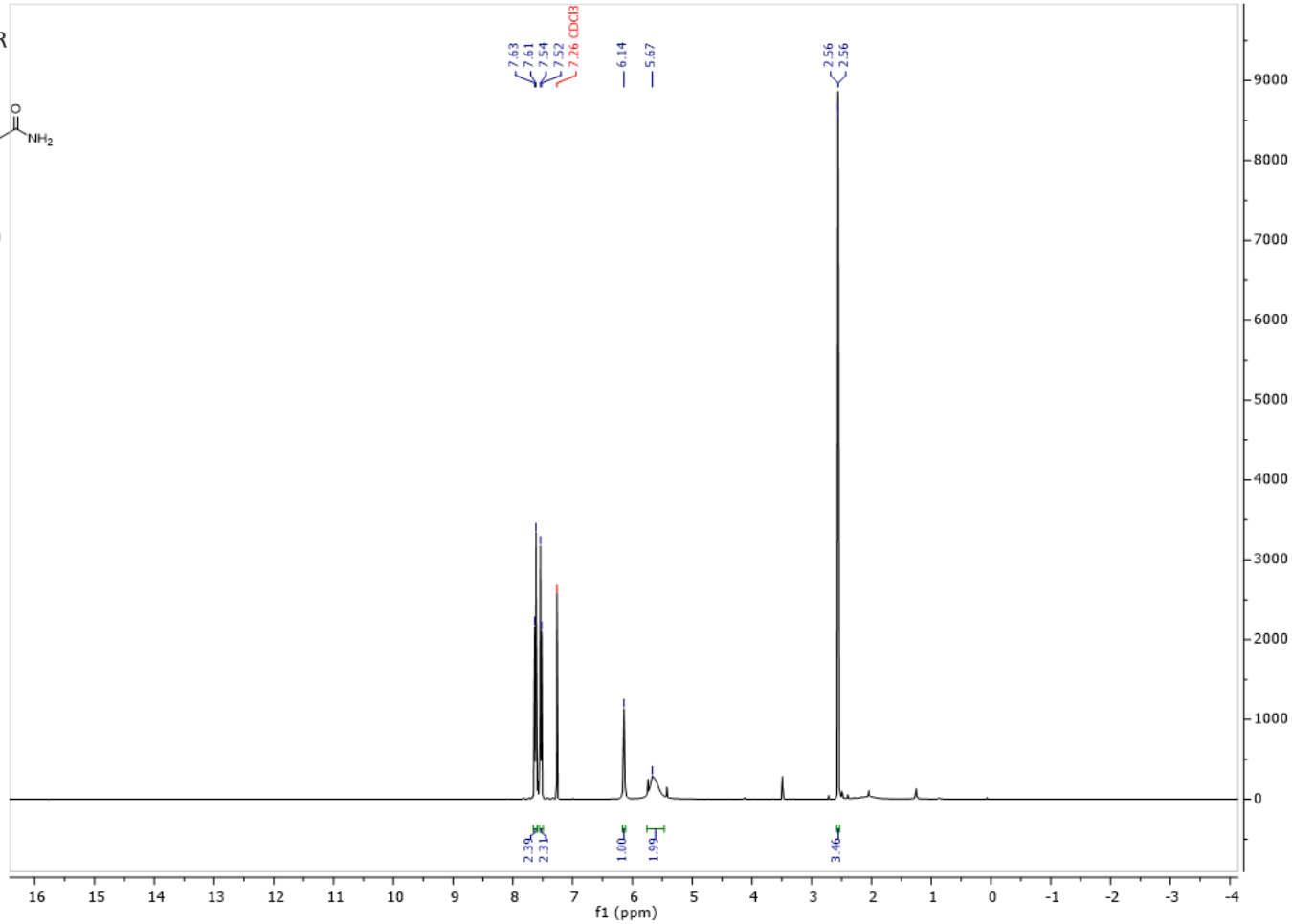
P17


157.89
157.87
142.21
141.93
141.90
137.76
137.60
135.95
135.13
129.37
129.28
127.03
126.86
126.27
125.47
123.30
123.07
120.57
120.51
120.36
120.32
113.55
113.27
112.33
112.27
77.32 CDCl3
77.16 CDCl3
77.00 CDCl3
57.17
57.05
55.61
55.53
55.40
55.34
50.78
40.77
40.75
40.62
40.60
21.51
21.50
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

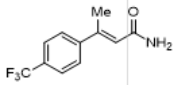
^{1}H NMR


Me
O
NH2
F3C

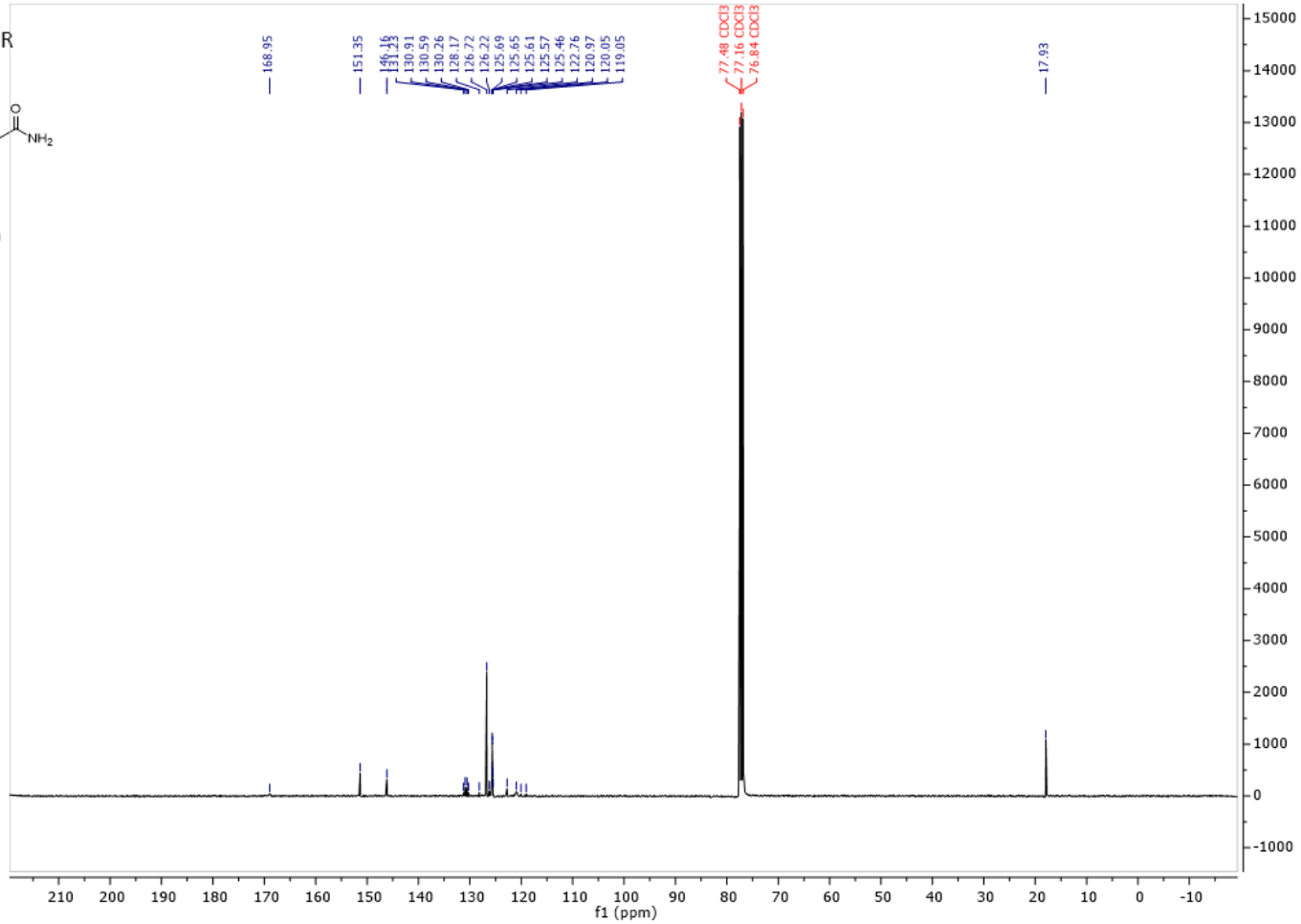
S20


7.63
7.61
7.54
7.52
7.26 CDCl3
6.14
5.67
2.56
2.56
2.39
2.31
1.00
1.99
3.46
f1 (ppm)

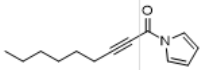
^{13}C NMR


Me
O
NH2
F3C

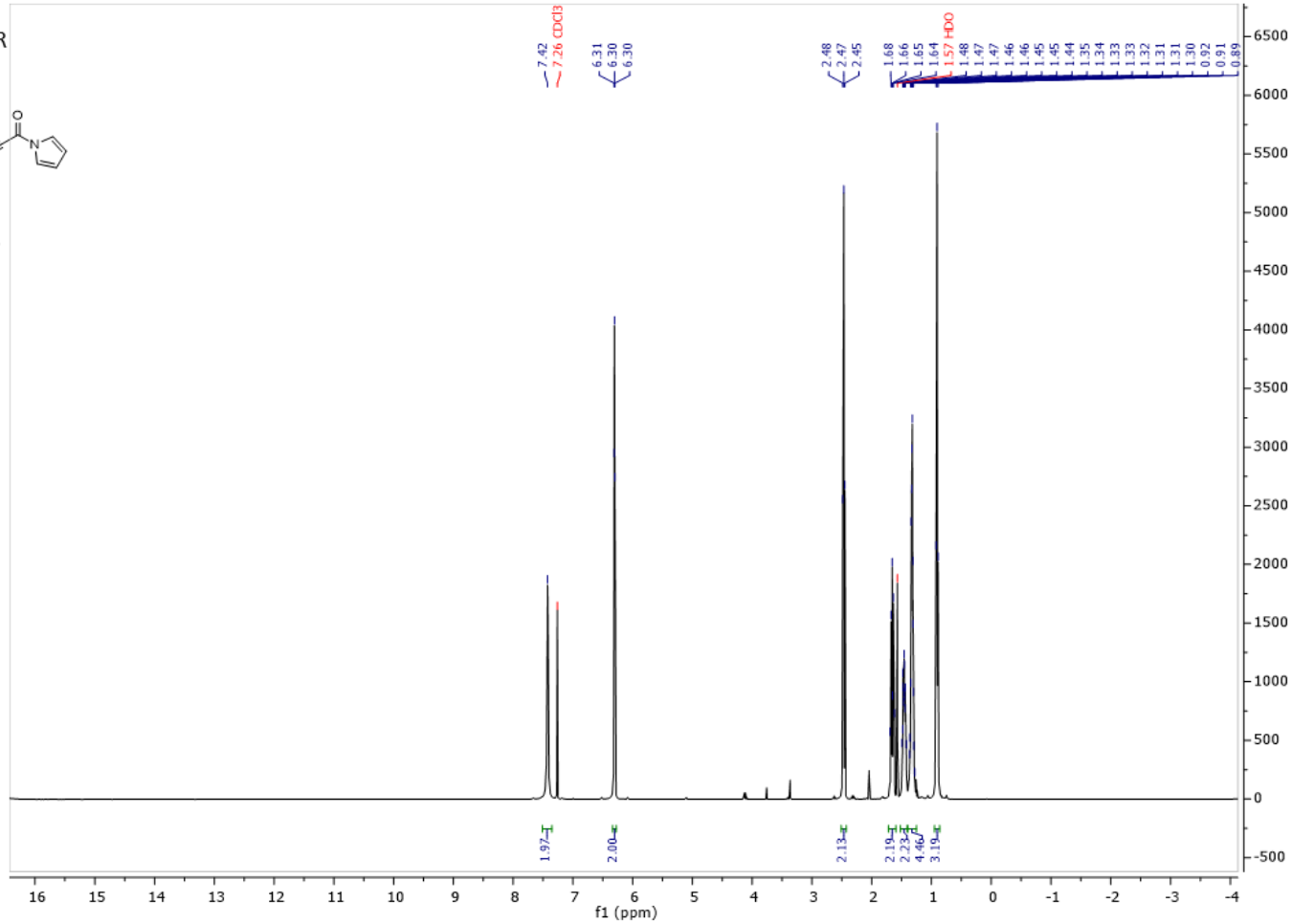
S20


168.95
151.35
146.16
141.23
130.91
130.59
130.26
128.17
126.72
126.22
125.69
125.65
125.61
125.57
125.46
122.76
120.97
120.05
119.05
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
17.93
f1 (ppm)

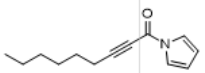
^{1}H NMR



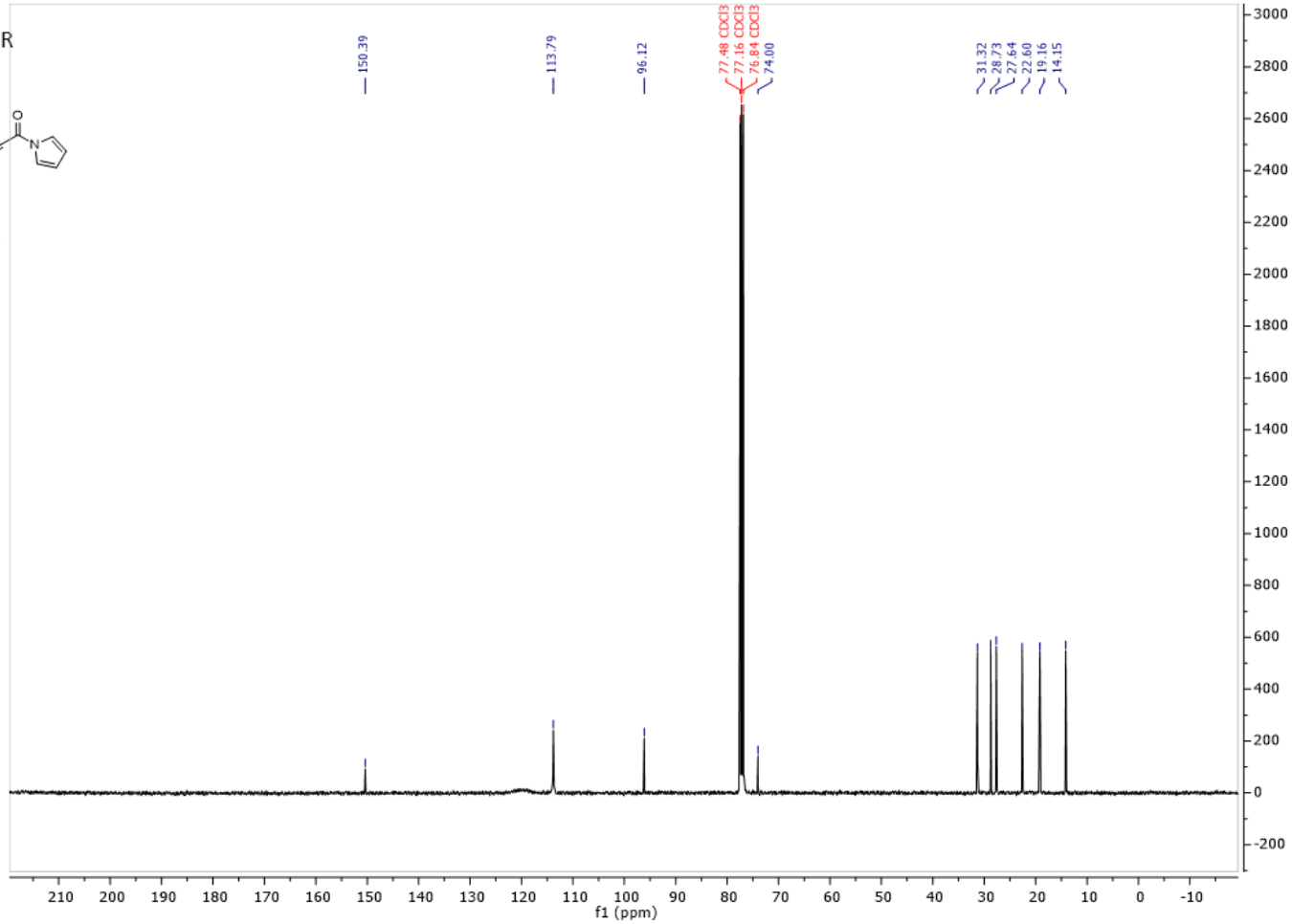
S22


7.42
7.26 CDCl3
6.31
6.30
6.30
2.48
2.47
2.45
1.68
1.66
1.65
1.64
1.57 HDO
1.48
1.47
1.47
1.46
1.46
1.45
1.45
1.44
1.35
1.34
1.33
1.33
1.32
1.31
1.31
1.30
0.92
0.91
0.89
1.97
2.00
2.13
2.19
2.23
4.46
3.19
f1 (ppm)

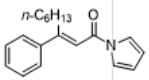
^{13}C NMR



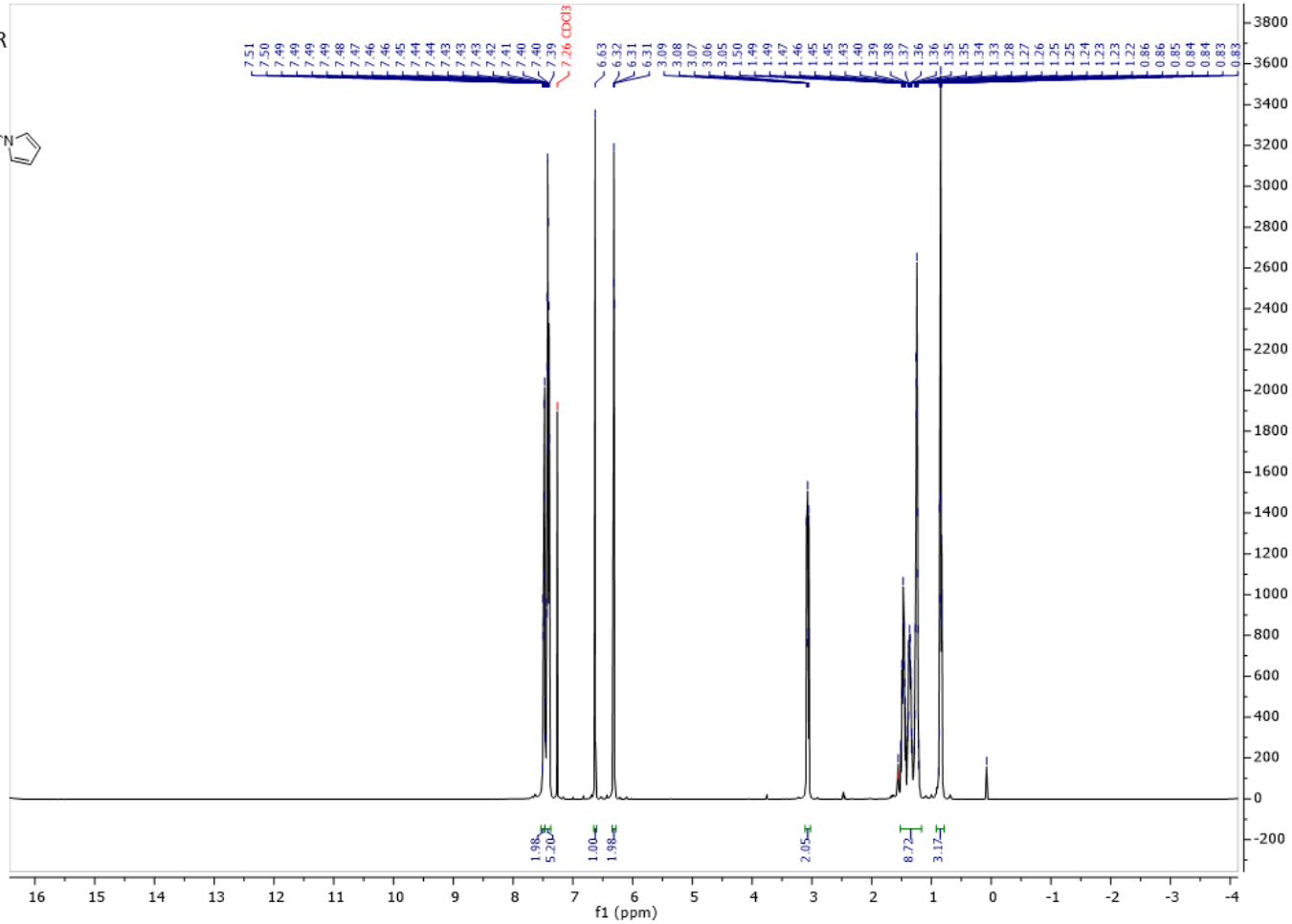
S22


150.39
113.79
96.12
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.00
31.32
28.73
27.64
22.60
19.16
14.15
f1 (ppm)

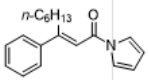
^{1}H NMR



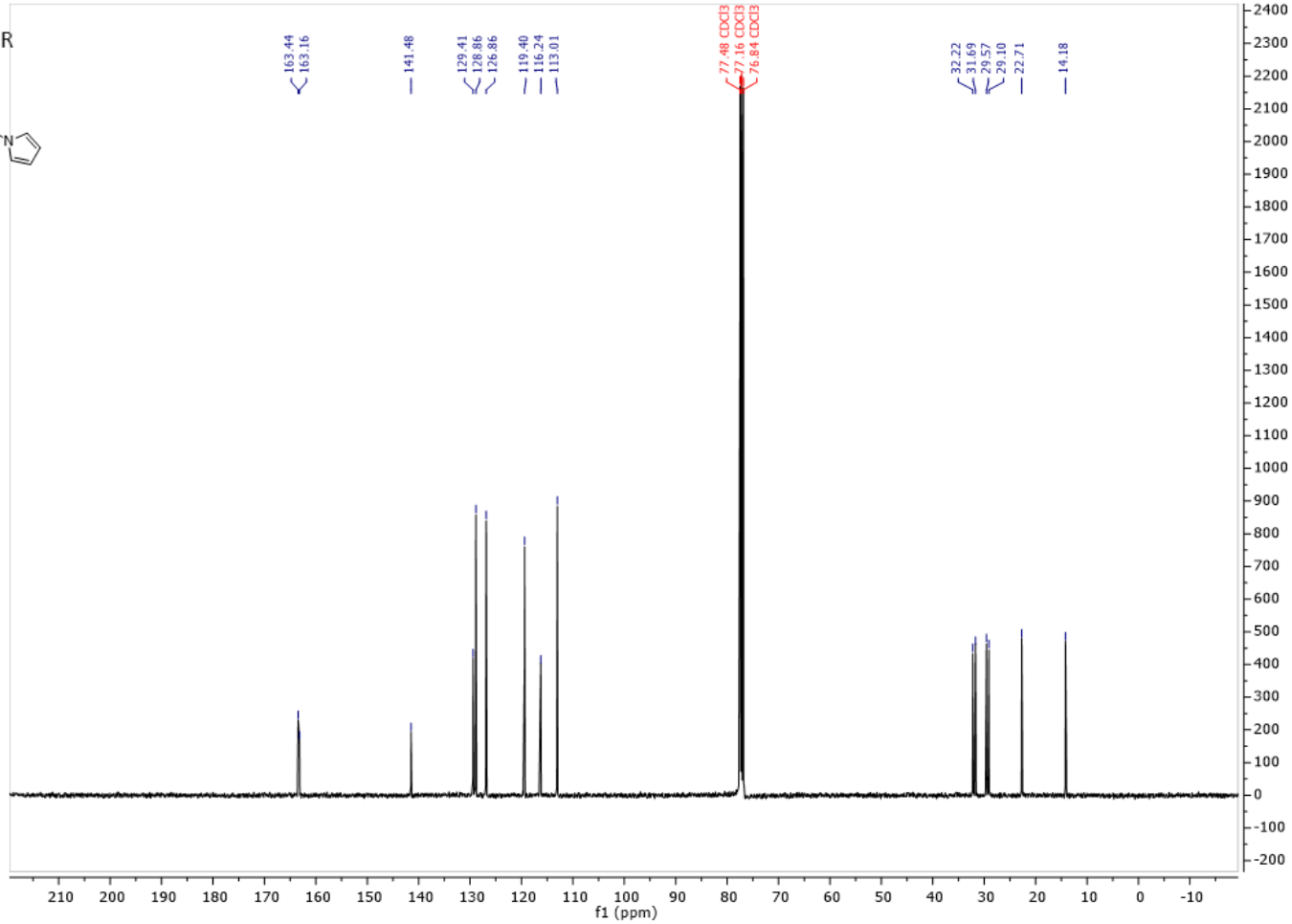
1b



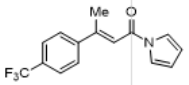
^{13}C NMR


n-C6H13
O
N

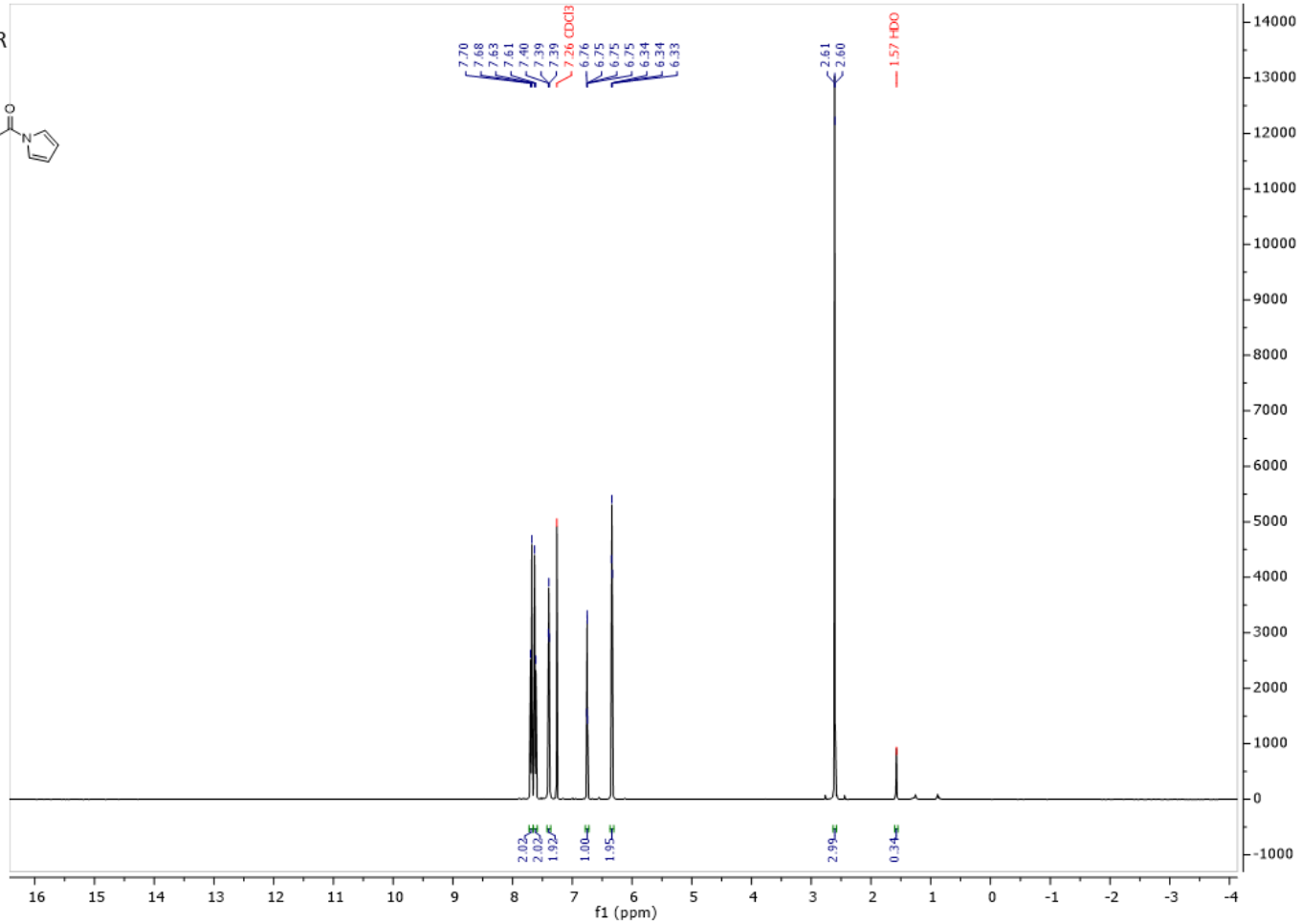
1b


163.44
163.16
141.48
129.41
128.86
126.86
119.40
116.24
113.01
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
32.22
31.69
29.57
29.10
22.71
14.18
f1 (ppm)

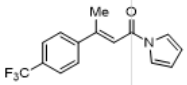
^{1}H NMR


Me
O
N
F3C

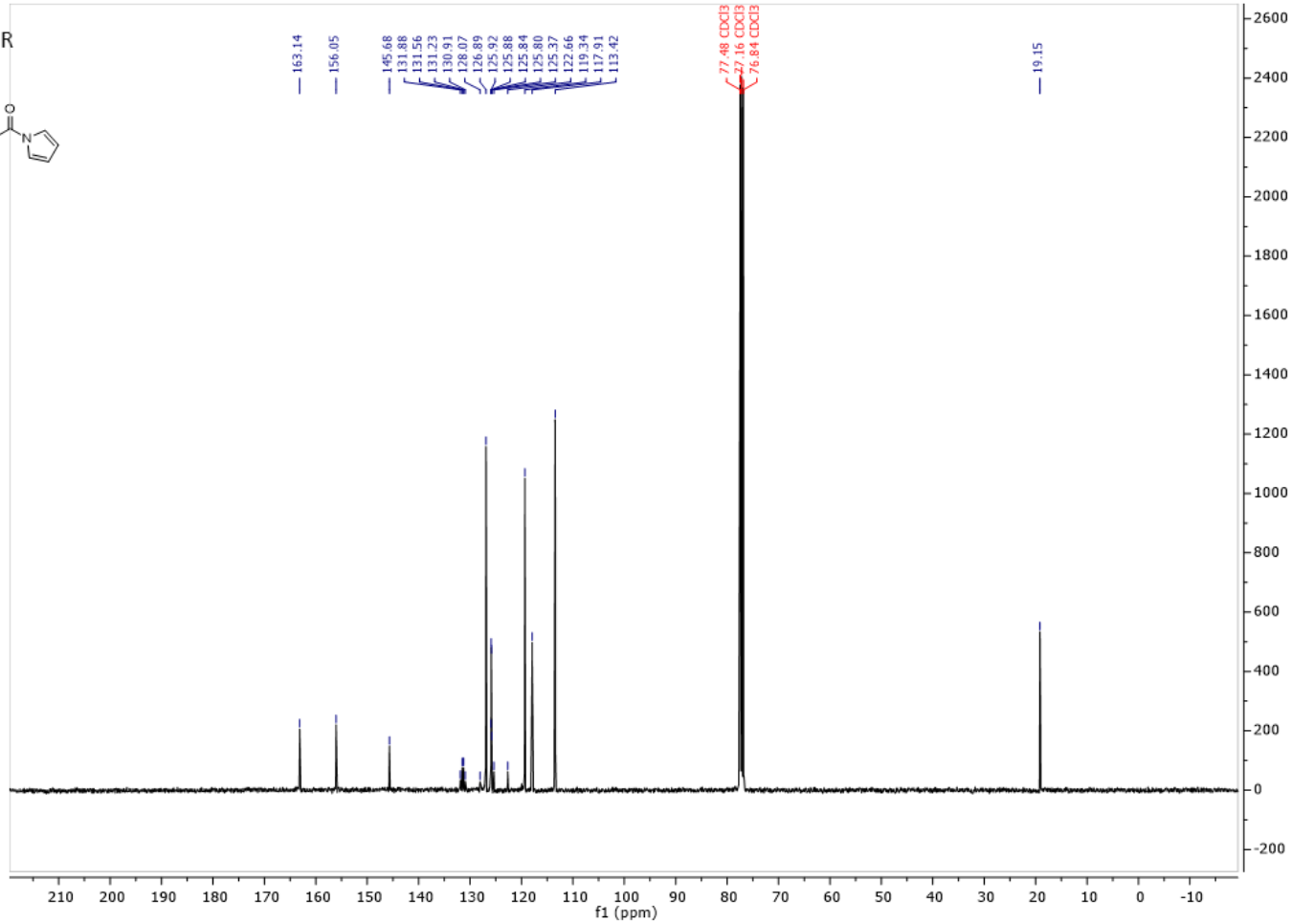
1c


7.70
7.68
7.63
7.61
7.40
7.39
7.39
7.26 CDCl3
6.76
6.75
6.75
6.75
6.34
6.34
6.33
2.61
2.60
1.57 HDO
2.02
2.02
1.92
1.00
1.95
2.99
0.34
f1 (ppm)

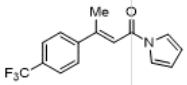
^{13}C NMR


Me
O
N
F3C

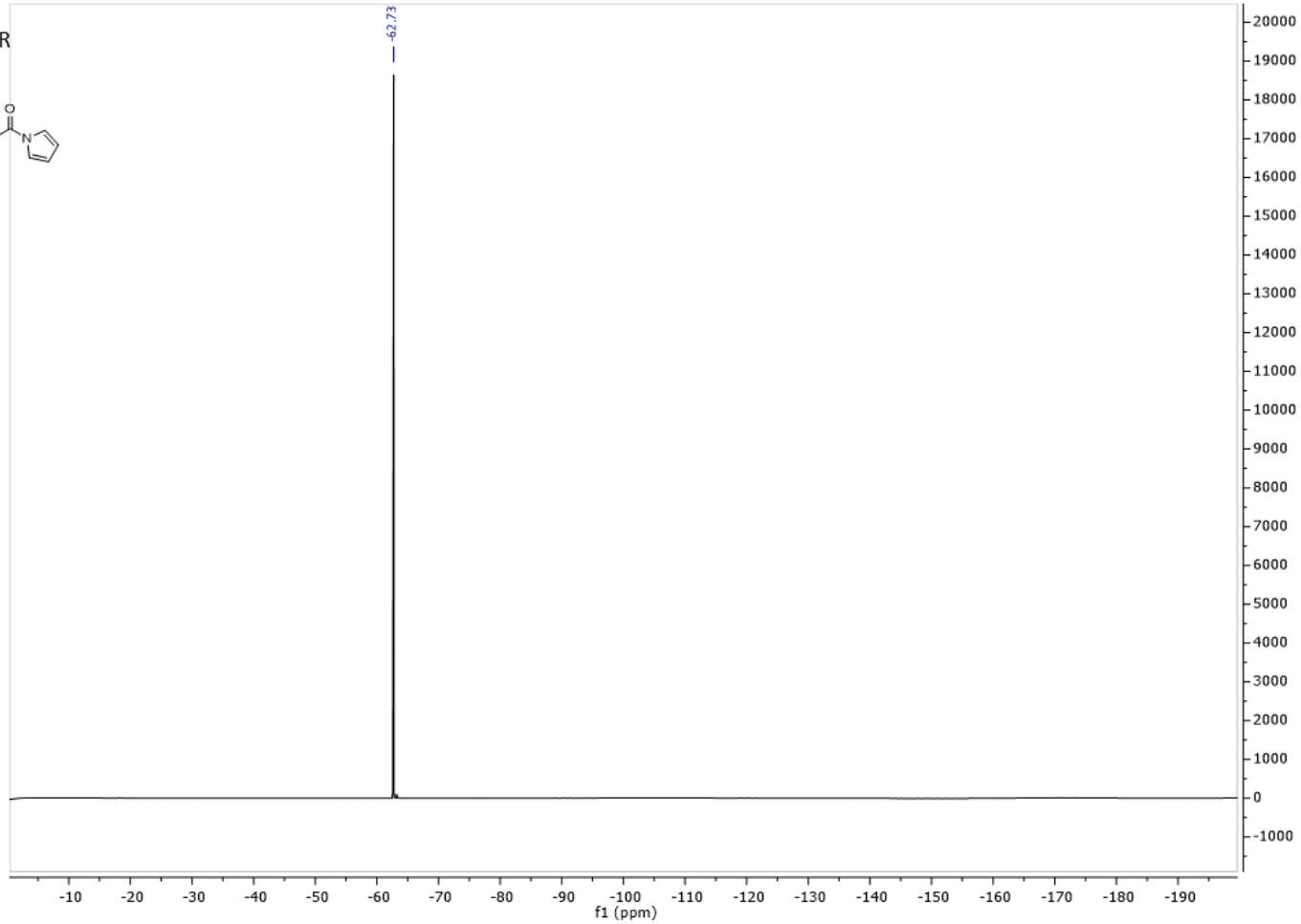
1c


163.14
156.05
145.68
131.88
131.56
131.23
130.91
128.07
126.89
125.92
125.88
125.84
125.80
125.37
122.66
119.34
117.91
113.42
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
19.15
f1 (ppm)

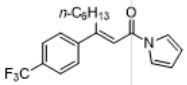
^{19}F NMR


Me
O
N
F3C

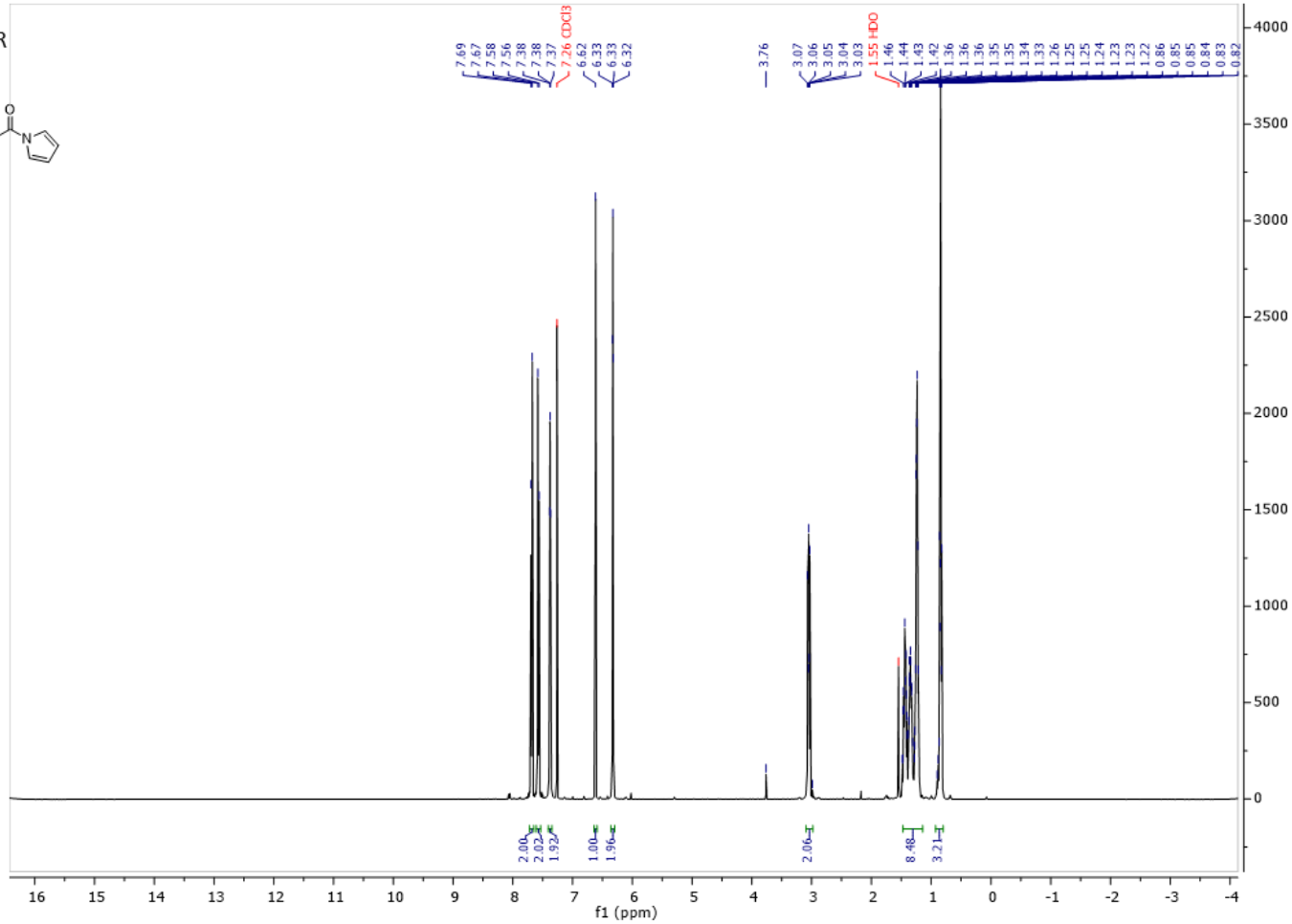
1c


-62.73
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

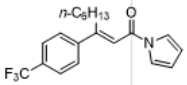
^{1}H NMR


n-C8H13
O
N
F3C

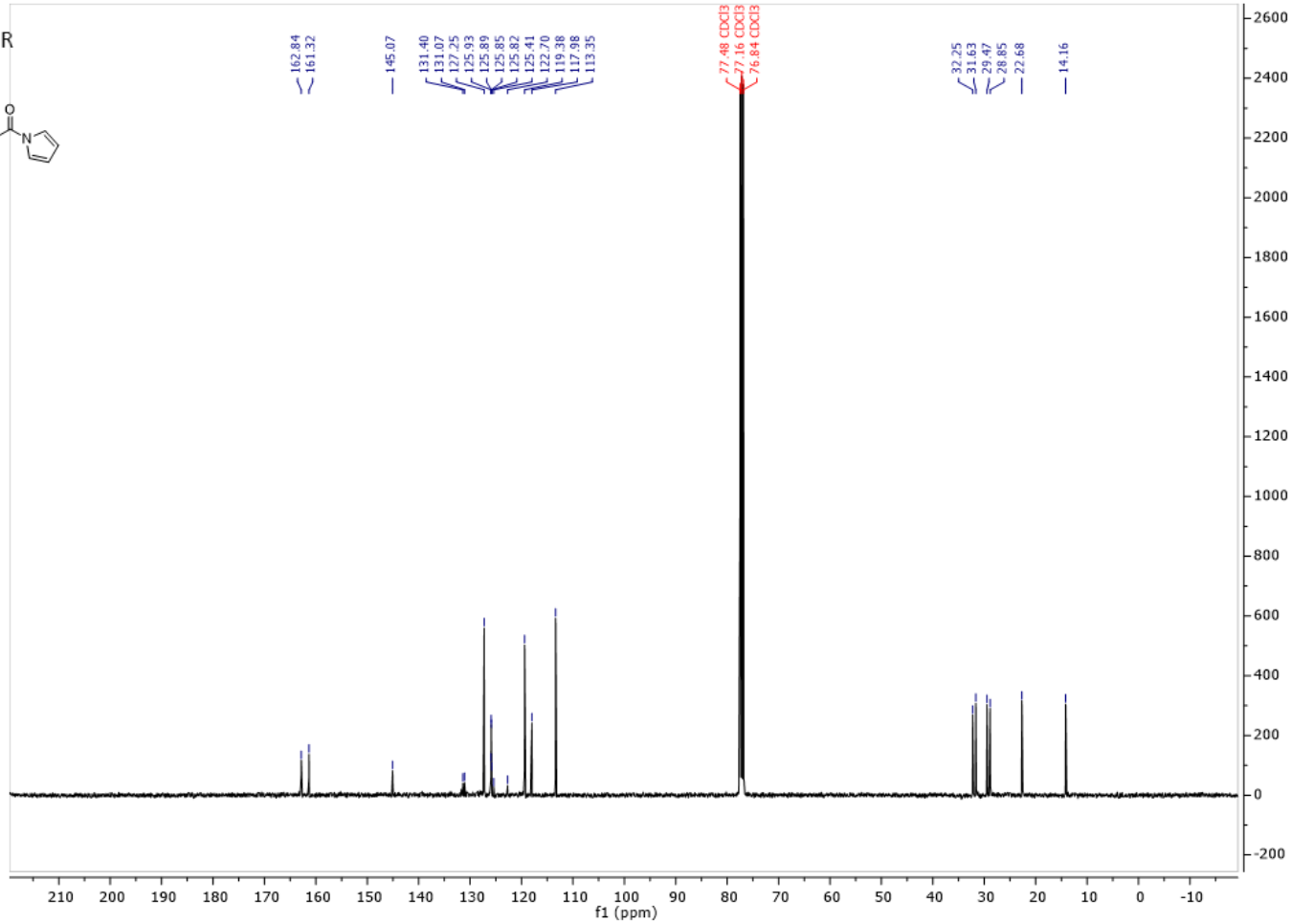
1d


7.69
7.67
7.58
7.56
7.38
7.38
7.37
7.26 CDCl3
6.62
6.33
6.33
6.32
3.76
3.07
3.06
3.05
3.04
3.03
1.55 HDO
1.46
1.44
1.43
1.42
1.36
1.36
1.36
1.35
1.35
1.34
1.33
1.26
1.25
1.25
1.24
1.23
1.23
1.22
0.86
0.85
0.85
0.84
0.83
0.82
2.00
2.02
1.92
1.00
1.96
2.06
8.48
3.21
f1 (ppm)

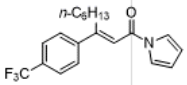
^{13}C NMR


n-C8H13
O
N
F3C

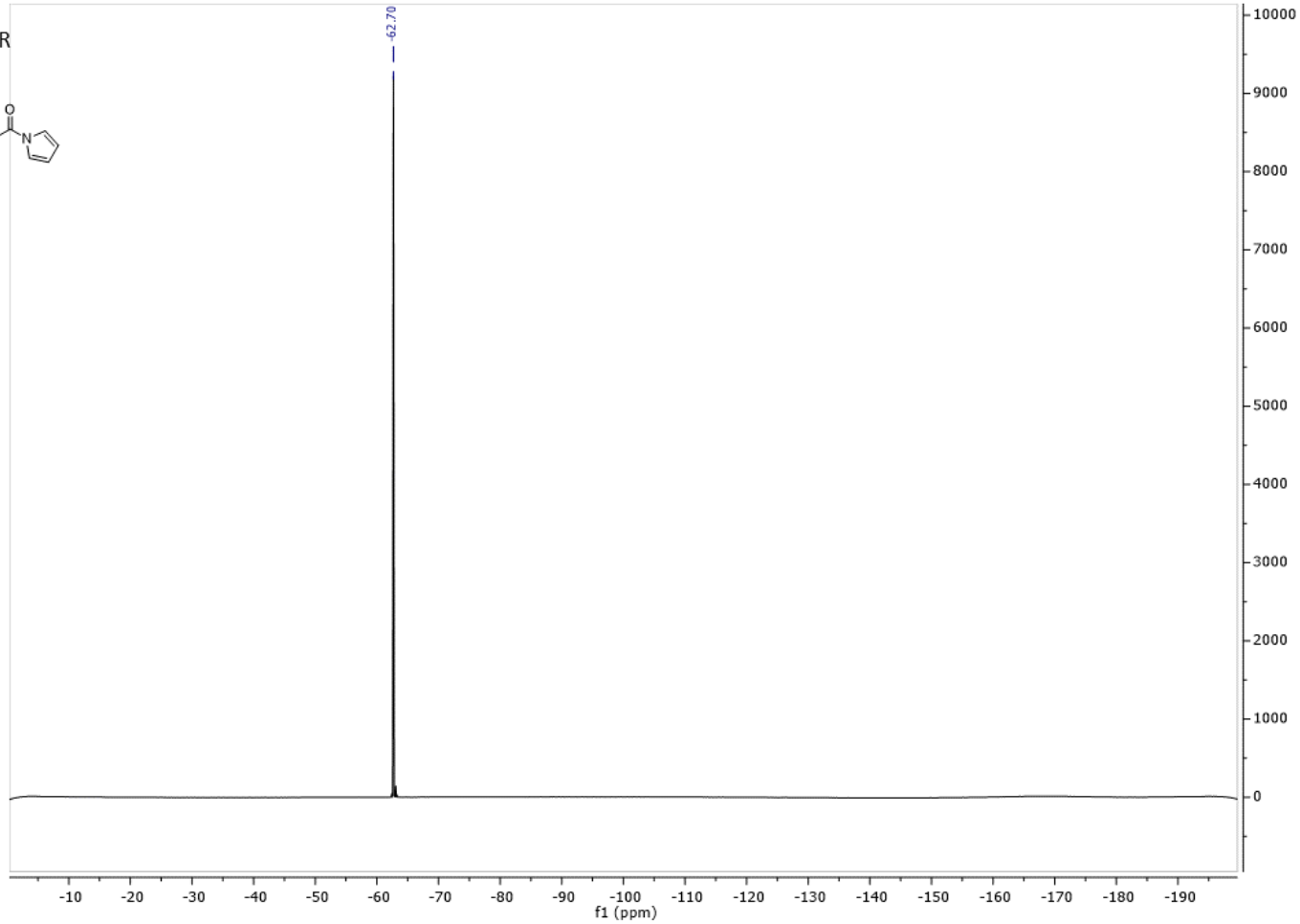
1d


162.84
161.32
145.07
131.40
131.07
127.25
125.93
125.89
125.85
125.82
125.41
122.70
119.38
117.98
113.35
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
32.25
31.63
29.47
28.85
22.68
14.16
f1 (ppm)

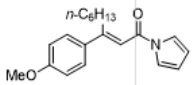
^{19}F NMR


n-C8H13
O
N
F3C

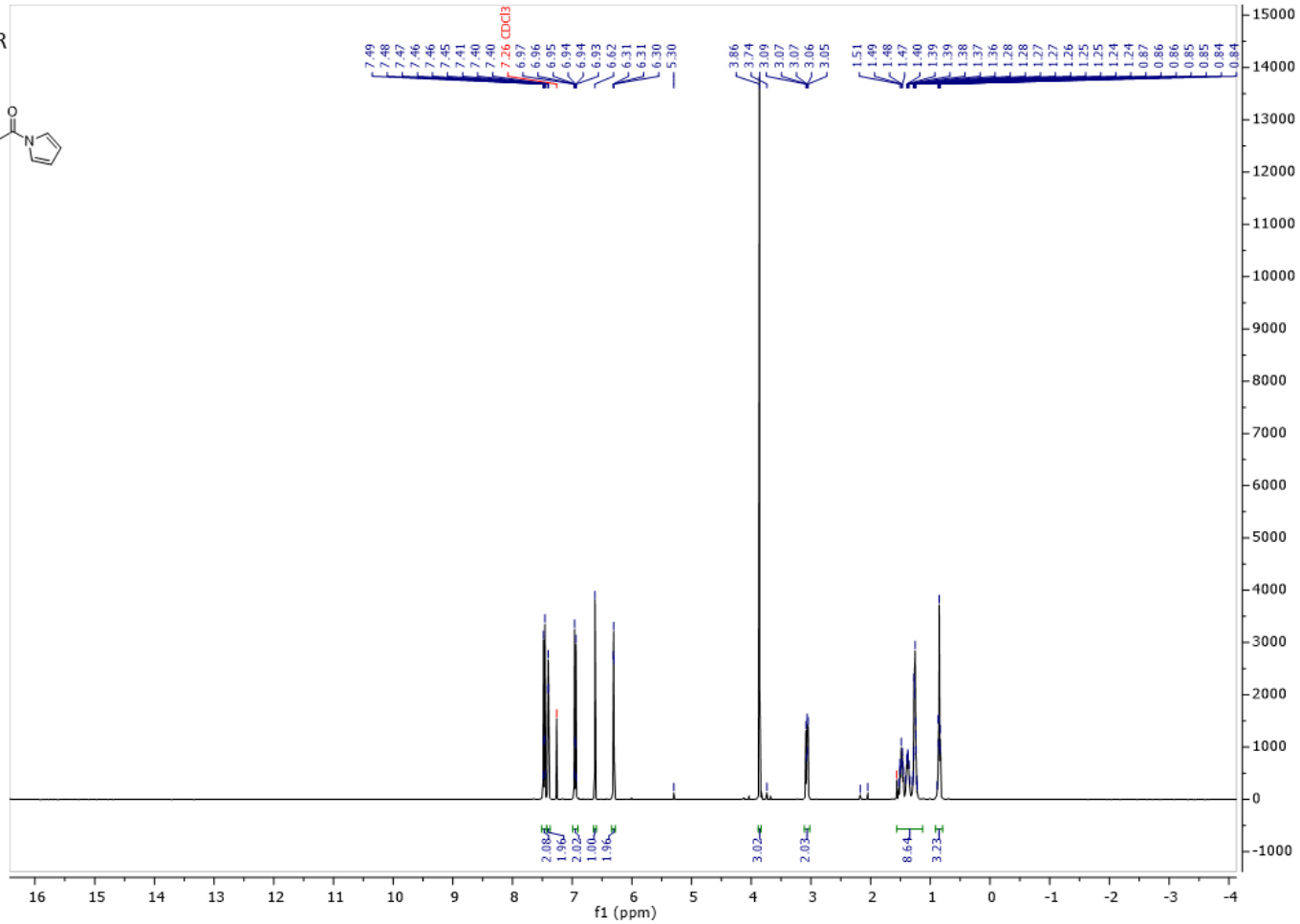
1d


-62.70
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

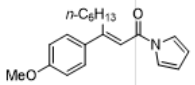
^{1}H NMR



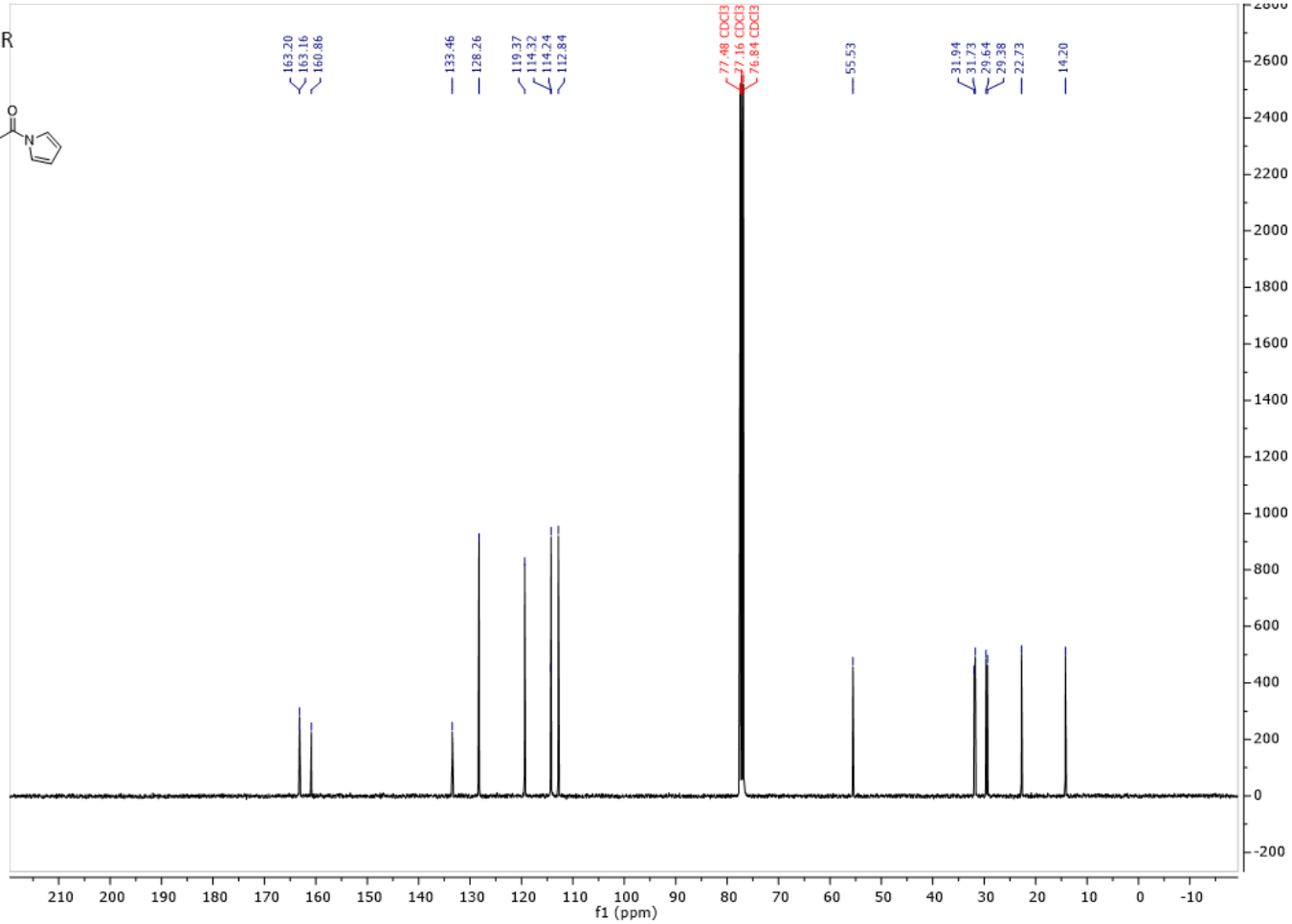
1f



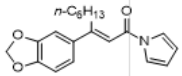
^{13}C NMR


n-C6H13
O
N
MeO

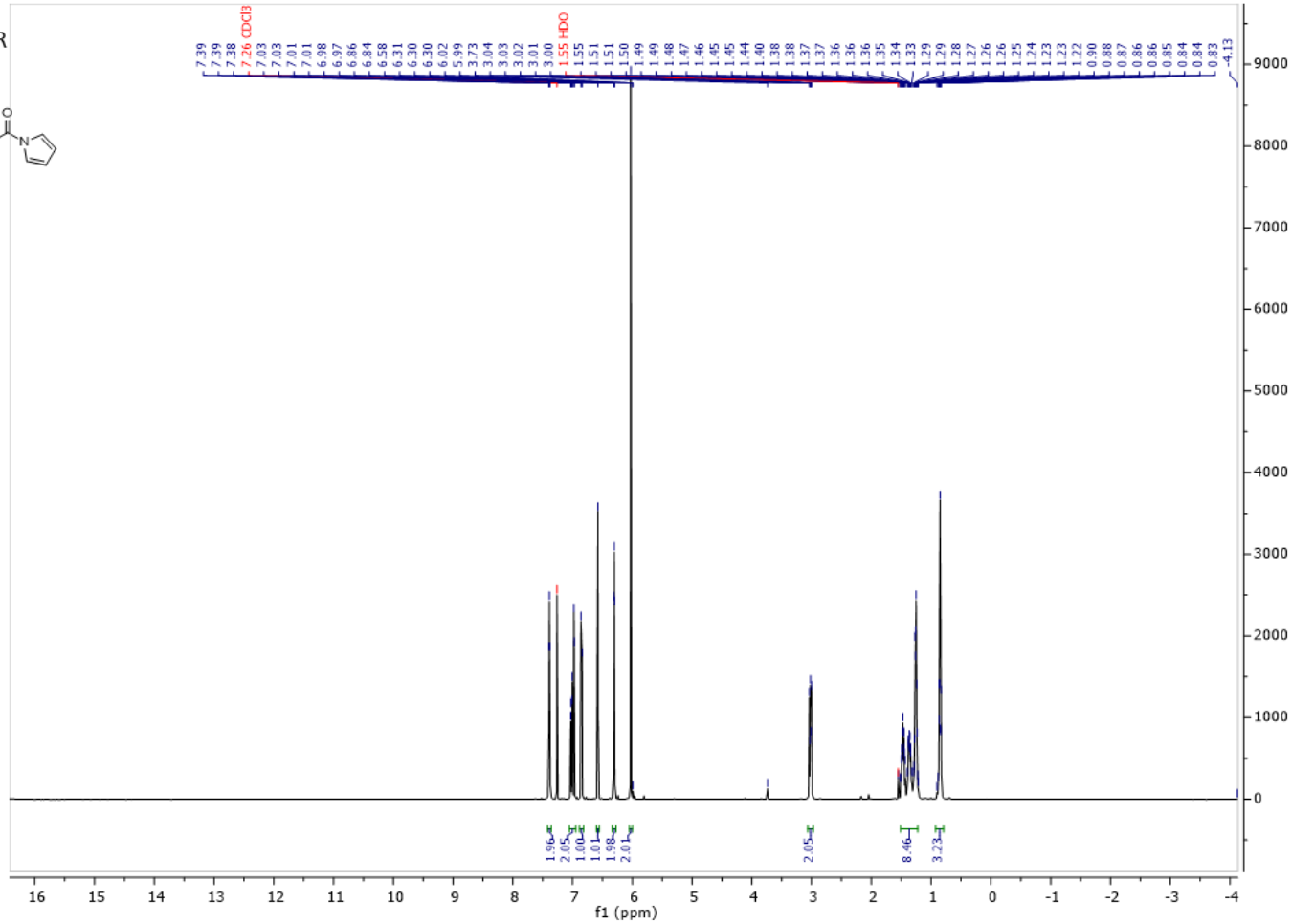
1f


163.20
163.16
160.86
133.46
128.26
119.37
114.32
114.24
112.84
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.53
31.94
31.73
29.64
29.38
22.73
14.20
f1 (ppm)

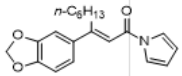
^{1}H NMR



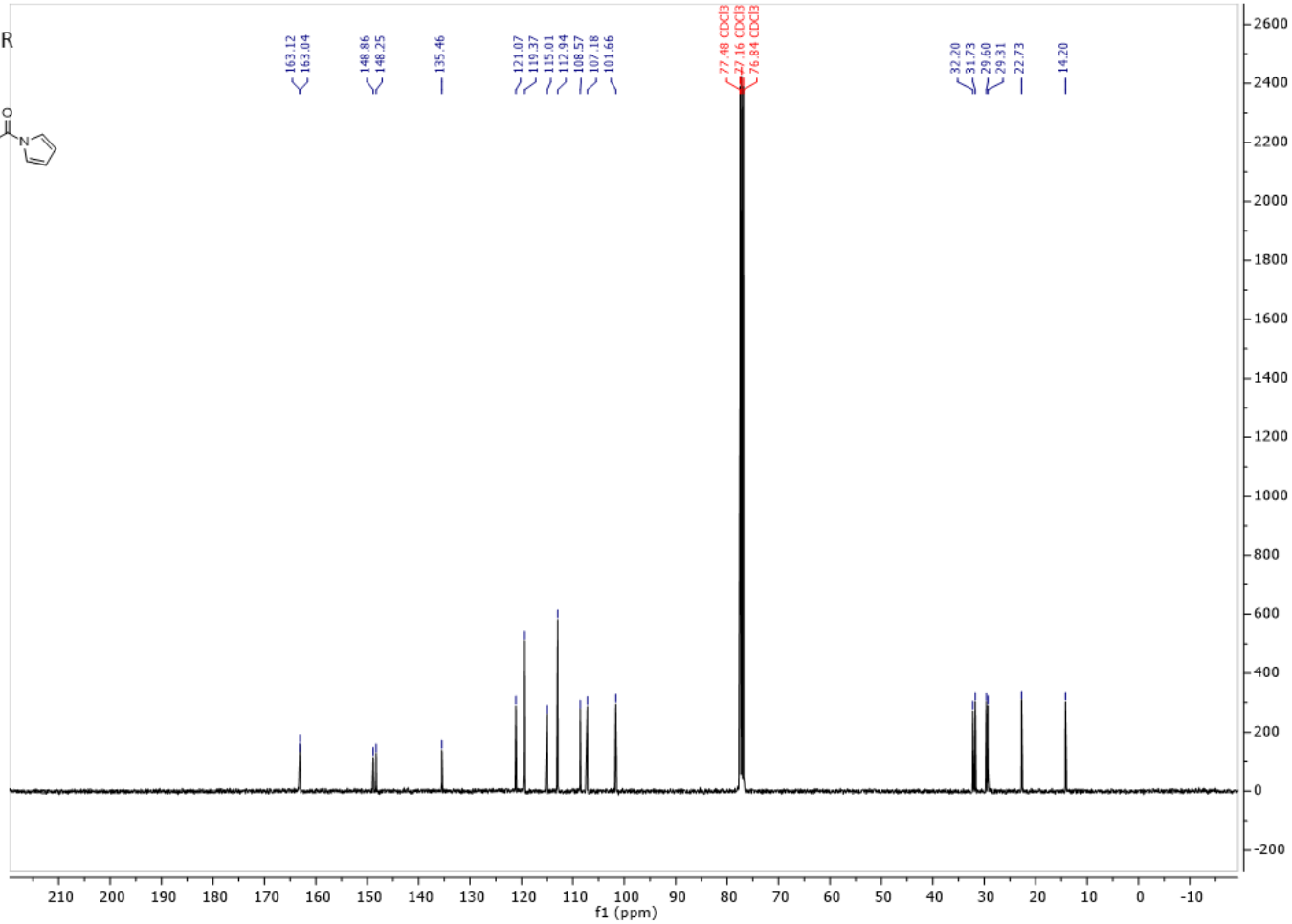
1g



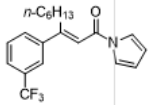
^{13}C NMR


n-C6H13
O
N
O
O

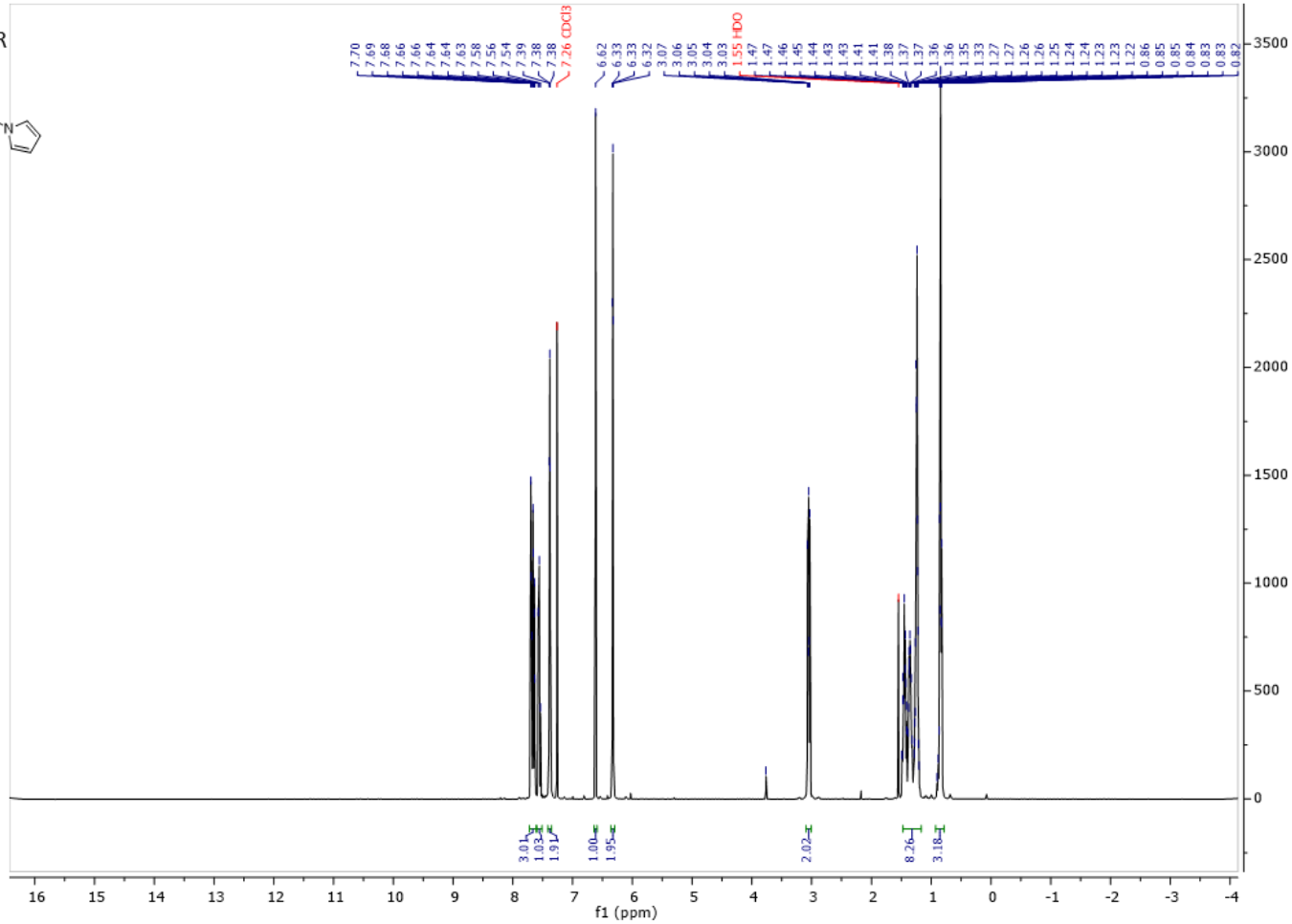
1g


163.12
163.04
148.86
148.25
135.46
121.07
119.37
115.01
112.94
108.57
107.18
101.66
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
32.20
31.73
29.60
29.31
22.73
14.20
f1 (ppm)

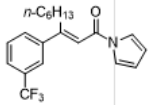
^{1}H NMR


n-C6H13
O
N
CF3

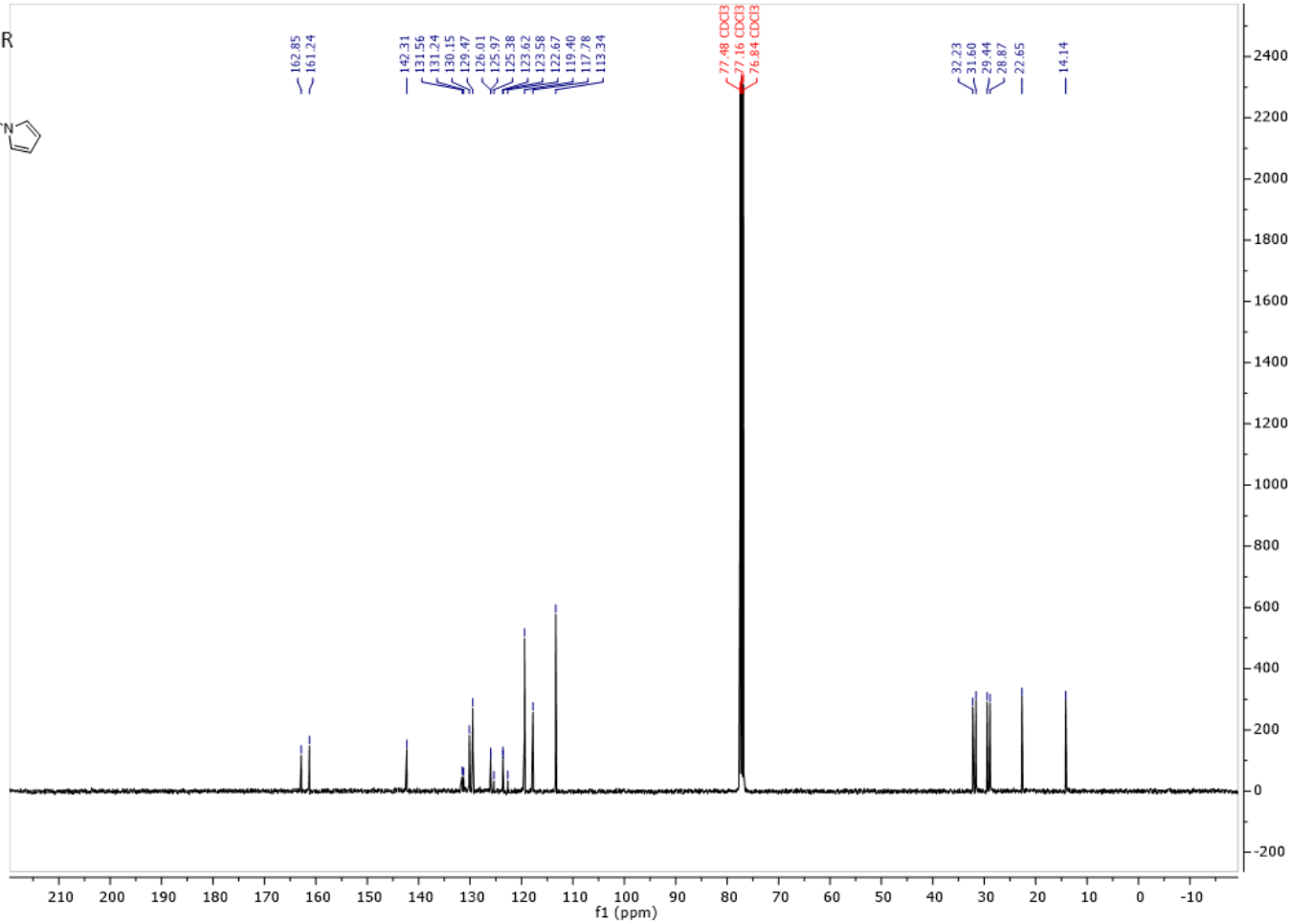
1h


7.70 7.69 7.68 7.66 7.66 7.64 7.64 7.63 7.58 7.56 7.54 7.39 7.38 7.38 7.26 CDCl3
6.62 6.33 6.33 6.32
3.07 3.06 3.05 3.04 3.03
1.55 HDO
1.47 1.47 1.46 1.45 1.44 1.43 1.43 1.41 1.41 1.38 1.37 1.37 1.36 1.36 1.35 1.33 1.27 1.27 1.26 1.26 1.25 1.24 1.24 1.23 1.23 1.22 0.86 0.85 0.85 0.84 0.83 0.83 0.82
3.01 1.03 1.91 1.00 1.95 2.02 8.26 3.18
f1 (ppm)

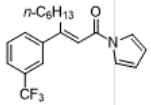
^{13}C NMR


n-C6H13
O
N
CF3

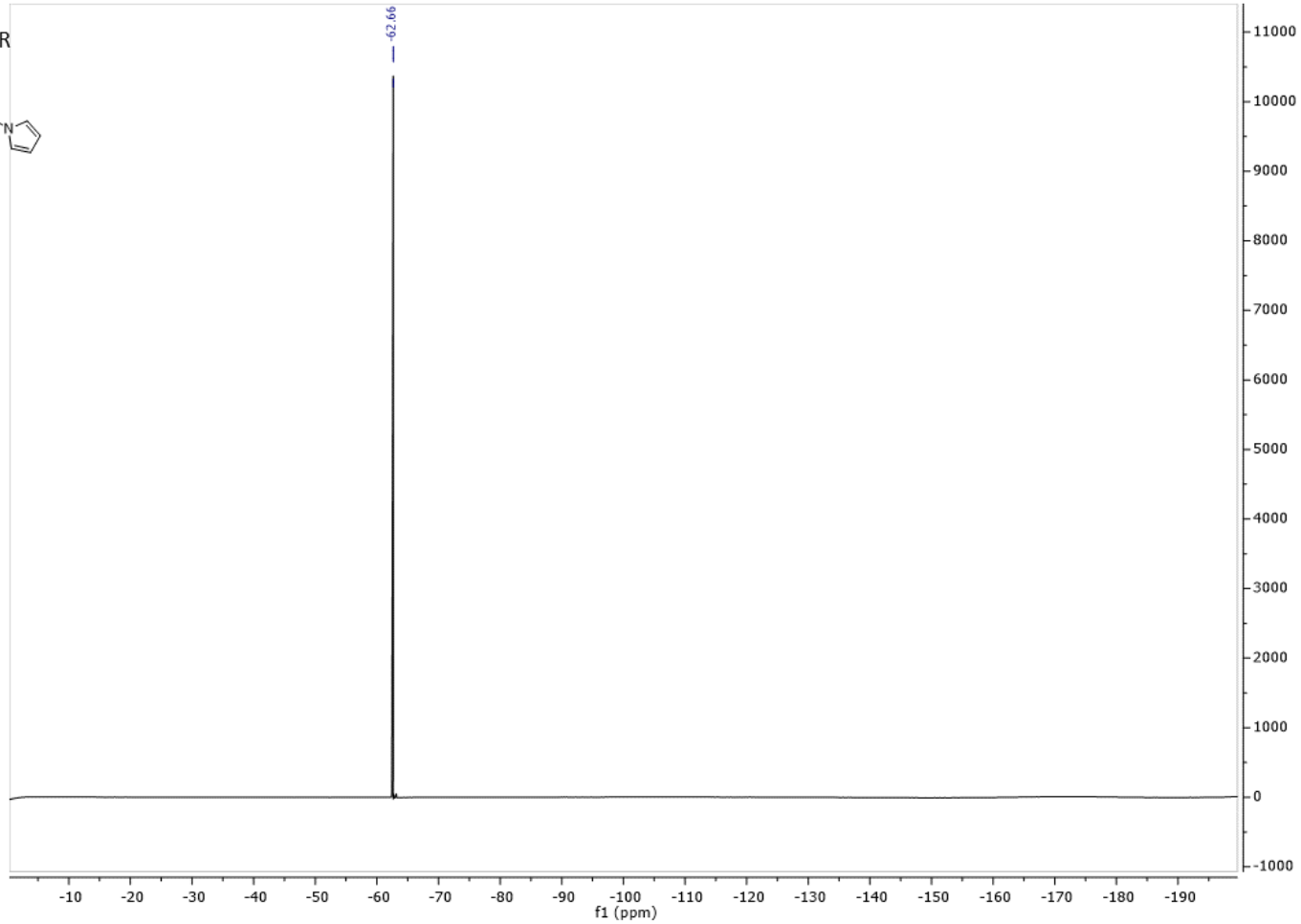
1h


162.85
161.24
142.31
131.56
131.24
130.15
129.47
126.01
125.97
125.38
123.62
123.58
122.67
119.40
117.78
113.34
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
32.23
31.60
29.44
28.87
22.65
14.14
f1 (ppm)

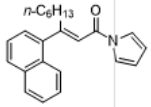
^{19}F NMR


n-C6H13
O
N
CF3

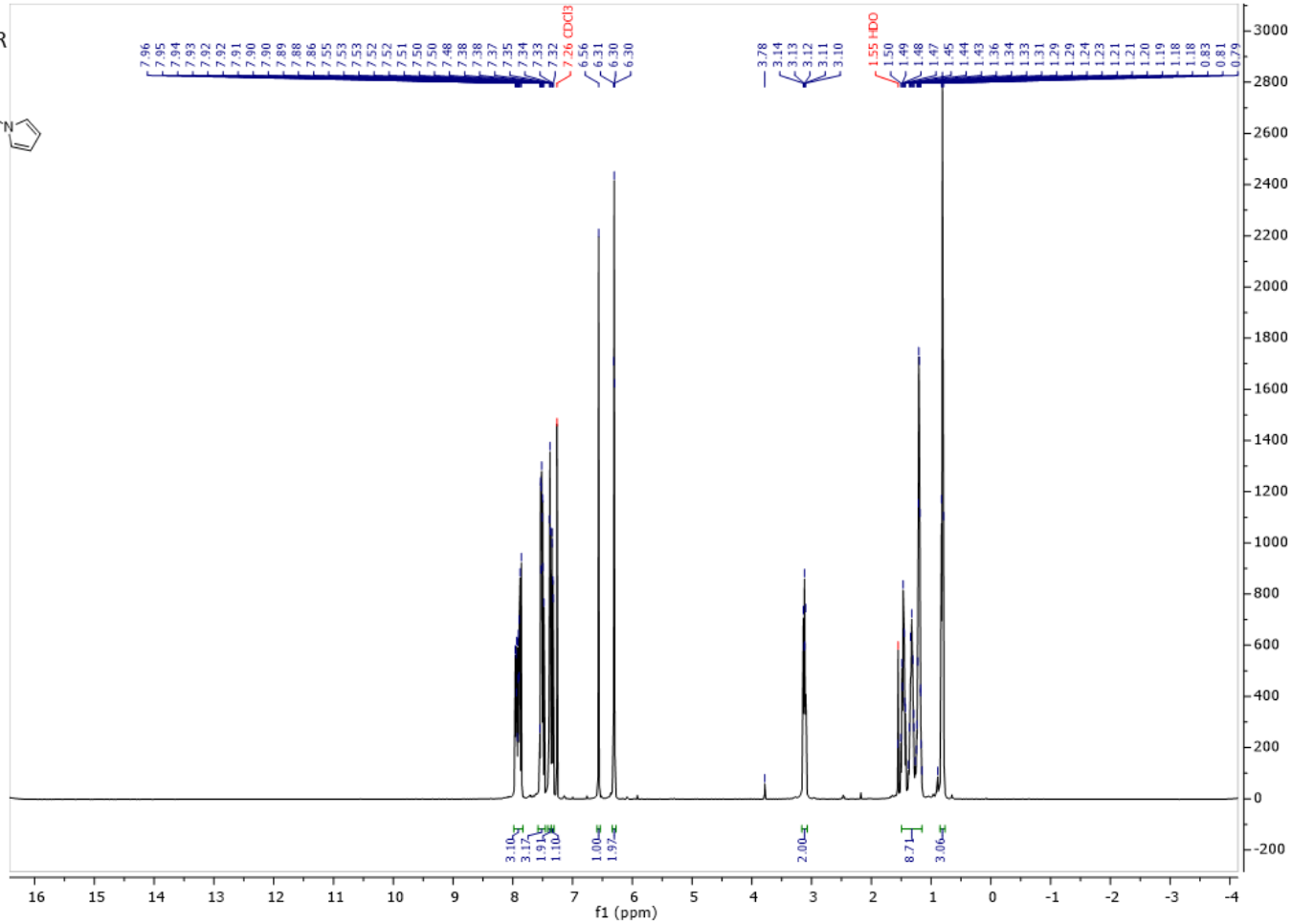
1h


-62.66
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

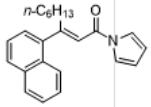
^{1}H NMR



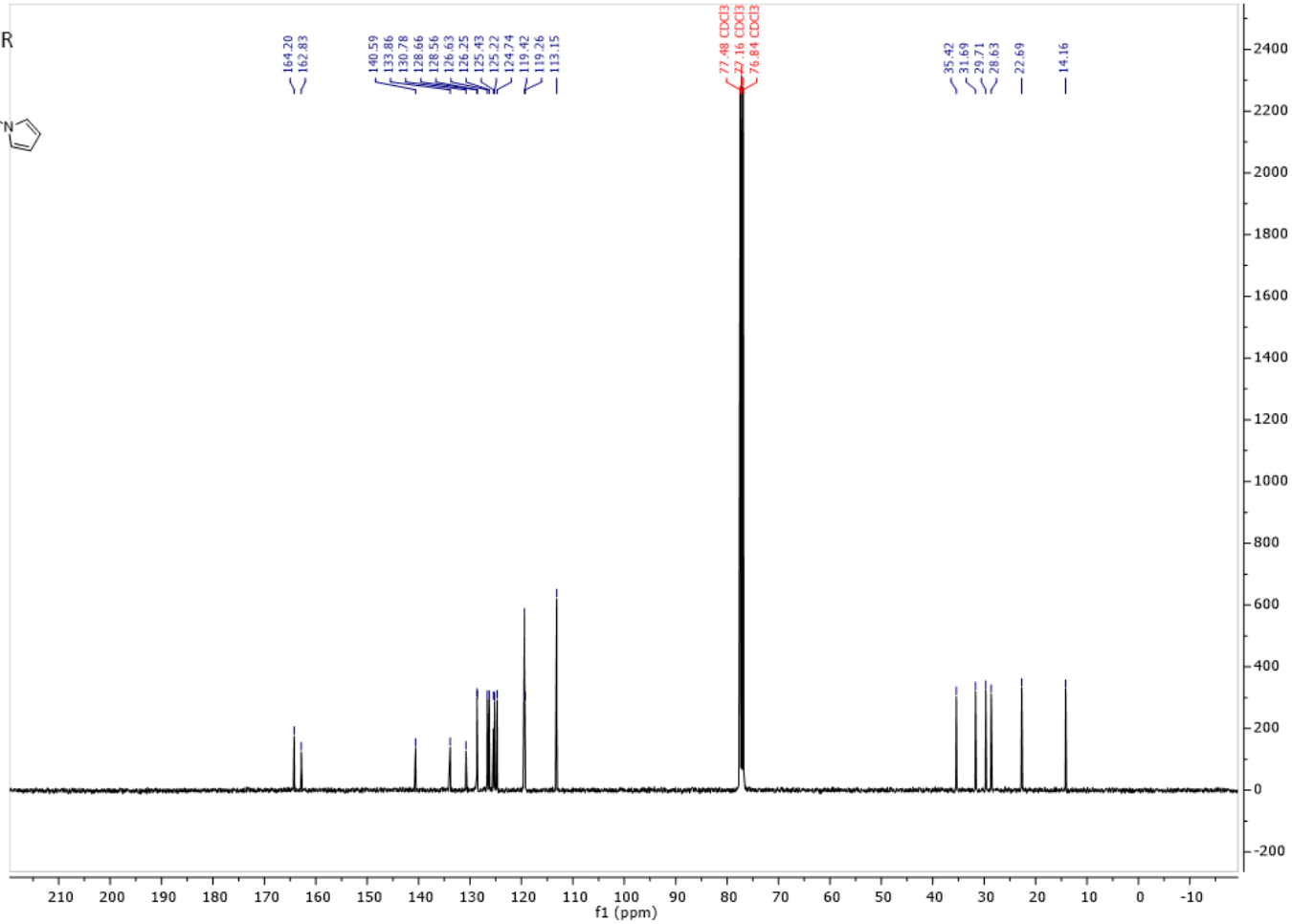
1i



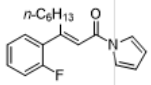
^{13}C NMR


n-C6H13
O
N

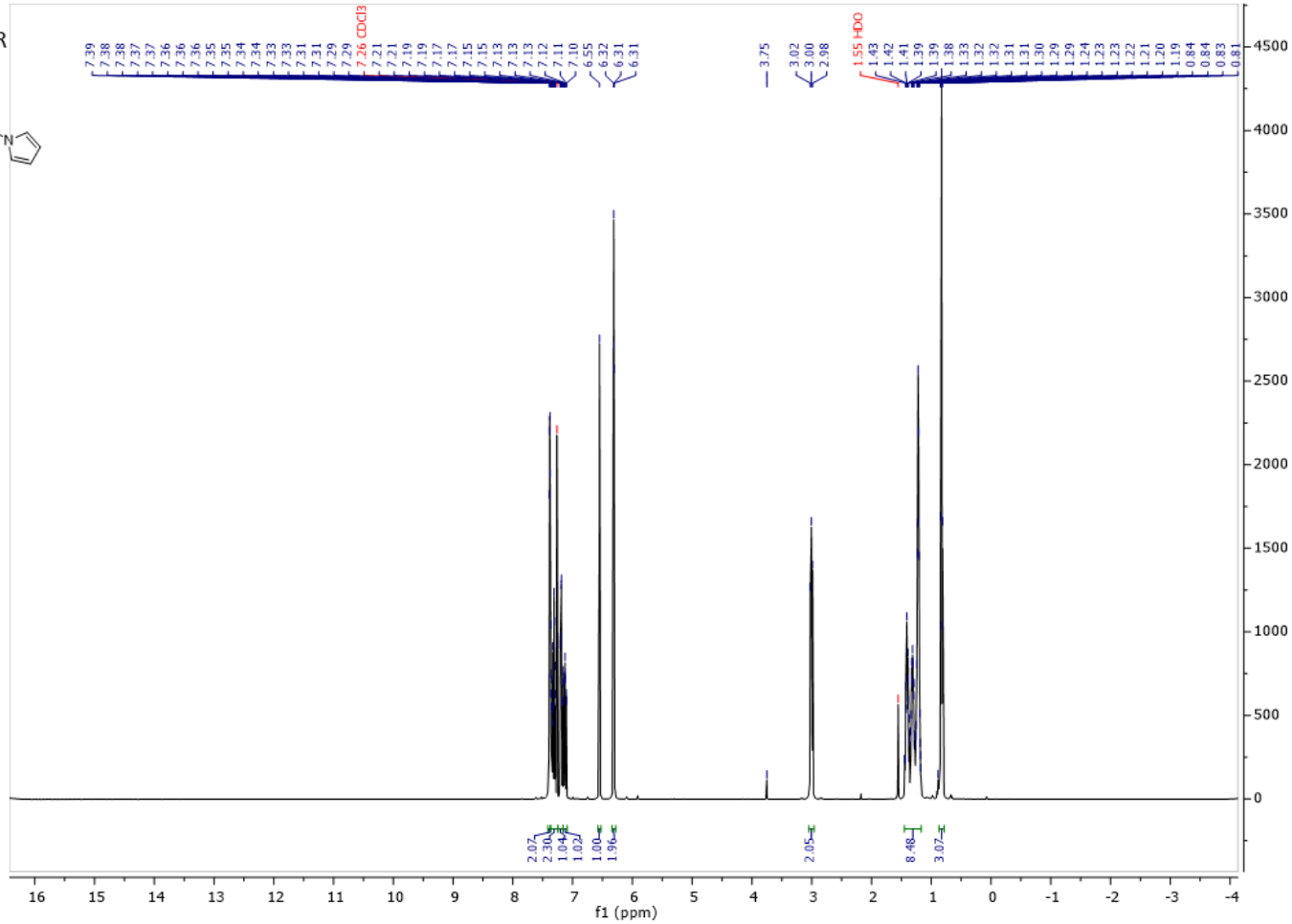
1i


164.20
162.83
140.59
133.86
130.78
128.66
128.56
126.63
126.25
125.43
125.22
124.74
119.42
119.26
113.15
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
35.42
31.69
29.71
28.63
22.69
14.16
f1 (ppm)

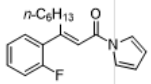
^{1}H NMR


n-C6H13
O
N
F

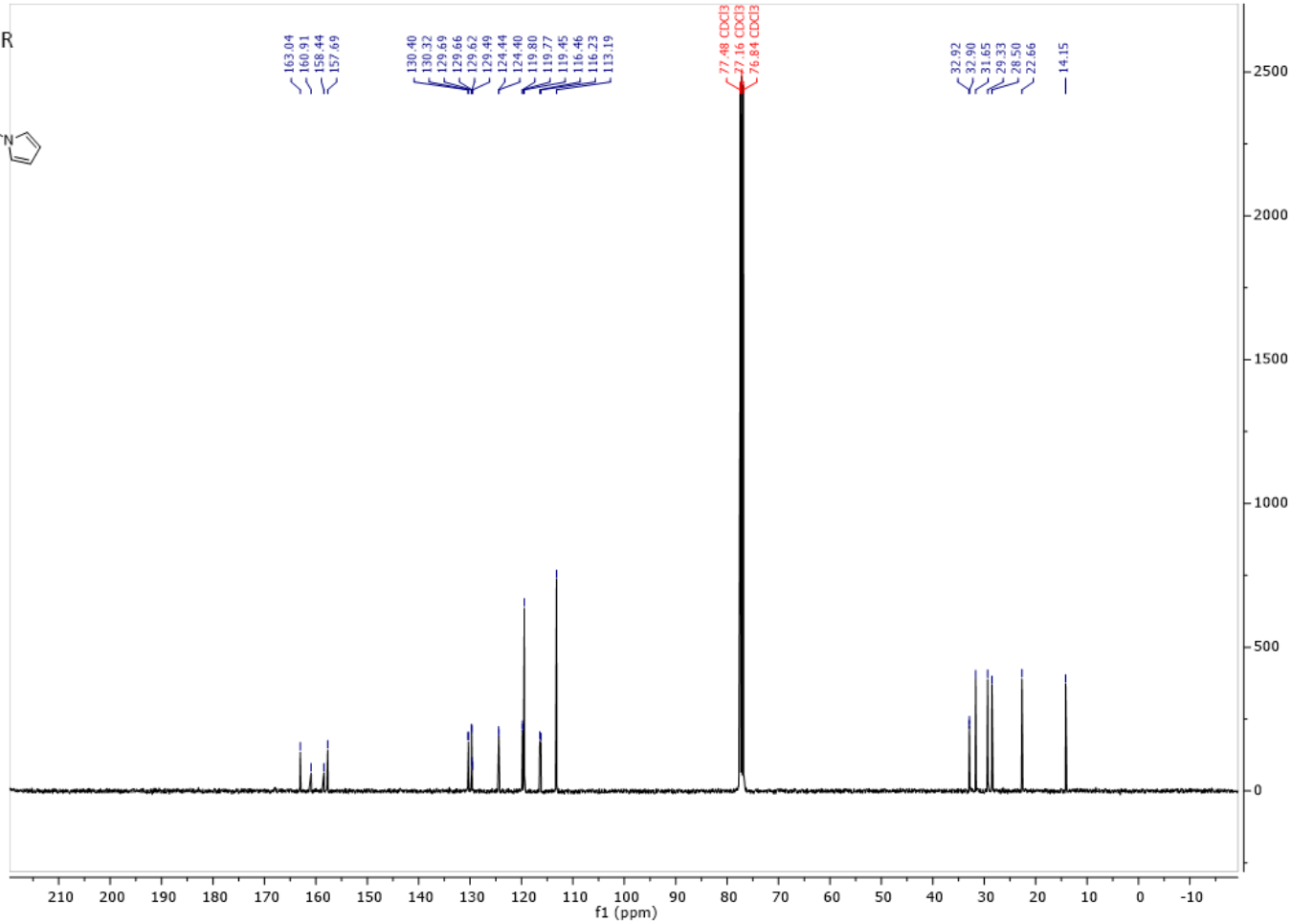
1j


7.26 CDCl3
1.55 H2O
3.75
3.02
3.00
2.98
6.55
6.32
6.31
6.31
2.07
2.30
1.04
1.02
1.00
1.96
2.05
8.48
3.07
f1 (ppm)

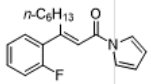
^{13}C NMR


n-C6H13
O
N
F

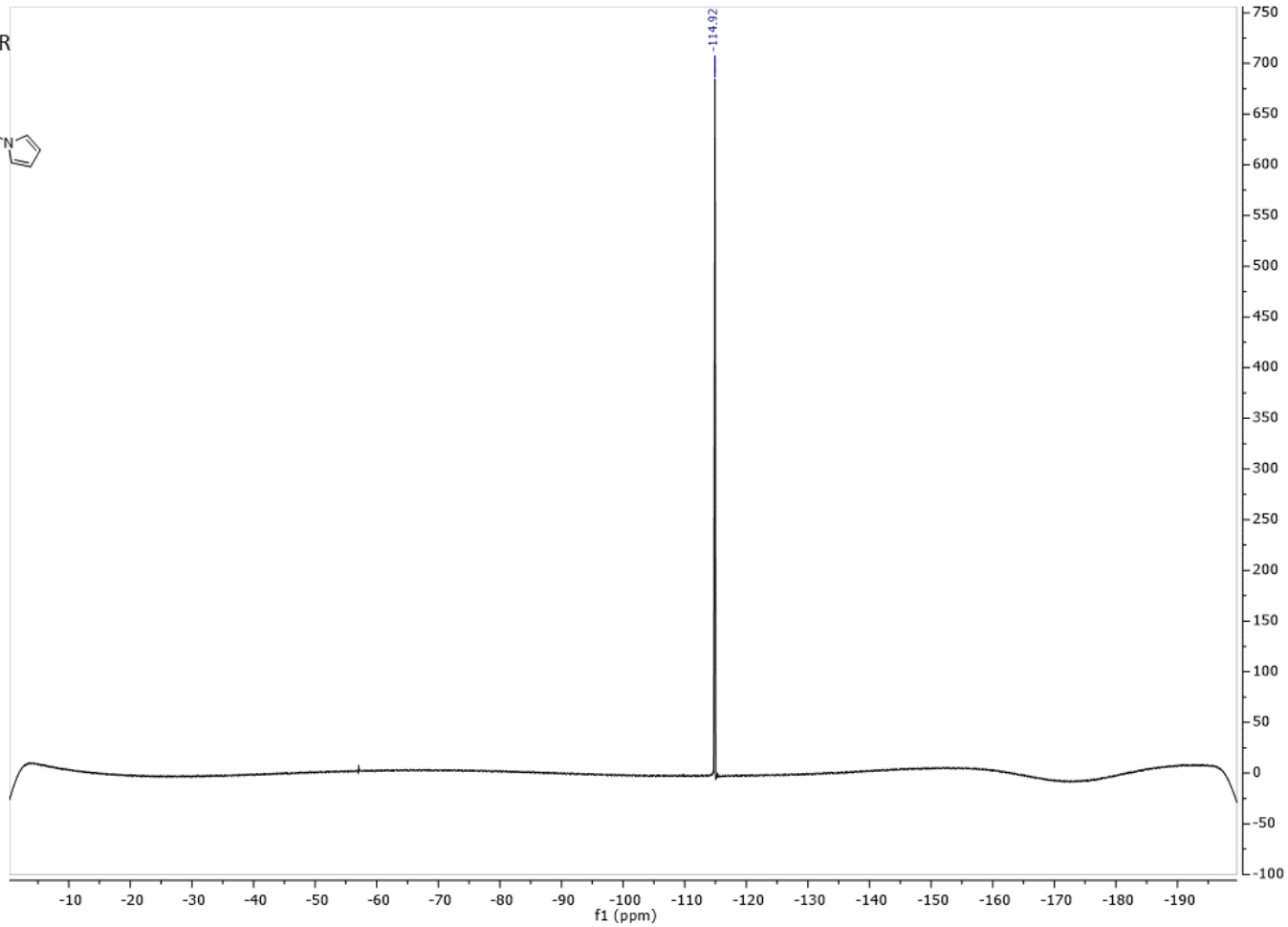
1j


163.04
160.91
158.44
157.69
130.40
130.32
129.69
129.66
129.62
129.49
124.44
124.40
119.80
119.77
119.45
116.46
116.23
113.19
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
32.92
32.90
31.65
29.33
28.50
22.66
14.15
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

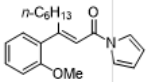
^{19}F NMR


n-C6H13
O
N
F

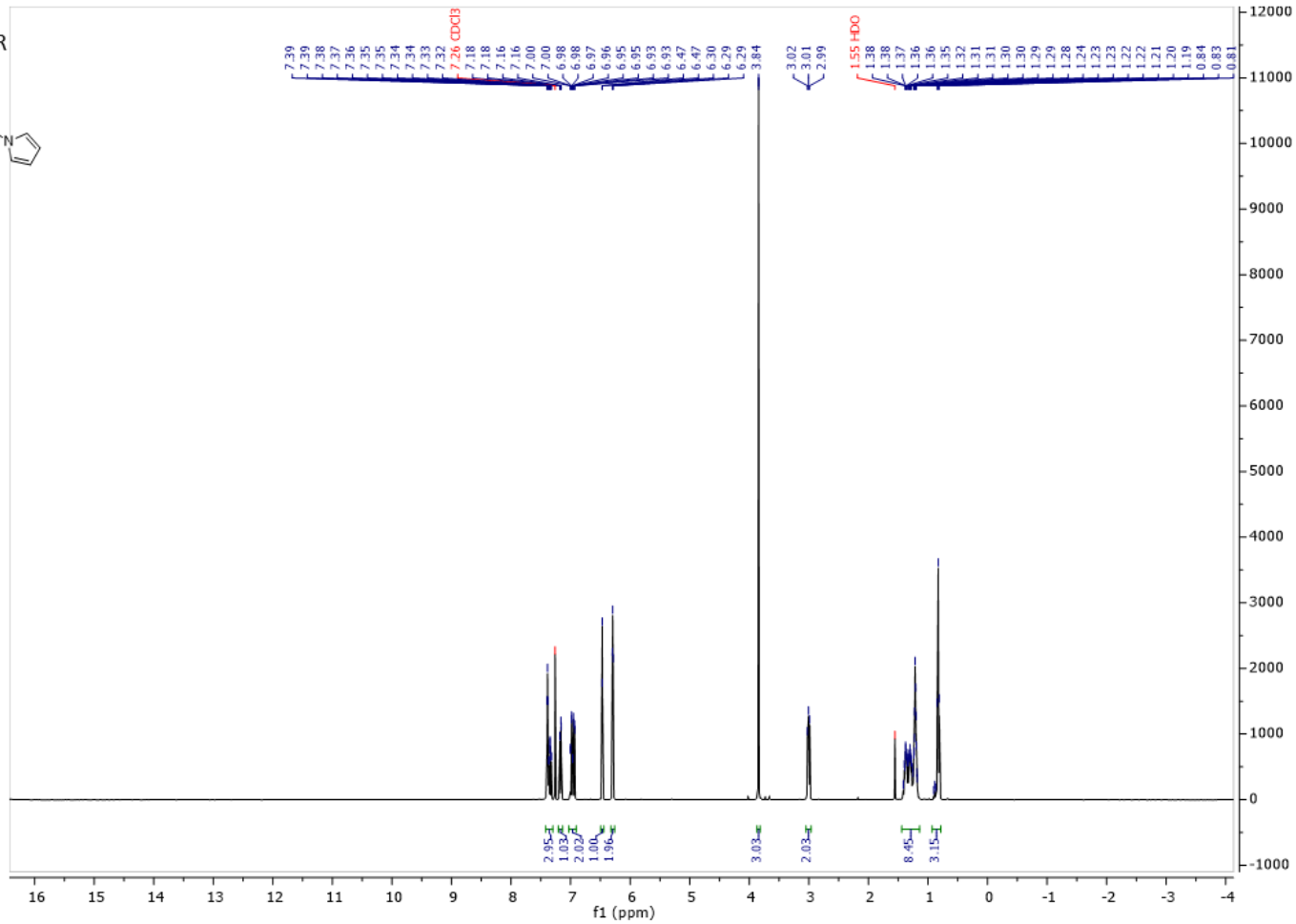
1j


-114.92
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

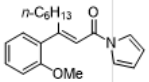
^{1}H NMR



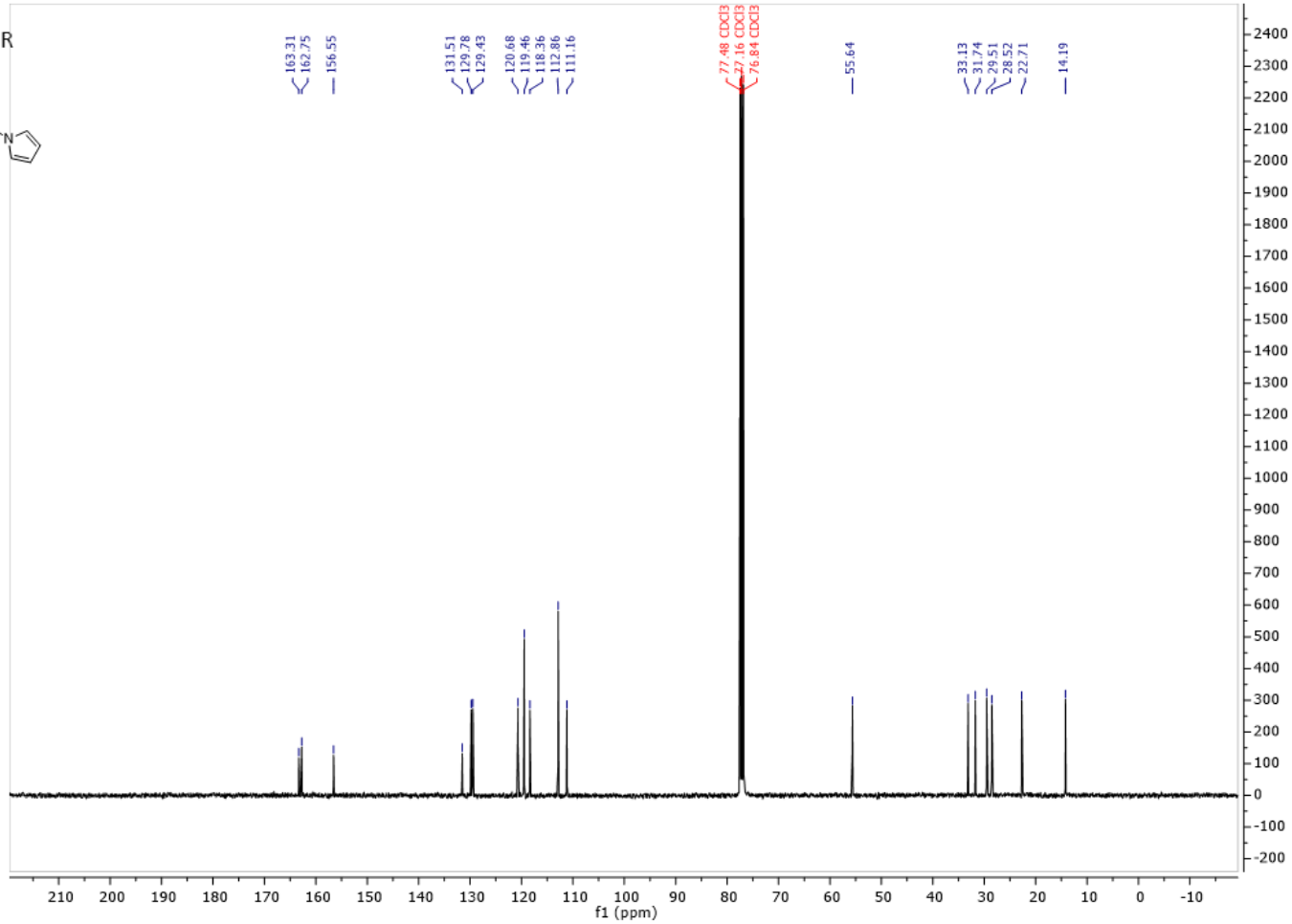
1k



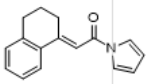
^{13}C NMR


n-C6H13
O
N
OMe

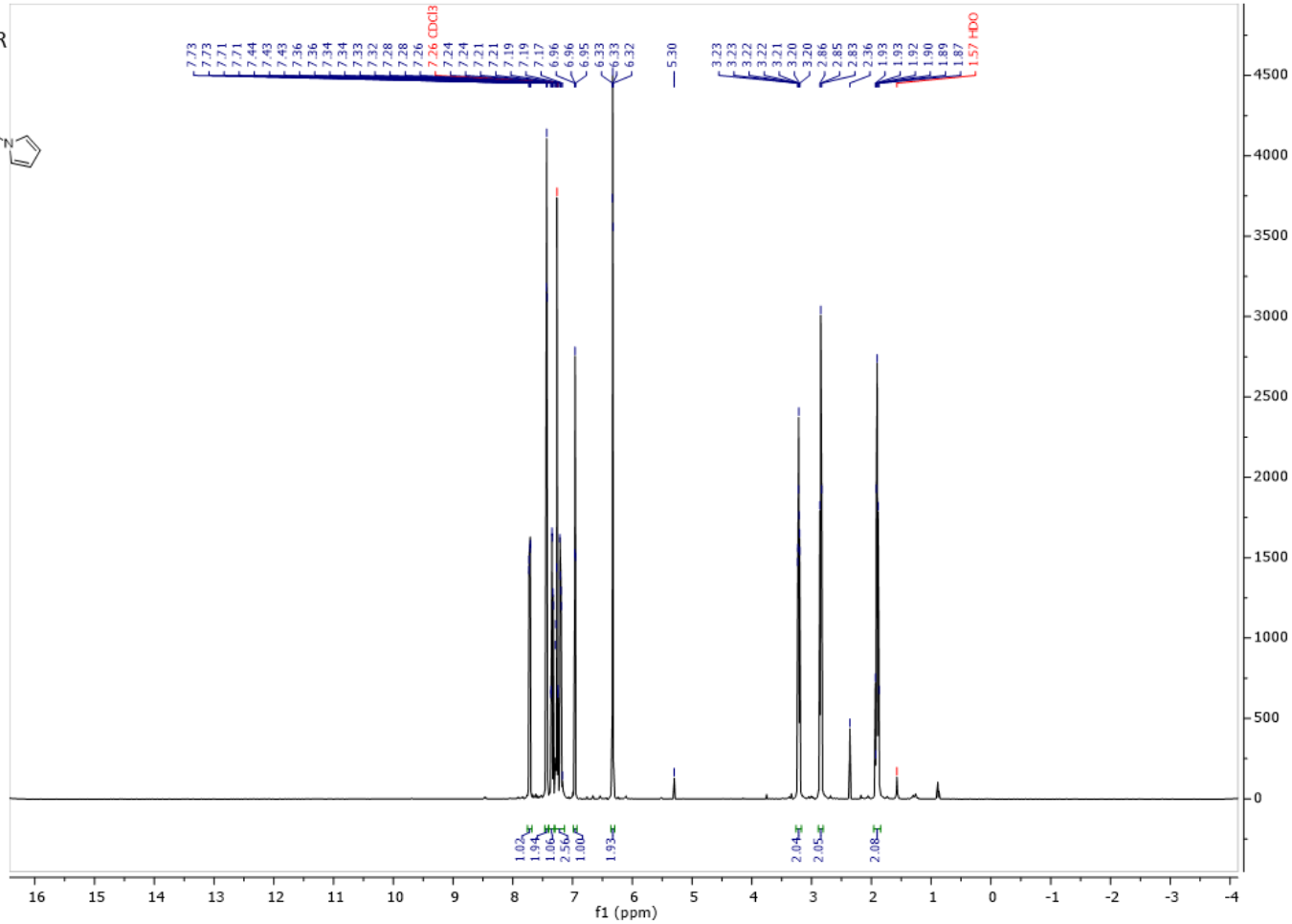
1k


163.31
162.75
156.55
131.51
129.78
129.43
120.68
119.46
118.36
112.86
111.16
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.64
33.13
31.74
29.51
28.52
22.71
14.19
f1 (ppm)

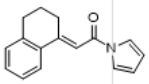
^{1}H NMR



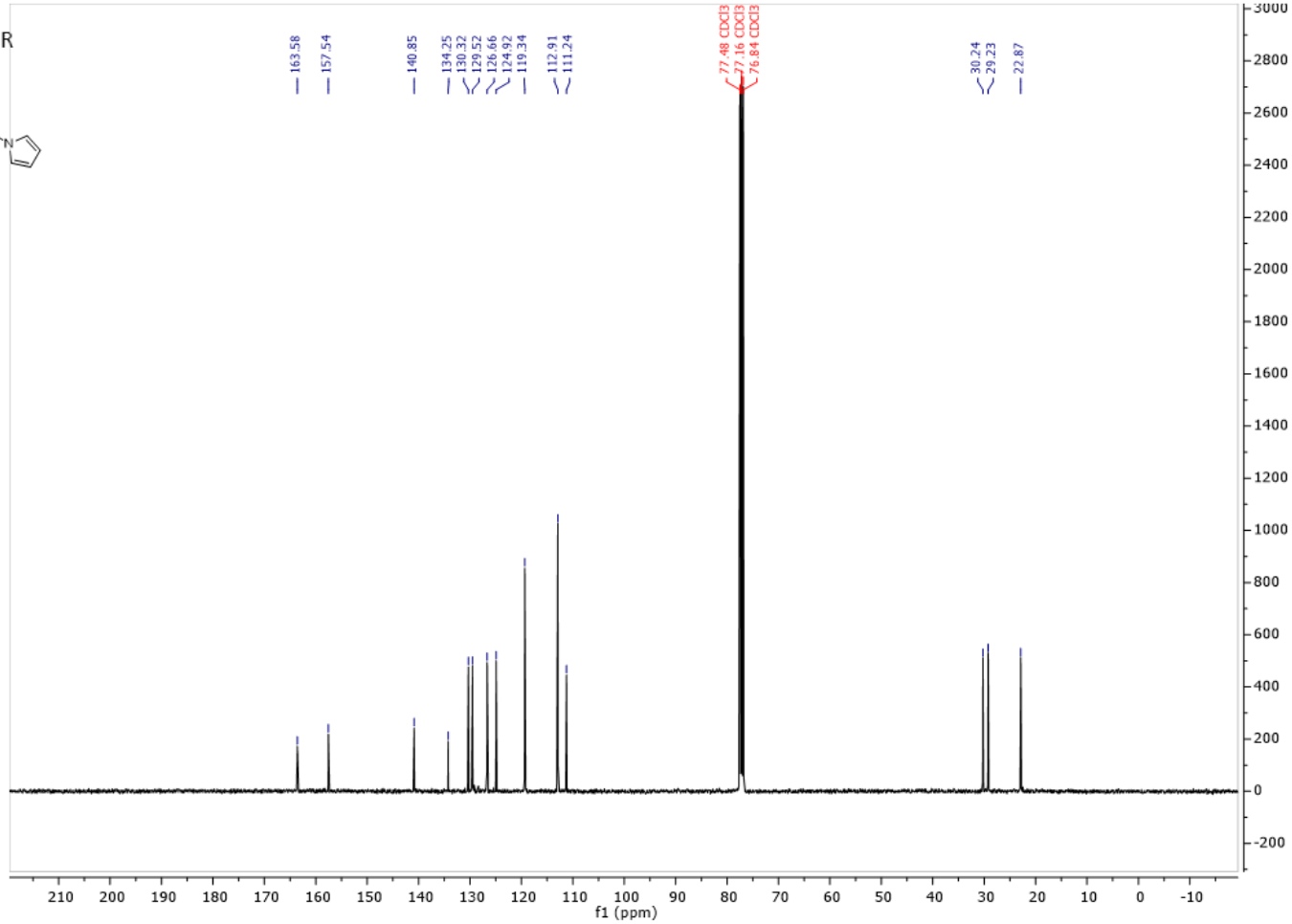
1l



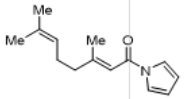
^{13}C NMR



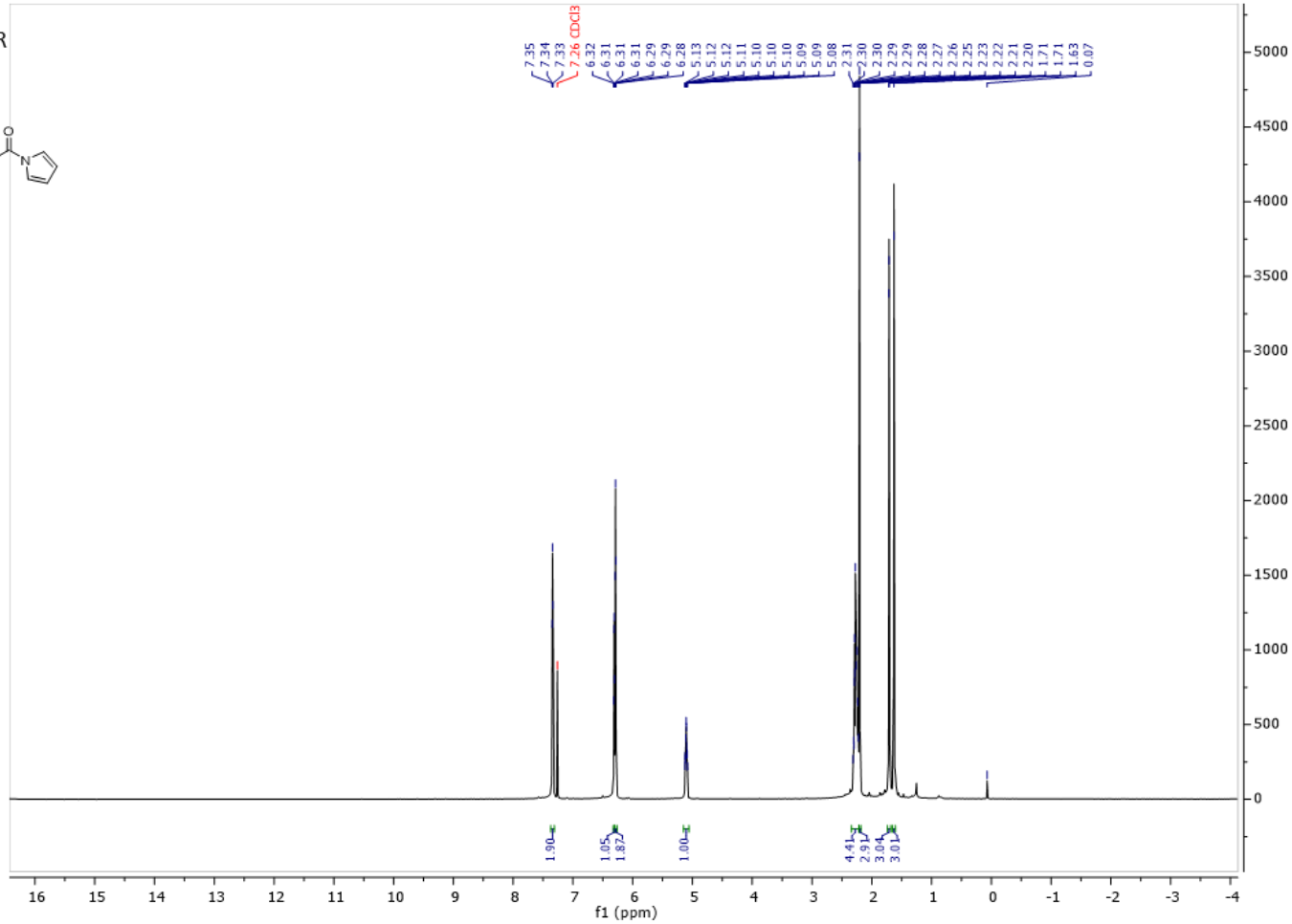
1l


163.58
157.54
140.85
134.25
130.32
129.52
126.66
124.92
119.34
112.91
111.24
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
30.24
29.23
22.87
f1 (ppm)

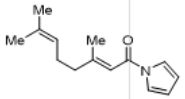
^{1}H NMR


Me
Me
Me
O
N

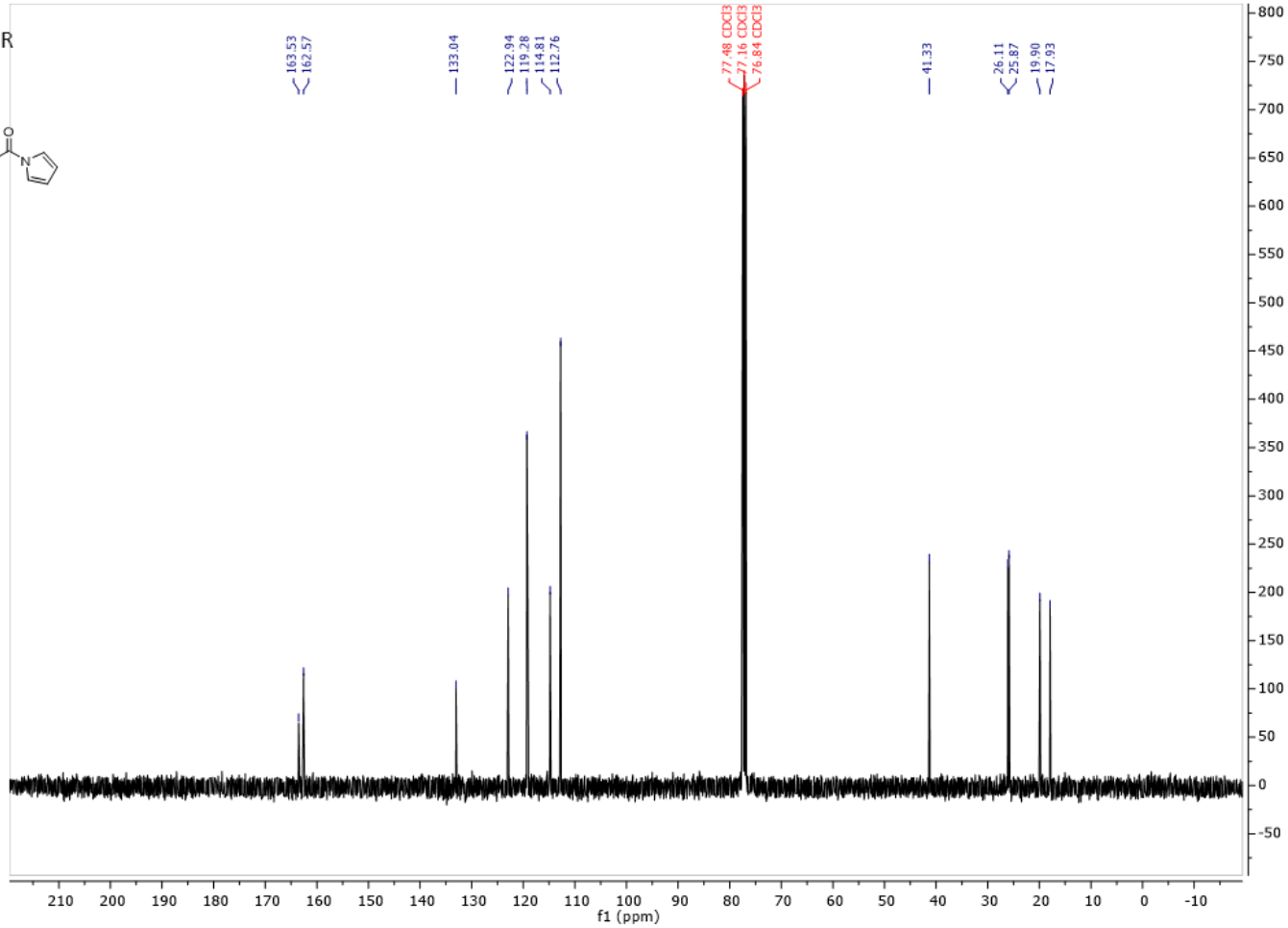
1m


7.35
7.34
7.33
7.26 CDCl3
6.32
6.31
6.31
6.31
6.29
6.29
6.28
5.13
5.12
5.12
5.11
5.10
5.10
5.10
5.09
5.09
5.08
2.31
2.30
2.30
2.30
2.29
2.29
2.28
2.27
2.26
2.25
2.23
2.22
2.21
2.20
1.71
1.71
1.63
0.07
1.90
1.05
1.87
1.00
4.41
2.91
3.04
3.01
f1 (ppm)

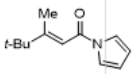
^{13}C NMR


Me
Me
Me
O
N

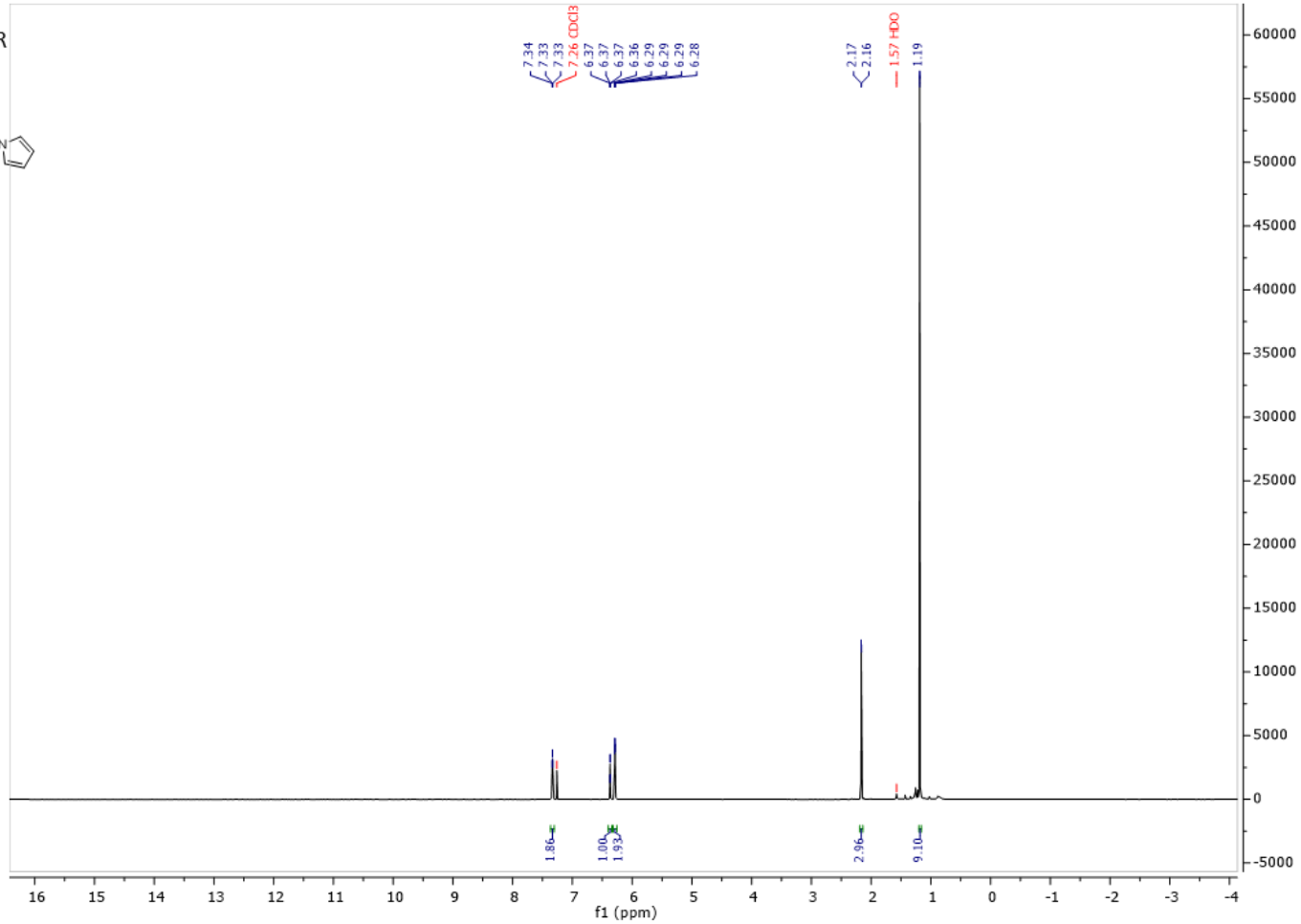
1m


163.53
162.57
133.04
122.94
119.28
114.81
112.76
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
41.33
26.11
25.87
19.90
17.93
f1 (ppm)

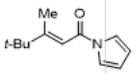
^{1}H NMR


Me
O
t-Bu
N

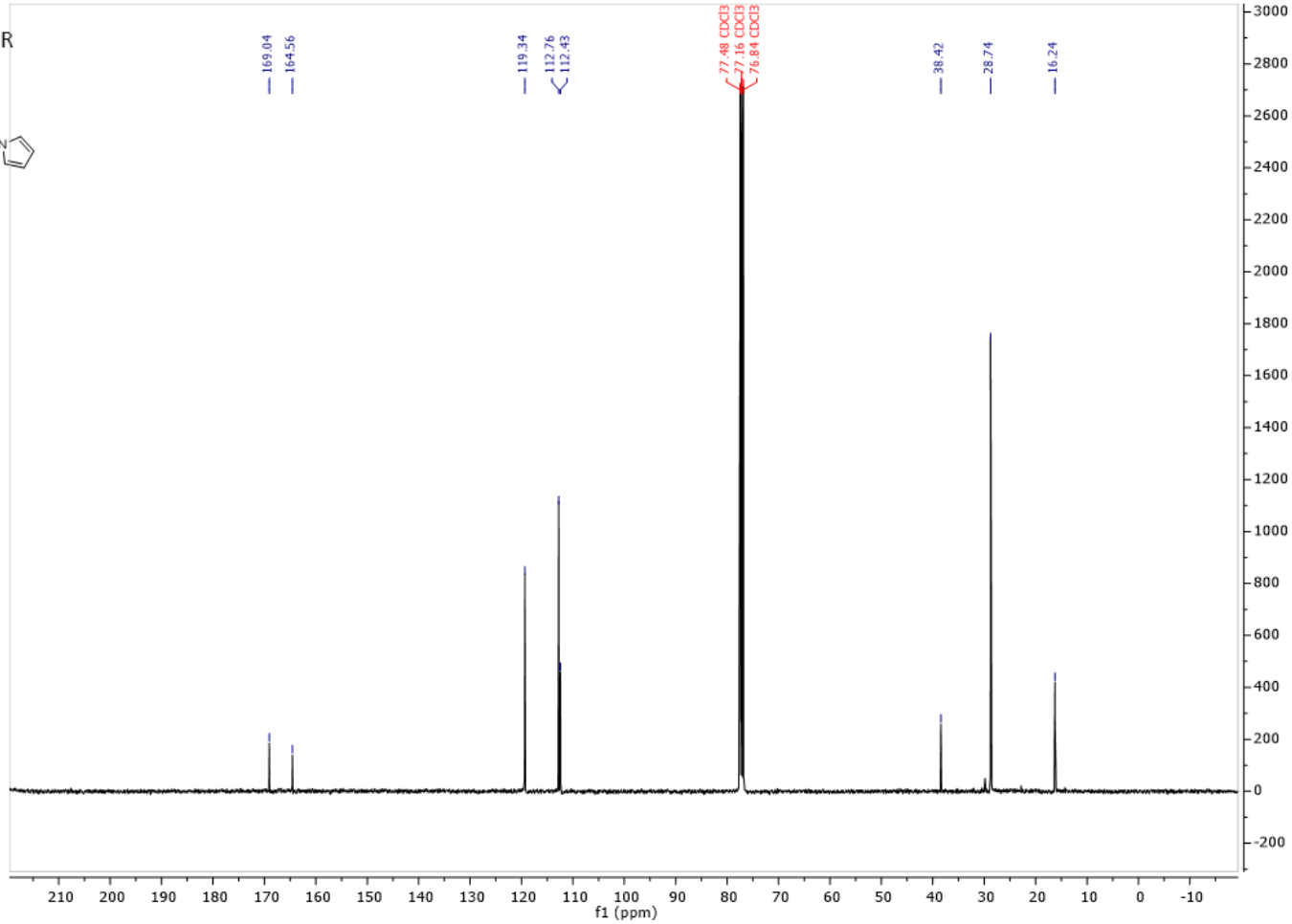
1n


7.34
7.33
7.33
7.26 CDCl3
6.37
6.37
6.37
6.36
6.29
6.29
6.29
6.28
2.17
2.16
1.57 HDO
1.19
1.86
1.00
1.93
2.96
9.10
f1 (ppm)

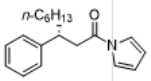
^{13}C NMR


Me
O
t-Bu
N

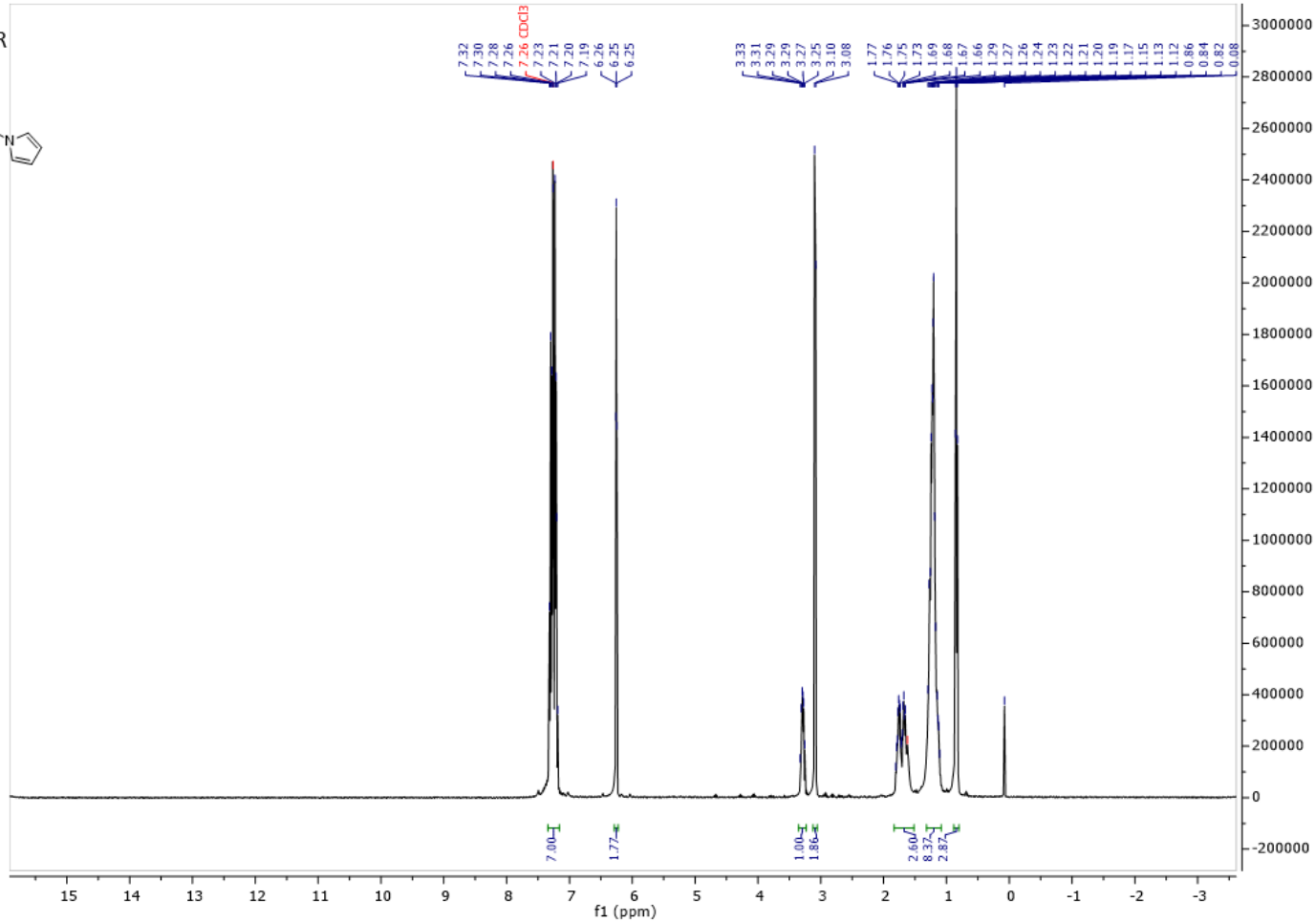
1n


169.04
164.56
119.34
112.76
112.43
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
38.42
28.74
16.24
f1 (ppm)

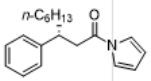
^{1}H NMR


n-C6H13
O
N

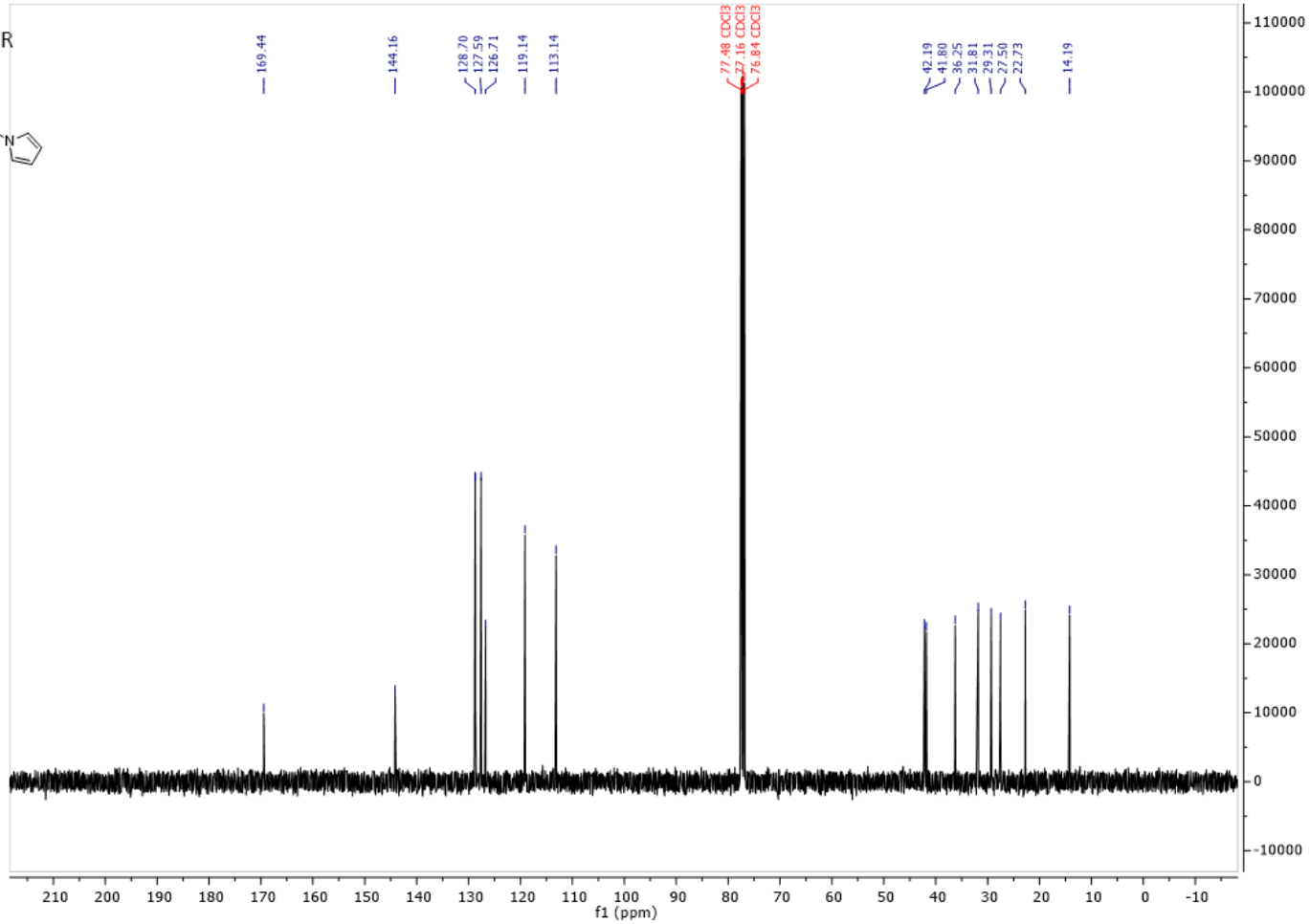
2b


7.32
7.30
7.28
7.26
7.26 CDCl3
7.23
7.21
7.20
7.19
6.26
6.25
6.25
3.33
3.31
3.29
3.29
3.27
3.25
3.10
3.08
1.77
1.76
1.75
1.73
1.69
1.68
1.67
1.66
1.29
1.27
1.26
1.24
1.23
1.22
1.21
1.20
1.19
1.17
1.17
1.15
1.13
1.12
0.86
0.84
0.82
0.08
7.00
1.77
1.00
1.86
2.60
8.37
2.87
f1 (ppm)

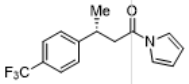
^{13}C NMR


n-C6H13
O
N

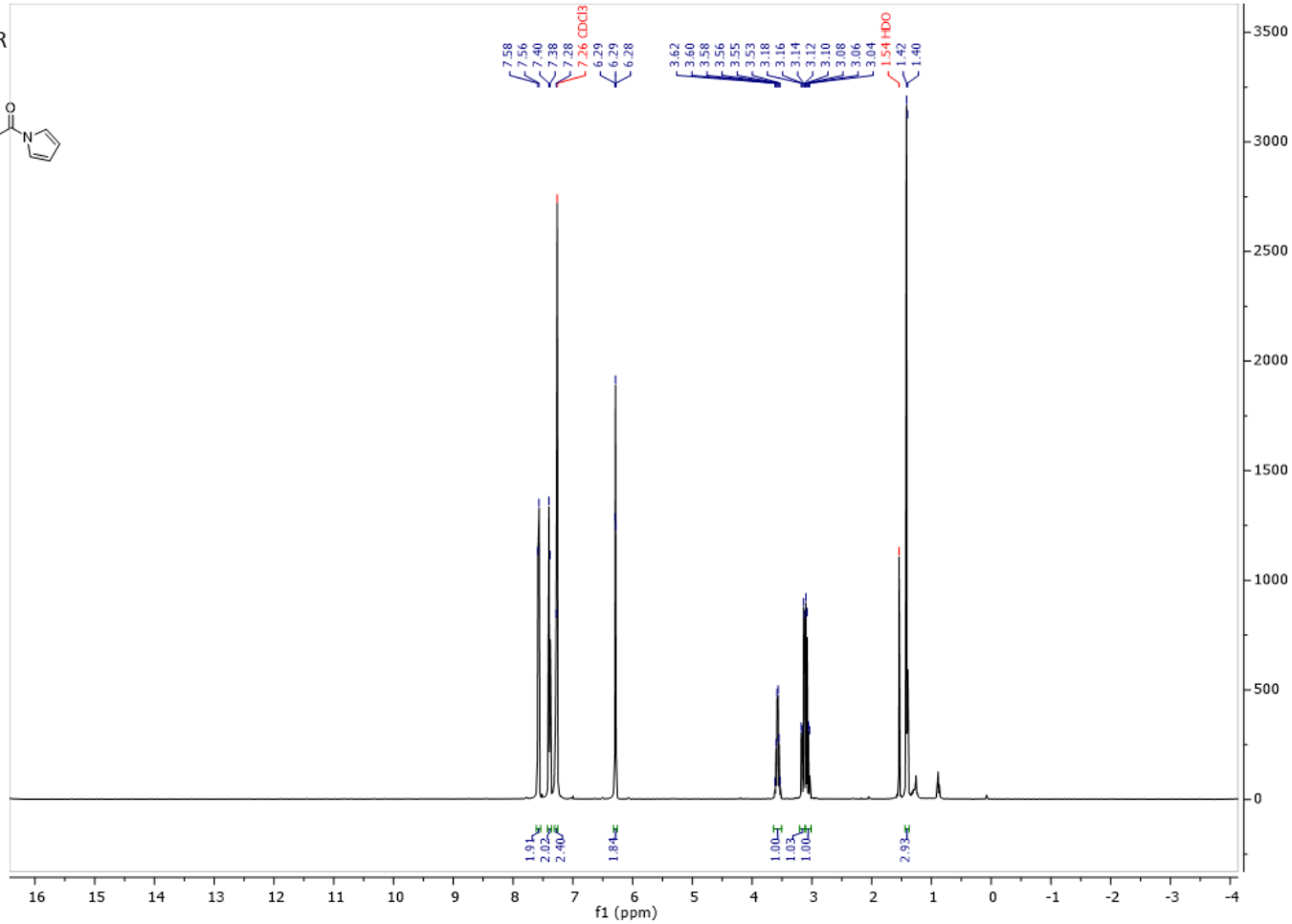
2b


169.44
144.16
128.70
127.59
126.71
119.14
113.14
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
42.19
41.80
36.25
31.81
29.31
27.50
22.73
14.19
f1 (ppm)

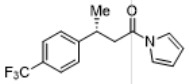
^{1}H NMR


Me
O
N
F3C

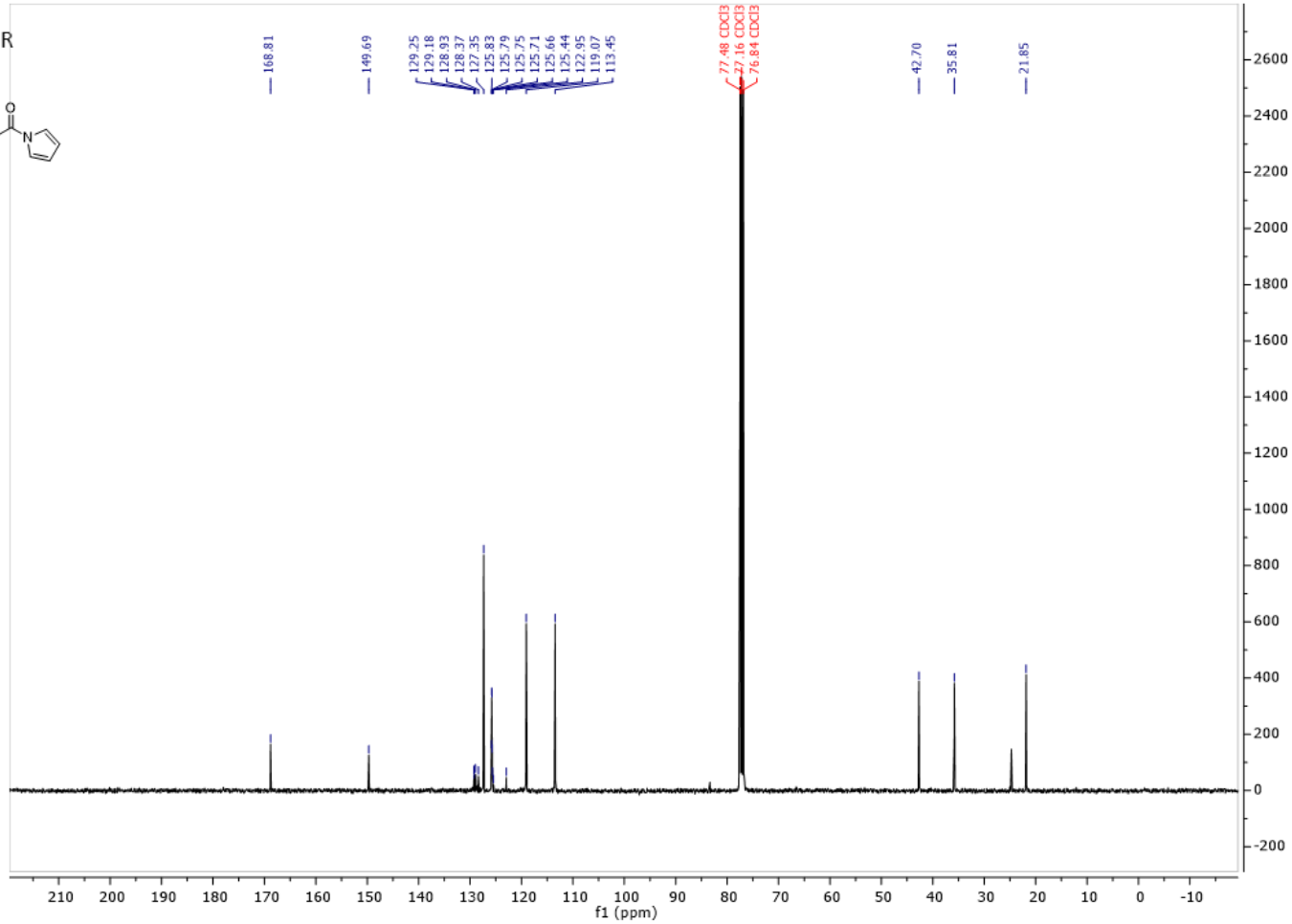
2c


7.58
7.56
7.40
7.38
7.28
7.26 CDCl3
6.29
6.29
6.28
3.62
3.60
3.58
3.56
3.55
3.53
3.18
3.16
3.14
3.12
3.10
3.08
3.06
3.04
1.54 HDO
1.42
1.40
1.91
2.02
2.40
1.84
1.00
1.03
1.00
2.93
f1 (ppm)

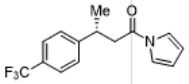
^{13}C NMR


Me
O
N
F3C

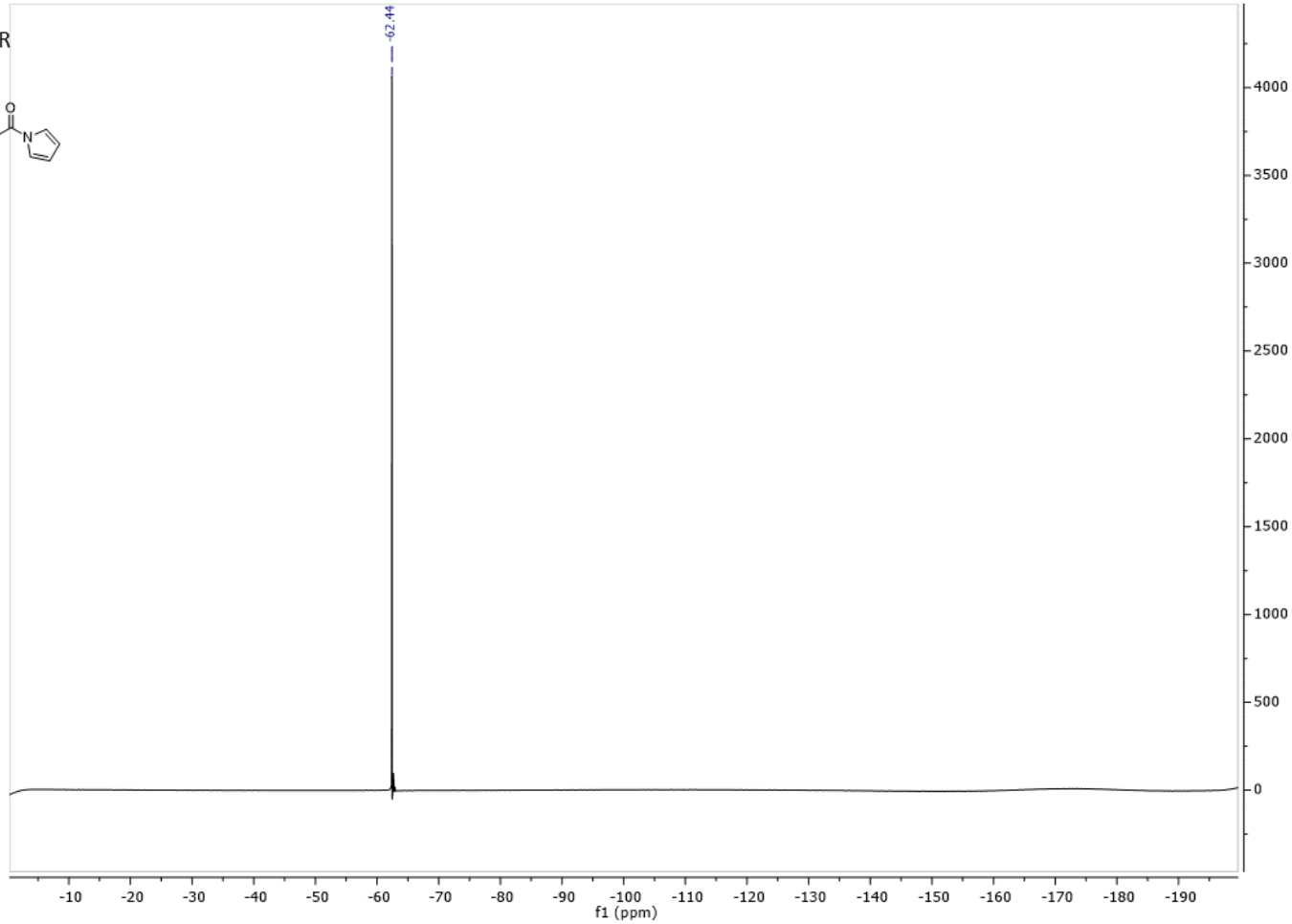
2c


168.81
149.69
129.25
129.18
128.93
128.37
127.35
125.83
125.79
125.75
125.71
125.66
125.44
122.95
119.07
113.45
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
42.70
35.81
21.85
f1 (ppm)

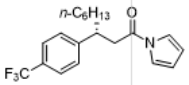
^{19}F NMR


Me
O
N
F3C

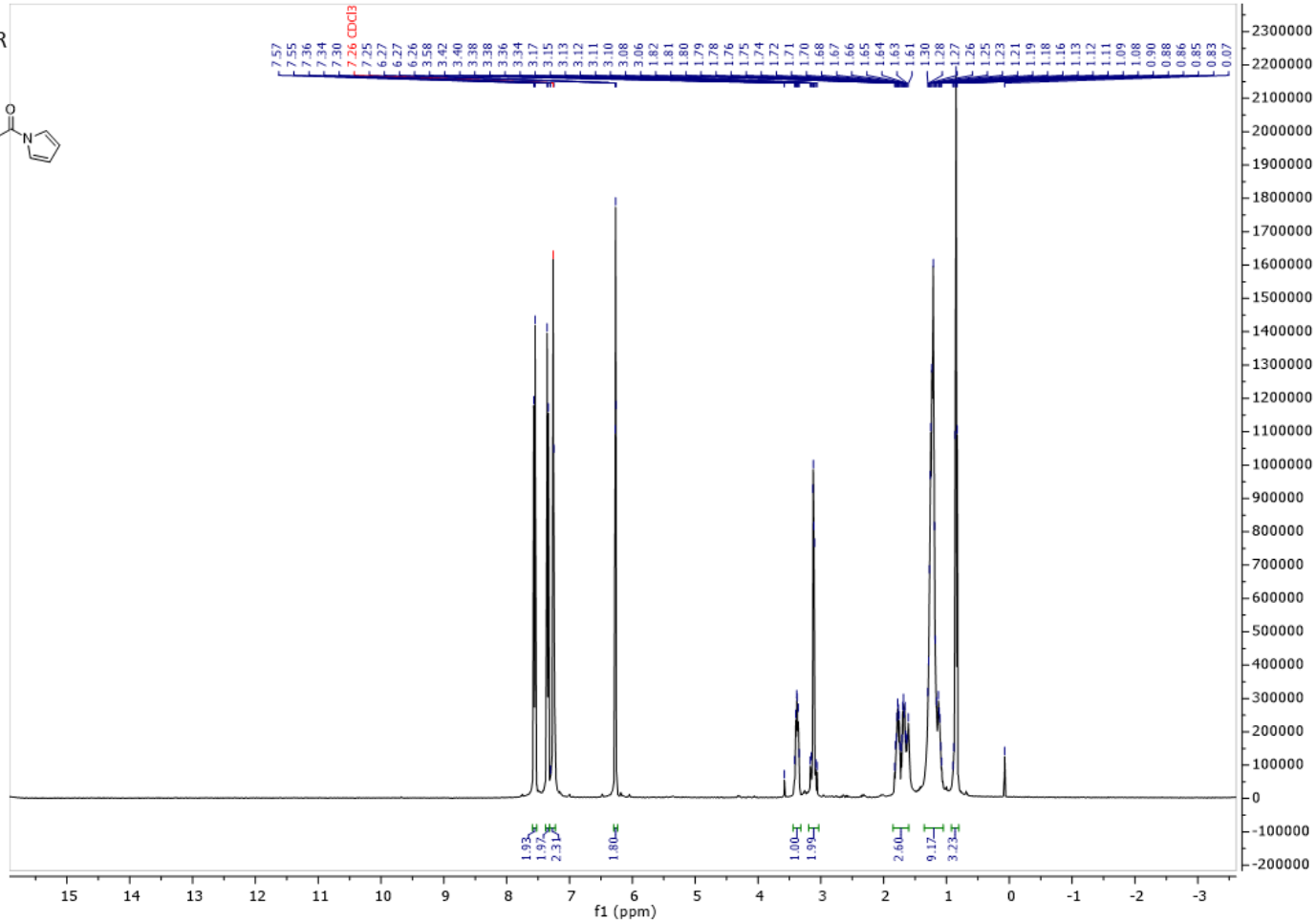
2c


-62.44
4000
3500
3000
2500
2000
1500
1000
500
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

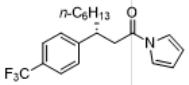
^{1}H NMR



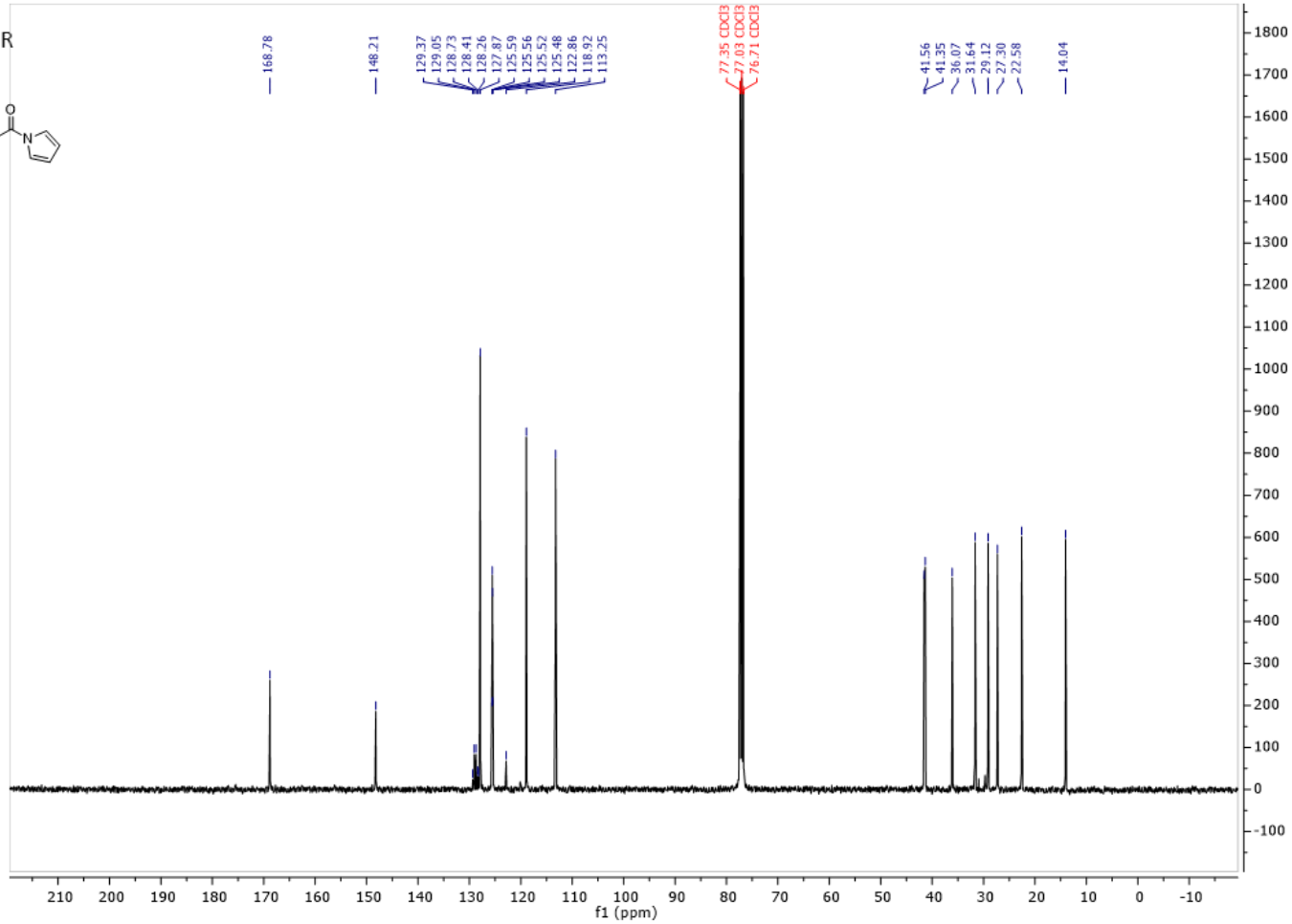
2d



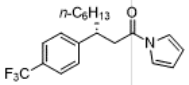
^{13}C NMR


n-C6H13
O
N
F3C

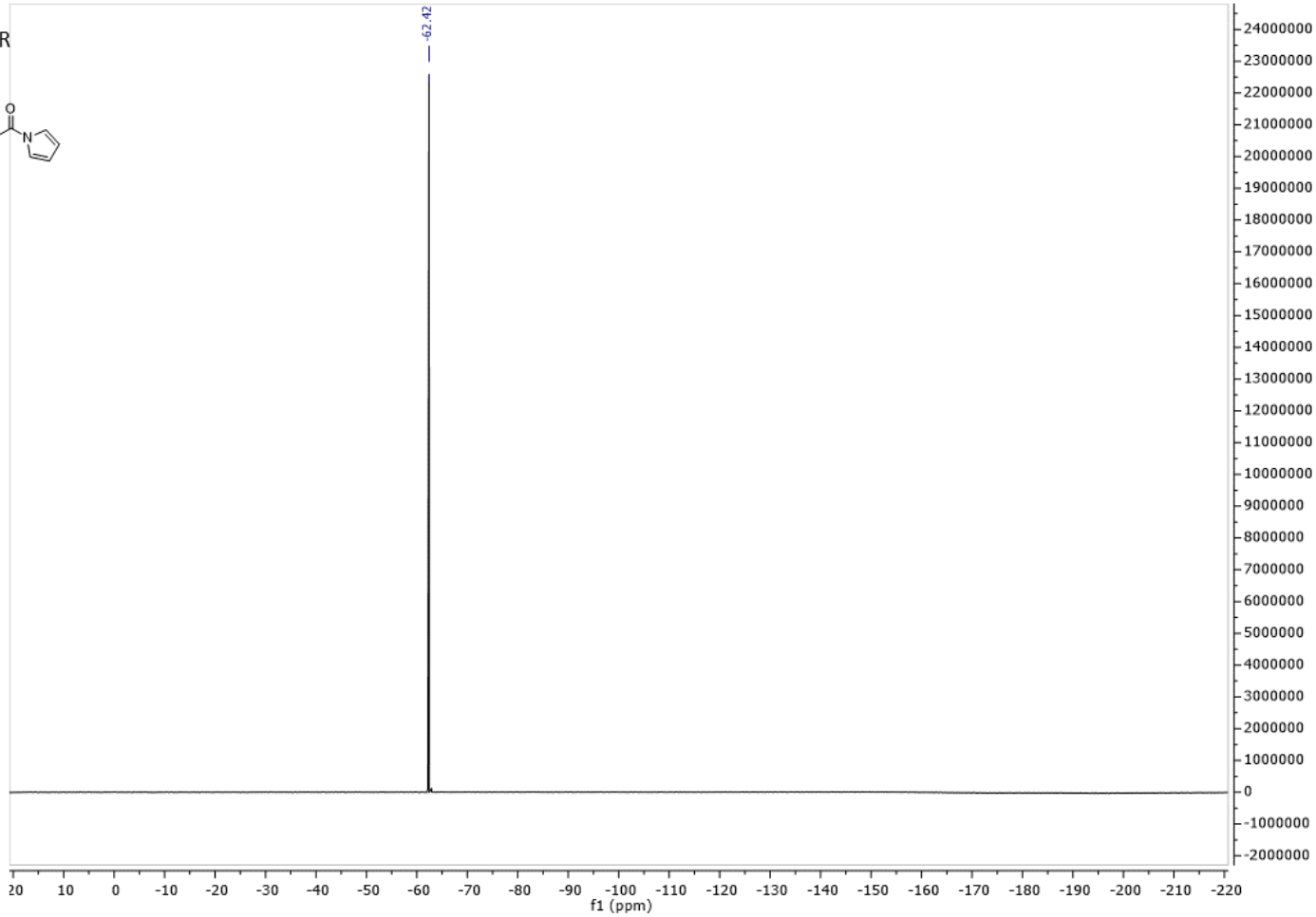
2d


168.78
148.21
129.37
129.05
128.73
128.41
128.26
127.87
125.59
125.56
125.52
125.48
122.86
118.92
113.25
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
41.56
41.35
36.07
31.64
29.12
27.30
22.58
14.04
f1 (ppm)

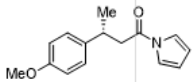
^{19}F NMR



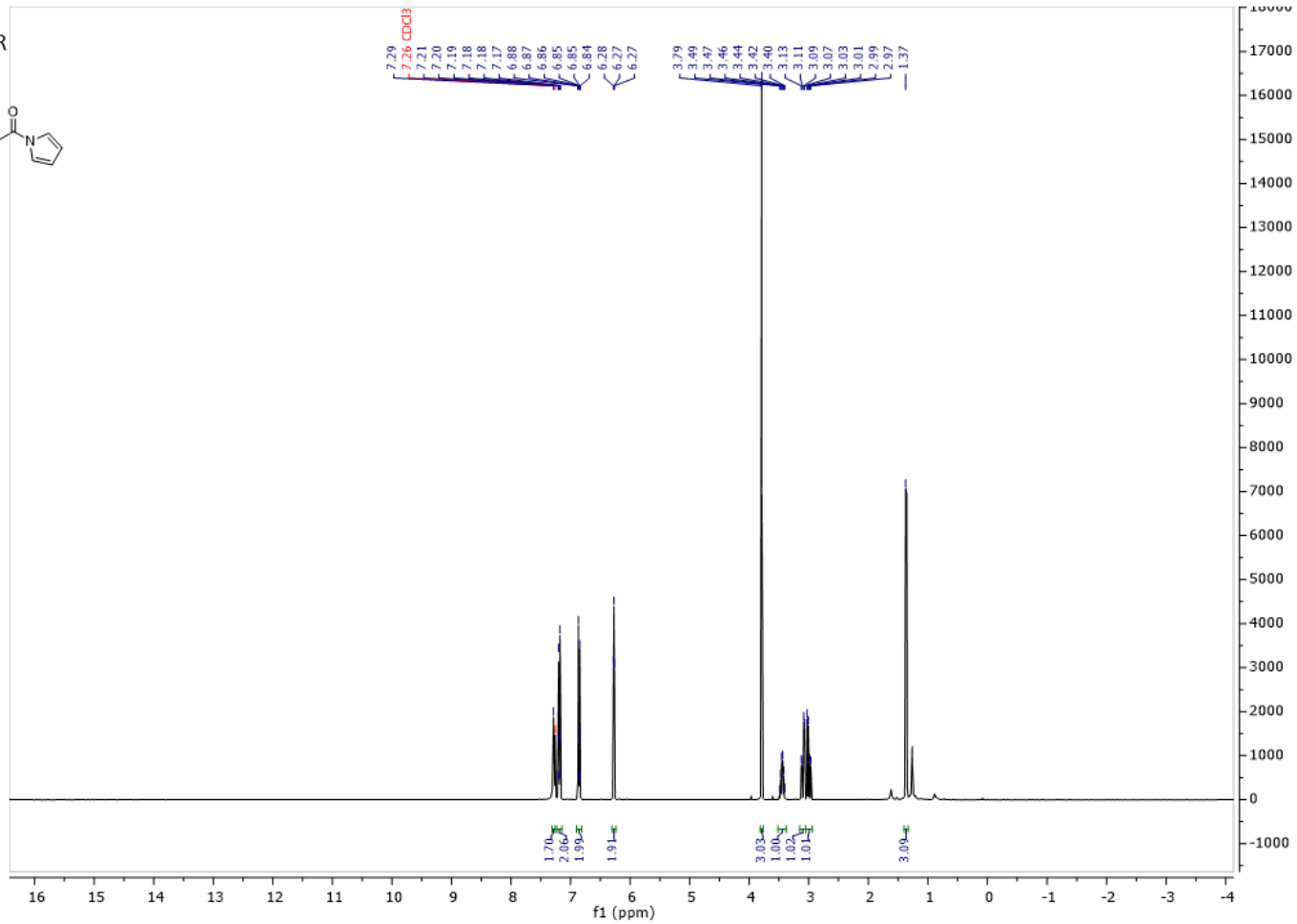
2d



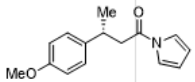
^{1}H NMR


Me
O
N
MeO

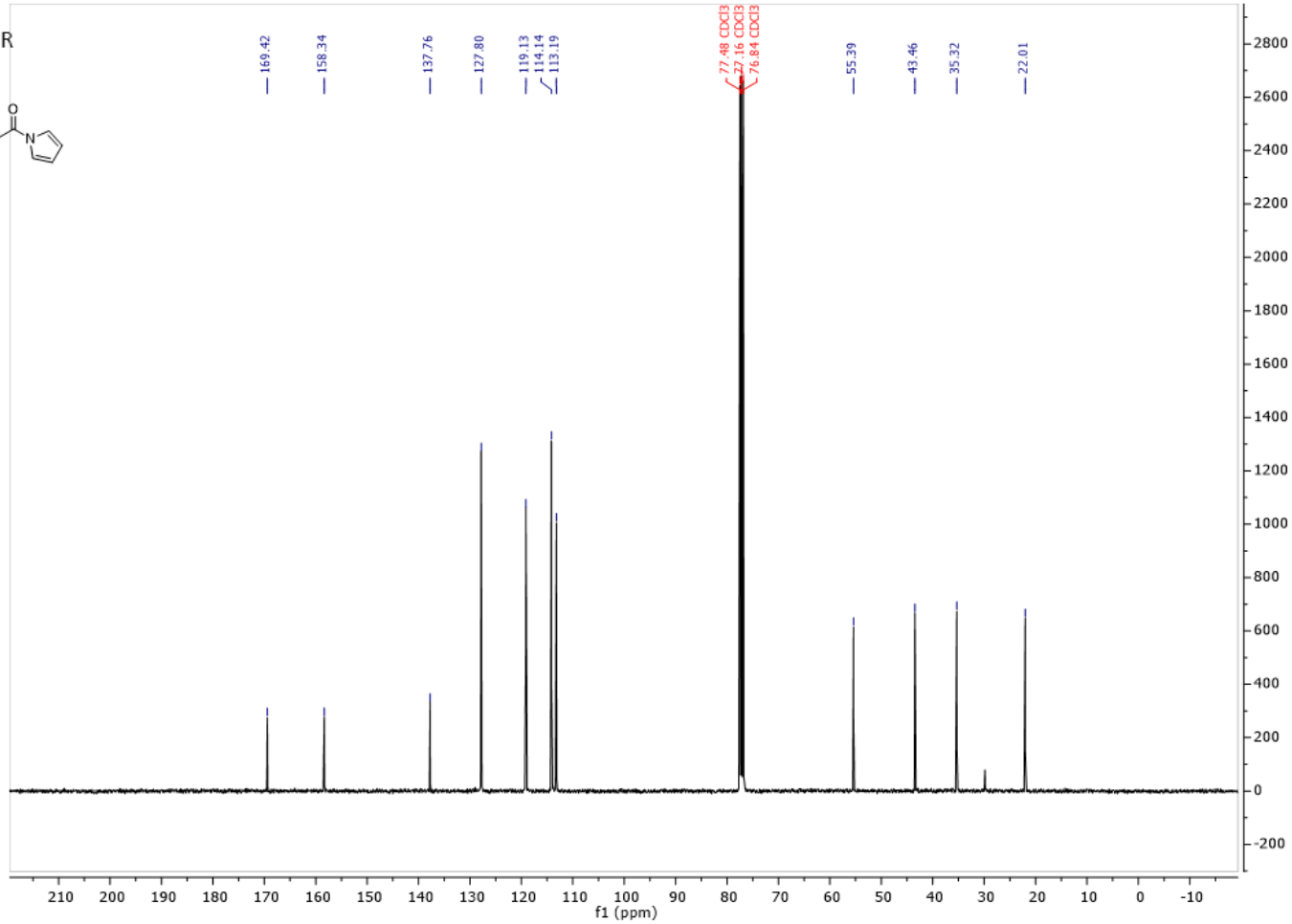
2e


7.29
7.26 CDCl3
7.21
7.20
7.19
7.18
7.18
7.17
6.88
6.87
6.86
6.85
6.85
6.84
6.28
6.27
6.27
3.79
3.49
3.47
3.46
3.44
3.42
3.40
3.13
3.11
3.09
3.07
3.03
3.01
2.99
2.97
1.37
1.70
2.06
1.99
1.91
3.03
1.00
1.02
1.01
3.09
f1 (ppm)

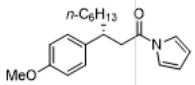
^{13}C NMR


Me
O
N
MeO

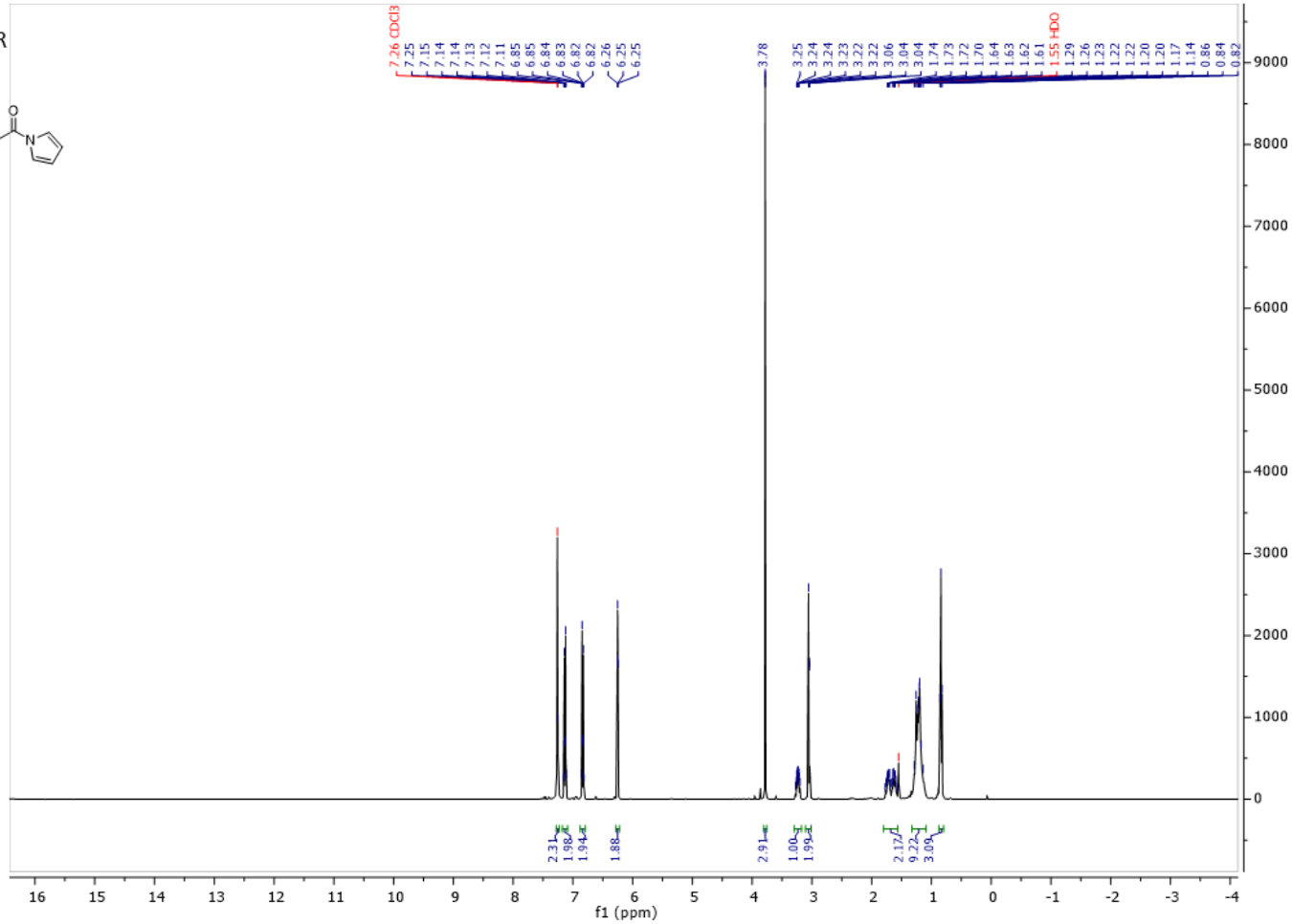
2e


169.42
158.34
137.76
127.80
119.13
114.14
113.19
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.39
43.46
35.32
22.01
f1 (ppm)

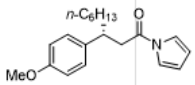
^{1}H NMR


n-C6H13
O
N
MeO

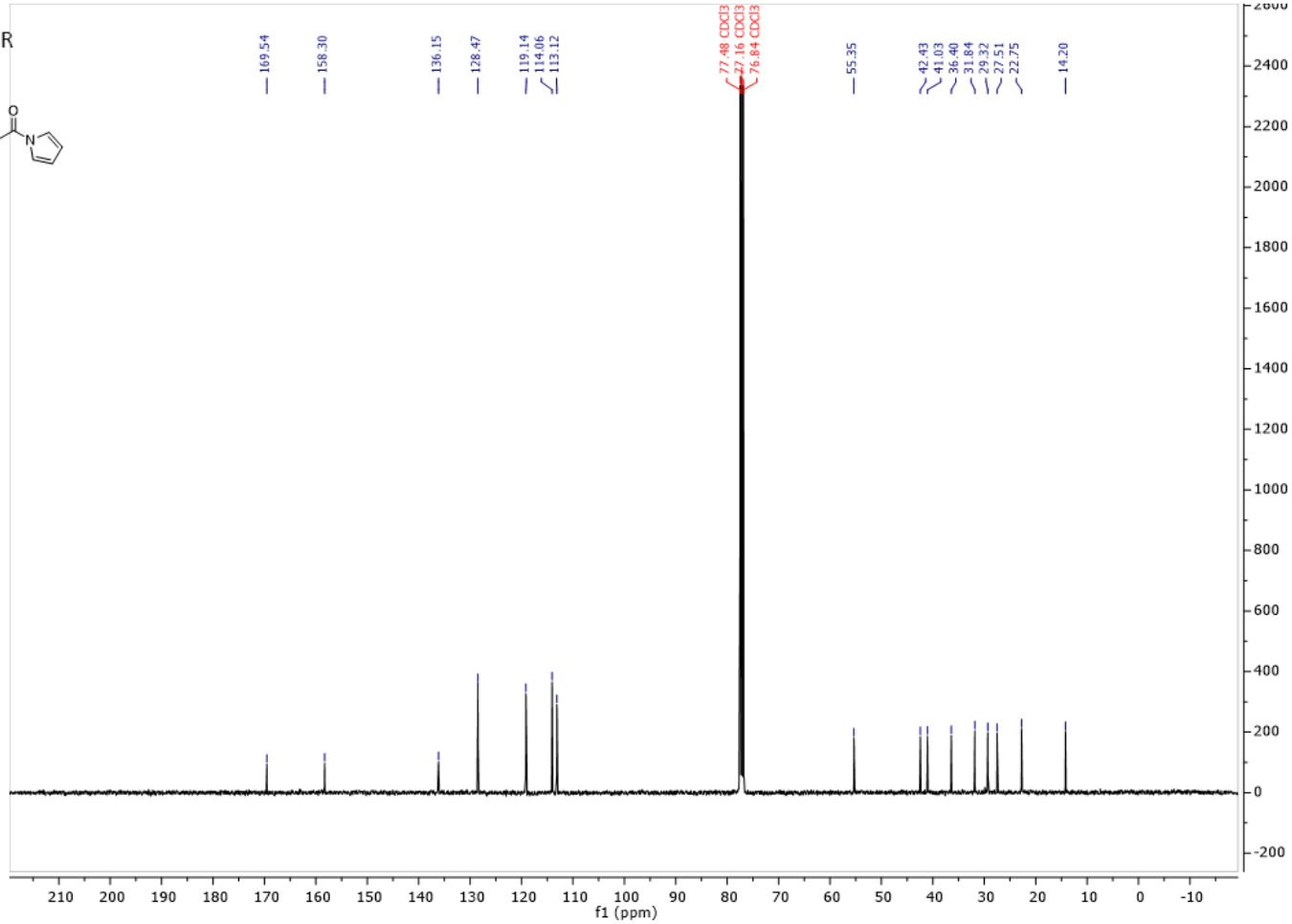
2f


7.26 CDCl3
7.25
7.15
7.14
7.14
7.13
7.12
7.11
6.85
6.85
6.84
6.83
6.82
6.82
6.26
6.25
6.25
3.78
3.25
3.24
3.24
3.23
3.22
3.22
3.06
3.04
3.04
1.74
1.73
1.72
1.70
1.64
1.63
1.62
1.61
1.55 HDO
1.29
1.26
1.23
1.22
1.22
1.20
1.20
1.17
1.14
0.86
0.84
0.82
2.31
1.98
1.94
1.88
2.91
1.00
1.99
2.17
9.22
3.09
f1 (ppm)

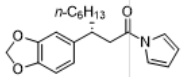
^{13}C NMR


n-C6H13
O
N
MeO

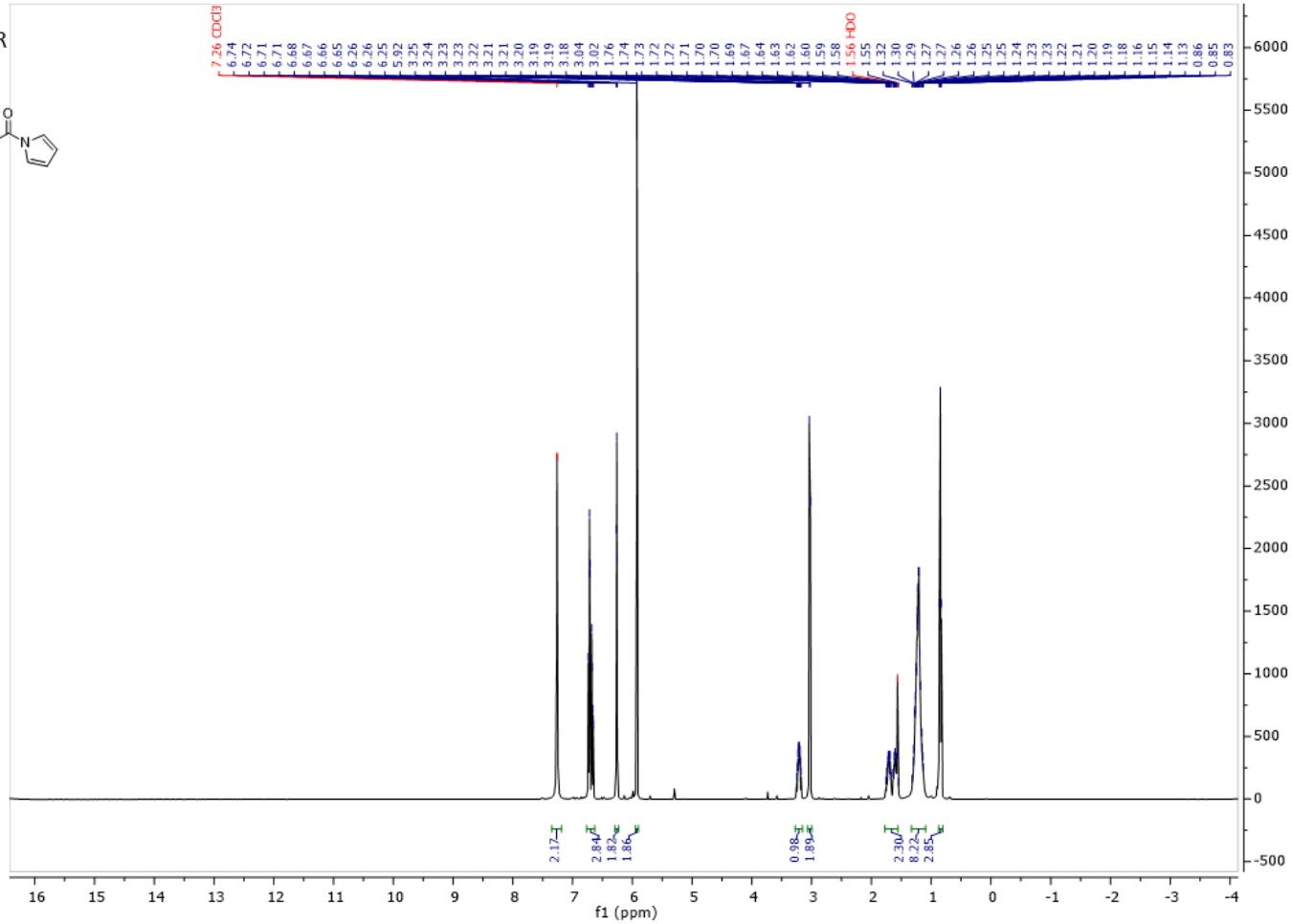
2f


169.54
158.30
136.15
128.47
119.14
114.06
113.12
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.35
42.43
41.03
36.40
31.84
29.32
27.51
22.75
14.20
f1 (ppm)

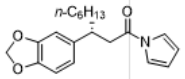
^{1}H NMR


n-C6H13
O
O
O
N

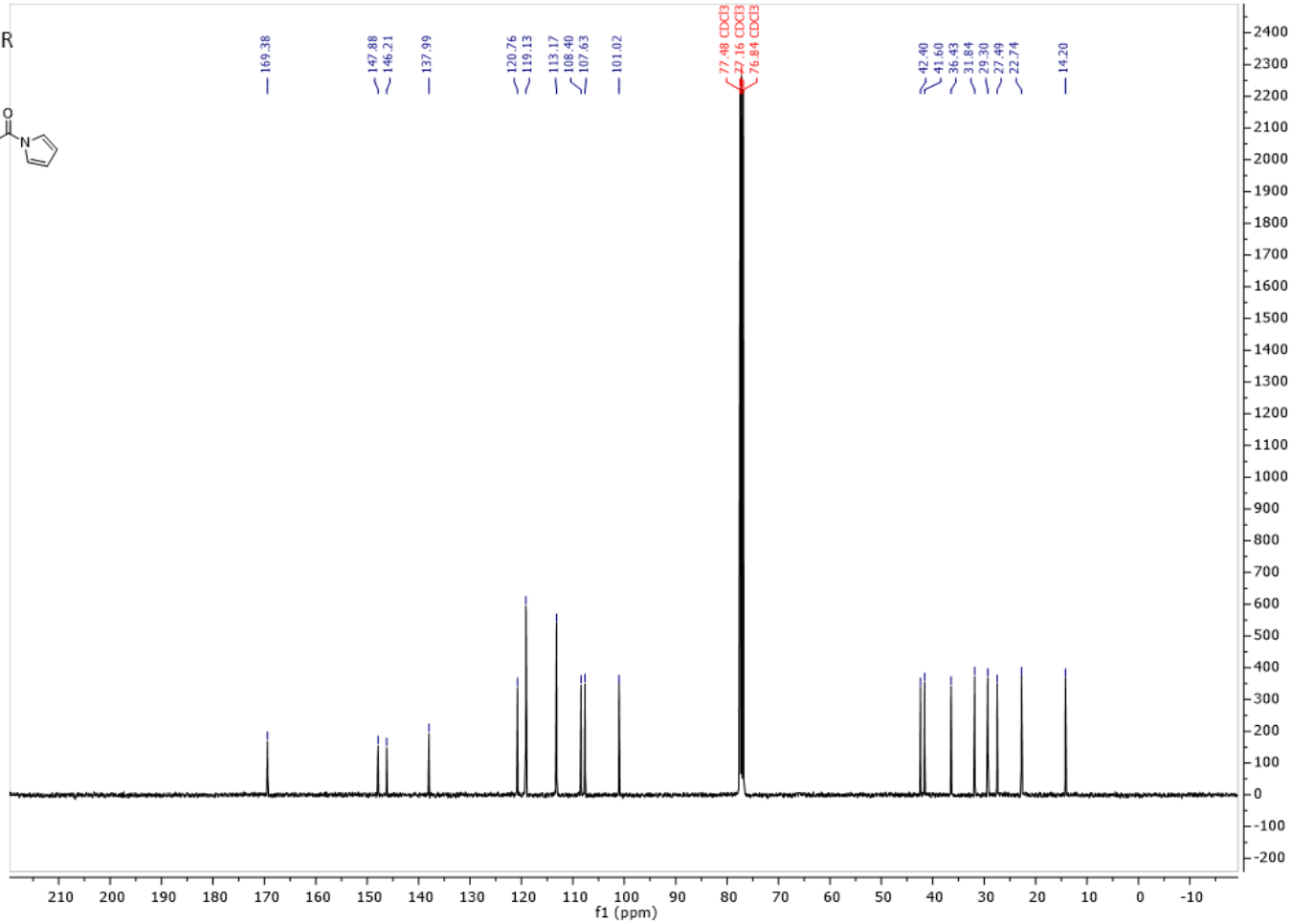
2g


7.26 CDCl3
1.56 HDO
2.17
2.84
1.82
1.86
0.98
1.89
2.30
8.22
2.85
f1 (ppm)

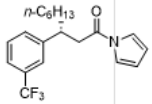
^{13}C NMR


n-C6H13
O
O
O
N

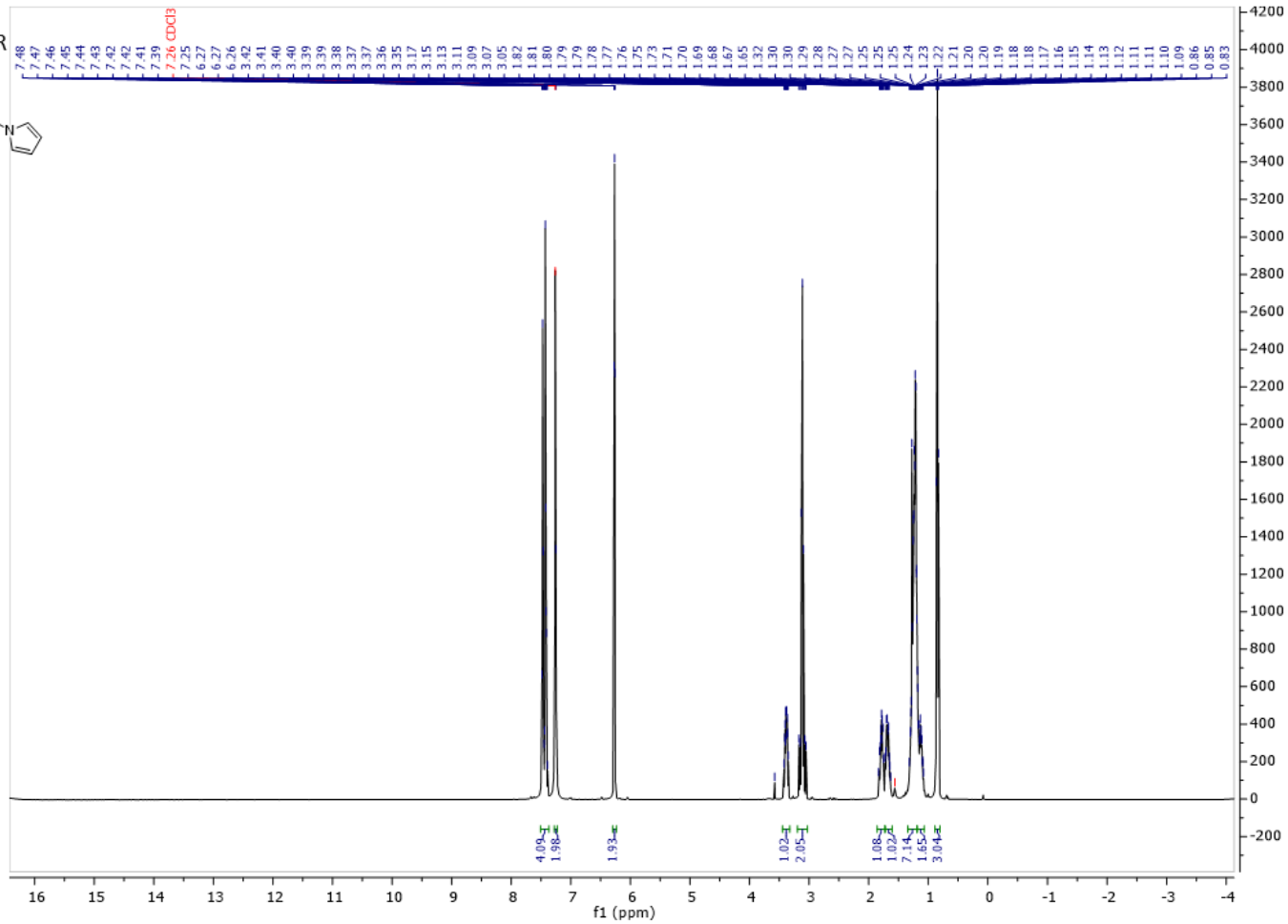
2g


169.38
147.88
146.21
137.99
120.76
119.13
113.17
108.40
107.63
101.02
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
42.40
41.60
36.43
31.84
29.30
27.49
22.74
14.20
f1 (ppm)

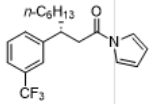
^{1}H NMR


n-C6H13
O
N
CF3

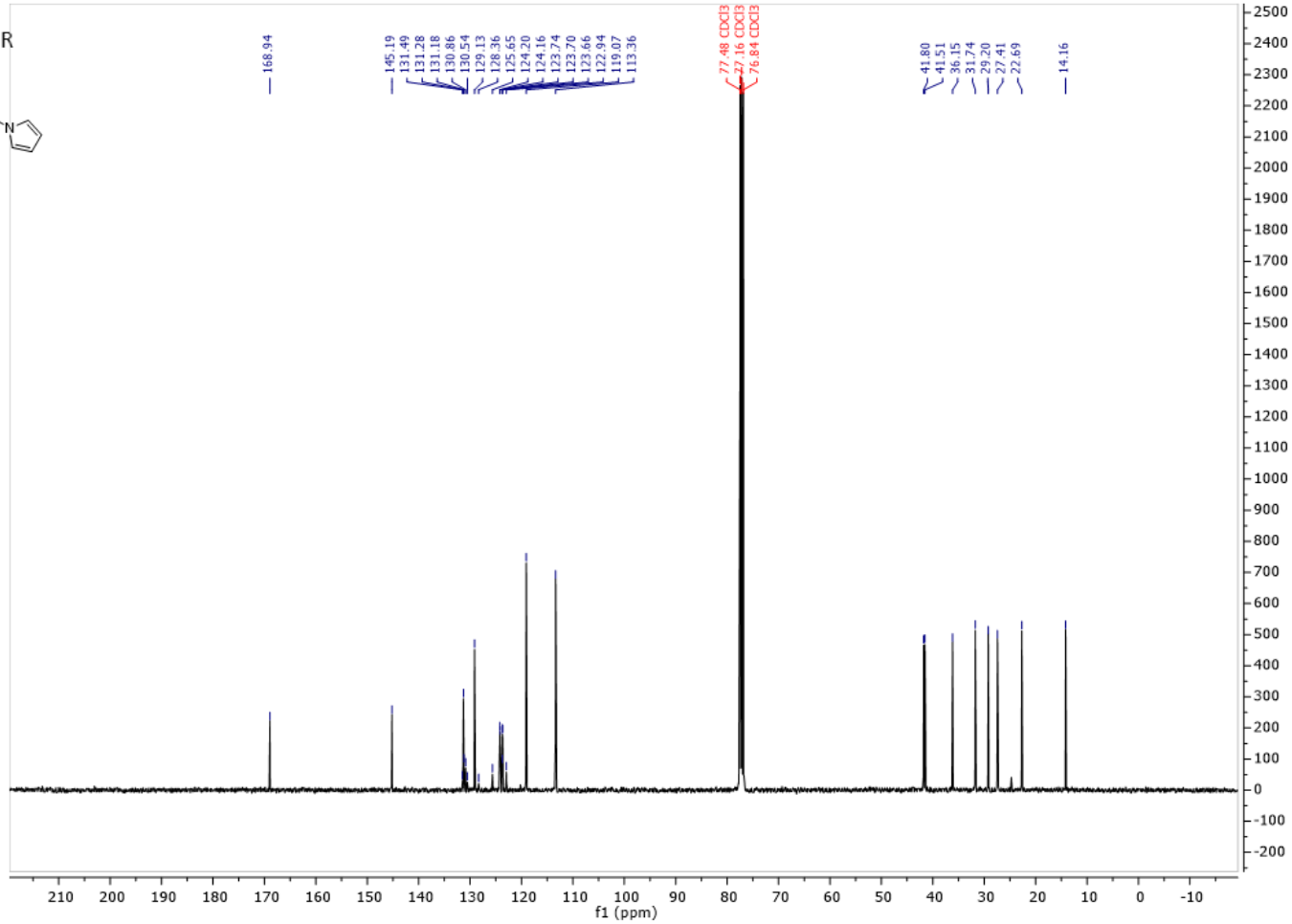
2h


CDCl3
4.09
1.98
1.93
1.02
2.05
1.08
1.02
7.14
1.65
3.04
f1 (ppm)

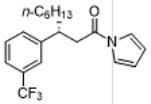
^{13}C NMR


n-C6H13
O
N
CF3

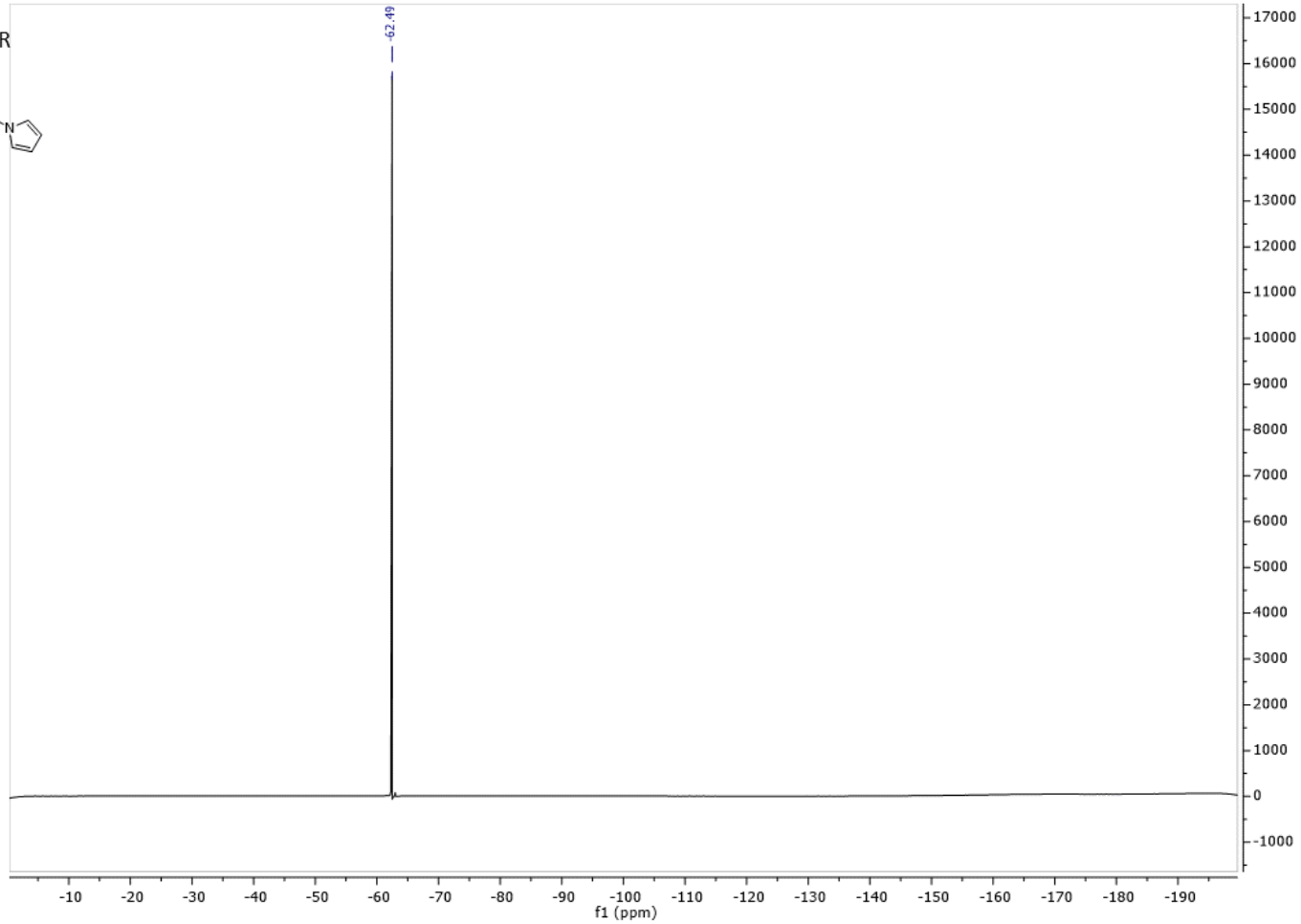
2h


168.94
145.19
131.49
131.28
131.18
130.86
130.54
129.13
128.36
125.65
124.20
124.16
123.74
123.70
123.66
122.94
119.07
113.36
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
41.80
41.51
36.15
31.74
29.20
27.41
22.69
14.16
f1 (ppm)

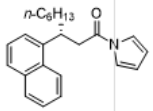
^{19}F NMR


n-C6H13
O
N
CF3

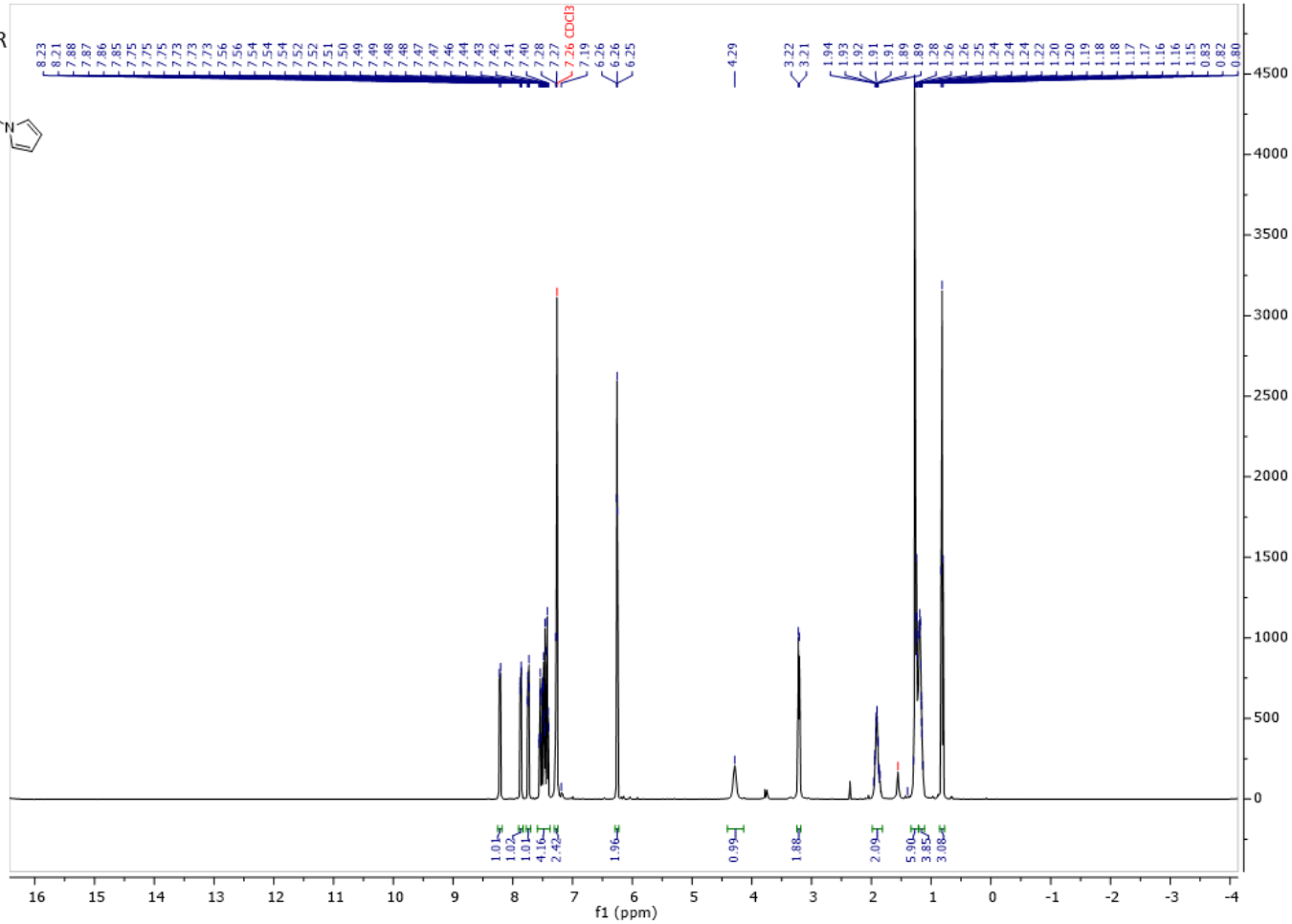
2h


-62.49
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

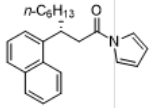
^{1}H NMR



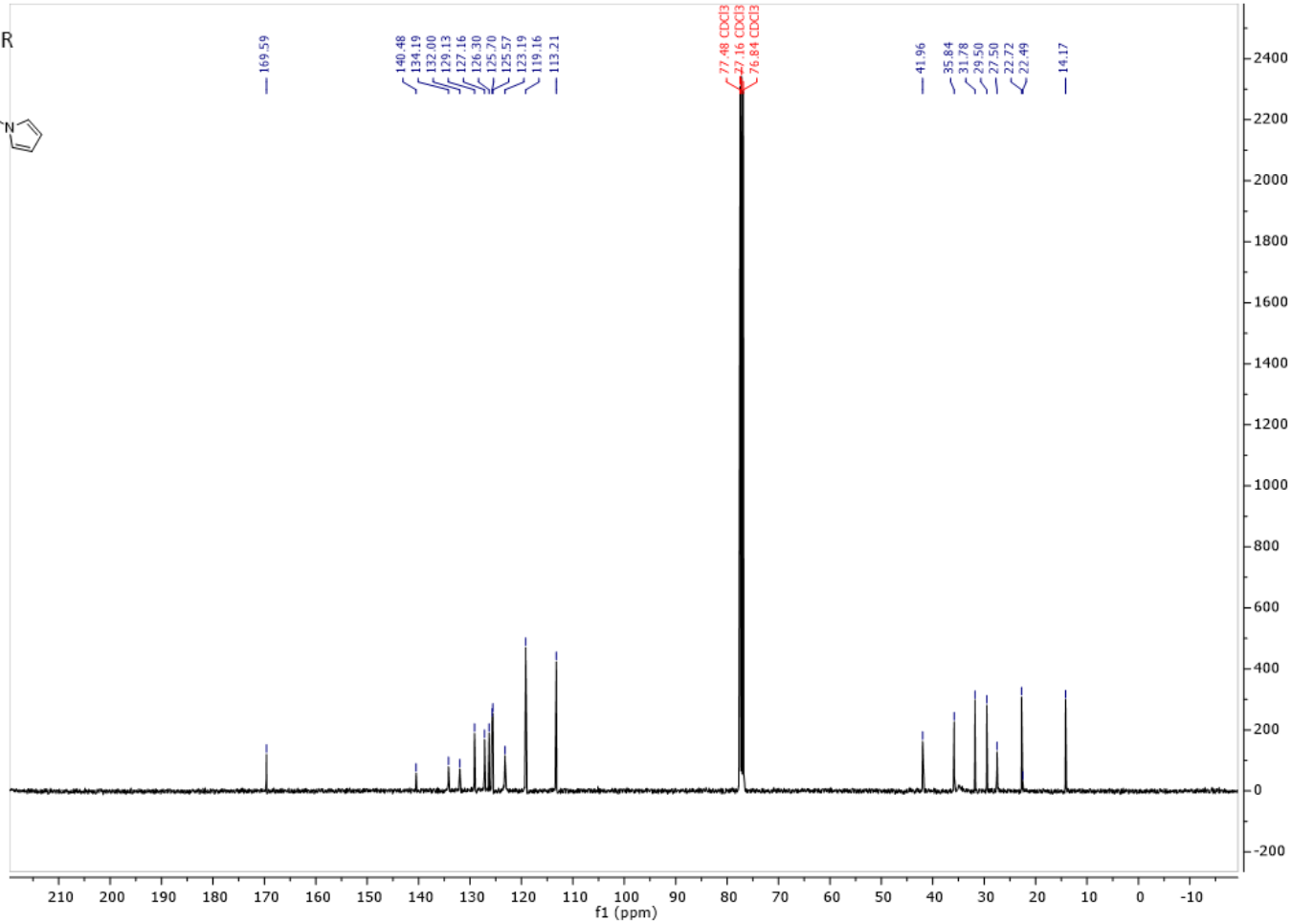
2i



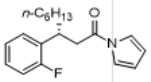
^{13}C NMR


n-C6H13
O
N

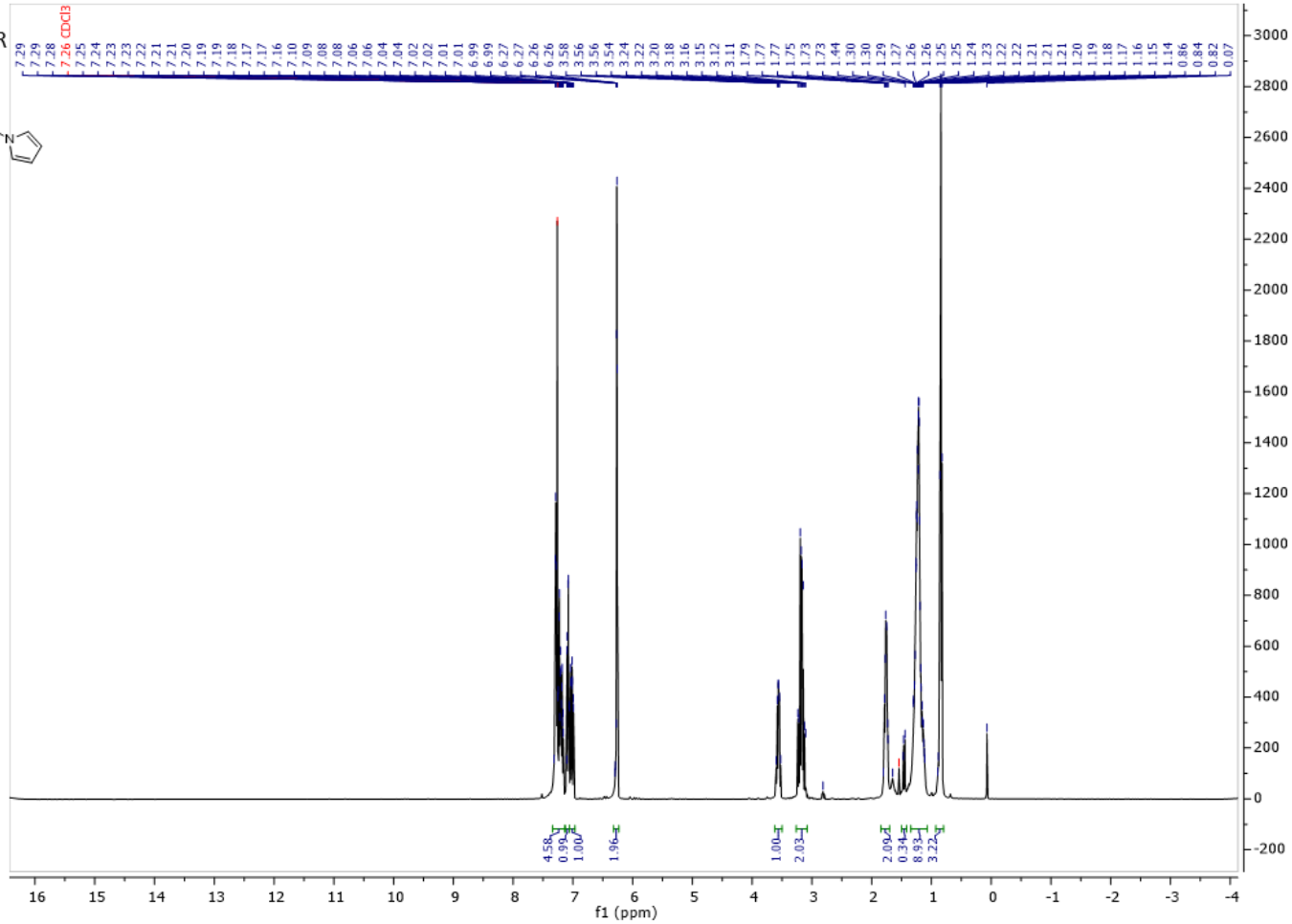
2i


169.59
140.48
134.19
132.00
129.13
127.16
126.30
125.70
125.57
123.19
119.16
113.21
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
41.96
35.84
31.78
29.50
27.50
22.72
22.49
14.17
f1 (ppm)

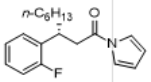
^{1}H NMR



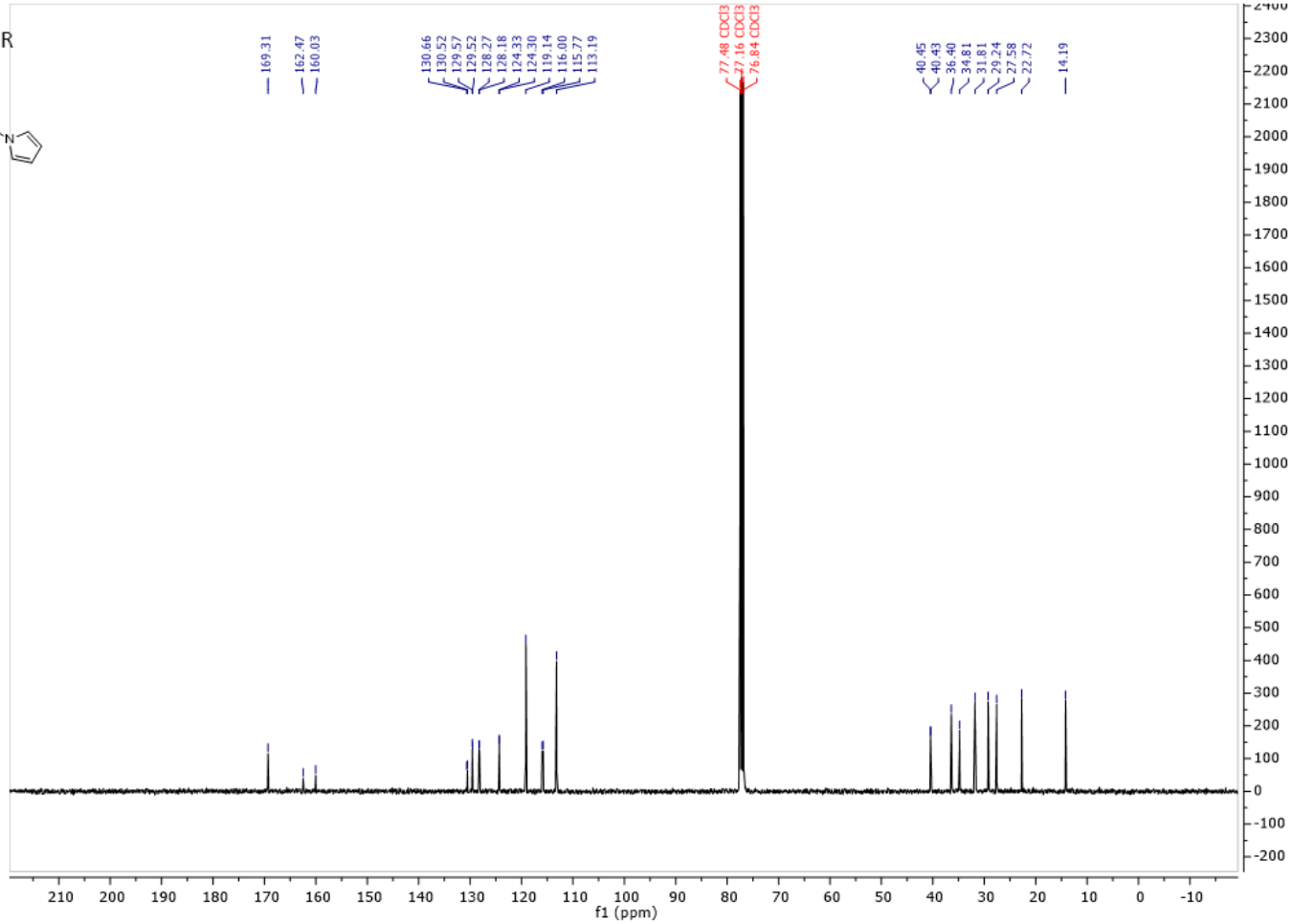
2j



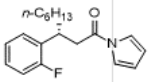
^{13}C NMR


n-C6H13
O
N
F

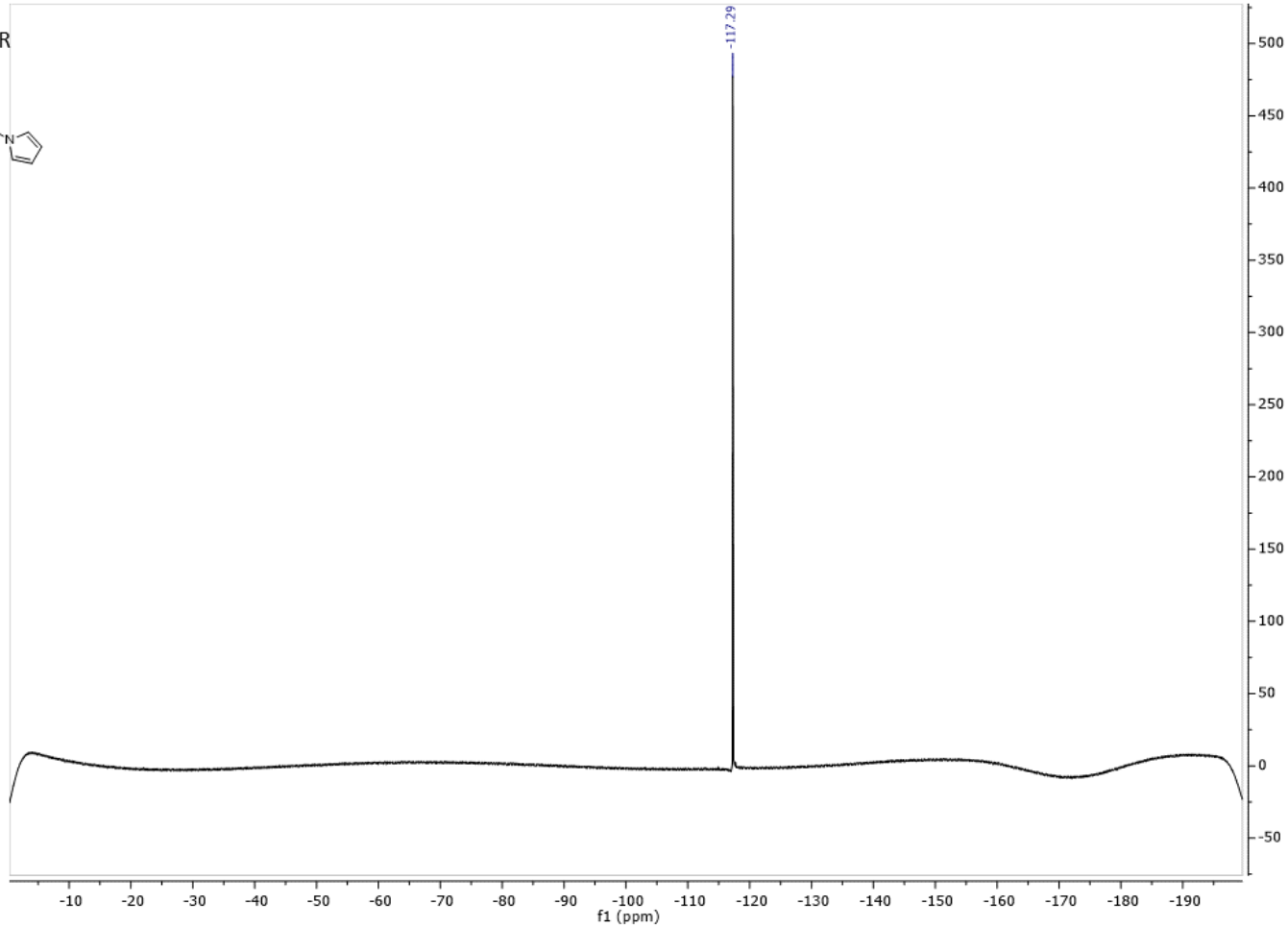
2j


169.31
162.47
160.03
130.66
130.52
129.57
129.52
128.27
128.18
124.33
124.30
119.14
116.00
115.77
113.19
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
40.45
40.43
36.40
34.81
31.81
29.24
27.58
22.72
14.19
f1 (ppm)

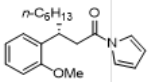
^{19}F NMR


n-C6H13
O
N
F

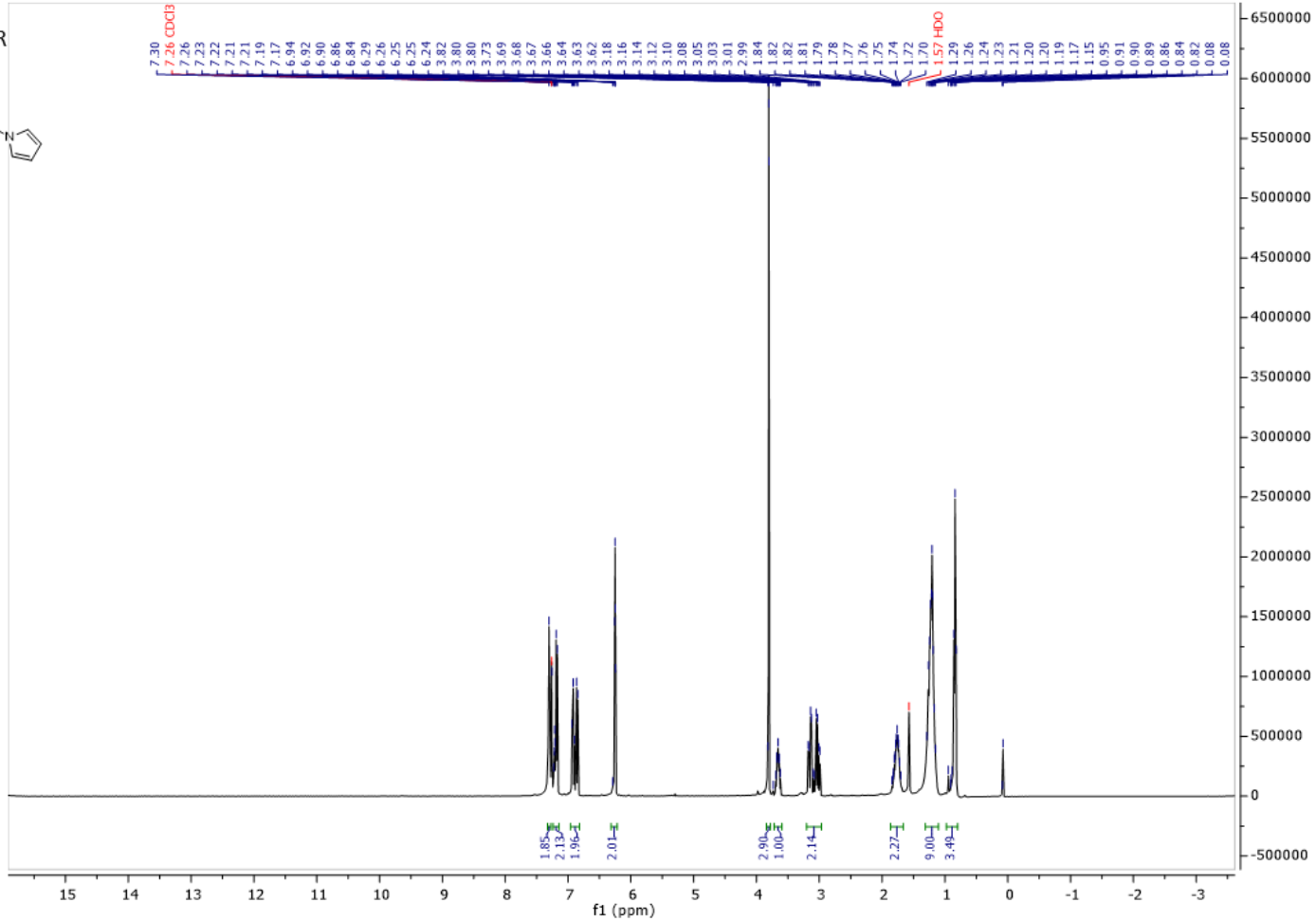
2j


-117.29
500
450
400
350
300
250
200
150
100
50
0
-50
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

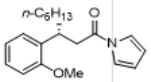
^{1}H NMR


n-C6H13
O
N
OMe

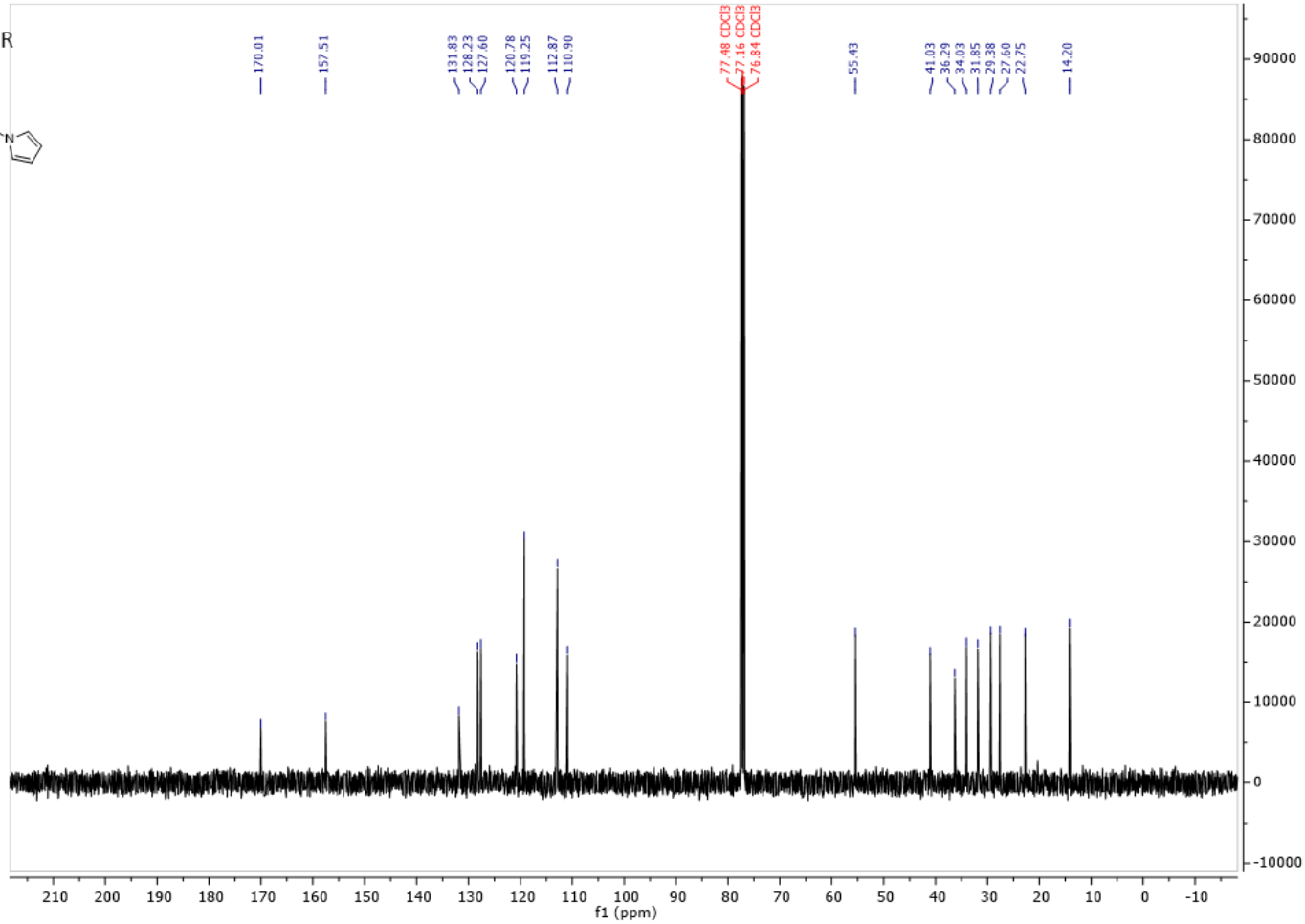
2k


7.30
7.26 CDCl3
7.23
7.22
7.21
7.21
7.19
7.17
6.94
6.92
6.90
6.86
6.84
6.29
6.26
6.25
6.25
6.24
3.82
3.80
3.80
3.73
3.69
3.68
3.67
3.66
3.64
3.63
3.62
3.18
3.16
3.14
3.12
3.10
3.08
3.05
3.03
3.01
2.99
1.84
1.82
1.82
1.81
1.79
1.78
1.77
1.76
1.75
1.74
1.72
1.70
1.57 HDO
1.29
1.26
1.24
1.23
1.21
1.20
1.20
1.19
1.17
1.15
0.95
0.91
0.90
0.89
0.86
0.84
0.82
0.08
0.08
1.85
2.13
1.96
2.01
2.90
1.00
2.14
2.27
9.00
3.49
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

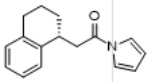
^{13}C NMR


n-C6H13
O
N
OMe

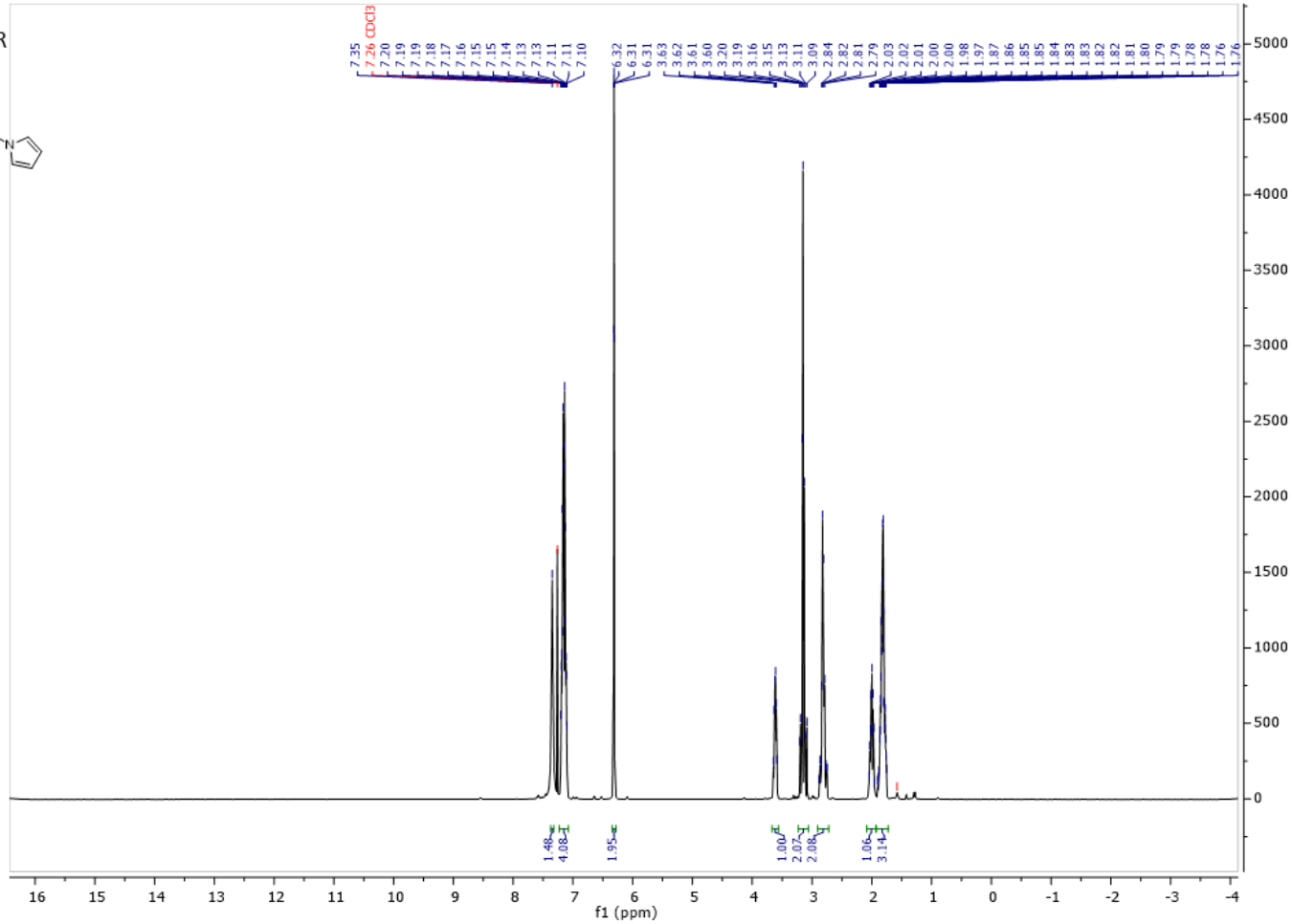
2k


170.01
157.51
131.83
128.23
127.60
120.78
119.25
112.87
110.90
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.43
41.03
36.29
34.03
31.85
29.38
27.60
22.75
14.20
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

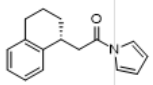
^{1}H NMR



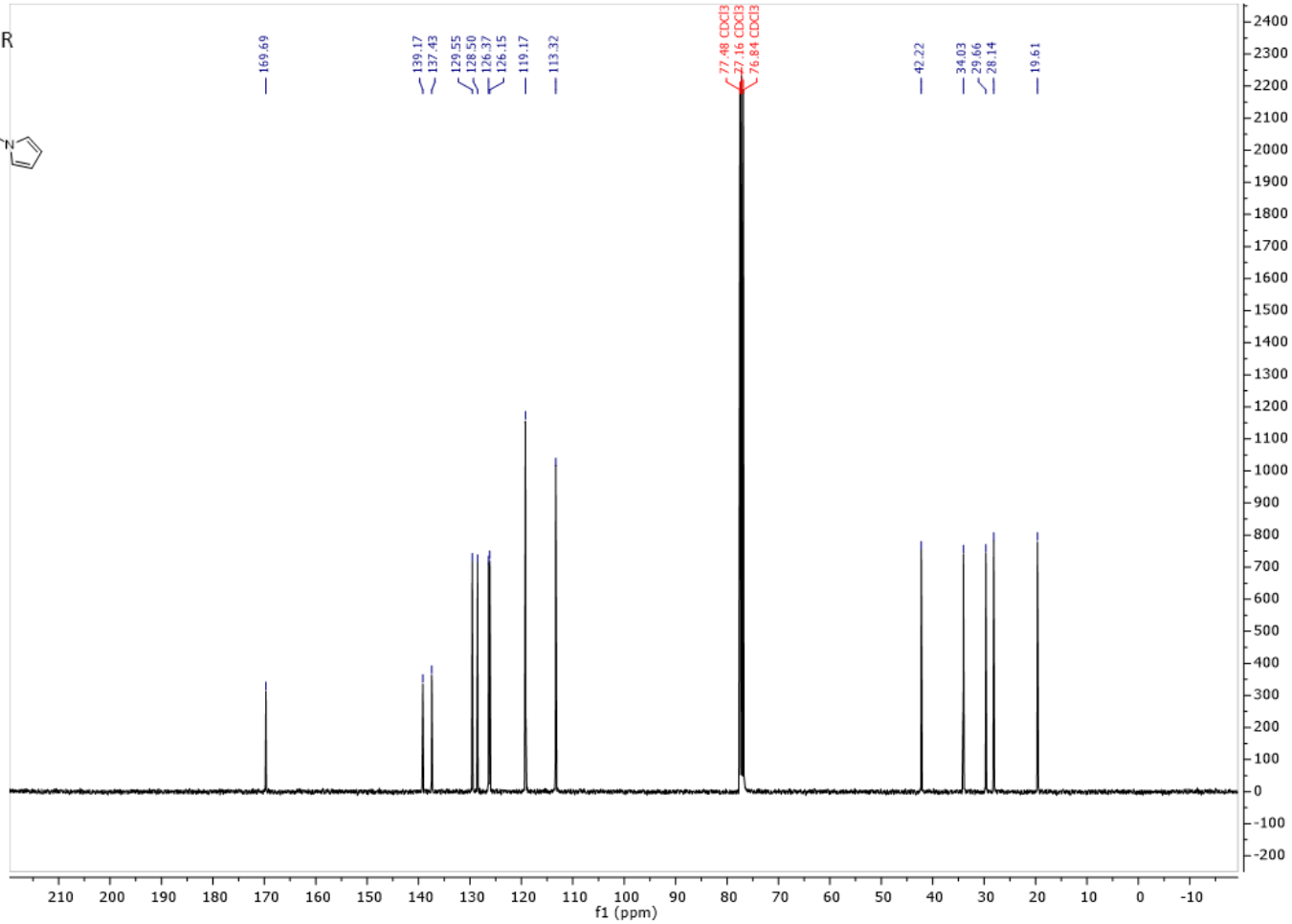
2l


7.35 7.26 CDCl3 7.20 7.19 7.19 7.18 7.17 7.16 7.15 7.15 7.14 7.13 7.13 7.11 7.11 7.10
6.32 6.31 6.31
3.63 3.62 3.61 3.60 3.20 3.19 3.16 3.15 3.13 3.11 3.09
2.84 2.82 2.81 2.79 2.03 2.02 2.01 2.00 2.00 1.98 1.97 1.87 1.86 1.85 1.85 1.84 1.83 1.83 1.82 1.82 1.81 1.80 1.79 1.79 1.78 1.78 1.76 1.76
1.48 4.08 1.95 1.00 2.07 2.08 1.06 3.14
f1 (ppm)

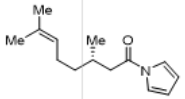
^{13}C NMR



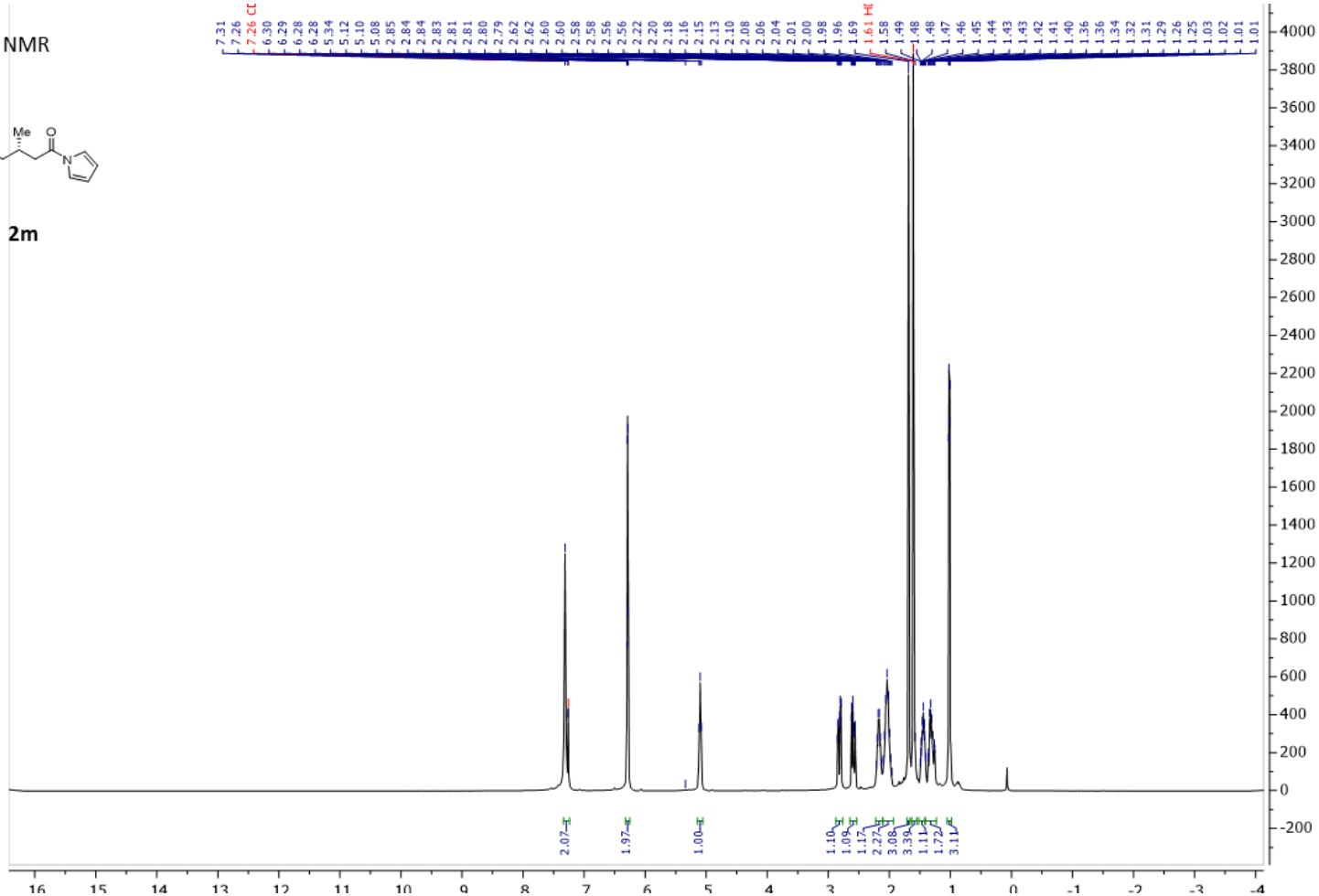
2l


169.69
139.17
137.43
129.55
128.50
126.37
126.15
119.17
113.32
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
42.22
34.03
29.66
28.14
19.61
f1 (ppm)

^{1}H NMR


Me
Me
Me
O
N

2m


7.31
7.26 CL
7.26
6.30
6.29
6.28
6.28
5.34
5.12
5.10
5.08
2.85
2.84
2.84
2.83
2.81
2.81
2.80
2.79
2.62
2.62
2.60
2.60
2.58
2.58
2.56
2.56
2.22
2.20
2.18
2.16
2.15
2.13
2.10
2.08
2.06
2.04
2.01
2.00
1.98
1.96
1.69
1.61 HI
1.58
1.49
1.48
1.48
1.47
1.46
1.45
1.44
1.43
1.43
1.42
1.41
1.40
1.36
1.36
1.34
1.32
1.31
1.29
1.26
1.25
1.03
1.02
1.01
1.01
2.07
1.97
1.00
1.10
1.09
1.17
2.27
3.08
3.39
1.11
1.72
3.11
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
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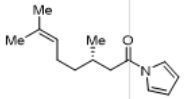
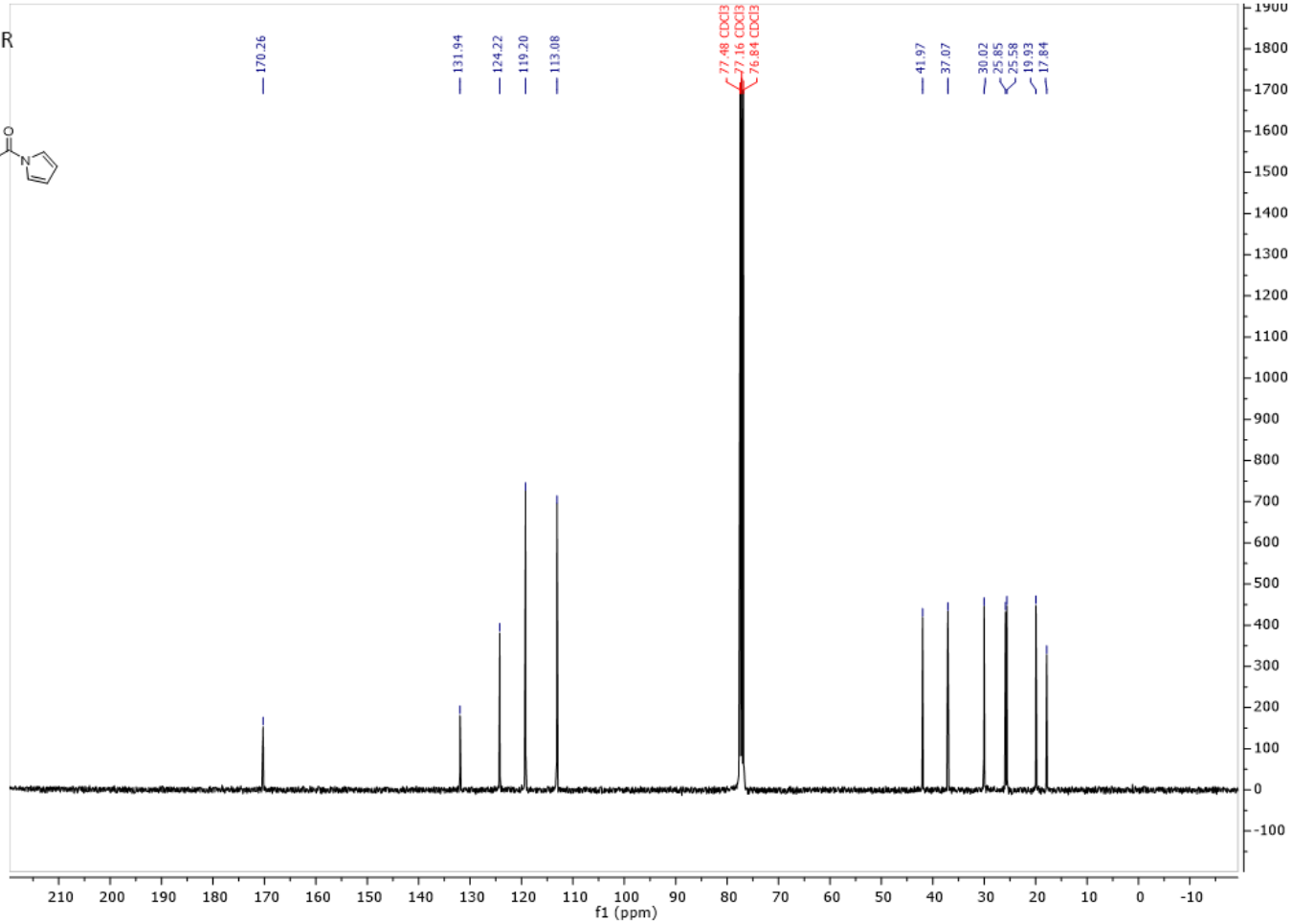
0
-1
-2
-3
-4

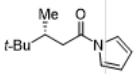
^{13}C NMR


Me
Me
Me
O
N

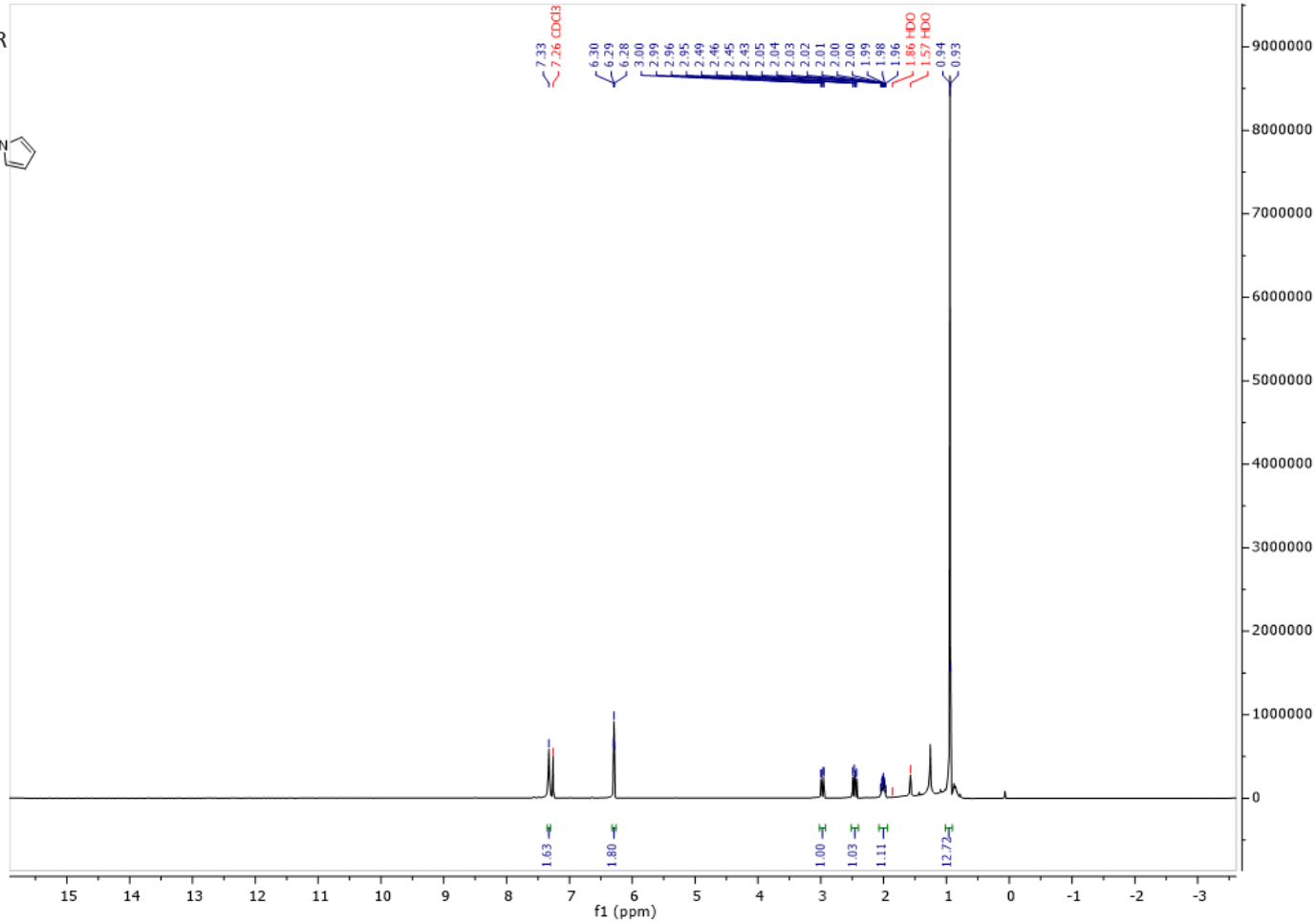
2m


170.26
131.94
124.22
119.20
113.08
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
41.97
37.07
30.02
25.85
25.58
19.93
17.84
f1 (ppm)

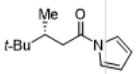
^{1}H NMR


Me
O
t-Bu
N

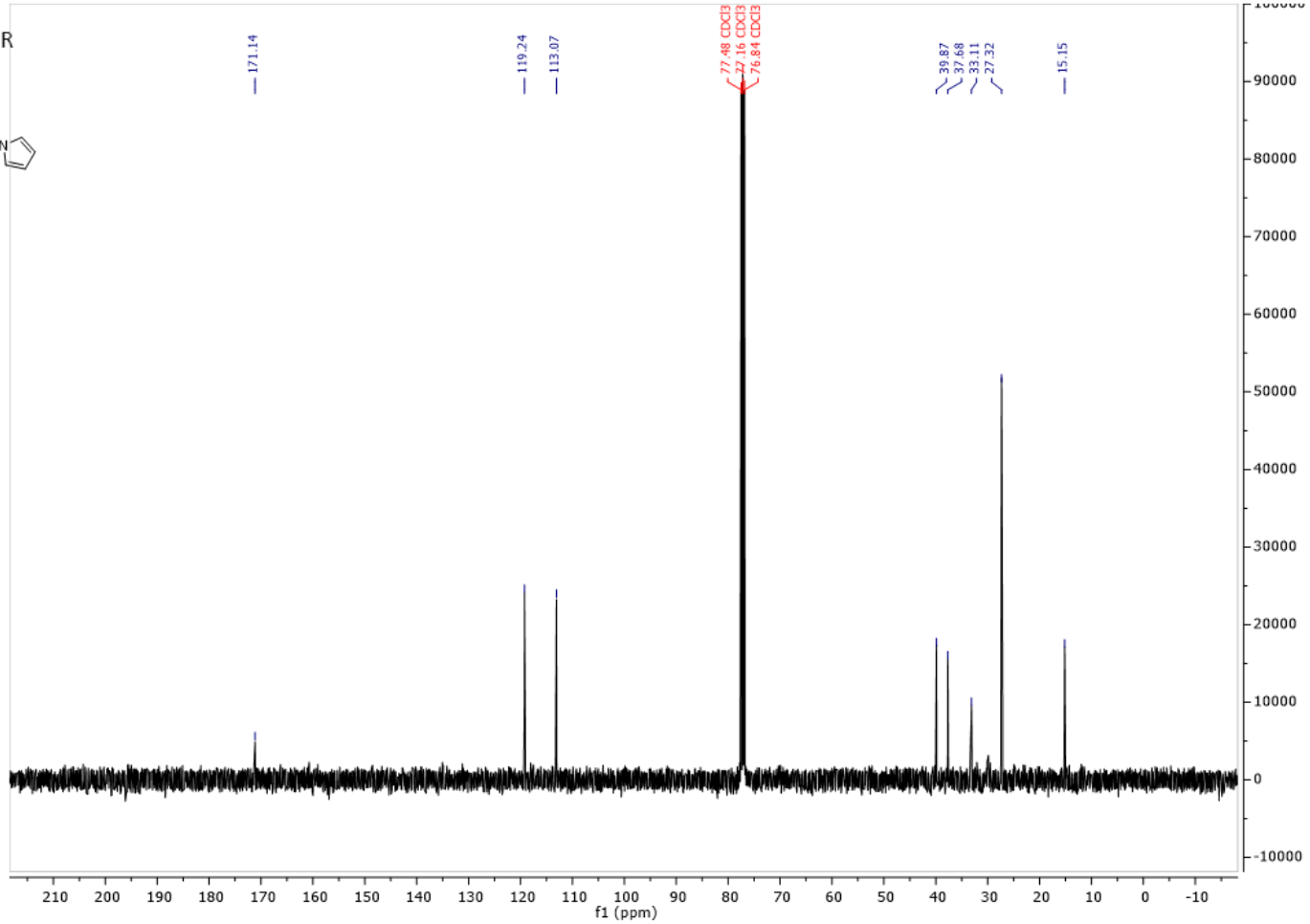
2n


7.33
7.26 CDCl3
6.30
6.29
6.28
3.00
2.99
2.96
2.95
2.49
2.46
2.45
2.43
2.05
2.04
2.03
2.02
2.01
2.00
2.00
1.99
1.98
1.96
1.86 HDO
1.57 HDO
0.94
0.93
1.63
1.80
1.00
1.03
1.11
12.72
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

^{13}C NMR


Me
O
t-Bu
N

2n


171.14
119.24
113.07
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
39.87
37.68
33.11
27.32
15.15
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)