Supporting Information

Ketene Aminal Phosphates: Competent Substrates for Enantioselective Pd(0)-Catalyzed C-H Functionalizations

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General Methods

Experimental procedures, reagents and glassware

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring, unless otherwise indicated. Toluene, THF, Et_2O and dichloromethane were purified by an Innovative Technology Solvent Delivery System. DMF was dried over 4A molecular sieves. Chemicals were used as obtained from the suppliers unless otherwise stated. Diphenyl phosphoryl chloride ($ClPO(OPh)_2$) and diethyl phosphoryl chloride ($ClPO(OEt)_2$) was distilled under reduced pressure and stored in a glovebox. Solvent compositions are given in (v/v).

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 visualised under UV-light at 254 nm and/or developed using standard $KMnO_4$ or vanillin stains, followed by heating. Where specified silica was buffered prior to use (method: silica (100 g) was suspended in 0.2 M Na_2HPO_4 (1 L), the pH was adjusted to 7 with phosphoric acid, and the silica filtered and oven-dried prior to use).

NMR Spectroscopy

Proton nuclear magnetic resonance (^{1}H NMR) data were acquired at 400 MHz on a Bruker AVANCEIII-400 spectrometer or at 600 MHz on a Bruker DRX-600 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual chloroform (s, 7.26 ppm), residual benzene (s, 7.16 ppm) or residual CD_3CN (m, 1.94 ppm). Proton decoupled Carbon-13 nuclear magnetic resonance ($^{13C\{1H\}}${^{1}H} NMR) data were acquired at 101 MHz on a Bruker AVANCEIII-400, at 151 MHz on a Bruker DRX-600 spectrometer or at 201 MHz on an AVANCEII-800. Chemical shifts are reported in ppm relative to residual chloroform (77.16 ppm), residual benzene (128.06 ppm) or residual CD_3CN (1.32 and 118.26 ppm). Proton decoupled Fluorine-19 nuclear magnetic resonance (^{19}F{^{1}H} NMR) were acquired at 377 MHz on a Bruker AV400 spectrometer. Proton decoupled Phosphorus-31 nuclear magnetic resonance (^{31}P{^{1}H} NMR) were acquired at 162 MHz on a Bruker AV400 spectrometer. The assignment of proton and carbon signals was assisted by COSY, HSQC, HMBC and DEPT-135 experiments where necessary. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; dd, doublet of doublets; dt, doublet of triplets; td, triplet of doublets; m, multiplet. All NMR data were recorded at 298 K.

Infrared Spectroscopy

Infrared (IR) data were recorded on an Alpha-P Bruker FT-IR Spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}).

Mass Spectrometry

HRMS measurements were performed on an Agilent LC-MS TOF (Multimode: ESI + APCI) or Waters Xevo G2-S QTOF (ESI or APPI). High resolution mass are given in *m/z*.

Melting Points

Melting points were measured on a Büchi B-540 and are uncorrected.

Enantiomeric excesses

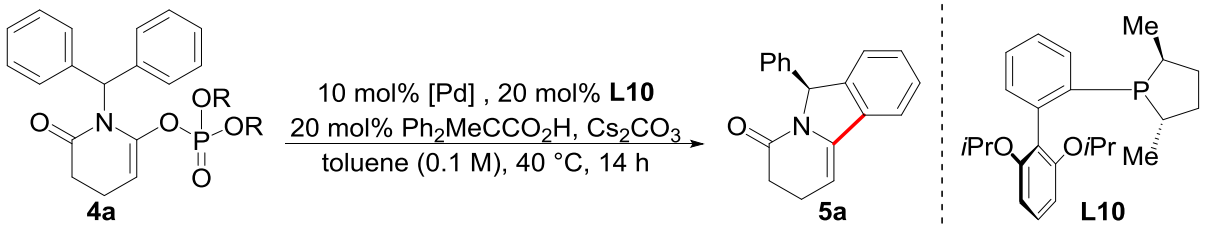
Enantiomeric excesses were measured on an Agilent HPLC. Optical rotations were measured on a Polartronic M polarimeter using a 0.5 cm cell with a Na 589 nm filter.

X-Ray analyses

X-ray analyses of compounds **L6** and **5e** were performed by Dr. R. Scopelliti and Dr. F. Fadaei Tirani at the EPF Lausanne.

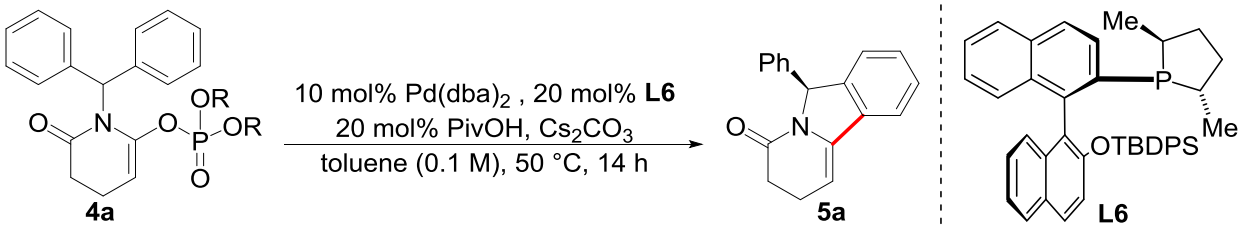
Additional Optimization Experiments

Pd source screening with L10 and Ph_2MeCCO_2H



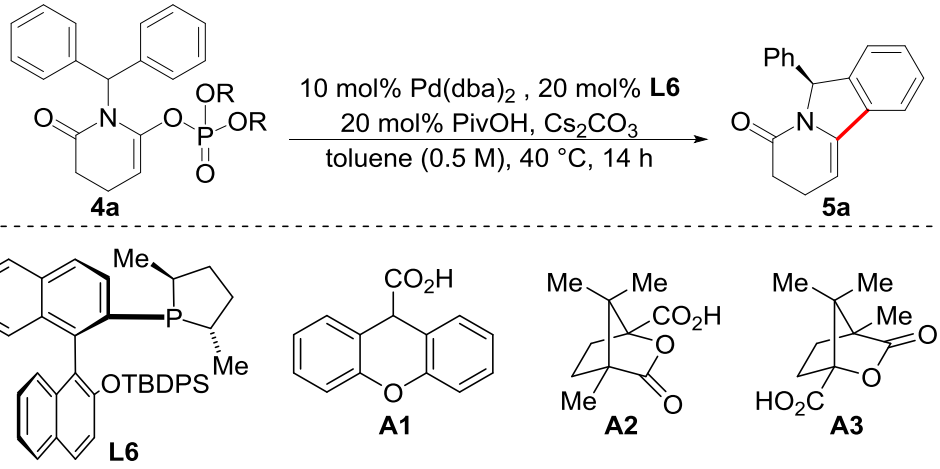
Entry	[Pd]	Conversion	Yield	er
1	$Pd(dba)_2$	100%	82%	89:11
2	Pd(cinnamyl)Cp	62%	52%	88.5:11.5
3	$Pd(OAc)_2$	100%	85%	71:29

Base screening



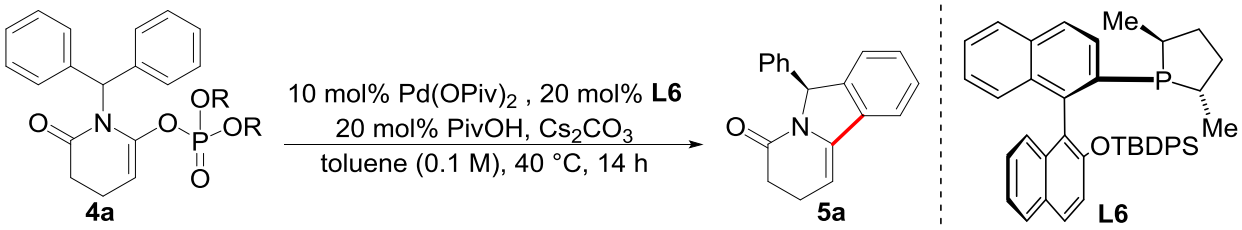
Entry	Base	Conversion	Yield	er
1	Li_2CO_3	30%	22%	69.5:30.5
2	Na_2CO_3	36%	30%	72.5:27.5
3	K_2CO_3	68%	65%	87:13
4	Cs_2CO_3	76%	76%	92.5 :7.5
5	Tl_2CO_3	84%	80%	92:8

Acid screening



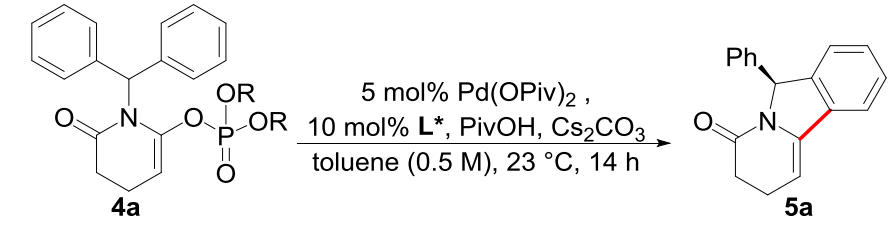
Entry	Acid	Conversion	Yield	er
1	Ph_2MeCCO_2H	30%	29%	90.5:9.5
2	$PhCO_2H$	39%	37%	93:7
3	PivOH	37%	36%	93.5:6.5
4	**A1**	28%	26%	91.5:8.5
5	**A2**	24%	22%	92.5:7.5
6	**A3**	30%	28%	90.5:9.5

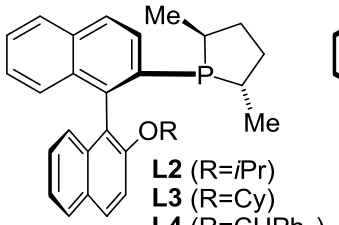
Relevant Control Experiments



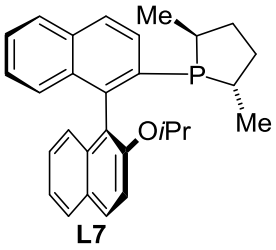
Entry	Deviation from Standard Conditions	Conversion	Yield	er
1	–	100%	95%	94:6
2	no Pd source	0%	0%	–
3	no ligand	0%	0%	–
4	no PivOH	95%	90%	92:8

Ligand Screening under Optimized Conditions

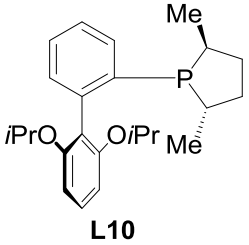




L2 (R=*i*Pr)
L3 (R=Cy)
L4 (R=$CHPh_2$)
L5 (R=TBS)
L6 (R=TBDPS)



L7

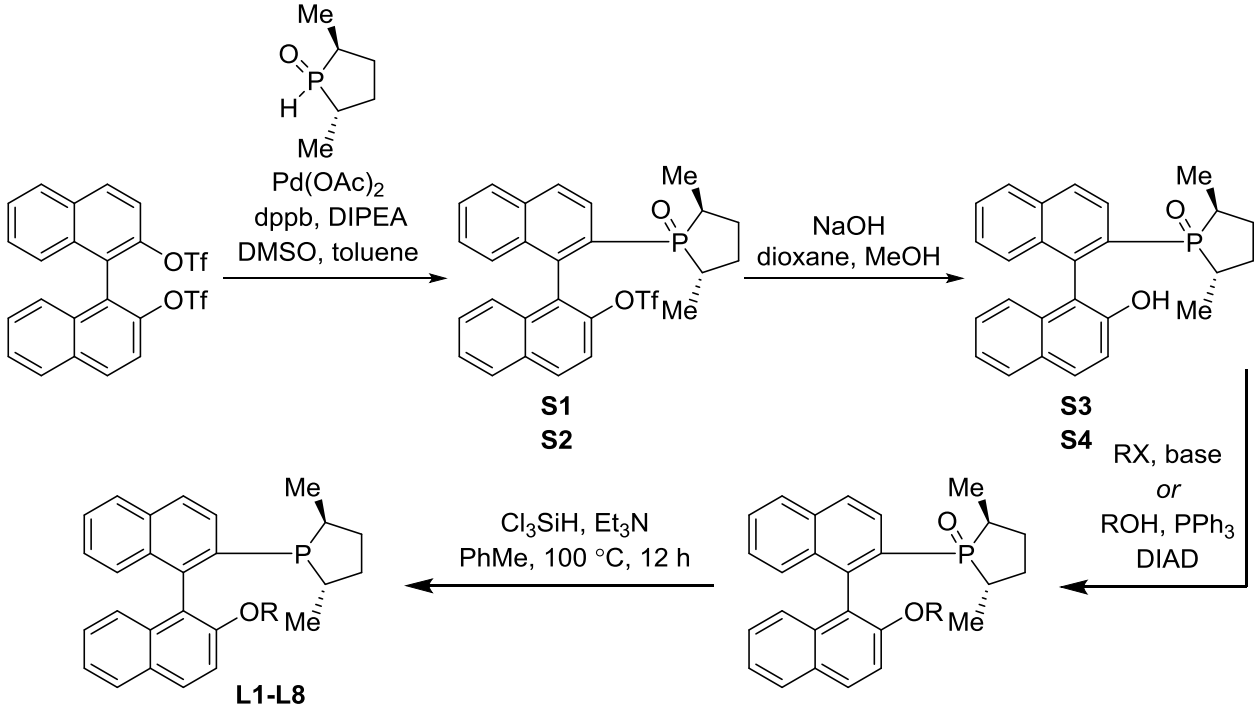


L10

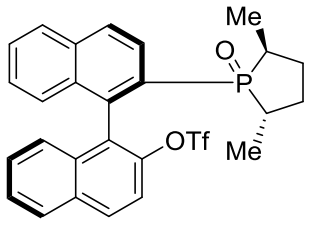
Entry	Ligand	Conversion	Yield	er
1	**L2**	60%	38%	71.5:28.5
2	**L3**	67%	39%	90.5:9.5
3	**L4**	82%	55%	73.5:26.5
4	**L5**	18%	8%	nd
5	**L6**	100%	93%	94.5 :5.5
6	**L7**	100%	72%	67.5 :32.5
7	**L10**	100%	62%	83.5:16.5

Experimental Procedures and Characterization Data

Chiral binaphthyl-substituted phospholane ligands



(*R*)-2'-((2*S*,5*S*)-2,5-dimethyl-1-oxidophospholan-1-yl)-[1,1'-binaphthalen]-2-yl trifluoromethanesulfonate:



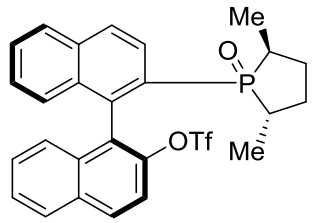
S1

Prepared according to a slight modification of the procedure reported by Buchwald.[1] A 10-20 mL microwave tube was charged with (*R*)-[1,1'-binaphthalene]-2,2'-diyl bis(trifluoromethanesulfonate) (2.08 g, 3.78 mmol, 1.0 eq.), $Pd(OAc)_2$ (170 mg, 0.757 mmol, 20 mol%) and 1,4-bis(diphenylphosphino)butane (dppb) (323 mg, 0.757 mmol, 20 mol%). This tube was transferred to a glovebox, (2*S*,5*S*)-2,5-dimethylphospholane 1-oxide[2] (1.00 g, 7.57 mmol, 2.0 eq.) and distilled toluene (3.0 mL) were added, the tube was closed and taken out of the glovebox. Freshly distilled *N*,*N*-diisopropylethylamine (DIPEA) (2.6 mL, 15.1 mmol, 4.0 eq.) and DMSO (5.0 ml) were added by syringe. The tube was sealed and the reaction was stirred for 48 h at 110 °C. The resulting mixture was cooled down to room temperature and diluted with EtOAc (70 mL). The organic phase was washed with water (4*50 mL) and brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification *via* flash chromatography (SiO_2, EtOAc) yielded (*R*)-2'-((2*S*,5*S*)-2,5-dimethyl-1-oxidophospholan-1-yl)-[1,1'-binaphthalen]-2-yl trifluoromethanesulfonate (**S1**) (1.49 g, 2.80 mmol, 74%).

Appearance: pale brown foam; $\mathbf{R_f}$: 0.2 (EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.12–8.01 (m, 2 H), 7.96 (d, *J* = 8.4 Hz, 2 H), 7.63–7.42 (m, 4 H), 7.38–7.20 (m, 3 H), 7.12 (d, *J* = 8.5 Hz, 1 H), 2.33–1.99 (m, 4 H), 1.63–1.39 (m, 2 H), 1.17 (dd, *J* = 7.1, 16.3 Hz, 3 H), 0.86 (dd, *J* = 6.8, 14.7 Hz, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): 145.6, 138.5 (d, *J* = 4.3 Hz), 134.6, 134.4 (d, *J* = 2.4 Hz), 133.5 (d, *J* = 10.1 Hz), 132.1, 130.7, 129.2 (d, *J* = 3.7 Hz), 128.8 (d, *J* = 11.8 Hz),

128.6, 128.4, 128.0, 127.4, 127.35, 127.3, 126.7, 126.6, 126.0 (d, *J* = 12.5 Hz), 119.8, 119.3, 116.6, 39.6 (d, *J* = 66.2 Hz), 36.5 (d, *J* = 68.2 Hz), 34.0 (d, *J* = 9.1 Hz), 32.5 (d, *J* = 8.3 Hz), 14.2, 12.1 (d, J = 2.8 Hz) ppm; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ -74.9 ppm; **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ 59.7 ppm; **IR** (ATR): ν_{max} = 3060, 2959, 2932, 2871, 1453, 1417, 1212, 1181, 1139, 956, 940, 834, 810, 748, 685, 499 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{27}H_{24}F_3O_4PS + H]^+$: 533.1158, found: 533.1157; **$[\alpha]_D^{20}$**: 62.3 (c = 1.0, $CHCl_3$).

(*S*)-2'-((2*S*,5*S*)-2,5-dimethyl-1-oxidophospholan-1-yl)-[1,1'-binaphthalen]-2-yl trifluoromethanesulfonate:

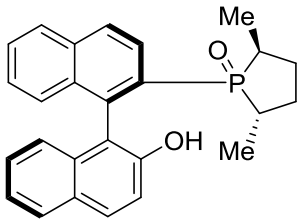


S2

Prepared according to a slight modification of the procedure reported by Buchwald.[1] A 10-20 mL microwave tube was charged with (*S*)-[1,1'-binaphthalene]-2,2'-diyl bis(trifluoromethanesulfonate) (1.10 g, 2.00 mmol, 1.0 eq.), $Pd(OAc)_2$ (90.0 mg, 0.400 mmol, 20 mol%) and 1,4-bis(diphenylphosphino)butane (dppb) (171 mg, 0.400 mmol, 20 mol%). This tube was transferred to a glovebox, and (2*S*,5*S*)-2,5-dimethylphospholane 1-oxide (529 mg, 4.00 mmol, 2.0 eq.) and distilled toluene (2.0 mL) were added, the tube was closed. Freshly distilled *N*,*N*-diisopropylethylamine (DIPEA) (1.4 mL, 8.00 mmol, 4.0 eq.) and DMSO (3.0 mL) were added by syringe. The tube was sealed and the reaction was stirred for 48 h at 110 °C. The resulting mixture was cooled down to room temperature and diluted with EtOAc (70 mL). The organic phase was washed with water (4*30 mL) and brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification *via* flash chromatography (SiO_2, EtOAc) yielded (*S*)-2'-((2*S*,5*S*)-2,5-dimethyl-1-oxidophospholan-1-yl)-[1,1'-binaphthalen]-2-yl trifluoromethanesulfonate (**S2**) (619 mg, 1.16 mmol, 58%).

Appearance: white foam; **R_f**: 0.2 (EtOAc); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.70 (ddd, *J* = 0.9, 2.4, 8.7 Hz, 1 H), 7.62 (d, *J* = 8.2 Hz, 1 H), 7.56–7.46 (m, 3 H), 7.36 (dd, *J* = 1.0, 8.5 Hz, 1 H), 7.21–7.07 (m, 4 H), 6.98–6.91 (m, 2 H), 1.95–1.83 (m, 1 H), 1.81 – 1.47 (m, 3 H), 1.30 (dd, *J* = 6.9, 14.5 Hz, 3 H), 1.30–1.17 (m, 1 H), 1.01–0.88 (m, 1 H), 0.74 (dd, *J* = 7.3, 15.8 Hz, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 145.5, 138.7 (d, *J* = 4.0 Hz), 134.63, 134.60, 134.01 (d, *J* = 9.9 Hz), 132.6, 130.6, 129.8, 129.2 (d, *J* = 3.7 Hz), 128.80, 128.7 (d, *J* = 11.4 Hz), 128.2, 127.9, 127.5, 127.2, 126.9, 126.40, 126.3 (d, *J* = 12.1 Hz), 120.4, 120.1, 117.2, 39.7 (d, *J* = 66.8 Hz), 35.5 (d, *J* = 67.9 Hz), 33.4 (d, *J* = 9.5 Hz), 32.8 (d, *J* = 8.1 Hz), 14.3, 12.8 (d, *J* = 2.6 Hz) ppm; **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ -75.5 ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ 56.9 ppm; **IR** (ATR): ν_{max} = 3059, 2961, 2932, 2872, 1624, 1586, 1560, 1509, 1454, 1416, 1247, 1211, 1180, 1138, 747, 686 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{27}H_{24}F_3O_4PS + H]^+$: 533.1158, found: 533.1156; **$[\alpha]_D^{20}$**: 43.2 (c = 1.0, $CHCl_3$).

(2*S*,5*S*)-1-((*R*)-2'-Hydroxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide:



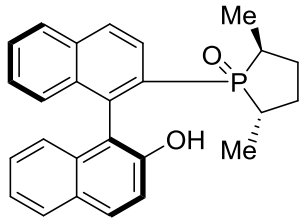
S3

To a solution of triflate **S1** (1.49 g, 2.80 mmol, 1.0 eq.) in a mixture of dioxane:MeOH (2:1, 30 mL) was added 4 M aqueous solution of NaOH (7.7 ml, 30.8 mmol, 11 eq.) at 23 °C. The resulting mixture was kept stirring overnight at this temperature. Then, the mixture was acidified (pH = 1) by the addition of concentrated HCl (aqueous) and product was extracted with EtOAc (50 mL). The organic fraction was dried over $MgSO_4$ and concentrated under reduced pressure to yield (2*S*,5*S*)-1-((*R*)-2'-hydroxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-

oxide (**S3**) (1.12 g, 2.80 mmol, 100%) which was used in the next step without further purification.

Appearance: pale brown foam; **^{1}H NMR** (400 MHz, CD_3CN): δ 8.28–8.20 (m, 1 H), 8.10 (d, *J* = 8.2 Hz, 1 H), 8.0 (d, *J* = 9.0 Hz, 1 H), 7.95–7.89 (m, 1 H), 7.77 (dd, *J* = 8.7, 11.1 Hz, 1 H), 7.72–7.67 (m, 1 H), 7.44–7.38 (m, 1 H), 7.38–7.28 (m, 1 H + 1 H), 7.26–7.15 (m, 2 H), 6.83–6.78 (m, 1 H), 2.13–1.99 (m, 1 H), 1.91–1.70 (m, 3 H), 0.99 (dd, *J* = 7.2, 18.4 Hz, 3 H), 0.98–0.85 (m, 1 H), 0.87 (dd, *J* = 6.7, 16.3 Hz, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, CD_3CN): δ 153.5, 143.0 (d, *J* = 7.7 Hz), 136.6 (d, *J* = 2.6 Hz), 135.5, 134.2 (d, *J* = 2.6 Hz), 131.7, 130.5, 129.8 (d, *J* = 12.5 Hz), 129.4, 129.3, 129.2, 128.9, 128.0, 127.8 (d, *J* = 12.5 Hz), 127.6, 125.3, 124.6, 118.8, 117.1 (d, *J* = 4.0 Hz), 37.8 (d, *J* = 62.0 Hz), 34.2 (d, *J* = 63.8 Hz), 32.5 (d, *J* = 10.3 Hz), 31.9 (d, *J* = 8.8 Hz), 14.6, 12.2 (d, *J* = 4.0 Hz) ppm; **^{31}P{^{1}H} NMR** (162 MHz, CD_3CN): δ 87.2 ppm; **HRMS** (Multimode): calculated for $[C_{26}H_{25}O_2P + H]^+$: 401.1665, found: 401.1663.

(2*S*,5*S*)-1-((*S*)-2'-Hydroxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide:

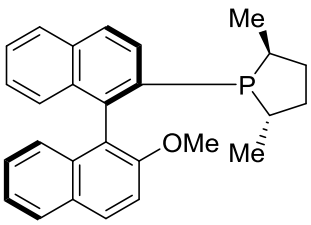


S4

To a solution of triflate **S2** (586 mg, 1.10 mmol, 1.0 eq.) in a mixture of dioxane:MeOH (2:1, 10 mL) was added 4 M aqueous solution of NaOH (3.0 mL, 12.1 mmol, 11 eq.) at 23 °C. The resulting mixture was kept stirring overnight at this temperature. Then, the mixture was acidified (pH = 1) by the addition of concentrated HCl (aqueous) and product was extracted with EtOAc (20 mL). The organic fraction was dried over $MgSO_4$ and concentrated under reduced pressure to yield crude (2*S*,5*S*)-1-((*S*)-2'-hydroxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (**S4**) (381 mg, 0.953 mmol, 87%) which was used in the next step without further purification.

Appearance: Pale brown foam; **^{1}H NMR** (400 MHz, CD_3CN): δ 8.33 – 8.29 (m, 1 H), 8.19–7.88 (m, 9 H), 7.74 – 7.69 (m, 1 H), 7.50 – 7.16 (m, 5 H), 6.89–6.77 (m, 1H), 2.65 – 2.50 (m, 1 H), 2.32–2.11 (m, 1 H), 2.01–1.81 (m, 1 H), 1.52–1.17 (m, 1 H), 1.05 (dd, *J* = 7.3, 19.3 Hz, 3 H), 0.39 (ddd, J = 1.8, 6.8 17.1 Hz, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, CD_3CN): δ 155.6, 140.5, 135.6, 134.0, 132.6, 131.5, 131.4, 131.2, 131.0, 130.4, 129.7, 129.62, 129.14, 129.05, 128.9, 128.4, 128.3, 127.9, 127.6, 127.3, 125.7, 124.5, 121.5, 114.0, 56.5, 55.3, 40.8, 40.1, 34.7, 34.0, 33.2, 33.1, 30.3, 14.6, 12.5, 12.44 ppm; **^{31}P{^{1}H} NMR** (162 MHz, CD_3CN): δ 87.2 ppm; **HRMS** (Multimode): calculated for $[C_{26}H_{25}O_2P + H]^+$: 401.1665, found: 401.1661.

(2*S*,5*S*)-1-((*R*)-2'-methoxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane:



L1

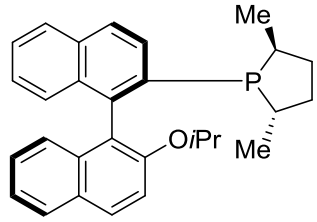
A mixture of (2*S*,5*S*)-1-((*R*)-2'-hydroxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (**S3**) (75.0 mg, 0.187 mmol, 1.0 eq), K_2CO_3 (104 mg, 0.749 mmol, 4.0 eq) and MeI (47 μL, 0.749 mmol, 4.0 eq) in acetone (0.94 mL, 0.2 M) was stirred for 10 h at 50 °C. The reaction mixture was cooled down, filtered through celite (eluting with Et_2O) and concentrated under reduced pressure to give (2*S*,5*S*)-1-((*R*)-2'-methoxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (66.0 mg, 0.159 mmol, 85%), which was used in the next step without further purification.

A 10–20 mL microwave vial was transferred to a glovebox and charged with a solution of (2*S*,5*S*)-1-((*R*)-2'-methoxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (66.0 mg, 0.159 mmol, 1.0 eq) in toluene (3.2 mL, 0.05 M). The tube was sealed and taken out of the glovebox. To this solution was added Et_3N (0.71 mL, 5.10 mmol, 32 eq), and the resulting

mixture was cooled down to 0 °C. Trichlorosilane (Cl_3SiH) (0.13 mL, 1.27 mmol, 8.0 eq) was added at this temperature, the tube was sealed, heated to 100 °C and the reaction was stirred for 10 h at this temperature. After this time the mixture was cooled down, diluted with Et_2O (5.0 mL), quenched with saturated $NaHCO_3$ (2.0 mL) and filtered through celite (eluting with Et_2O). The resulting filtrate was concentrated under reduced pressure and subjected to silica gel chromatography (pentane/EtOAc, 10:1) to afford (2*S*,5*S*)-1-((*R*)-2'-methoxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane (**L1**) (40.0 mg, 0.100 mmol, 63%).

Appearance: white foam; $\mathbf{R_f}$: 0.6 (pentane:EtOAc, 10:1); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.84–7.68 (m, 5 H), 7.46 (d, *J* = 8.5 Hz, 1 H) 7.26–7.17 (m, 3 H), 7.08–6.94 (m, 3 H), 3.21 (s, 3 H), 2.63–2.50 (m, 1 H), 2.24–2.08 (m, 1 H), 2.07–1.84 (m, 2 H), 1.79–1.61 (m, 1 H), 1.15 (dd, *J* = 7.1, 9.1 Hz, 3 H), 1.12–1.06 (m, 1 H), 1.00 (dd, *J* = 7.1, 18.1 Hz, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$,): δ 155.2 (d, *J* = 2.2 Hz), 144.4, 144.1, 137.1, 138.8, 135.3, 134.4, 133.9 (d, *J* = 7.3 Hz), 131.1 (d, *J* = 3.7 Hz), 129.6, 129.4, 128.7, 127.4 (d, *J* = 2.6 Hz), 127.2, 126.7 (d, *J* = 2.2 Hz), 126.5, 126.1, 123.8 (d, *J* = 9.5 Hz), 123.7, 113.0, 55.4, 39.0 (d, *J* = 11.7 Hz), 38.3 (d, *J* = 2.2 Hz), 37.5 (d, *J* = 2.9 Hz), 35.4 (d, *J* = 14.3 Hz), 20.4 (d, *J* = 36.7 Hz), 16.0 (d, *J* = 2.2 Hz) ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -2.9 ppm; **IR** (ATR): ν_{max} = 3054, 2922, 2858, 1736, 1593, 1509, 1456, 1345, 1268, 1249, 1147, 1080, 1020, 908, 809, 746 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{27}H_{27}OP + H]^+$: 399.1872, found: 399.1876; **$[\alpha]_D^{20}$**: 55.3 (c = 0.6, $CHCl_3$).

(2*S*,5*S*)-1-((*R*)-2'-isopropoxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane:



L2

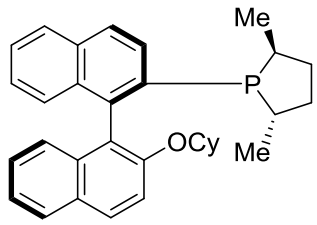
A mixture of (2*S*,5*S*)-1-((*R*)-2'-hydroxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (**S3**) (120 mg, 0.300 mmol, 1.0 eq), K_2CO_3 (166 mg, 1.20 mmol, 4.0 eq) and *i*PrI (204 mg, 1.20 mmol, 4.0 eq) in acetone (1.5 mL, 0.2 M) was stirred for 10 h at 50 °C. The reaction mixture was cooled down, filtered through celite (eluting with Et_2O) and concentrated under reduced pressure to give (2*S*,5*S*)-1-((*R*)-2'-isopropoxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (128 mg, 0.289 mmol, 96%), which was used in the next step without further purification.

A 10-20 mL microwave vial was transferred to a glovebox and charged with a solution of (2*S*,5*S*)-1-((*R*)-2'-isopropoxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (125 mg, 0.281 mmol, 1.0 eq) in toluene (5.6 mL, 0.05 M). The tube was sealed and taken out of the glovebox. To this solution was added Et_3N (1.3 mL, 9.02 mmol, 32 eq), and the resulting mixture was cooled down to 0 °C. Trichlorosilane (Cl_3SiH) (0.23 mL, 2.26 mmol, 8.0 eq) was added at this temperature, the tube was sealed, heated to 100 °C and the reaction was stirred for 10 h at this temperature. After this time the mixture was cooled down, diluted with Et_2O (8.0 mL), quenched with saturated $NaHCO_3$ (4.0 mL) and filtered through celite (eluting with Et_2O). The resulting filtrate was concentrated under reduced pressure and subjected to silica gel chromatography (pentane: CH_2Cl_2, 2:1) to afford (2*S*,5*S*)-1-((*R*)-2'-isopropoxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane (**L2**) (92.0 mg, 0.216 mmol, 76%).

Appearance: yellow oil; $\mathbf{R_f}$: 0.5 (pentane:EtOAc, 20:1); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.84–7.70 (m, 5 H), 7.43–7.38 (m, 1 H), 7.26–7.21 (m, 1 H), 7.19–7.12 (m, 3 H), 7.06–6.97 (m, 2 H), 4.32–4.21 (m, 1 H), 2.60–2.48 (m, 1 H), 2.32–2.15 (m, 1 H), 2.09–1.86 (m, 2 H), 1.78–1.60 (m, 1 H), 1.22 (dd, *J* = 7.3, 9.4 Hz, 3 H), 1.16–1.03 (m, 1 H), 1.03–0.90 (m, 3 H + 3 H), 0.73 (d, *J* = 6.0 Hz, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 153.6 (d, *J* = 2.2 Hz), 144.6 (d, *J* = 34.8 Hz), 137.3 (d, *J* = 28.6 Hz), 135.8, 135.7, 134.2, 133.7 (d, *J* = 7.3 Hz), 131.2 (d, *J* = 3.7 Hz), 129.43, 129.37, 128.20, 128.16, 127.9, 127.6 (d, *J* = 2.6 Hz), 127.1, 126.5 (d, *J* = 2.9 Hz), 126.2, 125.2

(d, *J* = 9.2 Hz), 123.7, 115.7, 70.3, 39.4 (d, *J* = 11.7 Hz), 38.5 (d, *J* = 2.2 Hz), 37.5 (d, *J* = 3.3 Hz), 35.2 (d, *J* = 14.3 Hz), 22.5, 22.1, 20.3 (d, *J* = 36.7 Hz), 16.3 (d, *J* = 2.2 Hz) ppm; **$^{31}P\{^{1}H\}$ NMR** (162 MHz, C_6D_6): δ -3.1 ppm; **IR** (ATR): ν_{max} = 3054, 2973, 2920, 2279, 1621, 1591, 1507, 1452, 1326, 1241, 1112, 1001, 809, 745, 499 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{29}H_{31}OP + H]^+$: 427.2185, found: 427.2188; **$[\alpha]_D^{20}$**: 249.9 (c = 1.0, $CHCl_3$).

(2*S*,5*S*)-1-((*R*)-2'-cyclohexyloxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane:



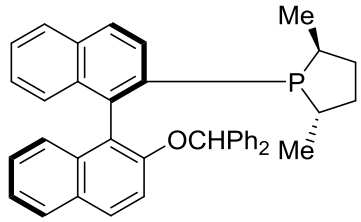
L3

A solution of diisopropyl azodicarboxylate (DIAD) (152 mg, 0.750 mmol, 1.5 eq) in THF (4 ml, 0.19 M) was added dropwise via a syringe to a stirring solution of cyclohexanol (460 mg, 2.50 mmol, 5 eq), (2*S*,5*S*)-1-((*R*)-2'-hydroxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (**S3**) (200 mg, 0.500 mmol) and PPh_3 (196 mg, 0.750 mmol) in THF (2 mL, 0.25 M) at 0 °C. After stirring for 45 h at 23 °C, the reaction mixture was diluted with EtOAc (50 mL), washed with water (2*25 mL), brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification *via* flash chromatography (SiO_2, pure EtOAc → EtOAc:MeOH, 100:1) yielded (2*S*,5*S*)-1-((*R*)-2'-cyclohexyloxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (101 mg, 0.209 mmol, 42%).

A 2-5 mL microwave vial was transferred to a glovebox and charged with a solution of (2*S*,5*S*)-1-((*R*)-2'-cyclohexyloxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (50 mg, 0.110 mmol, 1.0 eq) in toluene (2.20 mL, 0.05 M). The tube was sealed and taken out of the glovebox. To this solution was added Et_3N (491 μL, 3.52 mmol, 32 eq), and the resulting mixture was cooled down to 0 °C. Trichlorosilane (Cl_3SiH) (89.0 μL, 0.880 mmol, 8.0 eq) was added at this temperature, the tube was sealed, heated to 100 °C and the reaction was stirred for 10 h at this temperature. After this time the mixture was cooled down, diluted with Et_2O (2.0 mL), quenched with saturated $NaHCO_3$ (1.0 mL) and filtered through celite (eluting with Et_2O). The resulting filtrate was concentrated under reduced pressure and subjected to silica gel chromatography (pentane: CH_2Cl_2, 2:1) to afford (2*S*,5*S*)-1-((*R*)-2'-cyclohexyloxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane (**L3**) (36.0 mg, 0.080 mmol, 73%).

Appearance: white foam; **R_f**: 0.25 (pentane: CH_2Cl_2, 3:1); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.83–7.70 (m, 5 H), 7.44 – 7.39 (m, 1 H), 7.27–7.17 (m, 4 H), 7.08–6.97 (m, 2 H), 4.11 – 4.02 (m, 1 H), 2.59 – 2.47 (m, 1 H), 2.36 – 2.18 (m, 1 H), 2.09–1.87 (m, 2 H), 1.84–1.63 (m, 2 H), 1.56–1.44 (m, 1 H), 1.41–1.06 (m, 8 H), 1.04–0.64 (m, 7 H) ppm; **$^{13}C\{^{1}H\}$ NMR** (101 MHz, C_6D_6): δ 153.6 (d, *J* = 2.2 Hz), 144.6 (d, *J* = 34.5 Hz), 137.4 (d, *J* = 28.6 Hz), 135.8 (d, *J* = 2.6 Hz), 134.2, 133.7 (d, *J* = 7.3 Hz), 131.3 (d, *J* = 3.7 Hz), 129.4, 129.3, 128.20, 128.18, 127.9, 127.1, 126.6, 126.5, 126.2, 126.1, 125.2 (d, *J* = 9.2 Hz), 123.7, 116.0, 75.9, 39.5 (d, *J* = 11.4 Hz), 38.5 (d, *J* = 2.2 Hz), 37.5 (d, *J* = 3.3 Hz), 35.3 (d, *J* = 14.3 Hz), 32.8, 31.9, 25.6, 23.9, 23.7, 20.4 (d, *J* = 36.7 Hz), 16.3 (d, *J* = 2.2 Hz) ppm; **$^{31}P\{^{1}H\}$ NMR** (162 MHz, C_6D_6): δ -3.1 ppm; **IR** (ATR): ν_{max} = 3054, 2930, 2857, 1452, 1330, 1236, 1071, 1048, 1021, 812, 745, 684 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{32}H_{35}OP + H]^+$: 467.2498, found: 467.2497; **$[\alpha]_D^{20}$**: 167.0 (c = 1.0, $CHCl_3$).

(2*S*,5*S*)-1-((*R*)-2'-benzhydryloxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane:



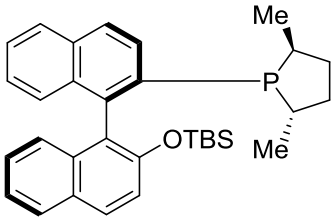
L4

A solution of diisopropyl azodicarboxylate (DIAD) (152 mg, 0.750 mmol, 1.5 eq) in THF (4.0 ml, 0.19 M) was added dropwise via a syringe to a stirring solution of diphenylmethanol (460 mg, 2.50 mmol, 5 eq), (2*S*,5*S*)-1-((*R*)-2'-hydroxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (**S3**) (200 mg, 0.500 mmol) and PPh_3 (196 mg, 0.750 mmol) in THF (5.0 mL, 0.1 M) at 0 °C. After stirring for 45 h at 23 °C, the reaction mixture was diluted with EtOAc (50 mL), washed with water (2*25 mL), brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification *via* flash chromatography (SiO_2, pure EtOAc → EtOAc:MeOH, 100:1) yielded (2*S*,5*S*)-1-((*R*)-2'-benzhydryloxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (107 mg, 0.189 mmol, 38%).

A 2-5 mL microwave vial was transferred to a glovebox and charged with a solution of (2*S*,5*S*)-1-((*R*)-2'-benzhydryloxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (50 mg, 0.090 mmol, 1.0 eq) in toluene (1.8 mL, 0.05 M). The tube was sealed and taken out of the glovebox. To this solution was added Et_3N (0.40 mL, 2.88 mmol, 32 eq), and the resulting mixture was cooled down to 0 °C. Trichlorosilane (Cl_3SiH) (73 µL, 0.720 mmol, 8.0 eq) was added at this temperature, the tube was sealed, heated to 100 °C and the reaction was stirred for 10 h at this temperature. After this time the mixture was cooled down, diluted with Et_2O (2.0 mL), quenched with saturated $NaHCO_3$ (1.0 mL) and filtered through celite (eluting with Et_2O). The resulting filtrate was concentrated under reduced pressure and subjected to silica gel chromatography (pentane: CH_2Cl_2, 2:1) to afford 2(2*S*,5*S*)-1-((*R*)-2'-benzhydryloxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane (**L4**) (37.0 mg, 0.067 mmol, 75%).

Appearance: colorless oil; $\mathbf{R_f}$: 0.15 (pentane: CH_2Cl_2, 3:1); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.85–7.74 (m, 3 H), 7.66–7.56 (m, 2 H), 7.44–7.40 (m, 1 H), 7.31–7.19 (m, 3 H), 7.15–7.10 (m, 3 H), 7.07–6.94 (m, 6 H), 6.94–6.82 (m, 4 H), 6.13 (s, 1 H), 2.56–2.44 (m, 1 H), 2.26–2.10 (m, 1 H), 2.05–1.80 (m, 2 H), 1.75–1.60 (m, 1 H), 1.14–1.01 (m, 1 H), 1.01–0.91 (m, 6 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 153.6 (d, *J* = 2.2 Hz), 144.2 (d, *J* = 34.8 Hz), 142.4, 142.2, 137.7 (d, *J* = 29.0 Hz), 135.6 (d, *J* = 2.9 Hz), 134.2, 133.7 (d, *J* = 7.3 Hz), 131.53, 131.49, 129.6, 129.3, 128.51 (2 C), 128.45 (2 C), 128.2, 127.9, 127.6, 127.5, 127.2, 126.93 (2 C), 126.86 (2 C), 126.7, 126.6, 126.3, 126.2, 125.1 (d, *J* = 9.2 Hz), 123.9, 116.1, 82.5, 40.2 (d, *J* = 11.7 Hz), 38.6 (d, *J* = 2.6 Hz), 37.7 (d, *J* = 2.6 Hz), 35.7 (d, *J* = 13.6 Hz), 20.4 (d, *J* = 36.3 Hz), 15.9 (d, *J* = 2.2 Hz) ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -2.2 ppm; **IR** (ATR): ν_{max} = 3057, 3031, 2921, 2860, 2278, 1621, 1591, 1494, 1467, 1453, 1329, 1265, 1194, 1147, 1084, 1044, 1017, 811, 744, 701, 499 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{39}H_{35}OP + H]^+$: 551.2498, found: 551.2496; **$[\alpha]_D^{20}$**: 86.4 (c = 1.0, $CHCl_3$).

(2*S*,5*S*)-1-((*R*)-2'-(*tert*-butyldimethylsilyl)oxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane:



L5

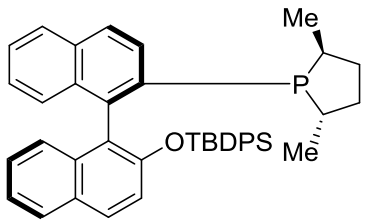
To a solution of (2*S*,5*S*)-1-((*R*)-2'-hydroxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (**S3**) (100 mg, 0.250 mmol, 1.0 eq) and imidazole (34.0 mg, 0.500 mmol, 2.0 eq) in DMF (1.0 mL, 0.25 M) was added *tert*-butyldimethylsilyl chloride (57 µL, 0.375 mmol, 1.5 eq). The reaction was stirred for 10 h at 50 °C. The resulting

mixture was cooled down, diluted with EtOAc (10 mL) and washed with water (5*8 mL). The combined organic fractions were dried over $MgSO_4$ and concentrated under reduced pressure to yield crude (2*S*,5*S*)-1-((*R*)-2'-(*tert*-butyldimethylsilyl)oxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (127 mg, 0.249 μmol, 99%) which was used in the next step without further purification.

A 10–20 mL microwave vial was transferred to a glovebox and charged with a solution of (2*S*,5*S*)-1-((*R*)-2'-(*tert*-butyldimethylsilyl)oxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (145 mg, 0.282 mmol, 1.0 eq) in toluene (5.6 mL, 0.05 M). The tube was sealed and taken out of the glovebox. To this solution was added Et_3N (1.3 mL, 9.01 mmol, 32 eq), and the resulting mixture was cooled down to 0 °C. Trichlorosilane (Cl_3SiH) (0.23 μL, 2.25 mmol, 8.0 eq) was added at this temperature, the tube was sealed, heated to 100 °C and the reaction was stirred for 10 h at this temperature. After this time the mixture was cooled down, diluted with Et_2O (10 mL), quenched with saturated $NaHCO_3$ (2 mL) and filtered through celite (eluting with Et_2O). The resulting filtrate was concentrated under reduced pressure and subjected to silica gel chromatography (pentane:EtOAc, 10:1) to afford (2*S*,5*S*)-1-((*R*)-2'-(*tert*-butyldimethylsilyl)oxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane (**L5**) (91.0 mg, 0.182 mmol, 65%).

Appearance: colorless oil; $\mathbf{R_f}$: 0.6 (pentane:EtOAc, 20:1); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.78–7.68 (m, 5 H), 7.37–7.32 (m, 1 H), 7.27–7.17 (m, 4 H), 7.10–7.04 (m, 1 H), 7.00–6.94 (m, 1 H), 2.54–2.42 (m, 1 H), 2.22–2.08 (m, 1 H), 2.05–1.94 (m, 1 H), 1.92–1.82 (m, 1 H), 1.76–1.64 (m, 1 H), 1.24 (dd, *J* = 7.3, 9.4 Hz, 3 H), 1.08–1.00 (m, 1 H), 0.99–0.92 (m, 3 H), 0.58 (s, 9 H), 0.12 (s, 3 H), -0.34 (s, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 151.6 (d, *J* = 2.2 Hz), 144.6, 144.2, 137.7, 137.4, 136.0 (d, *J* = 2.9 Hz), 134.2, 133.8 (d, *J* = 7.0 Hz), 131.5 (d, *J* = 3.3 Hz), 129.7, 129.3, 128.2, 127.9, 127.1, 126.6, 126.52, 126.48, 126.3, 123.9, 120.9, 39.9 (d, *J* = 12.1 Hz), 38.4 (d, *J* = 2.6 Hz), 37.7 (d, *J* = 2.6 Hz), 35.6 (d, *J* = 13.9 Hz), 25.6 (3 C), 20.5 (d, *J* = 36.7 Hz), 18.1, 16.4 (d, *J* = 1.8 Hz), -3.5, -4.6 ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -1.8 ppm; **IR** (ATR): ν_{max} = 3056, 2951, 2927, 2857, 1592, 1468, 1346, 1245, 996, 837, 812, 779, 745, 683 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{32}H_{39}OPSi + H]^+$: 499.2581, found: 499.2588; **$[\alpha]_D^{20}$**: 106.2 (c = 1.0, $CHCl_3$).

(2*S*,5*S*)-1-((*R*)-2'-(*tert*-butyldiphenylsilyl)oxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane:



L6

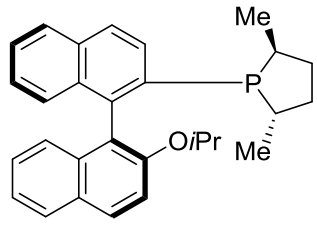
To a solution of (2*S*,5*S*)-1-((*R*)-2'-hydroxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (**S3**) (190 mg, 0.474 mmol, 1.0 eq) and imidazole (129 mg, 1.50 mmol, 4 eq) in DMF (1.9 mL, 0.25 M) was added *tert*-butyldiphenylchlorosilane (0.27 mL, 1.04 mmol, 2.2 eq). The reaction was stirred for 10 h at 80 °C. The resulting mixture was cooled down, diluted with EtOAc (30 mL) and washed with water (5*20 mL), dried over $MgSO_4$ and concentrated under reduced pressure to yield crude (2*S*,5*S*)-1-((*R*)-2'-(*tert*-butyldiphenylsilyl)oxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (286 mg, 0.459 μmol, 97%) which was used in the next step without further purification.

A 10–20 mL microwave vial was transferred to a glovebox and charged with a solution of (2*S*,5*S*)-1-((*R*)-2'-(*tert*-butyldiphenylsilyl)oxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (400 mg, 0.626 mmol, 1.0 eq) in toluene (7.8 mL, 0.08 M). The tube was sealed and taken out of the glovebox. To this solution was added Et_3N (2.8 mL, 20.0 mmol, 32 eq), and the resulting mixture was cooled down to 0 °C. Trichlorosilane (Cl_3SiH) (0.51 mL, 5.01 mmol, 8.0 eq) was added at this temperature, the tube was sealed, heated to 100 °C and the reaction was

stirred for 10 h at this temperature. After this time the mixture was cooled down, diluted with Et_2O (10 mL), quenched with saturated $NaHCO_3$ (5.0 mL) and filtered through celite (eluting with Et_2O). The resulting filtrate was concentrated under reduced pressure and subjected to silica gel chromatography (pentane:EtOAc, 10:1) to afford (2*S*,5*S*)-1-((*R*)-2'-(*tert*-butyldiphenylsilyl)oxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane (**L6**) (376 mg, 0.604 mmol, 96%).

Appearance: white solid; $\mathbf{R_f}$: 0.55 (pentane:EtOAc, 20:1); **m.p.**: 139.7–140.8; **^{1}H NMR** (400 MHz, C_6D_6): δ 7.88–7.75 (m, 7 H), 7.62 (d, *J* = 8.2 Hz, 1 H), 7.51–7.47 (m, 1 H), 7.33–7.17 (m, 9 H), 7.13–7.01 (m, 4 H), 2.51–2.41 (m, 1 H), 2.32–2.14 (m, 1 H), 2.09–1.97 (m, 1 H), 1.94–1.85 (m, 1 H), 1.82–1.70 (m, 1 H), 1.13 (dd, *J* = 7.2, 9.5 Hz, 3 H), 1.10–1.02 (m, 1 H), 0.93 (dd, *J* = 7.2, 17.9 Hz, 3 H), 0.61 (s, 9 H) ppm; **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6): δ 150.9 (d, *J* = 2.2 Hz), 144.6 (d, *J* = 34.1 Hz), 137.8 (d, J = 30.4 Hz), 136.1 (d, *J* = 3.3 Hz), 135.93 (2 C), 135.91 (2 C), 135.85 (4 C), 134.2, 133.9 (d, *J* = 7.3 Hz), 133.6, 133.4, 131.63, 131.59, 130.3, 130.1, 129.5, 129.0, 128.2, 127.9, 127.1, 126.8, 126.49, 126.46, 126.4, 125.7 (d, *J* = 9.2 Hz), 123.8, 120.8, 41.0 (d, *J* = 12.5 Hz), 38.7 (d, *J* = 2.9 Hz), 38.0, 36.0 (d, *J* = 13.9 Hz), 26.4 (3 C), 20.6 (d, *J* = 35.6 Hz), 19.3, 16.2 (d, *J* = 1.8 Hz) ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -3.4 ppm; **IR** (ATR): ν_{max} = 3053, 2927, 2858, 1592, 1469, 1428, 1346, 1273, 1247, 1113, 998, 812, 701, 500 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{42}H_{43}OPSi + H]^+$: 623.2894, found: 623.2895; **$[\alpha]_D^{20}$**: 28.1 (c = 1.0, $CHCl_3$).

(2*S*,5*S*)-1-((*S*)-2'-isopropoxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane:



L7

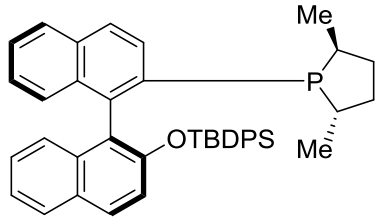
A mixture of (2*S*,5*S*)-1-((*S*)-2'-hydroxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (**S4**) (120 mg, 0.300 mmol, 1.0 eq), K_2CO_3 (166 mg, 1.20 mmol, 4.0 eq) and *i*PrI (204 mg, 1.20 mmol, 4.0 eq) in acetone (1.5 mL, 0.2 M) was stirred for 10 h at 50 °C. The reaction mixture was cooled down, filtered through celite (eluting with Et_2O) and concentrated under reduced pressure to give (2*S*,5*S*)-1-((*S*)-2'-isopropoxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane (119 mg, 0.279 mmol, 93%), which was used in the next step without further purification.

A 10-20 mL microwave vial was transferred to a glovebox and charged with a solution of (2*S*,5*S*)-1-((*S*)-2'-isopropoxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane (115 mg, 0.270 mmol, 1.0 eq) in toluene (5.4 mL, 0.05 M). The tube was sealed and taken out of the glovebox. To this solution was added Et_3N (1.2 mL, 8.64 mmol, 32 eq), and the resulting mixture was cooled down to 0 °C. Trichlorosilane (Cl_3SiH) (0.22 mL, 2.16 mmol, 8.0 eq) was added at this temperature, the tube was sealed, heated to 100 °C and the reaction was stirred for 10 h at this temperature. After this time the mixture was cooled down, diluted with Et_2O (6.0 mL), quenched with saturated $NaHCO_3$ (3.0 mL) and filtered through celite (eluting with Et_2O). The resulting filtrate was concentrated under reduced pressure and subjected to silica gel chromatography (pentane:EtOAc, 20:1) to afford (2*S*,5*S*)-1-((*S*)-2'-isopropoxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane (**L7**) (65.0 mg, 0.158 mmol, 59%).

Appearance: colorless oil; $\mathbf{R_f}$: 0.6 (pentane:EtOAc, 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00–7.76 (m, 5 H), 7.49–7.35 (m, 2 H), 7.31–7.24 (m, 1 H), 7.23–7.09 (m, 3 H), 6.98–6.92 (m, 1 H), 4.43 (dt, *J* = 6.0, 12.0 Hz, 1 H), 2.80–2.55 (m, 1 H), 2.32–2.11 (m, 1 H), 2.10–1.89 (m, 2 H), 1.89–1.68 (m, 1 H), 1.35–1.24 (m, 1 H), 1.24 (dd, *J* = 7.0, 18.2 Hz, 3 H), 1.11 (d, *J* = 6.1 Hz, 3 H), 0.93–0.72 (m, 6H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 153.5 (d, *J* = 2.2 Hz), 144.3 (d, *J* = 34.8 Hz), 137.4 (d, *J* = 29.3 Hz), 135.5 (d, *J* = 2.2 Hz), 134.2, 133.8 (d, *J* = 7.3 Hz), 131.21,

131.17, 129.6, 129.4, 127.1, 126.6, 126.5, 126.3, 128.2, 127.9, 126.2, 125.7 (d, *J* = 9.2 Hz), 123.8, 117.1, 71.0, 39.3 (d, *J* = 12.1 Hz), 38.2 (d, *J* = 2.2 Hz), 37.6 (d, *J* = 2.6 Hz), 35.4 (d, *J* = 14.3 Hz), 22.7, 22.3, 21.0 (d, *J* = 37.0 Hz), 16.2 (d, *J* = 1.8 Hz) ppm; **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ -2.2 ppm; **IR** (ATR): ν_{max} = 2920, 2861, 2279, 1619, 1591, 1506, 1452, 1329, 1257, 1241, 1113, 1001, 811, 747, 491 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{29}H_{31}OP + H]^+$: 427.2185, found: 427.2184; **$[\alpha]_D^{20}$**: 61.8 (c = 1.0, $CHCl_3$).

(2*S*,5*S*)-1-((*S*)-2'-(*tert*-butyldiphenylsilyl)oxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane:



L8

To a solution of (2*S*,5*S*)-1-((*S*)-2'-hydroxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (**S4**) (120 mg, 0.300 mmol, 1.0 eq) and imidazole (82.0 mg, 1.20 mmol, 4 eq) in DMF (1.2 mL, 0.25 M) was added *tert*-butyldiphenylchlorosilane (0.17 mL, 0.660 mmol, 2.2 eq). The reaction was stirred for 10 h at 80 °C. The resulting mixture was cooled down, diluted with EtOAc (15 mL) and washed with water (5*10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to yield crude (2*S*,5*S*)-1-((*S*)-2'-(*tert*-butyldiphenylsilyl)oxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (236 mg, 0.369 μmol, 74%).

A 2–5 mL microwave vial was transferred to a glovebox and charged with a solution of (2*S*,5*S*)-1-((*S*)-2'-(*tert*-butyldiphenylsilyl)oxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane 1-oxide (66.0 mg, 0.100 mmol, 1.0 eq) in toluene (0.74 mL, 0.14 M). The tube was sealed and taken out of the glovebox. To this solution was added Et_3N (0.46 mL, 3.20 mmol, 32 eq), and the resulting mixture was cooled to 0 °C. Trichlorosilane (Cl_3SiH) (83 μL, 0.800 mmol, 8.0 eq) was added at this temperature, the tube was sealed, heated to 100 °C and the reaction was stirred for 10 h at this temperature. After this time the mixture was cooled down, diluted with Et_2O (2.0 mL), quenched with saturated $NaHCO_3$ (1.0 mL) and filtered through celite (eluting with Et_2O). The resulting filtrate was concentrated under reduced pressure and subjected to silica gel chromatography (pentane:EtOAc, 50:1) to afford (2*S*,5*S*)-1-((*S*)-2'-(*tert*-butyldiphenylsilyl)oxy-[1,1'-binaphthalen]-2-yl)-2,5-dimethylphospholane (**L8**) (55.0 mg, 0.051 mmol, 85%).

Appearance: white foam; **R_f**: 0.55 (pentane:EtOAc, 20:1); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.96–7.90 (m, 2 H), 7.86–7.82 (m, 1 H), 7.80–7.73 (m, 4 H), 7.55–7.46 (m, 2 H), 7.32–7.22 (m, 6 H), 7.18–7.15 (m, 3 H) ,7.11–6.98 (m, 4 H), 2.75–2.60 (m, 1H), 2.16 – 2.04 (m, 1 H), 1.91–1.70 (m, 2 H), 1.70–1.55 (m, 1 H), 1.26 (dd, *J* = 7.2, 18.6 Hz, 3 H), 1.26–1.16 (m, 1 H), 0.89–0.82 (m, 3 H), 0.58 (s, 9 H); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 150.4 (d, *J* = 2.2 Hz), 144.3 (d, *J* = 33.7 Hz), 137.0 (d, *J* = 29.0 Hz), 136.17, 136.15, 135.9 (4 C), 135.5 (d, *J* = 2.6 Hz), 134.3, 133.9 (d, *J* = 7.0 Hz), 133.6, 133.1, 130.8 (d, *J* = 3.3 Hz), 130.2 (4 C), 129.5, 129.0, 128.2, 127.9, 127.6, 127.2, 126.7 (d, *J* = 4.0 Hz), 126.4, 126.1, 125.7, 125.6, 123.7, 121.0, 37.5, 37.1, 35.8 (d, *J* = 14.7 Hz), 30.5, 26.0 (3 C), 21.9 (d, *J* = 37.0 Hz), 19.3, 16.7 ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -0.3 ppm; **IR** (ATR): ν_{max} = 3051, 2925, 2857, 1621, 1504, 1469, 1346, 1275, 1248, 1113, 1002, 825, 811, 745, 701, 612, 502 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{42}H_{43}OPSi + H]^+$: 623.2894, found: 623.2902; **$[\alpha]_D^{20}$**: 72.3 (c = 0.9, $CHCl_3$).

Synthesis of Starting Materials

Typical Procedures for the Preparation of Substituted Benzhydryl Glutarimides S5a-S5r

Typical Procedure TP1

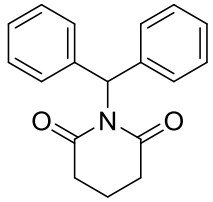
A mixture of glutarimide (1.0 eq.), TBAI (20 mol%), K_2CO_3 (2 eq.) and corresponding benzhydryl bromide (1.5 eq.) in dry acetone (0.5 M) was stirred at room temperature for 36 hours under inert atmosphere. The resulting mixture was concentrated under reduced pressure, suspended in water, extracted with EtOAc (*2), washed with water and brine. After drying over $MgSO_4$ the mixture was concentrated under reduced pressure. Desired product was purified by flash chromatography.

Typical Procedure TP2

To a mixture of corresponding diarylmethanol (1.0 eq), glutarimide (1.4 eq.), PPh_3 (1.33 eq) in dry THF (0.5 M) was added DIAD (1.3 eq) dropwise at 0 °C. The resulting mixture was stirred at room temperature for 12 hours under inert atmosphere. After that it was concentrated under reduced pressure, and the desired product was purified by flash chromatography.

Characterisation data for benzhydryl glutarimides S5a-S5r

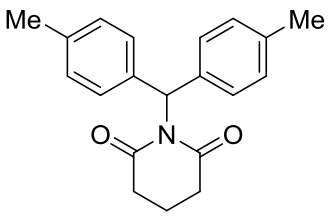
1-Benzhydrylpiperidine-2,6-dione:



S5a

Was obtained according to **TP1** from glutarimide (3.00 g, 26.5 mmol), TBAI (1.96 g, 5.30 mmol), K_2CO_3 (7.33 g, 53.0 mmol) and bromomethylenedibenzene (9.83 g, 39.8 mmol). **Yield**: 4.69 g, 63%; **appearance**: pale brown solid; $\mathbf{R_f}$: 0.2 (pentane:EtOAc, 4:1); **m.p.**: 124.3–124.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36–7.20 (m, 10 H), 7.18 (s, 1 H), 2.70 (t, *J* = 6.6 Hz, 4 H), 2.04–1.94 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 172.5 (2 C), 138.8 (2 C), 128.8 (4 C), 128.2 (4 C), 127.3 (2 C), 58.3, 33.8 (2 C), 17.2 ppm; **IR** (ATR): ν_{max} = 3060, 3028, 2942, 1727, 1677, 1345, 1240, 1169, 1135, 1000, 876, 813, 773, 700 cm^{-1}; **HRMS** (ESI): calculated for $[C_{18}H_{17}NO_2 + Na]^+$: 302.1151, found: 302.1157.

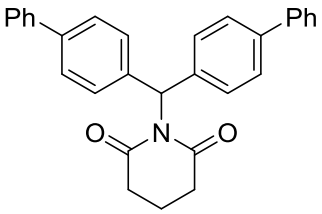
1-(Di-*p*-tolylmethyl)piperidine-2,6-dione:



S5b

Was obtained according to **TP1** from glutarimide (104 mg, 0.921 mmol), TBAI (68.0 mg, 0.184 mmol), K_2CO_3 (254 mg, 1.84 mmol) and 4,4'-(bromomethylene)bis(methylbenzene) (380 mg, 1.38 mmol). **Yield**: 64.0 mg, 23%; **appearance**: white solid; $\mathbf{R_f}$: 0.2 (pentane:EtOAc, 4:1); **m.p.**: 125.0–126.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.0 Hz, 4 H), 7.13–7.09 (m, 4 H + 1 H), 2.69 (t, *J* = 6.6 Hz, 4 H), 2.33 (s, 6 H), 2.01–1.93 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$,): δ 172.5 (2 C), 136.8 (2 C), 136.0 (2 C), 128.9 (4 C), 128.7 (4 C), 57.9, 33.9 (2 C), 21.2 (2 C), 17.2 ppm; **IR** (ATR): ν_{max} = 2943, 1674, 1513, 1342, 1317, 1239, 1167, 1134, 1000, 883, 761 cm^{-1}; **HRMS** (ESI): calculated for $[C_{20}H_{21}NO_2 + Na]^+$: 330.1465, found: 330.1470.

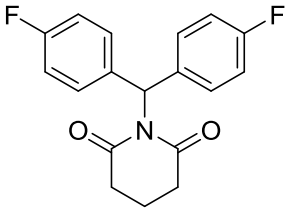
1-(Di([1,1'-biphenyl]-4-yl)methyl)piperidine-2,6-dione:



S5c

Was obtained according to **TP2** from di([1,1'-biphenyl]-4-yl)methanol (1.35 g, 4.00 mmol), glutarimide (633 mg, 5.60 mmol), PPh_3 (1.40 g, 5.32 mmol) and DIAD (1.05 mL, 5.20 mmol). **Yield**: 301 mg, 17%; **appearance**: white foam; $\mathbf{R_f}$: 0.1 (pentane:EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63–7.53 (m, 8 H), 7.47–7.38 (m, 8 H), 7.37–7.31 (m, 2 H), 7.27 (s, 1 H), 2.75 (t, *J* = 6.5 Hz, 4 H), 2.07–1.99 (m, 2 H) ppm; **^{13}C{^{1}H}** (101 MHz, $CDCl_3$,): δ 172.5 (2 C), 140.9 (2 C), 140.2 (2 C), 137.8 (2 C), 129.3 (4 C), 128.9 (4 C), 127.4 (2 C), 127.2 (4 C), 127.0 (4 C), 57.8, 33.9 (2 C), 17.3 ppm; **IR** (ATR): ν_{max} = 3028, 2963, 1673, 1519,1341, 1317, 1238, 1168, 1134, 1000, 766, 740, 698, 565 cm^{-1}; **HRMS** (ESI): calculated for $[C_{30}H_{25}NO_2 + Na]^+$: 454.1778, found: 454.1783.

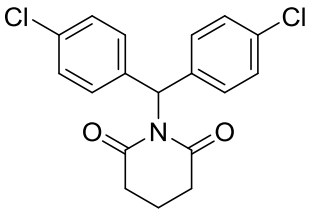
1-(Bis(4-fluorophenyl)methyl)piperidine-2,6-dione:



S5d

Was obtained according to **TP1** from glutarimide (146 mg, 1.30 mmol), TBAI (96.0 mg, 259 μmol), K_2CO_3 (358 mg, 2.59 mmol) and 4,4'-(bromomethylene)bis(fluorobenzene) (550 mg, 1.94 mmol). **Yield**: 198 mg, 49%; **appearance**: white solid; $\mathbf{R_f}$: 0.15 (pentane:EtOAc, 4:1); **m.p.**: 133.6–134.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31–7.20 (m, 4 H), 7.11 (s, 1 H), 7.05–6.94 (m, 4 H), 2.70 (t, *J* = 6.6 Hz, 4H), 2.03–1.95 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$,): δ 172.5 (2 C), 162.1 (d, *J* = 246.5 Hz, 2 C), 134.4 (d, *J* = 3.2 Hz, 2 C), 130.4 (d, *J* = 8.1 Hz, 4 C), 115.2 (d, *J* = 21.3 Hz, 4 C), 57.1, 33.8 (2 C), 17.1 ppm; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ -115.2 ppm; **IR** (ATR): ν_{max} = 2973, 2898, 1727, 1676, 1603, 1508, 1378, 1342, 1318, 1224, 1167, 1134, 1098, 1000 cm^{-1}; **HRMS** (APPI): calculated for $[C_{18}H_{15}F_2NO_2]^+$: 315.1065, found: 315.1057.

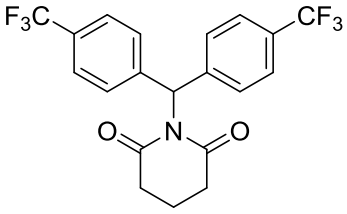
1-(Bis(4-chlorophenyl)methyl)piperidine-2,6-dione:



S5e

Was obtained according to **TP1** from glutarimide (597 mg, 5.27 mmol), TBAI (390 mg, 1.06 mmol), K_2CO_3 (1.46 g, 10.6 mmol) and 4,4'-(bromomethylene)bis(chlorobenzene) (2.50 g, 7.91 mmol). **Yield**: 1.45 g, 79%; **appearance**: colorless solid; $\mathbf{R_f}$: 0.2 (pentane:EtOAc, 4:1); **m.p.**: 130.7–131.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30–7.23 (m, 4 H), 7.22–7.16 (m, 4 H), 7.08 (s, 1 H), 2.69 (t, *J* = 6.6 Hz, 4 H), 2.04–1.91 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$,): δ 172.4 (2 C), 136.8 (2 C), 133.4 (2 C), 130.1 (4 C), 128.6 (4 C), 57.1, 33.7 (2 C), 17.1 ppm; **IR** (ATR): ν_{max} = 2967, 2884, 1728, 1679, 1491, 1376, 1342, 1318, 1238, 1168, 1168, 1134, 1091, 1001 cm^{-1}; **HRMS** (APPI): calculated for $[C_{18}H_{15}{}^{35}Cl_2NO_2]^+$: 347.0474, found: 347.0464.

1-(Bis(4-(trifluoromethyl)phenyl)methyl)piperidine-2,6-dione:

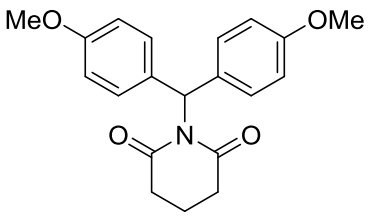


S5f

Was obtained according to **TP1** from glutarimide (528 mg, 4.67 mmol), TBAI (345 mg, 0.933 mmol), K_2CO_3 (1.29 g, 9.33 mmol) and 4,4'-(bromomethylene)bis((trifluoromethyl)benzene) (2.68 g, 7.00 mmol). **Yield**: 205 mg, 11%; **appearance**: yellow solid; $\mathbf{R_f}$: 0.3

(pentane:EtOAc, 4:1); **m.p.**: 134.3–136.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.4 Hz, 4 H), 7.42–7.34 (m, 4 H), 7.24 (s, 1 H), 2.74 (t, *J* = 6.5 Hz, 4 H), 2.07–1.93 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 172.4 (2 C), 141.9 (2 C), 129.9 (q, *J* = 32.5 Hz, 2 C), 129.1 (4 C), 125.5 (q, *J* = 3.7 Hz, 4 C), 122.8 (2 C), 57.3, 33.7 (2 C), 17.1 ppm; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ -62.7 ppm; **IR** (ATR): ν_{max} = 2941, 1732, 1681, 1619, 1414, 1377, 1321, 1240, 1165, 1111, 1068, 1018, 1001 cm^{-1}; **HRMS** (APPI): calculated for $[C_{20}H_{15}F_6NO_2]^+$: 415.1001, found: 415.0989.

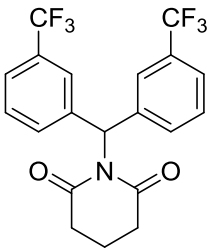
1-(Bis(4-methoxyphenyl)methyl)piperidine-2,6-dione:



S5g

Was obtained according to **TP2** from bis(4-methoxyphenyl)methanol (1.22 g, 5.00 mmol), glutarimide (792 mg, 7.00 mmol), PPh_3 (1.74 g, 6.65 mmol) and DIAD (1.3 mL, 6.50 mmol). **Yield**: 305 mg, 45%; **appearance**: white foam; **R_f**: 0.25 (pentane:EtOAc, 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.25–7.19 (m, 4 H), 7.07 (s, 1 H), 6.88–6.72 (m, 4 H), 3.79 (s, 6 H), 2.68 (t, *J* = 6.6 Hz, 4 H), 2.01–1.93 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$,): δ 172.5 (2 C), 158.7 (2 C), 131.2 (2 C), 130.0 (4 C), 113.6 (4 C), 57.5, 55.4 (2 C), 33.9 (2 C), 17.3 ppm; **IR** (ATR): ν_{max} = 2958, 2937, 2902, 2837, 1725, 1675, 1609, 1511, 1344, 1319, 1248, 1176, 1136, 1111, 834 cm^{-1}; **HRMS** (ESI): calculated for $[C_{20}H_{21}NO_4 + Na]^+$: 362.1363, found: 362.1365.

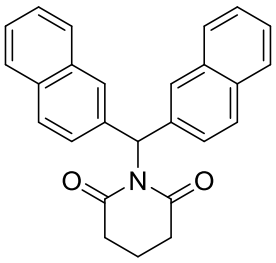
1-(Bis(3-(trifluoromethyl)phenyl)methyl)piperidine-2,6-dione:



S5h

Was obtained according to **TP1** from glutarimide (472 mg, 4.18 mmol), TBAI (309 mg, 835 μmol), K_2CO_3 (1.15 g, 8.35 mmol) and 3,3'-(bromomethylene)bis((trifluoromethyl)benzene) (2.40 g, 6.26 mmol). **Yield**: 1.30 g, 75%; **appearance**: colorless oil; **R_f**: 0.3 (pentane:EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64–7.42 (m, 8 H), 7.25 (s, 1 H), 2.74 (t, *J* = 6.6 Hz, 4 H), 2.02 (p, *J* = 6.5 Hz, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$,): δ 172.4 (2 C), 139.0 (2 C), 132.2 (2 C), 130.9 (q, *J* = 32.3 Hz, 2 C), 129.0 (2 C), 125.4 (q, *J* = 3.7 Hz, 2 C), 124.7 (q, *J* = 3.8 Hz, 2 C), 122.8 (2 C), 57.3, 33.7 (2 C), 17.1 ppm; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ -62.6 ppm; **IR** (ATR): ν_{max} = 2945, 1732, 1683, 1377, 1329, 1257, 1241, 1166, 1122, 1076, 1003, 927, 904 cm^{-1}; **HRMS** (ESI): calculated for $[C_{20}H_{15}F_6NO_2 + Na]^+$: 438.0899, found: 438.0895.

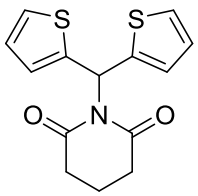
1-(Di(naphthalen-2-yl)methyl)piperidine-2,6-dione:



S5i

Was obtained according to **TP1** from glutarimide (754 mg, 6.67 mmol), TBAI (492 mg, 1.33 mmol), K_2CO_3 (1.84 g, 13.3 mmol) and 2,2'-(bromomethylene)dinaphthalene (3.47 g, 10.0 mmol). **Yield**: 815 mg, 32%; **appearance**: pale brown solid; **R_f**: 0.1 (pentane:EtOAc, 4:1); **m.p.**: 147.3–148.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92–7.67 (m, 8 H), 7.62–7.39 (m, 7 H), 2.75 (t, *J* = 6.5 Hz, 4 H), 2.07–1.99 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$,): δ 172.6 (2 C), 136.3 (2 C), 133.3 (2 C), 132.8 (2 C), 128.2, 127.9 (4 C), 127.7 (2 C), 126.9 (2 C), 126.2 (2 C), 126.1 (2 C), 58.7, 33.9 (2 C), 17.3 ppm; **IR** (ATR): ν_{max} = 3054, 2937, 1727, 1676, 1633, 1599, 1507, 1428, 1338, 1317, 1239, 1169, 1132, 1001, 820 cm^{-1}; **HRMS** (ESI): calculated for $[C_{26}H_{21}NO_2 + Na]^+$: 402.1465, found: 402.1470.

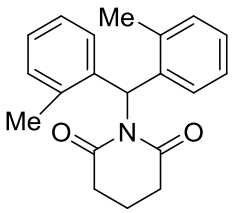
1-(Di(thiophen-2-yl)methyl)piperidine-2,6-dione:



S5j

Was obtained according to **TP2** from di(thiophen-2-yl)methanol (720 mg, 3.67 mmol), glutarimide (581 mg, 5.14 mmol), PPh_3 (1.28 g, 4.88 mmol) and DIAD (0.93 mL, 4.77 mmol). **Yield**: 95.0 mg, 9%; **appearance**: white solid; $\mathbf{R_f}$: 0.2 (pentane:EtOAc, 4:1); **m.p.**: 153.2 – 155.7 °C; **^{1}H NMR** (400 MHz, C_6D_6): δ 7.96 (s, 1 H), 7.13–7.11 (m, 2 H), 6.86–6.83 (m, 2 H), 6.68–6.64 (m, 2 H), 1.81 (t, *J* = 6.6 Hz, 4 H), 0.80–0.72 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 171.2 (2 C), 142.6 (2 C), 128.4 (2 C), 126.4 (2 C), 126.1 (2 C), 50.4, 33.0 (2 C), 16.4 ppm; **IR** (ATR): ν_{max} = 3098, 2943, 2882, 1725, 1675, 1430, 1387, 1337, 1316, 1239, 1169, 1133, 1045, 997, 851 cm^{-1}; **HRMS** (ESI): calculated for $[C_{14}H_{13}NO_2S_2 + Na]^+$: 314.0280, found: 314.0282.

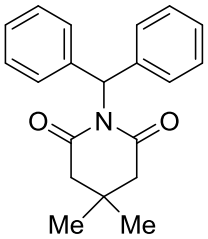
1-(Di-*o*-tolylmethyl)piperidine-2,6-dione:



S5k

Was obtained according to **TP1** from glutarimide (377 mg, 3.33 mmol), TBAI (246 mg, 667 μmol), K_2CO_3 (921 mg, 6.67 mmol) and 2,2'-(bromomethylene)bis(methylbenzene) (1.38 g, 5.00 mmol). **Yield**: 284 mg, 28%; **appearance**: white solid; $\mathbf{R_f}$: 0.2 (pentane:EtOAc, 4:1); **m.p.**: 134.5–137.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.22–7.03 (m, 9 H), 2.70 (t, *J* = 6.5 Hz, 4 H), 2.15 (s, 6 H), 2.02–1.93 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$,: δ 172.5 (2 C), 136.9 (2 C), 136.0 (2 C), 130.4 (2 C), 129.3 (2 C), 127.5 (2 C), 125.8 (2 C), 55.4, 33.8 (2 C), 19.5 (2 C), 17.5 ppm; **IR** (ATR): ν_{max} = 3021, 2956, 2878, 1727, 1677, 1488, 1460, 1377, 1342, 1317, 1240, 1169, 1137, 1111, 1000 cm^{-1}; **HRMS** (ESI): calculated for $[C_{20}H_{21}NO_2 + Na]^+$: 330.1465, found: 330.1470.

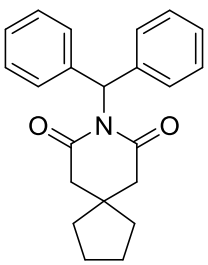
1-Benzhydryl-4,4-dimethylpiperidine-2,6-dione:



S5l

Was obtained according to **TP1** from 4,4-dimethylglutarimide (706 mg, 5.00 mmol), TBAI (369 mg, 1.00 mmol), K_2CO_3 (1.38 g, 10.0 mmol) and benzhydryl bromide (1.85 g, 7.50 mmol). **Yield**: 548 mg, 36%; **appearance**: white solid; $\mathbf{R_f}$: 0.45 (pentane:EtOAc, 4:1); **m.p.**: 134.1–135.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31–7.20 (m, 10 H), 7.17 (s, 1 H), 2.53 (s, 4 H), 1.06 (s, 6 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 172.0 (2 C), 138.8 (2 C), 128.8 (4 C), 128.2 (4 C), 127.3 (2 C), 58.3, 47.2 (2 C), 29.3, 27.9 (2 C) ppm; **IR** (ATR): ν_{max} = 3029, 2957, 2872, 1727, 1674, 1494, 1450, 1382, 1349, 1269, 1229, 1136, 1080 cm^{-1}; **HRMS** (ESI): calculated for $[C_{20}H_{21}NO_2 + Na]^+$: 330.1465, found: 330.1470.

8-Benzhydryl-8-azaspiro[4.5]decane-7,9-dione:

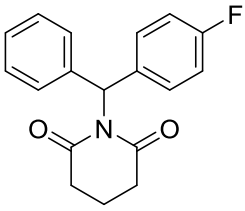


S5m

Was obtained according to **TP1** from 8-azaspiro[4.5]decane-7,9-dione (418 mg, 2.50 mmol), TBAI (185 mg, 0.50 mmol), K_2CO_3 (691 mg, 5.00 mmol) and (bromomethylene)dibenzene (927 mg, 3.75 mmol). **Yield**: 450 mg, 54%; **appearance**: white powder; $\mathbf{R_f}$: 0.4 (pentane:EtOAc, 4:1); **m.p.**: 157.1–160.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32–7.21 (m, 10 H), 7.18 (s, 1 H), 2.64 (s, 4 H), 1.76–1.64 (m, 4 H), 1.59–1.45 (m, 4 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz,

$CDCl_3$): δ 172.2 (2 C), 138.9 (2 C), 128.8 (4 C), 128.2 (4 C), 127.3 (2 C), 58.4, 45.8 (2 C), 39.6, 37.8 (2 C), 24.5 (2 C) ppm; **IR** (ATR): ν_{max} = 3088, 3061, 3028, 2950, 2863, 1728, 1674, 1601, 1494, 1450, 1382, 1351, 1335, 1265, 1143, 1079, 751, 720, 697, 578, 522 cm^{-1}; **HRMS** (ESI): calculated for $[C_{22}H_{23}NO_2 + Na]^+$: 356.1621, found: 356.1627.

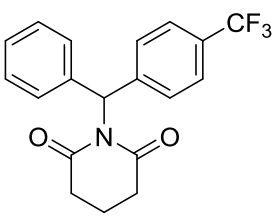
1-((4-fluorophenyl)(phenyl)methyl)piperidine-2,6-dione:



S5n

Was obtained according to **TP2** from (4-fluorophenyl)(phenyl)methanol (1.70 g, 8.41 mmol), glutarimide (1.33 g, 11.8 mmol), PPh_3 (2.93 g, 11.2 mmol) and DIAD (2.13 mL, 10.9 mmol). **Yield**: 421 mg, 17%; **appearance**: white solid; $\mathbf{R_f}$: 0.2 (pentane:EtOAc, 4:1); **m.p.**: 105.1–108.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41–7.17 (m, 7 H), 7.15 (s, 1 H), 7.02–6.96 (m, 2 H), 2.70 (t, *J* = 6.6 Hz, 4 H), 2.07–1.86 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 172.5 (2 C), 162.1 (d, *J* = 246.1 Hz), 138.5, 134.6 (d, *J* = 3.3 Hz), 130.9 (d, *J* = 8.1 Hz, 2 C), 128.33 (2 C), 128.27 (2 C), 127.3, 115.1 (d, *J* = 21.3 Hz, 2 C), 57.6, 33.8 (2 C), 17.2 ppm; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ -115 ppm; **IR** (ATR): ν_{max} = 3062, 2963, 2944, 2885, 1727, 1675, 1603, 1509, 1452, 1379, 1343, 1318, 1239, 1168, 1134, 1099, 1067, 1000, 881, 841, 792, 728, 701, 563 cm^{-1}; **HRMS** (ESI): calculated for $[C_{18}H_{16}FNO_2 + Na]^+$: 320.1057, found: 320.1063.

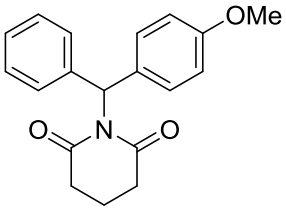
1-(Phenyl(4-(trifluoromethyl)phenyl)methyl)piperidine-2,6-dione:



S5o

Was obtained according to **TP2** from phenyl(4-(trifluoromethyl)phenyl)methanol (1.17 g, 4.64 mmol), glutarimide (735 mg, 6.49 mmol), PPh_3 (1.62 g, 6.17 mmol) and DIAD (1.17 mL, 6.03 mmol). **Yield**: 322 mg, 20%; **appearance**: colorless foam; $\mathbf{R_f}$: 0.15 (pentane:EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.2 Hz, 2 H), 7.41–7.26 (m, 7 H), 7.20 (s, 1 H), 2.72 (t, *J* = 6.6 Hz, 4 H), 2.00 (p, *J* = 6.6 Hz, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 172.4 (2 C) , 143.0, 137.8, 128.9 (4 C), 128.5 (2 C), 127.8, 125.2 (q, *J* = 3.4 Hz, 2 C), 57.8, 33.8 (2 C), 17.2 ppm, the signals of CF_3 and the adjacent carbon are missing; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ -62.5 ppm; **IR** (ATR): ν_{max} = 3304, 3032, 2982, 2939, 1707, 1619, 1495, 1467, 1454, 1385, 1324, 1248, 1165, 1108, 1067, 1018,, 951, 922, 840, 814, 760, 722, 699, 620 cm^{-1}; **HRMS** (ESI): calculated for $[C_{19}H_{16}F_3NO_2 + Na]^+$: 370.1025, found: 370.1031.

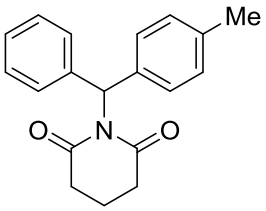
1-((4-Methoxyphenyl)(phenyl)methyl)piperidine-2,6-dione:



S5p

Was obtained according to **TP2** from (4-methoxyphenyl)(phenyl)methanol (1.07 g, 5.00 mmol), glutarimide (792 mg, 7.00 mmol), PPh_3 (1.74 g, 6.65 mmol) and DIAD (1.26 mL, 6.50 mmol). **Yield**: 241 mg, 16%; **appearance**: white solid; $\mathbf{R_f}$: 0.45 (pentane:EtOAc, 1:1); **m.p.**: 131.0–132.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33–7.17 (m, 7 H), 7.12 (s, 1 H), 6.88–6.75 (m, 2 H), 3.78 (s, 3 H), 2.67 (t, *J* = 6.5 Hz, 4 H), 1.99–1.91 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 172.4 (2 C), 158.8, 139.0, 130.9, 130.7 (2 C), 128.2 (2 C), 128.1 (2 C), 127.0, 113.5 (2 C), 57.8, 55.3, 33.8 (2 C), 17.2 ppm; **IR** (ATR): ν_{max} = 2966, 2901, 2836, 1727, 1676, 1608, 1584, 1512, 1461, 1381, 1344, 1318, 1248, 1170, 1135, 1112, 1066, 1032, 1000, 930, 880, 837, 780, 732, 703, 564 cm^{-1}; **HRMS** (ESI): calculated for $[C_{19}H_{19}NO_3 + Na]^+$: 332.1257, found: 332.1261.

1-(Phenyl(*p*-tolyl)methyl)piperidine-2,6-dione:



S5r

Was obtained according to **TP2** from phenyl(*p*-tolyl)methanol (1.59 g, 8.00 mmol), glutarimide (1.27 g, 11.2 mmol), PPh_3 (2.79 g, 10.6 mmol) and DIAD (2.02 mL, 10.4 mmol). **Yield:** 326 mg, 14%; **appearance**: colorless oil; $\mathbf{R_f}$: 0.6 (pentane:EtOAc, 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38–7.24 (m, 7 H), 7.21–7.14 (m, 3 H), 2.72 (t, *J* = 6.6 Hz, 4 H), 2.38 (s, 3 H), 2.05–1.95 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 172.4 (2 C), 138.9, 136.9, 135.7, 128.9 (2 C), 128.8 (2 C), 128.5 (2 C), 128.1 (2 C), 127.1, 58.0, 33.7 (2 C), 21.2, 17.1 ppm; **IR** (ATR): ν_{max} = 3027, 2943, 1727, 1676, 1514, 1379, 1344, 1318, 1240, 1168, 1134, 1000, 929, 880, 828, 746,m 725, 702, 593, 564, 510, 442 cm^{-1}; **HRMS** (ESI): calculated for $[C_{19}H_{19}NO_2 + Na]^+$: 316.1308, found: 316.1312.

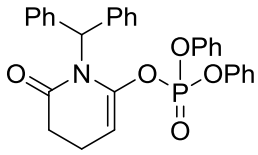
Typical Procedure for the Preparation of Substituted Ketene Aminal Phosphates 4a–4r (TP3)

A cold (-78 °C) solution of KHMDS (1.1 eq) in THF (0.5 M) was treated with a solution of the corresponding benzhydryl imide (1.0 eq) in THF (0.5 M) dropwise. The resulting mixture was stirred at this temperature for 1.5 h and then a solution of $ClPO(OPh)_2$ (1.2 eq) in THF (1 M) was added by a syringe pump over 30 min at -78 °C. The reaction mixture was stirred at -78 °C for 15 min and then allowed to warm to room temperature over 1.5 h. It was then quenched by the addition of 2% aqueous ammonia, diluted with water and the layers were separated. The aqueous layer was extracted with Et_2O (*2), combined organic fractions were washed with water, brine, dried over K_2CO_3 and concentrated under reduced pressure. Crude product was purified by flash chromatography (pentane:Et_2O) using phosphate buffered silica gel. The purified samples were stored in a glovebox freezer as 0.5 M solutions in distilled toluene, otherwise they hydrolyzed to the corresponding imides.

The obtained phosphates were sufficiently characterized by ^{1}H NMR, ^{31}P NMR, IR spectroscopy and mass spectrometry, the representative $^{13}C\{^1H\}$ NMR spectra for compounds **4a**, **4a′**, **4c** and **4n** are also included.

Characterisation data for ketene aminal phosphates 4a–4r

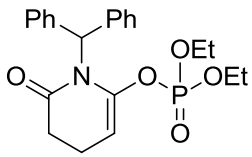
1-Benzhydryl-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:



4a

Was obtained according to **TP3** from KHMDS (329 mg, 1.65 mmol), 1-benzhydrylpiperidine-2,6-dione (**S5a**) (419 mg, 1.50 mmol) and $ClPO(OPh)_2$ (484 mg, 1.80 mmol). **Yield**: 609 mg, 79%; **Appearance**: colorless oil; $\mathbf{R}_f$: 0.4 (pentane:Et_2O, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.48–7.38 (m, 4 H), 7.32 (s, 1 H), 7.15–7.09 (m, 4 H), 7.08–6.98 (m, 6 H), 6.91–6.85 (m, 4 H), 6.82–6.73 (m, 2 H), 5.39 (td, *J* = 2.0, 5.2 Hz, 1 H), 2.18 (dd, *J* = 6.6, 8.3 Hz, 2 H), 1.66–1.56 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 170.1, 150.9, 150.8, 143.42, 143.40, 139.8, 130.0, 129.1, 128.4, 127.3, 125.69, 125.67, 120.4, 120.3, 91.03, 91.00, 59.4, 32.7, 17.3 ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.1 ppm; **IR** (ATR): ν_{max} = 3061, 3029, 2906, 2847, 1689, 1674, 1589, 1488, 1454, 1396, 1344, 1299, 1274, 11172, 1162, 1010, 966, 949, 769, 688, 516 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{30}H_{26}NO_5P + H]^+$: 512.1621, found: 512.1617.

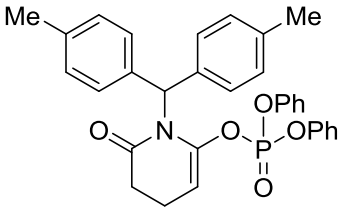
1-Benzhydryl-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diethyl phosphate:



4a′

Was obtained according to **TP3** from KHMDS (219 mg, 1.10 mmol), 1-benzhydrylpiperidine-2,6-dione (**S5a**) (279 mg, 1.00 mmol) and $ClPO(OEt)_2$ (207 mg, 1.20 mmol). **Yield**: 299 mg, 72%; **Appearance**: colorless oil; $\mathbf{R}_f$: 0.35 (pentane:Et_2O, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.51–7.44 (m, 5 H), 7.13 (d, *J* = 7.8 Hz, 4 H), 7.07–6.99 (m, 2 H), 5.33 (td, *J* = 1.9, 5.1 Hz, 1 H), 3.72–3.42 (m, 4 H), 2.26 (dd, *J* = 6.6, 8.3 Hz, 2 H), 1.69 (tdd, *J* = 1.1, 5.1, 7.3 Hz, 2 H), 0.82 (td, *J* = 1.0, 7.0 Hz, 6 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 170.3, 143.64, 143.63, 140.2, 129.1, 128.4, 127.2, 89.28, 89.27, 64.34, 64.31, 58.9, 32.8, 17.3, 15.94, 15.89 ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -8.0 ppm; **IR** (ATR): ν_{max} = 3061, 3029, 2982, 2930, 2910, 2848, 1686, 1672, 1495, 1448, 1394, 1345, 1272, 1180, 1163, 1025, 1004, 898, 845, 746, 695, 508 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{22}H_{26}NO_5P + H]^+$: 416.1621, found: 416.1625.

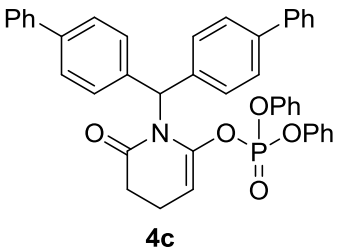
1-(Di-*p*-tolylmethyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:



4b

Was obtained according to **TP3** from KHMDS (105 mg, 0.526 mmol), 1-(di-*p*-tolylmethyl)piperidine-2,6-dione (**S5b**) (147 mg, 0.478 mmol) and $ClPO(OPh)_2$ (154 mg, 0.574 mmol). **Yield**: 162 mg, 63%; **appearance**: yellow oil; $\mathbf{R_f}$: 0.45 (pentane:Et_2O, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.44–7.38 (m, 5 H), 7.06–7.02 (m, 4 H), 6.97 (d, *J* = 7.9 Hz, 4 H), 6.91–6.85 (m, 4 H), 6.81–6.71 (m, 2 H), 5.41 (td, *J* = 1.9, 5.1 Hz, 1 H), 2.25–2.15 (m, 2 H), 2.09 (s, 6 H), 1.65–1.58 (m, 2 H) ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.1 ppm; **IR** (ATR): ν_{max} = 3085, 3059, 3025, 2919, 2864, 1690, 1674, 1591, 1492, 1456, 1393, 1344, 1299, 1185, 1128, 1025, 1009, 965, 949, 903, 840, 815, 755, 727, 692, 515, 463 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{32}H_{30}NO_5P + H]^+$: 540.1934, found: 540.1928.

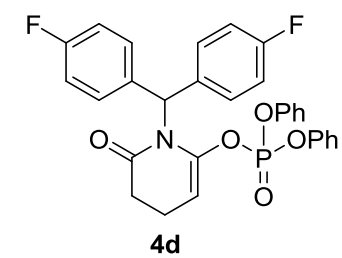
1-(Di([1,1'-biphenyl]-4-yl)methyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:



4c

Was obtained according to **TP3** from KHMDS (64.0 mg, 0.321 mmol), 1-(di([1,1'-biphenyl]-4-yl)methyl)piperidine-2,6-dione (**S5c**) (126 mg, 0.292 mmol) and $ClPO(OPh)_2$ (94.0 mg, 0.350 mmol). **Yield**: 64.0 mg, 33%; **appearance**: colorless oil; $\mathbf{R_f}$: 0.3 (pentane:Et_2O, 1:2); **^{1}H NMR** (600 MHz, C_6D_6): δ 7.57 (d, *J* = 8.4 Hz, 4 H), 7.52–7.45 (m, 9 H), 7.24–7.20 (m, 4 H), 7.15–7.12 (m, 2 H), 7.05–7.01 (m, 4 H), 6.85–6.80 (m, 4 H), 6.71–6.69 (m, 2 H), 5.45 (td, *J* = 1.9, 5.2 Hz, 1 H), 2.26 (dd, *J* = 6.5, 8.3 Hz, 2 H), 1.76–1.59 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 170.2, 150.8, 150.7, 143.4, 141.2, 140.4, 138.8, 130.0, 129.7, 129.1, 128.2, 128.0, 127.5, 127.4, 127.3, 125.7, 120.3, 120.3, 91.0, 58.8, 32.7, 17.3 ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.2 ppm; **IR** (ATR): ν_{max} = 3057, 3028, 2952, 2921, 2851, 1688, 1673, 1590, 1486, 1391, 1344, 1312, 1296, 1271, 1160, 1129, 1072, 1025, 1009, 946, 905, 846, 742, 731, 687, 561, 513, 465 cm^{-1}.

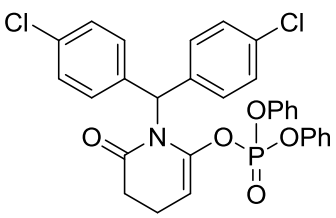
1-(Bis(4-fluorophenyl)methyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:



4d

Was obtained according to **TP3** from KHMDS (110 mg, 0.550 mmol), 1-(bis(4-fluorophenyl)methyl)piperidine-2,6-dione (**S5d**) (158 mg, 0.500 mmol) and $ClPO(OPh)_2$ (161 mg, 0.600 mmol). **Yield**: 126 mg, 46%; **appearance**: colorless oil; $\mathbf{R_f}$: 0.55 (pentane:Et_2O, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): 7.15–7.12 (m, 2 H), 7.08 (s, 1 H), 7.03–6.98 (m, 4 H), 6.90–6.84 (m, 4 H), 6.79–6.72 (m, 6 H), 5.37 (td, *J* = 2.0, 5.1 Hz, 1 H), 2.16 (dd, *J* = 6.6, 8.3 Hz, 1 H), 1.63–1.55 (m, 2 H) ppm; **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ -115.3 ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.2 ppm; **IR** (ATR): ν_{max} = 3070, 2904, 2849, 1688, 1675, 1601, 1589, 1508, 1487, 1391, 1298, 1273, 1225, 1159, 1127, 1099, 1010, 965, 949, 905, 833, 754, 687, 543, 516 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{30}H_{24}F_2NO_5P + H]^+$: 548.1433, found: 548.1441.

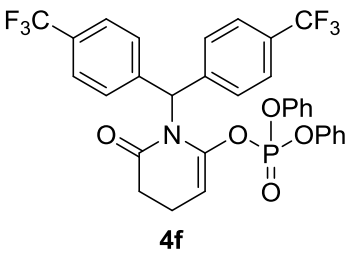
1-(Bis(4-chlorophenyl)methyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:



4e

Was obtained according to **TP3** from KHMDS (329 mg, 1.65 mmol), 1-(bis(4-chlorophenyl)methyl)piperidine-2,6-dione (**S5e**) (522 mg, 1.50 mmol) and $ClPO(OPh)_2$ (484 mg, 1.80 mmol). **Yield**: 576 mg, 66%; **appearance**: colorless oil; $\mathbf{R_f}$: 0.5 (pentane:Et_2O, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): 7.07–7.04 (m, 8 H), 7.02 (s, 1 H), 7.01–6.97 (m, 4 H), 6.92–6.87 (m, 4 H), 6.81–6.75 (m, 2 H), 5.36 (dt, *J* = 3.6, 7.2 Hz, 1 H), 2.20–2.06 (m, 2 H), 1.61–1.54 (m, 2 H) ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.3 ppm; **IR** (ATR): ν_{max} = 3464, 3088, 3061, 3028, 2950, 2863 1728, 1674, 1601, 1494, 1450, 1382, 1351, 1335, 1265, 1230, 1143, 1079, 1032, 919, 876, 795, 750, 720, 697, 629, 599, 578, 545, 522, 468, 452 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{30}H_{24}{}^{35}Cl_2NO_5P + H]^+$: 580.0842, found: 580.0849.

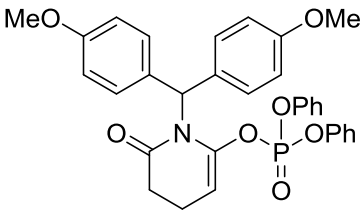
1-(Bis(4-(trifluoromethyl)phenyl)methyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:



4f

Was obtained according to **TP3** from KHMDS (110 mg, 0.550 mmol), 1-(bis(4-(trifluoromethyl)phenyl)methyl)piperidine-2,6-dione (**S5f**) (208 mg, 0.500 mmol) and $ClPO(OPh)_2$ (161 mg, 0.600 mmol), as a 5:1 mixture with starting material. **Yield** (calculated based on product:starting material ratio): 65.0 mg, 17%; **appearance**: yellow oil; $\mathbf{R_f}$: 0.6 (pentane:Et_2O, 1:2); **^{1}H NMR** (600 MHz, C_6D_6): 7.31 (d, *J* = 8.3 Hz, 4 H), 7.20–7.13 (m, 4 H), 7.05 (s, 1 H), 6.97–6.93 (m, 4 H), 6.90–6.82 (m, 4 H), 6.81–6.68 (m, 2 H), 5.35 (td, *J* = 2.0, 5.1 Hz, 1 H), 2.21–2.08 (m, 2 H), 1.67–1.53 (m, 2 H) ppm; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ –62.2 ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.2 ppm; **HRMS** (Multimode): calculated for $[C_{32}H_{25}F_6NO_5P]^+$: 648.1369, found: 648.1361.

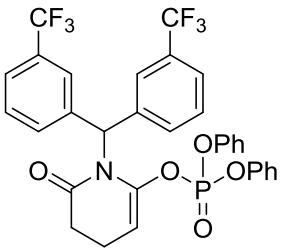
1-(Bis(4-methoxyphenyl)methyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:



4g

Was obtained according to **TP3** from KHMDS (110 mg, 0.550 mmol), 1-(bis(4-methoxyphenyl)methyl)piperidine-2,6-dion (**S5g**) (170 mg, 0.500 mmol) and $ClPO(OPh)_2$ (161 mg, 0.600 mmol), as a 4:1 mixture with starting material. **Yield** (calculated based on product:starting material ratio): 89.0 mg, 27%; **appearance**: colorless oil; $\mathbf{R_f}$: 0.3 (pentane:Et_2O, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): 7.45–7.37 (m, 4 H), 7.35 (s, 1 H), 7.07–7.02 (m, 4 H), 6.94–6.85 (m, 4 H), 6.81–6.71 (m, 6 H), 5.41 (td, *J* = 1.9, 5.1 Hz, 1 H), 3.27 (s, 6 H), 2.26–2.20 (m, 2 H), 1.70–1.59 (m, 2 H) ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.1 ppm; **IR** (ATR): ν_{max} = 3084, 3061, 3025, 3001, 2917, 2836, 1727, 1609, 1587, 1510, 1490, 1461, 1394, 1342, 1300, 1246, 1173, 1130, 1111, 1028, 1009, 948, 830, 769, 728, 688, 560, 515, 464 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{32}H_{30}NO_7P + Na]^+$: 594.1652, found: 594.1656.

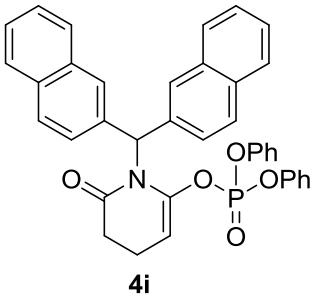
1-(Bis(3-(trifluoromethyl)phenyl)methyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:



4h

Was obtained according to **TP3** from KHMDS (110 mg, 0.550 mmol), 1-(bis(4-fluorophenyl)methyl)piperidine-2,6-dione (**S5h**) (208 mg, 0.500 mmol) and $ClPO(OPh)_2$ (161 mg, 0.600 mmol). **Yield**: 99.0 mg, 30%; **appearance**: yellow oil; $\mathbf{R_f}$: 0.55 (pentane:Et_2O, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): 7.78 (s, 2 H), 7.33 (d, *J* = 7.9 Hz, 2 H), 7.27–7.18 (m, 2 H), 7.03–7.00 (m, 4 H), 6.98 (s, 1 H), 6.92–6.81 (m, 6 H), 6.79–6.70 (m, 2 H), 5.30 (td, *J* = 2.0, 5.1 Hz, 1 H, 2.03 (dd, *J* = 6.7, 8.3 Hz, 2 H), 1.54–1.44 (m, 2 H) ppm; **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ -62.2 ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -18.7 ppm; **IR** (ATR): ν_{max} = 3067, 2922, 2852, 1695, 1678, 1591, 1489, 1446, 1393, 1329, 1270, 1163, 1124, 1099, 1076, 1011, 969, 950, 904, 858, 768, 701, 664, 653, 616, 595, 558, 517 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{32}H_{24}F_6NO_5P + H]^+$: 548.1433, found: 548.1441.

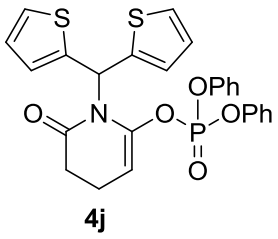
1-(Di(naphthalen-2-yl)methyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:



4i

Was obtained according to **TP3** from KHMDS (110 mg, 0.550 mmol), 1-(di(naphthalen-2-yl)methyl)piperidine-2,6-dione (**S4i**) (190 mg, 0.500 mmol) and $ClPO(OPh)_2$ (161 mg, 0.600 mmol). **Yield**: 248 mg, 81%; **appearance**: white foam; $\mathbf{R_f}$: 0.4 (pentane:Et_2O, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): 8.11–7.99 (m, 2 H), 7.79 (s, 1 H), 7.66–7.49 (m, 8 H), 7.31–7.16 (m, 4 H), 6.81–6.77 (m, 4 H), 6.73–6.61 (m, 6 H), 5.44 (td, *J* = 1.9, 5.1 Hz, 1 H), 2.34–2.23 (m, 2 H), 1.70–1.64 (m, 2 H) ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.0 ppm; **IR** (ATR): ν_{max} = 3066, 2925, 2851, 1698, 1672, 1590, 1489, 1445, 1398, 1330, 1281, 1163, 1128, 1100, 1071, 1000, 961, 950, 902, 858, 664, 653, 620, 534 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{38}H_{30}NO_5P + K]^+$: 650.1493, found: 650.1489.

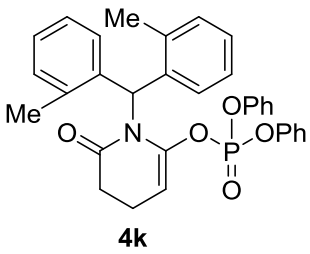
1-(Di(thiophen-2-yl)methyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:



4j

Was obtained according to **TP3** from KHMDS (45.0 mg, 0.227 mmol), 1-(di(thiophen-2-yl)methyl)piperidine-2,6-dione (**S4j)** (60.0 mg, 0.206 mmol) and $ClPO(OPh)_2$ (66.0 mg, 0.247 mmol). **Yield**: 72 mg, 67%; **appearance**: colorless oil; $\mathbf{R_f}$: 0.45 (pentane:Et_2O, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): 7.60 (s, 1 H), 7.15–7.09 (m, 4 H), 6.93–6.88 (m, 3 H), 6.83–6.76 (m, 3 H), 6.67–6.63 (m, 2 H), 5.40 (t, *J* = 5.1 Hz, 1 H), 2.08 (t, *J* = 7.3 Hz, 2 H), 1.61–1.49 (m, 2 H) ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.0 ppm; **IR** (ATR): ν_{max} = 3101, 3070, 2953, 2923, 2851, 1687, 1674, 1589, 1487, 1396, 1363, 1342, 1298, 1269, 1231, 1210, 1134, 1071, 1024, 1009, 946, 904, 856, 832, 757, 687, 616, 584, 565, 515 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{26}H_{22}NO_5PS_2 + Na]^+$: 546.0569, found: 546.0574.

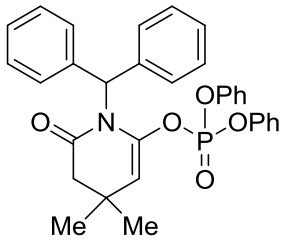
1-(Di-*o*-tolylmethyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:



4k

Was obtained according to **TP3** from KHMDS (110 mg, 0.550 mmol), 1-(di-*o*-tolylmethyl)piperidine-2,6-dione (**S4k**) (154 mg, 0.500 mmol) and $ClPO(OPh)_2$ (161 mg, 0.600 mmol). **Yield**: 168 mg, 62%; **appearance**: colorless oil; $\mathbf{R_f}$: 0.55 (pentane:Et_2O, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): 7.52–7.44 (m, 2 H), 7.39 (s, 1 H), 7.09–6.96 (m, 10 H), 6.90 (t, *J* = 7.9 Hz, 4 H), 6.83–6.73 (m, 2 H), 5.41 (td, *J* = 1.8, 5.2 Hz, 1 H), 2.22–2.14 (m, 2 H), 7.17 (s, 6 H), 1.72–1.60 (m, 2 H) ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.3 ppm; **IR** (ATR): ν_{max} = 3068, 3023, 2950, 2924, 2850, 1687, 1590, 1488, 1458, 1403, 1379, 1343, 1312, 1291, 1276, 1173, 1134, 1010, 966, 951, 851, 742, 688, 516, 497 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{32}H_{30}NO_5P + H]^+$: 540.1934, found: 540.1943.

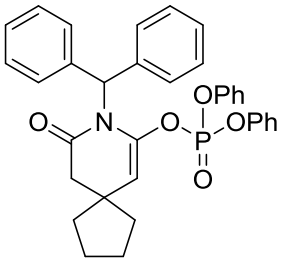
1-Benzhydryl-4,4-dimethyl-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:



4l

Was obtained according to **TP3** from KHMDS (197 mg, 0.550 mmol), 1-benzhydryl-4,4-dimethylpiperidine-2,6-dione (**S5l**) (277 mg, 0.900 mmol) and $ClPO(OPh)_2$ (290 mg, 1.08 mmol), as a 10:1 mixture with bisphosphate. **Yield** (calculated based on product:side-product ratio): 376 mg, 72%; **appearance**: colorless oil; $\mathbf{R_f}$: 0.55 (pentane:Et_2O, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): 7.48–7.44 (m, 4 H), 7.15–7.00 (m, 11 H), 6.91–6.84 (m, 4 H), 6.81–6.74 (m, 2 H), 5.37 (d, *J* = 2.0 Hz, 1 H), 2.21 (s, 2 H), 0.71 (s, 6H) ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.0 ppm; **HRMS** (Multimode): calculated for $[C_{32}H_{30}NO_5P + H]^+$: 540.1934, found: 540.1928.

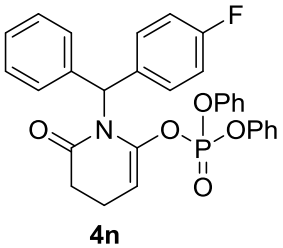
8-Benzhydryl-9-oxo-8-azaspiro[4.5]dec-6-en-7-yl diphenyl phosphate:



4m

Was obtained according to **TP3** from KHMDS (219 mg, 1.10 mmol), 8-benzhydryl-8-azaspiro[4.5]decane-7,9-dione (**S5m**) (333 mg, 1.00 mmol) and $ClPO(OPh)_2$ (322 mg, 1.20 mmol), as a 12:1 mixture with bisphosphate. **Yield** (calculated based on product:side-product ratio): 410 mg, 65%; **appearance**: colorless oil; $\mathbf{R_f}$: 0.5 (pentane:Et_2O, 1:1); **^{1}H NMR** (400 MHz, C_6D_6): 7.49–7.44 (m, 4 H), 7.39 (s, 1 H), 7.14–7.10 (m, 4 H), 7.08–7.03 (m, 6 H), 6.92–6.86 (m, 4 H), 6.82–6.75 (m, 2 H), 5.49–5.47 (m, 1 H), 2.32 (s, 2 H), 1.31–1.18 (m, 8 H) ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -18.9 ppm **HRMS** (Multimode): calculated for $[C_{34}H_{32}NO_5P + H]^+$: 566.2091, found: 566.2091.

1-((4-Fluorophenyl)(phenyl)methyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:

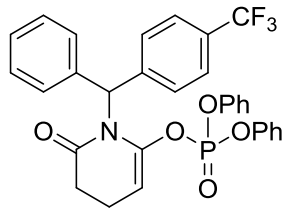


4n

Was obtained according to **TP3** from KHMDS (110 mg, 0.550 mmol), 1-((4-fluorophenyl)(phenyl)methyl)piperidine-2,6-dione (**S5n**) (149 mg, 0.500 mmol) and $ClPO(OPh)_2$ (161 mg, 0.600 mmol). **Yield**: 178 mg, 67%; **appearance**: yellowish oil; $\mathbf{R_f}$: 0.5 (pentane:Et_2O, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): 7.37–7.33 (m, 2 H), 7.24–7.18 (m, 3 H), 7.14–7.09 (m, 2 H), 7.07–6.97 (m, 5 H), 6.89–6.83 (m, 4 H), 6.78–6.70 (m, 4 H), 5.38 (td, *J* = 1.9, 5.1 Hz, 1 H), 2.17 (dd, *J* = 6.6, 8.3 Hz, 2 H), 1.64–1.54 (m, 2

H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6) δ 170.1, 163.2, 161.5, 150.74, 150.69, 143.21, 143.19, 139.5, 135.49, 135.47, 131.0, 130.9, 130.0, 128.8, 128.5, 128.4, 127.4, 125.79, 125.77, 120.29, 120.26, 120.22, 120.19, 115.2, 115.1, 91.20, 91.18, 58.7, 32.6, 17.2 ppm; **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ -115.5 ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.1 ppm; **IR** (ATR): ν_{max} = 3061, 3026, 2919, 2855, 1692, 1675, 1602, 1590, 1508, 1489, 1454, 1393, 1343, 1313, 1300, 1273, 1226, 1184, 1160, 1128, 1009, 965, 947, 836, 755, 727, 687, 555, 515, 501, 463 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{30}H_{26}FNO_5P]^+$: 530.1527, found: 530.1523.

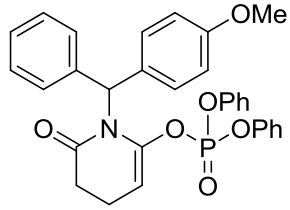
6-Oxo-1-(phenyl(4-(trifluoromethyl)phenyl)methyl)-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:



4o

Was obtained according to **TP3** from KHMDS (110 mg, 0.550 mmol), 1-(phenyl(4-(trifluoromethyl)phenyl)methyl)piperidine-2,6-dione (**S5o**) (174 mg, 0.500 mmol) and $ClPO(OPh)_2$ (161 mg, 0.600 mmol). **Yield**: 75.0 mg, 26%; **appearance**: yellowish oil; **R_f**: 0.45 (pentane:Et_2O, 1:2); **^{1}H NMR** (600 MHz, C_6D_6): 7.35–7.32 (m, 2 H), 7.29–7.23 (m, 4 H), 7.19 (s, 1 H), 7.14 – 7.11 (m, 2 H), 7.08 – 7.04 (m, 1 H), 6.99–6.96 (m, 4 H), 6.90–6.84 (m, 4 H), 6.79–6.74 (m, 2 H), 5.37 (td, *J* = 1.9, 5.1 Hz, 1 H), 2.17 (t, *J* = 7.8 Hz, 2 H), 1.62–1.57 (m, 2 H) ppm; **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ -62.0 ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.1 ppm; **IR** (ATR): ν_{max} = 3062, 3026, 2919, 2873, 1693, 1676, 1619, 1602, 1590, 1491, 1454, 1415, 1393, 1324, 1273, 1162, 1123, 1080, 1026, 1010, 966, 947, 840, 769, 755, 727, 692, 593, 559, 515, 463 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{31}H_{26}F_3NO_5P]^+$: 580.1495, found: 580.1504.

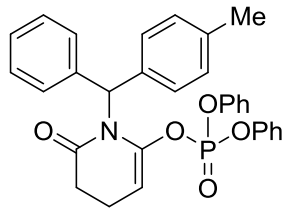
1-((4-Methoxyphenyl)(phenyl)methyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:



4p

Was obtained according to **TP3** from KHMDS (110 mg, 0.550 mmol), 1-((4-methoxyphenyl)(phenyl)methyl)piperidine-2,6-dione (**S5p**) (155 mg, 0.500 mmol) and $ClPO(OPh)_2$ (161 mg, 0.600 mmol). **Yield**: 178 mg, 66%; **appearance**: colorless oil; **R_f**: 0.4 (pentane:Et_2O, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): 7.47–7.32 (m, 5 H), 7.13 (d, *J* = 7.8 Hz, 2 H), 7.10–6.98 (m, 5 H), 6.91 – 6.84 (m, 4 H), 6.83–6.67 (m, 4 H), 5.40 (td, *J* = 2.0, 5.1 Hz, 1 H), 2.20 (t, *J* = 7.5 Hz, 2 H), 1.69–1.54 (m, 2 H) ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.1 ppm; **HRMS** (Multimode): calculated for $[C_{31}H_{28}NO_6P + H]^+$: 542.1727, found: 542.1736.

6-Oxo-1-(phenyl(*p*-tolyl)methyl)-1,4,5,6-tetrahydropyridin-2-yl diphenyl phosphate:

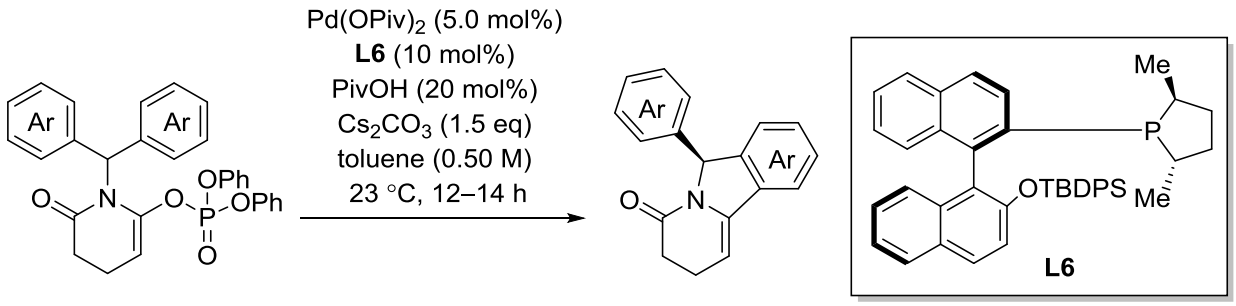


4r

Was obtained according to **TP3** from KHMDS (110 mg, 0.550 mmol), 1-(phenyl(p-tolyl)methyl)piperidine-2,6-dione (**S5r**) (147 mg, 0.500 mmol) and $ClPO(OPh)_2$ (161 mg, 0.600 mmol). **Yield**: 143 mg, 54%; **appearance**: colorless oil; **R_f**: 0.45 (pentane:Et_2O, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): 7.49–7.43 (m, 2 H), 7.41–7.35 (m, 3 H), 7.13–7.09 (m, 2 H), 7.07–6.99 (m, 5 H), 6.94 (d, *J* = 7.8 Hz, 2 H), 6.89 – 6.83 (m, 4 H), 6.80 – 6.70 (m, 2 H), 5.40 (td, *J* = 2.0, 5.1 Hz, 1H), 2.17 (dd, J = 6.7, 8.2 Hz, 2 H), 2.06 (s, 3 H), 1.63–1.52 (m, 2 H) ppm; **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -19.0 ppm; **IR** (ATR): ν_{max} = 3060, 3027, 2919, 2849, 1687, 1673, 1589, 1513, 1487, 1454, 1393, 1344, 1311, 1298, 1272, 1159, 1127, 1009, 945, 902, 853, 825, 753, 727, 686,

616, 582, 557, 513, 464 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{31}H_{28}NO_5P + H]^+$: 526.1778, found: 526.1780.

General procedure for the enantioselective C–H functionalization of enamide phosphates (GP1)



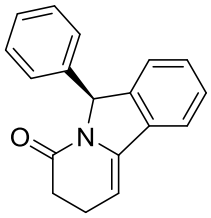
To an oven-dried 0.2-0.5 mL microwave vial equipped with a stir bar and open to air were added $Pd(OPiv)_2$ (1.54 mg, 5.00 μmol, 5.0 mol%), ligand **L6** (6.23 mg, 10.0 μmol, 10 mol%) and pivalic acid (2.04 mg, 20.0 μmol, 20 mol%). The vial was transferred to a glovebox, Cs_2CO_3 (49.0 mg, 150 μmol, 1.50 eq) was added followed by the addition of the corresponding phosphate (100 μmol, 1.00 eq) as a 0.50 M solution in toluene (200 μL). The vial was sealed, taken out of the glovebox and the reaction was stirred for 14 h at 23 °C. The reaction mixture was filtered through a plug of celite (eluting with EtOAc) and concentrated under reduced pressure. The resulting product was purified by chromatography on phosphate buffered silica gel (pentane:EtOAc or pentane: CH_2Cl_2) and stabilized by addition of 4-methoxyphenol.

Gram-scale preparation of 5a

A pressure tube with Teflon screw-cap equipped with a stir bar was charged with $Pd(OPiv)_2$ (78.0 mg, 0.250 mmol, 5.0 mol%), ligand **L6** (312 mg, 0.500 mmol, 10 mol%) and pivalic acid (102 mg, 1.00 mmol, 20 mol%). The tube was transferred to a glovebox, Cs_2CO_3 (2.44 g, 7.50 mmol, 1.50 eq) was added followed by the addition of phosphate **4a** (2.56 g, 5.00 mmol, 1.00 eq) and distilled toluene (10 mL, 0.5 M). The reaction tube was taken out of the glovebox and sealed. The reaction mixture was stirred for 48 h at 23 °C, then was filtered through a plug of celite (eluting with EtOAc) and concentrated under reduced pressure. Purification by column chromatography (pentane: CH_2Cl_2, 1:2) provided product **5a** in 80% yield (1.05 g) and 95.5:4.5 er.

Characterisation data for isoindolines 5a–5m

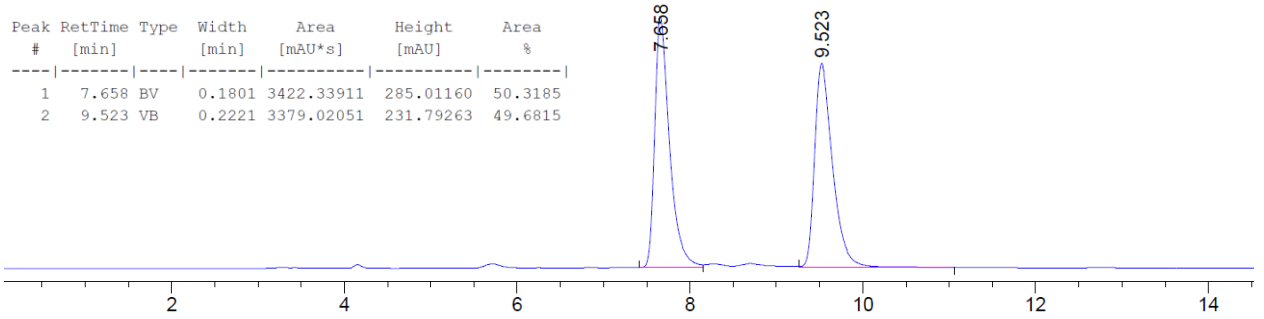
(*S*)-6-Phenyl-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one:

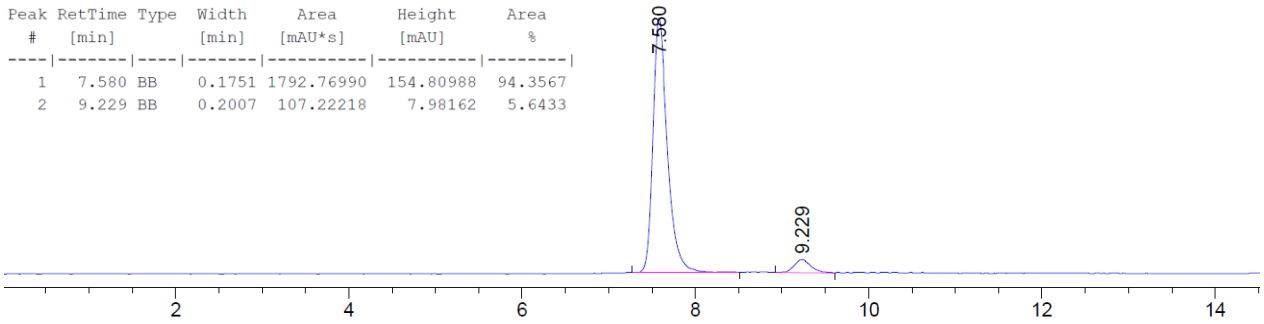


5a

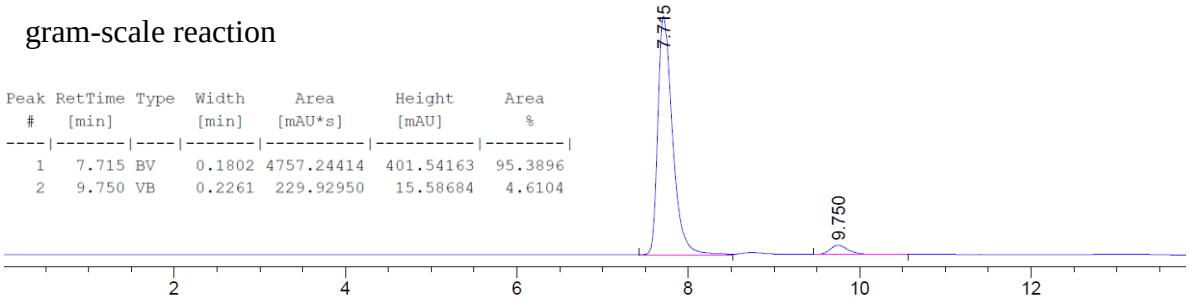
Yield: 22.5 mg, 86%; **appearance**: yellow powder; $\mathbf{R_f}$: 0.4 (CH_2Cl_2); **m.p.**: 89.6–90.5 °C; **^{1}H NMR** (400 MHz, C_6D_6): δ 7.30–7.19 (m, 3 H), 7.11–7.05 (m, 2 H), 7.03–6.98 (m, 2 H), 6.93–6.87 (m, 1 H), 6.78–6.75 (m, 1 H), 6.08 (s, 1 H), 5.16 (dd, *J* = 3.4, 5.9 Hz, 1 H), 2.33 – 2.25 (m, 1 H), 2.22–2.12 (m, 1 H), 2.08–1.96 (m, 1 H), 1.94–1.84 (m, 1 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 167.6, 142.5, 141.7, 141.0, 133.4, 129.3, 128.8 (2 C), 128.4 (2 C), 127.7 (2 C), 124.3, 120.4, 94.6, 65.8, 31.7, 21.0 ppm; **IR** (ATR): ν_{max} = 3061, 3029, 2928, 2895, 2838, 1729, 1668, 1612, 1600, 1493, 1467, 1454, 1381, 1343, 1313, 1267, 1210, 1178, 1141, 1107, 1075, 1029, 930, 749, 697, 609, 536, 477, 424 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{18}H_{15}NO + H]^+$: 262.1226, found: 262.1236; **$[\alpha]_D^{20}$**: 2.8 (c = 1.0, $CHCl_3$).

Chiral HPLC (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 284 nm): t_R (major) = 7.6 min, t_R (minor) = 9.2 min, 94.3:5.7 er.

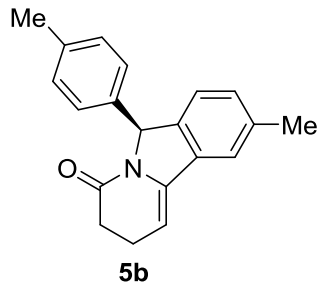




gram-scale reaction



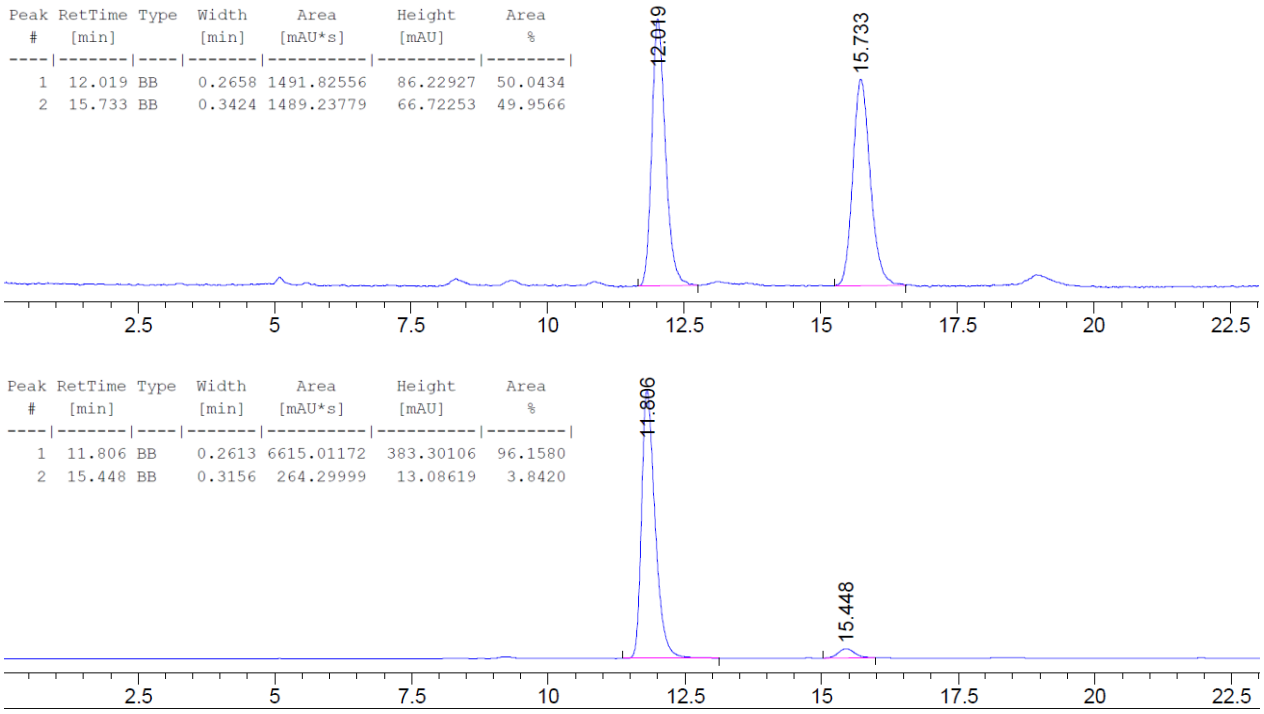
(*S*)-9-methyl-6-(*p*-tolyl)-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one:



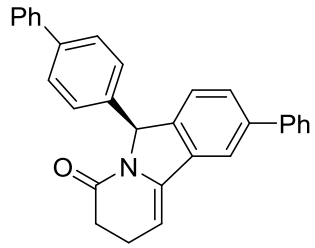
5b

Yield: 24.0 mg, 83%; **appearance**: yellow oil; **R_f**: 0.25 (CH_2Cl_2); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.26 (d, *J* = 8.2 Hz, 2 H), 7.14–7.09 (m, 1 H), 7.00–6.91 (m, 2 H), 6.77 (d, *J* = 1.3 Hz, 2 H), 6.15 (s, 1H), 5.20 (dd, *J* = 3.4, 5.8 Hz, 1 H), 2.37–2.29 (m, 1 H), 2.26–2.16 (m, 1 H), 2.11–2.00 (m, 1 H), 2.07 (s, 3 H), 2.03 (s, 3 H), 1.98–1.85 (m, 1 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 167.5, 141.3, 140.2, 139.1, 137.8, 137.3, 133.7, 130.4, 129.4 (2 C), 128.4 (2 C), 124.1, 120.7, 94.2, 65.5, 31.9, 21.3, 21.10, 21.06 ppm; **IR** (ATR): ν_{max} = 3061, 3028, 2896, 2833, 1728, 1667, 1600, 1498, 1472, 1380, 1341, 1268, 1210, 1179, 1030, 931, 748, 693 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{20}H_{19}NO + H]^+$: 290.1539, found: 290.1540; **$[\alpha]_D^{20}$**: 96 (c = 0.7, $CHCl_3$).

Chiral HPLC (Chiralpak IF, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 286 nm): t_R (major) = 11.8 min, t_R (minor) = 15.4 min, 96.2:3.8 er.



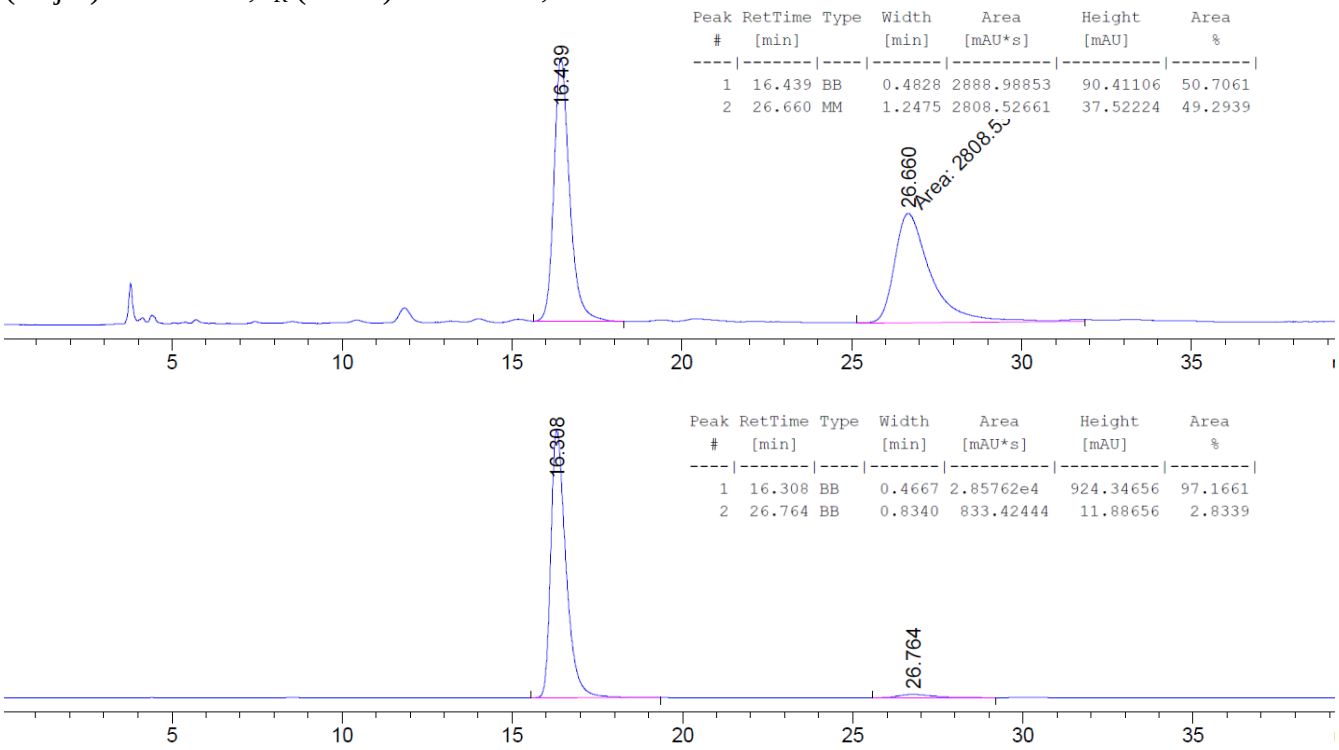
(*S*)-6-([1,1'-biphenyl]-4-yl)-9-phenyl-2,3-dihydropyrido[2,1-a]isoindol-4(6*H*)-one:



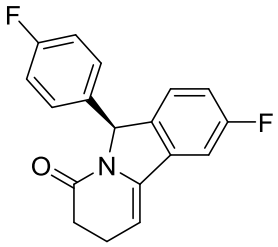
5c

Yield: 37.5 mg, 91%; **appearance**: colorless oil; $\mathbf{R_f}$: 0.3 (CH_2Cl_2); **^{1}H NMR** (600 MHz, C_6D_6): δ 7.64 (d, *J* = 1.9 Hz, 1 H), 7.52–7.38 (m, 8 H), 7.30–7.19 (m, 3 H), 7.19–7.16 (m, 3 H), 7.14–7.06 (m, 1 H), 6.88 (d, *J* = 7.9 Hz, 1 H), 6.23 (s, 1 H), 5.23 (dd, *J* = 3.3, 5.8 Hz, 1 H), 2.41–2.32 (m, 1 H), 2.30–2.19 (m, 1 H), 2.14–2.02 (m, 1 H), 1.98–1.88 (m, 1 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 172.2 (2 C), 138.9 (2 C), 128.8 (4 C), 128.2 (4 C), 127.3 (2 C), 58.4, 45.8 (2 C), 39.6, 37.8 (2 C), 24.5 (2 C); **IR** (ATR): ν_{max} = 3057, 3029, 2929, 2894, 2838, 2278, 2267, 1731, 1671, 1599, 1486, 1475, 1425, 1381, 1321, 1263, 1216, 1205, 1180, 1139, 1125, 1076, 1008, 865, 825, 813, 759, 737, 697, 556, 499 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{30}H_{23}NO + H]^+$: 414.1852, found: 414.1832; **$[\alpha]_D^{20}$**: 53 (c = 1.0, $CHCl_3$).

Chiral HPLC (Chiralpak IF, 4.6 x 250 mm; hexane:*i*-PrOH 70:30, 1.0 mL/min, 274 nm): t_R (major) = 16.3 min, t_R (minor) = 26.8 min, 97.2:2.8 er.



(*S*)-9-fluoro-6-(4-fluorophenyl)-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one:

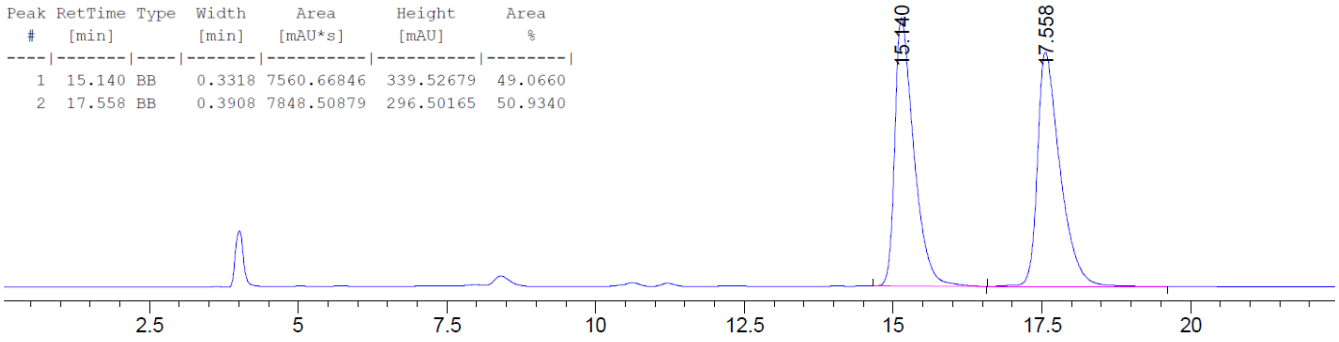


5d

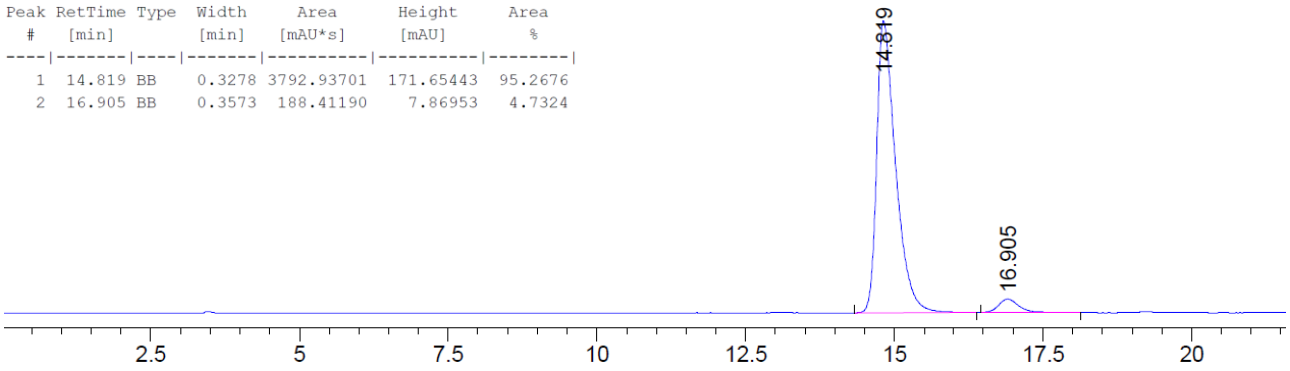
Yield: 26 mg, 87%; **appearance**: yellow oil; **R$_f$**: 0.35 (CH_2Cl_2); **^{1}H NMR** (400 MHz, C_6D_6): 7.03–6.95 (m, 2 H), 6.91–6.86 (m, 1 H), 6.78–6.71 (m, 2 H), 6.62–6.55 (m, 1 H), 6.42–6.36 (m, 1 H), 5.84 (s, 1 H), 4.95 (dd, *J* = 3.4, 5.9 Hz, 1 H), 2.28–2.19 (m, 1 H), 2.16–2.05 (m, 1 H), 1.99–1.87 (m, 1 H), 1.86–1.76 (m, 1 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 167.3, 163.9 (d, *J* = 89.0 Hz), 162.2 (d, *J* = 89.0 Hz), 140.0 (d, *J* = 4.1 Hz), 137.6 (d, *J* = 2.5 Hz), 137.1 (d, *J* = 3.6 Hz), 135.3 (d, *J* = 9.2 Hz), 129.5 (d, J = 8.1 Hz, 2 C), 125.8 (d, *J* = 9.2 Hz), 116.7 (d, *J* = 23.4 Hz), 115.6 (d, *J* = 21.4 Hz, 2 C), 107.1 (d, *J* = 23.9 Hz), 96.0, 64.5, 31.5, 21.0 ppm; **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ -113.9, -114.4 ppm; **IR** (ATR): ν_{max} = 1463, 3067, 2933, 2898, 2851, 1683, 1672, 1605, 1508, 1482, 1383, 1323, 1311, 1220, 1159, 863, 818, 579, 535 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{18}H_{13}F_2NO + H]^+$: 298.1038, found: 298.1047; **$[\alpha]_D^{20}$**: 16 (c = 0.2, $CHCl_3$).

Chiral HPLC (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 95:5, 1.0 mL/min, 304 nm): t_R (major) = 14.8 min, t_R (minor) = 16.9 min, 95.3:4.7 er.

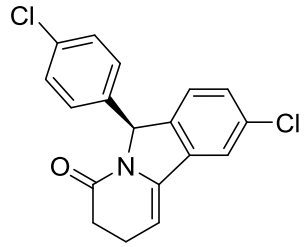
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.140	BB	0.3318	7560.66846	339.52679	49.0660
2	17.558	BB	0.3908	7848.50879	296.50165	50.9340



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.819	BB	0.3278	3792.93701	171.65443	95.2676
2	16.905	BB	0.3573	188.41190	7.86953	4.7324



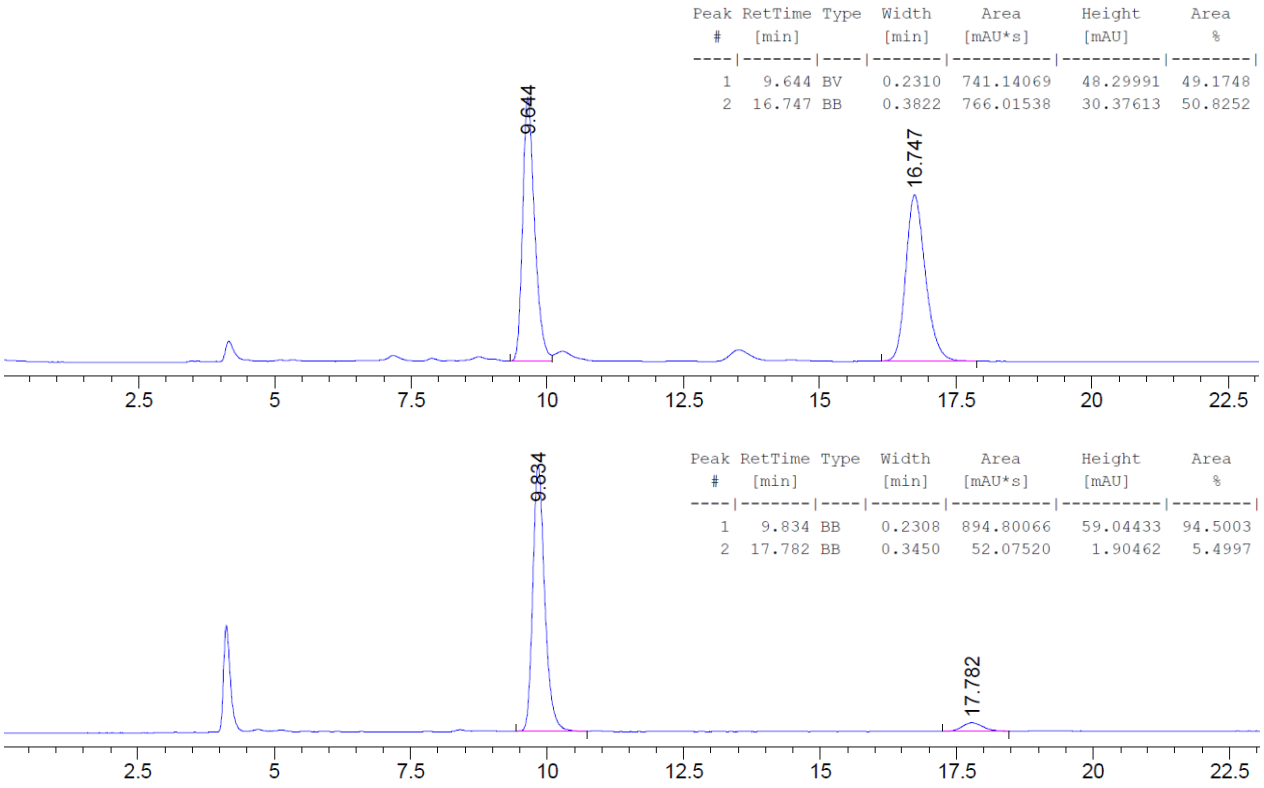
(*S*)-9-chloro-6-(4-chlorophenyl)-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one:



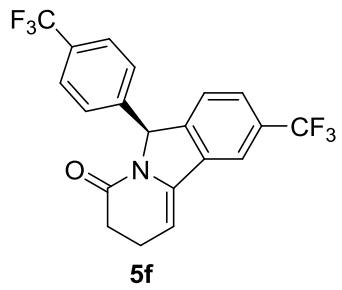
5e

Yield: 25.0 mg, 76%; **Appearance**: yellow powder; **R_f**: 0.3 (pentane:EtOAc, 4:1); **m.p.**: 179.6–181.3 °C; **^{1}H NMR** (600 MHz, C_6D_6): δ 7.23 (d, *J* = 1.9 Hz, 1 H), 7.07–7.03 (m, 2 H), 6.94–6.83 (m, 3 H), 6.32 (d, *J* = 8.7 Hz, 1 H), 5.76 (s, 1 H), 4.92 (dd, *J* = 3.7, 5.7 Hz, 1 H), 2.26–2.16 (m, 1 H), 2.12–2.05 (m, 1 H), 1.98–1.86 (m, 1 H), 1.86–1.76 (m, 1 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 166.9, 139.7, 139.2, 134.7, 134.2, 133.6, 129.1, 128.7 (2 C), 128.6 (2 C), 128.0, 125.1, 120.3, 95.8, 64.3, 31.0, 20.6 ppm; **IR** (ATR): ν_{max} = 2927, 2850, 1736, 1683, 1671, 1491, 1468, 1428, 1384, 1324, 1307, 1258, 1209, 1180, 1089, 1073, 1014, 815, 805, 532, 511, 452, cm^{-1}; **HRMS** (Multimode): calculated for $[C_{18}H_{13}{}^{35}Cl_2NO + H]^+$: 330.0447, found: 330.0441; **$[\alpha]_D^{20}$**: 231 (c = 0.6, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 322 nm): t_R (major) = 9.8 min, t_R (minor) = 17.8 min, 94.5:5.5 er.



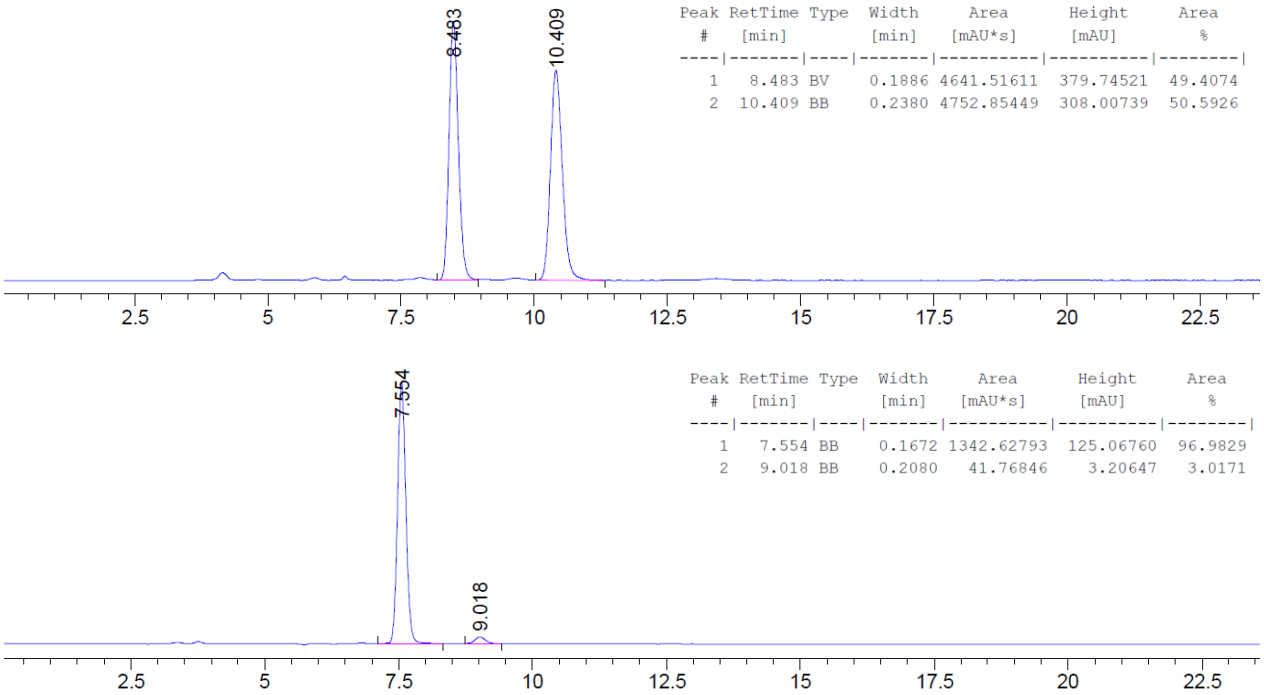
(*S*)-9-(trifluoromethyl)-6-(4-(trifluoromethyl)phenyl)-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one:



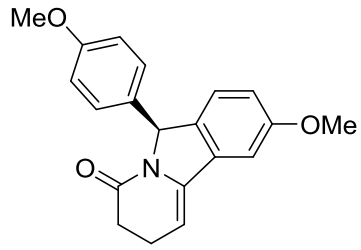
5f

Yield: 31.5 mg, 79%; **Appearance**: yellow oil; **R_f**: 0.15 (pentane:CH_2Cl_2, 1:2); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.57–7.49 (m, 1 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.13–7.08 (m, 1 H), 6.96 (d, *J* = 8.0 Hz, 2 H), 6.47–6.35 (m, 1 H), 5.79 (s, 1 H), 4.90 (dd, *J* = 3.5, 5.8 Hz, 1 H), 2.28–2.19 (m, 1 H), 2.15–2.05 (m, 1 H), 1.99–1.88 (m, 1 H), 1.87–1.73 (m, 1 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 167.3, 144.5, 144.4, 139.3, 134.1, 131.0 (q, *J* = 32.3), 130.3 (q, *J* = 32.4), 126.0 (q, *J* = 3.7), 125.9 (q, *J* = 3.7, 2 C), 124.7 (2 C), 117.77, 117.73, 96.9, 64.9, 31.2, 21.0 ppm, 2 signals are missing; **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ -62.1, -62.3 ppm; **IR** (ATR): ν_{max} = 3377, 2931, 2857, 1733, 1683, 1619, 1420, 1380, 1323, 1266, 1241, 1166, 1119, 1068, 1018, 1002, 855, 841, 766, 732, 705, 604, 563, 441 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{20}H_{13}F_6NO + H]^+$: 398.0974, found: 398.0974; **$[\alpha]_D^{20}$**: 12 (c = 0.5, $CHCl_3$).

Chiral HPLC (Chiralpak IC, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 290 nm): t_R (major) = 7.6 min, t_R (minor) = 9.0 min, 97.0:3.0 er.



(*S*)-9-methoxy-6-(4-methoxyphenyl)-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one:

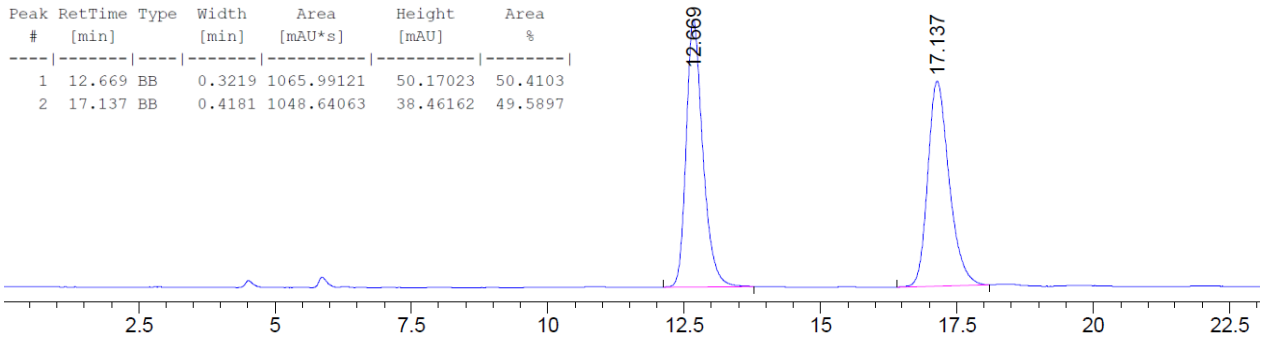


5g

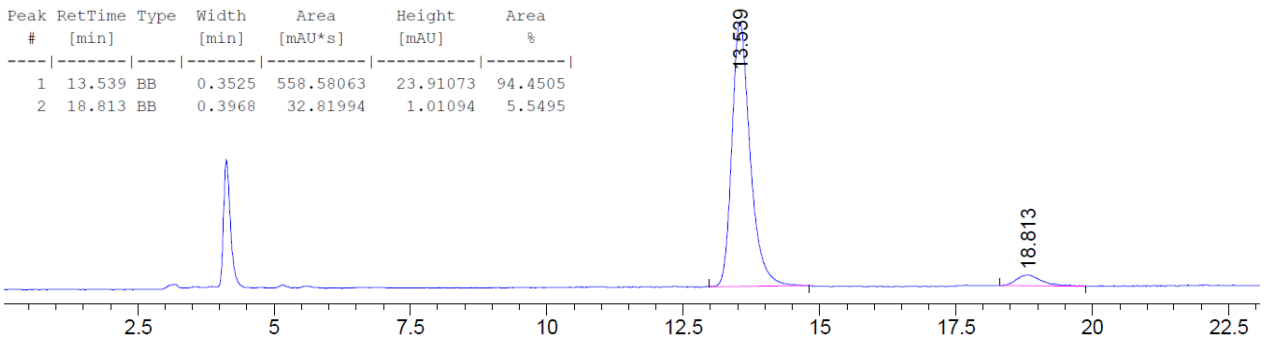
Yield: 26.5 mg, 82%; **Appearance**: yellow oil; $\mathbf{R_f}$: 0.1 (CH_2Cl_2); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.28 (d, *J* = 8.8 Hz, 2 H), 6.94 (d, *J* = 2.4 Hz, 1 H), 6.78–6.73 (m, 3 H), 6.69–6.65 (m, 1 H), 6.16 (s, 1 H), 5.12 (dd, *J* = 3.3, 5.9 Hz, 1 H), 3.30 (s, 3 H), 3.23 (s, 3 H), 2.37–2.29 (m, 1 H), 2.26–2.16 (m, 1 H), 2.08–1.97 (m, 1 H), 1.93–1.84 (m, 1 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 167.5, 160.4, 159.7, 141.1, 135.2, 134.9, 134.1, 129.3 (2 C), 125.3, 116.5, 114.2 (2 C), 104.6, 94.6, 65.0, 55.0, 54.7, 31.9, 21.1 ppm; **IR** (ATR): ν_{max} = 2995, 2923, 2836, 1728, 1670, 1610, 1511, 1490, 1385, 1319, 1245, 1174, 1031, 856, 814, 584, 553, 540, cm^{-1}; **HRMS** (Multimode): calculated for $[C_{20}H_{19}NO_3 + H]^{\bullet+}$: 322.1438, found: 322.1442; **$[\alpha]_D^{20}$**: 36 (c = 0.2, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 308 nm): t_R (major) = 13.5 min, t_R (minor) = 18.8 min, 94.5:5.5 er.

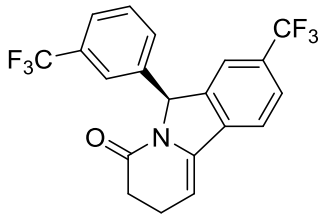
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.669	BB	0.3219	1065.99121	50.17023	50.4103
2	17.137	BB	0.4181	1048.64063	38.46162	49.5897



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.539	BB	0.3525	558.58063	23.91073	94.4505
2	18.813	BB	0.3968	32.81994	1.01094	5.5495



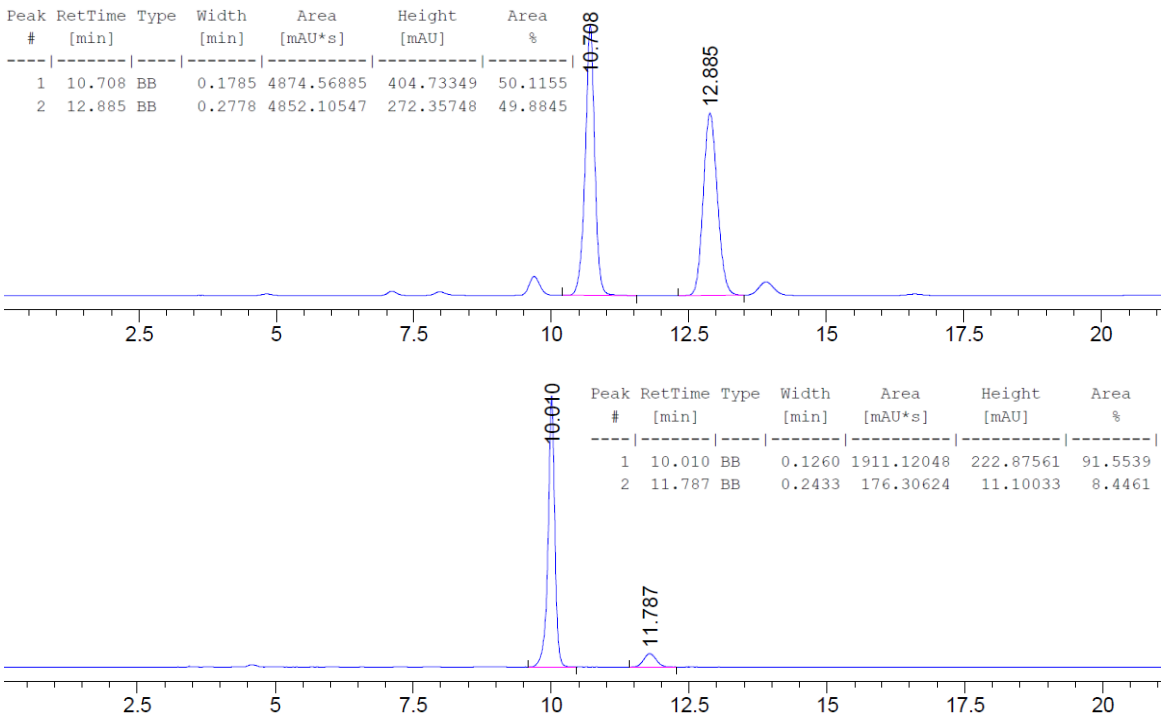
(*S*)-8-(trifluoromethyl)-6-(3-(trifluoromethyl)phenyl)-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one:



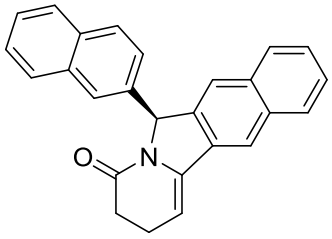
5h

Yield: 35.0 mg, 88%; **appearance**: colorless oil; **R_f**: 0.1 (pentane:EtOAc, 4:1); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.67 (d, *J* = 1.9 Hz, 1 H), 7.21 (d, *J* = 8.2 Hz, 1 H), 7.10–7.03 (m, 2 H), 6.92–6.89 (1 H), 6.80 – 6.76 (m, 1 H), 5.84 (s, 1 H), 5.03 (dt, *J* = 3.1, 6.1 Hz, 1H), 2.23–2.15 (m, 1 H), 2.08–2.03 (m, 1 H), 1.92–1.85 (m, 1 H), 1.82–1.76 (m, 1 H) ppm; **^{13}C{^{1}H} NMR** (201 MHz, C_6D_6): δ 167.4, 141.7, 139.4, 136.7, 131.4, 131.2, 130.7, 129.6, 128.4, 125.8 (q, *J* = 3.7 Hz), 125.4, 125.2 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 4.0 Hz), 124.0, 123.8, 121.3 (q, *J* = 4.0 Hz), 121.1, 97.7, 64.9, 31.2, 20.9 ppm; **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ -62.0, -62.3 ppm; **IR** (ATR): ν_{max} = 3367, 2923, 2852, 1741, 1684, 1436, 1384, 1327, 1283, 1164, 1121, 1073, 1063, 939, 919, 904, 838, 701, 662 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{20}H_{13}F_6NO + H]^+$: 398.0974, found: 398.0984; **$[\alpha]_D^{20}$**: 25 (c = 0.5, $CHCl_3$).

Chiral HPLC (Chiralpak IC, 4.6 x 250 mm; hexane:*i*-PrOH 90:10, 1.0 mL/min, 302 nm): t_R (major) = 10.0 min, t_R (minor) = 11.8 min, 91.6:8.4 er.



(*S*)-6-(naphthalen-2-yl)-2,6-dihydrobenzo[*f*]pyrido[2,1-*a*]isoindol-4(3*H*)-one:

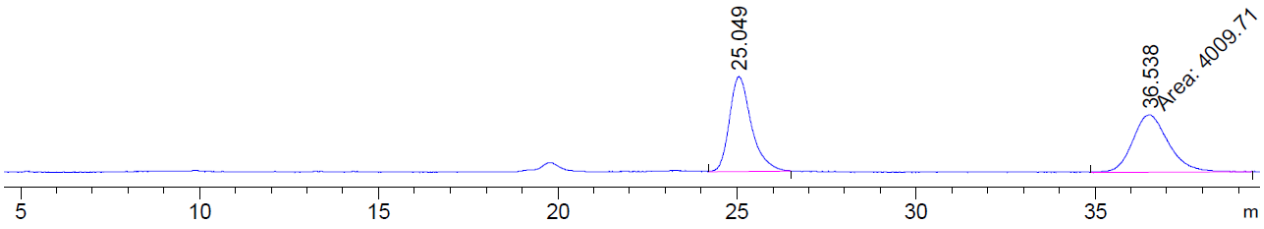


5i

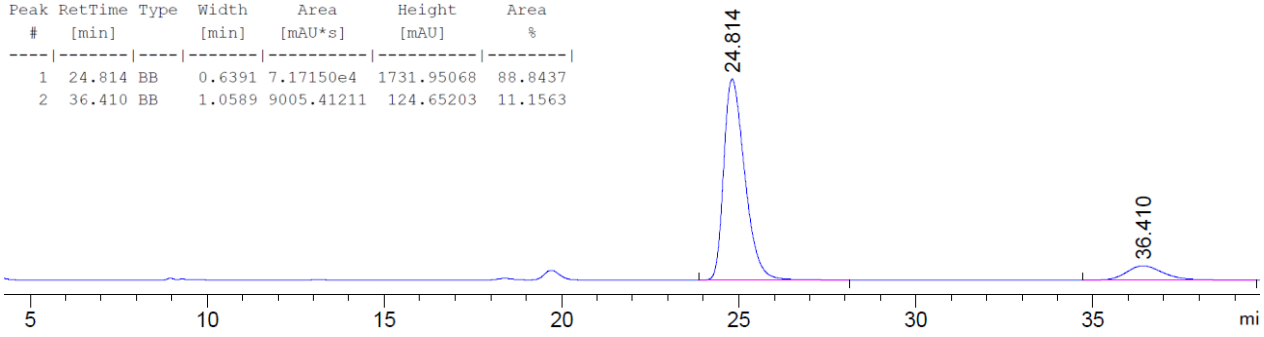
Yield: 26.5 mg, 73%; **appearance**: yellow oil; **R_f**: 0.2 (pentane:EtOAc, 4:1); **^{1}H NMR** (400 MHz, C_6D_6): δ 8.00–7.95 (m, 1 H), 7.79 (s, 1 H), 7.68–7.59 (m, 2 H), 7.57–7.48 (m, 2 H), 7.40–7.28 (m, 3 H), 7.26–7.18 (m, 4 H), 6.46 (s, 1 H), 5.39 (dd, *J* = 3.3, 5.9 Hz, 1 H), 2.41–2.33 (m, 1 H), 2.30–2.20 (m, 1 H), 2.17–2.06 (m, 1 H), 2.03–1.92 (m, 1 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 167.7, 140.6, 140.5, 139.7, 134.6, 133.9, 133.8, 133.6, 132.2, 128.9, 128.6, 128.5, 128.5, 127.6, 127.2, 126.50, 126.47, 126.4, 126.2, 125.2, 123.6, 119.3, 95.6, 65.6, 31.7, 21.2 ppm; **IR** (ATR): ν_{max} = 3347, 3055, 2966, 2925, 2854, 1730, 1702, 1637, 1509, 1453, 1374, 1341, 1318, 1267, 1214, 1171, 1143, 1126, 1040, 951, 919, 891, 859, 823, 758, 477 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{26}H_{19}NO + H]^{\bullet+}$: 362.1539, found: 362.1531; **$[\alpha]_D^{20}$**: 58 (c = 0.5, $CHCl_3$).

Chiral HPLC (Chiralpak ID, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 240 nm): t_R (major) = 25.0 min, t_R (minor) = 36.4 min, 88.8:11.2 er.

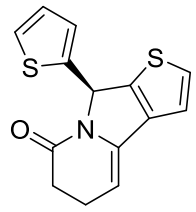
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.049	BB	0.5450	3959.76147	93.32450	49.6866
2	36.538	MM	1.1810	4009.70703	56.58869	50.3134



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.814	BB	0.6391	7.17150e4	1731.95068	88.8437
2	36.410	BB	1.0589	9005.41211	124.65203	11.1563



(*S*)-9-(thiophen-2-yl)-5,9-dihydrothieno[3,2-*a*]indolizin-7(6*H*)-one:

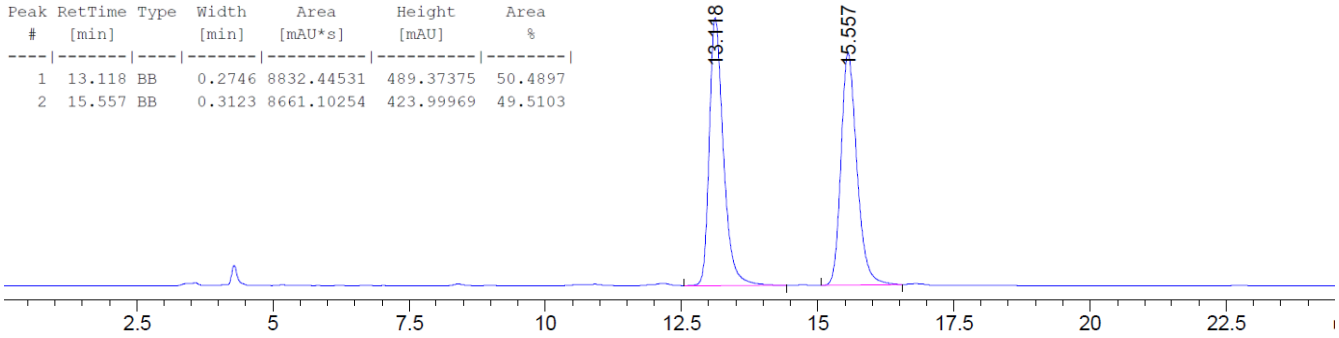


5j

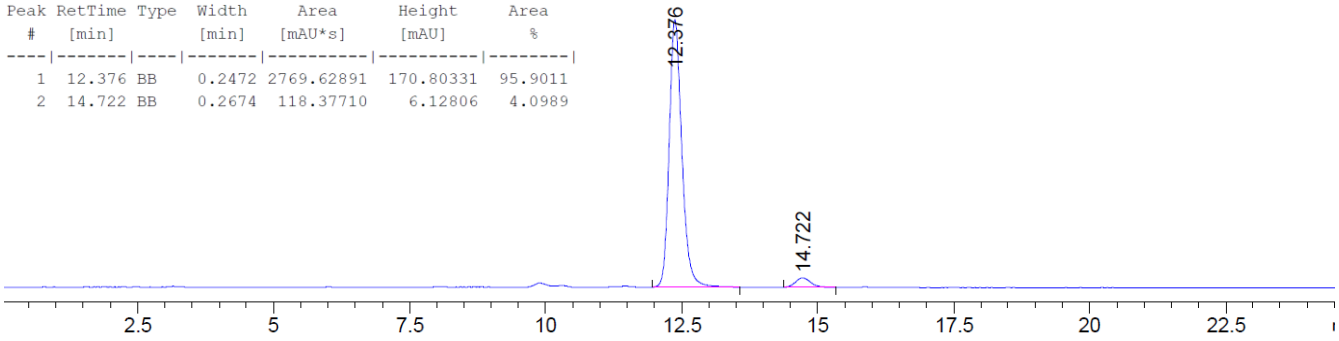
Yield: 16.0 mg, 59%; **appearance**: yellow oil; **R_f**: 0.3 (CH_2Cl_2); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.18–7.21 (m, 1 H), 6.76–6.70 (m, 2 H), 6.64 – 6.60 (m, 1 H), 6.59–6.55 (m, 1 H), 6.48 (s, 1 H), 4.84 (dd, J = 3.1, 6.1 Hz, 1 H), 2.30–2.21 (m, 1 H), 2.15–2.04 (m, 1 H), 1.95–1.82 (m, 1 H), 1.80–1.69 (m, 1 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 167.8, 143.7, 143.7, 139.8, 137.1, 131.2, 127.5, 126.7, 125.8, 118.2, 94.7, 59.1, 31.6, 20.7 ppm; **IR** (ATR): ν_{max} = 3101, 2955, 2917, 2896, 2848, 1727, 1667, 1597, 1537, 1464, 1403, 1374, 1318, 1292, 1208, 1117, 855, 756, 711, 672 cm^{-1}; **HRMS** (APPI): calculated for $[C_{14}H_{11}NOS_2 + H]^{\bullet+}$: 274.0355, found: 274.0365; **$[\alpha]_D^{20}$**: 5.0 (c = 1.0, $CHCl_3$).

Chiral HPLC (Chiralpak IF, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 276 nm): t_R (major) = 12.4 min, t_R (minor) = 14.7 min, 95.9:4.1 er.

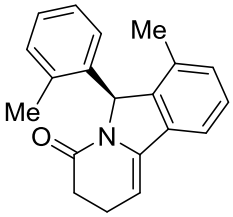
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.118	BB	0.2746	8832.44531	489.37375	50.4897
2	15.557	BB	0.3123	8661.10254	423.99969	49.5103



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.376	BB	0.2472	2769.62891	170.80331	95.9011
2	14.722	BB	0.2674	118.37710	6.12806	4.0989



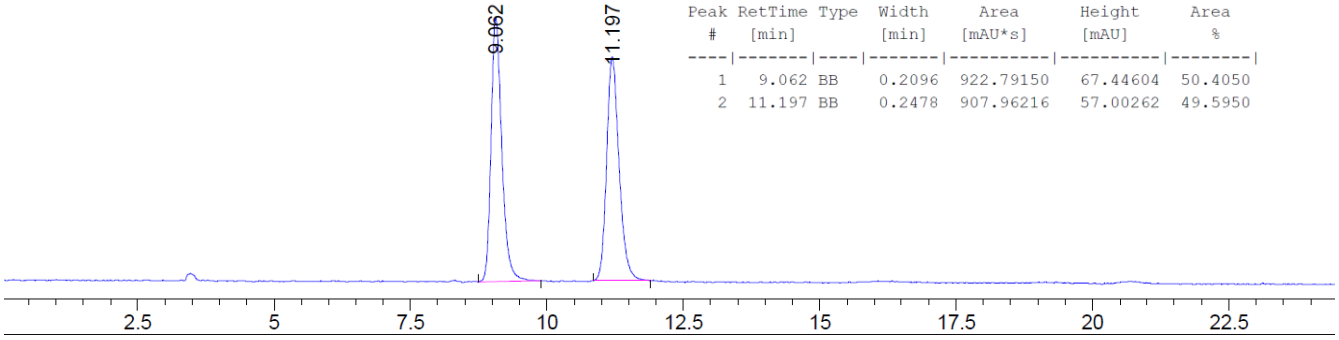
(*S*)-6-(*o*-tolyl)-2,3,6,11-tetrahydro-4*H*-pyrido[1,2-*b*]isoquinolin-4-one:



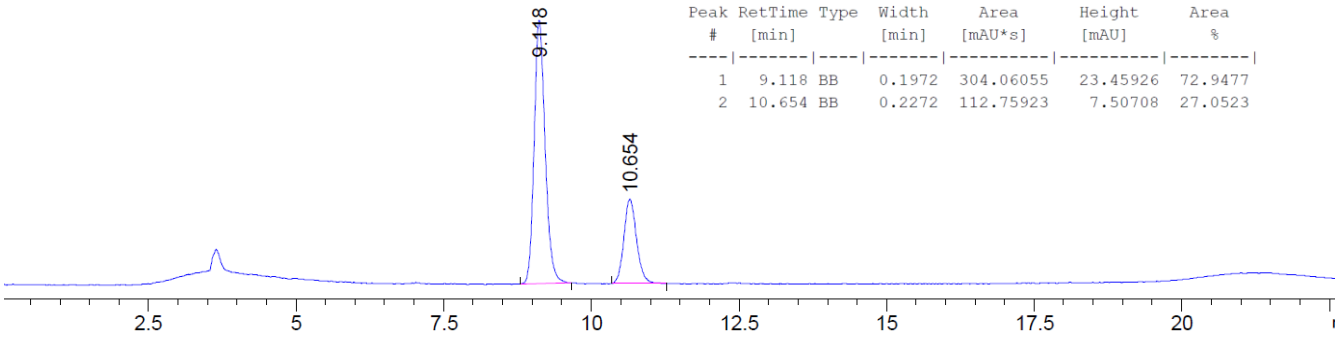
5k

Yield: 18.0 mg, 62%; **appearance**: colorless oil; **R_f**: 0.5 (pentane:EtOAc, 4:1); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.18 (d, *J* = 7.3 Hz, 1 H), 7.07–6.69 (m, 6 H), 6.10 (s, 1 H), 5.18 (dd, J = 3.6, 5.6 Hz, 1 H), 2.76 (br. s, 3 H), 2.27–2.10 (m, 2 H), 2.03–1.82 (m, 2 H), 1.64 (s, 3 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 167.1, 141.4, 138.5, 137.4, 134.13, 133.9, 130.7, 130.6, 128.5, 128.2, 127.9, 127.7 126.6, 117.8, 94.3, 60.1, 31.7, 21.1, 19.9, 18.0 ppm; **IR** (ATR): ν_{max} = 3018, 2946, 2900, 2841, 1732, 1681, 1670, 1485, 1463, 1384, 1354, 1321, 1308, 1208, 1140, 1108, 957, 777, 744, 726, 677, 621, 541, 501, 486, 469 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{20}H_{19}NO + H]^+$: 290.1539, found: 290.1541; **$[\alpha]_D^{20}$**: 19.2 (c = 0.2, $CHCl_3$).

Chiral HPLC (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 95:5, 1.0 mL/min, 288 nm): t_R (major) = 9.1 min, t_R (minor) = 10.7 min, 73:27 er.

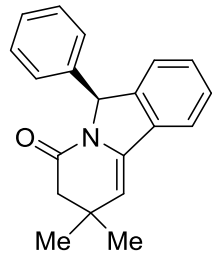


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.062	BB	0.2096	922.79150	67.44604	50.4050
2	11.197	BB	0.2478	907.96216	57.00262	49.5950



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.118	BB	0.1972	304.06055	23.45926	72.9477
2	10.654	BB	0.2272	112.75923	7.50708	27.0523

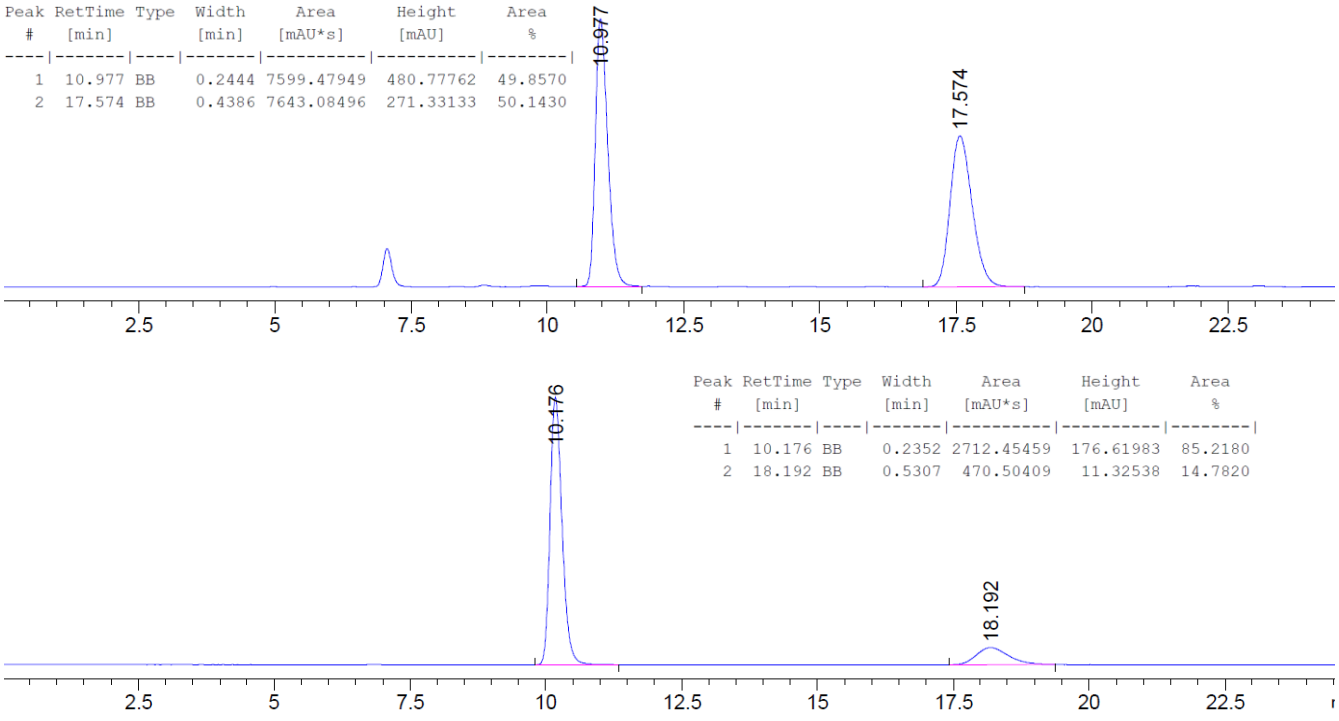
(*S*)-2,2-dimethyl-6-phenyl-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one:



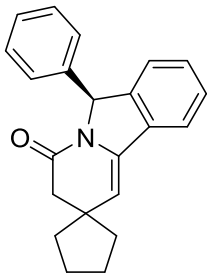
5l

Yield: 22.0 mg, 76%; **appearance**: yellow oil; **R_f**: 0.25 (CH_2Cl_2); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.31–7.21 (m, 3 H), 7.12–7.04 (m, 2 H), 7.03–6.96 (m, 2 H), 6.92 – 6.87 (m, 1 H), 6.78–6.74 (m, 1 H), 6.07 (s, 1 H), 5.18 (d, *J* = 1.0 Hz, 1 H), 2.36–2.16 (m, 2 H), 0.93 (s, 3 H), 0.92 (s, 3 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 167.0, 143.0, 141.8, 139.0, 133.3, 129.3, 128.8 (2 C), 128.4 (2 C), 127.5 (2 C), 124.3, 120.5, 105.8, 65.7, 46.8, 32.8, 29.2, 27.6 ppm; **IR** (ATR): ν_{max} = 3061, 3030, 2955, 2927, 2867, 1731, 1680, 1602, 1494, 1466, 1455, 1371, 1303, 1217, 1142, 961, 936, 750, 729, 697, 549 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{20}H_{19}NO + H]^+$: 290.1539, found: 290.1543; **$[\alpha]_D^{20}$**: 8.3 (c = 0.5, $CHCl_3$).

Chiral HPLC (Chiralpak ID, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 306 nm): t_R (major) = 10.2 min, t_R (minor) = 18.2 min, 85.2:14.8 er.



(*S*)-6'-phenyl-6'H-spiro[cyclopentane-1,2'-pyrido[2,1-*a*]isoindol]-4'(3'*H*)-one:

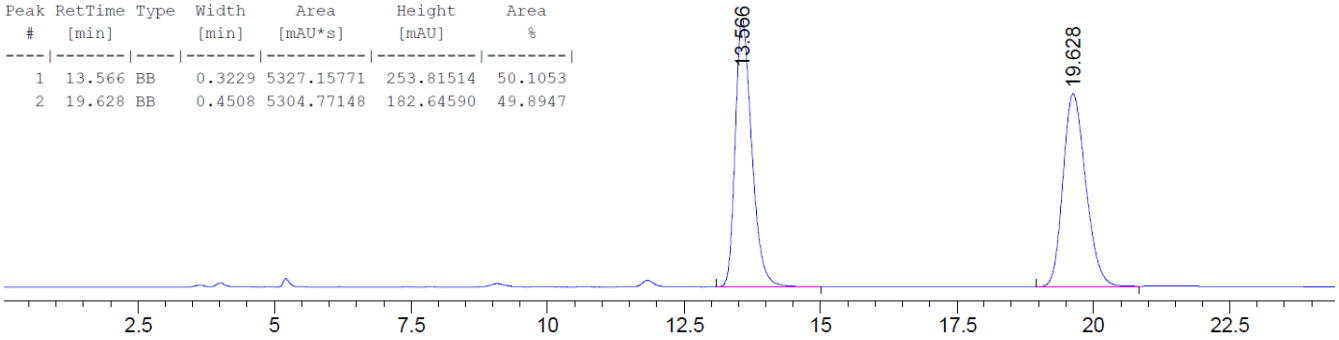


5m

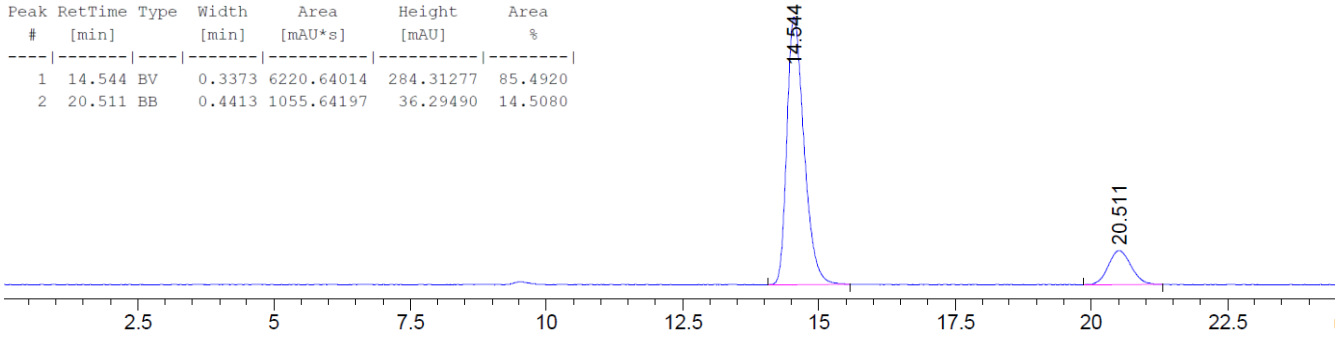
Yield: 24 mg, 83%; **appearance**: yellow oil; **R_f**: 0.3 (CH_2Cl_2); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.30–7.21 (m, 3 H), 7.12–7.06 (m, 2 H), 7.05–6.96 (m, 2 H), 6.93–6.87 (m, 1 H), 6.82–6.72 (m, 1 H), 6.09 (s, 1 H), 5.34 (s, 1 H), 2.46–2.27 (m, 2 H), 1.58–1.28 (m, 8 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 167.1, 142.9, 141.8, 139.4, 133.3, 129.3, 128.8 (2 C), 128.4 (2 C), 127.4 (2 C), 124.3, 120.5, 105.4, 65.7, 44.2, 43.9, 39.8, 39.0, 24.1, 23.9 ppm; **IR** (ATR): ν_{max} = 3058, 3030, 2952, 2874, 1679, 1493, 1467, 1454, 1375, 1302, 1188, 1145, 1113, 955, 750, 697, 542 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{22}H_{21}NO + H]^+$: 316.1696, found: 316.1702; **$[\alpha]_D^{20}$**: 5.3 (c = 0.5, $CHCl_3$).

Chiral HPLC (Chiralpak ID, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 286 nm): t_R (major) = 14.5 min, t_R (minor) = 20.5 min, 85.5:14.5 er.

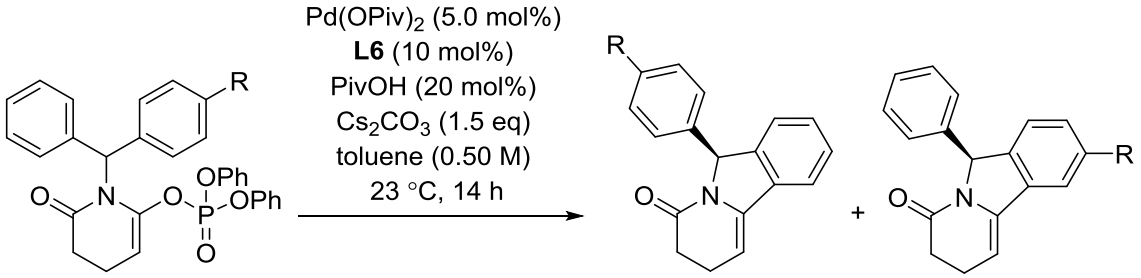
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.566	BB	0.3229	5327.15771	253.81514	50.1053
2	19.628	BB	0.4508	5304.77148	182.64590	49.8947



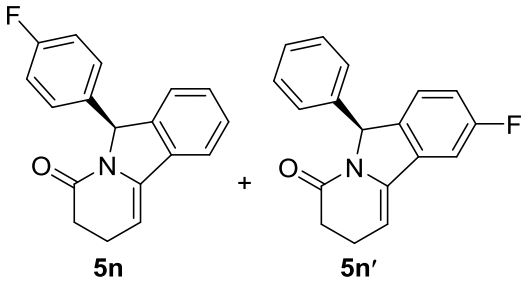
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.544	BV	0.3373	6220.64014	284.31277	85.4920
2	20.511	BB	0.4413	1055.64197	36.29490	14.5080



Parallel kinetic resolution



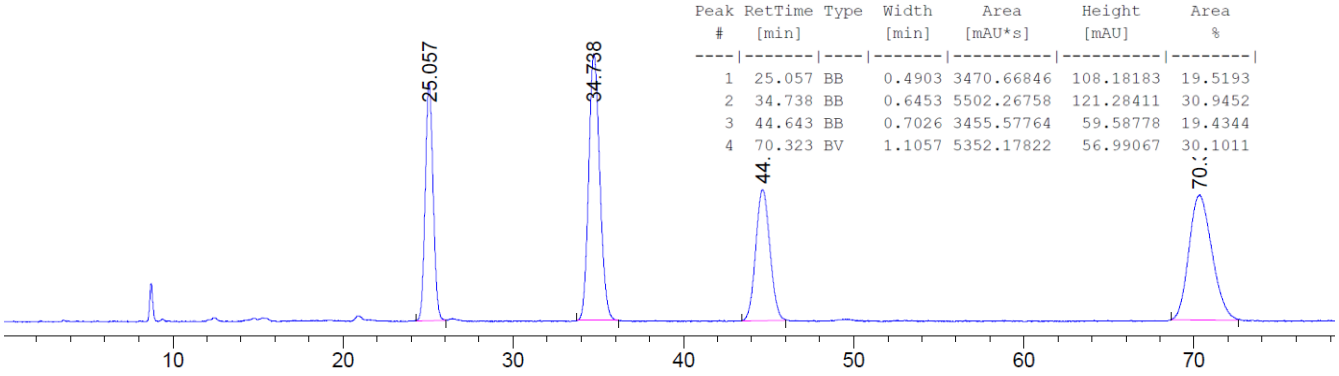
(*S*)-6-(4-fluorophenyl)-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one and (S)-9-fluoro-6-phenyl-2,6-dihydropyrido[2,1-a]isoindol-4(3H)-one



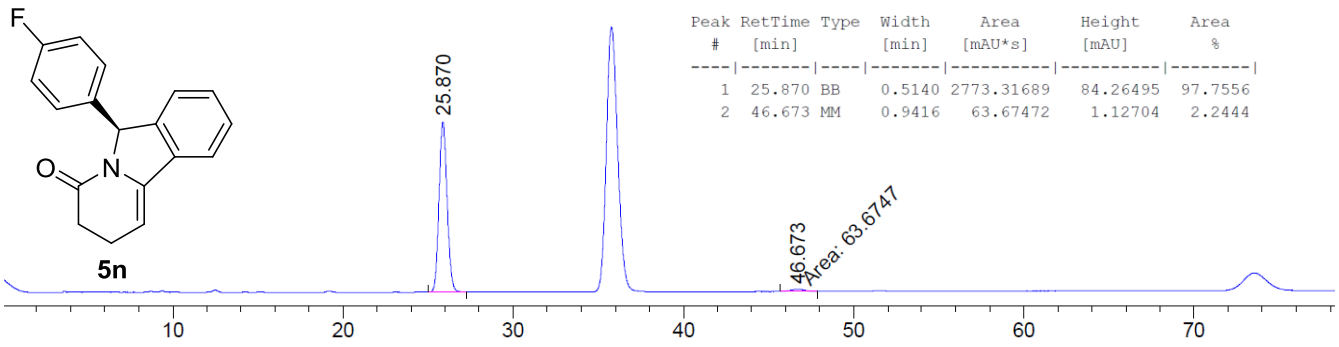
Following general procedure **GP1** (p. 27) column chromatography on phosphate-buffered silica gel delivered a mixture of **5n** and **5n′** in 90% combined yield (25.0 mg) and 1:1.3 ratio.

Appearance: yellow oil; **^{1}H NMR** (400 MHz, C_6D_6): 7.25–7.17 (m, 3.7 H), 7.13–6.97 (m, 7.5 H), 6.96–6.84 (m, 2.7 H), 6.76–6.66 (m, 3.2 H), 6.60–6.54 (m, 1.3 H), 6.48–6.43 (m, 1.3 H), 5.99 (s, 1 H), 5.95 (s, 1.3 H), 5.14 (dd, *J* = 3.3, 5.8 Hz, 1.0 H), 4.96 (dd, *J* = 3.4, 5.8 Hz, 1.3 H), 2.34–1.74 (m, 10 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 167.6, 167.3, 164.1, 163.51, 162.47, 142.1, 141.4, 140.8, 140.3, 140.2, 137.98, 137.96, 137.43, 137.41, 135.32, 135.26, 133.4, 129.62, 129.56, 129.3, 128.8, 128.4, 127.6, 125.91, 125.85, 124.2, 120.4, 116.7, 116.5, 115.6, 115.5, 107.1, 107.0, 95.9, 94.8, 65.3, 65.0, 31.7, 31.5, 21.02, 20.96 ppm; **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ -114.2, -114.7 ppm.

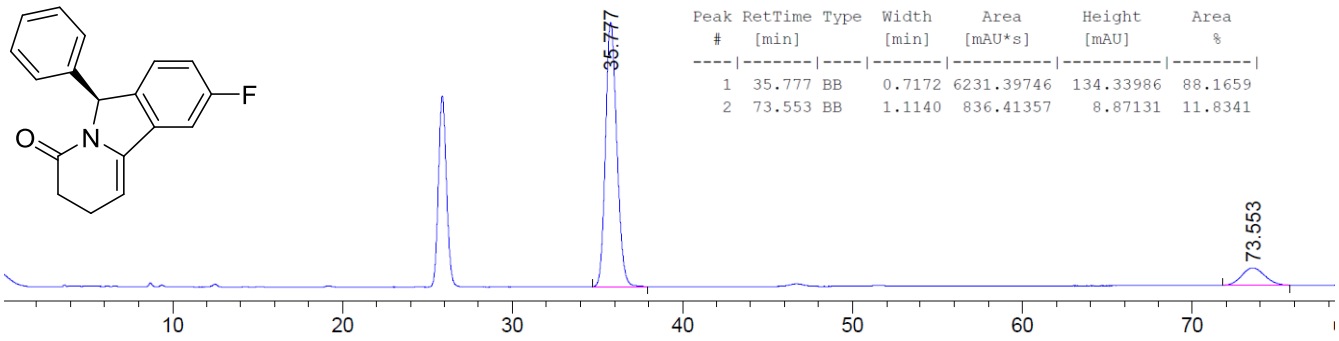
Chiral HPLC (Chiralpak IC, 4.6 x 250 mm; hexane:*i*-PrOH 90:10, 1.0 mL/min, 310 nm), **5n**: t_R (major) = 25.9 min, t_R (minor) = 46.7 min, 97.5:2.5 er; **5n′**: t_R (major) = 35.8 min, t_R (minor) = 73.6 min, 88.2:11.8 er.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.057	BB	0.4903	3470.66846	108.18183	19.5193
2	34.738	BB	0.6453	5502.26758	121.28411	30.9452
3	44.643	BB	0.7026	3455.57764	59.58778	19.4344
4	70.323	BV	1.1057	5352.17822	56.99067	30.1011

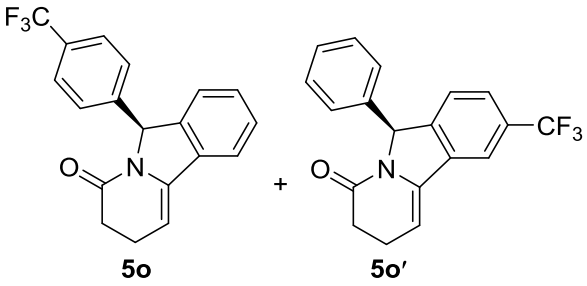


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.870	BB	0.5140	2773.31689	84.26495	97.7556
2	46.673	MM	0.9416	63.67472	1.12704	2.2444



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.777	BB	0.7172	6231.39746	134.33986	88.1659
2	73.553	BB	1.1140	836.41357	8.87131	11.8341

(*S*)-6-phenyl-9-(trifluoromethyl)-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one and (*S*)-6-(4-(trifluoromethyl)phenyl)-2,6-dihydropyrido[2, 1-*a*]isoindol-4(3*H*)-one

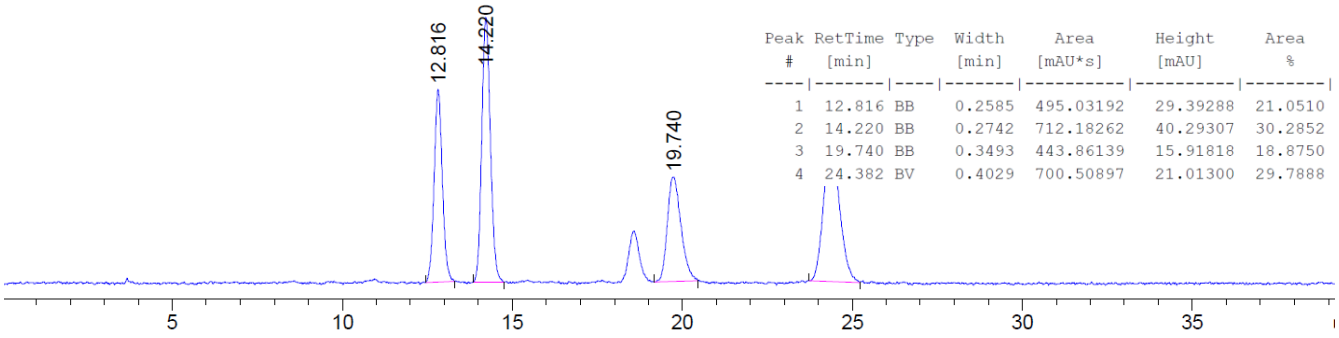


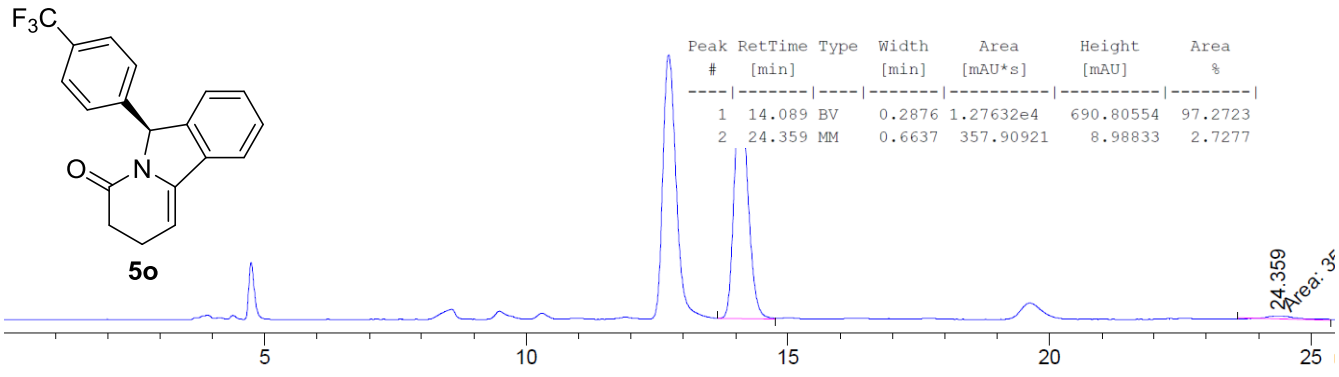
5o **5o′**

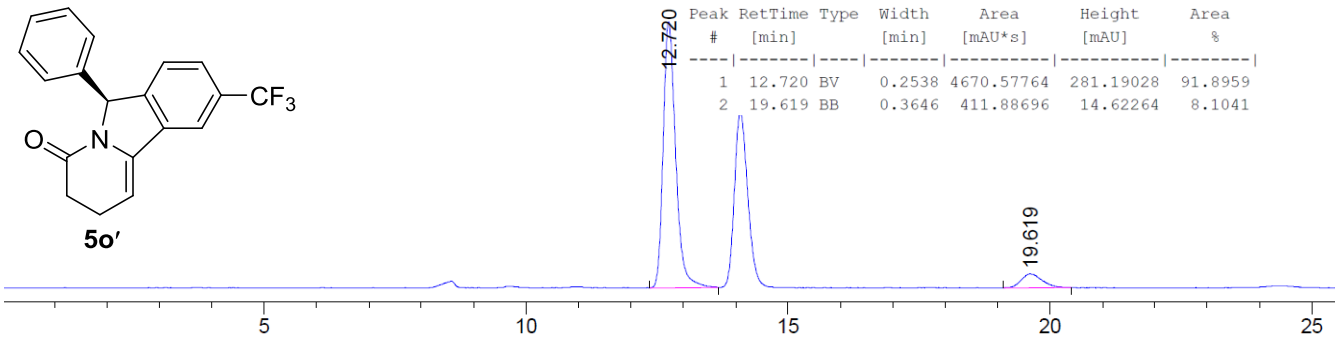
Following general procedure **GP1** (p. 27) column chromatography on phosphate-buffered silica gel delivered a mixture of **5o** and **5o′** in 96% combined yield (31.5 mg) and 1:1.1 ratio.

Appearance: yellow oil; a 1:2.1 mixture of **5o**:**5o′** was submitted to characterization: **^{1}H NMR** (400 MHz, C_6D_6): 7.55–7.49 (m, 2.1 H), 7.27 (d, *J* = 8.0 Hz, 2.1 H), 7.18 (d, *J* = 7.9 Hz, 1.5 H), 7.13 (d, *J* = 1.4 Hz, 3.1 H), 7.10–7.04 (m, 8.2 H), 7.03–6.97 (m, 3.1 H), 6.89 (td, *J* = 1.3, 7.5 Hz, 1 H), 6.66–6.61 (m, 1 H), 6.55–6.48 (m, 2.1 H), 5.94 (s, 3.1 H), 5.13 (dd, J = 3.3, 5.9 Hz, 1 H), 4.91 (dd, J = 3.4, 5.9 Hz, 2.1 H), 2.35–1.70 (m, 13.3 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 167.5, 167.3, 145.6, 145.4, 141.5, 140.8, 140.7, 139.6, 134.1, 133.4, 131.0, 130.7, 130.5, 130.3, 130.0, 129.8, 129.4, 128.9, 128.43, 128.35, 127.6, 125.92, 125.89, 125.87, 125.84, 125.79, 125.77, 125.74, 125.72, 125.0, 124.1, 123.9, 120.5, 117.59, 117.56, 96.5, 95.0, 65.6, 65.1, 31.51, 31.46, 21.1, 20.9 ppm; **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ -62.0, -62.2 ppm.

Chiral HPLC (Chiralpak ID, 4.6 x 250 mm; hexane:*i*-PrOH 90:10, 1.0 mL/min, 290 nm), **5o**: t_R (major) = 14.1 min, t_R (minor) = 24.4 min, 97.3:2.7 er; **5o′**: t_R (major) = 12.7 min, t_R (minor) = 19.6 min, 91.9:8.1 er.

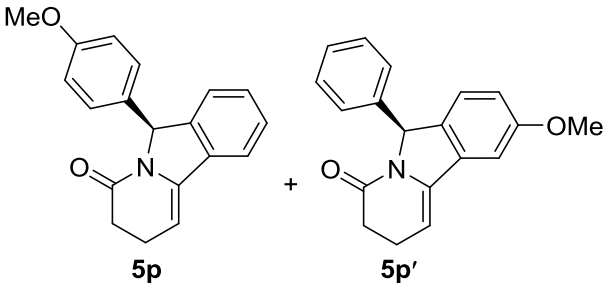






Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.720	BV	0.2538	4670.57764	281.19028	91.8959
2	19.619	BB	0.3646	411.88696	14.62264	8.1041

(*S*)6-(4-methoxyphenyl)-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one and (*S*)-9-methoxy-6-phenyl-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one

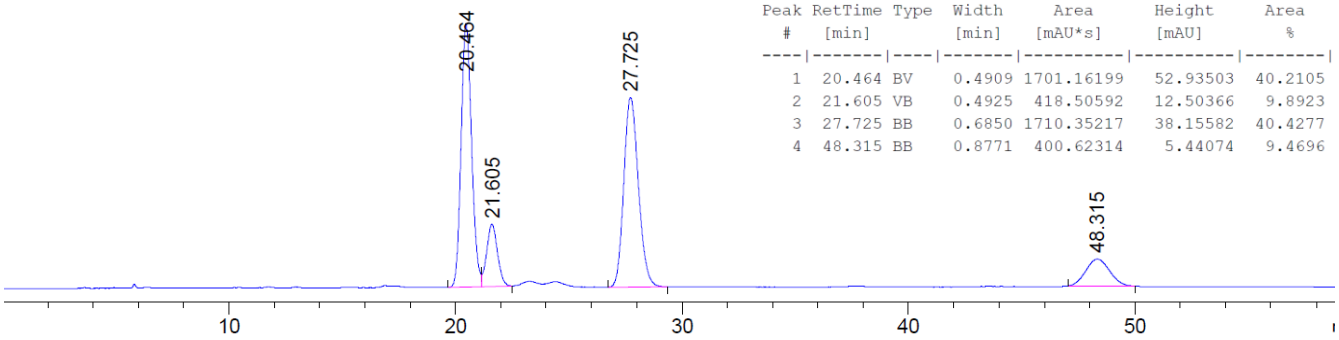


5p **5p′**

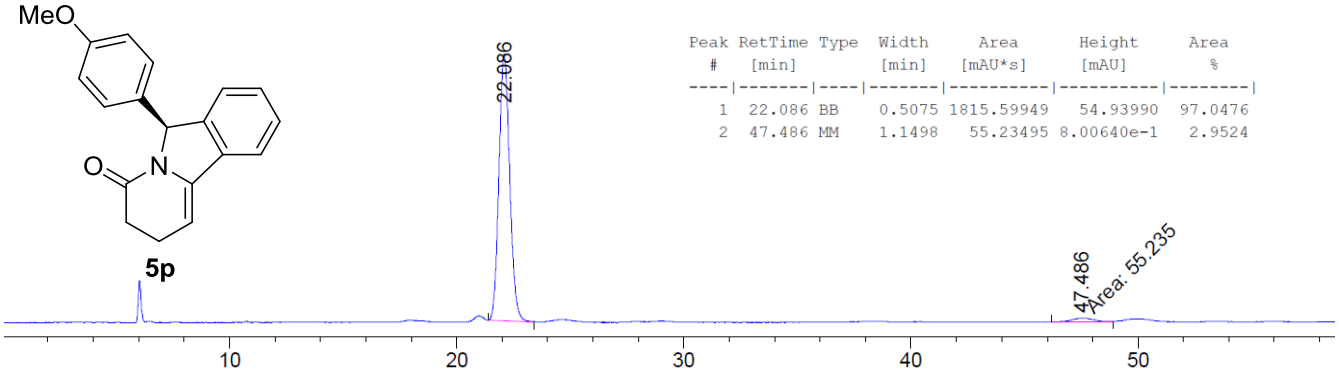
Following general procedure **GP1** (p. 27) column chromatography on phosphate-buffered silica gel delivered a mixture of **5p** and **5p′** in 93% combined yield (27.0 mg) and 1:1.1 ratio.

Appearance: yellow oil; a 1:1.4 mixture of **5o**:**5o′** was submitted to characterization **^{1}H NMR** (400 MHz, C_6D_6): 7.35–7.30 (m, 2.9 H), 7.25–7.20 (m, 3.4 H), 7.14–7.09 (m, 3.2 H), 7.05–6.99 (m, 2.6 H), 6.98–6.91 (m, 2.6 H), 6.85–6.81 (m, 1 H), 6.74–6.59 (m, 5.1 H), 6.14 (s, 1 H), 6.11 (s, 1.4 H), 5.16 (dd, *J* = 3.4, 5.9 Hz, 1 H), 5.11 (dd, J = 3.4, 5.9 Hz, 1.4 H), 3.28 (s, 4.2 H), 3.22 (s, 3 H), 2.38–1.81 (m, 10 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 167.6, 167.5, 160.4, 159.7, 142.8, 142.1, 141.2, 141.0, 135.0, 134.8, 133.8, 133.5, 129.2, 129.2, 128.7, 127.8, 127.6, 125.3, 124.4, 116.5, 114.2, 104.7, 94.7, 94.6, 65.4, 55.0, 54.7, 31.8, 31.7, 21.1, 21.0 ppm.

Chiral HPLC (Chiralpak IG, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 310 nm), **5p**: t_R (major) = 22.1 min, t_R (minor) = 47.5 min, 97.0:3.0 er; **5p′**: t_R (major) = 20.8 min, t_R (minor) = 27.6 min, 92.3:7.7 er.

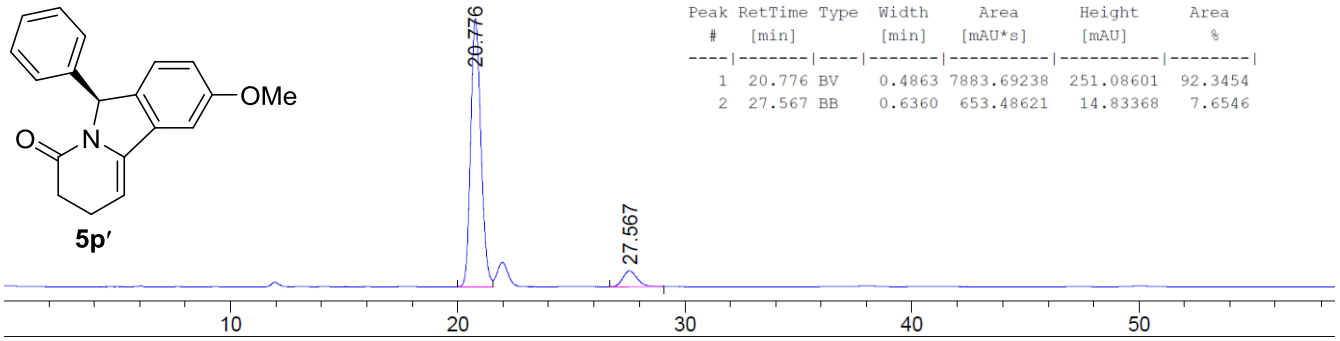


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.464	BV	0.4909	1701.16199	52.93503	40.2105
2	21.605	VB	0.4925	418.50592	12.50366	9.8923
3	27.725	BB	0.6850	1710.35217	38.15582	40.4277
4	48.315	BB	0.8771	400.62314	5.44074	9.4696



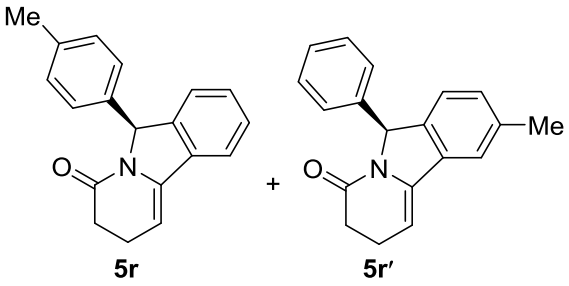
5p

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.086	BB	0.5075	1815.59949	54.93990	97.0476
2	47.486	MM	1.1498	55.23495	8.00640e-1	2.9524



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.776	BV	0.4863	7883.69238	251.08601	92.3454
2	27.567	BB	0.6360	653.48621	14.83368	7.6546

(*S*)-6-(*p*-tolyl)-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one and (*S*)-9-methyl-6-phenyl-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one

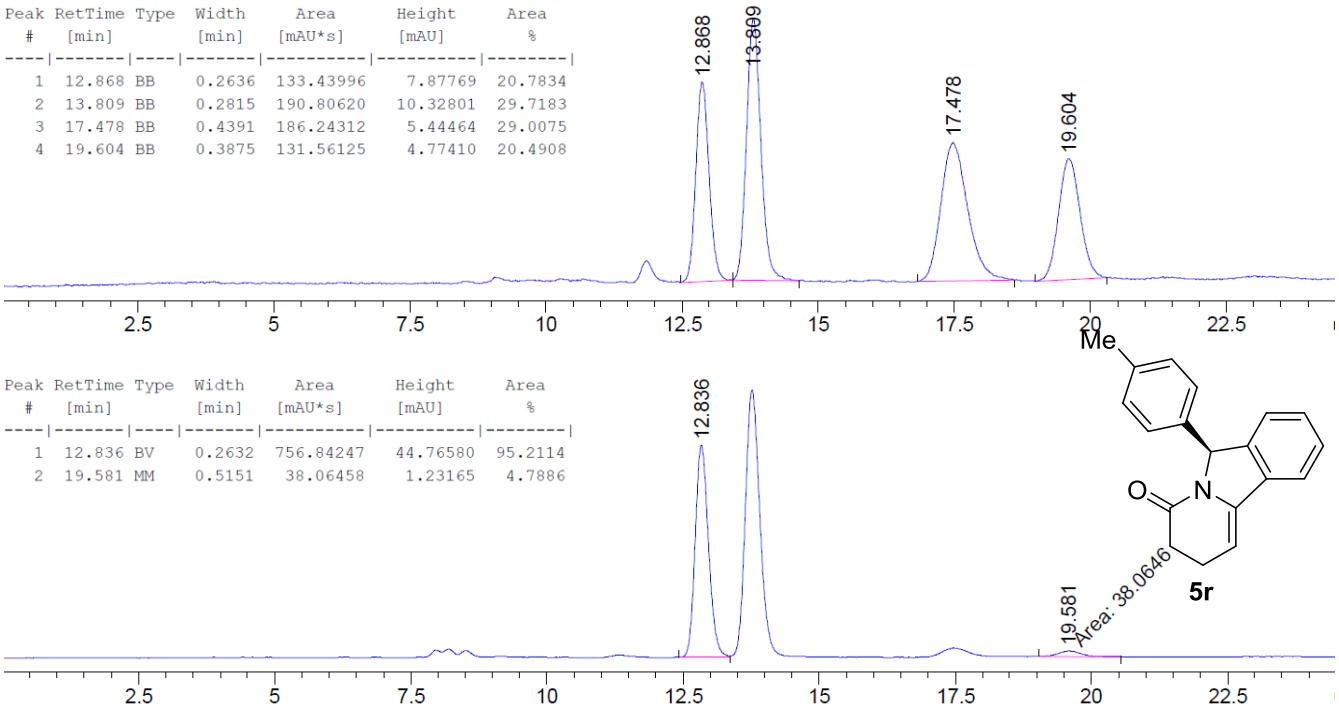


5r **5r′**

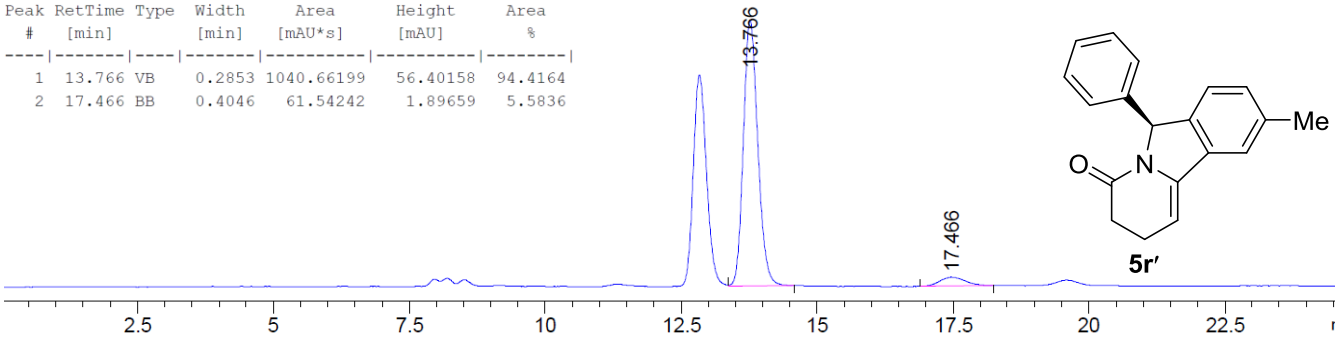
Following general procedure **GP1** (p. 27) column chromatography on phosphate-buffered silica gel delivered a mixture of **5r** and **5r′** in 94% combined yield (26.0 mg) and 1:1.1 ratio.

Appearance: yellow oil; **^{1}H NMR** (400 MHz, C_6D_6): 7.34–7.28 (m, 2.1 H), 7.24–7.20 (m, 3.2 H), 7.14–7.06 (m, 3.5 H), 7.04–6.97 (m, 2.5 H), 6.97–6.89 (m, 3.3 H), 6.84–6.79 (m, 1.1 H), 6.77–6.66 (m, 2.2 H), 6.13 (s, 2.1 H), 5.20 (dd, *J* = 3.3, 5.8 Hz, 1.1 H), 5.16 (dd, J = 3.4, 5.9 Hz, 1 H), 2.36–1.84 (m, 16.9 H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 167.54, 167.50, 142.7, 142.0, 141.20, 141.1, 139.9, 138.9, 137.8, 137.3, 133.6, 133.5, 130.4, 129.5, 129.2, 128.7, 128.4, 127.7, 124.4, 124.1, 120.7, 120.4, 94.5, 94.3, 65.69, 65.66, 31.8, 21.3, 21.08, 21.06 ppm.

Chiral HPLC (Chiralpak ID, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 314 nm), **5r**: t_R (major) = 12.8 min, t_R (minor) = 19.6 min, 95.2:4.8 er; **5p′**: t_R (major) = 13.8 min, t_R (minor) = 17.5 min, 94.4:5.6 er.

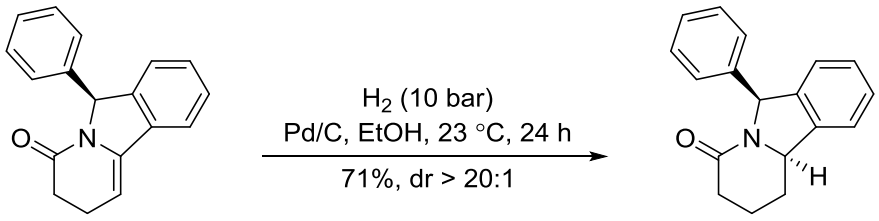


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.766	VB	0.2853	1040.66199	56.40158	94.4164
2	17.466	BB	0.4046	61.54242	1.89659	5.5836



5r′

Synthetic transformations of product 5a



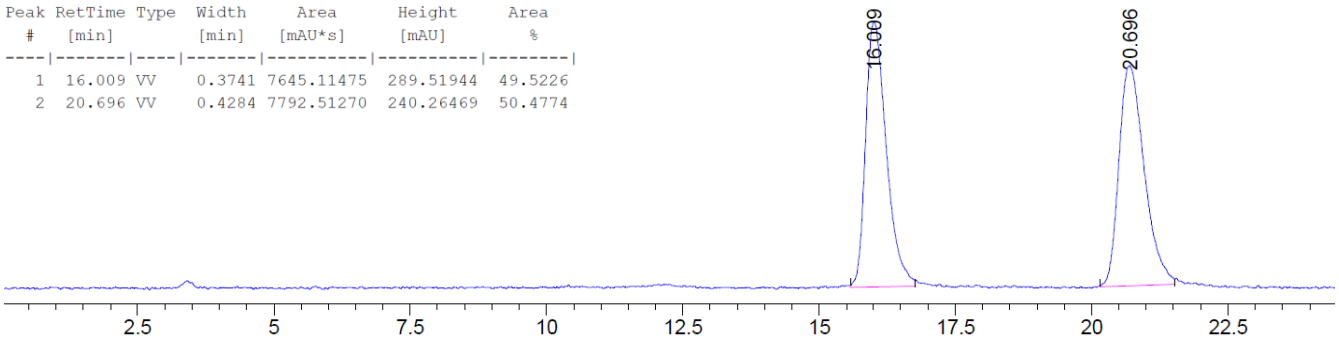
5a
98:2 er

6a
98:2 er

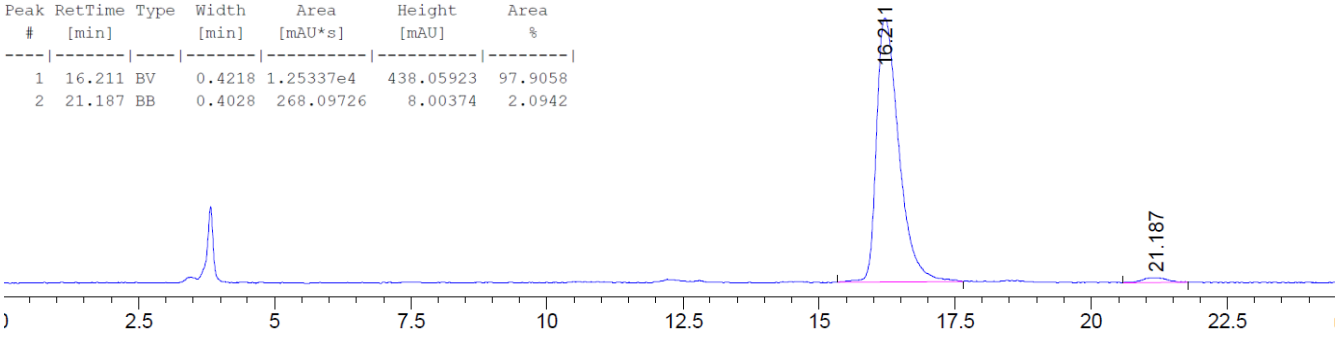
To a 5 mL microwave vial equipped with a stir bar and open to air were added (*S*)-6-phenyl-2,6-dihydropyrido[2,1-*a*]isoindol-4(3*H*)-one (**5a**) (39.0 mg, 150 µmol, 1.0 eq) and Pd/C 10%wt (16.0 mg, 15.0 µmol, 10 mol%). The tube was placed in an autoclave and the reaction mixture was kept stirring under pressure of H_2 (10 bar) for 24 h at 23 °C. The mixture was filtered through celite (eluting with EtOAc) and concentrated under reduced pressure. Purification by silica gel chromatography (pentane:EtOAc, 1:1 → pure EtOAc) afforded (6*S*,10b*R*)-6-phenyl-2,3,6,10b-tetrahydropyrido[2,1-*a*]isoindol-4(1*H*)-one (28.0 mg, 106 µmol, 71%) as a white solid. **R_f**: 0.3 (EtOAc); **m.p.**: 125.1–126.7 °C; **^{1}H NMR** (400 MHz, C_6D_6): δ 7.28–7.20 (m, 2 H), 7.18–7.12 (m, 2 H), 7.11–6.99 (m, 2 H), 6.95–6.82 (m, 2 H), 6.75–6.70 (m, 1 H), 5.93 (s, 1 H), 4.29–4.18 (m, 1 H), 2.14–1.94 (m, 2 H), 1.87–1.71 (m, 1 H), 1.48–1.22 (m, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 168.6, 143.0, 142.0, 140.0, 128.5 (2 C), 128.2, 127.9 (2 C), 127.4, 124.7, 121.6, 67.0, 62.3, 32.0, 29.0, 20.2 ppm; **IR** (ATR): ν_{max} = 3389, 3055, 3029, 2948, 2870, 1650, 1589, 1461, 1407, 1325, 1261, 1200, 1144, 1099, 1073, 1055, 1028, 932, 800, 747, 698 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{18}H_{17}NO + H]^{\bullet+}$: 264.1383, found: 264.1377; **$[\alpha]_D^{20}$**: 5.8 (c = 1.0, $CHCl_3$).

Chiral HPLC (Chiralpak IF, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 208 nm): t_R (major) = 16.2 min, t_R (minor) = 21.2 min, 97.9:2.1 er.

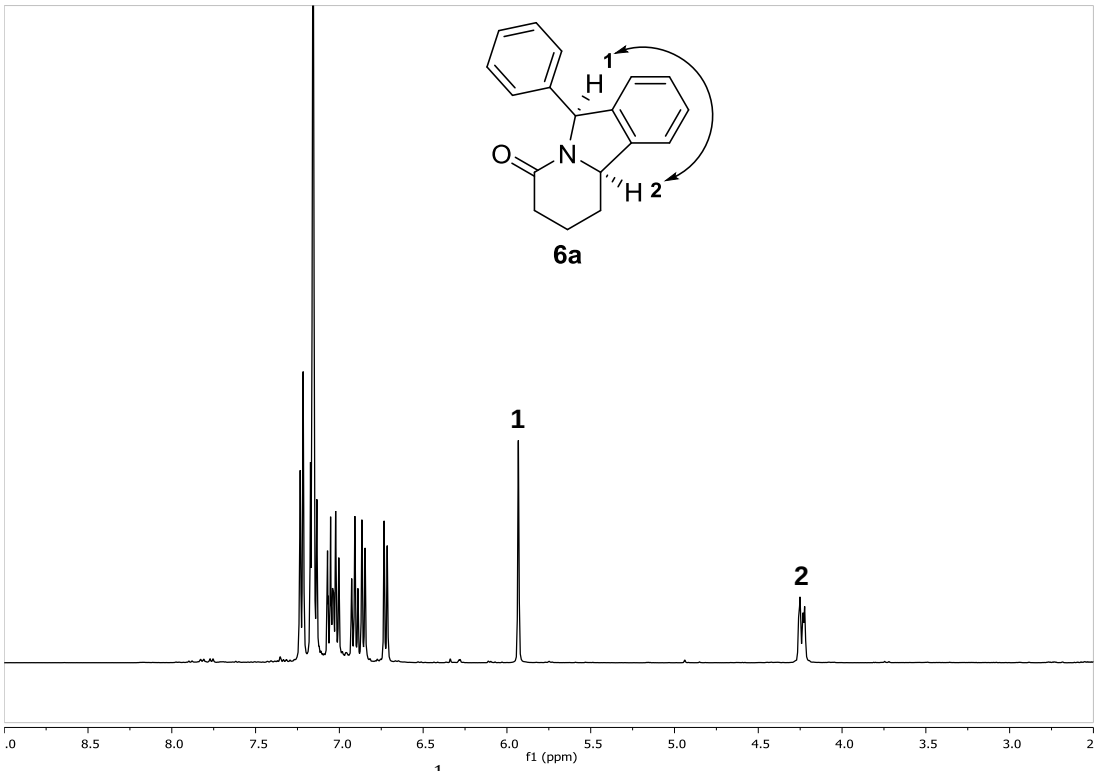
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.009	VV	0.3741	7645.11475	289.51944	49.5226
2	20.696	VV	0.4284	7792.51270	240.26469	50.4774



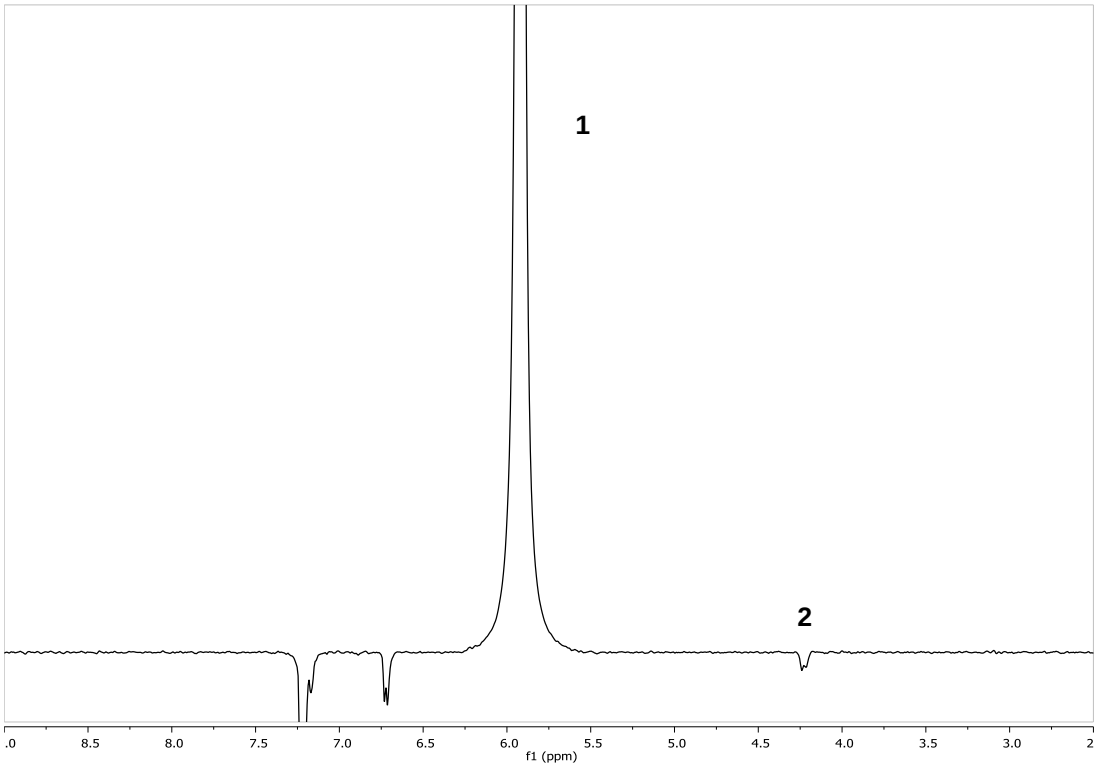
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.211	BV	0.4218	1.25337e4	438.05923	97.9058
2	21.187	BB	0.4028	268.09726	8.00374	2.0942



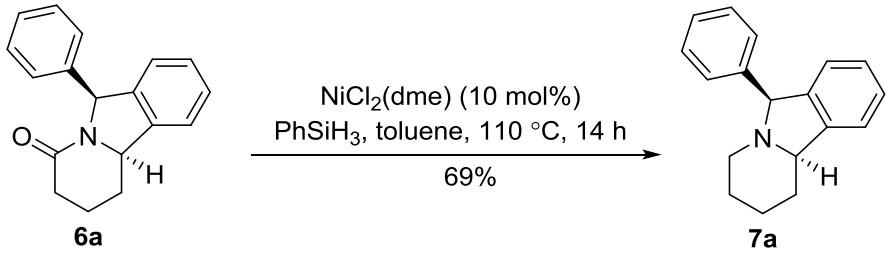
Determination of stereoconfiguration of 6a by 1D NOE spectroscopy



9.0–2.5 ppm fragment of ^{1}H NMR spectrum (C_6D_6, 400 MHz) of **6a.**



1D NOE spectrum of **6a**, irradiation at the frequency of H-1.



6a **7a**

Prepared according to a slight modification of the procedure reported by Garg.[3] A 0.2–0.5 mL microwave vial vial equipped with a stir bar was charged with (6*S*,10b*R*)-6-phenyl-2,3,6,10b-tetrahydropyrido[2,1-*a*]isoindol-4(1*H*)-one (**6a**) (12.0 mg, 46.0 μmol, 1.0 eq) and $NiCl_2$(dme) (1.0 mg, 4.56 μmol, 10 mol%), and the vial was flushed with N_2. $PhSiH_3$ (11 μL, 91.0 μmol, 2 eq) was added under a N_2 atmosphere followed by toluene (90 μL, 0.5 M). The vial was sealed, placed in a pre-heated aluminum block and allowed to stir at 110 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered through celite and concentrated under reduced pressure. Purification by silica gel chromatography (pentane:EtOAc, 4:1) afforded (6*S*,10b*R*)-6-phenyl-1,2,3,4,6,10*b*-hexahydropyrido[2,1-*a*]isoindole (8.0 mg, 32.0 μmol, 70%) as colorless oil along with an unindentified impurity. $\mathbf{R}_f$: 0.2 (pentane:EtOAc, 4:1); **^{1}H NMR** (400 MHz, C_6D_6): δ 7.43–7.39 (m, 2 H), 7.23–7.19 (m, 2 H), 7.11–7.05 (m, 3 H), 7.00–6.96 (m, 1 H), 6.81–6.77 (m, 1 H), 4.38 (d, *J* = 3.4 Hz, 1 H), 3.31–3.26 (m, 1 H), 2.89–2.83 (m, 1H), 2.28–2.17 (m, 1 H), 2.11–2.02 (m, 1 H), 1.75–1.70 (m, 1 H), 1.67–1.60 (m, 1H), 1.55–1.46 (m, 1 H), 1.42–1.37 (m, 1 H), 1.30–1.21 (m, 1 H) ppm; **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6): δ 145.0, 143.5, 141.7, 135.7, 128.9 (2 C), 128.3, 128.1, 126.7, 126.6, 122.8, 120.0, 72.3, 66.9, 48.7, 29.1, 26.0, 24.5 ppm; **IR** (ATR): ν_{max} = 3025, 2932, 2851, 2775, 2737, 2702, 2171, 2148, 1955, 1601, 1457, 1377, 1350, 1300, 1283, 1248, 1124, 1081, 1027, 842, 739, 699 cm^{-1}; **HRMS** (Multimode): calculated for $[C_{18}H_{19}NO + H]^{\bullet+}$: 250.1590, found: 250.1575; $\mathbf{[\alpha]_D^{20}}$: 32 (c = 0.6, $CHCl_3$).

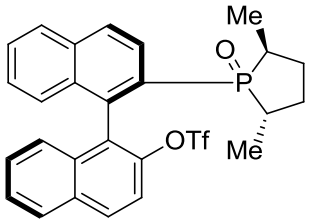
References

1. Hamada, T.; Chieffi, A.; Åhman, J.; Buchwald, S. L., *J. Am. Chem. Soc.* **2002**, *124*, 1261–1268.

2. Donets, P. A.; Cramer, N., *J. Am. Chem. Soc.* **2013**, *135*, 11772–11775.

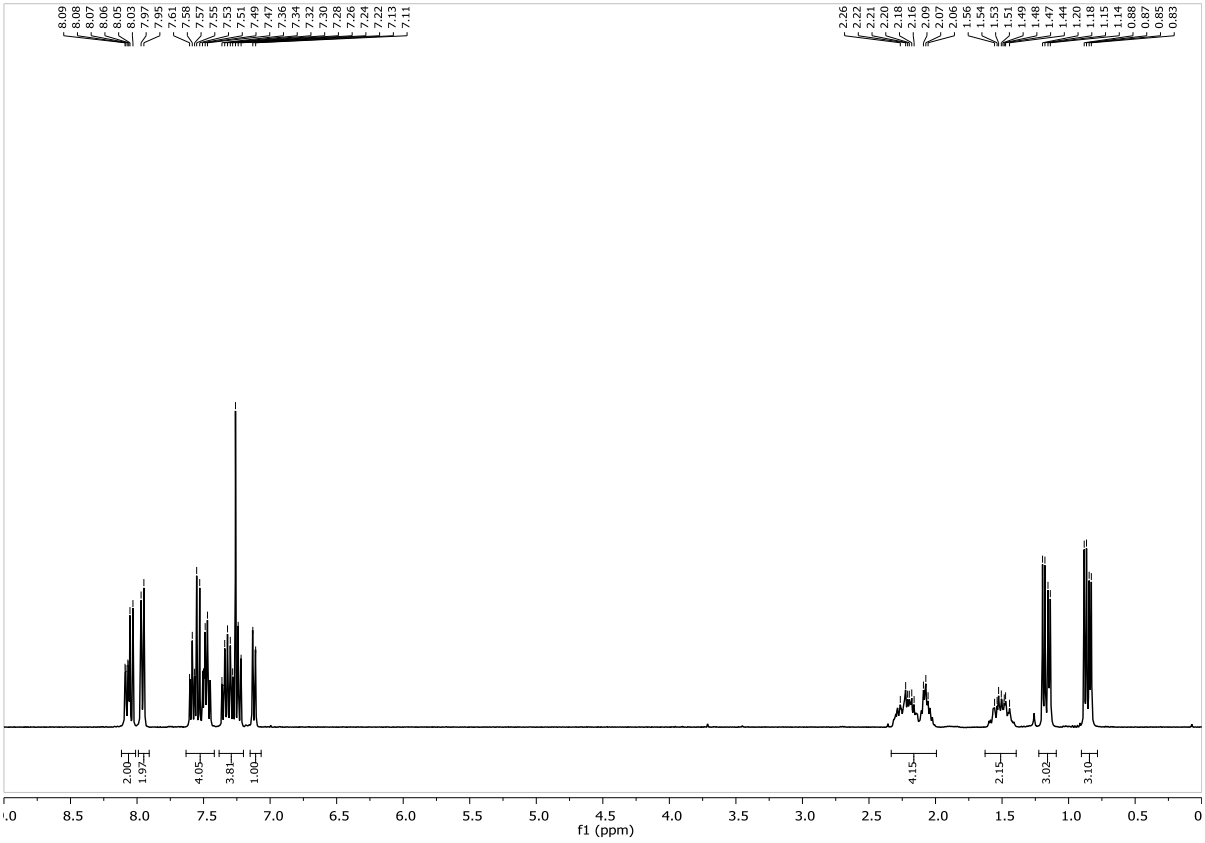
3. Simmons, B. J.; Hoffmann, M.; Hwang, J.; Jackl, M. K.; Garg, N. K., *Org. Lett.* **2017**, *19*, 1910–1913.

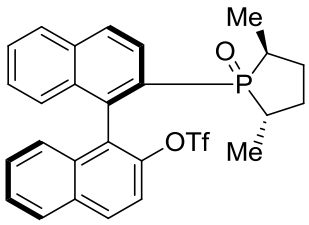
NMR Spectra



S1

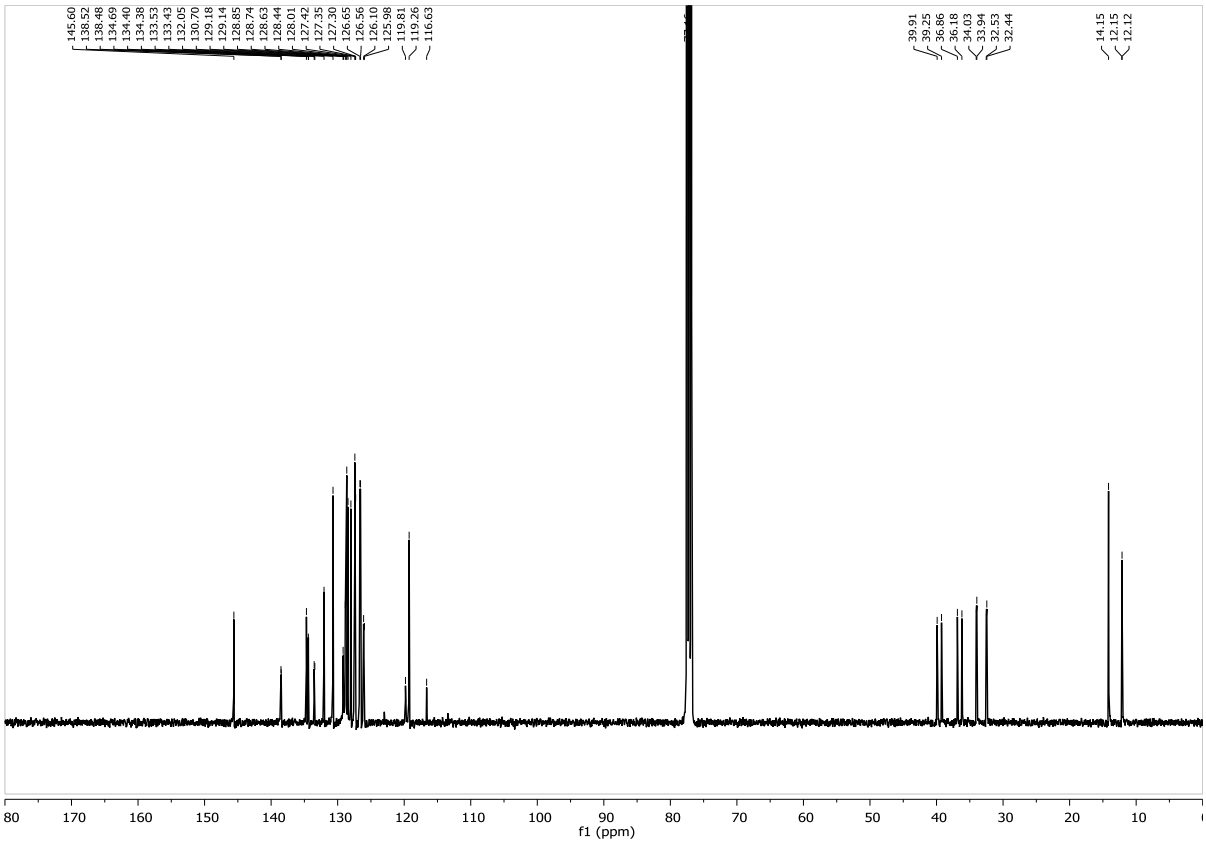
^{1}H NMR, 400 MHz, $CDCl_3$

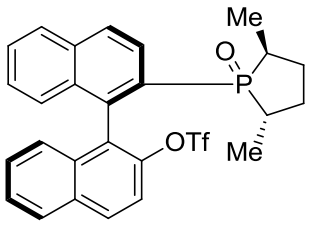




S1

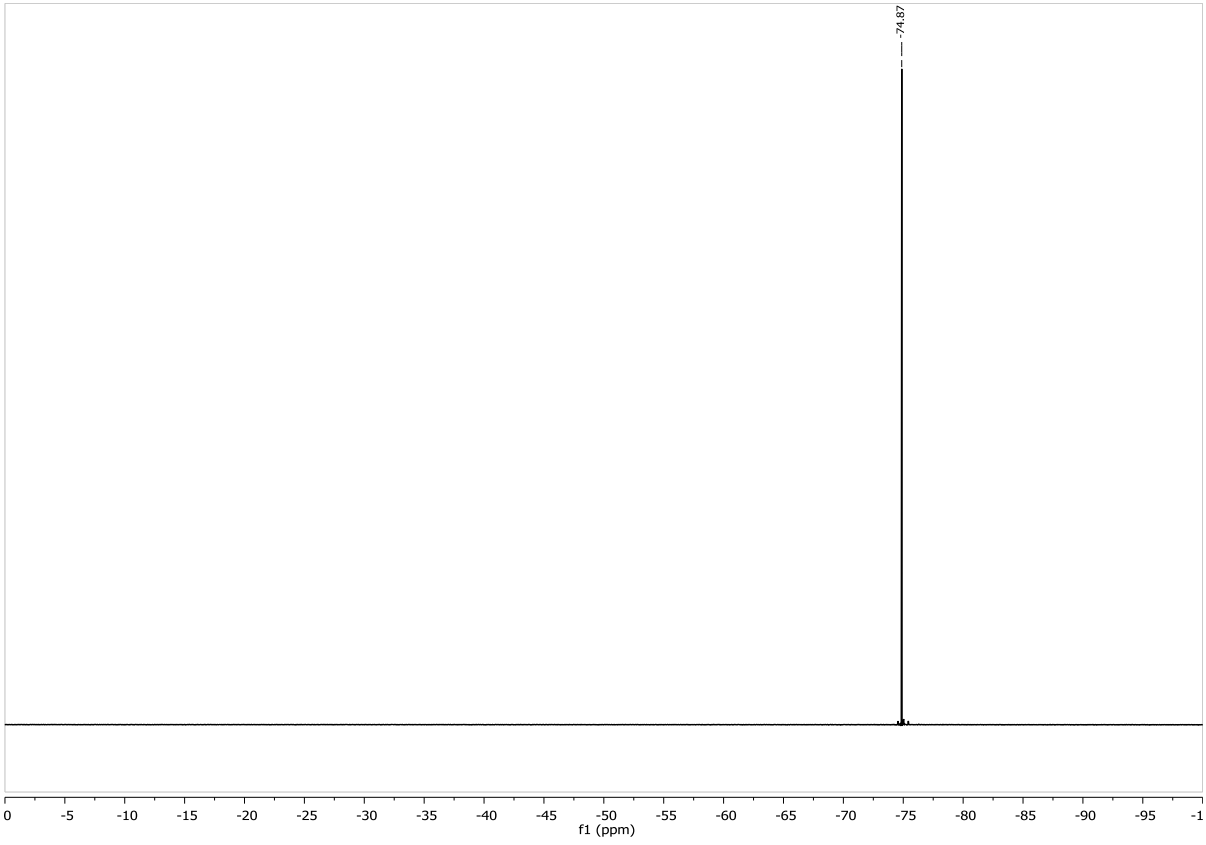
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

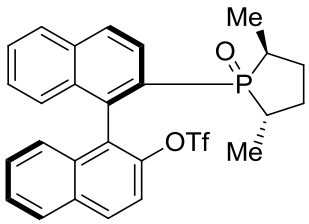




S1

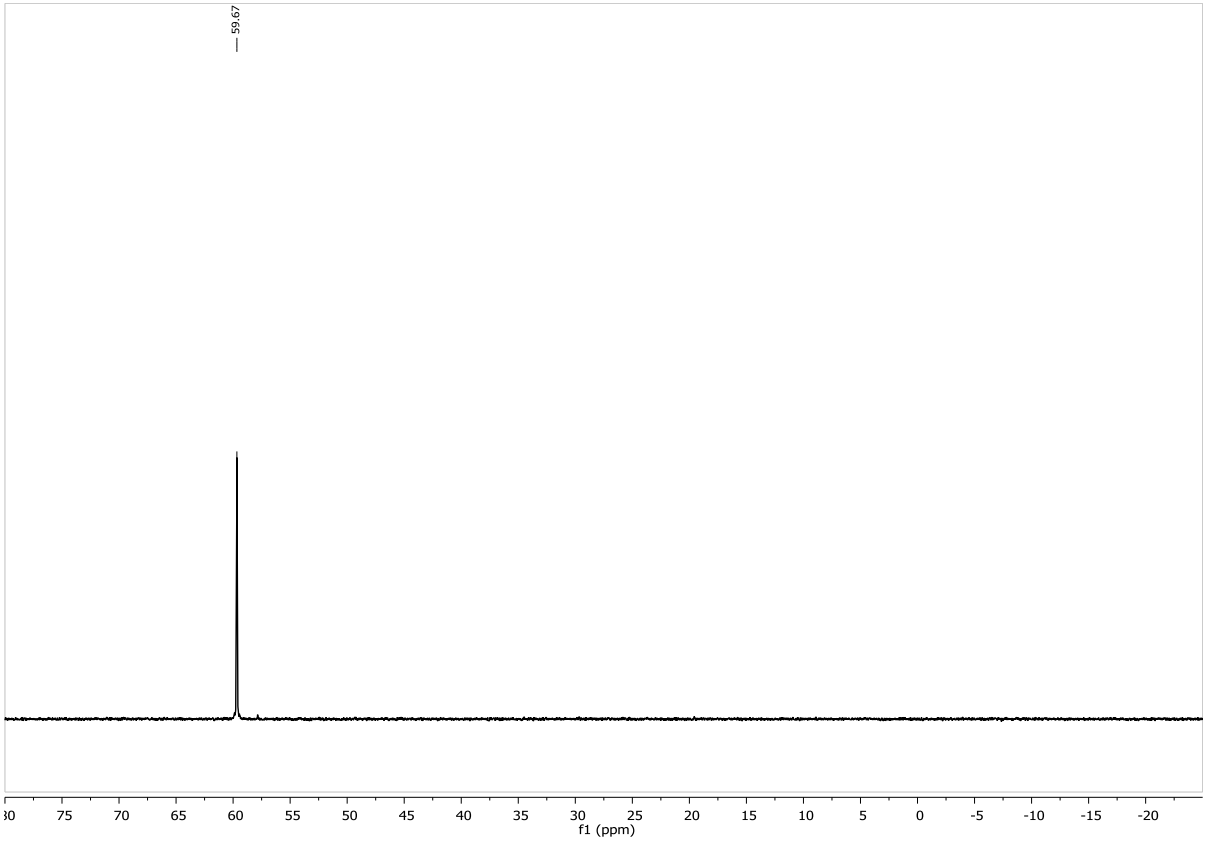
$^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

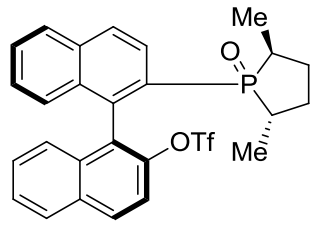




S1

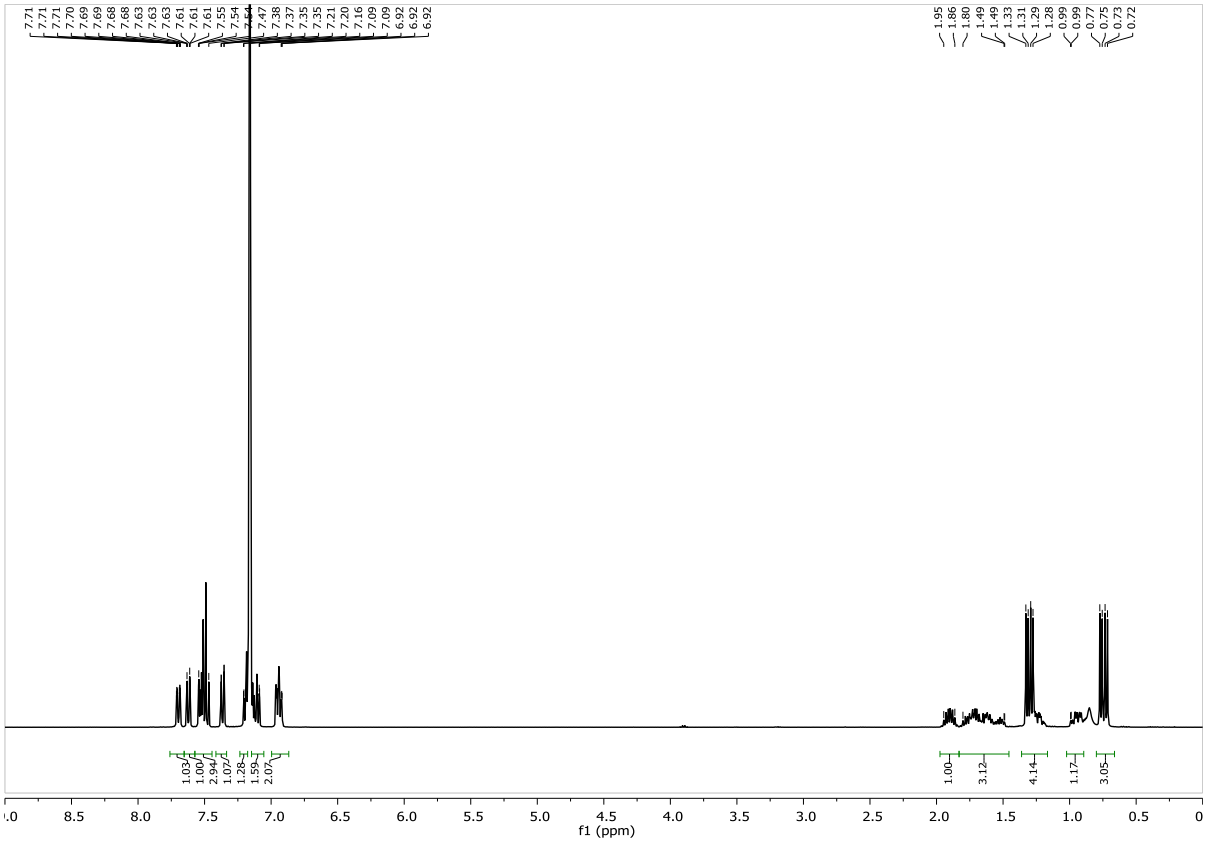
$^{31}P\{^{1}H\}$ NMR, 162 MHz, $CDCl_3$

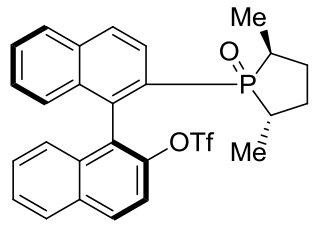




S2

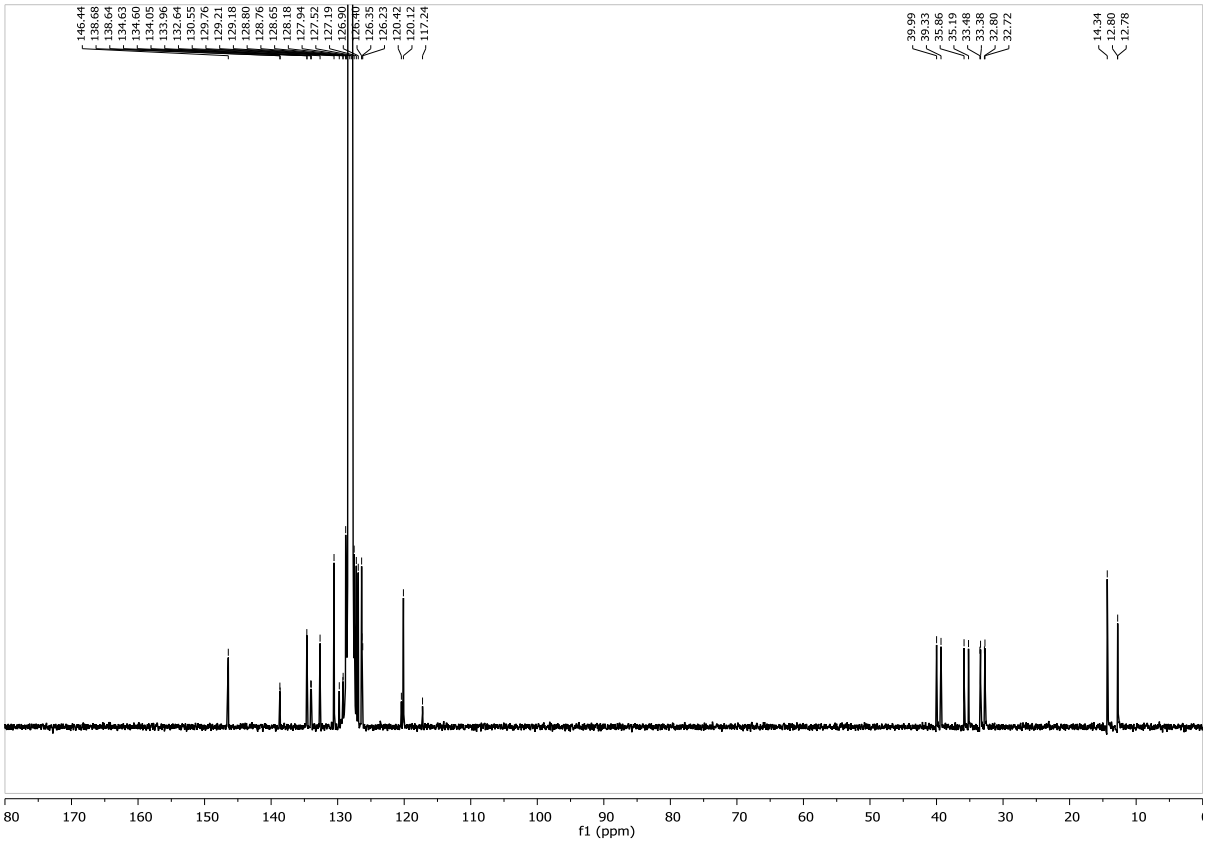
^{1}H NMR, 400 MHz, C_6D_6

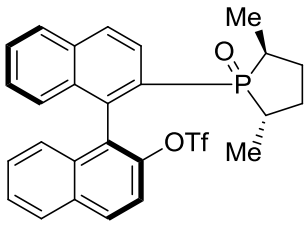




S2

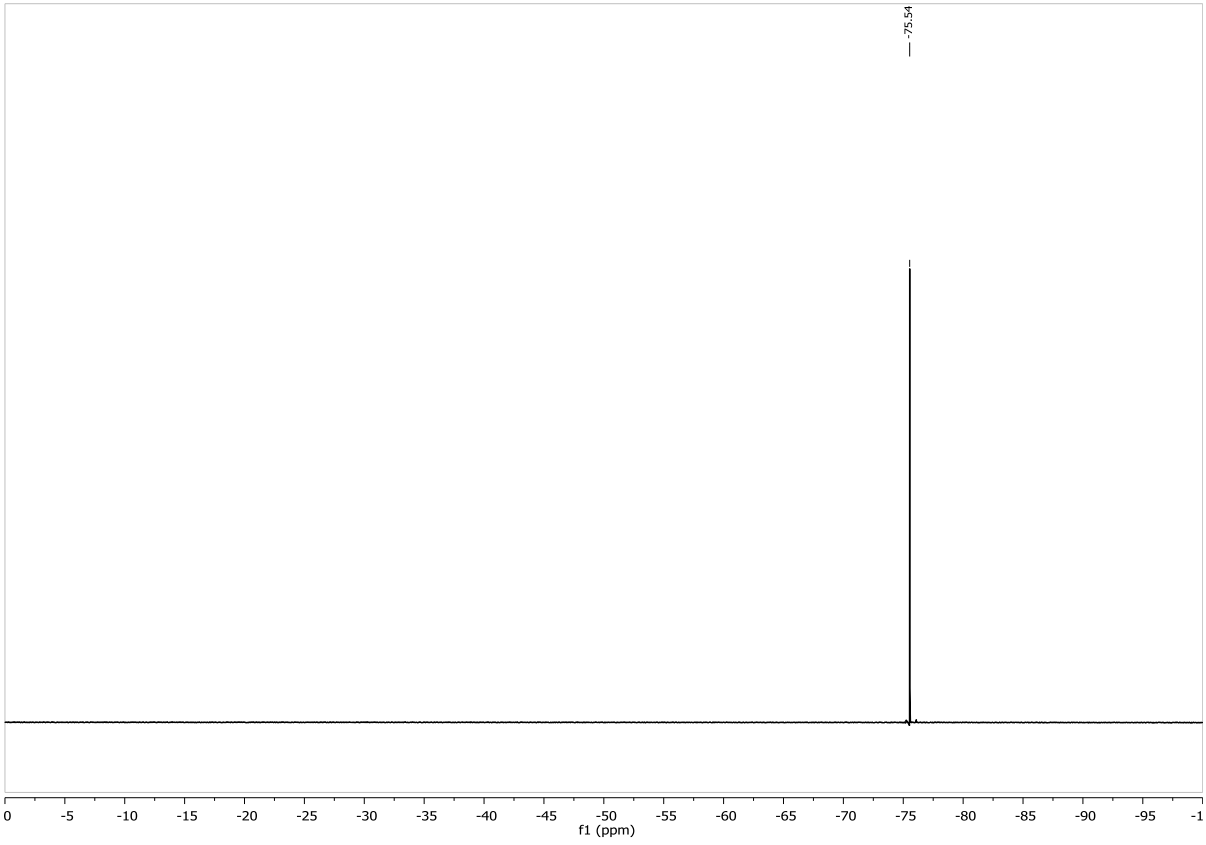
$^{13}C\{^{1}H\}$ NMR, 101 MHz, C_6D_6

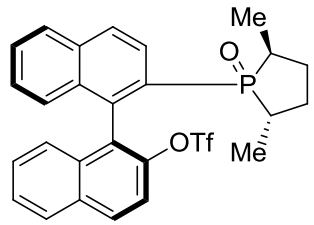




S2

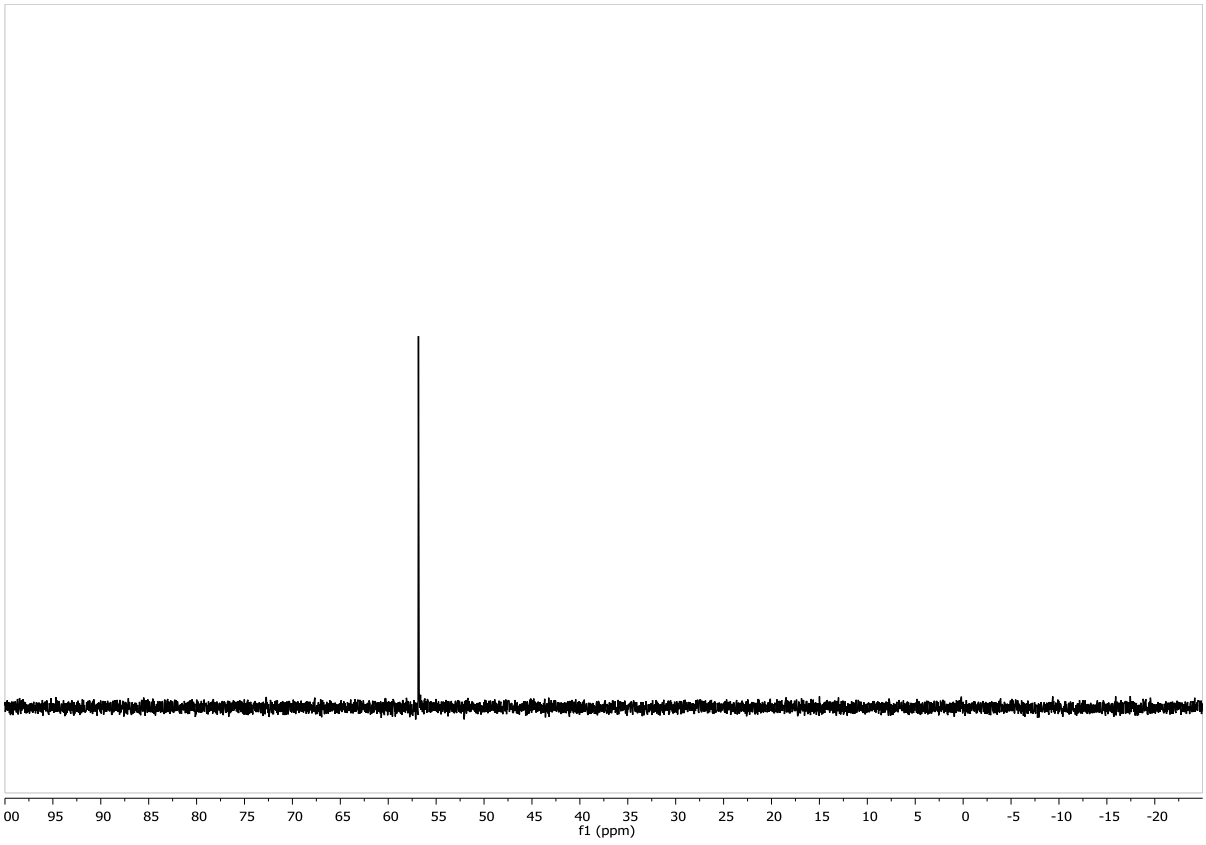
$^{19}F\{^{1}H\}$ NMR, 376 MHz, C_6D_6

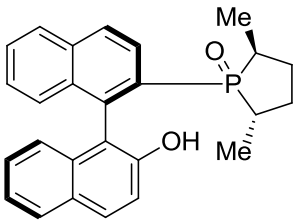




S2

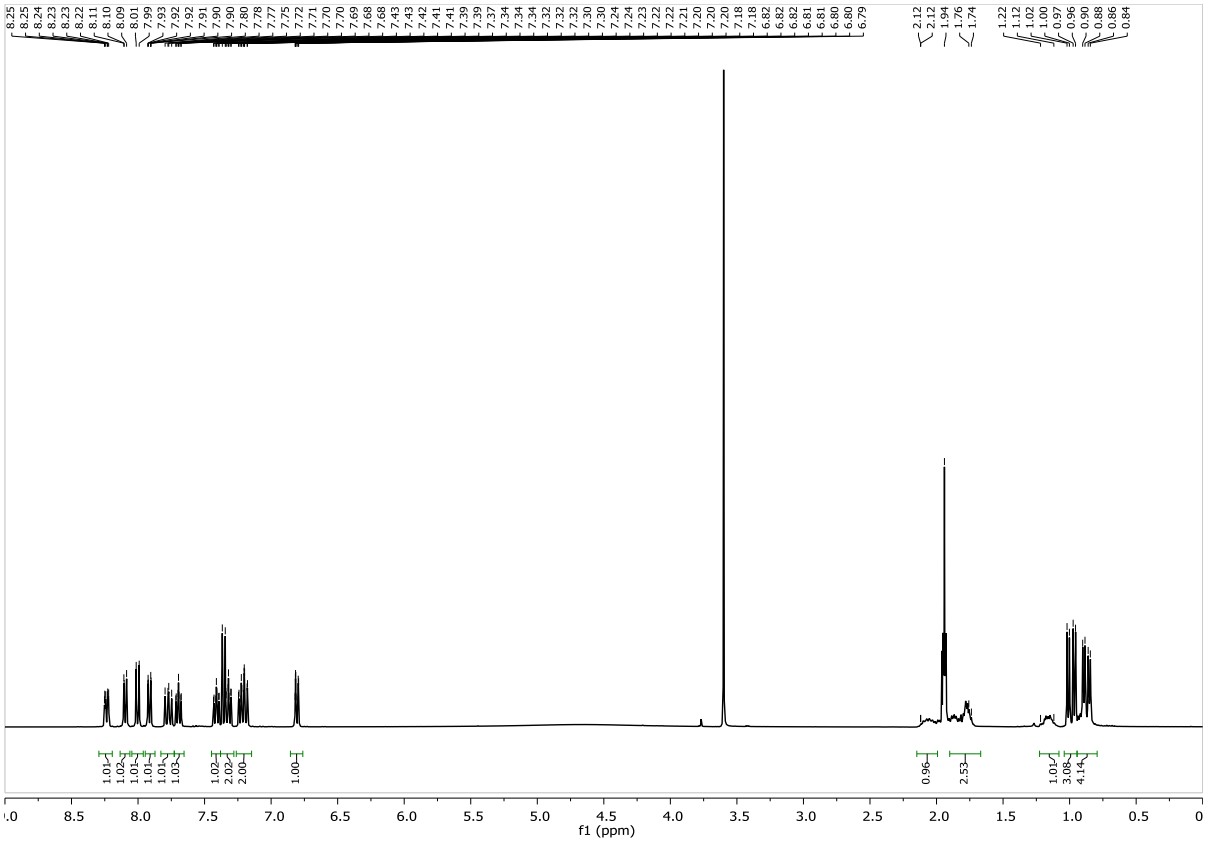
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

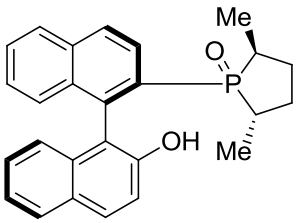




S3

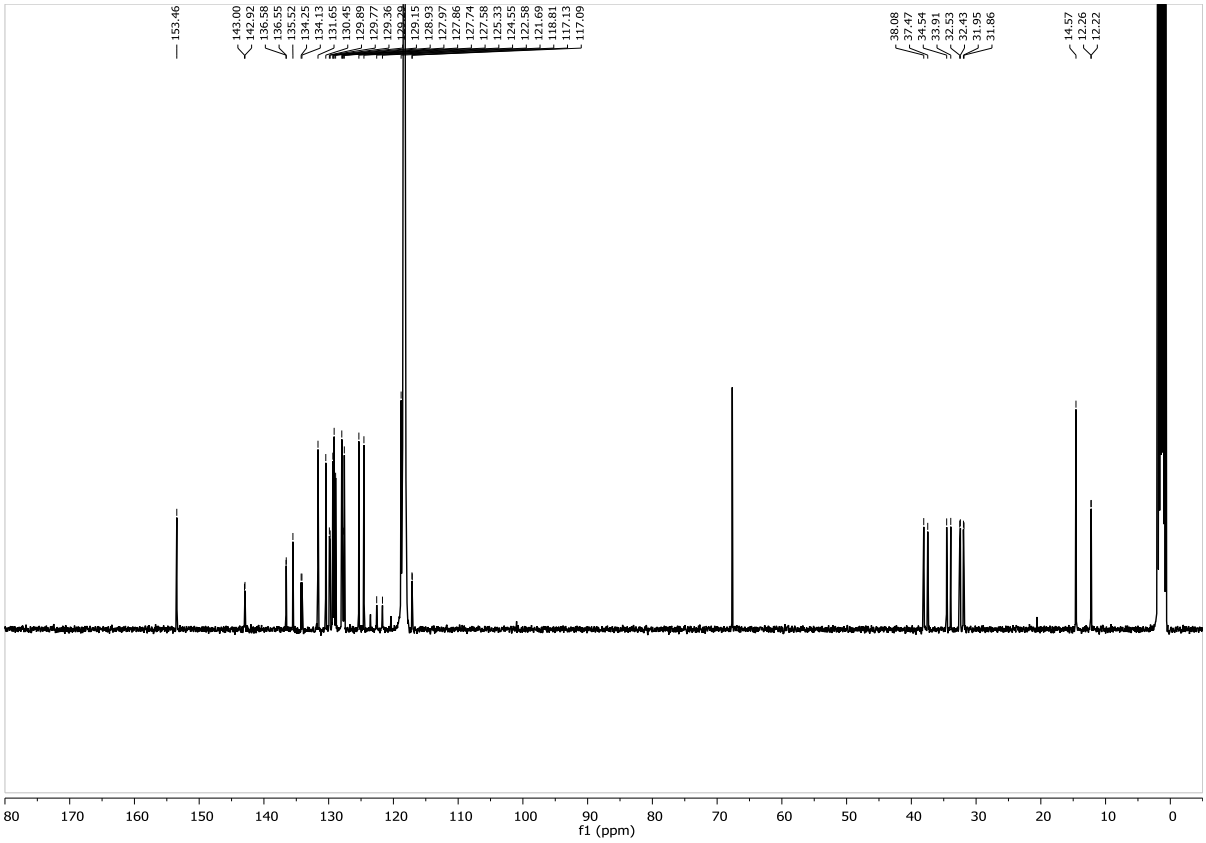
^{1}H NMR, 400 MHz, CD_3CN

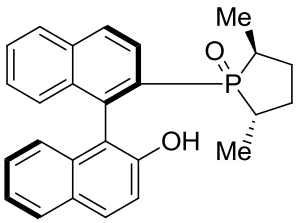




S3

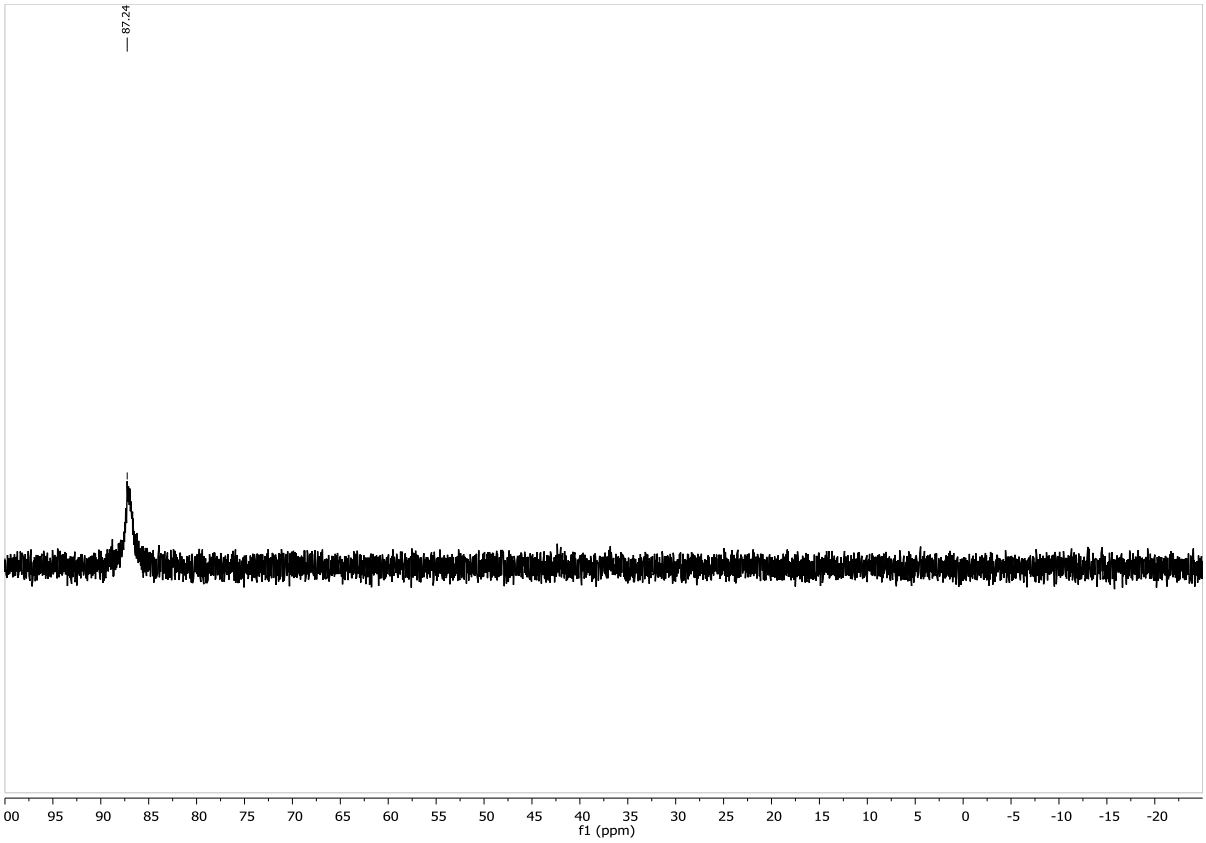
$^{13}C\{^{1}H\}$ NMR, 101 MHz, CD_3CN

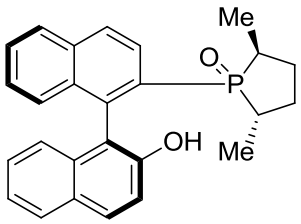




S3

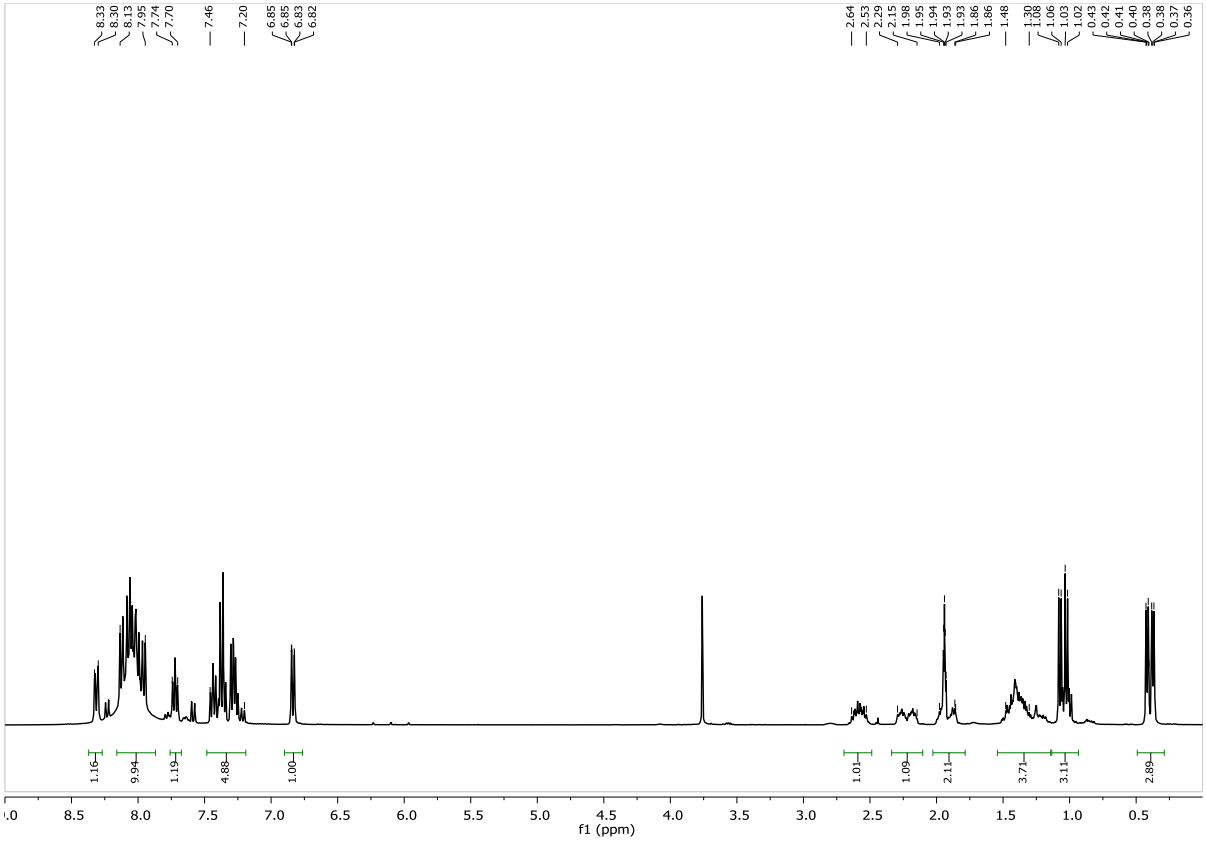
$^{31}P\{^{1}H\}$ NMR, 162 MHz, CD_3CN

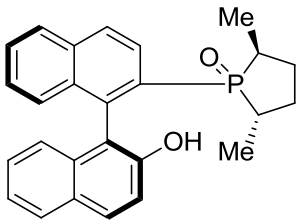




S4

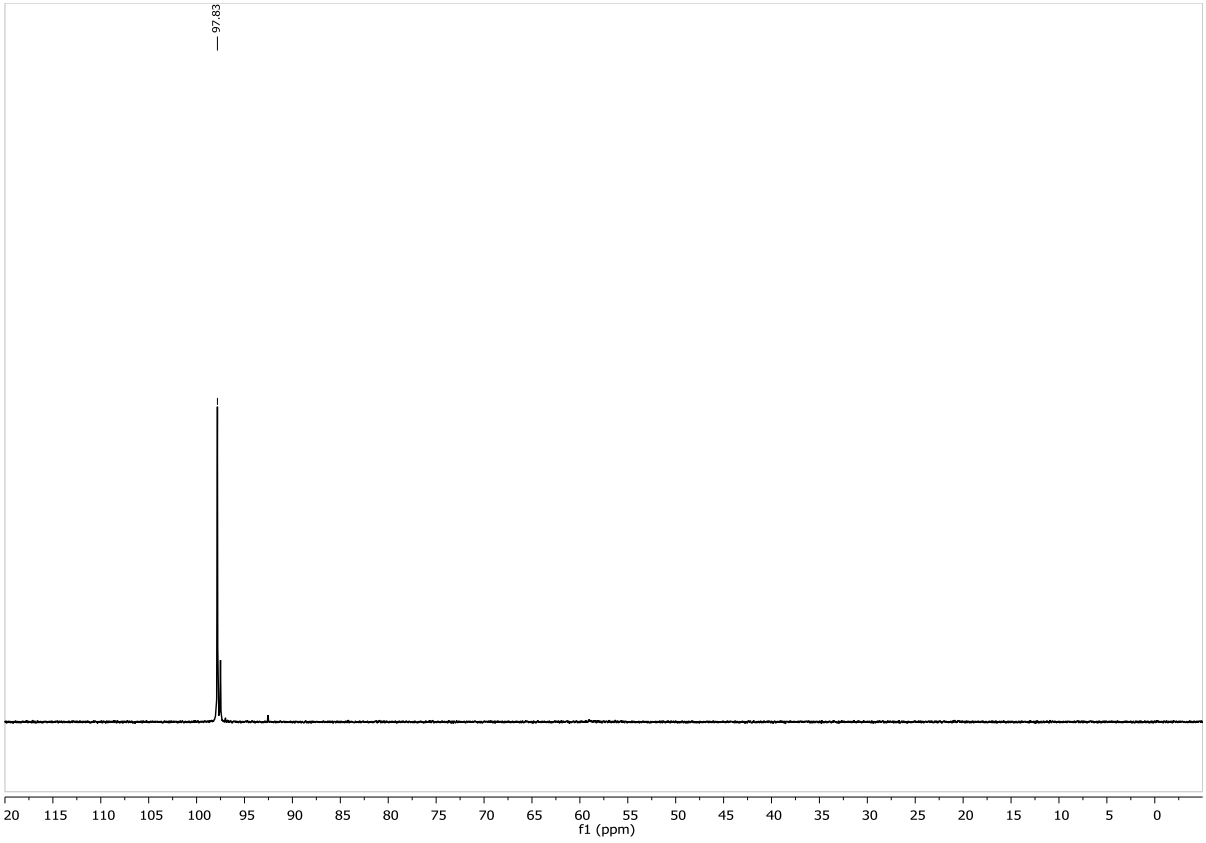
^{1}H NMR, 400 MHz, CD_3CN

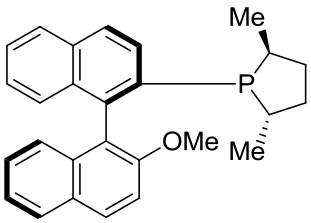




S4

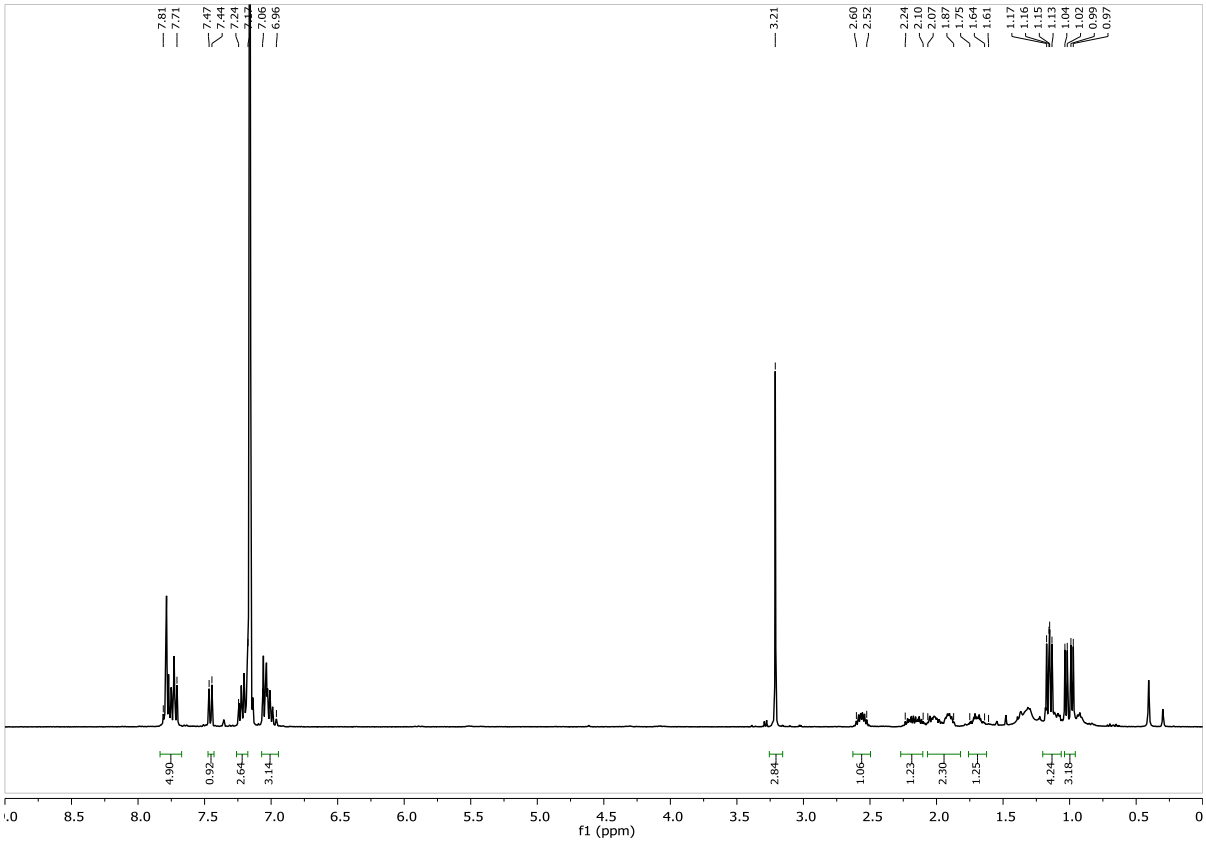
$^{31}P\{^{1}H\}$ NMR, 162 MHz, CD_3CN

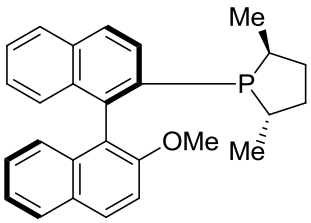




L1

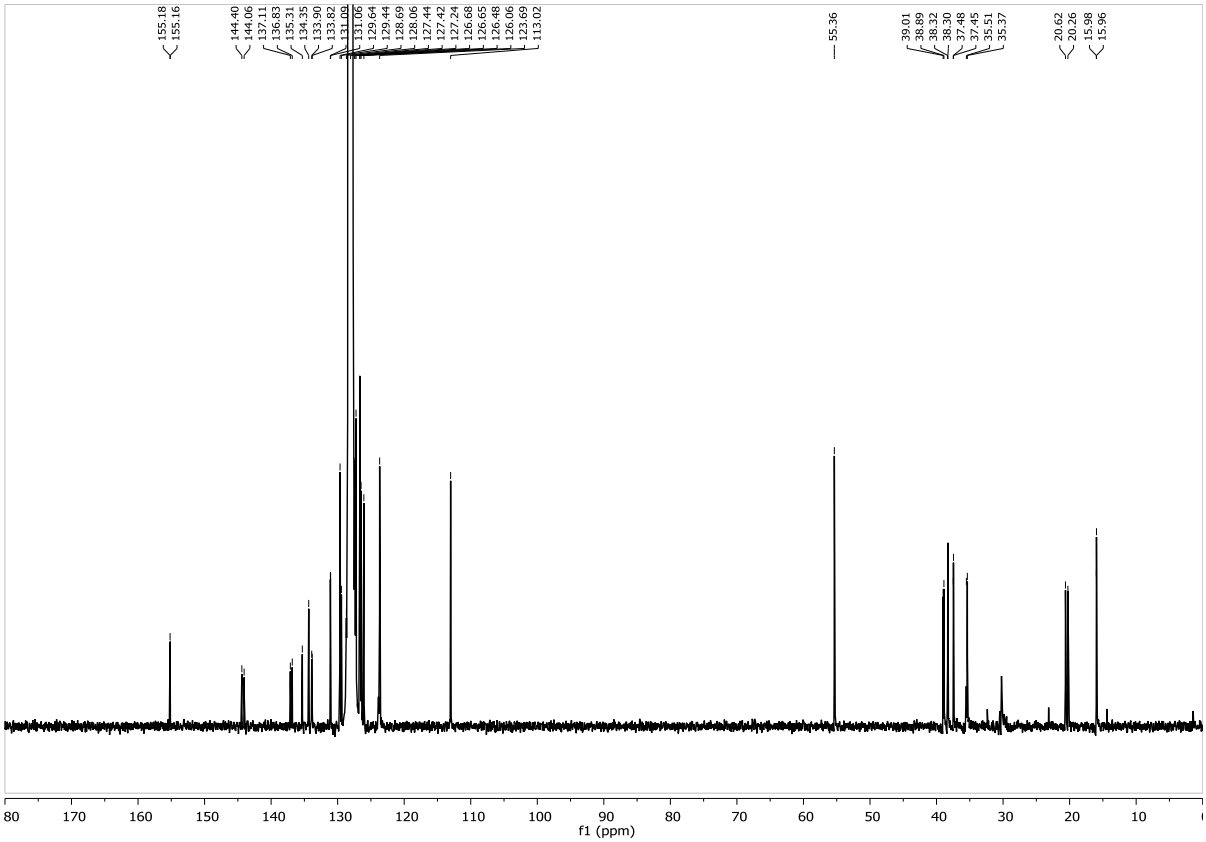
^{1}H NMR, 400 MHz, C_6D_6

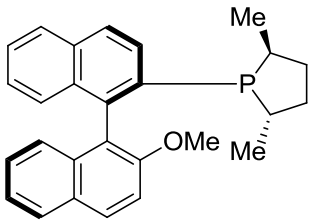




L1

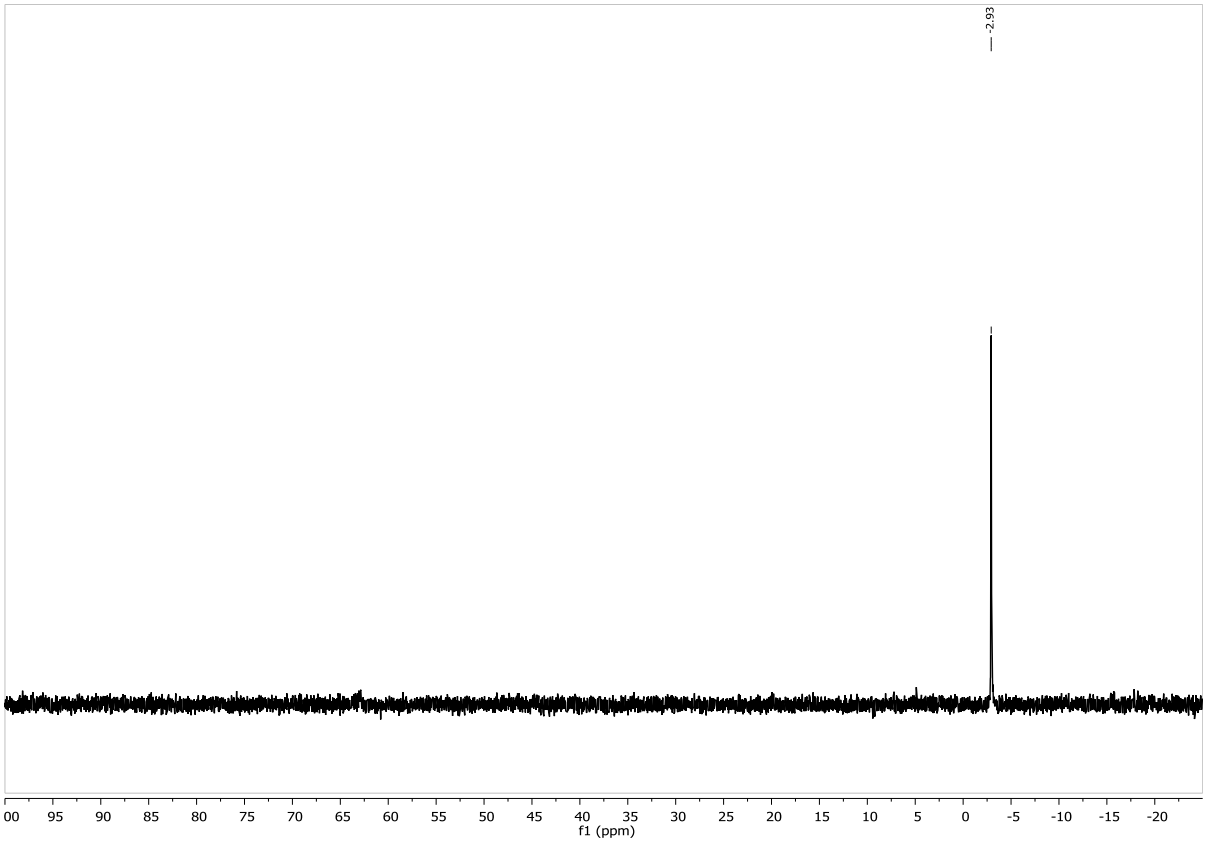
$^{13}C\{^{1}H\}$ NMR, 101 MHz, C_6D_6

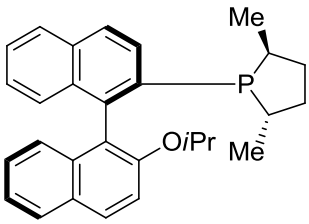




L1

$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6





L2

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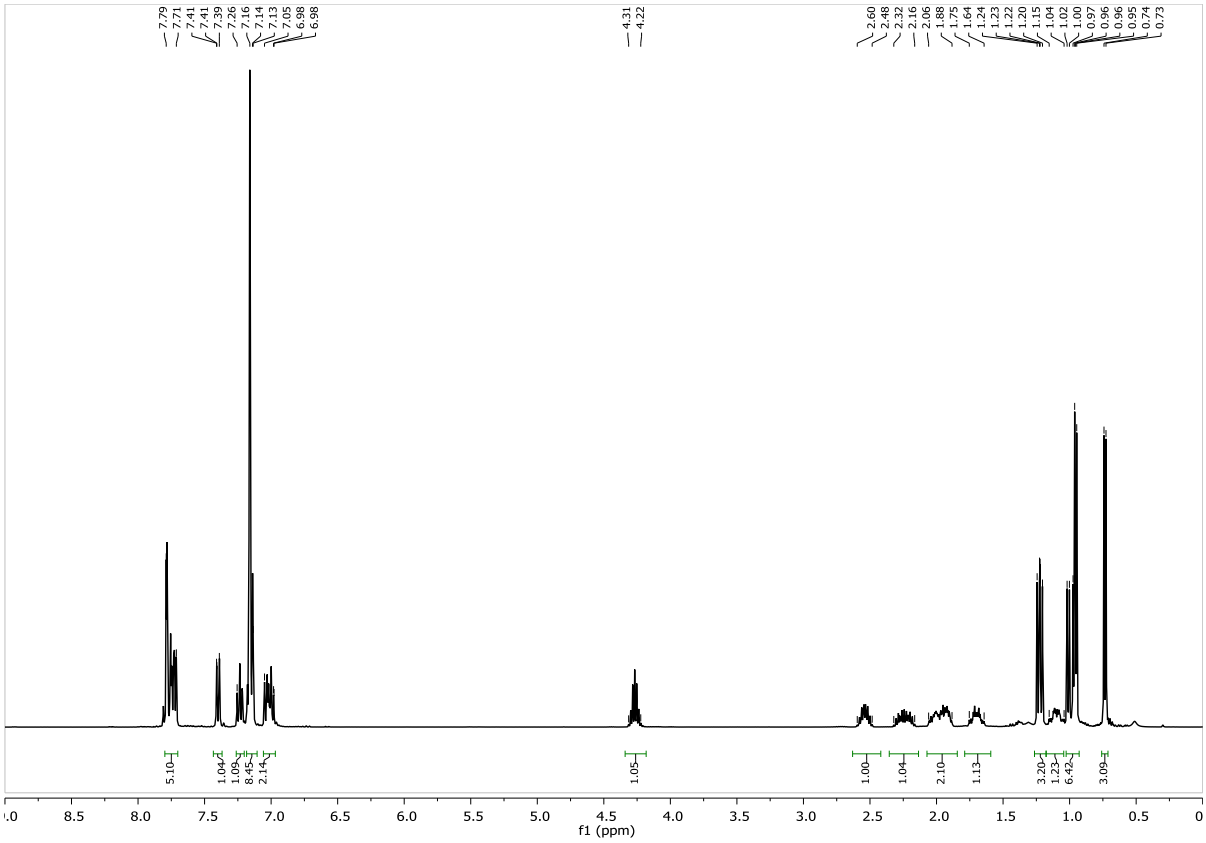

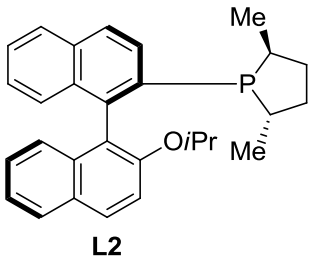

L2

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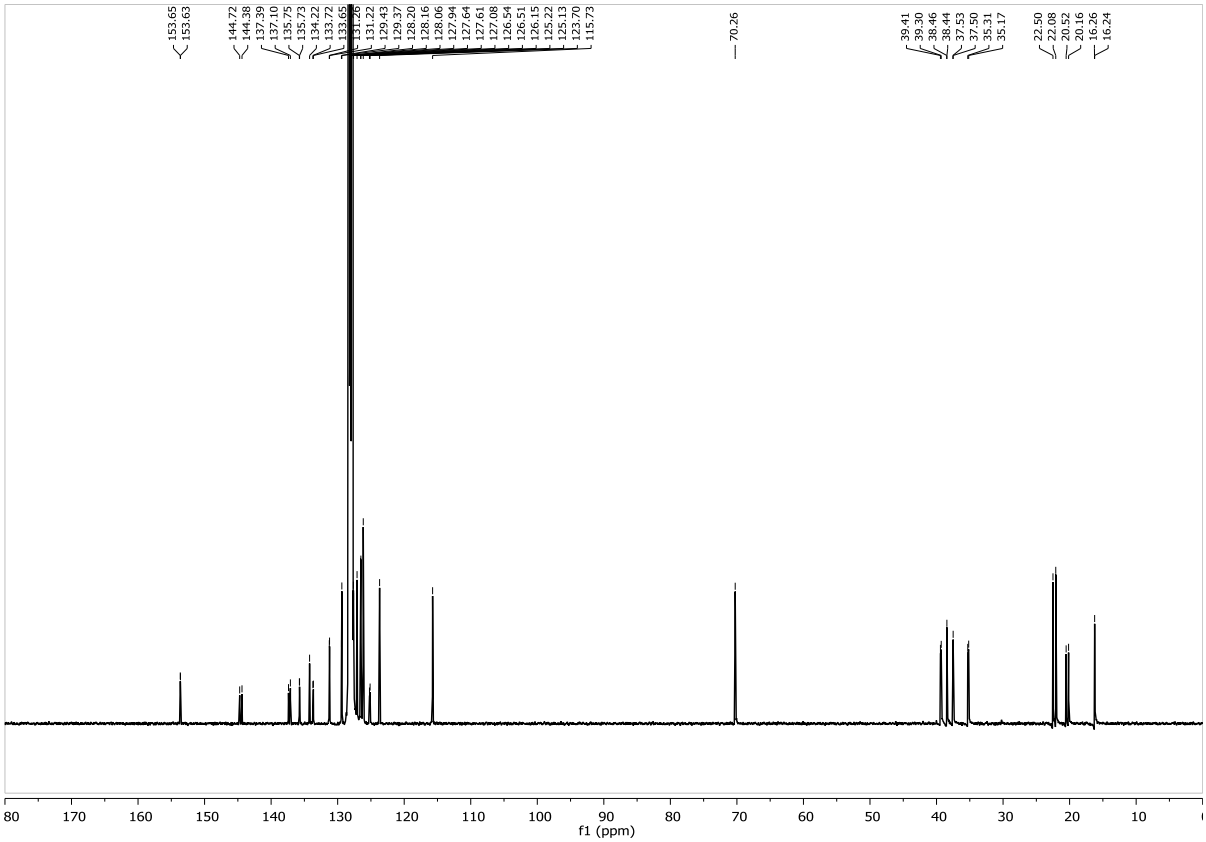

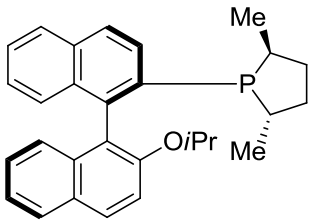

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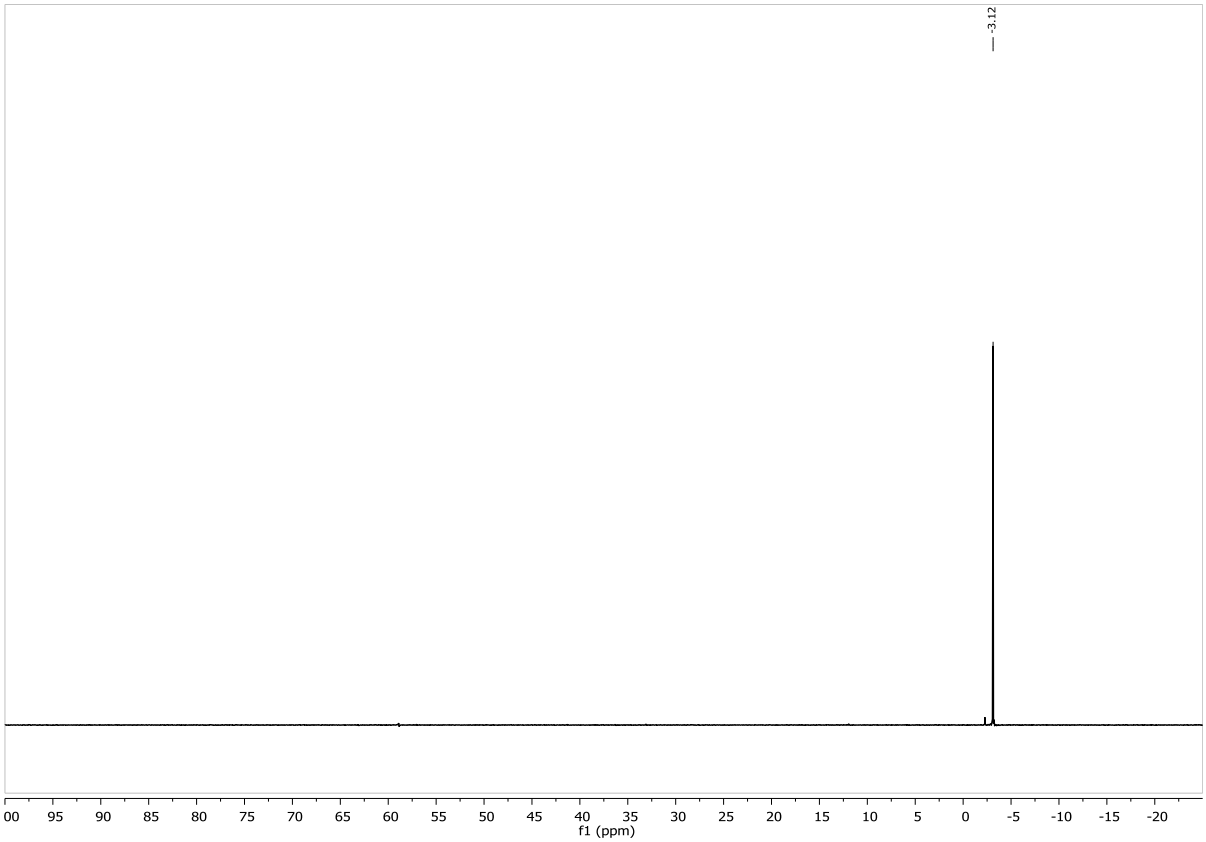

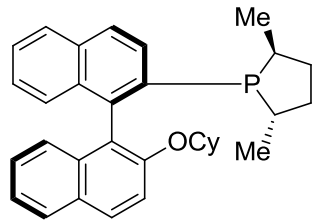

L3

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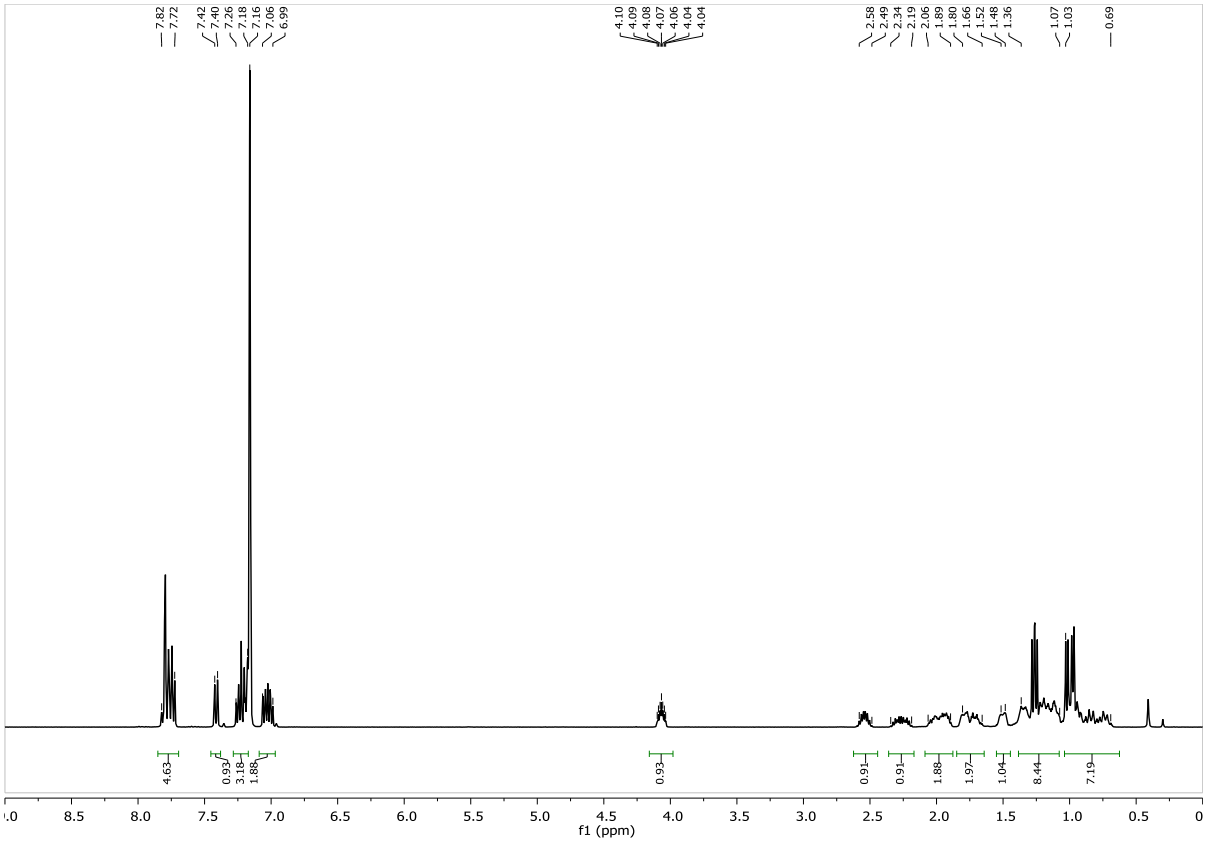
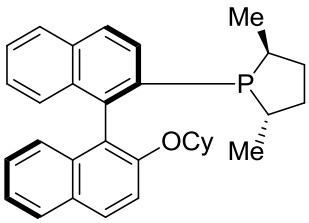
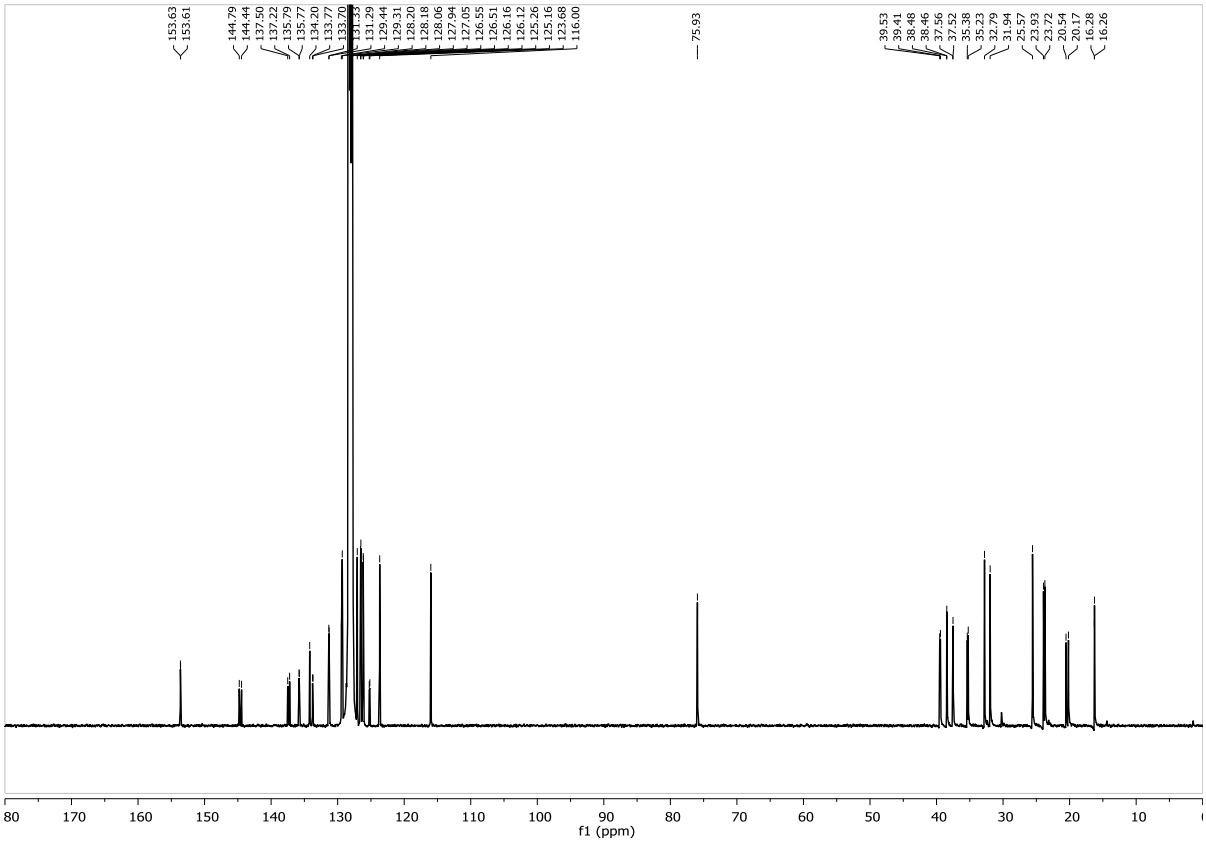
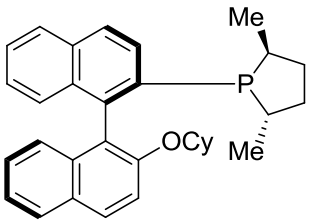




L3

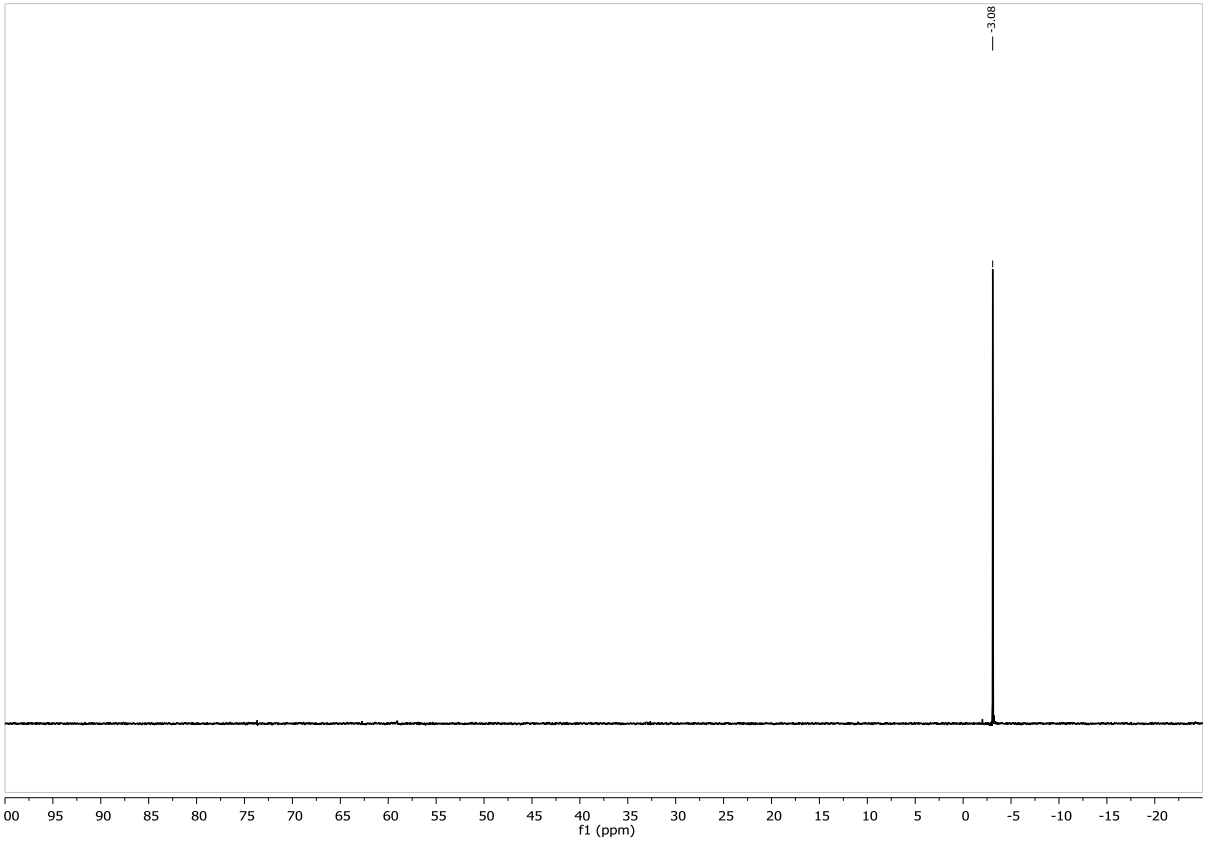
$^{13}C\{^{1}H\}$ NMR, 101 MHz, C_6D_6

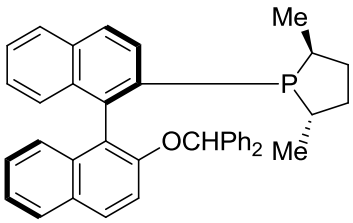




L3

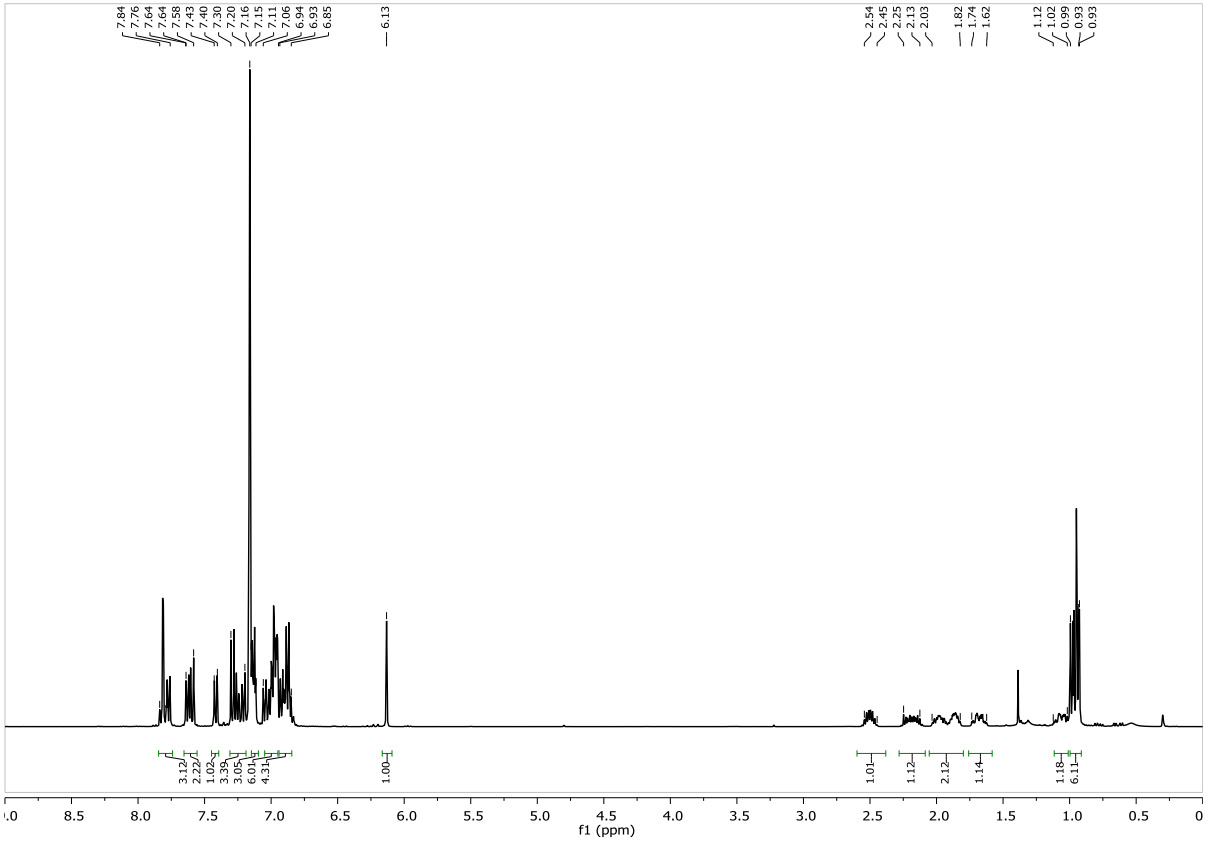
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

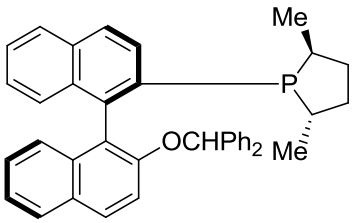




L4

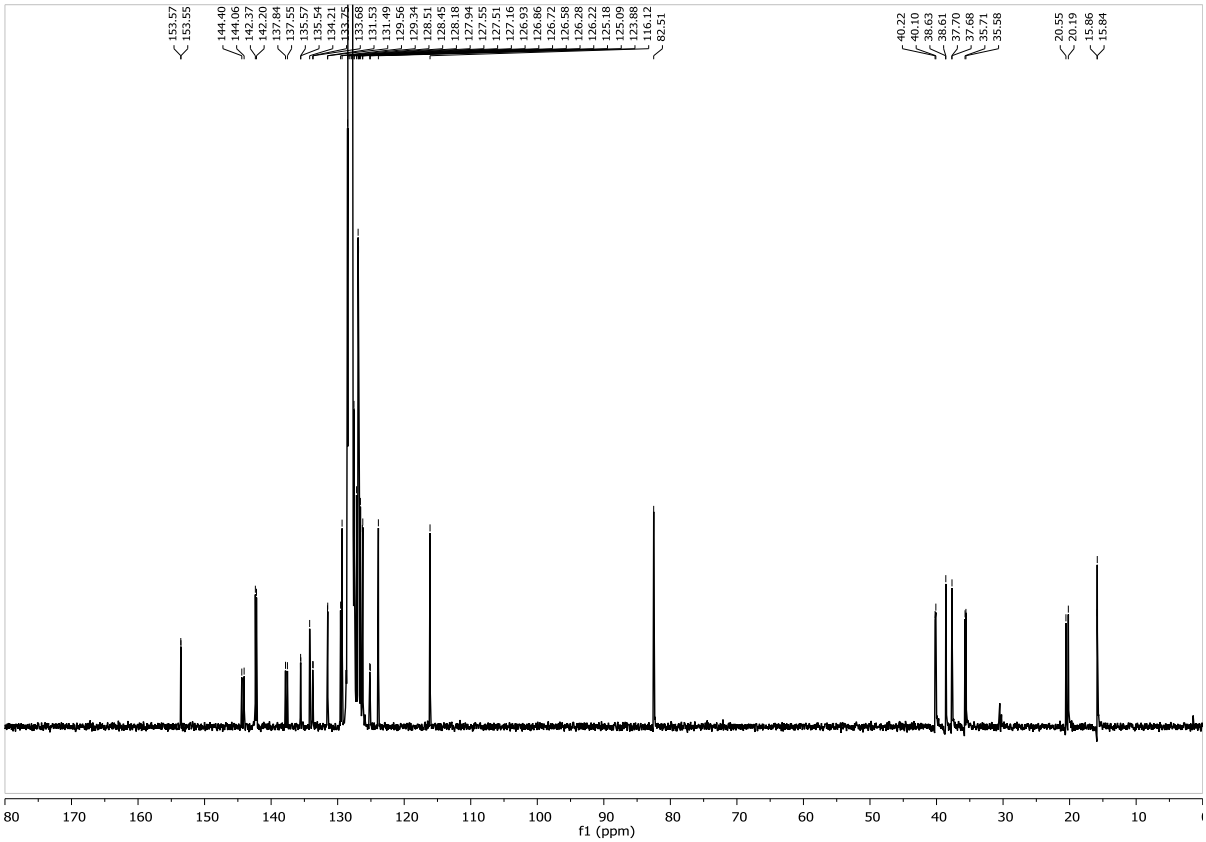
^{1}H NMR, 400 MHz, C_6D_6

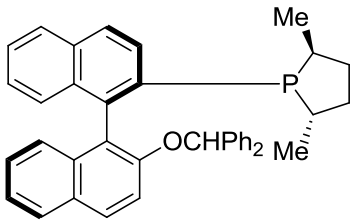




L4

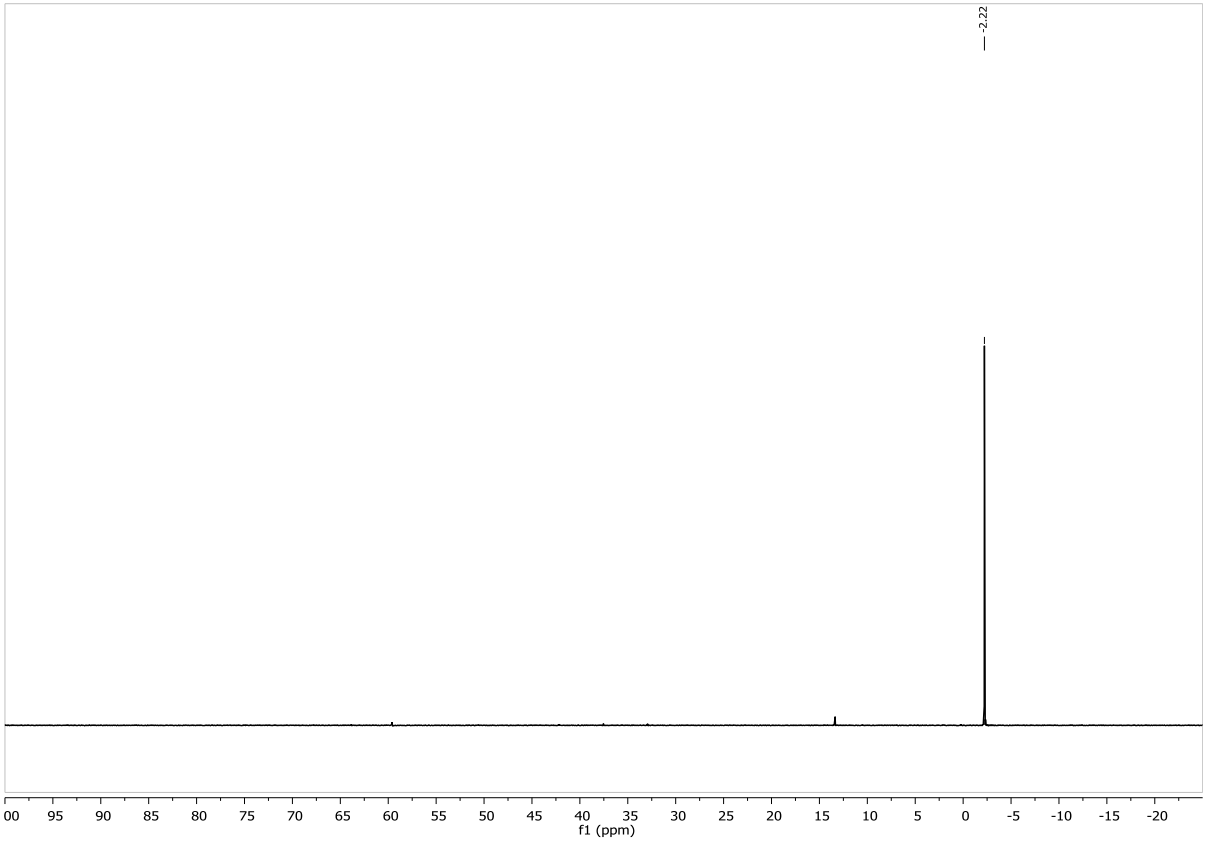
$^{13}C\{^{1}H\}$ NMR, 101 MHz, C_6D_6

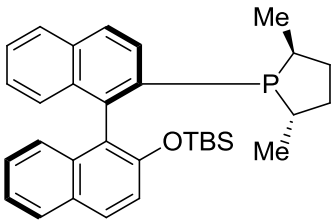




L4

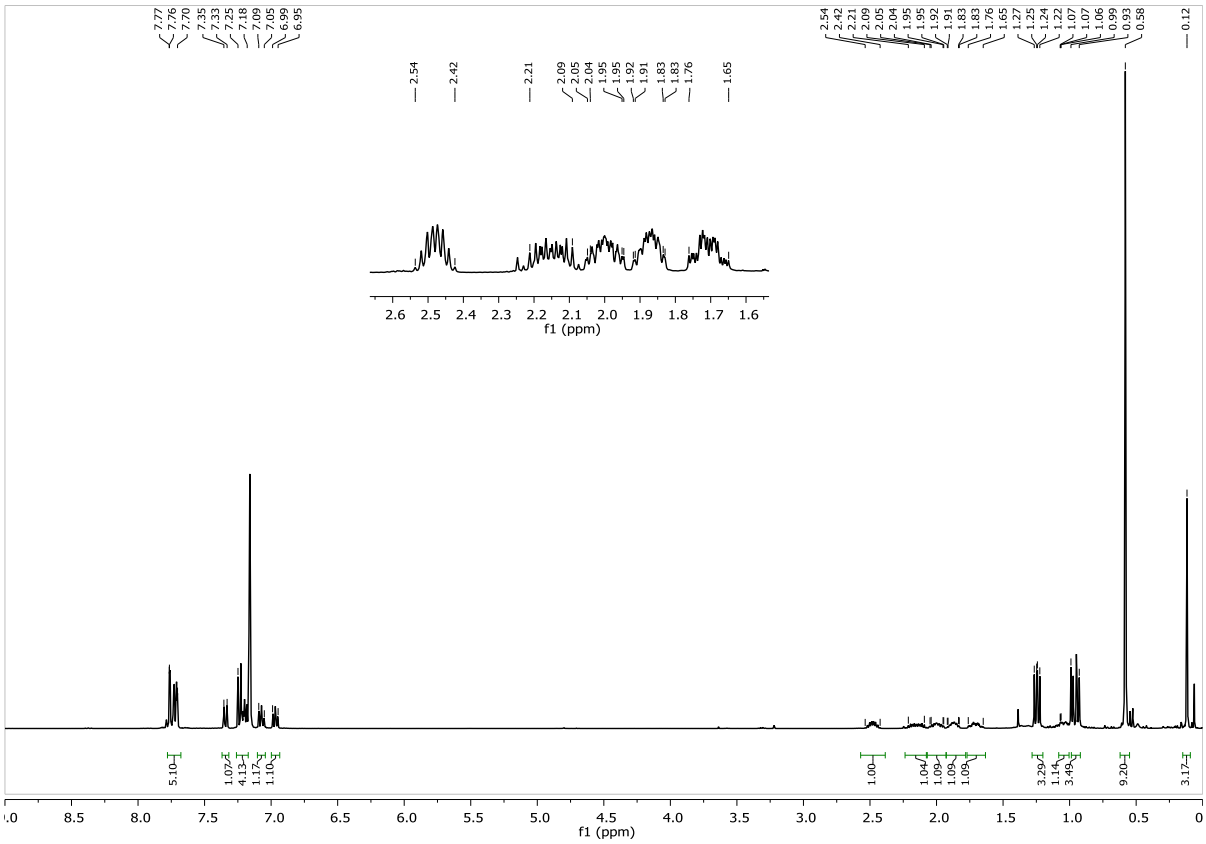
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

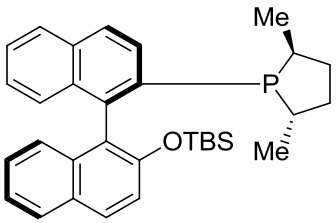




L5

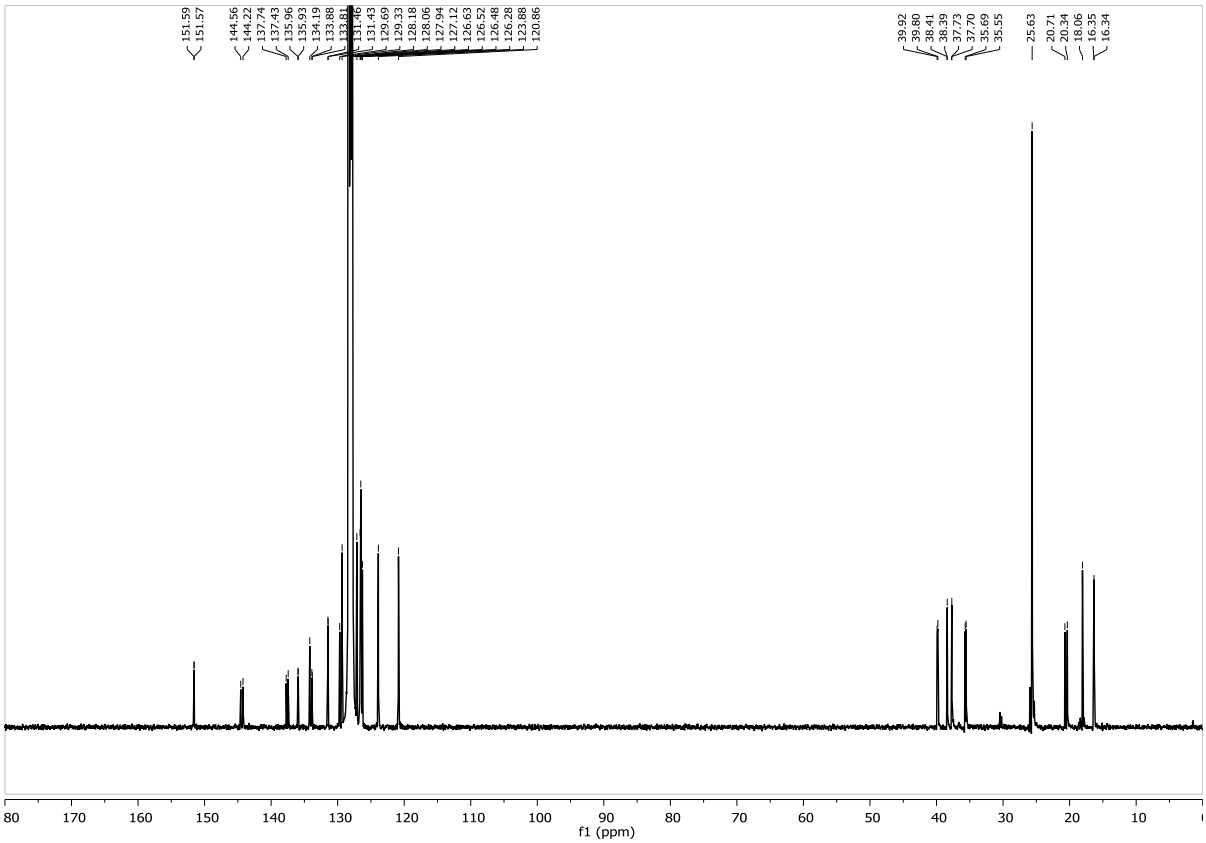
^{1}H NMR, 400 MHz, C_6D_6

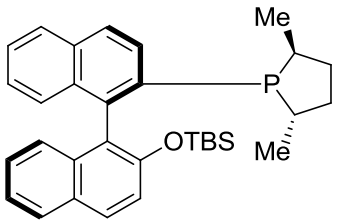




L5

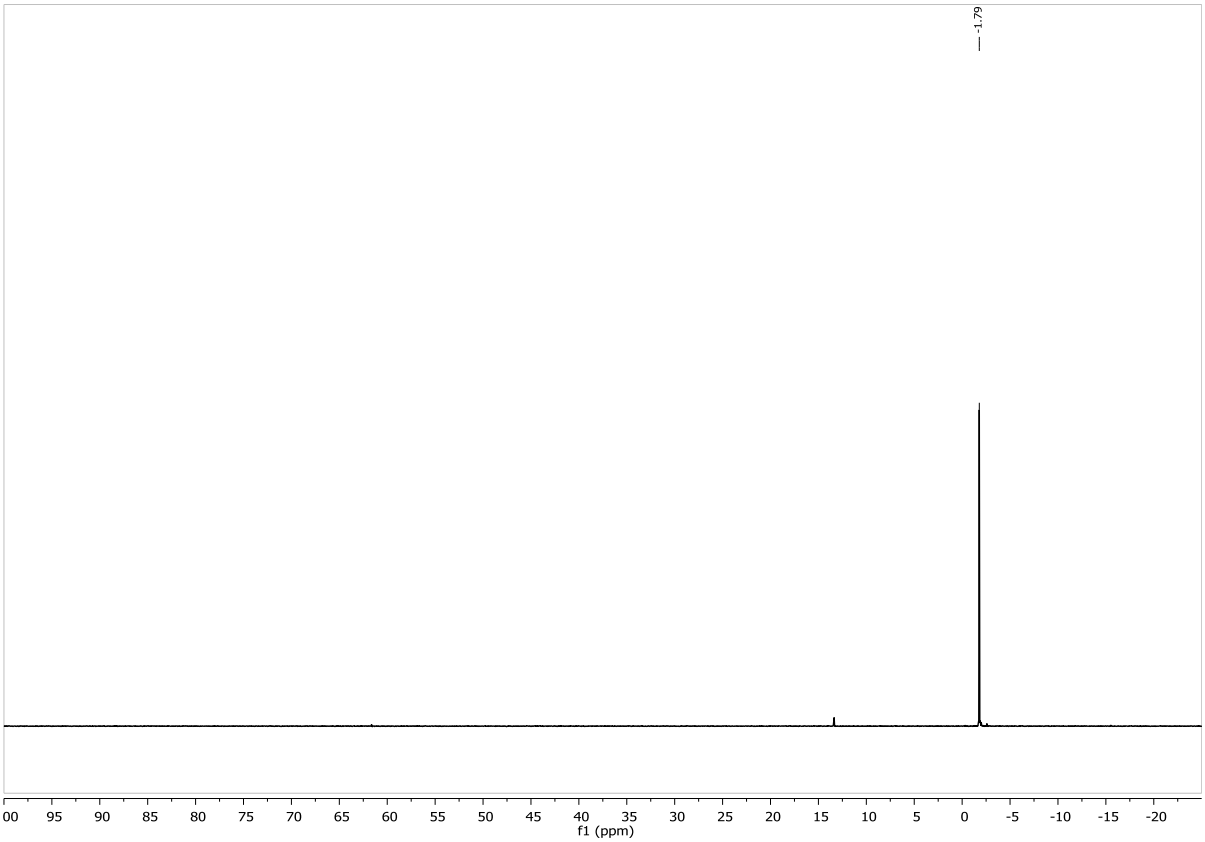
$^{13}C\{^{1}H\}$ NMR, 101 MHz, C_6D_6

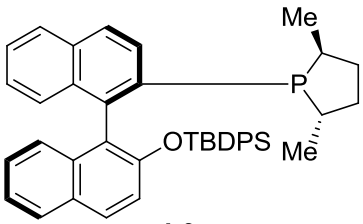




L5

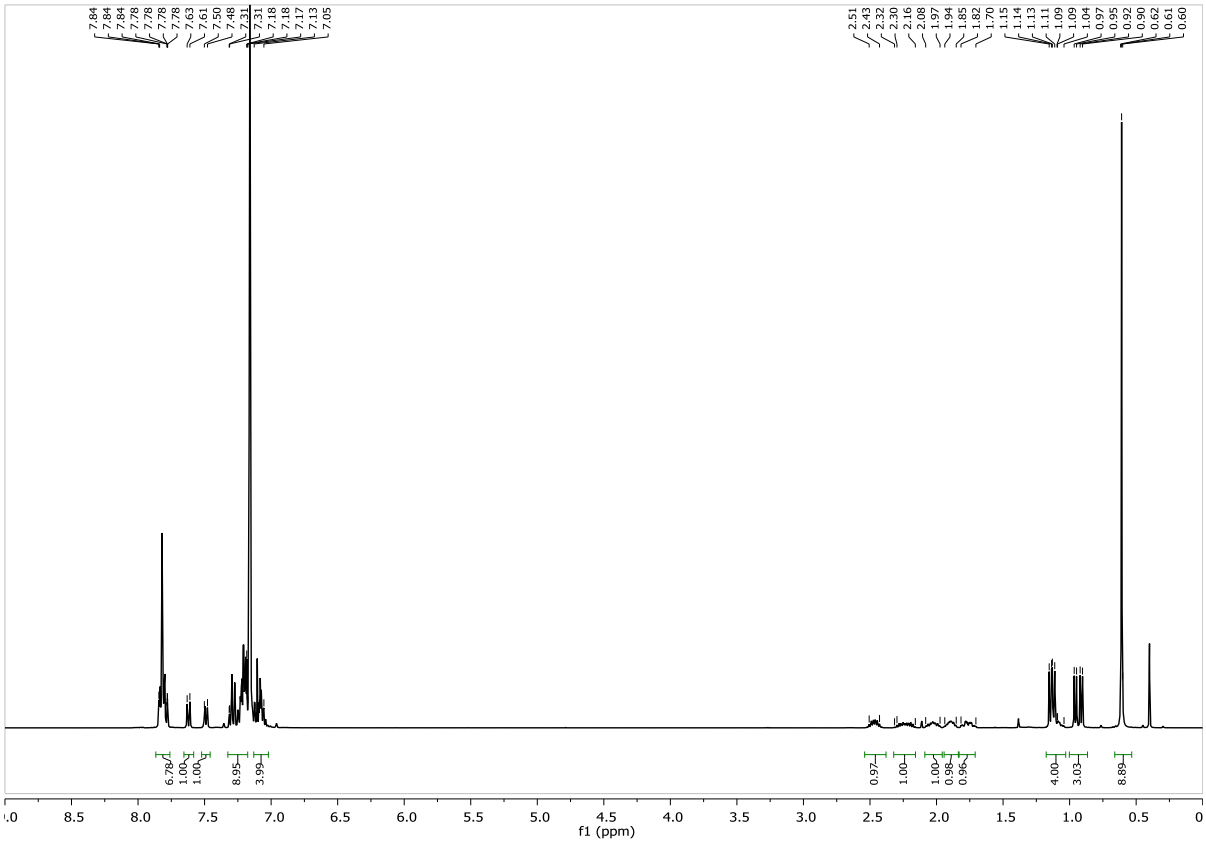
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

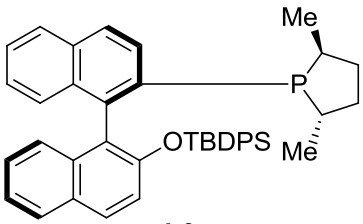




L6

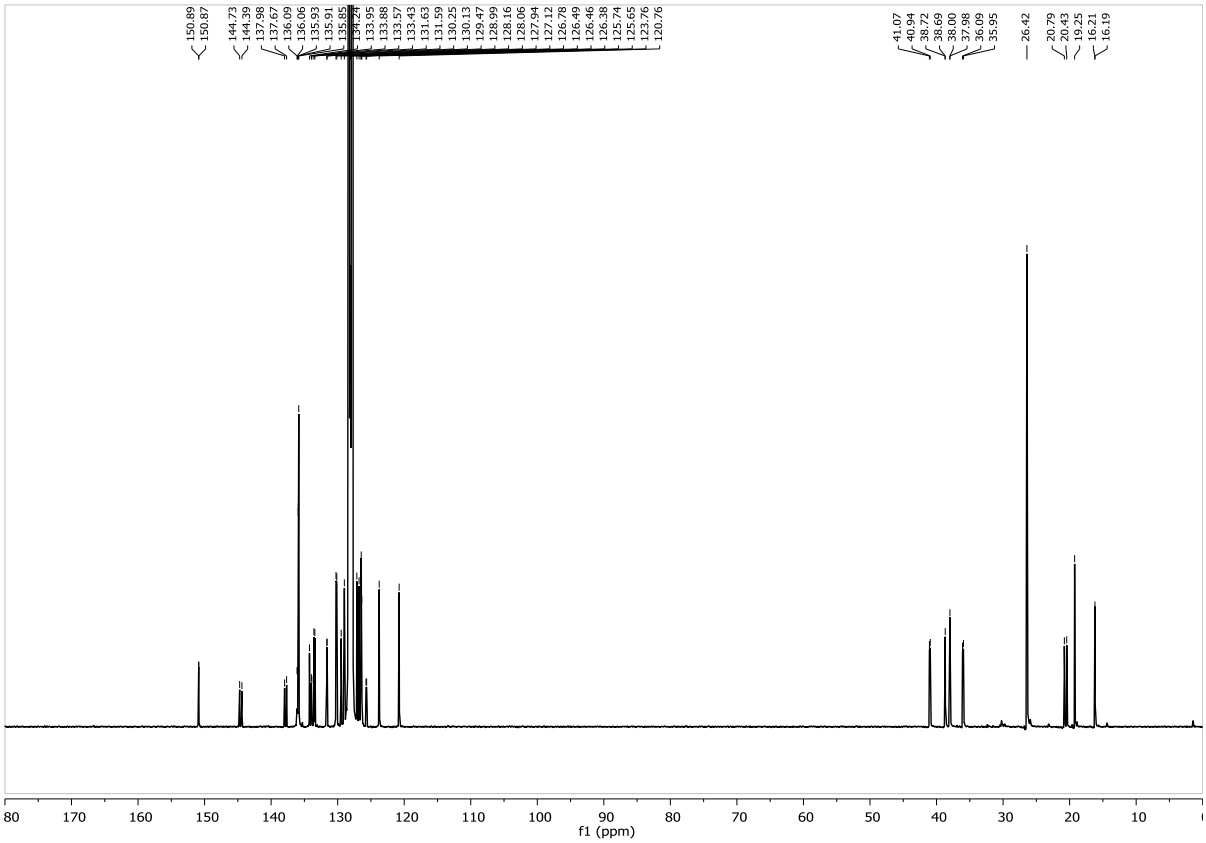
^{1}H NMR, 400 MHz, C_6D_6

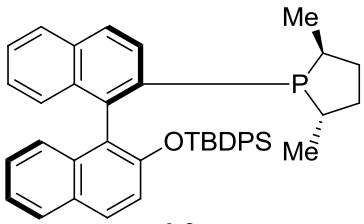




L6

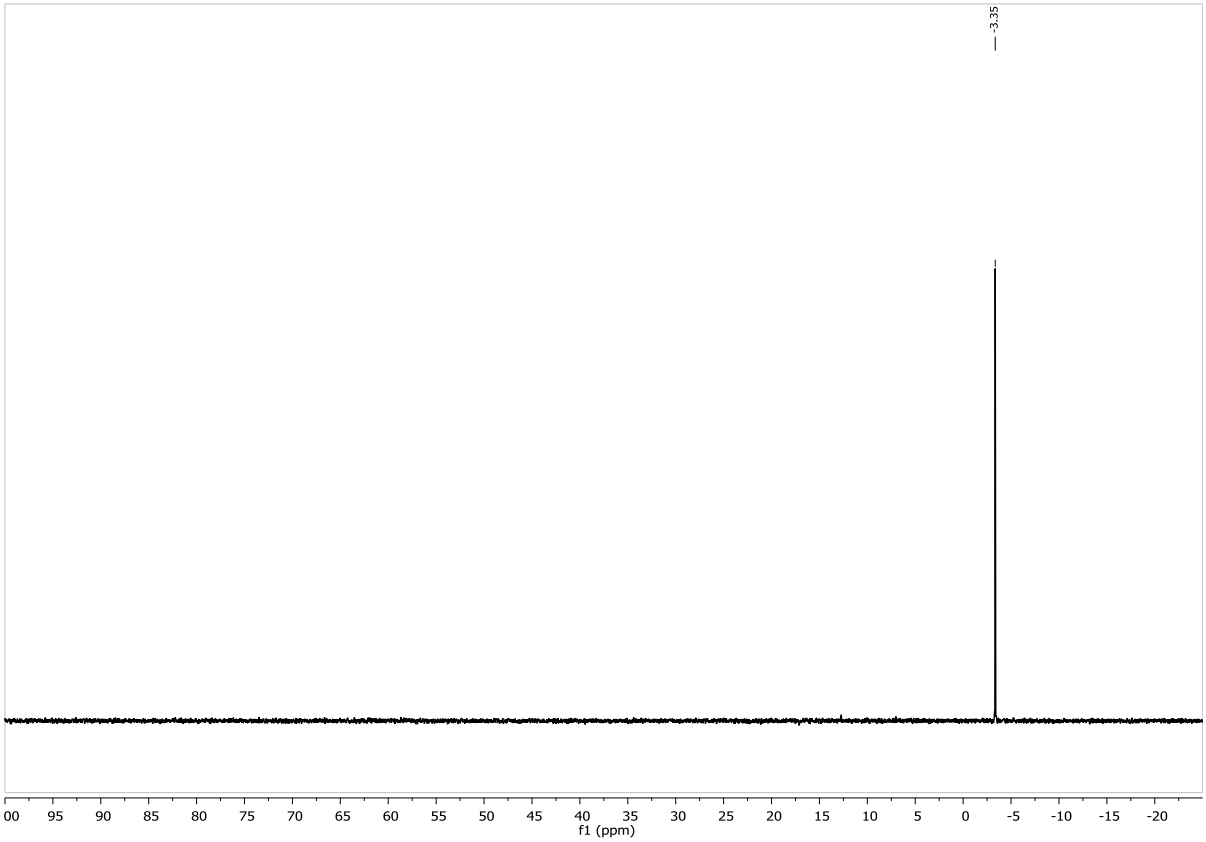
$^{13}C\{^{1}H\}$ NMR, 101 MHz, C_6D_6

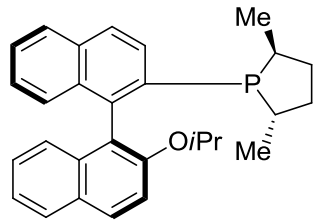




L6

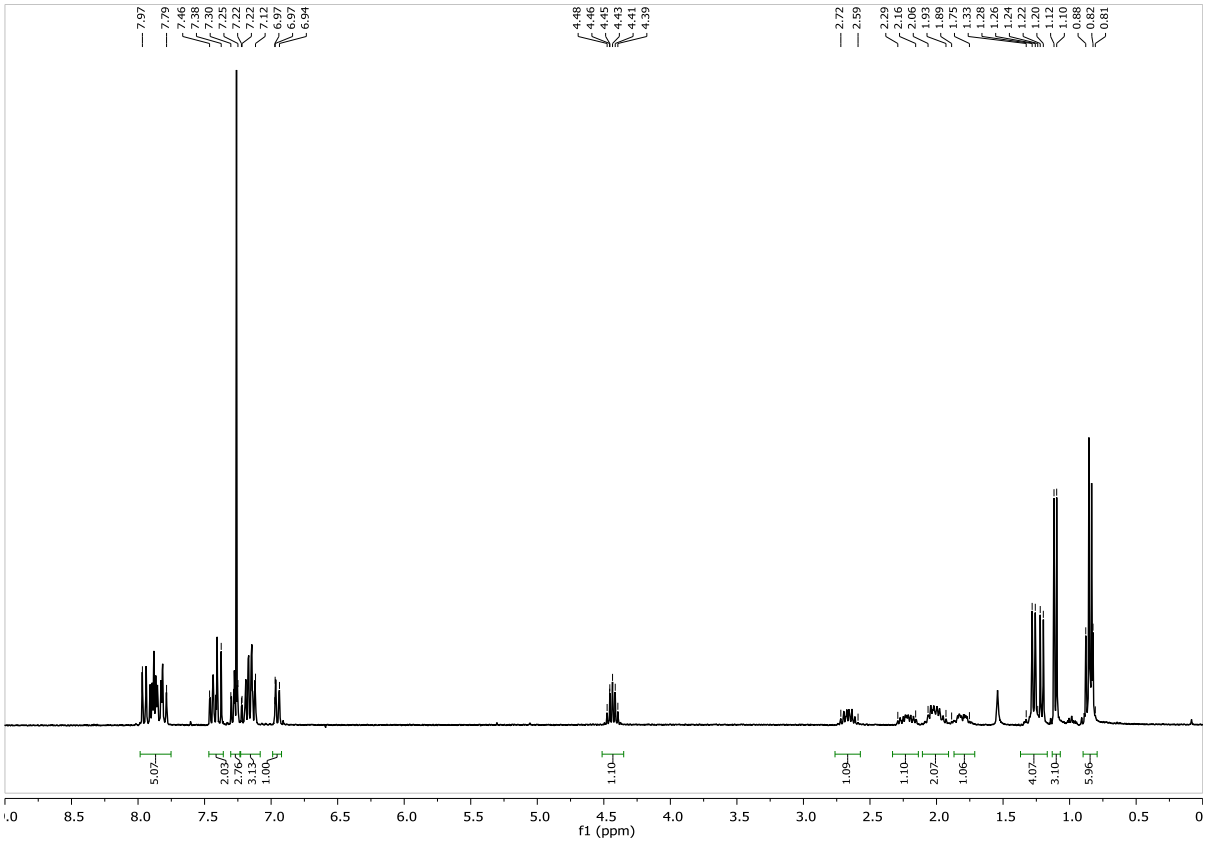
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

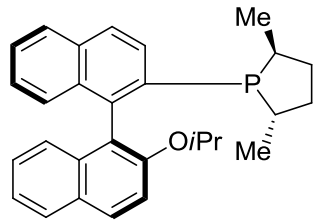




L7

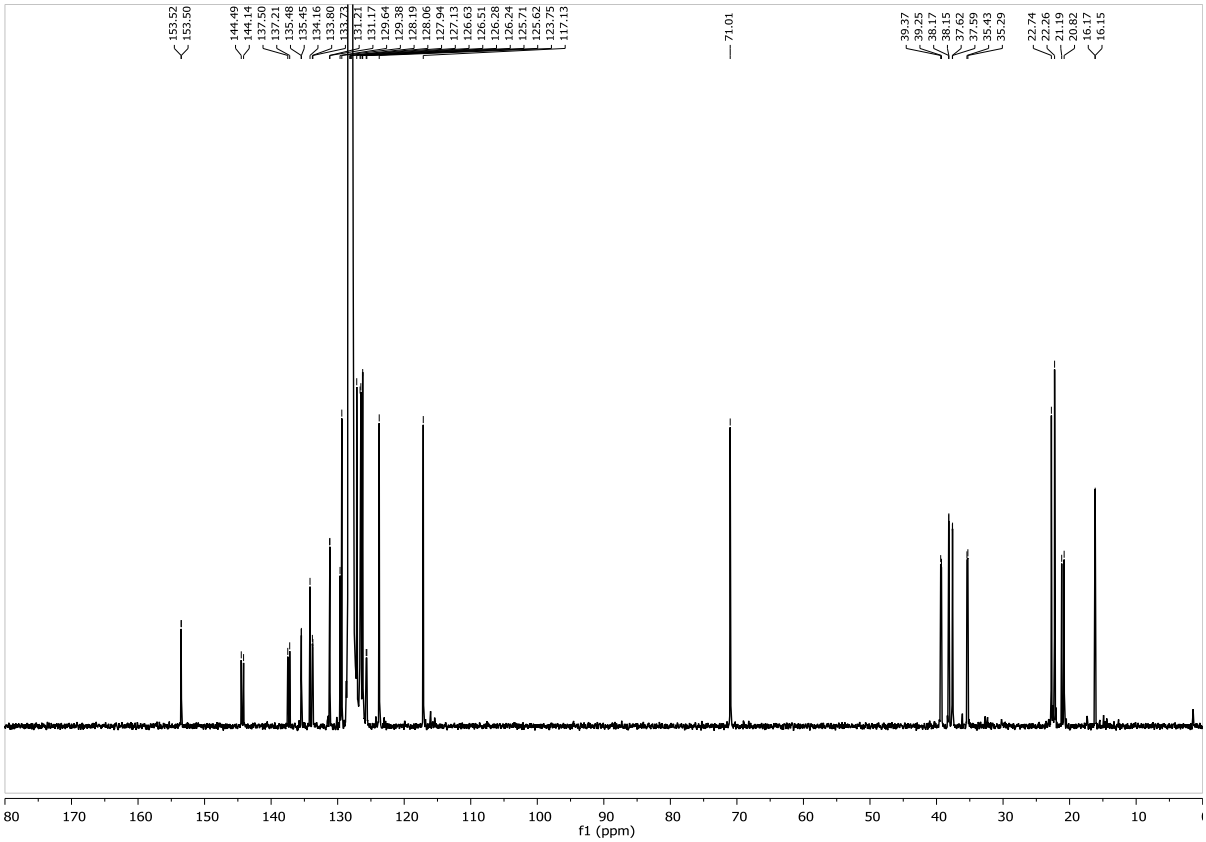
^{1}H NMR, 400 MHz, $CDCl_3$

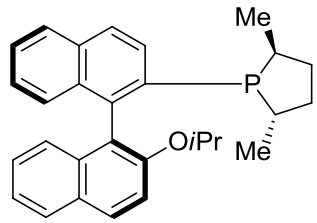




L7

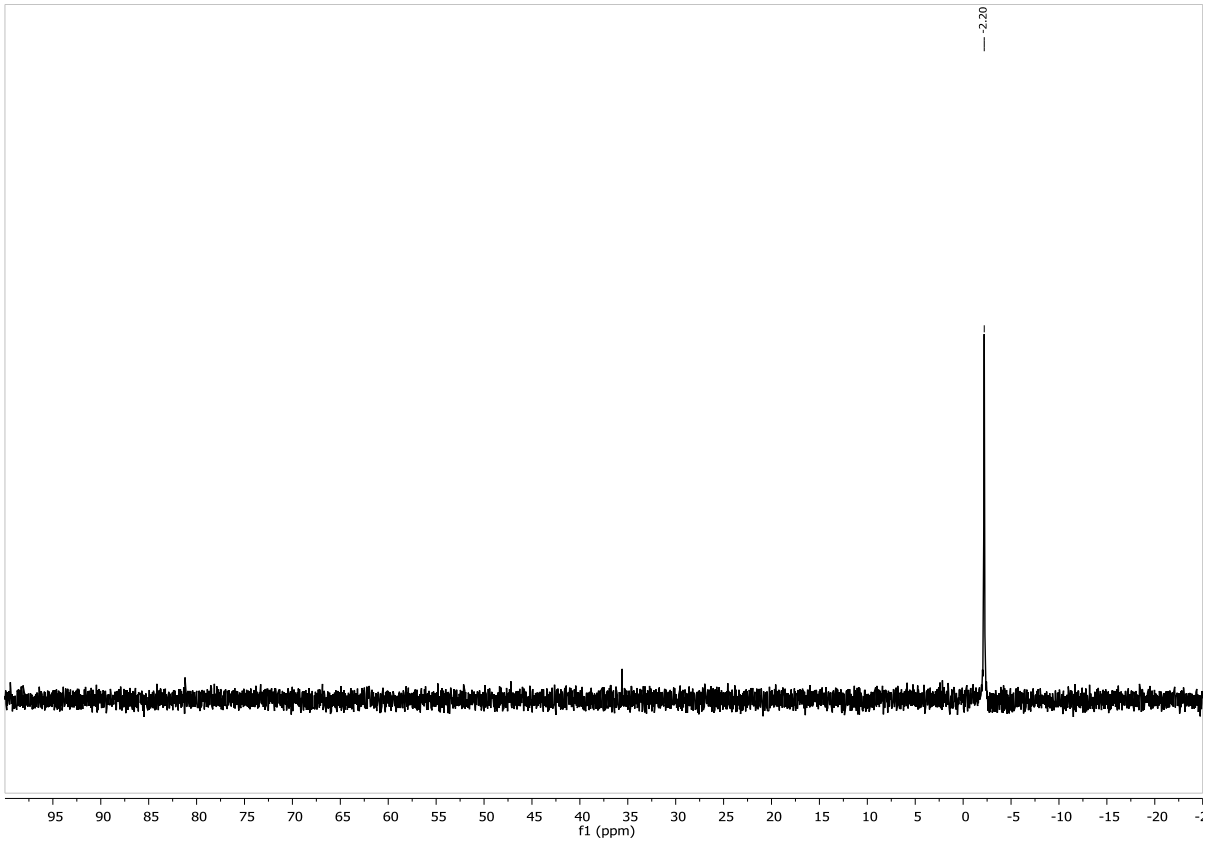
$^{13}C\{^{1}H\}$ NMR, 101 MHz, C_6D_6

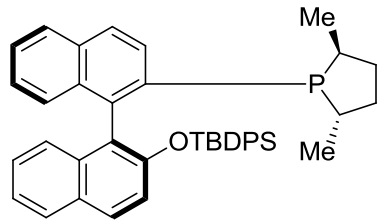




L7

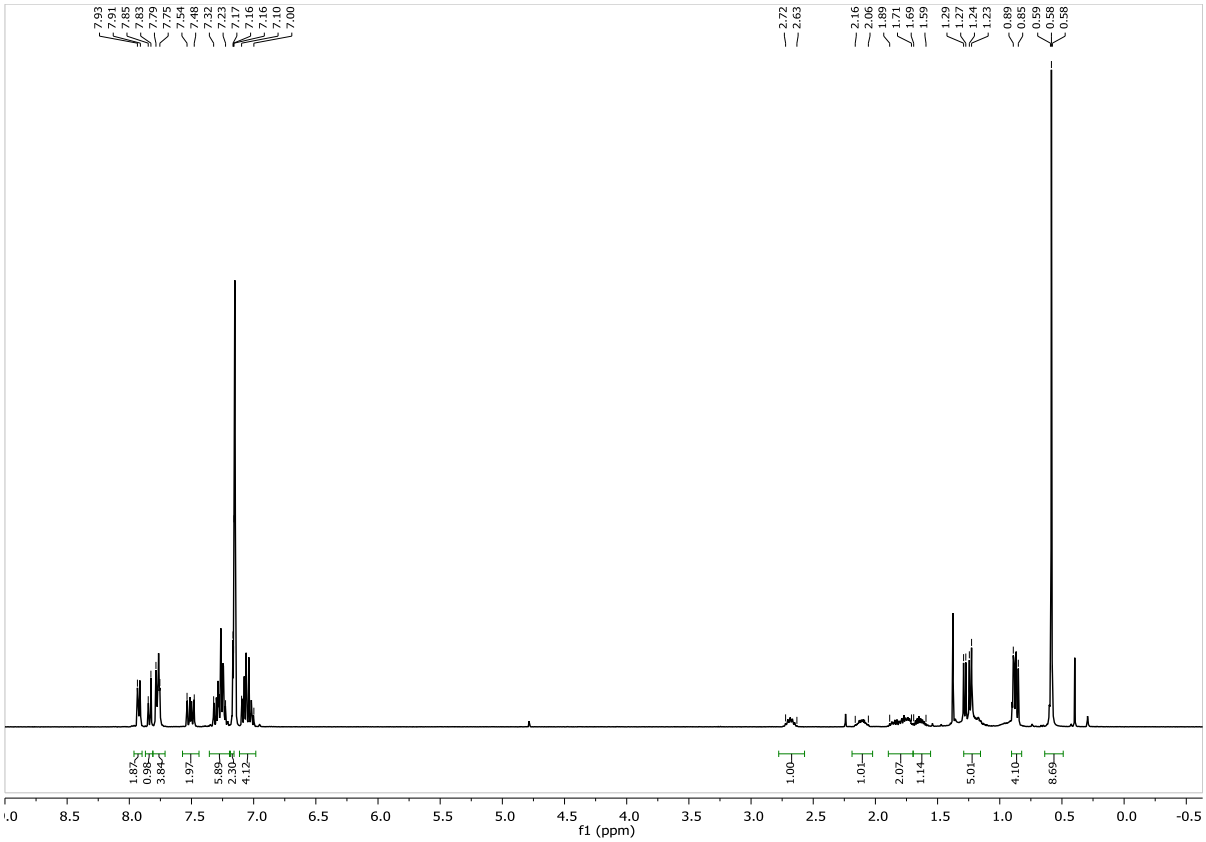
$^{31}P\{^{1}H\}$ NMR, 162 MHz, $CDCl_3$

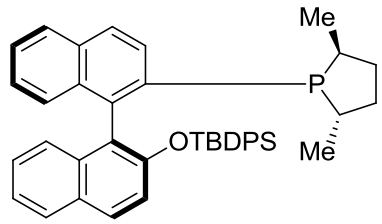




L8

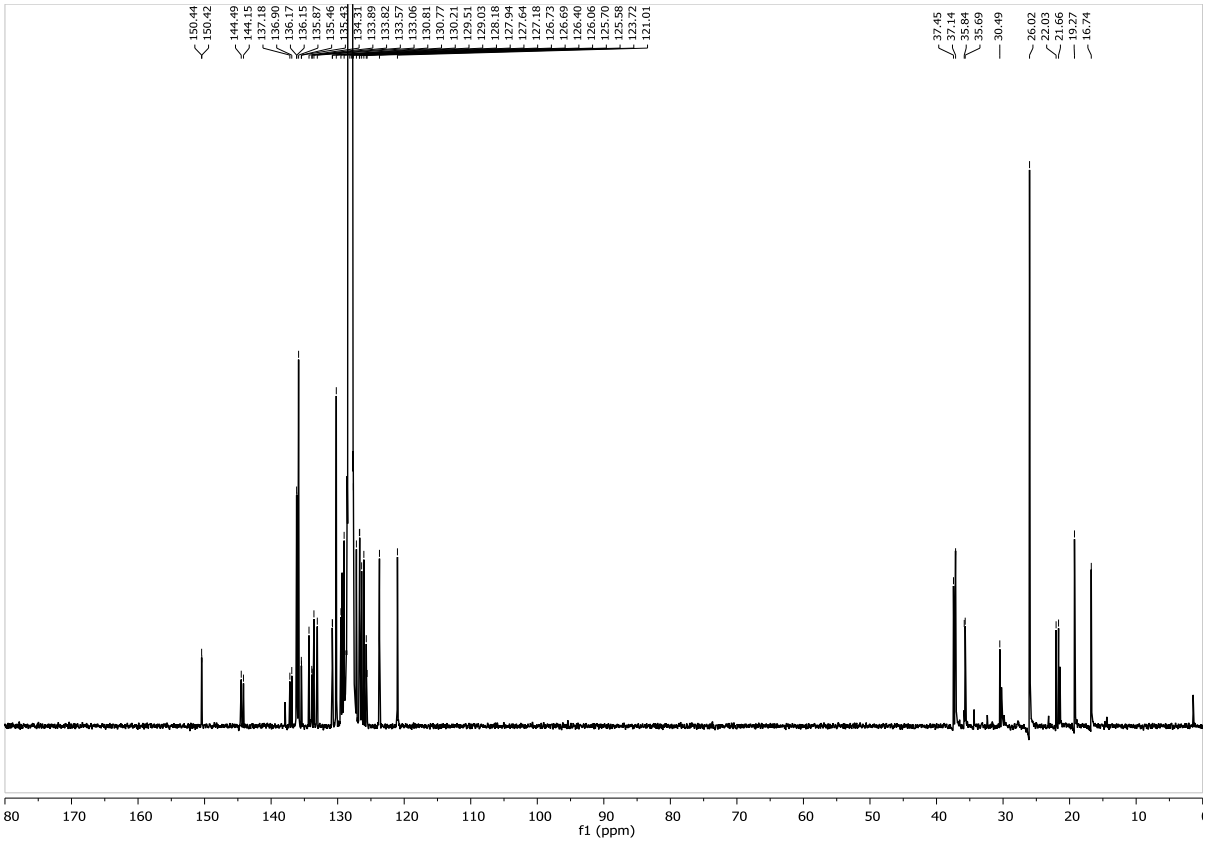
^{1}H NMR, 400 MHz, C_6D_6

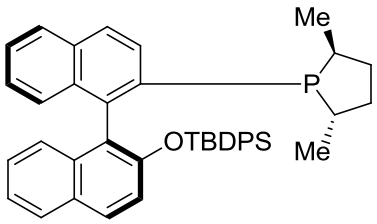




L8

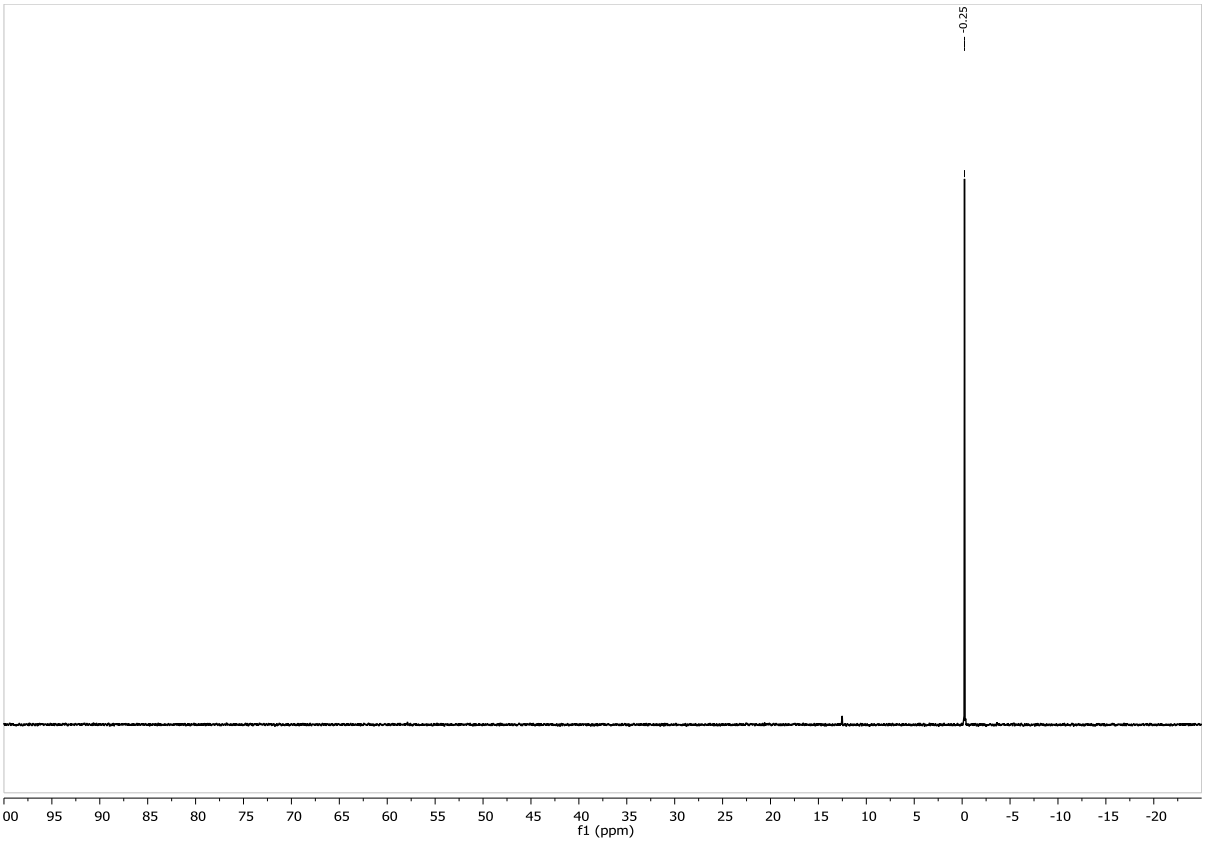
$^{13}C\{^{1}H\}$ NMR, 101 MHz, C_6D_6

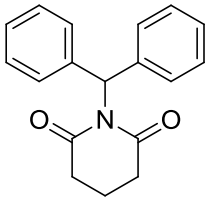




L8

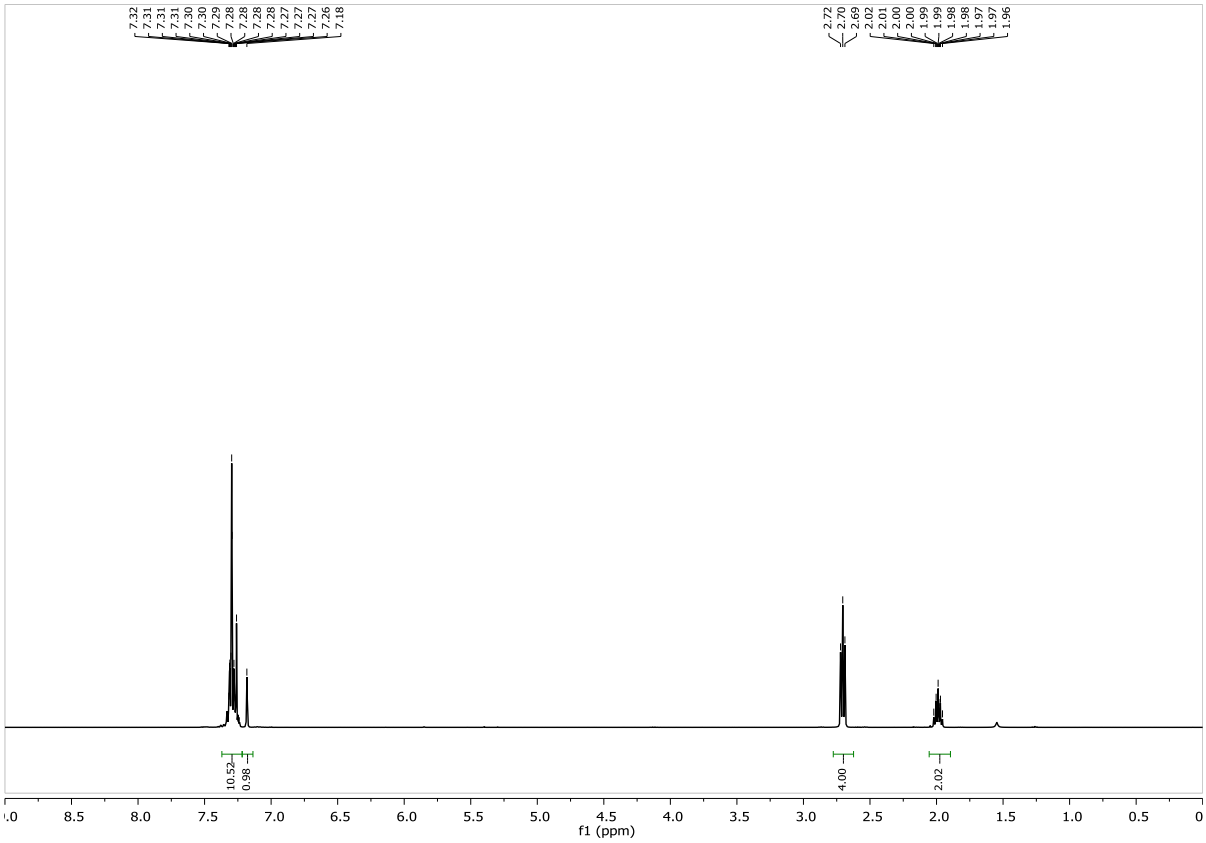
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

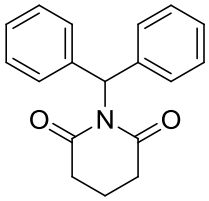




S5a

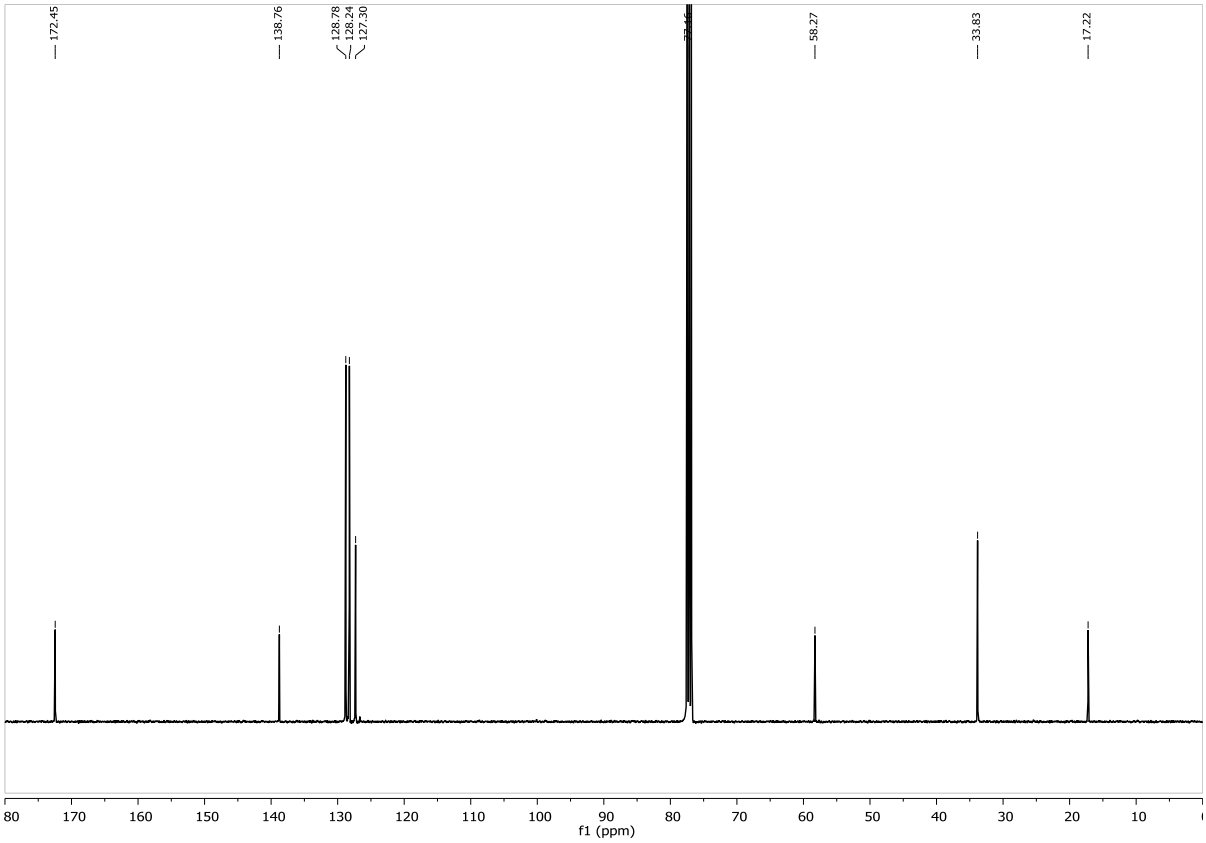
^{1}H NMR, 400 MHz, $CDCl_3$

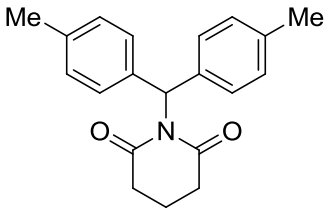




S5a

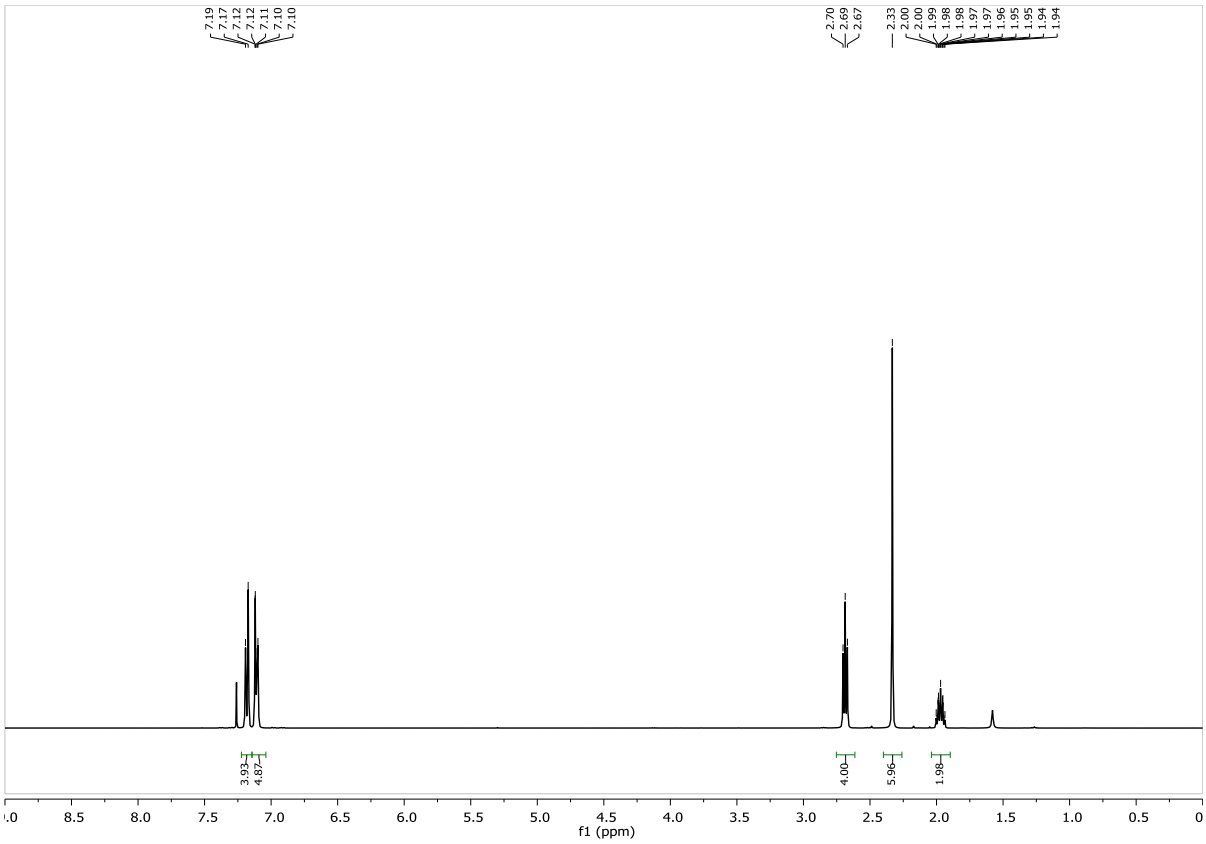
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

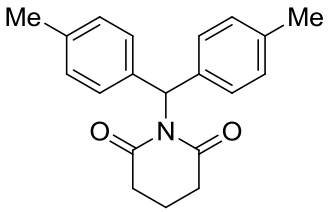




S5b

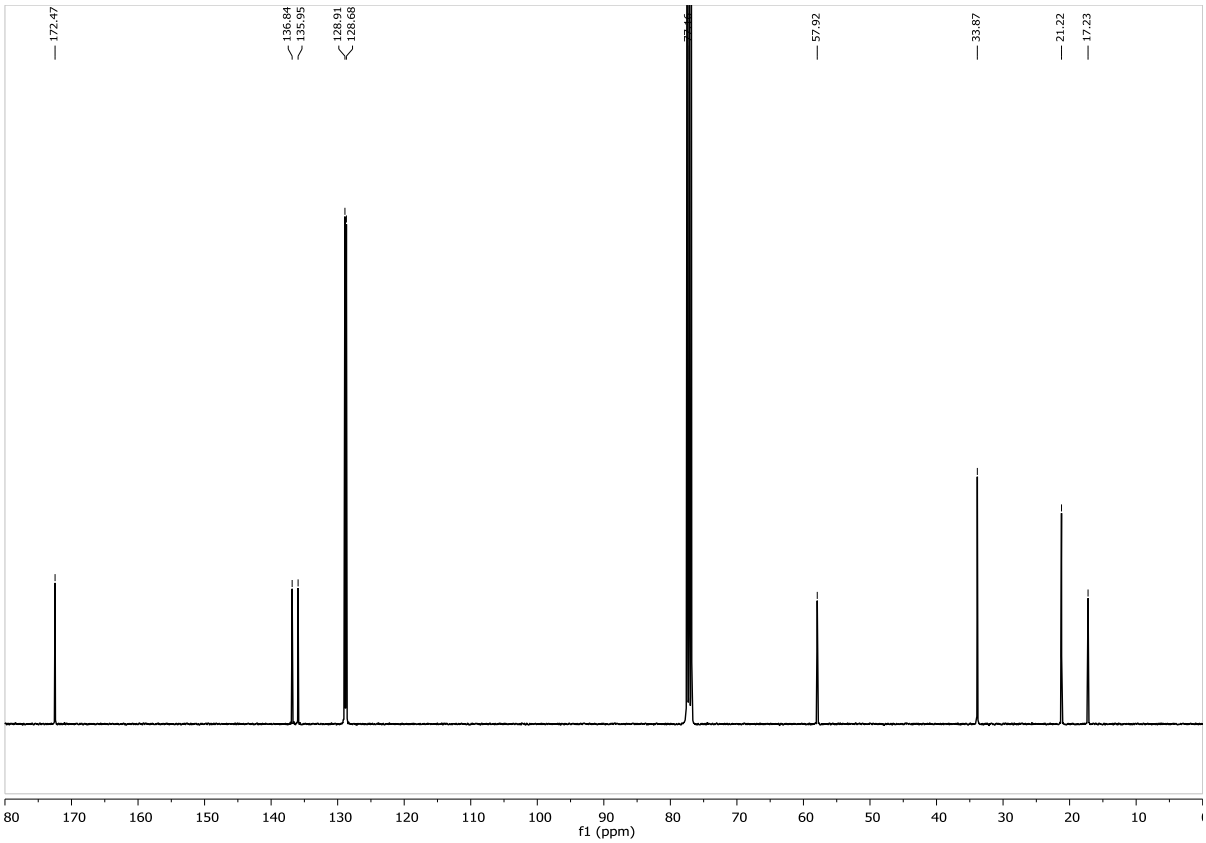
^{1}H NMR, 400 MHz, $CDCl_3$

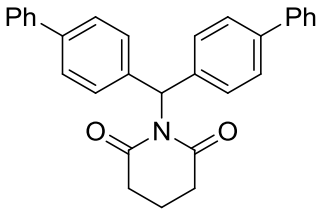




S5b

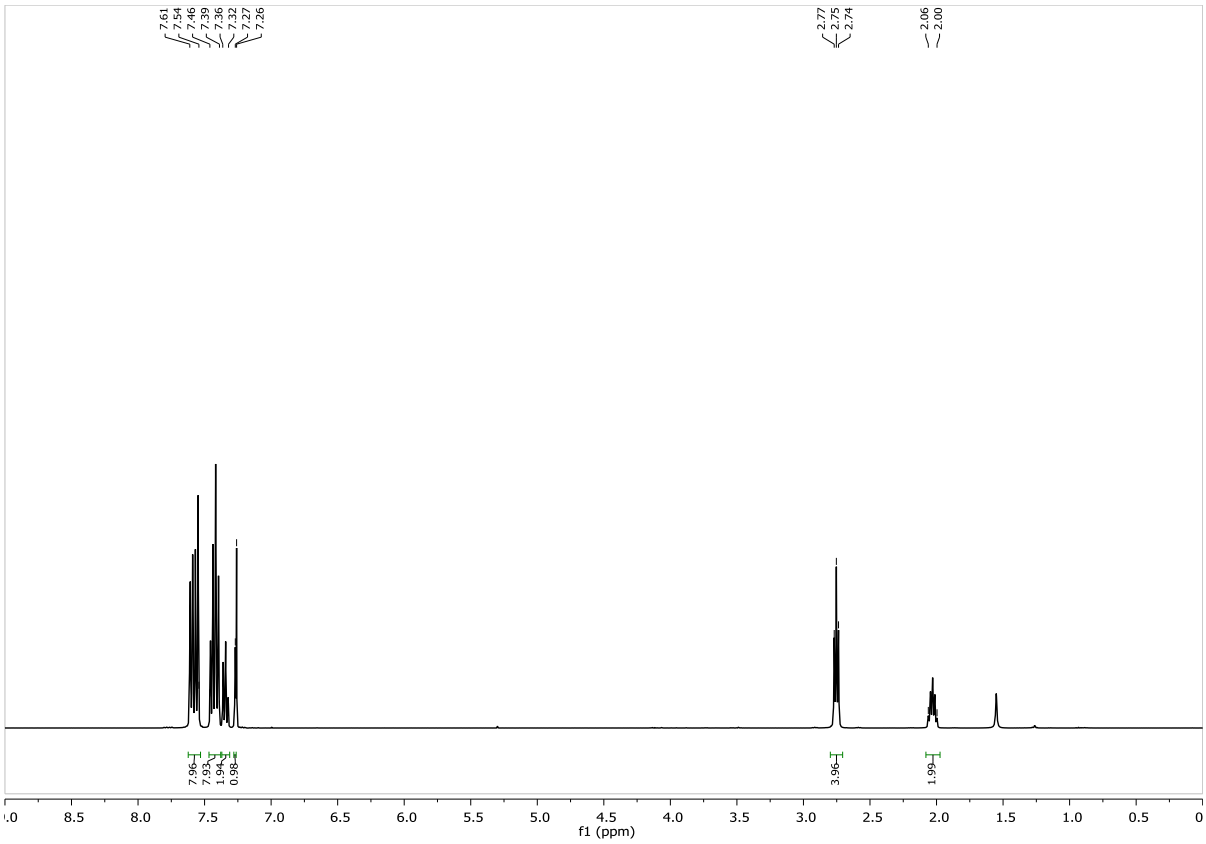
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

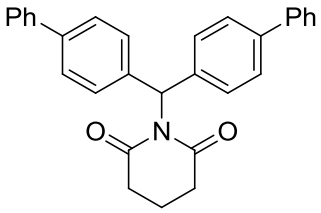




S5c

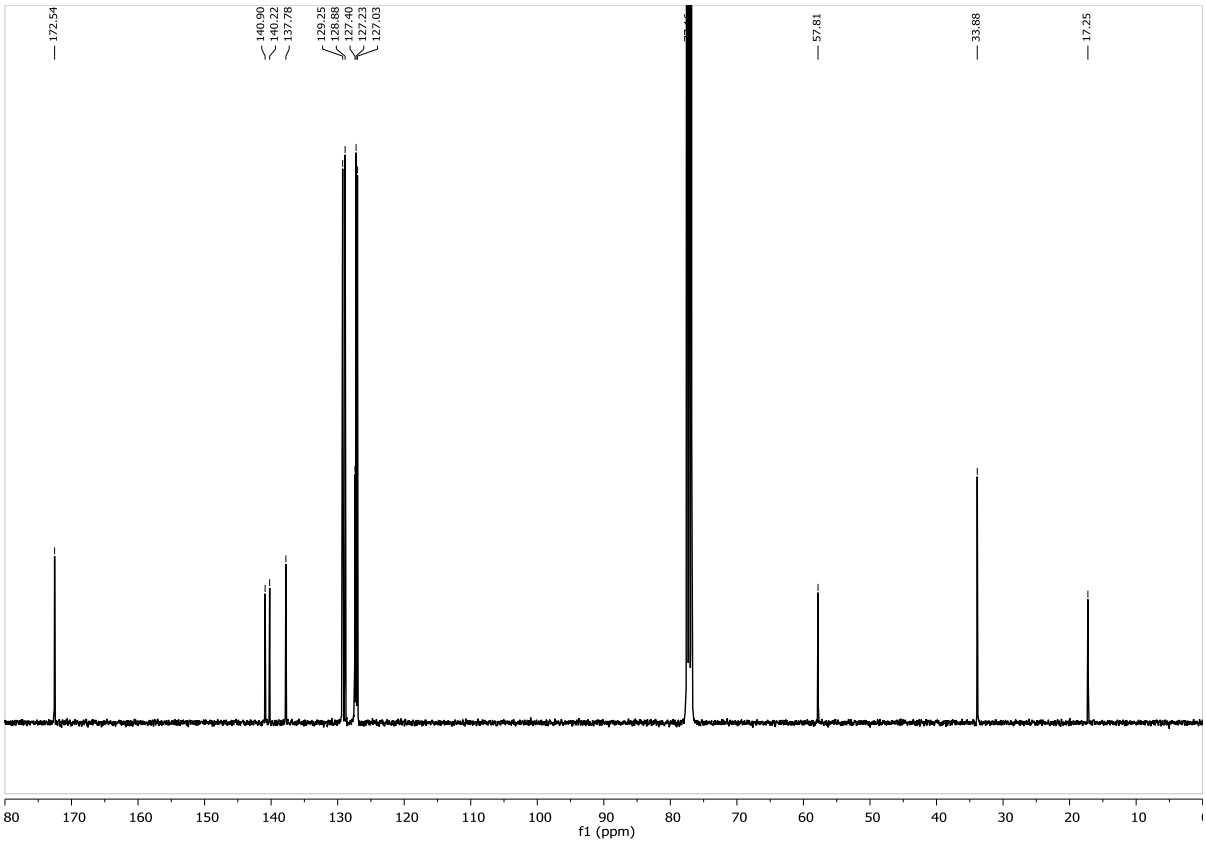
^{1}H NMR, 400 MHz, $CDCl_3$

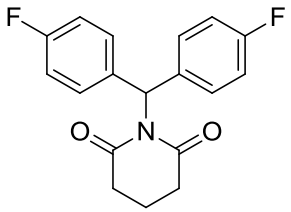




S5c

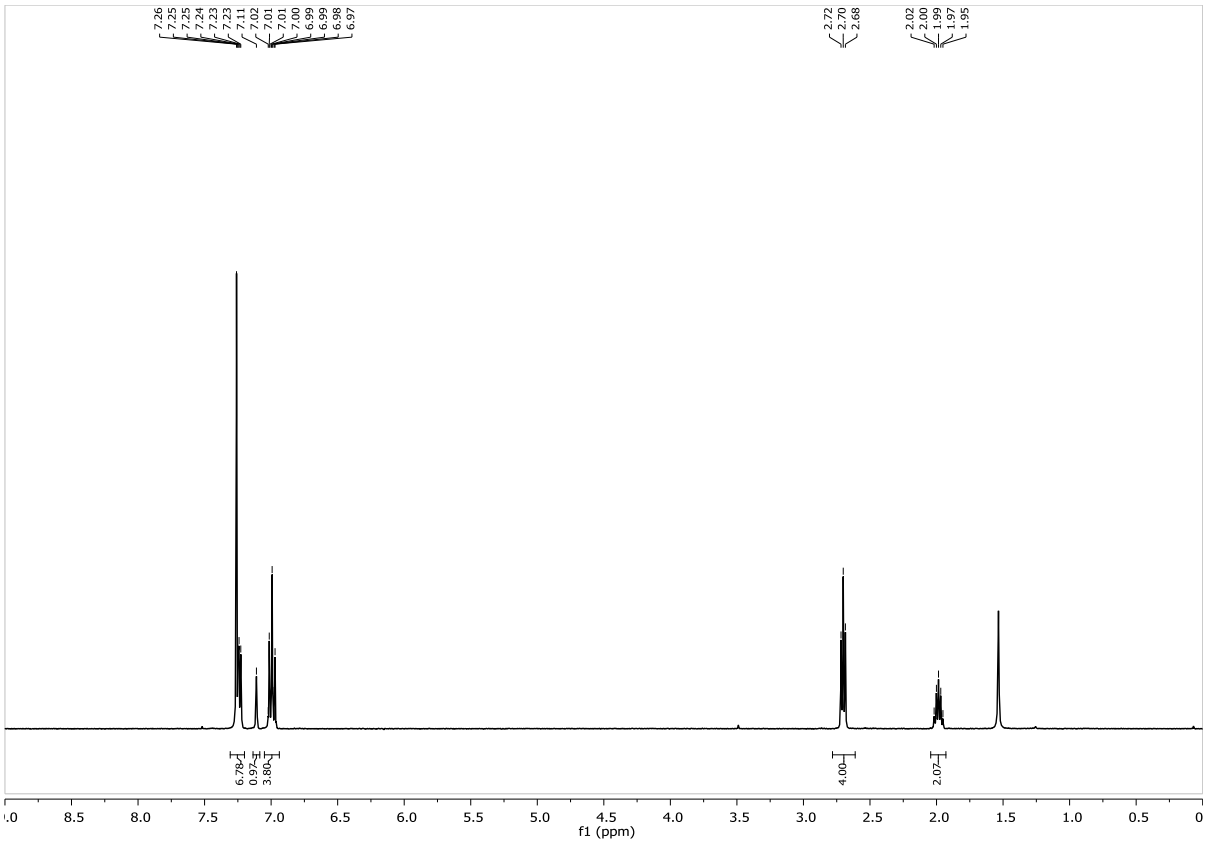
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

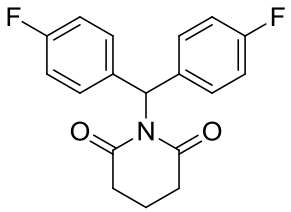




S5d

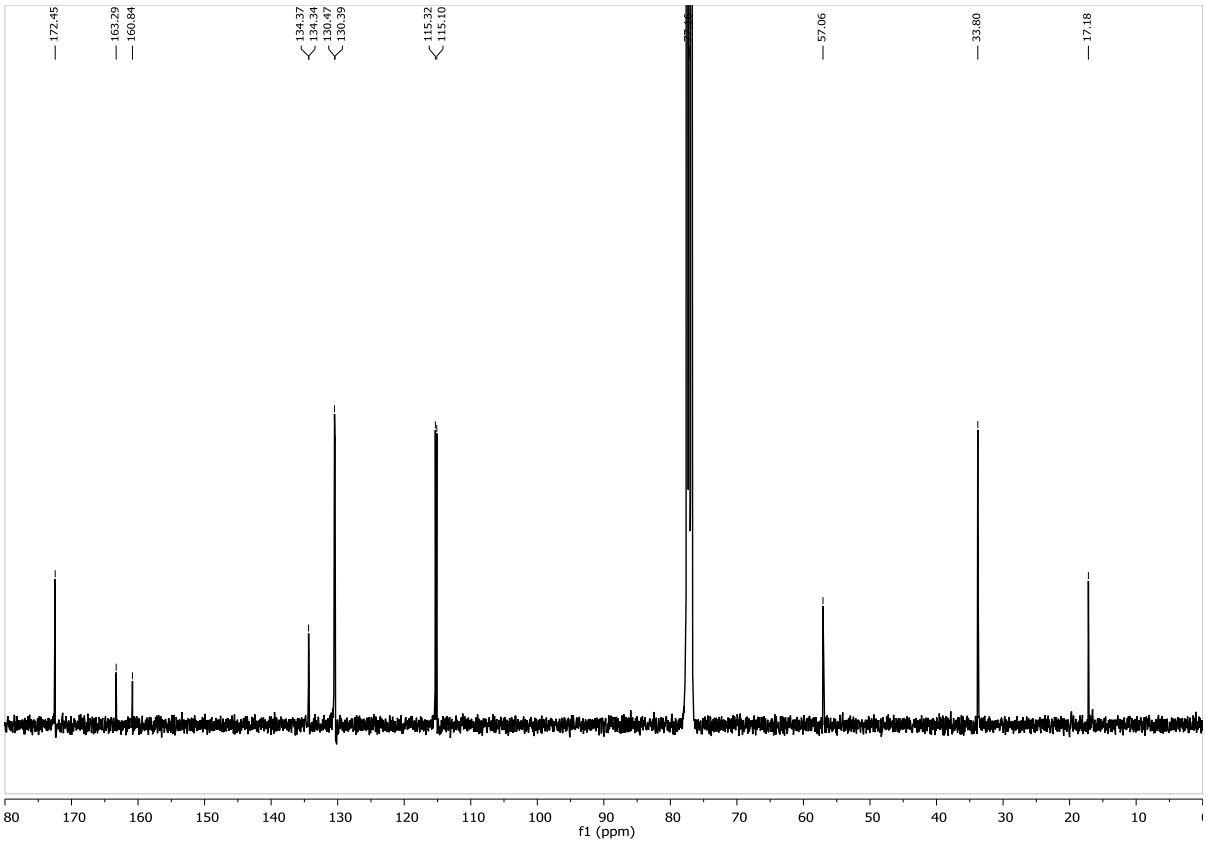
^{1}H NMR, 400 MHz, $CDCl_3$

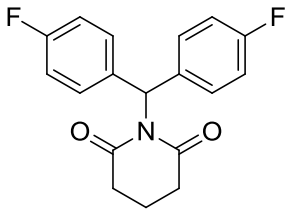




S5d

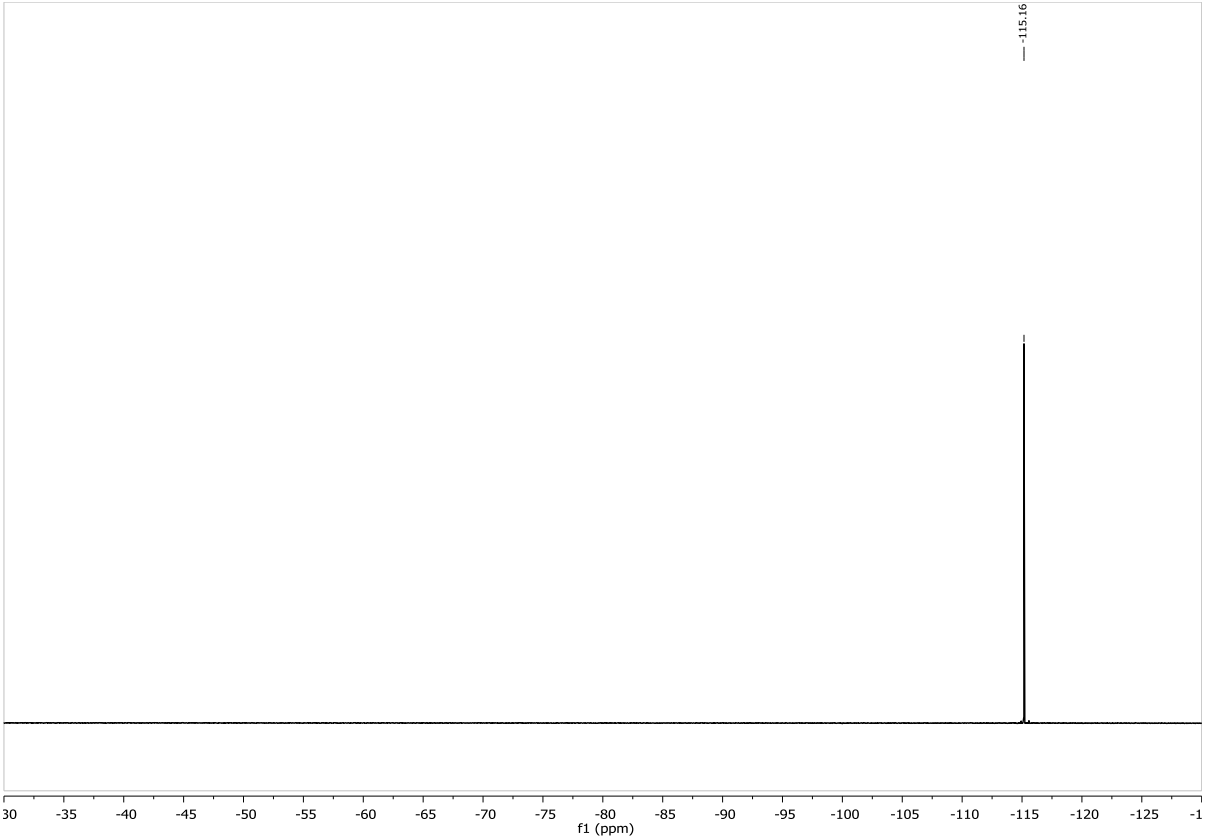
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

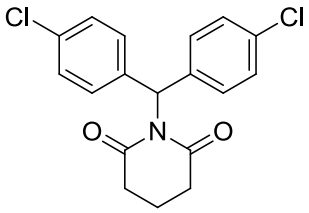




S5d

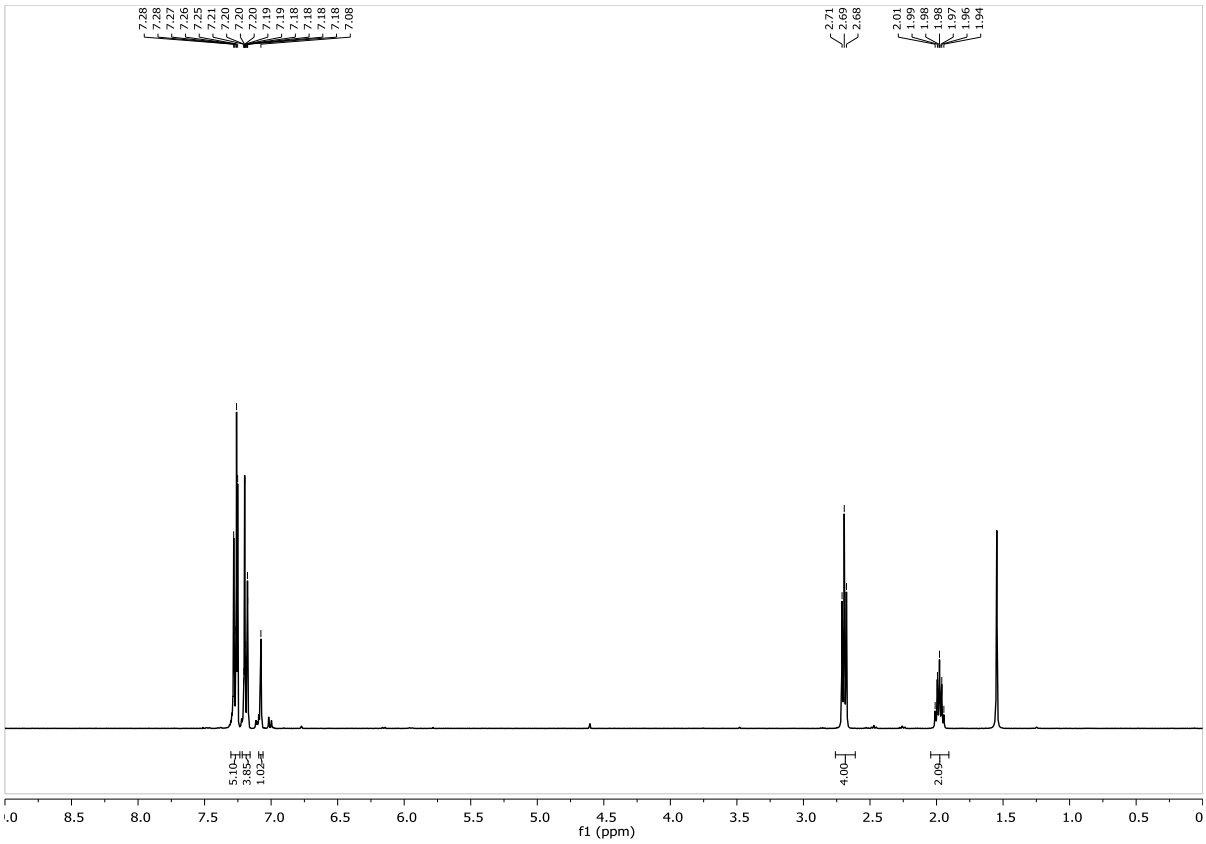
$^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

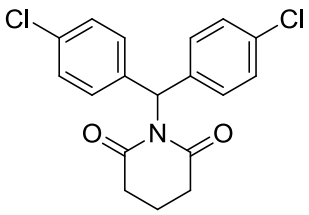




S5e

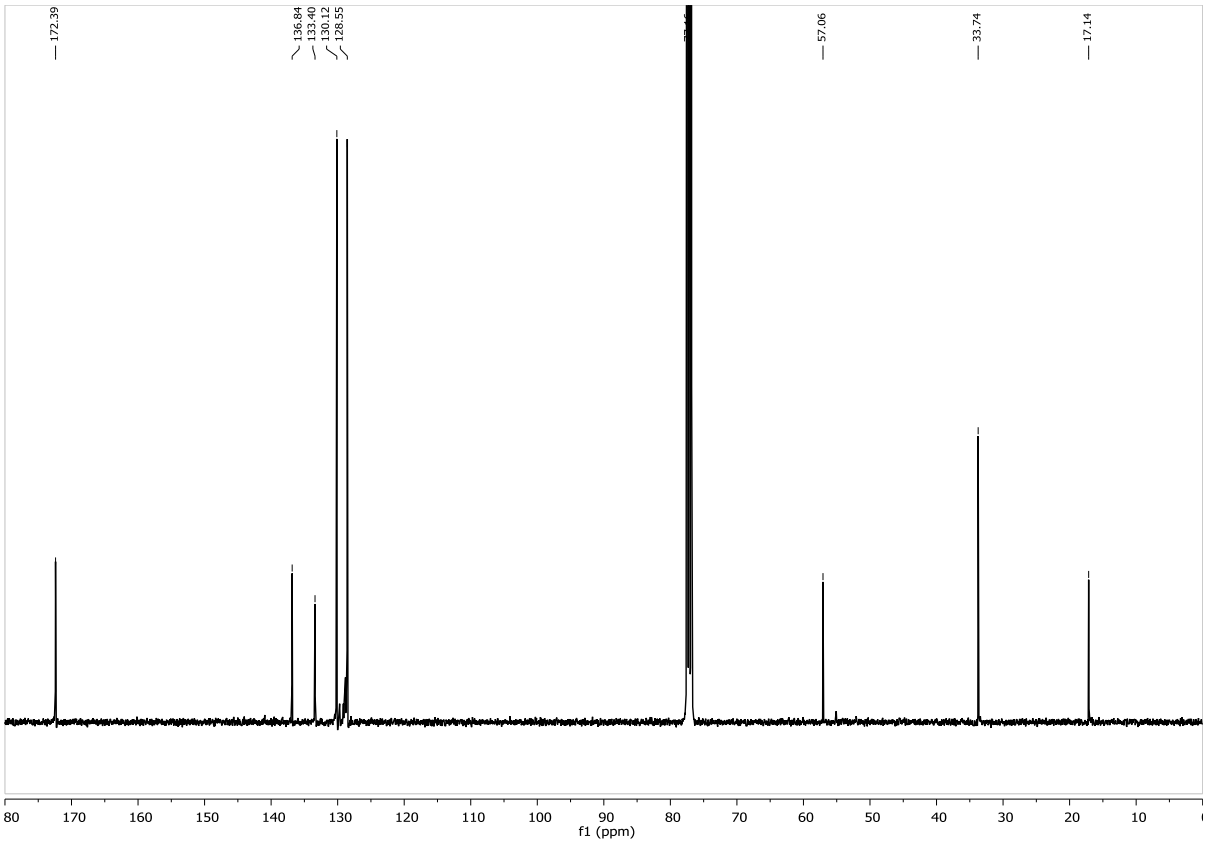
^{1}H NMR, 400 MHz, $CDCl_3$

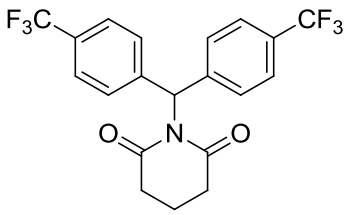




S5e

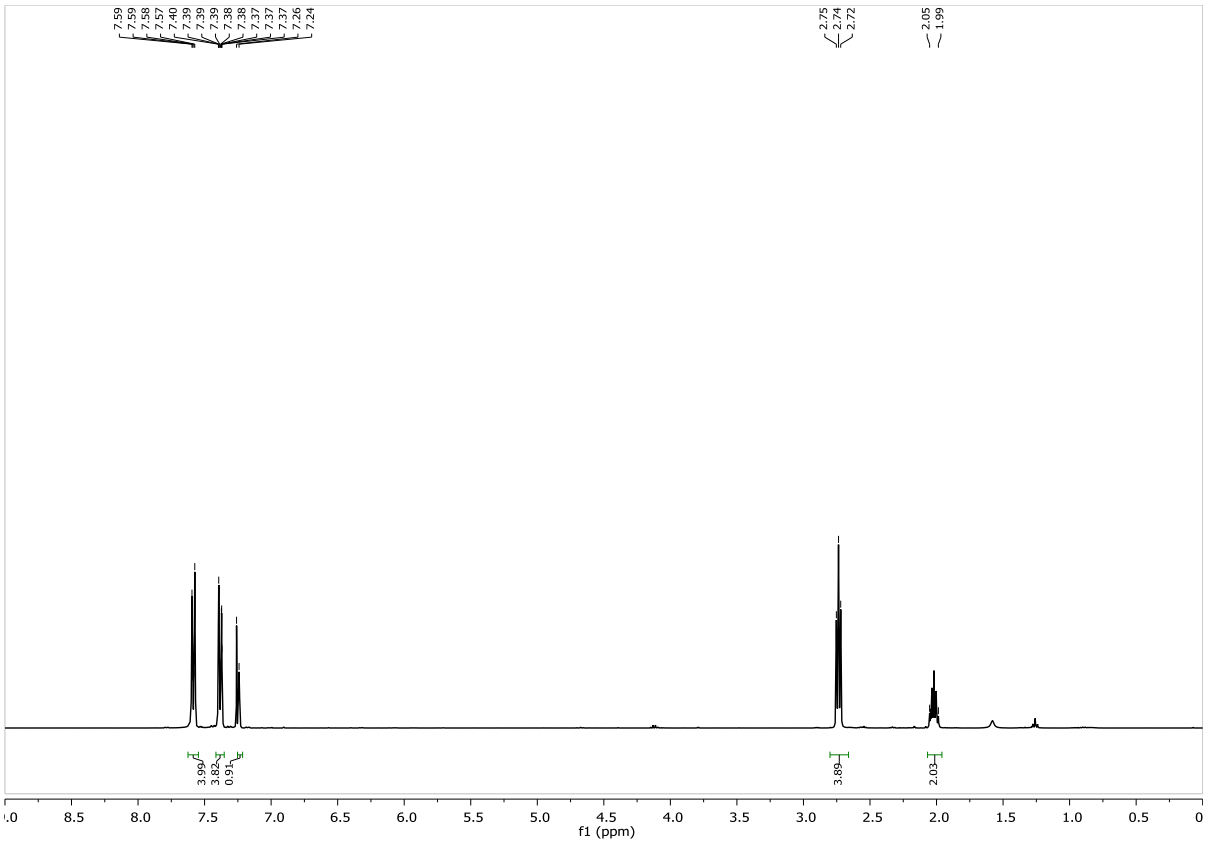
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

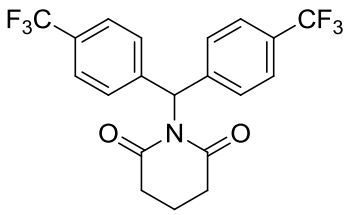




S5f

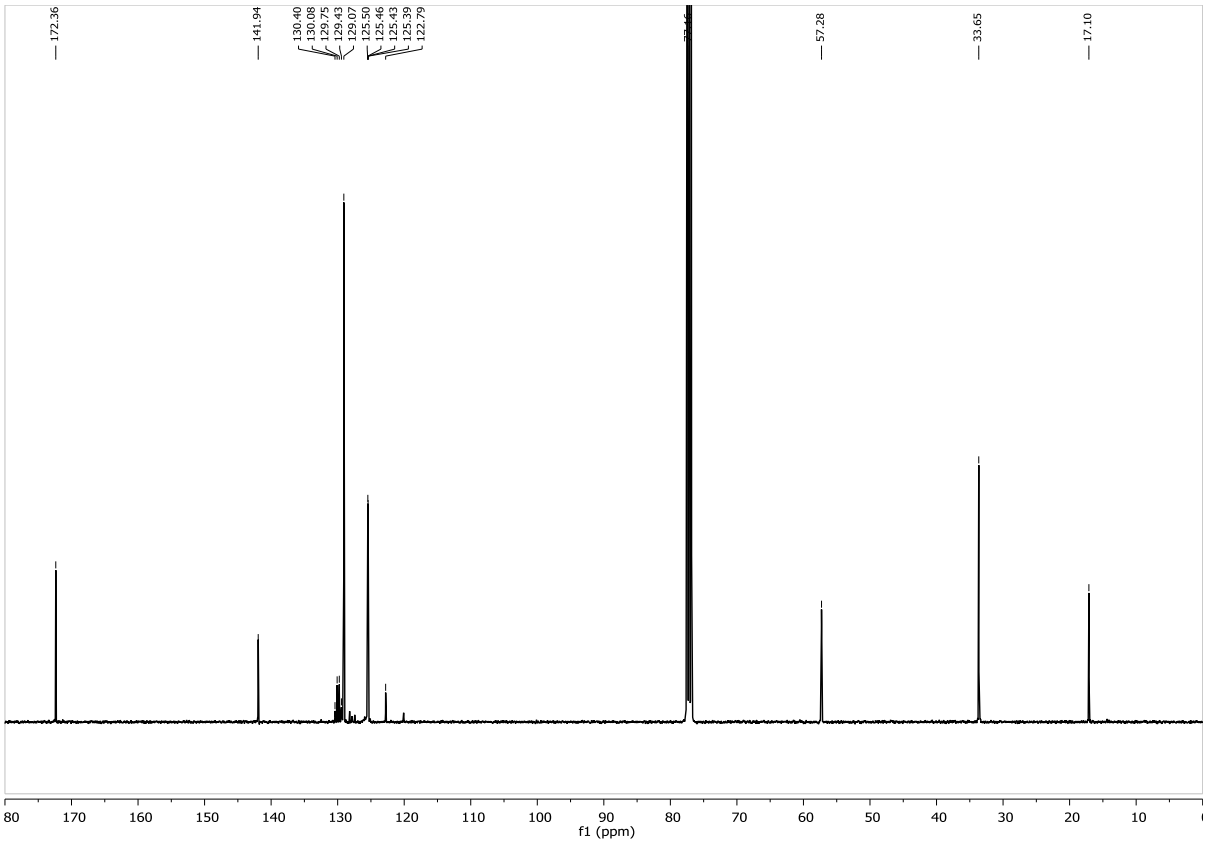
^{1}H NMR, 400 MHz, $CDCl_3$

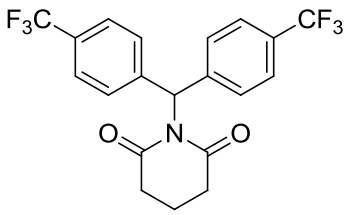




S5f

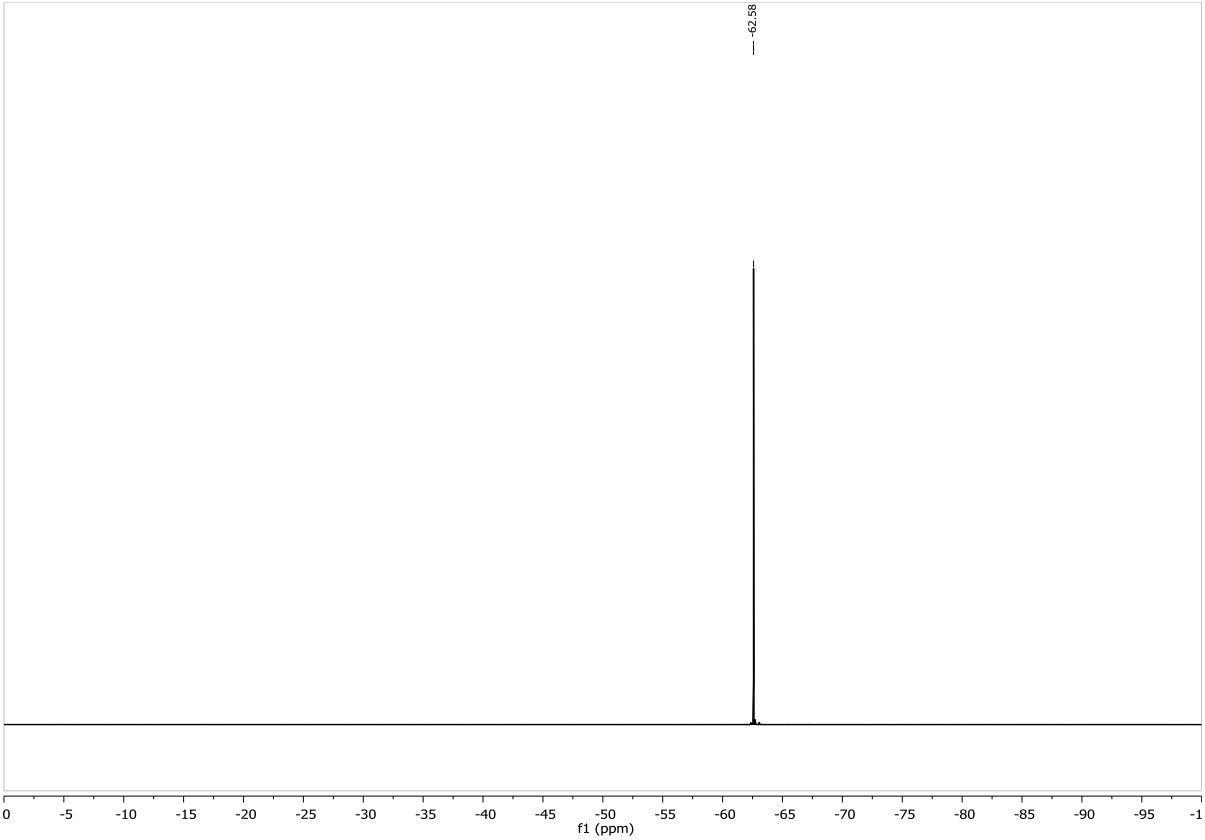
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

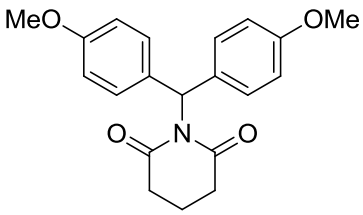




S5f

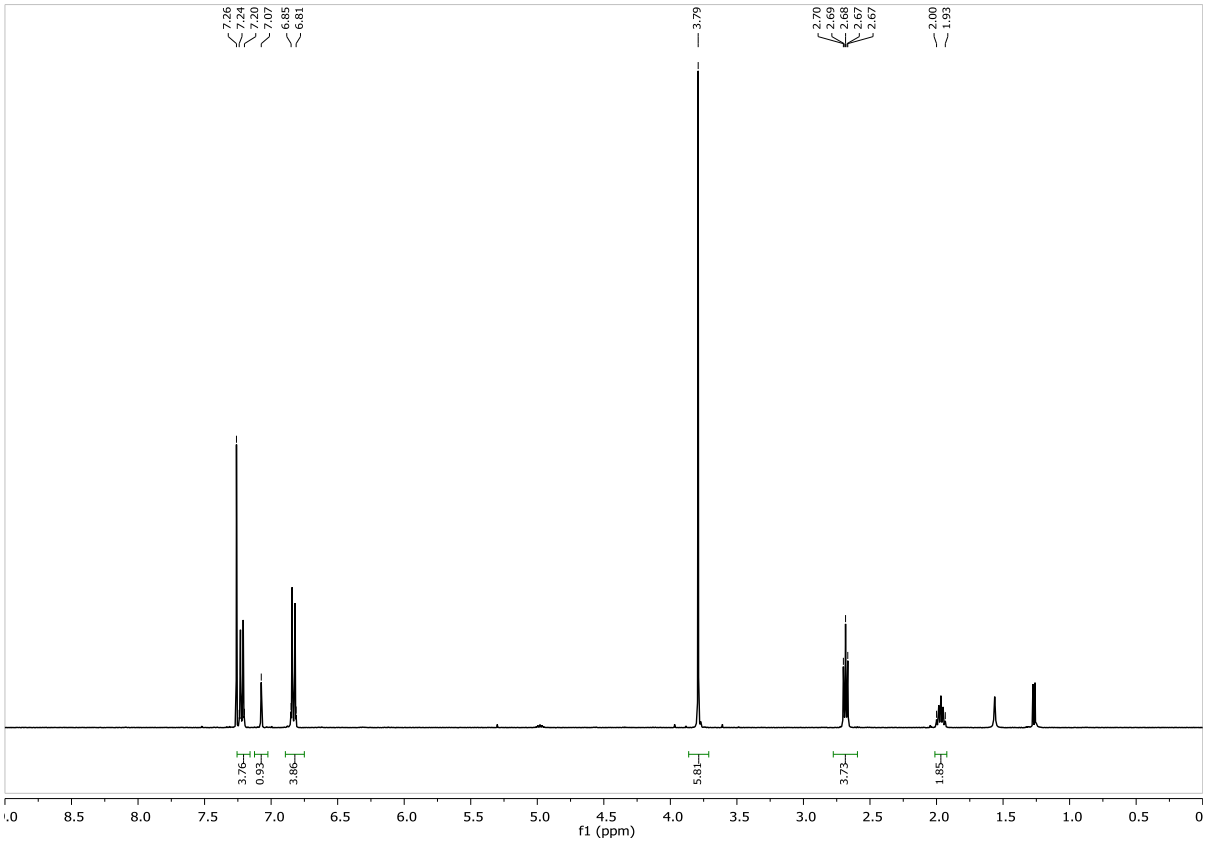
$^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

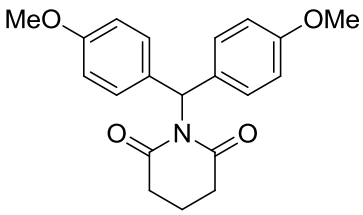




S5g

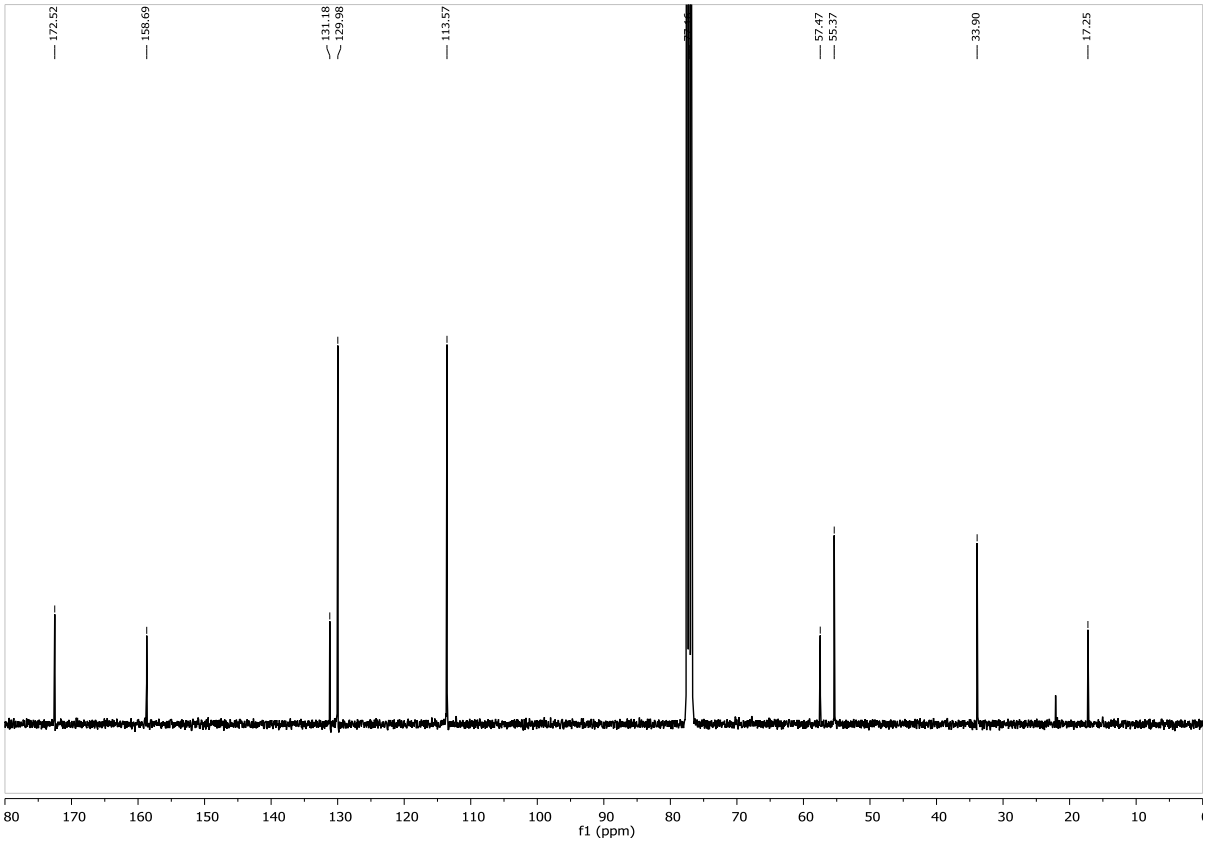
^{1}H NMR, 400 MHz, $CDCl_3$

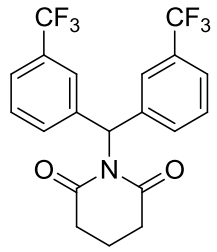




S5g

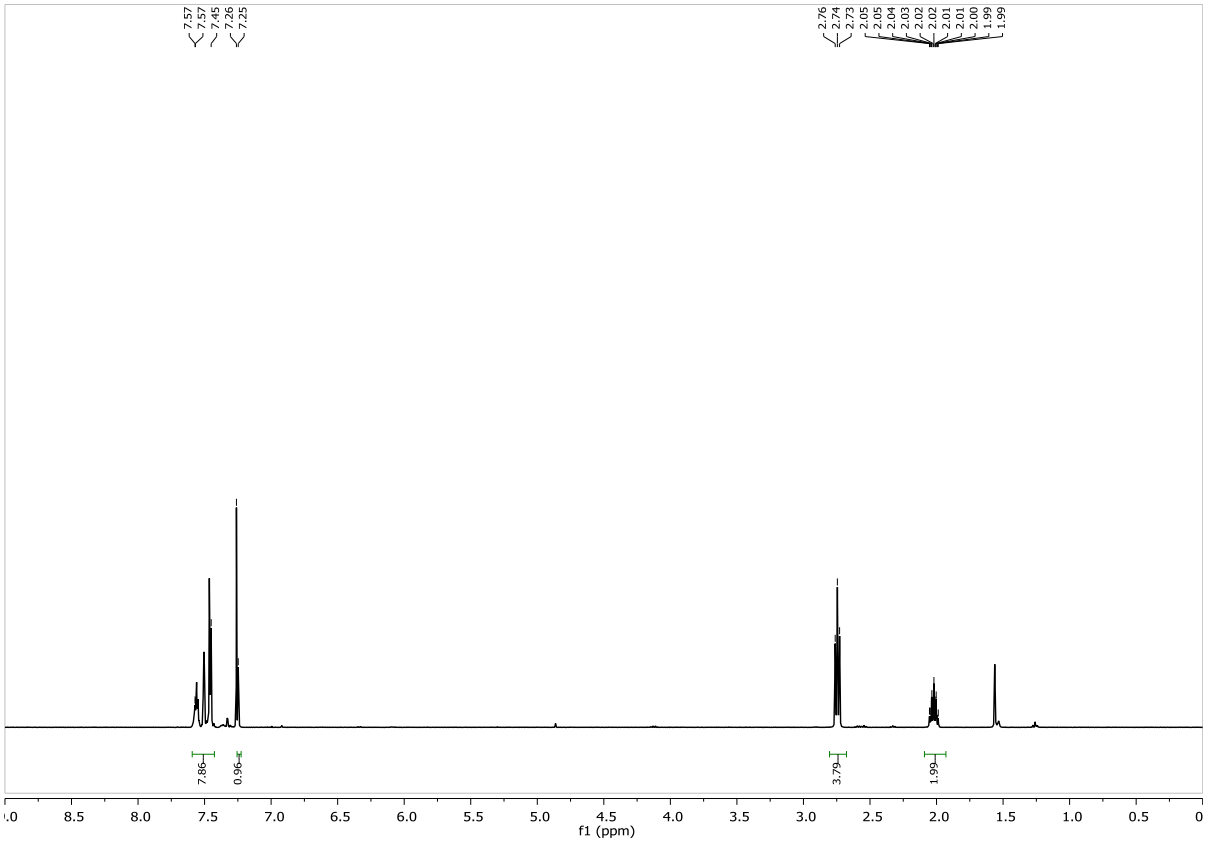
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

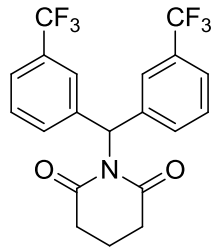




S5h

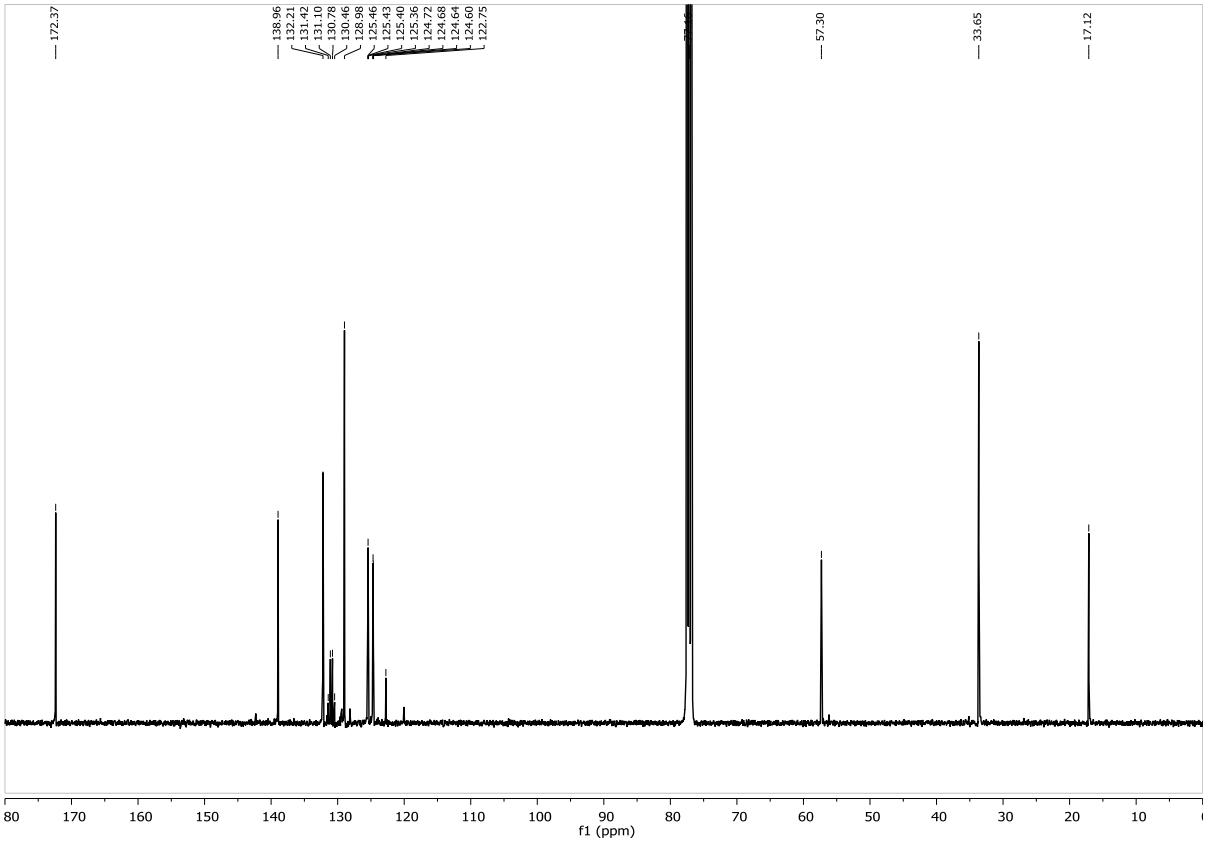
^{1}H NMR, 400 MHz, $CDCl_3$

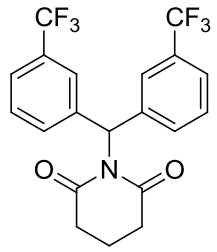




S5h

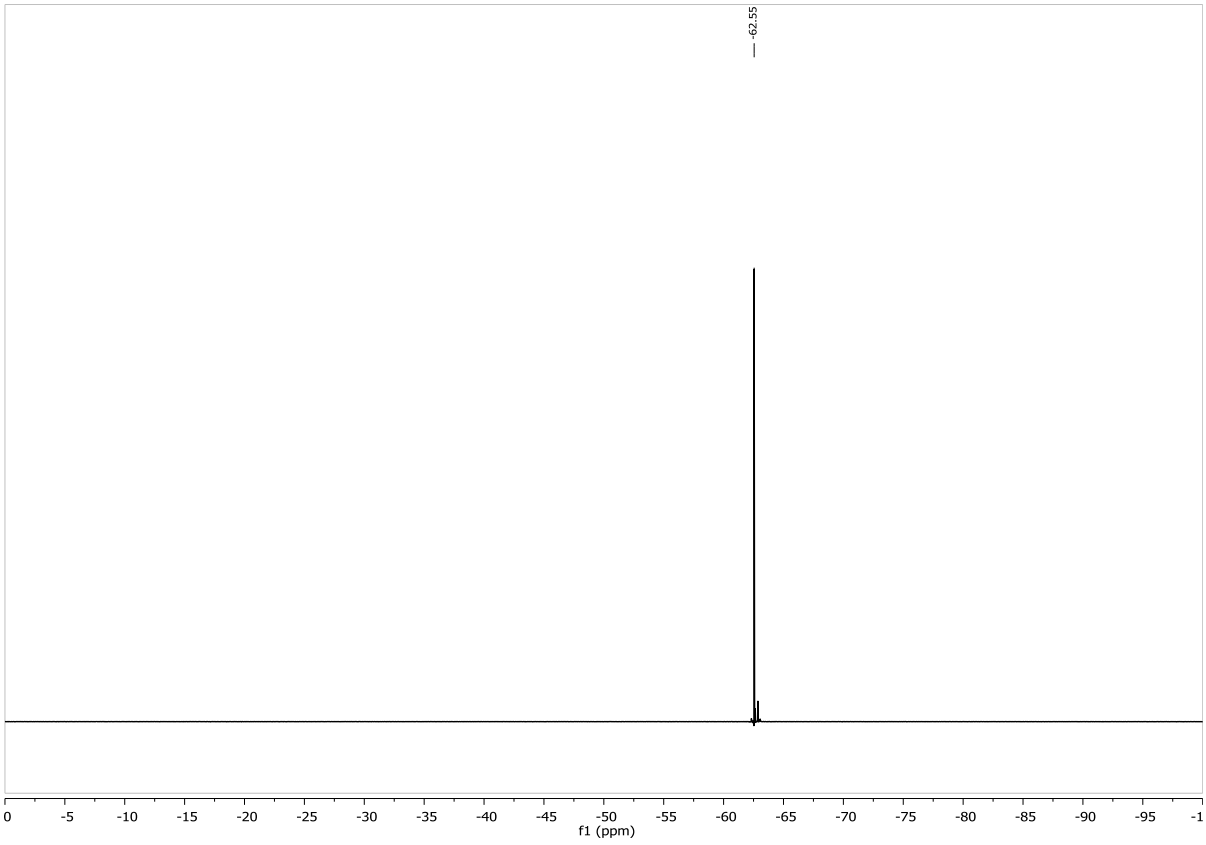
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

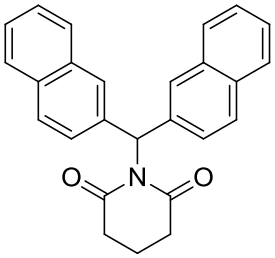




S5h

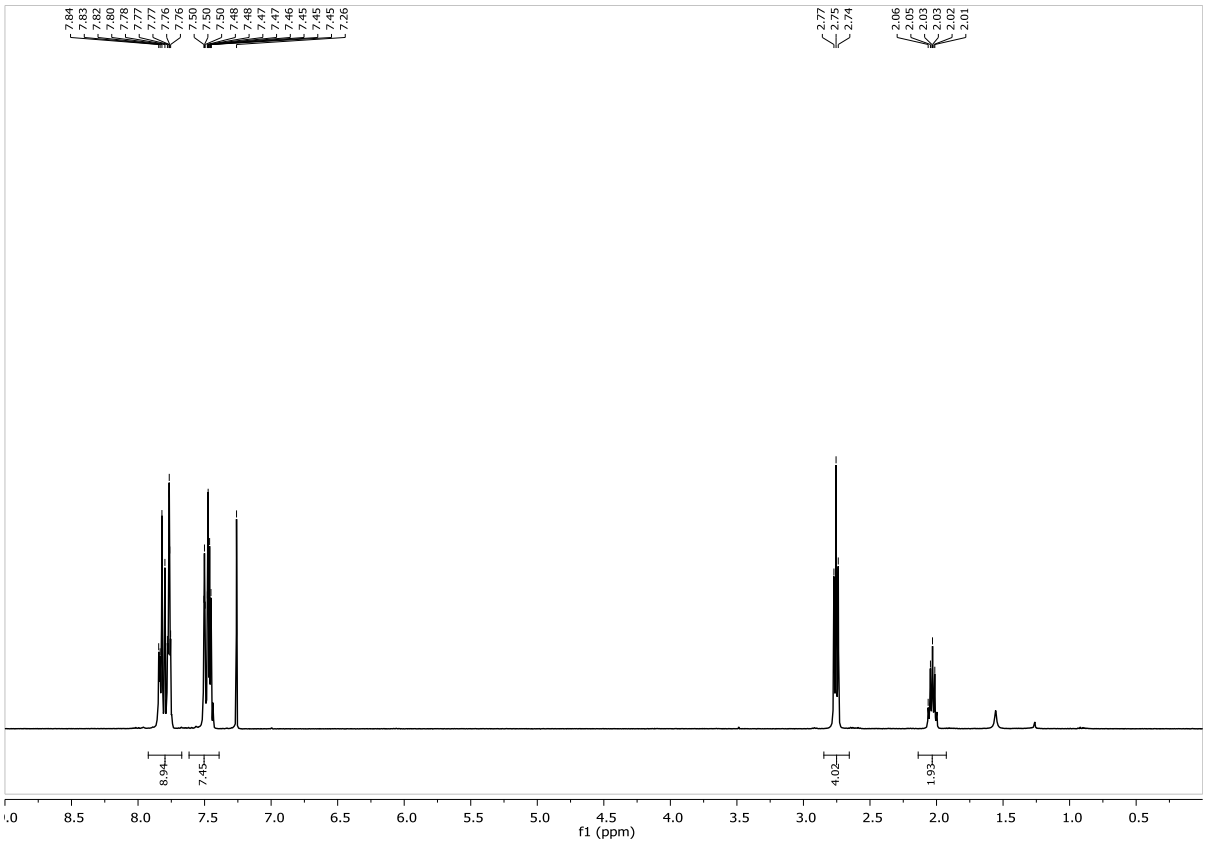
$^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

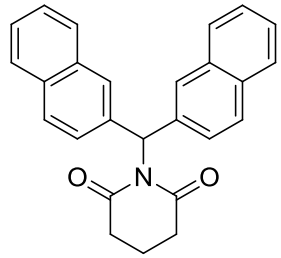




S5i

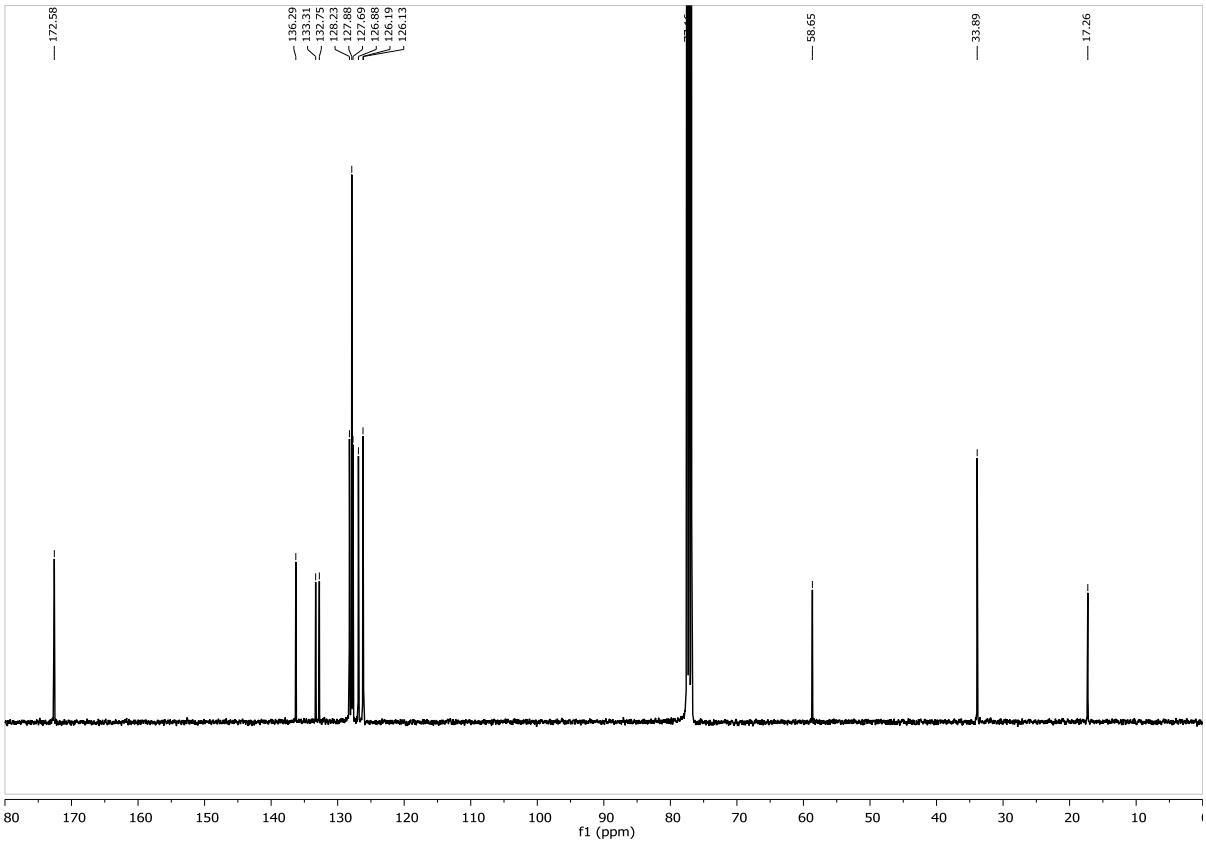
^{1}H NMR, 400 MHz, $CDCl_3$

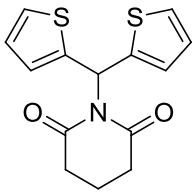




S5i

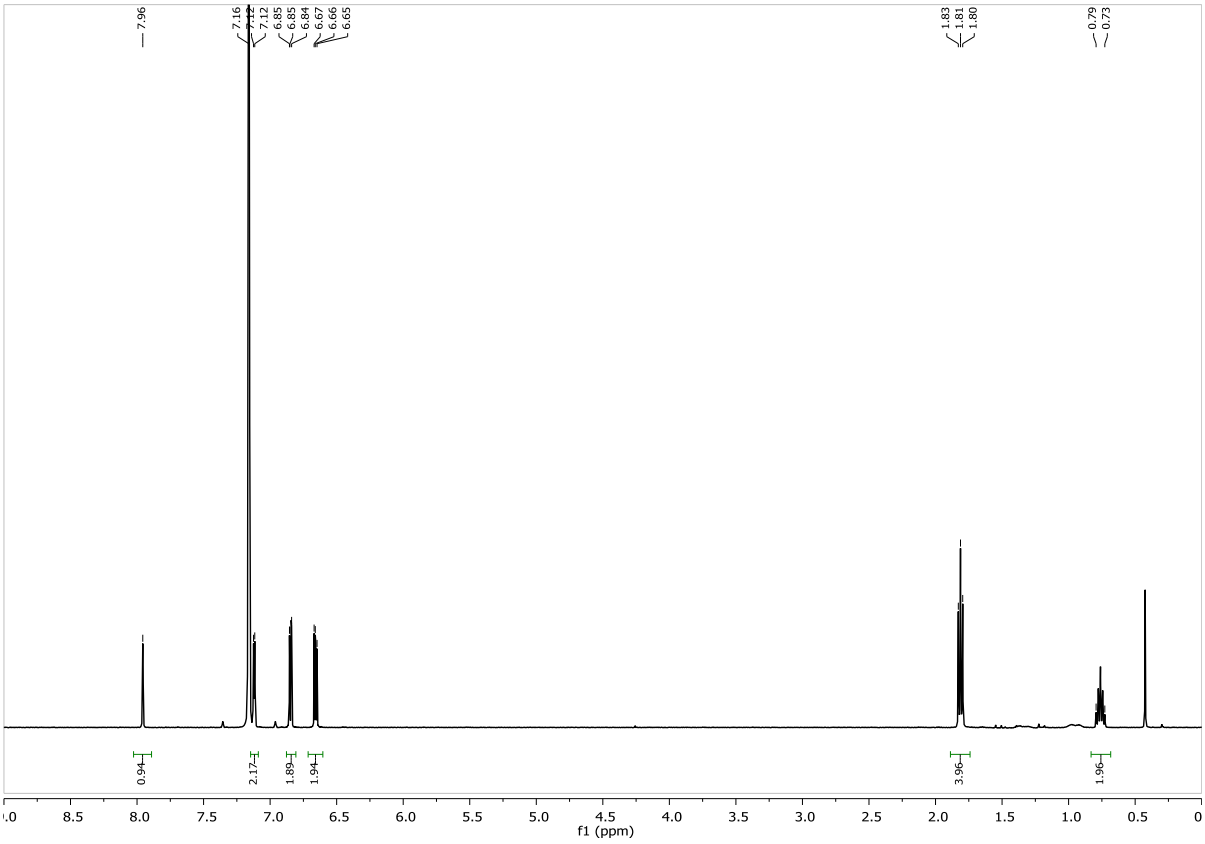
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

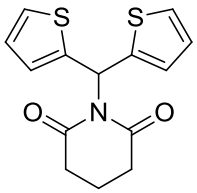




S5j

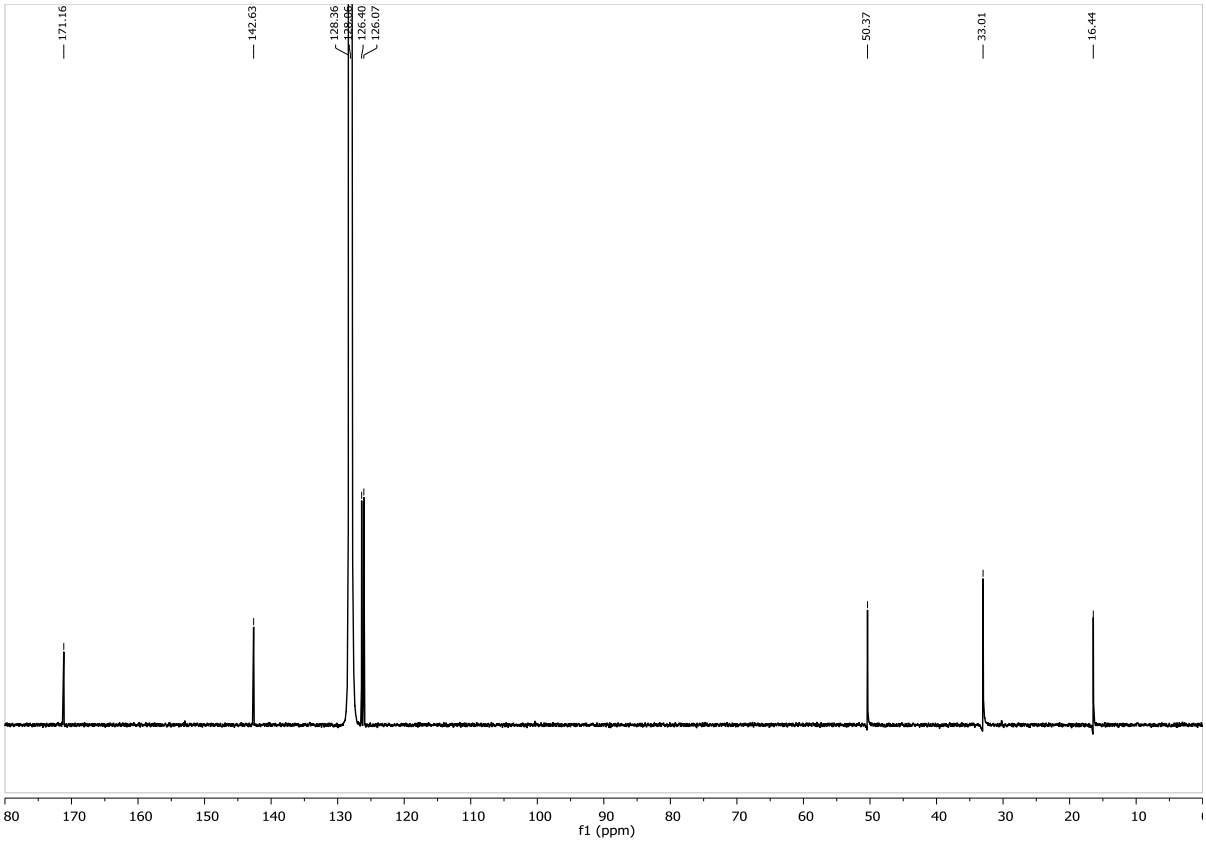
^{1}H NMR, 400 MHz, C_6D_6

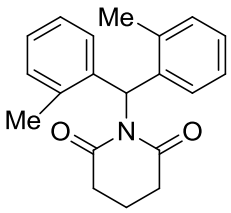




S5j

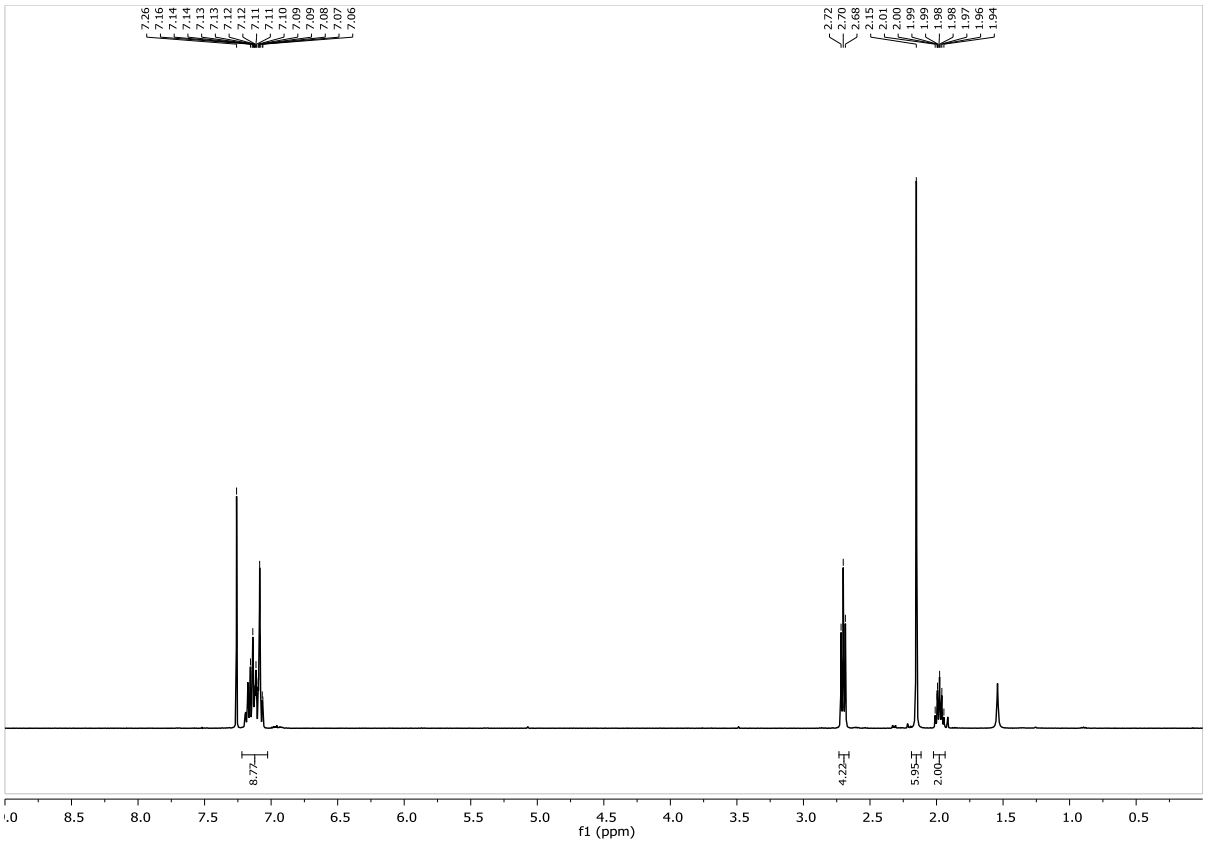
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

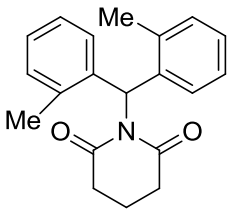




S5k

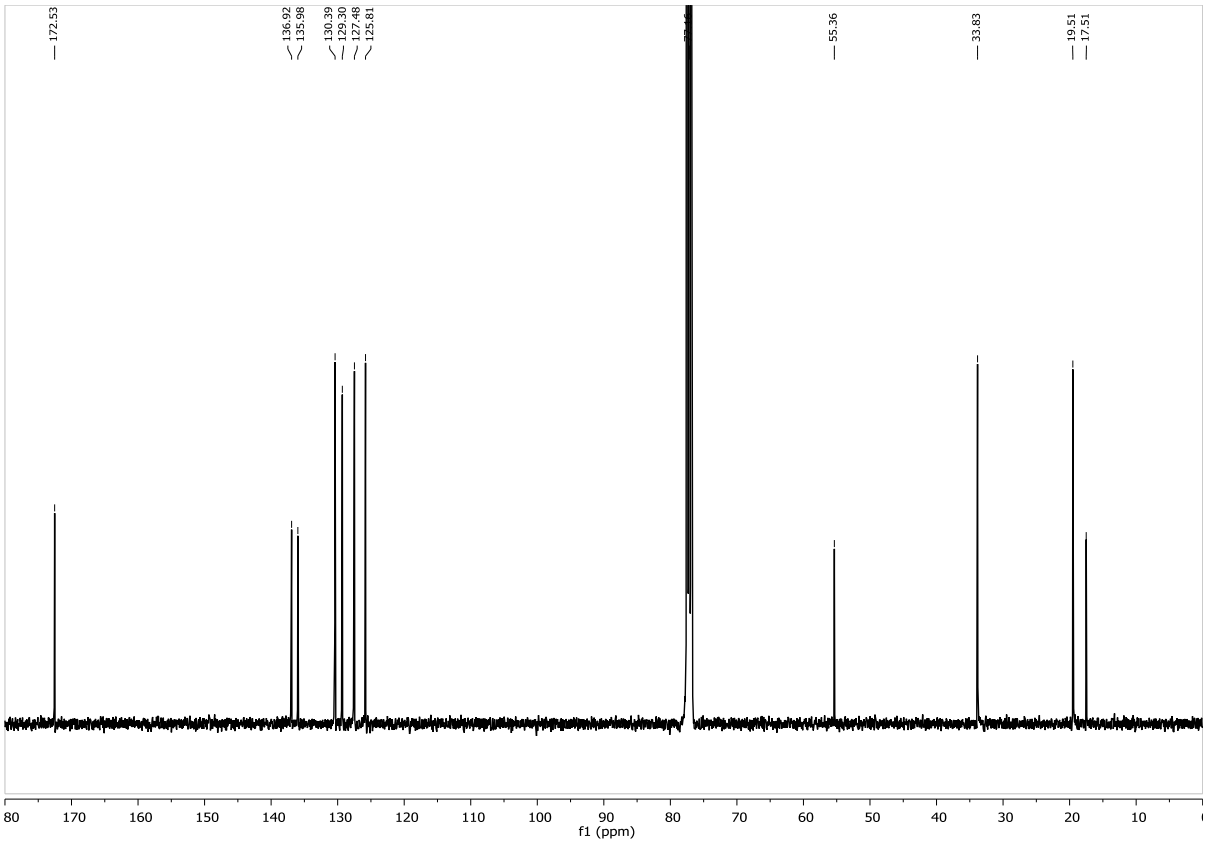
^{1}H NMR, 400 MHz, $CDCl_3$

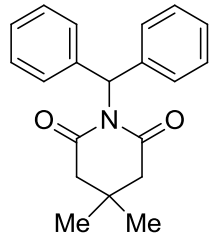




S5k

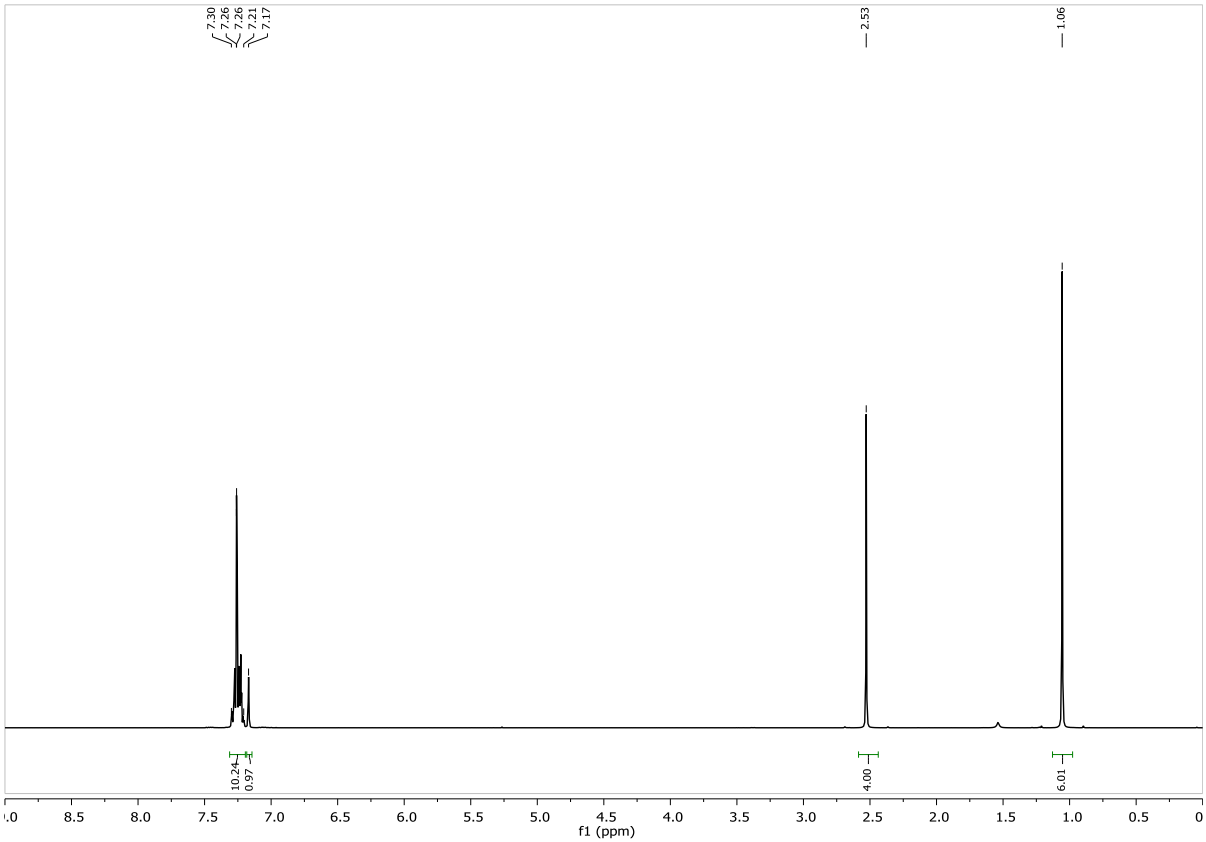
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

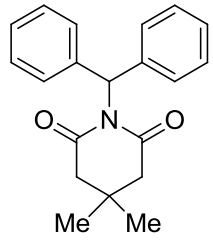




S5l

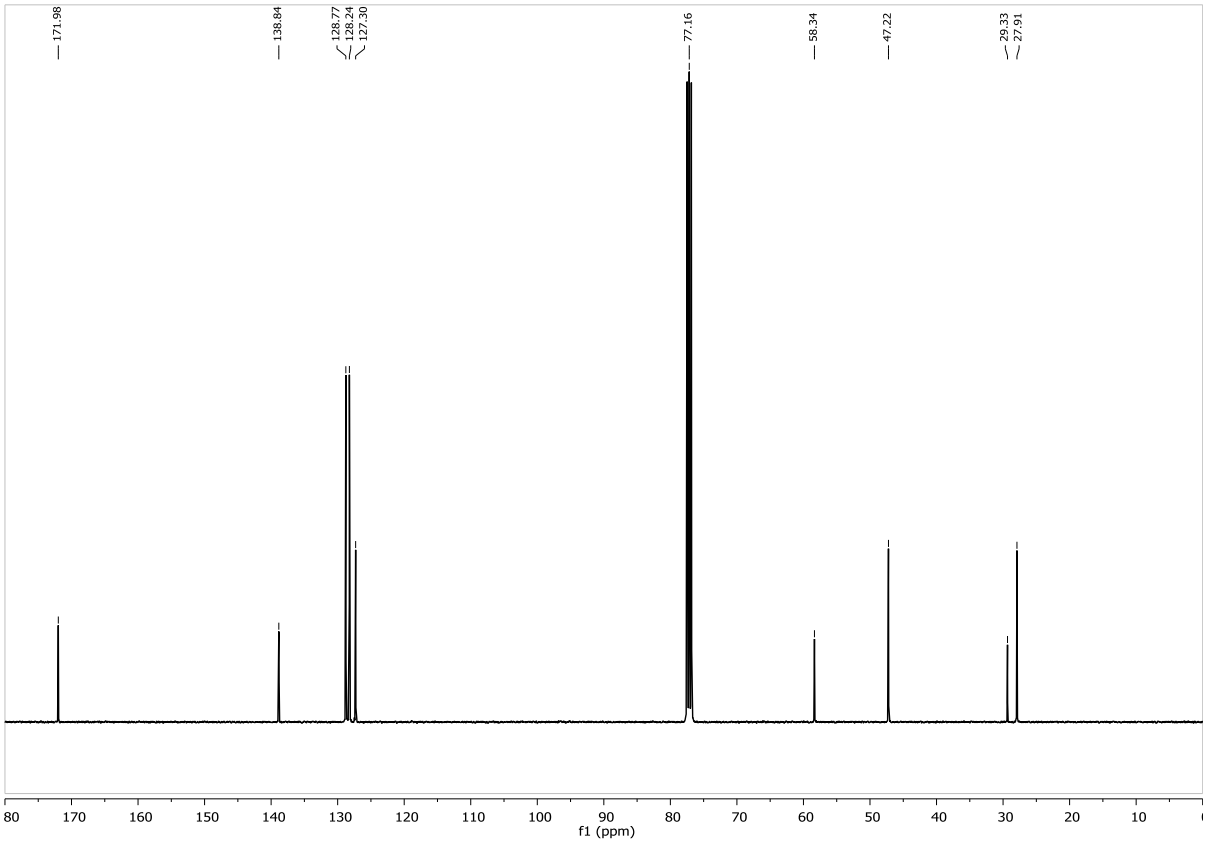
^{1}H NMR, 400 MHz, $CDCl_3$

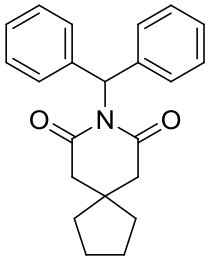




S5l

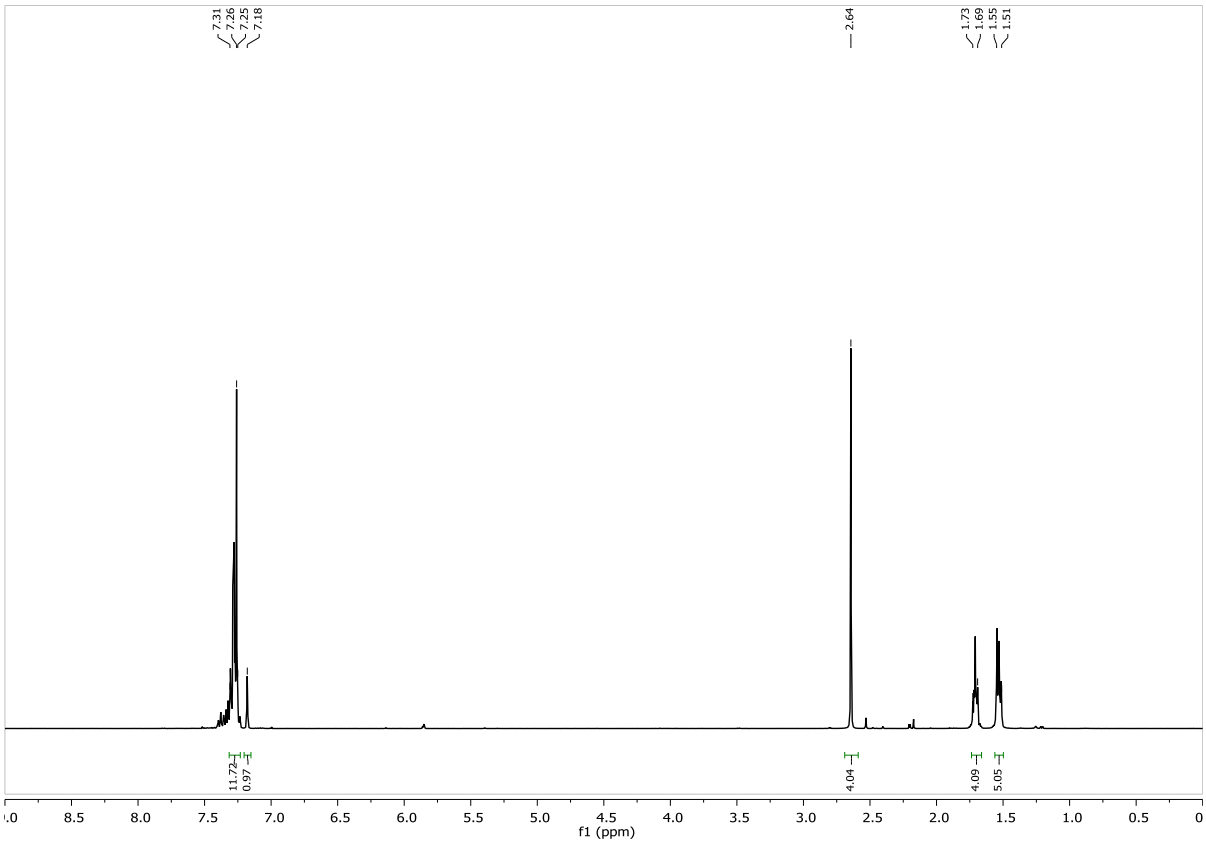
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

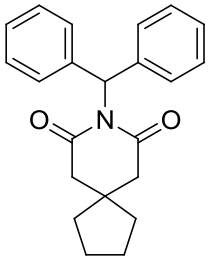




S5m

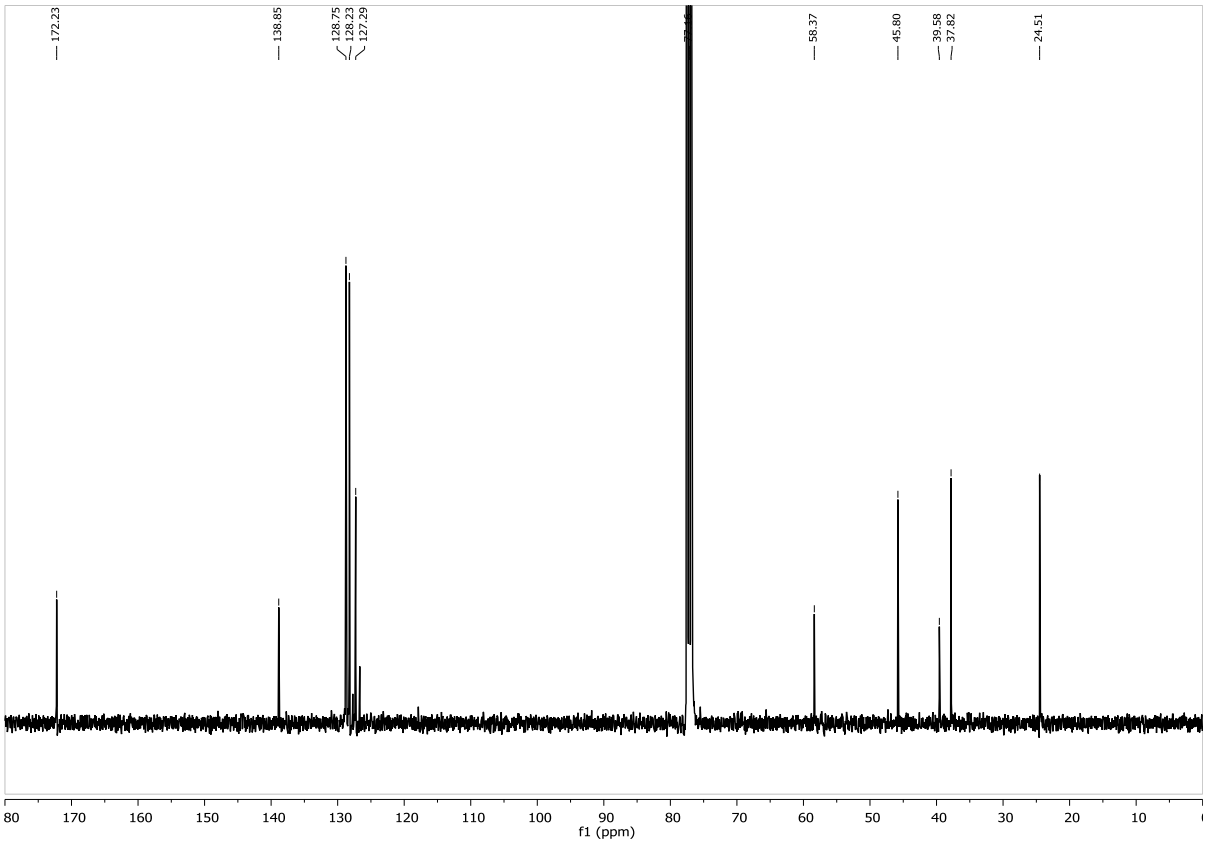
^{1}H NMR, 400 MHz, $CDCl_3$

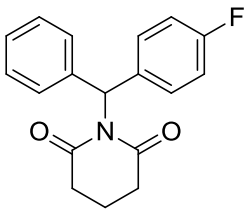




S5m

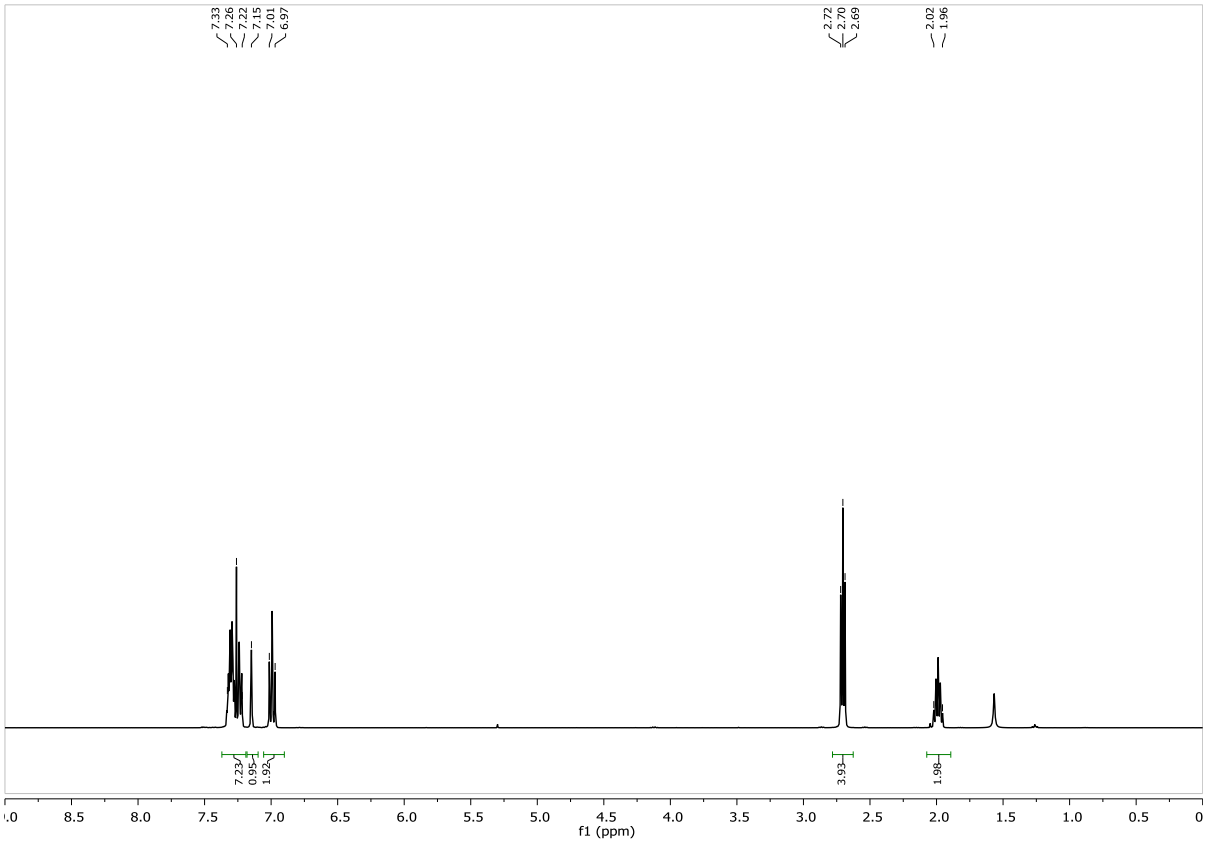
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

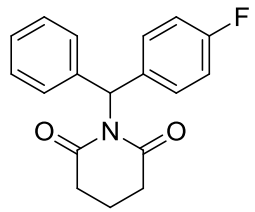




S5n

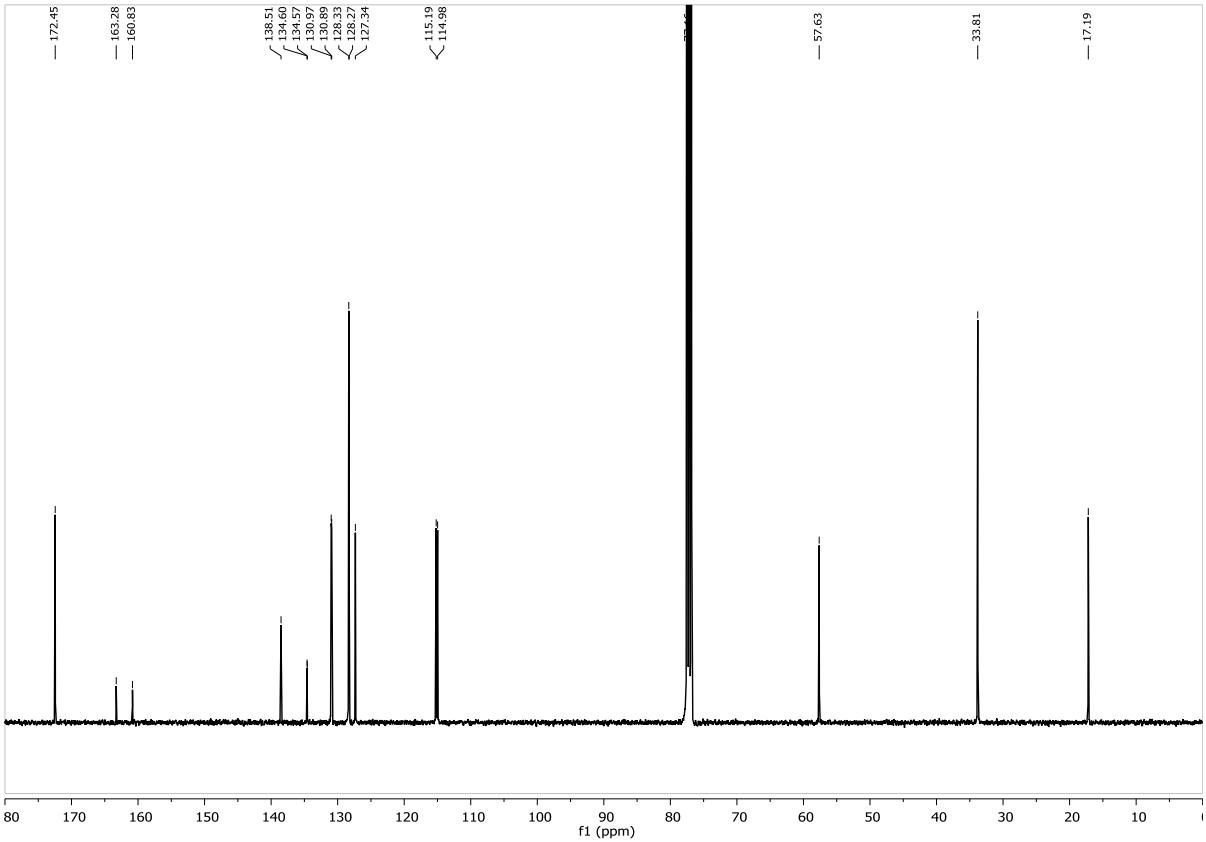
^{1}H NMR, 400 MHz, $CDCl_3$

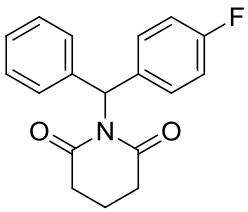




S5n

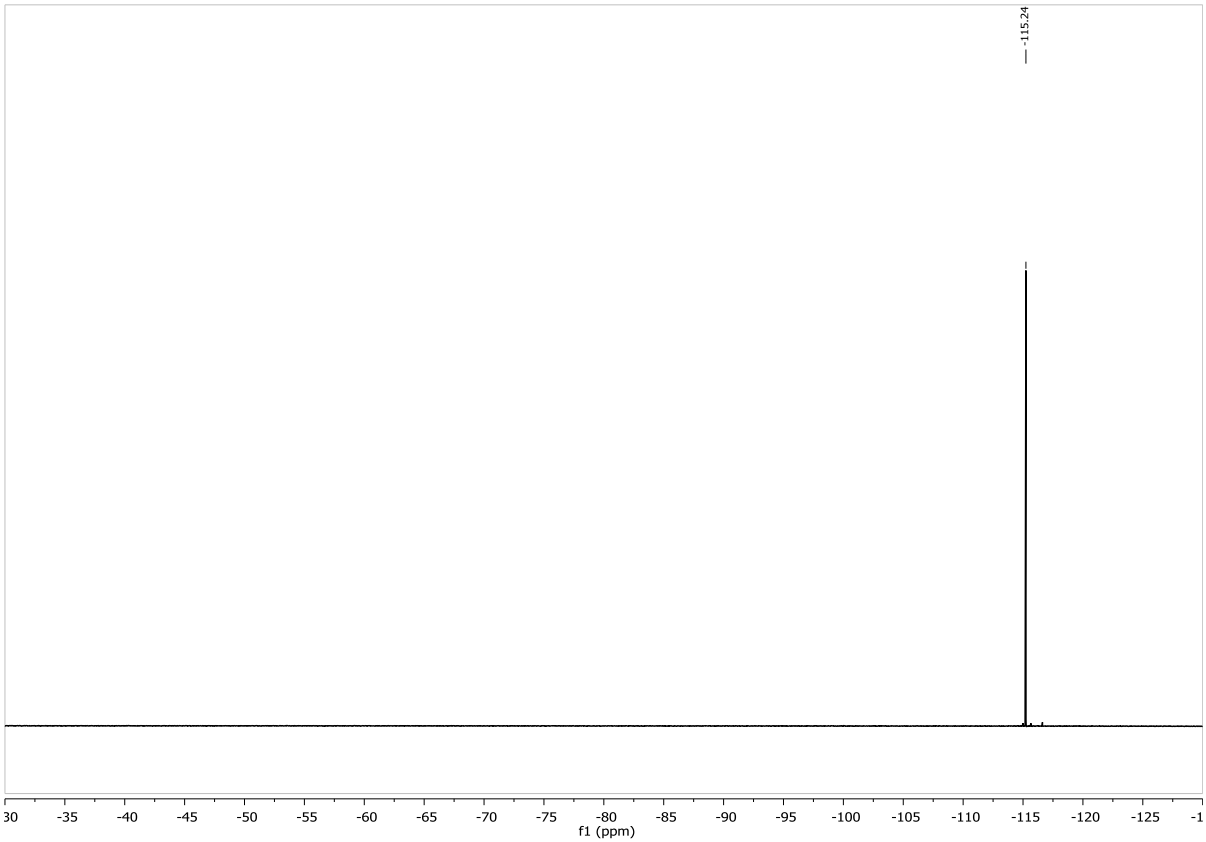
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

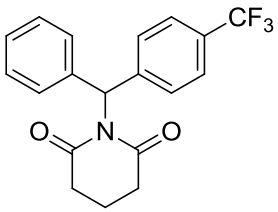




S5n

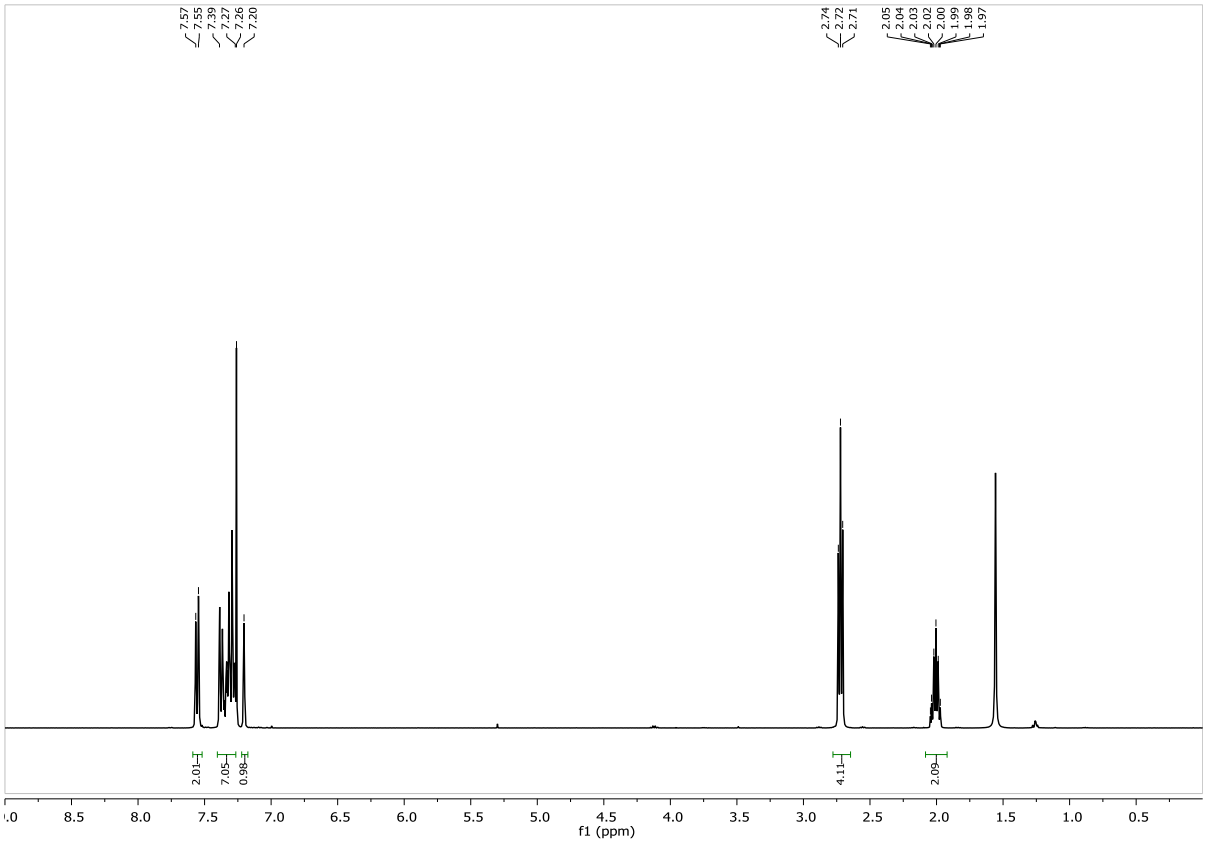
$^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

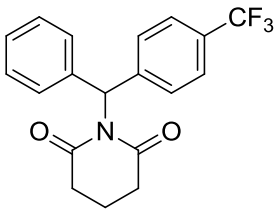




S5o

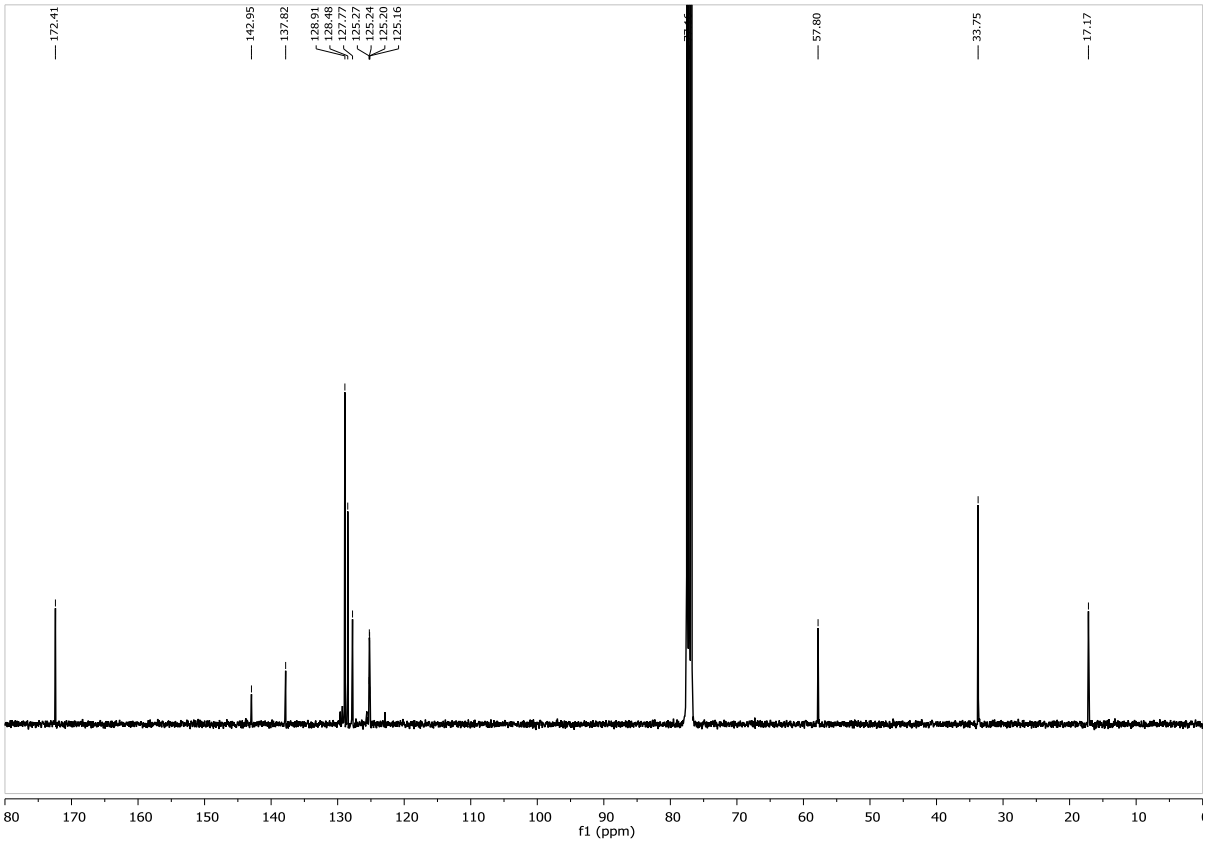
^{1}H NMR, 400 MHz, $CDCl_3$

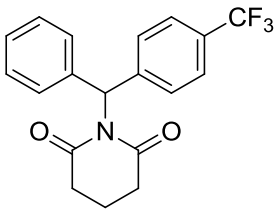




S5o

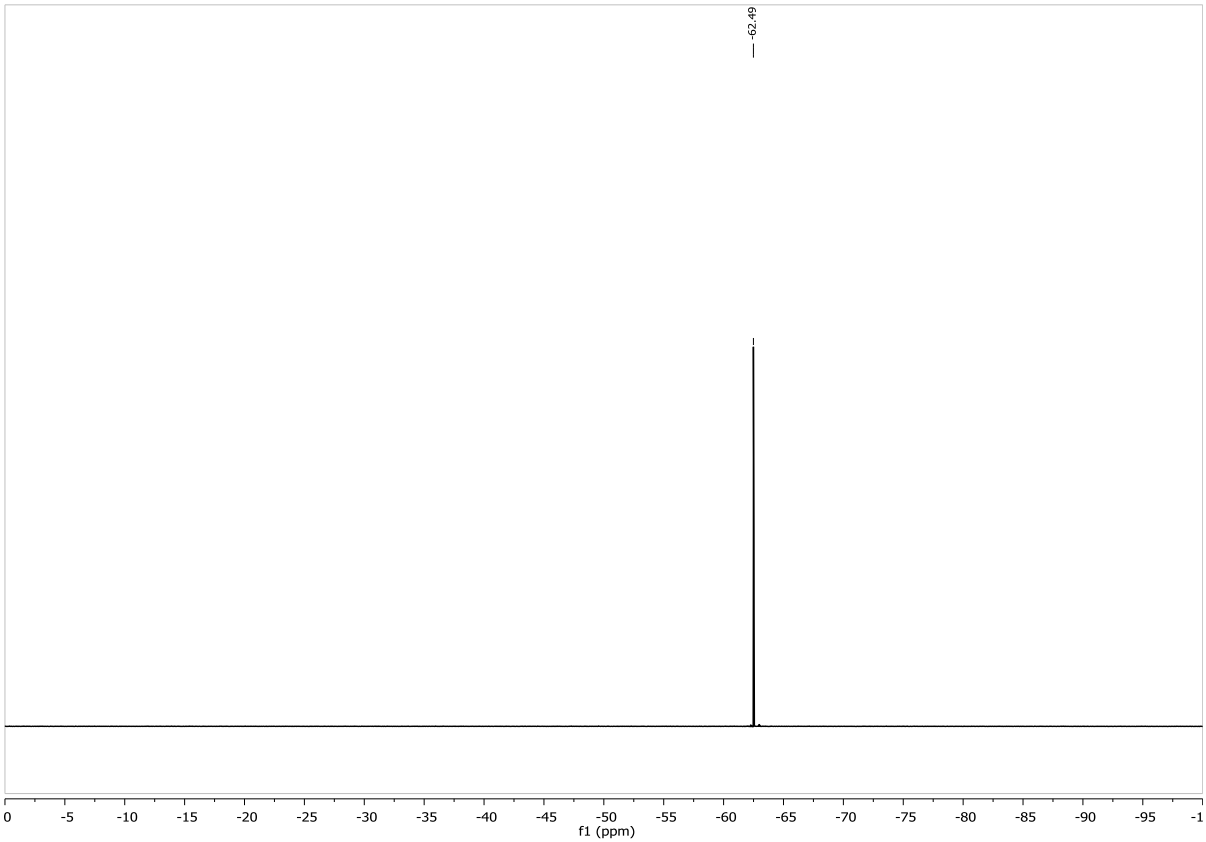
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

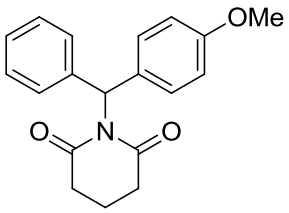




S5o

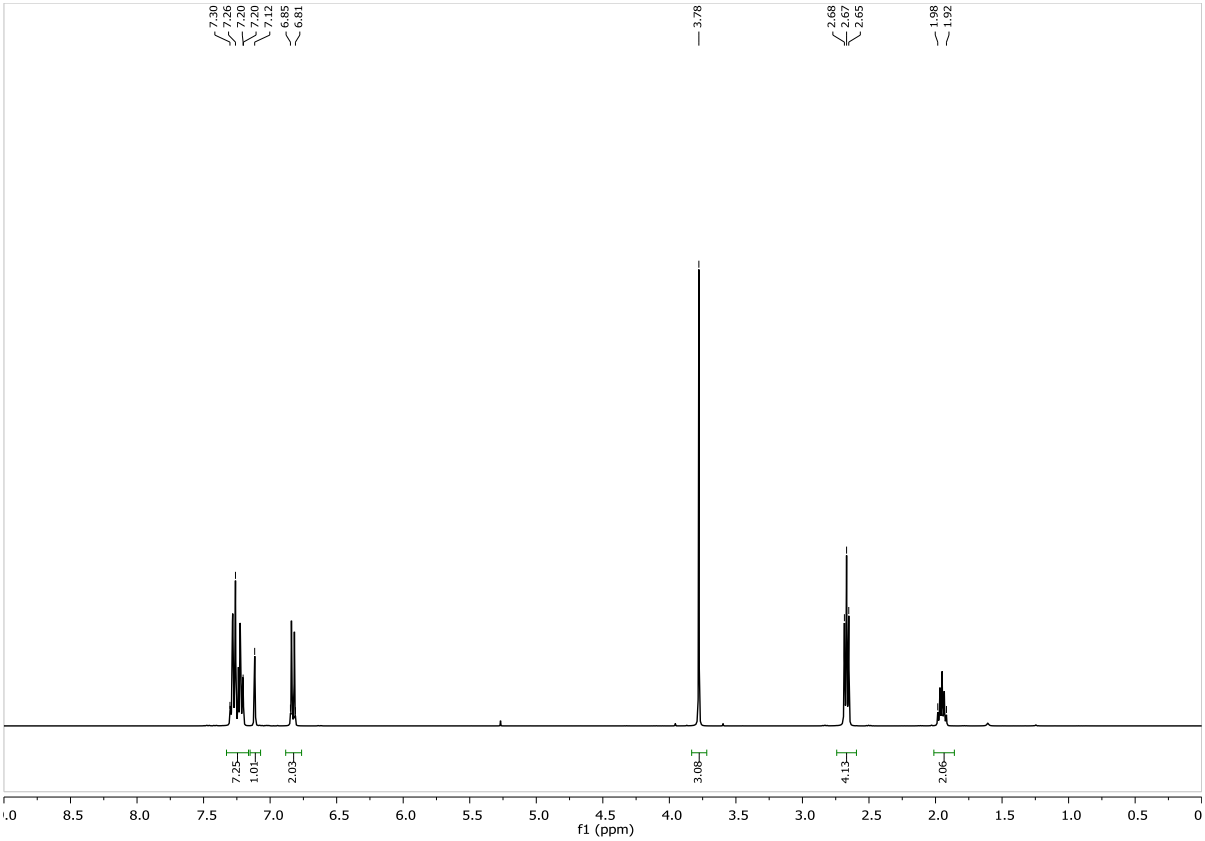
$^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

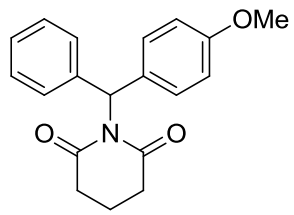




S5p

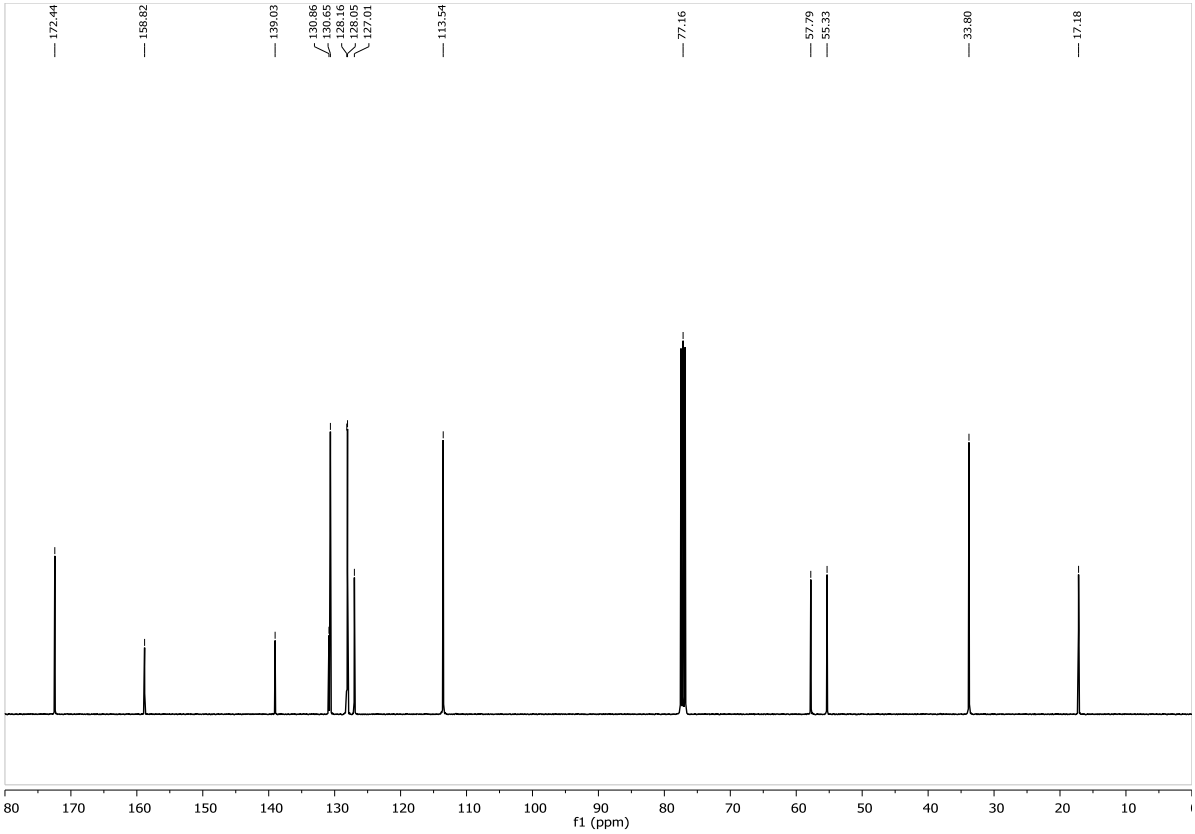
^{1}H NMR, 400 MHz, $CDCl_3$

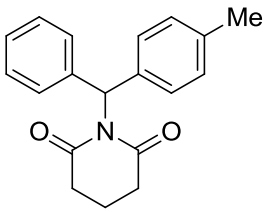




S5p

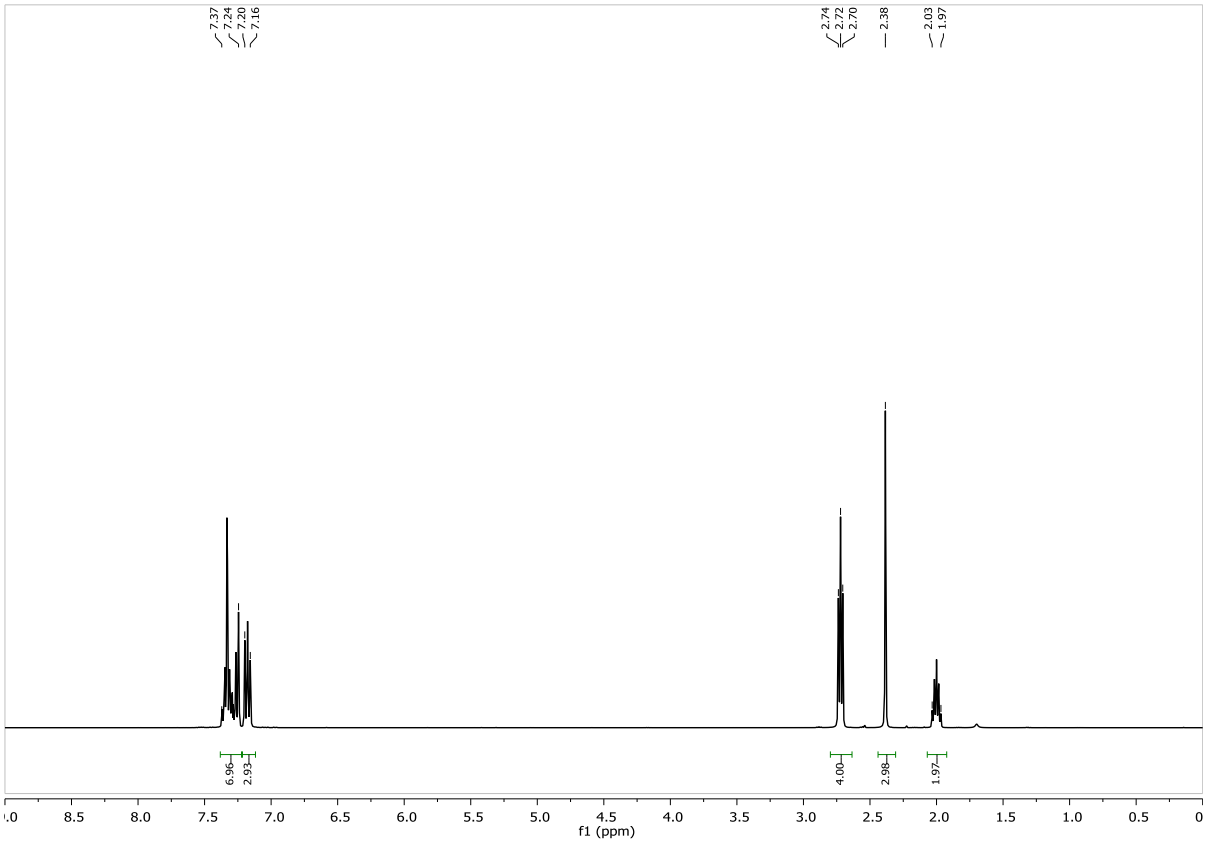
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

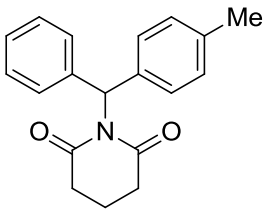




S5r

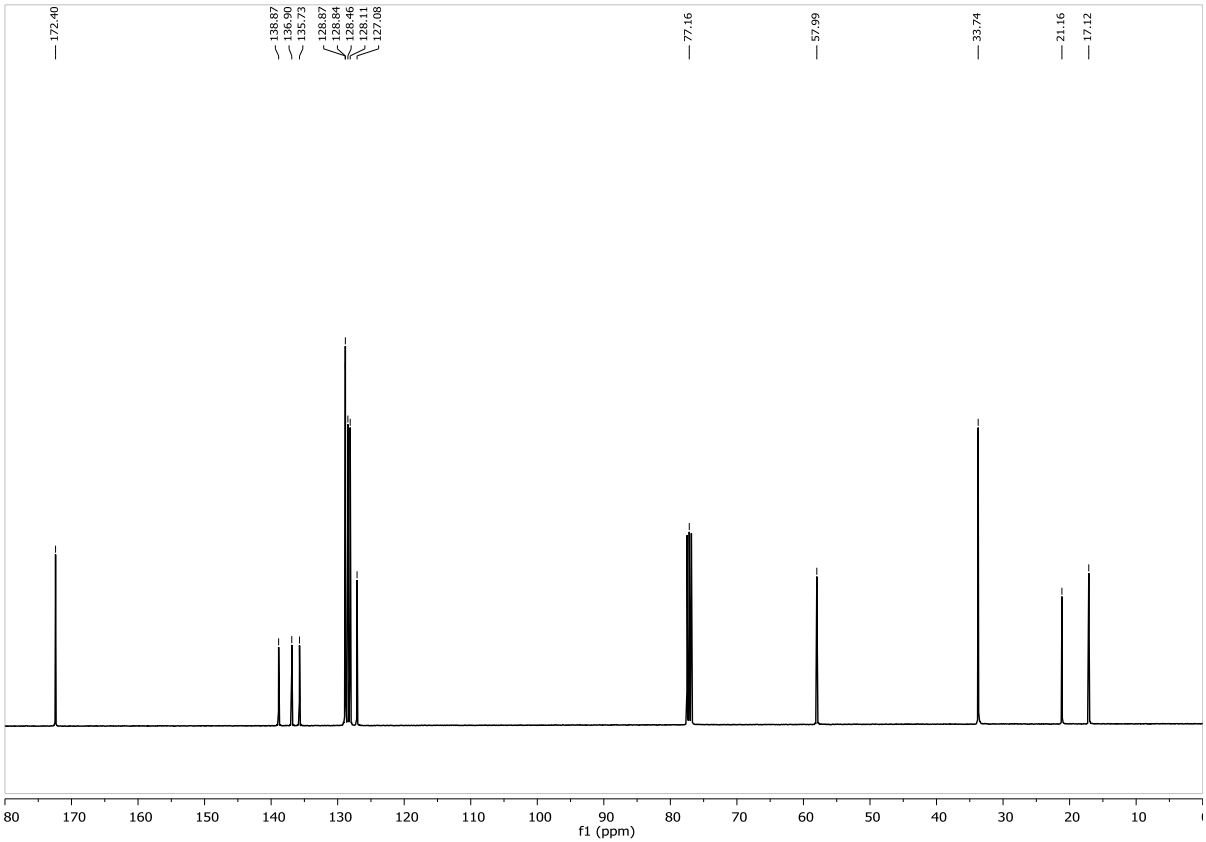
^{1}H NMR, 400 MHz, $CDCl_3$

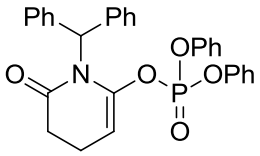




S5r

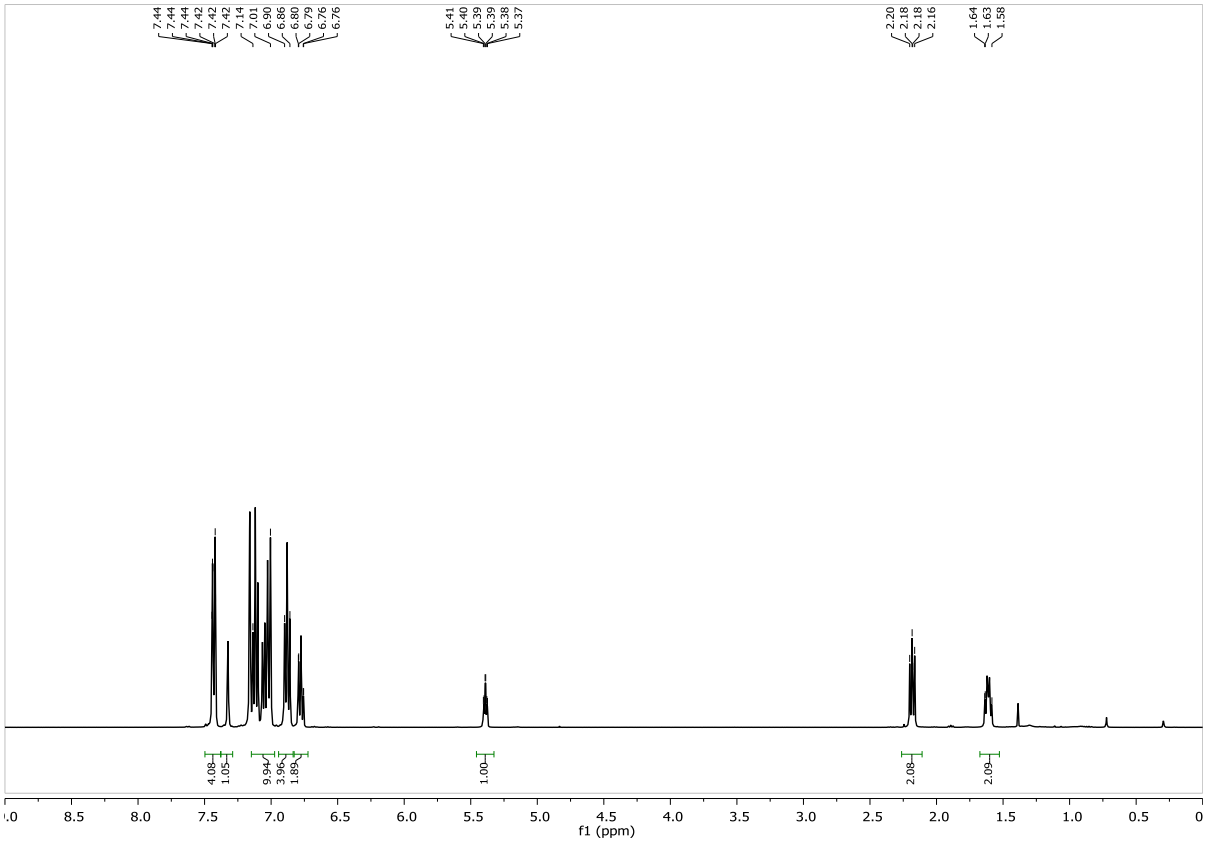
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

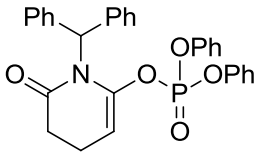




4a

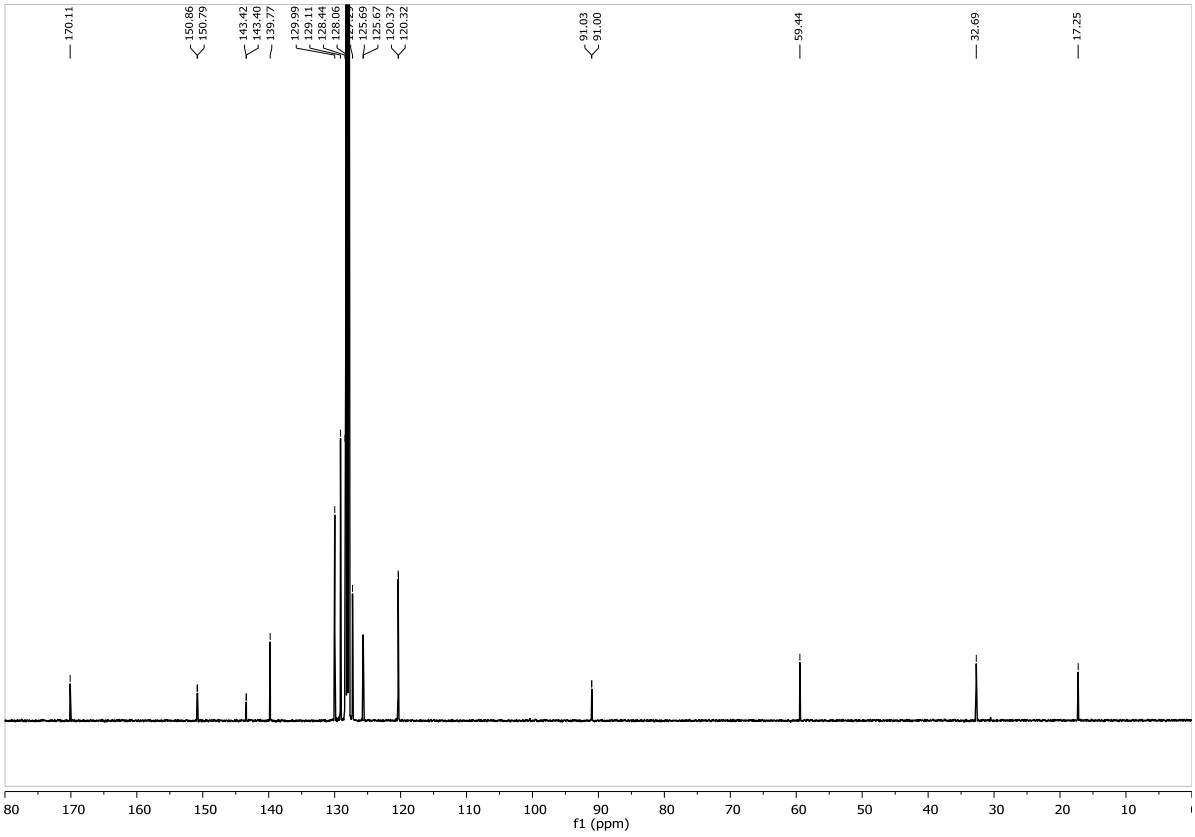
^{1}H NMR, 400 MHz, C_6D_6

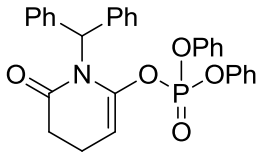




4a

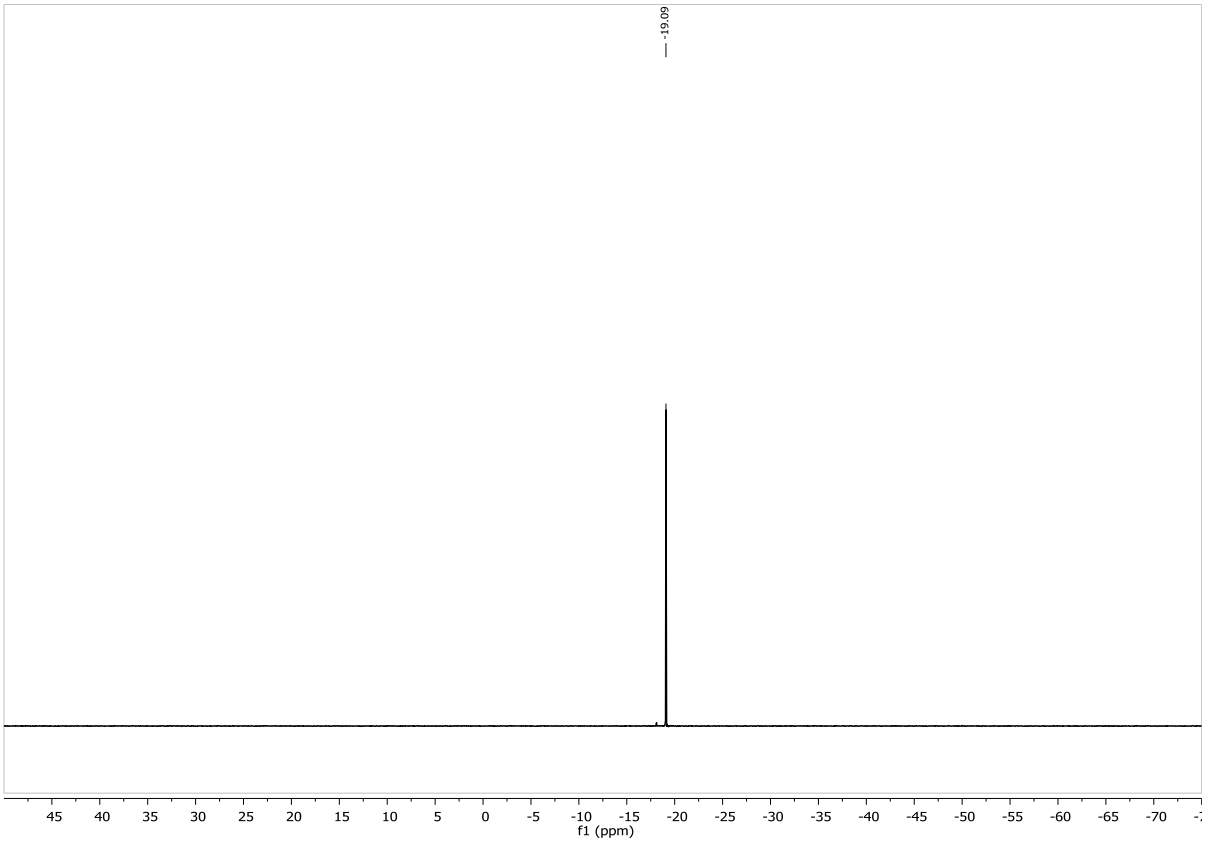
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

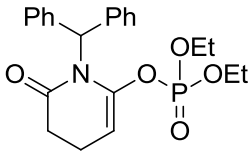




4a

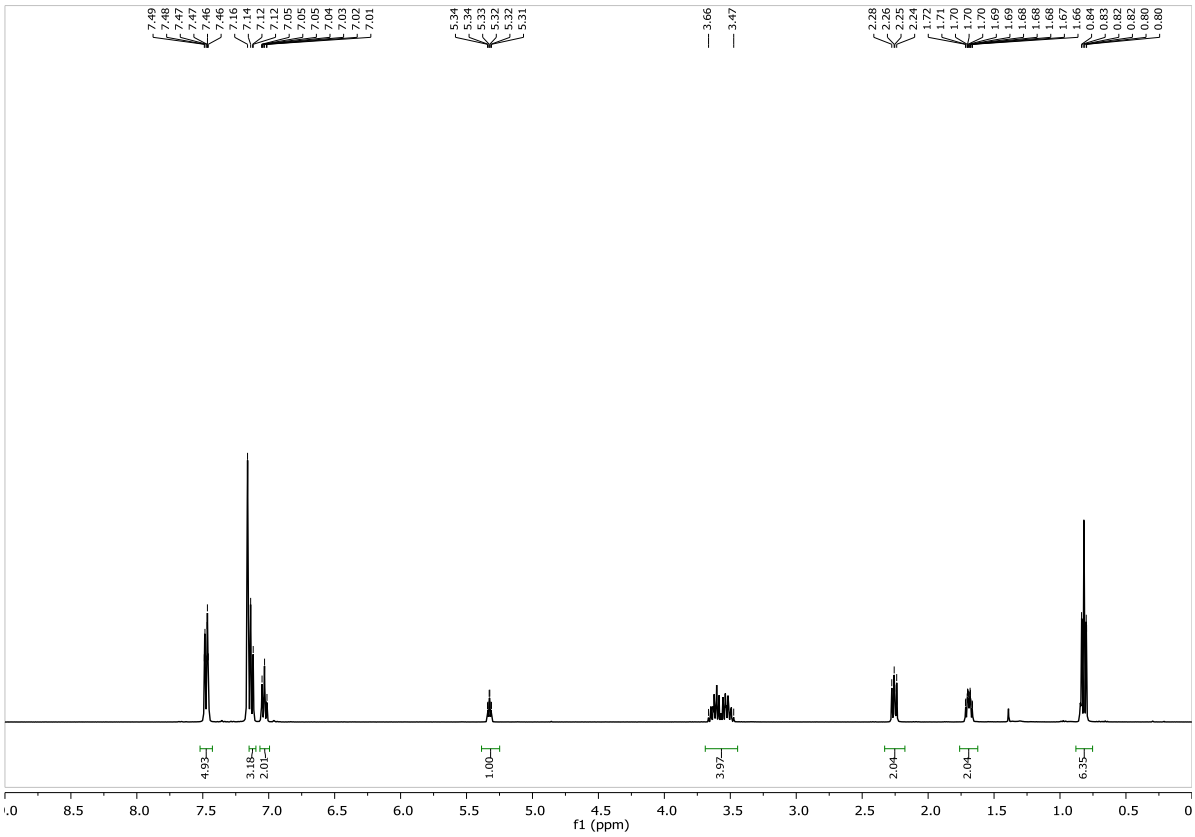
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

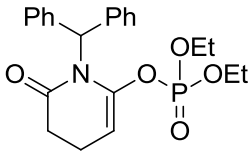




4a′

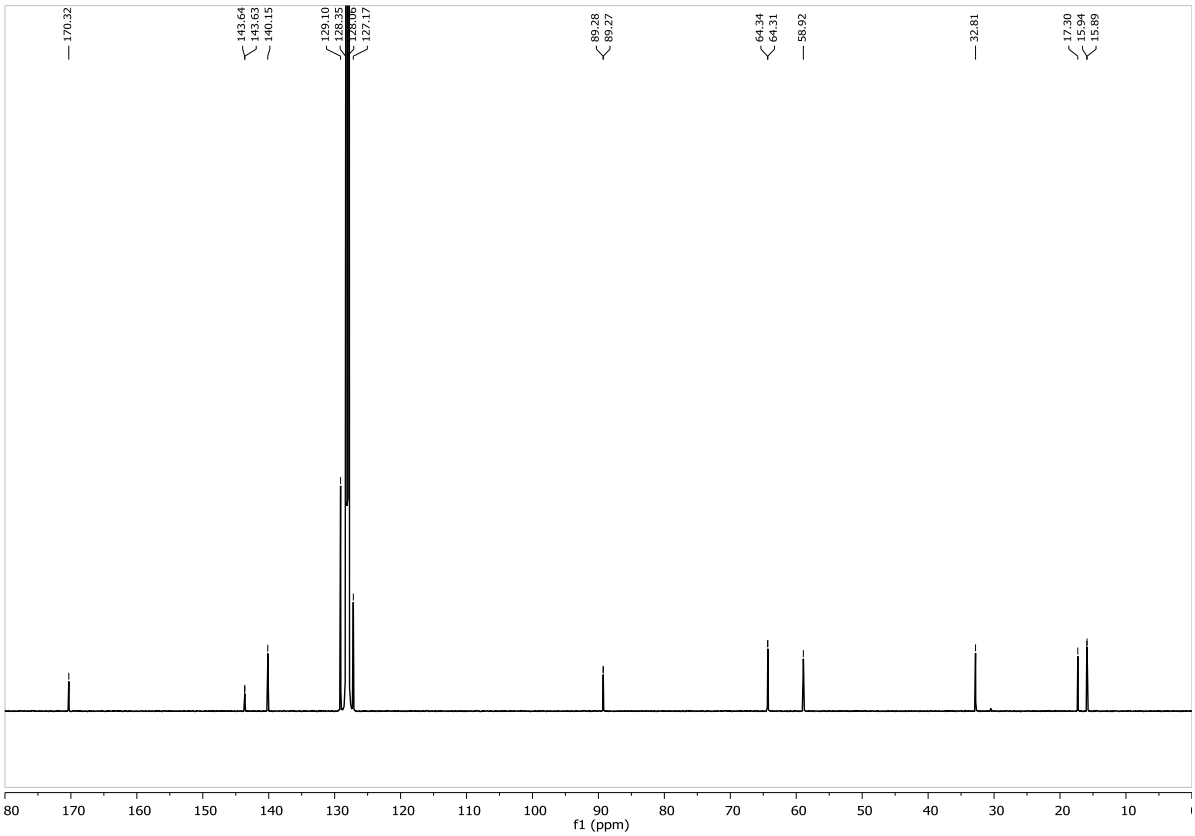
^{1}H NMR, 400 MHz, C_6D_6

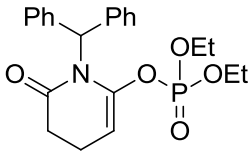




4a′

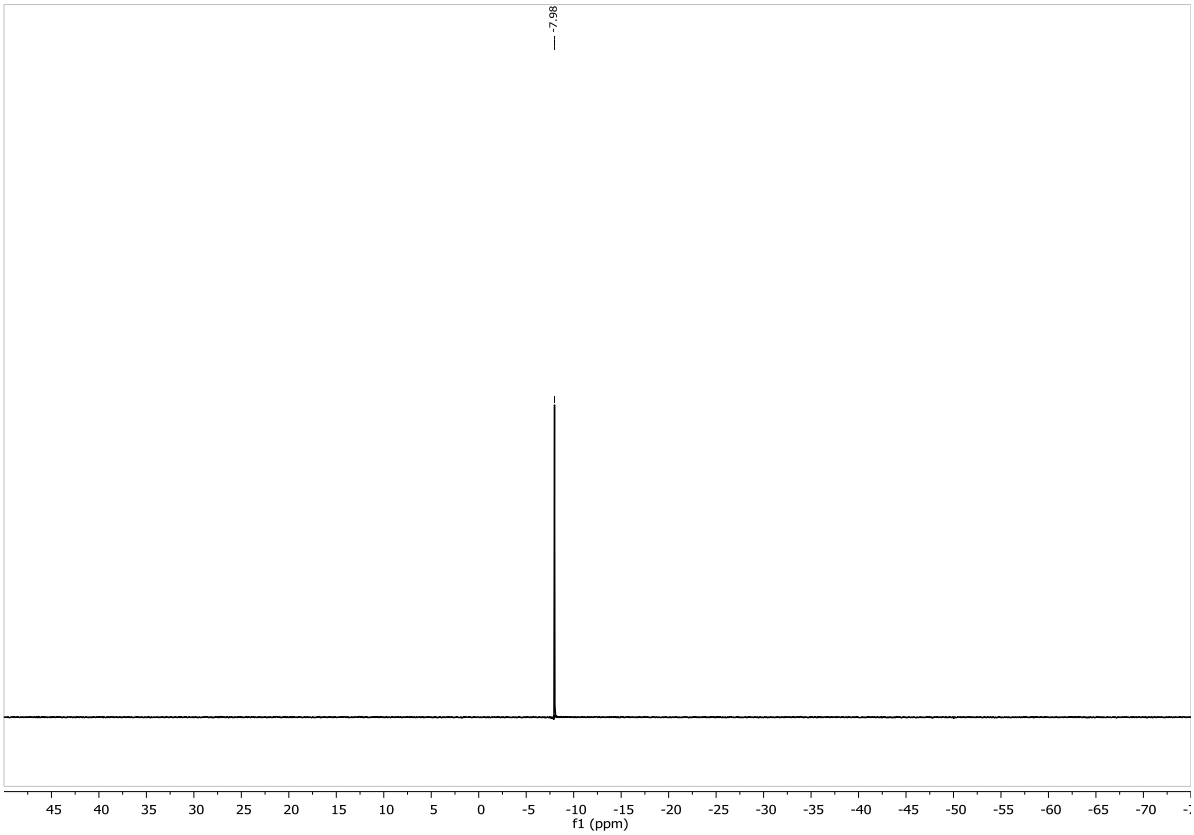
$^{13}C\{^{1}H\}$ NMR, 600 MHz, C_6D_6

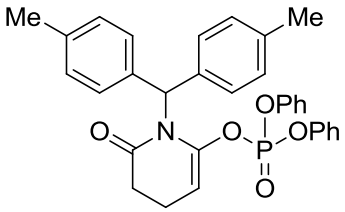




4a′

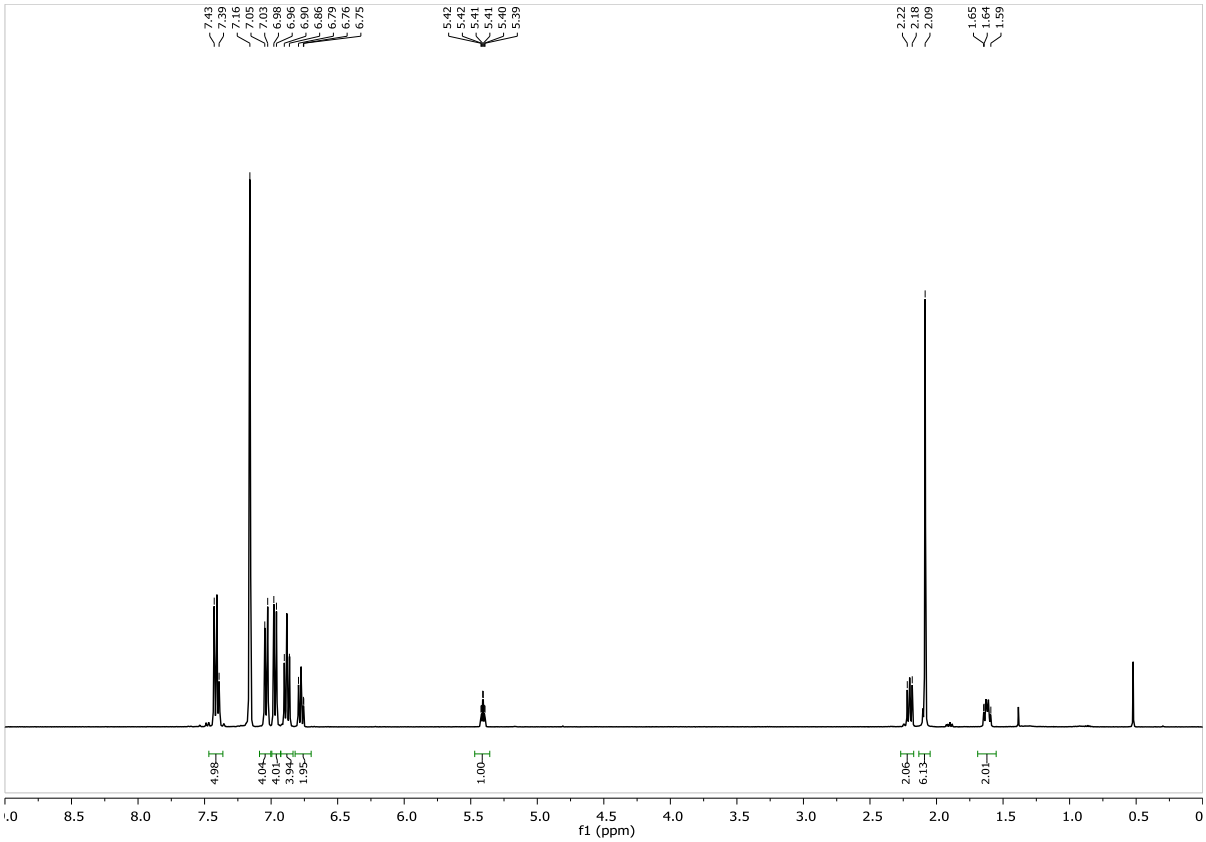
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

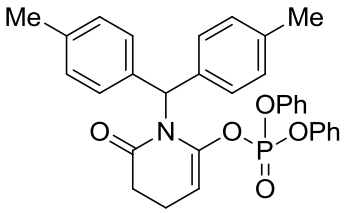




4b

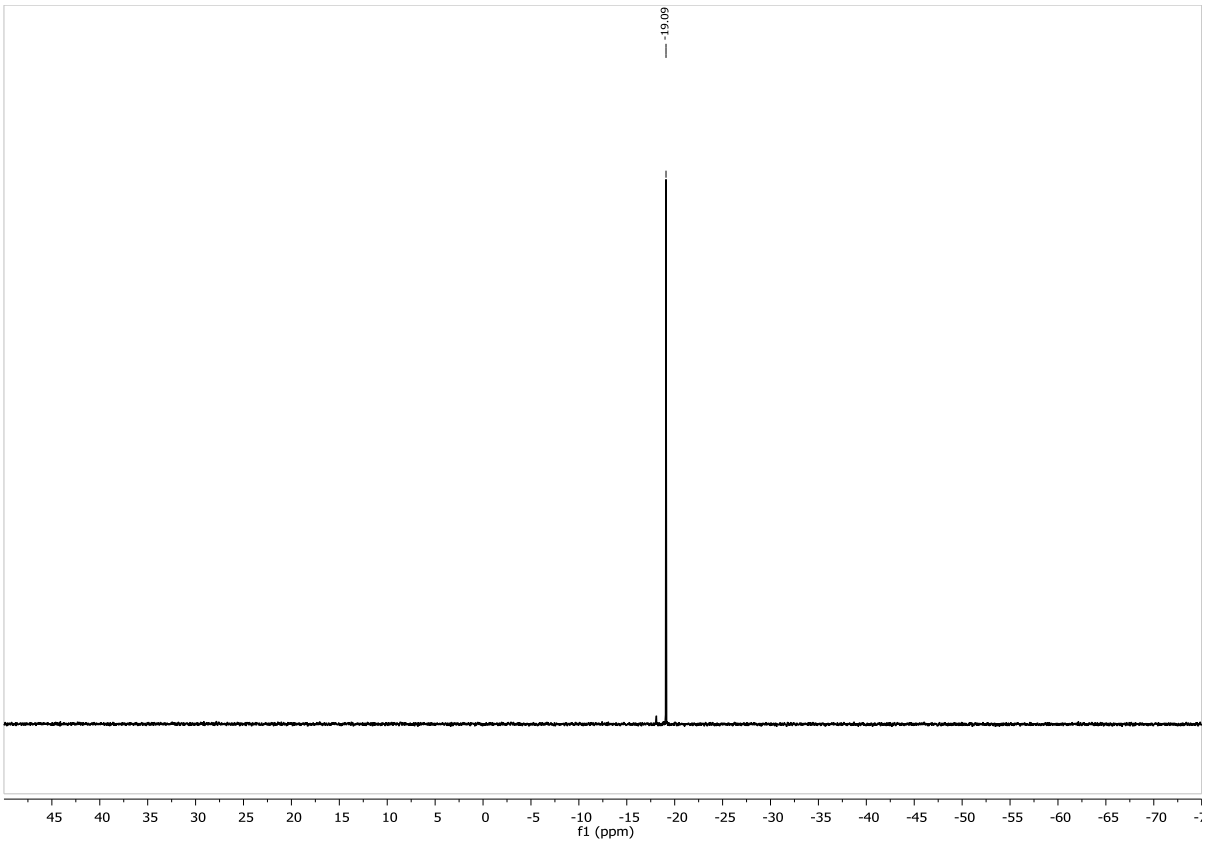
^{1}H NMR, 400 MHz, C_6D_6

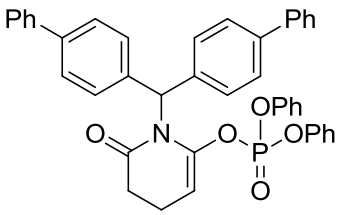




4b

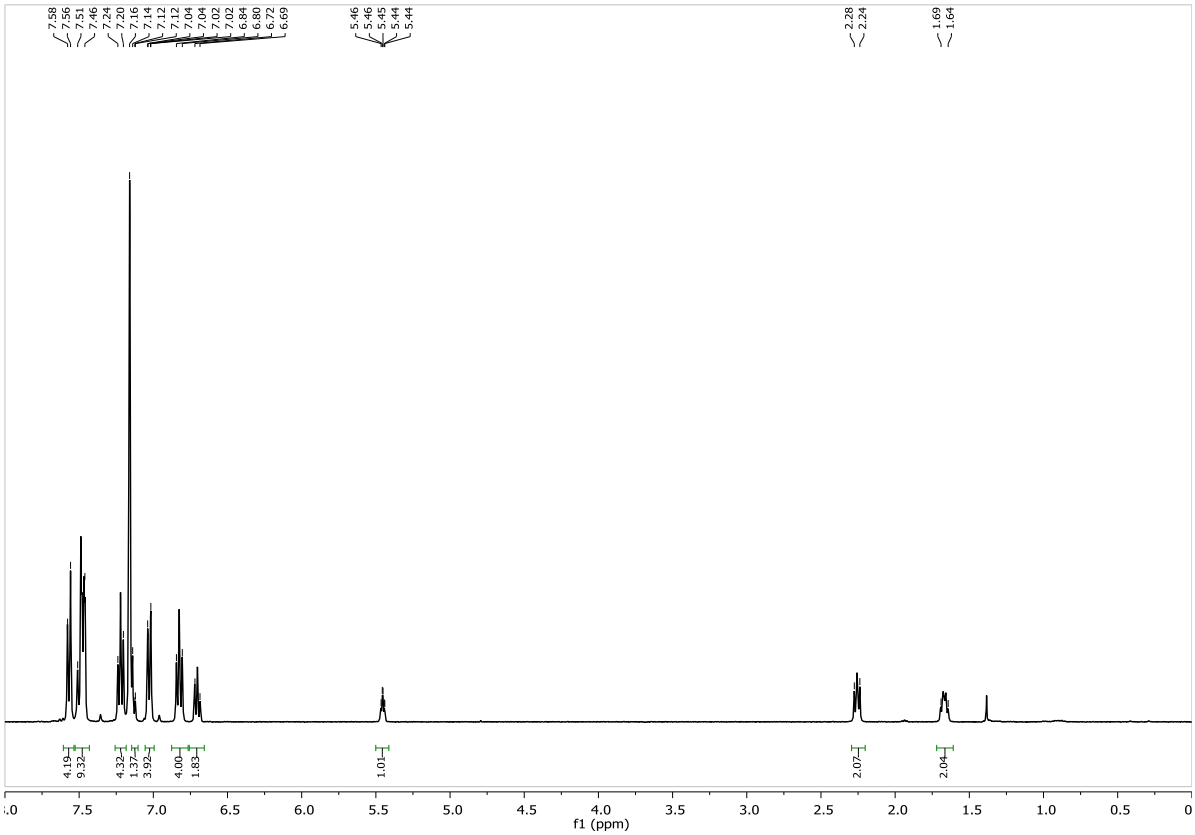
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

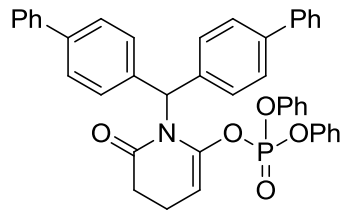




4c

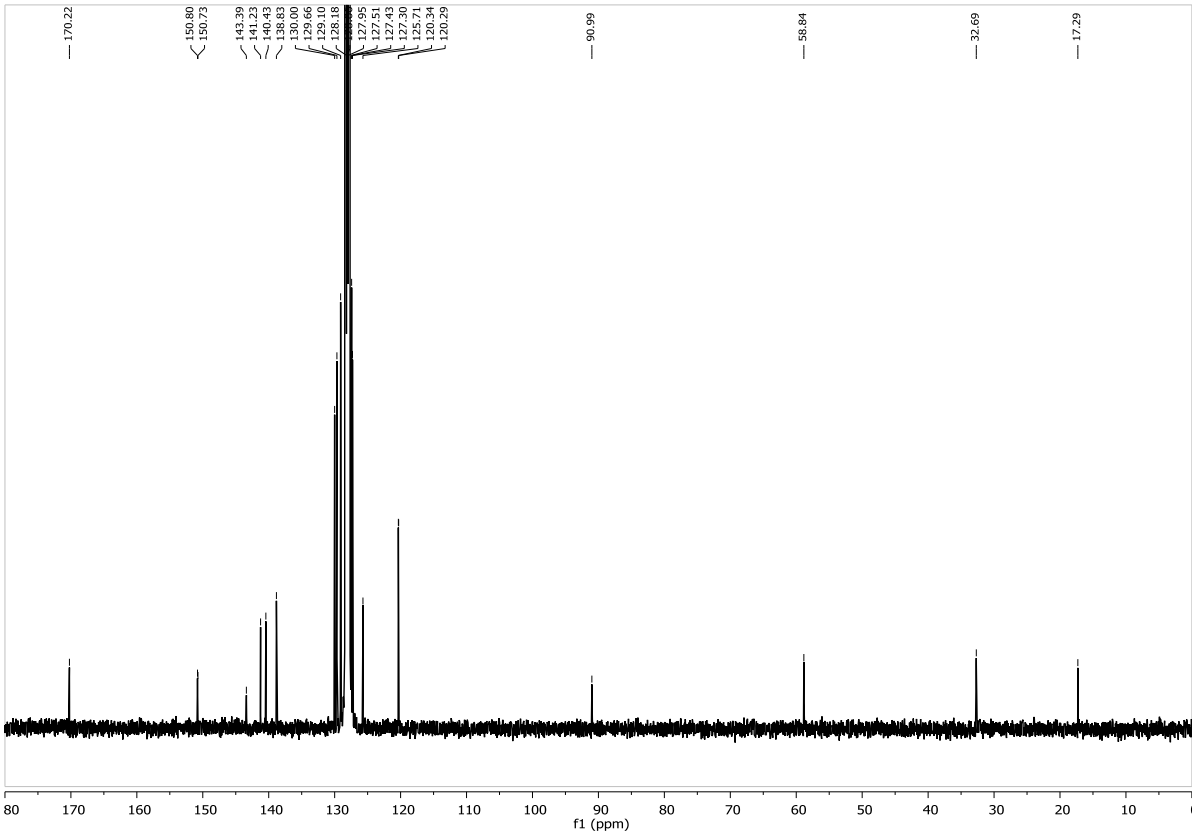
^{1}H NMR, 400 MHz, C_6D_6

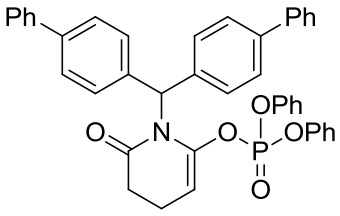




4c

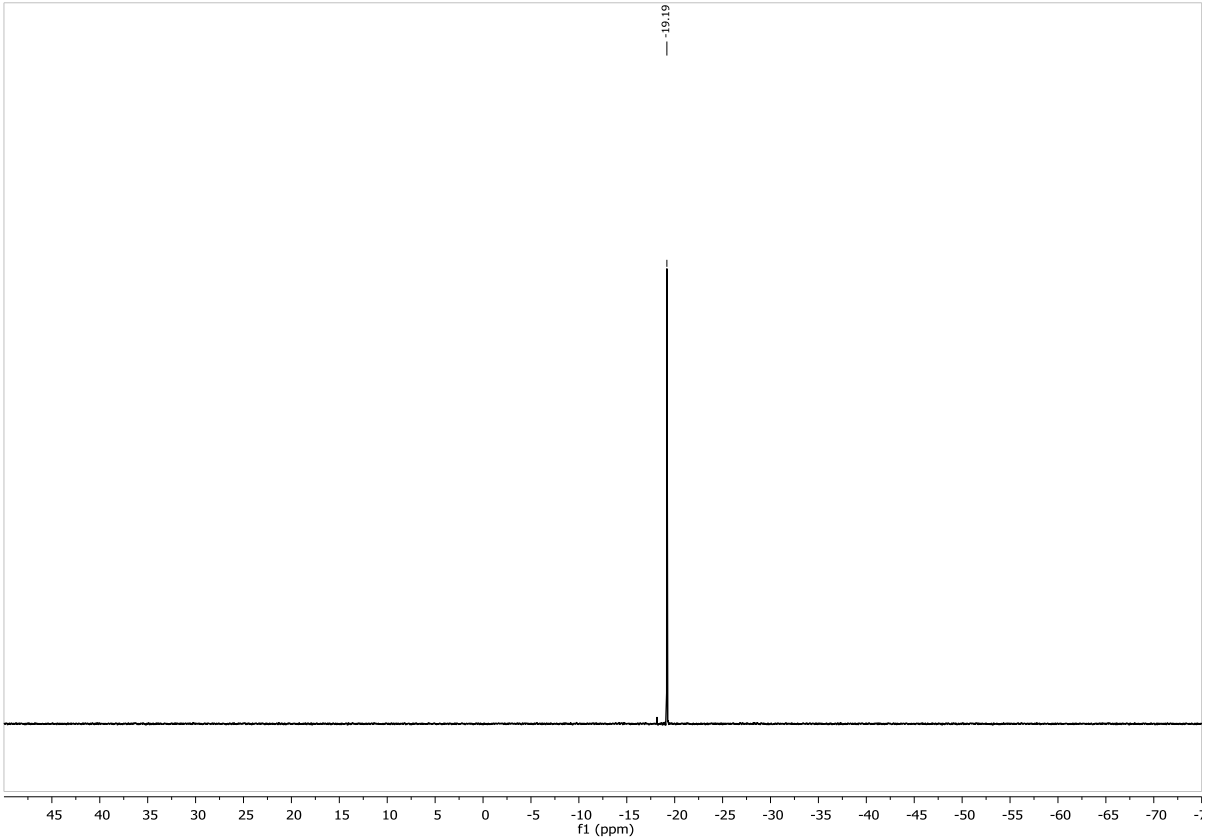
$^{13}C\{^{1}H\}$ NMR, 101 MHz, C_6D_6

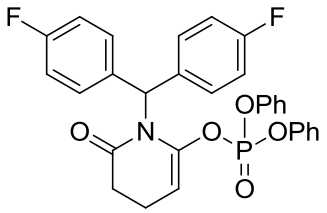




4c

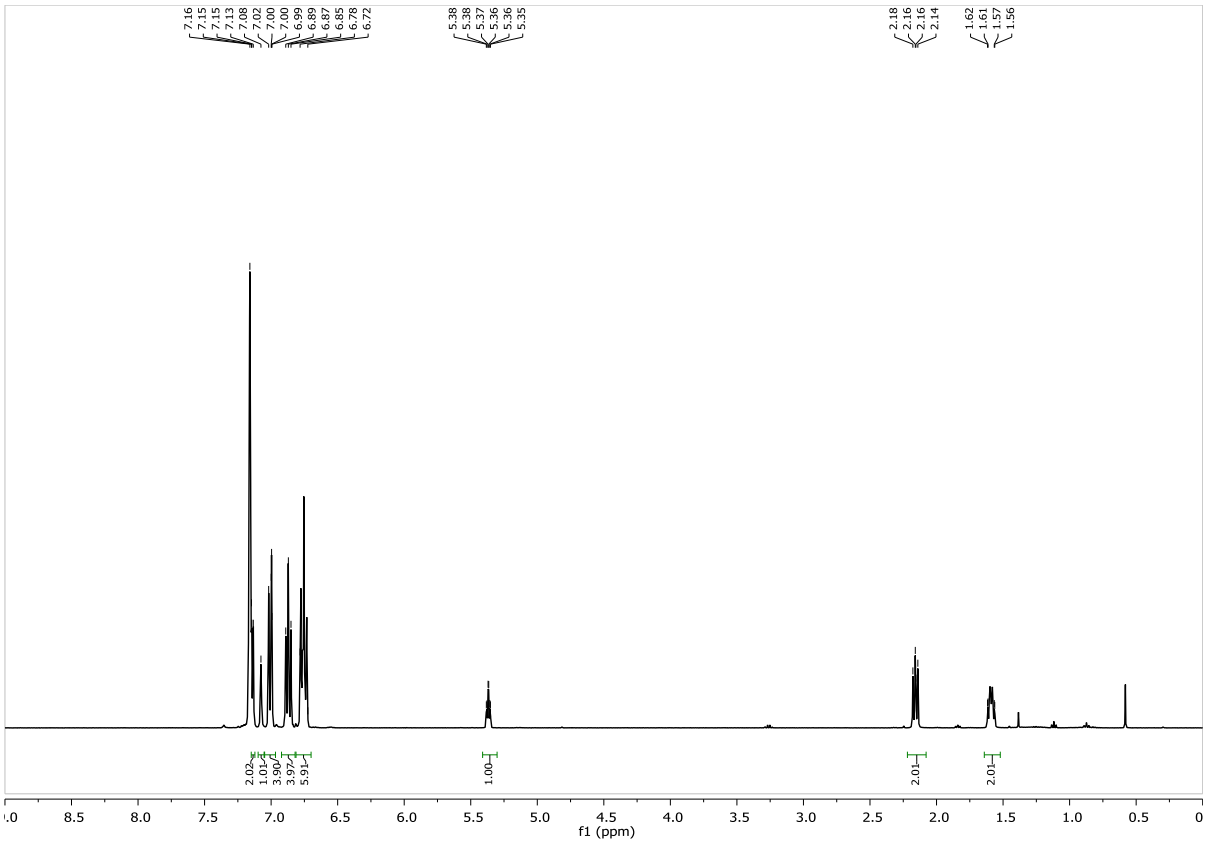
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

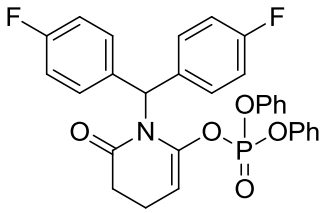




4d

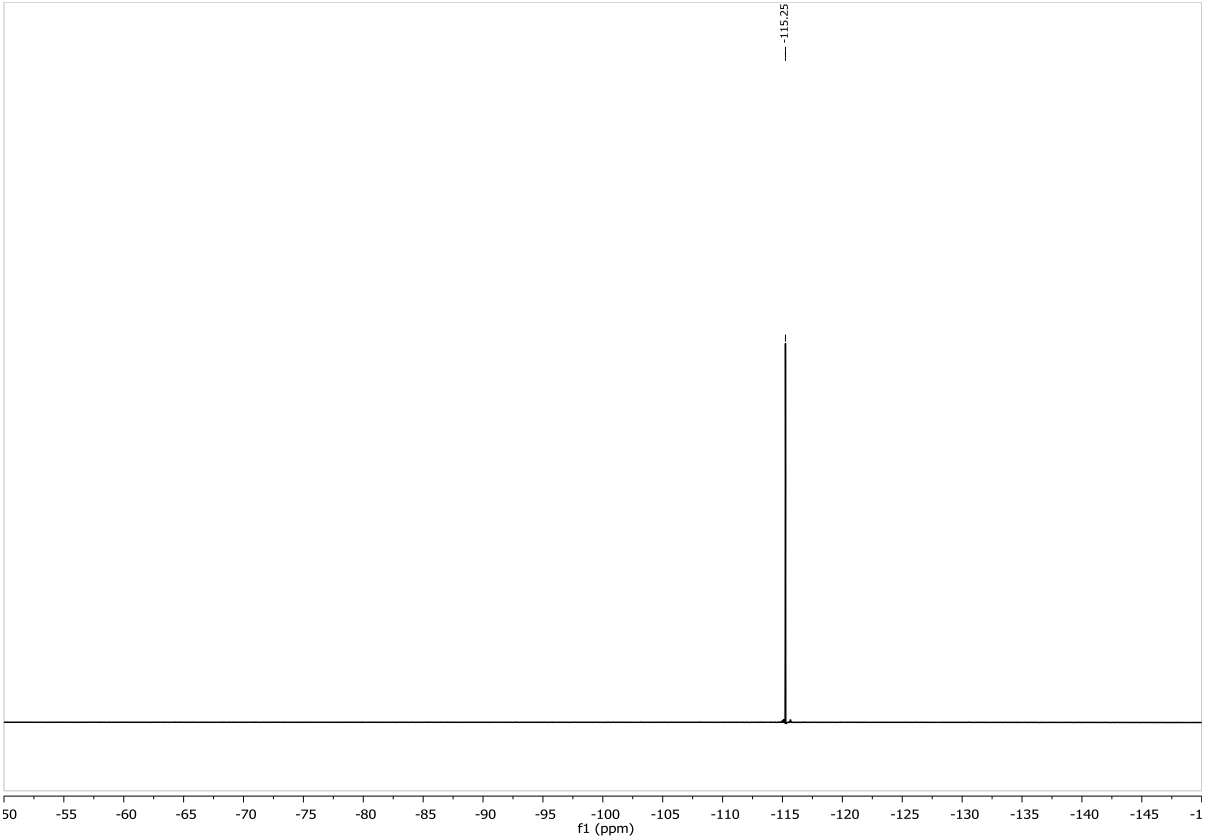
^{1}H NMR, 400 MHz, C_6D_6

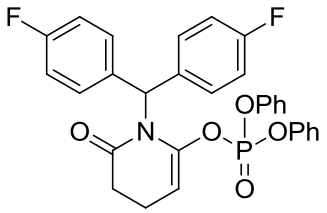




4d

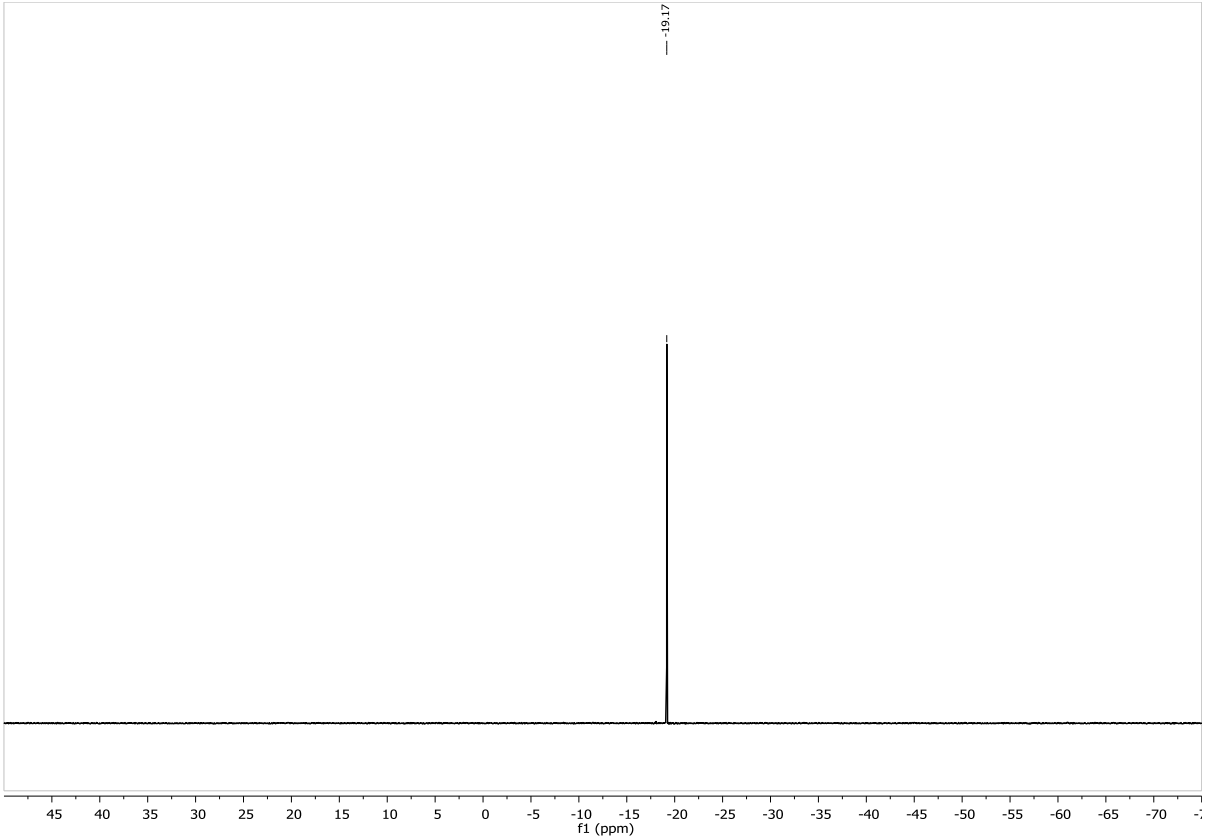
$^{19}F\{^{1}H\}$ NMR, 376 MHz, C_6D_6

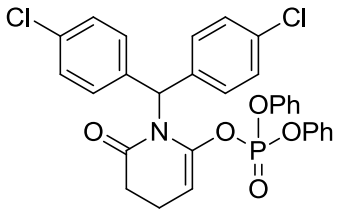




4d

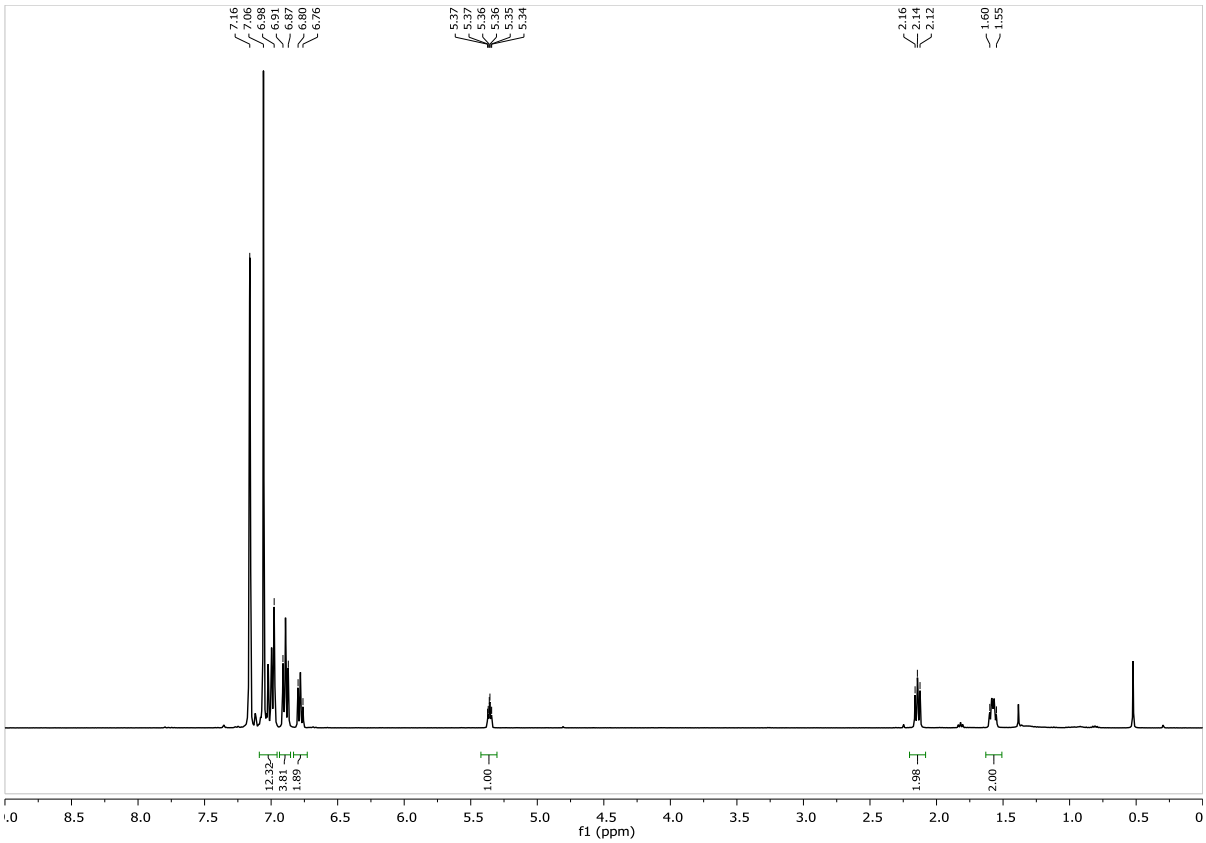
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

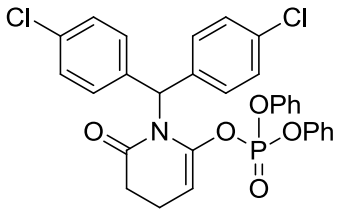




4e

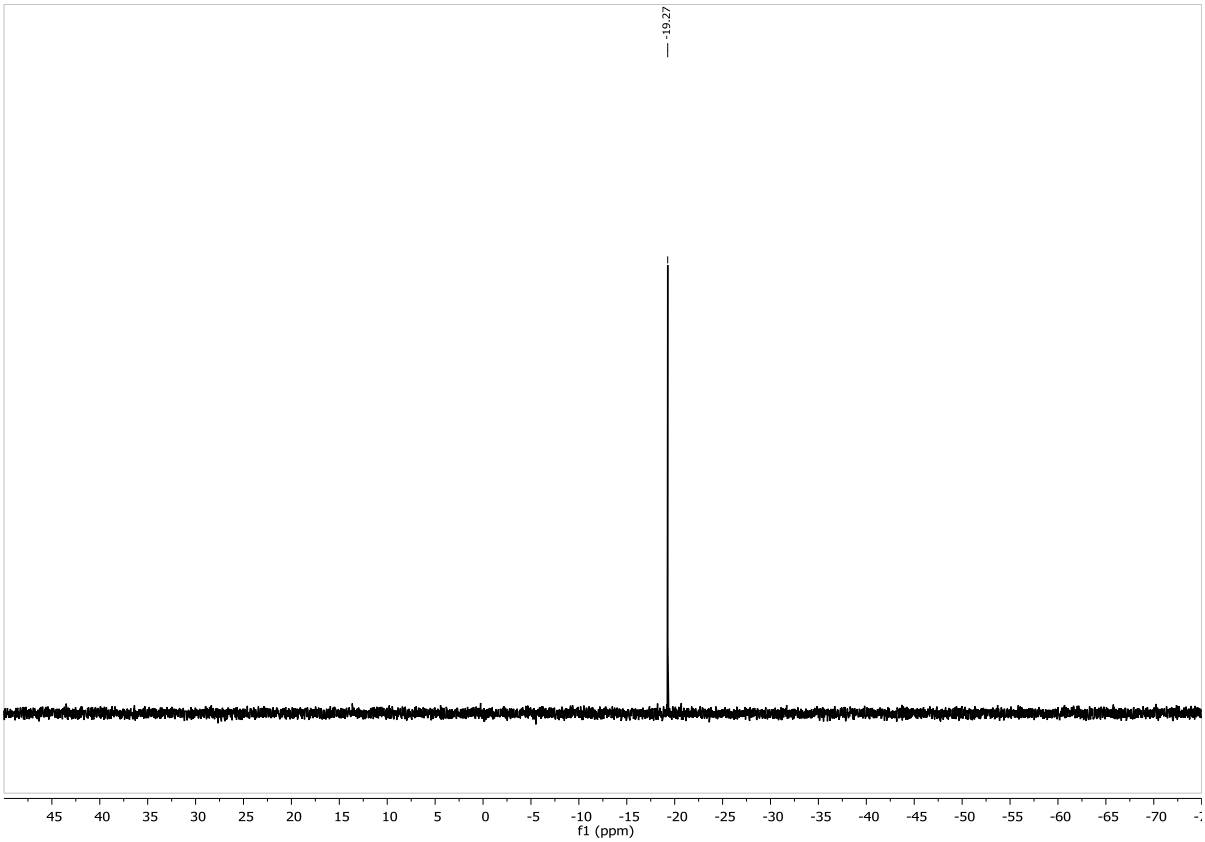
^{1}H NMR, 400 MHz, C_6D_6

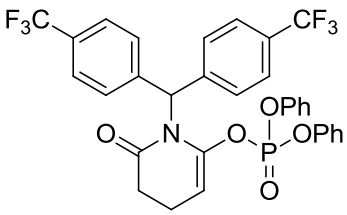




4e

$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

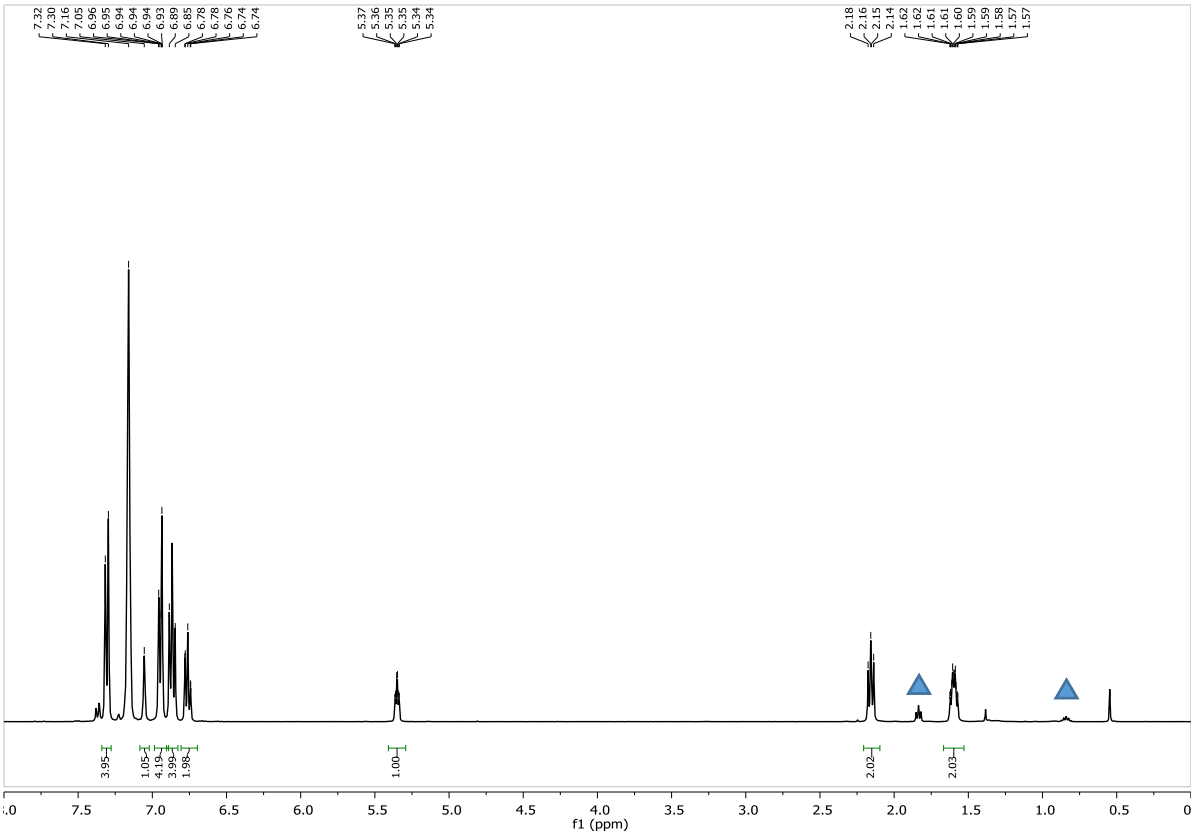


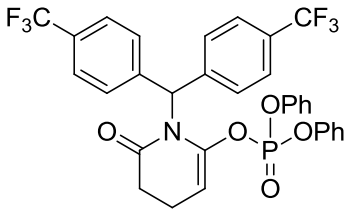


4f

^{1}H NMR, 400 MHz, C_6D_6

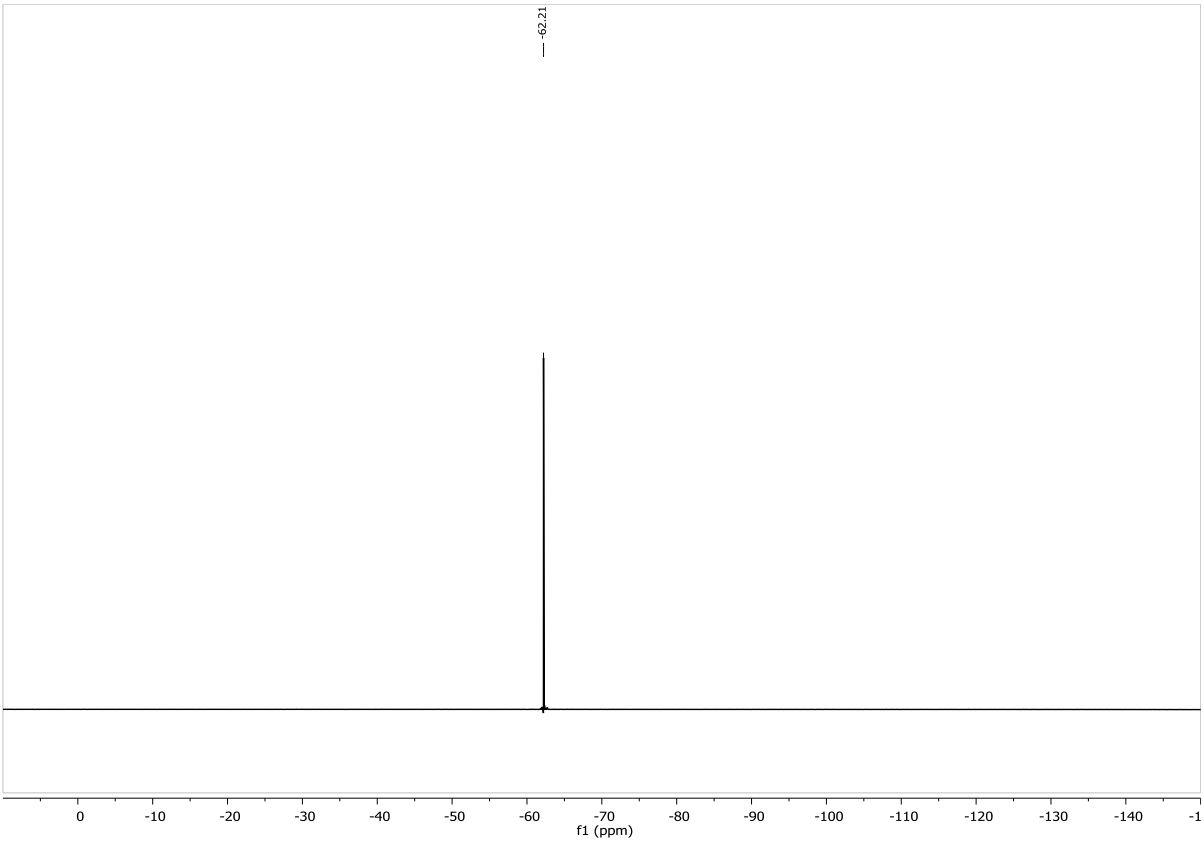
▲ starting material

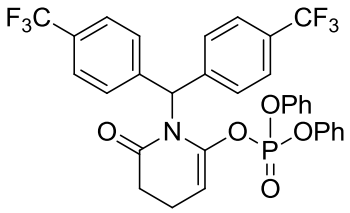




4f

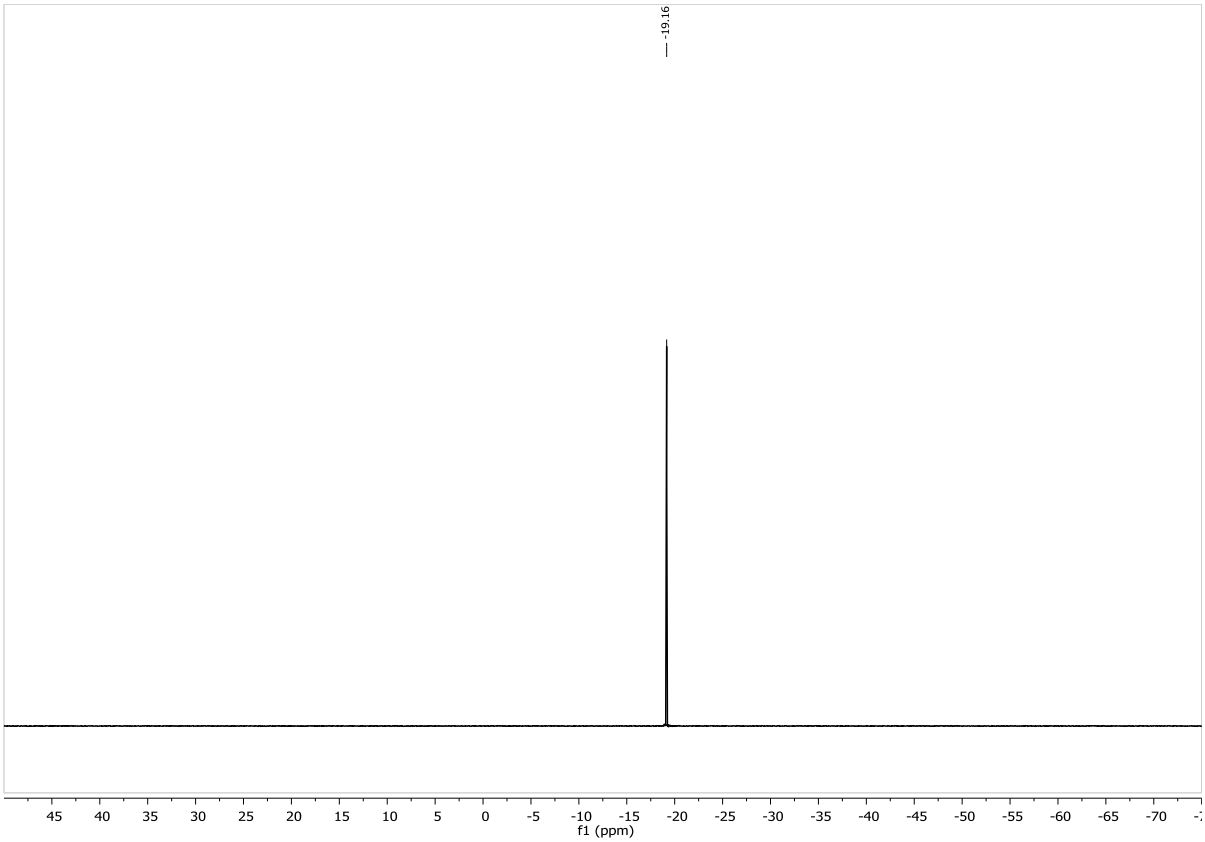
$^{19}F\{^{1}H\}$ NMR, 376 MHz, C_6D_6

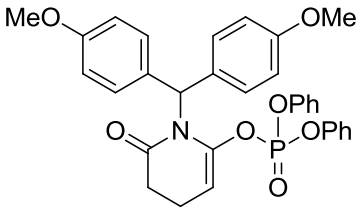




4f

$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

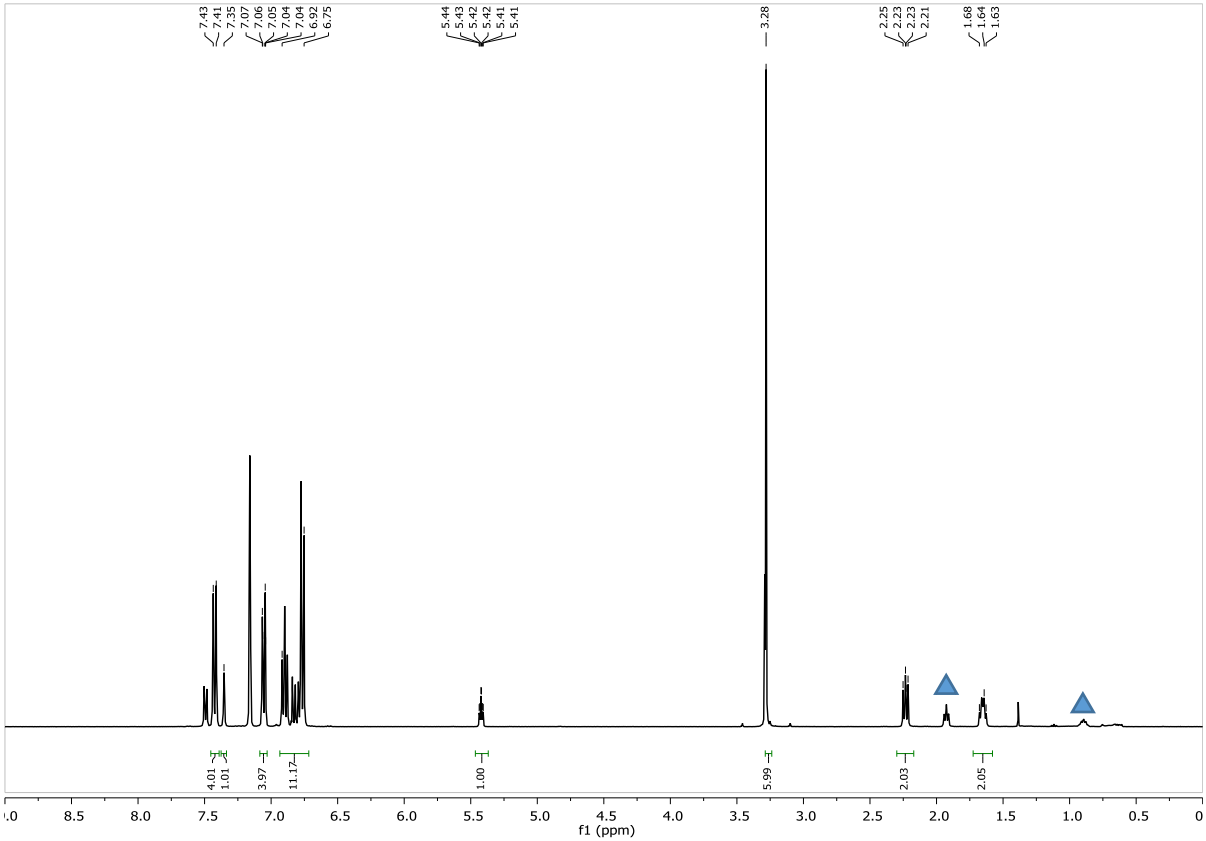


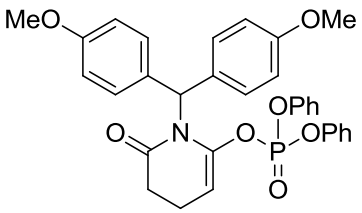


4g

^{1}H NMR, 400 MHz, C_6D_6

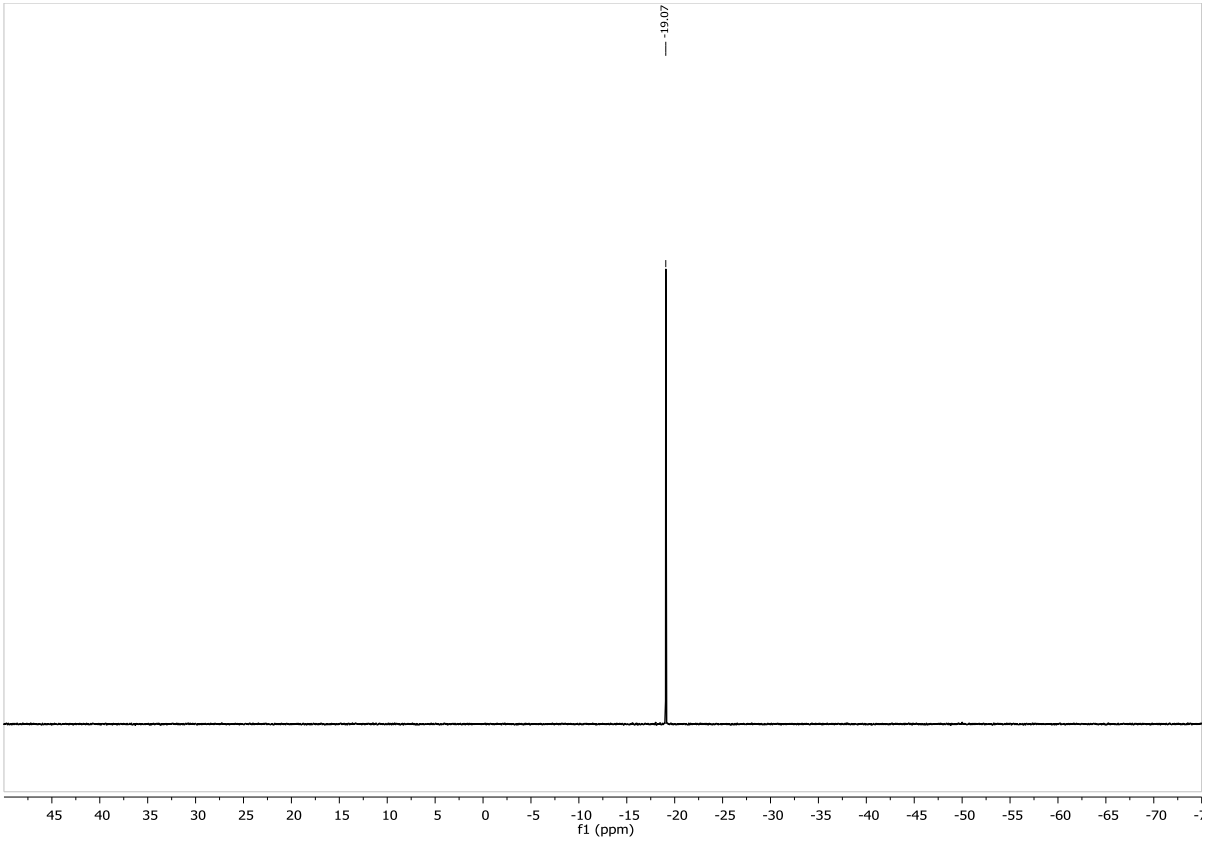
▲ starting material

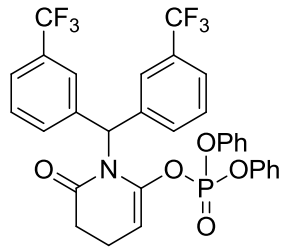




4g

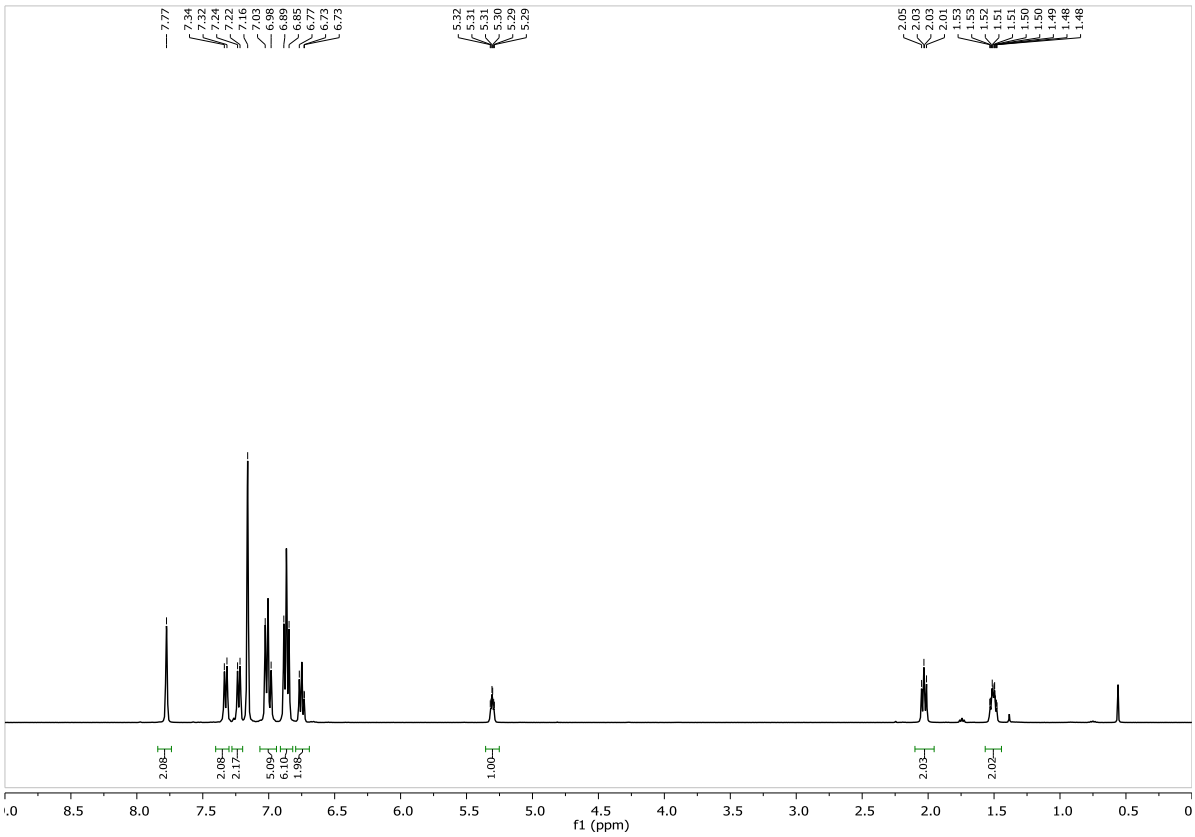
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

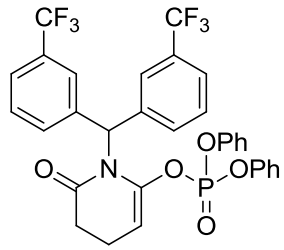




4h

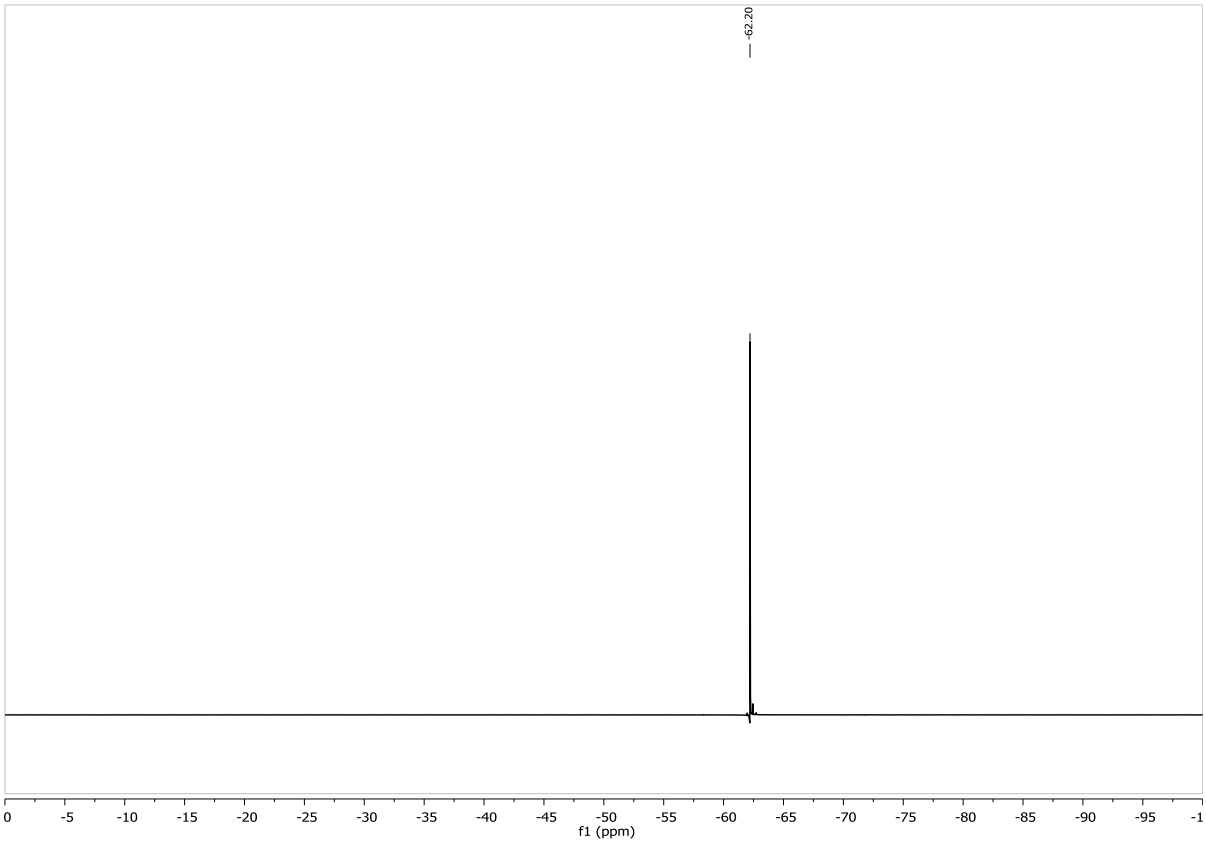
^{1}H NMR, 400 MHz, C_6D_6

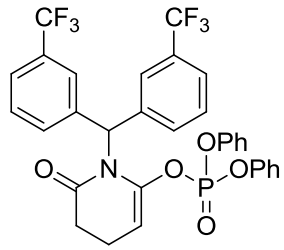




4h

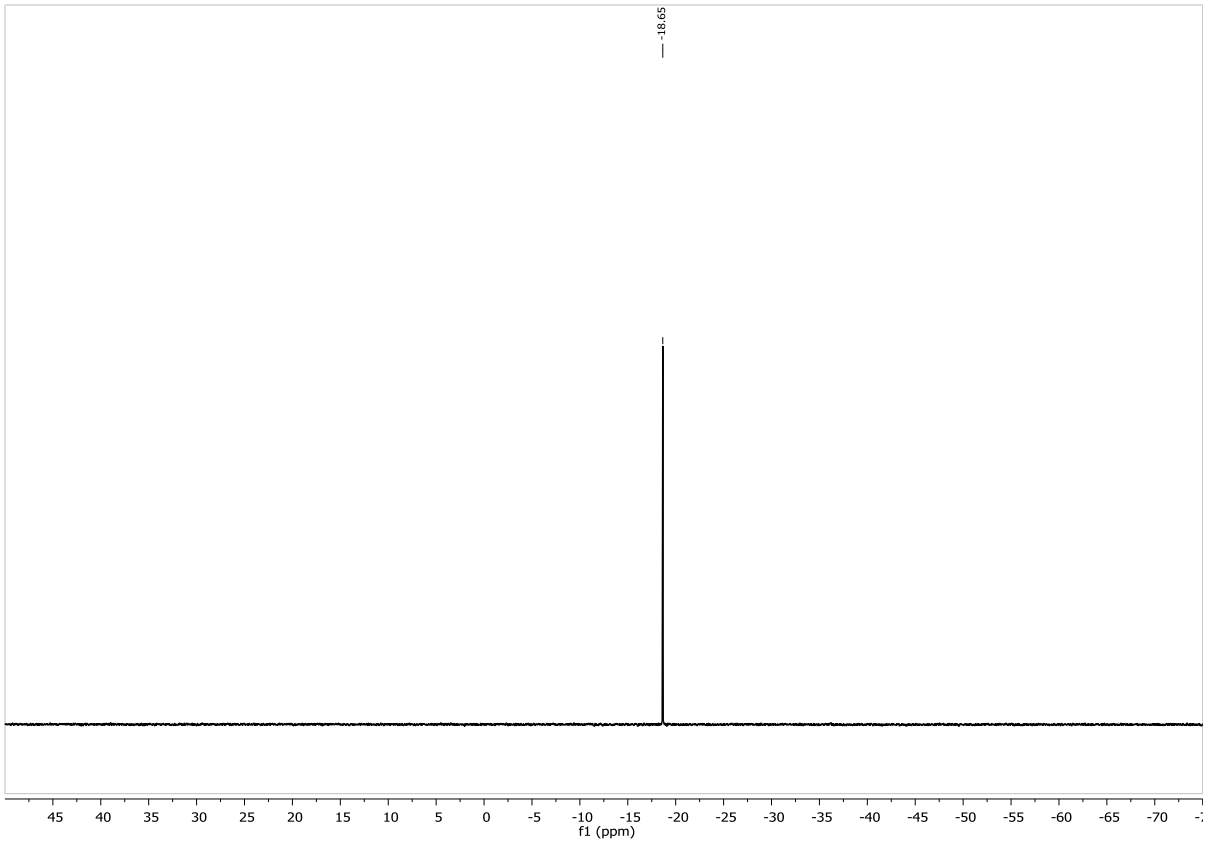
$^{19}F\{^{1}H\}$ NMR, 376 MHz, C_6D_6

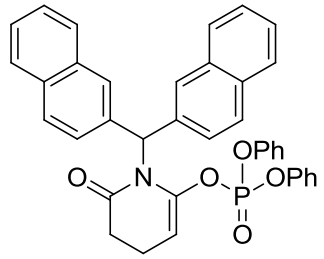




4h

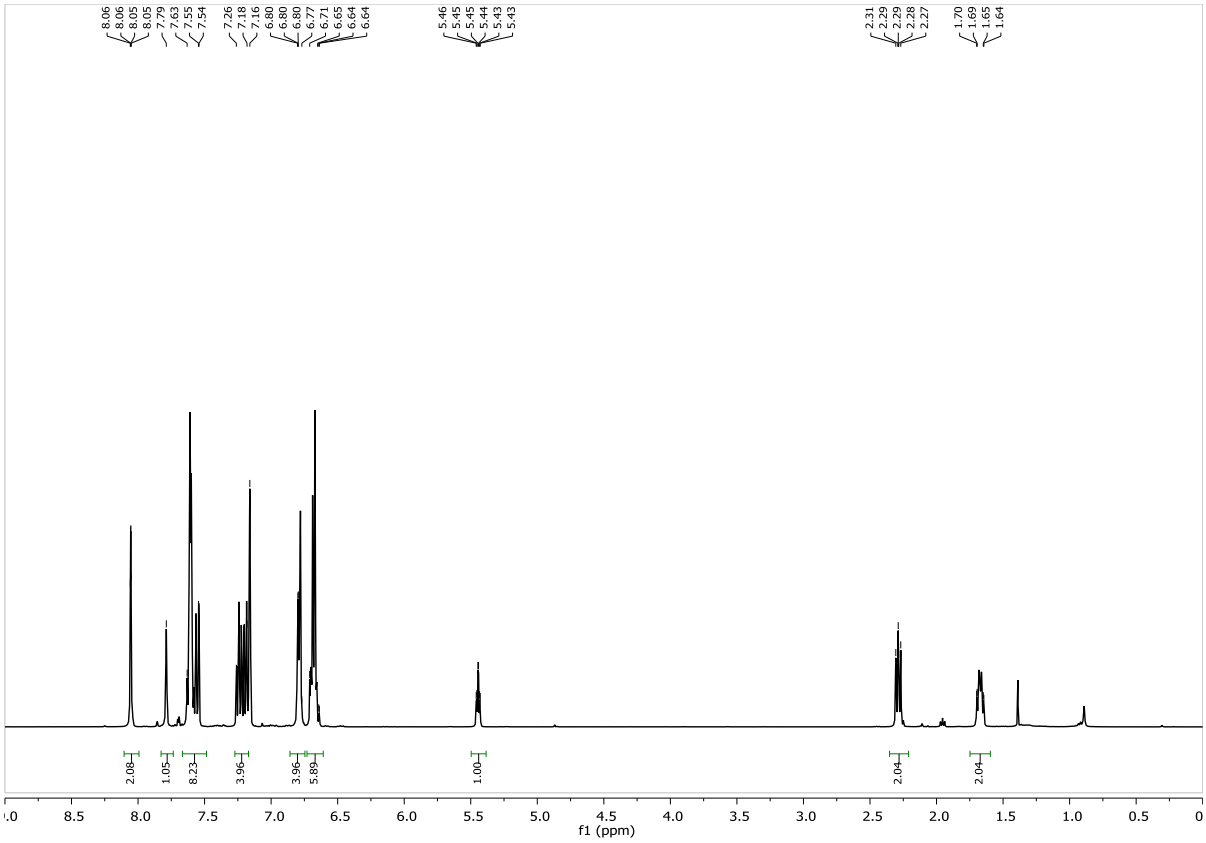
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

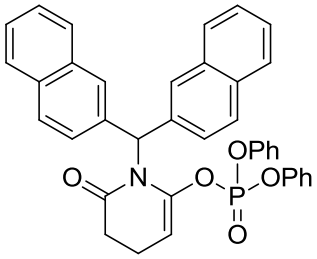




4i

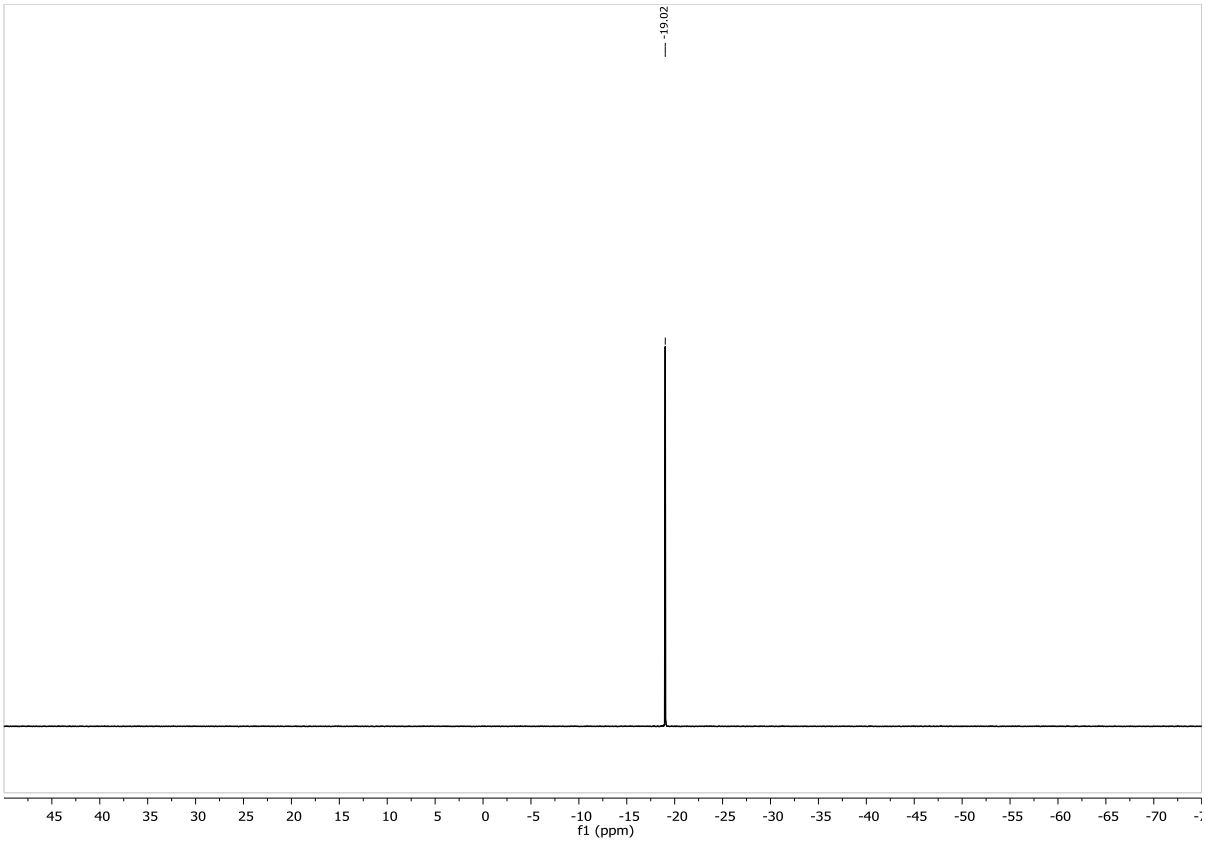
^{1}H NMR, 400 MHz, C_6D_6

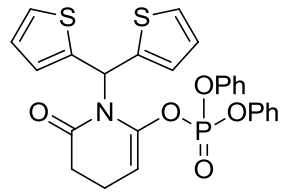




4i

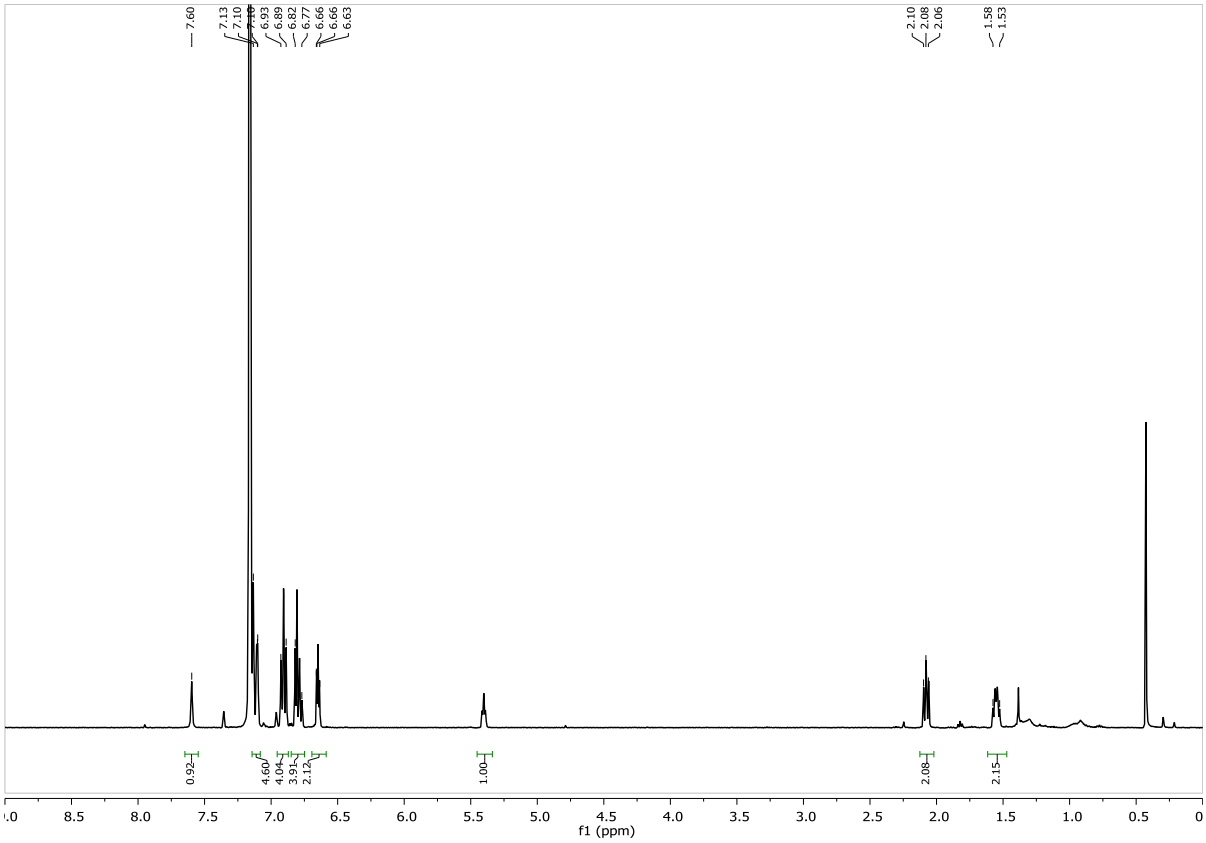
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

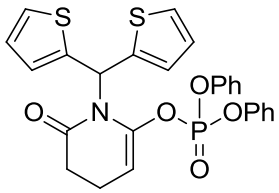




4j

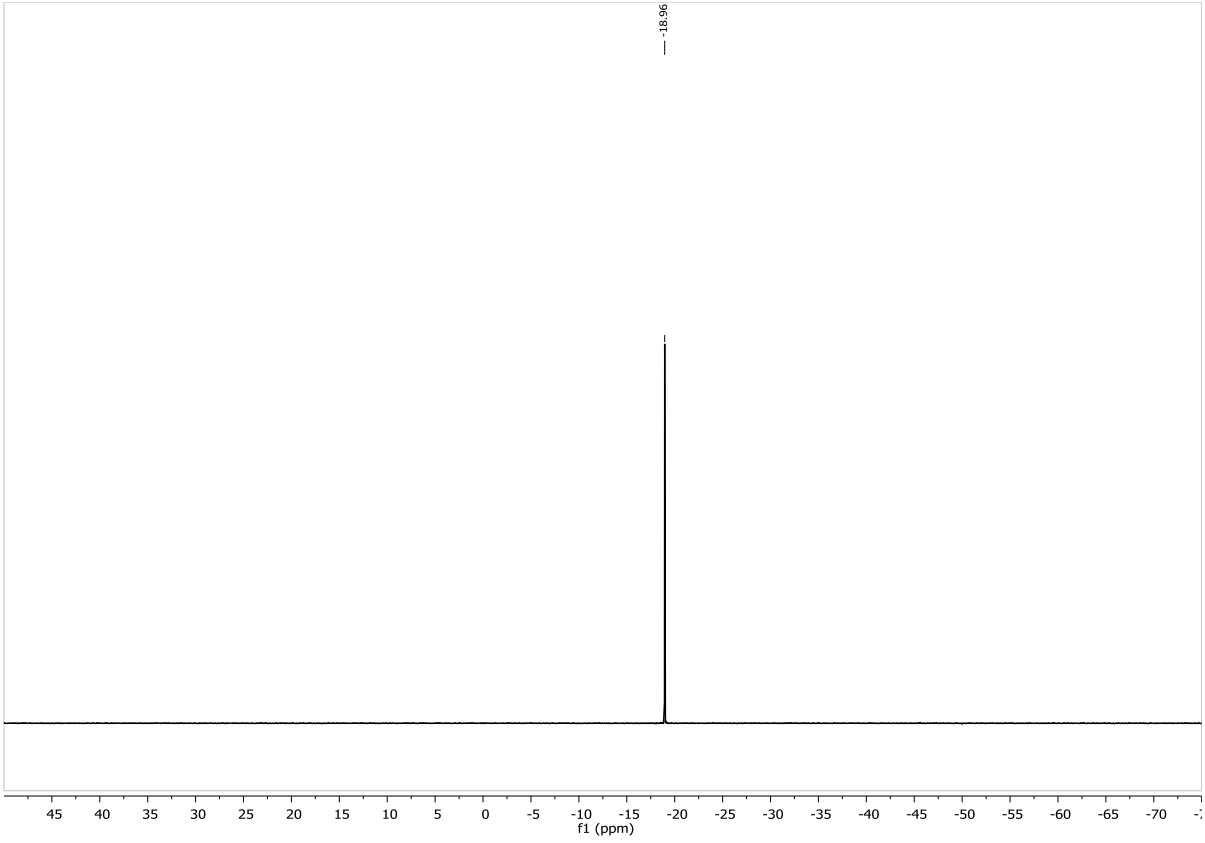
^{1}H NMR, 400 MHz, C_6D_6

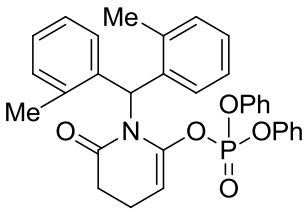




4j

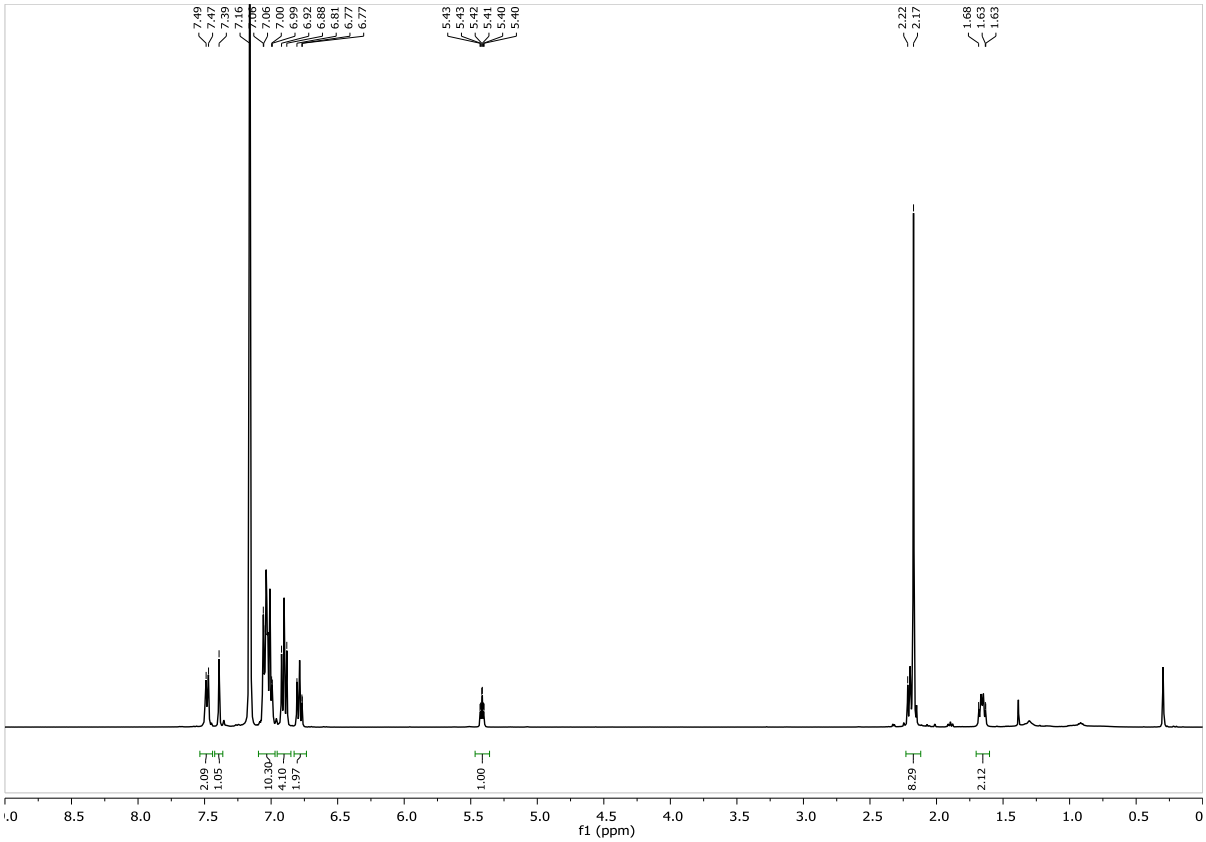
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

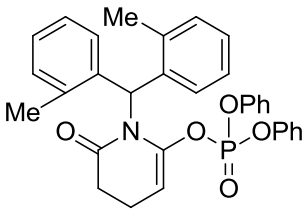




4k

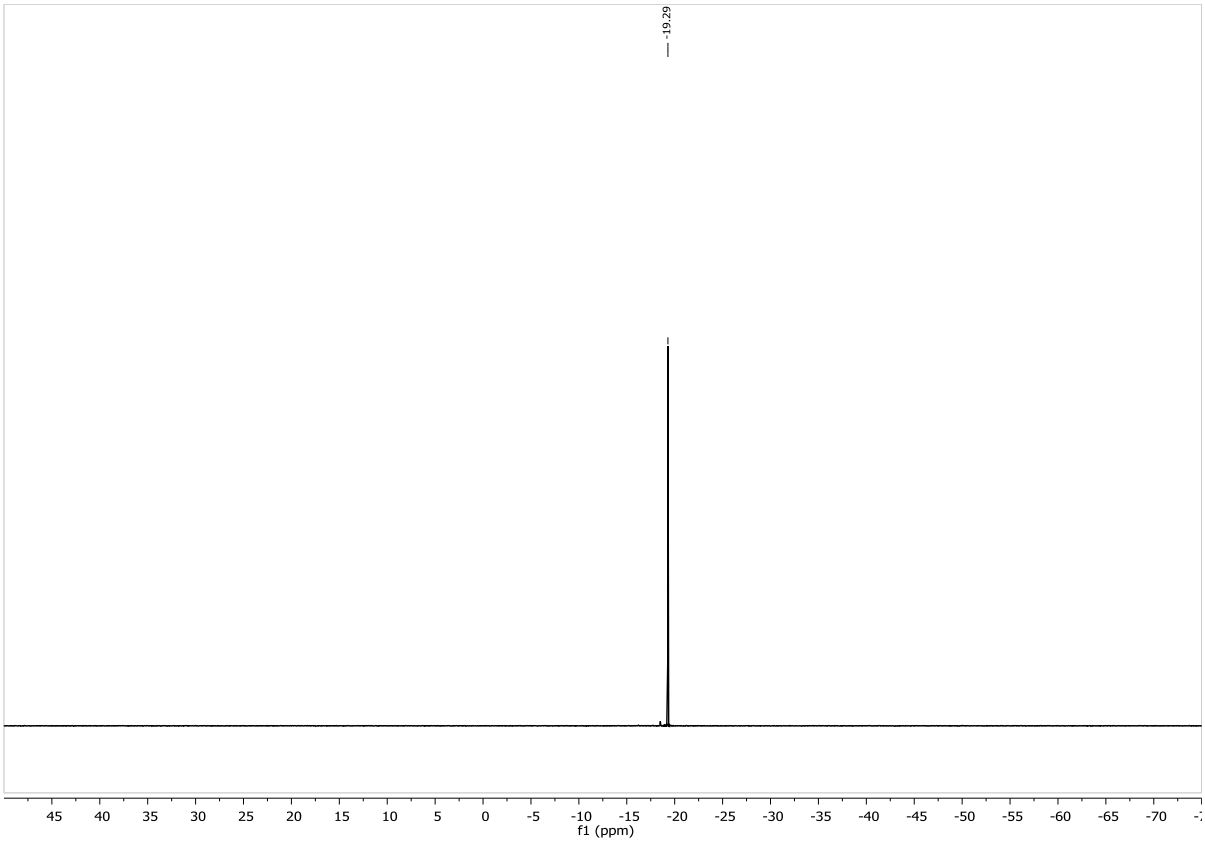
^{1}H NMR, 400 MHz, C_6D_6

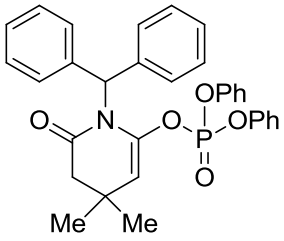




4k

$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

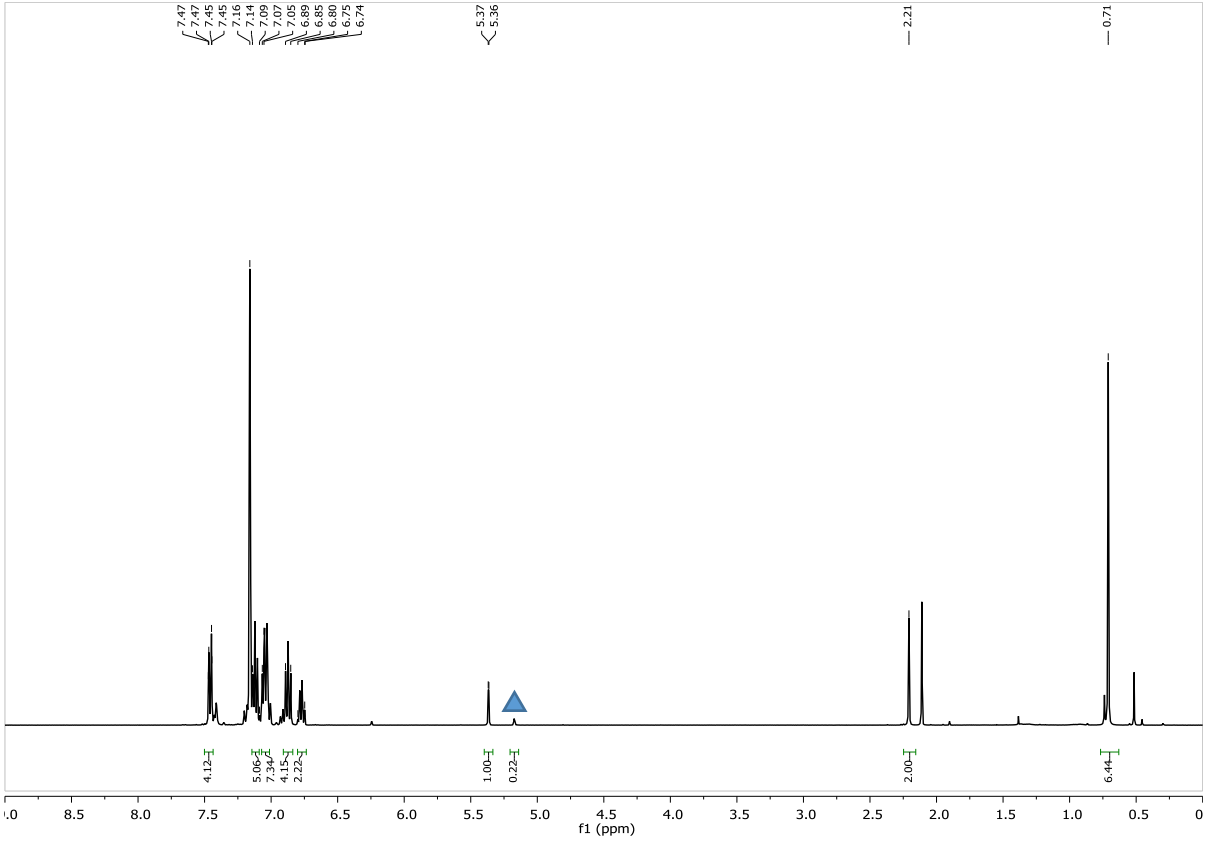


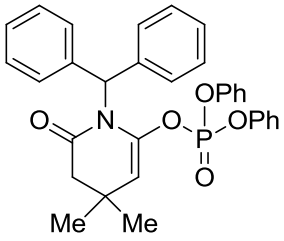


4l

^{1}H NMR, 400 MHz, C_6D_6

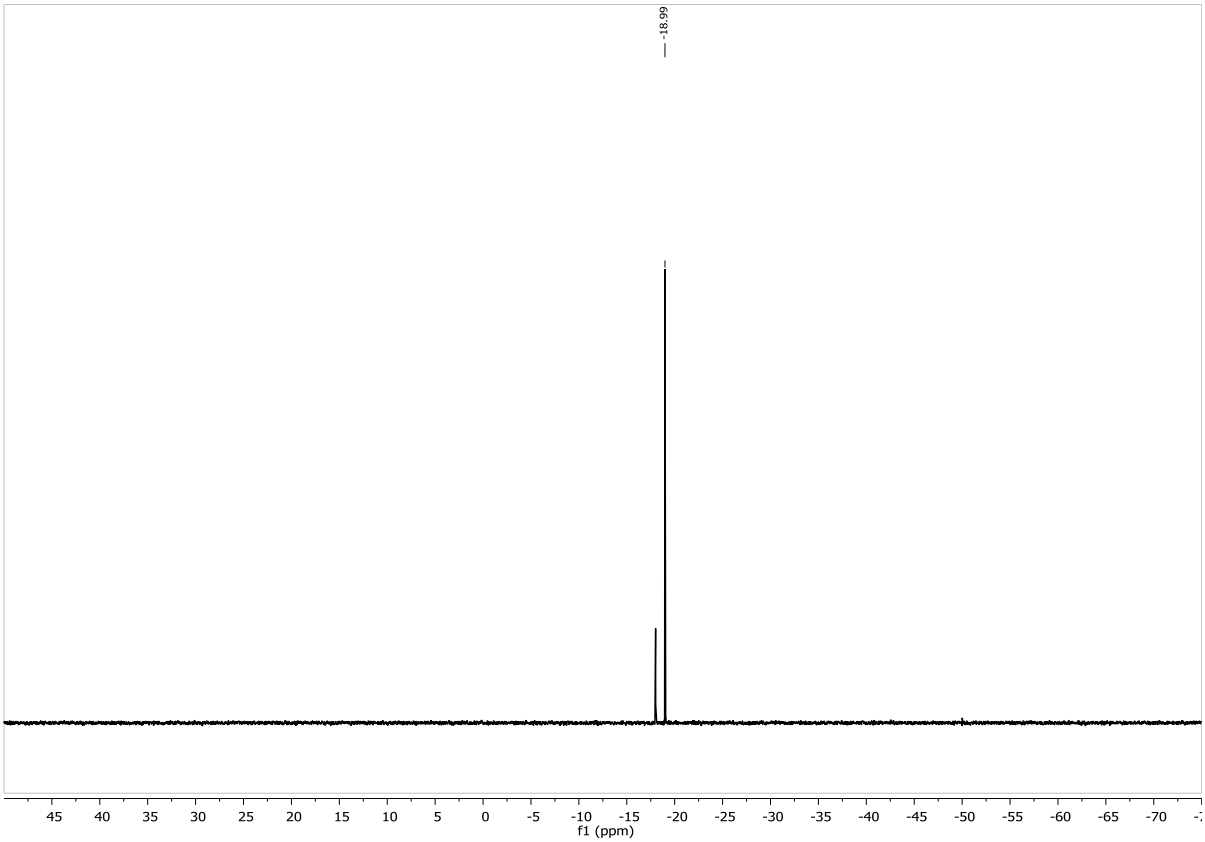
▲ bisphosphate

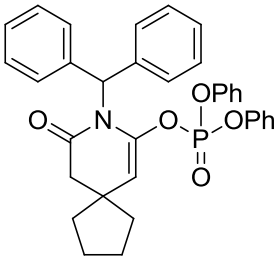




4l

$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

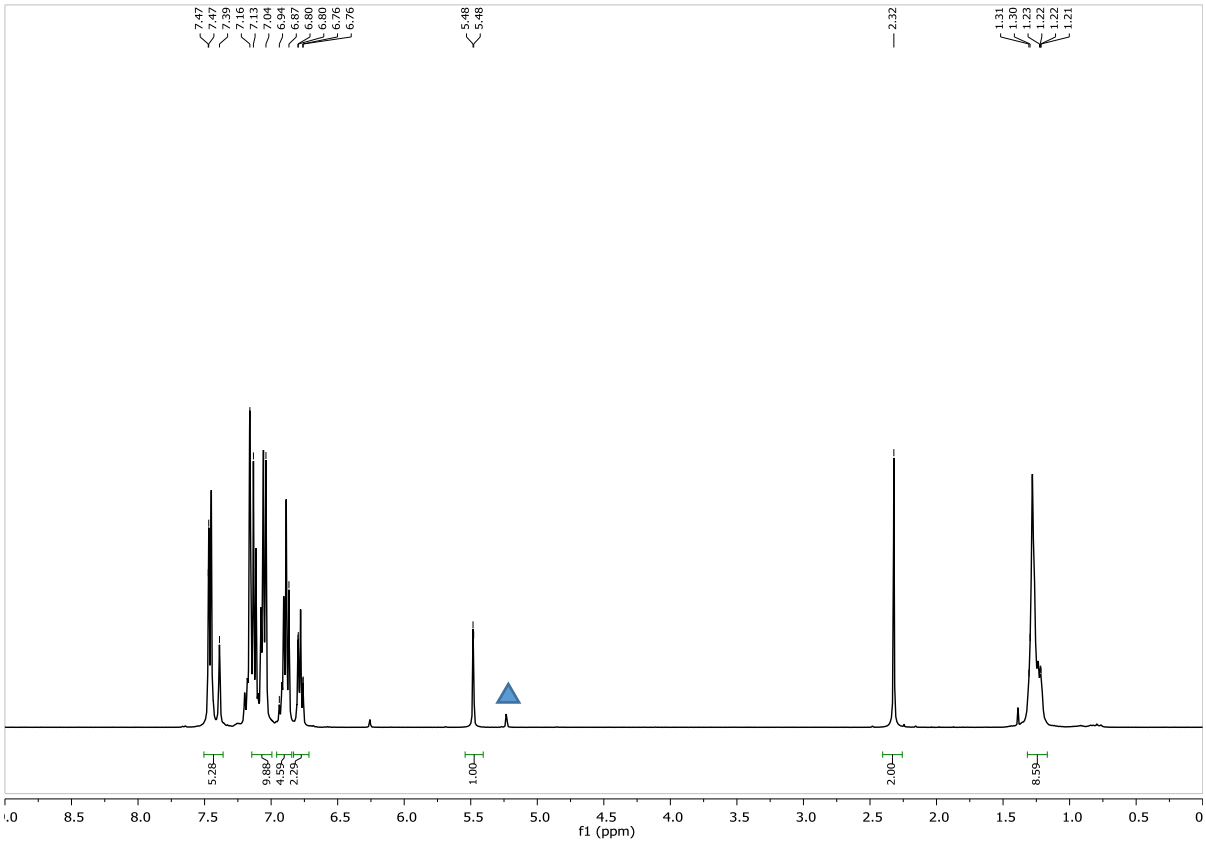


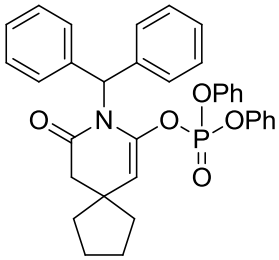


4m

^{1}H NMR, 400 MHz, C_6D_6

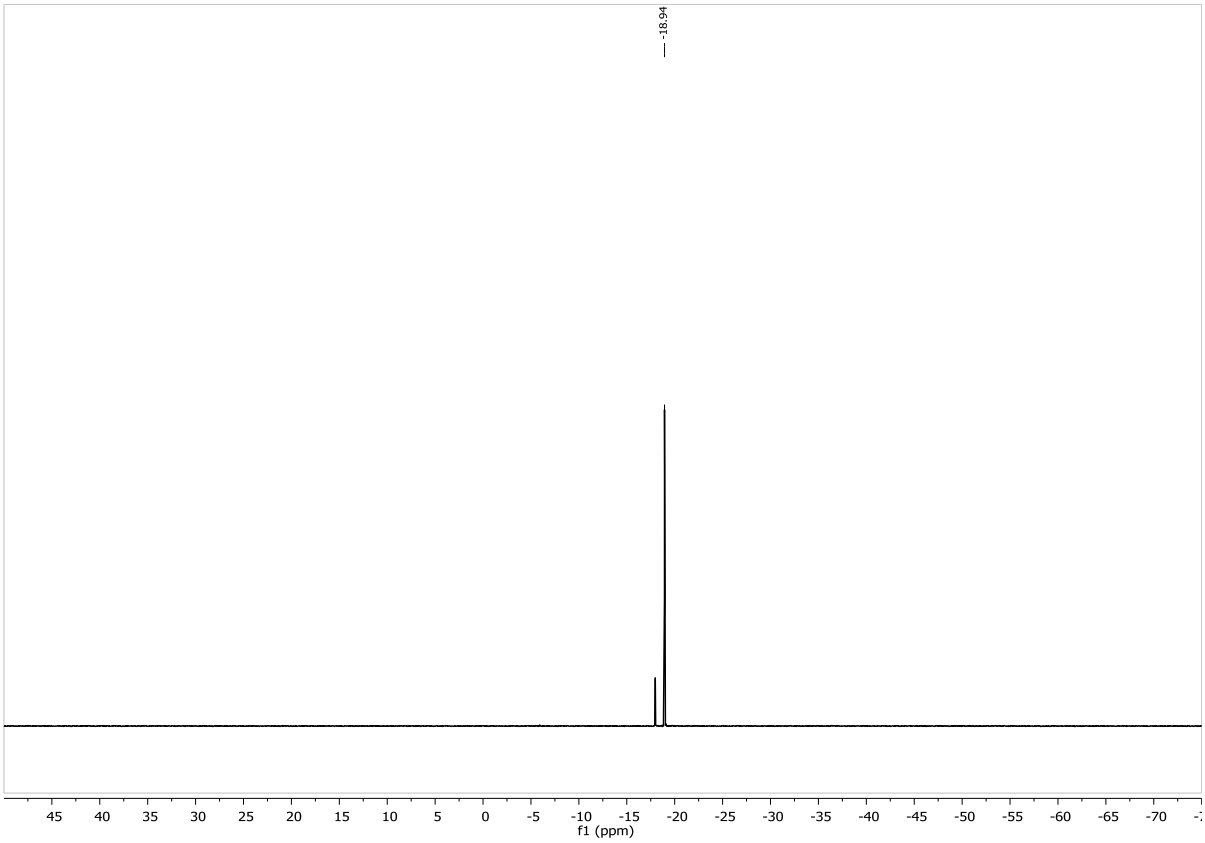
▲ bisphosphate

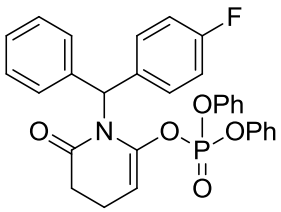




4m

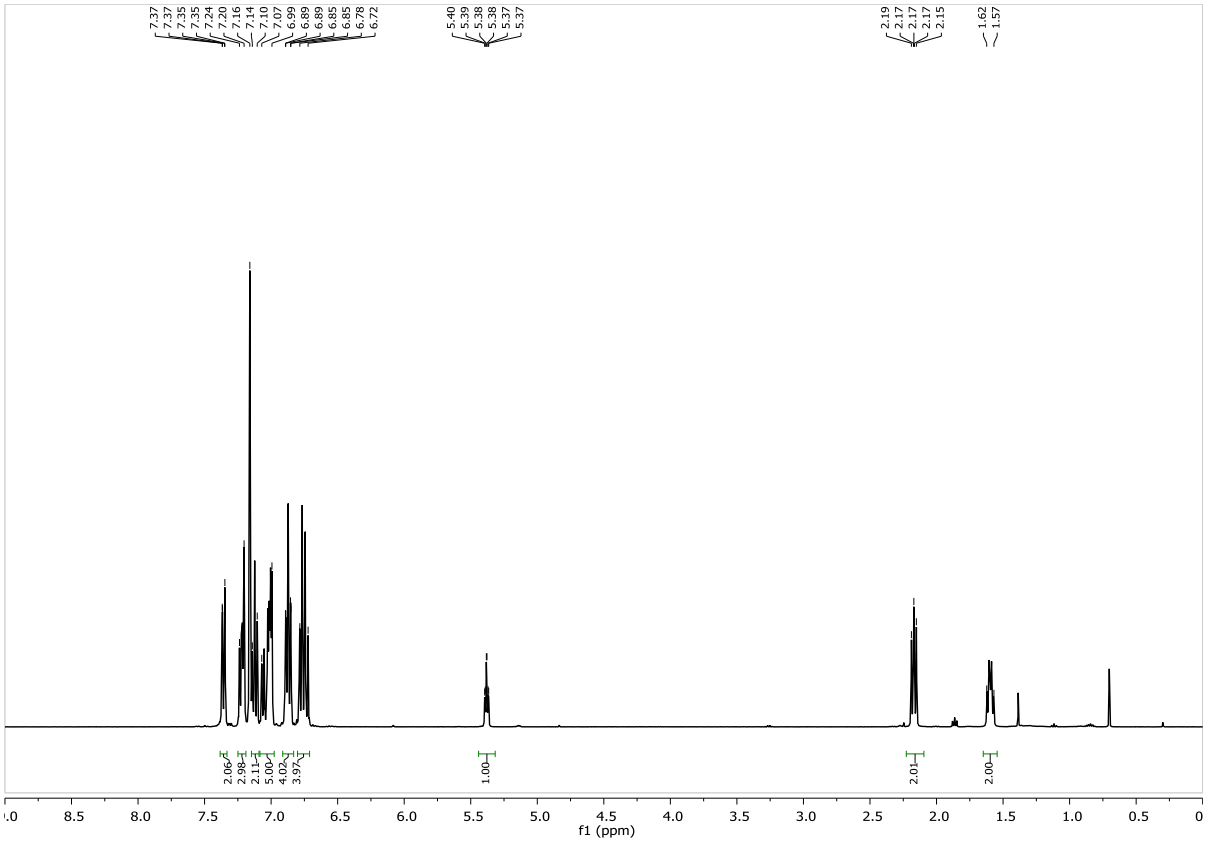
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

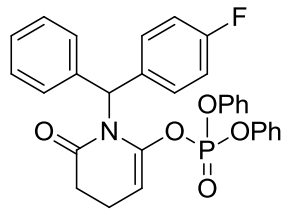




4n

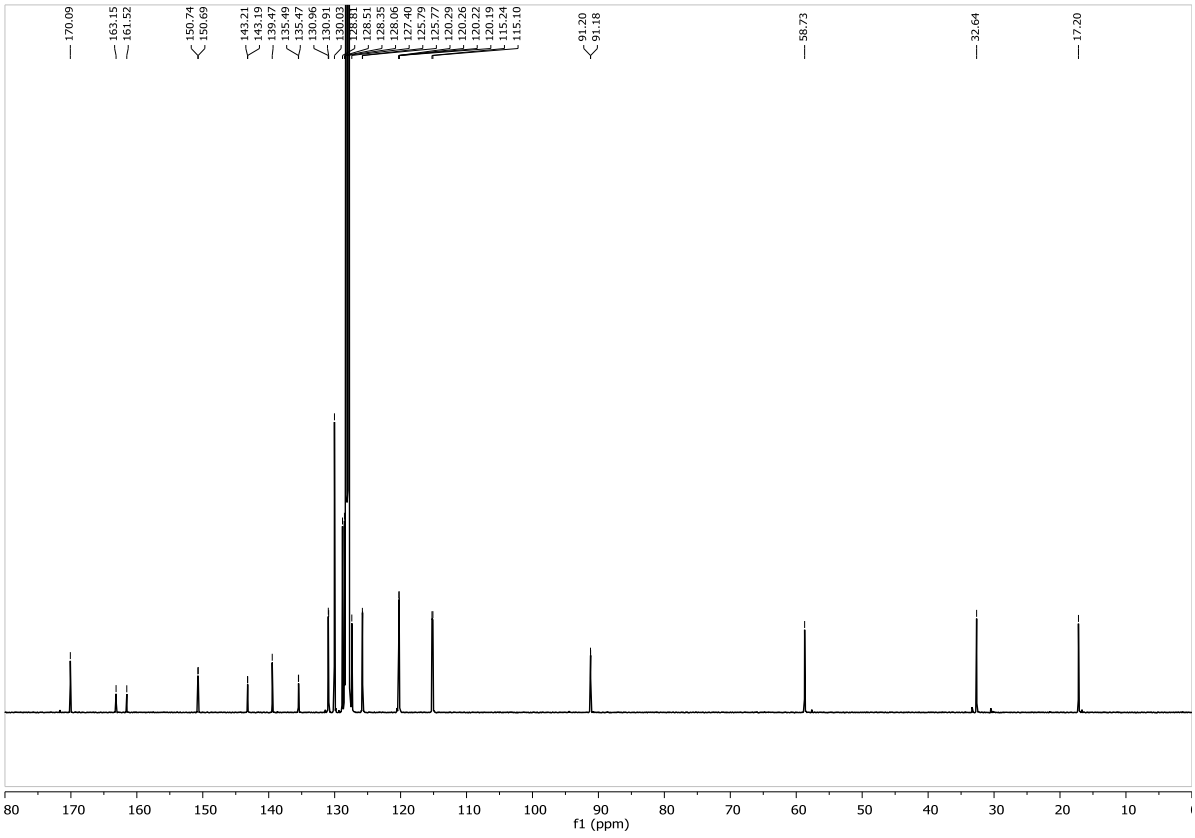
^{1}H NMR, 400 MHz, C_6D_6

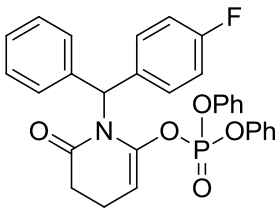




4n

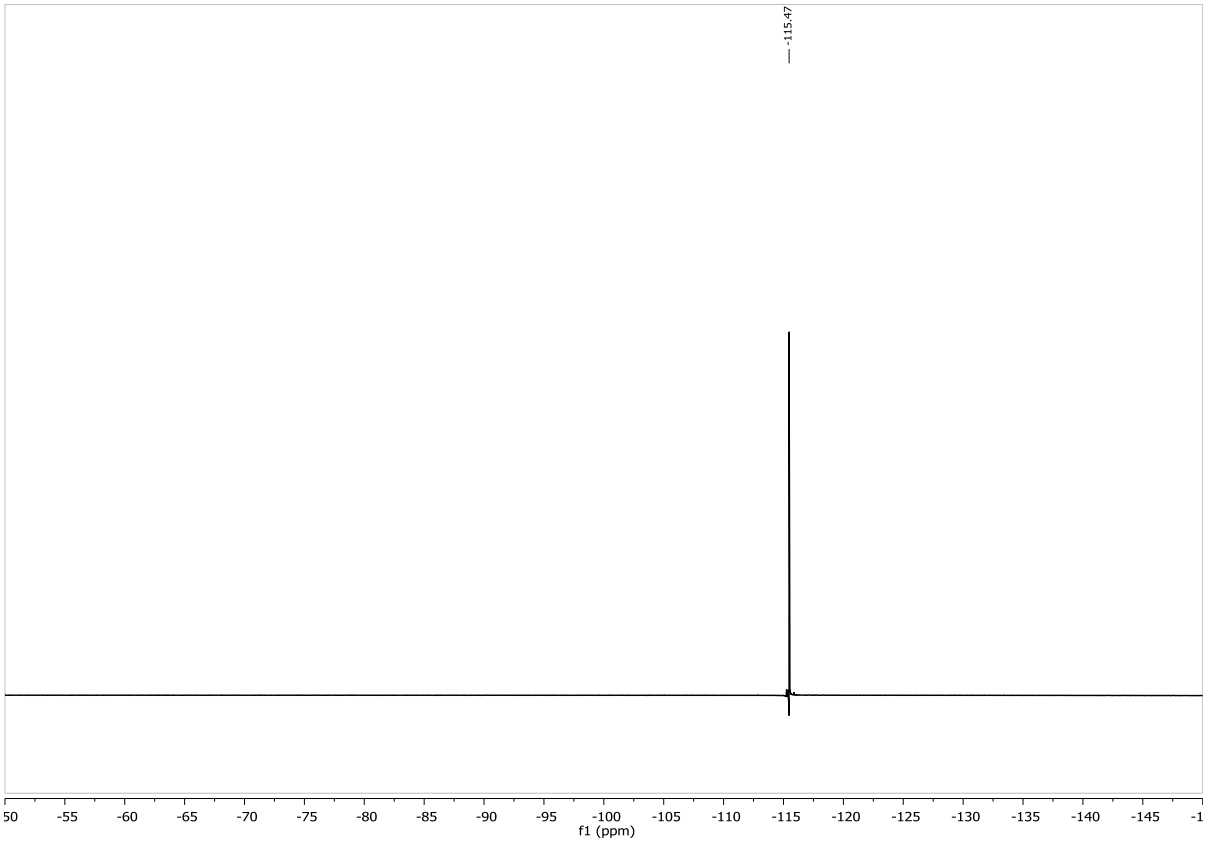
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

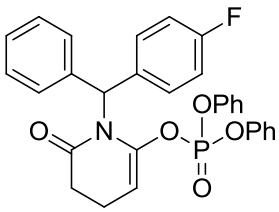




4n

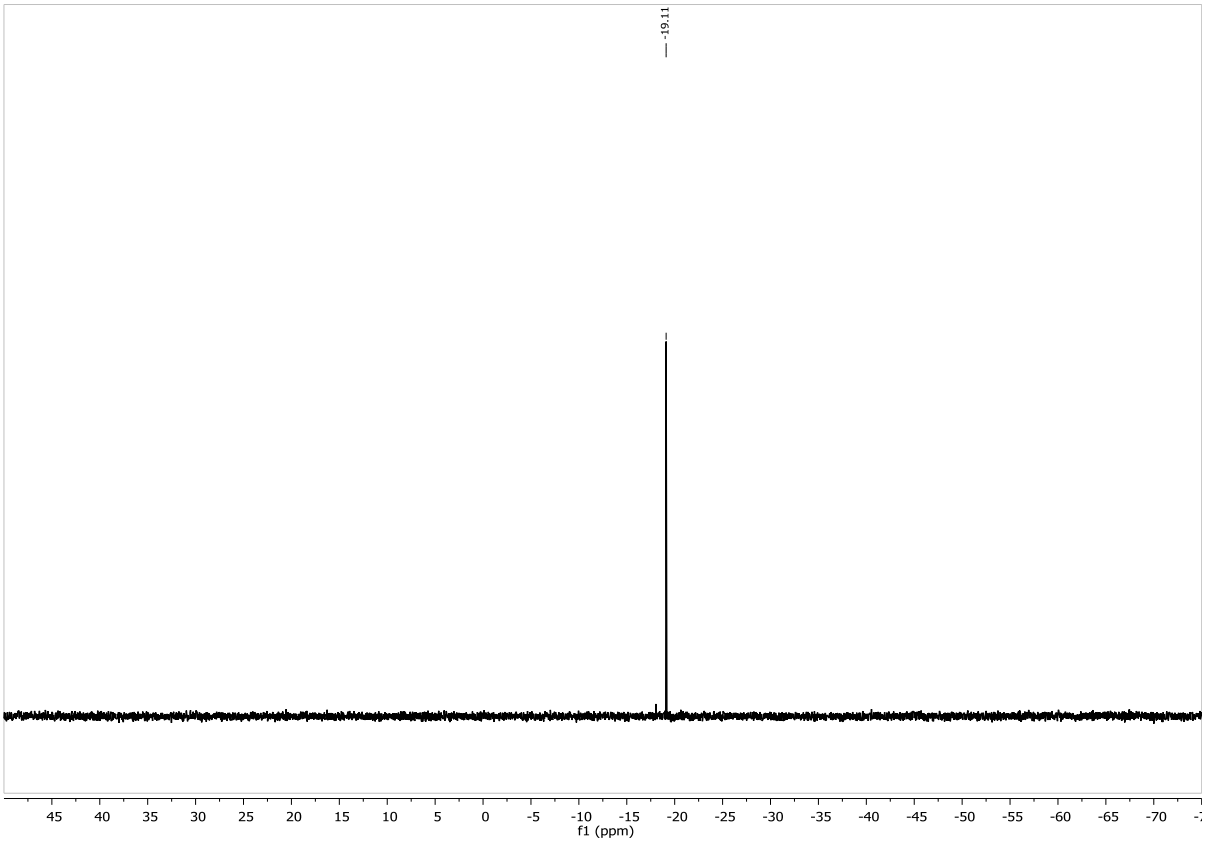
$^{19}F\{^{1}H\}$ NMR, 376 MHz, C_6D_6

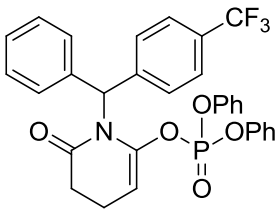




4n

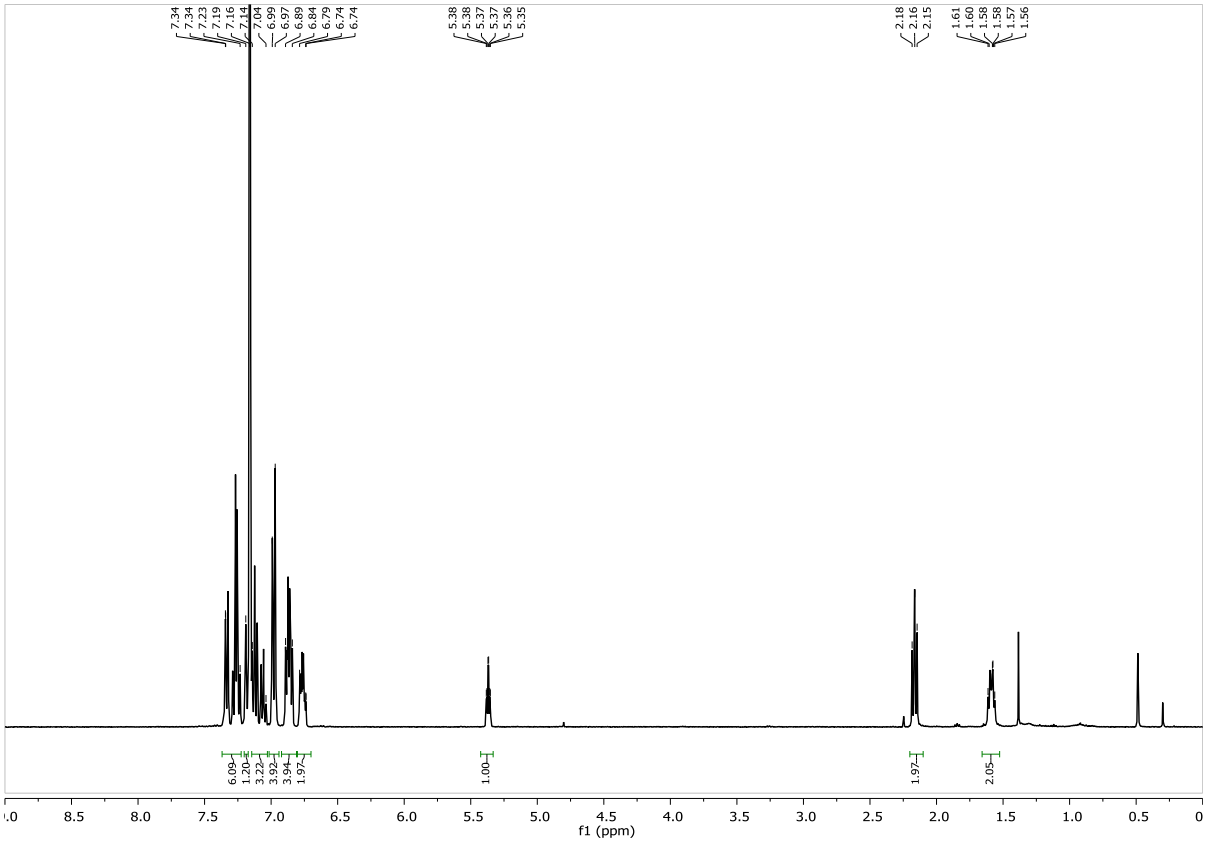
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

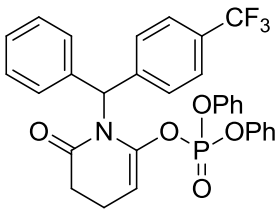




4o

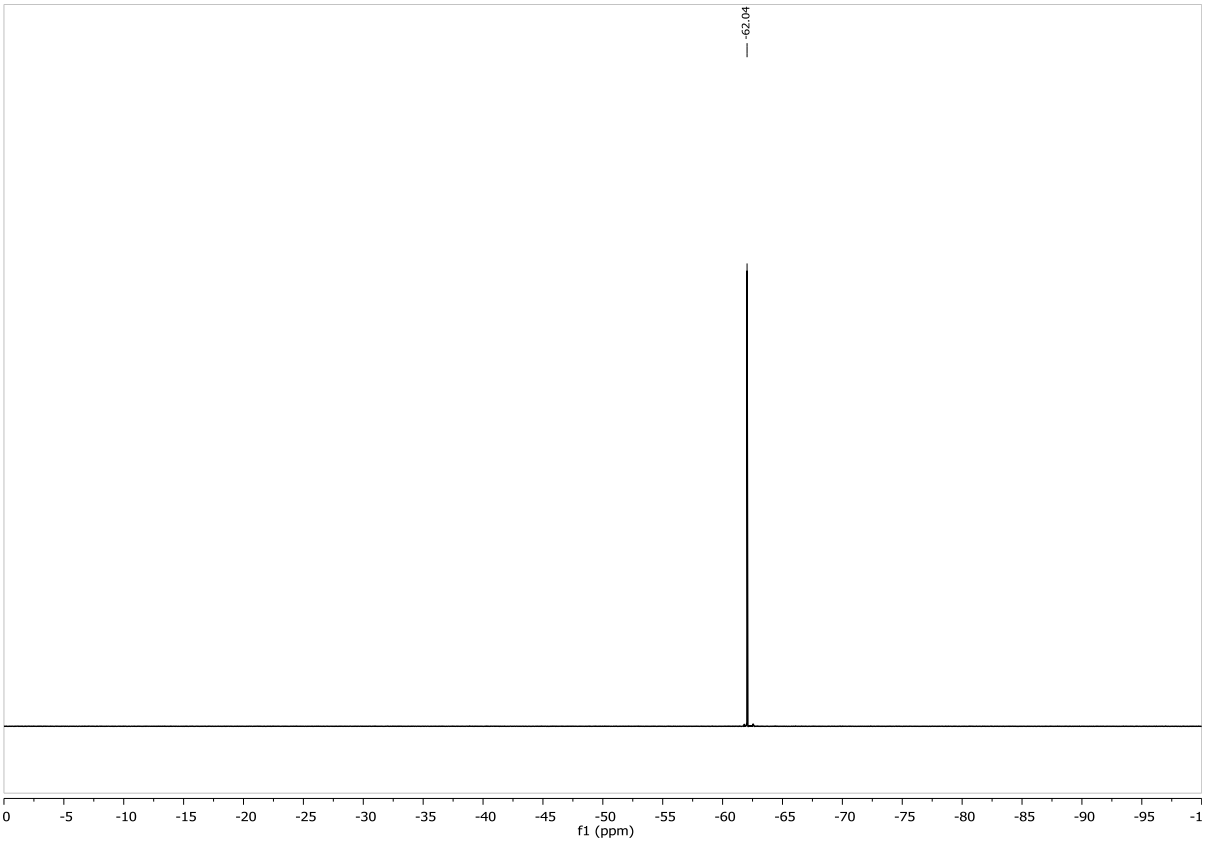
^{1}H NMR, 400 MHz, C_6D_6

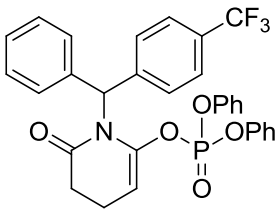




4o

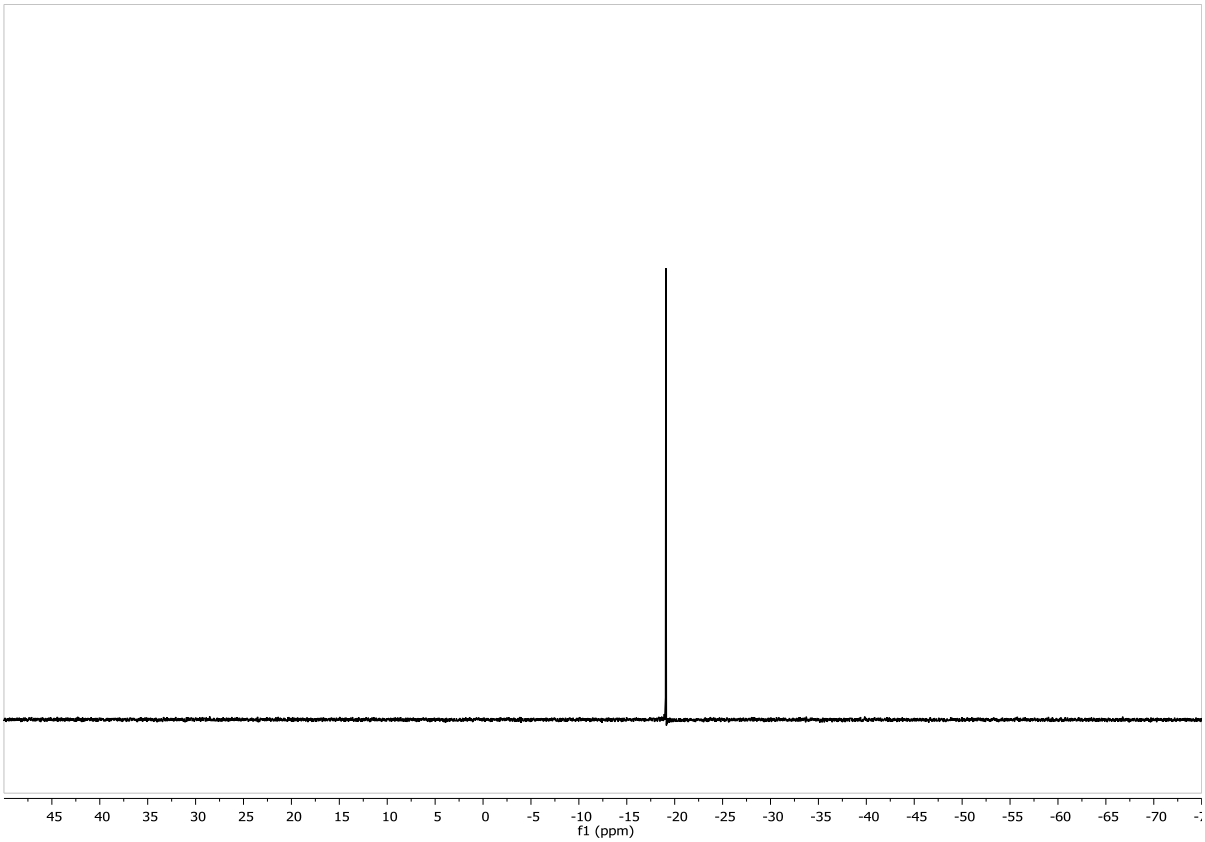
$^{19}F\{^{1}H\}$ NMR, 376 MHz, C_6D_6

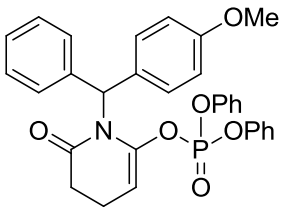




4o

$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

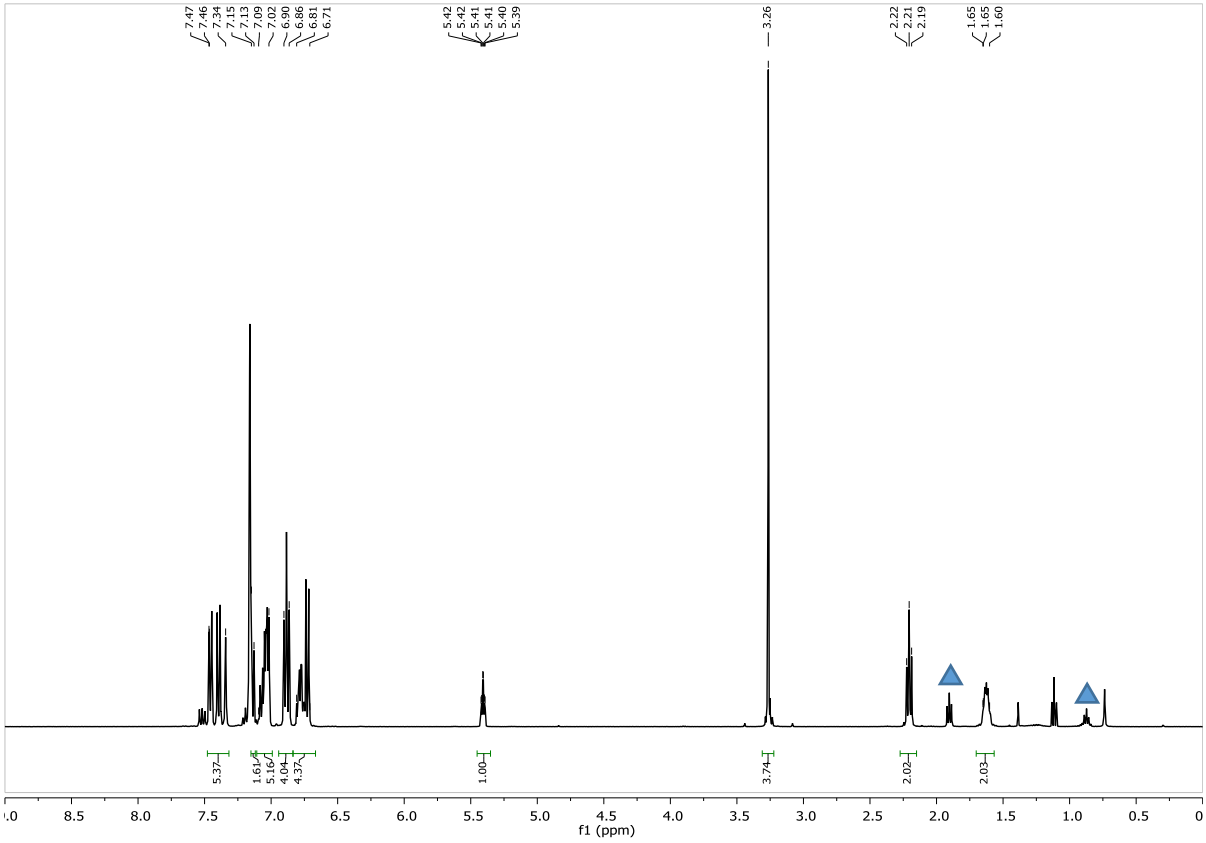


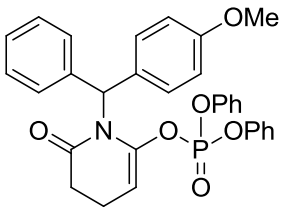


4p

^{1}H NMR, 400 MHz, C_6D_6

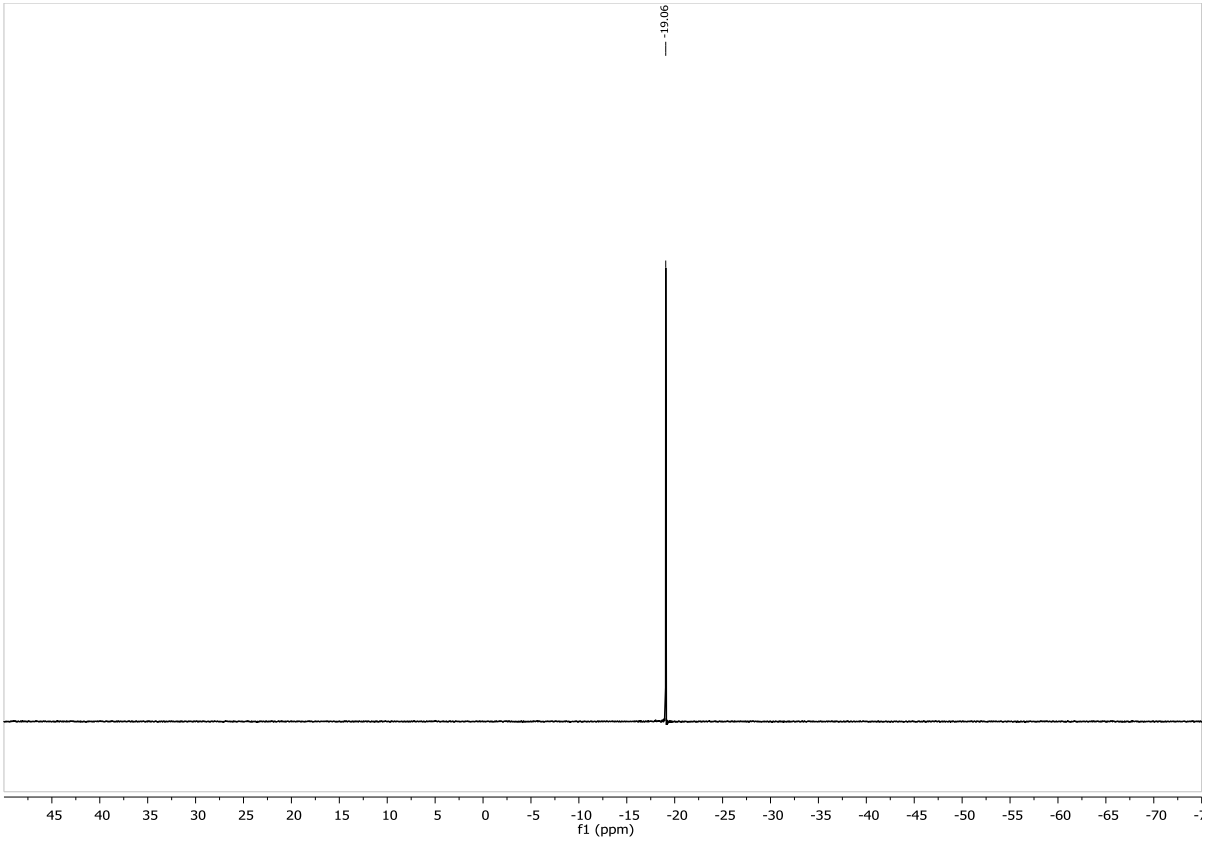
▲ starting material

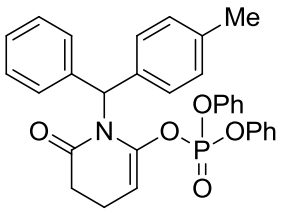




4p

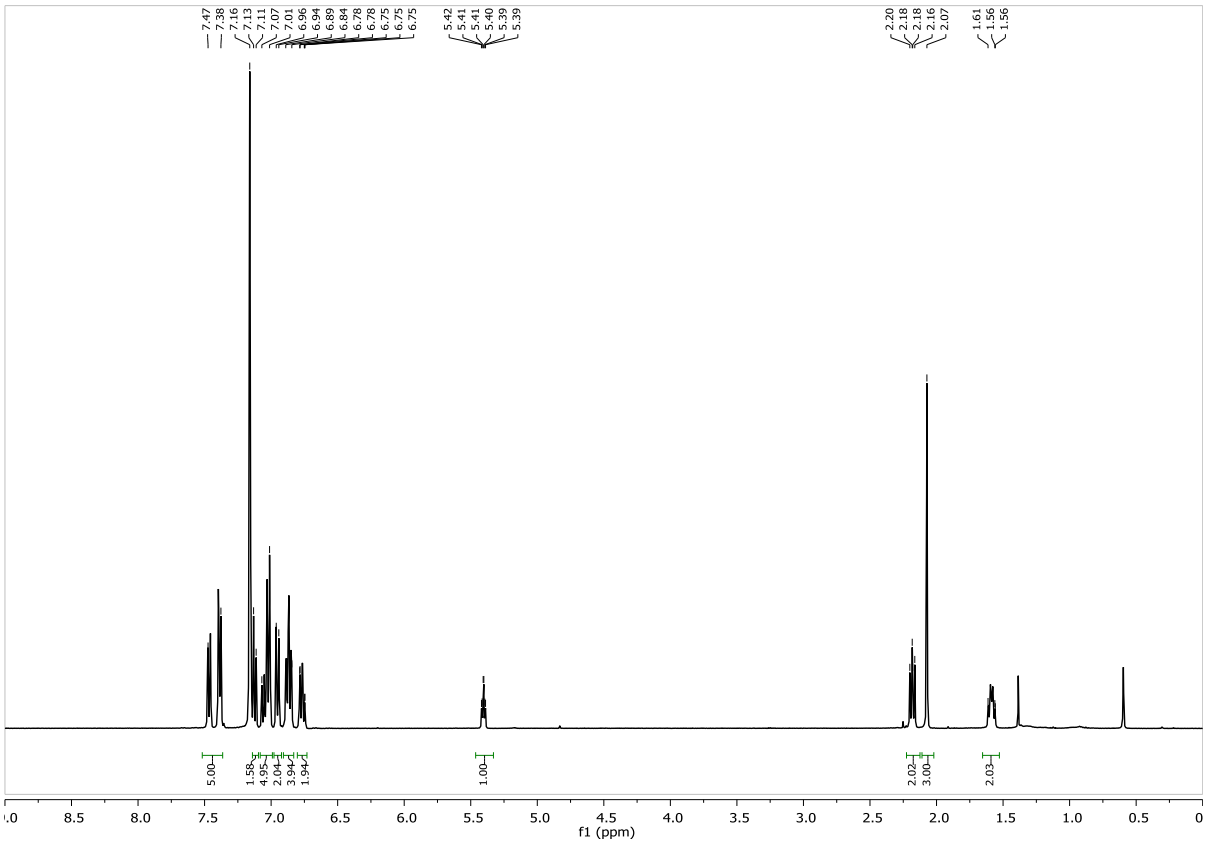
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

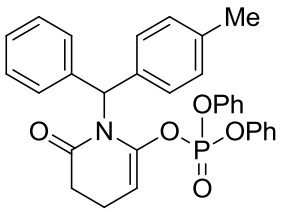




4r

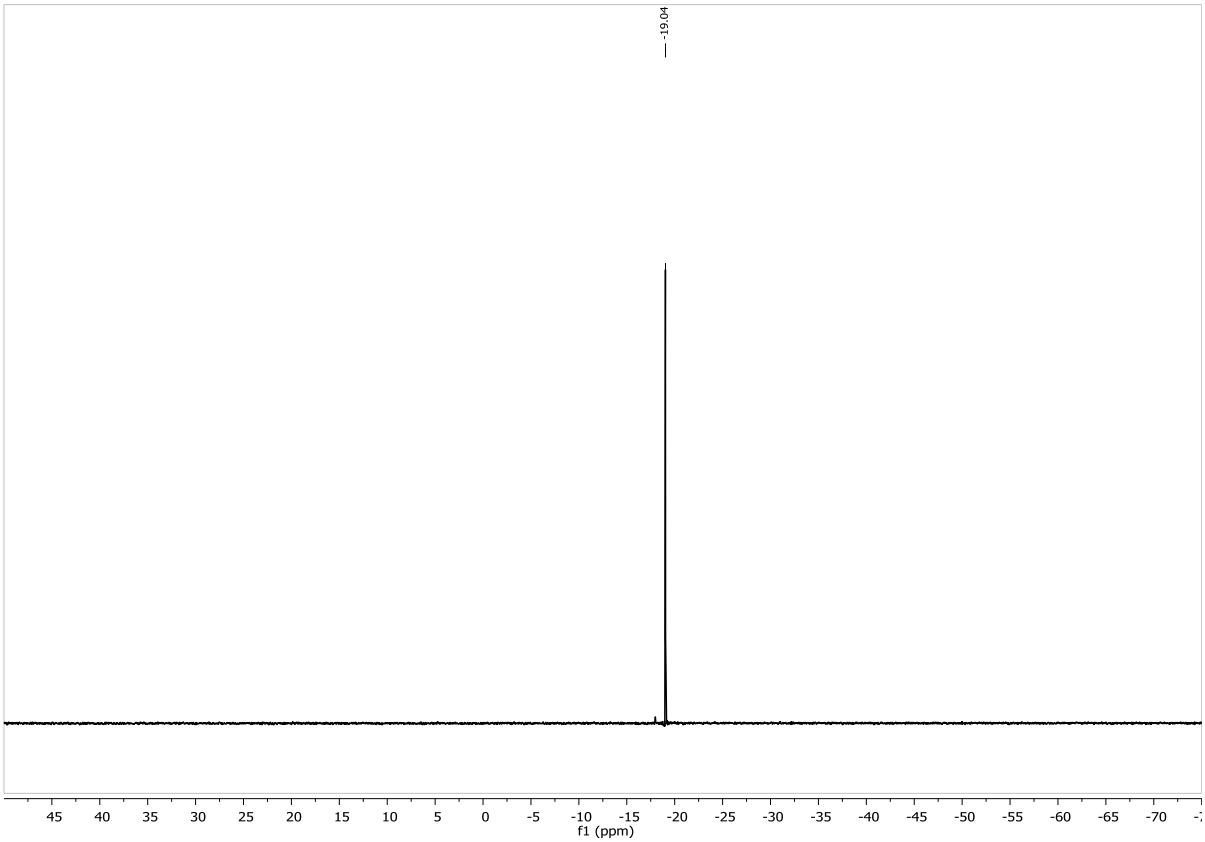
^{1}H NMR, 400 MHz, C_6D_6

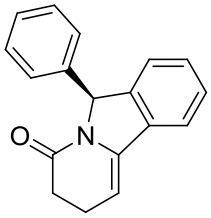




4r

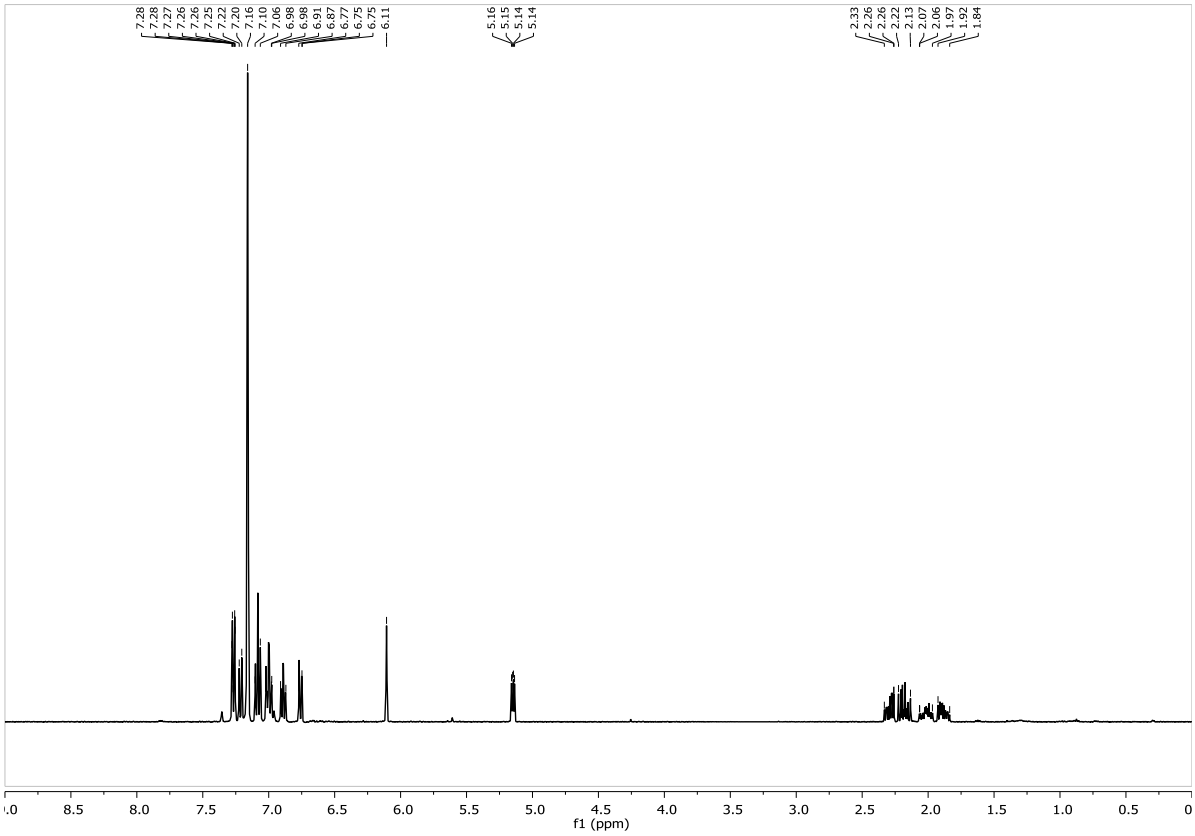
$^{31}P\{^{1}H\}$ NMR, 162 MHz, C_6D_6

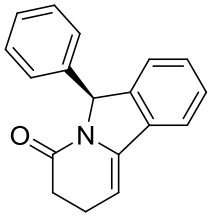




5a

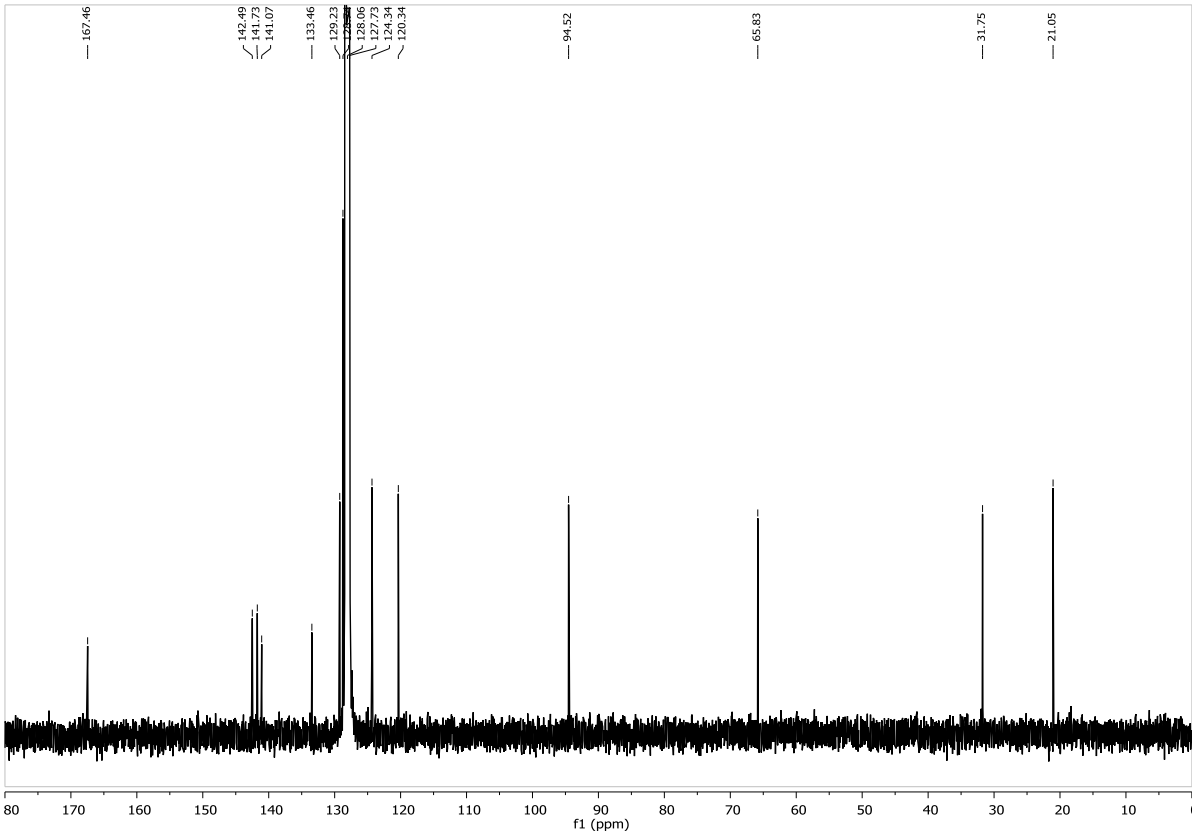
^{1}H NMR, 400 MHz, C_6D_6

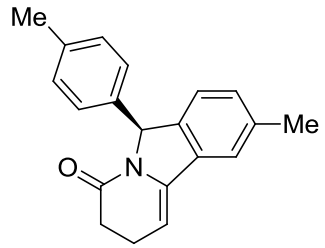




5a

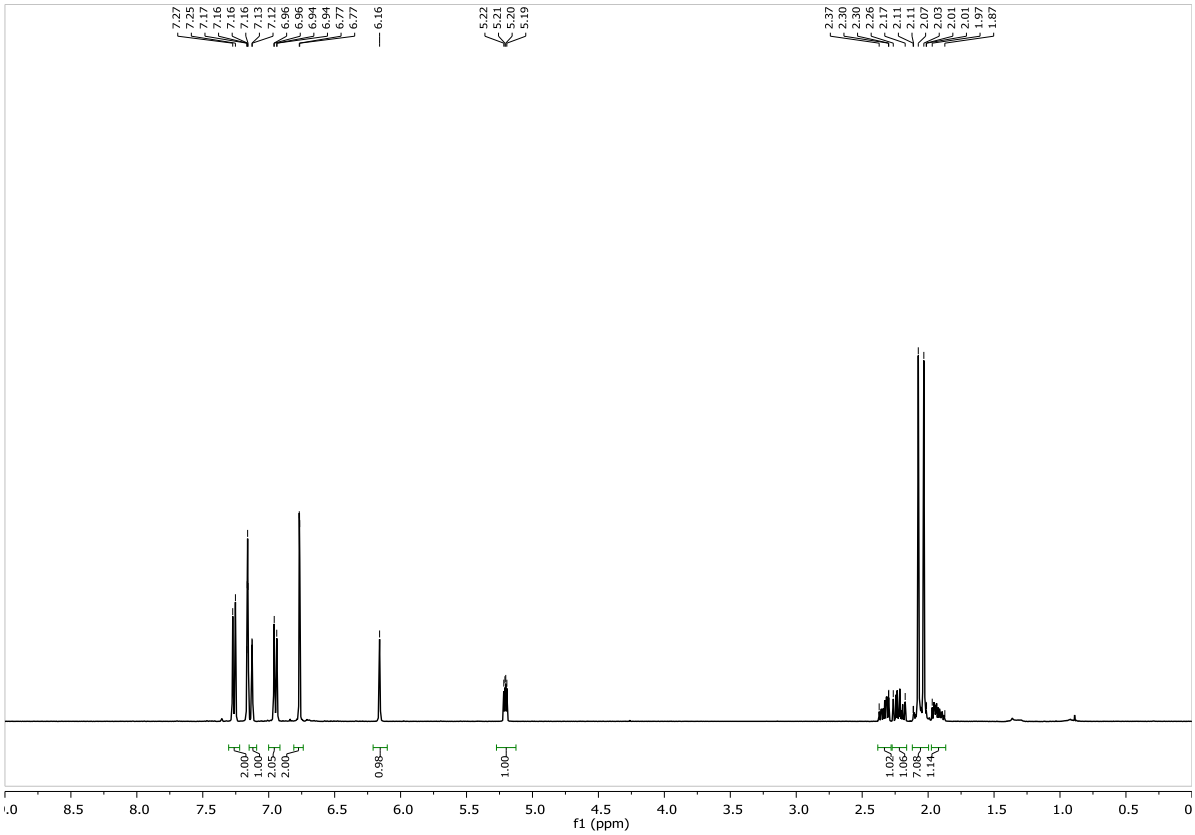
$^{13}C\{^{1}H\}$ NMR, 101 MHz, C_6D_6

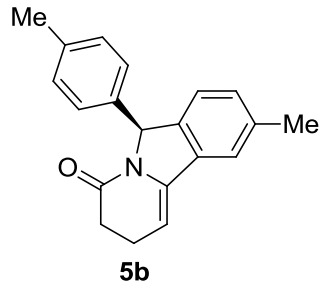




5b

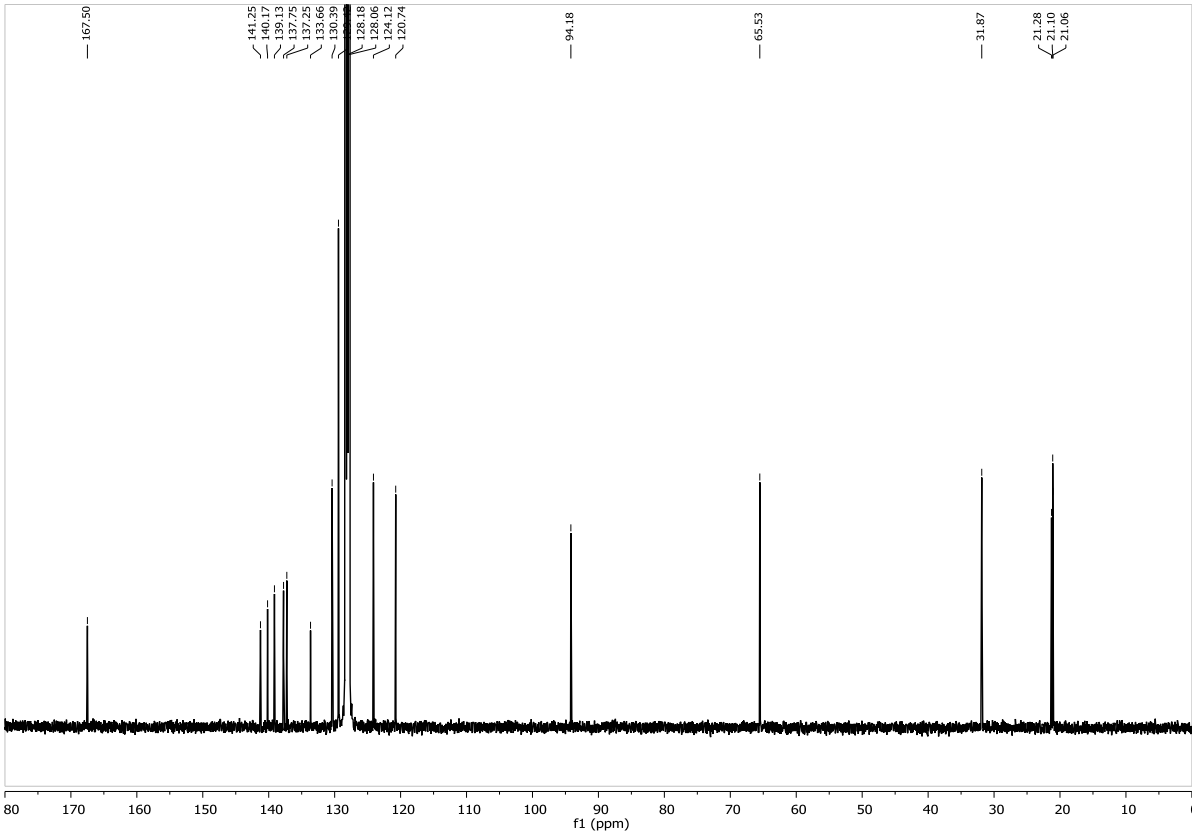
^{1}H NMR, 400 MHz, C_6D_6

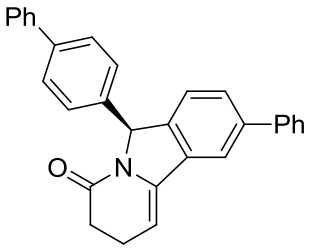




5b

$^{13}C\{^{1}H\}$ NMR, 101 MHz, C_6D_6

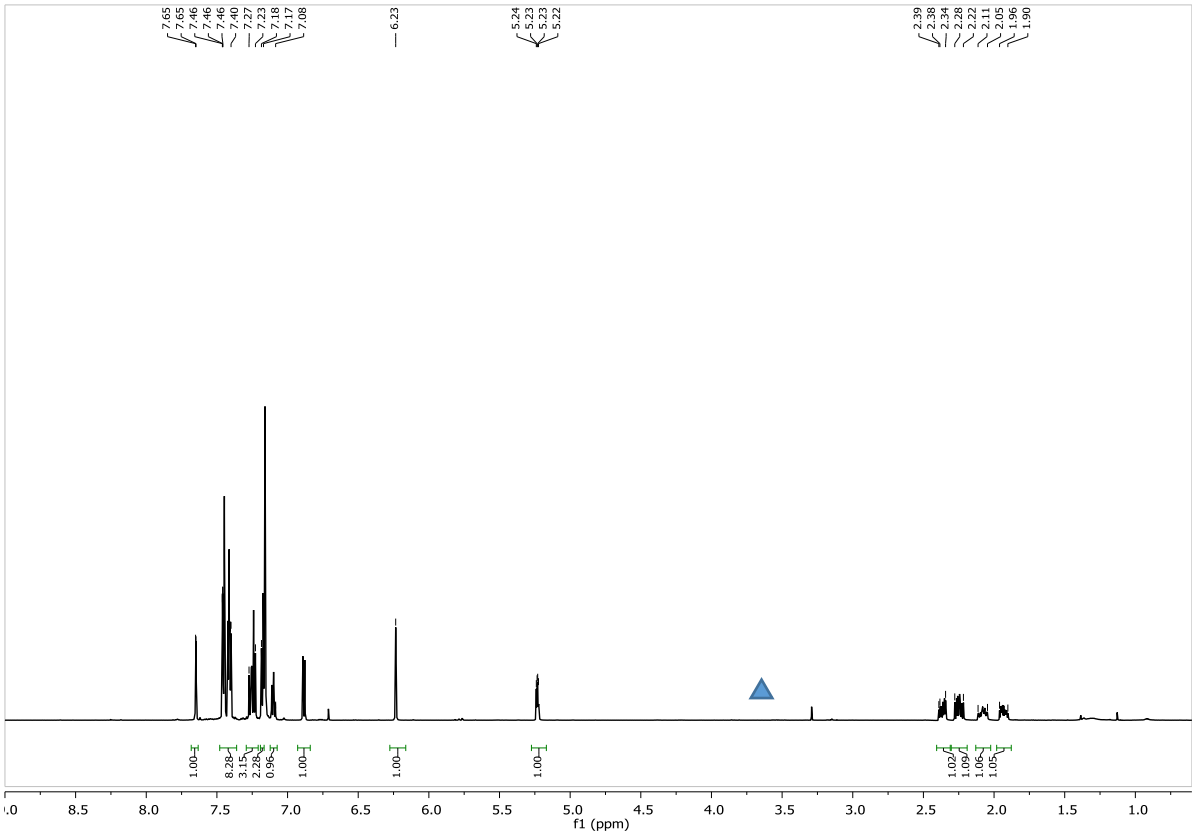


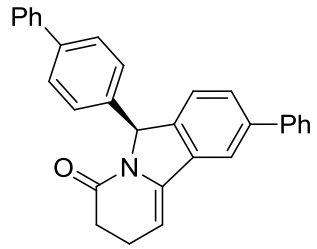


5c

^{1}H NMR, 600 MHz, C_6D_6

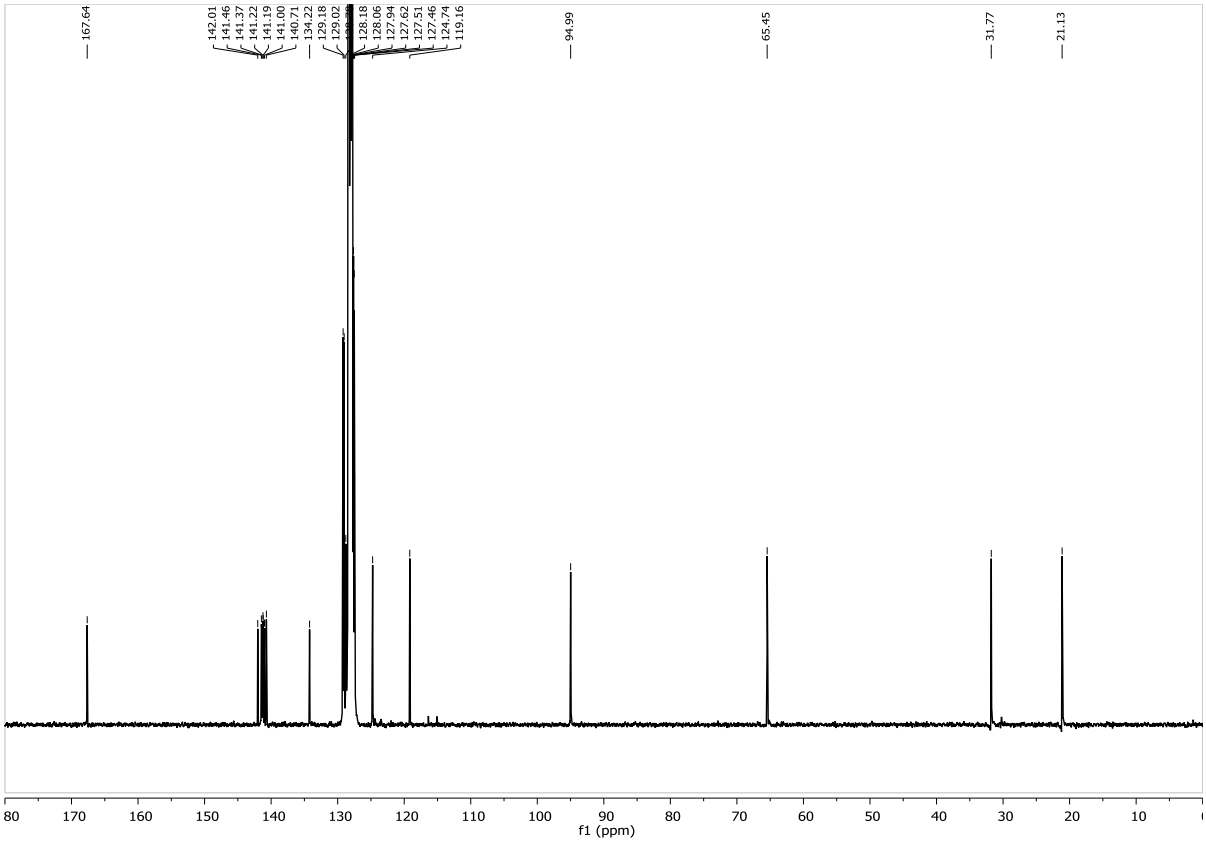
▲ 4-methoxyphenol

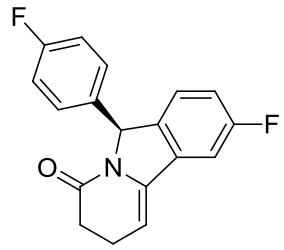




5c

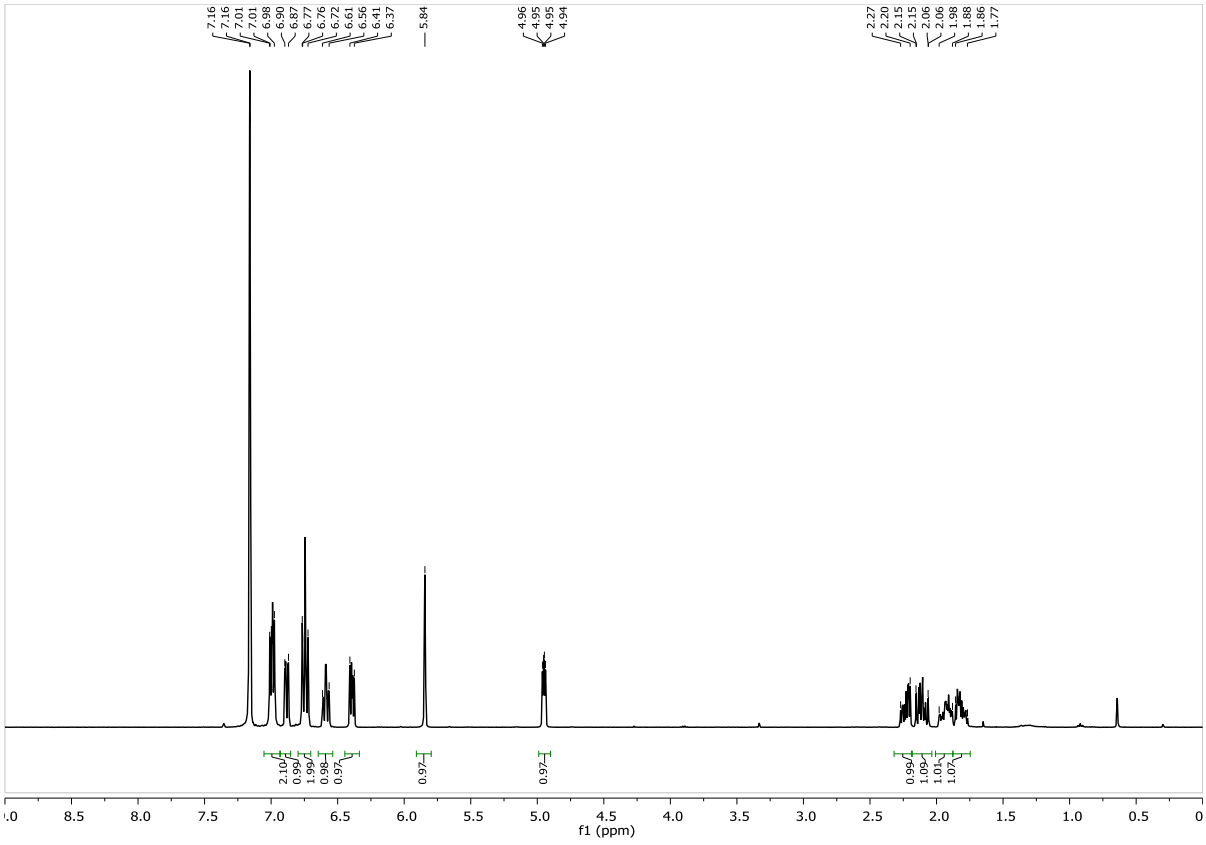
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

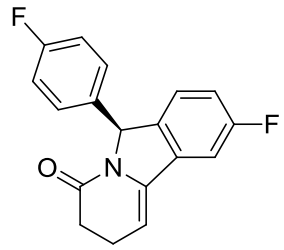




5d

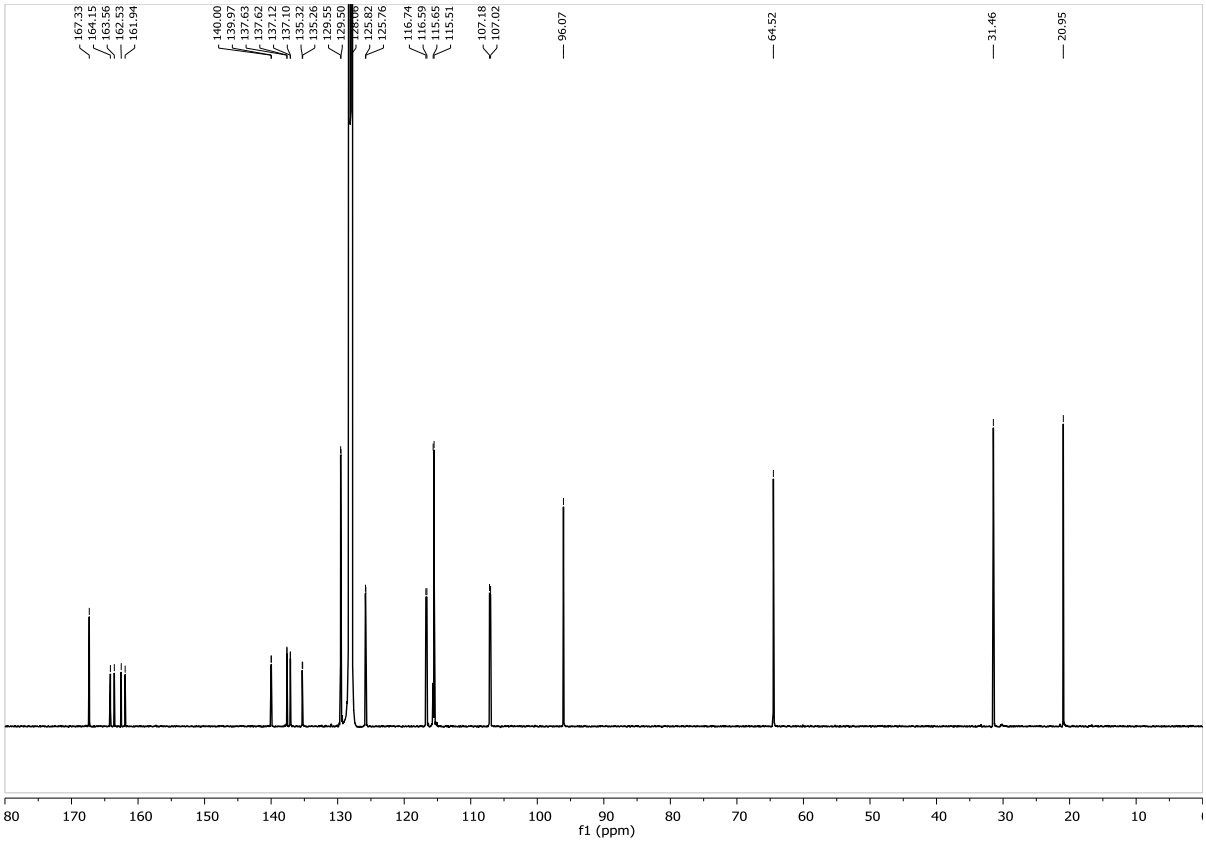
^{1}H NMR, 400 MHz, C_6D_6

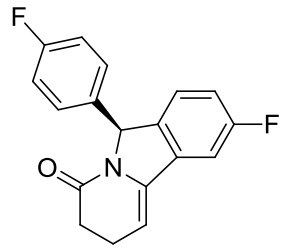




5d

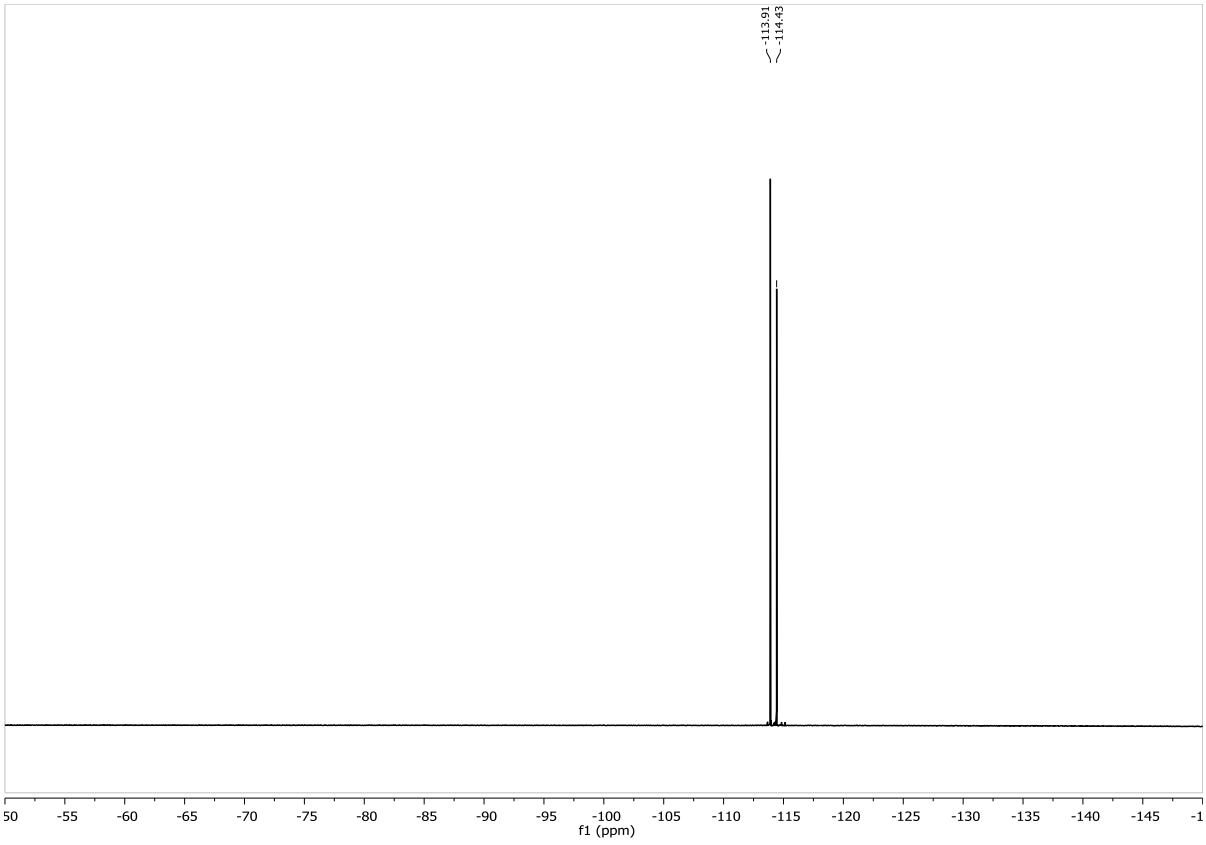
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

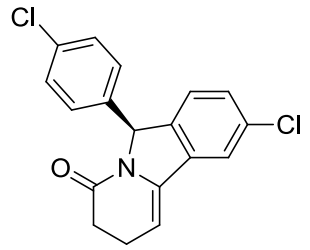




5d

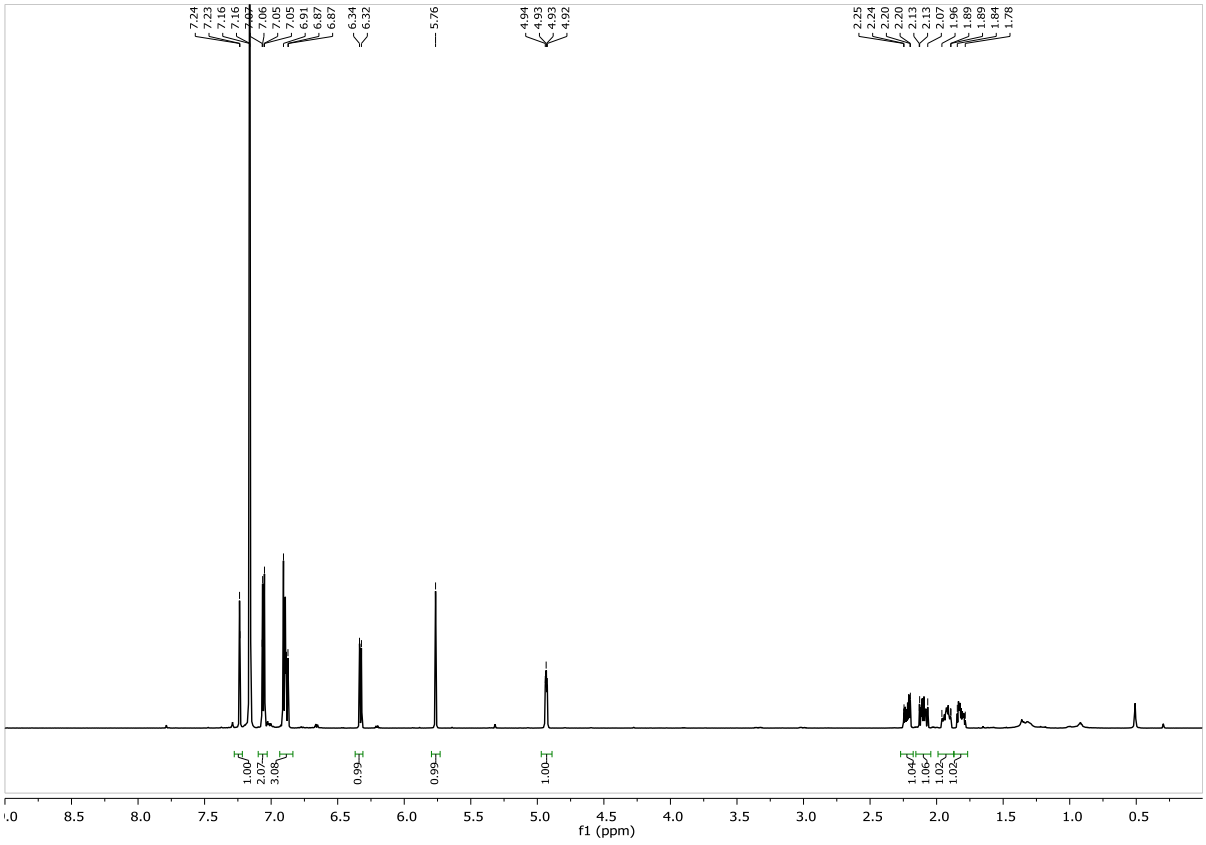
$^{19}F\{^{1}H\}$ NMR, 376 MHz, C_6D_6

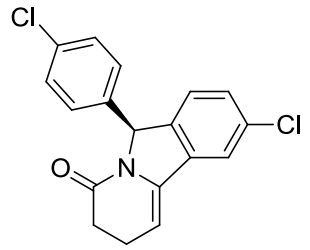




5e

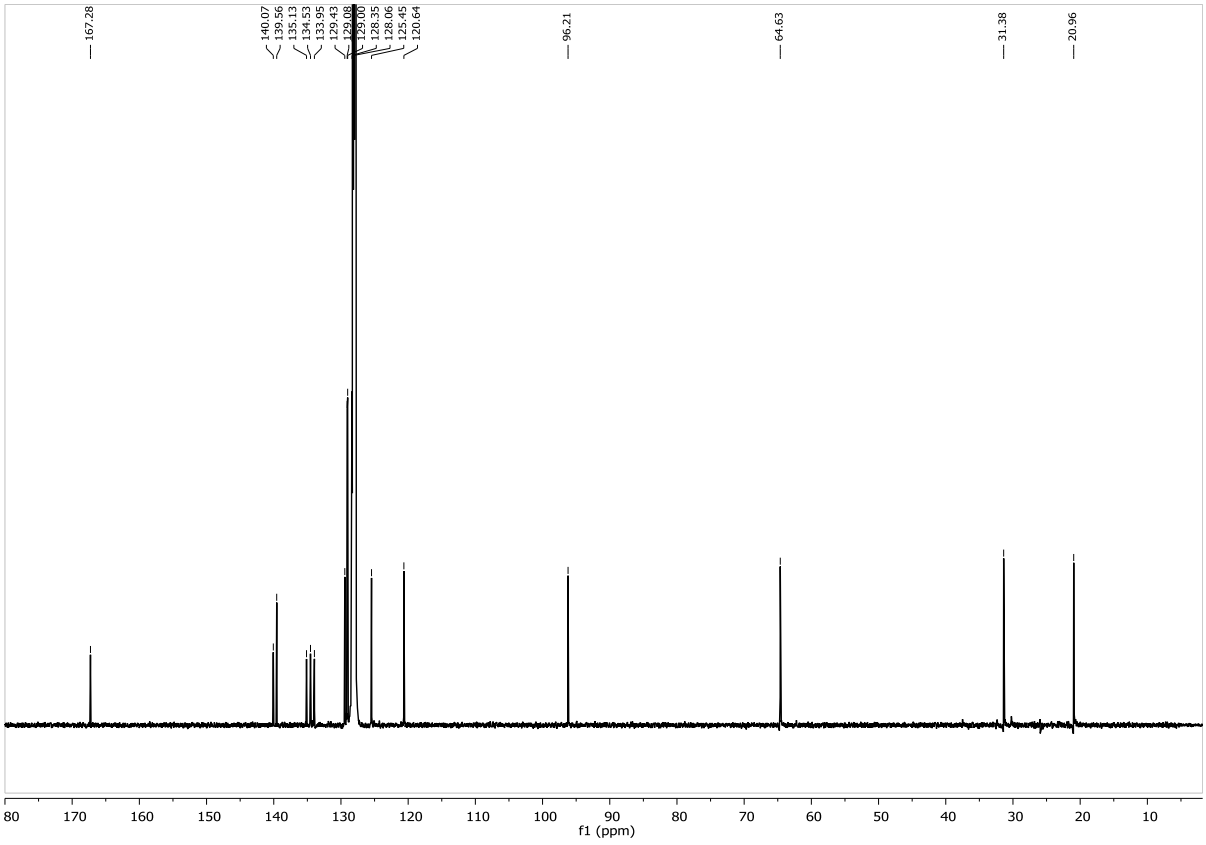
^{1}H NMR, 600 MHz, C_6D_6

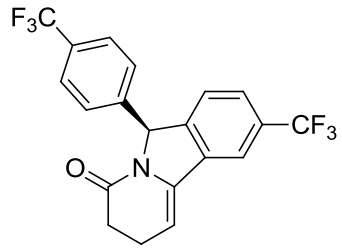




5e

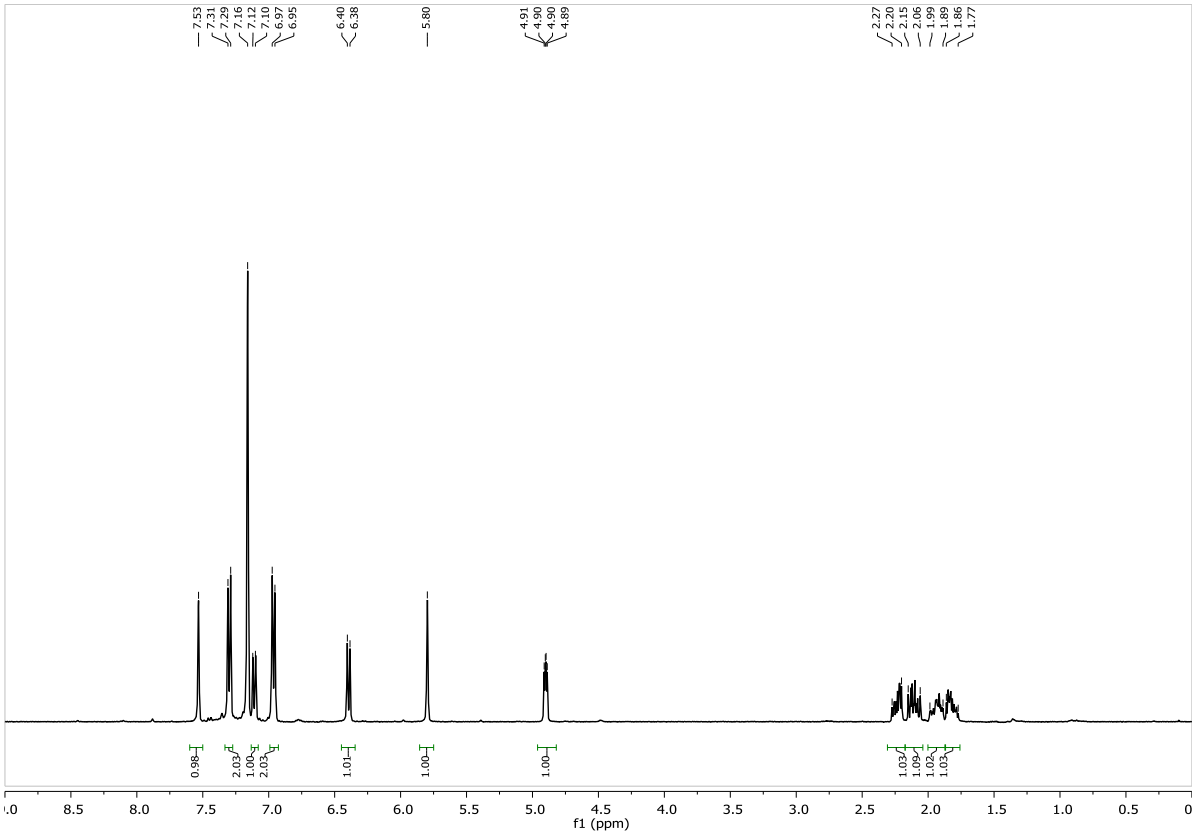
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

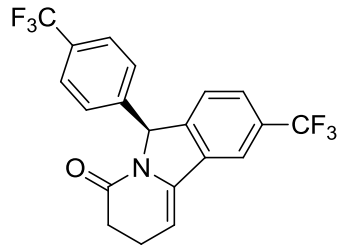




5f

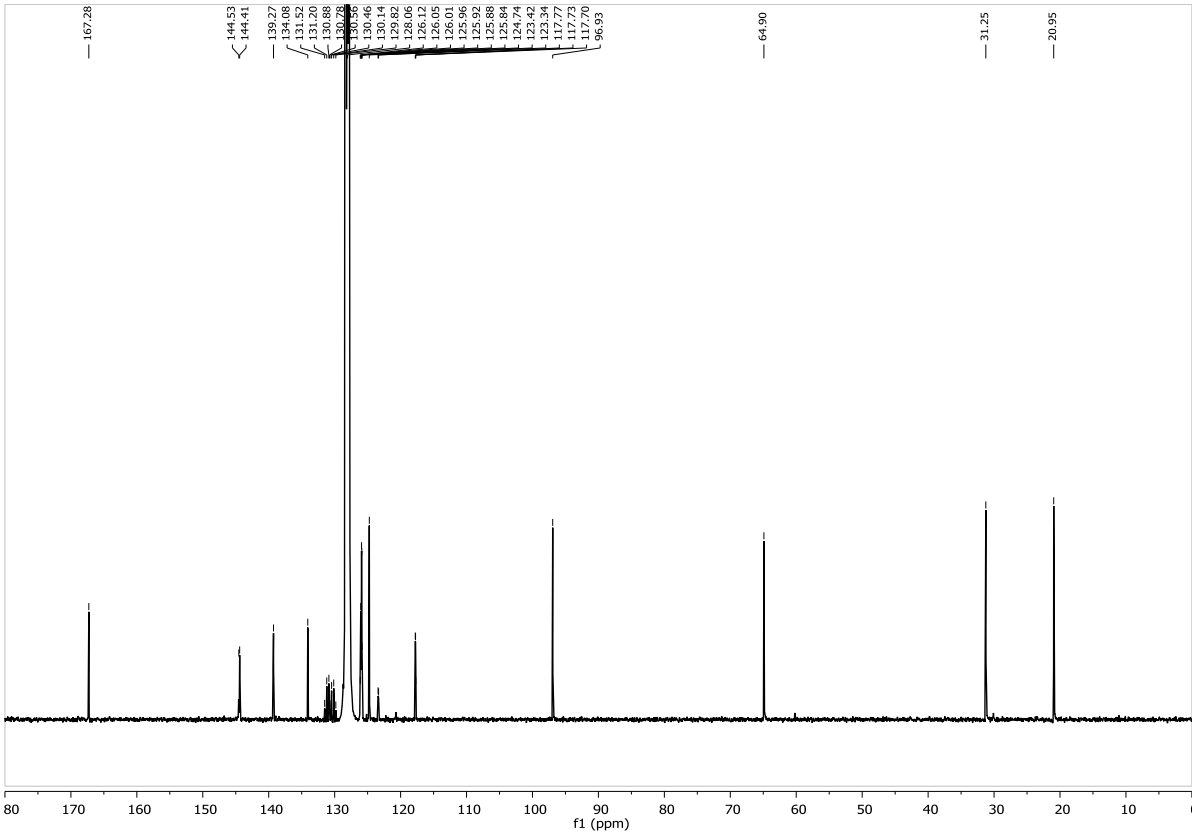
^{1}H NMR, 400 MHz, C_6D_6

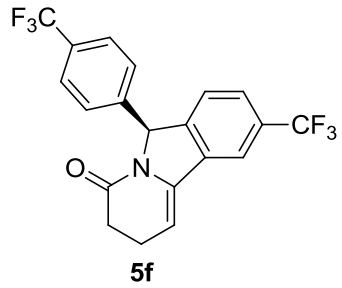




5f

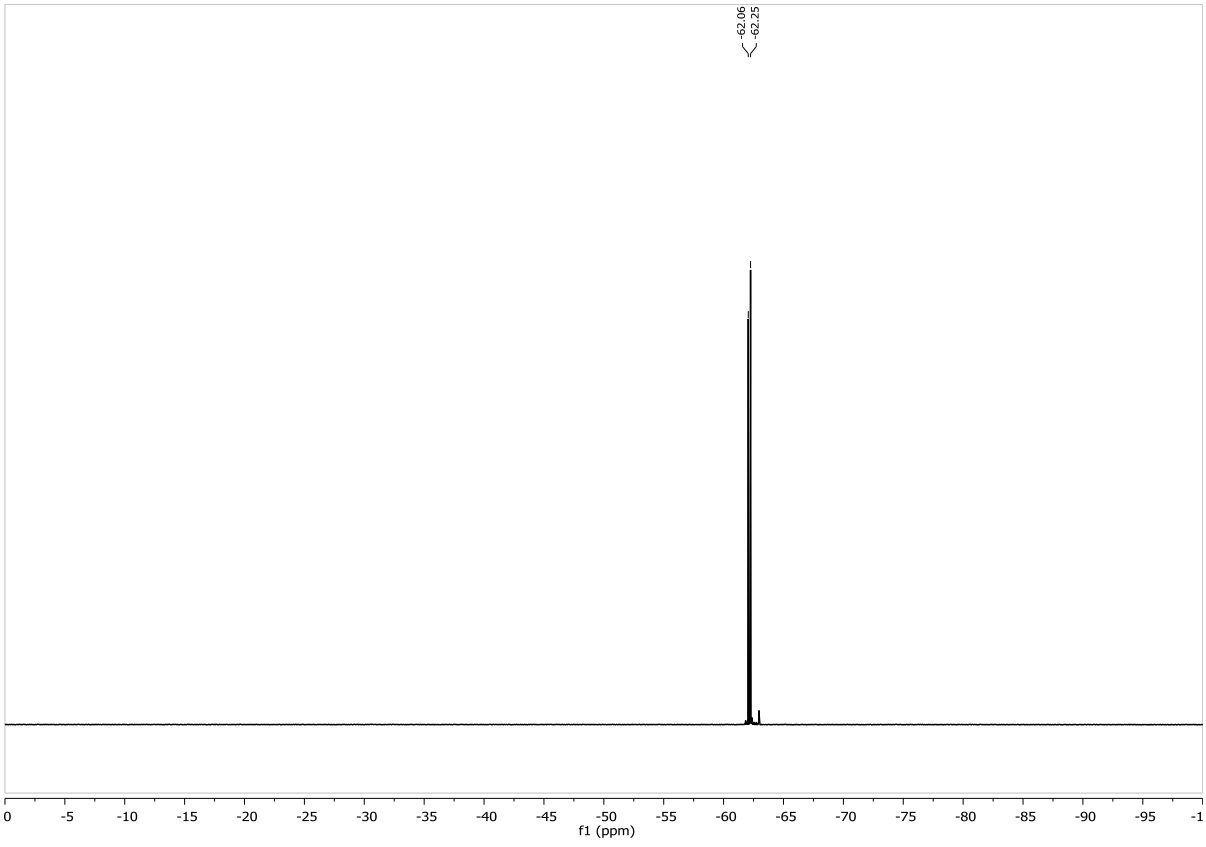
$^{13}C\{^{1}H\}$ NMR, 101 MHz, C_6D_6

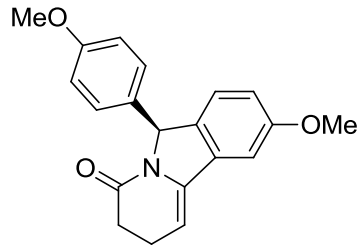




5f

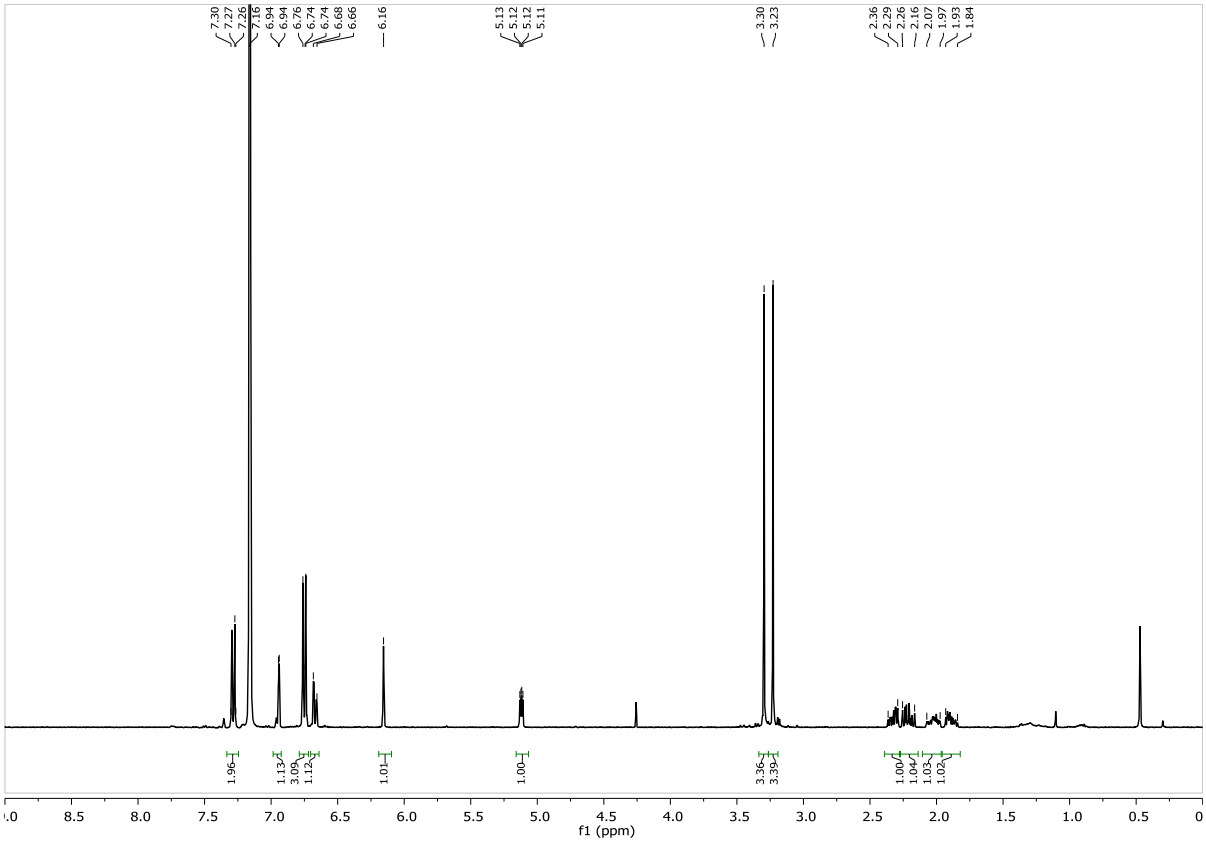
$^{19}F\{^{1}H\}$ NMR, 376 MHz, C_6D_6

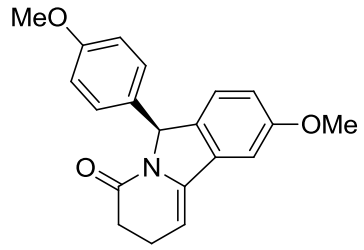




5g

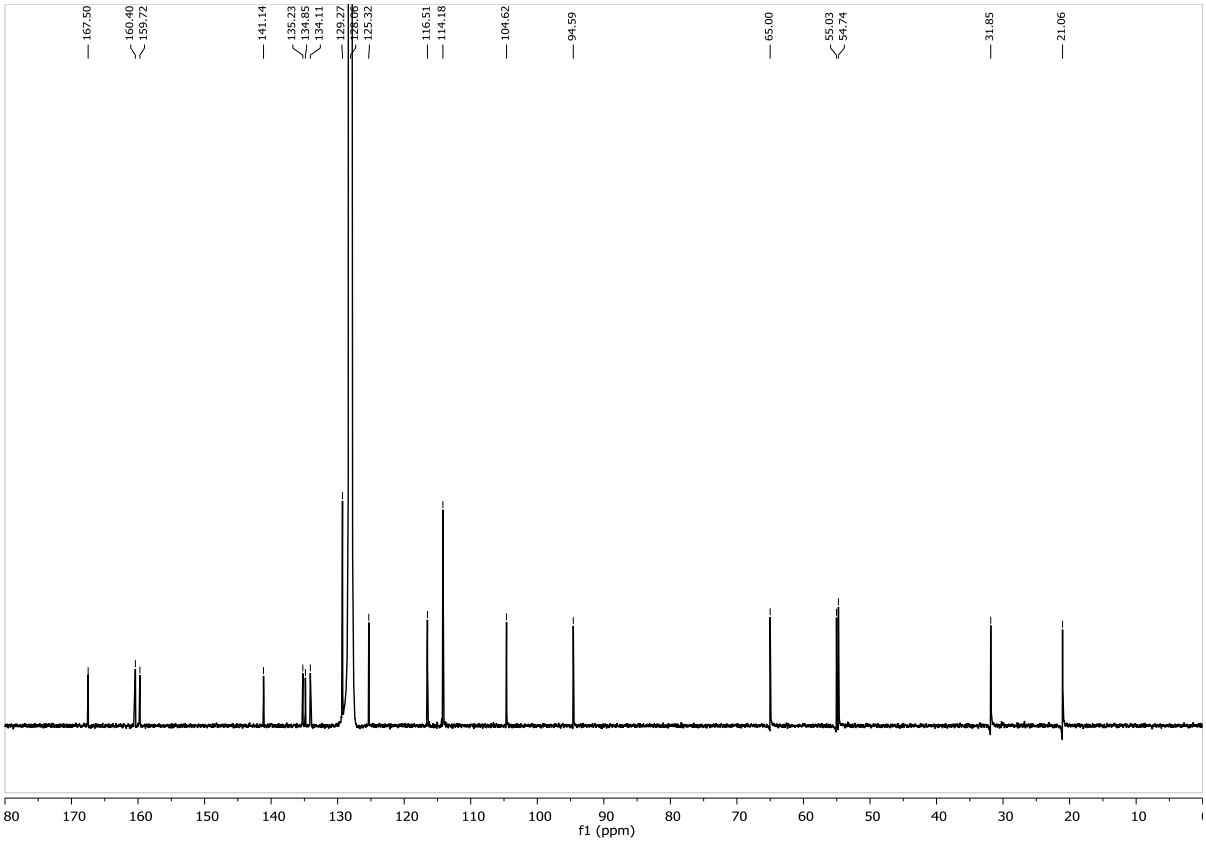
^{1}H NMR, 400 MHz, C_6D_6

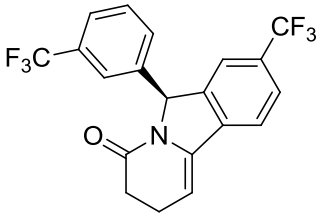




5g

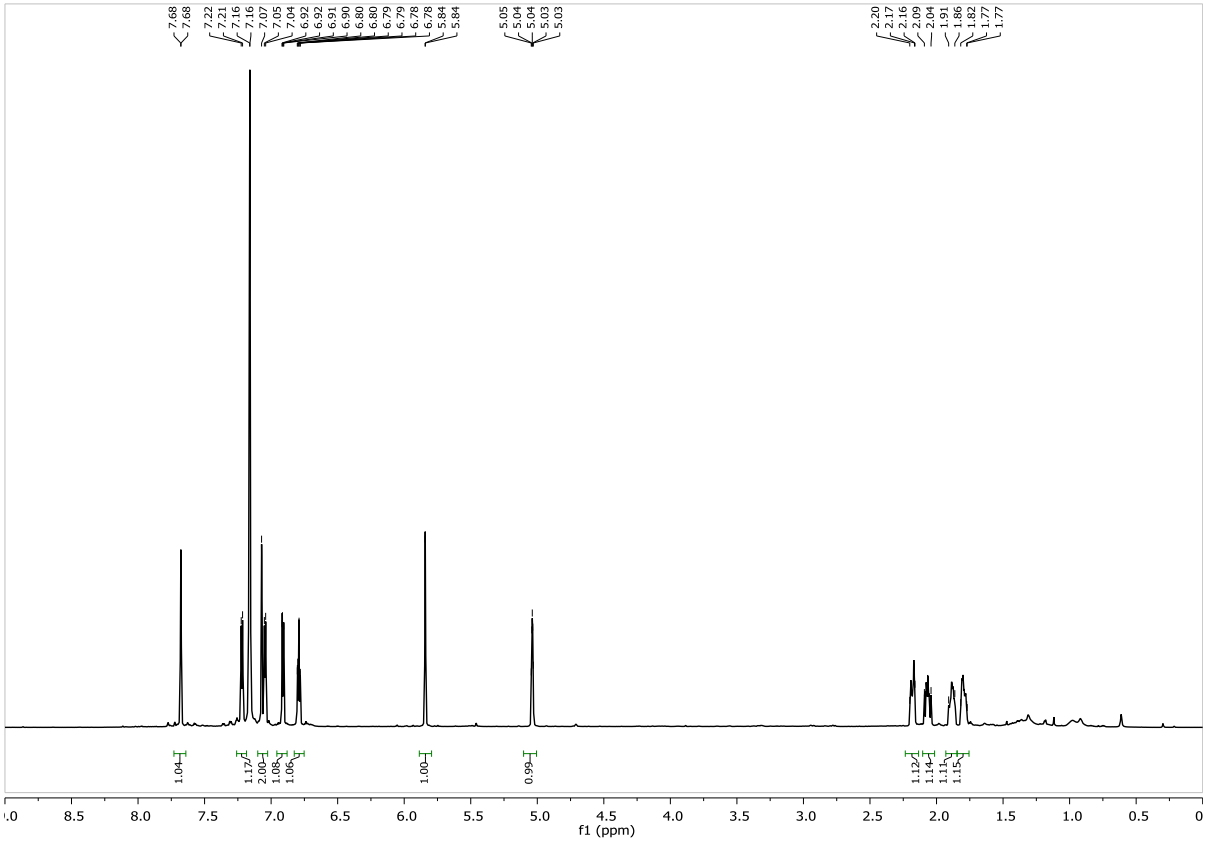
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

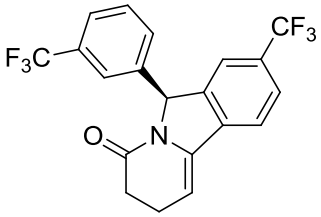




5h

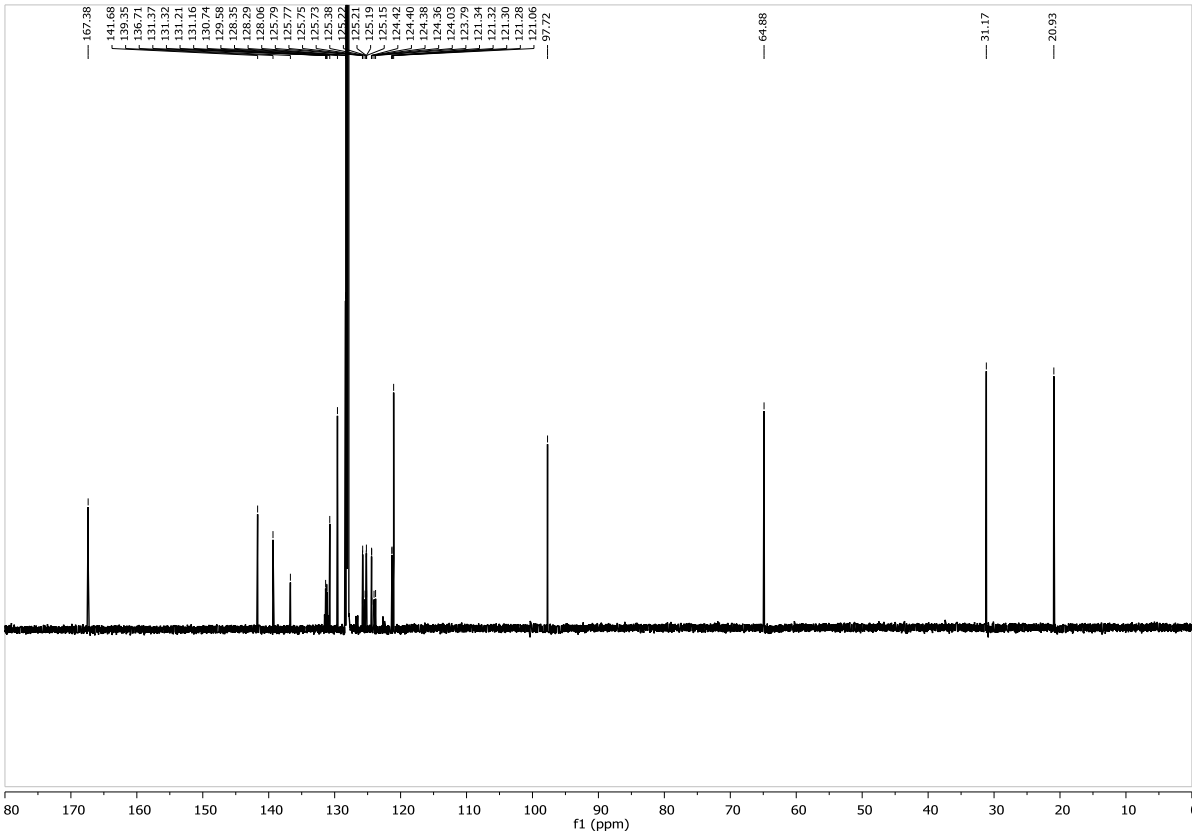
^{1}H NMR, 400 MHz, C_6D_6

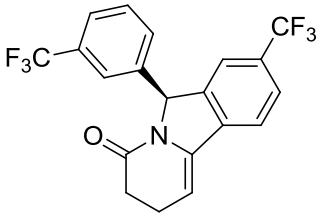




5h

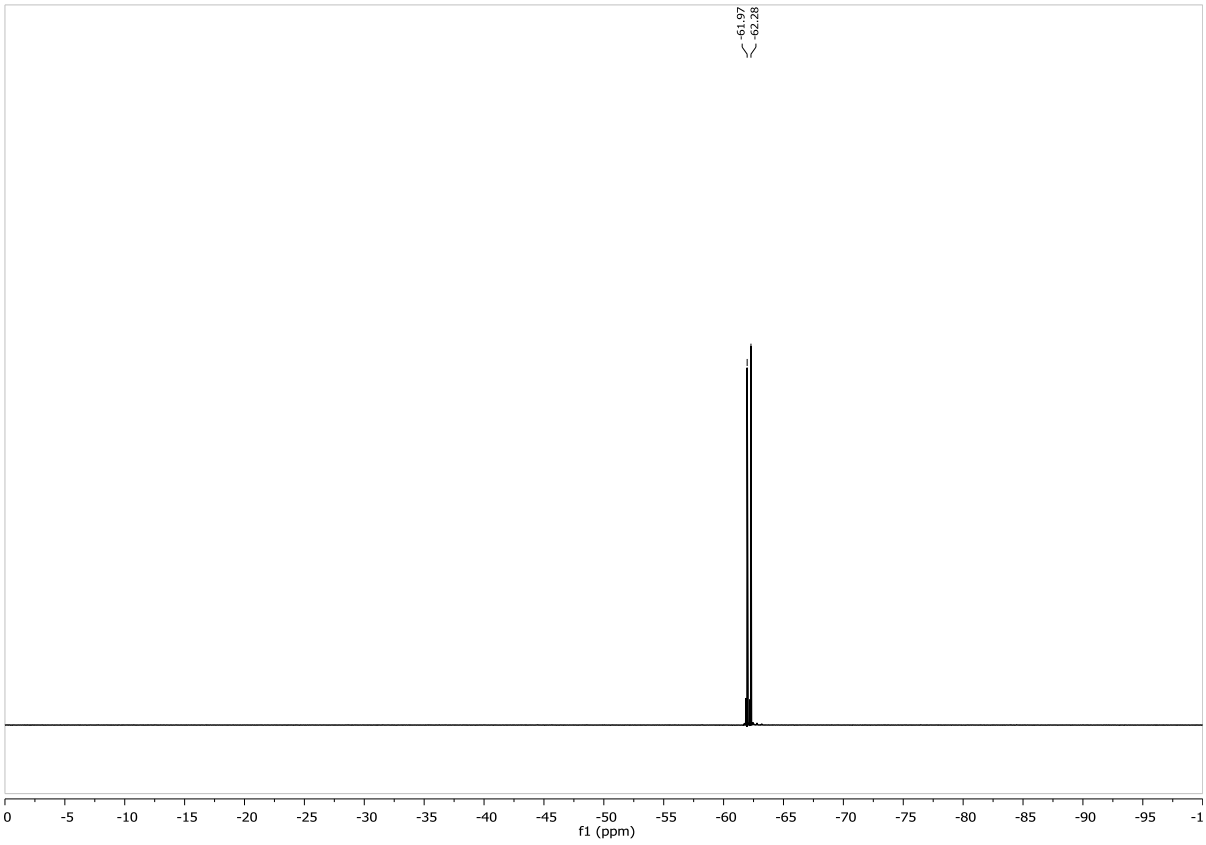
$^{13}C\{^{1}H\}$ NMR, 201 MHz, C_6D_6

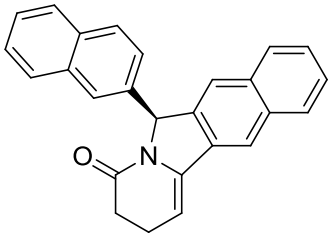




5h

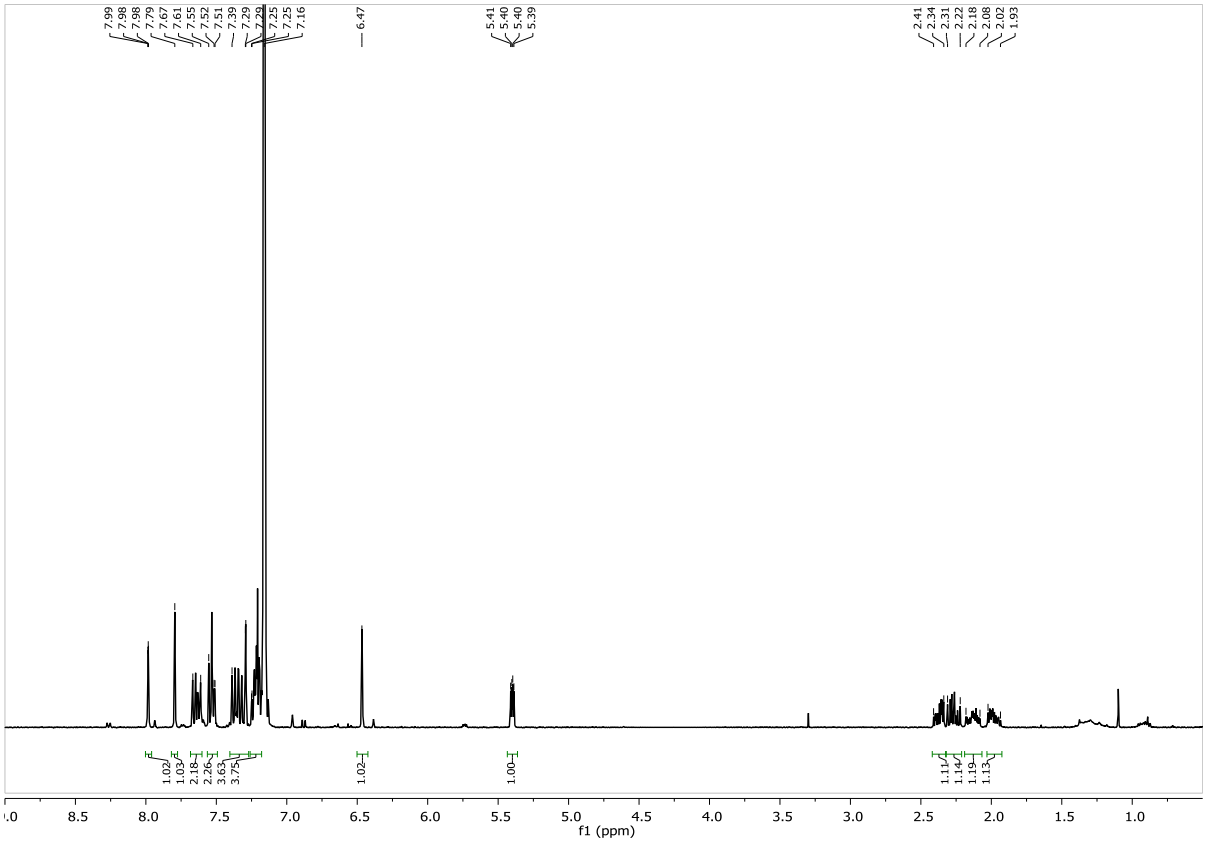
$^{19}F\{^{1}H\}$ NMR, 376 MHz, C_6D_6

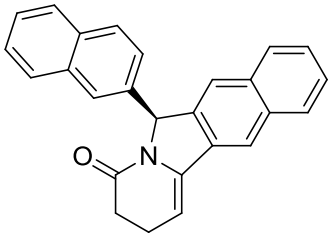




5i

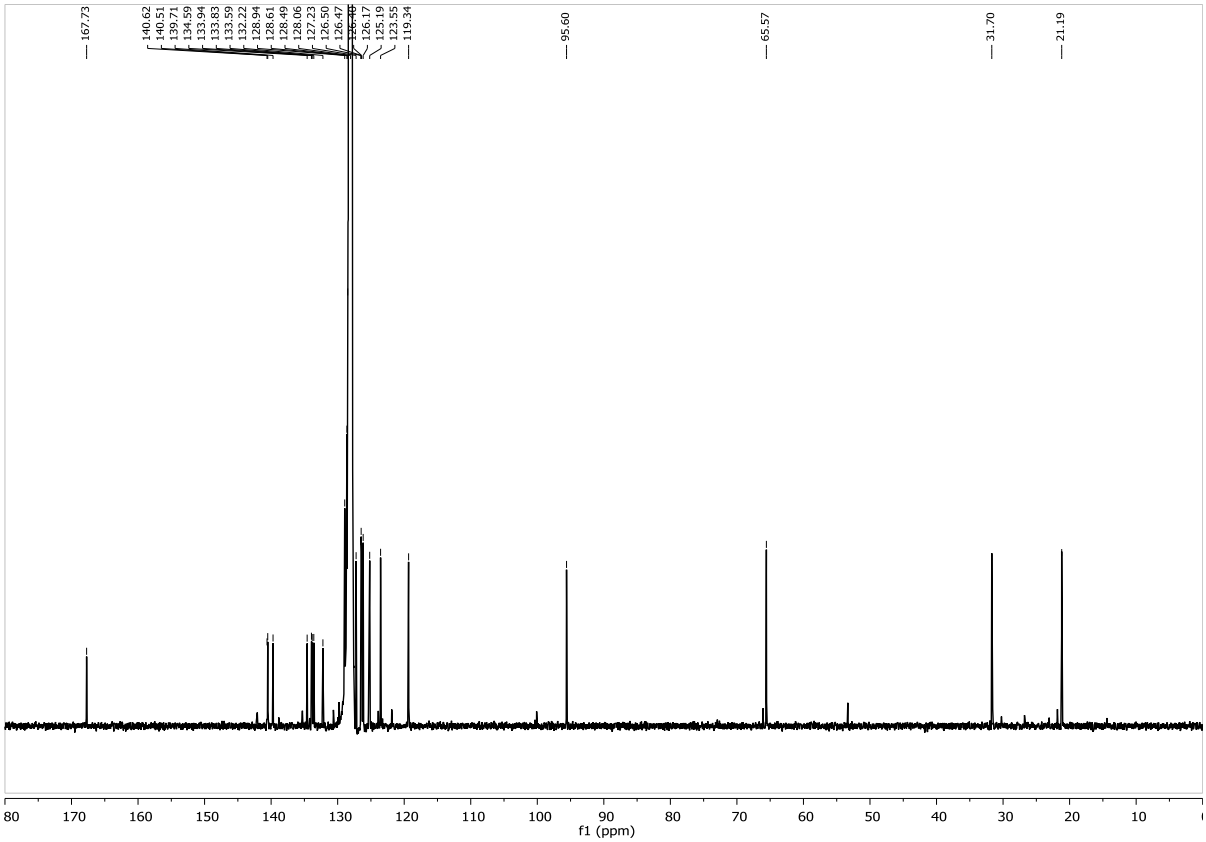
^{1}H NMR, 400 MHz, C_6D_6

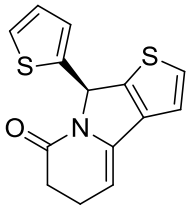




5i

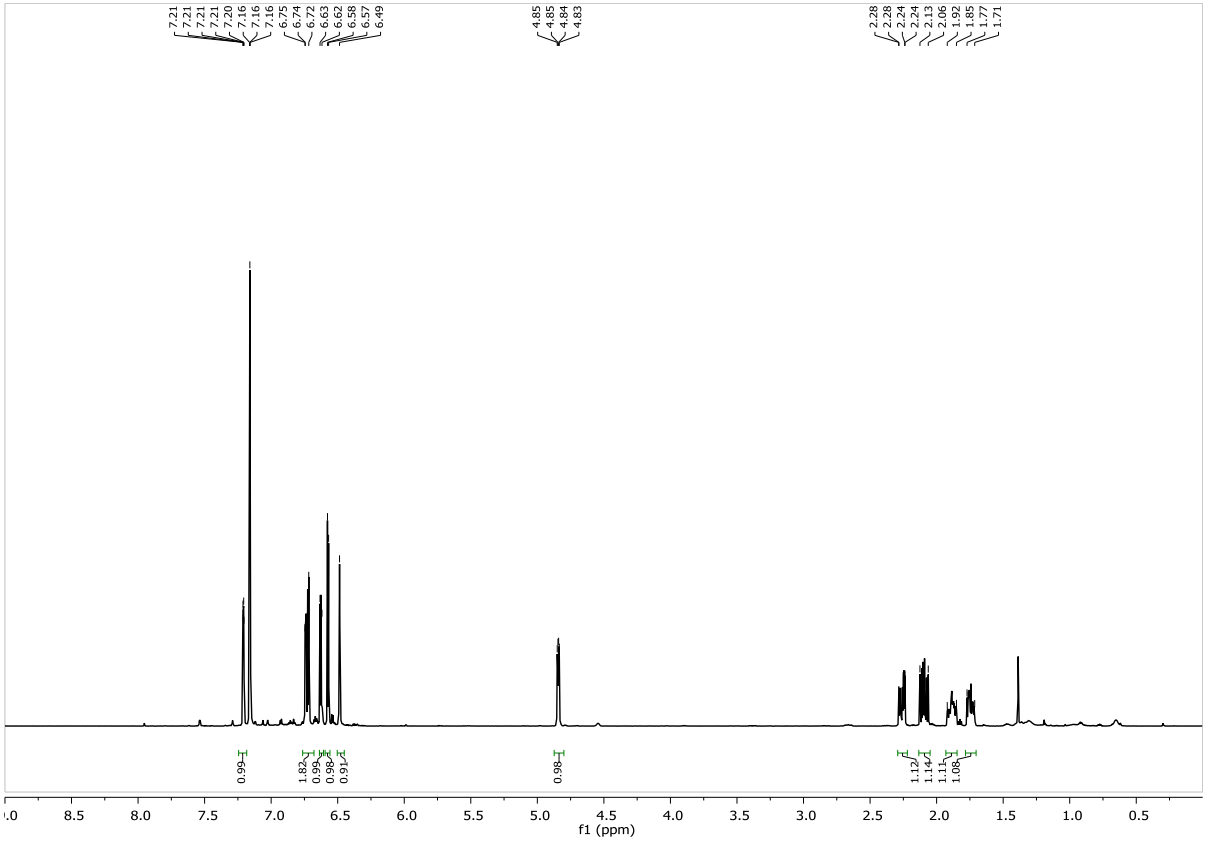
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

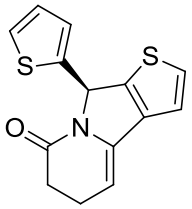




5j

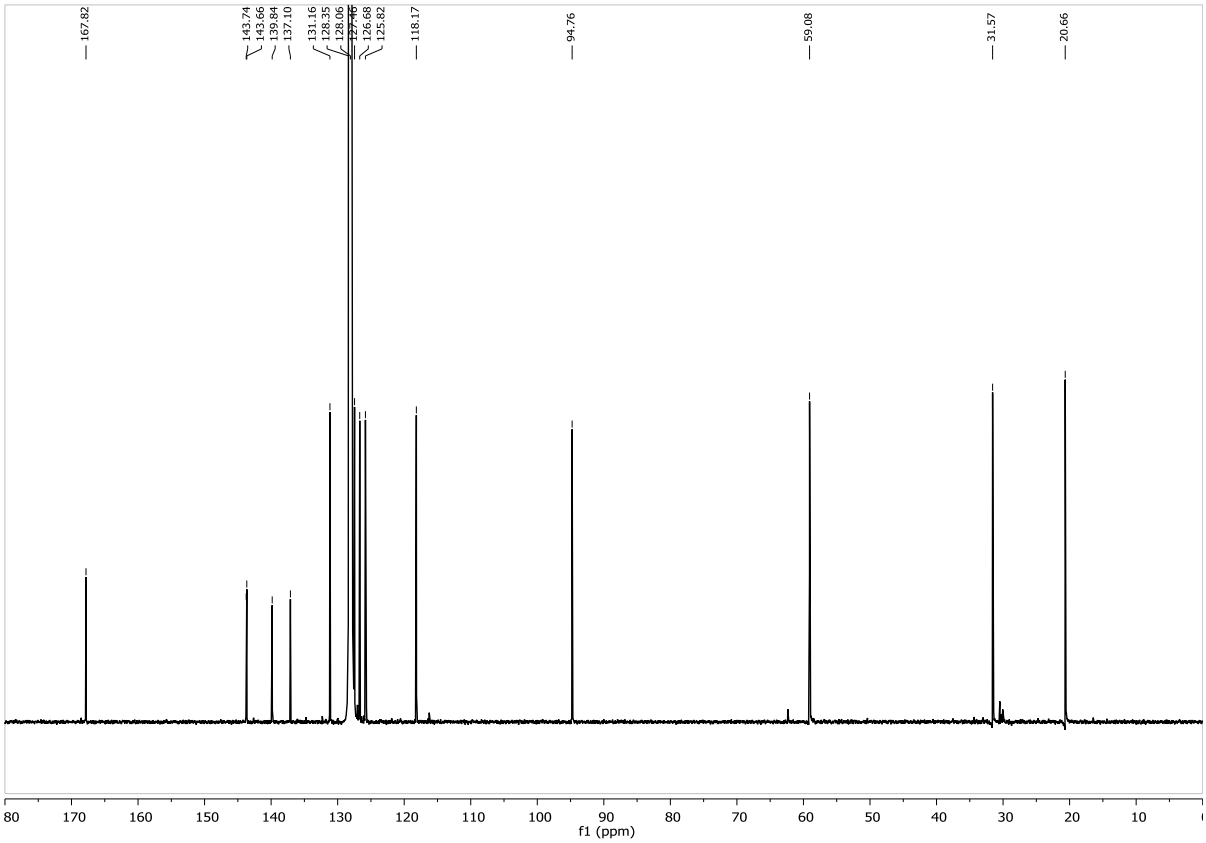
^{1}H NMR, 400 MHz, C_6D_6

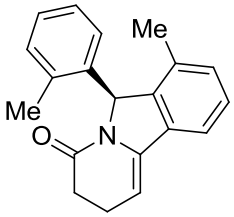




5j

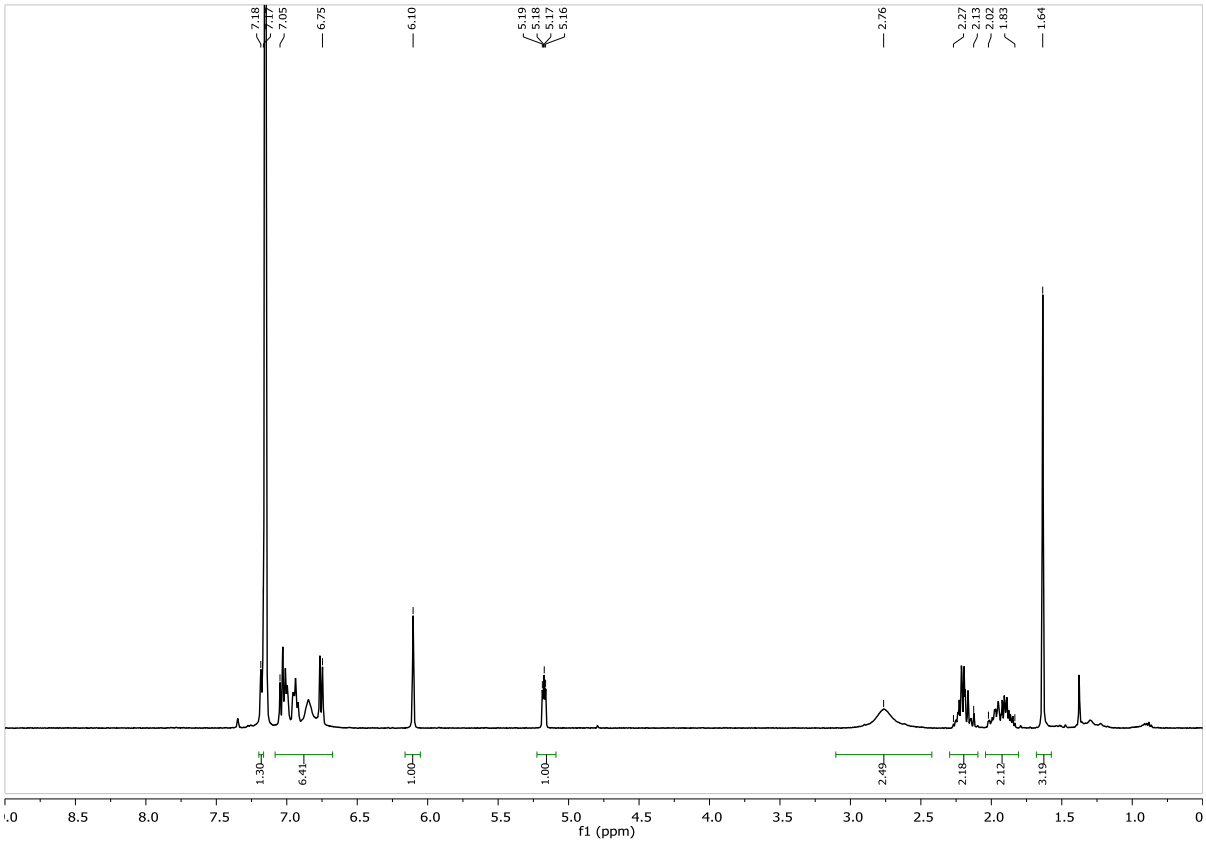
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

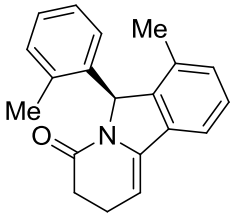




5k

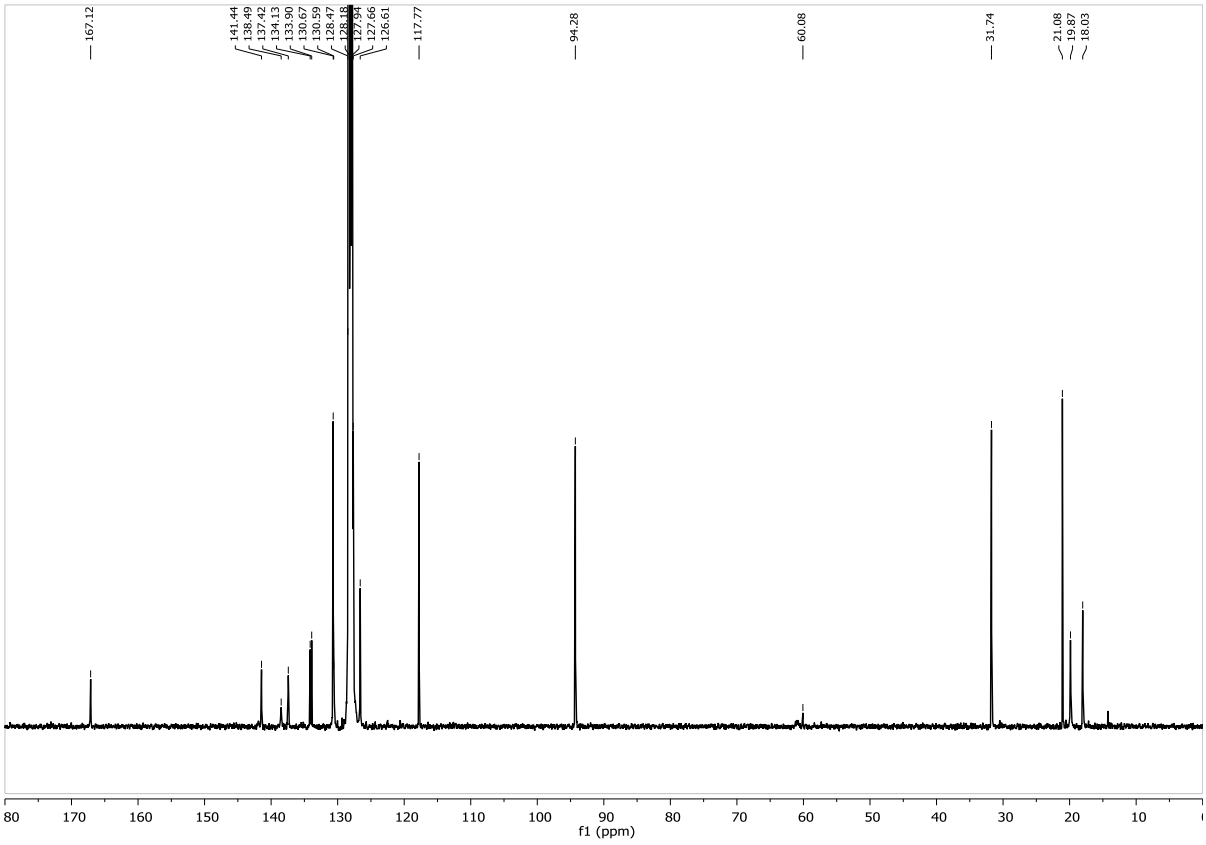
^{1}H NMR, 400 MHz, C_6D_6

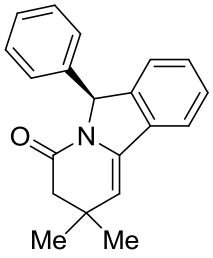




5k

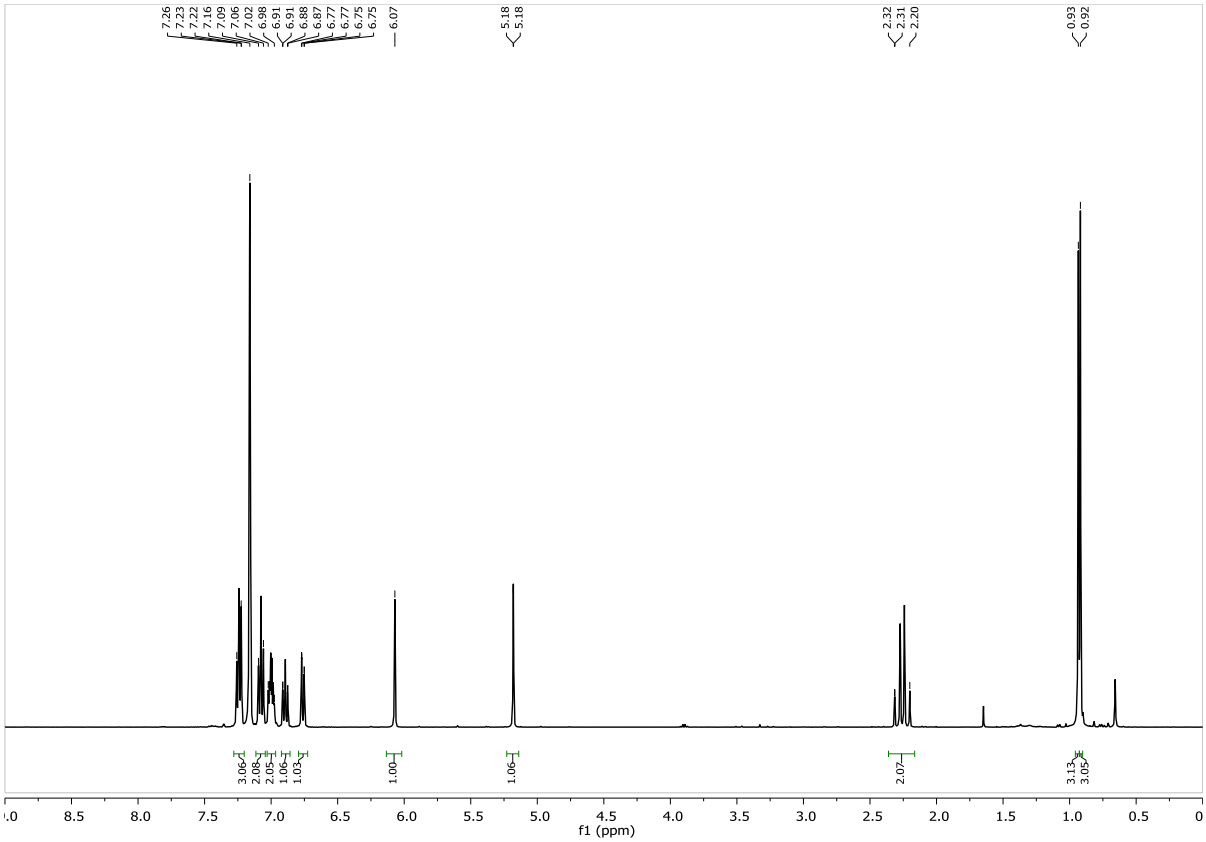
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

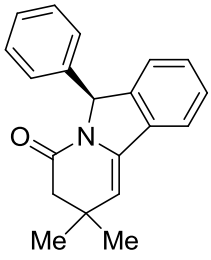




5l

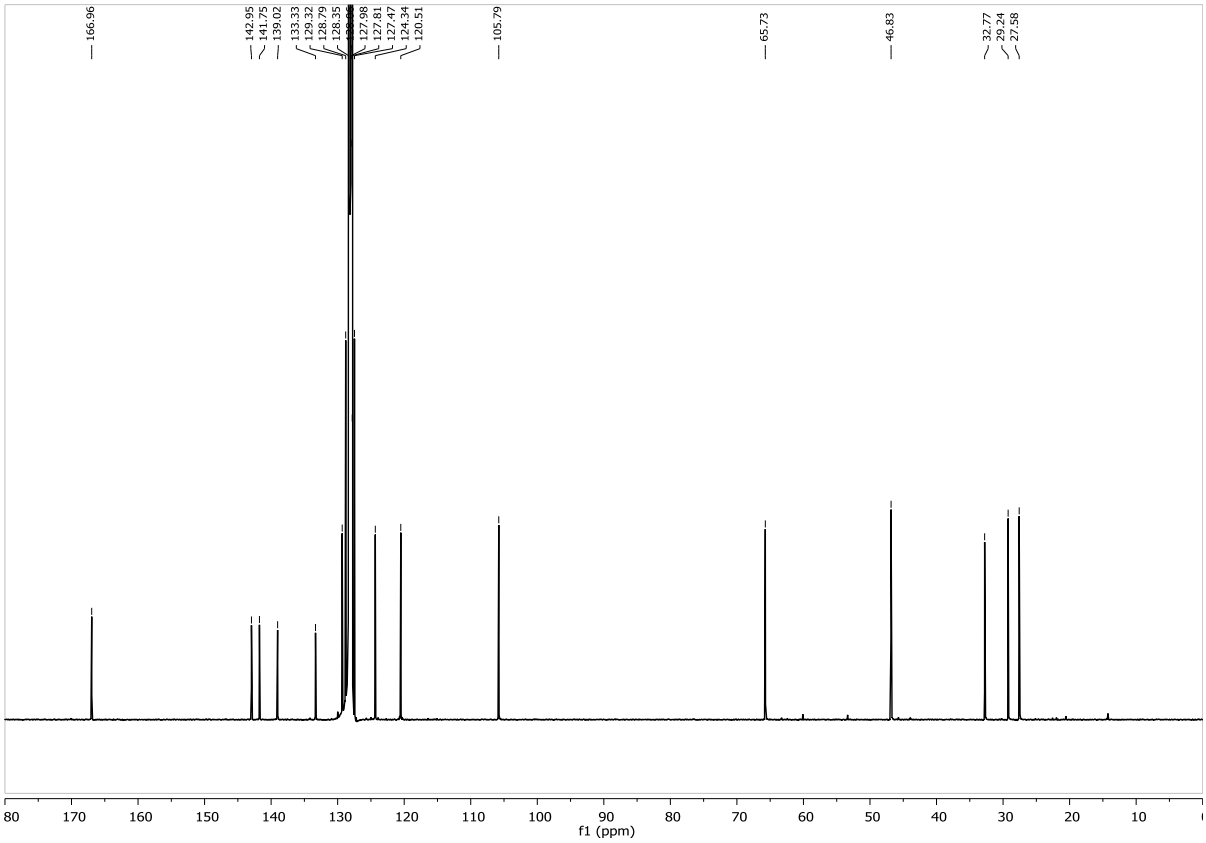
^{1}H NMR, 400 MHz, C_6D_6

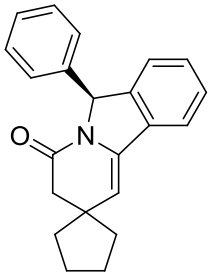




5l

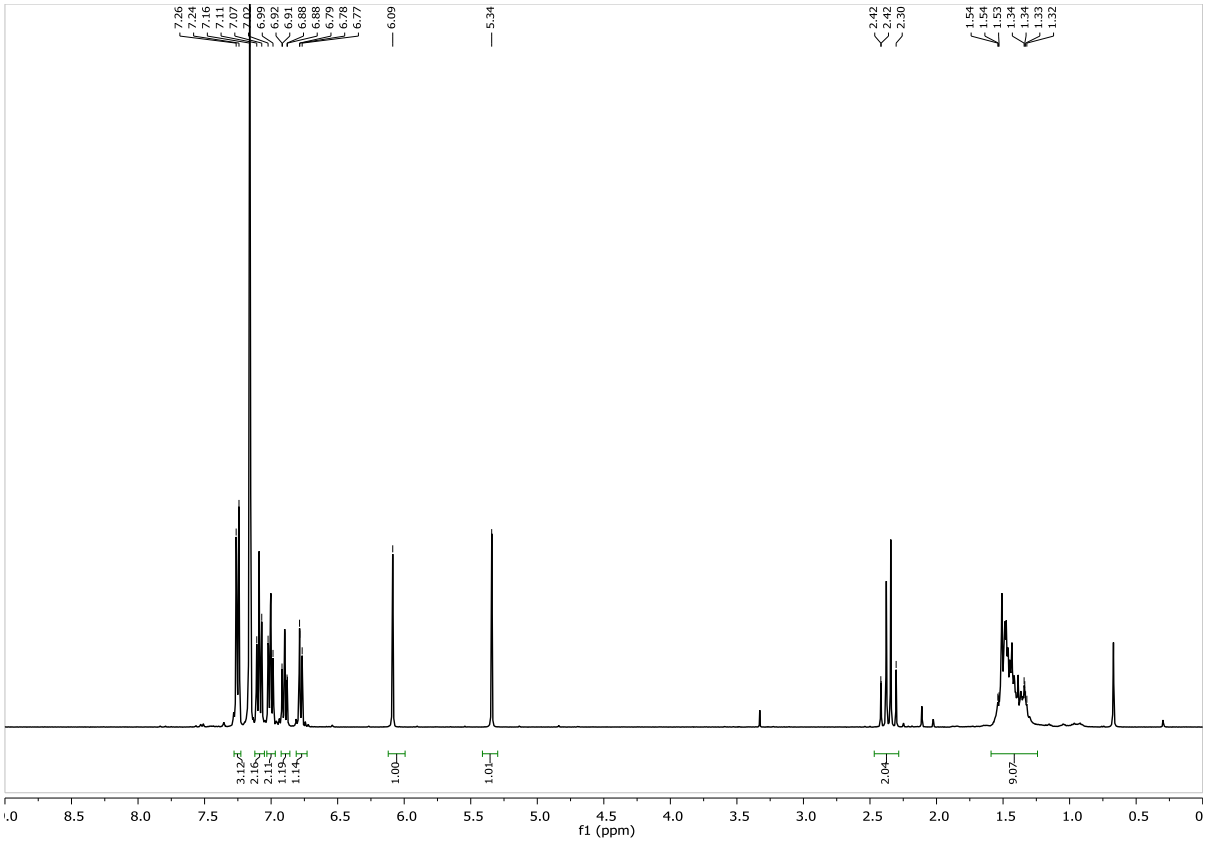
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

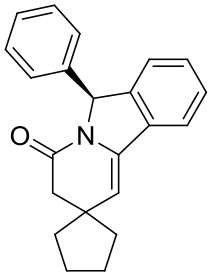




5m

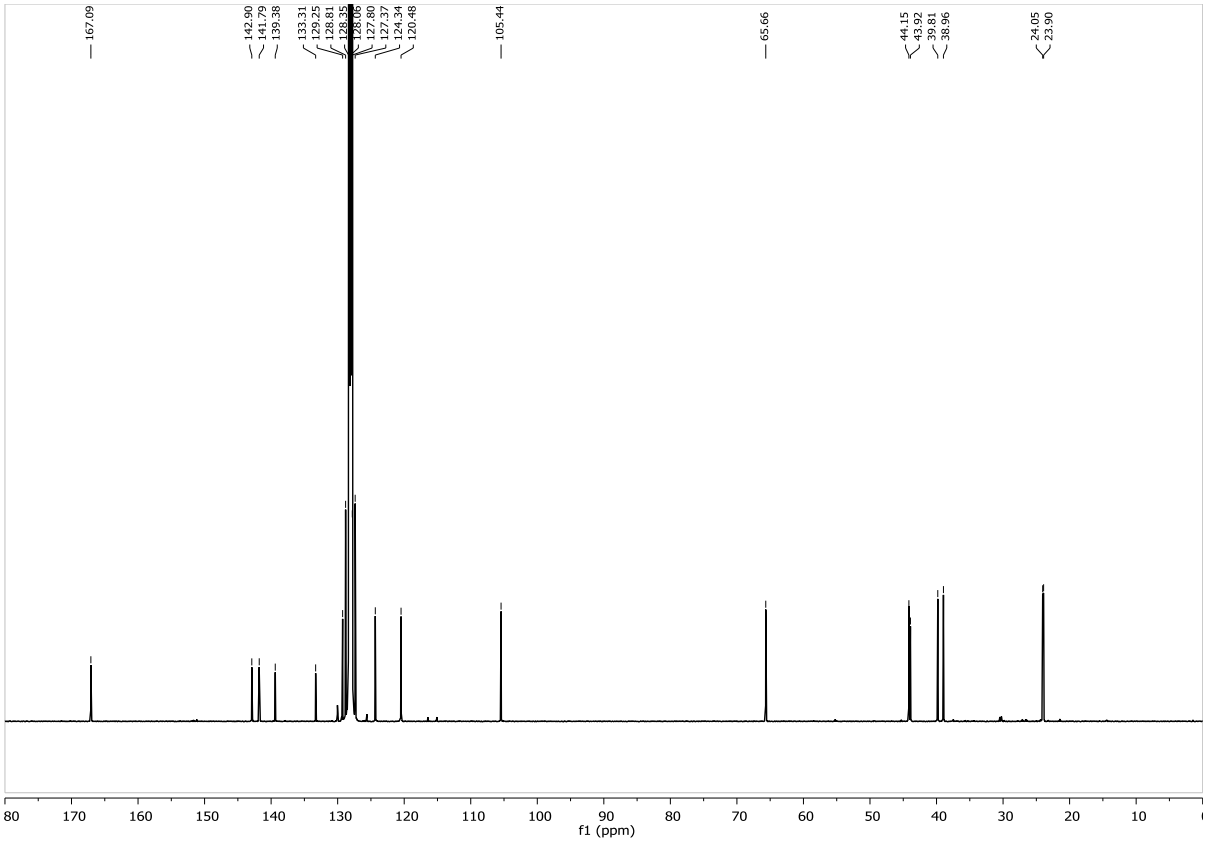
^{1}H NMR, 400 MHz, C_6D_6

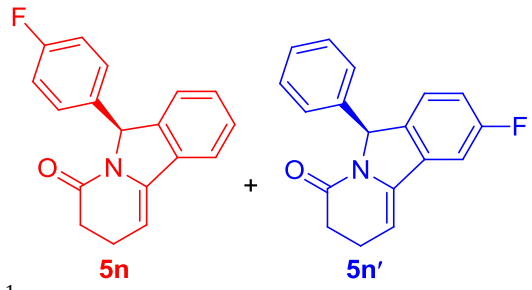




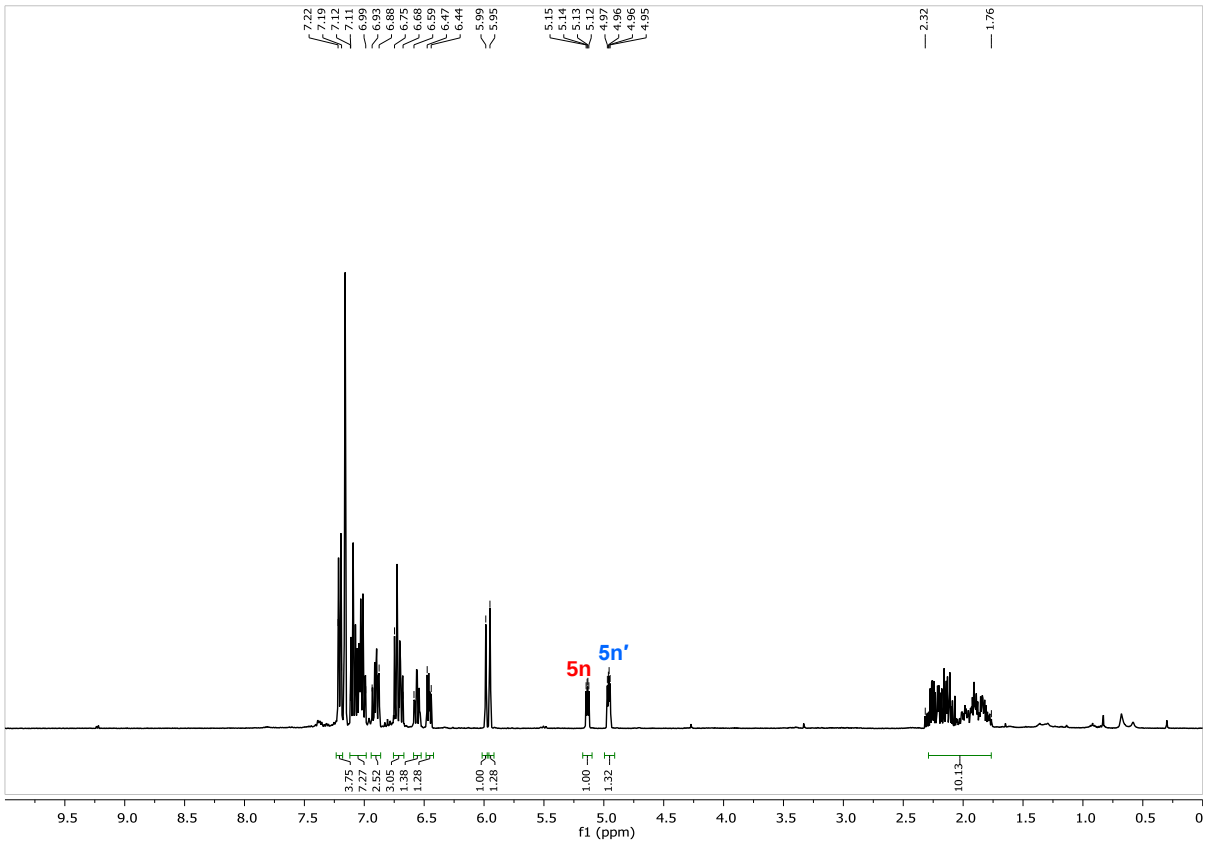
5m

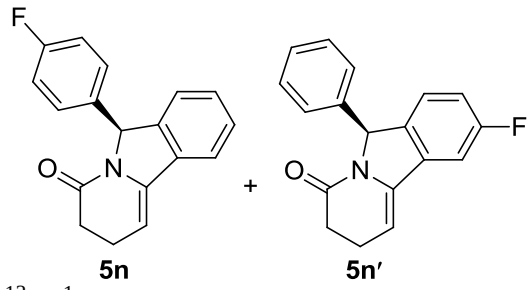
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6





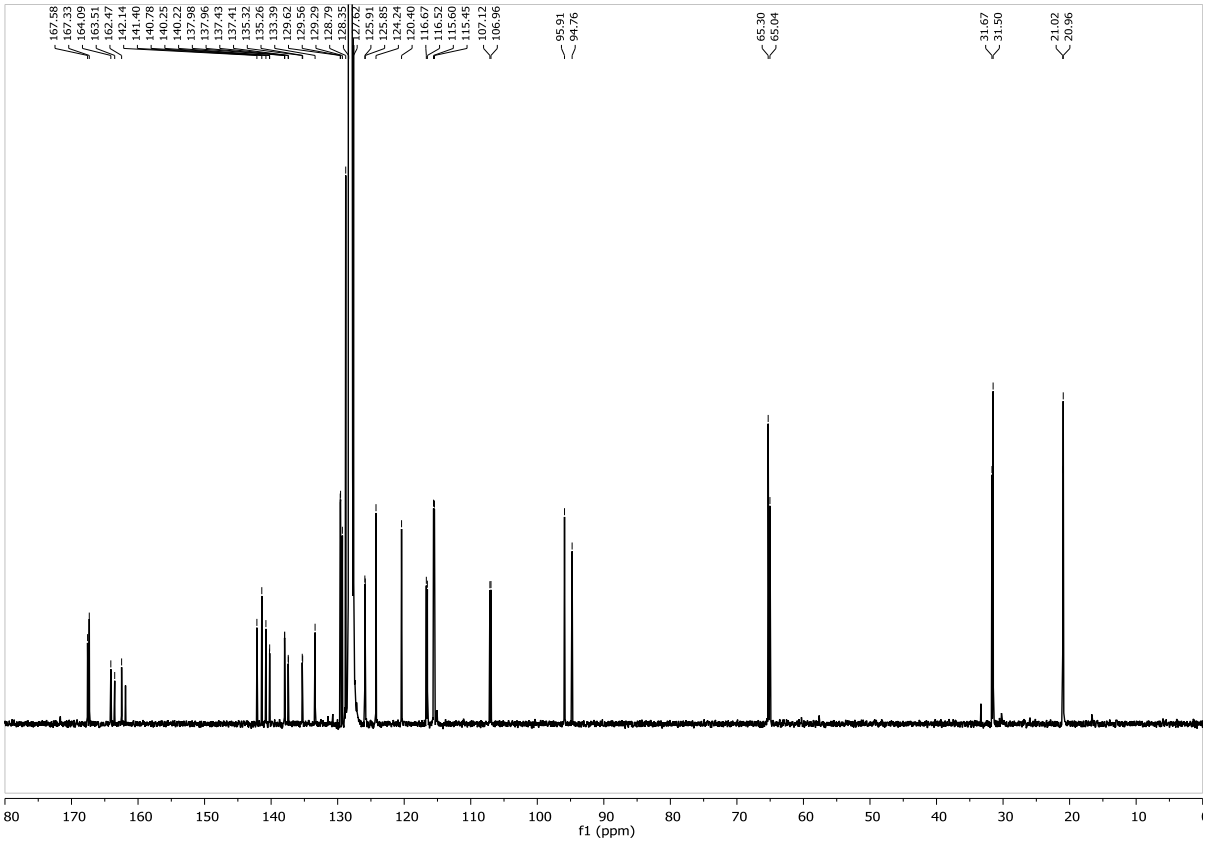
^{1}H NMR, 400 MHz, C_6D_6

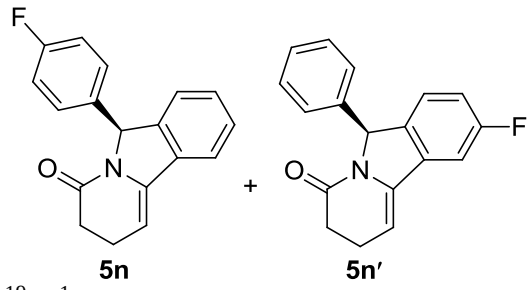




5n **5n′**

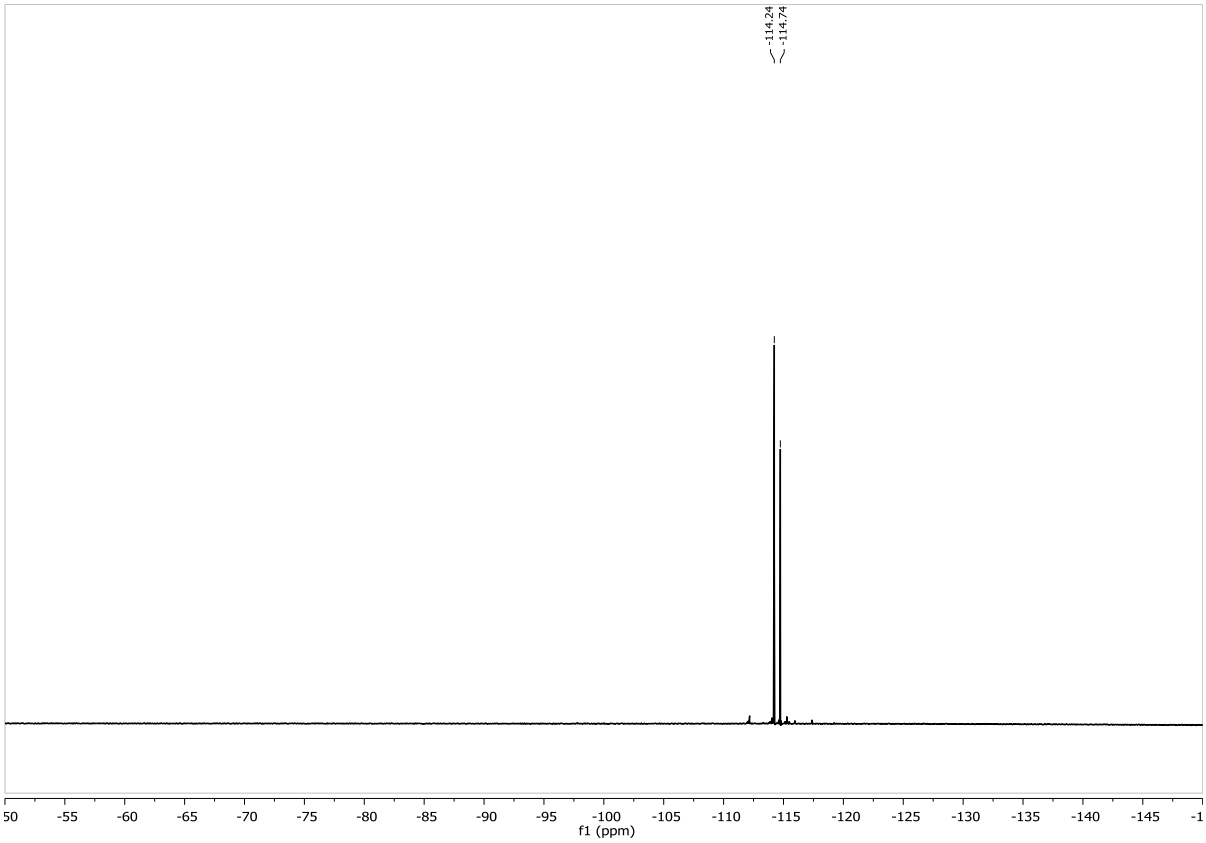
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

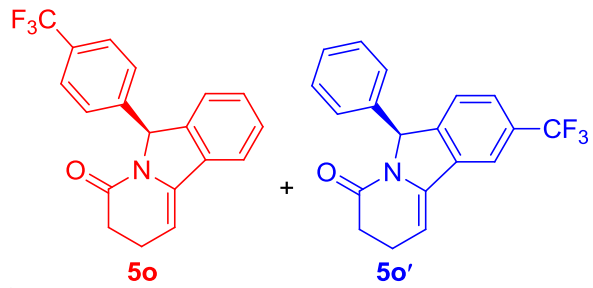




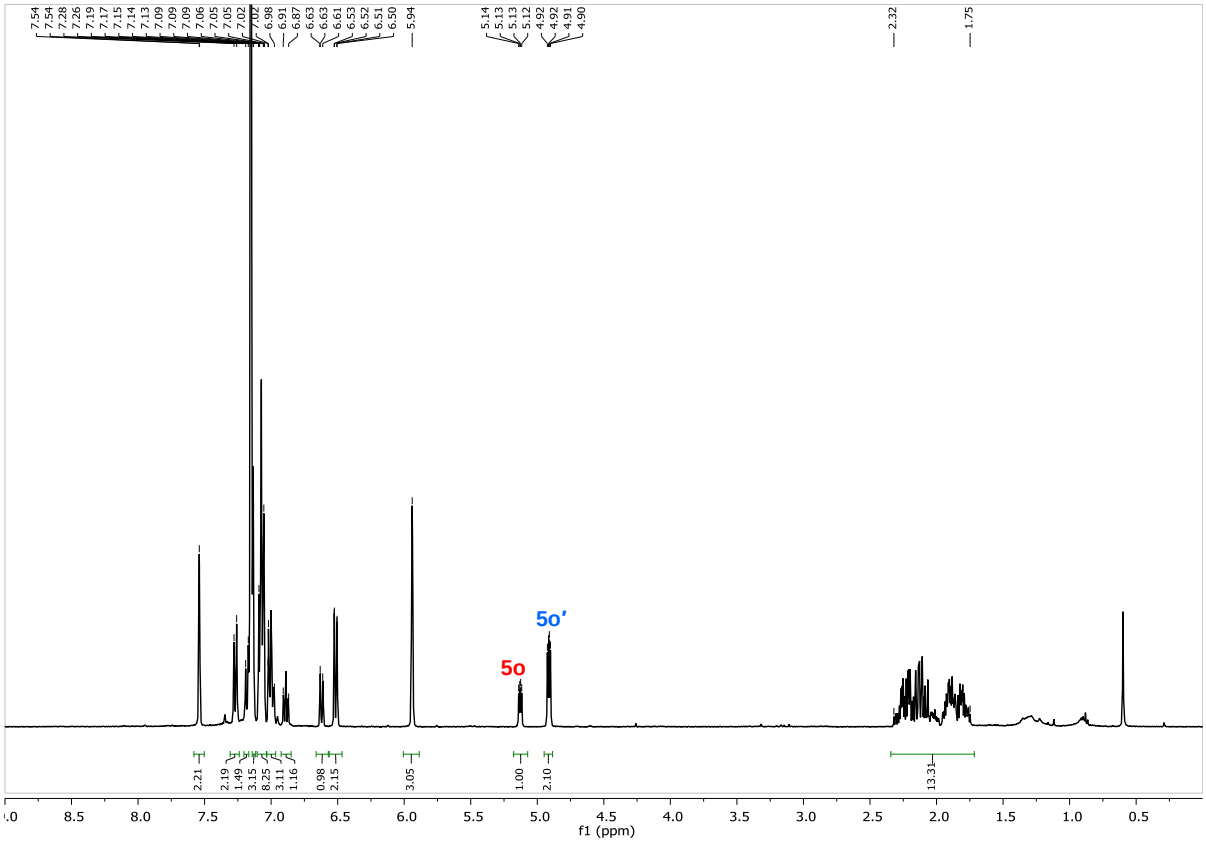
5n **5n′**

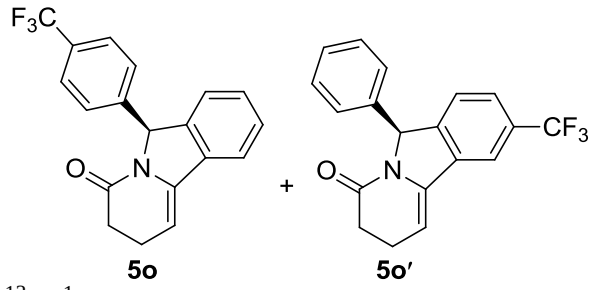
$^{19}F\{^{1}H\}$ NMR, 376 MHz, C_6D_6





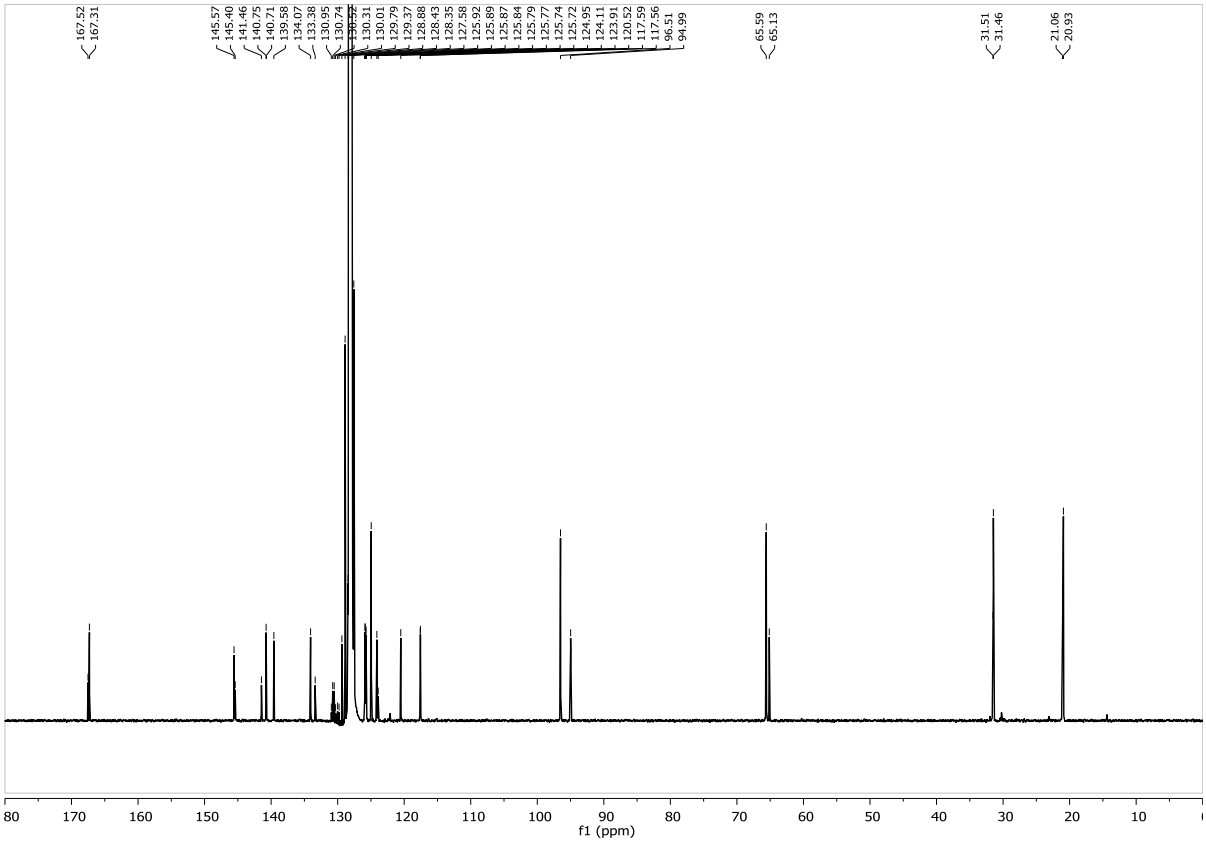
^{1}H NMR, 400 MHz, C_6D_6

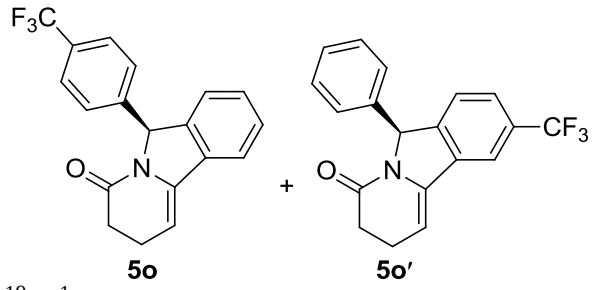




5o **5o′**

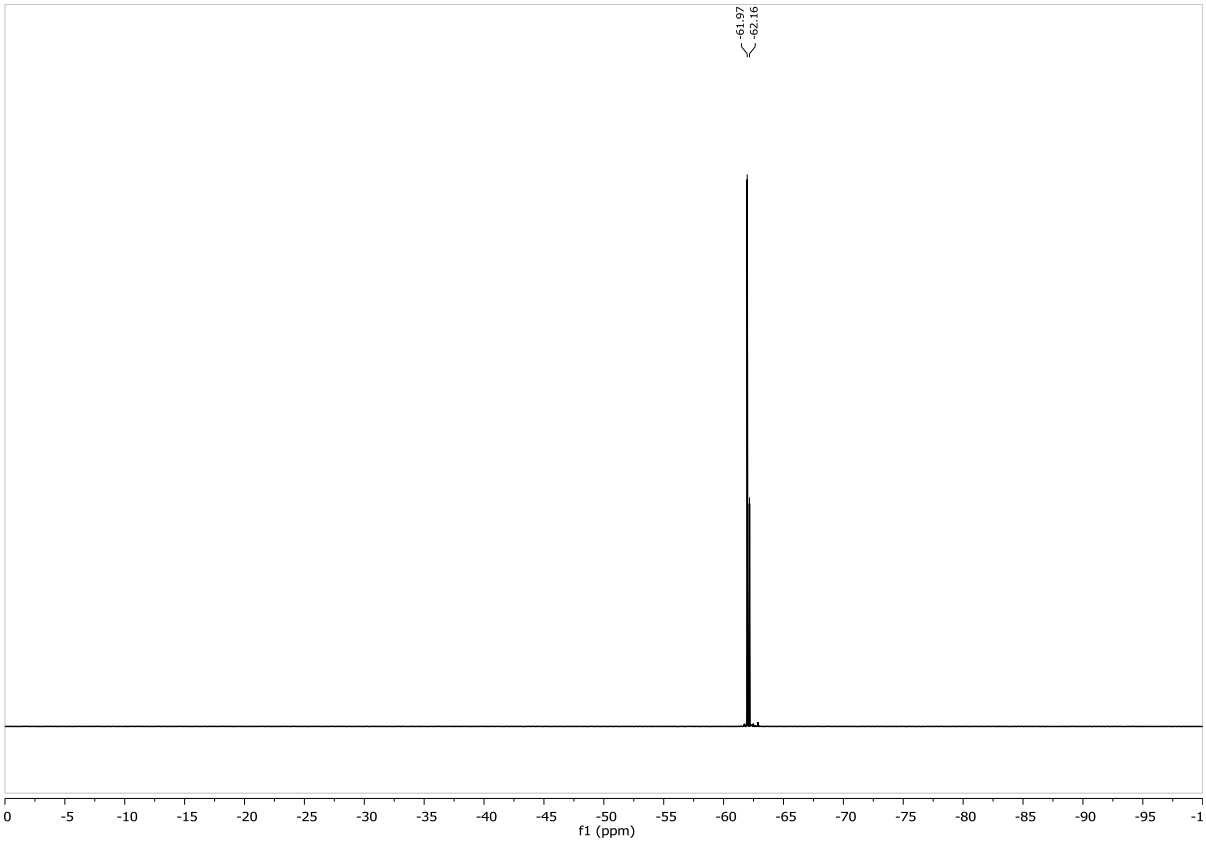
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

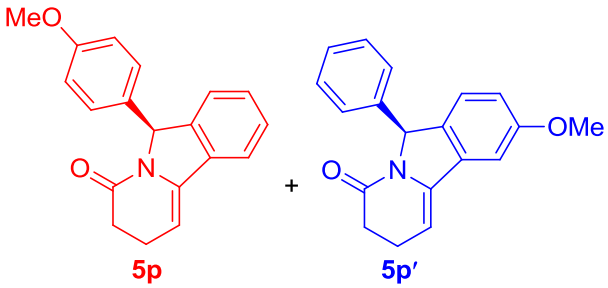




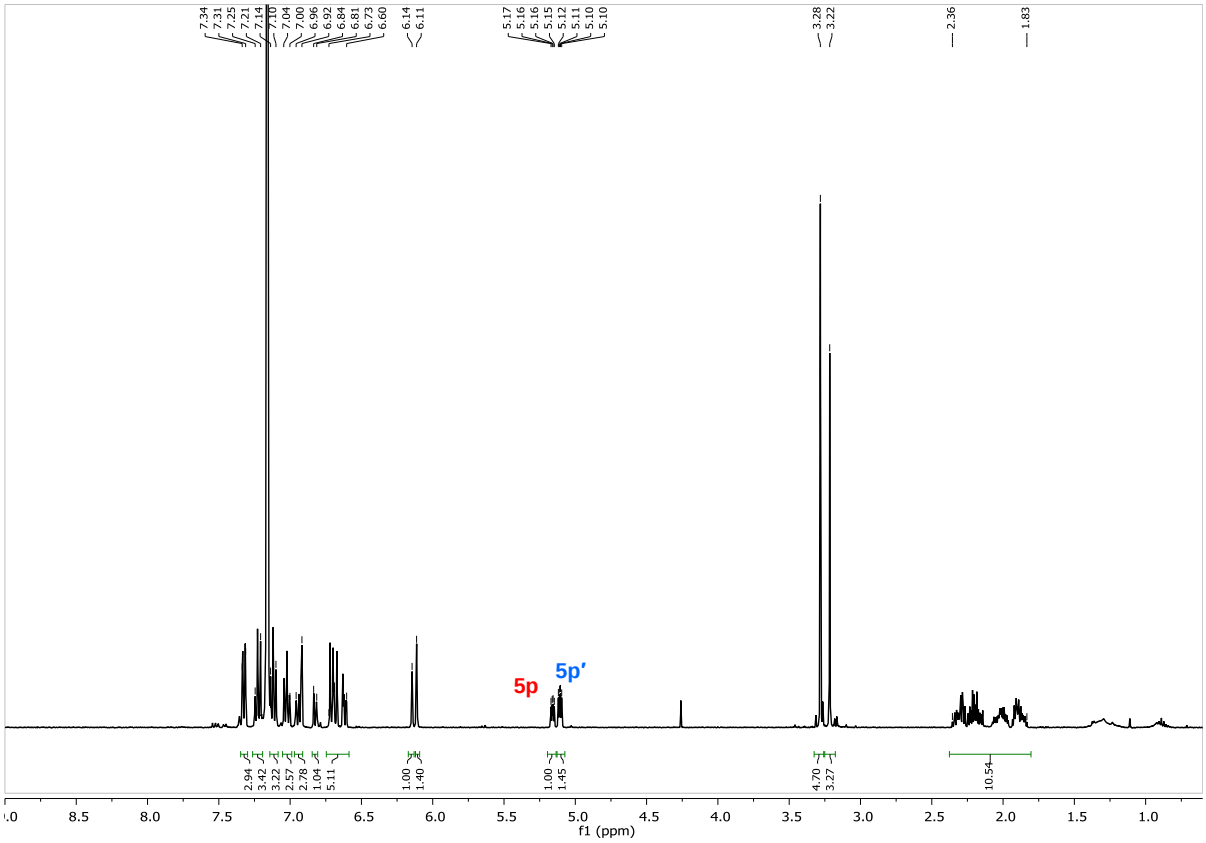
5o **5o′**

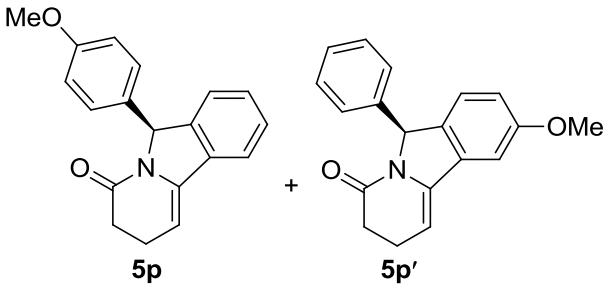
$^{19}F\{^{1}H\}$ NMR, 376 MHz, C_6D_6





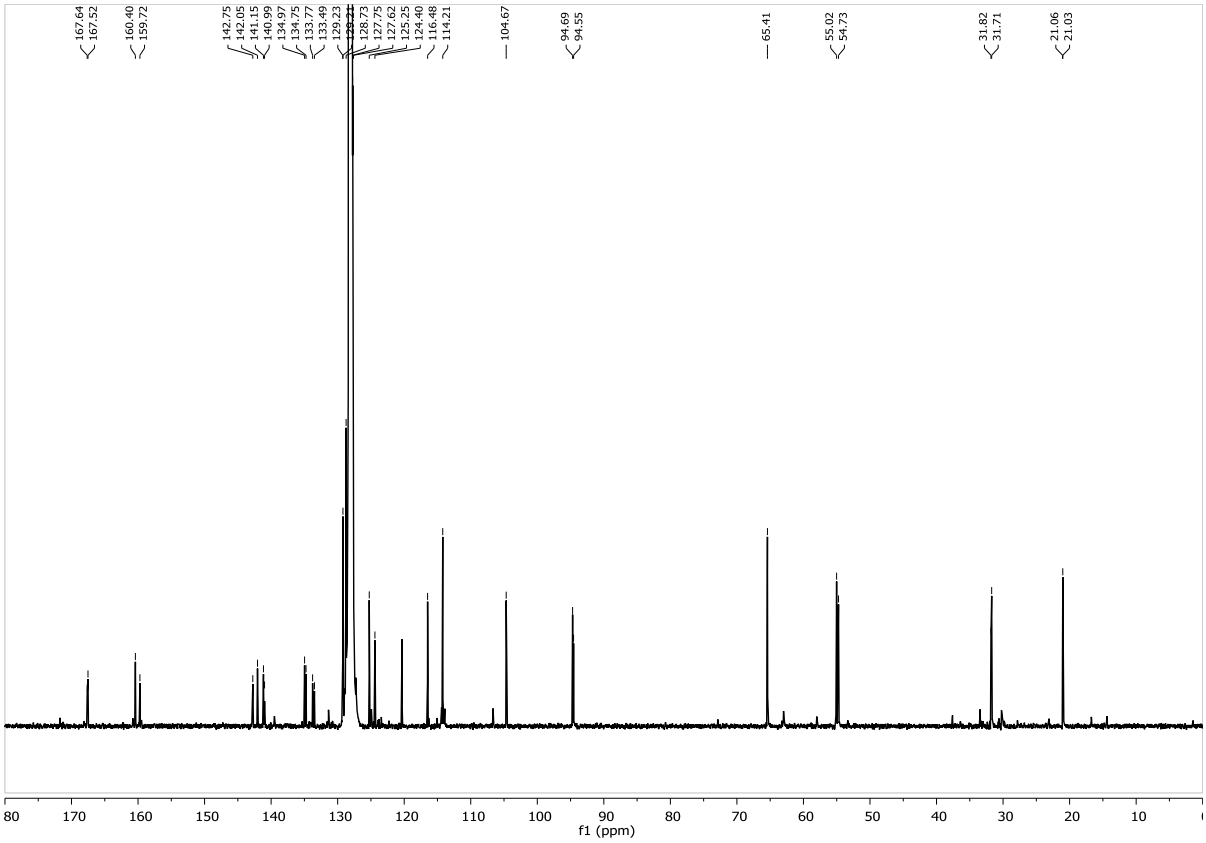
^{1}H NMR, 400 MHz, C_6D_6

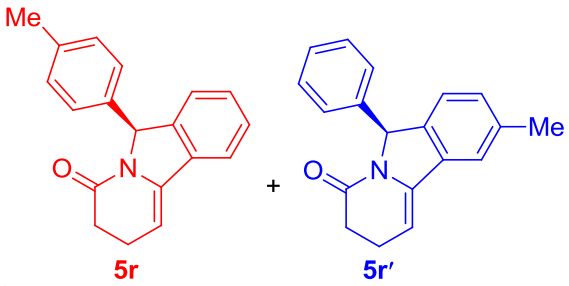




5p **5p′**

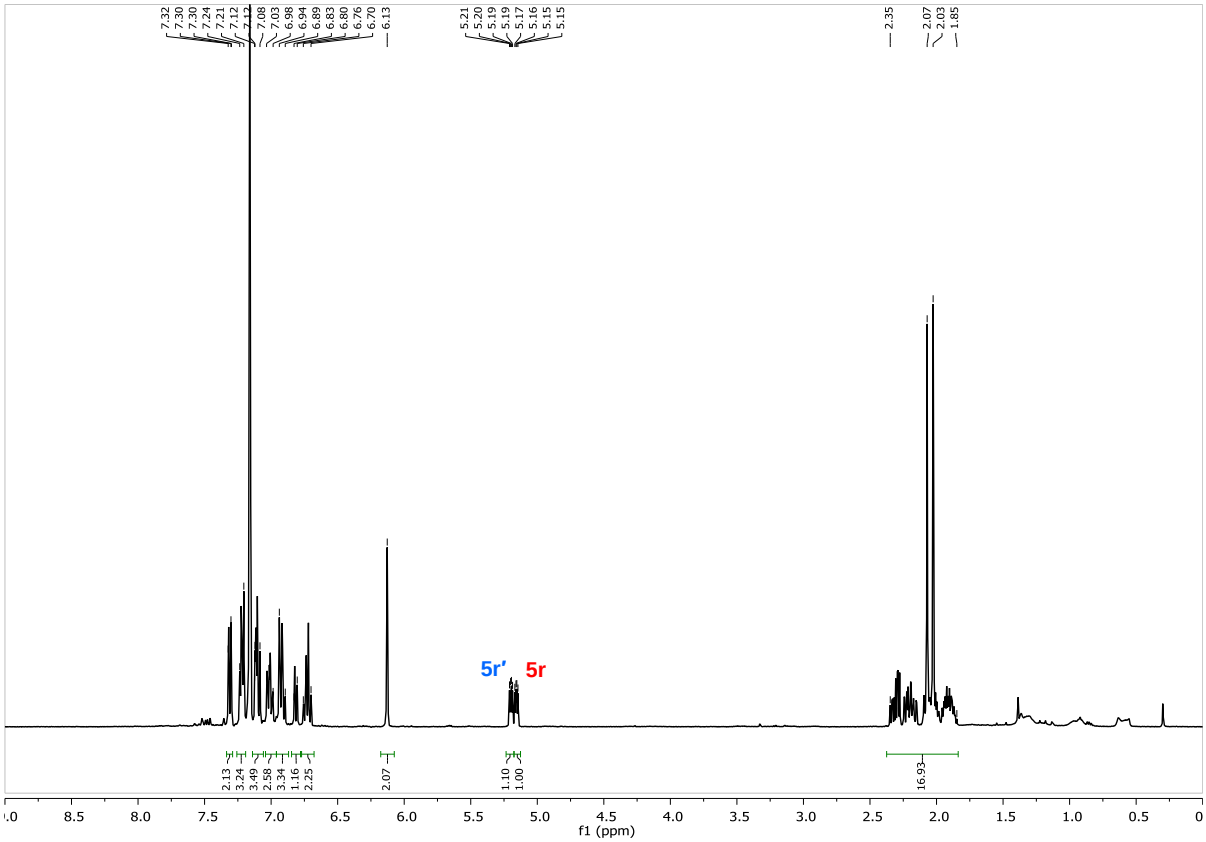
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

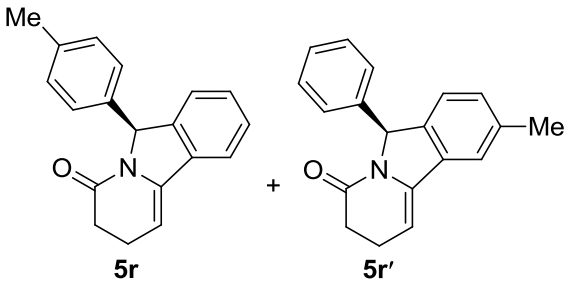




5r **5r′**

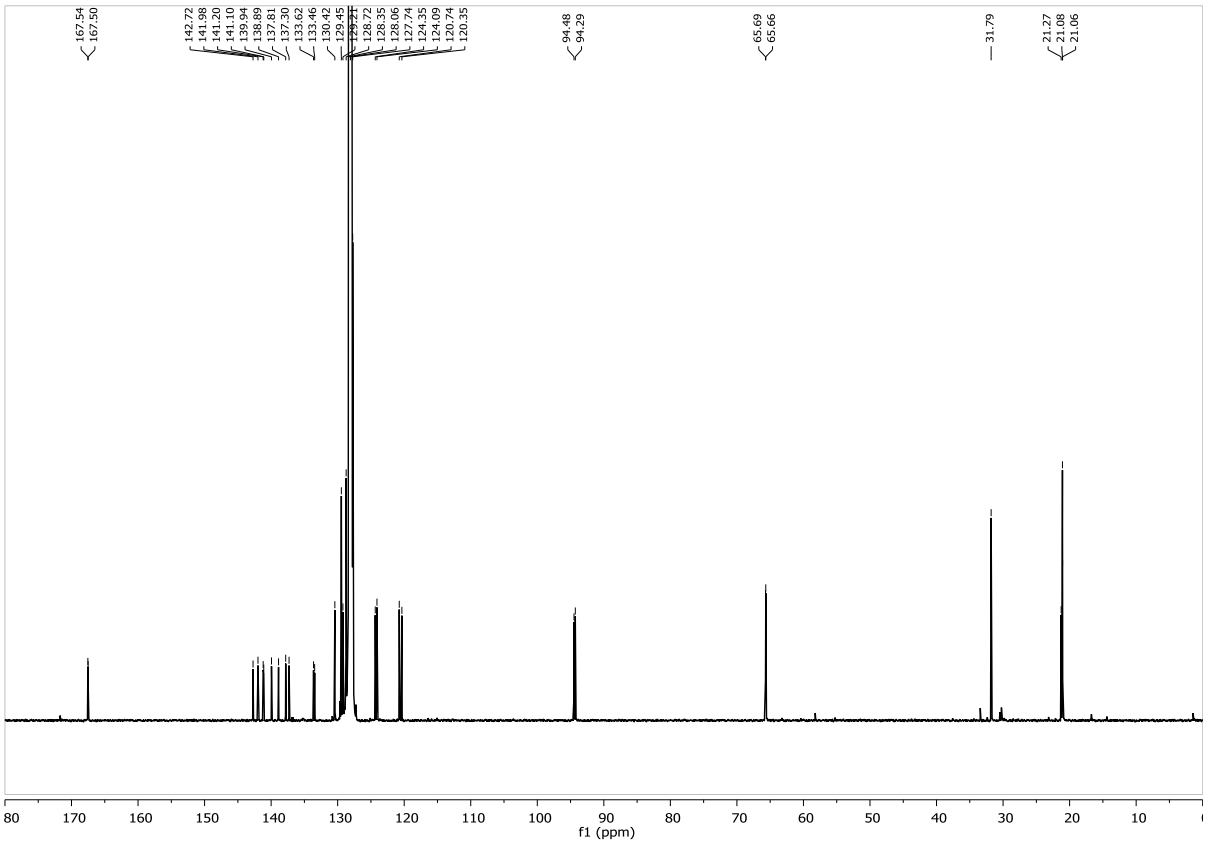
^{1}H NMR, 400 MHz, C_6D_6

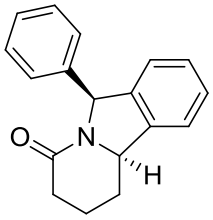




5r **5r′**

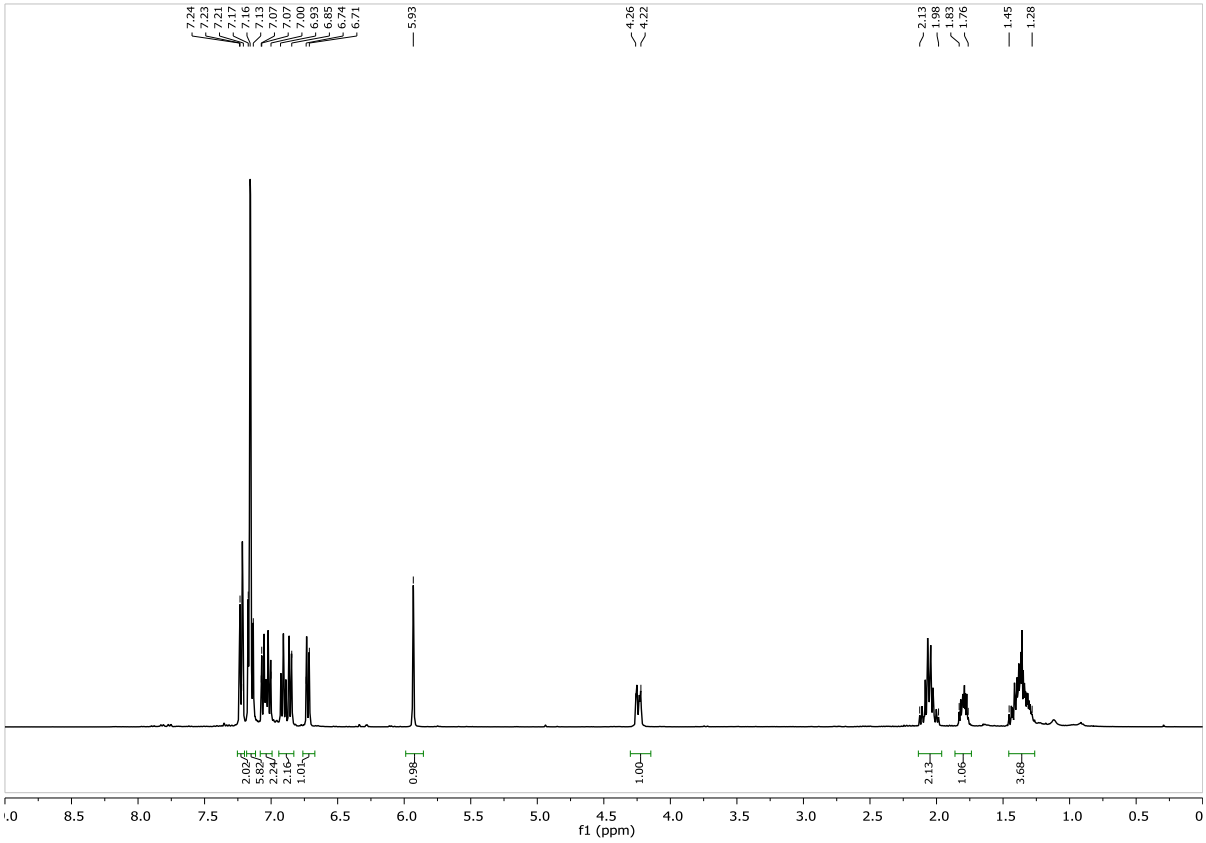
$^{13}C\{^{1}H\}$ NMR, 151 MHz, C_6D_6

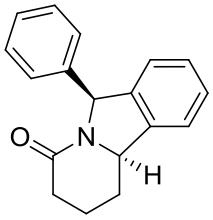




6a

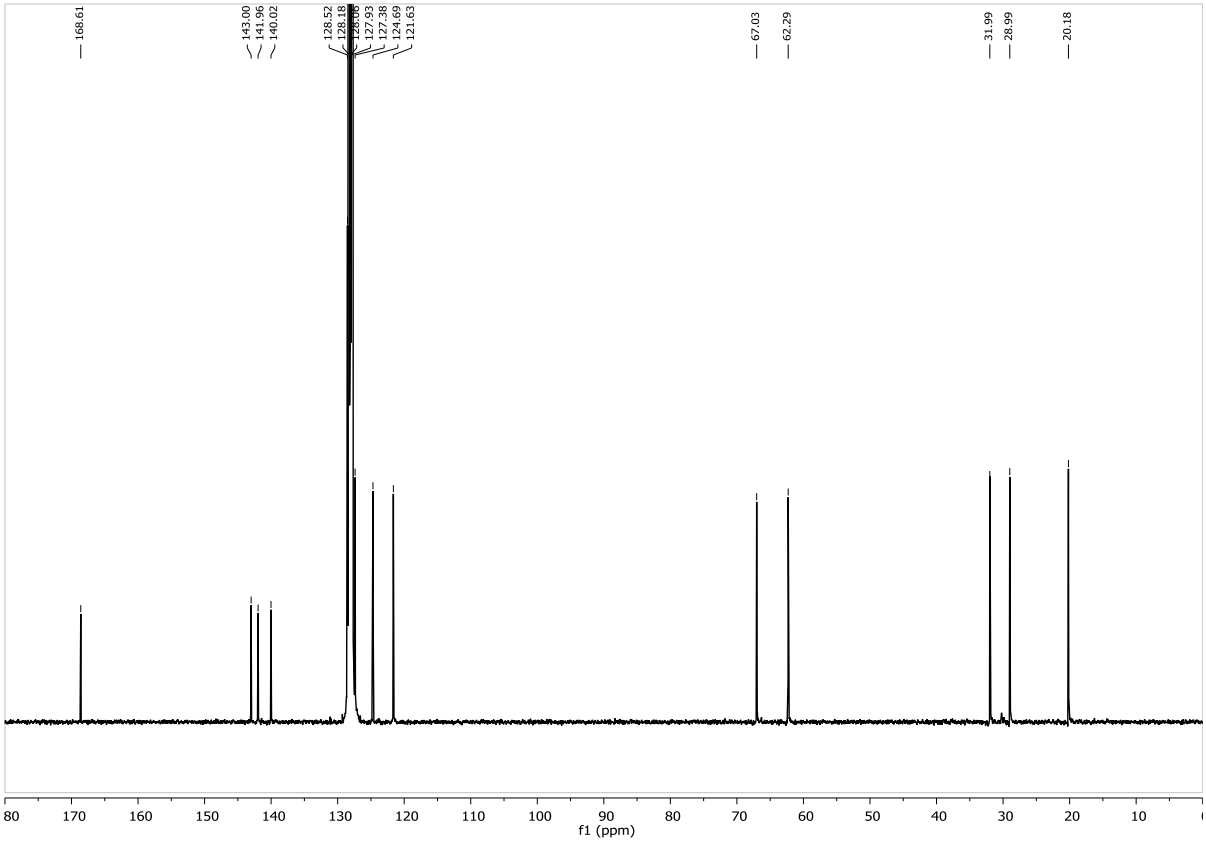
^{1}H NMR, 400 MHz, C_6D_6

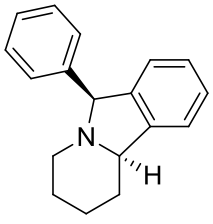




6a

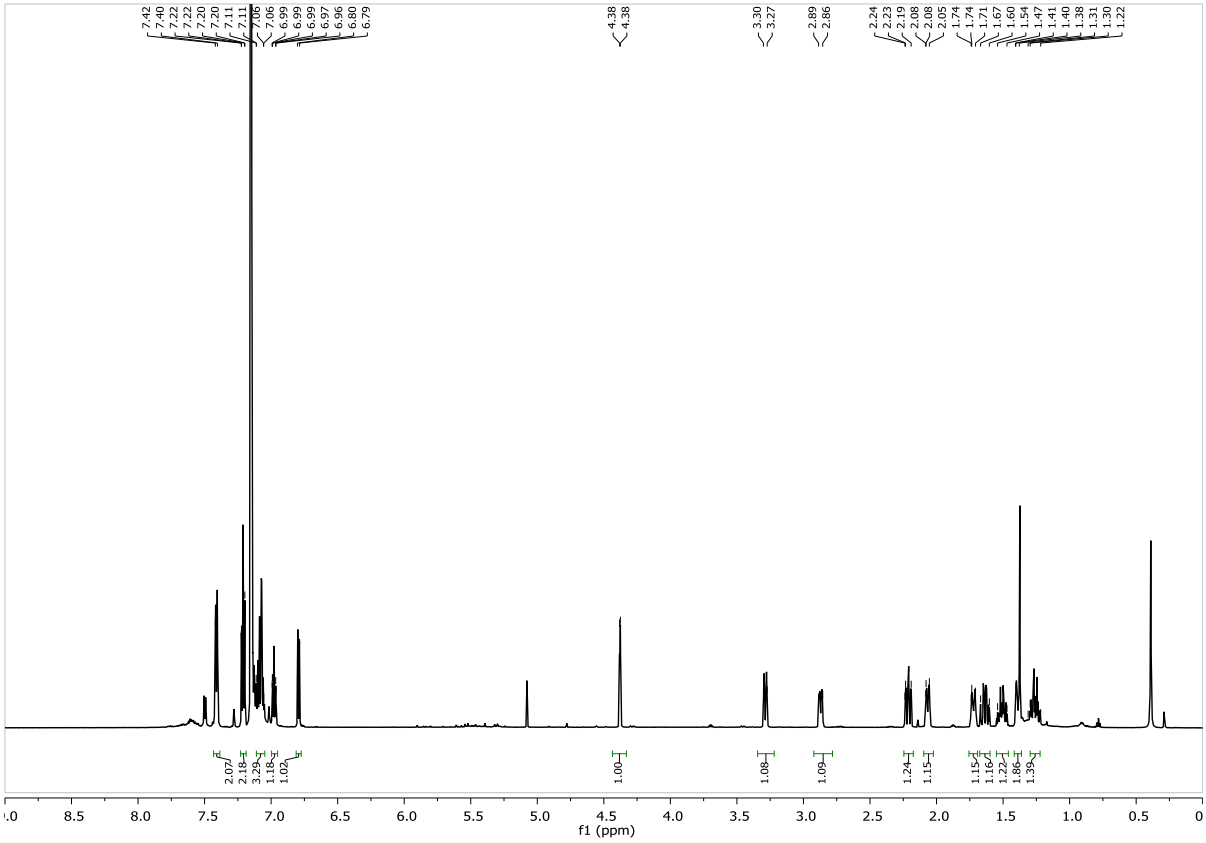
$^{13}C\{^{1}H\}$ NMR, 101 MHz, C_6D_6

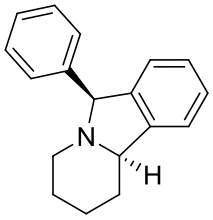




7a

^{1}H NMR, 400 MHz, C_6D_6





7a

$^{13}C\{^{1}H\}$ NMR, 101 MHz, C_6D_6