Supporting Information

Synthesis of Phosphoramidates: A Facile Approach Based on the C–N Bond Formation via Ir-catalyzed Direct C–H Amidation

Hyunwoo Kim,[†,‡] Juhyeon Park,[†,‡] Jeung Gon Kim,*[‡,†] and Sukbok Chang*[‡,†]

†Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea

‡Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS), Daejeon 305-701, Korea

Table of Contents ····· S1

I. General Methods ····· S2

II. Procedures for the Preparation of Starting Materials ····· S2

1. General Procedure for the Preparation of Aromatic Amides ····· S2
2. General Procedure for the Preparation of Arylpryidines ····· S3
3. General Procedure for the Preparation of Azides ····· S3

III. Procedure for the Optimization Study ····· S7

IV. Procedure for the Ir-Catalyzed C–H Amination with Azides ····· S8

1. Ir-Catalyzed Amination of Amides with Azides ····· S8
2. Ir-Catalyzed Amination of Ketones with Azides ····· S15
3. Ir-Catalyzed Amination of Pyridines with Azides ····· S18

V. Procedure of Mechanistic Studies ····· S21

VI. References ····· S22

Appendix I ····· S23

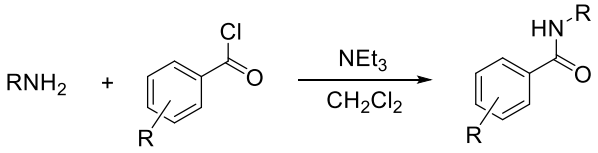
Spectral Copies of ^{1}H, ^{13}C and ^{31}P NMR of Compounds Obtained in this Study

I. General Methods

Unless otherwise stated, all commercial reagents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F_{254} plates. Visualization on TLC was achieved by the use of UV light (254 nm), exposure to iodine vapor, or treatment with acidic anisaldehyde or phosphomolybdic acid, ninhydrin or ceric ammonium molydate stain followed by heating. Column chromatography was undertaken on silica gel (400-630 mesh) using a proper eluent system. ^{1}H NMR was recorded on Agilent Technologies DD2 (600 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), td (triplet of doublet), ddd (doublet of doublet of doublet), m (multiplet). Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on Agilent Technologies DD2 (150 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the appropriate solvent peak. ^{31}P NMR was recorded on Agilent Technologies DD2 (243 MHz). Chemical shifts were reported in ppm referenced to external PPh_3 (-6.00 ppm). Infrared (IR) spectra were recorded on Bruker Alpha FT-IR Spectrometer. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. High resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using EI or FAB method, or from KAIST Research Analysis Center by using ESI method. 1,2-Dichloroethane was dried via activated alumina column. Dichloro(η^5-pentamethylcyclopentadienyl)iridium(III) dimer (98%) was purchased from Strem Chemicals Co., Ltd.

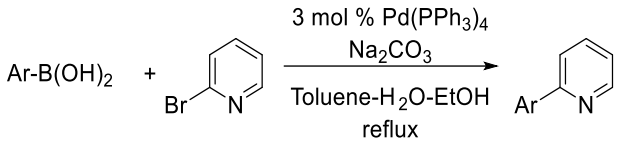
II. Procedures for the Preparation of Starting Materials

1. General Procedure for the Preparation of Aromatic Amides[1]



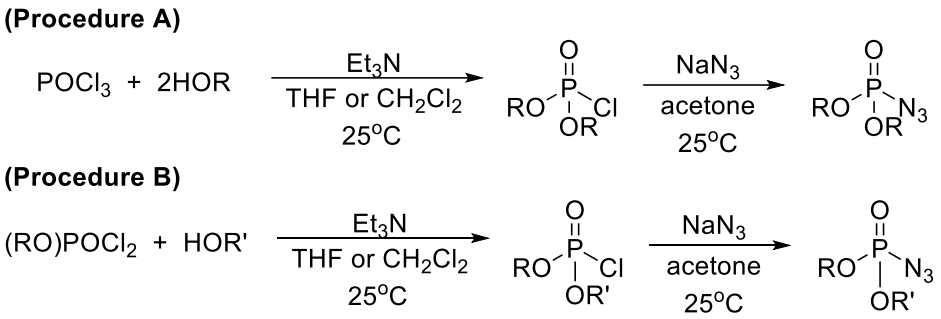
To a solution of acyl chloride (5.0 mmol) in dichloromethane (20 mL) were added dropwise appropriate alkylamine (6.0 mmol) and triethylamine (0.61 g, 6.0 mmol) at 0 °C under N_2 atmosphere. After stirring for 5 h at room temperature, the reaction mixture was quenched with 1N HCl (10 mL), extracted with CH_2Cl_2 three times, dried over $MgSO_4$, and evaporated under reduced pressure to afford crude product, which was purified by recrystallization (*n*-hexane/CH_2Cl_2).

2. General Procedure for the Preparation of Arylpyridines[2]



To a solution of 2-bromopyridine (0.32 g, 2.0 mmol) in toluene (7 mL), ethanol (1.5 mL), and H_2O (7 mL) was added Na_2CO_3 (1.6 g, 15 mmol) followed by $Pd(PPh_3)_4$ (0.069 g, 0.060 mmol) and appropriate arylboronic acid (2.6 mmol) under argon in a 50 mL two-necked flask. The reaction mixture was refluxed for 12 h, and then cooled to room temperature. To the reaction mixture was added aqueous NH_4Cl (15 mL), extracted by EtOAc for three times, dried over $MgSO_4$, and evaporated in vacuum to afford the crude product, which was purified by flash chromatography on silica gel with n-hexane/EtOAc to give quantitative yield of corresponding aryl pyridines

3. General Procedure for the Preparation of Azides[3]



3-1. Preparation of dialkylphosphorochloridate

3-1-1. Procedure A

To a stirred solution of an appropriate alcohol (10 mmol) and triethylamine (1.2 g, 12 mmol) in dichloromethane (10mL) was added phosphorus oxychloride (766.7 mg, 5.0 mmol) dropwise at room temperature. After stirring the reaction mixture for 5 h at room temperature, insoluble residues were filtered through Celite. The filtrate was diluted with diethyl ether (30 mL) and washed 3 times with water (20 mL). The collected aqueous layer was back-extracted with diethyl ether (10 mL) 2 times. Collected organic layer was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The isolated product was used in the further reaction without further purifications.

3-1-2. Procedure B

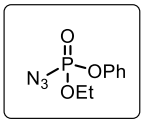
To a stirred solution of an appropriate alcohol (3.0 mmol) and triethylamine (3.3 mmol) in

dichloromethane (3 mL) was added alkyl dichlorophosphate (3.0 mmol) dropwise at room temperature. After stirring the reaction mixture for 5 h at room temperature, insoluble residues were filtered through Celite. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel.

3-2. Preparation of dialkylphosphoroazidate

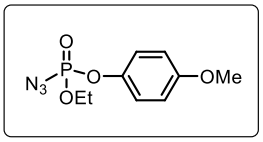
To a stirred solution of an appropriate dialkylphosphorochloridate (2.0 mmol) in acetone (5 mL) was added sodium azide (3.0 mmol) in one portion at room temperature. The resulting solution was stirred for 10 h during which time white salt precipitated. The insoluble residues were filtered through Celite. The filtrate was dried under reduced pressure, diluted with diethyl ether (20 mL) and then washed 3 times with water (20 mL). The collected aqueous layer was back-extracted with diethyl ether (10 mL) twice. Collected organic layer was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The isolated product was used without further purifications.

Ethyl phenyl phosphorazidate



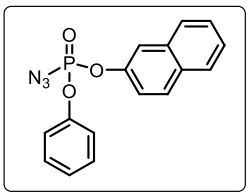
Colorless liquid (195 mg, 43%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.24 – 7.18 (m, 3H), 4.32 – 4.25 (m, 2H), 1.41 – 1.36 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.9 (d, *J* = 7.5 Hz), 129.9 (2C), 125.7, 120.1 (d, *J* = 4.8 Hz, 2C), 65.7 (d, *J* = 6.7 Hz), 15.9 (d, *J* = 6.7 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -5.57; **IR** (cm^{-1}) 3066, 2986, 2161, 1591, 1194, 939, 772; **High Resolution MS** (FAB): Calculated for $C_8H_{10}N_3O_3P$ $[M+H]^+$: 228.0538, Found: 228.0539.

Ethyl (4-methoxyphenyl) phosphorazidate



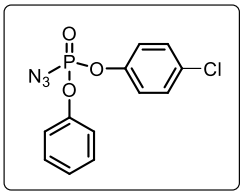
Colorless liquid (401 mg, 78%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.13 – 7.10 (m, 2H), 6.85 – 6.81 (m, 2H), 4.30 – 4.23 (m, 2H), 3.75 (s, 3H), 1.39 – 1.34 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.2, 143.3 (d, *J* = 7.7 Hz), 120.9 (m, 2C), 114.7 (2C), 65.6 (d, *J* = 5.4 Hz), 55.4 (d, *J* = 4.7 Hz), 15.8; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -4.95; **IR** (cm^{-1}) 2985, 2839, 2161, 1596, 1252, 1191, 942, 754; **High Resolution MS** (FAB): Calculated for $C_9H_{12}N_3O_4P$ $[M+H]^+$: 258.0644, Found: 258.0641.

Naphthalen-2-yl phenyl phosphorazidate



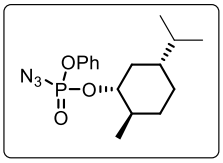
Colorless liquid (390 mg, 60%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 3H), 7.78 – 7.76 (m, 1H), 7.54 – 7.46 (m, 2H), 7.43 – 7.37 (m, 3H), 7.34 – 7.31 (m, 2H), 7.28 – 7.23 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.9 (d, *J* = 7.7 Hz), 147.5 (d, *J* = 8.0 Hz), 133.8, 131.4, 130.4, 130.1 (2C), 127.8, 127.7, 127.1, 126.2, 126.1, 120.3 (d, *J* = 5.2 Hz, 2C), 119.7 (d, *J* = 5.0 Hz), 117.1 (d, *J* = 5.1 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -10.23; **IR** (cm^{-1}) 2165, 1591, 1270, 1191, 956, 751; **High Resolution MS** (FAB): Calculated for $C_{16}H_{12}N_3O_3P$ $[M+H]^+$: 326.0695, Found: 326.0694.

4-Chlorophenyl phenyl phosphorazidate



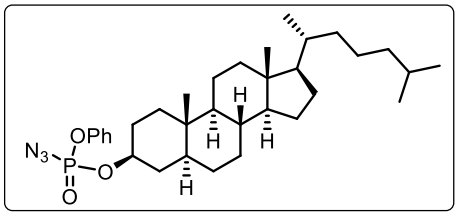
Colorless liquid (570 mg, 92%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.35 – 7.32 (m, 2H), 7.27 – 7.22 (m, 3H), 7.21 – 7.18 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.7 (d, *J* = 7.7 Hz), 148.3 (d, *J* = 7.7 Hz), 131.6 (d, *J* = 1.6 Hz), 130.1 (2C) 130.0 (2C), 126.2, 120.6 (d, *J* = 4.7 Hz, 2C), 120.1 (d, *J* = 4.8 Hz, 2C); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -10.25; **IR** (cm^{-1}) 2167, 1589, 1269, 1182, 1092, 960, 785; **High Resolution MS** (FAB): Calculated for $C_{12}H_9ClN_3O_3P$ $[M+H]^+$: 310.0148, Found: 310.0145.

(1R,2R,5R)-5-Isopropyl-2-methylcyclohexyl phenyl phosphorazidate



Colorless liquid (617 mg, 92%); 1:1 mixture of diastereomer; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.24 – 7.17 (m, 3H), 4.44 – 4.35 (m, 1H), 2.28 – 2.16 (m, 1H), 2.12 – 1.94 (m, 1H), 1.69 – 1.62 (m, 2H), 1.50 – 1.36 (m, 2H), 1.28 – 1.15 (m, 1H), 1.04 – 0.95 (m, 1H), 0.93 – 0.71 (m, 10H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ [150.1 (*J* = 7.5 Hz) + 150.0 (*J* = 7.5 Hz)] , 129.8 (2C), 125.7 (m), 120.3 (*J* = 5.0 Hz), 120.2 (*J* = 4.6 Hz), [82.3 (*J* = 7.7 Hz) + 82.1 (*J* = 7.6 Hz)], 48.3 (m), [42.5 + 42.3], 33.8, 31.6, [25.7 + 25.5], [22.9 (*J* = 1.1 Hz) + 22.8 (*J* = 1.1 Hz)], [21.8 + 21.8], [20.8 + 20.7], [15.6 + 15.5]); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -6.14; **IR** (cm^{-1}) 2927, 2870, 2159, 1592, 1196, 953, 772; **High Resolution MS** (FAB): Calculated for $C_{16}H_{24}N_3O_3P$ $[M+H]^+$: 338.1634 Found: 338.1632.

(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl phenyl phosphorazidate

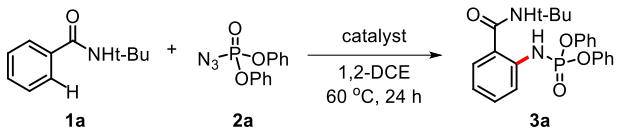


Colorless liquid (429 mg, 99%, 0.76 mmol scale); 1:1 mixture of diastereomer; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.23 – 7.17 (m, 3H), 4.54 – 4.46 (m, 1H), 2.00 – 1.92 (m, 2H), 1.83 – 1.62 (m, 5H), 1.60 – 1.47 (m, 3H), 1.47 – 1.43 (m, 1H), 1.39 – 1.15 (m, 9H), 1.15 – 1.05 (m, 6H), 1.05 – 0.93 (m, 4H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.81 (s, 3H), 0.63 (s, 3H), 0.61 – 0.56 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.0 (*J* = 7.9 Hz), 129.9 (2C), 125.7 (*J* = 1.7 Hz), 120.2 (*J* = 5.2 Hz, 2C), [81.0 (*J* = 6.9 Hz) + 81.0 (*J* = 6.9 Hz)], 56.4, 56.3, 54.1, 44.7, 42.6, 39.9, 39.5, [36.7+ 36.7], 36.1, 35.8, [35.7 (*J* = 4.0 Hz) + 35.6 (*J* = 4.0 Hz)], 35.4, 35.3, 31.9, 29.2 (*J* = 4.8 Hz), [28.5 + 28.4], 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 21.2, 18.7, 12.2, 12.0; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -6.52, -6.55; **IR** (cm^{-1}) 2930, 2160, 1592, 1198, 950, 774; **High Resolution MS** (FAB): Calculated for $C_{33}H_{52}N_3O_3P$ $[M+H]^+$: 570.3825, Found: 570.3822.

III. Procedure for the Optimization Study

To a screw capped vial with a spinvane triangular-shaped Teflon spinbar were added *N-tert*-butylbenzamide (**1a**, 0.20 mmol), diphenyl phosphoryl azide (**2a**), catalyst, additive, and solvent (0.5 mL) under atmospheric conditions. The reaction mixture was stirred in a pre-heated aluminium reaction block at the indicated temperature for 24 h. The reaction mixture was cooled to room temperature in case of heating, filtered through a plug of celite and then washed with CH_2Cl_2 (10 mL x 3). The solvent were removed under reduced pressure and the crude yield was measured by ^{1}H NMR using an internal standard (CH_2Br_2).

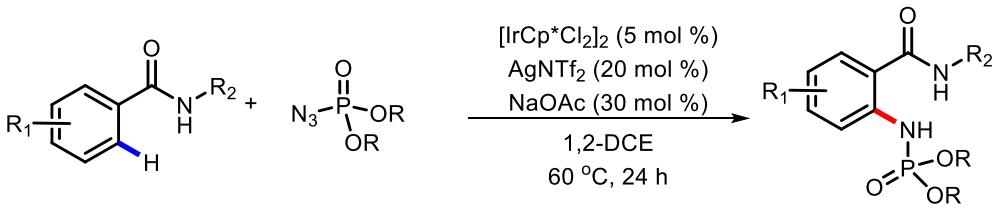
Table S1. Optimization of Reaction Parameters



Entry	Catalytic system (mol %)	Additive (mol %)	**2a** (equiv)	Solvent	Temp (°C)	Yield (%)
1	$[IrCp^*Cl_2]_2$ (5) / $AgNTf_2$ (20)	-	1.2	$ClCH_2CH_2Cl$	60	28
2	$[RhCp^*Cl_2]_2$ (5) / $AgNTf_2$ (20)	-	1.2	$ClCH_2CH_2Cl$	60	n.r.
3	$[Ru(p\text{-cymene})Cl_2]_2$ (5) / $AgNTf_2$ (20)	-	1.2	$ClCH_2CH_2Cl$	60	<1
4	$Pd(OAc)_2$ (5)	-	1.2	$ClCH_2CH_2Cl$	60	n.r.
5	$[IrCp^*Cl_2]_2$ (5) / $AgNTf_2$ (20)	NaOAc (30)	1.2	$ClCH_2CH_2Cl$	60	99
6	$[RhCp^*Cl_2]_2$ (5) / $AgNTf_2$ (20)	NaOAc (30)	1.2	$ClCH_2CH_2Cl$	60	<1
7	$[Ru(p\text{-cymene})Cl_2]_2$ (5) / $AgNTf_2$ (20)	NaOAc (30)	1.2	$ClCH_2CH_2Cl$	60	n.r.
8	$Pd(OAc)_2$ (5)	NaOAc (30)	1.2	$ClCH_2CH_2Cl$	60	n.r.
9	$[IrCp^*Cl_2]_2$ (2.5) / $AgNTf_2$ (10)	NaOAc (30)	1.2	$ClCH_2CH_2Cl$	60	13
10	$[IrCp^*Cl_2]_2$ (1) / $AgNTf_2$ (4)	NaOAc (30)	1.2	$ClCH_2CH_2Cl$	60	6

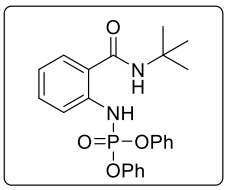
IV. Procedure for the Ir-Catalyzed C–H Amination with Azides

1. Ir-Catalyzed Amination of Amides with Azides (Scheme 2, **3a-3e, 3t** & Scheme 4)



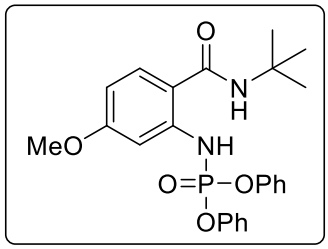
To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added amide (0.20 mmol), azide (0.24 mmol), $[IrCp^*Cl_2]_2$ (8.0 mg, 0.010 mmol, 5 mol %), $AgNTf_2$ (16 mg, 0.040 mmol, 20 mol %), NaOAc (4.9 mg, 0.060 mmol, 30 mol %) and 1,2-dichloroethane (0.50 mL) under atmospheric conditions. The reaction mixture was stirred at 60 °C for 24 h, filtered through a pad of celite and then washed with CH_2Cl_2 (10 mL x 3). Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc or *n*-hexane/EtOAc/CH_2Cl_2) to give the desired product.

Diphenyl (2-(*tert*-butylcarbamoyl)phenyl)phosphoramidate (Scheme 2, **3a**)



Brown liquid (84 mg, 99%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.92 (d, *J* = 11.9 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.26 (m, 4H) , 7.24 (d, *J* = 8.0 Hz, 4H), 7.14 (t, *J* = 7.3 Hz, 2H), 6.95 – 6.90 (m, 1H), 5.96 (s, 1H), 1.40 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.6, 150.5 (d, *J* = 6.9 Hz, 2C), 141.1, 132.2, 129.7 (4C), 126.8, 125.2 (2C), 121.1, 120.7 (d, *J* = 9.4 Hz), 120.4 (d, *J* = 5.1 Hz, 4C), 119.4, 52.0, 28.7 (3C); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.97; **IR** (cm^{-1}) 3316, 3066, 2969, 1635,1487, 1454, 1391, 1207, 1184, 935, 750; **High Resolution MS** (EI): Calculated for $C_{23}H_{25}N_2O_4P$ $[M]^+$: 424.1552, Found: 424.1554.

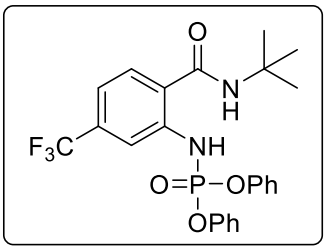
Diphenyl (2-(*tert*-butylcarbamoyl)-5-methoxyphenyl)phosphoramidate (Scheme 2, **3b**)



White solid (77 mg, 85%); m.p. 114 – 116 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.47 (d, *J* = 11.8 Hz, 1H), 7.32 – 7.24 (m, 9H), 7.21 (d, *J* = 2.4 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 2H), 6.44 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.92 (s, 1H), 3.78 (s, 3H), 1.40 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.6, 162.5, 150.5 (d, *J* = 6.8 Hz, 2C), 143.5, 129.7 (4C), 128.2, 125.2 (2C),

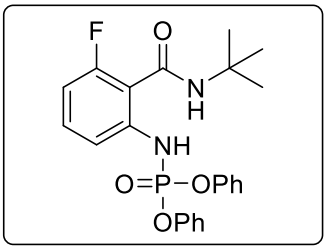
120.4 (d, *J* = 5.0 Hz, 4C), 112.8 (d, *J* = 10.1 Hz), 107.6, 103.9, 55.4, 51.8, 28.8 (3C); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -8.02; **IR** (cm^{-1}) 3333, 2967, 2930, 1629, 1487, 1264, 1206, 1185, 934, 766; **High Resolution MS** (EI): Calculated for $C_{24}H_{27}N_2O_5P$ $[M]^+$: 454.1658, Found: 454.1655.

Diphenyl (2-(*tert*-butylcarbamoyl)-5-(trifluoromethyl)phenyl)phosphoramidate (Scheme 2, **3c**)



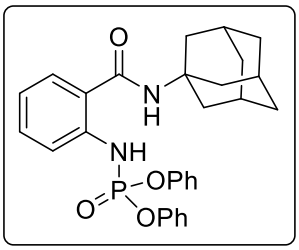
White solid (62 mg, 63%); m.p. 146 – 148 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.00 – 9.88 (m, 1H), 7.92 (s, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.28 (m, 4H), 7.24 (d, *J* = 7.9 Hz, 4H), 7.19 – 7.13 (m, 3H), 6.10 – 6.00 (m, 1H), 1.43 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.5, 150.3 (d, *J* = 7.2 Hz, 2C), 141.7, 133.9 (q, *J* = 32.7 Hz), 129.8 (4C), 127.4, 125.4 (2C), 123.4 (d, *J* = 9.9 Hz, 4C), 123.3 (q, *J* = 272.9 Hz), 120.3 (d, *J* = 5.0 Hz), 117.5 (q, *J* = 3.1 Hz), 116.2, 52.5, 28.6 (3C); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -8.87; **IR** (cm^{-1}) 3328, 3068, 2967, 1647, 1333, 1183, 932, 767; **High Resolution MS** (ESI): Calculated for $C_{24}H_{24}F_3N_2O_4P$ $[M+Na]^+$: 515.1323, Found: 515.1335.

Diphenyl (2-(*tert*-butylcarbamoyl)-3-fluorophenyl)phosphoramidate (Scheme 2, **3d**)



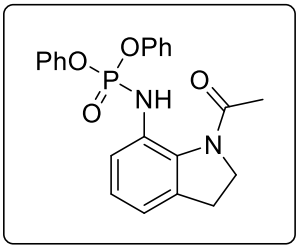
White solid (84 mg, 95%); m.p. 92 – 94 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.49 (d, *J* = 11.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.34 – 7.28 (m, 5H), 7.26 (d, *J* = 8.1 Hz, 4H), 7.18 – 7.14 (m, 2H), 6.69 (dd, *J* = 12.3, 8.3 Hz, 1H), 6.52 (d, *J* = 14.4 Hz, 1H), 1.41 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.6, 160.9 (d, *J* = 245.1 Hz), 150.4 (d, *J* = 7.0 Hz, 2C), 143.6 (m), 132.3 (d, *J* = 12.6 Hz), 129.7 (4C), 125.3 (2C), 120.4 (d, *J* = 4.8 Hz, 4C), 115.3 , 108.9 (m), 108.6 (d, *J* = 25.8 Hz), 52.3 , 28.7 (3C); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -8.30; **IR** (cm^{-1}) 3461, 3056, 2997, 2968, 1645, 1482, 1285, 1184, 933, 767; **High Resolution MS** (EI): Calculated for $C_{23}H_{24}FN_2O_4P$ $[M]^+$: 442.1458, Found: 442.1460.

Diphenyl (2-(((3s,5s,7s)-adamantan-1-yl)carbamoyl)phenyl)phosphoramidate (Scheme 2, **3e**)



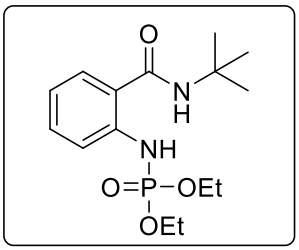
Colorless liquid (87 mg, 86%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.96 (d, *J* = 12.0 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.31 – 7.26 (m, 4H), 7.24 (d, *J* = 8.1 Hz, 4H), 7.13 (t, *J* = 7.3 Hz, 2H), 6.93 – 6.87 (m, 1H), 5.91 (s, 1H), 2.09 (s, 3H), 2.04 (s, 6H), 1.69 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.4, 150.5 (d, *J* = 6.9 Hz, 2C), 141.0, 132.2, 129.7 (4C), 126.9, 125.2 (2C), 121.1, 120.8 (d, *J* = 9.4 Hz), 120.4 (d, *J* = 4.6 Hz, 4C), 119.3, 52.8, 41.4 (3C), 36.3 (3C), 29.4 (3C); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.96; **IR** (cm^{-1}) 3067, 2905, 2849, 1634, 1488, 1269, 1185, 936, 751; **High Resolution MS** (ESI): Calculated for $C_{29}H_{31}N_2O_4P$ $[M+Na]^+$: 525.1919, Found: 525.1934.

Diphenyl (1-acetylindolin-7-yl)phosphoramidate (Scheme 2, **3t)**



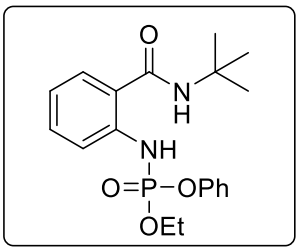
Light brown solid (80 mg, 98%); m.p. 109 – 111 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.98 (d, *J* = 11.7 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.24 (m, 4H), 7.21 (d, *J* = 8.1 Hz, 4H), 7.16 – 7.05 (m, 3H), 6.87 (d, *J* = 7.6 Hz, 1H), 3.85 (t, *J* = 7.9 Hz, 2H), 2.97 (t, *J* = 7.9 Hz, 2H), 2.13 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.3, 150.6 (d, *J* = 6.9 Hz, 2C), 135.2, 132.9 (d, *J* = 12.0 Hz), 129.6 (4C), 129.2, 126.7, 125.0 (2C), 120.4 (d, *J* = 4.7 Hz, 4C), 120.3, 119.2, 51.3, 28.8, 24.2; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -6.86; **IR** (cm^{-1}) 3066, 2854, 2698, 1627, 1486, 1187, 933, 751; **High Resolution MS** (EI): Calculated for $C_{22}H_{21}N_2O_4P$ $[M]^+$: 408.1239, Found: 408.1240.

Diethyl (2-(*tert*-butylcarbamoyl)phenyl)phosphoramidate (Scheme 3, **4a**)



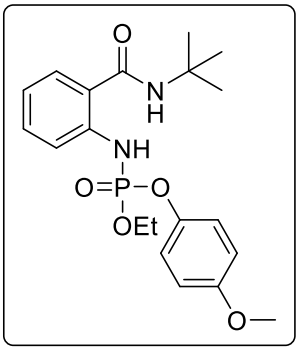
Brown liquid (47 mg, 71%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.26 (d, *J* = 11.1 Hz, 1H), 7.44 – 7.28 (m, 3H), 6.95 – 6.84 (t, *J* = 7.5 Hz, 1H), 6.00 (s, 1H), 4.17 – 4.07 (m, 4H), 1.44 (s, 9H), 1.34 – 1.29 (m, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.8, 141.8, 132.2, 126.7, 120.3, 120.2 (d, *J* = 9.5 Hz), 118.7, 62.9 (d, *J* = 5.4 Hz, 2C), 52.0, 28.8 (3C), 16.1 (d, *J* = 6.9 Hz, 2C); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -8.89; **IR** (cm^{-1}) 3395, 2983, 1638, 1525, 1251, 1189, 974, 754; **High Resolution MS** (EI): Calculated for $C_{15}H_{25}N_2O_4P$ $[M]^+$: 328.1552, Found: 328.1550.

Ethyl phenyl (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (Scheme 3, **4b**)



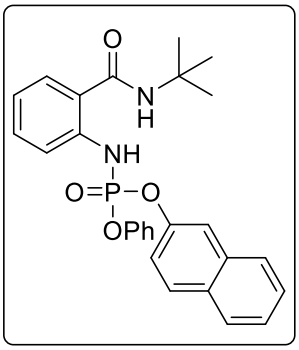
Brown liquid (39 mg, 52%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.57 (d, *J* = 11.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.28 – 7.23 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.13 – 7.08 (m, 1H), 6.89 (t, *J* = 7.6 Hz, 1H), 5.98 (s, 1H), 4.39 – 4.13 (m, 2H), 1.41 (s, 9H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.7, 150.6 (d, *J* = 6.6 Hz), 141.4, 132.2, 129.6 (2C), 126.7, 124.8, 120.7, 120.5 (d, *J* = 9.6 Hz), 120.3 (d, *J* = 4.7 Hz, 2C), 119.1, 63.7 (d, *J* = 5.5 Hz), 52.0, 28.7 (3C), 16.1 (d, *J* = 6.7 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -3.13; **IR** (cm^{-1}) 3299, 2971, 1635, 1584, 1257, 1163, 927, 753; **High Resolution MS** (EI): Calculated for $C_{19}H_{25}N_2O_4P$ $[M]^+$: 376.1552, Found: 376.1553.

Ethyl (4-methoxyphenyl) (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (Scheme 3, **4c**)



Brown liquid (42 mg, 51%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.50 (d, *J* = 11.4 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.11 – 7.06 (m, 2H), 6.92 – 6.87 (m, 1H), 6.78 – 6.74 (m, 2H), 5.96 (s, 1H), 4.29 – 4.13 (m, 2H), 3.72 (s, 3H), 1.41 (s, 9H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.7, 156.6, 144.2 (d, *J* = 6.9 Hz), 141.5, 132.2, 126.7, 121.2 (d, *J* = 4.4 Hz, 2C), 120.7, 120.5 (d, *J* = 9.9 Hz), 119.1, 114.6 (2C), 63.7 (d, *J* = 5.6 Hz), 55.5, 52.0, 28.7 (3C), 16.1 (d, *J* = 6.8 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -2.62; **IR** (cm^{-1}) 3293, 2970, 1635, 1584, 1252, 1194, 958, 753; **High Resolution MS** (EI): Calculated for $C_{20}H_{27}N_2O_5P$ $[M+X]^+$: 406.1658, Found: 406.1656.

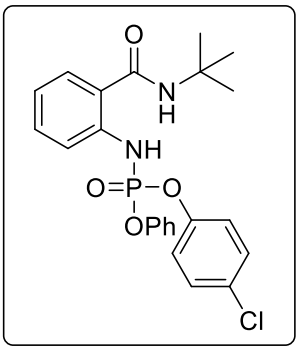
Naphthalen-2-yl phenyl (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (Scheme 3, **4d**)



Light yellow viscous liquid (76 mg, 80%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.05 (d, *J* = 11.8 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.75 – 7.70 (m, 3H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.37 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.19 – 7.12 (m, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 5.99 (s, 1H), 1.35 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.6, 150.5 (d, *J* = 6.8 Hz), 148.1 (d, *J* = 7.0 Hz), 141.1, 133.9, 132.3, 131.0, 129.8, 129.7 (2C), 127.7, 127.6, 126.9, 126.6, 125.5, 125.2, 121.2, 120.8 (d, *J* = 9.7 Hz), 120.4 (d, *J* = 4.6 Hz, 2C), 120.3 (d, *J* = 4.7 Hz), 119.4 , 117.0 (d, *J* = 5.3 Hz), 52.0, 28.7 (3C); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.77; **IR** (cm^{-1}) 3319, 2968, 1633, 1585, 1265, 1153, 968, 747; **High Resolution MS** (FAB):

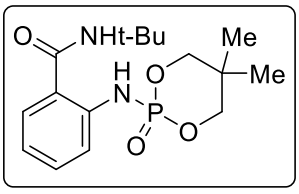
Calculated for $C_{27}H_{27}N_2O_4P$ [M+H]$^+$: 475.1787, Found: 475.1786.

4-chlorophenyl phenyl (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (Scheme 3, **4e**)



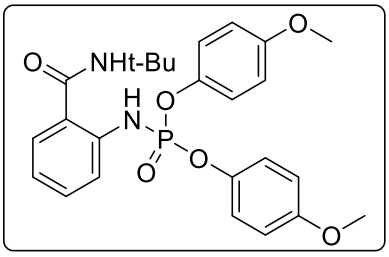
Light yellow liquid (58 mg, 64%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.99 (d, *J* = 11.8 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.20 (m, 4H), 7.20 – 7.12 (m, 3H), 6.94 (t, *J* = 7.5 Hz, 1H), 5.97 (s, 1H), 1.41 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.5, 150.3 (d, *J* = 6.8 Hz), 149.0, 140.9, 132.3, 130.5, 129.7 (2C), 129.7 (2C), 126.8, 125.3, 121.8 (d, *J* = 5.0 Hz, 2C), 121.3, 120.6 (d, *J* = 9.7 Hz), 120.3 (d, *J* = 4.9 Hz, 2C), 119.3, 52.1, 28.7 (3C); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.84; **IR** (cm^{-1}) 3318, 2969, 1636, 1534, 1266, 1188, 1071, 940, 753; **High Resolution MS** (FAB): Calculated for $C_{23}H_{24}ClN_2O_4P$ [M+H]$^+$: 459.1240, Found: 459.1237.

***N-tert*-butyl-2-((5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)amino)benzamide** (Scheme 3, **4f)**



Brown solid (45 mg, 66%); m.p. 144 –146 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.58 (d, *J* = 12.3 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.34 – 7.28 (m, 1H), 6.93 – 6.87 (m, 1H), 6.17 (s, 1H), 4.07 – 4.02 (m, 2H), 4.00 – 3.93 (m, 2H), 1.44 (s, 9H), 1.23 (s, 3H), 0.90 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.0, 141.4 (d, *J* = 2.0 Hz), 132.4, 126.9, 120.8, 120.1 (d, *J* = 9.2 Hz), 119.3, 77.4 (d, *J* = 6.7 Hz, 2C), 52.0, 32.4 (d, *J* = 5.7 Hz), 28.7 (3C), 21.7, 20.7; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -4.74; **IR** (cm^{-1}) 3348, 3066, 2976, 2962, 1634, 1479, 1192, 1053, 954, 750; **High Resolution MS** (EI): Calculated for $C_{16}H_{25}N_2O_4P$ [M]$^+$: 340.1552, Found: 340.1548.

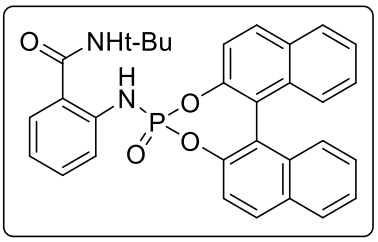
Bis(4-methoxyphenyl) (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (Scheme 3, **4g**)



Brown viscous liquid (74 mg, 76%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.83 (d, *J* = 11.7 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.13 (d, *J* = 8.7 Hz, 4H), 6.93 – 6.87 (m, 1H), 6.78 (d, *J* = 8.8 Hz, 4H), 6.02 (s, 1H), 3.72 (s, 6H), 1.39 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.6, 156.8, 144.1 (d, *J* = 7.6 Hz, 2C), 141.2, 132.2, 126.8, 121.3 (d, *J* = 4.3 Hz, 4C), 121.0, 120.6 (d, *J* = 9.8 Hz), 119.3 (2C), 114.6 (4C), 55.5 (2C), 52.0, 28.7 (3C); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -6.95; **IR** (cm^{-1}) 3309,

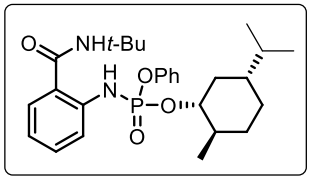
2965, 1635, 1596, 1250, 1176, 939, 751; **High Resolution MS** (FAB): Calculated for $C_{25}H_{29}N_2O_6P$ $[M+H]^+$: 485.1842, Found: 485.1838.

***N*-(*tert*-butyl)-2-((4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)amino)benzamide** (Scheme 3, **4h**)



Light brown solid (103 mg, 99%); m.p. 244 – 246 °C; **^{1}H NMR** (600 MHz, CD_2Cl_2) δ 10.04 (d, *J* = 11.2 Hz, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.99 – 7.93 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.47 – 7.37 (m, 4H), 7.37 – 7.27 (m, 3H), 7.05 – 6.99 (m, 1H), 6.10 (s, 1H), 1.34 (s, 9H); **^{13}C NMR** (150 MHz, CD_2Cl_2) δ 168.4 147.3 (d, *J* = 10.8 Hz), 146.0 (d, *J* = 8.1 Hz), 141.0 (d, *J* = 4.2 Hz), 132.4, 132.3 (d, *J* = 4.3 Hz, 2C), 131.9, 131.7, 131.2 (d, *J* = 6.0 Hz, 2C), 128.4 (d, *J* = 10.4 Hz, 2C), 127.0, 126.9, 126.8, 126.7 (d, *J* = 4.7 Hz, 2C), 125.7 (d, *J* = 7.6 Hz, 2C), 121.7, 121.6 (d, *J* = 1.8 Hz), 121.2, 120.8 (d, *J* = 1.8 Hz), 120.2, 120.2 (d, *J* = 1.8 Hz), 119.6, 51.9, 28.3 (3C); **^{31}P NMR** (243 MHz, CD_2Cl_2) δ 7.52; **IR** (cm^{-1}) 3318, 3051, 2963, 1540, 1272, 1204, 961, 747; **High Resolution MS** (EI): Calculated for $C_{31}H_{27}N_2O_4P$ $[M]^+$: 522.1708, Found: 522.1707.

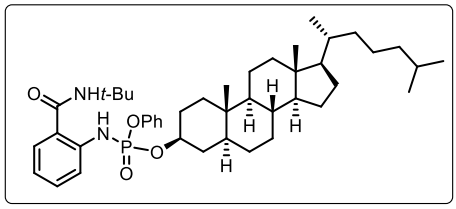
(1R,2R,5R)-5-Isopropyl-2-methylcyclohexyl phenyl (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (Scheme 4, **5a**)



White solid (43 mg, 44%); m.p. 78 – 80 °C; Mixture of diastereomers (major : minor = 2 : 1); **Major** : **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.49 (d, *J* = 11.2 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.27 – 7.22 (m, 2H), 7.22 – 7.19 (m, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.90 – 6.85 (m, 1H), 5.91 (s, 1H), 4.43 – 4.34 (m, 1H), 2.35 – 2.30 (m, 1H), 2.12 – 2.01 (m, 1H), 1.66 – 1.59 (m, 2H), 1.42 (s, 9H), 1.47 – 1.33 (m, 2H), 1.22 – 1.15 (m, 1H), 1.03 – 0.95 (m, 1H), 0.85 – 0.80 (m, 1H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 3H), 0.74 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.7, 150.9 (*J* = 6.9 Hz), 141.7 (*J* = 2.3 Hz), 132.0, 129.4 (2C), 126.6, 124.7, 120.6 (*J* = 9.9 Hz), 120.5, 120.4 (*J* = 4.7 Hz, 2C), 119.3 (*J* = 2.3 Hz), 79.8 (*J* = 6.4 Hz), 51.9, 48.5 (*J* = 7.5 Hz), 42.3, 34.0, 31.5, 28.7 (3C), 25.3, 22.8, 21.9, 20.9, 15.5; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -4.22; **Minor** : **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.55 (d, *J* = 11.2 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.27 – 7.22 (m, 2H), 7.22 – 7.19 (m, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.90 – 6.85 (m, 1H), 5.89 (s, 1H), 4.43 – 4.34 (m, 1H), 2.30 – 2.26 (m, 1H), 2.12 – 2.06 (m, 1H), 1.66 – 1.59 (m, 2H), 1.41 (s, 9H), 1.47 – 1.33 (m, 2H), 1.21 – 1.14 (m, 1H), 1.03 – 0.95 (m, 1H), 0.85 – 0.80 (m, 1H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 3H), 0.72 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.7, 150.8 (*J* = 6.9 Hz), 141.8 (*J*

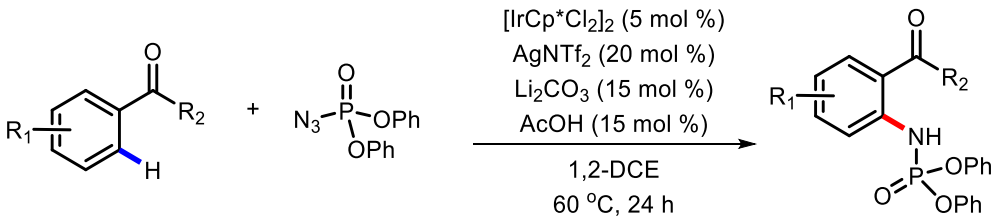
= 2.3 Hz), 132.0, 129.5 (2C), 126.5, 124.7, 120.5, 120.4 (*J* = 4.7 Hz, 2C), 120.3 (*J* = 9.9 Hz), 119.2 (*J* = 2.3 Hz), 79.9 (*J* = 6.4 Hz), 51.9, 48.4 (*J* = 7.5 Hz), 42.7, 34.0, 31.5, 28.7 (3C), 25.5, 22.8, 21.9, 20.9, 15.6; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -3.68; **IR** (cm^{-1}) 3304, 2926, 1639, 1596, 1257, 1162, 942, 753; **High Resolution MS** (EI): Calculated for $C_{27}H_{39}N_2O_4P$ $[M]^+$: 486.2647, Found: 486.2646.

(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl phenyl (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (1R,2R,5R)-5-Isopropyl-2-methylcyclohexyl phenyl (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (Scheme 4, **5b**)



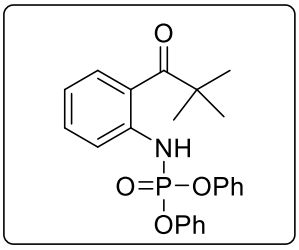
White solid (85 mg, 59%); m.p. 103 – 105 °C; 1 :1 Mixture of diastereomers; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.52 – 9.46 (m, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.27 – 7.23 (m, 2H), 7.20 – 7.16 (m, 2H), 7.11 – 7.07 (m, 1H), 6.90 – 6.86 (m, 1H), 5.93 (s, 1H), 4.52 – 4.45 (m, 1H), 2.00 – 1.90 (m, 2H), 1.83 – 1.74 (m, 2H), 1.73 – 1.68 (m, 1H), 1.67 – 1.60 (m, 2H), 1.56 – 1.47 (m, 3H), 1.46 – 1.40 (m, 1H), 1.41 (s, 9H), 1.37 – 1.27 (m, 4H), 1.27 – 1.17 (m, 4H), 1.15 – 0.91 (m, 11H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.79 (s, 3H), 0.62 (s, 3H), 0.61 – 0.56 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.7, [150.8 (*J* = 7.0 Hz) + 150.8 (*J* = 7.0 Hz)], [141.7 (*J* = 2.3 Hz) + 141.6 (*J* = 2.3 Hz)], [132.1 + 132.0], 129.5 (2C), 126.7, 124.7, 120.5 (*J* = 9.5 Hz), 120.5, 120.4 (*J* = 4.5 Hz, 2C), [119.2 (*J* = 2.3 Hz) + 119.2 (*J* = 2.3 Hz)], [78.6 (*J* = 5.8 Hz) + 78.6 (*J* = 5.8 Hz)], 56.4, 56.3, [54.2 + 54.1], 51.9, 44.7, 42.6, 39.9, 39.5, [36.8 + 36.8], 36.1, [35.9 (*J* = 4.0 Hz) + 35.8 (*J* = 4.0 Hz)], 35.7, 35.4, 35.3, 31.9, [29.4 (*J* = 4.6 Hz) + 29.3 (*J* = 4.6 Hz)], 28.7 (3C), 28.5, 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 21.2, 18.6, [12.2 + 12.2], 12.1; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -4.17; **IR** (cm^{-1}) 3296, 2929, 1638, 1595, 1164, 928, 752; **High Resolution MS** (FAB): Calculated for $C_{44}H_{67}N_2O_4P$ $[M+H]^+$: 719.4917, Found: 719.4914.

2. Ir-Catalyzed Amination of Ketones with Azides (Scheme 2, **3f-3m**)



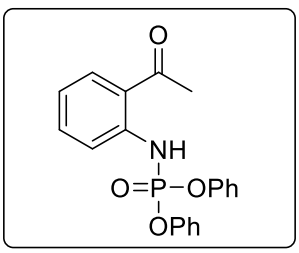
To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added ketone (0.20 mmol), azide (0.24 mmol), $[IrCp^*Cl_2]_2$ (8.0 mg, 0.010 mmol, 5 mol %), $AgNTf_2$ (16 mg, 0.040 mmol, 20 mol %), $LiCO_3$ (2.2 mg, 0.030 mmol, 15 mol %), AcOH (1.8 mg, 0.030 mmol, 15 mol %) and 1,2-dichloroethane (0.50 mL) under atmospheric conditions. The reaction mixture was stirred at 60 °C for 24 h, filtered through a pad of celite and then washed with CH_2Cl_2 (10 mL x 3). Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc or *n*-hexane/EtOAc/CH_2Cl_2) to give the desired product.

Diphenyl (2-pivaloylphenyl)phosphoramidate (Scheme 2, **3f**)



Colorless liquid (75 mg, 91%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.07 (d, *J* = 11.3 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.77 – 7.73 (m, 1H), 7.47 – 7.42 (m, 1H), 7.33 – 7.28 (m, 4H), 7.26 – 7.22 (m, 4H), 7.19 – 7.14 (m, 2H), 7.03 – 6.98 (m, 1H), 1.29 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 211.0, 150.4 (d, *J* = 7.0 Hz, 2C), 140.7 (d, *J* = 1.3Hz), 132.7, 129.8 (4C), 129.7, 125.3 (2C), 123.4 (d, *J* = 8.8 Hz), 120.5, 120.3 (d, *J* = 4.8 Hz, 4C), 120.0 (d, *J* = 1.9 Hz), 45.1, 28.6 (3C); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -8.18; **IR** (cm^{-1}) 3068, 2969, 1637, 1487, 1450, 1388, 1281, 1184, 936, 756; **High Resolution MS (**EI): Calculated for $C_{23}H_{24}NO_4P$ $[M]^+$: 409.1443, Found: 409.1445.

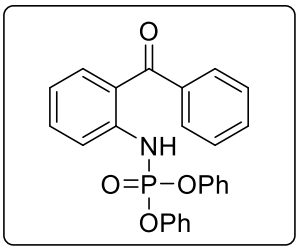
Diphenyl (2-acetylphenyl)phosphoramidate (Scheme 2, **3g**)



White solid (72 mg, 98%); m.p. 88 – 90 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.63 (d, *J* = 11.7 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.30 (t, *J* = 7.8 Hz, 4H), 7.24 (d, *J* = 8.1 Hz, 4H), 7.15 (t, *J* = 7.4 Hz, 2H), 7.04 – 6.99 (m, 1H), 2.59 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 202.2, 150.4 (d, *J* = 7.4 Hz, 2C), 142.7, 135.0, 132.0, 129.8 (4C), 125.3 (2C), 121.2 (d, *J* = 9.2 Hz), 120.9, 120.3 (d, *J* = 4.7 Hz, 4C), 118.9 (d, *J* = 1.6 Hz), 28.1;

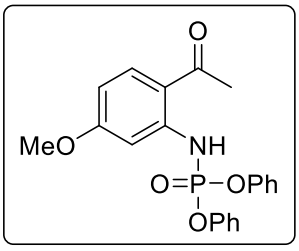
^{31}P NMR (243 MHz, $CDCl_3$) δ -8.53; **IR** (cm^{-1}) 3059, 1646, 1485, 1181, 941, 759; **High Resolution MS** (EI): Calculated for $C_{20}H_{18}NO_4P$ $[M]^+$: 367.0973, Found: 367.0974.

Diphenyl (2-benzoylphenyl)phosphoramidate (Scheme 2, **3h**)



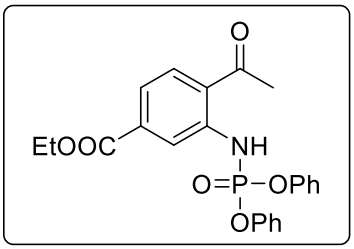
Yellow liquid (48 mg, 55%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.76 (d, *J* = 11.1 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.58 – 7.50 (m, 3H), 7.48 – 7.42 (m, 2H), 7.34 – 7.22 (m, 8H), 7.15 (t, *J* = 7.2 Hz, 2H), 7.01 – 6.96 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.5, 150.4 (d, *J* = 7.2 Hz, 2C), 142.7, 138.6, 134.4, 134.3, 132.1, 129.8 (4C), 129.6 (2C), 128.2 (2C), 125.4 (2C), 122.2 (d, *J* = 9.2 Hz), 120.6, 120.3 (d, *J* = 5.1 Hz, 4C), 119.2 (d, *J* = 1.3 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -8.40; **IR** (cm^{-1}) 3062, 1630, 1486, 1282, 1183, 934, 750; **High Resolution MS** (EI): Calculated for $C_{25}H_{20}NO_4P$ $[M]^+$: 429.1130, Found: 429.1127.

Diphenyl (2-acetyl-5-methoxyphenyl)phosphoramidate (Scheme 2, **3i**)



White solid (79 mg, 99%); m.p. 83 – 85 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.02 (d, *J* = 11.7 Hz, 1H), 7.74 (dd, *J* = 8.9, 1.6 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.26 (d, *J* = 8.9 Hz, 4H), 7.16 (t, *J* = 7.3 Hz, 2H), 6.52 (dd, *J* = 8.9, 2.3 Hz, 1H), 3.83 (s, 3H), 2.52 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.6, 164.6, 150.4 (d, *J* = 7.0 Hz, 2C), 145.5, 134.0, 129.8 (4C), 125.4 (2C), 120.3 (d, *J* = 4.8 Hz, 4C), 115.1 (d, *J* = 9.0 Hz), 108.0, 102.7, 55.5, 27.7; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -8.55; **IR** (cm^{-1}) 3068, 2941, 1634, 1488, 1270, 1187, 933, 756; **High Resolution MS** (EI): Calculated for $C_{21}H_{20}NO_5P$ $[M]^+$: 397.1079, Found: 397.1078.

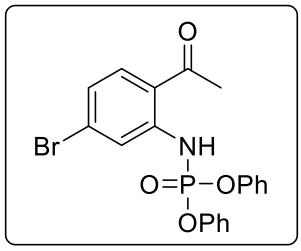
Ethyl 4-acetyl-3-((diphenoxyphosphoryl)amino)benzoate (Scheme 2, **3j**)



Yellow liquid (57 mg, 65%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.50 (d, *J* = 11.7 Hz, 1H), 8.41 (d, *J* = 1.8 Hz, 1H), 7.91 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.67 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.35 – 7.29 (m, 4H), 7.26 (d, *J* = 8.1 Hz, 4H), 7.17 (t, *J* = 7.3 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.64 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 201.9, 165.2, 150.3 (d, *J* = 7.0 Hz, 2C), 142.5, 135.8, 131.9, 129.8 (4C), 125.4 (2C), 123.7 (d, *J* = 8.6 Hz), 121.5, 120.3 (d, *J* = 4.6 Hz, 4C), 119.92 (d, *J* = 1.8 Hz), 61.7, 28.4, 14.2; **^{31}P NMR** (243 MHz, $CDCl_3$)

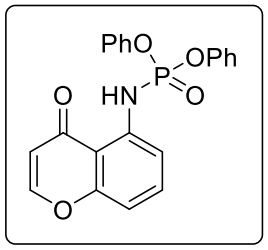
δ -9.16; **IR** (cm^{-1}) 3069, 2982, 1719, 1655, 1487, 1300, 1234, 1184, 933, 763; **High Resolution MS** (EI): Calculated for $C_{23}H_{22}NO_6P$ $[M]^+$: 439.1185, Found:439.1183.

Diphenyl (2-acetyl-5-bromophenyl)phosphoramidate (Scheme 2, **3k**)



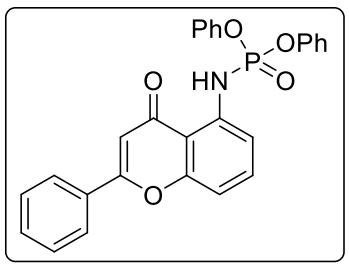
Colorless solid (71 mg, 80%); m.p. 116 – 118 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.67 (d, *J* = 11.2 Hz, 1H), 7.94 (d, *J* = 1.8 Hz, 1H), 7.68 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.36 – 7.30 (m, 4H), 7.25 (d, *J* = 7.8 Hz, 4H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.15 (dd, *J* = 8.5, 1.8 Hz, 1H), 2.57 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 201.5, 150.2 (d, *J* = 7.1 Hz, 2C), 143.9, 133.0, 129.9, 129.9 (4C), 125.5 (2C), 124.2, 121.9 (d, *J* = 1.8 Hz), 120.3 (d, *J* = 5.1 Hz, 4C), 119.9 (d, *J* = 9.0 Hz), 28.1; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -9.34; **IR** (cm^{-1}) 3069, 1641, 1488, 1283, 1183, 928, 753; **High Resolution MS** (EI): Calculated for $C_{20}H_{17}BrNO_4P$ $[M]^+$: 445.0079, Found: 445.0078.

Diphenyl (4-oxo-4H-chromen-5-yl)phosphoramidate (Scheme 2, **3l**)



Brown liquid (60 mg, 76%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.31 (d, *J* = 11.8 Hz, 1H), 7.75 (d, *J* = 5.8 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.35 – 7.29 (m, 4H), 7.27 (d, *J* = 8.4 Hz, 4H), 7.17 (t, *J* = 7.3 Hz, 2H), 7.02 – 6.97 (m, 1H), 6.23 (d, *J* = 5.9 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 181.4, 157.5, 154.9, 150.34 (d, *J* = 6.9 Hz, 2C), 142.7 (d, *J* = 3.1 Hz), 134.6, 129.8 (4C), 125.4 (2C), 120.3 (d, *J* = 4.8 Hz, 4C), 112.8 (2C), 112.3 (d, *J* = 10.3 Hz), 109.9; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -8.89; **IR** (cm^{-1}); 3067, 1638, 1483, 1262, 1183, 931,760; **High Resolution MS** (EI): Calculated for $C_{21}H_{16}NO_5P$ $[M]^+$: 393.0766, Found: 393.0767.

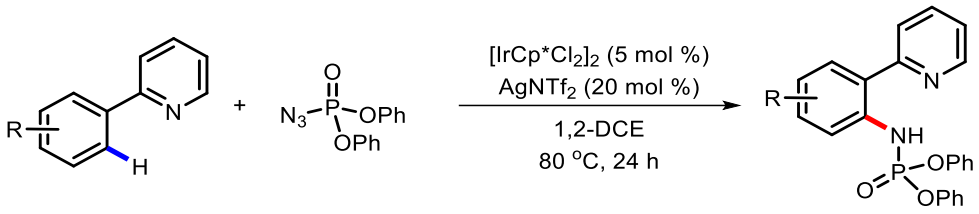
Diphenyl (4-oxo-2-phenyl-4H-chromen-5-yl)phosphoramidate (Scheme 2, **3m**)



Light yellow solid (84 mg, 90%); m.p. 140 – 142 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.49 (d, *J* = 12.0 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.61 – 7.55 (m, 2H), 7.55 – 7.46 (m, 3H), 7.36 – 7.28 (m, 8H), 7.17 (t, *J* = 7.0 Hz, 2H), 7.13 – 7.07 (m, 1H), 6.70 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 182.0, 163.1, 157.3 (d, *J* = 1.5 Hz), 150.4 (d, *J* = 6.9 Hz, 2C), 142.6 (d, *J* = 1.9 Hz), 134.6, 131.9, 131.0, 129.8 (4C), 129.1 (2C), 126.3 (2C), 125.4 (2C), 120.4 (d, *J* = 4.6 Hz, 4C), 112.8 (d, *J* = 1.5 Hz), 111.3 (d, *J* = 10.4 Hz), 109.8, 107.2;

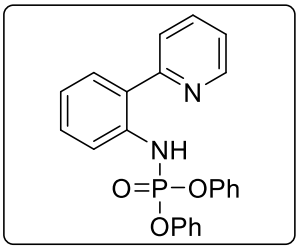
^{31}P NMR (243 MHz, $CDCl_3$) δ -8.72; **IR** (cm^{-1}) 3059, 1632, 1484, 1282, 1183, 931, 766; **High Resolution MS** (EI): Calculated for $C_{27}H_{20}NO_5P$ $[M]^+$: 469.1079, Found: 469.1078.

3. Ir-Catalyzed Amination of Pyridines with Azides (Scheme 2, **3n**-**3s** & **3u**)



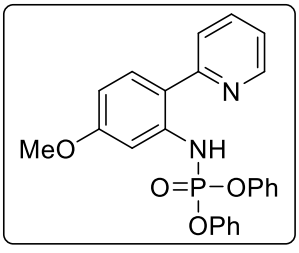
To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added ketone (0.20 mmol), azide (0.24 mmol), $[IrCp^*Cl_2]_2$ (8.0 mg, 0.010 mmol, 5 mol %), $AgNTf_2$ (16 mg, 0.040 mmol, 20 mol %) and 1,2-dichloroethane (0.50 mL) under atmospheric conditions. The reaction mixture was stirred at 80 °C for 24 h, filtered through a pad of celite and then washed with CH_2Cl_2 (10 mL x 3). Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc or *n*-hexane/EtOAc/CH_2Cl_2) to give the desired product.

Diphenyl (2-(pyridin-2-yl)phenyl)phosphoramidate (Scheme 2, **3n**)



Brown liquid (45 mg, 56%); **^{1}H NMR** (600 MHz, CD_2Cl_2) δ 11.60 (d, *J* = 12.0 Hz, 1H), 8.51 (d, *J* = 4.3 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.79 – 7.71 (m, 3H), 7.44 – 7.39 (m, 1H), 7.33 – 7.28 (m, 4H), 7.27 – 7.21 (m, 5H), 7.19 – 7.14 (m, 2H), 7.14 – 7.10 (m, 1H); **^{13}C NMR** (150 MHz, CD_2Cl_2) δ 157.5, 150.6 (d, *J* = 6.9 Hz, 2C), 146.9, 139.4, 137.7, 130.3, 129.6 (4C), 128.7, 125.1 (2C), 123.9 (d, *J* = 9.9 Hz), 122.0, 121.9, 121.8, 120.3 (d, *J* = 4.8 Hz, 4C), 119.5; **^{31}P NMR** (243 MHz, CD_2Cl_2) δ -7.50; **IR** (cm^{-1}) 3062, 1487, 1185, 931, 751; **High Resolution MS** (ESI): Calculated for $C_{23}H_{19}N_2O_3P$ $[M+Na]^+$: 425.1031, Found: 425.1021.

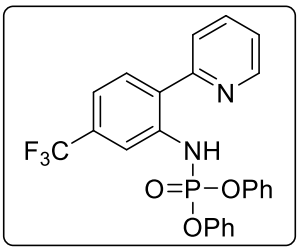
Diphenyl (5-methoxy-2-(pyridin-2-yl)phenyl)phosphoramidate (Scheme 2, **3o**)



Yellow liquid (59 mg, 68%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 12.09 (d, *J* = 12.1 Hz, 1H), 8.41 (d, *J* = 4.9 Hz, 1H), 7.74 – 7.68 (m, 1H), 7.68 – 7.61 (m, 2H), 7.30 (d, *J* = 2.4 Hz, 1H), 7.29 – 7.23 (m, 8H), 7.16 – 7.07 (m, 3H), 6.62 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.85 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.1, 157.6, 150.6 (d, *J* = 6.9 Hz, 2C), 146.7, 141.3, 137.3, 129.6 (4C),

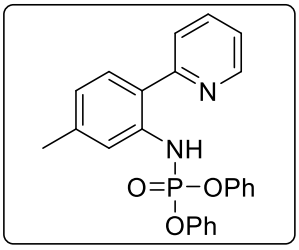
129.6, 125.1 (2C), 120.9, 120.8, 120.4 (d, *J* = 4.6 Hz, 4C), 116.6 (d, *J* = 10.0 Hz), 108.2, 104.4 (d, *J* = 1.6 Hz), 55.34; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.69; **IR** (cm^{-1}) 3065, 1487, 1277, 1185, 929, 771; **High Resolution MS** (EI): Calculated for $C_{24}H_{21}N_2O_4P$ $[M]^+$: 432.1239, Found: 432.1237.

Diphenyl (2-(pyridin-2-yl)-5-(trifluoromethyl)phenyl)phosphoramidate (Scheme 2, **3p**)



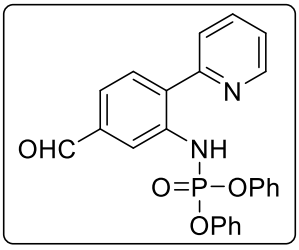
Colorless liquid (71 mg, 75%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.69 (d, *J* = 11.7 Hz, 1H), 8.55 (d, *J* = 4.7 Hz, 1H), 8.00 (s, 1H), 7.85 – 7.80 (m, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.24 (m, 5H), 7.23 (d, *J* = 8.1 Hz, 4H), 7.16 – 7.10 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.4, 150.4 (d, *J* = 6.8 Hz, 2C), 147.3, 140.0, 137.8, 132.0 (q, *J* = 32.4 Hz), 129.7 (4C), 129.1, 126.6 (d, *J* = 10.1 Hz), 125.2 (2C), 123.73 (q, *J* = 272.5 Hz), 122.6, 122.3, 120.3 (d, *J* = 4.7 Hz, 4C), 118.1 (q, *J* = 3.6 Hz), 116.4; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -8.52; **IR** (cm^{-1}) 3065, 1488, 1333, 1185, 931, 771; **High Resolution MS** (EI): Calculated for $C_{24}H_{18}F_3N_2O_3P$ $[M]^+$: 470.1007, Found: 470.1005.

Diphenyl (5-methyl-2-(pyridin-2-yl)phenyl)phosphoramidate (Scheme 2, **3q**)



Colorless liquid (67 mg, 80%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.77 (d, *J* = 11.9 Hz, 1H), 8.42 (d, *J* = 5.4 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.30 – 7.23 (m, 8H), 7.15 – 7.09 (m, 3H), 6.88 (d, *J* = 7.9 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.7, 150.7 (d, *J* = 7.1 Hz, 2C), 146.9, 140.7, 139.5, 137.3, 129.6 (4C), 128.5, 125.1 (2C), 122.8, 121.4, 121.3, 121.1 (d, *J* = 9.9 Hz), 120.4 (d, *J* = 4.9 Hz, 4C), 120.1, 21.6; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.44; **IR** (cm^{-1}) 3059, 2950, 1274, 1185, 927, 753; **High Resolution MS** (EI): Calculated for $C_{24}H_{21}N_2O_3P$ $[M]^+$: 416.1290, Found: 416.1287.

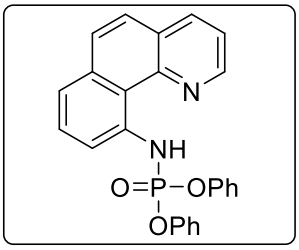
Diphenyl (5-formyl-2-(pyridin-2-yl)phenyl)phosphoramidate (Scheme 2, **3r**)



Yellow liquid (42 mg, 49%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.69 (d, *J* = 11.7 Hz, 1H), 10.04 (s, 1H), 8.53 (d, *J* = 4.8 Hz, 1H), 8.23 (s, 1H), 7.88 – 7.79 (m, 2H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.21 (m, 9H), 7.12 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 191.6, 156.5, 150.4 (d, *J* = 6.9 Hz, 2C), 147.3, 140.3, 137.8, 137.3, 129.7 (4C), 129.7, 129.3, 128.8 (d, *J* = 10.3 Hz), 125.3 (2C), 122.7 (d, *J* = 13.5 Hz), 121.9, 121.1, 120.3 (d, *J* = 4.6

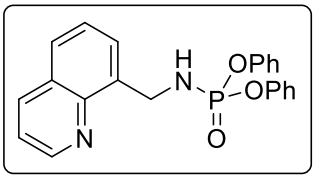
Hz, 4C); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -8.21; **IR** (cm^{-1}) 3062, 2849, 1693, 1486, 1184, 926, 766; **High Resolution MS** (ESI): Calculated for $C_{24}H_{19}N_2O_4P$ $[M+Na]^+$: 453.0980, Found: 453.0995.

Diphenyl benzo[h]quinolin-10-ylphosphoramidate (Scheme 2, **3s)**



Yellow solid (51 mg, 60%); m.p. 113 – 115 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) 14.08 (d, *J* = 8.4 Hz, 1H), 8.78 – 8.71 (m, 1H), 8.19 – 8.14 (m, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.36 – 7.30 (m, 4H), 7.29 – 7.24 (m, 4H), 7.11 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.8 (d, *J* = 7.1 Hz, 2C), 147.8, 145.5, 140.7, 136.3, 135.4, 129.7 (4C), 129.1, 128.8, 127.1, 125.3, 125.1 (2C), 121.2, 120.8, 120.5 (d, *J* = 4.5 Hz, 4C), 117.1 (d, *J* = 10.4 Hz), 116.0 (d, *J* = 3.2 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.45; **IR** (cm^{-1}) 3429, 3241, 1485, 1188, 950, 755; **High Resolution MS** (EI): Calculated for $C_{25}H_{19}N_2O_3P$ $[M]^+$: 426.1133, Found: 426.1130.

Diphenyl (quinolin-8-ylmethyl)phosphoramidate (Scheme 2, **3u**)

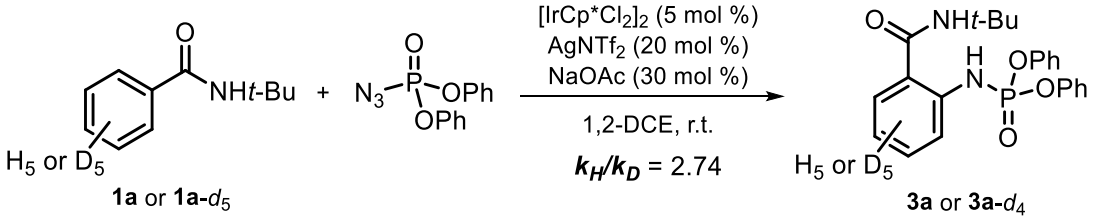


Yellow solid (32 mg, 41%); m.p. 81 – 83 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.85 – 8.82 (m, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 6.9 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.19 (dd, *J* = 7.8 Hz, 4H), 7.12 (d, *J* = 8.0 Hz, 4H), 7.08 – 7.03 (m, 2H), 4.92 (s, 1H), 4.80 – 4.74 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.8 (d, *J* = 7.0 Hz, 2C), 149.2, 129.4 (4C), 136.7, 136.5, 128.8, 128.4, 127.6 (2C), 126.4, 124.6 (2C), 121.1, 120.2 (d, *J* = 4.7 Hz, 4C), 44.0; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -0.54; **IR** (cm^{-1}) 3216, 2063, 2922, 1589, 1487, 1189, 924, 766; **High Resolution MS** (EI): Calculated for $C_{22}H_{19}N_2O_3P$ $[M]^+$: 390.1133, Found: 390.1135

VI. Experimental Procedures of Mechanistic Studies

Kinetic Isotope Effects: Initial Rate Comparison Test

To a J-Young NMR tube were added *N-tert*-butylbenzamide (**1a**, 35 mg, 0.20 mmol) or *N-tert*-butyl-d_5-benzamide (**1a**-d_5, 37 mg, 0.20 mmol), diphenyl phosphoryl azide (52 μL, 0.24 mmol), $[IrCp^*Cl_2]_2$ (8.0 mg, 0.010 mmol, 5.0 mol %), $AgNTf_2$ (16 mg, 0.040 mmol, 20 mol %), NaOAc (4.9 mg, 0.060 mmol, 30 mol %) and 1,2-dichloroethane(d_4) (0.5 mL) under atmospheric conditions. The NMR tube was gently shaken to insure through mixing and started to measure its conversion over 190 min at 25 °C using an internal standard (dibromomethane). The KIE value (k_H/k_D = 2.7) was determined by comparing the relative initial rates.



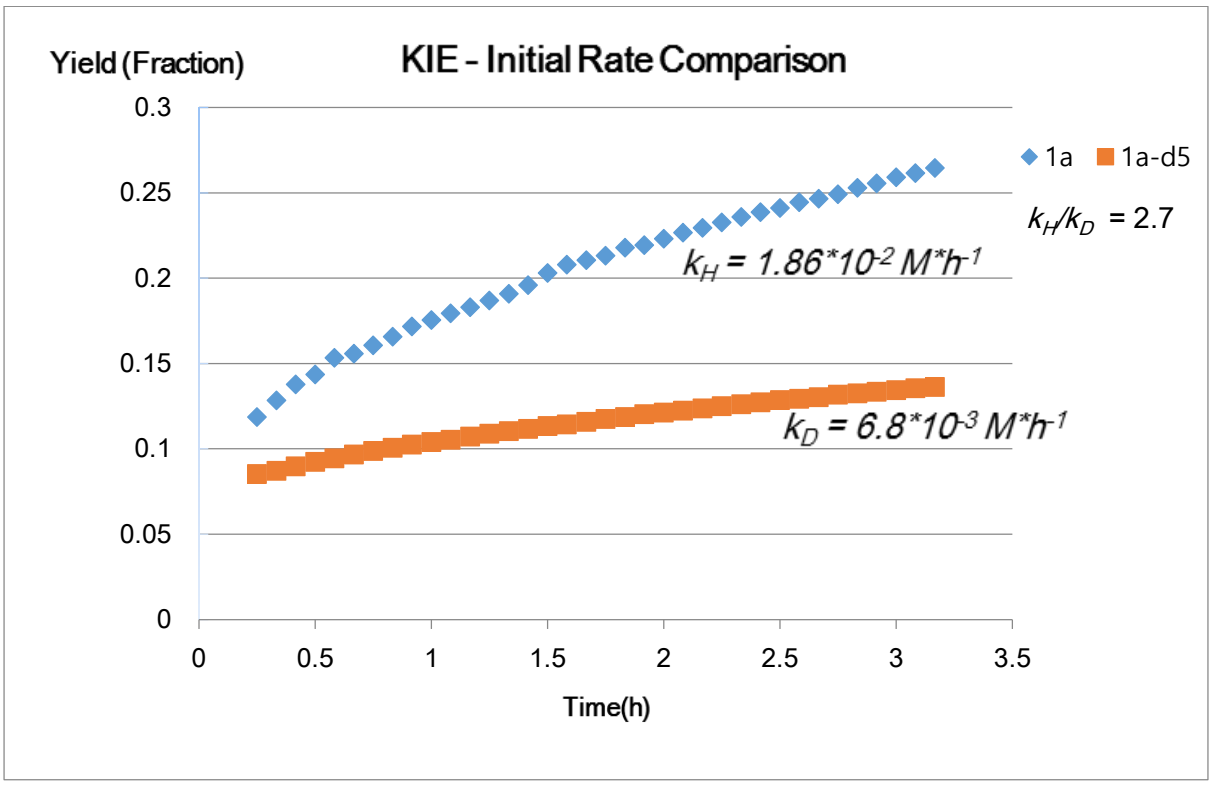


Figure S1. Initial rate of *N-tert*-butylbenzamide (**1a**, blue diamond) or *N-tert*-butylbenzamide-d_5 (**1a-*d*$_5$**, red square).

VII. References

(1) Ryu, J.; Shin, K.; Park, S. H.; Kim, J. Y.; Chang, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 9904.

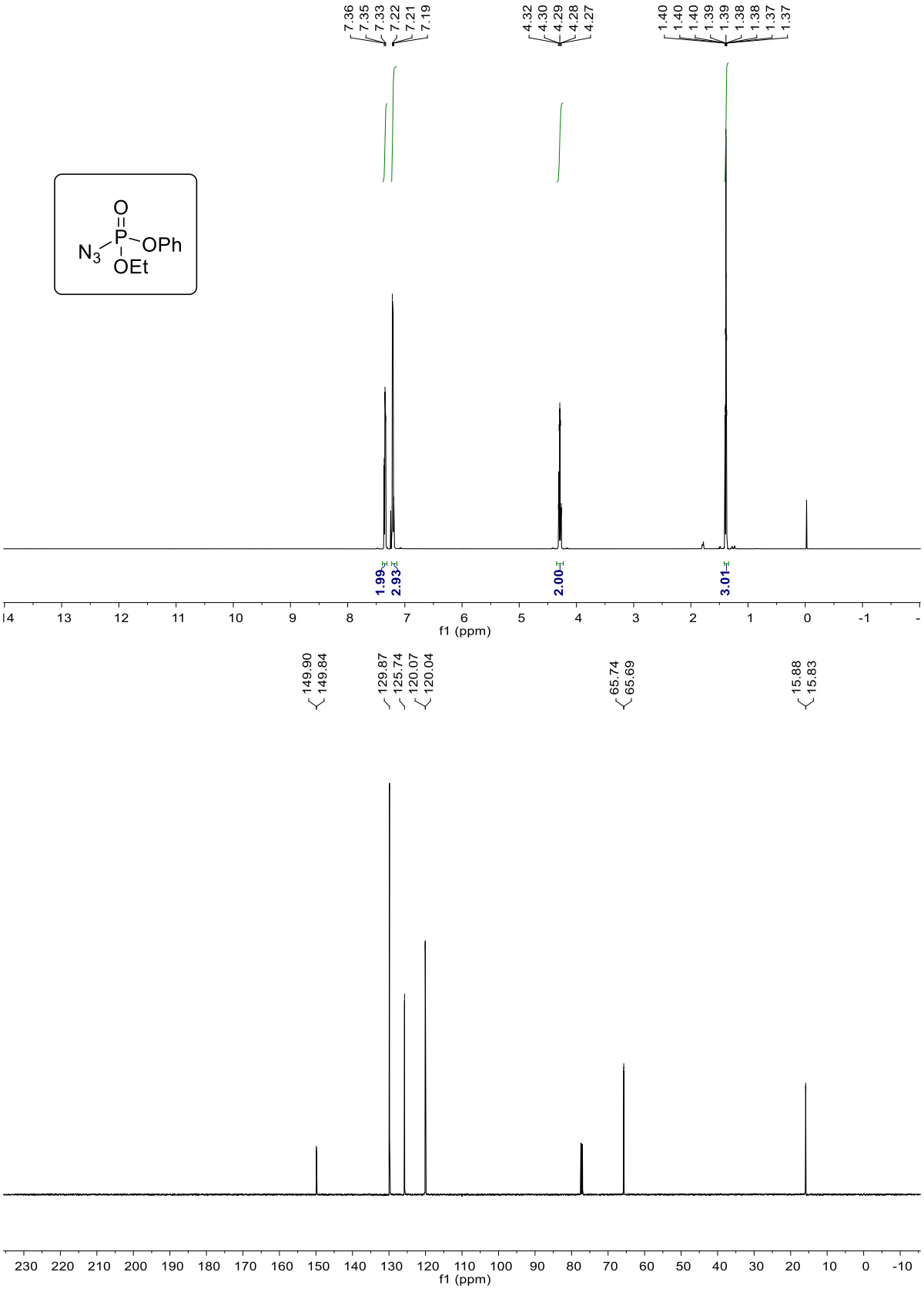
(2) Kim, J. Y.; Park, S. H.; Ryu, J.; Cho, S. H.; Kim, S. H; Chang, S. *J. Am. Chem. Soc.* **2012**, *134*, 9110.

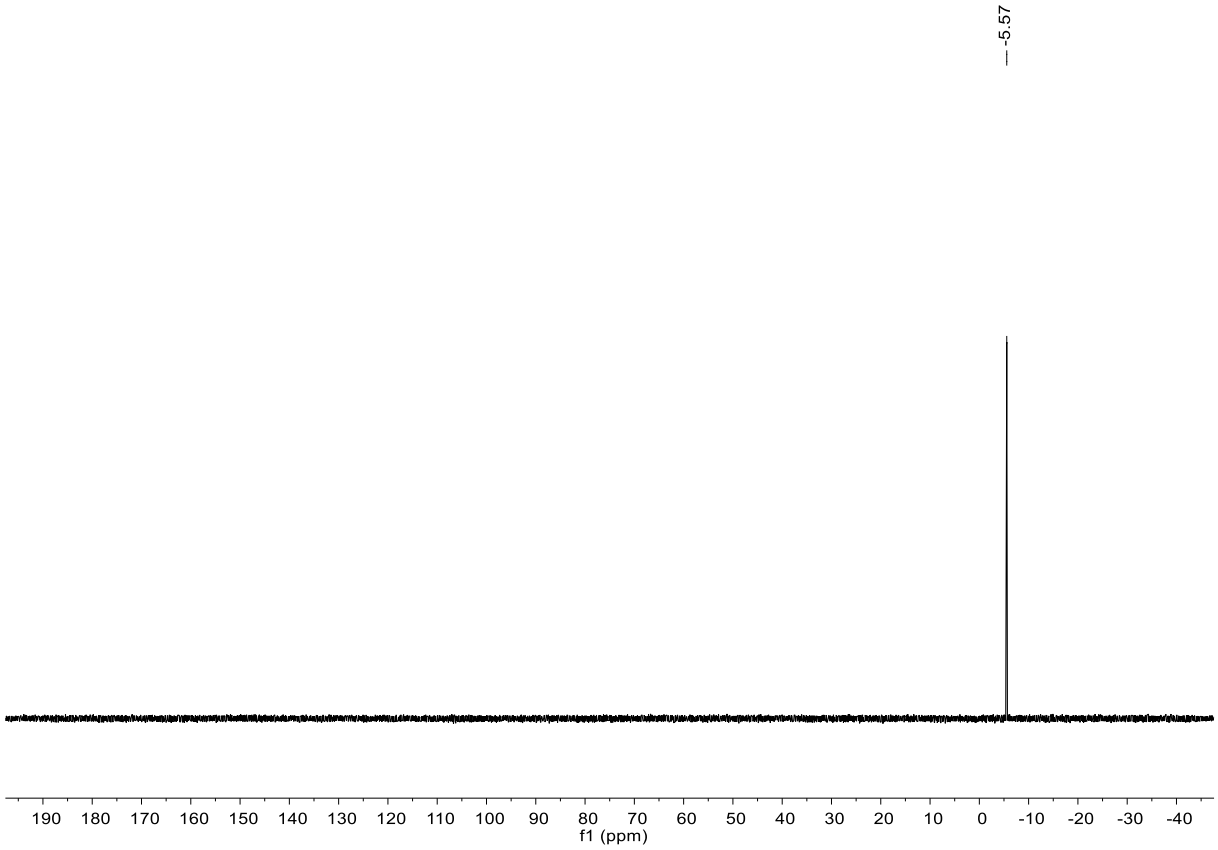
(3) Kim, S. H.; Jung, D. Y.; Chang S. *J. Org. Chem.* **2007**, *72*, 9769.

Appendix I

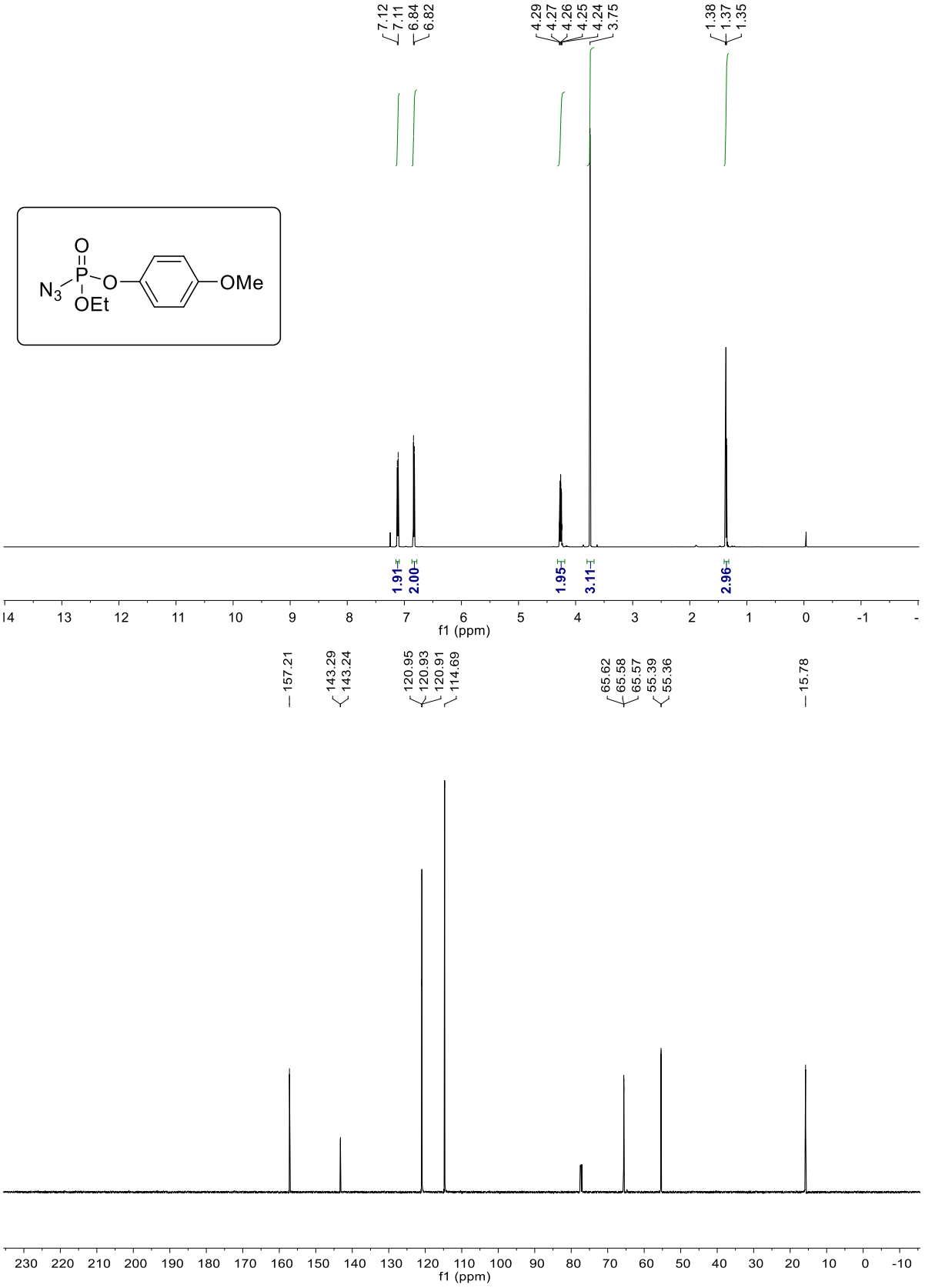
Spectral Copies of ^{1}H, ^{13}C and ^{31}P NMR of Compounds Obtained in this Study

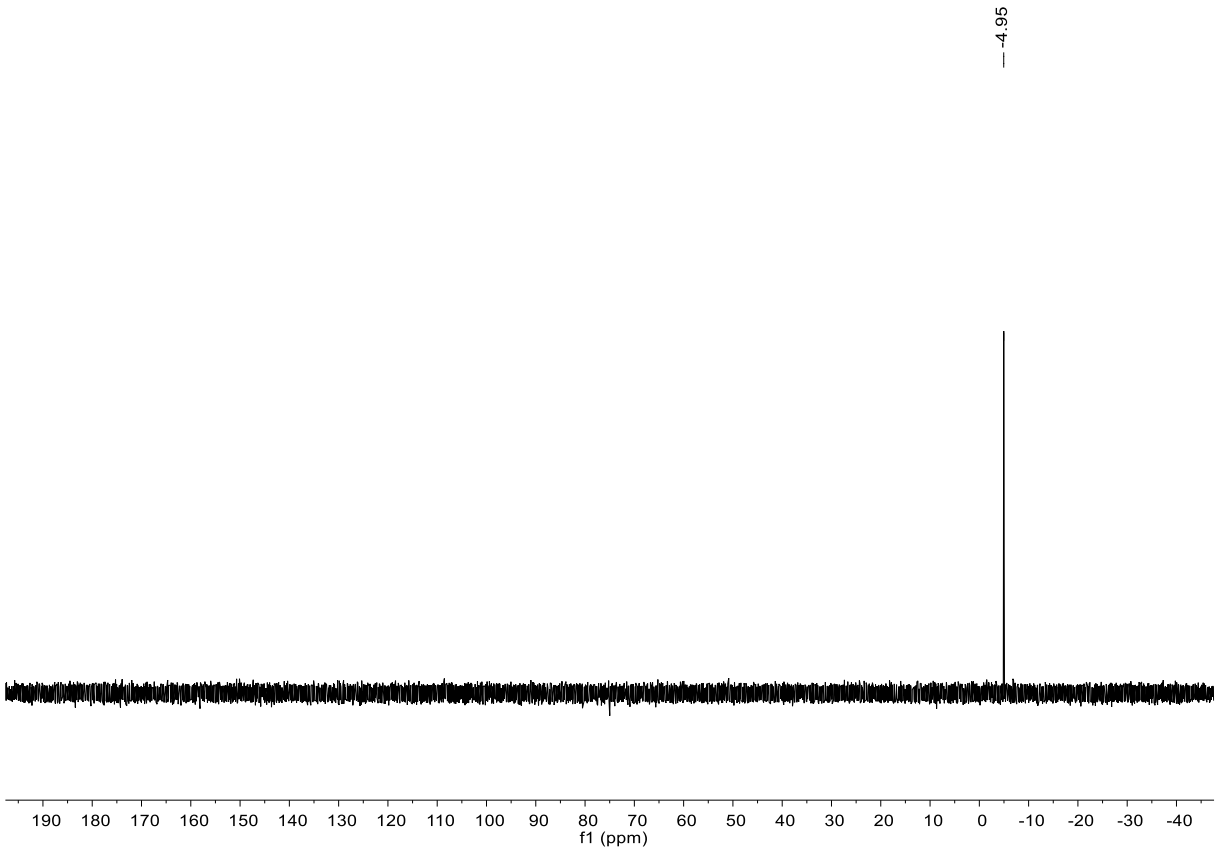
Ethyl phenyl phosphorazidate



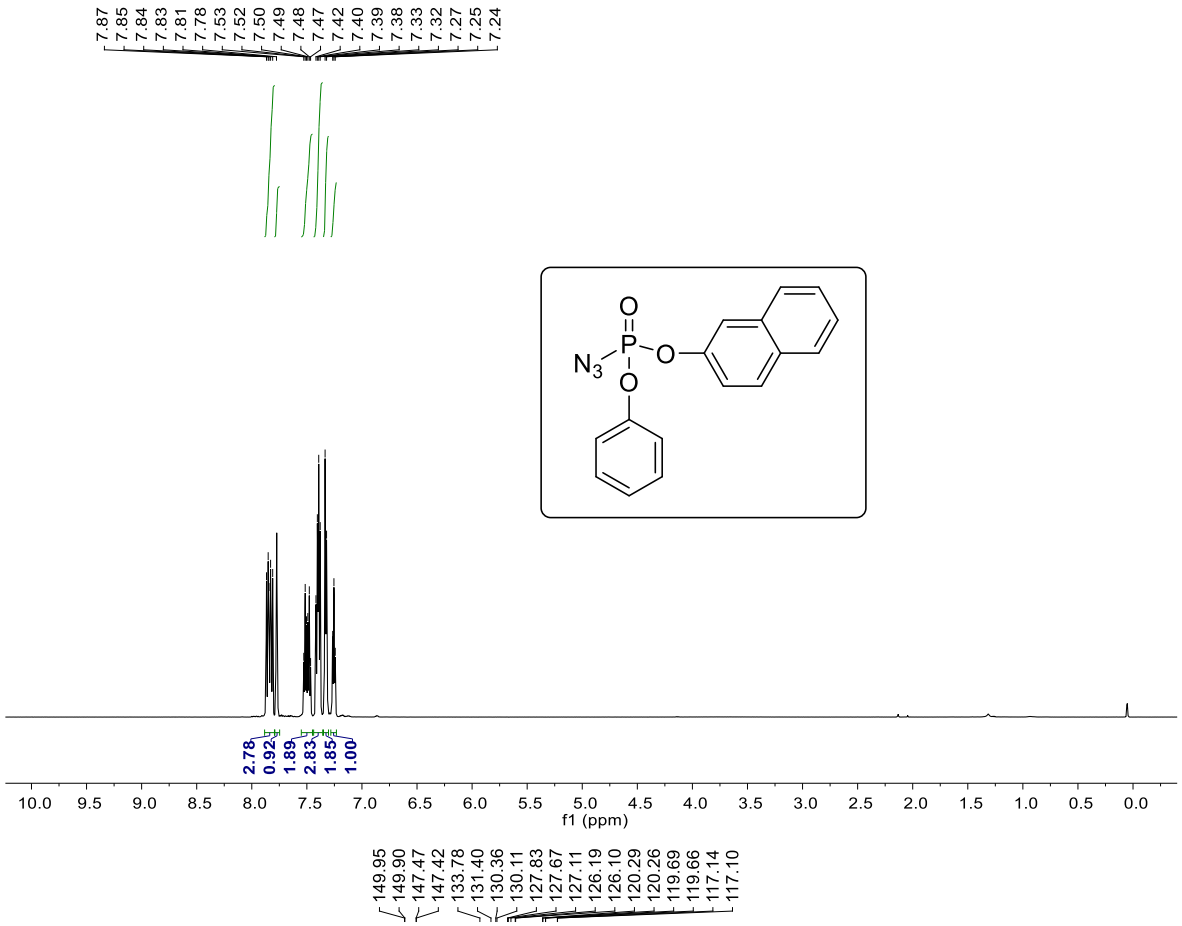

-5.57
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

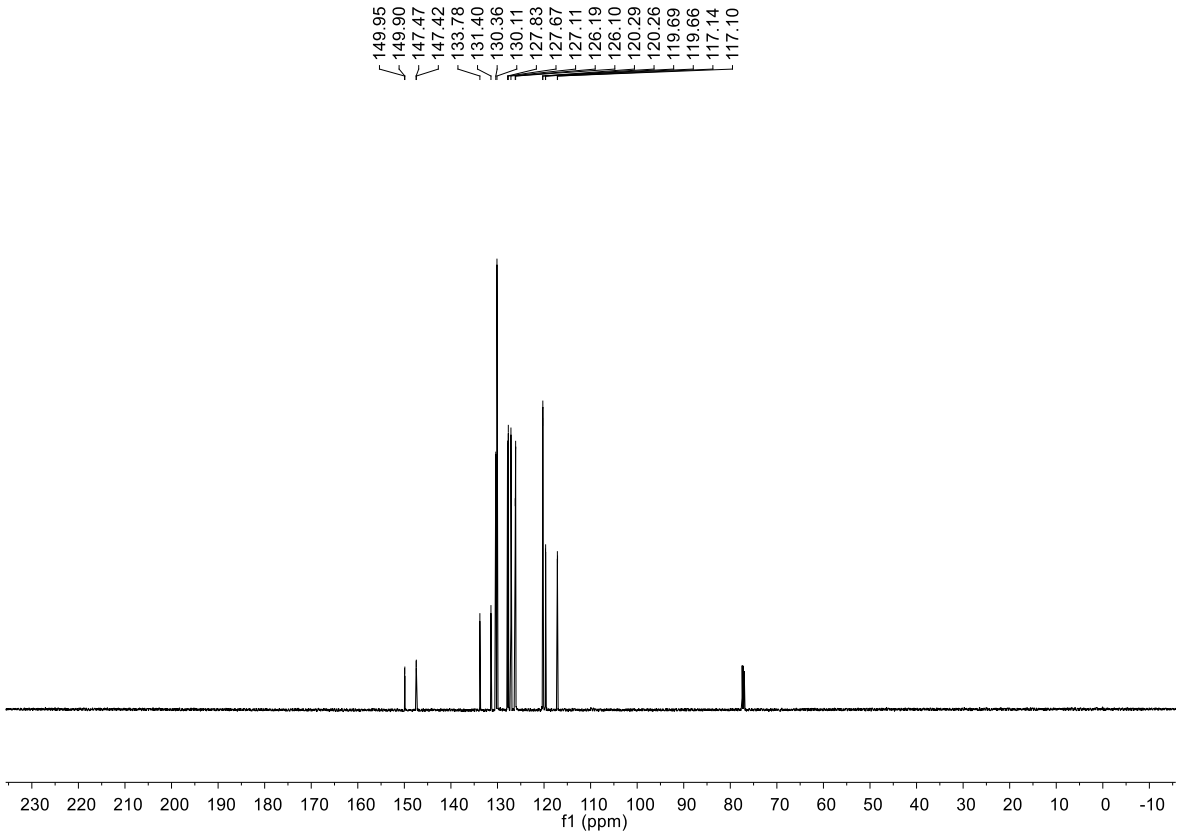
Ethyl (4-methoxyphenyl) phosphorazidate

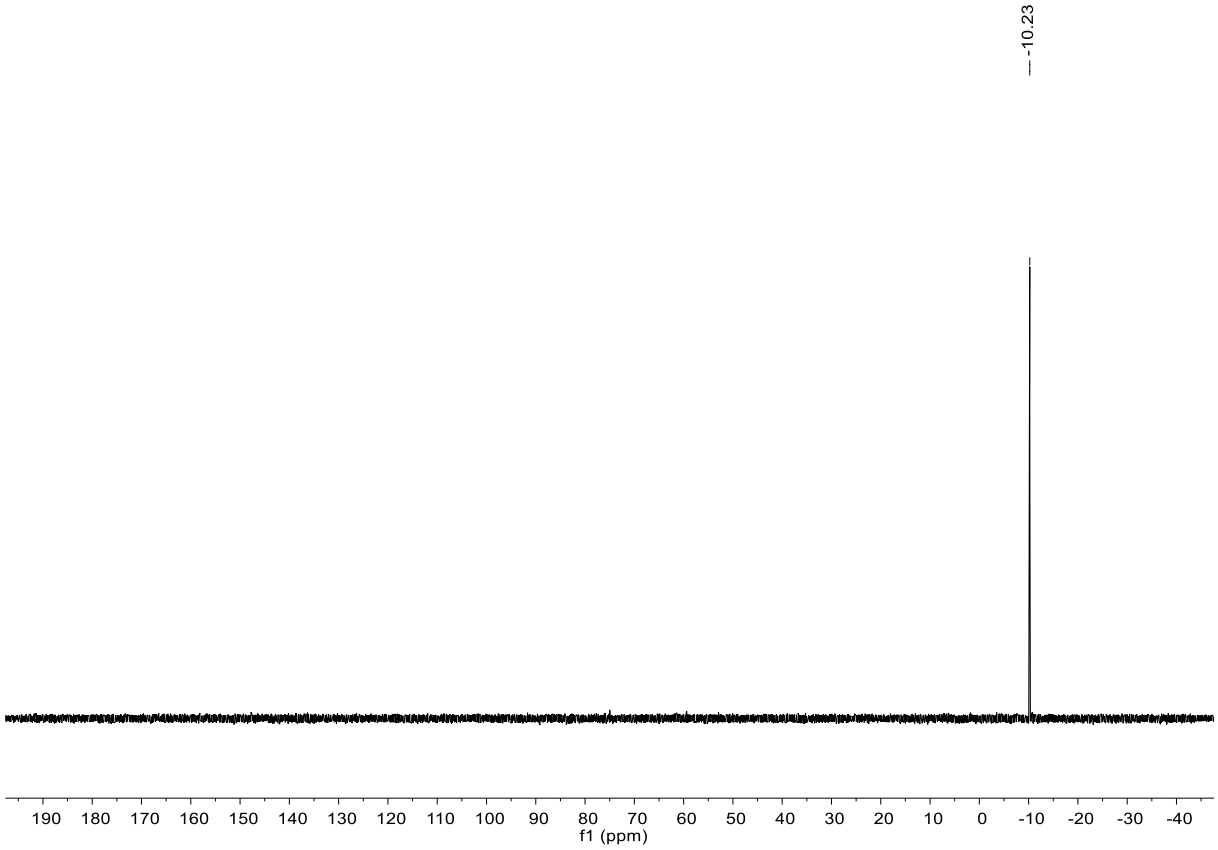



-4.95
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

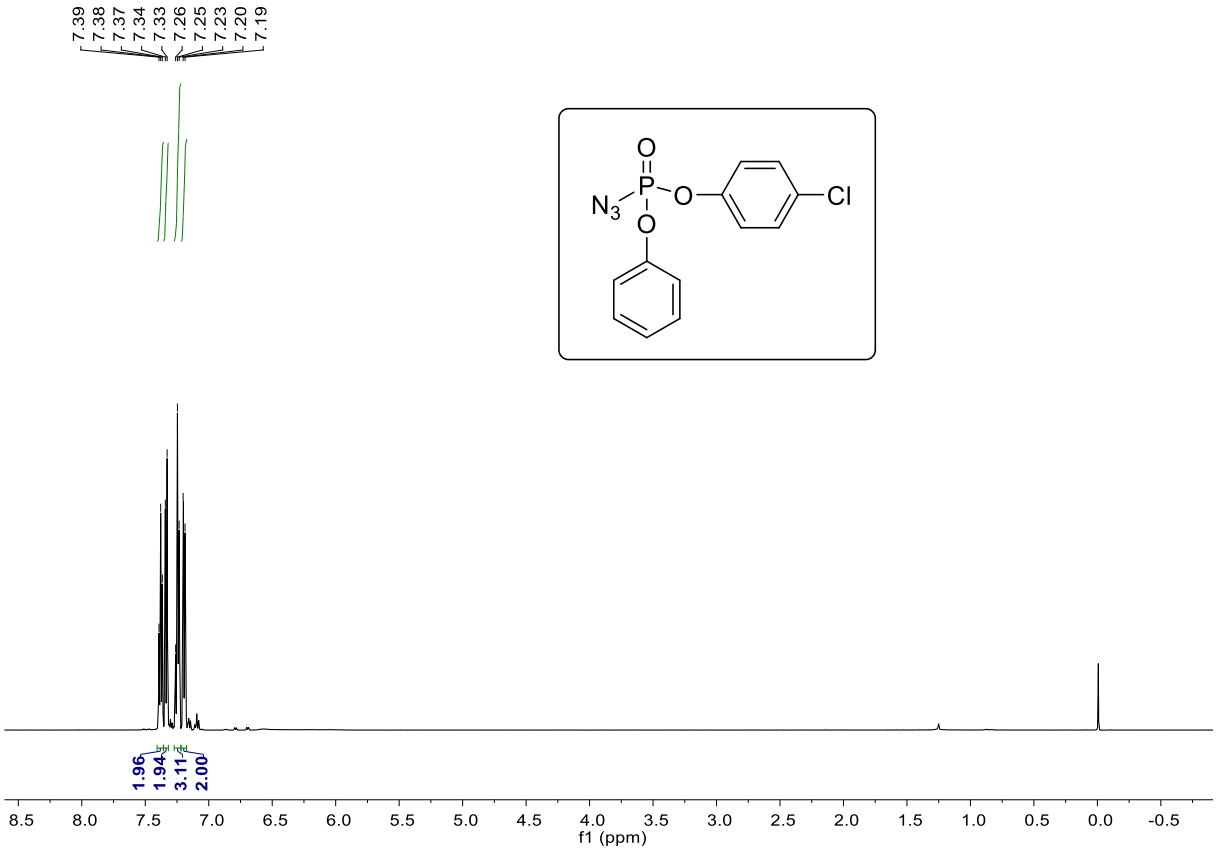
Naphthalen-2-yl phenyl phosphorazidate

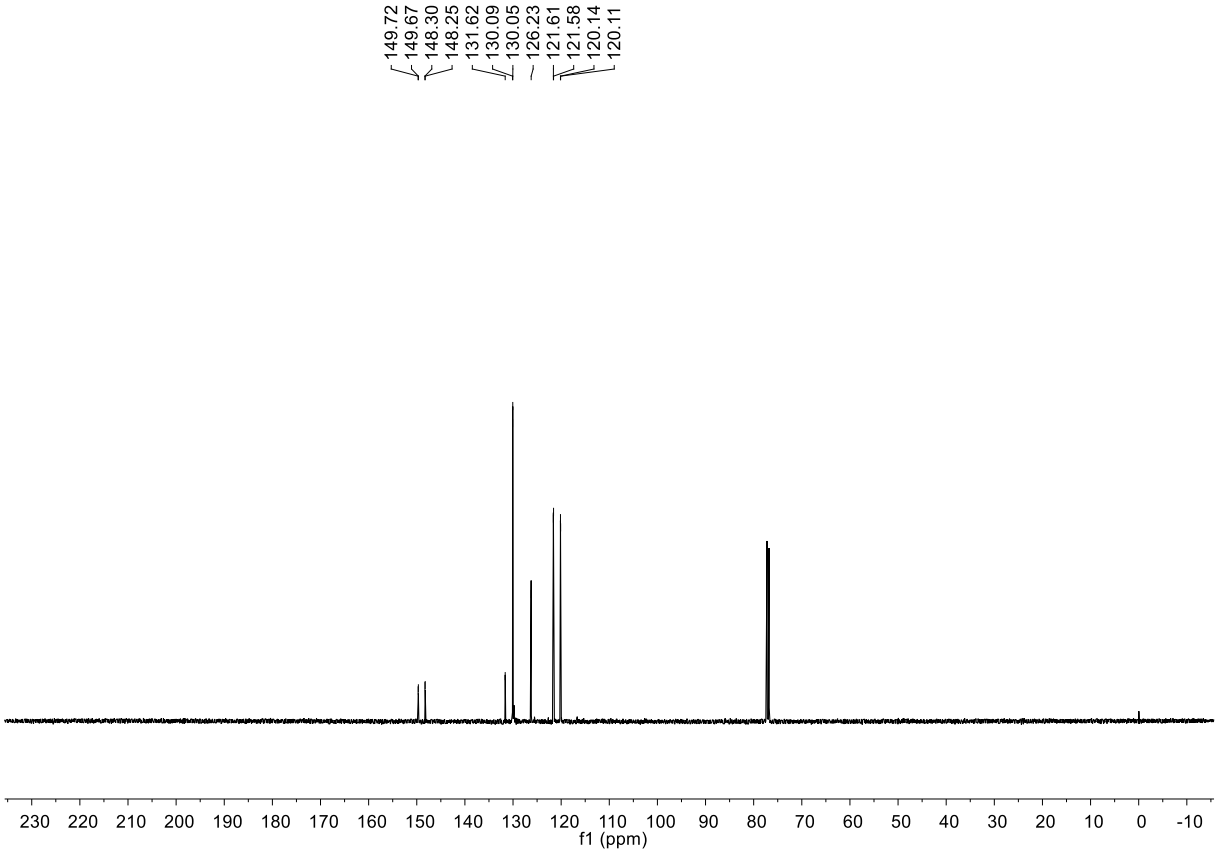


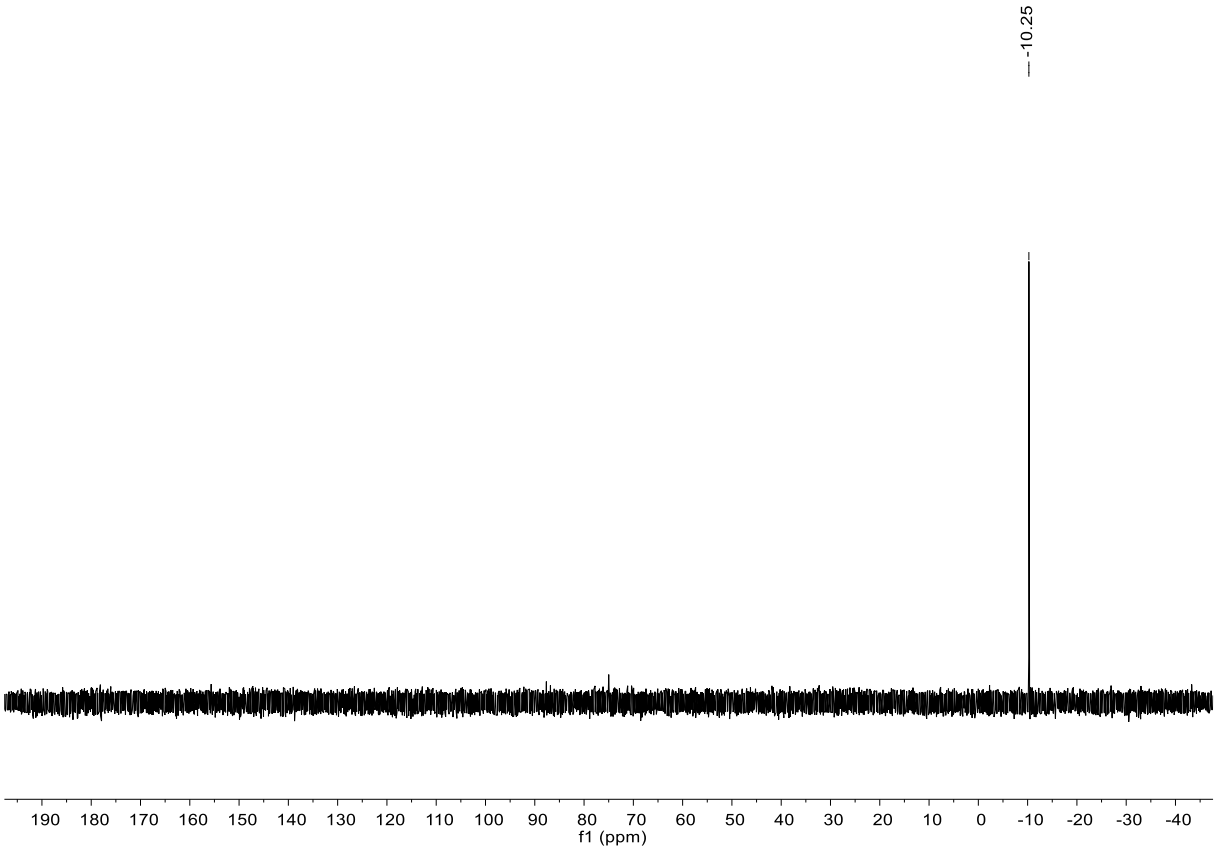



-10.23
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

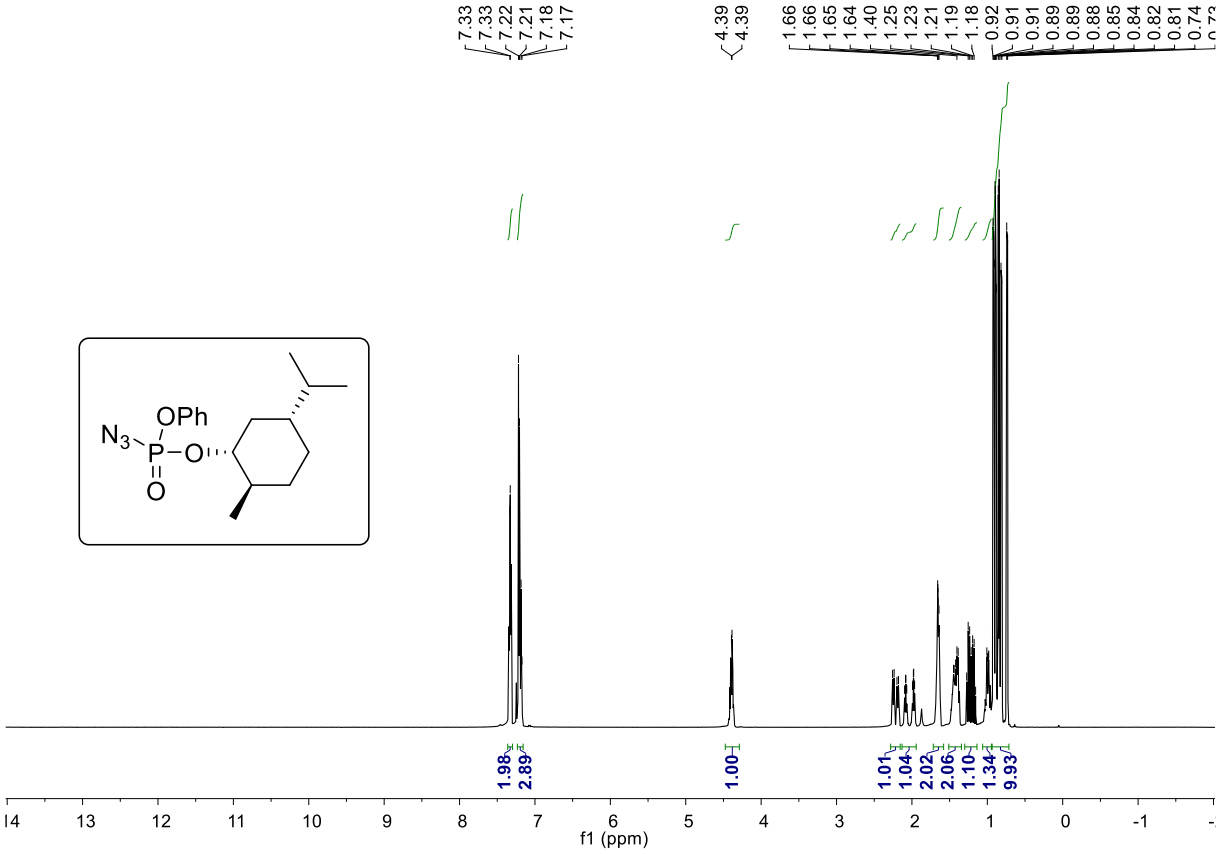
4-Chlorophenyl phenyl phosphorazidate

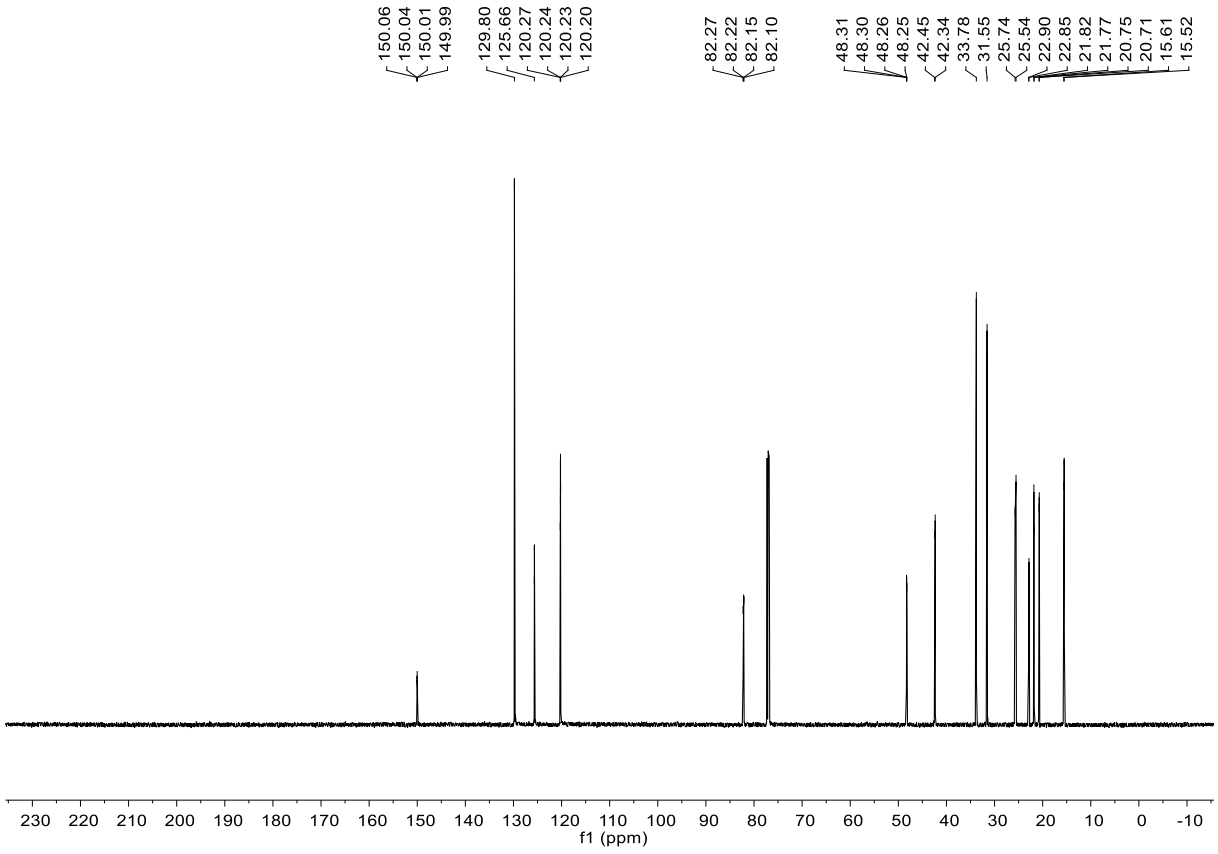


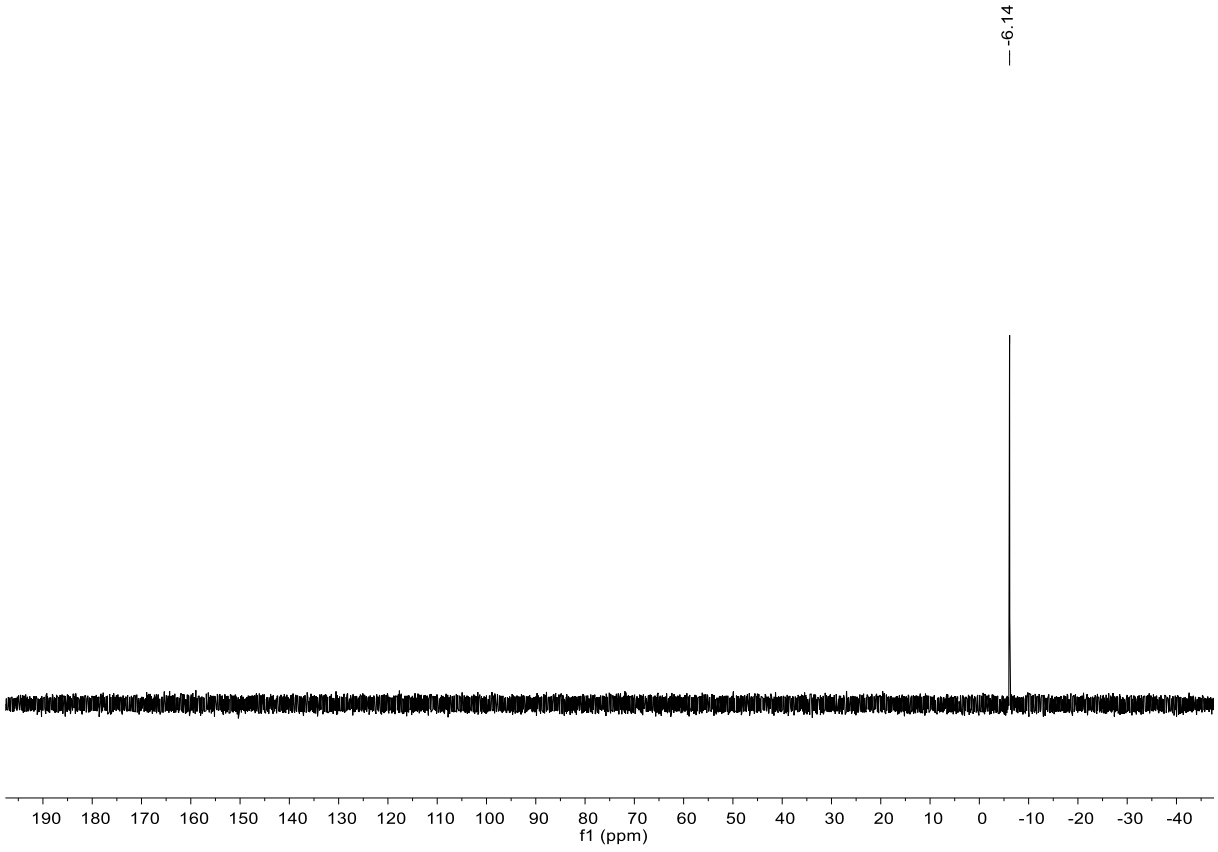

149.72
149.67
148.30
148.25
131.62
130.09
130.05
126.23
121.61
121.58
120.14
120.11
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-10.25
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

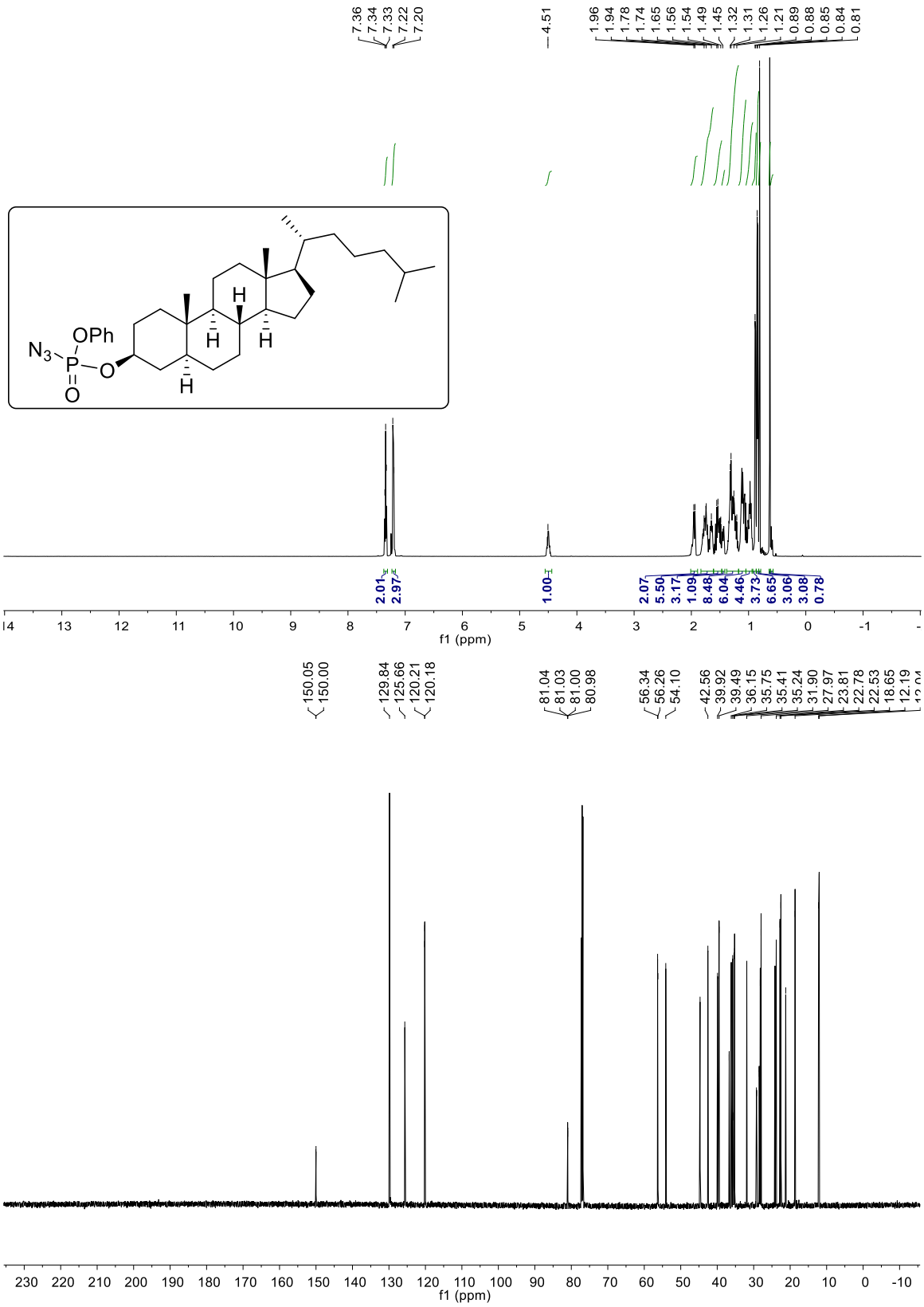
(1R,2R,5R)-5-Isopropyl-2-methylcyclohexyl phenyl phosphorazidate

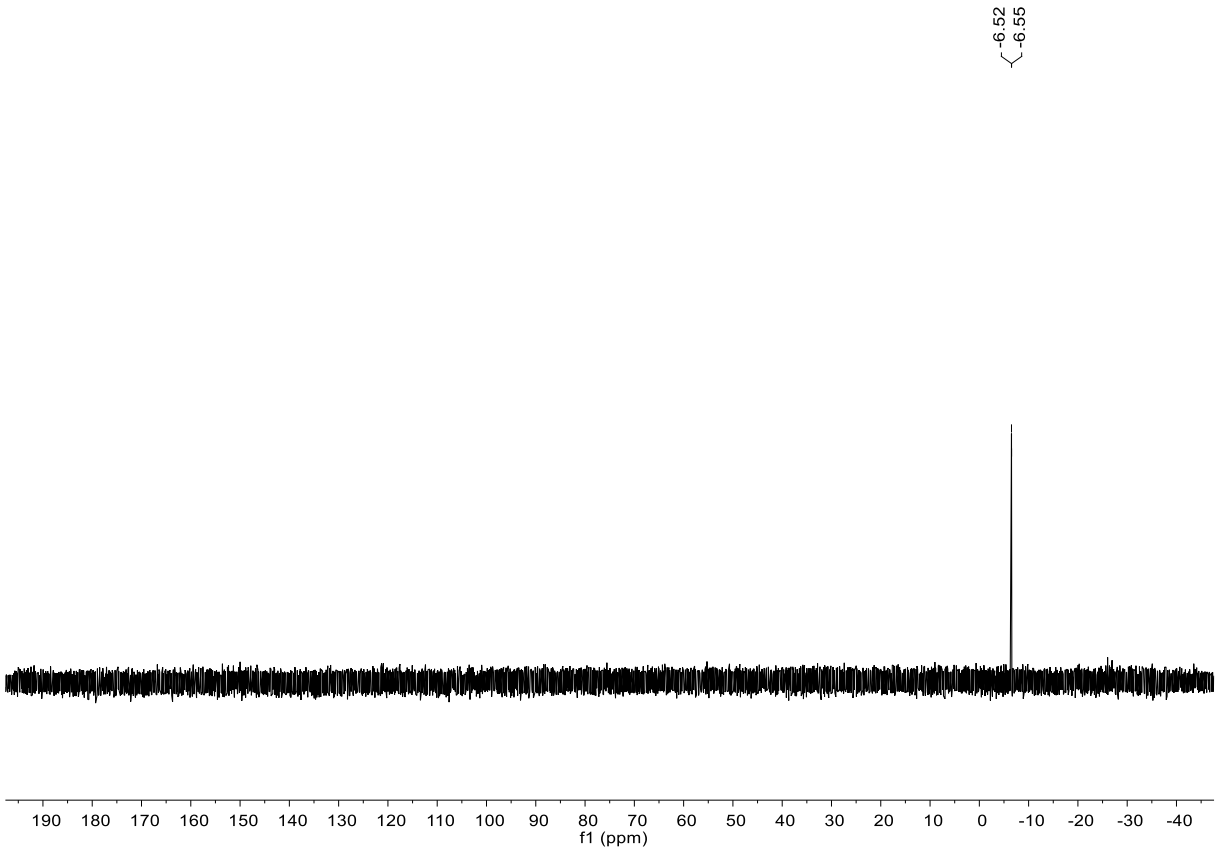



150.06
150.04
150.01
149.99
129.80
125.66
120.27
120.24
120.23
120.20
82.27
82.22
82.15
82.10
48.31
48.30
48.26
48.25
42.45
42.34
33.78
31.55
25.74
25.54
22.90
22.85
21.82
21.77
20.75
20.71
15.61
15.52
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

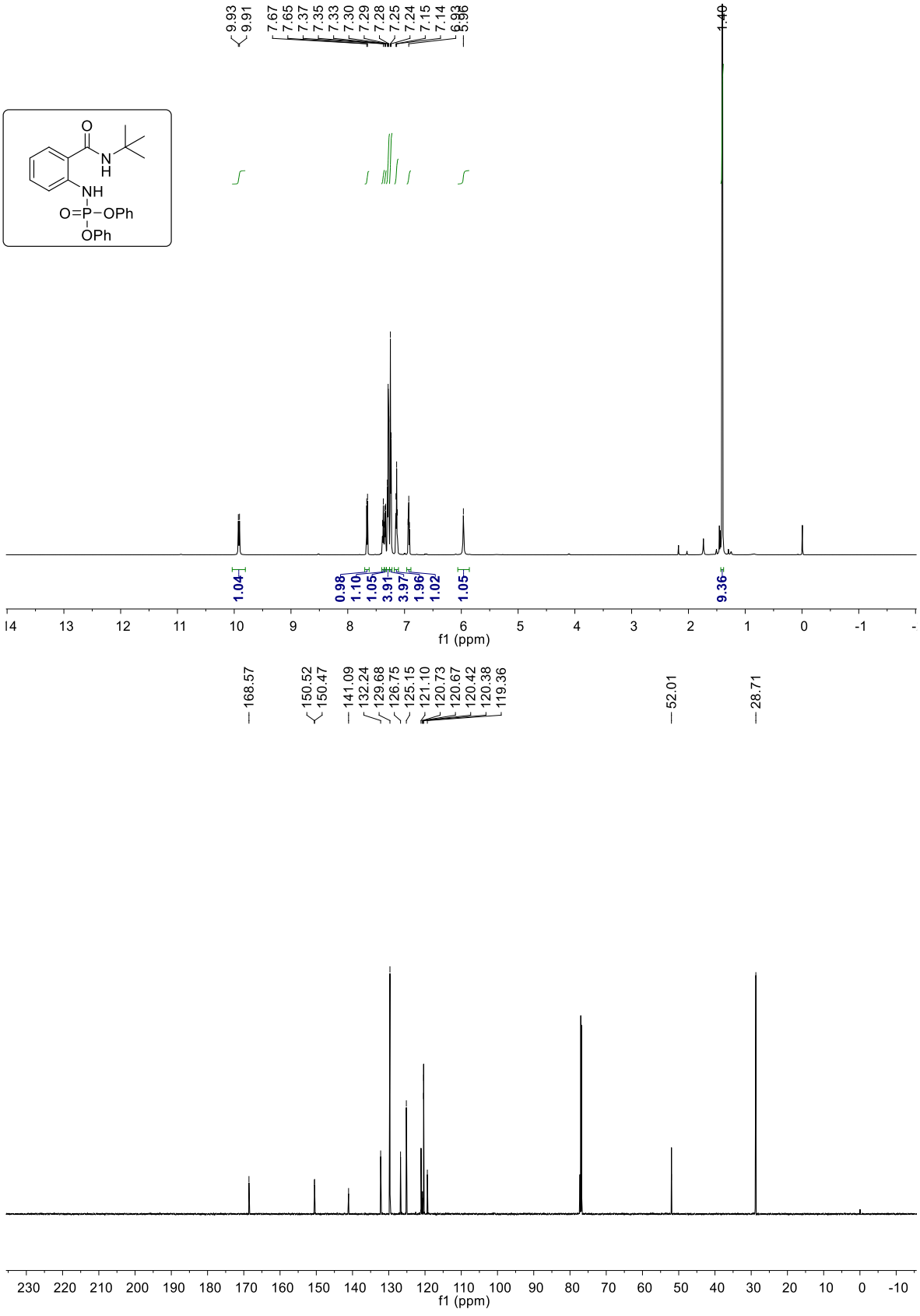

-6.14
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

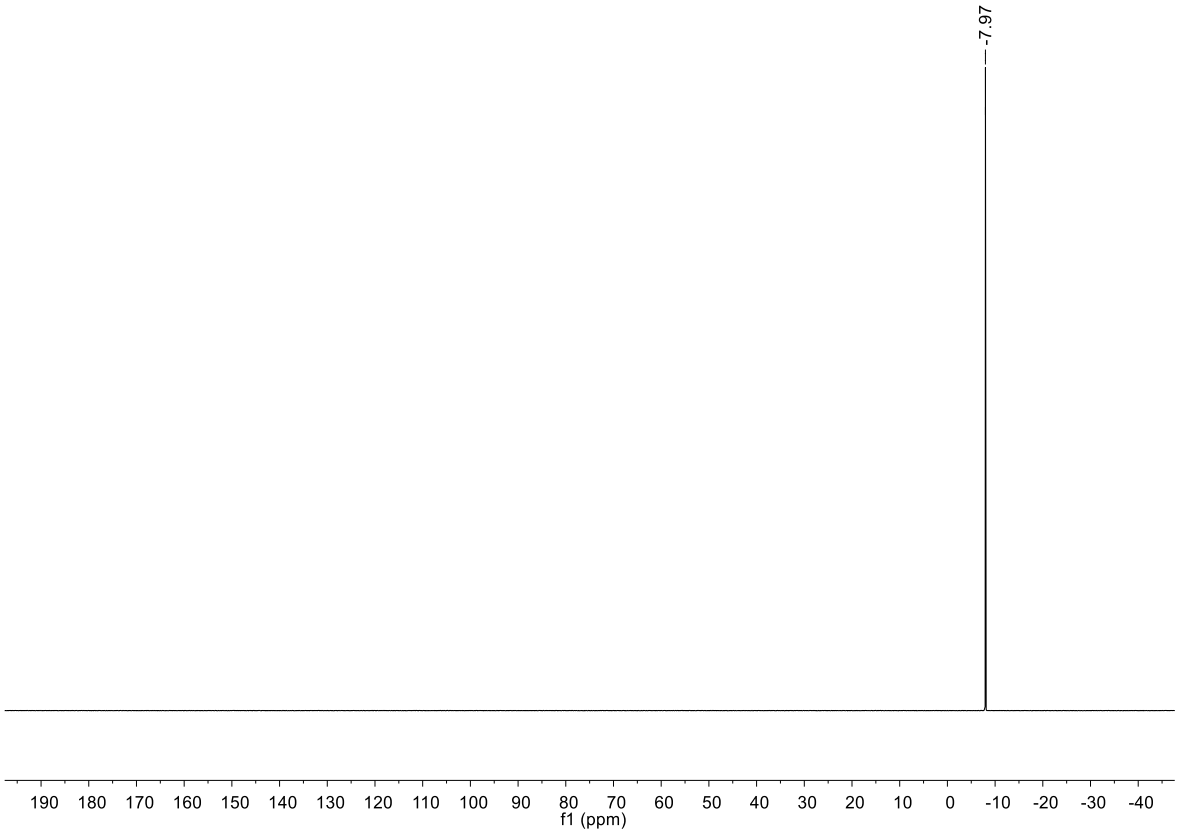
(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl phenyl phosphorazidate



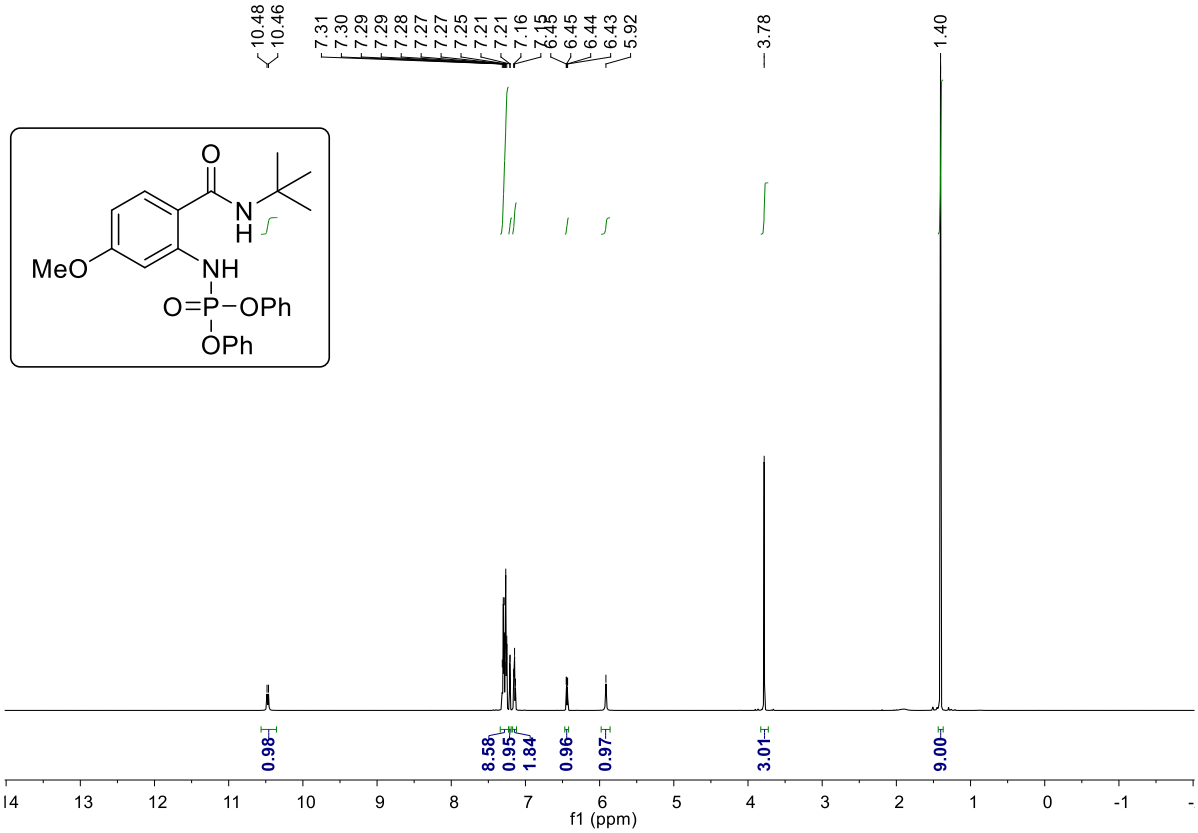

-6.52
-6.55
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

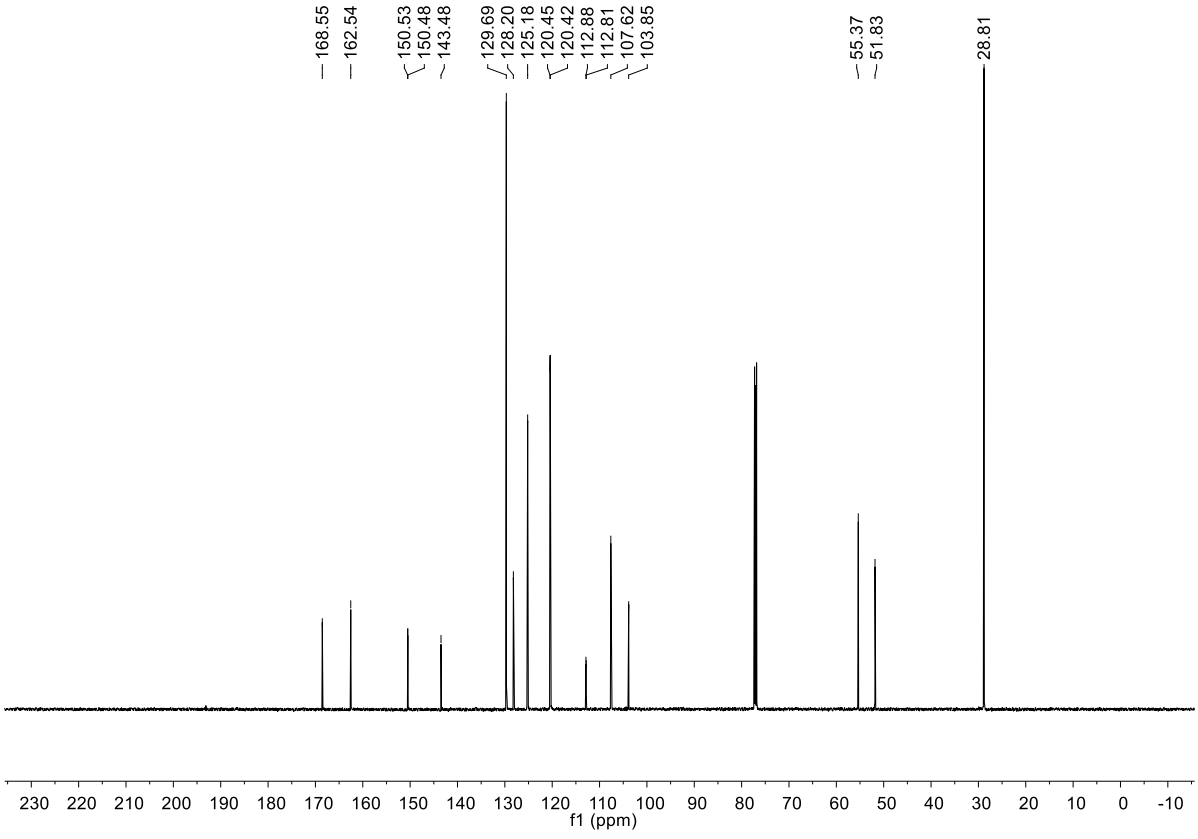
Diphenyl (2-(*tert*-butylcarbamoyl)phenyl)phosphoramidate (Scheme 2, **3a**)

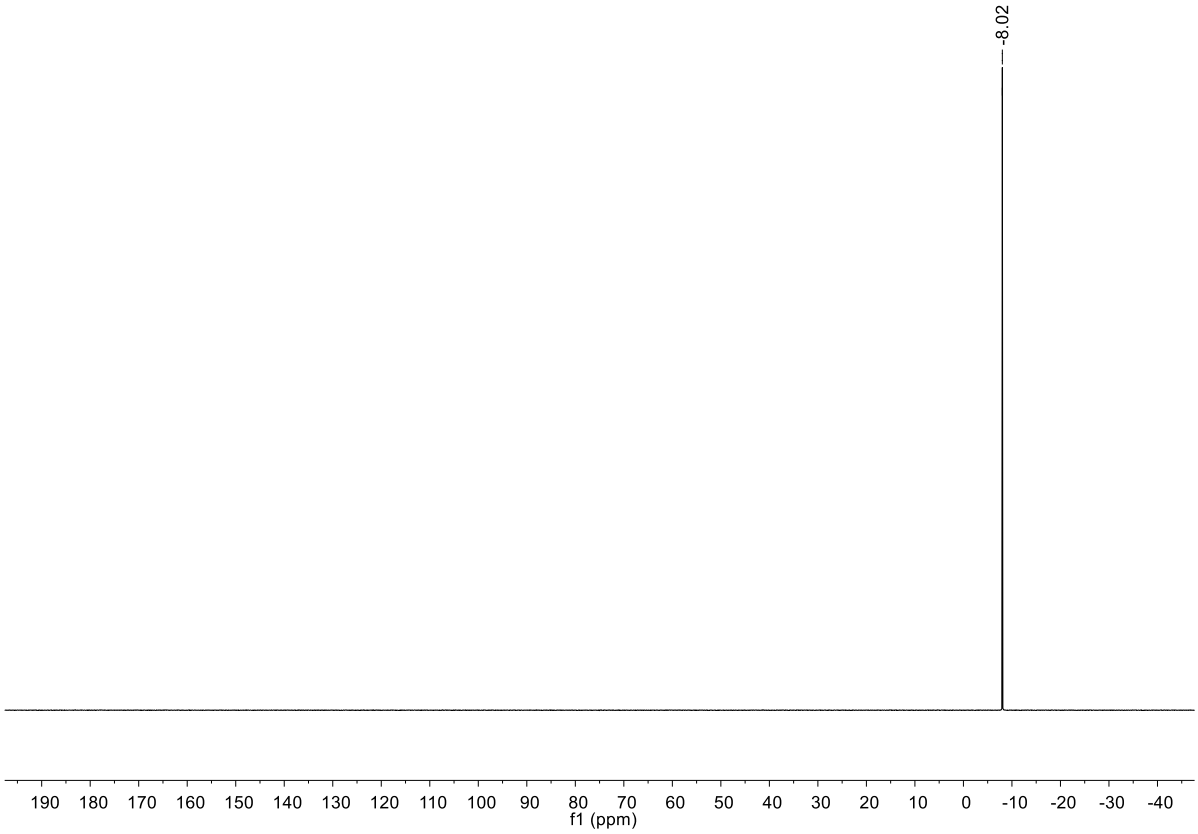



-7.97
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

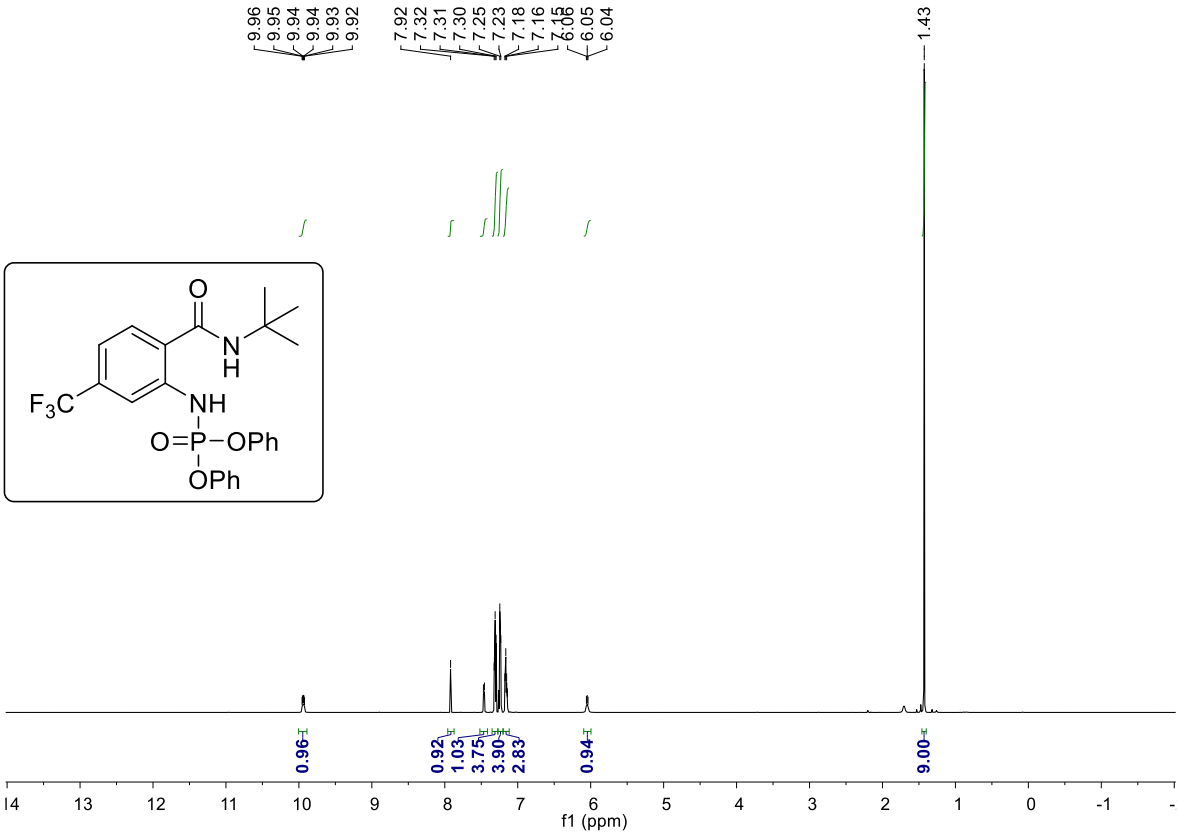
Diphenyl (2-(*tert*-butylcarbamoyl)-5-methoxyphenyl)phosphoramidate (Scheme 2, **3b**)

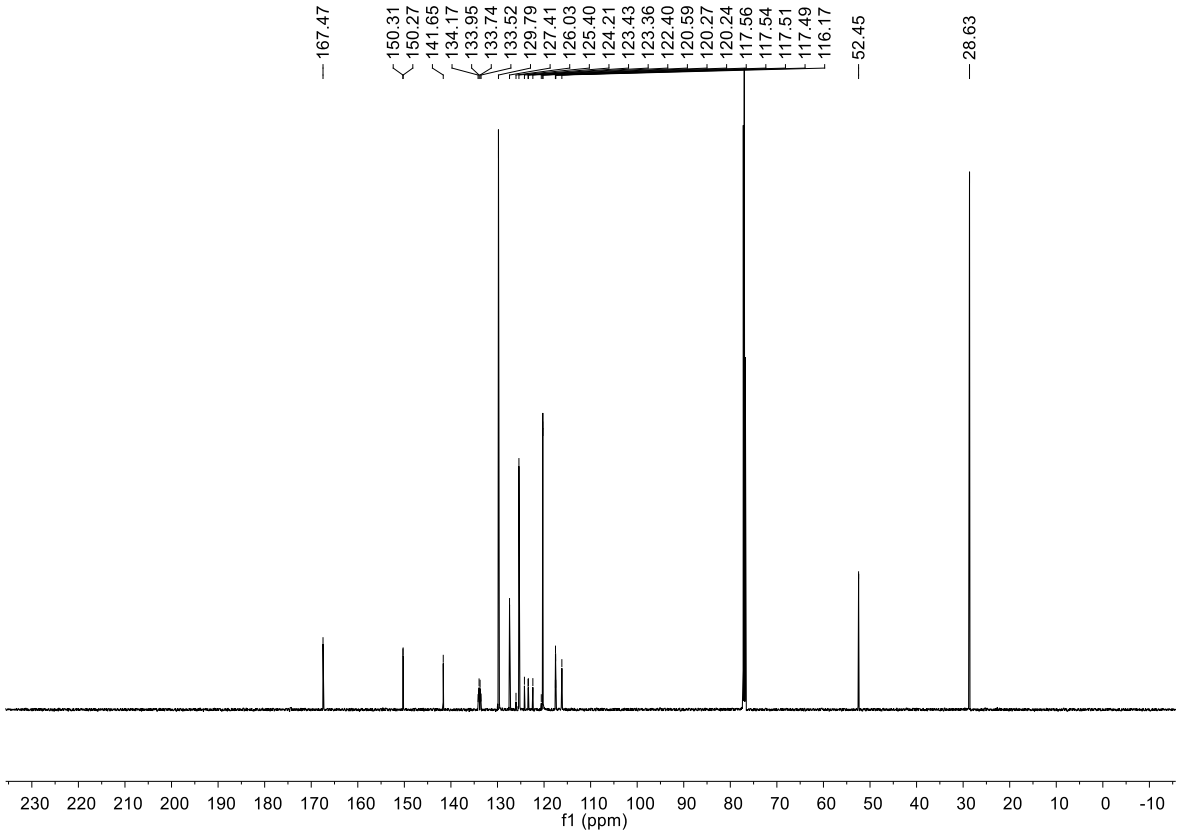


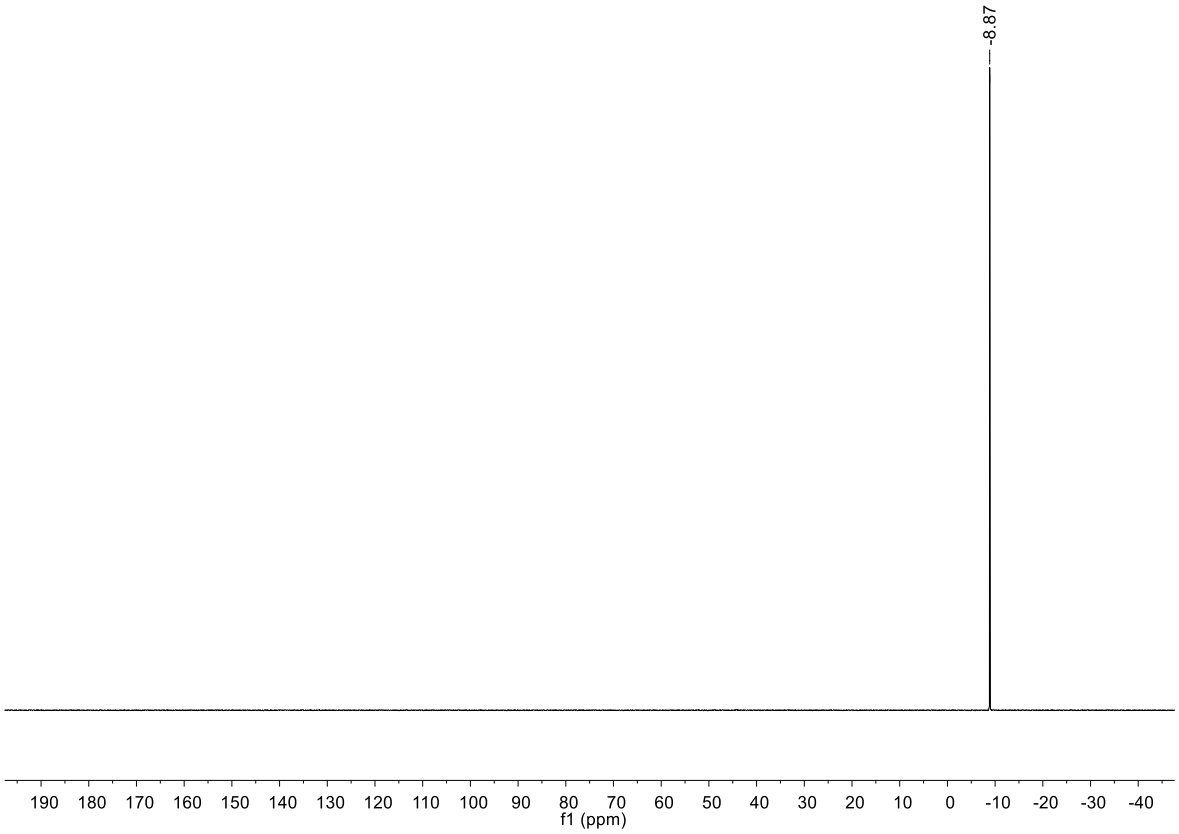



-8.02
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

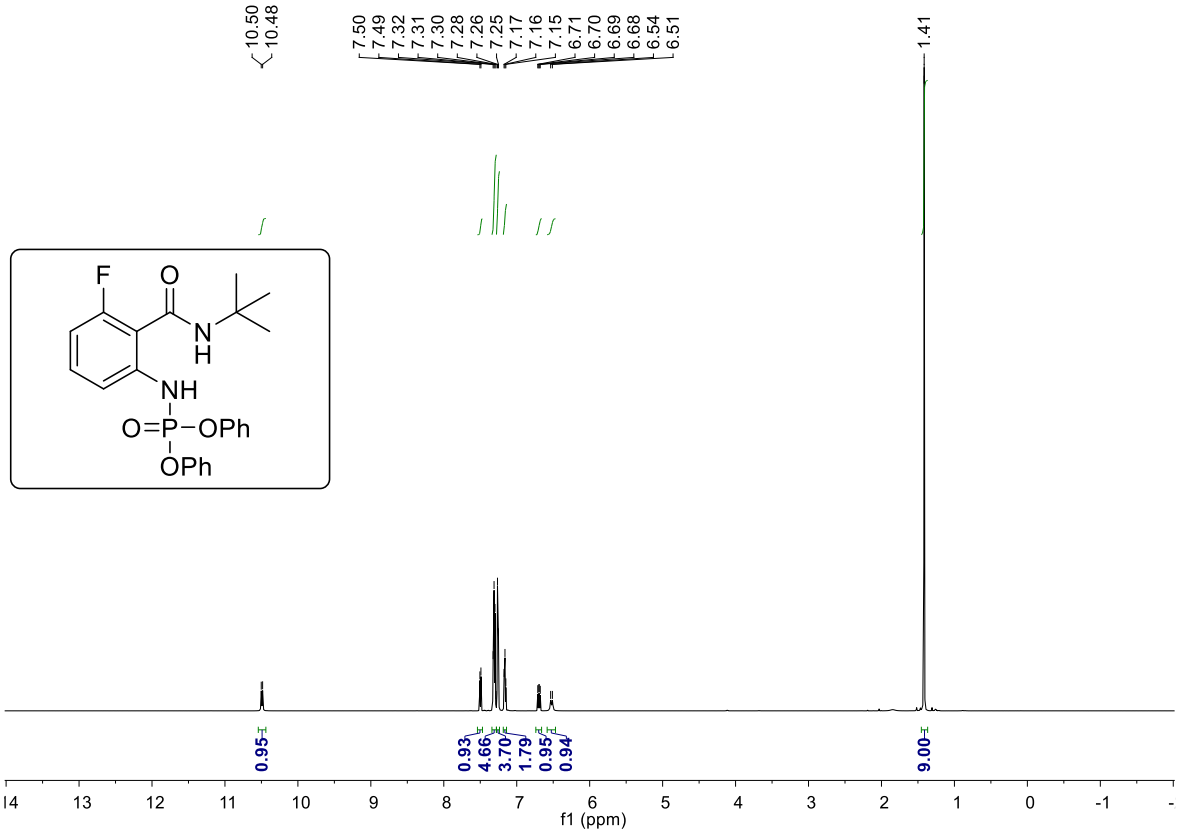
Diphenyl (2-(*tert*-butylcarbamoyl)-5-(trifluoromethyl)phenyl)phosphoramidate (Scheme 2, **3c**)

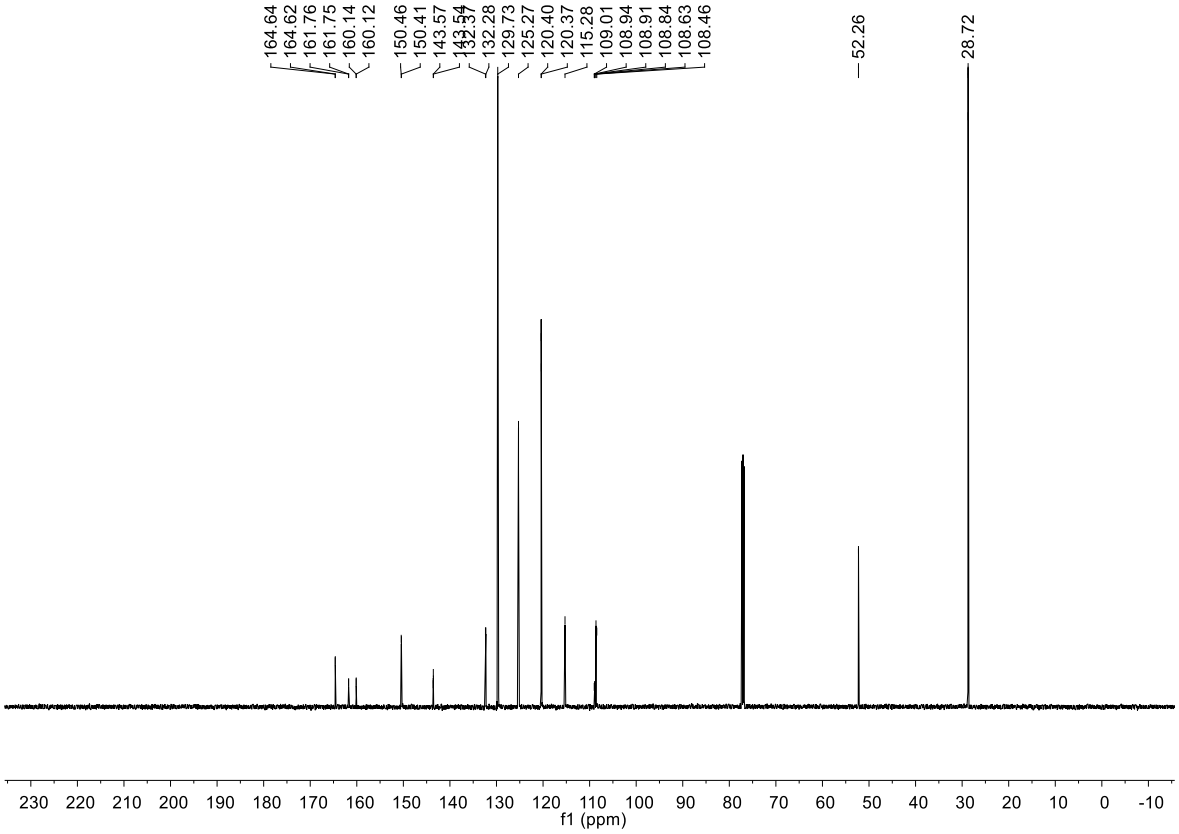


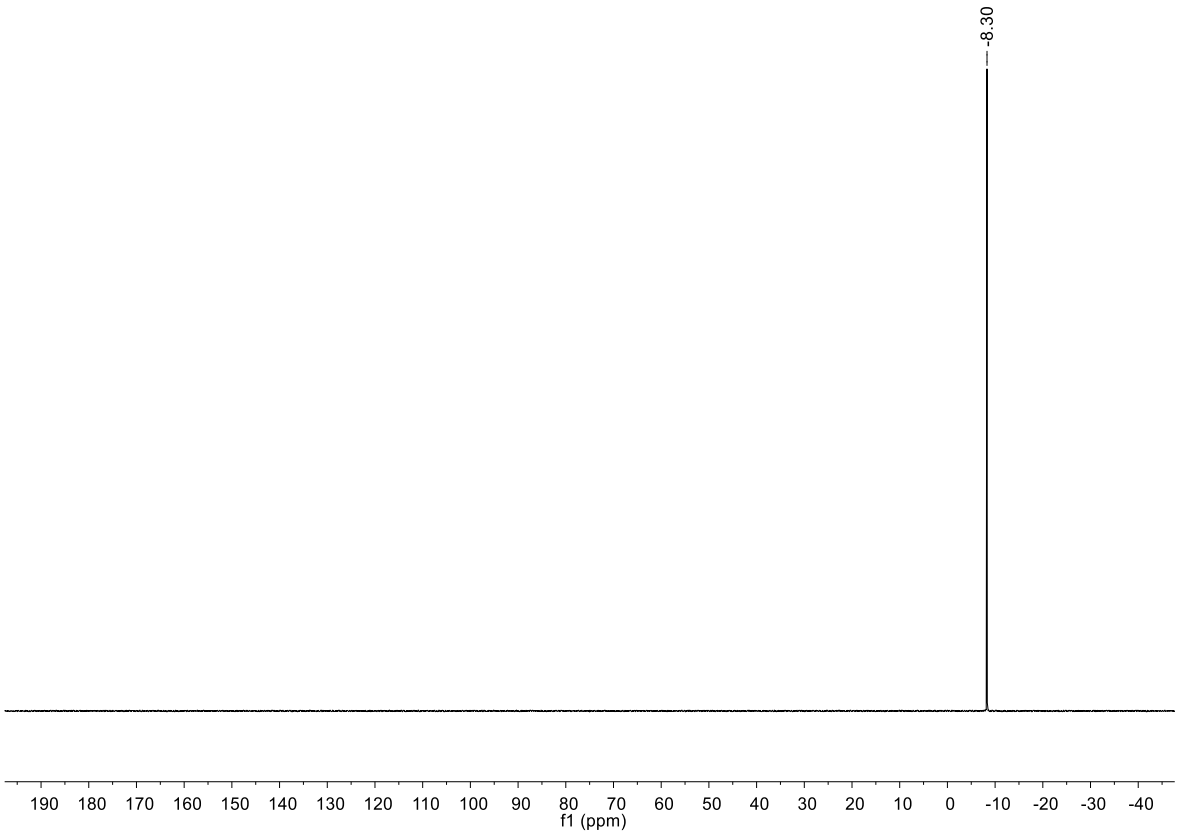



-8.87
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

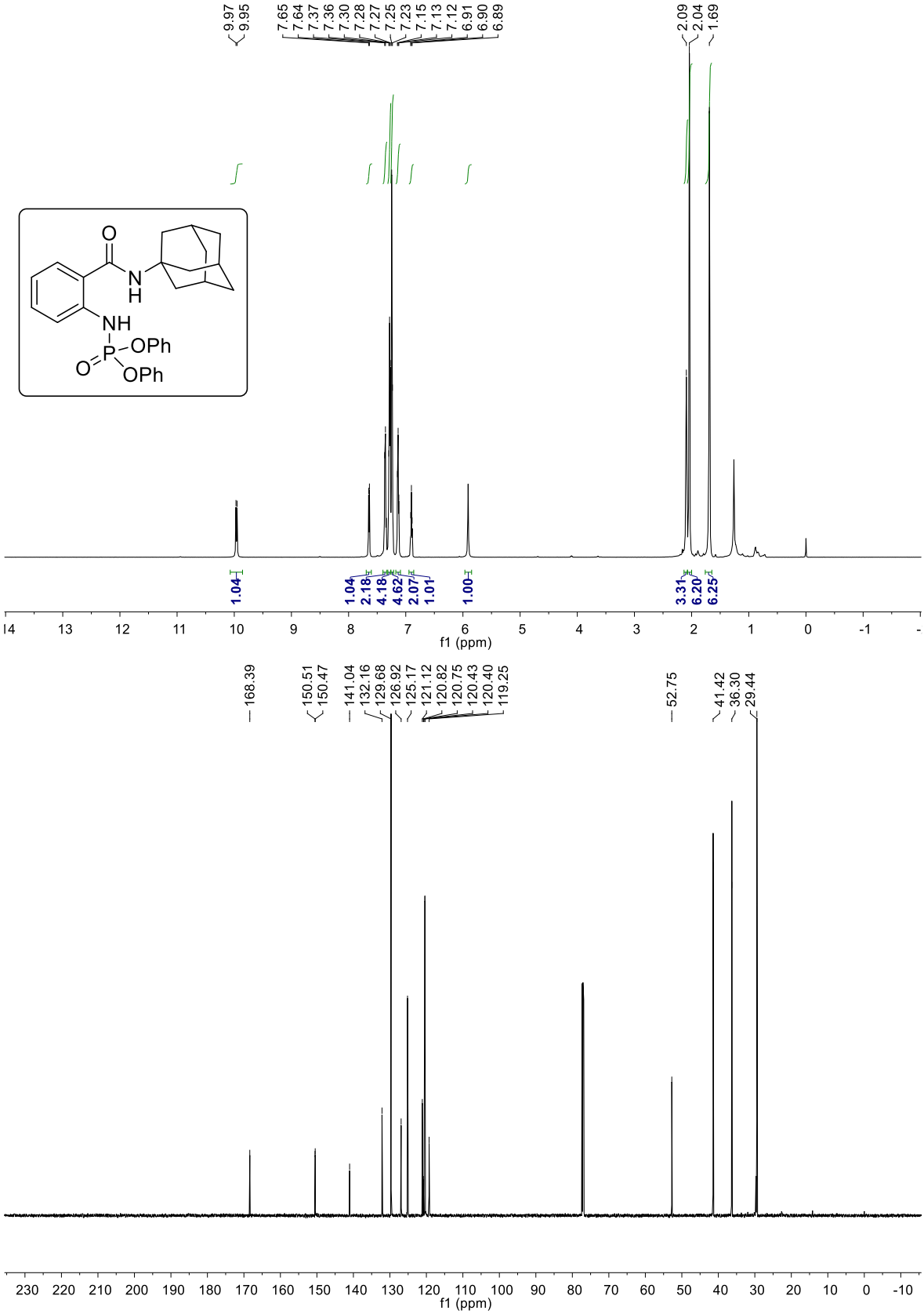
Diphenyl (2-(*tert*-butylcarbamoyl)-3-fluorophenyl)phosphoramidate (Scheme 2, **3d**)

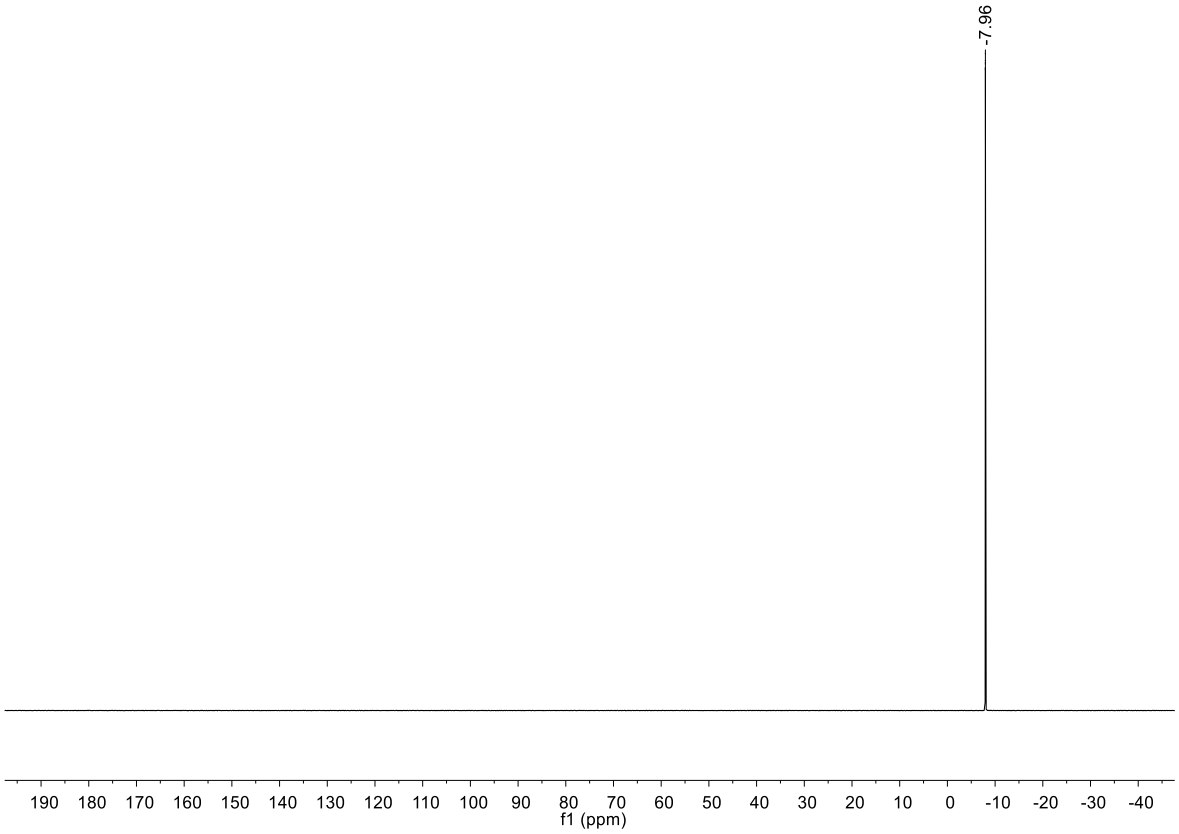



164.64
164.62
161.76
161.75
160.14
160.12
150.46
150.41
143.57
132.37
132.28
129.73
125.27
120.40
120.37
115.28
109.01
108.94
108.91
108.84
108.63
108.46
52.26
28.72
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

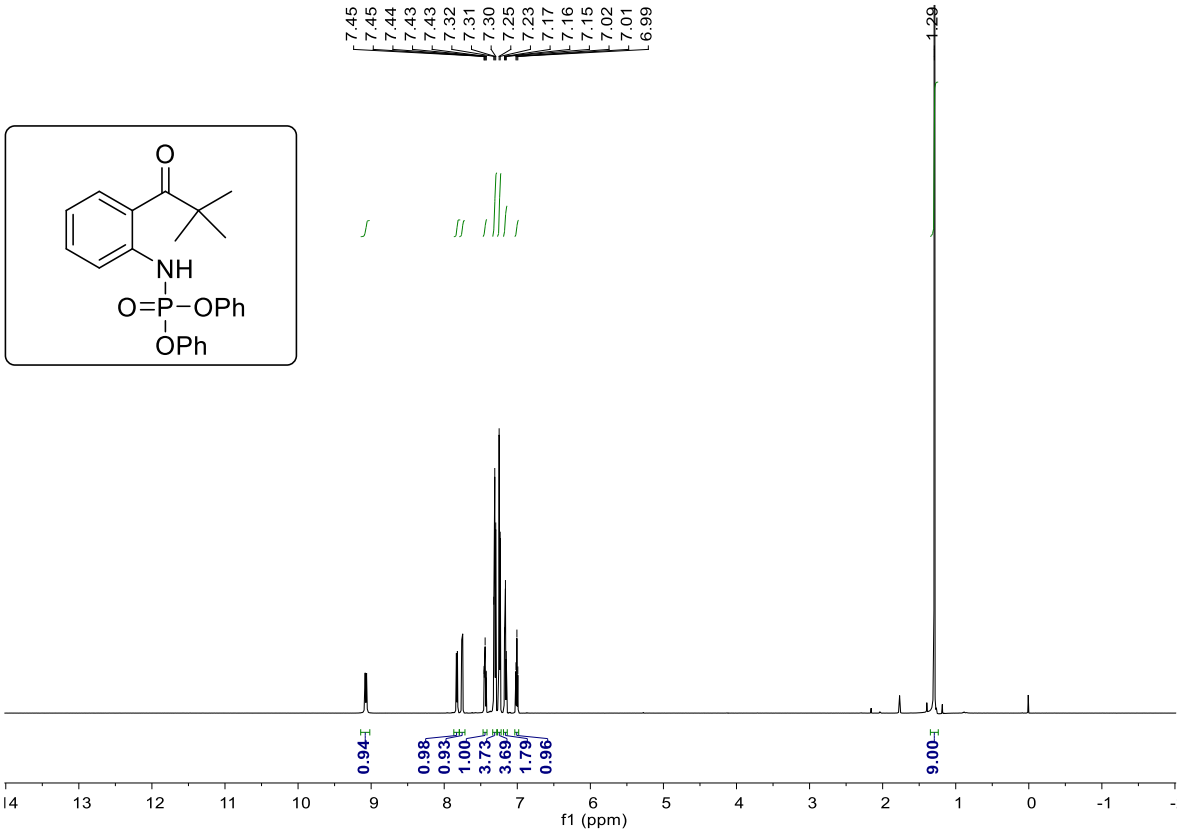

-8.30
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

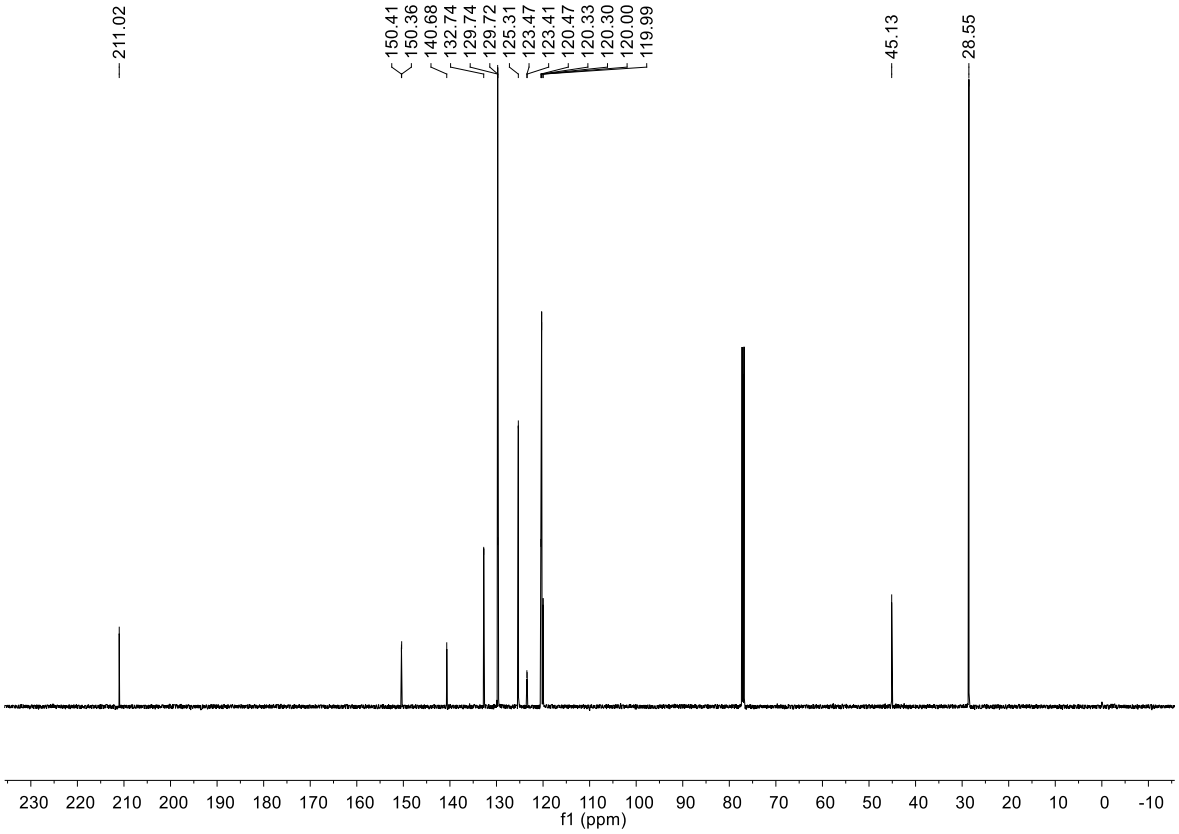
Diphenyl (2-(((3s,5s,7s)-adamantan-1-yl)carbamoyl)phenyl)phosphoramidate (Scheme 2, **3e**)

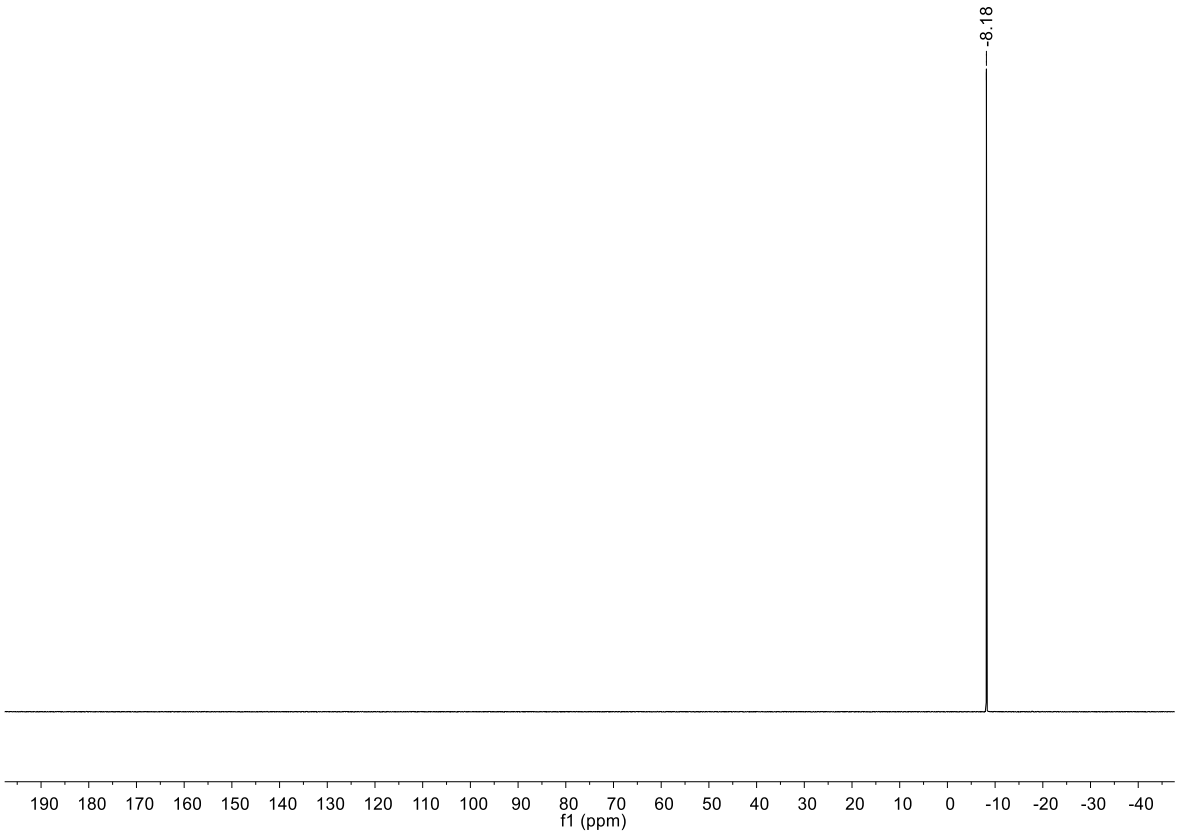



-7.96
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

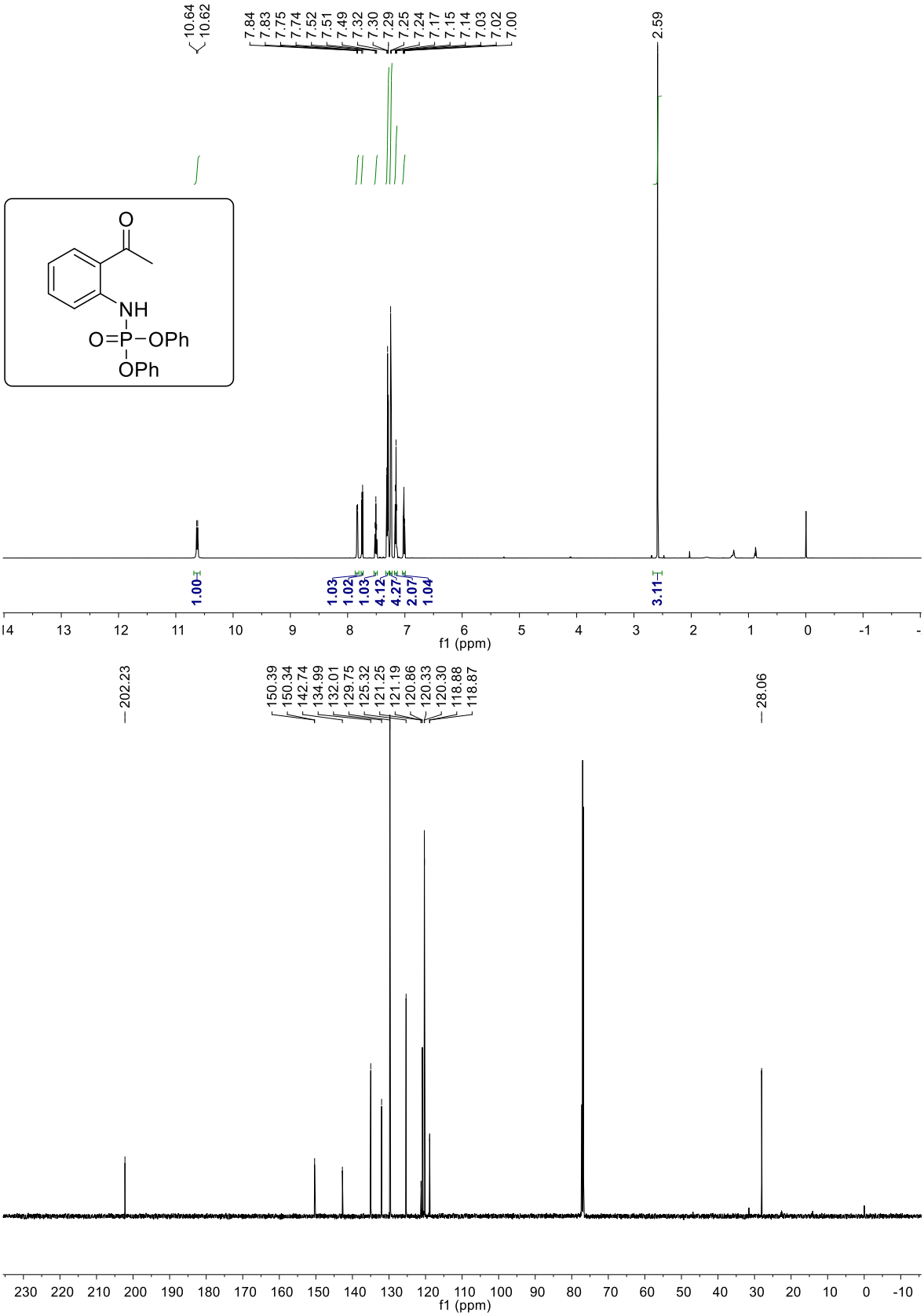
Diphenyl (2-pivaloylphenyl)phosphoramidate (Scheme 2, **3f**)

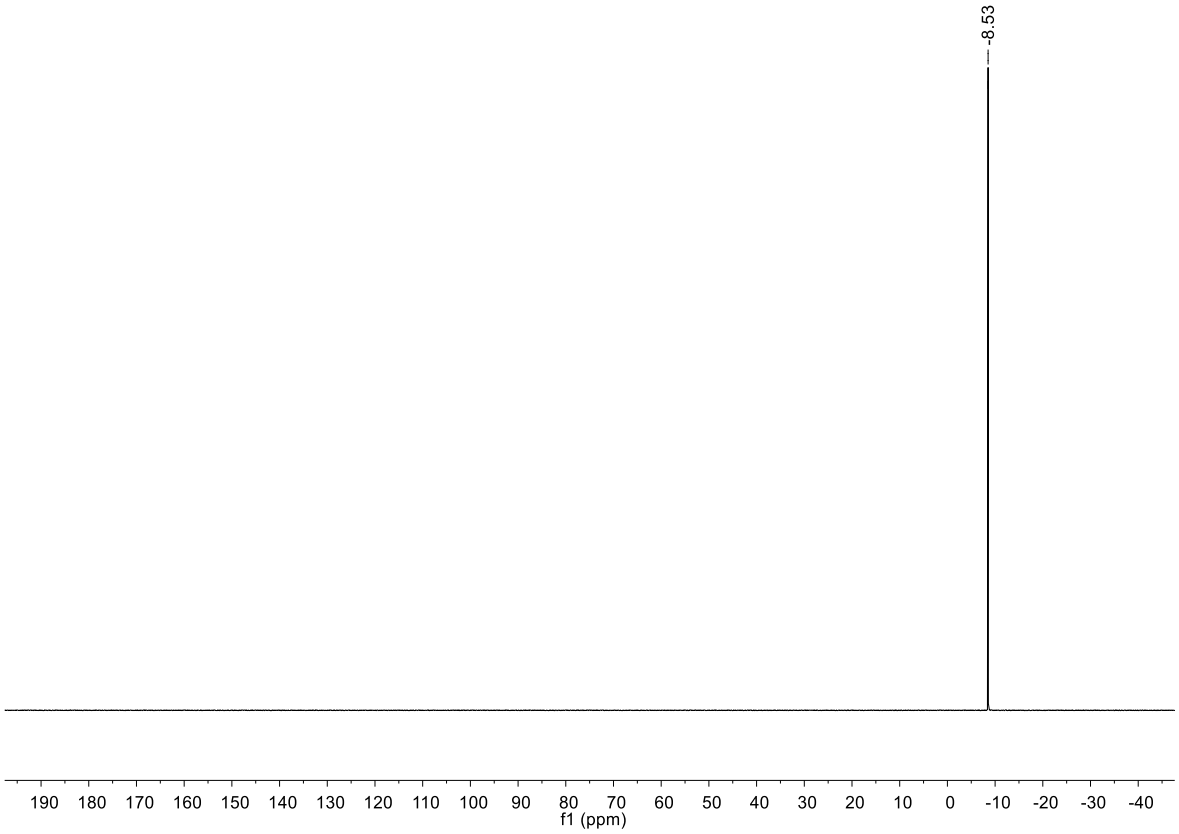



211.02
150.41
150.36
140.68
132.74
129.74
129.72
125.31
123.47
123.41
120.47
120.33
120.30
120.00
119.99
45.13
28.55
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

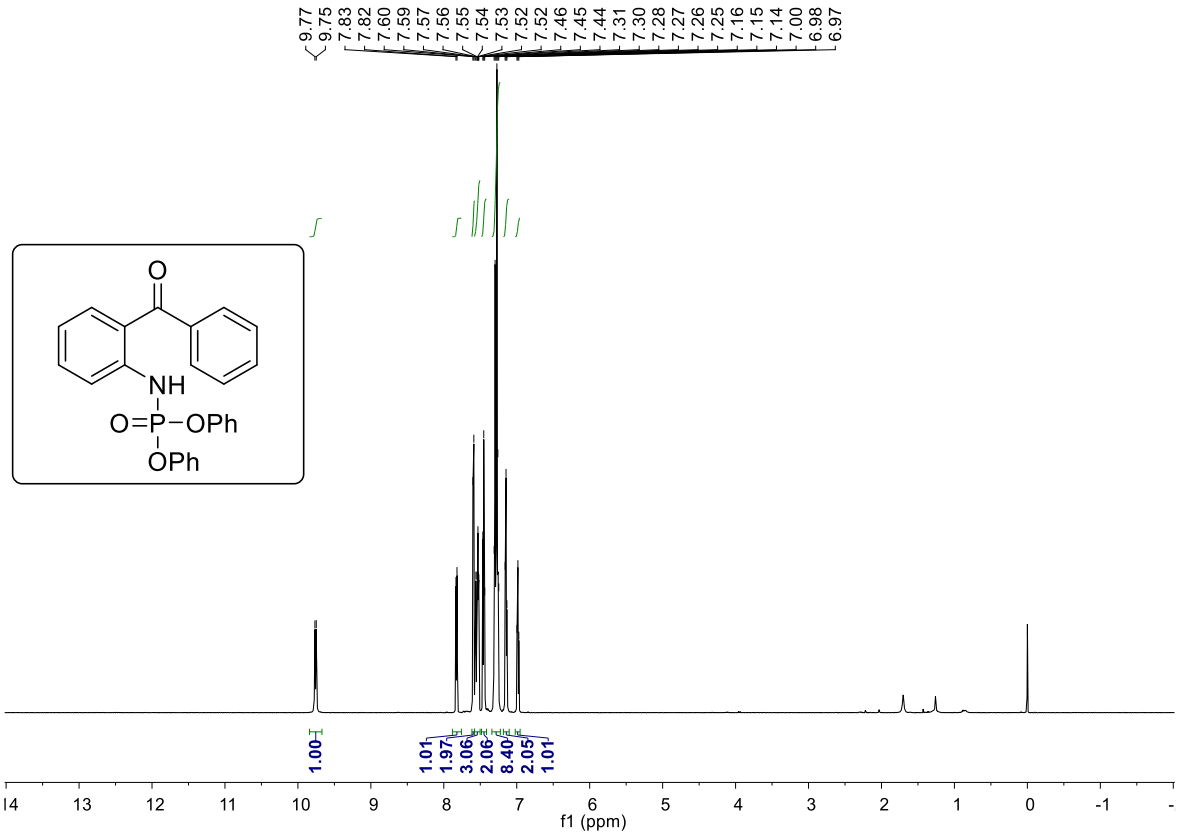

-8.18
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

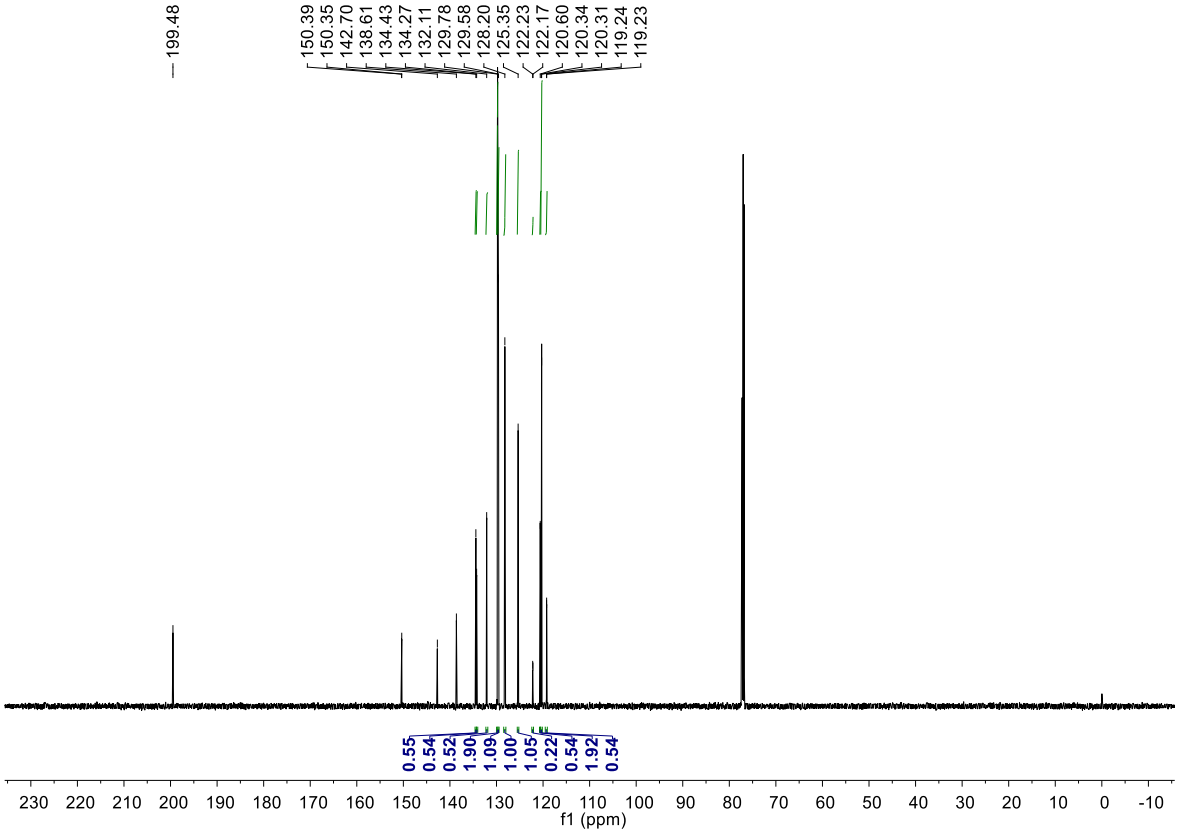
Diphenyl (2-acetylphenyl)phosphoramidate (Scheme 2, **3g**)

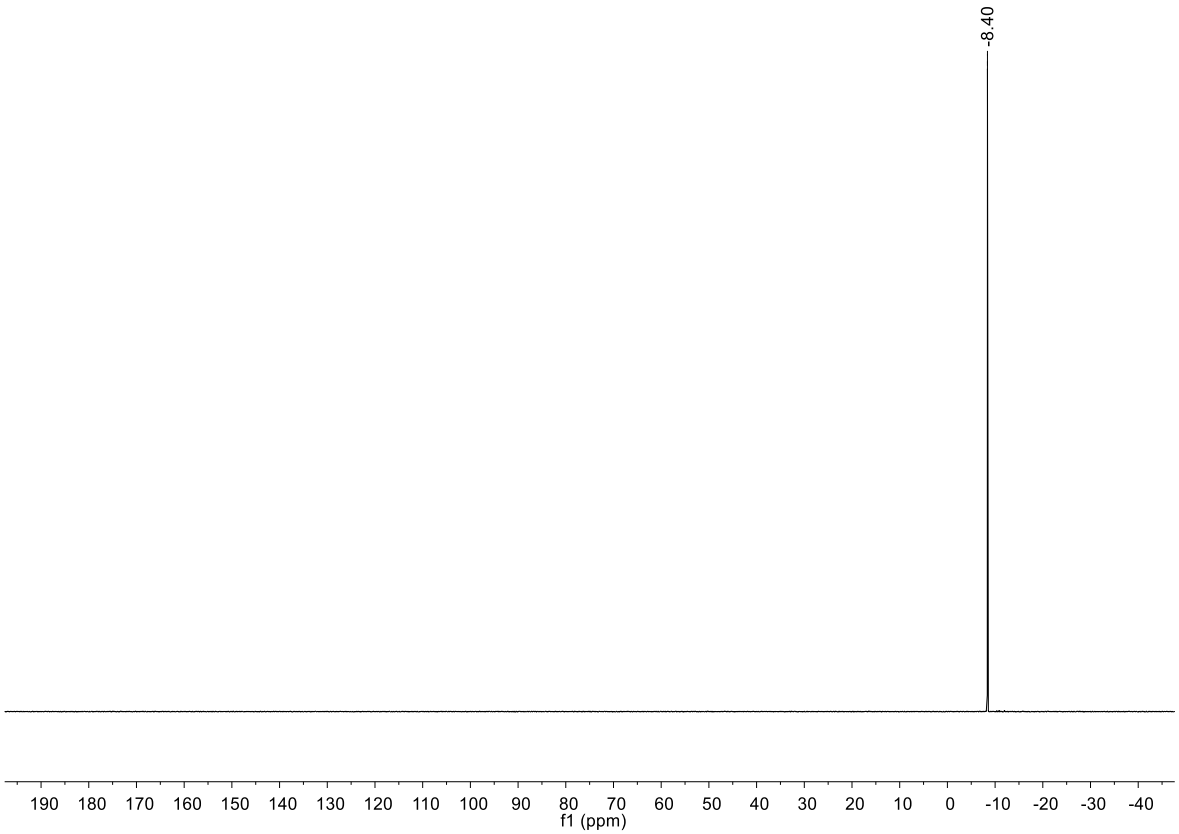



-8.53
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

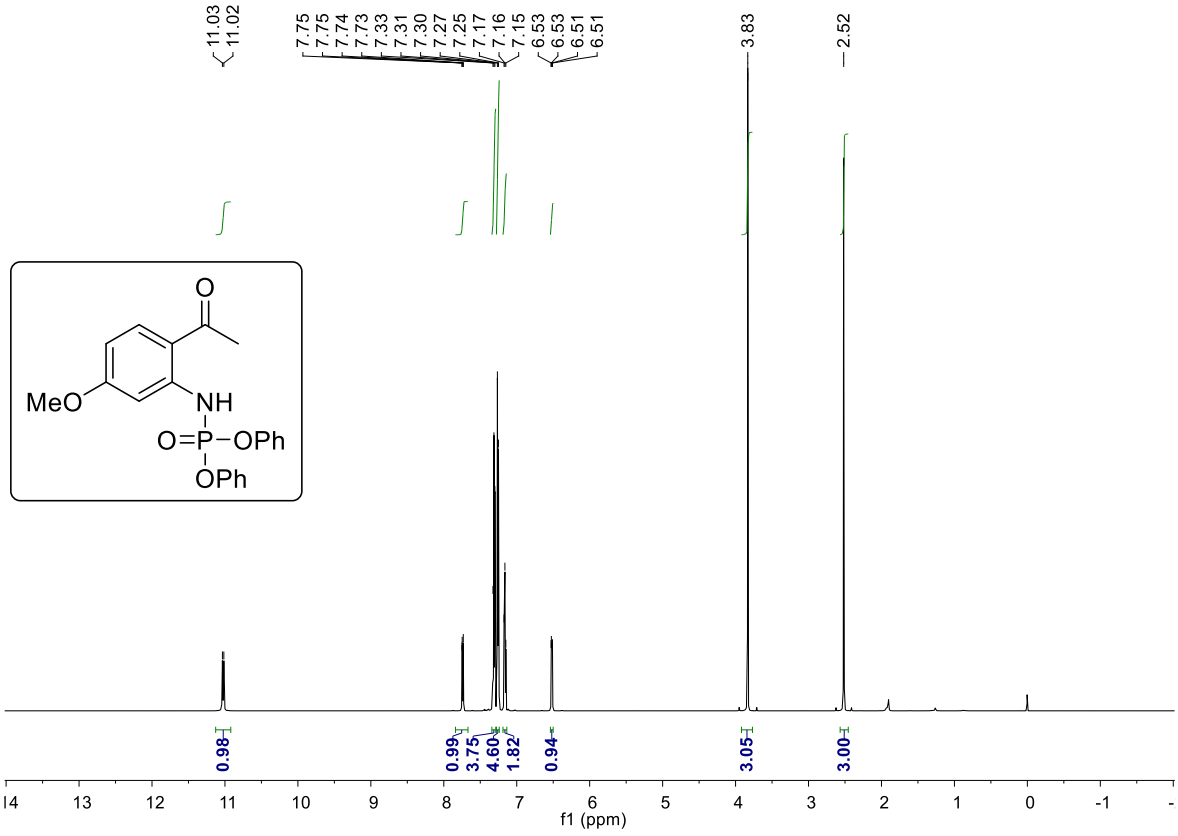
Diphenyl (2-benzoylphenyl)phosphoramidate (Scheme 2, **3h**)

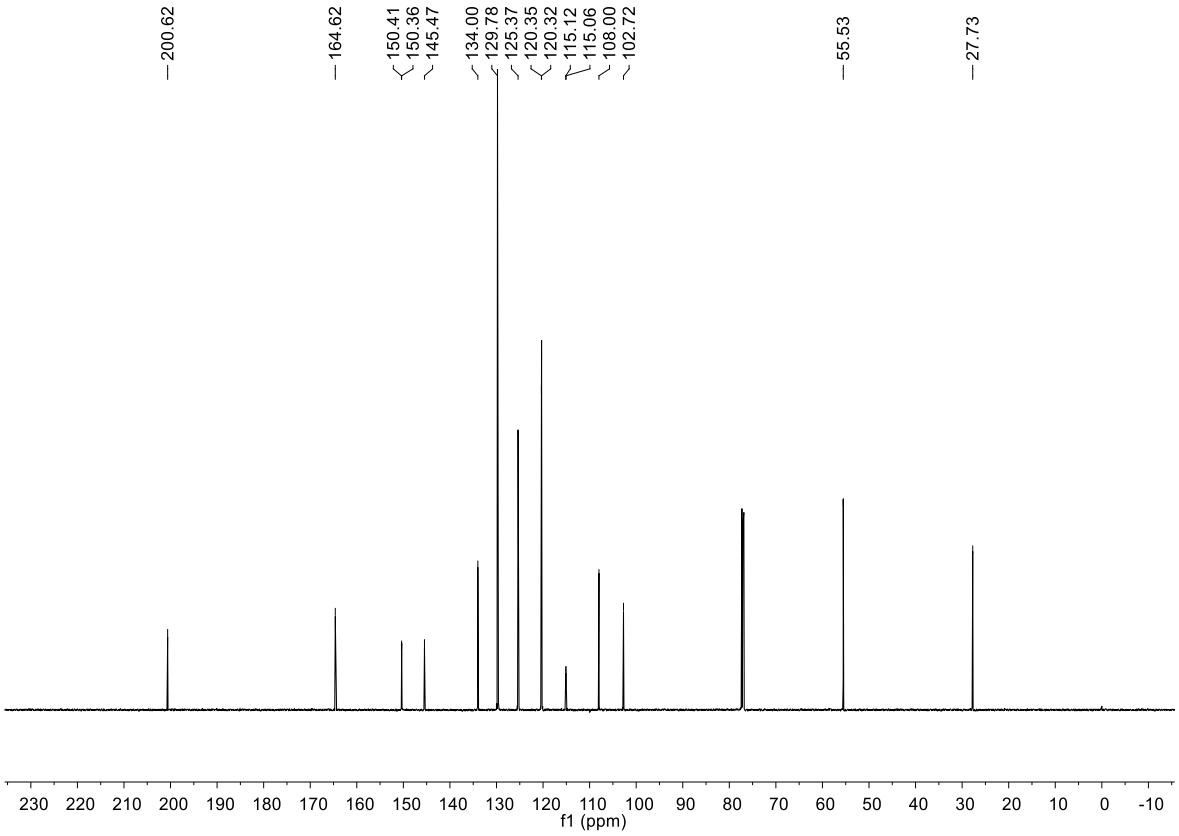


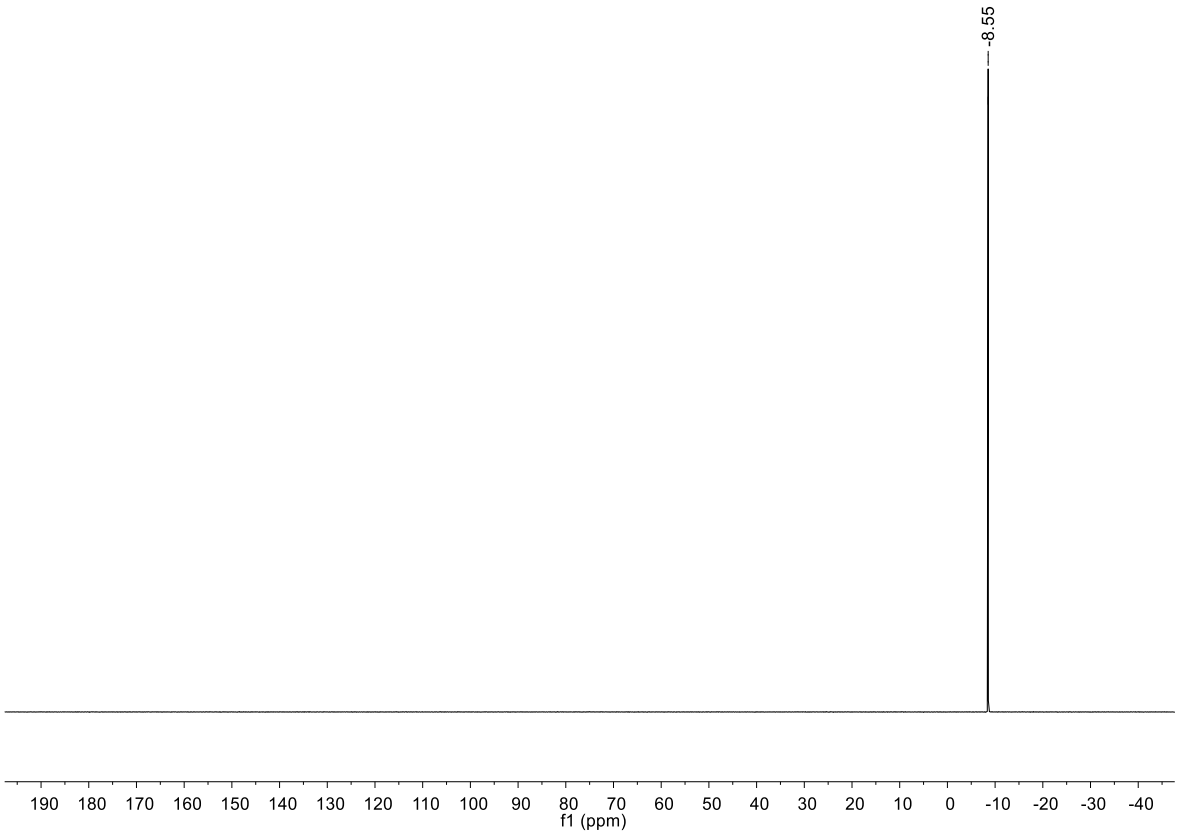

199.48
150.39
150.35
142.70
138.61
134.43
134.27
132.11
129.78
129.58
128.20
125.35
122.23
122.17
120.60
120.34
120.31
119.24
119.23
0.55
0.54
0.52
1.90
1.09
1.00
1.05
0.22
0.54
1.92
0.54
f1 (ppm)


-8.40
f1 (ppm)

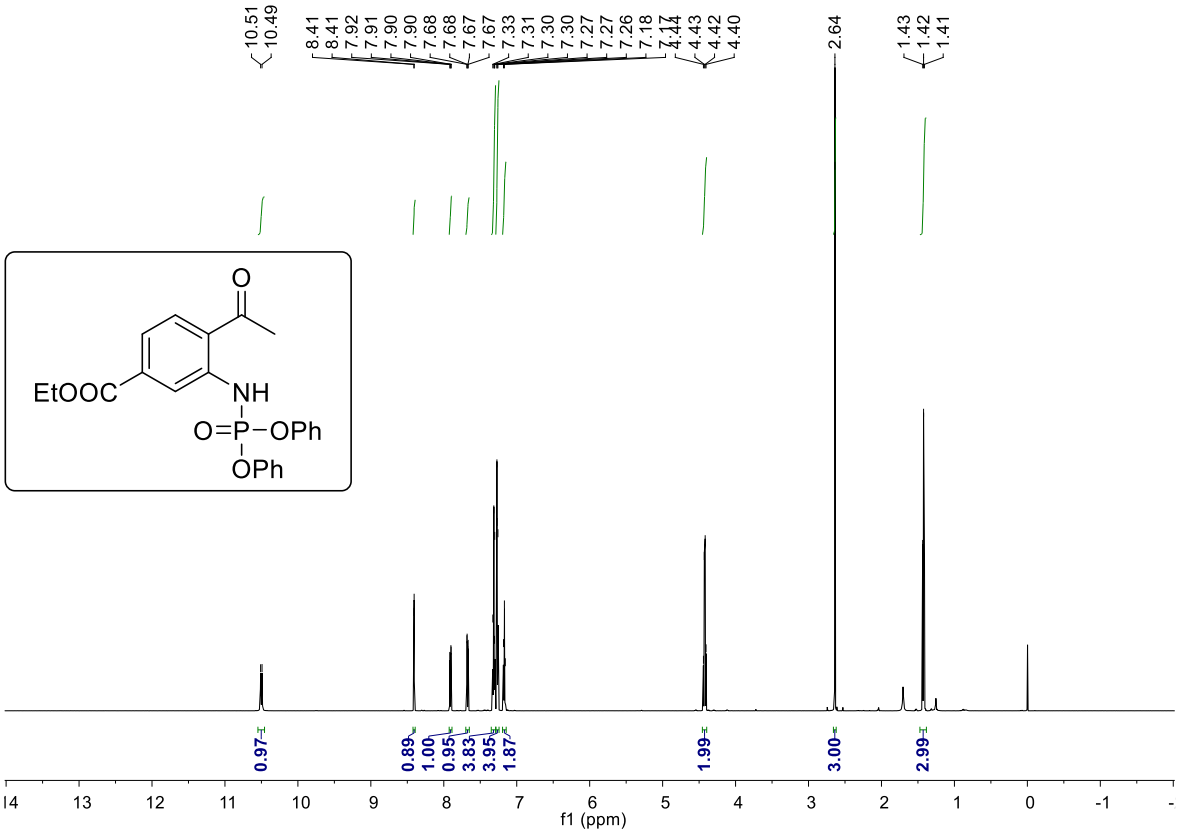
Diphenyl (2-acetyl-5-methoxyphenyl)phosphoramidate (Scheme 2, **3i**)

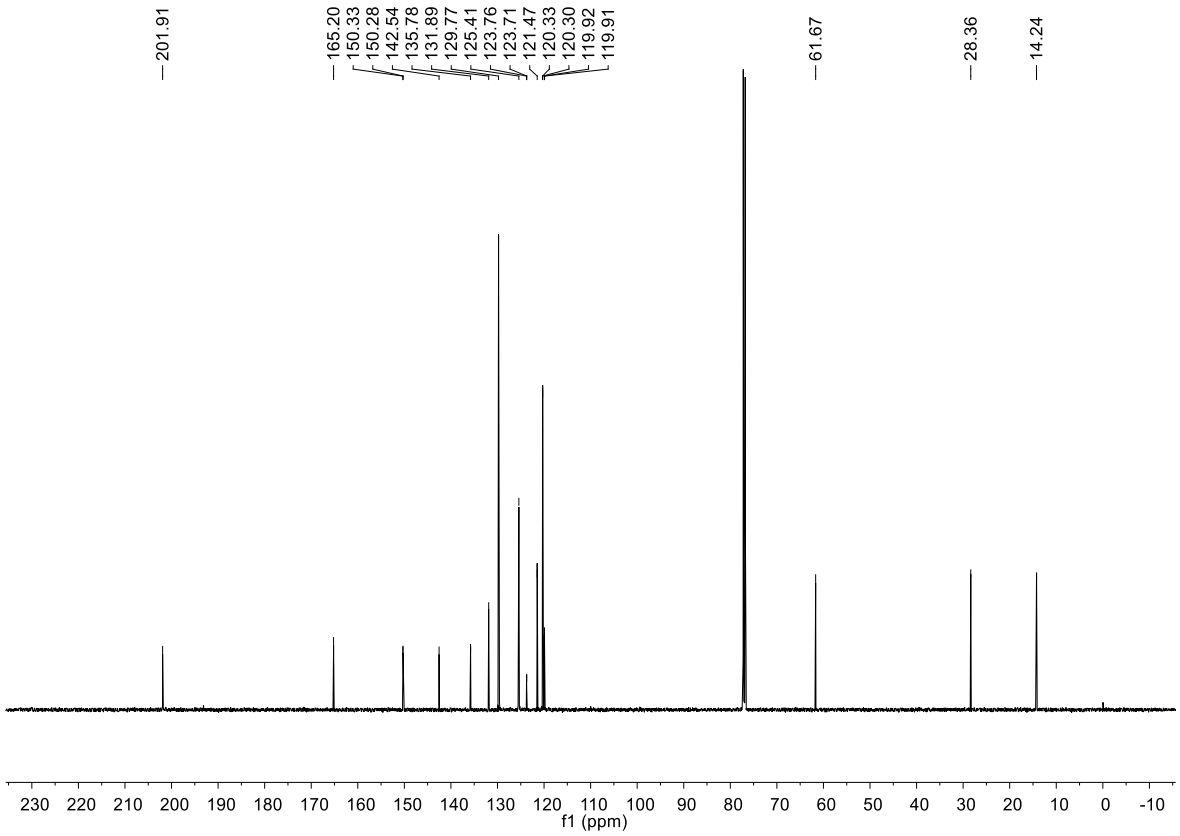


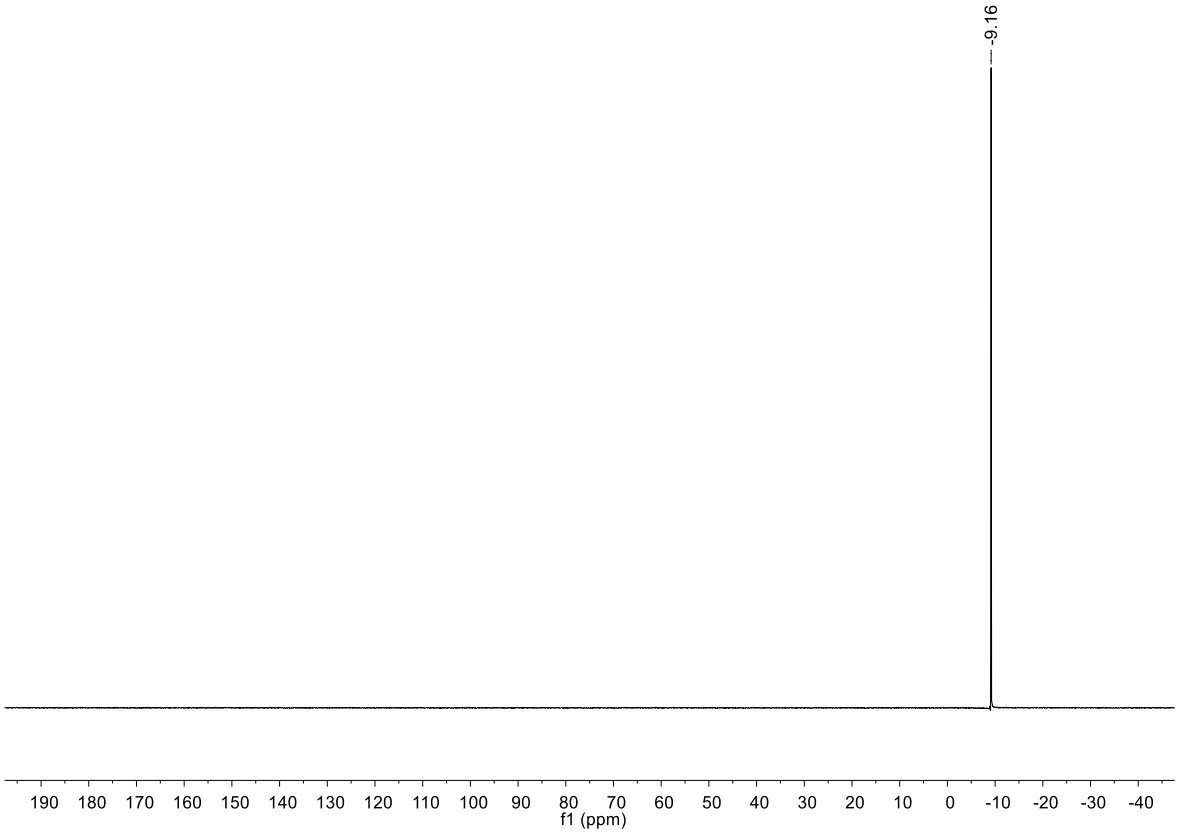

200.62
164.62
150.41
150.36
145.47
134.00
129.78
125.37
120.35
120.32
115.12
115.06
108.00
102.72
55.53
27.73
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-8.55
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

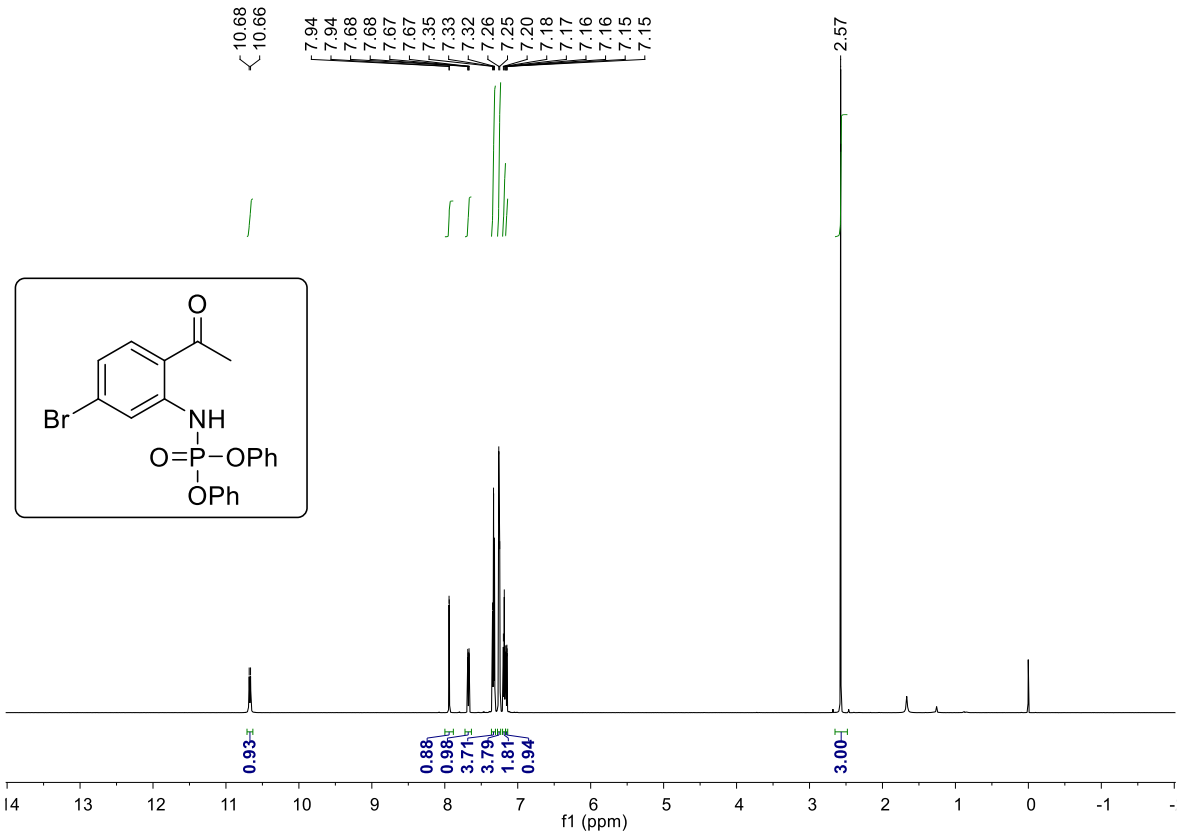
Ethyl 4-acetyl-3-((diphenoxyphosphoryl)amino)benzoate (Scheme 2, **3j**)

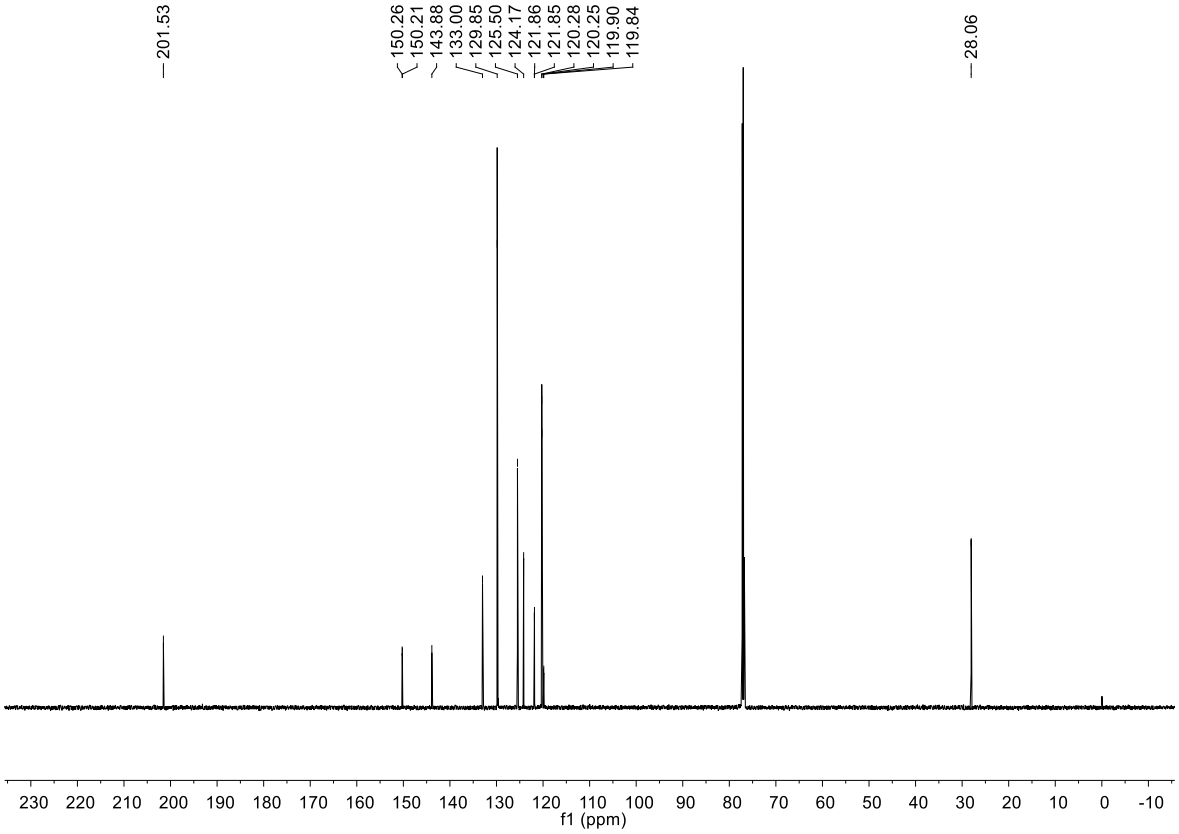


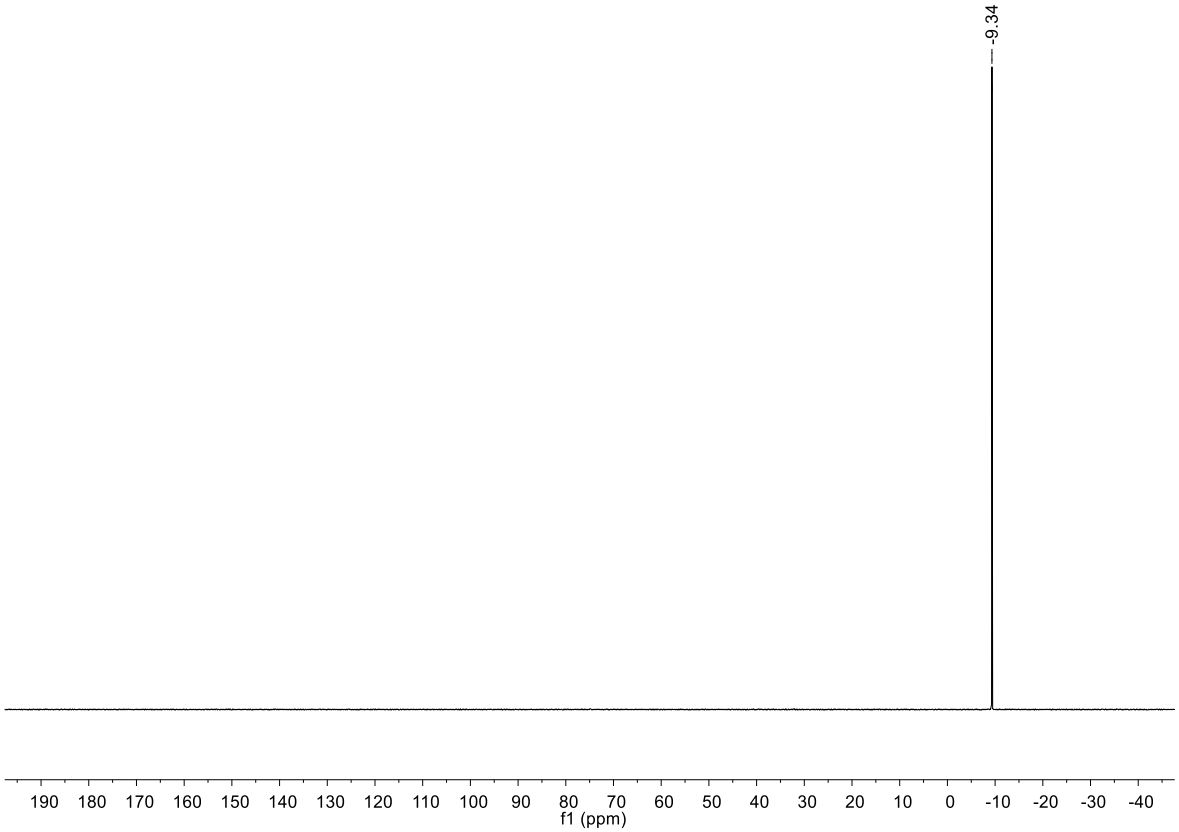

201.91
165.20
150.33
150.28
142.54
135.78
131.89
129.77
125.41
123.76
123.71
121.47
120.33
120.30
119.92
119.91
61.67
28.36
14.24
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-9.16
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

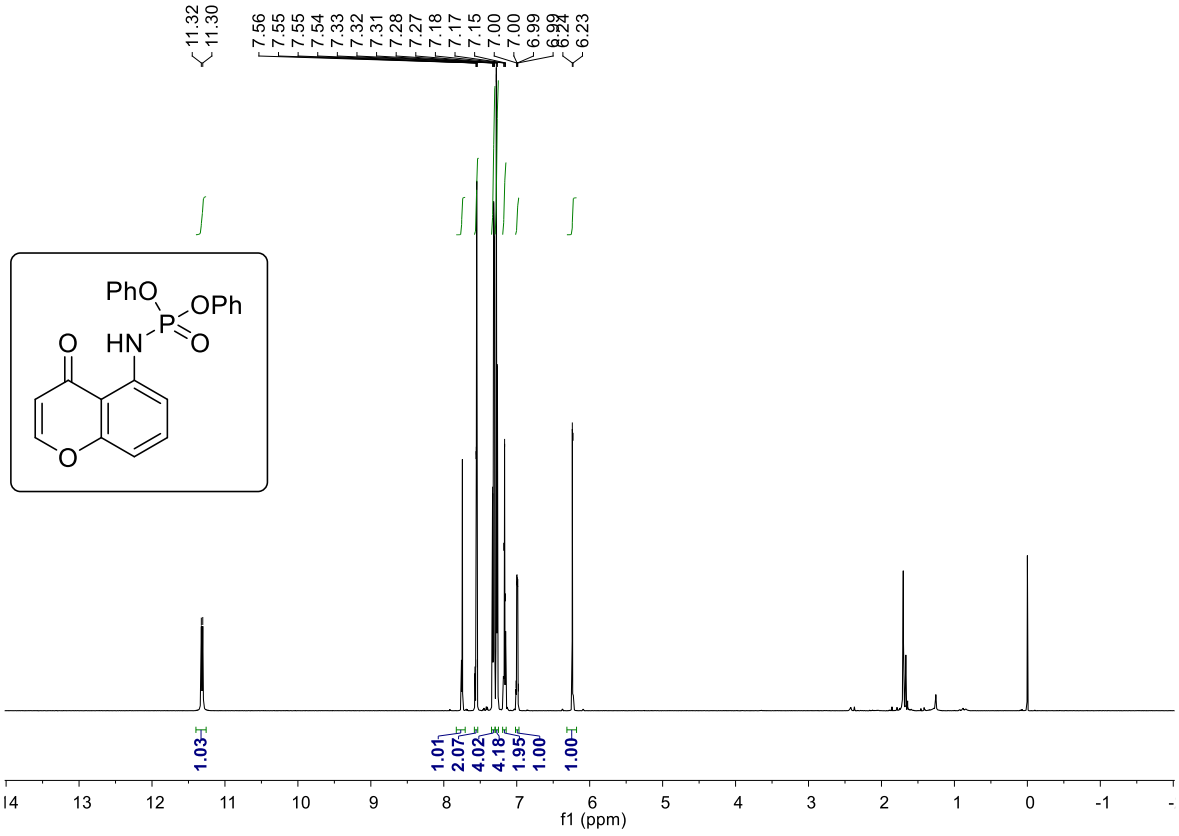
Diphenyl (2-acetyl-5-bromophenyl)phosphoramidate (Scheme 2, **3k**)

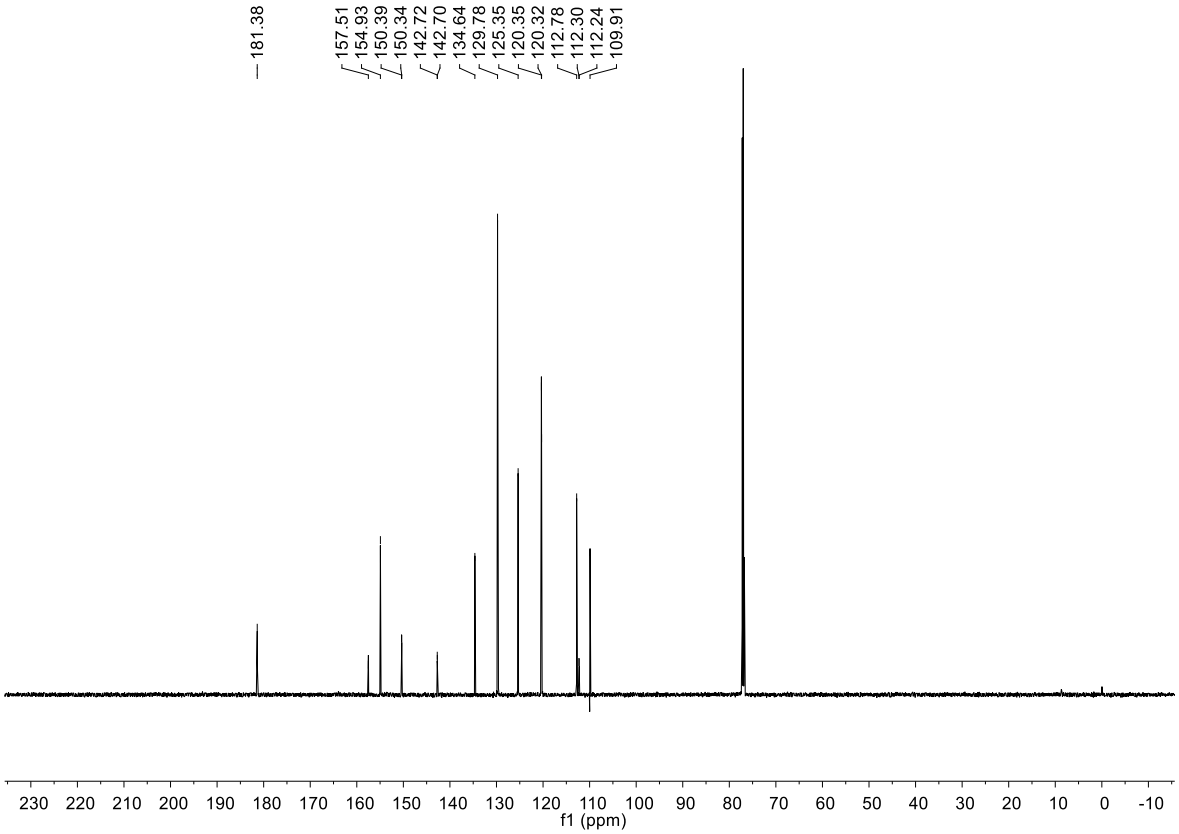


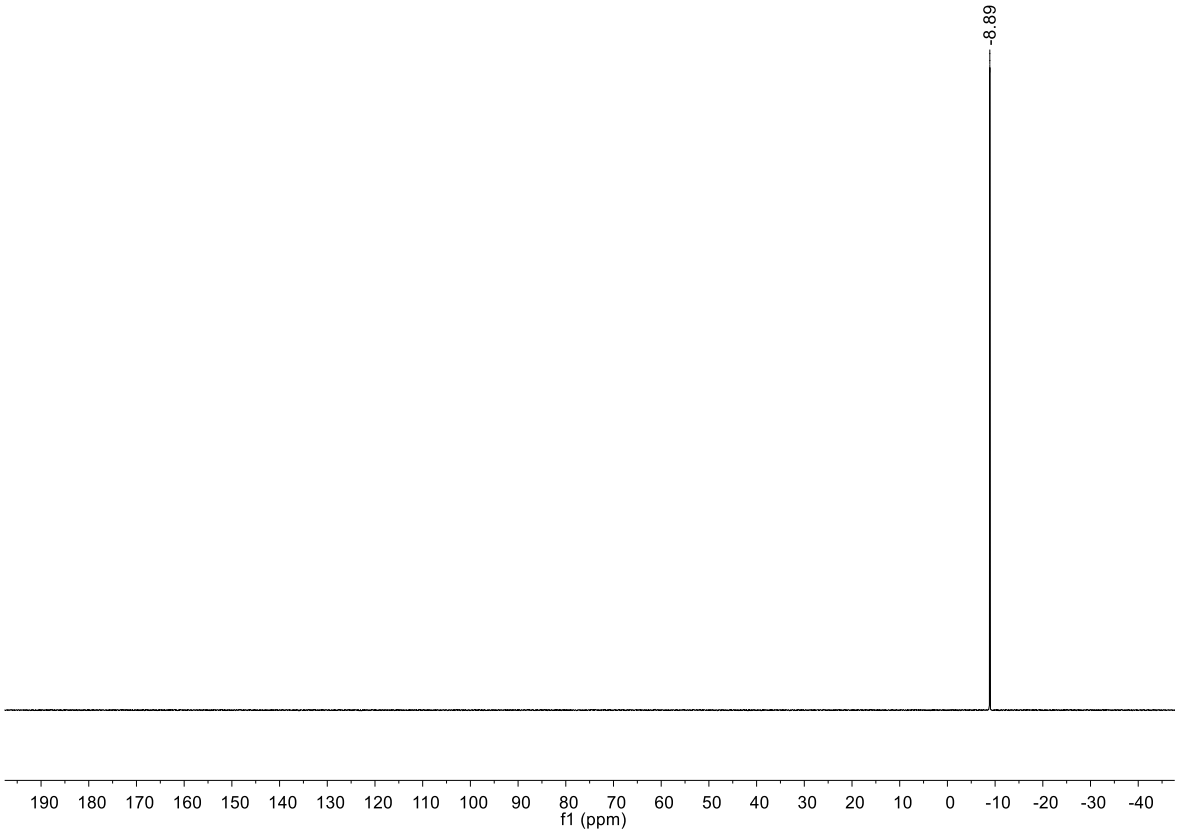

201.53
150.26
150.21
143.88
133.00
129.85
125.50
124.17
121.86
121.85
120.28
120.25
119.90
119.84
28.06
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-9.34
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

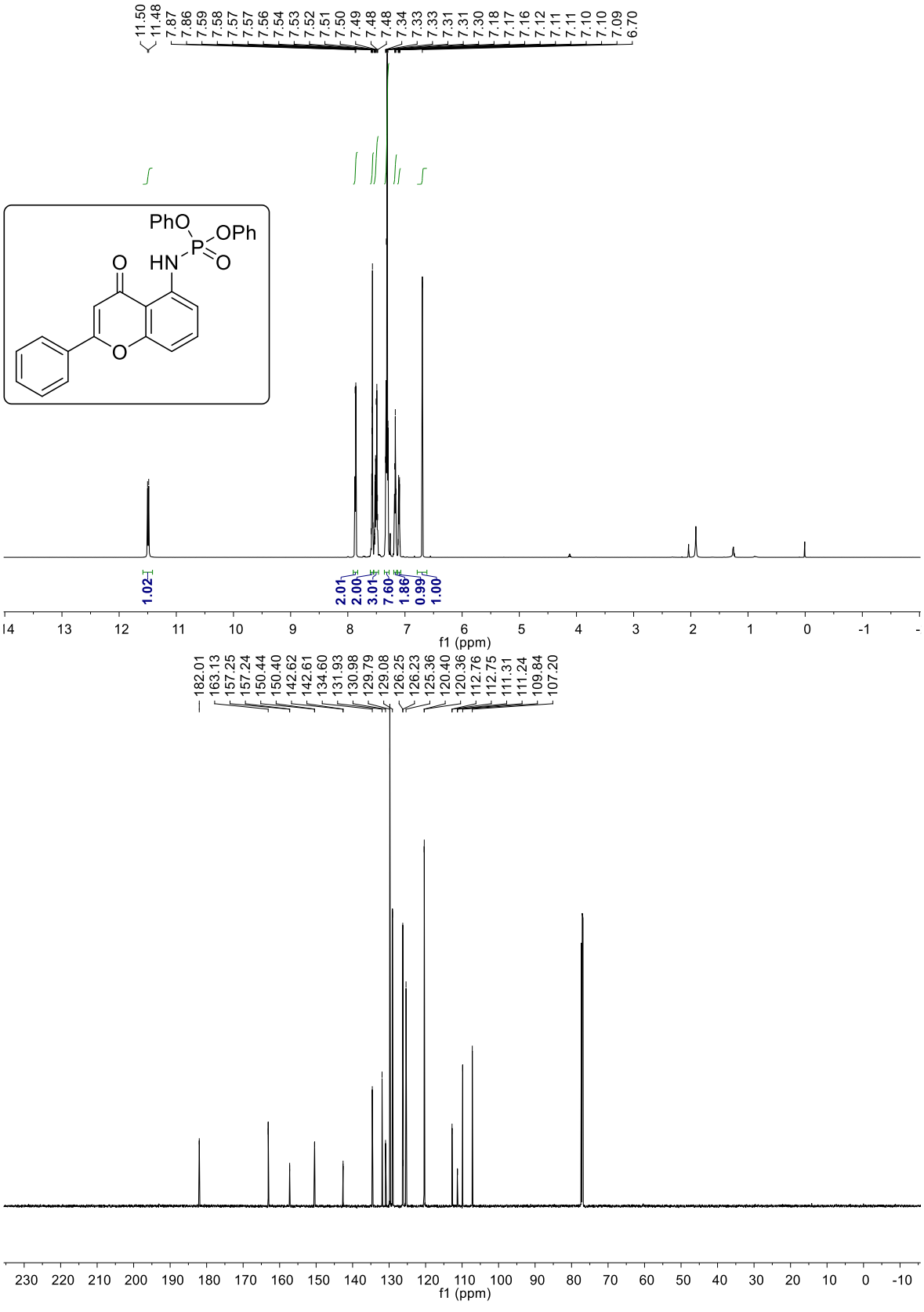
Diphenyl (4-oxo-4H-chromen-5-yl)phosphoramidate (Scheme 2, **3l**)

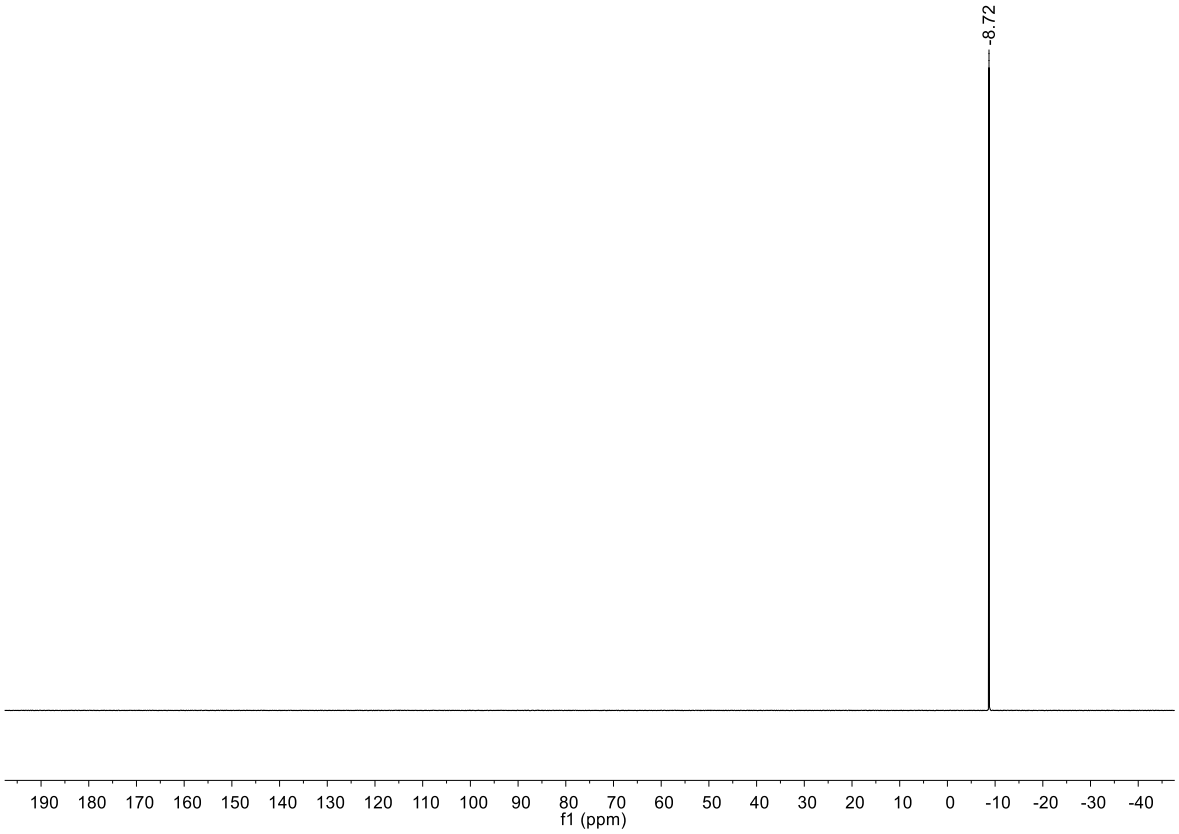




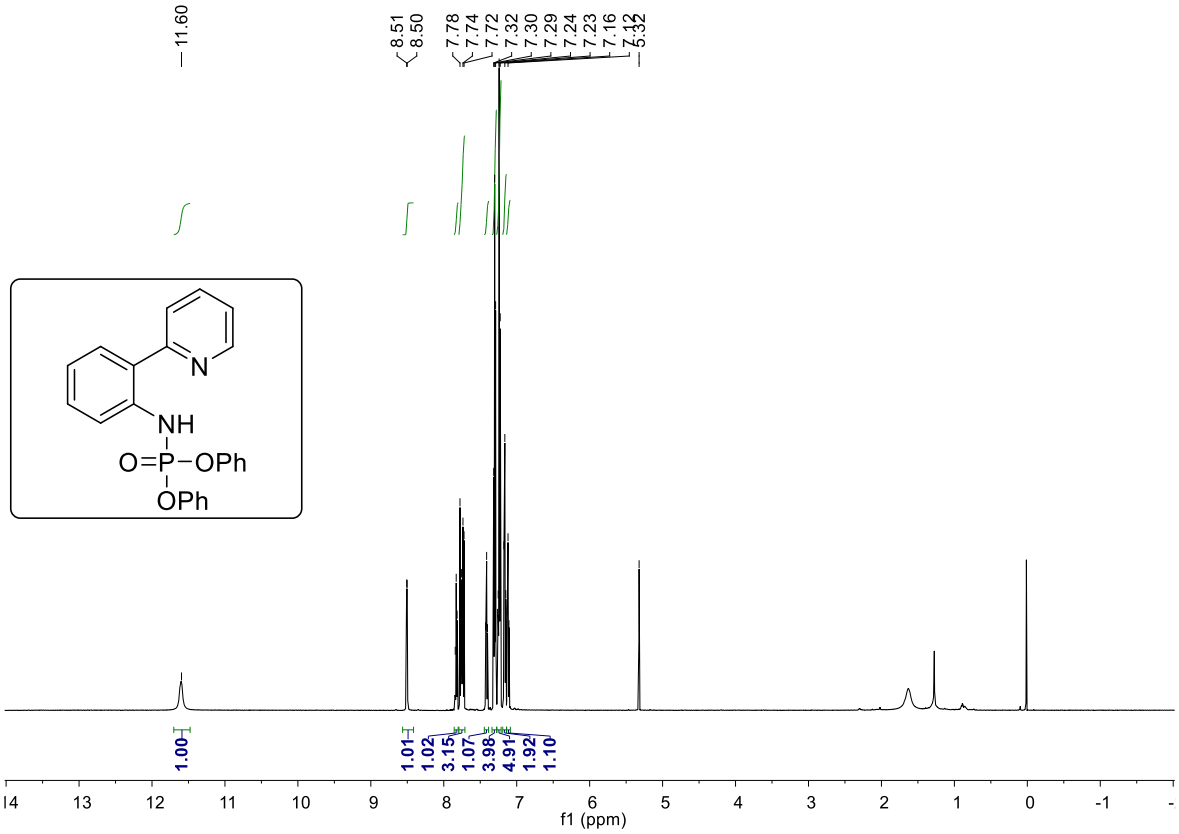

-8.89
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

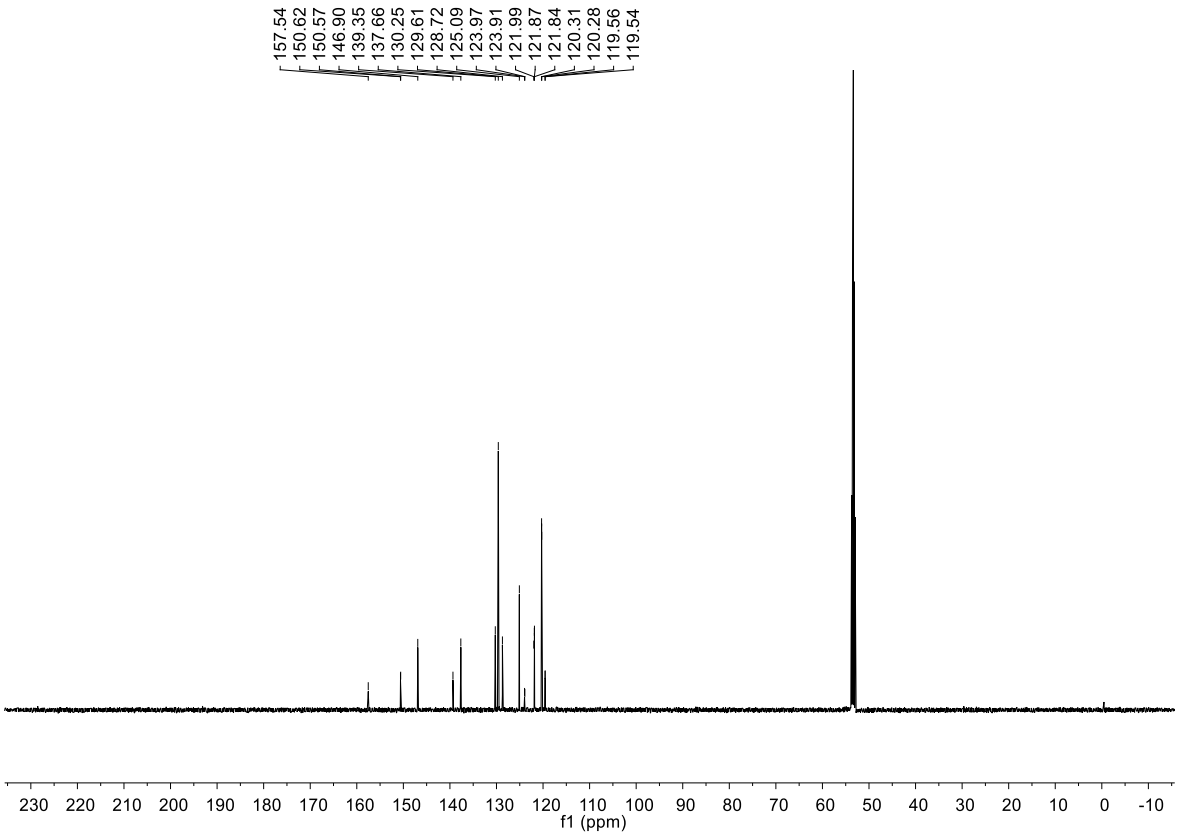
Diphenyl (4-oxo-2-phenyl-4H-chromen-5-yl)phosphoramidate (Scheme 2, **3m**)

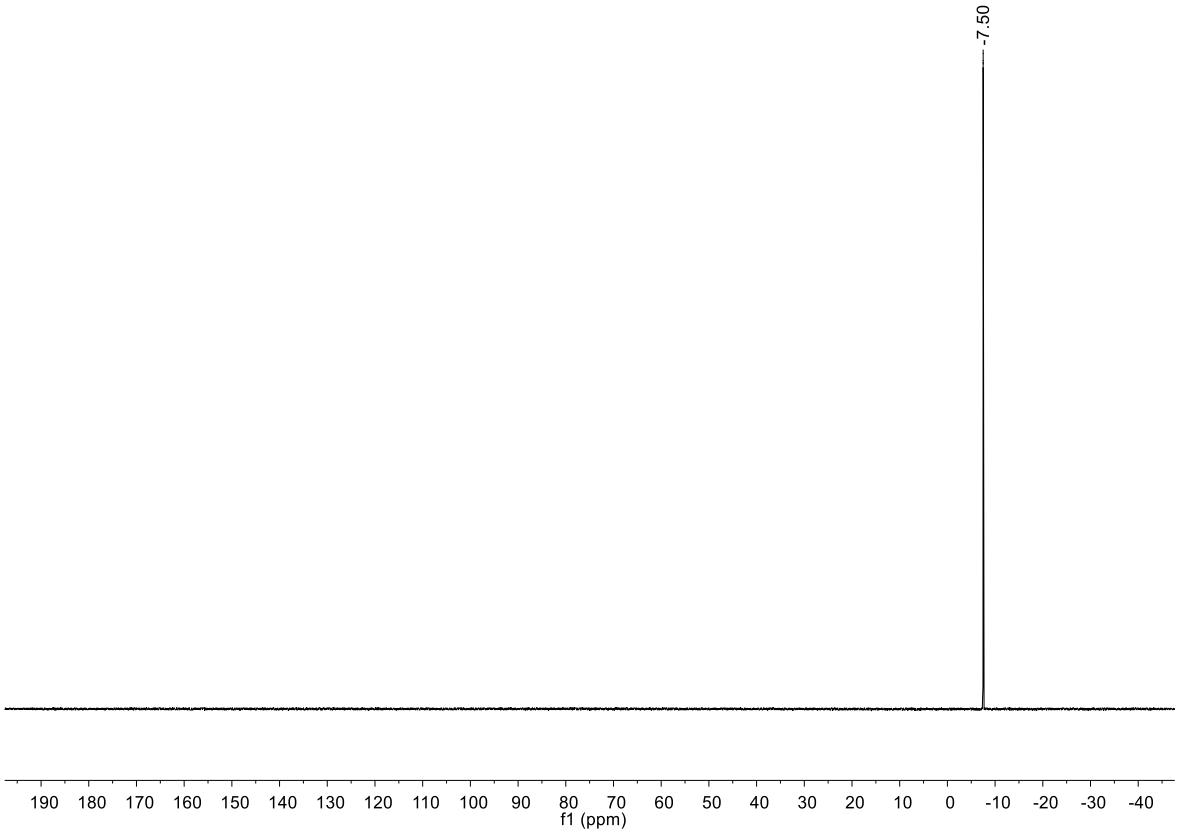



-8.72
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

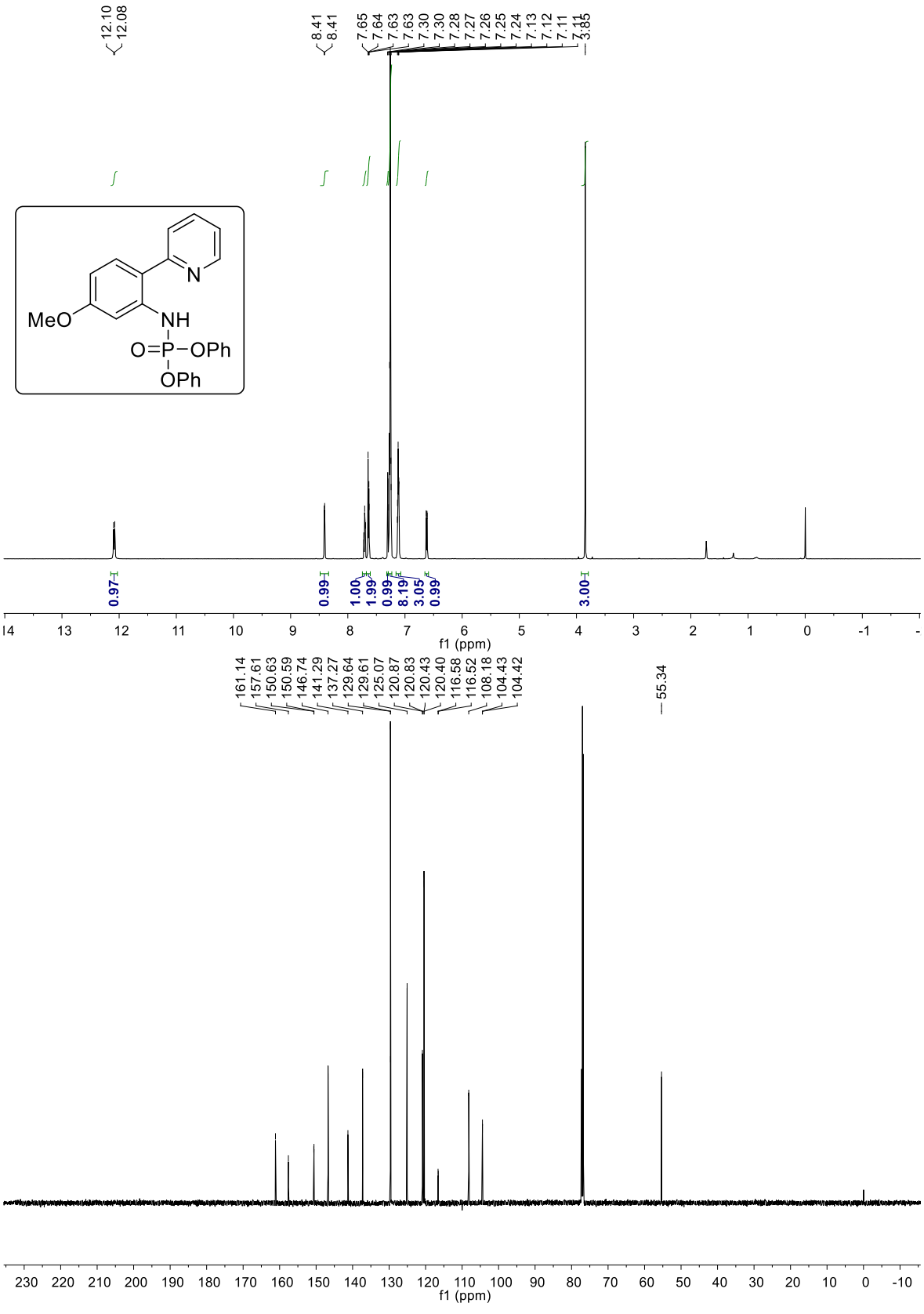
Diphenyl (2-(pyridin-2-yl)phenyl)phosphoramidate (Scheme 2, **3n**)

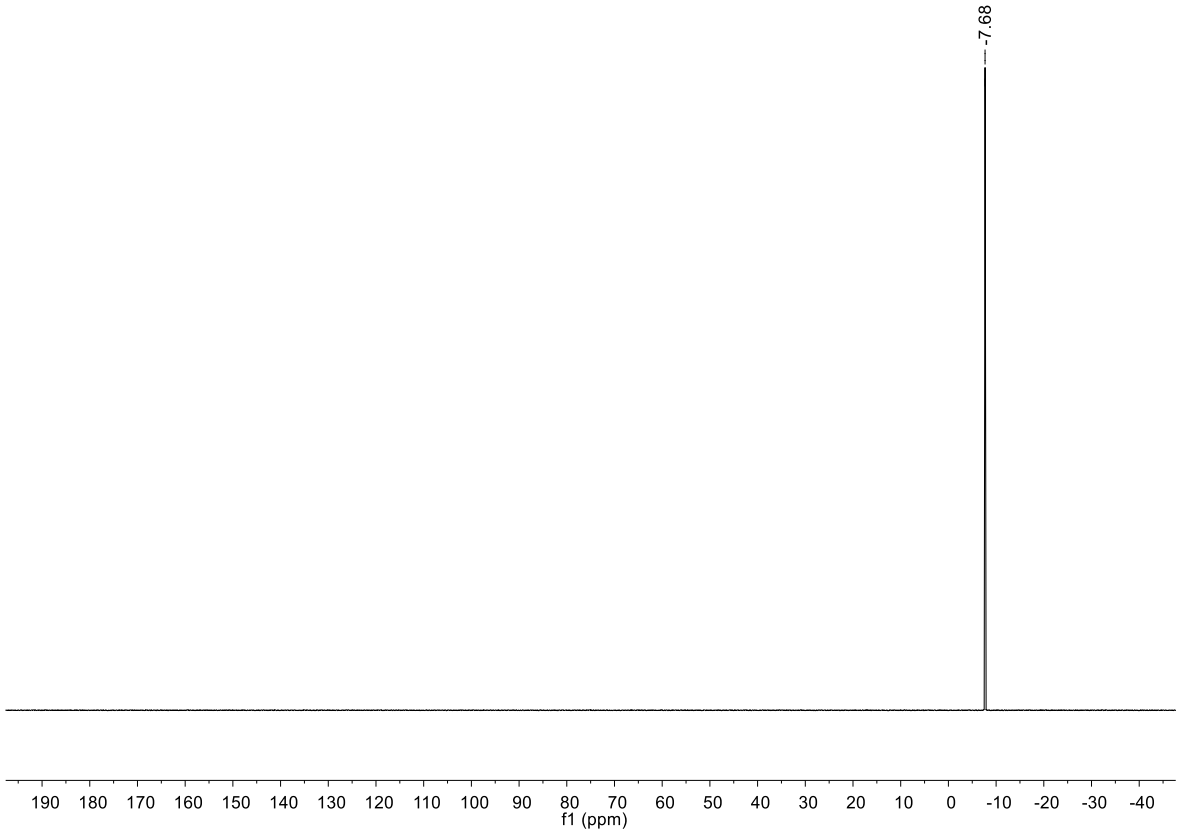




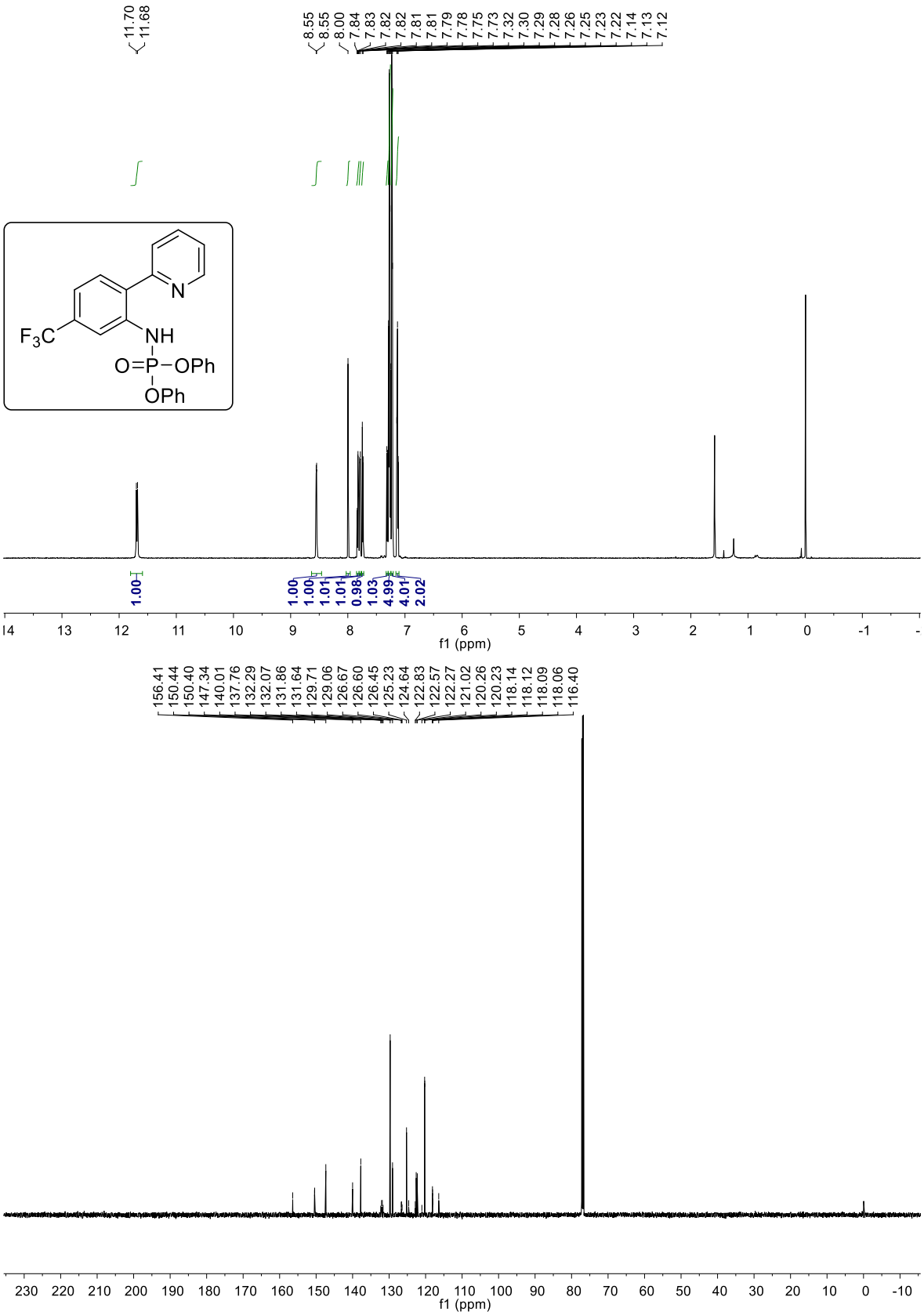

-7.50
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

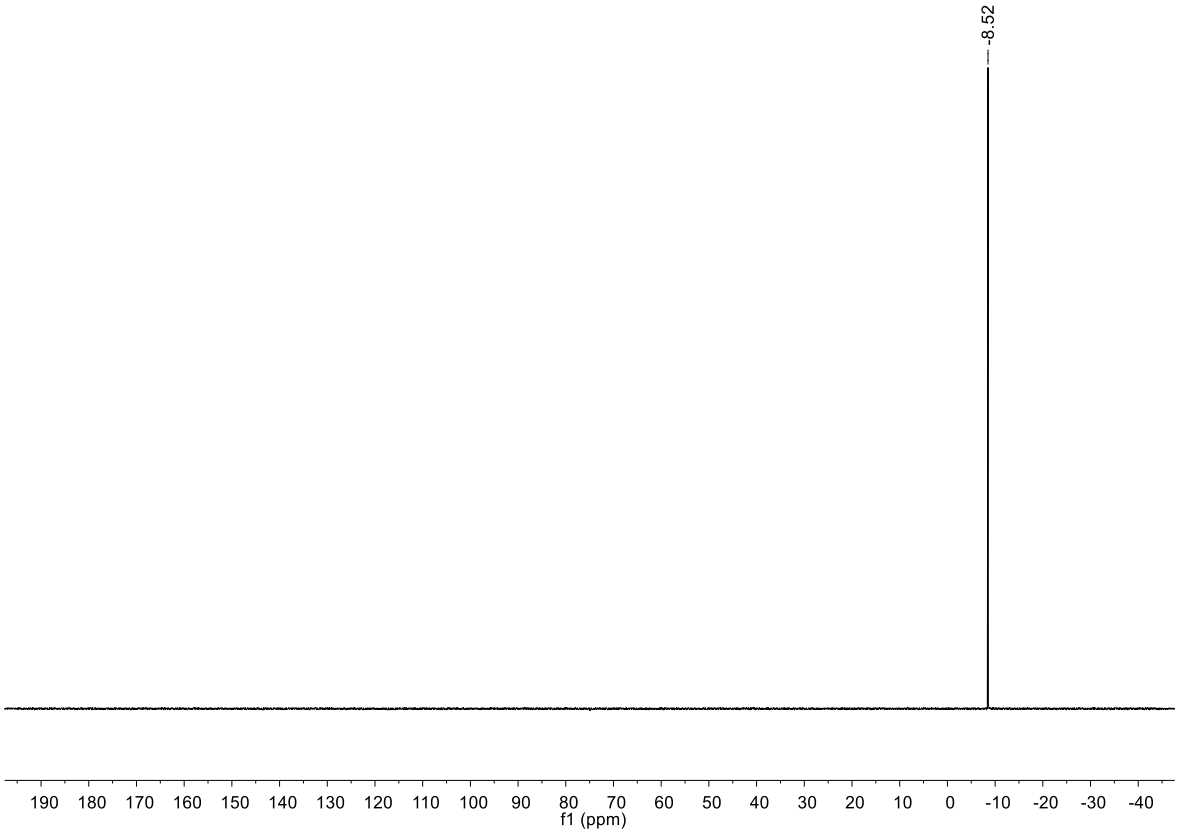
Diphenyl (5-methoxy-2-(pyridin-2-yl)phenyl)phosphoramidate (Scheme 2, **3o**)



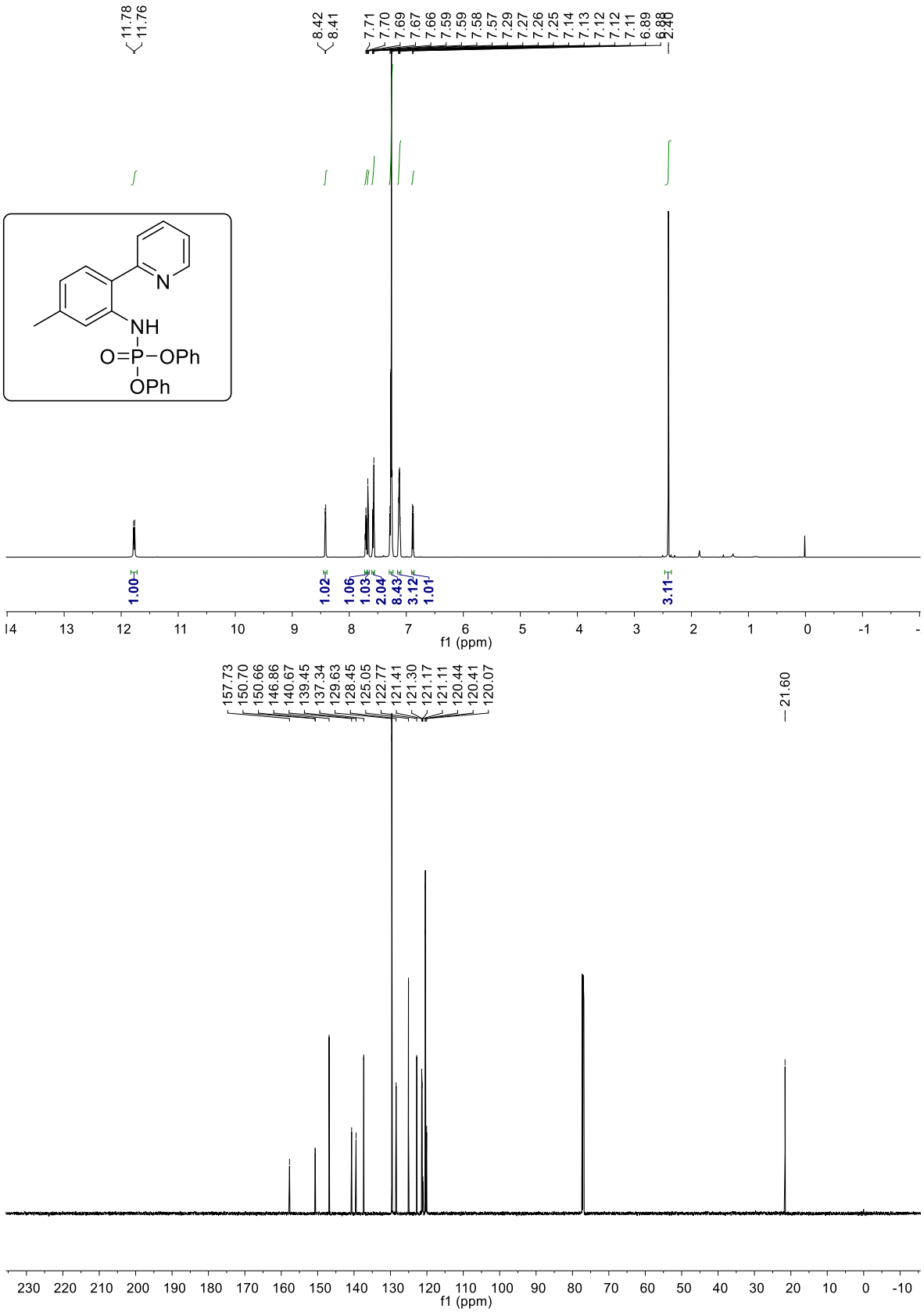

-7.68
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

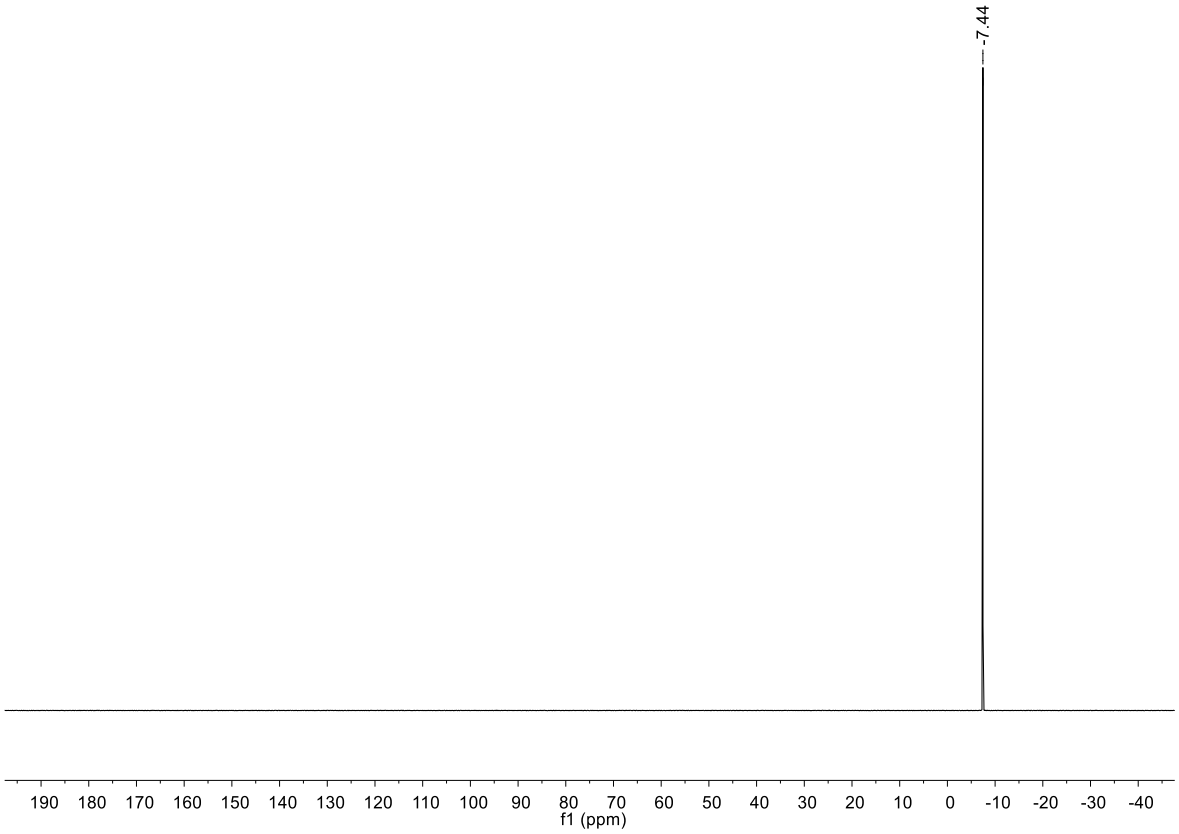
Diphenyl (2-(pyridin-2-yl)-5-(trifluoromethyl)phenyl)phosphoramidate (Scheme 2, **3p**)



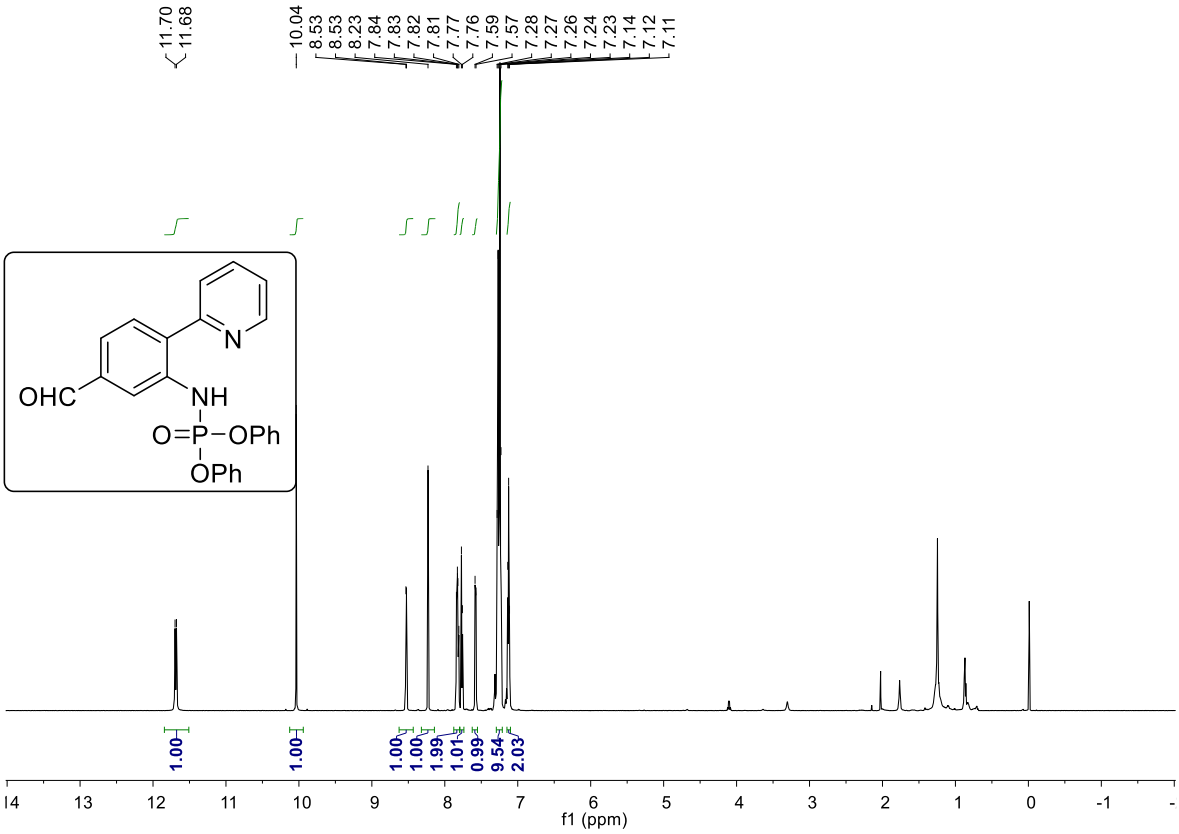

-8.52
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

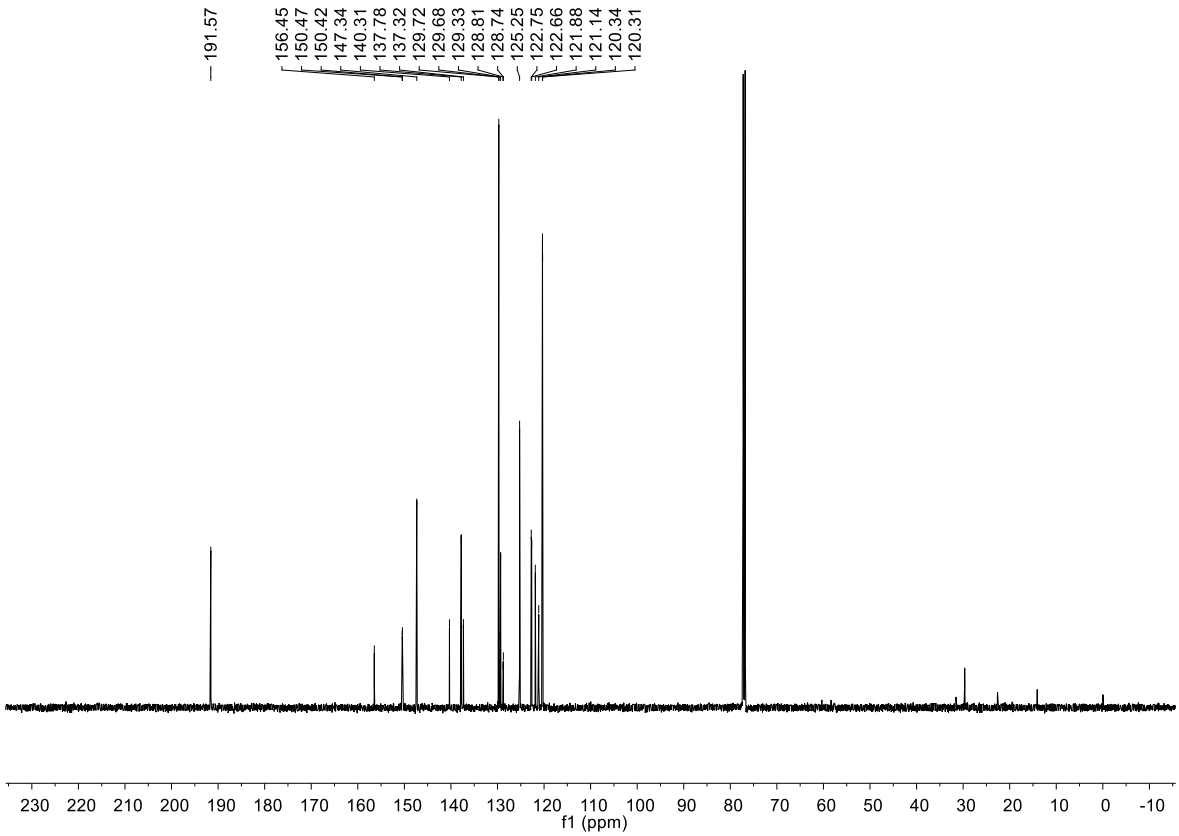
Diphenyl (5-methyl-2-(pyridin-2-yl)phenyl)phosphoramidate (Scheme 2, **3q**)

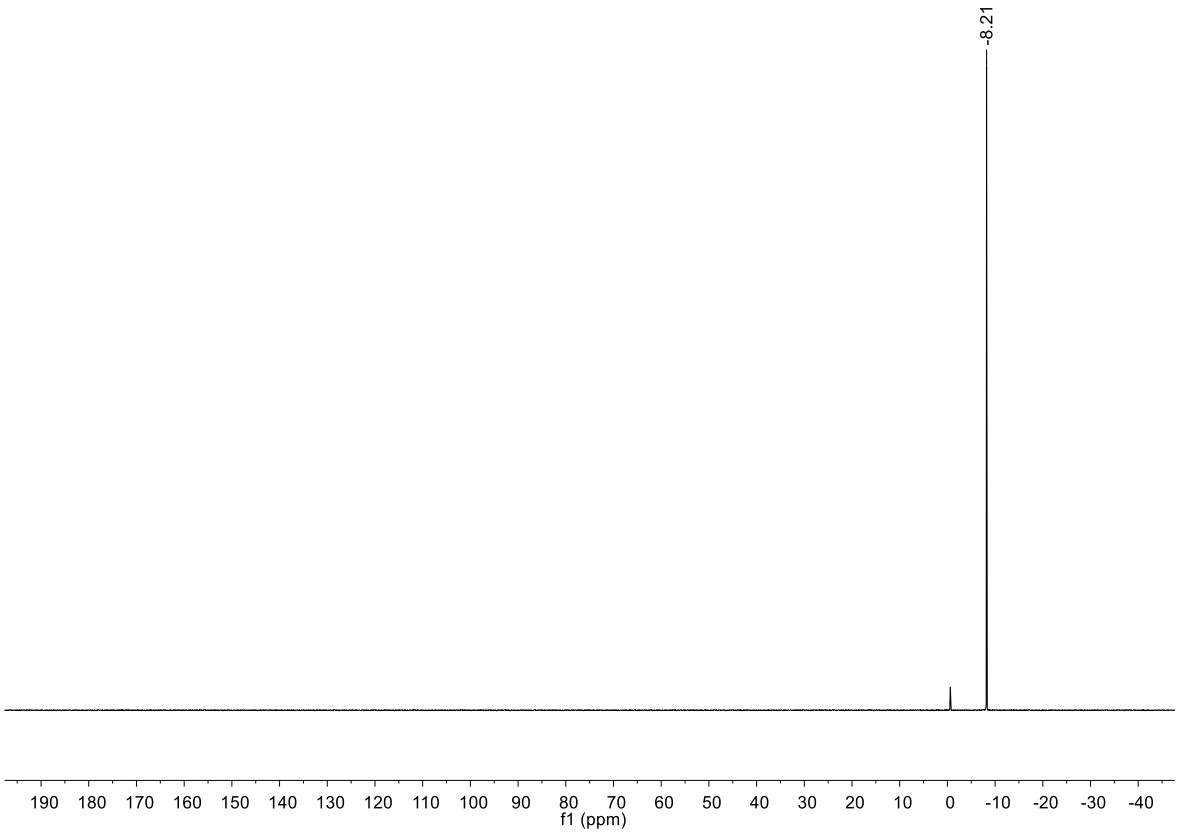



-7.44
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

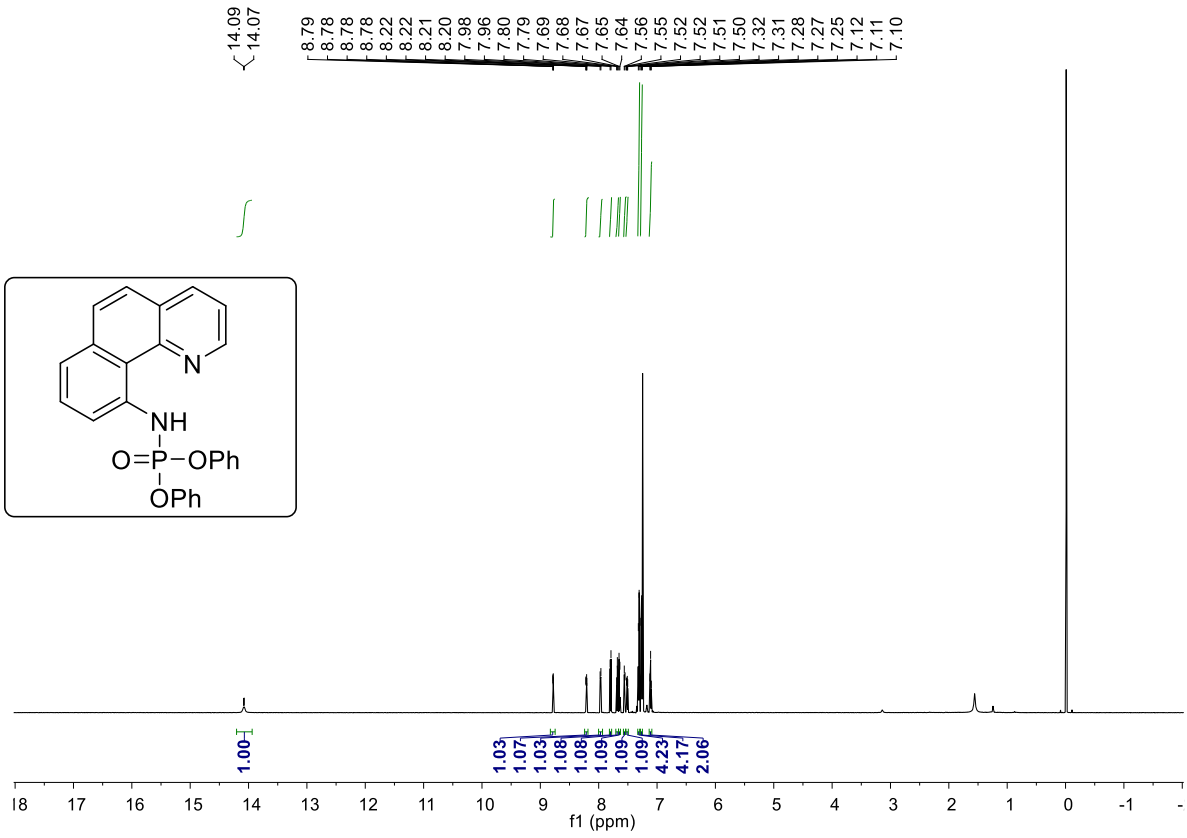
Diphenyl (5-formyl-2-(pyridin-2-yl)phenyl)phosphoramidate (Scheme 2, **3r**)

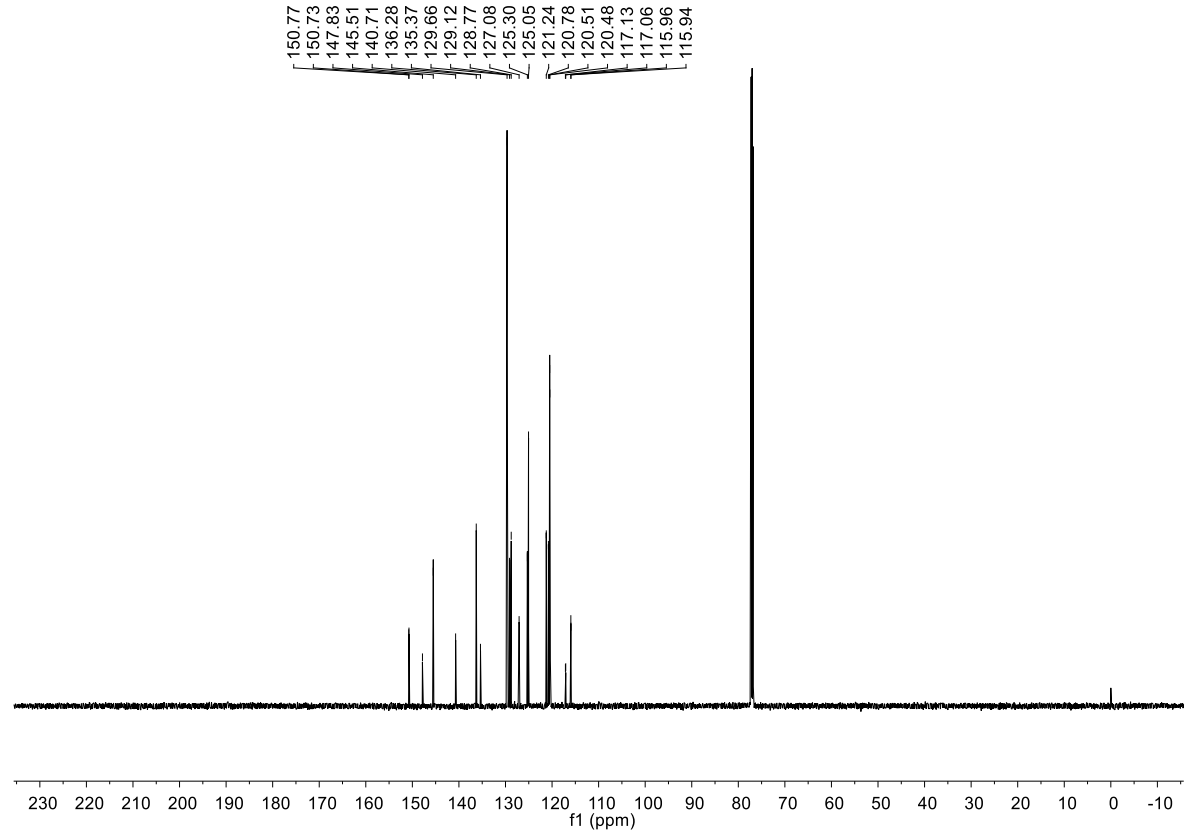


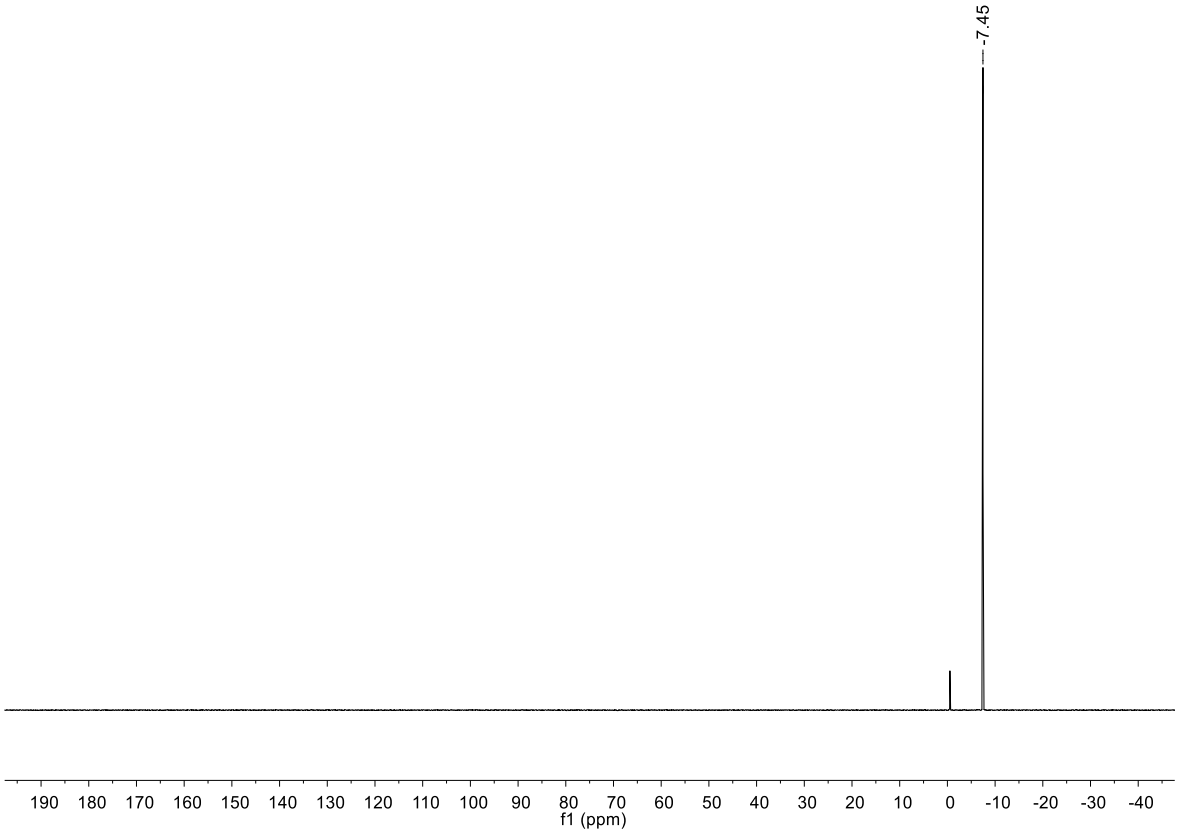



-8.21
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

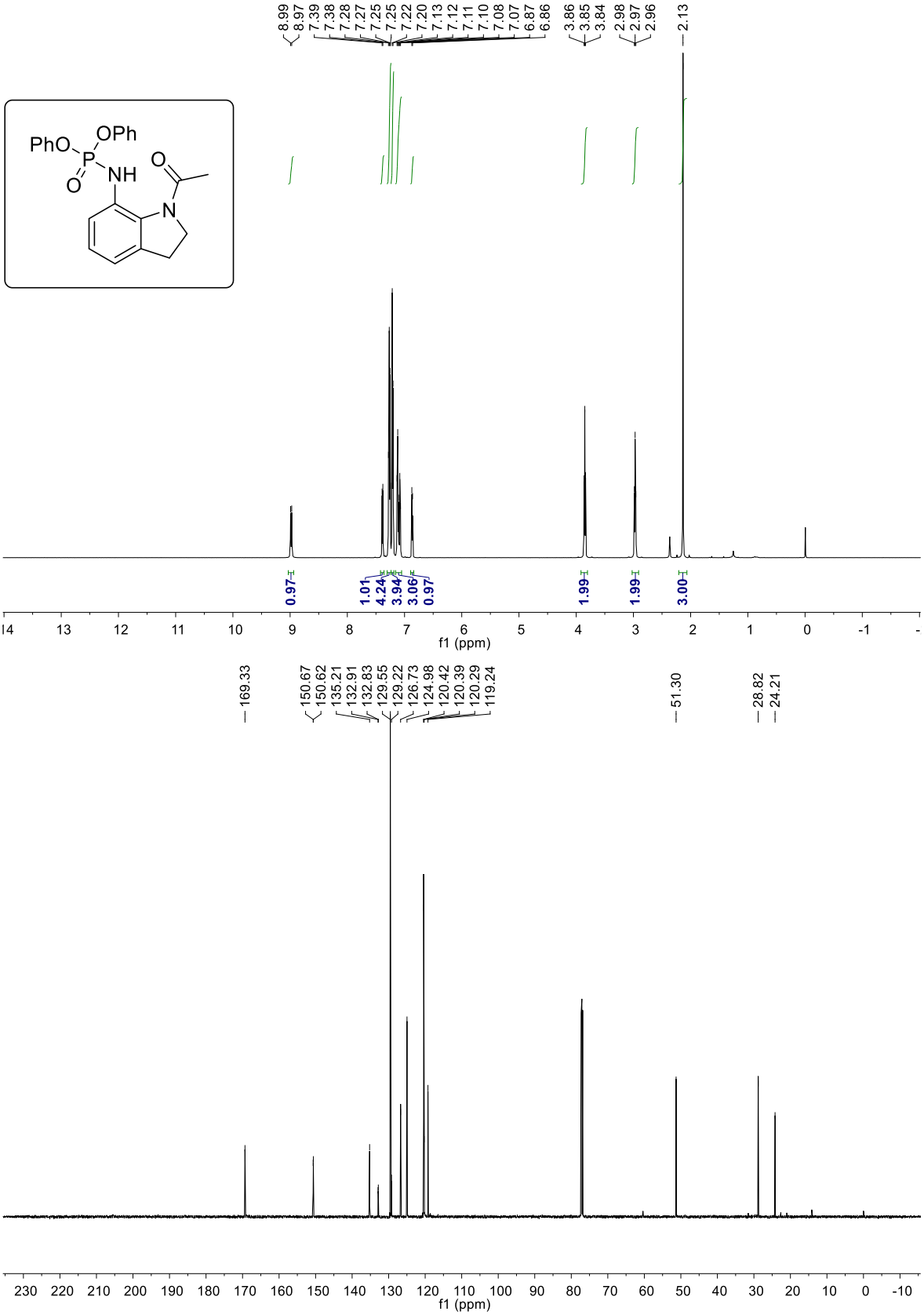
Diphenyl benzo[h]quinolin-10-ylphosphoramidate (Scheme 2, **3s)**

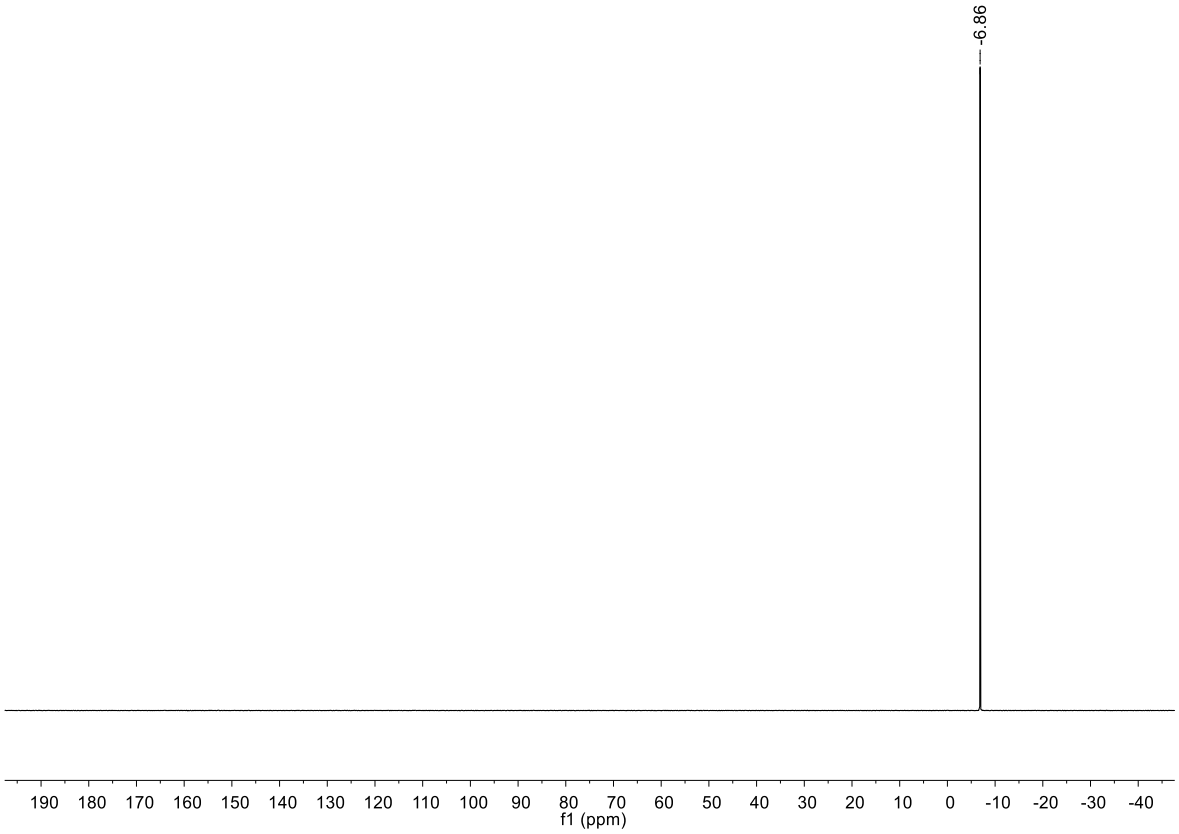




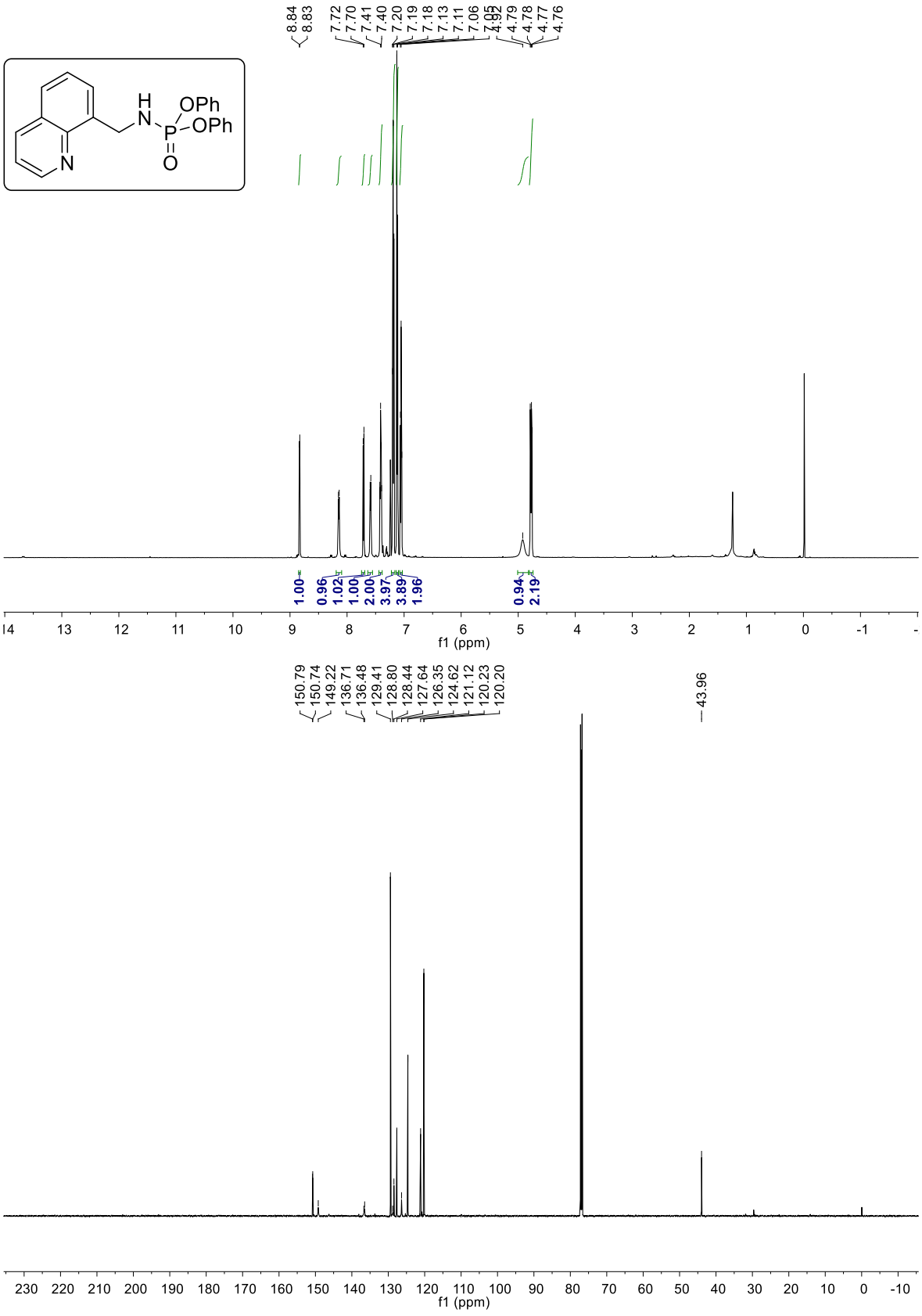

-7.45
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

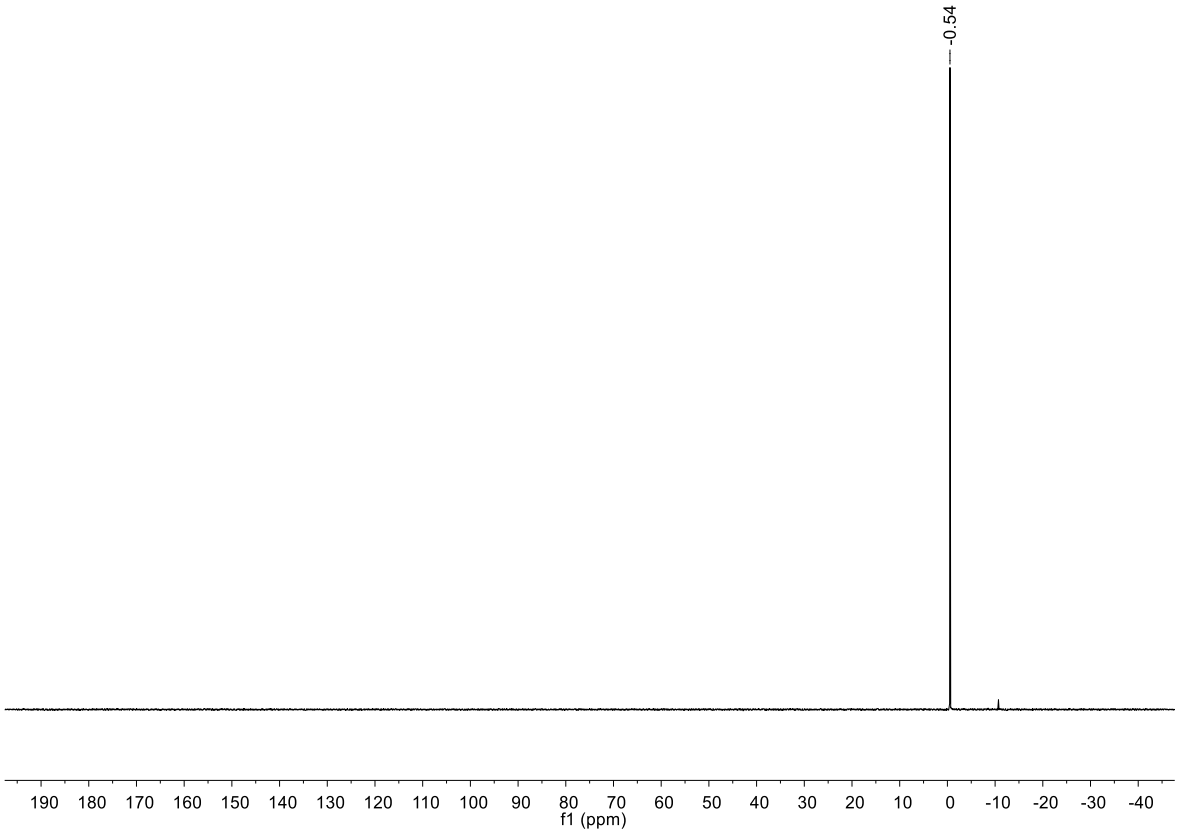
Diphenyl (1-acetylindolin-7-yl)phosphoramidate (Scheme 2, **3t)**



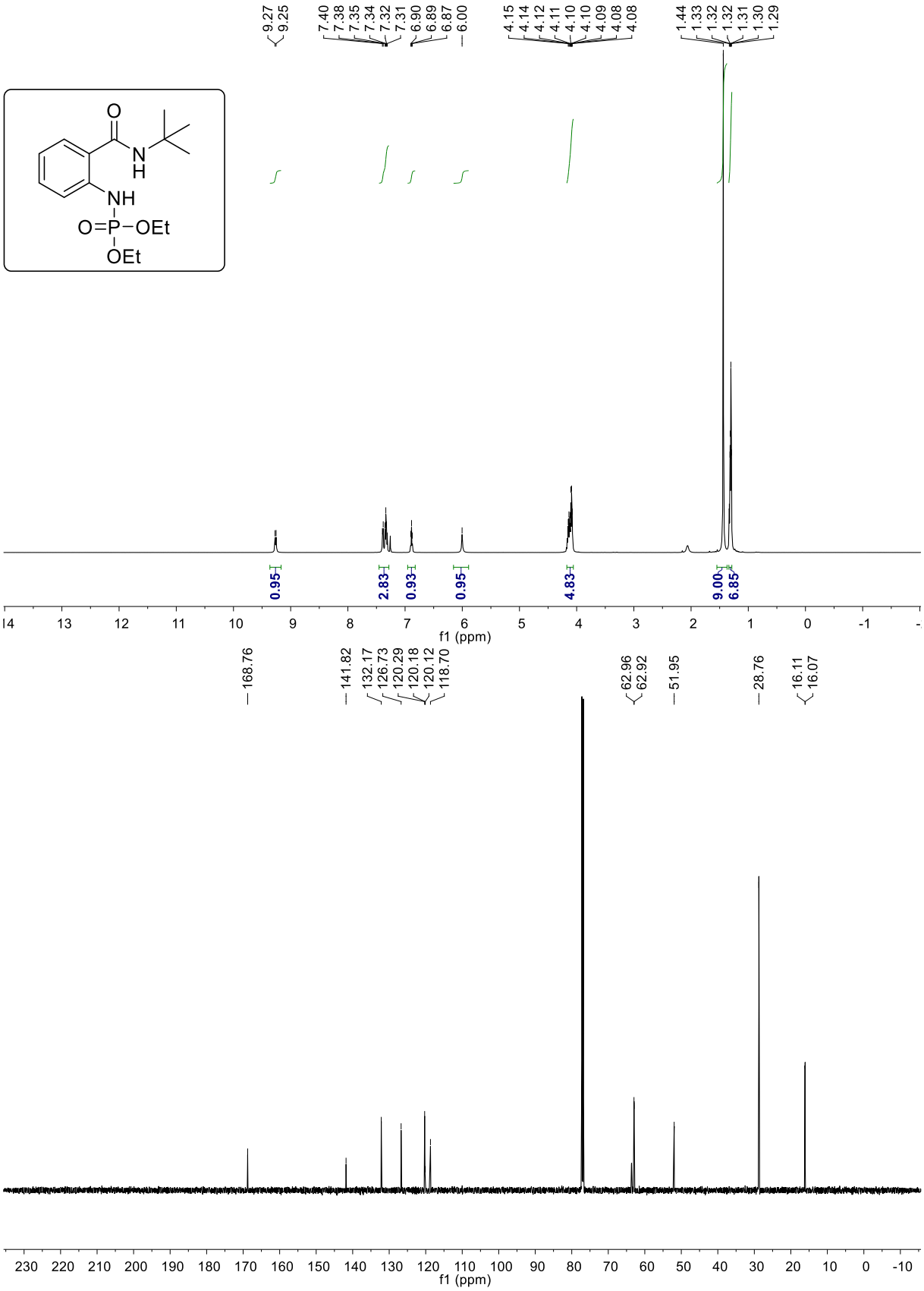

-6.86
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

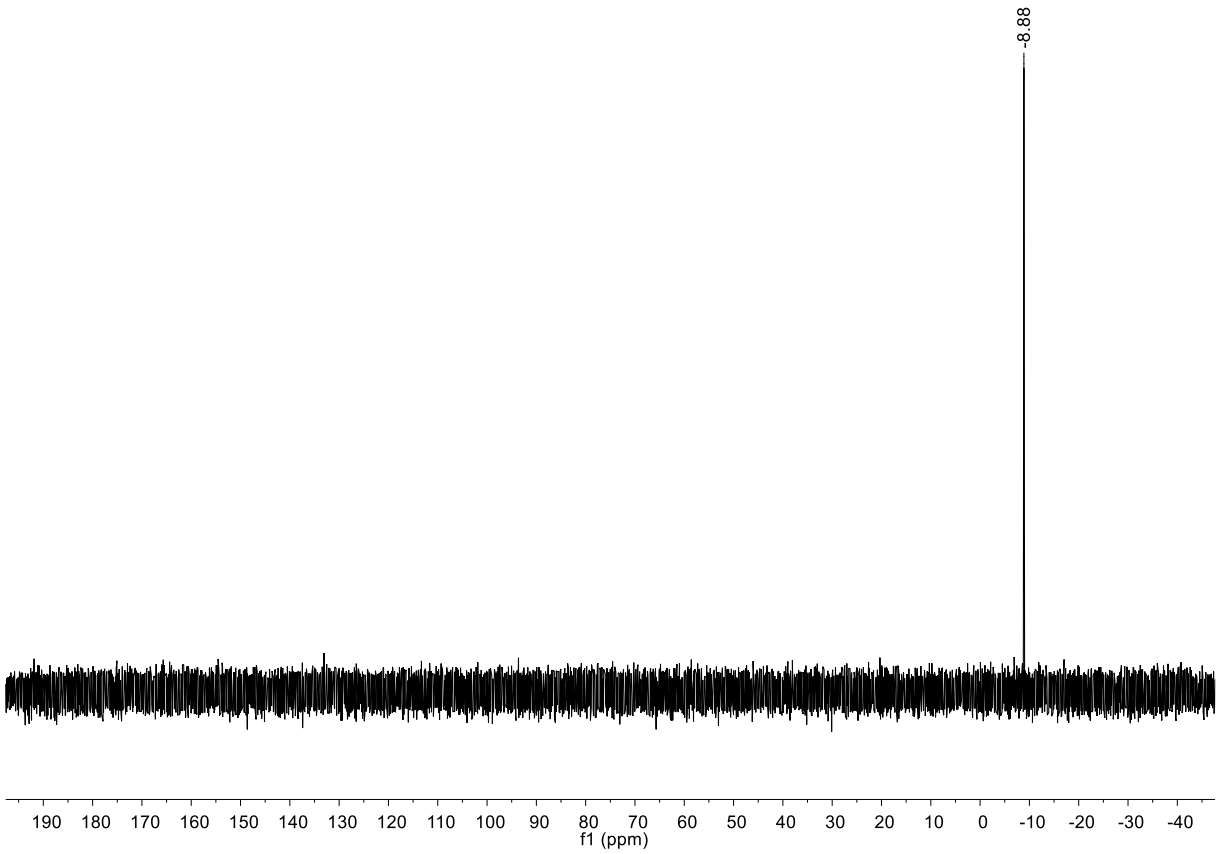
Diphenyl (quinolin-8-ylmethyl)phosphoramidate (Scheme 2, **3u**)



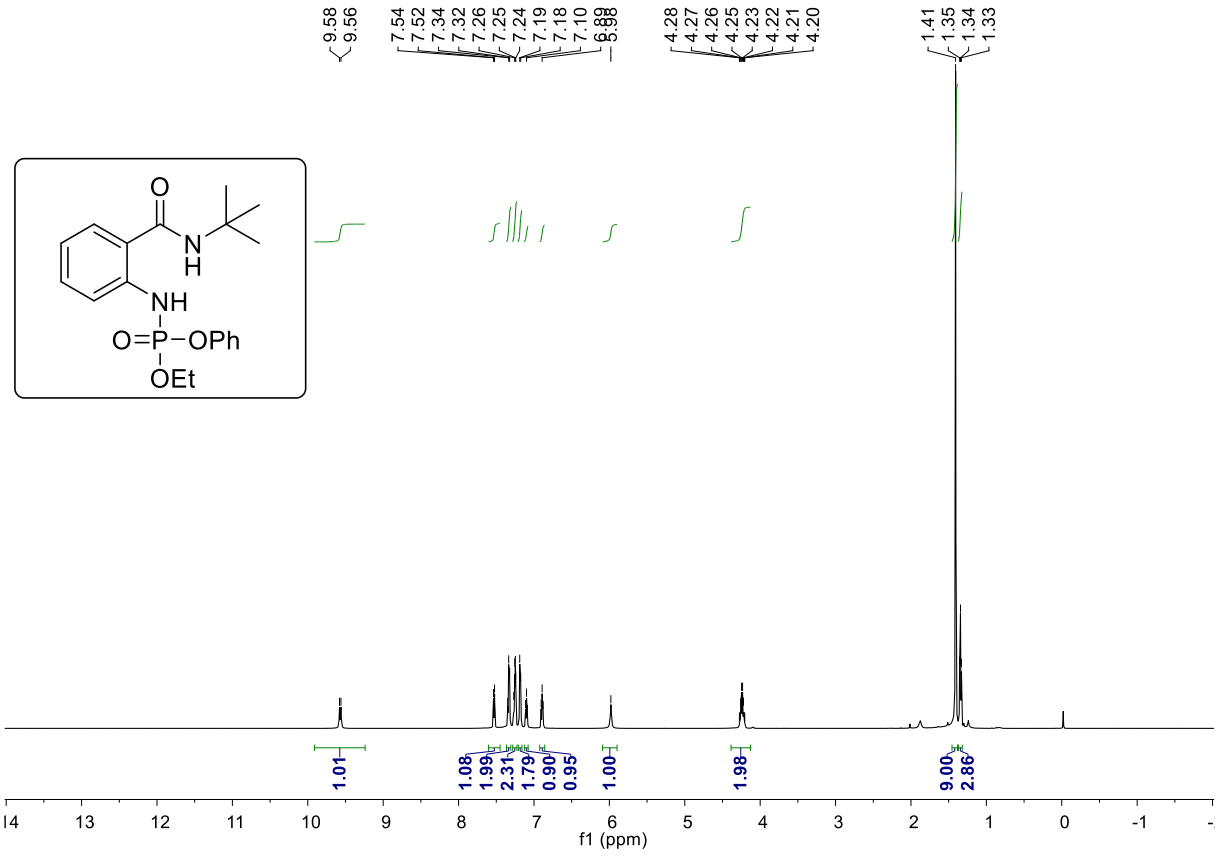

-0.54
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

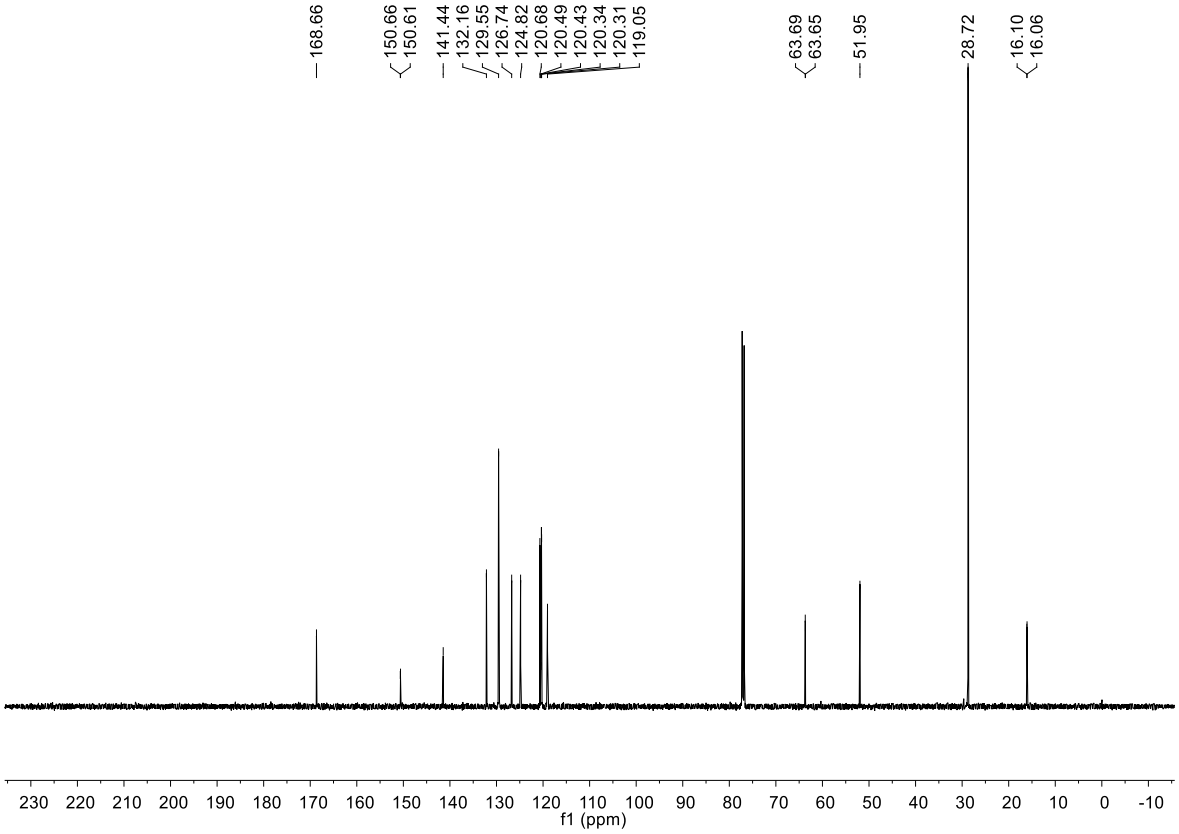
Diethyl (2-(*tert*-butylcarbamoyl)phenyl)phosphoramidate (Scheme 3, **4a**)

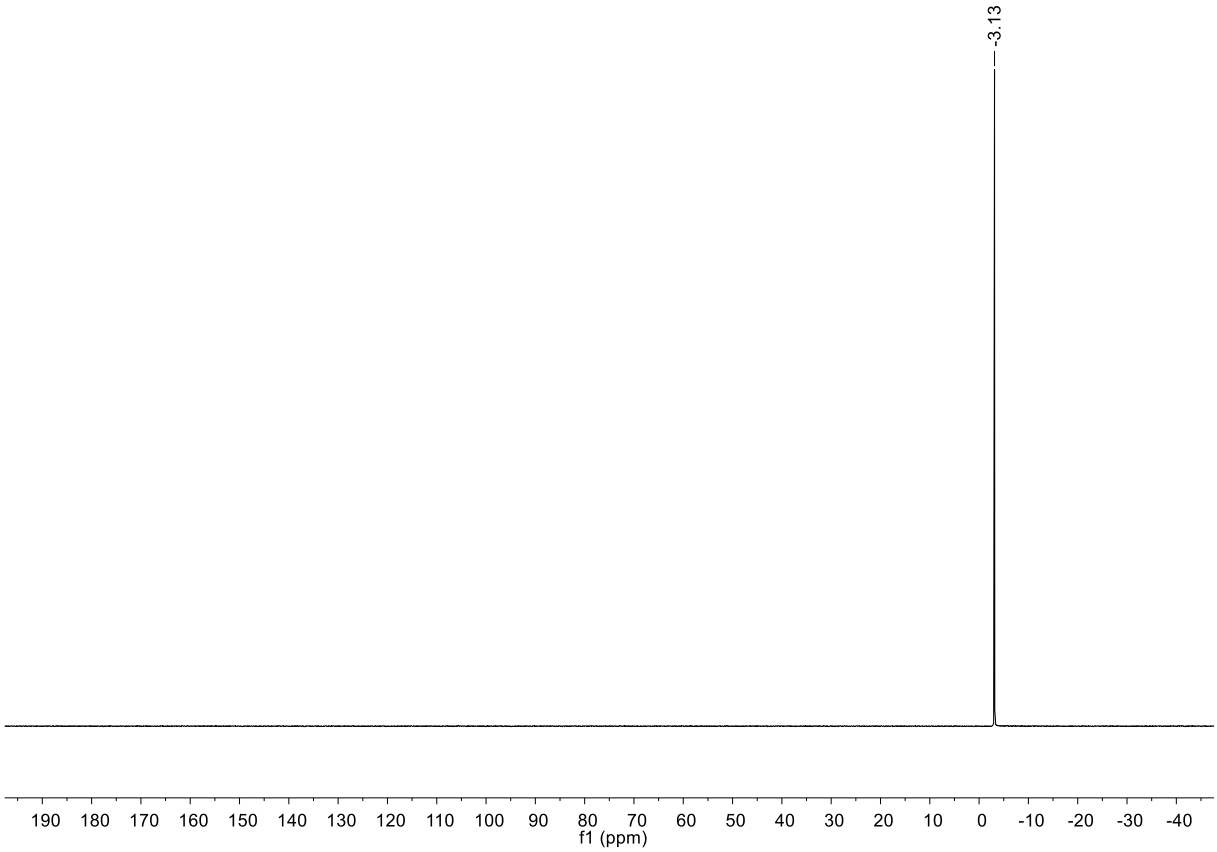



-8.88
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

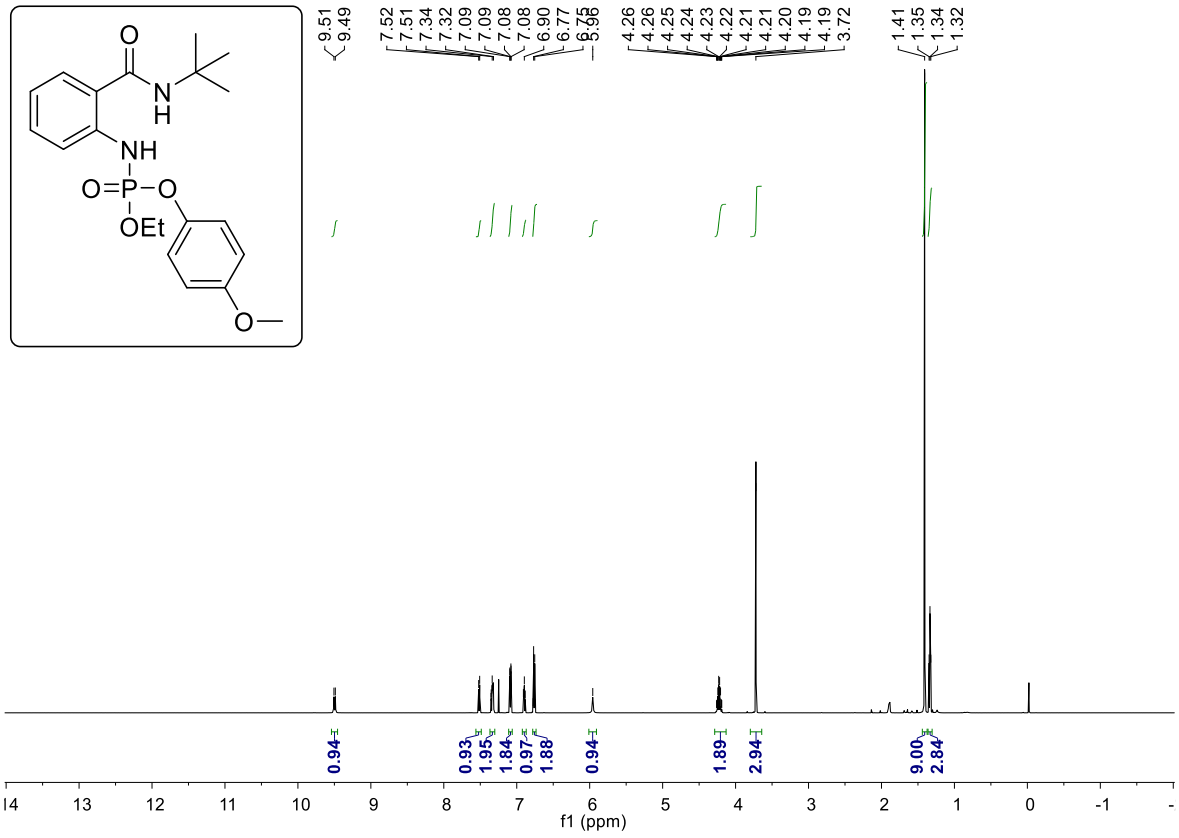
Ethyl phenyl (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (Scheme 3, **4b**)

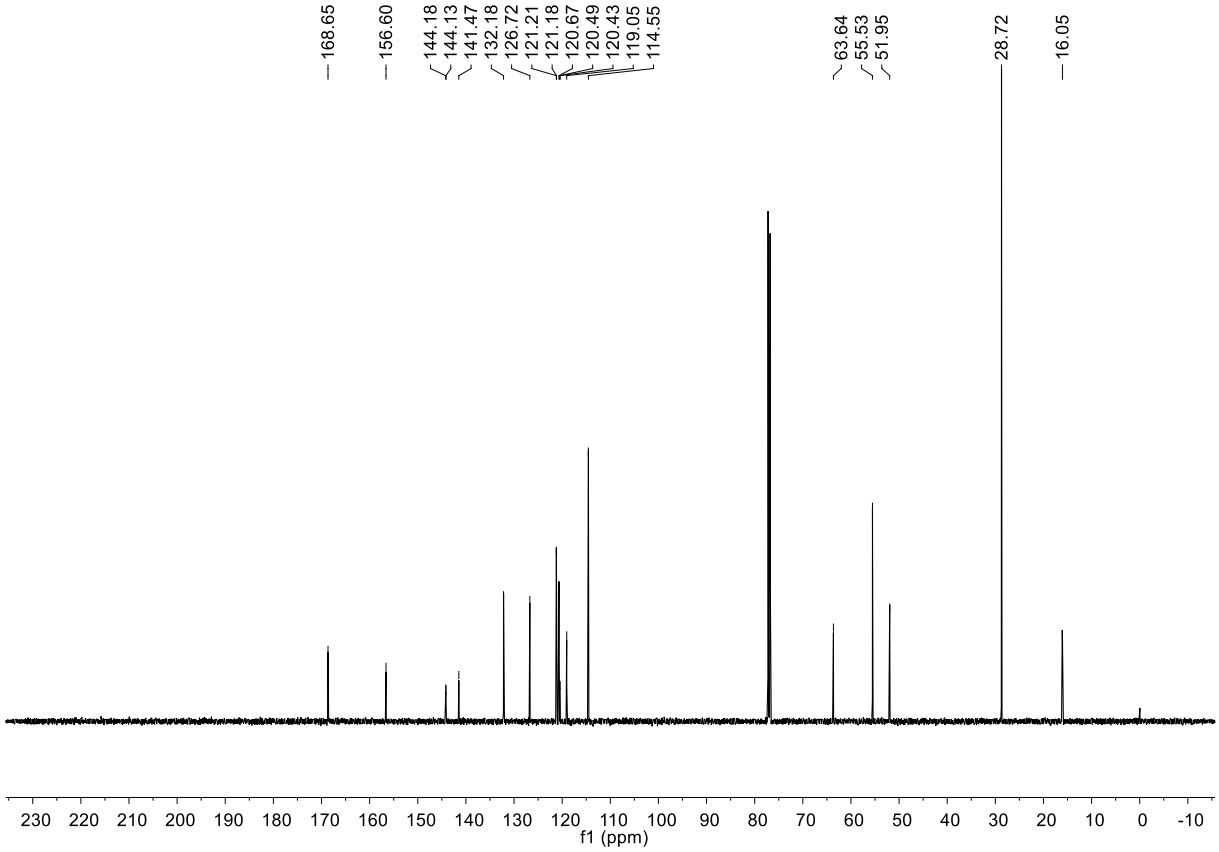


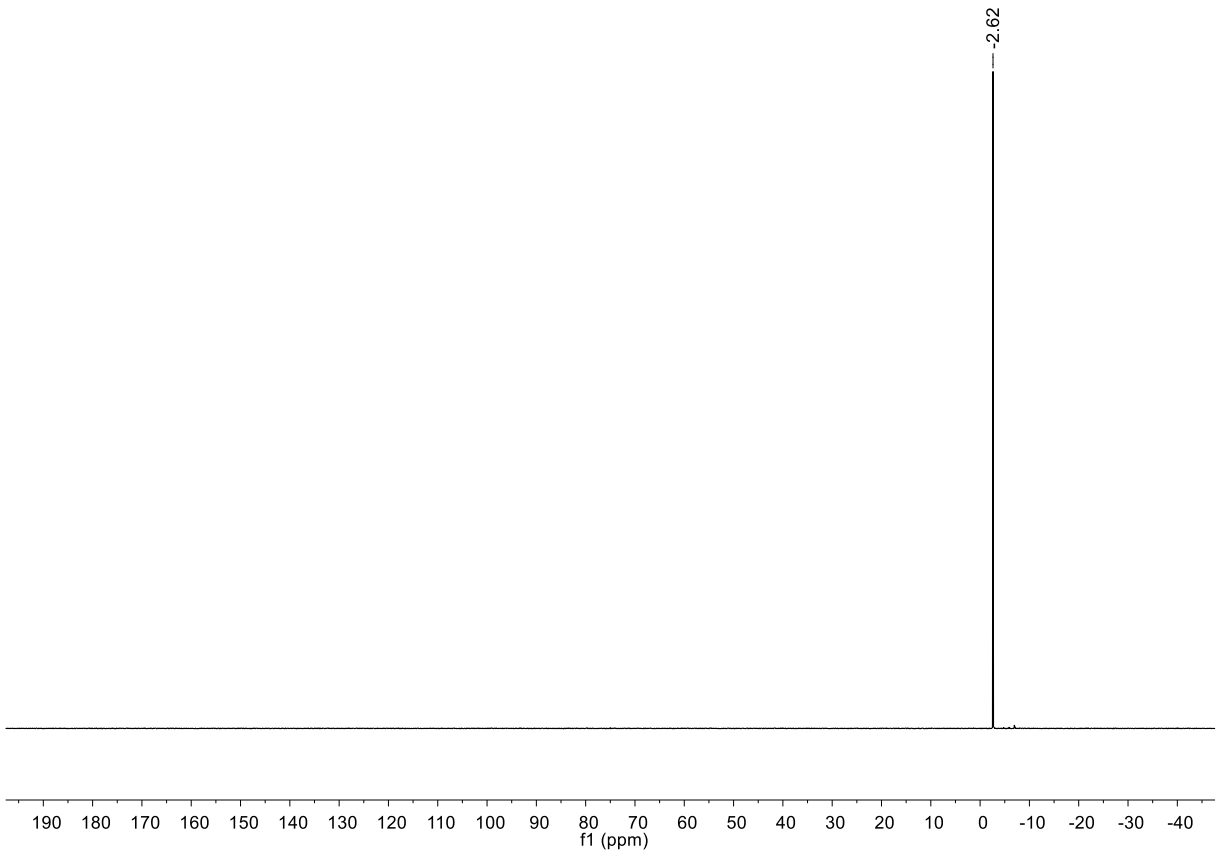

168.66
150.66
150.61
141.44
132.16
129.55
126.74
124.82
120.68
120.49
120.43
120.34
120.31
119.05
63.69
63.65
51.95
28.72
16.10
16.06
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-3.13
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

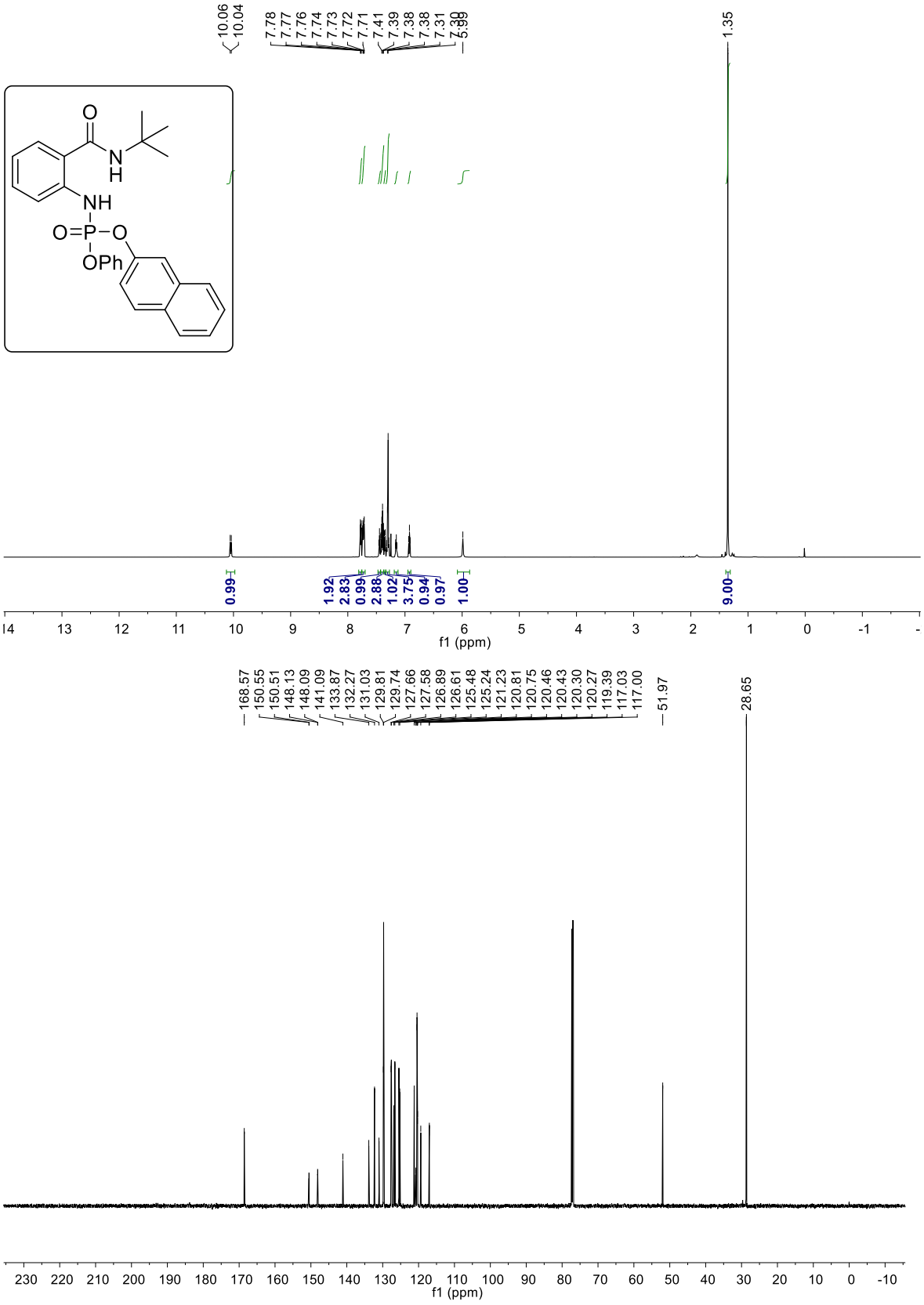
Ethyl (4-methoxyphenyl) (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (Scheme 3, **4c**)

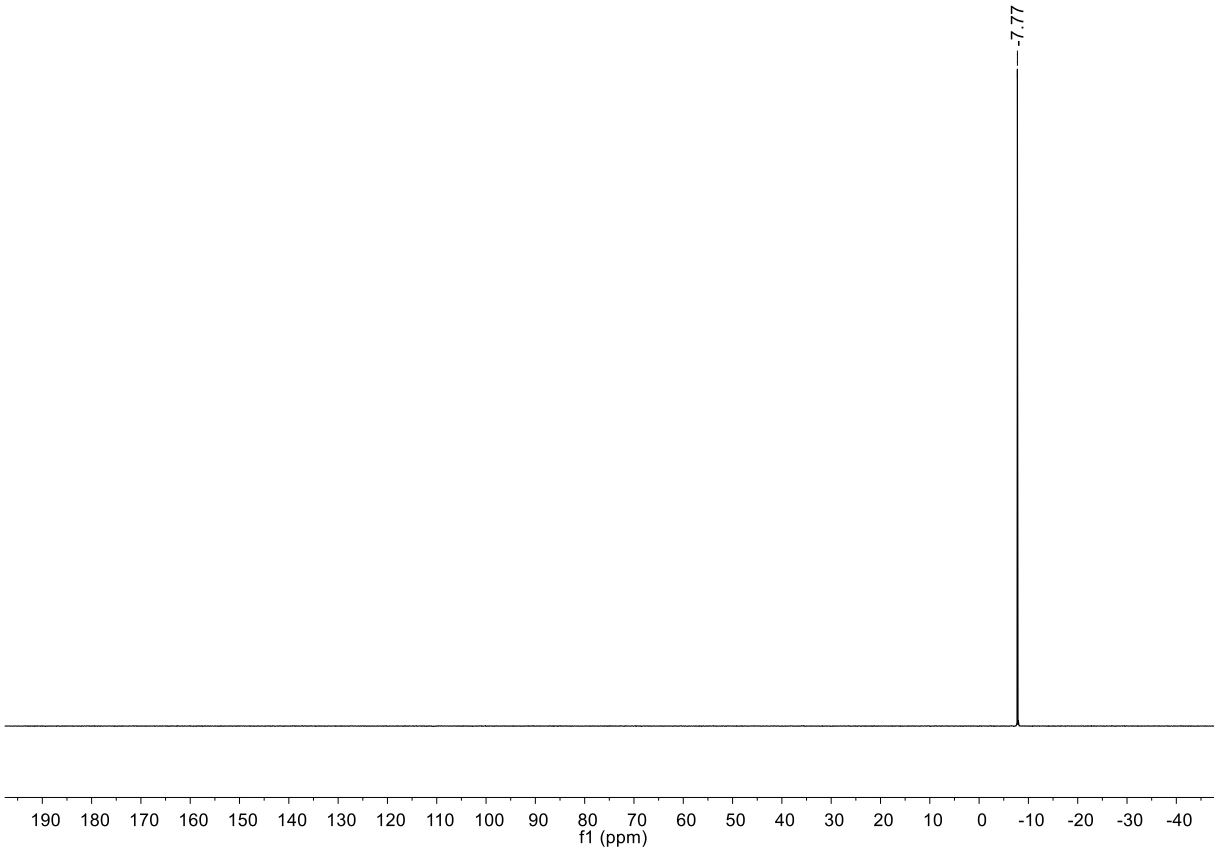



168.65
156.60
144.18
144.13
141.47
132.18
126.72
121.21
121.18
120.67
120.49
120.43
119.05
114.55
63.64
55.53
51.95
28.72
16.05
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

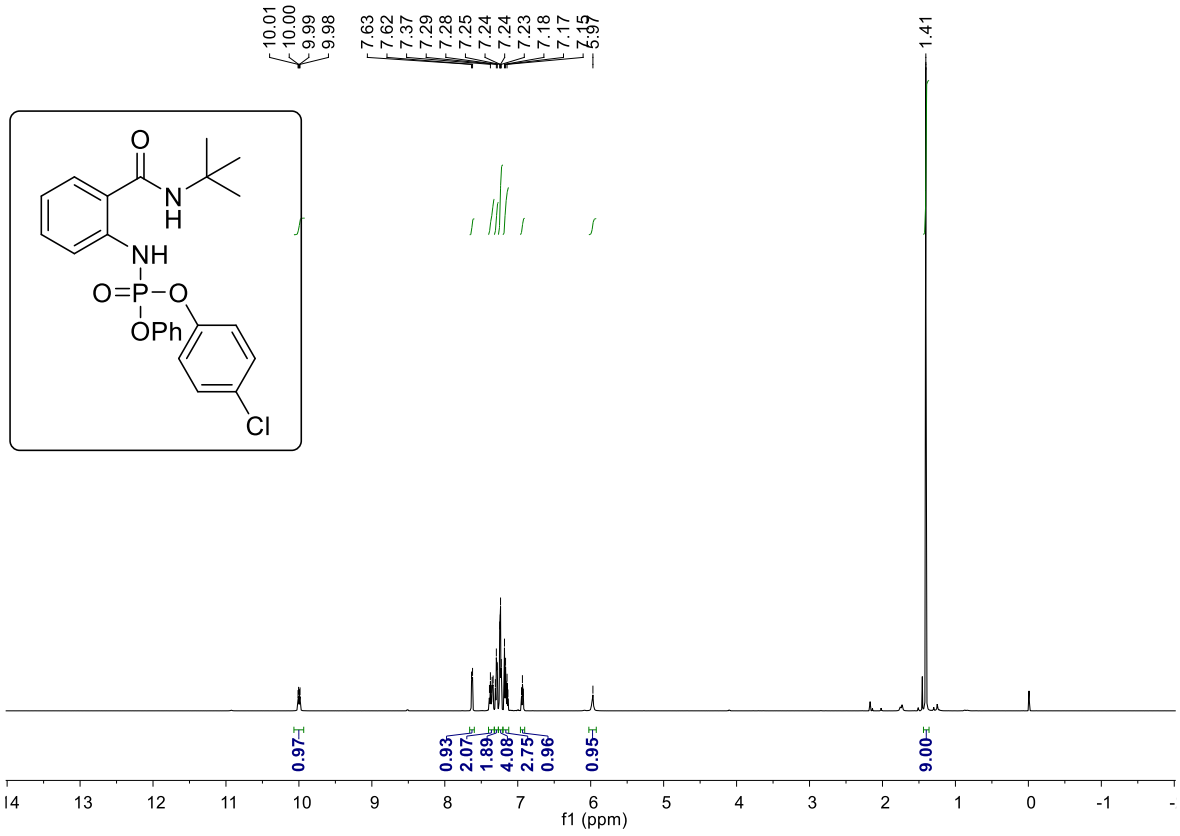

-2.62
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

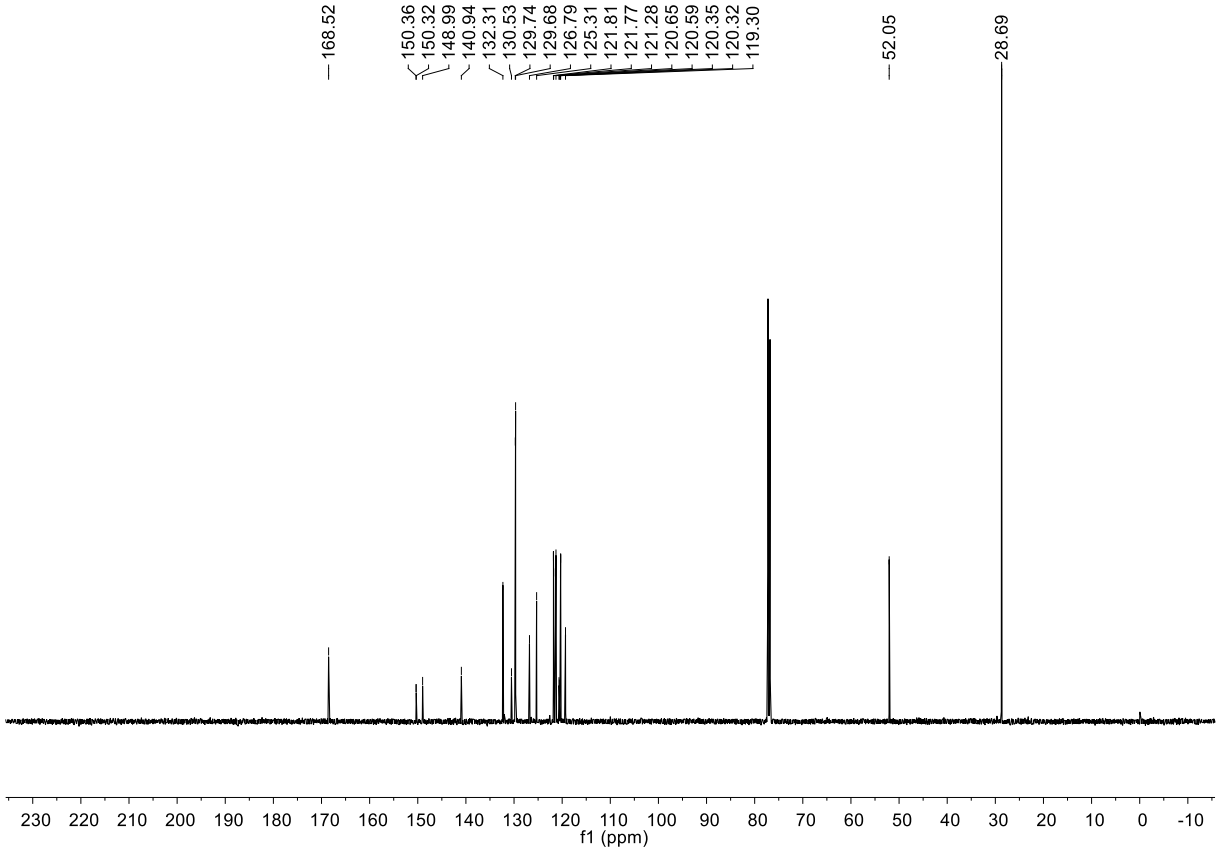
Naphthalen-2-yl phenyl (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (Scheme 3, **4d**)

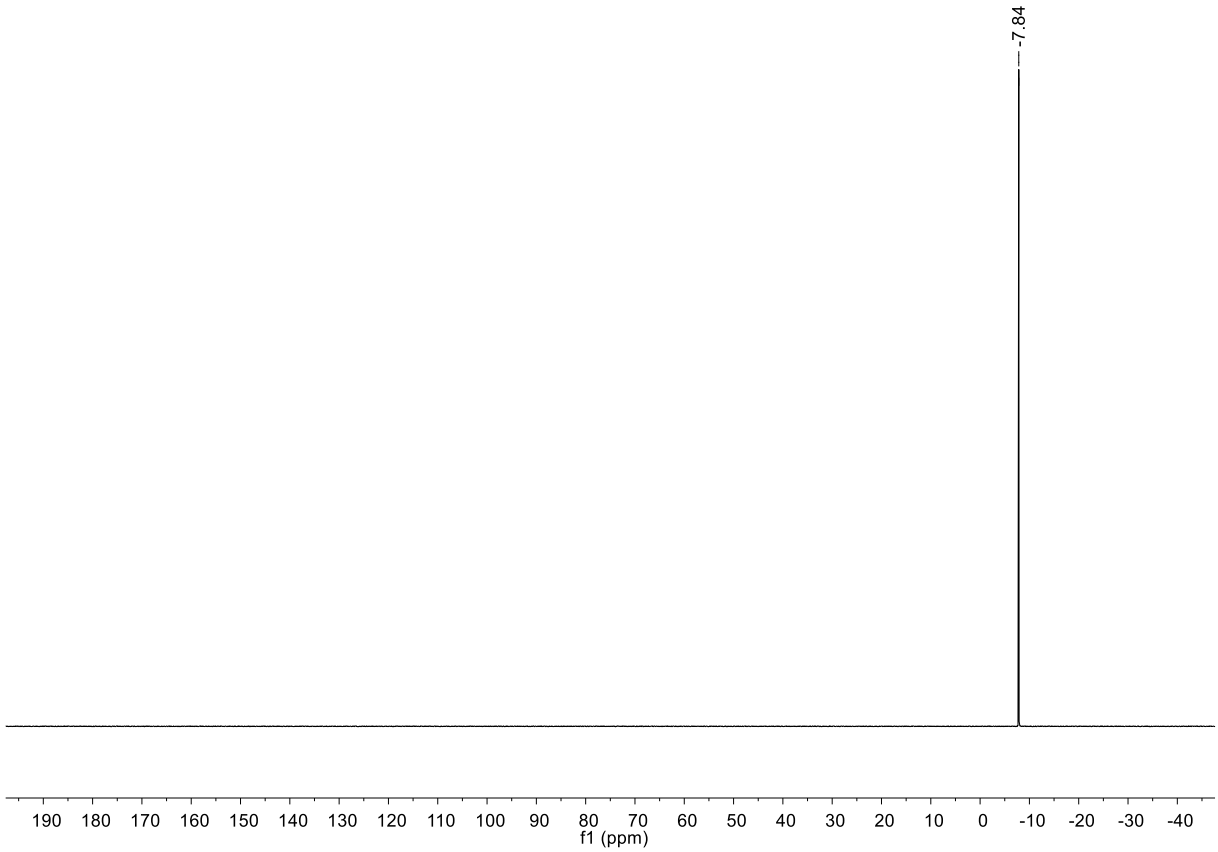



-7.77
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

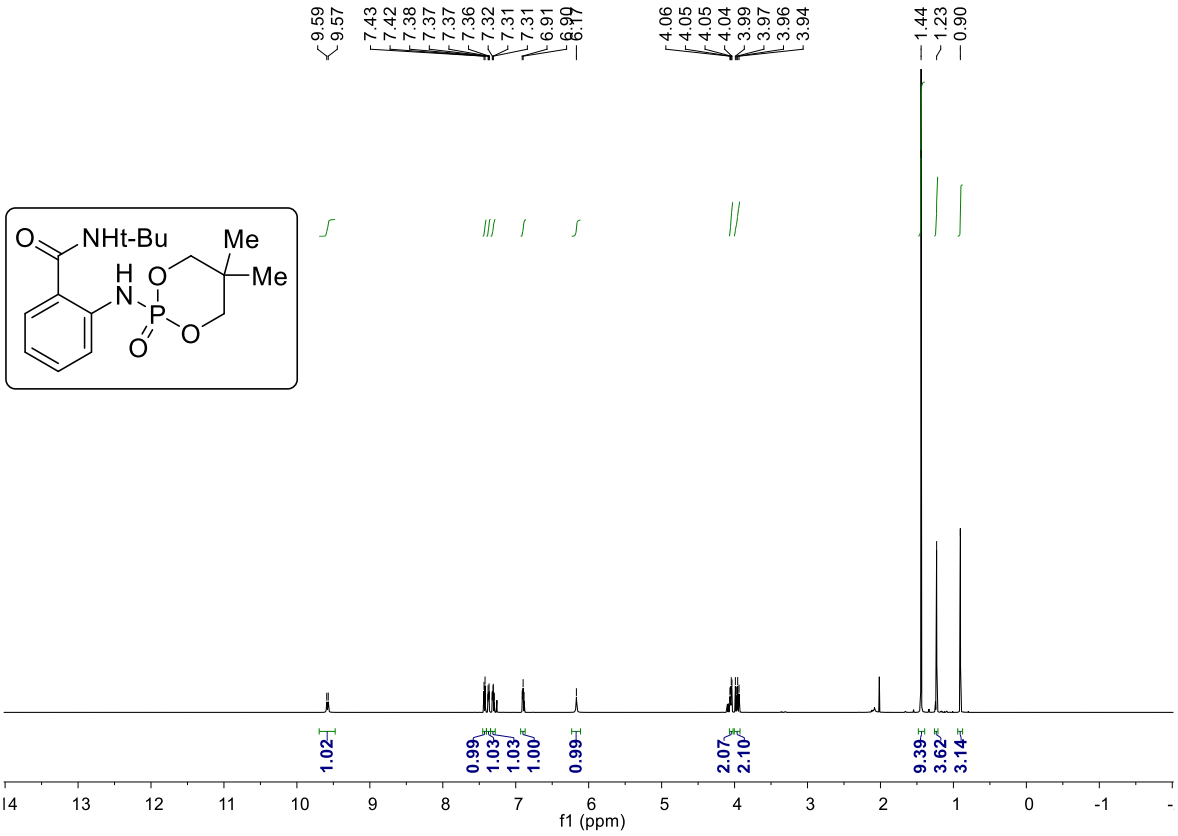
4-chlorophenyl phenyl (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (Scheme 3, **4e**)

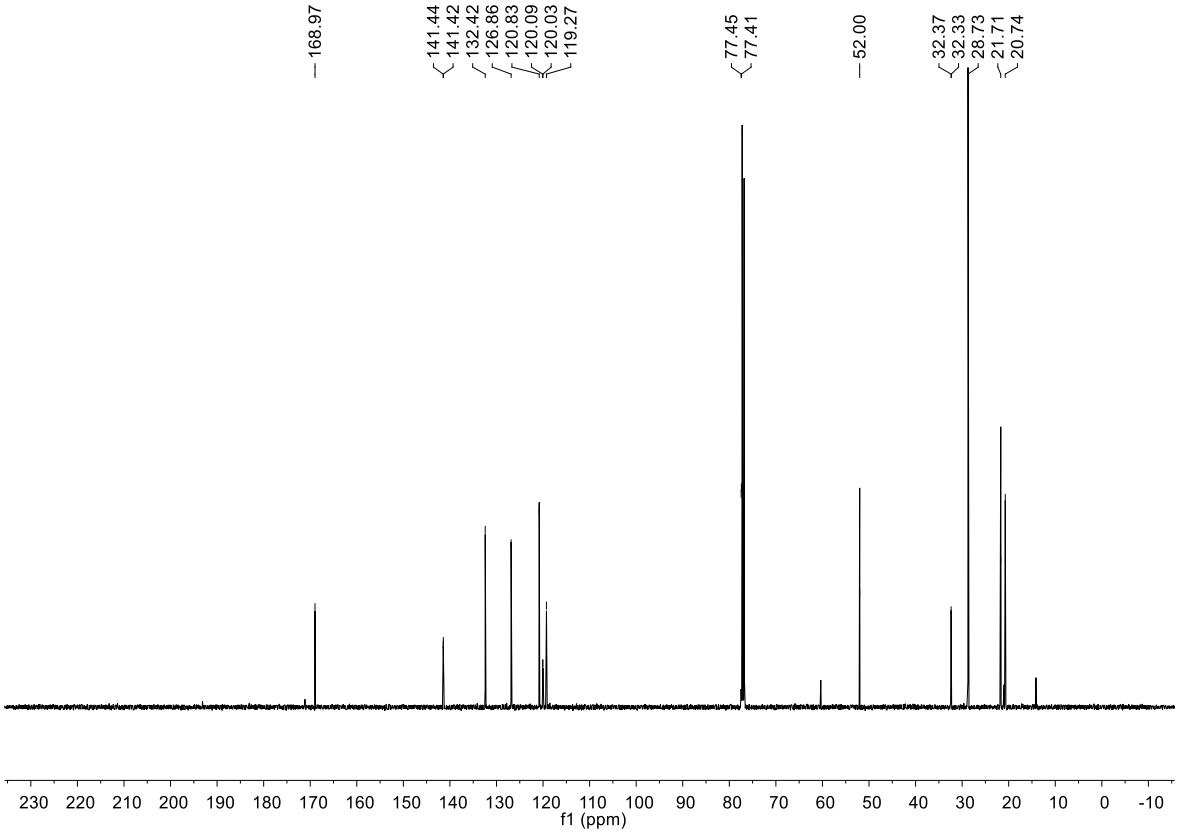


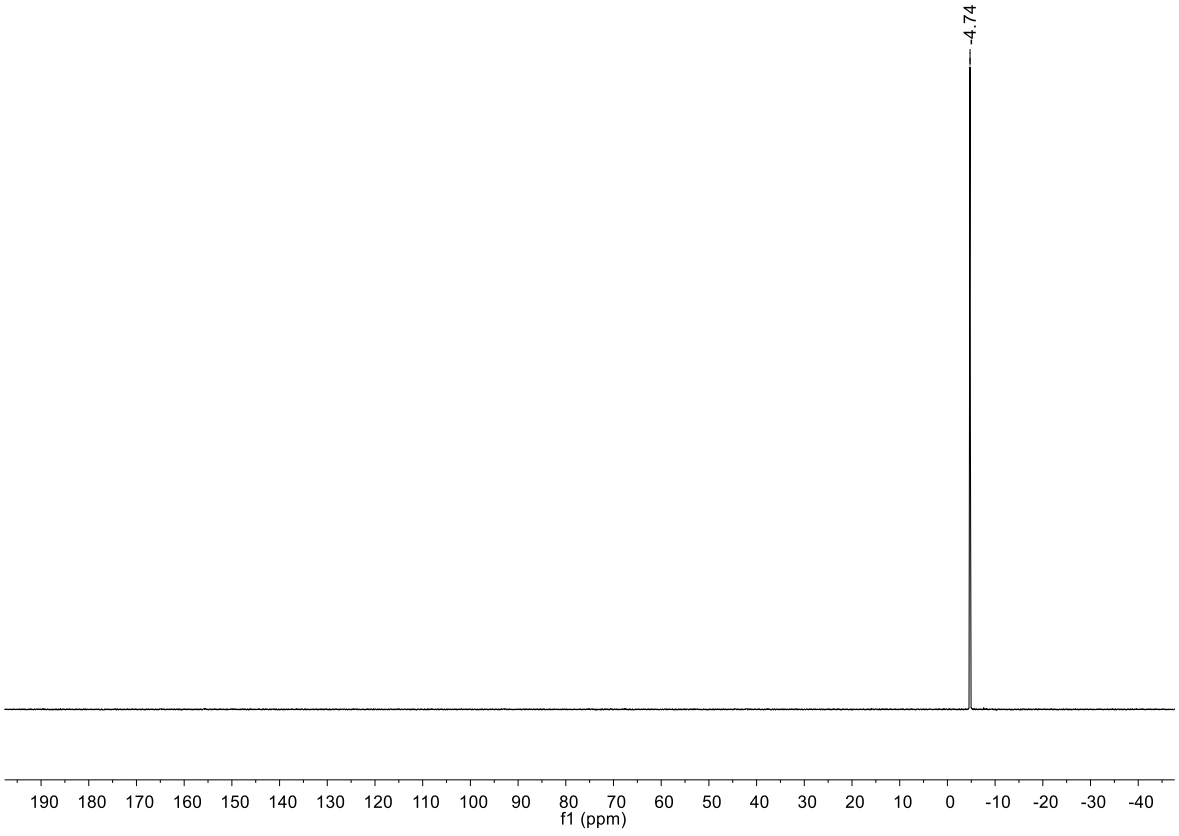

168.52
150.36
150.32
148.99
140.94
132.31
130.53
129.74
129.68
126.79
125.31
121.81
121.77
121.28
120.65
120.59
120.35
120.32
119.30
52.05
28.69
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-7.84
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

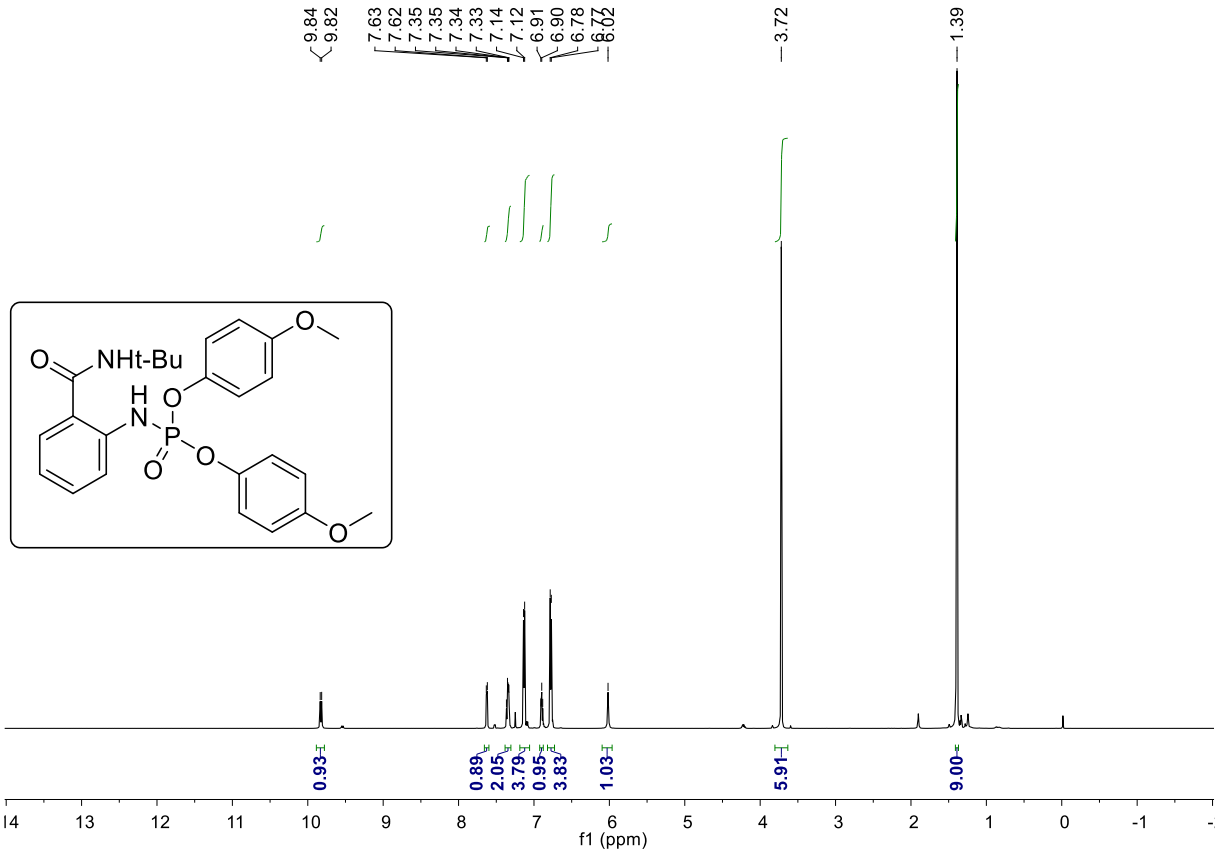
***N*-*tert*-butyl-2-((5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)amino)benzamide** (Scheme 3, **4f)**

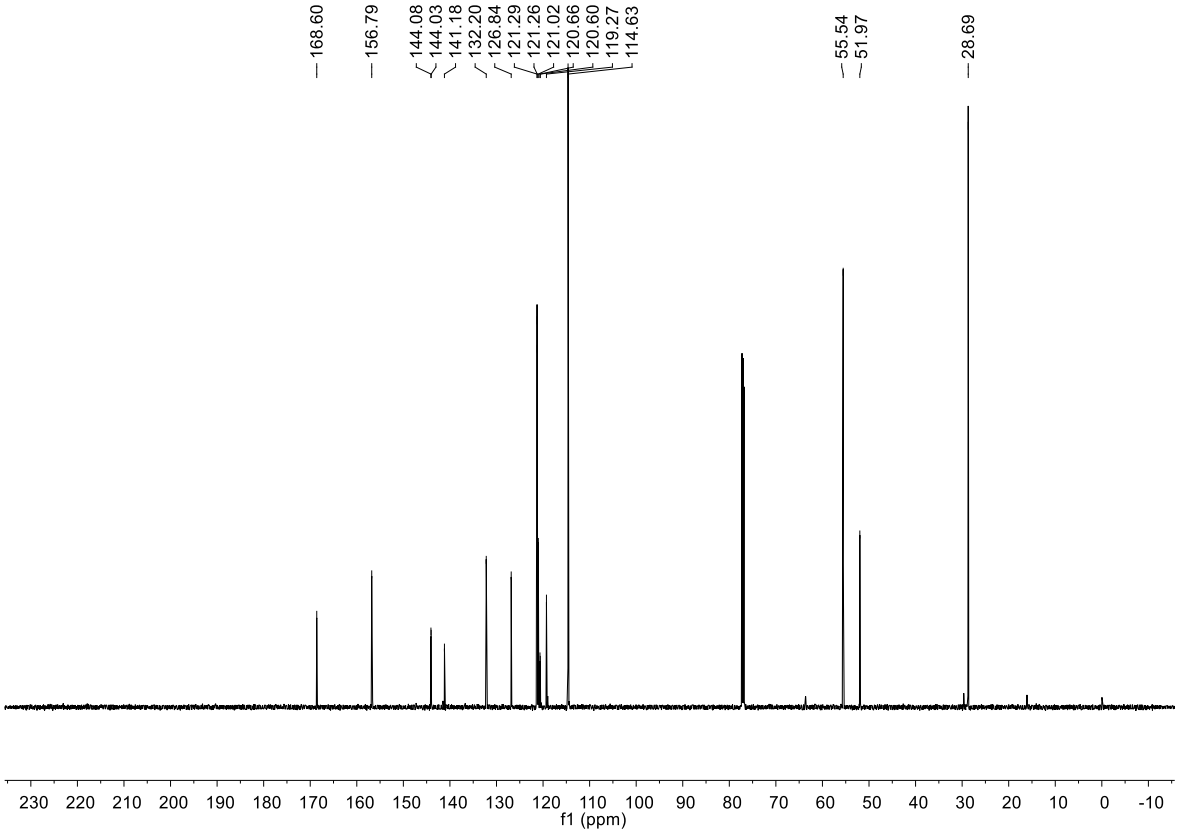


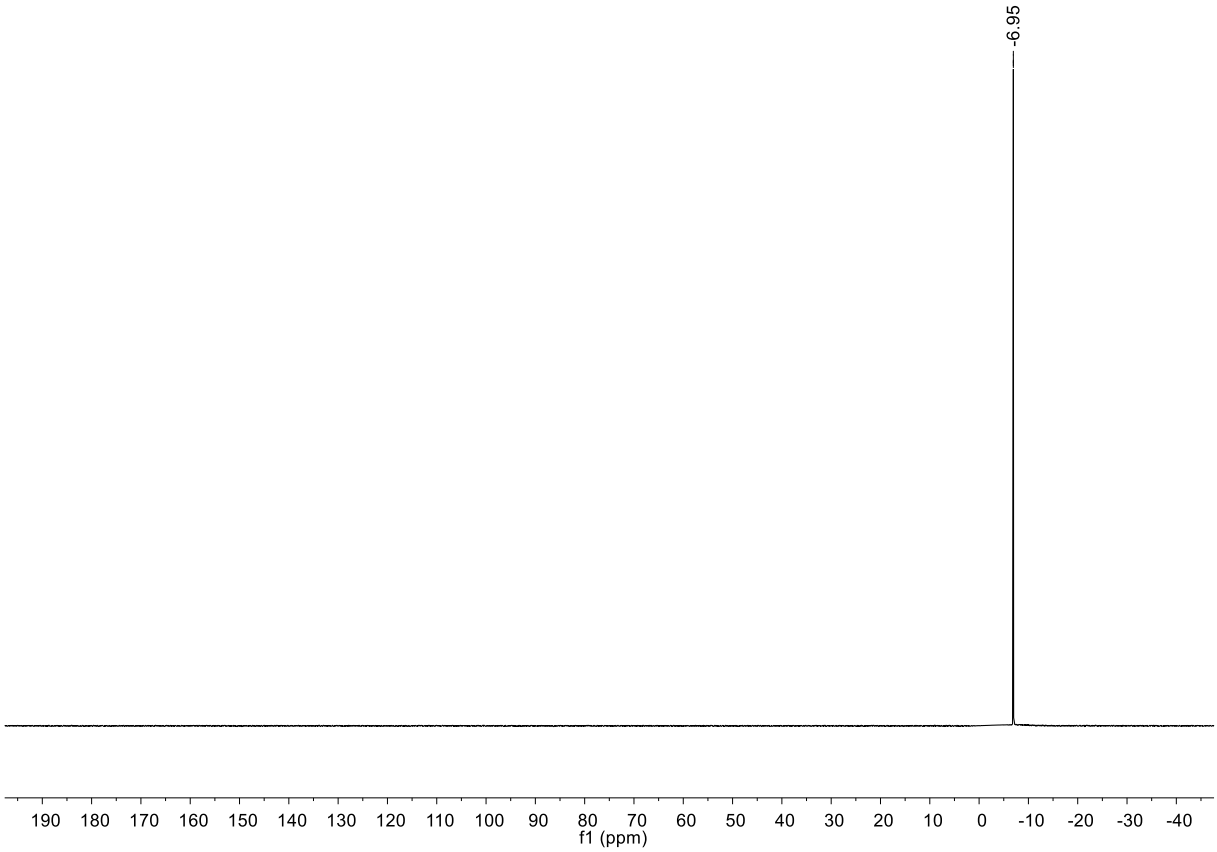

168.97
141.44
141.42
132.42
126.86
120.83
120.09
120.03
119.27
77.45
77.41
52.00
32.37
32.33
28.73
21.71
20.74
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-4.74
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

Bis(4-methoxyphenyl) (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (Scheme 3, **4g**)

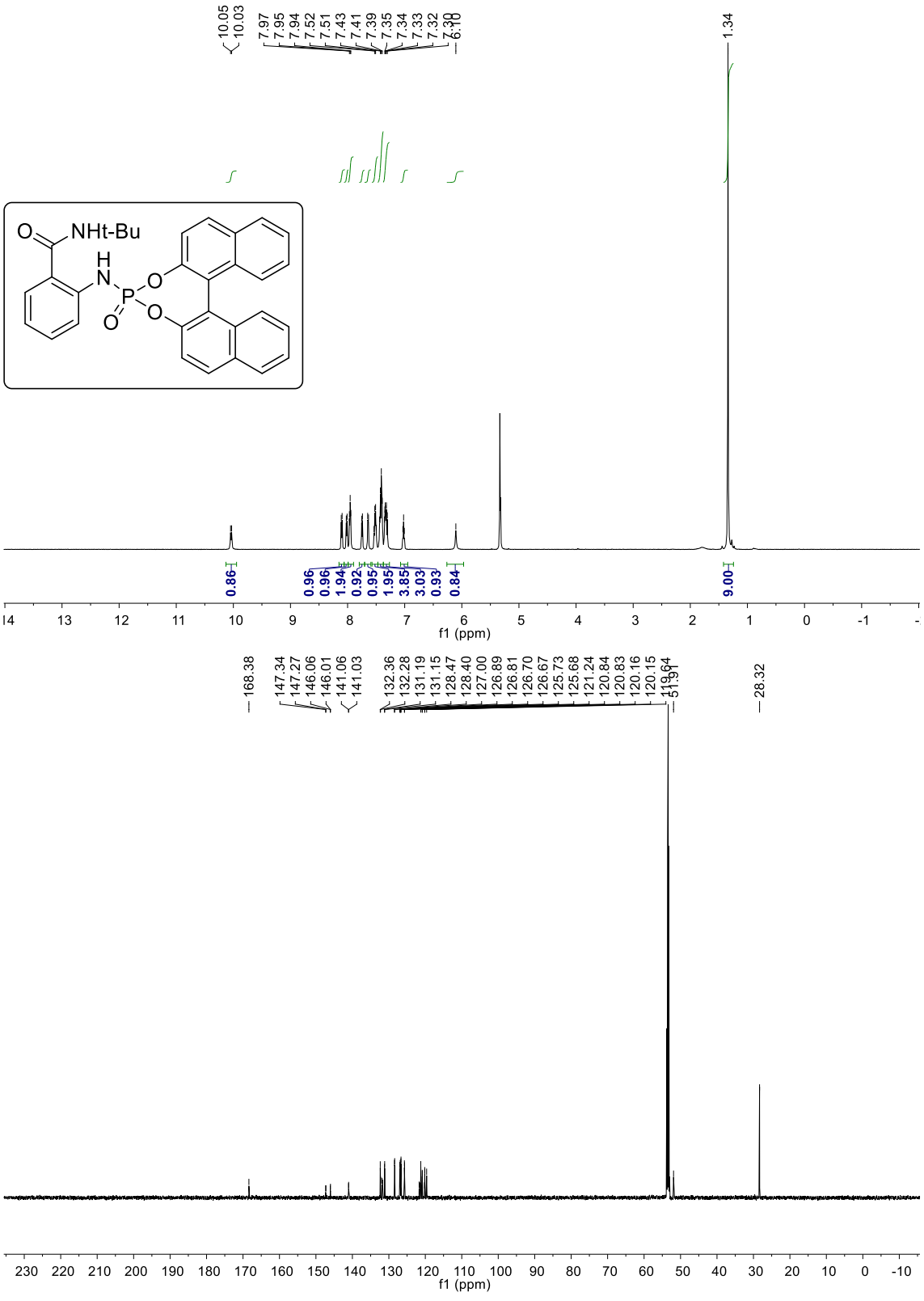


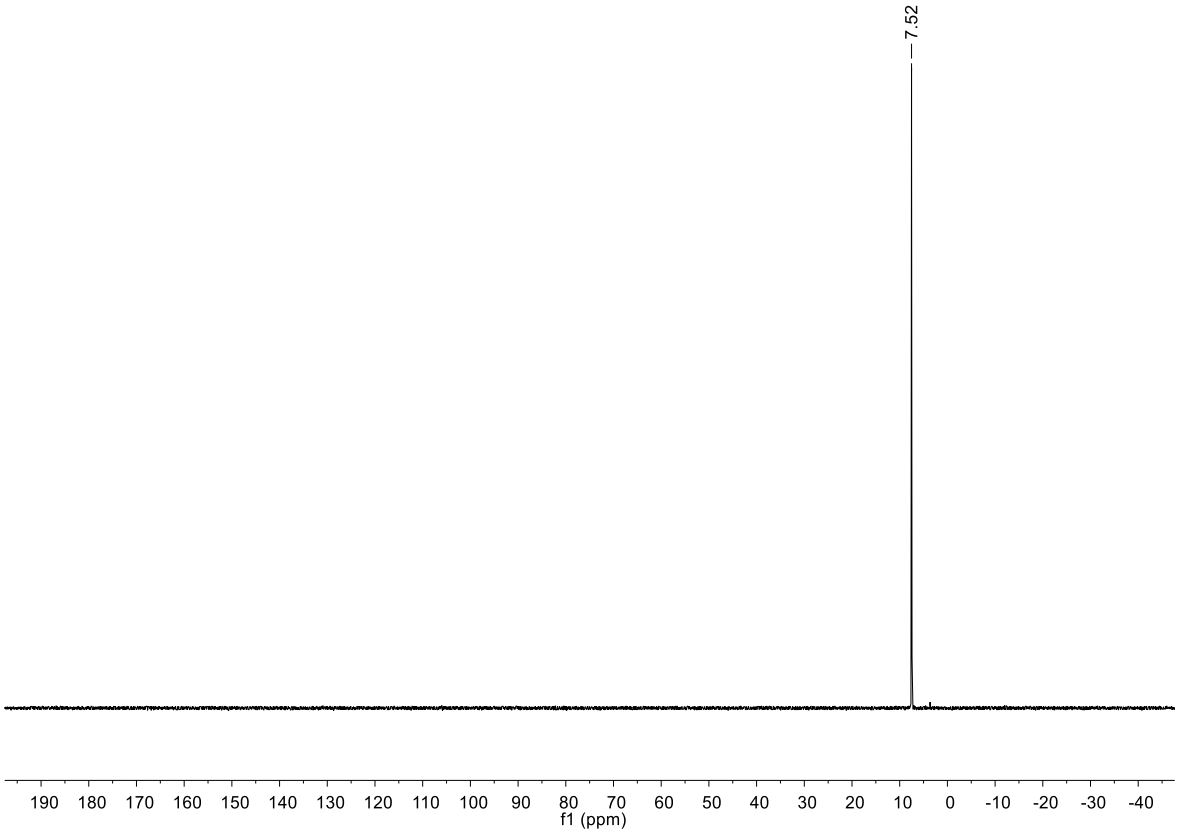

168.60
156.79
144.08
144.03
141.18
132.20
126.84
121.29
121.26
121.02
120.66
120.60
119.27
114.63
55.54
51.97
28.69
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-6.95
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

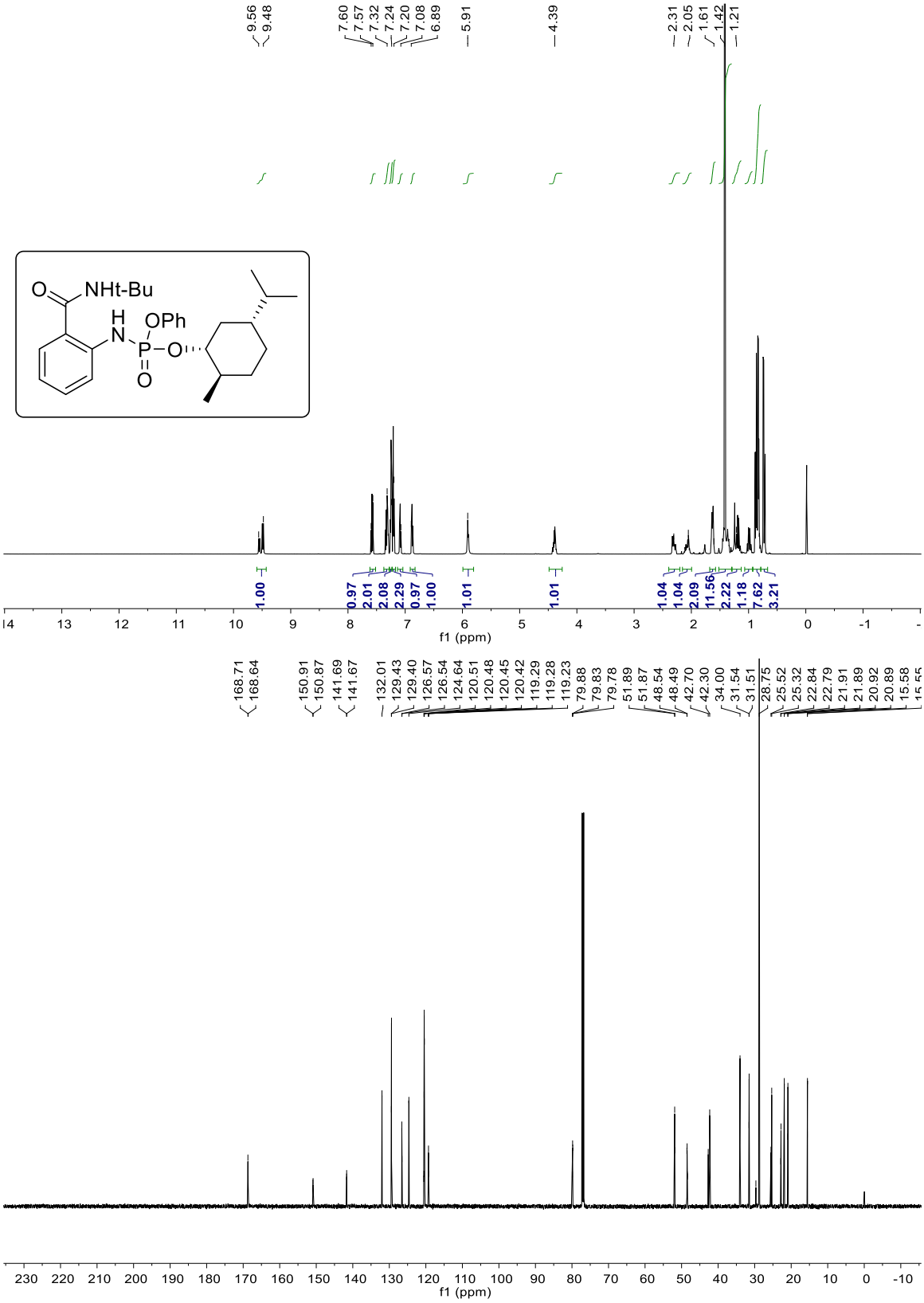
***N*-(*tert*-butyl)-2-((4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)amino)benzamide**

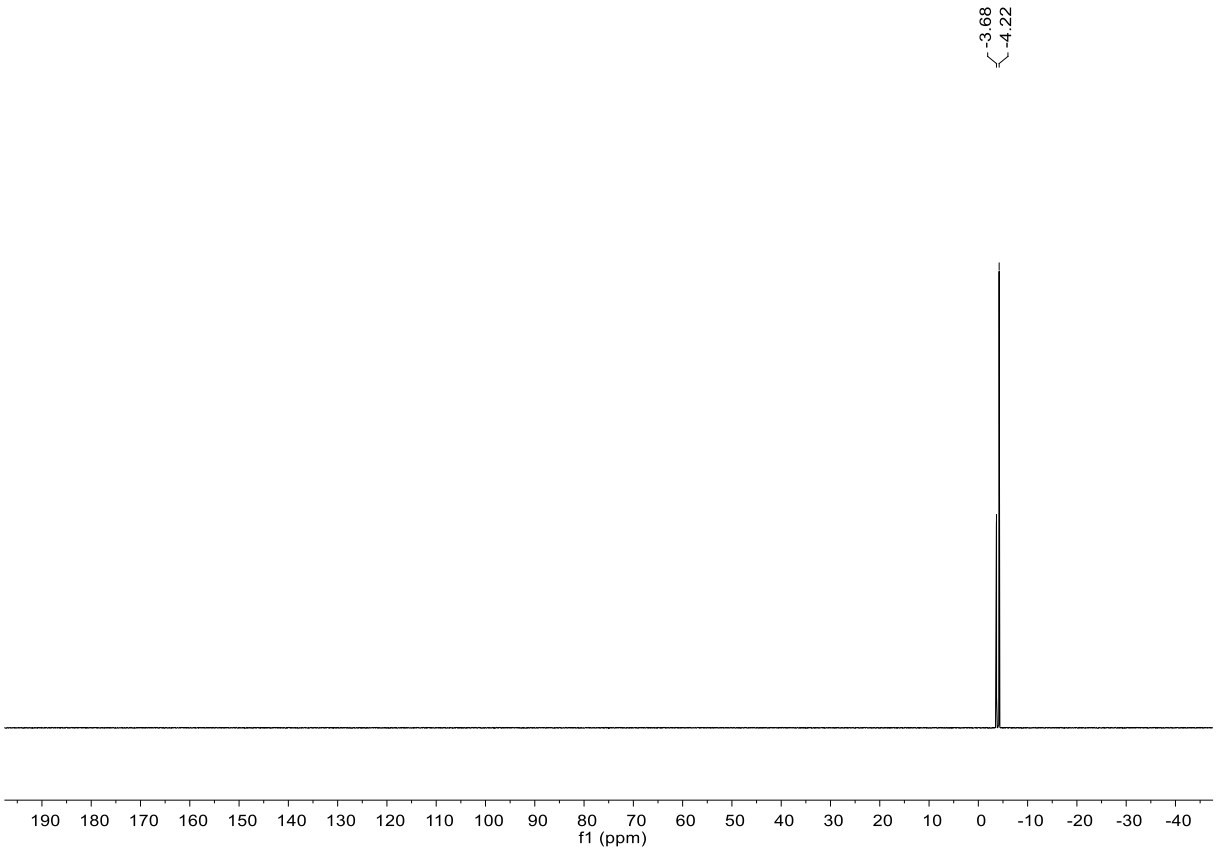
(Scheme 3, **4h**)



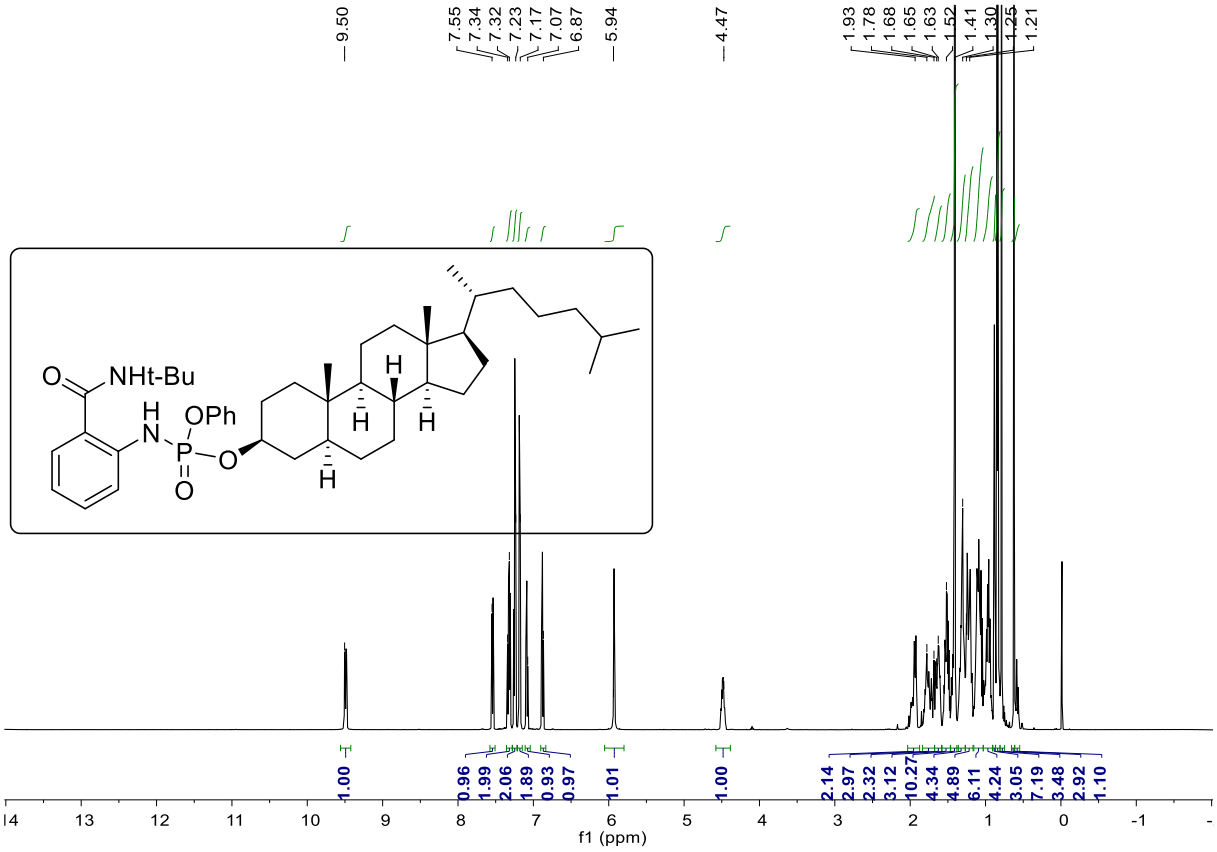

7.52
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

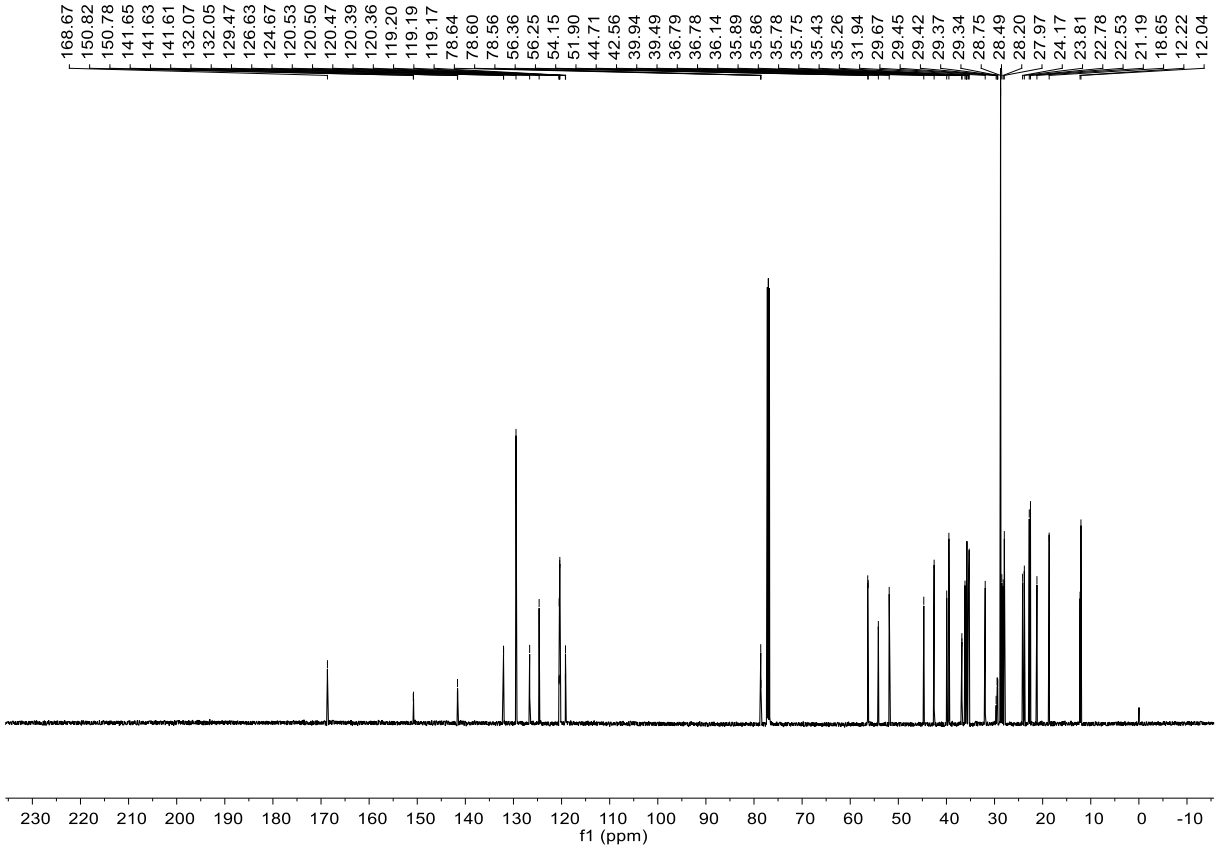
(1R,2R,5R)-5-Isopropyl-2-methylcyclohexyl phenyl (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (Scheme 4, **5a**)

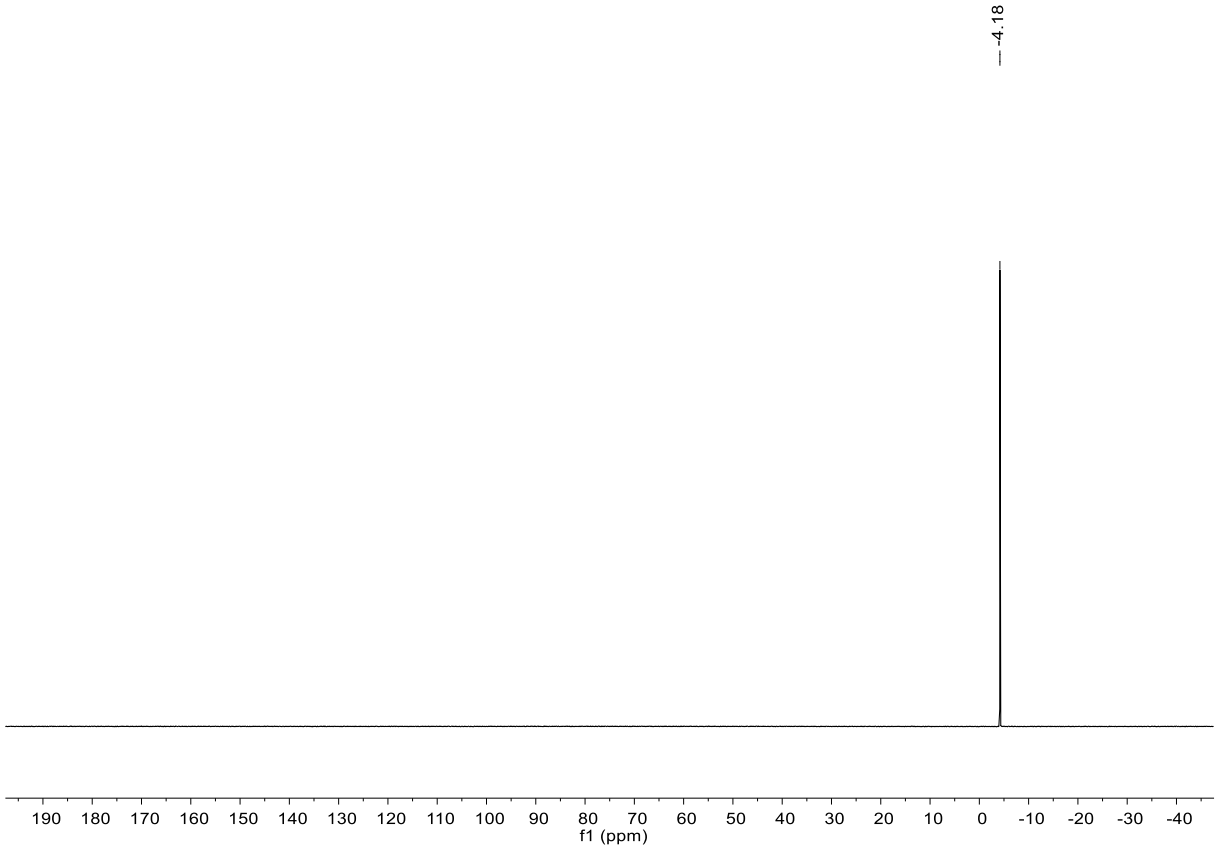



-3.68
-4.22
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl phenyl (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (1R,2R,5R)-5-Isopropyl-2-methylcyclohexyl phenyl (2-(tert-butylcarbamoyl)phenyl)phosphoramidate (Scheme 4, **5b**)




168.67
150.82
150.78
141.65
141.63
141.61
132.07
132.05
129.47
126.63
124.67
120.53
120.50
120.47
120.39
120.36
119.20
119.19
119.17
78.64
78.60
78.56
56.36
56.25
54.15
51.90
44.71
42.56
39.94
39.49
36.79
36.78
36.14
35.89
35.86
35.78
35.75
35.43
35.26
31.94
29.67
29.45
29.42
29.37
29.34
28.75
28.49
28.20
27.97
24.17
23.81
22.78
22.53
21.19
18.65
12.22
12.04
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-4.18
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)