Supporting Information

Synthesis of *ortho*-Phosphated (Hetero)Arylamines through Cascade Atherton-Todd Reaction/[3,3]-Rearrangement from Arylhydroxylamines and Dialkyl Phosphites

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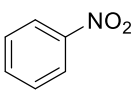
Content

General remarks

All reactions were carried out in oven-dried glassware under air with magnetic stirring. Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography (TLC) with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Silica gel (particle size 0.032-0.063 mm) purchased from SiliCycle was used for flash chromatography. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Bruker AV-500 spectrometer operating at 500 MHz for proton and 126 MHz for carbon nuclei using $CDCl_3$ or DMSO-*d*$_6$ as solvent, respectively. Chemical shifts were referenced to the residual proton solvent peaks (^{1}H: $CDCl_3$, δ 7.26; DMSO-*d*$_6$, δ 2.50), solvent ^{13}C signals ($CDCl_3$, δ 77.16; DMSO-*d*$_6$, δ 39.60). Proton signal data uses the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet and *J* = coupling constant. High Resolution Mass Spectrometry was performed on a Bruker Apex II mass instrument with quadrupole mass analyzer under the conditions of electrospray ionization (ESI) in both positive and negative mode. ^{35}Cl was used to calculate the theoretical m/z for all chlorine containing compounds. ^{79}Br was used to calculate the theoretical m/z for all bromine containing compounds.

Materials and Methods: Nitro compounds **S1-1**~**S1-24**, **S1-26**~**S1-29**, **S3-1**, **S3-3**, **S3-6**, **S3-7** were purchased from commercial sources and used without further purification. Nitro compounds **S1-25**, **S3-2**, **S3-4**, **S3-5**, **S3-8**, **S3-9**, **S3-10** were prepared according to the literature procedures.[1-4] Arylhydroxylamine substrates **1a-1ap** were prepared according to the literature procedures.[5-12] Dialkyl phosphites **2a-2f** were purchased from commercial sources and used without further purification. All heating reactions were carried out in an oil bath.

List of nitro compounds



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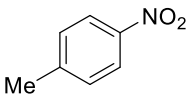

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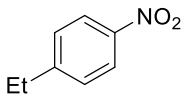

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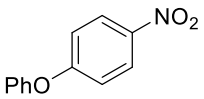

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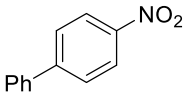

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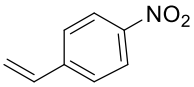

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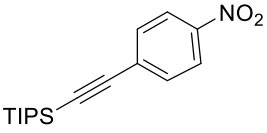

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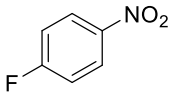

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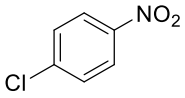

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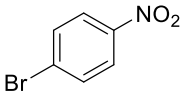

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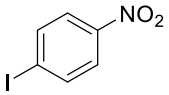

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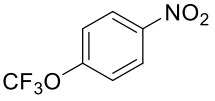

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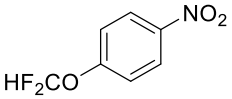

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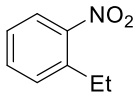

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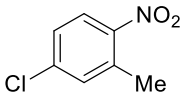

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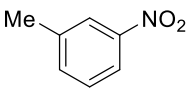

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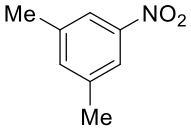

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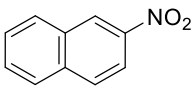

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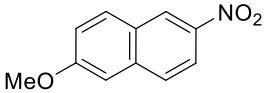

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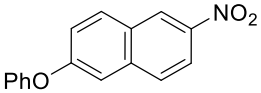

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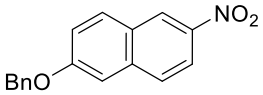

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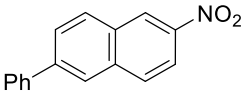

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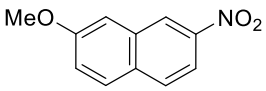

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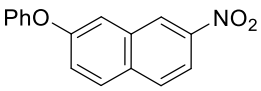

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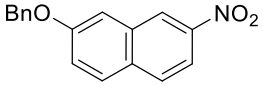

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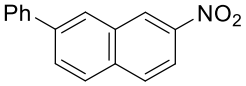

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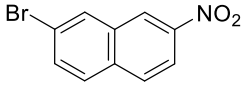

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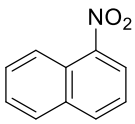

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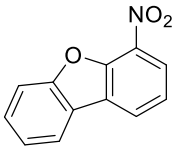

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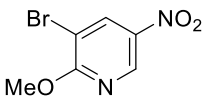

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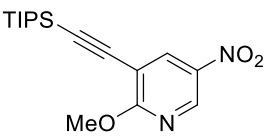

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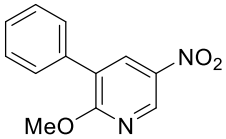

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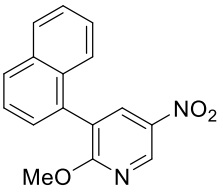

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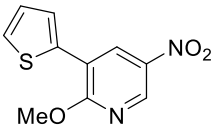

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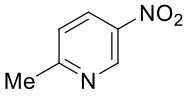

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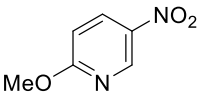

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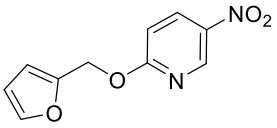

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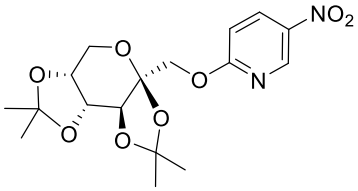

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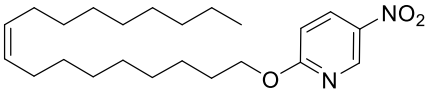
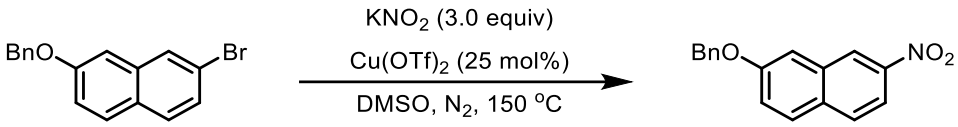


S3-10

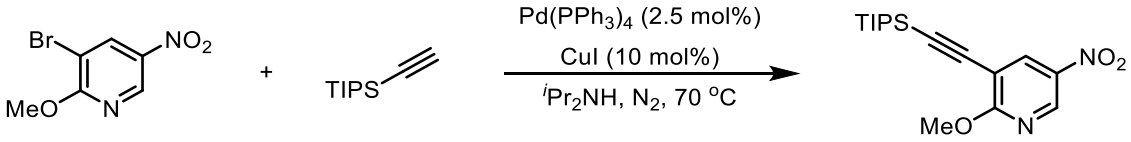
General procedure for the synthesis of new nitro compounds

Method A: [1]



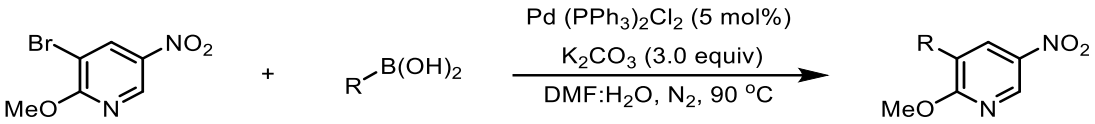
2-(benzyloxy)-7-bromonaphthalene (3.13 g, 10 mmol, 1.0 equiv), $Cu(OTf)_2$ (904 mg, 2.5 mmol, 25 mol%), KNO_2 (2.55 g, 30 mmol, 3.0 equiv) and anhydrous DMSO (30 mL) were added to the reaction device under nitrogen atmosphere. Then it was stirred at 150 °C in an oil bath for 12 h. The reaction mixture was then cooled to room temperature, washed with excess water and extracted with ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give the crude product which was purified by column chromatography using silica gel to afford the desired product 2-(benzyloxy)-7-nitronaphthalene.

Method B:[2]



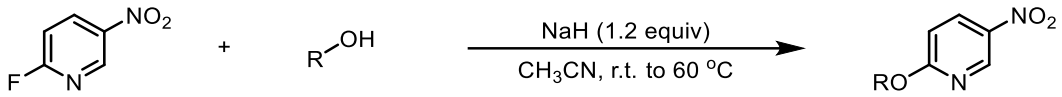
3-bromo-2-methoxy-5-nitropyridine (2.33 g, 10 mmol, 1.0 equiv), ethynyltriisopropylsilane (2.7 mL, 12 mmol, 1.2 equiv), Pd $(PPh_3)_4$ (289 mg, 0.25 mmol, 2.5 mol%), CuI (190 mg, 1 mmol, 10 mol%) and $^{i}Pr_2NH$ (20 mL) were added to a clean, dry, round-bottom flask equipped with a stirring bar under nitrogen atmosphere. Then the reaction mixture was stirred and heated at 70 °C in an oil bath for 10 h. The reaction mixture was then cooled to room temperature, washed with excess water and extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified by flash column chromatography to afford the desired product 2-methoxy-5-nitro-3-((triisopropylsilyl)ethynyl)pyridine.

Method C:[3]



3-bromo-2-methoxy-5-nitropyridine (2.33 g, 10 mmol, 1.0 equiv), arylboronic acid (12 mmol, 1.2 equiv), Pd $(PPh_3)_2Cl_2$ (350 mg, 0.5 mmol, 5 mol%), K_2CO_3 (4.15 g, 30 mmol, 3.0 equiv) and DMF: H_2O (*V* : *V*= 40 mL : 10 mL) were added to a clean, dry, round-bottom flask equipped with a stirring bar under nitrogen atmosphere. Then the reaction mixture was stirred and heated at 90 °C in an oil bath for 10 h. The reaction mixture was then cooled to room temperature, washed with excess water and extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified by flash column chromatography to afford the desired product.

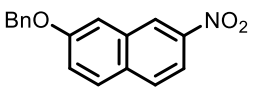
Method D:[4]



2-fluoro-5-nitropyridine (1.42 g, 10 mmol, 1.0 equiv), alcohol (12 mmol, 1.2 equiv), NaH (288 mg, 12 mmol, 1.2 equiv) and CH_3CN (50 mL) were added to a clean, dry, round-bottom flask equipped with a stirring bar under nitrogen atmosphere. Then the reaction mixture was stirred and heated at 60 °C in an oil bath for 10 h. The reaction mixture was then cooled to room temperature, concentrated under reduced pressure and purified by flash column chromatography to afford the desired product.

Analytical data of new nitro compounds

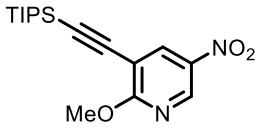
1. 2-(benzyloxy)-7-nitronaphthalene (S1-25)



S1-25

Followed **Method A**; 1.78 g, 64% yield; Yellow solid, m.p. = 119-121 ºC; R_f = 0.5 (PE:EtOAc = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (d, *J* = 2.0 Hz, 1H), 8.09 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.86 (dd, *J* = 10.9, 9.1 Hz, 2H), 7.51-7.49 (m, 2H), 7.45–7.41 (m, 3H), 7.39–7.35 (m, 2H), 5.22 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.3, 146.2, 136.3, 133.6, 131.7, 129.6, 129.3, 128.9, 128.5, 127.7, 123.4, 123.3, 117.3, 108.8, 70.4. HRMS (ESI) m/z calcd for $[C_{17}H_{14}NO_3]^+$ $[M+H]^+$: 280.0968, found 280.0982.

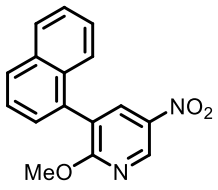
2. 2-methoxy-5-nitro-3-((triisopropylsilyl)ethynyl)pyridine (S3-2)



S3-2

Followed **Method B**; 2.34 g, 70% yield; Colorless oil; R_f = 0.5 (PE:EtOAc = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.96 (d, *J* = 2.8 Hz, 1H), 8.41 (d, *J* = 2.8 Hz, 1H), 4.09 (s, 3H), 1.13 (s, 18H), 1.12 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.3, 143.3, 138.9, 136.4, 108.5, 100.5, 98.8, 55.5, 18.7, 11.4. HRMS (ESI) m/z calcd for $[C_{17}H_{27}N_2O_3Si]^+$ $[M+H]^+$: 335.1785, found 335.1805.

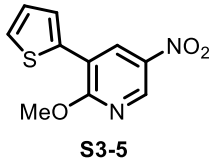
3. 2-methoxy-3-(naphthalen-1-yl)-5-nitropyridine (S3-4)



S3-4

Followed **Method C**; 2.10 g, 75% yield; White solid, m.p. = 122-124 ºC; R_f = 0.3 (PE:EtOAc = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.23 (d, *J* = 2.8 Hz, 1H), 8.45 (d, *J* = 2.8 Hz, 1H), 7.95 (t, *J* = 8.0 Hz, 2H), 7.59–7.47 (m, 4H), 7.44 (dd, *J* = 7.0, 1.0 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.1, 143.8, 139.5, 134.9, 133.5, 132.3, 131.3, 129.3, 128.6, 127.7, 126.6, 126.2, 125.3, 125.1, 124.1, 55.1. HRMS (ESI) m/z calcd for $[C_{16}H_{13}N_2O_3]^+$ $[M+H]^+$: 281.0921, found 281.0929.

4. 2-methoxy-5-nitro-3-(thiophen-2-yl)pyridine (S3-5)

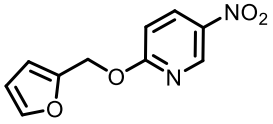


S3-5

Followed **Method C**; 1.70 g, 72% yield; Yellow solid, m.p. = 113-115 ºC; R_f = 0.3 (PE:EtOAc = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.92 (d, *J* = 2.6 Hz, 1H), 8.58 (d, *J* = 2.6 Hz, 1H), 7.63 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.43 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.12 (dd, *J* = 5.1, 3.8 Hz, 1H), 4.17 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.3, 141.7, 139.7, 135.1, 130.0, 127.9, 127.7, 127.6, 118.4, 55.2. HRMS (ESI) m/z

calcd for $[C_{10}H_9N_2O_3S]^+$ $[M+H]^+$: 237.0328, found 237.0341.

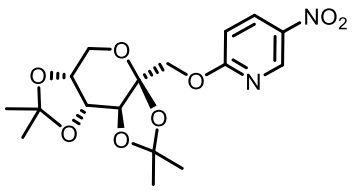
5. 2-(furan-2-ylmethoxy)-5-nitropyridine (S3-8)



S3-8

Followed **Method D**; 0.84 g, 38% yield; Light red solid, m.p. = 92-94 °C; R_f = 0.5 (PE:EtOAc = 5:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.09 (d, *J* = 2.7 Hz, 1H), 8.35 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.45 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.85 (d, *J* = 9.1 Hz, 1H), 6.50 (d, *J* = 3.2 Hz, 1H), 6.39 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.45 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.5, 149.5, 144.7, 143.6, 139.9, 134.2, 111.6, 111.2, 110.8, 61.1. HRMS (ESI) m/z calcd for $[C_{10}H_9N_2O_4]^+$ $[M+H]^+$: 221.0557, found 221.0571.

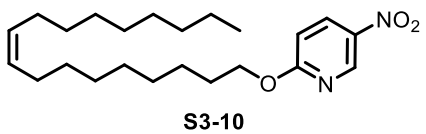
6. 5-nitro-2-(((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)-[4,5-*b*:4',5'-*d*]pyran-3a-yl)methoxy)pyridine (S3-9)



S3-9

Followed **Method D**; 1.60 g, 42% yield; White solid, m.p. = 45-47 °C; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.02 (d, *J* = 2.8 Hz, 1H), 8.32 (dd, *J* = 9.1, 2.8 Hz, 1H), 6.83 (d, *J* = 9.1 Hz, 1H), 4.78 (d, *J* = 11.5 Hz, 1H), 4.59 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.41 (d, *J* = 2.6 Hz, 1H), 4.35 (d, *J* = 11.5 Hz, 1H), 4.23 (dd, *J* = 8.0, 1.8 Hz, 1H), 3.91 (dd, *J* = 13.0, 1.8 Hz, 1H), 3.76 (d, *J* = 13.0 Hz, 1H), 1.50 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.5, 144.8, 139.8, 134.1, 111.3, 109.2, 108.9, 101.8, 70.8, 70.7, 70.1, 68.0, 61.3, 26.5, 25.9, 25.3, 24.1. HRMS (ESI) m/z calcd for $[C_{17}H_{23}N_2O_8]^+$ $[M+H]^+$: 383.1449, found 383.1469.

7. (Z)-5-nitro-2-(octadec-9-en-1-yloxy)pyridine (S3-10)

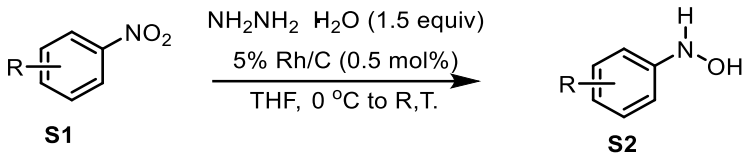


S3-10

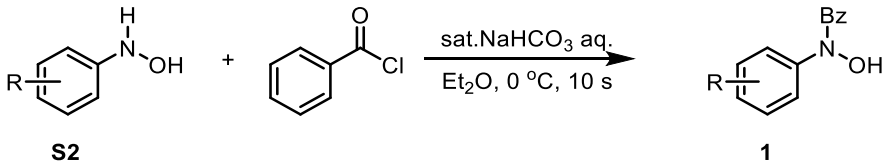
Followed **Method D**; 1.80 g, 46% yield; Yellow oil; R_f = 0.3 (PE:EtOAc = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.06 (d, *J* = 2.8 Hz, 1H), 8.33 (dd, *J* = 9.1, 2.8 Hz, 1H), 6.79 (d, *J* = 9.1 Hz, 1H), 5.38–5.31 (m, 2H), 4.41 (t, *J* = 6.7 Hz, 2H), 2.06–1.95 (m, 4H), 1.79 (p, *J* = 6.8 Hz, 2H), 1.47–1.25 (m, 22H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.5, 145.0, 139.4, 133.9, 130.2, 129.9, 111.4, 68.0, 32.1, 29.91, 29.87, 29.7, 29.6, 29.5, 29.43, 29.35, 28.9, 27.4, 27.3, 26.1, 22.8, 14.3. HRMS (ESI) m/z calcd for $[C_{23}H_{39}N_2O_3]^+$ $[M+H]^+$: 391.2955, found 391.2970.

General procedure for the synthesis of arylhydroxylamines

Method E:

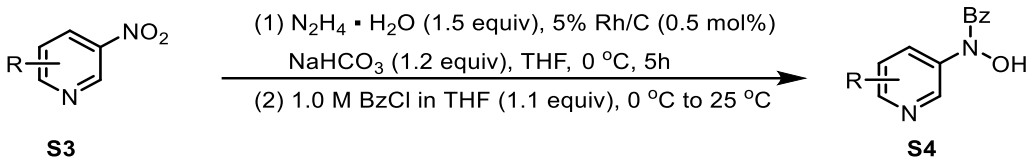


A solution of nitroarene **S1** (10 mmol, 1.0 equiv) and 5% Rh/C (100 mg, 0.05 mmol, 0.5 mol%) in THF (20 mL) under N_2 atmosphere was cooled to 0 °C. Hydrazine monohydrate (0.8 mL, 15 mmol, 1.5 equiv) was added dropwise. The reaction mixture was slowly warmed up to 25 °C and stirred at room temperature for 4 h. The reaction mixture was filtered through diatomite and concentrated *in vacuo*. Recrystallization from CH_2Cl_2/PE at r.t. afforded the title compound **S2**. The resulting crude residue was used directly for the next step.



To a solution of **S2** in ether (20 mL), saturated aqueous solution (10 mL) of sodium bicarbonate was added. Then the solution was cooled to 0 °C and benzoyl chloride (1.3 mL, 11 mmol, 1.1 equiv) was added dropwise. After stirring for 10 s at 0 °C, the reaction was quenched by saturated aqueous ammonium chloride. The mixture was extracted with CH_2Cl_2, the organic layer was washed by brine and dried over sodium sulfate. After the solvent was removed *in vacuo*, the crude product was purified by flash column chromatography (PE/CH_2Cl_2) to obtain **1**.

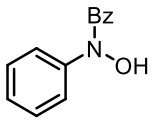
Method F:



S3 **S4**

S3 (10 mmol, 1.0 equiv), 5% Rh/C (100 mg, 0.05 mmol, 0.5 mol%), and $NaHCO_3$ (1.01g, 12 mmol, 1.2 equiv) in THF (50 mL) was cooled to 0 °C under N_2. Hydrazine monohydrate (0.8 mL, 15 mmol, 1.5 equiv) was then added dropwise and the reaction mixture was stirred vigorously with a stir bar at 0 °C for 2 h. While the reaction flask was still in the ice bath, a solution of benzoyl chloride (1.3 mL, 11 mmol, 1.1 equiv) in THF (10 mL) was added dropwise and the resulting mixture was stirred at 0 °C for 5 min and then warmed up to 25 °C. Afterwards, the reaction mixture was filtered through diatomite and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford **S4**.

Previously reported arylhydroxylamines



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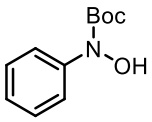

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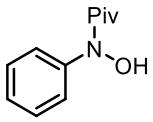

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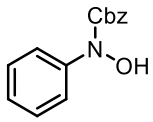

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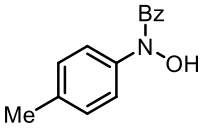

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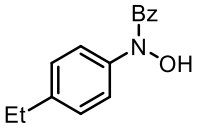

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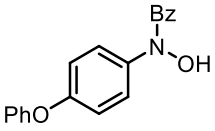

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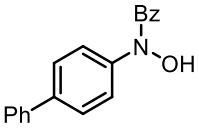

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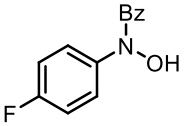

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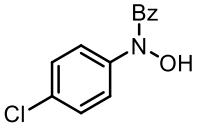

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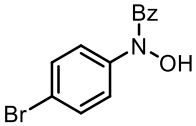

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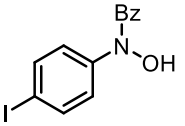

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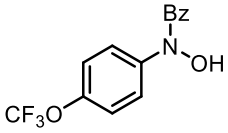

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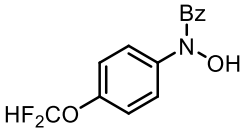

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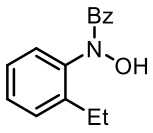

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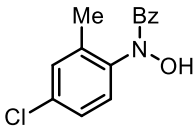

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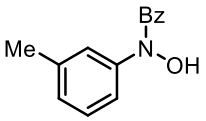

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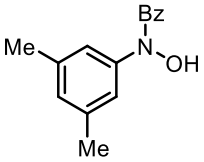

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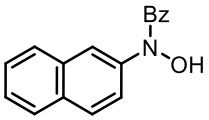

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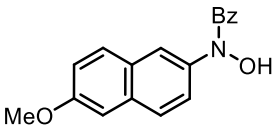

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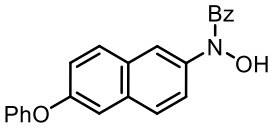

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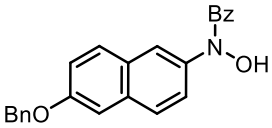

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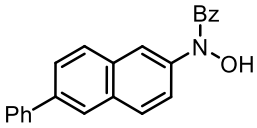

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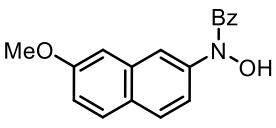

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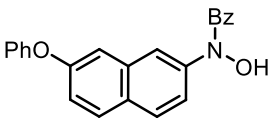

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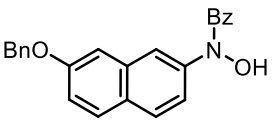

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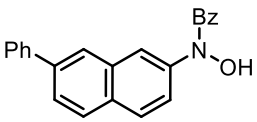

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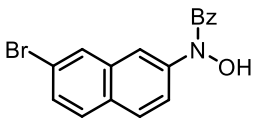

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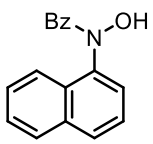

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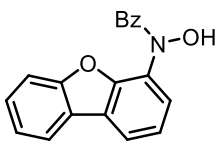

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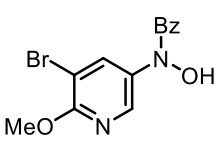

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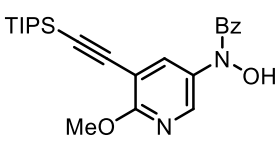
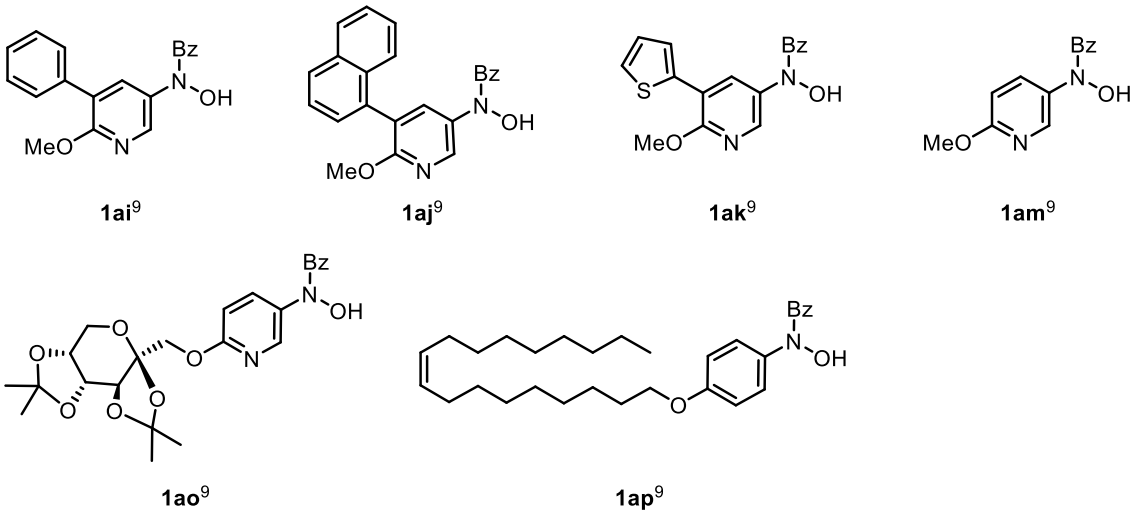


1ah[9]

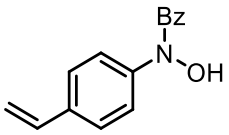


1ai[9] **1aj**[9] **1ak**[9] **1am**[9]

1ao[9] **1ap**[9]

Analytical data of new arylhydroxylamines

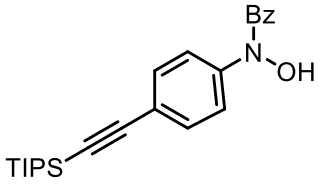
1. *N*-hydroxy-*N*-(4-vinylphenyl)benzamide (1i)



1i

Followed **Method E**; 1.34 g, 56% yield; White solid, m.p. = 141-143 °C; R_f = 0.3 (DCM:EtOAc = 50:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.36 (s, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (d, *J* = 17.5 Hz, 1H), 5.28 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 138.9, 137.4, 135.8, 132.4, 131.1, 129.0, 128.3, 126.9, 125.9, 115.3. HRMS (ESI) m/z calcd for $[C_{15}H_{14}NO_2]^+$ $[M+H]^+$: 240.1019, found 240.1021.

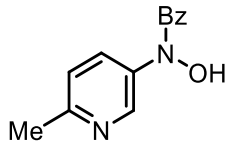
2. *N*-hydroxy-*N*-(4-((triisopropylsilyl)ethynyl)phenyl)benzamide (1j)



1j

Followed **Method E**; 1.96 g, 50% yield; Light yellow solid, m.p. = 160-162 °C; R_f = 0.3 (DCM:EtOAc = 50:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.29 (s, 1H), 7.43-7.39 (m, 3H), 7.38-7.36 (m, 2H), 7.31-7.28 (m, 2H), 7.13–7.12 (m, 2H), 1.11 (s, 18H), 1.11 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 139.2, 132.8, 132.2, 131.4, 129.0, 128.5, 125.2, 123.2, 106.0, 92.6, 18.8, 11.4. HRMS (ESI) m/z calcd for $[C_{24}H_{32}NO_2Si]^+$ $[M+H]^+$: 394.2197, found 394.2202.

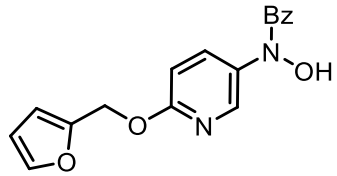
3. *N*-hydroxy-*N*-(6-methylpyridin-3-yl)benzamide (1al)



1al

Followed **Method F**; 685 mg, 30% yield; Light red solid, m.p. = 162-164 °C; R_f = 0.2 (DCM:EtOAc = 50:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.87 (s, 1H), 8.66 (s, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 6.8 Hz, 2H), 7.46 (dt, *J* = 14.5, 7.0 Hz, 3H), 7.29 (d, *J* = 7.9 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 168.2, 154.6, 142.4, 136.4, 134.9 130.4, 129.4, 128.4, 127.8, 122.6, 23.4. HRMS (ESI) m/z calcd for $[C_{13}H_{13}N_2O_2]^+$ $[M+H]^+$: 229.0972, found 229.0975.

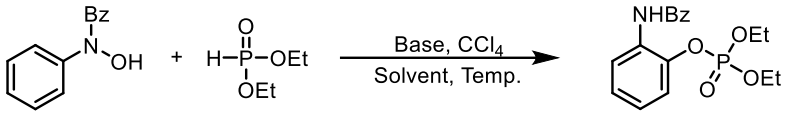
4. *N*-(6-(furan-2-ylmethoxy)pyridin-3-yl)-*N*-hydroxybenzamide (1an)



1an

Followed **Method F**; 1.74 g, 56% yield; Light red solid, m.p. = 118-120 °C; R_f = 0.3 (DCM:EtOAc = 50:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.22 (s, 1H), 8.00 (d, *J* = 1.7 Hz, 1H), 7.52 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.44–7.41 (m, 3H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 1H), 6.42 (d, *J* = 3.2 Hz, 1H), 6.37 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.28 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.3, 162.5, 150.2, 145.0, 143.3, 137.1, 131.7, 131.4, 131.0, 129.0, 128.5, 111.9, 110.7, 110.6, 60.3. HRMS (ESI) m/z calcd for $[C_{17}H_{15}N_2O_4]^+$ $[M+H]^+$: 311.1026, found 311.1027.

Optimization of the reaction conditions



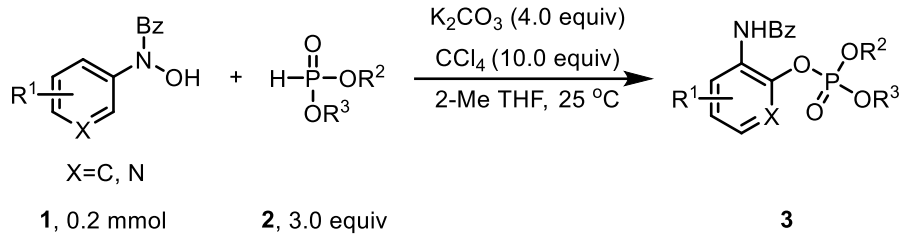
1a **2a** **3a**

entry[a]	**2a** (equiv)	base	solvent	temp.	**3a** yield[b]
1	5.0	No Base	THF	25 ºC	N.P.
2	5.0	Et_3N	THF	25 ºC	44%
3	5.0	DBU	THF	25 ºC	54%
4	5.0	DMAP	THF	25 ºC	51%
5	5.0	4-NH_2 Pyridine	THF	25 ºC	57%
6	5.0	DABCO	THF	25 ºC	57%
7	5.0	TMG	THF	25 ºC	59%
8	5.0	DIPEA	THF	25 ºC	52%
9	5.0	^{t}BuOK	THF	25 ºC	50%
10	5.0	^{t}BuONa	THF	25 ºC	62%
11	5.0	KF	THF	25 ºC	Trace
12	5.0	NaOH	THF	25 ºC	60%
13	5.0	K_3PO_4	THF	25 ºC	59%
14	5.0	CH_3COOK	THF	25 ºC	23%
15	5.0	NaH	THF	25 ºC	59%
16	5.0	Na_2CO_3	THF	25 ºC	59%
17	5.0	K_2CO_3	THF	25 ºC	64%
18	5.0	K_2CO_3	2-Me THF	25 ºC	69%
19	5.0	K_2CO_3	CH_3CN	25 ºC	66%
20	5.0	K_2CO_3	Et_2O	25 ºC	67%
21	5.0	K_2CO_3	Toluene	25 ºC	67%
22	5.0	K_2CO_3	CH_2Cl_2	25 ºC	56%
23	5.0	K_2CO_3	DCE	25 ºC	59%
24	5.0	K_2CO_3	EtOAc	25 ºC	64%
25	5.0	K_2CO_3	PhH	25 ºC	57%

26	5.0	K_2CO_3	PhCl	25 °C	64%
27	5.0	K_2CO_3	$CHCl_3$	25 °C	64%
28	5.0	K_2CO_3	DME	25 °C	63%
29	5.0	K_2CO_3	Acetone	25 °C	66%
30	5.0	K_2CO_3	CH_3OH	25 °C	14%
31	5.0	K_2CO_3	TFE	25 °C	Trace
32	5.0	K_2CO_3	HFIP	25 °C	N.P.
33	5.0	K_2CO_3	NMP	25 °C	21%
34	5.0	K_2CO_3	DMF	25 °C	20%
35	5.0	K_2CO_3	DMSO	25 °C	27%
36	5.0	K_2CO_3	1,4-Dioxane	25 °C	53%
37	5.0	K_2CO_3 (1.0)	2-Me THF	25 °C	60%
38	5.0	K_2CO_3 (1.5)	2-Me THF	25 °C	59%
39	5.0	K_2CO_3 (2.0)	2-Me THF	25 °C	66%
40	5.0	K_2CO_3 (3.0)	2-Me THF	25 °C	66%
41	5.0	K_2CO_3 (6.0)	2-Me THF	25 °C	64%
42	1.0	K_2CO_3	2-Me THF	25 °C	66%
43	2.0	K_2CO_3	2-Me THF	25 °C	63%
44	**3.0**	**K_2CO_3**	**2-Me THF**	**25 °C**	**72%**
45	4.0	K_2CO_3	2-Me THF	25 °C	59%
46	3.0	K_2CO_3	2-Me THF	-40 °C	59%
47	3.0	K_2CO_3	2-Me THF	-20 °C	59%
48	3.0	K_2CO_3	2-Me THF	0 °C	67%
49	3.0	K_2CO_3	2-Me THF	50 °C	70%

[a]Unless otherwise noted, all reactions were carried out under the following conditions: **1a** (43 mg, 0.2 mmol, 1.0 equiv), **2a** (129 µL, 1.0 mmol, 5.0 equiv), base (0.8 mmol, 4.0 equiv), CCl_4 (0.2 mL, 2 mmol, 10.0 equiv) in 2-Me THF (2 mL), 10 hours. [b]Yields of isolated products. Bz = benzoyl; DBU = 1,8-Diazabicyclo[5.4.0]undecane-7-ene; DMAP = 4-(Dimethylamino)pyridine; DABCO = 1,4-Diaza[2.2.2]bicyclooctane; TMG = *N,N'*-Tetramethylguanidine; DIPEA = *N,N*-diisopropylethylamine; THF = Tetrahydrofuran; DCE = 1,2-Bichloroethane; DME = 1,2-dimethoxy-ethan; TFE = 2,2,2-Trifluoroethanol; HFIP = 1,1,1,3,3,3-Hexafluoro-2-propanol; NMP = 1-Methyl-2-pyrrolidinone; DMF = *N,N*-dimethylformamide; DMSO = dimethyl sulfoxide.

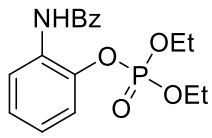
General procedure for the synthesis of *ortho*-phosphated (hetero)arylamines



The system of a mixture of **1** (0.2 mmol, 1.0 equiv), **2** (0.6 mmol, 3.0 equiv), K_2CO_3 (111 mg, 0.8 mmol, 4.0 equiv) and CCl_4 (0.2 mL, 2 mmol, 10.0 equiv) in 2-Me THF (2 mL) was stirred at 25℃ for 10 h. The reaction mixture was evaporated under reduced pressure and purified by column chromatography to give the desired product **3**.

Analytical data of *ortho*-phosphated (hetero)arylamines

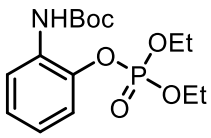
1. 2-benzamidophenyl diethyl phosphate (3a)



3a

50 mg, 72% yield; Colorless oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.37 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.05–8.03 (m, 2H), 7.56–7.53 (m, 1H), 7.51–7.48 (m, 2H), 7.27–7.24 (m, 1H), 7.21 (dt, *J* = 8.1, 1.5 Hz, 1H), 7.13–7.10 (m, 1H), 4.27–4.15 (m, 4H), 1.31 (td, *J* = 7.1, 1.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 140.7 (d, $J_{C\text{-}P}$ = 8.1 Hz), 134.5, 132.0, 130.3 (d, $J_{C\text{-}P}$ = 4.0 Hz), 128.8, 127.4, 126.2 (d, $J_{C\text{-}P}$ = 1.8 Hz), 125.0 (d, $J_{C\text{-}P}$ = 1.8 Hz), 124.0 (d, $J_{C\text{-}P}$ = 1.2 Hz), 121.4 (d, $J_{C\text{-}P}$ = 3.2 Hz), 65.5 (d, $J_{C\text{-}P}$ = 6.2 Hz), 16.2 (d, $J_{C\text{-}P}$ = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.37; HRMS (ESI) m/z calcd for $[C_{17}H_{21}NO_5P]^+$ $[M+H]^+$: 350.1152, found 350.1160.

2. *tert*-butyl (2-((diethoxyphosphoryl)oxy)phenyl)carbamate (3b)

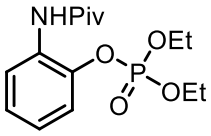


3b

45 mg, 65% yield; Colorless oil; R_f = 0.2 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.22 (dt, *J* = 8.3, 1.3 Hz, 2H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.97 (td, *J* = 7.8, 1.7 Hz, 1H), 4.27–4.16 (m, 4H), 1.51 (s, 9H), 1.34 (td, *J* = 7.1, 1.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.8, 139.6 (d, $J_{C\text{-}P}$ = 7.5 Hz), 130.3 (d, $J_{C\text{-}P}$ = 5.5 Hz), 125.8 (d, $J_{C\text{-}P}$ = 0.9 Hz), 123.1 (d, $J_{C\text{-}P}$ = 1.0

Hz), 120.8, 120.1 (d, $J_{C\text{-}P}$ = 2.7 Hz), 80.8, 65.2 (d, $J_{C\text{-}P}$ = 5.9 Hz), 28.4, 16.2 (d, $J_{C\text{-}P}$ = 6.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -5.33. HRMS (ESI) m/z calcd for $[C_{15}H_{25}NO_6P]^+$ $[M+H]^+$: 346.1414, found 346.1413.

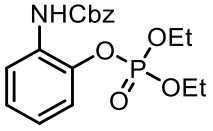
3. diethyl (2-pivalamidophenyl) phosphate (3c)



3c

28 mg, 43% yield; Colorless oil; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 7.20–7.16 (m, 2H), 7.05 (td, *J* = 7.8, 1.5 Hz, 1H), 4.27–4.15 (m, 4H), 1.35–1.32 (m, 15H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 177.1, 140.4 (d, $J_{C\text{-}P}$ = 7.9 Hz), 130.4 (d, $J_{C\text{-}P}$ = 4.5 Hz), 126.0 (d, $J_{C\text{-}P}$ = 1.7 Hz), 124.4 (d, $J_{C\text{-}P}$ = 1.9 Hz), 123.5, 121.0 (d, $J_{C\text{-}P}$ = 3.1 Hz), 65.4 (d, $J_{C\text{-}P}$ = 6.2 Hz), 40.1, 27.7, 16.2 (d, $J_{C\text{-}P}$ = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.60. HRMS (ESI) m/z calcd for $[C_{15}H_{25}NO_5P]^+$ $[M+H]^+$: 330.1465, found 330.1465.

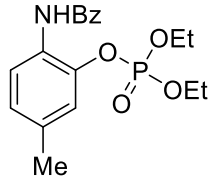
4. benzyl (2-((diethoxyphosphoryl)oxy)phenyl)carbamate (3d)



3d

36 mg, 47% yield; Colorless oil; R_f = 0.2 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 5.9 Hz, 1H), 7.55 (s, 1H), 7.42-7.40 (m, 2H), 7.39–7.36 (m, 2H), 7.35–7.31 (m, 1H), 7.25 (dt, *J* = 8.3, 1.4 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.02 (td, *J* = 7.9, 1.7 Hz, 1H), 5.21 (s, 2H), 4.26–4.14 (m, 4H), 1.31 (td, *J* = 7.1, 0.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.5, 139.9 (d, $J_{C\text{-}P}$ = 7.1 Hz), 136.2, 129.8 (d, $J_{C\text{-}P}$ = 5.4 Hz), 128.7, 128.4, 125.9, 123.7, 121.2, 120.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 67.1, 65.2 (d, $J_{C\text{-}P}$ = 6.0 Hz), 16.1 (d, $J_{C\text{-}P}$ = 6.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -5.15. HRMS (ESI) m/z calcd for $[C_{18}H_{23}NO_6P]^+$ $[M+H]^+$: 380.1258, found 380.1267.

5. 2-benzamido-5-methylphenyl diethyl phosphate (3e)

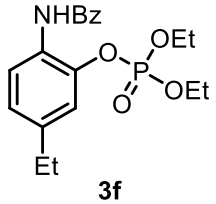


3e

54 mg, 74% yield; Light green oil; R_f = 0.5 (PE:EtOAc =2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.28 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 8.02–8.01 (m, 2H), 7.54–7.51 (m, 1H), 7.49-7.46 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 7.02 (s, 1H), 4.26–4.14 (m, 4H), 2.33 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.3, 140.5 (d, $J_{C\text{-}P}$ = 8.2 Hz), 135.2 (d, $J_{C\text{-}P}$ = 1.7 Hz), 134.5, 131.9, 128.8, 127.5 (d, $J_{C\text{-}P}$ = 4.1 Hz), 127.3, 126.8 (d, $J_{C\text{-}P}$ = 1.8 Hz), 123.8, 121.7 (d, $J_{C\text{-}P}$ = 3.2 Hz), 65.4 (d, $J_{C\text{-}P}$= 6.3 Hz), 21.0, 16.1 (d, $J_{C\text{-}P}$ = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.37. HRMS (ESI) m/z calcd

for $[C_{18}H_{23}NO_5P]^+$ $[M+H]^+$: 364.1308, found 364.1302.

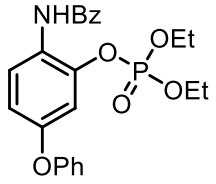
6. 2-benzamido-5-ethylphenyl diethyl phosphate (3f)



3f

53 mg, 70% yield; Colorless oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.31 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.04–8.02 (m, 2H), 7.55–7.52 (m, 1H), 7.50 –7.47 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.04 (s, 1H), 4.27–4.15 (m, 4H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.31 (td, *J* = 7.1, 1.0 Hz, 6H), 1.23 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 141.7 (d, $J_{C\text{-}P}$ = 1.7 Hz), 140.7 (d, $J_{C\text{-}P}$ = 8.2 Hz), 134.6, 131.9, 128.8, 127.7 (d, $J_{C\text{-}P}$ = 3.9 Hz), 127.4, 125.6 (d, $J_{C\text{-}P}$ = 1.8 Hz), 124.0, 120.6 (d, $J_{C\text{-}P}$ = 3.2 Hz), 65.5 (d, $J_{C\text{-}P}$ = 6.3 Hz), 28.4, 16.2 (d, *J* = 6.4 Hz), 15.6; ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.34. HRMS (ESI) m/z calcd for $[C_{19}H_{25}NO_5P]^+$ $[M+H]^+$: 378.1465, found 378.1462.

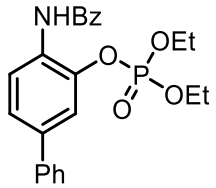
7. 2-benzamido-5-phenoxyphenyl diethyl phosphate (3g)



3g

54 mg, 61% yield; Light yellow oil; R_f = 0.4 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.38 (s, 1H), 8.20 (d, *J* = 8.9 Hz, 1H), 8.05–8.03 (m, 2H), 7.56–7.53 (m, 1H), 7.51–7.48 (m, 2H), 7.37–7.33 (m, 2H), 7.14–7.11 (m, 1H), 7.04– 7.01 (m, 2H), 6.93 (ddd, *J* = 8.9, 2.6, 0.9 Hz, 1H), 6.89 (dd, *J* = 2.6, 1.3 Hz, 1H), 4.26–4.14 (m, 4H), 1.31 (td, *J* = 7.1, 1.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 157.0, 154.2 (d, $J_{C\text{-}P}$ = 1.8 Hz), 141.7 (d, $J_{C\text{-}P}$ = 8.2 Hz), 134.4, 132.0, 130.0, 128.8, 127.4, 125.7 (d, $J_{C\text{-}P}$ = 3.9 Hz), 125.4, 123.8, 119.0, 116.5 (d, $J_{C\text{-}P}$ = 1.8 Hz), 112.4 (d, $J_{C\text{-}P}$ = 3.2 Hz), 65.6 (d, $J_{C\text{-}P}$ = 6.2 Hz), 16.2 (d, $J_{C\text{-}P}$ = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.55. HRMS (ESI) m/z calcd for $[C_{23}H_{25}NO_6P]^+$ $[M+H]^+$: 442.1414, found 442.1404.

8. 4-benzamido-[1,1'-biphenyl]-3-yl diethyl phosphate (3h)

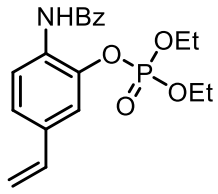


3h

49 mg, 58% yield; White solid, m.p. = 110-112 °C; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.43 (s, 1H), 8.41 (d, *J* = 8.5 Hz, 1H), 8.08–8.06 (m, 2H), 7.60–7.55 (m, 3H), 7.53–7.50 (m, 3H), 7.46–7.43 (m, 3H), 7.38–7.34 (m, 1H), 4.31-4.19 (m, 4H), 1.34 (td, *J* = 7.1, 1.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 140.9 (d, $J_{C\text{-}P}$ = 8.2 Hz), 139.7, 138.2 (d, $J_{C\text{-}P}$ = 1.6 Hz), 134.5, 132.1, 129.4 (d, $J_{C\text{-}P}$ = 4.0 Hz), 129.0, 128.9, 127.7, 127.5, 127.0, 124.8 (d, $J_{C\text{-}P}$

= 1.7 Hz), 124.2, 119.9 (d, $J_{C\text{-}P}$ = 3.2 Hz), 65.7 (d, $J_{C\text{-}P}$ = 6.3 Hz), 16.2 (d, $J_{C\text{-}P}$ = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.28. HRMS (ESI) m/z calcd for $[C_{23}H_{25}NO_5P]^+$ $[M+H]^+$: 426.1465, found 426.1460.

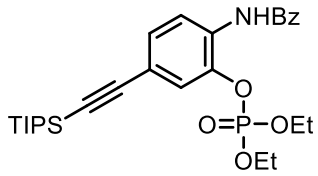
9. 2-benzamido-5-vinylphenyl diethyl phosphate (3i)



3i

31 mg, 41% yield; Light yellow oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.35 (s, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 8.04–8.02 (m, 2H), 7.56–7.53 (m, 1H), 7.51–7.48 (m, 2H), 7.30 (dt, *J* = 8.5, 1.6 Hz, 1H), 7.26 (d, *J* = 1.6 Hz, 1H), 6.66 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 (d, *J* = 17.5 Hz, 1H), 5.26 (d, *J* = 10.9 Hz, 1H), 4.29–4.16 (m, 4H), 1.32 (td, *J* = 7.0, 1.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 140.7 (d, $J_{C\text{-}P}$ = 8.1 Hz), 135.6, 134.8 (d, $J_{C\text{-}P}$ = 1.9 Hz), 134.5, 132.1, 129.7 (d, $J_{C\text{-}P}$ = 4.0 Hz), 128.9, 127.4, 124.1 (d, $J_{C\text{-}P}$ = 1.8 Hz), 123.6, 118.8 (d, $J_{C\text{-}P}$ = 3.2 Hz), 114.4, 65.6 (d, $J_{C\text{-}P}$ = 6.3 Hz), 16.2 (d, $J_{C\text{-}P}$ = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.37. HRMS (ESI) m/z calcd for $[C_{19}H_{23}NO_5P]^+$ $[M+H]^+$: 376.1308, found 376.1307.

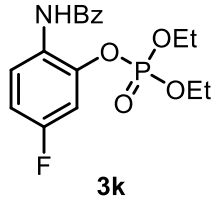
10. 2-benzamido-5-((triisopropylsilyl)ethynyl)phenyl diethyl phosphate (3j)



3j

64 mg, 60% yield; Light yellow oil; R_f = 0.2 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.36 (s, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 8.04–8.02 (m, 2H), 7.57–7.54 (m, 1H), 7.51–7.48 (m, 2H), 7.37 (dt, *J* = 8.6, 1.5 Hz, 1H), 7.30 (t, *J* = 1.6 Hz, 1H), 4.30–4.17 (m, 4H), 1.33 (td, *J* = 7.0, 0.8 Hz, 6H), 1.13 (s, 21H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 139.9 (d, $J_{C\text{-}P}$ = 8.1 Hz), 134.4, 132.2, 130.8 (d, $J_{C\text{-}P}$ = 3.9 Hz), 130.2 (d, $J_{C\text{-}P}$ = 1.8 Hz), 128.9, 127.5, 124.7 (d, $J_{C\text{-}P}$ = 3.3 Hz), 123.1, 120.0 (d, $J_{C\text{-}P}$ = 1.7 Hz), 105.9, 91.4, 65.7 (d, $J_{C\text{-}P}$ = 6.1 Hz), 18.8, 16.2 (d, $J_{C\text{-}P}$ = 6.4 Hz), 11.5; ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.55. HRMS (ESI) m/z calcd for $[C_{28}H_{41}NO_5PSi]^+$ $[M+H]^+$: 530.2486, found 530.2483.

11. 2-benzamido-5-fluorophenyl diethyl phosphate (3k)

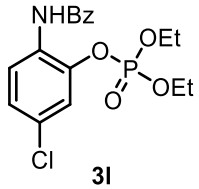


3k

48 mg, 65% yield; Colorless oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.28 (s, 1H), 8.24 (dd, *J* = 8.7, 6.0 Hz, 1H), 8.03–8.00 (m, 2H), 7.56–7.53 (m, 1H), 7.51–7.47 (m, 2H), 7.01–6.96 (m, 2H), 4.28–4.16

(m, 4H), 1.33 (td, J = 7.1, 1.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): 165.5, 159.0 (dd, $J_{C\text{-}F}$ = 246.1 Hz, $J_{C\text{-}P}$ = 1.8 Hz), 141.3 (dd, $J_{C\text{-}F}$ = 11.1 Hz, $J_{C\text{-}P}$ = 8.1 Hz), 134.2, 132.1, 128.9, 127.4, 126.6 (t, $J_{C\text{-}P}$ = 3.9 Hz), 125.3 (d, $J_{C\text{-}F}$ = 9.0 Hz), 113.0 (dd, $J_{C\text{-}F}$ = 21.6 Hz, $J_{C\text{-}P}$ = 1.8 Hz), 109.3 (dd, $J_{C\text{-}F}$ = 25.8 Hz, $J_{C\text{-}P}$ = 3.2 Hz), 65.8 (d, $J_{C\text{-}P}$ = 6.3 Hz), 16.2 (d, $J_{C\text{-}P}$ = 6.4 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ -115.28; ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.64. HRMS (ESI) m/z calcd for $[C_{17}H_{20}FNO_5P]^+$ $[M+H]^+$:368.1058, found 368.1055.

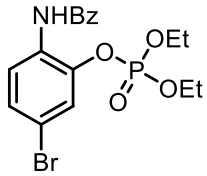
12. 2-benzamido-5-chlorophenyl diethyl phosphate (3l)



3l

59 mg, 77% yield; Colorless oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.33 (s, 1H), 8.29 (d, J = 8.4 Hz, 1H), 8.03–8.00 (m, 2H), 7.57–7.53 (m, 1H), 7.51–7.48 (m, 2H), 7.25-7.22 (m, 2H), 4.29-4.17 m, 4H), 1.33 (td, J = 7.1, 1.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 140.9 (d, $J_{C\text{-}P}$ = 8.1 Hz), 134.2, 132.2, 129.4 (d, $J_{C\text{-}P}$ = 1.9 Hz), 129.2 (d, $J_{C\text{-}P}$ = 4.0 Hz), 128.9, 127.4, 126.3 (d, $J_{C\text{-}P}$ = 1.7 Hz), 124.7, 121.8 (d, $J_{C\text{-}P}$ = 3.2 Hz), 65.8 (d, $J_{C\text{-}P}$ = 6.2 Hz), 16.7 (d, $J_{C\text{-}P}$ = 6.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.59. HRMS (ESI) m/z calcd for $[C_{17}H_{20}ClNO_5P]^+$ $[M+H]^+$: 384.0762, found 384.0764.

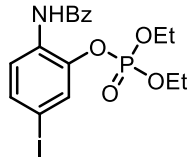
13. 2-benzamido-5-bromophenyl diethyl phosphate (3m)



3m

49 mg, 57% yield; Light yellow oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.33 (s, 1H), 8.24 (d, J = 8.8 Hz, 1H), 8.02–8.00 (m, 2H), 7.57–7.53 (m, 1H), 7.51–7.48 (m, 2H), 7.39-7.37 (m, 2H), 4.30-4.17 (m , 4H), 1.33 (td, J = 7.1, 1.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 140.9 (d, $J_{C\text{-}P}$ = 8.3 Hz), 134.1, 132.2, 129.7 (d, $J_{C\text{-}P}$ = 4.0 Hz), 129.3 (d, $J_{C\text{-}P}$ = 1.8 Hz), 128.9, 127.4, 124.9, 124.6 (d, $J_{C\text{-}P}$ = 3.2 Hz), 116.6 (d, $J_{C\text{-}P}$ = 2.0 Hz), 65.8 (d, $J_{C\text{-}P}$ = 6.3 Hz), 16.2 (d, $J_{C\text{-}P}$ = 6.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.57. HRMS (ESI) m/z calcd for $[C_{17}H_{20}BrNO_5P]^+$ $[M+H]^+$: 428.0257, found 428.0242.

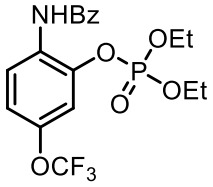
14. 2-benzamido-5-iodophenyl diethyl phosphate (3n)



3n

72 mg, 76% yield; Light yellow oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.33 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 8.02–8.00 (m, 2H), 7.57–7.53 (m, 3H), 7.50–7.47 (m, 2H), 4.28-4.16 (m, 4H), 1.33 (td, *J* = 7.1, 1.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 140.8 (d, J_{C-P} = 8.2 Hz), 135.3 (d, J_{C-P} = 1.8 Hz), 134.2, 132.2, 130.4 (d, J_{C-P} = 4.0 Hz), 130.3 (d, J_{C-P} = 3.2 Hz), 128.9, 127.4, 125.2, 86.6 (d, J_{C-P} = 2.1 Hz), 65.8 (d, J_{C-P} = 6.2 Hz), 16.2 (d, J_{C-P} = 6.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.59. HRMS (ESI) m/z calcd for $[C_{17}H_{20}INO_5P]^+$ $[M+H]^+$: 476.0118, found 476.0117.

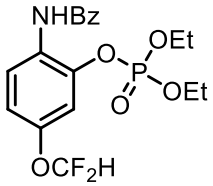
15. 2-benzamido-5-(trifluoromethoxy)phenyl diethyl phosphate (3o)



3o

49 mg, 57% yield; Colorless oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.41 (s, 1H), 8.36 (d, *J* = 9.0 Hz, 1H), 8.04–8.02 (m, 2H), 7.58–7.54 (m, 1H), 7.52–7.49 (m, 2H), 7.15 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.12 (d, *J* = 1.7 Hz, 1H), 4.29–4.17 (m, 4H), 1.33 (td, *J* = 7.1, 1.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 145.1 (t, J_{C-P} = 2.1 Hz), 140.9 (d, J_{C-P} = 8.1 Hz), 134.1, 132.3, 129.4 (d, J_{C-P} = 4.0 Hz), 128.9, 127.5, 124.7, 120.5 (q, J_{C-F} = 257.7 Hz), 118.9, 115.0 (d, J_{C-P} = 3.2 Hz), 65.9 (d, J_{C-P} = 6.2 Hz), 16.1 (d, J_{C-P} = 6.4 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ -58.24; ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.61. HRMS (ESI) m/z calcd for $[C_{18}H_{20}F_3NO_6P]^+$ $[M+H]^+$: 434.0975, found 434.0977.

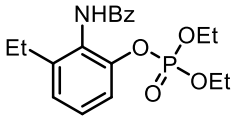
16. 2-benzamido-5-(difluoromethoxy)phenyl diethyl phosphate (3p)



3p

54 mg, 65% yield; White solid, m.p. = 75-77 °C; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.36 (s, 1H), 8.30 (d, *J* = 8.6 Hz, 1H), 8.04–8.01 (m, 2H), 7.57–7.54 (m, 1H), 7.52–7.48 (m, 2H), 7.06-7.04 (m, 2H), 6.50 (t, *J* = 73.5 Hz, 1H), 4.29–4.17 (m, 4H), 1.33 (td, *J* = 7.1, 0.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 147.3 (d, J_{C-P} = 1.4 Hz), 141.2 (d, J_{C-P} = 8.1 Hz), 134.3, 132.2, 128.9, 128.1 (d, J_{C-P} = 4.1 Hz), 127.5, 125.0, 117.5, 115.9 (t, J_{C-F} = 261.3 Hz), 113.9 (d, J_{C-P} = 3.3 Hz), 65.8 (d, J_{C-P} = 6.1 Hz), 16.1 (d, J_{C-P} = 6.4 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ -81.24; ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.59. HRMS (ESI) m/z calcd for $[C_{18}H_{21}F_2NO_6P]^+$ $[M+H]^+$: 416.1069, found 416.1069.

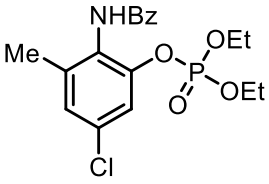
17. 2-benzamido-3-ethylphenyl diethyl phosphate (3q)



3q

23 mg, 30% yield; Colorless oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.08 (s, 1H), 8.06 (dd, *J* = 7.1, 1.9 Hz, 2H), 7.56–7.52 (m, 1H), 7.50-7.47 (m, 2H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.05 (dt, *J* = 7.9, 1.6 Hz, 1H), 4.15–4.04 (m, 4H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.23 (td, *J* = 7.0, 1.0 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.9, 145.4 (d, J_{C-P} = 8.0 Hz), 144.5, 134.1, 131.9, 128.8, 128.0 (d, J_{C-P} = 3.9 Hz), 127.8 (d, *J* = 1.3 Hz), 127.7, 126.0 (d, J_{C-P} = 2.2 Hz), 119.1 (d, J_{C-P} = 3.4 Hz), 65.3 (d, J_{C-P} = 6.4 Hz), 24.8, 16.1 (d, J_{C-P} = 6.5 Hz), 14.0; ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.47. HRMS (ESI) m/z calcd for $[C_{19}H_{25}NO_5P]^+$ $[M+H]^+$: 378.1465, found 378.1476.

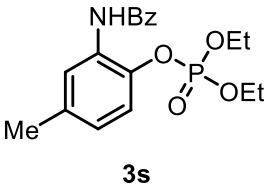
18. 2-benzamido-5-chloro-3-methylphenyl diethyl phosphate (3r)



3r

25 mg, 32% yield; Light yellow oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.26 (s, 1H), 8.04 (dd, *J* = 7.1, 1.4 Hz, 2H), 7.57–7.53 (m, 1H), 7.50–7.47 (m, 2H), 7.16 (s, 1H), 7.05 (s, 1H), 4.18–4.06 (m, 4H), 2.31 (s, 3H), 1.26 (td, *J* = 7.1, 1.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 145.3 (d, J_{C-P} = 8.2 Hz), 140.2 (d, J_{C-P} = 1.3 Hz), 133.7, 132.2 (d, J_{C-P} = 2.0 Hz), 132.1, 128.8, 128.2 (d, J_{C-P} = 2.0 Hz), 127.7, 127.6 (d, J_{C-P} = 3.6 Hz), 119.7 (d, J_{C-P} = 3.6 Hz), 65.6 (d, J_{C-P} = 6.4 Hz), 19.0, 16.1 (d, J_{C-P} = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.45; HRMS (ESI) m/z calcd for $[C_{18}H_{22}ClNO_5P]^+$ $[M+H]^+$: 398.0919, found 398.0914.

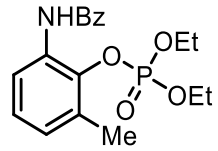
19. 2-benzamido-4-methylphenyl diethyl phosphate (3s)



3s

26 mg, 36% yield; Colorless oil; R_f = 0.2 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.32 (s, 1H), 8.14 (s, 1H), 8.05–8.03 (m, 2H), 7.56–7.48 (m, 3H), 7.09–7.07 (m, 1H), 6.91 (dd, *J* = 8.3, 1.8 Hz, 1H), 4.27–4.14 (m, 4H), 2.37 (s, 3H), 1.31 (td, *J* = 7.1, 1.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): 165.4, 138.6 (d, J_{C-P} = 8.1 Hz), 136.1 (d, J_{C-P} = 1.9 Hz), 134.6, 132.0, 129.9 (d, J_{C-P} = 4.0 Hz), 128.8, 127.4, 125.6 (d, J_{C-P} = 1.7 Hz), 124.4, 121.0 (d, J_{C-P} = 3.3 Hz), 65.5 (d, J_{C-P} = 5.9 Hz), 21.3, 16.2 (d, J_{C-P} = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.16. HRMS (ESI) m/z calcd for $[C_{18}H_{23}NO_5P]^+$ $[M+H]^+$: 364.1308, found 364.1309.

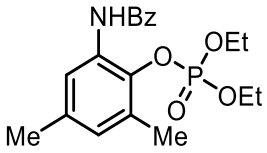
2-benzamido-6-methylphenyl diethyl phosphate (3s′)



3s'

17 mg, 23% yield; Colorless oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.92 (s, 1H), 8.11 (dt, *J* = 7.2, 1.3 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.55–7.48 (m, 3H), 7.17–7.14 (m, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 4.27–4.14 (m, 4H), 2.34 (s, 3H), 1.29 (td, *J* = 7.1, 1.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.6, 139.9 (d, J_{C-P} = 8.8 Hz), 134.7, 131.9, 131.0 (d, J_{C-P} = 3.7 Hz), 130.5 (d, J_{C-P} = 3.1 Hz), 128.7, 127.7, 127.1, 125.7 (d, J_{C-P} = 2.1 Hz), 122.8 (d, J_{C-P} = 2.0 Hz), 65.6 (d, J_{C-P} = 6.4 Hz), 16.9, 16.1 (d, J_{C-P} = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -3.39. HRMS (ESI) m/z calcd for $[C_{18}H_{23}NO_5P]^+$ $[M+H]^+$: 364.1308, found 364.1310.

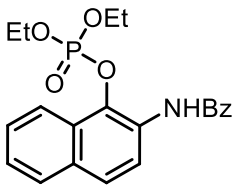
20. 2-benzamido-4,6-dimethylphenyl diethyl phosphate (3t)



3t

39 mg, 52% yield; Light yellow oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.11–8.09 (m, 2H), 7.85 (s, 1H), 7.54–7.47 (m, 3H), 6.81 (s, 1H), 4.26–4.12 (m, 4H), 2.32 (s, 3H), 2.29 (s, 3H), 1.29 (td, *J* = 7.1, 1.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.6, 137.7 (d, J_{C-P} = 8.9 Hz), 135.4 (d, J_{C-P} = 2.1 Hz), 134.6, 131.8, 130.4 (d, J_{C-P} = 3.7 Hz), 129.9 (d, J_{C-P} = 2.8 Hz), 128.7, 127.9 (d, J_{C-P} = 1.8 Hz), 127.6, 123.2 (d, J_{C-P} = 1.9 Hz), 65.6 (d, J_{C-P} = 6.3 Hz), 21.2, 16.8, 16.1 (d, J_{C-P} = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -3.21; HRMS (ESI) m/z calcd for $[C_{19}H_{25}NO_5P]^+$ $[M+H]^+$: 378.1465, found 378.1465.

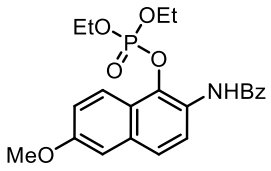
21. 2-benzamidonaphthalen-1-yl diethyl phosphate (3u)



3u

57 mg, 71% yield; White solid, m.p. = 95-97 ºC; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.28 (s, 1H), 8.27 (d, *J* = 8.9 Hz, 1H), 8.18 (dt, *J* = 7.0, 1.4 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.58–7.51 (m, 4H), 7.49–7.46 (m, 1H), 4.29–4.11 (m, 4H), 1.23 (td, *J* = 7.0, 1.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.7, 135.7 (d, J_{C-P} = 9.4 Hz), 134.3, 132.0, 131.9 (d, J_{C-P} = 1.1 Hz), 128.8, 127.8, 127.7, 127.3 (d, J_{C-P} = 3.2 Hz), 127.2 (d, J_{C-P} = 3.9 Hz), 126.6, 125.8, 125.7 (d, J_{C-P} = 2.1 Hz), 123.6 (d, J_{C-P} = 2.1 Hz), 121.7, 65.8 (d, J_{C-P} = 6.1 Hz), 16.1 (d, J_{C-P} = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -3.15; HRMS (ESI) m/z calcd for $[C_{21}H_{23}NO_5P]^+$ $[M+H]^+$: 400.1308, found 400.1318.

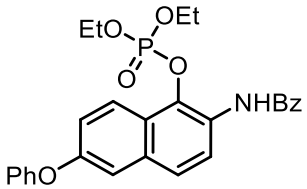
22. 2-benzamido-6-methoxynaphthalen-1-yl diethyl phosphate (3v)



3v

58 mg, 68% yield; Light green oil; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.18 (s, 1H), 8.19 (d, *J* = 8.9 Hz, 1H), 8.17–8.15 (m, 2H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.57–7.50 (m, 3H), 7.19 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 4.28–4.10 (m, 4H), 3.92 (s, 3H), 1.23 (td, *J* = 7.0, 1.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.7, 157.8, 136.3 (d, $J_{C\text{-}P}$ = 9.5 Hz), 134.4, 133.4 (d, $J_{C\text{-}P}$ = 1.0 Hz), 132.0, 128.8, 127.7, 125.1 (d, $J_{C\text{-}P}$ = 3.7 Hz), 124.5, 123.4, 122.5 (d, $J_{C\text{-}P}$ = 3.2 Hz), 119.5, 105.9, 65.8 (d, $J_{C\text{-}P}$ = 6.3 Hz), 55.5, 16.1 (d, $J_{C\text{-}P}$ = 6.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -3.19; HRMS (ESI) m/z calcd for $[C_{22}H_{25}NO_6P]^+$ $[M+H]^+$: 430.1414, found 430.1427.

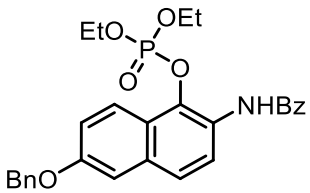
23. 2-benzamido-6-phenoxynaphthalen-1-yl diethyl phosphate (3w)



3w

57 mg, 58% yield; White solid, m.p. = 98-100 °C; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.20 (s, 1H), 8.21 (d, *J* = 8.9 Hz, 1H), 8.17–8.15 (m, 2H), 8.06 (d, *J* = 9.1 Hz, 1H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.58–7.51 (m, 3H), 7.42-7.38 (m, 2H), 7.32 (dd, *J* = 9.1, 2.4 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.18 (tt, *J* = 7.7, 1.0 Hz, 1H), 7.11–7.08 (m, 2H), 4.30–4.13 (m, 4H), 1.26 (td, *J* = 7.1, 1.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.8, 156.9, 155.6, 136.2 (d, $J_{C\text{-}P}$ = 9.4 Hz), 134.4, 133.1, 132.0, 130.1, 128.8, 127.7, 126.2 (d, $J_{C\text{-}P}$ = 3.5 Hz), 124.9 (d, $J_{C\text{-}P}$ = 1.6 Hz), 124.7 (d, $J_{C\text{-}P}$ = 2.0 Hz), 124.0 (d, $J_{C\text{-}P}$ = 2.7 Hz), 123.9 (d, $J_{C\text{-}P}$ = 3.1 Hz), 120.5, 119.6, 113.7, 65.9 (d, $J_{C\text{-}P}$ = 6.1 Hz), 16.2 (d, $J_{C\text{-}P}$ = 6.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -3.17; HRMS (ESI) m/z calcd for $[C_{27}H_{27}NO_6P]^+$ $[M+H]^+$: 492.1571, found 492.1584.

24. 2-benzamido-6-(benzyloxy)naphthalen-1-yl diethyl phosphate (3x)

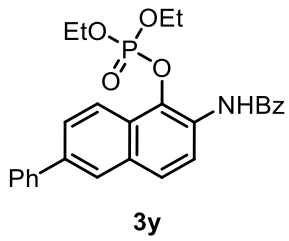


3x

58 mg, 57% yield; Light red solid, m.p. = 130-132 °C; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.19 (s, 1H), 8.20 (d, *J* = 8.9 Hz, 1H), 8.17 (dt, *J* = 6.9, 1.4 Hz, 2H), 8.00 (d, *J* = 9.2 Hz, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.58–7.49 (m, 5H), 7.44-7.41 (m, 2H), 7.38–7.34 (m, 1H), 7.29 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 5.19 (s, 2H), 4.29–4.12 (m, 4H), 1.24 (td, *J* = 7.1, 1.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$):

δ 165.7, 157.0, 136.7, 136.3 (d, J_{C-P} = 9.4 Hz), 134.4, 133.3 (d, J_{C-P} = 1.1 Hz), 132.0, 128.8, 128.3, 127.8, 127.7, 125.2 (d, J_{C-P} = 3.7 Hz), 124.6 (d, J_{C-P} = 2.0 Hz), 124.5 (d, J_{C-P} = 2.1 Hz), 123.5, 122.7 (d, J_{C-P} = 3.2 Hz), 119.8, 107.2, 70.2, 65.8 (d, J_{C-P} = 6.2 Hz), 16.1 (d, J_{C-P} = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -3.16; HRMS (ESI) m/z calcd for $[C_{28}H_{29}NO_6P]^+$ $[M+H]^+$: 506.1727, found 506.1739.

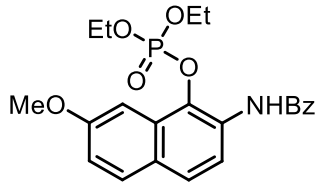
25. 2-benzamido-6-phenylnaphthalen-1-yl diethyl phosphate (3y)



3y

77 mg, 81% yield; White solid, m.p. = 96-98 °C; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.27 (s, 1H), 8.31 (d, *J* = 8.9 Hz, 1H), 8.18 (dt, *J* = 6.8, 1.4 Hz, 2H), 8.14 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 1.6 Hz, 1H), 7.82 (dd, *J* = 8.8, 1.8 Hz, 2H), 7.74 (dt, *J* = 8.2, 1.6 Hz, 2H), 7.59–7.49 (m, 5H), 7.40 (tt, *J* = 6.8, 1.1 Hz, 1H), 4.32–4.15 (m, 4H), 1.27 (td, *J* = 7.0, 1.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.8, 140.7, 138.6, 135.8 (d, J_{C-P} = 9.6 Hz), 134.4, 132.3 (d, J_{C-P} = 0.7 Hz), 132.1, 129.1, 128.8, 127.8, 127.7, 127.5, 127.4 (d, J_{C-P} = 3.7 Hz), 126.5 (d, J_{C-P} = 3.2 Hz), 126.4, 126.1 (d, J_{C-P} = 1.6 Hz), 125.7, 124.1 (d, J_{C-P} = 1.3 Hz), 122.4, 65.9 (d, J_{C-P} = 6.0 Hz), 16.2 (d, J_{C-P} = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -3.13; HRMS (ESI) m/z calcd for $[C_{27}H_{27}NO_5P]^+$ $[M+H]^+$: 476.1621, found 476.1640.

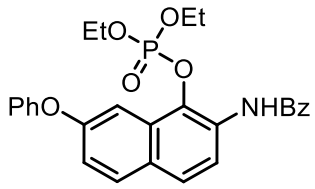
26. 2-benzamido-7-methoxynaphthalen-1-yl diethyl phosphate (3z)



3z

57 mg, 66% yield; White solid, m.p. = 99-101 °C; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.15 (s, 1H), 8.18–8.15 (m, 2H), 8.12 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.58–7.50 (m, 3H), 7.36 (d, *J* = 2.6 Hz, 1H), 7.13 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.29–4.12 (m, 4H), 3.94 (s, 3H), 1.25 (td, *J* = 7.0, 1.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.7, 158.4, 135.1 (d, J_{C-P} = 9.5 Hz), 134.4, 132.0, 129.5, 128.8, 128.5 (d, J_{C-P} = 3.1 Hz), 127.8 (d, J_{C-P} = 3.7 Hz), 127.7, 127.5 (d, J_{C-P} = 1.1 Hz), 125.5 (d, J_{C-P} = 2.1 Hz), 121.0 (d, J_{C-P} = 2.0 Hz), 118.5, 100.3, 65.7 (d, J_{C-P} = 6.1 Hz), 55.4, 16.2 (d, J_{C-P} = 6.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -2.81; HRMS (ESI) m/z calcd for $[C_{22}H_{25}NO_6P]^+$ $[M+H]^+$: 430.1414 found 430.1412.

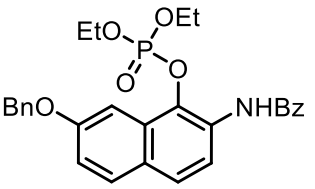
27. 2-benzamido-7-phenoxynaphthalen-1-yl diethyl phosphate (3aa)



3aa

82 mg, 83% yield; White solid, m.p. = 72-74 °C; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.23 (s, 1H), 8.21 (d, *J* = 8.9 Hz, 1H), 8.15 (dt, *J* = 6.9, 1.4 Hz, 2H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.57–7.50 (m, 3H), 7.42-7.38 (m, 3H), 7.26 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.17 (tt, *J* = 7.6, 1.0 Hz, 1H), 7.12–7.10 (m, 2H), 4.14–3.96 (m, 4H), 1.17 (td, *J* = 7.1, 1.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.7, 156.7, 156.5, 134.9 (d, $J_{C\text{-}P}$ = 9.4 Hz), 134.4, 132.0, 130.0, 128.7, 128.38, 128.36, 128.1 (d, $J_{C\text{-}P}$ = 3.6 Hz), 127.7, 125.5 (d, $J_{C\text{-}P}$ = 2.0 Hz), 124.0, 122.0 (d, $J_{C\text{-}P}$ = 2.1 Hz), 119.9, 119.5, 107.6, 65.7 (d, $J_{C\text{-}P}$ = 6.6 Hz), 16.0 (d, $J_{C\text{-}P}$ = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -3.78; HRMS (ESI) m/z calcd for $[C_{27}H_{27}NO_6P]^+$ $[M+H]^+$: 492.1571, found 492.1563.

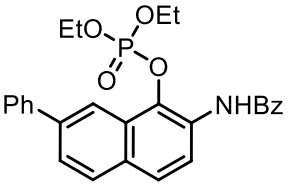
28. 2-benzamido-7-(benzyloxy)naphthalen-1-yl diethyl phosphate (3ab)



3ab

68 mg, 67% yield; Light red solid, m.p. = 108-110 °C; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.18 (s, 1H), 8.18–8.13 (m, 3H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.58–7.49 (m, 5H), 7.45–7.40 (m, 3H), 7.37–7.33 (m, 1H), 7.23 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.22 (s, 2H), 4.24–4.07 (m, 4H), 1.23 (td, *J* = 7.1, 1.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.7, 157.5, 136.8, 135.1 (d, $J_{C\text{-}P}$ = 9.4 Hz), 134.4, 132.0, 129.6, 128.8, 128.7, 128.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.2, 127.8 (d, $J_{C\text{-}P}$ = 3.7 Hz), 127.7, 127.6, 127.5 (d, $J_{C\text{-}P}$ = 0.9 Hz), 125.5 (d, $J_{C\text{-}P}$ = 2.1 Hz), 121.1 (d, $J_{C\text{-}P}$ = 2.0 Hz), 118.9, 101.6, 70.2, 65.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 16.2 (d, $J_{C\text{-}P}$ = 6.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -2.84; HRMS (ESI) m/z calcd for $[C_{28}H_{29}NO_6P]^+$ $[M+H]^+$: 506.1727, found 506.1741.

29. 2-benzamido-7-phenylnaphthalen-1-yl diethyl phosphate (3ac)

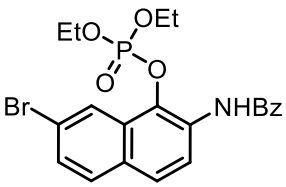


3ac

75 mg, 79% yield; Light green oil; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.25 (s, 1H), 8.30–8.28 (m, 2H), 8.20-8.18 (m, 2H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.76-7.73 (m, 3H), 7.60–7.50 (m, 5H), 7.41 (tt, *J* = 6.8, 1.1 Hz, 1H), 4.31–4.14 (m, 4H), 1.25 (td, *J* = 7.1, 1.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.7, 141.1, 139.3, 136.0 (d, $J_{C\text{-}P}$ = 9.5 Hz), 134.4, 132.0, 131.1 (d, $J_{C\text{-}P}$ = 1.0 Hz), 129.0, 128.8,

128.4, 127.71, 127.69, 127.66, 127.6 (d, J_{C-P} = 3.1 Hz), 127.5, 125.6, 125.5 (d, J_{C-P} = 2.3 Hz), 123.6 (d, J_{C-P} = 2.3 Hz), 119.7, 65.8 (d, J_{C-P} = 6.4 Hz), 16.1 (d, J_{C-P} = 6.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -3.02; HRMS (ESI) m/z calcd for $[C_{27}H_{27}NO_5P]^+$ $[M+H]^+$: 476.1621, found 476.1622.

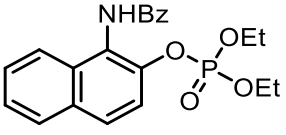
30. 2-benzamido-7-bromonaphthalen-1-yl diethyl phosphate (3ad)



3ad

67 mg, 70% yield; Light red oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.25 (s, 1H), 8.29 (d, *J* = 9.0 Hz, 1H), 8.21 (d, *J* = 1.9 Hz, 1H), 8.17–8.14 (m, 2H), 7.73-7.70 (m, 2H), 7.59–7.51 (m, 4H), 4.31–4.14 (m, 4H), 1.27 (td, *J* = 7.1, 1.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.8, 134.8 (d, J_{C-P} = 9.4 Hz), 134.2, 132.2, 130.3 (d, J_{C-P} = 1.1 Hz), 129.6, 129.3, 128.9, 128.5 (d, J_{C-P} = 3.2 Hz), 128.4 (d, J_{C-P} = 3.7 Hz), 127.7, 125.7 (d, J_{C-P} = 2.3 Hz), 124.2, 124.1 (d, J_{C-P} = 2.0 Hz), 121.1, 66.0 (d, J_{C-P} = 6.2 Hz), 16.1 (d, J_{C-P} = 6.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -3.26; HRMS (ESI) m/z calcd for $[C_{21}H_{22}BrNO_5P]^+$ $[M+H]^+$: 478.0413, found 478.0408.

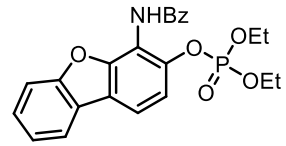
31. 1-benzamidonaphthalen-2-yl diethyl phosphate (3ae)



3ae

58 mg, 73% yield; White solid, m.p. = 114-116 °C; R_f = 0.2 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.59 (s, 1H), 8.19–8.17 (m, 2H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.9 Hz, 1H), 7.61–7.57 (m, 1H), 7.56-7.52 (m, 3H), 7.51-7.48 (m, 1H), 7.35 (dd, *J* = 8.9, 1.0 Hz, 1H), 4.21–4.09 (m, 4H), 1.27 (td, *J* = 7.1, 1.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.3, 142.5 (d, J_{C-P} = 8.1 Hz), 133.9, 132.14, 132.10 (d, J_{C-P} = 1.2 Hz), 131.2, 128.8, 128.2, 127.9, 127.2, 126.1, 125.1 (d, J_{C-P} = 4.7 Hz), 124.7, 120.6 (d, J_{C-P} = 2.9 Hz), 65.5 (d, J_{C-P} = 6.4 Hz), 16.1 (d, J_{C-P} = 6.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.03; HRMS (ESI) m/z calcd for $[C_{21}H_{23}NO_5P]^+$ $[M+H]^+$: 400.1308, found 400.1322.

32. 4-benzamidodibenzo[*b*,*d*]furan-3-yl diethyl phosphate (3af)

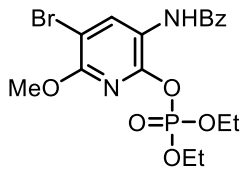


3af

22mg, 25% yield; Light yellow solid, m.p. = 146-148 °C; R_f = 0.2 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.63 (s, 1H), 8.17–8.15 (m, 2H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.59-

7.56 (m, 2H), 7.54-7.51 (m, 2H), 7.45-7.41 (m, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.21 (dd, J = 8.4, 1.4 Hz, 1H), 4.25–4.11 (m, 4H), 1.29 (td, J = 7.0, 1.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.1, 157.2, 151.9, 143.2 (d, $J_{C\text{-}P}$ = 8.4 Hz), 133.7, 132.1, 128.8, 128.0, 127.3, 123.9, 123.5 (d, $J_{C\text{-}P}$ = 1.8 Hz), 123.2, 120.5, 118.3, 116.8 (d, $J_{C\text{-}P}$ = 3.6 Hz), 116.1 (d, $J_{C\text{-}P}$ = 3.7 Hz), 112.4, 65.6 (d, $J_{C\text{-}P}$ = 6.1 Hz), 16.1 (d, $J_{C\text{-}P}$ = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -3.85; HRMS (ESI) m/z calcd for $[C_{23}H_{23}NO_6P]^+$ $[M+H]^+$: 440.1258, found 440.1268.

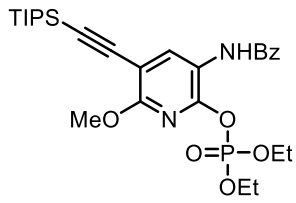
33. 3-benzamido-5-bromo-6-methoxypyridin-2-yl diethyl phosphate (3ag)



3ag

74 mg, 81% yield; White solid, m.p. = 112-114 ºC; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.10 (s, 1H), 8.82 (s, 1H), 7.99–7.97 (m, 2H), 7.58–7.54 (m, 1H), 7.51–7.48 (m, 2H), 4.38–4.25 (m, 4H), 3.97 (s, 3H), 1.37 (td, J = 7.1, 1.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 154.9, 144.0 (d, $J_{C\text{-}P}$ = 7.1 Hz), 138.9, 133.7, 132.4, 128.9, 127.4, 118.9 (d, $J_{C\text{-}P}$ = 4.9 Hz), 102.5 (d, $J_{C\text{-}P}$ = 1.9 Hz), 65.7 (d, $J_{C\text{-}P}$ = 6.3 Hz), 55.1, 16.2 (d, $J_{C\text{-}P}$ = 7.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.46; HRMS (ESI) m/z calcd for $[C_{17}H_{21}BrN_2O_6P]^+$ $[M+H]^+$: 459.0315, found 459.0321.

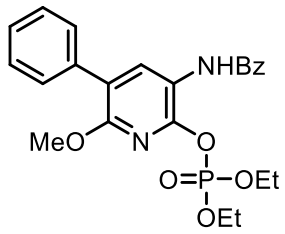
34. 3-benzamido-6-methoxy-5-((triisopropylsilyl)ethynyl)pyridin-2-yl diethyl phosphate (3ah)



3ah

70 mg, 62% yield; White solid, m.p. = 113-115 ºC; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.02 (s, 1H), 8.63 (s, 1H), 7.99–7.97 (m, 2H), 7.57–7.53 (m, 1H), 7.50–7.47 (m, 2H), 4.37–4.24 (m, 4H), 3.94 (s, 3H), 1.36 (td, J = 7.1, 1.1 Hz, 6H), 1.13 (s, 21H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 159.6 (d, $J_{C\text{-}P}$ = 0.8 Hz), 144.5 (d, $J_{C\text{-}P}$ = 7.3 Hz), 139.2, 133.9, 132.3, 128.9, 127.4, 117.5 (d, $J_{C\text{-}P}$ = 5.0 Hz), 105.4 (d, $J_{C\text{-}P}$ = 1.0 Hz), 100.1, 97.3, 65.6 (d, $J_{C\text{-}P}$ = 6.3 Hz), 54.5, 18.8, 16.2 (d, $J_{C\text{-}P}$ = 6.9 Hz), 11.4; ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.60; HRMS (ESI) m/z calcd for $[C_{28}H_{42}N_2O_6PSi]^+$ $[M+H]^+$: 561.2544, found 561.2537.

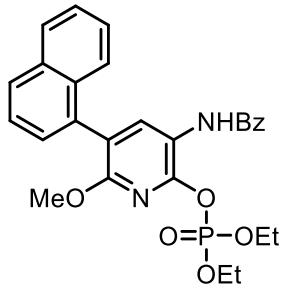
35. 3-benzamido-6-methoxy-5-phenylpyridin-2-yl diethyl phosphate (3ai)



3ai

55 mg, 60% yield; Light yellow solid, m.p. = 127-129 ºC; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.15 (s, 1H), 8.60 (s, 1H), 8.03–8.00 (m, 2H), 7.61–7.59 (m, 2H), 7.57–7.54 (m, 1H), 7.51-7.48 (m, 2H), 7.43–7.40 (m, 2H), 7.36–7.33 (m, 1H), 4.43–4.29 (m, 4H), 3.94 (s, 3H), 1.39 (td, J = 7.1, 1.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 155.7, 144.2 (d, $J_{C\text{-}P}$ = 7.3 Hz), 136.8, 135.6, 134.1, 132.1, 129.4, 128.9, 128.3, 127.8, 127.4, 122.4 (d, $J_{C\text{-}P}$ = 0.9 Hz), 118.1 (d, $J_{C\text{-}P}$ = 4.9 Hz), 65.5 (d, $J_{C\text{-}P}$ = 6.2 Hz), 54.2, 16.1 (d, $J_{C\text{-}P}$ = 6.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.22; HRMS (ESI) m/z calcd for $[C_{23}H_{26}N_2O_6P]^+$ $[M+H]^+$: 457.1523, found 457.1537.

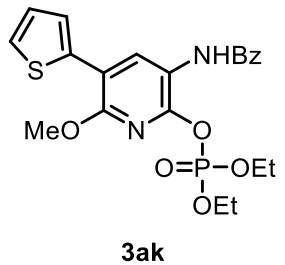
36. 3-benzamido-6-methoxy-5-(naphthalen-1-yl)pyridin-2-yl diethyl phosphate (3aj)



3aj

66 mg, 65% yield; White solid, m.p. = 158-160 ºC; R_f = 0.2 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.14 (s, 1H), 8.58 (s, 1H), 8.01–7.99 (m, 2H), 7.89 (dd, J = 7.9, 3.1 Hz, 2H), 7.63 (d, J = 8.3 Hz, 1H), 7.57–7.43 (m, 7H), 4.48-4.33 (m, 4H), 3.84 (s, 3H), 1.43 (td, J = 7.0, 2.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): 165.5, 156.5, 144.8 (d, $J_{C\text{-}P}$ = 7.2 Hz), 138.4, 134.1, 133.62, 133.55, 132.2, 131.8, 128.9, 128.6, 128.4, 128.0, 127.3, 126.2, 125.9 (d, $J_{C\text{-}P}$ = 6.2 Hz), 125.4, 121.2, 117.8 (d, $J_{C\text{-}P}$ = 5.0 Hz), 65.6–65.5 (m), 54.2, 16.2 (d, $J_{C\text{-}P}$ = 6.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.15; HRMS (ESI) m/z calcd for $[C_{27}H_{28}N_2O_6P]^+$ $[M+H]^+$: 507.1679, found 507.1688.

37. 3-benzamido-6-methoxy-5-(thiophen-2-yl)pyridin-2-yl diethyl phosphate (3ak)

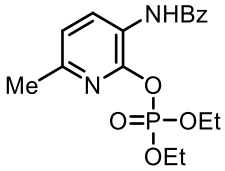


3ak

82 mg, 89% yield; Light green oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.08 (s, 1H), 8.90 (s, 1H), 8.02–8.00 (m, 2H), 7.58–7.54 (m, 2H), 7.52-7.48 (m, 2H), 7.35 (dd, J = 5.1, 1.2 Hz, 1H), 7.09 (dd, J = 5.1, 3.7 Hz, 1H), 4.40–4.27 (m, 4H), 4.04 (s, 3H), 1.38 (td, J = 7.0, 1.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.6, 154.2, 143.6 (d, $J_{C\text{-}P}$ = 7.3 Hz), 136.8, 134.2, 133.8, 132.2, 128.9, 127.4, 127.3, 126.5, 126.3, 118.3 (d, $J_{C\text{-}P}$ = 5.0 Hz), 115.9 (d, $J_{C\text{-}P}$ = 1.2 Hz), 65.5 (d, $J_{C\text{-}P}$ = 6.3 Hz), 54.3, 16.2 (d, $J_{C\text{-}P}$ = 6.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.35; HRMS (ESI) m/z calcd for $[C_{21}H_{24}N_2O_6PS]^+$ $[M+H]^+$:

463.1087, found 463.1084.

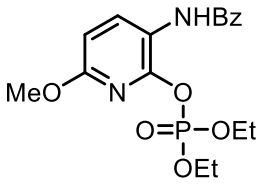
38. 3-benzamido-6-methylpyridin-2-yl diethyl phosphate (3al)



3al

30 mg, 41% yield; White solid, m.p. = 249-251 °C; R_f = 0.3 (PE:EtOAc = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.06 (s, 1H), 8.59 (d, *J* = 8.1 Hz, 1H), 7.99 –7.96 (m, 2H), 7.57–7.54 (m, 1H), 7.51–7.47 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 4.40–4.29 (m, 4H), 2.47 (s, 3H), 1.36 (td, *J* = 7.1, 1.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.7, 151.9, 146.5 (d, $J_{C\text{-}P}$ = 6.8 Hz), 134.2, 132.3, 128.9, 127.4, 122.4 (d, $J_{C\text{-}P}$ = 5.2 Hz), 121.4, 65.6 (d, $J_{C\text{-}P}$ = 6.1 Hz), 23.5, 16.1 (d, $J_{C\text{-}P}$ = 6.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.15; HRMS (ESI) m/z calcd for $[C_{17}H_{22}N_2O_5P]^+$ $[M+H]^+$: 365.1261, found 365.1265.

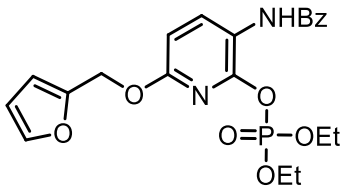
39. 3-benzamido-6-methoxypyridin-2-yl diethyl phosphate (3am)



3am

53mg, 70% yield; White solid, m.p. = 77-79 °C; R_f = 0.2 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.07 (s, 1H), 8.47 (d, *J* = 8.8 Hz, 1H), 8.00–7.97 (m, 2H), 7.56–7.52 (m, 1H), 7.50–7.46 (m, 2H), 6.69 (d, *J* = 8.7 Hz, 1H), 4.38–4.25 (m, 4H), 3.89 (s, 3H), 1.35 (td, *J* = 7.1, 1.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.6, 159.2, 145.3 (d, $J_{C\text{-}P}$ = 7.2 Hz), 136.7, 134.1, 132.1, 128.9, 127.4, 117.8 (d, $J_{C\text{-}P}$ = 4.9 Hz), 108.1 (d, $J_{C\text{-}P}$ = 1.0 Hz), 65.5 (d, $J_{C\text{-}P}$ = 6.3 Hz), 54.0, 16.1 (d, $J_{C\text{-}P}$ = 6.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.35; HRMS (ESI) m/z calcd for $[C_{17}H_{22}N_2O_6P]^+$ $[M+H]^+$: 381.1210, found 381.1211.

40. 3-benzamido-6-(furan-2-ylmethoxy)pyridin-2-yl diethyl phosphate (3an)

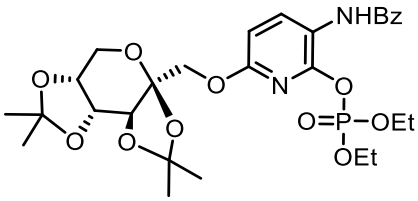


3an

70 mg, 78% yield; Light red solid, m.p. = 97-99 °C; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.07 (s, 1H), 8.49 (d, *J* = 8.7 Hz, 1H), 8.00–7.97 (m, 2H), 7.56–7.53 (m, 1H), 7.49 (td, *J* = 6.8, 1.5 Hz, 2H), 7.43–7.42 (m, 1H), 6.72 (d, *J* = 8.7 Hz, 1H), 6.49 (d, *J* = 3.2 Hz, 1H), 6.36 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.27 (s, 2H), 4.38–4.25 (m, 4H), 1.36 (td, *J* = 7.1, 1.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.6, 158.0, 150.3, 145.0 (d, $J_{C\text{-}P}$ = 7.2 Hz), 143.2, 136.8, 134.1, 132.1, 128.9, 127.4, 118.2 (d, $J_{C\text{-}P}$ = 4.9 Hz), 110.6, 110.5, 108.6, 65.5 (d, $J_{C\text{-}P}$ = 6.3 Hz), 60.3, 16.2 (d, $J_{C\text{-}P}$ = 6.8 Hz); ^{31}P NMR

(202 MHz, $CDCl_3$) δ -6.37; HRMS (ESI) m/z calcd for $[C_{21}H_{24}N_2O_7P]^+$ $[M+H]^+$: 447.1316, found 447.1316.

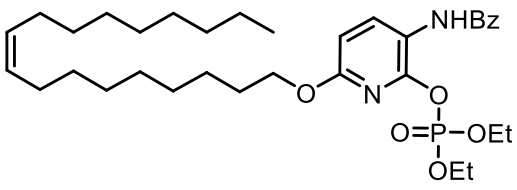
41. 3-benzamido-6-(((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]-dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methoxy)pyridin-2-yl diethyl phosphate (3ao)



3ao

85 mg, 70% yield; Colorless oil; R_f = 0.2 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.18 (s, 1H), 8.51 (d, *J* = 8.7 Hz, 1H), 8.00–7.98 (m, 2H), 7.56–7.52 (m, 1H), 7.50-7.47 (m, 2H), 6.72 (d, *J* = 8.7 Hz, 1H), 4.64–4.59 (m, 2H), 4.51 (d, *J* = 2.6 Hz, 1H), 4.37–4.24 (m, 5H), 4.20 (d, *J* = 11.2 Hz, 1H), 3.95 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.78 (d, *J* = 12.9 Hz, 1H), 1.54 (s, 3H), 1.48 (s, 3H), 1.44 (s, 3H), 1.36–1.33 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.6, 158.1, 145.0 (d, *J* = 7.1 Hz), 136.8, 134.2, 132.1, 128.9, 127.4, 118.6 (d, *J* = 4.6 Hz), 109.2, 108.9, 108.4, 102.2, 71.1, 70.5 (d, *J* = 21.6 Hz), 67.1, 65.63 (d, *J* = 2.5 Hz), 65.57 (d, *J* = 2.7 Hz), 61.4, 26.7, 26.1, 25.5, 24.2, 16.1 (d, *J* = 6.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.36; HRMS (ESI) m/z calcd for $[C_{28}H_{38}N_2O_{11}P]^+$ $[M+H]^+$: 609.2208, found 609.2222.

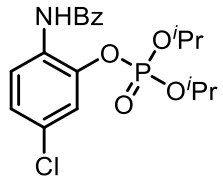
42. (*Z*)-3-benzamido-6-(octadec-9-en-1-yloxy)pyridin-2-yl diethyl phosphate (3ap)



3ap

103 mg, 83% yield; White solid, m.p. = 42-44 °C; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.08 (s, 1H), 8.47 (d, *J* = 8.7 Hz, 1H), 8.00–7.98 (m, 2H), 7.56–7.53 (m, 1H), 7.50-7.47 (m, 2H), 6.68 (d, *J* = 8.6 Hz, 1H), 5.39–5.31 (m, 2H), 4.38–4.24 (m, 4H), 4.22 (t, *J* = 6.6 Hz, 2H), 2.04-1.99 (m, 3H), 1.75 (p, *J* = 6.8 Hz, 2H), 1.44–1.39 (m, 2H), 1.37–1.23 (m, 27H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): 165.6, 159.2, 145.3 (d, J_{C-P} = 7.2 Hz), 136.7, 134.2, 132.1, 130.0 (d, J_{C-P} = 23.2 Hz), 128.9, 127.4, 117.7 (d, J_{C-P} = 4.8 Hz), 108.4, 66.9, 65.4 (d, J_{C-P} = 6.3 Hz), 32.0, 29.904, 29.896, 29.8, 29.7, 29.6, 29.52, 29.46, 29.44, 29.39, 29.1, 27.4, 27.3, 26.2, 22.8, 16.2 (d, J_{C-P} = 6.9 Hz), 14.2; ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.25; HRMS (ESI) m/z calcd for $[C_{34}H_{54}N_2O_6P]^+$ $[M+H]^+$: 617.3714, found 617.3706.

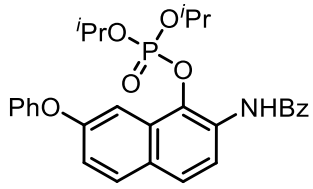
43. 2-benzamido-5-chlorophenyl diisopropyl phosphate (3aq)



3aq

63 mg, 76% yield; Colorless oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.41 (s, 1H), 8.29 (d, *J* = 9.4 Hz, 1H), 8.04–8.02 (m, 2H), 7.56–7.53 (m, 1H), 7.51-7.47 (m, 2H), 7.24-7.22 (m, 2H), 4.79–4.70 (m, *J* = 6.3 Hz, 2H), 1.38 (d, *J* = 6.2 Hz, 6H), 1.26 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 141.1 (d, $J_{C\text{-}P}$ = 8.3 Hz), 134.3, 132.2, 129.33 (d, $J_{C\text{-}P}$ = 1.2 Hz), 129.31, 128.9, 127.5, 126.2 (d, $J_{C\text{-}P}$ = 2.0 Hz), 124.6, 122.0 (d, $J_{C\text{-}P}$ = 3.5 Hz), 75.1 (d, $J_{C\text{-}P}$ = 6.4 Hz), 23.7 (d, $J_{C\text{-}P}$ = 4.9 Hz), 23.6 (d, $J_{C\text{-}P}$ = 5.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.20; HRMS (ESI) m/z calcd for $[C_{19}H_{24}ClNO_5P]^+$ $[M+H]^+$: 412.1075, found 412.1056.

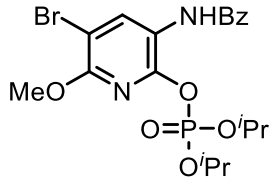
44. 2-benzamido-7-phenoxynaphthalen-1-yl diisopropyl phosphate (3ar)



3ar

79 mg, 76% yield; White solid, m.p. = 120-122 °C; R_f = 0.3 (PE:EtOAc = 5:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.35 (s, 1H), 8.22 (d, *J* = 9.0 Hz, 1H), 8.18–8.16 (m, 2H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.57–7.49 (m, 3H), 7.44 (d, *J* = 2.4 Hz, 1H), 7.41–7.37 (m, 2H), 7.26 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.17 (tt, *J* = 7.3, 1.2 Hz, 1H), 7.13–7.10 (m, 2H), 4.62-4.53 (m, 2H), 1.27 (d, *J* = 6.2 Hz, 6H), 1.03 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.8, 156.8, 156.3, 135.1 (d, $J_{C\text{-}P}$ = 9.4 Hz), 134.4, 132.0, 130.0, 129.9, 128.8, 128.6 (d, $J_{C\text{-}P}$ = 3.0 Hz) 128.4, 128.2 (d, $J_{C\text{-}P}$ = 3.7 Hz), 127.8, 125.4 (d, $J_{C\text{-}P}$ = 2.2 Hz), 123.9, 122.1 (d, $J_{C\text{-}P}$ = 2.0 Hz), 119.9, 119.6, 108.0, 75.0 (d, $J_{C\text{-}P}$ = 6.8 Hz), 23.7 (d, $J_{C\text{-}P}$ = 4.7 Hz), 23.4 (d, $J_{C\text{-}P}$ = 5.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -5.23; HRMS (ESI) m/z calcd for $[C_{29}H_{31}NO_6P]^+$ $[M+H]^+$: 520.1884, found 520.1881.

45. 3-benzamido-5-bromo-6-methoxypyridin-2-yl diisopropyl phosphate (3as)

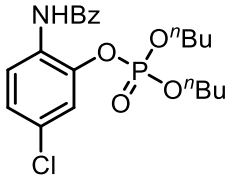


3as

81 mg, 83% yield; Light yellow solid, m.p. = 127-129 °C; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.22 (s, 1H), 8.82 (s, 1H), 8.00-7.98 (m, 2H), 7.58–7.54 (m, 1H), 7.49 (tt, *J* = 7.0, 1.4 Hz, 2H), 4.89-4.80 (m, 2H), 3.98 (s, 3H), 1.39 (d, *J* = 6.2 Hz, 6H), 1.33 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 154.9, 144.3 (d, $J_{C\text{-}P}$ = 7.3 Hz), 138.8, 133.8, 132.3, 128.9, 127.4, 119.0 (d, $J_{C\text{-}P}$ = 4.9 Hz), 102.3 (d, $J_{C\text{-}P}$ = 1.8 Hz), 74.9 (d, $J_{C\text{-}P}$ = 6.4 Hz), 55.0, 23.8 (d, $J_{C\text{-}P}$ = 5.1 Hz), 23.6 (d, $J_{C\text{-}P}$ = 5.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -8.17; HRMS

(ESI) m/z calcd for $[C_{19}H_{25}BrN_2O_6P]^+$ $[M+H]^+$: 487.0628, found 487.0628.

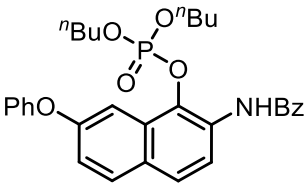
46. 2-benzamido-5-chlorophenyl dibutyl phosphate (3at)



3at

55 mg, 63% yield; White solid, m.p. = 49-51 °C; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.33 (s, 1H), 8.30–8.28 (m, 1H), 8.03–8.00 (m, 2H), 7.57–7.53 (m, 1H), 7.49 (tt, *J* = 7.1, 1.7 Hz, 2H), 7.25–7.23 (m, 2H), 4.21–4.10 (m, 4H), 1.67-1.62 (m, 4H), 1.39-1.32 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 141.0 (d, J_{C-P} = 8.2 Hz), 134.3, 132.2, 129.5 (d, J_{C-P} = 1.8 Hz), 129.2 (d, J_{C-P} = 4.0 Hz), 128.9, 127.5, 126.3 (d, J_{C-P} = 1.8 Hz), 124.7, 121.8 (d, J_{C-P} = 3.2 Hz), 69.5 (d, J_{C-P} = 6.4 Hz), 32.3 (d, J_{C-P} = 6.4 Hz), 18.7, 13.6; ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.50; HRMS (ESI) m/z calcd for $[C_{21}H_{28}ClNO_5P]^+$ $[M+H]^+$: 440.1388, found 440.1392.

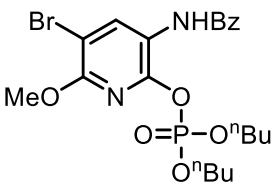
47. 2-benzamido-7-phenoxynaphthalen-1-yl dibutyl phosphate (3au)



3au

53 mg, 48% yield; Light red oil; R_f = 0.5 (PE:EtOAc = 5:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.27 (s, 1H), 8.20 (d, *J* = 8.9 Hz, 1H), 8.16–8.14 (m, 2H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.57–7.49 (m, 3H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.40–7.37 (m, 2H), 7.25 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.16 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.11-7.09 (m, 2H), 4.08-3.90 (m, 4H), 1.54–1.43 (m, 4H), 1.29–1.17 (m, 4H), 0.80 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.8, 156.8, 156.4, 135.1 (d, J_{C-P} = 9.4 Hz), 134.4, 132.0, 130.0, 128.8, 128.5, 128.1 (d, J_{C-P} = 3.5 Hz), 127.8, 125.6 (d, J_{C-P} = 2.2 Hz), 124.0, 122.2 (d, J_{C-P} = 2.1 Hz), 119.8, 119.6, 107.9, 69.4 (d, J_{C-P} = 6.8 Hz), 32.2 (d, J_{C-P} = 6.7 Hz), 18.6, 13.5; ^{31}P NMR (202 MHz, $CDCl_3$) δ -3.37; HRMS (ESI) m/z calcd for $[C_{31}H_{35}NO_6P]^+$ $[M+H]^+$: 548.2197, found 548.2177.

48. 3-benzamido-5-bromo-6-methoxypyridin-2-yl dibutyl phosphate (3av)

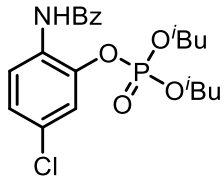


3av

54 mg, 52% yield; Light red solid, m.p. = 81-83 °C; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.10 (s, 1H), 8.80 (s, 1H), 7.98–7.96 (m, 2H), 7.57–7.53 (m, 1H), 7.50–7.46 (m, 2H), 4.29–4.17 (m, 4H), 3.96 (s, 3H), 1.70–1.64 (m, 4H), 1.42-1.32 (m, 4H), 0.89 (t, *J* = 7.4 Hz,

6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 154.9, 144.2 (d, J_{C-P} = 7.2 Hz), 138.9, 133.8, 132.3, 128.9, 127.4, 118.8 (d, J_{C-P} = 5.0 Hz), 102.4 (d, J_{C-P} = 1.7 Hz), 69.3 (d, J_{C-P} = 6.4 Hz), 55.0, 32.2 (d, J_{C-P} = 6.8 Hz), 18.7, 13.5; ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.28; HRMS (ESI) m/z calcd for $[C_{21}H_{29}BrN_2O_6P]^+$ $[M+H]^+$: 515.0941, found 515.0938.

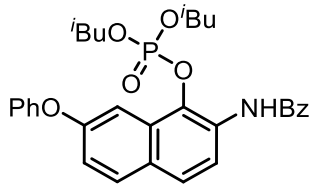
49. 2-benzamido-5-chlorophenyl diisobutyl phosphate (3aw)



3aw

76 mg, 86% yield; Colorless oil; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.32 (s, 1H), 8.29 (d, *J* = 9.3 Hz, 1H), 8.03-8.00 (m, 2H), 7.57–7.53 (m, 1H), 7.51–7.47 (m, 2H), 7.25–7.23 (m, 2H), 3.97–3.87 (m, 4H), 2.00-1.89 (m, 2H), 0.92 (d, *J* = 1.6 Hz, 6H), 0.90 (d, *J* = 1.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 141.0 (d, J_{C-P} = 8.1 Hz), 134.3, 132.2, 129.5 (d, J_{C-P} = 1.8 Hz), 129.2 (d, J_{C-P} = 4.3 Hz), 128.9, 127.5, 126.3 (d, J_{C-P} = 1.8 Hz), 124.7, 121.8 (d, J_{C-P} = 3.2 Hz), 75.5 (d, J_{C-P} = 6.8 Hz), 29.2 (d, J_{C-P} = 6.8 Hz), 18.6 (d, J_{C-P} = 1.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.52; HRMS (ESI) m/z calcd for $[C_{21}H_{28}ClNO_5P]^+$ $[M+H]^+$: 440.1388, found 440.1354.

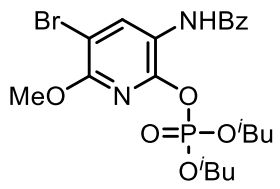
50. 2-benzamido-7-phenoxynaphthalen-1-yl diisobutyl phosphate (3ax)



3ax

64 mg, 58% yield; Light yellow oil; R_f = 0.5 (PE:EtOAc = 5:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.29 (s, 1H), 8.20 (d, *J* = 9.0 Hz, 1H), 8.18–8.15 (m, 2H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.57–7.50 (m, 4H), 7.40–7.36 (m, 2H), 7.25 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.17-7.14 (m, 1H), 7.11–7.08 (m, 2H), 3.87-3.70 (m, 4H), 1.85-1.77 (m, 2H), 0.80 (d, *J* = 2.7 Hz, 6H), 0.78 (d, *J* = 2.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.8, 156.9, 156.3, 135.2 (d, J_{C-P} = 9.6 Hz), 134.4, 132.0, 130.0, 128.8, 128.51, 128.48, 128.1 (d, J_{C-P} = 3.8 Hz), 127.8, 125.5 (d, J_{C-P} = 2.1 Hz), 123.9, 122.3 (d, J_{C-P} = 2.1 Hz), 119.7, 119.6, 108.0, 75.4 (d, J_{C-P} = 6.9 Hz), 29.1 (d, J_{C-P} = 7.0 Hz), 18.5; ^{31}P NMR (202 MHz, $CDCl_3$) δ -3.32; HRMS (ESI) m/z calcd for $[C_{31}H_{35}NO_6P]^+$ $[M+H]^+$: 548.2197, found 548.2190.

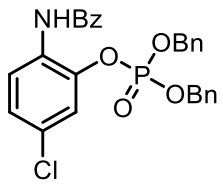
51. 3-benzamido-5-bromo-6-methoxypyridin-2-yl diisobutyl phosphate (3ay)



3ay

86 mg, 83% yield; White solid, m.p. = 70-71 ºC; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.09 (s, 1H), 8.81 (s, 1H), 7.99–7.96 (m, 2H), 7.58–7.54 (m, 1H), 7.51–7.47 (m, 2H), 4.06–3.94 (m, 4H), 3.97 (s, 3H), 2.03-1.92 (m, 2H), 0.92 (d, J = 6.7 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 154.9, 144.2 (d, $J_{C\text{-}P}$ = 7.2 Hz), 138.9, 133.8, 132.4, 128.9, 127.4, 118.9 (d, $J_{C\text{-}P}$ = 5.0 Hz), 102.4 (d, $J_{C\text{-}P}$ = 1.7 Hz), 75.3 (d, $J_{C\text{-}P}$ = 6.8 Hz), 55.0, 29.2 (d, $J_{C\text{-}P}$ = 7.1 Hz), 18.6; ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.30; HRMS (ESI) m/z calcd for $[C_{21}H_{29}BrN_2O_6P]^+$ $[M+H]^+$: 515.0941, found 515.0935.

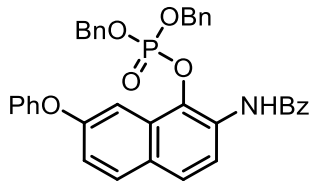
52. 2-benzamido-5-chlorophenyl dibenzyl phosphate (3az)



3az

54 mg, 53% yield; Light yellow solid, m.p. = 120-122 ºC; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.08 (s, 1H), 8.26 (d, J = 8.8 Hz, 1H), 7.94–7.92 (m, 2H), 7.55–7.52 (m, 1H), 7.46-7.43 (m, 2H), 7.32–7.25 (m, 10H), 7.19 (ddd, J = 8.8, 2.4, 1.1 Hz, 1H), 7.10 (dd, J = 2.4, 1.4 Hz, 1H), 5.12 (s, 2H), 5.11 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 140.6 (d, $J_{C\text{-}P}$ = 8.0 Hz), 134.8 (d, $J_{C\text{-}P}$ = 6.0 Hz), 134.3, 132.2, 129.4 (d, $J_{C\text{-}P}$ = 2.0 Hz), 129.2, 129.1 (d, $J_{C\text{-}P}$ = 4.3 Hz), 128.90, 128.89, 128.4, 127.5, 126.4 (d, $J_{C\text{-}P}$ = 1.9 Hz), 124.4, 121.8 (d, $J_{C\text{-}P}$ = 3.1 Hz), 71.2 (d, $J_{C\text{-}P}$ = 6.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -4.53; HRMS (ESI) m/z calcd for $[C_{27}H_{24}ClNO_5P]^+$ $[M+H]^+$: 508.1075, found 508.1069.

53. 2-benzamido-7-phenoxynaphthalen-1-yl dibenzyl phosphate (3aaa)

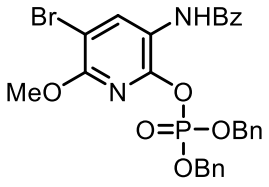


3aaa

72 mg, 58% yield; Light yellow oil; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.17 (s, 1H), 8.22 (d, J = 8.9 Hz, 1H), 8.15–8.13 (m, 2H), 7.81 (d, J = 9.0 Hz, 1H), 7.73 (d, J = 8.9 Hz, 1H), 7.57–7.54 (m, 1H), 7.52-7.49 (m, 2H), 7.41 (d, J = 2.4 Hz, 1H), 7.30–7.22 (m, 9H), 7.11–7.09 (m, 4H), 7.07–7.04 (m, 1H), 6.99–6.97 (m, 2H), 5.00 (dd, J = 11.5, 8.1 Hz, 2H), 4.89 (dd, J = 11.5, 8.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.8, 156.6, 156.5, 134.8 (d, $J_{C\text{-}P}$ = 7.2 Hz), 134.7, 134.4, 132.0, 130.0, 129.0, 128.8, 128.7, 128.4, 128.3 (d, $J_{C\text{-}P}$ = 3.1 Hz) 128.2, 127.8, 125.7 (d, $J_{C\text{-}P}$ = 2.2 Hz), 124.0, 122.0 (d, $J_{C\text{-}P}$ = 2.1 Hz), 119.9, 119.5, 107.6, 71.1 (d, $J_{C\text{-}P}$ = 6.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ -3.75; HRMS

(ESI) m/z calcd for $[C_{37}H_{31}NO_6P]^+$ $[M+H]^+$: 616.1884, found 616.1897.

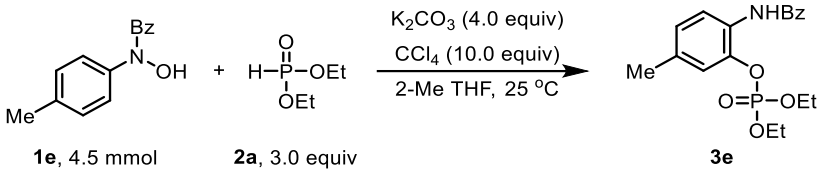
54. 3-benzamido-5-bromo-6-methoxypyridin-2-yl dibenzyl phosphate (3aab)



3aab

82 mg, 70% yield; Light red solid, m.p. = 93-95 °C; R_f = 0.3 (PE:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.78 (s, 1H), 7.91–7.89 (m, 2H), 7.58–7.54 (m, 1H), 7.48-7.45 (m, 2H), 7.32-7.28 (m, 10H), 5.23 (s, 2H), 5.21 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 154.7, 143.7 (d, $J_{C\text{-}P}$ = 7.4 Hz), 138.4, 135.0 (d, $J_{C\text{-}P}$ = 6.6 Hz), 133.8, 132.3, 129.04, 128.95, 128.8, 128.1, 127.4, 118.6 (d, $J_{C\text{-}P}$ = 5.4 Hz), 102.5 (d, $J_{C\text{-}P}$ = 1.7 Hz), 70.9 (d, $J_{C\text{-}P}$ = 6.0 Hz), 55.0; ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.40; HRMS (ESI) m/z calcd for $[C_{27}H_{25}BrN_2O_6P]^+$ $[M+H]^+$: 583.0628, found 583.0614.

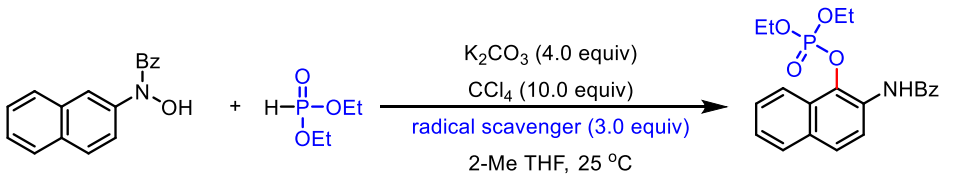
Experimental procedure for gram scale reaction



1e, 4.5 mmol **2a**, 3.0 equiv **3e**

The system of a mixture of **1e** (1.02 g, 4.5 mmol, 1.0 equiv), **2a** (1.74 mL, 13.5 mmol, 3.0 equiv), K_2CO_3 (2.50 g, 18.0 mmol, 4.0 equiv) and CCl_4 (4.5 mL, 45 mmol, 10.0 equiv) in 2-Me THF (45 mL) was stirred at 40℃ for 18 h. After the completion of the reaction was detected by TLC, the mixture was evaporated under reduced pressure and purified by column chromatography to give the desired product **3e** (1.02 g, 62%).

Control experiment with radical scavenger

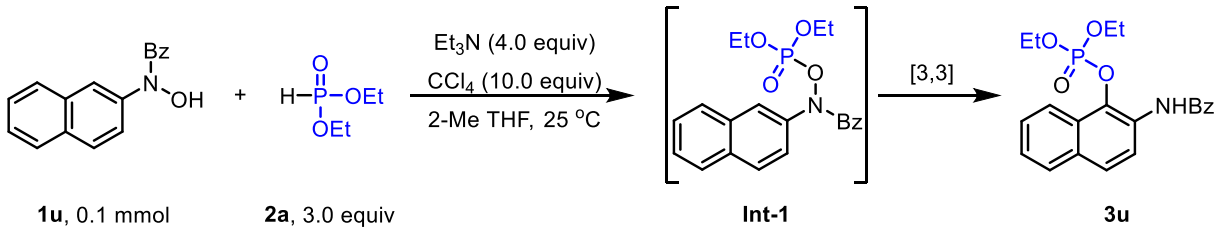


1u **2a** **3u**, 69%, Phloroglucinol
75%, TEMPO
76%, BHT

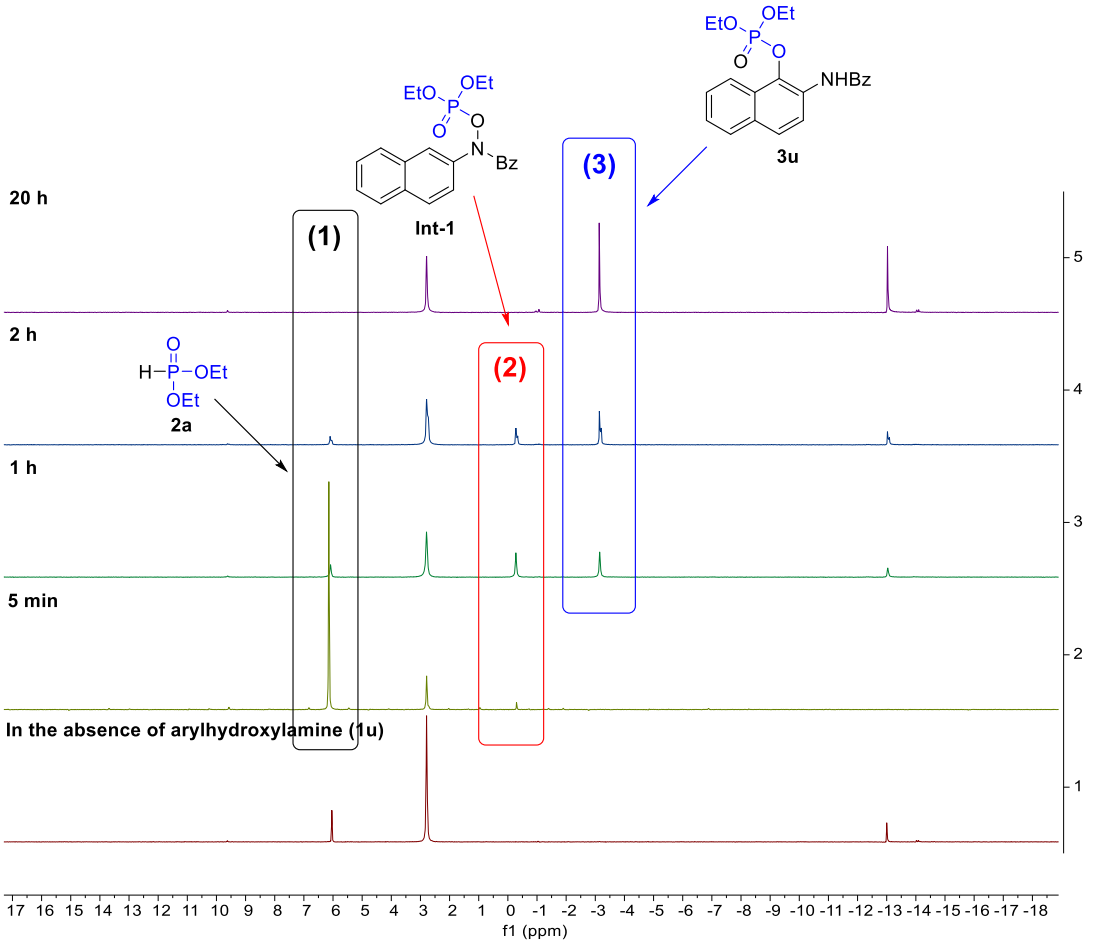
TEMPO = 2,2,6,6-Tetramethylpiperidinooxy; BHT = 2,6-di-*tert*-butyl-4-methylphenol

To a solution of **1u** (53 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (111mg, 0.8 mmol, 4.0 equiv), radical scavenger (0.6 mmol, 3.0 equiv), CCl_4 (0.2 mL, 2 mmol, 10.0 equiv) in 2-Me THF (2 mL), **2a** (77 μL, 0.6 mmol, 3.0 equiv) was added. The reaction mixture was stirred at room temperature for 10 h. Then the reaction mixture was evaporated under reduced pressure and purified by column chromatography to give the desired product.

Reaction of 1u with diethyl phosphite 2a monitored by ^{31}P NMR



1u, 0.1 mmol **2a**, 3.0 equiv **Int-1** **3u**



Procedure:

To a solution of **1u** (26 mg, 0.1 mmol, 1.0 equiv), Et_3N (56 μL, 0.4 mmol, 4.0 equiv) and CCl_4 (0.1 mL, 1 mmol, 10.0 equiv) in 2-Me THF (1 mL), **2a** (39 μL, 0.3 mmol, 3.0 equiv) was added at room temperature. The reaction process was monitored by ^{31}P NMR at room temperature.

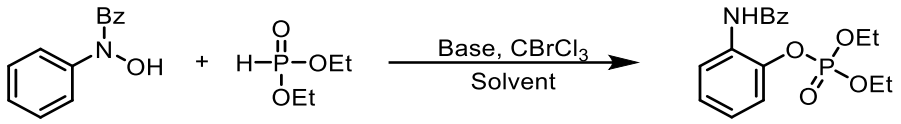
Result:

(1) The phosphorus spectrum signal at 6.1 ppm represents the starting material (**2a**). With the progress of the reaction, diethyl phosphite (**2a**) was gradually consumed with decreasing signal.

(2) The phosphorus spectrum signal at -0.2 ppm was getting stronger in the beginning of the reaction and getting weaker until disappeared at the end of the reaction. We speculate that this signal around -0.2 ppm might be the *O*-phosphorylated intermediate (**Int-1**).

(3) The phosphorus spectrum signal at -3.1 ppm represents the final product 2-benzamidonaphthalen-1-yl diethyl phosphate (**3u**). With the progress of the reaction, the *ortho*-phosphated arylamine (**3u**) was gradually produced with increasing signal.

Optimization of the reaction with $CBrCl_3$ instead of CCl_4[13]

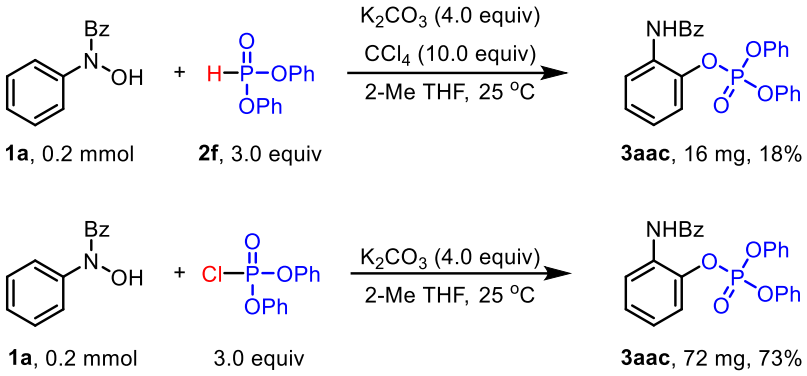


1a **2a** **3a**

entry[a]	**2a** (equiv)	base	$CBrCl_3$	solvent	**3a** yield[b]
1	3.0	K_2CO_3 (4.0)	1.5	2-Me THF	10%.
2	3.0	K_2CO_3 (4.0)	3.0	2-Me THF	11%
3	3.0	K_2CO_3 (4.0)	5.0	2-Me THF	10%
4	3.0	K_2CO_3 (1.5)	1.5	2-Me THF	10%
5	3.0	K_2CO_3 (2.0)	1.5	2-Me THF	11%
6	3.0	K_2CO_3 (3.0)	1.5	2-Me THF	9%
7	1.5	K_2CO_3	1.5	2-Me THF	9%
8	2.0	K_2CO_3	1.5	2-Me THF	10%
9	4.0	K_2CO_3	1.5	2-Me THF	9%
10	2.0	K_2CO_3	1.5	THF	19%
11	2.0	K_2CO_3	1.5	CH_2Cl_2	60%
12	2.0	K_2CO_3	1.5	Toluene	49%
13	2.0	K_2CO_3	1.5	$CHCl_3$	67%
14	2.0	K_2CO_3	1.5	CH_3CN	57%
15	2.0	K_2CO_3	1.5	Et_2O	53%
16	2.0	K_2CO_3	1.5	EtOAc	66%
17	2.0	K_2CO_3	1.5	Acetone	49%
18	2.0	^{t}BuOK	1.5	$CHCl_3$	42%
19	2.0	DIPEA	1.5	$CHCl_3$	52%
20	2.0	DMAP	1.5	$CHCl_3$	52%
21	2.0	NaH	1.5	$CHCl_3$	50%
22	2.0	KOH	1.5	$CHCl_3$	64%
23	**2.0**	**Et_3N**	**1.5**	**$CHCl_3$**	**67%**

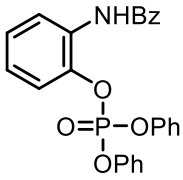
[a]Unless otherwise noted, all reactions were carried out under the following conditions: **1a** (43 mg, 0.2 mmol, 1.0 equiv), **2a** (53 μL, 0.4 mmol, 2.0 equiv), base (0.4 mmol, 2.0 equiv), $CBrCl_3$ (30 μL, 0.3 mmol, 1.5 equiv) in $CHCl_3$ (2 mL), 10 hours. [b]Yields of isolated products. Bz = benzoyl; DMAP = 4-(Dimethylamino)pyridine; DIPEA = *N,N*-diisopropylethylamine; THF = Tetrahydrofuran.

Control experiment with (P(O)-Cl instead of P(O)-H and CCl_4)



NOTE: We tried the reaction of **1a** with slightly excess of $(PhO)_2P(O)$-Cl in the presence of base. To our delight, the corresponding product could be successfully isolated in reasonable yield. Since $(RO)_2P(O)$-Cl compounds are toxic, less commercially available and much more expensive than the corresponding $(RO)_2P(O)$-H compounds, we think the current protocol using $(RO)_2P(O)$-H compounds may be more practical and useful.

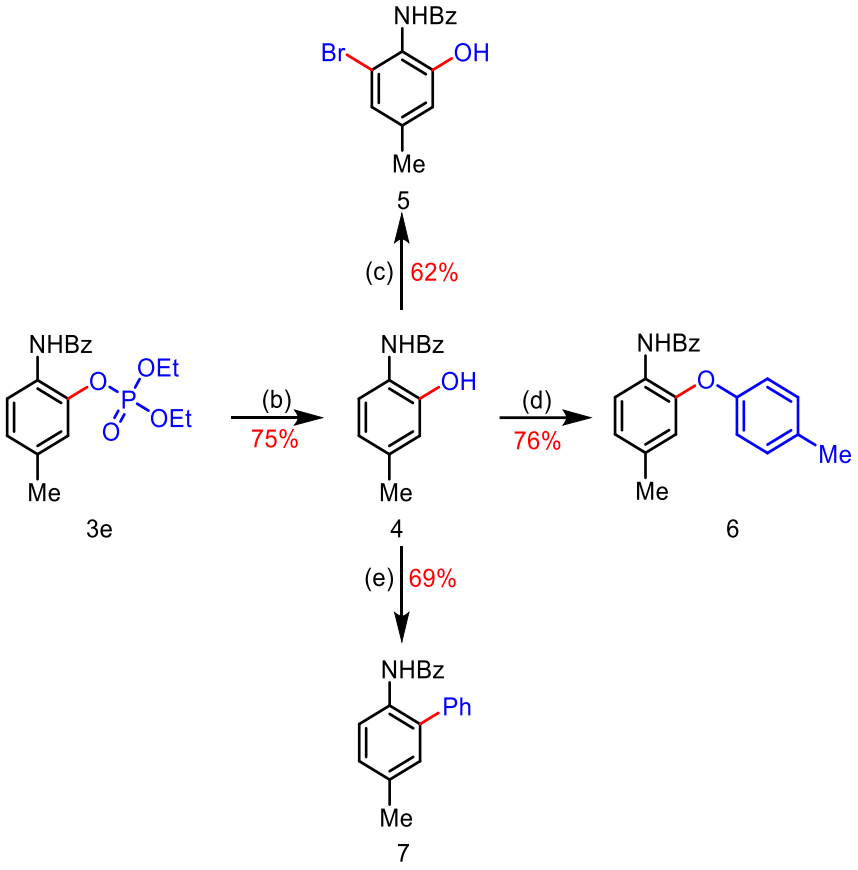
2-benzamidophenyl diphenyl phosphate (3aac)



3aac

72 mg, 73% yield; Colorless oil; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.02 (s, 1H), 7.94–7.92 (m, 2H), 7.67 (dd, J = 5.6, 3.7 Hz, 1H), 7.61–7.57 (m, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.45–7.42 (m, 1H), 7.35–7.30 (m, 6H), 7.23–7.20 (m, 6H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 165.2, 149.8 (d, $J_{C\text{-}P}$ = 7.6 Hz), 144.0 (d, $J_{C\text{-}P}$ = 6.7 Hz), 133.9, 131.7, 130.1, 129.3 (d, $J_{C\text{-}P}$ = 6.7 Hz), 128.4, 127.8, 127.6, 126.9, 125.9, 125.8, 120.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 119.8 (d, $J_{C\text{-}P}$ = 4.8 Hz); ^{31}P NMR (202 MHz, DMSO-d_6) δ -17.32; HRMS (ESI) m/z calcd for $[C_{25}H_{21}NO_5P]^+$ $[M+H]^+$: 446.1152, found 446.1169.

Synthetic applications



(b) LDA, THF, -55 ºC to r. t; (c) NBS, DMF, -10 ºC to r. t.; (d) 4-tolylboronic acid, $Cu(OAc)_2$, Et_3N, 4 Å MS, CH_2Cl_2, r. t.; (e) (i) Tf_2O, Et_3N, $CHCl_3$, 0 ºC to r. t.; (ii) phenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, 70 ºC.

(b) General Procedure for the Synthesis of 4.[14]

To a solutuon of **3e** (73 mg, 0.20 mmol, 1.0 equiv) in THF (3 mL), LDA (0.5 mL, 1.00 mmol, 5.0 equiv) was added dropwise at -55 ºC. After being stirred at -55 ºC for 30 min, the reaction mixture was warmed to room temperature and stirred for further 12h. Then it was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, evaporated in *vacuo*, and purified by column chromatography on silica using EtOAc/petroleum ether (*V*∶*V*＝1∶7) to give product **4** (34 mg, 75%).

(c) General Procedure for the Synthesis of 5.[15]

To a solutuon of **4** (23 mg, 0.10 mmol, 1.0 equiv) in dry DMF (1 mL), *N*-bromosuccinimide (20 mg, 0.11 mmol, 1.1 equiv) was added at -10 ºC. The reaction mixture was warmed to room temperature and stirred for further 12h. Water (10mL) was added to the reaction system, and the

mixture was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4, evaporated in *vacuo*, and purified by column chromatography on silica using EtOAc/petroleum ether (*V*：*V*＝1：7) to give product **5** (19 mg, 62%).

(d) General Procedure for the Synthesis of 6.[16]

To a mixture of $Cu(OTf)_2$ (36 mg, 0.10 mmol, 1.0 equiv), 4 Å MS (50 mg), **4** (23 mg, 0.10 mmol, 1.0 equiv) and 4-tolylboronic acid (27 mg, 0.20 mmol, 2.0 equiv) in CH_2Cl_2 (2 mL), Et_3N (69 μL, 0.50 mmol, 5.0 equiv) was added. The system was stirred at room temperature for 12 h under air. The resulting mixture was filtered on celite, evaporated under reduced pressure. The crude residue was purified by flash column chromatography using EtOAc/petroleum ether (*V*：*V*＝1：7) to give product **6** (24 mg, 76%).

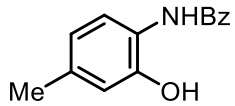
(e) General Procedure for the Synthesis of 7.[3, 17]

To a mixture of **4** (23 mg, 0.10 mmol, 1.0 equiv) and Et_3N (28 μL,0.20 mmol, 2.0 equiv) in $CHCl_3$ (1.5 mL), Tf_2O (34 μL, 0.20 mmol, 2.0 equiv) was added dropwise at 0 °C under N_2. The system was stirred at room temperature for 12 h. The resulting mixture was evaporated under reduced pressure and purified by flash column chromatography using EtOAc/petroleum ether (*V*：*V*＝1：7) to give triflate product (31 mg, 86%).

Add the triflate product (36 mg, 0.10 mmol, 1.0 equiv), phenylboronic acid (18 mg, 0.15 mmol, 1.5 equiv), $Pd(PPh_3)_4$ (3 mg, 0.0025 mmol, 2.5 mol%), and K_2CO_3 (55 mg, 0.40 mmol, 4.0 equiv) to a microwave vial. It was sealed, evacuated and backfilled with nitrogen 3 times. Then, 1.5 mL of THF and 0.3 mL of H_2O were added. The mixture was stirred and heated at 70 °C in an oil bath for 12 h. The reaction was determined to be complete by TLC. After the reaction was cooled to room temperature, the resulting mixture was evaporated under reduced pressure and purified by flash column chromatography using EtOAc/petroleum ether (*V*：*V*＝1：7) to give product **7** (23 mg, 80%).

Analytical data of synthetic application products

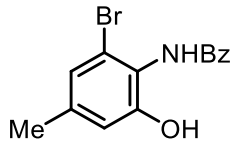
1. *N*-(2-hydroxy-4-methylphenyl)benzamide (4)[18]



4

34 mg, 75% yield; White solid, m.p. = 124-126 ºC; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.60 (s, 1H), 9.51 (s, 1H), 7.98–7.96 (m, 2H), 7.60–7.57 (m, 1H), 7.54–7.50 (m, 3H), 6.75 (d, *J* = 1.8 Hz, 1H), 6.65 (dd, *J* = 8.2, 1.9 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 165.2, 149.2, 135.1, 134.4, 131.5, 128.4, 127.4, 124.0, 123.3, 119.6, 116.7, 20.7; HRMS (ESI) m/z calcd for $[C_{14}H_{14}NO_2]^+$ $[M+H]^+$: 228.1019, found 228.1010.

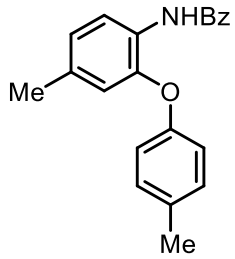
2. *N*-(2-bromo-6-hydroxy-4-methylphenyl)benzamide (5)



5

19 mg, 62% yield; White solid, m.p. = 220-222 ºC; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.00 (s, 1H), 9.50 (s, 1H), 7.97–7.95 (m, 2H), 7.91 (s, 1H), 7.61–7.58 (m, 1H), 7.54–7.51 (m, 2H), 6.90 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 165.2, 148.7, 134.1, 134.0, 131.7, 128.5, 127.5, 126.7, 125.2, 117.9, 111.9, 22.0; HRMS (ESI) m/z calcd for $[C_{14}H_{13}BrNO_2]^+$ $[M+H]^+$: 306.0124, found 306.0119.

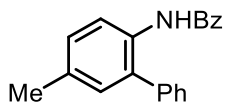
3. *N*-(4-methyl-2-(*p*-tolyloxy)phenyl)benzamide (6)



6

24 mg, 76% yield; White solid, m.p. = 110-112 ºC; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (d, *J* = 8.3 Hz, 1H), 8.46 (s, 1H), 7.83–7.80 (m, 2H), 7.53–7.50 (m, 1H), 7.46–7.43 (m, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.98–6.95 (m, 3H), 6.69 (d, *J* = 1.5 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.3, 154.4, 146.4, 135.3, 134.4, 133.7, 131.8, 130.6, 128.9, 127.4, 127.2, 124.5, 120.8, 118.8, 118.2, 21.2, 20.8; HRMS (ESI) m/z calcd for $[C_{21}H_{20}NO_2]^+$ $[M+H]^+$: 318.1489, found 318.1491.

4. *N*-(5-methyl-[1,1'-biphenyl]-2-yl)benzamide (7)[19]



7

69% yield (two steps); White solid, m.p. = 122-124 ºC; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.3 Hz, 1H), 7.92 (s, 1H), 7.61–7.60 (m, 2H), 7.52–7.42 (m, 6H), 7.38 (tt, *J* = 7.9, 1.6 Hz, 2H), 7.25 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.13 (d, *J* = 2.1 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ

165.1, 138.4, 135.1, 134.2, 132.7, 132.5, 131.7, 130.7, 129.5, 129.3, 129.2, 128.8, 128.2, 126.9, 121.5, 21.0; HRMS (ESI) m/z calcd for $[C_{20}H_{18}NO]^+$ $[M+H]^+$: 288.1383, found 288.1389.

References

(1) Amal Joseph, P. J.; Priyadarshini, S.; Lakshmi Kantam, M.; Maheswaran, H., Copper catalyzed ipso-nitration of iodoarenes, bromoarenes and heterocyclic haloarenes under ligand-free conditions. *Tetrahedron Lett.* **2012,** *53*, 1511-1513.

(2) Akula, H. K.; Lakshman, M. K., Synthesis of deuterated 1,2,3-Triazoles. *J. Org. Chem.* **2012,** *77*, 8896-8904.

(3) Bodunov, V. A.; Galenko, E. E.; Sakharov, P. A.; Novikov, M. S.; Khlebnikov, A. F., Selective Cu-Catalyzed Intramolecular Annulation of 3-Aryl/Heteryl-2-(diazoacetyl)-1*H*-pyrroles: Synthesis of Benzo/Furo/Thieno [*e*]-Fused 1*H*-Indol-7-oles and Their Transformations. *J. Org. Chem.* **2019,** *84*, 10388-10401.

(4) Feng, P.; Lee, K. N.; Lee, J. W.; Zhan, C.; Ngai, M.-Y., Access to a new class of synthetic building blocks via trifluoromethoxylation of pyridines and pyrimidines. *Chem. Sci.* **2016,** *7*, 424-429.

(5) Yuan, H.; Guo, L.; Liu, F.; Miao, Z.; Feng, L.; Gao, H., Copper-Catalyzed Tandem *O*-Vinylation of Arylhydroxylamines/3,3-Rearrangement/Cyclization: Synthesis of Highly Substituted Indoles and Benzoindoles. *ACS Catal.* **2019,** *9*, 3906-3912.

(6) Fang, W. Y.; Zha, G. F.; Zhao, C.; Qin, H. L., Regioselective installation of fluorosulfate (-OSO_2F) functionality into aromatic C(sp^2)-H bonds for the construction of para-amino-arylfluorosulfates. *Chem Commun (Camb)* **2019,** *55*, 6273-6276.

(7) Chuang, H. Y.; Schupp, M.; Meyrelles, R.; Maryasin, B.; Maulide, N., Redox-Neutral Selenium-Catalysed Isomerisation of para-Hydroxamic Acids into para-Aminophenols. *Angew. Chem. Int. Ed. Engl.* **2021,** *60*, 13778-13782.

(8) Guo, L.; Liu, F.; Wang, L.; Yuan, H.; Feng, L.; Kurti, L.; Gao, H., Cascade Approach to Highly Functionalized Biaryls by a Nucleophilic Aromatic Substitution with Arylhydroxylamines. *Org. Lett.* **2019,** *21*, 2894-2898.

(9) Zhang, Z.; Luo, J.; Gao, H., Rapid Access to Fluorinated Anilides via DAST-Mediated

Deoxyfluorination of Arylhydroxylamines. *Org. Lett.* **2021,** *23*, 9332-9336.

(10) Du, Y.; Xi, Z.; Guo, L.; Lu, H.; Feng, L.; Gao, H., Practical bromination of arylhydroxylamines with $SOBr_2$ towards ortho-bromo-anilides. *Tetrahedron Lett.* **2021,** *72,* 153074.

(11) Guo, L.; Liu, F.; Wang, L.; Yuan, H.; Feng, L.; Lu, H.; Gao, H., Transition-metal-free aerobic C-O bond formation via C-N bond cleavage. *Org. Chem. Front.* **2020,** *7*, 1077-1081.

(12) Wang, M.; Liu, X.; Wang, L.; Lu, H.; Gao, H., Cooperative Gold/Zinc-catalyzed Cascade Approach to Tryptophan Derivatives from N-arylhydroxylamines and Alkynes. *Asian J. Org. Chem.* **2022,** *11*, e202200054.

(13) Le Corre, S. S.; Berchel, M.; Couthon-Gourvès, H.; Haelters, J.-P.; Jaffrès, P.-A., Atherton–Todd reaction: mechanism, scope and applications. *Beilstein J. Org. Chem.* **2014,** *10*, 1166-1196.

(14) Xie, L.; Ding, Y.; Wang, Y.; Ding, Y., Synthetic Strategy *o*-Hydroxyphenyl(ethynyl)phosphinates. *Chin. J. Chem* . **2009,** *27*, 1387-1390.

(15) Polley, A.; Varalaxmi, K.; Nandi, A.; Jana, R., Divergent Total Synthesis of (±)-Mahanine and Other Carbazole Alkaloids. *Asian J. Org. Chem.* **2021,** *10*, 1207-1215.

(16) Wang, M.; Liu, Y.; Wang, L.; Lu, H.; Feng, L.; Gao, H., Cascade Chan-Lam C−O Coupling/[3,3]-Rearrangement of Arylhydroxylamines with Arylboronic Acids Toward NOBIN Analogues. *Adv. Synth. Catal.* **2021,** *363*, 1733-1738.

(17) Li, F.; Basile, V. M.; Rose, M. J., Electron Transfer through Surface-Grown, Ferrocene-Capped Oligophenylene Molecular Wires (5-50 Å) on n-Si(111) Photoelectrodes. *Langmuir* **2015,** *31*, 7712-7716.

(18) Yang, D.; Fu, H., A simple and practical copper-catalyzed approach to substituted phenols from aryl halides by using water as the solvent. *Chem. Eur. J.* **2010,** *16*, 2366-2370.

(19) Jiang, J.; Zhang, W.-M.; Dai, J.-J.; Xu, J.; Xu, H.-J., Visible-Light-Promoted C–H Arylation by Merging Palladium Catalysis with Organic Photoredox Catalysis. *J. Org. Chem.* **2017,** *82*, 3622-3630.

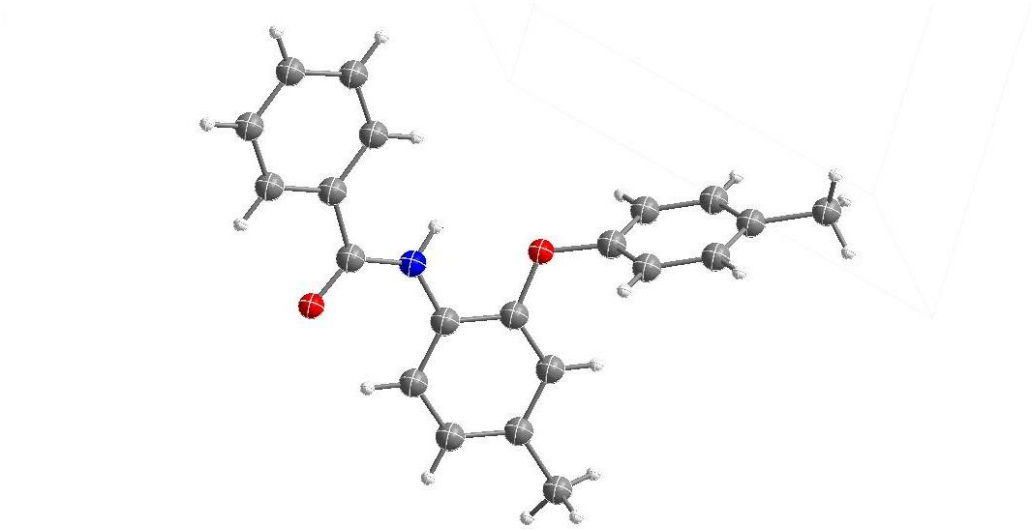
X-ray crystal structure data

Suitable crystal of compound **6** were obtained by slowly evaporating a mixture of CH_2Cl_2 and hexane solution at ambient temperature. Single crystal was chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) to prevent decomposition. Intensity data and cell parameters were recorded at 173 K on a Bruker Apex II single crystal diffractometer, employing a Mo K_α radiation (λ = 0.71073 Å) and a CCD area detector. The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[1] The structure was solved using the charge-flipping algorithm, as implemented in the program *SUPERFLIP*[2] and refined by full-matrix least-squares techniques against F_o^2 using the SHELXL program[3] through the OLEX2 interface.[4] Hydrogen atoms at carbon were placed in calculated positions and refined isotropically by using a riding model. Appropriate restraints or constraints were applied to the geometry and the atomic displacement parameters of the atoms in the cluster. All structures were examined using the Addsym subroutine of PLATON[5] to ensure that no additional symmetry could be applied to the models. **CCDC 2181778 (6)** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

References

1. *APEX3*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA, **2015**.
2. Palatinus, L.; Chapuis, G., SUPERFLIP – a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *J. Appl. Crystallogr.* **2007**, *40*, 786-790.
3. .Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta. Crystallogr. Sect. C.* **2015**, *71*, 3-8.
4. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339-341.
5. Spek, A. L., Structure validation in chemical crystallography. *Acta. Crystallogr. Sect. D.* **2009**, *65*, 148-155.

Crystal data and structure refinement for 6 (Thermal ellipsoids at the 30% probability level)



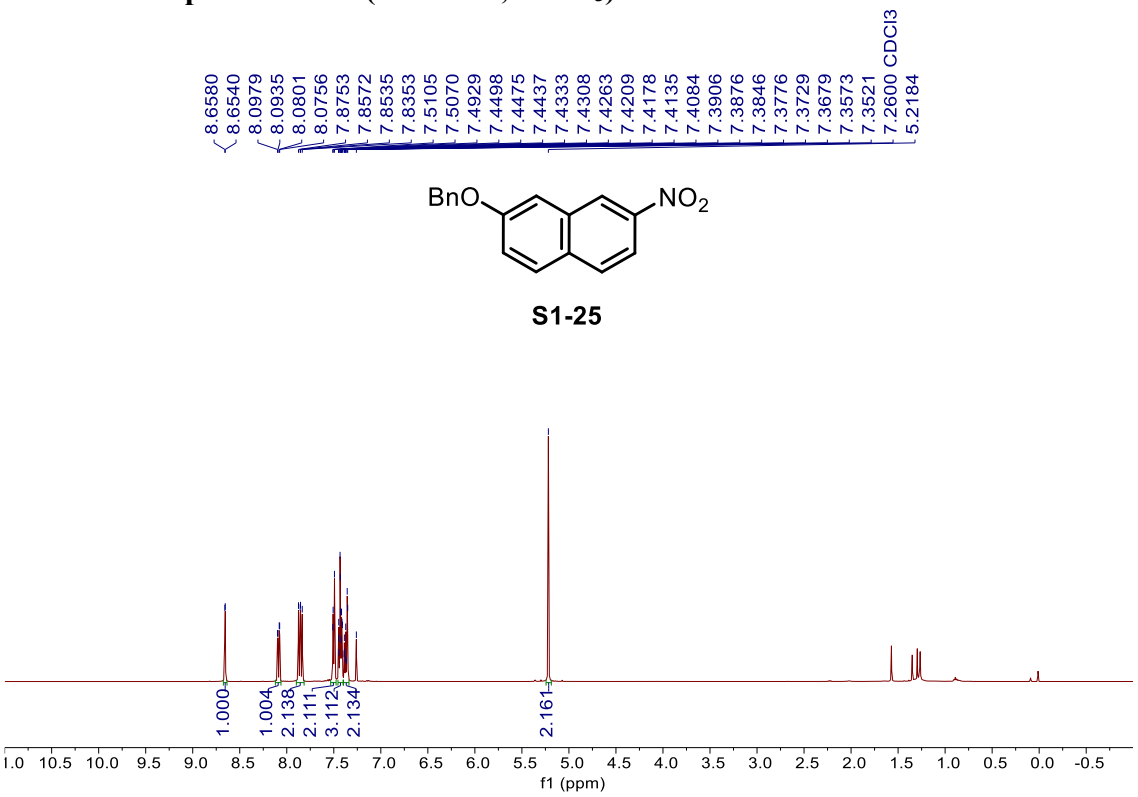
CCDC: 2181778

Identification code	**6**
Empirical formula	$C_{21}H_{19}NO_2$
Formula weight	317.37
Temperature/K	293.0
Crystal system	triclinic
Space group	P-1
a/Å	9.238(3)
b/Å	9.252(3)
c/Å	11.277(3)
α/°	71.838(17)
β/°	71.309(16)
γ/°	85.794(19)
Volume/Å^3	867.2(5)
Z	2
ρ_{calc}mg/mm^3	1.215

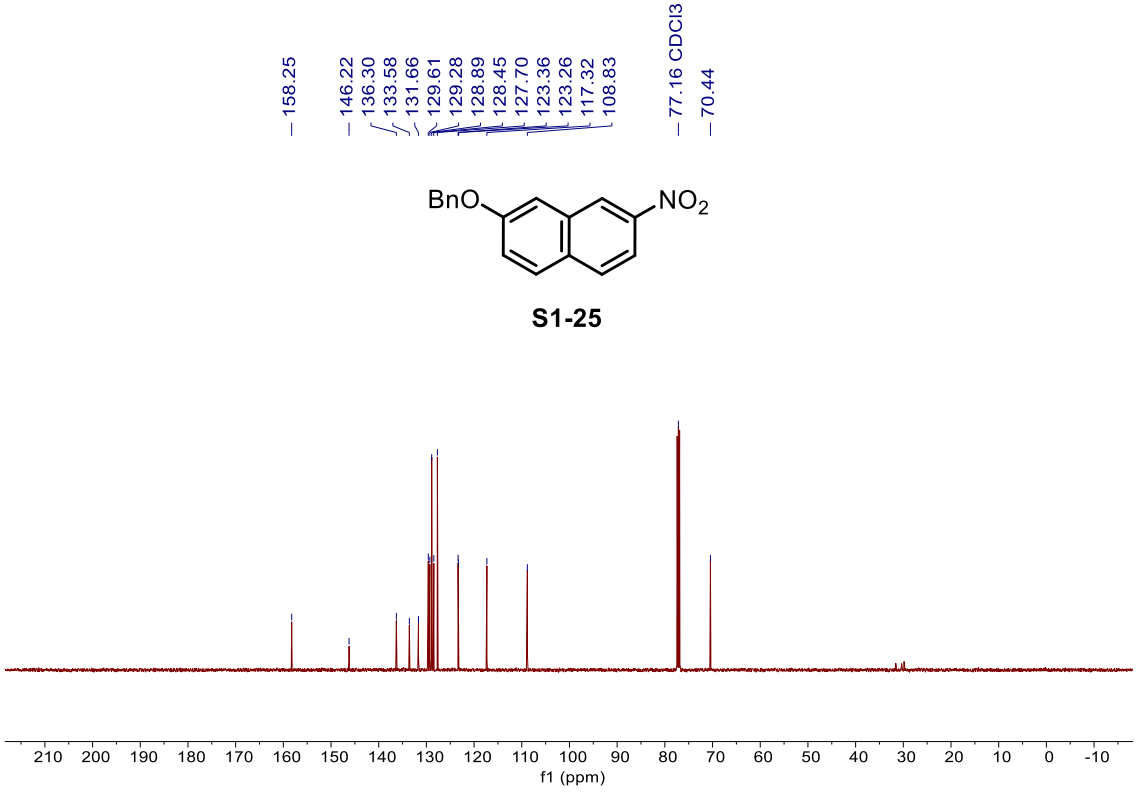
μ/mm^{-1}	0.618
F(000)	336.0
Crystal size/mm^3	0.04 × 0.02 × 0.01
2Θ range for data collection	8.692 to 133.152 °
Index ranges	$-10 \leq h \leq 10$, $-10 \leq k \leq 11$, $-13 \leq l \leq 13$
Reflections collected	6799
Independent reflections	3009[R(int) = 0.0449]
Data/restraints/parameters	3009/0/220
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0597, wR_2 = 0.1715
Final R indexes [all data]	R_1 = 0.0805, wR_2 = 0.1929
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.21

NMR spectra

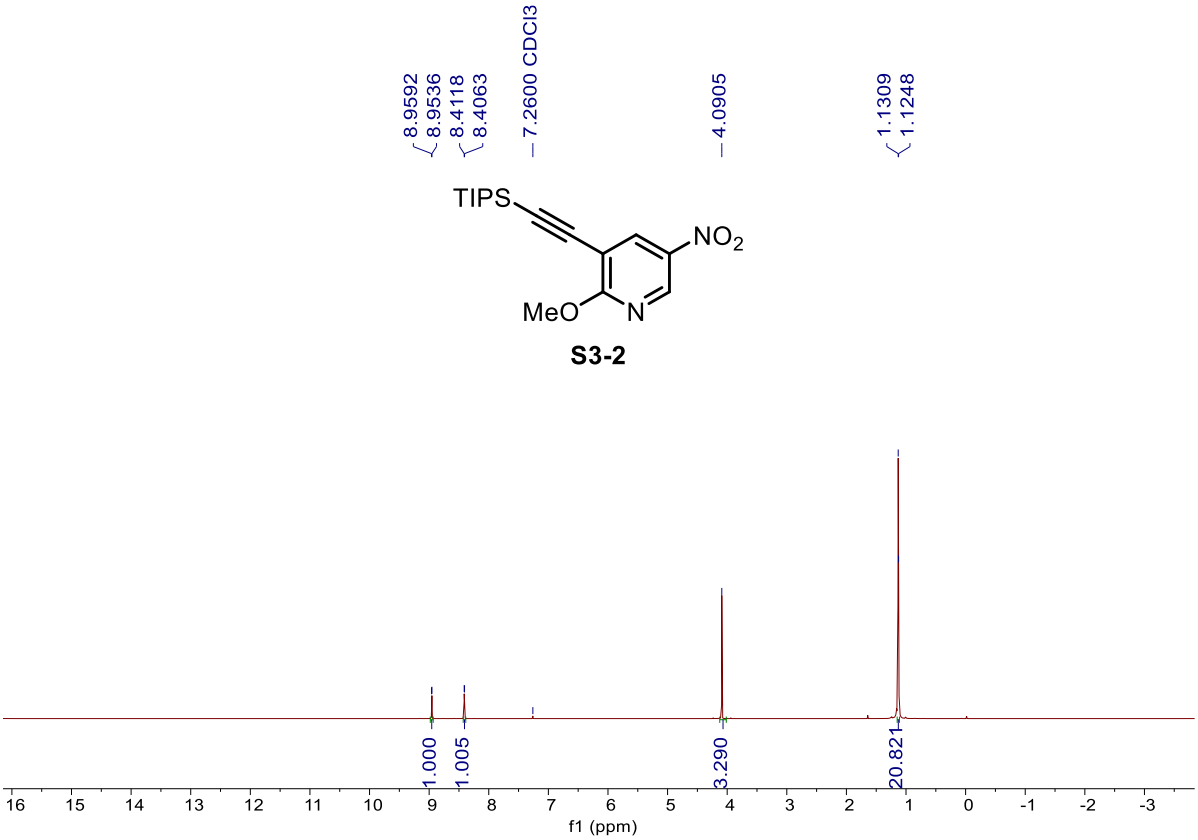
^{1}H NMR of Compound S1-25 (500 MHz, $CDCl_3$)



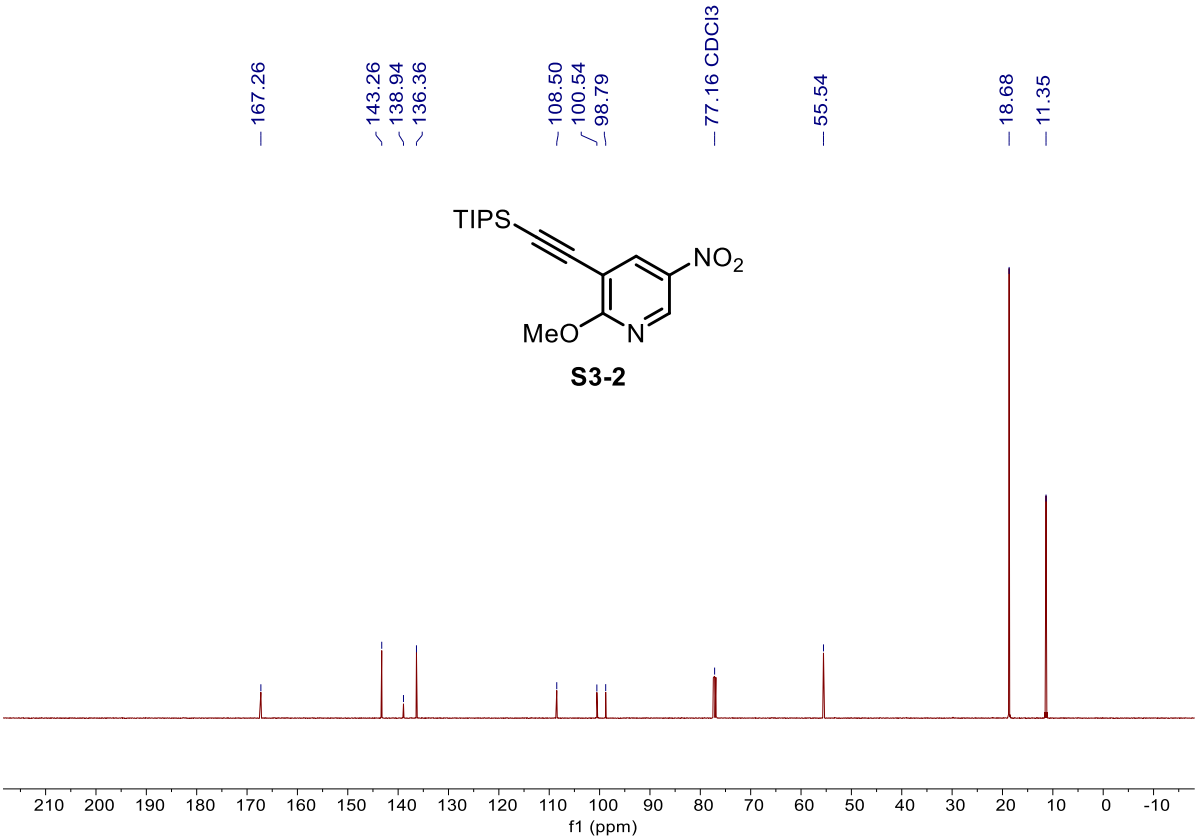
^{13}C NMR of Compound S1-25 (126 MHz, $CDCl_3$)



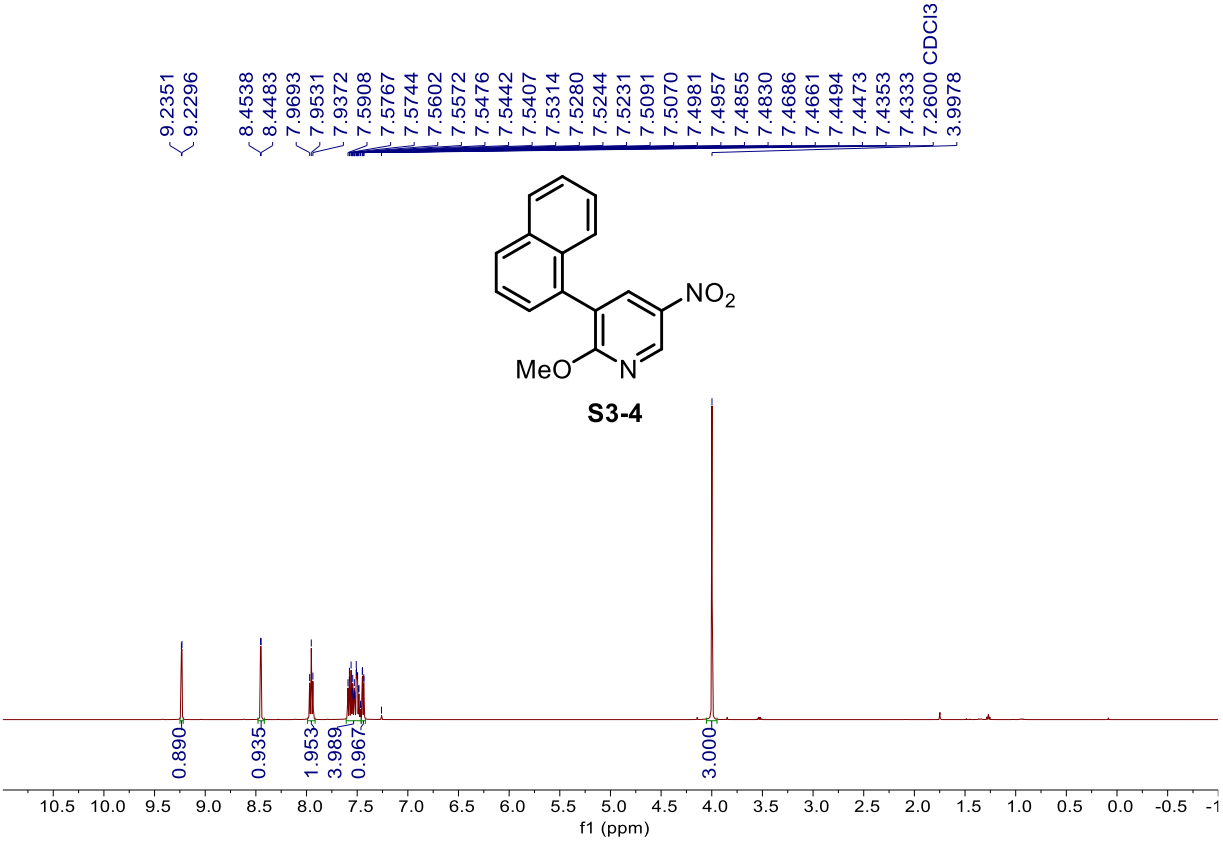
^{1}H NMR of Compound S3-2 (500 MHz, $CDCl_3$)



^{13}C NMR of Compound S3-2 (126 MHz, $CDCl_3$)

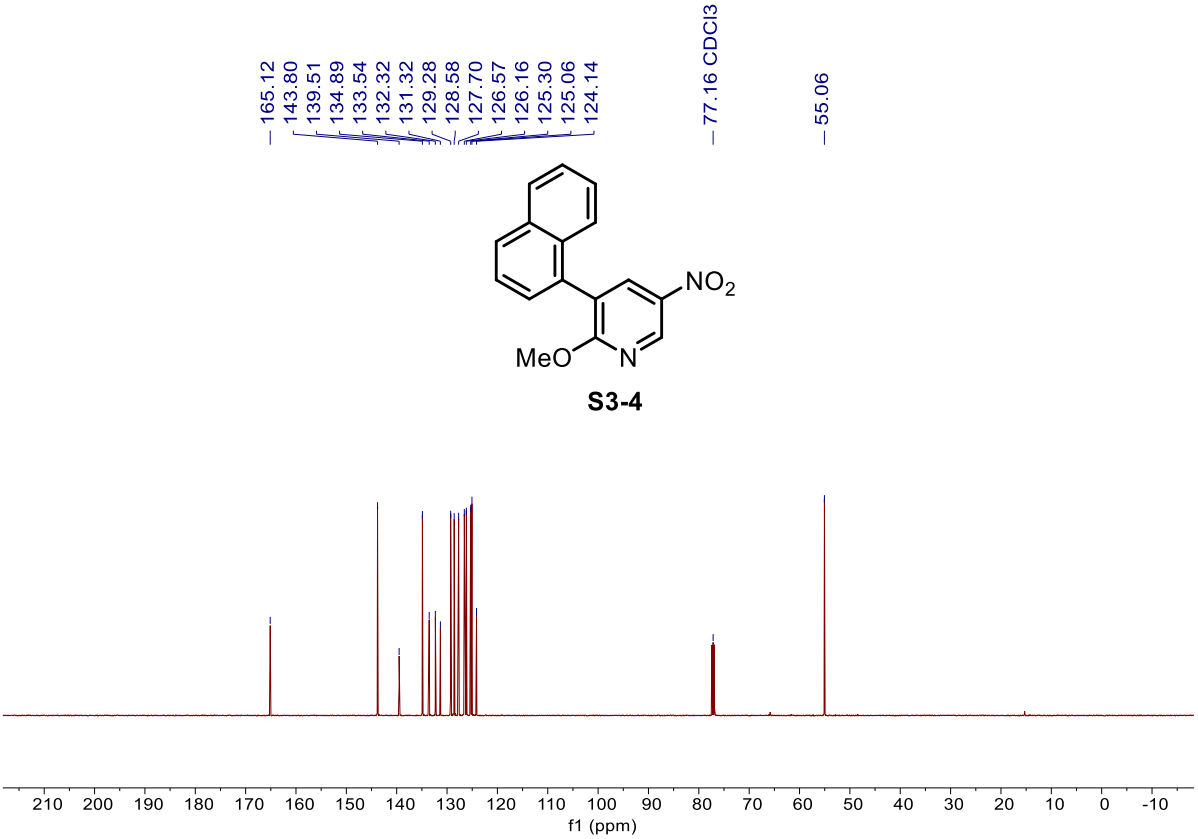


^{1}H NMR of Compound S3-4 (500 MHz, $CDCl_3$)



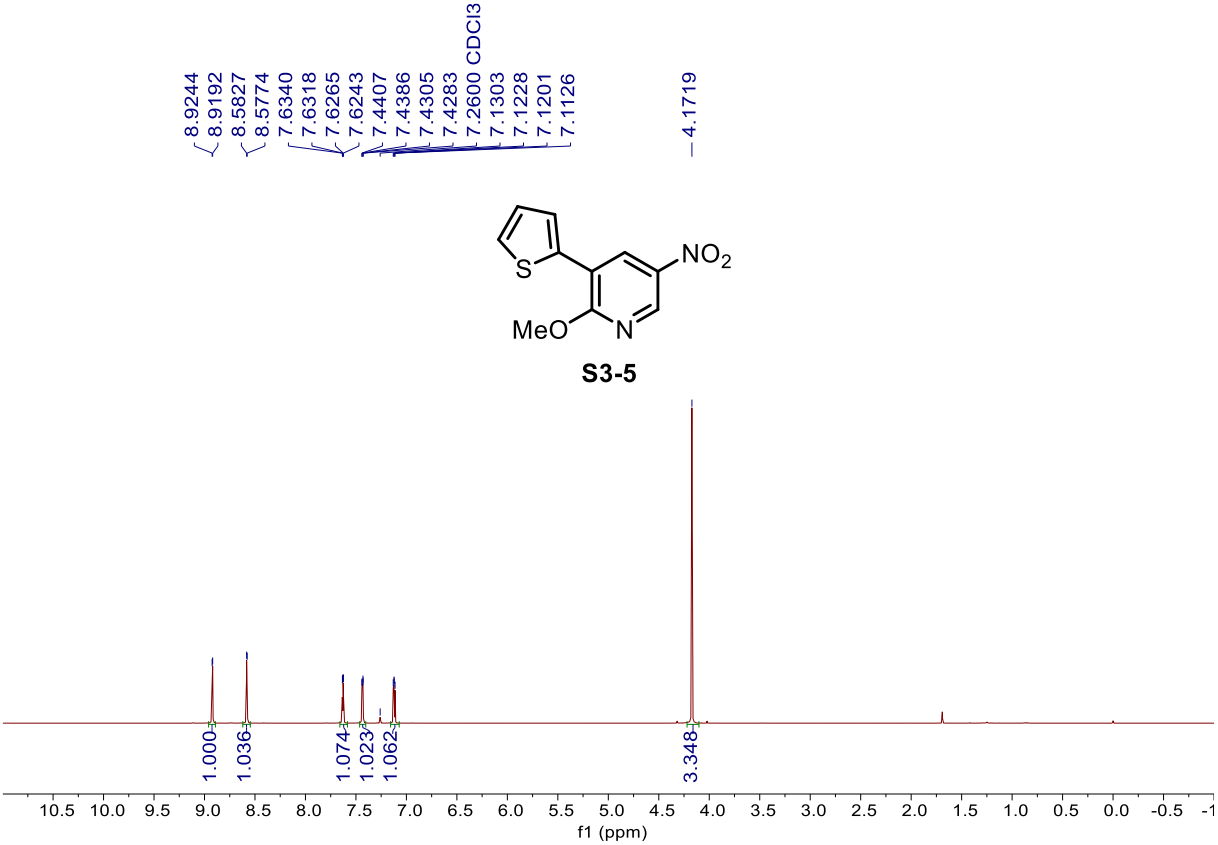
S3-4

^{13}C NMR of Compound S3-4 (126 MHz, $CDCl_3$)

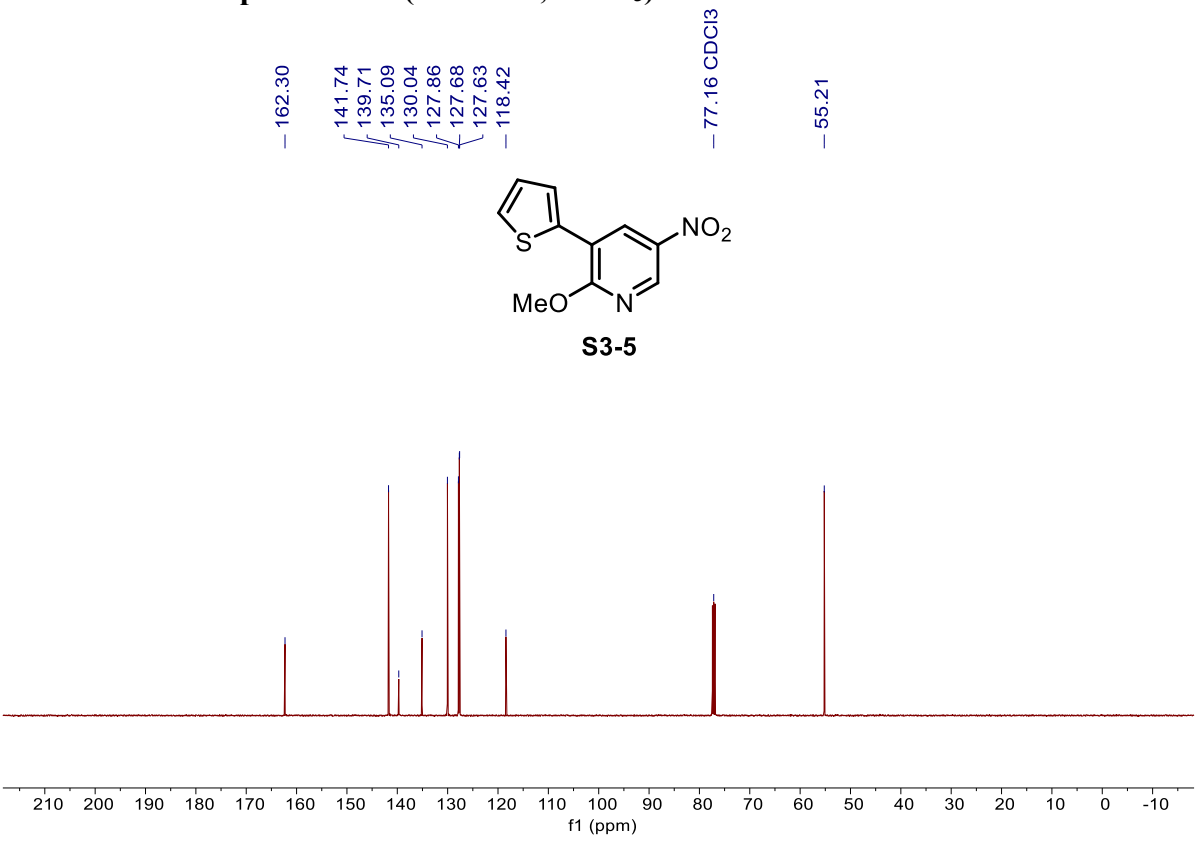


S3-4

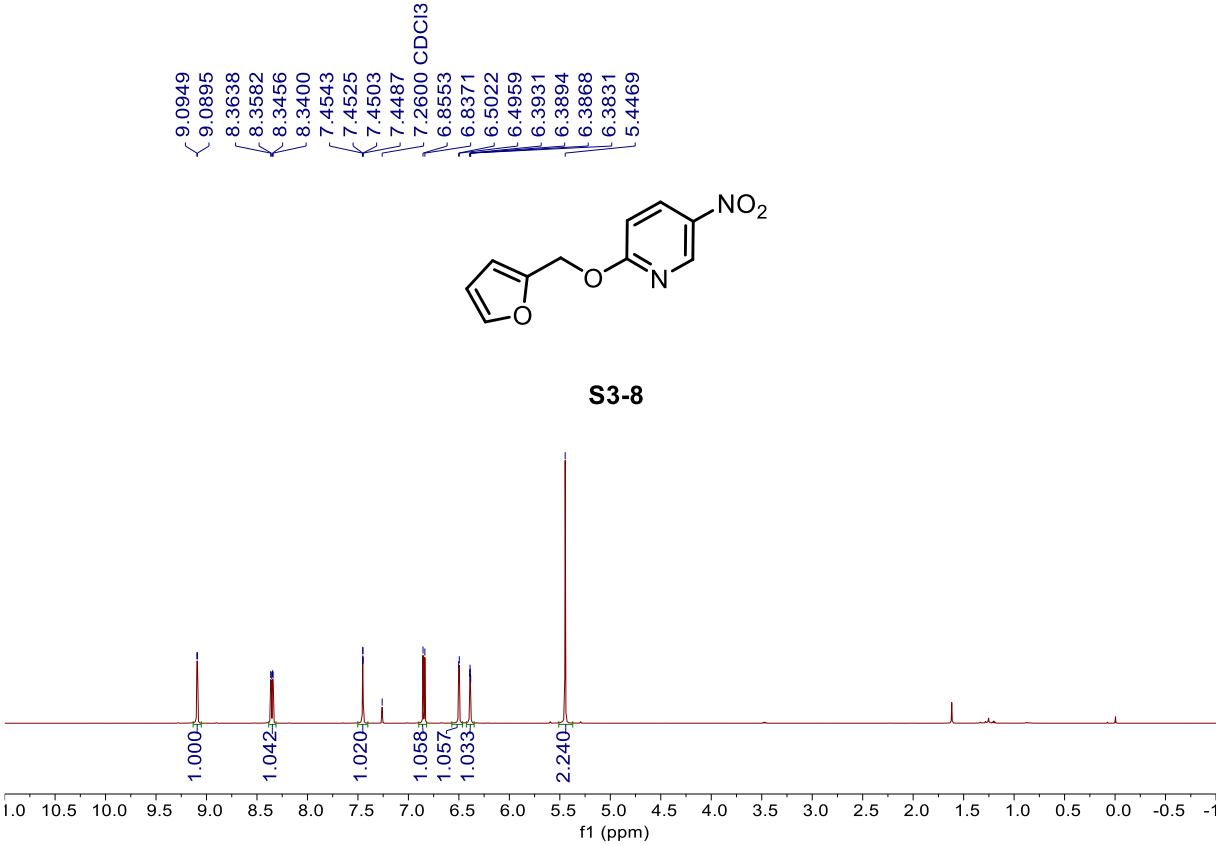
^{1}H NMR of Compound S3-5 (500 MHz, $CDCl_3$)



^{13}C NMR of Compound S3-5 (126 MHz, $CDCl_3$)

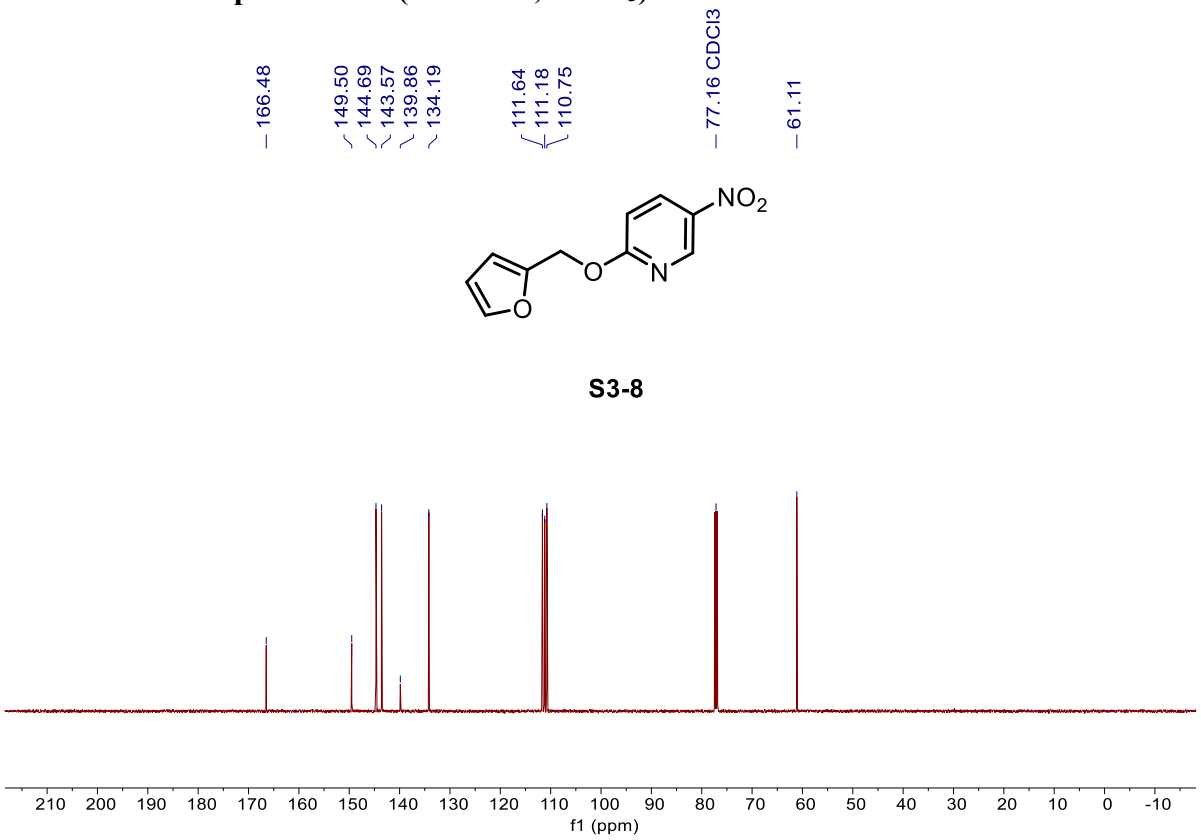


^{1}H NMR of Compound S3-8 (500 MHz, $CDCl_3$)



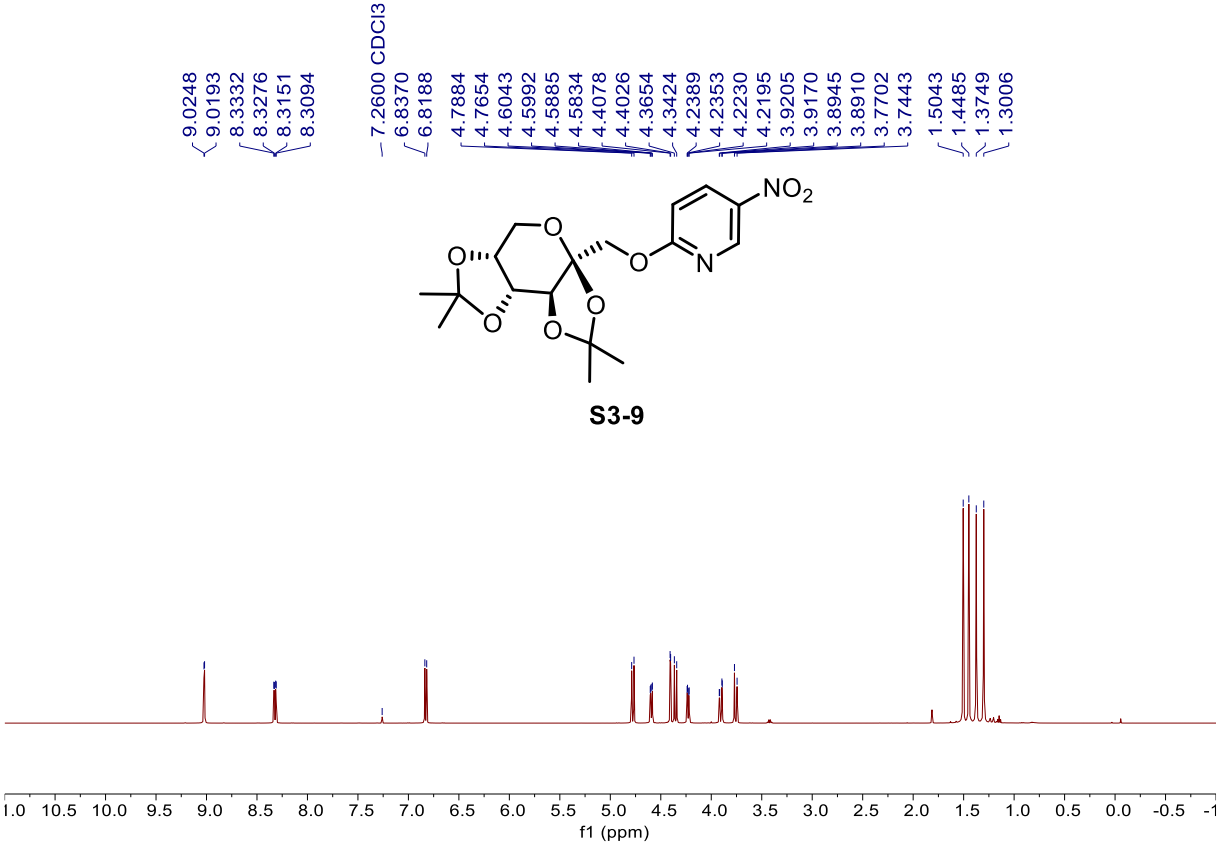
S3-8

^{13}CNMR of Compound S3-8 (126 MHz, $CDCl_3$)

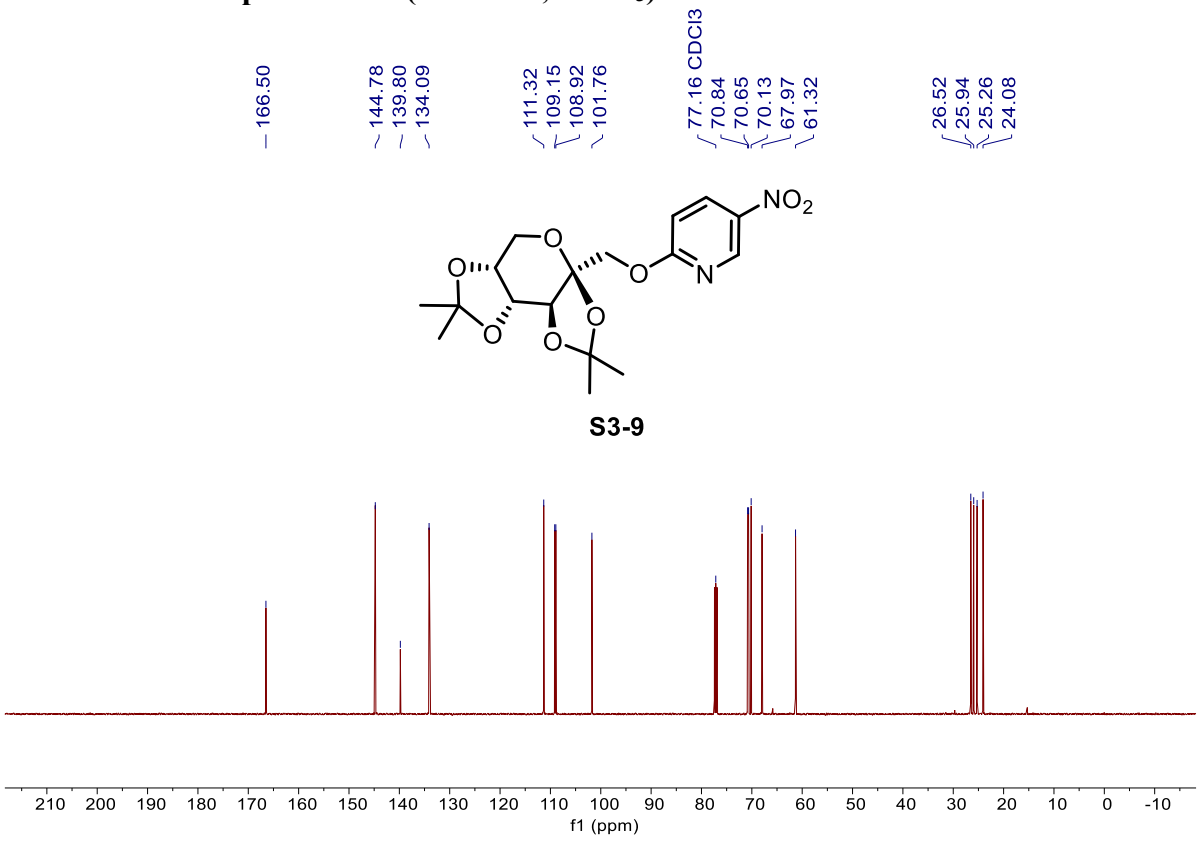


S3-8

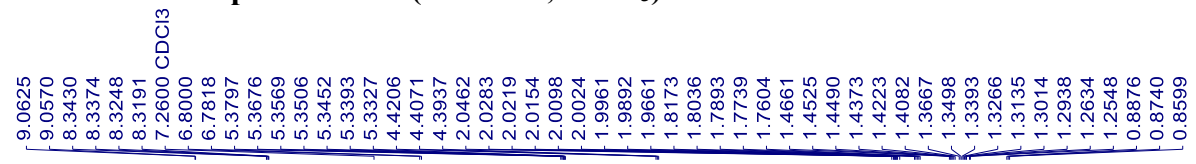
^{1}H NMR of Compound S3-9 (500 MHz, $CDCl_3$)

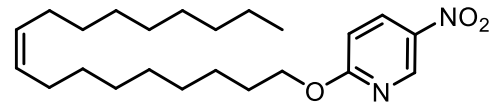


^{13}C NMR of Compound S3-9 (126 MHz, $CDCl_3$)

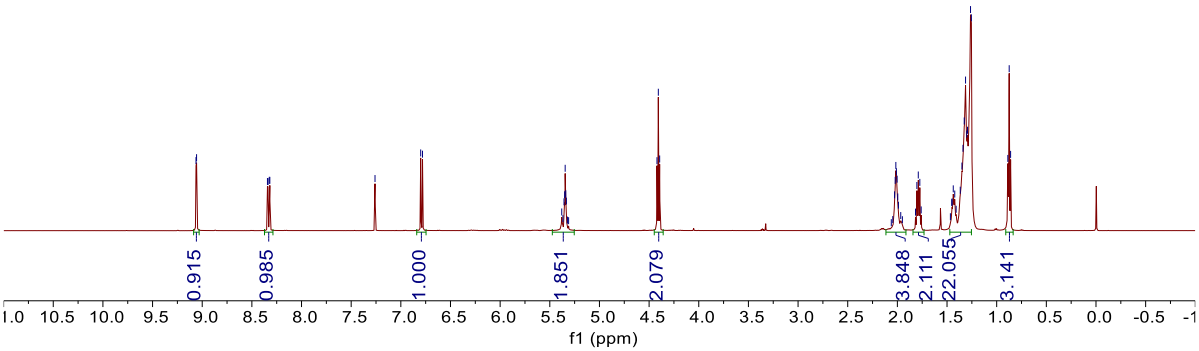


^{1}H NMR of Compound S3-10 (500 MHz, $CDCl_3$)

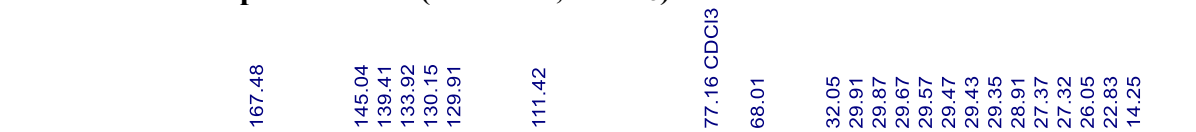


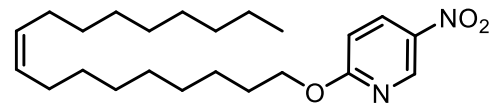


S3-10

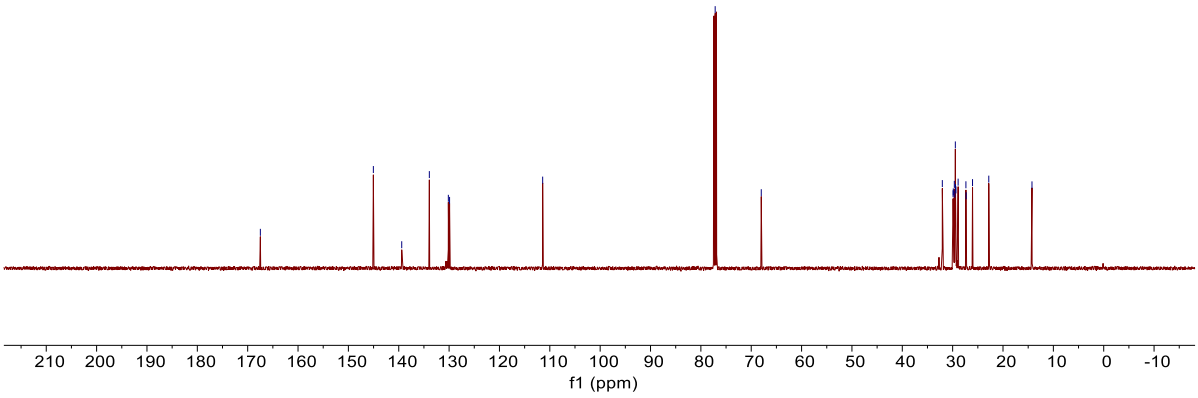


^{13}C NMR of Compound S3-10 (126 MHz, $CDCl_3$)

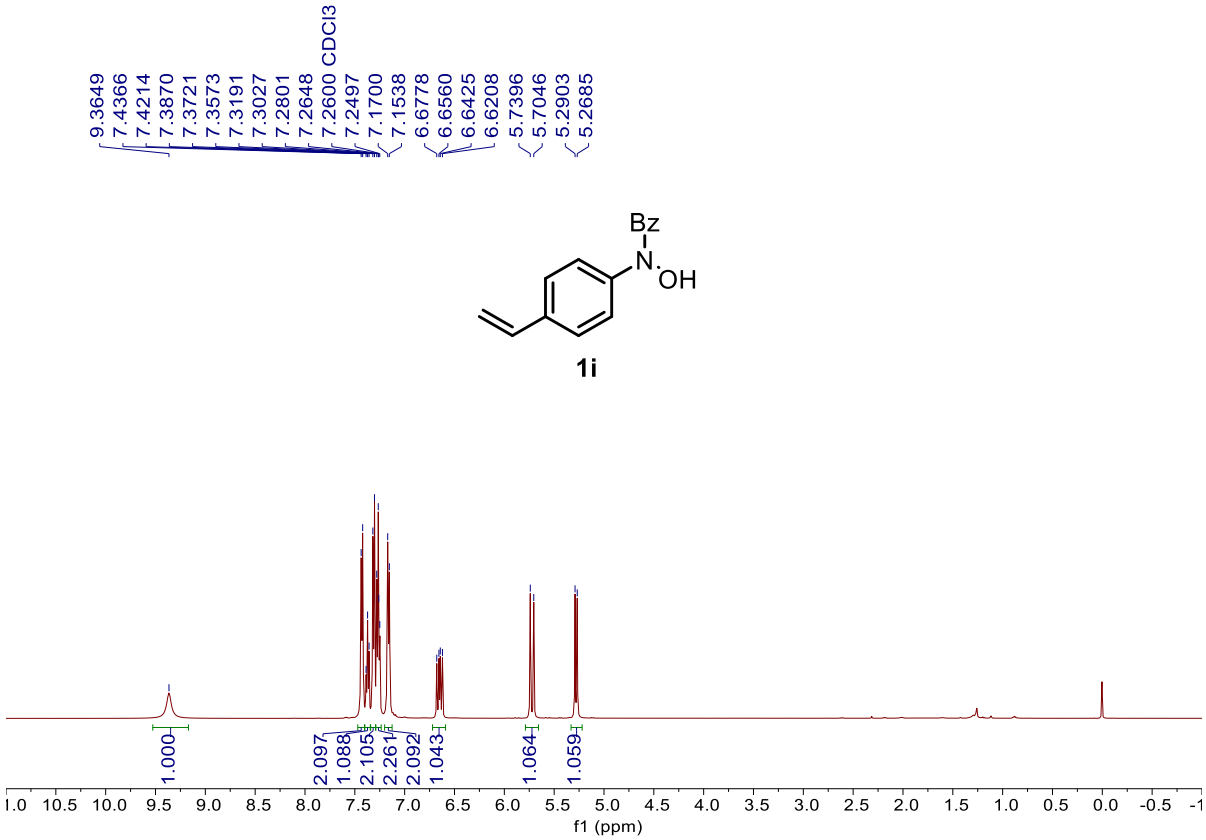




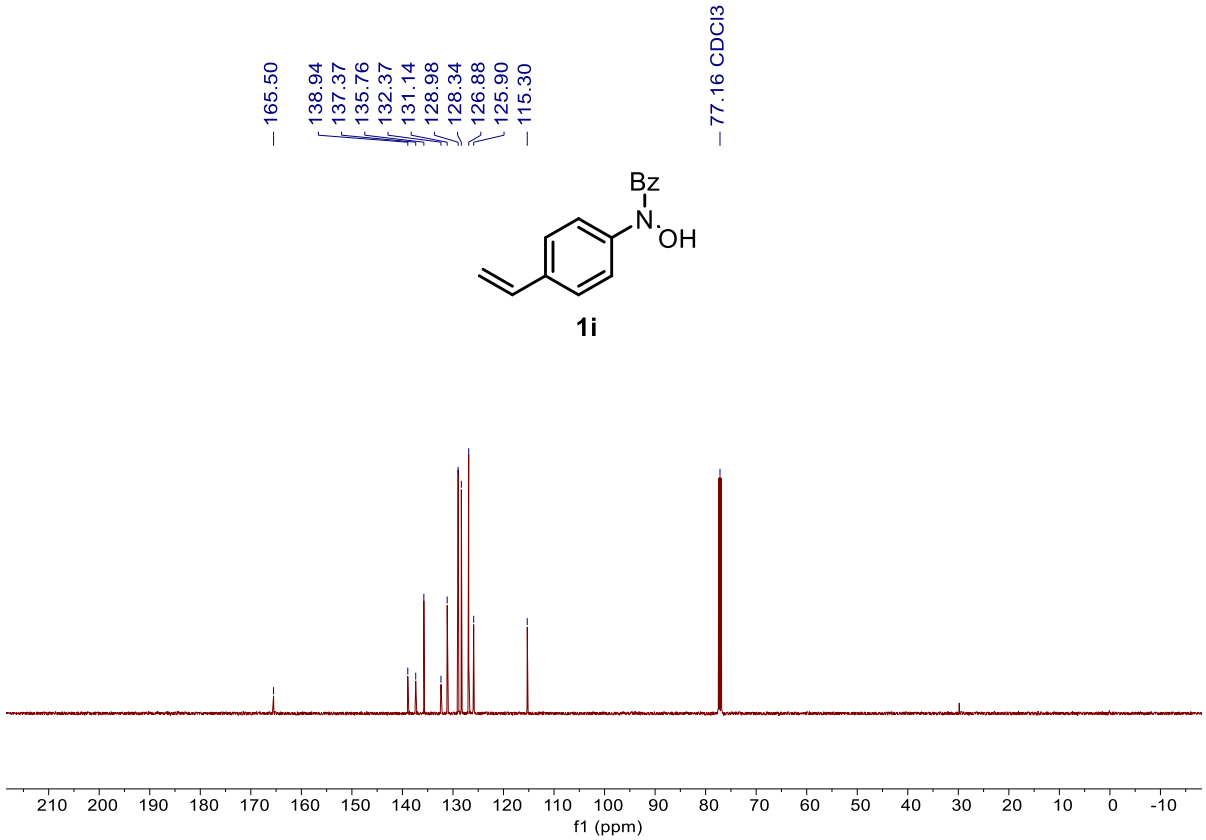
S3-10



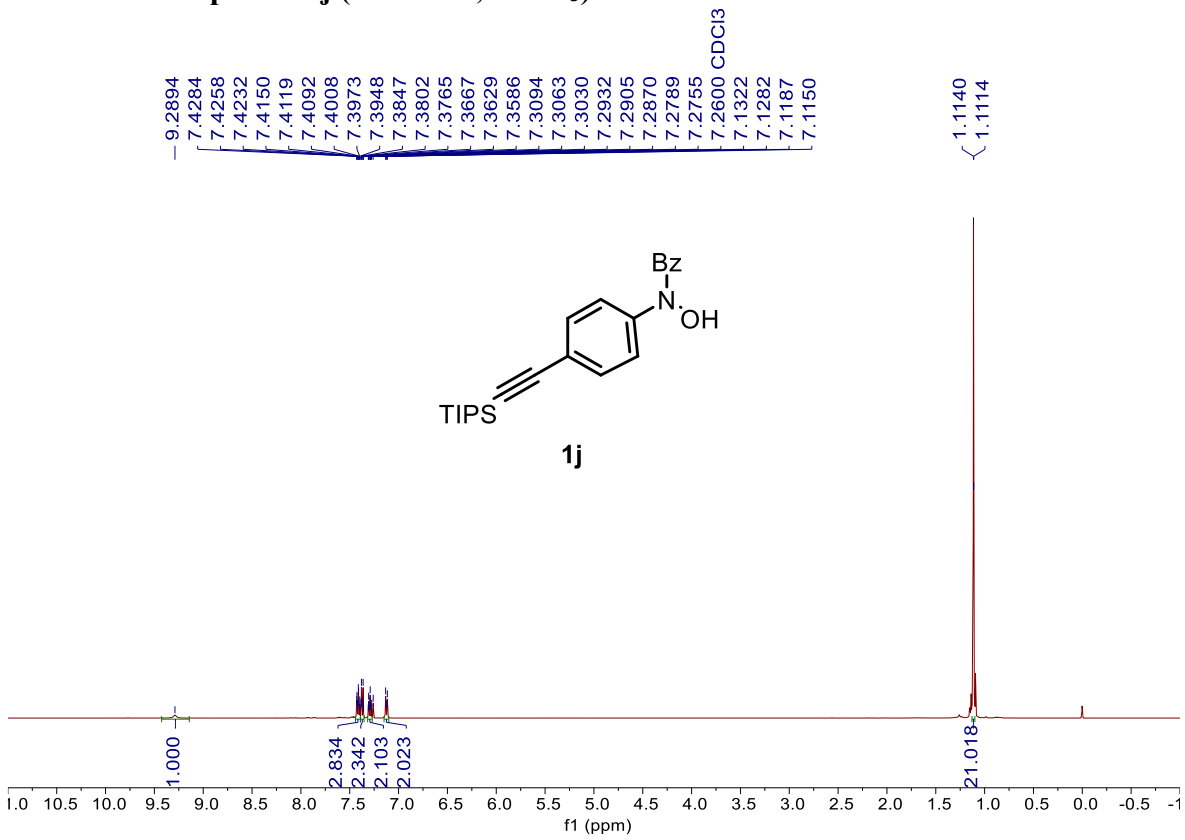
^{1}H NMR of Compound 1i (500 MHz, $CDCl_3$)



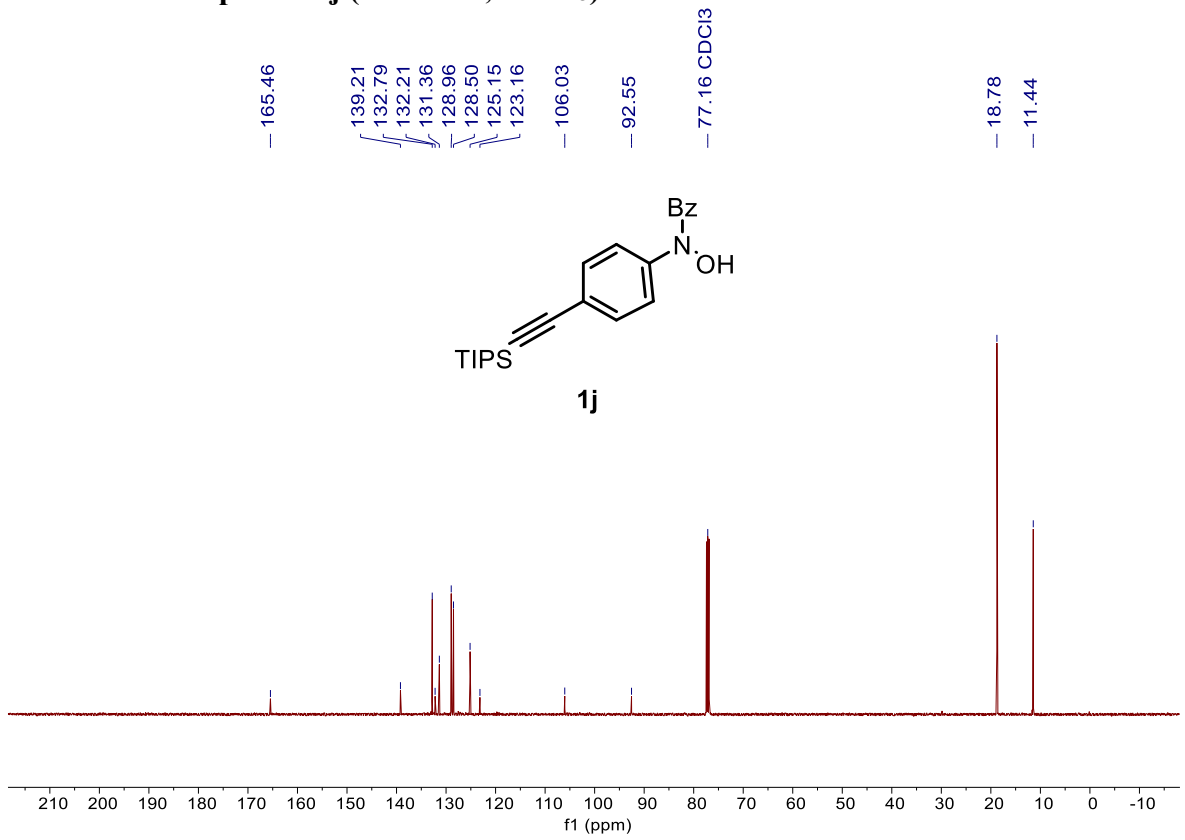
^{13}C NMR of Compound 1i (126 MHz, $CDCl_3$)



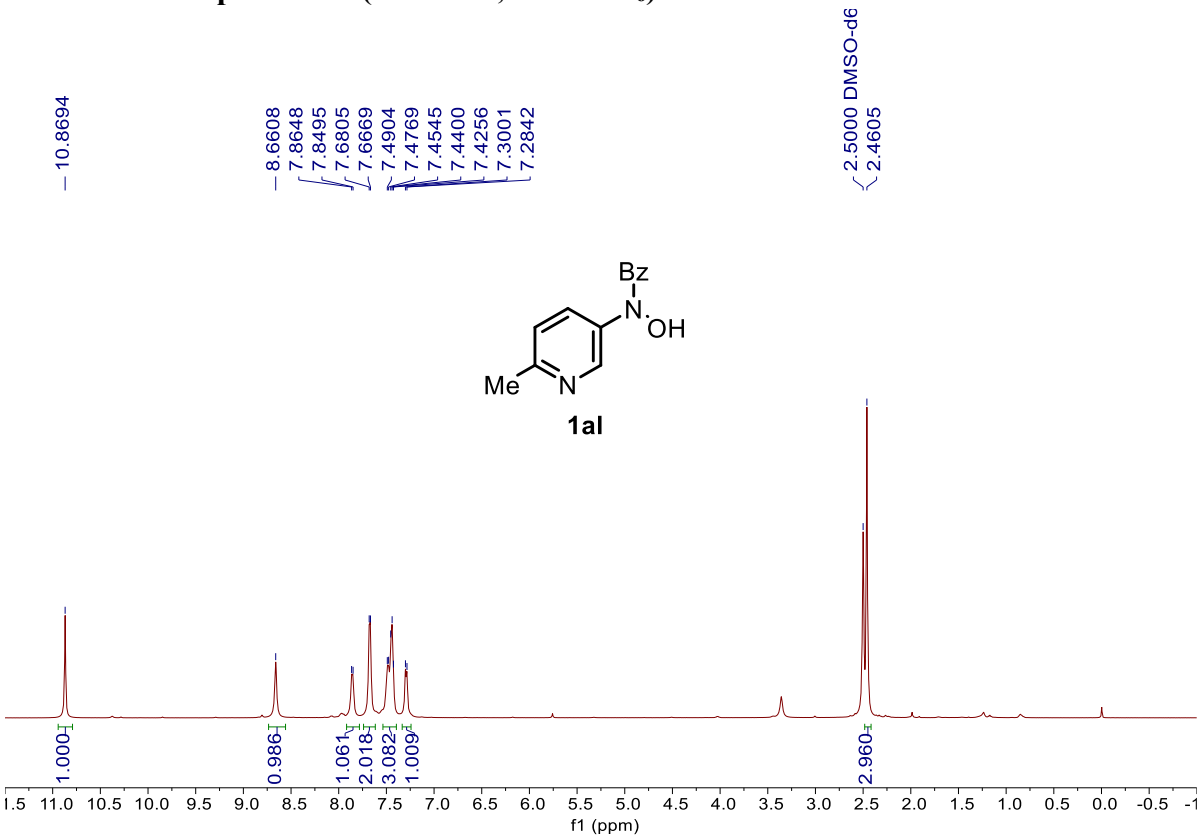
^{1}H NMR of Compound 1j (500 MHz, $CDCl_3$)



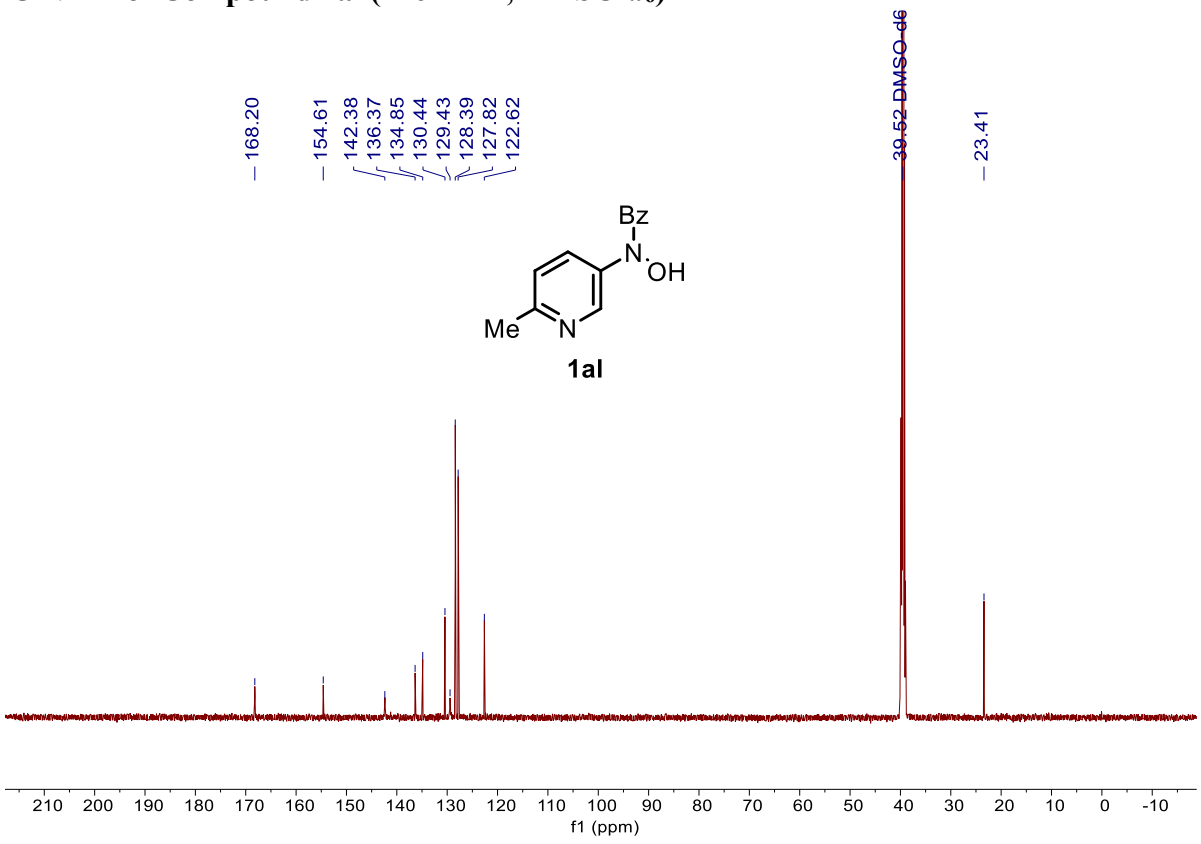
^{13}C NMR of Compound 1j (126 MHz, $CDCl_3$)



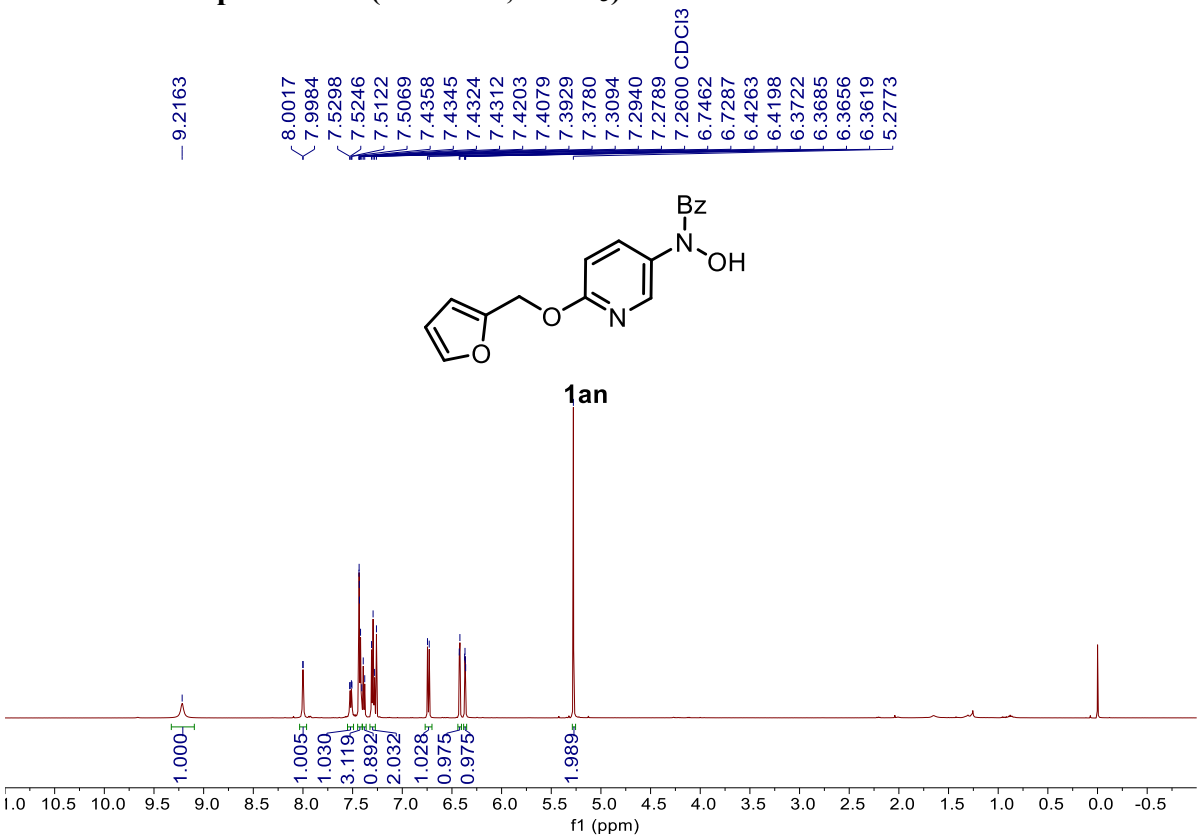
^{1}H NMR of Compound 1al (500 MHz, DMSO-d_6)



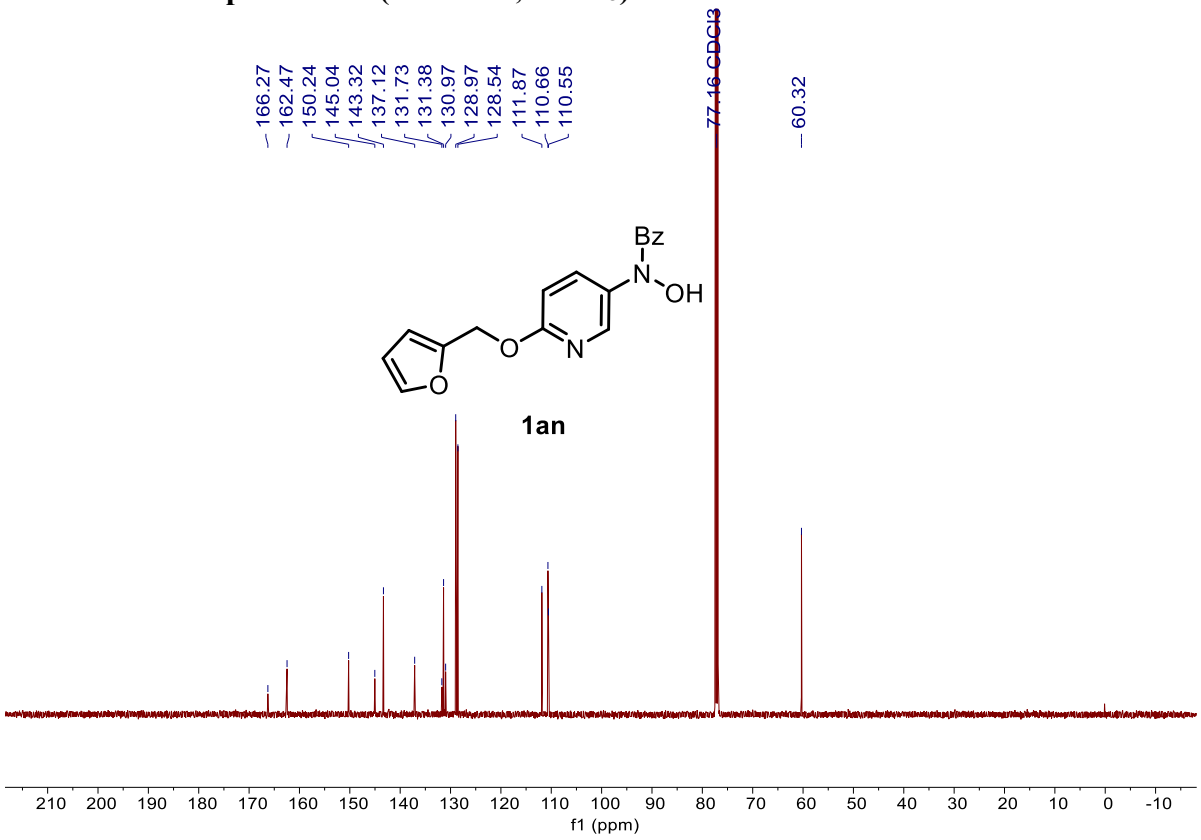
^{13}C NMR of Compound 1al (126 MHz, DMSO-d_6)



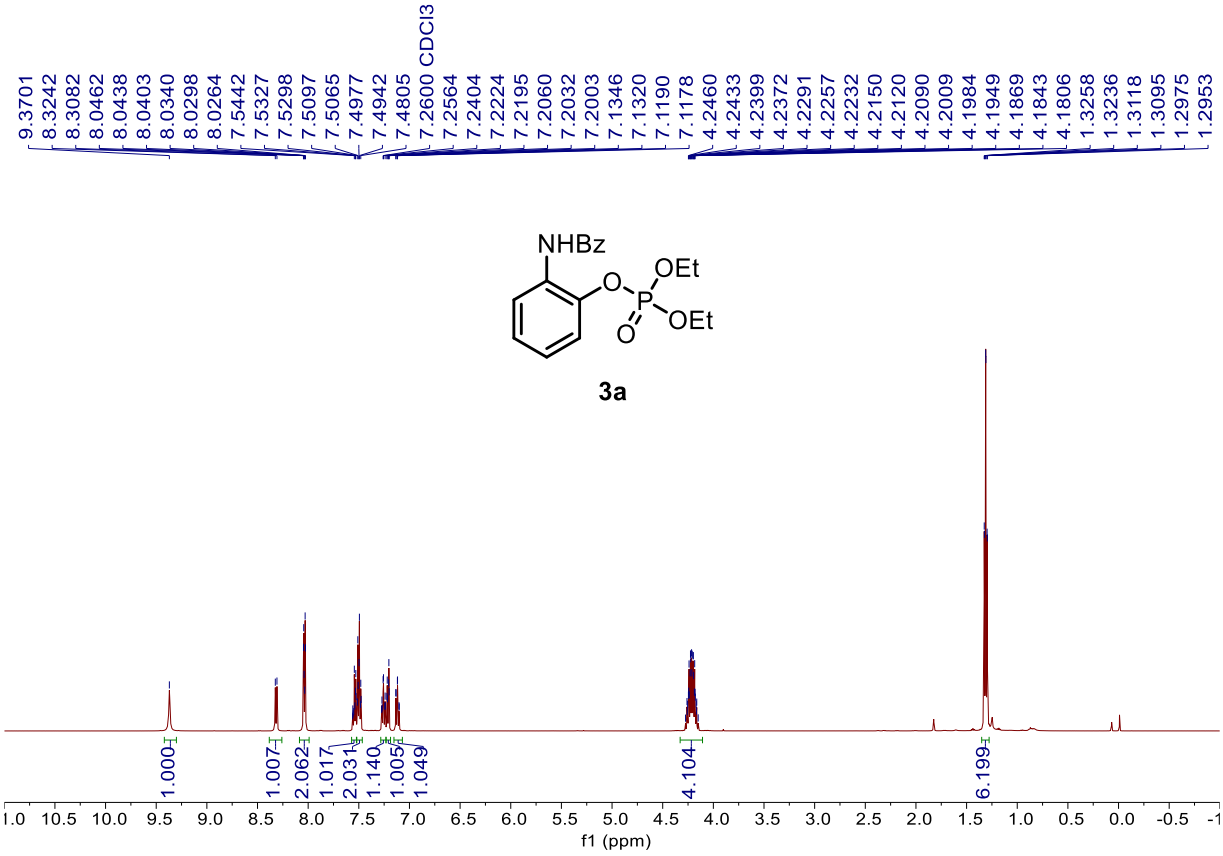
^{1}H NMR of Compound 1an (500 MHz, $CDCl_3$)



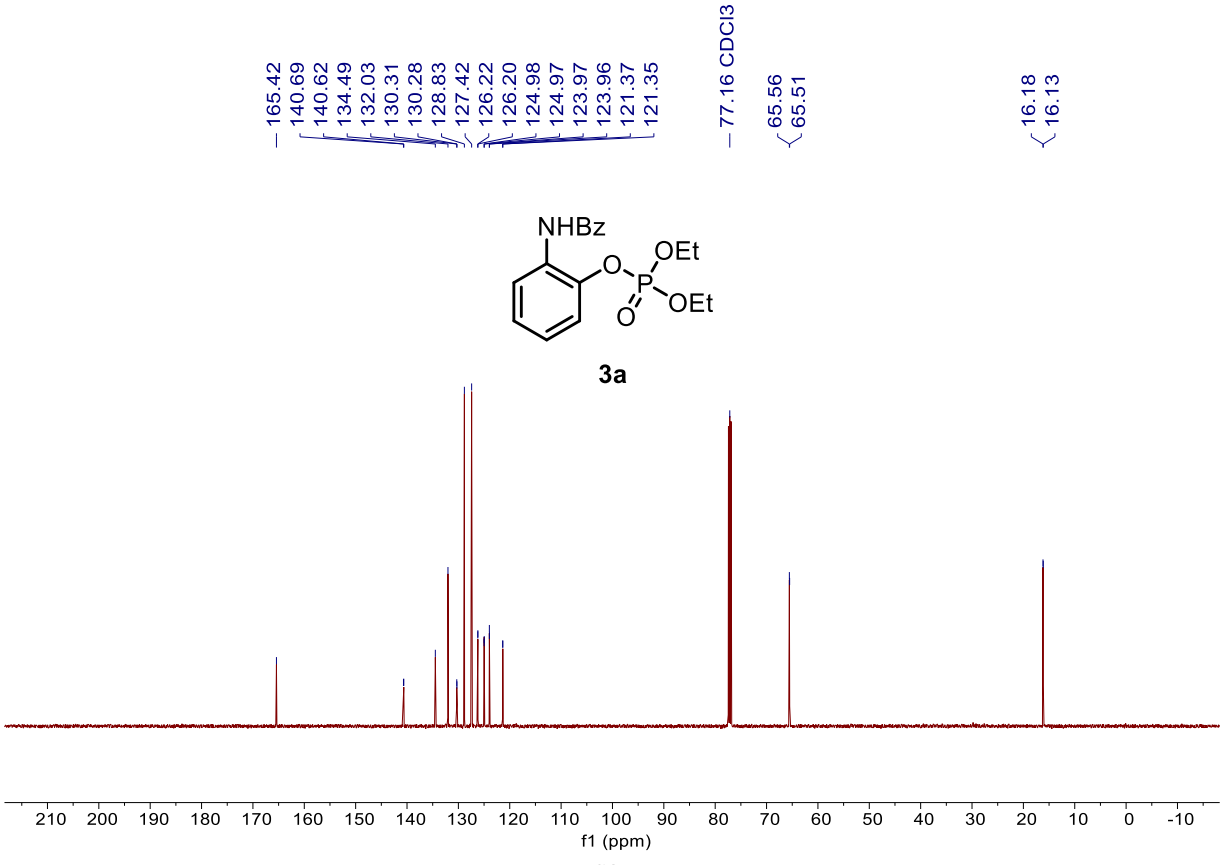
^{13}C NMR of Compound 1an (126 MHz, $CDCl_3$)



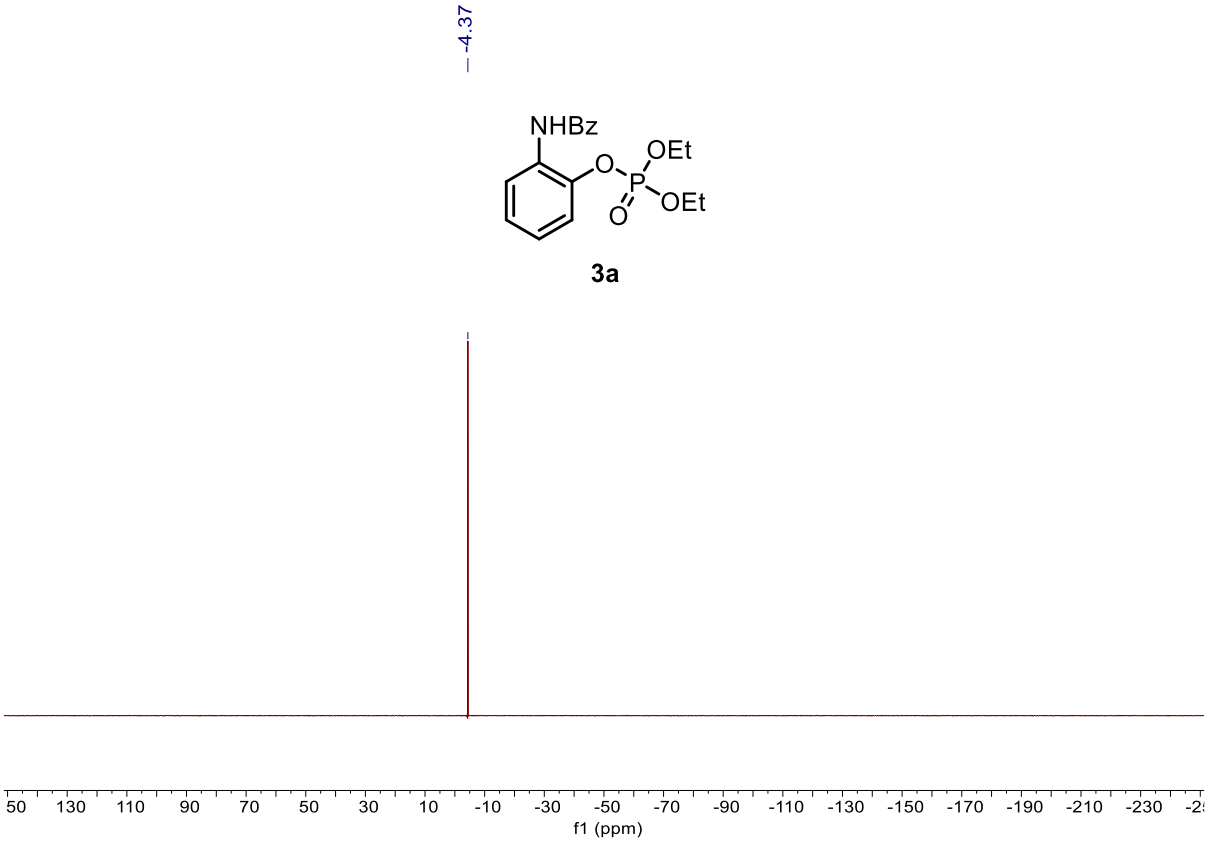
^{1}H NMR of Compound 3a (500 MHz, $CDCl_3$)



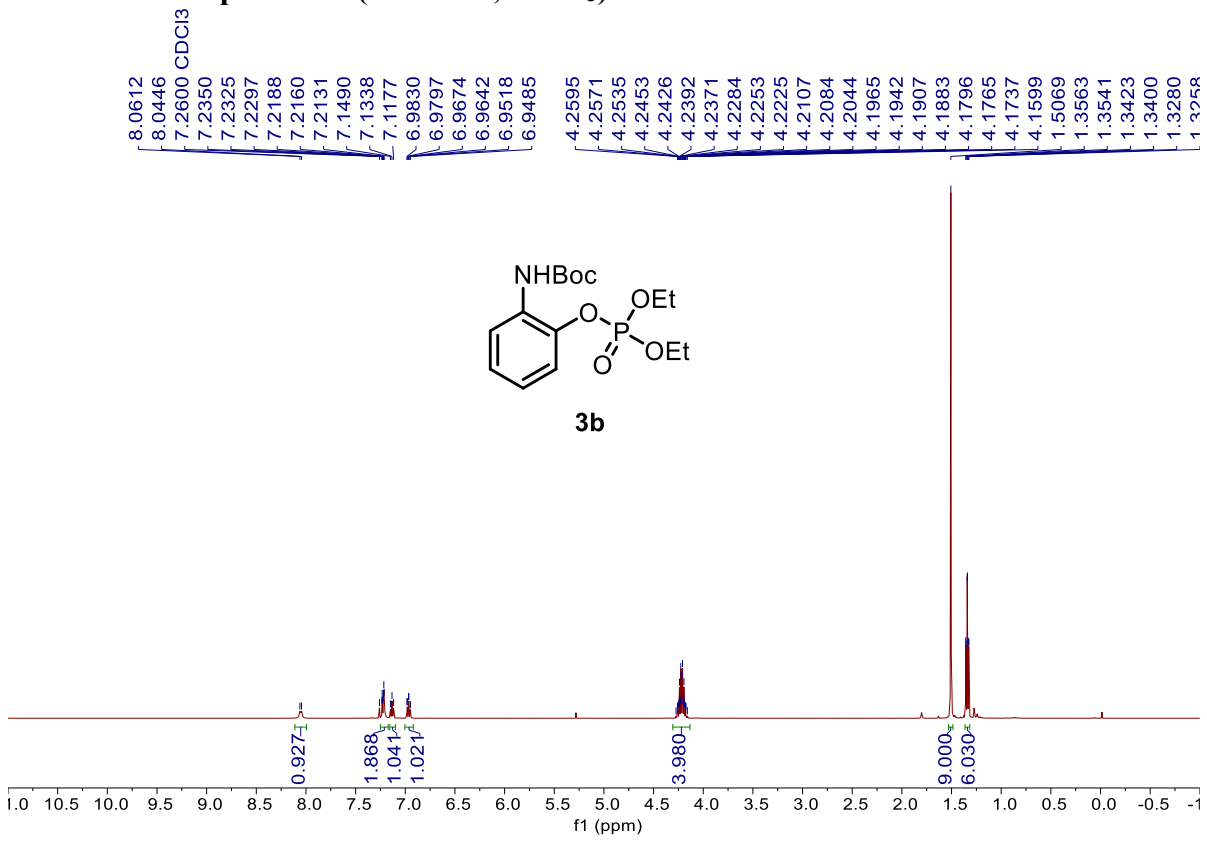
^{13}C NMR of Compound 3a (126 MHz, $CDCl_3$)



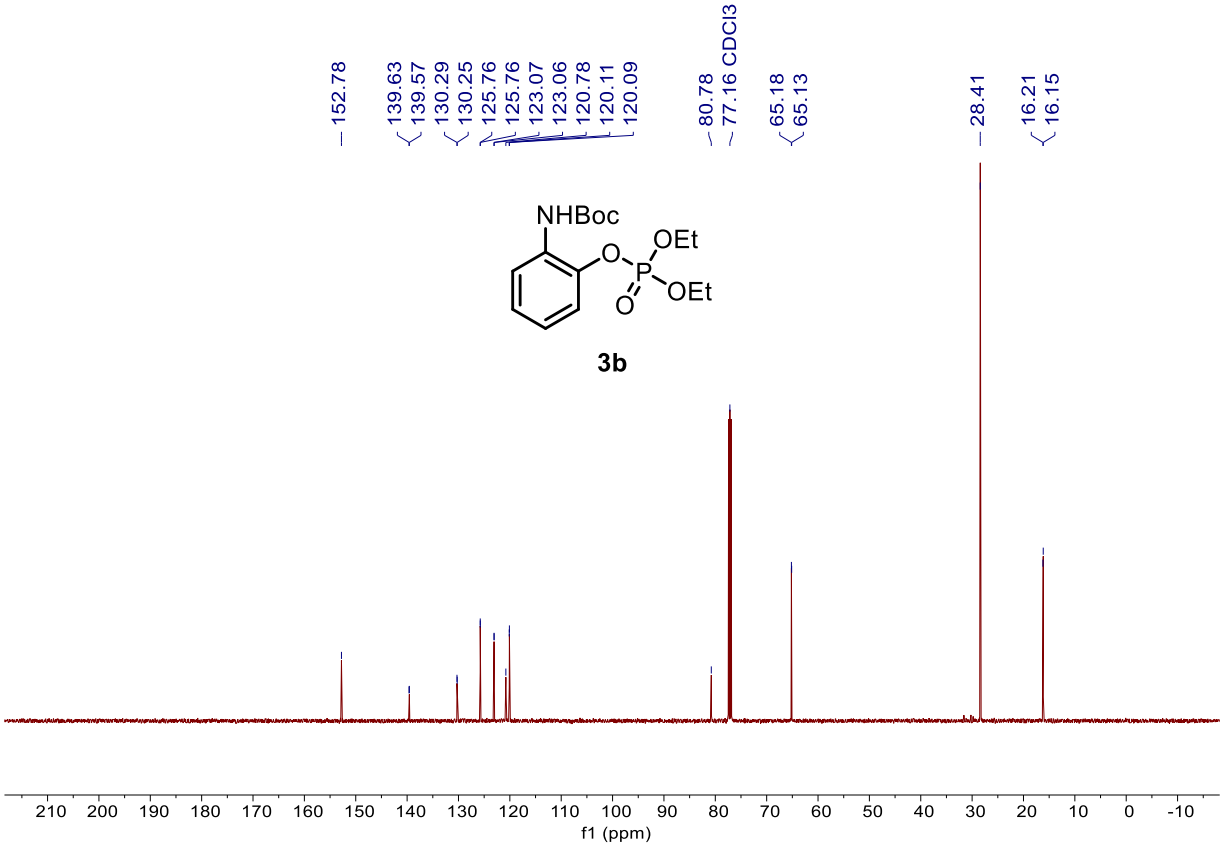
^{31}P NMR of Compound 3a (202 MHz, $CDCl_3$)



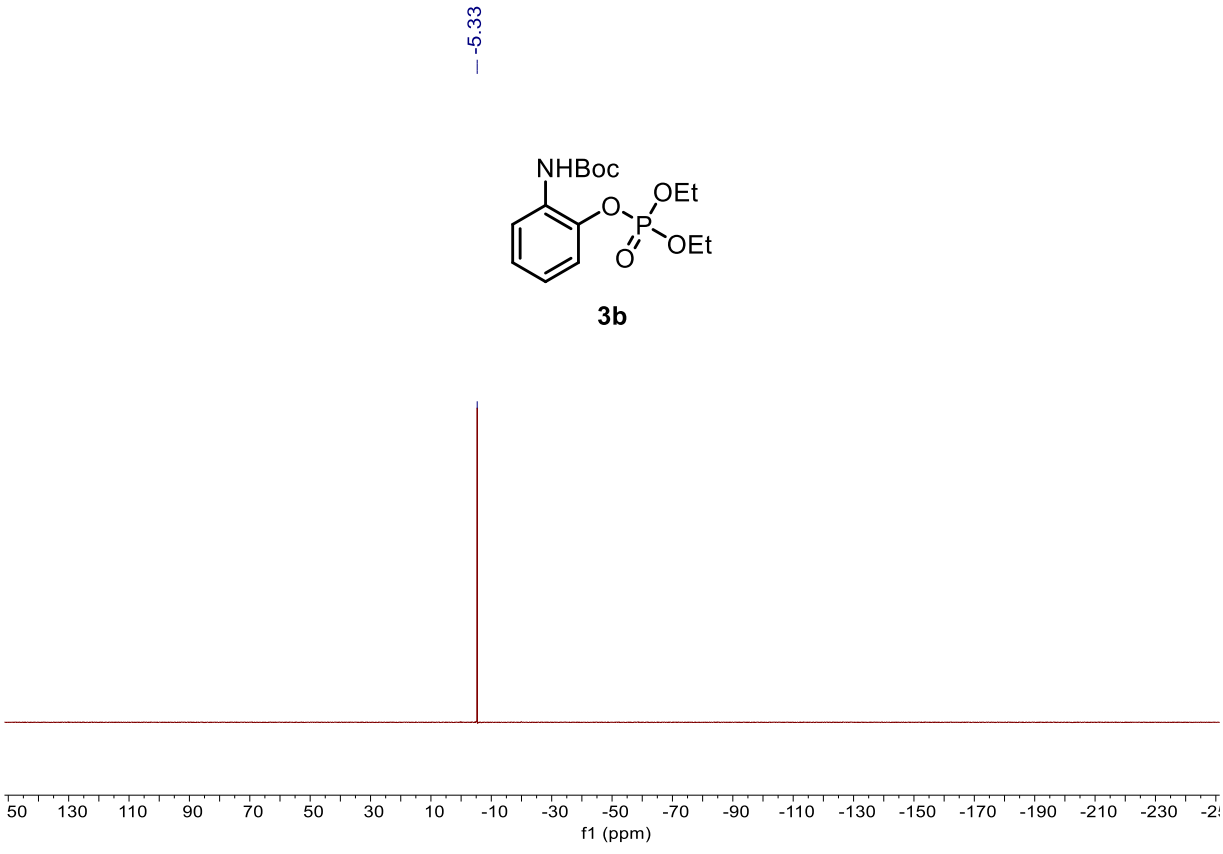
^{1}H NMR of Compound 3b (500 MHz, $CDCl_3$)



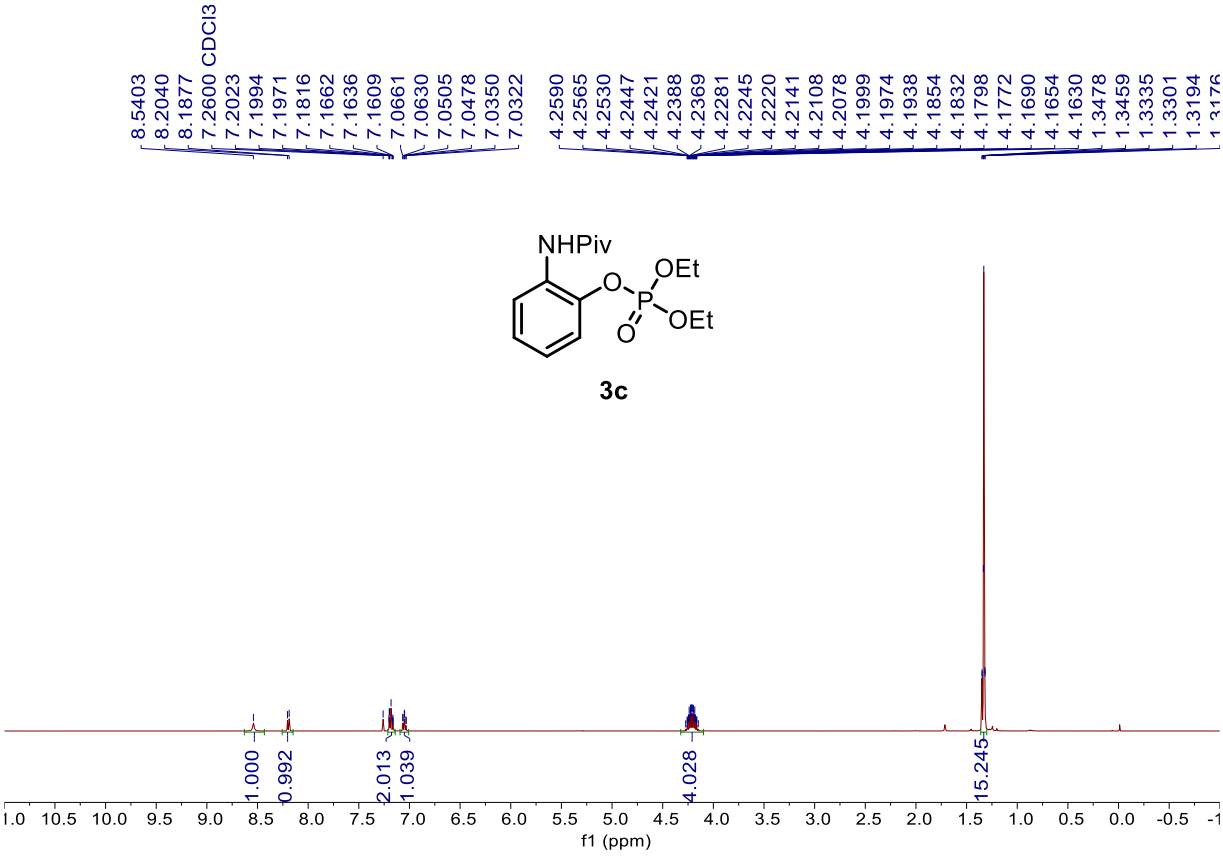
^{13}C NMR of Compound 3b (126 MHz, $CDCl_3$)



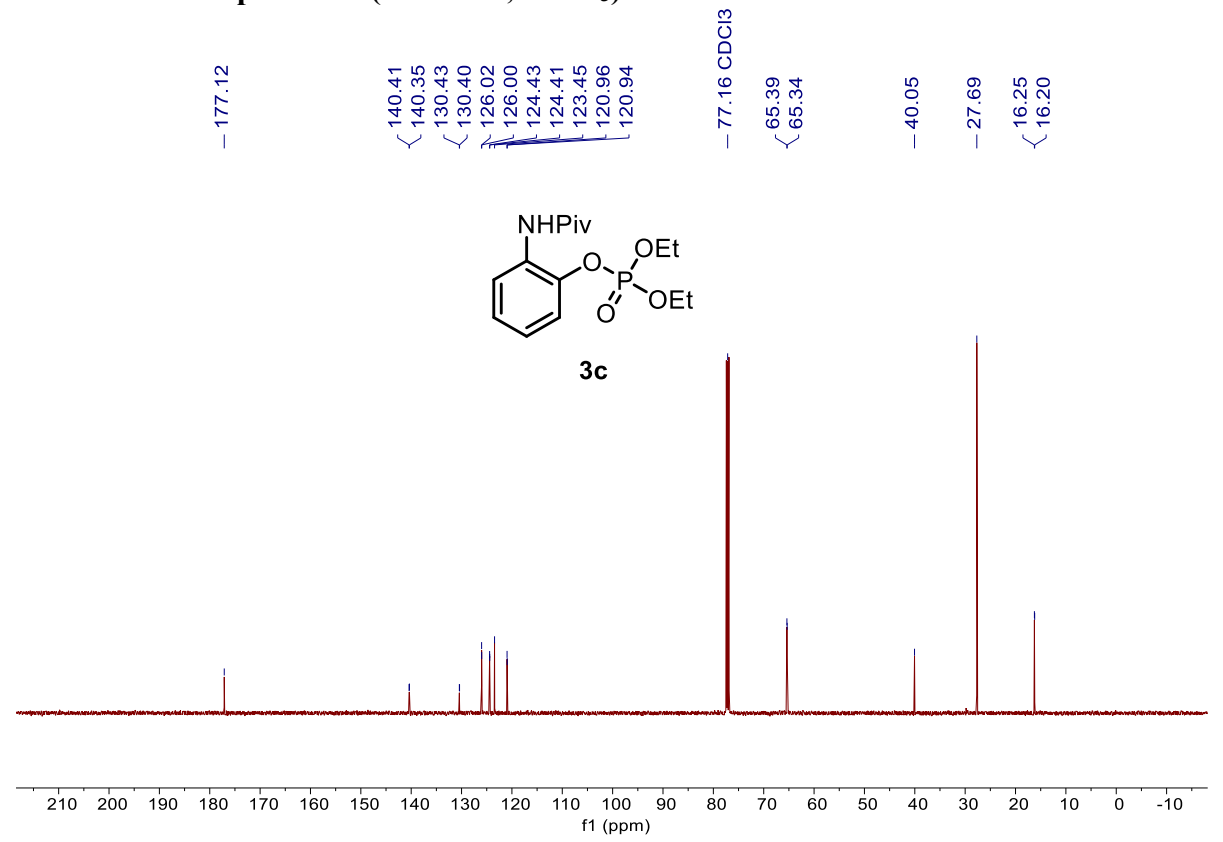
^{31}P NMR of Compound 3b (202 MHz, $CDCl_3$)



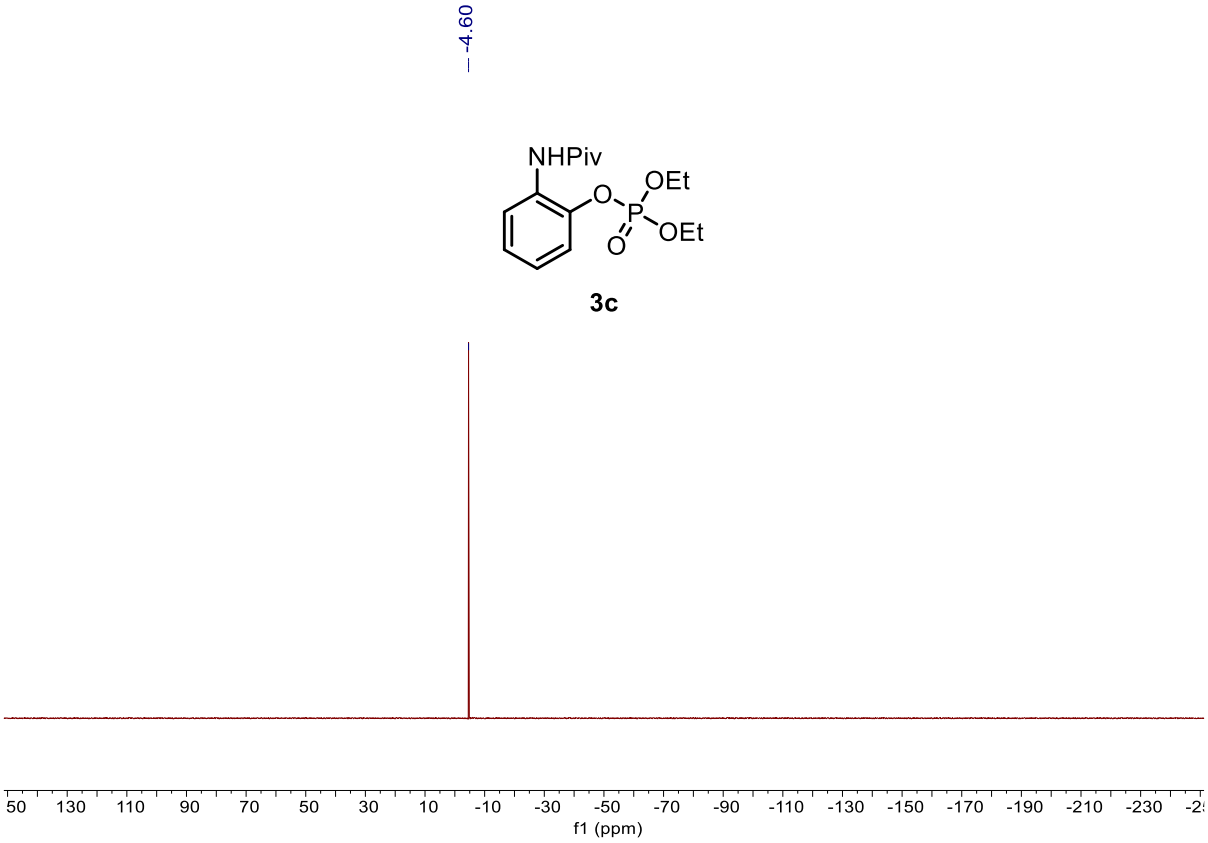
^{1}H NMR of Compound 3c (500 MHz, $CDCl_3$)



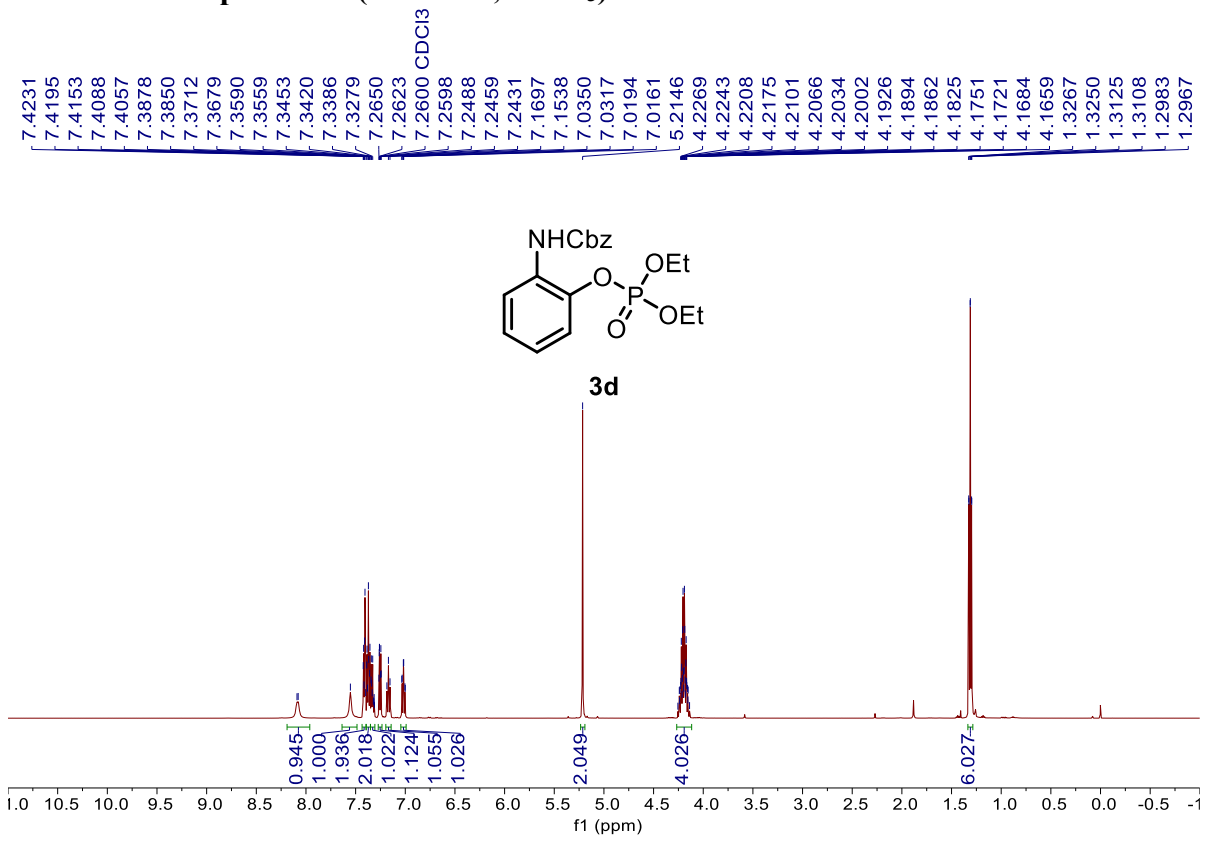
^{13}C NMR of Compound 3c (126 MHz, $CDCl_3$)



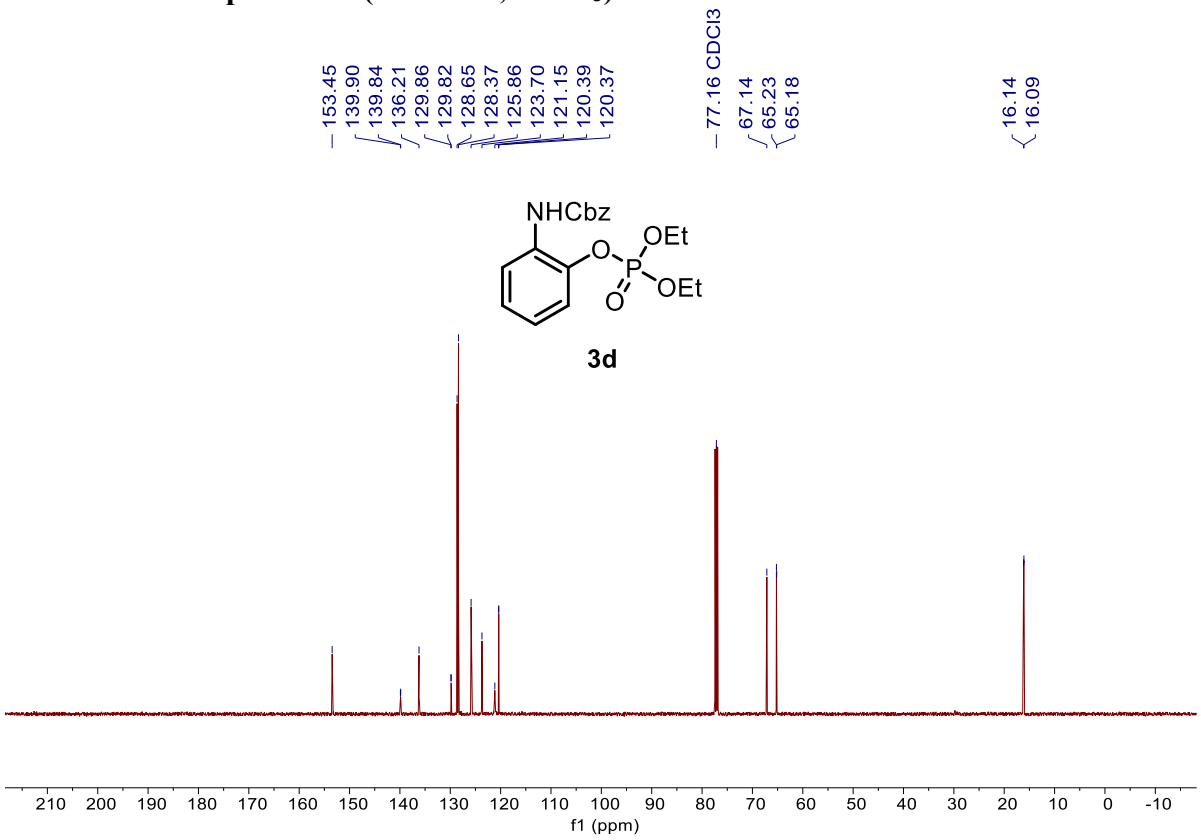
^{31}P NMR of Compound 3c (202 MHz, $CDCl_3$)



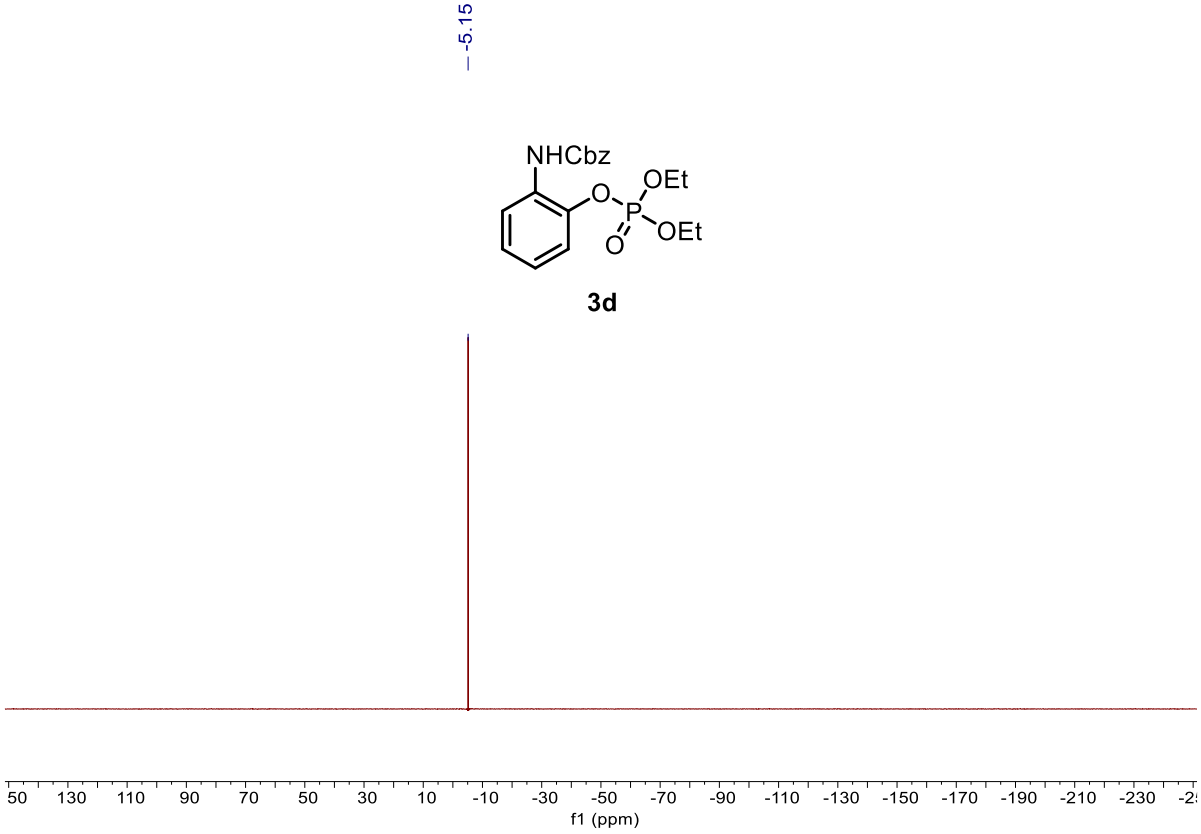
^{1}H NMR of Compound 3d (500 MHz, $CDCl_3$)



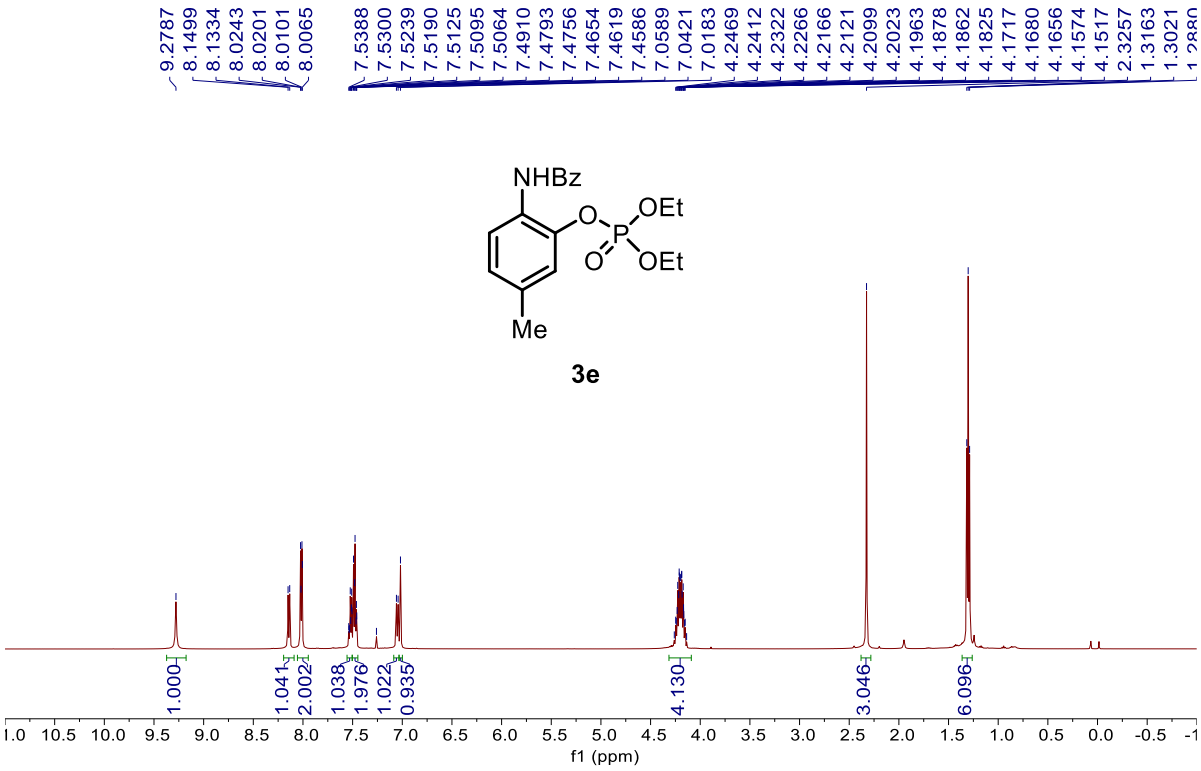
^{13}C NMR of Compound 3d (126 MHz, $CDCl_3$)



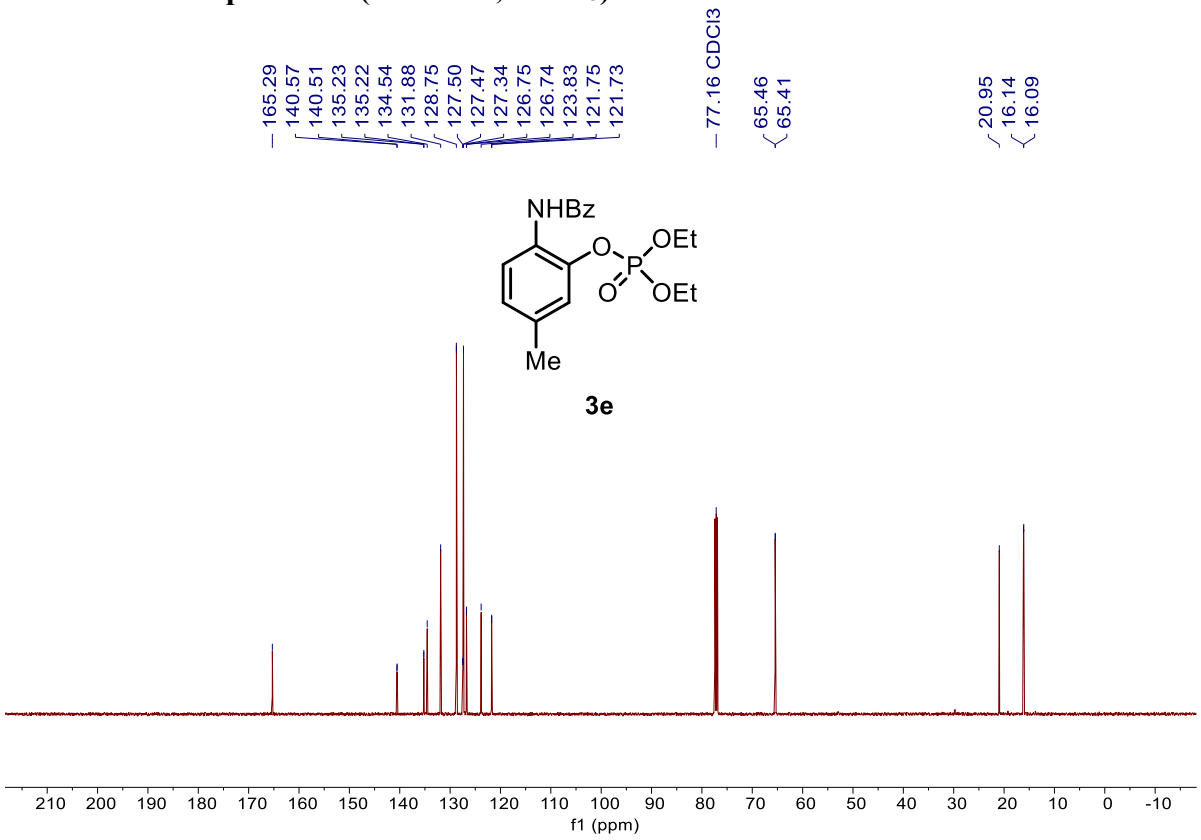
^{31}P NMR of Compound 3d (202 MHz, $CDCl_3$)



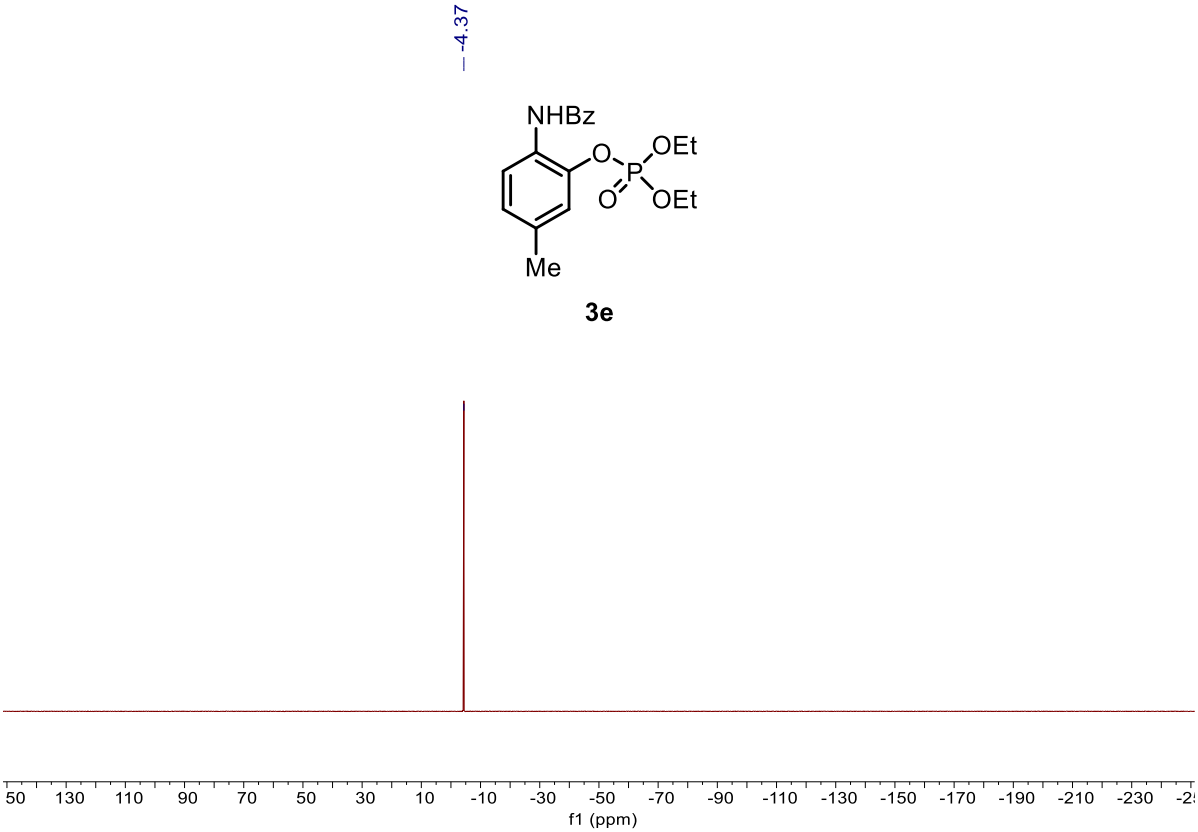
^{1}H NMR of Compound 3e (500 MHz, $CDCl_3$)



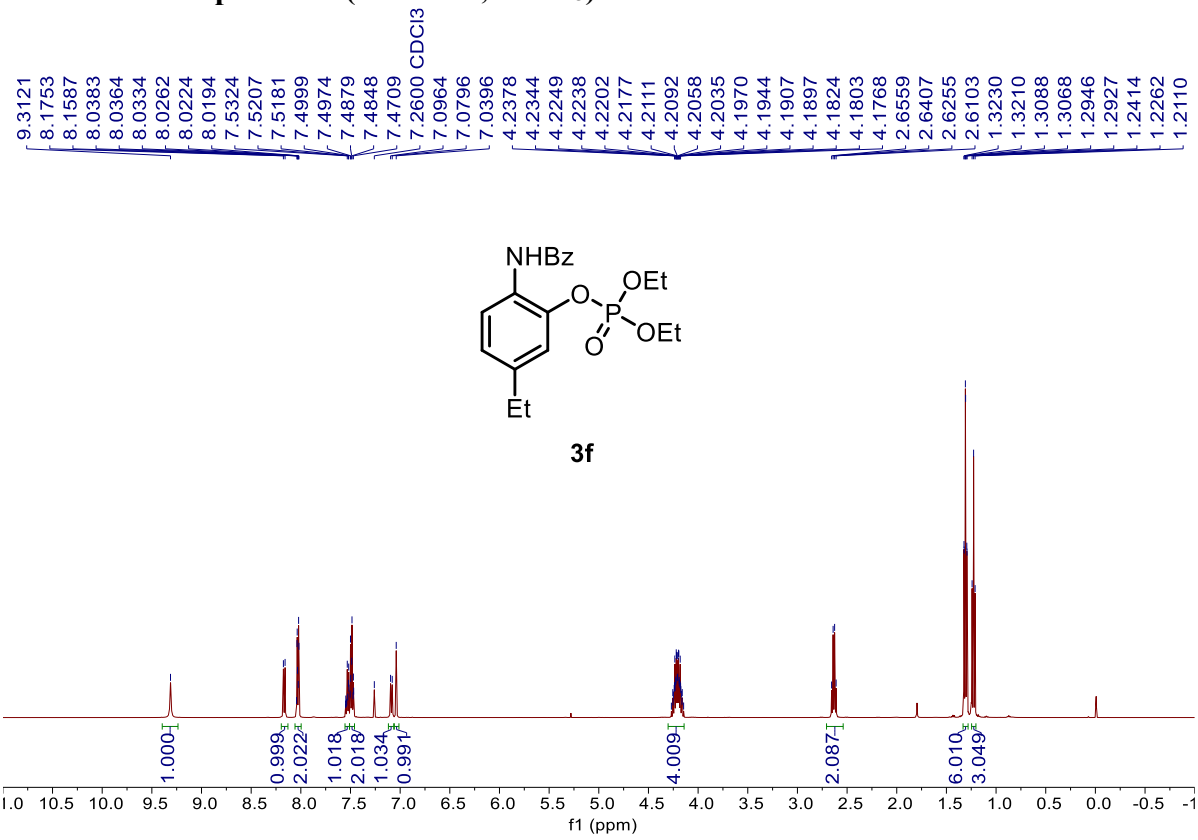
^{13}C NMR of Compound 3e (126 MHz, $CDCl_3$)



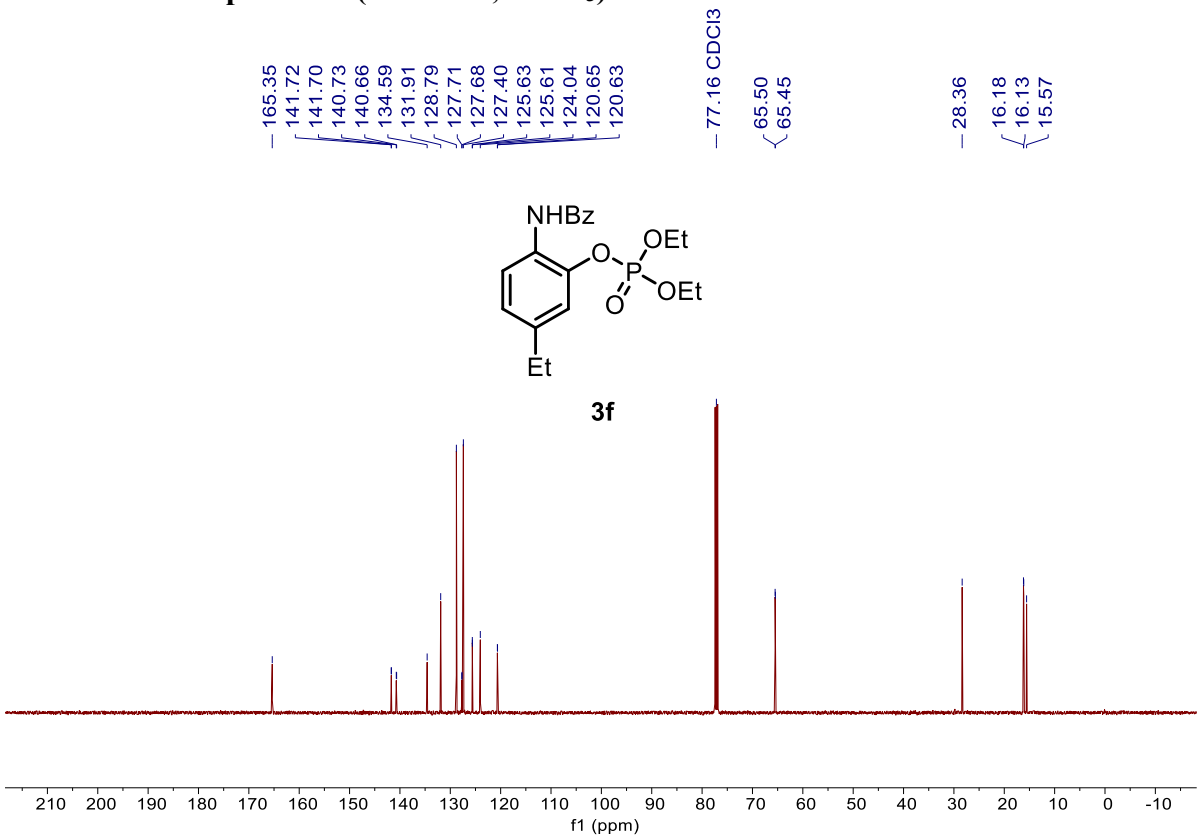
^{31}P NMR of Compound 3e (202 MHz, $CDCl_3$)



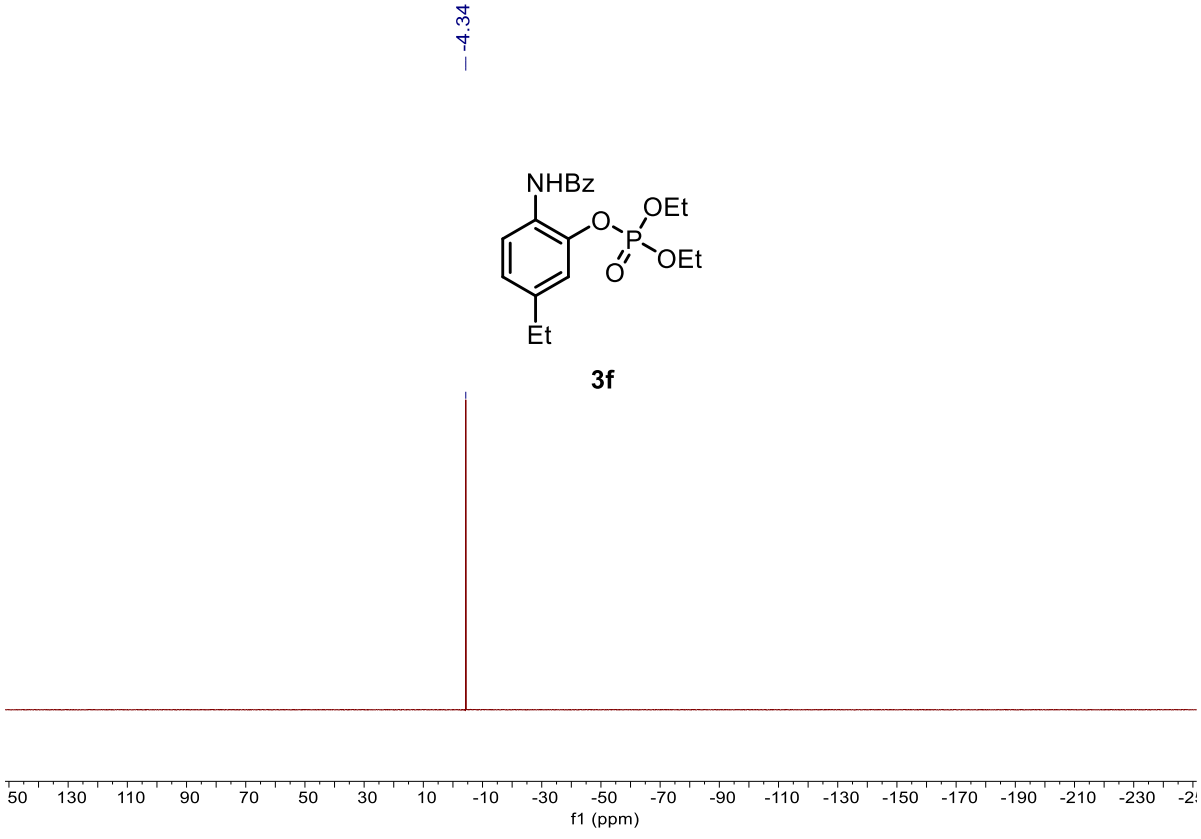
^{1}H NMR of Compound 3f (500 MHz, $CDCl_3$)



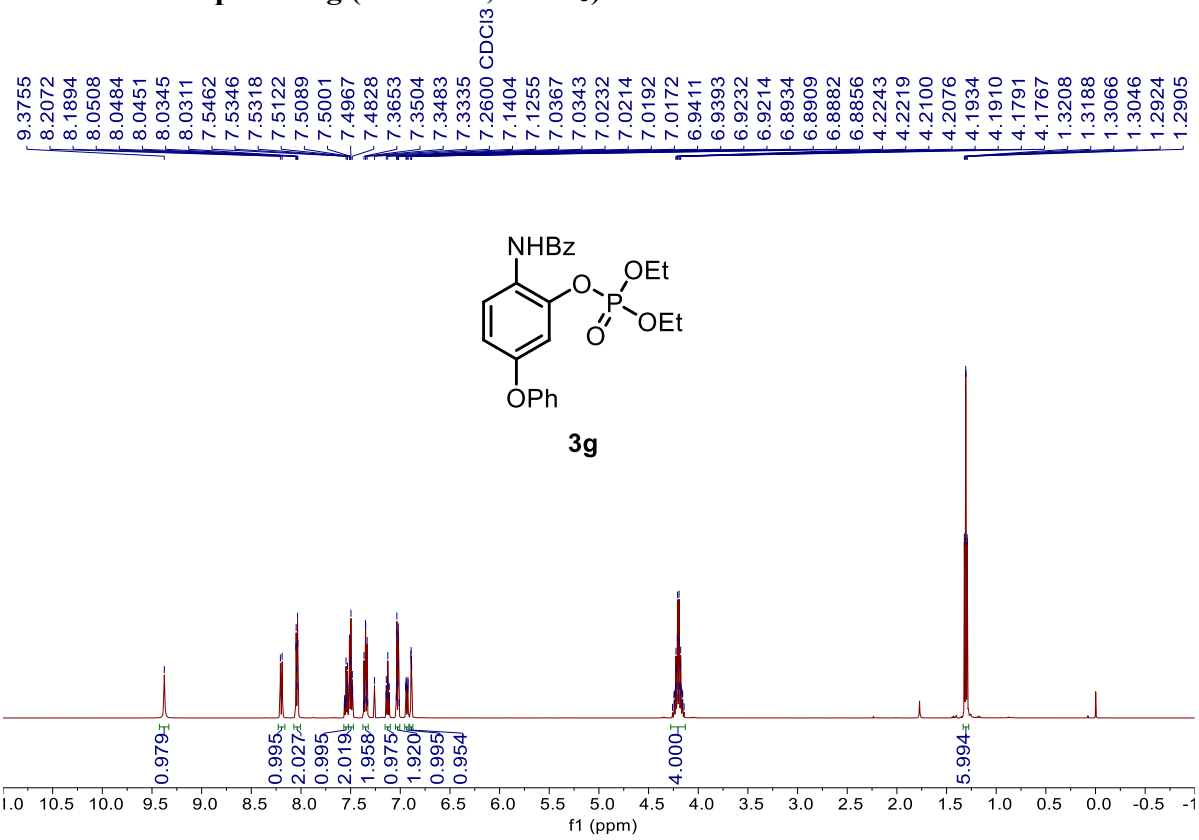
^{13}C NMR of Compound 3f (126 MHz, $CDCl_3$)



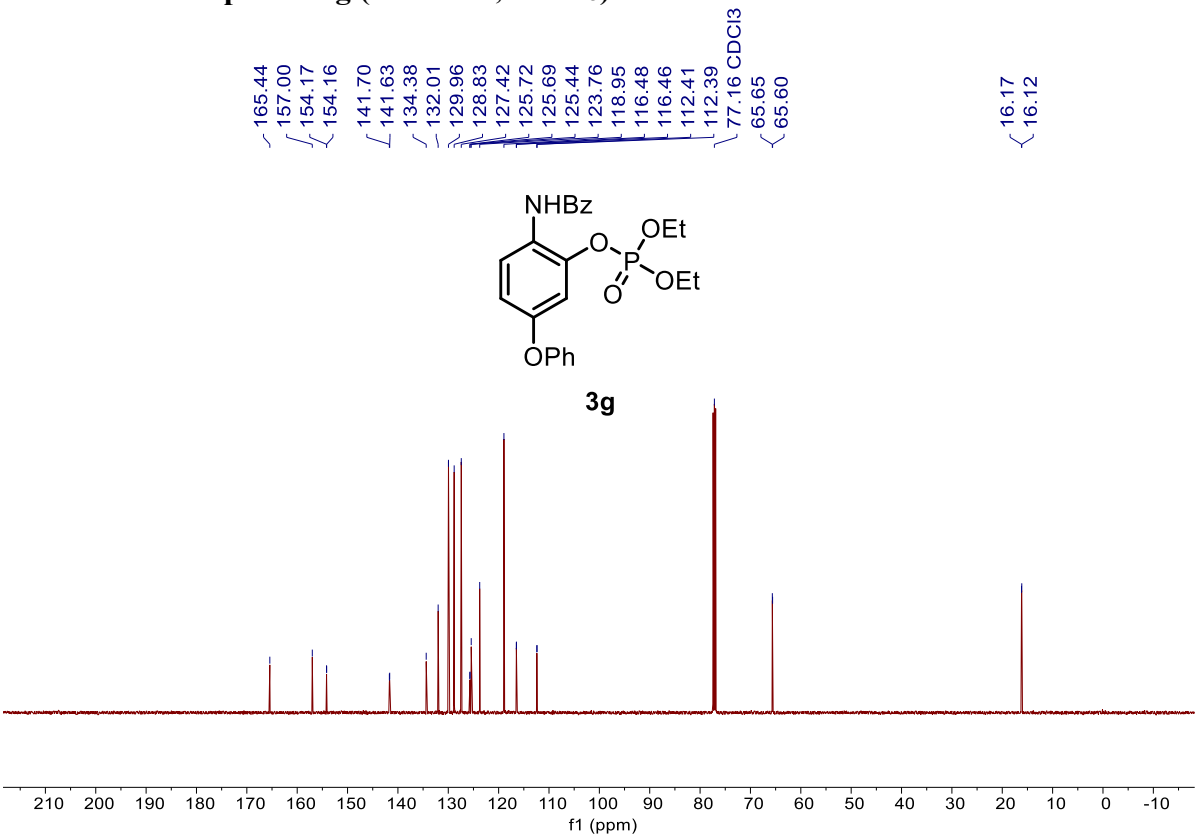
^{31}P NMR of Compound 3f (202 MHz, $CDCl_3$)



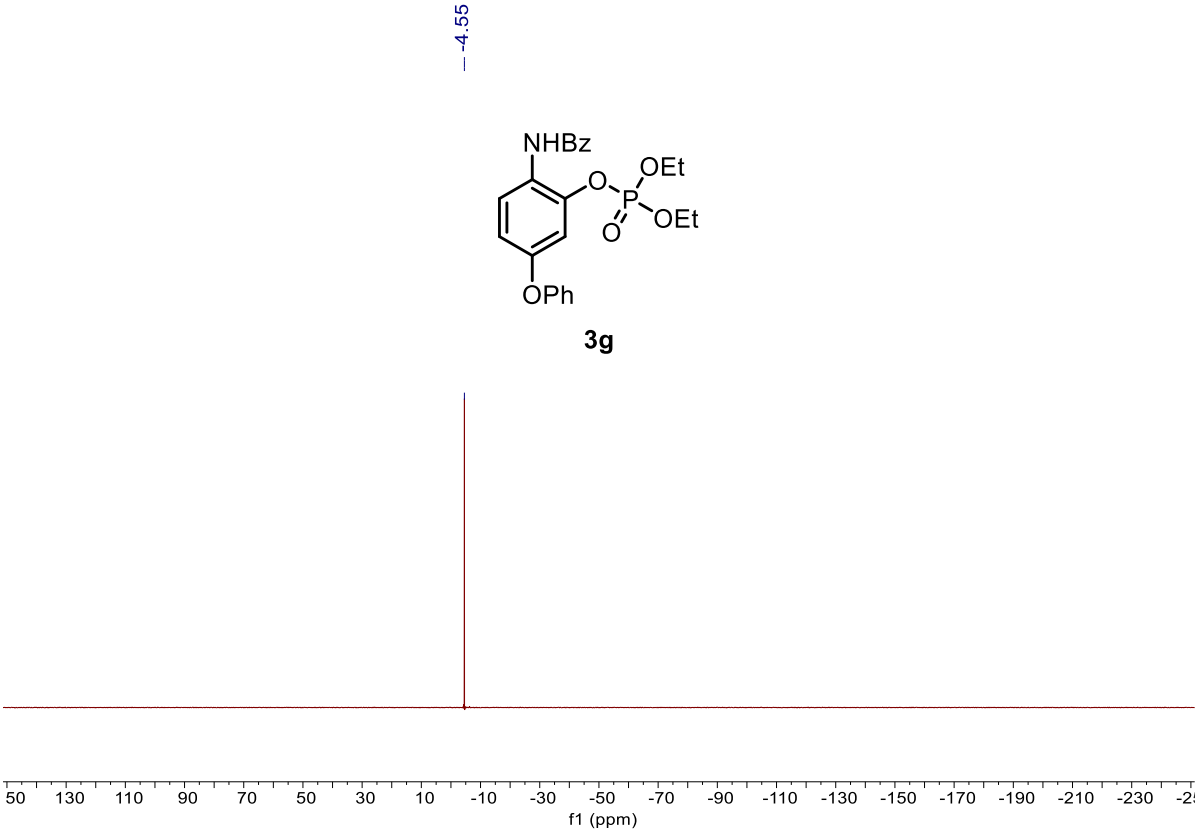
^{1}H NMR of Compound 3g (500 MHz, $CDCl_3$)



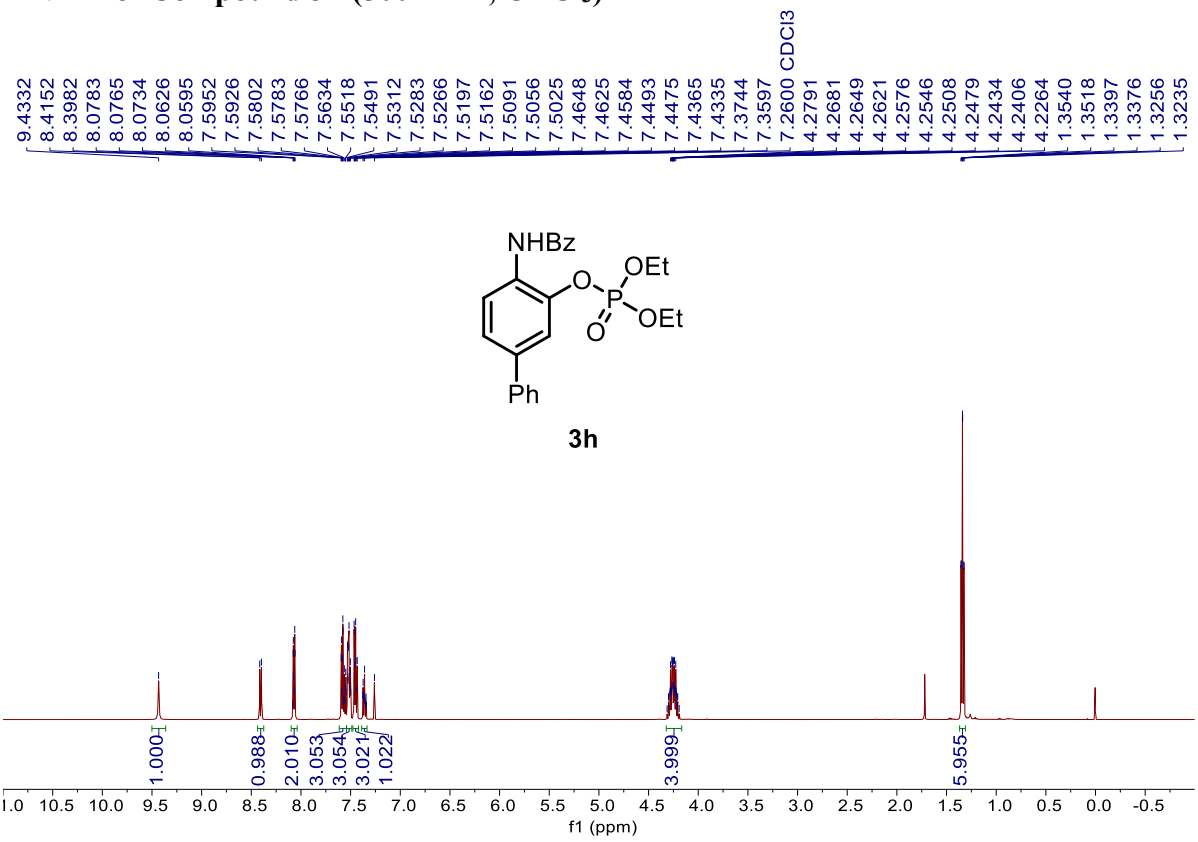
^{13}C NMR of Compound 3g (126 MHz, $CDCl_3$)



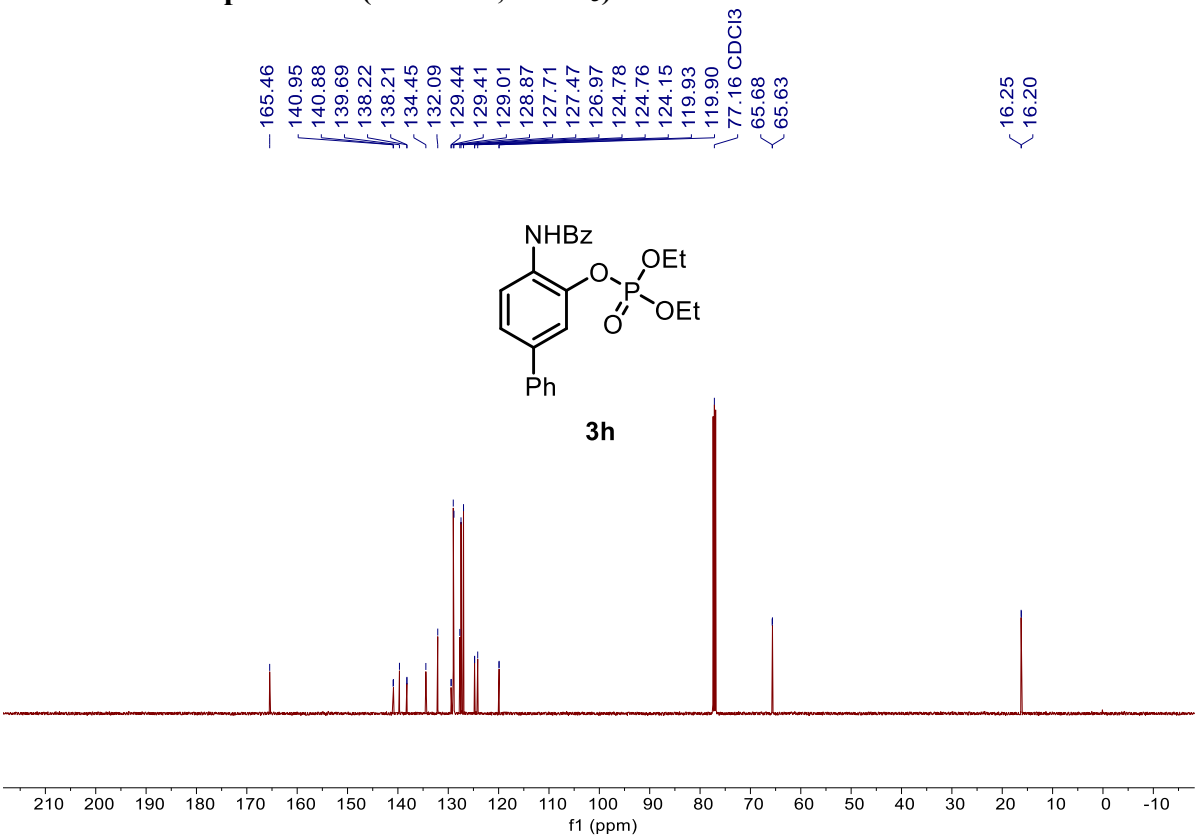
^{31}P NMR of Compound 3g (202 MHz, $CDCl_3$)



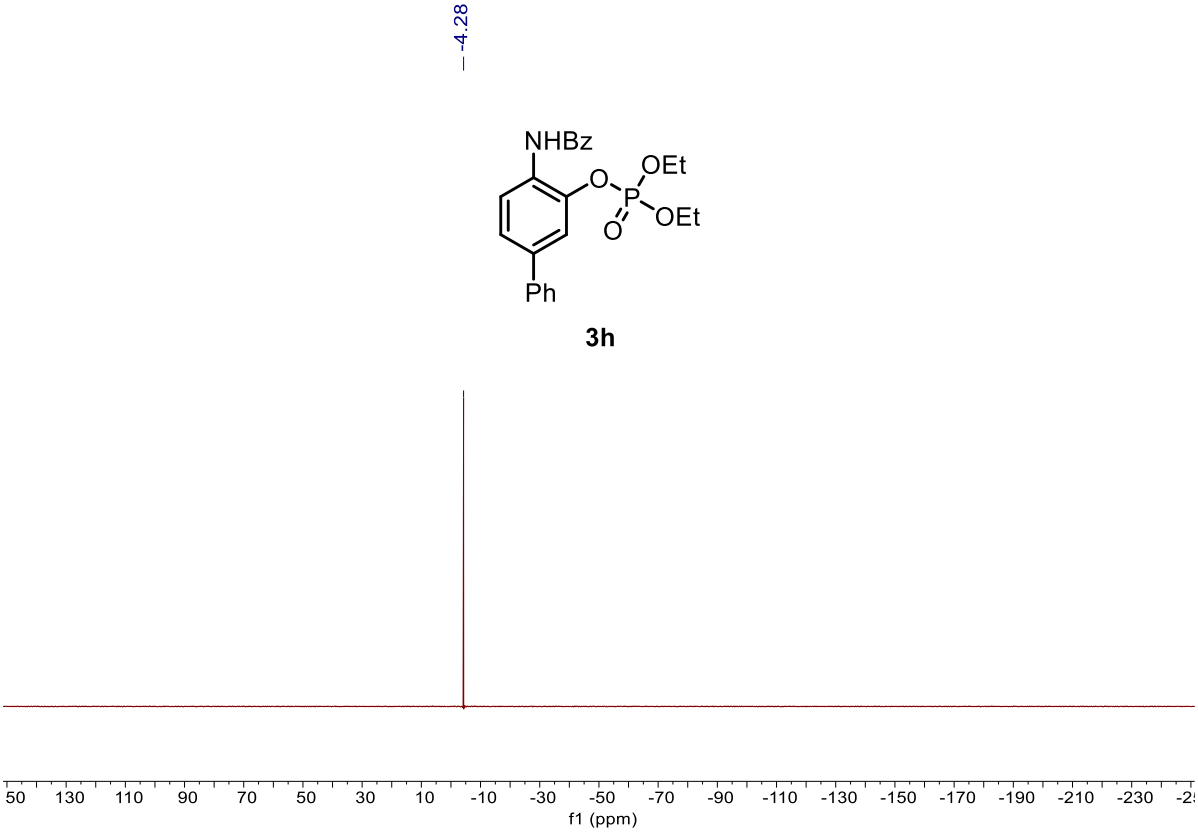
^{1}H NMR of Compound 3h (500 MHz, $CDCl_3$)



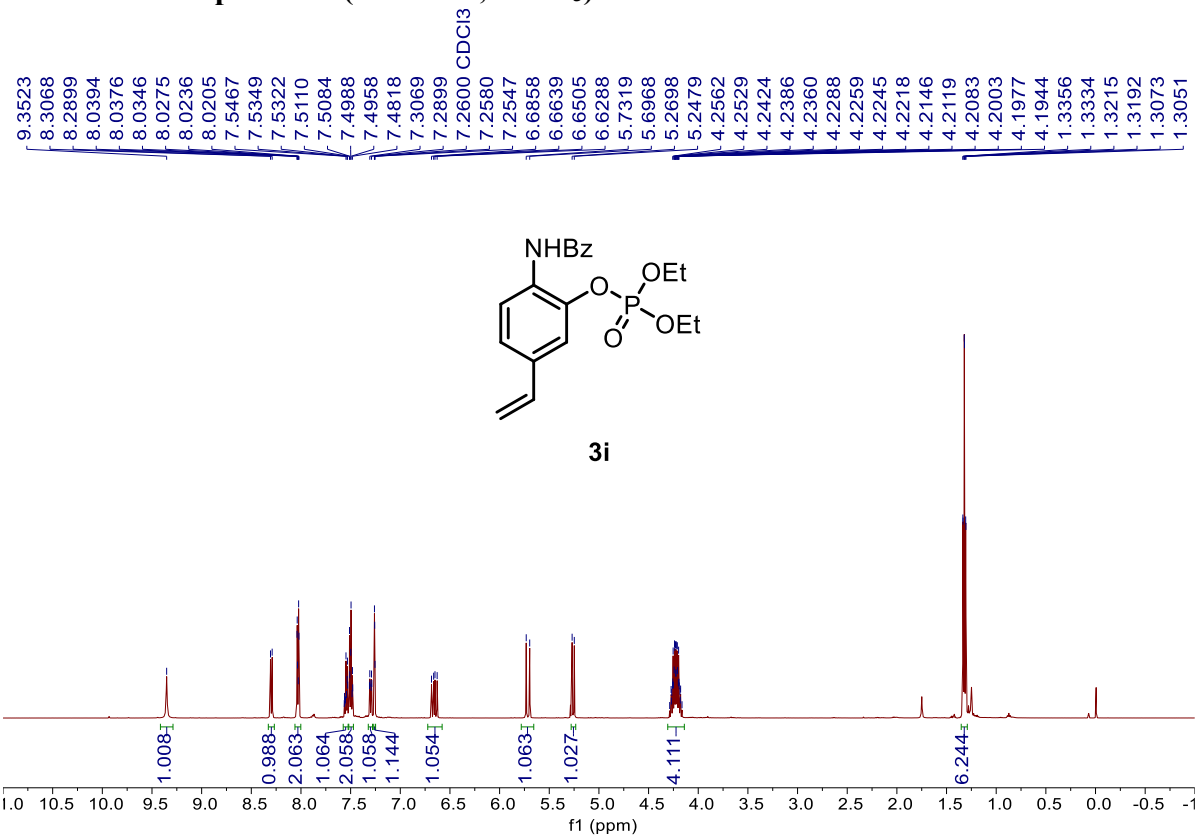
^{13}C NMR of Compound 3h (126 MHz, $CDCl_3$)



^{31}P NMR of Compound 3h (202 MHz, $CDCl_3$)

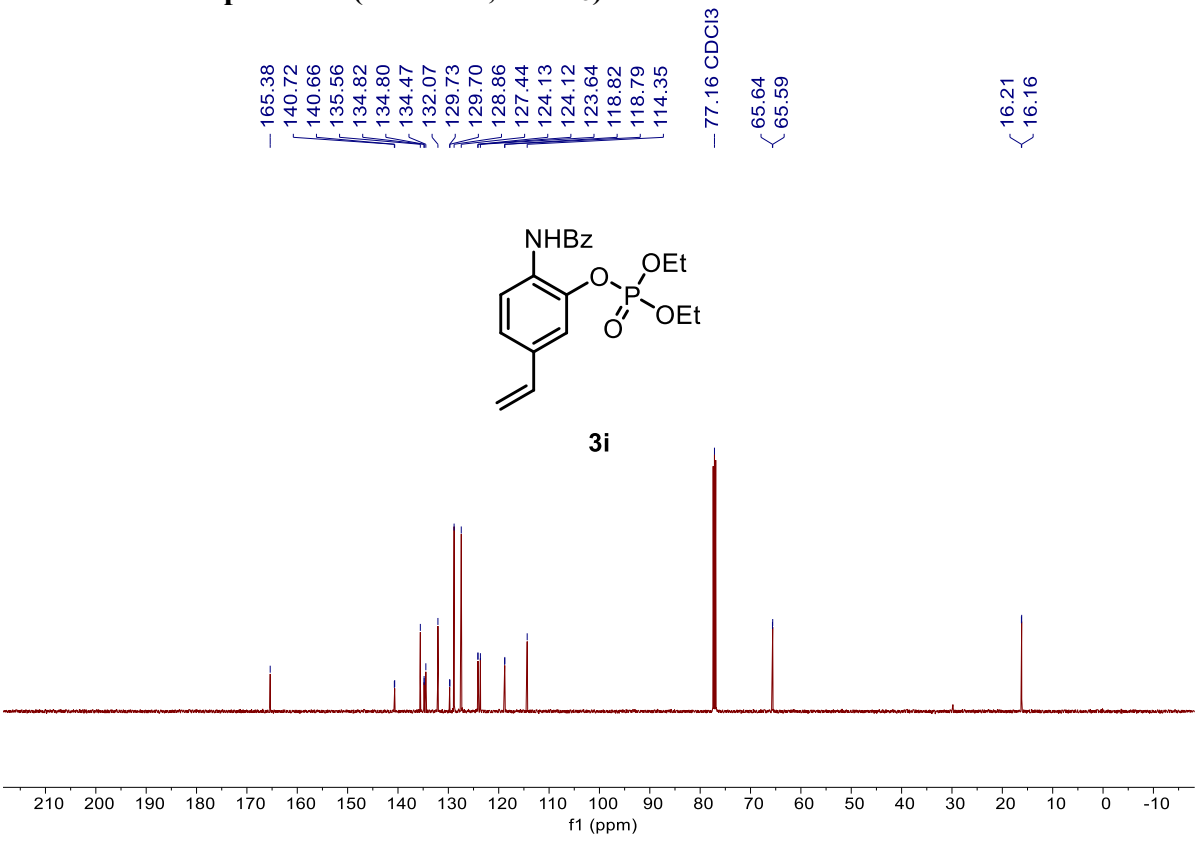


^{1}H NMR of Compound 3i (500 MHz, $CDCl_3$)



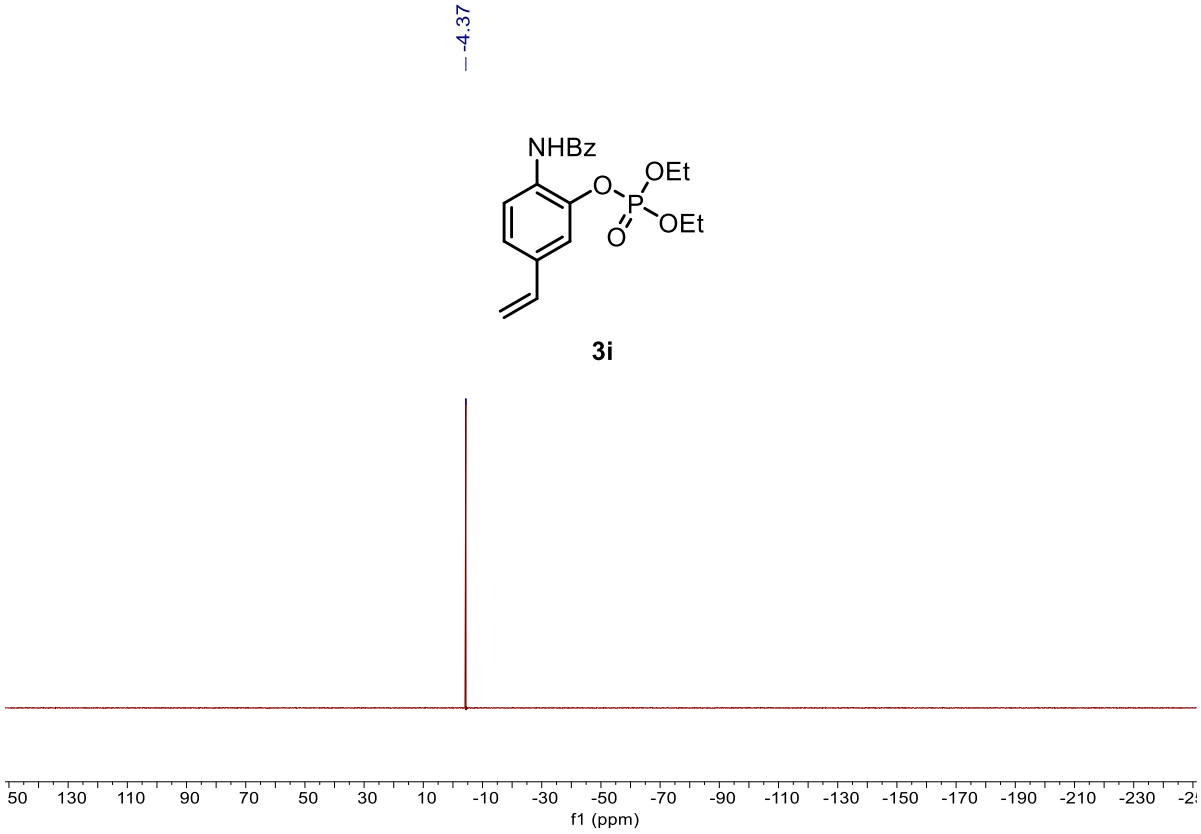
3i

^{13}C NMR of Compound 3i (126 MHz, $CDCl_3$)



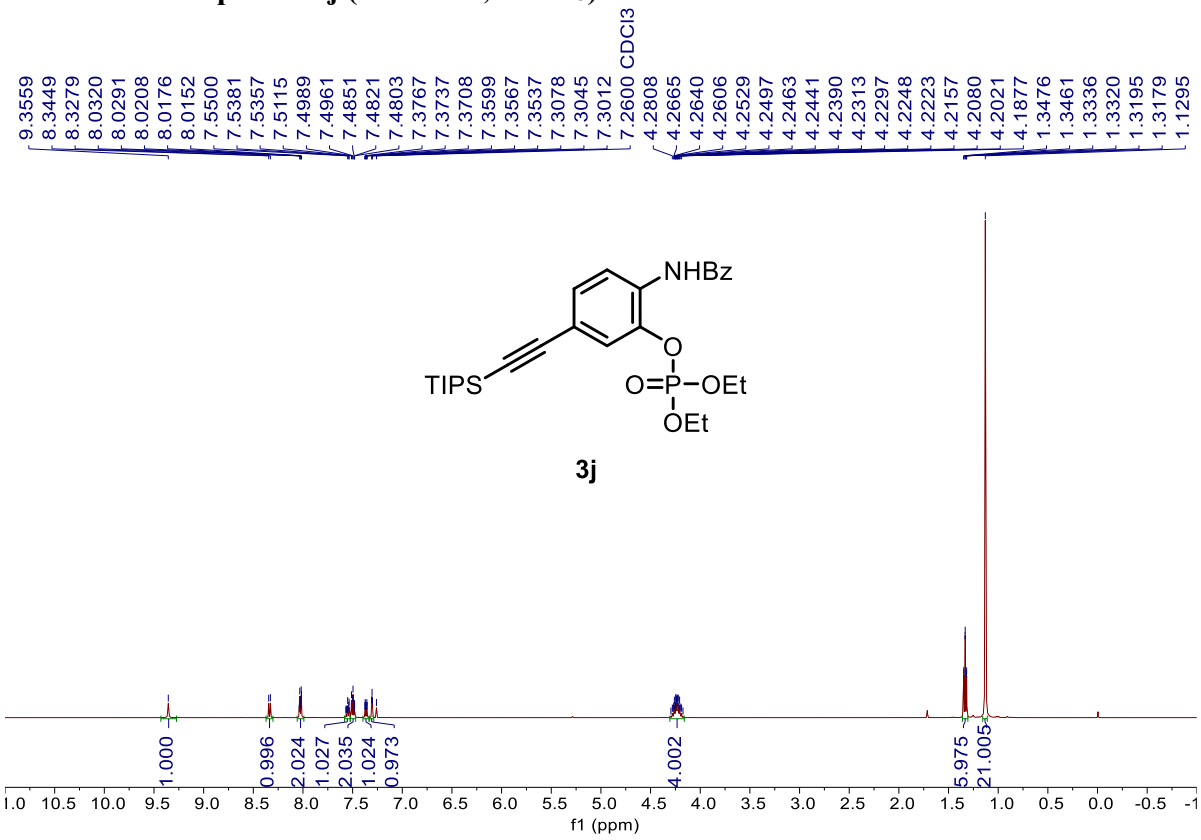
3i

^{31}P NMR of Compound 3i (202 MHz, $CDCl_3$)



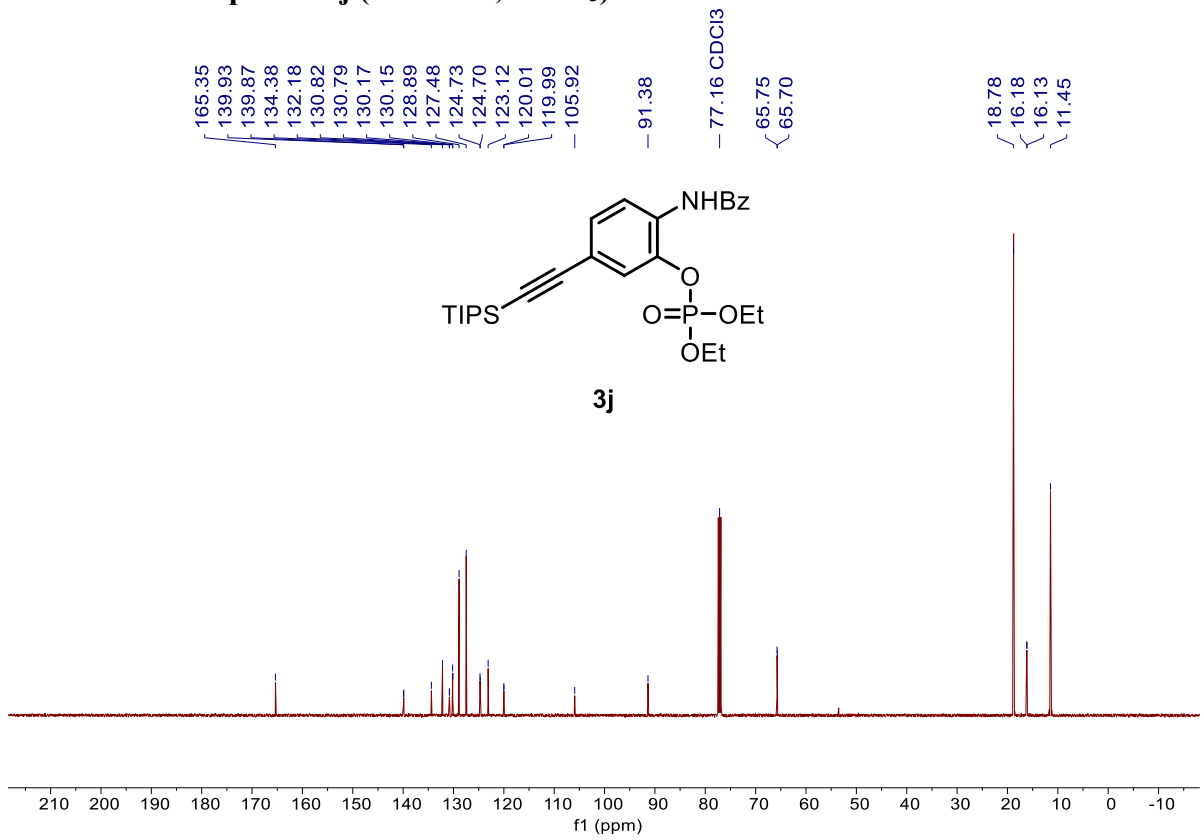
3i

^{1}H NMR of Compound 3j (500 MHz, $CDCl_3$)

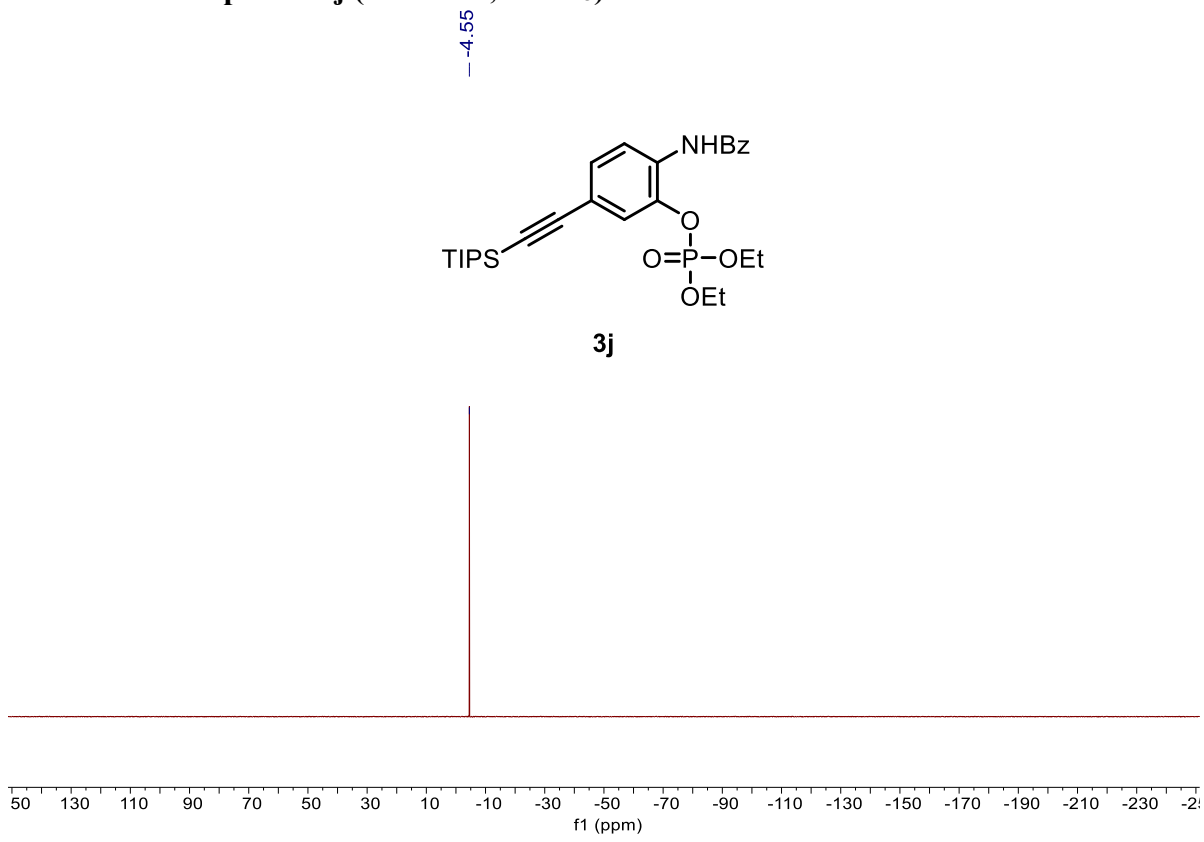


3j

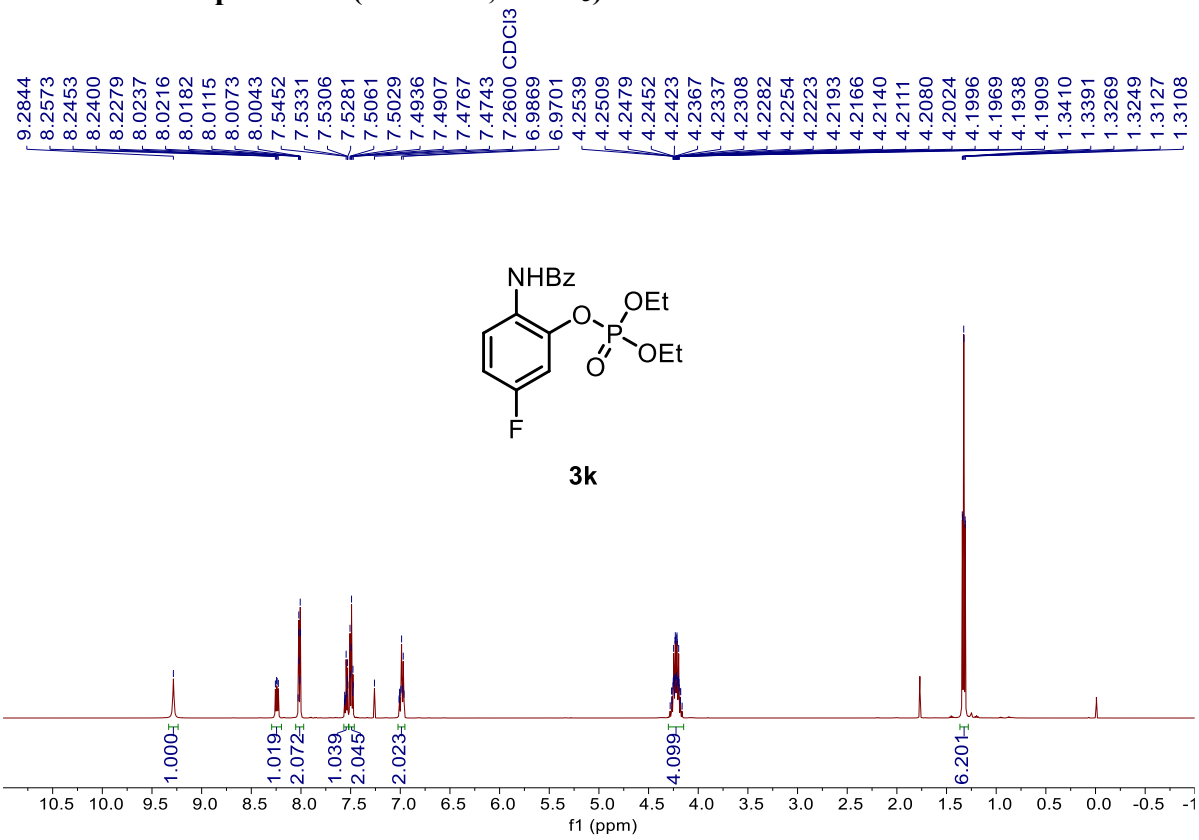
^{13}C NMR of Compound 3j (126 MHz, $CDCl_3$)



^{31}P NMR of Compound 3j (202 MHz, $CDCl_3$)

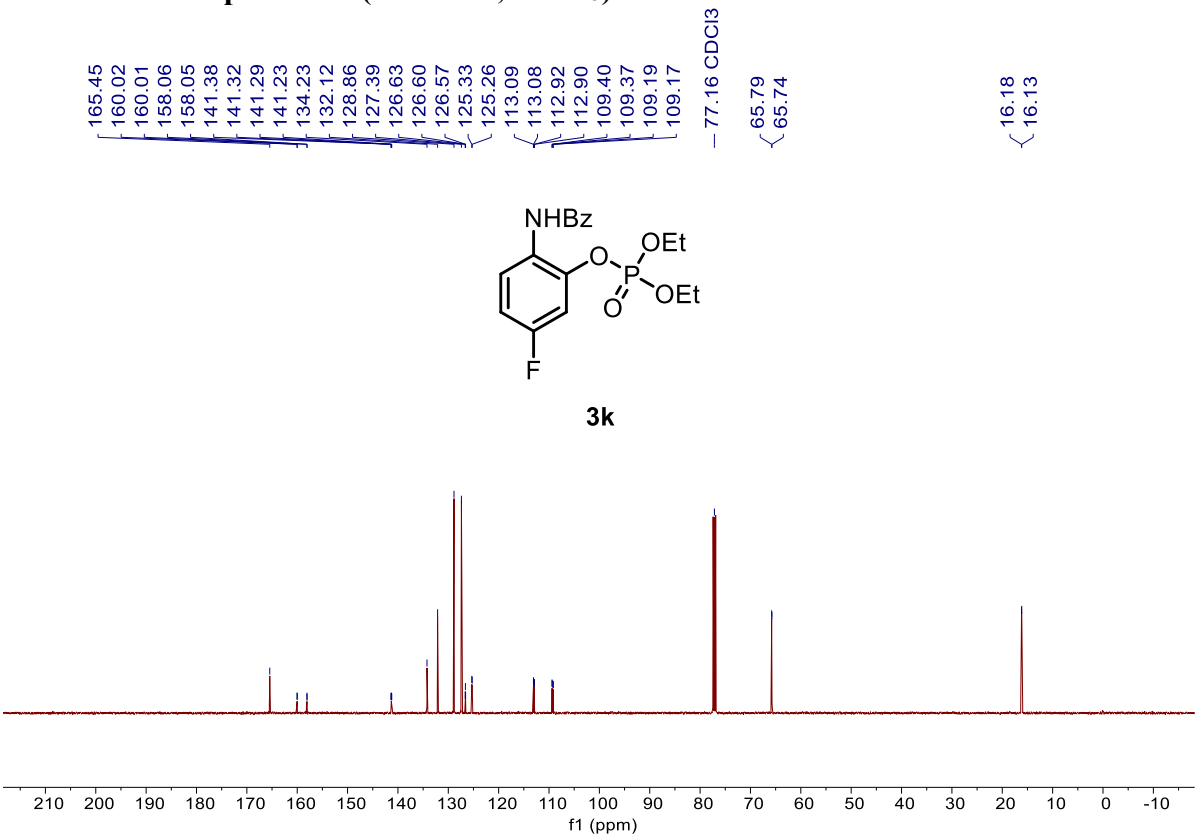


^{1}H NMR of Compound 3k (500 MHz, $CDCl_3$)



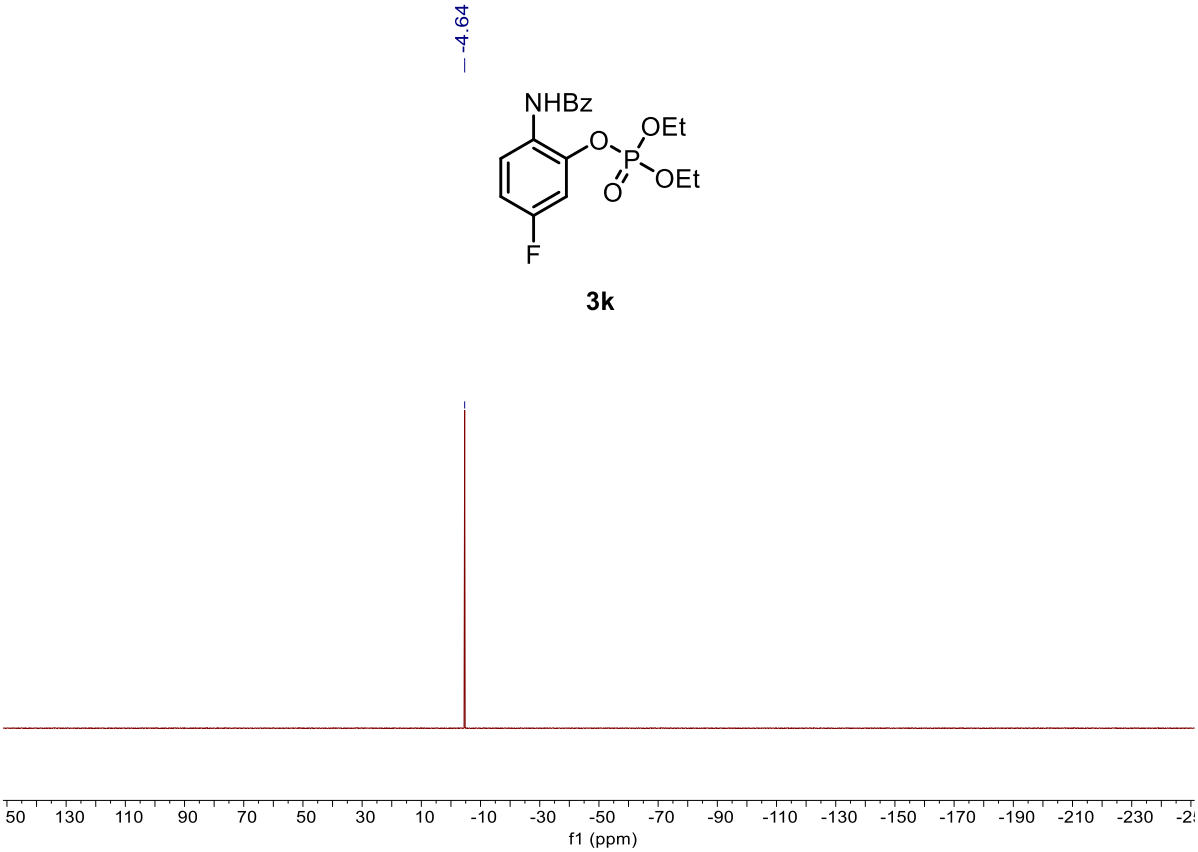
3k

^{13}C NMR of Compound 3k (126 MHz, $CDCl_3$)



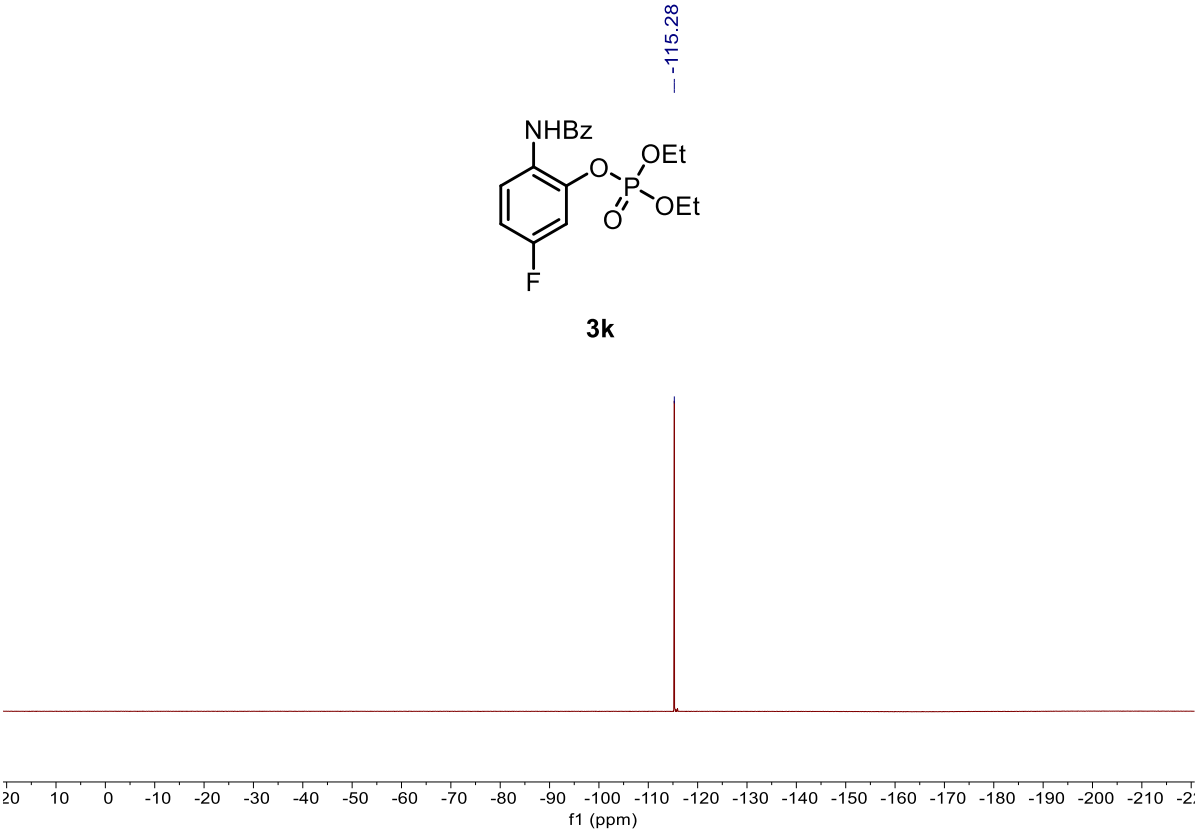
3k

^{31}P NMR of Compound 3k (202 MHz, $CDCl_3$)



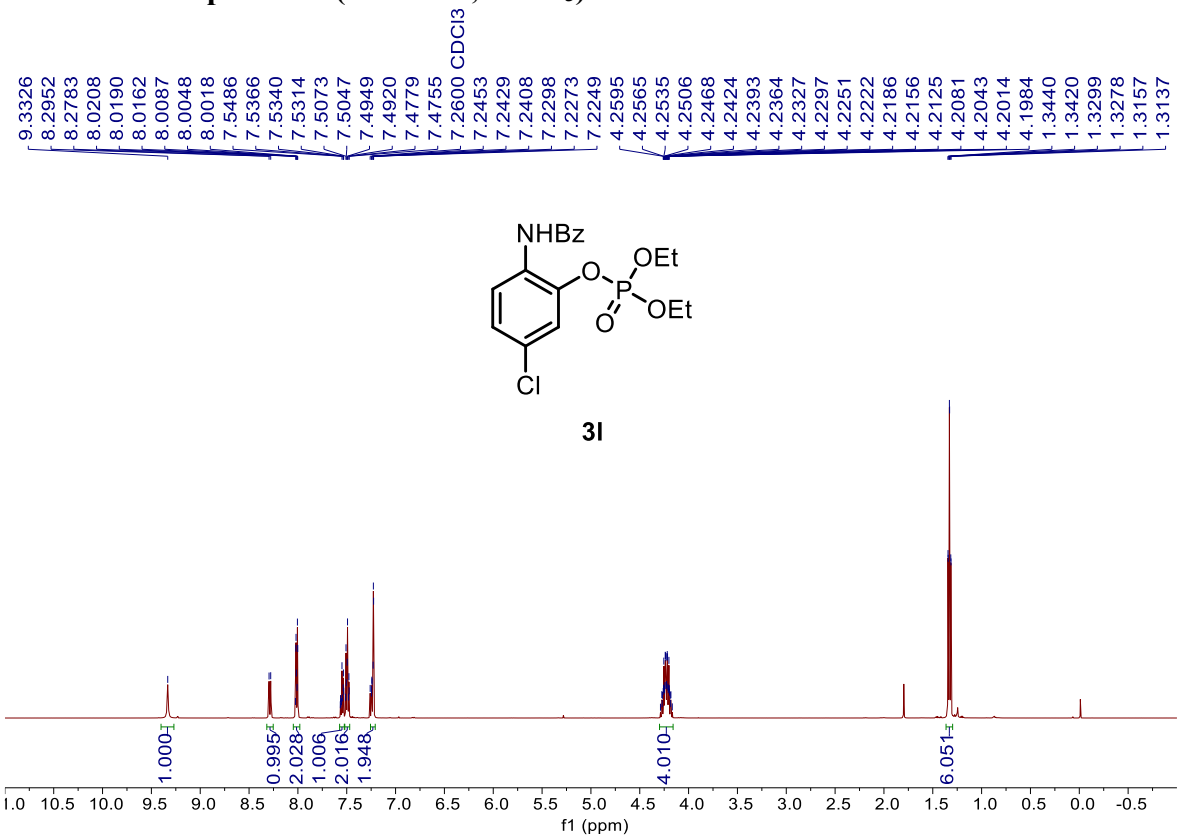
3k

^{19}F NMR of Compound 3k (471 MHz, $CDCl_3$)



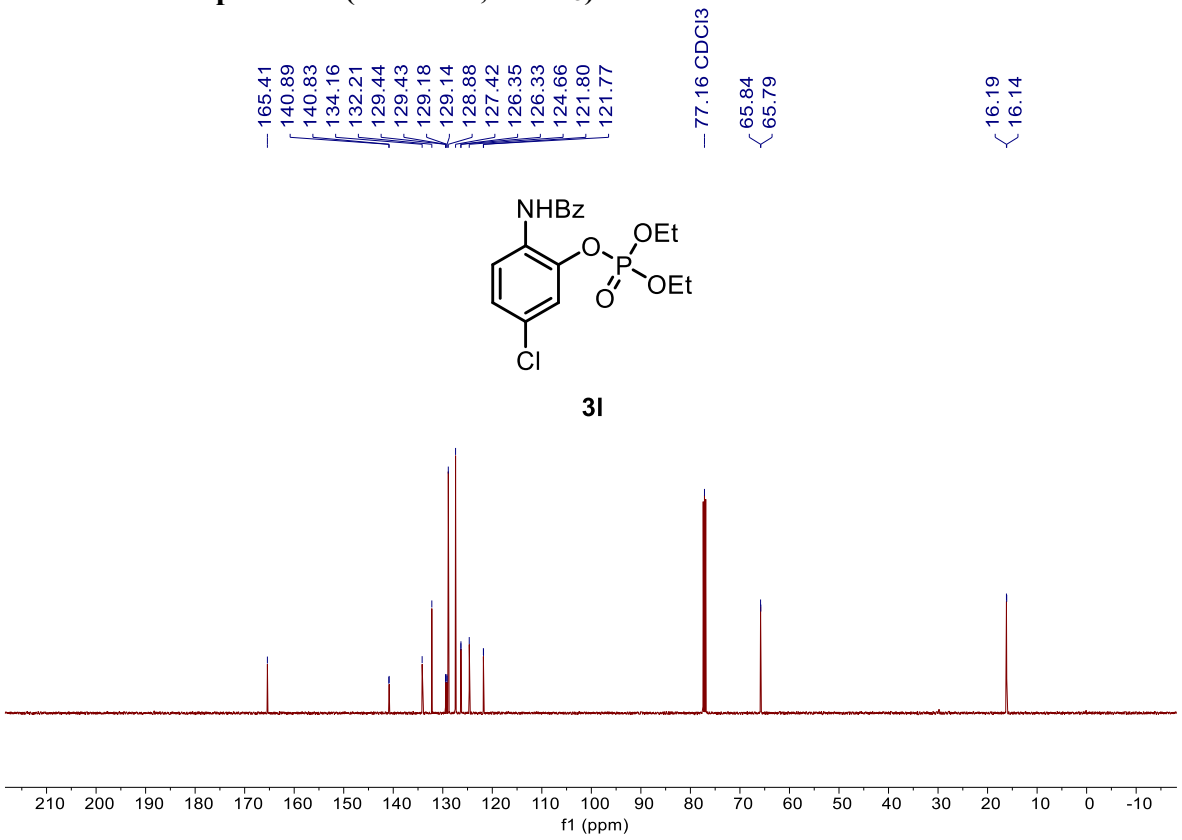
3k

^{1}H NMR of Compound 3l (500 MHz, $CDCl_3$)



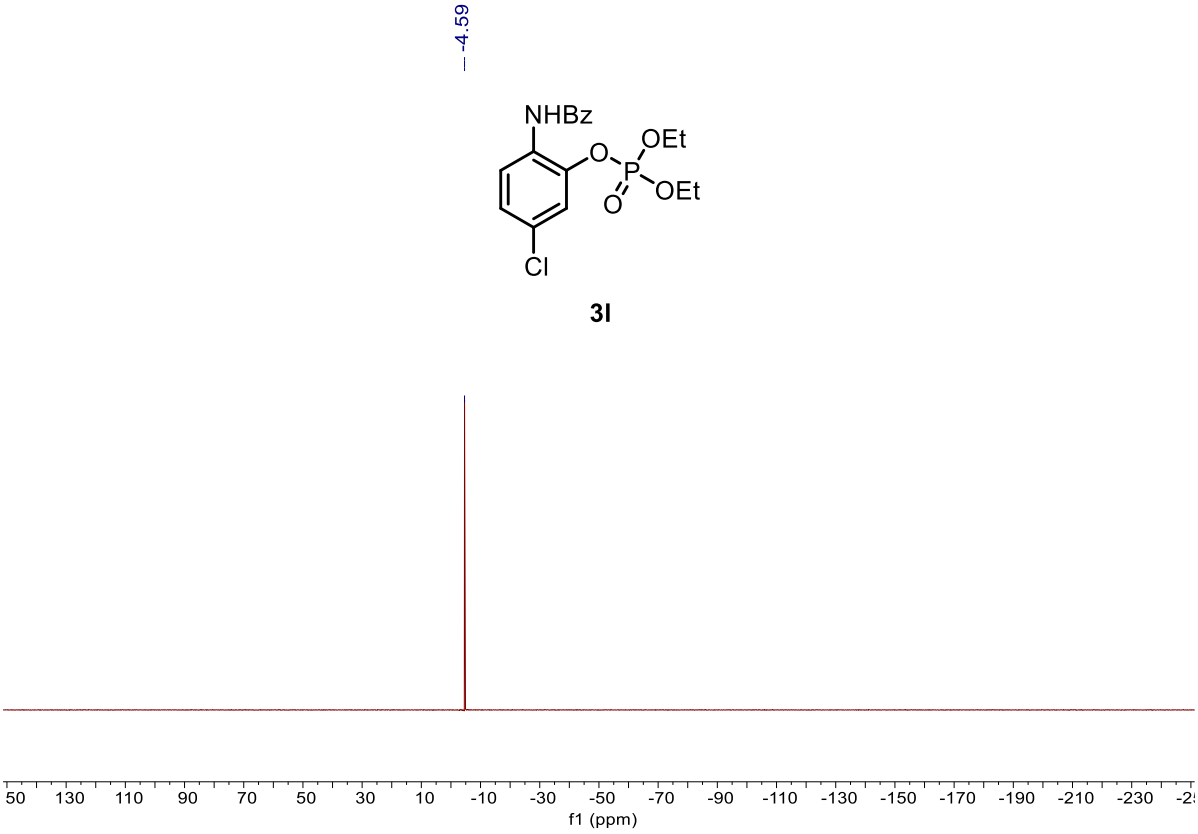
3l

^{13}C NMR of Compound 3l (126 MHz, $CDCl_3$)



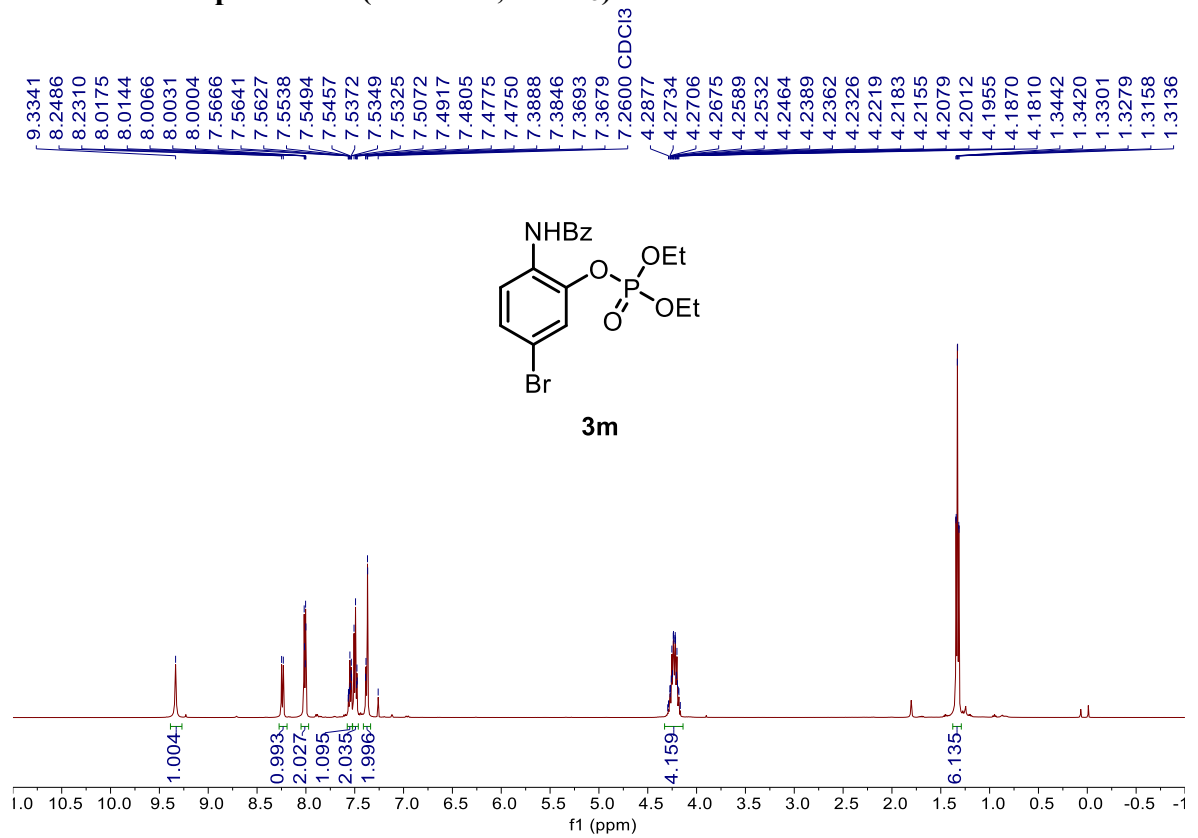
3l

^{31}P NMR of Compound 3l (202 MHz, $CDCl_3$)



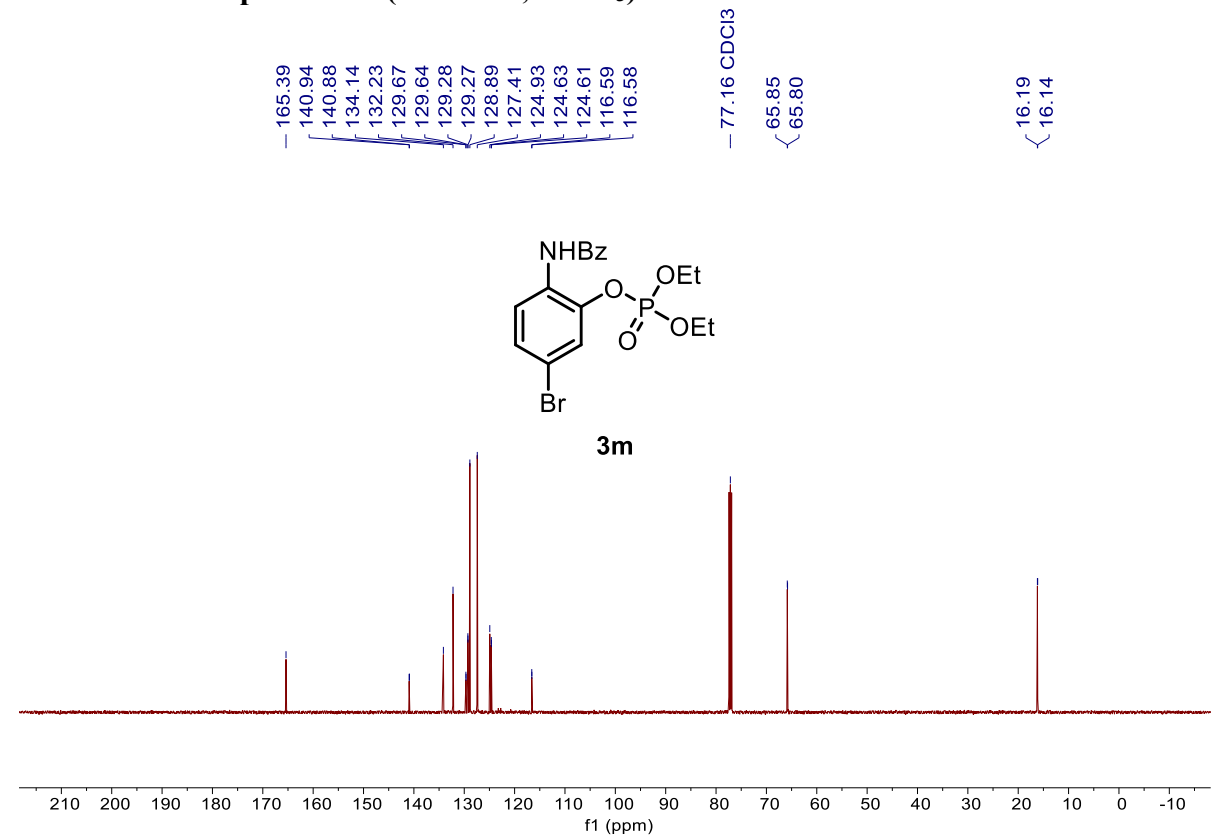
3l

^{1}H NMR of Compound 3m (500 MHz, $CDCl_3$)

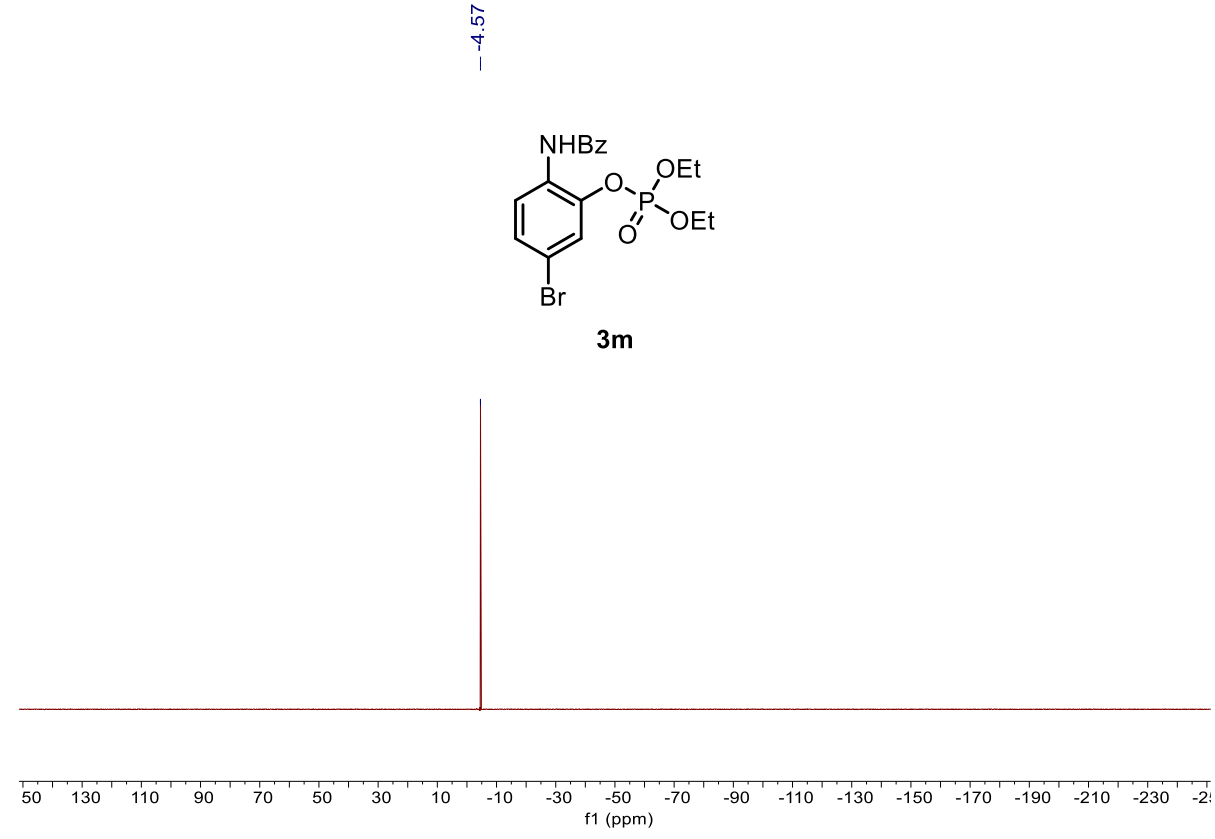


3m

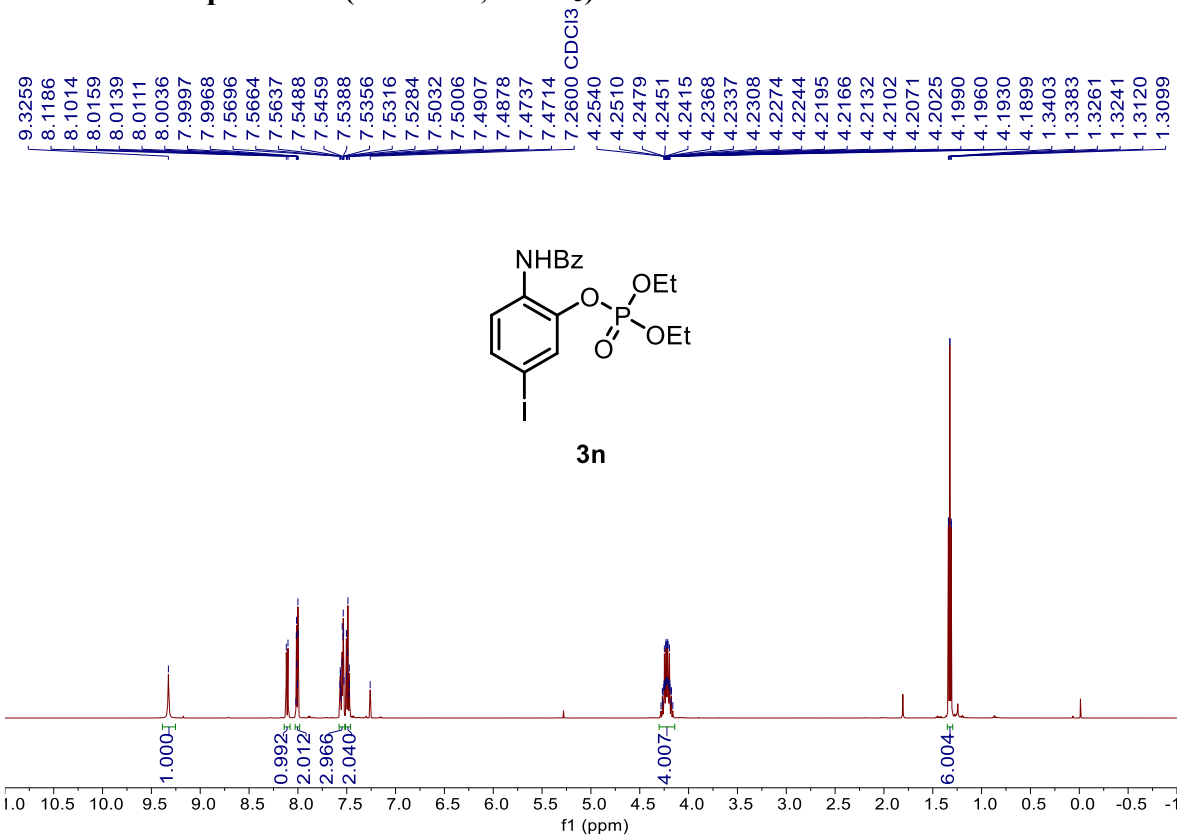
^{13}C NMR of Compound 3m (126 MHz, $CDCl_3$)



^{31}P NMR of Compound 3m (202 MHz, $CDCl_3$)

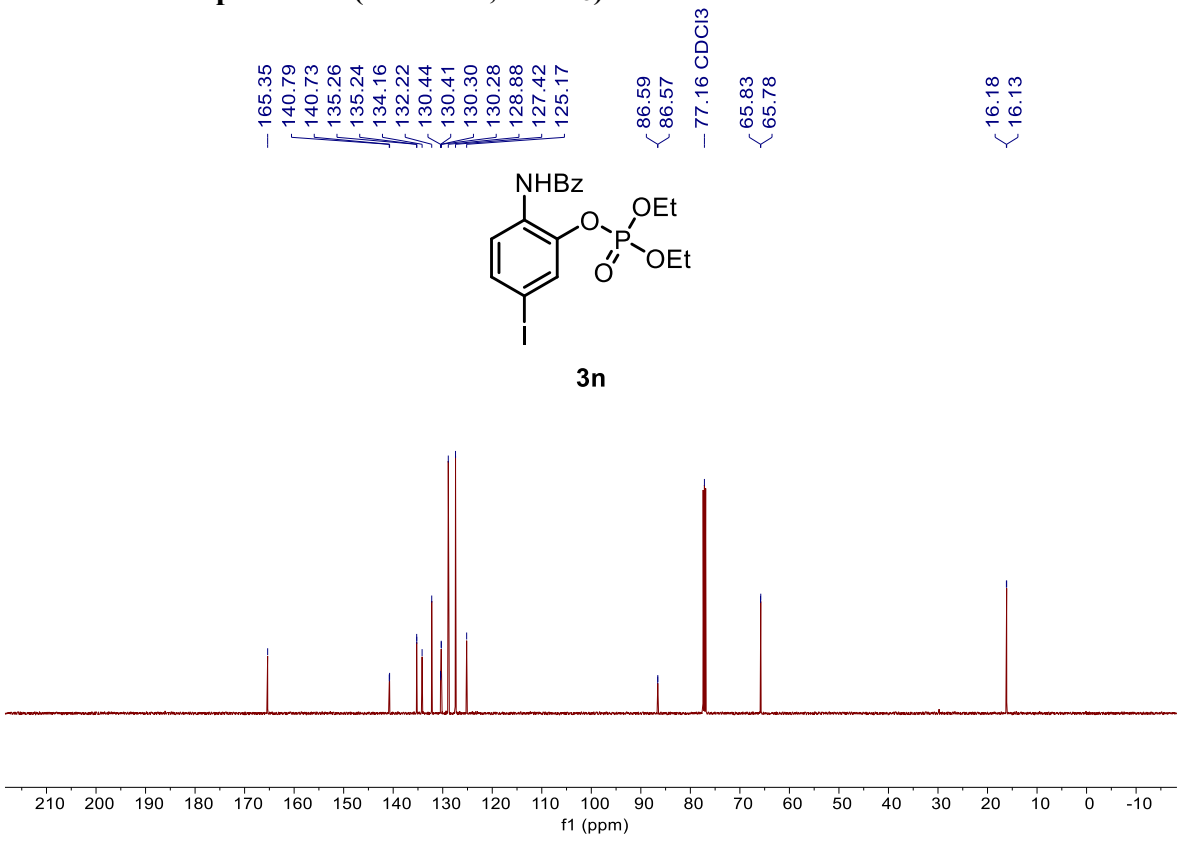


^{1}H NMR of Compound 3n (500 MHz, $CDCl_3$)



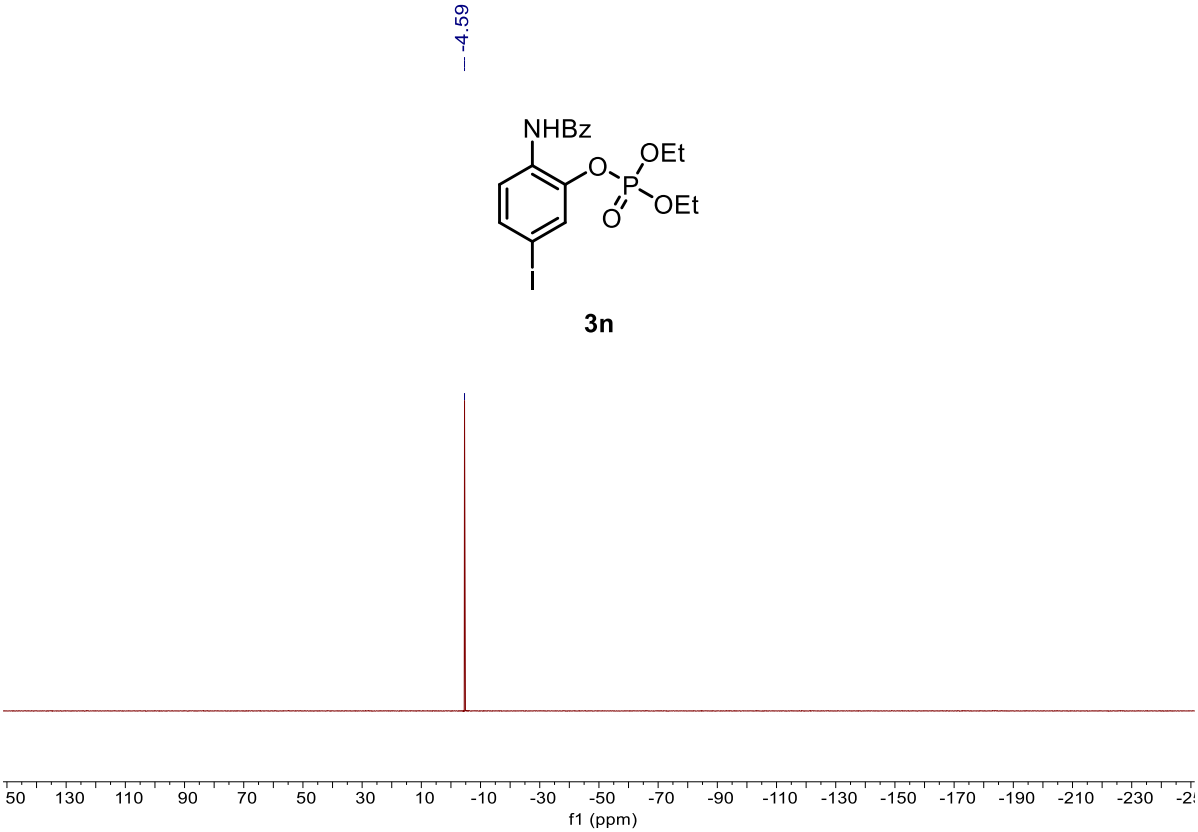
3n

^{13}C NMR of Compound 3n (126 MHz, $CDCl_3$)

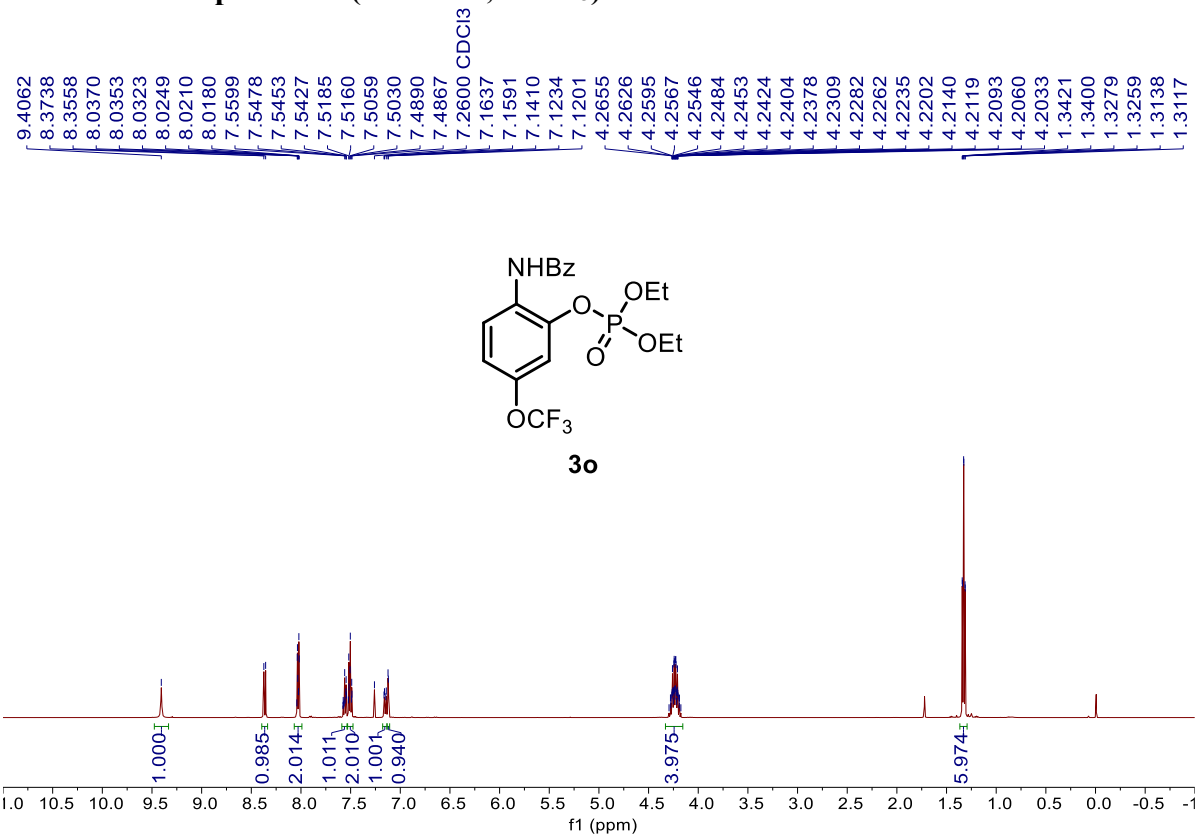


3n

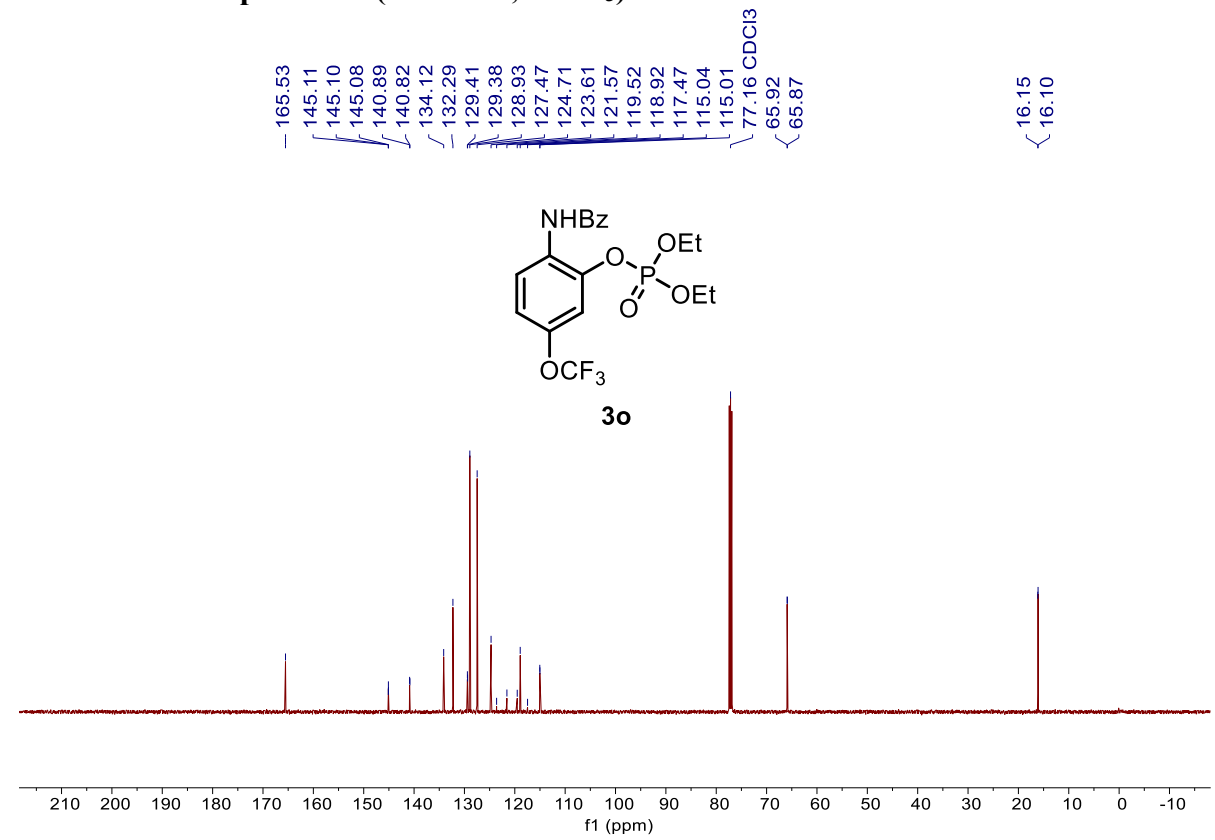
^{31}P NMR of Compound 3n (202 MHz, $CDCl_3$)



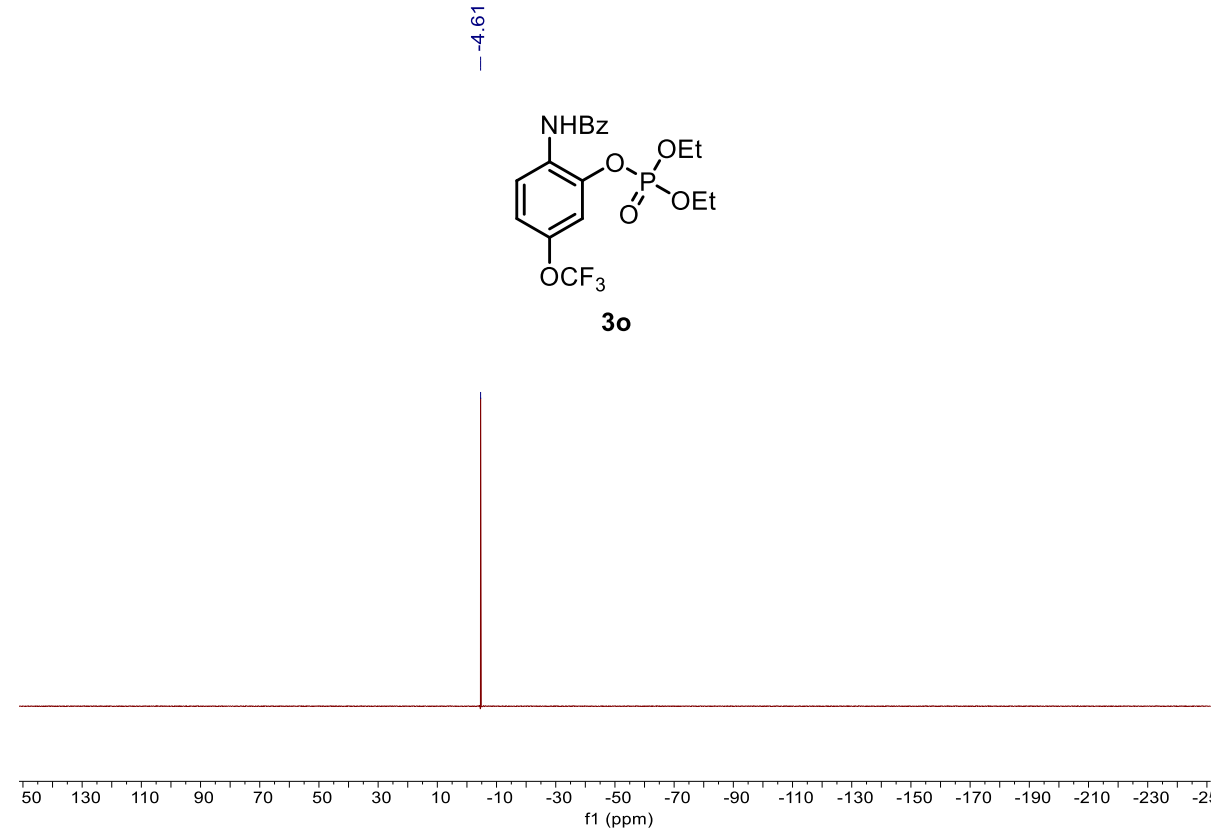
^{1}H NMR of Compound 3o (500 MHz, $CDCl_3$)



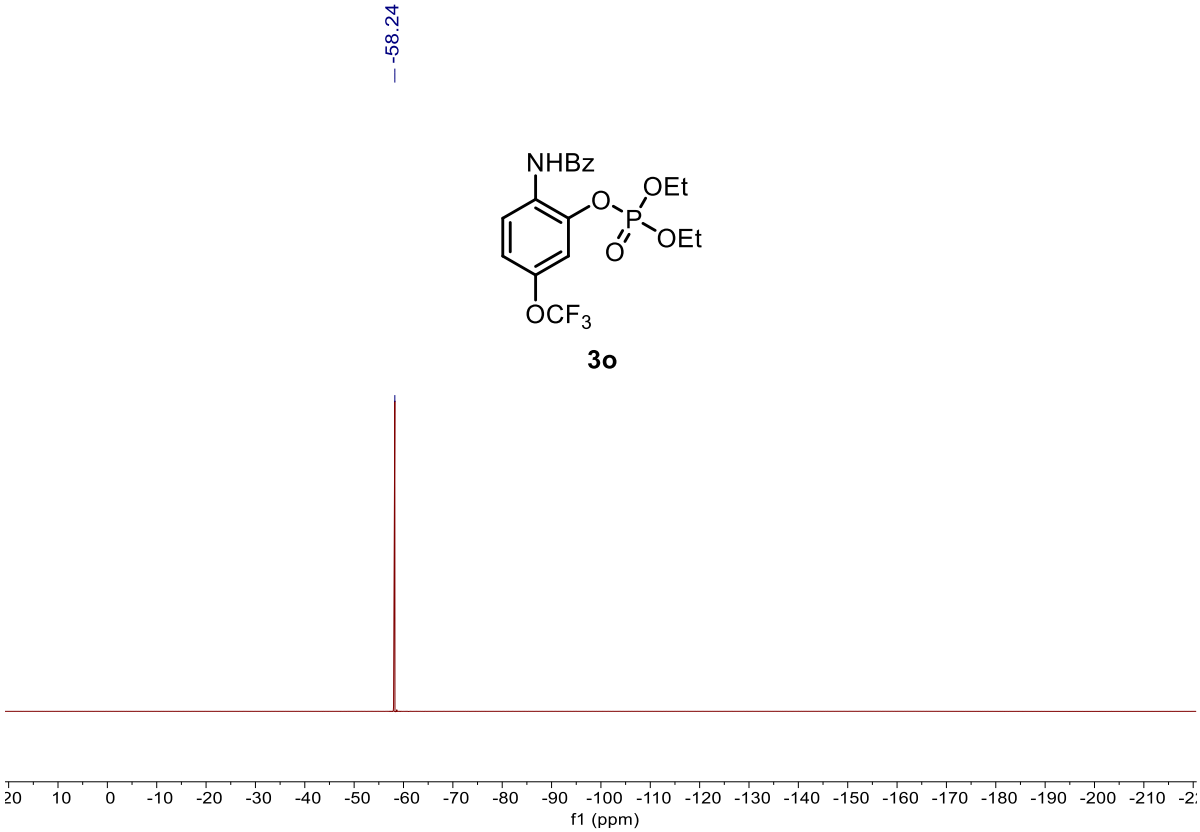
^{13}C NMR of Compound 3o (126 MHz, $CDCl_3$)



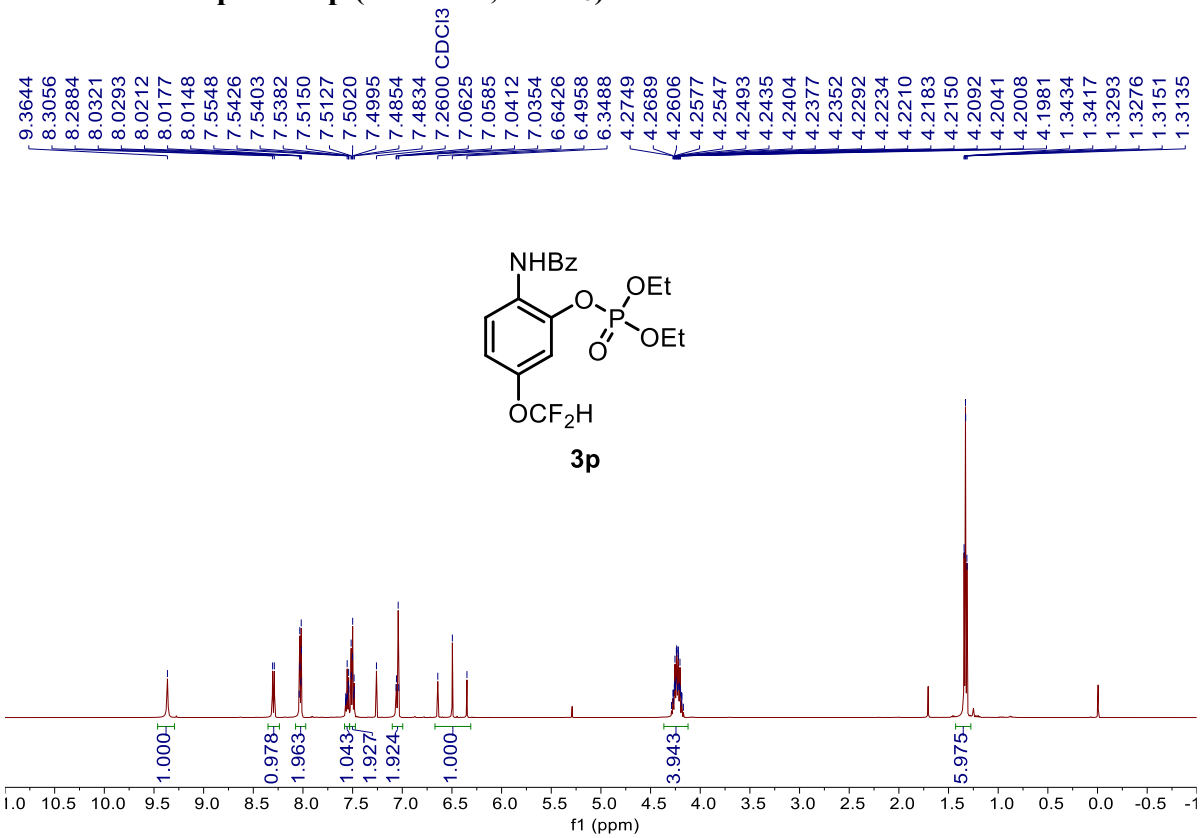
^{31}P NMR of Compound 3o (202 MHz, $CDCl_3$)



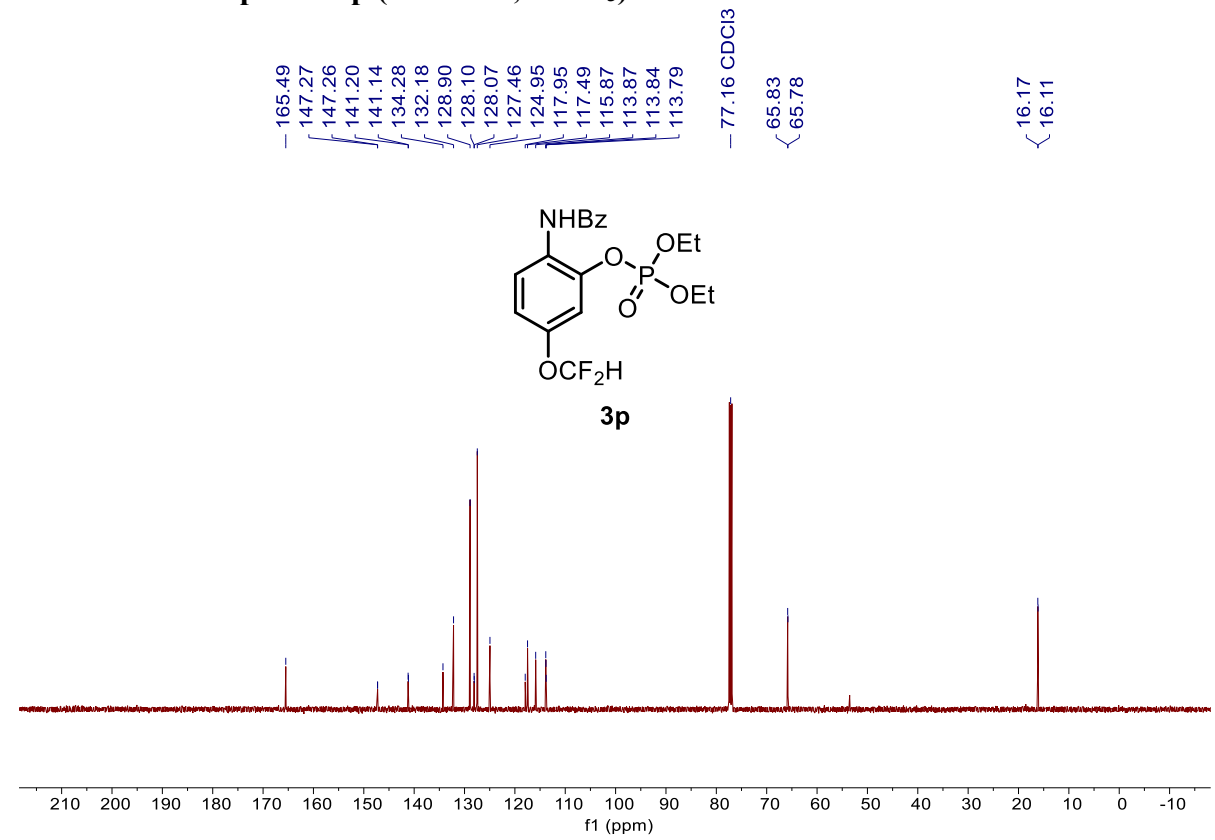
^{19}F NMR of Compound 3o (471 MHz, $CDCl_3$)



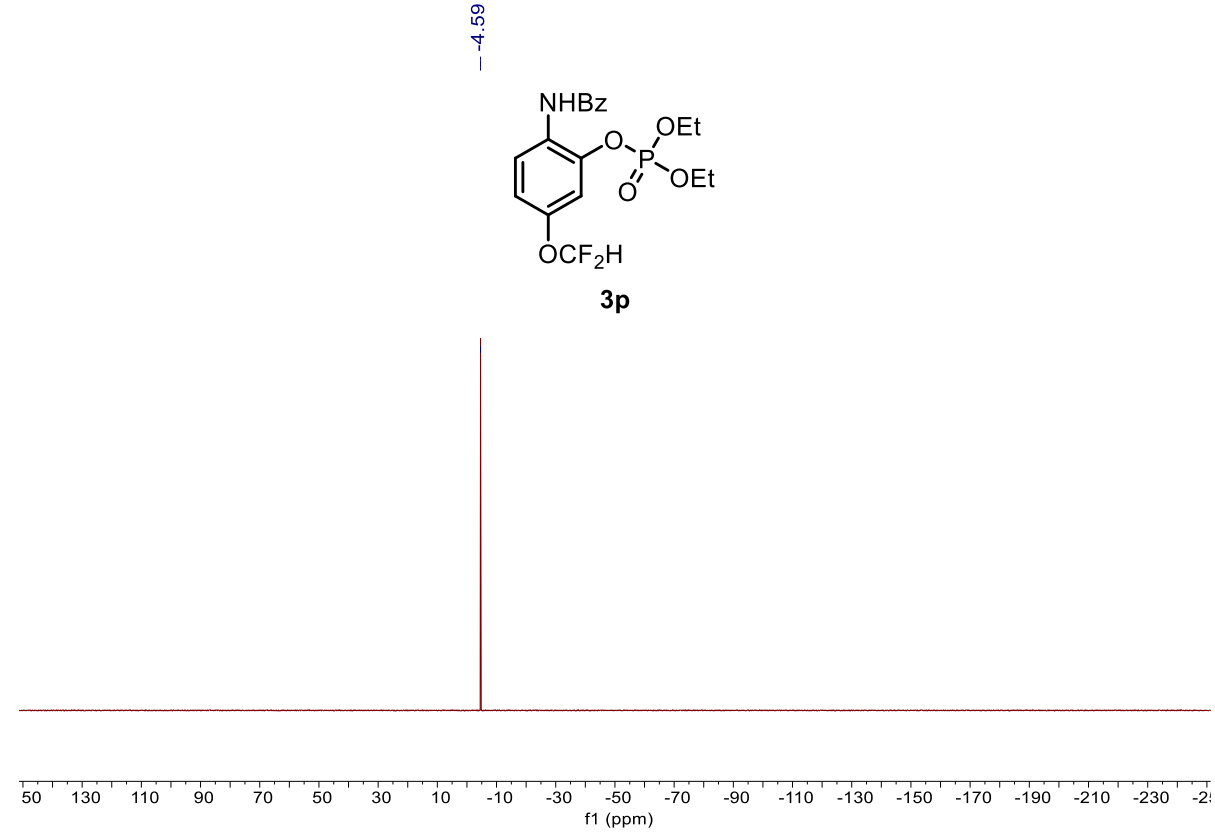
^{1}H NMR of Compound 3p (500 MHz, $CDCl_3$)



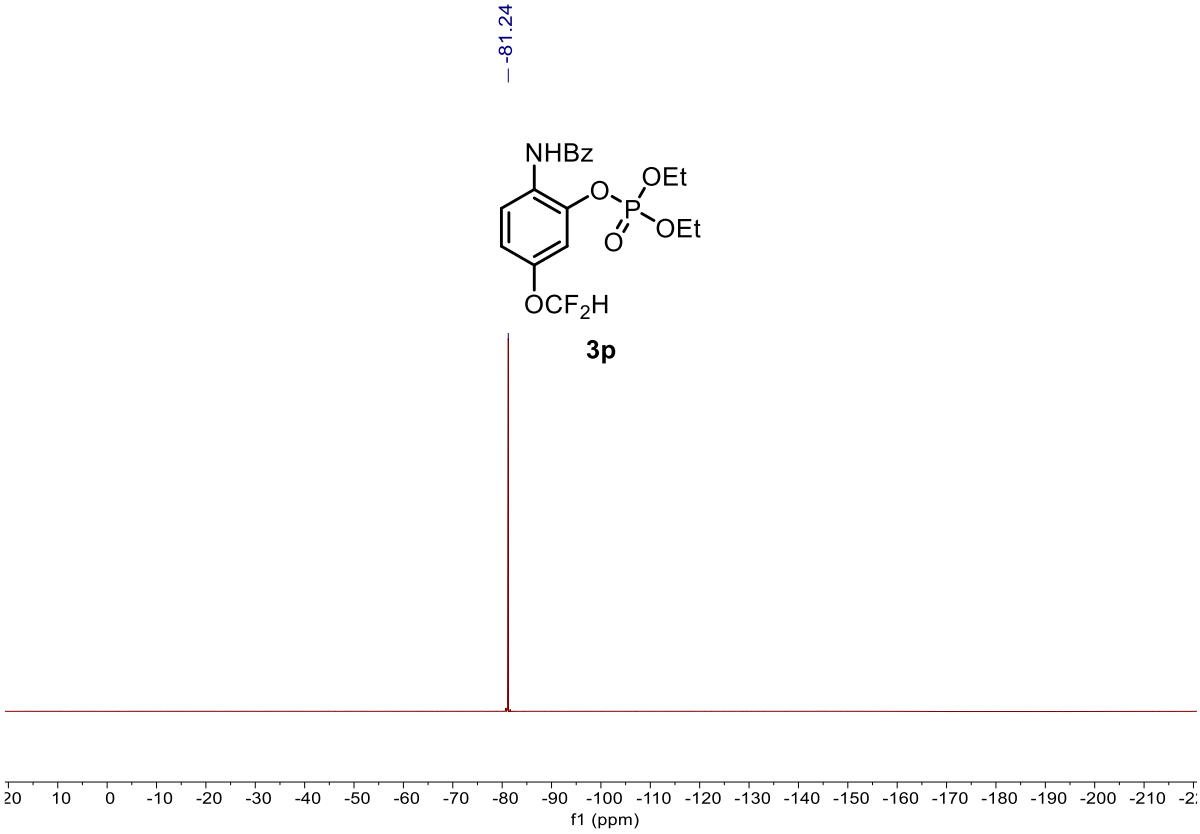
^{13}C NMR of Compound 3p (126 MHz, $CDCl_3$)



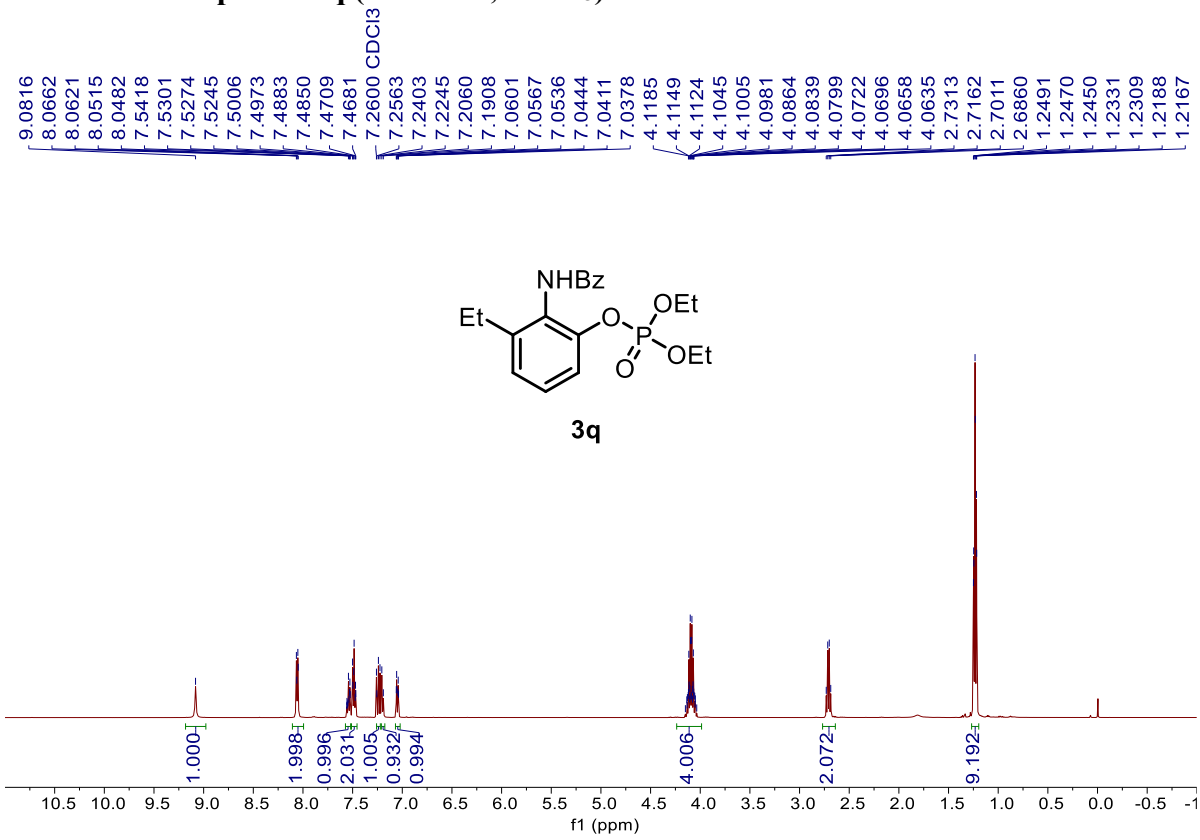
^{31}P NMR of Compound 3p (202 MHz, $CDCl_3$)



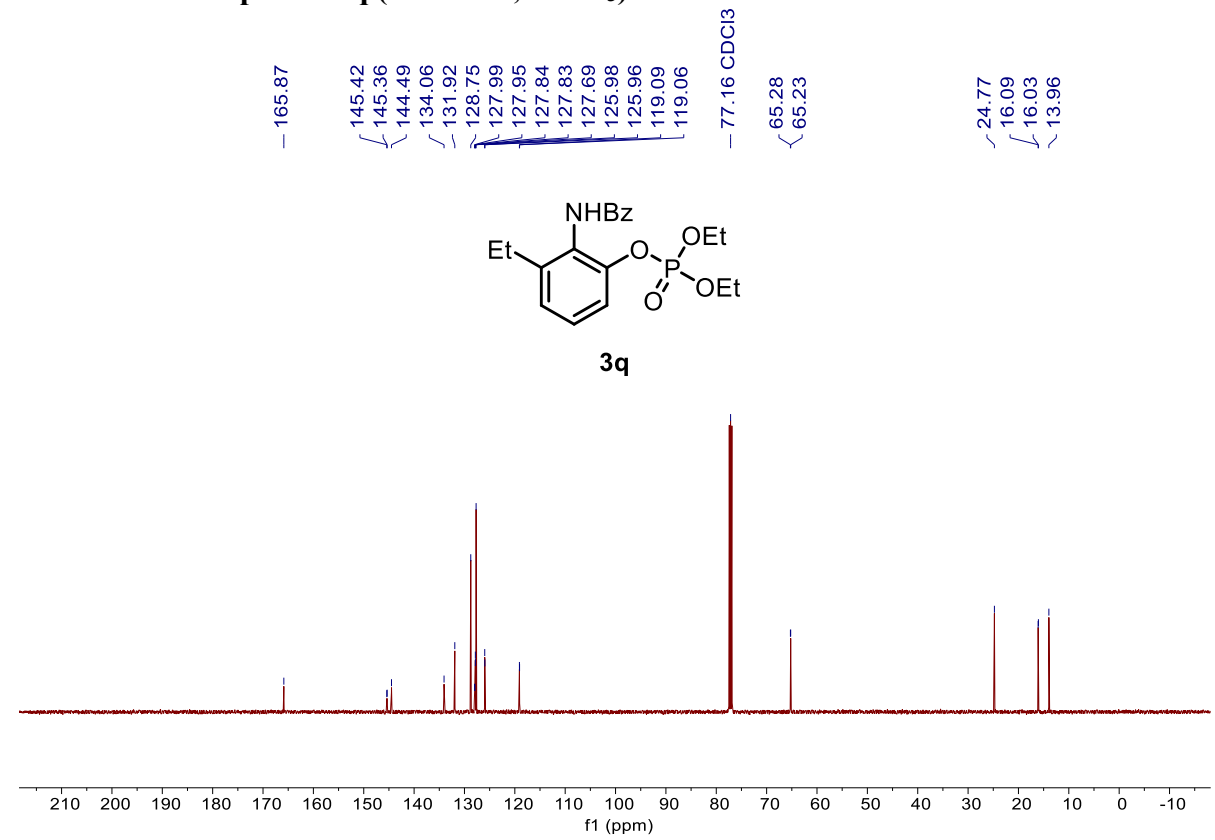
^{19}F NMR of Compound 3p (471 MHz, $CDCl_3$)



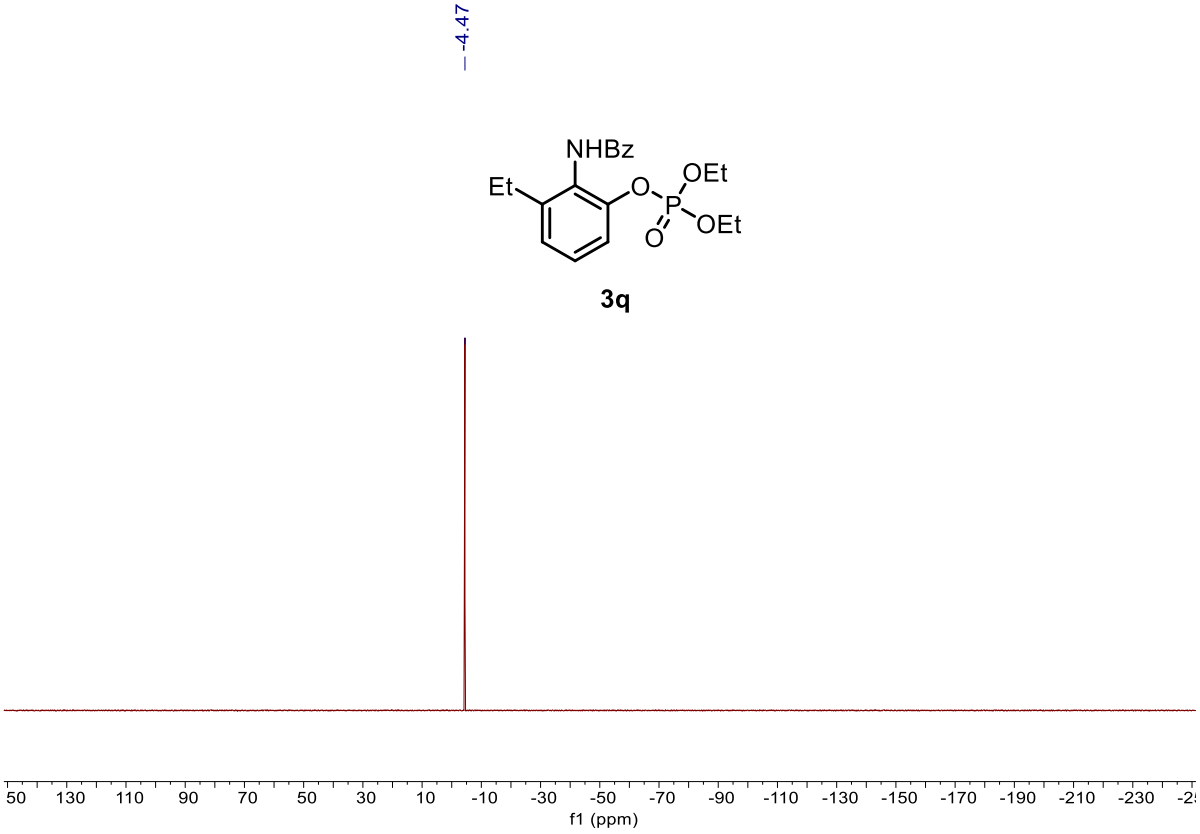
^{1}H NMR of Compound 3q (500 MHz, $CDCl_3$)



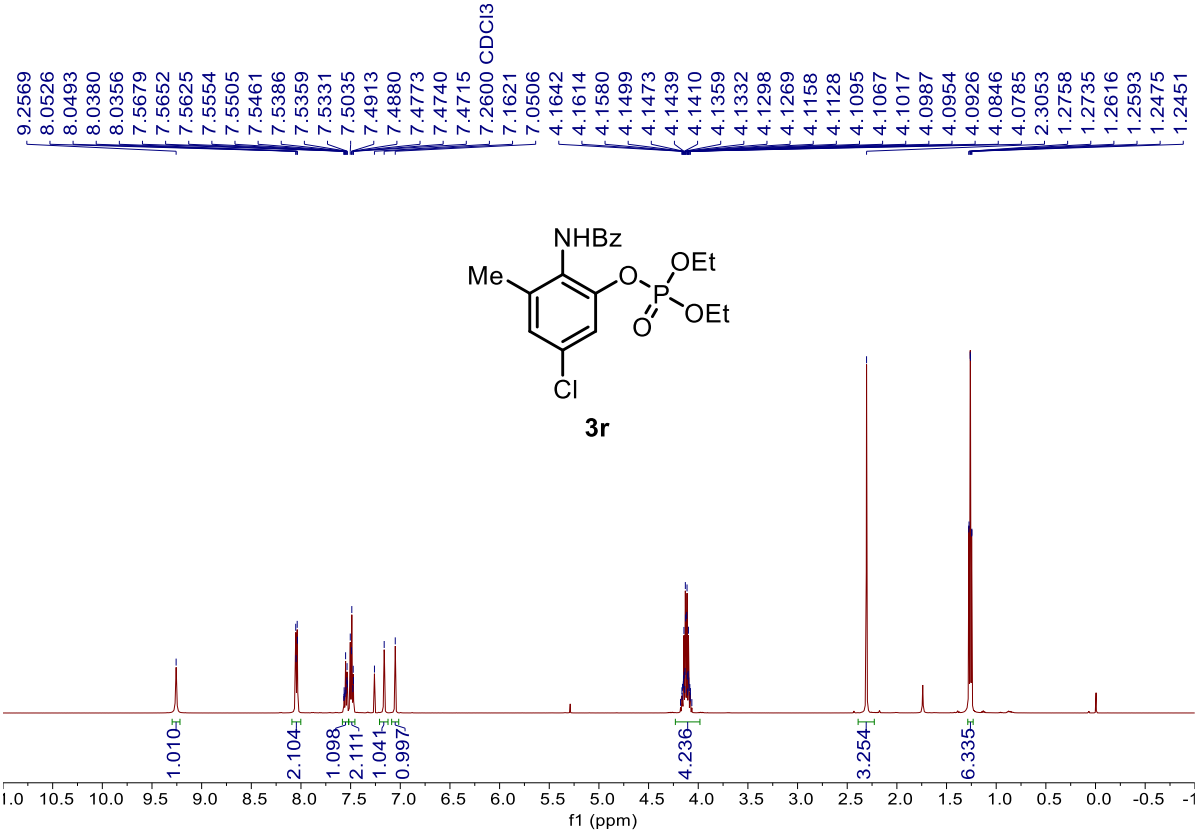
^{13}C NMR of Compound 3q (126 MHz, $CDCl_3$)



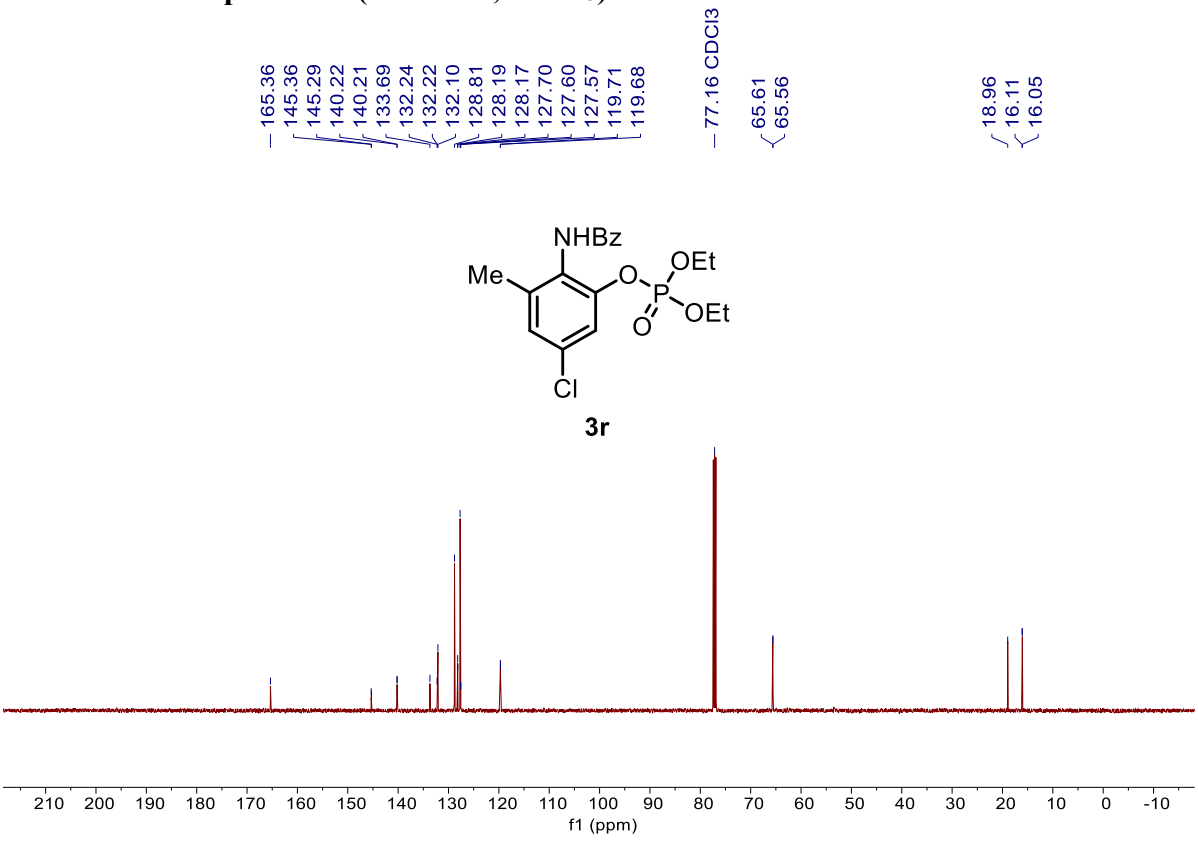
^{31}P NMR of Compound 3q (202 MHz, $CDCl_3$)



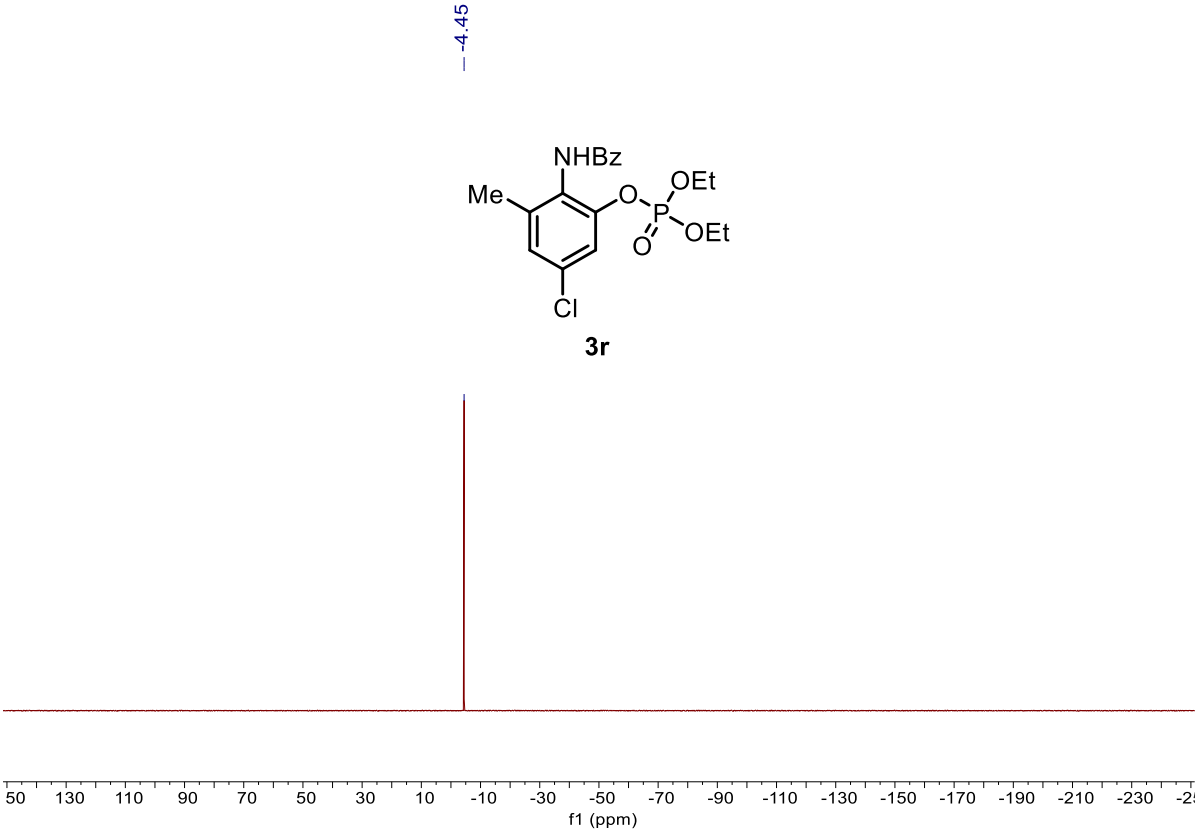
^{1}H NMR of Compound 3r (500 MHz, $CDCl_3$)



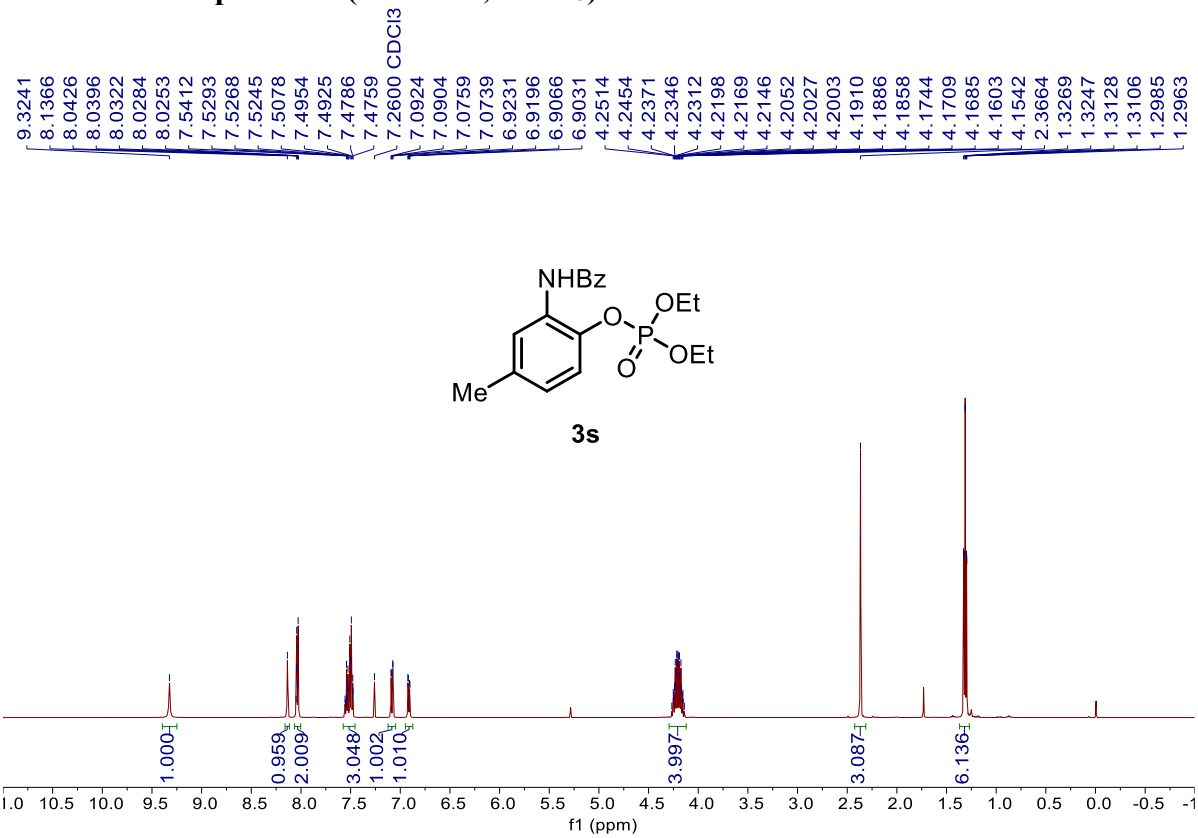
^{13}C NMR of Compound 3r (126 MHz, $CDCl_3$)



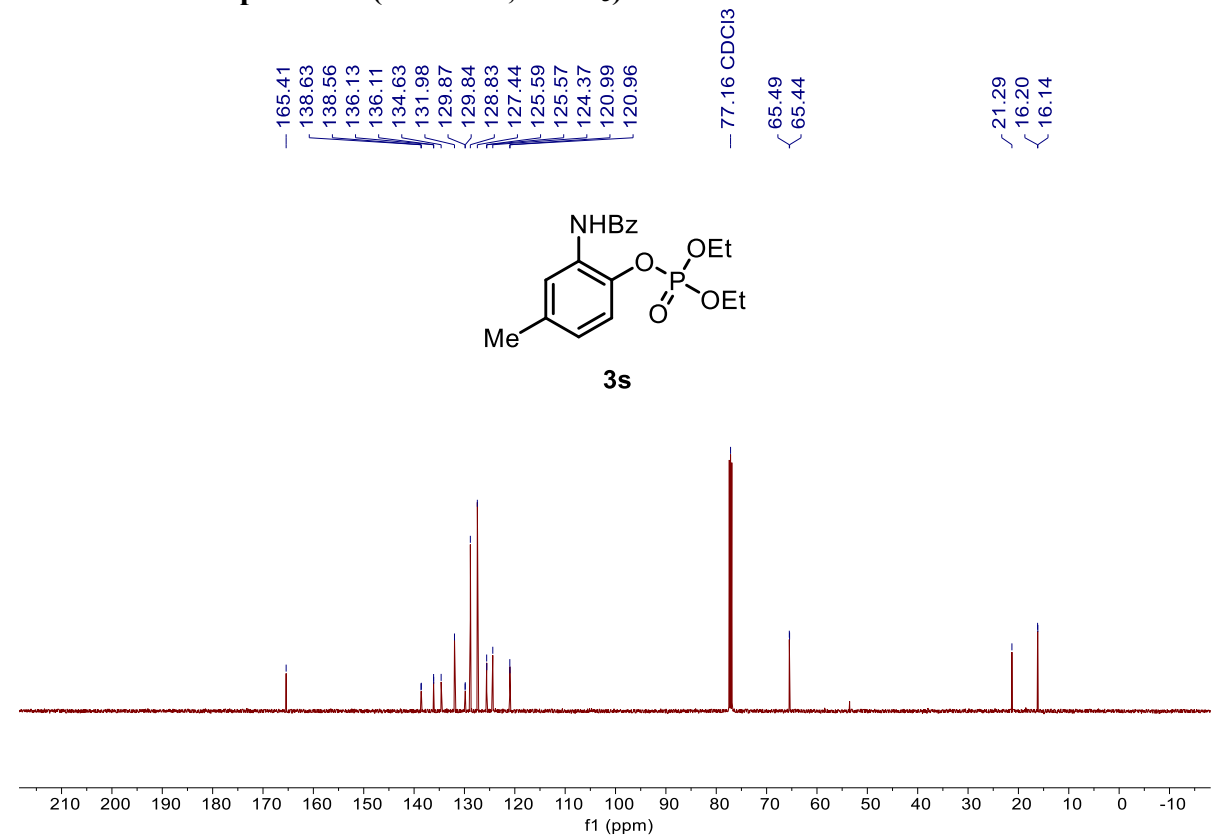
^{31}P NMR of Compound 3r (202 MHz, $CDCl_3$)



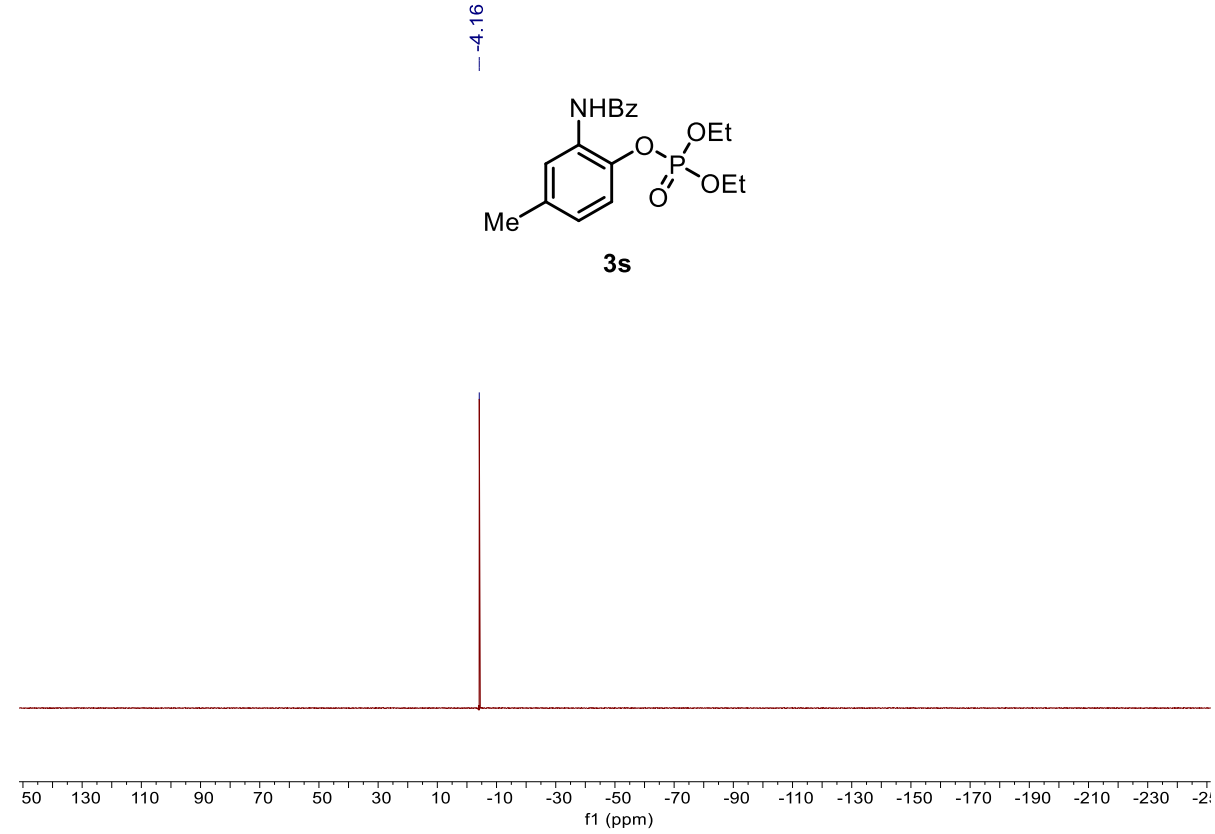
^{1}H NMR of Compound 3s (500 MHz, $CDCl_3$)



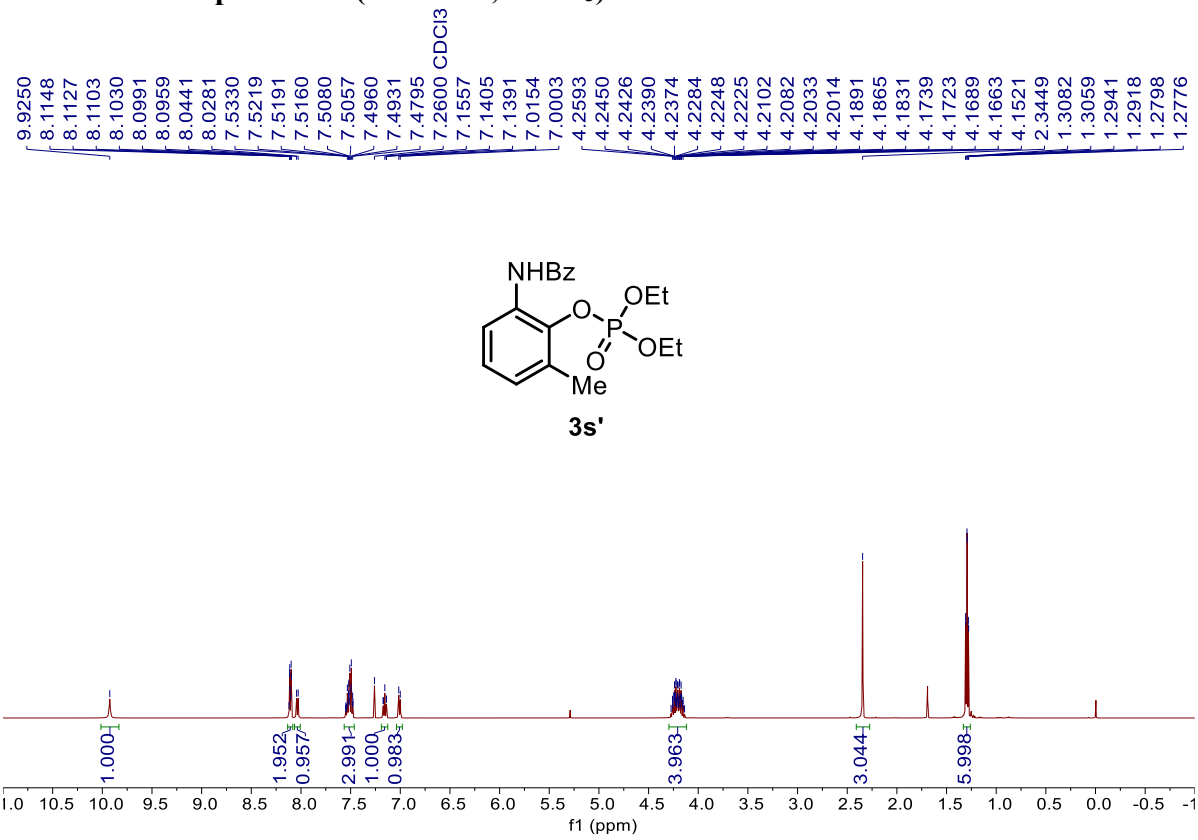
^{13}C NMR of Compound 3s (126 MHz, $CDCl_3$)



^{31}P NMR of Compound 3s (202 MHz, $CDCl_3$)

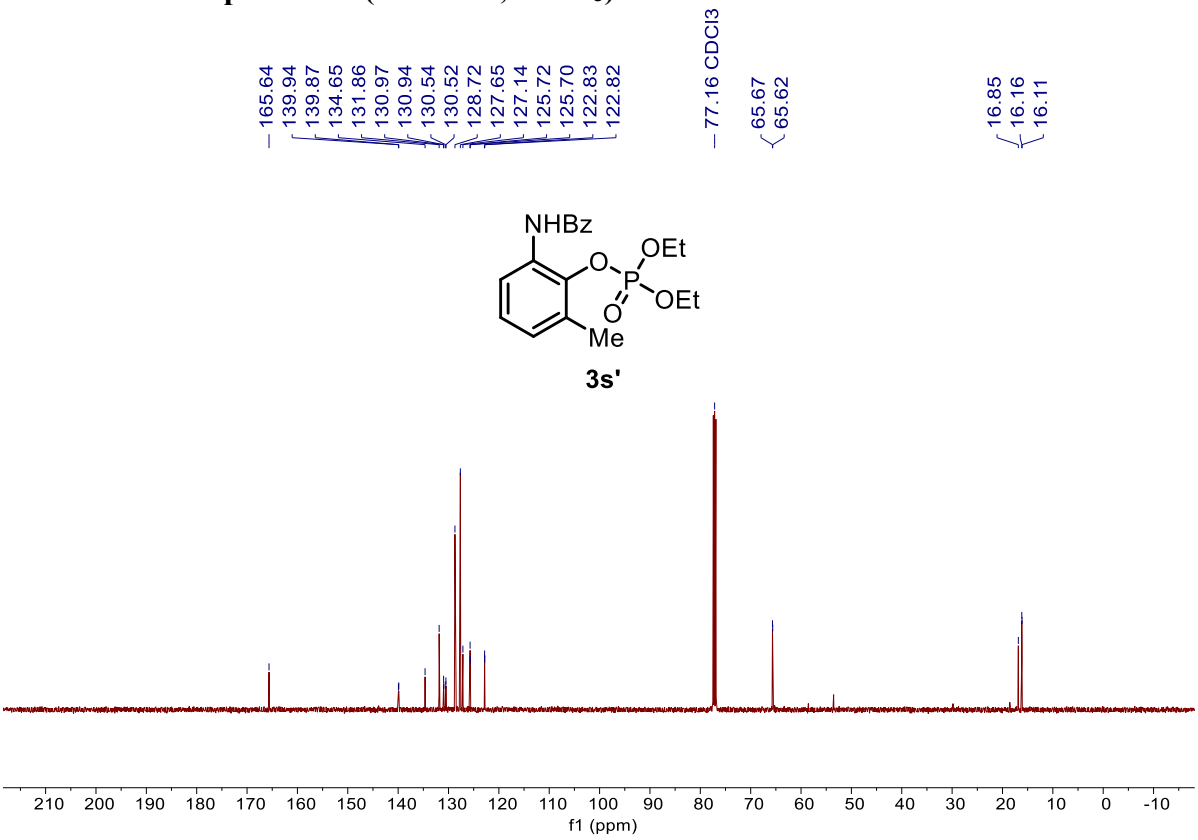


^{1}H NMR of Compound 3s' (500 MHz, $CDCl_3$)



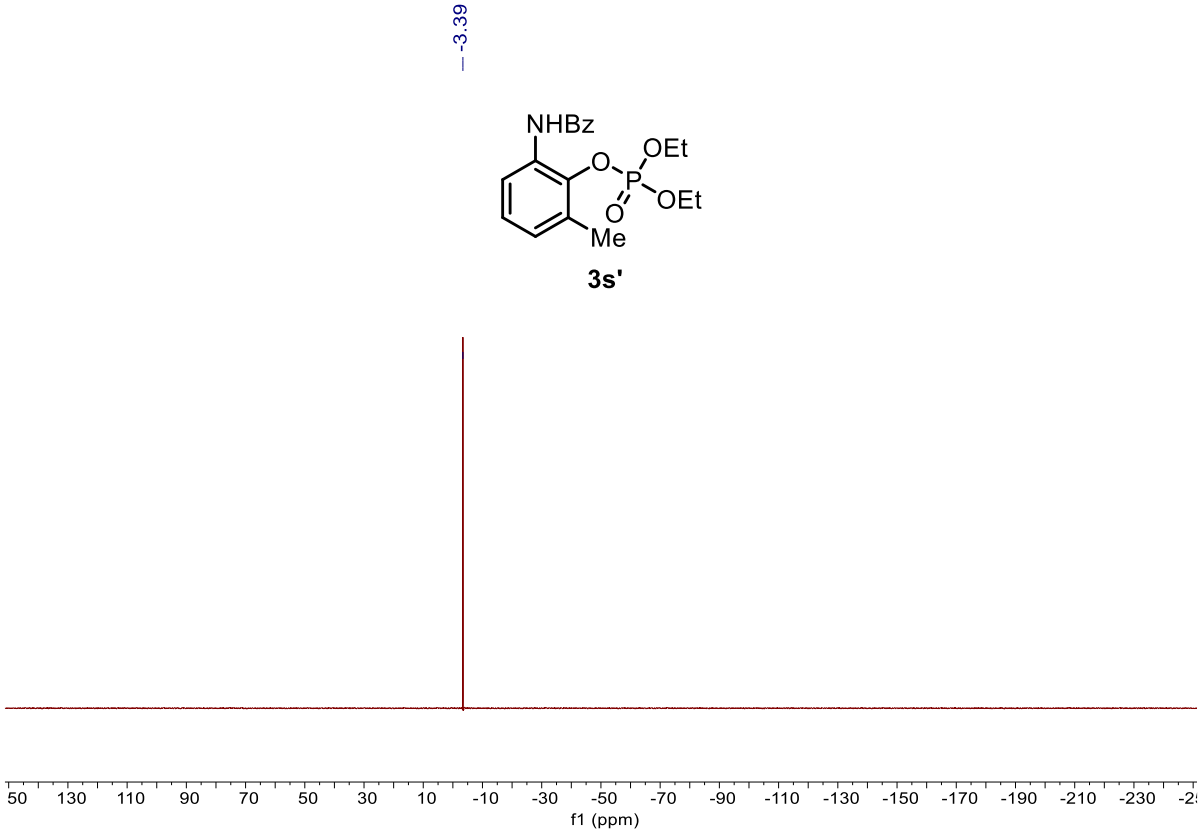
3s'

^{13}C NMR of Compound 3s' (126 MHz, $CDCl_3$)

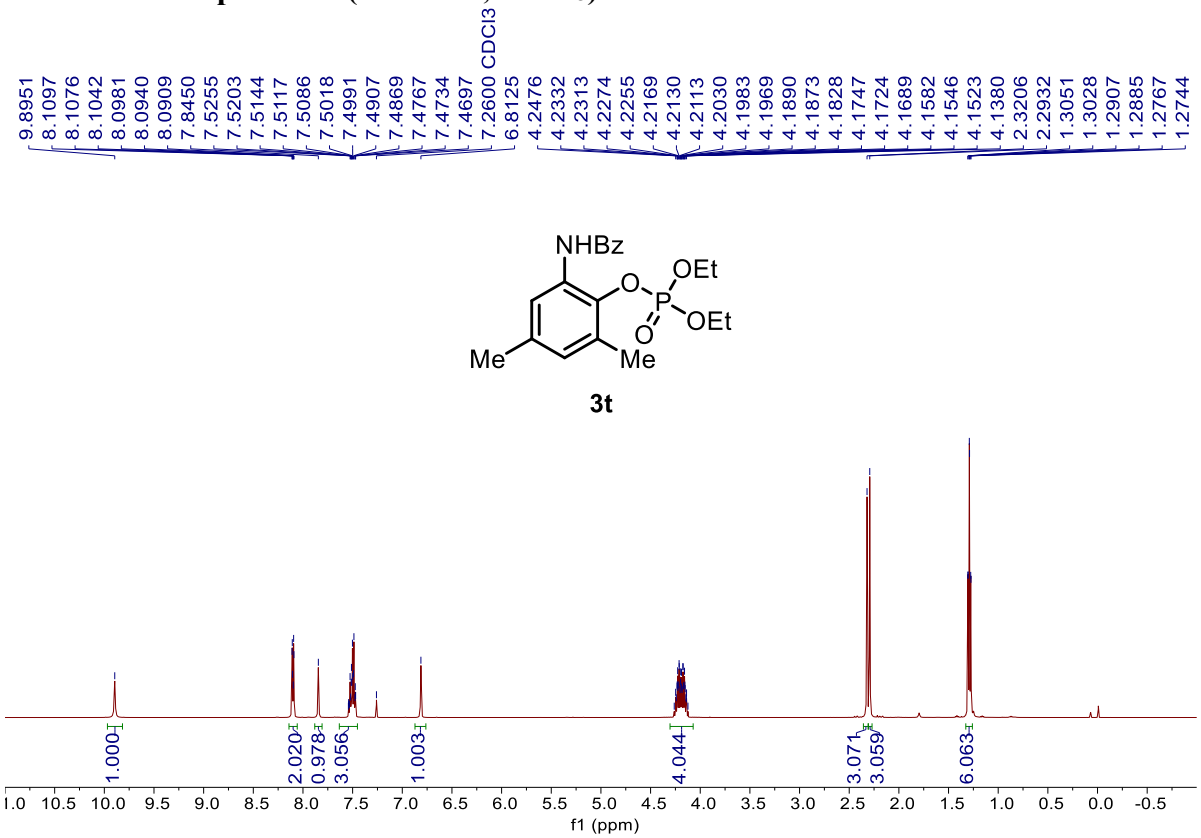


3s'

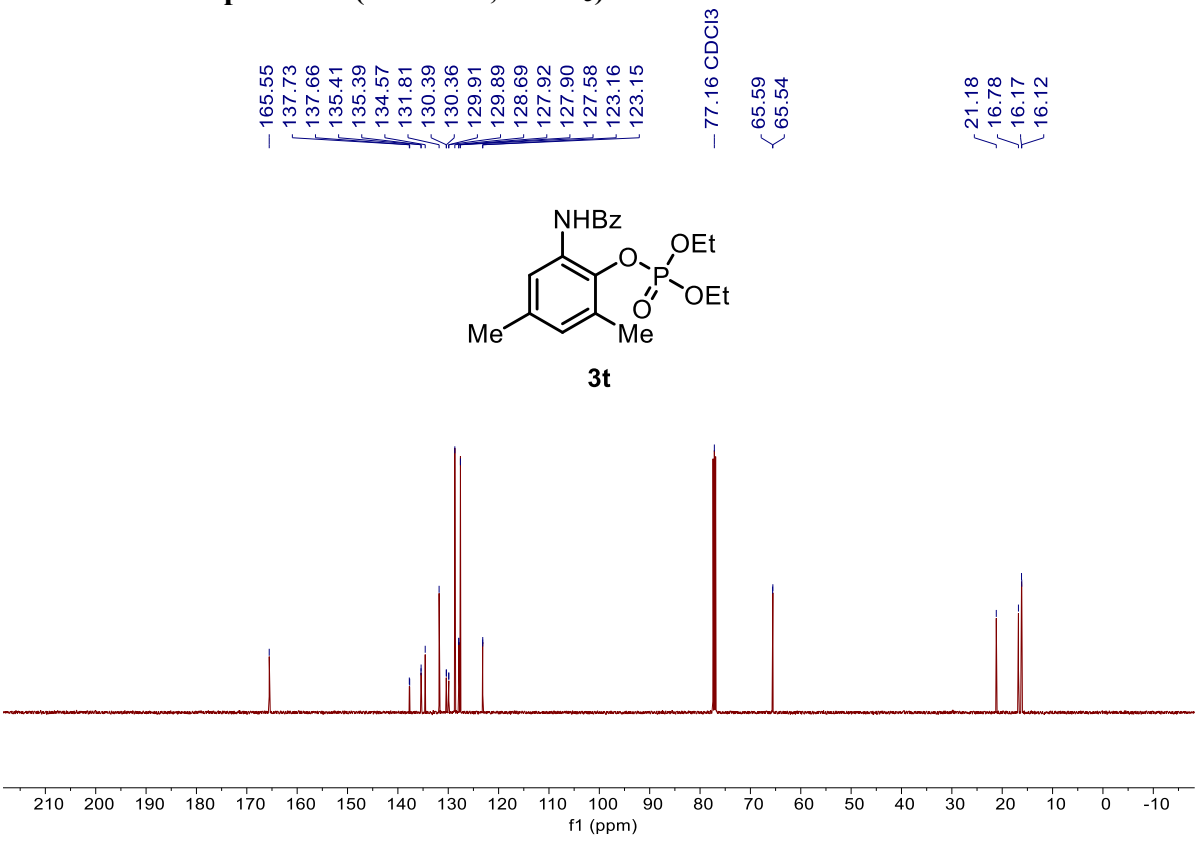
^{31}P NMR of Compound 3s' (202 MHz, $CDCl_3$)



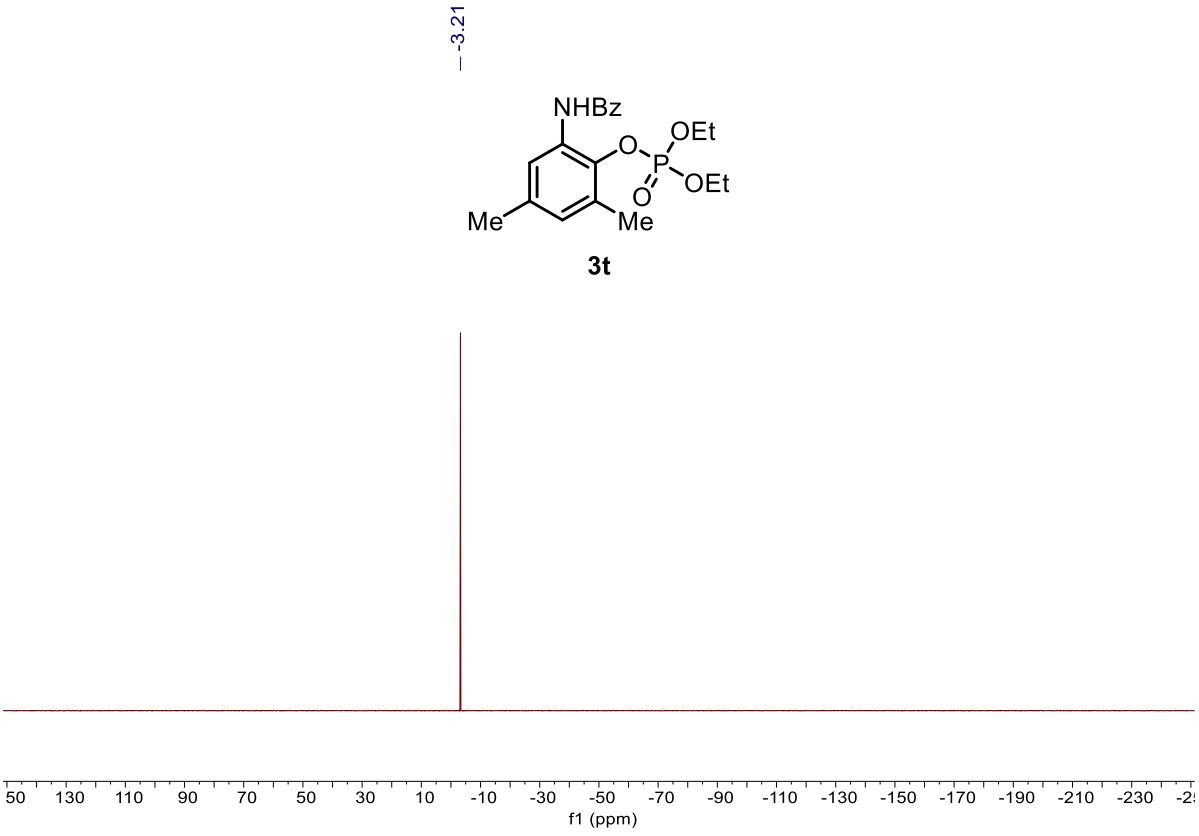
^{1}H NMR of Compound 3t (500 MHz, $CDCl_3$)



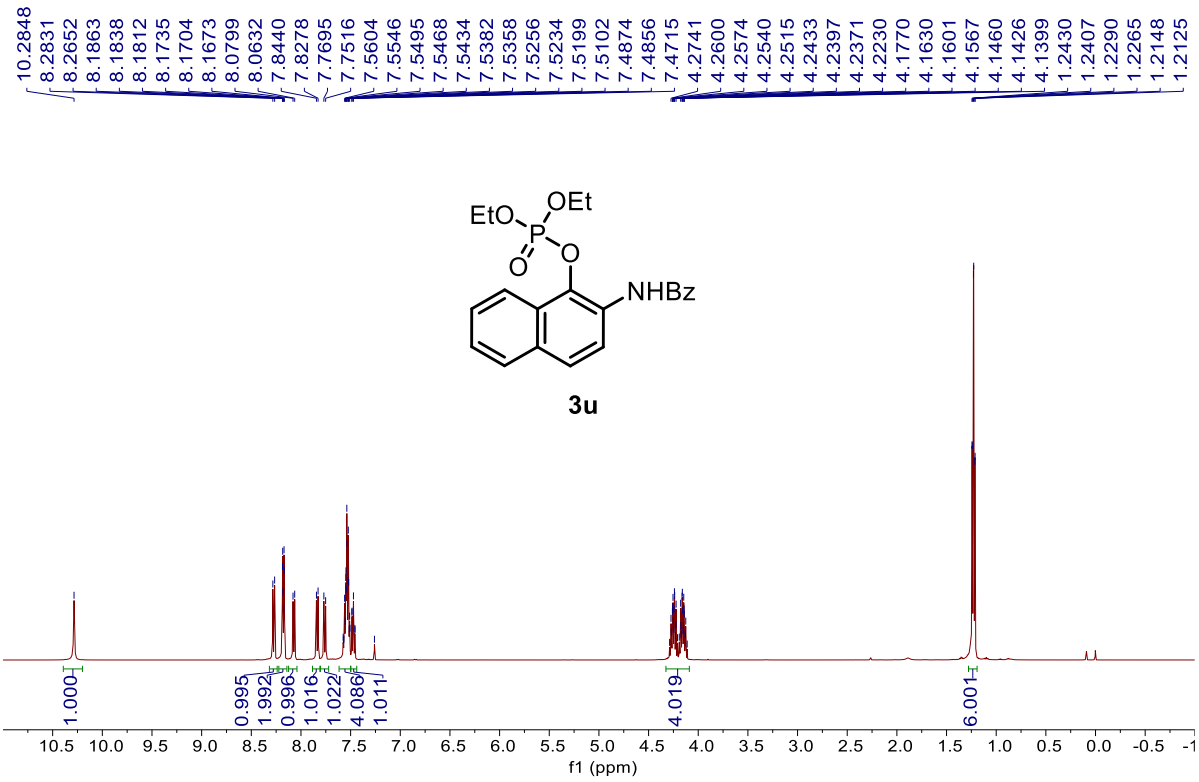
^{13}C NMR of Compound 3t (126 MHz, $CDCl_3$)



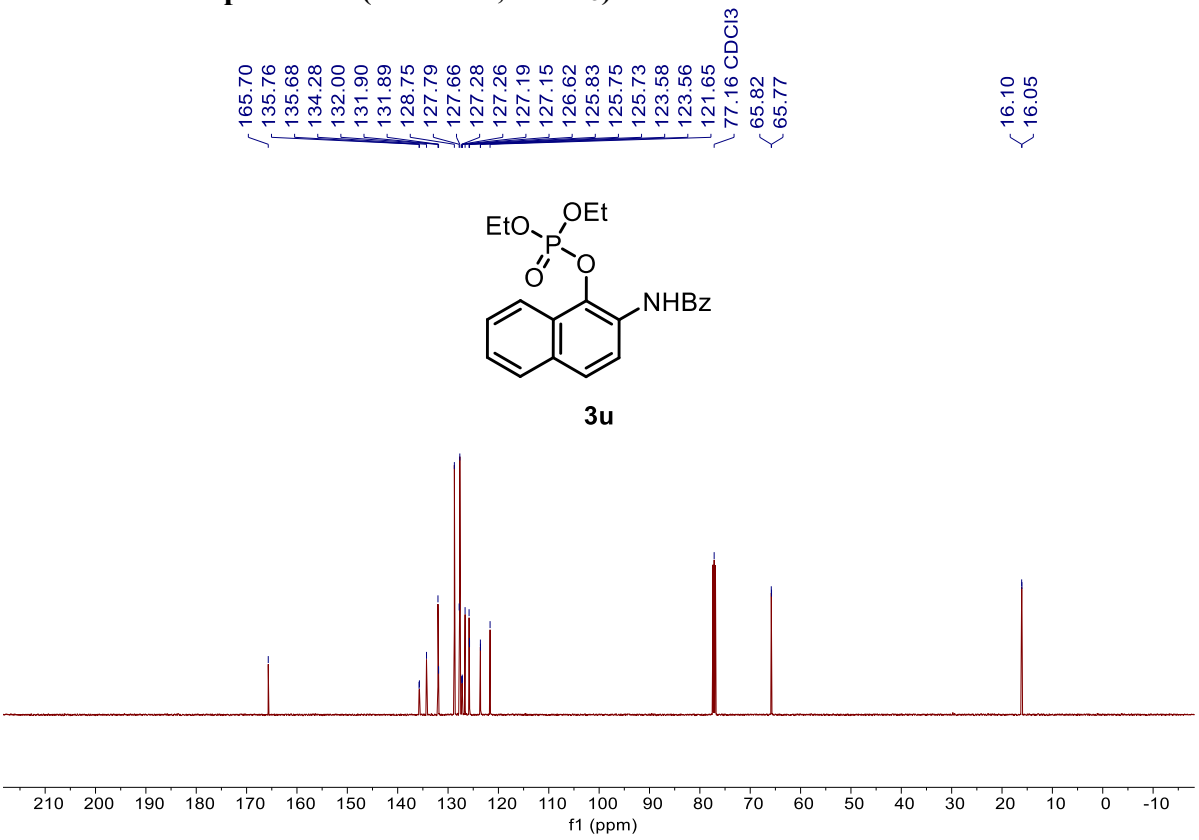
^{31}P NMR of Compound 3t (202 MHz, $CDCl_3$)



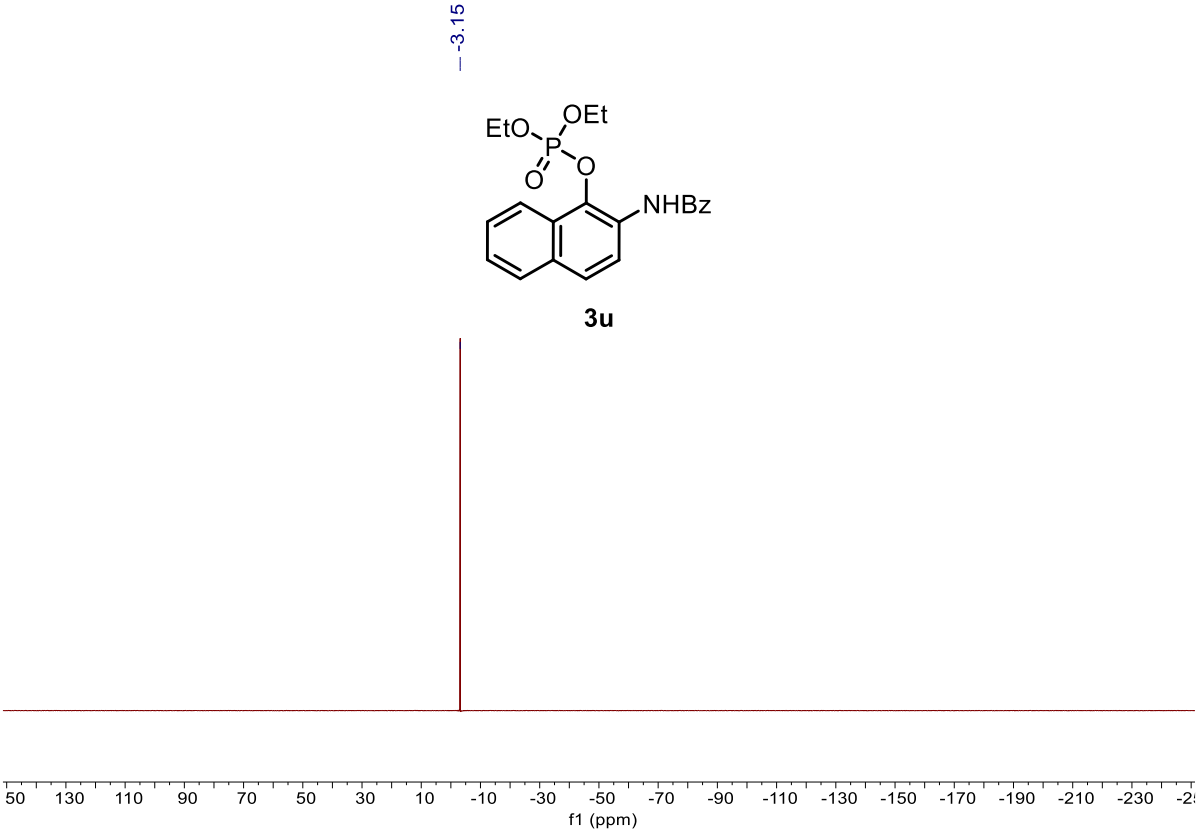
^{1}H NMR of Compound 3u (500 MHz, $CDCl_3$)



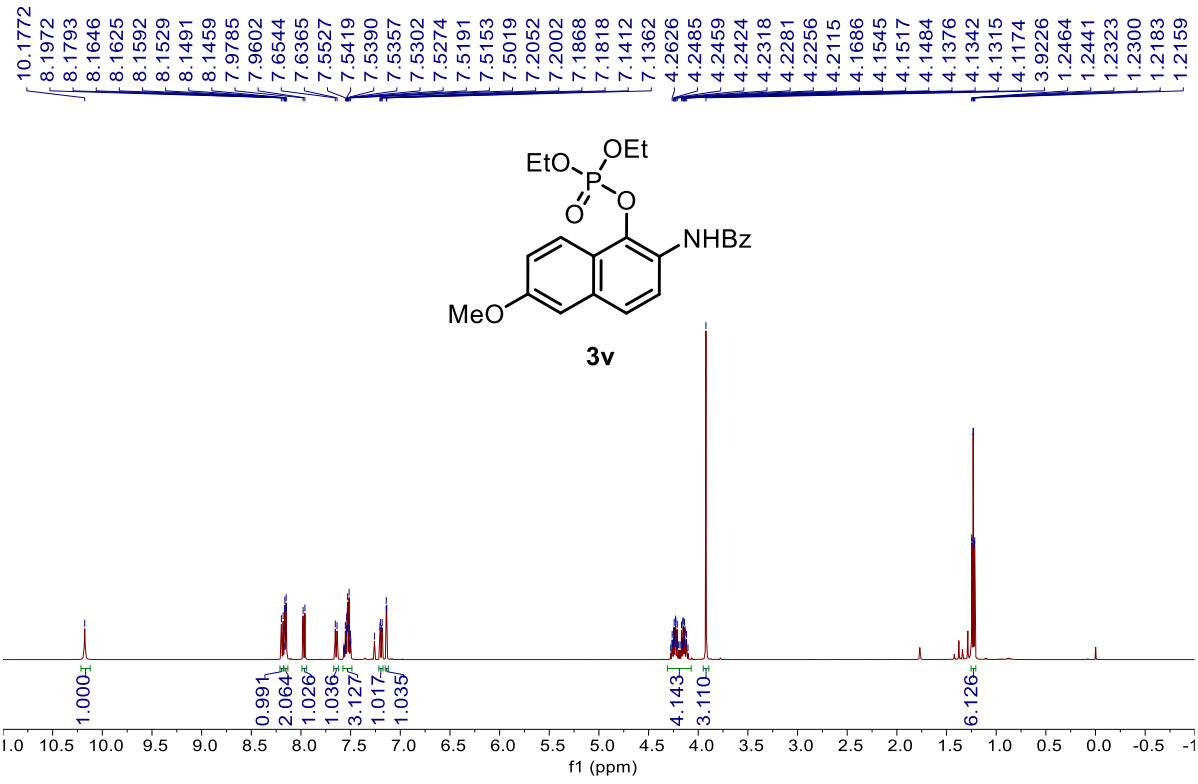
^{13}C NMR of Compound 3u (126 MHz, $CDCl_3$)



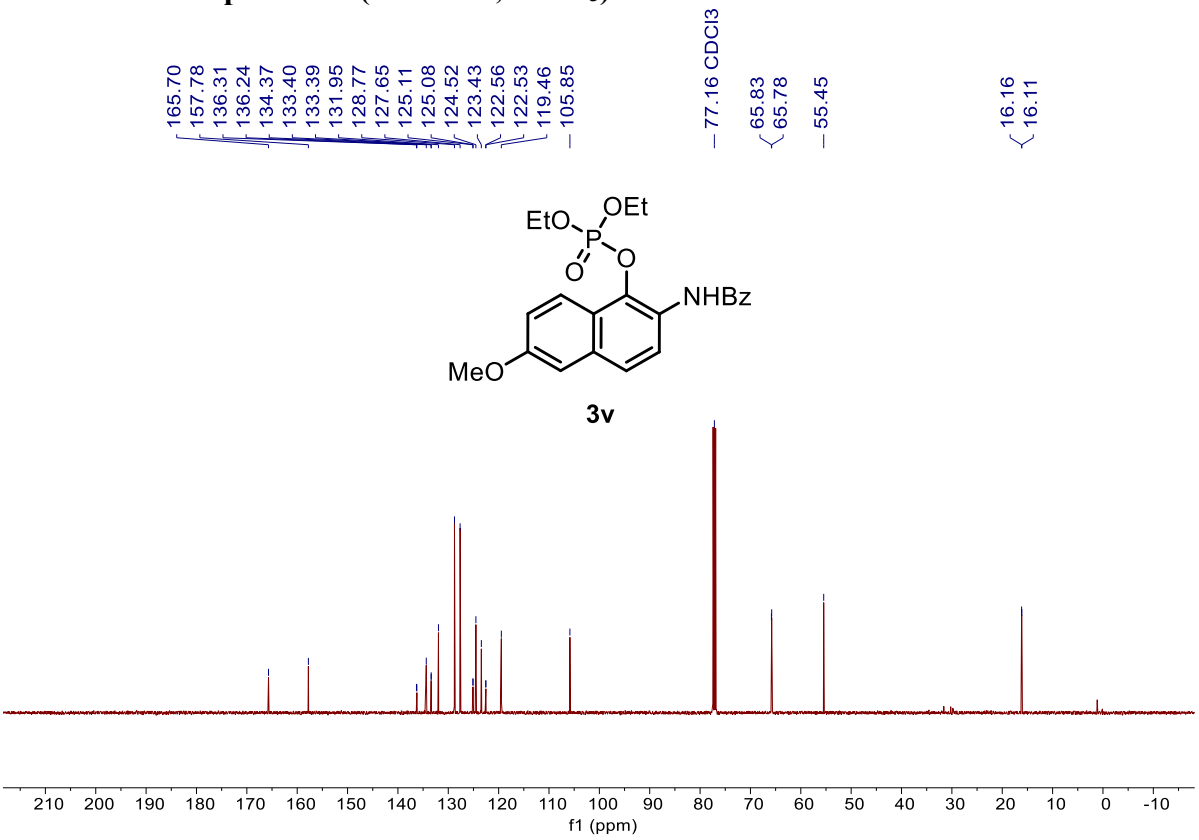
^{31}P NMR of Compound 3u (202 MHz, $CDCl_3$)



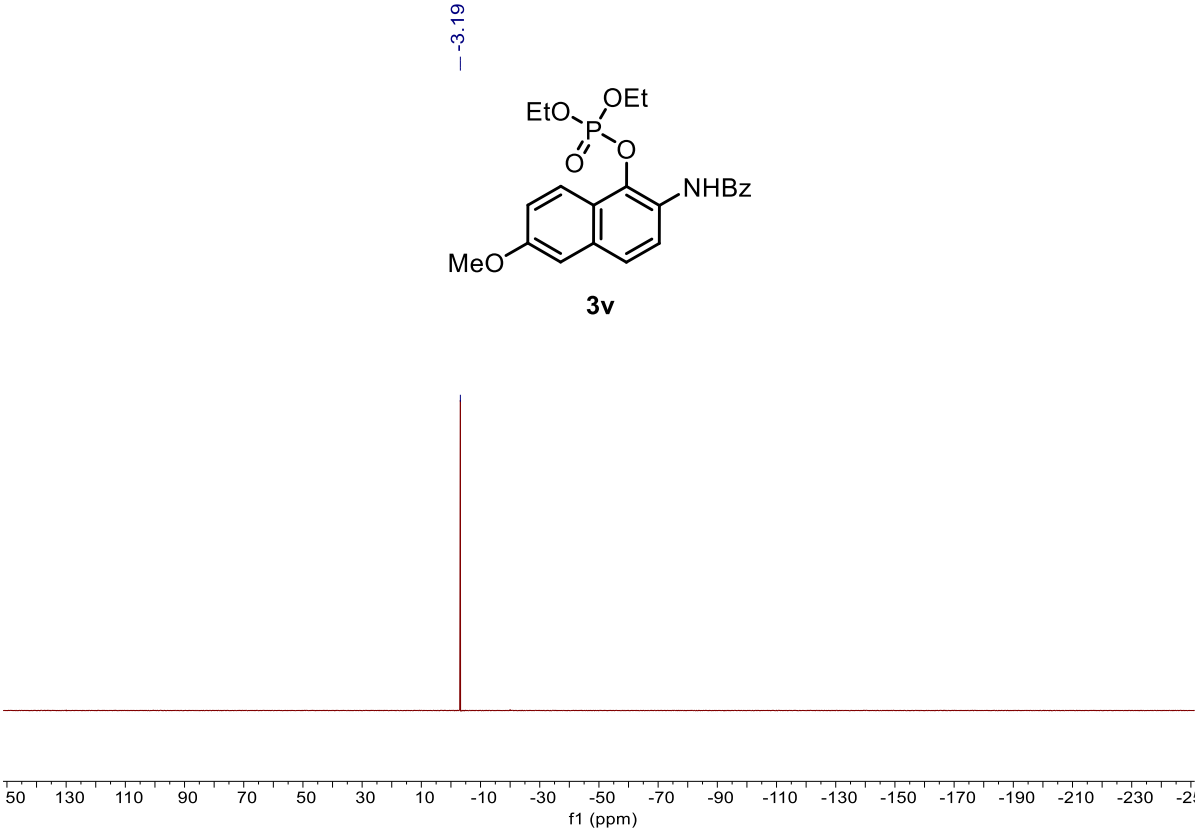
^{1}H NMR of Compound 3v (500 MHz, $CDCl_3$)



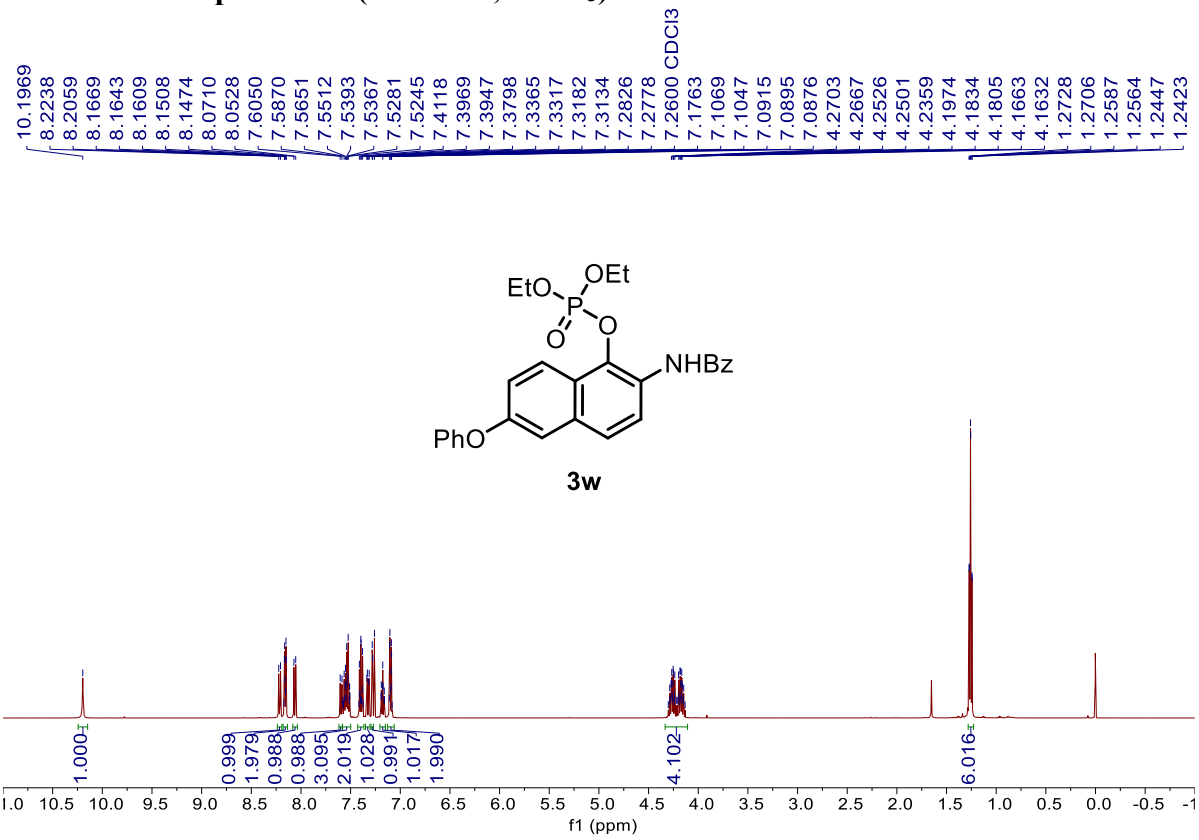
^{13}C NMR of Compound 3v (126 MHz, $CDCl_3$)



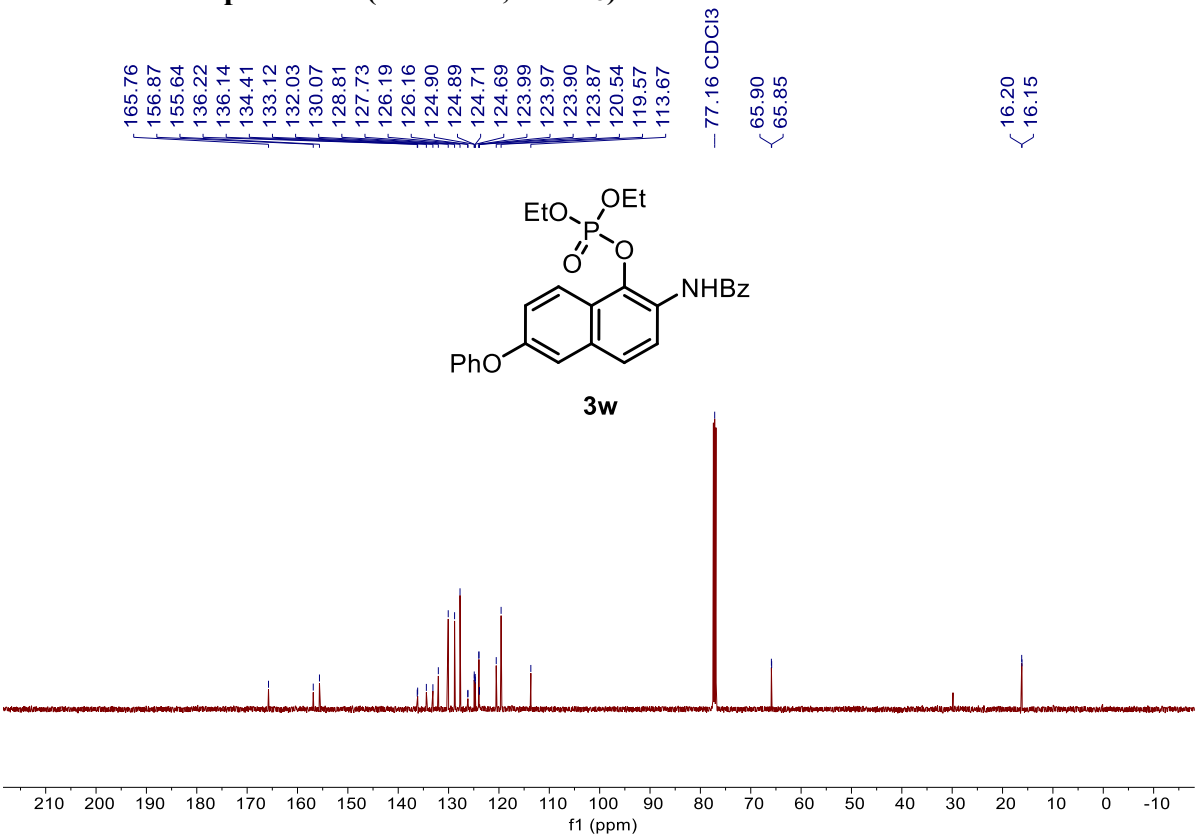
^{31}P NMR of Compound 3v (202 MHz, $CDCl_3$)



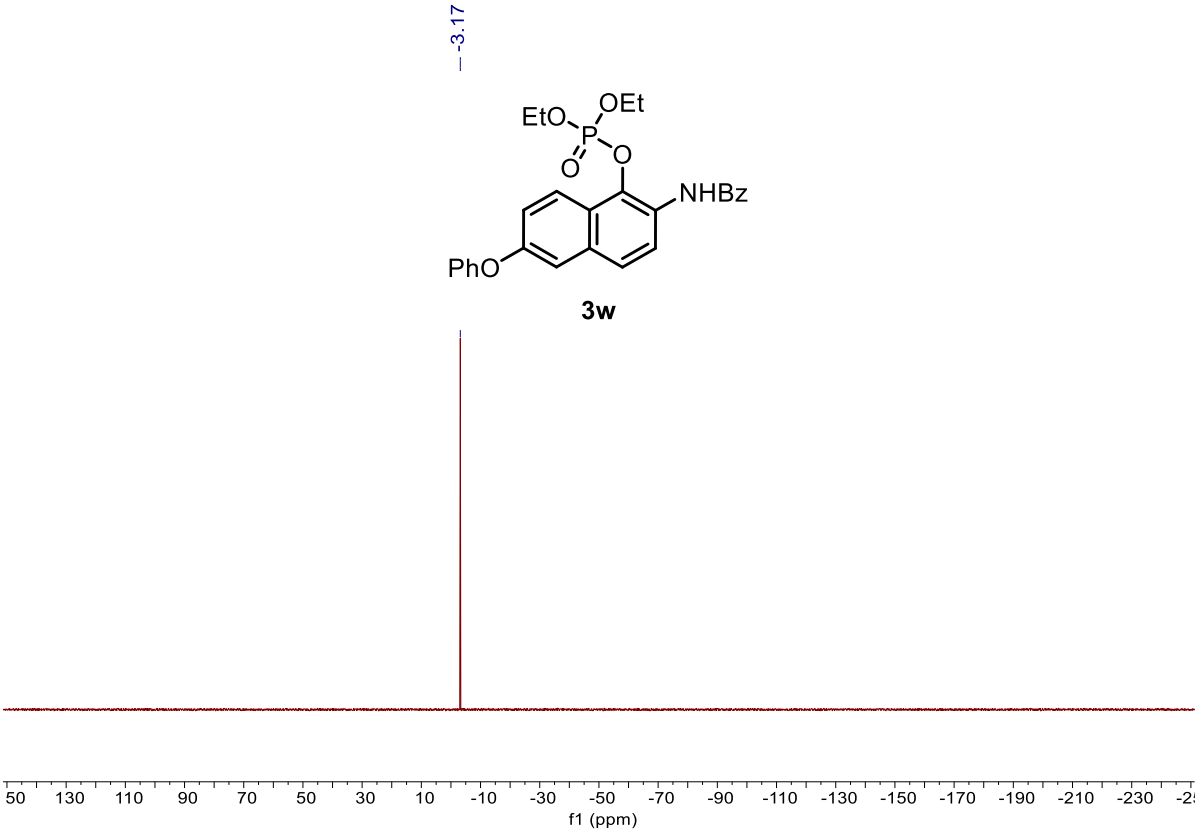
^{1}H NMR of Compound 3w (500 MHz, $CDCl_3$)



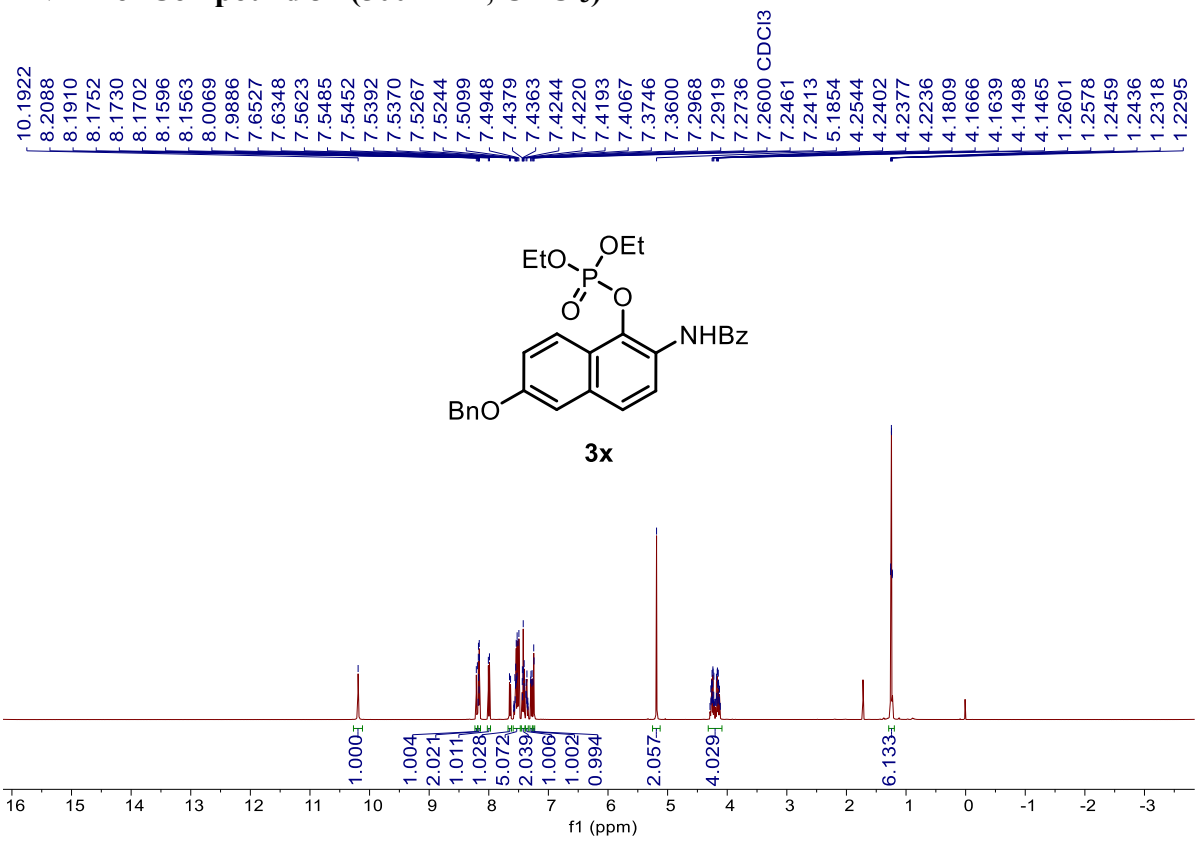
^{13}C NMR of Compound 3w (126 MHz, $CDCl_3$)



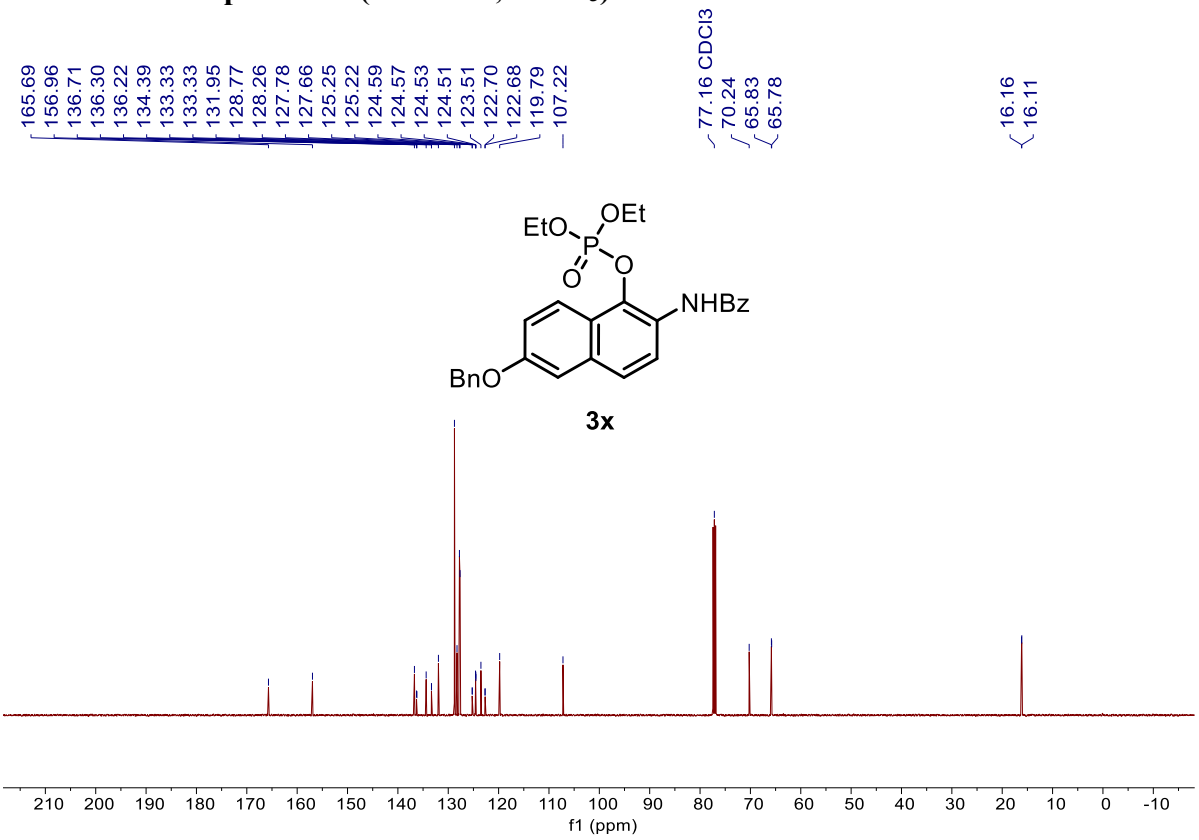
^{31}P NMR of Compound 3w (202 MHz, $CDCl_3$)



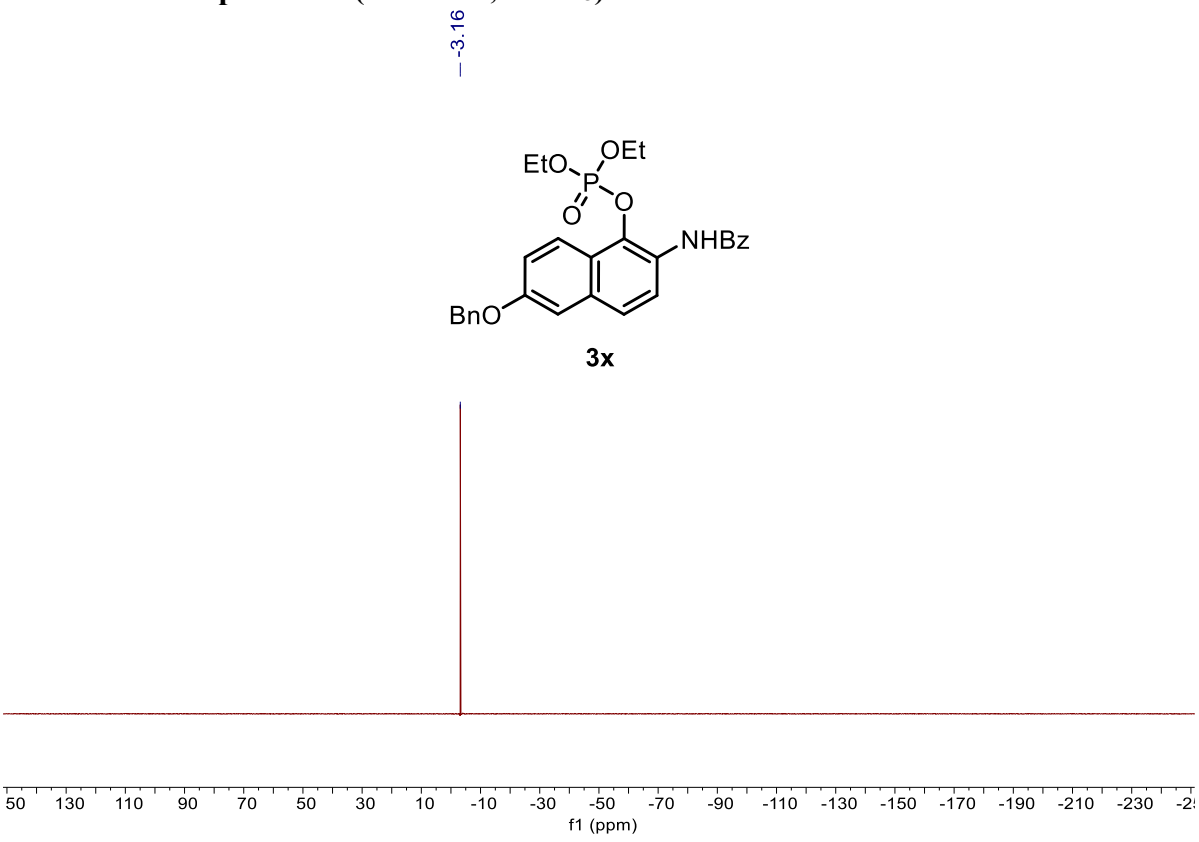
^{1}H NMR of Compound 3x (500 MHz, $CDCl_3$)



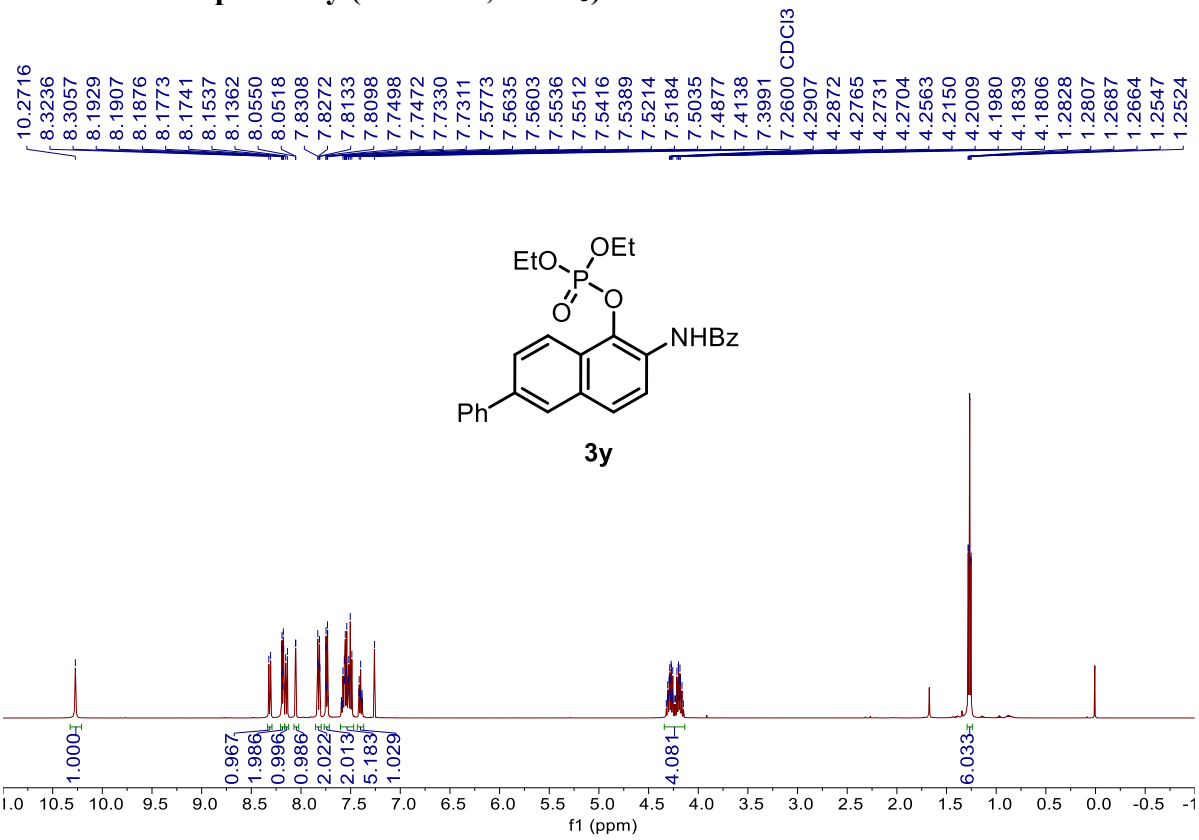
^{13}C NMR of Compound 3x (126 MHz, $CDCl_3$)



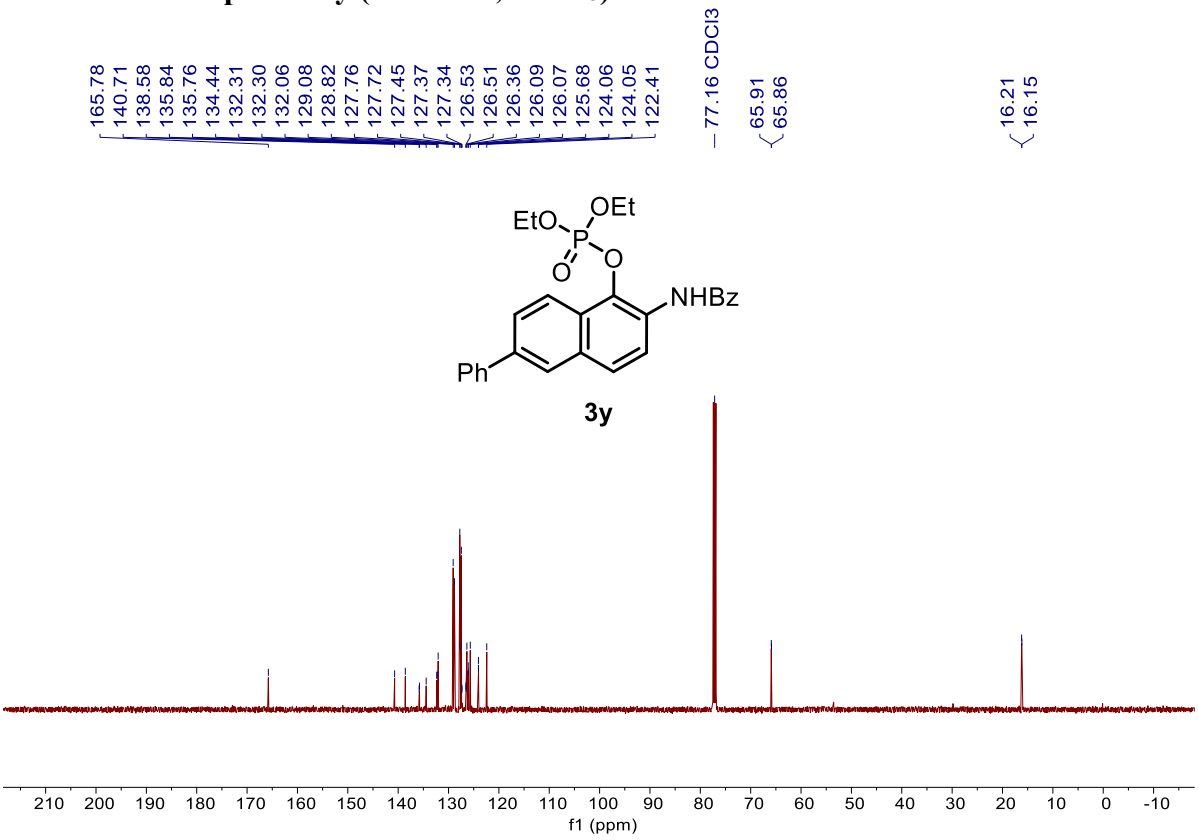
^{31}P NMR of Compound 3x (202 MHz, $CDCl_3$)



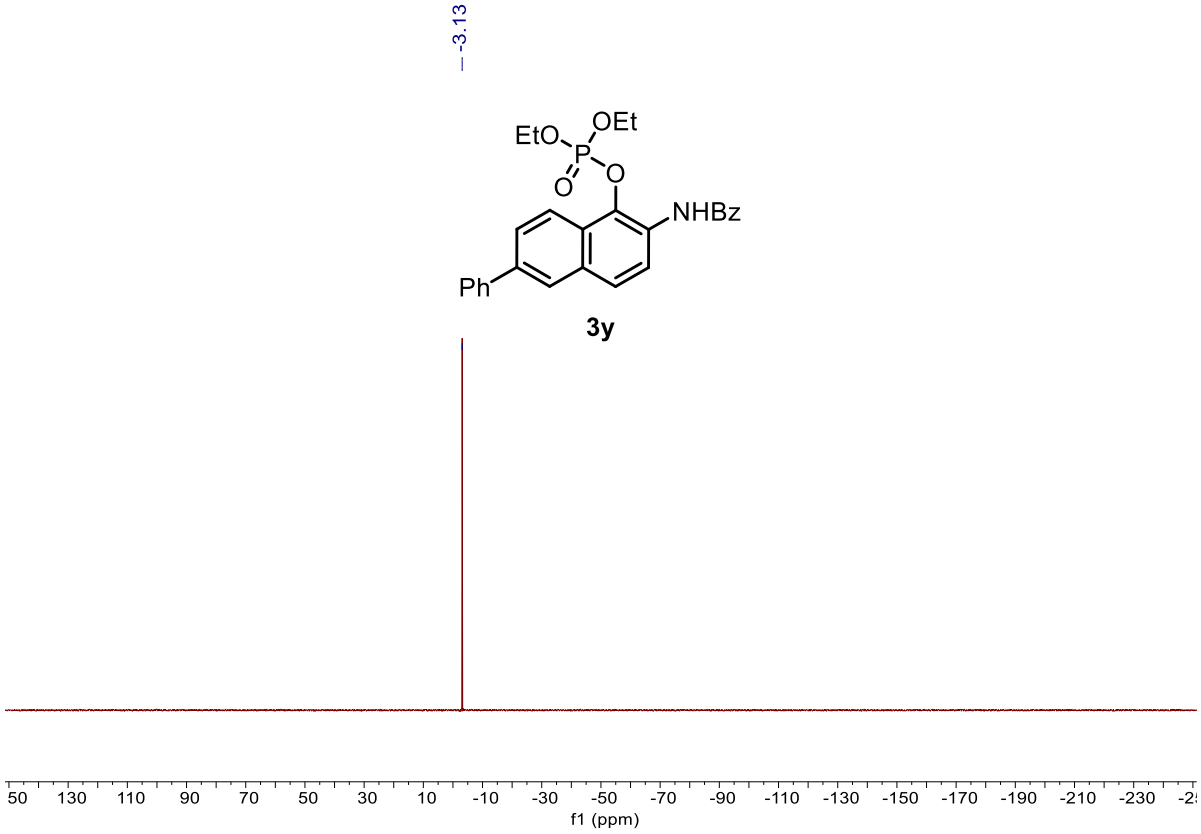
^{1}H NMR of Compound 3y (500 MHz, $CDCl_3$)



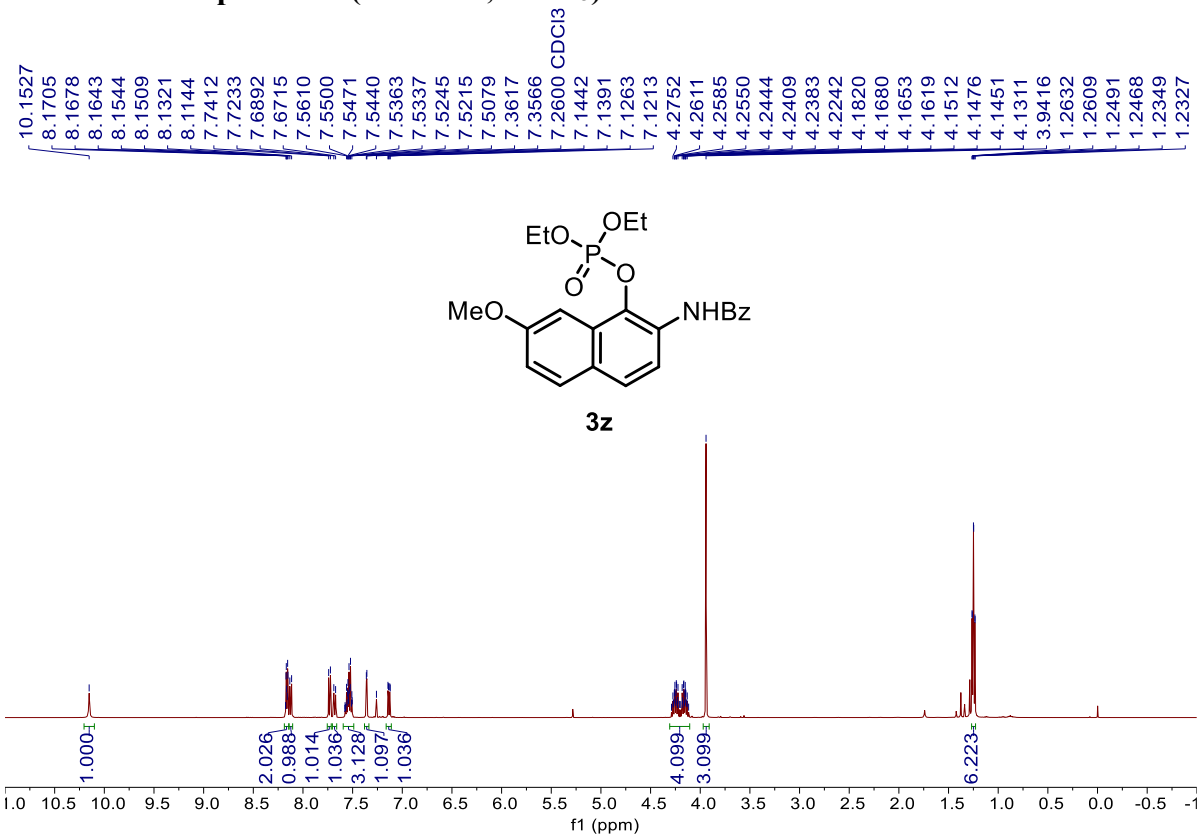
^{13}C NMR of Compound 3y (126 MHz, $CDCl_3$)



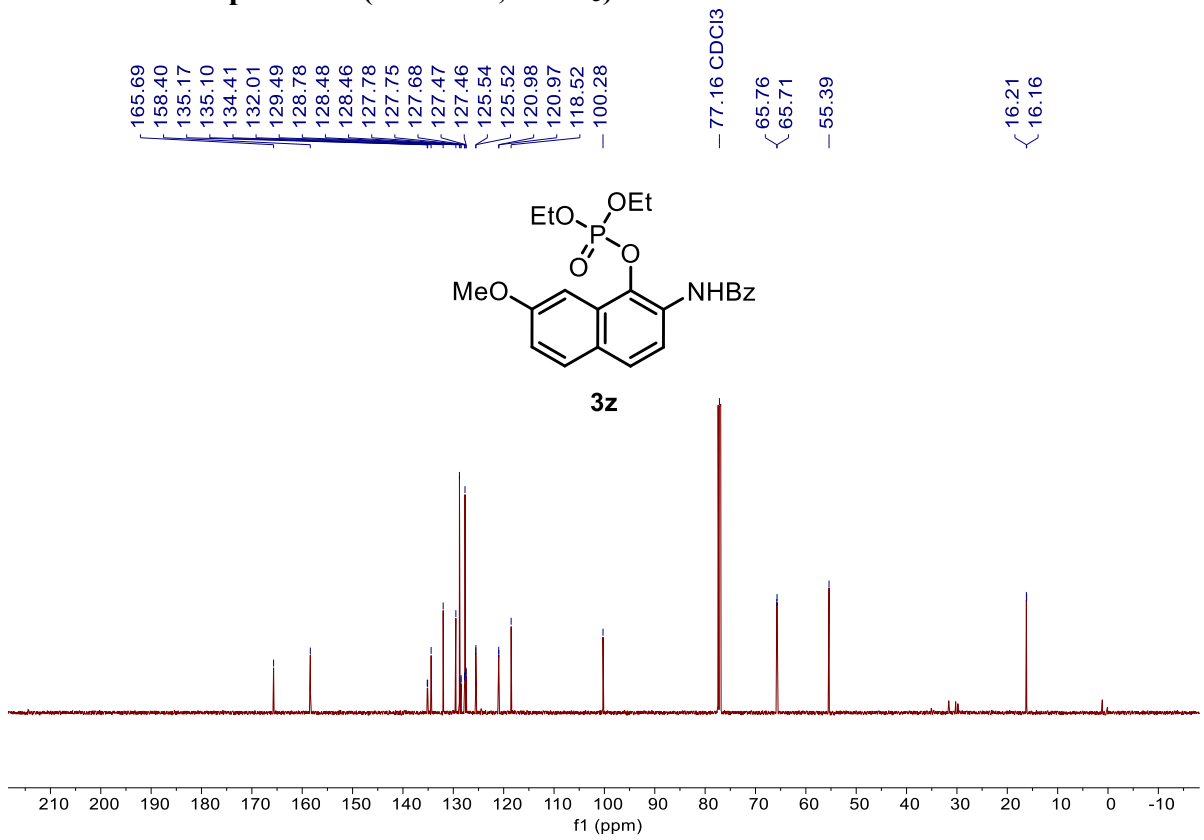
^{31}P NMR of Compound 3y (202 MHz, $CDCl_3$)



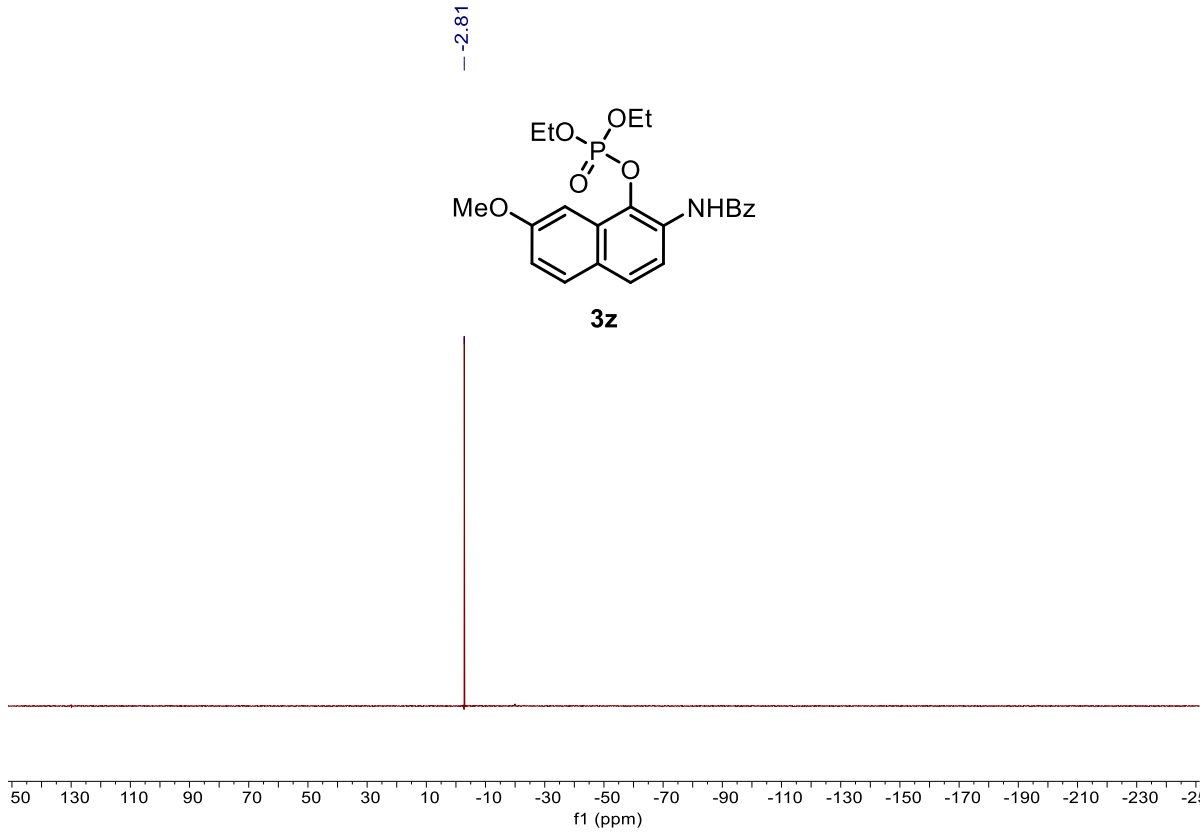
^{1}H NMR of Compound 3z (500 MHz, $CDCl_3$)



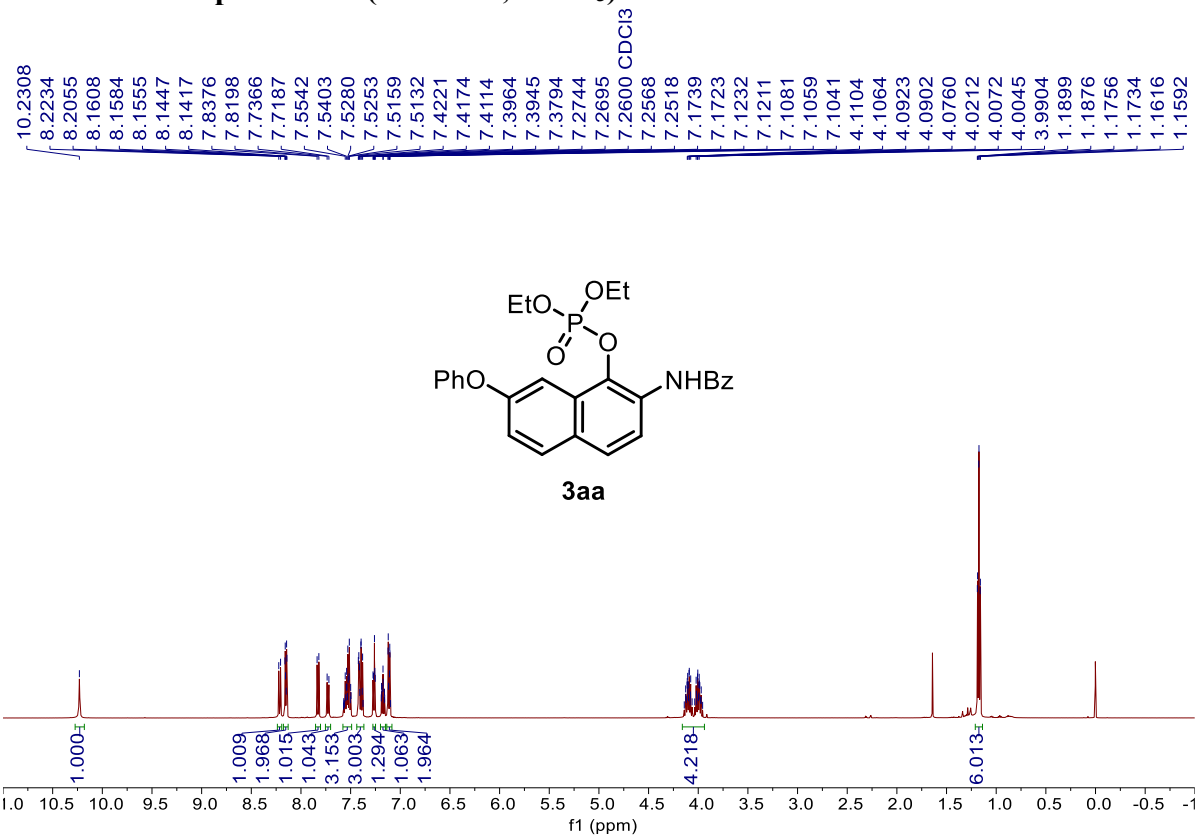
^{13}C NMR of Compound 3z (126 MHz, $CDCl_3$)



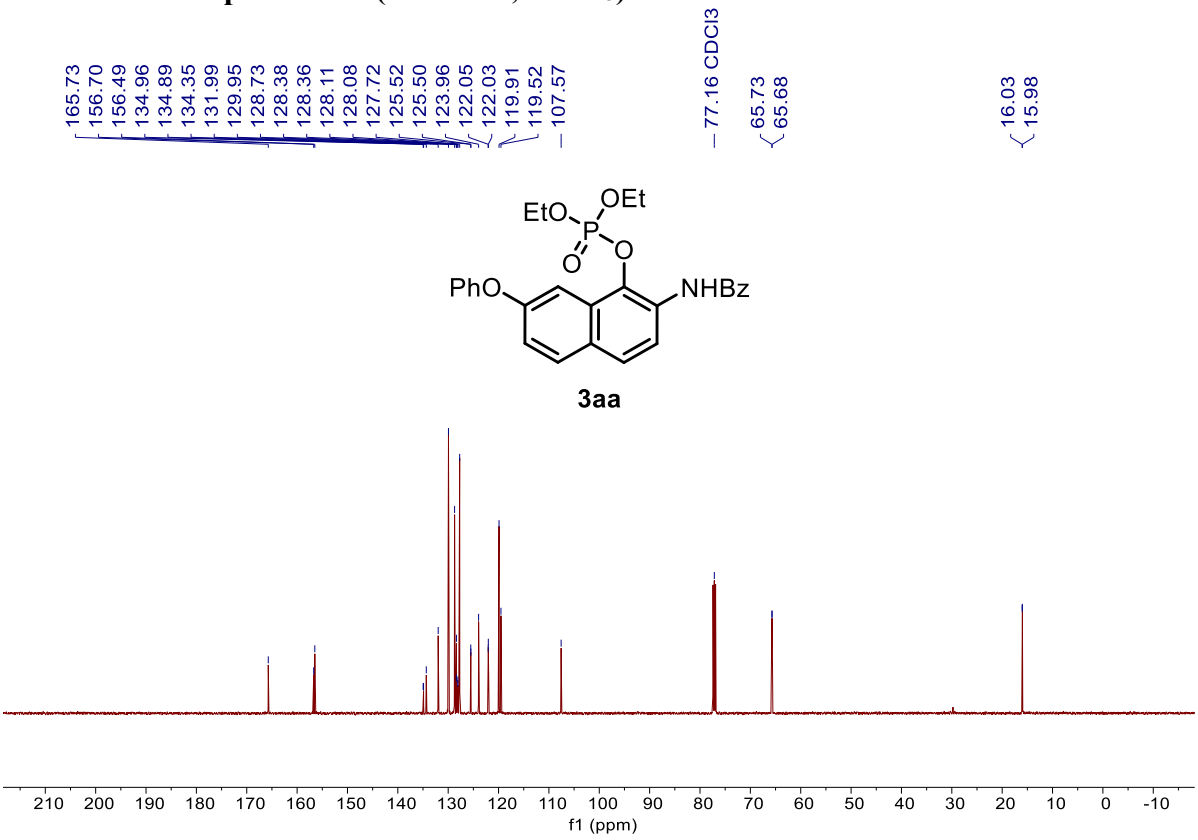
^{31}P NMR of Compound 3z (202 MHz, $CDCl_3$)



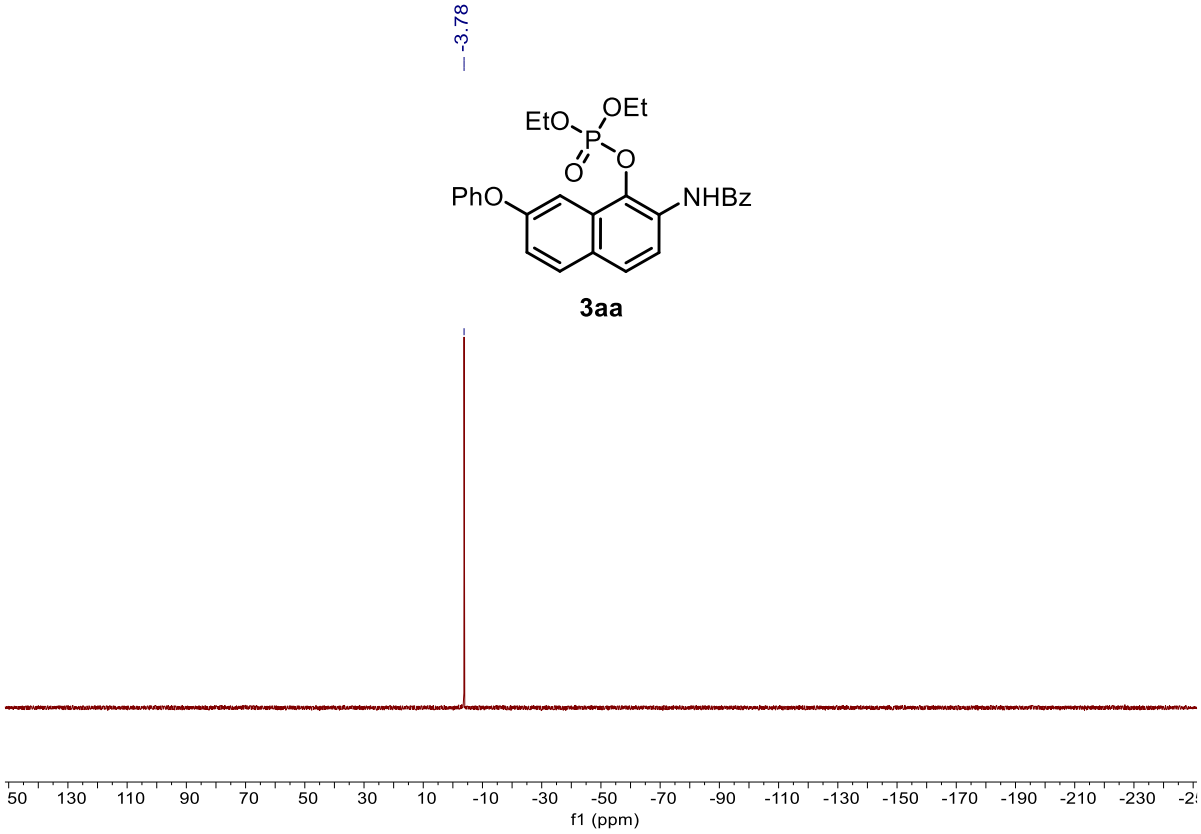
^{1}H NMR of Compound 3aa (500 MHz, $CDCl_3$)



^{13}C NMR of Compound 3aa (126 MHz, $CDCl_3$)

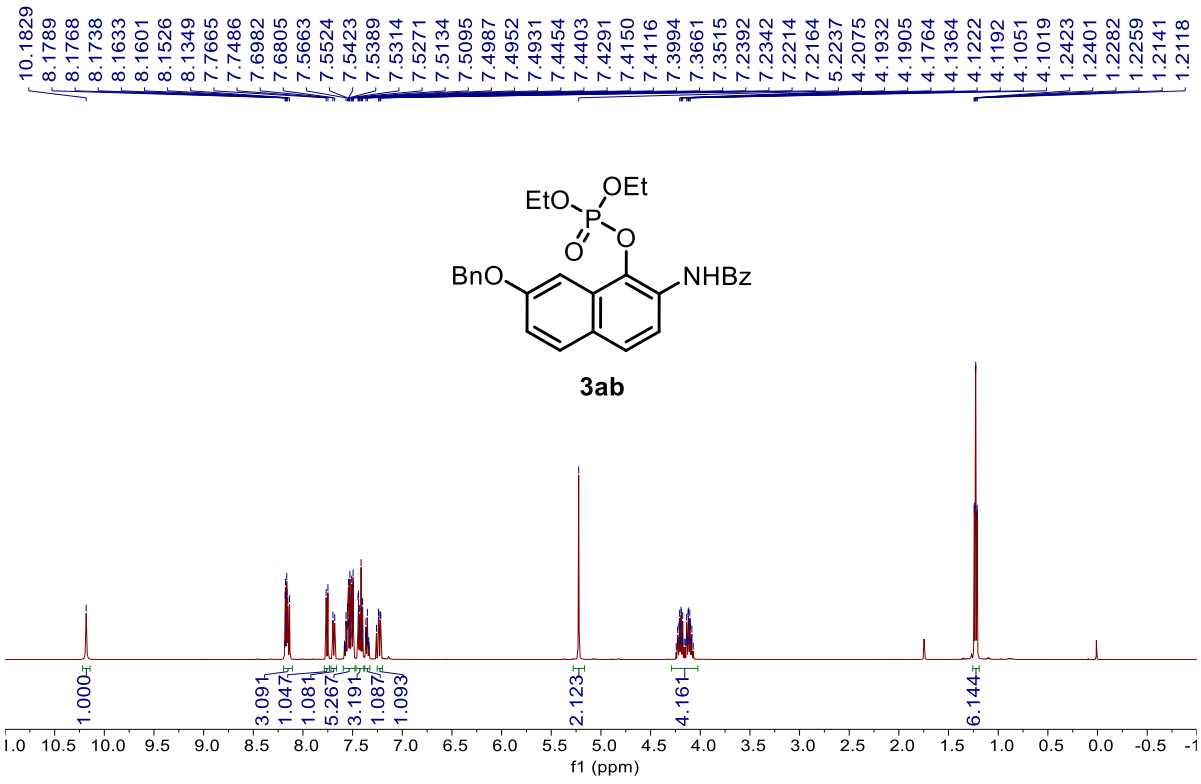


^{31}P NMR of Compound 3aa (202 MHz, $CDCl_3$)



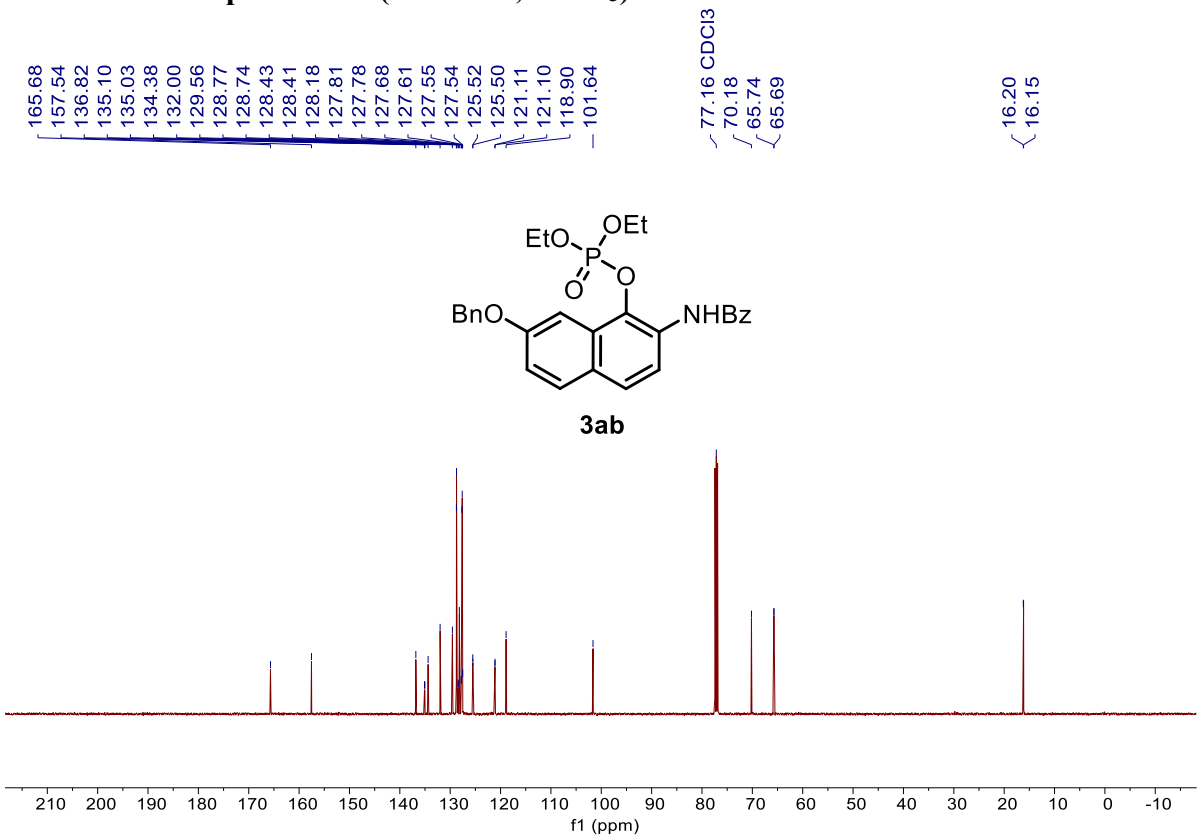
3aa

^{1}H NMR of Compound 3ab (500 MHz, $CDCl_3$)

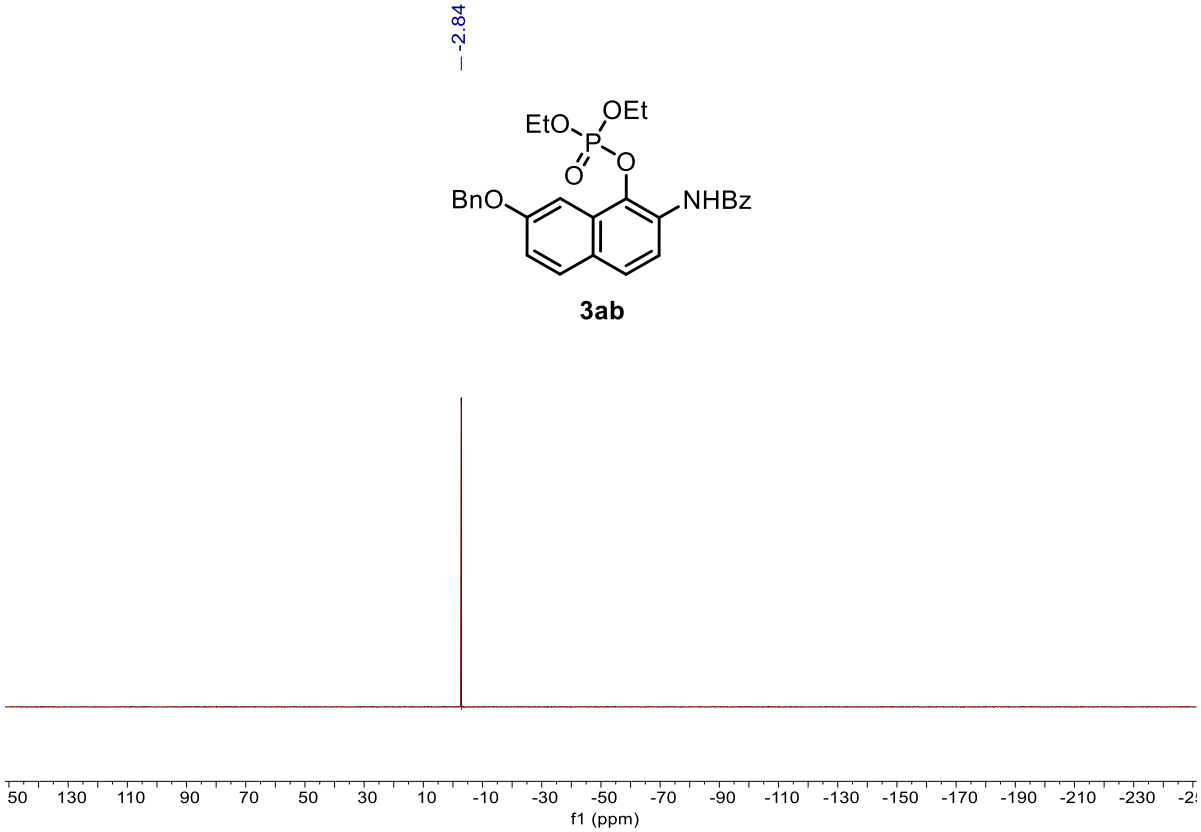


3ab

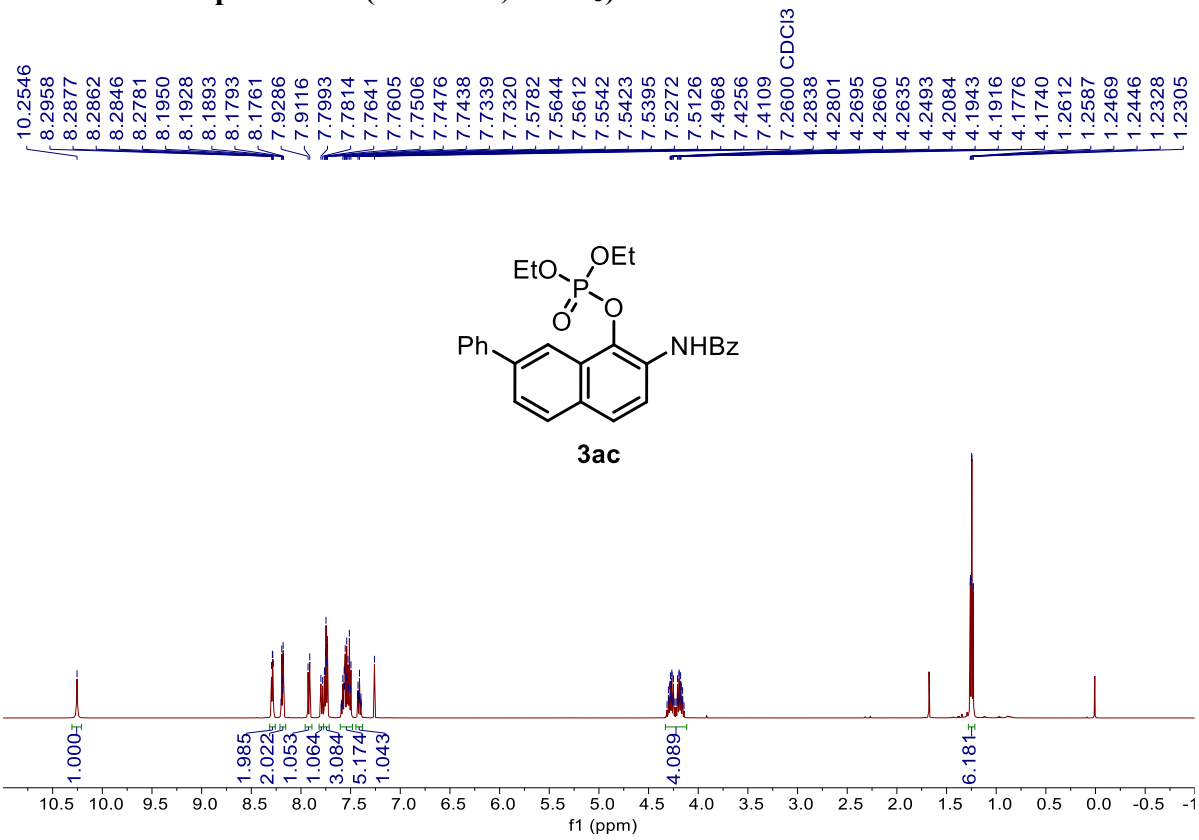
^{13}C NMR of Compound 3ab (126 MHz, $CDCl_3$)



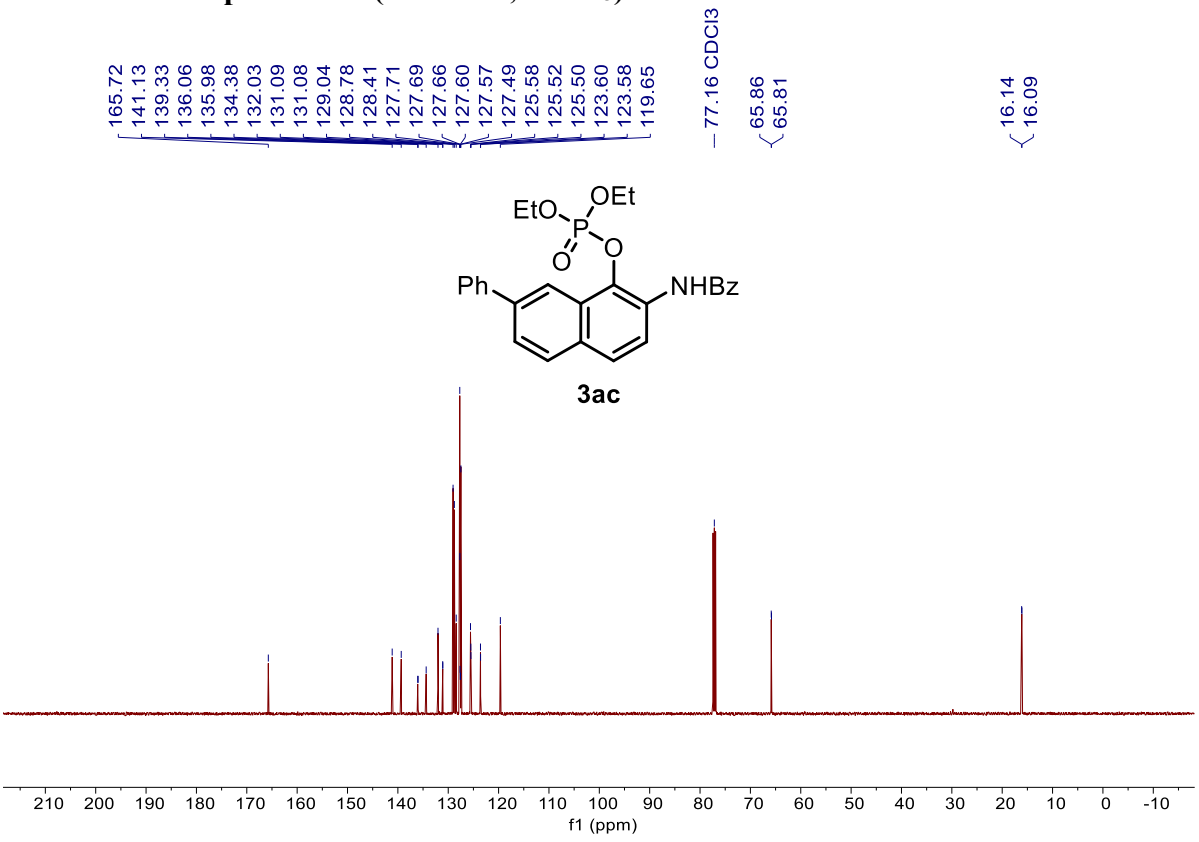
^{31}P NMR of Compound 3ab (202 MHz, $CDCl_3$)



^{1}H NMR of Compound 3ac (500 MHz, $CDCl_3$)



^{13}C NMR of Compound 3ac (126 MHz, $CDCl_3$)



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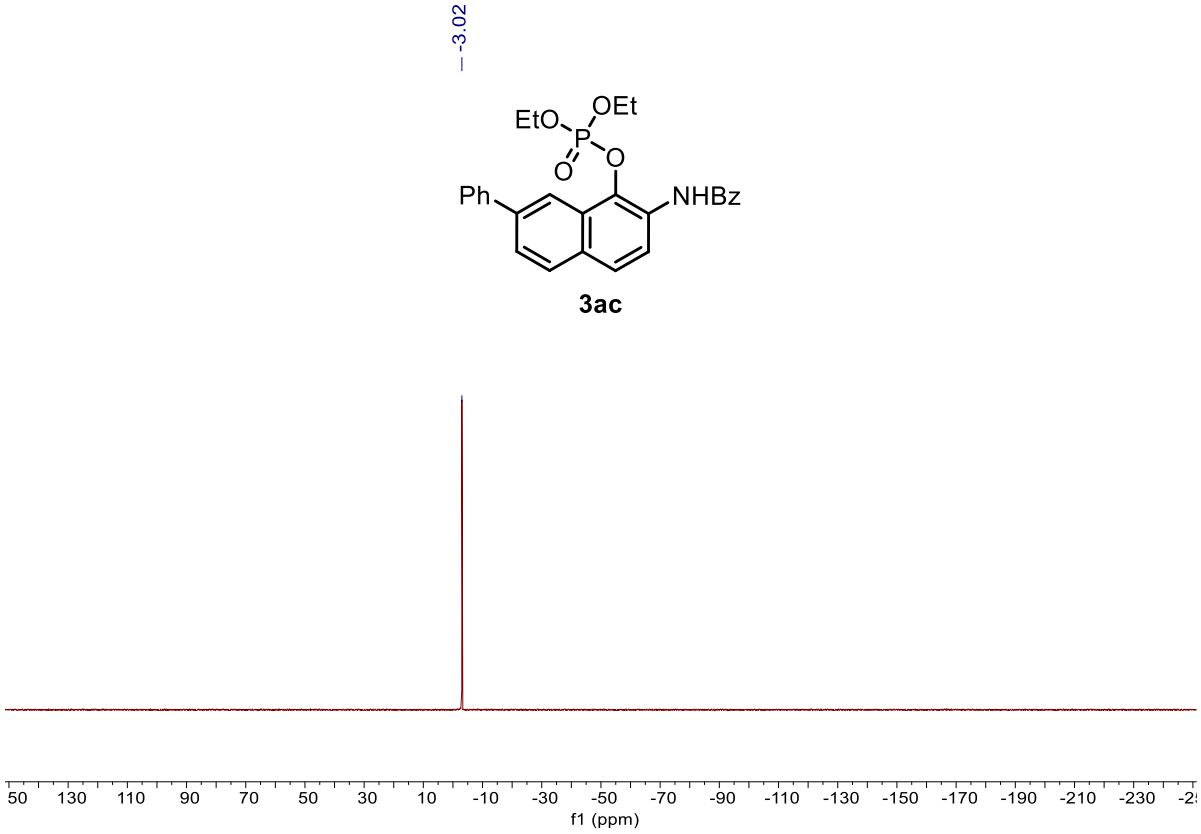
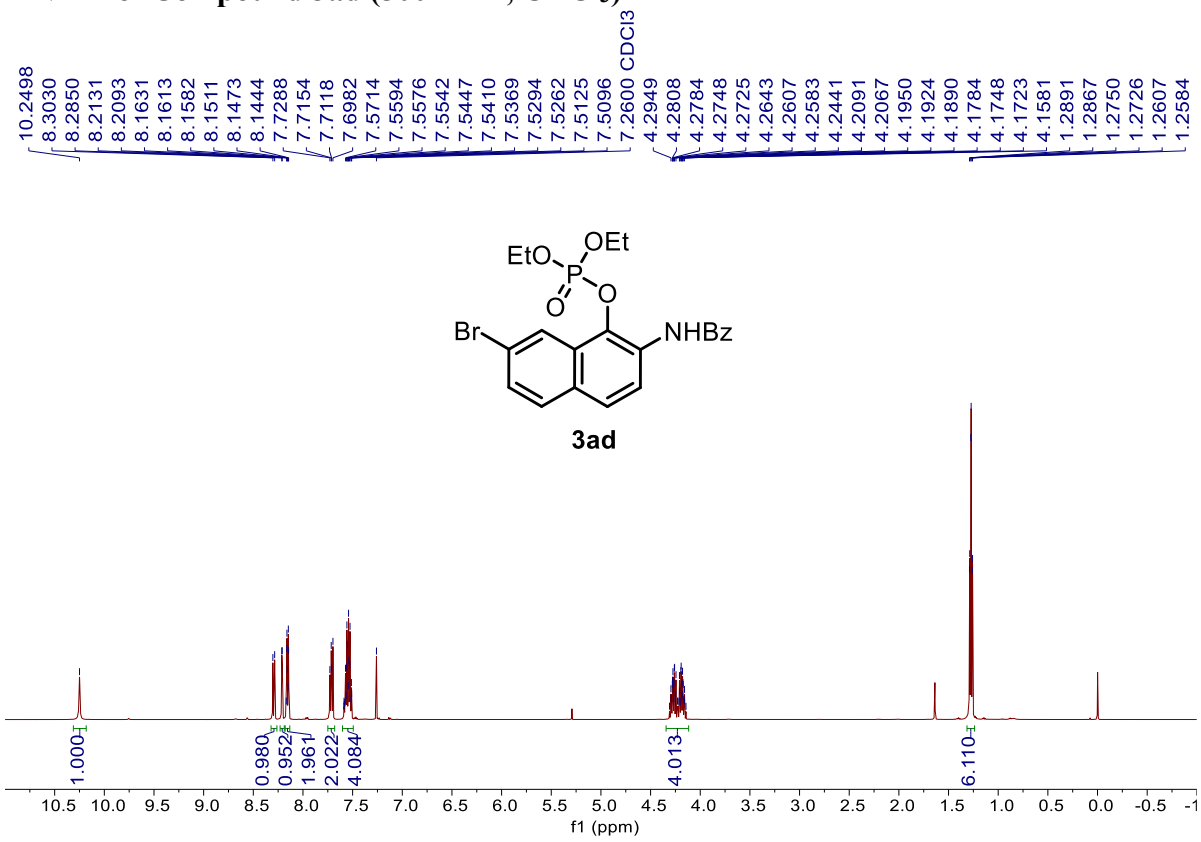
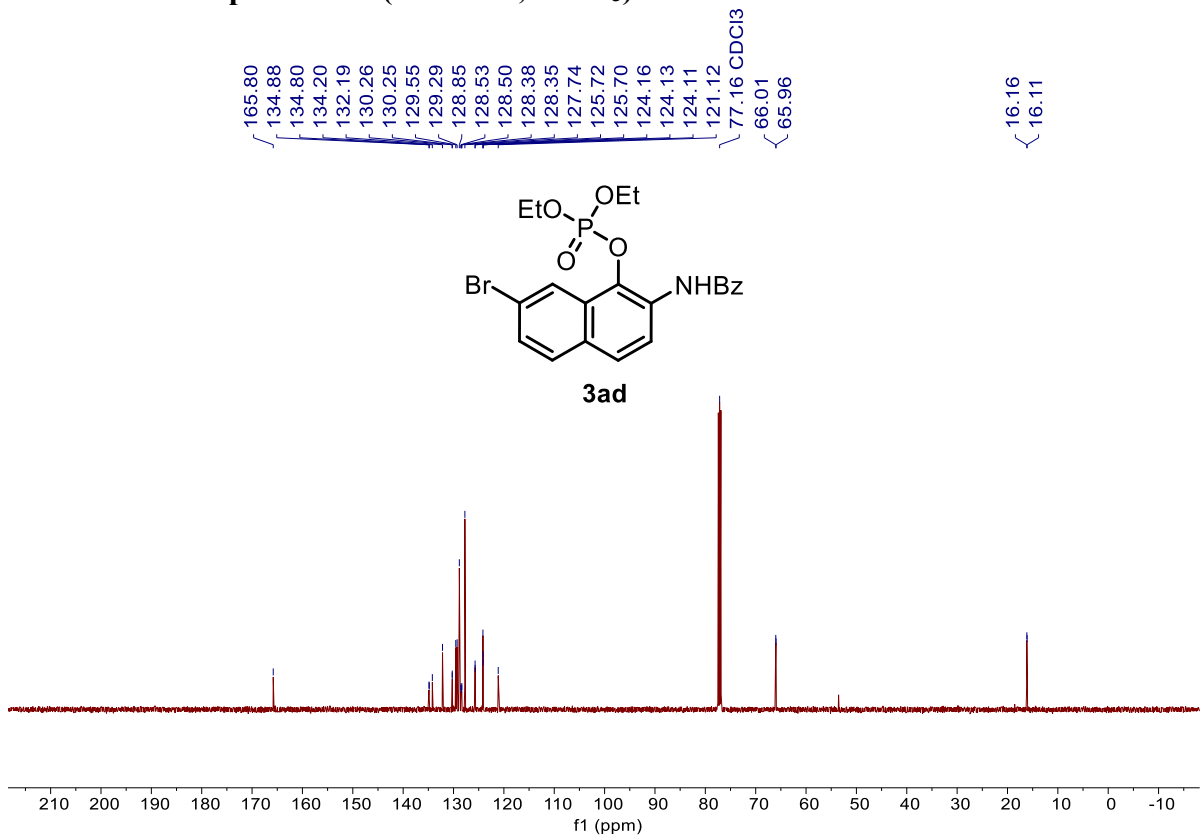


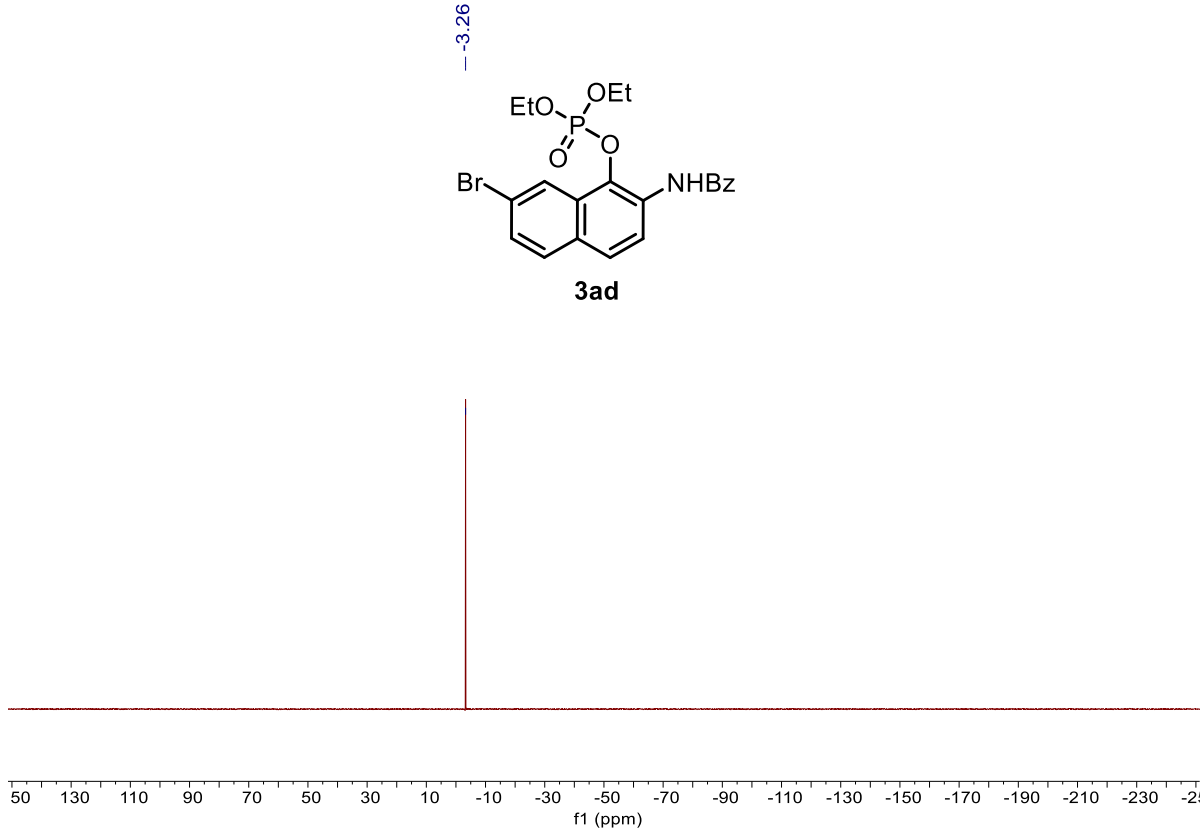
^{1}H NMR of Compound 3ad (500 MHz, $CDCl_3$)



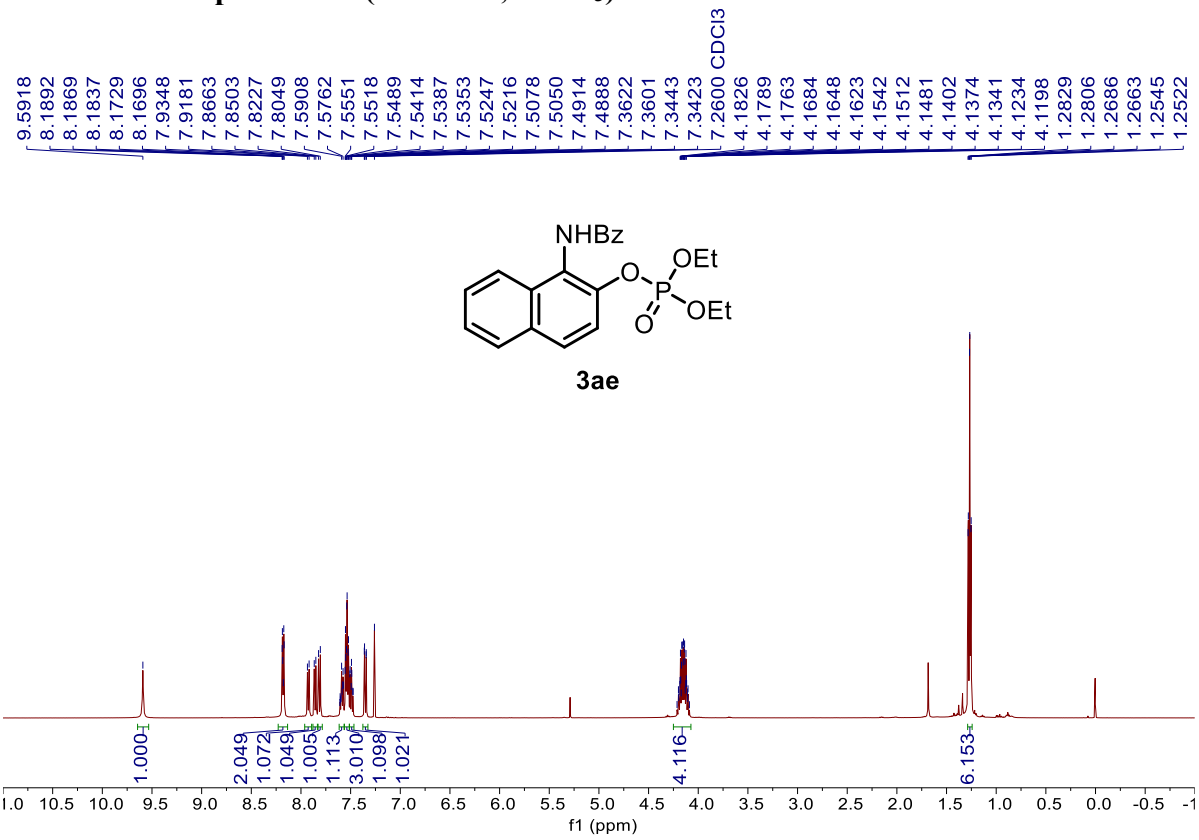
^{13}C NMR of Compound 3ad (126 MHz, $CDCl_3$)



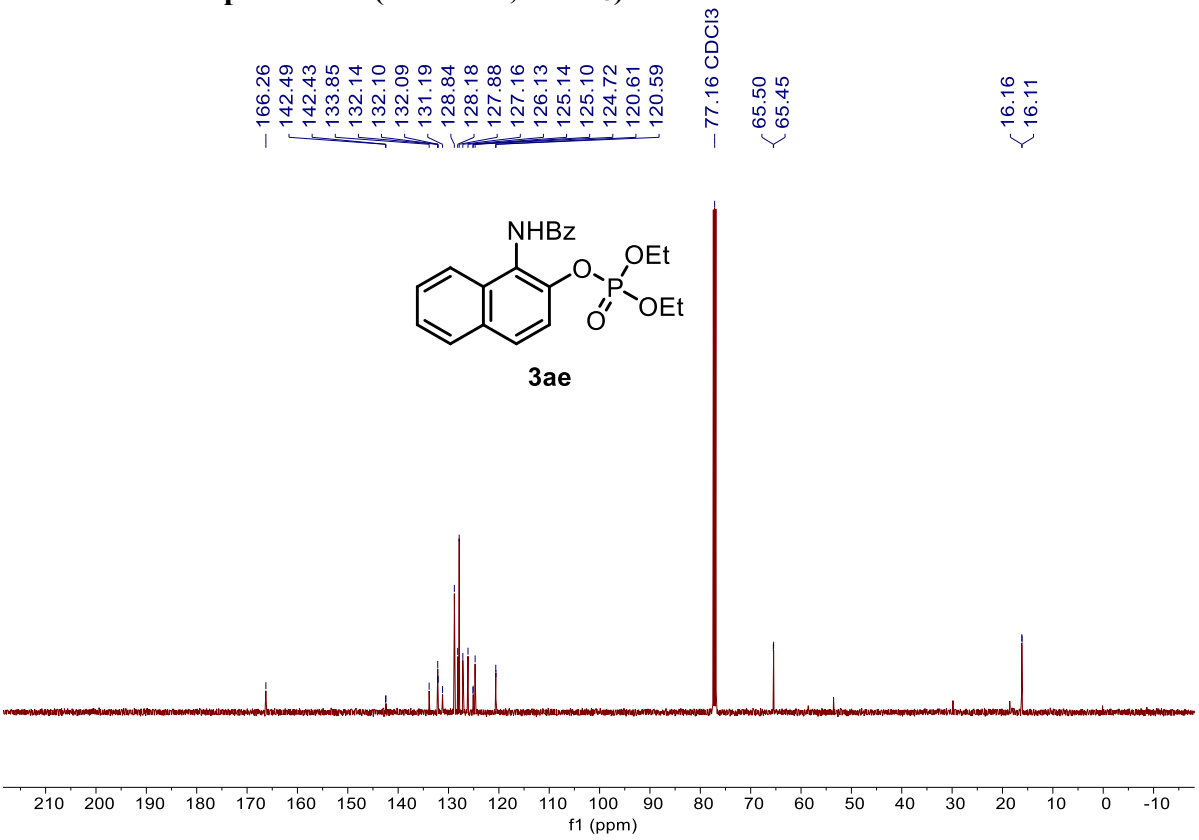
^{31}P NMR of Compound 3ad (202 MHz, $CDCl_3$)



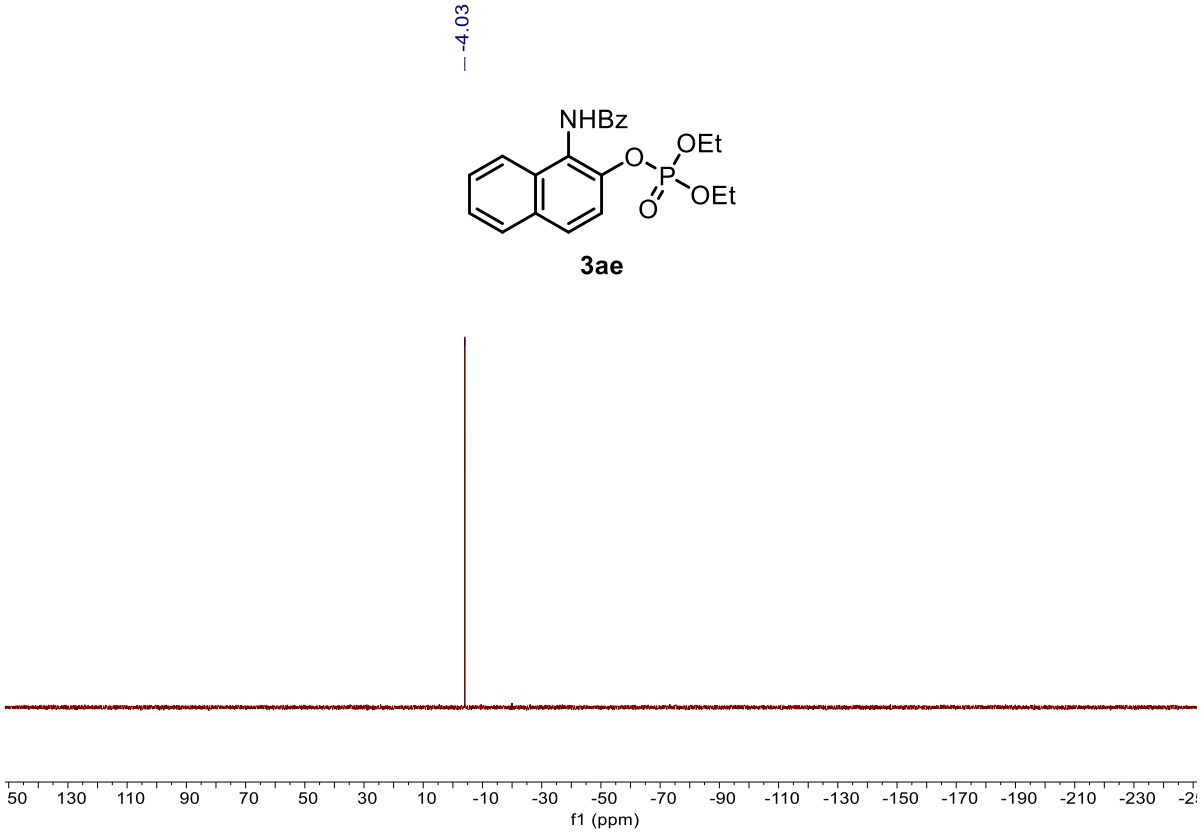
^{1}H NMR of Compound 3ae (500 MHz, $CDCl_3$)



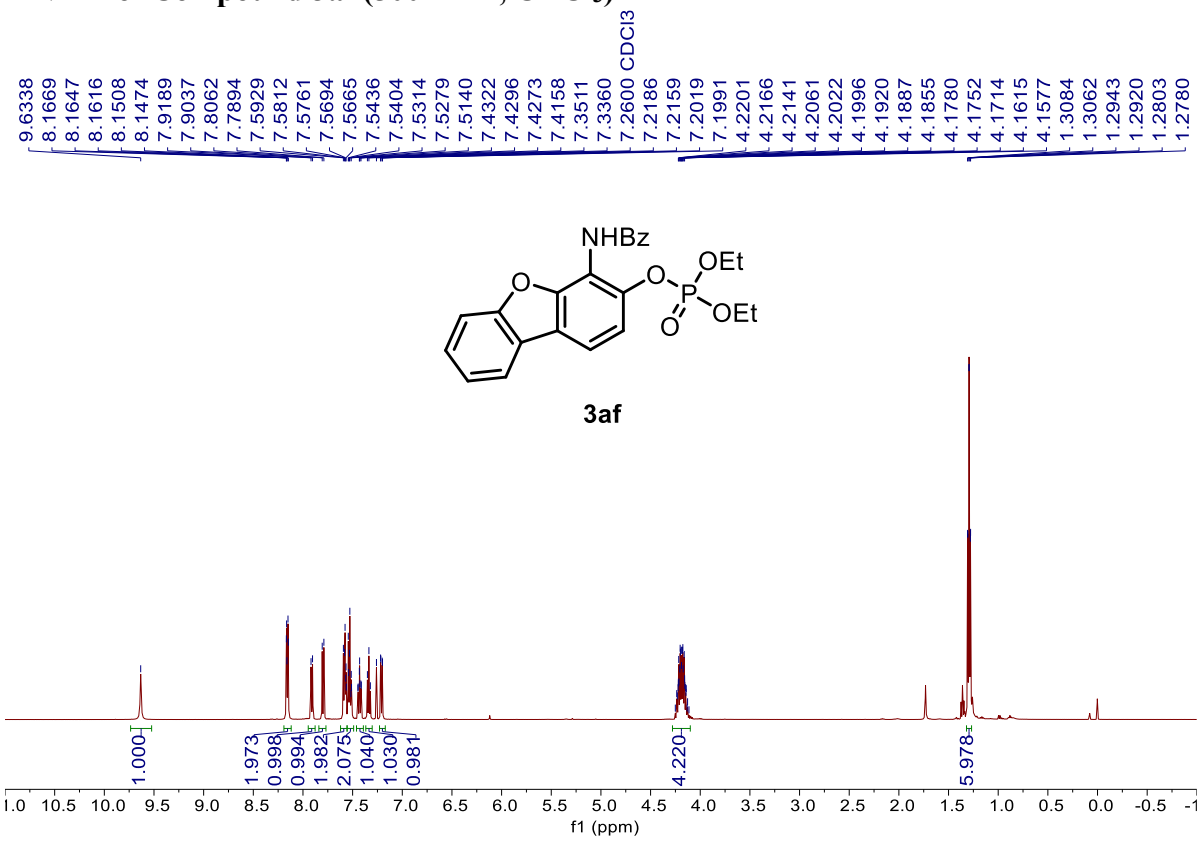
^{13}C NMR of Compound 3ae (126 MHz, $CDCl_3$)



^{31}P NMR of Compound 3ae (202 MHz, $CDCl_3$)



^{1}H NMR of Compound 3af (500 MHz, $CDCl_3$)



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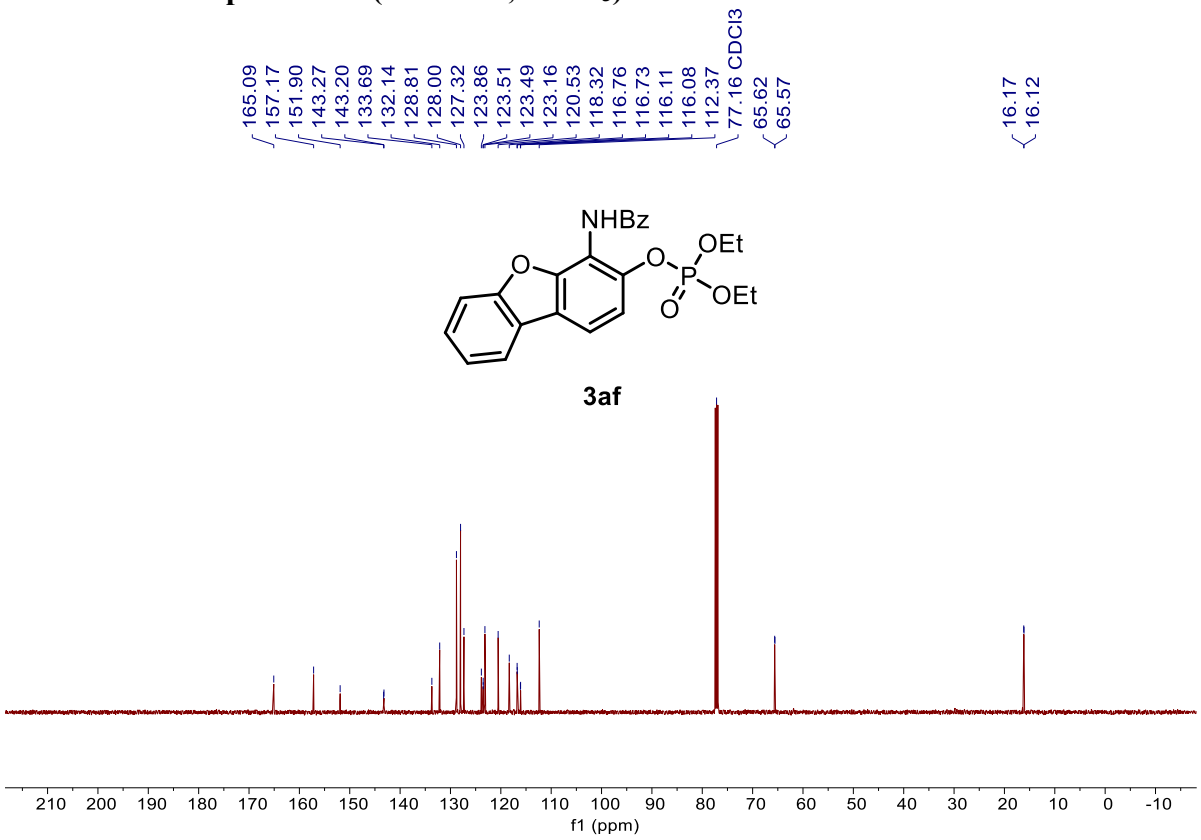
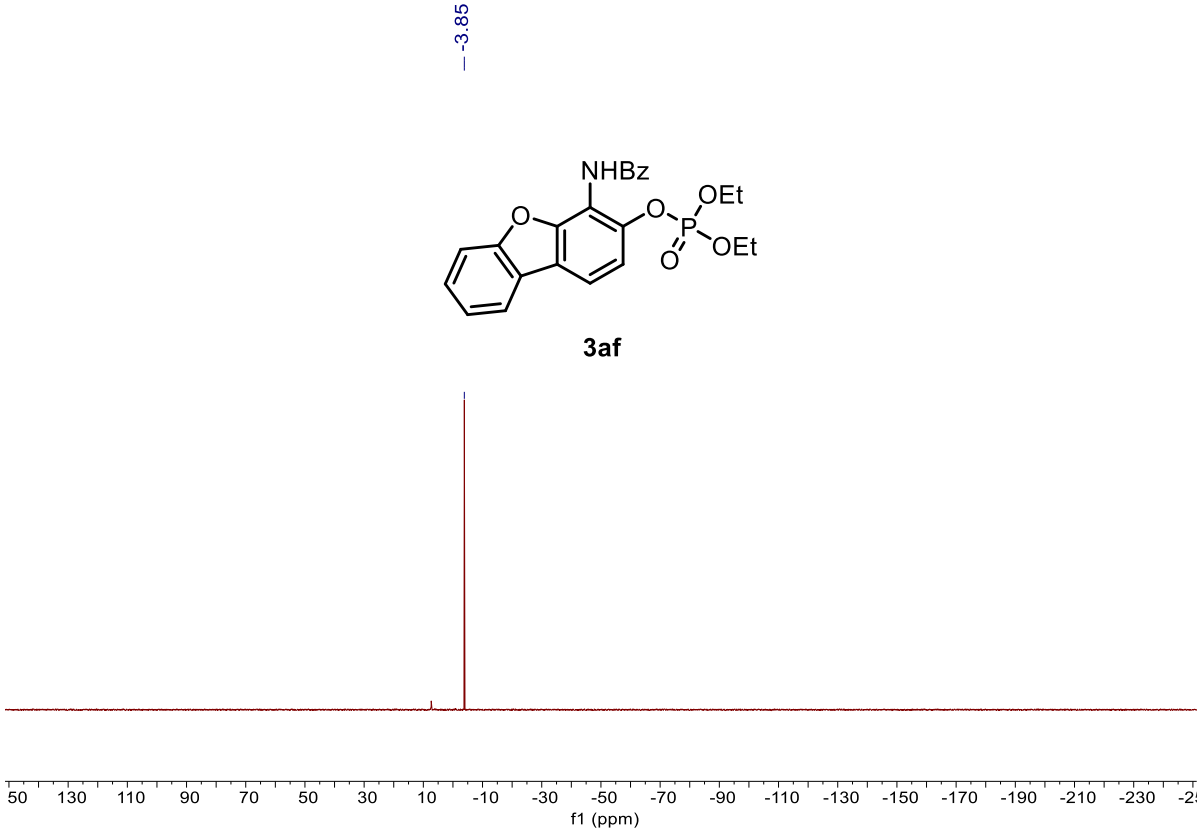
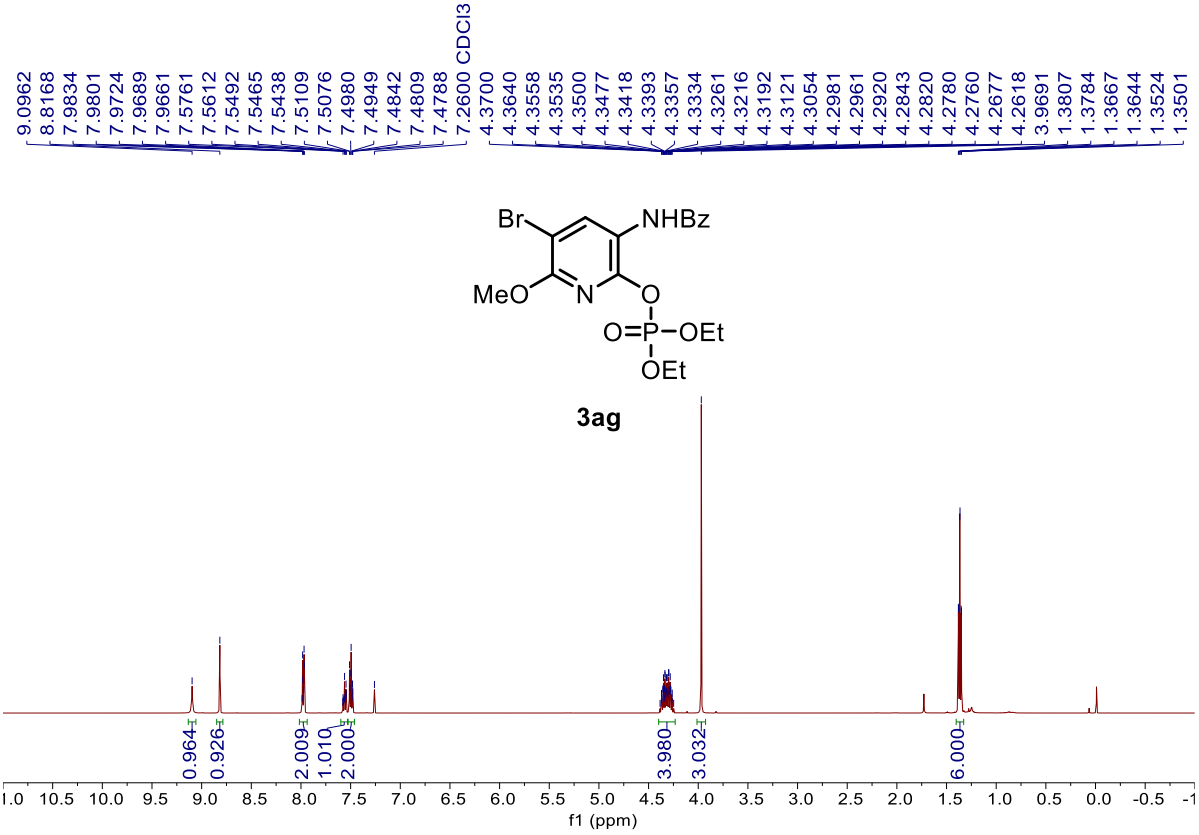


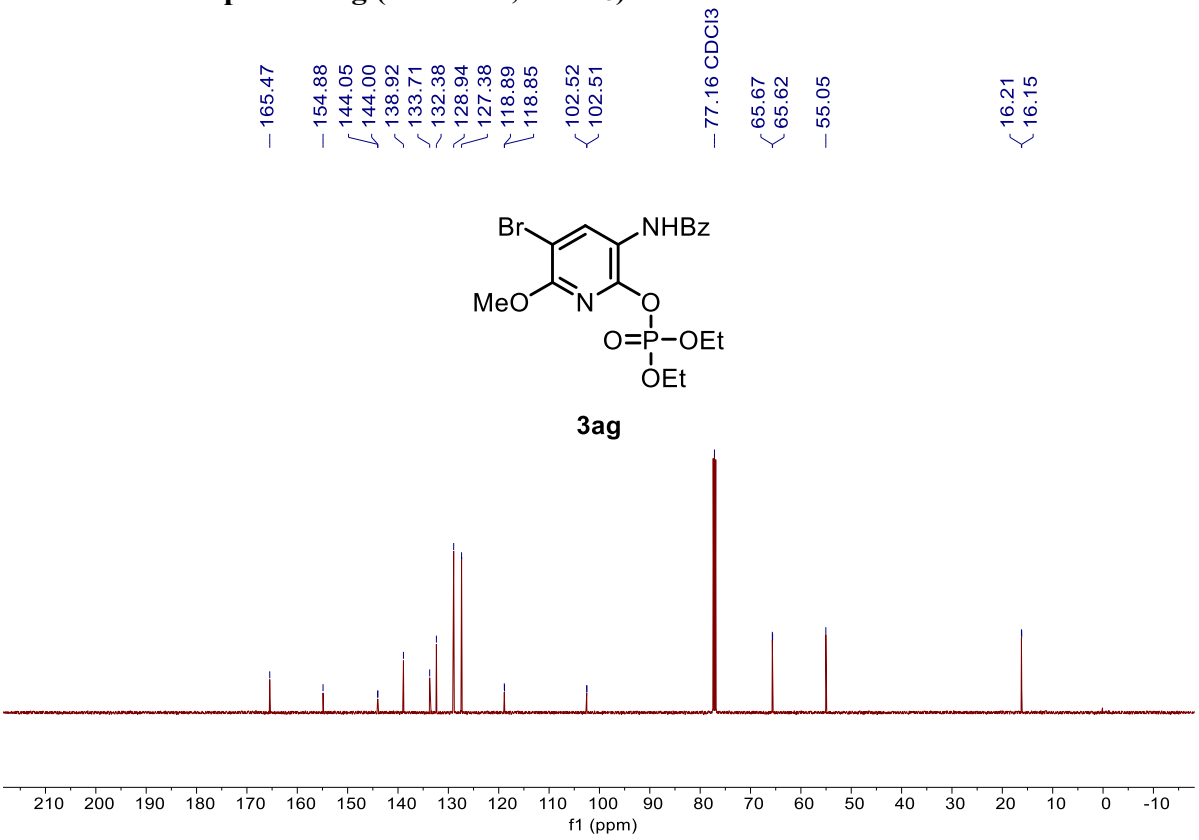
^{31}P NMR of Compound 3af (202 MHz, $CDCl_3$)



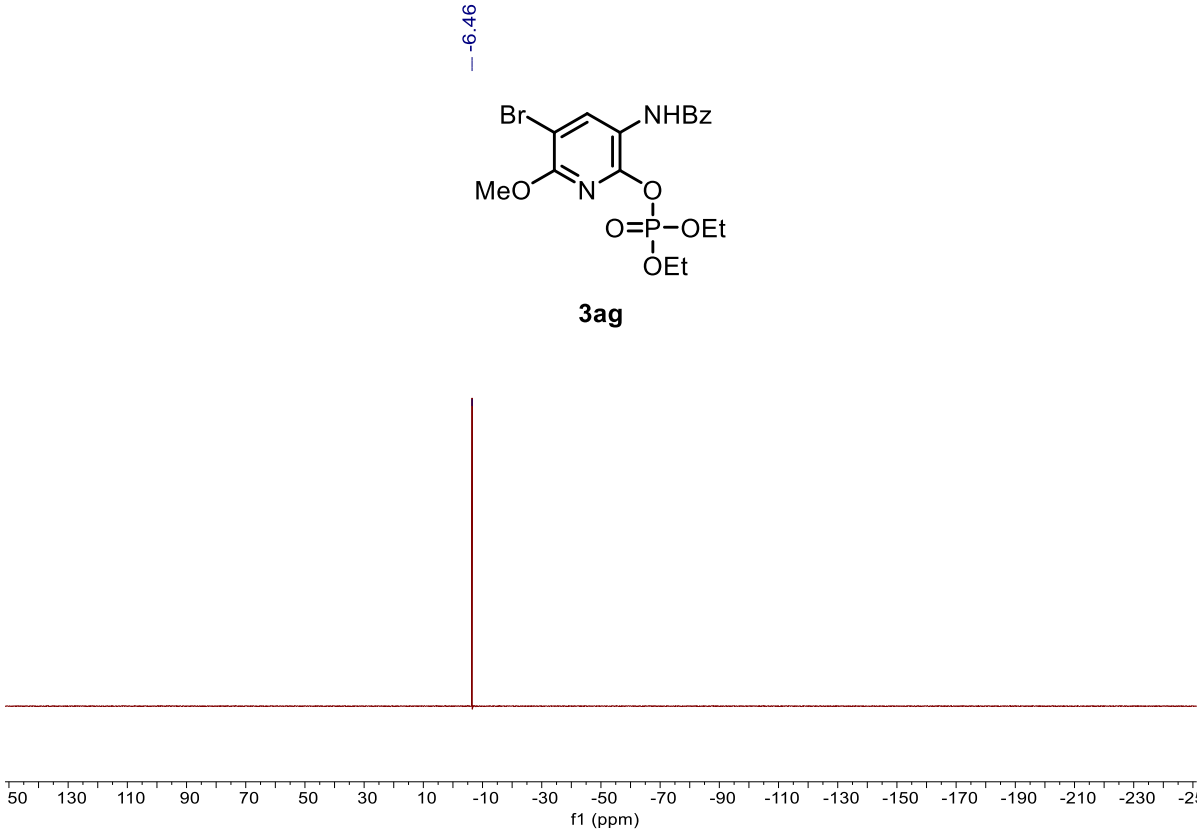
^{1}H NMR of Compound 3ag (500 MHz, $CDCl_3$)



^{13}C NMR of Compound 3ag (126 MHz, $CDCl_3$)

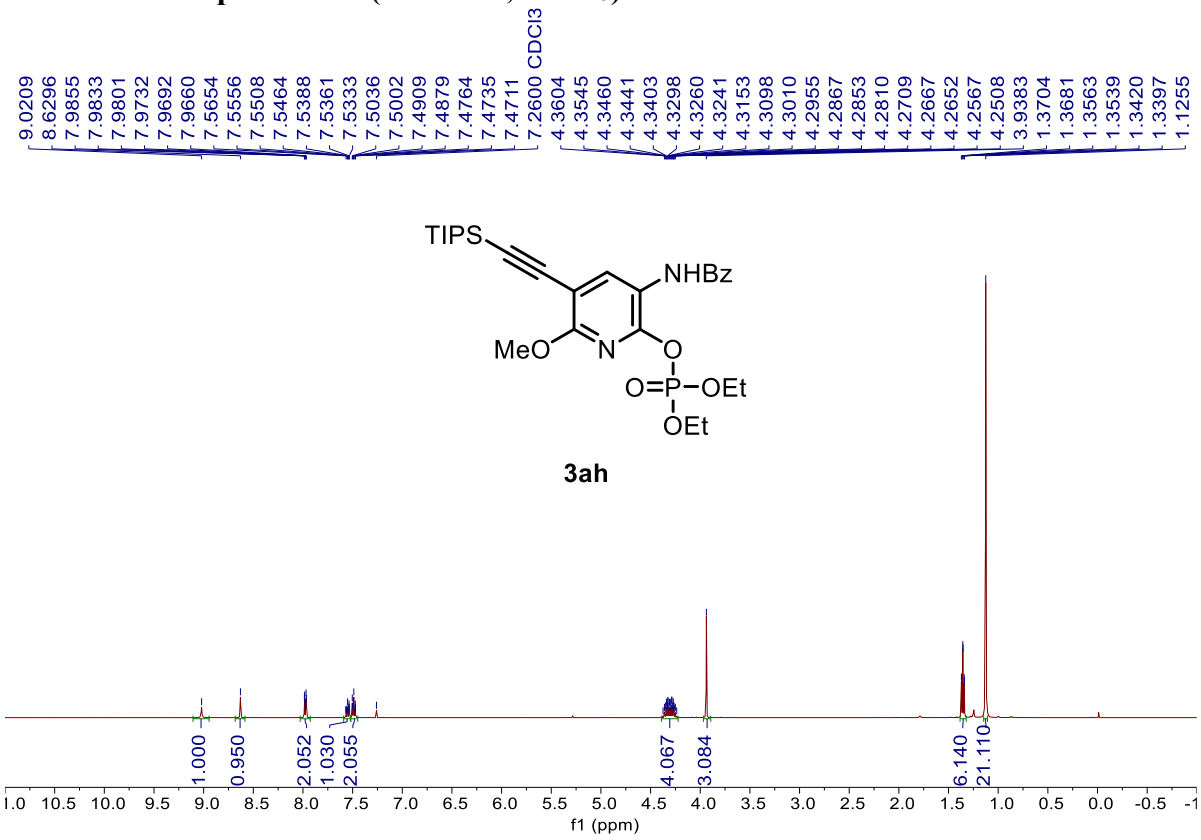


^{31}P NMR of Compound 3ag (202 MHz, $CDCl_3$)



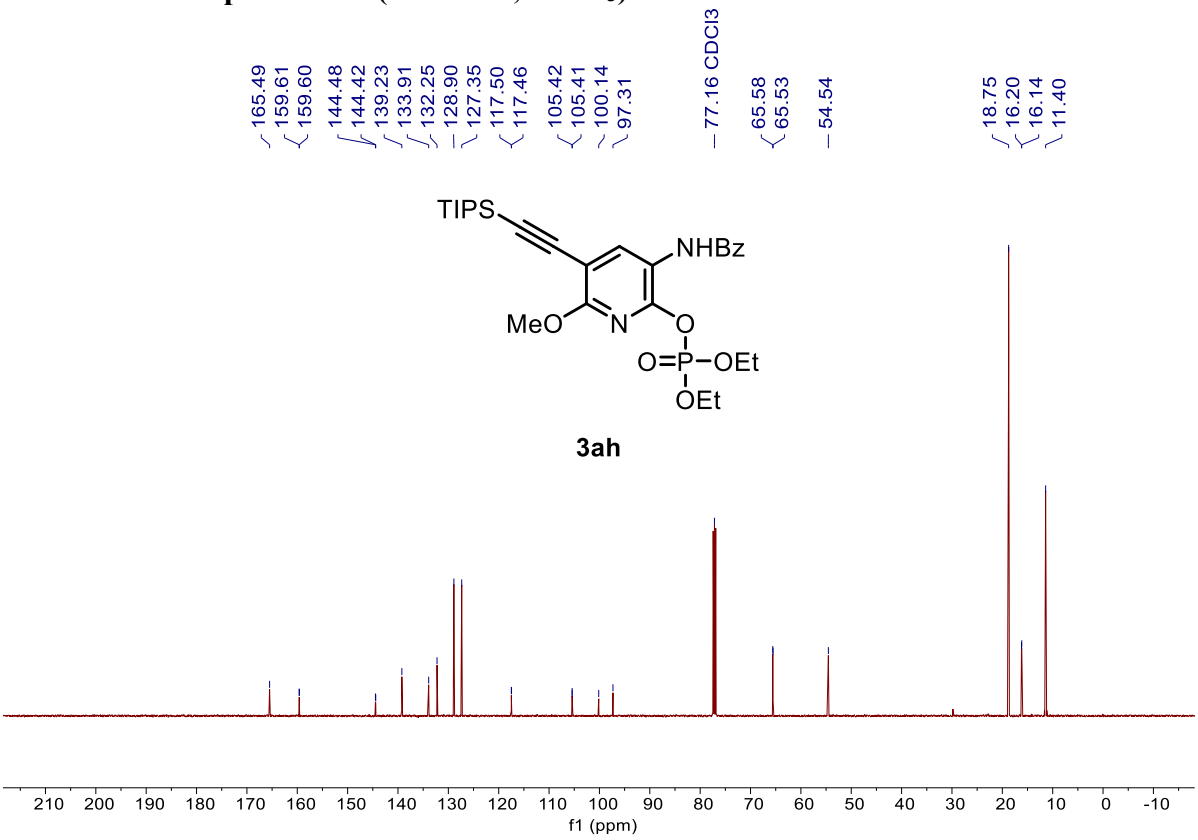
3ag

^{1}H NMR of Compound 3ah (500 MHz, $CDCl_3$)

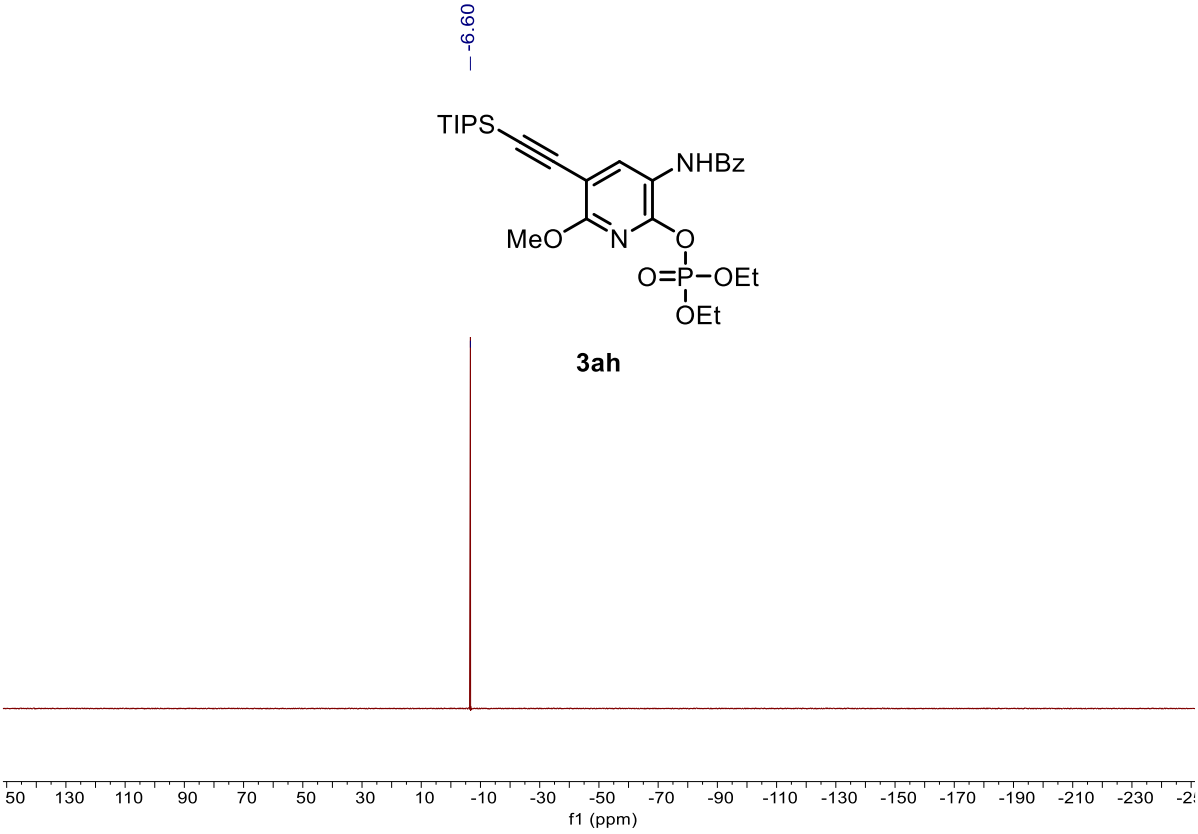


3ah

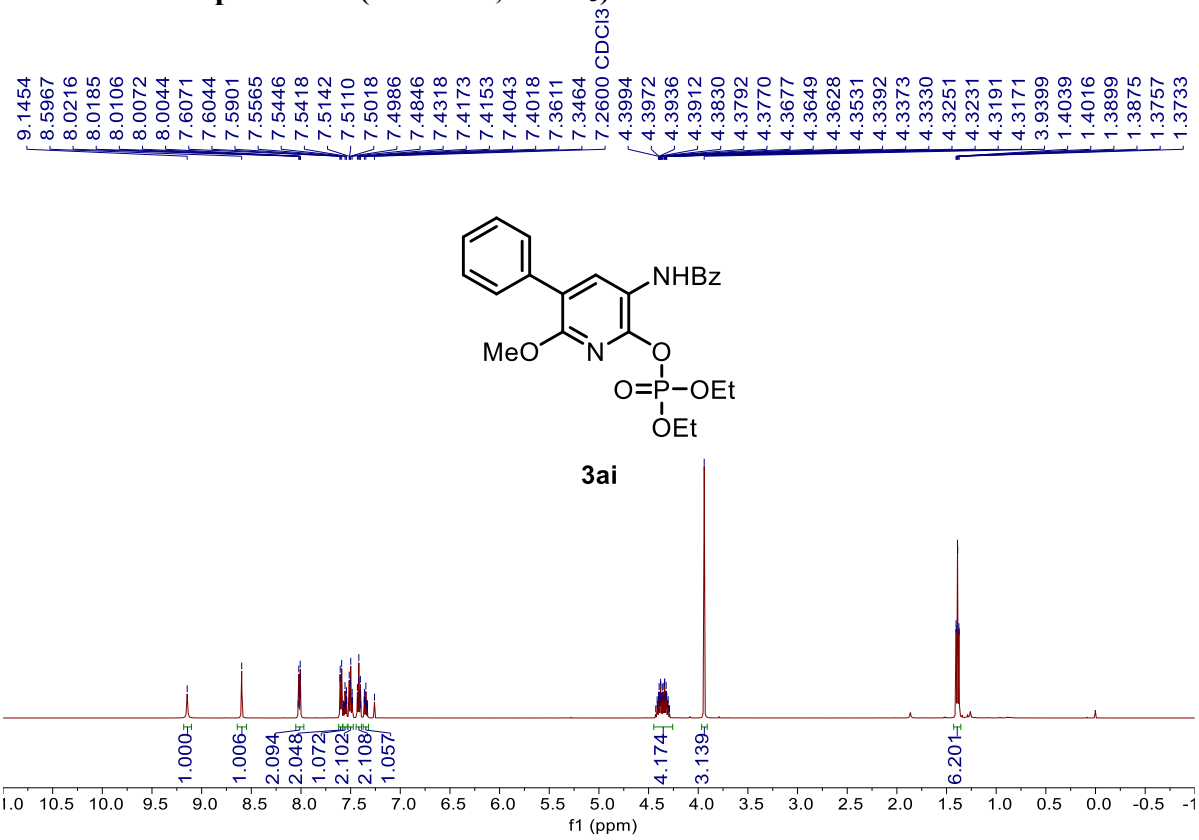
^{13}C NMR of Compound 3ah (126 MHz, $CDCl_3$)



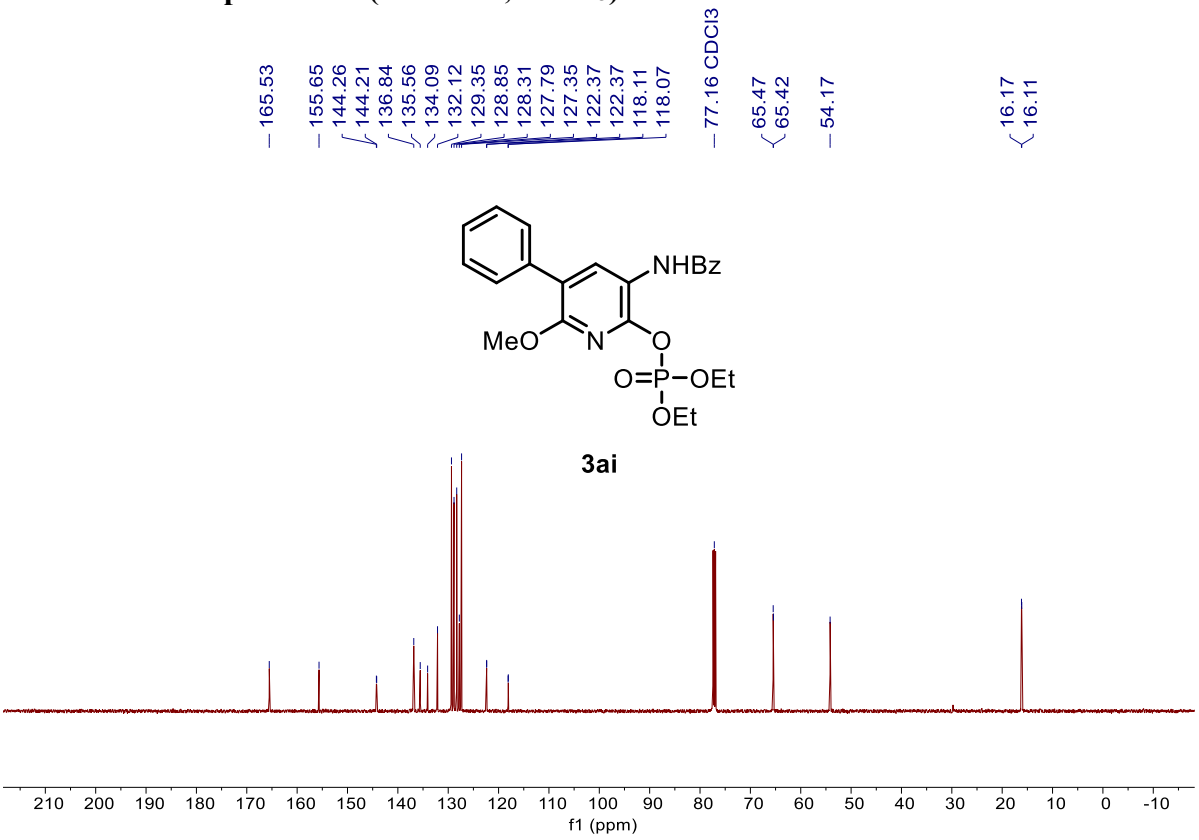
^{31}P NMR of Compound 3ah (202 MHz, $CDCl_3$)



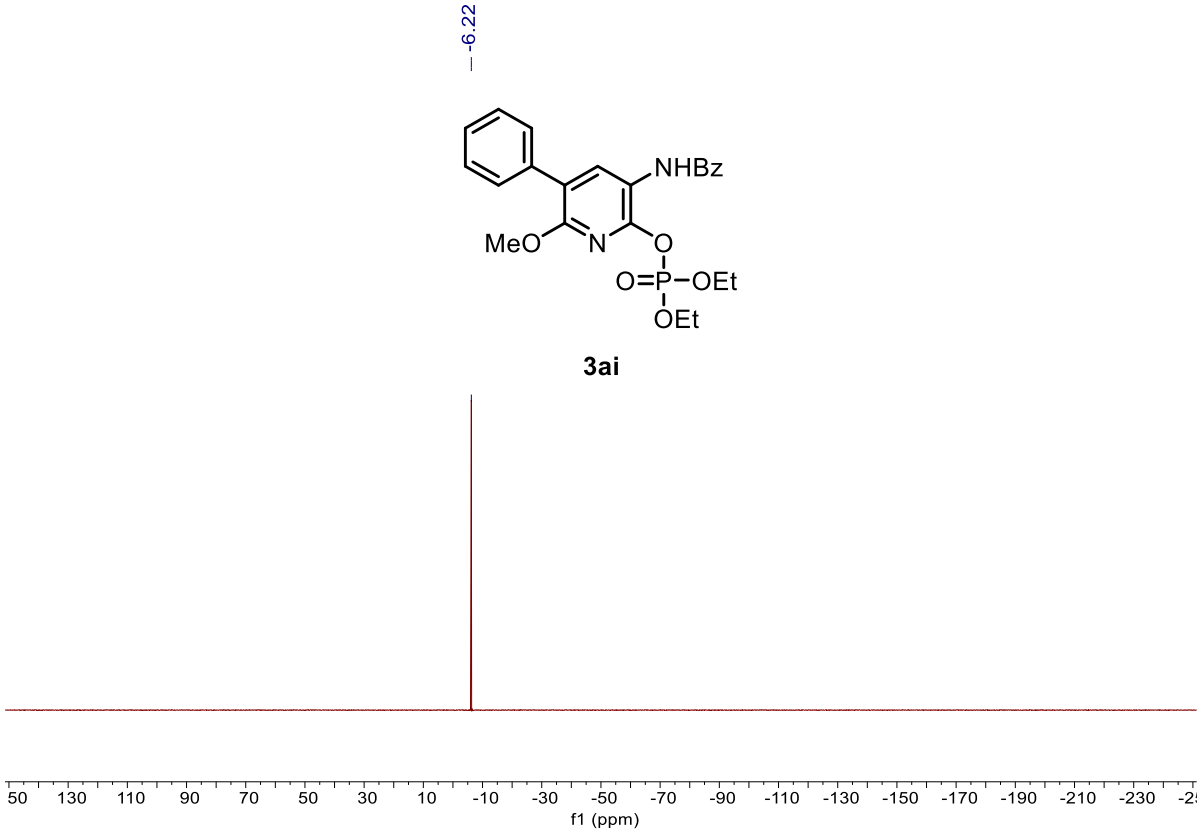
^{1}H NMR of Compound 3ai (500 MHz, $CDCl_3$)



^{13}C NMR of Compound 3ai (126 MHz, $CDCl_3$)

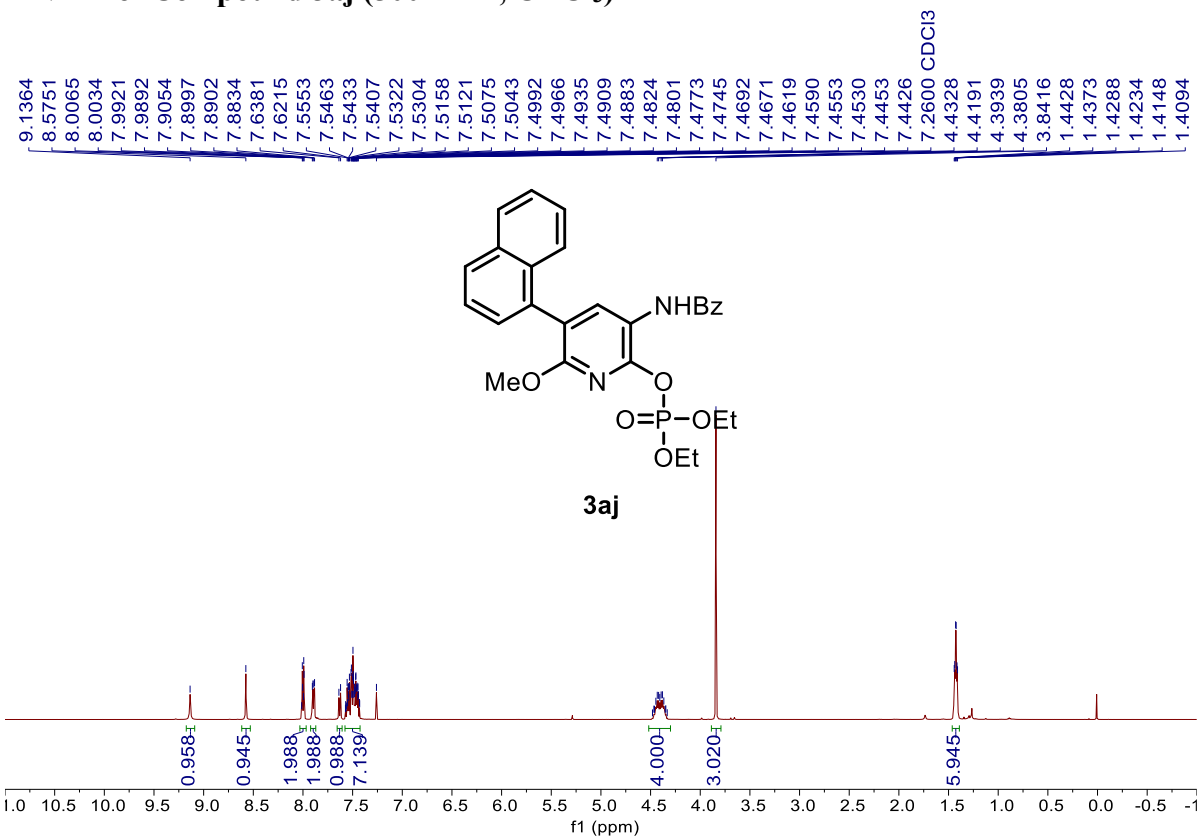


^{31}P NMR of Compound 3ai (202 MHz, $CDCl_3$)



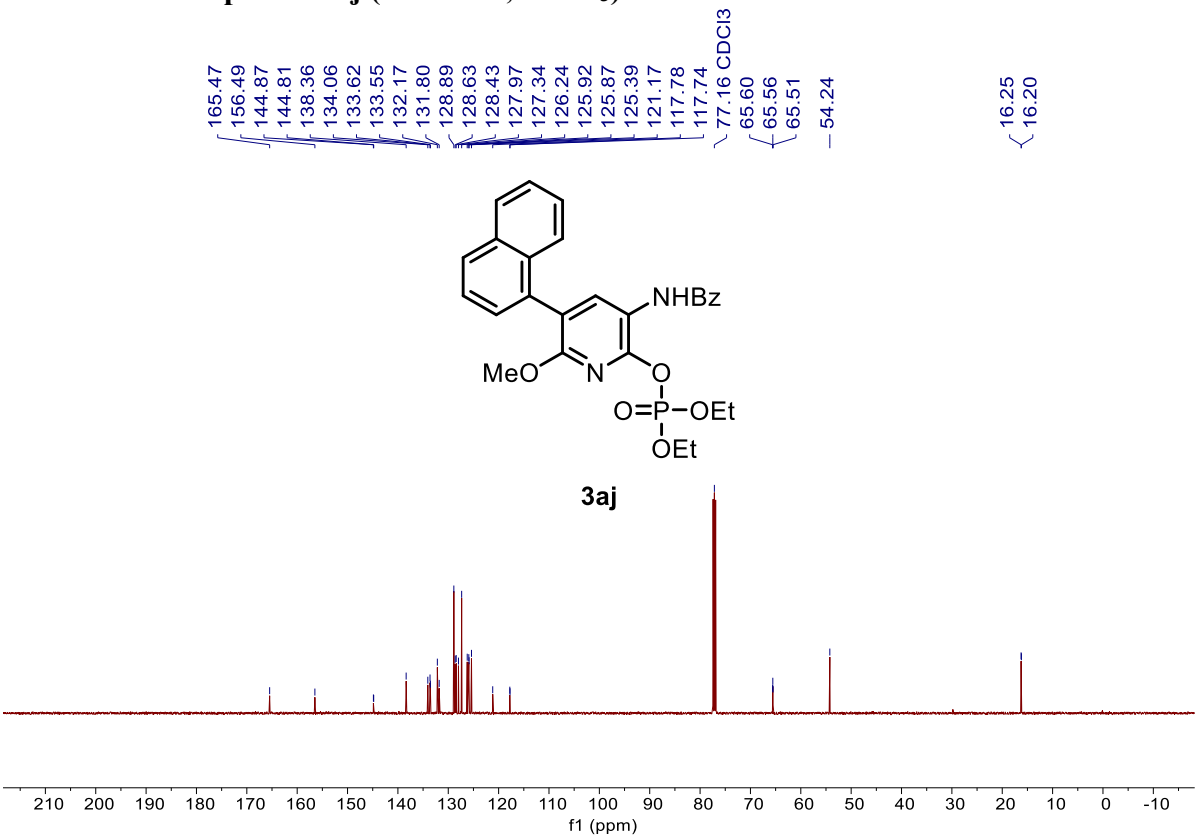
3ai

^{1}H NMR of Compound 3aj (500 MHz, $CDCl_3$)

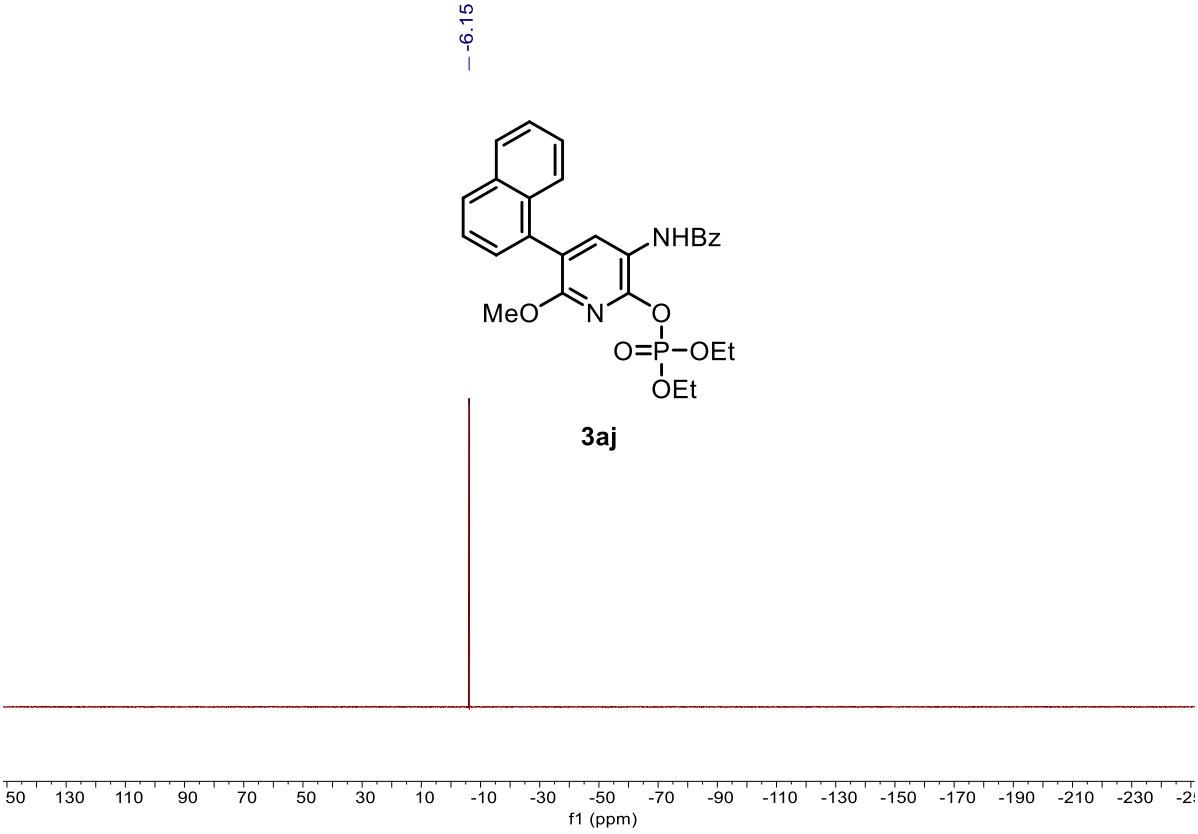


3aj

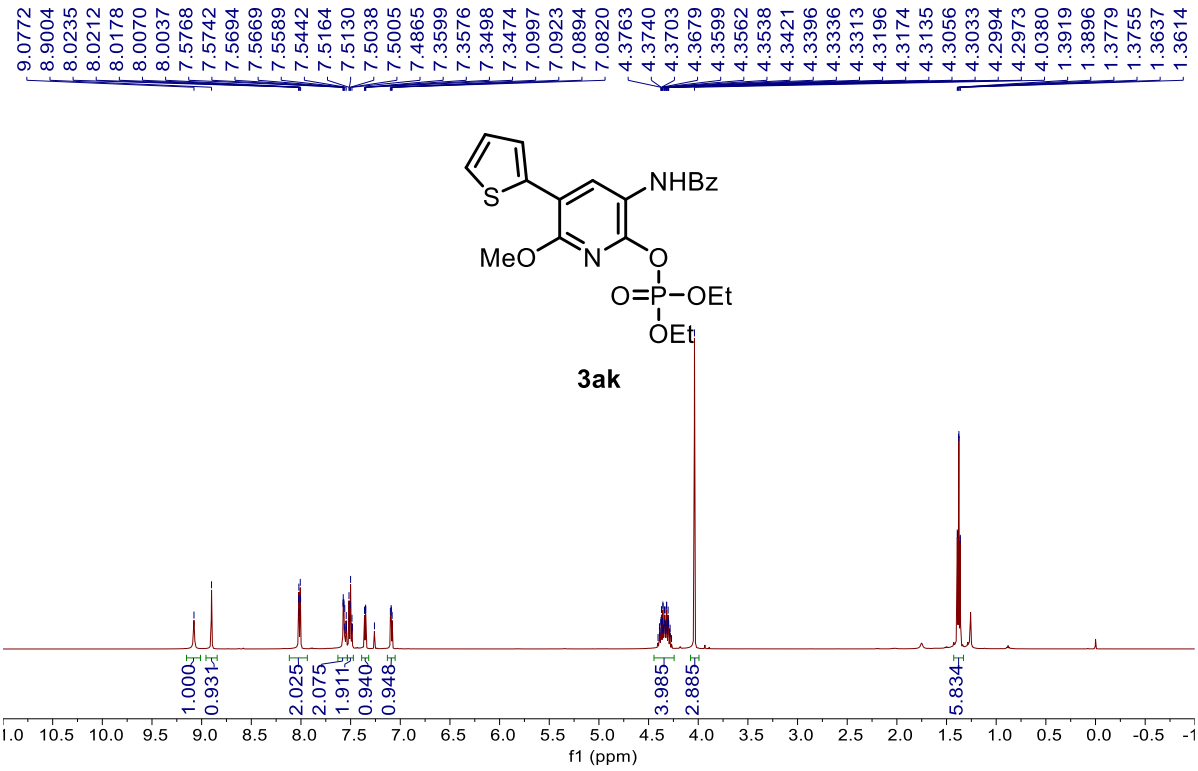
^{13}C NMR of Compound 3aj (126 MHz, $CDCl_3$)



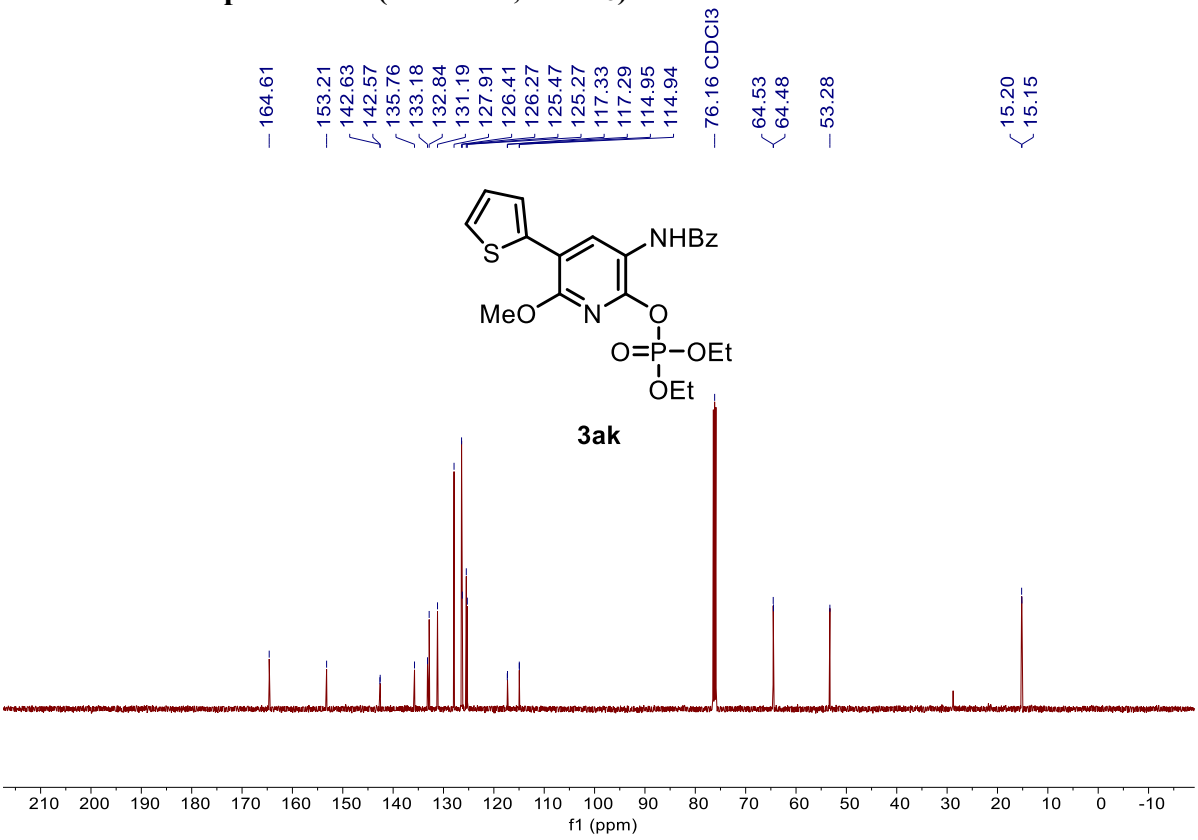
^{31}P NMR of Compound 3aj (202 MHz, $CDCl_3$)



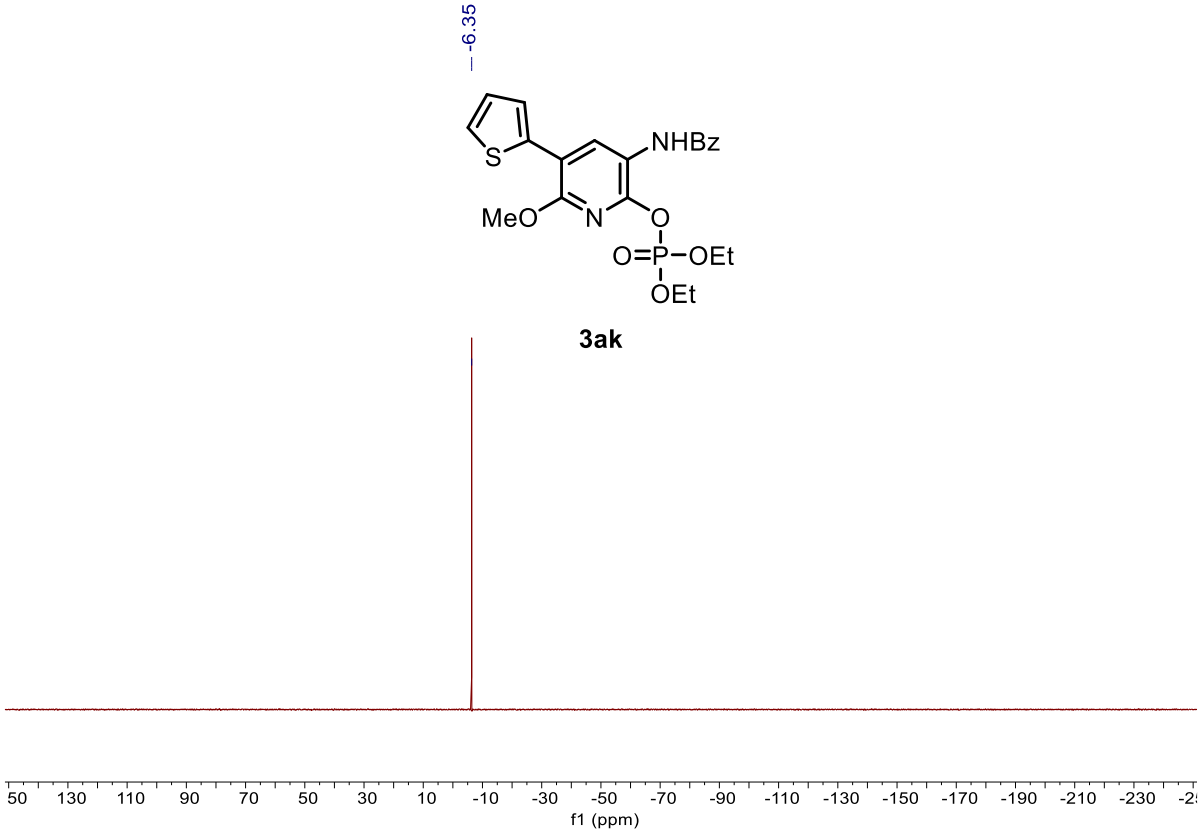
^{1}H NMR of Compound 3ak (500 MHz, $CDCl_3$)



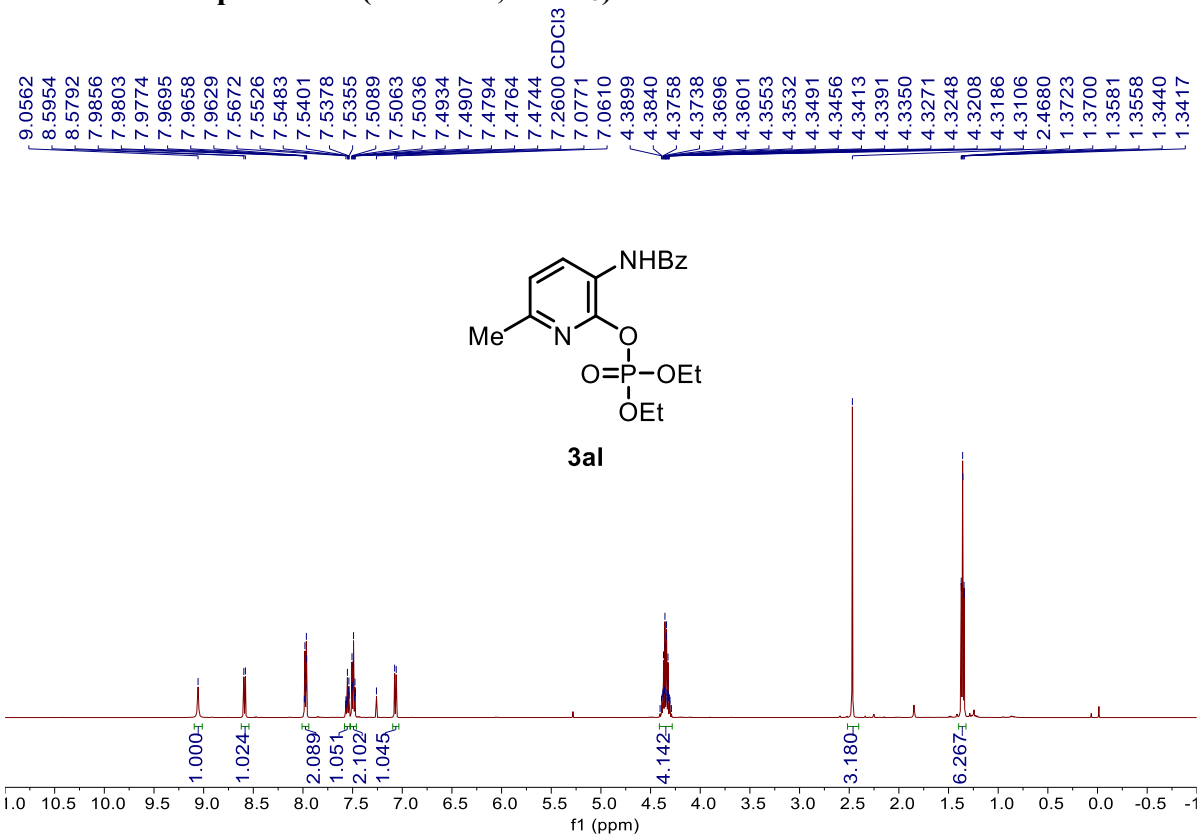
^{13}C NMR of Compound 3ak (126 MHz, $CDCl_3$)



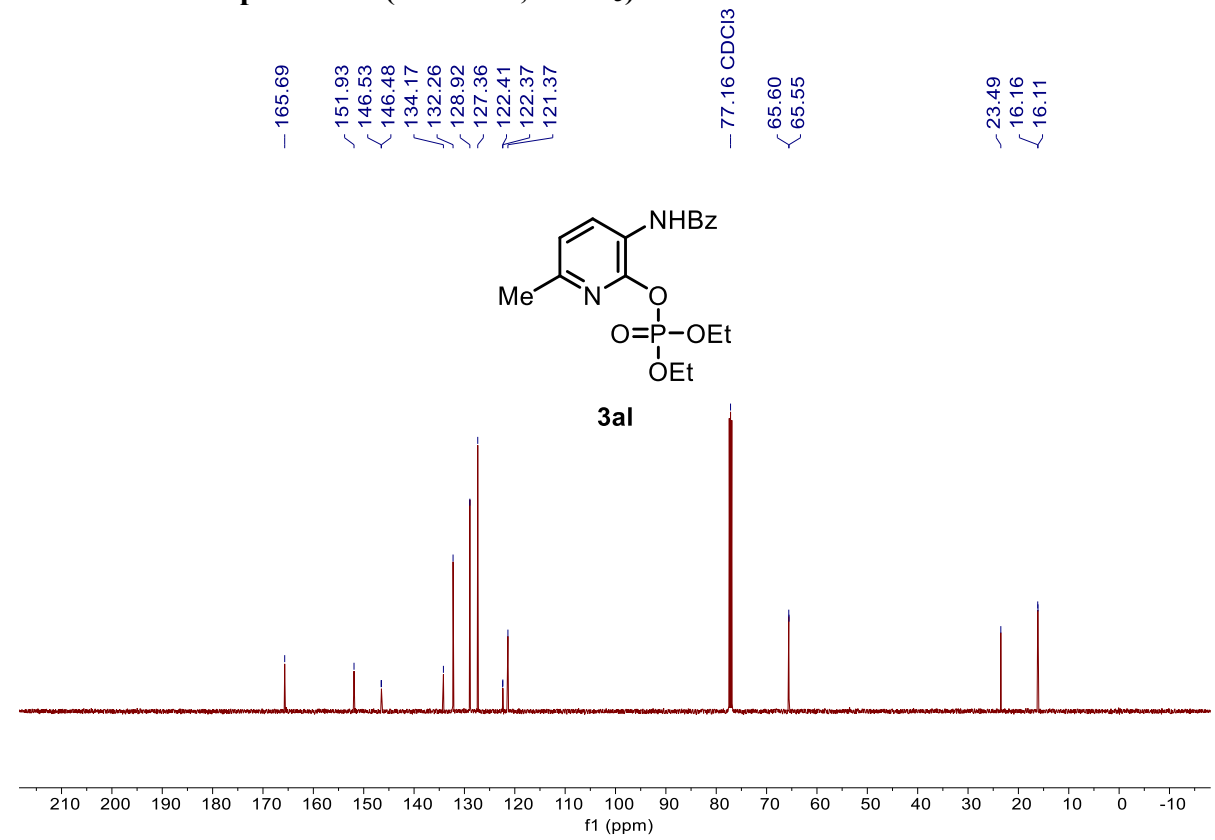
^{31}P NMR of Compound 3ak (202 MHz, $CDCl_3$)



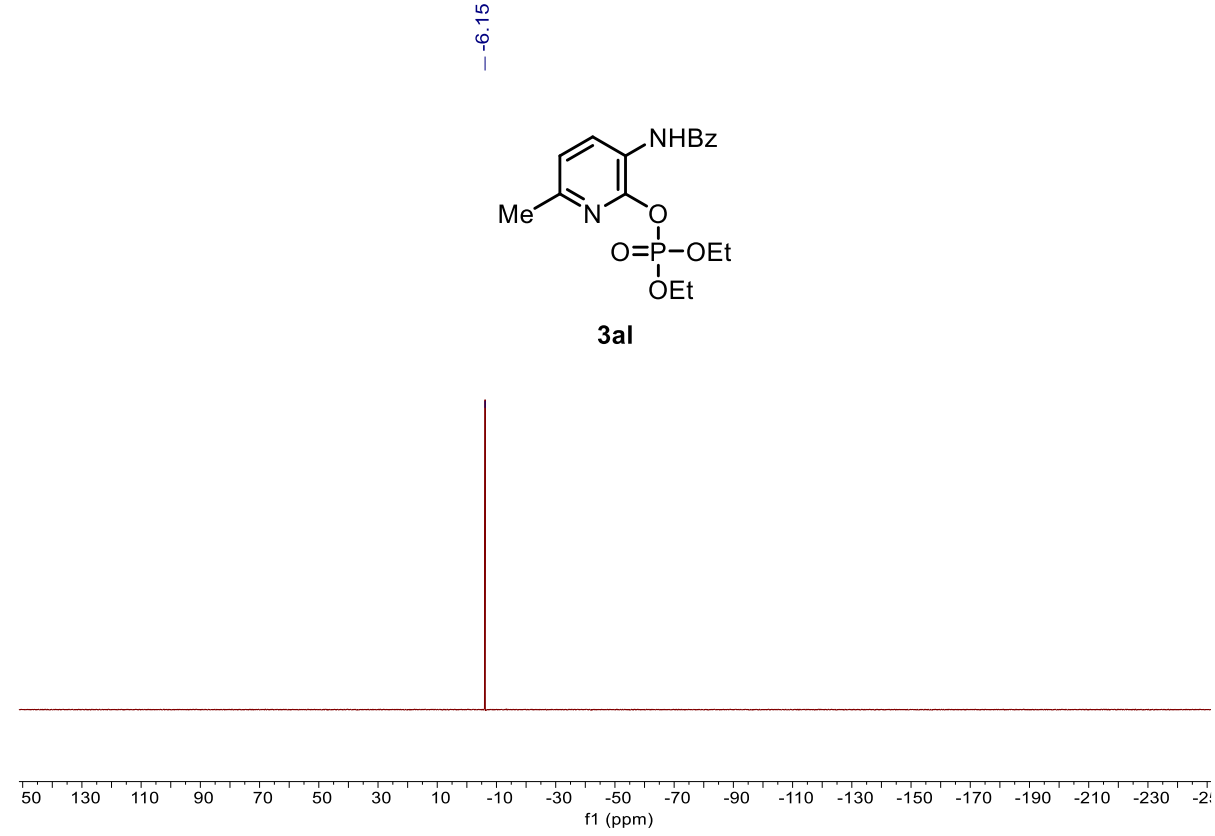
^{1}H NMR of Compound 3al (500 MHz, $CDCl_3$)



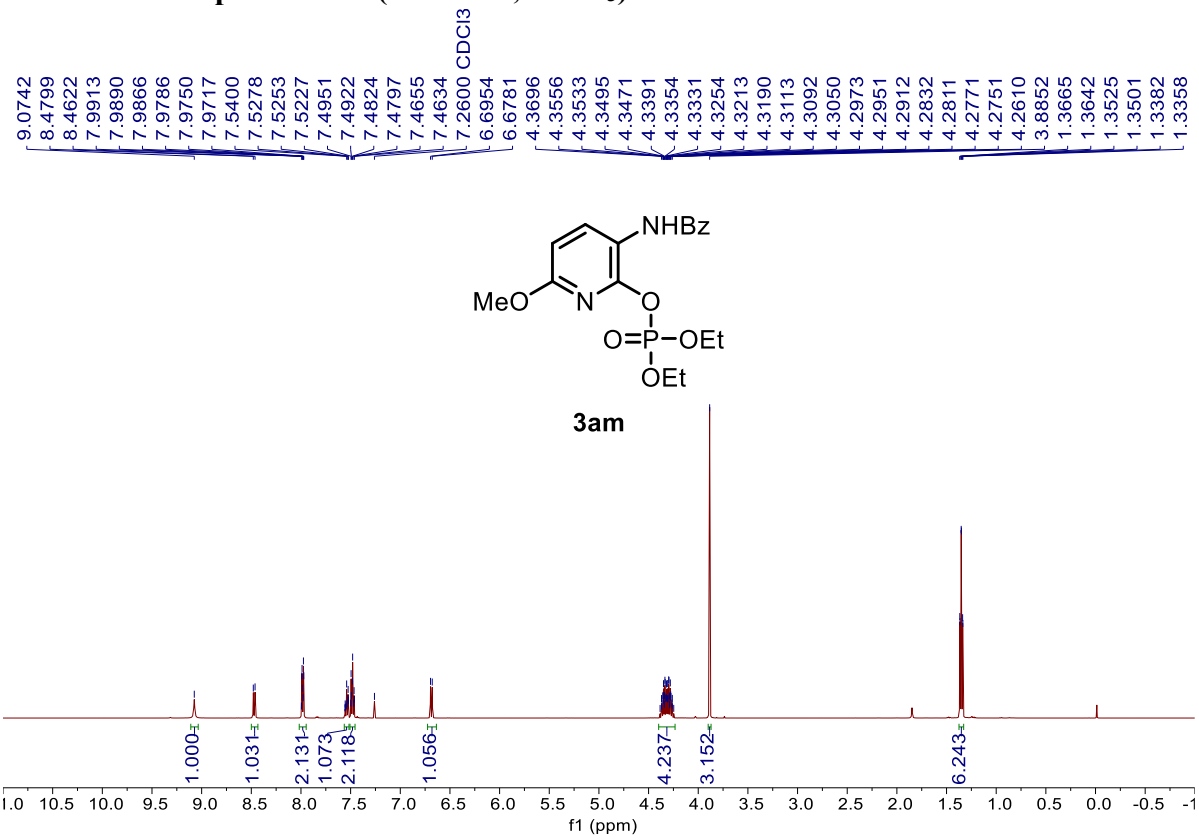
^{13}C NMR of Compound 3al (126 MHz, $CDCl_3$)



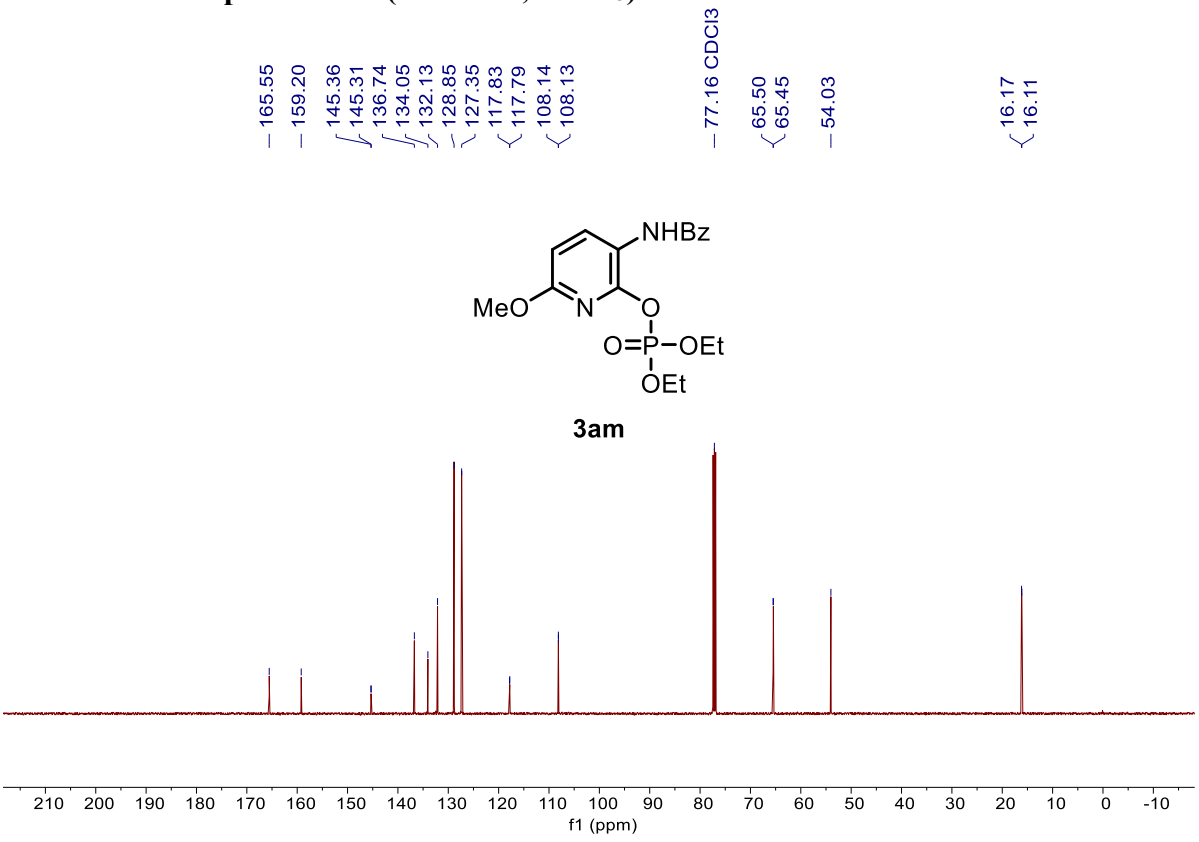
^{31}P NMR of Compound 3al (202 MHz, $CDCl_3$)



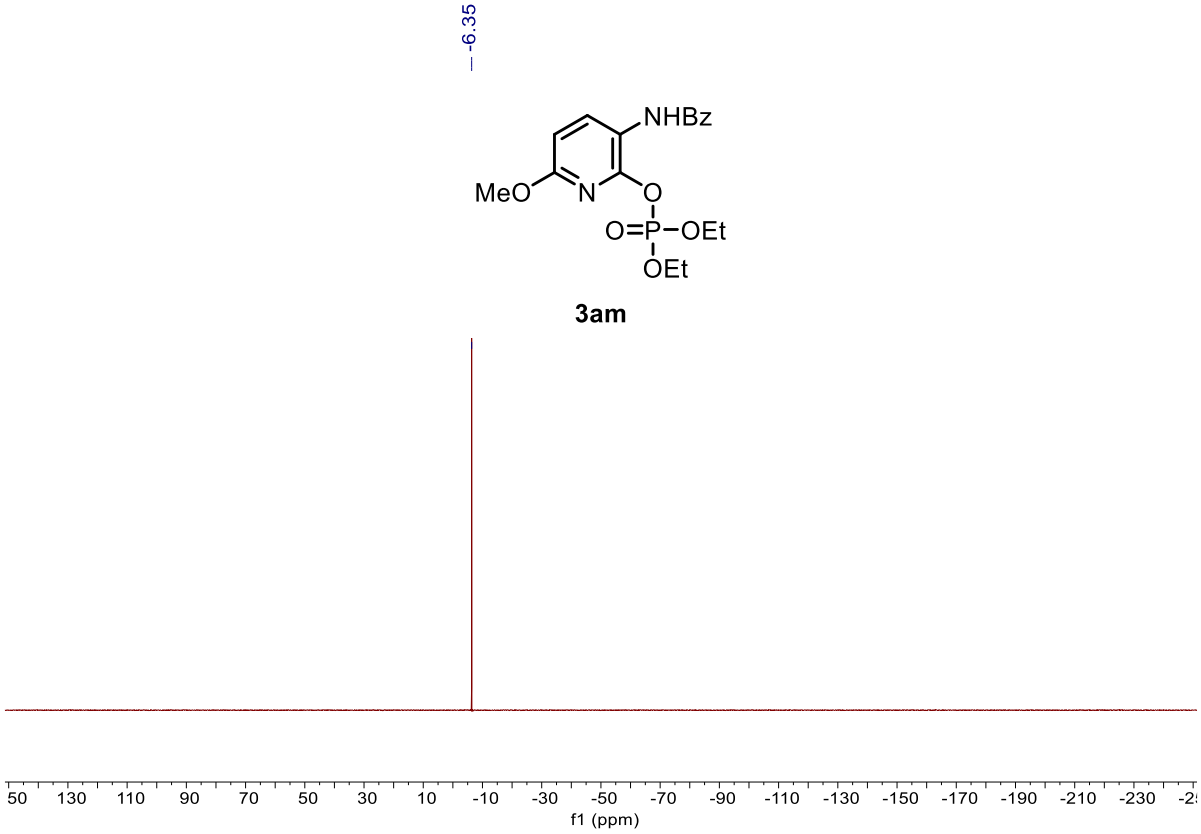
^{1}H NMR of Compound 3am (500 MHz, $CDCl_3$)



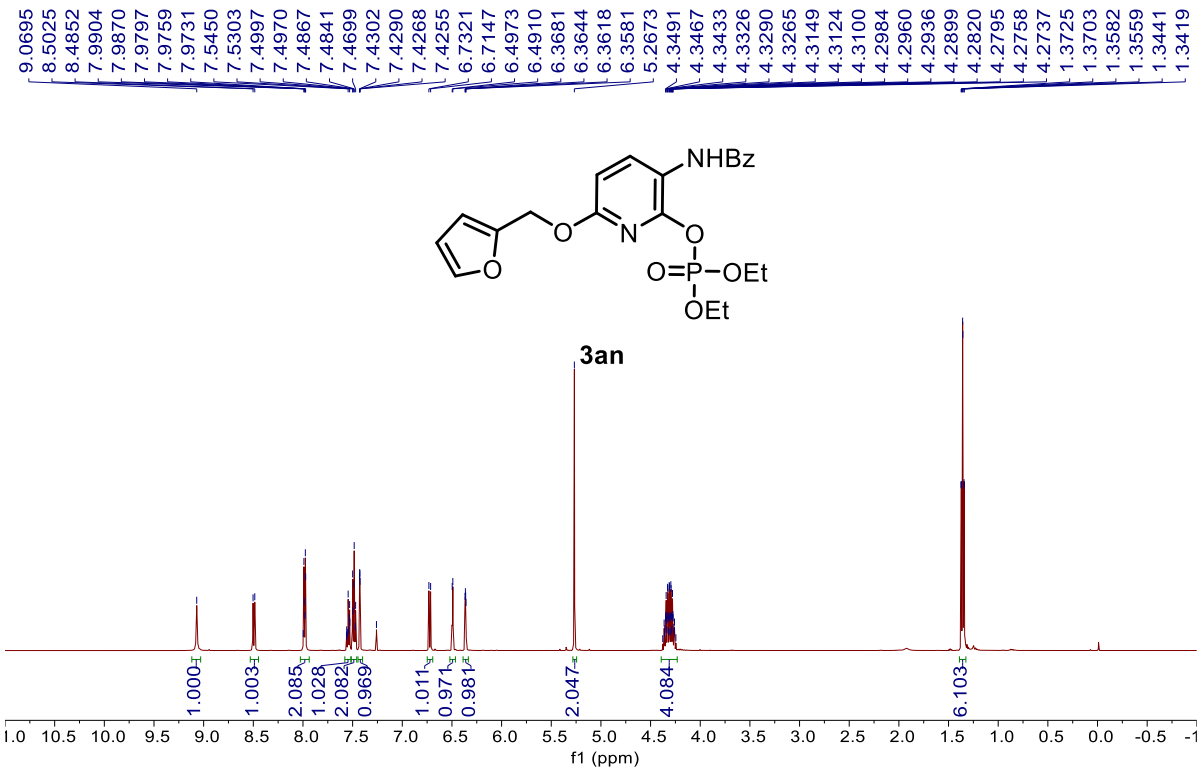
^{13}C NMR of Compound 3am (126 MHz, $CDCl_3$)



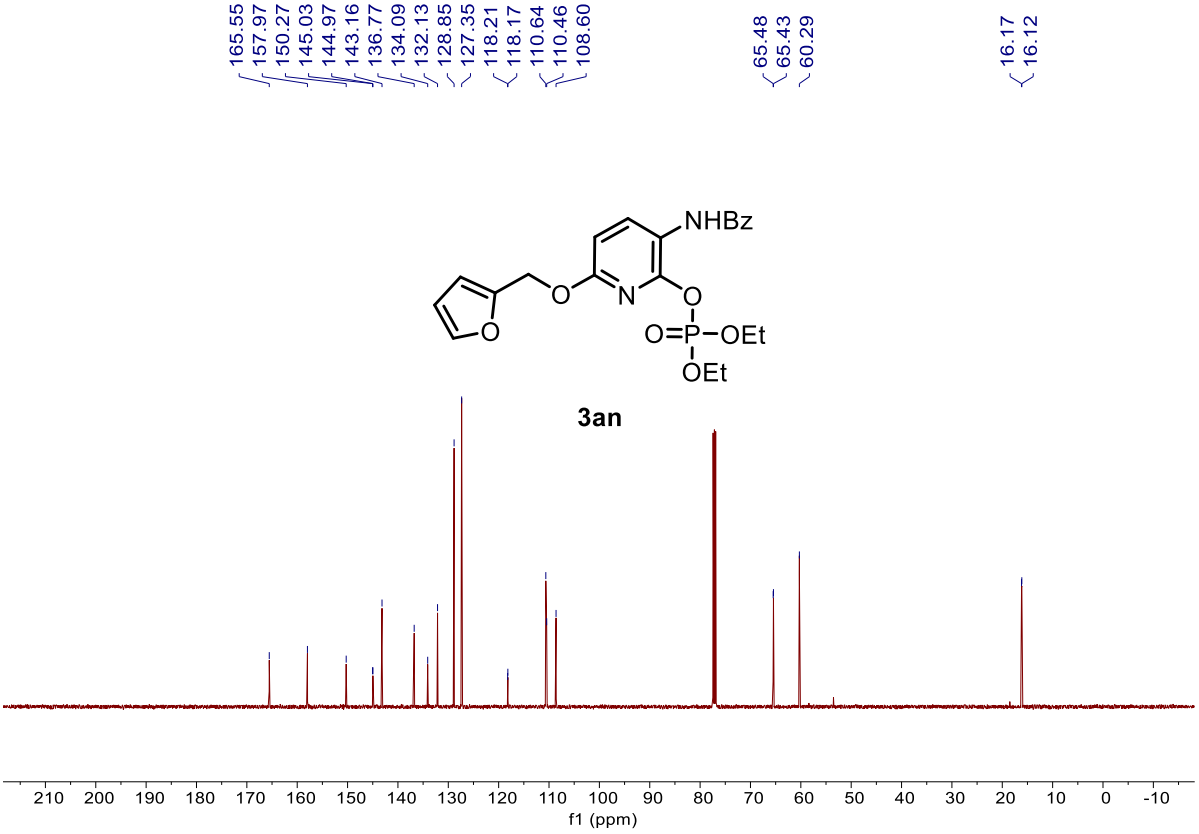
^{31}P NMR of Compound 3am (202 MHz, $CDCl_3$)



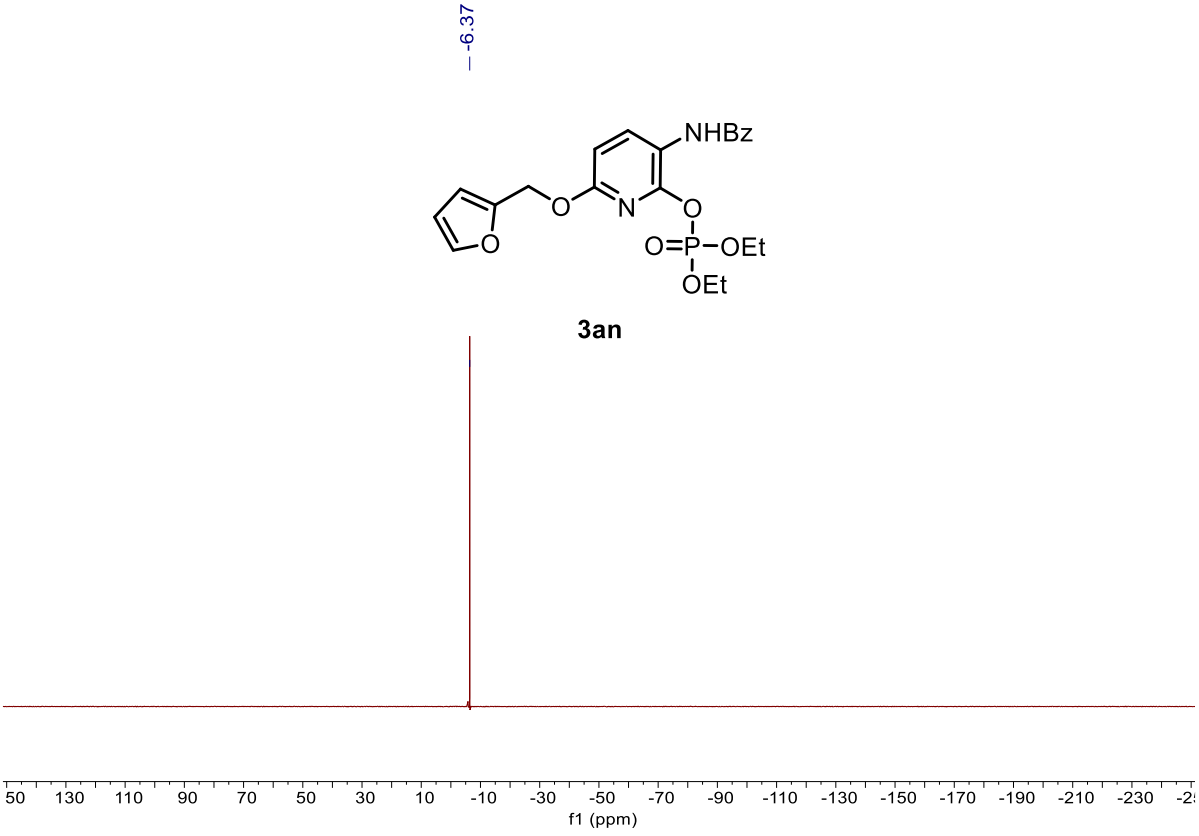
^{1}H NMR of Compound 3an (500 MHz, $CDCl_3$)



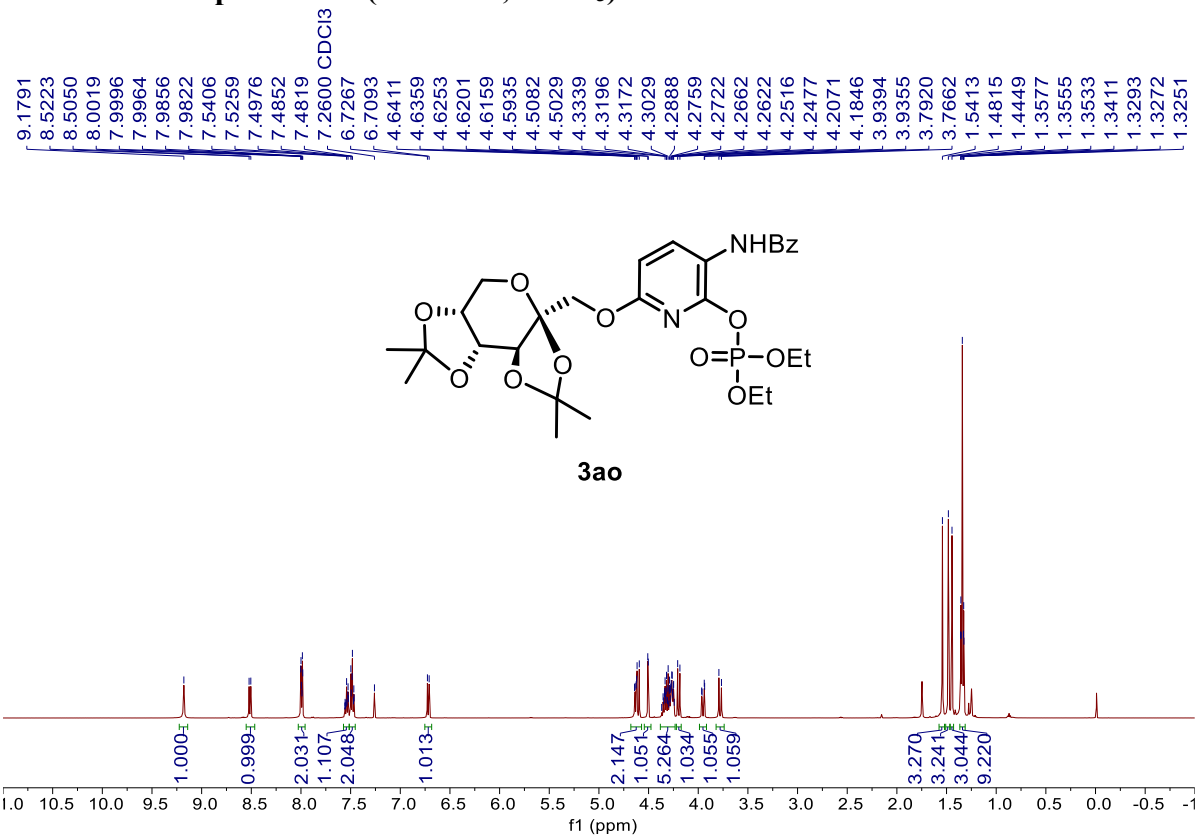
^{13}C NMR of Compound 3an (126 MHz, $CDCl_3$)



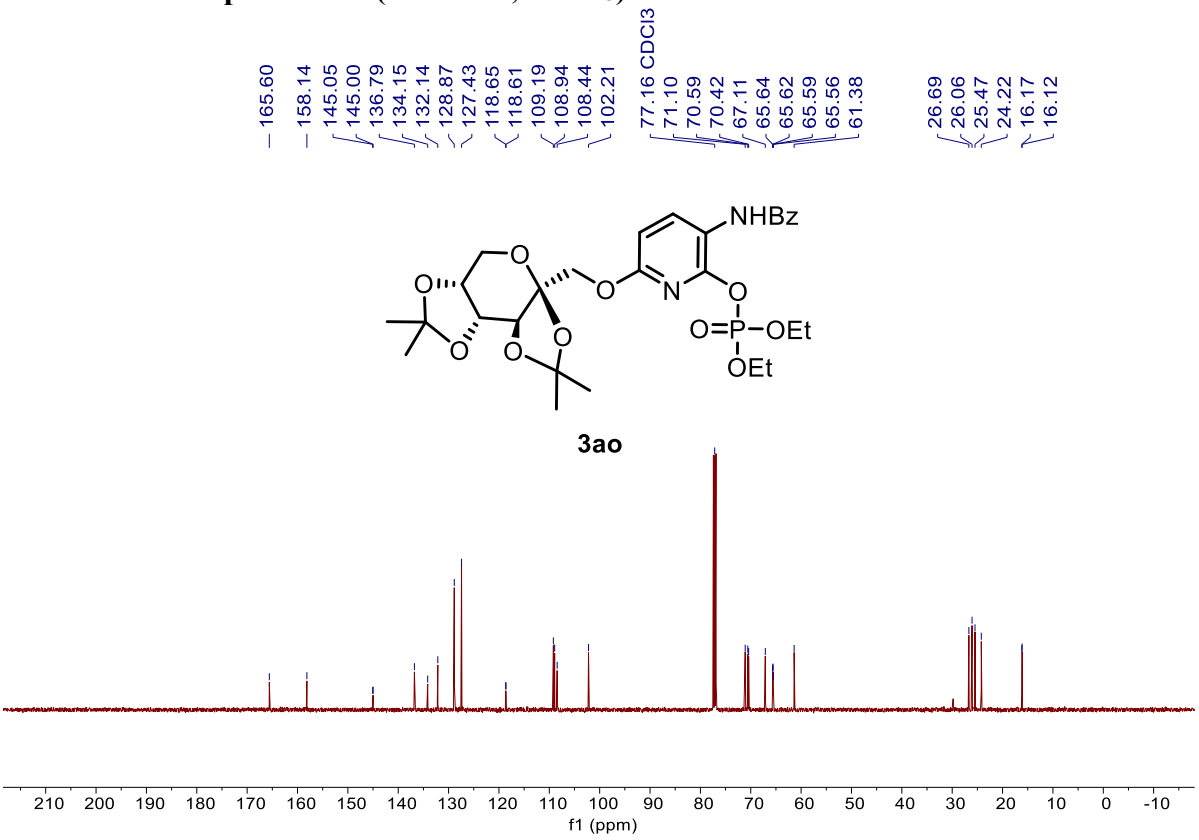
^{31}P NMR of Compound 3an (202 MHz, $CDCl_3$)



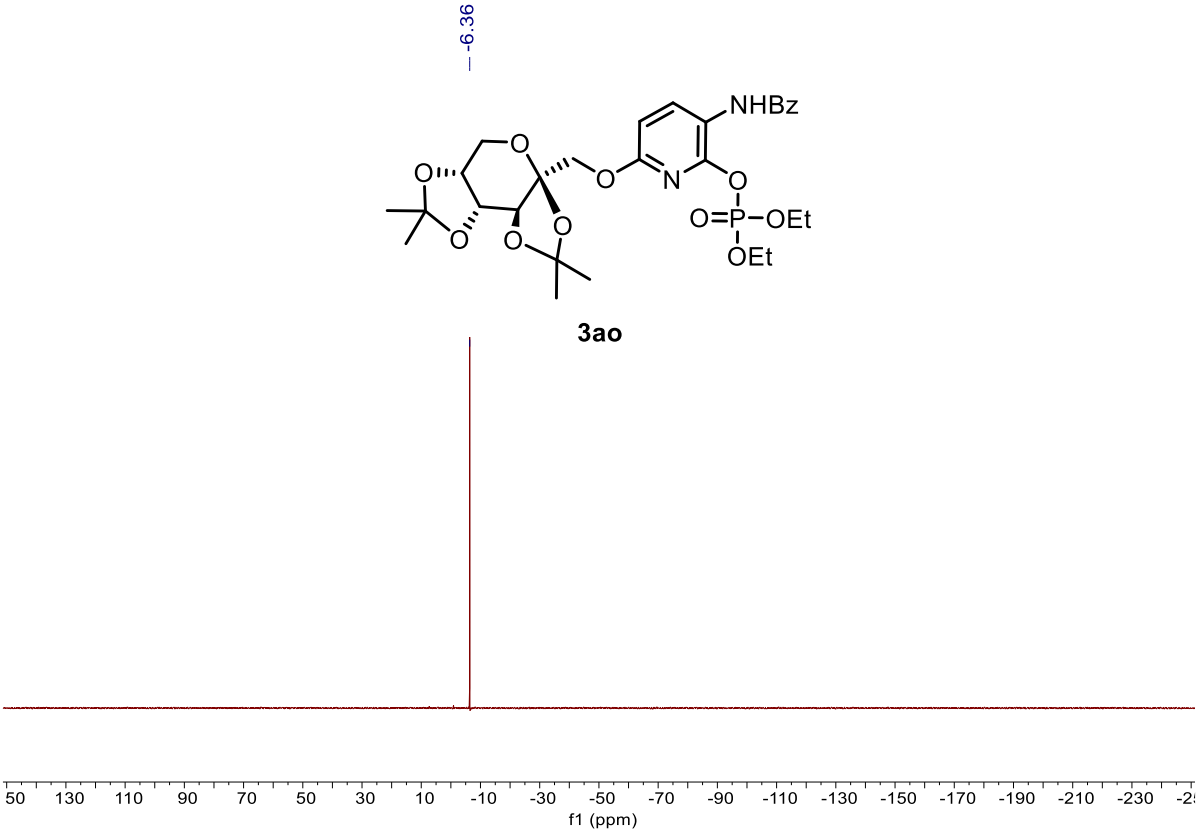
^{1}H NMR of Compound 3ao (500 MHz, $CDCl_3$)



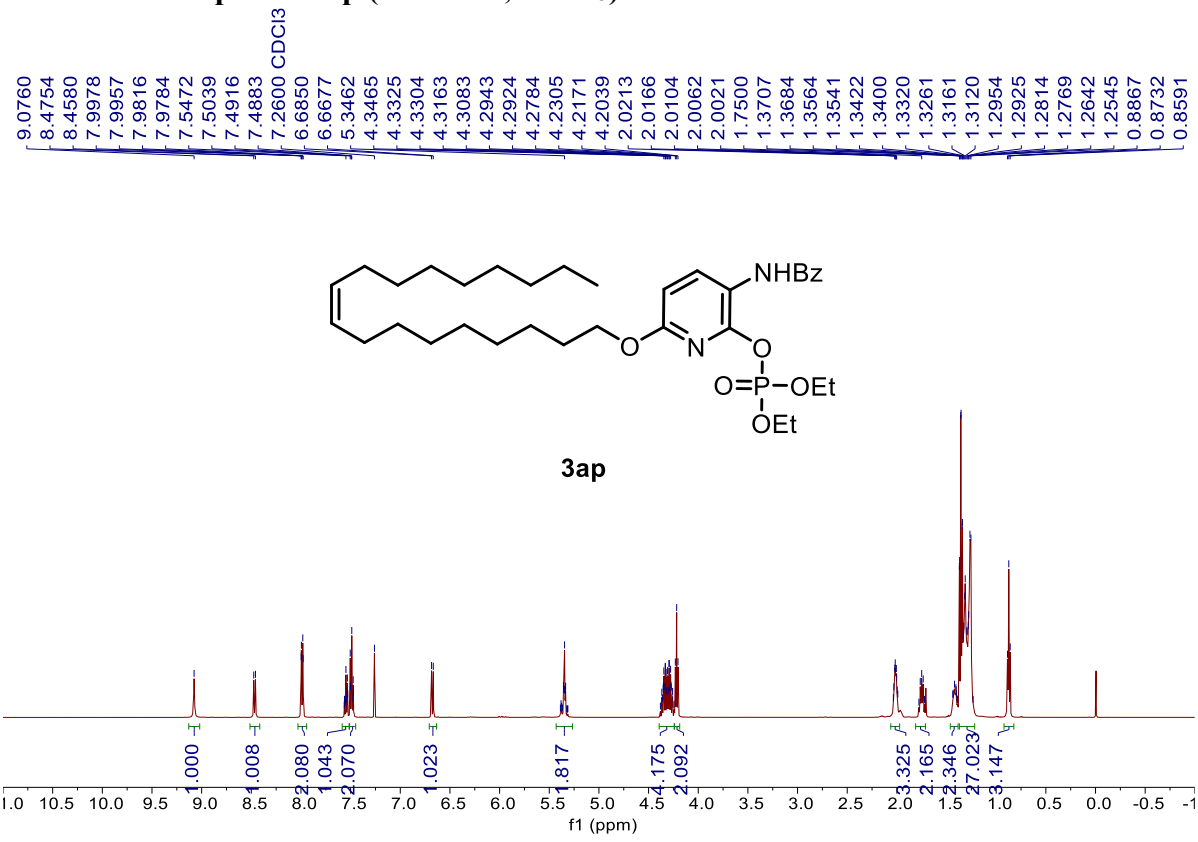
^{13}C NMR of Compound 3ao (126 MHz, $CDCl_3$)



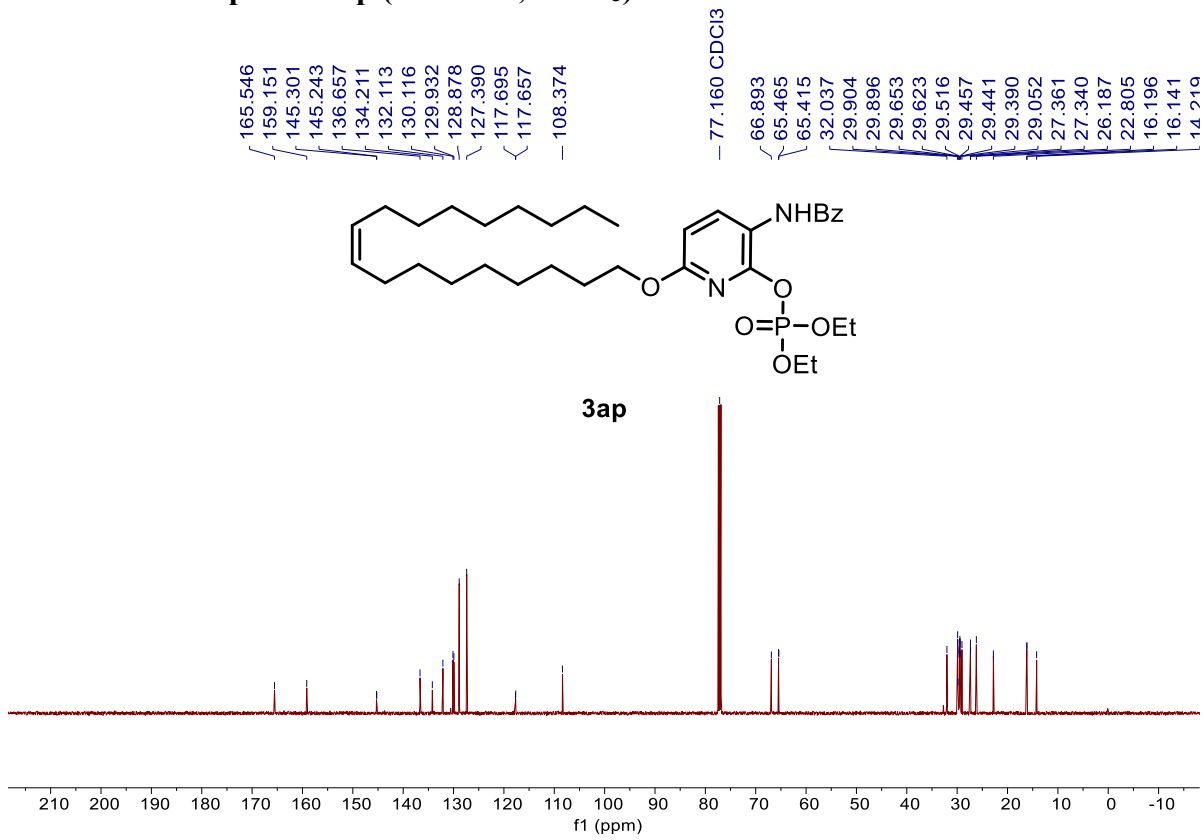
^{31}P NMR of Compound 3ao (202 MHz, $CDCl_3$)



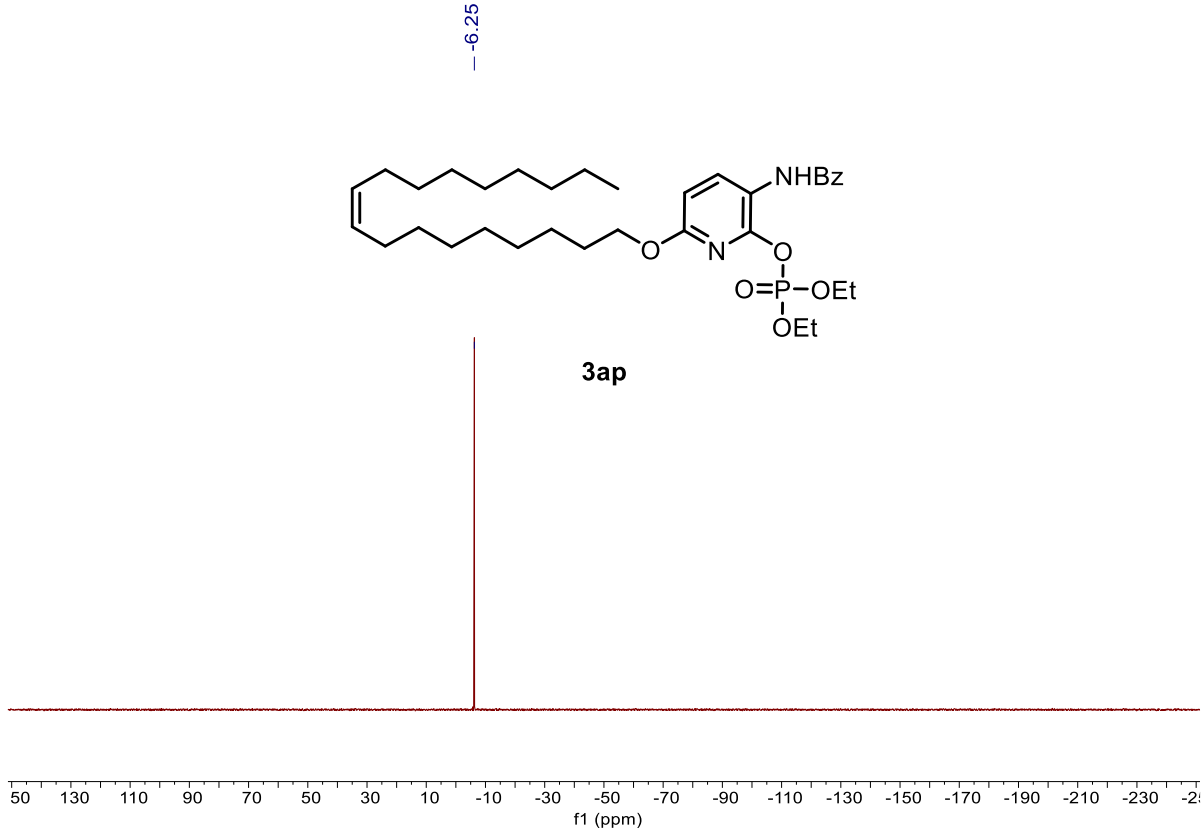
^{1}H NMR of Compound 3ap (500 MHz, $CDCl_3$)



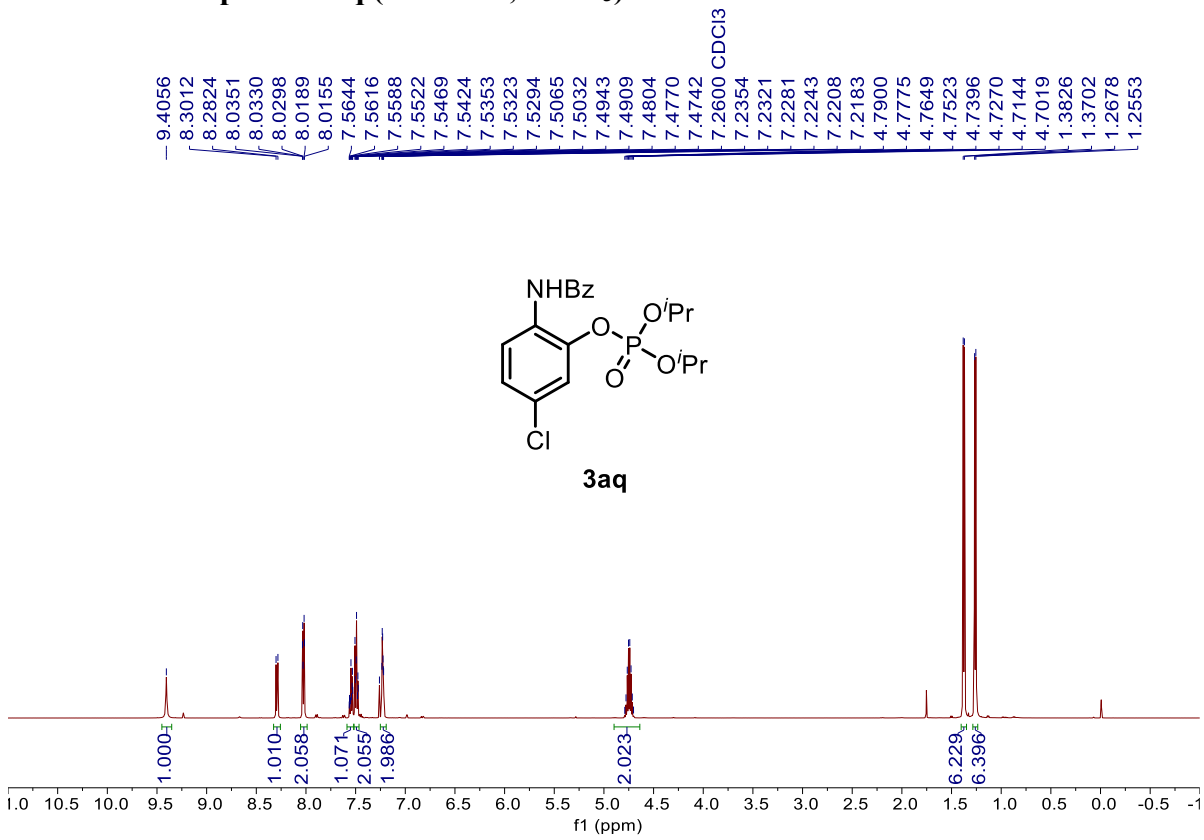
^{13}C NMR of Compound 3ap (126 MHz, $CDCl_3$)



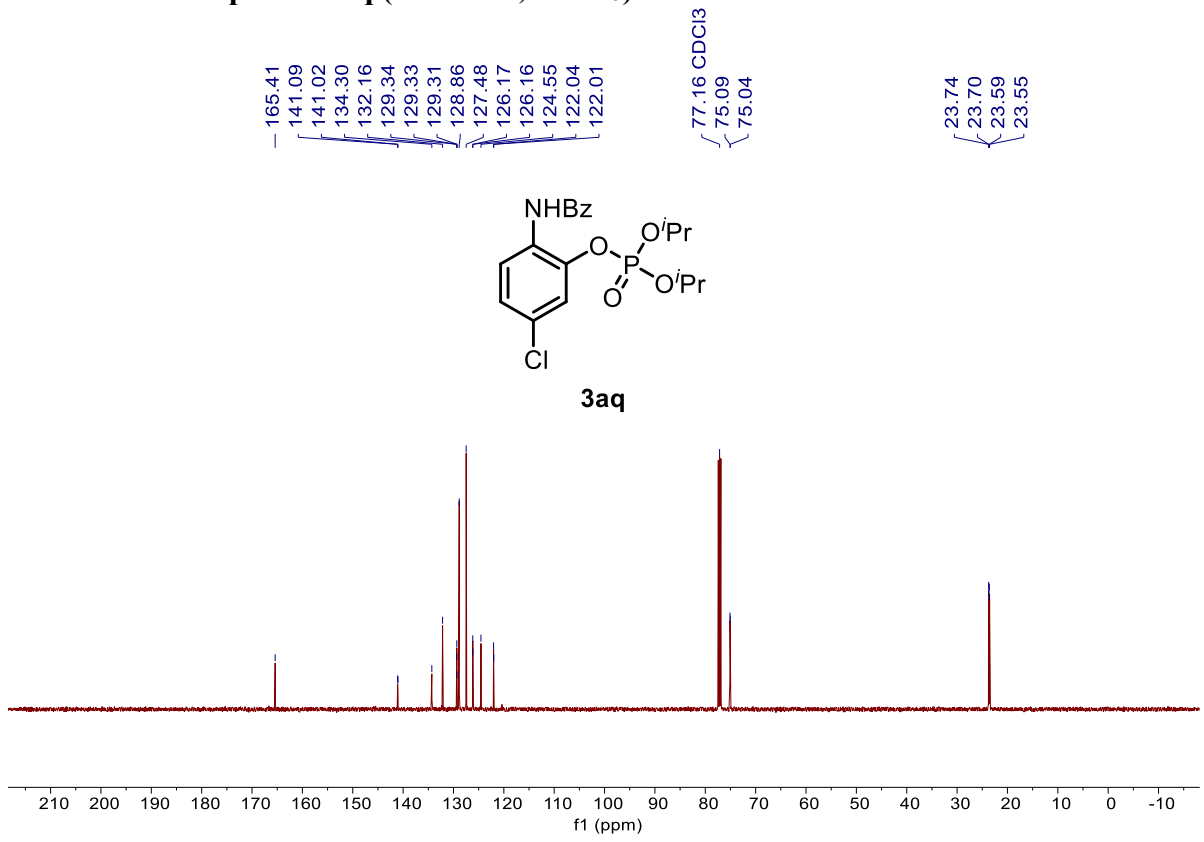
^{31}P NMR of Compound 3ap (202 MHz, $CDCl_3$)



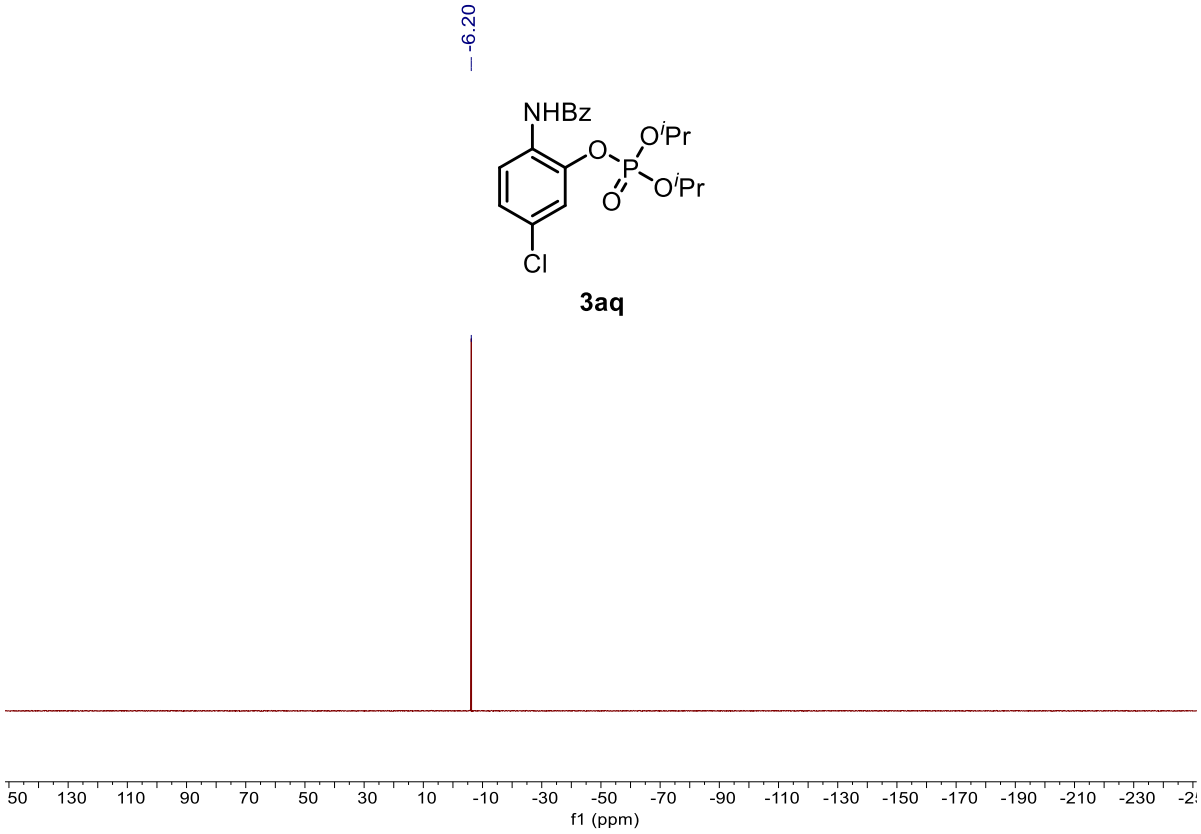
^{1}H NMR of Compound 3aq (500 MHz, $CDCl_3$)



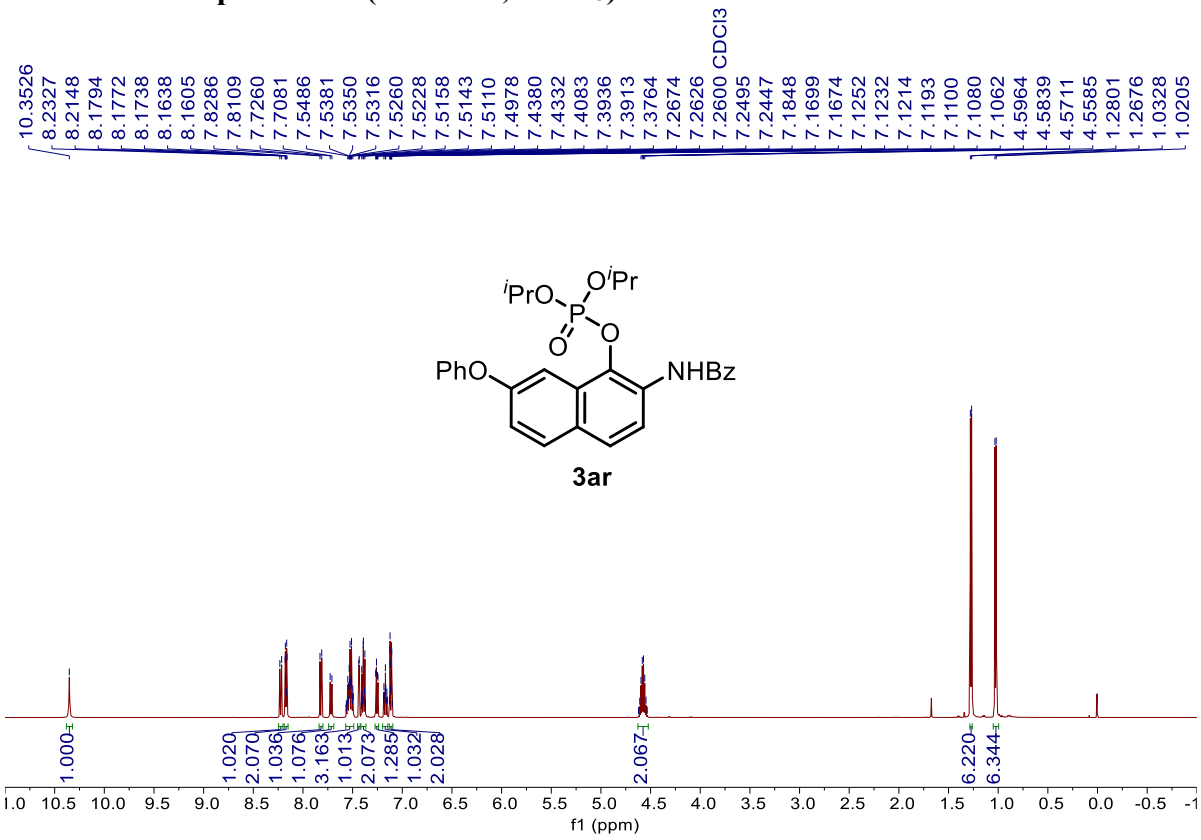
^{13}C NMR of Compound 3aq (126 MHz, $CDCl_3$)



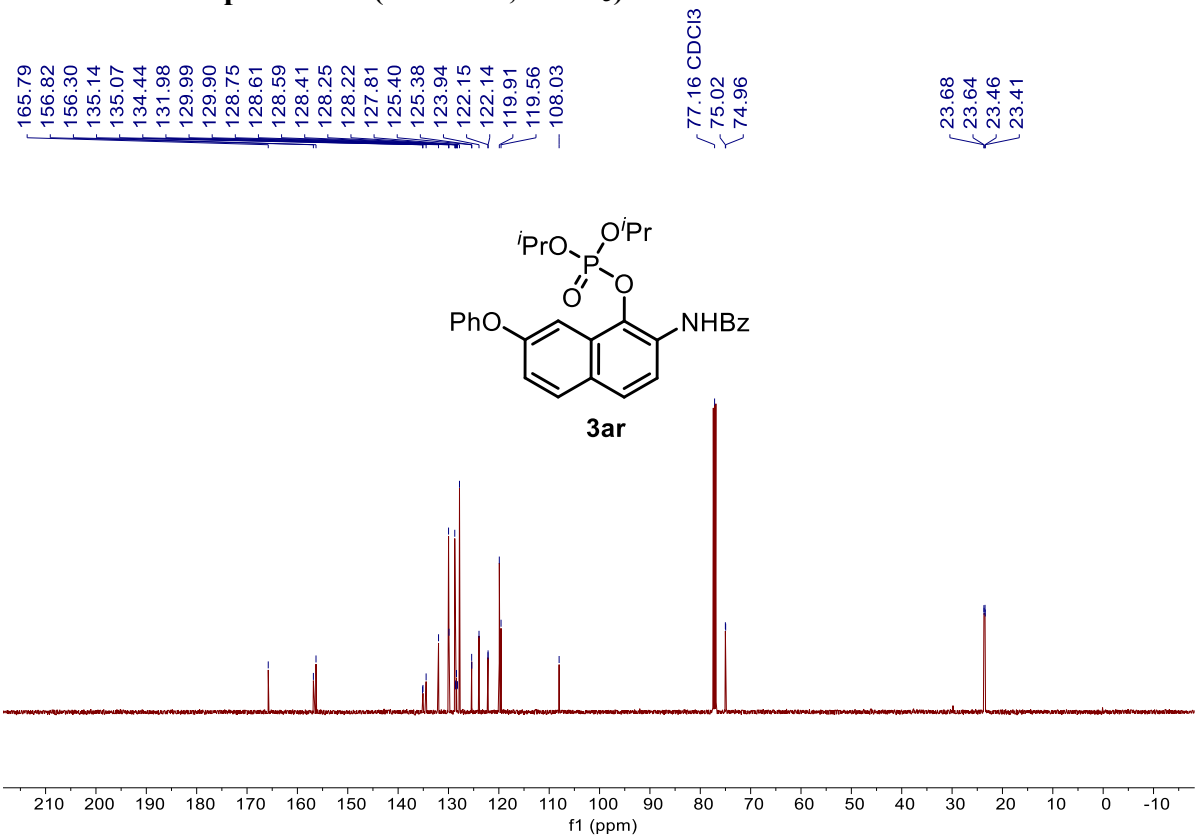
^{31}P NMR of Compound 3aq (202 MHz, $CDCl_3$)



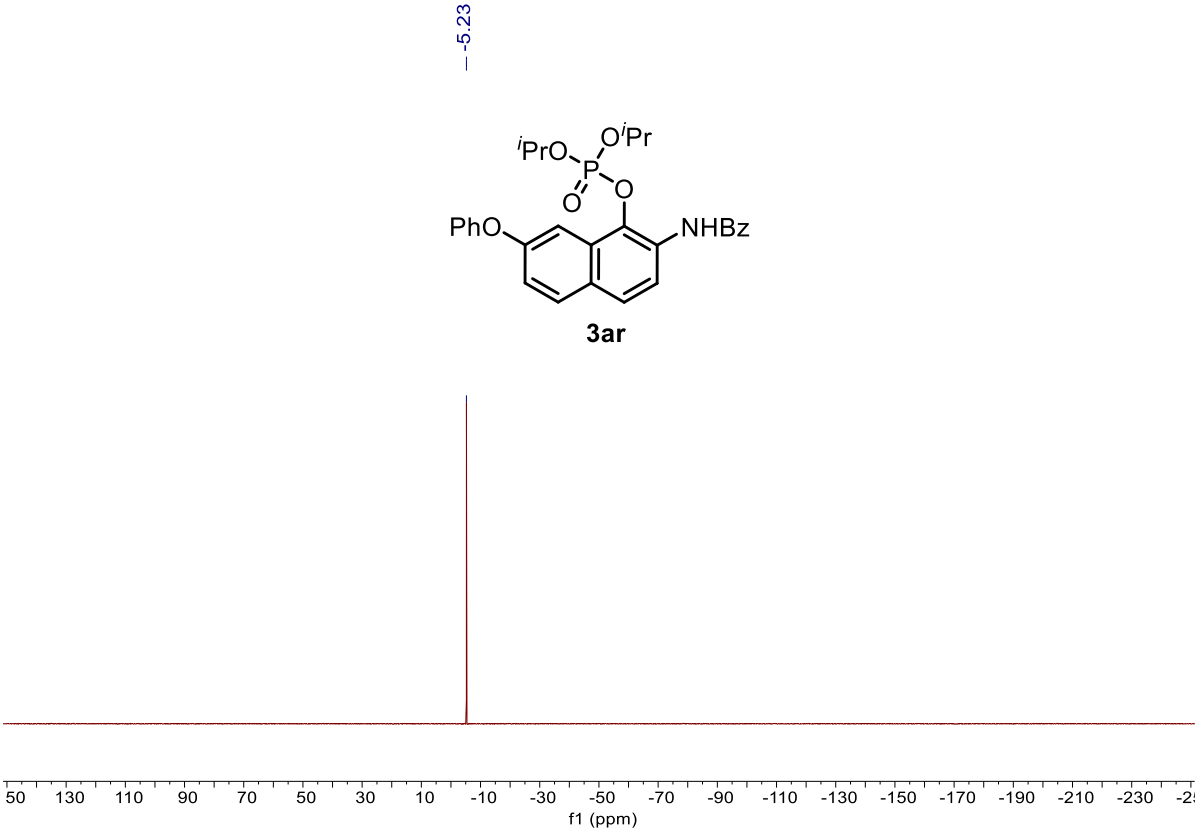
^{1}H NMR of Compound 3ar (500 MHz, $CDCl_3$)



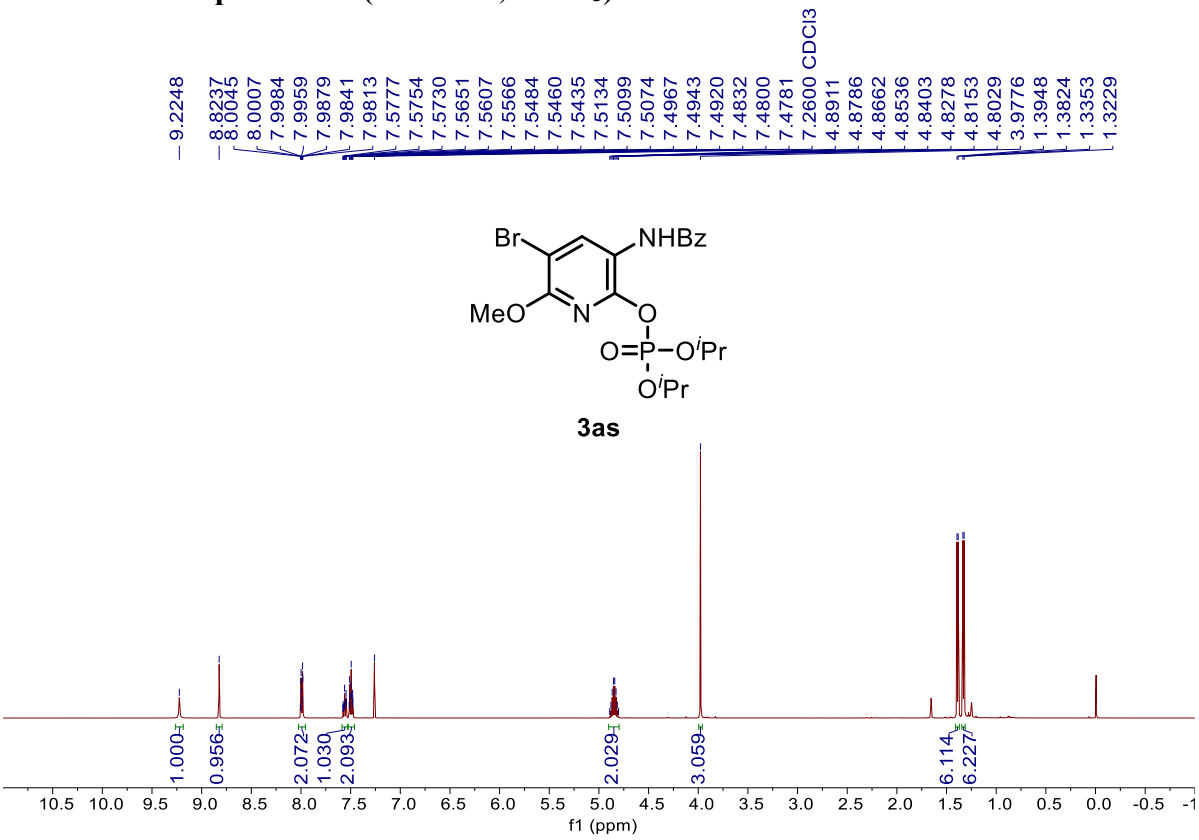
^{13}C NMR of Compound 3ar (126 MHz, $CDCl_3$)



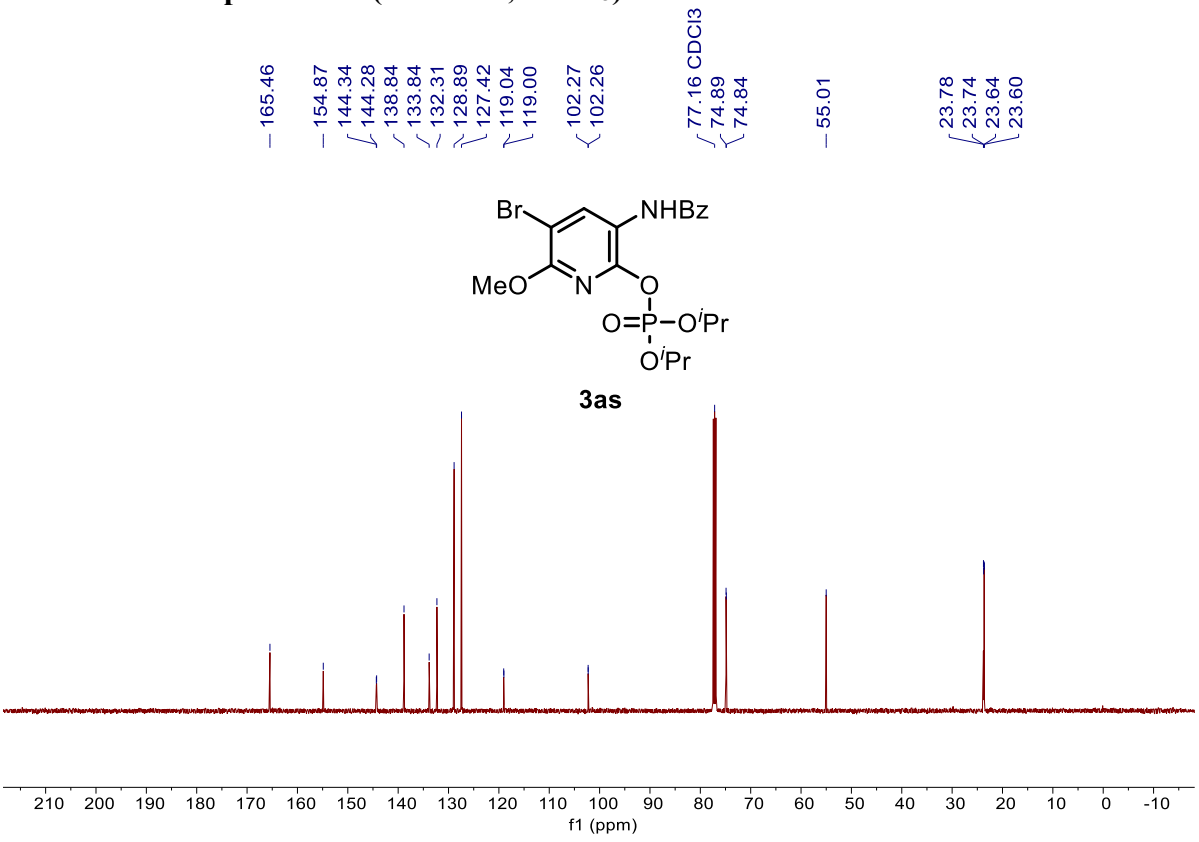
^{31}P NMR of Compound 3ar (202 MHz, $CDCl_3$)



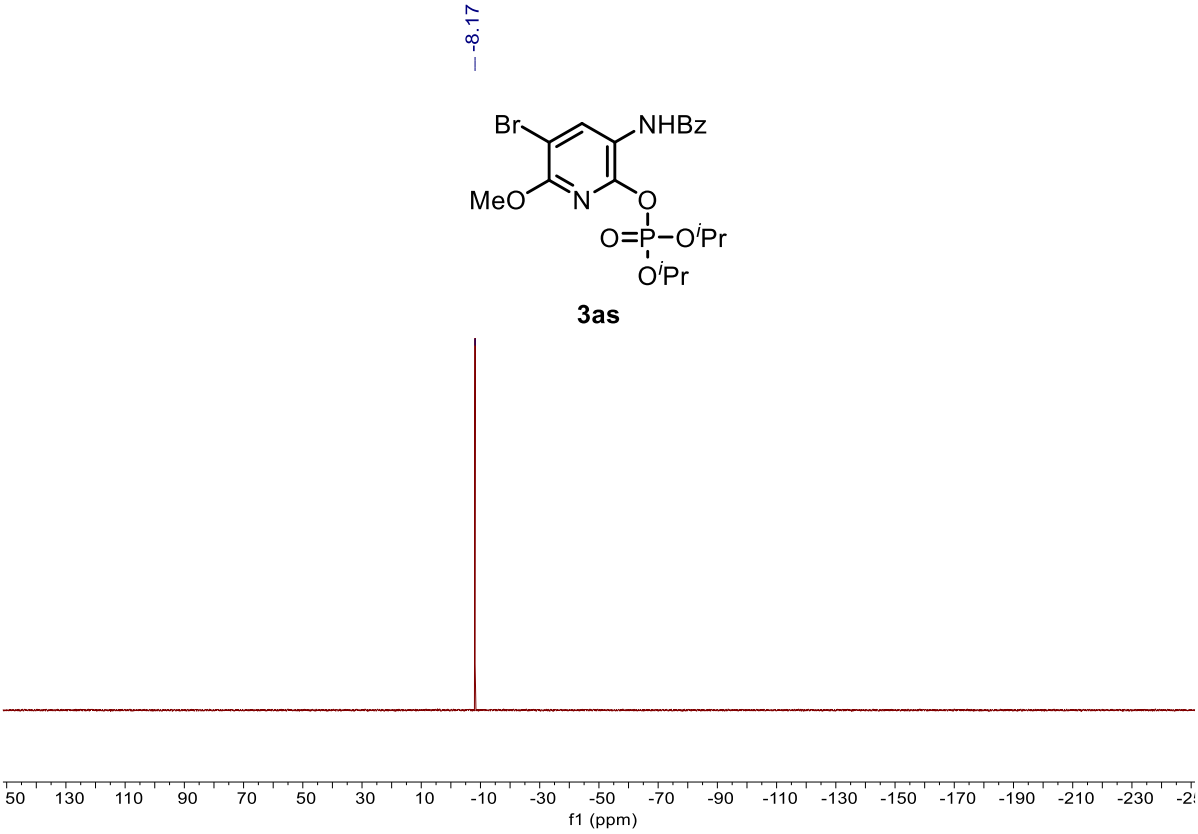
^{1}H NMR of Compound 3as (500 MHz, $CDCl_3$)



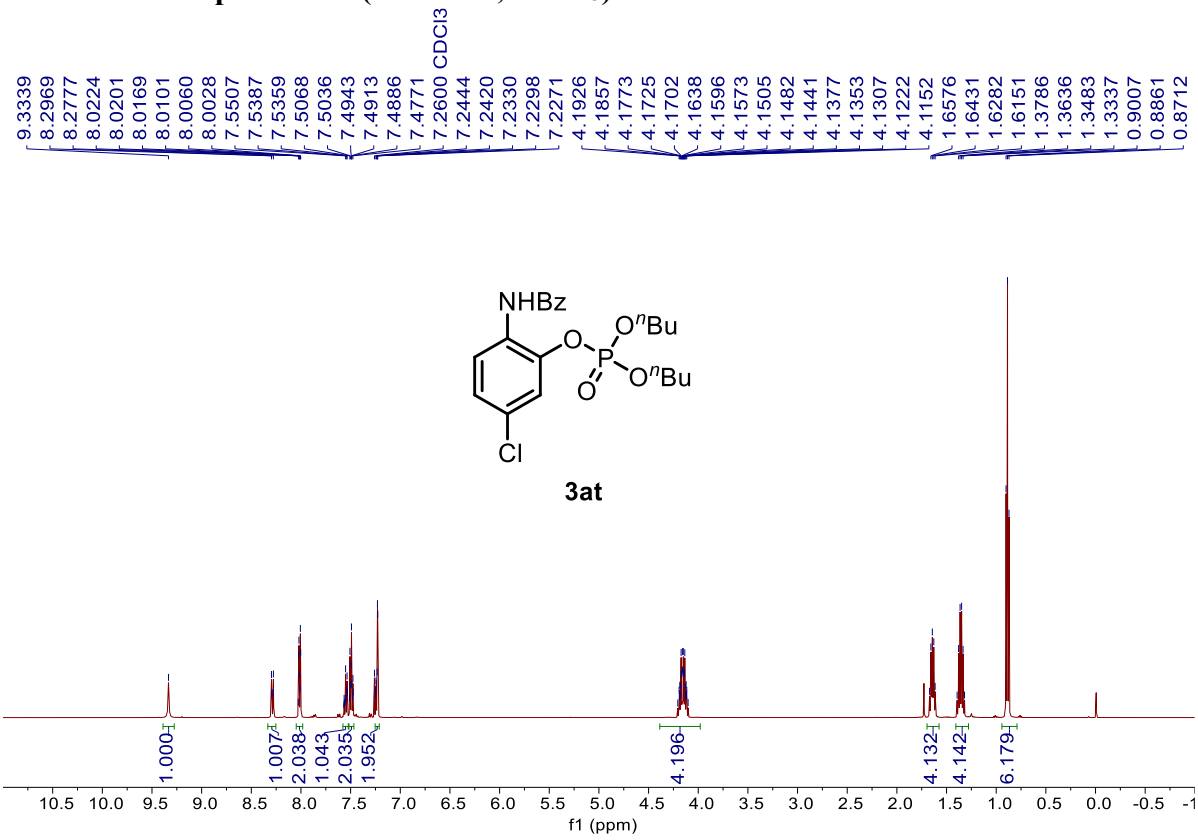
^{13}C NMR of Compound 3as (126 MHz, $CDCl_3$)



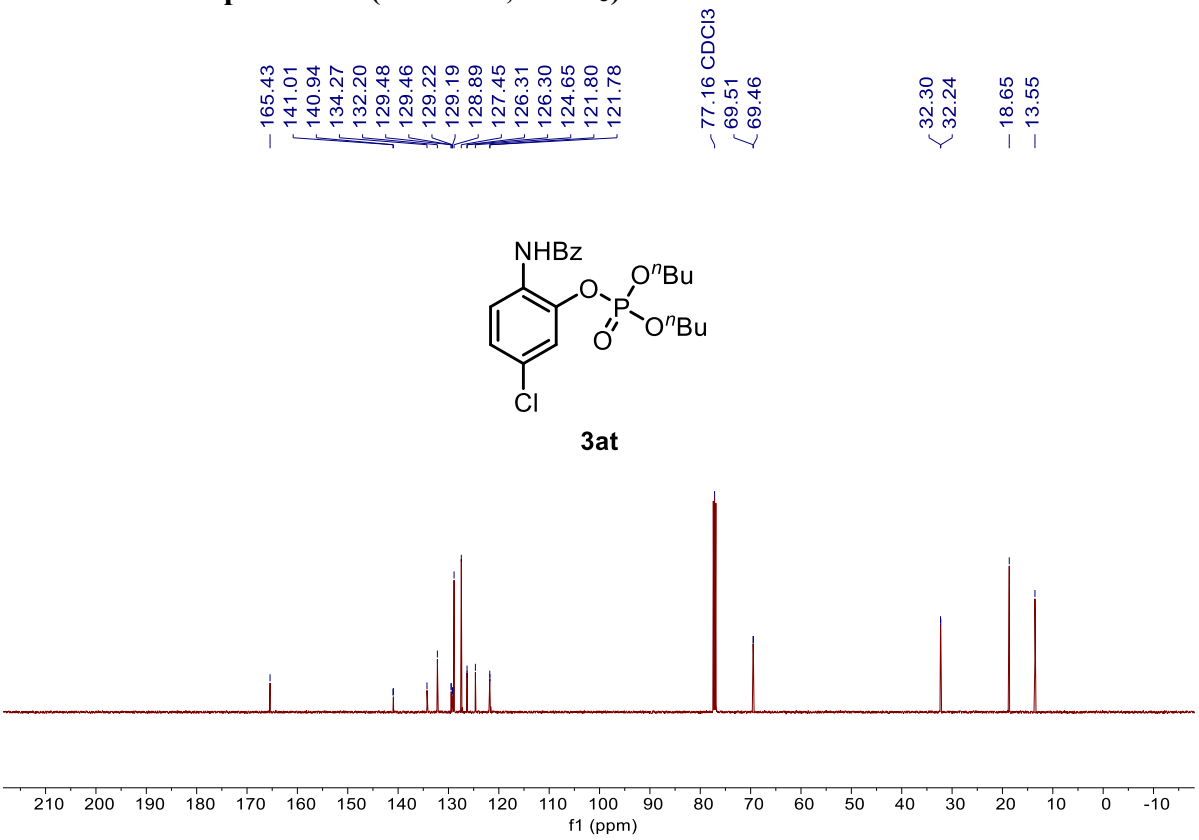
^{31}P NMR of Compound 3as (202 MHz, $CDCl_3$)



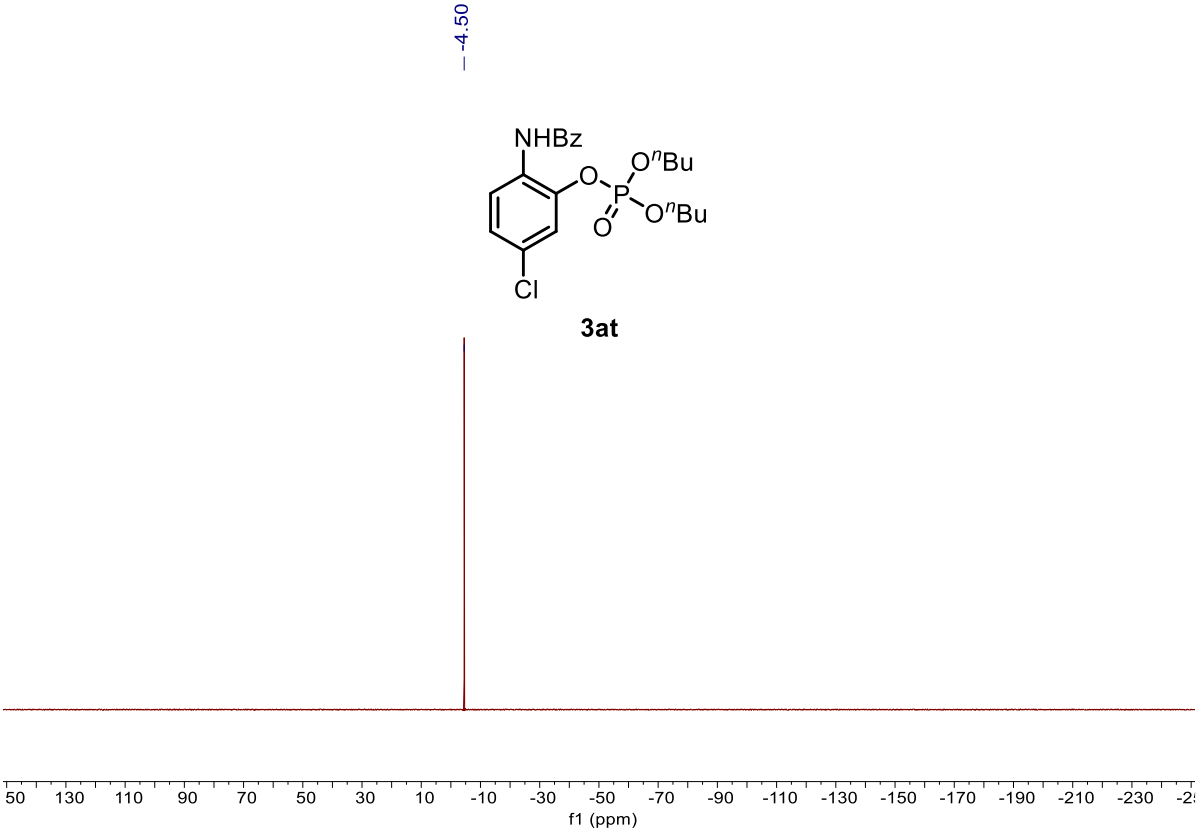
^{1}H NMR of Compound 3at (500 MHz, $CDCl_3$)



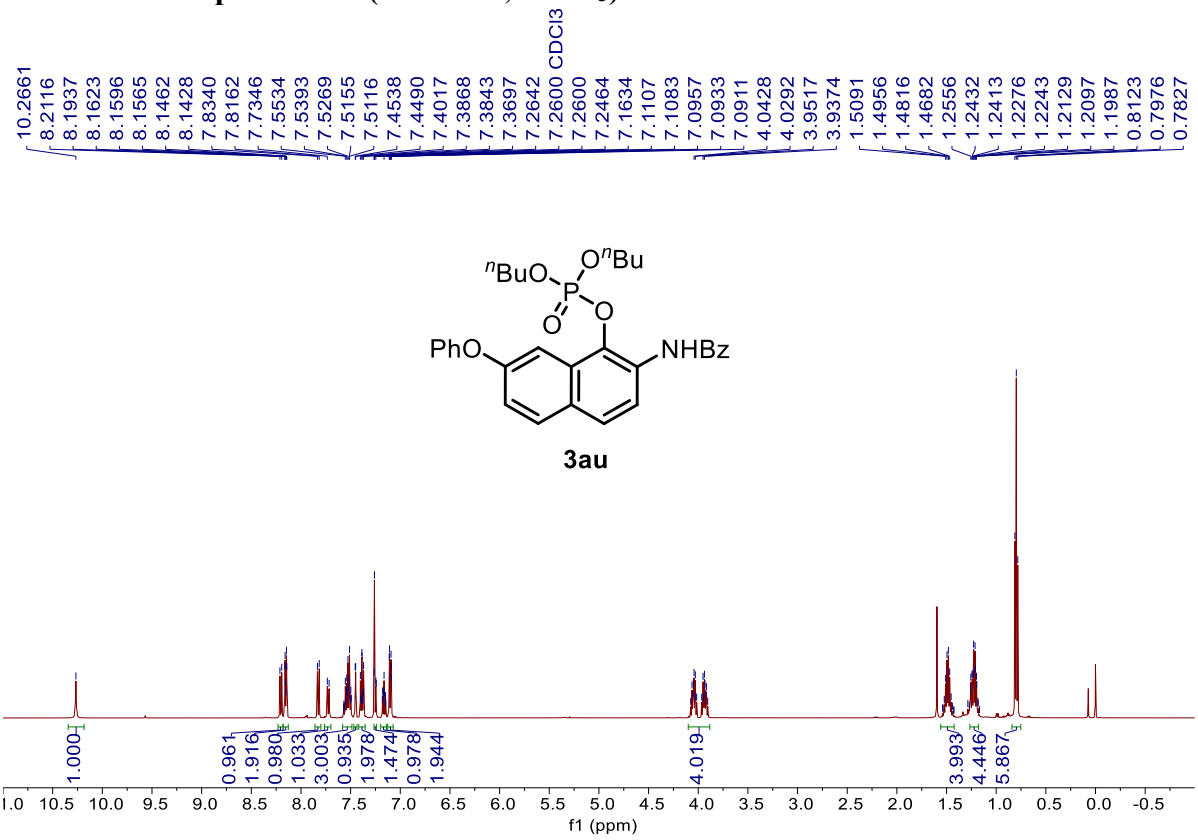
^{13}C NMR of Compound 3at (126 MHz, $CDCl_3$)



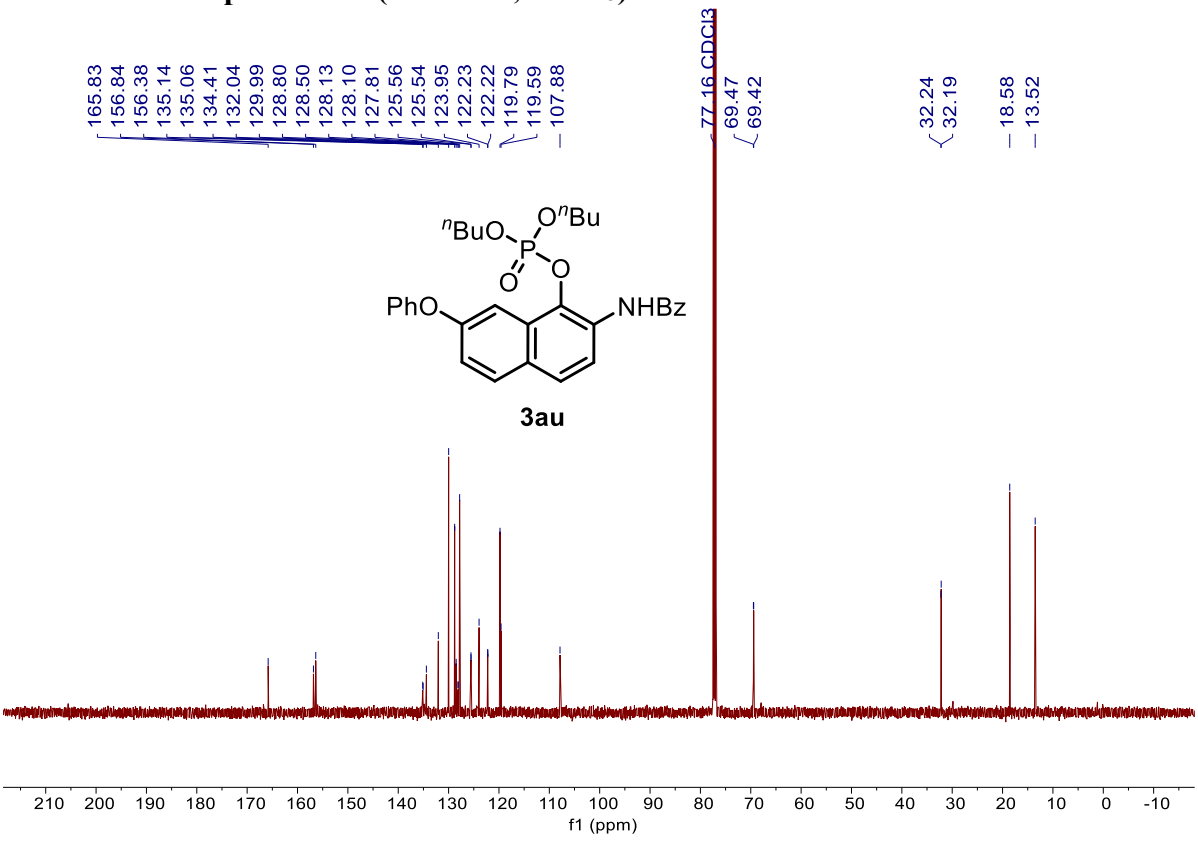
^{31}P NMR of Compound 3at (202 MHz, $CDCl_3$)



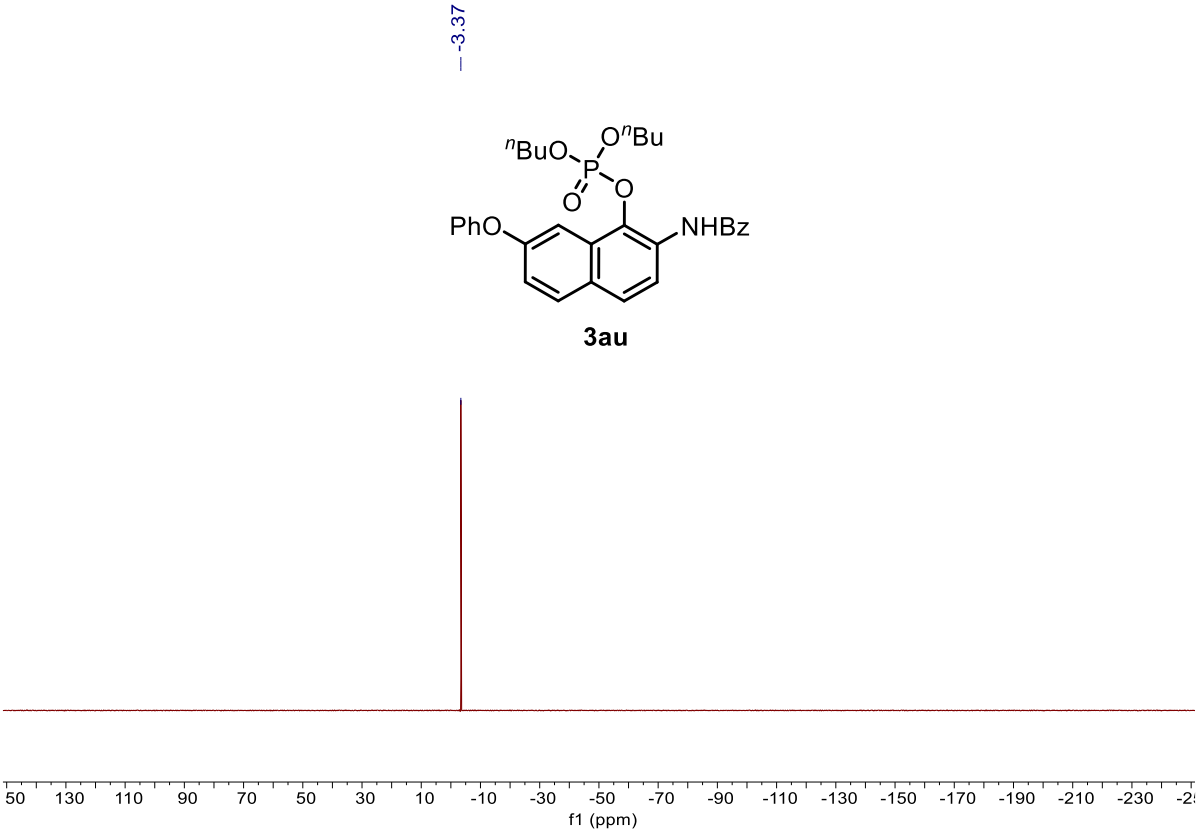
^{1}H NMR of Compound 3au (500 MHz, $CDCl_3$)



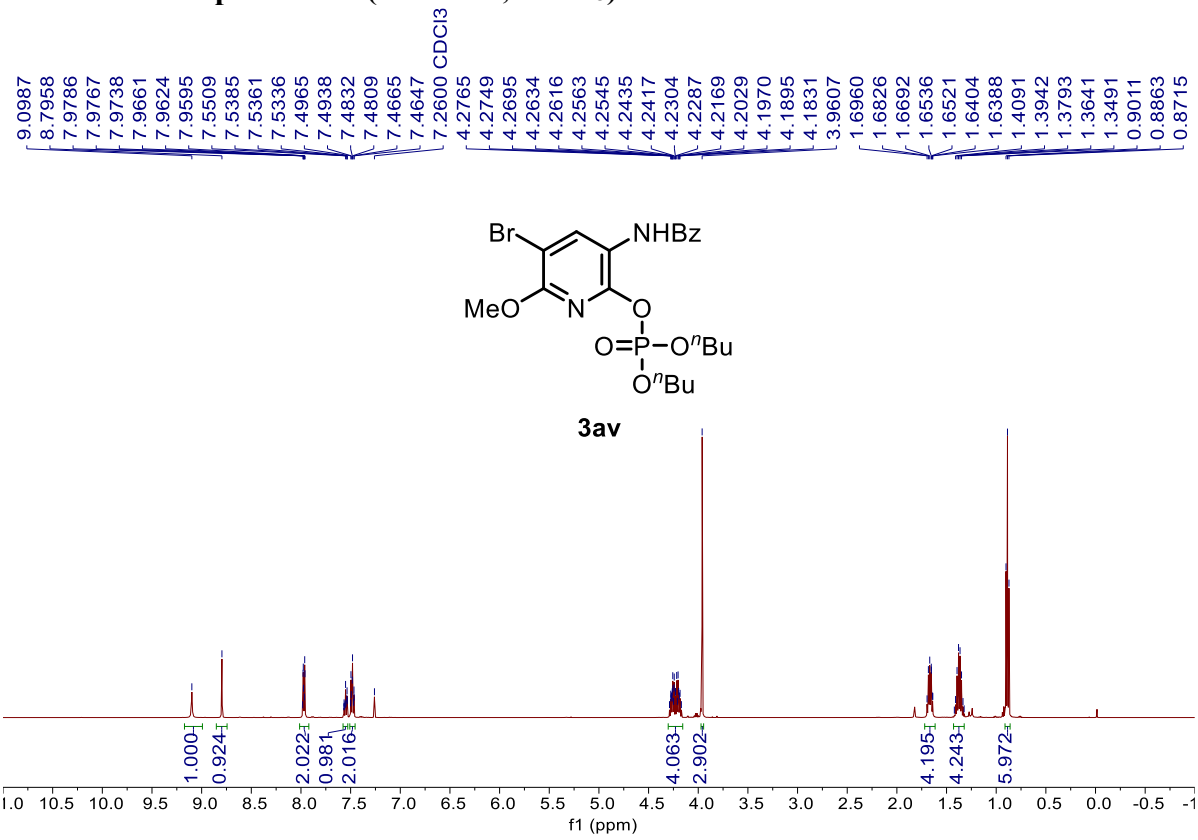
^{13}C NMR of Compound 3au (126 MHz, $CDCl_3$)



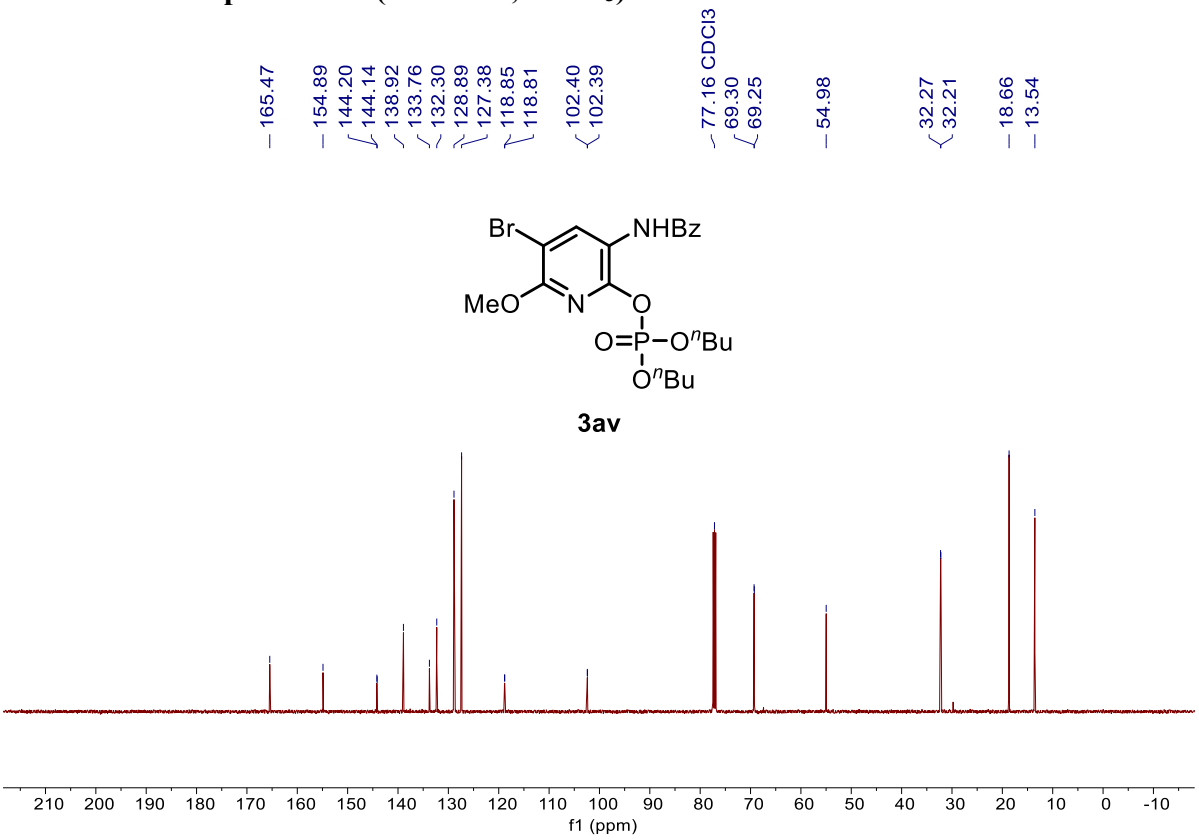
^{31}P NMR of Compound 3au (202 MHz, $CDCl_3$)



^{1}H NMR of Compound 3av (500 MHz, $CDCl_3$)

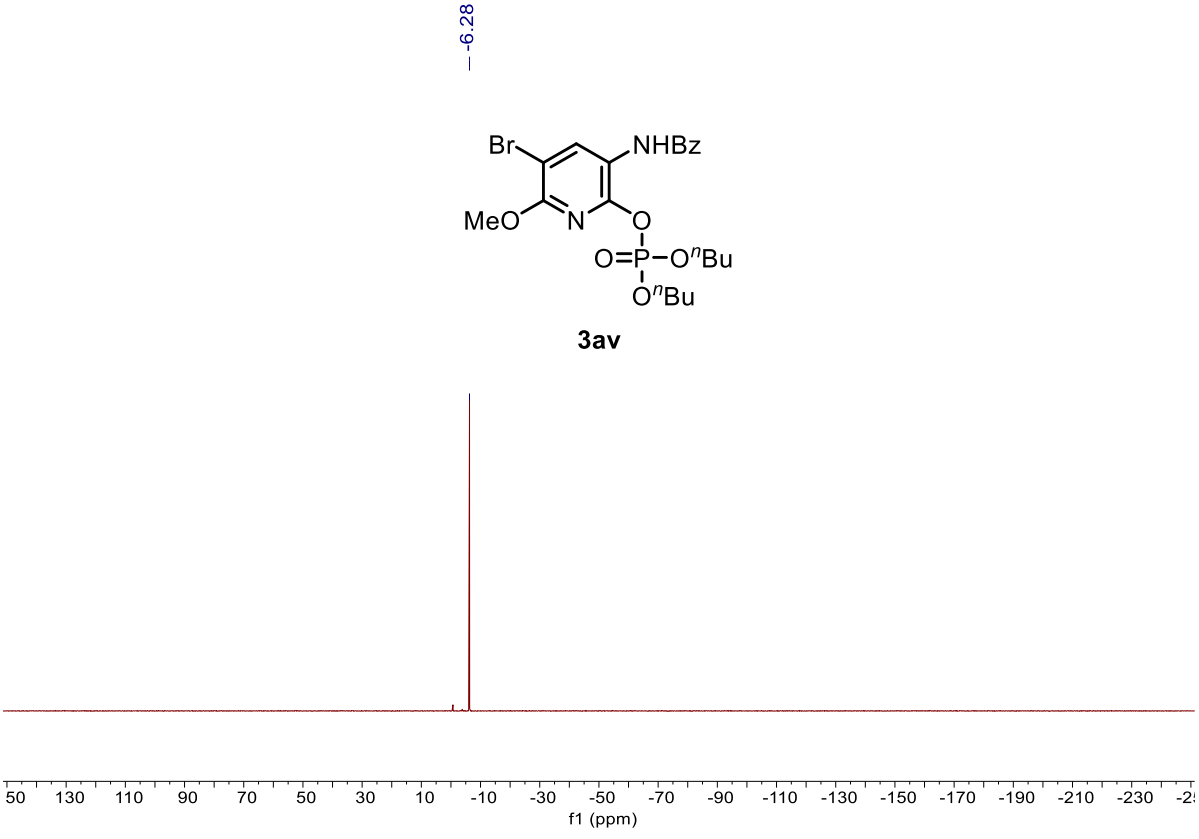


^{13}C NMR of Compound 3av (126 MHz, $CDCl_3$)



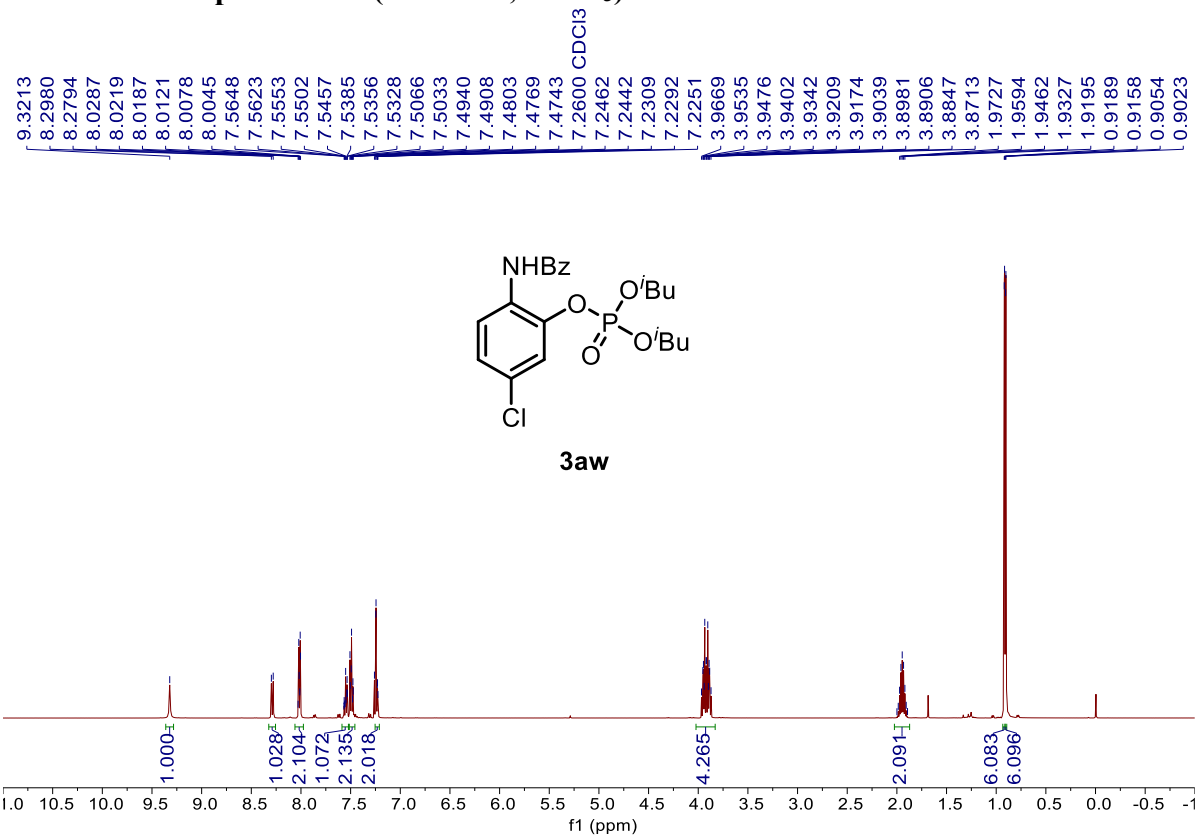
3av

^{31}P NMR of Compound 3av (202 MHz, $CDCl_3$)



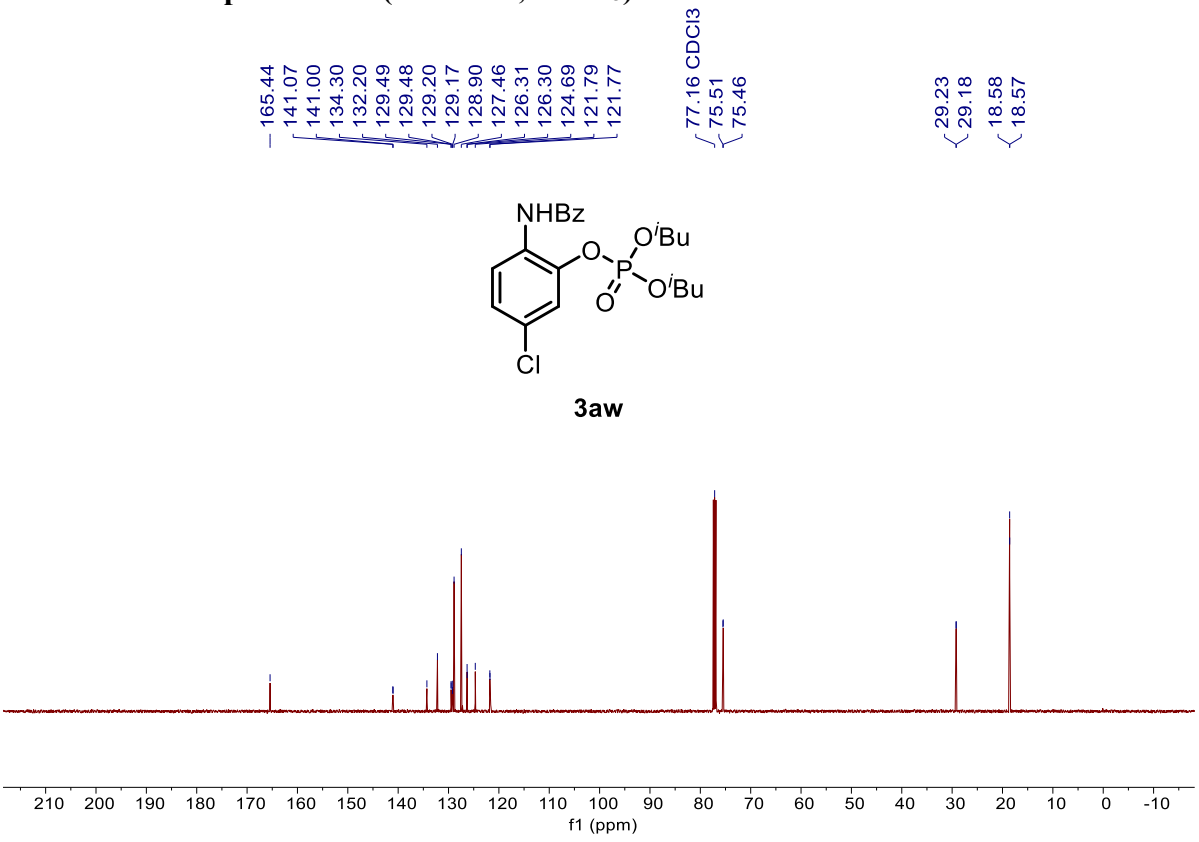
3av

^{1}H NMR of Compound 3aw (500 MHz, $CDCl_3$)



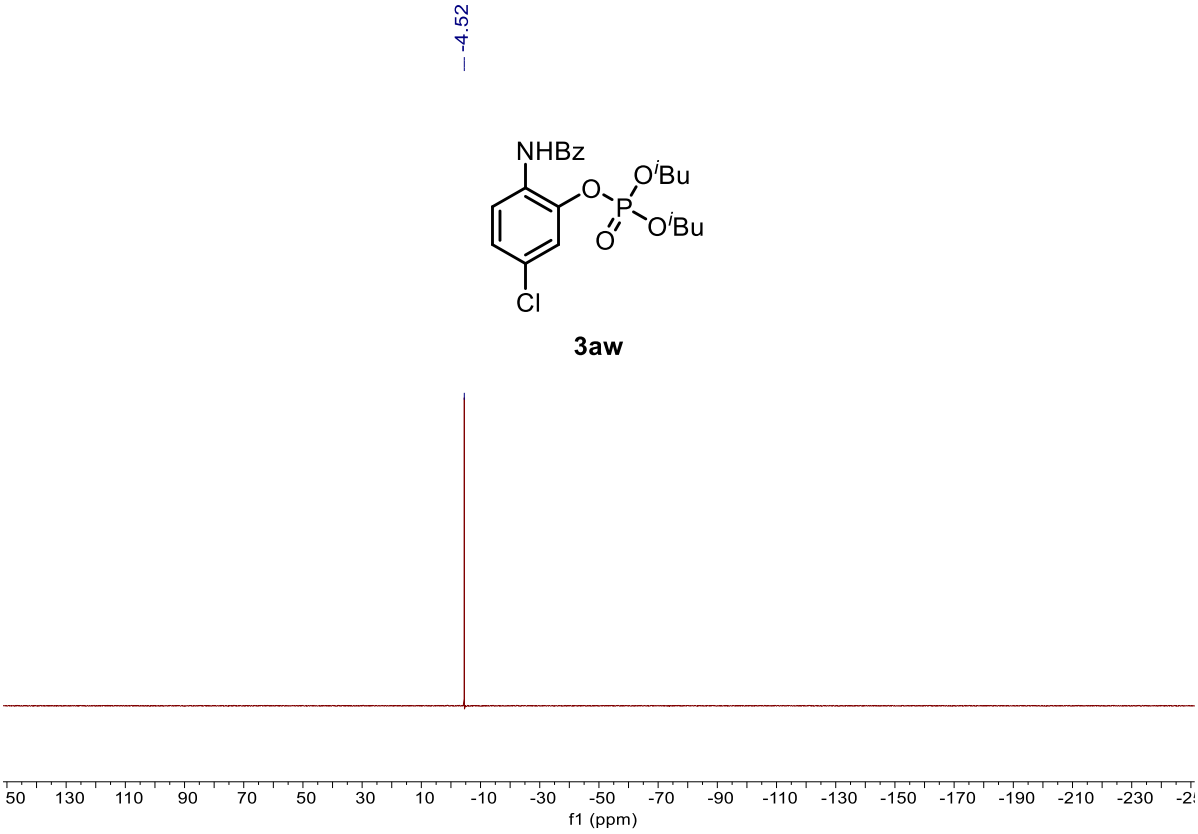
3aw

^{13}C NMR of Compound 3aw (126 MHz, $CDCl_3$)

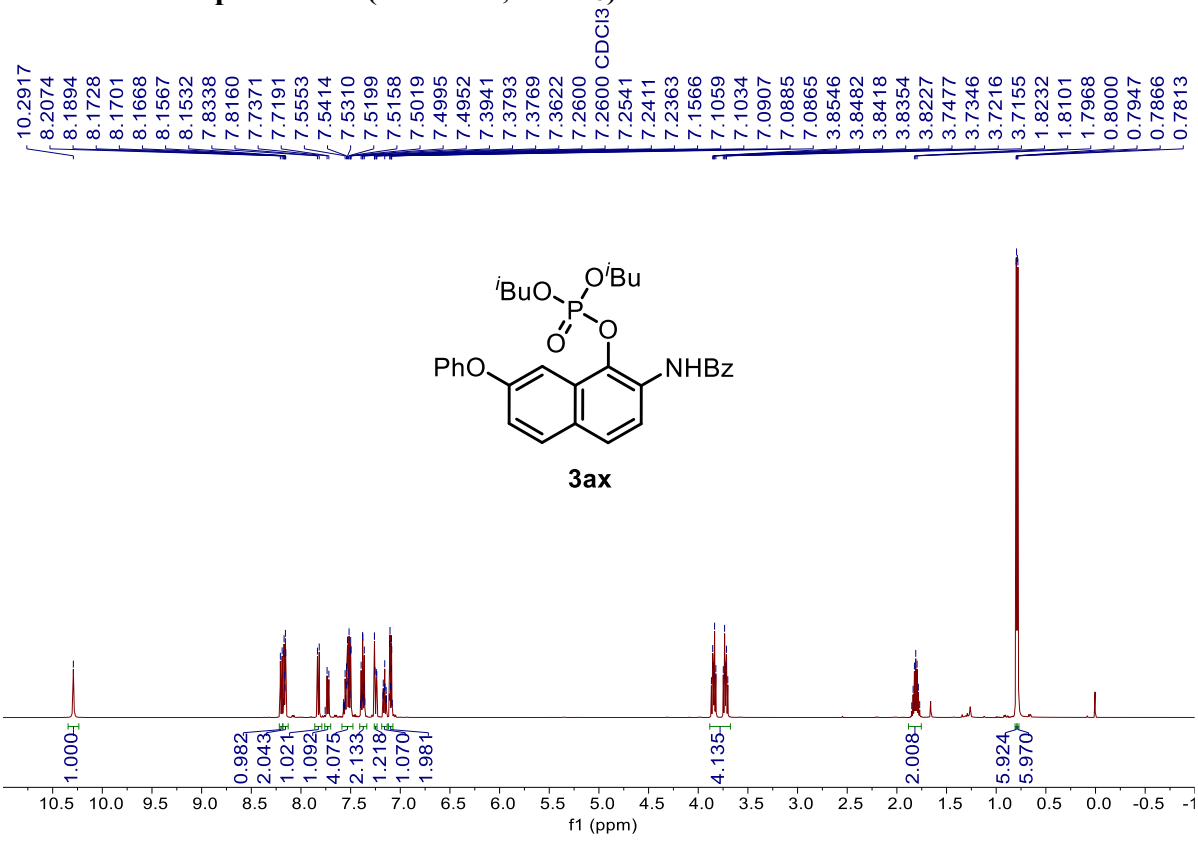


3aw

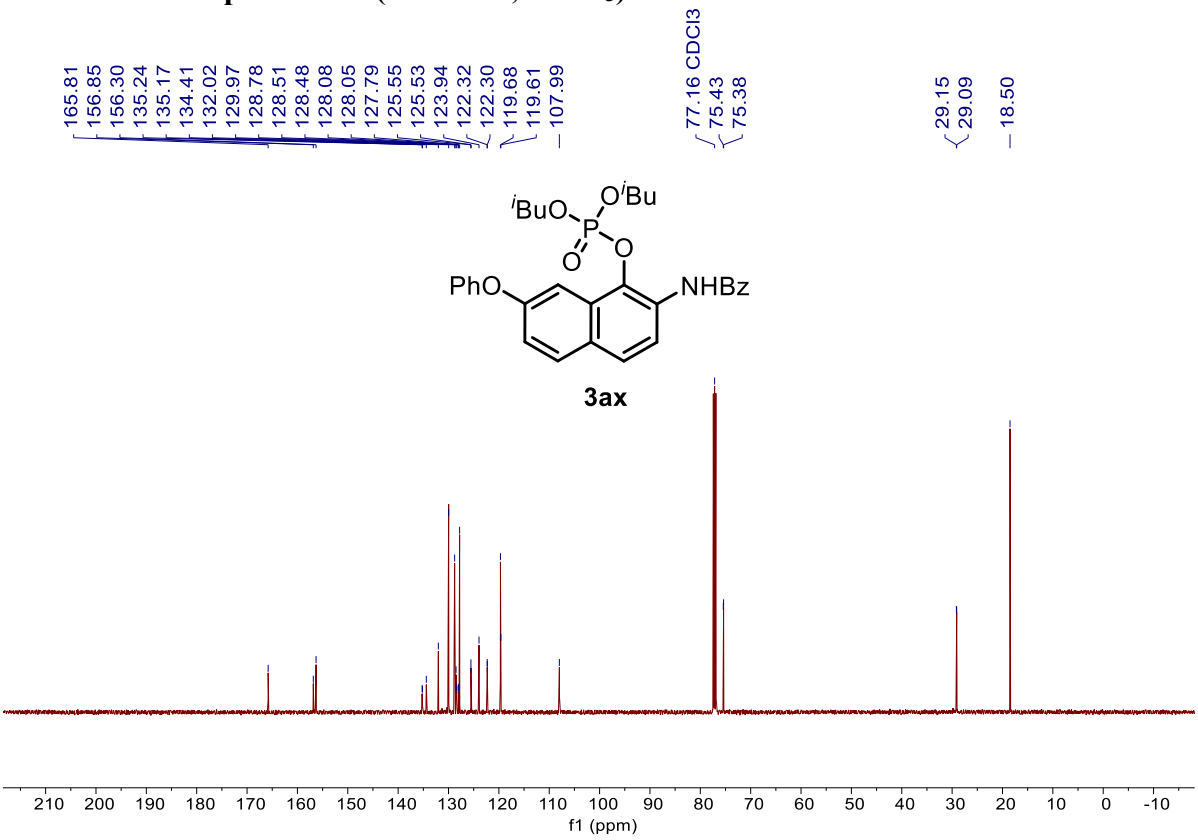
^{31}P NMR of Compound 3aw (202 MHz, $CDCl_3$)



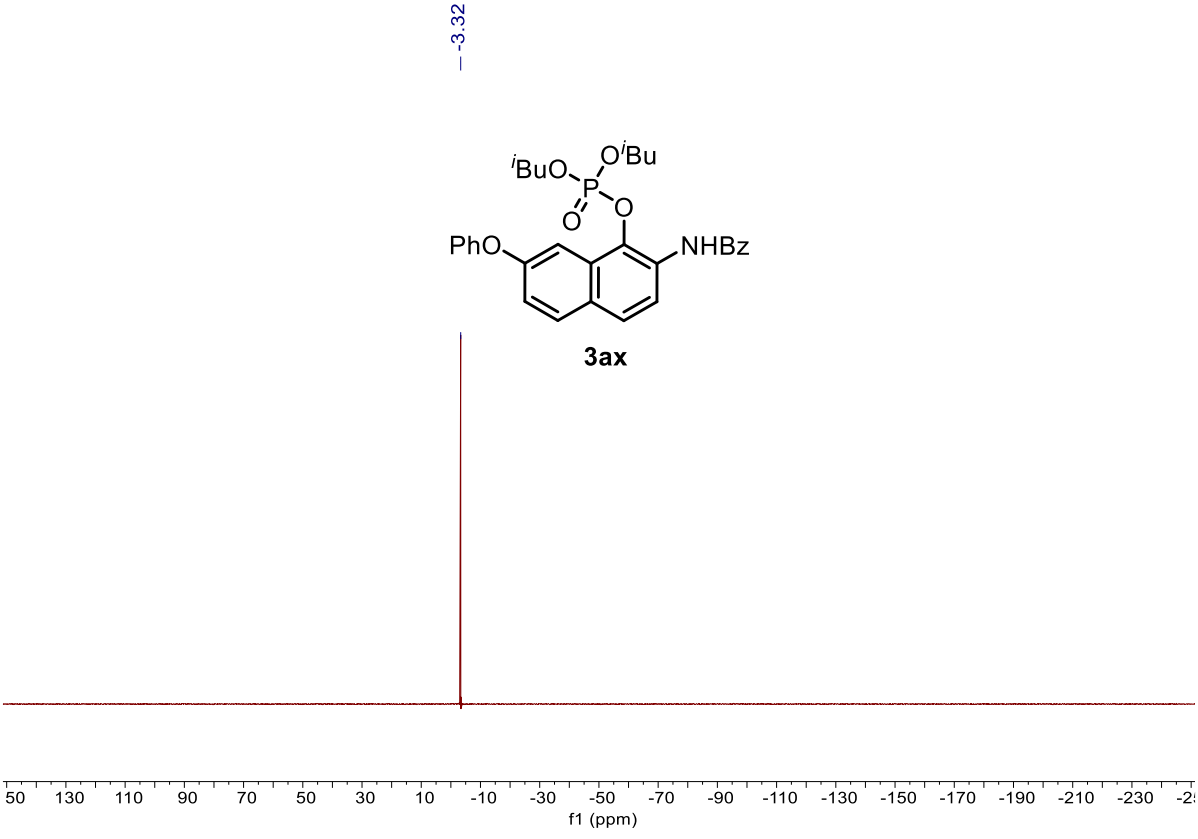
^{1}H NMR of Compound 3ax (500 MHz, $CDCl_3$)



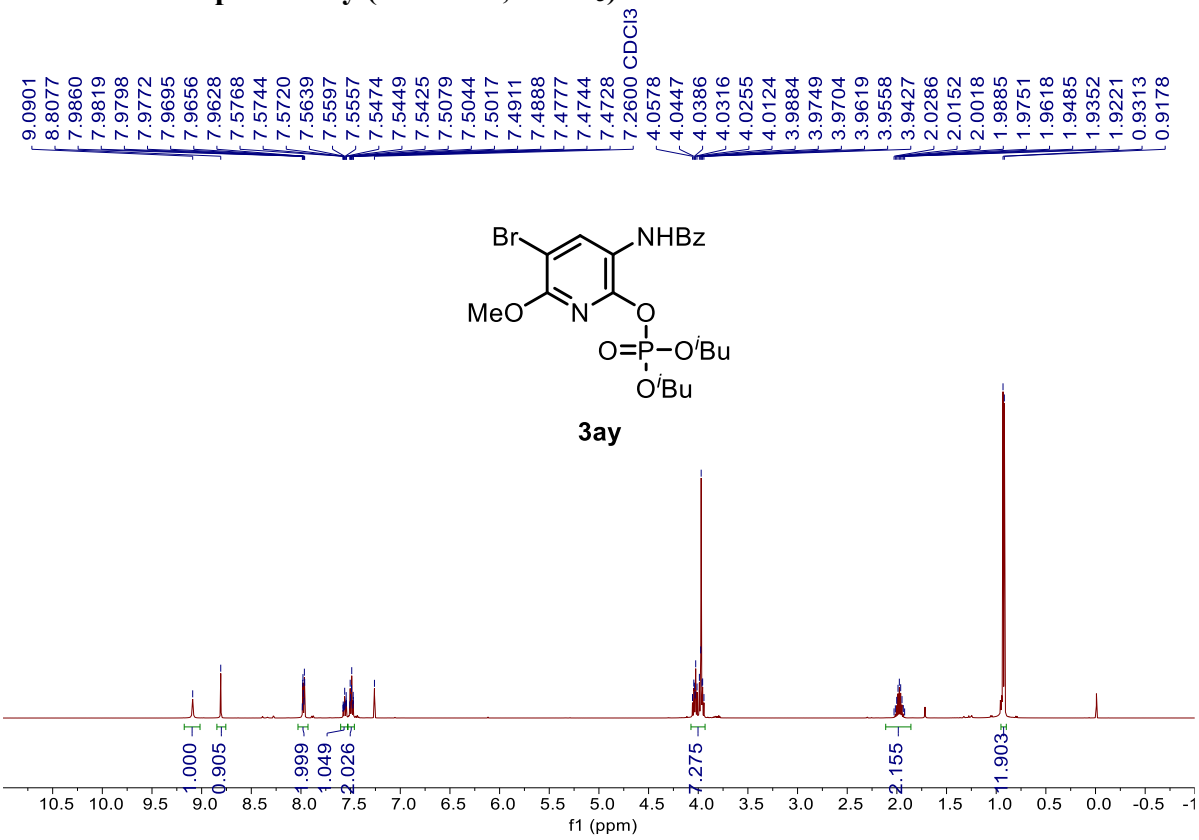
^{13}C NMR of Compound 3ax (126 MHz, $CDCl_3$)



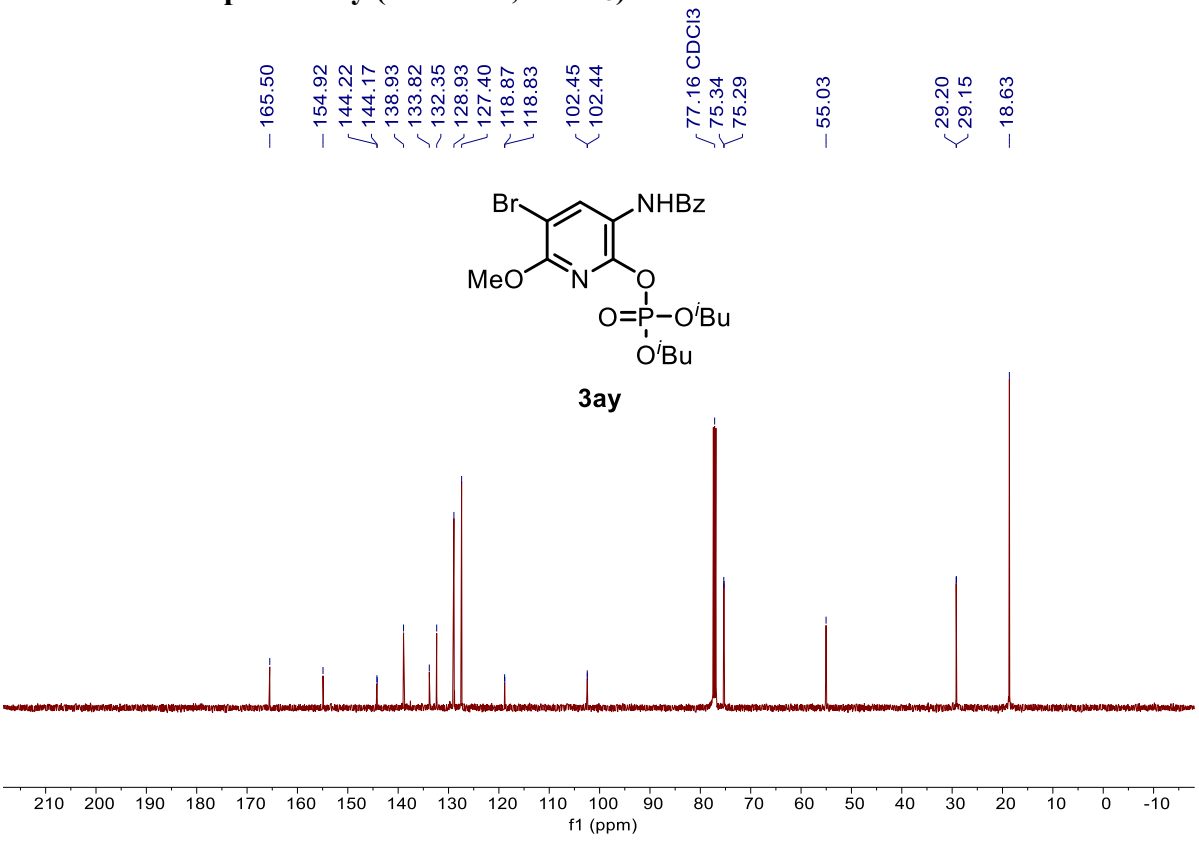
^{31}P NMR of Compound 3ax (202 MHz, $CDCl_3$)



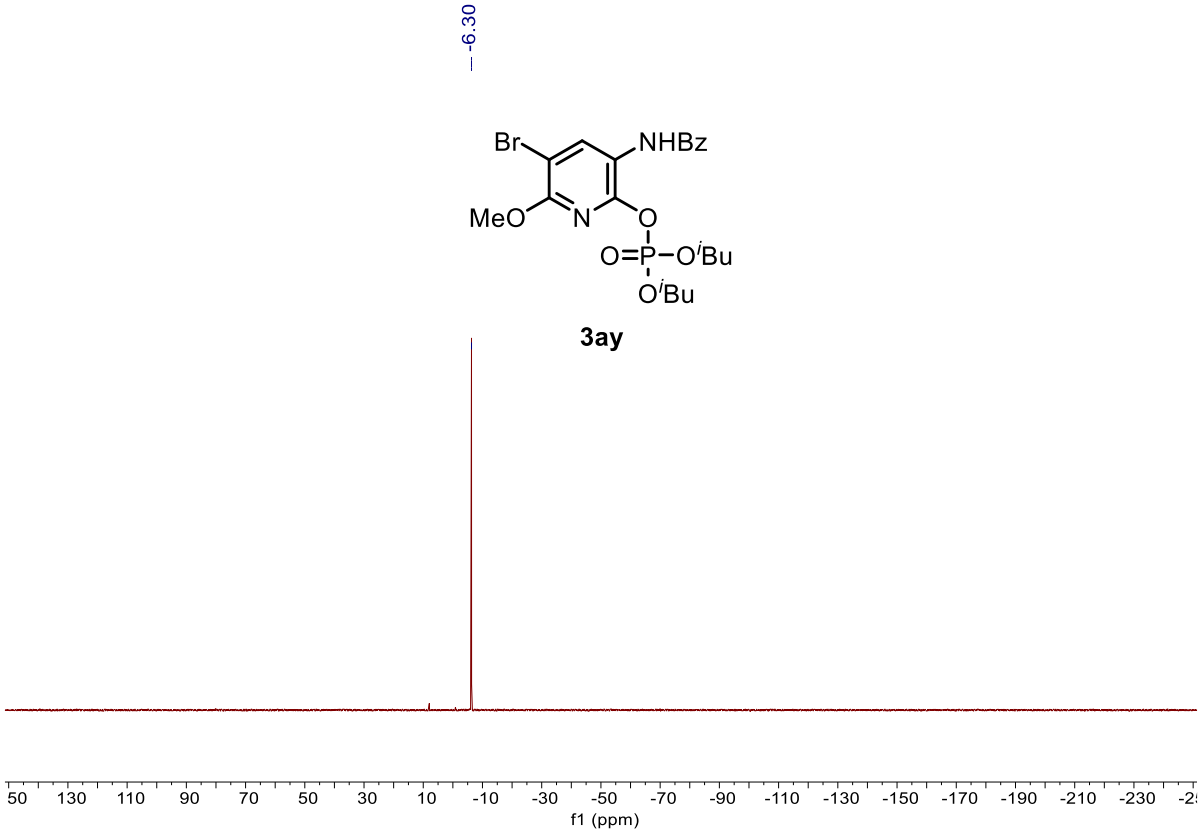
^{1}H NMR of Compound 3ay (500 MHz, $CDCl_3$)



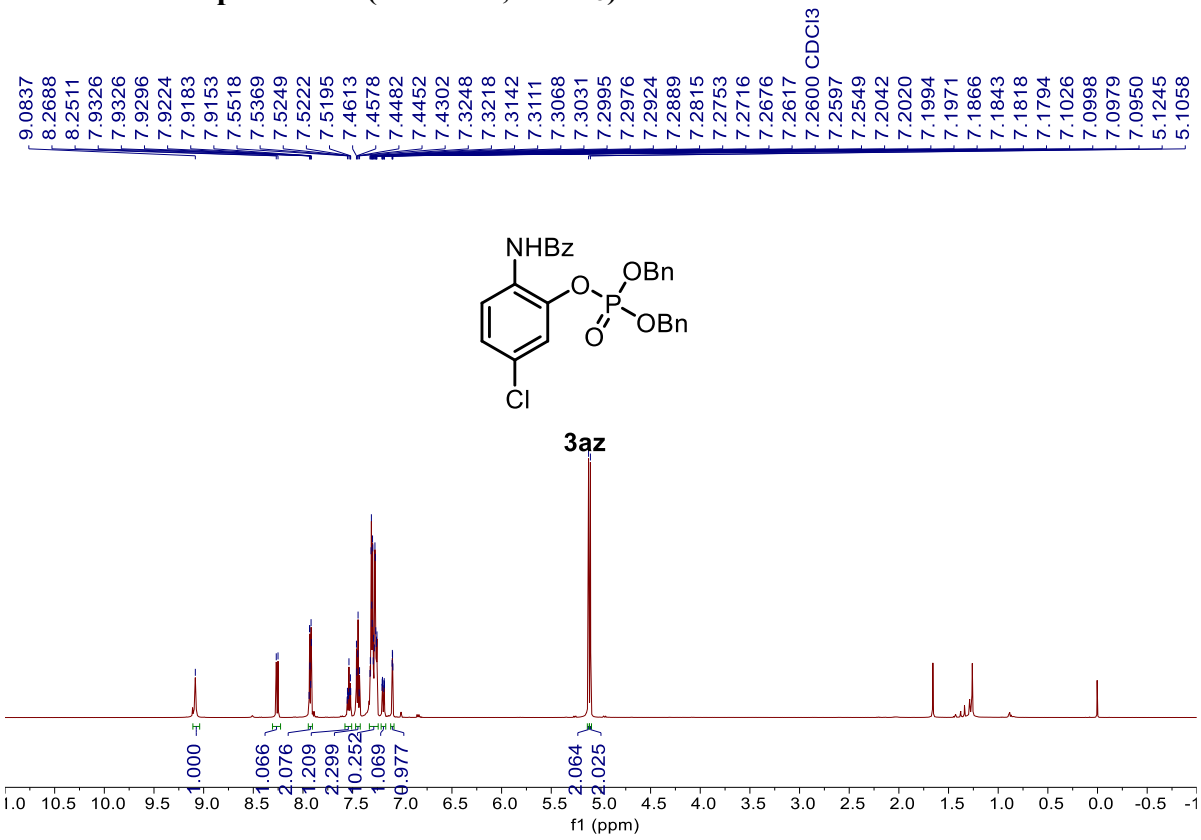
^{13}C NMR of Compound 3ay (126 MHz, $CDCl_3$)



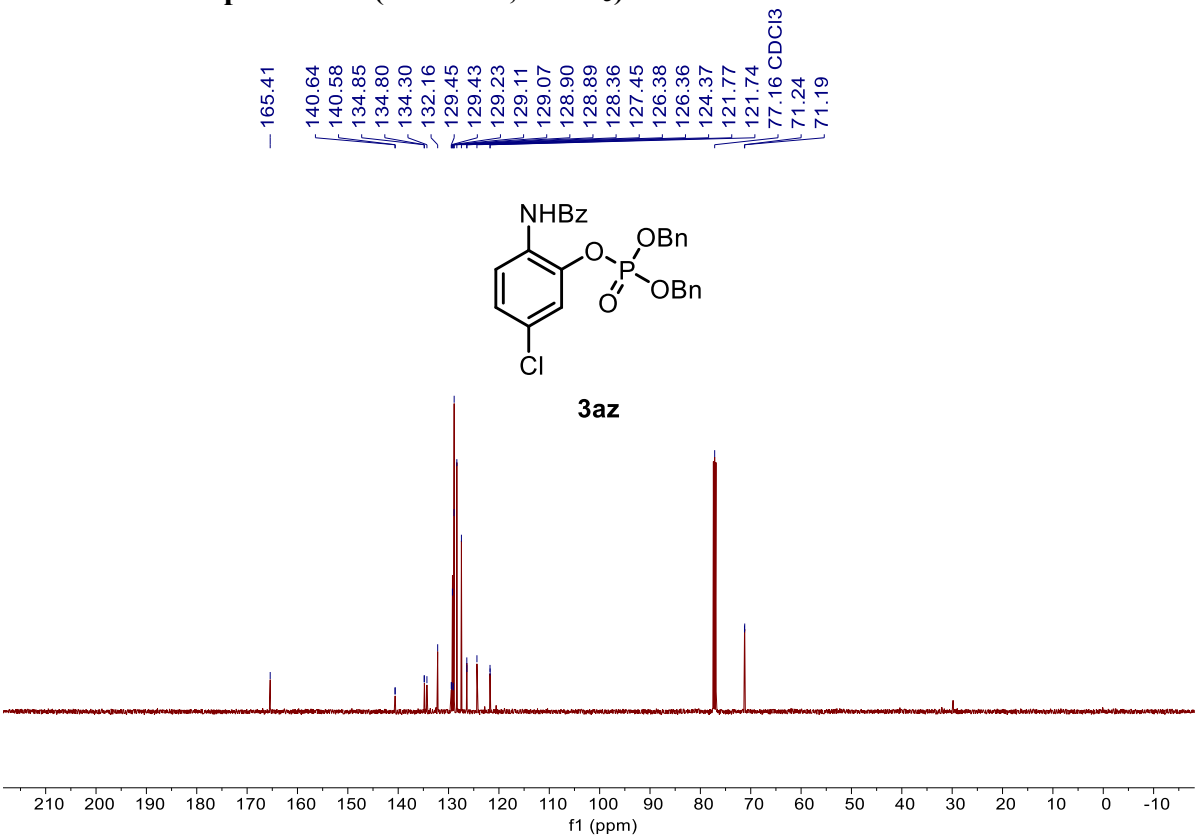
^{31}P NMR of Compound 3ay (202 MHz, $CDCl_3$)



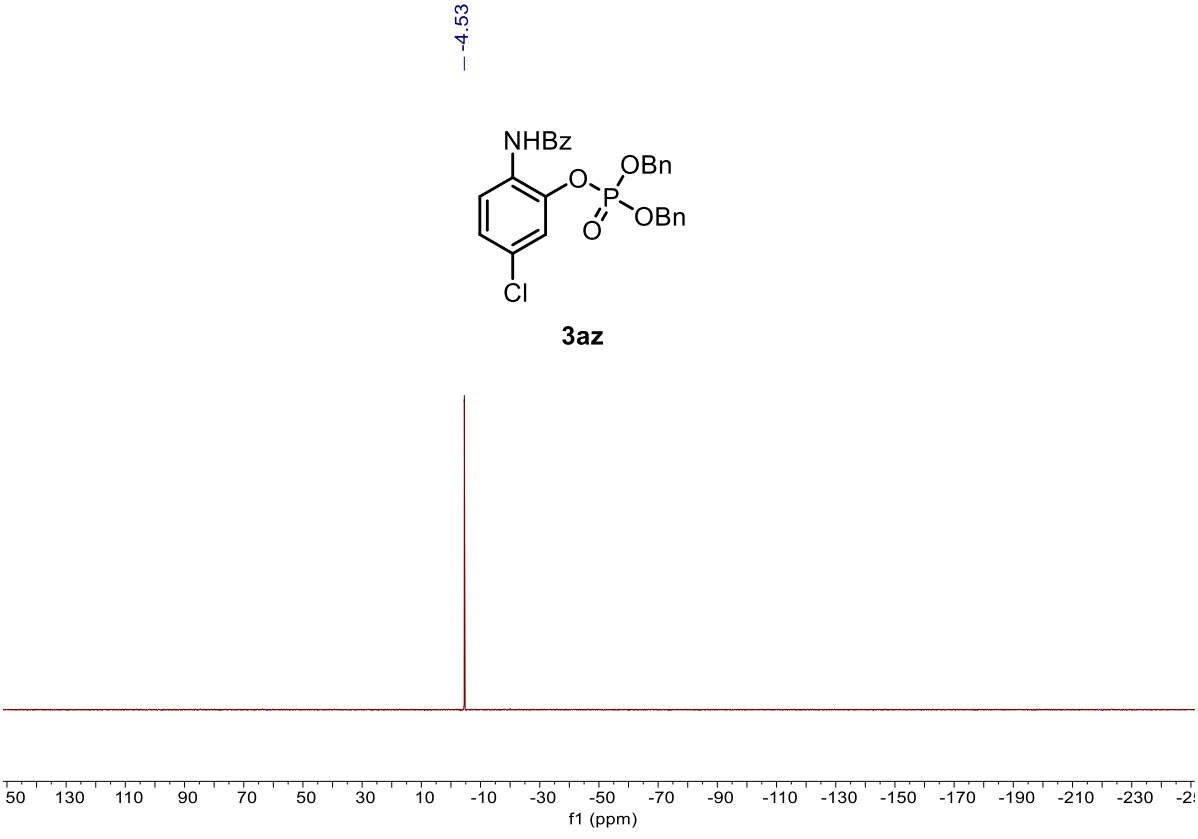
^{1}H NMR of Compound 3az (500 MHz, $CDCl_3$)



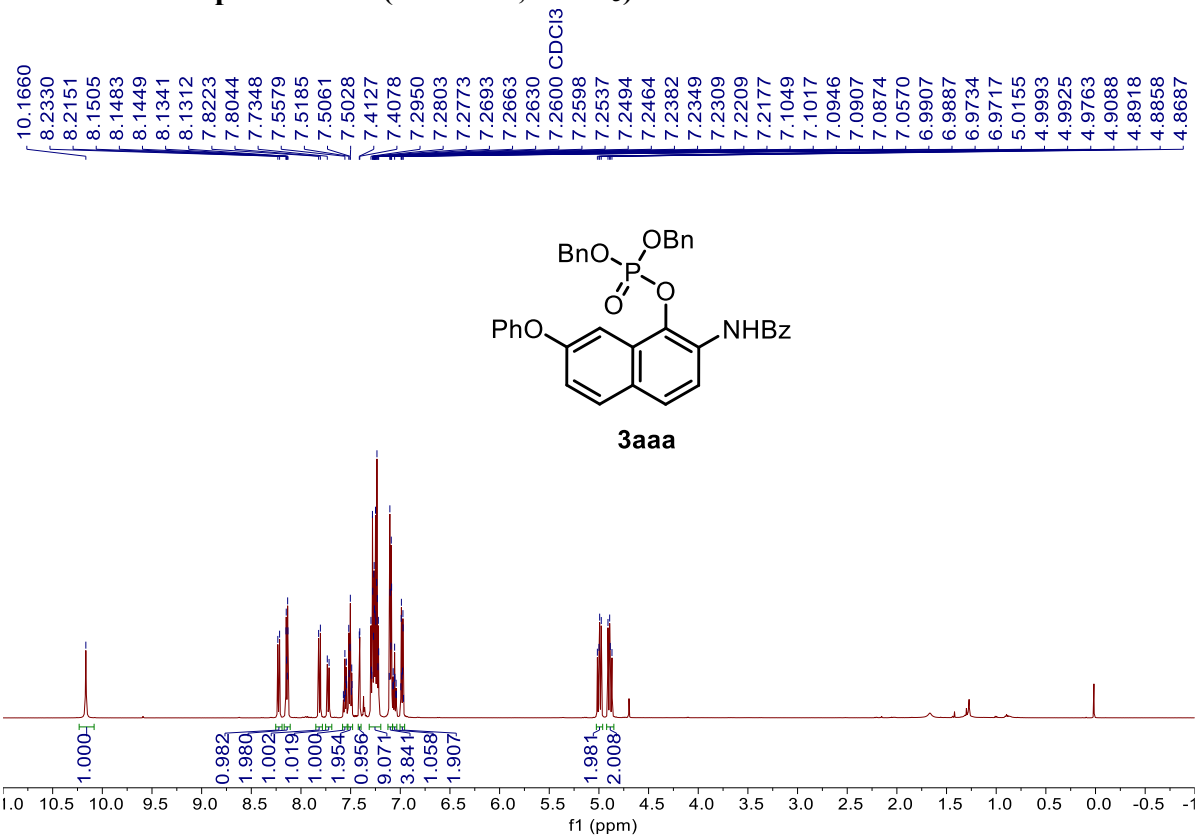
^{13}C NMR of Compound 3az (126 MHz, $CDCl_3$)



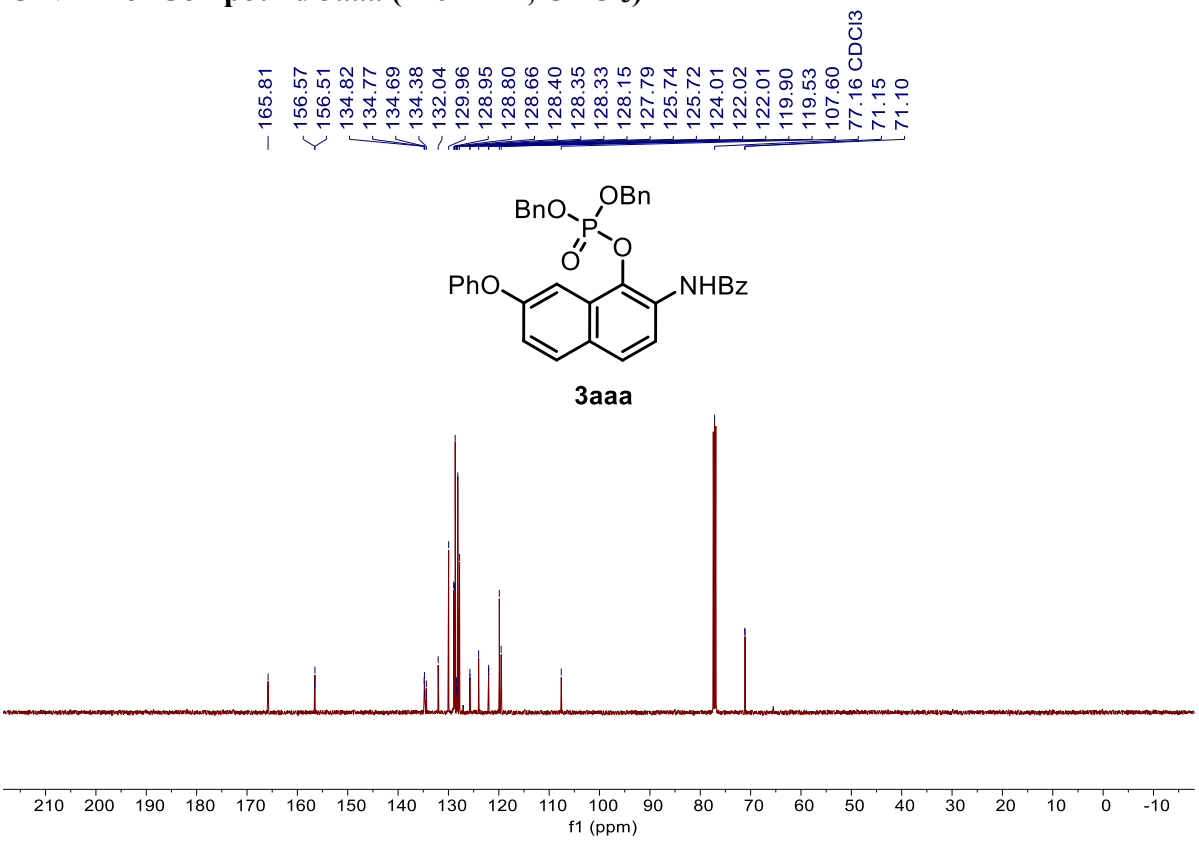
^{31}P NMR of Compound 3az (202 MHz, $CDCl_3$)



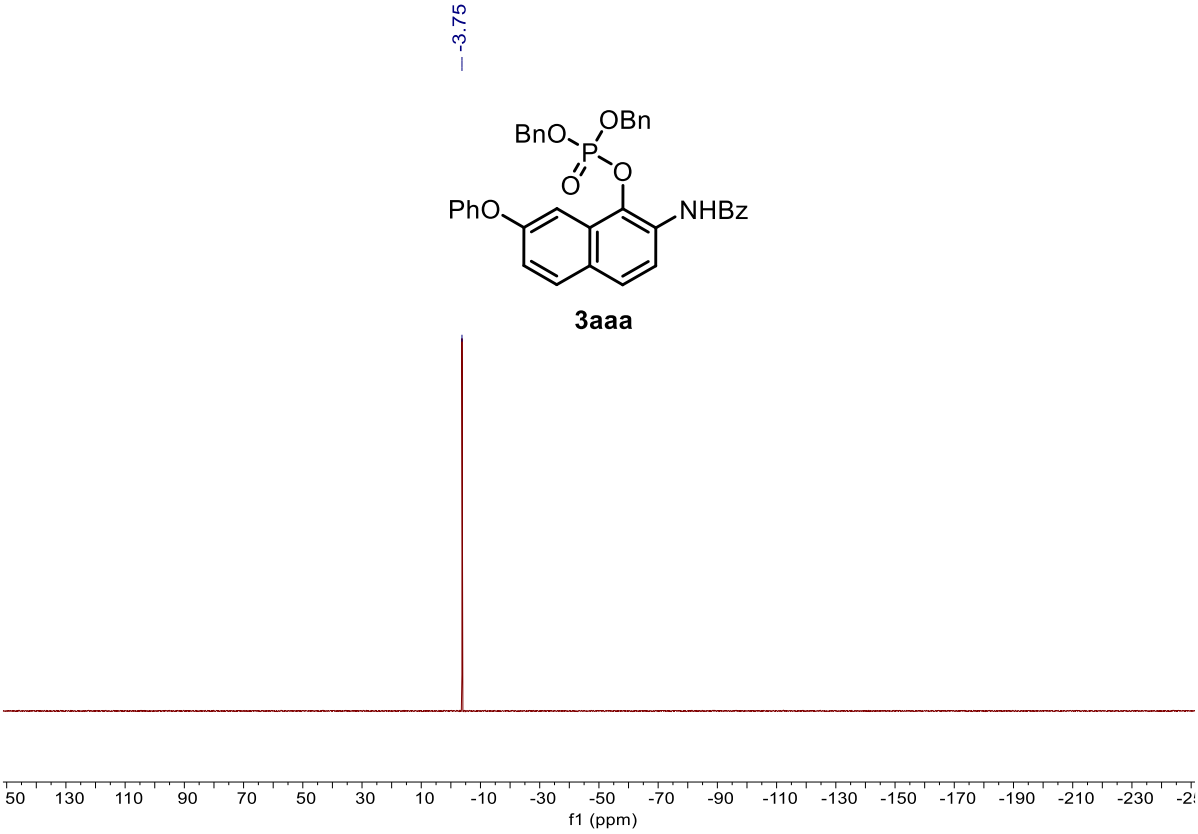
^{1}H NMR of Compound 3aaa (500 MHz, $CDCl_3$)



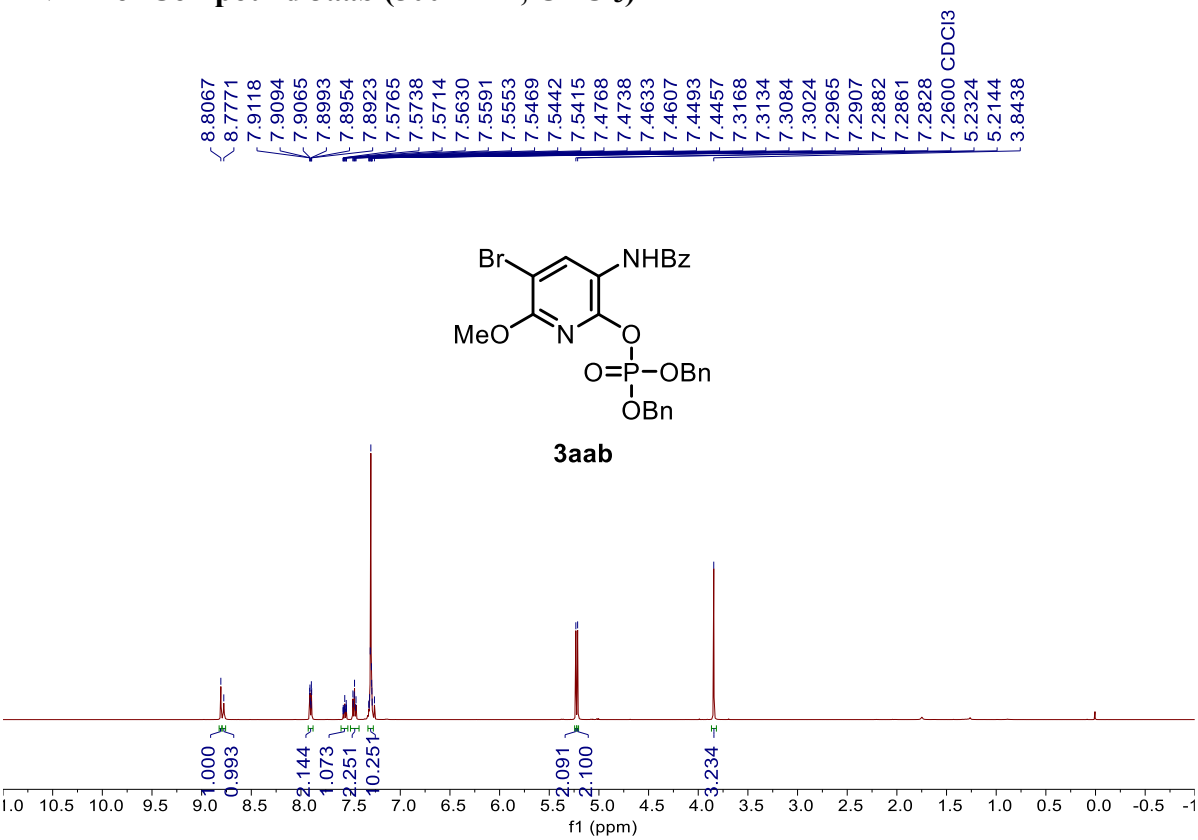
^{13}C NMR of Compound 3aaa (126 MHz, $CDCl_3$)



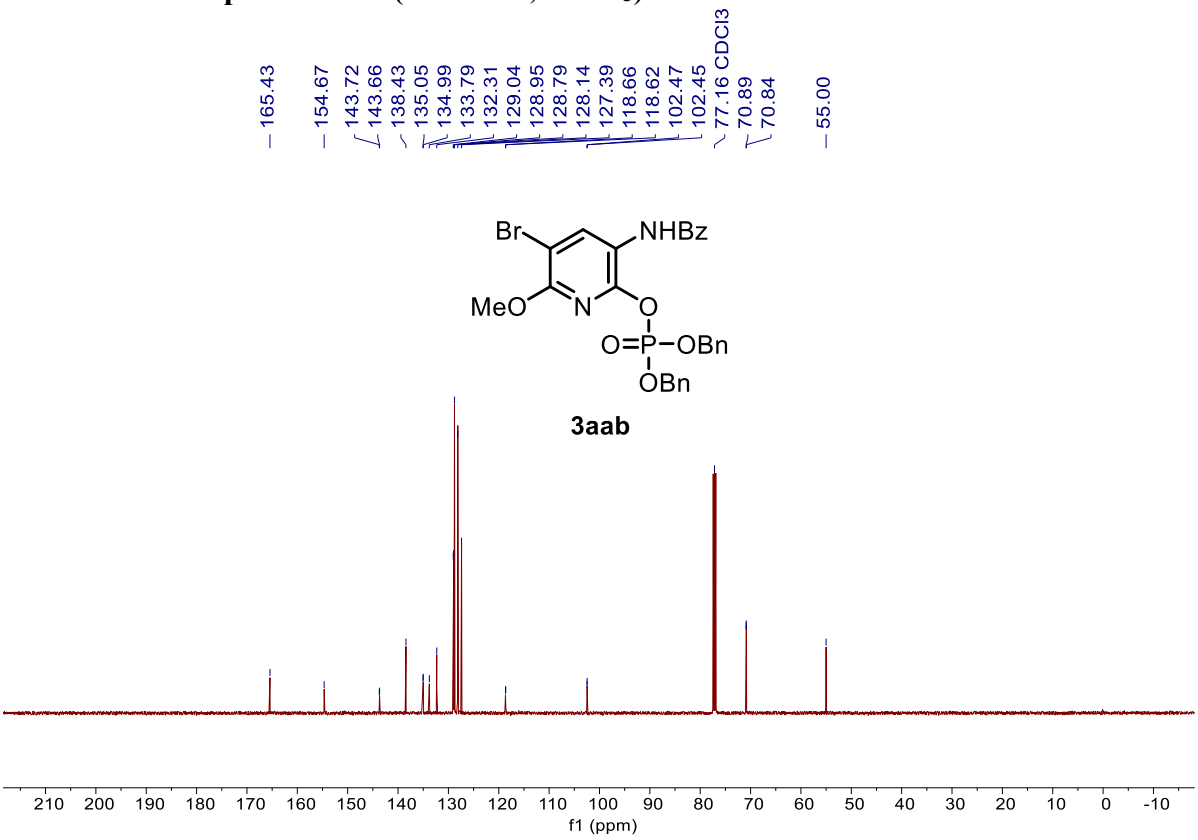
^{31}P NMR of Compound 3aaa (202 MHz, $CDCl_3$)



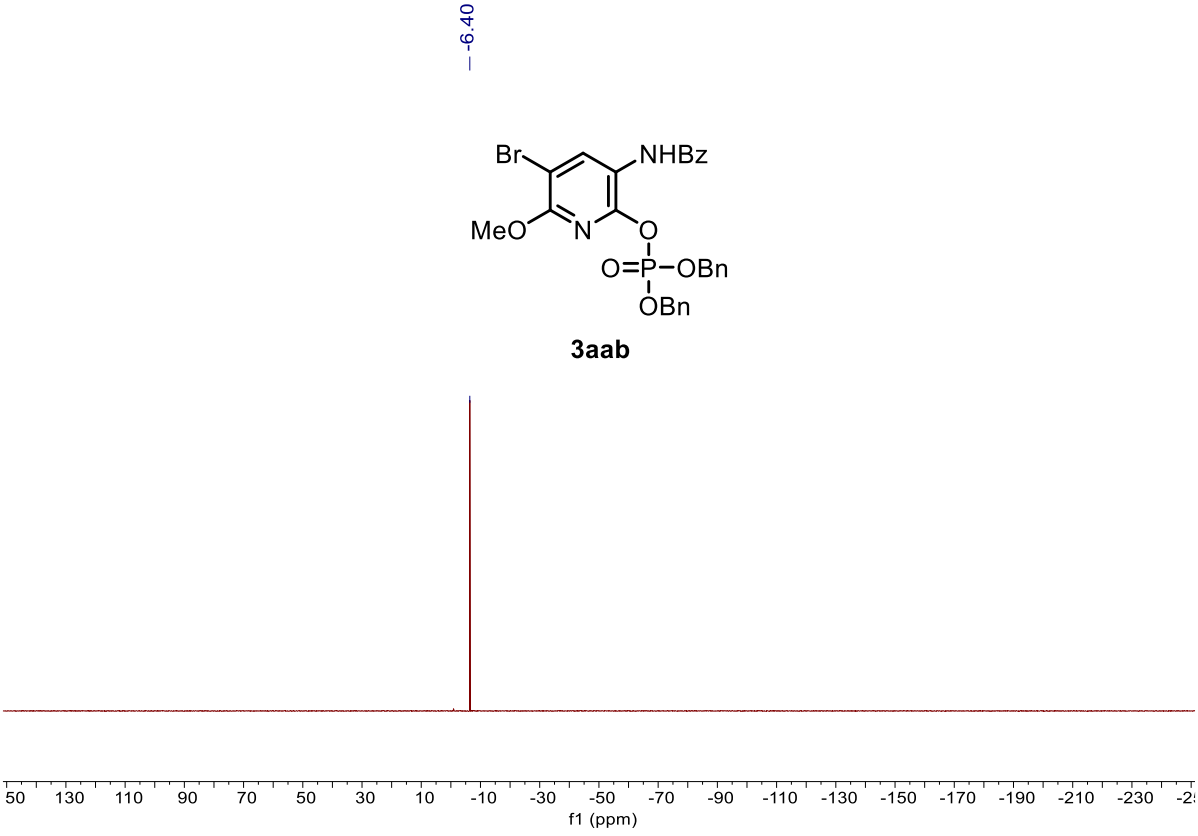
^{1}H NMR of Compound 3aab (500 MHz, $CDCl_3$)



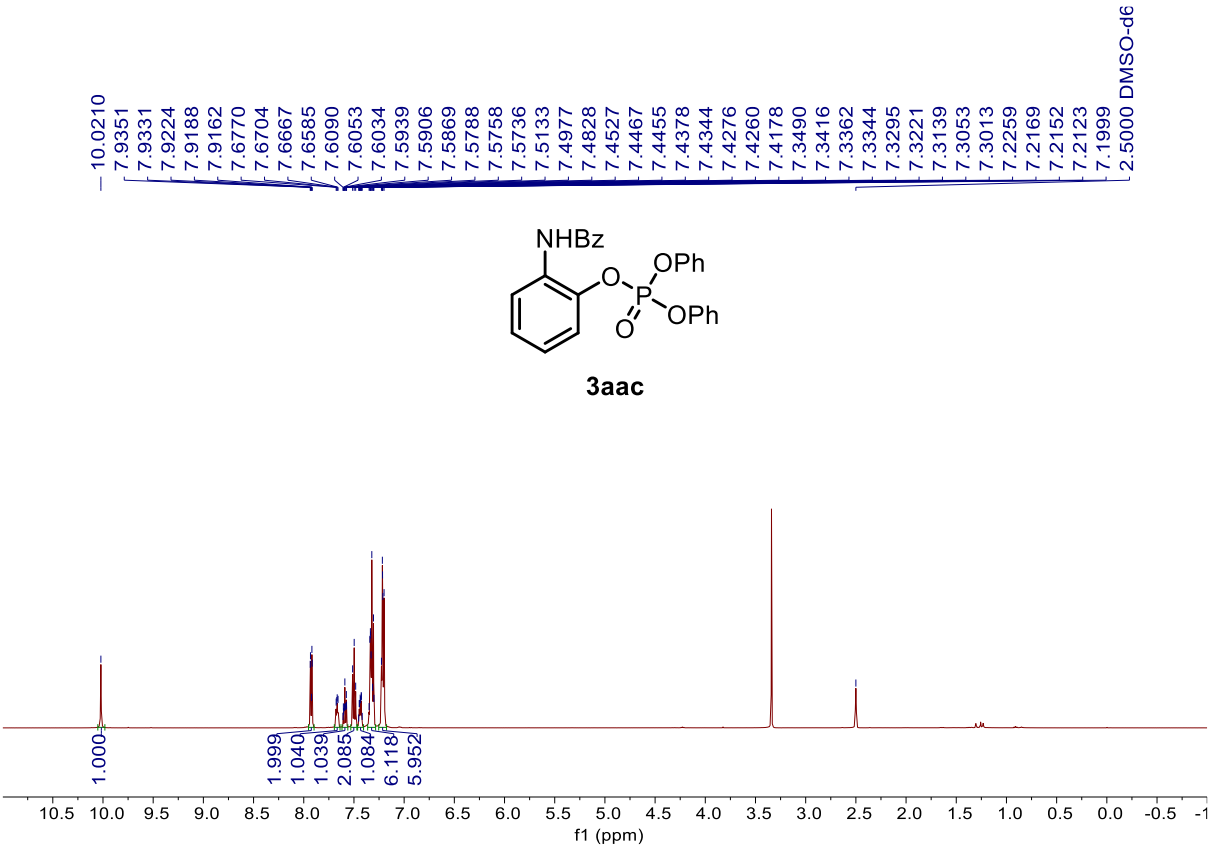
^{13}C NMR of Compound 3aab (126 MHz, $CDCl_3$)



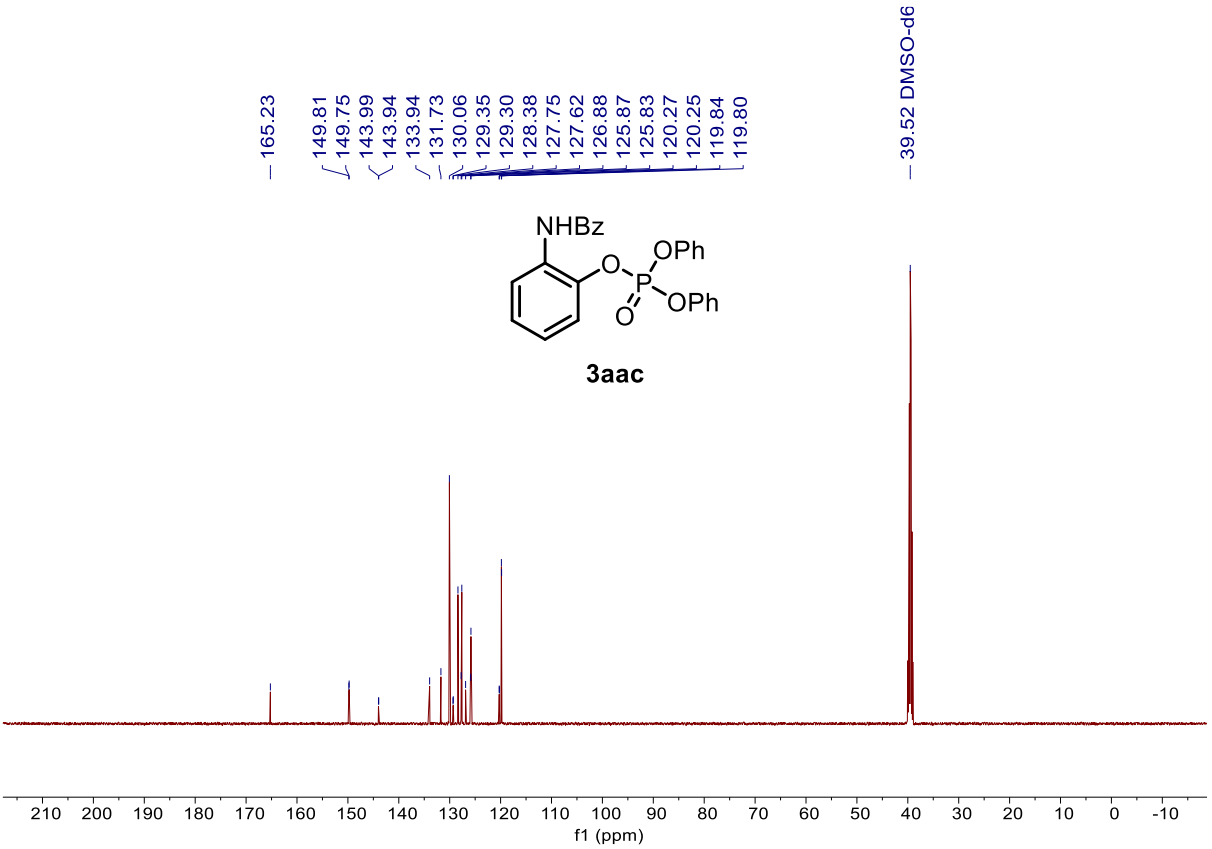
^{31}P NMR of Compound 3aab (202 MHz, $CDCl_3$)



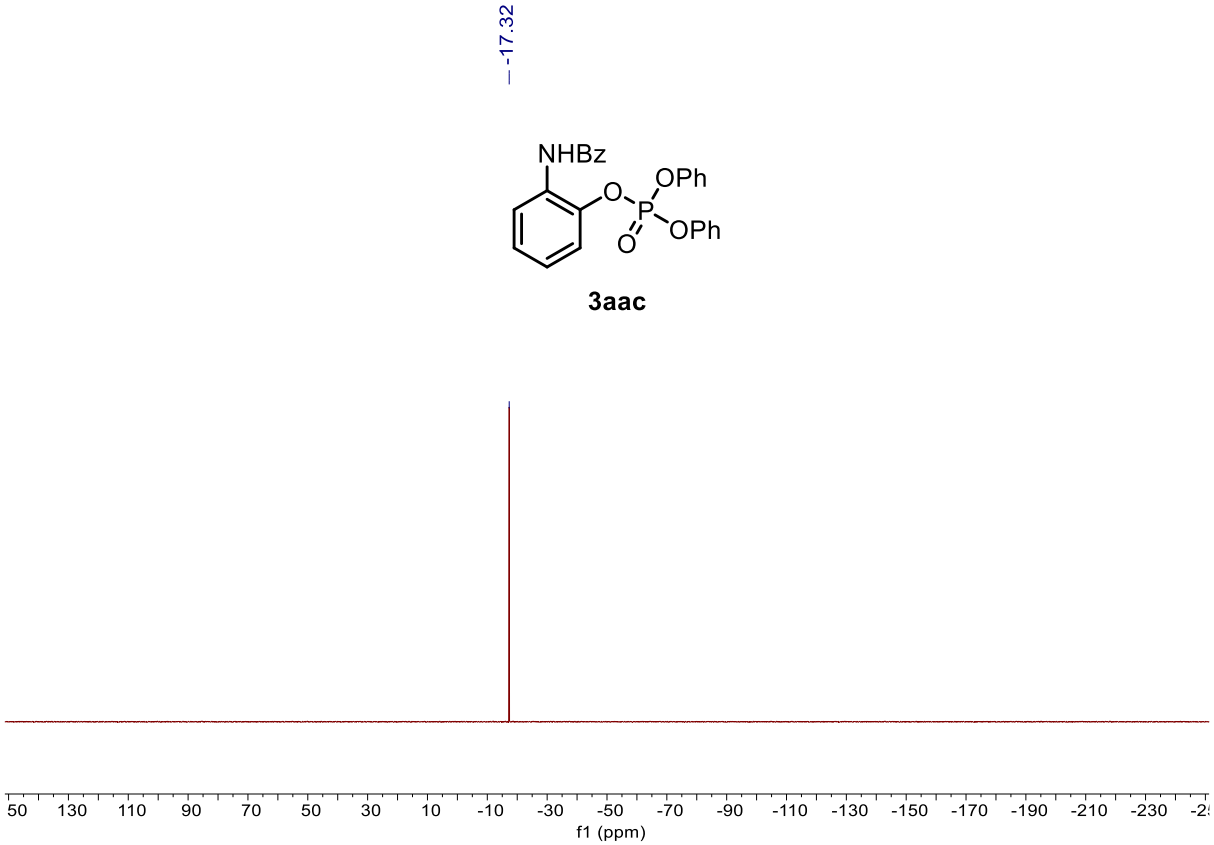
^{1}H NMR of Compound 3aac (500 MHz, DMSO-d_6)



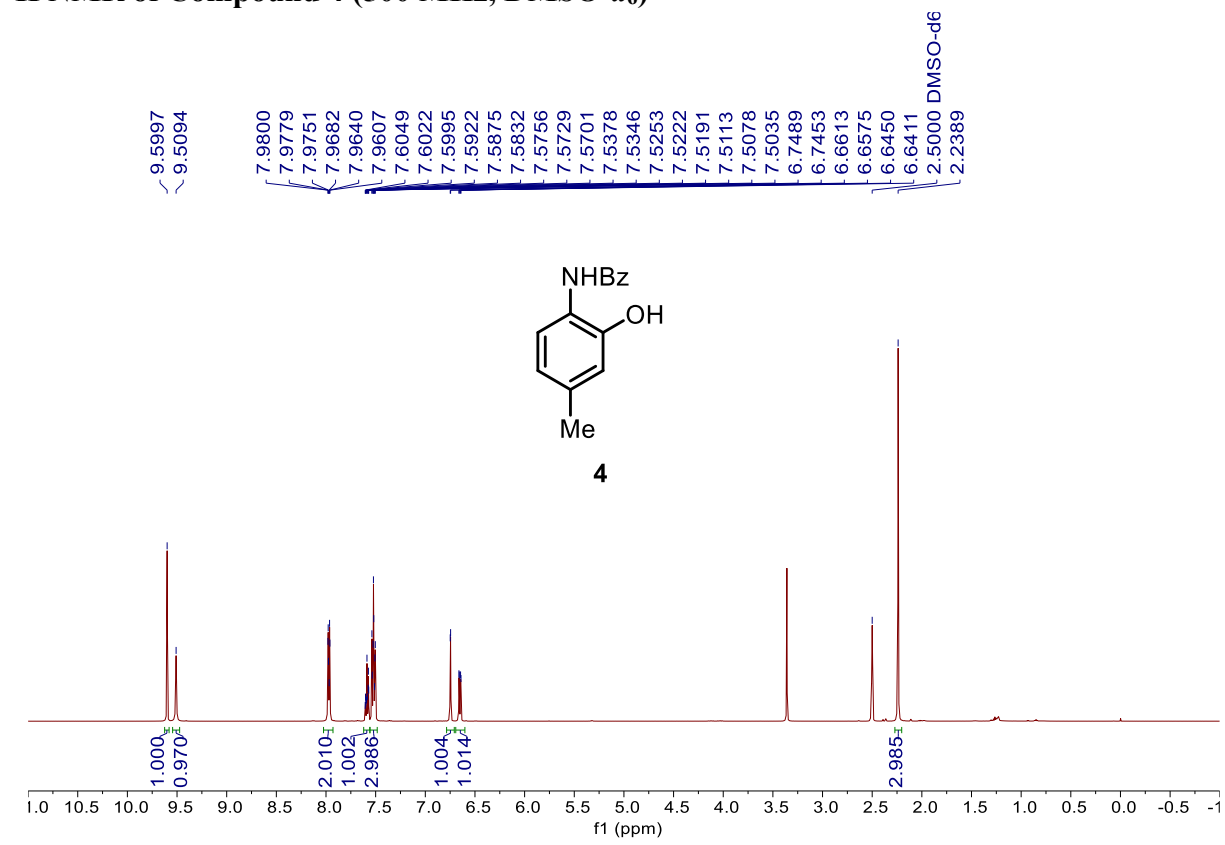
^{13}C NMR of Compound 3aac (126 MHz, DMSO-d_6)



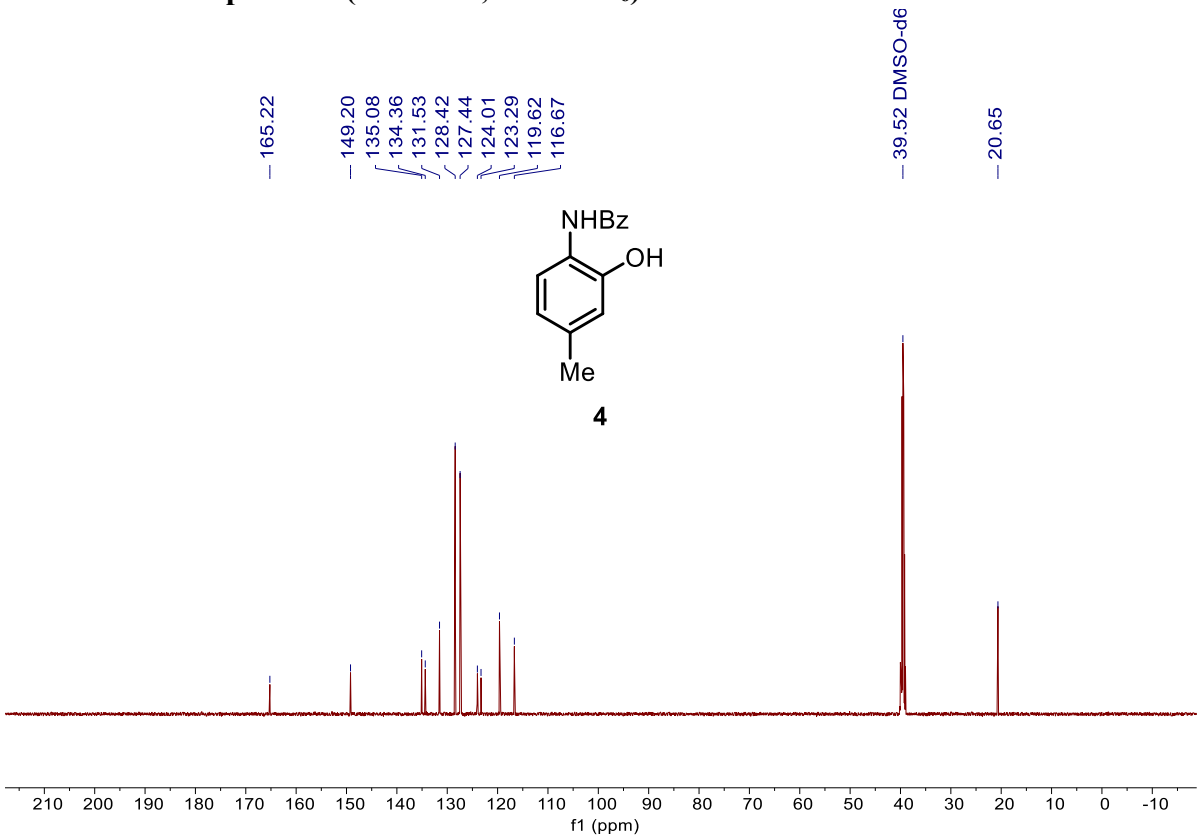
^{31}P NMR of Compound 3aac (202 MHz, DMSO-d_6)



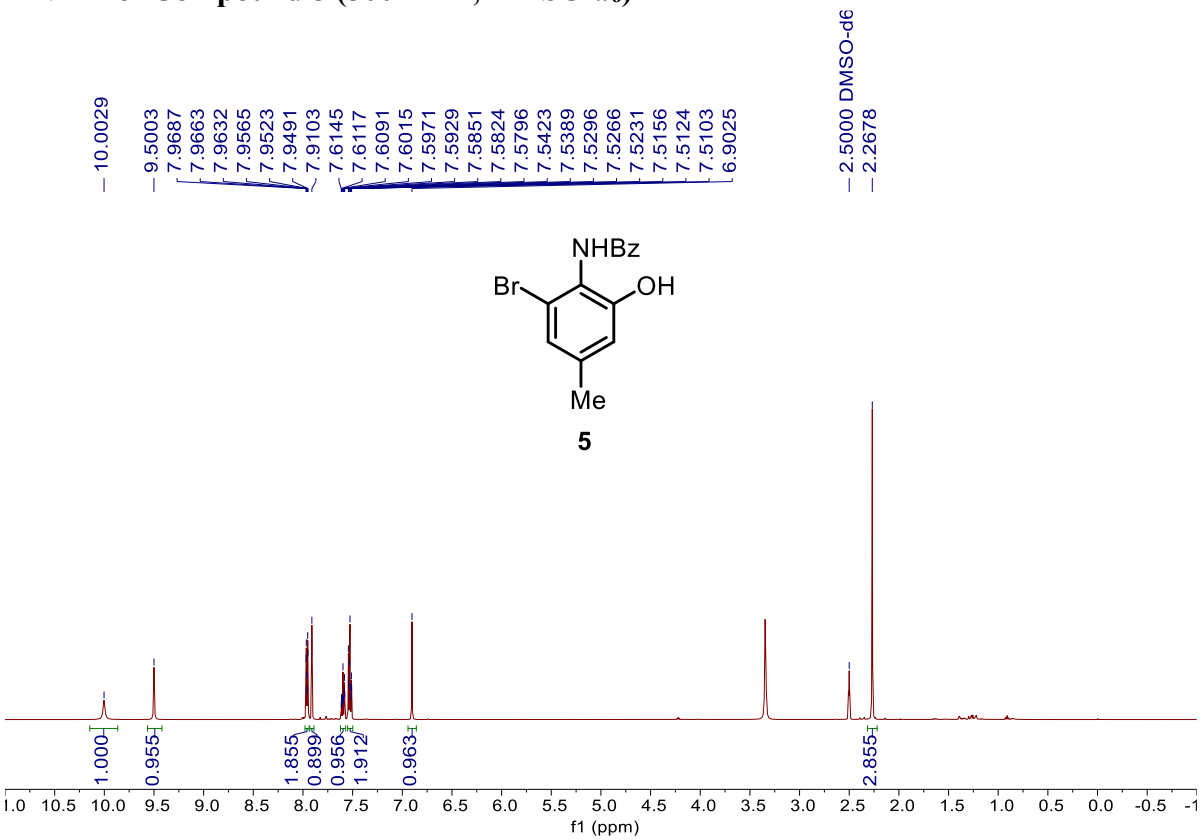
^{1}H NMR of Compound 4 (500 MHz, DMSO-d_6)



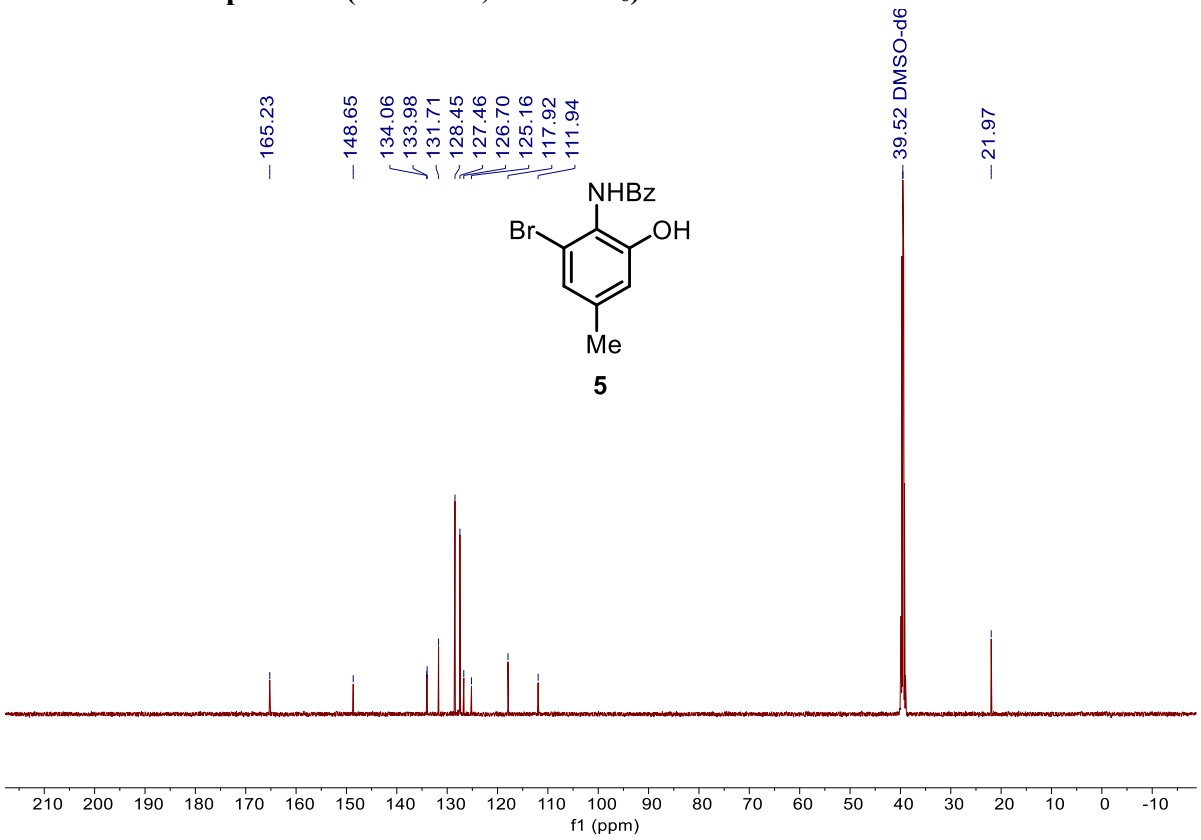
^{13}C NMR of Compound 4 (126 MHz, DMSO-d_6)



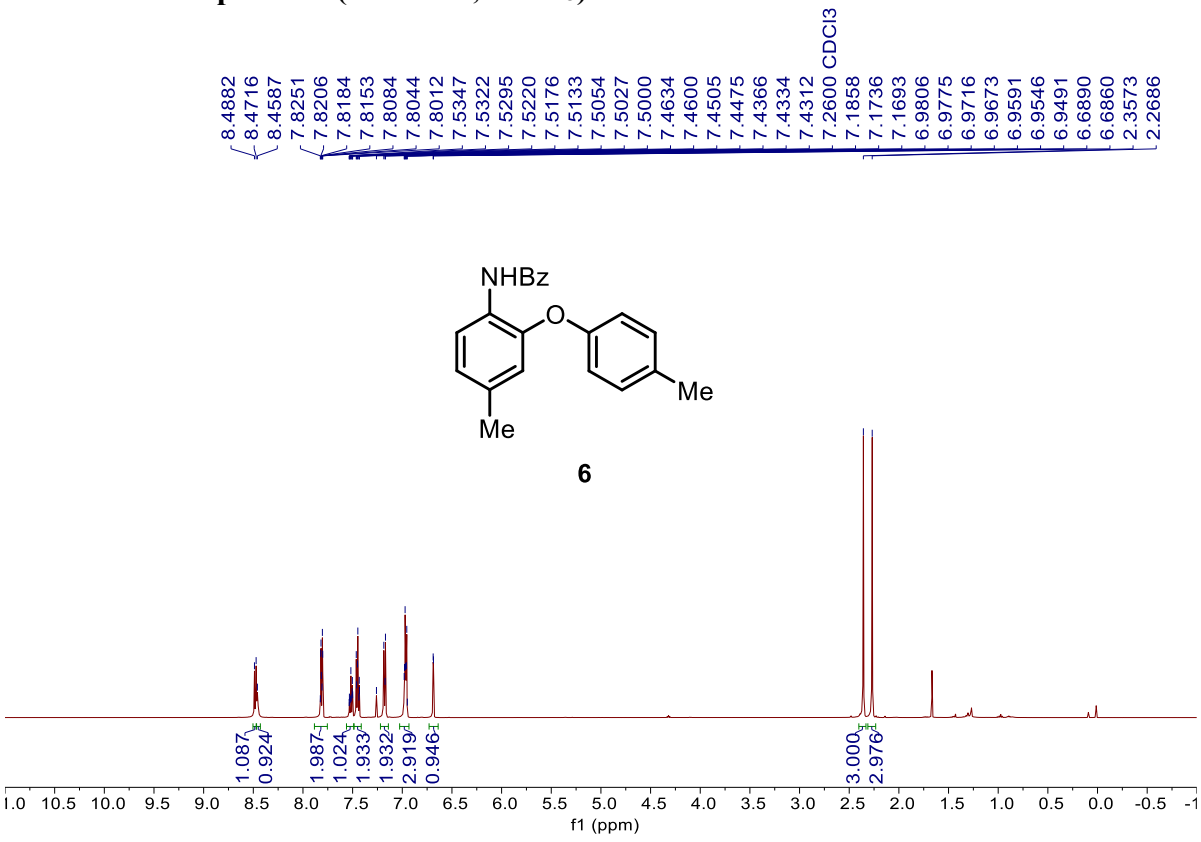
^{1}H NMR of Compound 5 (500 MHz, DMSO-d_6)



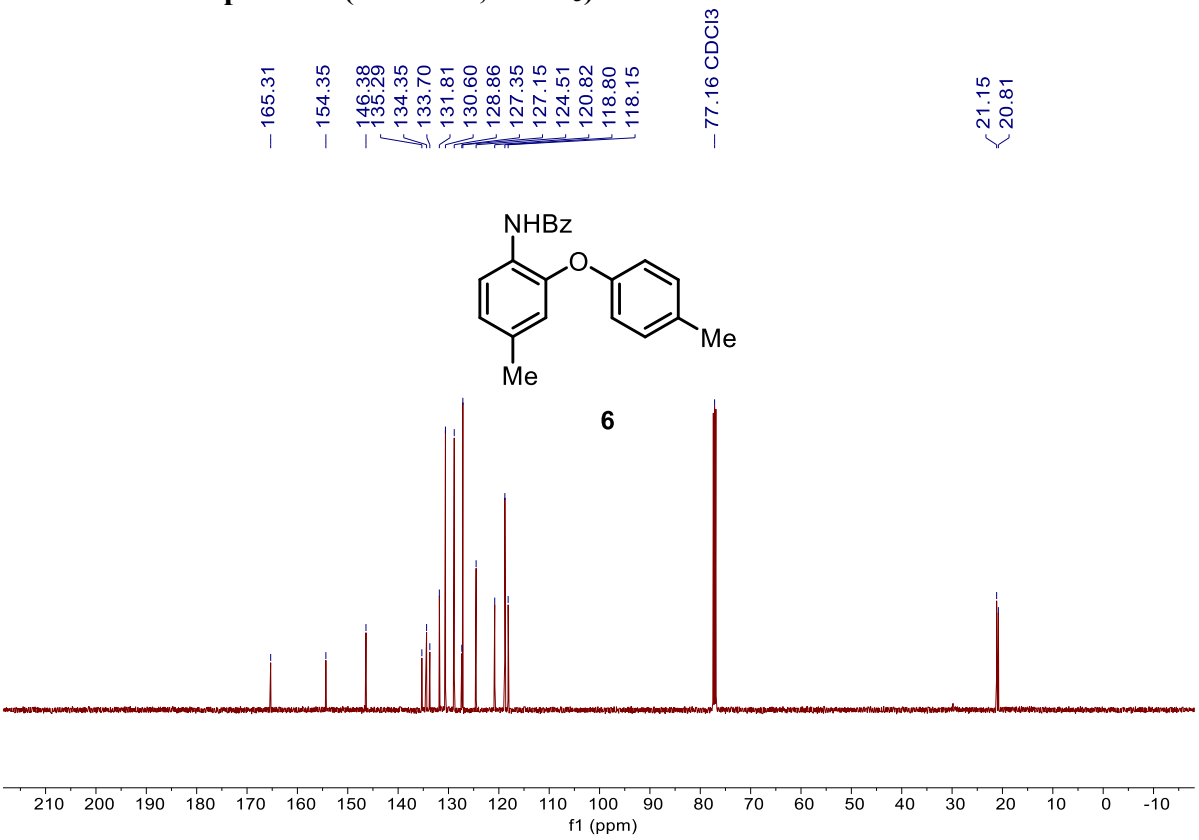
^{13}C NMR of Compound 5 (126 MHz, DMSO-d_6)



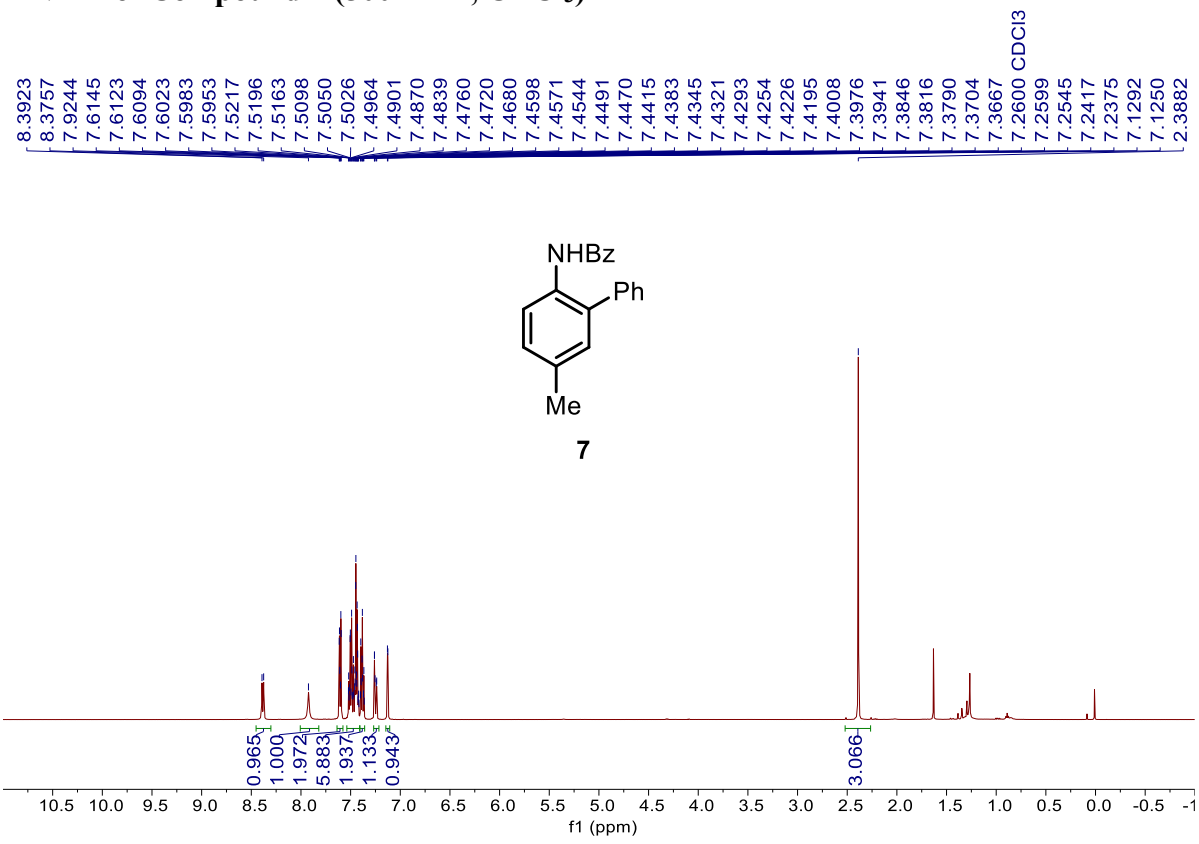
^{1}H NMR of Compound 6 (500 MHz, $CDCl_3$)



^{13}C NMR of Compound 6 (126 MHz, $CDCl_3$)



^{1}H NMR of Compound 7 (500 MHz, $CDCl_3$)



^{13}C NMR of Compound 7 (126 MHz, $CDCl_3$)