Supporting Information
for
The synthesis of α-aryl-α-aminophosphonates and α-aryl-α-aminophosphine oxides by the microwave-assisted Pudovik reaction

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Experimental, X-ray crystallographic data, and NMR spectra

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General information

The reactions were carried out in a 300 W CEM Discover focused microwave reactor (CEM Microwave Technology Ltd., Buckingham, UK) equipped with a pressure controller using 20–30 W irradiation under isothermal conditions.

GC measurements were performed on an HP5890 series 2 GC-FID chromatograph, using a 15 m × 0.18 mm Restek, Rtx-5 column with a film layer of 0.20 μm. The temperature of the column was initially held at 40 °C for 1 min, followed by programming at 25 °C/min up to 300 °C, and a final period at 300 °C (isothermal) for 10 min. The temperature of the injector was 290 °C, and of the FID detector 300 °C. The carrier gas was N_2.

GC–MS measurements were performed on an Agilent 6890 N-GC-5973 N-MSD chromatograph, using a 30 m × 0.25 mm Restek, Rtx-5SILMS column with a film layer of 0.25 μm. The initial temperature of column was 45 °C for 1 min, followed by programming at 10 °C/min up to 310 °C and a final period at 310 °C (isothermal) for 17 min. The temperature of the injector was 250 °C. The carrier gas was He and the operation mode was splitless.

LC–MS experiments were performed with an Agilent 1200 liquid chromatography system coupled with a 6130 quadrupole mass spectrometer equipped with an ESI ion source (Agilent Technologies, Palo Alto, CA, USA). Analysis was performed at 40 °C on a Gemini C18 column (150 mm × 4.6 mm, 3 μm; Phenomenex, Torrance, CA, USA) with a mobile phase flow rate of 0.6 mL/min. The composition of eluent A was 0.1% NH_4HCO_3 in water; eluent B was 0.1% NH_4HCO_3 and 8% water in acetonitrile; 0→3 min 5% B, 3→13 min gradient, 13→20 min 95% B. The injection volume was 20 μL. The chromatographic profile was registered at 222 nm. The MSD operating parameters were as follows: positive ionization mode, scan spectra from *m*/*z* 100 to 1000, drying gas temperature 300 °C, nitrogen-flow rate 12 L/min, nebulizer pressure 60 psi, capilary voltage 2500 V.

High resolution mass spectrometric measurements were performed using a Q-TOF Premier mass spectrometer in positive electrospray mode.

The ^{31}P, ^{13}C, ^{1}H NMR spectra were taken in $CDCl_3$ solution on a Bruker AV-300 or DRX-500 spectrometer operating at 121.5, 75.5 and 300 or 202.4, 125.7 and 500 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 and TMS. Non-equivalence effects were observed in ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra. Corresponding pairs of resonances were marked with (I) and (II), respectively.

In situ FTIR measurements were conducted using a ReactIR 1000 equipment (Mettler-Toledo Inc., Columbus, OH). An attenuated total reflectance (ATR) diamond probe was placed in a

100-mL four-necked flask equipped with a dropping funnel, a condenser, a thermometer, and a magnetic stirrer. The temperature was maintained by using an appropriately adjusted oil bath.

General procedure for the preparation of *N*-benzylideneamines

A mixture of 25 mmol of amine [butylamine (2.5 mL), cyclohexylamine (2.9 mL), aniline (2.3 mL)] and 25 mmol of aldehyde [benzaldehyde (2.6 mL), 2-chlorobenzaldehyde (2.8 mL), 3-chlorobenzaldehyde (2.8 mL), 4-chlorobenzaldehyde (3.5 g)] was stirred for 6–10 min at rt (25 °C). After completion, 10 mL of dichloromethane were added to the mixture, dried (Na_2SO_4) and filtered. Evaporation of the volatile components provided the products **1a–f**.

***N*-Benzylidene(butyl)amine (1a)**

Yield: 97% (3.9 g) of compound **1a** as pale yellow oil; ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3), 20.5 (CH_3CH_2), 33.0 (CH_2CH_2N), 61.5 (CH_2N), 128.0 (C_2), 128.6 (C_3), 130.4 (C_4), 136.4 (C_1), 160.7 (CH=N); δ [S1] ($CDCl_3$) 13.5, 20.1, 32.6, 61.1, 127.6, 128.1, 130.0, 136.0, 160.2; $[M+H]^+_{found}$ = 162.1282, $C_{11}H_{16}N$ requires 162.1277.

***N*-Benzylidene(cyclohexyl)amine (1b)**

Yield: 96% (4.5 g) of compound **1b** as yellow oil; ^{13}C NMR ($CDCl_3$) δ 24.8 (C_3), 25.7 (C_4), 34.4 (C_2), 70.0 (C_1), 128.1 ($C_{3'}$), 128.5 ($C_{2'}$), 130.3 ($C_{4'}$), 136.6 ($C_{1'}$), 158.6 (CH=N); δ [S1] ($CDCl_3$) 24.8, 25.6, 34.4, 70.0, 128.0, 128.5, 130.3, 136.6, 158.5; $[M+H]^+_{found}$ = 188.1441, $C_{13}H_{18}N$ requires 188.1434.

***N*-Benzylideneaniline (1c)**

Yield: 96% (4.3 g) of compound **1c** as yellow crystal; Mp: 47-48 °C; Mp [S2]: 50-51 °C; ^{13}C NMR ($CDCl_3$) δ 120.9 (C_2), 125.9 (C_4), 128.77 (C_3'), 128.81 (C_3), 129.1 (C_2'), 131.4 (C_4'), 136.2 (C_1'), 152.1 (C_1), 160.4 (CH=N); δ [S1] ($CDCl_3$) 120.9, 125.9, 128.79, 128.83, 129.2, 131.4, 136.3, 152.1, 160.4; $[M+H]^+_{found}$ = 182.0972, $C_{13}H_{12}N$ requires 182.0964.

***N*-2-Chlorobenzylidene(butyl)amine (1d)**

Yield: 95% (4.6 g) of compound **1d** as pale yellow oil; ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3), 20.5 (CH_3CH_2), 32.9 (CH_2CH_2N), 61.6 (CH_2N), 127.0 (C_5), 128.3 (C_6), 129.7 (C_3), 131.3 (C_4), 133.4 (C_2), 134.9 (C_1), 157.5 (CH=N); δ [S3] (DMSO) 13.85, 20.42, 32.92, 61.56, 126.92, 128.26, 129.68, 131.21, 133.40, 134.88, 157.44; $[M+H]^+_{found}$ = 196.0895, $C_{11}H_{15}NCl$ requires 196.0888.

***N*-3-Chlorobenzylidene(butyl)amine (1e)**

Yield: 97% (4.7 g) of compound **1e** as yellow oil; ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3), 20.5 (CH_3CH_2), 32.9 (CH_2CH_2N), 61.4 (CH_2N), 126.3 (C_6), 127.7 (C_2), 129.8 (C_5), 130.4 (C_4), 134.8 (C_1), 138.2 (C_3), 159.2 (CH=N); ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J_{HH} = 7.3, 3H, CH_3), 1.31-1.46 (m, 2H, CH_3CH_2), 1.61-1.75 (m, 2H, CH_2CH_2N), 3.62 (t, J_{HH} = 7.0, 2H, CH_2N), 7.29-7.41 (m, 2H, C_4H, C_5H), 7.53-7.59 (m, 1H, C_6H), 7.75 (s, 1H, C_2H), 8.22 (s, 1H, CH=N); $[M+H]^+_{found}$ = 196.0892, $C_{11}H_{15}NCl$ requires 196.0888.

***N*-4-chlorobenzylidene(butyl)amine (1f)**

Yield: 96% (4.7 g) of compound **1f** as yellow oil; ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3), 20.5 (CH_3CH_2), 33.0 (CH_2CH_2N), 61.4 (CH_2N), 128.8 (C_3), 129.2 (C_2), 134.9 (C_1), 136.3 (C_4), 159.3 (CH=N); δ [S4] ($CDCl_3$) 13.9, 20.4, 32.9, 61.4, 128.8, 129.2, 134.9, 136.3, 159.3; $[M+H]^+_{found}$ = 196.0887, $C_{11}H_{15}NCl$ requires 196.0888.

General procedure for the synthesis of the α-aminophosphonates and α-aminophosphine oxides

A mixture of 1 mmol imine derivate [**1a** (0.16 g), **1b** (0.19 g), **1c** (0.18 g), **1d-e** (0.20 g)] and >P(O)H derivative (1.0 mmol [dimethyl phosphite (0.092 mL), diethyl phosphite (0.13 mL)] or 1.2 mmol [dimethyl phosphite (0.11 mL), diethyl phosphite (0.15 mL), dibutyl phosphite (0.23 mL), dibenzyl phosphite (0.27 mL), diphenylphosphine oxide (0.24 g)] or 1.5 mmol [dimethyl phosphite (0.14 mL)]) was irradiated in a sealed tube at 80–100 °C for 10–60 min in a CEM Microwave reactor equipped with a pressure controller. The volatile components were removed under reduced pressure. The residue obtained was purified by flash column chromatography using silica gel and dichloromethane/methanol 97:3 or ethyl acetate/hexane 1:1 as the eluent to afford α-aminophosphonates and α-aminophosphine oxides.

Dimethyl ((butylamino)(phenyl)methyl)phosphonate (2a)

Yield: 73% (0.20 g) of compound **2a** as colorless oil; ^{31}P NMR ($CDCl_3$) δ 26.0; ^{13}C NMR ($CDCl_3$) 13.9 (CH_3CH_2), 20.3 (CH_3CH_2), 32.0 (d, J_{CP} = 0.5, CH_2CH_2N), 47.7 (d, $^3J_{CP}$ = 16.7, CH_2N), 53.5 (d, $^2J_{CP}$ = 7.0, CH_3O^I), 53.7 (d, $^2J_{CP}$ = 7.1, CH_3O^{II}), 60.8 (d, $^1J_{CP}$ = 153.4, CHP), 127.9 (d, J_{CP} = 3.2, C_4), 128.4 (d, $^3J_{CP}$ = 6.2, C_2), 128.5 (d, J_{CP} = 2.5, C_3), 136.0 (d, $^2J_{CP}$ = 3.8, C_1); ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J_{HH} = 7.2, 3H, CH_3CH_2), 1.21-1.38 (m, 2H, CH_3CH_2), 1.38-1.50 (m, 2H, CH_2CH_2N), 1.94 (s, 1H, NH), 2.36-2.59 (m, 2H, CH_2N), 3.55 (d, J_{HP} = 10.4, 3H,

CH_3O^I), 3.74 (d, J_{HP} = 10.5, 3H, CH_3O^{II}), 4.05 (d, J_{HP} = 20.1, 1H, CHP), 7.26-7.45 (m, 5H, ArH); $[M+H]^+_{found}$ = 272.1408, $C_{13}H_{23}NO_3P$ requires 272.1410.

Diethyl ((butylamino)(phenyl)methyl)phosphonate (2b)

Yield: 85% (0.25 g) of compound **2b** as colorless oil; ^{31}P NMR ($CDCl_3$) δ 23.8; δ [S5] ($CDCl_3$) 23.6; $[M+H]^+_{found}$ = 300.1734, $C_{15}H_{27}NO_3P$ requires 300.1723.

Dibutyl ((butylamino)(phenyl)methyl)phosphonate (2c)

Yield: 90% (0.32 g) of compound **2c** as colorless oil; ^{31}P NMR ($CDCl_3$) δ 24.2; ^{13}C NMR ($CDCl_3$) 13.6 ($CH_3(CH_2)_3O^I$), 13.7 ($CH_3(CH_2)_3O^{II}$), 14.0 ($CH_3(CH_2)_3N$), 18.6 ($CH_2(CH_2)_2O^I$), 18.7 ($CH_2(CH_2)_2O^{II}$), 20.3 ($CH_2(CH_2)_2N$), 32.0 (d, J_{CP} = 0.5, CH_2CH_2N), 32.5 (d, $^3J_{CP}$ = 5.8, $CH_2CH_2O^I$), 32.6 (d, $^3J_{CP}$ = 5.8, $CH_2CH_2O^{II}$), 47.8 (d, $^3J_{CP}$ = 16.5, CH_2N), 61.2 (d, $^1J_{CP}$ = 152.7, CHP), 66.4 (d, $^2J_{CP}$ = 7.2, CH_2O^I), 66.6 (d, $^2J_{CP}$ = 7.3, CH_2O^{II}), 127.7 (d, J_{CP} = 3.2, C_4), 128.3 (d, J_{CP} = 2.5, C_3), 128.5 (d, $^3J_{CP}$ = 6.2, C_2), 136.5 (d, $^2J_{CP}$ = 4.1, C_1); ^1H NMR ($CDCl_3$) δ 0.84 (t, J_{HH} = 7.2, 3H, $CH_3(CH_2)_3O^I$), 0.86 (t, J_{HH} = 6.8, 3H, $CH_3(CH_2)_3N$), 0.90 (t, J_{HH} = 7.2, 3H, $CH_3(CH_2)_3O^{II}$), 1.16-1.53 (m, 10H, $CH_2CH_2CH_2N$, $CH_2CH_2CH_2O$, $CH_2CH_2O^I$), 1.54-1.67 (m, 2H, $CH_2CH_2O^{II}$), 1.98 (s, 1H, NH), 2.37-2.60 (m, 2H, CH_2N) 3.69-3.82 (m, 1H, CH_A, CH_2O^I), 3.84-3.95 (m, 1H, CH_B, CH_2O^I), 3.95-4.09 [4.02 (d, J_{HP} = 19.6, CHP) overlapped by the multiplet of CH_2O^{II} total int. 3H], 7.23-7.37 (m, 3H, C_2H, C_4H), 7.37-7.46 (m, 2H, C_3H); $[M+H]^+_{found}$ = 356.2360, $C_{19}H_{35}NO_3P$ requires 356.2349.

Dibenzyl ((butylamino)(phenyl)methyl)phosphonate (2d)

Yield: 69% (0.29 g) of compound **2d** as colorless oil; ^{31}P NMR ($CDCl_3$) δ 25.3; ^{13}C NMR ($CDCl_3$) 13.9 (CH_3), 20.2 (CH_3CH_2), 32.0 (d, J_{CP} = 0.4, CH_2CH_2N), 47.8 (d, $^3J_{CP}$ = 16.7, CH_2N), 61.4 (d, $^1J_{CP}$ = 152.6, CHP), 68.1 (d, $^2J_{CP}$ = 6.8, CH_2O^I), 68.3 (d, $^2J_{CP}$ = 7.1, CH_2O^{II}), 127.7 ($C_{2'}{}^I$), 127.85 (d, J_{CP} = 3.1, C_4), 127.88 ($C_{2'}{}^{II}$), 128.15 ($C_{4'}{}^I$), 128.22 ($C_{4'}{}^{II}$), 128.37 ($C_{3'}{}^I$), 128.440 (d, J_{CP} = 2.5, C_3), 128.444 ($C_{3'}{}^{II}$), 125.5 (d, $^3J_{CP}$ = 6.3, C_2), 136.0 (d, $^2J_{CP}$ = 3.7, C_1), 136.3 (d, $^3J_{CP}$ = 6.2, $C_{1'}{}^I$), 136.5 (d, $^3J_{CP}$ = 6.2, $C_{1'}{}^{II}$); ^1H NMR ($CDCl_3$) δ 0.84 (t, J_{HH} = 7.2, 3H, CH_3), 1.17-1.33 (m, 2H, CH_3CH_2), 1.33-1.45 (m, 2H, CH_2CH_2N), 1.84 (s, 1H, NH), 2.34-2.58 (m, 2H, CH_2N), 4.06 (d, J_{HP} = 20.0, 1H, CHP), 4.73 (dd, J_{HP} = 11.9, J_{HH} = 8.1, 1H, CH_A, CH_2O^I), 4.88 (dd, J_{HP} = 11.9, J_{HH} = 7.2, 1H, CH_B, CH_2O^I), 5.02 (qd, J_{HP} = 11.9, J_{HH} = 8.0, 2H, CH_2O^{II}), 7.08-7.19 (m, 2H, $C_{4'}H$), 7.21-7.46 (m, 13H, $C_{2\text{-}4}H$, $C_{2'}H$ and $C_{3'}H$), $[M+H]^+_{found}$ = 424.2037, $C_{25}H_{31}NO_3P$ requires 424.2036.

((Butylamino)(phenyl)methyl)diphenylphosphine oxide (2e)

Yield: 89% (0.32 g) of compound **2e** as white crystal; Mp: 166-167 °C; ^{31}P NMR ($CDCl_3$) δ 31.1; ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3), 20.2 (CH_3CH_2), 31.9 (CH_2CH_2N), 47.7 (d, $^3J_{CP}$ = 13.8, CH_2N), 63.5 (d, $^1J_{CP}$ = 79.4, CHP), 127.6 (d, J_{CP} = 2.7, C_4), 128.0 (d, $^2J_{CP}$ = 11.5, $C_{2'}^{I}$), 128.1 (d, J_{CP} = 2.1, C_3), 128.3 (d, $^2J_{CP}$ = 11.4, $C_{2'}^{II}$), 128.8 (d, $^3J_{CP}$ = 5.2, C_2), 131.2 (d, $^1J_{CP}$ = 95.6, $C_{1'}^{I}$), 131.3 (d, $^1J_{CP}$ = 97.0, $C_{1'}^{II}$), 131.5 (d, J_{CP} = 2.8, $C_{4'}^{I}$), 131.7 (d, $^3J_{CP}$ = 8.7, $C_{3'}^{I}$), 131.8 (d, J_{CP} = 3.0, $C_{4'}^{II}$), 132.1 (d, $^3J_{CP}$ = 8.6, $C_{3'}^{II}$), 135.6 (d, $^2J_{CP}$ = 1.8, C_1); ^{1}H NMR ($CDCl_3$) δ 0.82 (t, J_{HH} = 7.2, 3H, CH_3), 1.16-1.31 (m, 2H, CH_3CH_2), 1.32-1.46 (m, 2H, CH_2CH_2N), 1.76 (s, 1H, NH), 2.34-2.48 (m, 1H, CH_A, CH_2N), 2.50-2.64 (m, 1H, CH_B, CH_2N), 4.45 (d, J_{HP} = 11.3, 1H, CHP), 7.09-7.22 (m, 5H, $C_{2\text{-}4}H$), 7.27-7.62 (m, 8H, $C_{2'}H$, $C_{4'}H$, $C_{3'}H^{I}$), 7.80-7.92 (m, 2H, $C_{3'}H^{II}$); $[M+H]^+_{found}$ = 364.1830, $C_{23}H_{27}NOP$ requires 364.1825.

Dimethyl ((cyclohexylamino)(phenyl)methyl)phosphonate (4a)

Yield: 87% (0.26 g) of compound **4a** as colorless oil; ^{31}P NMR ($CDCl_3$) δ 26.5; δ [S6] ($CDCl_3$) 26.5; $[M+H]^+_{found}$ = 298.1559, $C_{15}H_{25}NO_3P$ requires 298.1567.

Diethyl ((cyclohexylamino)(phenyl)methyl)phosphonate (4b)

Yield: 91% (0.30 g) of compound **4b** as colorless; ^{31}P NMR ($CDCl_3$) δ 24.1; δ [S5] ($CDCl_3$) 24.3; $[M+H]^+_{found}$ = 326.1890, $C_{17}H_{29}NO_3P$ requires 326.1880.

Dibutyl ((cyclohexylamino)(phenyl)methyl)phosphonate (4c)

Yield: 93% (0.35 g) of compound **4c** as colorless oil; ^{31}P NMR ($CDCl_3$) δ 24.2; ^{13}C NMR ($CDCl_3$) 13.6 (CH_3^{I}), 13.7 (CH_3^{II}), 18.6 ($CH_3CH_2^{I}$), 18.7 ($CH_3CH_2^{II}$), 24.4 (C_3^{I}), 24.9 (C_3^{II}), 26.1 (C_4), 32.0 (C_2^{I}), 32.4 (d, $^3J_{CP}$ = 5.9, $CH_2CH_2O^{I}$), 32.6 (d, $^3J_{CP}$ = 5.9, $CH_2CH_2O^{II}$), 34.4 (C_2^{II}), 53.5 (d, $^3J_{CP}$ = 15.5, C_1), 57.6 (d, $^1J_{CP}$ = 153.5, CHP), 66.3 (d, $^2J_{CP}$ = 7.3, CH_2O^{I}), 66.8 (d, $^2J_{CP}$ = 7.2, CH_2O^{II}), 127.6 (d, J_{CP} = 3.2, $C_{4'}$), 128.3 (d, J_{CP} = 2.5, $C_{3'}$), 128.5 (d, $^3J_{CP}$ = 6.2, $C_{2'}$), 137.0 (d, $^2J_{CP}$ = 2.8, $C_{1'}$); ^{1}H NMR ($CDCl_3$) δ 0.82 (t, J_{HH} = 7.3, 3H, CH_3^{I}), 0.91 (t, J_{HH} = 7.3, 3H, CH_3^{II}), 0.99-1.29 (m, 7H, $C_{2\text{-}4}H_{eq}$, $CH_3CH_2^{I}$), 1.30-1.47 (m, 4H, $CH_3CH_2^{II}$, $CH_2CH_2O^{I}$), 1.48-1.73 (m, 6H, C_2H_{ax}, C_3H_{ax}, $CH_2CH_2O^{II}$), 1.88 (bs, 2H, NH, C_4H_{ax}), 2.28-2.43 (m, 1H, C_1H), 3.63-3.76 (m, 1H, CH_A, CH_2O^{I}), 3.80-3.93 (m, 1H, CH_B, CH_2O^{I}), 3.96-4.14 (m, 2H, CH_2O^{II}), 4.19 (d, J_{HP} = 22.0, CHP), 7.23-7.36 (m, 3H, $C_{2'}H$, $C_{4'}H$), 7.37-7.43 (m, 2H, $C_{3'}H$); $[M+H]^+_{found}$ = 382.2501, $C_{21}H_{37}NO_3P$ requires 382.2506.

Dibenzyl ((cyclohexylamino)(phenyl)methyl)phosphonate (4d)

Yield: 68% (0.31 g) of compound **4d** as colorless oil; ^{31}P NMR ($CDCl_3$) δ 25.0; ^{13}C NMR ($CDCl_3$) 24.4 (C_3^{I}), 24.8 (C_3^{II}), 26.0 (C_4), 32.0 (C_2^{I}), 34.3 (C_2^{II}), 53.6 (d, $^3J_{CP}$ = 15.0, C_1), 57.9 (d, $^1J_{CP}$ = 153.3, CHP), 67.9 (d, $^2J_{CP}$ = 7.0, CH_2O^{I}), 68.6 (d, $^2J_{CP}$ = 7.0, CH_2O^{II}), 127.7 ($C_{2''}^{I}$), 127.8 (d, J_{CP} = 3.2, $C_{4'}$), 127.9 ($C_{2''}^{II}$), 128.1 ($C_{4''}^{I}$), 128.2 ($C_{4''}^{II}$), 128.4 ($C_{3''}^{I}$), 128.44 ($C_{3''}^{II}$), 128.45 (d, J_{CP} = 2.4, $C_{3'}$), 128.50 (d, $^3J_{CP}$ = 6.3, $C_{2'}$), 136.4 (d, $^3J_{CP}$ = 6.2, $C_{1''}^{I}$), 136.6 (d, $^2J_{CP}$ = 2.5, $C_{1'}$), 136.7 (d, $^3J_{CP}$ = 6.1, $C_{1''}^{II}$); ^{1}H NMR ($CDCl_3$) δ 0.89-1.24 (m, 5H, $C_{2\text{-}4}H_{ax}$), 1.44-1.73 (m, 4H, C_2H_{ax}, C_3H_{ax}), 1.76-1.90 (m, 2H, NH, C_4H_{ax}), 2.35 (bs, 1H, C_1H) 4.26 (d, J_{HP} = 22.1, 1H, CHP), 4.68 (dd, J_{HP} = 11.7, J_{HH} = 8.1, 1H, CH_A, CH_2O^{I}), 4.86 (dd, J_{HP} = 11.8, J_{HH} = 7.1, 1H, CH_B, CH_2O^{I}), 5.07 (qd, J_{HP} = 11.9, J_{HH} = 7.7, 2H, CH_2O^{II}), 7.12 (bs, 2H, $C_{4''}H$), 7.21-7.44 (m, 13H, $C_{2'\text{-}4'}H$, $C_{2''}H$, $C_{3''}H$), $[M+H]^+_{found}$ = 450.2207, $C_{27}H_{33}NO_3P$ requires 450.2193.

((Cyclohexylamino)(phenyl)methyl)diphenylphosphine oxide (4e)

Yield: 88% (0.34 g) of compound **4e** as white crystal; Mp: 189-190 °C; ^{31}P NMR ($CDCl_3$) δ 31.5; ^{13}C NMR ($CDCl_3$) δ 24.2 (C_3^{I}), 24.7 (C_3^{II}), 26.0 (C_4), 31.7 (C_2^{I}), 34.4 (C_2^{II}), 53.6 (d, $^3J_{CP}$ = 12.8, C_1), 59.9 (d, $^1J_{CP}$ = 79.8, CHP), 127.4 (d, J_{CP} = 2.7, $C_{4'}$), 127.9 (d, $^2J_{CP}$ = 11.5, $C_{2''}^{I}$), 128.1 (d, J_{CP} = 2.1, $C_{3'}$), 128.3 (d, $^2J_{CP}$ = 11.4, $C_{2''}^{II}$), 128.8 (d, $^3J_{CP}$ = 5.1, $C_{2'}$), 131.41 (d, J_{CP} = 2.7, $C_{4''}^{I}$), 131.42 (d, $^1J_{CP}$ = 96.4, $C_{1''}^{I}$), 131.63 (d, $^3J_{CP}$ = 8.7, $C_{3''}^{I}$), 131.64 (d, $^1J_{CP}$ = 97.2, $C_{1''}^{II}$), 131.7 (d, J_{CP} = 2.8, $C_{4''}^{II}$), 132.1 (d, $^3J_{CP}$ = 8.6, $C_{3''}^{II}$), 136.0 (d, $^2J_{CP}$ = 1.6, $C_{1'}$); ^{1}H NMR ($CDCl_3$) δ 0.97-1.21 (m, 5H, $C_{2\text{-}4}H_{eq}$), 1.48-1.60 (m, 4H, C_2H_{ax} and C_3H_{ax}), 1.87 (bs, 1H, C_4H_{ax}), 2.04 (s, 1H, NH), 2.34 (bs, 1H, C_1H), 4.63 (d, J_{HP} = 11.6, 1H, CHP), 7.16 (bs, 5H, $C_{2'\text{-}4'}H$), 7.22-7.31 (m, 2H, $C_{3''}H^{I}$), 7.33-7.42 (m, 1H, $C_{4''}H^{I}$), 7.43-7.59 (m, 5H, $C_{2''}H$, $C_{4''}H^{II}$), 7.85-7.97 (m, 2H, $C_{3''}H^{II}$); $[M+H]^+_{found}$ = 390.1968, $C_{25}H_{29}NOP$ requires 390.1981.

Dimethyl ((phenylamino)(phenyl)methyl)phosphonate (5a)

Yield: 92% (0.27 g) of compound **5a** as yellow crystal; Mp: 94-95 °C; Mp [S7]: 90-92 °C; ^{31}P NMR ($CDCl_3$) δ 25.2; δ [S8] ($CDCl_3$) 25.3; $[M+H]^+_{found}$ = 292.1103, $C_{15}H_{19}NO_3P$ requires 292.1097.

Diethyl ((phenylamino)(phenyl)methyl)phosphonate (5b)

Yield: 93% (0.29 g) of compound **5b** as pale blue crystal; Mp: 91-92 °C; Mp [S9]: 90-91 °C; ^{31}P NMR ($CDCl_3$) δ 22.8; δ [S9] ($CDCl_3$) 23.2; $[M+H]^+_{found}$ = 320.1418, $C_{17}H_{23}NO_3P$ requires 320.1410.

Dibutyl ((phenylamino)(phenyl)methyl)phosphonate (5c)

Yield: 97% (0.36 g) of compound **5c** as greenish-blue oil; ^{31}P NMR ($CDCl_3$) δ 22.7; ^{13}C NMR ($CDCl_3$) 13.5 (CH_3^{I}), 13.6 (CH_3^{II}), 18.6 ($CH_3CH_2^{I}$), 18.7 ($CH_3CH_2^{II}$), 32.4 (d, $^3J_{CP}$ = 5.7, $CH_2CH_2O^{I}$), 32.6 (d, $^3J_{CP}$ = 5.7, $CH_2CH_2O^{II}$), 56.1 (d, $^1J_{CP}$ = 150.8, CHP), 67.0 (d, $^2J_{CP}$ = 7.4, CH_2O^{I}), 67.1 (d, $^2J_{CP}$ = 7.5, CH_2O^{II}), 113.9 (C_2), 118.4 (C_4), 127.90 (d, $^3J_{CP}$ = 5.6, $C_{2'}$), 127.92 (d, J_{CP} = 2.8, $C_{4'}$), 128.6 (d, J_{CP} = 2.7, $C_{3'}$), 129.2 (C_3), 136.0 (d, $^2J_{CP}$ = 2.7, $C_{1'}$), 146.4 (d, $^3J_{CP}$ = 14.5, C_1); δ [S10] ($CDCl_3$) 13.33, 13.37, 13.39, 18.35, 18.49, 18.55, 32.13, 32.2, 32.26, 32.33, 32.39, 55.13, 56.63, 65.28, 65.35, 66.65, 66.72, 66.74, 66.81, 113.66, 113.69, 118.16, 127.72, 128.37, 128.43, 135.86, 135.88, 146.14, 146.28; ^{1}H NMR ($CDCl_3$) δ 0.82 (t, J_{HH} = 7.3, 3H, CH_3^{I}), 0.88 (t, J_{HH} = 7.3, 3H, CH_3^{II}), 1.16-1.29 (m, 2H, $CH_3CH_2^{I}$), 1.29-1.49 (m, 4H, $CH_3CH_2^{II}$, $CH_2CH_2O^{I}$), 1.51-1.72 (m, 2H, $CH_2CH_2O^{II}$), 3.53-3.68 (m, 1H, CH_A, CH_2O^{I}), 3.81-3.94 (m, 1H, CH_B, CH_2O^{I}), 3.95-4.14 (m, 2H, CH_2O^{II}), 4.77 (d, J_{HP} = 24.2, CHP), 5.32 (bs, 1H, NH), 6.60 (d, J_{HH} = 7.8, 2H, C_2H), 6.68 (t, J_{HH} = 7.3, 1H, C_4H), 7.09 (t, J_{HH} = 7.9, 2H, C_3H), 7.20-7.38 (m, 3H, $C_{2'}H$, $C_{4'}H$), 7.42-7.51 (m, 2H, $C_{3'}H$); δ [S10] ($CDCl_3$) 0.82 (t, J = 7.4, 3H), 0.88 (t, J = 7.4, 3H), 1.17-1.27 (m, 8H), 3.54-4.14 (m, 5H), 4.73 (d, J = 24.2, 1H), 6.57-6.60 (m, 2H), 6.66-6.70 (m, 1H), 7.07-7.11 (m, 2H), 7.30-7.33 (m, 3H), 7.45-7.48 (m, 2H); $[M+H]^+_{found}$ = 376.2044, $C_{21}H_{31}NO_3P$ requires 376.2036.

Dibenzyl ((phenylamino)(phenyl)methyl)phosphonate (5d)

Yield: 70% (0.31 g) of compound **5d** as yellow crystal; Mp: 118-119 °C; ^{31}P NMR ($CDCl_3$) δ 23.6; ^{13}C NMR ($CDCl_3$) 56.3 (d, $^1J_{CP}$ = 150.4, CHP), 68.5 (d, $^2J_{CP}$ = 6.9, CH_2O^{I}), 68.6 (d, $^2J_{CP}$ = 7.0, CH_2O^{II}), 113.9 (C_2), 118.5 (C_4), 127.88 ($C_{2''}^{I}$), 127.93 (d, $^3J_{CP}$ = 5.6, $C_{2'}$), 127.98 (d, J_{CP} = 2.4, $C_{4'}$), 128.05 ($C_{2''}^{II}$), 128.4 ($C_{4''}^{I}$), 128.46 ($C_{4''}^{II}$), 128.49 ($C_{3''}^{I}$), 128.6 ($C_{3''}^{II}$), 128.7 (d, J_{CP} = 2.7, $C_{3'}$), 129.1 (C_3), 135.7 (d, $^2J_{CP}$ = 2.6, $C_{1'}$), 135.9 (d, $^3J_{CP}$ = 6.0, $C_{1''}^{I}$), 136.0 (d, $^3J_{CP}$ = 5.8, $C_{1''}^{II}$), 146.1 (d, $^3J_{CP}$ = 14.5, C_1); ^{1}H NMR ($CDCl_3$) δ 4.59 (dd, J_{HP} = 11.7, J_{HH} = 8.3, 1H, CH_A, CH_2O^{I}), 4.69 (bs, 1H, NH), 4.80 (d, J_{HP} = 24.5, 1H, CHP), 4.86 (dd, J_{HP} = 11.7, J_{HH} = 7.6, 1H, CH_B, CH_2O^{I}), 5.00 (qd, J_{HP} = 11.7, J_{HH} = 8.4, 2H, CH_2O^{II}), 6.53 (d, J_{HH} = 7.7, 2H, C_2H), 6.68 (t, J_{HH} = 7.3, 1H, C_4H), 7.03-7.16 [7.08 (t, J_{HH} = 7.6, 2H, C_2H) overlapped by the multiplet of $C_{4''}H$ total int. 4H], 7.20-7.38 (m, 11H, $C_{2'}H$, $C_{4'}H$, $C_{2''}H$, $C_{3''}H$), 7.40-7.49 (m, 2H, $C_{3'}H$); $[M+H]^+_{found}$ = 444.1717, $C_{27}H_{27}NO_3P$ requires 444.1723.

((Phenylamino)(phenyl)methyl)diphenylphosphine oxide (5e)

Yield: 89% (0.34 g) of compound **5e** as yellow crystal; Mp: 252-253 °C; Mp [S11]: 252 °C; ^{31}P NMR ($CDCl_3$) δ 33.2; δ [S12] ($CDCl_3$) 33.6; $[M+H]^+_{found}$ = 384.1525, $C_{25}H_{23}NOP$ requires 384.1512.

Dimethyl ((butylamino)(2-chlorophenyl)methyl)phosphonate (6a)

Yield: 91% (0.28 g) of compound **6a** as colorless oil; ^{31}P NMR ($CDCl_3$) δ 25.5; ^{13}C NMR ($CDCl_3$) 13.9 (CH_3CH_2), 20.2 (CH_3CH_2), 31.9 (d, J_{CP} = 0.6, CH_2CH_2N), 47.5 (d, $^3J_{CP}$ = 16.4, CH_2N), 53.3 (d, $^2J_{CP}$ = 6.8, CH_3O^I), 53.9 (d, $^2J_{CP}$ = 6.8, CH_3O^{II}), 55.8 (d, $^1J_{CP}$ = 155.7, CHP), 127.2 (d, J_{CP} = 2.8, C_5), 128.9 (d, J_{CP} = 3.1, C_3), 129.3 (d, $^3J_{CP}$ = 4.3, C_6), 129.5 (d, J_{CP} = 2.2, C_4), 134.3 (d, $^2J_{CP}$ = 1.2, C_1), 134.6 (d, $^3J_{CP}$ = 9.0, C_2); ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J_{HH} = 7.3, 3H, CH_3CH_2), 1.23-1.37 (m, 2H, CH_3CH_2), 1.37-1.49 (m, 2H, CH_2CH_2N), 1.69 (bs, 1H, NH), 2.46 (t, J_{HH} = 6.9, 2H, CH_2N), 3.54 (d, J_{HP} = 10.5, 3H, CH_3O^I), 3.84 (d, J_{HP} = 10.6, 3H, CH_3O^{II}), 4.74 (d, J_{HP} = 21.4, 1H, CHP), 7.23 (t, J_{HH} = 7.6, 1H, C_4H), 7.32 (t, J_{HH} = 7.5, 1H, C_5H), 7.38 (d, J_{HH} = 7.9, 1H, C_6H), 7.64 (d, J_{HH} = 7.8, 1H, C_3H); $[M+H]^+_{found}$ = 306.1029, $C_{13}H_{22}NO_3PCl$ requires 306.1020.

Diethyl ((butylamino)(2-chlorophenyl)methyl)phosphonate (6b)

Yield: 72% (0.24 g) of compound **6b** as colorless oil; ^{31}P NMR ($CDCl_3$) δ 21.4; ^{13}C NMR ($CDCl_3$) 13.9 ($CH_3CH_2CH_2$), 16.2 (d, $^3J_{CP}$ = 5.8, $CH_3CH_2O^I$), 16.5 (d, $^3J_{CP}$ = 5.9, $CH_3CH_2O^{II}$), 20.2 ($CH_3CH_2CH_2$), 32.0 (d, J_{CP} = 0.6, CH_2CH_2N), 47.6 (d, $^3J_{CP}$ = 16.3, CH_2N), 56.1 (d, $^1J_{CP}$ = 155.3, CHP), 62.8 (d, $^2J_{CP}$ = 7.1, CH_2O^I), 63.2 (d, $^2J_{CP}$ = 6.9, CH_2O^{II}), 127.1 (d, J_{CP} = 3.0, C_5), 128.8 (d, J_{CP} = 3.0, C_3), 129.37 (d, $^3J_{CP}$ = 4.3, C_6), 129.40 (d, J_{CP} = 2.1, C_4), 134.7 (d, $^2J_{CP}$ = 1.6, C_1), 134.8 (d, $^3J_{CP}$ = 8.7, C_2); ^{1}H NMR ($CDCl_3$) δ 0.85 (t, J_{HH} = 7.2, 3H, $CH_3CH_2CH_2$), 1.11 (t, J_{HH} = 7.1, 3H, $CH_3CH_2O^I$), 1.22-1.48 [1.33 (t, J_{HH} = 7.1, $CH_3CH_2O^{II}$) overlapped by the multiplet of $CH_3CH_2CH_2$ total int. 7H], 1.88 (bs, 1H, NH), 2.47 (t, J_{HH} = 6.9, 2H, CH_2N), 3.73-3.87 (m, 1H, CH_A, CH_2O^I), 3.87-4.02 (m, 1H, CH_B, CH_2O^I), 4.09-4.31 (m, 2H, CH_2O^{II}), 4.70 (d, J_{HP} = 21.3, 1H, CHP), 7.21 (t, J_{HH} = 7.6, 1H, C_4H), 7.29 (d, J_{HH} = 7.7, 1H, C_6H), 7.35 (t, J_{HH} = 7.8, 1H, C_5H), 7.66 (d, J_{HH} = 7.7, 1H, C_3H); $[M+H]^+_{found}$ = 334.1318, $C_{15}H_{26}NO_3PCl$ requires 334.1333.

Dibutyl ((butylamino)(2-chlorophenyl)methyl)phosphonate (6c)

Yield: 74% (0.29 g) of compound **6c** as colorless oil; ^{31}P NMR ($CDCl_3$) δ 23.2; ^{13}C NMR ($CDCl_3$) 13.5 ($CH_3(CH_2)_3O^I$), 13.6 ($CH_3(CH_2)_3O^{II}$), 13.9 ($CH_3(CH_2)_3N$), 18.5 ($CH_2(CH_2)_2O^I$),

18.7 ($CH_2(CH_2)_2O^{II}$), 20.2 ($CH_2(CH_2)_2N$), 32.0 (d, J_{CP} = 0.6, CH_2CH_2N), 32.4 (d, $^3J_{CP}$ = 5.9, $CH_2CH_2O^I$), 32.7 (d, $^3J_{CP}$ = 5.8, $CH_2CH_2O^{II}$), 47.6 (d, $^3J_{CP}$ = 16.4, CH_2N), 56.1 (d, $^1J_{CP}$ = 155.6, CHP), 66.4 (d, $^2J_{CP}$ = 7.4, CH_2O^I), 66.9 (d, $^2J_{CP}$ = 7.1, CH_2O^{II}), 127.1 (d, J_{CP} = 2.9, C_5), 128.7 (d, J_{CP} = 2.9, C_3), 129.3 (d, J_{CP} = 2.0, C_4), 129.4 (d, $^3J_{CP}$ = 4.3, C_6), 134.7 (d, $^3J_{CP}$ = 8.8, C_2), 134.9 (d, $^2J_{CP}$ = 1.5, C_1); ^{1}H NMR ($CDCl_3$) δ 0.82 (t, J_{HH} = 7.3, 3H, $CH_3(CH_2)_3O^I$), 0.86 (t, J_{HH} = 7.0, 3H, $CH_3(CH_2)_3N$), 0.93 (t, J_{HH} = 7.3, 3H, $CH_3(CH_2)_3O^{II}$), 1.14-1.51 (m, 10H, $CH_2CH_2CH_2N$, $CH_2CH_2CH_2O$, $CH_2CH_2O^I$), 1.60-1.72 (m, 2H, $CH_2CH_2O^{II}$), 1.88 (bs, 1H, NH), 2.47 (t, J_{HH} = 6.6, 2H, CH_2N), 3.67-3.80 (m, 1H, CH_A, CH_2O^I), 3.81-3.95 (m, 1H, CH_B, CH_2O^I), 4.03-4.23 (m, 2H, CH_2O^{II}), 4.70 (d, J_{HP} = 21.3, CHP), 7.22 (t, J_{HH} = 7.6, 1H, C_4H), 7.29 (d, J_{HH} = 6.8, 1H, C_6H), 7.35 (t, J_{HH} = 7.7, 1H, C_5H), 7.65 (d, J_{HH} = 7.7, 1H, C_3H); $[M+H]^+_{found}$ = 390.1950, $C_{19}H_{34}NO_3PCl$ requires 390.1959.

Dimethyl ((butylamino)(3-chlorophenyl)methyl)phosphonate (7a)

Yield: 80% (0.24 g) of compound **7a** as pale yellow oil; ^{31}P NMR ($CDCl_3$) δ 25.2; ^{13}C NMR ($CDCl_3$) 13.9 (CH_3CH_2), 20.2 (CH_3CH_2), 31.9 (d, J_{CP} = 0.7, CH_2CH_2N), 47.8 (d, $^3J_{CP}$ = 16.5, CH_2N), 53.6 (d, $^2J_{CP}$ = 6.9, CH_3O^I), 53.8 (d, $^2J_{CP}$ = 7.1, CH_3O^{II}), 60.5 (d, $^1J_{CP}$ = 153.1, CHP), 126.6 (d, $^3J_{CP}$ = 6.0, C_6), 128.1 (d, J_{CP} = 3.2, C_5), 128.5 (d, $^3J_{CP}$ = 6.3, C_2), 129.7 (d, J_{CP} = 2.6, C_4), 134.5 (d, $^2J_{CP}$ = 2.8, C_1), 138.4 (d, J_{CP} = 9.0, C_3); ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J_{HH} = 7.2, 3H, CH_3CH_2), 1.23-1.37 (m, 2H, CH_3CH_2), 1.37-1.51 (m, 2H, CH_2CH_2N), 1.88 (bs, 1H, NH), 2.37-2.57 (m, 2H, CH_2N), 3.62 (d, J_{HP} = 10.5, 3H, CH_3O^I), 3.75 (d, J_{HP} = 10.5, 3H, CH_3O^{II}), 4.03 (d, J_{HP} = 20.3, 1H, CHP), 7.25-7.33 (m, 3H, $C_{4\text{-}6}H$), 7.41 (s, 1H, C_2H); $[M+H]^+_{found}$ = 306.1016, $C_{13}H_{22}NO_3PCl$ requires 306.1020.

Diethyl ((butylamino)(3-chlorophenyl)methyl)phosphonate (7b)

Yield: 94% (0.31 g) of compound **7b** as pale yellow oil; ^{31}P NMR ($CDCl_3$) δ 22.7; ^{13}C NMR ($CDCl_3$) 13.9 ($CH_3CH_2CH_2$), 16.3 (d, $^3J_{CP}$ = 5.8, $CH_3CH_2O^I$), 16.4 (d, $^3J_{CP}$ = 5.8, $CH_3CH_2O^{II}$), 20.3 ($CH_3CH_2CH_2$), 31.9 (d, J_{CP} = 0.5, CH_2CH_2N), 47.9 (d, $^3J_{CP}$ = 16.4, CH_2N), 60.9 (d, $^1J_{CP}$ = 152.2, CHP), 62.9 (d, $^2J_{CP}$ = 6.9, CH_2O^I), 63.1 (d, $^2J_{CP}$ = 7.1, CH_2O^{II}), 126.7 (d, $^3J_{CP}$ = 5.9, C_6), 127.9 (d, J_{CP} = 3.2, C_5), 128.6 (d, $^3J_{CP}$ = 6.1, C_2), 129.6 (d, J_{CP} = 2.6, C_4), 134.3 (d, $^2J_{CP}$ = 3.0, C_1), 138.6 (d, J_{CP} = 4.5, C_3); ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J_{HH} = 7.2, 3H, $CH_3CH_2CH_2$), 1.19 (t, J_{HH} = 7.0, 3H, $CH_3CH_2O^I$), 1.24-1.37 [1.28 (t, J_{HH} = 7.1, $CH_3CH_2O^{II}$) overlapped by the multiplet of $CH_3CH_2CH_2$ total int. 5H], 1.38-1.50 (m, 2H, CH_2CH_2N), 2.02 (bs, 1H, NH), 2.38-2.58 (m, 2H, CH_2N), 3.85-4.16 [4.01 (d, J_{HP} = 19.9, CHP) overlapped by

the multiplet of CH_2O total int. 5H], 7.22-7.36 (m, 3H, $C_{4\text{-}6}H$), 7.42 (s, 1H, C_2H); $[M+H]^+_{found}$ = 334.1336, $C_{15}H_{26}NO_3PCl$ requires 334.1333.

Dibutyl ((butylamino)(3-chlorophenyl)methyl)phosphonate (7c)

Yield: 73% (0.28 g) of compound **7c** as pale yellow oil; ^{31}P NMR ($CDCl_3$) δ 22.8; ^{13}C NMR ($CDCl_3$) 13.56 ($CH_3(CH_2)_3O^I$), 13.60 ($CH_3(CH_2)_3O^{II}$), 13.9 ($CH_3(CH_2)_3N$), 18.6 ($CH_2(CH_2)_2O^I$), 18.7 ($CH_2(CH_2)_2O^{II}$), 20.2 ($CH_2(CH_2)_2N$), 32.0 (d, J_{CP} = 0.5, CH_2CH_2N), 32.5 (d, $^3J_{CP}$ = 5.9, $CH_2CH_2O^I$), 32.6 (d, $^3J_{CP}$ = 5.9, $CH_2CH_2O^{II}$), 47.9 (d, $^3J_{CP}$ = 16.4, CH_2N), 60.9 (d, $^1J_{CP}$ = 152.2, CHP), 66.6 (d, $^2J_{CP}$ = 7.2, CH_2O^I), 66.8 (d, $^2J_{CP}$ = 7.3, CH_2O^{II}), 126.7 (d, $^3J_{CP}$ = 5.9, C_6), 127.9 (d, J_{CP} = 3.2, C_5), 128.6 (d, $^3J_{CP}$ = 6.1, C_2), 129.6 (d, J_{CP} = 2.7, C_4), 134.3 (d, $^2J_{CP}$ = 2.9, C_1), 138.8 (d, J_{CP} = 4.6, C_3); ^1H NMR ($CDCl_3$) δ 0.866 (t, J_{HH} = 7.3, 3H, $CH_3(CH_2)_3O^I$), 0.870 (t, J_{HH} = 7.2, 3H, $CH_3(CH_2)_3N$), 0.91 (t, J_{HH} = 7.2, 3H, $CH_3(CH_2)_3O^{II}$), 1.20-1.55 (m, 10H, $CH_2CH_2CH_2N$, $CH_2CH_2CH_2O$, $CH_2CH_2O^I$), 1.55-1.64 (m, 2H, $CH_2CH_2O^{II}$), 1.85 (bs, 1H, NH), 2.38-2.57 (m, 2H, CH_2N), 3.80-3.96 (m, 2H, CH_2O^I), 3.96-4.09 [4.01 (d, J_{HP} = 20.0, CHP) overlapped by the multiplet of CH_2O^{II} total int. 3H], 7.22-7.34 (m, 3H, $C_{4\text{-}6}H$), 7.41 (s, 1H, C_2H); $[M+H]^+_{found}$ = 390.1946, $C_{19}H_{34}NO_3PCl$ requires 390.1959.

Dimethyl ((butylamino)(4-chlorophenyl)methyl)phosphonate (8a)

Yield: 75% (0.23 g) of compound **8a** as pale yellow oil; ^{31}P NMR ($CDCl_3$) δ 25.4; ^{13}C NMR ($CDCl_3$) 13.9 (CH_3CH_2), 20.3 (CH_3CH_2), 32.0 (d, J_{CP} = 0.5, CH_2CH_2N), 47.7 (d, $^3J_{CP}$ = 16.6, CH_2N), 53.5 (d, $^2J_{CP}$ = 7.0, CH_3O^I), 53.8 (d, $^2J_{CP}$ = 7.1, CH_3O^{II}), 60.3 (d, $^1J_{CP}$ = 153.4, CHP), 128.7 (d, J_{CP} = 2.6, C_3), 129.7 (d, $^3J_{CP}$ = 6.2, C_2), 133.7 (d, $^2J_{CP}$ = 3.9, C_1), 134.6 (d, J_{CP} = 4.5, C_4); ^1H NMR ($CDCl_3$) δ 0.86 (t, J_{HH} = 7.2, 3H, CH_3CH_2), 1.24-1.35 (m, 2H, CH_3CH_2), 1.37-1.48 (m, 2H, CH_2CH_2N), 1.85 (bs, 1H, NH), 2.35-2.55 (m, 2H, CH_2N), 3.60 (d, J_{HP} = 10.5, 3H, CH_3O^I), 3.74 (d, J_{HP} = 10.5, 3H, CH_3O^{II}), 4.04 (d, J_{HP} = 20.0, 1H, CHP), 7.30-7.40 (m, 4H, ArH); $[M+H]^+_{found}$ = 306.1014, $C_{13}H_{22}NO_3PCl$ requires 306.1020.

Diethyl ((butylamino)(4-chlorophenyl)methyl)phosphonate (8b)

Yield: 80% (0.27 g) of compound **8b** as pale yellow oil; ^{31}P NMR ($CDCl_3$) δ 23.0; ^{13}C NMR ($CDCl_3$) 13.9 ($CH_3CH_2CH_2$), 16.4 (d, $^3J_{CP}$ = 5.7, $CH_3CH_2O^I$), 16.5 (d, $^3J_{CP}$ = 5.7, $CH_3CH_2O^{II}$), 20.3 ($CH_3CH_2CH_2$), 32.0 (d, J_{CP} = 0.7, CH_2CH_2N), 47.8 (d, $^3J_{CP}$ = 16.5, CH_2N), 60.7 (d, $^1J_{CP}$ = 152.6, CHP), 62.9 (d, $^2J_{CP}$ = 7.0, CH_2O^I), 63.0 (d, $^2J_{CP}$ = 7.1, CH_2O^{II}), 128.6 (d, J_{CP} = 2.6, C_3), 129.8 (d, $^3J_{CP}$ = 6.1, C_2), 133.5 (d, $^2J_{CP}$ = 3.9, C_1), 135.0 (d, J_{CP} = 4.8, C_4); δ [S10] ($CDCl_3$) 16,16; 16,21; 16,33; 53,43; 54,72; 56,22; 63,23; 63,30; 63,33; 63,40; 113,78;

118,60; 118,74; 128,71; 128,74; 129,06; 129,11; 129,16; 129,36; 133,66; 134,53; 134,56; 145,89; 146,03; 152,64; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J_{HH} = 7.2, 3H, CH_3CH$_2$CH$_2$), 1.19 (t, J_{HH} = 7.1, 3H, CH_3CH$_2$O^{I}), 1.23-1.36 [1.28 (t, J_{HH} = 7.0, CH_3CH$_2$O^{II}) overlapped by the multiplet of CH_3CH_2CH$_2$ total int. 5H], 1.36-1.50 (m, 2H, CH_2CH$_2$N), 1.90 (bs, 1H, NH), 2.36-2.56 (m, 2H, CH$_2$N), 3.83-4.15 [4.01 (d, J_{HP} = 19.9, CHP) overlapped by the multiplet of CH$_2$O total int. 5H], 7.28-7.42 (m, 4H, ArH); δ [S10] ($CDCl_3$) 1,15 (t, J = 7.09, 3H), 1,28 (t, J = 7,09, 3H), 3,72–4,18 (m, 4H), 4,73 (d, J = 24,49, 1H), 6,54–6,57 (m, 2H), 6,68–6,72 (m, 1H), 7,07–7,12 (m, 2H), 7,29–7,31 (m, 2H), 7,39–7,42 (m, 2H); $[M+H]^{+}_{found}$ = 334.1337, $C_{15}H_{26}NO_3PCl$ requires 334.1333.

Dibutyl ((butylamino)(4-chlorophenyl)methyl)phosphonate (8c)

Yield: 81% (0.32 g) of compound **8c** as colorless oil; ^{31}P NMR ($CDCl_3$) δ 23.5; ^{13}C NMR ($CDCl_3$) 13.56 (*C*H$_3$(CH$_2$)$_3$O^{I}), 13.60 (*C*H$_3$(CH$_2$)$_3$O^{II}), 13.9 (*C*H$_3$(CH$_2$)$_3$N), 18.6 (*C*H$_2$(CH$_2$)$_2$O^{I}), 18.7 (*C*H$_2$(CH$_2$)$_2$O^{II}), 20.3 (*C*H$_2$(CH$_2$)$_2$N), 32.0 (d, J_{CP} = 0.5, *C*H$_2$CH$_2$N), 32.5 (d, $^{3}J_{CP}$ = 5.8, *C*H$_2$CH$_2$O^{I}), 32.6 (d, $^{3}J_{CP}$ = 5.8, *C*H$_2$CH$_2$O^{II}), 47.9 (d, $^{3}J_{CP}$ = 16.5, CH$_2$N), 60.7 (d, $^{1}J_{CP}$ = 152.7, CHP), 66.5 (d, $^{2}J_{CP}$ = 7.2, CH$_2$O^{I}), 66.7 (d, $^{2}J_{CP}$ = 7.4, CH$_2$O^{II}), 128.5 (d, J_{CP} = 2.6, C$_3$), 129.8 (d, $^{3}J_{CP}$ = 6.1, C$_2$), 133.5 (d, $^{2}J_{CP}$ = 4.0, C$_1$), 135.1 (d, J_{CP} = 4.7, C$_4$); ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J_{HH} = 7.2, 6H, CH_3(CH$_2$)$_3$O^{I}, CH_3(CH$_2$)$_3$N), 0.91 (t, J_{HH} = 7.4, 3H, CH_3(CH$_2$)$_3$O^{II}), 1.20-1.53 (m, 10H, CH_2CH_2CH$_2$N, CH_2CH$_2$CH$_2$O, CH_2CH$_2$O^{I}), 1.53-1.68 (m, 2H, CH_2CH$_2$O^{II}), 1.81 (bs, 1H, NH), 2.36-2.56 (m, 2H, CH$_2$N), 3.77-3.95 (m, 2H, CH$_2$O^{I}), 3.95-4.08 [4.00 (d, J_{HP} = 19.8, CHP) overlapped by the multiplet of CH$_2$O^{II} total int. 3H], 7.26-7.40 (m, 4H, ArH); $[M+H]^{+}_{found}$ = 390.1962, $C_{19}H_{34}NO_3PCl$ requires 390.1959.

Real time monitoring of the addition of diethyl phosphite to *N*-benzylidene(butyl)amine

To the mixture of imine **1a** (30 mmol, 4.8 g) in 20 mL acetonitrile, diethyl phosphite (30 mmol, 3.9 mL) was added drop wise at rt with intensive stirring. After complete addition the mixture was heated gradually from 25 °C to 80 °C and stirred for 3.5 h at this temperature.

Single crystal X-ray diffraction measurements

A crystal of **5b** was mounted on a glass fiber. Cell parameters were determined by least-squares from the respective setting angles. Completeness was equal or greater to $2\theta = 99.4\%$ for **5b** and 99.6% for **5d**. Multi-scan absorption correction was applied to the data with minimum and maximum transmission factors of 0.809 and 1.00 for **5b** and 0.988 and 1.00 for **5d**, respectively. Initial structure models were obtained by direct methods [S13] and subsequent difference syntheses. Anisotropic full-matrix least-squares refinements on F^2 were applied for all non-hydrogen atoms and the model was refined to convergence [S13]. Hydrogen atomic positions were calculated from assumed geometries where appropriate. N–H hydrogen atoms were located from difference electron density maps. Hydrogen atoms were included in structure factor calculations and the non-trivial hydrogen positions and their isotropic displacements were refined. Other H atoms were kept riding on their anchor atoms, with isotropic displacement parameters of these hydrogen atoms were approximated from the U(eq) value of the atom they were bonded. The maximum and minimum residual electron densities in the final difference maps range 0.6 and −0.4 $e \cdot Å^{-3}$ and were normal for both. All further calculations and drawings were done by using PLATON [S14] and Diamond [S15]. Crystal structure data are deposited with the Cambridge Crystallographic Data Centre under CCDC 1508647 (**5b**) and 1508648 (**5d**) and can be obtained free of charge upon application.

Table S1: Essential crystallographic data of the **5b** and **5d** single crystal diffraction experiments and model refinements.

	5b	**5d**
Formula	$C_{17}H_{22}NO_3P$	$C_{27}H_{26}NO_3P$
F. W.	319.32	443.46
Space grp.	P-1 (No. 2)	P-1 (No. 2)
a, b, c [Å]	8.7262(5) 9.8627(6) 10.0063(6)	9.7723(5) 10.7780(6) 11.1060(7)
α, β, γ [^{o}]	94.125(5) 94.790(5) 91.430(5)	101.830(5) 94.026(4) 90.170(4)
V [Å^3]	855.54(9)	1141.90(11)
Z	2	2
$D_{(c)}$ [Mg/m^3]	1.240	1.290
μ(MoKα) [/mm]	0.172	0.150
Cryst. Size [mm]	0.06 x 0.35 x 0.40	0.08 x 0.15 x 0.15
Temp. (K)	173	173
Radiation λ [Å]	MoKa 0.71073	MoKa 0.71073
θ Min-Max [^{o}]	4.5, 26.4	4.2, 26.4
Tot., Uniq. Data, R(int)	10779, 3477, 0.044	14708, 4650, 0.043
Obsd data [I > 2.0 σ(I)]	2578	3473
Nref, Npar	3477, 219	4650, 315
R_1, wR^2, S	0.0524, 0.1427, 1.06	0.0427, 0.1054, 1.03
Max./ Av. Shift/Error	0.00, 0.00	0.00, 0.00
Min/Max Res.Den. [e/Å^3]	-0.34, 0.62	-0.36, 0.41

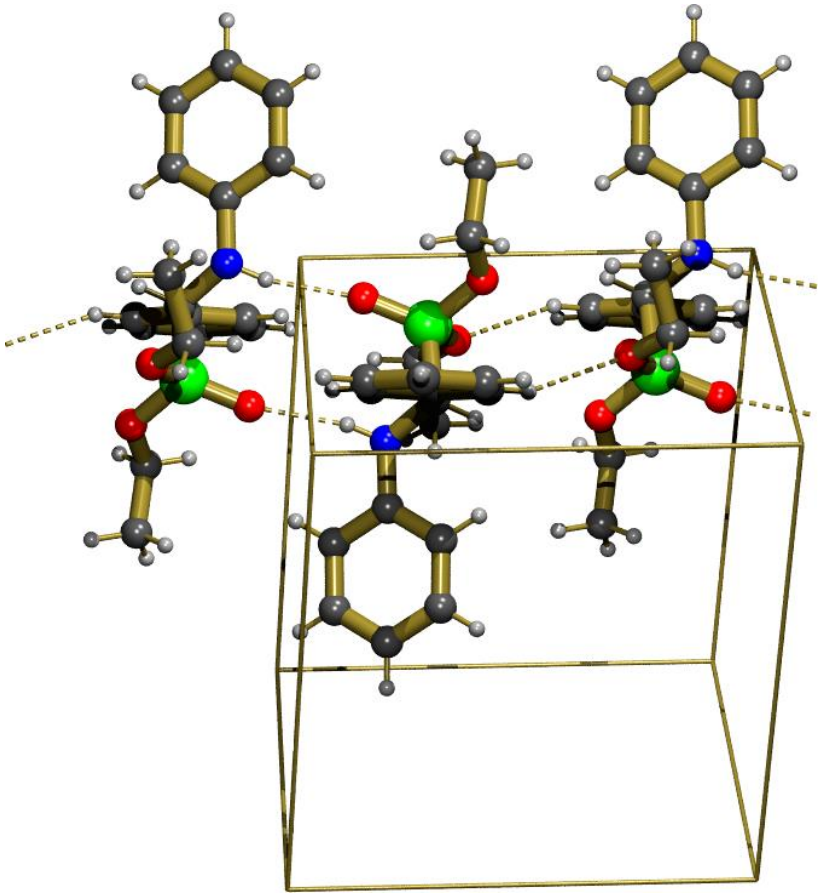


Figure S1: Pairs of **5b** molecules fused through N–H···O and C–H···O hydrogen bridges into *RS*-centrosymmetric dimeric infinite sheets. Broken lines indicate H-bridges.

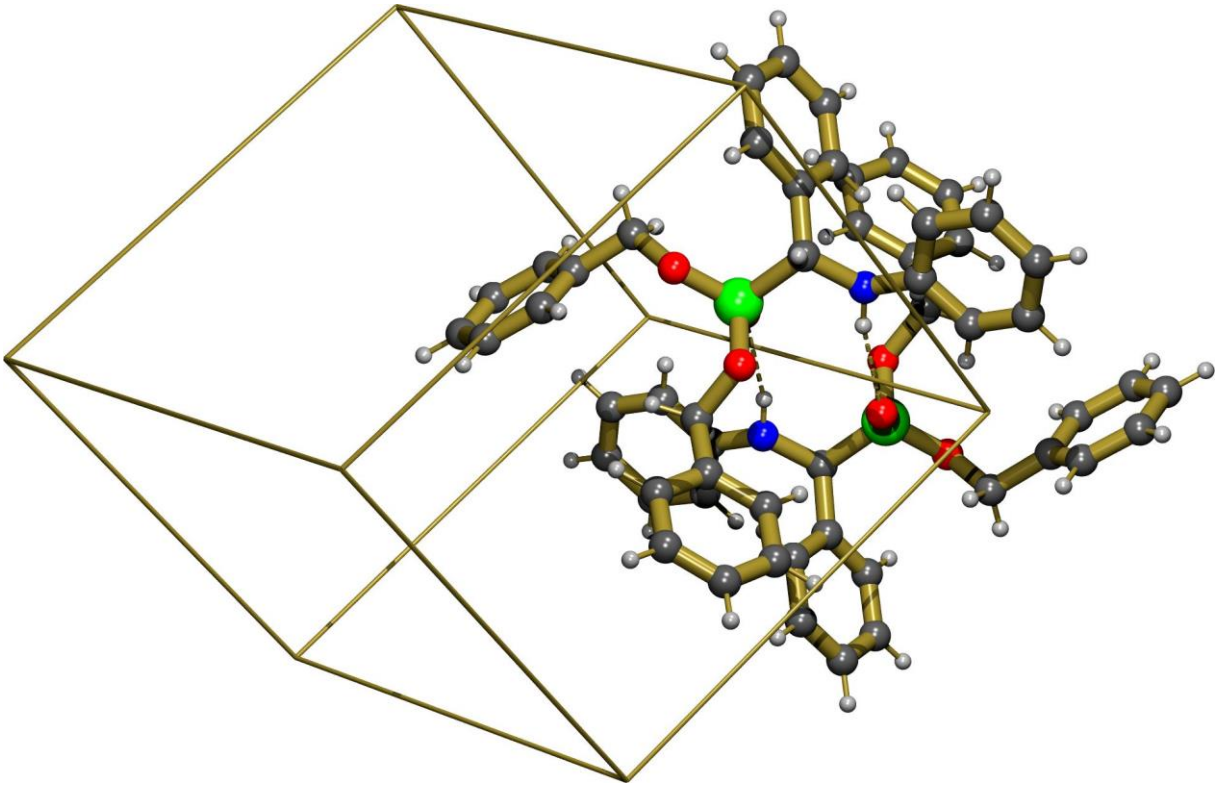
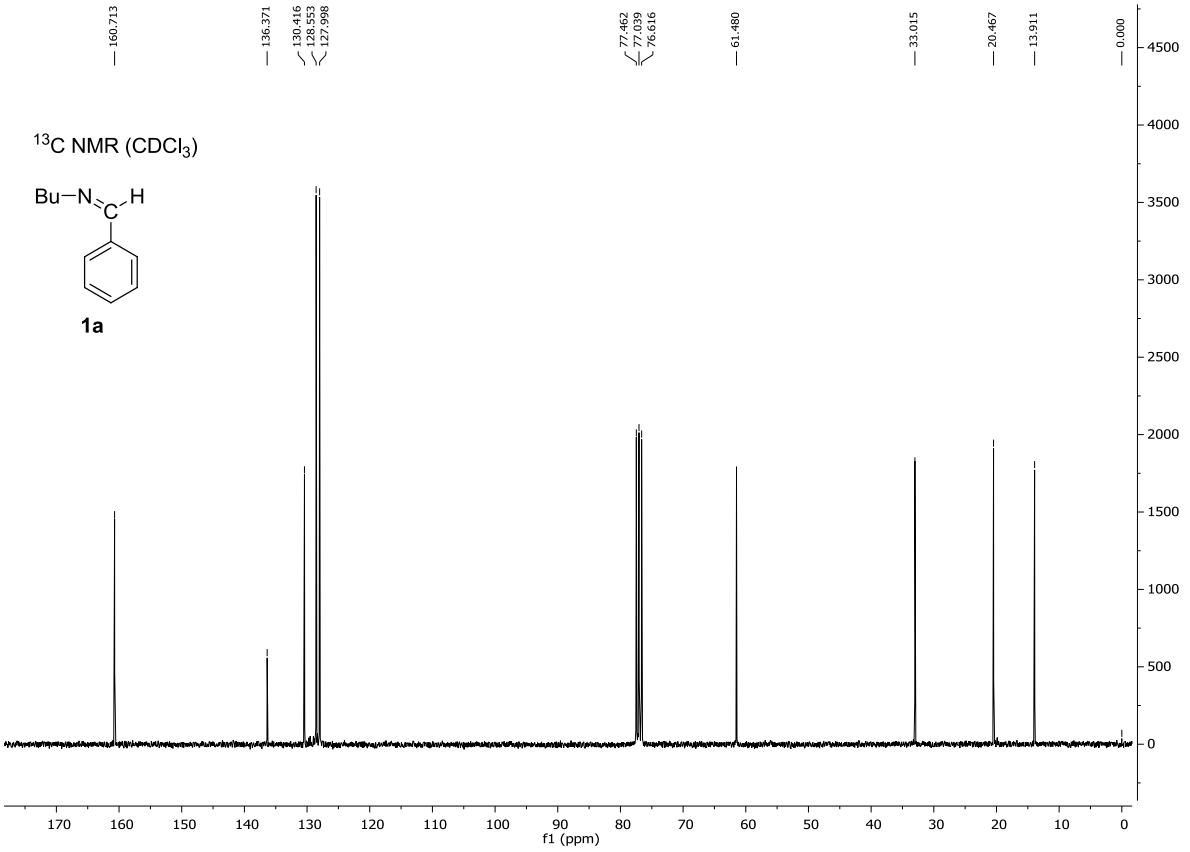


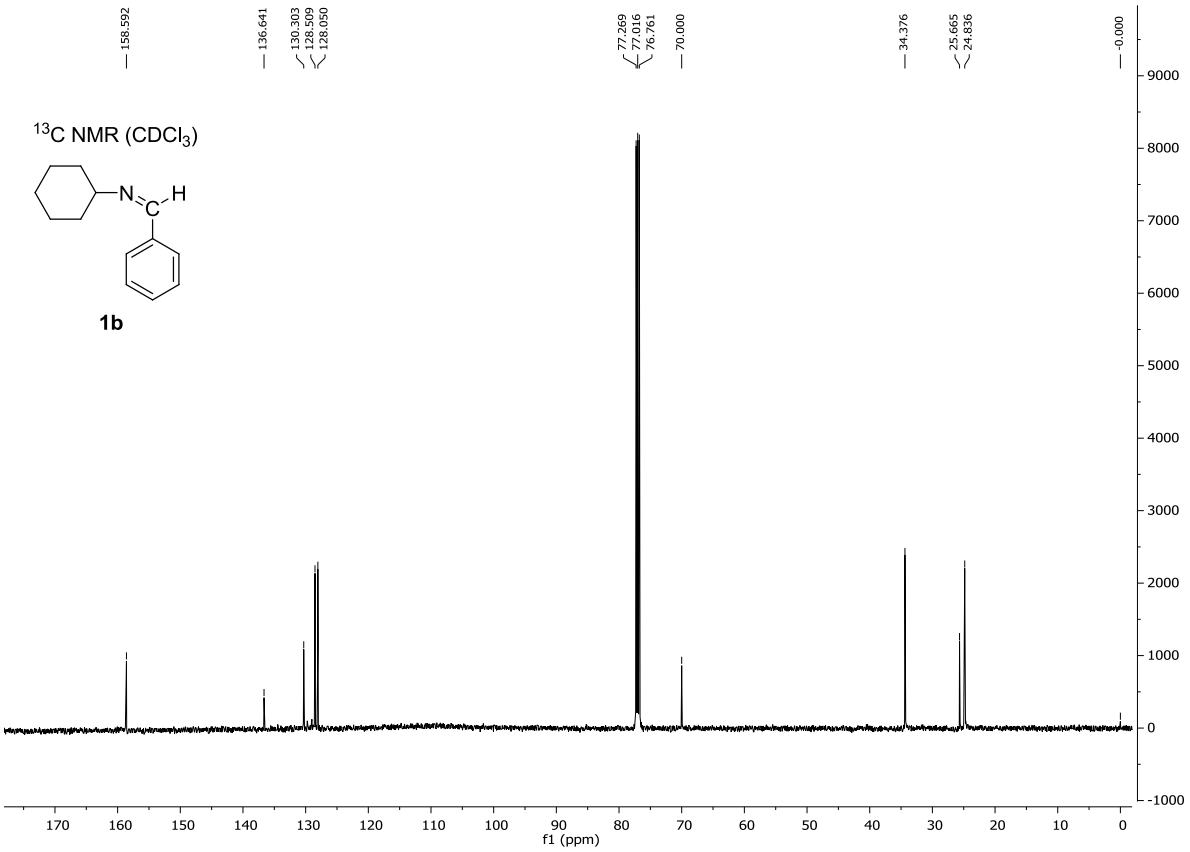
Figure S2: An isolated *RS* dimer of **5d** molecules formed around a symmetry center.

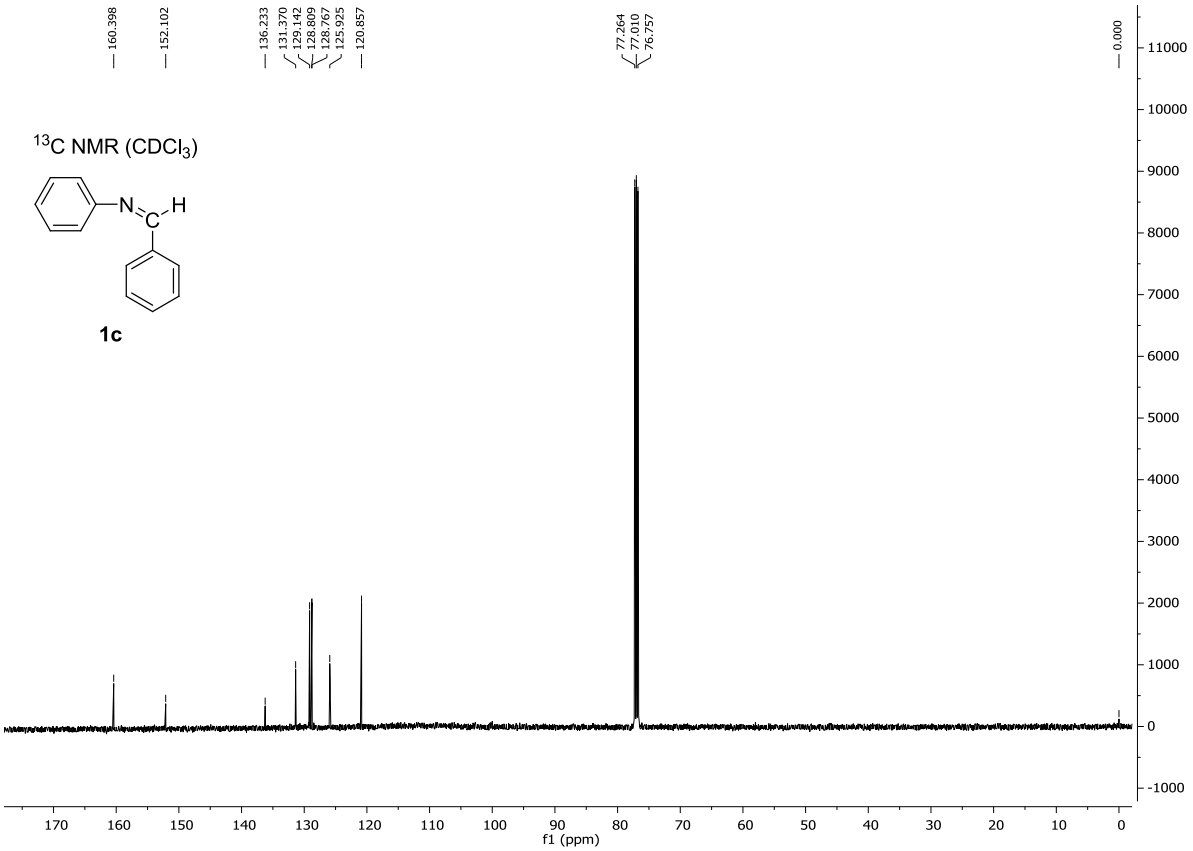
Quantum chemical calculations

In all quantum chemical calculations, the B3LYP/6-31G(d,p) method [S16-S20] was used implemented in the Gaussian09 program package [S21]. During the calculations including geometry optimizations, scanning and IRC optimizations, transition-state determinations and frequency calculations, the IEFPCM [S22,S23] implicit method was used taking into account the effect of water as the solvent, approximating the dielectric constant of the reaction mixture. The reaction pathways and energetics were calculated by scanning and IRC calculations to verify that a calculated transition state indeed connects the two corresponding minima. The transition states were optimized with the QST3 method. Transition states were identified by having one imaginary frequency in the Hessian matrix. All the geometries and transition states were optimized and frequency calculations were made to assure that the structures are in a local minimum on a saddle point, respectively.

^{31}P NMR, ^{1}H NMR and ^{13}C NMR spectra



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131.370
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125.925
120.857
77.264
77.010
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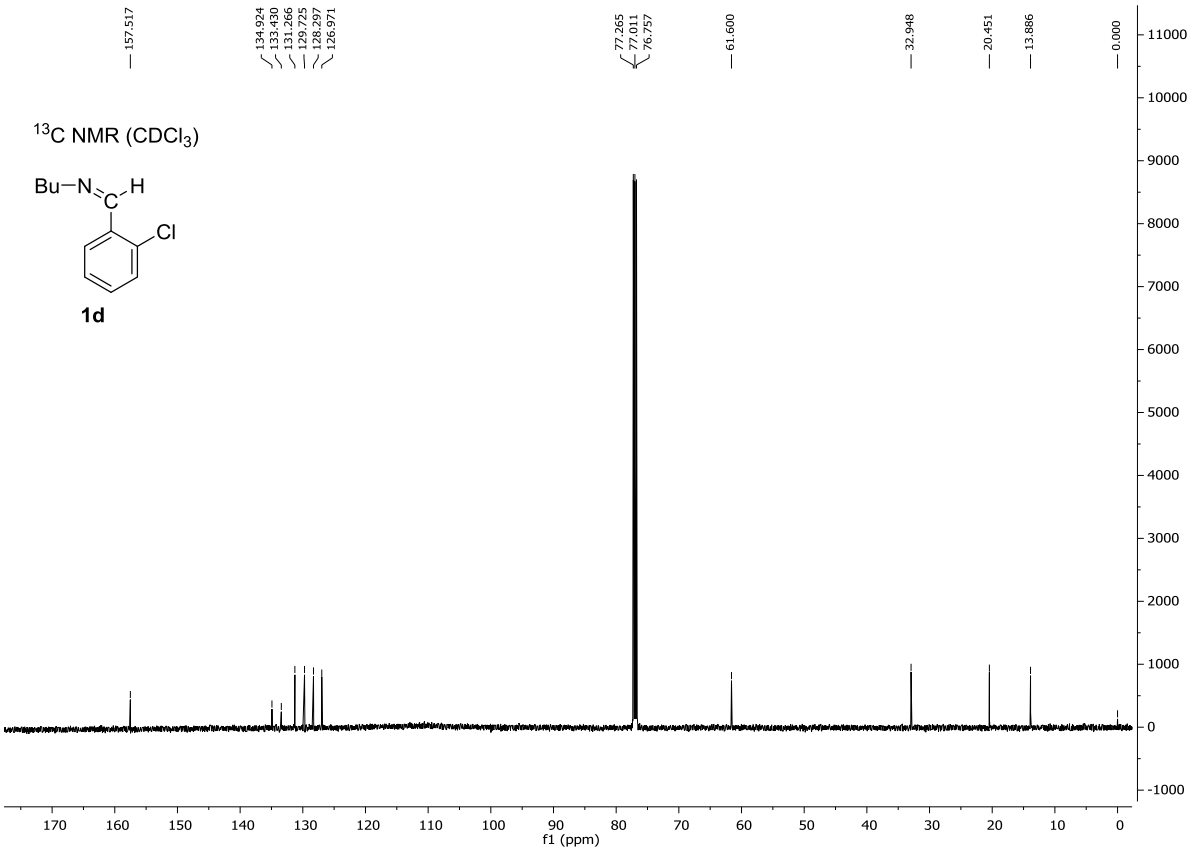
0.000
^{13}C NMR ($CDCl_3$)
N
H
1c
f1 (ppm)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129.725
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77.265
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76.757
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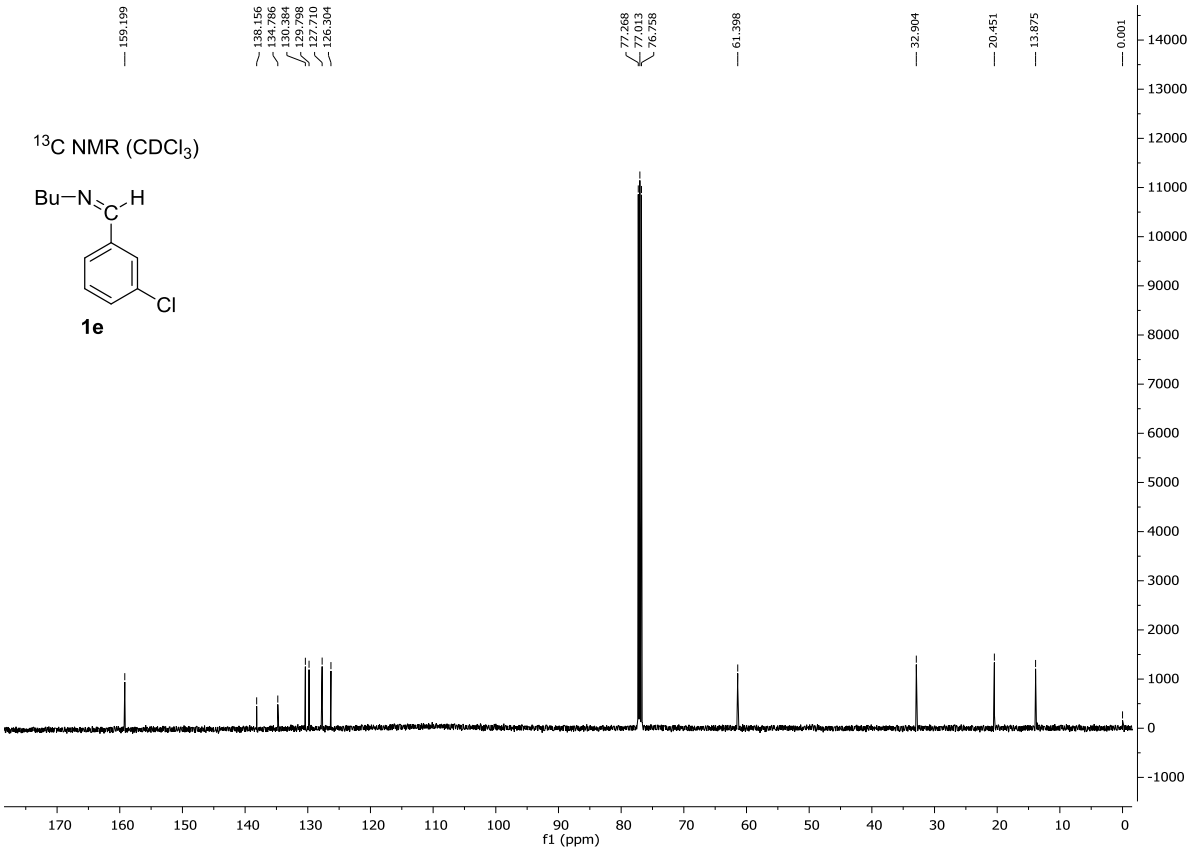
13.886
0.000
^{13}C NMR ($CDCl_3$)
Bu
N
H
Cl
1d
f1 (ppm)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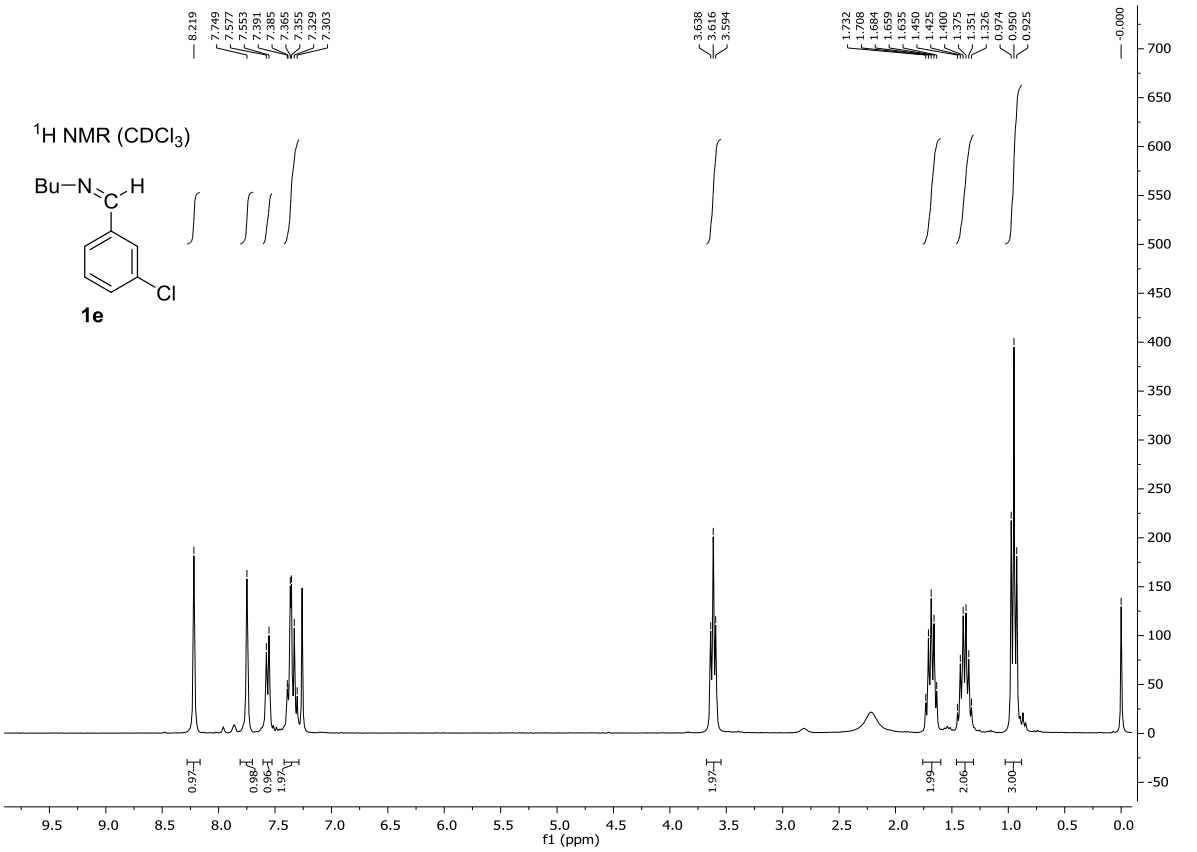
129.798
127.710
126.304
77.268
77.013
76.758
61.398
32.904
20.451
13.875
0.001
^{13}C NMR ($CDCl_3$)
Bu—N=C—H
Cl
1e
f1 (ppm)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1.732
1.708
1.684
1.659
1.635
1.450
1.425
1.400
1.375
1.351
1.326
0.974
0.950
0.925
-0.000
^{1}H NMR ($CDCl_3$)
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Cl
1e
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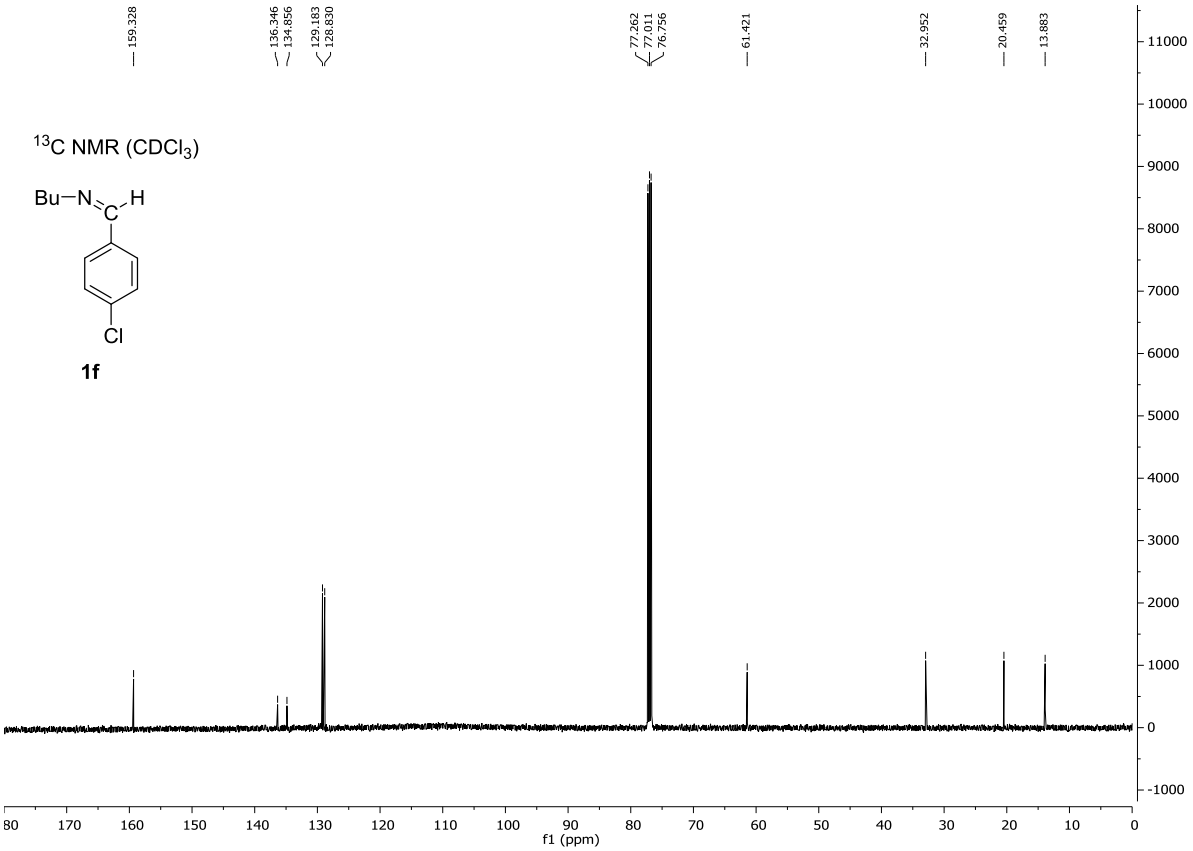
0.98
0.96
1.97
1.97
1.99
2.06
3.00
f1 (ppm)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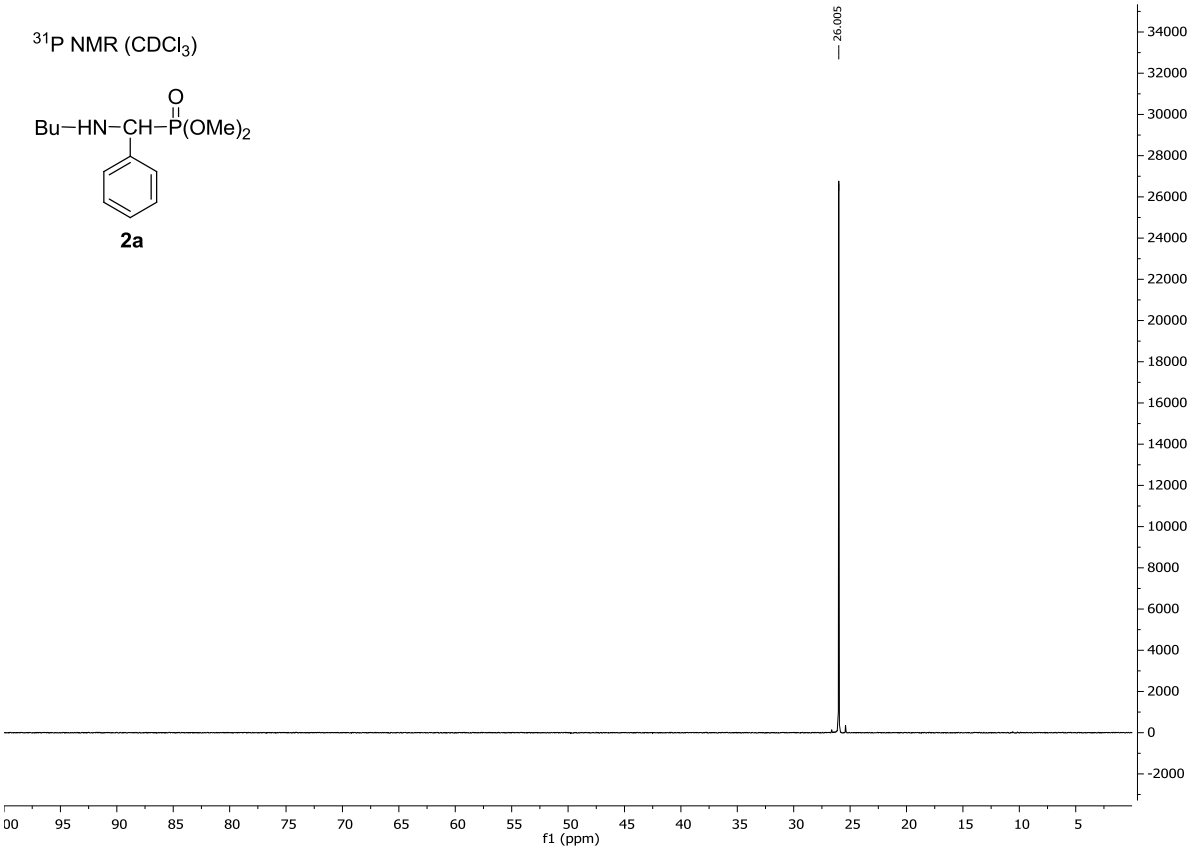
Bu–N=C(H)
Cl
1f
f1 (ppm)


26.005
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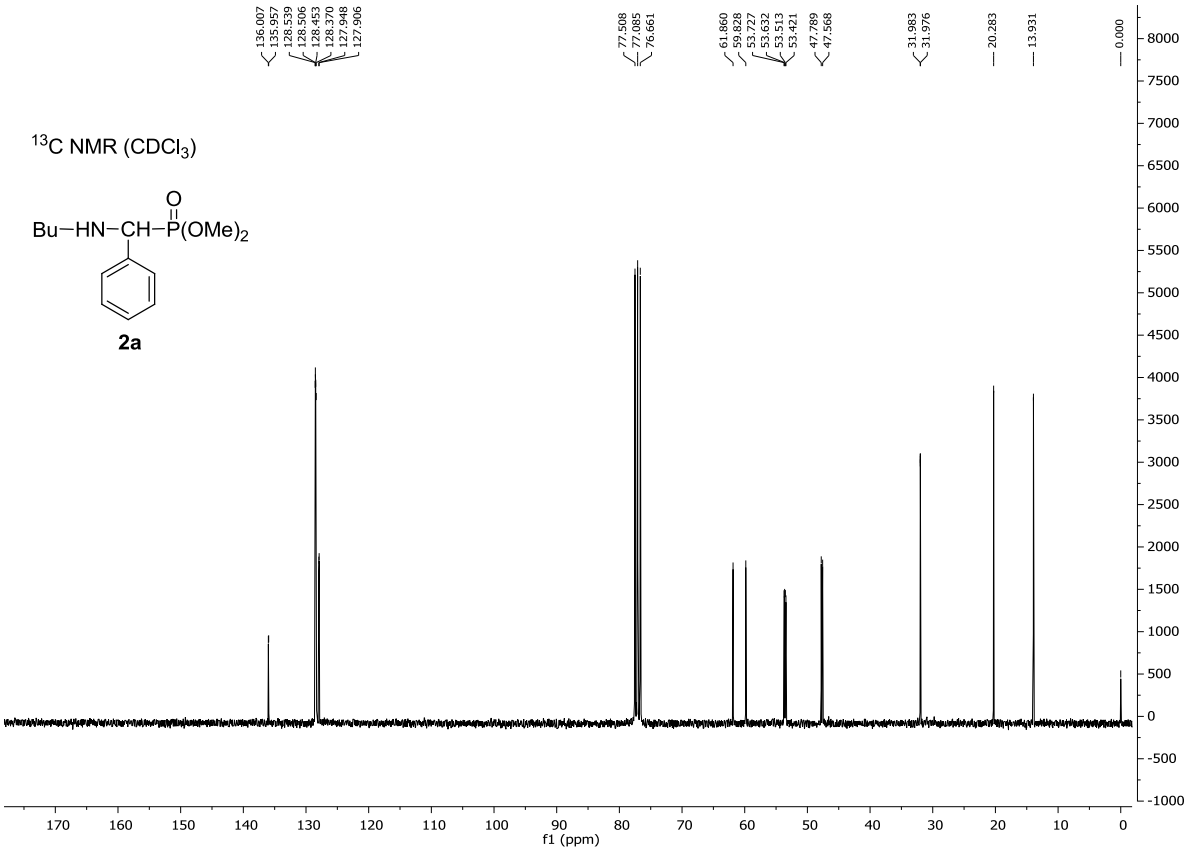
Bu–HN–CH(O=P(OMe)$_2$)
2a
f1 (ppm)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53.727
53.632
53.513
53.421
47.789
47.568
31.983
31.976
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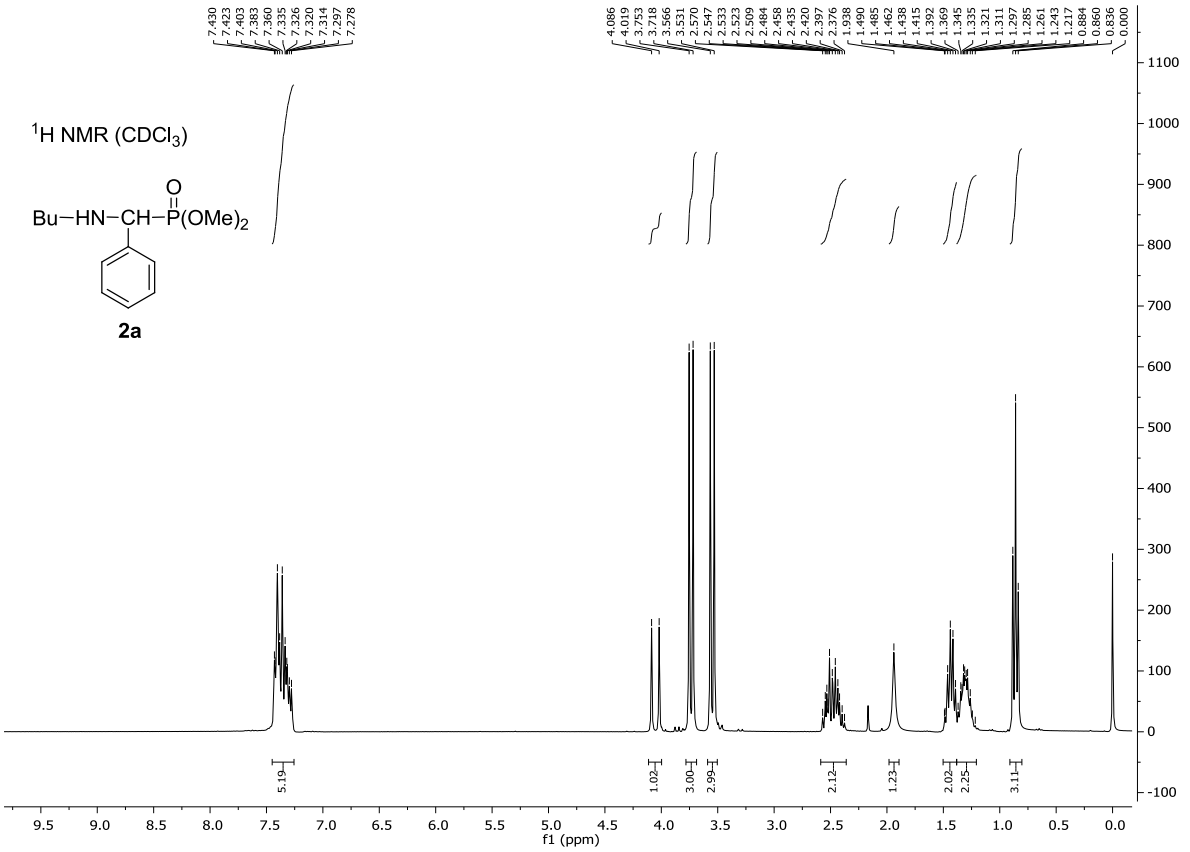
Bu−HN−CH−P(OMe)$_2$
O
2a
f1 (ppm)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1.369
1.345
1.335
1.321
1.311
1.297
1.285
1.261
1.243
1.217
0.884
0.860
0.836
0.000
^{1}H NMR ($CDCl_3$)
Bu−HN−CH−P(OMe)$_2$
O
2a
5.19
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3.00
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2.12
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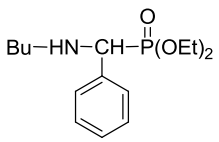
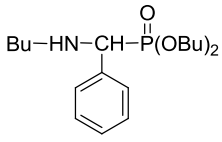
3.11
f1 (ppm)

^{31}P NMR ($CDCl_3$)



2b

^{31}P NMR ($CDCl_3$)



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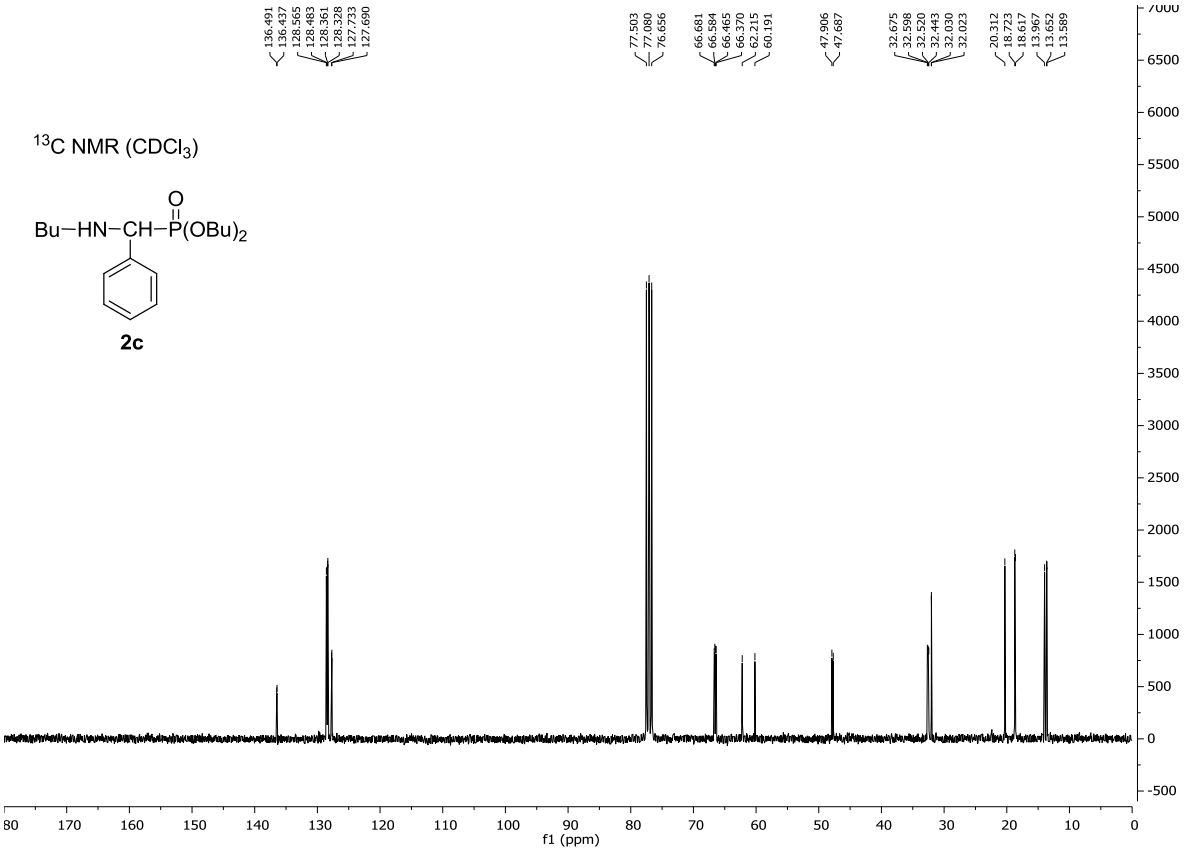
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32.598
32.520
32.443
32.059
32.023
20.312
18.723
18.617
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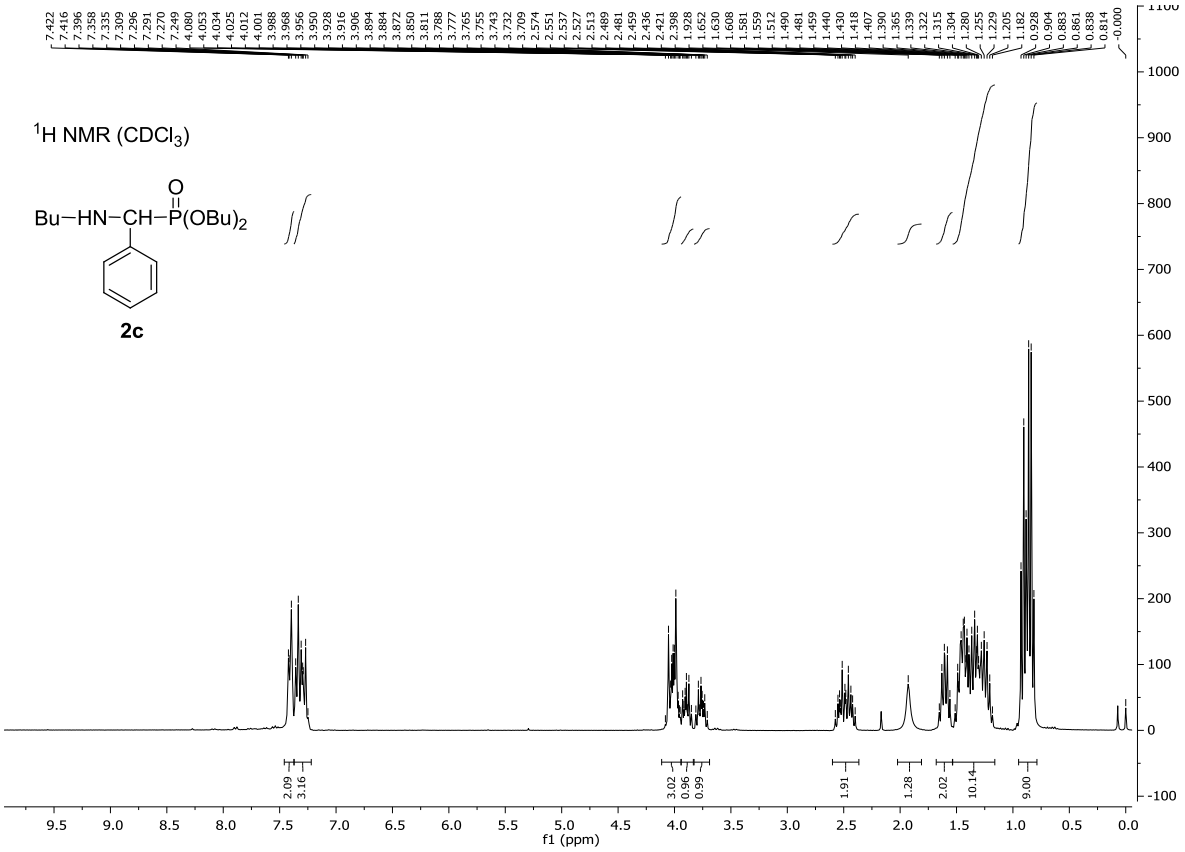
13.589
^{13}C NMR ($CDCl_3$)
Bu–HN–CH–P(OBu)$_2$
O
2c
f1 (ppm)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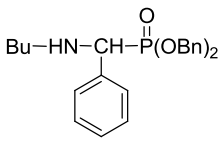
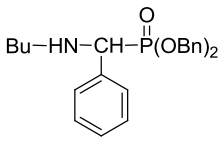
0.814
-0.000
^{1}H NMR ($CDCl_3$)
Bu–HN–CH–P(OBu)$_2$
O
2c
2.09
3.16
3.02
0.96
0.99
1.91
1.28
2.02
10.14
9.00
f1 (ppm)

^{31}P NMR ($CDCl_3$)

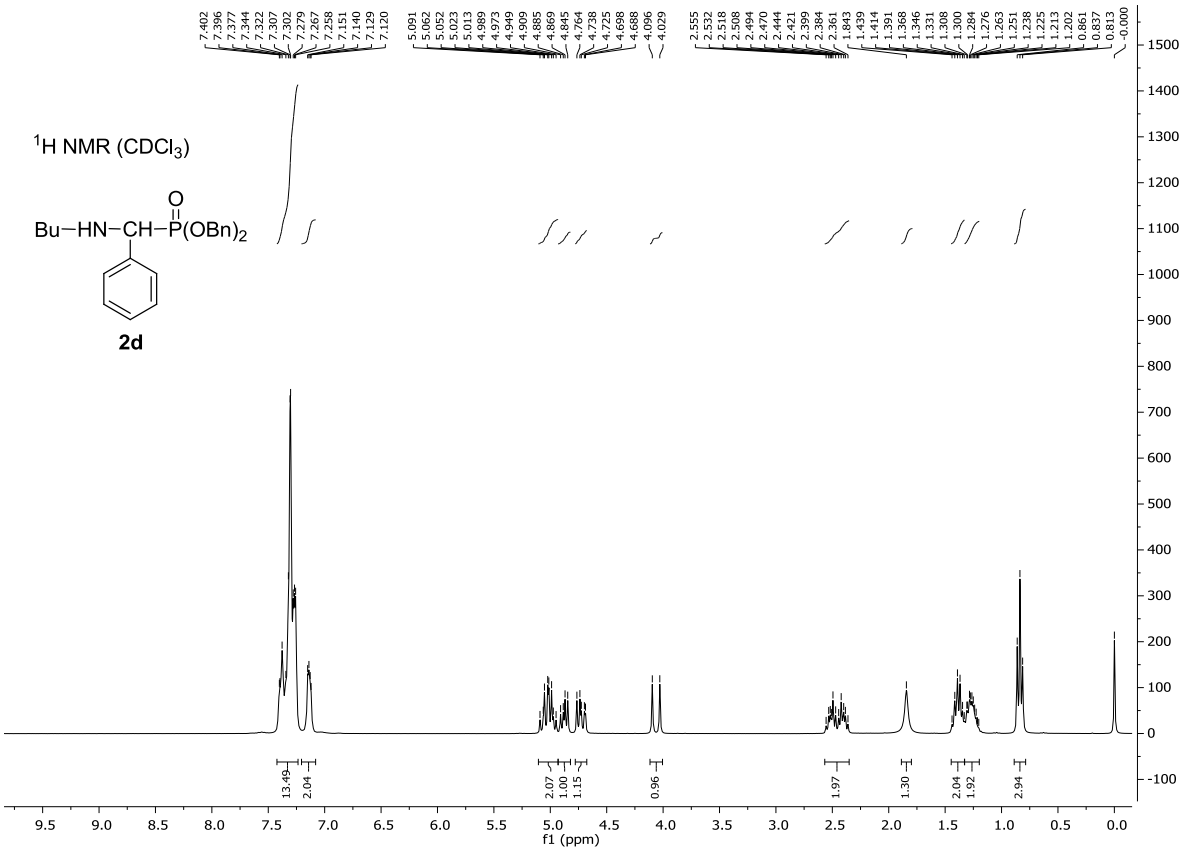


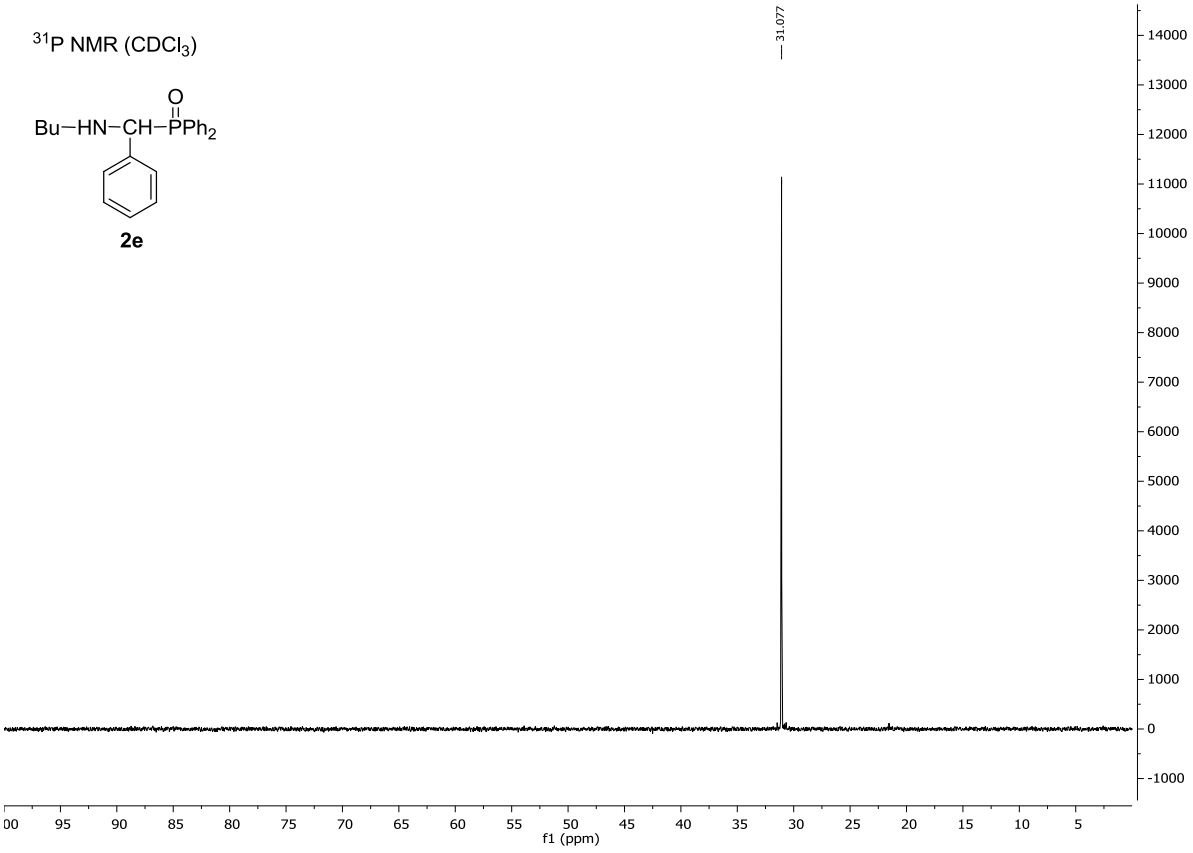
2d

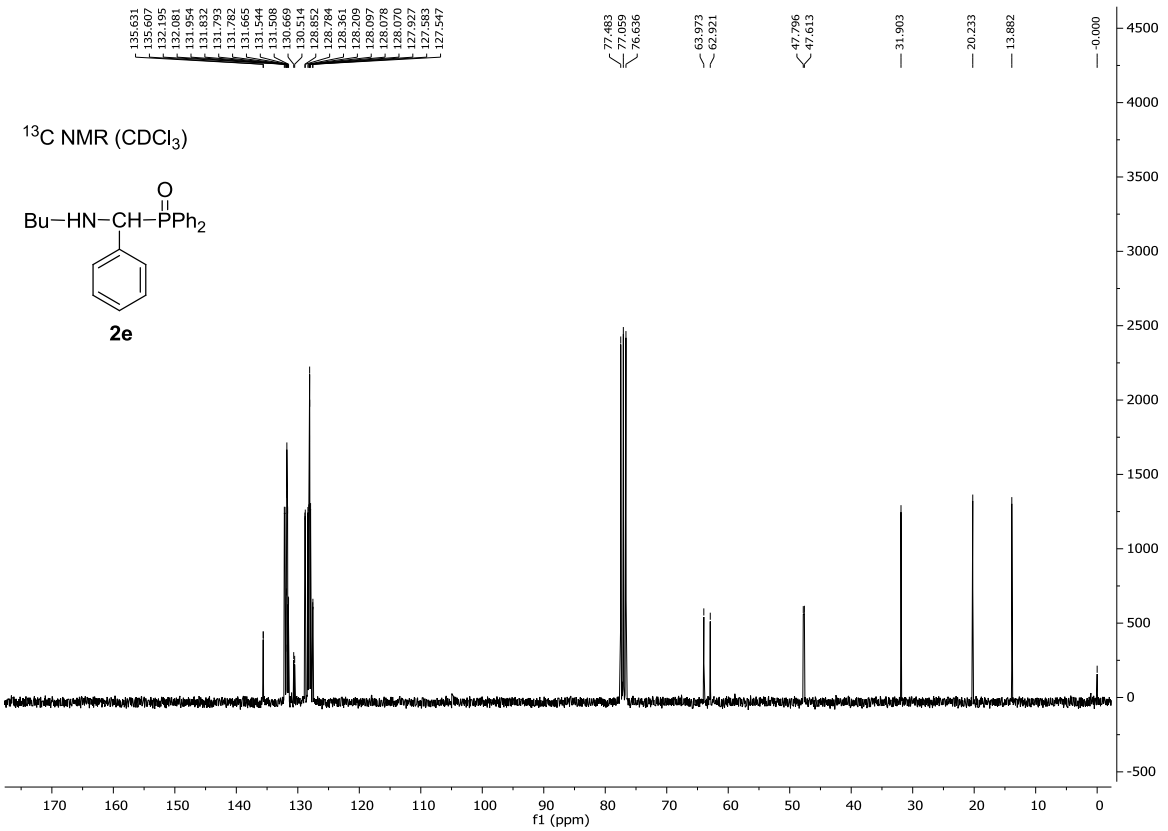
^{13}C NMR ($CDCl_3$)

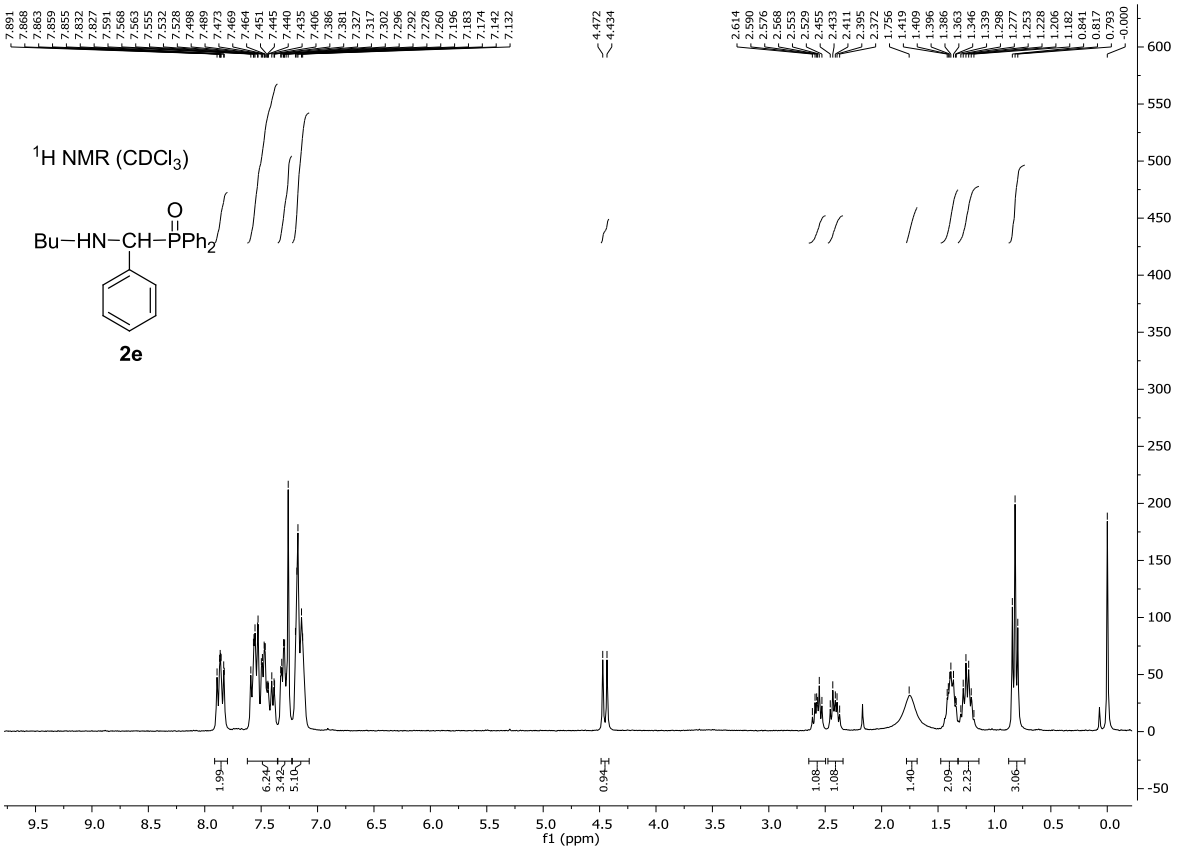


2d

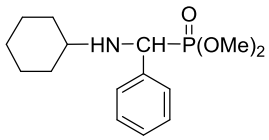

^{1}H NMR ($CDCl_3$)
Bu–HN–CH–P(OBn)$_2$
O
2d
f1 (ppm)


^{31}P NMR ($CDCl_3$)
Bu–HN–CH–PPh$_2$
O
2e
31.077
f1 (ppm)


135.631
135.607
132.195
132.081
131.954
131.832
131.793
131.782
131.665
131.544
131.508
130.669
130.514
128.852
128.784
128.361
128.209
128.097
128.078
128.070
127.927
127.583
127.547
77.483
77.059
76.636
63.973
62.921
47.796
47.613
31.903
20.233
13.882
-0.000
^{13}C NMR ($CDCl_3$)
Bu–HN–CH–PPh$_2$
O
2e
f1 (ppm)

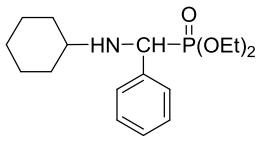

7.891
7.868
7.863
7.859
7.855
7.832
7.827
7.591
7.568
7.563
7.555
7.532
7.528
7.498
7.489
7.473
7.469
7.464
7.451
7.445
7.440
7.435
7.406
7.386
7.381
7.327
7.317
7.302
7.296
7.292
7.278
7.260
7.196
7.183
7.174
7.142
7.132
4.472
4.434
2.614
2.590
2.576
2.568
2.553
2.529
2.455
2.433
2.411
2.395
2.372
1.756
1.419
1.409
1.396
1.386
1.363
1.346
1.339
1.298
1.277
1.253
1.228
1.206
1.182
0.841
0.817
0.793
-0.000
^{1}H NMR ($CDCl_3$)
Bu–HN–CH–PPh$_2$
O
2e
1.99
6.24
3.42
5.10
0.94
1.08
1.08
1.40
2.09
2.23
3.06
f1 (ppm)

^{31}P NMR ($CDCl_3$)



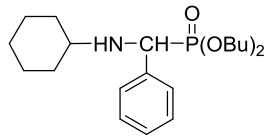
4a

^{31}P NMR ($CDCl_3$)



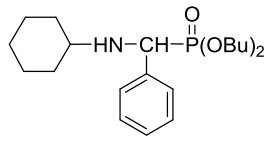
4b

^{31}P NMR ($CDCl_3$)

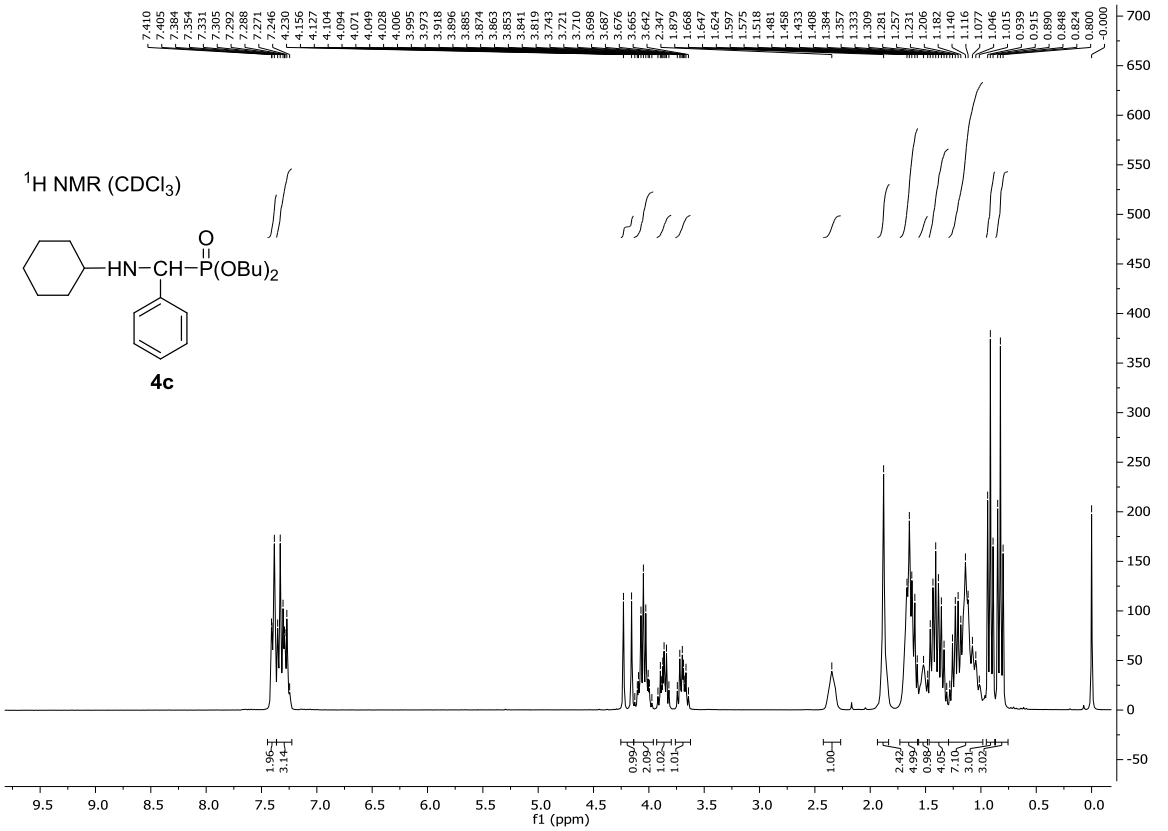


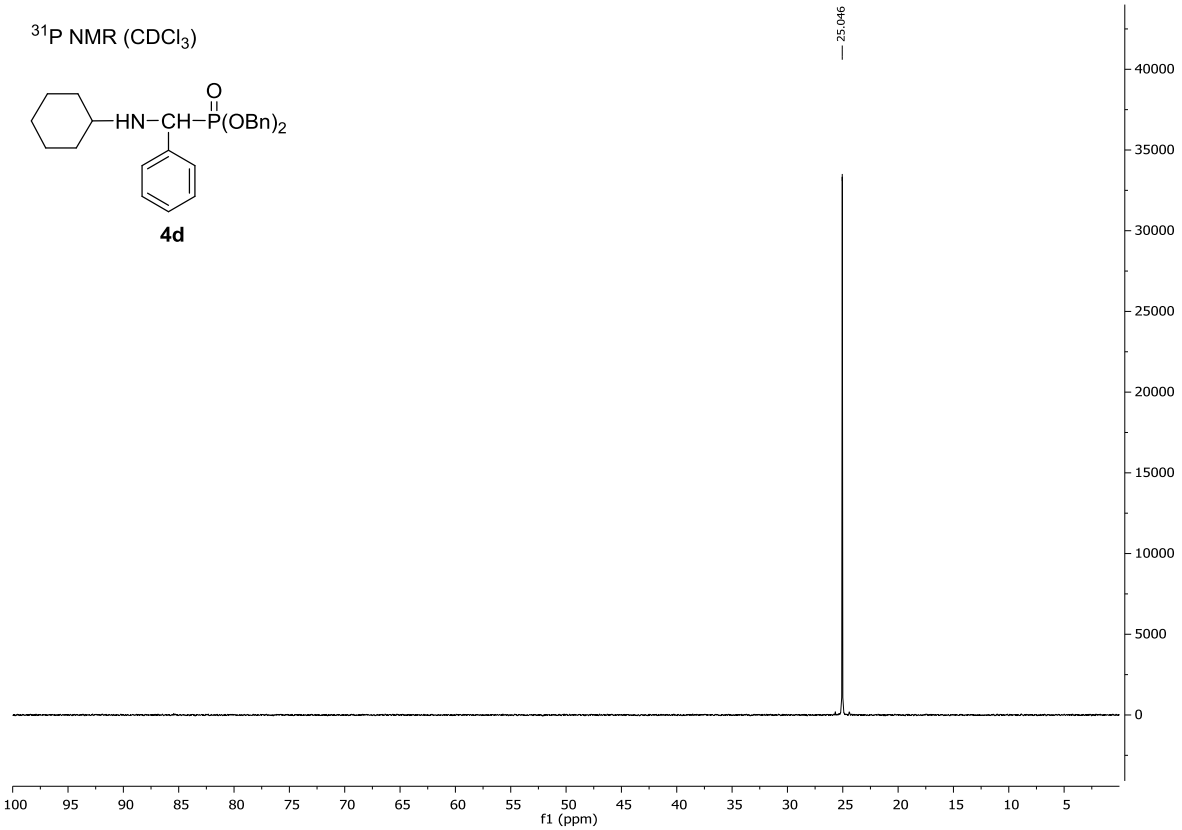
4c

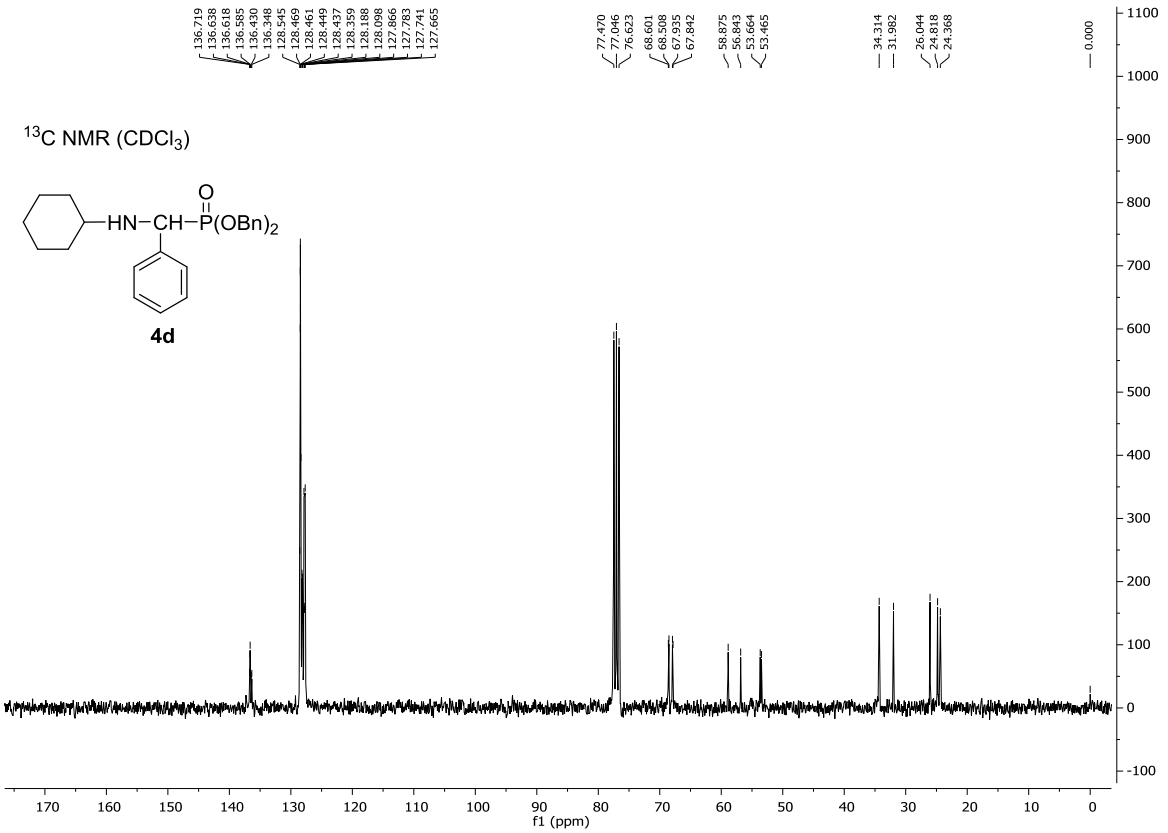
^{13}C NMR ($CDCl_3$)

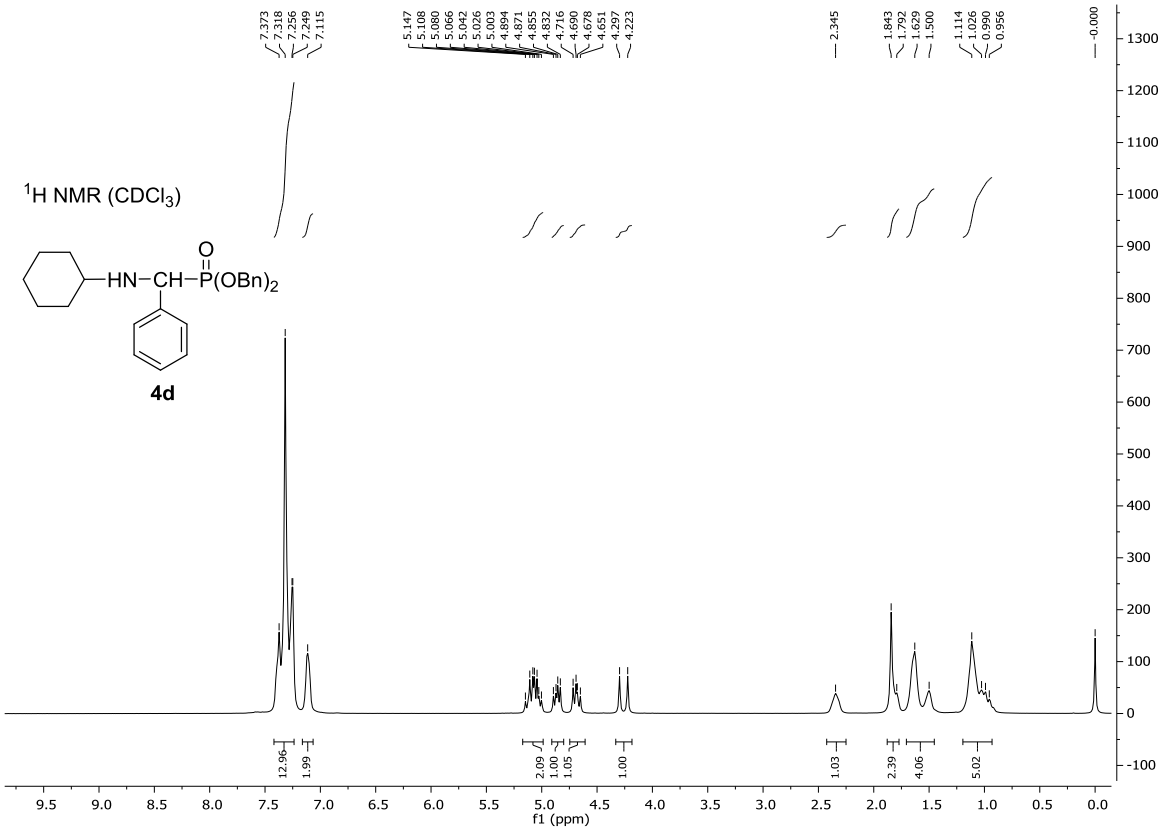


4c

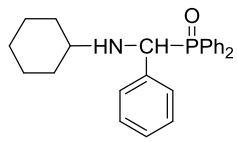

^{1}H NMR ($CDCl_3$)
HN−CH−P(OBu)$_2$
O
4c
f1 (ppm)


^{31}P NMR ($CDCl_3$)
HN−CH−P(OBn)$_2$
O
4d
25.046
f1 (ppm)


136.719
136.638
136.618
136.585
136.430
136.348
128.545
128.469
128.461
128.449
128.437
128.359
128.188
128.098
127.866
127.783
127.741
127.665
77.470
77.046
76.623
68.601
68.508
67.935
67.842
58.875
56.843
53.664
53.465
34.314
31.982
26.044
24.818
24.368
0.000
^{13}C NMR ($CDCl_3$)
HN−CH−P(OBn)$_2$
O
4d
f1 (ppm)

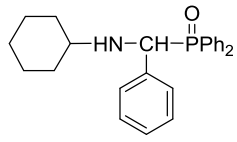

7.373
7.318
7.256
7.249
7.115
5.147
5.108
5.080
5.066
5.042
5.026
5.003
4.894
4.871
4.855
4.832
4.716
4.690
4.678
4.651
4.297
4.223
2.345
1.843
1.792
1.629
1.500
1.114
1.026
0.990
0.956
-0.000
^{1}H NMR ($CDCl_3$)
HN−CH−P(OBn)$_2$
O
4d
12.96
1.99
2.09
1.00
1.05
1.00
1.03
2.39
4.06
5.02
f1 (ppm)

^{31}P NMR ($CDCl_3$)

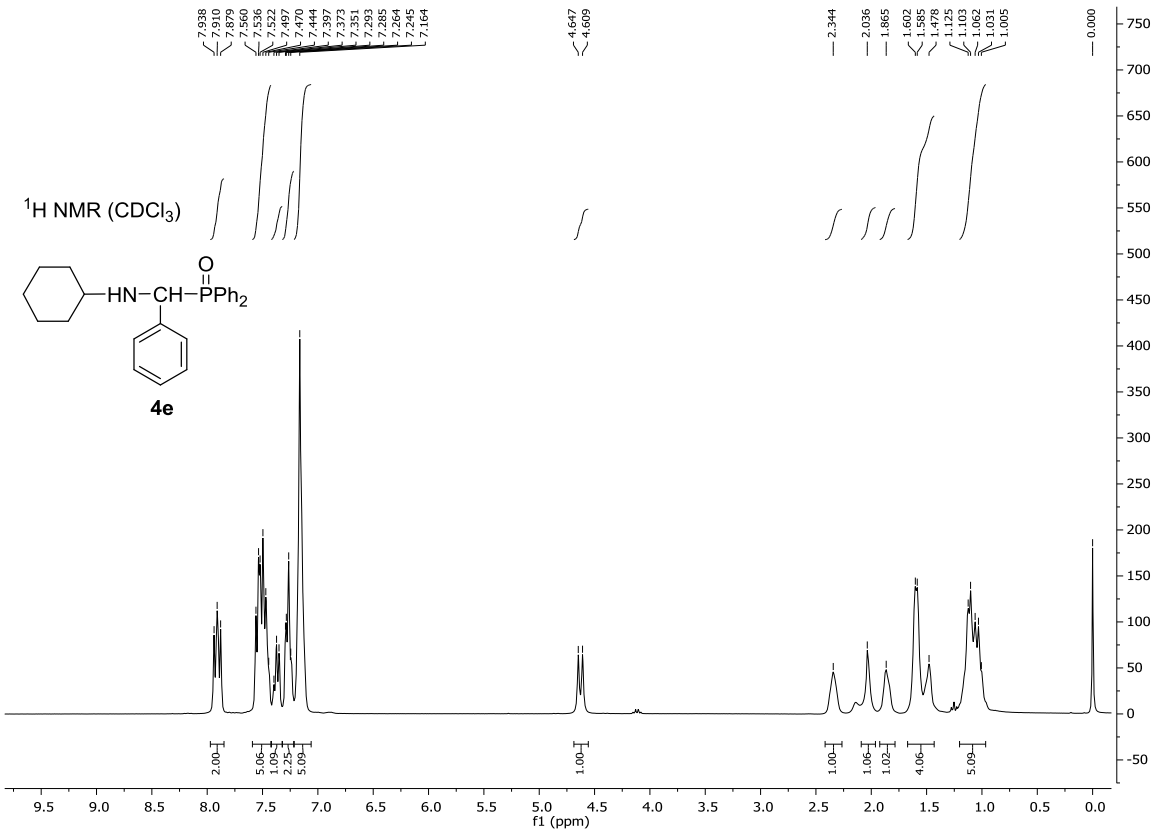


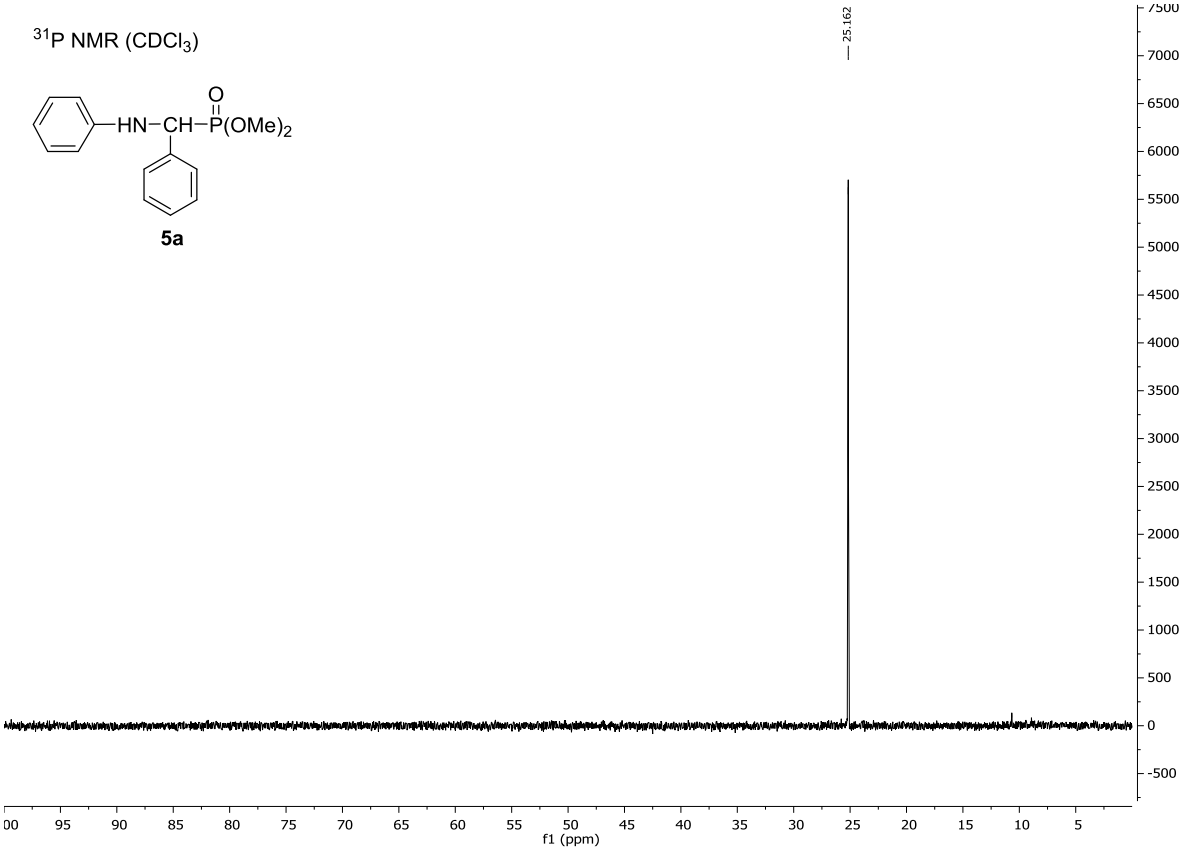
4e

^{13}C NMR ($CDCl_3$)

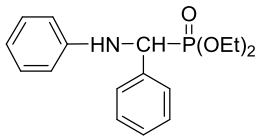


4e


^{1}H NMR ($CDCl_3$)
HN−CH−PPh$_2$
O
4e
7.938
7.910
7.879
7.560
7.536
7.522
7.497
7.470
7.444
7.397
7.373
7.351
7.293
7.285
7.264
7.245
7.164
4.647
4.609
2.344
2.036
1.865
1.602
1.585
1.478
1.125
1.103
1.062
1.031
1.005
0.000
2.00
5.06
1.09
2.25
5.09
1.00
1.00
1.06
1.02
4.06
5.09
f1 (ppm)

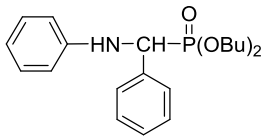

^{31}P NMR ($CDCl_3$)
HN−CH−P(OMe)$_2$
O
5a
25.162
f1 (ppm)

^{31}P NMR ($CDCl_3$)

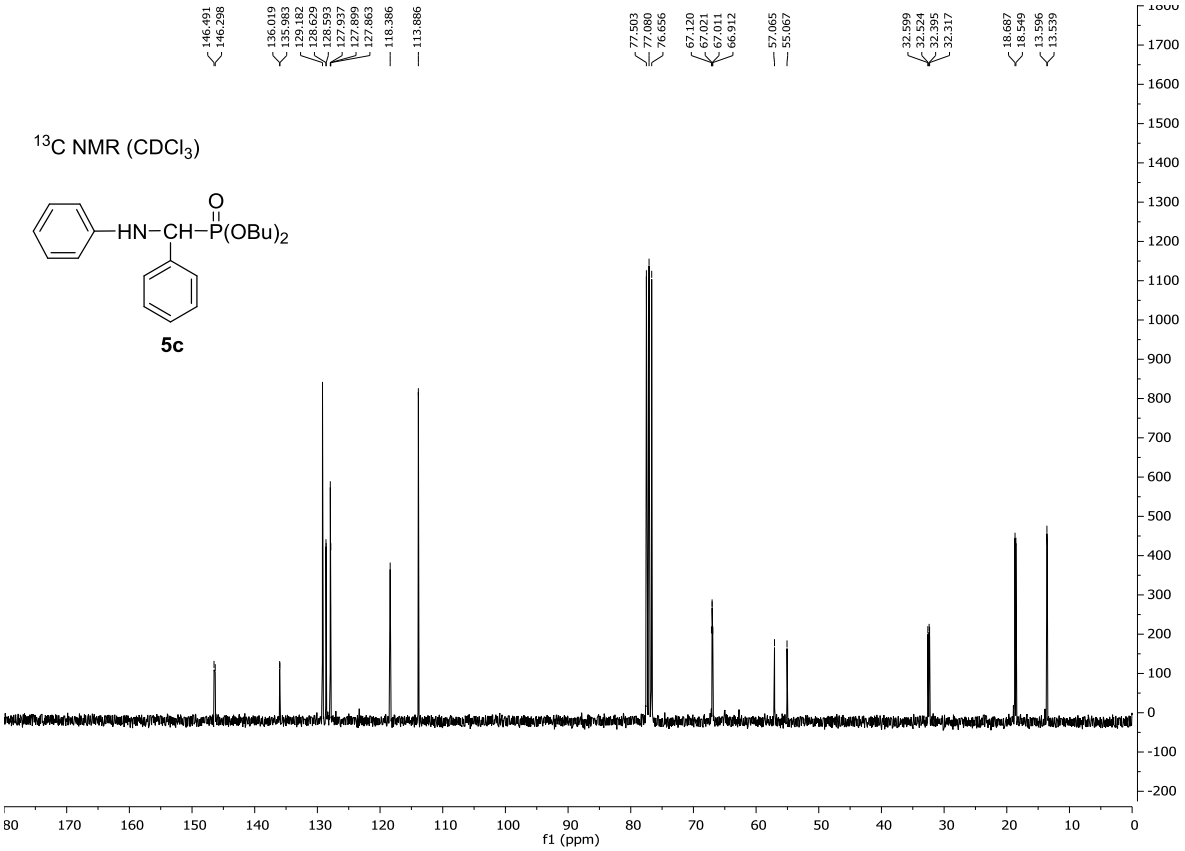


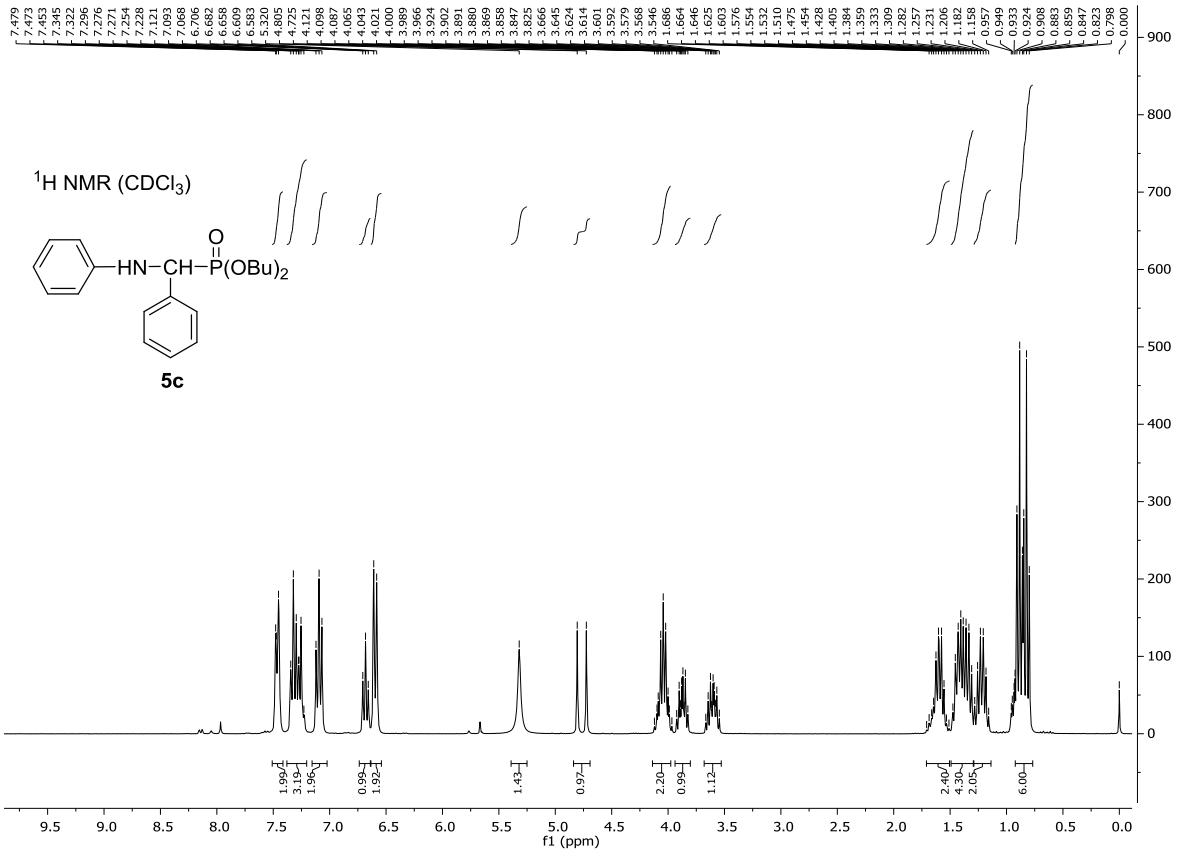
5b

^{31}P NMR ($CDCl_3$)

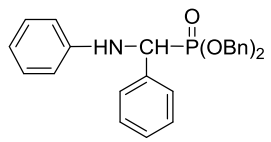


5c

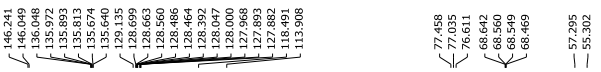

146.491
146.298
136.019
135.983
129.182
128.629
128.593
127.937
127.899
127.863
118.386
113.886
77.503
77.080
76.656
67.120
67.021
67.011
66.912
57.065
55.067
32.599
32.524
32.395
32.317
18.687
18.549
13.596
13.539
13C NMR (CDCl3)
HN−CH−P(OBu)2
O
5c
f1 (ppm)


1H NMR (CDCl3)
HN−CH−P(OBu)2
O
5c
1.99
3.19
1.96
0.99
1.92
1.43
0.97
2.20
0.99
1.12
2.40
4.30
2.05
6.00
f1 (ppm)

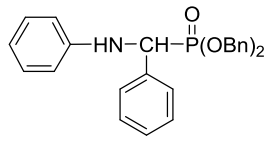
^{31}P NMR ($CDCl_3$)



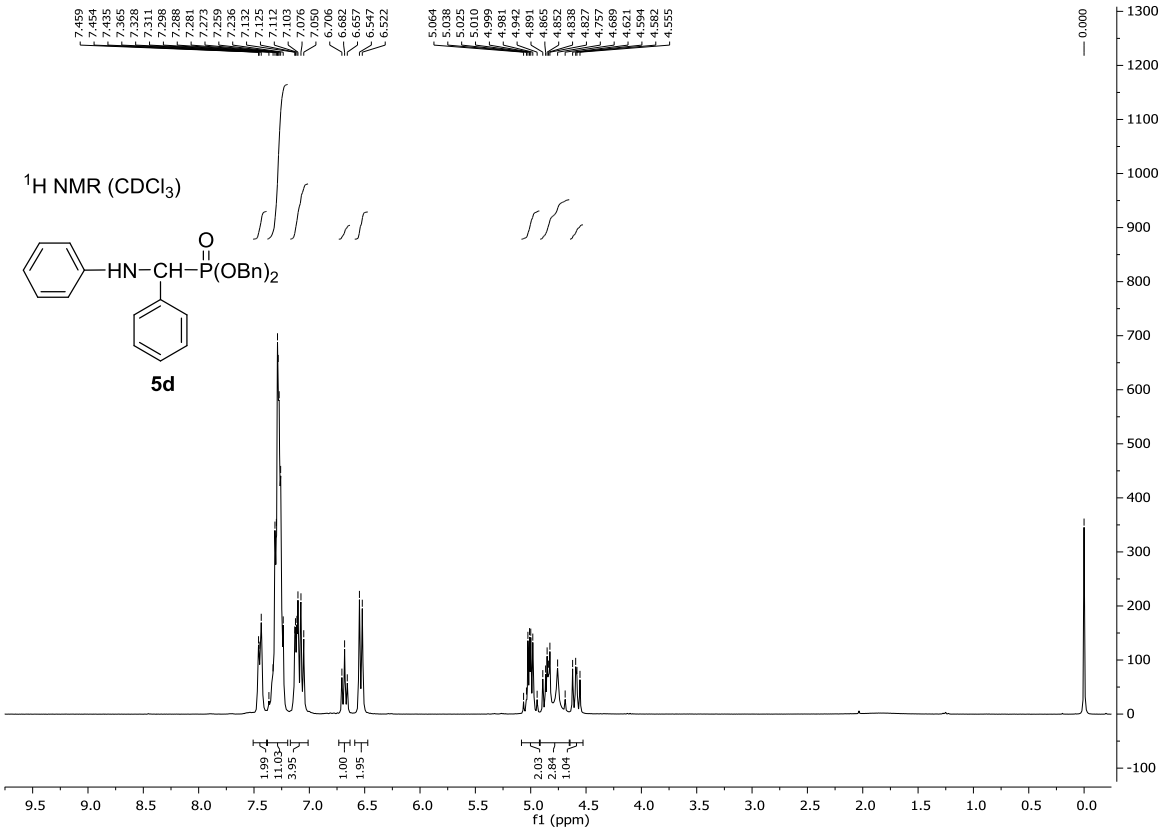
5d

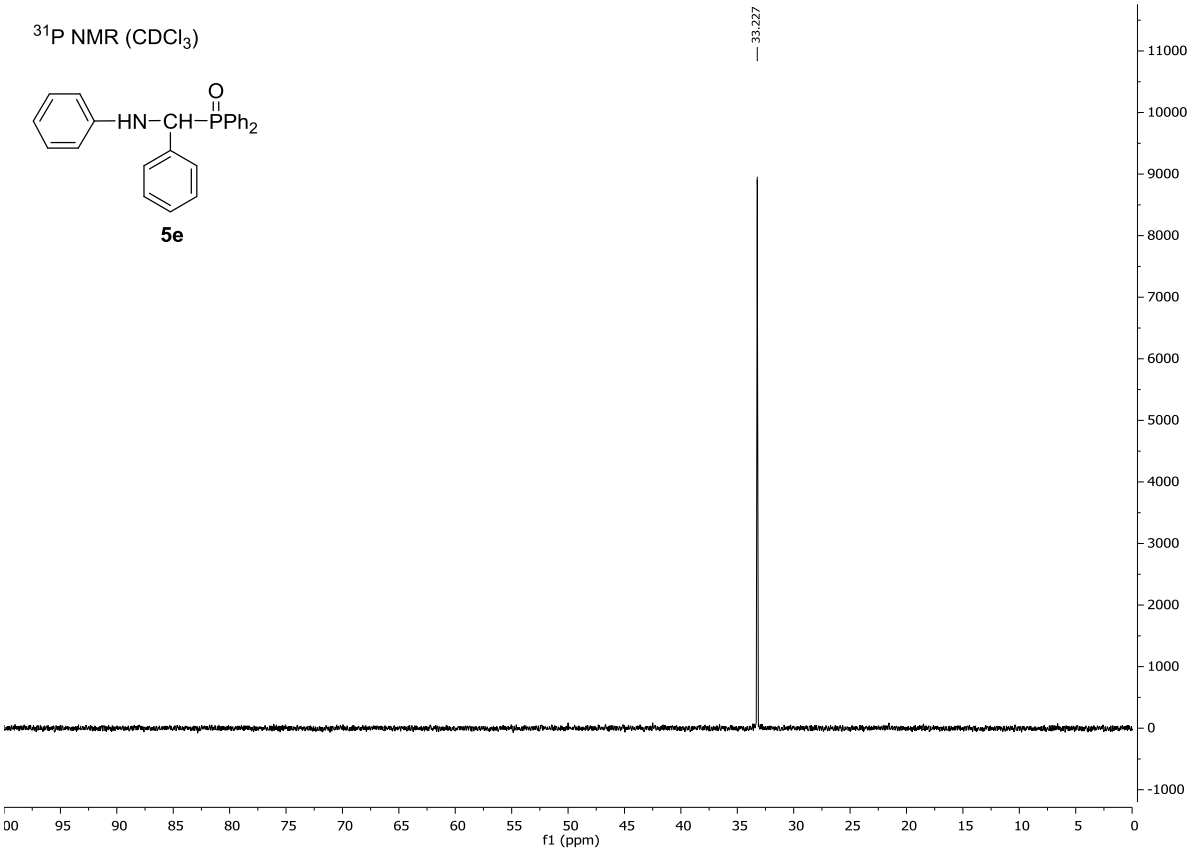


^{13}C NMR ($CDCl_3$)

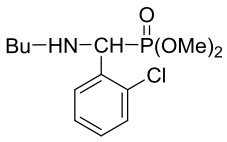


5d


7.459
7.454
7.435
7.365
7.328
7.311
7.298
7.288
7.281
7.273
7.259
7.236
7.132
7.125
7.112
7.103
7.076
7.050
6.706
6.682
6.657
6.547
6.522
5.064
5.038
5.025
5.010
4.999
4.981
4.942
4.891
4.865
4.852
4.838
4.827
4.757
4.689
4.621
4.594
4.582
4.555
0.000
1H NMR (CDCl3)
HN−CH−P(OBn)2
O
5d
1.99
11.03
3.95
1.00
1.95
2.03
2.84
1.04
f1 (ppm)

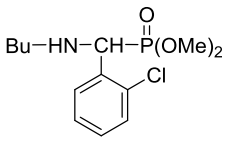

31P NMR (CDCl3)
HN−CH−PPh2
O
5e
33.227
f1 (ppm)

^{31}P NMR ($CDCl_3$)

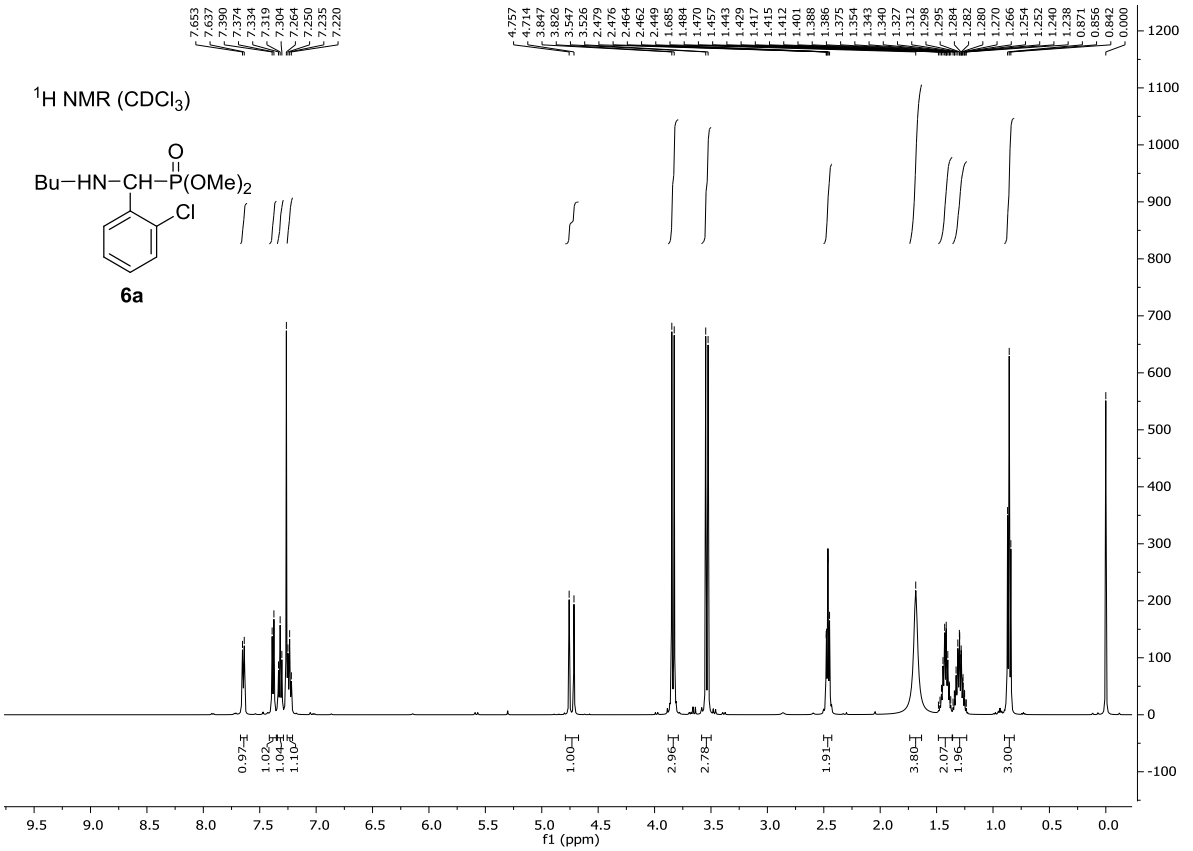


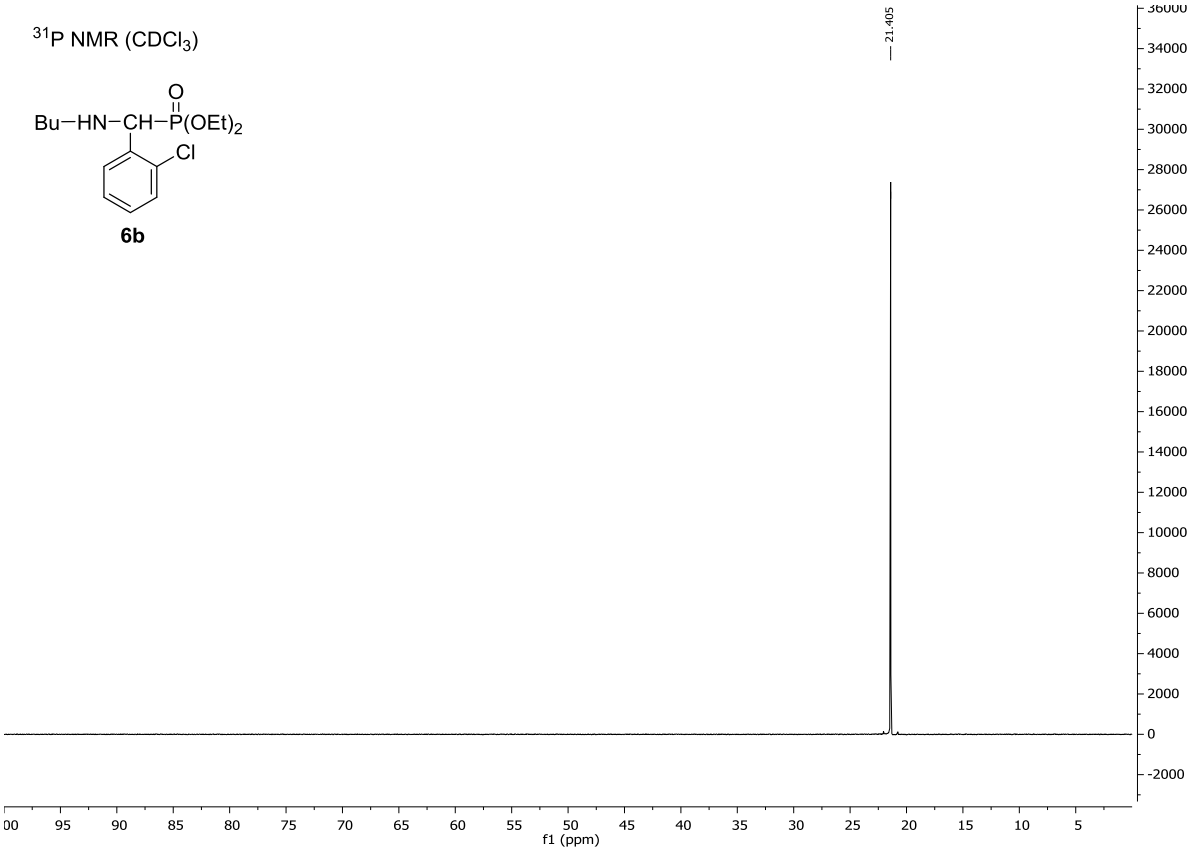
6a

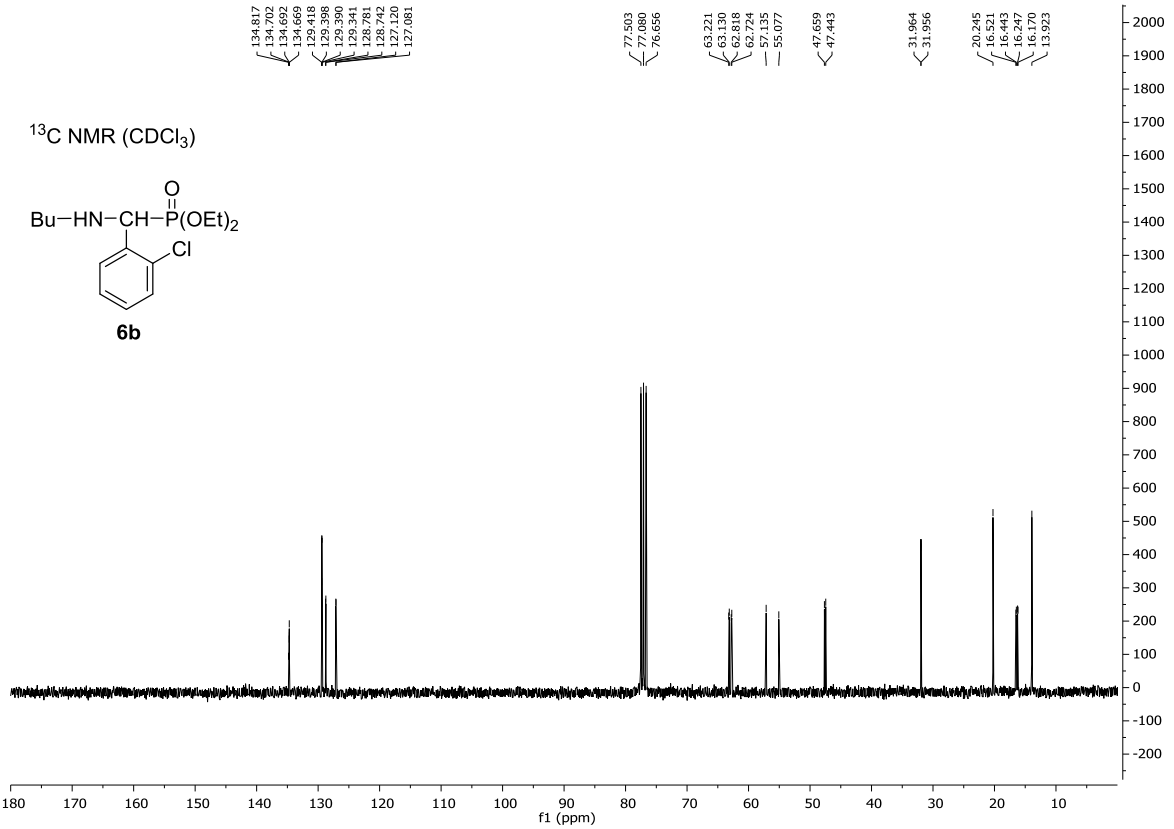
^{13}C NMR ($CDCl_3$)

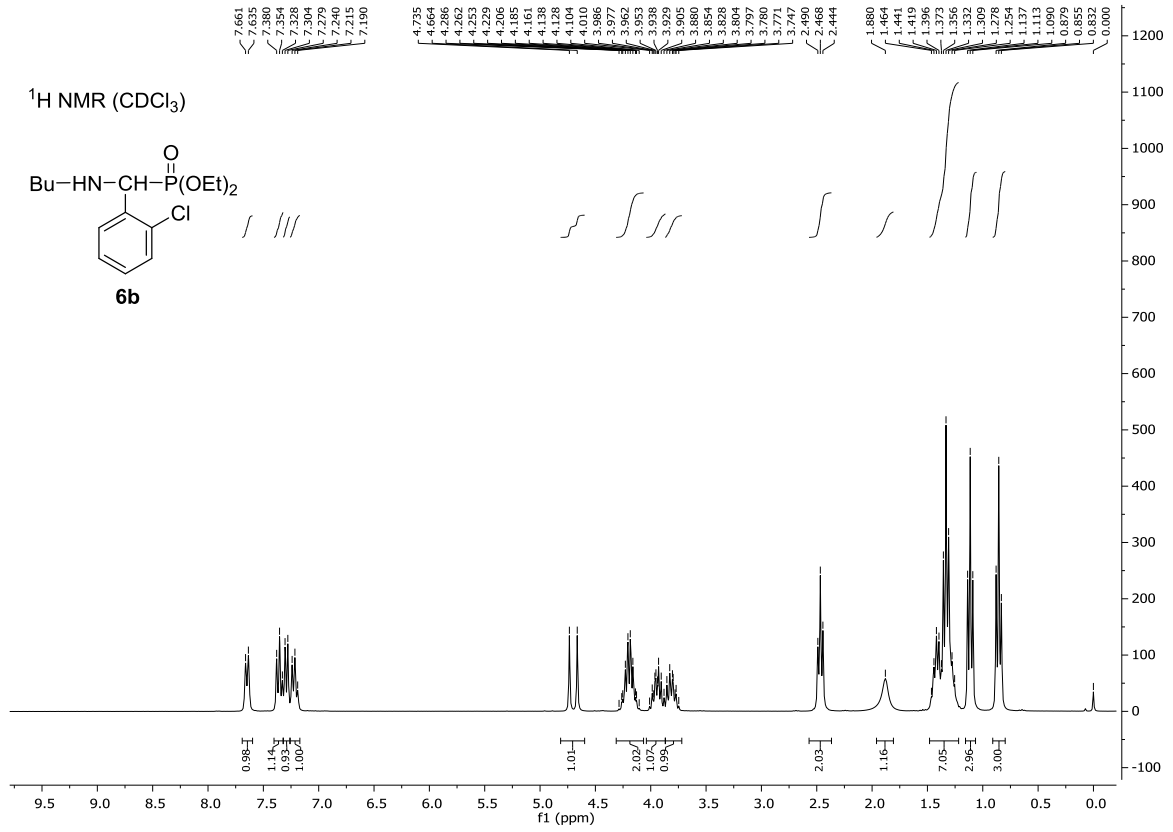


6a

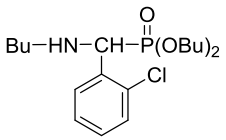

^{1}H NMR ($CDCl_3$)
Bu–HN–CH–P(OMe)$_2$
O
Cl
6a
f1 (ppm)


^{31}P NMR ($CDCl_3$)
Bu–HN–CH–P(OEt)$_2$
O
Cl
6b
21.405
f1 (ppm)


134.817
134.702
134.692
134.669
129.418
129.398
129.390
129.341
128.781
128.742
127.120
127.081
77.503
77.080
76.656
63.221
63.130
62.818
62.724
57.135
55.077
47.659
47.443
31.964
31.956
20.245
16.521
16.443
16.247
16.170
13.923
^{13}C NMR ($CDCl_3$)
Bu−HN−CH−P(OEt)$_2$
O
Cl
6b
f1 (ppm)

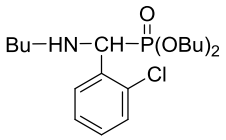

7.661
7.635
7.380
7.354
7.328
7.304
7.279
7.240
7.215
7.190
4.735
4.664
4.286
4.262
4.253
4.229
4.206
4.185
4.161
4.138
4.128
4.104
4.010
3.986
3.977
3.962
3.953
3.938
3.929
3.905
3.880
3.854
3.828
3.804
3.797
3.780
3.771
3.747
2.490
2.468
2.444
1.880
1.464
1.441
1.419
1.396
1.373
1.356
1.332
1.309
1.278
1.254
1.137
1.113
1.090
0.879
0.855
0.832
0.000
^{1}H NMR ($CDCl_3$)
Bu−HN−CH−P(OEt)$_2$
O
Cl
6b
0.98
1.14
0.93
1.00
1.01
2.02
1.07
0.99
2.03
1.16
7.05
2.96
3.00
f1 (ppm)

^{31}P NMR ($CDCl_3$)

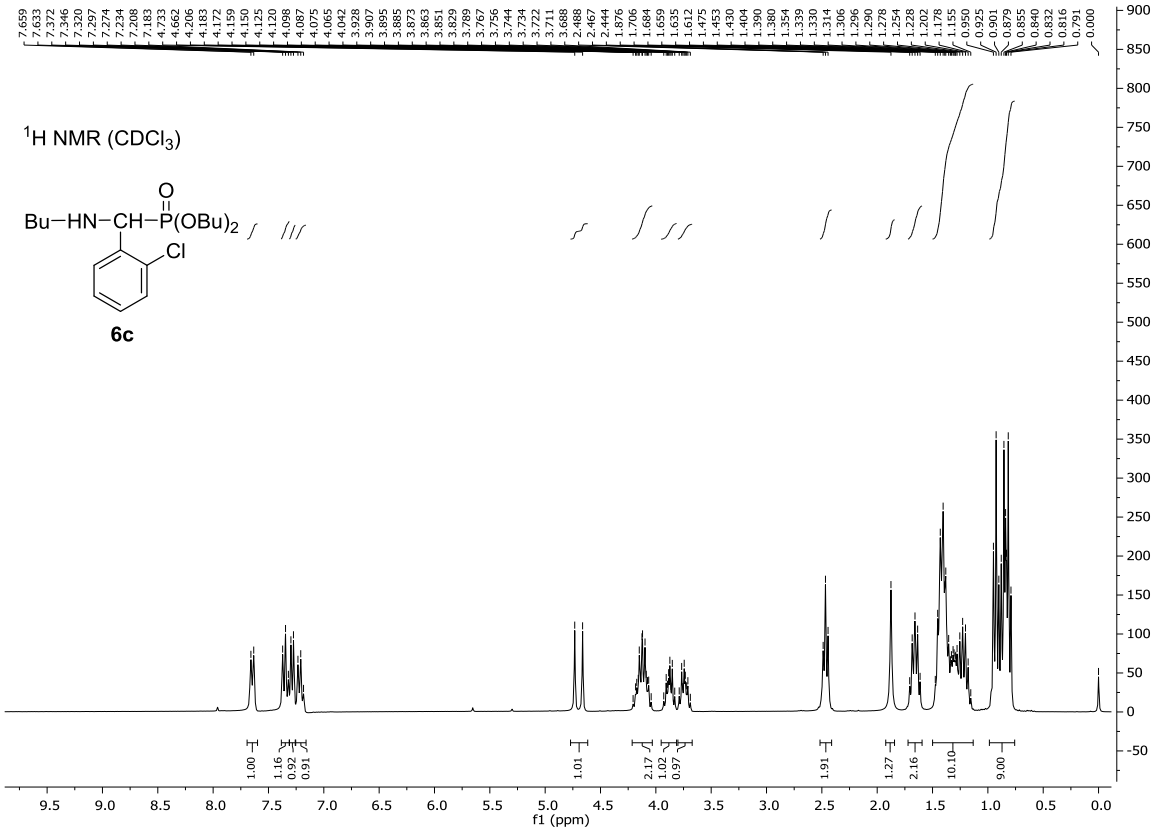


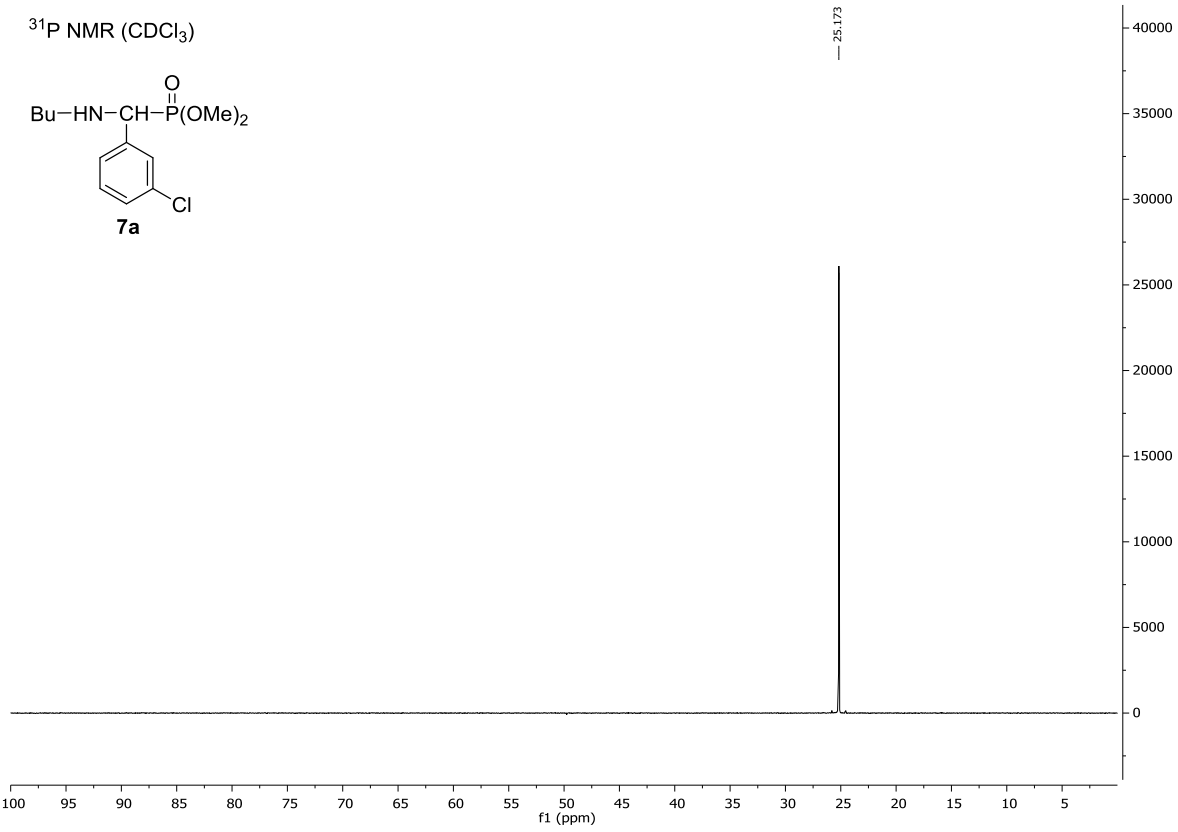
6c

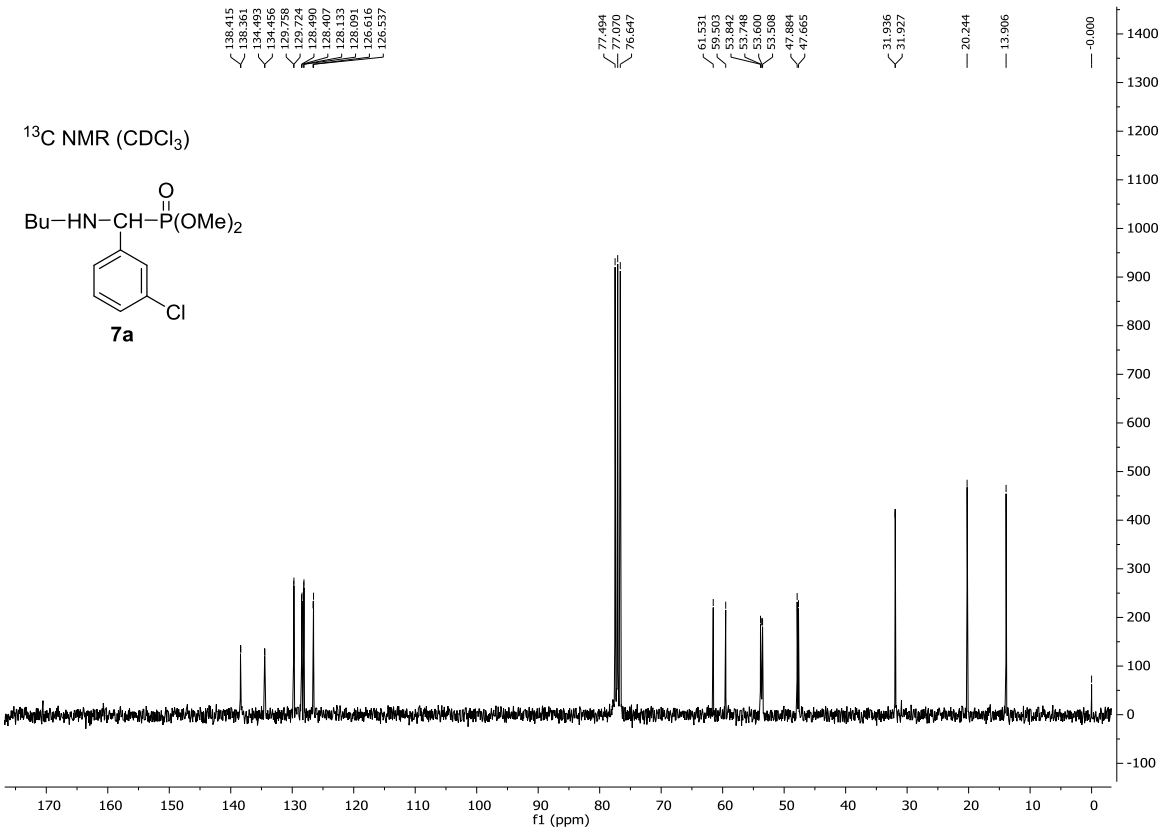
^{13}C NMR ($CDCl_3$)

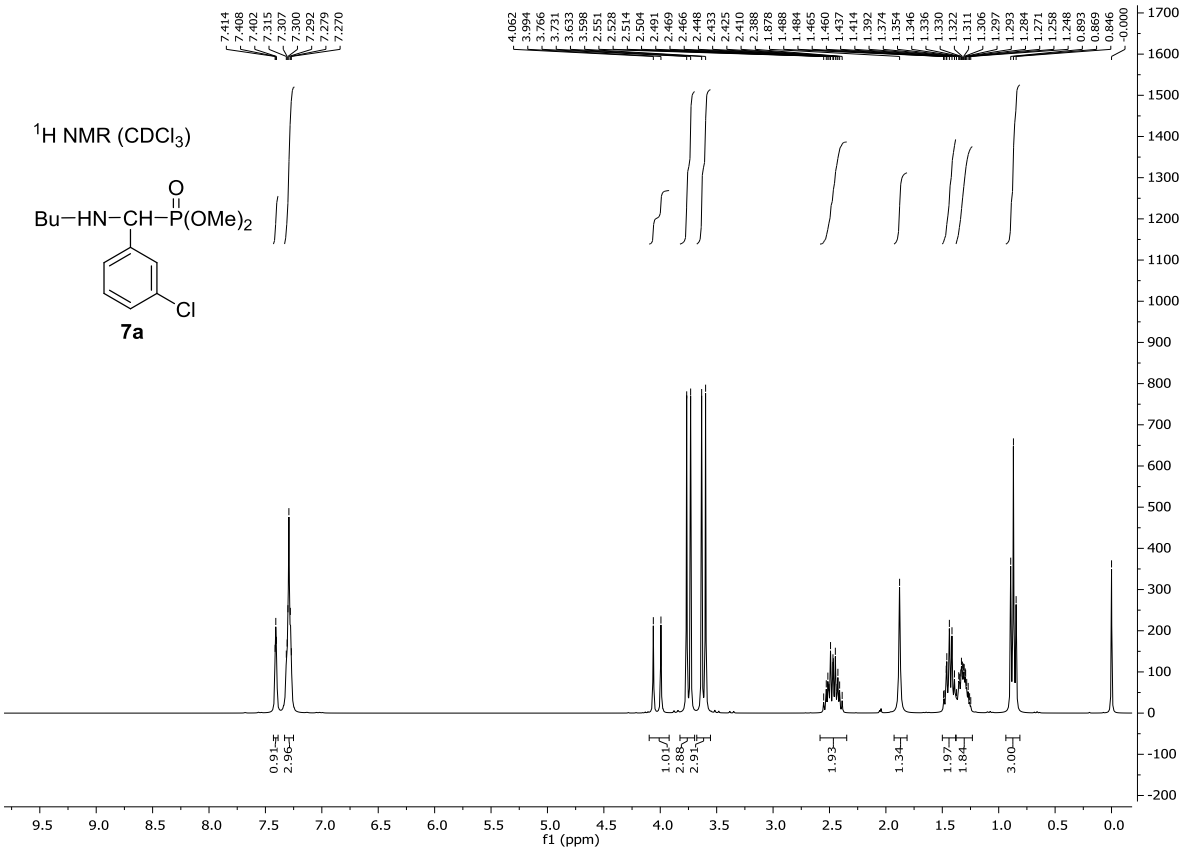


6c

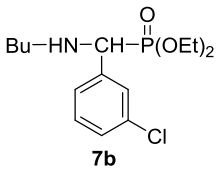

^{1}H NMR ($CDCl_3$)
Bu–HN–CH–P(OBu)$_2$
O
Cl
6c
f1 (ppm)


^{31}P NMR ($CDCl_3$)
Bu–HN–CH–P(OMe)$_2$
O
Cl
7a
25.173
f1 (ppm)


^{13}C NMR ($CDCl_3$)
Bu–HN–CH–P(OMe)$_2$
O
Cl
7a
f1 (ppm)

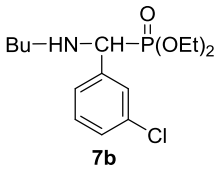

^{1}H NMR ($CDCl_3$)
Bu–HN–CH–P(OMe)$_2$
O
Cl
7a
f1 (ppm)

^{31}P NMR ($CDCl_3$)

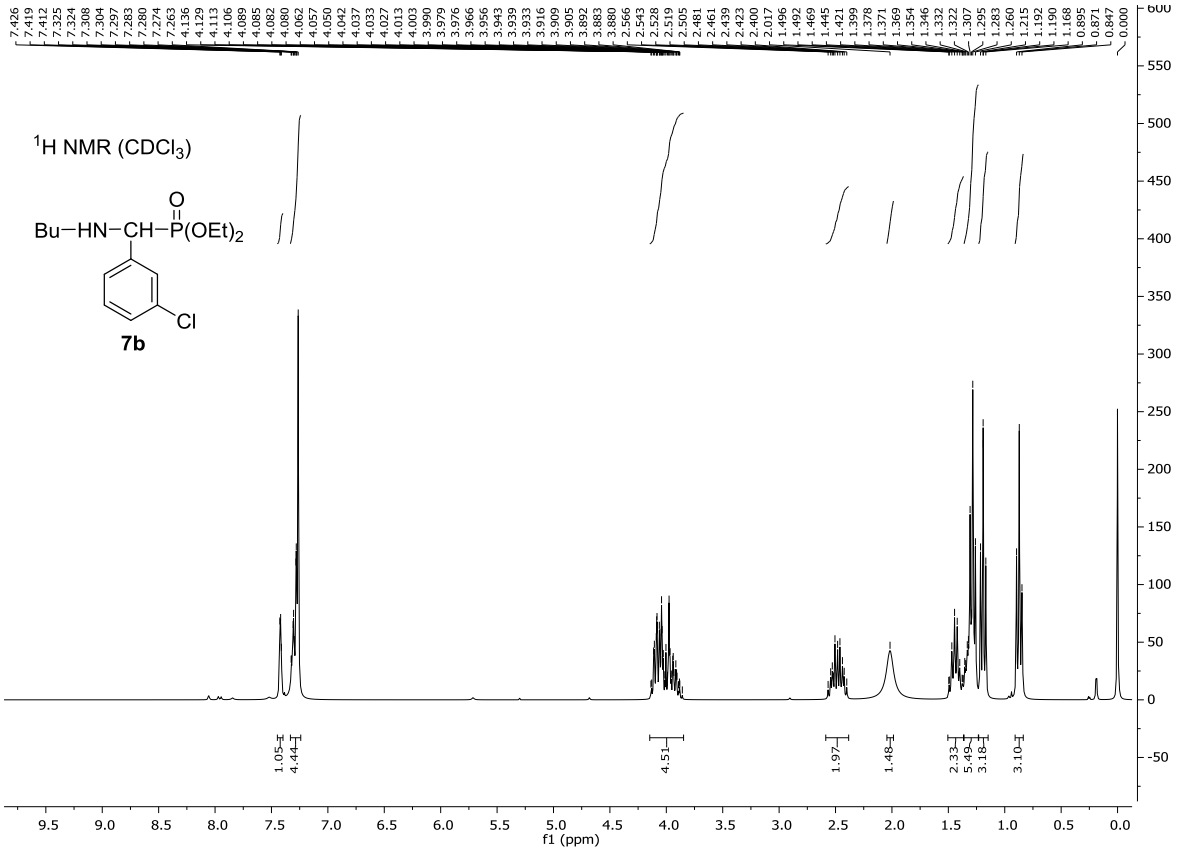


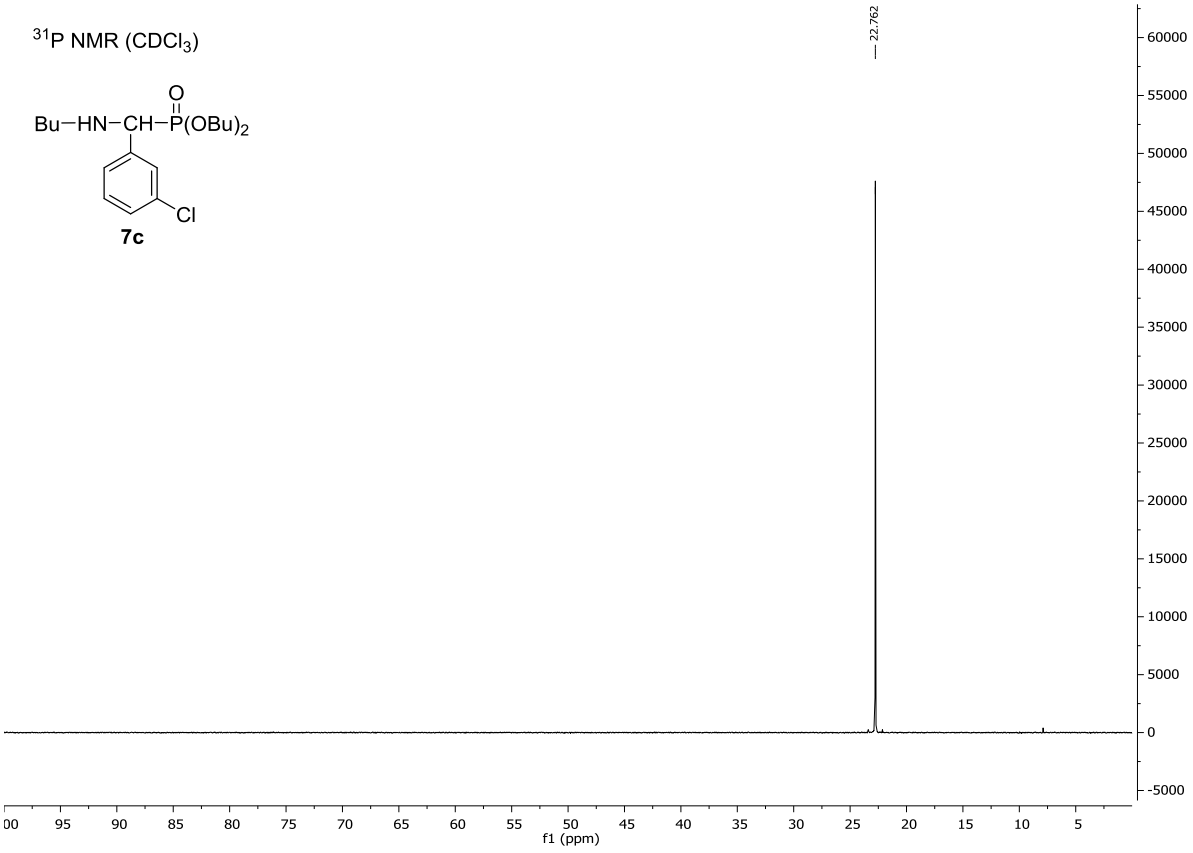
7b

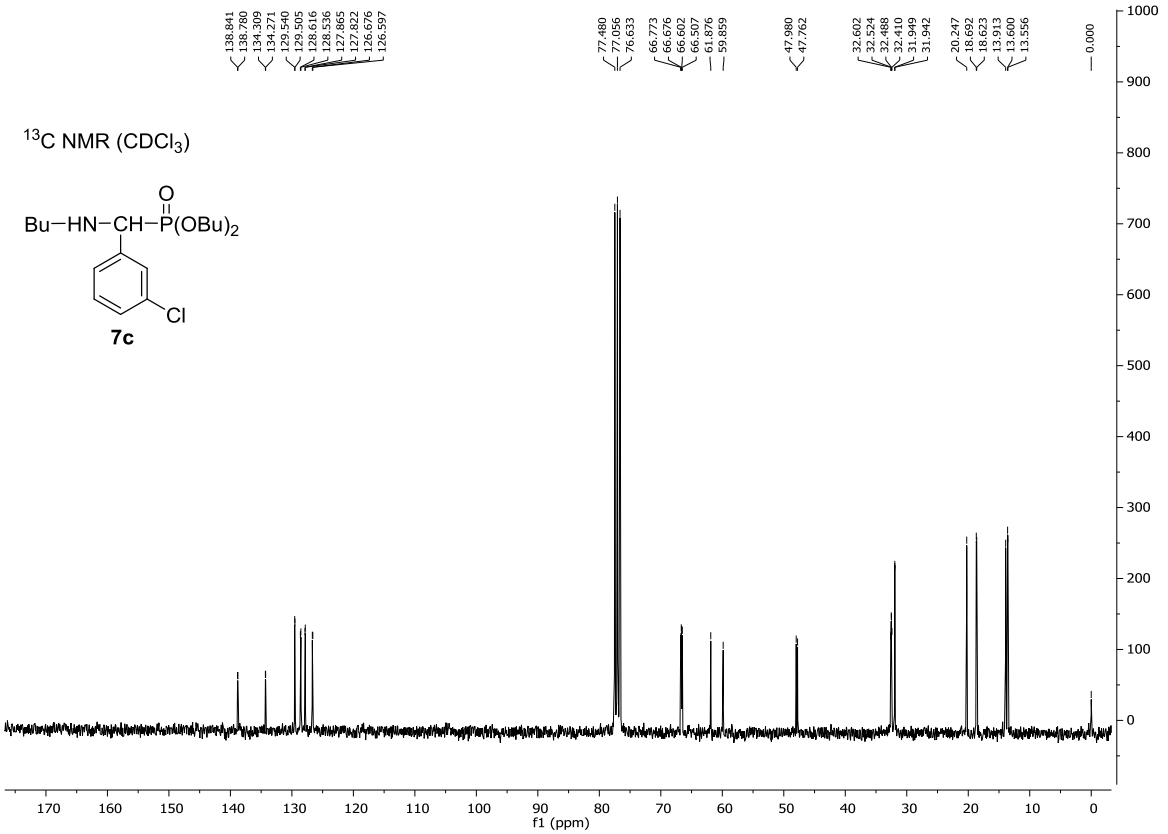
^{13}C NMR ($CDCl_3$)

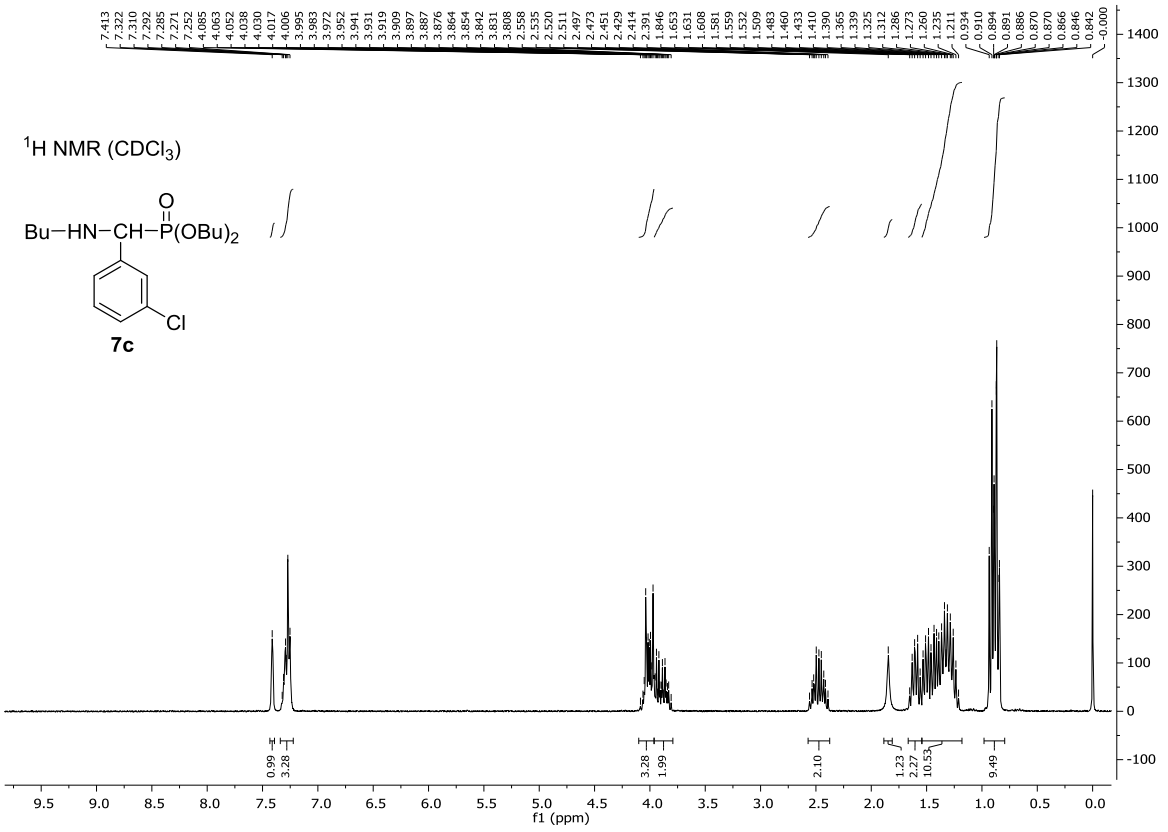


7b

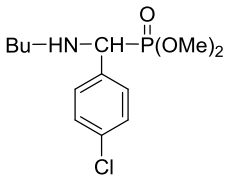

^{1}H NMR ($CDCl_3$)
Bu–HN–CH–P(OEt)$_2$
O
Cl
7b
f1 (ppm)


^{31}P NMR ($CDCl_3$)
Bu–HN–CH–P(OBu)$_2$
O
Cl
7c
22.762
f1 (ppm)


^{13}C NMR ($CDCl_3$)
Bu–HN–CH–P(OBu)$_2$
O
Cl
7c
f1 (ppm)

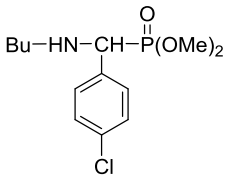

^{1}H NMR ($CDCl_3$)
Bu–HN–CH–P(OBu)$_2$
O
Cl
7c
f1 (ppm)

^{31}P NMR ($CDCl_3$)

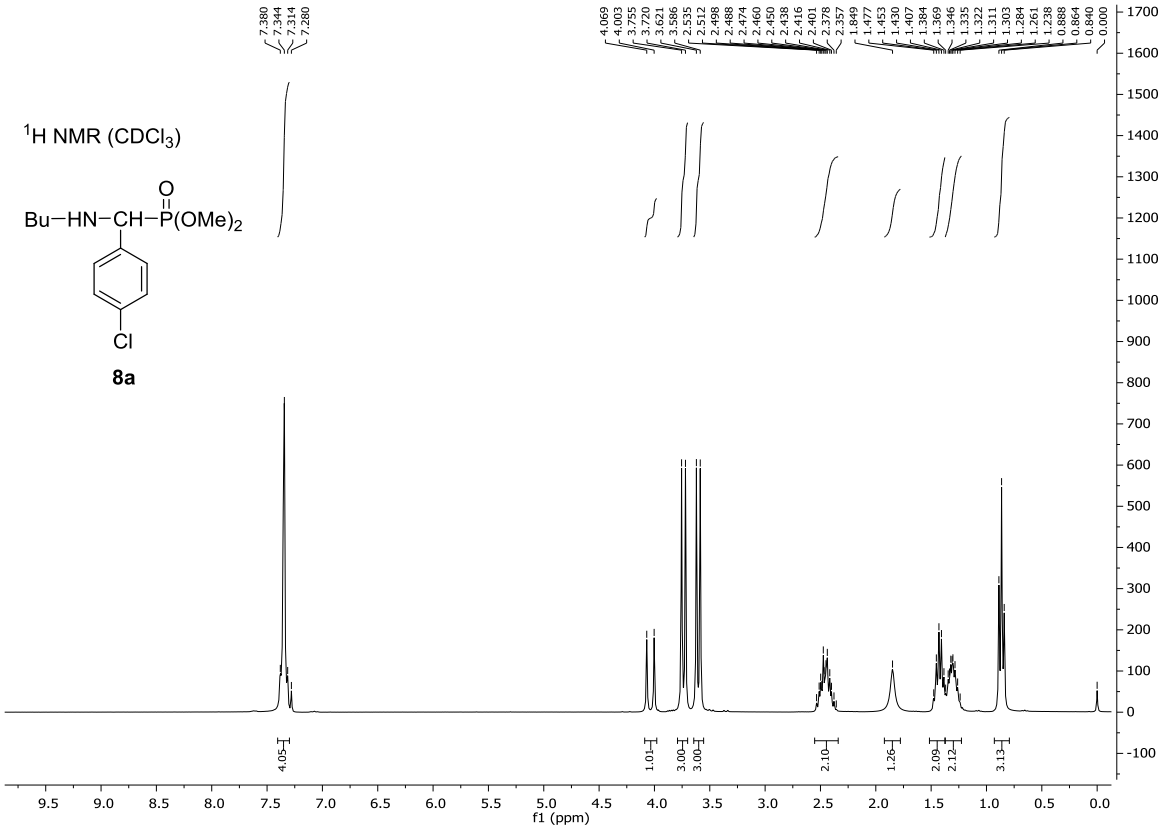


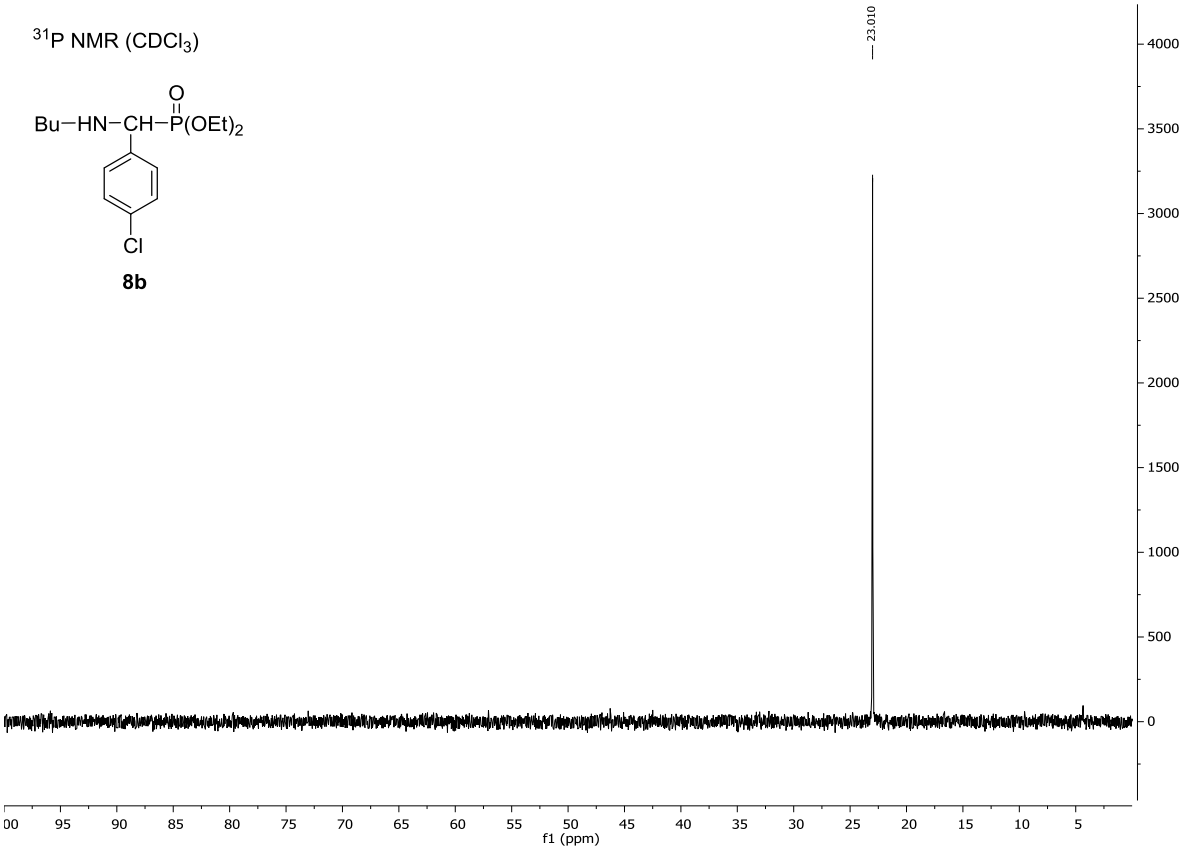
8a

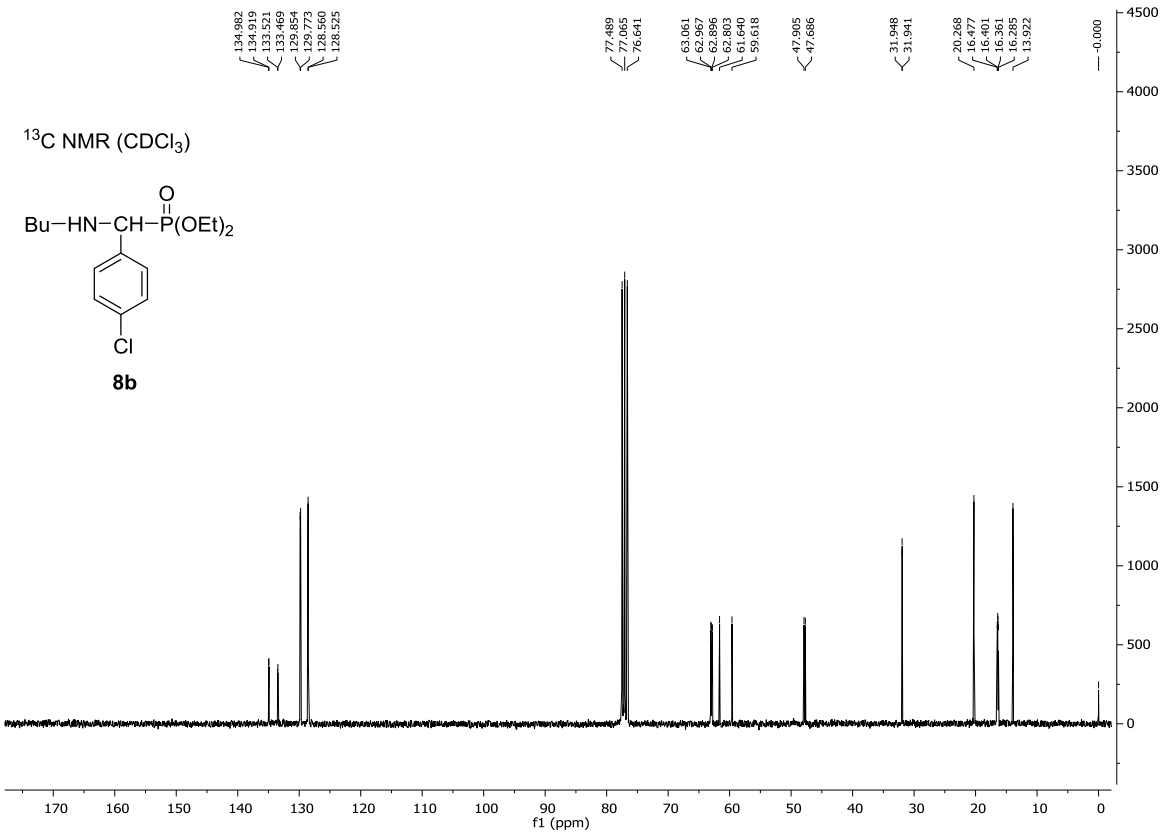
^{13}C NMR ($CDCl_3$)

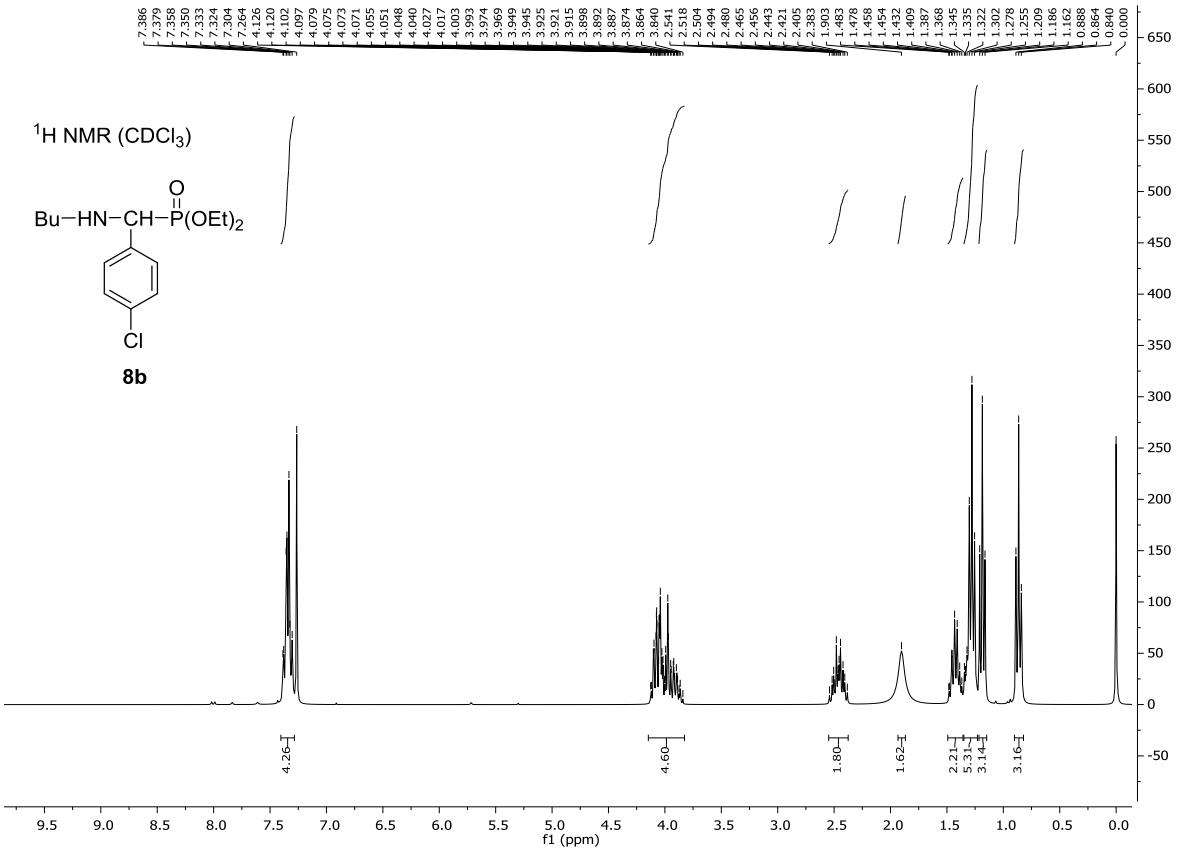


8a

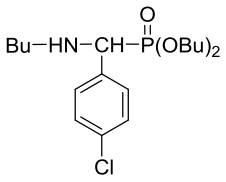

^{1}H NMR ($CDCl_3$)
Bu–HN–CH–P(OMe)$_2$
O
Cl
8a
f1 (ppm)


^{31}P NMR ($CDCl_3$)
Bu–HN–CH–P(OEt)$_2$
O
Cl
8b
23.010
f1 (ppm)


134.982
134.919
133.521
133.469
129.854
129.773
128.560
128.525
77.489
77.065
76.641
63.061
62.967
62.896
62.803
61.640
59.618
47.905
47.686
31.948
31.941
20.268
16.477
16.401
16.361
16.285
13.922
-0.000
13C NMR (CDCl3)
Bu−HN−CH−P(OEt)2
O
Cl
8b
f1 (ppm)

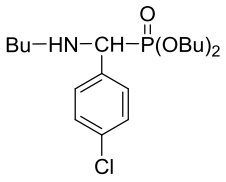

7.386
7.379
7.358
7.350
7.333
7.324
7.304
7.264
4.126
4.120
4.102
4.097
4.079
4.075
4.073
4.071
4.055
4.051
4.048
4.040
4.027
4.017
4.003
3.993
3.974
3.969
3.949
3.945
3.925
3.921
3.915
3.898
3.892
3.887
3.874
3.864
3.840
2.518
2.504
2.494
2.460
2.465
2.456
2.443
2.421
2.405
2.383
1.903
1.483
1.478
1.458
1.454
1.432
1.409
1.387
1.368
1.345
1.335
1.322
1.302
1.278
1.255
1.209
1.186
1.162
0.888
0.864
0.840
0.000
1H NMR (CDCl3)
Bu−HN−CH−P(OEt)2
O
Cl
8b
4.26
4.60
1.80
1.62
2.21
5.31
3.14
3.16
f1 (ppm)

^{31}P NMR ($CDCl_3$)

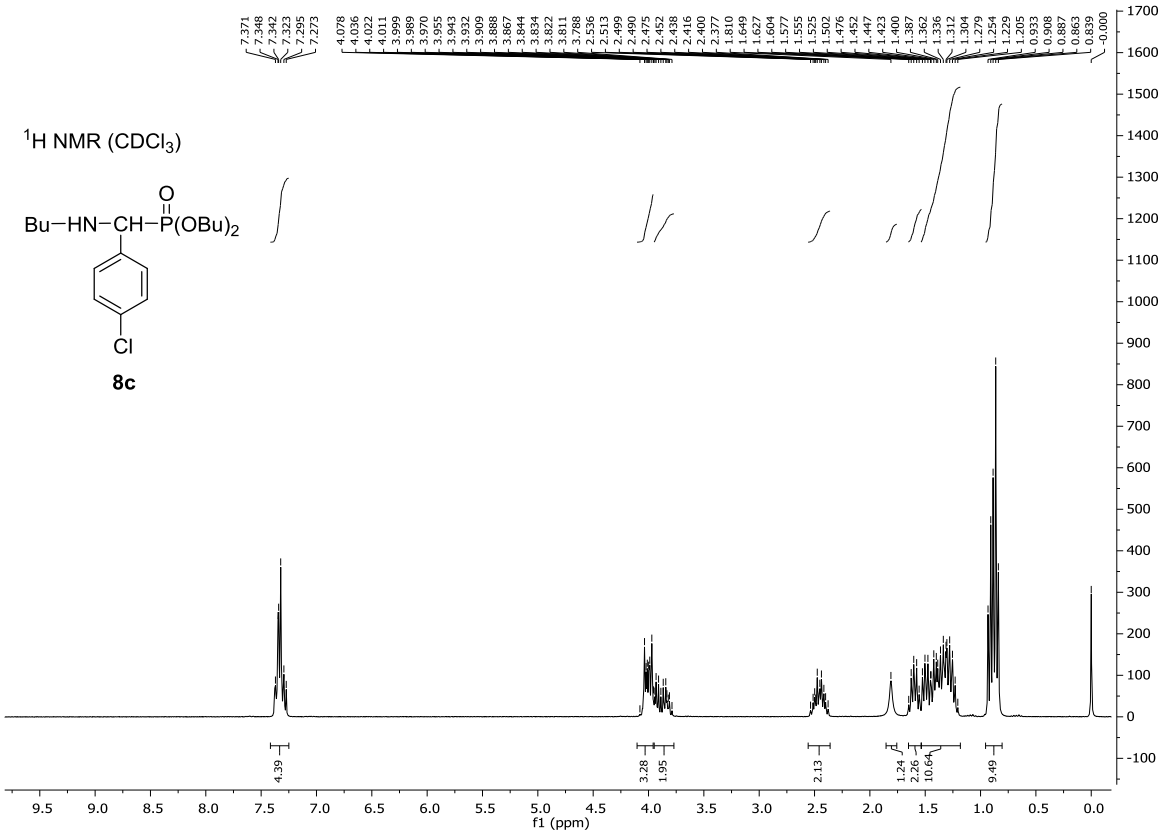


8c

^{13}C NMR ($CDCl_3$)



8c


^{1}H NMR ($CDCl_3$)
Bu−HN−CH−P(OBu)$_2$
O
Cl
8c
f1 (ppm)

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