Supplementary Information

Phosphazene base-catalyzed telescopic three-component reaction involving 1,1-difunctionalization of electron-deficient alkenes

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Contents

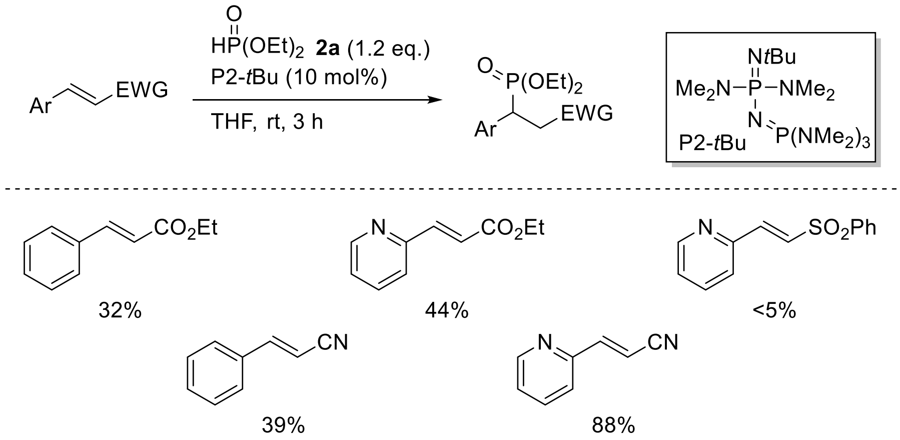
General Information

Unless otherwise noted, the reactions were carried out with dried glassware under argon atmosphere. ^{1}H NMR spectra were recorded on a JEOL JNM-ECA600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: 7.26 ppm, TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on a JEOL JNM-ECA600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). ^{31}P NMR spectra were recorded on a JEOL JNM-ECA600 (243 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with 85% H_3PO_4 solution as an external standard (0.0 ppm in $CDCl_3$). ^{19}F NMR spectra were recorded on a JEOL JNM-ECA600 (565 MHz) spectrometer. Chemical shifts are reported in ppm from the $C_6F_5CF_3$ (-67.2 ppm) resonance as the external standard. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was performed on silica gel 60N (spherical, neutral, 40-50 μm; Kanto Chemical Co., Inc.). Gel permeation chromatography (GPC) was performed on JAI LaboACE LC-7080 Plus with JAIGEL-2HR-40. Optically rotations were measured on a Jasco P-1020 digital polarimeter with a sodium lamp and reported as follows; $[\alpha]^{T°C}{}_{D}$ (c = g/100 mL, solvent). HPLC was performed on JASCO HPLC systems consisting of the following: pump, PU-2080 plus; degasser, DG-2080-53; mixer, MX-2080-32; UV/Vis detector, UV2077 plus; CD detector, CD-2095; Oven, CO-2067 plus. SFC was performed on JASCO SFC systems consisting of the following: HPLC pump, PU-2080 plus; CO_2 delivery pump, PU-2080-CO_2 plus; solvent selection unit, LV-2080-03; Back Pressure Regulators, BP-2080 and BP-2080 plus; Photodiode detector, MD-2018 plus; Oven, CO-4065. Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. High resolution mass spectra analysis was performed on a Bruker Daltonics solariX 9.4T FT-ICR-MS spectrometer at Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

Materials: Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., LTD., Merck KGaA, and other commercial suppliers and were used without purification. Dichloromethane, diethyl ether, tetrahydrofuran and toluene were supplied from Kanto Chemical Co., Inc. as "Dehydrated solvent system". Other solvents were purchased from commercial suppliers as dehydrated solvents, and used under argon atmosphere.

Additional Experimental Results

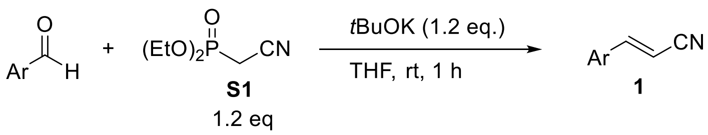
Preliminary Screening of Electron-deficient Alkenes



Experimental Procedure

Substrate Synthesis

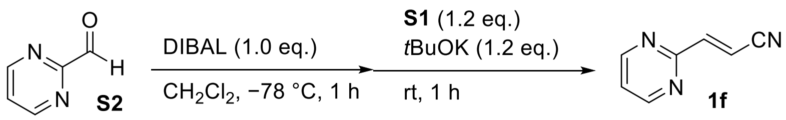
General Procedure for Synthesis of Cinnamonitrile Derivative 1



Synthesis of **1a** (Ar = 2-pyridyl, R = Ph) is representative.

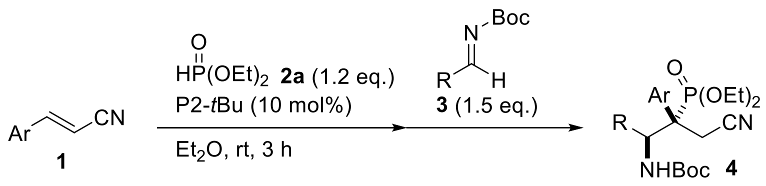
To a solution of 2-pyridinecarboxaldehyde (0.48 mL, 5.0 mmol) in THF (13 mL) were sequentially added **S1** (0.93 mL, 6.0 mmol) and *t*BuOK (0.67 g, 6.0 mmol) at 0 °C. After stirring at room temperature for 1 h, the reaction was quenched with sat. aq. NH_4Cl. The product was extracted with AcOEt. The combined organic layer was dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/AcOEt = 2/1) to afford **1a** (0.44 g, 3.4 mmol, 68%) as a white solid.

*Synthesis of **1f***



To a solution of methyl pyrimidine-2-carboxylate (**S2**, 0.41 g, 3.0 mmol) in CH_2Cl_2 (40 mL) was added DIBAL (1.0 M in hexane, 3.0 mL, 3.0 mmol) at −78 °C. After stirred at −78 °C for 1 h, **S2** (0.56 mL, 3.6 mmol) and *t*BuOK (0.41 g, 3.6 mmol) were added to the solution. The resulting mixture was then warmed to room temperature and stirred at that temperature for 1 h. The reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt = 2/1) to afford **1f** (50 mg, 0.39 mmol, 13%) as a white solid.

General Procedure for Telescopic Three Component Reaction of Diethyl phosphite, Cinnamonitrile Derivatives, and *N*-Boc Imine

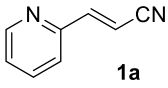
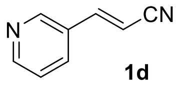


The reaction of **1a** (Ar = 2-pyridyl), **2a**, and **3a** (R =Ph) is representative (Table 1, entry 12).

To a solution of diethyl phosphite (**2a**, 17 mg, 0.12 mmol) and **1a** (13 mg, 0.10 mmol) in Et_2O (1.0 mL) was added a solution of P2-*t*Bu (2.0 M in THF, 5.0 µL, 0.010 mmol) at room temperature. The reaction mixture was stirred at room temperature for 3 h. **3a** (31 mg, 0.15 mmol) was then added, and the resulting mixture was further stirred at room temperature for 3 h. The reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt = 1/1). Further purification was carried out by using preparative HPLC, and **4aa** (33 mg, 0.070 mmol, 70%) was isolated as a white solid.

Analytical Data

^{1}H NMR data of **1a**,[S1] **1d**,[S1] **1e**,[S1] **1f**,[S2] **1h**,[S3] **1i**[S1] and **1j**[S1] were identical with those reported in literature.


1a

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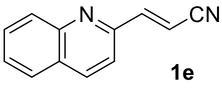
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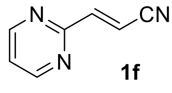
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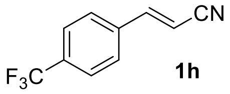
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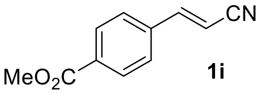
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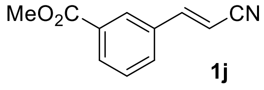
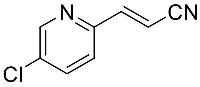
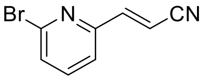

1j

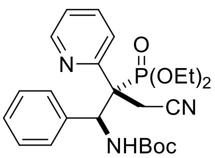
(*E*)-3-(5-Chloropyridin-2-yl)acrylonitrile (1b):


White solid; ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.57 (d, J = 16.2 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.37 (d, J = 16.2 Hz, 1H), 7.73 (dd, J = 8.4, 2.4 Hz, 1H), 8.57 (d, J = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 101.3, 117.6, 124.7, 133.5, 136.5, 147.1, 149.1, 149.3; IR (ATR): 3055, 2213, 1554, 1461, 1369, 1269, 1105, 1012, 957, 857, 816, 737 cm^{-1}; HRMS (ESI) Calcd for $C_8H_5ClN_2$ [M+Na]$^+$ 187.0033, Found 187.0033; Mp. 100.0-102.0 °C.

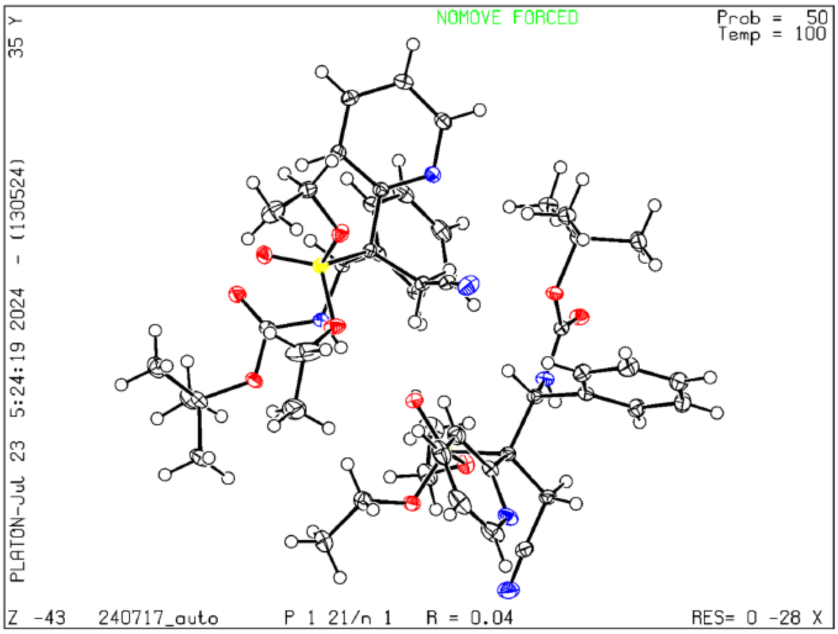
(*E*)-3-(6-Bromopyridin-2-yl)acrylonitrile (1c):


White solid; ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.62 (d, J = 16.2 Hz, 1H), 7.29 (d, J = 7.2 Hz, 1H), 7.31 (d, J = 16.2 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.61 (dd, J = 7.8, 7.2 Hz, 1H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 102.3, 117.4, 123.1, 129.6, 139.2, 142.8, 146.6, 152.0; IR (ATR): 3020, 2217, 1626, 1544, 1406, 1266, 1122, 960, 898, 747, 682 cm^{-1}; HRMS (ESI) Calcd for $C_8H_5BrN_2$ [M+Na]$^+$ 230.9528, Found 230.9528; Mp. 130.0-132.0 °C.

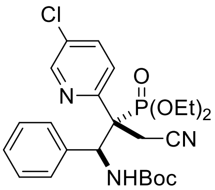
(3*R,4*S**)-4-(*tert*-Butoxycarbonylamino)-3-diethoxyphosphoryl-4-phenyl-3-(pyridin-2-yl)butylonitrile (4aa):**


White solid; ^{1}H NMR (600 MHz, CDCl$_3$) δ 1.10-1.20 (m, 6H), 1.32 (s, 9H), 2.89 (dd, J = 15.0, 11.4 Hz, 1H), 3.28 (dd, J = 21.6, 16.2 Hz, 1H), 3.73-3.97 (m, 1H), 3.99-4.23 (m, 3H), 5.24 (dd, J = 18.6, 7.8 Hz, 1H), 6.76 (d, J = 6.6 Hz, 1H), 7.10 (brs, 2H), 7.19-7.24 (m, 3H), 7.26 (dd, J = 7.8, 5.4 Hz, 1H), 7.73 (dd, J = 7.8, 7.2, 1.8 Hz, 1H), 7.97 (d, J = 7.8 Hz, 1H), 8.54-8.59 (m, 1H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 15.9 (d, J = 7.2 Hz), 16.2 (d, J = 5.7 Hz), 21.5 (d, J = 2.9 Hz), 28.3, 53.7 (d, J = 139.2 Hz), 60.5, 62.5 (d, J = 7.2 Hz), 64.0 (d, J = 8.7 Hz), 79.6, 118.1 (d, J = 4.4 Hz), 122.9, 124.3, 127.9 (2C), 128.1, 136.0, 137.3, 148.7, 154.5, 154.9; ^{31}P NMR (243 MHz, CDCl$_3$) δ 24.3; IR (ATR): 2976, 2935, 1716, 1585, 1507, 1366, 1241, 1166, 1019, 792, 775 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{32}N_3O_5P$ [M+Na]$^+$ 496.1972, Found 496.1972; Mp. 133.0-135.0 °C.

ORTEP drawing of (3*R**,4*S**)-**4aa** showing thermal elipsoids at the 50% probability level. CCDC No. 2374658. Recrystallization from hexane/toluene.

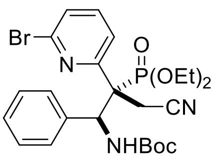


4-(*tert*-Butoxycarbonylamino)-3-(5-chloropyridin-2-yl)-3-diethoxyphosphoryl-4-phenylbutylonitrile (4ba):



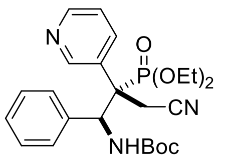
83:17 Diastereomer mixture; White solid; ^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer* δ 1.14 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.32 (s, 9H), 2.89 (dd, *J* = 15.0, 10.2 Hz, 1H), 3.28 (dd, *J* = 22.8, 16.8 Hz, 1H), 3.90-4.23 (m, 4H), 5.15 (dd, *J* = 20.4, 8.4 Hz, 1H), 6.70 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 3.0 Hz, 2H), 7.23-7.26 (m, 3H), 7.71 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 2.4 Hz, 1H); *minor diastereomer* δ 1.04 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H), 1.30 (s, 9H), 3.08 (dd, *J* = 15.0, 13.2 Hz, 1H), 3.20-3.30 (m, 1H), 3.42-3.53 (m, 1H), 3.80-4.20 (m, 3H), 5.86 (brs, 1H), 6.28 (brs, 1H), 7.20-7.30 (m, 5H), 7.69 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.80 (brs, 1H), 8.64 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) *major diastereomer* δ 15.9 (d, *J* = 7.2 Hz), 16.2 (d, *J* = 5.9 Hz), 21.7, 28.3, 53.4 (d, *J* = 142.2 Hz), 60.5, 62.7 (d, *J* = 5.7 Hz), 64.0 (d, *J* = 7.2 Hz), 79.8, 117.7 (d, *J* = 4.4 Hz), 125.2, 128.0, 128.06, 128.13, 131.6, 135.7, 137.0, 147.6, 153.2, 154.4; *minor diastereomer* δ 15.9 (d, *J* = 5.9 Hz), 16.1 (d, *J* = 5.9 Hz), 20.5, 28.2, 53.4 (d, *J* = 142.2 Hz), 58.2, 62.9 (d, *J* = 7.2 Hz), 63.5 (d, *J* = 7.2 Hz), 79.8, 117.7 (d, *J* = 4.4 Hz), 125.2, 128.1, 128.2, 128.4, 131.7, 136.1, 137.9, 147.5, 152.4 (d, *J* = 4.5 Hz), 154.7; ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer* δ 23.9; *minor diastereomer* δ 23.1; IR (ATR): 2976, 2935, 1716, 1503, 1461, 1369, 1248, 1137, 1162, 1012, 967, 778, 706 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{31}ClN_3O_5P$ $[M+Na]^+$ 530.1581, Found 530.1581; Mp. 72.0-74.0 °C.

(3*R,4*S**)-3-(6-Bromopyridin-2-yl)-4-(*tert*-butoxycarbonylamino)-3-diethoxyphosphoryl-4-phenylbutylonitrile (4ca):**



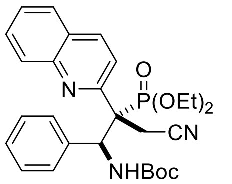
Major diastereomer; White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.14 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 9H), 2.88 (dd, *J* = 16.2, 10.8 Hz, 1H), 3.20 (dd, *J* = 21.6, 16.8 Hz, 1H), 3.91-4.00 (m, 1H), 4.01-4.13 (m, 2H), 4.14-4.25 (m, 1H), 5.21 (dd, *J* = 20.4, 8.4 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 7.14-7.20 (m, 2H), 7.24-7.26 (m, 3H), 7.46 (d, J = 7.8 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.88 (d, J = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.9 (d, J = 7.2 Hz), 16.2 (d, J = 4.4 Hz), 21.7 (d, J = 4.4 Hz), 28.3, 53.5 (d, J = 140.7 Hz), 60.4, 62.7 (d, J = 7.2 Hz), 64.2 (d, J = 5.7 Hz), 79.7, 117.4 (d, J = 4.2 Hz), 123.0, 127.5, 128.0, 128.1, 128.2, 137.0, 138.4, 140.8, 154.5, 156.5; ^{31}P NMR (243 MHz, $CDCl_3$) δ 23.5; IR (ATR): 2987, 2928, 1716, 1575, 1499, 1437, 1362, 1252, 1159, 1019, 778 cm^{-1} ; HRMS (ESI) Calcd for $C_{24}H_{31}BrN_3O_5P$ [M+Na]$^+$ 574.1076, Found 574.1076; Mp. 77.0-79.0 °C.

(3*S,4*S**)-4-(*tert*-Butoxycarbonylamino)-3-diethoxyphosphoryl-4-phenyl-3-(pyridin-3-yl)butylonitrile (4da):**



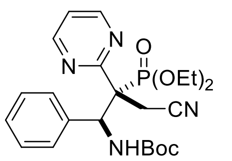
White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.19 (t, J = 7.2 Hz, 6H), 1.33 (s, 9H), 2.92-3.12 (m, 2H), 3.87-3.99 (m, 1H), 4.03-4.21 (m, 3H), 5.15 (dd, J = 16.8, 8.4 Hz, 1H), 6.59 (brs, 1H), 7.03 (brs, 2H), 7.21-7.26 (m, 3H), 7.33 (dd, J = 7.8, 4.8 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H), 8.61 (d, J = 4.2 Hz, 1H), 8.69 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.9 (d, J = 5.7 Hz), 16.2 (d, J = 5.7 Hz), 20.9, 28.2, 49.4 (d, J = 137.9 Hz), 61.1, 62.9 (d, J = 5.7 Hz), 64.4 (d, J = 8.7 Hz), 80.1, 116.5 (d, J = 4.4 Hz), 123.1, 128.07, 128.14, 128.2, 131.7 (d, J = 4.4 Hz), 135.4, 136.5, 149.2, 149.3 (d, J = 4.4 Hz), 154.5; ^{31}P NMR (243 MHz, $CDCl_3$) δ 24.1; IR (ATR): 2983, 2941, 1716, 1507, 1245, 1217, 1159, 1050, 1015, 973, 775 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{32}N_3O_5P$ [M+Na]$^+$ 496.1971, Found 496.1971; Mp. 155.0-157.0 °C.

4-(*tert*-Butoxycarbonylamino)-3-diethoxyphosphoryl-4-phenyl-3-(quinolin-2-yl)butylonitrile (4ea):



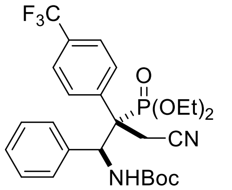
90:10 Diastereomer mixture; Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer* δ 1.12 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.2 Hz, 3H), 1.29 (s, 9H), 2.99 (dd, J = 15.6, 12.0 Hz, 1H), 3.40 (dd, J = 21.6, 16.2 Hz, 1H), 3.84-3.92 (m, 1H), 4.04-4.24 (m, 3H), 5.42 (dd, J = 17.4, 9.0 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 7.09 (d, J = 7.2 Hz, 2H), 7.13-7.20 (m, 3H), 7.57 (dd, J = 7.2 Hz, 1H), 7.71 (ddd, J = 7.8, 7.2, 1.2 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 8.12 (d, J = 9.0 Hz, 1H), 8.20 (d, J = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) *major diastereomer* δ 15.9 (d, J = 5.7 Hz), 16.2 (d, J = 5.9 Hz), 21.5, 28.2, 54.4 (d, J = 137.9 Hz), 60.1, 62.6 (d, J = 7.2 Hz), 63.9 (d, J = 7.2 Hz), 79.6, 118.3 (d, J = 4.4 Hz), 121.4, 127.0, 127.1, 127.2, 127.87, 127.92, 128.0, 129.66, 129.72, 136.0, 137.3, 146.9, 154.5, 154.9; ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer* δ 24.5; *minor diastereomer* δ 23.3; IR (ATR): 3343, 2980, 2945, 1688, 1520, 1252, 1166, 1022, 960, 833, 775, 702 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{34}N_3O_5P$ [M+Na]$^+$ 546.2128, Found 546.2128; Mp. 182.0-184.0 °C.

(3*R,4*S**)-4-(*tert*-Butoxycarbonylamino)-3-diethoxyphosphoryl-4-phenyl-3-(pyrimidin-2-yl)butylonitrile (4fa):**



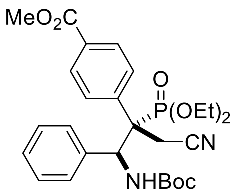
White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.06 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.26 (s, 9H), 2.85 (dd, J = 15.6, 9.0 Hz, 1H), 3.43 (dd, J = 22.8, 16.2 Hz, 1H), 3.95-4.09 (m, 2H), 4.12-4.19 (m, 1H), 4.40-4.46 (m, 1H), 5.32 (dd, J = 23.4, 9.6 Hz, 1H), 6.85 (d, J = 6.6 Hz, 1H), 7.19-7.29 (m, 6H), 8.80 (d, J = 4.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.7 (d, J = 7.2 Hz), 16.4 (d, J = 4.4 Hz), 22.7, 28.2, 56.1 (d, J =143.6 Hz), 61.1, 61.9 (d, J = 4.4 Hz), 64.6 (d, J = 7.2 Hz), 79.4, 117.6 (d, J = 2.9 Hz), 119.9, 128.0 (2C), 128.3, 137.4 (d, J = 2.8 Hz), 154.5, 156.8, 166.3; ^{31}P NMR (243 MHz, $CDCl_3$) δ 22.8; IR (ATR): 2983, 2941, 1709, 1564, 1507, 1410, 1245, 1162, 1060, 1022, 967, 709 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{31}N_4O_5P$ [M+Na]$^+$ 497.1924, Found 497.1924; Mp. 198.0-200.0 °C.

4-(*tert*-Butoxycarbonylamino)-3-diethoxyphosphoryl-4-phenyl-3-(4-trifluoromethyl)phenylbutylonitrile (4ha):



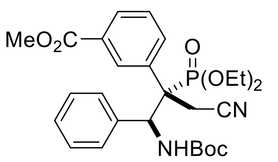
88:12 Diastereomer mixture; White solid; [1]H NMR (600 MHz, $CDCl_3$) *major diastereomer* δ 1.10-1.23 (m, 6H), 1.31 (s, 9H), 2.89-3.06 (m, 2H), 3.82-3.93 (m, 1H), 4.00-4.21 (m, 3H), 5.17 (dd, *J* = 17.4, 9.0 Hz, 1H), 6.53 (brs, 1H), 7.01 (brs, 2H), 7.16-7.25 (m, 3H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H); [13]C NMR (150 MHz, $CDCl_3$) *major diastereomer* δ 15.9 (d, *J* = 5.7 Hz), 16.2 (d, *J* = 5.9 Hz), 21.3, 28.2, 51.0 (d, *J* = 137.7 Hz), 61.2, 62.9 (d, *J* = 7.2 Hz), 64.4 (d, *J* = 7.1 Hz), 80.0, 116.7 (d, *J* = 4.4 Hz), 123.8 (q, *J* = 270.0 Hz), 125.3 (q, *J* = 3.0 Hz), 128.0, 128.1, 128.2, 128.6 (d, *J* = 5.7 Hz), 130.3 (q, *J* = 33.0 Hz), 136.6, 139.7, 154.5; [19]F NMR (565 MHz, $CDCl_3$) *major diastereomer* δ –62.65; *minor diastereomer* δ –62.67; [31]P NMR (243 MHz, $CDCl_3$) *major diastereomer* δ 24.1; *minor diastereomer* δ 23.1; IR (ATR): 2979, 2928, 1717, 1691, 1500, 1330, 1243, 1166, 1122, 1015, 767, 708 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{32}F_3N_2O_5P$ $[M+Na]^+$ 563.1893, Found 563.1893; Mp. 207.0-209.0 °C.

4-(*tert*-Butoxycarbonylamino)-3-diethoxyphosphoryl-3-(4-methoxycarbonyl)phenyl-4-phenylbutylonitrile (4ia):



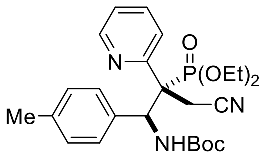
88:12 Diastereomer mixture; White solid; [1]H NMR (600 MHz, $CDCl_3$) *major diastereomer* δ 1.15 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.34 (s, 9H), 2.87-3.03 (m, 2H), 3.77-3.87 (m, 1H), 3.94 (s, 3H), 4.06-4.20 (m, 3H), 5.29 (dd, *J* = 13.8, 7.8 Hz, 1H), 6.49 (brs, 1H), 6.93 (brs, 2H), 7.16 (dd, *J* = 7.2, 6.6 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 2H); [13]C NMR (150 MHz, $CDCl_3$) *major diastereomer* δ 16.0 (d, *J* = 5.7 Hz), 16.2 (d, *J* = 5.7 Hz), 20.8, 28.2, 51.0 (d, *J* = 137.9 Hz), 52.3, 60.9, 62.9 (d, *J* = 5.7 Hz), 64.4 (d, *J* = 7.2 Hz), 80.0, 116.9 (d, *J* = 2.9 Hz), 127.9, 127.96, 128.03, 128.2 (d, J = 5.7 Hz), 129.6, 129.8, 136.6, 140.6 (d, *J* = 2.9 Hz), 154.5, 166.4; [31]P NMR (243 MHz, $CDCl_3$) *major diastereomer* δ 24.2; *minor diastereomer* δ 23.2; IR (ATR): 2992, 2941, 1726, 1702, 1507, 1307, 1366, 1248, 1166, 1046, 1012, 964, 826, 770, 702, 651 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{35}N_2O_7P$ $[M+Na]^+$ 553.2073, Found 553.2073; Mp. 188.0-190.0 °C.

4-(*tert*-Butoxycarbonylamino)-3-diethoxyphosphoryl-3-(3-methoxycarbonyl)phenyl-4-phenylbutylonitrile (4ja):



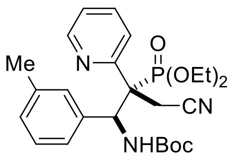
80:20 Diastereomer mixture; White solid; [1]H NMR (600 MHz, $CDCl_3$) *major diastereomer* δ 1.17 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 9H), 2.89-3.03 (m, 2H), 3.80-3.91 (m, 1H), 3.94 (s, 3H), 4.05-4.21 (m, 3H), 5.24 (dd, *J* = 15.6, 7.8 Hz, 1H), 6.62 (brs, 1H), 6.97 (d, *J* = 5.4 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 8.07 (dd, *J* = 8.4, 0.6 Hz, 1H), 8.23 (s, 1H); *minor diastereomer* δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H), 1.27 (s, 9H), 3.10-3.25 (m, 2H), 3.67-3.70 (m, 1H), 3.80-4.20 (m, 3H), 3.94 (s, 3H), 5.74 (d, *J* = 2.4 Hz, 1H), 5.90 (brs, 1H), 7.28-7.35 (m, 5H), 7.54 (t, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 8.05 (dd, *J* = 7.8, 0.6 Hz, 1H), 8.23 (s, 1H); [13]C NMR (150 MHz, $CDCl_3$) *major diastereomer* δ 16.0 (d, *J* = 5.7 Hz), 16.2 (d, *J* = 5.7 Hz), 21.0, 28.2, 50.6 (d, *J* = 137.9 Hz), 52.3, 61.1, 62.9 (d, *J* = 7.2 Hz), 64.3 (d, *J* = 7.2 Hz), 79.8, 116.9 (d, *J* = 4.2 Hz), 127.96, 128.03 (2C), 128.6, 128.9 (d, *J* = 5.7 Hz), 129.4, 130.4, 132.7 (d, *J* = 4.4 Hz), 136.1 (d, *J* = 4.2 Hz), 136.7 (d, *J* = 5.7 Hz), 154.5, 166.5; *minor diastereomer* δ 15.9 (d, *J* = 5.7 Hz), 16.0 (d, *J* = 5.7 Hz), 20.2, 28.1, 51.3 (d, *J* = 136.8 Hz), 52.3, 61.1, 62.5 (d, J = 7.0 Hz), 64.0 (d, J = 7.3 Hz), 80.0, 116.9 (d, J = 4.2 Hz), 127.8-128.1 (3C), 128.6, 128.7, 129.5, 130.5, 133.6 (d, J = 2.7 Hz), 134.6 (d, J = 4.4 Hz), 137.9 (d, J = 5.7 Hz), 154.7, 166.6; ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer* δ 24.4; *minor diastereomer* δ 23.5; IR (ATR): 2980, 2925, 1719, 1503, 1373, 1283, 1170, 1050, 1019, 964, 744, 709 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{35}N_2O_7P$ $[M+Na]^+$ 553.2074, Found 553.2074; Mp. 83.0-85.0 °C.

(3*R,4*S**)-4-(*tert*-Butoxycarbonylamino)-3-diethoxyphosphoryl-4-(4-methylphenyl)-3-(pyridin-2-yl)butylonitrile (4ab):**



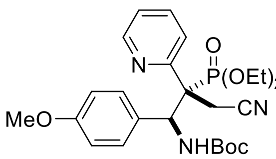
White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.15 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H), 1.32 (s, 9H), 2.28 (s, 3H), 2.88 (dd, J = 15.0, 10.8 Hz, 1H), 3.26 (dd, J = 22.8, 16.8 Hz, 1H), 3.82-3.94 (m, 1H), 4.04-4.22 (m, 3H), 5.22 (dd, J = 18.0, 7.8 Hz, 1H), 6.70 (d, J = 7.2 Hz, 1H), 6.94 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 7.8 Hz, 2H), 7.25 (dd, J = 7.2, 4.8 Hz, 1H), 7.73 (td, J = 7.8, 1.8 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 8.56 (d, J = 4.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.9 (d, J = 5.9 Hz), 16.2 (d, J = 5.7 Hz), 21.0, 21.3 (d, J = 2.9 Hz), 28.3, 53.7 (d, J = 139.3 Hz), 60.2, 62.5 (d, J = 7.2 Hz), 63.9 (d, J = 7.2 Hz), 79.5, 118.2 (d, J = 4.4 Hz), 122.8, 124.3, 127.9, 128.6, 134.2, 136.0, 137.5, 148.7, 154.5, 155.0; ^{31}P NMR (243 MHz, $CDCl_3$) δ 24.7; IR (ATR): 2983, 2935, 2310, 1716, 1513, 1430, 1366, 1241, 1032, 967, 775 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{34}N_3O_5P$ $[M+Na]^+$ 510.2128, Found 510.2128; Mp. 165.0-167.0 °C.

(3*R,4*S**)-4-(*tert*-Butoxycarbonylamino)-3-diethoxyphosphoryl-4-(3-methylphenyl)-3-(pyridin-2-yl)butylonitrile (4ac):**



Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.17 (t, J = 7.2 Hz, 6H), 1.32 (s, 9H), 2.24 (s, 3H), 2.86 (dd, J = 14.4, 11.4 Hz, 1H), 3.28 (dd, J = 22.8, 16.8 Hz, 1H), 3.86-3.92 (m, 1H), 4.02-4.22 (m, 3H), 5.18 (dd, J = 19.2, 8.4 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 6.85 (s, 1H), 6.90 (d, J = 6.6 Hz, 1H), 7.03 (d, J = 7.8 Hz, 1H), 7.10 (dd, J = 7.8, 7.2 Hz, 1H), 7.26 (dd, J = 7.8, 5.4 Hz, 1H), 7.73 (ddd, J = 7.8, 7.2, 1.2 Hz, 1H), 7.97 (d, J = 7.8 Hz, 1H), 8.57 (d, J = 4.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.9 (d, J = 5.7 Hz), 16.2 (d, J = 5.9 Hz), 21.4, 21.5 (d, J = 4.4 Hz), 28.3, 53.6 (d, J = 140.9 Hz), 60.5, 62.5 (d, J = 7.2 Hz), 63.9 (d, J = 8.7 Hz), 79.5, 118.1 (d, J = 4.4 Hz), 122.8, 124.4, 125.1, 127.8, 128.6, 128.8, 135.9, 137.1, 137.4, 148.7, 154.5, 155.0; ^{31}P NMR (243 MHz, $CDCl_3$) δ 24.6; IR (ATR): 2980, 2935, 1712, 1509, 1366, 1245, 1166, 1050, 1015, 970, 788 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{34}N_3O_5P$ $[M+Na]^+$ 510.2128, Found 510.2128; Mp. 131.0-133.0 °C.

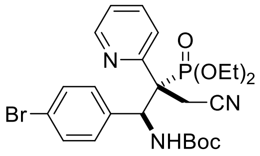
(3*R,4*S**)-4-(*tert*-Butoxycarbonylamino)-3-diethoxyphosphoryl-4-(4-methoxyphenyl)-3-(pyridin-2-yl)butylonitrile (4ad):**



White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.15 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H), 1.33 (s, 9H), 2.89 (dd, J = 14.4, 11.4 Hz, 1H), 3.25 (dd, J = 22.2, 16.8 Hz, 1H), 3.76 (s, 3H), 3.82-3.93 (m, 1H), 4.05-4.20 (m, 3H), 5.20 (dd, J = 18.0, 7.8 Hz, 1H), 6.66-6.75 (m, 1H), 6.73 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 7.26 (dd, J = 7.8, 4.8 Hz, 1H), 7.73 (td, J = 7.8, 1.8 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.90 (dd, J = 4.2, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, CDCl3) δ 16.0 (d, J = 7.2 Hz), 16.2 (d, J = 5.7 Hz), 21.4 (d, J = 4.2 Hz), 28.3, 53.7 (d, J = 139.2 Hz), 55.2, 60.0, 62.5 (d, J = 7.2 Hz), 63.9 (d, J = 8.7 Hz), 79.5, 113.2, 118.2 (d, J = 4.2 Hz), 122.9, 124.3, 129.2, 129.4, 136.0, 148.7, 154.5, 155.0, 159.1; ^{31}P NMR (243 MHz, $CDCl_3$) δ 24.7; IR (ATR): 2983, 2932, 1716, 1585, 1513, 1366, 1248, 1166, 1022, 967, 788 cm^{-1}; HRMS

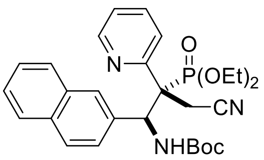
(ESI) Calcd for $C_{25}H_{34}N_3O_6P$ $[M+Na]^+$ 526.2077, Found 526.2077; Mp. 140.0-142.0 °C.

(3*R,4*S**)-4-(4-Bromophenyl)-4-(*tert*-butoxycarbonylamino)-3-diethoxyphosphoryl-3-(pyridin-2-yl)butylonitrile (4ae):**



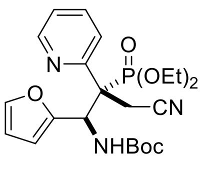
White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.17 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H), 1.34 (s, 9H), 2.92 (dd, J = 14.4, 12.0 Hz, 1H), 3.22 (dd, J = 21.0, 16.2 Hz, 1H), 3.82-3.95 (m, 1H), 4.05-4.20 (m, 3H), 5.26 (dd, J = 16.8, 8.4 Hz, 1H), 6.75 (d, J = 6.0 Hz, 1H), 6.93 (d, J = 8.4 Hz, 2H), 7.28 (dd, J = 7.2, 5.4 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.74 (td, J = 7.8, 1.8 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 8.57 (d, J = 3.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.0 (d, J = 5.7 Hz), 16.2 (d, J = 5.7 Hz), 21.3, 28.3, 53.3 (d, J = 139.2 Hz), 59.9, 62.7 (d, J = 7.2 Hz), 64.1 (d, J = 7.2 Hz), 79.9, 117.9 (d, J = 4.2 Hz), 122.0, 123.1, 124.3, 129.8, 131.0, 136.2, 136.6, 148.8, 154.5, 154.6; ^{31}P NMR (243 MHz, $CDCl_3$) δ 24.2; IR (ATR): 2980, 2941, 1716, 1599, 1507, 1245, 1159, 1028, 1008, 977, 795 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{31}BrN_3O_5P$ $[M+Na]^+$ 574.1077, Found 574.1077; Mp. 183.0-185.0 °C.

4-(*tert*-Butoxycarbonylamino)-3-diethoxyphosphoryl-4-(2-naphthyl)-3-(pyridin-2-yl)butylonitrile (4af):



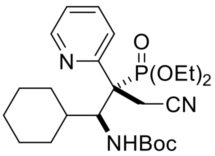
83:17 Diastereomer mixture; White solid; ^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer* δ 1.07 (t, J = 7.2 Hz, 3H), 1.16 (t, J = 5.7 Hz, 3H), 1.33 (s, 9H), 2.93 (dd, J = 15.0, 11.4 Hz, 1H), 3.32 (dd, J = 21.6, 16.2 Hz, 1H), 3.80-3.95 (m, 1H), 4.01-4.13 (m, 2H), 4.14-4.23 (m, 1H), 5.42 (dd, J = 18.6, 8.4 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.28 (dd, J = 7.2, 4.8 Hz, 1H), 7.43-7.46 (m, 2H), 7.58 (s, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.70-7.73 (m, 1H), 7.76-7.79 (m, 2H), 8.02 (d, J = 7.8 Hz, 1H), 8.56 (d, J = 4.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) *major diastereomer* δ 15.8 (d, J = 5.7 Hz), 16.2 (d, J = 5.9 Hz), 21.6 (d, J = 4.2 Hz), 28.3, 53.7 (d, J = 139.4 Hz), 60.7, 62.6 (d, J = 7.2 Hz), 64.0 (d, J = 7.2 Hz), 79.7, 118.0 (d, J = 4.4 Hz), 122.9, 124.3, 125.8, 126.1 (2C), 127.4 (2C), 127.5, 128.0, 132.7, 132.8, 134.8, 136.1, 148.8, 154.5, 155.0; ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer* δ 24.6; *minor diastereomer* δ 23.6; IR (ATR): 2976, 1712, 1589, 1507, 1369, 1241, 1162, 1015, 970, 861, 823, 747 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{34}N_3O_5P$ $[M+Na]^+$ 546.2128, Found 546.2128; Mp. 185.0-187.0 °C.

(3*R,4*S**)-4-(*tert*-Butoxycarbonylamino)-3-diethoxyphosphoryl-4-(2-furyl)-3-(pyridin-2-yl)butylonitrile (4ag):**



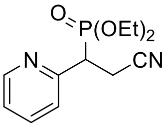
Brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.14 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H), 1.32 (s, 9H), 3.21 (dd, J = 16.8, 10.2 Hz, 1H), 3.45 (dd, J = 21.0, 16.8 Hz, 1H), 3.80-3.92 (m, 1H), 3.92-3.98 (m, 1H), 4.03-4.16 (m, 2H), 5.36 (dd, J = 22.2, 10.2 Hz, 1H), 6.16 (d, J = 3.0 Hz, 1H), 6.28 (dd, J = 3.0, 1.8 Hz, 1H), 6.47 (d, J = 8.4 Hz, 1H), 7.25 (dd, J = 6.6, 5.4 Hz, 1H), 7.31 (dd, J = 1.8, 1.2 Hz, 1H), 7.70 (td, J = 7.8, 1.8 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 8.61 (ddd, J = 4.8, 1.2, 0.6 Hz, 1H); ^{13}C NMR (150 MHz, CDCl3) δ 16.0 (d, J = 7.2 Hz), 16.1 (d, J = 5.9 Hz), 21.8 (d, J = 4.4 Hz), 28.2, 53.6 (d, J =142.2 Hz), 54.4, 62.6 (d, J = 7.2 Hz), 63.7 (d, J = 7.1 Hz), 79.8, 108.7, 110.3, 117.9 (d, J = 5.7 Hz), 122.9, 124.2, 136.0, 142.0, 148.7, 151.2 (d, J = 5.7 Hz), 154.4, 154.6; ^{31}P NMR (243 MHz, $CDCl_3$) δ 23.9; IR (ATR): 3429, 2983, 1723, 1513, 1375, 1239, 1156, 1052, 1012, 950, 781 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{30}N_3O_6P$ $[M+Na]^+$ 486.1764, Found 486.1764; Mp. 158.0-160.0 °C.

4-(*tert*-Butoxycarbonylamino)-4-cylohexyl-3-diethoxyphosphoryl-3-(pyridin-2-yl)butylonitrile (4ah):



86:14 Diastereomer mixture; White solid; ^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer* δ 0.81-1.10 (m, 6H), 1.15 (t, J = 7.2 Hz, 3H), 1.30-1.37 (m, 1H), 1.40 (t, J = 7.2 Hz, 3H), 1.44 (s, 9H), 1.49-1.60 (m, 3H),1.79-1.87 (m, 1H), 3.22 (dd, J = 16.8, 15.0 Hz, 1H), 3.43 (dd, J = 19.2, 16.8 Hz, 1H), 3.76-3.83 (m, 1H), 4.03-4.09 (m, 1H), 4.20-4.28 (m, 3H), 5.55 (d, J = 10.8 Hz, 1H), 7.24 (dd, J = 7.8, 4.8 Hz, 1H), 7.69 (td, J = 7.8, 1.8 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 8.59 (ddd, J = 4.8, 1.8, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, CDCl3) *major diastereomer* δ 16.2 (d, J = 5.9 Hz), 16.4 (d, J = 5.9 Hz), 21.2 (d, J = 4.4 Hz), 25.9, 26.0, 26.6, 28.2, 28.4, 33.3, 40.0 (d, J = 4.2 Hz), 53.3 (d, J = 140.7 Hz), 59.3, 62.9 (d, J = 7.2 Hz), 63.3 (d, J = 7.2 Hz), 79.3, 118.7 (d, J = 2.9 Hz), 122.8, 124.2, 136.3, 148.8, 155.5, 155.7; ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer* δ 25.3; *minor diastereomer* δ 25.6; IR (ATR): 2981, 1661, 1594, 1493, 1448, 1307, 1255, 1137, 1029, 1006, 968, 910, 829, 748, 690 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{38}N_3O_5P$ [M+Na]$^+$ 502.2441, Found 502.2441; Mp. 120.0-122.0 °C.

3-Diethoxyphosphoryl-3-(pyridin-2-yl)propionitrile (5a):



Brown oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.25 (t, J = 7.2 Hz, 3H), 7.26 (t, J = 7.2 Hz, 3H), 3.06 (ddd, J = 16.8, 9.6, 4.2 Hz, 1H), 3.40 (td, J = 16.8, 10.8 Hz, 1H), 3.67 (ddd, J = 22.8, 10.8, 4.8 Hz, 1H), 3.97-4.10 (m, 4H), 7.25 (m, 1H), 7.41 (dt, J = 7.8, 1.2 Hz, 1H), 7.70 (td, J = 7.8, 1.8 Hz, 1H), 8.62 (dd, J = 4.8, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.2 (d, J = 7.2 Hz), 16.3 (d, J = 5.7 Hz), 17.4, 43.0 (d, J = 138.0 Hz), 62.9 (d, J = 7.2 Hz), 63.1 (d, J = 7.2 Hz), 118.0 (d, J = 20.1 Hz), 122.9 (d, J = 2.9 Hz), 124.7 (d, J = 5.9 Hz), 136.7, 149.6, 152.8 (d, J = 7.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 23.3; IR (ATR): 2983, 2935, 2911, 2255, 1589, 1476, 1434, 1252, 1022, 960, 850, 799, 751 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{17}N_2O_3P$ [M+Na]$^+$ 291.0868, Found 291.0868.

References

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S2 K. Bhansali, S. Raut, S. Barange, P. Bhagat, *New. J. Chem.* **2020**, *44*, 19690-19712.

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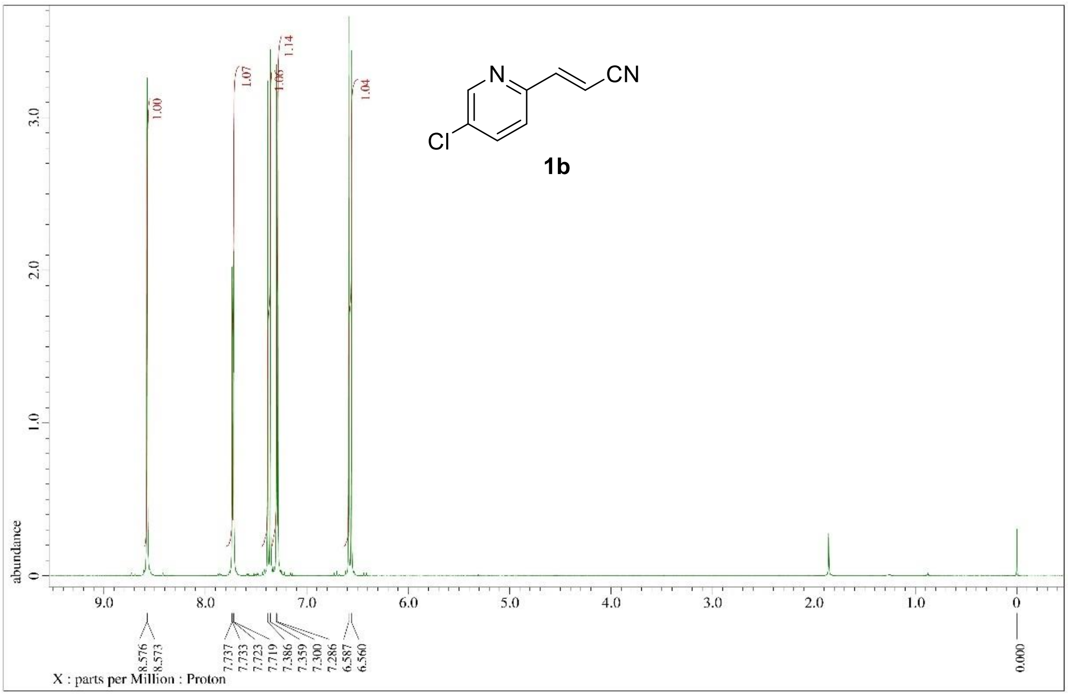
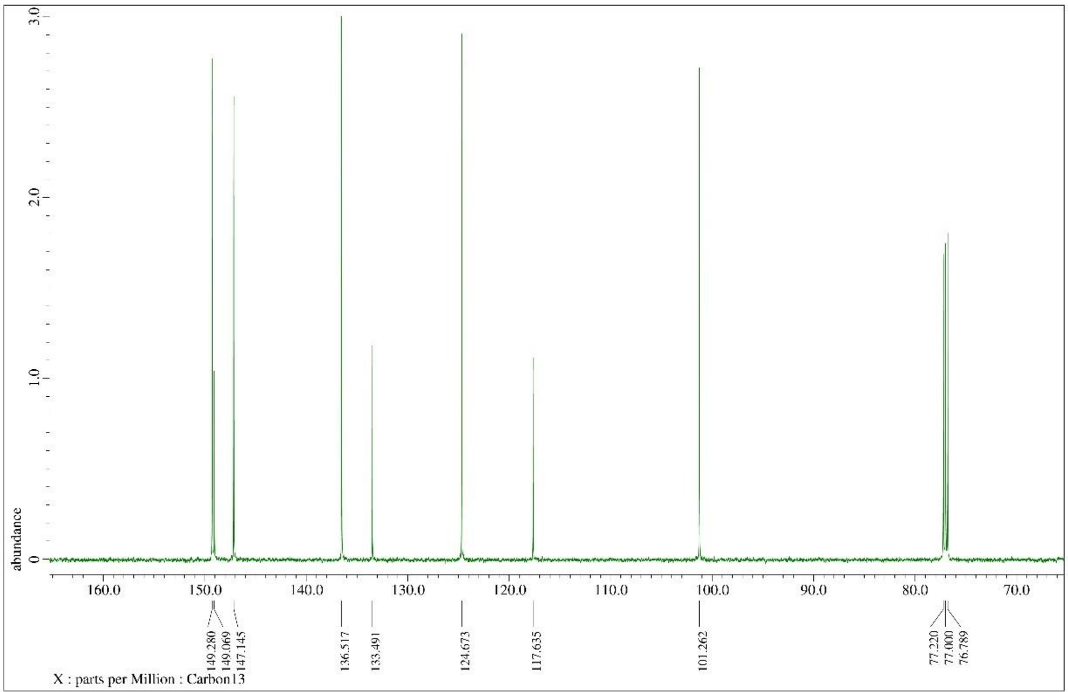
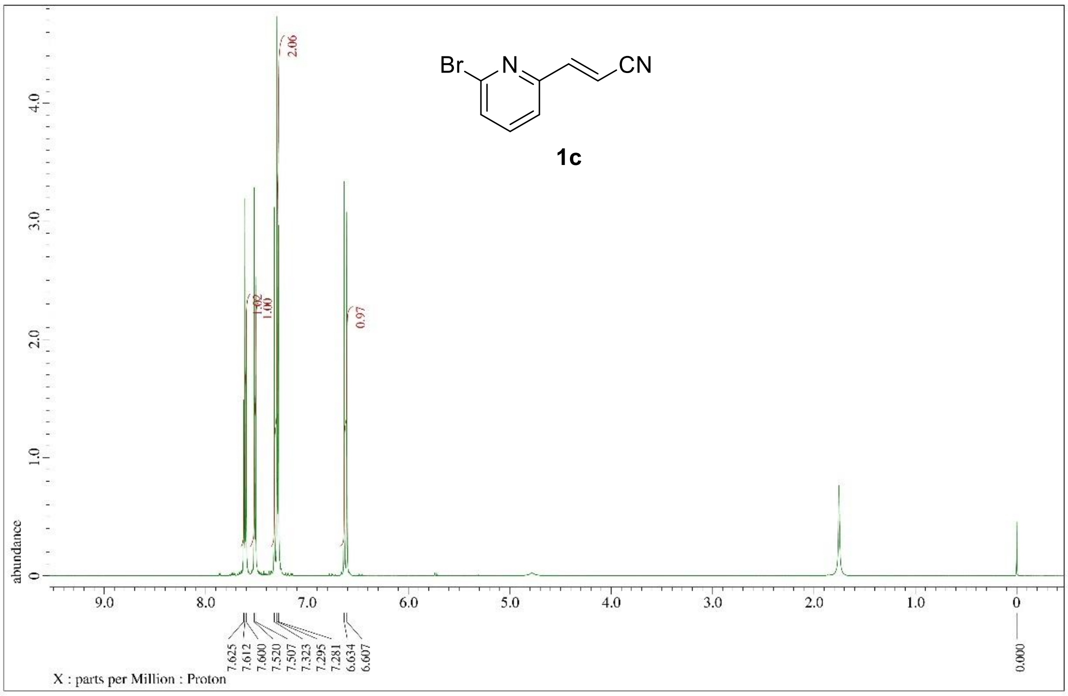


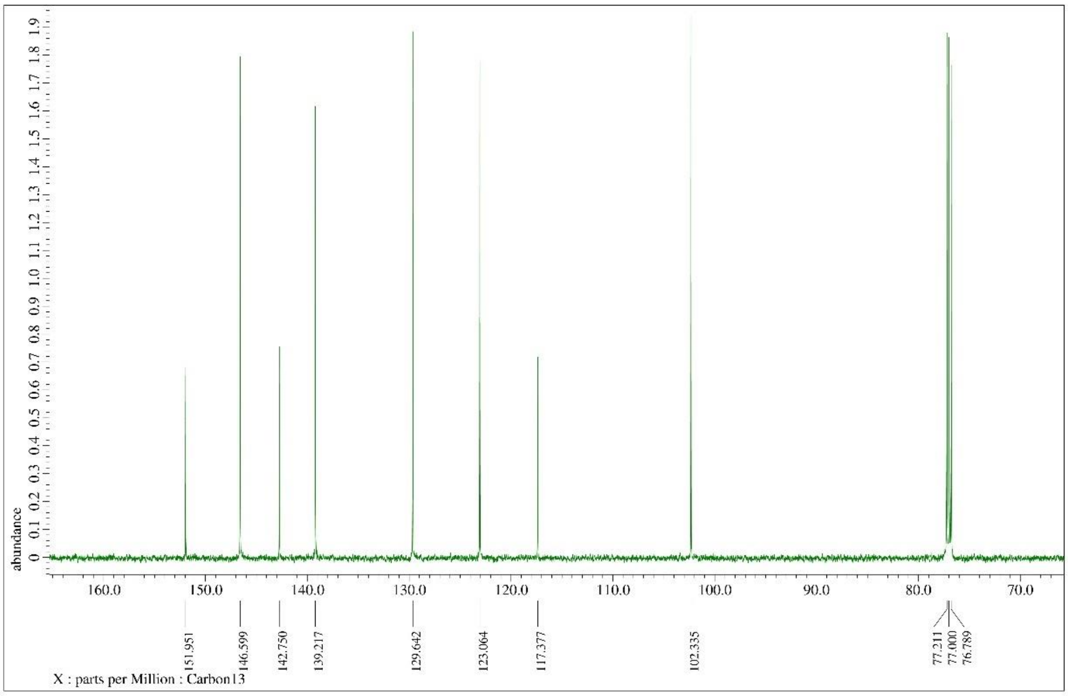
600 MHz, $CDCl_3$



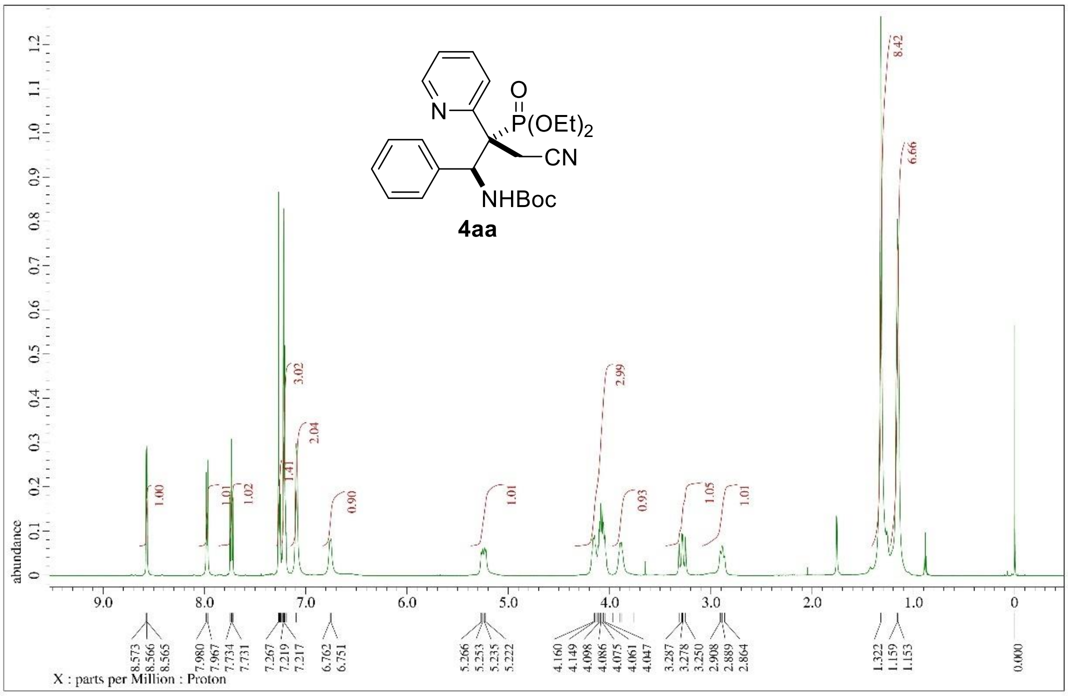
150 MHz, $CDCl_3$



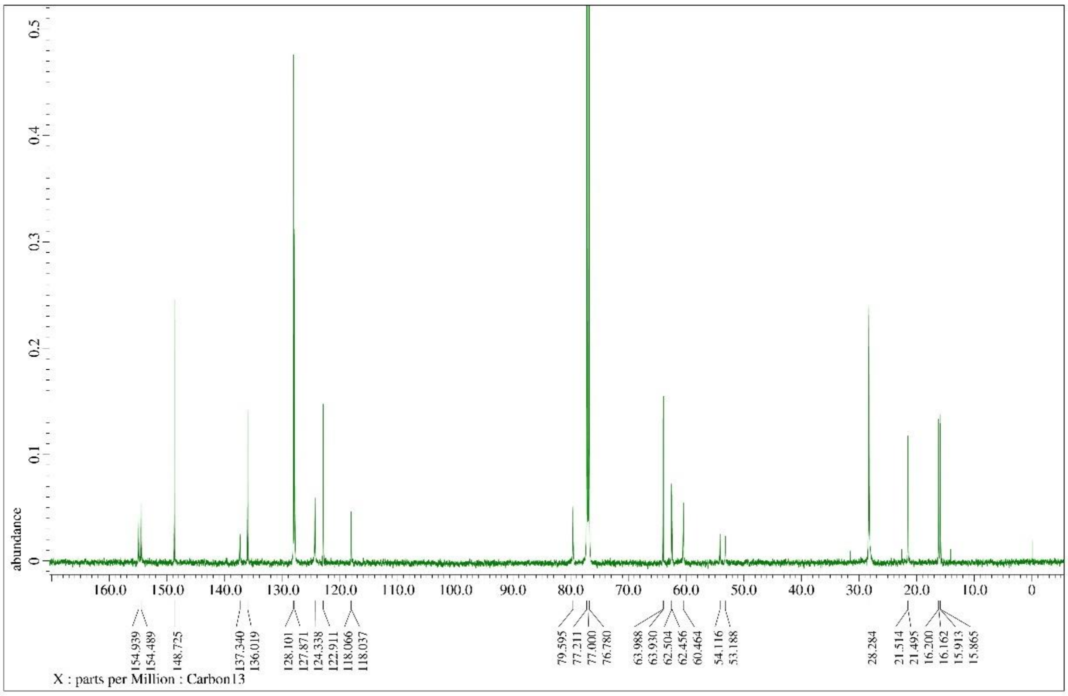
600 MHz, $CDCl_3$



150 MHz, $CDCl_3$



600 MHz, $CDCl_3$



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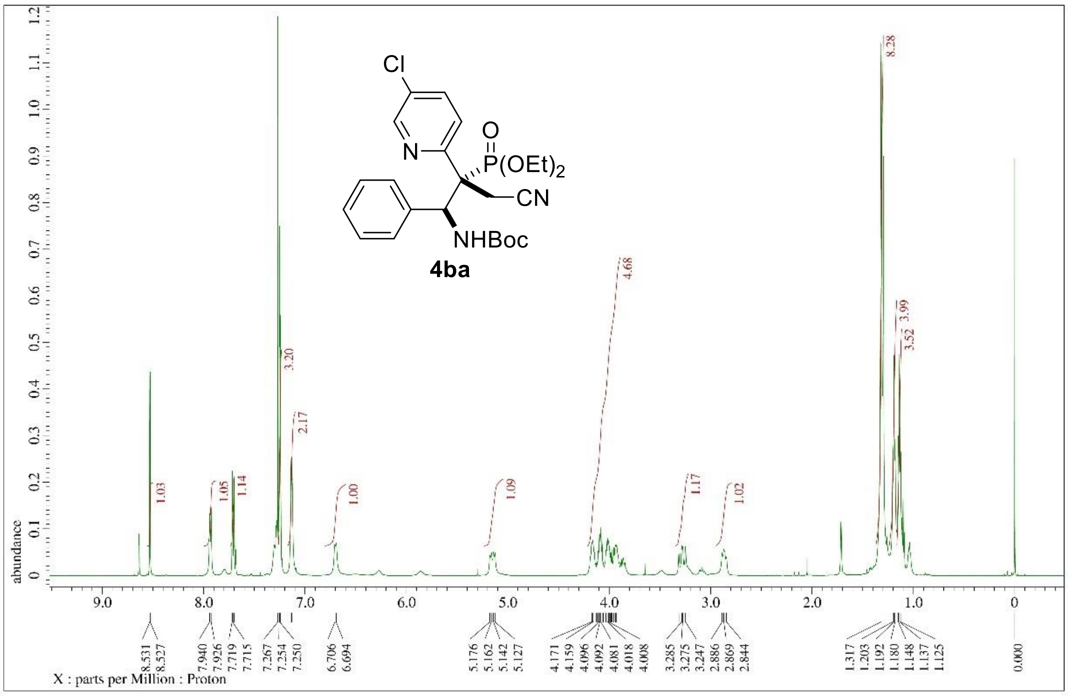
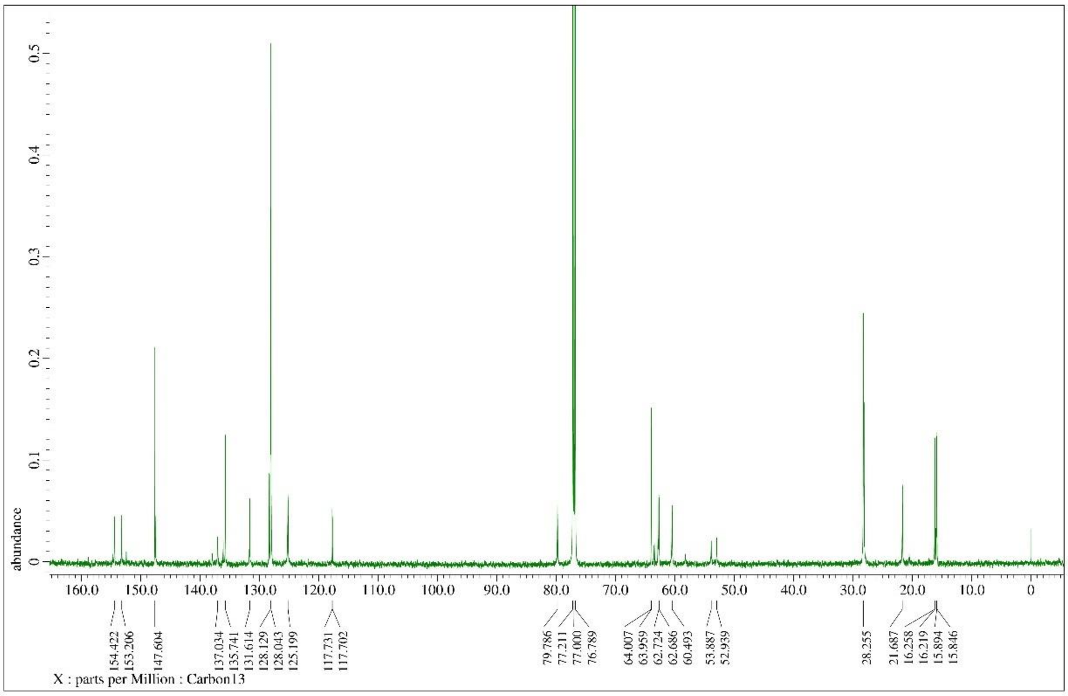


600 MHz, $CDCl_3$



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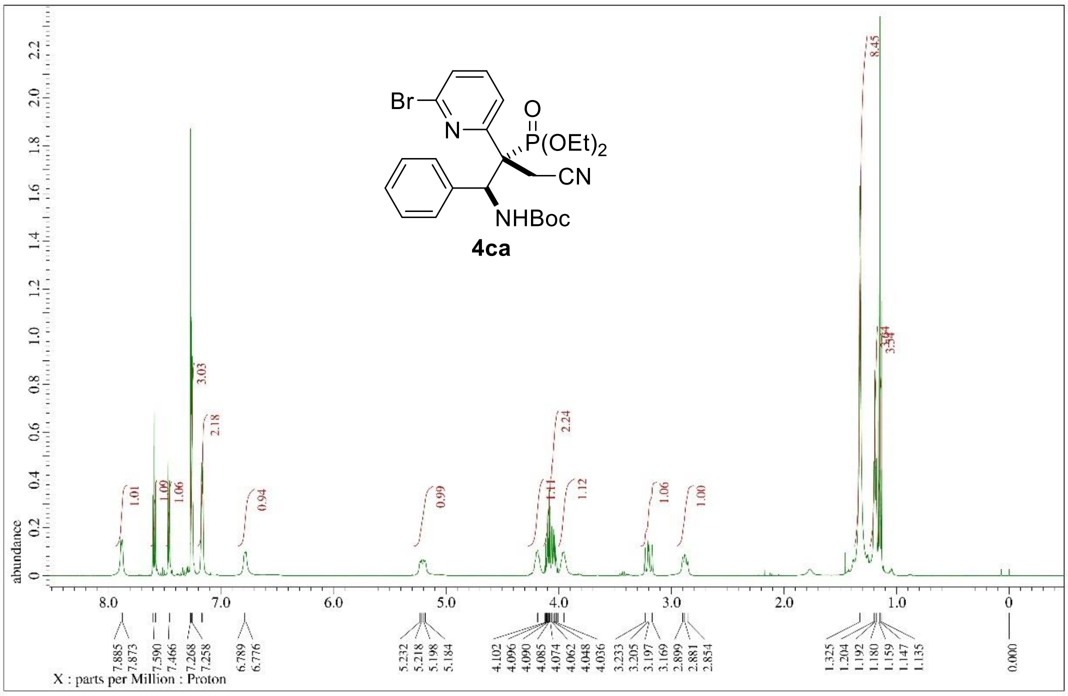

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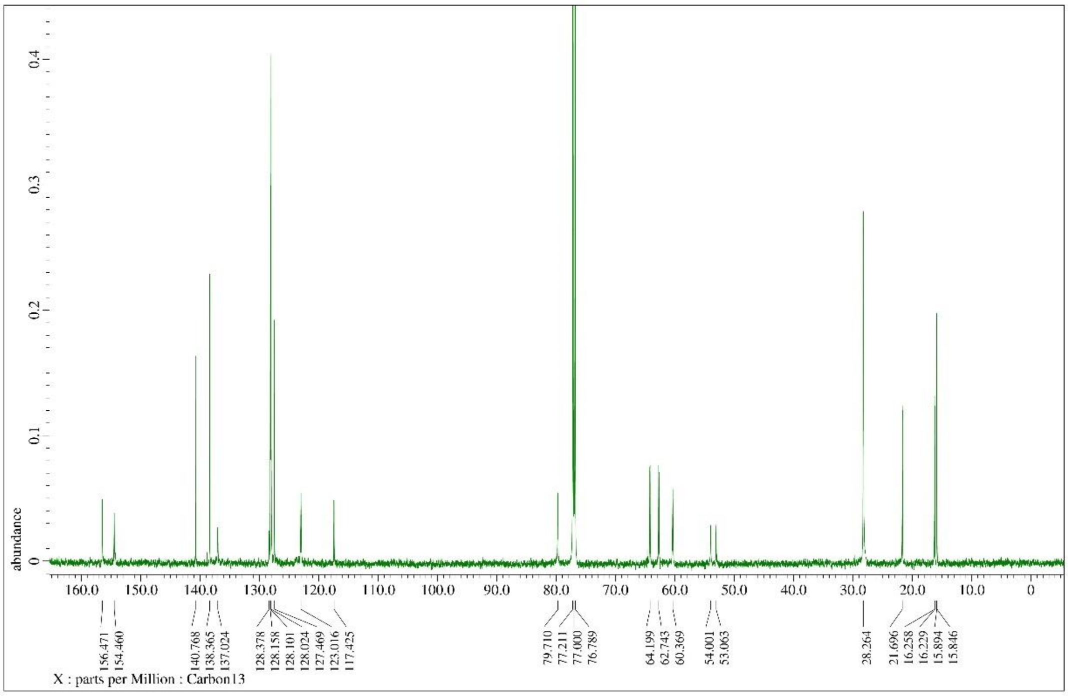
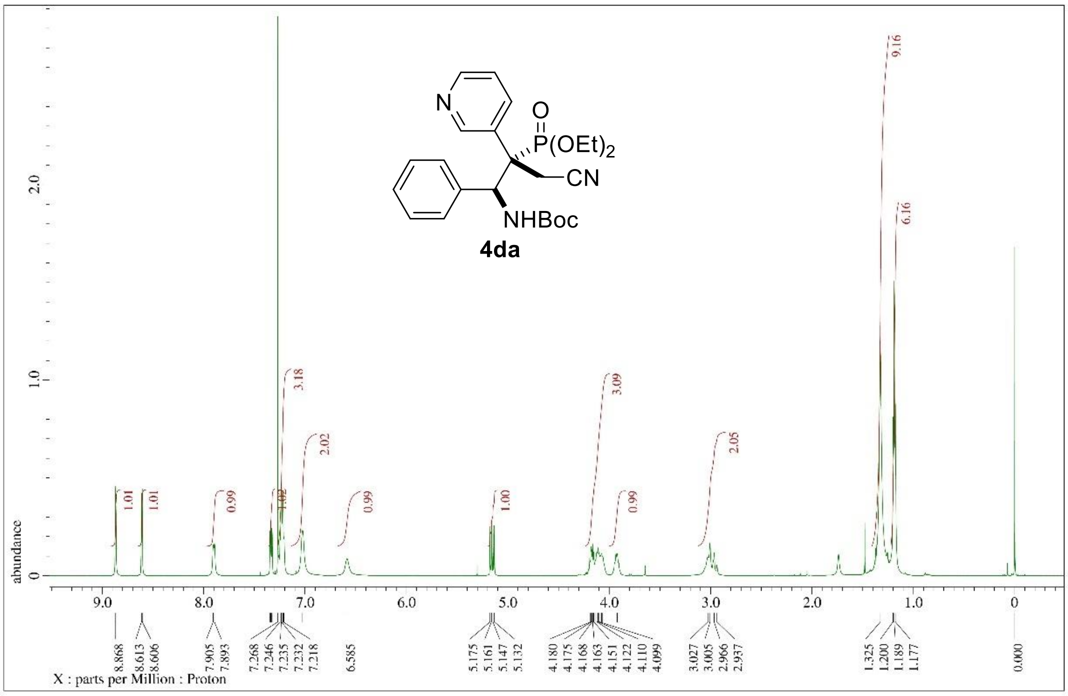


150 MHz, $CDCl_3$



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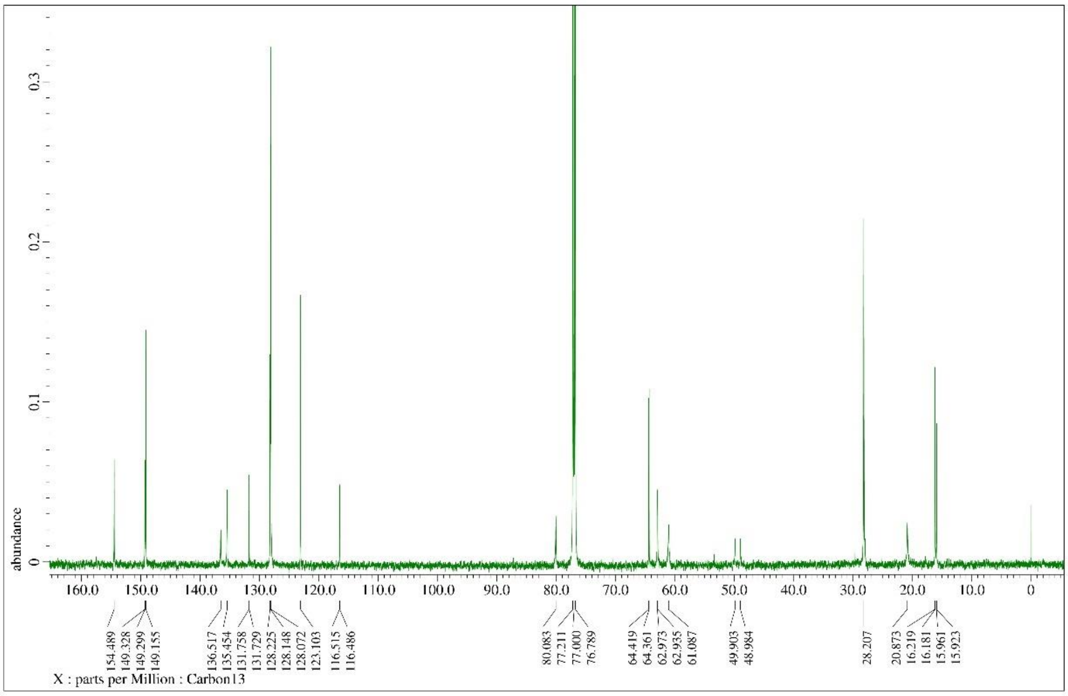

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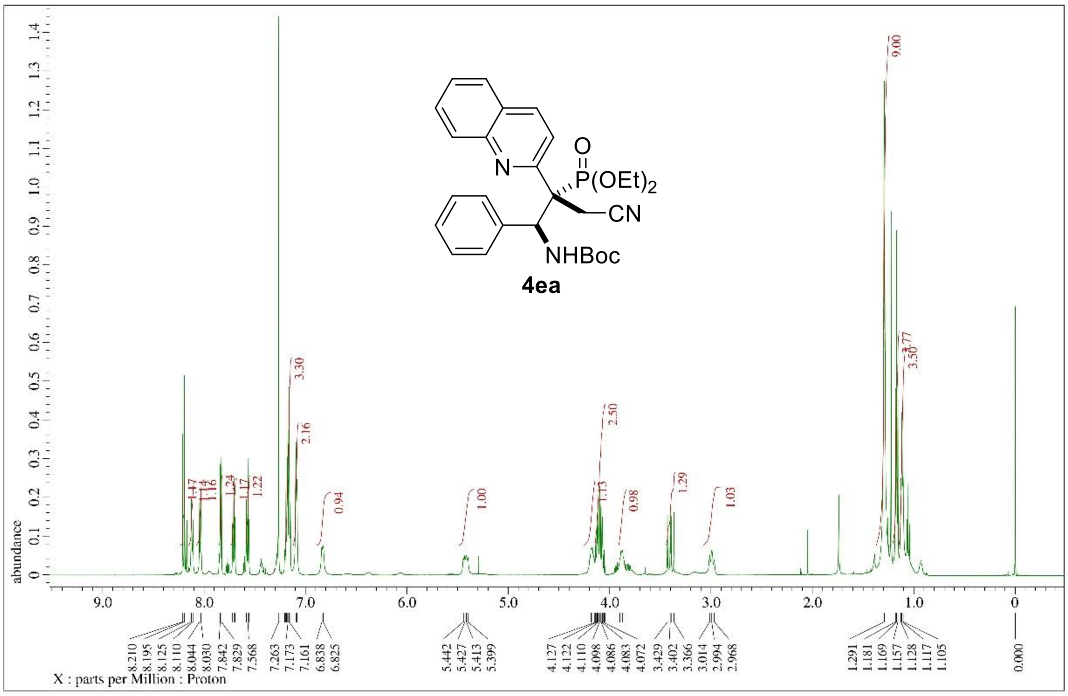

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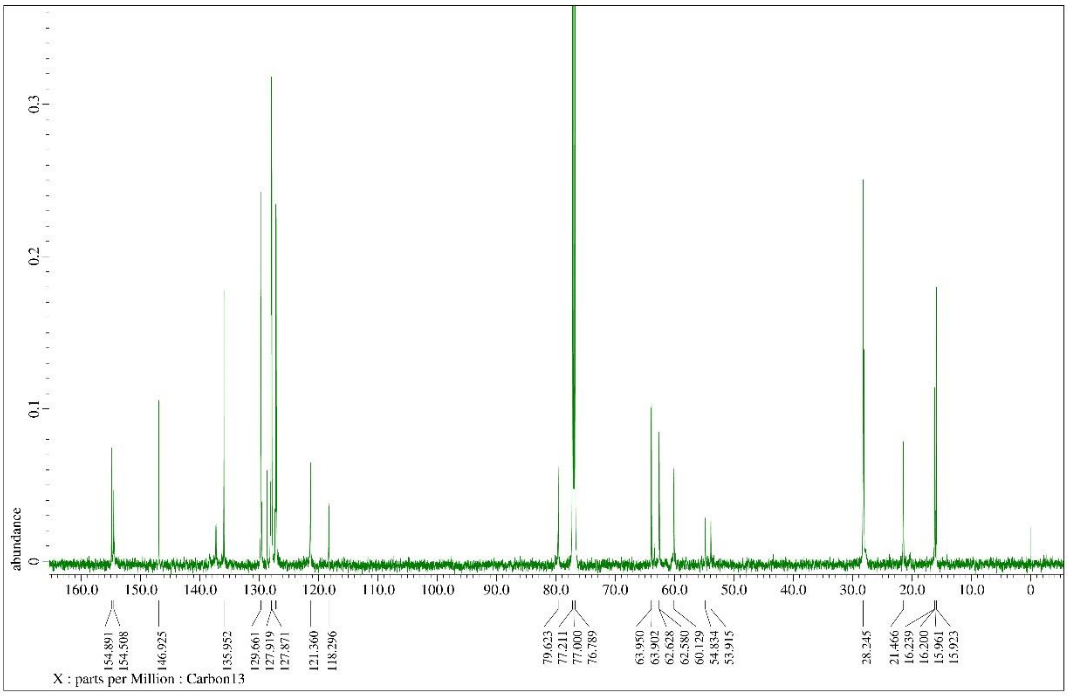

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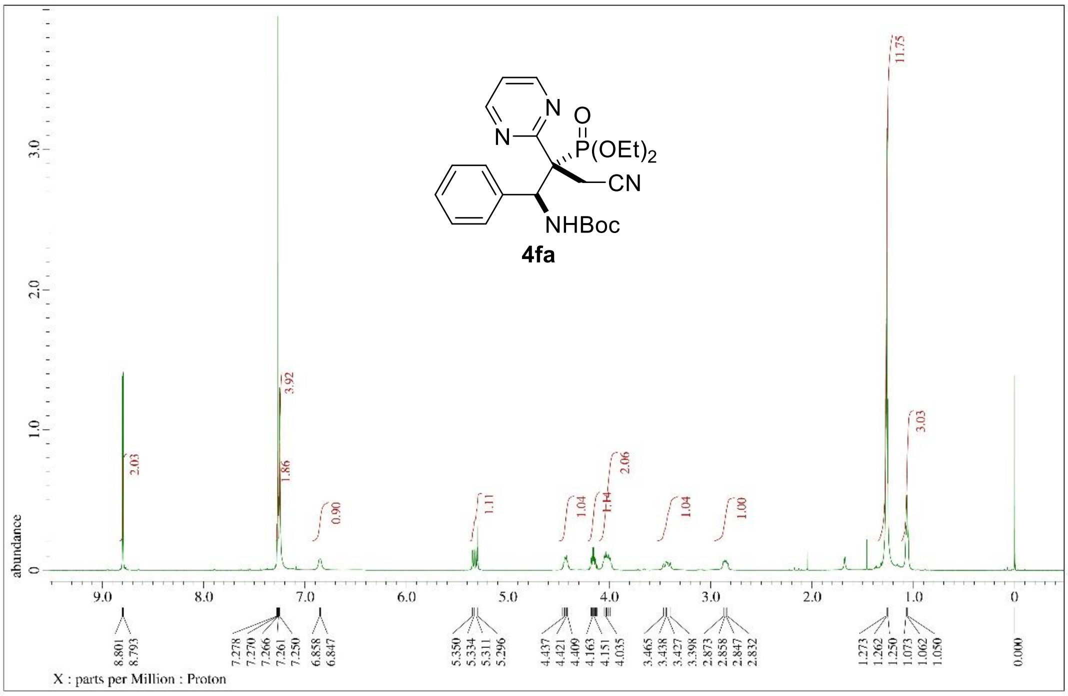

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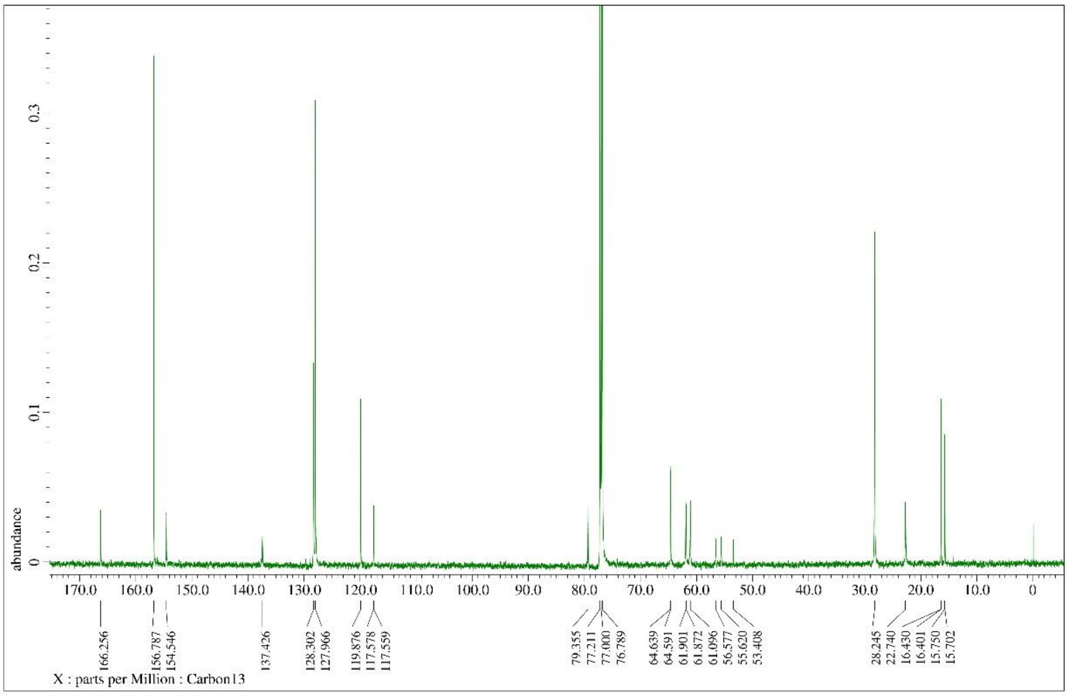

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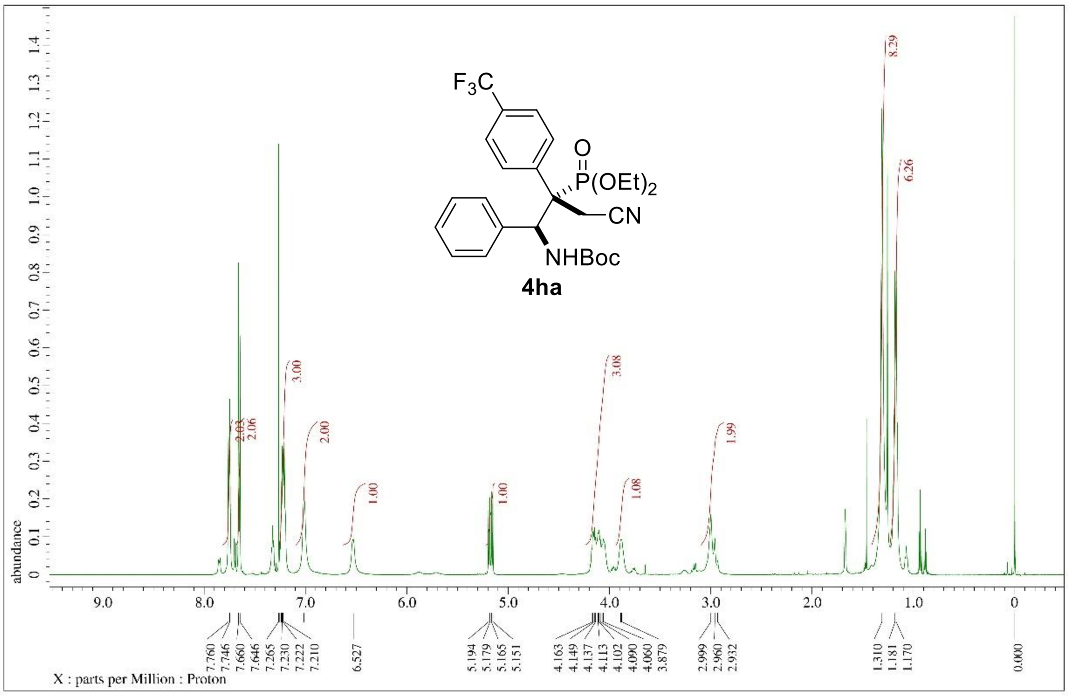

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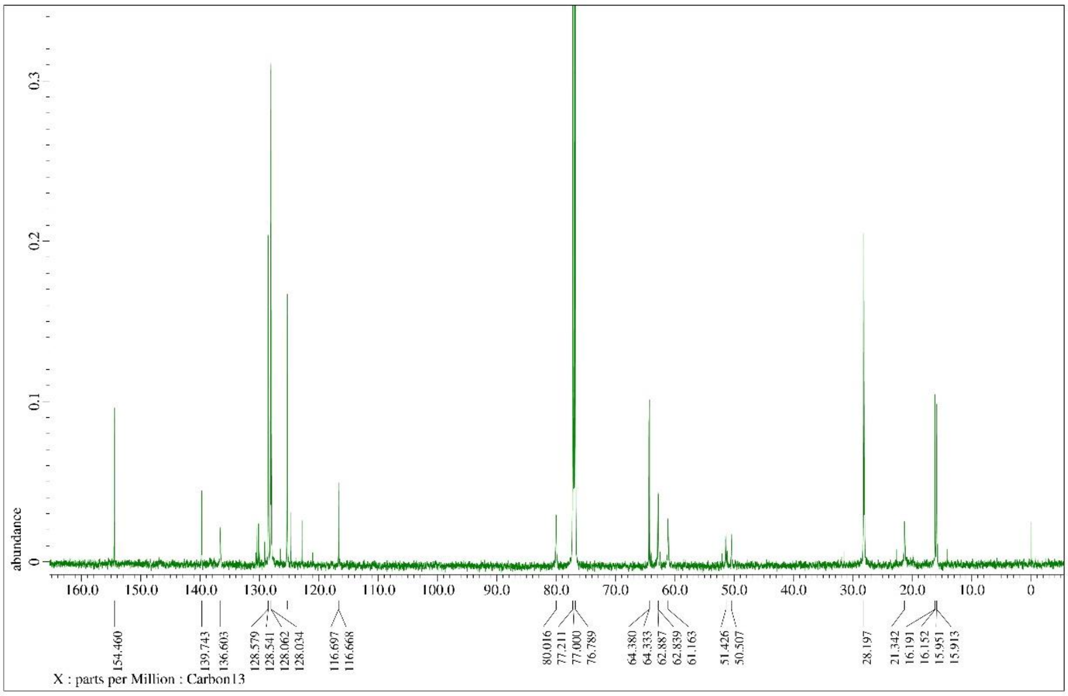

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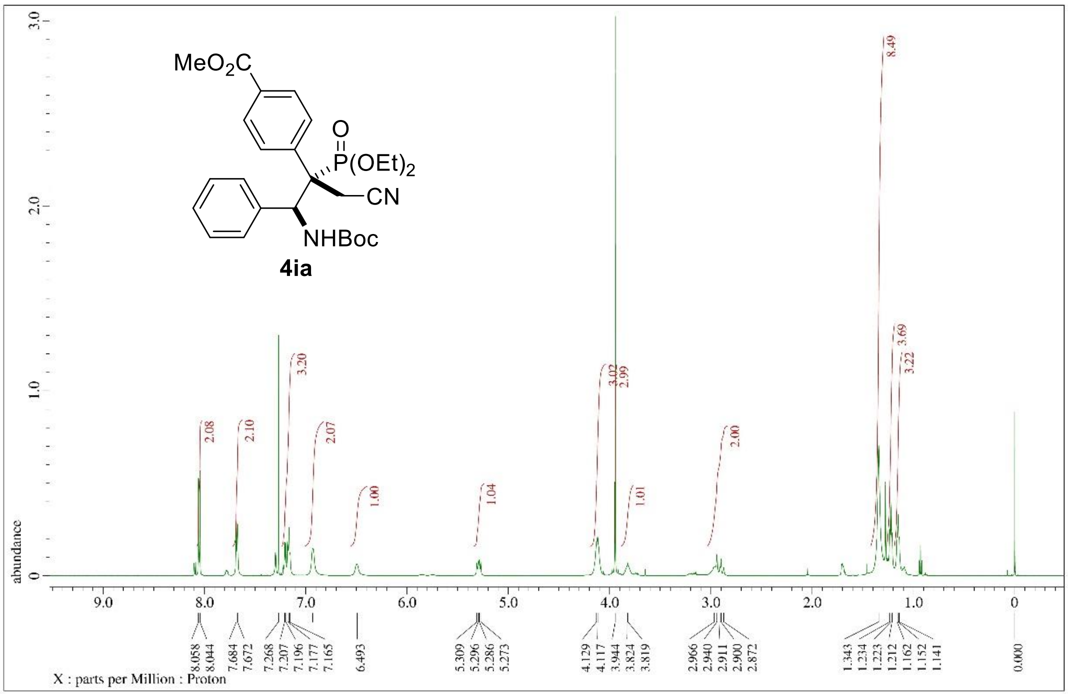

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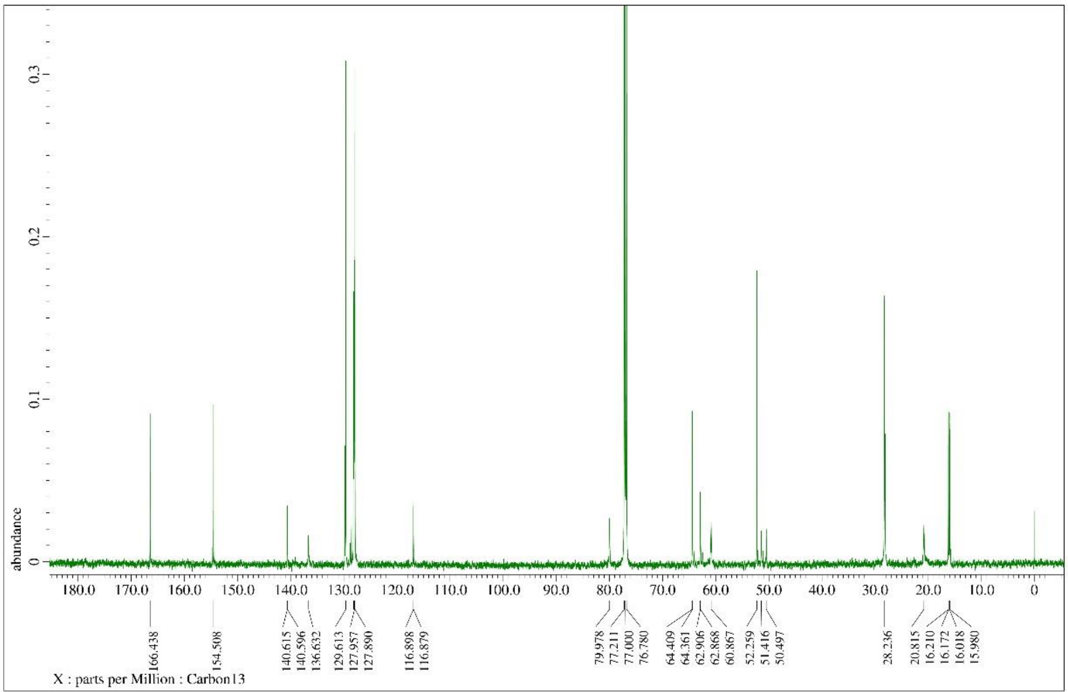

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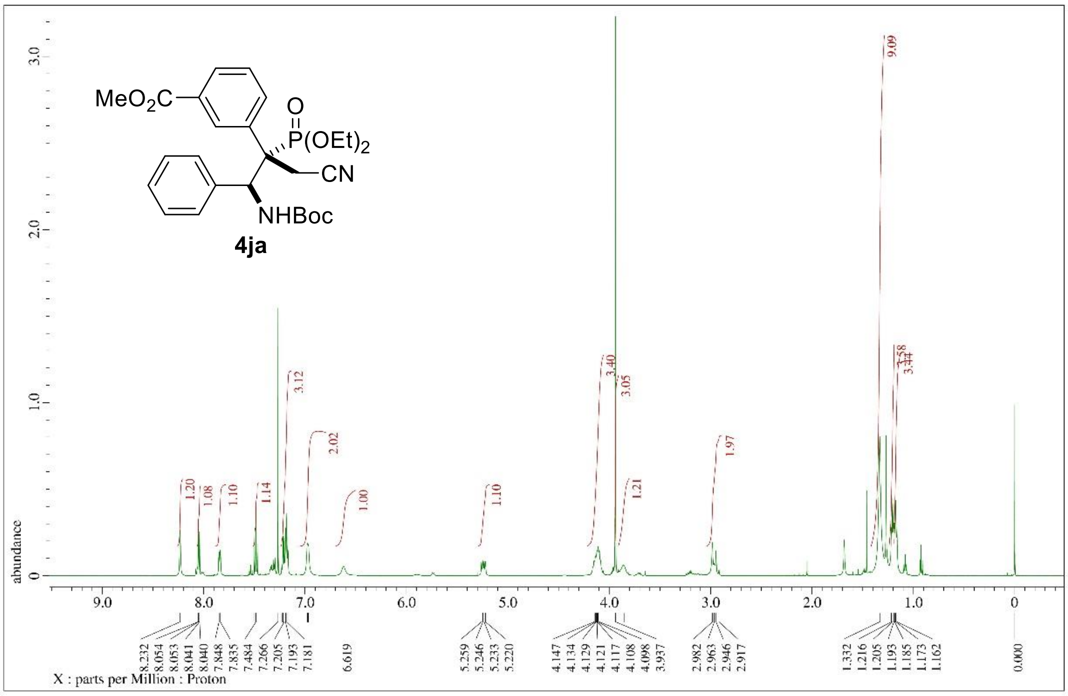

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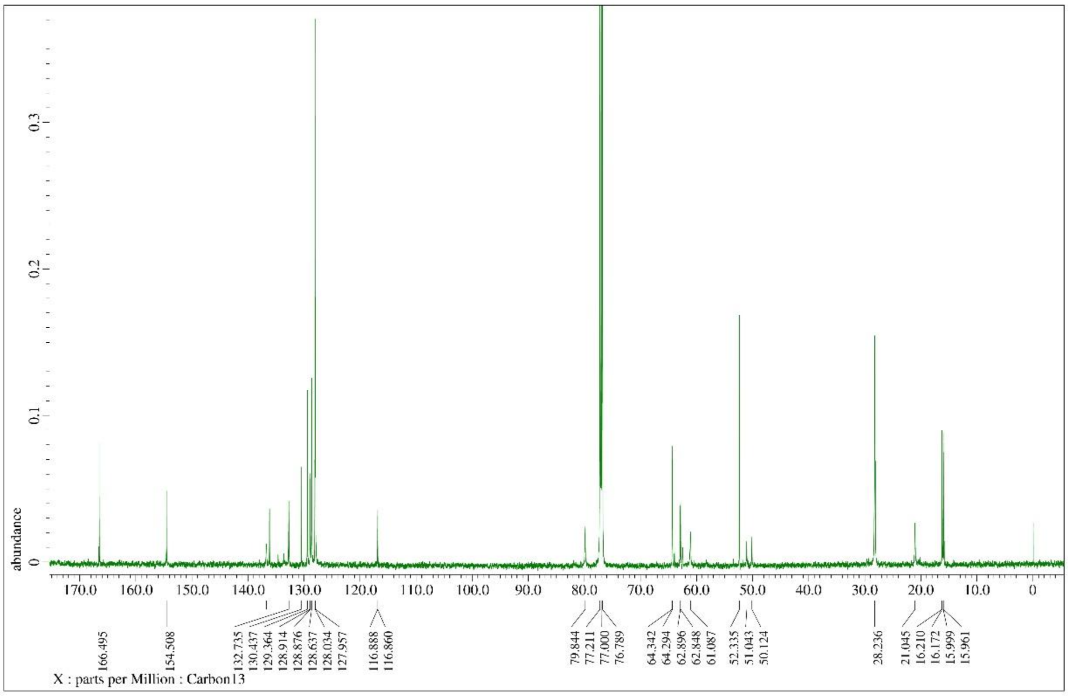

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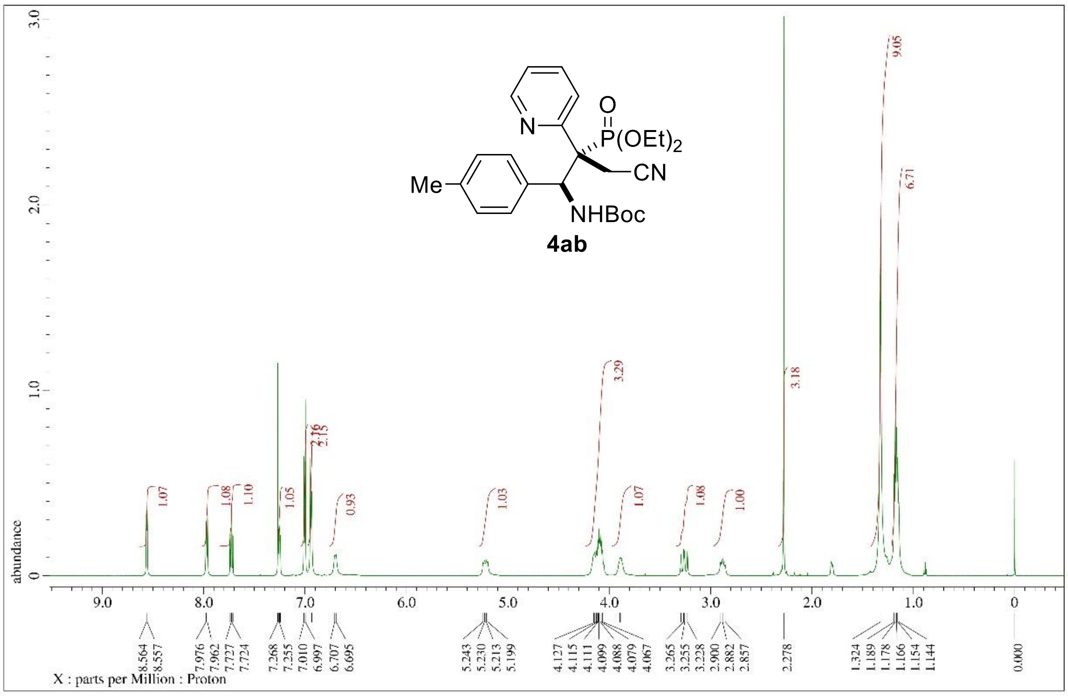

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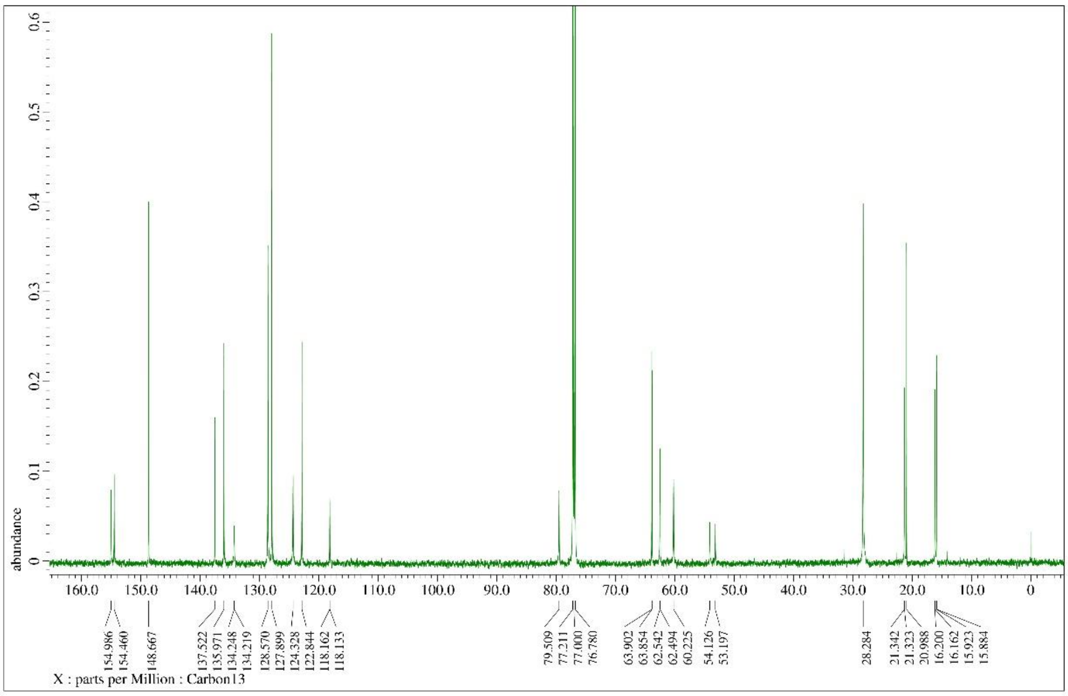

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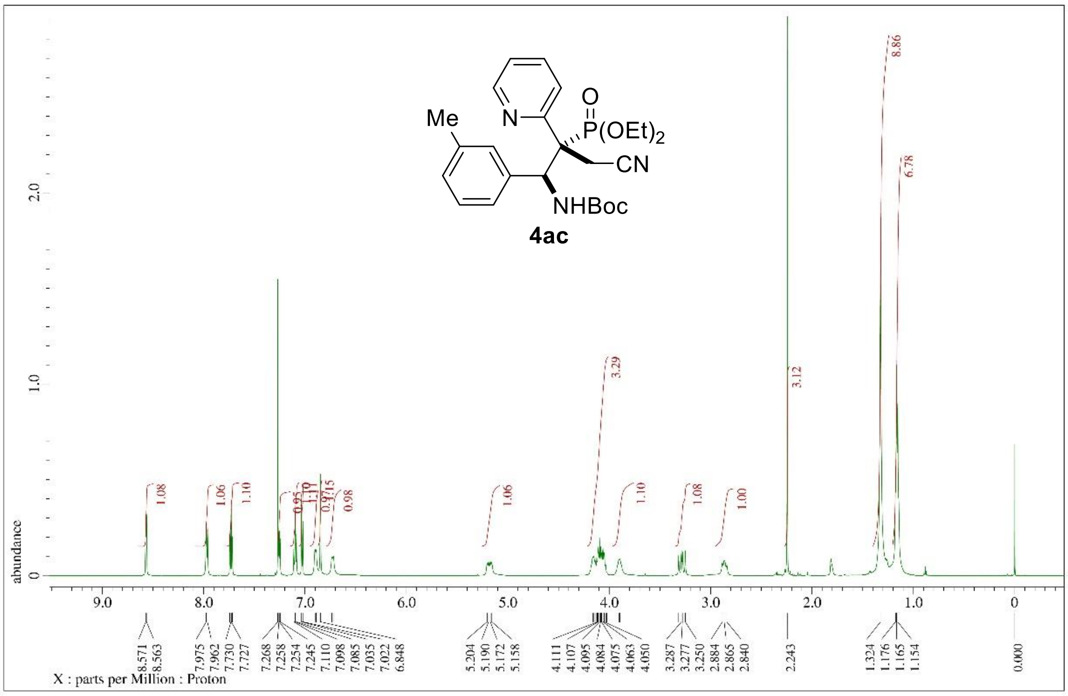

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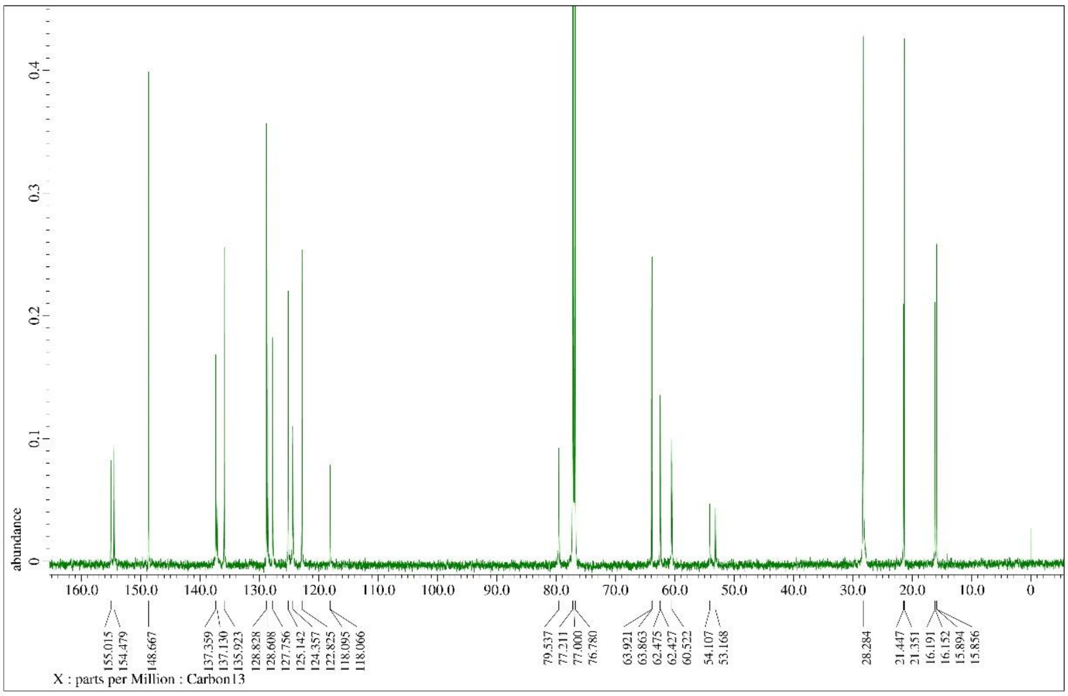

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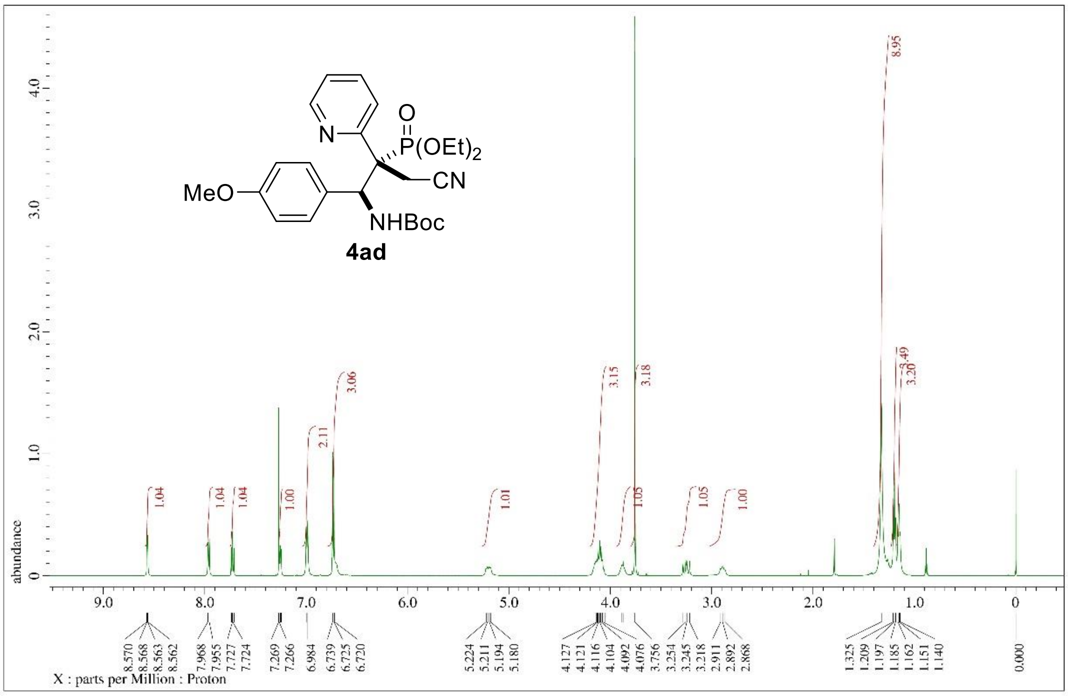

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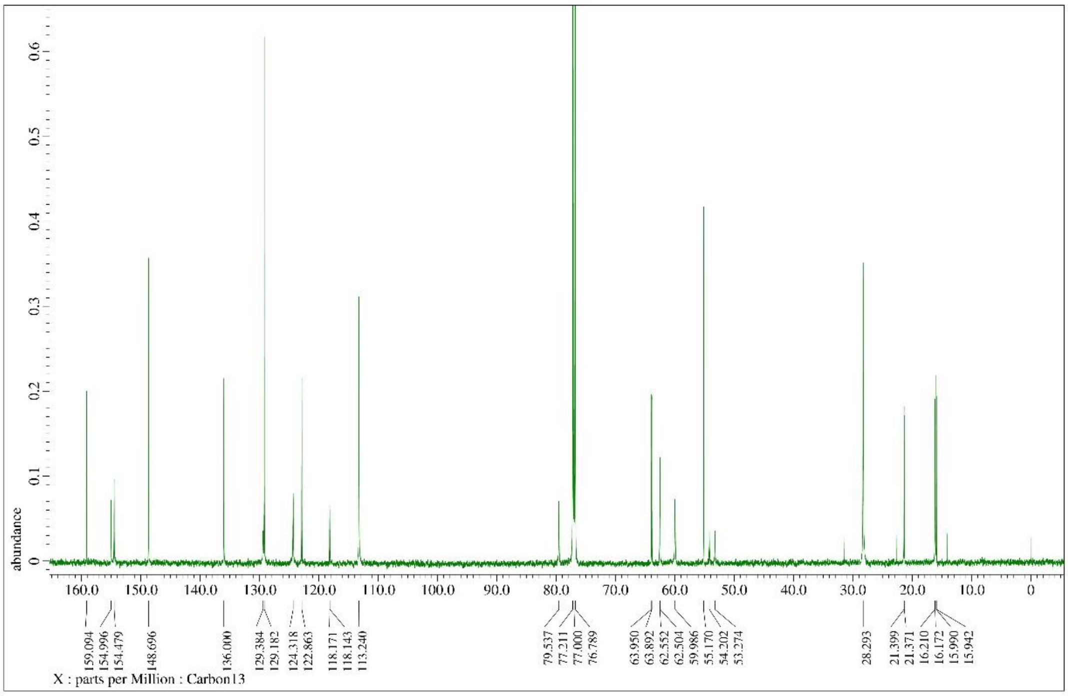

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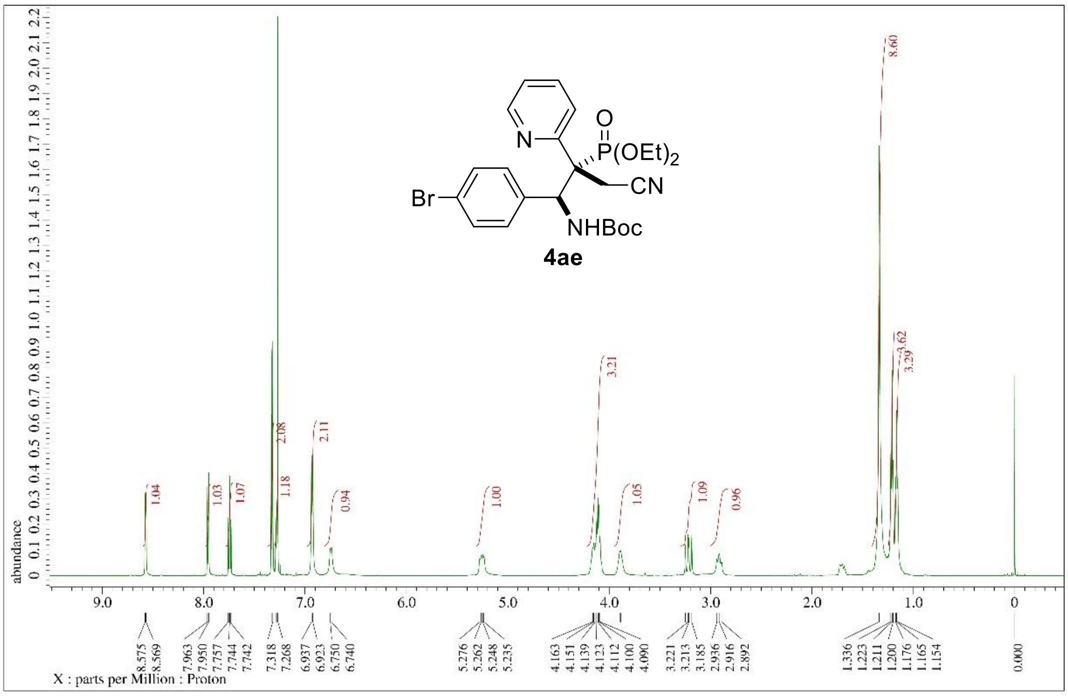

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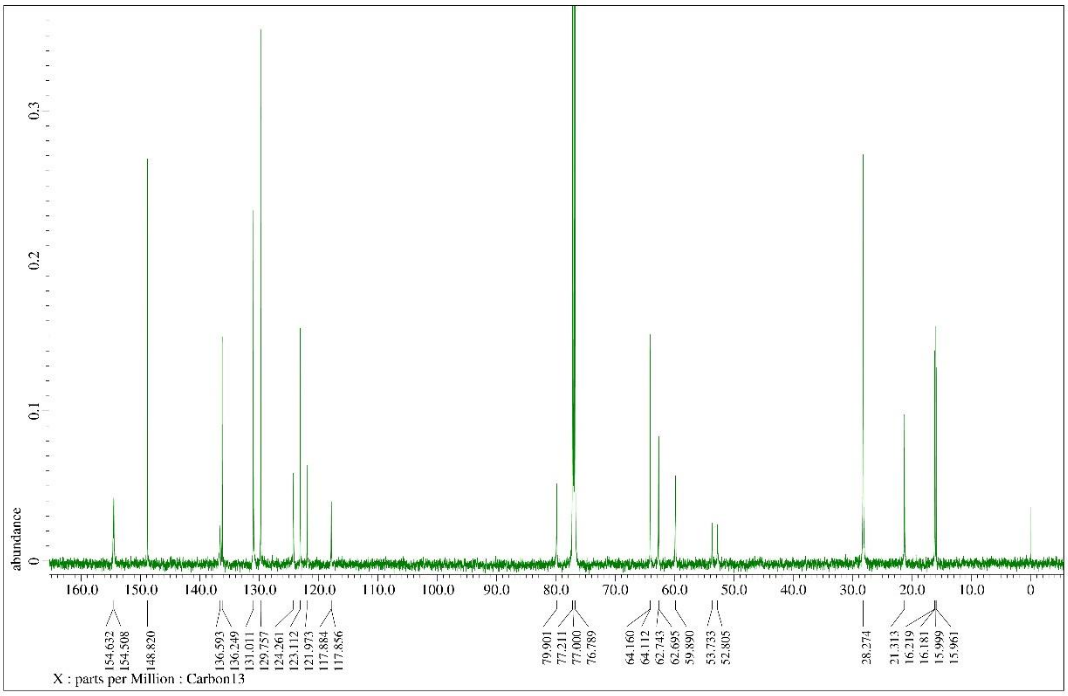

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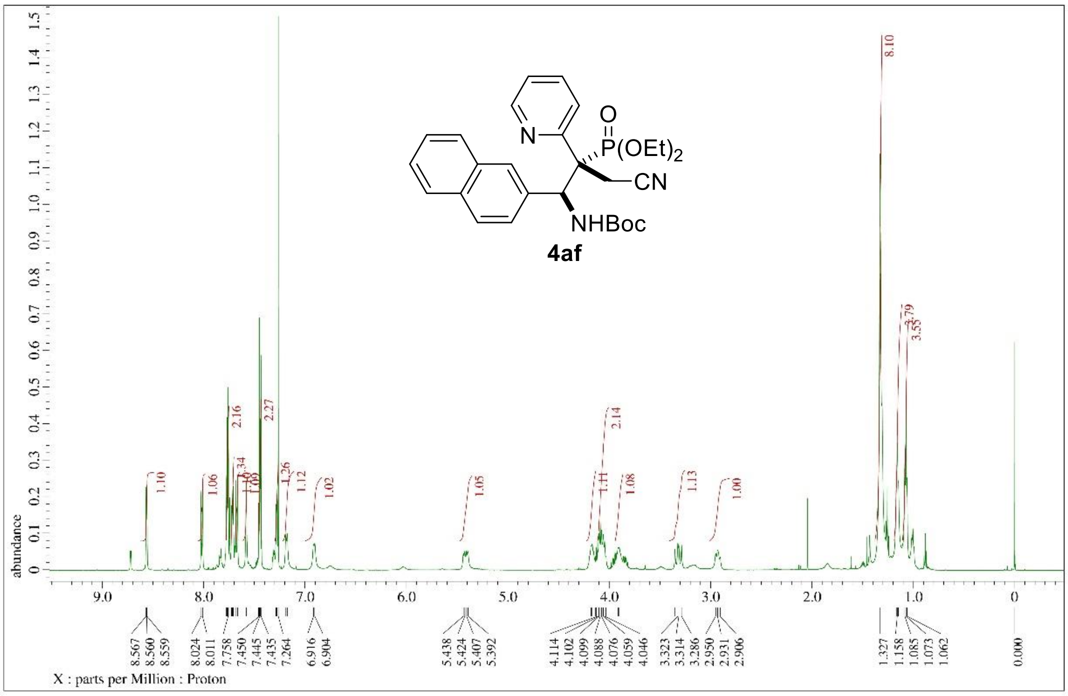

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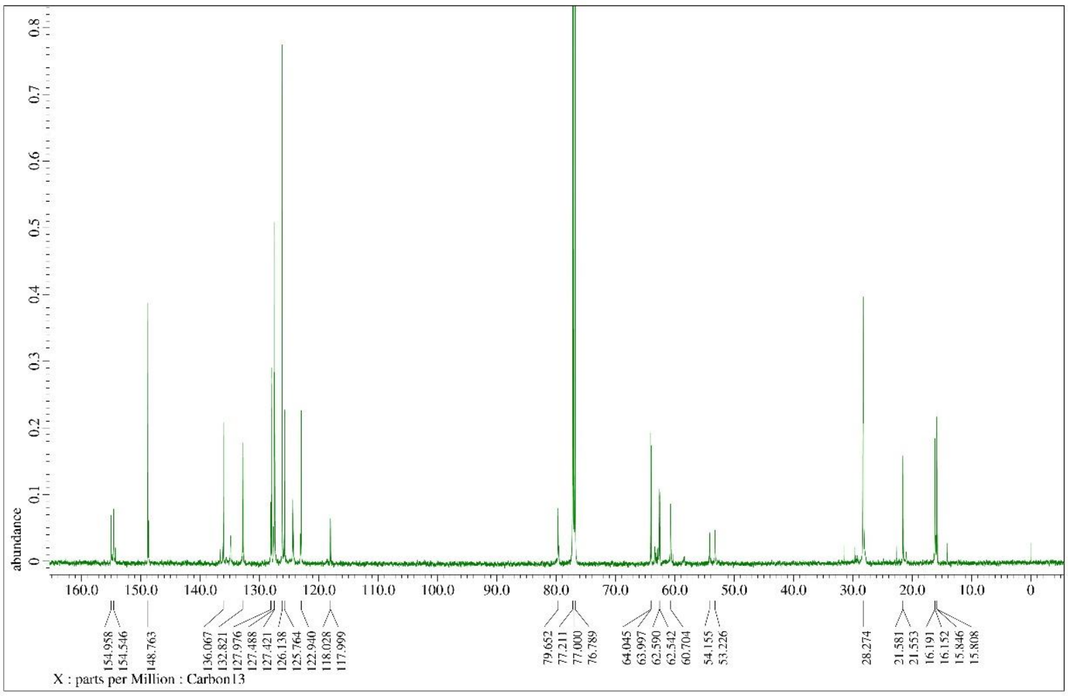

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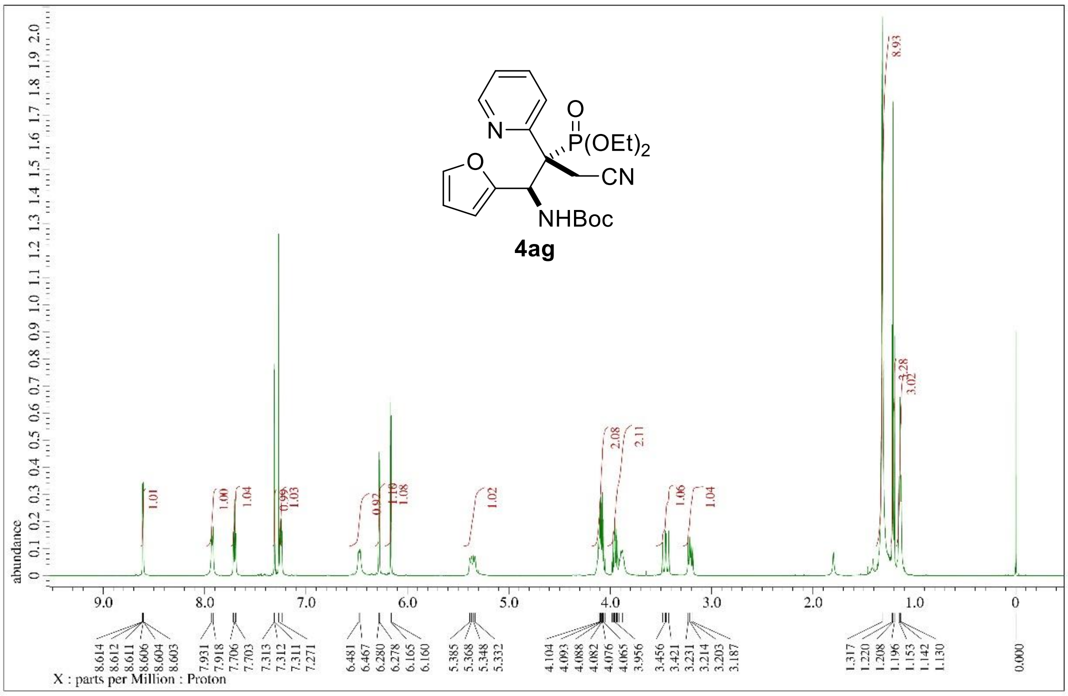

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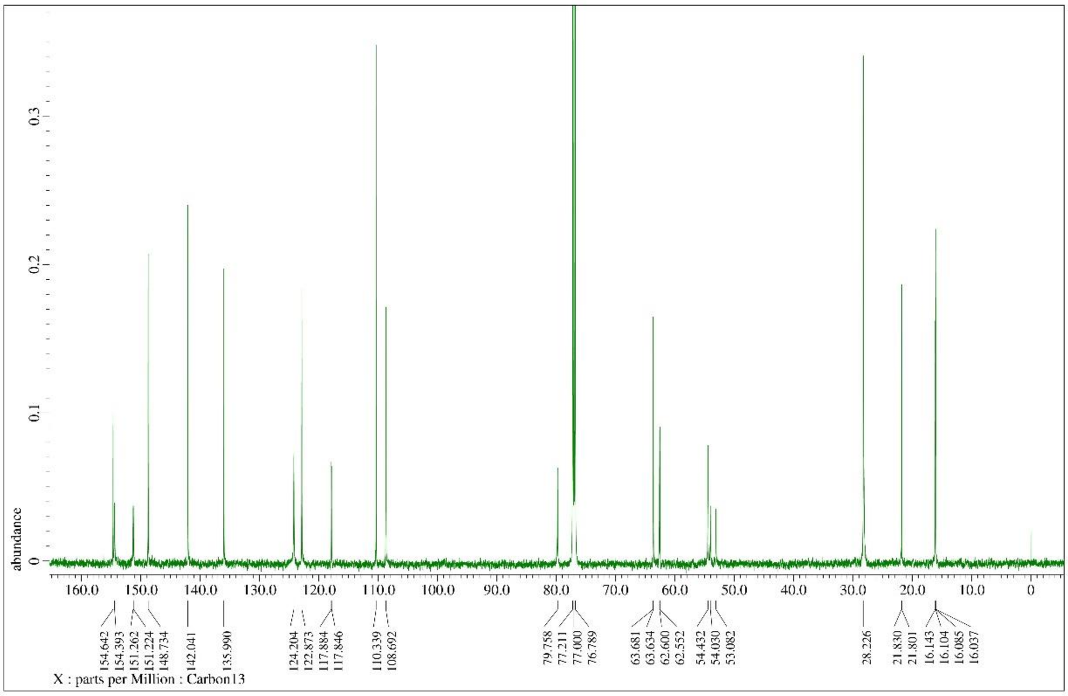

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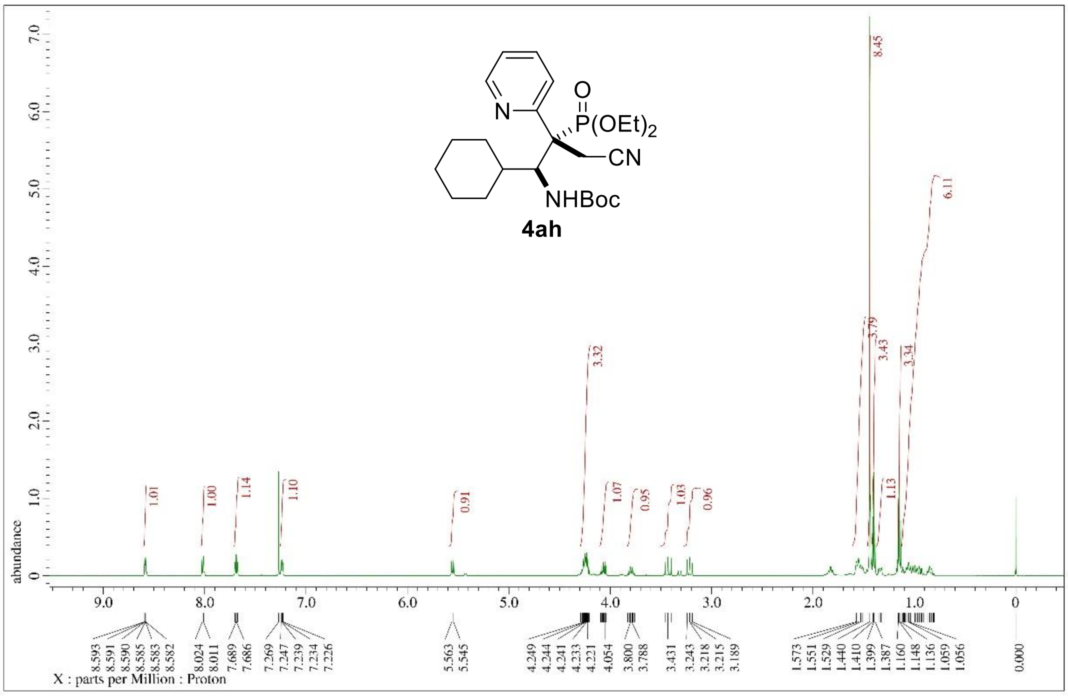

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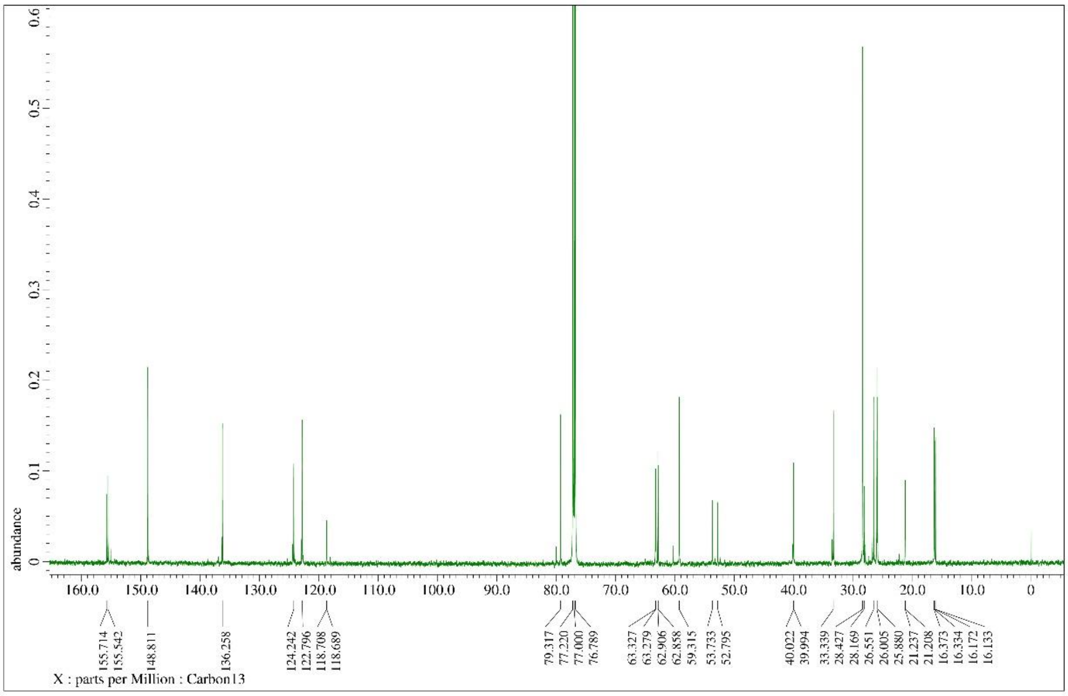

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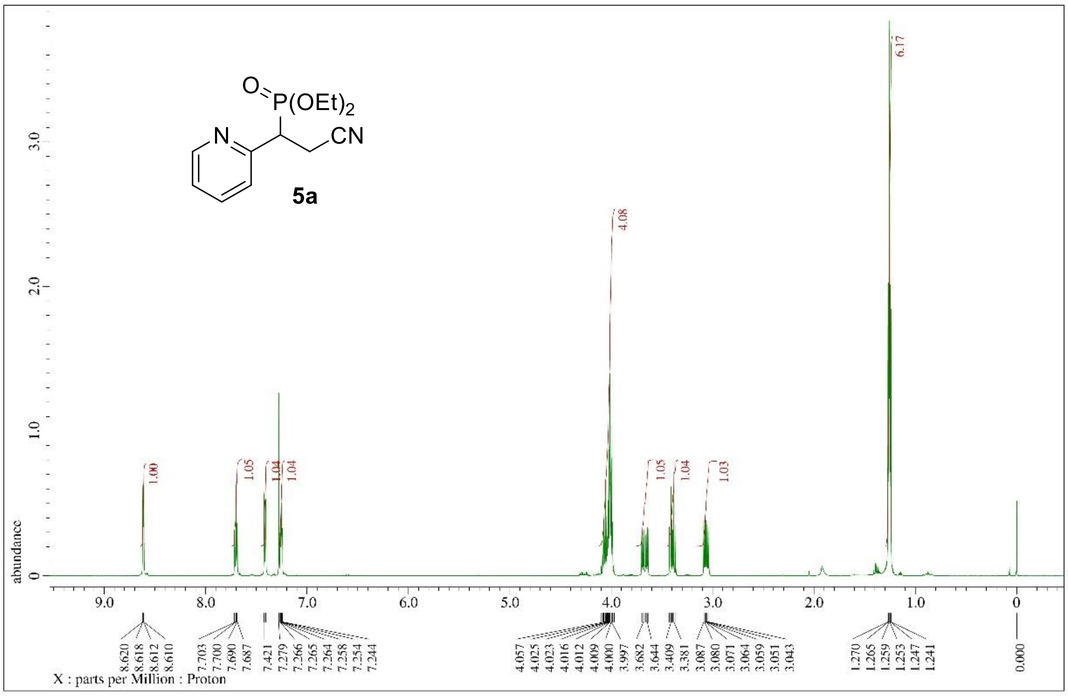

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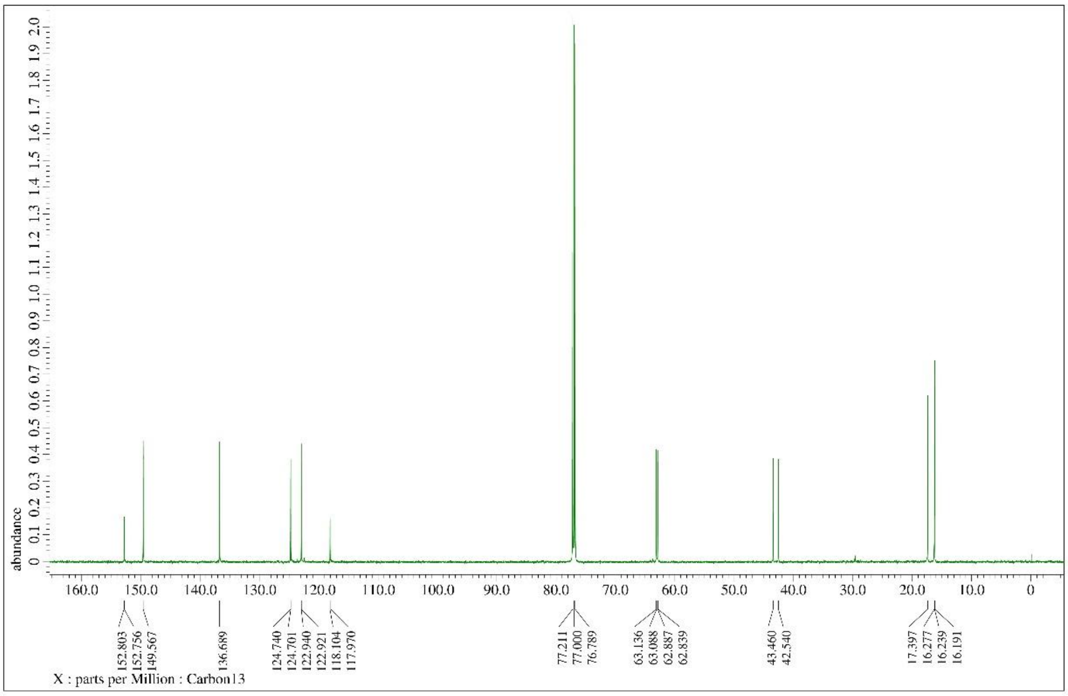

150 MHz, $CDCl_3$

X-ray Structure Reports

Table S1. Crystal data and structure refinement for 4aa.

Identification code	**4aa**
Empirical formula	$C_{48}H_{64}N_6O_{10}P_2$
Formula weight	946.99
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.38560(10)
b/Å	21.6393(3)
c/Å	20.1707(3)
α/°	90
β/°	96.0230(10)
γ/°	90
Volume/Å^3	4942.15(11)
Z	4
ρ_{calc}g/cm^3	1.273
μ/mm^{-1}	0.150
F(000)	2016.0
Crystal size/mm^3	0.2 × 0.15 × 0.05
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.476 to 61.904
Index ranges	$-15 \leq h \leq 16$, $-30 \leq k \leq 30$, $-28 \leq l \leq 27$
Reflections collected	135824
Independent reflections	13787 [R_{int} = 0.0631, R_{sigma} = 0.0350]
Data/restraints/parameters	13787/0/613
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0374, wR_2 = 0.0932
Final R indexes [all data]	R_1 = 0.0513, wR_2 = 0.1003
Largest diff. peak/hole / e Å^{-3}	0.52/-0.41

Table S2. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²× 10³) for 4aa. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
P15	5341.2(3)	3957.2(2)	5807.7(2)	14.92(7)
P48	3474.4(2)	1380.4(2)	6375.1(2)	14.11(6)
O43	6710.0(7)	1250.8(4)	5069.2(4)	15.65(16)
O25	4518.0(7)	4462.2(4)	5614.8(4)	19.29(17)
O27	2013.2(7)	3959.0(4)	4880.9(4)	18.65(17)
O10	1750.1(7)	3488.9(4)	5867.1(4)	18.52(17)
O60	5561.8(7)	523.2(4)	4500.5(4)	18.76(17)
O49	2772.2(7)	863.9(4)	5956.6(4)	18.68(17)
O52	2715.8(7)	1482.9(4)	6974.8(4)	17.78(16)
O16	5084.8(8)	3575.3(4)	6445.2(4)	21.64(18)
O19	6664.6(7)	4170.8(4)	5972.7(4)	18.87(17)
O58	3712.3(7)	1955.7(4)	6025.2(4)	19.60(17)
N8	3226.1(8)	3187.6(5)	5306.1(5)	15.46(18)
N41	5293.3(9)	771.6(5)	5563.8(5)	15.53(18)
N28	7026.4(8)	3182.6(4)	4520.8(5)	16.25(19)
N61	5238.0(9)	977.8(5)	7926.2(5)	20.8(2)
N24	7714.6(10)	2713.5(5)	6318.4(6)	25.5(2)
N57	2637.5(10)	19.5(5)	7406.9(6)	26.4(2)
C42	5850.6(10)	826.5(5)	5003.5(5)	14.5(2)
C9	2297.1(10)	3582.4(5)	5314.0(5)	15.2(2)
C14	5365.2(9)	3345.1(5)	5175.2(5)	13.3(2)
C1	3967.7(9)	2791.2(5)	4270.6(6)	15.4(2)
C7	4070.8(9)	3276.0(5)	4822.4(5)	14.0(2)
C29	6161.4(9)	3564.4(5)	4655.5(5)	14.2(2)
C34	6954.3(10)	724.7(5)	6466.5(5)	15.4(2)
C55	4556.6(10)	277.8(5)	6860.9(6)	16.7(2)
C62	5252.8(9)	1306.7(5)	7364.7(5)	16.0(2)
C22	5796.4(10)	2723.9(5)	5487.5(6)	15.6(2)
C39	7166.4(11)	96.0(5)	6385.6(6)	19.9(2)
C33	7721.1(10)	3365.7(6)	4061.1(6)	19.4(2)
C6	3795.9(10)	2166.7(5)	4402.8(6)	19.3(2)
C40	5772.2(10)	1017.8(5)	6211.7(5)	14.3(2)

Table S2. Fractional Atomic Coordinates (×10[4]) and Equivalent Isotropic Displacement Parameters (Å[2]× 10[3]) for 4aa. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C47	4815.5(10)	967.0(5)	6715.3(5)	14.1(2)
C23	6892.8(10)	2741.1(5)	5941.9(6)	17.7(2)
C32	7593.4(10)	3920.8(6)	3723.1(6)	20.1(2)
C2	4006.2(10)	2974.3(6)	3609.6(6)	19.1(2)
C30	5969.9(10)	4136.3(5)	4343.0(6)	17.1(2)
C56	3483.4(11)	151.3(5)	7184.0(6)	18.7(2)
C31	6699.1(10)	4315.5(5)	3869.7(6)	18.9(2)
C44	7540.4(10)	1311.0(5)	4552.0(6)	17.1(2)
C35	7864.9(11)	1096.3(6)	6756.0(6)	20.0(2)
C11	654.7(10)	3836.2(6)	5954.1(6)	18.6(2)
C5	3677.7(11)	1737.7(6)	3884.8(7)	23.6(2)
C45	8429.9(11)	1777.8(6)	4865.3(7)	21.7(2)
C46	8131.0(11)	690.4(6)	4455.7(7)	23.3(2)
C63	5596.7(10)	1923.1(6)	7364.1(6)	21.8(2)
C4	3710.3(11)	1925.5(6)	3230.8(6)	24.6(3)
C38	8271.1(11)	-153.9(6)	6593.2(6)	23.6(2)
C37	9176.3(11)	220.7(6)	6877.3(6)	24.1(3)
C20	7038.0(11)	4800.8(5)	5829.0(6)	20.4(2)
C3	3868.8(11)	2544.6(6)	3093.2(6)	23.1(2)
C59	6897.1(11)	1560.6(6)	3909.0(6)	22.4(2)
C66	5585.3(11)	1256.5(7)	8506.4(6)	26.6(3)
C36	8969.0(11)	846.0(6)	6960.1(7)	24.5(3)
C65	5943.8(11)	1860.3(7)	8554.7(7)	28.8(3)
C64	5952.6(11)	2202.0(6)	7978.7(7)	27.2(3)
C12	-308.8(11)	3649.1(6)	5412.8(7)	25.0(3)
C53	2605.3(11)	2088.3(6)	7285.5(6)	22.7(2)
C13	356.0(12)	3613.9(7)	6630.9(7)	27.2(3)
C26	889.7(12)	4527.3(6)	5973.2(7)	27.1(3)
C54	1366.5(12)	2149.8(6)	7467.3(7)	26.5(3)
C21	6998.9(13)	5199.7(6)	6437.2(7)	28.9(3)
C50	1549.3(11)	968.3(6)	5681.1(7)	25.4(3)
C51	1502.5(13)	994.3(8)	4940.2(7)	36.2(3)

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2× 10^3) for 4aa. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C18	4130.0(17)	3650.7(7)	7444.0(8)	40.5(4)
C17	5043(2)	3906.8(8)	7062.2(8)	54.6(6)

Table S3. Anisotropic Displacement Parameters (Å^2×10^3) for 4aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P15	17.76(14)	12.30(13)	15.25(13)	-1.07(10)	4.35(10)	-1.58(10)
P48	14.90(13)	14.42(13)	13.30(13)	0.61(10)	2.8(1)	-1.25(10)
O43	18.2(4)	15.4(4)	14.4(4)	-1.1(3)	6.2(3)	-3.2(3)
O25	20.4(4)	14.4(4)	23.9(4)	-2.7(3)	5.8(3)	0.6(3)
O27	18.1(4)	21.6(4)	16.5(4)	2.5(3)	2.8(3)	2.4(3)
O10	15.4(4)	24.2(4)	16.9(4)	2.9(3)	6.3(3)	3.4(3)
O60	24.4(4)	18.5(4)	13.9(4)	-2.6(3)	4.3(3)	-4.4(3)
O49	15.7(4)	20.1(4)	19.6(4)	-3.3(3)	-1.1(3)	0.1(3)
O52	20.0(4)	15.9(4)	18.5(4)	-1.2(3)	7.0(3)	-2.2(3)
O16	32.0(5)	19.1(4)	14.7(4)	-1.5(3)	6.2(3)	-7.0(3)
O19	19.4(4)	13.8(4)	23.1(4)	-0.4(3)	0.9(3)	-2.2(3)
O58	20.1(4)	18.9(4)	20.6(4)	5.7(3)	6.1(3)	0.8(3)
N8	16.4(4)	14.9(4)	16.1(4)	2.4(4)	5.9(4)	0.6(3)
N41	17.1(4)	17.2(5)	12.7(4)	-1.4(3)	3.6(3)	-4.6(4)
N28	16.0(4)	16.6(4)	16.4(4)	-0.5(4)	3.3(4)	0.3(3)
N61	17.9(5)	30.9(6)	13.8(4)	0.1(4)	2.6(4)	1.4(4)
N24	25.3(5)	23.6(5)	27.0(6)	5.6(4)	-1.0(4)	-2.1(4)
N57	31.4(6)	22.5(5)	26.7(6)	1.1(4)	9.9(5)	-5.2(4)
C42	15.8(5)	13.4(5)	14.6(5)	1.3(4)	2.8(4)	0.9(4)
C9	14.5(5)	17.4(5)	13.8(5)	-2.5(4)	2.2(4)	-2.2(4)
C14	15.0(5)	10.8(5)	14.6(5)	-0.3(4)	3.4(4)	0.0(4)
C1	11.8(5)	17.9(5)	16.7(5)	-1.6(4)	2.9(4)	0.2(4)
C7	14.2(5)	13.8(5)	14.6(5)	0.5(4)	3.8(4)	0.1(4)
C29	14.7(5)	13.3(5)	14.9(5)	-0.9(4)	2.4(4)	-2.1(4)
C34	16.8(5)	17.2(5)	12.7(5)	0.6(4)	4.1(4)	0.4(4)
C55	21.4(5)	15.7(5)	13.7(5)	0.4(4)	5.4(4)	-1.0(4)
C62	13.0(5)	21.0(5)	14.2(5)	-3.3(4)	2.2(4)	0.7(4)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 4aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C22	16.1(5)	12.3(5)	18.6(5)	1.2(4)	3.5(4)	-0.9(4)
C39	22.6(6)	18.2(5)	19.0(5)	-1.6(4)	2.8(4)	0.5(4)
C33	16.8(5)	22.1(6)	20.0(6)	-0.5(4)	5.6(4)	1.8(4)
C6	20.6(5)	19.0(5)	18.5(5)	-1.8(4)	3.0(4)	-1.1(4)
C40	16.3(5)	14.8(5)	12.0(5)	-0.9(4)	2.3(4)	-1.0(4)
C47	16.1(5)	14.3(5)	12.1(5)	-0.3(4)	2.8(4)	-1.0(4)
C23	20.4(5)	13.4(5)	20.0(5)	3.4(4)	5.4(4)	-0.8(4)
C32	18.6(5)	23.8(6)	18.9(5)	1.4(4)	6.6(4)	-1.9(4)
C2	16.3(5)	23.3(6)	18.2(5)	0.9(4)	4.0(4)	-0.7(4)
C30	18.5(5)	13.3(5)	20.4(5)	0.1(4)	5.3(4)	0.4(4)
C56	26.5(6)	14.9(5)	14.8(5)	0.1(4)	3.6(4)	-2.1(4)
C31	21.7(6)	15.5(5)	20.2(5)	2.5(4)	4.8(4)	-1.8(4)
C44	17.1(5)	16.9(5)	18.7(5)	0.6(4)	8.1(4)	-0.5(4)
C35	20.6(6)	18.6(5)	20.6(6)	1.0(4)	1.6(4)	-1.6(4)
C11	14.7(5)	23.0(6)	19.0(5)	-2.5(4)	6.3(4)	1.5(4)
C5	23.6(6)	19.4(6)	27.8(6)	-5.6(5)	2.2(5)	-1.8(5)
C45	18.9(5)	17.8(5)	29.2(6)	-0.7(5)	6.8(5)	-2.2(4)
C46	20.8(6)	18.5(6)	31.6(7)	-3.2(5)	7.7(5)	2.0(4)
C63	18.9(5)	20.8(6)	26.1(6)	-2.7(5)	4.2(5)	-1.1(4)
C4	19.1(6)	31.5(7)	23.3(6)	-11.8(5)	2.8(5)	0.0(5)
C38	28.3(6)	20.4(6)	22.5(6)	1.2(5)	4.1(5)	6.1(5)
C37	20.5(6)	29.3(7)	22.5(6)	6.5(5)	2.3(5)	5.6(5)
C20	19.7(5)	15.5(5)	26.4(6)	1.4(4)	4.6(5)	-4.7(4)
C3	18.2(5)	35.3(7)	16.0(5)	-3.1(5)	3.5(4)	0.3(5)
C59	24.3(6)	24.9(6)	19.1(6)	3.7(5)	7.7(5)	-0.1(5)
C66	19.5(6)	45.1(8)	15.1(5)	-2.2(5)	0.8(4)	2.0(5)
C36	19.6(6)	26.7(6)	26.4(6)	2.6(5)	-1.3(5)	-3.0(5)
C65	18.5(6)	45.5(8)	21.8(6)	-13.7(6)	-0.5(5)	1.5(5)
C64	16.8(6)	26.3(6)	38.7(7)	-12.4(6)	3.5(5)	-2.1(5)
C12	16.6(5)	32.8(7)	25.7(6)	-4.6(5)	2.9(5)	-1.6(5)
C53	26.0(6)	19.2(6)	23.8(6)	-6.6(5)	7.0(5)	-2.6(5)
C13	23.4(6)	37.6(7)	22.5(6)	2.2(5)	11.2(5)	3.6(5)

Table S3. Anisotropic Displacement Parameters (Å^2×10^3) for 4aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C26	27.4(6)	23.8(6)	31.8(7)	-6.4(5)	10.3(5)	0.3(5)
C54	25.8(6)	26.0(6)	28.3(7)	-4.1(5)	6.2(5)	4.4(5)
C21	38.7(7)	19.7(6)	27.1(7)	-2.7(5)	-1.6(6)	-8.1(5)
C50	15.3(5)	31.2(7)	29.2(7)	-5.5(5)	0.6(5)	-0.5(5)
C51	24.9(7)	53.6(10)	28.2(7)	3.4(6)	-5.8(5)	1.2(6)
C18	63.9(11)	29.8(8)	32.1(8)	-2.4(6)	25.4(7)	3.0(7)
C17	104.6(16)	40.9(9)	22.4(7)	-13.3(7)	25.3(9)	-37.1(10)

Table S4. Bond Lengths for 4aa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P15	O25	1.4654(9)	C29	C30	1.3956(15)
P15	O16	1.5813(9)	C34	C39	1.3942(16)
P15	O19	1.5777(9)	C34	C40	1.5273(15)
P15	C14	1.8413(11)	C34	C35	1.3912(16)
P48	O49	1.5681(8)	C55	C47	1.5542(15)
P48	O52	1.5740(8)	C55	C56	1.4697(16)
P48	O58	1.4703(8)	C62	C47	1.5386(15)
P48	C47	1.8392(11)	C62	C63	1.3902(17)
O43	C42	1.3381(13)	C22	C23	1.4696(16)
O43	C44	1.4852(13)	C39	C38	1.3925(17)
O27	C9	1.2134(14)	C33	C32	1.3814(17)
O10	C9	1.3488(13)	C6	C5	1.3937(17)
O10	C11	1.4822(14)	C40	C47	1.5692(15)
O60	C42	1.2240(14)	C32	C31	1.3845(17)
O49	C50	1.4615(14)	C2	C3	1.3928(17)
O52	C53	1.4633(14)	C30	C31	1.3847(16)
O16	C17	1.4416(16)	C44	C45	1.5201(16)
O19	C20	1.4661(14)	C44	C46	1.5234(16)
N8	C9	1.3610(14)	C44	C59	1.5202(17)
N8	C7	1.4527(14)	C35	C36	1.3908(17)
N41	C42	1.3580(14)	C11	C12	1.5193(17)
N41	C40	1.4628(14)	C11	C13	1.5193(17)

Table S4. Bond Lengths for 4aa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N28	C29	1.3351(14)	C11	C26	1.5190(18)
N28	C33	1.3402(15)	C5	C4	1.3845(19)
N61	C62	1.3393(15)	C63	C64	1.3999(18)
N61	C66	1.3389(16)	C4	C3	1.3838(19)
N24	C23	1.1432(16)	C38	C37	1.3870(19)
N57	C56	1.1412(16)	C37	C36	1.3867(19)
C14	C7	1.5750(15)	C20	C21	1.5045(18)
C14	C29	1.5314(15)	C66	C65	1.369(2)
C14	C22	1.5426(15)	C65	C64	1.378(2)
C1	C7	1.5249(15)	C53	C54	1.5001(18)
C1	C6	1.3953(16)	C50	C51	1.491(2)
C1	C2	1.3960(16)	C18	C17	1.466(2)

Table S5. Bond Angles for 4aa.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O25	P15	O16	115.98(5)	N61	C62	C63	122.62(11)
O25	P15	O19	114.06(5)	C63	C62	C47	121.58(10)
O25	P15	C14	114.09(5)	C23	C22	C14	116.47(9)
O16	P15	C14	101.82(5)	C38	C39	C34	120.38(11)
O19	P15	O16	103.61(5)	N28	C33	C32	124.01(11)
O19	P15	C14	105.88(5)	C5	C6	C1	120.42(11)
O49	P48	O52	102.96(5)	N41	C40	C34	112.46(9)
O49	P48	C47	102.16(5)	N41	C40	C47	109.50(9)
O52	P48	C47	106.43(5)	C34	C40	C47	113.59(9)
O58	P48	O49	117.02(5)	C55	C47	P48	111.76(8)
O58	P48	O52	113.15(5)	C55	C47	C40	110.35(9)
O58	P48	C47	113.79(5)	C62	C47	P48	105.49(7)
C42	O43	C44	120.23(8)	C62	C47	C55	110.39(9)
C9	O10	C11	119.29(9)	C62	C47	C40	109.45(9)
C50	O49	P48	120.41(8)	C40	C47	P48	109.27(7)
C53	O52	P48	122.28(7)	N24	C23	C22	174.59(12)
C17	O16	P15	117.88(9)	C33	C32	C31	118.21(11)
C20	O19	P15	121.40(7)	C3	C2	C1	120.84(11)

Table S5. Bond Angles for 4aa.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	N8	C7	119.69(9)	C31	C30	C29	118.89(10)
C42	N41	C40	123.28(9)	N57	C56	C55	175.36(13)
C29	N28	C33	117.35(10)	C32	C31	C30	118.82(11)
C66	N61	C62	118.10(11)	O43	C44	C45	102.23(9)
O43	C42	N41	112.23(9)	O43	C44	C46	109.53(9)
O60	C42	O43	125.45(10)	O43	C44	C59	110.19(9)
O60	C42	N41	122.30(10)	C45	C44	C46	110.79(10)
O27	C9	O10	125.80(10)	C45	C44	C59	111.03(10)
O27	C9	N8	124.18(10)	C59	C44	C46	112.58(10)
O10	C9	N8	110.02(10)	C36	C35	C34	120.65(11)
C7	C14	P15	107.47(7)	O10	C11	C12	109.44(9)
C29	C14	P15	107.70(7)	O10	C11	C13	102.49(9)
C29	C14	C7	108.25(8)	O10	C11	C26	110.73(9)
C29	C14	C22	111.33(9)	C12	C11	C13	110.41(10)
C22	C14	P15	111.79(7)	C26	C11	C12	113.11(11)
C22	C14	C7	110.14(8)	C26	C11	C13	110.14(10)
C6	C1	C7	121.90(10)	C4	C5	C6	120.57(12)
C6	C1	C2	118.45(11)	C62	C63	C64	117.93(12)
C2	C1	C7	119.62(10)	C3	C4	C5	119.50(11)
N8	C7	C14	111.29(9)	C37	C38	C39	120.39(12)
N8	C7	C1	113.20(9)	C36	C37	C38	119.44(11)
C1	C7	C14	113.06(9)	O19	C20	C21	109.78(10)
N28	C29	C14	116.73(9)	C4	C3	C2	120.20(12)
N28	C29	C30	122.71(10)	N61	C66	C65	123.40(13)
C30	C29	C14	120.56(10)	C37	C36	C35	120.28(12)
C39	C34	C40	121.54(10)	C66	C65	C64	118.72(12)
C35	C34	C39	118.85(11)	C65	C64	C63	119.22(12)
C35	C34	C40	119.53(10)	O52	C53	C54	108.03(10)
C56	C55	C47	116.45(9)	O49	C50	C51	108.63(10)
N61	C62	C47	115.75(10)	O16	C17	C18	110.80(13)

Table S6. Torsion Angles for 4aa.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
P15	O16	C17	C18	143.06(13)	C7	N8	C9	O10	-169.06(9)
P15	O19	C20	C21	93.89(11)	C7	C14	C29	N28	-116.89(10)
P15	C14	C7	N8	-52.70(10)	C7	C14	C29	C30	62.81(13)
P15	C14	C7	C1	178.58(7)	C7	C14	C22	C23	-168.67(9)
P15	C14	C29	N28	127.19(9)	C7	C1	C6	C5	178.48(11)
P15	C14	C29	C30	-53.10(12)	C7	C1	C2	C3	-177.51(10)
P15	C14	C22	C23	-49.27(12)	C29	N28	C33	C32	0.01(17)
P48	O49	C50	C51	112.56(11)	C29	C14	C7	N8	-168.77(9)
P48	O52	C53	C54	142.87(9)	C29	C14	C7	C1	62.51(11)
O25	P15	O16	C17	-57.66(14)	C29	C14	C22	C23	71.24(12)
O25	P15	O19	C20	-9.97(10)	C29	C30	C31	C32	-0.01(17)
O25	P15	C14	C7	-34.95(8)	C34	C39	C38	C37	-0.58(18)
O25	P15	C14	C29	81.48(8)	C34	C40	C47	P48	176.25(7)
O25	P15	C14	C22	-155.92(7)	C34	C40	C47	C55	-60.48(12)
O49	P48	O52	C53	-146.48(9)	C34	C40	C47	C62	61.20(12)
O49	P48	C47	C55	-33.59(8)	C34	C35	C36	C37	-0.01(19)
O49	P48	C47	C62	-153.59(7)	C62	N61	C66	C65	0.58(18)
O49	P48	C47	C40	88.84(8)	C62	C63	C64	C65	-0.29(18)
O52	P48	O49	C50	59.96(9)	C22	C14	C7	N8	69.30(11)
O52	P48	C47	C55	74.03(8)	C22	C14	C7	C1	-59.42(12)
O52	P48	C47	C62	-45.96(8)	C22	C14	C29	N28	4.31(13)
O52	P48	C47	C40	-163.54(7)	C22	C14	C29	C30	-175.99(10)
O16	P15	O19	C20	-136.96(9)	C39	C34	C40	N41	-39.59(14)
O16	P15	C14	C7	90.77(8)	C39	C34	C40	C47	85.49(13)
O16	P15	C14	C29	-152.80(7)	C39	C34	C35	C36	0.14(17)
O16	P15	C14	C22	-30.20(8)	C39	C38	C37	C36	0.70(19)
O19	P15	O16	C17	68.11(13)	C33	N28	C29	C14	179.22(10)
O19	P15	C14	C7	-161.21(7)	C33	N28	C29	C30	-0.47(16)
O19	P15	C14	C29	-44.78(8)	C33	C32	C31	C30	-0.42(18)
O19	P15	C14	C22	77.82(8)	C6	C1	C7	N8	-41.99(14)
O58	P48	O49	C50	-64.81(10)	C6	C1	C7	C14	85.74(12)
O58	P48	O52	C53	-19.22(10)	C6	C1	C2	C3	0.41(17)
O58	P48	C47	C55	-160.66(7)	C6	C5	C4	C3	0.38(19)

Table S6. Torsion Angles for 4aa.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O58	P48	C47	C62	79.34(8)	C40	N41	C42	O43	-15.41(15)
O58	P48	C47	C40	-38.23(9)	C40	N41	C42	O60	165.85(10)
N41	C40	C47	P48	-57.10(10)	C40	C34	C39	C38	176.83(11)
N41	C40	C47	C55	66.17(11)	C40	C34	C35	C36	-176.61(11)
N41	C40	C47	C62	-172.15(9)	C47	P48	O49	C50	170.23(9)
N28	C29	C30	C31	0.48(17)	C47	P48	O52	C53	106.47(9)
N28	C33	C32	C31	0.44(19)	C47	C62	C63	C64	178.28(10)
N61	C62	C47	P48	115.55(9)	C2	C1	C7	N8	135.86(10)
N61	C62	C47	C55	-5.34(13)	C2	C1	C7	C14	-96.41(12)
N61	C62	C47	C40	-127.00(10)	C2	C1	C6	C5	0.61(17)
N61	C62	C63	C64	0.78(17)	C56	C55	C47	P48	-43.27(12)
N61	C66	C65	C64	-0.1(2)	C56	C55	C47	C62	73.81(12)
C42	O43	C44	C45	-173.33(9)	C56	C55	C47	C40	-165.07(9)
C42	O43	C44	C46	-55.80(13)	C44	O43	C42	O60	-10.70(16)
C42	O43	C44	C59	68.57(12)	C44	O43	C42	N41	170.61(9)
C42	N41	C40	C34	-61.76(14)	C35	C34	C39	C38	0.16(17)
C42	N41	C40	C47	170.95(10)	C35	C34	C40	N41	137.06(11)
C9	O10	C11	C12	64.34(13)	C35	C34	C40	C47	-97.85(12)
C9	O10	C11	C13	-178.47(10)	C11	O10	C9	O27	4.42(17)
C9	O10	C11	C26	-61.02(13)	C11	O10	C9	N8	-175.33(9)
C9	N8	C7	C14	123.50(10)	C5	C4	C3	C2	0.64(18)
C9	N8	C7	C1	-107.86(11)	C63	C62	C47	P48	-62.11(12)
C14	P15	O16	C17	177.88(13)	C63	C62	C47	C55	176.99(10)
C14	P15	O19	C20	116.30(9)	C63	C62	C47	C40	55.34(13)
C14	C29	C30	C31	-179.21(10)	C38	C37	C36	C35	-0.41(19)
C1	C6	C5	C4	-1.01(19)	C66	N61	C62	C47	-178.55(10)
C1	C2	C3	C4	-1.04(18)	C66	N61	C62	C63	-0.91(17)
C7	N8	C9	O27	11.19(17)	C66	C65	C64	C63	-0.01(19)

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4aa.

Atom	*x*	*y*	*z*	U(eq)
H7	3869.11	3680.95	4600.2	17
H55A	4500.47	48.85	6433.77	20

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4aa.

Atom	*x*	*y*	*z*	U(eq)
H55B	5240.66	108.62	7147.4	20
H22A	5162.5	2553.79	5734.52	19
H22B	5910.42	2432.28	5121.47	19
H39	6553.77	-163.35	6187.74	24
H33	8339.14	3097.25	3961.62	23
H6	3759.3	2033.03	4848.81	23
H40	5922.19	1468.04	6147.45	17
H32	8105.5	4028.85	3398.76	24
H2	4127.68	3397.27	3510.75	23
H30	5349.53	4398.31	4453.06	21
H31	6587.78	4702.42	3649.47	23
H35	7731.25	1525.22	6814.79	24
H5	3573.78	1312.65	3981.23	28
H45A	8032.76	2173.1	4922.29	33
H45B	9058.82	1835.84	4574.63	33
H45C	8771.45	1625.26	5300.86	33
H46A	8489.49	537.12	4887.38	35
H46B	8744.08	741.21	4153.39	35
H46C	7539.32	393.79	4264.23	35
H63	5590.39	2148.06	6959.3	26
H4	3624.56	1631.54	2879.23	29
H38	8405.5	-583.41	6539.81	28
H37	9931.91	50.31	7014.14	29
H20A	6508.31	4974.19	5454.25	24
H20B	7851.05	4793.56	5696.74	24
H3	3883.89	2676.93	2645.06	28
H59A	6335.2	1250.51	3714.98	34
H59B	7470.89	1653.98	3593.32	34
H59C	6470.63	1938.37	4004.31	34
H66	5582.84	1023.23	8905.3	32
H36	9583.71	1104.63	7157.07	29
H65	6181.79	2040.22	8977.14	35
H64	6197.25	2621.95	7998.4	33

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4aa.

Atom	*x*	*y*	*z*	U(eq)
H12A	-130.12	3818.57	4984.11	37
H12B	-1069.78	3810.62	5521.06	37
H12C	-347.85	3197.33	5383.95	37
H53A	2774.74	2420.02	6971.16	27
H53B	3175.19	2123.77	7689.52	27
H13A	219.34	3166.75	6615.24	41
H13B	-358.04	3824.25	6745	41
H13C	1014.15	3707.29	6969.14	41
H26A	1575.36	4614.93	6294.97	41
H26B	196.56	4743.97	6107.17	41
H26C	1048.63	4668.74	5529.8	41
H54A	811.38	2132.26	7062.2	40
H54B	1280.45	2546.06	7692.53	40
H54C	1198.45	1811.39	7766.13	40
H21A	7289.31	5614.29	6346.33	43
H21B	7498.11	5017.21	6811.94	43
H21C	6183.65	5227.53	6549.36	43
H50A	1256.78	1361.5	5853.45	30
H50B	1041.84	628.58	5815.24	30
H51A	676.92	989.54	4745.4	54
H51B	1916.27	635.89	4779.66	54
H51C	1883.4	1374.69	4808.38	54
H18A	3357.35	3686.48	7182.64	61
H18B	4120.89	3879.93	7862.45	61
H18C	4301.41	3214.46	7542.21	61
H17A	4872.4	4348.25	6965.4	66
H17B	5820.58	3879.87	7330.39	66
H41	4851(14)	458(8)	5543(8)	26(4)
H8	3311(15)	2899(8)	5602(9)	33(4)