Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Allylation of ß-amino Phosphonic Acid Precursor via Palladium-NHC Catalyzed Allylic C-H Activation

Wei Ren, [†]Ming Jin, [†] Qian-Ming Zuo, [†] Shang-Dong Yang*[†‡]

[†]State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R. China.

‡State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, P. R. China.

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1. General Information

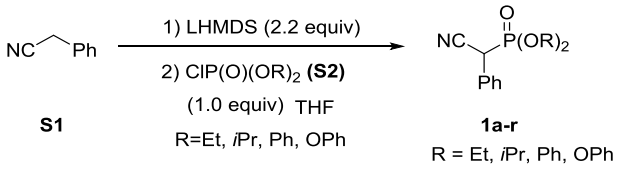
All solvents were treated according to standard procedures prior to use unless otherwise noted. Palladium acetate was purchased from Shanghai Darui Fine Chemistry Co., Ltd. Other Reagents were obtained from commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance Ⅲ400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C), Bruker advance Ⅲ600 spectrometer (600 MHz for ^{1}H and 151 MHz for ^{13}C) or Varian instrucment (300 MHz) in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C as internal standard. ^{31}P NMR spectra were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants, *J*, are reported in hertz. The desired products were purified by column chromatography on silica gel (200-300 mesh). Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm).

2. Experimental Procedure

2.1 Methods for the Synthesis of Substrates

Substrates **2a, 2b, 2c, 2f, 2k, 2l, 2t** are commercially available and used directly without further purification. **2d-e** [1], **2g** [2], **2h-j**[1b,c], **2m** [3], **2n** [2], **2o** [4], **2p** [5], **2q** [6], **2r** [4], **2s** [7], **2u** [2], **1s** [8], **1t** [9], **1u** [10] were prepared according to the literature method.

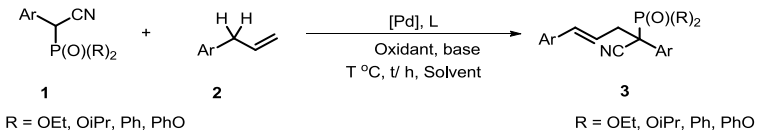
2.2 Procedure for preparation of a-cyano-phosphate ester [11]



1a-r were synthesized via deprotonation of phenylacetonitrile (**S1**) by LHMDS followed by Phosphorylation with the Dialkyl phosphorochloridate. For the synthesis of **1a**, to a solution of LHMDS (1.0 M in THF, 110 mL, 110 mmol) was added phenylacetonitrile (**S1**, 5.9 g, 50 mmol) dropwise at -78 ℃, after stirred for 60 min, Diethyl chlorophosphate **(S2)** (8.6 g, 50 mmol) was added and the mixture was allowed to stir at 0 ℃ for 40 min. After completion of the reaction, the reaction mixture was quenched with 2N HCl aq. and the mixture was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, solvent was removed on a rotary evaporator, and the residue was purified by column chromatography (Petroleum ether / Ethyl acetate. = 1:1) to afford **1a** (9.2 g, 36 mmol, 72 %) as a colorless oil.

3. Experimental details

General Procedure

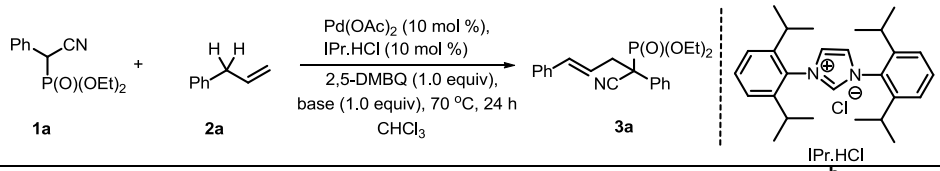


1 2 3

R = OEt, OiPr, Ph, PhO R = OEt, OiPr, Ph, PhO

The indicated catalyst, base, oxidant and a-cyano-phosphate ester (**1)** were added to an oven-dried 10 mL glass tube equipped with a stirring bar. The tube was filled with a rubber plug to ensure inert (argon) atmosphere. With stirring, solvent was added following by allylbenzene (**2)**. The reaction mixture was vigorously stirred and after completion of the reaction indicated by thin-layer chromatography analysis, the product was achieved by column chromatography on silica gel.

3.1 Table S1: The Effect of Base[a]

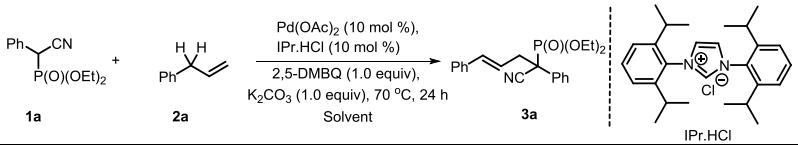


1a 2a 3a

Entry	Base	Yield[b][%]
1	**K_2CO_3**	**58**
2	Cs_2CO_3	49
3	^{t}BuONa	33
4	^{t}BuOLi	trace
5	^{t}BuOK	24
6	Na_2CO_3	trace
7	K_3PO_4	31
8	$KHCO_3$	trace
9	NaOAc	trace
10	KOAc	<10

[a] The reactions were carried out by using **1a** (0.15 mmol), **2a** (0.225 mmol), $Pd(OAc)_2$ (10 mol %), IPr.HCl (10 mol %), 2,5-DMBQ (1.0 equiv), and base (1.0 equiv) in $CHCl_3$ (2.0 mL) at 70 ℃ for 24 h under argon. [b]Isolated yields.

3.2 Table S2: The Effect of Solvent[a]

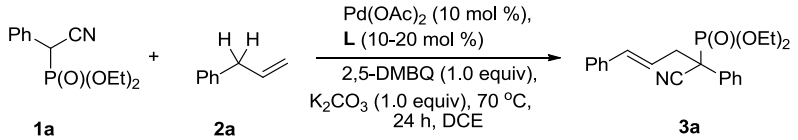


1a 2a 3a

Entry	Solvent	Yield[b][%]
1	**DCE**	**75**
2	THF	40
3	Toluene	64
4	Acetonitrile	45
5	DCM	70
6	DME	49
7	Dioxane	Trace
8	CH_3OH	Trace
9	DMF	N.R
10	Et_2O	67

[a] The reactions were carried out by using **1a** (0.15 mmol), **2a** (0.225 mmol), $Pd(OAc)_2$ (10 mol %), IPr.HCl (10 mol %), 2,5-DMBQ (1.0 equiv), and K_2CO_3 (1.0 equiv) in Solvent (2.0 mL) at 70 ℃ for 24 h under argon. [b]Isolated yields.

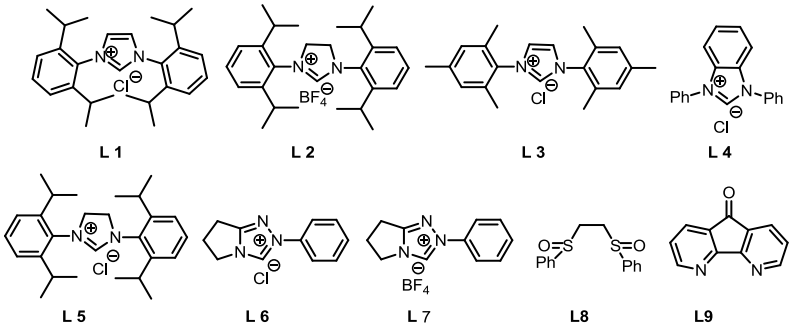
3.3 Table S3: The Effect of ligands[a]



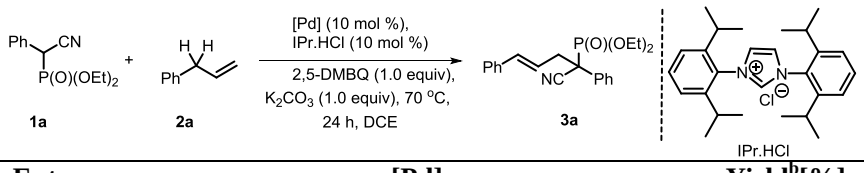
1a **2a** **3a**

Entry	Ligand	Yield[b][%]
1	**L1**	**75**
2	L2	50
3	L3	63
4	L4	32
5	L5	64
6	L6	51
7	L7	61
8	L8	Trace
9	L9	10 (L:B = 7:1)

[a] The reactions were carried out by using **1a** (0.15 mmol), **2a** (0.225 mmol), $Pd(OAc)_2$ (10 mol %), **L1-L9** (10-20 mol %), 2,5-DMBQ (1.0 equiv), K_2CO_3 (1.0 equiv) in DCE (2.0 mL) at 70 ℃ for 24 h under argon. [b]Isolated yields.



3.4 Table S4: The Effect of [Pd][a]

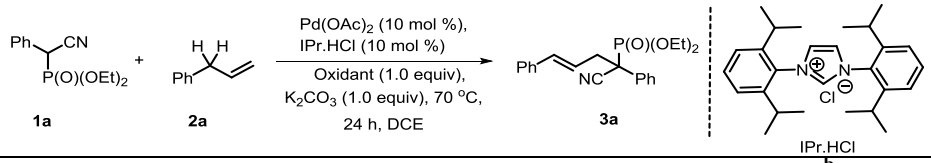


1a **2a** **3a**

Entry	[Pd]	Yield[b][%]
1	$Pd(dba)_2$	34
2	$PdCl_2$	37
3	$(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$	62
4	$Pd(CF_3COO)_2$	70
5	PdI_2	Trace
6	$PdBr_2$	Trace
7	$Pd(NO_3)_2$	36
8	$PdCl_2(CH_3CN)_2$	8
9	$PdCl_2(C_6H_5CN)_2$	Trace
10	**$Pd(OAc)_2$**	**75**
11	Pd (η^3-cin)(IPr)Cl	76

[a] The reactions were carried out by using **1a** (0.15 mmol), **2a** (0.225 mmol), [Pd] (10 mol %), IPr.HCl (10 mol %), 2,5-DMBQ (1.0 equiv), and K_2CO_3 (1.0 equiv) in DCE (2.0 mL) at 70 ℃ for 24 h under argon. [b]Isolated yields.

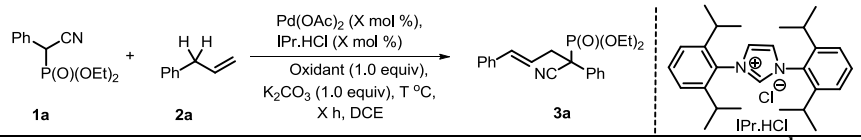
3.5 Table S5: The Effect of Oxidant[a]



Entry	Oxidant	Yield[b][%]
1	2,5-dichloro-1,4-benzoquinone	Trace
2	2,6-Dichloro-1,4-benzoquinone	Trace
3	BQ	<10
4	2,6-dimethoxy-1,4-benzoquinone	54
5	2,3,5,6-tetramethyl-1,4-benzoquinone	10
6	Methyl-p-benzoquinone	30
7	Tetrachloro-p-benzoquinone	N.R[c]
8	2,6-Di-tert-butyl-p-benzoquinone	18
9	Anthraquinone	Trace
10	1,4-Naphthoquinone	52
11	MnO_2	Trace
12	2,6-DMBQ	40
13	**2,5-DMBQ**	**75**
14	Oxone	Trace
15	Ag_2CO_3	N.R[c]
16	$Cu(OAc)_2$	N.R[c]
17	Ag_2O	N.R[c]
18	Ag_2CO_3+2,5-DMBQ	N.R[c,d]

[a] The reactions were carried out by using **1a** (0.15 mmol), **2a** (0.225 mmol), $Pd(OAc)_2$ (10 mol %), IPr.HCl (10 mol %), Oxidant (1.0 equiv), and K_2CO_3 (1.0 equiv) in DCE (2.0 mL) at 70 ℃ for 24 h under argon. [b]Isolated yields. [c] No reaction, [d]Ag_2CO_3 (1.0 equiv) +2,5-DMBQ (10 mol %).

3.6 Table S6: The Effect of Other Reaction Conditions[a]

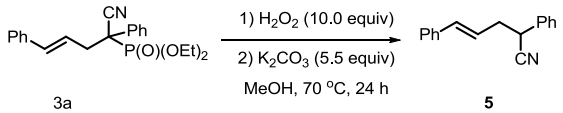


Entry	T(°C)	Yield[b][%]
1	25	Trace
2	30	Trace
3	40	Trace
4	50	<10
5	60	72[c]
6	70	75
7	80	84
8	90	84
9	80	67[d]
10	80	84[e]
11	80	84[f]
12	80	65[g]
13	80	84[h]
14	80	84[i]
15	80	73[j]
16	**80**	**91[k]**

[a] The reactions were carried out by using **1a** (0.15 mmol), **2a** (0.225 mmol), Pd $(OAc)_2$ (10 mol %), IPr.HCl (10 mol %), 2,5-DMBQ (1.0 equiv), and K_2CO_3 (1.0 equiv) in DCE (2.0 mL) for 24 h under argon. [b]Isolated yields. [c]60 °C for 60 h, [d][Pd] (5 mol %), IPr.HCl (5 mol %), [e]Pd $(OAc)_2$ (10.0 mol %), IPr.HCl (10.0 mol %), [f]Pd $(OAc)_2$ (12.5 mol %), IPr.HCl (12.5 mol %), [g] 2a (0.15 mmol), [h]K_2CO_3 (1.5 equiv), [i]2,5-DMBQ (1.5 equiv), [j]for 12 h, [k]for 36 h.

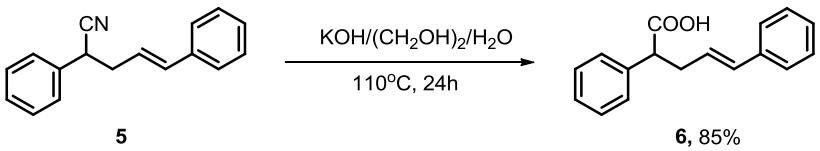
4. The derivatization of reaction products

4.1 Procedure for preparation of 2,5-diphenylpent-4-enenitrile (5)



To a solution of **3a** (277.5 mg, 0.75 mmol) in MeOH (22.5 mL), H_2O_2 (0.3 mL) and K_2CO_3 (0.55 g, 4.1 mmol) was added at 0°C. Then the mixture was allowed to stir at 70 ℃ for 24 h. After completion of the reaction indicated by thin-layer chromatography analysis, the mixture was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography (hexane/ ethyl acetate = 15: 1) to afford 2,5-diphenylpent-4-enenitrile **5** [12] (0.149 g, 85 %) as a white solid.

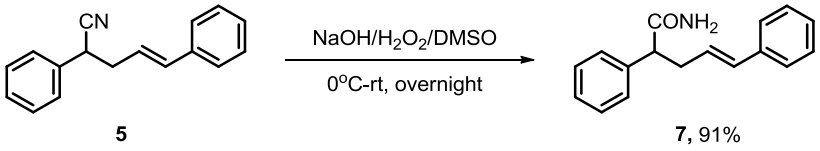
4.2 Procedure for preparation of 2,5-diphenylpent-4-enoic acid (6)



5 **6**, 85%

According to the reported procedure and a little modification, [13] An ethylene glycol solution (3.0 mL) of 2,5-diphenylpent-4-enenitrile (155 mg, 0.67 mmol), KOH (223mg, 3.99 mmol) and water (1.0 mL) was heated at 110 ℃ for 24 h. After completion of the reaction indicated by thin-layer chromatography analysis and the mixture was cooled to room temperature. Then, the mixture was acidified with HCl (6N) to PH = 3, and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography (Methanol / Ethyl acetate = 1/ 30) to afford **6** [14] (0.142 g, 85 %) as a white solid.

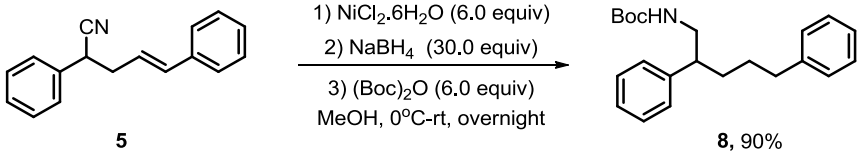
4.3 Procedure for preparation of 2,5-diphenylpent-4-enamide (7)



5 **7**, 91%

According to the reported procedure and a little modification, [15] An oven dried reaction flask containing a magnetic stir bar was charged with 2,5-diphenylpent-4-enenitrile (51.0 mg, 0.219 mmol) and DMSO (2.0 mL). The mixture was cooled to 0 °C before NaOH (0.3 mL, 0.5 M) and H_2O_2 aq. (30 wt% in water, 0.1 mL) were added and stirred at room temperature for overnight. The reaction mixture was quenched by the addition of water, the mixture extracted with ethyl acetate. The organic layers were combined and washed with water and NaCl aq, dried over Na_2SO_4, filtered and concentrated in vacuo to afford the crude product. Purification by flash column chromatography on silica gel (Petroleum ether / Ethyl acetate = 1:1) gave the product **7** (50 mg, 91% yield) as a white solid.

4.4 Procedure for preparation of tert-butyl (2,5-diphenylpentyl) carbamate (8)

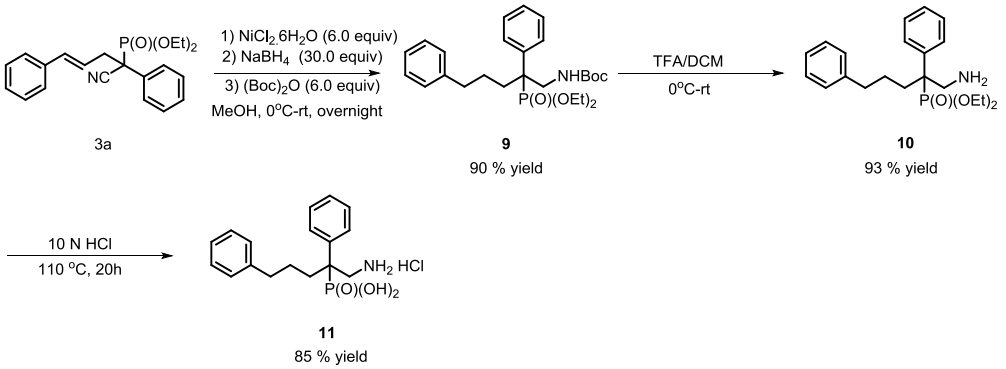


5 **8**, 90%

According to the reported procedure and a little modification, [16] A dry reaction tube was charged with (116.5 mg, 0.5 mmol) 2,5-diphenylpent-4-enenitrile, 0.714 g $NiCl_2.6H_2O$ (3.0 mmol), 0.654 g $(Boc)_2O$ (3.0 mmol) and 10 mL MeOH. Then, the mixture was cooled to 0 ℃ and 0.57 g $NaBH_4$ (15.0 mmol) was added in portions. The reaction was allowed to stir at room temperature for overnight, after completion of the reaction indicated by thin-layer chromatography analysis

and the mixture was concentrated at room temperature. Then quenched with water and extracted with ethyl acetate, the organic layers were combined and washed with water and NaCl aq, dried over Na_2SO_4, filtered and concentrated in vacuo to afford the crude product. Purification by flash column chromatography on silica gel (Petroleum ether / Ethyl acetate = 20:1) gave the product **9** (0.149 g, 90% yield) as a white solid.

4.5 Procedure for preparation of (1-amino-2,5-diphenylpentan-2-yl) phosphonic acid hydrochloride.[16, 17]



3a

9
90 % yield

10
93 % yield

11
85 % yield

A dry reaction tube was charged with 679 mg **3a** (1.84 mmol), 1.43 g $NiCl_2.6H_2O$ (11.04 mmol), 2.7g $(Boc)_2O$ (11.04 mmol) and 100 mL MeOH. Then, the mixture was cooled to 0 ℃ and 2.1 g $NaBH_4$ (55.2 mmol) was added in portions. The reaction mixture was allowed to stir at room temperature for overnight. Then quenched with water and filtered over celite (washings with ethyl acetate). The crude product was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to provide the product **9** (786 mg, 90 % yield) as a colorless oil.

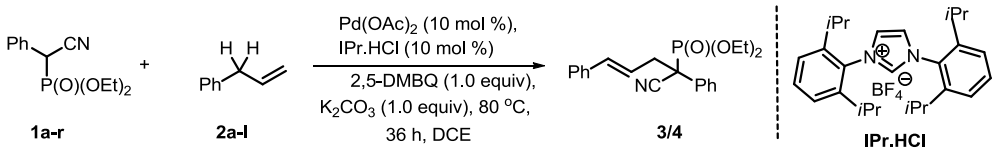
A CH_2Cl_2 solution (5 mL) of **9** (0.475 g, 1 mmol) was treated with trifluoroacetic acid (2.5 mL) at 0 ℃, and then stirred at room temperature for 6 h. The solution was evaporated, and the mixture was basicitied with aqueous saturated Na_2CO_3 to PH = 7-8, and extracted with CH_2Cl_2 (3 x 15 mL). The organics layers were combined and dried over Na_2SO_4, filtered and concentrated in vacuum and the crude product was purified by column chromatography (methanol/ethyl acetate 1:15) to provide the product **10** (348 mg, 93 % yield) as a colorless oil.

The solution of diethyl (1-amino-2,5-diphenylpentan-2-yl) phosphonate **10** (300 mg, 0.8 mmol) in conc. HCl (10 mL) was allowed to refluxed for 20 h. After completion of the reaction and the reaction mixture was cooled to room temperature, volatile compound was removed under reduced pressure. Then the residue was dissolved in hot EtOH (5.0 mL), propylene oxide (0.5 mL) was added at 0 ℃ and allowed to stir at room temperature for 3 h. the solvents were removed under reduced pressure and the residue was recrystallization from ethyl acetate and the precipitate was collected as off-white solid.

5. Experimental details and Analytical Data

5.1. Experimental details

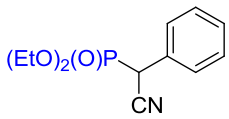
General Procedure for Allylation of *ß*-amino Phosphonic Acid Precursor via Palladium-NHC Catalyzed Allylic *C-H* Activation



A 10 mL Schlenk tube equipped with a magnetic stir bar was equipped with $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 10 mol %), IPr.HCl (6.4 mg, 0.015 mmol, 10 mol %), **1a-r** (0.15 mmol, 1.0 equiv) and K_2CO_3 (20.7 mg, 0.15 mmol, 1.0 equiv), 2,5-DMBQ (20.4 mg, 0.15 mmol, 1.0 equiv). Then the tube was transferred into glove-box with standard procedures and filled with a rubber plug to insure inert (argon) atmosphere. Subsequently the tube was moved outside, Allylbenzene **2a-l** (0.225 mmol, 1.5 equiv) and 2.0 mL DCE was added and the mixture was transferred to oil bath, the reaction mixture was allowed to warm to 80 ^{o}C and stirred for 36 h. Then, the resulting mixture was concentrated in vacuo to afford the crude product. Purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate 4:1 to 3:1) to afford the target products.

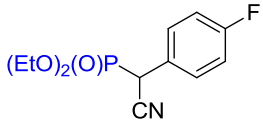
5.2. Analytical Data

Diethyl (cyano (phenyl) methyl) phosphonate (1a) [11]**:**



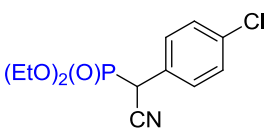
Colorless oil, 72 % yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.47-7.34 (m, 5H), 4.30-4.21 (d, *J* = 26.5 Hz, 1H), 4.18-3.95 (m, 4H), 1.31-1.20 (m, 6H); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 14.74; **MS (ESI)**: $[M+H]^+$ 254.2.

Diethyl (cyano (4-fluorophenyl) methyl) phosphonate (1b) [18]**:**



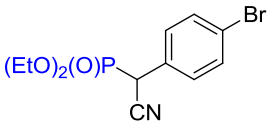
white solid, 67 % yield; **M.p.** 73-75 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.41 (m, 2H), 7.08 (t, *J* = 8.4 Hz, 2H) 4.27-4.20 (d, *J* = 26.2 Hz, 1H), 4.17-4.00 (m, 4H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8.0 (dd, *J* = 3.4, 249.7 Hz), 130.4 (dd, *J* = 4.9, 8.4 Hz), 123.5 (dd, *J* = 3.3, 8.3 Hz), 116.0 (dd, *J* = 2.7, 22.1 Hz), 115.2 (d, *J* = 9.8 Hz); 64.8 (d, *J* = 7.1 Hz); 64.4 (d, *J* = 7.1 Hz); 35.9 (d, *J* = 139.4 Hz); 16.2 (d, *J* = 5.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 14.01; **MS (ESI)**: $[M+ Na]^+$ 294.2.

Diethyl ((4-chlorophenyl) (cyano) methyl) phosphonate (1c) [18]**:**



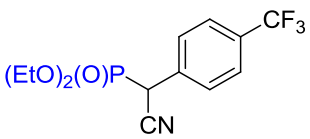
white solid, 63 % yield; **M.p.** 60-63 ^{o}C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42-7.36 (m, 4H), 4.27-4.18 (d, *J* = 26.2 Hz, 1H), 4.17-3.99 (m, 4H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 14.83; **MS (ESI)**: $[M+ Na]^+$ 310.1.

Diethyl ((4-bromophenyl) (cyano)methyl) phosphonate (1d):



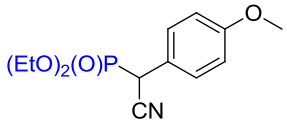
white solid, 53 % yield; **M.p.** 74-78 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.35-7.31 (m, 2H), 4.20 (d, *J* = 26.4 Hz, 1H), 4.15-4.02 (m, 4H), 1.33-1.23 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.1, 130.1 (d, *J* = 4.9 Hz), 126.9, 122.9, 115.0 (d, *J* = 10.1 Hz), 64.8 (d, *J* = 7.4 Hz), 64.4 (d, *J* = 7.4 Hz), 36.1 (d, *J* = 138.4 Hz), 16.1 (d, *J* = 5.5 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 14.45; **HRMS** (ESI) calcd for $C_{12}H_{15}BrNO_3P$ $[M+H]^+$ 332.0045; found 332.0040.

Diethyl (cyano (4-(trifluoromethyl) phenyl) methyl) phosphonate (1e):



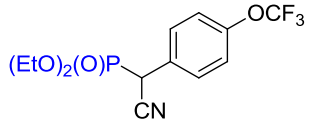
Colorless oil, 62 % yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.28-7.26 (m, 2H), 4.32-4.23 (d, *J* = 26.3 Hz, 1H), 4.21-4.02 (m, 4H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.0 (d, *J* = 8.1 Hz), 129.1 (d, *J* = 5.1 Hz), 125.9, 124.4, 122.2, 114.1 (d, *J* = 10.1 Hz), 64.9 (d, *J* = 7.1 Hz), 64.5 (d, *J* = 7.1 Hz), 36.6 (d, *J* = 137.4 Hz), 16.1 (d, *J* = 5.8 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 14.72; **HRMS** (ESI) calcd for $C_{13}H_{15}F_3NO_3P$ $[M+H]^+$ 322.0814; found 322.0810.

Diethyl (cyano (4-methoxyphenyl) methyl) phosphonate (1f) [18]:



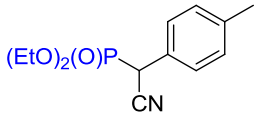
white solid, 63 % yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37-7.33 (m, 2H), 6.92-6.88 (m, 2H), 4.22 (d, *J* = 26.4 Hz, 1H), 4.14-3.96 (m, 4H), 3.79 (s, 3H), 1.28 (d, *J* = 7.2 Hz, 3H), 1.24 (d, *J* = 7.2 Hz, 3H); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 15.69; **MS (ESI)**: $[M+H]^+$ 284.3.

Diethyl (cyano (4-(trifluoromethoxy) phenyl) methyl) phosphonate (1g):



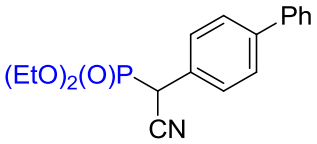
white solid, 66 % yield; **M.p.** 62-64 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.26 (d, *J* = 26.3 Hz, 1H), 4.21-4.02 (m, 4H), 1.31 (d, *J* = 7.1 Hz, 3H), 1.25 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.5, 130.2 (d, *J* = 5.1 Hz), 126.5 (d, *J* = 8.1 Hz), 121.4, 115.0 (d, *J* = 10.1 Hz), 64.9 (d, *J* = 7.1 Hz), 64.5 (d, *J* = 7.1 Hz), 36.1 (d, *J* = 138.4 Hz), 16.2 (d, *J* = 5.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 13.73; **HRMS** (ESI) calcd for $C_{13}H_{15}F_3NO_4P$ $[M+H]^+$ 338.0763; found 338.0761.

Diethyl (cyano (p-tolyl) methyl) phosphonate (1h) [18]:



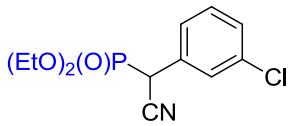
white solid, 71 % yield; **M.p.** 63-66 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.22 (d, *J* = 26.4 Hz, 1H), 4.16-3.95 (m, 4H), 2.34 (s, 3H), 1.32-1.22 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.6, 129.6 (d, *J* = 2.7 Hz), 128.4 (d, *J* = 5.0 Hz), 124.5 (d, *J* = 8.5 Hz), 115.5 (d, *J* = 9.7 Hz), 64.6 (d, *J* = 7.2 Hz), 64.2 (d, *J* = 7.2 Hz), 36.8 (d, *J* = 138.4 Hz), 21.0, 16.2 (d, *J* = 5.8 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 14.47; **MS (ESI)**: $[2M+Na]^+$ 557.1.

Diethyl ([1, 1'-biphenyl]-4-yl (cyano) methyl) phosphonate (1i):



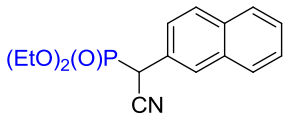
white solid, 58 % yield; **M.p.** 86-90 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63-7.52 (m, 6H), 7.46-7.34 (m, 3H), 4.32 (d, *J* = 26.5 Hz, 1H), 4.21-4.03 (m, 4H), 1.34-1.30 (d, *J* = 8.0 Hz, 3H), 1.29-1.25 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.6 (d, *J* = 3.1 Hz), 139.8, 128.9, 128.7, 127.6, 126.9, 126.6, 126.5, 115.4, 64.7 (d, *J* = 7.1 Hz), 64.3 (d, *J* = 6.8 Hz), 36.4 (d, *J* = 138.8 Hz), 16.1 (d, *J* = 5.5 Hz); **^{31}P NMR** (162 MHz, CDCl3) δ 14.28; **HRMS** (ESI) calcd for $C_{18}H_{20}NO_3P$ $[M+H]^+$ 330.1181; found 330.1251.

Diethyl ((3-chlorophenyl) (cyano) methyl) phosphonate (1j) [19]:



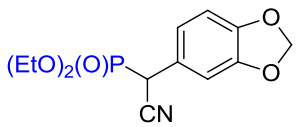
white solid, 35 % yield; **M.p.** 40-45 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.48-7.47 (m, 1H), 7.41-7.30 (m, 3H), 4.29 (d, *J* = 26.3 Hz, 1H), 4.24-4.04 (m, 4H), 1.35-1.26 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.8, 133.2 (d, *J* = 2.0 Hz), 129.8 (d, *J* = 8.1 Hz), 128.9, 128.7 (d, *J* = 5.1 Hz), 126.8 (d, *J* = 5.1 Hz), 114.9 (d, *J* = 10.1 Hz), 64.8 (d, *J* = 7.1 Hz), 64.5 (d, *J* = 6.8 Hz), 36.2 (d, *J* =137.4 Hz), 16.1 (d, *J* = 5.5 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 14.73; **MS (ESI)**: $[M+H]^+$ 288.4.

Diethyl (cyano (naphthalen-2-yl) methyl) phosphonate (1k) [19]:



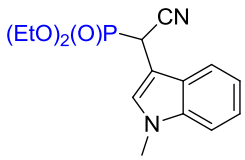
white solid, 34 % yield; **M.p.** 71-73 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.88-7.82 (m, 3H), 7.55-7.50 (m, 3H), 4.43 (d, *J* = 26.5 Hz, 1H), 4.21-3.95 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.03 (d, *J* = 3.0 Hz), 132.93 (d, *J* = 2.0 Hz), 128.89 (d, *J* = 2.0 Hz), 128.06 (d, *J* = 7.1 Hz), 127.90, 127.66 (d, *J* = 2.0 Hz), 126.83, 126.76, 125.72 (d, *J* = 3.1 Hz), 124.97 (d, *J* = 8.1Hz), 115.50 (d, *J* = 10.1 Hz), 64.77 (d, *J* = 7.1 Hz), 64.36 (d, *J* = 7.1 Hz), 36.89 (d, *J* = 138.37 Hz), 16.21 (d, *J* = 5.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 14.33; **HRMS (ESI)** calcd for $C_{16}H_{18}NO_3P$ $[M+Na]^+$: 326.0914. Found: 326.0916.

Diethyl (benzo[d] [1,3] dioxol-5-yl(cyano)methyl) phosphonate (1l):



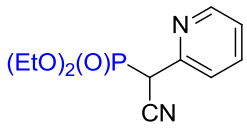
white solid, 64 % yield; **M.p.** 49-53 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.93-6.92 (m, 1H), 6.90-6.87 (m, 1H), 6.80-6.78 (d, *J* = 8.0 Hz, 1H), 5.97 (s, 2H), 4.18-4.04 (m, 5H), 1.30 (t, *J* = 5.4 Hz, 3H), 1.27 (t, *J* = 5.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.19 (d, *J* = 2.7 Hz), 148.11 (d, *J* = 3.2 Hz), 122.3 (d, *J* = 6.1 Hz), 120.9 (d, *J* = 8.5 Hz), 115.5 (d, *J* = 9.1 Hz), 109.0 (d, *J* = 4.1 Hz), 108.5 (d, *J* = 2.9 Hz), 101.5, 64.7 (d, *J* = 7.3 Hz), 64.3 (d, *J* = 7.2 Hz), 36.3 (d, *J* =140.4 Hz), 16.2 (d, *J* = 5.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 14.33; **HRMS** (ESI) calcd for $C_{13}H_{16}NO_5P$ $[M+H]^+$ 298.0838; found 298.0836.

Diethyl (cyano (1-methyl-1H-indol-3-yl) methyl) phosphonate (1m):



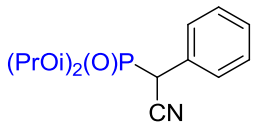
reddish brown solid, 25 % yield; **M.p.** 70-74 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.33-7.24 (m, 3H), 7.17 (t, *J* = 7.5 Hz, 1H), 4.53 (d, *J* = 25.9 Hz, 1H), 4.17-3.95 (m, 4H), 3.78 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.8, 128.7 (d, *J* = 6.1 Hz), 126.0 (d, *J* = 4.0 Hz), 122.3, 119.9, 118.8, 115.7 (d, *J* = 7.1 Hz), 109.6, 100.1 (d, *J* = 8.1 Hz), 64.4 (d, *J* = 7.2 Hz), 64.1 (d, *J* = 7.1 Hz), 32.9, 28.1 (d, *J* = 146.5 Hz), 16.2 (t, *J* = 5.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.12; **HRMS** (ESI) calcd for $C_{15}H_{19}N_2O_3P$ $[M+H]^+$ 307.1206; found 307.1202.

Diethyl (1-cyano-4-phenyl-1-(pyridin-2-yl) but-3-en-1-yl) phosphonate (1n) [20]:



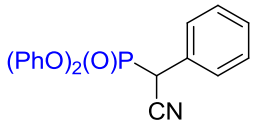
brow solid, 40 % yield; **M.p.** 74-80 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.0 (s, 1H), 7.42 (t, *J* = 6.9 Hz, 2H), 7.28-7.26 (m, 1H), 6.43 (t, *J* = 6.6 Hz, 1H), 4.16-4.12 (m, 4H), 1.38 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1 (d, *J* = 8.7 Hz), 138.9, 134.2, 120.5 (d, *J* = 13.7 Hz), 119.8 (d, *J* = 8.8 Hz), 110.3, 62.4 (d, *J* = 5.4 Hz), 46.4 (d, *J* = 212.1 Hz), 16.0 (d, *J* = 7.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.46; **MS (ESI)**: $[M+H]^+$ 255.1.

Diisopropyl (cyano (phenyl)methyl) phosphonate (1o) [21]:



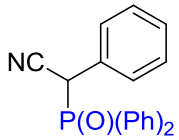
pale yellow solid, 23 % yield; **M.p.** 44-48 ^{o}C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.48-7.25 (m, 5H), 4.70-4.56 (m, 2H), 4.20 (d, *J* = 26.5 Hz, 1H), 1.31 (dd, *J* = 6.2, 13.9 Hz, 6H), 1.18 (dd, *J* = 6.2, 13.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 128.7 (d, *J* = 3.0 Hz), 128.6 (d, *J* = 5.0 Hz), 128.5 (d, *J* = 3.0 Hz), 128.0 (d, *J* = 7.1 Hz), 115.6 (d, *J* = 10.1 Hz), 73.5 (d, *J* = 7.1 Hz), 73.2 (d, *J* = 7.1 Hz), 37.3 (d, *J* = 140.4 Hz), 23.8 (dd, *J*= 5.1, 12.1 Hz), 23.3 (dd, *J* = 6.1, 12.1 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 13.11; **MS (ESI)**: $[2M+H]^+$ 563.2.

Diphenyl (cyano(phenyl)methyl) phosphonate (1p) [21]:



white solid, 71 % yield; **M.p.** 90-92 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 7.44-7.40 (m, 3H) 7.32-7.11 (m, 8H), 6.95-6.92 (m, 2H), 4.69-4.59 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.8 (d, *J* = 10.1 Hz), 149.6 (d, *J* = 9.1 Hz), 129.8, 129.6, 129.1 (d, *J* = 3.0 Hz), 129.0 (d, *J* = 4.0 Hz), 128.9 (d, *J* = 5.1 Hz), 126.4 (d, *J* = 7.1 Hz), 125.8, 125.6, 120.2 (d, *J* = 4.0 Hz), 120.0 (d, *J* = 4.0 Hz), 114.5, 36.6 (d, *J* = 143.4 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 6.76; **MS (ESI)**: $[M+Na]^+$ 372.2.

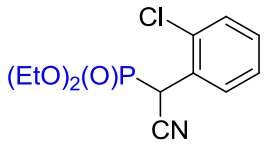
2-(diphenylphosphoryl)-2-phenylacetonitrile (1q):



white solid, 65 % yield; **M.p.** 223-229 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.78 (m, 4H), 7.61-7.57 (m, 2H), 7.51-7.44 (m, 4H), 7.27-7.17 (m, 5H), 4.82-4.78 (d, *J* = 17.9 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.9 (dd, *J* = 2.9, 6.2 Hz), 132.1 (d, *J* = 9.1 Hz), 131.6 (d, *J* = 9.5 Hz), 131.1 (d, *J* = 10.5 Hz), 129.8, 129.0 (d, *J* = 4.0 Hz), 128.8 (d, *J* = 12.1 Hz), 128.5 (d, *J* = 2.0 Hz), 128.4, 128.2 (d, *J* =

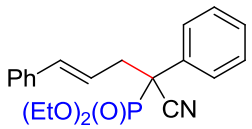
13.1 Hz), 127.8, 127.1 (d, *J* = 6.1 Hz), 126.8, 116.5 (d, *J* = 3.9 Hz), 40.1 (d, *J* = 57.3 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 27.48; **HRMS** (ESI) calcd for $C_{20}H_{16}NOP$ $[M+H]^+$ 318.1042; found 318.1040.

Diethyl ((2-chlorophenyl) (cyano) methyl) phosphonate (1r):



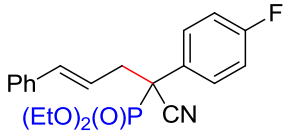
pale yellow oil, 29 % yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.76-7.72 (m, 1H), 7.45-7.28 (m, 3H), 4.91 (d, *J* = 25.8 Hz, 1H), 4.28-4.18 (m, 2H), 4.16-3.98 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 133.4 (d, *J* = 6.8 Hz), 130.5 (d, *J* = 4.2 Hz), 130.2 (d, *J* = 3.1 Hz), 129.8 (d, *J* = 2.5 Hz), 127.6 (d, *J* = 3.0 Hz), 126.5 (d, *J* = 8.5 Hz), 115.3 (d, *J* = 9.6 Hz), 64.6 (d, *J* = 7.1 Hz), 64.5 (d, *J* = 7.1 Hz), 34.13 (d, *J* = 138.8 Hz), 16.2 (d, *J* = 5.8 Hz), 16.1 (d, *J* = 5.6 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 14.45; **HRMS** (ESI) calcd for $C_{12}H_{15}ClNO_3P$ $[M+H]^+$ 288.0550; found 288.0552.

Diethyl (1-cyano-1,4-diphenylbut-3-en-1-yl) phosphonate (3a):



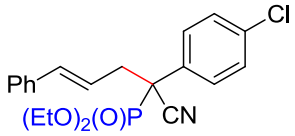
Colorless oil, 91 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.33-7.29 (m, 1H), 7.19-7.12 (m, 5H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.00-5.92 (m, 1H), 4.25-4.16 (m, 2H), 3.90-3.80 (m, 1H), 3.67-3.53 (m, 1H), 3.30-3.17 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.2, 135.2, 130.5 (d, *J* = 6.7 Hz), 128.5 (d, *J* = 2.0 Hz), 128.3 (d, *J* = 2.0 Hz), 128.1, 127.6 (d, *J* = 4.9 Hz), 127.4, 126.0, 121.4 (d, *J* = 11.7 Hz), 117.5 (d, *J* = 9.6 Hz), 64.8 (d, *J* = 7.4 Hz), 64.0 (d, *J* = 7.9 Hz), 47.6 (d, *J* = 138.4 Hz), 37.8 (d, *J* = 3.4 Hz), 15.9 (d, *J* = 5.8 Hz), 15.7 (d, *J* = 5.6 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 18.50; **HRMS** (ESI) calcd for $C_{21}H_{24}NO_3P$ $[M+H]^+$ 370.1567; found 370.1567.

Diethyl (1-cyano-1-(4-fluorophenyl)-4-phenylbut-3-en-1-yl)phosphonate (3b):



yellow oil, 89 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.64 (m, 2H), 7.27-7.18 (m, 5H), 7.11 (t, *J* = 8.5 Hz, 2H), 6.52 (d, *J* = 15.7 Hz, 1H), 5.99-5.92 (m, 1H), 4.30-4.22 (m, 2H), 3.97-3.88 (m, 1H), 3.73-3.63 (m, 1H), 3.24-3.20 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.6 (dd, *J* = 2.8, 249.9 Hz), 136.4, 135.7, 129.8 (dd, *J* = 4.9, 8.3 Hz), 128.5, 127.8, 126.8 (dd, *J* = 3.3, 6.6 Hz), 126.3, 121.3 (d, *J* = 11.9 Hz), 117.8 (d, *J* = 9.8 Hz), 115.9 (dd, *J* = 2.4, 21.8 Hz), 65.1 (d, *J* = 7.4 Hz), 64.4 (d, *J* = 7.9 Hz), 47.2 (d, *J* = 138.6 Hz), 38.2 (d, *J* = 3.2 Hz), 16.3 (d, *J* = 5.8 Hz), 16.1 (d, *J* = 5.7 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 17.2; **HRMS** (ESI) calcd for $C_{21}H_{23}FNO_3P$ $[M+H]^+$ 388.1472; found 388.1468.

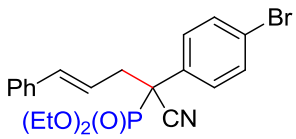
Diethyl (1-(4-chlorophenyl)-1-cyano-4-phenylbut-3-en-1-yl)phosphonate(3c):



Colorless oil, 84 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63-7.60 (m, 2H), 7.39 (d,

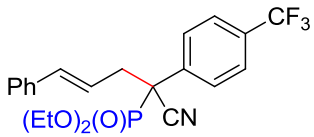
J = 8.5 Hz, 2H), 7.28-7.18 (m, 5H), 6.52 (d, *J* = 15.7 Hz, 1H), 5.98-5.91 (m, 1H), 4.30-4.23 (m, 2H), 3.99-3.89 (m, 1H), 3.75-3.65 (m, 1H), 3.24-3.20 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.3, 135.8, 134.8 (d, *J* = 3.3 Hz), 129.6 (d, *J* = 6.7 Hz), 129.4 (d, *J* = 5.0 Hz), 129.0 (d, *J* = 2.4 Hz), 128.5, 127.8, 126.4, 121.3 (d, *J* = 11.8 Hz), 117.6 (d, *J* = 9.7 Hz), 65.2 (d, *J* = 7.3 Hz), 64.5 (d, *J* = 7.8 Hz), 47.5 (d, *J* = 137.4 Hz), 38.2 (d, *J* = 3.5 Hz), 16.3 (d, *J* = 5.8 Hz), 16.1 (d, *J* = 5.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.93; **HRMS** (ESI) calcd for $C_{21}H_{23}ClNO_3P$ $[M+H]^+$ 404.1177; found 404.1173.

Diethyl (1-(4-bromophenyl)-1-cyano-4-phenylbut-3-en-1-yl) phosphonate (3d):



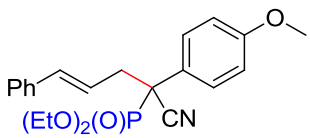
Colorless oil, 72 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.54 (m, 4H), 7.32-7.18 (m, 5H), 6.55 (d, *J* = 15.7 Hz, 1H), 5.98-5.90 (m, 1H), 4.30-4.21 (m, 2H), 3.99-3.89 (m, 1H), 3.75-3.67 (m, 1H), 3.24-3.20 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.3, 135.7, 132.0 (d, *J* = 2.4 Hz), 130.1 (d, *J* = 6.7 Hz), 129.6 (d, *J* = 5.0 Hz), 128.4, 127.8, 126.4, 123.0 (d, *J* = 3.5 Hz), 121.1 (d, *J* = 11.9 Hz), 117.5 (d, *J* = 9.7 Hz), 65.2 (d, *J* = 7.4 Hz), 64.5 (d, *J* = 7.9 Hz), 47.5 (d, *J* = 138.4 Hz), 38.0 (d, *J* = 3.4 Hz), 16.2 (d, *J* = 5.8 Hz), 16.1 (d, *J* = 5.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.78; **HRMS** (ESI) calcd for $C_{21}H_{23}BrNO_3P$ $[M+H]^+$ 448.0672; found 448.0668.

Diethyl (1-cyano-4-phenyl-1-(4-(trifluoromethyl) phenyl) but-3-en-1yl) phosphonate (3e):



Colorless oil, 74 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.0 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.27-7.18 (m, 5H), 6.54 (d, *J* = 15.7 Hz, 1H), 5.98-5.90 (m, 1H), 4.32-4.24 (m, 2H), 4.00-3.91 (m, 1H), 3.79-3.68 (m, 1H), 3.27 (t, *J* = 7.7 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.2, 136.0, 135.4 (d, *J* = 6.1 Hz), 131.1, 130.7, 128.5, 128.4, 127.8, 126.3, 125.7 (t, *J* = 6.1 Hz), 120.9 (d, *J* = 11.1 Hz), 117.4 (d, *J* = 11.1 Hz), 65.2 (d, *J* = 7.5 Hz), 64.7 (d, *J* = 7.9 Hz), 47.9 (d, *J* = 137.4 Hz), 38.2 (d, *J* = 3.6 Hz), 16.3 (d, *J* = 5.7 Hz), 16.0 (d, *J* = 5.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.64; **HRMS** (ESI) calcd for $C_{22}H_{23}F_3NO_3P$ $[M+H]^+$ 438.1440; found 438.1440.

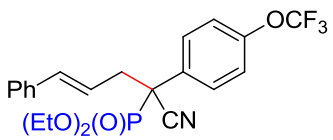
Diethyl (1-cyano-1-(4-methoxyphenyl)-4-phenylbut-3-en-1-yl) phosphonate (3f):



Colorless oil, 83 % yield (petroleum ether/ethyl acetate = 4:1-2:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 6.7 Hz, 2H), 7.26-7.18 (m, 5H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.02-5.94 (m, 1H), 4.28-4.21 (m, 2H), 3.94-3.85 (m, 1H), 3.81(s, 3H), 3.68-3.58 (m, 1H), 3.28-3.15 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6 (d, *J* = 2.6 Hz), 136.5, 135.3, 129.2 (d, *J* = 4.9 Hz), 128.4, 127.6, 126.3, 122.4 (d, *J* = 6.9 Hz), 121.8 (d, *J* = 11.8 Hz), 118.1 (d, *J* = 9.6 Hz), 114.1 (d, *J* = 2.3 Hz), 65.1 (d, *J* = 7.4 Hz), 64.2

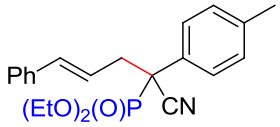
(d, *J* = 8.0 Hz), 55.2, 47.1 (d, *J* = 139.4 Hz), 38.1 (d, *J* = 3.1 Hz), 16.3 (d, *J* = 5.8 Hz), 16.1 (d, *J* = 5.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.58; **HRMS** (ESI) calcd for $C_{22}H_{26}NO_4P$ $[M+H]^+$ 400.1672; found 400.1668.

Diethyl (1-cyano-4-phenyl-1-(4-(trifluoromethoxy) phenyl) but-3-en-1-yl) phosphonate (3g):



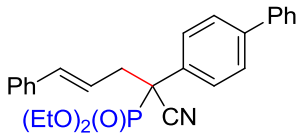
Colorless oil, 82 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.7 Hz, 2H), 7.28-7.20 (m, 7H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.00-5.92 (m, 1H), 4.31-4.24 (m, 2H), 3.79-3.91 (m, 1H), 3.76-3.68 (m, 1H), 3.25-3.21 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.3, 136.3, 135.8, 129.8 (d, *J* = 6.7 Hz), 129.6 (d, *J* = 4.9 Hz), 128.4, 127.8, 126.3, 121.2, 121.1, 121.0, 117.6 (d, *J* = 9.7 Hz), 65.1 (d, *J* = 7.4 Hz), 64.6 (d, *J* = 7.9 Hz), 47.4 (d, *J* = 138.4 Hz), 38.2 (d, *J* = 3.4 Hz), 16.3 (d, *J* = 5.7 Hz), 16.0 (d, *J* = 5.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.97; **HRMS** (ESI) calcd for $C_{22}H_{23}F_3NO_4P$ $[M+H]^+$ 454.1390; found 454.1386.

Diethyl (1-cyano-4-phenyl-1-(p-tolyl) but-3-en-1-yl) phosphonate (3h):



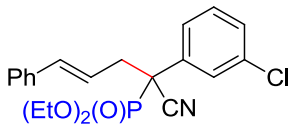
Colorless oil, 45 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55-7.52 (m, 2H), 7.25-7.15 (m, 7H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.01-5.93 (m, 1H), 4.30-4.20 (m, 2H), 3.93-3.83 (m, 1H), 3.66-3.562 (m, 1H), 3.29-3.16 (m, 2H), 2.34 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.5 (d, *J* = 2.9 Hz), 136.6, 135.3, 129.5 (d, *J* = 2.4 Hz), 128.3, 127.8 (d, *J* = 3.9 Hz), 127.7, 127.5, 126.3, 121.9 (d, *J* = 11.8 Hz), 118.1 (d, *J* = 9.6 Hz), 65.0 (d, *J* = 7.4 Hz), 64.2 (d, *J* = 7.9 Hz), 47.5 (d, *J* = 138.4 Hz), 38.1 (d, *J* = 3.4 Hz), 21.0, 16.3 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.52; **HRMS** (ESI) calcd for $C_{22}H_{26}NO_3P$ $[M+H]^+$ 384.1723; found 384.1721.

Diethyl (1-([1,1'-biphenyl]-4-yl)-1-cyano-4-phenylbut-3-en-1-yl) phosphonate (3i):



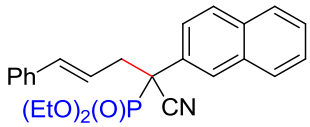
Colorless oil, 62% yield (petroleum ether/ethyl acetate = 4:1-2:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2H), 7.67-7.64 (m, 2H), 7.62-7.60 (m, 2H), 7.46-7.43 (m, 2H), 7.38-7.34 (m, 1H), 7.27-7.16 (m, 5H), 6.57 (d, *J* = 15.7 Hz, 1H), 6.06-5.98 (m, 1H), 4.31-4.24 (m, 2H), 3.98-3.87 (m, 1H), 3.73-3.63 (m, 1H), 3.36-3.26 (m, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3 (d, *J* = 2.9 Hz), 139.7, 136.4, 135.5, 129.8 (d, *J* = 6.8 Hz), 128.8, 128.4, 128.3, 127.7, 127.6, 127.3 (d, *J* = 2.5 Hz), 126.9, 126.3, 121.7 (d, *J* = 11.7 Hz), 117.9 (d, *J* = 9.6 Hz), 65.1 (d, *J* = 7.5 Hz), 64.3 (d, *J* = 7.9 Hz), 47.6 (d, *J* = 137.4 Hz), 38.1 (d, *J* = 3.4 Hz), 16.3 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.33; **HRMS** (ESI) calcd for $C_{27}H_{28}NO_3P$ $[M+H]^+$ 446.1879; found 446.2812.

Diethyl (1-(3-chlorophenyl)-1-cyano-4-phenylbut-3-en-1-yl) phosphonate (3j):



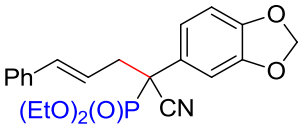
Colorless oil, 80 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.58-7.55 (m, 1H), 7.38-7.35 (m, 2H), 7.26-7.19 (m, 5H), 6.54 (d, *J* = 15.7 Hz, 1H), 6.00-5.92 (m, 1H), 4.30-4.23 (m, 2H), 4.01-3.91 (m, 1H), 3.78-3.68 (m, 1H), 3.25-3.21 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.3, 135.8, 134.9, 133.2 (d, *J* = 7.1 Hz), 130.0, 128.9 (d, *J* = 2.0 Hz), 128.4, 128.1 (d, *J* = 5.1 Hz), 127.8, 126.4, 126.2 (d, *J* = 5.1 Hz), 121.2 (d, *J* = 12.1 Hz), 117.5 (d, *J* = 9.1 Hz), 65.2 (d, *J* = 8.1 Hz), 64.6 (d, *J* = 8.1 Hz), 47.7 (d, *J* = 138.4 Hz), 38.1 (d, *J* = 4.0 Hz), 16.3 (d, *J* = 5.8 Hz), 16.1 (d, *J* = 5.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.77; **HRMS** (ESI) calcd for $C_{21}H_{23}ClNO_3P$ $[M+H]^+$ 404.1177; found 404.1175.

Diethyl (1-cyano-1-(naphthalen-2-yl)-4-phenylbut-3-en-1-yl) phosphonate (3k):



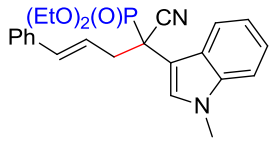
Colorless oil, 84 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.92-7.78 (m, 4H), 7.54-7.51 (m, 2H), 7.21-7.14 (m, 5H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.02-5.95 (m, 1H), 4.32-4.25 (m, 2H), 3.91-3.81 (m, 1H), 3.66-3.52 (m, 1H), 3.46-3.37 (m, 1H), 3.34-3.27 (m, 1H), 1.41 (t, *J* = 8.0 Hz, 3H), 1.01 (t, *J* = 8.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.38, 135.49, 132.94 (d, *J* = 3.0 Hz), 132.88 (d, *J* = 2.0 Hz), 128.63 (d, *J* = 2.0 Hz), 128.34, 128.25, 128.18, 127.80 (d, *J* = 7.1 Hz), 127.55 (d, *J* = 9.1 Hz), 126.87, 126.80, 126.66, 126.31, 124.64 (d, *J* = 3.0 Hz), 121.58 (d, *J* = 12.1 Hz), 118.02 (d, *J* = 9.1 Hz), 65.09 (d, *J* = 7.1 Hz), 64.35 (d, *J* = 7.1 Hz), 48.10 (d, *J* = 137.4 Hz), 38.16 (d, *J* = 3.0 Hz), 16.31 (d, *J* = 6.1 Hz), 16.02 (d, *J* = 6.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.2; **HRMS** (ESI) calcd for $C_{25}H_{26}NO_3P$ $[M+H]^+$ 420.1723; found 420.1720.

Diethyl (1-(benzo[d][1,3] dioxol-5-yl)-1-cyano-4-phenylbut-3-en-1-yl) phosphonate (3l):



Colorless oil, 55 % yield (petroleum ether/ethyl acetate = 4:1-2:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.26 (m, 4H), 7.24-7.13 (m, 3H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 15.7 Hz, 1H), 6.02-5.94 (m, 3H), 4.29-4.22 (m, 2H), 4.02-3.92 (m, 1H), 3.78-3.68 (m, 1H), 3.20-3.16 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.2 (d, *J* = 3.0 Hz), 147.9 (d, *J* = 3.0 Hz), 136.5, 135.4, 128.4, 127.6, 126.3, 124.3 (d, *J* = 7.1 Hz), 121.8 (d, *J* = 6.1 Hz), 121.6, 121.5, 118.0 (d, *J* = 9.1 Hz), 108.3, 101.5, 65.2 (d, *J* = 7.1 Hz), 64.3 (d, *J* = 8.1 Hz), 47.5 (d, *J* = 138.4 Hz), 38.3 (d, *J* = 3.2 Hz), 16.3 (d, *J* = 5.8 Hz), 16.2 (d, *J* = 5.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.37; **HRMS** (ESI) calcd for $C_{22}H_{24}NO_5P$ $[M+H]^+$ 414.1464; found 414.2605.

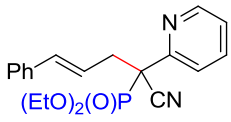
Diethyl (1-cyano-1-(1-methyl-1H-indol-3-yl)-4-phenylbut-3-en-1-yl) phosphonate (3m):



Colorless oil, 47 % yield (petroleum ether/ethyl acetate = 4:1-1.5:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 1H),

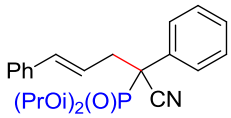
7.32-7.30 (d, *J* = 8.1 Hz, 1H), 7.28-7.15 (m, 8H), 6.56 (d, *J* = 15.7 Hz, 1H), 6.13-6.05 (m, 1H), 4.28-4.18 (m, 2H), 3.94-3.86 (m, 1H), 3.77 (s, 3H), 3.68-3.57 (m, 1H), 3.49-3.41 (m, 1H), 3.29-3.22 (m, 1H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.5, 136.7, 134.9, 129.1 (d, *J* = 6.8 Hz), 128.3, 127.5, 126.4, 125.4 (d, *J* = 2.9 Hz), 122.6 (d, *J* = 11.1 Hz), 122.2, 121.1, 119.9, 118.4 (d, *J* = 8.8 Hz), 109.5, 103.9 (d, *J* = 7.7 Hz), 64.8 (d, *J* = 7.5 Hz), 64.0 (d, *J* = 8.0 Hz), 42.4 (d, *J* = 144.4 Hz), 37.3 (d, *J* = 2.8 Hz), 33.0, 16.3 (d, *J* = 6.1 Hz), 16.0 (d, *J* = 6.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.68; **HRMS** (ESI) calcd for $C_{24}H_{27}N_2O_3P$ $[M+H]^+$ 423.1832; found 423.1829.

Diethyl (1-cyano-4-phenyl-1-(pyridin-2-yl) but-3-en-1-yl) phosphonate (3n):



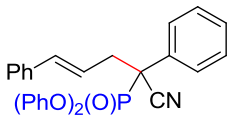
Colorless oil, 27 % yield (petroleum ether/ethyl acetate = 4:1-2:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67-8.66 (m, 1H), 7.75-7.73 (m, 2H), 7.29-7.17 (m, 6H), 6.56-6.52 (d, *J* = 16.0 Hz, 1H), 6.09-6.01 (m, 1H), 4.32-4.17 (m, 2H), 4.13-4.03 (m, 1H), 4.00-3.89 (m, 1H), 3.58-3.49 (m, 1H), 3.26-3.19 (m, 1H), 1.39-1.35 (t, *J* = 8.0 Hz, 3H), 1.22-1.18 (t, *J* = 8.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6 (d, *J* = 7.1 Hz), 149.3 (d, *J* = 2.0 Hz), 136.9 (d, *J* = 2.0 Hz), 136.6, 135.4, 128.3, 127.5, 126.3, 123.5 (d, *J* = 4.0 Hz), 123.2 (d, *J* = 2.0 Hz), 122.1 (d, *J* = 11.1 Hz), 117.7 (d, *J* = 9.1 Hz), 64.7 (d, *J* = 4.0 Hz), 64.6 (d, *J* = 4.0 Hz), 50.8 (d, *J* = 136.4 Hz), 37.2 (d, *J* = 3.0 Hz), 16.2 (d, *J* = 6.1 Hz), 16.1 (d, *J* = 6.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.3; **HRMS** (ESI) calcd for $C_{20}H_{23}N_2O_3P$ $[M+H]^+$ 371.1519; found 371.1519.

Diisopropyl (1-cyano-1,4-diphenylbut-3-en-1-yl) phosphonate (3o):



Colorless oil, 66 % yield (petroleum ether/ethyl acetate = 4:1-2:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69-7.67 (m, 2H), 7.41-7.33 (m, 3H), 7.27-7.14 (m, 5H), 6.49 (d, *J* = 15.7 Hz, 1H), 5.98-5.91 (m, 1H), 4.84-4.76 (m, 1H), 4.31-4.23 (m, 1H), 3.30-3.15 (m, 2H), 1.41-1.38 (m, 6H), 1.23 (d, *J* = 6.2 Hz, 3H), 0.80 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.6, 135.2, 131.2 (d, *J* = 6.4 Hz), 128.7 (d, *J* = 2.1 Hz), 128.5 (d, *J* = 2.1 Hz), 128.3, 128.0 (d, *J* = 5.1 Hz), 127.5, 126.3, 122.0 (d, *J* = 12.0 Hz), 118.1 (d, *J* = 9.8 Hz), 74.1 (d, *J* = 7.7 Hz), 73.2 (d, *J* = 8.2 Hz), 48.2 (d, *J* = 138.4 Hz), 38.5 (d, *J* = 3.4 Hz), 24.2 (d, *J* = 2.6 Hz), 23.9 (d, *J* = 5.1 Hz), 23.7 (d, *J* = 4.9 Hz), 22.7 (d, *J* = 7.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.70; **HRMS** (ESI) calcd for $C_{23}H_{28}NO_3P$ $[M+H]^+$ 398.1879; found 398.1875.

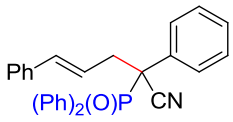
Diphenyl (1-cyano-1,4-diphenylbut-3-en-1-yl) phosphonate (3p):



Colorless oil, 42 % yield (petroleum ether/ethyl acetate = 6:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77-7.75 (m, 2H), 7.43-7.32 (m, 5H), 7.28-7.19 (m, 8H), 7.09 (t, *J* = 7.7 Hz, 2H), 7.02 (t, *J* = 7.0 Hz, 1H), 6.59-6.55 (m, 3H), 6.05-5.97 (m, 1H), 3.50-3.38 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150. 2 (d, *J* = 6.5 Hz), 150.1 (d, *J* = 6.8 Hz), 136.4, 136.1, 129.9, 129.8, 129.4, 129.1 (d, *J* = 2.5 Hz), 129.0 (d, *J* = 2.8 Hz), 128.4, 128.2 (d, *J* = 5.1 Hz), 127.8, 126.4, 125.8, 125.3, 120.9 (d, *J* = 12.8 Hz), 120.4 (d, *J* = 4.4 Hz), 119.9 (d, *J* = 4.4 Hz), 117.3 (d, *J* = 10.2 Hz), 48.5 (d, *J* = 142.4 Hz), 38.3; **^{31}P**

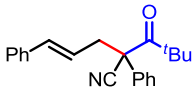
NMR (162 MHz, $CDCl_3$) δ 9.96; **HRMS** (ESI) calcd for $C_{29}H_{24}NO_3P$ $[M+H]^+$ 466.1567; found 466.1565.

2-(diphenylphosphoryl)-2,5-diphenylpent-4-enenitrile (3q):



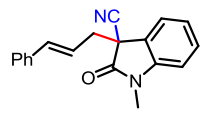
Colorless oil, 44 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31-8.27 (m, 2H), 7.69-7.54 (m, 7H), 7.43 (t, *J* = 7.1 Hz, 1H), 7.33-7.27 (m, 5H), 7.20-7.10 (m, 5H), 6.39 (d, *J* = 15.7 Hz, 1H), 5.85-5.78 (m, 1H), 3.55-3.48 (m, 1H), 3.03-2.96 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.5, 135.5, 132.9 (d, *J* = 8.5 Hz), 132.8 (d, *J* = 2.8 Hz), 132.4 (d, *J* = 2.8 Hz), 131.9 (d, *J* = 8.7 Hz), 130.6 (d, *J* = 4.5 Hz), 129.2 (d, *J* = 7.4 Hz), 128.8 (d, *J* = 11.9 Hz), 128.5 (d, *J* = 4.0 Hz), 128.41, 128.38, 128.32, 128.26, 128.1 (d, *J* = 12.1 Hz), 127.5, 126.3, 121.5 (d, *J* = 9.7 Hz), 119.7, 49.6 (d, *J* = 58.6 Hz), 37.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.54; **HRMS** (ESI) calcd for $C_{29}H_{24}NOP$ $[M+H]^+$ 434.1668; found 434.1918.

4-cyano-2, 2-dimethyl-4,7-diphenylhept-6-en-3-one (3s):



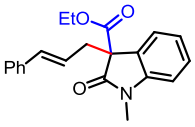
White solid, 77 % yield (petroleum ether/ethyl acetate = 50:1 as the eluent); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.33 (m, 5H), 7.28-7.19 (m, 5H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.03-5.95 (m, 1H), 3.22-3.17 (m, 1H), 2.83-2.78 (m, 1H), 1.20 (s, 9H); **MS (ESI)**: $[M+H]^+$ 318.1.

3-cinnamyl-1-methyl-2-oxoindoline-3-carbonitrile (3t):



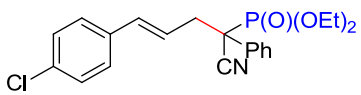
Colorless oil, 32 % yield (petroleum ether/ethyl acetate = 4:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.31-7.22 (m, 5H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.09-6.01 (m, 1H), 3.23 (s, 3H), 3.20-3.15 (m, 1H), 2.87-2.81 (m, 1H); **MS (ESI)**: $[M+H]^+$ 289.2.

Ethyl 3-cinnamyl-1-methyl-2-oxoindoline-3-carboxylate (3u):



White solid, 78 % yield (petroleum ether/ethyl acetate = 8:1 as the eluent). **M.p.** 138-141 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 2H), 7.23-7.19 (m, 2H), 7.16-7.13 (m, 3H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.82 - 6.80 (m, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 5.84-5.76 (m, 1H), 4.20-4.11 (m, 2H), 3.19 (s, 3H), 3.16-3.14 (m, 1H), 3.08-3.02 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.6, 168.9, 143.9, 136.9, 134.5, 129.0, 128.3, 127.6, 127.2, 126.1, 123.6, 122.7, 122.5, 108.3, 61.9, 59.4, 37.7, 26.4, 13.9; **HRMS** (ESI) calcd for $C_{21}H_{21}NO_3$ $[M+H]^+$ 336.1594; found 336.1593.

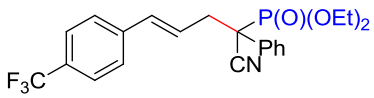
Diethyl (4-(4-chlorophenyl)-1-cyano-1-phenylbut-3-en-1-yl) phosphonate (4b):



Colorless oil, 63 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.65 (m, 2H), 7.42-7.39 (m, 2H), 7.37-7.33 (m, 1H),7.20-7.18 (m, 2H), 7.15-7.13 (m, 2H), 6.47 (d, *J* = 15.7 Hz, 1H), 5.98-5.90 (m, 1H), 4.28-4.20 (m, 2H), 3.91-3.82 (m, 1H), 3.63-3.53 (m, 1H), 3.30-3.16 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.9, 134.2, 133.3, 130.8 (d, *J* = 6.6 Hz), 128.8 (d, *J* = 2.0 Hz), 128.7 (d, *J* = 3.0 Hz), 128.5, 127.9 (d, *J*

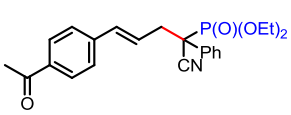
= 4.9 Hz), 127.5, 122.5 (d, *J* = 11.7 Hz), 117.9 (d, *J* = 9.7 Hz), 65.1 (d, *J* = 7.4 Hz), 64.3 (d, *J* = 8.0 Hz), 47.8 (d, *J* = 138.4 Hz), 38.1 (d, *J* = 3.4 Hz), 16.3 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.24; **HRMS** (ESI) calcd for $C_{21}H_{23}ClNO_3P$ $[M+H]^+$ 404.1177; found 404.1175.

Diethyl (1-cyano-1-phenyl-4-(4-(trifluoromethyl) phenyl) but-3-en-1-yl) phosphonate (4c):



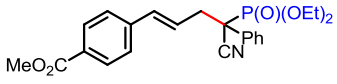
Colorless oil, 83 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.5 Hz,, 2H), 7.38-7.34 (m, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.10-6.03 (m, 1H), 4.29-4.21 (m, 2H), 3.92-3.82 (m, 1H), 3.63-3.53 (m, 1H), 3.33-3.20 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.8, 134.1, 130.7 (d, *J* = 6.7 Hz), 129.6, 128.9 (d, *J* = 2.3 Hz), 128.7 (d, *J* = 2.6 Hz), 127.9 (d, *J* = 4.9 Hz), 126.5, 125.4 (d, *J* = 3.8 Hz), 124.7 (d, *J* = 11.7 Hz), 122.7, 117.8 (d, *J* = 9.7 Hz), 65.2 (d, *J* = 7.4 Hz), 64.3 (d, *J* = 7.9 Hz), 47.4 (d, *J* = 138.4 Hz), 38.1 (d, *J* = 3.3 Hz), 16.3 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.13; **HRMS** (ESI) calcd for $C_{22}H_{23}F_3NO_3P$ $[M+H]^+$ 438.1440; found 438.1440.

Diethyl (4-(4-acetylphenyl)-1-cyano-1-phenylbut-3-en-1-yl) phosphonate (4d):



Colorless oil, 77 % yield (petroleum ether/ethyl acetate = 4:1-1.5:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.67-7.65 (m, 2H), 7.43-7.33 (m, 3H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.13-6.06 (m, 1H), 4.27-4.18 (m, 2H), 3.89-3.81 (m, 1H), 3.60 -3.55 (m, 1H), 3.33-3.20 (m, 2H), 2.53 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.4, 140.9, 136.1, 134.4, 130.6 (d, *J* = 6.7 Hz), 128.9 (d, *J* = 2.3 Hz), 128.7 (d, *J* = 2.7 Hz), 128.6, 127.84 (d, *J* = 4.9 Hz), 126.4, 124.9 (d, *J* = 11.6 Hz), 117.8 (d, *J* = 9.7 Hz), 65.2 (d, *J* = 7.4 Hz), 64.3 (d, *J* = 7.9 Hz), 47.7 (d, *J* = 138.2 Hz), 38.2 (d, *J* = 3.4 Hz), 26.5, 16.3 (d, *J* = 5.9 Hz), 16.0 (d, *J* = 5.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.14; **HRMS** (ESI) calcd for $C_{23}H_{26}NO_4P$ $[M+H]^+$ 412.1672; found 412.1672.

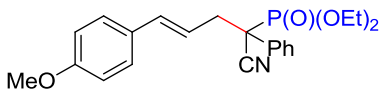
Methyl 4-(4-cyano-4-(diethoxyphosphoryl)-4-phenylbut-1-en-1-yl) benzoate (4e):



Colorless oil, 84 % yield (petroleum ether/ethyl acetate = 4:1-2:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.70-7.68 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.40-7.36 (m, 1H), 7.31-7.28 (m, 2H), 6.58 (d, *J* = 15.8 Hz, 1H), 6.15-6.07 (m, 1H), 4.30-4.22 (m, 2H), 3.93-3.83 (m, 4H), 3.62-3.56 (m, 1H), 3.36-3.22 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 140.8, 134.5, 130.6 (d, *J* = 6.6 Hz), 129.7, 129.0, 128.9 (d, *J* = 2.3 Hz), 128.7 (d, *J* = 2.7 Hz), 127.8 (d, *J* = 4.9 Hz), 126.2, 124.6 (d, *J* = 11.6 Hz), 117.8 (d, *J* = 9.7 Hz), 65.2 (d, *J* = 7.4 Hz), 64.3 (d, *J* = 8.0 Hz), 51.9, 47.7 (d, *J* = 138.2 Hz), 38.2 (d, *J* = 3.3 Hz), 16.3 (d, *J* = 5.9 Hz),

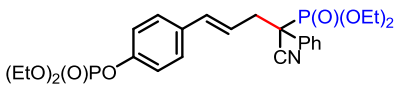
16.0 (d, *J* = 5.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.16; **HRMS** (ESI) calcd for $C_{23}H_{26}NO_5P$ $[M+H]^+$ 428.1621; found 428.1622.

Diethyl (1-cyano-4-(4-methoxyphenyl)-1-phenylbut-3-en-1-yl) phosphonate (4f):



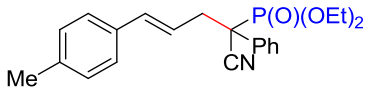
Colorless oil, 89 % yield (petroleum ether/ethyl acetate = 4:1-2:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.65 (m, 2H), 7.42-7.32 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.46 (d, *J* = 15.7 Hz, 1H), 5.86-5.78 (m, 1H), 4.28-4.21 (m, 2H), 3.93-3.82 (m, 1H), 3.75 (s, 3H), 3.63-3.53 (m, 1H), 3.29-3.15 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 134.8, 130.9 (d, *J* = 6.6 Hz), 129.4, 128.8 (d, *J* = 3.0 Hz), 128.6 (d, *J* = 3.0 Hz), 128.0 (d, *J* = 5.1 Hz), 127.5, 119.4 (d, *J* = 12.1 Hz), 118.0 (d, *J* = 10.1 Hz), 113.8, 65.0 (d, *J* = 7.4 Hz), 64.3 (d, *J* = 7.9 Hz), 55.2, 48.0 (d, *J* = 137.4 Hz), 38.2 (d, *J* = 3.4 Hz), 16.3 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.46; **HRMS** (ESI) calcd for $C_{22}H_{26}NO_4P$ $[M+H]^+$ 400.1672; found 400.1672.

4-(4-cyano-4-(diethoxyphosphoryl)-4-phenylbut-1-en-1-yl) phenyl diethyl phosphate (4g):



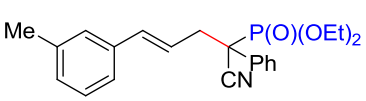
Colorless oil, 88 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.36-7.32 (m, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.47 (d, *J* = 15.7 Hz, 1H), 5.92- 5.84 (m, 1H), 4.27- 4.10 (m, 6H), 3.87-3.82 (m, 1H), 3.62-3.52 (m, 1H), 3.29-3.15 (m, 2H), 1.37 (t, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 6H), 1.03 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.1 (d, *J* = 7.0 Hz), 134.3, 133.5, 130.7 (d, *J* = 6.7 Hz), 128.8 (d, *J* = 2.3 Hz), 128.6 (d, *J* = 2.6 Hz), 127.9 (d, *J* = 4.9 Hz), 127.6, 121.7 (d, *J* = 11.7 Hz), 119.9 (d, *J* = 5.0 Hz), 117.8 (d, *J* = 9.6 Hz), 65.1 (d, *J* = 7.4 Hz), 64.5 (d, *J* = 6.1 Hz), 64.3 (d, *J* = 7.9 Hz), 47.8 (d, *J* = 137.9 Hz), 38.1 (d, *J* = 3.4 Hz), 16.3 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 6.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.31, -6.39; **HRMS** (ESI) calcd for $C_{25}H_{33}NO_7P_2$ $[M+H]^+$ 522.1805; found 522.1805.

Diethyl (1-cyano-1-phenyl-4-(p-tolyl) but-3-en-1-yl) phosphonate (4h):



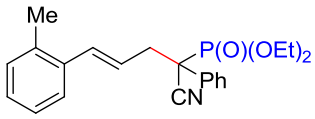
Colorless oil, 82% yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.65 (m, 2H), 7.42-7.36 (m, 2H),7.35-7.32 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.49 (d, *J* = 15.7 Hz, 1H), 5.95-5.87 (m, 1H), 4.28-4.21 (m, 2H), 3.92-3.82 (m, 1H), 3.64-3.53 (m, 1H), 3.30-3.17 (m, 2H), 2.28 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.4, 135.2, 133.7, 130.8 (d, *J* = 7.1 Hz), 129.0, 128.7 (d, *J* = 2.3 Hz), 128.5 (d, *J* = 2.6 Hz), 127.9 (d, *J* = 5.1 Hz), 126.2, 120.6 (d, *J* = 12.1 Hz) ,117.9 (d, *J* = 10.1 Hz), 65.0 (d, *J* = 8.1 Hz), 64.2 (d, *J* = 8.1 Hz), 47.8 (d, *J* = 138.4 Hz), 38.1(d, *J* = 3.0 Hz), 21.0, 16.3 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.44; **HRMS** (ESI) calcd for $C_{22}H_{26}NO_3P$ $[M+H]^+$ 384.1723; found 384.1721.

Diethyl (1-cyano-1-phenyl-4-(m-tolyl) but-3-en-1-yl) phosphonate (4i):



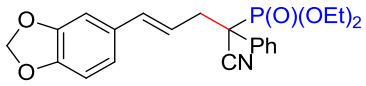
Colorless oil, 55 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2H), 7.43-7.39 (m, 2H), 7.36-7.33 (m, 1H), 7.14-7.10 (m, 1H), 7.05-6.99 (m, 3H), 6.49 (d, *J* = 15.7 Hz, 1H), 6.00-5.92 (m,1H), 4.28-4.21 (m, 2H), 3.92-3.82 (m, 1H), 3.64-3.54 (m, 1H), 3.31-3.18 (m, 2H), 2.27 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.9, 136.4, 135.5, 130.8 (d, *J* = 7.1 Hz), 128.8 (d, *J* = 2.0 Hz), 128.6 (d, *J* = 3.0 Hz), 128.4, 128.2, 127.9 (d, *J* = 5.1 Hz), 127.0, 123.4, 121.4 (d, *J* = 12.1 Hz), 117.9 (d, *J* = 10.1 Hz), 65.0 (d, *J* = 8.1 Hz), 64.3 (d, *J* = 8.1 Hz), 47.8 (d, *J* = 138.4 Hz), 38.1 (d, *J* = 4.0 Hz), 21.2, 16.3 (d, *J* = 5.9 Hz), 16.0 (d, *J* = 5.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.42; **HRMS** (ESI) calcd for $C_{22}H_{26}NO_3P$ $[M+H]^+$ 384.1723; found 384.1721.

Diethyl (1-cyano-1-phenyl-4-(o-tolyl) but-3-en-1-yl) phosphonate (4j):



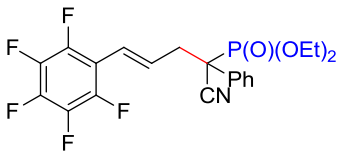
Colorless oil, 37 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69-7.67 (m, 2H), 7.43-7.32 (m, 3H), 7.20-7.18 (m, 1H), 7.11-7.07 (m, 3H), 6.69 (d, *J* = 15.7 Hz, 1H), 5.85-5.77 (m, 1H), 4.30-4.23 (m, 2H), 3.93-3.84 (m, 1H), 3.66-3.56 (m, 1H), 3.34-3.19 (m, 2H), 2.19 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.9, 135.3, 133.9, 130.8 (d, *J* = 7.1 Hz), 130.0, 128.8 (d, *J* = 3.0 Hz), 128.5 (d, *J* = 3.0 Hz), 128.0 (d, *J* = 5.1 Hz), 127.5, 125.8, 123.2, 123.0, 117.9 (d, *J* = 10.1 Hz), 65.1 (d, *J* = 7.1 Hz), 64.3 (d, *J* = 7.1 Hz), 48.0 (d, *J* = 137.4 Hz), 38.3 (d, *J* = 4.0 Hz), 19.6, 16.3 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.47; **HRMS** (ESI) calcd for $C_{22}H_{26}NO_3P$ $[M+H]^+$ 384.1723; found 384.1721.

Diethyl (4-(benzo[d][1,3] dioxol-5-yl)-1-cyano-1-phenylbut-3-en-1-yl) phosphornate (4k):



Colorless oil, 62% yield (petroleum ether/ethyl acetate = 4:1-2:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 2H), 7.42-7.32 (m, 3H), 6.70 (s, 1H), 6.66 (s, 2H), 6.42 (d, *J* = 15.7 Hz, 1H), 5.88 (s, 2H), 5.81-5.73 (m, 1H), 4.27-4.20 (m, 2H), 3.91-3.81 (m, 1H), 3.63-3.53 (m, 1H), 3.28-3.13 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 147.2, 134.9, 131.0, 130.9 (d, *J* = 6.1 Hz), 128.8 (d, *J* = 3.0 Hz), 128.6 (d, *J* = 3.0 Hz), 127.9 (d, *J* = 5.1 Hz), 121.0, 119.8 (d, *J* = 12.1 Hz), 117.9 (d, *J* = 10.1 Hz), 108.0, 105.6, 100.9, 65.0 (d, *J* = 8.1 Hz), 64.3 (d, *J* = 8.1 Hz), 47.9 (d, *J* = 137.4 Hz), 38.1 (d, *J* = 3.4 Hz), 16.3 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.40; **HRMS** (ESI) calcd for $C_{22}H_{24}NO_5P$ $[M+H]^+$ 414.1465; found 414.1465.

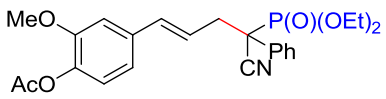
Diethyl (1-cyano-4-(perfluorophenyl)-1-phenylbut-3-en-1-yl) phosphonate (4l):



Colorless oil, 58 % yield (petroleum ether/ethyl acetate = 4:1-2:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 2H),

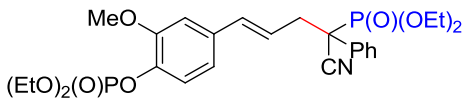
7.43-7.34 (m, 3H), 6.41 (d, *J* = 15.7 Hz, 1H), 6.33-6.21 (m, 1H), 4.30-4.22 (m, 2H), 3.90-3.84 (m, 1H), 3.61-3.55 (m, 1H), 3.31-3.25 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.3 (d, *J* = 4.0 Hz), 138.7 (d, *J* = 5.1 Hz), 136.3, 131.9 (d, *J* = 8.1 Hz), 130.5 (d, *J* = 6.1 Hz), 128.9 (d, *J* = 3.0 Hz), 128.8 (d, *J* = 3.0 Hz), 127.8 (d, *J* = 5.1 Hz), 119.4, 117.5 (d, *J* = 10.1 Hz), 111.3 (d, *J* = 4.0 Hz), 65.3 (d, *J* = 8.1 Hz), 64.3 (d, *J* = 8.1 Hz), 47.5 (d, *J* = 138.4 Hz), 39.3 (d, *J* = 4.0 Hz), 16.2 (d, *J* = 6.1 Hz), 16.0 (d, *J* = 6.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.96; **HRMS** (ESI) calcd for $C_{21}H_{19}F_5NO_3P$ $[M+H]^+$ 460.1095; found 460.1090.

4-(4-cyano-4-(diethoxyphosphoryl)-4-phenylbut-1-en-1-yl)-2-methoxyphenyl acetate (4m):



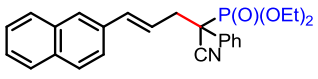
Colorless oil, 72 % yield (petroleum ether/ethyl acetate = 4:1-2:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.43-7.33 (m, 3H), 6.90-6.88 (m, 1H), 6.81-6.80 (m, 2H), 6.47 (d, *J* = 15.7 Hz, 1H), 5.95-5.87 (m, 1H), 4.29-4.21 (m, 2H), 3.90-3.84 (m, 1H), 3.77 (s, 3H), 3.61-3.57 (m, 1H), 3.26-3.21 (m, 2H), 2.27 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.8, 150.9, 139.2, 135.5, 134.8, 130.7 (d, *J* = 6.7 Hz), 128.8 (d, *J* = 2.3 Hz), 128.6 (d, *J* = 2.4 Hz), 127.9 (d, *J* = 4.9 Hz), 122.6, 122.0 (d, *J* = 11.8 Hz), 118.8, 117.8 (d, *J* = 9.7 Hz), 110.2, 65.1 (d, *J* = 7.4 Hz), 64.3 (d, *J* = 7.9 Hz), 55.5 (d, *J* = 2.1 Hz), 47.8 (d, *J* = 138.4 Hz), 38.1 (d, *J* = 3.4 Hz), 20.5 (d, *J* = 1.8 Hz), 16.2 (d, *J* = 5.8 Hz), 15.9 (d, *J* = 5.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.30; **HRMS** (ESI) calcd for $C_{24}H_{28}NO_6P$ $[M+H]^+$ 458.1727; found 458.1723.

4-(4-cyano-4-(diethoxyphosphoryl)-4-phenylbut-1-en-1-yl)-2-methoxyphenyl diethyl phosphate (4n):



Colorless oil, 72 % yield (petroleum ether/ethyl acetate = 4:1-0:100 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66-7.63 (m, 2H), 7.41-7.31 (m, 3H), 7.13-7.11 (m, 1H), 6.77-6.73 (m, 2H), 6.44 (d, *J* = 15.7 Hz, 1H), 5.91-5.84 (m, 1H), 4.26-4.13 (m, 6H), 3.90-3.82 (m, 1H), 3.78 (s, 3H), 3.62-3.52 (m, 1H), 3.24-3.17 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.32-1.29 (m, 6H), 1.03 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5 (d, *J* = 5.5 Hz), 139.5 (d, *J* = 7.2 Hz), 134.7, 134.3 (d, *J* = 2.1 Hz), 130.7 (d, *J* = 6.6 Hz), 128.8 (d, *J* = 2.3 Hz), 128.6 (d, *J* = 2.4 Hz), 127.9 (d, *J* = 4.9 Hz), 121.8 (d, *J* = 11.7 Hz), 121.1 (d, *J* = 2.9 Hz), 118.9, 117.8 (d, *J* = 9.7 Hz), 110.5, 65.0 (d, *J* = 7.4 Hz), 64.4 (d, *J* = 6.1 Hz), 64.3 (d, *J* = 8.1 Hz), 55.8, 47.8 (d, *J* = 138.4 Hz), 38.1 (d, *J* = 3.4 Hz), 16.2 (d, *J* = 5.8 Hz), 15.9 (d, *J* = 6.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.27, -6.01; **HRMS** (ESI) calcd for $C_{26}H_{35}NO_8P_2$ $[M+H]^+$ 552.1911; found 552.1907.

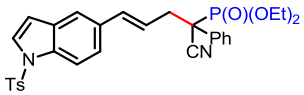
Diethyl (1-cyano-4-(naphthalen-2-yl)-1-phenylbut-3-en-1-yl) phosphonate (4o):



Colorless oil, 85 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75- 7.68 (m, 5H), 7.61 (s, 1H), 7.44-7.34 (m, 6H), 6.69 (d, *J* = 15.7 Hz, 1H), 6.15- 6.08 (m, 1H), 4.30-4.23 (m, 2H),

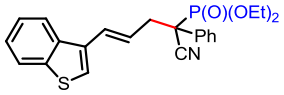
3.92-3.86 (m, 1H), 3.66-3.58 (m, 1H), 3.37-3.27 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.5, 133.9, 133.4, 132.9, 130.9 (d, *J* = 6.7 Hz), 128.8 (d, *J* = 2.4 Hz), 128.6 (d, *J* = 2.7 Hz), 128.1, 128.0, 127.9 (d, *J* = 1.9 Hz), 127.6, 126.3, 126.1, 125.9, 123.5, 122.1 (d, *J* = 11.6 Hz), 117.9 (d, *J* = 9.8 Hz), 65.1 (d, *J* = 7.4 Hz), 64.3 (d, *J* = 7.9 Hz), 47.9 (d, *J* =137.9 Hz), 38.4 (d, *J* = 3.4 Hz), 16.3 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.6 Hz);**^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.38; **HRMS** (ESI) calcd for $C_{25}H_{26}NO_3P$ $[M+H]^+$ 420.1723; found 420.1720.

Diethyl (1-cyano-1-phenyl-4-(1-tosyl-1H-indol-5-yl)but-3-en-1-yl)phosphonate(4p)



Colorless oil, 28 % yield (petroleum ether/ethyl acetate = 4:1-2:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.6 Hz, 1H), 7.70-7.65 (m, 4H), 7.48 (d, *J* = 3.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.36-7.32 (m, 2H), 7.20-7.15 (m, 3H), 6.59-6.54(m, 2H), 5.96-5.89 (m, 1H), 4.28-4.20 (m, 2H), 3.90-3.84 (m, 1H), 3.64-3.56 (m, 1H), 3.32-3.17 (m, 2H), 2.29 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9, 135.3, 135.0, 134.2, 132.0, 130.9, 130.7 (d, *J* = 6.8 Hz), 129.8, 128.8 (d, *J* = 2.3 Hz), 128.6 (d, *J* = 2.8 Hz), 127.9 (d, *J* = 4.9 Hz), 126.8, 126.6, 122.9, 120.9 (d, *J* = 11.9 Hz), 119.2, 117.9 (d, *J* = 9.6 Hz), 113.4, 109.1, 65.1 (d, *J* = 7.4 Hz), 64.3 (d, *J* = 7.9 Hz), 47.9 (d, *J* = 137.8 Hz), 38.1 (d, *J* = 3.2 Hz), 21.4, 16.3 (d, *J* = 5.7 Hz), 15.9 (d, *J* = 5.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.40; **HRMS** (ESI) calcd for $C_{30}H_{31}N_2O_5PS$ $[M+H]^+$ 563.1764; found 563.1764.

Diethyl (4-(benzo[b]thiophen-3-yl)-1-cyano-1-phenylbut-3-en-1-yl)phosphonate(4q):



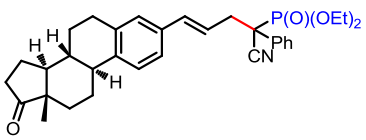
Colorless oil, 32 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.79 (m, 1H), 7.72-7.69 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.39-7.30 (m, 3H), 7.26 (s, 1H), 6.77 (d, *J* = 15.8 Hz, 1H), 6.06-5.99 (m, 1H), 4.32-4.17 (m, 2H), 3.93 -3.86 (m, 1H), 3.62-3.59 (m, 1H), 3.39-3.25 (m, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 137.4, 133.3, 130.8 (d, *J* = 6.6 Hz), 128.8 (d, *J* = 2.4 Hz), 128.7 (d, *J* = 2.6 Hz), 127.9 (d, *J* = 4.9 Hz), 127.8, 124.4, 124.2, 123.6 (d, *J* = 11.8 Hz), 122.7, 122.4, 121.9, 117.9 (d, *J* = 9.6 Hz), 65.1 (d, *J* = 7.4 Hz), 64.3 (d, *J* = 7.9 Hz), 47.9 (d, *J* = 138.1 Hz), 38.4 (d, *J* = 3.4 Hz), 16.3 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.40; **HRMS** (ESI) calcd for $C_{23}H_{24}NO_3PS$ $[M+H]^+$ 426.1287; found 426.1287.

Diethyl (1-cyano-1-phenyl-4-(thiophen-2-yl)but-3-en-1-yl)phosphonate (4r) :

Colorless oil, 30 % yield (petroleum ether/ethyl acetate = 4:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.65 (m, 2H), 7.43-7.34 (m, 3H), 7.08 (d, *J* = 4.9 Hz, 1H), 6.90-6.86 (m, 2H), 6.64 (d, *J* = 15.6 Hz, 1H), 5.84-5.77 (m, 1H), 4.29-4.21 (m, 2H), 3.90-3.80 (m, 1H), 3.60-3.50 (m, 1H), 3.24-3.16 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4, 130.8 (d, *J* = 6.6 Hz), 128.8

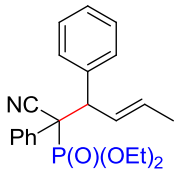
(d, *J* = 2.3 Hz), 128.6 (d, *J* = 2.7 Hz), 128.4, 127.9 (d, *J* = 4.9 Hz), 127.2, 125.8, 124.3, 121.3 (d, *J* = 11.4 Hz), 117.9 (d, *J* = 9.7 Hz), 65.1 (d, *J* = 7.6 Hz), 64.3 (d, *J* = 8.1 Hz), 47.8 (d, *J* = 137.9 Hz), 38.2 (d, *J* = 3.3 Hz), 16.3 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.27; **HRMS** (ESI) calcd for $C_{19}H_{22}NO_3PS$ $[M+H]^+$ 376.1131; found 376.1131.

diethyl ((E)-1-cyano-4-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,-16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-1-phenylbut-3-en-1-yl) pho -sphonate (4s):



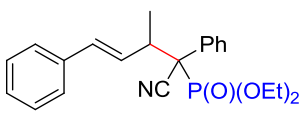
Colorless oil, 82 % yield (petroleum ether/ethyl acetate = 4:1-2:1 as the eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 6.0 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.03-7.00 (m, 1H), 6.97 (d, *J* = 4.9 Hz, 1H), 6.46 (d, *J* = 15.7 Hz, 1H), 5.96-5.89 (m, 1H), 4.28 -4.21 (m, 2H), 3.91-3.82 (m, 1H), 3.63-3.53 (m, 1H), 3.30-3.16 (m, 2H), 2.85-2.82 (m, 2H), 2.51-2.44 (m, 1H), 2.37-2.35 (m, 1H), 2.26-2.20 (m, 1H), 2.16-1.89 (m, 4H), 1.63- 1.44 (m, 6H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.4, 136.5, 135.2, 134.1, 130.7 (d, *J* = 6.9 Hz), 128.7 (d, *J* = 2.3 Hz), 128.5 (d, *J* = 2.6 Hz), 127.9 (d, *J* = 4.9 Hz), 126.9 (d, *J* = 6.0 Hz), 125.4, 123.7 (d, *J* = 6.3 Hz), 120.9 (d, *J* = 2.6 Hz), 120.8 (d, *J* = 2.6 Hz), 117.9 (d, *J* = 9.7 Hz), 65.1 (d, *J* = 7.4 Hz), 64.3 (d, *J* = 8.0 Hz), 50.4, 47.9 (d, *J* = 137.8 Hz), 47.8, 44.3, 38.0, 35.8, 31.5, 29.2, 26.4, 25.6, 21.5, 16.3 (d, *J* = 5.9 Hz), 16.0 (d, *J* = 5.6 Hz), 13.7; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.45; **HRMS** (ESI) calcd for $C_{33}H_{40}NO_4P$ $[M+H]^+$ 546.2768; found 546.2768.

Diethyl (1-cyano-1,2-diphenylpent-3-en-1-yl) phosphonate (4t):



Colorless oil, 27 % yield (petroleum ether/ethyl acetate = 5:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69-7.67 (m, 2H), 7.38-7.35 (m, 2H), 7.31-7.26 (m, 1H), 7.22-7.10 (m, 5H), 6.17 (d, *J* = 15.7 Hz, 1H), 5.90-5.84 (m, 1H), 4.32-4.24 (m, 2H), 3.82-3.74 (m, 1H), 3.60-3.48 (m, 1H), 3.30-3.22 (m, 1H), 1.57 (d, *J* = 5.1 Hz, 3H), 1.42 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7, 132.4, 132.2 (d, *J* = 6.1 Hz), 128.9, 128.7 (d, *J* = 2.0 Hz), 128.4 (d, *J* = 3.0 Hz), 128.3, 128.0 (d, *J* = 5.1 Hz), 127.3, 126.2, 116.9 (d, *J* = 9.1 Hz), 65.0 (d, *J* = 8.1 Hz), 64.0 (d, *J* = 8.1 Hz), 53.0 (d, *J* = 137.4 Hz), 43.3, 18.2, 16.2 (d, *J* = 6.1 Hz), 15.9 (d, *J* = 6.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.59; **HRMS** (ESI) calcd for $C_{22}H_{26}NO_3P$ $[M+H]^+$ 384.1723; found 384.1720.

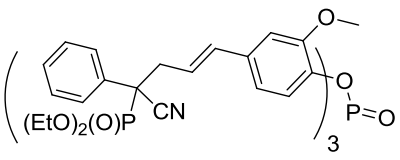
Diethyl (1-cyano-2-methyl-1,4-diphenylbut-3-en-1-yl) phosphonate (4t'):



Colorless oil, 37 % yield (petroleum ether/ethyl acetate = 5:1-3:1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76-7.74 (m, 2H), 7.45-7.42 (m, 4H), 7.40-7.37 (m, 3H), 7.36-7.30 (m, 2H), 7.26-7.22 (m, 1H), 6.70 (d, *J* = 15.7 Hz, 1H), 6.43-6.37 (m, 1H), 4.13-4.03 (m, 1H), 4.00-3.90 (m, 1H), 3.78-3.69 (m, 1H), 3.54-3.45 (m, 1H), 3.32-3.22 (m, 1H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 8.0 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9, 132.0 (d, *J* = 6.1 Hz), 131.7,

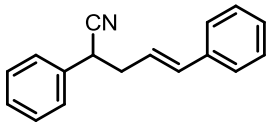
129.7 (d, *J* = 2.0 Hz), 128.9 (d, *J* = 2.0 Hz), 128.6 (d, *J* = 2.0 Hz), 128.5, 127.7 (d, *J* = 5.1 Hz), 127.5, 126.4, 116.9 (d, *J* = 10.1 Hz), 64.6 (d, *J* = 8.1 Hz), 63.7 (d, *J* = 8.1 Hz), 53.4 (d, *J* = 139.4 Hz), 43.6 (d, *J* = 2.0 Hz), 17.2 (d, *J* = 12.1 Hz), 15.9 (d, *J* = 6.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.57; **HRMS** (ESI) calcd for $C_{22}H_{26}NO_3P$ $[M+H]^+$ 384.1723; found 384.1720.

tris (4-(4-cyano-4-(diethoxyphosphoryl)-4-phenylbut-1-en-1-yl)-2-methoxyphenyl) phosphate (4u):



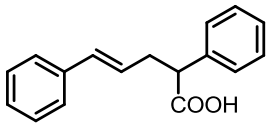
Colorless oil, 63 % yield (petroleum ether/ethyl acetate = 4:1-1:5 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.4 Hz, 6H), 7.41-7.32 (m, 9H), 7.2 (t, *J* = 8.7 Hz, 3H), 6.72 (d, *J* = 6.0 Hz, 6H), 6.43 (d, *J* = 15.7 Hz, 3H), 5.90-5.83 (m, 3H), 4.26-4.19 (m, 6H), 3.90-3.81 (m, 3H), 3.69-3.52 (m, 12H), 3.27-3.15 (m, 6H), 1.37 (t, *J* = 7.1 Hz, 9H), 1.03 (t, *J* = 7.1 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4 (d, *J* = 6.7 Hz), 139.5 (d, *J* = 7.7 Hz), 134.7, 134.5, 130.7 (d, *J* = 6.7 Hz), 128.8 (d, *J* = 2.0 Hz), 128.6 (d, *J* = 2.0 Hz), 127.8 (d, *J* = 4.9 Hz), 121.8 (d, *J* = 11.7 Hz), 121.2 (d, *J* = 2.9 Hz), 118.6, 117.9 (d, *J* = 9.6 Hz), 110.4, 65.1 (d, *J* = 7.4 Hz), 64.3 (d, *J* = 8.0 Hz), 55.8, 47.8 (d, *J* = 138.4 Hz), 38.1 (d, *J* = 3.0 Hz), 16.2 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.29, -16.56; **HRMS** (ESI) calcd for $C_{66}H_{75}N_3O_{16}P_4$ $[M+H]^+$ 1290.4170 found 1290.4175.

2,5-diphenylpent-4-enenitrile (5)[12]**:**



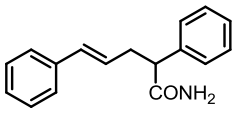
White solid, 85% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.21 (m, 10H), 6.47 (d, *J* = 15.7 Hz, 1H), 6.17-6.10 (m, 1H), 3.87 (t, *J* = 6.9 Hz, 1H), 2.80-2.74 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.4, 135.0, 134.1, 128.9, 128.4, 128.0, 127.5, 127.2, 126.2, 123.7, 120.2, 39.0, 37.7; **MS (ESI)**: $[M+H]^+$ 234.1.

2,5-diphenylpent-4-enoic acid (6)[14]



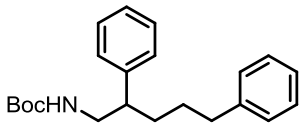
White solid, 85 % yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35-7.31 (m, 4H), 7.29-7.24 (m, 5H), 7.20-7.17 (m, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.11-6.06 (m, 1H), 3.70 (t, *J* = 7.6 Hz, 1H), 2.97 (dt, *J* = 7.7, 15.1 Hz, 1H), 2.67 (dt, *J* = 6.9, 14.0 Hz, 1H); **MS (ESI)**: $[M-H]^-$ 251.1.

2,5-diphenylpent-4-enamide (7)



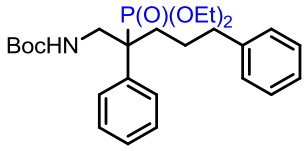
White solid, 91 % yield; **M.p.** 138-141 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34-7.31 (m, 4H), 7.28-7.23 (m, 5H), 7.18-7.15 (m, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.13-6.08 (m, 1H), 5.84 (s, 1H), 5.48 (s, 1H), 3.51 (t, *J* = 7.5 Hz, 1H), 3.06-3.01 (m, 1H), 2.68-2.63 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.3, 139.2, 137.3, 132.0, 128.8, 128.3, 127.9, 127.4, 127.3, 127.0, 126.0, 52.8, 36.5; **HRMS** (ESI) calcd for $C_{17}H_{17}NO$ $[M+H]^+$ 252.1382; found 252.1382.

Tert-butyl (2,5-diphenylpentyl)carbamate (8)



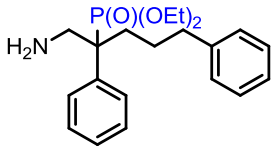
White solid, 90 % yield; **M.p.** 58-63 ^{o}C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.23-7.19 (m, 3H), 7.13 (t, *J* = 6.2 Hz, 3H), 7.08 (d, *J* = 7.4 Hz, 2H), 4.37 (s, 1H), 3.49-3.47 (m, 1H), 3.13-3.08 (m, 1H), 2.75 (s, 1H), 2.59-2.49 (m, 2H), 1.71-1.66 (m, 1H), 1.62-1.55 (m, 1H), 1.54-1.46 (m, 2H), 1.39 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.7, 142.6, 142.1, 128.5, 128.2, 128.1, 127.7, 126.5, 125.5, 78.9, 46.2, 46.0, 35.7, 33.0, 28.9, 28.3; **HRMS** (ESI) calcd for $C_{22}H_{29}NO_2$ $[M+H]^+$ 340.2271; found 340.2282.

Tert-butyl (2-(diethoxyphosphoryl)-2,5-diphenylpentyl) carbamate (9):



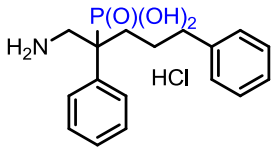
Colorless oil, 90 % yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2H), 7.31-7.27 (m, 2H), 7.24-7.20 (m, 3H), 7.15-7.09 (m, 3H), 5.57 (s, 1H), 4.00-3.75 (m, 6H), 2.64-2.47 (m, 2H), 2.18-2.05 (m, 2H), 1.69-1.60 (m, 1H), 1.45 (s, 9H), 1.29-1.26 (m, 1H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.7, 141.7, 136.8 (d, *J* = 6.1 Hz), 128.3, 128.1 (d, *J* = 3.0 Hz), 128.0, 127.8 (d, *J* = 6.1 Hz), 126.8 (d, *J* = 2.0 Hz), 125.5, 78.9, 62.9 (d, *J* = 7.1 Hz), 62.5 (d, *J* = 7.1 Hz), 46.4 (d, *J* = 133.3 Hz), 41.8, 35.9, 30.3, 28.2, 24.1 (d, *J* = 12.1 Hz), 16.11 (d, *J* = 5.1Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.82; **HRMS** (ESI) calcd for $C_{26}H_{38}NO_5P$ $[M+H]^+$ 476.2560 found 476.2557.

Diethyl (1-amino-2,5-diphenylpentan-2-yl) phosphonate (10):



Colorless oil, 93 % yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2H), 7.32-7.19 (m, 5H), 7.17-7.12 (m, 3H), 3.94-3.73 (m, 4H), 3.56-3.50 (m, 1H), 3.23-3.13 (m, 1H), 2.70-2.56 (m, 2H), 2.28-2.10 (m, 2H), 1.71 (s, 2H), 1.66-1.58 (m, 1H), 1.52-1.45 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.6, 137.5 (d, *J* = 6.1 Hz), 128.2, 128.1, 128.0, 126.6 (d, *J* = 3.0 Hz), 125.6, 62.3 (d, *J* = 8.1 Hz), 62.0 (d, *J* = 8.1 Hz), 48.1 (d, *J* = 133.3 Hz), 44.3 (d, *J* = 3.0 Hz), 35.9, 29.6, 24.8 (d, *J* = 10.1 Hz), 16.11 (d, *J* = 5.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.44; **HRMS** (ESI) calcd for $C_{21}H_{30}NO_3P$ $[M+H]^+$ 376.2036 found 376.2032.

(1-amino-2,5-diphenylpentan-2-yl) phosphonic acid hydrochloride (11):



off-white solid, 85 % yield; **M.p.** 229-232 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (s, 3.5H), 7.37 (s, 2H), 7.17-7.04 (m, 10H), 3.54 (m, 1H), 3.02 (m, 1H), 2.58 (m, 1H), 2.36 (m, 1H), 2.22 (m, 1H), 1.96 (m, 1H), 1.42 (m, 1H), 1.03-1.00 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.2, 140.7, 128.2, 128.0, 127.5, 125.5, 125.3, 40.8, 40.0, 39.8, 35.5, 24.8 (d, *J* = 10.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.83; **HRMS** (ESI) calcd for $C_{17}H_{22}NO_3P$ $[M+H]^+$ 320.1410 found 320.1407.

6. References

[1] (a) V. Hoogenband, J. J. Hartog, N. Faber-Hilhorst, J. M. Lange, J. W. Terpstra, *Tetrahedron Lett*., 2009**, 50**, 5040-5043; (b) X. X. Qi, P. H. Chen and G. S. Liu, *Angew. Chem. Int. Ed*., 2017, **56**, 9517-9521; (c) S. A. Reed, M. C. White, *J. Am. Chem. Soc*., 2008, **130**, 3316-3318.

[2] I. Faye, M. Decostanzi, Y. Ecochard and S. Caillol, *Green Chem*., 2017, **19**, 5236-5242.

[3] J. M. Álvarez-Calero, Z. D. Jorge and G. M. Massanet, *Org. Lett.,* 2016, **18**, 6344-6347.

[4]W. F. Yang, H. J. Chen, J. X. Li, C. S. Li, W. Q. Wu and H. F. Jiang, *Chem. Commun.*, 2015, **51**, 9575-9578.

[5] N. J. Race and J. F. Bower, *Org. Lett*., 2013, **15**, 4616-4619.

[6] S. Dhiman, U. K. Mishra and S. S. V. Ramasastry, *Angew. Chem. Int. Ed*., 2016, **55**, 7737-7741.

[7] M. Jin, W. Ren, D. W. Qian and S. D. Yang, *Org. Lett.*, 2018, **20**, 7015-7019.

[8] S. Jautze, R. Peters, *Angew. Chem., Int. Ed*., 2008, **47**, 9284-9288.

[9] (a) H.-L.Wang, Z. Li, G.-W.Wang, S.-D. Yang, *Chem. Commun*., 2011, **47**, 11336-11338; (b) M. Kischkewitz, C. G. Daniliuc, A. Studer, *Org. Lett*., 2016, **18**, 1206-1209.

[10] (a) S. Ghosh, S. Chaudhuri and A. Bisai, *Org. Lett*., 2015, **17**, 1373-1376; (b) M. Jackson, C. Q. O'Broin, H. Müller-Bunz and P. J. Guiry, *Org. Biomol. Chem*., 2017, **15**, 8166-8178.

[11] B. Iorga, L. Ricard and P. Savignac, *J. Chem. Soc., Perkin Trans. 1*., 2000, 3311-3316.

[12] T. Maji and J. A. Tunge, *Org. Lett.,* 2014, **16**, 5072-5075.

[13] Y. Huang, G. H. Chan and S. Chiba, *Angew. Chem. Int. Ed*., 2017, **56**, 1-5.

[14] X. Yu, Z. Liu, Z. L. Xia, Z. G. Shen, X. X. Pan, H. Zhang and W. Q. Xie, *RSC Adv*., 2014, **4**, 53397-53401.

[15] K. Kiyokawa, S. Hata, S. Kainuma and S. Minakata, *Chem. Commun*., 2019, **55**, 458-461.

[16] J.-C. Zhang, K. Fu, L.-L. Lin, Y. Lu, X.-H. Liu and X.-M. Feng, *Chem. Eur., J.,* 2018, **24**, 4289-4293.

[17] Ma. Hayashi, N. Shiomi, Y. Funahashi and S. Nakamura, *J. Am. Chem. Soc.*, 2012, **134**, 19366-19369.

[18] S. M. Kim, Y. K. Kang, M. J. Cho, J. Y. Mang and D. Y. Kim, *Bull. Korean Chem. Soc*., 2007, **28**, 2435-2441.

[19] K. Moriya, Y. Hamashima and M. Sodeoka, *Synlett.*, 2007, **7**. 1139-1142.

[20] T. Sakamoto, E. Katoh, Y. Kondo and H. Yamanaka, *Heterocycles.*, 1988, **27**, 1353-1356.

[21] S. M. Kim, Y. K. Kang, M. J. Cho, J. Y. Mang and D. Y. Kim, *Bulletin of the Korean Chemical Society.*, 2007, **28**, 2435-2441.

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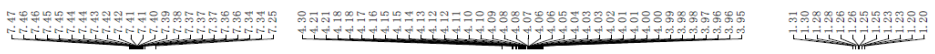
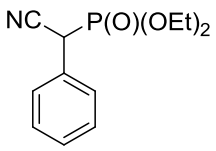
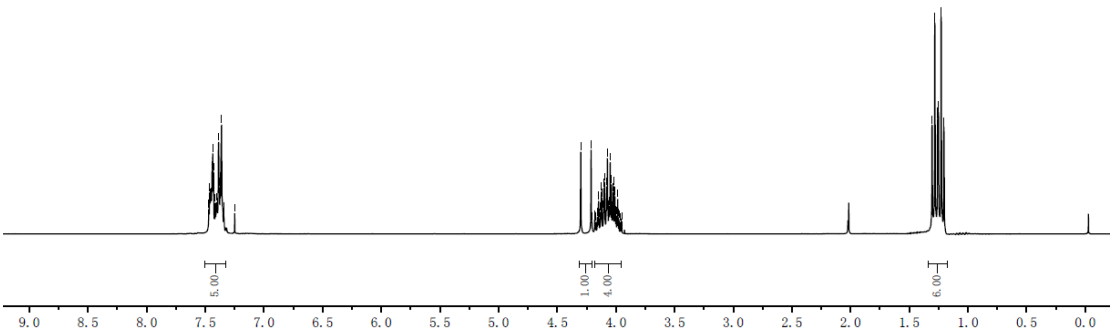
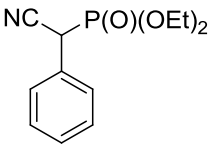
7. NMR charts:



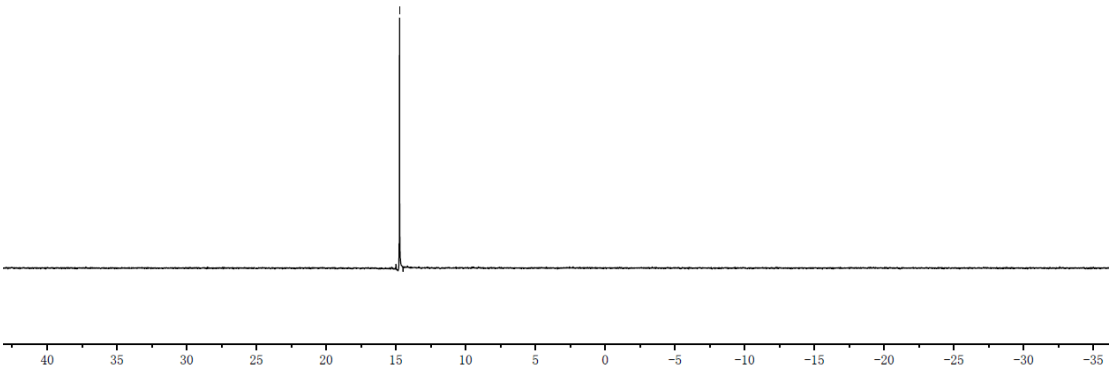


1a

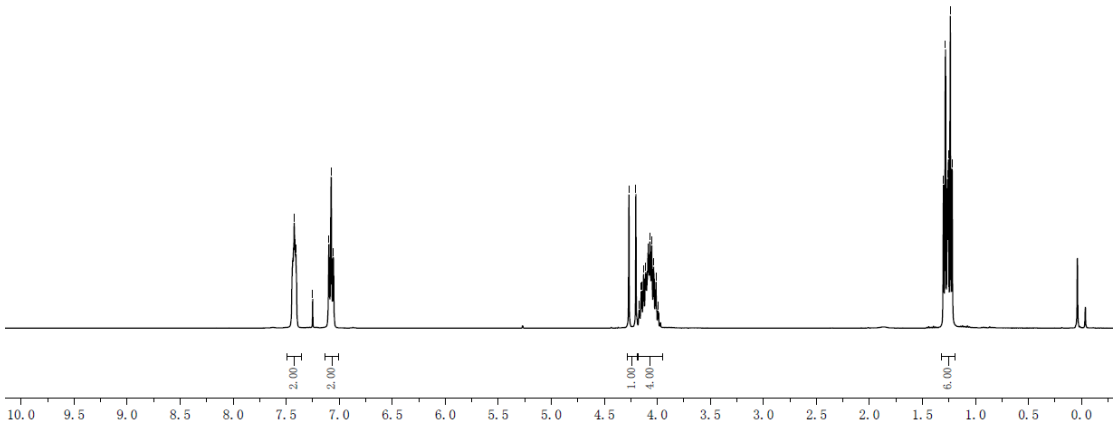


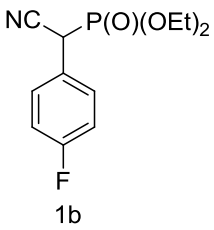


1a

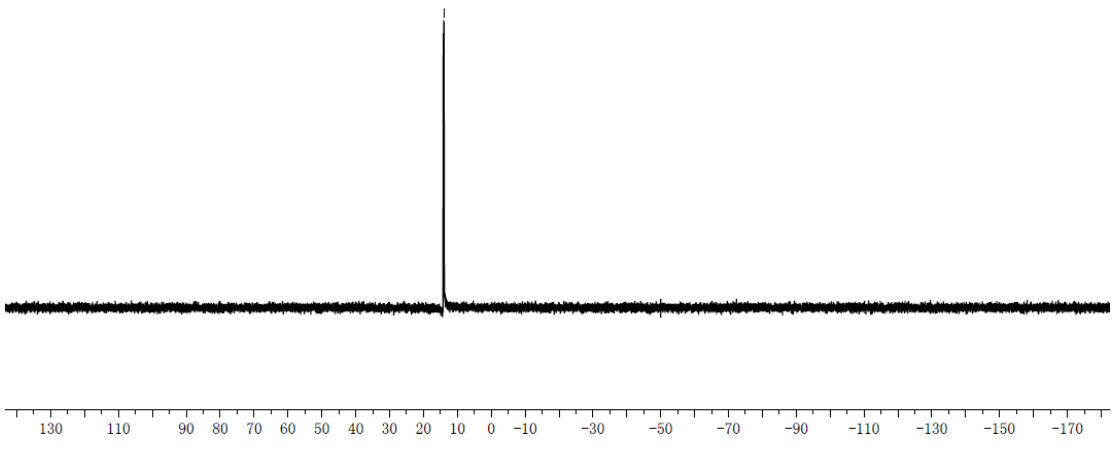


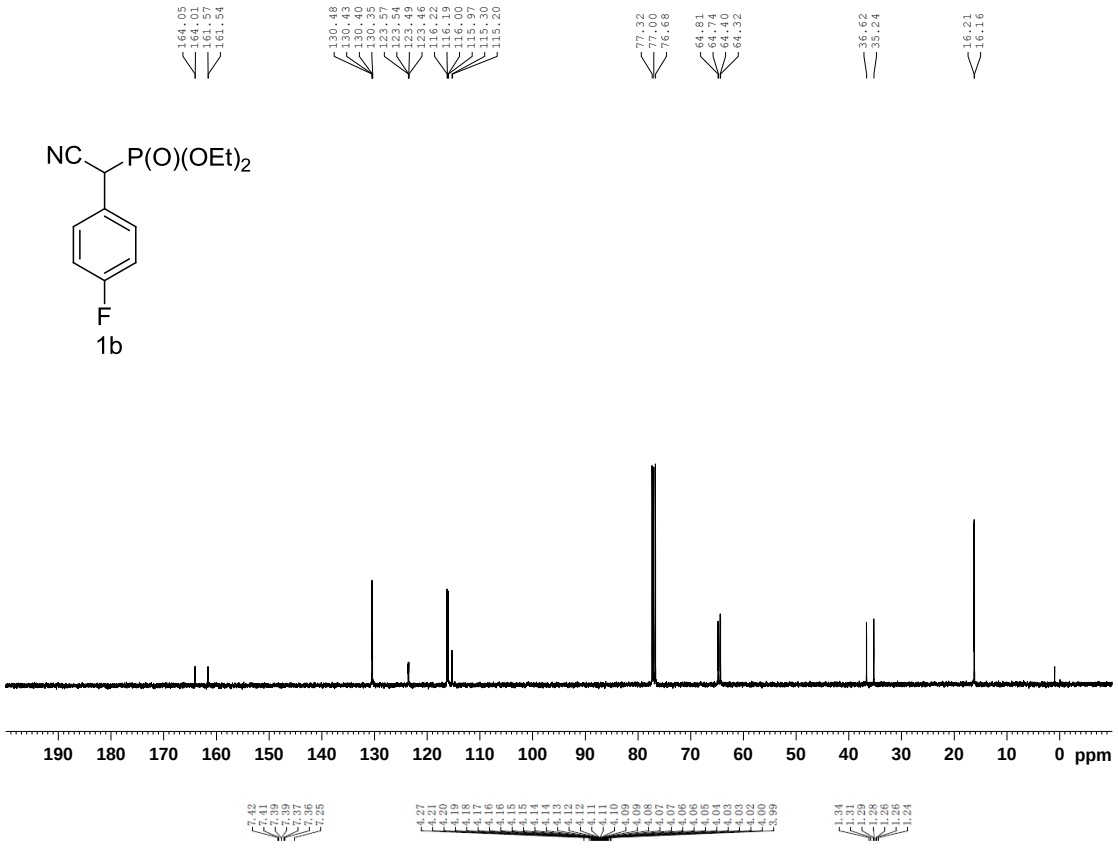
1b

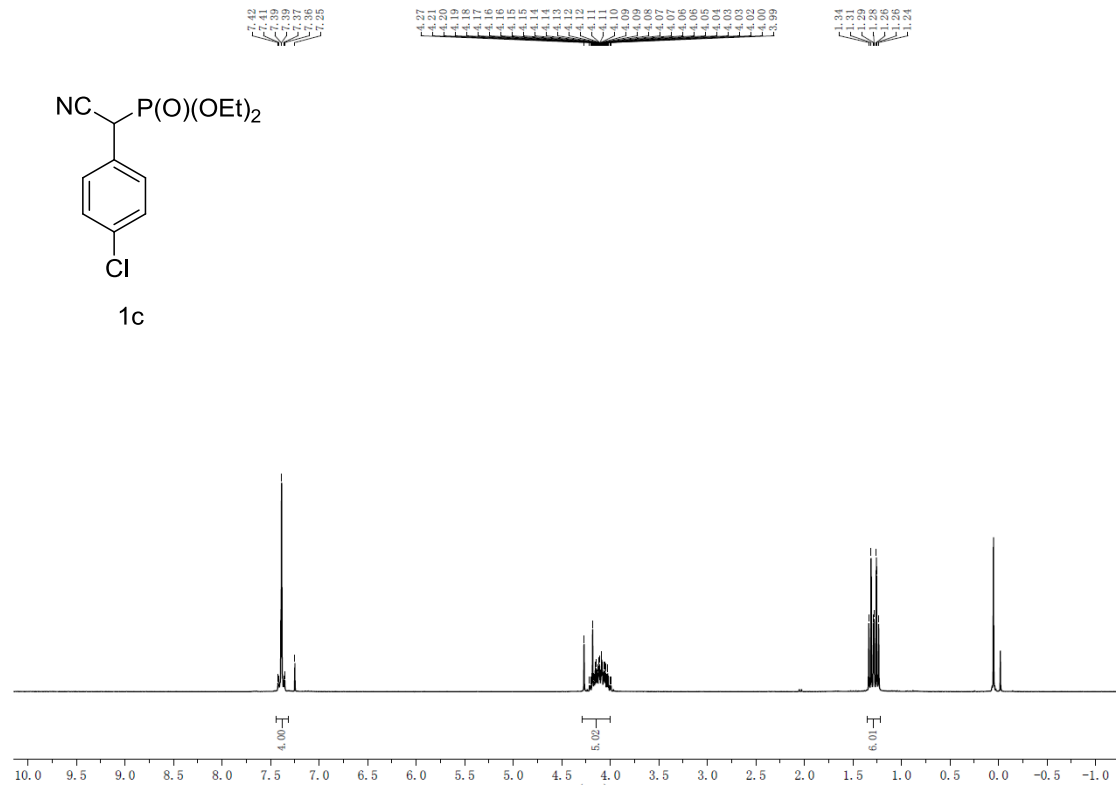


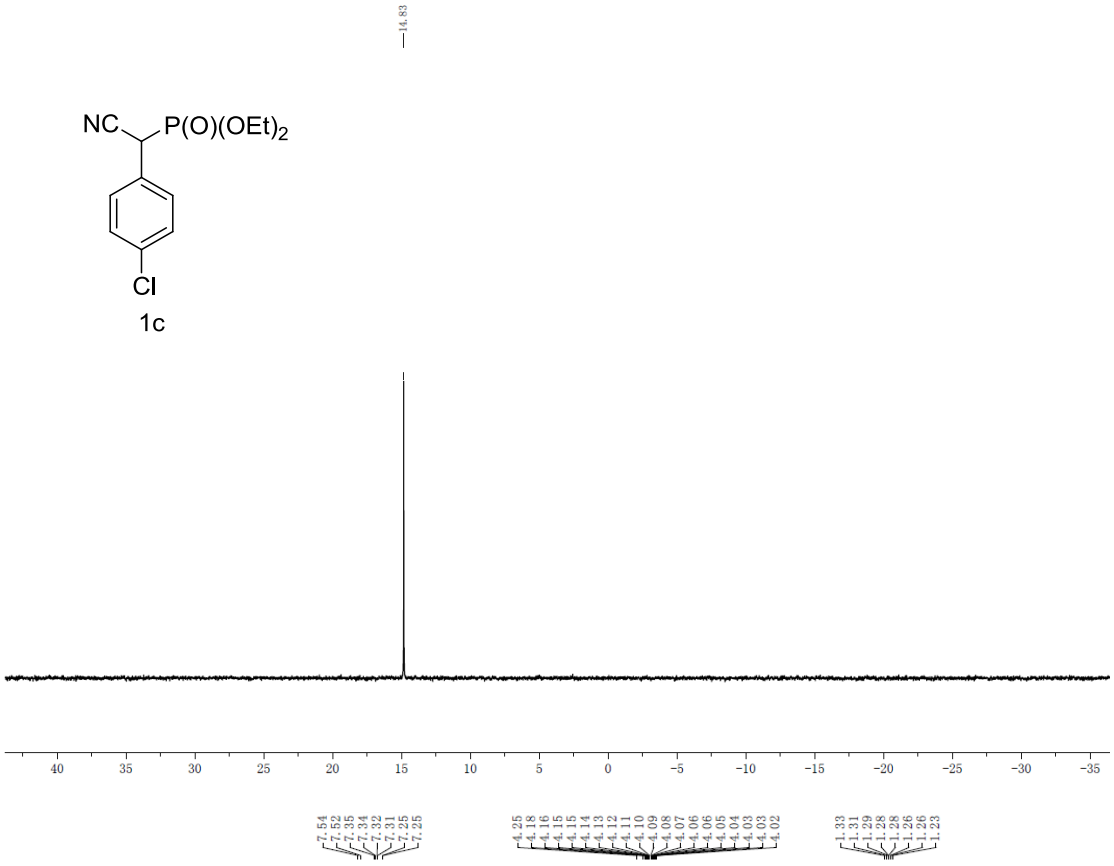


1b

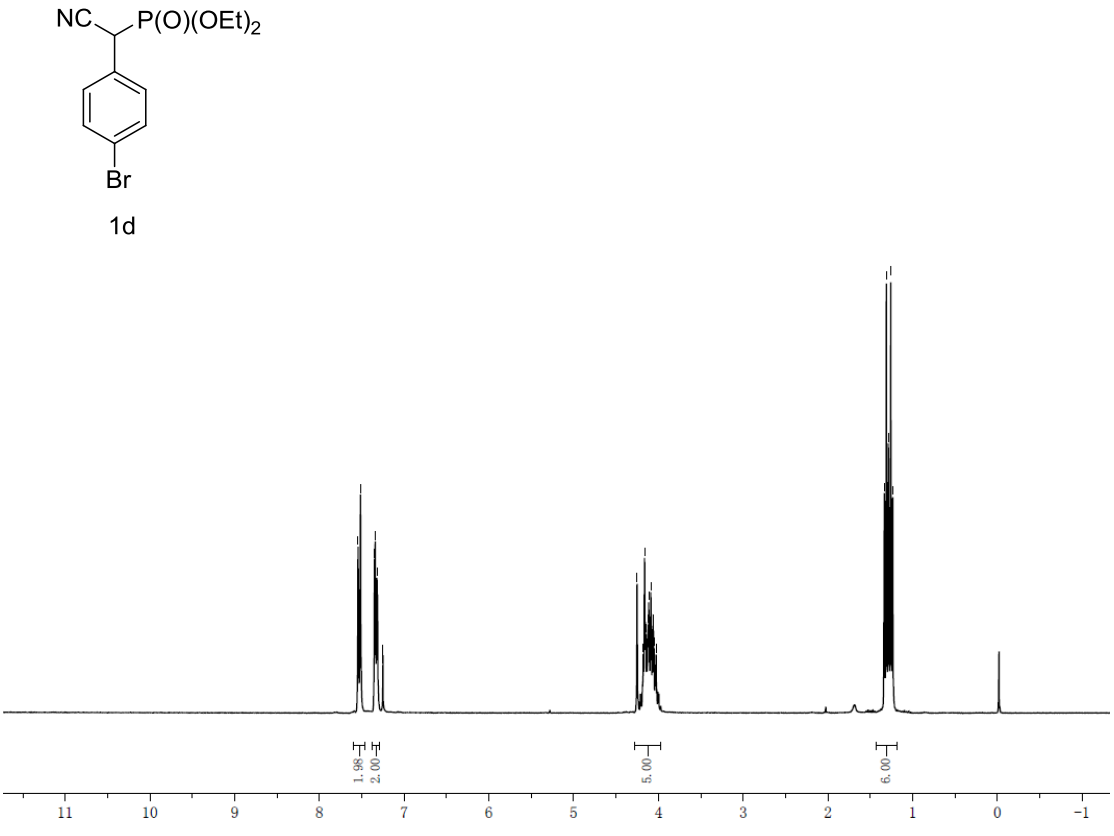



164.05
164.01
161.57
161.54
130.48
130.43
130.40
130.35
123.57
123.54
123.49
123.46
116.22
116.19
116.00
115.97
115.30
115.20
77.32
77.00
76.68
64.81
64.74
64.40
64.32
36.62
35.24
16.21
16.16
NC
P(O)(OEt)2
F
1b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

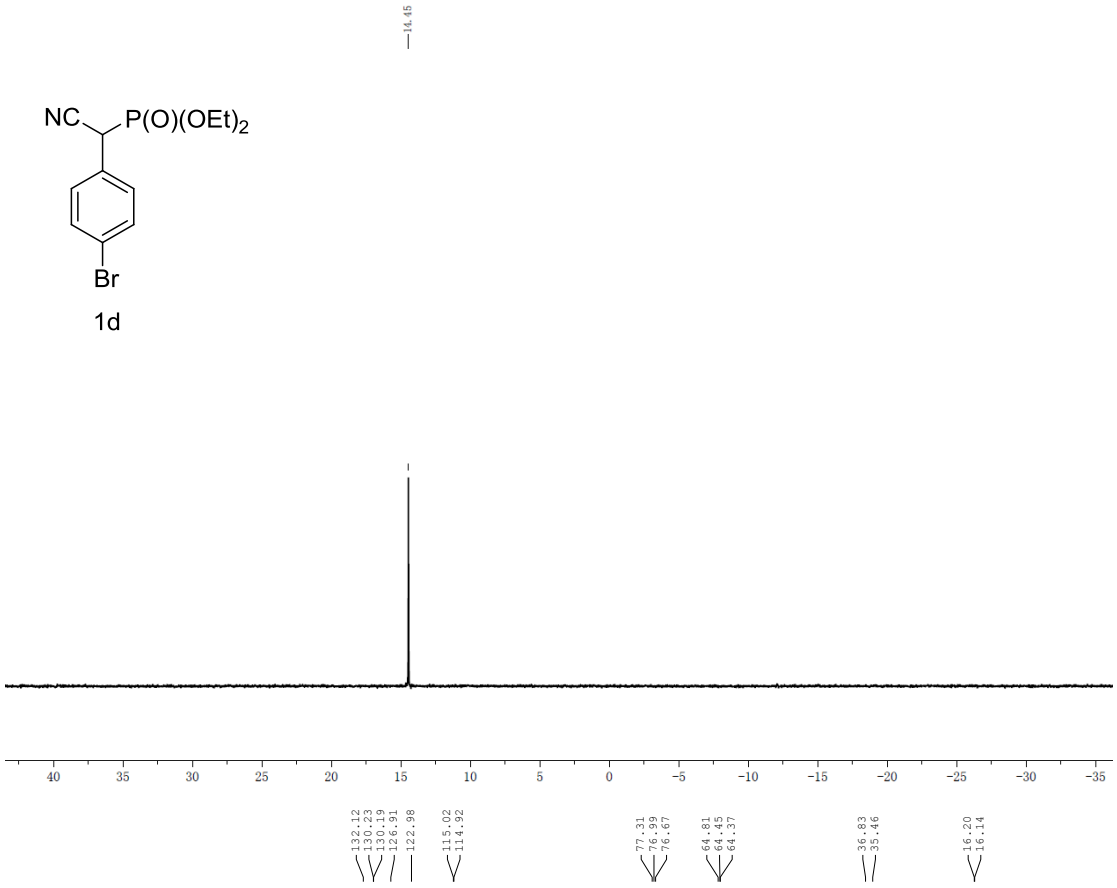

7.42
7.41
7.39
7.38
7.37
7.36
7.25
4.27
4.21
4.20
4.19
4.18
4.17
4.16
4.16
4.15
4.15
4.14
4.13
4.12
4.12
4.11
4.11
4.10
4.09
4.09
4.08
4.07
4.07
4.06
4.06
4.05
4.04
4.03
4.03
4.02
4.00
3.99
1.34
1.31
1.29
1.28
1.26
1.26
1.24
NC
P(O)(OEt)2
Cl
1c
4.00
5.02
6.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

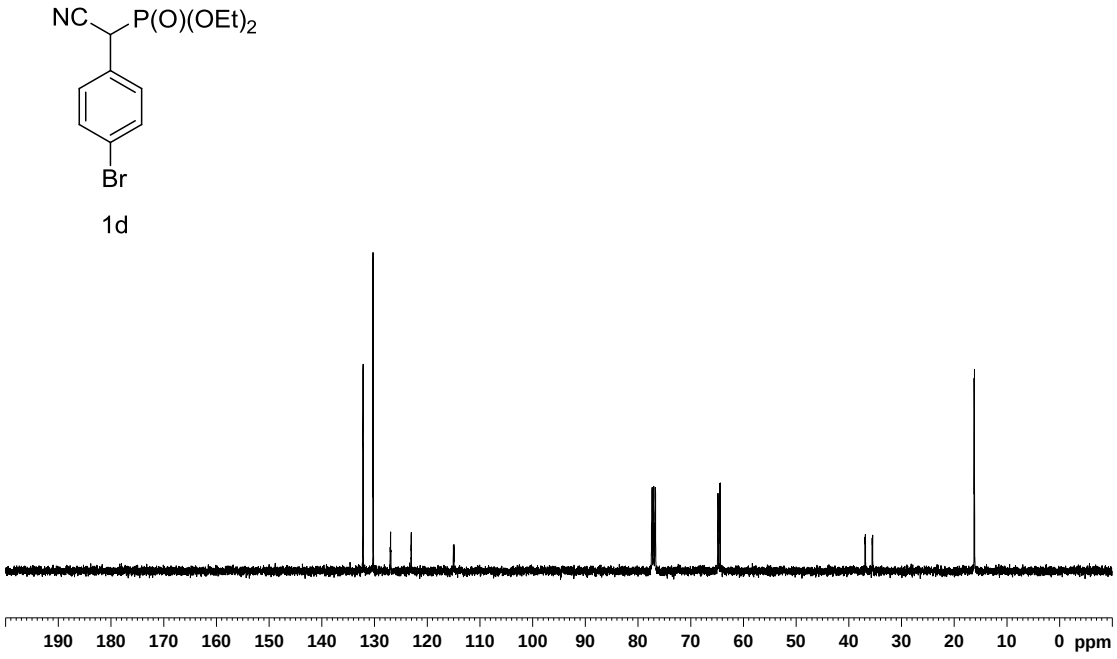

14.83
NC
P(O)(OEt)2
Cl
40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35
7.54 7.52 7.35 7.34 7.32 7.31 7.25 7.25
4.25 4.18 4.16 4.15 4.14 4.13 4.12 4.11 4.10 4.09 4.08 4.07 4.06 4.06 4.05 4.04 4.03 4.03 4.02
1.33 1.31 1.29 1.28 1.28 1.26 1.26 1.23

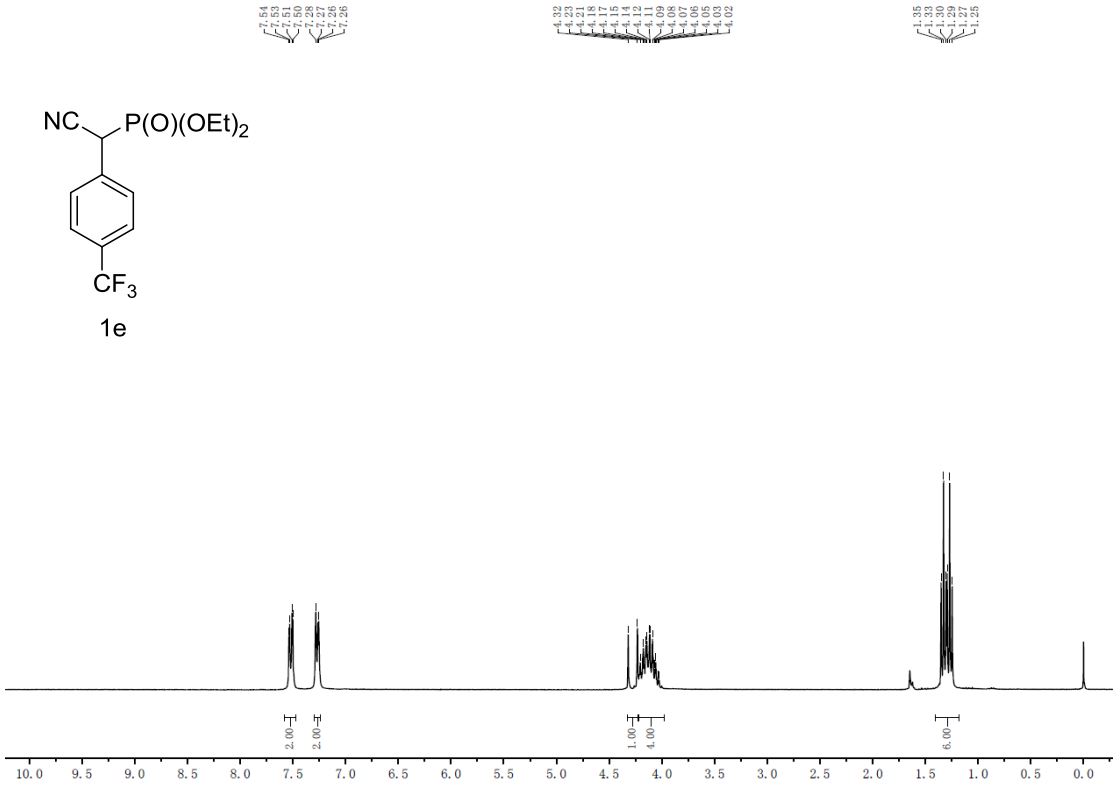
1c

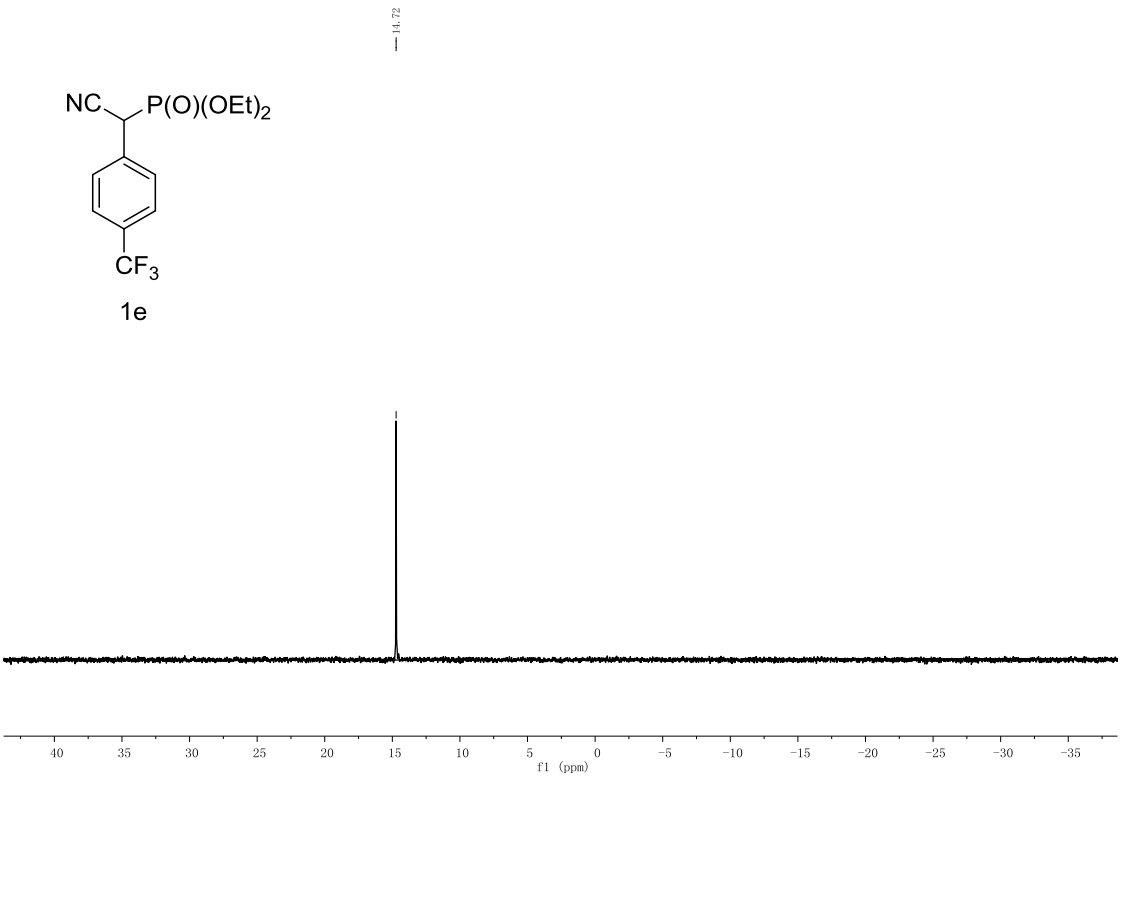

NC
P(O)(OEt)2
Br
1.98
2.00
5.00
6.00
11 10 9 8 7 6 5 4 3 2 1 0 −1

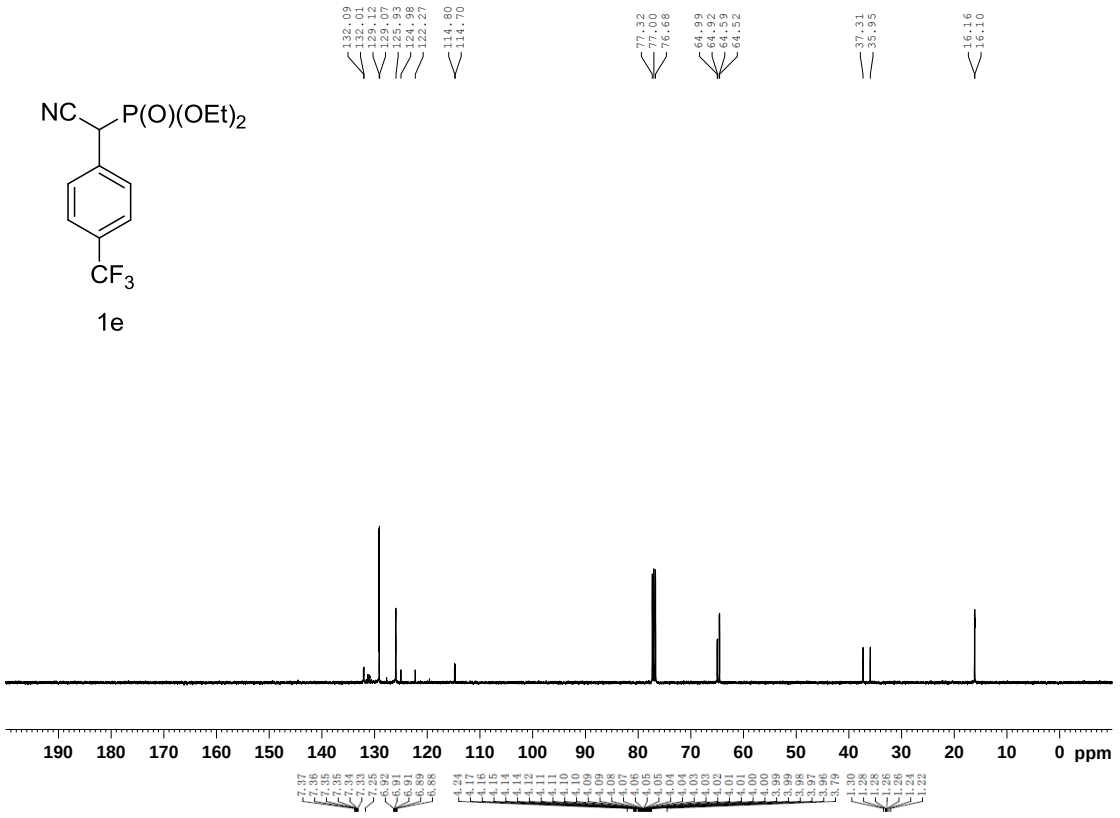
1d

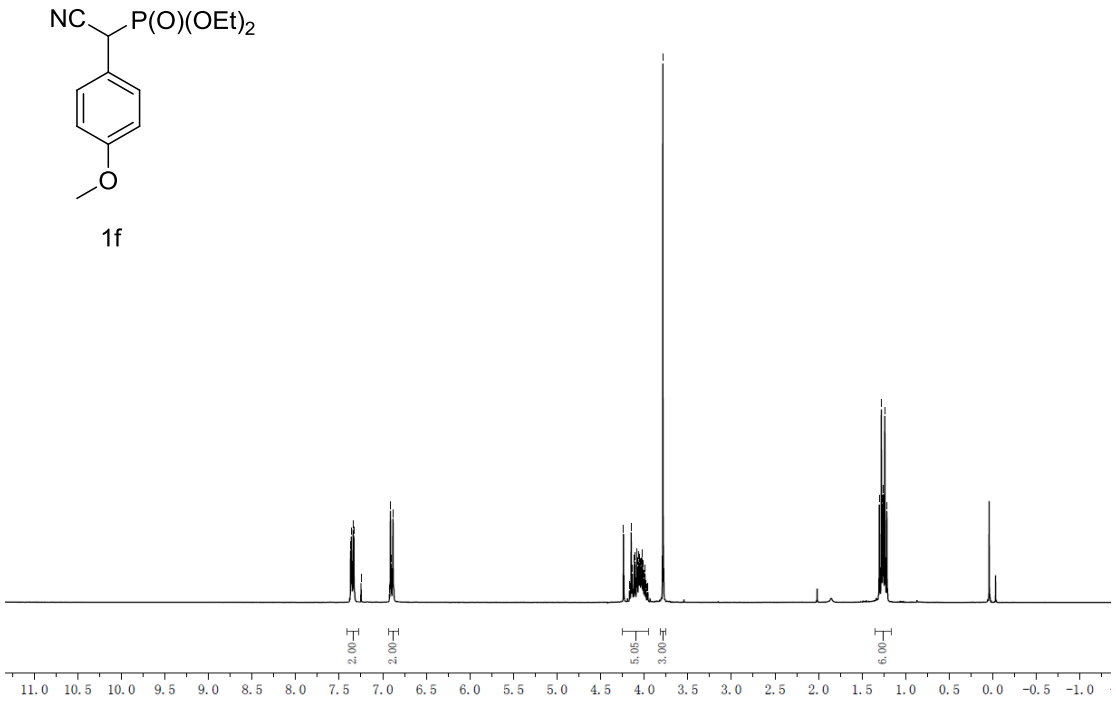

14.45
NC
P(O)(OEt)2
Br
1d
40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35
132.12
130.23
130.19
126.91
122.98
115.02
114.92
77.31
76.99
76.67
64.81
64.45
64.37
36.83
35.46
16.20
16.14


NC
P(O)(OEt)2
Br
1d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

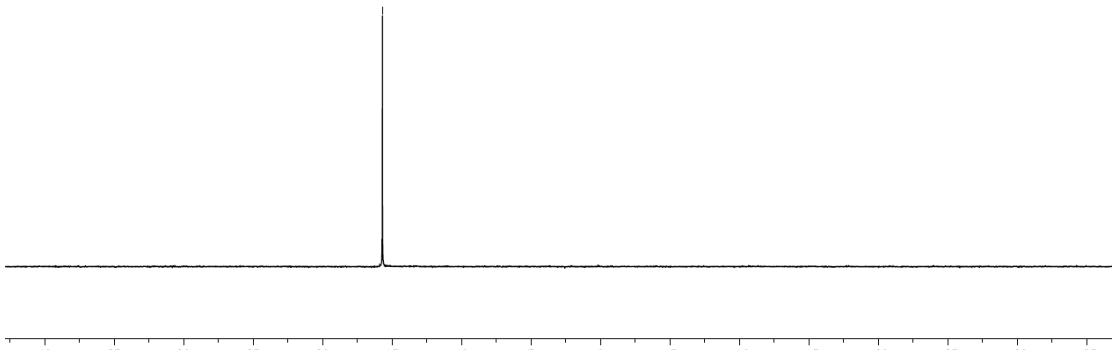

NC
P(O)(OEt)2
CF3
1e

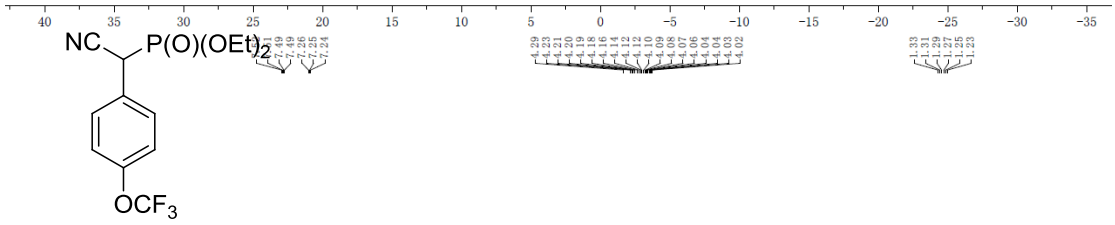

NC
P(O)(OEt)2
CF3
1e
f1 (ppm)


NC
P(O)(OEt)2
CF3
1e
132.09
132.01
129.12
129.07
125.93
124.98
122.27
114.80
114.70
77.32
77.00
76.68
64.99
64.92
64.59
64.52
37.31
35.95
16.16
16.10
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

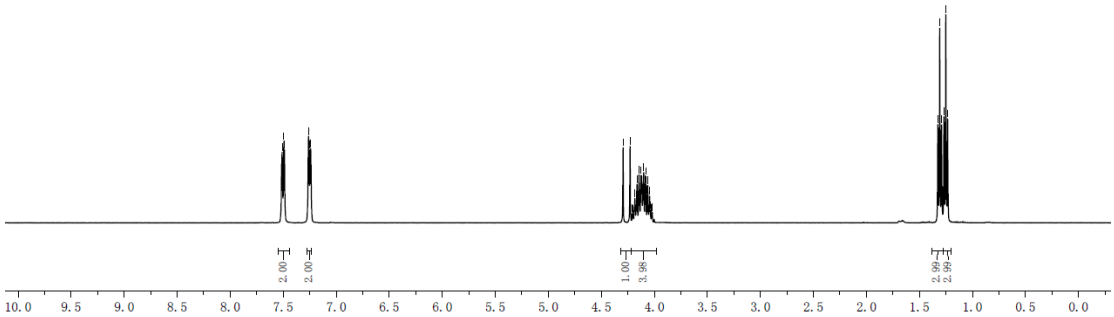

NC
P(O)(OEt)2
O
1f
2.00
2.00
5.05
3.00
6.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

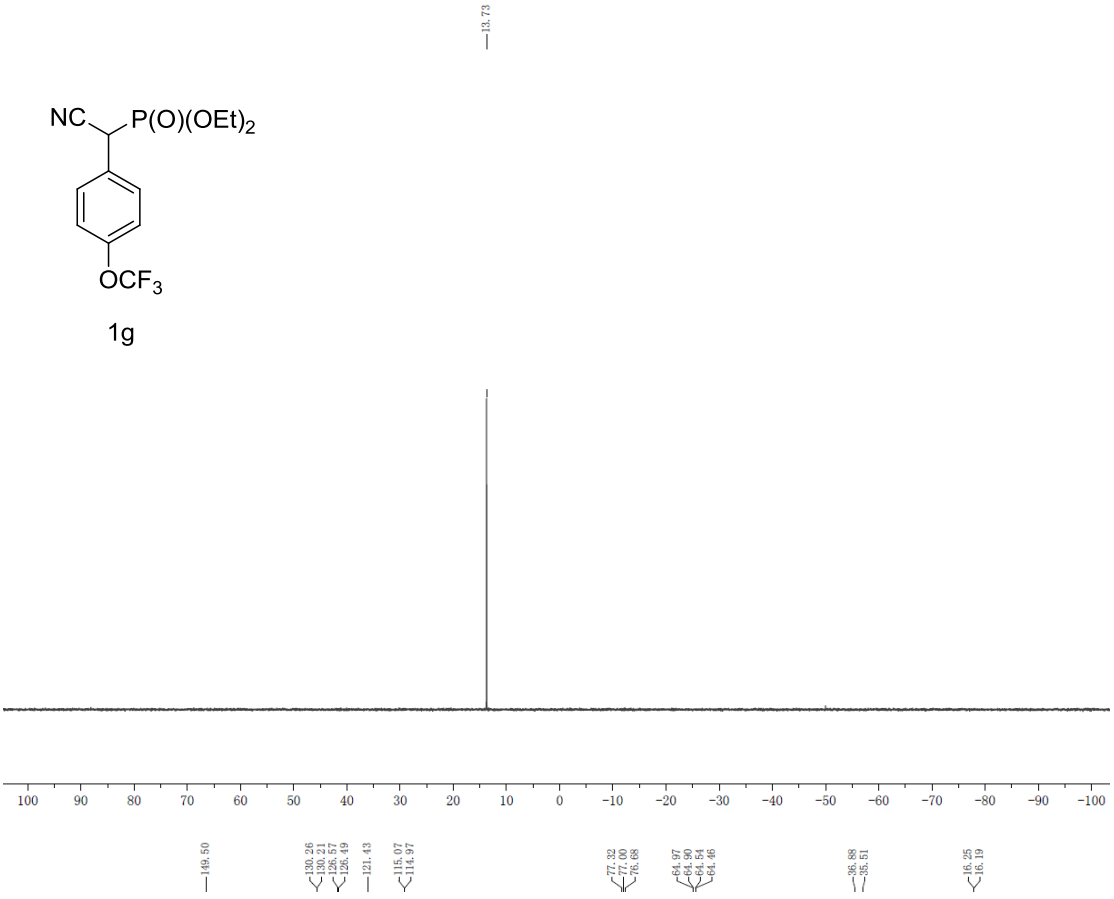
1f

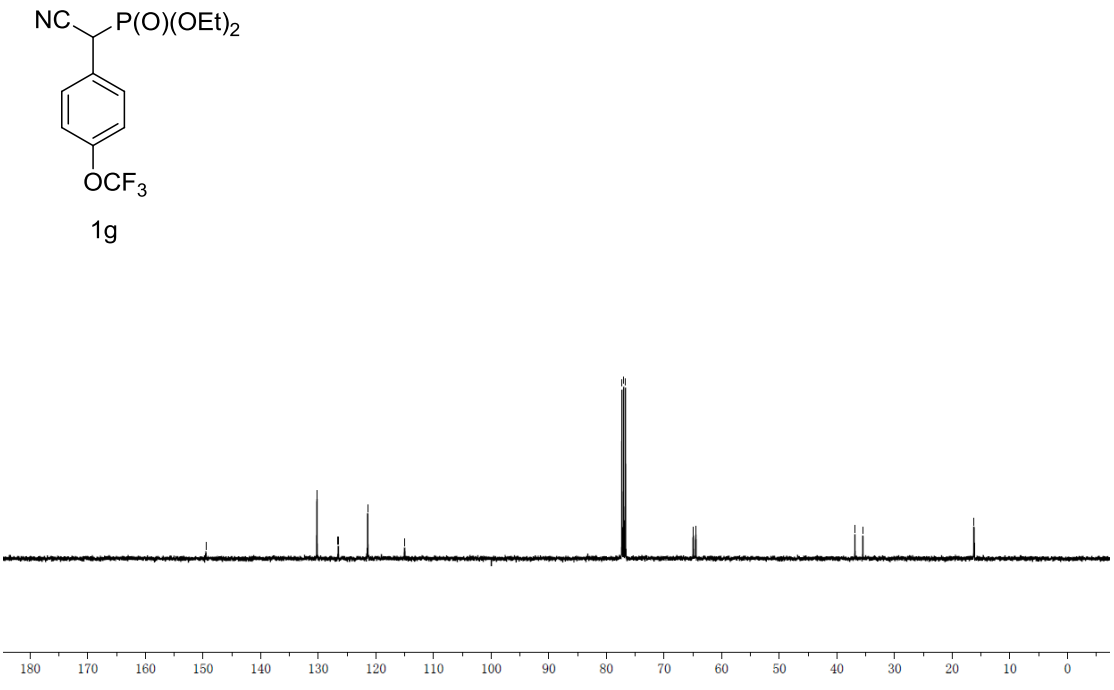


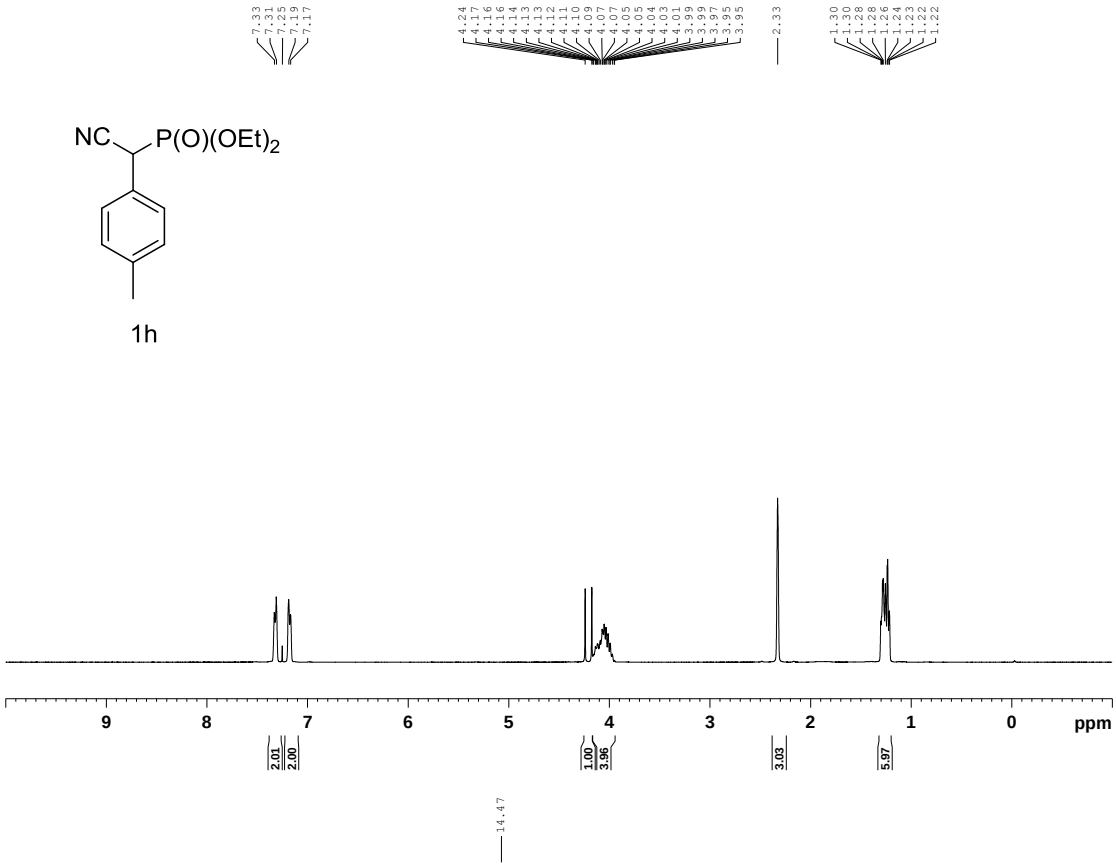


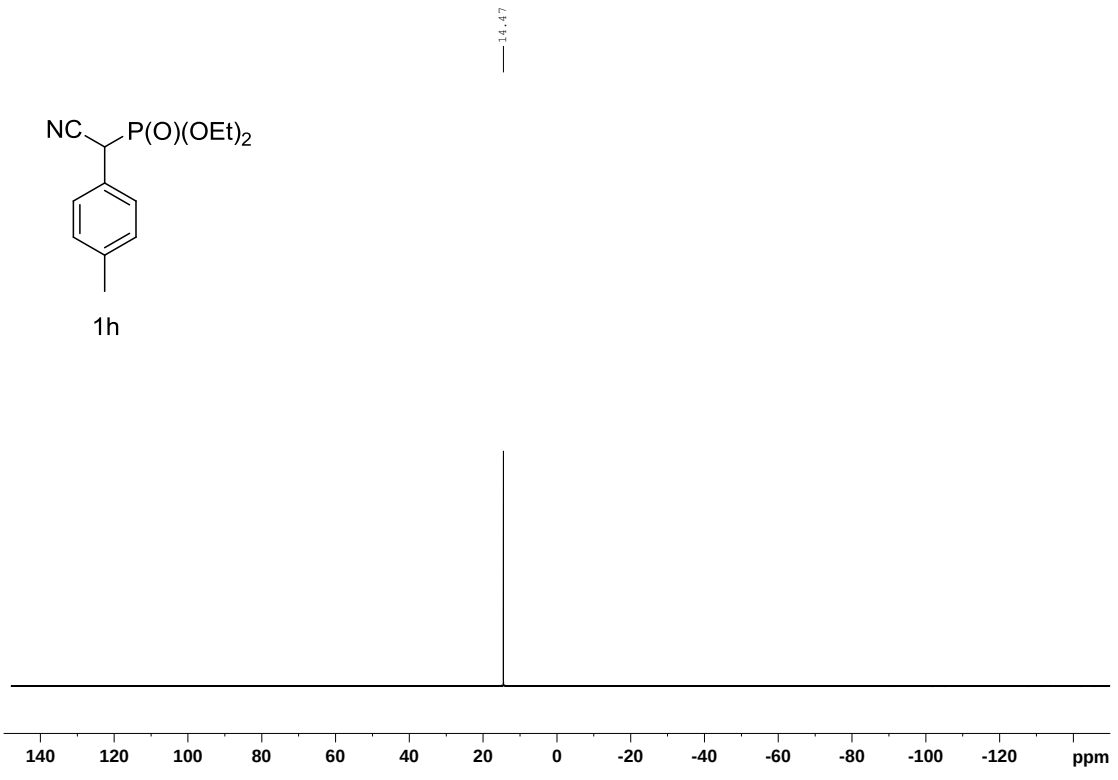
1g

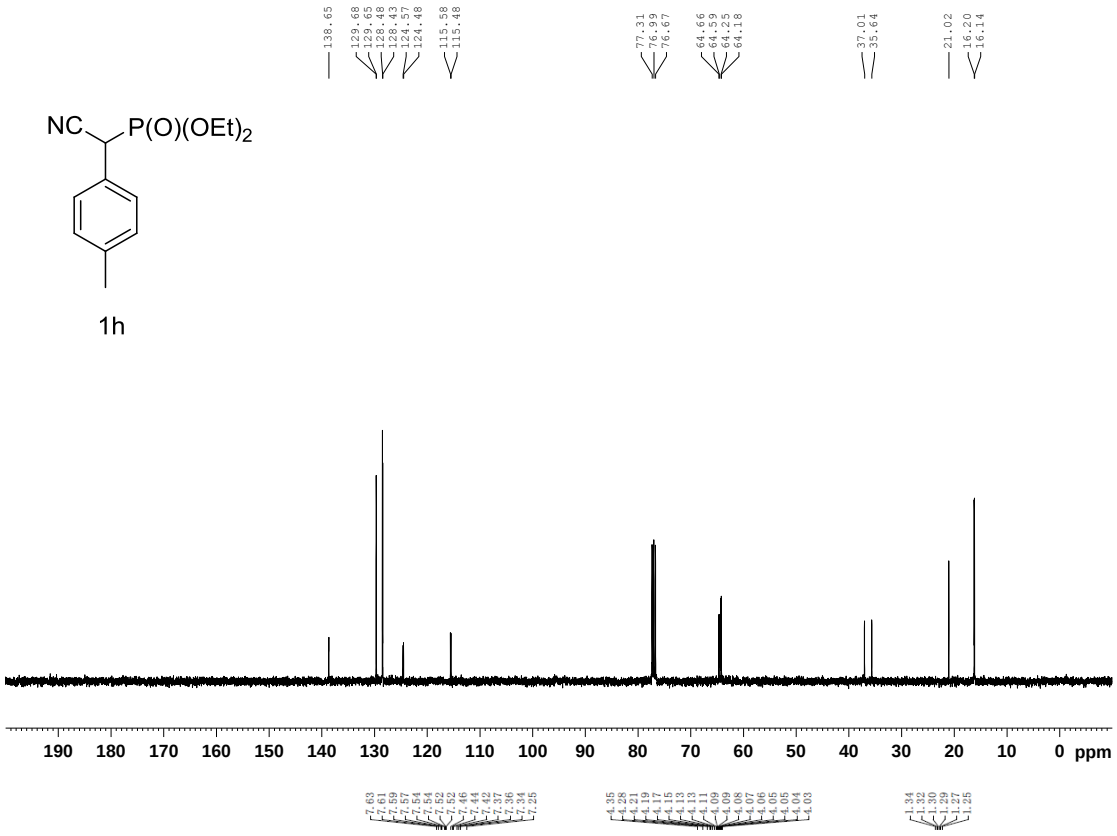


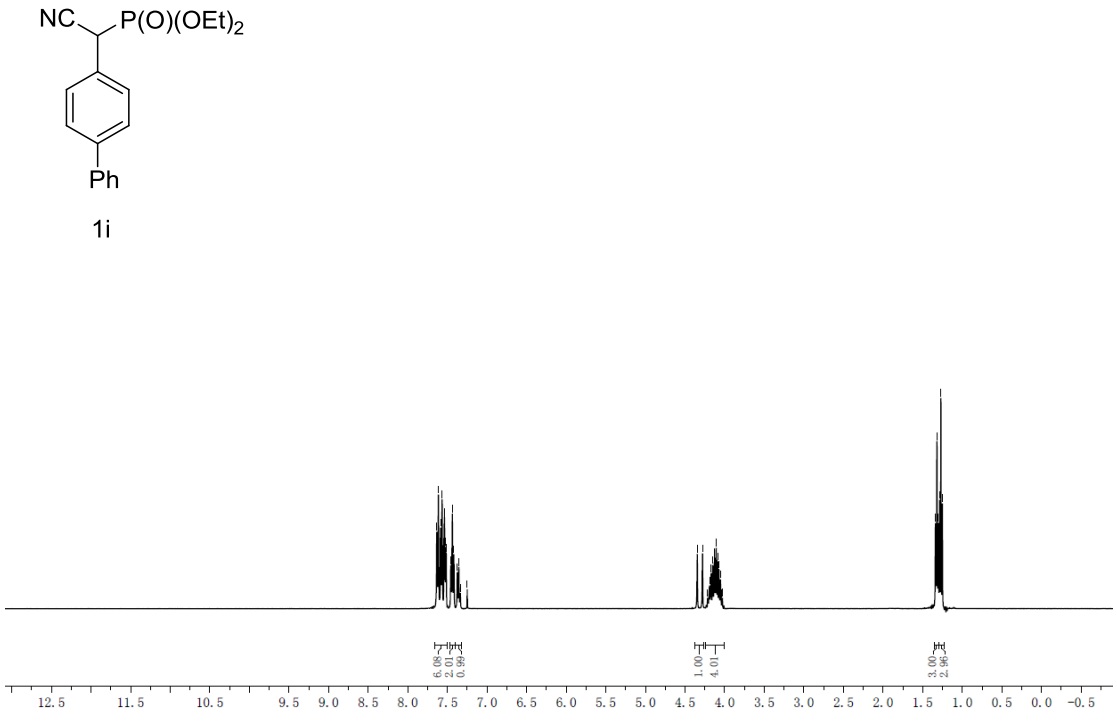

NC
P(O)(OEt)2
OCF3
1g
13.73
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
149.50
130.26
130.21
126.57
126.49
121.43
115.07
114.97
77.32
77.00
76.68
64.97
64.90
64.54
64.46
36.68
35.51
16.25
16.19

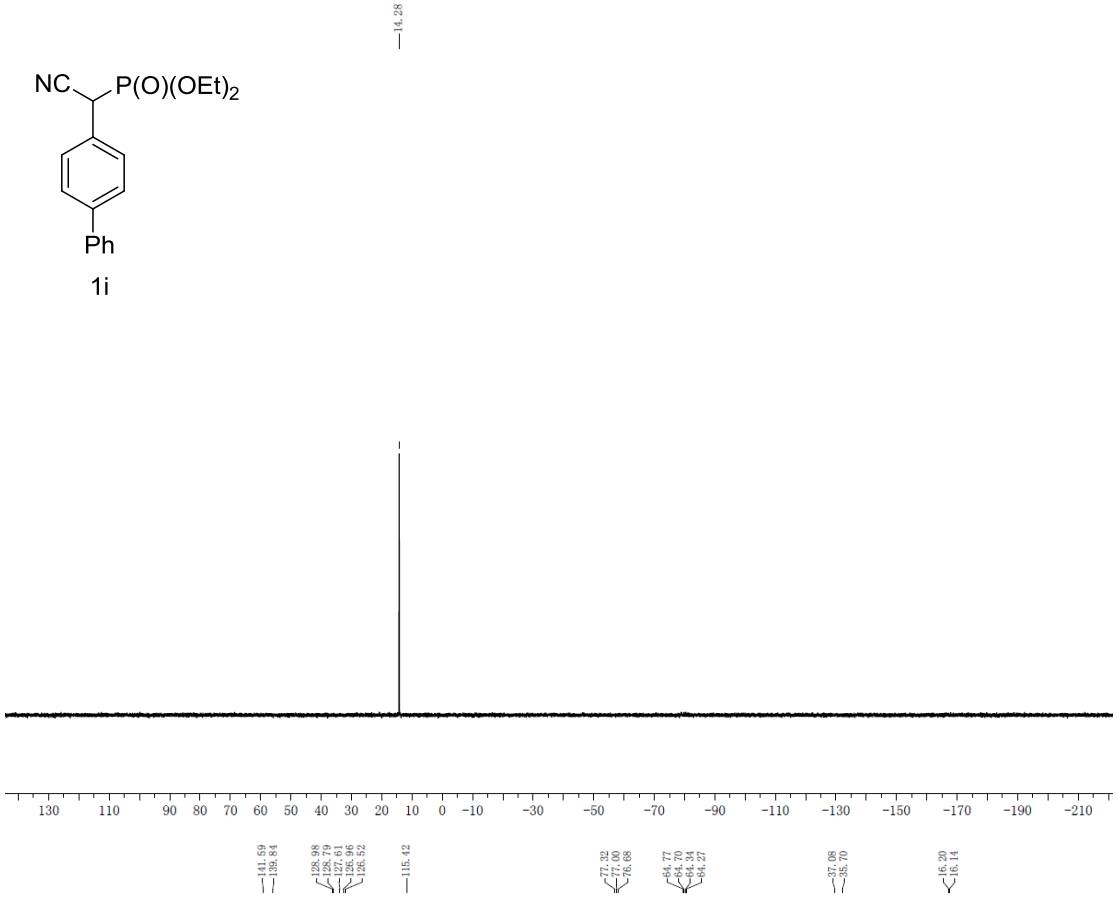

NC
P(O)(OEt)2
OCF3
1g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

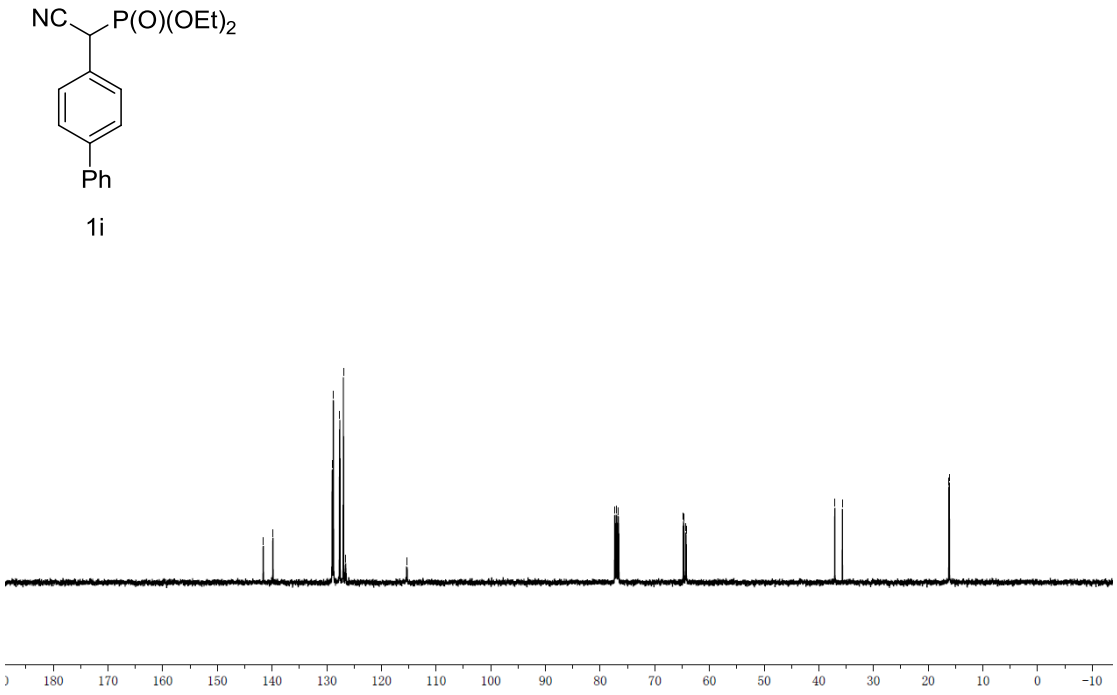

7.33
7.31
7.25
7.19
7.17
4.24
4.17
4.16
4.16
4.14
4.13
4.12
4.11
4.10
4.09
4.07
4.07
4.05
4.05
4.04
4.03
4.01
3.99
3.99
3.97
3.95
3.95
2.33
1.30
1.30
1.28
1.28
1.26
1.24
1.23
1.22
1.22
NC
P(O)(OEt)2
1h
9
8
7
6
5
4
3
2
1
0
ppm
2.01
2.00
1.00
3.96
3.03
5.97

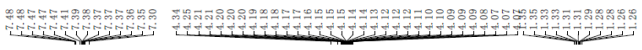

14.47
NC
P(O)(OEt)2
1h
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm

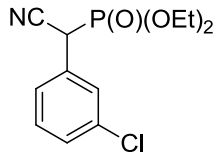

NC
P(O)(OEt)2
1h
138.65
129.68
129.65
128.48
128.43
124.57
124.48
115.58
115.48
77.31
76.99
76.67
64.66
64.59
64.25
64.18
37.01
35.64
21.02
16.20
16.14
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


NC
P(O)(OEt)2
Ph
1i
6.06
2.01
0.98
1.00
4.01
3.00
2.96
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

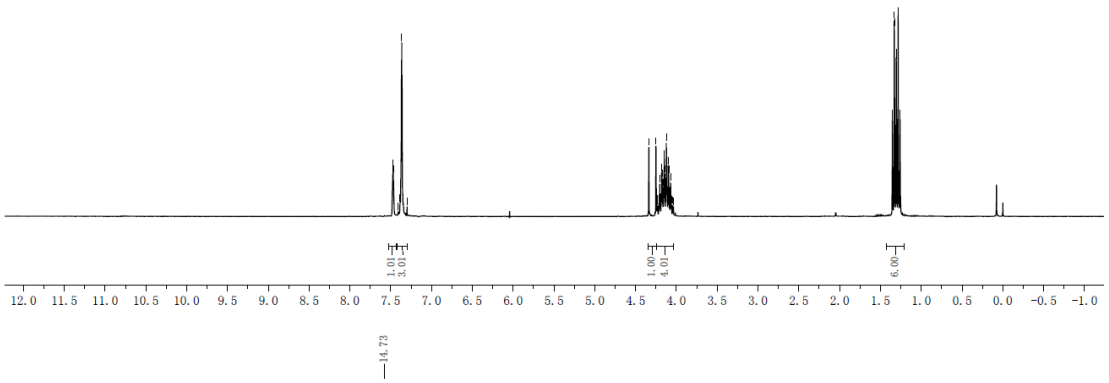

NC
P(O)(OEt)2
Ph
1i
14.28
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
141.59
139.84
128.98
128.79
127.61
126.96
126.52
115.42
77.32
77.00
76.68
64.77
64.70
64.34
64.27
37.08
35.70
16.20
16.14

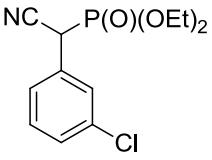

NC
P(O)(OEt)2
Ph
1i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



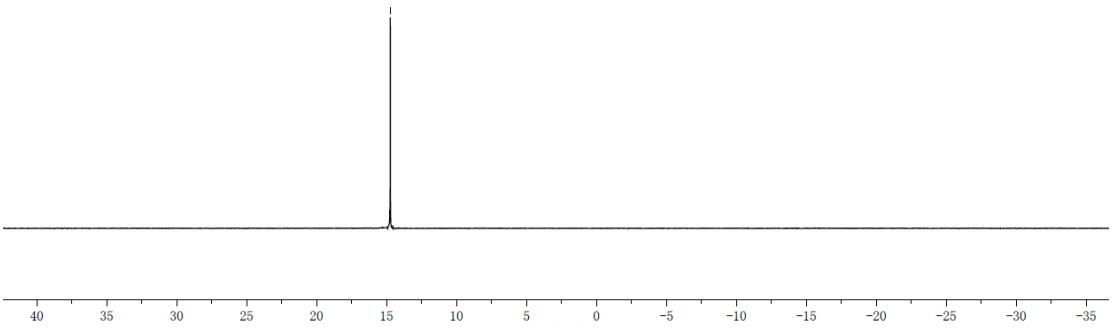

NC
P(O)(OEt)2
Cl

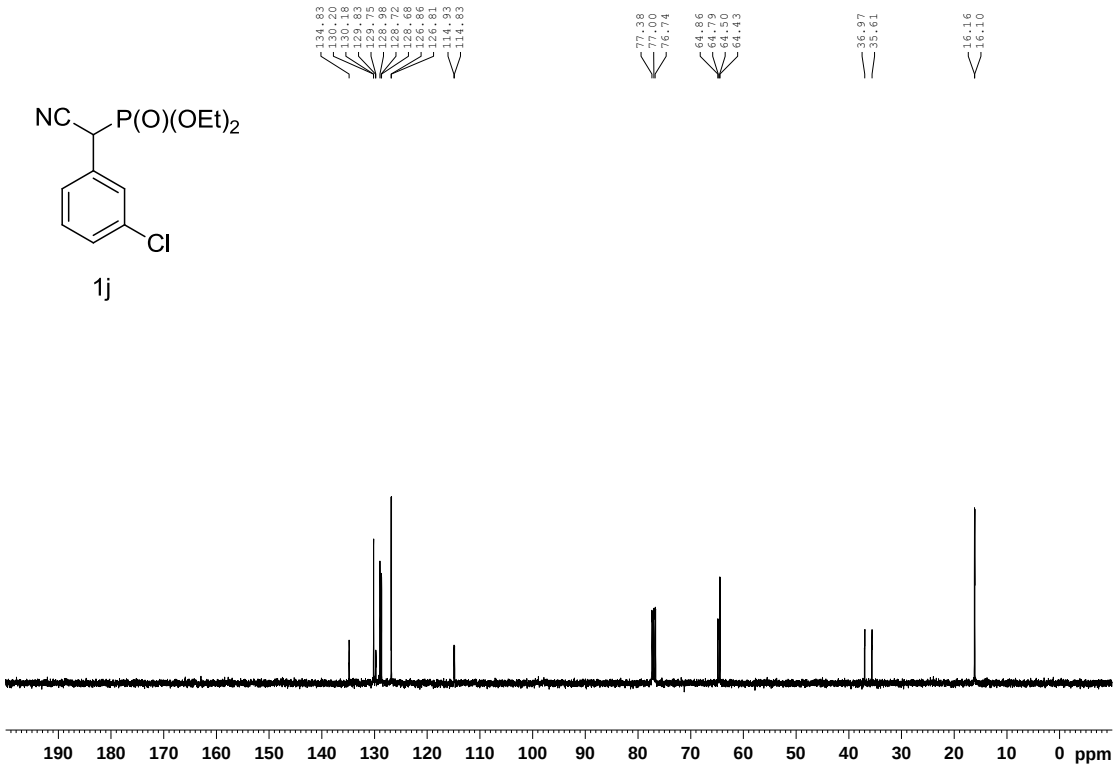
1j


1.01
3.01
1.00
4.01
6.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

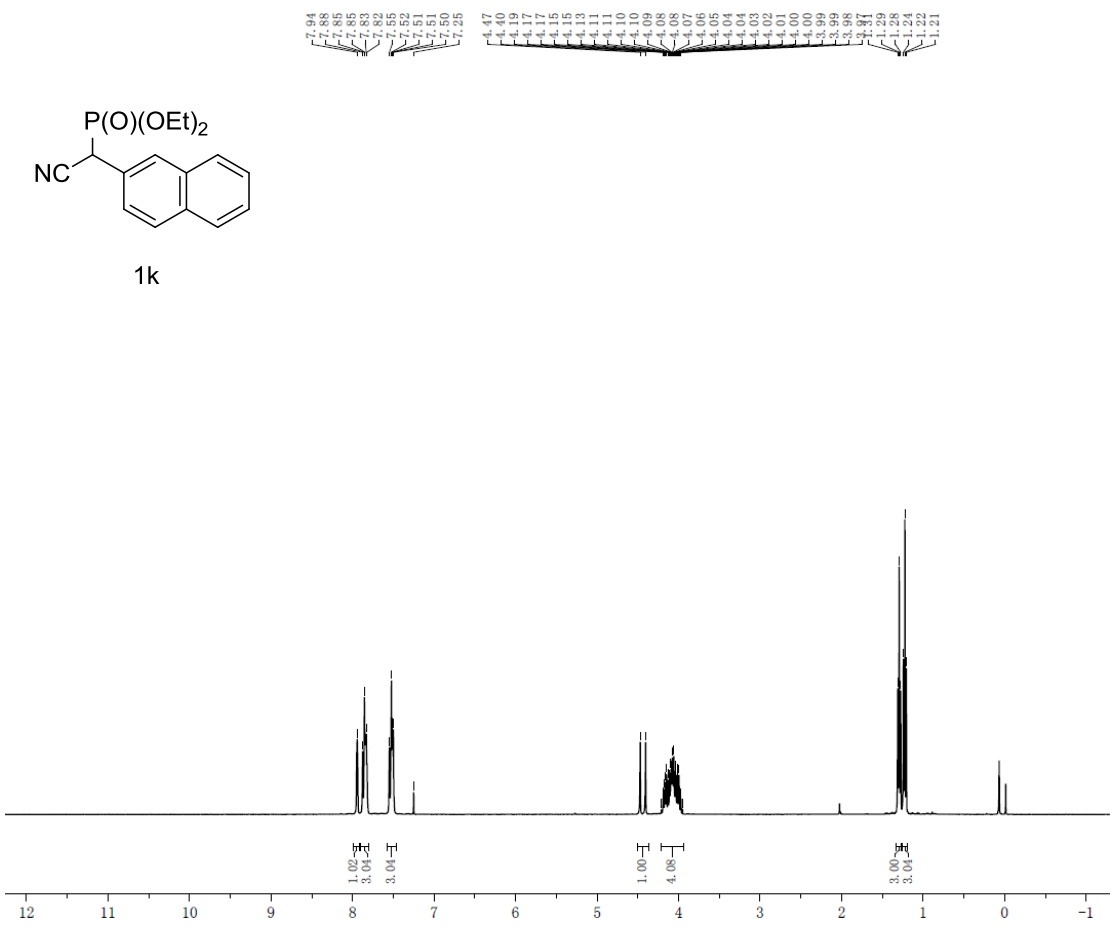

NC
P(O)(OEt)2
Cl

1j

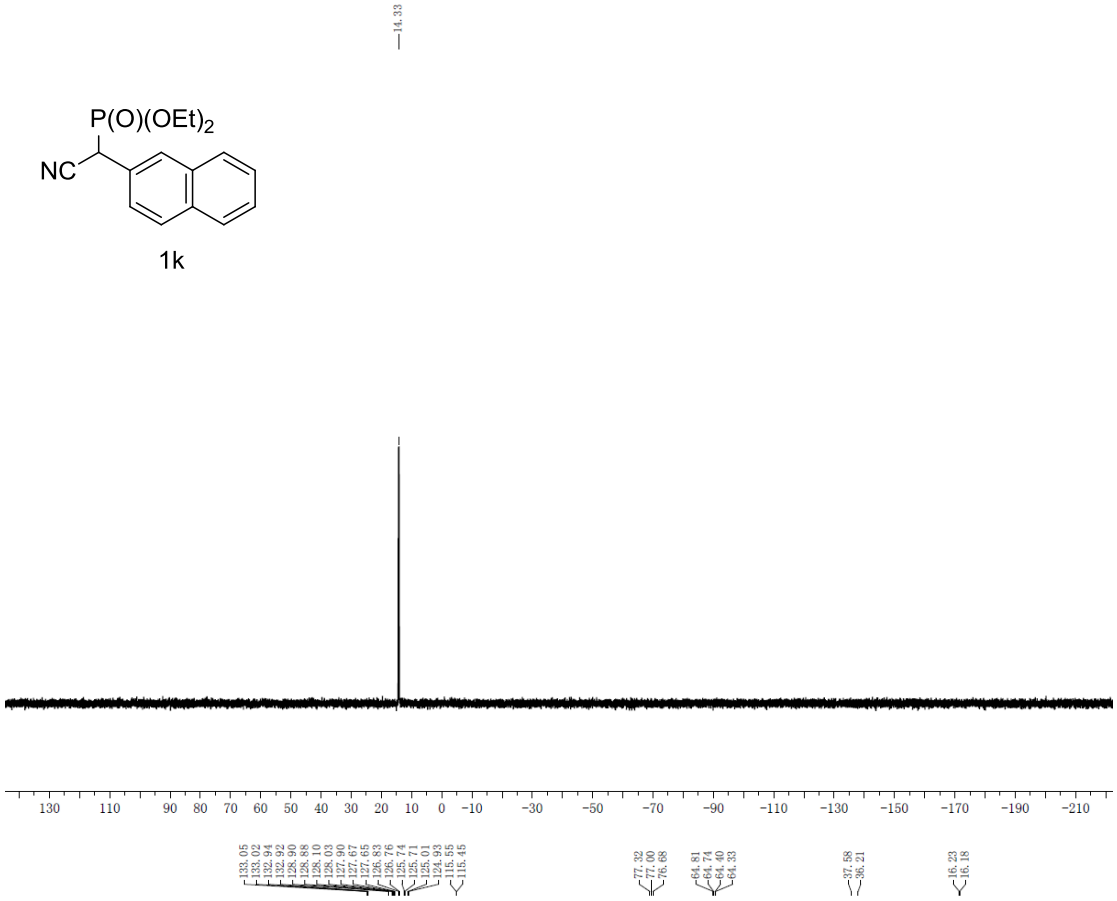

40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35

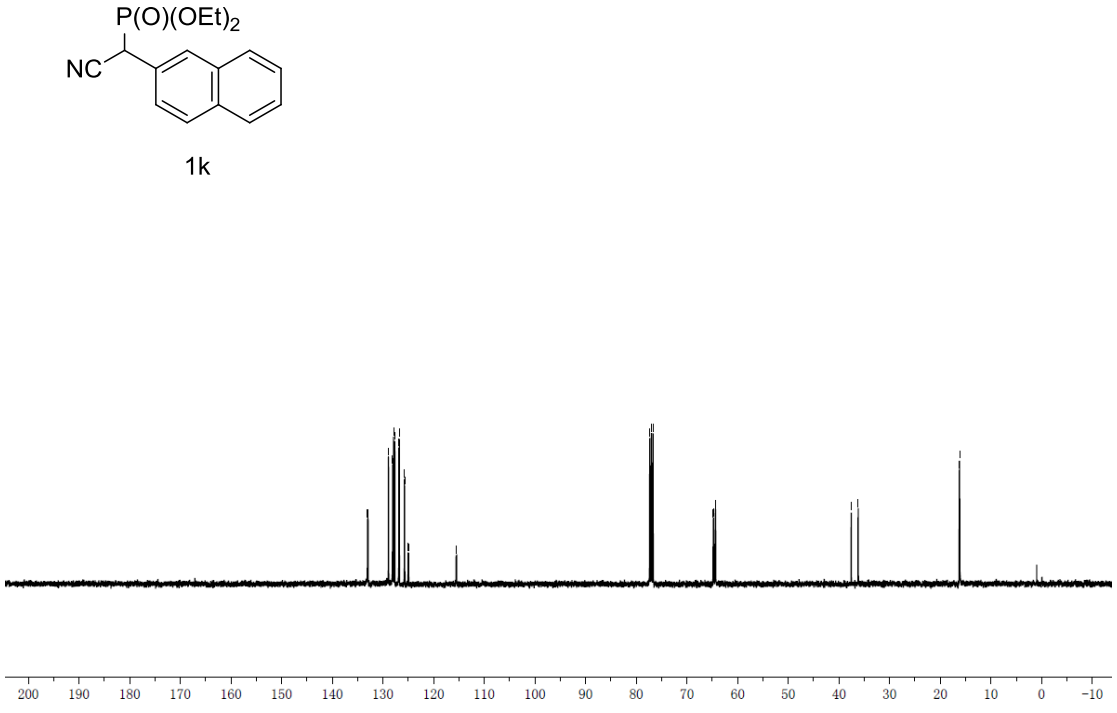

134.83
130.20
130.18
129.83
129.75
128.98
128.72
128.46
126.86
126.81
114.93
114.83
77.38
77.00
76.74
64.86
64.79
64.50
64.43
36.97
35.61
16.16
16.10
NC
P(O)(OEt)2
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

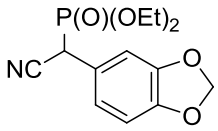
1j


7.94
7.88
7.85
7.85
7.83
7.82
7.55
7.52
7.51
7.51
7.50
7.25
4.47
4.40
4.19
4.17
4.17
4.15
4.15
4.13
4.11
4.11
4.10
4.10
4.09
4.08
4.08
4.07
4.06
4.05
4.04
4.04
4.03
4.02
4.01
4.00
4.00
3.99
3.99
3.98
1.31
1.29
1.28
1.24
1.22
1.21
P(O)(OEt)2
NC
1.02
3.04
3.04
1.00
4.08
3.00
3.04
12 11 10 9 8 7 6 5 4 3 2 1 0 −1

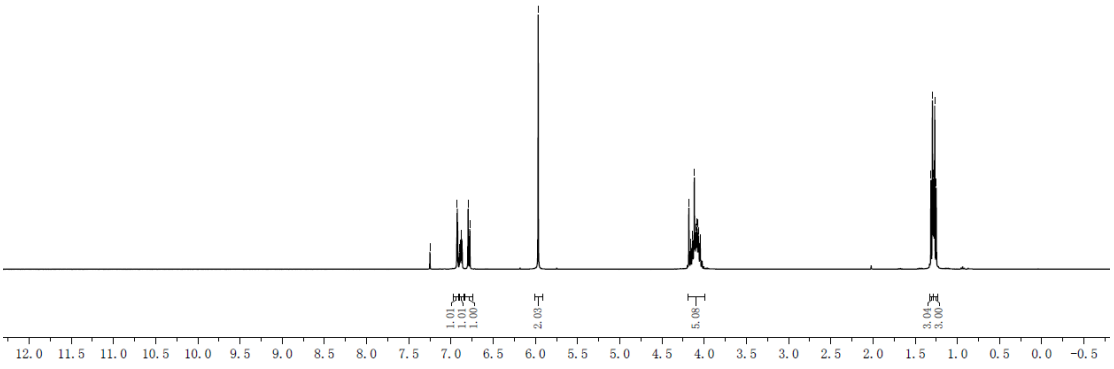
1k

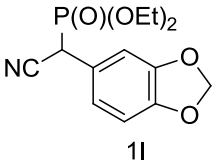

14.33
P(O)(OEt)2
NC
1k
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
133.05
133.02
132.94
132.92
129.90
128.88
128.10
128.03
127.90
127.67
127.65
126.83
126.76
125.74
125.71
125.01
124.93
116.55
116.45
77.32
77.00
76.68
64.81
64.74
64.40
64.33
37.58
36.21
16.23
16.18


P(O)(OEt)2
NC
1k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

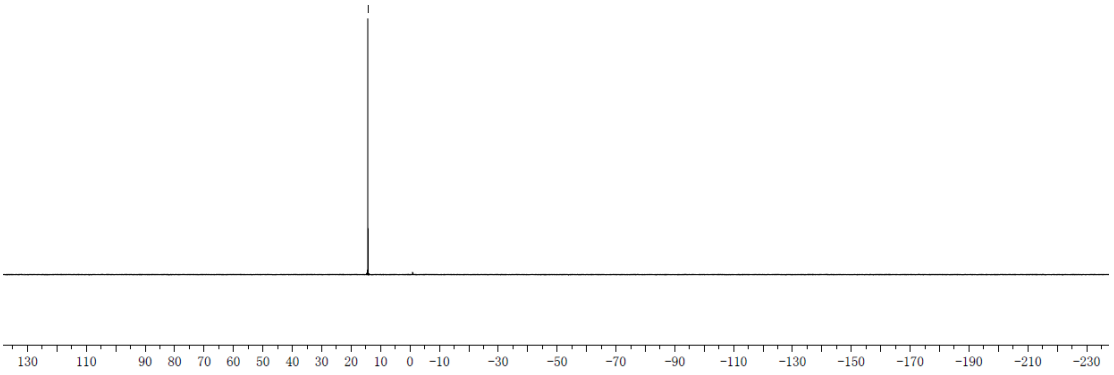


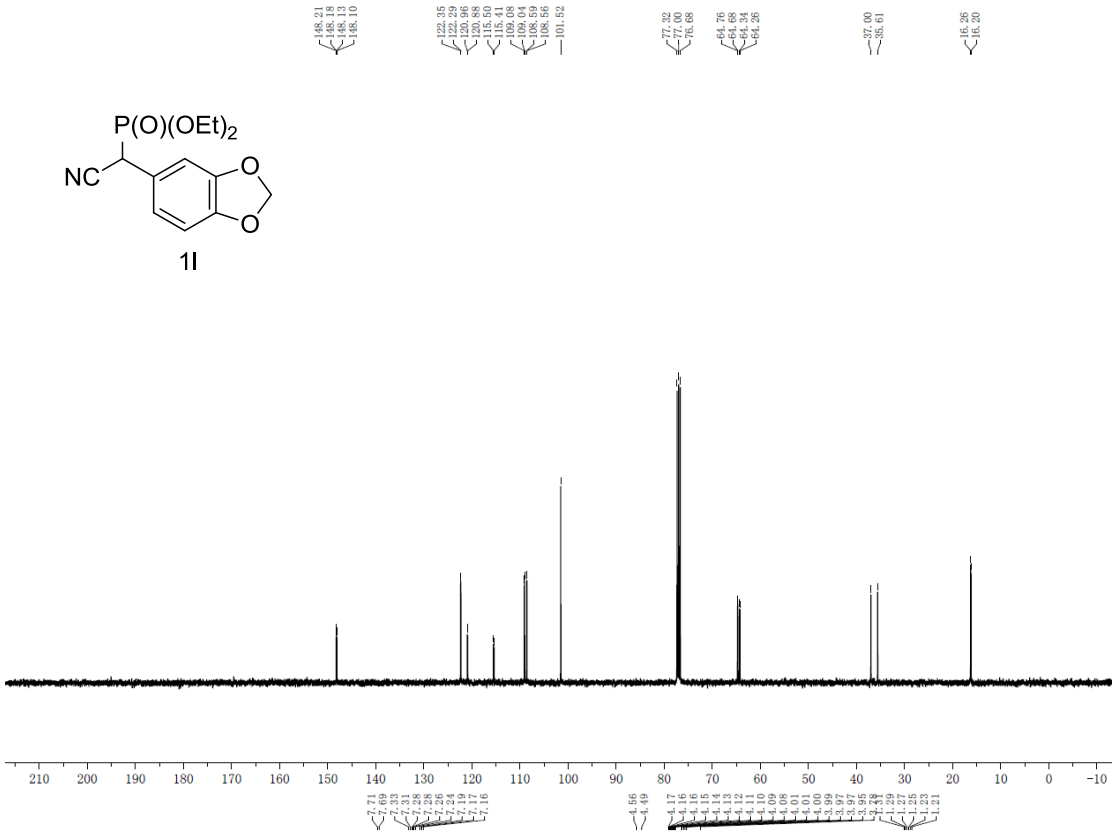
1l

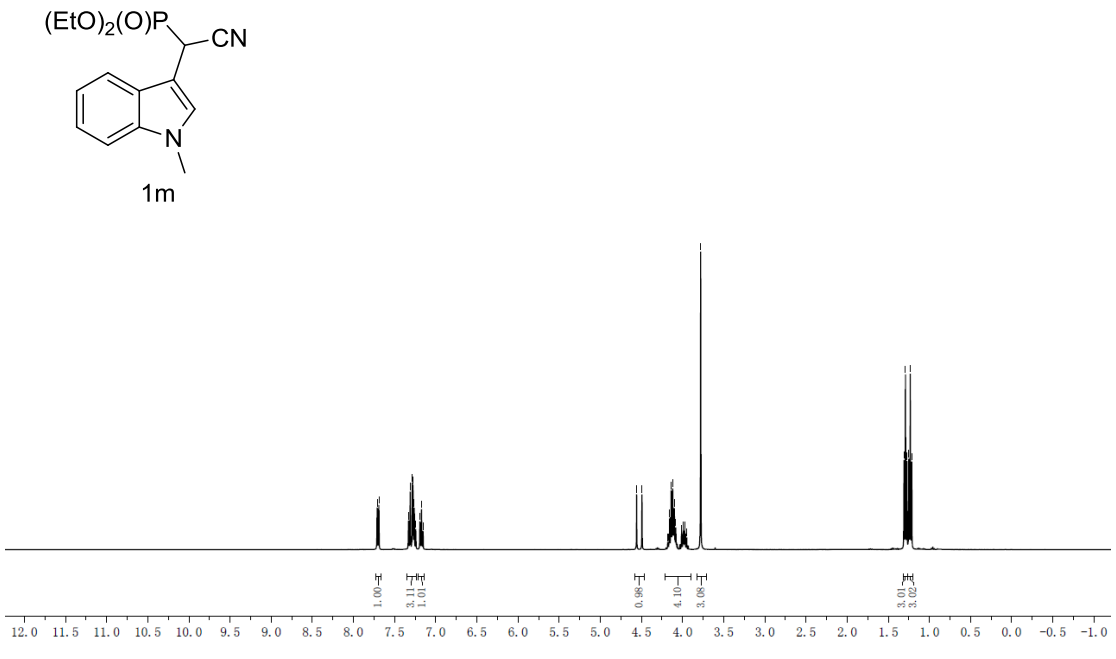


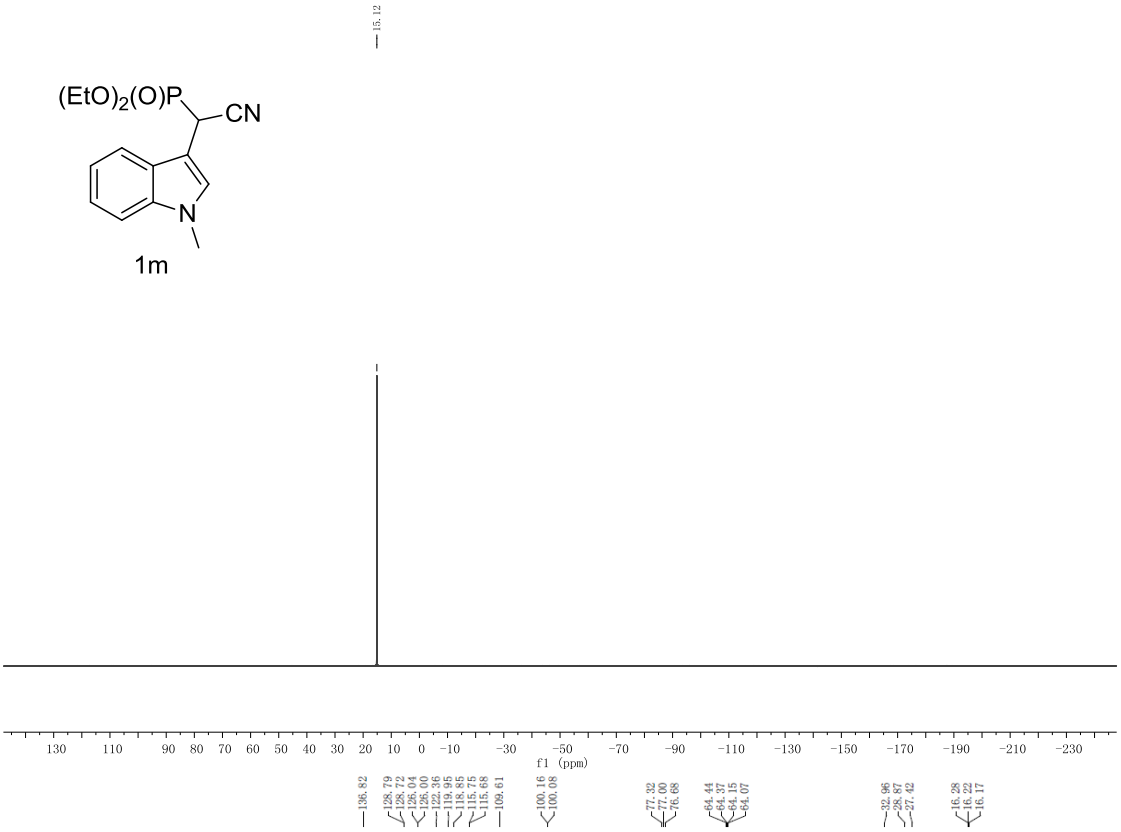


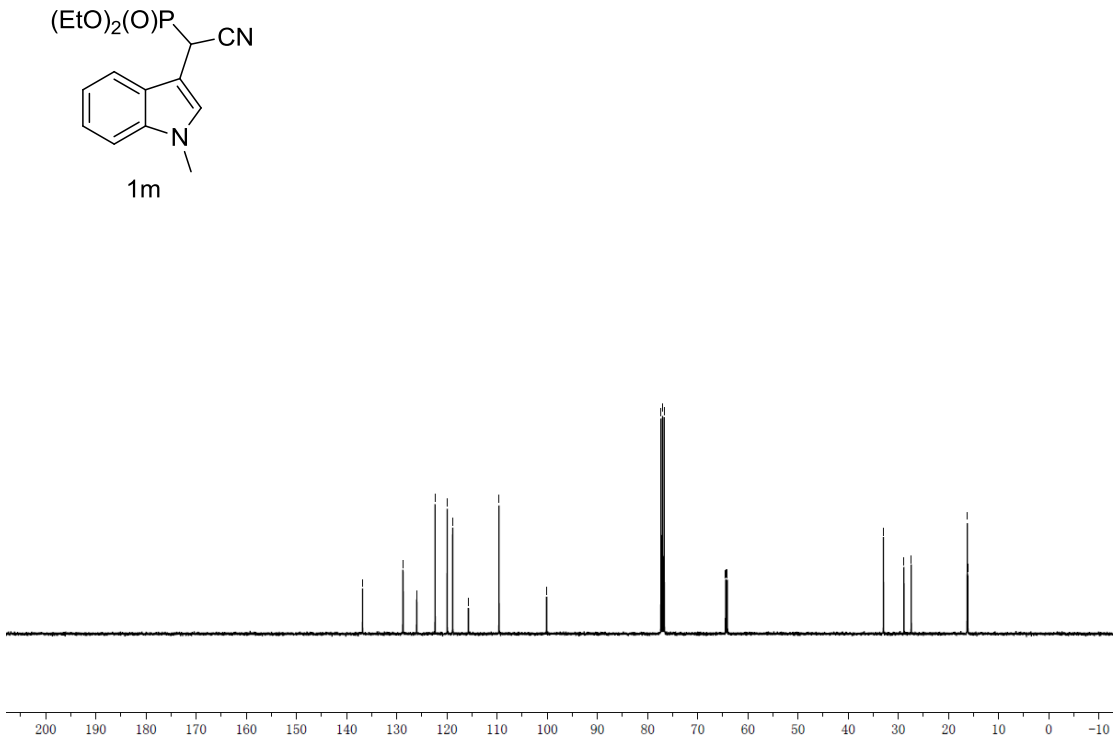
1l

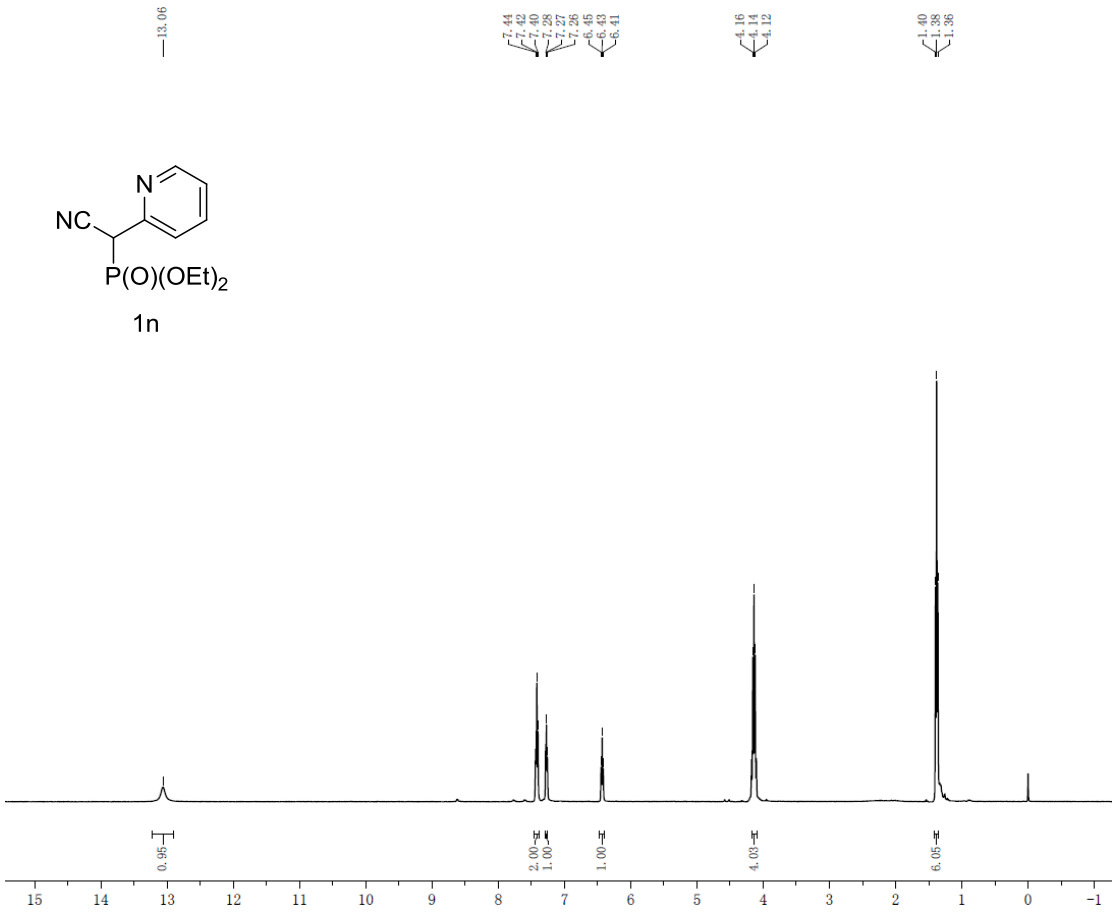


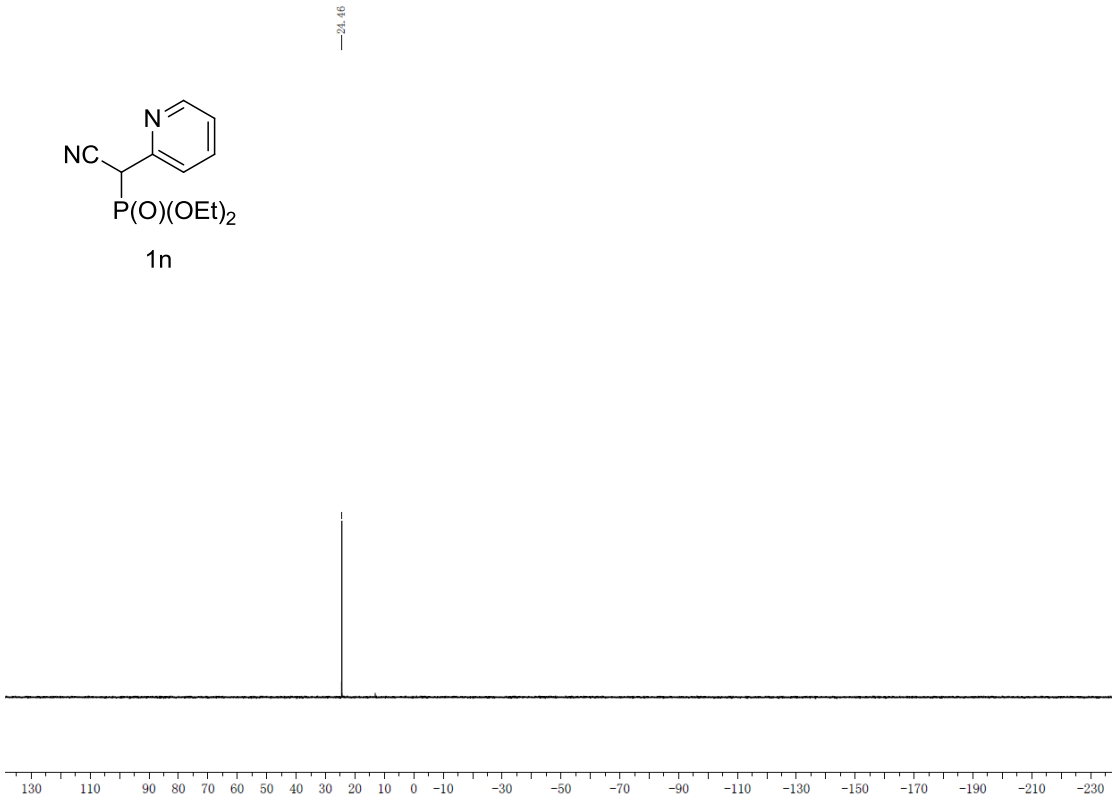

148.21
148.18
148.13
148.10
122.35
122.29
120.96
120.88
115.69
115.41
109.08
109.04
108.59
108.55
101.52
77.32
77.00
76.68
64.76
64.68
64.34
64.26
37.00
35.61
16.36
16.20
P(O)(OEt)2
NC
O
O
1l
7.71
7.69
7.33
7.31
7.28
7.26
7.24
7.19
7.17
7.16
4.56
4.49
4.17
4.16
4.16
4.15
4.14
4.13
4.12
4.11
4.10
4.09
4.08
4.01
4.00
3.99
3.97
3.97
3.95
2.43
2.41
1.29
1.27
1.25
1.23
1.21

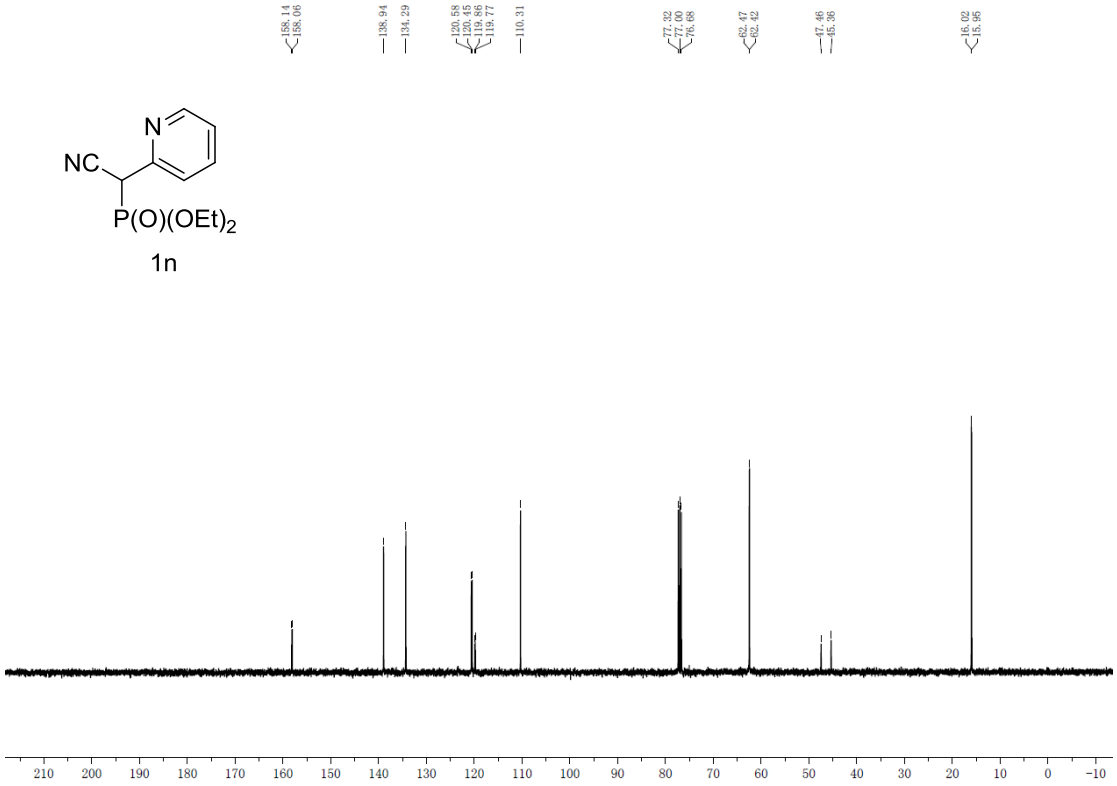

(EtO)2(O)P
CN
N
1m
1.00
3.11
1.01
0.98
4.10
3.08
3.01
3.02


(EtO)2(O)P
CN
N
1m
15.12
f1 (ppm)
136.82
128.79
128.72
126.04
126.00
122.36
119.45
118.85
115.75
115.68
109.61
100.16
100.08
77.32
77.00
76.68
64.44
64.37
64.15
64.07
32.96
28.87
27.42
16.28
16.22
16.17

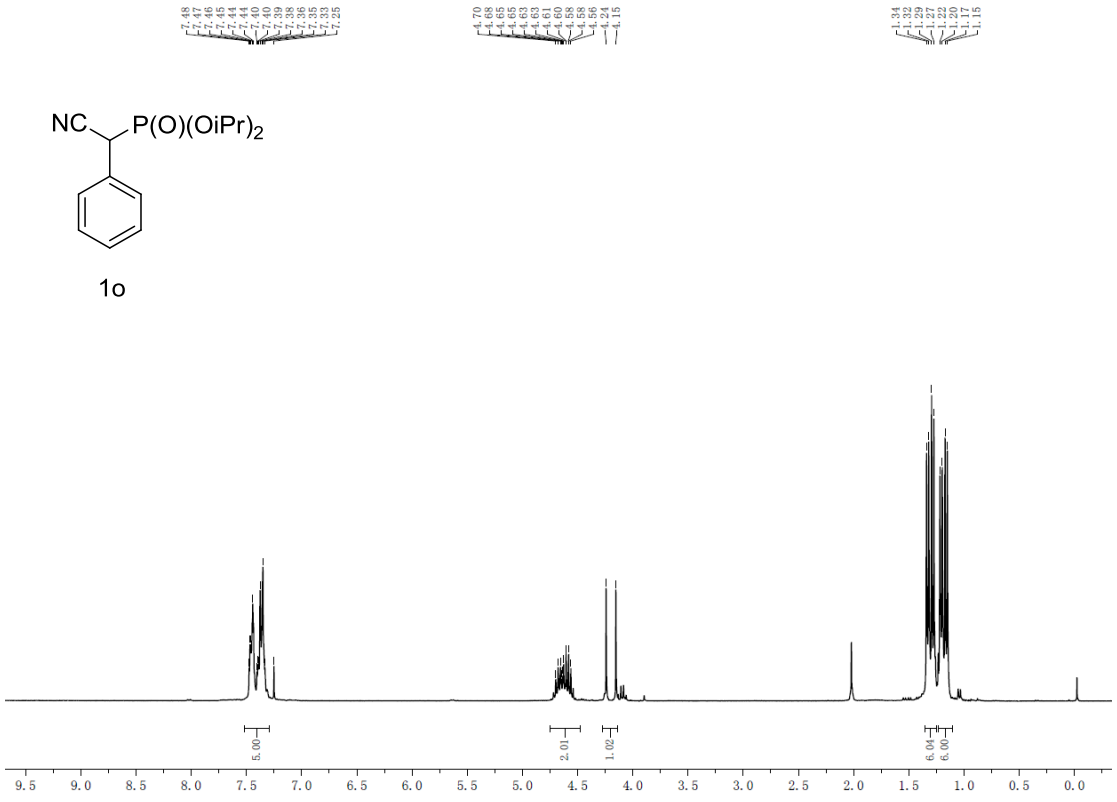

(EtO)2(O)P
CN
N
1m


13.06
7.44
7.42
7.40
7.28
7.27
7.26
6.45
6.43
6.41
4.16
4.14
4.12
1.40
1.38
1.36
N
NC
P(O)(OEt)2
1n
0.95
2.00
1.00
1.00
4.03
6.05
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1

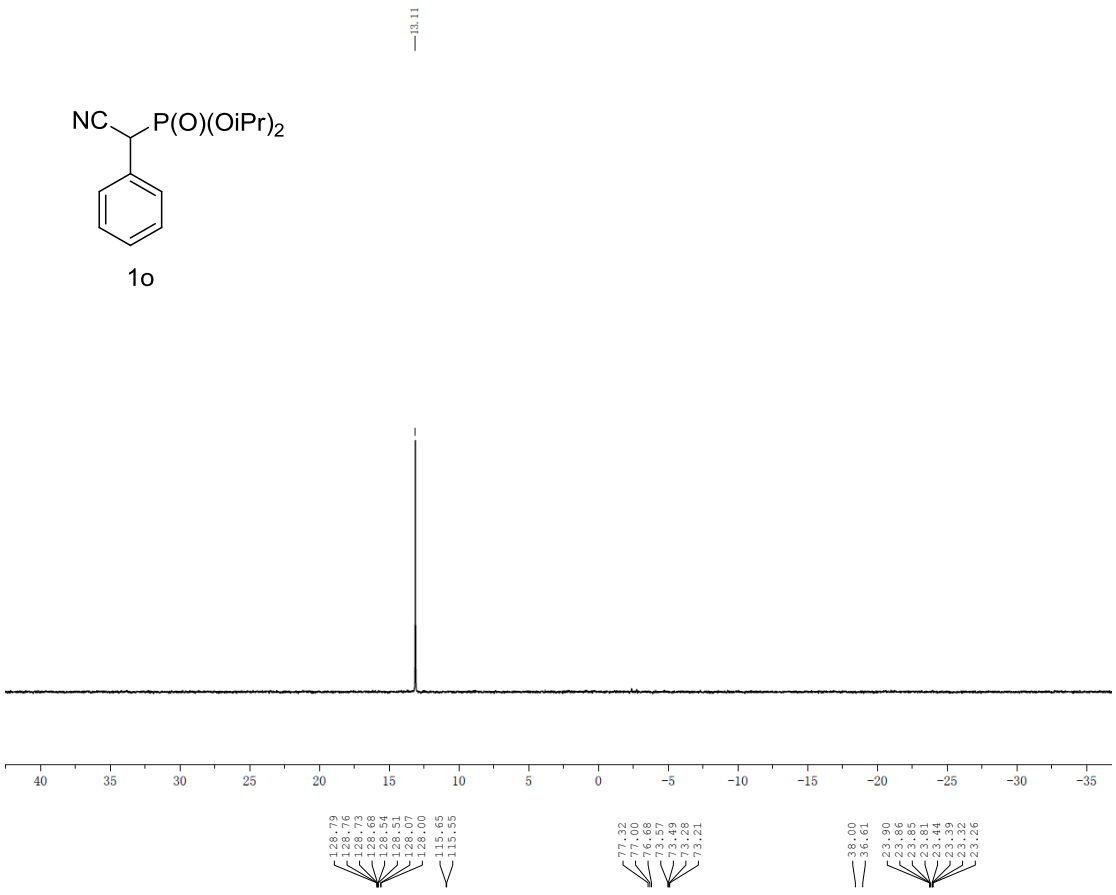

24.46
N
NC
P(O)(OEt)2
1n
130 110 90 80 70 60 50 40 30 20 10 0 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230


158.14
158.06
138.94
134.29
120.58
120.45
119.86
119.77
110.31
77.32
77.00
76.68
62.47
62.42
47.46
45.36
16.02
15.95
N
NC
P(O)(OEt)2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

1n


7.48
7.47
7.46
7.45
7.44
7.40
7.39
7.38
7.36
7.35
7.33
7.25
4.70
4.68
4.65
4.65
4.63
4.61
4.60
4.58
4.58
4.56
4.24
4.15
1.34
1.32
1.29
1.27
1.22
1.20
1.17
1.15
NC
P(O)(OiPr)2
5.00
2.01
1.02
6.04
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

1o


NC
P(O)(OiPr)2
1o
13.11
40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
128.79
128.76
128.73
128.68
128.54
128.51
128.07
128.00
115.65
115.55
77.32
77.00
76.68
73.57
73.49
73.28
73.21
38.00
36.61
23.90
23.86
23.85
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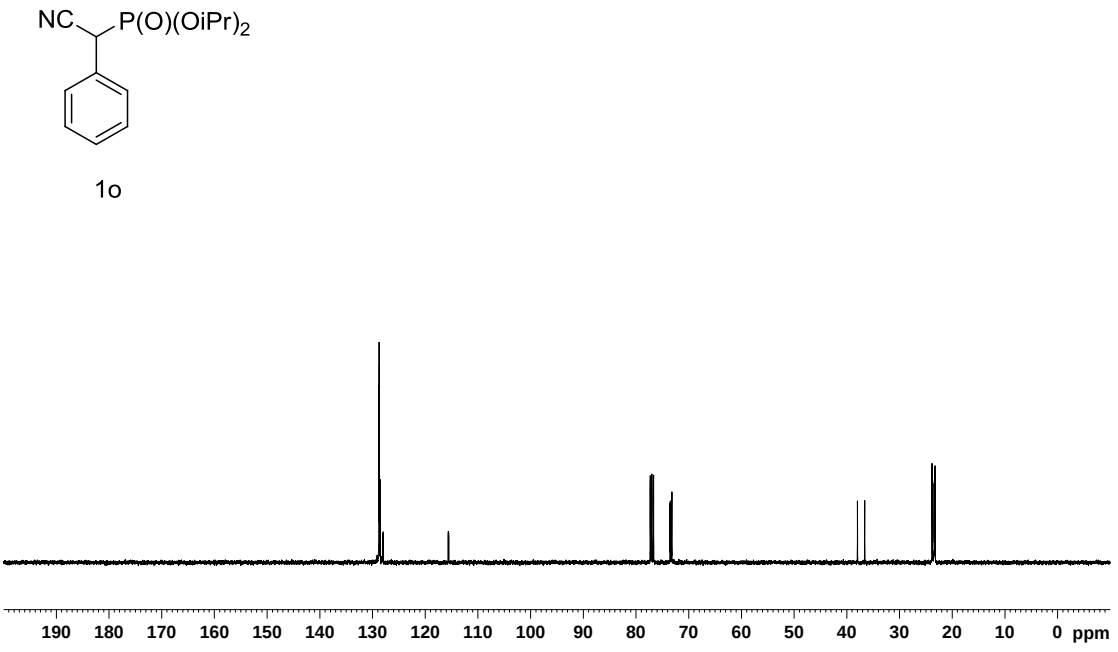
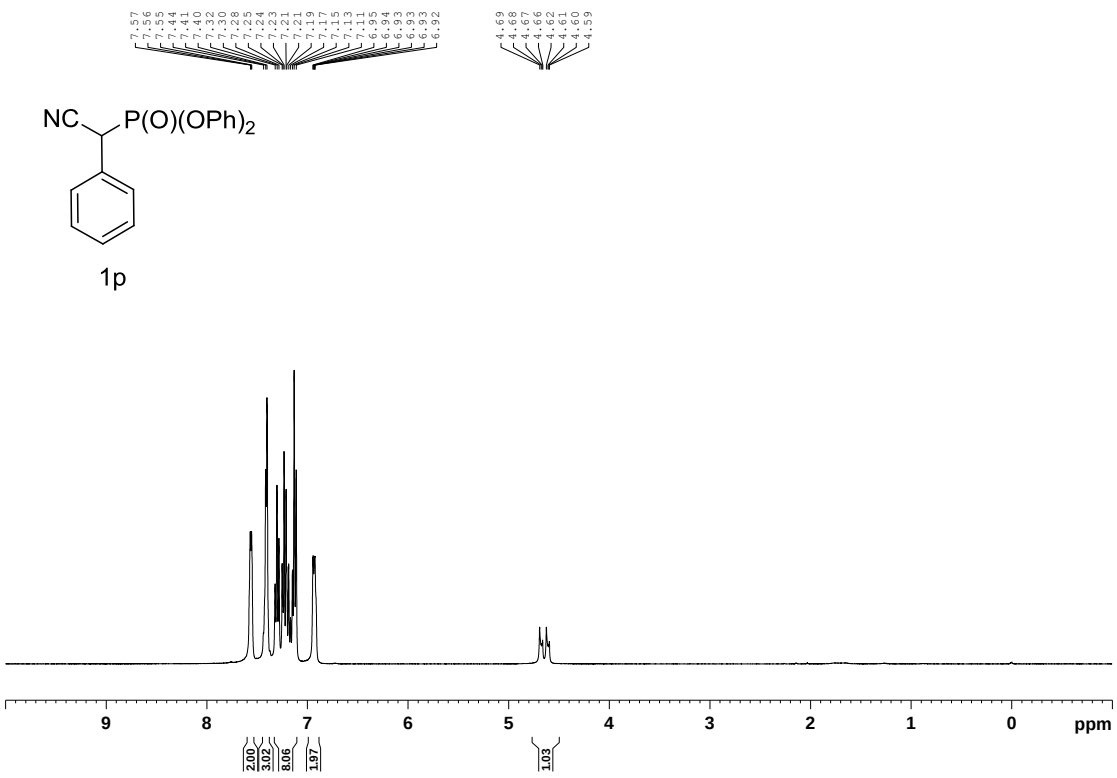
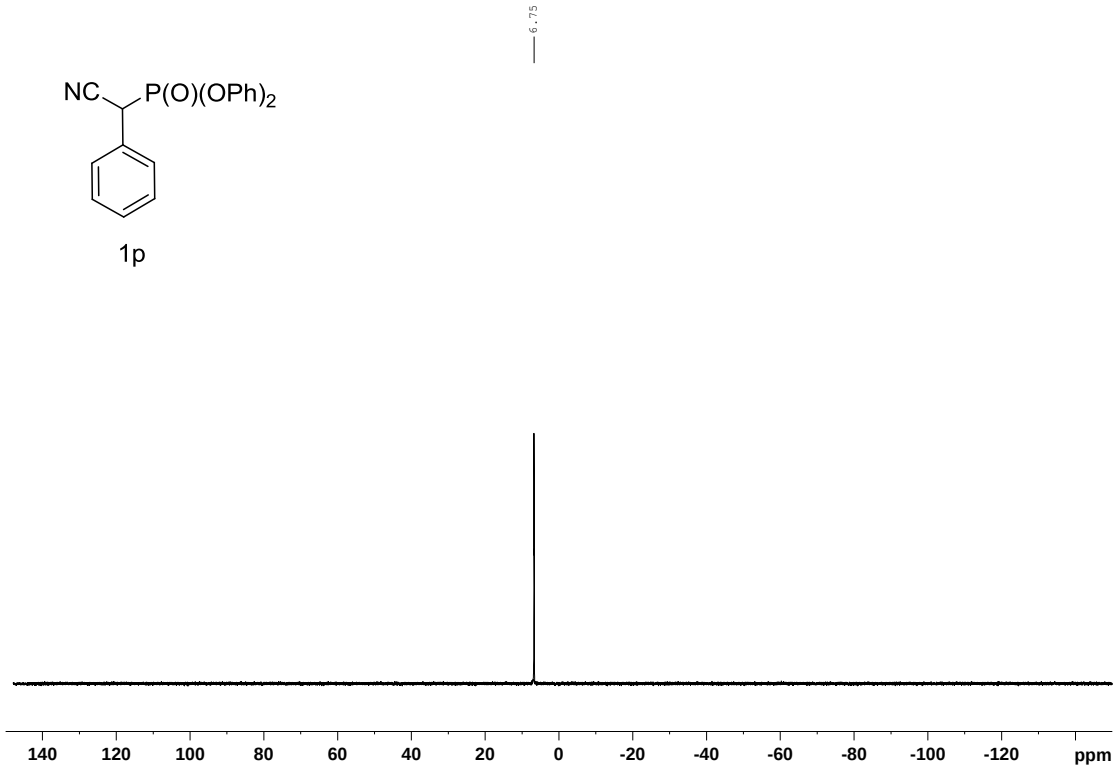
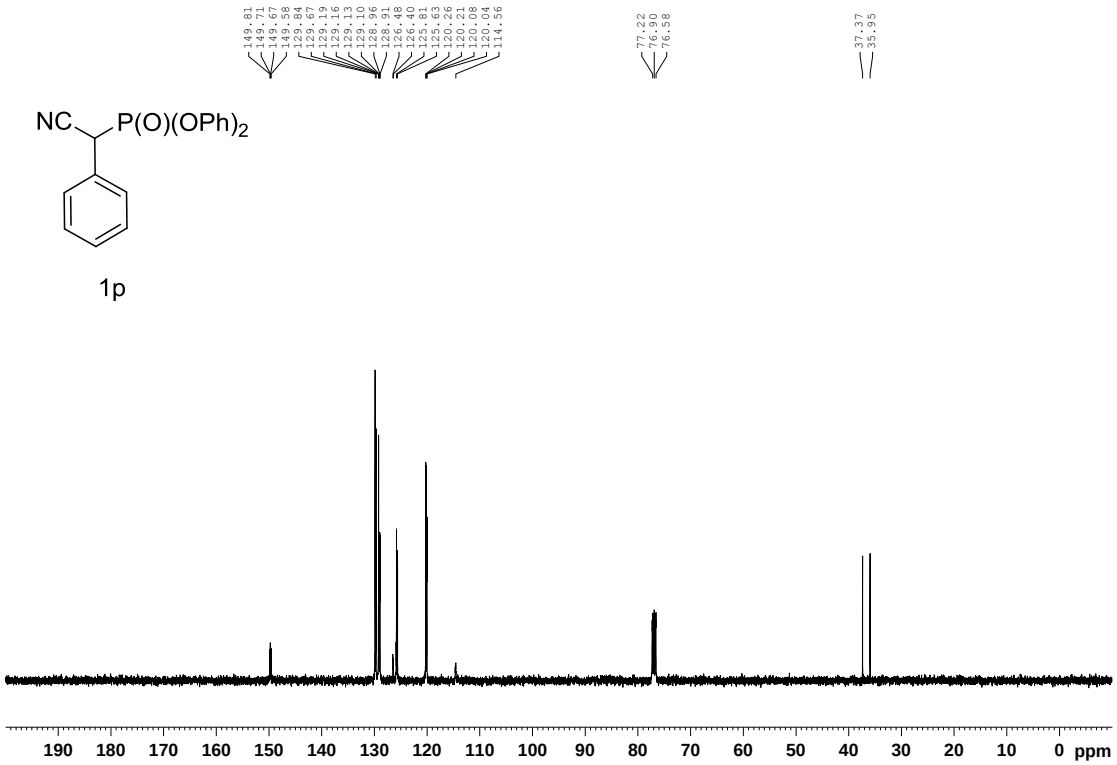
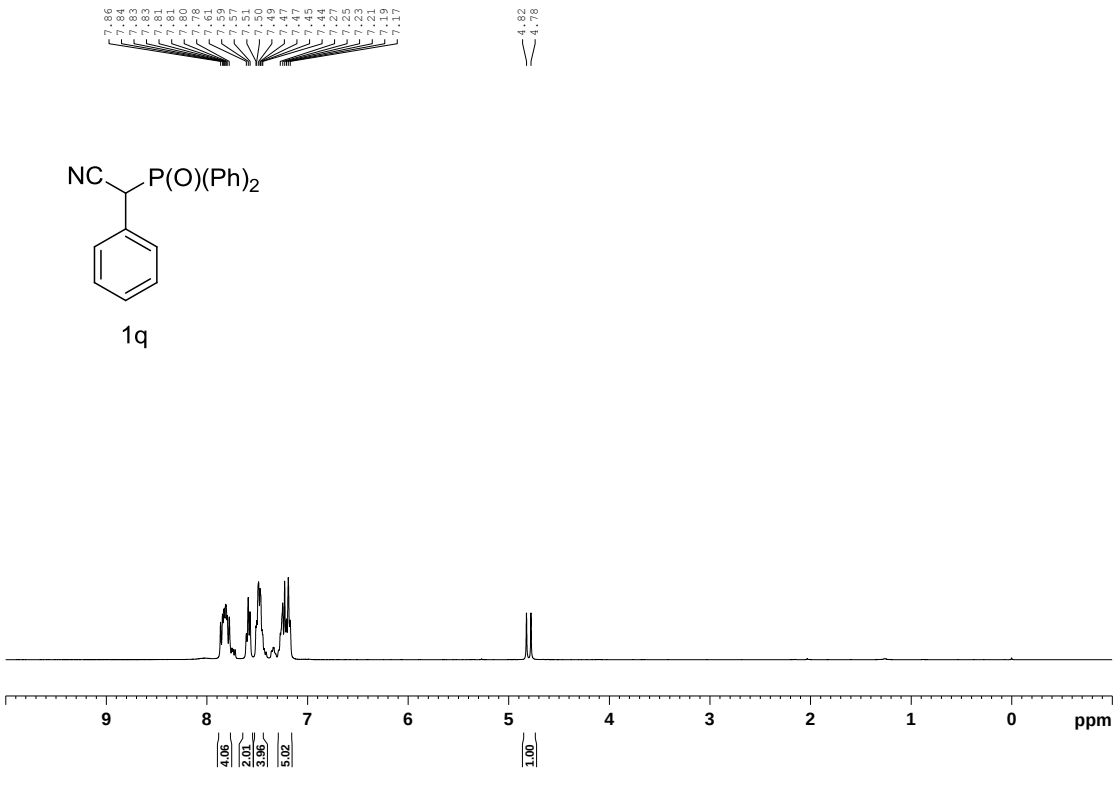
23.44
23.39
23.32
23.26

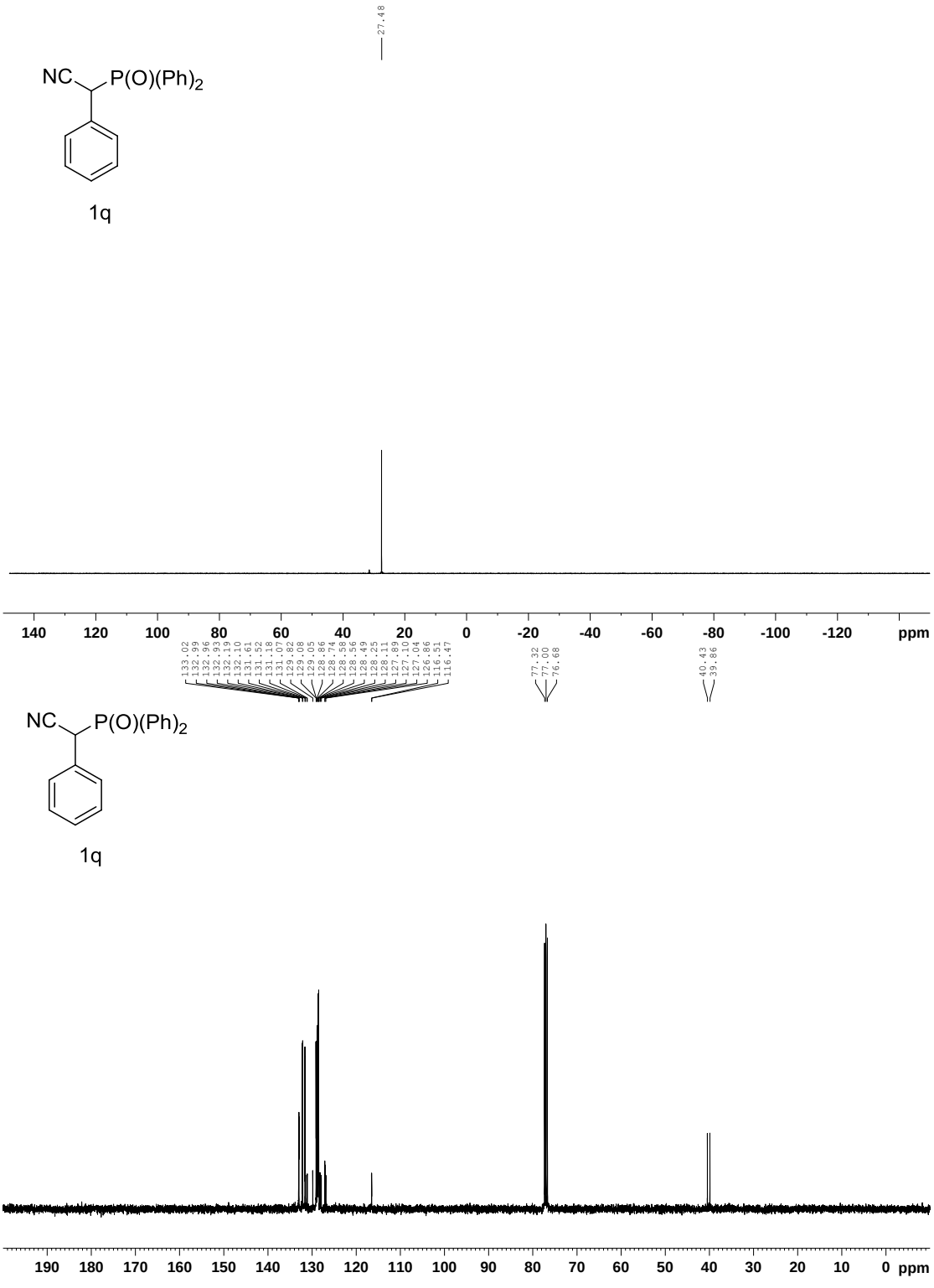

NC
P(O)(OiPr)2
1o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

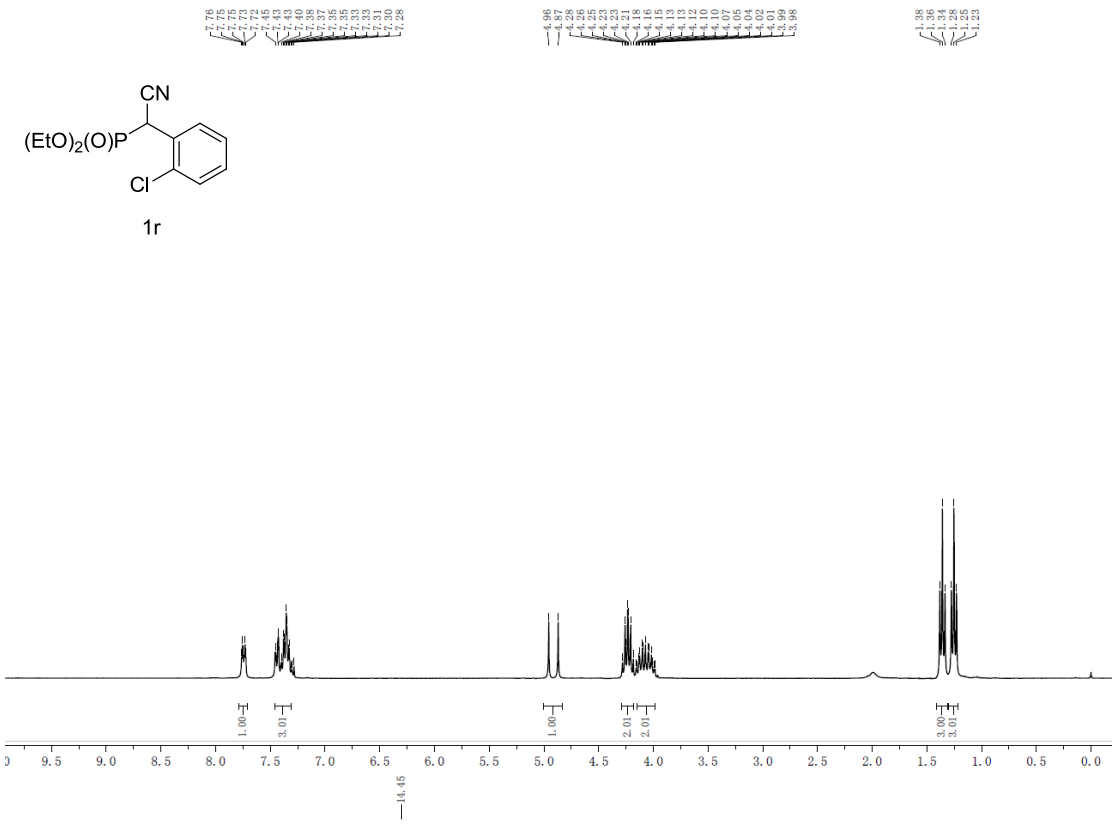

7.57
7.56
7.55
7.44
7.41
7.40
7.32
7.30
7.28
7.25
7.24
7.23
7.21
7.21
7.19
7.17
7.15
7.13
7.11
6.95
6.94
6.93
6.93
6.93
6.92
4.69
4.68
4.67
4.66
4.62
4.61
4.60
4.59
NC
P(O)(OPh)2
1p
9
8
7
6
5
4
3
2
1
0
ppm
2.00
3.02
8.06
1.97
1.03

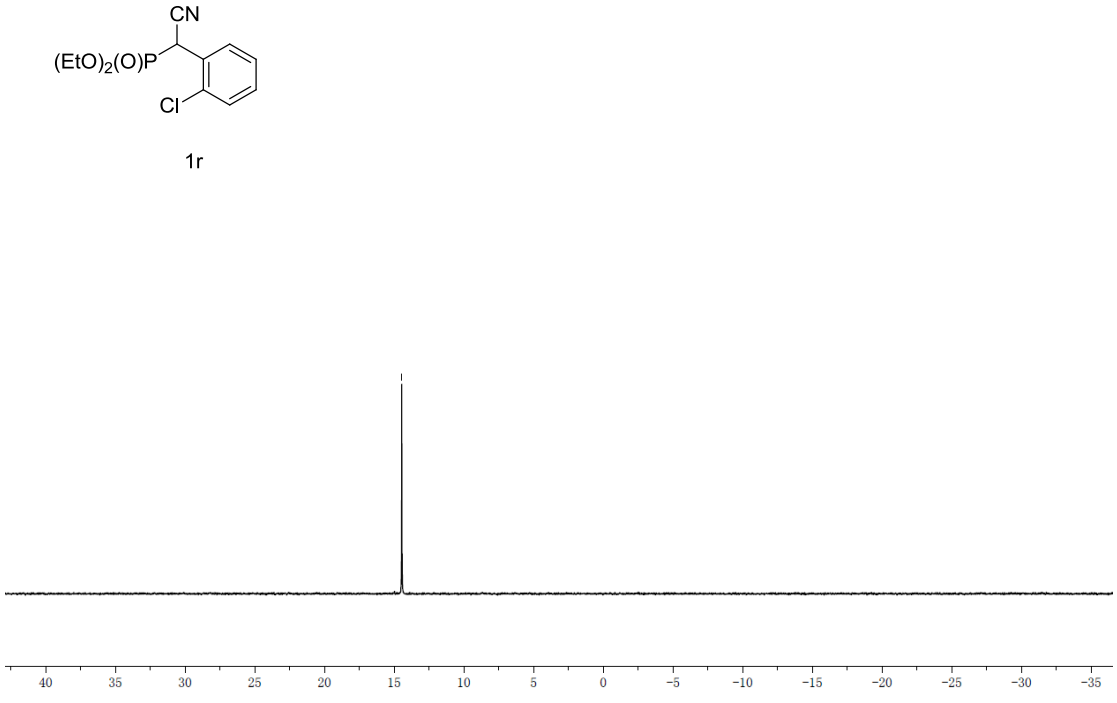

6.75
NC
P(O)(OPh)2
1p
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm

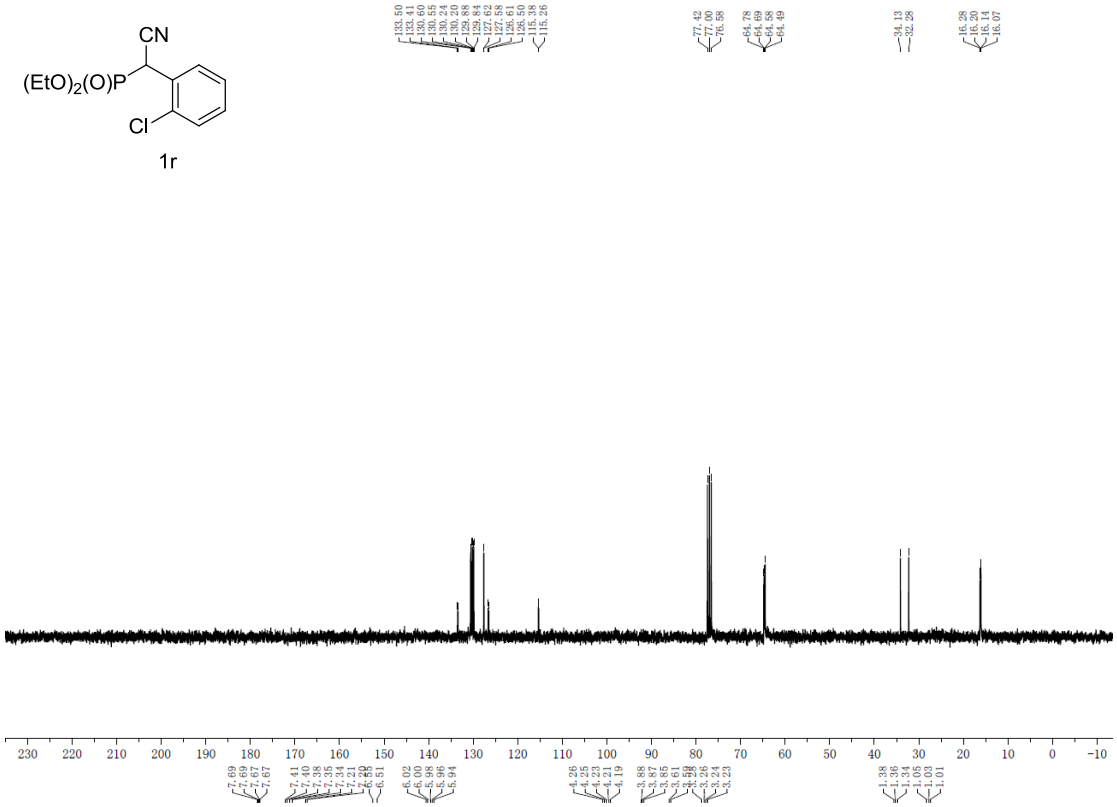

149.81
149.71
149.67
149.58
129.84
129.67
129.19
129.16
129.13
129.10
128.96
128.91
126.48
126.40
125.81
125.63
120.26
120.21
120.08
120.04
114.56
77.22
76.90
76.58
37.37
35.95
NC
P(O)(OPh)2
1p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

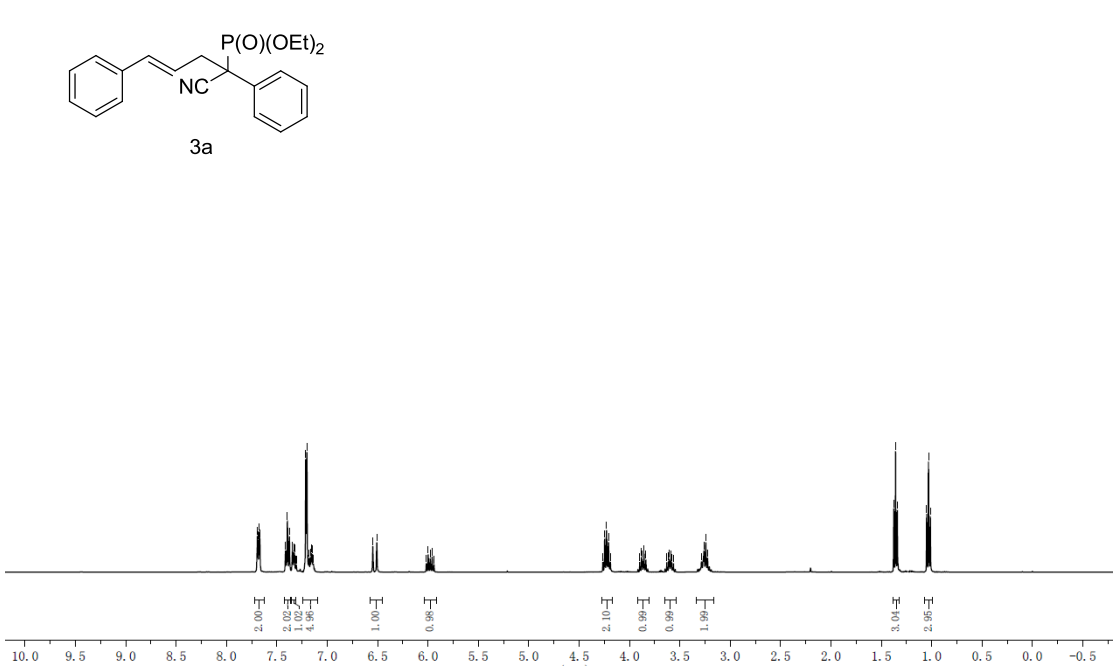

7.86
7.84
7.83
7.83
7.81
7.81
7.80
7.78
7.61
7.59
7.57
7.51
7.50
7.49
7.47
7.47
7.45
7.44
7.27
7.25
7.23
7.21
7.19
7.17
4.82
4.78
NC
P(O)(Ph)2
1q
9 8 7 6 5 4 3 2 1 0 ppm
4.06
2.01
3.96
5.02
1.00

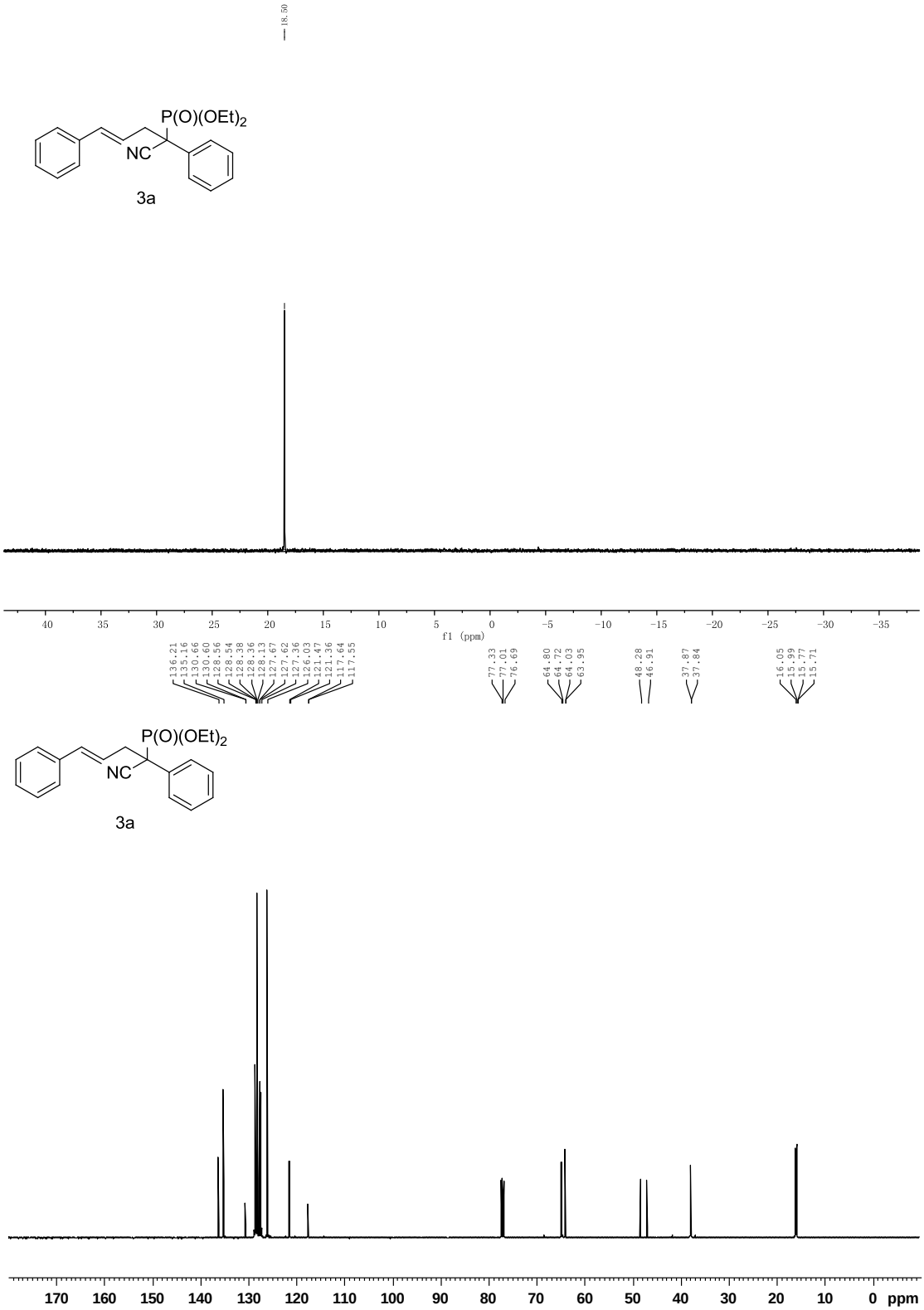

27.48
NC
P(O)(Ph)2
1q
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 ppm
133.02
132.99
132.96
132.93
132.19
132.10
131.61
131.52
131.18
131.07
130.82
129.08
129.05
128.86
128.74
128.58
128.56
128.49
128.25
128.11
127.89
127.10
127.04
126.86
116.51
116.47
77.32
77.00
76.68
40.43
39.86
NC
P(O)(Ph)2
1q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

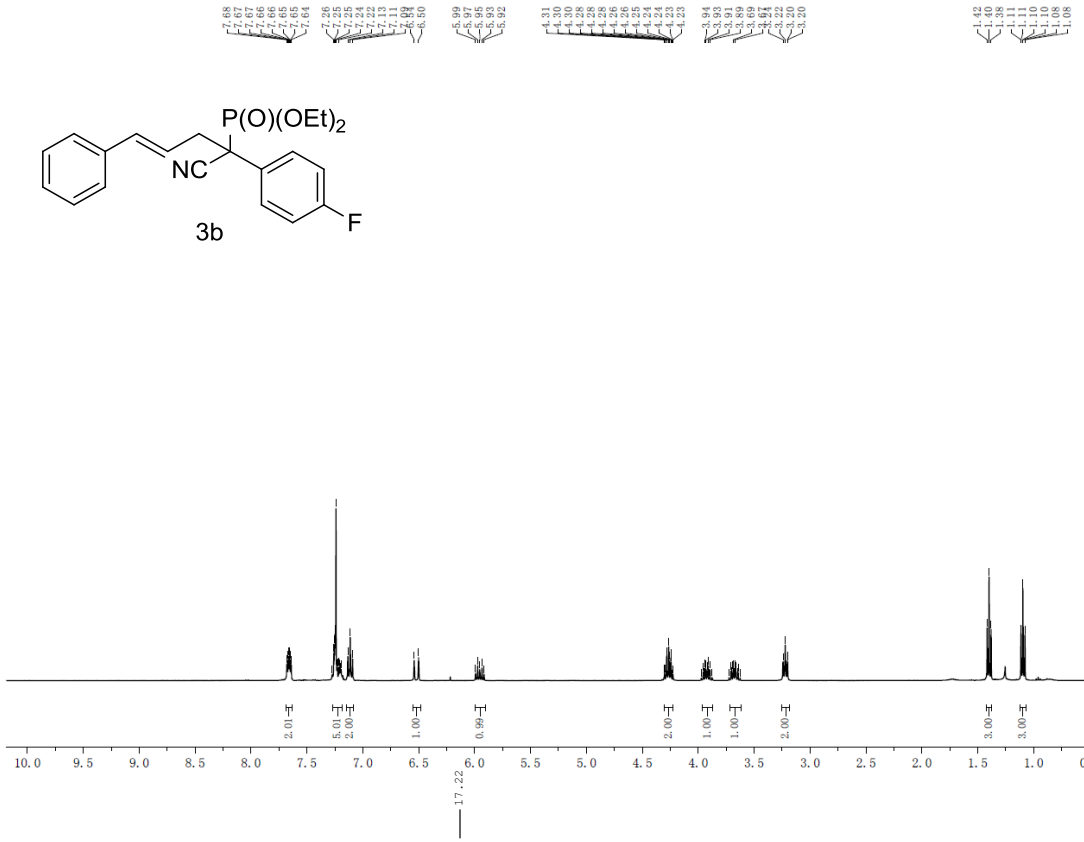

CN
(EtO)2(O)P
Cl
1r

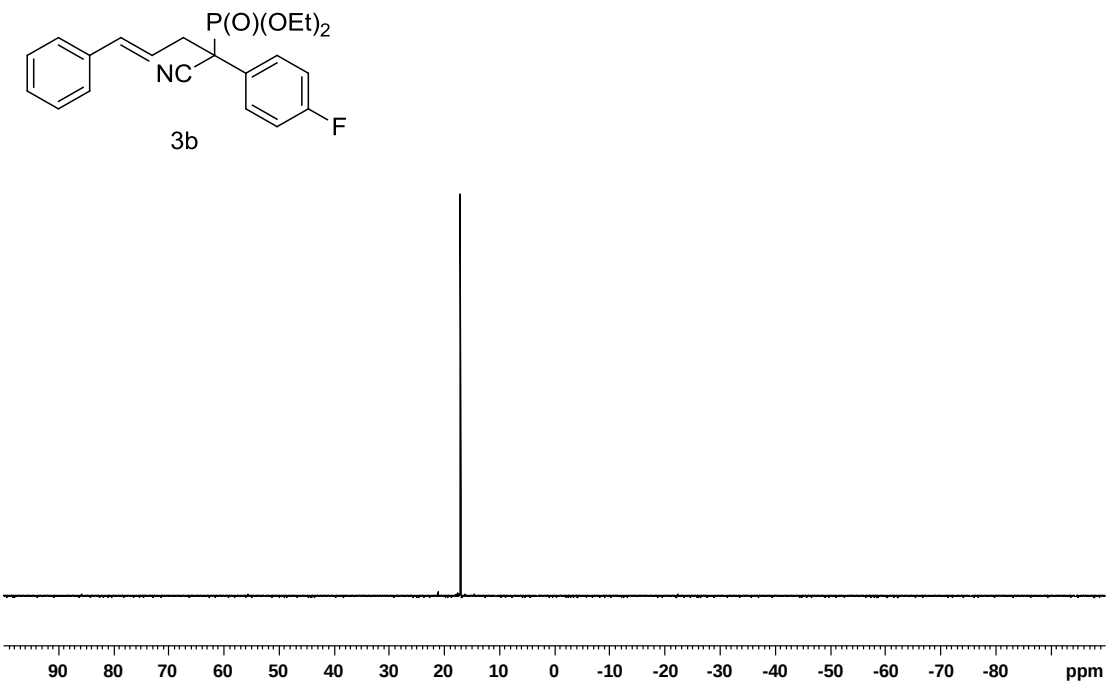

CN
(EtO)2(O)P
Cl
1r

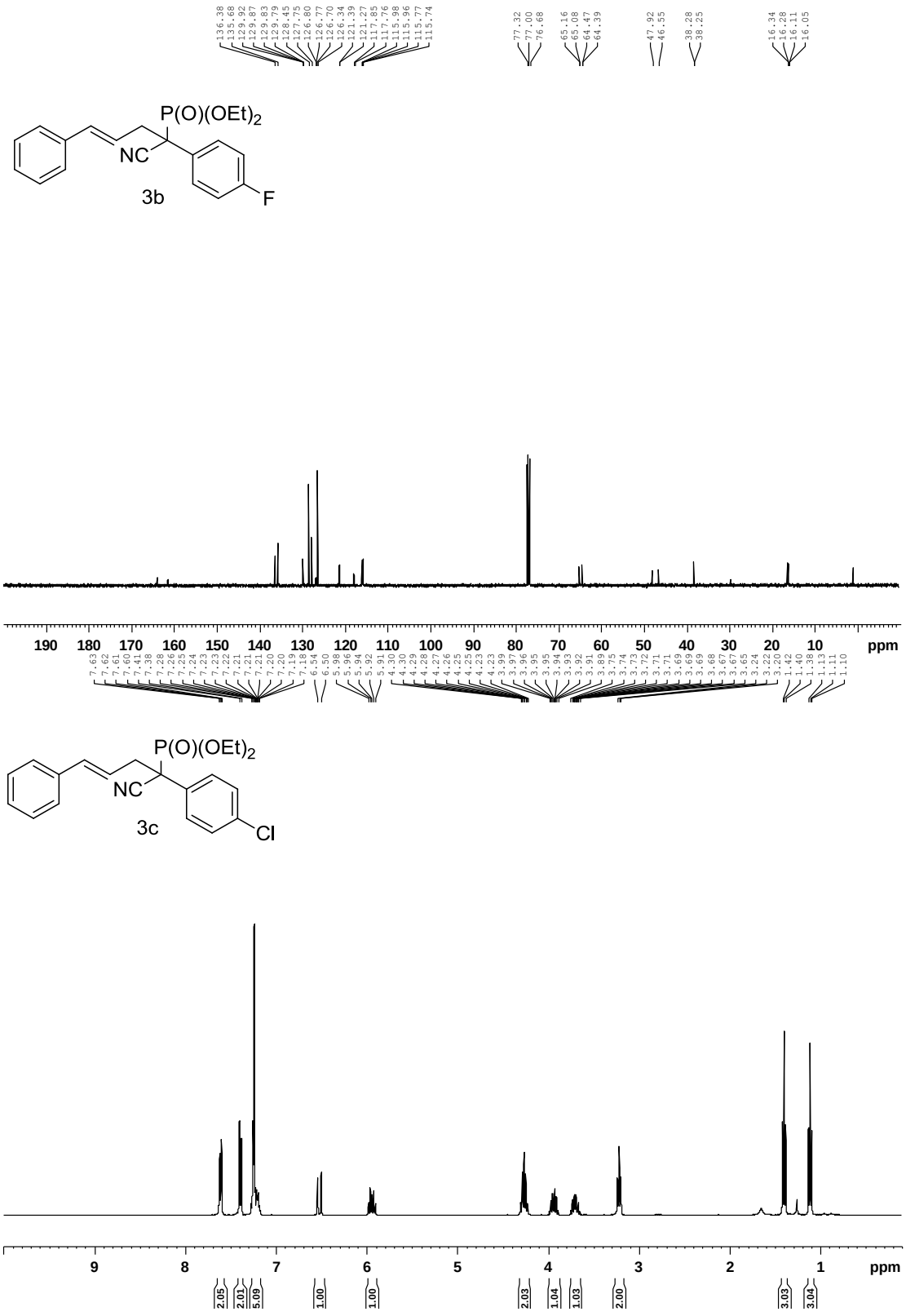

CN
(EtO)2(O)P
Cl
1r

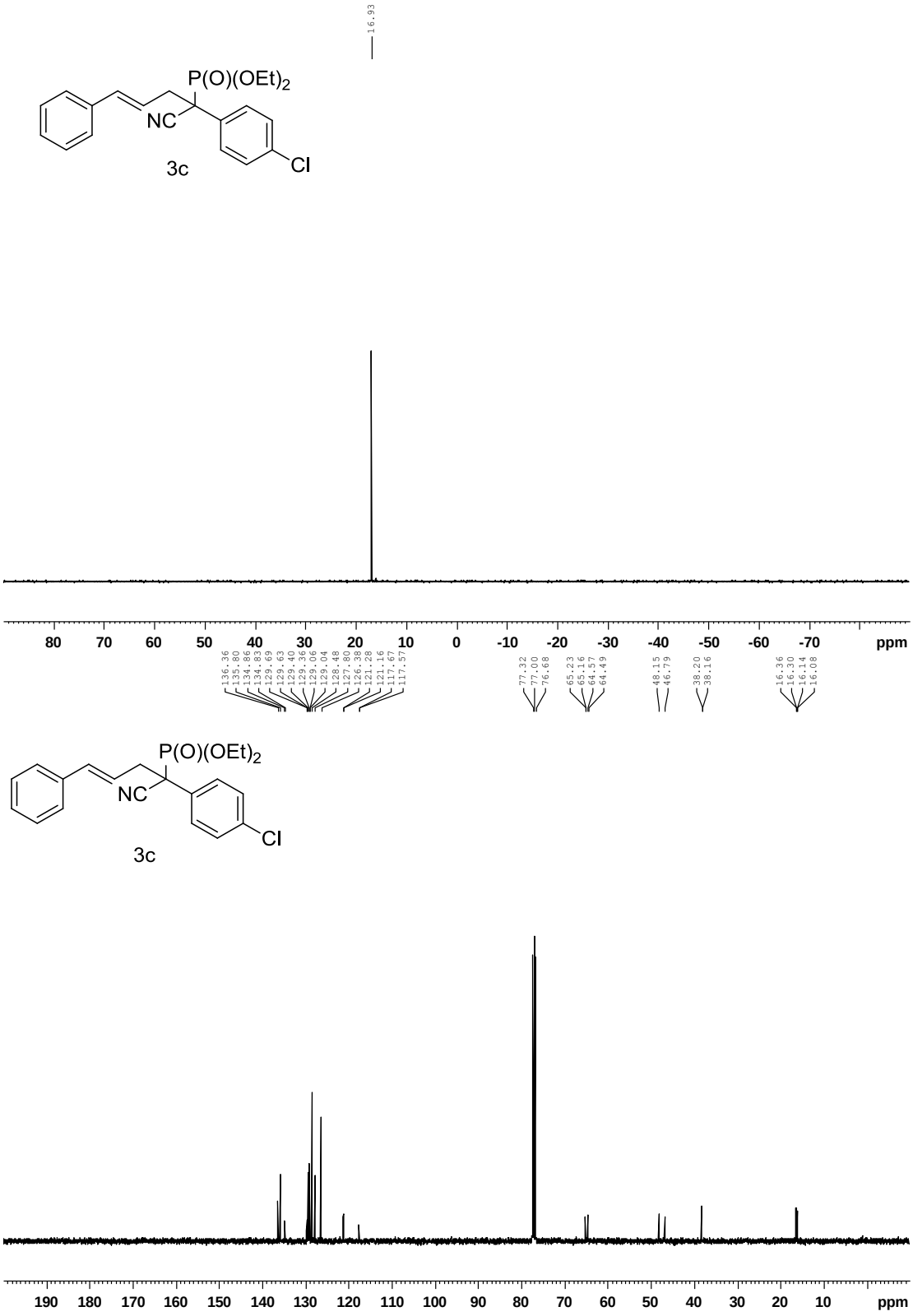

P(O)(OEt)2
NC
3a

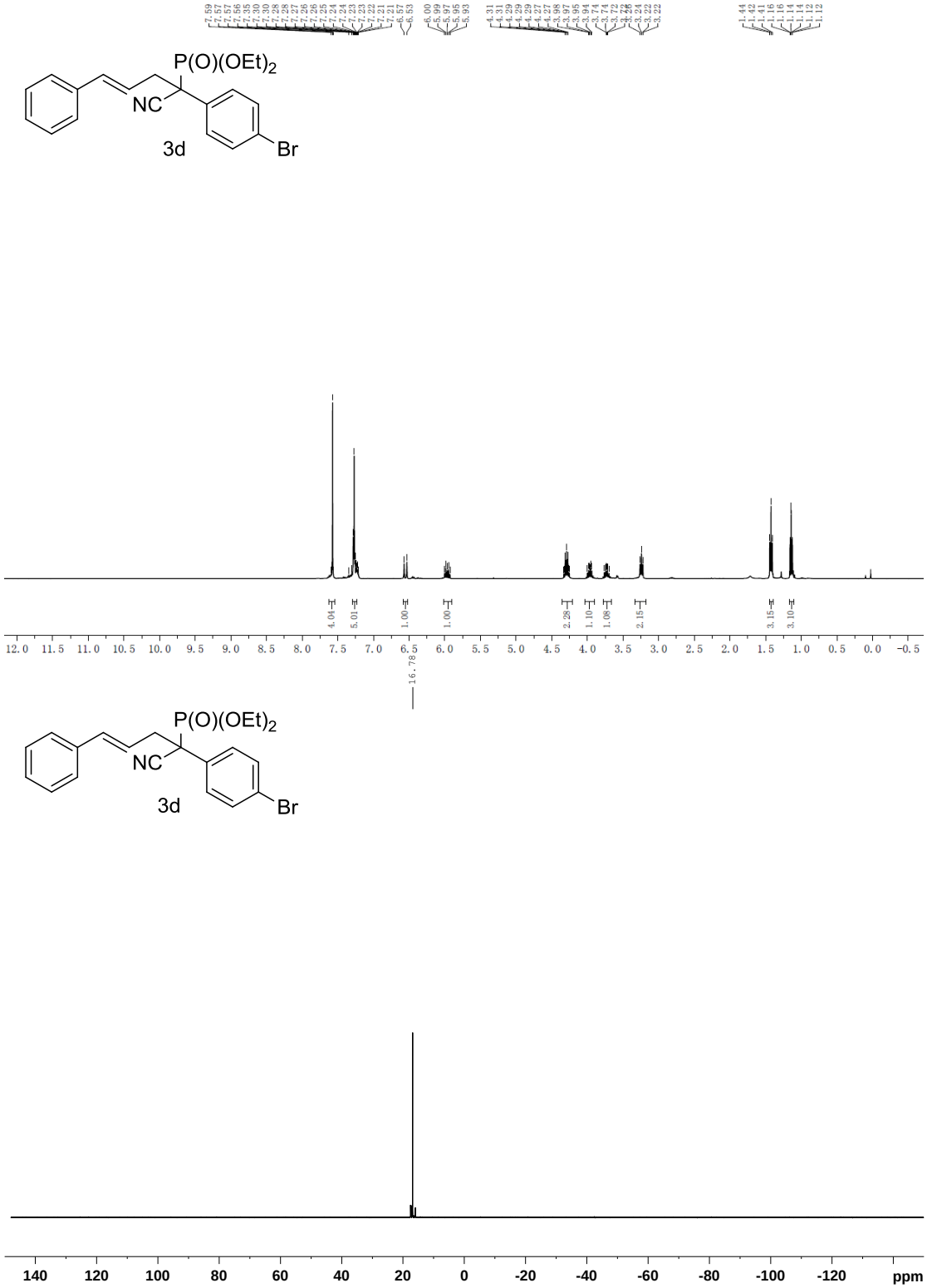

18.50
P(O)(OEt)2
NC
3a
40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35
f1 (ppm)
136.21
135.16
130.66
130.60
128.56
128.54
128.38
128.36
128.13
127.67
127.62
127.36
126.03
121.47
121.36
117.64
117.55
77.33
77.01
76.69
64.80
64.72
64.03
63.95
48.28
46.91
37.87
37.84
16.05
15.99
15.77
15.71
P(O)(OEt)2
NC
3a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


P(O)(OEt)2
NC
F
3b
2.01
5.01
2.00
1.00
0.99
2.00
1.00
1.00
2.00
3.00
3.00
17.22


P(O)(OEt)2
NC
F
3b
ppm

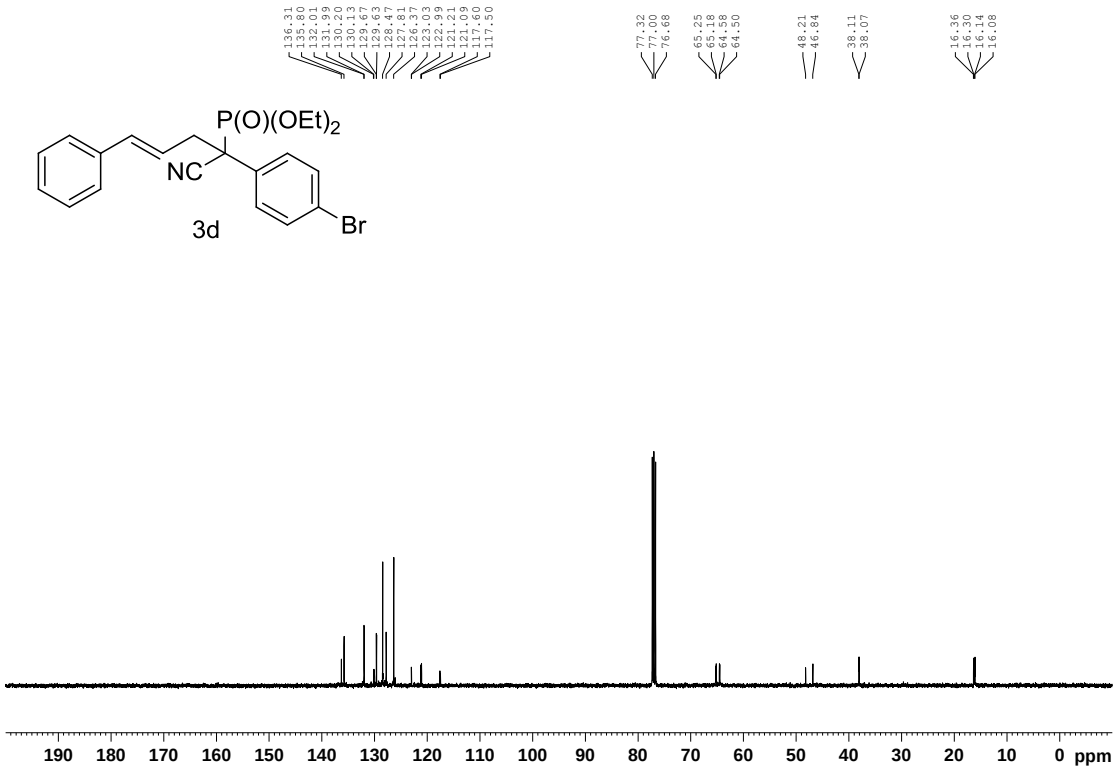

136.38
135.68
129.92
129.87
129.83
129.79
128.45
127.75
126.80
126.77
126.70
126.34
121.39
121.27
117.85
117.76
115.98
115.96
115.77
115.74
77.32
77.00
76.68
65.16
65.08
64.47
64.39
47.92
46.55
38.28
38.25
16.34
16.28
16.11
16.05
P(O)(OEt)2
NC
3b
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
7.63
7.62
7.61
7.60
7.41
7.38
7.28
7.26
7.25
7.24
7.23
7.22
7.21
7.21
7.21
7.20
7.20
7.19
7.18
6.54
6.50
5.98
5.96
5.94
5.92
5.91
4.30
4.29
4.28
4.27
4.26
4.25
4.25
4.23
4.23
3.99
3.97
3.96
3.95
3.95
3.94
3.93
3.92
3.91
3.89
3.75
3.74
3.73
3.72
3.71
3.71
3.69
3.69
3.69
3.68
3.67
3.67
3.65
3.24
3.22
3.20
1.42
1.40
1.38
1.13
1.11
1.10
P(O)(OEt)2
NC
3c
Cl
9 8 7 6 5 4 3 2 1 ppm
2.05
2.01
5.09
1.00
1.00
2.03
1.04
1.03
2.00
3.03
3.04

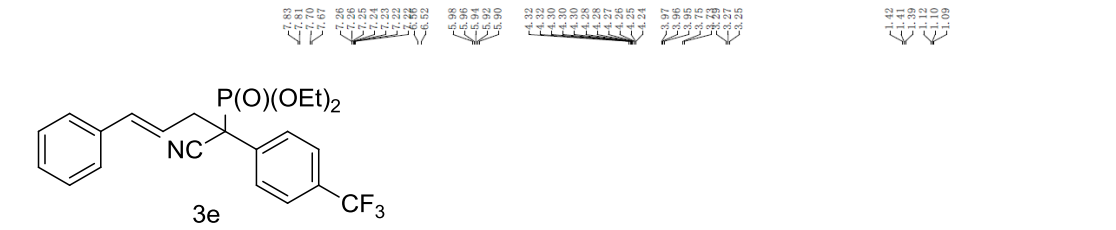

16.93
P(O)(OEt)2
NC
Cl
3c
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm
136.36
135.80
134.86
134.83
129.69
129.63
129.40
129.36
129.06
129.04
128.48
127.80
126.38
121.28
121.16
117.67
117.57
77.32
77.00
76.68
65.23
65.16
64.57
64.49
48.15
46.79
38.20
38.16
16.36
16.30
16.14
16.08
P(O)(OEt)2
NC
Cl
3c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


P(O)(OEt)2
NC
3d
Br
4.04
5.01
1.00
1.00
2.28
1.10
1.08
2.15
3.15
3.10
16.78
P(O)(OEt)2
NC
3d
Br
ppm

P(O)(OEt)2
NC
Br

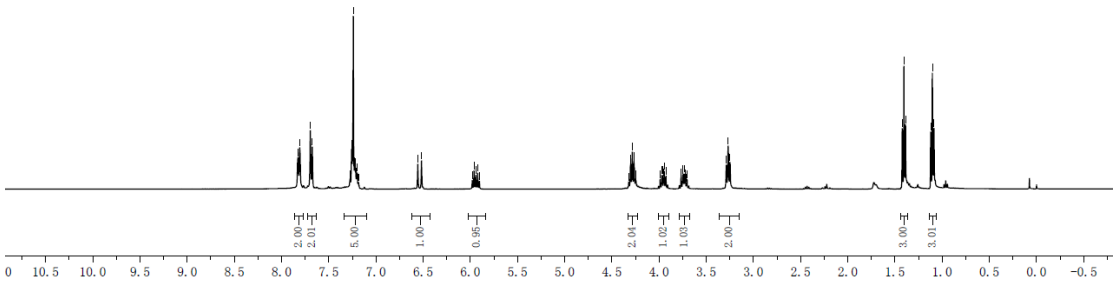
3d

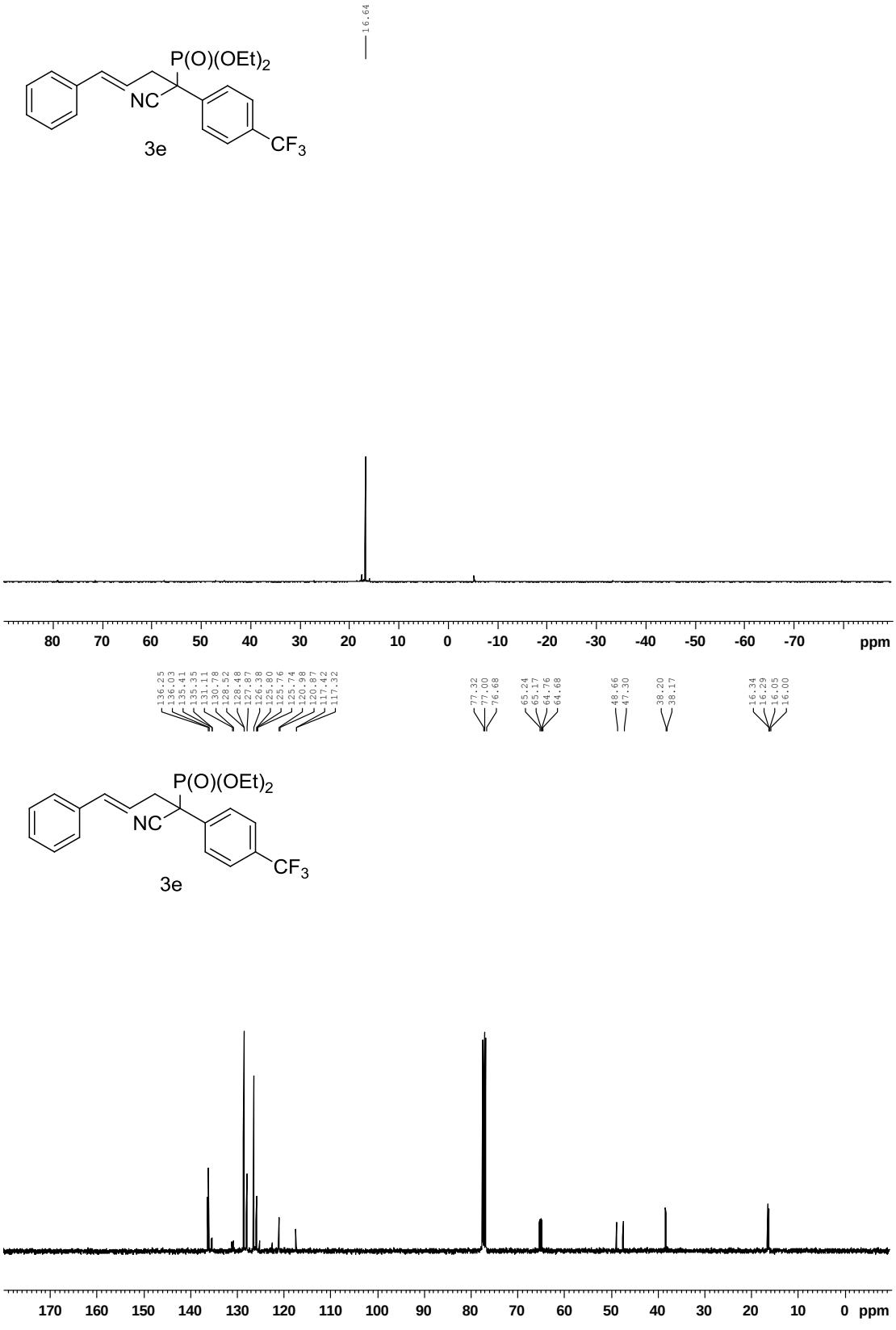

136.31
135.80
132.01
131.99
130.20
130.13
129.67
128.63
128.47
127.81
126.37
123.03
122.99
121.21
121.09
117.60
117.50
77.32
77.00
76.68
65.25
65.18
64.58
64.50
48.21
46.84
38.11
38.07
16.36
16.30
16.14
16.08
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

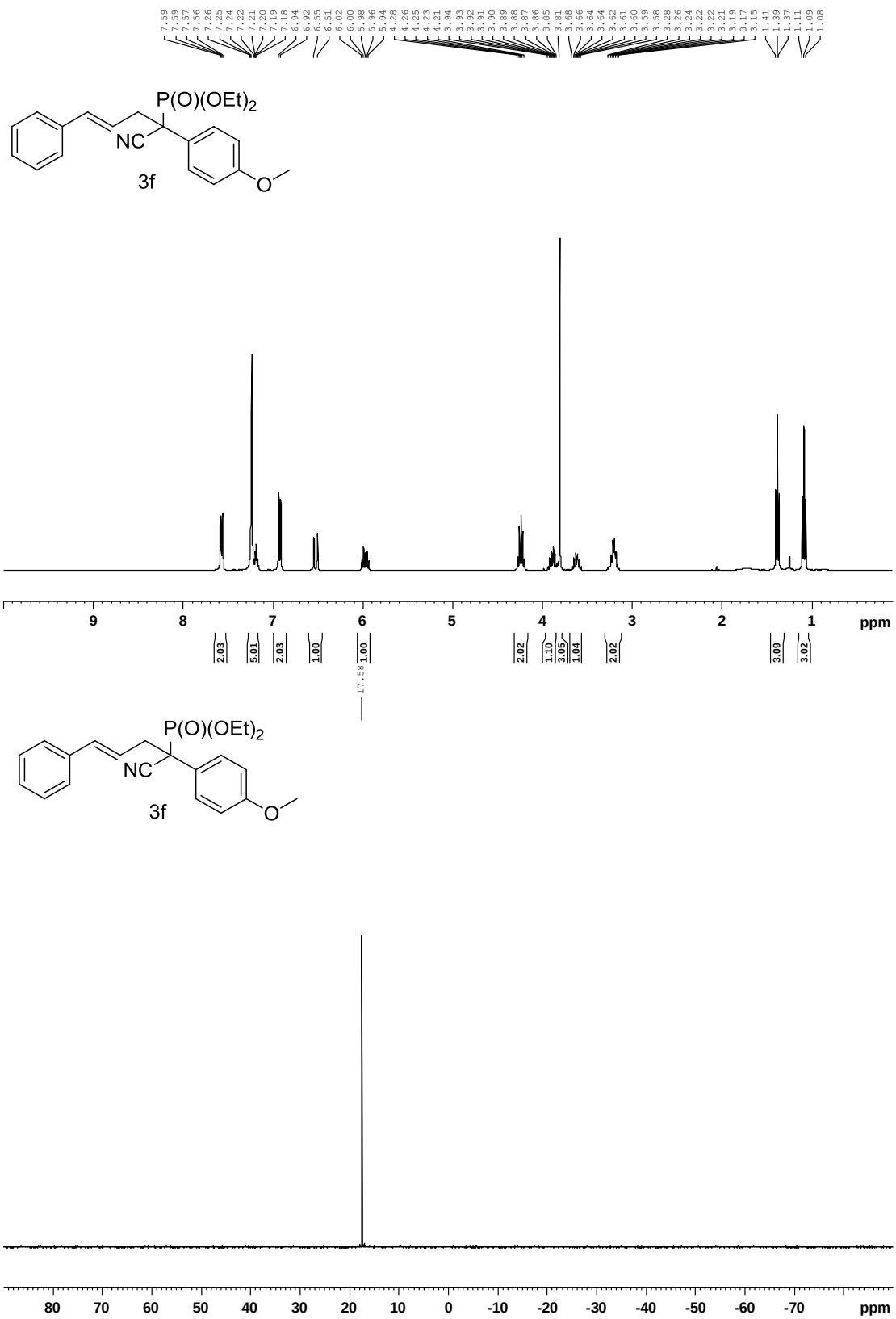

7.83
7.81
7.70
7.68
7.67
7.26
7.25
7.24
7.23
7.22
6.52
5.98
5.96
5.94
5.92
5.90
4.32
4.30
4.28
4.27
4.26
4.25
4.24
3.97
3.96
3.95
3.75
3.29
3.28
3.27
3.25
1.42
1.41
1.39
1.12
1.10
1.09

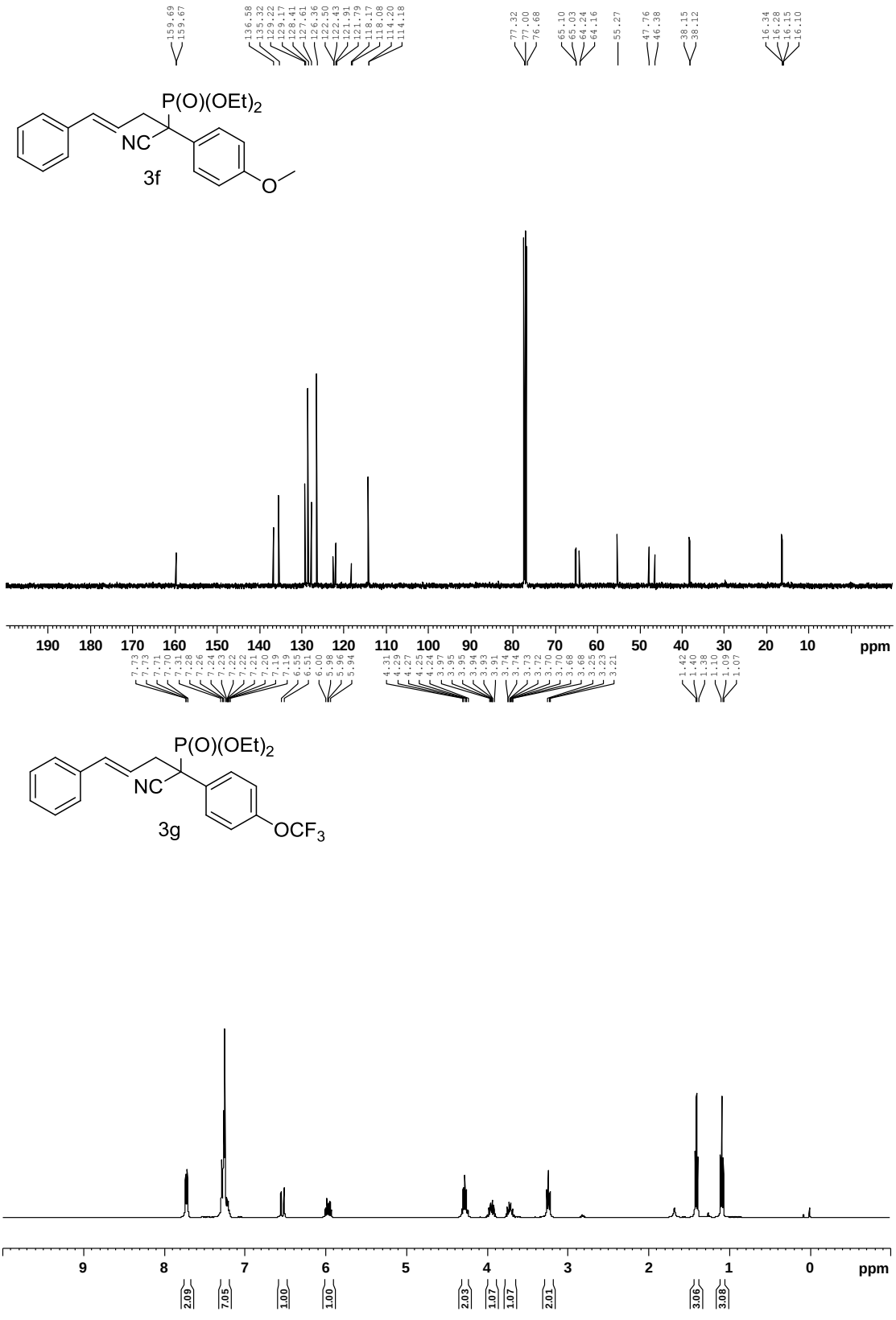
P(O)(OEt)2
NC
CF3

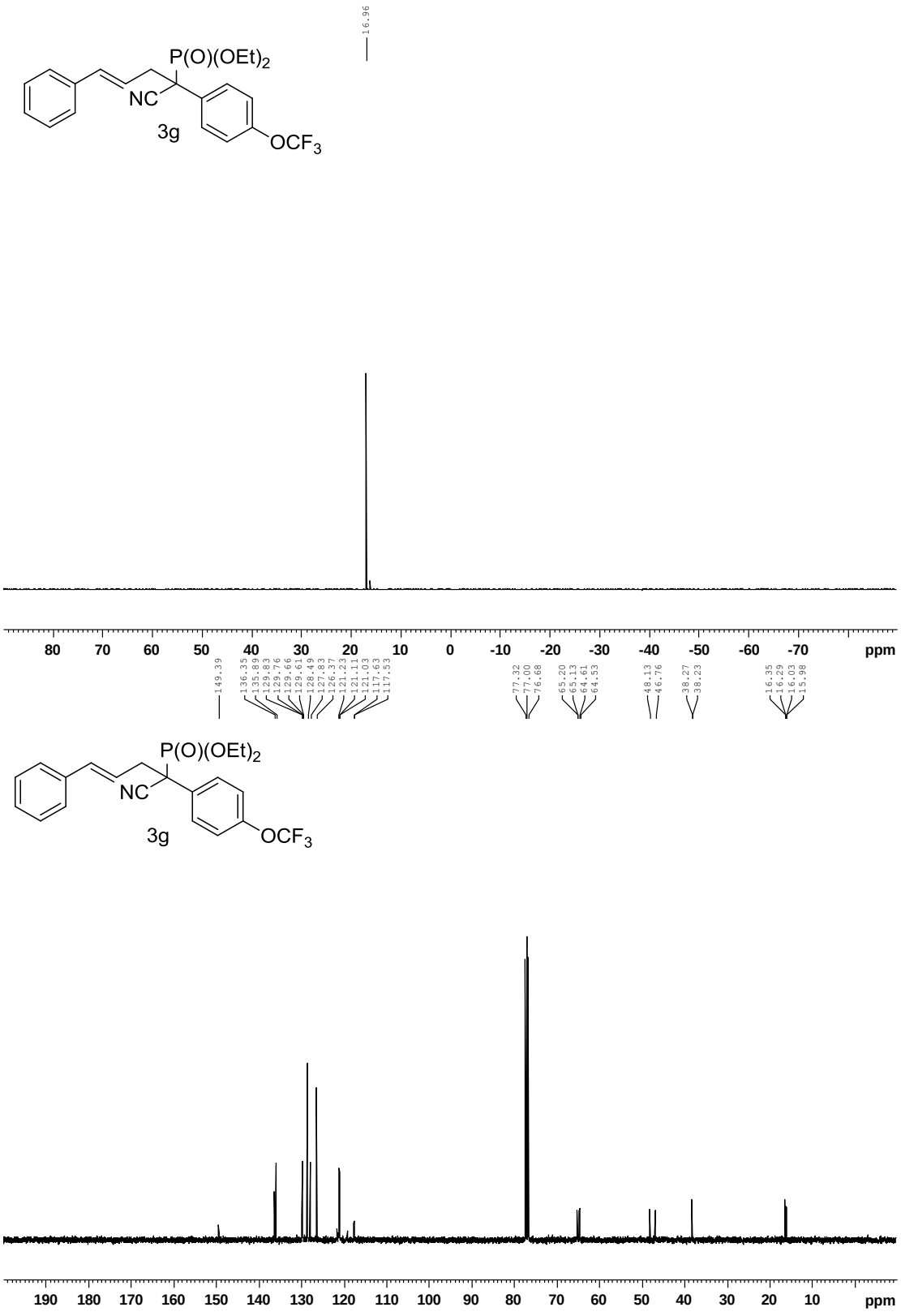
3e

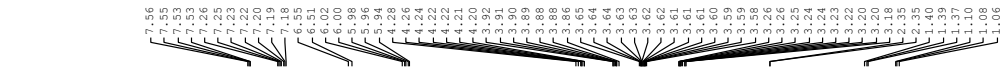

2.00
2.01
5.00
1.00
0.95
2.04
1.02
1.03
2.00
3.00
3.01
0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

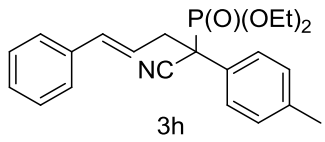

16.64
P(O)(OEt)2
NC
CF3
3e
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm
136.25
136.03
135.41
135.35
131.11
130.78
128.52
128.48
127.87
126.38
125.80
125.76
125.74
120.98
120.97
117.42
117.32
77.32
77.00
76.68
65.24
65.17
64.76
64.68
48.66
47.30
38.20
38.17
16.34
16.29
16.05
16.00
P(O)(OEt)2
NC
CF3
3e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

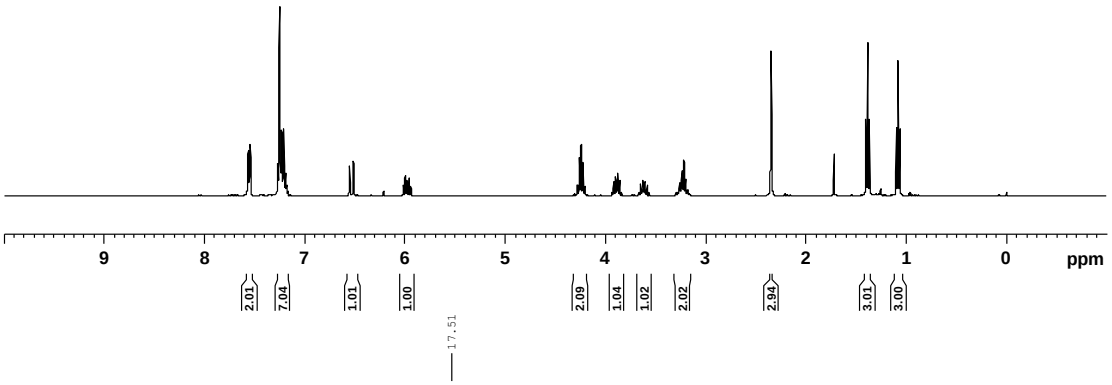

7.59
7.59
7.57
7.56
7.26
7.25
7.24
7.22
7.21
7.20
7.19
7.18
6.94
6.92
6.55
6.51
6.02
6.00
5.98
5.96
5.94
4.28
4.26
4.25
4.23
4.21
3.94
3.93
3.92
3.91
3.90
3.89
3.88
3.87
3.86
3.85
3.81
3.68
3.66
3.64
3.64
3.62
3.61
3.60
3.59
3.58
3.28
3.26
3.24
3.22
3.22
3.21
3.19
3.17
3.15
1.41
1.39
1.37
1.11
1.09
1.08
P(O)(OEt)2
NC
3f
O
9
8
7
6
5
4
3
2
1
ppm
2.03
5.01
2.03
1.00
1.00
17.58
2.02
1.10
3.05
1.04
2.02
3.09
3.02
P(O)(OEt)2
NC
3f
O
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
ppm

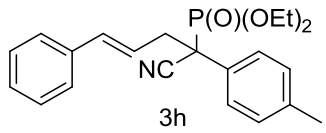

159.69
159.67
136.58
135.32
129.22
129.17
129.41
127.36
125.56
122.50
122.43
121.91
121.79
118.17
118.08
114.20
114.18
77.32
77.00
76.68
65.10
65.03
64.24
64.16
55.27
47.76
46.38
38.15
38.12
16.34
16.28
16.15
16.10
P(O)(OEt)2
NC
3f
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
7.73
7.73
7.71
7.71
7.70
7.31
7.28
7.26
7.24
7.23
7.22
7.22
7.21
7.20
7.19
7.19
6.55
6.51
6.00
5.98
5.96
5.94
4.31
4.29
4.27
4.25
4.24
3.97
3.95
3.95
3.94
3.93
3.91
3.74
3.74
3.73
3.72
3.70
3.70
3.68
3.68
3.25
3.23
3.21
1.42
1.40
1.38
1.10
1.09
1.07
P(O)(OEt)2
NC
3g
OCF3
9 8 7 6 5 4 3 2 1 0 ppm
2.09
7.05
1.00
1.00
2.03
1.07
1.07
2.01
3.06
3.08

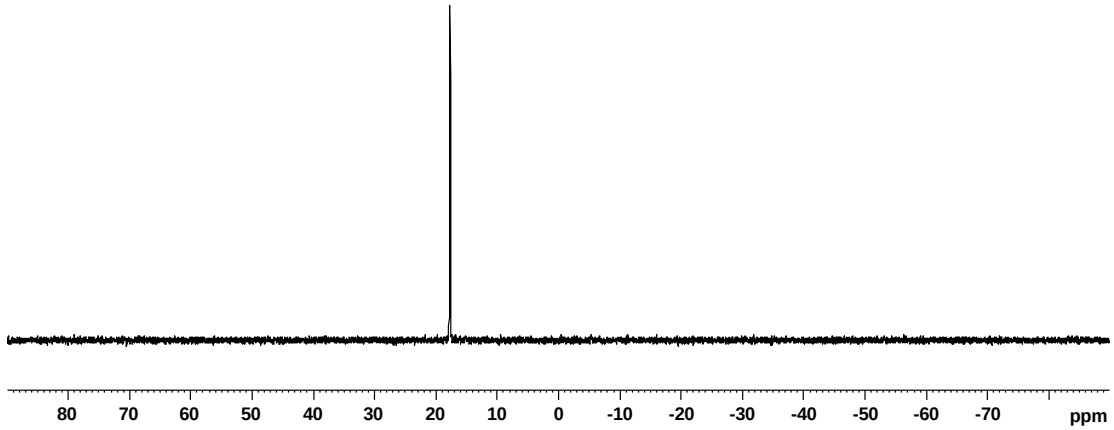

P(O)(OEt)2
NC
3g
OCF3
16.96
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm
149.39
136.35
135.89
129.83
129.76
129.66
129.61
128.49
127.83
126.37
121.23
121.11
121.03
117.63
117.53
77.32
77.00
76.68
65.20
65.13
64.61
64.53
48.13
46.76
38.27
38.23
16.35
16.29
16.03
15.98
P(O)(OEt)2
NC
3g
OCF3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

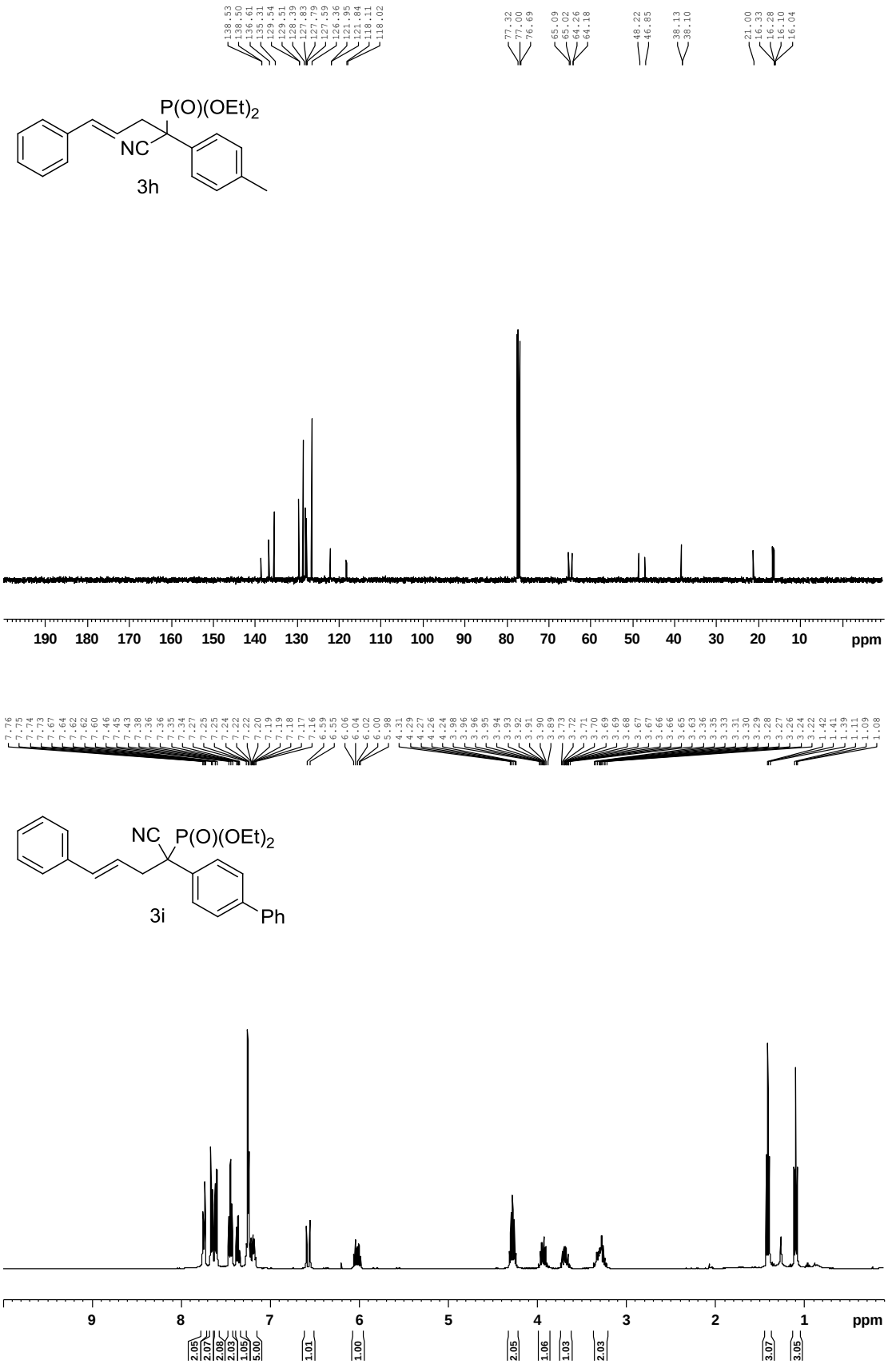

7.56
7.55
7.53
7.53
7.26
7.25
7.23
7.22
7.20
7.19
7.18
6.55
6.51
6.02
6.00
5.98
5.96
5.94
4.28
4.26
4.24
4.22
4.21
4.20
3.92
3.91
3.90
3.89
3.88
3.88
3.86
3.65
3.64
3.64
3.63
3.63
3.62
3.62
3.61
3.61
3.61
3.60
3.59
3.59
3.58
3.26
3.25
3.24
3.24
3.23
3.22
3.20
3.20
3.18
2.35
1.40
1.39
1.37
1.10
1.08
1.06

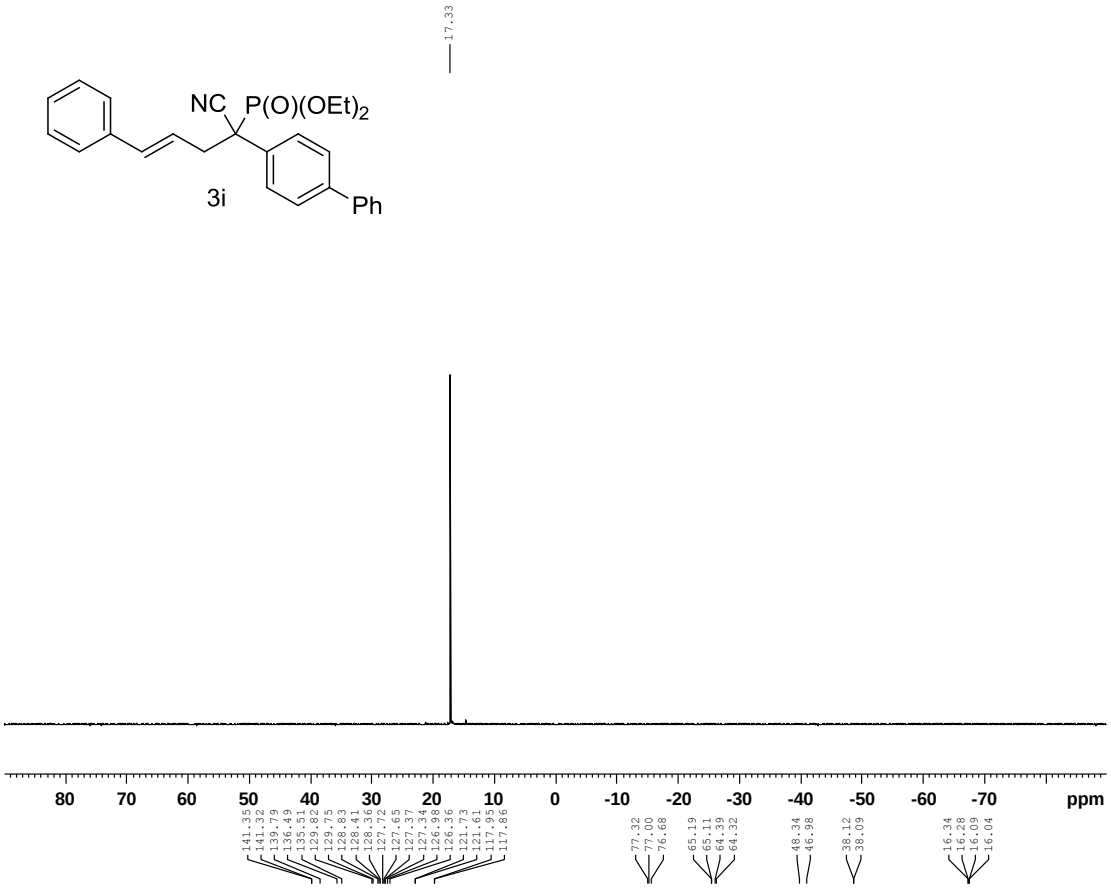

P(O)(OEt)2
NC
3h


9
8
7
6
5
4
3
2
1
0
ppm
2.01
7.04
1.01
1.00
2.09
1.04
1.02
2.02
2.94
3.01
3.00
17.51


P(O)(OEt)2
NC
3h


80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
ppm


138.53
138.50
136.61
135.31
129.54
129.51
128.39
127.83
127.79
127.59
126.36
121.95
121.84
118.11
118.02
77.32
77.00
76.69
65.09
65.02
64.26
64.18
48.22
46.85
38.13
38.10
21.00
16.33
16.28
16.10
16.04
P(O)(OEt)2
NC
3h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
7.76
7.75
7.74
7.73
7.67
7.64
7.62
7.62
7.60
7.46
7.45
7.43
7.38
7.36
7.36
7.35
7.34
7.27
7.25
7.25
7.24
7.22
7.22
7.20
7.19
7.19
7.18
7.17
7.16
6.59
6.55
6.06
6.04
6.02
6.00
5.98
4.31
4.29
4.27
4.26
4.24
3.98
3.96
3.96
3.95
3.94
3.93
3.93
3.91
3.90
3.89
3.73
3.72
3.71
3.70
3.69
3.69
3.68
3.67
3.67
3.66
3.66
3.65
3.63
3.36
3.35
3.33
3.31
3.30
3.29
3.28
3.27
3.26
3.24
3.22
1.42
1.41
1.39
1.11
1.09
1.08
NC
P(O)(OEt)2
3i
Ph
9 8 7 6 5 4 3 2 1 ppm
2.05
2.07
2.08
2.03
1.05
5.00
1.01
1.00
2.05
1.06
1.03
2.03
3.07
3.05


17.33
NC
P(O)(OEt)2
3i
Ph
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm
141.35
141.32
139.79
136.49
135.51
129.82
129.75
128.83
128.41
128.36
127.72
127.65
127.37
127.34
126.98
126.36
121.73
121.61
117.95
117.86
77.32
77.00
76.68
65.19
65.11
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64.32
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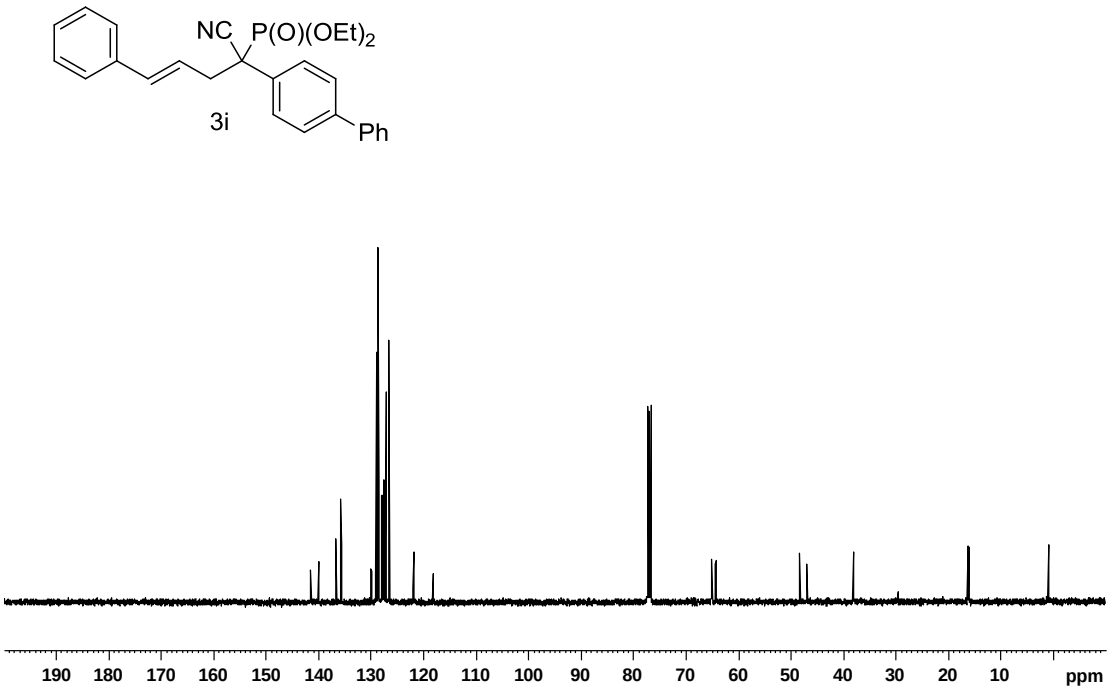
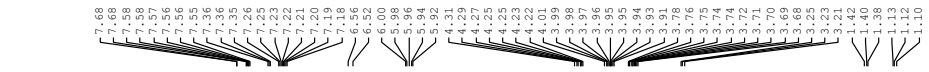
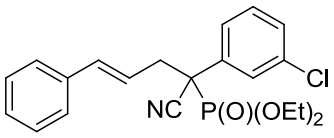
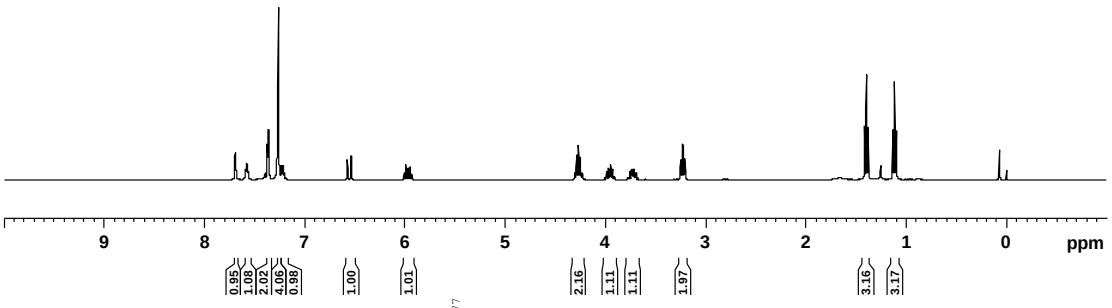
46.98
38.12
38.09
16.34
16.28
16.09
16.04

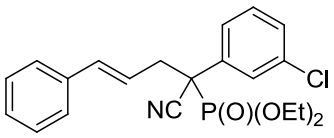

NC
P(O)(OEt)2
3i
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.68
7.68
7.58
7.58
7.57
7.56
7.56
7.55
7.36
7.35
7.26
7.25
7.23
7.22
7.21
7.20
7.19
7.18
6.56
6.52
6.00
5.98
5.96
5.94
5.92
4.31
4.29
4.27
4.25
4.23
4.22
4.01
3.99
3.98
3.97
3.96
3.95
3.95
3.94
3.93
3.91
3.78
3.76
3.75
3.74
3.74
3.72
3.71
3.70
3.69
3.68
3.25
3.23
3.21
1.42
1.40
1.38
1.13
1.12
1.10

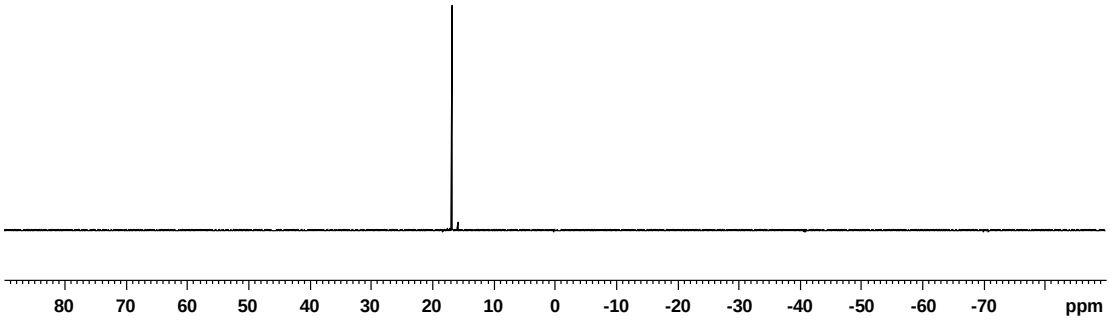

Cl
NC
P(O)(OEt)2

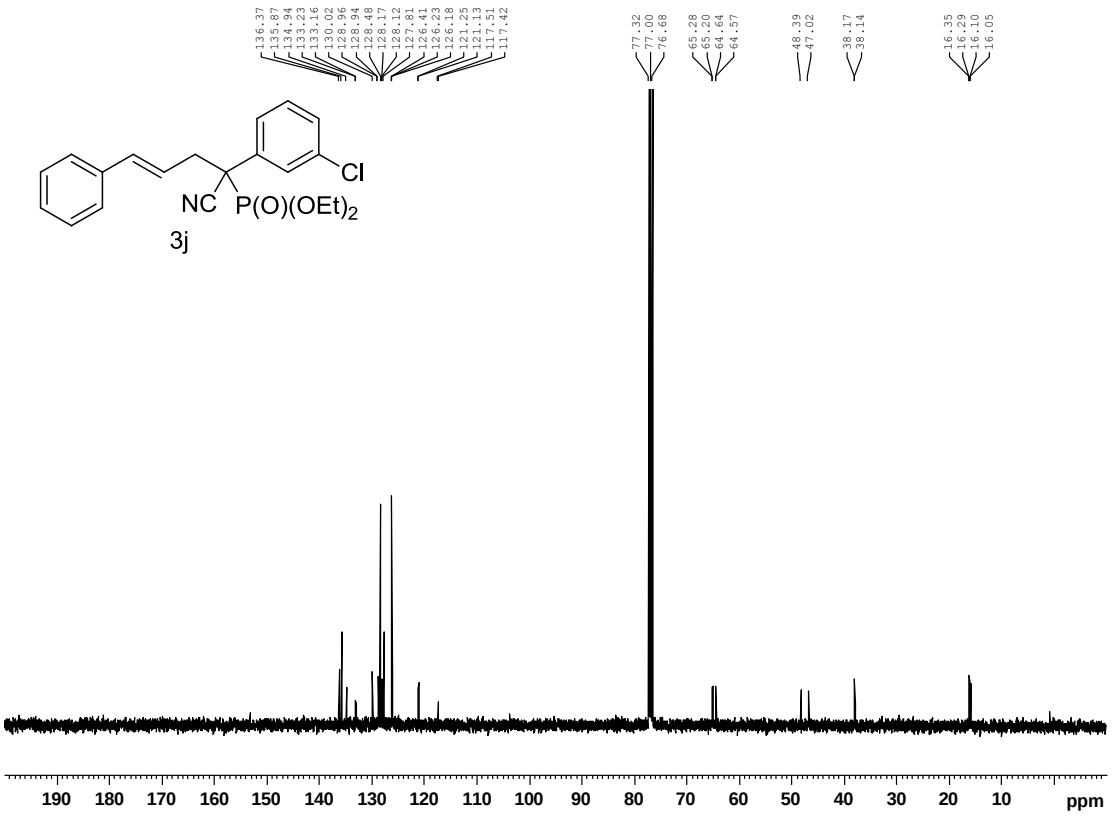
3j


9
8
7
6
5
4
3
2
1
0
ppm
0.95
1.08
2.02
4.06
0.98
1.00
1.01
2.16
1.11
1.11
1.97
3.16
3.17

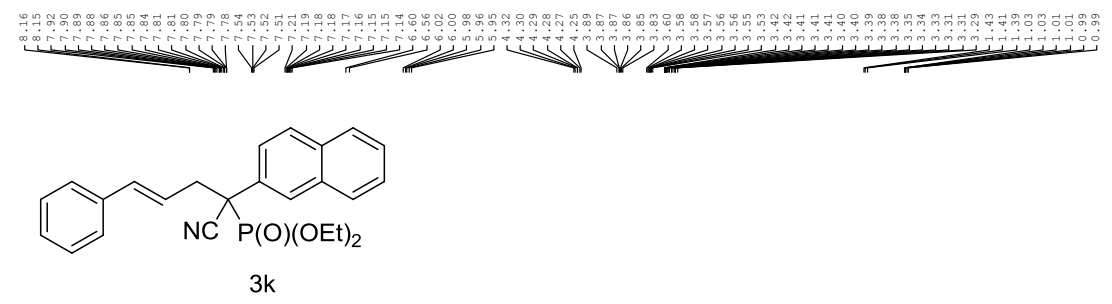

Cl
NC
P(O)(OEt)2

3j

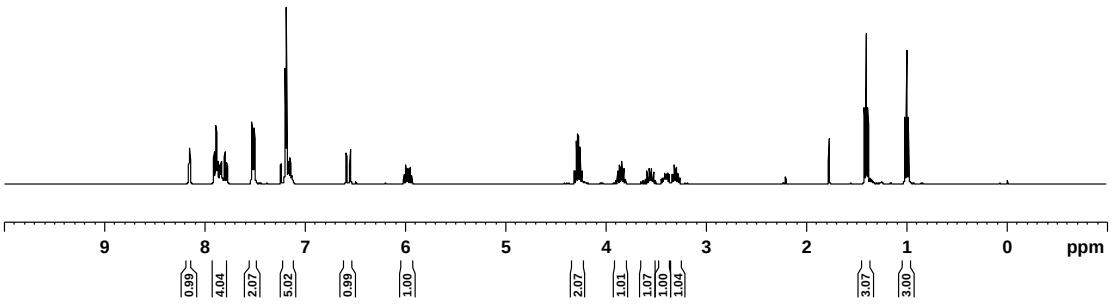

16.77
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
ppm

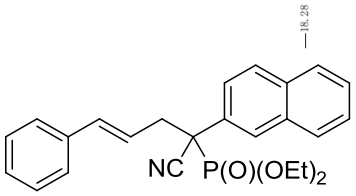


3j

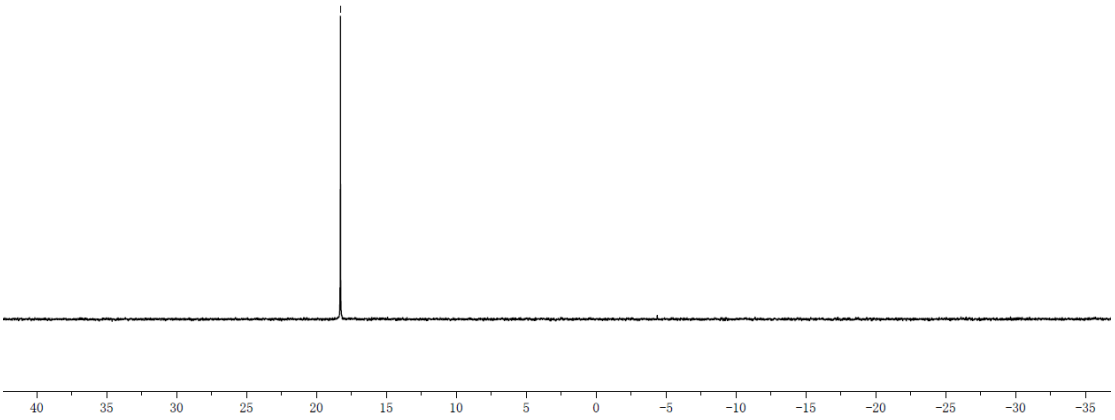


3k

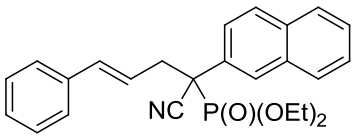



18.28
NC
P(O)(OEt)2

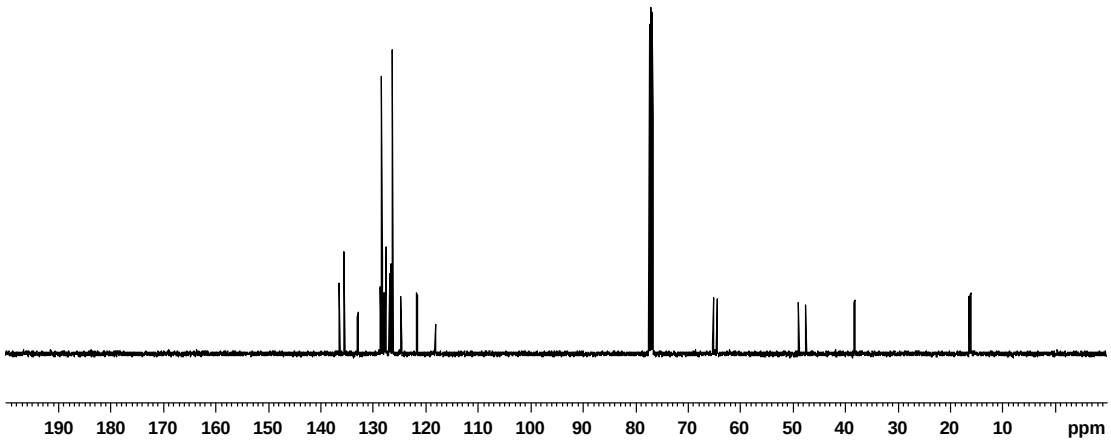
3k

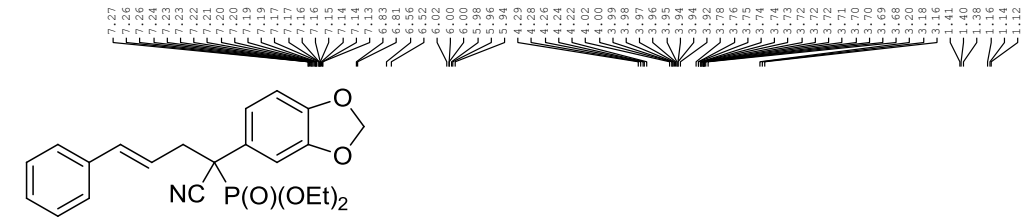

40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35


136.41
135.50
132.97
132.94
132.90
132.89
128.65
128.63
128.35
128.27
127.85
127.78
127.62
127.53
126.89
126.67
126.33
124.67
124.64
121.67
121.55
118.07
117.98
77.32
77.00
76.68
65.13
65.06
64.40
64.33
48.80
47.44
38.20
38.17
16.35
16.29
16.05
16.00


NC
P(O)(OEt)2

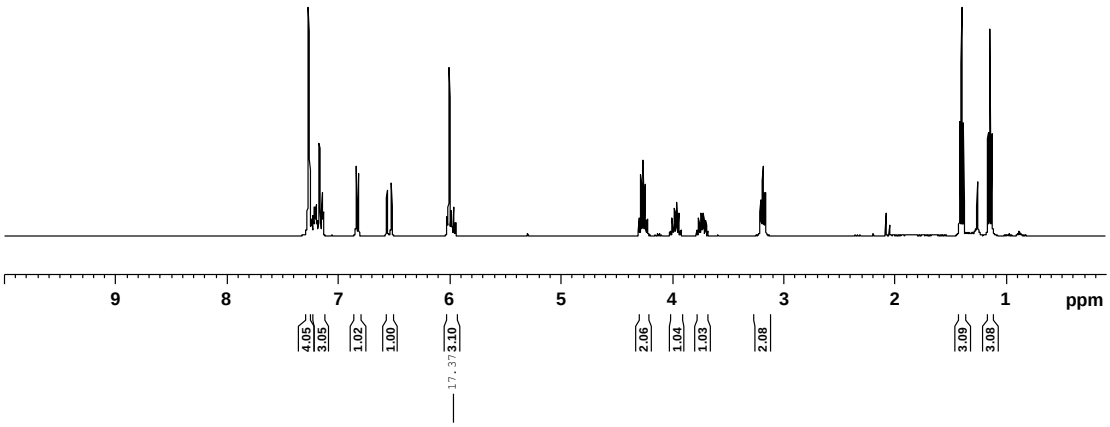
3k

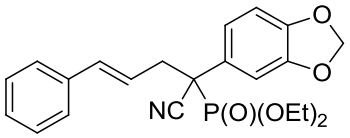

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



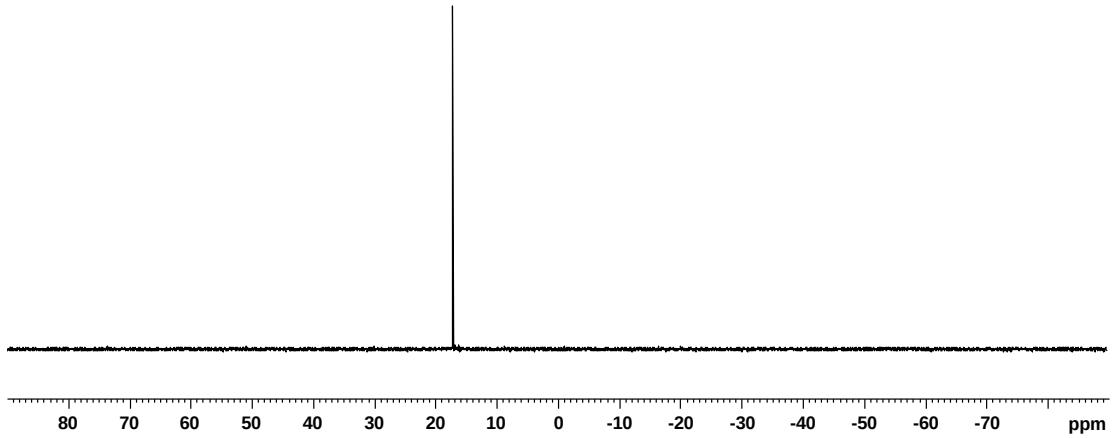
O
O
NC
P(O)(OEt)2

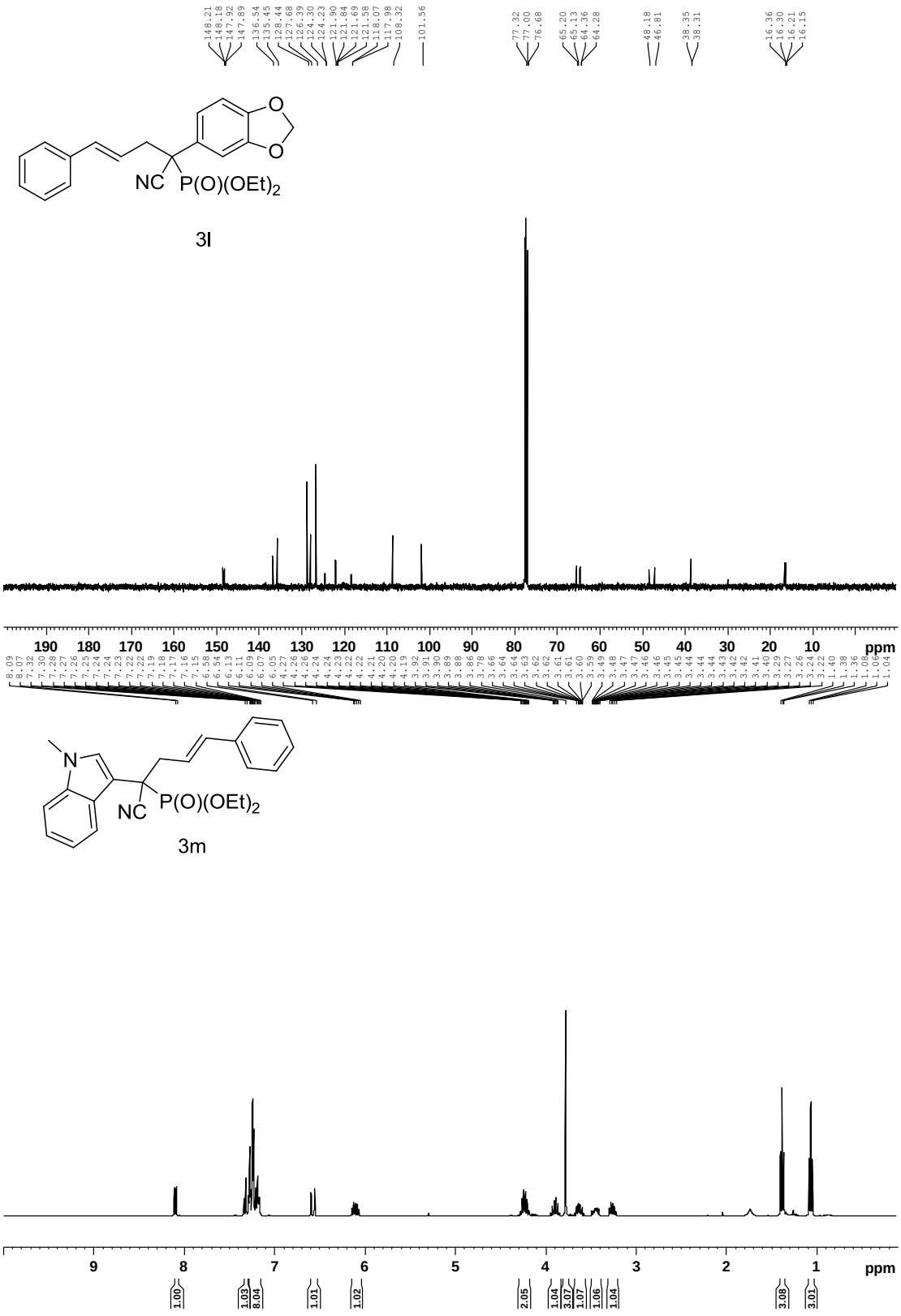
3l

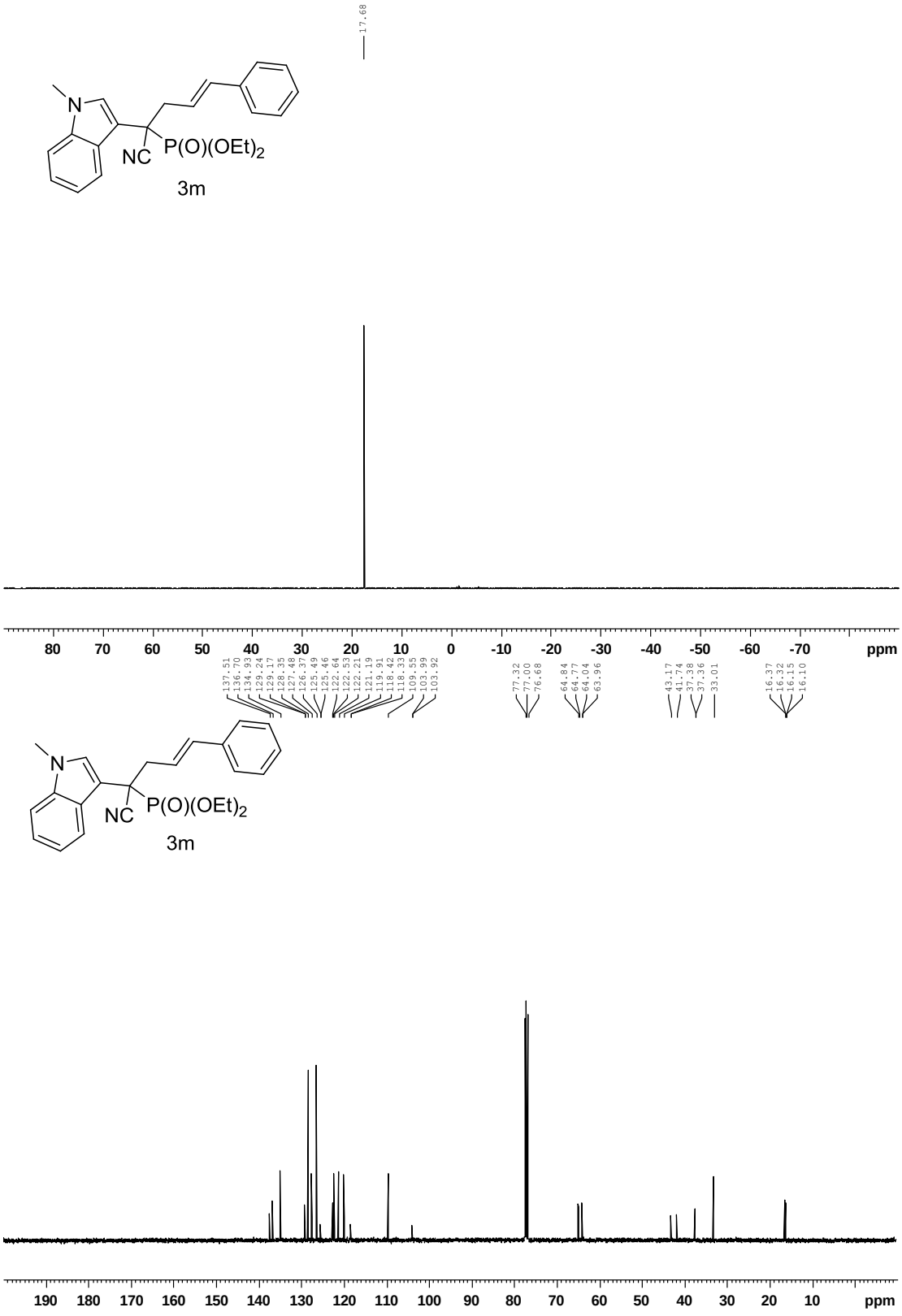

9
8
7
6
5
4
3
2
1
ppm
4.05
3.05
1.02
1.00
17.37
3.10
2.06
1.04
1.03
2.08
3.09
3.08

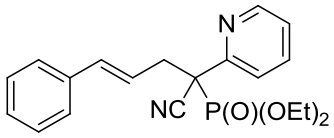

O
O
NC
P(O)(OEt)2

3l

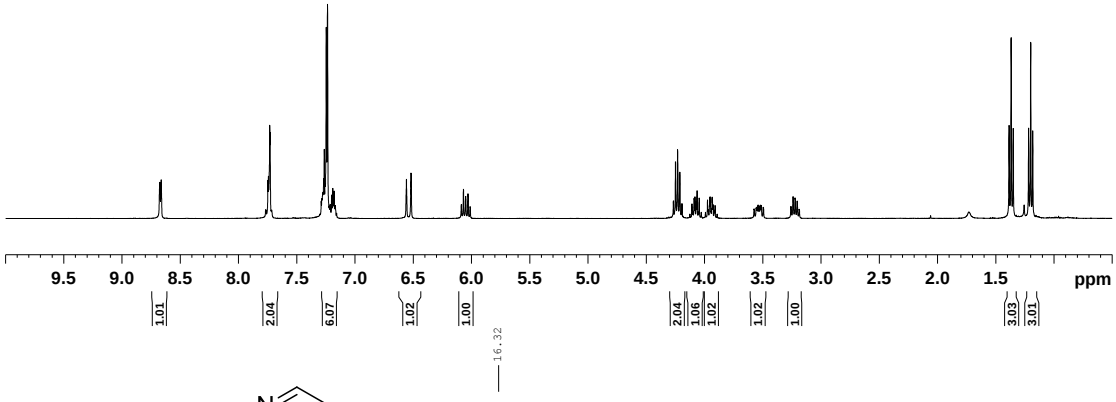

80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
ppm

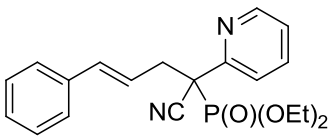

148.21
148.18
147.92
147.89
136.54
135.45
128.44
127.68
126.39
124.30
124.23
121.90
121.84
121.69
121.58
118.07
117.98
108.32
101.56
77.32
77.00
76.68
65.20
65.13
64.36
64.28
48.18
46.81
38.35
38.31
16.36
16.30
16.21
16.15
O
O
O
NC
P(O)(OEt)2
3l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
N
NC
P(O)(OEt)2
3m
9 8 7 6 5 4 3 2 1 ppm
1.00
1.03
8.04
1.01
1.02
2.05
1.04
3.07
1.07
1.06
1.04
3.08
3.01


17.68
N
NC
P(O)(OEt)2
3m
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm
137.51
136.70
134.93
129.24
129.17
127.43
126.37
125.49
125.46
122.64
122.53
122.21
121.19
119.91
118.42
118.33
109.55
103.99
103.92
77.32
77.00
76.68
64.84
64.77
64.04
63.96
43.17
41.74
41.38
37.36
33.01
16.37
16.32
16.15
16.10
N
NC
P(O)(OEt)2
3m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

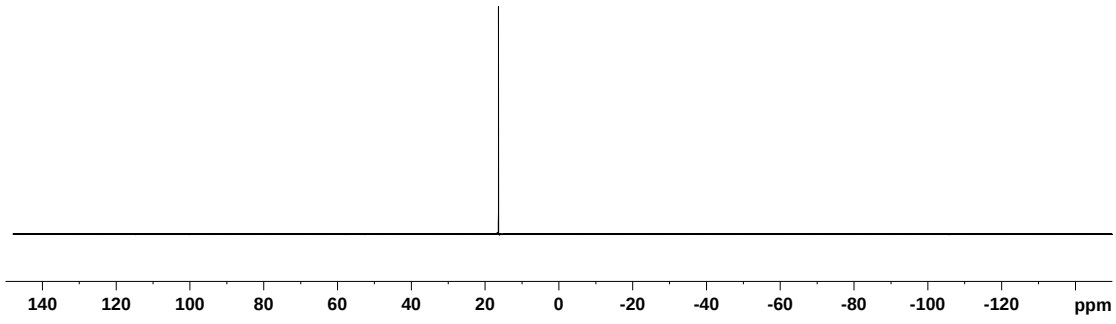

N
NC
P(O)(OEt)2

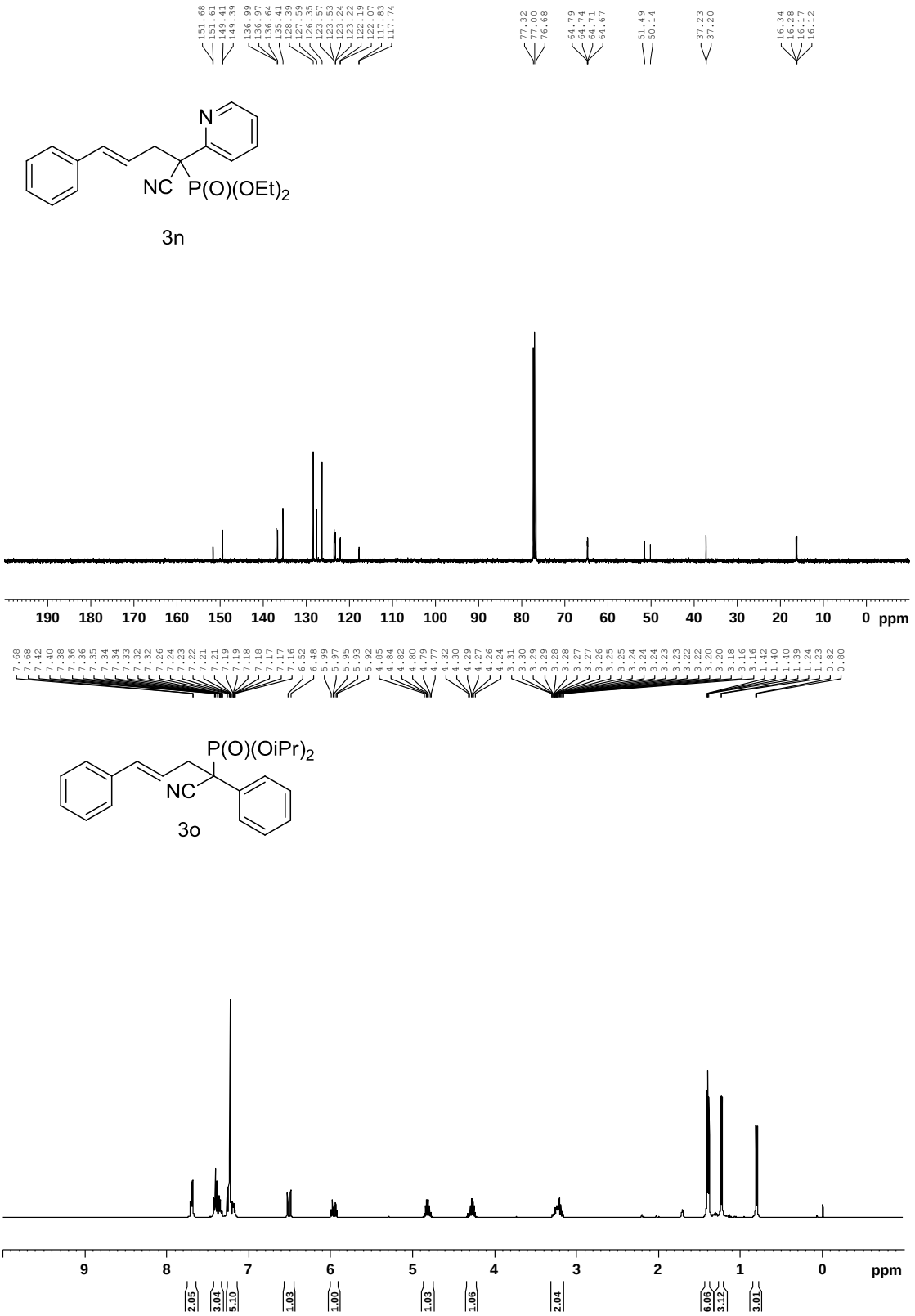
3n

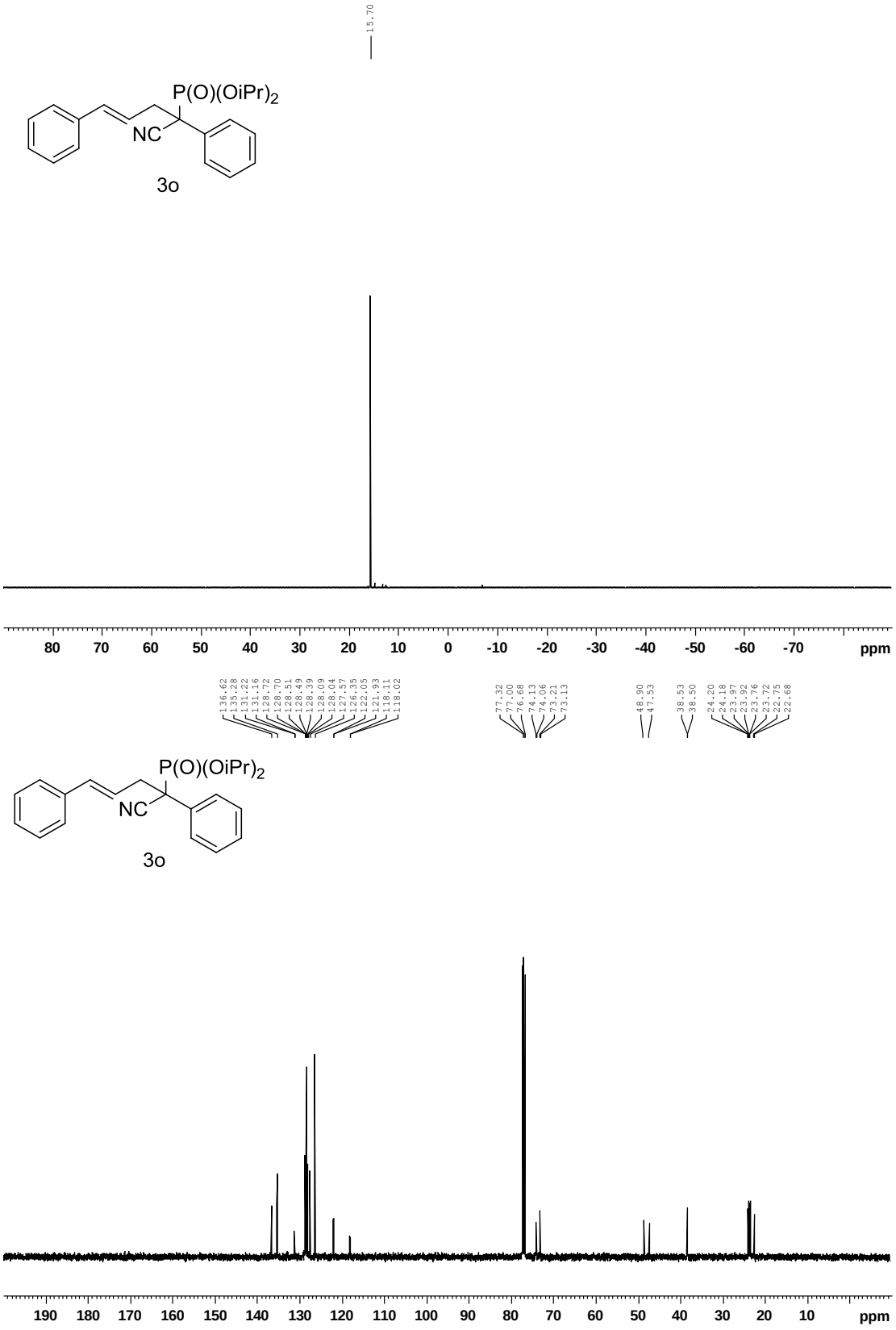

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.01
2.04
6.07
1.02
1.00
2.04
1.06
1.02
1.02
1.00
3.03
3.01

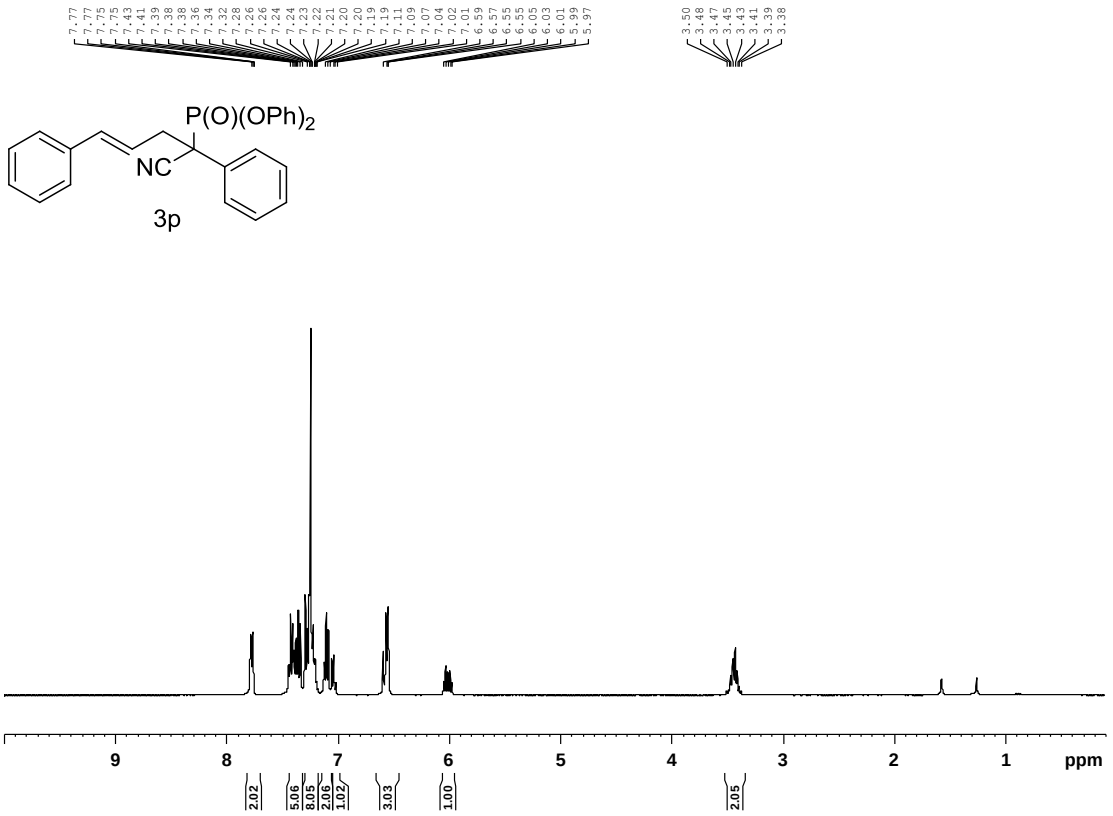

N
NC
P(O)(OEt)2

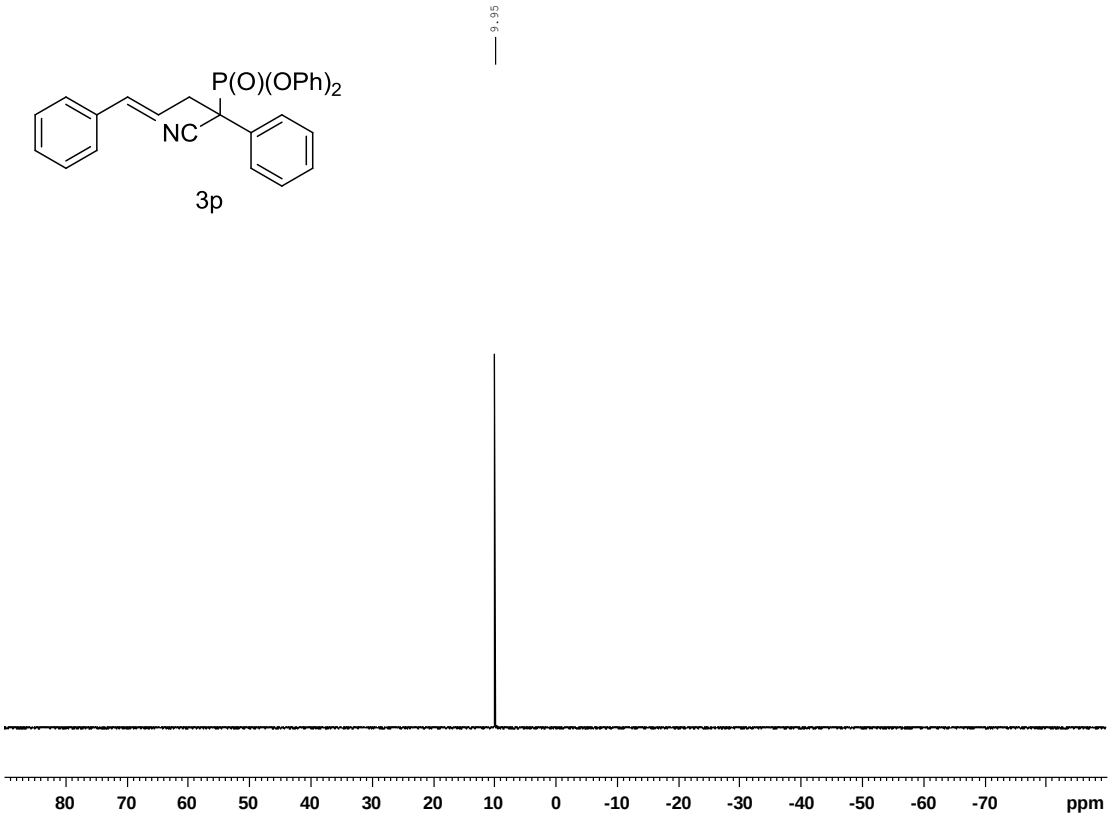
3n

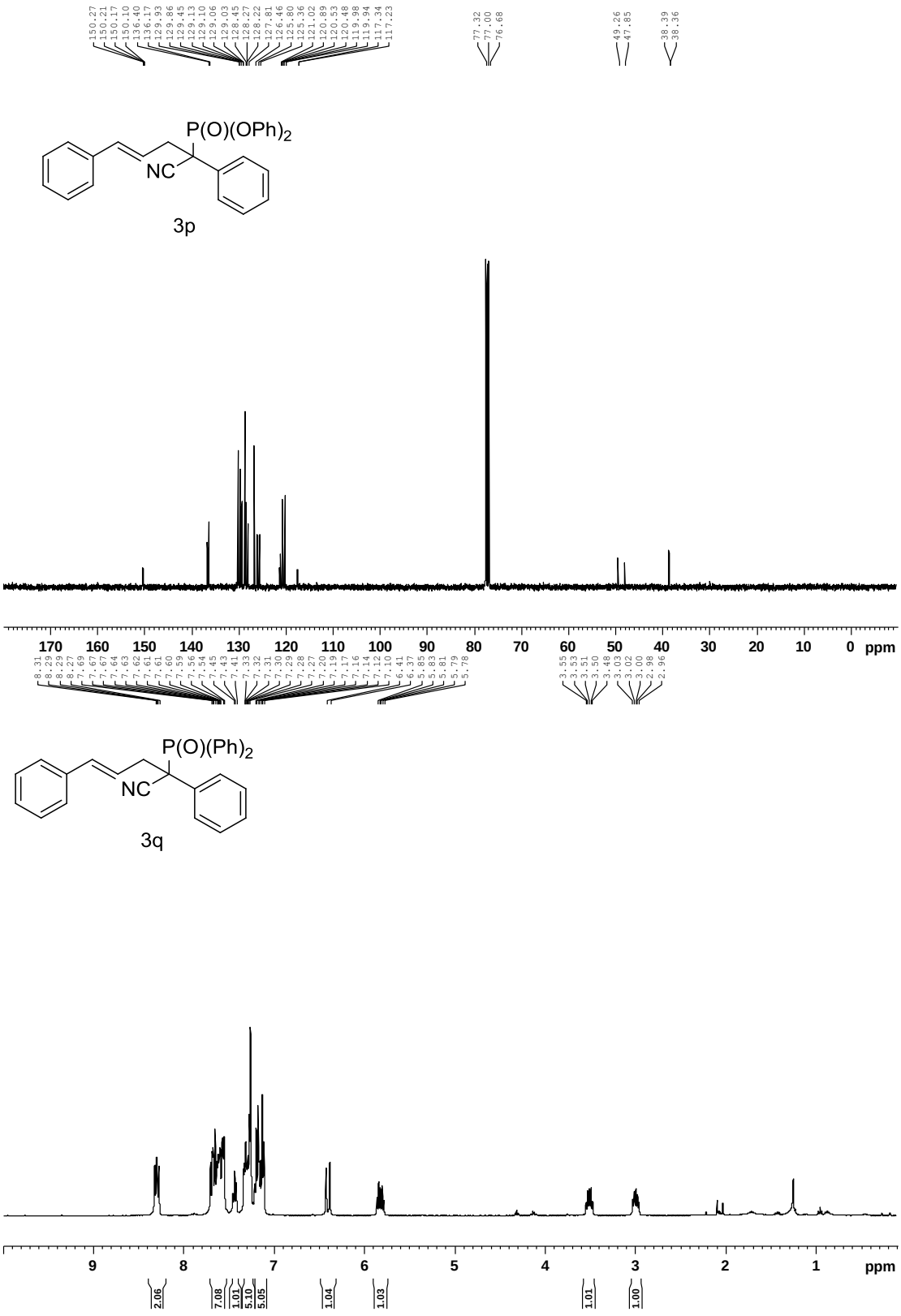

16.32
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm

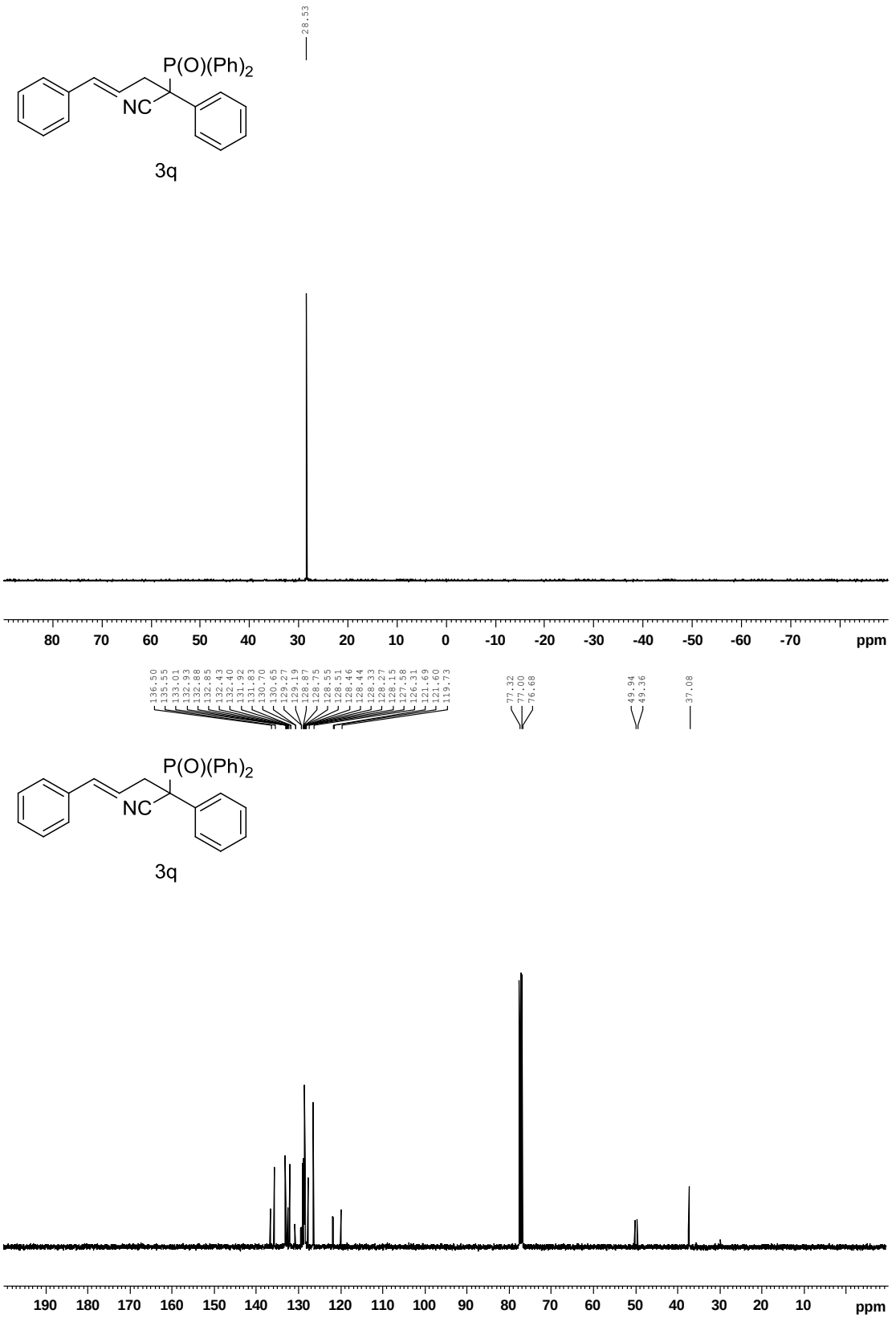

151.68
151.61
149.41
149.39
136.99
136.97
136.64
135.41
128.39
127.59
126.35
123.57
123.53
123.24
123.22
122.19
122.07
117.83
117.74
77.32
77.00
76.68
64.79
64.74
64.71
64.67
51.49
50.14
37.23
37.20
16.34
16.28
16.17
16.12
N
NC
P(O)(OEt)2
3n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
7.68
7.68
7.42
7.40
7.38
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.26
7.24
7.23
7.22
7.21
7.21
7.19
7.19
7.18
7.18
7.17
7.17
7.16
6.52
6.48
5.99
5.97
5.95
5.93
5.92
4.85
4.84
4.82
4.80
4.79
4.77
4.32
4.30
4.29
4.27
4.26
4.24
3.31
3.30
3.29
3.29
3.28
3.28
3.27
3.27
3.26
3.25
3.25
3.24
3.24
3.24
3.23
3.23
3.22
3.22
3.20
3.20
3.18
3.16
3.16
1.42
1.40
1.40
1.39
1.24
1.23
0.82
0.80
P(O)(OiPr)2
NC
3o
9 8 7 6 5 4 3 2 1 0 ppm
2.05
3.04
5.10
1.03
1.00
1.03
1.06
2.04
6.06
3.12
3.01

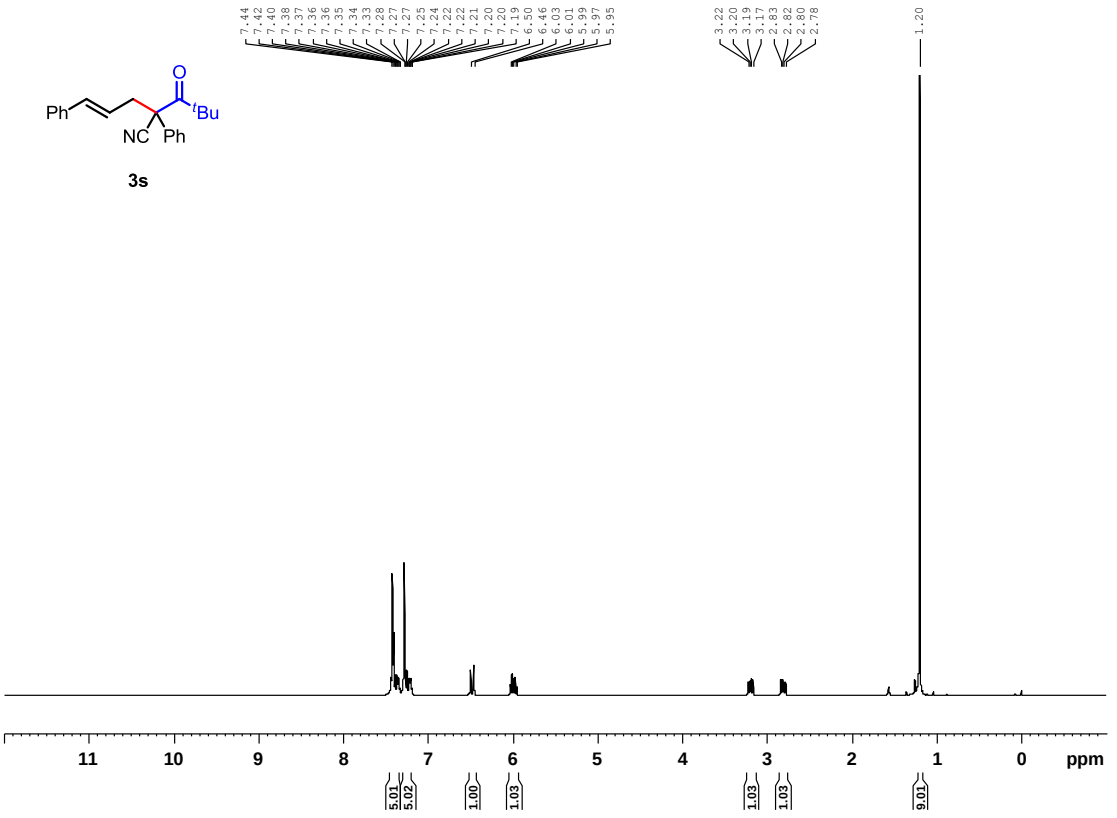

15.70
P(O)(OiPr)2
NC
3o
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm
136.62
135.28
135.22
131.16
128.72
128.70
128.51
128.49
128.39
128.09
128.04
127.57
126.35
122.05
121.93
118.11
118.02
77.32
77.00
76.68
74.13
74.06
73.21
73.13
48.90
47.53
38.53
38.50
24.20
24.18
23.97
23.92
23.76
23.72
22.75
22.68
P(O)(OiPr)2
NC
3o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

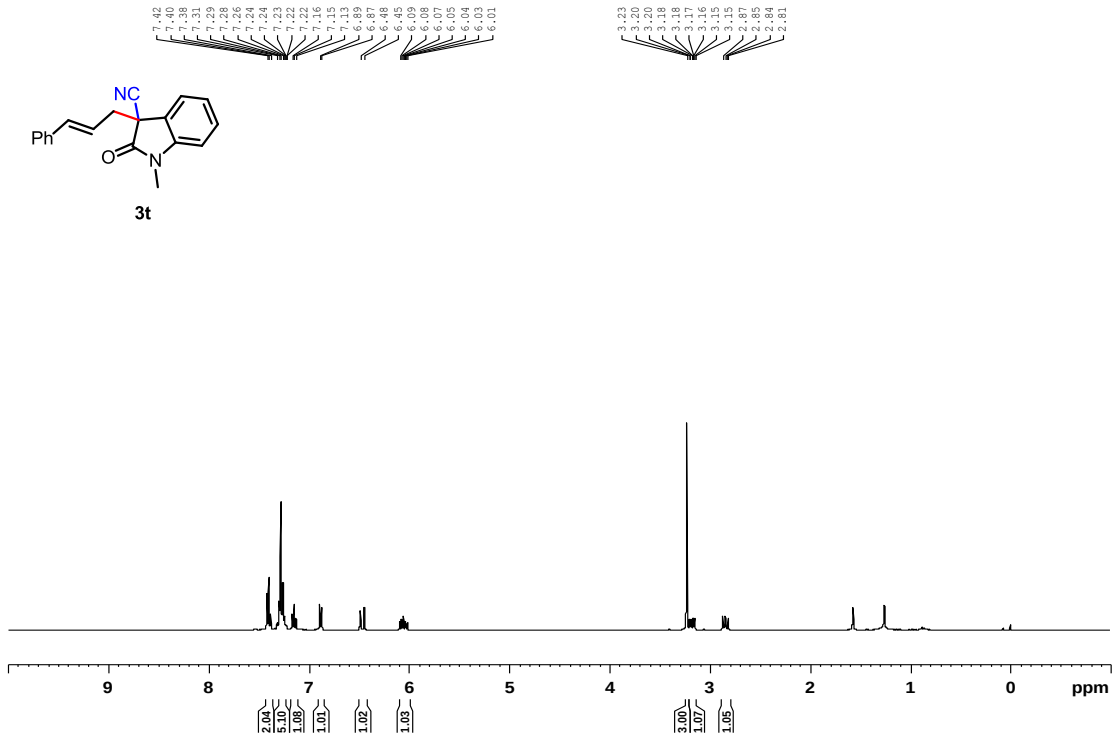

7.77
7.77
7.75
7.75
7.43
7.41
7.39
7.38
7.38
7.36
7.34
7.32
7.28
7.26
7.26
7.24
7.24
7.23
7.22
7.21
7.20
7.20
7.19
7.19
7.11
7.09
7.07
7.04
7.02
7.01
6.59
6.57
6.55
6.55
6.05
6.03
6.01
5.99
5.97
3.50
3.48
3.47
3.45
3.43
3.41
3.39
3.38
P(O)(OPh)2
NC
3p
9
8
7
6
5
4
3
2
1
ppm
2.02
5.06
8.05
2.06
1.02
3.03
1.00
2.05

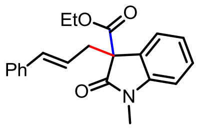

9.95
P(O)(OPh)2
NC
3p
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
ppm


150.27
150.21
150.17
150.10
136.40
136.17
129.93
129.86
129.45
129.13
129.10
129.06
129.03
128.45
128.27
128.22
127.81
126.46
125.80
125.36
121.02
120.89
120.53
120.48
119.98
119.94
117.34
117.23
77.32
77.00
76.68
49.26
47.85
38.39
38.36
P(O)(OPh)2
NC
3p
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
8.31
8.29
8.29
8.27
7.69
7.67
7.67
7.64
7.63
7.62
7.61
7.61
7.60
7.59
7.56
7.54
7.45
7.43
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.20
7.19
7.17
7.16
7.14
7.12
7.10
6.41
6.37
5.85
5.83
5.81
5.79
5.78
3.55
3.53
3.51
3.50
3.48
3.03
3.02
3.00
2.98
2.96
P(O)(Ph)2
NC
3q
9
8
7
6
5
4
3
2
1
ppm
2.06
7.08
1.01
5.10
5.05
1.04
1.03
1.01
1.00

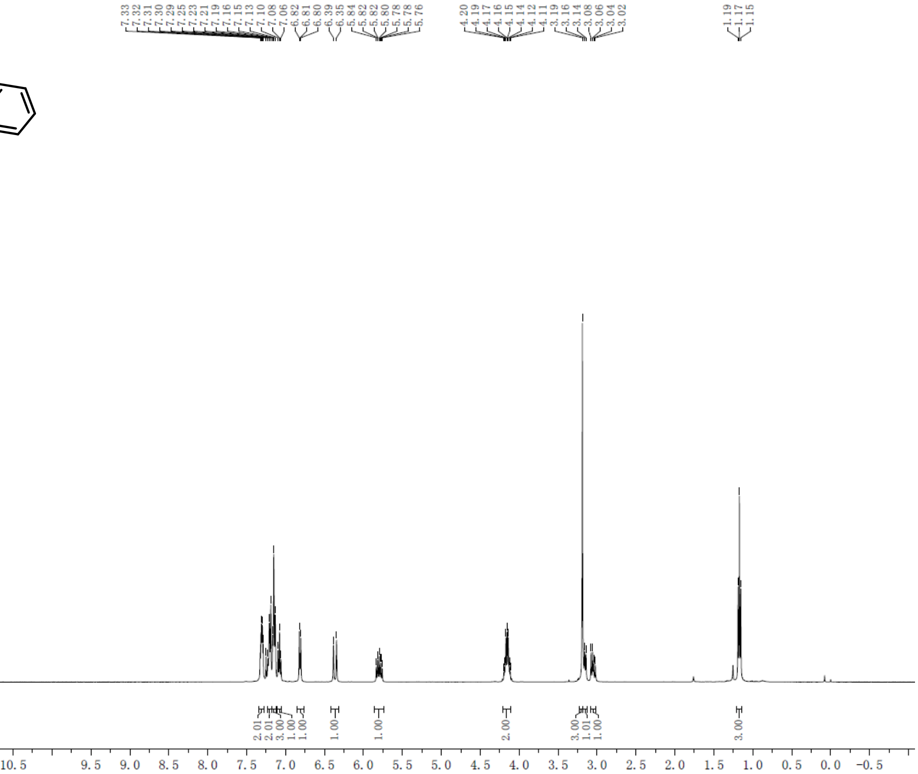

28.53
P(O)(Ph)2
NC
3q
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm
136.50
135.55
133.01
132.93
132.88
132.85
132.43
132.40
131.92
131.83
130.70
130.65
129.27
129.19
128.87
128.75
128.55
128.51
128.46
128.44
128.33
128.27
128.15
127.58
126.31
121.69
121.60
119.73
77.32
77.00
76.68
49.94
49.36
37.08
P(O)(Ph)2
NC
3q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

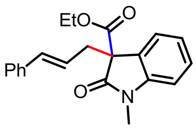

Ph
O
tBu
NC
Ph
3s
11
10
9
8
7
6
5
4
3
2
1
0
ppm


NC
Ph
O
N
3t
9
8
7
6
5
4
3
2
1
0
ppm

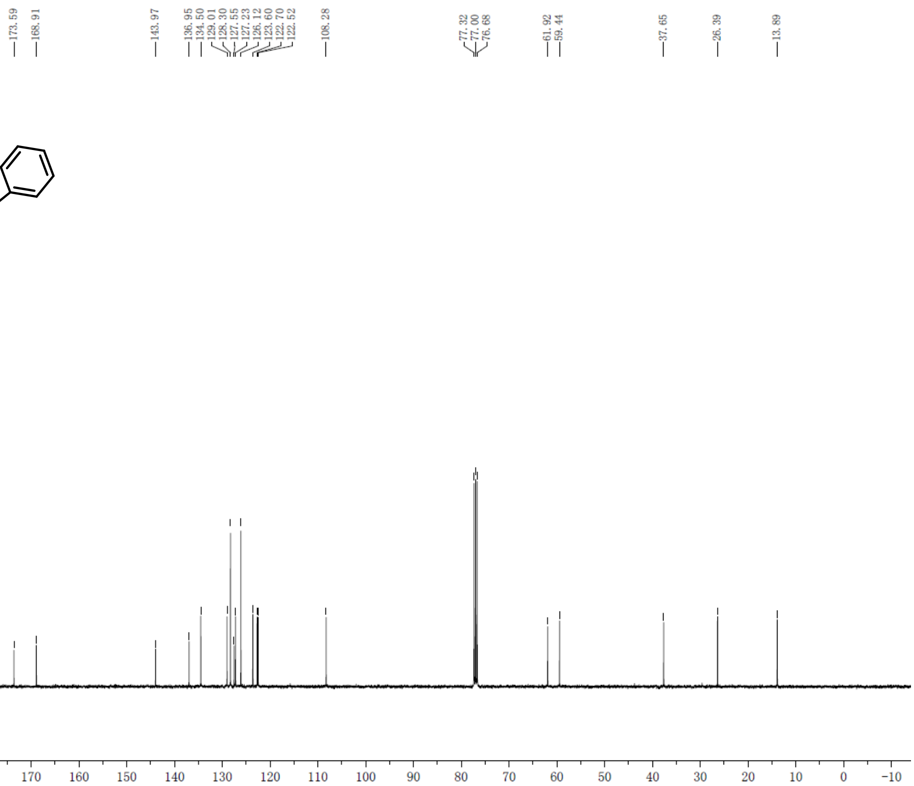

EtO
O
Ph
O
N

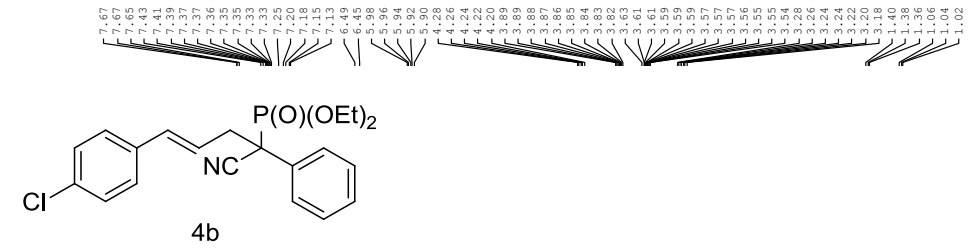
3u


7.33 7.32 7.31 7.30 7.29 7.25 7.23 7.21 7.19 7.16 7.15 7.13 7.10 7.08 7.06 6.82 6.81 6.80 6.39 6.35 5.84 5.82 5.82 5.80 5.78 5.78 5.76
4.20 4.19 4.17 4.16 4.15 4.14 4.12 4.11 3.19 3.16 3.14 3.08 3.06 3.04 3.02
1.19 1.17 1.15
2.01 2.01 3.00 1.00 1.00 1.00 1.00 2.00 3.00 1.01 1.00 3.00
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


EtO
O
Ph
O
N

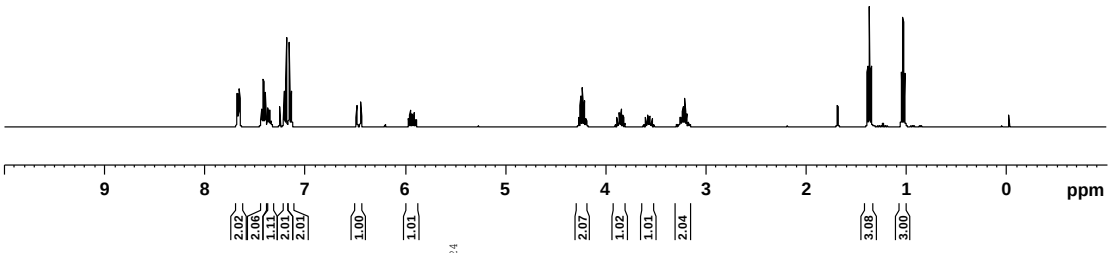
3u

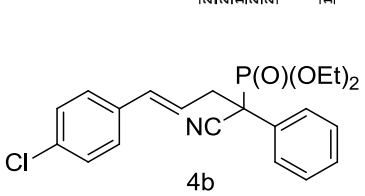

173.59 168.91 143.97 136.95 134.50 129.01 128.30 127.55 127.23 126.12 123.60 122.70 122.52 108.28
77.32 77.00 76.68 61.92 59.44 37.65 26.39 13.89
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.67
7.67
7.65
7.43
7.41
7.39
7.37
7.37
7.36
7.35
7.35
7.33
7.33
7.25
7.20
7.18
7.15
7.13
6.49
6.45
5.98
5.96
5.94
5.92
5.90
4.28
4.26
4.24
4.22
4.20
3.89
3.89
3.88
3.87
3.86
3.85
3.84
3.83
3.82
3.63
3.61
3.61
3.59
3.59
3.59
3.59
3.57
3.57
3.56
3.55
3.55
3.54
3.28
3.26
3.24
3.24
3.22
3.20
3.18
1.40
1.38
1.36
1.06
1.04
1.02

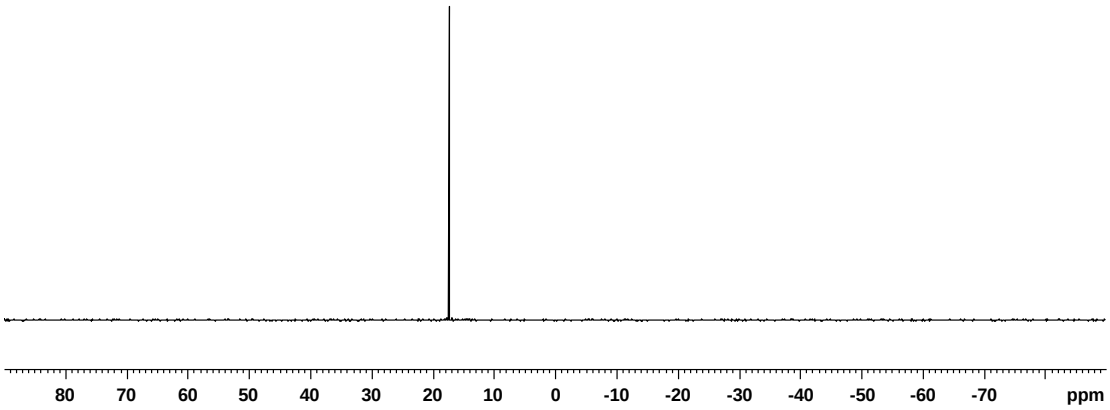
P(O)(OEt)2
NC
Cl

4b


9
8
7
6
5
4
3
2
1
0
ppm
2.02
2.06
1.11
2.01
2.01
1.00
1.01
2.07
1.02
1.01
2.04
3.08
3.00

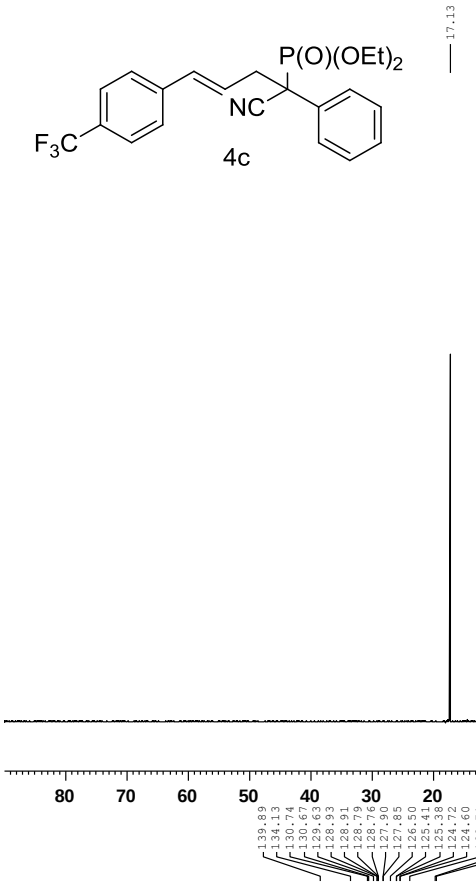

17.24
P(O)(OEt)2
NC
Cl

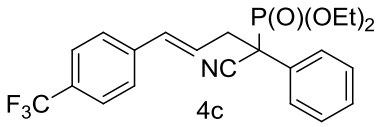
4b

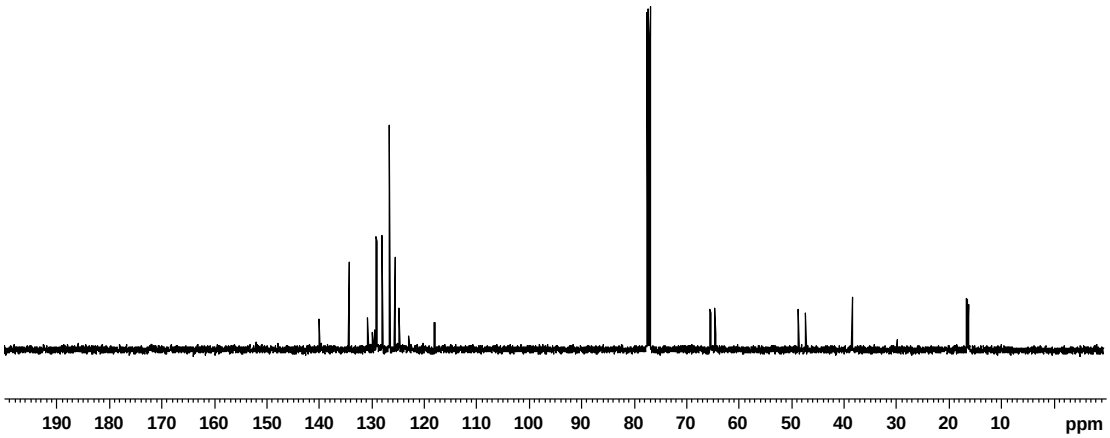

80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
ppm

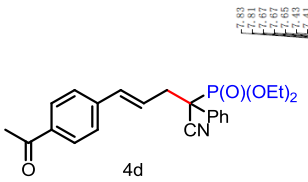

134.99
134.21
133.32
130.83
130.77
128.89
128.87
128.73
128.70
128.58
127.93
127.88
127.55
122.55
122.44
117.91
117.81
77.32
77.00
76.69
65.18
65.11
64.36
64.28
48.50
47.13
38.18
38.15
16.34
16.28
16.05
16.00
P(O)(OEt)2
NC
Cl
4b
ppm
P(O)(OEt)2
NC
F3C
4c
ppm

P(O)(OEt)2
NC
F3C
4c

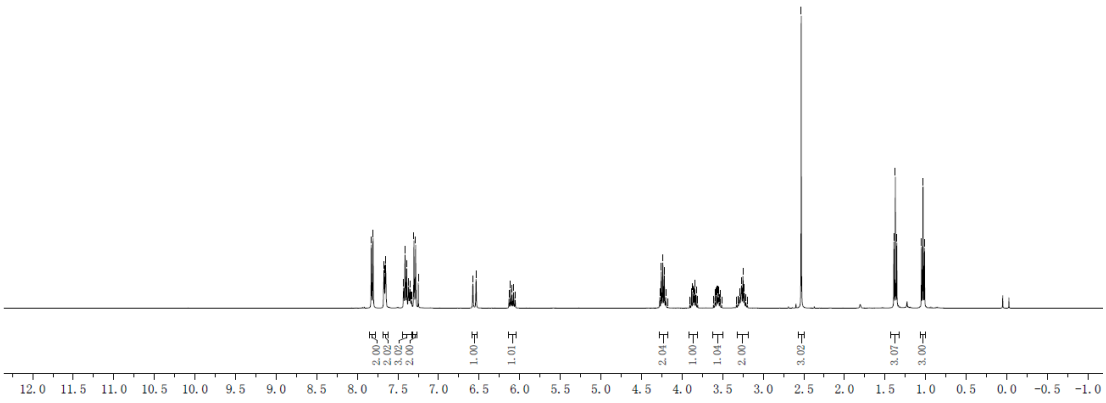

17.13
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm
139.89
134.13
131.74
130.67
129.63
128.93
128.91
128.79
128.76
127.90
127.85
126.50
125.41
125.38
124.72
124.60
122.71
117.85
117.75
77.32
77.00
76.68
65.25
65.17
64.39
64.32
48.42
47.05
38.18
38.15
16.33
16.27
16.04
15.98

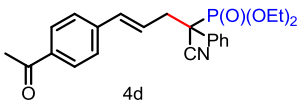

P(O)(OEt)2
NC
F3C
4c


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

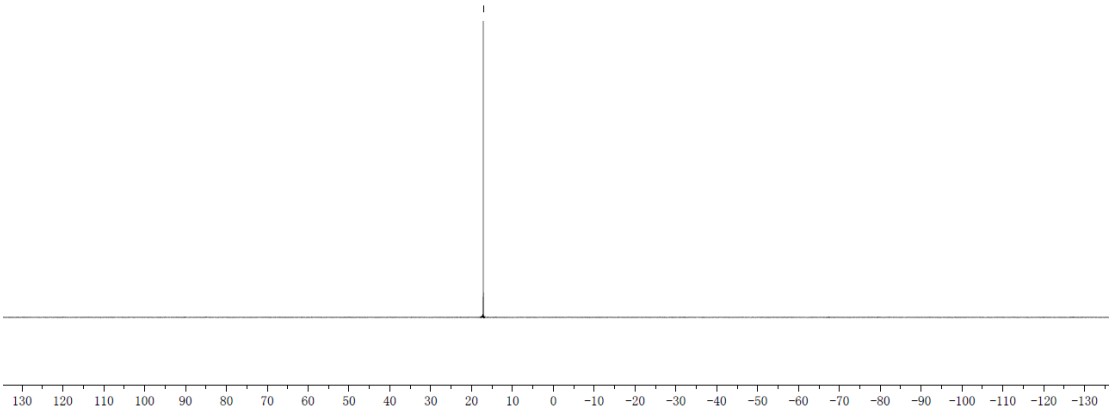


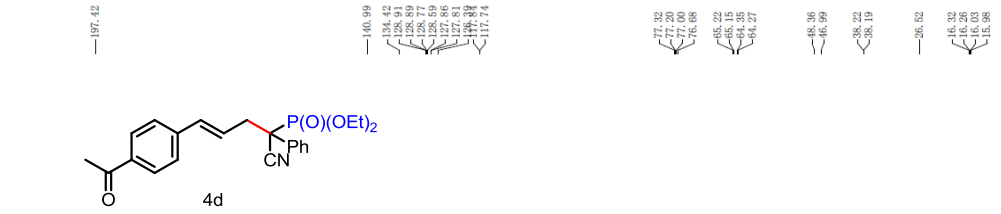
4d



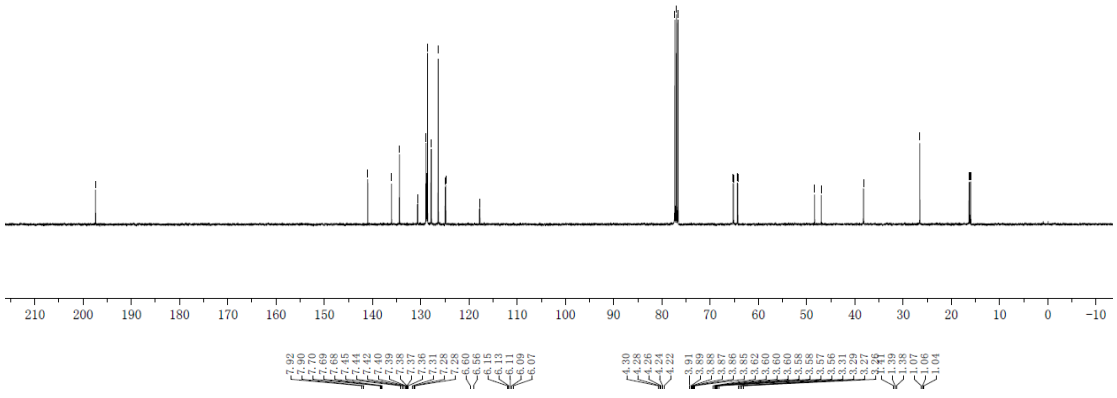


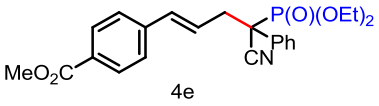
4d



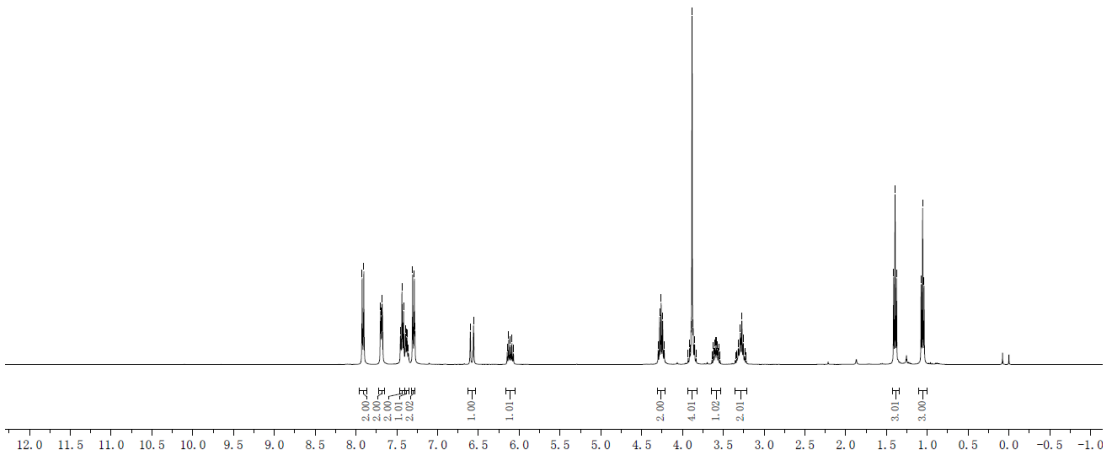


4d



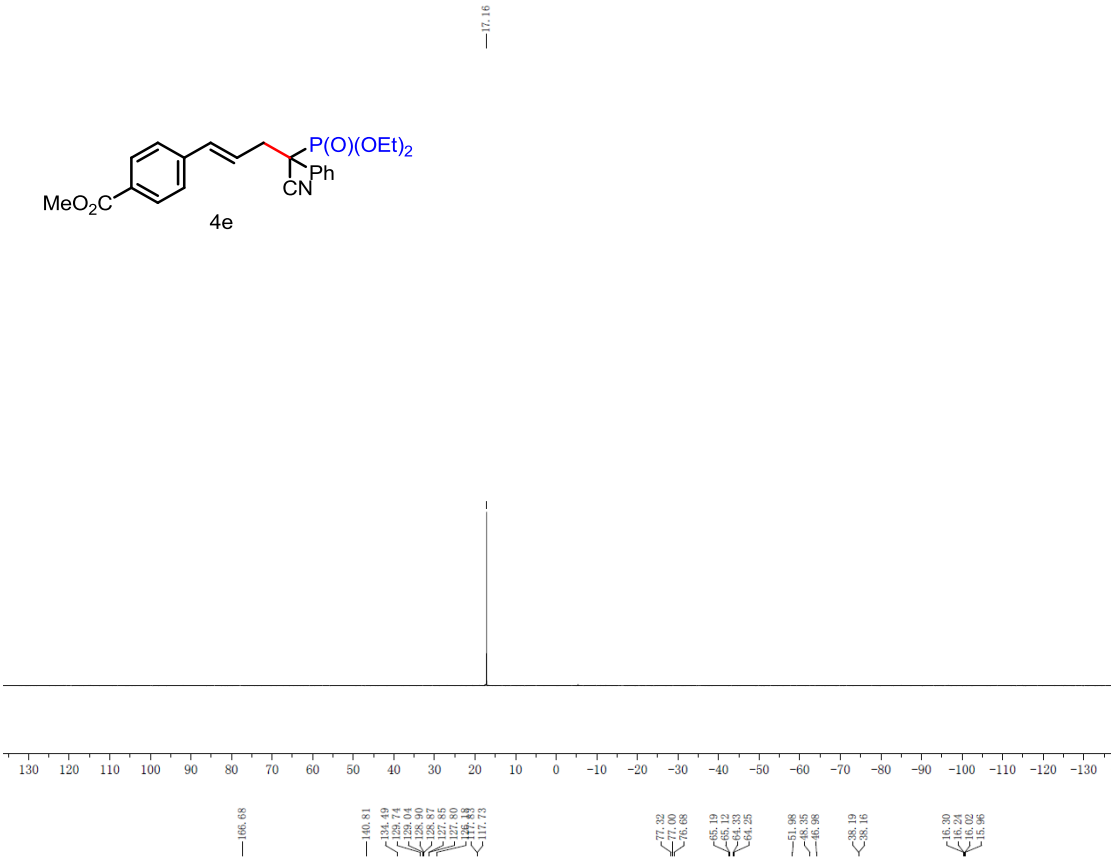


4e



P(O)(OEt)2
Ph
CN
MeO2C

4e


17.16
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
166.68
140.81
134.49
129.74
129.04
128.90
128.57
127.85
127.80
117.73
77.32
77.00
76.68
65.19
65.12
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51.98
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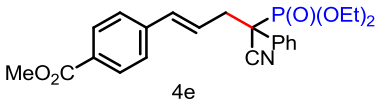
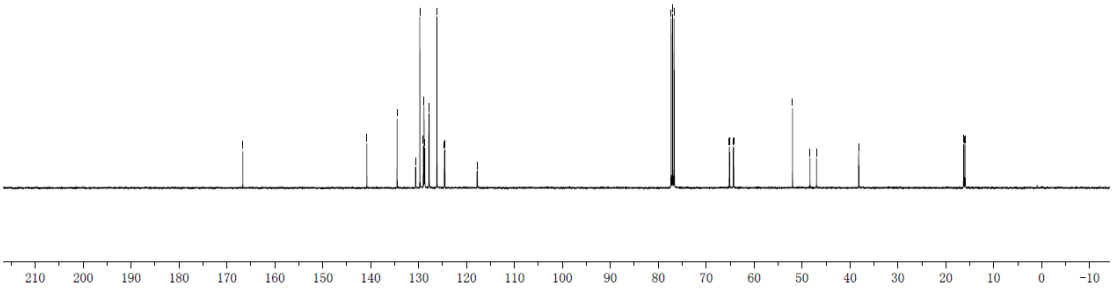
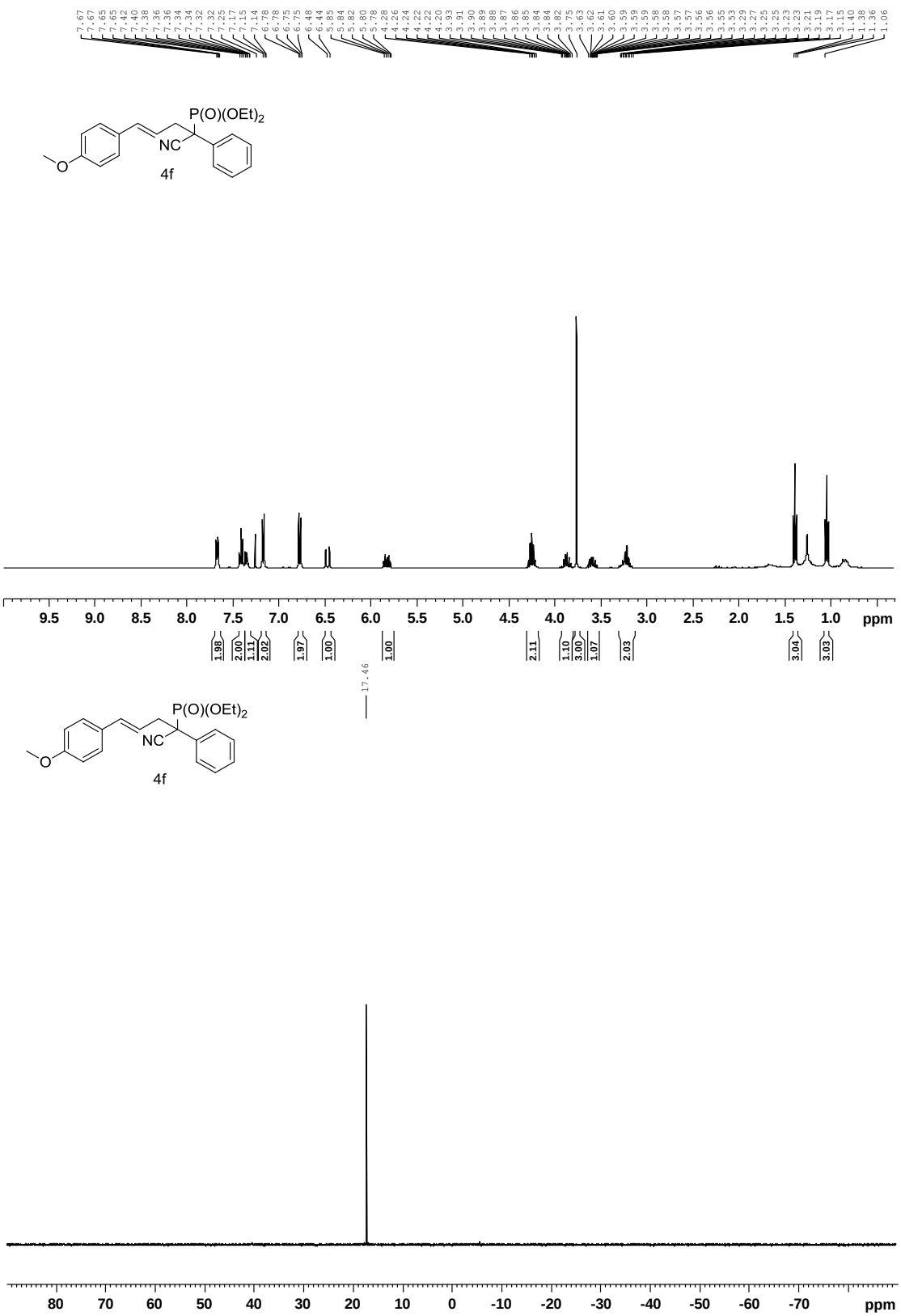
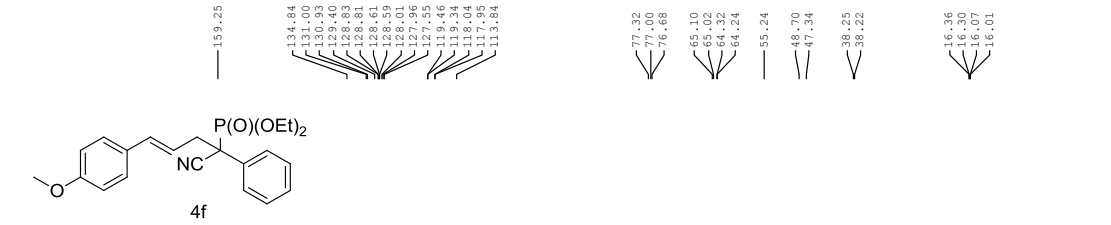
38.19
38.16
16.30
16.24
16.02
15.96


P(O)(OEt)2
Ph
CN
MeO2C

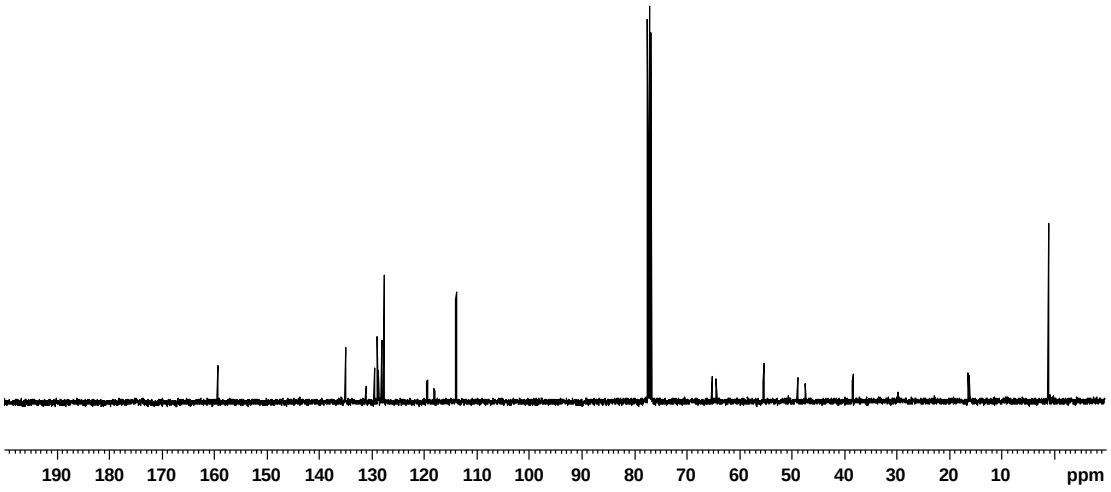
4e

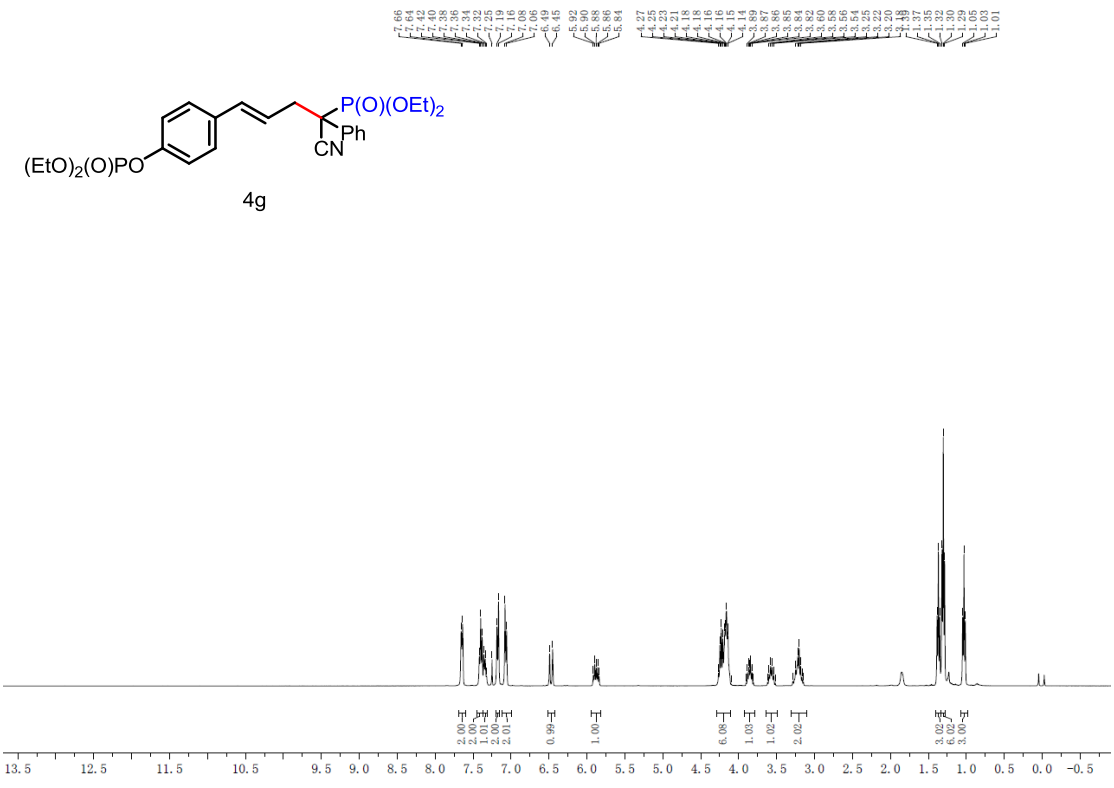

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.67 7.67 7.65 7.65 7.42 7.40 7.38 7.36 7.36 7.34 7.34 7.32 7.32 7.25 7.17 7.15 7.14 6.78 6.78 6.75 6.75 6.48 6.44 5.85 5.84 5.82 5.80 5.78 4.26 4.24 4.22 4.22 4.20 3.93 3.91 3.90 3.89 3.88 3.87 3.86 3.85 3.84 3.84 3.82 3.75 3.63 3.62 3.61 3.60 3.59 3.59 3.59 3.58 3.57 3.57 3.56 3.56 3.55 3.53 3.29 3.27 3.25 3.25 3.23 3.23 3.21 3.19 3.17 3.15 1.40 1.38 1.36 1.06
P(O)(OEt)2
NC
O
4f
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.98 2.00 1.11 2.02 1.97 1.00 1.00 2.11 1.10 3.00 1.07 2.03 3.04 3.03
17.46
P(O)(OEt)2
NC
O
4f
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm


159.25
134.84
131.00
130.93
129.40
128.83
128.81
128.61
128.59
128.01
127.96
127.55
119.46
119.34
118.04
117.95
113.84
77.32
77.00
76.68
65.10
65.02
64.32
64.24
55.24
48.70
47.34
38.25
38.22
16.36
16.30
16.07
16.01
P(O)(OEt)2
NC
O

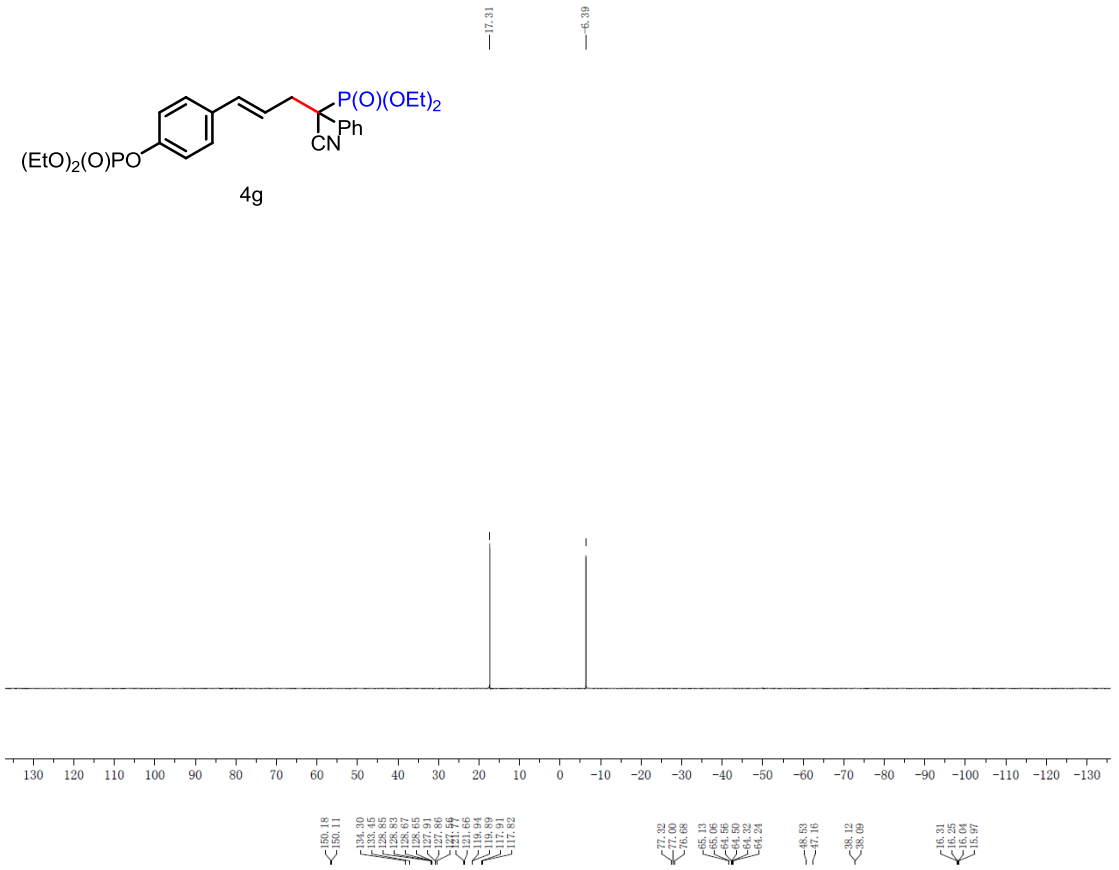
4f

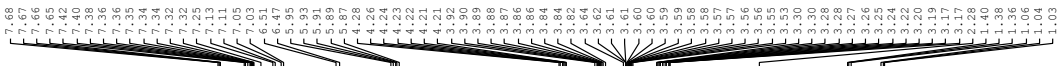

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

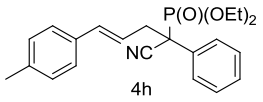

7.66
7.64
7.42
7.40
7.38
7.36
7.34
7.32
7.25
7.19
7.16
7.08
7.06
6.49
6.45
5.92
5.90
5.88
5.86
5.84
4.27
4.25
4.23
4.21
4.18
4.16
4.15
4.14
3.89
3.87
3.86
3.85
3.84
3.82
3.60
3.58
3.56
3.54
3.25
3.22
3.20
1.37
1.35
1.32
1.30
1.29
1.05
1.03
1.01
2.00
2.00
1.01
1.03
2.00
2.01
0.99
1.00
6.08
1.03
1.02
2.02
3.02
6.02
3.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

P(O)(OEt)2
Ph
CN
(EtO)2(O)PO

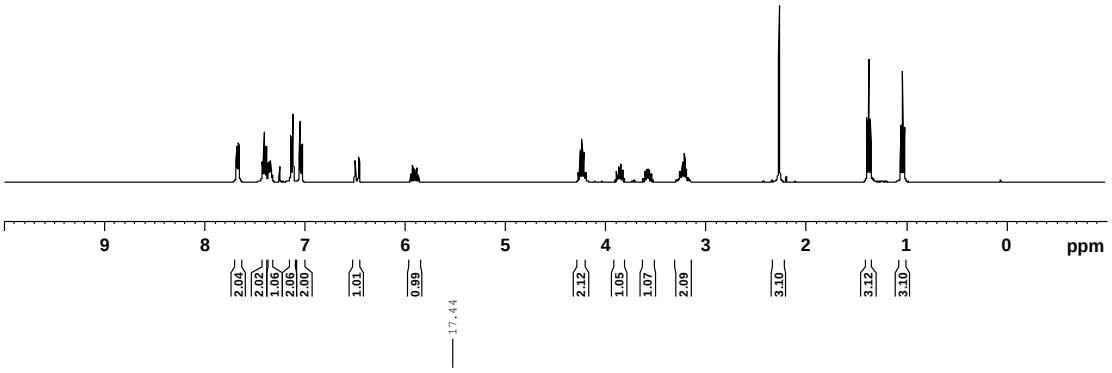
4g

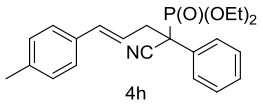

17.31
6.39
P(O)(OEt)2
Ph
CN
(EtO)2(O)PO
4g
130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130
150.18
150.11
134.30
133.45
128.85
128.83
128.67
128.65
127.91
127.86
121.66
118.94
118.89
117.91
117.82
77.32
77.00
76.68
65.13
65.06
64.56
64.50
64.32
64.24
48.53
47.16
38.12
38.09
16.31
16.25
16.04
15.97
P(O)(OEt)2
Ph
CN
(EtO)2(O)PO
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10



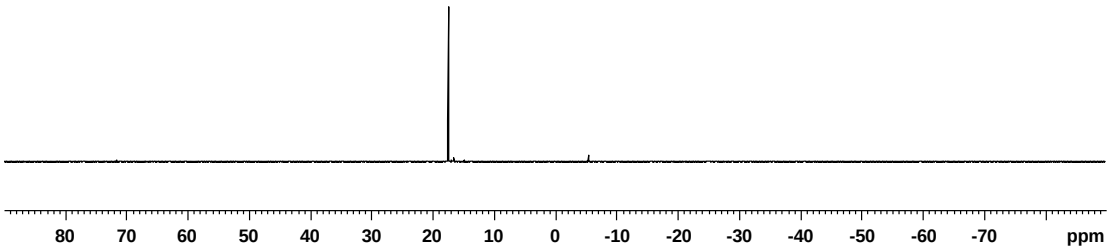

P(O)(OEt)2
NC

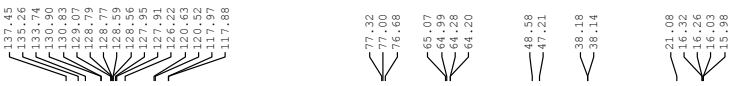
4h

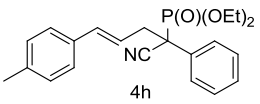

9
8
7
6
5
4
3
2
1
0
ppm
2.04
2.02
1.06
2.06
2.00
1.01
0.99
2.12
1.06
1.07
2.09
3.10
3.12
3.10
17.44


P(O)(OEt)2
NC

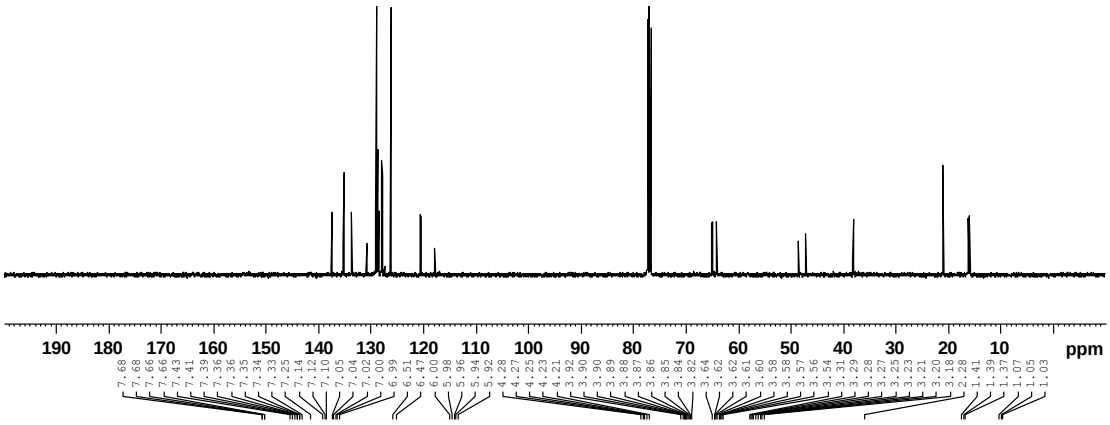
4h

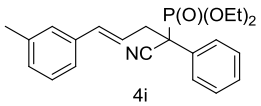

80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
ppm


137.45
135.26
133.74
130.90
130.83
129.07
128.79
128.77
128.59
128.56
127.95
127.91
126.22
120.63
120.52
117.97
117.88
77.32
77.00
76.68
65.07
64.99
64.28
64.20
48.58
47.21
38.18
38.14
21.08
16.32
16.26
16.03
15.98

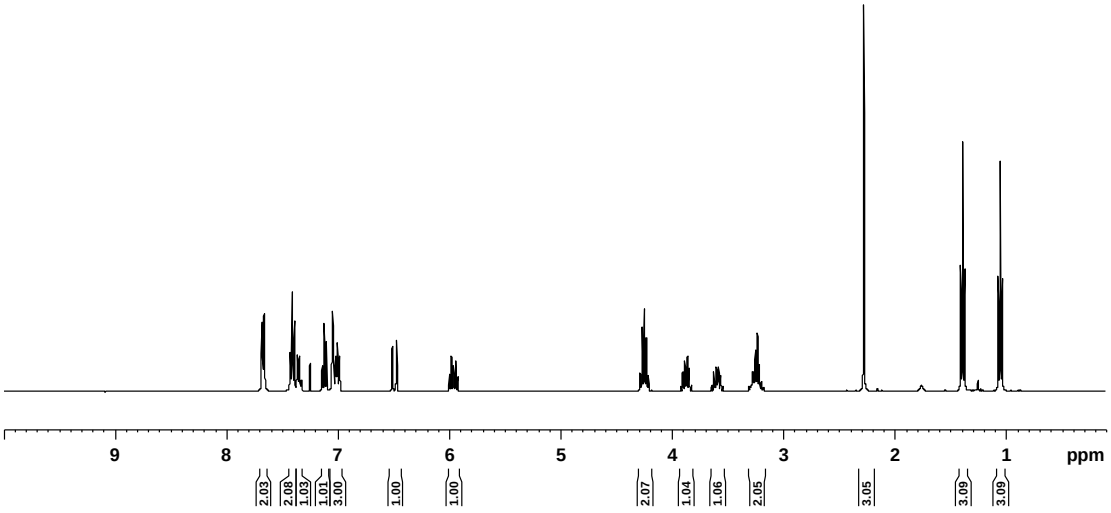

P(O)(OEt)2
NC

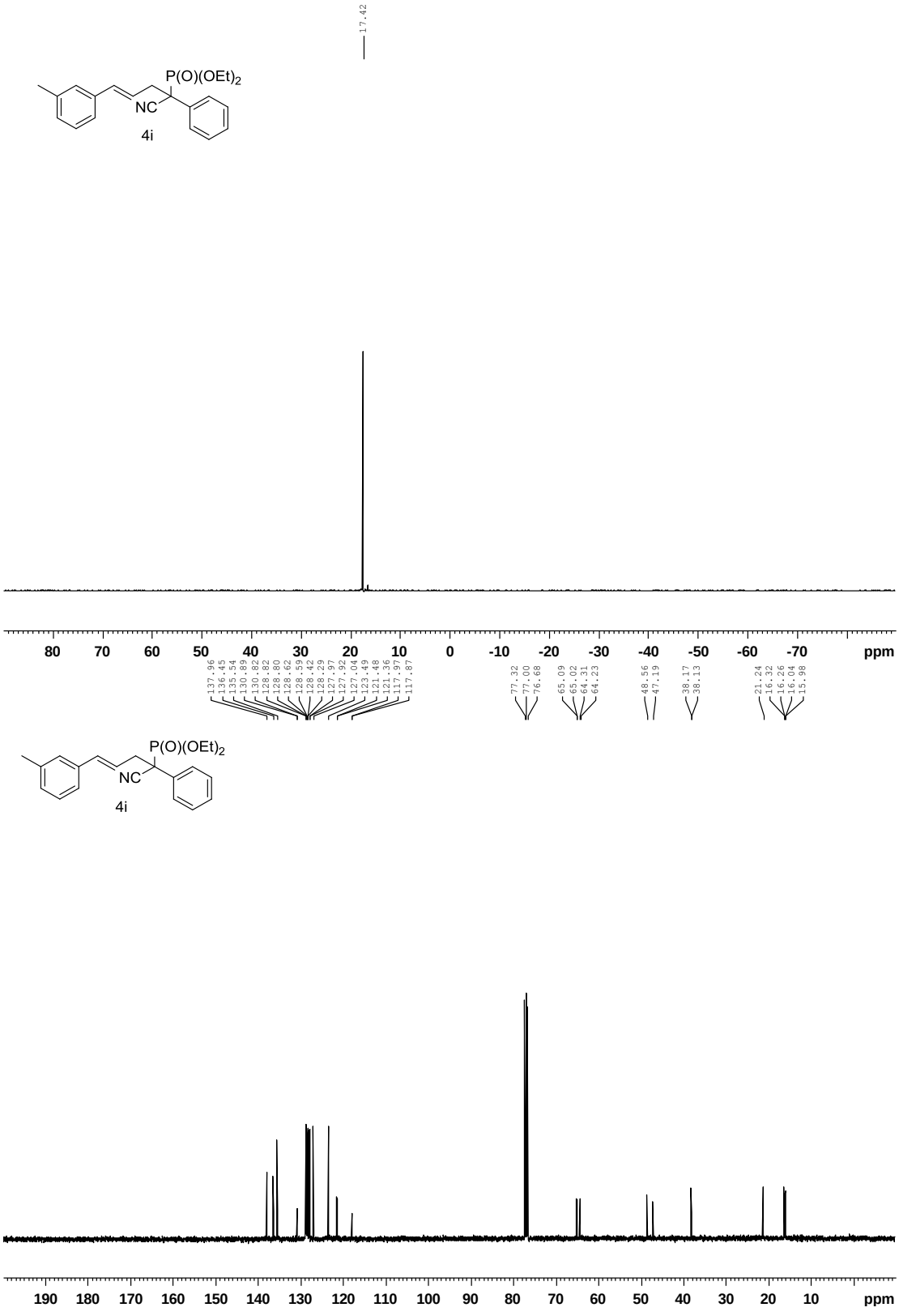
4h

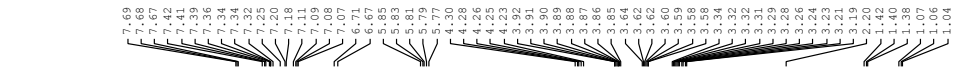

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
7.68
7.68
7.66
7.66
7.43
7.41
7.39
7.36
7.36
7.35
7.34
7.33
7.25
7.14
7.12
7.10
7.05
7.04
7.02
7.00
6.99
6.51
6.47
6.00
5.98
5.96
5.94
5.92
4.28
4.27
4.25
4.23
4.21
4.02
3.90
3.90
3.89
3.88
3.87
3.86
3.85
3.84
3.82
3.64
3.62
3.62
3.61
3.60
3.58
3.58
3.57
3.56
3.54
3.31
3.29
3.28
3.27
3.25
3.23
3.21
3.20
3.18
2.28
1.41
1.39
1.07
1.05
1.03

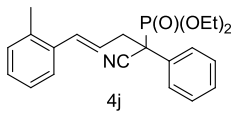

P(O)(OEt)2
NC

4i

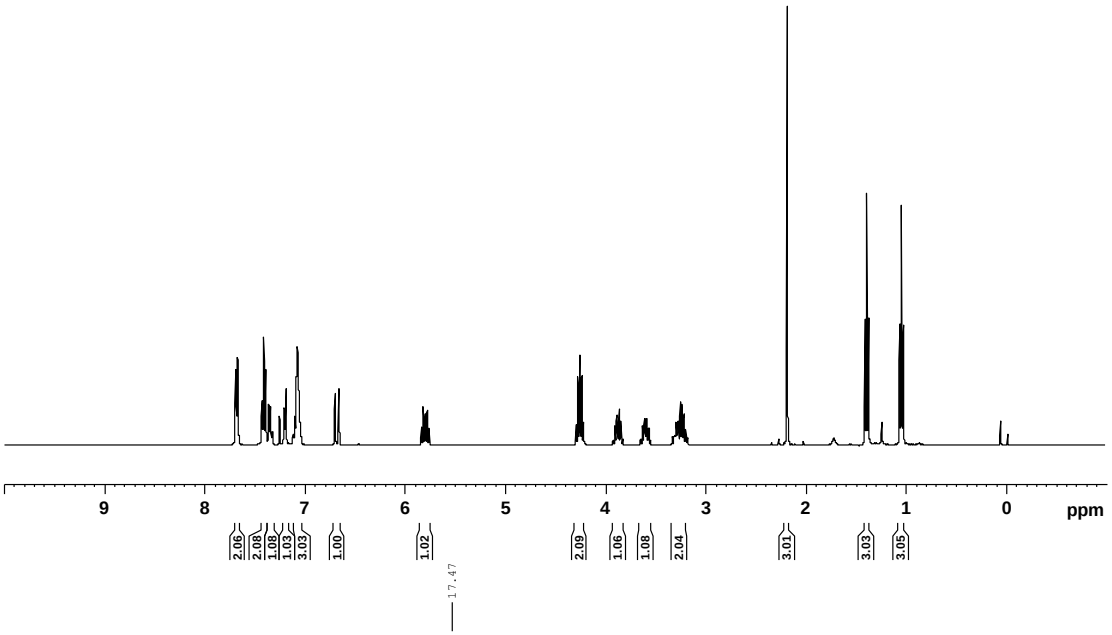

9 8 7 6 5 4 3 2 1 ppm
2.03
2.08
1.03
1.01
3.00
1.00
1.00
2.07
1.04
1.06
2.05
3.05
3.09
3.09

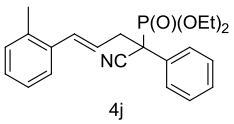

17.42
P(O)(OEt)2
NC
4i
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm
137.96
136.45
135.54
130.89
130.82
128.82
128.80
128.62
128.59
128.42
128.29
127.97
127.92
127.04
123.49
121.48
121.36
117.97
117.87
77.32
77.00
76.68
65.09
65.02
64.31
64.23
48.56
47.19
38.17
38.13
21.24
16.32
16.26
16.04
15.98
P(O)(OEt)2
NC
4i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.69
7.68
7.67
7.42
7.41
7.39
7.36
7.34
7.34
7.32
7.25
7.20
7.18
7.11
7.09
7.08
7.07
6.71
6.67
5.85
5.83
5.81
5.79
5.77
4.30
4.28
4.26
4.25
4.23
4.22
3.91
3.90
3.89
3.88
3.87
3.86
3.85
3.64
3.62
3.62
3.60
3.59
3.58
3.58
3.34
3.32
3.32
3.31
3.29
3.28
3.26
3.24
3.23
3.21
3.19
2.20
1.42
1.40
1.38
1.07
1.06
1.04

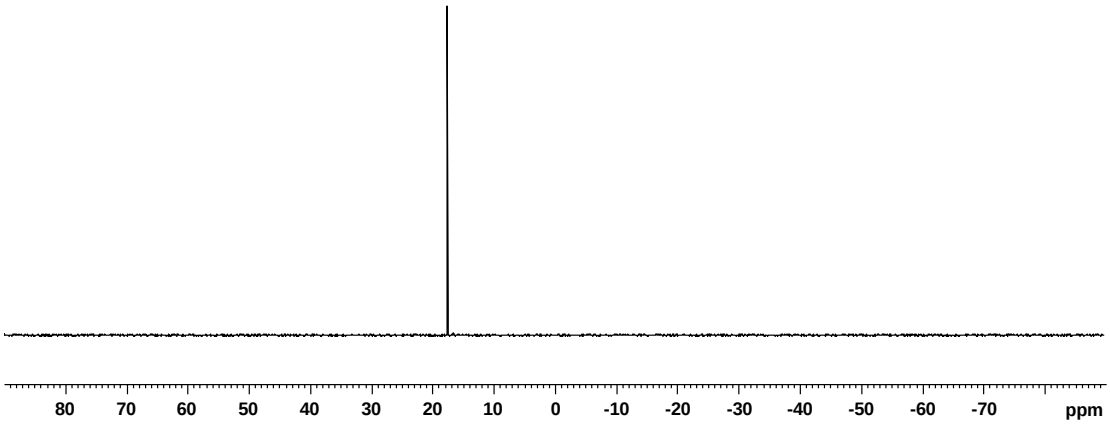

P(O)(OEt)2
NC

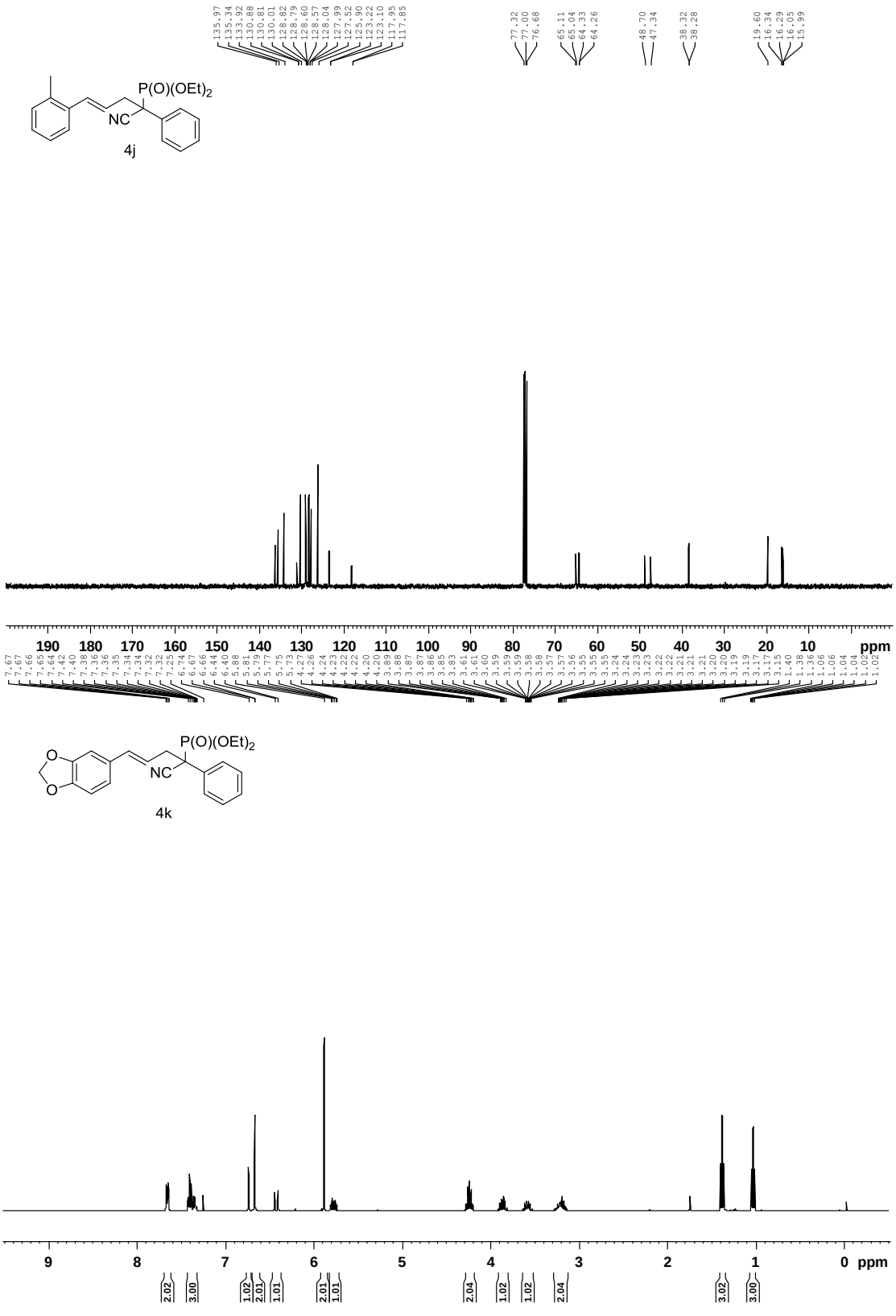
4j

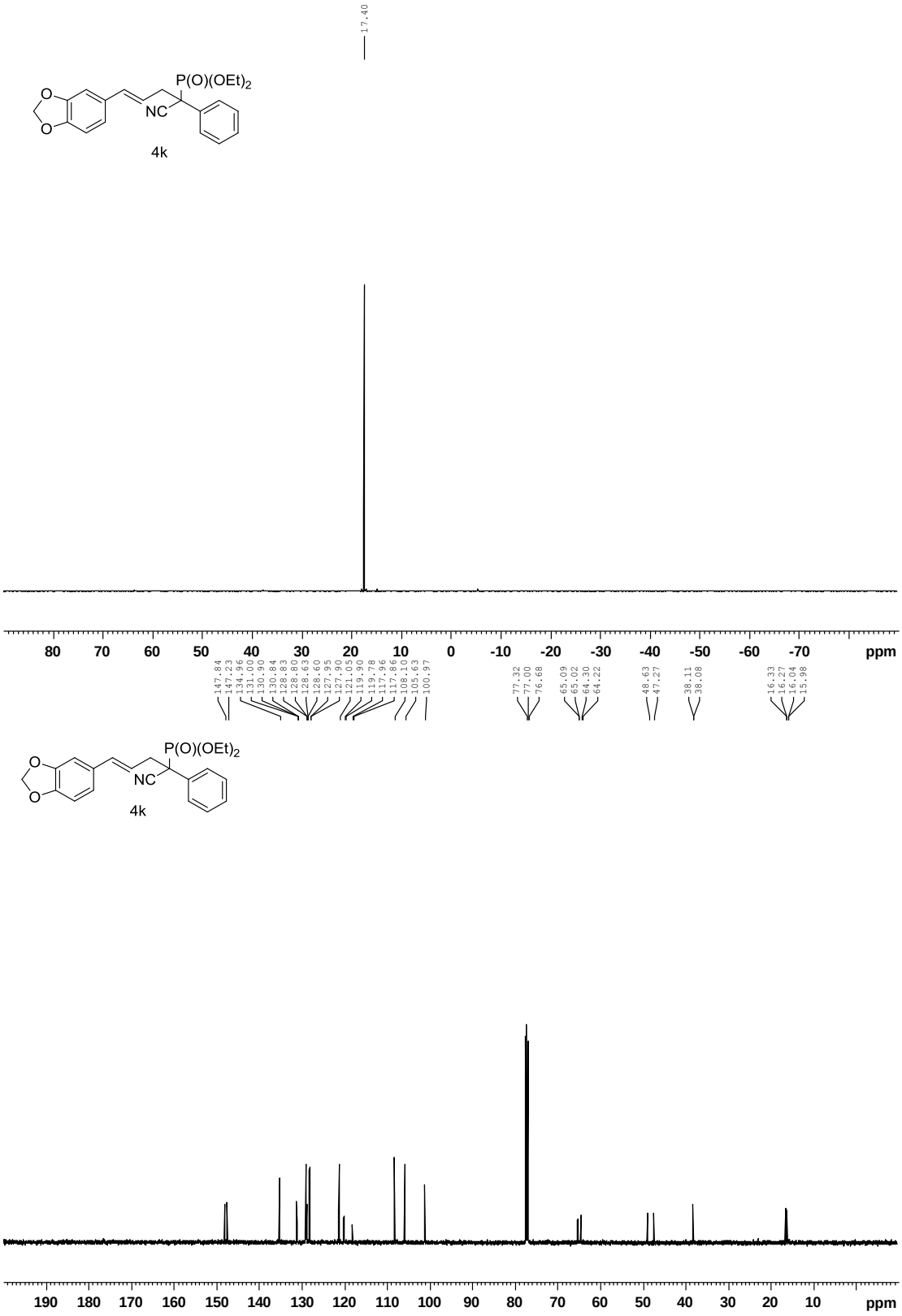

9
8
7
6
5
4
3
2
1
0
ppm
2.06
2.08
1.08
1.03
3.03
1.00
1.02
2.09
1.06
1.08
2.04
3.01
3.03
3.05
17.47

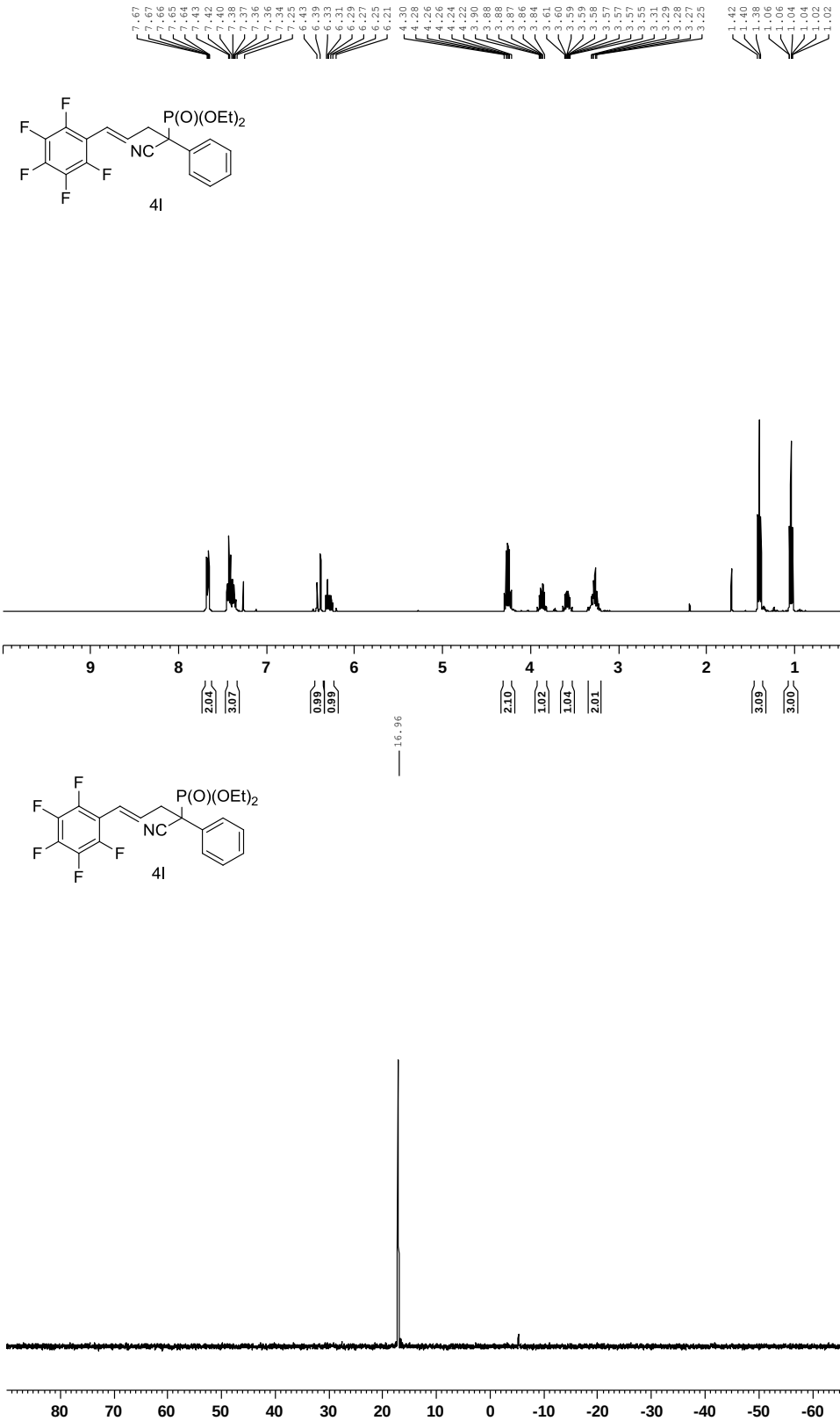

P(O)(OEt)2
NC

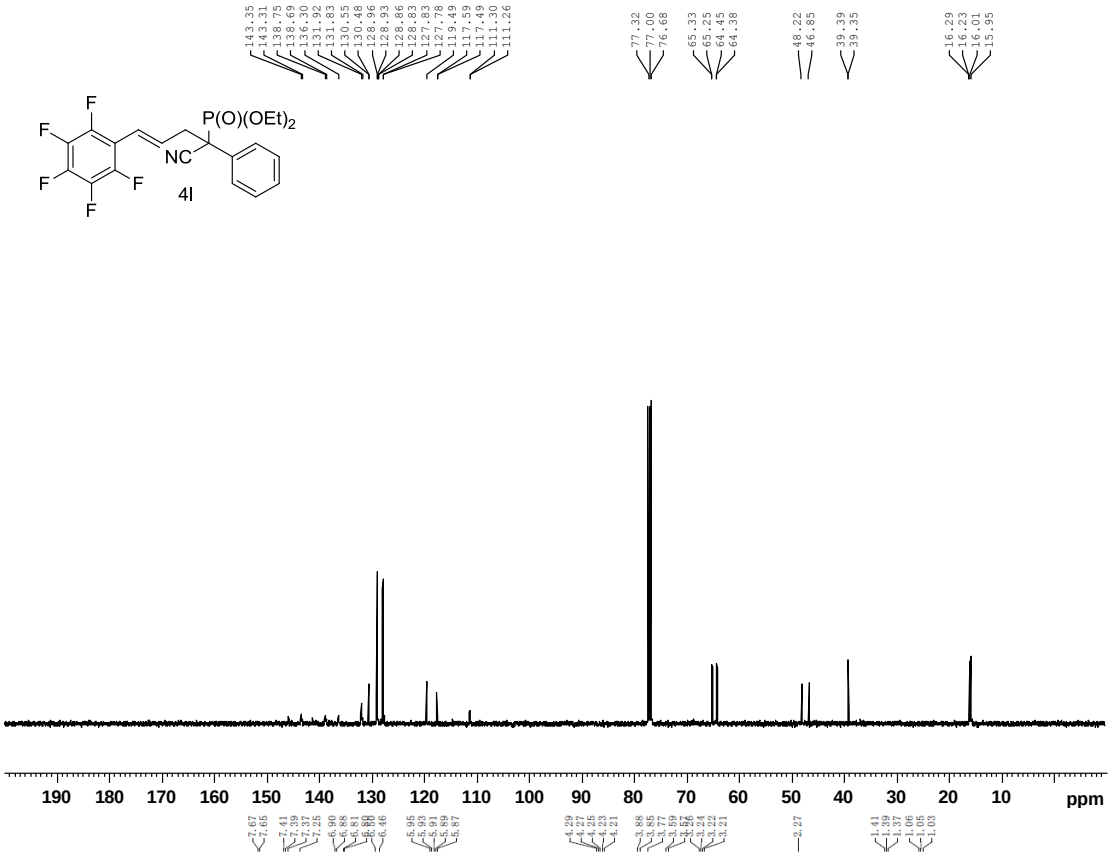
4j

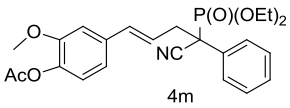

80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
ppm

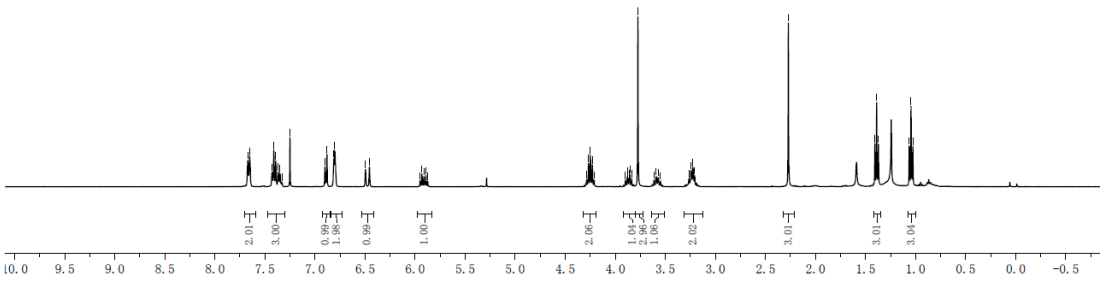

135.97
135.34
133.92
130.88
130.81
130.01
128.82
128.79
128.60
128.57
128.04
127.99
127.52
127.30
123.22
123.10
117.95
117.85
77.32
77.00
76.68
65.11
65.04
64.33
64.26
48.70
47.34
38.32
38.28
19.60
16.34
16.29
16.05
15.99
P(O)(OEt)2
NC
4j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
7.67
7.67
7.66
7.65
7.64
7.42
7.40
7.38
7.36
7.36
7.35
7.34
7.34
7.32
7.32
7.25
6.74
6.67
6.66
6.44
6.40
5.88
5.87
5.79
5.77
5.75
5.73
4.27
4.26
4.24
4.23
4.22
4.22
4.20
4.20
3.89
3.88
3.87
3.87
3.86
3.85
3.83
3.61
3.61
3.60
3.59
3.59
3.59
3.58
3.57
3.57
3.56
3.55
3.55
3.55
3.24
3.24
3.23
3.23
3.22
3.22
3.21
3.21
3.21
3.20
3.20
3.19
3.19
3.17
3.15
1.40
1.38
1.36
1.06
1.04
1.04
1.02
1.02
O
O
P(O)(OEt)2
NC
4k
9 8 7 6 5 4 3 2 1 0 ppm
2.02
3.00
1.02
2.01
1.01
2.01
1.01
2.04
1.02
1.02
2.04
3.02
3.00

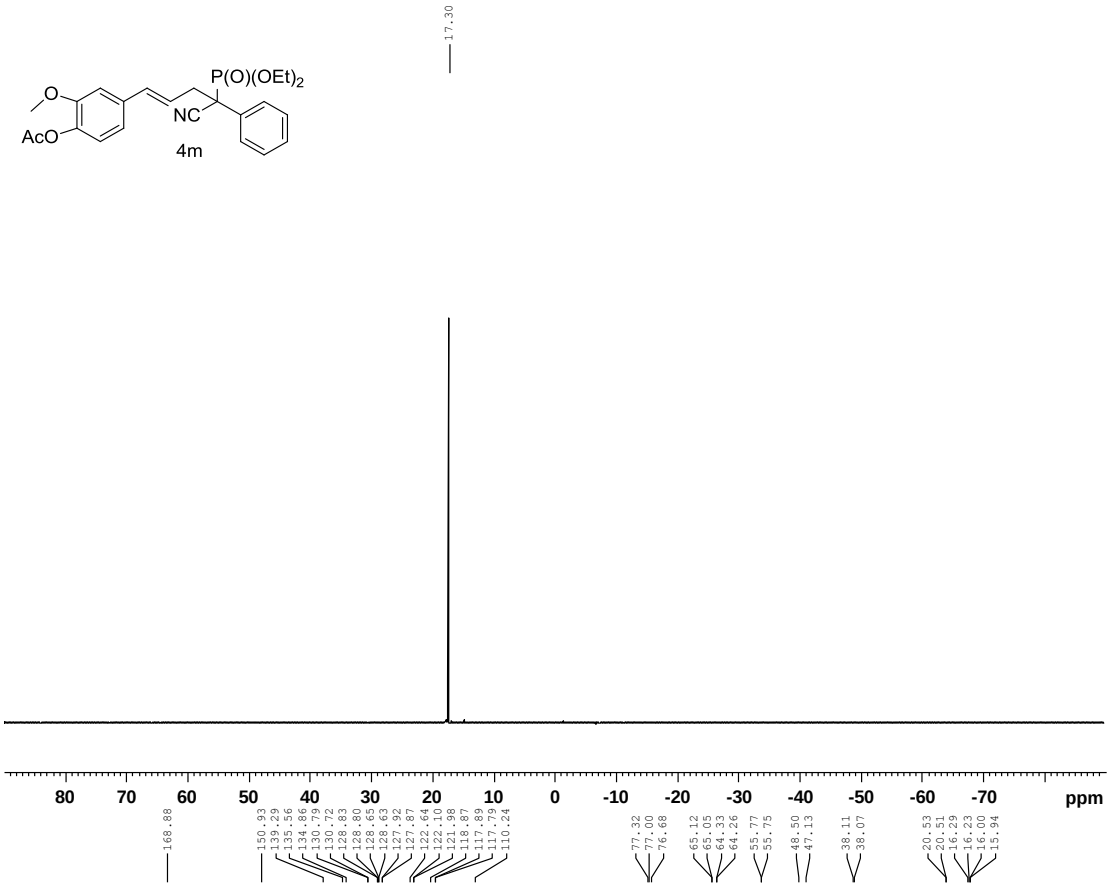

17.40
P(O)(OEt)2
NC
O
O
4k
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm
147.84
147.23
134.96
131.00
130.90
130.84
128.83
128.80
128.63
128.60
127.95
127.90
121.00
119.99
119.79
117.96
117.86
108.10
105.63
100.97
77.32
77.00
76.68
65.09
65.02
64.30
64.22
48.63
47.27
38.11
38.08
16.33
16.27
16.04
15.98
P(O)(OEt)2
NC
O
O
4k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

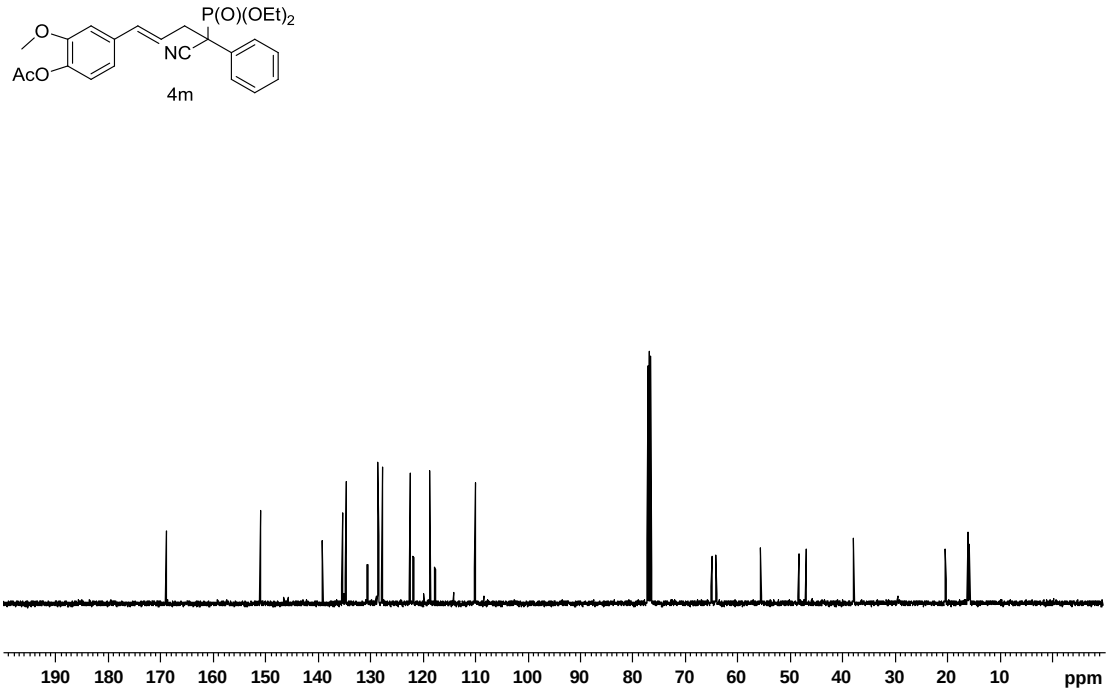

7.67
7.67
7.66
7.65
7.64
7.43
7.42
7.40
7.38
7.37
7.36
7.36
7.34
7.25
6.43
6.39
6.33
6.31
6.29
6.27
6.25
6.21
4.30
4.28
4.26
4.26
4.24
4.22
3.90
3.88
3.87
3.86
3.84
3.61
3.60
3.59
3.59
3.58
3.57
3.57
3.55
3.31
3.29
3.28
3.27
3.25
1.42
1.40
1.38
1.06
1.06
1.04
1.04
1.02
1.02
F
F
F
F
F
P(O)(OEt)2
NC
4l
9
8
7
6
5
4
3
2
1
0
ppm
2.04
3.07
0.99
0.99
2.10
1.02
1.04
2.01
3.09
3.00
16.96
F
F
F
F
F
P(O)(OEt)2
NC
4l
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
ppm

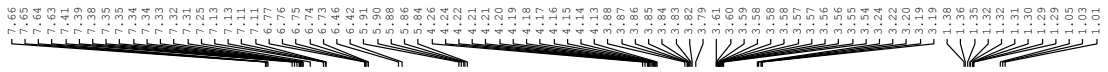

143.35
143.31
138.75
138.69
136.90
136.32
131.83
130.55
130.48
128.96
128.93
128.86
128.83
127.83
127.78
119.49
117.59
117.49
111.30
111.26
77.32
77.00
76.68
65.33
65.25
64.45
64.38
48.22
46.85
39.39
39.35
16.29
16.23
16.01
15.95
F
F
F
F
F
P(O)(OEt)2
NC
4l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
7.67
7.65
7.41
7.39
7.37
7.35
6.90
6.88
6.81
6.79
6.46
5.95
5.93
5.91
5.89
5.87
4.29
4.27
4.25
4.23
4.21
3.88
3.85
3.77
3.59
3.57
3.24
3.22
3.21
2.27
1.41
1.39
1.37
1.06
1.05
1.03

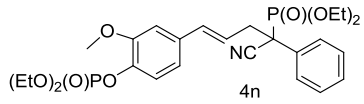

O
AcO
P(O)(OEt)2
NC
4m


2.01
3.00
0.99
1.98
0.99
1.00
2.06
1.04
2.04
1.06
2.02
3.01
3.01
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

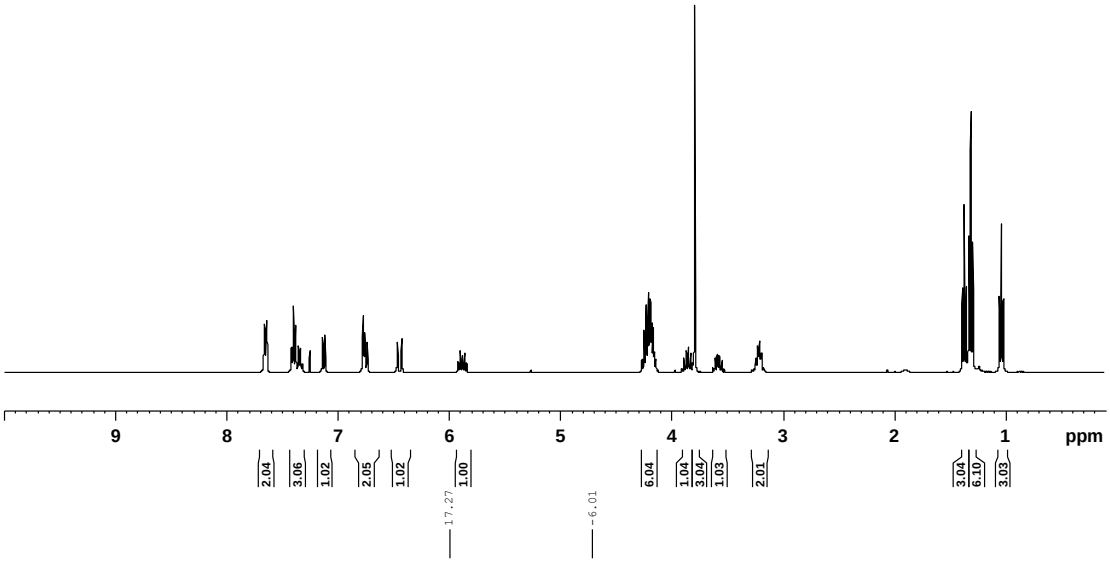

P(O)(OEt)2
O
NC
AcO
4m
17.30
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm
168.88
150.93
139.29
135.56
134.86
130.79
130.72
128.83
128.80
128.65
128.63
127.92
127.87
122.64
122.10
121.98
118.87
117.89
117.79
110.24
77.32
77.00
76.68
65.12
65.05
64.33
64.26
55.77
55.75
48.50
47.13
38.11
38.07
20.53
20.51
16.29
16.23
16.00
15.94

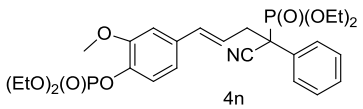

P(O)(OEt)2
O
NC
AcO
4m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.66 7.65 7.64 7.63 7.41 7.39 7.38 7.35 7.35 7.34 7.34 7.33 7.32 7.31 7.25 7.13 7.13 7.11 7.11 6.77 6.76 6.75 6.74 6.73 6.46 6.42 5.91 5.90 5.88 5.86 5.84 4.26 4.24 4.22 4.21 4.20 4.19 4.18 4.17 4.16 4.15 4.14 4.13 3.88 3.87 3.86 3.85 3.84 3.83 3.82 3.79 3.61 3.60 3.59 3.58 3.58 3.58 3.57 3.57 3.56 3.56 3.55 3.54 3.24 3.22 3.20 3.19 3.19 1.38 1.36 1.35 1.32 1.32 1.31 1.30 1.29 1.29 1.05 1.03 1.01

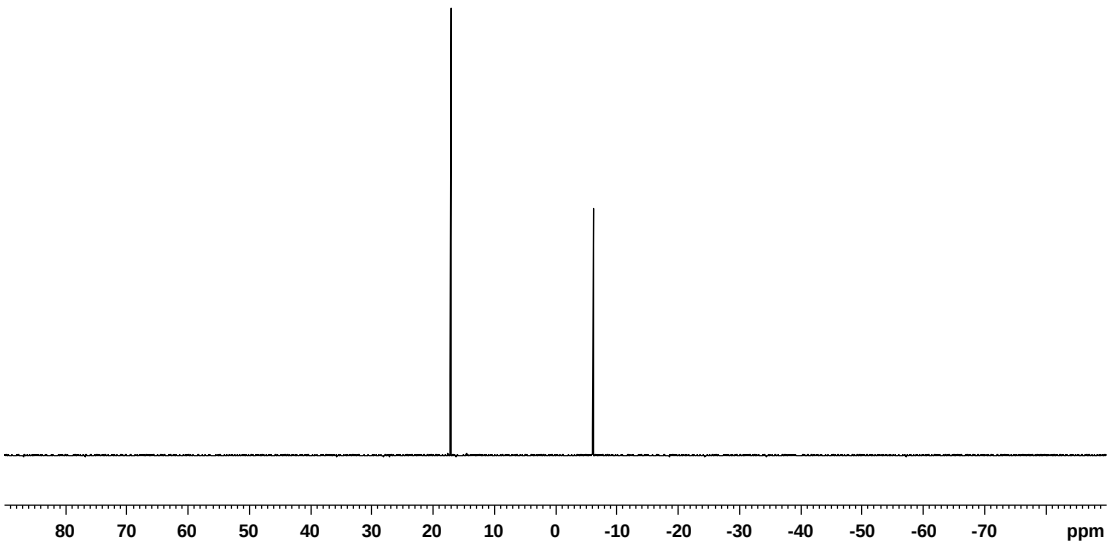

P(O)(OEt)2
O
NC
(EtO)2(O)PO

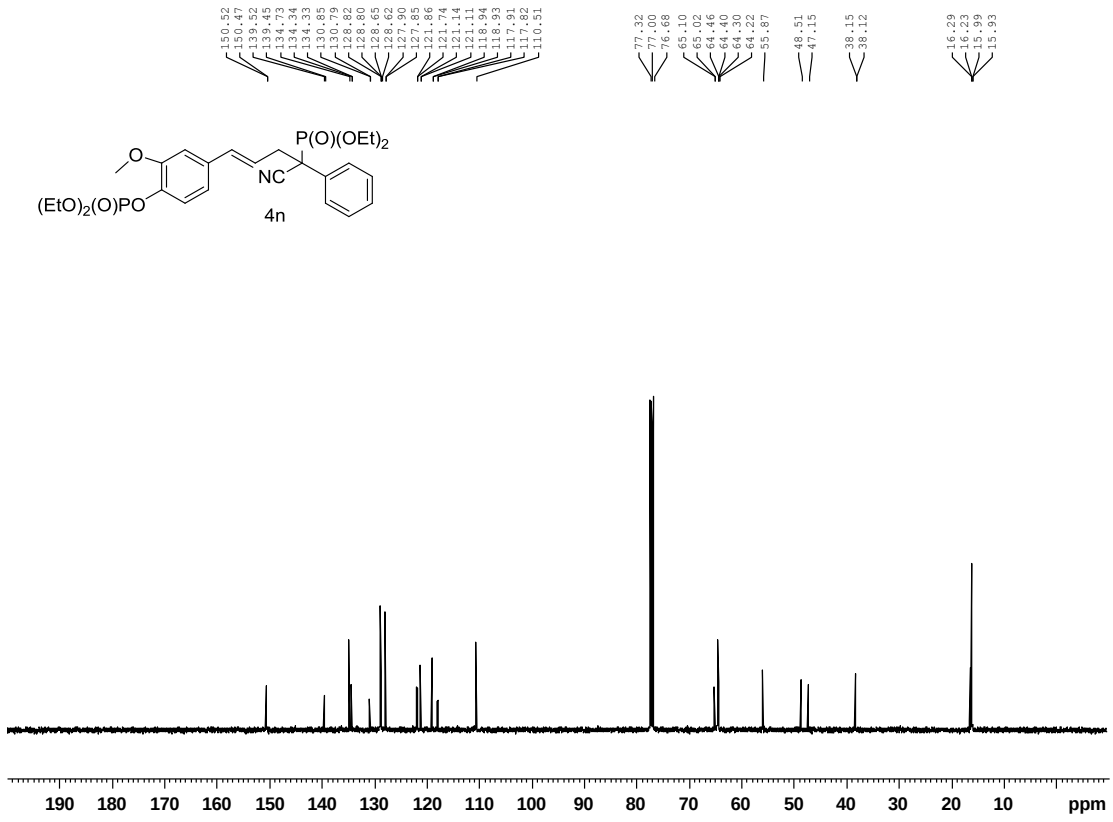
4n

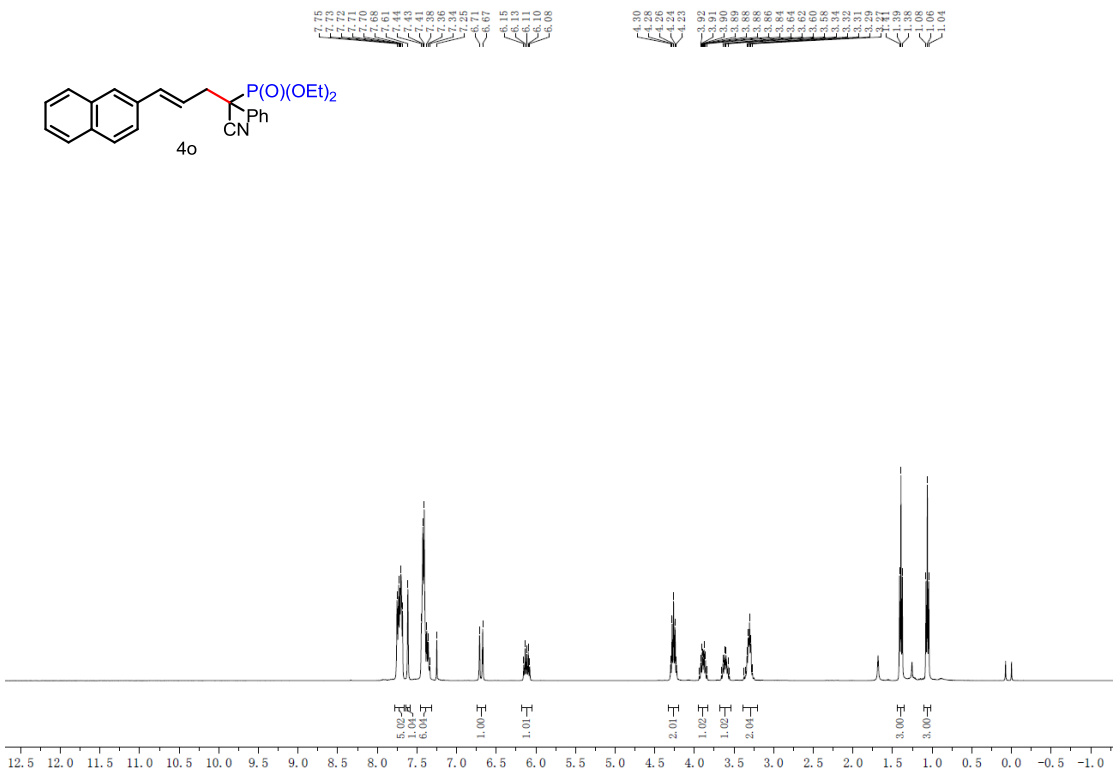

9
8
7
6
5
4
3
2
1
ppm
2.04
3.06
1.02
2.05
1.02
1.00
6.04
1.04
3.04
1.03
2.01
3.04
6.10
3.03
17.27
6.01

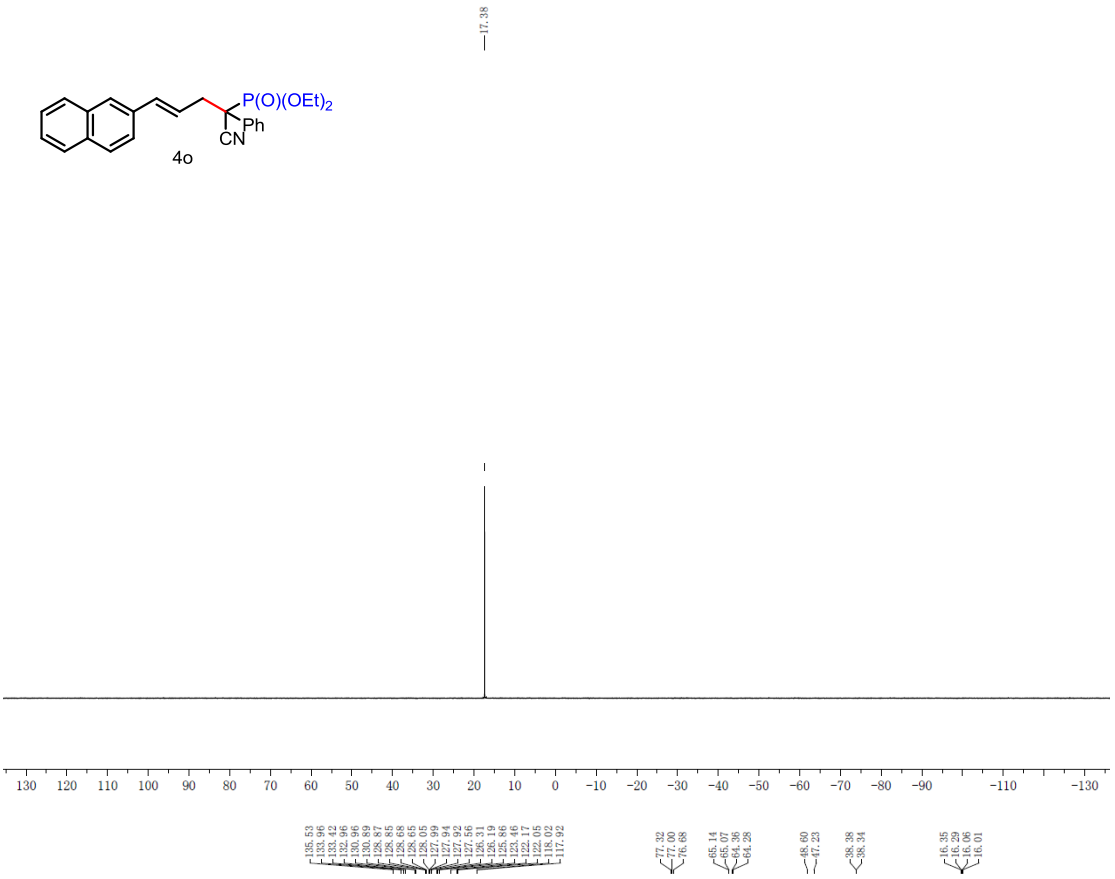

P(O)(OEt)2
O
NC
(EtO)2(O)PO

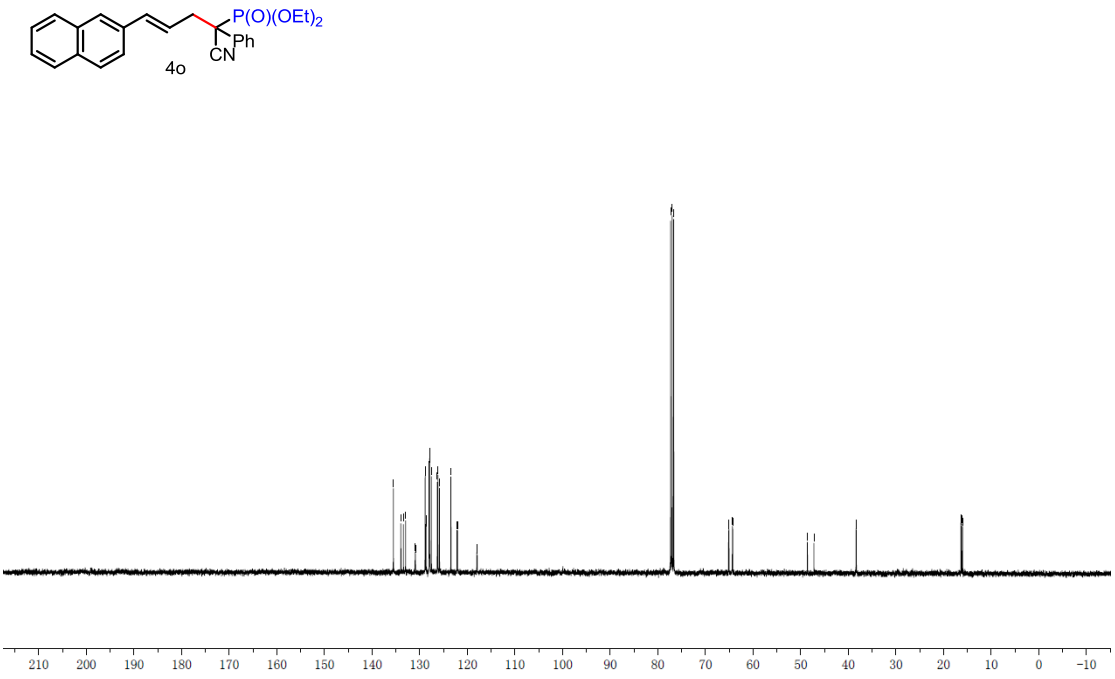
4n

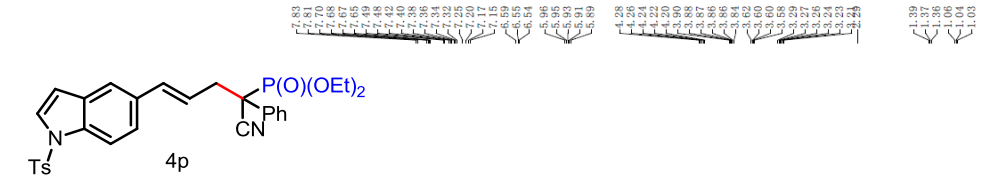

80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
ppm

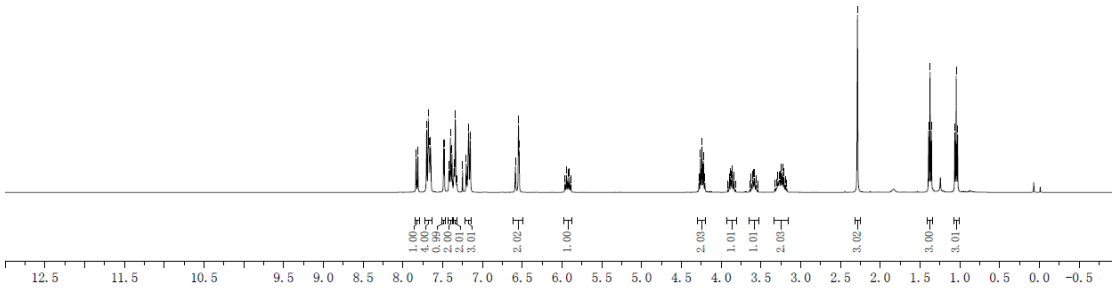

150.52
150.47
139.52
139.45
134.73
134.54
134.33
134.25
130.79
128.82
128.80
128.65
128.62
127.90
127.85
121.86
121.74
121.14
121.11
118.94
118.93
117.91
117.82
110.51
77.32
77.00
76.68
65.10
65.02
64.46
64.40
64.30
64.22
55.87
48.51
47.15
38.15
38.12
16.29
16.23
15.99
15.93
P(O)(OEt)2
O
NC
(EtO)2(O)PO
4n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

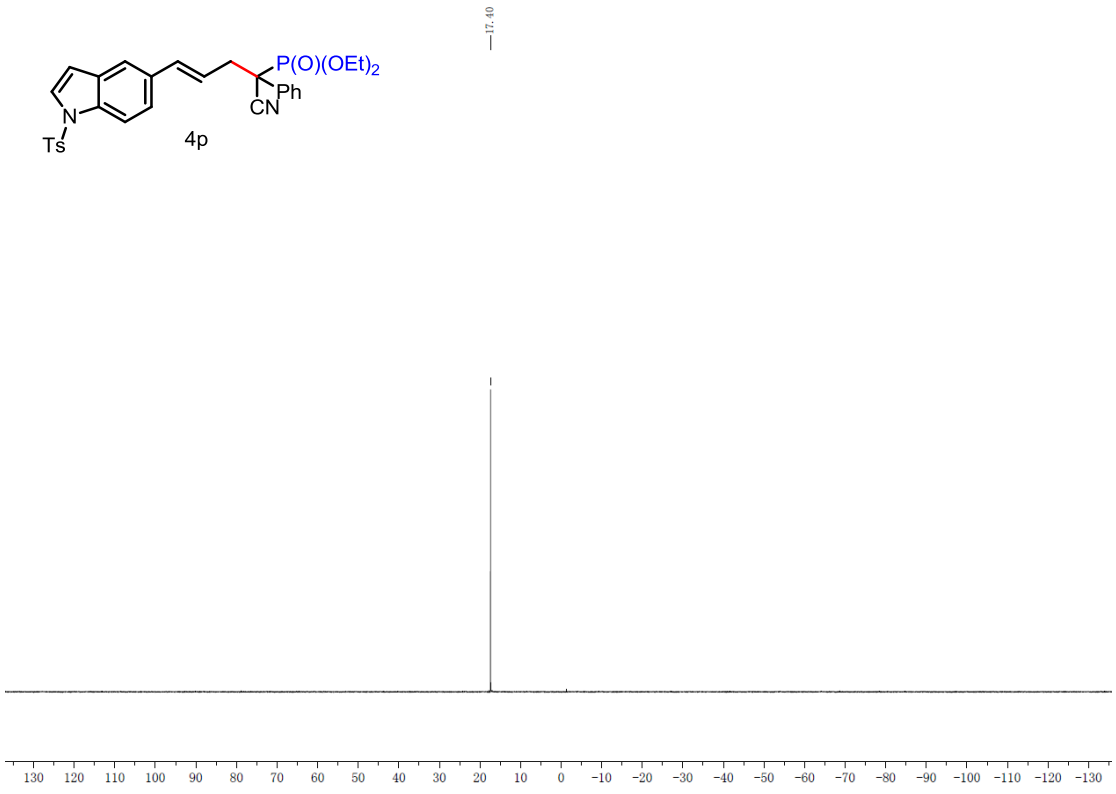

7.75
7.73
7.72
7.71
7.70
7.68
7.61
7.44
7.43
7.41
7.38
7.36
7.34
7.25
7.11
6.67
6.15
6.13
6.11
6.10
6.08
4.30
4.28
4.26
4.24
4.23
3.92
3.91
3.90
3.89
3.88
3.86
3.84
3.64
3.62
3.60
3.58
3.34
3.32
3.31
3.29
3.27
1.41
1.39
1.38
1.08
1.06
1.04
P(O)(OEt)2
Ph
CN
4o
5.02
1.04
6.04
1.00
1.01
2.01
1.02
1.02
2.04
3.00
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

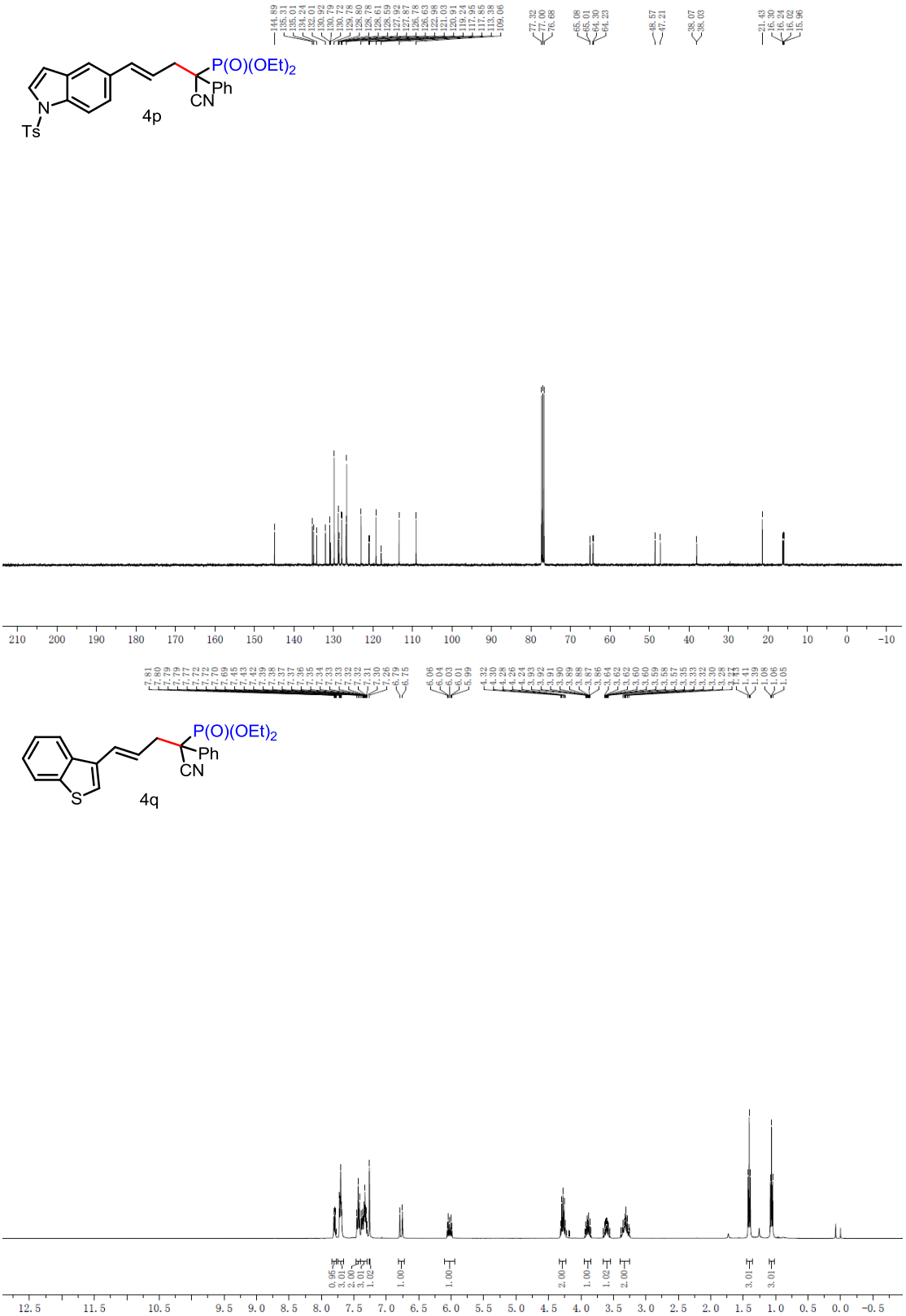

17.38
P(O)(OEt)2
Ph
CN
4o
135.53
133.96
133.43
132.96
130.96
130.89
128.87
128.65
128.05
127.99
127.94
127.92
127.56
126.31
126.19
125.86
125.46
122.17
122.05
118.02
117.92
77.32
77.00
76.68
65.14
65.07
64.36
64.28
48.60
47.23
38.38
38.34
16.35
16.29
16.06
16.01

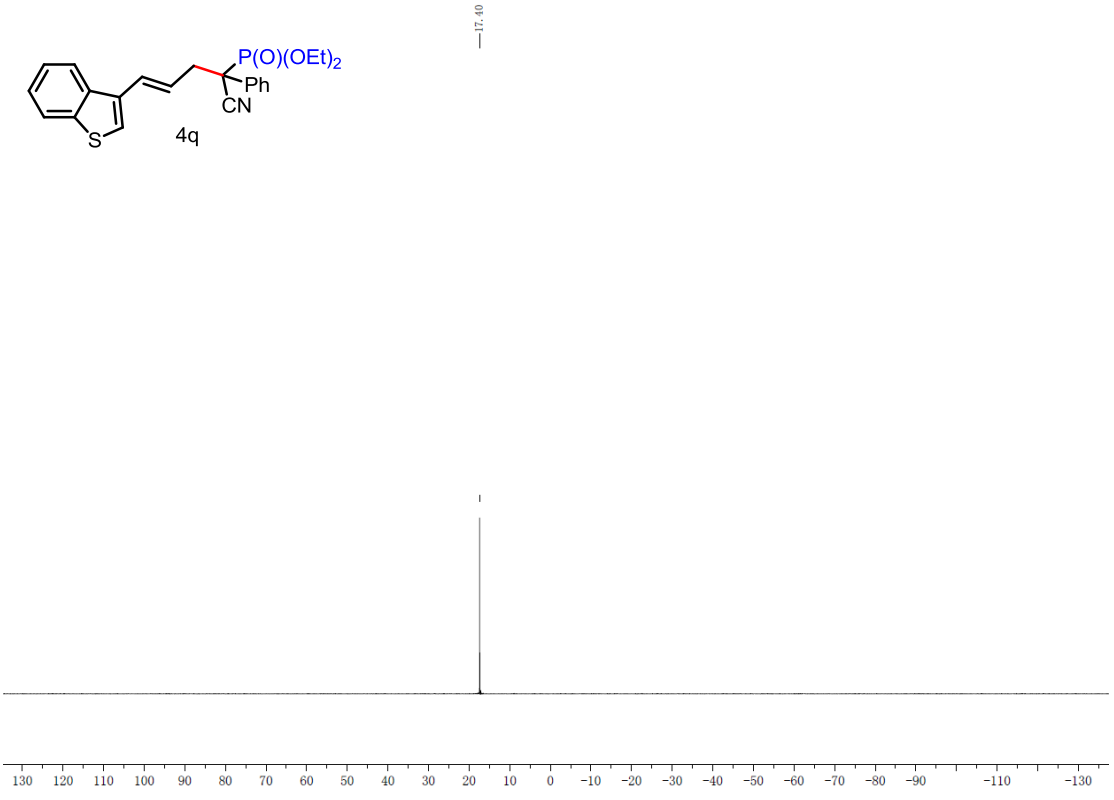

P(O)(OEt)2
Ph
CN
4o

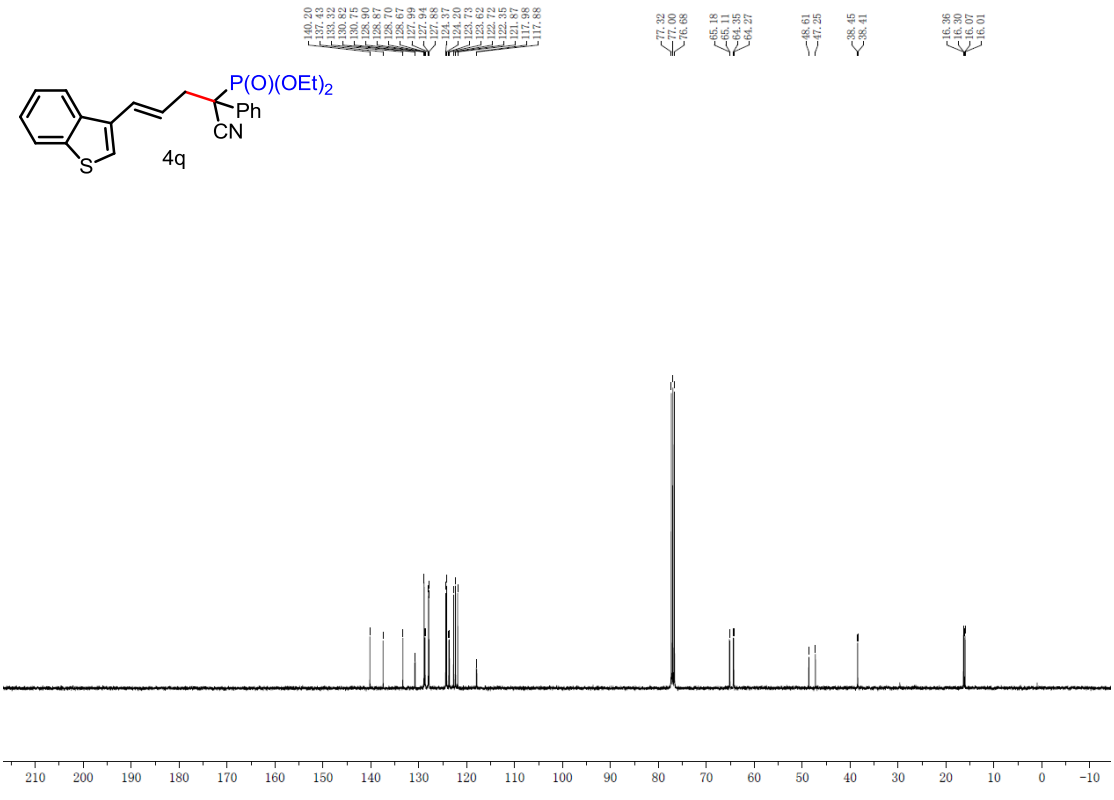




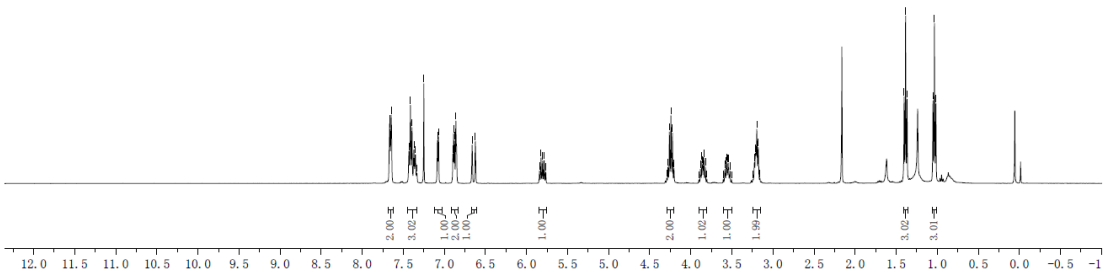


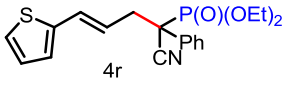

P(O)(OEt)2
Ph
CN
N
Ts
4p
P(O)(OEt)2
Ph
CN
S
4q


P(O)(OEt)2
Ph
CN
S
4q
17.40
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130

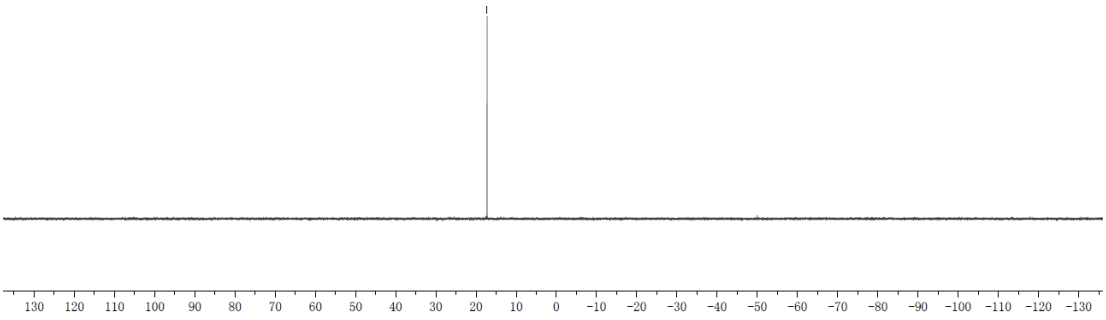

140.20
137.43
135.32
130.82
130.75
128.90
128.87
128.70
128.67
127.99
127.94
127.88
124.37
124.20
123.73
123.62
122.72
122.35
121.87
117.98
117.88
77.32
77.00
76.68
65.18
65.11
64.35
64.27
48.61
47.25
38.45
38.41
16.36
16.30
16.07
16.01
P(O)(OEt)2
Ph
CN
S
4q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

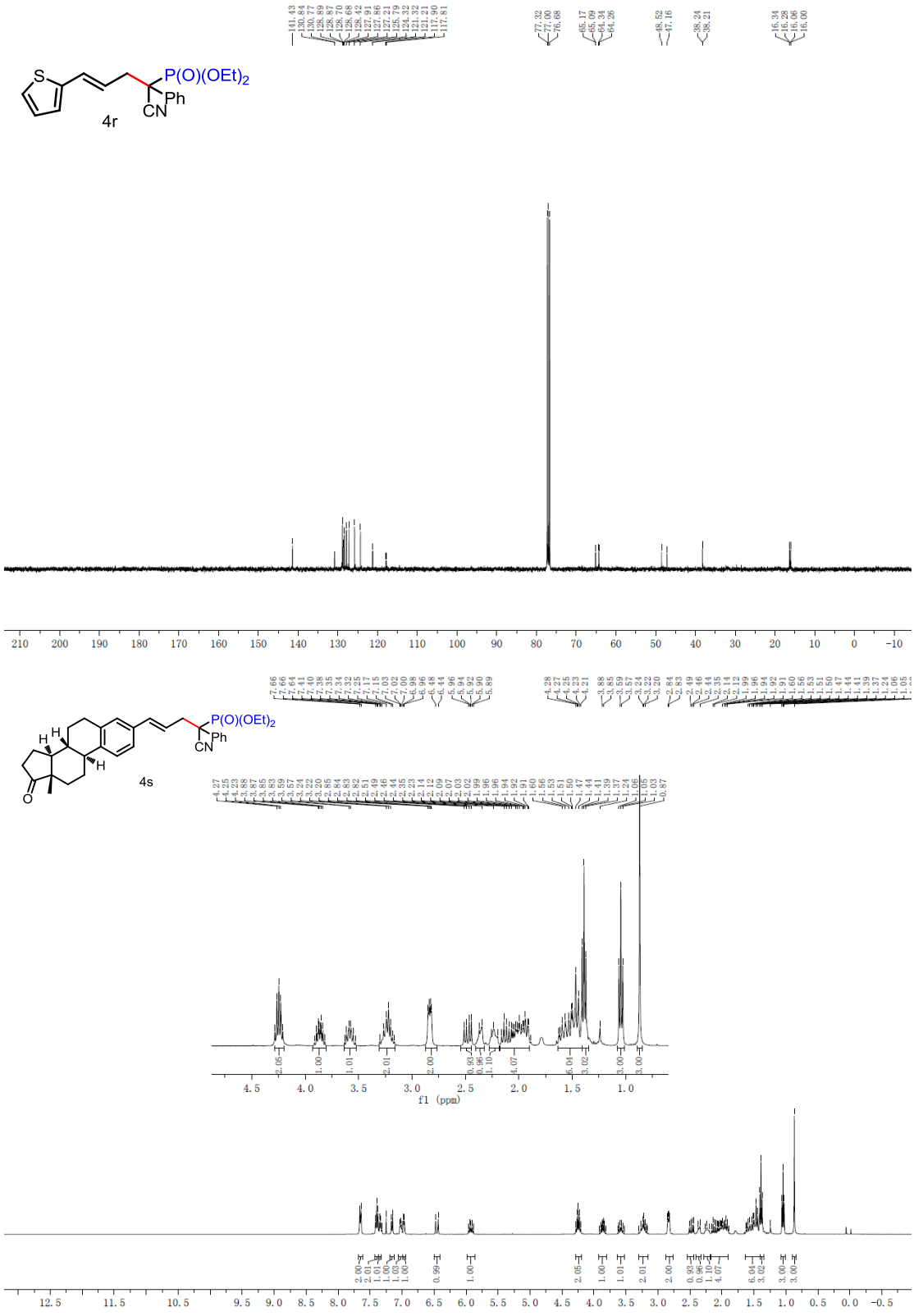
4r



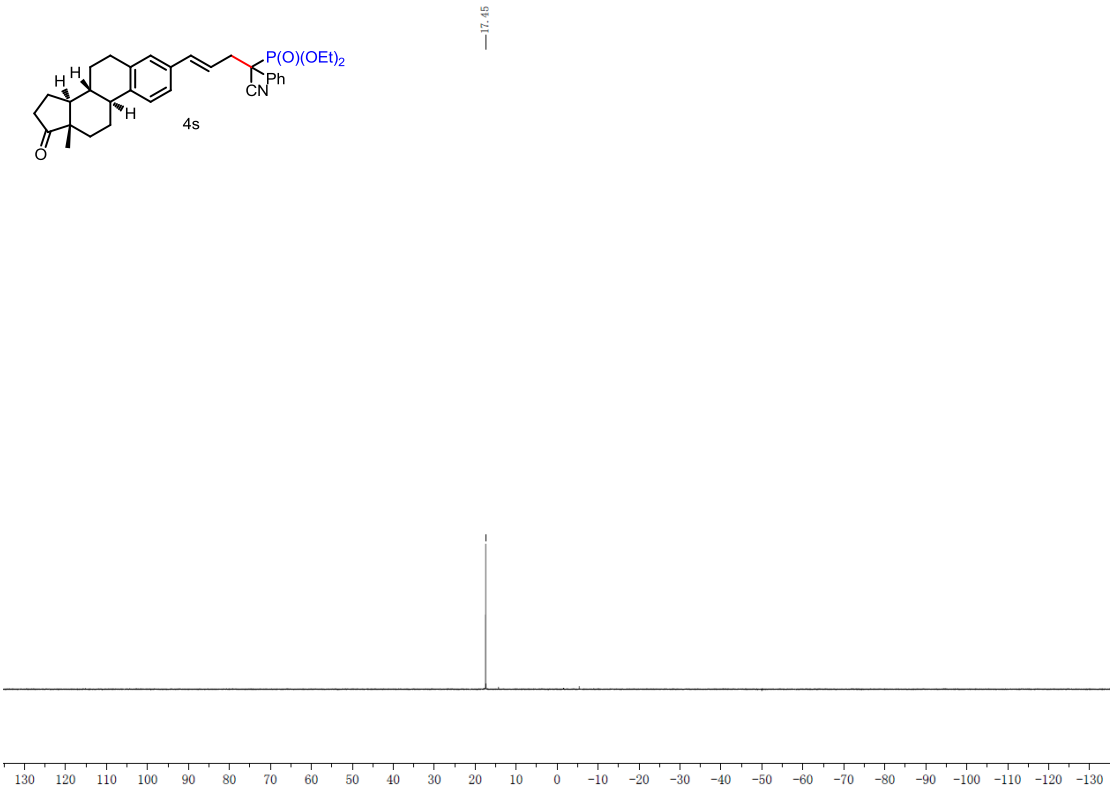


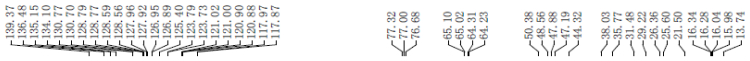
4r




P(O)(OEt)2
Ph
CN
4r
P(O)(OEt)2
Ph
CN
4s
f1 (ppm)

P(O)(OEt)2
Ph
CN
H
H
H
O
4s


17.45
130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130


139.37
138.48
135.15
134.10
130.77
130.70
128.79
128.77
128.59
126.56
127.96
127.92
126.95
126.89
125.40
123.79
123.73
121.02
121.00
120.90
120.88
117.97
117.87
77.32
77.00
76.68
65.10
65.02
64.31
64.23
50.38
48.56
47.88
47.19
44.32
38.03
35.77
31.48
29.22
26.36
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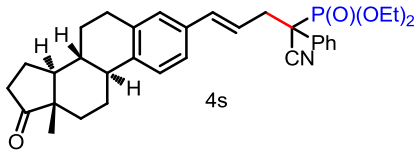
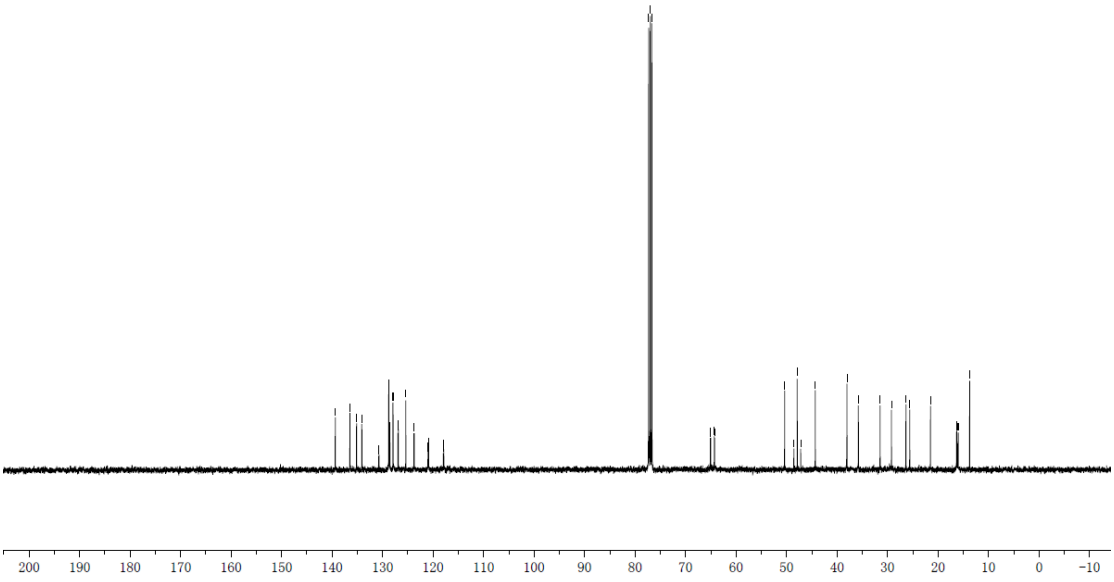
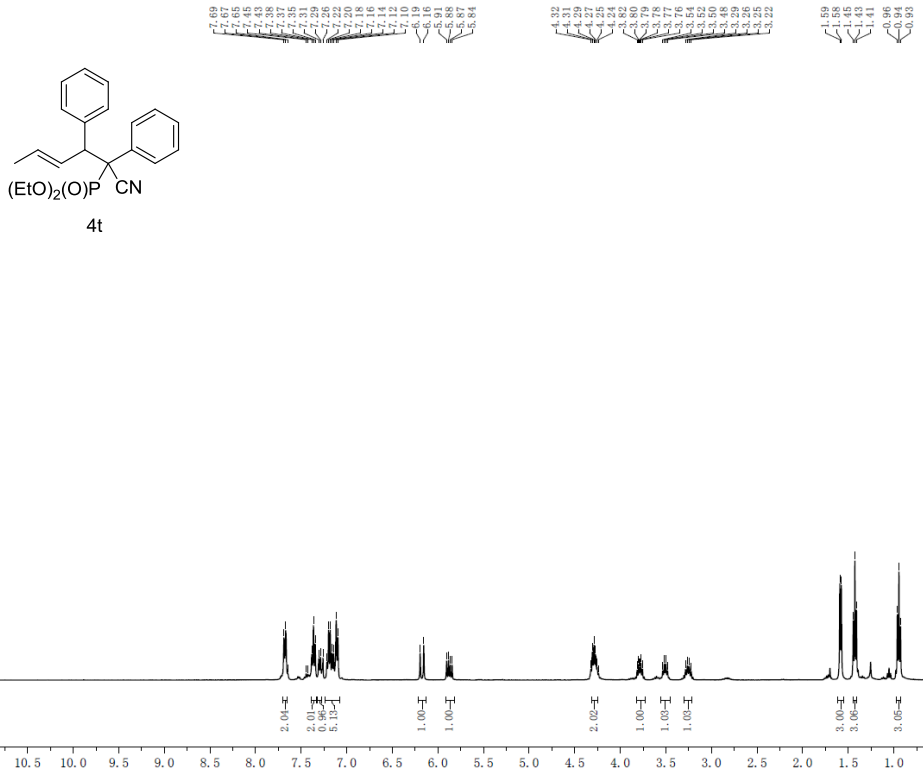
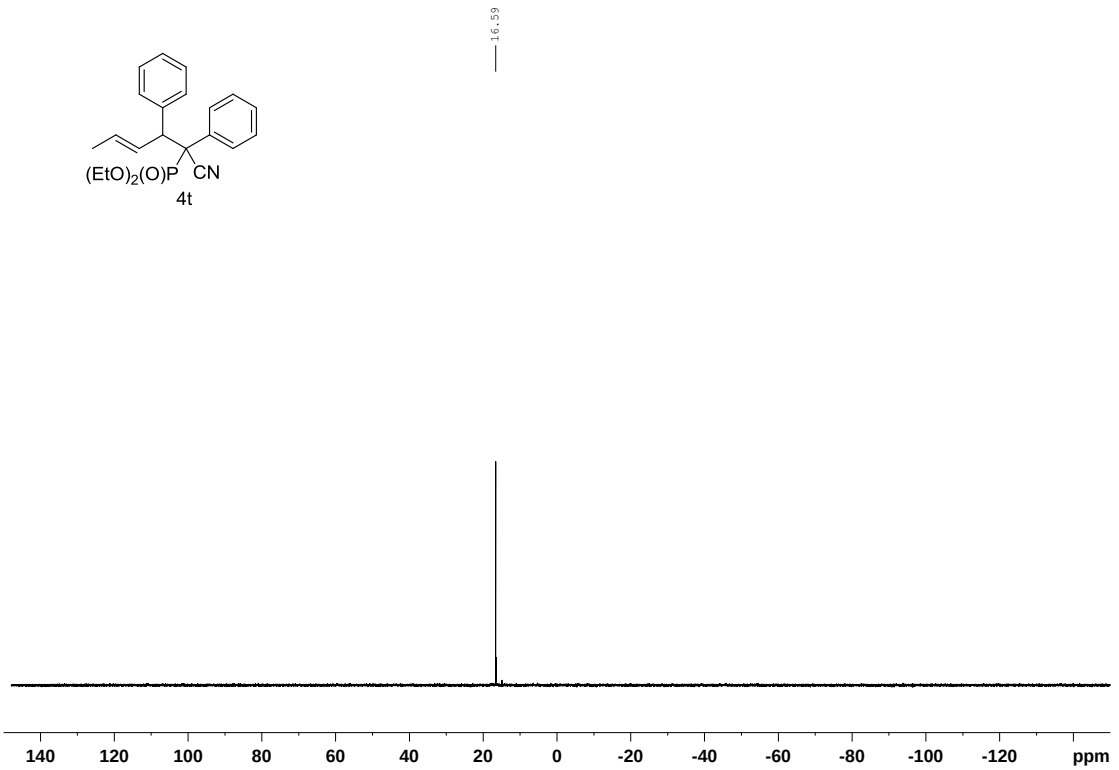
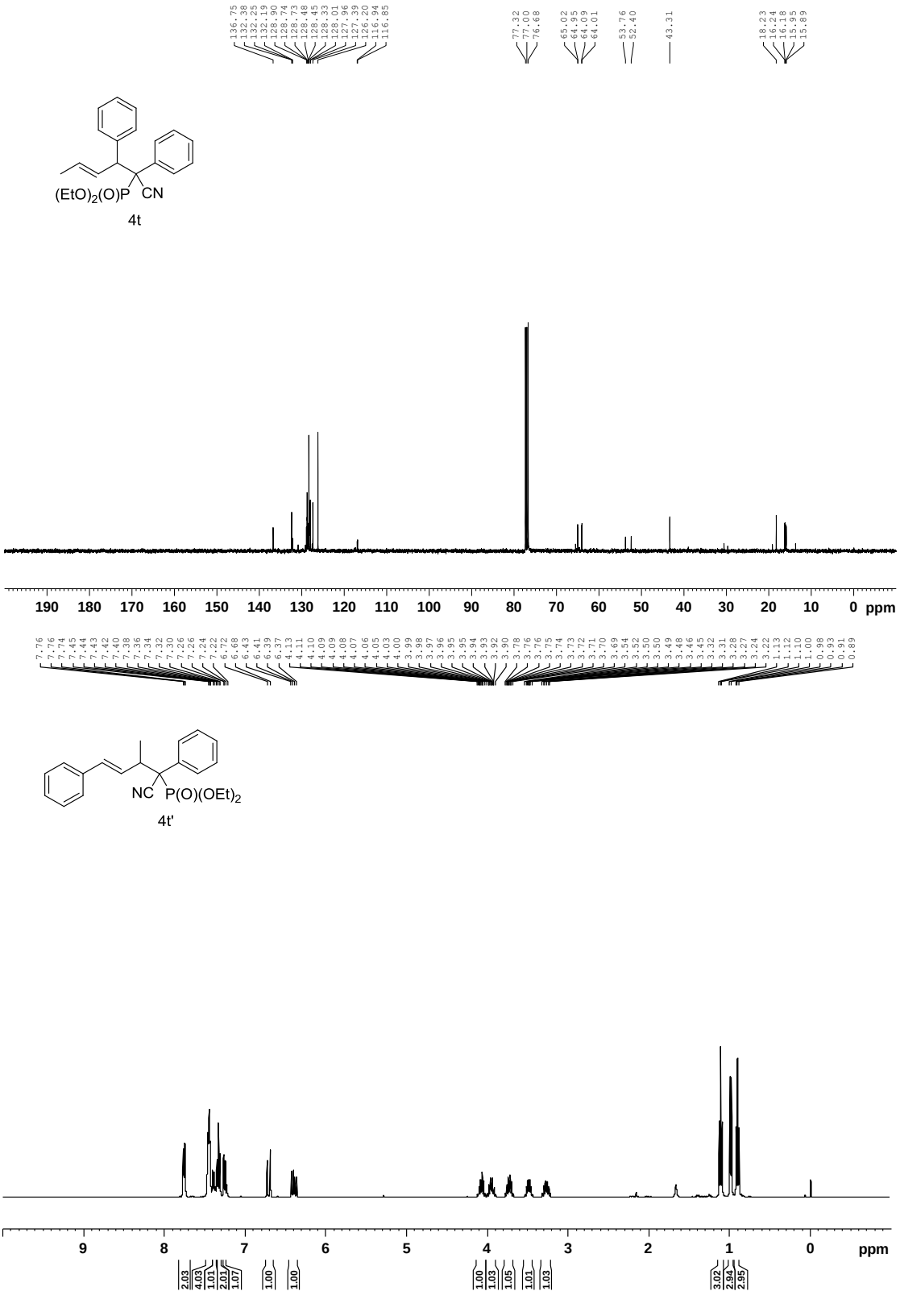
21.50
16.34
16.28
16.04
15.98
13.74

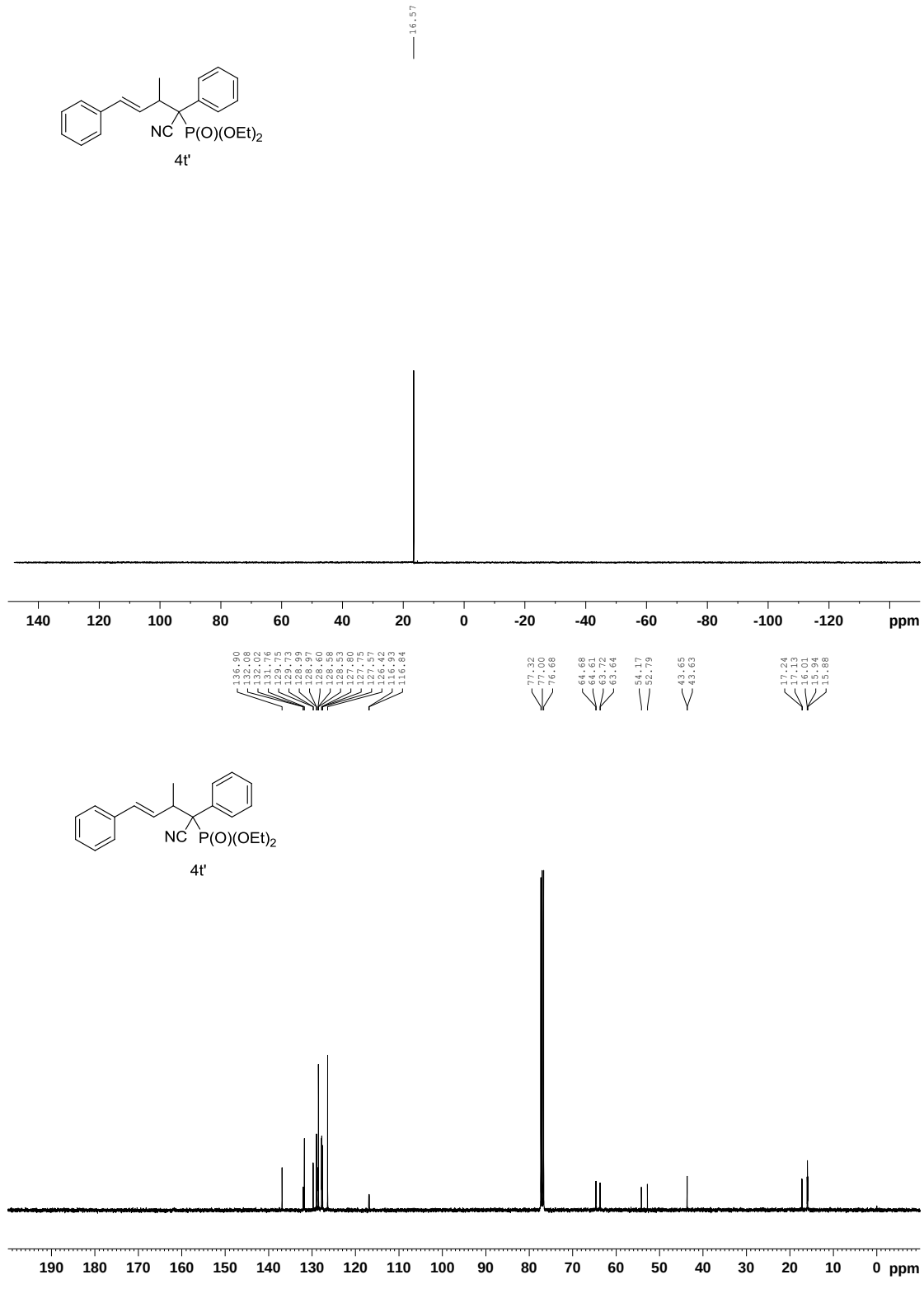

P(O)(OEt)2
Ph
CN
H
H
H
O
4s

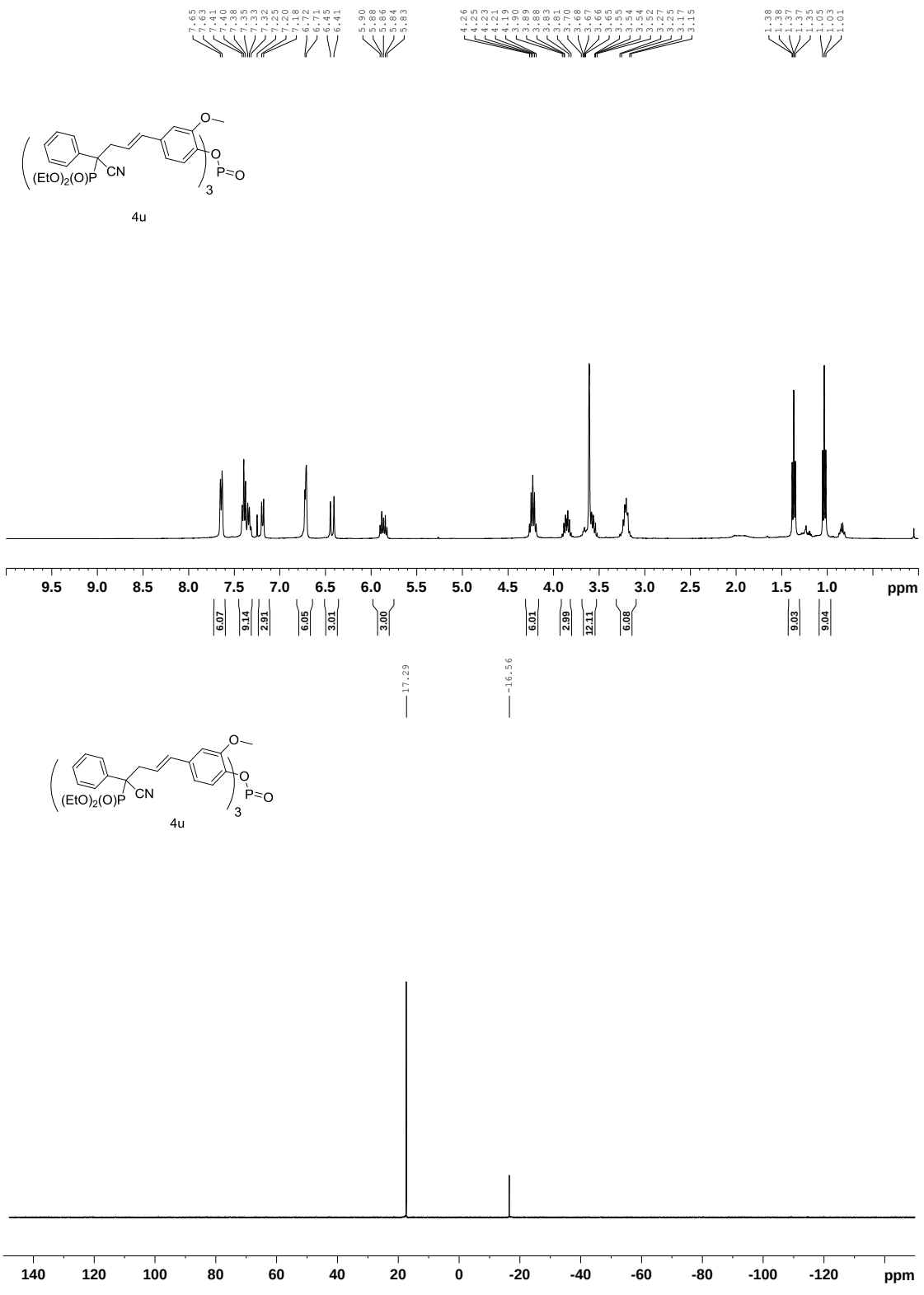

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

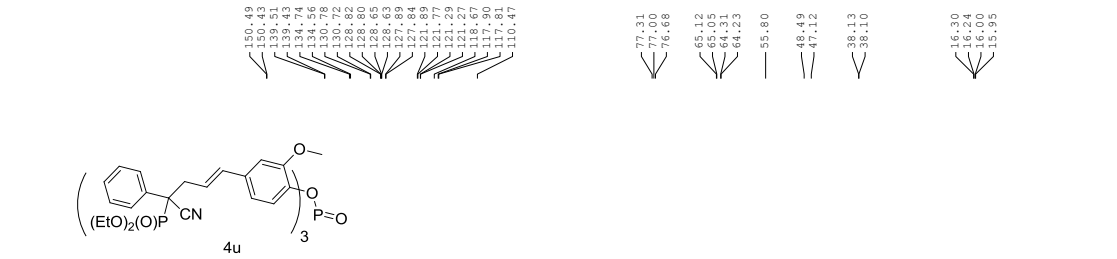

(EtO)2(O)P CN
4t


(EtO)2(O)P CN
4t
16.59
ppm


136.75
132.38
132.25
132.19
128.90
128.74
128.73
128.48
128.45
128.33
128.01
127.96
127.39
126.20
116.94
116.85
77.32
77.00
76.68
65.02
64.95
64.09
64.01
53.76
52.40
43.31
18.23
16.24
16.18
15.95
15.89
(EtO)2(O)P CN
4t
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
7.76
7.76
7.74
7.45
7.44
7.43
7.42
7.40
7.38
7.36
7.34
7.32
7.30
7.26
7.26
7.24
7.22
7.22
6.68
6.43
6.41
6.39
6.37
4.13
4.11
4.10
4.09
4.09
4.08
4.07
4.06
4.05
4.03
4.00
3.99
3.98
3.97
3.96
3.95
3.95
3.94
3.93
3.92
3.90
3.78
3.76
3.76
3.75
3.74
3.73
3.72
3.71
3.70
3.69
3.54
3.52
3.50
3.50
3.49
3.48
3.46
3.45
3.32
3.31
3.28
3.27
3.24
3.22
3.13
1.12
1.10
1.00
0.98
0.93
0.91
0.89
NC P(O)(OEt)2
4t'
9 8 7 6 5 4 3 2 1 0 ppm
2.03
4.03
1.01
2.01
1.07
1.00
1.00
1.00
1.03
1.05
1.01
1.03
3.02
2.94
2.95

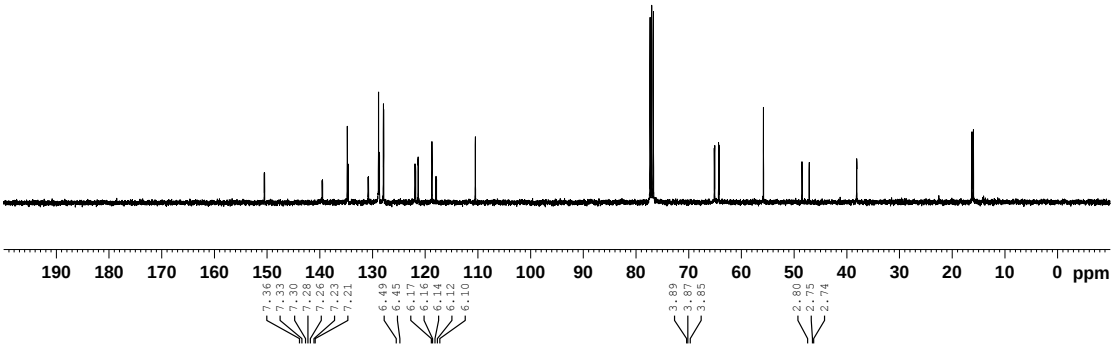

16.57
NC P(O)(OEt)2
4t'
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 ppm
136.90
132.08
132.02
131.76
129.75
129.73
128.99
128.97
128.60
128.58
128.53
127.80
127.57
127.57
126.42
116.93
116.84
77.32
77.00
76.68
64.68
64.61
63.72
63.64
54.17
52.79
43.65
43.63
17.24
17.13
16.01
15.94
15.88
NC P(O)(OEt)2
4t'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

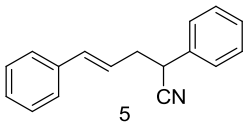

7.65
7.63
7.41
7.40
7.38
7.35
7.33
7.32
7.25
7.20
7.18
6.72
6.71
6.45
6.41
5.90
5.88
5.86
5.84
5.83
4.26
4.25
4.23
4.21
4.19
3.90
3.89
3.88
3.83
3.81
3.70
3.68
3.67
3.66
3.65
3.55
3.54
3.54
3.52
3.27
3.25
3.17
3.15
1.38
1.38
1.37
1.37
1.35
1.35
1.03
1.01
(EtO)2(O)P
CN
O
P=O
3
4u
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
6.07
9.14
2.91
6.05
3.01
3.00
6.01
2.99
12.11
6.08
9.03
9.04
17.29
-16.56
(EtO)2(O)P
CN
O
P=O
3
4u
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 ppm


150.49
150.43
139.51
139.43
134.74
134.56
130.78
130.72
128.82
128.80
128.65
128.63
127.89
127.84
121.89
121.77
121.29
121.27
118.67
117.90
117.81
110.47
77.31
77.00
76.68
65.12
65.05
64.31
64.23
55.80
48.49
47.12
38.13
38.10
16.30
16.24
16.00
15.95

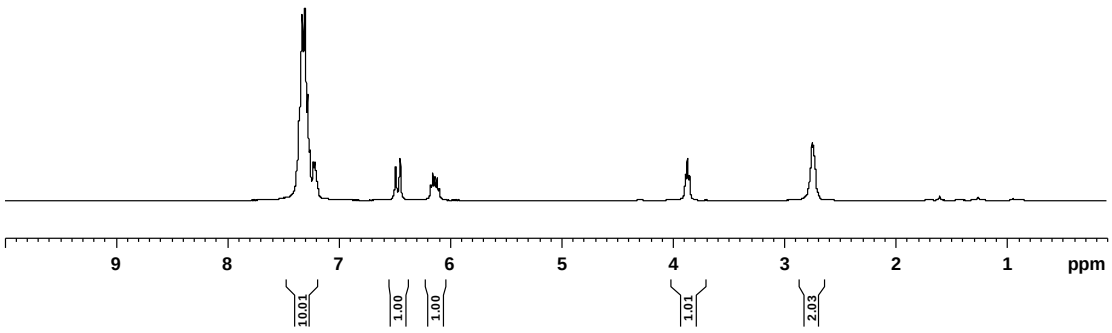
O
O
P=O
(EtO)2(O)P
CN
3

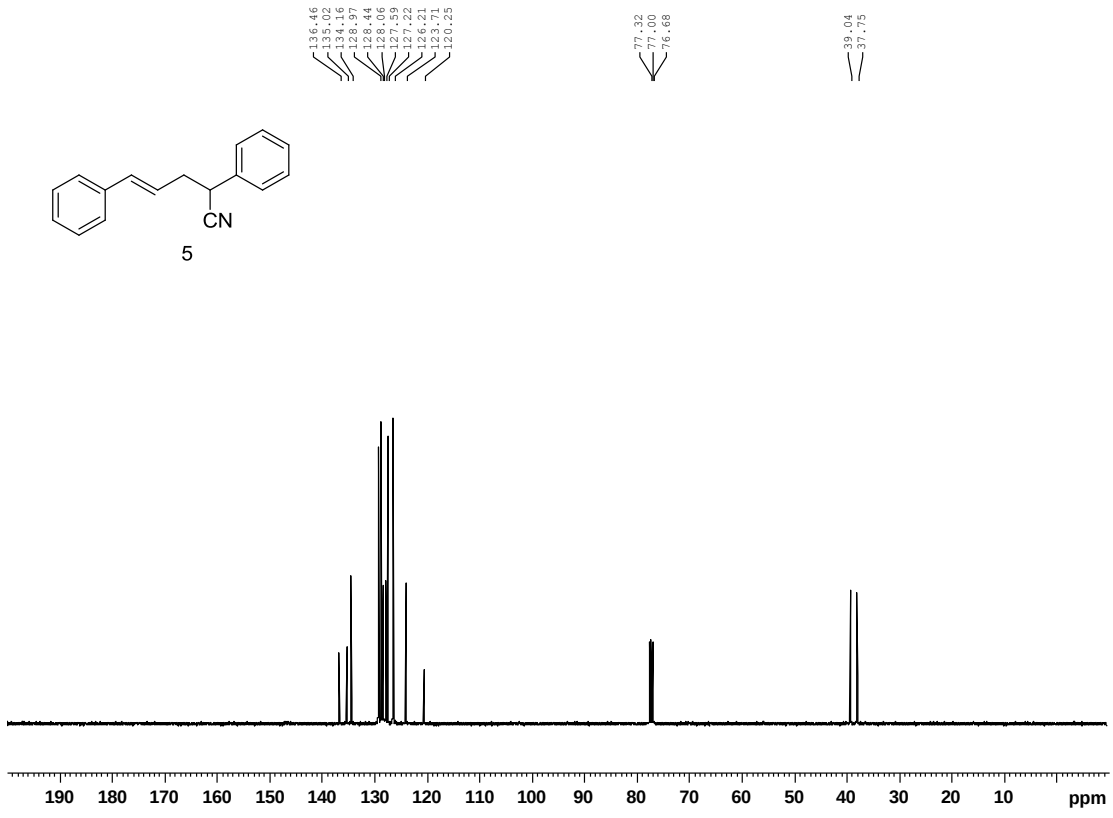
4u

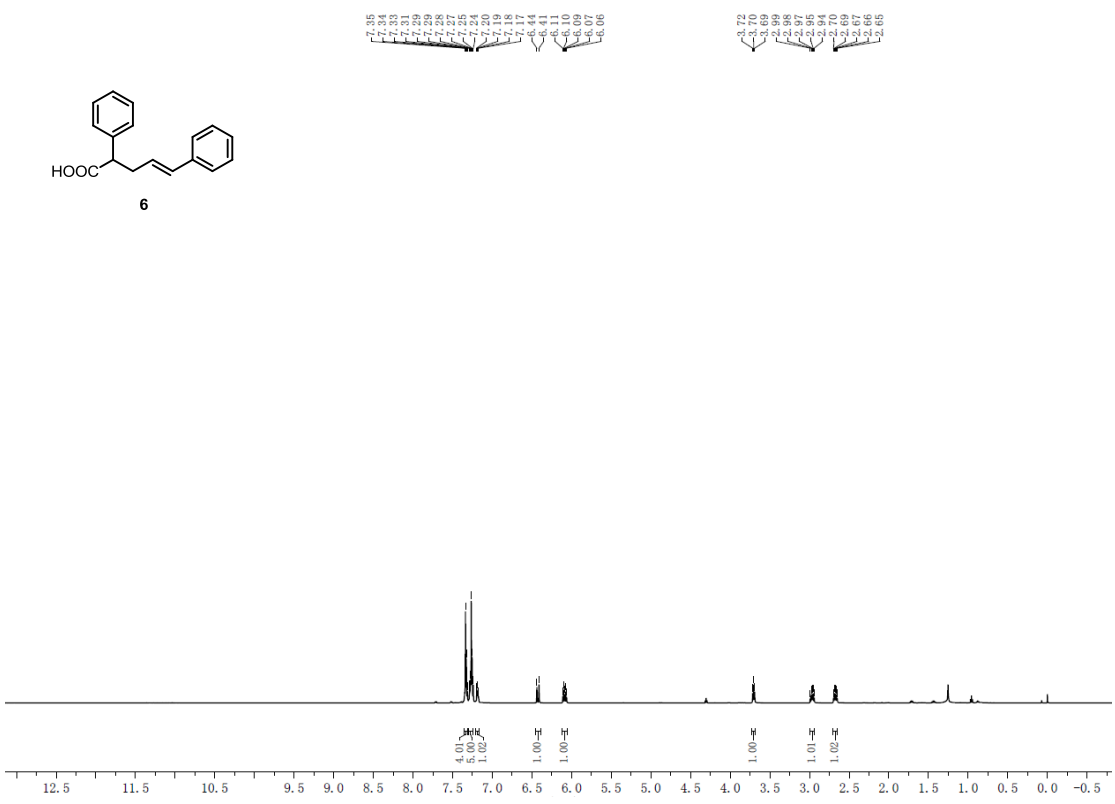

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
7.36
7.33
7.30
7.28
7.26
7.23
7.21
6.49
6.45
6.17
6.16
6.14
6.12
6.10
3.89
3.87
3.85
2.80
2.75
2.74

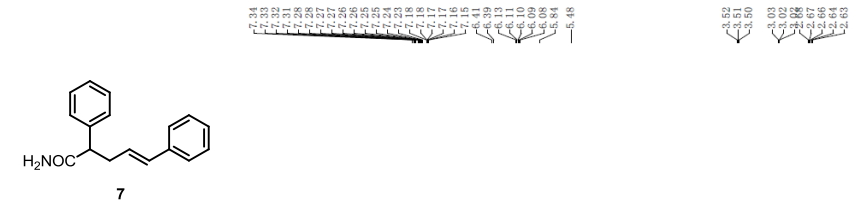

CN

5

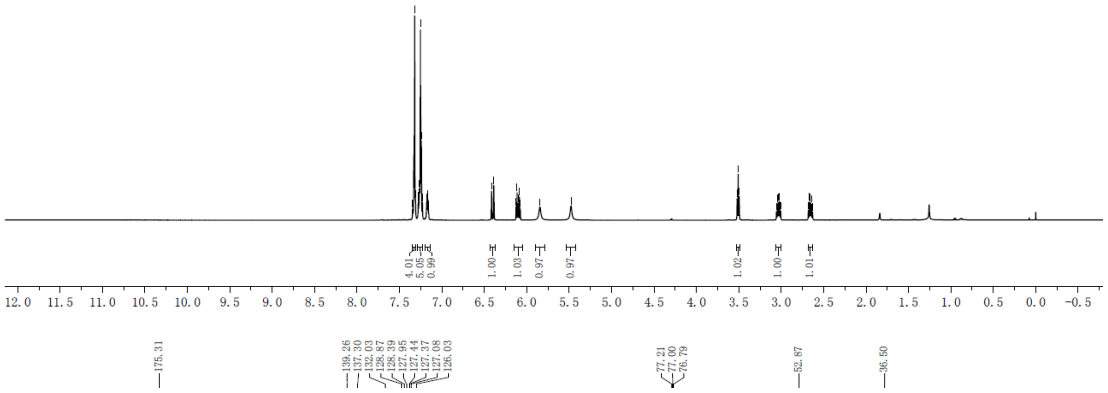

9 8 7 6 5 4 3 2 1 ppm
10.01
1.00
1.00
1.01
2.03

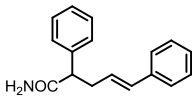

136.46
135.02
134.16
128.97
128.44
128.06
127.59
127.22
126.21
123.71
120.25
77.32
77.00
76.68
39.04
37.75
CN
5
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.35
7.34
7.33
7.31
7.29
7.29
7.28
7.27
7.25
7.24
7.20
7.19
7.18
7.17
6.44
6.41
6.11
6.10
6.09
6.07
6.06
3.72
3.70
3.69
2.99
2.98
2.97
2.95
2.94
2.70
2.69
2.67
2.66
2.65
HOOC
6
4.01
5.00
1.02
1.00
1.00
1.00
1.01
1.02
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

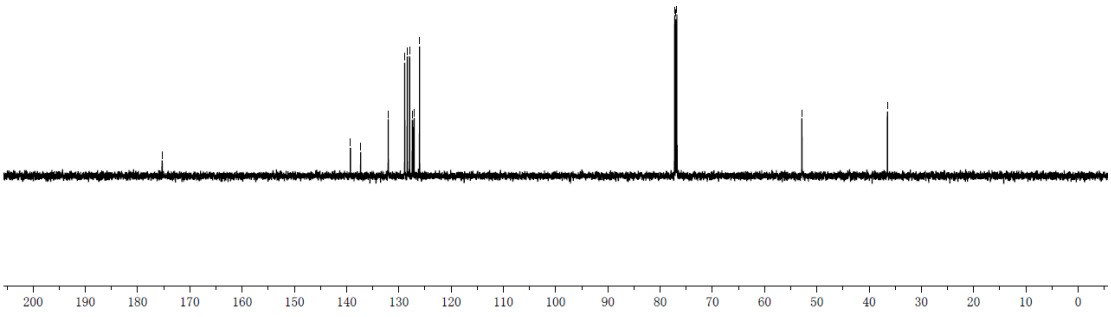


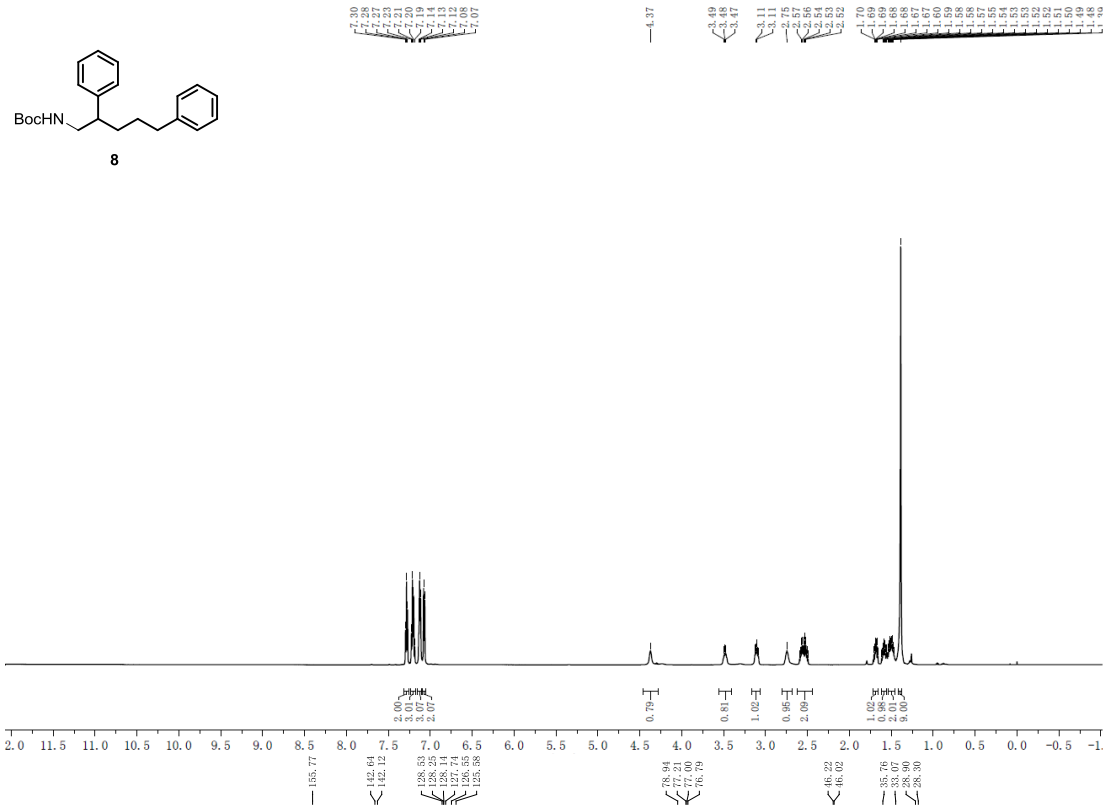
7

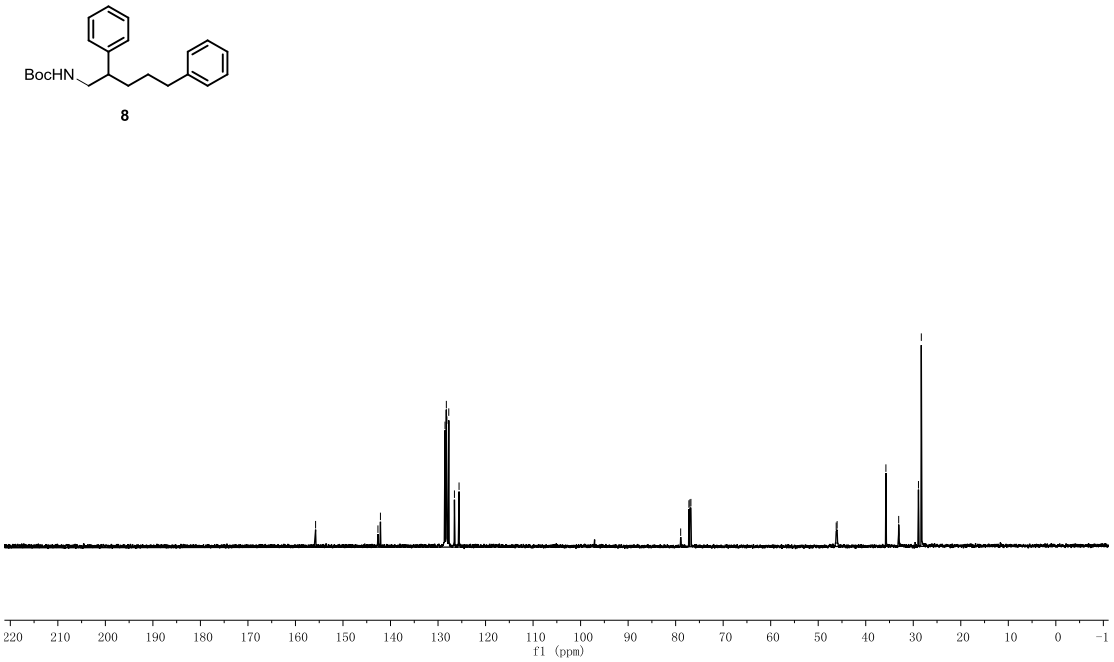


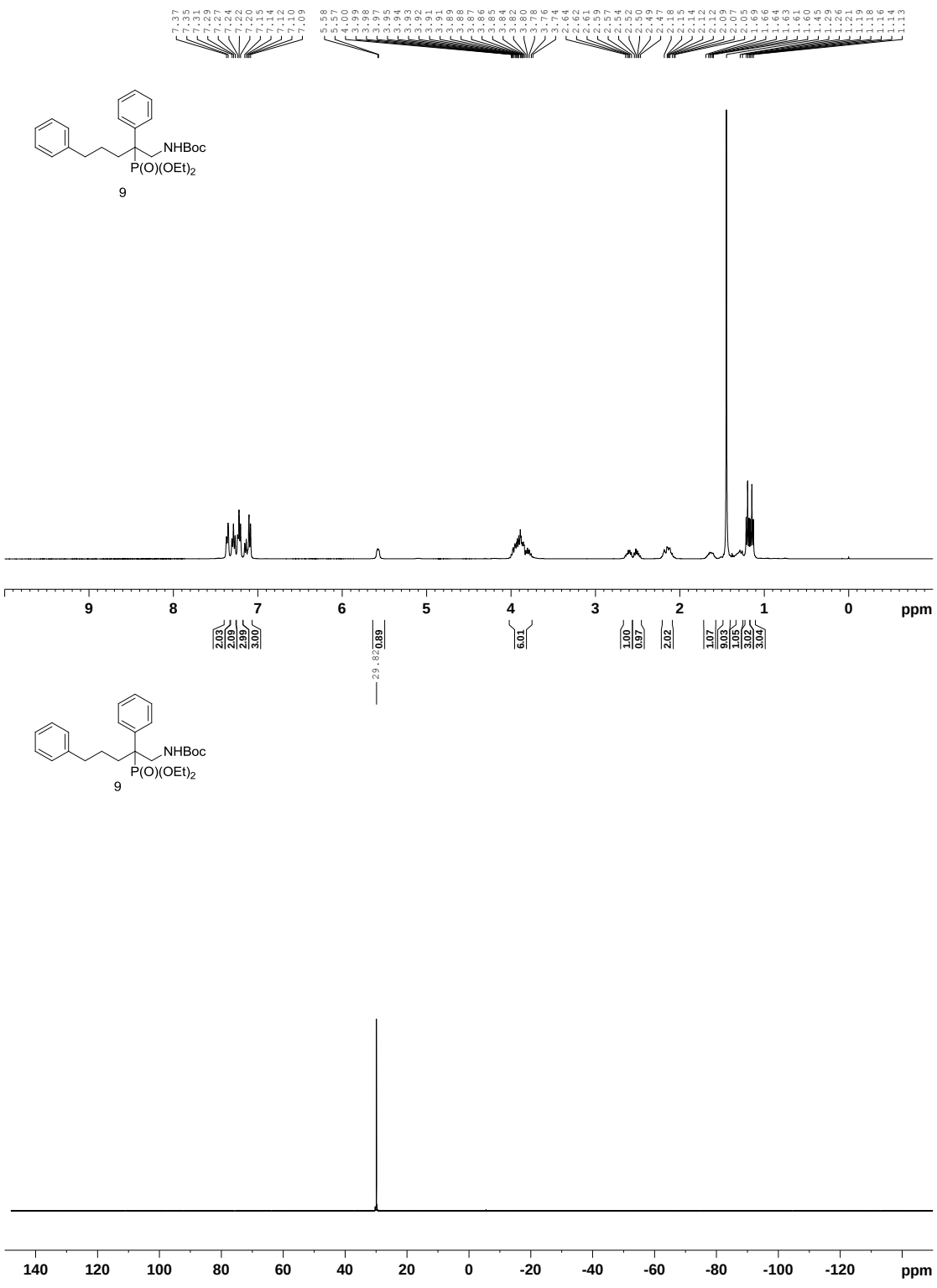


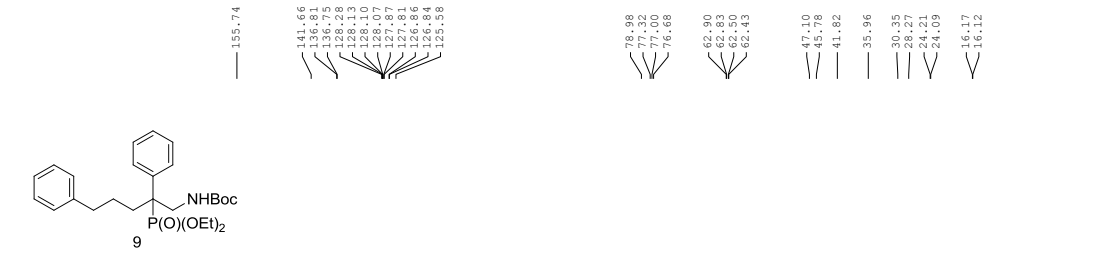
7




BocHN
8

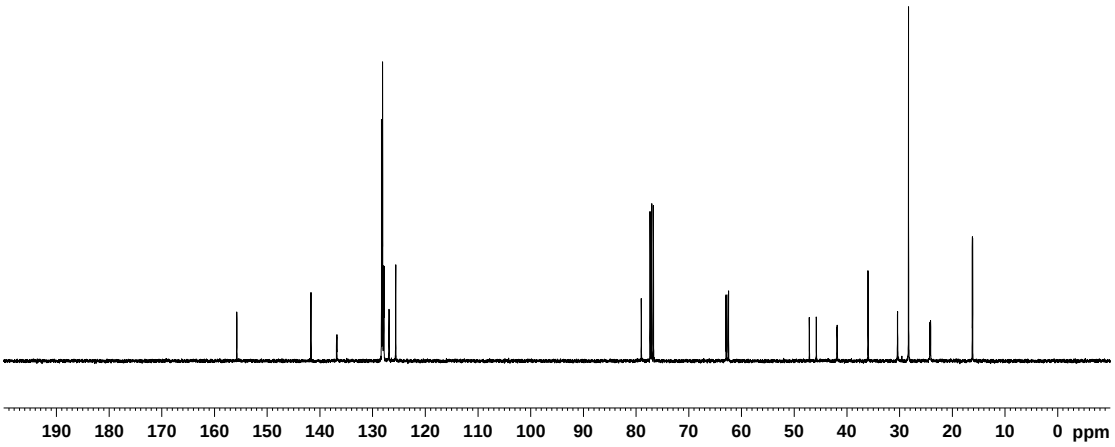

BocHN
8
f1 (ppm)

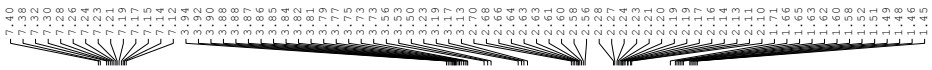

NHBoc
P(O)(OEt)2
9
ppm
NHBoc
P(O)(OEt)2
9
ppm

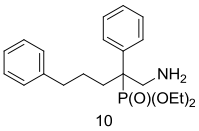

155.74
141.66
136.81
136.75
128.28
128.13
128.10
128.07
127.87
127.81
126.86
126.84
125.58
78.98
77.32
77.00
76.68
62.90
62.83
62.50
62.43
47.10
45.78
41.82
35.96
30.35
28.27
24.21
24.09
16.17
16.12

NHBoc
P(O)(OEt)2

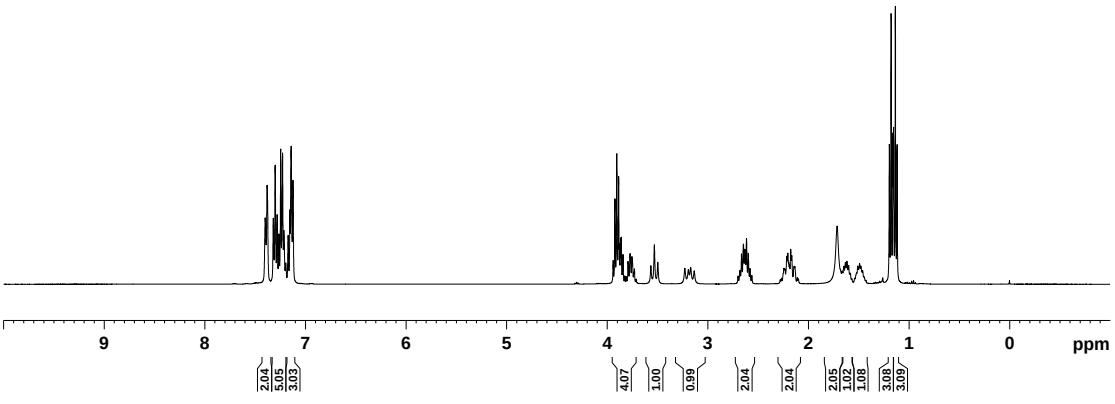
9

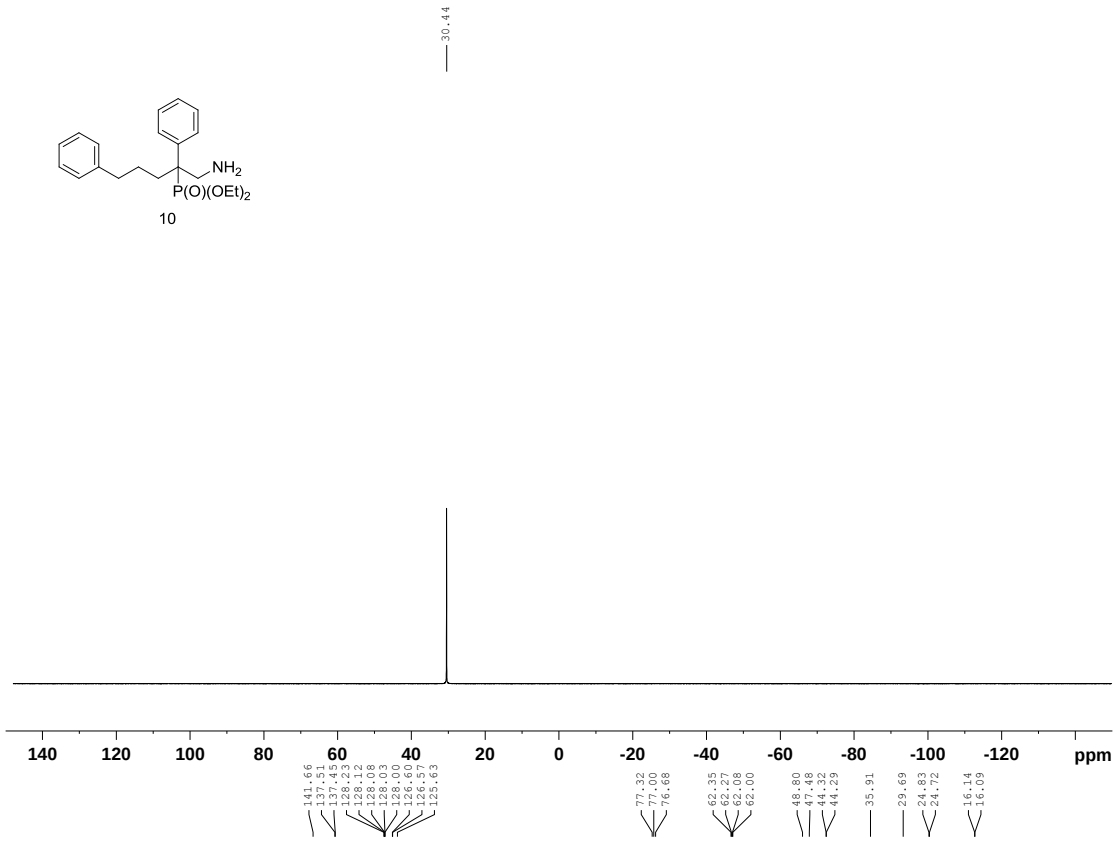

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

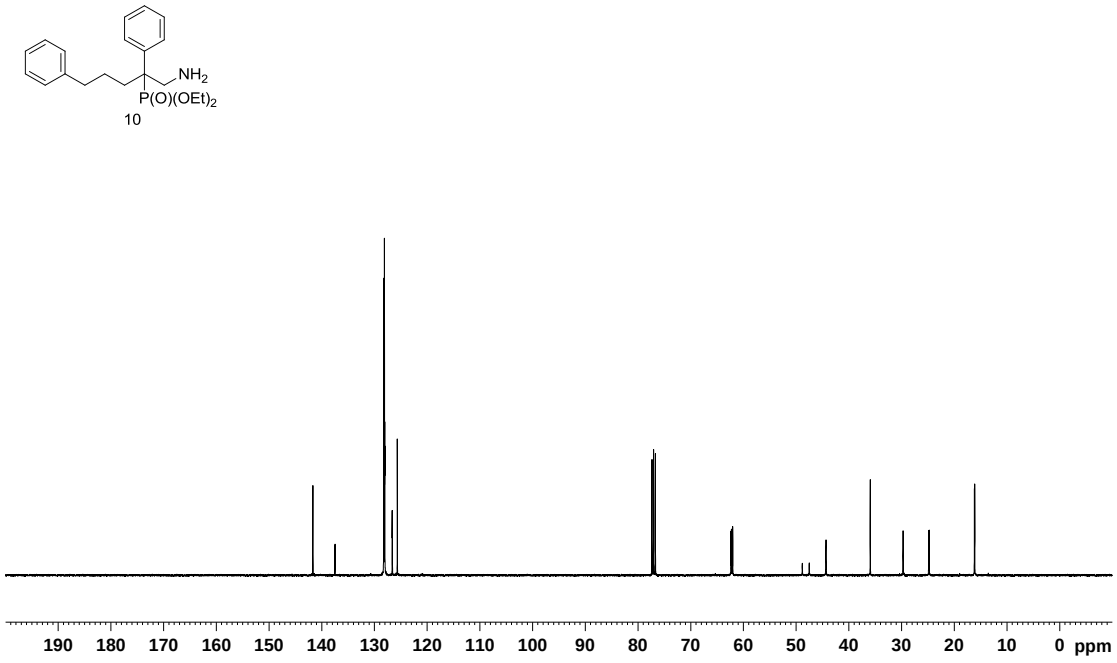

7.40
7.38
7.32
7.30
7.28
7.26
7.24
7.23
7.21
7.19
7.17
7.15
7.14
7.12
3.94
3.92
3.90
3.88
3.87
3.86
3.85
3.84
3.82
3.81
3.79
3.77
3.75
3.73
3.56
3.53
3.50
3.23
3.19
3.17
3.13
3.10
2.68
2.66
2.64
2.63
2.61
2.60
2.58
2.56
2.27
2.24
2.23
2.21
2.20
2.19
2.17
2.16
2.14
2.13
2.11
2.10
1.71
1.66
1.65
1.63
1.62
1.60
1.58
1.52
1.51
1.49
1.48
1.46
1.45

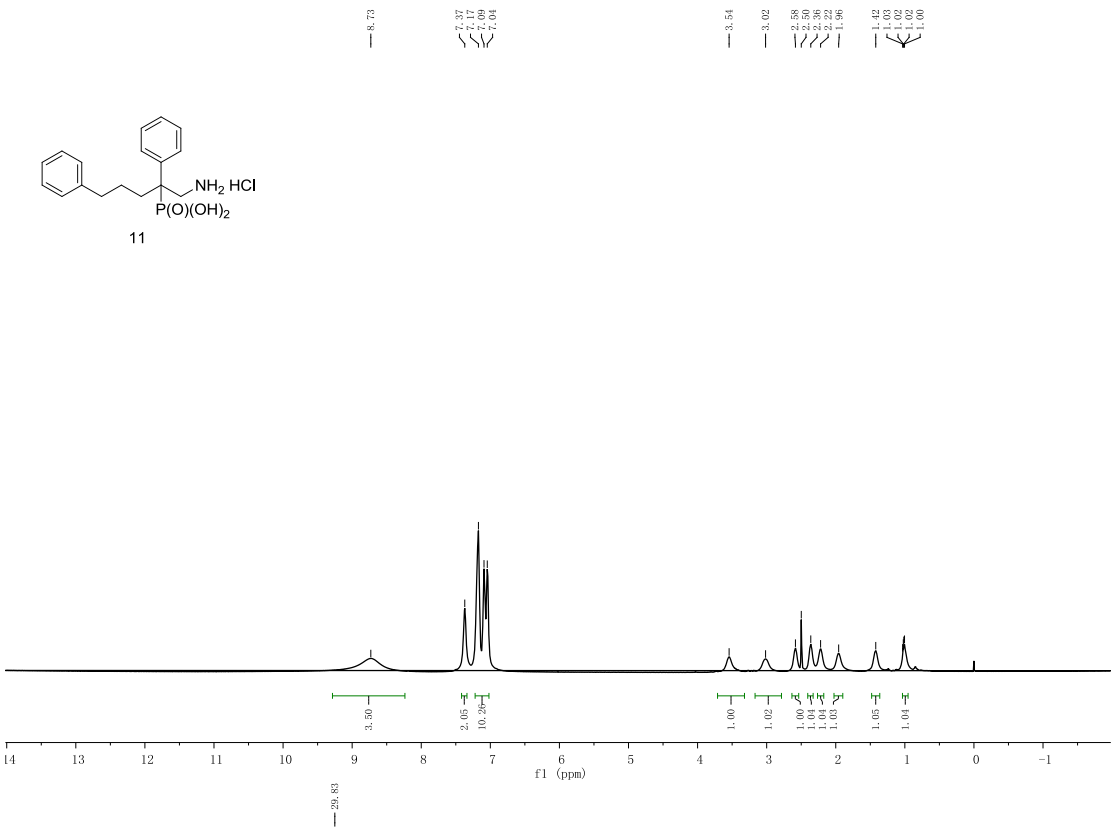

NH2
P(O)(OEt)2

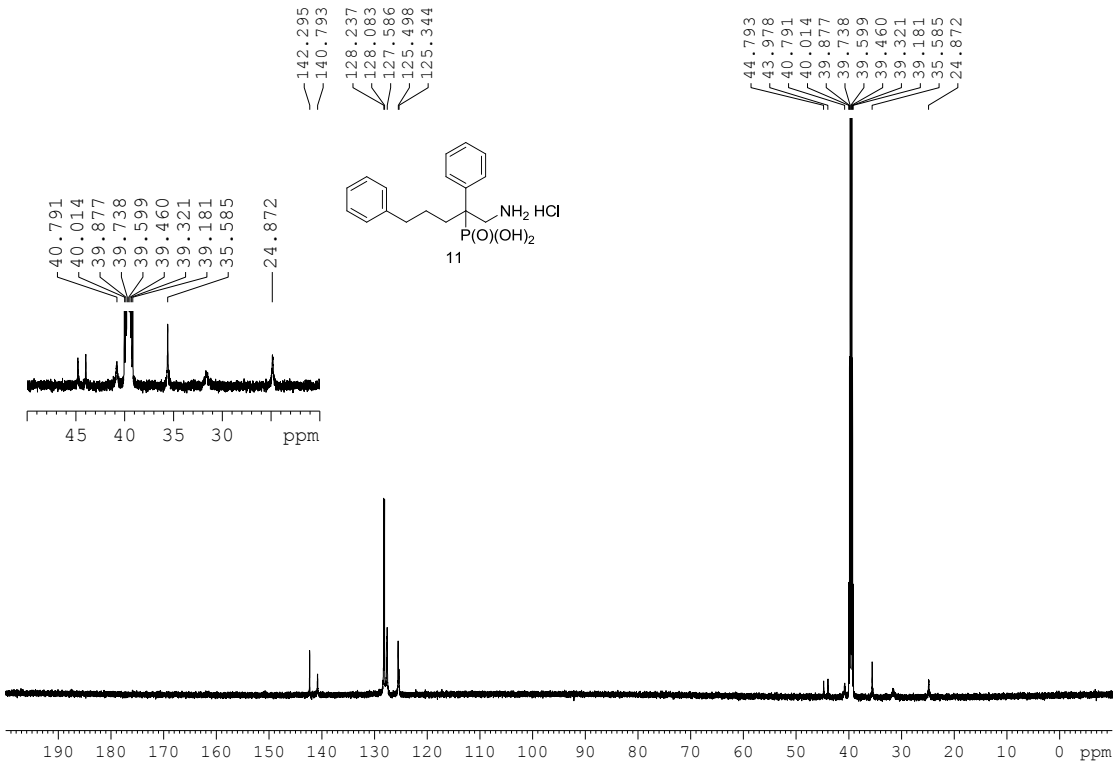
10


9 8 7 6 5 4 3 2 1 0 ppm
2.04
5.05
3.03
4.07
1.00
0.99
2.04
2.04
2.05
1.02
1.08
3.08
3.09


30.44
NH2
P(O)(OEt)2
10
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 ppm
141.66
137.51
137.45
128.23
128.12
128.08
128.03
128.00
126.60
126.57
125.63
77.32
77.00
76.68
62.35
62.27
62.08
62.00
48.80
47.48
44.32
44.29
35.91
29.69
24.83
24.72
16.14
16.09


NH2
P(O)(OEt)2
10
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.73
7.37
7.17
7.09
7.04
3.54
3.02
2.58
2.50
2.36
2.22
1.96
1.42
1.03
1.02
1.02
1.00
NH2 HCl
P(O)(OH)2
11
3.50
2.05
10.26
1.00
1.02
1.00
1.04
1.04
1.03
1.05
1.04
f1 (ppm)
29.83
NH2 HCl
P(O)(OH)2
11
f1 (ppm)


142.295
140.793
128.237
128.083
127.586
125.498
125.344
44.793
43.978
40.791
40.014
39.877
39.738
39.599
39.460
39.321
39.181
35.585
24.872
NH2 HCl
P(O)(OH)2
11
ppm
ppm