Supporting Information

One-Pot Bifunctionalization of Unactivated Alkenes, P(O)–H Compounds, and *N*-Heteroarenium Salts for the Construction of *β*-Pyridyl Alkylphosphonates

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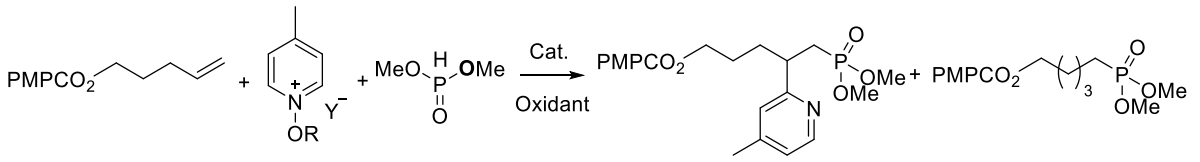
I. General Methods and Materials.

Unless stated otherwise, reactions were performed in flame-dried glassware. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F^{254} plates and visualization on TLC was achieved by UV light (254 and 365 nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). ^{1}H NMR was recorded on 400 MHz or 600 MHz and chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on 100 MHz or 150 MHz and was fully decoupled by broad band proton decoupling. Signals of ^{13}C spectra of carbon atom adjacent to phosphorus atom of organophosphorus compounds appeared as a doublet with varied coupling constants between C and P (J_{CP}). Chemical shifts were reported in ppm referenced to the centerline of a triplet at 77.0 ppm of $CDCl_3$. ^{31}P NMR was recorded on 162 MHz or 243 MHz and was fully decoupled by broad band proton decoupling. Mass spectral data were obtained from the KAIST Basic Science Institute by using ESI method. Commercial grade reagents and solvents were used without further purification except as indicated below.

II. Optimization of the reaction conditions

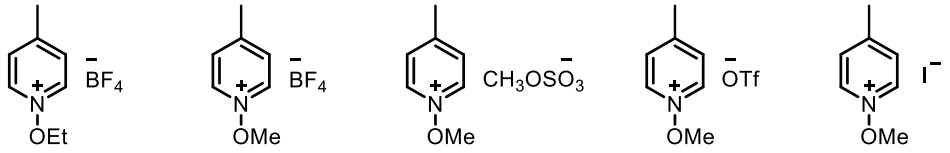
Table S1[a]



entry	catalyst (0.2 equiv)	oxidant (1.5 equiv)	2	solvent	temp/time	yield (%)[b]
1	$AgNO_3$	$Mn(OAc)_3{\cdot}2H_2O$	2a	DMF	60°C/16 h	56 (65/35)
2	$AgNO_3$	$Mn(OAc)_3{\cdot}2H_2O$	2a	DCM	60°C/16 h	86 (43/57)
3	$AgNO_3$	$Mn(OAc)_3{\cdot}2H_2O$	2a	toluene	60°C/16 h	68 (>5/95)
4	$AgNO_3$	$Mn(OAc)_3{\cdot}2H_2O$	2a	dioxane	60°C/16 h	77 (13/87)
5	$AgNO_3$	$Mn(OAc)_3{\cdot}2H_2O$	2a	MeCN	60°C/16 h	75 (69/31)
6	$AgNO_3$	$Mn(OAc)_3{\cdot}2H_2O$	2b	MeCN	60°C/16 h	80 (69/31)
7	$AgNO_3$	$Mn(OAc)_3{\cdot}2H_2O$	2c	MeCN	60°C/16 h	83 (72/28)
8	$AgNO_3$	$Mn(OAc)_3{\cdot}2H_2O$	2d	MeCN	60°C/16 h	83 (70/30)

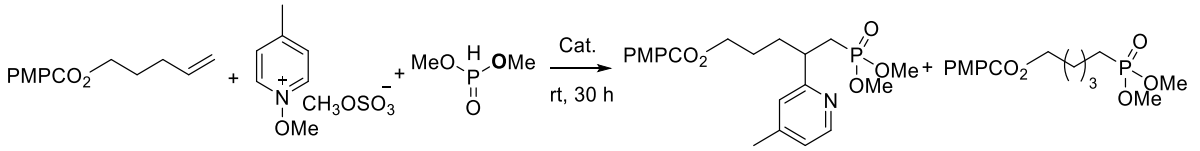
9	$AgNO_3$	$Mn(OAc)_3·2H_2O$	2e	MeCN	60°C/16 h	trace
10	$AgNO_3$	$Mn(OAc)_3·2H_2O$	2c	MeCN	80°C/16 h	78 (62/38)
11	$AgNO_3$	$Mn(OAc)_3·2H_2O$	2c	MeCN	rt/30 h	88 (81/19)
12	—	$Mn(OAc)_3·2H_2O$	2c	MeCN	rt/30 h	31 (71/29)
13	$AgNO_3$	—	2c	MeCN	rt/30 h	<5%
14	$AgNO_3$	$Mn(OAc)_3·2H_2O$	2c	MeCN/H_2O	80°C/16 h	14%
15	$AgNO_3$	$Mn(OAc)_3·2H_2O$	2c	MeCN/HOAc	rt/30 h	<5%
16[c]	$AgNO_3$	—	2c	MeCN	rt/30 h	22 (78/22)
17	$AgNO_3$	DTBP	2c	MeCN	rt/30 h	28 (55/45)
18	$AgNO_3$	$K_2S_2O_8$	2c	MeCN	rt/30 h	11 (89/11)
19	$AgNO_3$	BPO	2c	MeCN	rt/30 h	30 (60/40)
20	$AgNO_3$	MnO_2	2c	MeCN	rt/30 h	25 (65/35)
21	$AgNO_3$	$Mn(OAc)_2$	2c	MeCN	rt/30 h	25 (65/35)
22	$AgNO_3$	TBHP	2c	MeCN	rt/30 h	trace
23	AgOAc	$Mn(OAc)_3·2H_2O$	2c	MeCN	rt/30 h	86 (79/21)
24	$AgSbF_6$	$Mn(OAc)_3·2H_2O$	2c	MeCN	rt/30 h	85 (79/21)
25	$Pd(OAc)_2$	$Mn(OAc)_3·2H_2O$	2c	MeCN	rt/30 h	20 (78/22)
26	$Cu(OAc)_2$	$Mn(OAc)_3·2H_2O$	2c	MeCN	rt/30 h	trace

[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.5 mmol), **3a** (0.4 mmol), Oxidant (0.4 mmol), catalyst (20 mmol %), sovent (1.0 mL), under nitrogen. [b]Yields were determined by ^1H NMR spectroscope with caffeine as an internal standard. [c]$AgNO_3$ (1.0 equiv) was used.



2a **2b** **2c** **2d** **2e**

Table S2[a]



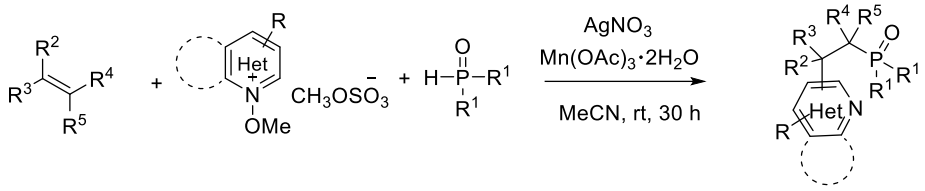
1a **2c** **3a** **4a** **5**

entry	catalyst	oxidant	additive	solvent	yield (%)[b]
1	$AgNO_3$	$Mn(OAc)_3·2H_2O$	K_2CO_3	MeCN	45 (74/26)
2	$AgNO_3$	$Mn(OAc)_3·2H_2O$	NaOAc	MeCN	75 (78/22)
3	$AgNO_3$	$Mn(OAc)_3·2H_2O$	Cs_2CO_3	MeCN	10 (75/25)
4	$AgNO_3$	$Mn(OAc)_3·2H_2O$	^{t}BuOK	MeCN	12 (76/24)
5	$AgNO_3$	$Mn(OAc)_3·2H_2O$	K_2HPO_4	MeCN	73 (79/21)

6	$AgNO_3$	$Mn(OAc)_3{\cdot}2H_2O$	DBU	MeCN	15 (77/23)
7	$AgNO_3$	$Mn(OAc)_3{\cdot}2H_2O$	TMEDA	MeCN	25 (78/22)
8	$AgNO_3$	$Mn(OAc)_3{\cdot}2H_2O$	Et_3N	MeCN	trace
9	$AgNO_3$	$Mn(OAc)_3{\cdot}2H_2O$	DABCO	MeCN	12 (76/24)
10	$AgNO_3$	$Mn(OAc)_3{\cdot}2H_2O$	4A MS	MeCN	70 (79/21)

[a]Reaction conditions: **1a** (0.2 mmol), **2c** (0.5 mmol), **3a** (0.4 mmol), additive (0.4 mmol), oxidant (0.3 mmol), catalyst (20 mmol %), sovent (1.0 mL), under nitrogen. [b]Yields were determined by ^{1}H NMR spectroscope with caffeine as an internal standard.

III. General experimental procedure

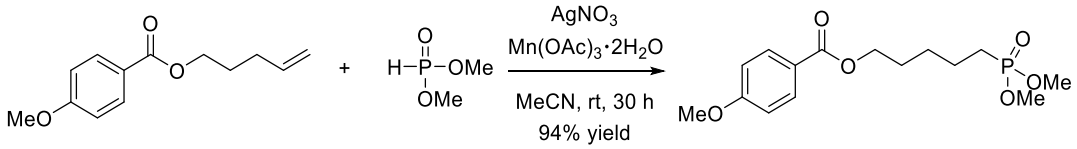


1 **2** **3** **4 or 6**

An oven-dried tube was charged with alkene **1** (0.2 mmol), N-methoxyheteroarenium salts **2** (0.5 mmol), $Mn(OAc)_3{\cdot}H_2O$ (0.3 mmol), and $AgNO_3$ (0.04 mmol). The tube was evacuated and backfilled with nitrogen (repeated three times). Then, dialkyl phosphonate **3** (0.4 mmol), and acetonitrile (1.0 mL) was added into the reaction via syringe. The reaction mixture was stirring at room temperature for 30 h. The reaction mixture was extracted by ethyl acetate, the combined organic layers were washed with saturated brine, dried over Na_2SO_4, concentrated in vacuumand purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH) to afford final the product **4** or **6**.

IV. Control Experiments

The reaction without N-methoxyheteroarenium salt

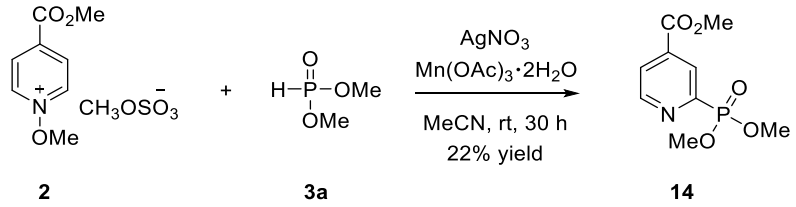


1a **3a** **5a**

An oven-dried tube was charged with alkene **1a** (0.2 mmol), $Mn(OAc)_3{\cdot}H_2O$ (0.3 mmol), and $AgNO_3$ (0.04 mmol). The tube was evacuated and backfilled with nitrogen (repeated three times). Then, dimethyl phosphonate **3a** (0.4 mmol), and acetonitrile (1.0 mL) was added into the reaction via syringe. The reaction mixture was stirring at room temperature for 30 h. The reaction mixture was extracted by

ethyl acetate, the combined organic layers were washed with saturated brine, dried over Na_2SO_4, concentrated in vacuum and purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH) to afford the product **5a** in 94% yield.

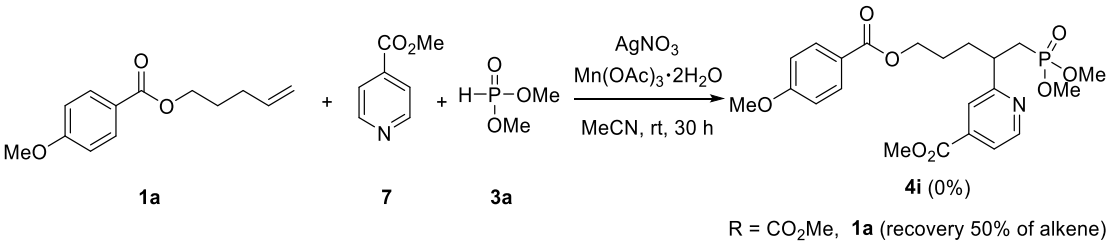
The reaction without alkene



2 **3a** **14**

An oven-dried tube was charged with N-methoxyheteroarenium salt **2** (0.2 mmol), $Mn(OAc)_3 \cdot H_2O$ (0.3 mmol), and $AgNO_3$ (0.04 mmol). The tube was evacuated and backfilled with nitrogen (repeated three times). Then, dimethyl phosphonate **3a** (0.4 mmol), and acetonitrile (1.0 mL) was added into the reaction via syringe. The reaction mixture was stirring at room temperature for 30 h. The reaction mixture was extracted by ethyl acetate, the combined organic layers were washed with saturated brine, dried over Na_2SO_4, concentrated in vacuum and purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH) to afford the product **14** in 22% yield.

Pyridine 7 was used in the reaction

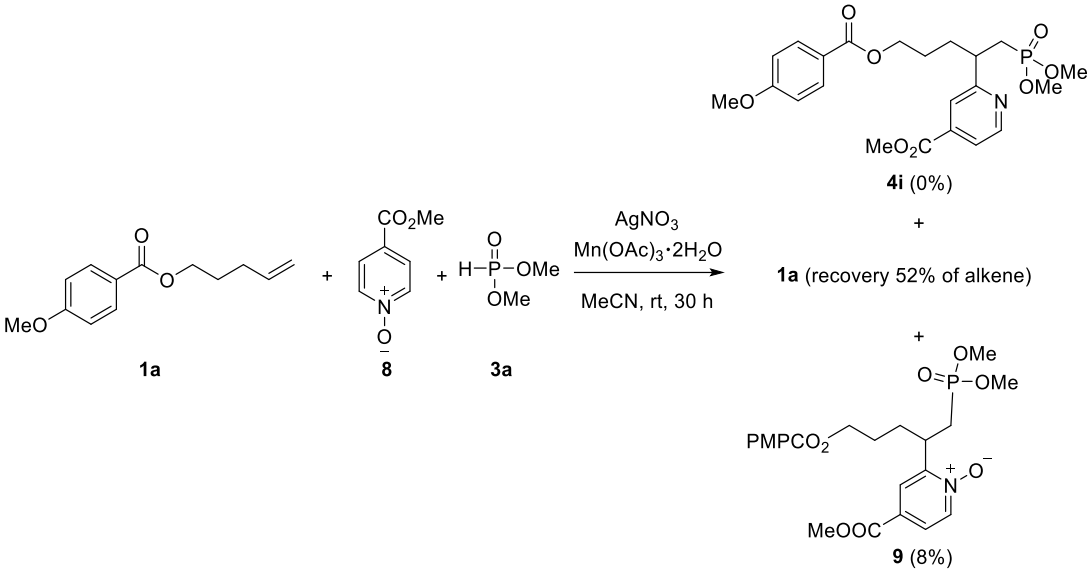


1a **7** **3a** **4i** (0%)

R = CO_2Me, **1a** (recovery 50% of alkene)

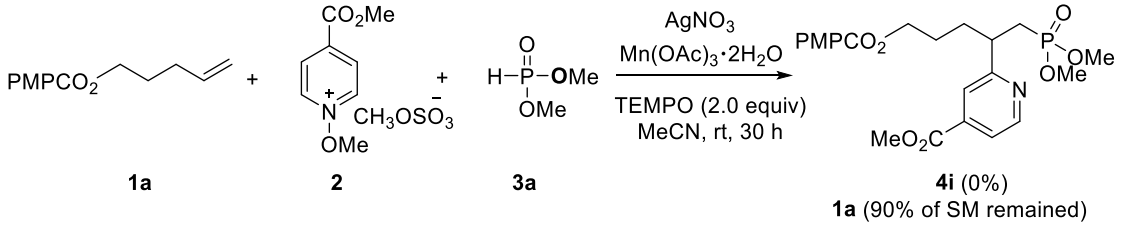
An oven-dried tube was charged with alkene **1a** (0.2 mmol), $Mn(OAc)_3 \cdot H_2O$ (0.3 mmol), and $AgNO_3$ (0.04 mmol). The tube was evacuated and backfilled with nitrogen (repeated three times). Then, dimethyl phosphonate **3a** (0.4 mmol), pyridine **7** (0.5 mmol), and acetonitrile (1.0 mL) was added into the reaction via syringe. The reaction mixture was stirring at room temperature for 30 h. The reaction mixture was extracted by ethyl acetate, the combined organic layers were washed with saturated brine, dried over Na_2SO_4, concentrated in vacuum and purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH).

Pyridine 1-oxide 8 was used in the reaction



An oven-dried tube was charged with alkene **1a** (0.2 mmol), pyridine 1-oxide **8** (0.5 mmol), $Mn(OAc)_3 \cdot H_2O$ (0.3 mmol), and $AgNO_3$ (0.04 mmol). The tube was evacuated and backfilled with nitrogen (repeated three times). Then, dimethyl phosphonate **3a** (0.4 mmol), and acetonitrile (1.0 mL) was added into the reaction via syringe. The reaction mixture was stirring at room temperature for 30 h. The reaction mixture was extracted by ethyl acetate, the combined organic layers were washed with saturated brine, dried over Na_2SO_4, concentrated in vacuum and purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH) to afford the product **9** in 8% yield.

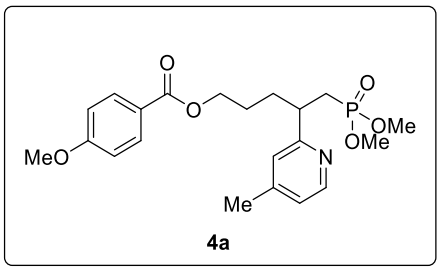
TEMPO experiment



An oven-dried tube was charged with alkene **1a** (0.2 mmol), N-methoxypyridinium salt **2** (0.5 mmol), TEMPO (0.4 mmol), $Mn(OAc)_3 \cdot H_2O$ (0.3 mmol), and $AgNO_3$ (0.04 mmol). The tube was evacuated and backfilled with nitrogen (repeated three times). Then, dimethyl phosphonate **3a** (0.4 mmol), and acetonitrile (1.0 mL) was added into the reaction via syringe. The reaction mixture was stirring at room temperature for 30 h. The reaction mixture was extracted by ethyl acetate, the combined organic layers

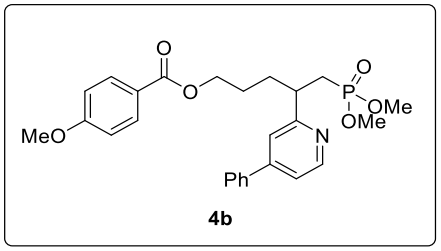
were washed with saturated brine, dried over Na_2SO_4, concentrated in vacuum and purified by flash column chromatography on silica gel.

V. Compound Characterizations



4a

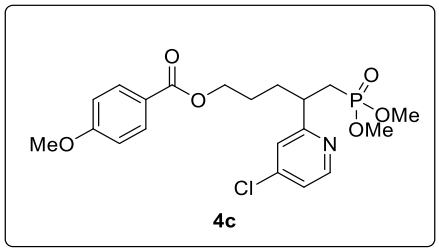
5-(dimethoxyphosphoryl)-4-(4-methylpyridin-2-yl)pentyl 4-methoxybenzoate (4a). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4a** (60.1 mg, 71%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 5.0 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 2H), 6.99 (s, 1H), 6.93 (d, *J* = 5.7 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 2H), 4.18 (t, *J* = 6.6 Hz, 2H), 3.83 (s, 3H), 3.55 (d, *J* = 10.8 Hz, 3H), 3.47 (d, *J* = 10.9 Hz, 3H), 3.15 – 3.12 (m, 1H), 2.44 – 2.38 (m, 1H), 2.30 (s, 3H), 2.11 – 2.05 (m, 1H), 1.92 – 1.88 (m, 2H), 1.65 – 1.60 (m, 1H), 1.49 – 1.45 (m, 1H). 13C NMR (101 MHz, Chloroform-d) δ 166.2, 163.2, 162.1 (d, J = 7.4 Hz), 149.2, 147.4, 131.5, 124.4, 122.7, 122.7, 113.5, 64.3, 55.3, 52.0 (d, *J* = 6.7 Hz), 51.9 (d, *J* = 6.5 Hz), 41.3 (d, J = 3.3 Hz), 33.0 (d, J = 13.6 Hz), 30.1 (d, J = 138.9 Hz), 26.5, 20.9. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 33.7. HRMS (ESI) Calcd for $C_{21}H_{28}NO_6P$: [M] + Na^+ = 444.1546. Found: 444.1575.



4b

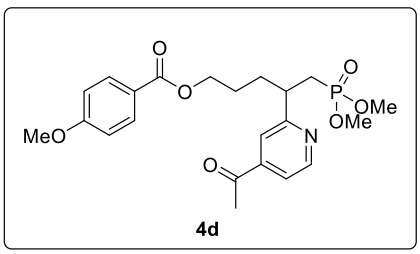
5-(dimethoxyphosphoryl)-4-(4-phenylpyridin-2-yl)pentyl 4-methoxybenzoate (4b). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4b** (66.9 mg, 70%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H),

7.47 (t, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 9.9 Hz, 2H), 7.36 (d, *J* = 5.1 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.22 (t, *J* = 6.5 Hz, 2H), 3.83 (s, 3H), 3.57 (d, *J* = 10.8 Hz, 3H), 3.49 (d, *J* = 10.9 Hz, 3H), 3.30 – 3.28 (m, 1H), 2.49 – 2.46 (m, 1H), 2.18 – 2.17 (m, 1H), 2.01 – 1.98 (m, 2H), 1.69 – 1.67 (m, 1H), 1.56 – 1.54 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.2, 163.2, 163.0 (d, *J* = 7.1 Hz), 149.9, 148.7, 138.0, 131.5, 129.0, 129.0, 127.0, 122.7, 121.4, 119.7, 113.5, 64.2, 55.3, 52.0 (d, *J* = 6.6 Hz), 52.0 (d, *J* = 6.5 Hz), 41.6 (d, *J* = 3.4 Hz), 33.1 (d, *J* = 13.7 Hz), 30.3 (d, *J* = 139.3 Hz), 26.5. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 33.0. HRMS (ESI) Calcd for $C_{26}H_{30}NO_6P$: [M] + Na^+ = 506.1703. Found: 506.1779.



4c

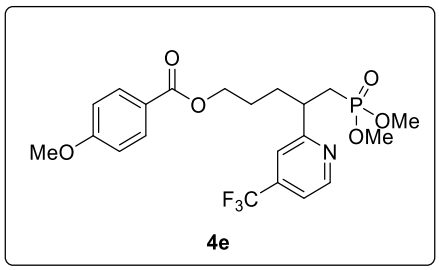
4-(4-chloropyridin-2-yl)-5-(dimethoxyphosphoryl)pentyl 4-methoxybenzoate (4c). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4c** (56.5 mg, 64%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 5.3 Hz, 1H), 7.95 (d, *J* = 8.9 Hz, 2H), 7.20 (d, *J* = 1.9 Hz, 1H), 7.15 (dd, *J* = 5.3, 2.0 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 2H), 4.20 (t, *J* = 6.5 Hz, 2H), 3.84 (s, 3H), 3.56 (d, *J* = 10.9 Hz, 3H), 3.52 (d, *J* = 10.8 Hz, 3H), 3.17 – 3.15 (m, 1H), 2.41 – 2.39 (m, 1H), 2.11 – 2.10 (m, 1H), 1.92 – 1.91 (m, 2H), 1.65 – 1.63 (m, 1H), 1.50 – 1.48 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-d) δ 166.2, 164.3 (d, J = 7.0 Hz), 163.3, 150.4, 144.1, 131.5, 123.7, 122.6, 122.1, 113.5, 64.1, 55.4, 52.0 (d, *J* = 2.7 Hz), 52.0 (d, *J* = 2.7 Hz), 41.5 (d, J = 3.5 Hz), 33.0 (d, J = 13.8 Hz), 30.0 (d, J = 139.9 Hz), 26.4. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.3. HRMS (ESI) Calcd for $C_{20}H_{25}ClNO_6P$: [M] + Na^+ = 464.1000. Found: 464.1016.



4d

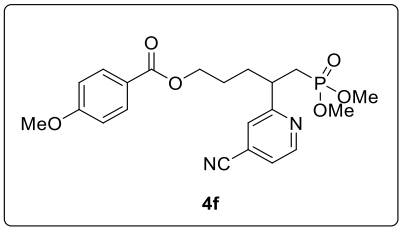
4-(4-acetylpyridin-2-yl)-5-(dimethoxyphosphoryl)pentyl 4-methoxybenzoate (4d). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-

enoate (44.0 mg, 0.2 mmol), compound **4d** (58.4 mg, 65%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.75 (d, *J* = 5.0 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.60 (s, 1H), 7.57 (d, *J* = 4.9 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 2H), 4.24 – 4.18 (m, 2H), 3.84 (s, 3H), 3.56 (d, *J* = 10.8 Hz, 3H), 3.51 (d, *J* = 10.9 Hz, 3H), 3.31 – 3.30 (m, 1H), 2.61 (s, 3H), 2.45 – 2.43 (m, 1H), 2.16 – 2.14 (m, 1H), 1.96 – 1.94 (m, 2H), 1.67 – 1.64 (m, 1H), 1.48 – 1.46 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 197.4, 166.2, 164.2 (d, *J* = 7.0 Hz), 163.3, 150.7, 143.1, 131.5, 122.6, 121.0, 119.4, 113.5, 64.1, 55.4, 52.1 (d, *J* = 3.8 Hz), 52.0 (d, *J* = 4.4 Hz), 41.7 (d, *J* = 3.4 Hz), 33.1 (d, *J* = 13.8 Hz), 30.1 (d, *J* = 139.8 Hz), 26.7, 26.5. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.4. HRMS (ESI) Calcd for $C_{22}H_{28}NO_7P$: [M] + Na^+ = 472.1496. Found: 472.1506.



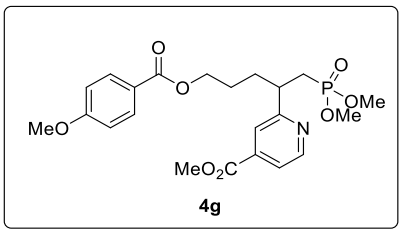
4e

5-(dimethoxyphosphoryl)-4-(4-(trifluoromethyl)pyridin-2-yl)pentyl 4-methoxybenzoate (4e). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound 4e (78.8 mg, 83%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 (d, *J* = 5.0 Hz, 1H), 7.95 (d, *J* = 8.9 Hz, 2H), 7.40 (s, 1H), 7.37 (d, *J* = 5.0 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 4.22 (t, *J* = 6.5 Hz, 2H), 3.85 (s, 3H), 3.56 (d, *J* = 10.8 Hz, 3H), 3.52 (d, *J* = 10.9 Hz, 3H), 3.31 – 3.29 (m, 1H), 2.44 – 2.40 (m, 1H), 2.16 – 2.14 (m, 1H), 1.97 – 1.95 (m, 2H), 1.69 – 1.66 (m, 1H), 1.50 – 1.48 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 164.3, 163.3, 150.5, 138.5 (q, *J* = 34.0 Hz), 131.5, 122.8 (q, *J* = 272.0 Hz), 122.6, 119.1 (q, *J* = 30.0 Hz), 117.4 (q, *J* = 30.0 Hz), 113.5, 64.1, 55.4, 52.1 (d, *J* = 6.6 Hz), 52.0 (d, *J* = 6.7 Hz), 41.8 (d, *J* = 3.6 Hz), 33.1 (d, *J* = 14.3 Hz), 30.2 (d, *J* = 140.3 Hz), 26.4. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 32.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.7. HRMS (ESI) Calcd for $C_{21}H_{25}F_3NO_6P$: [M] + Na^+ = 498.1264. Found: 498.1260.



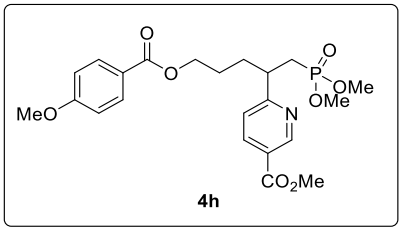
4f

4-(4-cyanopyridin-2-yl)-5-(dimethoxyphosphoryl)pentyl 4-methoxybenzoate (4f). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4f** (68.2 mg, 80%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.74 (d, *J* = 4.9 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.41 (s, 1H), 7.38 (d, *J* = 4.9 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.21 – 4.20 (m, 2H), 3.85 (s, 3H), 3.55 (dd, *J* = 16.1, 10.9 Hz, 6H), 3.27 – 3.24 (m, 1H), 2.42 – 2.40 (m, 1H), 2.15 – 2.10 (m, 1H), 1.94 – 1.91 (m, 2H), 1.67 – 1.64 (m, 1H), 1.47 – 1.45 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.1, 164.3 (d, *J* = 6.3 Hz), 163.3, 150.5, 131.5, 125.0, 123.2, 122.5, 120.5, 116.4, 113.6, 63.9, 55.4, 52.2 (d, *J* = 6.6 Hz), 52.1 (d, *J* = 6.6 Hz), 41.7 (d, *J* = 3.6 Hz), 33.0 (d, *J* = 14.5 Hz), 29.9 (d, *J* = 140.4 Hz), 26.4. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 31.9. HRMS (ESI) Calcd for $C_{21}H_{25}N_2O_6P$: [M] + Na^+ = 455.1342. Found: 455.1367.



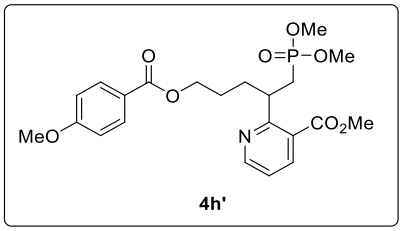
4g

methyl 2-(1-(dimethoxyphosphoryl)-5-((4-methoxybenzoyl)oxy)pentan-2-yl) isonicotinate (4g). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4g** (74.2 mg, 80%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 2H), 7.71 (dd, *J* = 1.6, 0.9 Hz, 1H), 7.67 (dd, *J* = 5.0, 1.6 Hz, 1H), 6.87 (d, *J* = 8.9 Hz, 2H), 4.17 (t, *J* = 6.5 Hz, 2H), 3.91 (s, 3H), 3.81 (s, 3H), 3.53 (d, *J* = 10.8 Hz, 3H), 3.49 (d, *J* = 10.9 Hz, 3H), 3.29 – 3.26 (m, 1H), 2.44 – 2.39 (m, 1H), 2.13 – 2.11 (m, 1H), 1.94 – 1.90 (m, 2H), 1.69 – 1.58 (m, 1H), 1.46 – 1.42 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1, 165.5, 163.7 (d, *J* = 7.0 Hz), 163.2, 150.3, 137.5, 131.4, 122.5, 122.4, 120.9, 113.4, 64.1, 55.3, 52.6, 52.0 (d, *J* = 2.6 Hz), 52.0 (d, *J* = 2.6 Hz), 41.6 (d, *J* = 3.5 Hz), 33.1 (d, *J* = 14.0 Hz), 30.0 (d, *J* = 139.8 Hz), 26.4. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 33.1. HRMS (ESI) Calcd for $C_{22}H_{28}NO_8P$: [M] + Na^+ = 488.1445. Found: 488.1443.



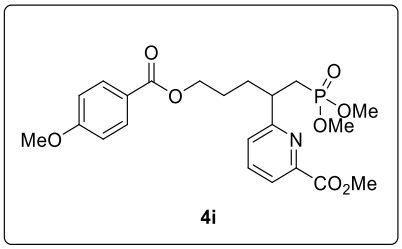
4h

methyl 6-(1-(dimethoxyphosphoryl)-5-((4-methoxybenzoyl)oxy)pentan-2-yl)nicotinate (4h). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4h** (47.8 mg, 52%) (major) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 9.16 (d, *J* = 1.9 Hz, 1H), 8.20 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 2H), 4.20 – 4.17 (m, 2H), 3.93 (s, 3H), 3.84 (s, 3H), 3.55 (d, *J* = 10.8 Hz, 3H), 3.49 (d, *J* = 10.9 Hz, 3H), 3.28 – 3.26 (m, 1H), 2.47 – 2.44 (m, 1H), 2.15 – 2.11 (m, 1H), 1.94 – 1.92 (m, 2H), 1.63 – 1.62 (m, 1H), 1.46 – 1.45 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.1 (d, *J* = 6.4 Hz), 166.2, 165.7, 163.3, 150.8, 137.3, 131.5, 124.2, 123.2, 122.7, 113.5, 64.1, 55.4, 52.3, 52.1 (d, *J* = 6.0 Hz), 52.0 (d, *J* = 6.4 Hz), 41.7 (d, *J* = 3.5 Hz), 33.1 (d, *J* = 14.0 Hz), 30.0 (d, *J* = 140.0 Hz), 26.5. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.3. HRMS (ESI) Calcd for $C_{22}H_{28}NO_8P$: [M] + Na^+ = 488.1445. Found: 488.1455.



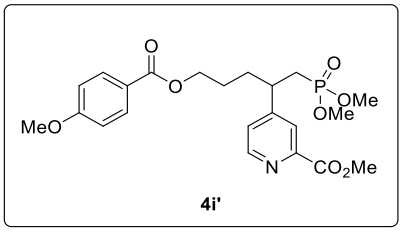
4h'

methyl 2-(1-(dimethoxyphosphoryl)-5-((4-methoxybenzoyl)oxy)pentan-2-yl)nicotinate (4h'). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4h'** (20.4 mg, 22%) (minor) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.70 (dd, *J* = 4.7, 1.8 Hz, 1H), 8.12 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.97 (d, *J* = 8.9 Hz, 2H), 7.22 (dd, *J* = 7.9, 4.7 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.29 – 4.27 (m, 1H), 4.22 (t, *J* = 6.6 Hz, 2H), 3.94 (s, 3H), 3.86 (s, 3H), 3.55 (d, *J* = 10.8 Hz, 3H), 3.50 (d, *J* = 10.7 Hz, 3H), 2.55 – 2.52 (m, 1H), 2.13 – 2.09 (m, 2H), 1.93 – 1.91 (m, 1H), 1.78 – 1.77 (m, 1H), 1.53 – 1.51 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.1, 166.3, 163.3 (d, *J* = 6.0 Hz), 163.2, 151.9, 138.0, 131.6, 126.7, 122.9, 121.0, 113.5, 64.5, 55.4, 52.5, 52.1 (d, *J* = 6.4 Hz), 52.0 (d, *J* = 6.9 Hz), 36.6 (d, *J* = 3.0 Hz), 33.3 (d, *J* = 15.0 Hz), 30.1 (d, *J* = 139.3 Hz), 26.4. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 33.0. HRMS (ESI) Calcd for $C_{22}H_{28}NO_8P$: [M] + Na^+ = 488.1445. Found: 488.1455.



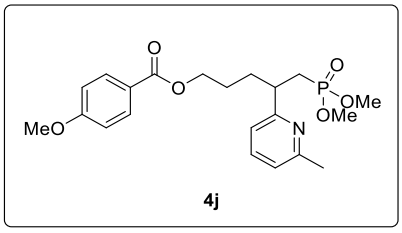
4i

methyl 6-(1-(dimethoxyphosphoryl)-5-((4-methoxybenzoyl)oxy)pentan-2-yl) picolinate (4i). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4i** (28.3 mg, 30%) (minor) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 8.1, 4.2 Hz, 3H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.21 – 4.20 (m, 2H), 3.97 (s, 3H), 3.86 (s, 3H), 3.56 (d, *J* = 10.8 Hz, 3H), 3.52 (d, *J* = 10.8 Hz, 3H), 3.33 – 3.31 (m, 1H), 2.56 – 2.54 (m, 1H), 2.17 – 2.16 (m, 1H), 1.99 – 1.96 (m, 2H), 1.68 – 1.66 (m, 1H), 1.52 – 1.49 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.2, 165.8, 163.3, 163.1 (d, *J* = 7.0 Hz), 148.0, 137.0, 131.5, 126.5, 123.3, 122.7, 113.5, 64.2, 55.4, 52.6, 52.1, 52.0, 41.6 (d, *J* = 3.5 Hz), 33.1 (d, *J* = 13.8 Hz), 29.8 (d, *J* = 139.3 Hz), 26.5. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.7. HRMS (ESI) Calcd for $C_{22}H_{28}NO_8P$: [M] + Na^+ = 488.1445. Found: 488.1447.



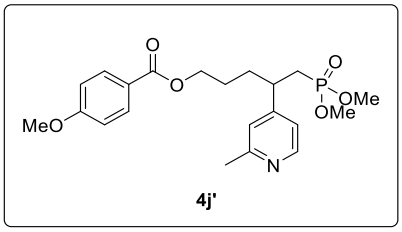
4i'

methyl 4-(1-(dimethoxyphosphoryl)-5-((4-methoxybenzoyl)oxy)pentan-2-yl)picolinate (4i'). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4i'** (44.8 mg, 48%) (major) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.67 (d, *J* = 4.9 Hz, 1H), 8.01 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 3.4 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.21 (t, *J* = 6.4 Hz, 2H), 4.00 (s, 3H), 3.85 (s, 3H), 3.59 (d, *J* = 10.9 Hz, 3H), 3.51 (d, *J* = 10.9 Hz, 3H), 3.16 – 3.15 (m, 1H), 2.18 – 2.10 (m, 2H), 2.02 – 2.00 (m, 1H), 1.82 – 1.79 (m, 1H), 1.64 – 1.62 (m, 1H), 1.50 – 1.48 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.1, 165.6, 163.3, 154.4 (d, *J* = 8.1 Hz), 150.0, 148.3, 131.5, 126.4, 123.9, 122.5, 113.6, 63.8, 55.4, 52.9, 52.2, 52.1, 39.6 (d, *J* = 3.7 Hz), 33.4 (d, *J* = 12.4 Hz), 31.5 (d, *J* = 141.3 Hz), 26.5. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 30.8. HRMS (ESI) Calcd for $C_{22}H_{28}NO_8P$: [M] + Na^+ = 488.1445. Found: 488.1457.



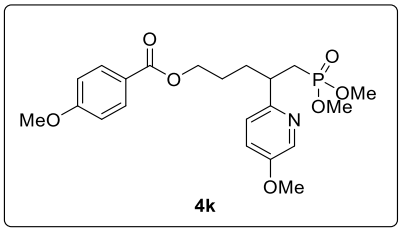
4j

5-(dimethoxyphosphoryl)-4-(6-methylpyridin-2-yl)pentyl 4-methoxybenzoate (4j). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4j** (38.7 mg, 46%) (major) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.9 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 4.21 (t, *J* = 6.6 Hz, 2H), 3.86 (s, 3H), 3.56 (d, *J* = 10.8 Hz, 3H), 3.52 (d, *J* = 10.8 Hz, 3H), 3.20 (s, 1H), 2.54 – 2.45 (m, 4H), 2.18 – 2.09 (m, 1H), 1.96 – 1.90 (m, 2H), 1.69 – 1.63 (m, 1H), 1.54 – 1.50 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.2, 163.2, 161.7 (d, *J* = 7.5 Hz), 158.1, 136.4, 131.5, 122.8, 121.2, 120.2, 113.5, 64.3, 55.4, 52.0 (d, *J* = 6.5 Hz), 51.9 (d, *J* = 6.4 Hz), 41.4 (d, *J* = 3.4 Hz), 33.0 (d, *J* = 13.5 Hz), 30.1 (d, *J* = 138.7 Hz), 26.5, 24.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 33.8. HRMS (ESI) Calcd for $C_{21}H_{28}NO_6P$: [M] + Na^+ = 444.1546. Found: 444.1559.



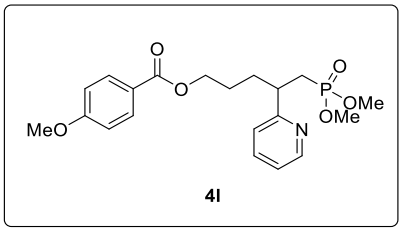
4j'

5-(dimethoxyphosphoryl)-4-(2-methylpyridin-4-yl)pentyl 4-methoxybenzoate (4j'). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4j'** (19.7 mg, 23%) (minor) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 (d, *J* = 5.1 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 2H), 7.00 (s, 1H), 6.94 (d, *J* = 5.2 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 2H), 4.20 (t, *J* = 6.4 Hz, 2H), 3.84 (s, 3H), 3.59 (d, *J* = 10.9 Hz, 3H), 3.49 (d, *J* = 10.9 Hz, 3H), 3.01 – 2.99 (m, 1H), 2.52 (s, 3H), 2.10 – 2.06 (m, 2H), 1.97 – 1.93 (m, 1H), 1.76 – 1.72 (m, 1H), 1.61 – 1.57 (m, 1H), 1.54 – 1.50 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 163.3, 158.6, 153.1 (d, *J* = 8.7 Hz), 149.2, 131.5, 122.5, 122.4, 119.8, 113.5, 63.9, 55.4, 52.1 (d, *J* = 6.8 Hz), 52.0 (d, *J* = 6.6 Hz), 39.3 (d, *J* = 3.4 Hz), 33.2 (d, *J* = 12.0 Hz), 31.6 (d, *J* = 140.6 Hz), 26.5, 24.3. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 32.2. HRMS (ESI) Calcd for $C_{21}H_{28}NO_6P$: [M] + Na^+ = 444.1546. Found: 444.1548.



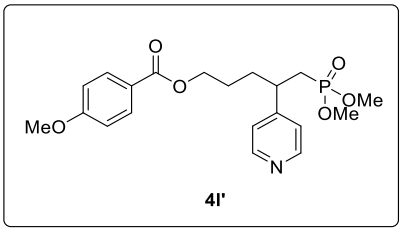
4k

5-(dimethoxyphosphoryl)-4-(5-methoxypyridin-2-yl)pentyl 4-methoxybenzoate (4k). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4k** (45.1 mg, 52%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 3.9, 2.2 Hz, 1H), 7.97 (d, *J* = 9.1 Hz, 2H), 7.15 – 7.14 (m, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 4.22 (t, *J* = 6.6 Hz, 2H), 3.87 (s, 3H), 3.85 – 3.81 (m, 4H), 3.58 (d, *J* = 2.2 Hz, 3H), 3.56 (d, *J* = 2.2 Hz, 3H), 2.56 – 2.52 (m, 1H), 2.15 – 2.13 (m, 1H), 1.94 – 1.92 (m, 2H), 1.69 – 1.65 (m, 1H), 1.56 – 1.53 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 163.2, 153.5, 152.4 (d, *J* = 7.6 Hz), 140.6, 131.5, 122.9, 122.2, 117.3, 113.5, 64.5, 55.5, 55.4, 52.1, 52.0, 33.2 (d, *J* = 2.9 Hz), 32.2 (d, *J* = 13.1 Hz), 28.9 (d, *J* = 138.9 Hz), 26.2. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 34.3. HRMS (ESI) Calcd for $C_{21}H_{28}NO_7P$: [M] + Na^+ = 460.1496. Found: 460.1514.



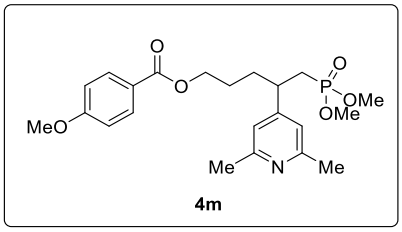
4l

5-(dimethoxyphosphoryl)-4-(pyridin-2-yl)pentyl 4-methoxybenzoate (4l). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4l** (39.3 mg, 49%) (major) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 4.8 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.14 – 7.12 (m, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 4.19 (t, *J* = 6.6 Hz, 2H), 3.84 (s, 3H), 3.55 (d, *J* = 10.8 Hz, 3H), 3.48 (d, *J* = 10.8 Hz, 3H), 3.21 – 3.18 (m, 4.9 Hz, 1H), 2.46 – 2.41 (m, 1H), 2.16 – 2.09 (m, 1H), 1.94 – 1.92 (m, 2H), 1.66 – 1.63 (m, 1H), 1.49 – 1.46 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.2, 163.3, 162.4 (d, *J* = 7.0 Hz), 149.6, 136.3, 131.5, 123.6, 122.7, 121.8, 113.5, 64.3, 55.4, 52.0 (d, *J* = 4.9 Hz), 52.0 (d, *J* = 4.7 Hz), 41.5 (d, *J* = 3.4 Hz), 33.2 (d, *J* = 14.0 Hz), 30.2 (d, *J* = 139.3 Hz), 26.5. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.9. HRMS (ESI) Calcd for $C_{20}H_{26}NO_6P$: [M] + Na^+ = 430.1390. Found: 430.1393.



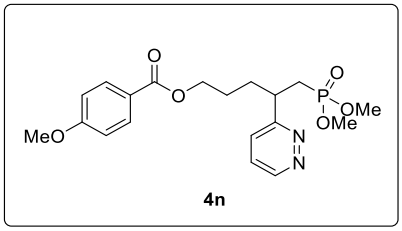
4l'

5-(dimethoxyphosphoryl)-4-(pyridin-4-yl)pentyl 4-methoxybenzoate (4l'). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4l'** (17.1 mg, 21%) (minor) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 6.1 Hz, 2H), 7.95 (d, *J* = 9.0 Hz, 2H), 7.16 (d, *J* = 6.1 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 4.22 (t, *J* = 6.4 Hz, 2H), 3.86 (s, 3H), 3.59 (d, *J* = 10.9 Hz, 3H), 3.50 (d, *J* = 10.8 Hz, 3H), 3.06 – 3.04 (m, 1H), 2.16 – 2.09 (m, 2H), 1.99 – 1.96 (m, 1H), 1.79 – 1.76 (m, 1H), 1.66 – 1.62 (m, 1H), 1.55 – 1.51 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 163.3, 152.7 (d, *J* = 8.5 Hz), 150.1, 131.5, 122.8, 122.6, 113.6, 63.9, 55.4, 52.2 (d, *J* = 6.7 Hz), 52.1 (d, *J* = 6.6 Hz), 39.5 (d, *J* = 3.5 Hz), 33.4 (d, *J* = 12.5 Hz), 31.7 (d, *J* = 140.9 Hz), 26.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 32.0. HRMS (ESI) Calcd for $C_{20}H_{26}NO_6P$: [M] + H^+ = 408.1571. Found: 408.1589.



4m

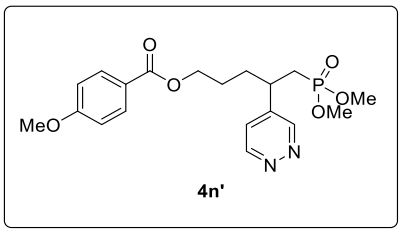
5-(dimethoxyphosphoryl)-4-(2,6-dimethylpyridin-4-yl)pentyl 4-methoxybenzoate (4m). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4m** (53.1 mg, 61%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.81 (s, 2H), 4.21 (t, *J* = 6.5 Hz, 2H), 3.85 (s, 3H), 3.60 (d, *J* = 10.9 Hz, 3H), 3.51 (d, *J* = 10.9 Hz, 3H), 2.97 – 2.95 (m, 1H), 2.50 (s, 6H), 2.09 – 2.06 (m, 2H), 1.97 – 1.95 (m, 1H), 1.74 – 1.72 (m, 1H), 1.63 – 1.60 (m, 1H), 1.53 – 1.51 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.2, 163.3, 157.9, 153.5 (d, *J* = 9.0 Hz), 131.5, 122.6, 119.4, 113.6, 64.0, 55.4, 52.2 (d, *J* = 6.8 Hz), 52.1 (d, *J* = 6.7 Hz), 39.3 (d, *J* = 3.5 Hz), 33.1 (d, *J* = 11.5 Hz), 31.7 (d, *J* = 140.4 Hz), 26.5, 24.3. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 31.7. HRMS (ESI) Calcd for $C_{22}H_{30}NO_6P$: [M] + Na^+ = 458.1703. Found: 458.1712.



4n

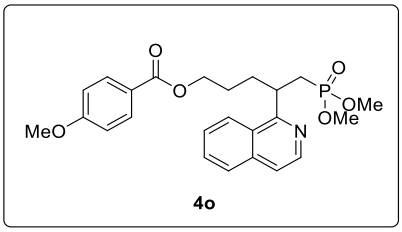
5-(dimethoxyphosphoryl)-4-(pyridazin-3-yl)pentyl 4-methoxybenzoate (4n). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate

(44.0 mg, 0.2 mmol), compound **4n** (46.0 mg, 57%) (major) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 9.10 (d, *J* = 3.2 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.42 (t, *J* = 6.6 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.23 (t, *J* = 6.6 Hz, 2H), 3.86 (s, 3H), 3.58 (d, *J* = 10.9 Hz, 3H), 3.51 (d, *J* = 10.9 Hz, 3H), 3.38 – 3.35 (m, 1H), 2.62 – 2.58 (m, 1H), 2.29 – 2.23 (m, 1H), 2.11 – 2.02 (m, 2H), 1.71 – 1.68 (m, 1H), 1.56 – 1.52 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.2, 164.6 (d, *J* = 5.0 Hz), 163.3, 150.1, 131.5, 126.9, 126.3, 122.6, 113.6, 64.0, 55.4, 52.2 (d, *J* = 4.0 Hz), 52.1 (d, *J* = 3.7 Hz), 40.7 (d, *J* = 3.6 Hz), 33.3 (d, *J* = 14.4 Hz), 29.9 (d, *J* = 139.9 Hz), 26.4. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 31.9. HRMS (ESI) Calcd for $C_{19}H_{25}N_2O_6P$: [M] + Na^+ = 431.1342. Found: 431.1353.



4n'

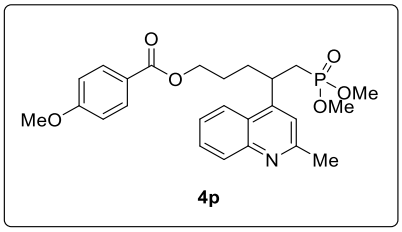
5-(dimethoxyphosphoryl)-4-(pyridazin-4-yl)pentyl 4-methoxybenzoate (4n'). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1), From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4n'** (17.7 mg, 21%) (C4:C3 = 2.6:1) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 9.11 – 9.09 (m, 2H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.32 (d, *J* = 4.2 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 1H), 4.21 (t, *J* = 6.4 Hz, 2H), 3.83 (s, 2H), 3.58 (d, *J* = 10.9 Hz, 2H), 3.50 (d, *J* = 10.9 Hz, 2H), 3.09 – 3.07 (m, 1H), 2.18 – 2.14 (m, 1H), 2.08 – 2.06 (m, 1H), 1.99 – 1.98 (m, 1H), 1.81 – 1.79 (m, 1H), 1.65 – 1.63 (m, 1H), 1.52 – 1.50 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.1, 163.4, 151.8, 151.1, 143.0 (d, *J* = 7.0 Hz), 131.5, 125.1, 122.4, 113.6, 63.6, 55.4, 52.3 (d, *J* = 6.7 Hz), 52.2 (d, *J* = 6.7 Hz), 37.6 (d, *J* = 3.9 Hz), 33.1 (d, *J* = 13.3 Hz), 31.1 (d, *J* = 142.1 Hz), 26.4. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 30.2. HRMS (ESI) Calcd for $C_{19}H_{25}N_2O_6P$: [M] + Na^+ = 431.1342. Found: 431.1342.



4o

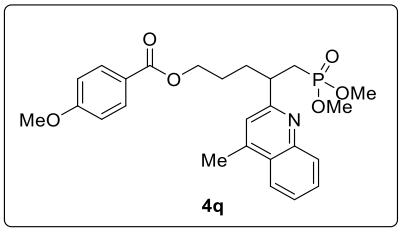
5-(dimethoxyphosphoryl)-4-(isoquinolin-1-yl)pentyl 4-methoxybenzoate (4o). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate

(44.0 mg, 0.2 mmol), compound **4o** (58.0 mg, 64%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 5.6 Hz, 1H), 8.31 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 9.1 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.68 (t, *J* = 6.9 Hz, 1H), 7.61 (t, *J* = 7.0 Hz, 1H), 7.54 (d, *J* = 5.7 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 2H), 4.26 – 2.24 (m, 1H), 4.18 (t, *J* = 6.5 Hz, 2H), 3.85 (s, 3H), 3.50 (d, *J* = 10.8 Hz, 3H), 3.38 (d, *J* = 10.8 Hz, 3H), 2.74 – 2.69 (m, 1H), 2.31 – 2.26 (m, 1H), 2.19 – 2.16 (m, 1H), 2.06 – 2.02 (m, 1H), 1.68 – 1.65 (m, 1H), 1.52 – 1.48 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 163.3, 162.5 (d, *J* = 6.9 Hz), 141.8, 136.3, 131.5, 129.9, 127.5, 127.4, 127.2, 124.6, 122.7, 119.6, 113.5, 64.3, 55.4, 52.0 (d, *J* = 5.0 Hz), 52.0 (d, *J* = 5.4 Hz), 35.3, 33.4 (d, *J* = 13.5 Hz), 29.9 (d, *J* = 138.9 Hz), 26.4. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 34.0. HRMS (ESI) Calcd for $C_{24}H_{28}NO_6P$: [M] + Na^+ = 480.1546. Found: 480.1546.



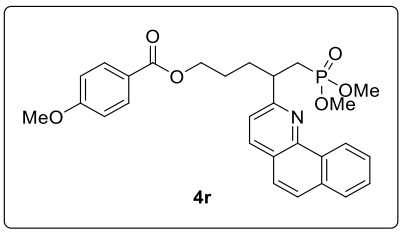
4p

5-(dimethoxyphosphoryl)-4-(2-methylquinolin-4-yl)pentyl 4-methoxybenzoate (4p). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4p** (76.0 mg, 81%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 2H), 7.68 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.52 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.19 (s, 1H), 6.88 (d, *J* = 9.0 Hz, 2H), 4.21 (t, *J* = 6.4 Hz, 2H), 4.02 – 3.98 (m, 1H), 3.84 (s, 3H), 3.56 (d, *J* = 10.8 Hz, 3H), 3.47 (d, *J* = 10.8 Hz, 3H), 2.72 (s, 3H), 2.22 – 2.18 (m, 3H), 2.01 – 1.98 (m, 1H), 1.66 – 1.62 (m, 1H), 1.58 – 1.54 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 163.3, 158.5, 150.1 (d, *J* = 7.5 Hz), 148.3, 131.5, 131.5, 129.6, 129.2, 125.8, 125.3, 122.7, 122.5, 113.5, 64.0, 55.4, 52.2 (d, *J* = 6.7 Hz), 52.1 (d, *J* = 6.6 Hz), 32.7 (d, *J* = 9.6 Hz), 32.4, 31.0, 26.4, 25.4. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 32.3. HRMS (ESI) Calcd for $C_{25}H_{30}NO_6P$: [M] + H^+ = 472.1884. Found: 472.1899.



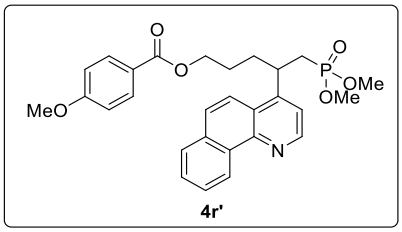
4q

5-(dimethoxyphosphoryl)-4-(4-methylquinolin-2-yl)pentyl 4-methoxybenzoate (4q). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4q** (61.3 mg, 65%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.97 – 7.89 (m, 3H), 7.66 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.50 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.15 (s, 1H), 6.87 (d, *J* = 8.9 Hz, 2H), 4.21 (t, *J* = 6.5 Hz, 2H), 3.83 (s, 3H), 3.51 (dd, *J* = 12.0, 10.8 Hz, 6H), 3.39 – 3.36 (m, 1H), 2.69 – 2.65 (m, 4H), 2.21 – 2.19 (m, 1H), 2.03 – 2.00 (m, 2H), 1.71 – 1.69 (m, 1H), 1.59 – 1.55 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 163.2, 162.6 (d, *J* = 7.8 Hz), 147.7, 144.3, 131.4, 129.5, 129.0, 127.1, 125.7, 123.6, 122.7, 122.1, 113.4, 64.3, 55.3, 52.1 (d, *J* = 6.7 Hz), 52.0 (d, *J* = 6.5 Hz), 41.8 (d, *J* = 3.3 Hz), 33.1 (d, *J* = 12.9 Hz), 29.6 (d, *J* = 139.1 Hz), 26.4, 18.7. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 33.9. HRMS (ESI) Calcd for $C_{25}H_{30}NO_6P$: [M] + Na^+ = 494.1703. Found: 494.1715.



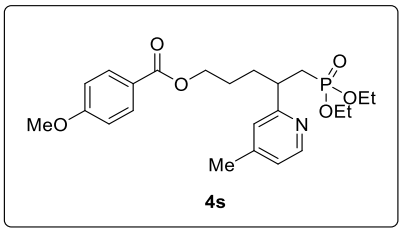
4r

4-(benzo[h]quinolin-2-yl)-5-(dimethoxyphosphoryl)pentyl 4-methoxybenzoate (4r). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4r** (53.6 mg, 53%) (major) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 9.36 (d, *J* = 7.4 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.91 – 7.90 (m, 3H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.72 – 7.67 (m, 3H), 7.44 (d, *J* = 8.1 Hz, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 4.23 (q, *J* = 6.3 Hz, 2H), 3.82 (s, 3H), 3.48 (dd, *J* = 10.8, 7.9 Hz, 7H), 2.85 – 2.83 (m, 1H), 2.33 – 2.31 (m, 1H), 2.22 – 2.20 (m, 1H), 2.08 – 2.06 (m, 1H), 1.75 – 1.73 (m, 1H), 1.60 – 1.58 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.2, 163.2, 161.5 (d, *J* = 7.1 Hz), 146.0, 136.0, 133.7, 131.4, 131.4, 128.0, 127.7, 127.0, 126.8, 125.2, 124.9, 124.5, 122.7, 122.3, 113.4, 64.3, 55.3, 52.0 (d, *J* = 5.5 Hz), 52.0 (d, *J* = 5.2 Hz), 42.0 (d, *J* = 3.4 Hz), 33.8 (d, *J* = 13.8 Hz), 30.3 (d, *J* = 139.0 Hz), 26.40. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 33.3. HRMS (ESI) Calcd for $C_{28}H_{30}NO_6P$: [M] + Na^+ = 530.1703. Found: 530.1728.



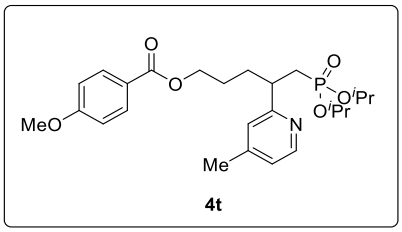
4r'

4-(benzo[h]quinolin-4-yl)-5-(dimethoxyphosphoryl)pentyl 4-methoxybenzoate (4r'). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4r'** (27.4 mg, 27%) (minor) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 9.34 (d, *J* = 8.1 Hz, 1H), 8.98 (d, *J* = 4.6 Hz, 1H), 8.10 (d, *J* = 9.2 Hz, 1H), 7.92 – 7.86 (m, 4H), 7.75– 7.70 (m, 2H), 7.44 (d, *J* = 4.7 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.21 (q, *J* = 3.6 Hz, 2H), 4.15 – 4.09 (m, 1H), 3.83 (s, 3H), 3.56 (d, *J* = 10.9 Hz, 3H), 3.45 (d, *J* = 10.9 Hz, 3H), 2.30 – 2.21 (m, 3H), 2.04 – 2.02 (m, 1H), 1.69 – 1.66 (m, 1H), 1.57 – 1.53 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.2, 163.3, 149.9 (d, *J* = 9.1 Hz), 148.8, 148.4, 146.9, 133.2, 131.9, 131.5, 128.3, 127.9, 127.6, 127.1, 124.9, 124.9, 122.5, 120.3, 113.5, 64.0, 55.4, 52.2 (d, *J* = 6.9 Hz), 52.1 (d, *J* = 6.5 Hz), 33.2 (d, *J* = 10.5 Hz), 32.2, 31.3, 26.4. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 31.5. HRMS (ESI) Calcd for $C_{28}H_{30}NO_6P$: [M] + Na^+ = 530.1703. Found: 530.1733.



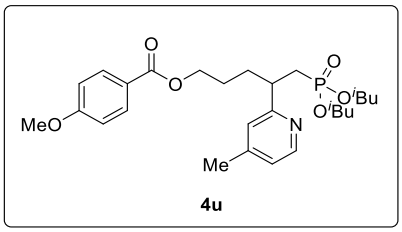
4s

5-(diethoxyphosphoryl)-4-(4-methylpyridin-2-yl)pentyl 4-methoxybenzoate (4s). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4s** (69.4 mg, 74%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 4.9 Hz, 1H), 7.94 (d, *J* = 8.9 Hz, 2H), 7.00 (s, 1H), 6.94 (d, *J* = 4.9 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.19 (t, *J* = 6.4 Hz, 2H), 3.96 – 3.91 (m, 2H), 3.85 – 3.83 (m, 5H), 3.17 – 3.13 (m, 1H), 2.41 – 2.39 (m, 1H), 2.30 (s, 3H), 2.12 – 2.06 (m, 1H), 1.93 – 1.90 (m, 2H), 1.64 – 1.62 (m, 1H), 1.49 – 1.46 (m, 1H), 1.17 (t, *J* = 7.0 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.2, 163.2, 162.3 (d, *J* = 7.1 Hz), 149.1, 147.3, 131.5, 124.5, 122.7, 122.7, 113.5, 64.3, 61.3 (d, *J* = 6.4 Hz), 61.2 (d, *J* = 6.5 Hz), 55.3, 41.4 (d, *J* = 3.3 Hz), 33.1 (d, *J* = 13.8 Hz), 31.1 (d, *J* = 139.3 Hz), 26.5, 20.90, 16.2 (T, *J* = 7.6 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.0. HRMS (ESI) Calcd for $C_{23}H_{32}NO_6P$: [M] + Na^+ = 472.1859. Found: 472.1854.



4t

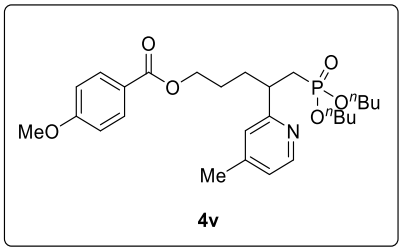
5-(diisopropoxyphosphoryl)-4-(4-methylpyridin-2-yl)pentyl 4-methoxybenzoate (4t). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4t** (66.4 mg, 70%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.40 (d, J = 5.1 Hz, 1H), 7.94 (d, J = 8.9 Hz, 2H), 7.01 (s, 1H), 6.96 (d, *J* = 4.4 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 4.58 – 4.51 (m, 2H), 4.18 (t, *J* = 6.6 Hz, 2H), 3.83 (s, 3H), 3.19 – 3.12 (m, 1H), 2.38 – 2.31 (m, 4H), 2.07 – 2.04 (m, 1H), 1.98 – 1.92 (m, 2H), 1.64 – 1.59 (m, 1H), 1.50 – 1.44 (m, 1H), 1.19 (dd, *J* = 6.2, 4.9 Hz, 6H), 1.13 (dd, *J* = 11.9, 6.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 163.2, 162.2 (d, *J* = 6.7 Hz), 148.6, 147.9, 131.5, 124.7, 122.7, 113.5, 69.8 (d, *J* = 6.7 Hz), 69.7 (d, *J* = 6.8 Hz), 64.3, 55.3, 41.6 (d, *J* = 3.7 Hz), 33.0 (d, *J* = 13.1 Hz), 32.7 (d, *J* = 140.9 Hz), 26.6, 23.8 (ddd, *J* = 7.9, 4.5, 2.1 Hz), 21.0. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 28.7. HRMS (ESI) Calcd for $C_{25}H_{36}NO_6P$: [M] + Na^+ = 500.2172. Found: 500.2189.



4u

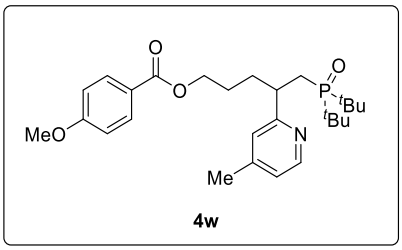
5-(diisobutoxyphosphoryl)-4-(4-methylpyridin-2-yl)pentyl 4-methoxybenzoate (4u). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4u** (70.1 mg, 70%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.42 (d, J = 4.9 Hz, 1H), 7.95 (d, J = 8.9 Hz, 2H), 7.04 (s, 1H), 6.98 (d, J = 3.4 Hz, 1H), 6.89 (d, J = 8.9 Hz, 2H), 4.19 (t, J = 6.5 Hz, 2H), 3.84 (s, 3H), 3.65 (q, J = 6.5 Hz, 2H), 3.56 (t, J = 6.3 Hz, 2H), 3.21 – 3.18 (m, 1H), 2.46 (q, J = 8.9 Hz, 1H), 2.32 (s, 3H), 2.18 – 2.10 (m, 1H), 1.97 – 1.93 (m, 2H), 1.79 – 1.69 (m, 3H), 1.50 – 1.43 (m, 1H), 0.84 (dd, J = 6.7, 2.7 Hz, 6H), 0.80 (dd, J = 6.7, 1.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 163.2, 162.2 (d, *J* = 6.4 Hz), 148.9, 147.8, 131.5, 124.7, 122.8, 122.7, 113.5, 71.3 (t, *J* = 7.2 Hz), 64.3, 55.4, 41.5 (d, *J* = 3.5 Hz), 33.2 (d, *J* = 13.4 Hz), 31.0 (d, *J* = 139.4 Hz), 29.1 (d, *J* = 5.1 Hz), 29.0 (d, *J* = 5.3 Hz), 26.6, 21.0,

18.6 (d, *J* = 2.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 30.6. HRMS (ESI) Calcd for $C_{27}H_{40}NO_6P$: [M] + Na^+ = 528.2485. Found: 528.2506.



4v

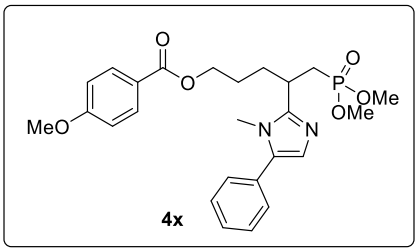
5-(dibutoxyphosphoryl)-4-(4-methylpyridin-2-yl)pentyl 4-methoxybenzoate (4v). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4v** (67.86 mg, 67%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 5.0 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 2H), 6.98 (s, 1H), 6.93 (d, *J* = 4.9 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 2H), 4.16 (t, *J* = 6.5 Hz, 2H), 3.81 – 3.75 (m, 7H), 3.15 – 3.12 (m, 1H), 2.42 – 2.37 (m, 1H), 2.28 (s, 3H), 2.11 – 2.06 (m, 1H), 1.91 – 1.88 (m, 2H), 1.63 – 1.59 (m, 1H), 1.46 – 1.42 (m, 5H), 1.26 – 1.21 (m, 4H), 0.83 (td, *J* = 7.4, 5.3 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1, 163.1, 162.1 (d, *J* = 6.9 Hz), 148.8, 147.6, 131.4, 124.6, 122.6, 122.6, 113.4, 64.9 (dd, *J* = 11.6, 6.7 Hz), 64.2, 55.2, 41.4 (d, *J* = 3.3 Hz), 33.1 (d, *J* = 13.7 Hz), 32.3 (d, *J* = 4.3 Hz), 32.2 (d, *J* = 4.2 Hz), 30.9 (d, *J* = 139.3 Hz), 26.5, 20.9, 18.5 (d, *J* = 2.9 Hz), 13.4. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 30.9. HRMS (ESI) Calcd for $C_{27}H_{40}NO_6P$: [M] + H^+ = 506.2666. Found: 506.2679.



4w

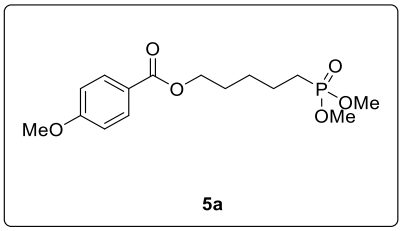
5-(di-tert-butylphosphoryl)-4-(4-methylpyridin-2-yl)pentyl 4-methoxybenzoate (4w). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4w** (45.3 mg, 48%) (single isomer) was obtained. White solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.40 (d, J = 5.0 Hz, 1H), 7.94 (d, J = 9.0 Hz, 2H), 7.07 (s, 1H), 6.92 (d, *J* = 4.4 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 4.19 – 4.15 (m, 2H), 3.82 (s, 3H), 3.29 – 3.25 (m, 1H), 2.33 – 2.29 (m, 4H), 2.00 – 1.96 (m, 3H), 1.64 – 1.61 (m, 1H), 1.45 – 1.41 (m, 1H), 1.24 (d, *J* = 13.0 Hz, 9H), 1.05 (d, *J* = 13.2 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 163.3 (d, *J* = 4.4 Hz), 163.1, 148.8, 147.5, 131.5, 125.5, 122.8, 122.5, 113.4, 64.5, 55.3, 41.4 (d, *J* = 3.6 Hz), 35.9 (d, *J*

= 15.9 Hz), 35.3 (d, *J* = 16.2 Hz), 33.8 (d, *J* = 6.4 Hz), 26.9, 26.3, 26.2 (d, *J* = 54.3 Hz), 26.1, 21.0. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 60.0. HRMS (ESI) Calcd for $C_{27}H_{40}NO_4P$: [M] + Na^+ = 496.2587. Found: 496.2584.



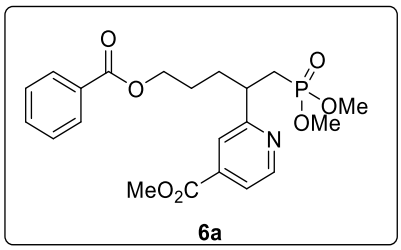
4x

5-(dimethoxyphosphoryl)-4-(1-methyl-5-phenyl-1H-imidazol-2-yl)pentyl 4-methoxybenzoate (**4x**). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1), From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **4x** (48.5 mg, 50%) (single isomer) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.35 (m, 3H), 7.05 (s, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.25 (t, *J* = 6.5 Hz, 2H), 3.85 (s, 3H), 3.63 (s, 3H), 3.61 (d, *J* = 10.9 Hz, 3H), 3.49 (d, *J* = 10.9 Hz, 3H), 3.36 – 3.34 (m, 1H), 2.51 – 2.50 (m, 1H), 2.21 – 2.16 (m, 1H), 2.10 – 2.08 (m, 1H), 1.97 – 1.94 (m, 1H), 1.75 – 1.72 (m, 1H), 1.67 – 1.65 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.3, 163.3, 150.5 (d, *J* = 5.6 Hz), 133.2, 131.6, 130.3, 128.8, 128.6, 127.7, 126.6, 122.7, 113.6, 64.1, 55.4, 52.3 (d, *J* = 6.7 Hz), 52.1 (d, *J* = 6.4 Hz), 33.2 (d, *J* = 15.4 Hz), 31.6 (d, *J* = 3.8 Hz), 31.1, 30.1 (d, *J* = 138.9 Hz), 26.5. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.3. HRMS (ESI) Calcd for $C_{25}H_{31}N_2O_6P$: [M] + H^+ = 487.1992. Found: 487.1942.



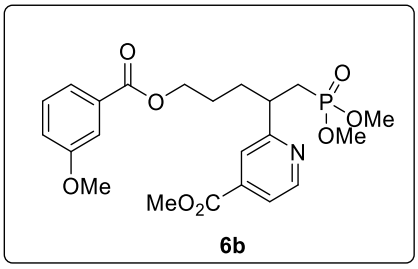
5a

5-(dimethoxyphosphoryl)pentyl 4-methoxybenzoate (5a). Purified by flash column chromatography on silica gel (DCM : MeOH = 35 : 1), colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.29 (t, *J* = 6.5 Hz, 2H), 3.86 (s, 3H), 3.74 (d, *J* = 10.8 Hz, 6H), 1.79 – 1.75 (m, 4H), 1.71 – 1.68 (m, 2H), 1.56 – 1.51 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.2, 163.2, 131.4, 122.7, 113.5, 64.2, 55.3, 52.3, 52.3, 28.3, 27.0 (d, *J* = 16.8 Hz), 24.5 (d, *J* = 140.7 Hz), 22.0 (d, *J* = 5.0 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 35.3. HRMS (ESI) Calcd for $C_{15}H_{23}O_6P$: [M] + Na^+ = 353.1124. Found: 353.1124.



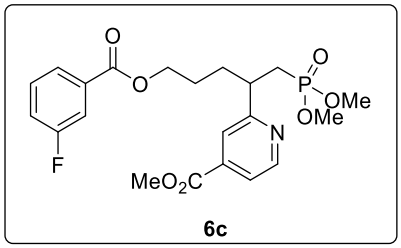
6a

methyl 2-(5-(benzoyloxy)-1-(dimethoxyphosphoryl)pentan-2-yl)isonicotinate (6a). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From pent-4-en-1-yl benzoate (38.0 mg, 0.2 mmol), compound **6a** (64.4 mg, 74%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 5.0 Hz, 1H), 7.99 (d, *J* = 7.3 Hz, 2H), 7.73 (s, 1H), 7.69 (d, *J* = 3.7 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 4.23 (t, *J* = 6.5 Hz, 2H), 3.94 (s, 3H), 3.55 (d, *J* = 10.8 Hz, 3H), 3.51 (d, *J* = 10.9 Hz, 3H), 3.31 – 3.29 (m, 1H), 2.46 – 2.41 (m, 1H), 2.18 – 2.12 (m, 1H), 1.97 – 1.94 (m, 2H), 1.69 – 1.66 (m, 1H), 1.49 – 1.47 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.4, 165.6, 163.8 (d, *J* = 7.3 Hz), 150.4, 137.6, 132.8, 130.2, 129.5, 128.3, 122.5, 121.0, 64.4, 52.6, 52.1 (d, *J* = 3.6 Hz), 52.0 (d, *J* = 4.0 Hz), 41.7 (d, *J* = 3.4 Hz), 33.1 (d, *J* = 13.9 Hz), 30.1 (d, *J* = 139.9 Hz), 26.4. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.4. HRMS (ESI) Calcd for $C_{21}H_{26}NO_7P$: [M] + Na^+ = 458.1339. Found: 458.1359.



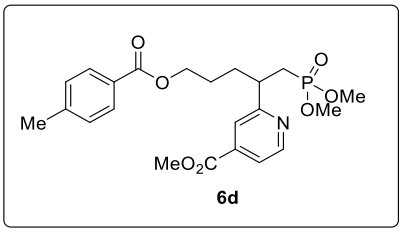
6b

methyl 2-(1-(dimethoxyphosphoryl)-5-((3-methoxybenzoyl)oxy)pentan-2-yl)isonicotinate (6b). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From pent-4-en-1-yl 3-methoxybenzoate (44.0 mg, 0.2 mmol), compound **6b** (73.5 mg, 79%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 5.0 Hz, 1H), 7.73 (s, 1H), 7.69 (d, *J* = 5.0 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.51 (s, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.08 (dd, *J* = 8.1, 2.5 Hz, 1H), 4.22 (t, *J* = 6.6 Hz, 2H), 3.94 (s, 3H), 3.83 (s, 3H), 3.53 (dd, *J* = 22.0, 10.8 Hz, 6H), 3.30 – 3.28 (m, 1H), 2.47 – 2.43 (m, 1H), 2.17 – 2.12 (m, 1H), 1.96 – 1.93 (m, 2H), 1.68 – 1.66 (m, 1H), 1.48 – 1.47 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.3, 165.6, 163.8 (d, *J* = 7.1 Hz), 159.5, 150.4, 131.5, 129.3, 122.5, 121.9, 121.0, 119.2, 114.1, 64.5, 55.4, 52.6, 52.1 (d, *J* = 3.9 Hz), 52.0 (d, *J* = 4.1 Hz), 41.7 (d, *J* = 3.5 Hz), 33.1 (d, *J* = 13.8 Hz), 30.2 (d, *J* = 139.9 Hz), 26.4. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.4. HRMS (ESI) Calcd for $C_{22}H_{28}NO_8P$: [M] + Na^+ = 488.1445. Found: 488.1454.



6c

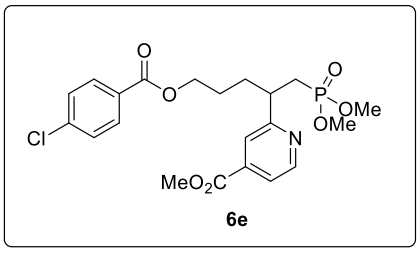
methyl 2-(1-(dimethoxyphosphoryl)-5-((3-fluorobenzoyl)oxy)pentan-2-yl)isonicotinate (6c). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From pent-4-en-1-yl 3-fluorobenzoate (41.6 mg, 0.2 mmol), compound **6c** (65.6 mg, 73%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 5.0 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.72 (s, 1H), 7.69 (d, *J* = 4.1 Hz, 1H), 7.65 (d, *J* = 9.2 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.23 (td, *J* = 8.3, 2.6 Hz, 1H), 4.22 (t, *J* = 6.5 Hz, 2H), 3.93 (s, 3H), 3.53 (dd, *J* = 23.7, 10.8 Hz, 6H), 3.30 – 3.28 (m, 1H), 2.44 – 2.42 (m, 1H), 2.16 – 2.11 (m, 1H), 1.96 – 1.95 (m, 2H), 1.68 – 1.65 (m, 1H), 1.48 – 1.46 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.6, 165.2 (d, *J* = 3.0 Hz), 163.7 (d, *J* = 7.4 Hz), 162.4 (d, *J* = 247.0 Hz), 150.4, 137.6, 132.4 (d, *J* = 7.3 Hz), 129.9 (d, *J* = 7.6 Hz), 125.2 (d, *J* = 3.0 Hz), 122.5, 121.0, 119.9 (d, *J* = 21.3 Hz), 116.3 (d, *J* = 22.8 Hz), 64.8, 52.6, 52.1 (d, *J* = 3.3 Hz), 52.0 (d, *J* = 3.5 Hz), 41.6 (d, *J* = 3.4 Hz), 33.0 (d, *J* = 13.6 Hz), 30.2 (d, *J* = 139.8 Hz), 26.3. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.3. ^{19}F NMR (564 MHz, Chloroform-*d*) δ -112.5 (d, *J* = 5.6 Hz). HRMS (ESI) Calcd for $C_{21}H_{25}FNO_7P$: [M] + Na^+ = 476.1245. Found: 476.1258.



6d

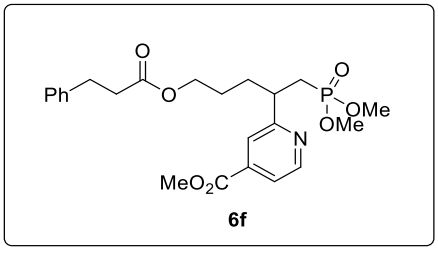
methyl 2-(1-(dimethoxyphosphoryl)-5-((4-methylbenzoyl)oxy)pentan-2-yl)isonicotinate (6d). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From pent-4-en-1-yl 4-methylbenzoate (40.8 mg, 0.2 mmol), compound **6d** (75.4 mg, 84%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 5.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.73 (s, 1H), 7.70 (d, *J* = 5.0 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 4.21 (t, *J* = 6.6 Hz, 2H), 3.94 (s, 3H), 3.53 (dd, *J* = 21.8, 10.8 Hz, 6H), 3.30 – 3.28 (m, 1H), 2.49 – 2.43 (m, 1H), 2.39 (s, 3H), 2.17 – 2.12 (m, 1H), 1.97 – 1.93 (m, 2H), 1.68 – 1.65 (m, 1H), 1.48 – 1.46 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.5, 165.6, 163.8 (d, *J* = 7.0 Hz), 150.3, 143.4, 137.6, 129.5, 129.0, 127.5, 122.5, 121.0, 64.3, 52.6, 52.1 (d, *J* = 4.0

Hz), 52.0 (d, *J* = 4.0 Hz), 41.7 (d, *J* = 3.5 Hz), 33.2 (d, *J* = 13.9 Hz), 30.1 (d, *J* = 139.9 Hz), 26.4, 21.6. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.4. HRMS (ESI) Calcd for $C_{22}H_{28}NO_7P$: [M] + Na^+ = 472.1496. Found: 472.1488.



6e

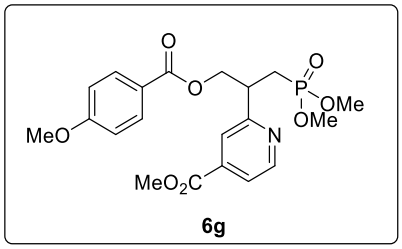
methyl 2-(5-((4-chlorobenzoyl)oxy)-1-(dimethoxyphosphoryl)pentan-2-yl)isonicotinate (6e). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From pent-4-en-1-yl 4-chlorobenzoate (44.8 mg, 0.2 mmol), compound **6e** (75.0 mg, 80%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 6.0 Hz, 2H), 7.91 (d, *J* = 8.1 Hz, 3H), 7.72 (s, 2H), 7.69 (d, *J* = 3.5 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 3H), 4.21 (t, *J* = 6.3 Hz, 2H), 3.93 (s, 2H), 3.55 (d, *J* = 10.9 Hz, 1H), 3.51 (d, *J* = 10.9 Hz, 1H), 3.30 – 3.28 (m, 1H), 2.47 – 2.40 (m, 1H), 2.17 – 2.10 (m, 1H), 1.97 – 1.91 (m, 3H), 1.70 – 1.62 (m, 1H), 1.50 – 1.40 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.6, 165.5, 163.7 (d, *J* = 7.3 Hz), 150.4, 139.2, 137.6, 130.9, 128.7, 128.6, 122.5, 121.0, 64.7, 52.6, 52.1 (d, *J* = 4.2 Hz), 52.0 (d, *J* = 4.4 Hz), 41.6 (d, *J* = 3.4 Hz), 33.0 (d, *J* = 13.5 Hz), 30.2 (d, *J* = 140.3 Hz), 26.3. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.3. HRMS (ESI) Calcd for $C_{21}H_{25}ClNO_7P$: [M] + Na^+ = 492.0949. Found: 492.0978.



6f

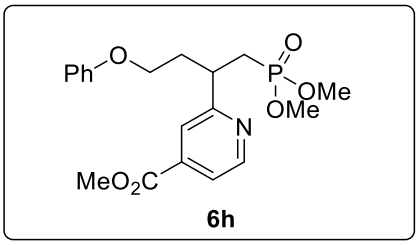
methyl 2-(1-(dimethoxyphosphoryl)-5-((3-phenylpropanoyl)oxy)pentan-2-yl)isonicotinate (6f). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From pent-4-en-1-yl 3-phenylpropanoate (43.6 mg, 0.2 mmol), compound **6f** (67.6 mg, 73%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 4.9 Hz, 1H), 7.69 – 7.68 (m, 2H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 8.5 Hz, 3H), 3.96 (t, *J* = 6.6 Hz, 2H), 3.93 (s, 3H), 3.54 (d, *J* = 10.8 Hz, 3H), 3.50 (d, *J* = 10.8 Hz, 3H), 3.23 – 3.20 (m, 1H), 2.90 (t, *J* = 7.8 Hz, 2H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.44 – 2.40 (m, 1H), 2.12 – 2.06 (m, 1H), 1.81 – 1.78 (m, 2H), 1.50 – 1.47 (m, 1H), 1.31 – 1.29 (m, 1H). ^{13}C NMR (151

MHz, Chloroform-*d*) δ 172.74, 165.6, 163.8 (d, *J* = 6.8 Hz), 150.3, 140.4, 137.6, 128.4, 128.2, 126.2, 122.5, 121.0, 64.0, 52.6, 52.1 (d, *J* = 6.2 Hz), 52.0 (d, *J* = 6.4 Hz), 41.6 (d, *J* = 3.5 Hz), 35.8, 33.1 (d, *J* = 14.1 Hz), 30.9, 30.1 (d, *J* = 139.8 Hz), 26.3. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.4. HRMS (ESI) Calcd for $C_{22}H_{30}NO_7P$: [M] + Na^+ = 486.1652. Found: 486.1685.



6g

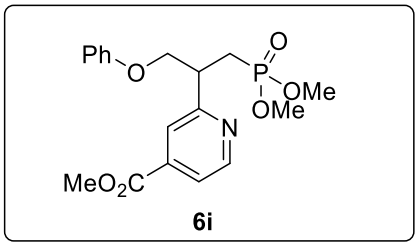
methyl 2-(1-(dimethoxyphosphoryl)-3-((4-methoxybenzoyl)oxy)propan-2-yl)isonicotinate (6g). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From allyl 4-methoxybenzoate (38.4 mg, 0.2 mmol), compound **6g** (61.1 mg, 70%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 4.9 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.85 (s, 1H), 7.73 (d, *J* = 5.0 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.53 (d, *J* = 6.7 Hz, 2H), 3.94 (s, 3H), 3.84 (s, 3H), 3.75 – 3.72 (m, 1H), 3.57 (dd, *J* = 10.9, 5.7 Hz, 6H), 2.61 – 2.54 (m, 1H), 2.35 – 2.29 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.7, 165.5, 163.4, 161.0 (d, *J* = 6.5 Hz), 150.2, 137.7, 131.5, 123.0, 122.1, 121.4, 113.6, 67.4 (d, *J* = 16.0 Hz), 55.4, 52.7, 52.2 (d, *J* = 6.4 Hz), 41.4 (d, *J* = 3.2 Hz), 26.1 (d, *J* = 142.3 Hz). ^{31}P NMR (243 MHz, Chloroform-*d*) δ 31.9. HRMS (ESI) Calcd for $C_{20}H_{24}NO_8P$: [M] + H = 460.1132. Found: 460.1148.



6h

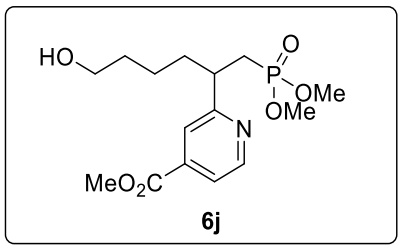
methyl 2-(1-(dimethoxyphosphoryl)-4-phenoxybutan-2-yl)isonicotinate (6h). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From (but-3-en-1-yloxy)benzene (29.6 mg, 0.2 mmol), compound **6h** (62.9 mg, 80%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 4.9 Hz, 1H), 7.74 (s, 1H), 7.69 (d, *J* = 5.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H), 3.87 – 3.85 (m, 1H), 3.70 – 3.68 (m, 1H), 3.59 – 3.52 (m, 7H), 2.50 – 3.48 (m, 1H), 2.31 – 2.29 (m, 2H), 2.23 – 2.18 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.6, 163.5 (d, *J* = 6.9 Hz), 158.6, 150.3, 137.6, 129.3, 122.8, 121.0, 120.6,

114.4, 65.0, 52.6, 52.1, 52.1, 38.8 (d, *J* = 3.4 Hz), 35.9 (d, *J* = 14.0 Hz), 30.1 (d, *J* = 140.0 Hz).[31]P NMR (243 MHz, Chloroform-*d*) δ 32.2. HRMS (ESI) Calcd for $C_{19}H_{24}NO_6P$: [M] + Na^+ = 416.1233. Found: 416.1230.



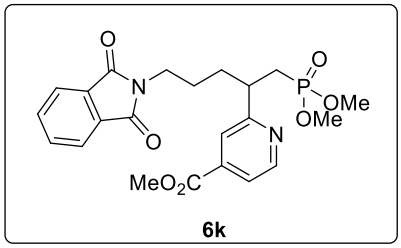
6i

methyl 2-(1-(dimethoxyphosphoryl)-3-phenoxypropan-2-yl)isonicotinate (6i). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From (allyloxy)benzene (26.8 mg, 0.2 mmol), compound **6i** (60.6 mg, 80%) was obtained. Colorless oil. [1]H NMR (599 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 5.0 Hz, 1H), 7.87 (s, 1H), 7.73 (d, *J* = 5.0 Hz, 1H), 7.24 (t, *J* = 8.0 Hz, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.24 (d, *J* = 6.3 Hz, 2H), 3.96 (s, 3H), 3.75 – 3.73 (m, 1H), 3.59 (dd, *J* = 10.9, 3.1 Hz, 6H), 2.52 – 2.43 (m, 2H). [13]C NMR (151 MHz, Chloroform-*d*) δ 165.6, 161.4 (d, *J* = 7.0 Hz), 158.4, 150.1, 137.7, 129.4, 123.1, 121.3, 121.0, 114.7, 70.9 (d, *J* = 14.6 Hz), 52.6, 52.2 (d, *J* = 4.3 Hz), 52.2 (d, *J* = 4.3 Hz), 41.9 (d, *J* = 3.0 Hz), 26.0 (d, *J* = 142.0 Hz). [31]P NMR (243 MHz, Chloroform-*d*) δ 32.3. HRMS (ESI) Calcd for $C_{18}H_{22}NO_6P$: [M] + Na^+ = 402.1077. Found: 402.1080.



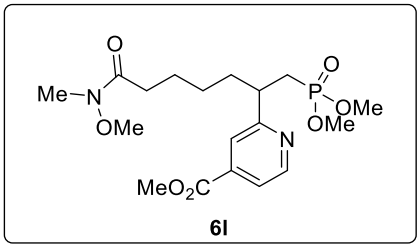
6j

methyl 2-(1-(dimethoxyphosphoryl)-6-hydroxyhexan-2-yl)isonicotinate (6j). Purified by flash column chromatography on silica gel (DCM : MeOH = 20 : 1). From hex-5-en-1-ol (20.0 mg, 0.2 mmol), compound **6j** (44.1 mg, 64%) was obtained. Colorless oil. [1]H NMR (599 MHz, Chloroform-*d*) δ 8.70 (d, *J* = 4.9 Hz, 1H), 7.69 – 7.67 (m, 2H), 3.94 (s, 3H), 3.55 – 3.50 (m, 8H), 3.24 – 3.22 (m, 1H), 2.41 – 2.39 (m, 1H), 2.13 – 2.12 (m, 1H), 2.00 (s, 1H), 1.82 – 1.80 (m, 2H), 1.50 – 1.48 (m, 2H), 1.26 – 1.24 (m, 1H), 1.11 – 1.09 (m, 1H). [13]C NMR (151 MHz, Chloroform-*d*) δ 165.7, 164.3 (d, *J* = 7.3 Hz), 150.2, 137.5, 122.4, 120.8, 62.3, 52.6, 52.1 (d, *J* = 6.0 Hz), 52.0 (d, *J* = 6.3 Hz), 41.8 (d, *J* = 3.5 Hz), 36.4 (d, *J* = 13.3 Hz), 32.4, 29.9 (d, *J* = 139.6 Hz), 23.2. [31]P NMR (243 MHz, Chloroform-*d*) δ 32.8. HRMS (ESI) Calcd for $C_{15}H_{24}NO_6P$: [M] + Na^+ = 368.1233. Found: 368.1260.



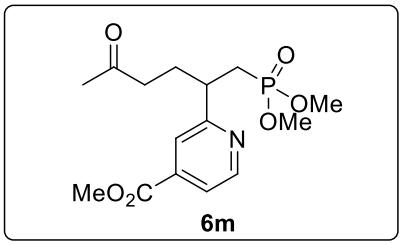
6k

methyl 2-(1-(dimethoxyphosphoryl)-5-(1,3-dioxoisoindolin-2-yl)pentan-2-yl)isonicotinate (6k). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 2-(pent-4-en-1-yl)isoindoline-1,3-dione (43.0 mg, 0.2 mmol), compound **6k** (68.5 mg, 75%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-d) δ 8.65 (d, J = 4.9 Hz, 1H), 7.78 (dd, J = 5.5, 3.0 Hz, 2H), 7.68 – 7.64 (m, 4H), 3.91 (s, 3H), 3.59 (t, *J* = 7.2 Hz, 2H), 3.50 (dd, *J* = 14.8, 10.8 Hz, 6H), 3.25 – 2.22 (m, 1H), 2.42 – 2.40 (m, 1H), 2.11 – 2.06 (m, 1H), 1.84 – 1.79 (m, 2H), 1.58 – 1.55 (m, 1H), 1.36 – 1.34 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.2, 165.6, 163.6 (d, *J* = 6.5 Hz), 150.3, 137.6, 133.8, 132.0, 123.1, 122.5, 121.0, 52.6, 52.1 (d, *J* = 4.1 Hz), 52.0 (d, *J* = 4.0 Hz), 41.6 (d, *J* = 3.5 Hz), 37.6, 33.9 (d, *J* = 14.2 Hz), 29.9 (d, *J* = 139.8 Hz), 26.2. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.4. HRMS (ESI) Calcd for $C_{22}H_{25}N_2O_7P$: [M] + Na^+ = 483.1295. Found: 483.1309.



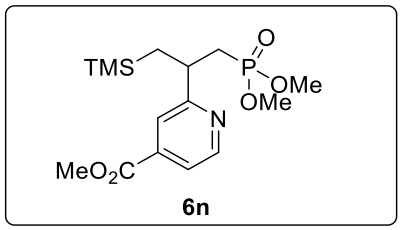
6l

methyl 2-(1-(dimethoxyphosphoryl)-7-(methoxy(methyl)amino)-7-oxoheptan-2-yl)isonicotinate(6l). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From N-methoxy-N-methylhept-6-enamide (34.2 mg, 0.2 mmol), compound **6l** (66.6 mg, 80%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-d) δ 8.70 (d, J = 5.0 Hz, 1H), 7.68 (s, 1H), 7.66 (d, *J* = 5.0 Hz, 1H), 3.93 (s, 3H), 3.62 (s, 3H), 3.51 (dd, *J* = 17.9, 10.8 Hz, 6H), 3.22 – 3.20 (m, 1H), 3.12 (s, 3H), 2.43 – 2.41 (m, 1H), 2.31 (t, *J* = 7.8 Hz, 2H), 2.10 (dd, *J* = 4.9, 2.9 Hz, 1H), 1.80 – 1.78 (m, 2H), 1.58 – 1.53 (m, 2H), 1.23 – 1.22 (m, 1H), 1.05 – 1.03 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.3, 165.7, 164.3 (d, *J* = 6.5 Hz), 150.2, 137.4, 122.5, 120.8, 61.1, 52.6, 52.0 (d, *J* = 5.7 Hz), 52.0 (d, *J* = 5.9 Hz), 41.8 (d, *J* = 3.5 Hz), 36.7 (d, *J* = 14.0 Hz), 32.1, 31.6, 29.9 (d, *J* = 139.5 Hz), 26.9, 24.3. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.7. HRMS (ESI) Calcd for $C_{18}H_{29}N_2O_7P$: [M] + Na^+ = 439.1605. Found: 439.1620.



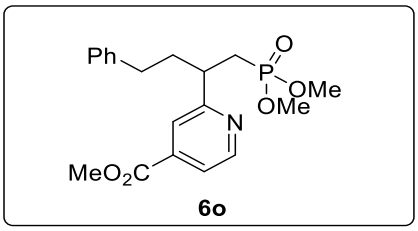
6m

methyl 2-(1-(dimethoxyphosphoryl)-5-oxohexan-2-yl)isonicotinate (6m). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From hex-5-en-2-one (19.6 mg, 0.2 mmol), compound **6m** (53.5 mg, 78%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 5.8 Hz, 1H), 7.69 – 7.69 (m, 2H), 3.94 (s, 3H), 3.55 (d, *J* = 10.9 Hz, 3H), 3.52 (d, *J* = 10.8 Hz, 3H), 3.25 – 3.22 (m, 1H), 2.45 – 2.42 (m, 1H), 2.30 – 2.28 (m, 1H), 2.20 – 2.18 (m, 1H), 2.14 – 2.11 (m, 1H), 2.08 – 2.03 (s, 5H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 207.6, 165.6, 163.5 (d, *J* = 7.1 Hz), 150.3, 137.7, 122.4, 121.0, 52.7, 52.1 (d, *J* = 2.4 Hz), 52.1 (d, *J* = 2.8 Hz), 41.1 (d, *J* = 3.4 Hz), 40.8, 30.5, 30.5 (d, *J* = 14.4 Hz), 29.8, 29.6. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.2. HRMS (ESI) Calcd for $C_{15}H_{22}NO_6P$: [M] + Na^+ = 366.1077. Found: 366.1073.



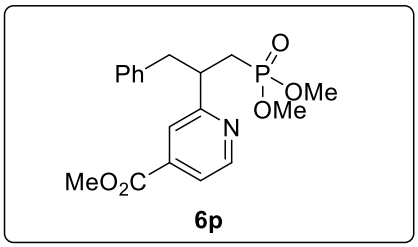
6n

methyl 2-(1-(dimethoxyphosphoryl)-3-(trimethylsilyl)propan-2-yl)isonicotinate (6n). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From allyltrimethylsilane (22.8 mg, 0.2 mmol), compound **6n** (54.6 mg, 76%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 5.0 Hz, 1H), 7.72 (s, 1H), 7.66 (d, *J* = 5.1 Hz, 1H), 3.94 (s, 3H), 3.51 (dd, *J* = 12.2, 10.9 Hz, 6H), 3.40 – 3.37 (m, 1H), 2.45 – 2.41 (m, 1H), 2.14 – 2.10 (m, 1H), 1.24 – 1.20 (m, 1H), 1.08 (dd, *J* = 14.6, 5.1 Hz, 1H), -0.22 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.7, 165.7, 150.1, 137.5, 122.0, 120.8, 52.6, 52.0 (d, *J* = 4.1 Hz), 52.0 (d, *J* = 4.2 Hz), 38.6 (d, *J* = 3.9 Hz), 33.8 (d, *J* = 136.7 Hz), 25.8 (d, *J* = 12.9 Hz), -1.3. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.0. HRMS (ESI) Calcd for $C_{15}H_{26}NO_5PSi$: [M] + Na^+ = 382.1210. Found: 382.1232.



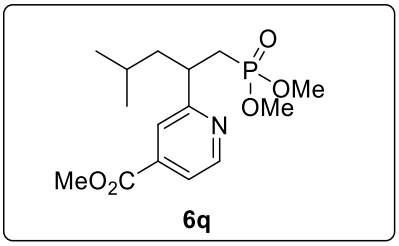
6o

methyl 2-(1-(dimethoxyphosphoryl)-4-phenylbutan-2-yl)isonicotinate (6o). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From but-3-en-1-ylbenzene (26.4 mg, 0.2 mmol), compound **6o** (61.8 mg, 82%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.75 (d, *J* = 4.9 Hz, 1H), 7.71 (d, *J* = 4.9 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 2H), 3.96 (s, 3H), 3.55 (d, *J* = 10.8 Hz, 3H), 3.50 (d, *J* = 10.8 Hz, 3H), 3.30 – 3.27 (m, 1H), 2.49 – 2.44 (m, 2H), 2.40 – 2.36 (m, 1H), 2.19 – 2.12 (m, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.7, 164.0 (d, *J* = 6.8 Hz), 150.3, 141.4, 137.5, 128.3, 128.3, 125.9, 122.7, 120.9, 52.7, 52.1 (d, *J* = 3.4 Hz), 52.0 (d, *J* = 3.6 Hz), 41.6 (d, *J* = 3.5 Hz), 38.4 (d, *J* = 13.9 Hz), 33.4, 30.1 (d, *J* = 139.8 Hz). ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.5. HRMS (ESI) Calcd for $C_{19}H_{24}NO_5P$: [M] + Na^+ = 400.1284. Found: 400.1301.



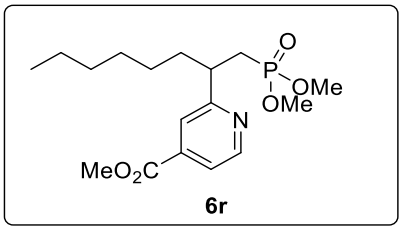
6p

methyl 2-(1-(dimethoxyphosphoryl)-3-phenylpropan-2-yl)isonicotinate (6p). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From allylbenzene (23.6 mg, 0.2 mmol), compound **6p** (54.5 mg, 75%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 5.0 Hz, 1H), 7.66 (dd, *J* = 5.0, 1.6 Hz, 1H), 7.53 (s, 1H), 7.19 (t, *J* = 7.3 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 3.50 (d, *J* = 10.9 Hz, 4H), 3.45 (d, *J* = 10.8 Hz, 3H), 3.06 – 3.03 (m, 2H), 2.54 – 2.47 (m, 1H), 2.18 – 2.12 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.6, 163.5 (d, *J* = 5.3 Hz), 150.0, 138.8, 137.3, 129.1, 128.3, 126.3, 122.8, 120.9, 52.5, 52.0 (d, *J* = 1.6 Hz), 52.0 (d, *J* = 1.8 Hz), 43.9 (d, *J* = 3.4 Hz), 43.2 (d, *J* = 15.5 Hz), 28.8 (d, *J* = 140.5 Hz). ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.6. HRMS (ESI) Calcd for $C_{18}H_{22}NO_5P$: [M] + Na^+ = 386.1128. Found: 386.1138.



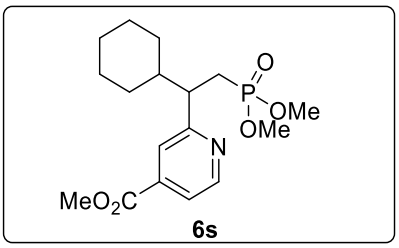
6q

methyl 2-(1-(dimethoxyphosphoryl)-4-methylpentan-2-yl)isonicotinate (6q). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From 4-methylpent-1-ene (16.8 mg, 0.2 mmol), compound **6q** (48.0 mg, 73%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 4.9 Hz, 1H), 7.71 (s, 1H), 7.67 (d, *J* = 4.1 Hz, 1H), 3.94 (s, 3H), 3.51 (dd, *J* = 20.0, 10.8 Hz, 6H), 3.32 – 3.31 (m, 1H), 2.41 – 2.38 (m, 1H), 2.10 – 2.04 (m, 1H), 1.75 – 1.73 (m, 1H), 1.55 – 1.54 (m, 1H), 1.25 – 1.22 (m, 1H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.81 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.7, 164.6 (d, *J* = 6.1 Hz), 150.2, 137.5, 122.4, 120.7, 52.6, 52.0 (d, *J* = 5.8 Hz), 52.0 (d, *J* = 5.8 Hz), 46.3 (d, *J* = 14.3 Hz), 39.8 (d, *J* = 3.6 Hz), 30.3 (d, *J* = 139.3 Hz), 25.4, 23.1, 21.9. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.7. HRMS (ESI) Calcd for $C_{15}H_{24}NO_5P$: [M] + Na^+ = 352.1284. Found: 352.1290.



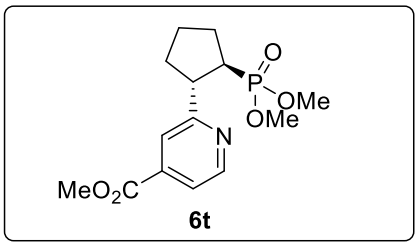
6r

methyl 2-(1-(dimethoxyphosphoryl)octan-2-yl)isonicotinate (6r). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From oct-1-ene (22.4 mg, 0.2 mmol), compound **6r** (54.3 mg, 76%) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 5.0 Hz, 1H), 7.69 (s, 1H), 7.67 (d, *J* = 5.0 Hz, 1H), 3.94 (s, 3H), 3.51 (dd, *J* = 14.7, 10.8 Hz, 6H), 3.22 – 3.19 (m, 1H), 2.44 – 2.40 (m, 1H), 2.16 – 2.06 (m, 1H), 1.76 – 1.74 (m, 2H), 1.19 – 1.16 (m, 7H), 1.00 – 0.97 (m, 1H), 0.83 – 0.79 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 164.5 (d, *J* = 6.2 Hz), 150.1, 137.4, 122.5, 120.7, 52.6, 52.0 (d, *J* = 3.6 Hz), 52.0 (d, *J* = 4.0 Hz), 41.9 (d, *J* = 3.6 Hz), 37.0 (d, *J* = 14.2 Hz), 31.5, 29.9 (d, *J* = 139.3 Hz), 29.0, 27.1, 22.5, 14.0. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 33.6. HRMS (ESI) Calcd for $C_{17}H_{28}NO_5P$: [M] + Na^+ = 380.1597. Found: 380.1625.



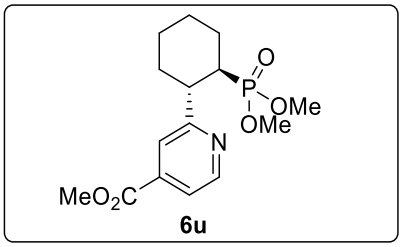
6s

methyl 2-(1-cyclohexyl-2-(dimethoxyphosphoryl)ethyl)isonicotinate (6s). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From vinylcyclohexane (22.0 mg, 0.2 mmol), compound **6s** (48.5 mg, 68%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 4.9 Hz, 1H), 7.68 – 7.67 (m, 2H), 3.94 (s, 3H), 3.47 (d, *J* = 10.8 Hz, 3H), 3.43 (d, *J* = 10.8 Hz, 3H), 3.04 – 2.98 (m, 1H), 2.57 – 2.53 (m, 1H), 2.25 – 2.20 (m, 1H), 1.88 (d, *J* = 12.3 Hz, 1H), 1.73 (d, *J* = 13.8 Hz, 1H), 1.63 – 1.60 (m, 3H), 1.30 (d, *J* = 12.7 Hz, 1H), 1.20 (d, *J* = 12.8 Hz, 1H), 1.09 – 1.06 (m, 2H), 0.93 – 0.91 (m, 1H), 0.85 – 0.83 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.8, 163.6 (d, *J* = 2.9 Hz), 149.8, 137.1, 123.5, 120.6, 52.6, 52.0 (d, *J* = 6.3 Hz), 52.0 (d, *J* = 6.7 Hz), 47.6 (d, *J* = 4.0 Hz), 43.4 (d, *J* = 15.7 Hz), 30.6 (d, *J* = 3.3 Hz), 26.5 (d, *J* = 139.9 Hz), 26.3, 26.2. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 34.0. HRMS (ESI) Calcd for $C_{17}H_{26}NO_5P$: [M] + Na^+ = 378.1441. Found: 378.1441.



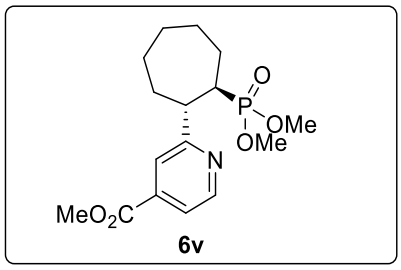
6t

methyl 2-((1S,2R)-2-(dimethoxyphosphoryl)cyclopentyl)isonicotinate (6t). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From cyclopentene (13.6 mg, 0.2 mmol), compound **6t** (46.6 mg, 75%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 5.0 Hz, 1H), 7.75 (s, 1H), 7.66 (d, *J* = 5.0 Hz, 1H), 3.94 (s, 3H), 3.58 – 3.50 (m, 7H), 2.90 – 2.86 (m, 1H), 2.17 – 2.15 (m, 2H), 2.07 – 2.04 (m, 1H), 1.92 – 1.89 (m, 1H), 1.85 – 1.82 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.8, 164.4(d, *J* = 2.7 Hz), 150.1, 137.5, 122.3 120.7 52.6, 52.3 (d, *J* = 6.4 Hz), 52.2 (d, *J* = 6.9 Hz), 48.7, 40.3 (d, *J* = 144.9 Hz), 36.0, *J* = 13.0 Hz), 27.7, 26.2 (d, *J* = 10.8 Hz). ^{31}P NMR (243 MHz, Chloroform-*d*) δ 36.3. MS (ESI) Calcd for $C_{14}H_{20}NO_5P$: [M] + Na^+ = 336.0971. Found: 336.0992.



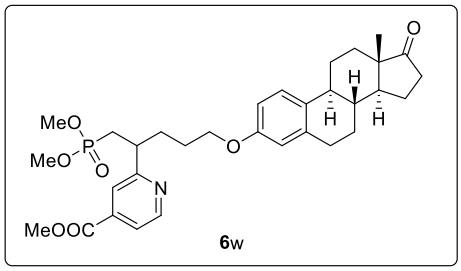
6u

methyl 2-((1S,2R)-2-(dimethoxyphosphoryl)cyclohexyl)isonicotinate (6u). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From cyclohexene (16.4 mg, 0.2 mmol), compound **6u** (46.9 mg, 77%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.68 (d, *J* = 5.0 Hz, 1H), 7.71 (s, 1H), 7.65 (d, *J* = 5.0 Hz, 1H), 3.92 (s, 3H), 3.41 (d, *J* = 10.6 Hz, 3H), 3.34 (d, *J* = 10.6 Hz, 3H), 2.99 – 2.97 (m, 1H), 2.49 – 2.46 (m, 1H), 2.19 – 2.17 (m, 1H), 1.84 – 1.81 (m, 3H), 1.66 – 1.63 (m, 1H), 1.58 – 1.56 (m, 1H), 1.40 – 1.36 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.8, 165.5 (d, *J* = 2.1 Hz), 149.7, 137.5, 122.1, 120.5, 52.5, 52.2 (d, *J* = 6.4 Hz), 51.7 (d, *J* = 7.4 Hz), 46.0 (d, *J* = 4.1 Hz), 38.3 (d, *J* = 139.3 Hz), 34.2 (d, *J* = 15.0 Hz), 26.1 (d, *J* = 4.6 Hz), 25.6, 25.5 (d, *J* = 15.7 Hz). ^{31}P NMR (243 MHz, Chloroform-*d*) δ 33.8. MS (ESI) Calcd for $C_{15}H_{22}NO_5P$: [M] + Na^+ = 350.1128. Found: 350.1128.



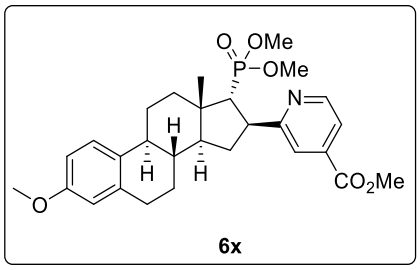
6v

methyl 2-((1S,2R)-2-(dimethoxyphosphoryl)cycloheptyl)isonicotinate (6v). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From cycloheptene (19.2 mg, 0.2 mmol), compound **6v** (53.1 mg, 78%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.67 (d, *J* = 5.0 Hz, 1H), 7.71 (s, 1H), 7.64 (d, *J* = 5.0 Hz, 1H), 3.94 (s, 3H), 3.48 (d, *J* = 10.6 Hz, 3H), 3.44 – 3.41 (m, 1H), 3.37 (d, *J* = 10.7 Hz, 3H), 3.08 – 3.05 (m, 1H), 2.17 – 2.14 (m, 1H), 1.90 – 1.87 (m, 2H), 1.71 – 1.70 (m, 1H), 1.64 – 1.60 (m, 1H), 1.53 – 1.48 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.8 (d, *J* = 1.5 Hz), 165.8, 149.4, 137.6, 122.1, 120.2, 52.6, 52.3 (d, *J* = 6.4 Hz), 51.9 (d, *J* = 7.4 Hz), 46.6 (d, *J* = 2.2 Hz), 39.0 (d, *J* = 134.5 Hz), 35.1 (d, *J* = 15.1 Hz), 30.1, 28.3 (d, *J* = 13.1 Hz), 26.2 (d, *J* = 3.8 Hz), 25.6. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 37.1. MS (ESI) Calcd for $C_{16}H_{24}NO_5P$: [M] + Na^+ = 364.1284. Found: 364.1311.



6w

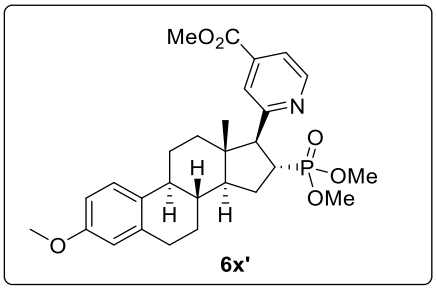
methyl2-(1-(dimethoxyphosphoryl)-5-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)pentan-2-yl)isonicotinate (6w). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From (8R,9S,13S,14S)-13-methyl-3-(pent-4-en-1-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (67.6 mg, 0.2 mmol), compound **6w** (84.4 mg, 73%) was obtained. White solid. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 5.0 Hz, 1H), 7.74 (s, 1H), 7.70 (d, *J* = 5.0 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 6.64 (d, *J* = 8.6 Hz, 1H), 6.58 (s, 1H), 3.95 (s, 3H), 3.85 (t, *J* = 6.6 Hz, 2H), 3.56 (d, *J* = 10.8 Hz, 3H), 3.52 (d, *J* = 10.9 Hz, 3H), 3.31 – 3.30 (m, 1H), 2.86 – 2.85 (m, 2H), 2.50 – 2.47 (m, 2H), 2.37 (d, *J* = 10.0 Hz, 1H), 2.23 (t, *J* = 9.2 Hz, 1H), 2.15 – 2.13 (m, 2H), 2.06 – 2.04 (m, 1H), 1.97 – 1.95 (m, 4H), 1.68 – 1.65 (m, 1H), 1.62 – 1.58 (m, 2H), 1.51 – 1.48 (m, 5H), 0.90 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 220.8, 165.6, 164.0 (d, *J* = 6.8 Hz), 156.8, 150.3, 137.6, 137.5, 131.9, 126.2, 122.6, 120.9, 114.4, 112.0, 67.4, 52.6, 52.1 (d, *J* = 6.1 Hz), 52.0 (d, *J* = 6.4 Hz), 50.4, 48.0, 43.9, 41.7 (d, *J* = 3.4 Hz), 38.3, 35.8, 33.4 (d, *J* = 14.2 Hz), 31.5, 30.1 (d, *J* = 139.7 Hz), 29.6, 27.0, 26.5, 25.9, 21.5, 13.8. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.5. MS (ESI) Calcd for $C_{32}H_{42}NO_7P$: [M] + Na^+ = 606.2591. Found: 606.2593.



6x

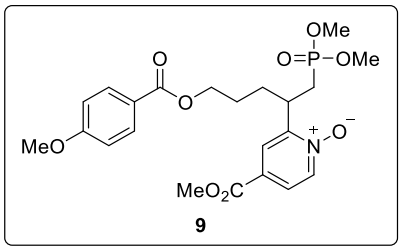
Methyl 2-((8R,9S,13S,14S,16R,17R)-17-(dimethoxyphosphoryl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-16-yl)isonicotinate (6x). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From (8S,9S,13R,14S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[a]phenanthrene (53.6 mg, 0.2 mmol), compound **6x** (40.5 mg, 40%) was obtained. White solid. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.70 (d, *J* = 5.0 Hz, 1H), 7.80 (s, 1H), 7.67 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 1H), 6.72

(dd, *J* = 8.6, 2.8 Hz, 1H), 6.63 (d, *J* = 2.7 Hz, 1H), 3.97 (s, 3H), 3.78 – 3.76 (m, 4H), 3.65 (dd, *J* = 23.8, 10.6 Hz, 6H), 2.85 (t, *J* = 4.9 Hz, 2H), 2.76 (dd, *J* = 19.6, 6.2 Hz, 1H), 2.37 – 2.34 (m, 3H), 2.16 – 2.13 (m, 1H), 2.04 – 2.01 (m, 1H), 1.93 – 1.90 (m, 2H), 1.78 – 1.76 (m, 1H), 1.60 – 1.57 (m, 1H), 1.52 – 1.49 (m, 2H), 1.14 (d, *J* = 3.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.9, 164.7 (d, *J* = 5.6 Hz), 157.5, 150.1, 137.9, 137.5, 132.7, 126.3, 122.2, 120.5, 113.7, 111.5, 55.2, 52.8, 52.7, 52.1 (d, *J* = 2.8 Hz), 52.1 (d, *J* = 2.2 Hz), 50.4 (d, *J* = 137.7 Hz), 46.7, 44.3, 43.0, 38.6, 35.8 (d, *J* = 5.2 Hz), 34.9 (d, *J* = 5.4 Hz), 29.8, 28.0, 26.8, 21.7 (d, *J* = 17.4 Hz). ^{31}P NMR (243 MHz, Chloroform-*d*) δ 34.9. MS (ESI) Calcd for $C_{28}H_{36}NO_6P$: [M] + Na^+ = 536.2172. Found: 536.2171.



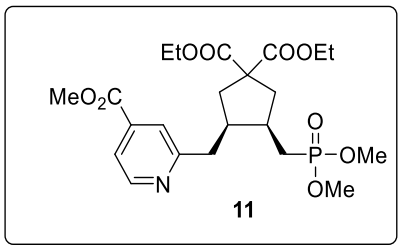
6x'

methyl 2-((8S,9S,13S,14S,16R,17S)-16-(dimethoxyphosphoryl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)isonicotinate (6x'). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From (8S,9S,13R,14S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[a]phenanthrene (53.6 mg, 0.2 mmol), compound **6x'** (21.4 mg, 21%) was obtained. White solid. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 4.9 Hz, 1H), 7.71 – 7.69 (m, 2H), 7.18 (d, *J* = 8.6 Hz, 1H), 6.70 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.64 (d, *J* = 2.7 Hz, 1H), 3.98 (s, 3H), 3.78 (s, 3H), 3.67 – 3.63 (m, 1H), 3.57 (d, *J* = 10.5 Hz, 3H), 3.51 (d, *J* = 10.5 Hz, 3H), 3.29 (dd, *J* = 19.8, 10.1 Hz, 1H), 2.89 – 2.87 (m, 2H), 2.29 (dd, *J* = 23.5, 8.6 Hz, 3H), 1.95 – 1.93 (m, 1H), 1.84 – 1.78 (m, 2H), 1.69 – 1.66 (m, 2H), 1.50 – 1.49 (m, 2H), 1.42 – 1.39 (m, 1H), 0.49 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.9, 159.9, 157.5, 149.3, 137.9, 137.1, 132.3, 126.2, 123.0, 120.7, 113.8, 111.5, 59.3, 55.2, 54.3 (d, *J* = 3.3 Hz), 52.7, 52.4 (d, *J* = 6.3 Hz), 52.3 (d, *J* = 6.7 Hz), 46.4 (d, *J* = 11.5 Hz), 43.5, 38.8, 37.7, 33.3 (d, *J* = 143.8 Hz), 29.8, 27.6, 26.6, 26.2, 13.4. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 32.5. MS (ESI) Calcd for $C_{28}H_{36}NO_6P$: [M] + Na^+ = 536.2172. Found: 536.2198.



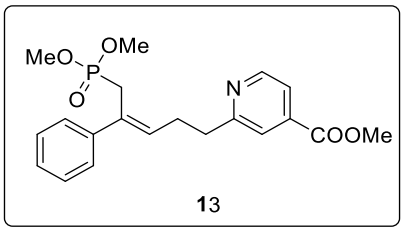
9

2-(1-(dimethoxyphosphoryl)-5-((4-methoxybenzoyl)oxy)pentan-2-yl)-4-(methoxycarbonyl)pyridine 1-oxide (9). Purified by flash column chromatography on silica gel (DCM : MeOH = 20 : 1). From 4-methoxyphenyl hex-5-enoate (44.0 mg, 0.2 mmol), compound **9** (7.7 mg, 8%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-d) δ 8.23 (d, J = 6.8 Hz, 1H), 7.98 (d, *J* = 7.1 Hz, 2H), 7.88 (s, 1H), 7.77 (d, *J* = 6.9 Hz, 1H), 6.92 (d, *J* = 7.1 Hz, 2H), 4.27 (t, *J* = 6.2 Hz, 2H), 3.93 (s, 3H), 3.86 (s, 3H), 3.76 – 3.71 (m, 1H), 3.63 (dd, *J* = 10.9, 1.8 Hz, 6H), 2.26 – 2.19 (m, 2H), 2.10 – 2.06 (m, 1H), 1.76 – 1.70 (m, 2H), 1.62 – 1.60 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.7 (d, *J* = 9.2 Hz), 166.2, 164.1, 163.3, 152.5, 140.2, 131.6, 125.9, 124.1, 122.6, 113.6, 64.0, 55.4, 52.7, 52.4 (d, *J* = 6.5 Hz), 52.3 (d, *J* = 6.6 Hz), 36.0, 28.7, 26.8, 25.9. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 31.3. MS (ESI) Calcd for $C_{22}H_{28}NO_9P$: [M] + Na^+ = 504.1394. Found: 504.1394.



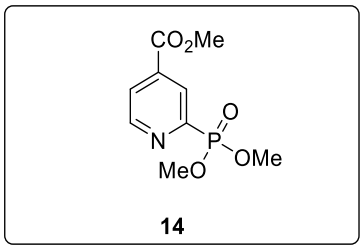
11

diethyl (3R,4R)-3-((dimethoxyphosphoryl)methyl)-4-((4-(methoxycarbonyl)pyridin-2-yl)methyl)cyclopentane-1,1-dicarboxylate (11). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From diethyl 2,2-diallylmalonate (48.0 mg, 0.2 mmol), compound **11** (61.9 mg, 64%) (cis/trans > 10:1) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 5.0 Hz, 1H), 7.69 (s, 1H), 7.65 (d, *J* = 5.0 Hz, 1H), 4.21 – 4.12 (m, 4H), 3.93 (s, 3H), 3.73 (dd, *J* = 10.8, 8.9 Hz, 6H), 2.95 – 2.90 (m, 1H), 2.66 – 2.64 (m, 2H), 2.55 – 2.53 (m, 1H), 2.49 – 2.46 (m, 1H), 2.30 – 2.27 (m, 2H), 2.03 – 2.01 (m, 2H), 1.79 – 1.77 (m, 1H), 1.21 (dt, *J* = 19.1, 7.1 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.7, 172.3, 165.7, 161.7, 150.1, 137.6, 122.5, 120.4, 61.6, 61.7, 58.5, 52.6, 52.4 (d, *J* = 6.7 Hz), 52.2 (d, *J* = 6.7 Hz), 43.0 (d, *J* = 13.7 Hz), 39.1 (d, *J* = 6.0 Hz), 37.7, 37.4, 36.7 (d, *J* = 4.6 Hz), 24.8 (d, *J* = 141.0 Hz), 14.0, 14.0. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 33.8. MS (ESI) Calcd for $C_{22}H_{32}NO_9P$: [M] + Na^+ = 508.1707. Found: 508.1783.



13

methyl (Z)-2-(5-(dimethoxyphosphoryl)-4-phenylpent-3-en-1-yl)isonicotinate (13). Purified by flash column chromatography on silica gel (DCM : MeOH = 25 : 1). From (1-cyclopropylvinyl)benzene (28.8 mg, 0.2 mmol), compound **13** (36.4 mg, 47%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 5.1 Hz, 1H), 7.74 (s, 1H), 7.67 (d, *J* = 4.6 Hz, 1H), 7.36 (d, *J* = 6.8 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 5.90 (q, *J* = 7.0 Hz, 1H), 3.94 (s, 3H), 3.55 (d, *J* = 10.9 Hz, 6H), 3.09 (s, 1H), 3.06 – 3.03 (m, 3H), 2.75 – 2.73 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.8, 162.4, 150.1, 142.3, 137.6, 131.8 (d, *J* = 11.9 Hz), 130.7 (d, *J* = 11.4 Hz), 128.3, 127.1, 126.5, 122.1, 120.4, 52.6, 52.5 (d, *J* = 6.8 Hz), 37.7 (d, *J* = 3.4 Hz), 29.2 (d, *J* = 3.2 Hz), 28.2 (d, *J* = 139.1 Hz). ^{31}P NMR (243 MHz, Chloroform-*d*) δ 29.2. MS (ESI) Calcd for $C_{20}H_{24}NO_5P$: [M] + Na^+ = 412.1284. Found: 412.1292.



14

methyl 2-(dimethoxyphosphoryl)isonicotinate (14). Purified by flash column chromatography on silica gel (DCM : MeOH = 30 : 1). From 1-methoxy-4-(methoxycarbonyl)pyridin-1-ium methyl sulfate (55.8 mg, 0.2 mmol), compound **14** (10.8 mg, 22%) was obtained. Colorless oil. ^{1}H NMR (599 MHz, Chloroform-*d*) δ 8.97 (d, *J* = 4.7 Hz, 1H), 8.48 (d, *J* = 6.9 Hz, 1H), 8.00 (d, *J* = 4.9 Hz, 1H), 3.98 (s, 3H), 3.90 (dd, *J* = 11.0, 1.4 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-d) δ 164.7 (d, *J* = 3.3 Hz), 152.4 (d, *J* = 230.2 Hz), 151.4 (d, *J* = 23.2 Hz), 137.7 (d, *J* = 13.0 Hz), 127.2 (d, *J* = 26.3 Hz), 125.3 (d, *J* = 4.0 Hz), 53.7, 53.6, 53.0. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 16.0. MS (ESI) Calcd for $C_9H_{12}NO_5P$: [M] + Na^+ = 268.0345. Found: 268.0345.

VI. Computational Details

Computational details

All calculations were conducted using DFT[1] as implemented in the Jaguar 9.1 suite[2] of ab initio quantum chemistry programs with Minnesota functional M06 including Grimme's D3 dispersion correction levels of theory.[3,4] Geometry optimizations were proceeded using the 6-31G** basis set. The energies of the optimized structures were reevaluated by additional single point calculations on each optimized geometry using M06 including Grimme's D3 dispersion correction and Dunning's correlation consistent triple-ζ basis set cc-pVTZ(-f)[5] which includes a double set of polarization functions. Analytical vibrational frequencies within the harmonic approximation were calculated using the 6-31G** basis to confirm proper convergence to well-defined minima or saddle points on the potential energy surface. At last, solvation energies were calculated using a self-consistent reaction field (SCRF)[6-8] approach based on accurate numerical solutions of the Poisson-Boltzmann equation and were performed with the 6-31G** basis at the optimized gas phase geometry with the dielectric constant of ε = 37.5 for acetonitrile. As is the case for all continuum models, the solvation energies are subject to empirical parametrization of the atomic radii that are used to generate the solute surface. The standard set of optimized radii in Jaguar was used for H (1.150 Å), C (1.900 Å), N (1.600Å), O (1.600Å), and P (2.074 Å).[9] The Gibbs free energies in solution phase G(sol) were computed with the following protocol.

$$G(sol) = G(gas) + G^{solv} \quad (1)$$

$$G(gas) = H(gas) - TS(gas) \quad (2)$$

$$H(gas) = E(SCF) + ZPE \quad (3)$$

$$\Delta E(SCF) = \Sigma E(SCF) \text{ for products} - \Sigma E(SCF) \text{ for reactants} \quad (4)$$

$$\Delta G(sol) = \Sigma G(sol) \text{ for products} - \Sigma G(sol) \text{ for reactants} \quad (5)$$

G(gas) is the free energy in gas phase; G^{solv} is the free energy of solvation; H(gas) is the enthalpy in gas phase; T is the temperature (298.15K); S(gas) is the entropy in gas phase; E(SCF) is "raw" electronic energy as computed from the SCF procedure which is the self-consistent field energy, and ZPE is the zero point energy. The entropy we refer is specifically vibrational/rotational/translational entropy of the solute(s), and the entropy of the solvent is implicitly comprised in the continuum solvation model.

Fragment analysis of A1-TS and A1'-TS

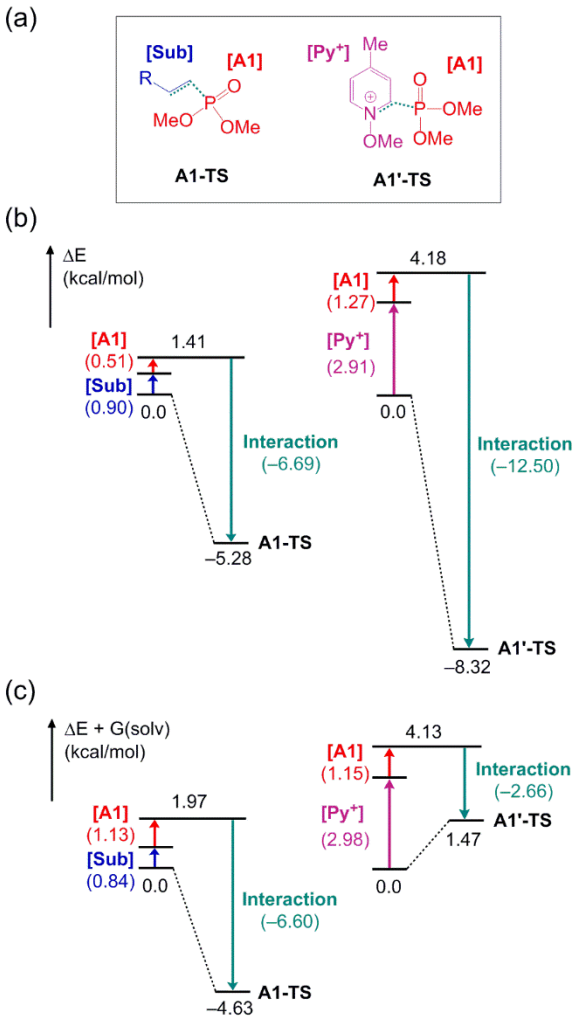


Figure S1. (a) Separating transition states into two fragments and nomination of them. (b) Fragment analysis using only electronic energy. (c) Fragment analysis after solvation correction.

Starting from the reactant states **A1**, the terminal alkene and pyridinium substrates, we calculated the energies required to distort the structures of these reactants to what is found in the transition states and labeled them as **[A1]**, **[Sub]**, and **[Py$^+$]**, respectively. Next, these distorted fragments were assembled into the transition states **A1-TS** and **A1'-TS**, allowing for the interaction energies to be calculated. Considering only the electronic energies, the terminal alkene and **A1** substrates undergo structural distortions that are worth only 0.9 and 0.5 kcal/mol, respectively. The interaction energy is –6.7 kcal/mol for **A1-TS**. These energies are easy to understand considering that the C–P bond is formed by a radical

attack on a fairly localized π-orbital, which should cause only minimal structural change.

A much more pronounced electronic change is needed to engage pyridinium, as the initially delocalized and aromatic π-orbital must be forced to localize and match the localized phosphonyl radical **A1**. Our calculations suggest structural distortion energies of 2.9 and 1.3 kcal/mol in **[Py$^+$]** and **[A1]**, respectively. The fragment interaction energy in **A1'-TS** is found to be –12.5 kcal/mol. As shown in Figure 4, the optimized P–C distances in **A1-TS** and **A1'-TS** are 2.72 and 2.59 Å, respectively, in good agreement with the much stronger interaction energy in **A1'-TS** over that of **A1-TS**. These computed results are internally consistent and easy to understand, given the localized vs. delocalized nature of the π-orbitals in the alkene and pyridinium substrates, respectively. When solvation energy was considered as illustrated in (c), the interaction energy of **A1'-TS** was significantly changed to –2.7 kcal/mol, whereas the interaction energy in **A1-TS** is nearly same. The reason of this critical role of solvation energy is written in main text.

Computationally calculated isosurface plots

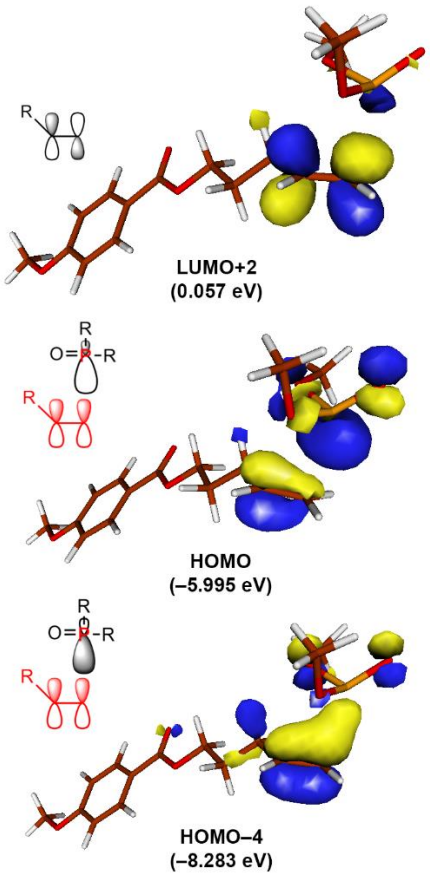


Figure S2. Isosurface plots of **A1-TS** (isodensity value = 0.05).

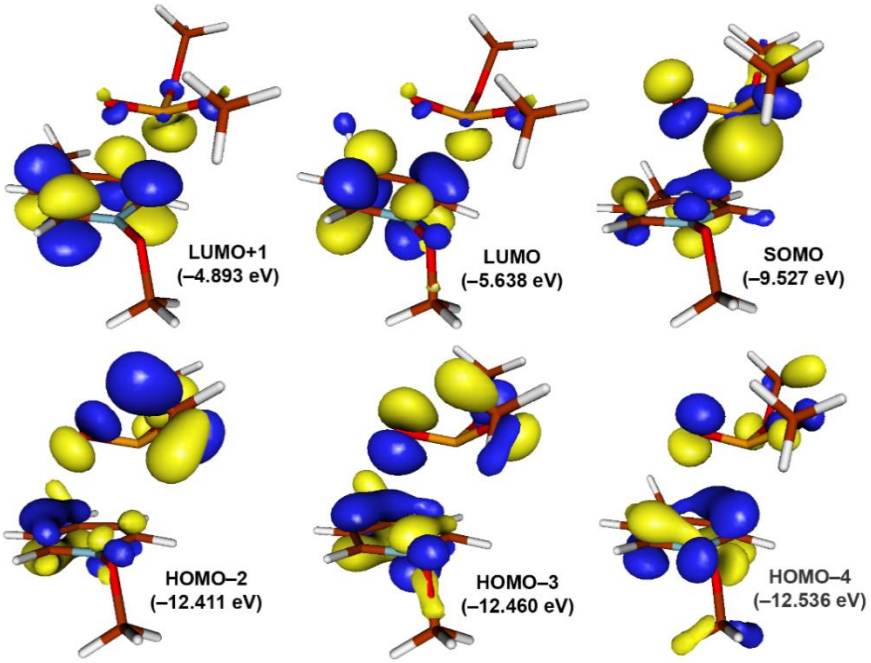


Figure S3. Isosurface plots of **A1'-TS** (isodensity value = 0.05).

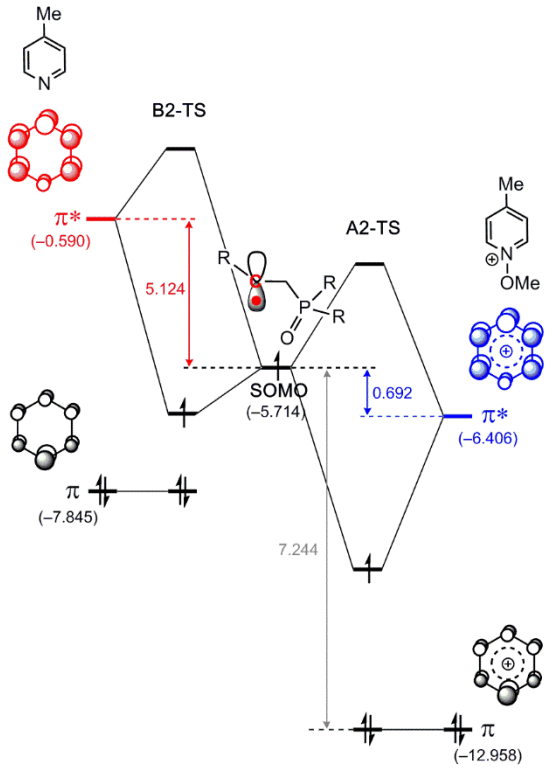


Figure S4. Qualitative MO diagram of radical interaction between alkyl radical **A2** and pyridinium (Energies are given in eV).

Similar to phosphonyl radical **A1**, transient alkyl radical intermediate **A2** will act as a nucleophile to interact with pyridine or pyridinium at first as mentioned in main text. Highly located LUMO energy of pyridine analogue is in good agreement with energy difference between **A2-TS** and **B2-TS** described in Figure 1.

Computational study of diverse pathway after C–C bond formation

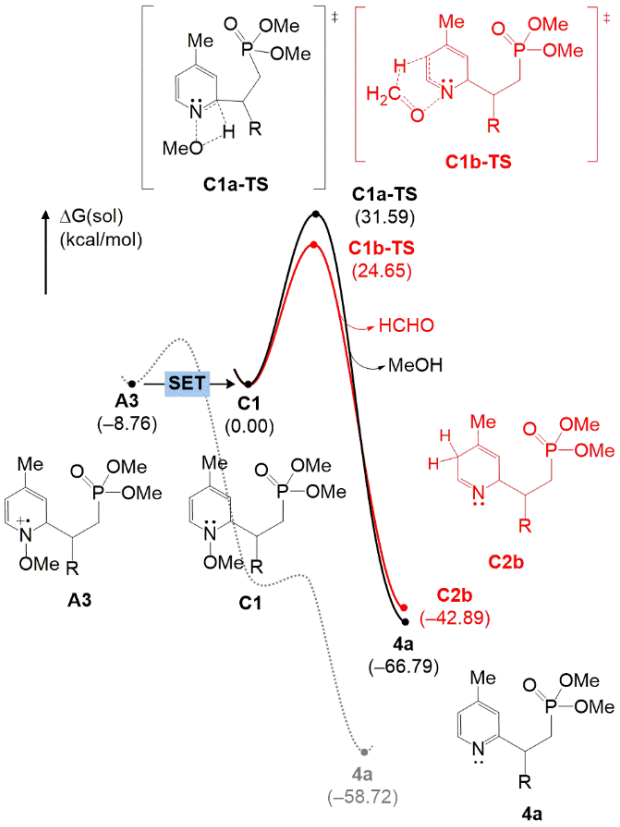


Figure S5. Other reaction pathways after formation of **A3** intermediate.

There is also a probability that a single electron transfer occurs in **A3**, and the associated energy profile is shown above. After being reduced of **A3**, it is impossible to be charge-separated by deprotonation due to the electroneutrality of **C1**. Instead, two different types of decomposition *via* metathesis, **C1a-TS** and **C1b-TS** could occur. Two metathesis reactions showed 31.6 and 24.7 kcal/mol of activation barrier respectively. Although the generation of aromaticity of products compensates the energy barriers of transition states, their values are quite high due to high structural strain in the structures of transition states. Therefore **C1** is hard to proceed to the next reactions. Deprotonation on **A3**, on the other hand, with acetate from Mn(OAc)3, occurs almost immediately. Thus it is reasonable that intermolecular deprotonation occurs dominantly and irreversibly. After deprotonation,

electroneutral radical intermediate **A4** undergoes barrierless homolytic cleavage to finally make a product **4a**.

Table S3. Computed energy components for optimized structures

	E(SCF)/(eV)	ZPE/(kcal/mol)	S(gas)/(cal/mol)	G(solv)/(kcal/mol)
	cc-pVTZ(-f)/LACV3P**	6-31G**/LACVP**	6-31G**/LACVP**	6-31G**/LACVP**
Terminal Alkene	-19875.195	166.616	135.583	-9.86
N-methoxypyridinium	-10946.475	100.479	88.162	-52.56
AcOH	-6232.411	38.976	68.687	-9.02
AcO^-	-6216.767	30.254	69.238	-74.82
•OMe	-3129.780	22.698	56.682	-3.86
4-methylpyridine	-7822.261	70.384	73.212	-6.26
3a	-17617.703	63.108	87.433	-11.31
A1	-17599.928	56.027	90.895	-9.07
A1-TS	-37475.352	222.957	183.185	-18.28
A2	-37476 540	224.315	179.767	-17.42
A2-TS	-48423.754	326.198	224.130	-50.61
A3	-48424.250	327.927	216.796	-53.07
A4	-48413.910	319.437	215.679	-20.21
A4-TS	-48413.887	318.567	211.958	-20.51

4a	-45284.625	293.881	191.185	-19.51
A1'-TS	-28546.764	156.793	145.486	-51.84
A5	-28547.313	155.123	135.384	-53.28
A6	-28537.238	149.721	140.329	-12.46
A2'-TS	-55093.965	286.169	226.167	-27.35
5a	-37494.492	233.224	177.523	-18.36
B1-TS	-25422.234	128.718	131.393	-12.68
B2	-25422.889	129.651	124.595	-12.55
B2-TS	-45298.703	298.214	209.912	-18.86
B3	-45299.367	298.923	193.862	-18.94
[A1] for A1-TS	-17599.906	-	-	-8.45
[Sub] for A1-TS	-19875.156	-	-	-9.92
[A1] for A1'-TS	-17599.873	-	-	-9.19
[Py^-] for A1'-TS	-10946.349	-	-	-52.49
[A1] for B1-TS	-17599.916	-	-	-8.61
[Py] for B1-TS	-7822.133	-	-	-6.19
C1	-48430.590	327.738	214.74	-19.70
C1a-TS	-48428.949	323.539	204.51	-24.80
C1b-TS	-48429.254	325.016	202.95	-26.65

C2b	-45316.516	308.011	205.88	-20.57

Table S4. Cartesian coordinates of the optimized geometries

The Cartesian coordinates of optimized geometries are given below in the standard XYZ format, and units are in Å

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================================
Terminal Alkene
================================
  C  -11.521351814  20.644306183   4.904490948
  C  -12.671218872  20.163919449   5.536429882
  C  -10.394090652  20.980697632   5.663475990
  H  -13.555590630  19.897346497   4.966016769
  H   -9.515980721  21.350675583   5.140699863
  C  -12.679127693  20.027162552   6.917237759
  C  -10.415908813  20.840747833   7.036854744
  H  -13.561959267  19.655868530   7.432218075
  H   -9.542123795  21.102640152   7.626879215
  C  -11.563039780  20.361085892   7.680323124
  O  -11.398137093  20.819774628   3.570338726
  C  -12.501939774  20.502878189   2.754052877
  H  -12.772815704  19.441244125   2.836078405
  H  -13.378118515  21.116544724   3.004869699
  H  -12.197964668  20.716060638   1.727502227
  C  -11.653382301  20.190776825   9.144140244
  O  -12.628444672  19.772930145   9.729846001
  O  -10.521397591  20.556035995   9.775820732
  C  -10.550807953  20.428565979  11.199486732
  H  -10.717603683  19.374948502  11.464841843
  H  -11.403974533  20.996107101  11.596021652
  C   -9.238547325  20.940980911  11.738993645
  H   -8.413756371  20.355667114  11.307426453
  H   -9.089897156  21.979612350  11.413717270
  C   -9.197201729  20.862390518  13.263438225
  H   -9.381662369  19.819675446  13.569818497
  H  -10.014464378  21.461629868  13.691795349
  C   -7.889837265  21.325269699  13.818906784
  H   -7.007808208  20.776065826  13.477978706
  C   -7.738047123  22.336658478  14.668234825
  H   -8.593214035  22.907320023  15.028964996
  H   -6.760002613  22.635354996  15.036756516

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Prydinium
================================
  C  -15.817765236   9.450723648  12.849877357
  C  -15.825049400  10.648455620  13.578764915
  C  -15.812279701  10.628487587  14.954562187
  N  -15.789124489   9.441808701  15.590767860
  C  -15.793006897   8.258952141  14.946773529
  C  -15.804556847   8.248073578  13.570919037
  H  -15.849179268  11.607464790  13.068708420
  H  -15.836642265  11.505366325  15.594453812
  H  -15.804986000   7.377139091  15.580308914
  H  -15.813331604   7.292233944  13.054448128
  C  -15.810677528   9.455904961  11.361762047
  H  -14.775117874   9.468031883  10.997719765
  H  -16.289432526   8.562040329  10.952937126
  H  -16.307958603  10.342556000  10.959379196
  O  -15.859109879   9.438712120  16.955110550
  C  -14.541271210   9.435117722  17.545576096
  H  -13.992975235   8.531832695  17.256814957
  H  -13.988074303  10.335425377  17.256156921
  H  -14.725853920   9.435386658  18.619771957

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AcOH
================================
  H  -12.310276031   8.670559883   3.532675743
  O  -12.310271263   8.166206360   4.360433102
  O  -12.310263634  10.269226074   5.133139133
  C  -12.310267448   9.083036423   5.349727631
  C  -12.310272217   8.427042007   6.695249081
  H  -11.429916382   7.785067558   6.796719551
  H  -12.310274124   9.189065933   7.475049496
  H  -13.190621376   7.785058975   6.796716690

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ACO⁻
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  O  -12.313472748   8.178046227   4.342724323
  O  -12.306834221  10.292366982   5.193414688
  C  -12.310469627   9.037668228   5.262367249
  C  -12.310425758   8.425977707   6.716212273
  H  -11.428895950   7.783079624   6.848137856
  H  -12.312383652   9.194140434   7.499892235
  H  -13.188919067   7.778820515   6.846951008

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•OMe
================================
  C   -1.276499152   0.005725105  -1.707090139
  H   -1.276446342  -0.843156040  -2.424370050
  H   -2.186100006   0.589112103  -1.934671283
  H   -0.366844416   0.589048922  -1.934664726
  O   -1.276383042  -0.559975863  -0.476628512

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pyridine
================================
  C   -5.588545322  23.778491974  12.417137146
  C   -6.130966663  24.866254807  13.102938652
  C   -6.481184483  22.808771133  11.965572357
  C   -7.502877235  24.924289703  13.309493065
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H	-5.484239101	25.666135788	13.462476730
N	-8.362779617	23.996620178	12.881690025
H	-7.936291695	25.776350021	13.836273193
C	-7.839528561	22.961675644	12.224221230
H	-8.547472000	22.210206985	11.868839264
H	-6.118187428	21.939016342	11.420926094
C	-4.110197544	23.654642105	12.211667061
H	-3.630988359	23.036495209	13.172302246
H	-3.905821800	23.042917252	11.180226326
H	-3.608176470	24.782997131	12.171600342

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3a

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P	-9.506259918	9.262967110	7.110801220
O	-10.442438126	8.005697250	7.473832130
O	-9.430193901	10.246900558	8.199023247
O	-10.059033394	9.786651611	5.692063808
C	-10.629548073	6.998232841	6.493062496
H	-9.670803070	6.649164677	6.082849026
H	-11.125844002	6.157337666	6.981164932
H	-11.251768112	7.358708858	5.664864540
C	-11.244074821	10.581050873	5.727045536
H	-11.422454834	10.938740730	4.711642742
H	-12.103495598	9.982652664	6.057592869
H	-11.120107651	11.432462692	6.404432774
H	-8.316870689	8.674837112	6.653928280

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A1

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P	-9.686430931	9.324294090	7.190940857
O	-10.060279846	7.765695095	7.406436920
O	-10.012427330	10.190062523	8.352016449
O	-10.529404640	9.641372681	5.828360081
C	-10.051469803	6.877927780	6.295254230
H	-9.127081871	6.969864845	5.710341930
H	-10.114775658	5.864920616	6.697468281
H	-10.906907082	7.071787357	5.640263081
C	-10.799750328	11.009169579	5.539074898
H	-11.445662498	11.025456429	4.658847332
H	-11.304450035	11.492768288	6.381834030
H	-9.876955032	11.557757378	5.312453270

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A1-TS

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C	-11.619331360	19.533327103	5.080024242
C	-12.461357117	18.617189407	5.720238209
C	-10.544341087	20.104864120	5.774565220
H	-13.300213814	18.163440704	5.198777199
H	-9.909474373	20.813476563	5.245893478
C	-12.217735291	18.284696579	7.045086384
C	-10.313105583	19.765304565	7.092885017
H	-12.858579636	17.574449539	7.565371990
H	-9.479101181	20.208181381	7.632473469
C	-11.150523186	18.848178864	7.744369507
O	-11.760233879	19.930250168	3.796722412
C	-12.826095581	19.387983322	3.050181627
H	-12.744559288	18.293516159	2.961395025
H	-13.802024841	19.638681412	3.494050741
H	-12.762474060	19.832471848	2.054735899
C	-10.960801125	18.439683914	9.150162697
O	-11.668259621	17.649129868	9.739088058
O	-9.901376724	19.043731689	9.726919174
C	-9.668888092	18.677984238	11.087437630
H	-9.522860527	17.590183258	11.152224541
H	-10.561375618	18.912813187	11.684969902
C	-8.455567360	19.431335449	11.573506355
H	-7.598872185	19.194435120	10.926007271
H	-8.630151749	20.511943817	11.478489876
C	-8.129531860	19.070924759	13.020272255
H	-7.982732296	17.979623795	13.099032402
H	-8.980452538	19.312063217	13.676775932
C	-6.896888733	19.741451263	13.520761490
H	-6.010467529	19.658805847	12.887066841
C	-6.781932831	20.343654633	14.718627930
H	-7.650308609	20.495141983	15.360386848
H	-5.862474918	20.839742661	15.019908905
O	-4.736972809	17.932352066	15.132202148
P	-6.002316952	18.149141312	16.119138718
O	-5.757310390	17.837556839	17.559104919
O	-7.058542252	17.111902237	15.409073830
C	-3.964716673	16.745328903	15.325071335
C	-8.284904480	16.916704178	16.099269867
H	-4.566683292	15.857135773	15.093553543
H	-3.116816282	16.799203873	14.637850761
H	-3.599891424	16.681100845	16.356380463
H	-8.899560928	16.250150681	15.487613678
H	-8.116278648	16.468585968	17.085102081
H	-8.824339867	17.867895126	16.231956482

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A2

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C	-10.945592880	19.652900696	5.666683197
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C	-9.865454674	19.928176880	6.513554096
H	-13.105011940	19.615411758	5.482589245
H	-8.860700607	19.783956528	6.125224590
C	-12.465977669	20.265529633	7.422723293
C	-10.090134621	20.366256714	7.803652287
H	-13.474760056	20.404588699	7.804057121
H	-9.253310204	20.576351166	8.463841438
C	-11.397603035	20.539834976	8.273262024
O	-10.620820045	19.226205826	4.426170826
C	-11.668064117	18.923641205	3.535542250
H	-12.305503845	18.114826202	3.919625282
H	-12.293926239	19.803806305	3.331401587
H	-11.199079514	18.596511841	2.605481386
C	-11.707654953	20.995918274	9.643459320
O	-12.828409195	21.149570465	10.079314232
O	-10.599646568	21.223897934	10.372553825
C	-10.832586288	21.632835388	11.721940041
H	-11.442034721	20.872734070	12.230138779
H	-11.416473389	22.564378738	11.723685265
C	-9.490938187	21.801216125	12.389334679
H	-8.935707092	20.854967117	12.337175369
H	-8.907006264	22.563251495	11.851037979
C	-9.649184227	22.200563431	13.860116005
H	-10.198538780	21.404804230	14.385473251
H	-10.280015945	23.105157852	13.915650368
C	-8.348988533	22.443782806	14.541554451
H	-7.720160484	23.266809464	14.201125145
C	-7.835270405	21.549392700	15.611056328
H	-8.634440422	21.205368042	16.283851624

H	-7.054000854	22.019662857	16.219697952
O	-6.457957745	19.349830627	16.139858246
P	-7.104001999	20.070257187	14.860378265
O	-7.994009972	19.251171112	14.006667137
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C	-5.788324356	18.110170364	15.924201012
C	-5.841565609	20.810144424	12.687738419
H	-4.874126911	18.267324448	15.340002060
H	-5.527804852	17.710372925	16.905809402
H	-6.441670418	17.403549194	15.400253296
H	-4.813180923	20.921651840	12.336881638
H	-6.316951275	19.960460663	12.186306000
H	-6.403398514	21.723899841	12.449661255

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A2-TS

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C	-11.052367210	20.039436340	5.616864204
C	-10.207585335	21.094697952	5.985687256
C	-11.745305061	19.316570282	6.600877285
H	-9.664113045	21.664468765	5.237572193
H	-12.391795158	18.504486084	6.277976036
C	-10.067747116	21.411214828	7.326597214
C	-11.599238396	19.641931534	7.931489944
H	-9.415748596	22.226854324	7.632135868
H	-12.137420654	19.081239700	8.690968513
C	-10.754612923	20.697492599	8.312188148
O	-11.263311386	19.643522263	4.353138924
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H	-10.885971069	21.389951706	3.282224417
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O	-11.259492874	20.340051651	10.577018738
C	-11.105606079	20.675666809	11.955523491
H	-12.011454582	20.309968948	12.449233055
H	-11.076985359	21.769454956	12.058137894
C	-9.850249290	20.052495956	12.548810005
H	-10.004335403	18.977823257	12.697227478
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H	-6.578137398	22.438539505	14.922530174
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O	-8.426455498	19.922275543	16.832738876
O	-5.970912457	20.032249451	15.921029091
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C	-5.541645527	23.616514206	12.309393883
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C	-7.818078518	22.751081467	12.226147652
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H	-3.743481398	24.382410049	11.433753014
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H	-11.283176422	24.735010147	12.323410988
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C	-10.872416496	19.234134674	7.628273964
H	-9.899230003	22.452655792	7.172845364
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C	-10.492860794	20.547233582	7.949615479
O	-10.722876549	19.236421585	4.036566257
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H	-9.408628464	20.447950363	2.967839003
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O	-10.064488411	22.152217865	9.664608002
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H	-11.370205879	23.161867142	17.685453415
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C	-7.864638329	23.533672333	10.939257622
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H	-9.312979698	23.760520935	14.000236511
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H	-10.600105286	25.011869431	12.392542839
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H	-12.080479622	22.297950745	10.018253326
H	-9.196454048	19.328964233	8.932301521
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C	-10.585871696	23.809469223	5.638900280
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H	-10.199744225	24.094675064	4.658363819
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C	-10.182784081	18.366159439	12.391095161
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H	-10.676071167	24.726322174	6.400497913
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H	-7.831318378	22.406187057	16.094945908
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C	-7.431497097	22.681573868	9.809389114
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C	-10.499570847	21.834299088	7.845417976
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H	-9.080203056	22.261499405	4.002530575
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H	-11.279335022	18.595018387	12.343213081
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H	-6.825876236	25.617223740	15.371299744
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C	-7.866810799	23.794452667	11.832097054
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C	-15.974157333	8.438343048	14.899209976
C	-16.310777664	8.478205681	13.569401741
H	-15.836585999	11.804375648	13.044535637
H	-15.155218124	11.603265762	15.479012489
H	-16.017173767	7.555361271	15.528799057
H	-16.635663986	7.564629078	13.080438614
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C	-15.665939331	9.426069260	12.767734528
C	-15.659790039	10.619835854	13.445247650
C	-15.691160202	10.706363678	14.920944214
N	-15.445311546	9.431862831	15.553765297
C	-15.429431915	8.276544571	14.905241013
C	-15.586369514	8.228219986	13.525053978
H	-15.722461700	11.567329407	12.914157867
H	-14.976768494	11.437364578	15.332869530
H	-15.255599976	7.389532566	15.508795738
H	-15.583672523	7.258491039	13.035038948
C	-15.717493057	9.358840942	11.277340889
H	-14.833484650	8.847098351	10.880152702
H	-16.592428207	8.785804749	10.948468208
H	-15.770913124	10.352798462	10.827292442
O	-15.148438454	9.500647545	16.878667831
C	-16.119169235	8.844220161	17.722038269
H	-17.128074646	9.195506096	17.486740112
H	-16.047641754	7.755054474	17.632940292
H	-15.835850716	9.143867493	18.731109619
O	-17.170118332	11.706983566	16.902423859
P	-17.389348984	11.403662682	15.363847733
O	-17.758903503	12.494316101	14.448358536
O	-18.316131592	10.102087021	15.358250618
C	-18.187503815	12.462661743	17.598606110
C	-19.276023865	9.856250763	14.310253143
H	-19.092132568	11.855675697	17.704935074
H	-17.777917862	12.696567535	18.580560684
H	-18.409137726	13.385405540	17.055179596
H	-20.382621765	9.978018761	14.822204590
H	-19.092388153	10.683487892	13.433870316
H	-19.083354950	8.704730988	13.927601814

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A6

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C	-15.572784424	9.505921364	12.744935036
C	-15.573019981	10.696508408	13.471717834
C	-15.749917984	10.731269836	14.843874931
N	-15.998684883	9.534355164	15.540100098
C	-15.915936470	8.334965706	14.839567184
C	-15.748105049	8.305459976	13.494342804
H	-15.448106766	11.654438972	12.968852043
H	-16.021986008	7.448467731	15.458272934
H	-15.750853539	7.341579914	12.988822937
C	-15.375486374	9.464323997	11.265427589
H	-14.432239532	8.971653938	10.991792679
H	-16.178272247	8.902956963	10.768661499
H	-15.357601166	10.471719742	10.837399483
O	-15.364718437	9.457316399	16.805904388
C	-16.346696854	9.335227013	17.821107864
H	-16.990417480	10.222176552	17.862525940
H	-16.962028503	8.435195923	17.675567627
H	-15.786157608	9.240163803	18.754678726
O	-14.871380806	12.348010063	16.830425262
P	-15.946516037	12.308945656	15.646380424
O	-15.918089867	13.443522453	14.697808266
O	-17.308992386	12.191967010	16.520553589
C	-14.715439796	13.586275101	17.517999649
C	-18.524501801	12.143070221	15.783608437
H	-15.611310959	13.813168526	18.108459473
H	-13.859869003	13.471953392	18.186180115
H	-14.528469086	14.402621269	16.812074661
H	-19.343118668	12.226041794	16.501186371
H	-18.579547882	12.970589638	15.067243576
H	-18.612358093	11.188670158	15.246732712

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A2'-TS

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C	-12.257213593	20.670097351	5.131645203
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C	-11.164428711	21.297428131	5.741492271
H	-13.922140121	19.310745239	5.415001392
H	-10.555230141	21.965467453	5.138500214
C	-12.779825211	19.581897736	7.208505154
C	-10.887420654	21.066373825	7.074291229
H	-13.398360252	18.916336060	7.805933952
H	-10.043884277	21.557804108	7.550775528
C	-11.695185661	20.202619553	7.823828220
O	-12.445156097	20.964443207	3.826178074
C	-13.538830757	20.373743057	3.165843725
H	-13.462460518	19.277276993	3.155403376
H	-14.493885994	20.659751892	3.628656864
H	-13.516285896	20.742193222	2.138330221
C	-11.461181641	19.921588898	9.253915787
O	-12.154911041	19.197862625	9.936140060
O	-10.380623817	20.565420151	9.734880447
C	-10.129020691	20.371572495	11.125765800
H	-9.959897995	19.303031921	11.321762085
H	-11.020875931	20.662031174	11.698886871
C	-8.933015823	21.210454941	11.502948761
H	-8.057952881	20.884733200	10.921879768
H	-9.130387306	22.255620956	11.223181725
C	-8.643119812	21.096698761	12.994233131
H	-8.503851891	20.037572861	13.270247459
H	-9.518911362	21.438915253	13.573472023
C	-7.437250614	21.884866714	13.422579765
H	-6.539382935	21.704486847	12.821072578
C	-7.176213264	22.044942856	14.893461227
H	-8.042379379	22.506307602	15.394256592
H	-6.319183350	22.703691483	15.085669518
O	-5.838187695	19.756290436	14.812884331
P	-6.821232796	20.526002884	15.817854881
O	-6.356045246	20.732772827	17.205577850
O	-8.141737938	19.598237991	15.699605942
C	-5.316004753	18.500045776	15.244378090
C	-9.180612564	19.802568436	16.650295258
H	-6.109992027	17.745113373	15.264665604
H	-4.550599098	18.206859589	14.523735046
H	-4.868943214	18.589376450	16.240716934
H	-9.879167557	18.969385147	16.550275803
H	-8.778873444	19.830175400	17.668636322
H	-9.716747284	20.740184784	16.445940018
O	-7.637492657	25.818994522	13.204622269
P	-8.642363548	24.584476471	12.883827209
O	-9.506196976	24.873378754	11.718876839
O	-9.430131912	24.351419449	14.290508270
H	-7.809020042	23.188203812	13.009247780
C	-6.736483097	25.697397232	14.293236732
C	-10.450966835	25.296863556	14.615773201
H	-6.014484406	24.885457993	14.124643326
H	-6.187084675	26.638044357	14.365428925
H	-7.266375065	25.513864517	15.237174034
H	-10.948449135	24.939205170	15.519208908
H	-10.013437271	26.285024643	14.807830811

H	-11.175625801	25.377220154	13.798678398

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5a
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C	-11.800296783	20.620141983	4.920408726
C	-12.776162148	19.909030914	5.623317242
C	-10.693709373	21.147525787	5.597204208
H	-13.641107559	19.492261887	5.116194725
H	-9.953388214	21.694345474	5.019217491
C	-12.633592606	19.735301971	6.992768288
C	-10.564757347	20.968652725	6.960333824
H	-13.379414558	19.186000824	7.562335014
H	-9.707304001	21.378608704	7.486638546
C	-11.537162781	20.258193970	7.675203800
O	-11.835929871	20.851282120	3.590090275
C	-12.929878235	20.348848343	2.860253811
H	-12.987093925	19.252717972	2.918013334
H	-13.880811691	20.774171829	3.210922718
H	-12.770228386	20.642698288	1.820930243
C	-11.462694168	20.033611298	9.133047104
O	-12.284226418	19.415874481	9.776412010
O	-10.372195244	20.597650528	9.686722755
C	-10.249453545	20.426794052	11.099829674
H	-10.193249702	19.354103088	11.333150864
H	-11.155791283	20.809238434	11.590317726
C	-9.014924049	21.164054871	11.557662010
H	-8.134795189	20.760766983	11.035672188
H	-9.095042229	22.220548630	11.261439323
C	-8.829813957	21.050268173	13.063602448
H	-8.766067505	19.990821838	13.350852966
H	-9.721809387	21.454252243	13.572303772
C	-7.594110012	21.792335510	13.556014061
H	-6.692305565	21.362575531	13.097206116
C	-7.438333035	21.810186386	15.075899124
H	-8.384487152	22.081665039	15.567314148
H	-6.710953712	22.569471359	15.389873505
O	-5.538423061	19.975669861	15.045855522
P	-6.877071857	20.291236877	15.872763634
O	-6.761478424	20.361831665	17.345396042
O	-7.824695587	19.081596375	15.355657578
C	-4.768355846	18.847669601	15.453913689
C	-9.024342537	18.824584961	16.074857712
H	-5.288770676	17.917306900	15.198988914
H	-3.819605112	18.893844604	14.915792465
H	-4.580260277	18.877683640	16.533067703
H	-9.375263214	17.832956314	15.780657768
H	-8.846147537	18.849340439	17.155065536
H	-9.797212601	19.563081741	15.816719055
H	-7.645204067	22.833709717	13.205314636

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C	-15.920877457	10.727292061	13.567619324
C	-15.791568756	10.835457802	14.970298767
N	-15.658923149	9.757672310	15.786930084
C	-15.872631073	8.574604034	15.227874756
C	-16.145257950	8.380837440	13.872809410
H	-15.925935745	11.628731728	12.957483292
H	-15.495458603	11.794875145	15.403248787
H	-15.809282303	7.710972786	15.891908646
H	-16.321180344	7.377489090	13.489852905
C	-16.395015717	9.305462837	11.541060448
H	-15.870254517	8.428484917	11.146401405
H	-17.464925766	9.154338837	11.352610588
H	-16.079179764	10.184318542	10.970690727
O	-18.136560440	12.855835915	14.743241310
P	-18.076759338	11.466813087	15.568930626
O	-19.247182846	10.557615280	15.430496216
O	-17.852319717	12.054633141	17.071060181
C	-19.291143417	13.678059578	14.925119400
C	-17.826480865	11.093100548	18.124917984
H	-19.300275803	14.102993011	15.935371399
H	-19.232450485	14.483547211	14.190058708
H	-20.207090378	13.098723412	14.762065887
H	-16.983882904	10.402598381	17.989294052
H	-17.697893143	11.646528244	19.057466507
H	-18.763713837	10.526117325	18.157276154

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B2
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C	-15.392765999	9.683361053	12.710859299
C	-15.339730263	10.670367241	13.656498909
C	-15.786263466	10.411798477	15.048490524
N	-16.007429123	9.042468071	15.452838898
C	-16.042072296	8.153400421	14.504421234
C	-15.793725967	8.394789696	13.128661156
H	-15.030669212	11.682282448	13.398279190
H	-15.133236885	10.907132149	15.787322998
H	-16.262578964	7.129078388	14.817961693
H	-15.872200012	7.579732418	12.412252426
C	-15.030116081	9.929244041	11.279848099
H	-14.240144730	9.245448112	10.946803093
H	-15.896699905	9.759275436	10.629461288
H	-14.685304642	10.955603600	11.121279716
O	-16.981313705	12.769259453	15.129292488
P	-17.417242050	11.236031532	15.328115463
O	-18.543249130	10.740549088	14.510178566
O	-17.652252197	11.185540199	16.917270660
C	-18.002820969	13.756833076	15.242544174
C	-18.359893799	10.071306229	17.463762283
H	-18.341415405	13.838434219	16.281816483
H	-17.568824768	14.706968307	14.925154686
H	-18.853487015	13.508082390	14.598048210
H	-18.597951889	10.325165749	18.498722076
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H	-17.728128433	9.177083969	17.430608749

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B2-TS
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C	-9.880050659	20.666191101	5.051643848
C	-9.715157509	22.013490677	5.390424252
C	-10.213626862	19.729482651	6.038910389
H	-9.456047058	22.754627228	4.639479160
H	-10.334392548	18.690429688	5.740317822
C	-9.888139725	22.406324387	6.710228920
C	-10.379433632	20.132949829	7.348572254
H	-9.770579338	23.450296402	6.996070862
H	-10.636288643	19.407165527	8.115958214
C	-10.219469070	21.480978012	7.699398994
O	-9.739702225	20.169603348	3.803666115
C	-9.404144287	21.063520432	2.766992331

H	-10.172278404	21.840402603	2.637540102
H	-8.432844162	21.547603607	2.947139025
H	-9.341204643	20.467464447	1.854118109
C	-10.381737709	21.972848892	9.080863953
O	-10.268659592	23.138444901	9.408340454
O	-10.668993950	20.983932495	9.948287964
C	-10.763159752	21.378744125	11.322106361
H	-11.401843071	20.626075745	11.798124313
H	-11.261477470	22.355123520	11.380970001
C	-9.391586304	21.450502396	11.959275246
H	-8.941770554	20.448778152	12.005246162
H	-8.744510651	22.056734085	11.312402725
C	-9.444265366	22.077070236	13.346131325
H	-9.894538879	21.370038986	14.064868927
H	-10.130508423	22.943670273	13.343592644
C	-8.098962784	22.518913269	13.843939781
H	-7.241593361	22.058427811	13.342152596
C	-7.887012005	22.698602676	15.319003105
H	-6.983994484	23.302181244	15.484371185
H	-7.741497040	21.735031128	15.833717346
O	-8.573227882	23.859464645	17.633850098
P	-9.225854874	23.532880783	16.193780899
O	-9.878928185	24.703100204	15.558874130
O	-10.217430115	22.295370102	16.507305145
C	-8.771507263	25.138946533	18.226289749
C	-11.399031639	22.599672318	17.238107681
H	-9.695621490	25.147930145	18.817422867
H	-7.922002316	25.324281693	18.887441635
H	-8.832312584	25.922513962	17.464847565
H	-11.152663231	22.842123032	18.280334473
H	-11.934764862	23.440923691	16.782550812
H	-12.033040047	21.710895538	17.219993591
C	-6.917132854	24.165243149	10.810752869
C	-5.621815205	24.179893494	11.345707893
C	-7.968299866	24.359640121	11.692779541
C	-5.450259209	24.447431564	12.707728386
H	-4.755804062	24.037101746	10.701185226
N	-6.437300682	24.632331848	13.567898750
H	-4.438044548	24.534442902	13.110892296
C	-7.710073471	24.463062286	13.087389946
H	-8.506049156	24.845209122	13.734387398
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C	-7.146451473	23.934326172	9.348225594
H	-7.141374111	22.857818604	9.122054100
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H	-6.358390331	24.395196915	8.741637230

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B3

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H	-9.218075752	22.575834274	4.556911945
H	-10.829300880	18.922260284	6.143517017
C	-9.671613693	22.572566986	6.652939796
C	-10.573454857	20.531236649	7.561297894
H	-9.349311829	23.599546432	6.811520576
H	-10.949905396	19.967464447	8.410167694
C	-10.157726288	21.856309891	7.744658947
O	-10.007764816	20.015352249	4.042112827
C	-9.544517517	20.700225830	2.902545214
H	-10.158408165	21.585645676	2.685340643
H	-8.496239662	21.010829926	3.014680386
H	-9.621288300	19.999841690	2.068670988
C	-10.215359688	22.535871506	9.053285599
O	-9.903943062	23.696712494	9.235918045
O	-10.658290863	21.725067139	10.030447006
C	-10.682055473	22.299045563	11.342969894
H	-11.411552429	21.708623886	11.907229424
H	-11.042799950	23.333524704	11.270095825
C	-9.307719231	22.264558792	11.975272179
H	-9.016163826	21.228813171	12.202179909
H	-8.585067749	22.643259048	11.240005493
C	-9.240150452	23.102678299	13.245136261
H	-9.757946968	22.570333481	14.053667068
H	-9.785781860	24.051630020	13.105822563
C	-7.796441555	23.411281586	13.665806770
H	-7.122047424	22.651752472	13.234551430
C	-7.627138615	23.399364471	15.184391975
H	-8.390449524	24.029409409	15.664308548
H	-6.643559456	23.795640945	15.465275764
O	-7.370287418	21.996662140	17.441633224
P	-7.777400017	21.755912781	15.892812729
O	-9.052090645	21.007987976	15.731451988
O	-6.485305786	21.032476425	15.243159294
C	-8.046278000	21.273904800	18.465311050
C	-6.250940323	19.679204941	15.607033730
H	-7.571714401	20.295042038	18.622264862
H	-7.964060783	21.862806320	19.386257172
H	-9.103288651	21.117870331	18.210165024
H	-5.859447956	19.622526169	16.634117126
H	-7.173341751	19.085336685	15.529620171
H	-5.500933170	19.279420853	14.916845322
C	-6.560632706	24.775243759	10.705484390
C	-5.241153717	24.731033325	11.194254875
C	-7.574157238	24.882322311	11.626793861
C	-5.014126301	24.889251709	12.592280388
H	-4.396115780	24.648542404	10.512594223
N	-5.929606915	24.960298538	13.506127357
H	-3.978076696	24.972951889	12.937888145
C	-7.308384895	24.785385132	13.092280388
H	-7.914136410	25.545513153	13.625393867
H	-8.604258537	24.974592209	11.277249336
C	-6.842913151	24.687263489	9.234787941
H	-6.980044842	23.548135757	8.925096512
H	-7.838037491	25.235088348	8.997155190
H	-5.947920799	25.135389328	8.622410774

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C1

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C	-11.171760559	19.703538895	5.760352612
C	-10.233585358	20.730812073	5.887507439
C	-11.846017838	19.227109909	6.890913010
H	-9.700442314	21.113918304	5.022602558
H	-12.569303513	18.427120209	6.756313801
C	-9.982918739	21.268411636	7.142183304
C	-11.588453293	19.772079468	8.133165359
H	-9.258563995	22.069839478	7.266236305
H	-12.112640381	19.404695511	9.011031151
C	-10.650411606	20.802564621	8.272862434
O	-11.497138023	19.106414795	4.592910767
C	-10.857585907	19.551156998	3.419881344
H	-11.066589355	20.611927032	3.221671820
H	-9.769332886	19.405950546	3.471290588

H	-11.258724213	18.949979782	2.601517916
C	-10.338065147	21.435447693	9.570905685
O	-9.528059959	22.329059601	9.712671280
O	-11.065062523	20.921012878	10.577248573
C	-10.838809967	21.483413696	11.876531601
H	-11.773322105	21.314128876	12.425302505
H	-10.675595284	22.564891815	11.778285027
C	-9.659653664	20.842037201	12.572260857
H	-9.818531036	19.757249832	12.661291122
H	-8.765429497	20.978349686	11.951592445
C	-9.461626053	21.444480896	13.959582329
H	-10.247364044	21.052843094	14.620871544
H	-9.614279747	22.533882141	13.930013657
C	-8.084910393	21.161279678	14.572373390
H	-7.696331978	20.219058990	14.155988693
C	-8.167534828	21.024732590	16.098056793
H	-8.868712425	21.754280090	16.526758194
H	-7.195025444	21.215692520	16.576229095
O	-7.378949642	18.531444550	16.194568634
P	-8.637366295	19.392606735	16.702857971
O	-8.978283882	19.299158096	18.139429092
O	-9.800601006	18.817041397	15.729060173
C	-7.376295567	17.139101028	16.489648819
C	-11.147904396	18.924961090	16.172714233
H	-8.155333519	16.623567581	15.915672302
H	-6.396442413	16.751049042	16.202983856
H	-7.538412094	16.970203400	17.560684204
H	-11.764219284	18.367633820	15.463533401
H	-11.264034271	18.510736465	17.179040909
H	-11.480235100	19.972990036	16.183149338
C	-7.872198582	24.623485565	14.100454330
C	-8.063488007	24.462892532	12.669278145
C	-7.357169151	23.610349655	14.826210976
C	-7.542945385	23.367179871	12.079301834
H	-8.593258858	25.206716537	12.082240105
N	-6.816594124	22.458486557	12.812801361
H	-7.633225918	23.134756088	11.020293236
C	-7.034569740	22.258010864	14.240429878
H	-6.077800274	21.890722275	14.656023979
H	-7.194904804	23.736389160	15.896172523
O	-6.491390228	21.285470963	12.135161400
C	-5.132748127	21.342546463	11.740857124
H	-4.923392773	20.391466141	11.243601799
H	-4.959370136	22.171314240	11.041114807
H	-4.469799519	21.459632874	12.609020233
C	-8.236792564	25.936723709	14.718025208
H	-9.291315079	26.176347733	14.526546478
H	-8.077053070	25.939680099	15.801121712
H	-7.647739410	26.753284454	14.280462265

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C1a-TS

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C	-11.065260887	19.987318039	6.662705421
C	-11.150757790	21.215393066	7.328808308
C	-10.952473640	18.798740387	7.395575523
H	-11.237293243	22.147987366	6.778262138
H	-10.884501457	17.861759186	6.846034050
C	-11.127044678	21.237417221	8.716854095
C	-10.927053452	18.835599899	8.775907516
H	-11.197827339	22.182664871	9.254195213
H	-10.833558083	17.914838791	9.345110893
C	-11.017800331	20.059356689	9.455306053
O	-11.081310272	19.844039917	5.320147514
C	-11.197081566	21.005039215	4.529893398
H	-12.135837555	21.541347504	4.733895779
H	-10.351164818	21.690437317	4.689198017
H	-11.194719315	20.671247482	3.489641905
C	-10.973077774	20.165964127	10.927504539
O	-11.029005051	21.218011856	11.537686348
O	-10.843785286	18.966648102	11.528943062
C	-10.580489159	19.018335342	12.939739227
H	-10.895137787	18.044176102	13.327834129
H	-11.204935074	19.800735474	13.388876915
C	-9.107007027	19.305023193	13.173256874
H	-8.501702309	18.401359558	13.016390800
H	-8.804745674	20.010135651	12.391962051
C	-8.820310593	19.929473877	14.529645920
H	-9.005344391	19.209526062	15.339447975
H	-9.524883270	20.767452240	14.678210258
C	-7.391950130	20.472793579	14.666551590
H	-6.673804283	19.639728546	14.621936798
C	-7.203298092	21.216485977	15.995993614
H	-8.088607788	21.812023163	16.265407562
H	-6.364762306	21.924627304	15.933663368
O	-5.463054180	19.484708786	16.927326202
P	-6.801412582	20.205482483	17.435272217
O	-6.737590790	20.930768967	18.722110748
O	-7.827751637	18.949550629	17.453363419
C	-4.783326149	18.629152298	17.842178345
C	-9.035747528	19.114055634	18.186903000
H	-5.365009308	17.716522217	18.016290665
H	-3.825857639	18.370803833	17.386127472
H	-4.611169338	19.142288208	18.795248032
H	-9.531079292	18.140819550	18.215961456
H	-8.831004143	19.460315704	19.205169678
H	-9.701813698	19.835803986	17.690860748
C	-8.229634285	22.815284729	11.877331734
C	-7.611390591	22.048940659	10.854096413
C	-7.932331085	22.464565277	13.161193848
C	-6.730942249	21.027273178	11.152744293
H	-7.864239693	22.248142242	9.812397003
N	-6.440085888	20.633955002	12.397950172
H	-6.266572952	20.452339172	10.351662636
C	-7.011310577	21.376295090	13.474061966
H	-6.001270294	21.900390625	13.743125916
H	-8.355249405	23.028978348	13.993991852
O	-4.628501415	21.611980438	12.846648216
C	-3.821190596	20.700485229	13.466526985
H	-3.012825489	21.204687119	14.032924652
H	-4.359217644	20.042890549	14.187264442
H	-3.304271460	20.039520264	12.743628502
C	-9.200201988	23.897192001	11.528464317
H	-10.115735054	23.446657181	11.122145653
H	-9.478907585	24.482067108	12.411128044
H	-8.790102959	24.583133698	10.776565552

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C1b-TS

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C	-10.772510529	20.192104340	5.696019650
C	-10.084339142	21.357545853	6.046061039
C	-11.388947487	19.416801453	6.686753273
H	-9.598915100	21.971311569	5.292726517
H	-11.914998055	18.516475677	6.378988743
C	-10.022517204	21.731998444	7.380370617

C	-11.318210602	19.799930573	8.011461258
H	-9.493995667	22.635297775	7.676797390
H	-11.793992043	19.198331833	8.781521797
C	-10.632292747	20.966663361	8.373473167
O	-10.898126602	19.732387543	4.432790279
C	-10.289329529	20.467327118	3.396007776
H	-10.701112747	21.484415054	3.324762821
H	-9.200140953	20.531528473	3.530515671
H	-10.502870560	19.930110931	2.469710112
C	-10.521126747	21.436227798	9.767215729
O	-9.942248344	22.454202652	10.096173286
O	-11.140108109	20.619964600	10.641678810
C	-11.058058739	21.013107300	12.016924858
H	-11.966817856	20.618280411	12.487584114
H	-11.080075264	22.110446930	12.068833351
C	-9.797733307	20.487831116	12.678689957
H	-9.868838310	19.403644562	12.849119186
H	-8.952720642	20.642831802	11.998005867
C	-9.541220665	21.204513550	13.999336243
H	-10.280120850	20.860160828	14.736070633
H	-9.723916054	22.284812927	13.877540588
C	-8.131434441	21.012601852	14.568973541
H	-7.741591454	20.032697678	14.254404068
C	-8.140750885	21.079490662	16.101882935
H	-8.834002495	21.851362228	16.466758728
H	-7.150087357	21.338006973	16.502355576
O	-7.393118382	18.588956833	16.428546906
P	-8.568787575	19.545434952	16.951198578
O	-8.756718636	19.654922485	18.413780212
O	-9.845606804	18.899944305	16.187288284
C	-7.371962070	17.247817993	16.909694672
C	-11.131940842	19.121046066	16.754055023
H	-8.207934380	16.677824020	16.488426208
H	-6.428195953	16.805923462	16.585102081
H	-7.429409027	17.229171753	18.004056931
H	-11.832987785	18.473066330	16.223514557
H	-11.135589600	18.884138107	17.822513580
H	-11.446389198	20.166801453	16.623517990
C	-7.829648972	24.372692108	13.486801147
C	-7.843110561	23.957036972	12.109144211
C	-7.453719616	23.453884125	14.403216362
C	-7.429429054	22.673389435	11.758896828
H	-8.284568787	24.601953506	11.350021362
N	-6.893208981	21.828445435	12.613059998
H	-7.408953190	22.394378662	10.704471588
C	-7.104502201	22.057237625	14.023655891
H	-6.146754265	21.799446106	14.502635956
H	-7.411640167	23.727922440	15.458690643
O	-4.960057735	22.762928009	12.692272186
C	-4.934880257	24.008584976	12.275893211
H	-4.240641117	24.218402863	11.433128357
H	-5.965747833	24.320831299	11.826714516
H	-4.829941273	24.780303955	13.077045441
C	-8.145962715	25.796361923	13.816352844
H	-9.130984306	26.087789536	13.431249619
H	-8.132559776	25.973169327	14.896295547
H	-7.410835266	26.469274521	13.353728294

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C2b

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C	-10.825003624	20.130760193	5.723255157
C	-10.020807266	21.229215622	6.043638706
C	-11.511682510	19.445014954	6.733379364
H	-9.479640007	21.772857666	5.274517536
H	-12.127685547	18.594736099	6.448863029
C	-9.915139198	21.628414154	7.368399620
C	-11.397054672	19.851852417	8.047774315
H	-9.297086716	22.481353760	7.642031193
H	-11.928697586	19.320453644	8.832925797
C	-10.595389366	20.952919006	8.380437851
O	-11.003777504	19.655363083	4.471793652
C	-10.335042953	20.303661346	3.414638281
H	-10.645654678	21.354991913	3.323010206
H	-9.242943764	20.263488770	3.539929867
H	-10.609021187	19.769300461	2.502418041
C	-10.440650940	21.442983627	9.763818741
O	-9.764476776	22.405805588	10.073710442
O	-11.144099236	20.713548660	10.647928238
C	-11.043783188	21.128999710	12.015365601
H	-11.966717720	20.777458191	12.491581917
H	-11.028471947	22.227033615	12.047145844
C	-9.805356026	20.571239471	12.686329842
H	-9.905632019	19.487684250	12.845518112
H	-8.947551727	20.716804504	12.020966530
C	-9.547711372	21.269678116	14.016274452
H	-10.297568321	20.933925629	14.746659279
H	-9.705991745	22.355464935	13.905157089
C	-8.138598442	21.047872543	14.580534935
H	-7.766178131	20.068483353	14.241426468
C	-8.146433830	21.071048737	16.114511490
H	-8.837748528	21.832521439	16.503435135
H	-7.154900074	21.317779541	16.521406174
O	-7.368530750	18.583099365	16.394615173
P	-8.574165344	19.509677887	16.910766602
O	-8.803149223	19.566701889	18.371189117
O	-9.818280220	18.864055634	16.092792511
C	-7.351173878	17.226978302	16.829227448
C	-11.122653961	19.032207489	16.635036469
H	-8.166003227	16.663496017	16.359222412
H	-6.391983509	16.803834915	16.523620605
H	-7.447238922	17.168798447	17.919887543
H	-11.795941353	18.394870758	16.056781769
H	-11.148954391	18.745990753	17.691267014
H	-11.457180023	20.076030731	16.544778824
C	-7.825631142	24.433879852	13.550915718
C	-7.856862068	24.103153229	12.090957642
C	-7.473496437	23.495981216	14.433192253
C	-7.242542267	22.769123077	11.791336060
H	-8.888543129	24.084802628	11.696999550
N	-6.914865494	21.866586685	12.622062683
H	-7.093179226	22.543600082	10.728610039
C	-7.119534969	22.091367722	14.046564102
H	-6.161355972	21.826282501	14.528841972
H	-7.435105324	23.747642517	15.495839119
H	-7.350925446	24.886352539	11.501306534
C	-8.181263924	25.832519531	13.934958458
H	-9.190292358	26.093019485	13.585763931
H	-8.146104813	25.978284836	15.020019531
H	-7.497011662	26.555633545	13.468991280

Table S5. Vibrational frequencies (in cm^{-1}) of the optimized structures

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Terminal Alkene
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11.13	27.74	47.70	57.33	83.49	91.24
115.28	128.62	150.83	185.44	207.10	243.75
248.10	314.67	323.86	354.20	401.58	425.46
438.32	495.13	516.97	544.01	622.15	642.15
650.71	701.09	742.07	779.31	810.78	825.21
844.08	856.19	884.16	927.17	935.79	970.13
976.60	1013.08	1018.81	1028.20	1050.10	1071.52
1107.88	1110.73	1119.60	1165.42	1166.45	1176.26
1183.48	1196.77	1221.06	1247.53	1289.02	1294.43
1301.29	1304.25	1326.05	1329.62	1362.99	1396.89
1423.02	1431.23	1459.18	1461.20	1465.44	1466.64
1475.22	1481.62	1493.39	1564.98	1650.35	1688.21
1740.77	1848.50	3001.09	3005.46	3025.38	3034.83
3057.08	3074.95	3084.43	3096.22	3120.82	3137.74
3152.47	3194.81	3196.31	3210.79	3214.78	3231.83

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Prydinium
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8.82	82.56	100.79	189.46	230.45	321.43
390.79	413.39	451.55	466.88	554.79	666.23
697.37	746.58	833.09	845.63	860.11	966.86
985.26	1003.11	1013.90	1038.80	1061.46	1127.18
1154.57	1186.30	1191.19	1228.87	1261.83	1313.10
1357.87	1392.03	1431.68	1436.10	1443.41	1459.57
1469.22	1498.70	1526.90	1627.04	1686.94	3035.06
3044.57	3129.15	3138.71	3163.72	3193.16	3207.54
3207.82	3225.82	3227.22			

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AcOH
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75.78	420.28	542.21	588.42	687.54	888.56
994.73	1057.93	1223.02	1342.25	1420.57	1447.52
1451.25	1906.08	3061.68	3146.42	3188.19	3821.90

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AcO-
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41.79	418.91	601.64	623.41	877.07	974.14
1016.39	1293.58	1409.90	1450.03	1462.68	1820.78
2995.72	3081.29	3095.33			

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•OMe
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649.72	964.45	1159.91	1348.95	1349.35	1508.66
2899.39	2978.26	3018.83			

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pyridine
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257.18	383.91	414.65	513.15	533.70	679.93
755.13	810.51	823.24	826.10	881.40	974.04
992.84	1006.82	1090.56	1103.65	1197.91	1222.07
1233.27	1254.11	1333.41	1350.21	1450.36	1494.34

1503.03 1514.02 1533.47 1637.28 1669.58 1989.58
2026.32 2160.08 3133.99 3137.79 3168.26 3178.14
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3a
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89.11 94.20 110.95 149.55 229.16 233.85
399.93 429.21 546.14 784.50 842.81 995.61
1013.44 1130.77 1134.25 1168.02 1171.24 1190.01
1197.12 1351.72 1457.33 1462.21 1466.04 1468.77
1473.46 1480.62 2507.38 3011.02 3026.03 3095.73
3118.64 3153.37 3162.45
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A1
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64.19 79.85 96.13 133.15 183.42 239.37
375.66 416.71 465.61 748.27 811.09 1106.95
1123.18 1164.40 1166.02 1178.70 1187.89 1258.36
1455.13 1459.83 1464.57 1464.81 1473.48 1475.76
3024.28 3027.00 3116.34 3118.52 3156.19 3156.52
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A1-TS
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-129.26 10.12 16.23 24.43 38.41 45.30
58.57 63.15 74.90 80.71 90.40 92.96
118.23 125.90 131.20 137.30 140.51 152.13
186.82 189.02 206.05 217.66 256.48 270.58
278.04 320.05 327.52 354.64 367.80 407.68
427.02 432.57 452.82 496.72 505.91 520.79
545.31 623.56 642.16 678.02 703.39 743.06
746.23 780.62 804.12 810.41 831.04 844.23
859.61 881.48 890.20 931.14 973.99 981.13
989.40 1016.01 1027.23 1051.63 1073.02 1082.06
1105.20 1108.67 1113.58 1121.85 1162.26 1166.40
1167.99 1168.31 1176.15 1178.81 1182.13 1185.01
1198.48 1218.23 1225.29 1244.00 1283.58 1287.48
1298.42 1302.34 1324.40 1328.46 1357.14 1388.31
1421.05 1429.47 1451.03 1452.76 1455.86 1460.43
1463.18 1464.72 1466.51 1468.10 1475.03 1475.41
1476.28 1483.05 1494.04 1562.22 1642.68 1649.03
1685.04 1838.25 2987.50 2991.10 2997.40 3022.22
3022.28 3033.04 3045.02 3063.25 3069.78 3092.31
3092.77 3115.63 3128.55 3136.19 3139.04 3146.95
3147.24 3181.07 3182.58 3198.77 3202.48 3231.17
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A2
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10.91 14.27 25.30 37.06 53.24 65.78
80.47 86.36 91.22 97.47 117.62 122.55
124.66 128.68 137.53 155.90 186.27 198.76
217.27 241.53 248.30 252.13 267.32 303.27
324.89 329.38 364.06 390.46 400.31 425.61
428.73 462.39 490.46 494.17 517.09 534.71
544.48 624.22 642.83 701.27 724.24 741.00
778.40 800.26 810.97 825.42 827.46 849.98
855.98 866.10 883.89 958.14 969.59 976.78
1018.23 1035.17 1056.01 1062.02 1101.95 1110.94

1112.94 1119.27 1133.80 1150.67 1165.97 1166.73
1169.34 1170.69 1179.11 1183.64 1189.80 1192.91
1197.39 1209.89 1232.41 1246.16 1289.88 1301.28
1301.98 1309.61 1323.25 1328.92 1346.55 1395.70
1401.62 1419.84 1426.06 1453.28 1456.71 1457.95
1459.57 1464.42 1465.62 1465.62 1467.06 1470.86
1477.03 1479.63 1482.10 1493.95 1565.28 1650.65
1688.42 1846.00 2978.63 3002.56 3020.07 3021.78
3029.82 3030.73 3031.56 3055.68 3077.15 3080.15
3100.93 3112.30 3113.08 3122.88 3150.39 3151.51
3153.57 3157.95 3195.58 3197.20 3211.24 3214.63

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A2-TS

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-242.57 10.53 13.14 20.35 33.85 39.40
45.23 47.26 55.12 57.71 67.83 72.34
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116.75 129.96 136.61 144.80 152.55 168.93
182.17 202.12 227.22 234.67 241.64 246.70
249.80 262.41 282.93 300.73 312.44 318.78
327.40 360.59 374.28 381.72 390.01 413.80
424.57 425.06 447.71 459.84 463.74 478.18
517.03 525.19 540.25 555.25 559.89 630.37
642.06 655.37 676.68 705.47 728.07 730.77
745.77 781.00 786.37 800.39 806.05 809.95
827.56 832.64 838.78 855.99 859.75 864.23
869.27 900.57 953.03 963.77 973.28 978.50
997.05 997.79 1011.52 1014.47 1042.58 1045.18
1053.40 1065.55 1075.35 1088.30 1096.98 1097.37
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1165.27 1166.90 1167.22 1168.27 1178.52 1184.73
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1236.28 1242.97 1270.51 1284.91 1303.95 1314.46
1317.23 1318.46 1335.05 1341.40 1353.48 1362.54
1395.44 1398.80 1407.83 1425.56 1432.13 1438.03
1445.28 1447.72 1450.94 1453.40 1455.61 1457.86
1462.09 1466.31 1467.27 1467.69 1469.95 1471.19
1472.90 1474.42 1474.45 1477.04 1481.44 1486.93
1518.47 1566.47 1587.76 1636.99 1664.33 1681.64
1767.16 2980.98 3005.62 3022.58 3032.66 3033.98
3037.21 3040.98 3041.26 3042.59 3050.25 3087.66
3099.52 3106.45 3118.23 3118.67 3123.53 3126.65
3127.97 3134.12 3140.77 3153.81 3162.43 3167.18
3168.15 3176.09 3189.33 3193.42 3196.09 3206.31
3209.31 3211.39 3223.88

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A3

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14.19 20.74 32.39 34.29 40.16 48.20
48.89 63.91 69.84 74.70 83.91 93.68
99.63 111.19 113.93 121.13 132.53 142.51
147.13 154.89 168.30 169.10 177.90 183.66
203.65 212.46 223.45 236.50 248.31 254.10
263.82 290.27 304.45 312.93 328.08 338.24
351.49 376.18 379.93 388.71 415.25 423.61
424.60 459.79 474.33 478.25 496.07 511.69

520.92 529.53 536.82 560.12 621.17 636.89
642.77 647.31 702.88 704.03 726.85 737.26
763.67 769.74 781.04 794.90 797.28 824.73
827.68 836.29 855.36 857.62 864.94 872.24
906.73 949.76 967.96 976.11 985.38 1000.27
1011.01 1014.88 1021.76 1038.02 1047.63 1054.29
1059.92 1066.58 1080.99 1091.33 1099.65 1101.24
1120.04 1123.12 1148.79 1152.06 1162.88 1162.91
1166.28 1169.05 1177.00 1181.80 1187.76 1191.61
1194.31 1194.58 1204.27 1219.98 1228.65 1237.66
1256.59 1280.50 1297.35 1302.08 1310.20 1317.30
1322.27 1325.50 1335.45 1339.76 1350.07 1366.44
1377.03 1393.25 1395.31 1401.10 1422.21 1426.07
1433.45 1446.99 1449.18 1453.06 1458.66 1459.35
1462.96 1464.74 1465.33 1466.39 1467.81 1469.11
1469.57 1472.74 1477.58 1479.69 1480.11 1481.53
1527.87 1565.32 1571.38 1609.51 1639.85 1682.03
1790.80 2985.33 2991.70 3011.86 3028.12 3028.90
3038.28 3039.18 3039.96 3043.31 3050.30 3058.70
3091.77 3092.55 3094.58 3107.07 3107.88 3122.11
3124.82 3129.03 3131.24 3139.16 3154.35 3162.73
3170.55 3184.24 3185.27 3194.44 3201.71 3203.79
3215.37 3217.34 3227.61

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A4

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11.90 18.39 26.51 33.67 48.83 58.15
64.91 70.79 77.41 79.24 91.63 93.18
96.42 103.02 107.62 118.69 125.23 130.44
145.43 150.07 158.38 180.17 186.00 196.49
208.62 229.44 232.38 238.56 242.90 249.08
277.16 286.22 306.45 314.19 321.92 328.72
344.35 355.28 375.93 387.08 398.14 423.75
434.25 460.67 474.63 480.89 500.28 509.31
513.71 524.91 543.76 559.32 605.57 619.89
641.39 653.71 688.74 699.83 711.66 731.97
744.26 767.04 776.85 785.35 794.23 823.86
836.16 848.09 854.98 863.14 873.03 896.11
914.12 922.08 957.63 963.79 964.36 972.04
986.45 1004.91 1018.13 1026.62 1043.59 1071.50
1086.82 1090.98 1099.98 1108.89 1111.95 1118.70
1128.38 1141.68 1156.43 1161.71 1165.27 1169.47
1171.90 1172.52 1176.32 1181.63 1194.95 1195.31
1196.78 1200.27 1215.12 1219.09 1238.27 1280.42
1288.87 1298.57 1299.47 1312.42 1318.84 1320.19
1330.24 1330.81 1356.14 1373.46 1393.40 1398.84
1404.27 1411.49 1417.55 1422.65 1434.66 1446.30
1448.37 1451.61 1454.36 1454.53 1458.14 1459.06
1463.90 1464.24 1465.43 1465.85 1466.74 1467.73
1469.89 1473.59 1480.44 1480.76 1491.28 1529.28
1563.15 1646.70 1650.10 1685.06 1828.34 2988.72
3004.01 3004.51 3007.35 3011.14 3021.27 3028.21
3035.64 3044.19 3055.52 3060.61 3075.04 3080.90
3082.72 3100.16 3102.81 3113.26 3114.53 3122.49
3130.68 3144.79 3146.72 3151.70 3154.34 3166.41
3176.44 3191.85 3195.15 3196.19 3212.72 3213.87

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A4-TS
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-522.00	14.10	22.97	30.84	34.88	50.10
57.73	67.69	75.98	78.33	85.00	90.93
96.60	103.38	104.44	122.44	126.32	135.42
149.92	157.88	159.44	169.64	183.25	190.53
200.70	207.20	231.23	239.01	242.49	247.91
254.37	276.68	280.64	303.03	315.39	323.48
328.30	337.10	354.89	373.18	389.01	419.12
426.36	428.36	462.01	475.79	479.42	513.68
516.01	519.73	528.85	540.61	556.19	619.56
641.14	642.18	691.08	700.52	721.47	730.89
764.96	777.51	783.69	787.59	795.59	827.02
836.82	847.01	855.71	859.86	865.33	881.90
918.06	921.58	926.63	958.95	969.75	976.22
991.75	1011.81	1017.73	1033.07	1043.39	1074.60
1085.42	1086.33	1105.05	1105.79	1114.36	1119.18
1124.70	1138.14	1160.71	1161.46	1165.74	1171.54
1172.03	1173.12	1175.65	1179.72	1180.98	1195.64
1196.84	1200.39	1215.71	1219.56	1240.60	1281.01
1294.56	1298.32	1299.38	1310.50	1316.71	1318.03
1329.03	1329.90	1354.00	1372.24	1390.63	1396.55
1404.70	1414.11	1420.38	1430.24	1443.68	1447.14
1450.62	1451.79	1454.28	1459.24	1459.34	1462.36
1463.26	1464.28	1466.24	1466.62	1466.98	1467.47
1471.76	1475.22	1481.37	1484.76	1487.90	1529.13
1561.96	1636.94	1643.88	1684.10	1828.72	2956.77
2999.39	3001.26	3007.41	3011.33	3013.30	3021.47
3030.22	3036.20	3044.27	3054.73	3077.25	3081.36
3082.06	3088.36	3096.92	3102.13	3103.30	3117.09
3121.79	3138.86	3140.94	3145.38	3151.23	3162.81
3174.89	3179.54	3184.43	3191.57	3206.24	3208.47

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4a
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2.90	12.87	17.00	33.90	49.62	51.79
63.91	70.90	76.58	78.53	105.35	107.57
124.09	127.44	133.04	145.90	150.71	162.49
183.98	200.41	209.43	226.58	237.90	243.28
249.42	261.73	275.67	300.51	307.01	327.61
329.95	362.38	386.08	402.01	417.29	425.68
453.28	465.98	480.14	499.64	514.60	518.21
524.36	529.66	546.21	566.20	603.39	627.86
643.12	678.37	695.11	702.16	727.34	753.82
768.26	780.66	794.53	804.02	825.82	837.75
842.59	849.73	856.71	871.27	890.27	919.64
938.28	970.48	975.69	976.03	1004.82	1011.03
1018.73	1032.50	1054.33	1071.16	1079.32	1104.54
1109.33	1111.13	1119.48	1125.41	1128.24	1130.35
1142.59	1156.25	1165.89	1169.64	1172.07	1174.24
1192.51	1194.00	1196.10	1197.19	1209.89	1221.80
1229.68	1271.40	1283.57	1300.83	1305.14	1311.04
1314.67	1320.61	1329.46	1334.81	1336.54	1343.48
1371.05	1393.58	1397.92	1418.66	1422.43	1450.69
1452.37	1457.19	1459.65	1463.16	1464.56	1466.04

1466.63 1467.06 1467.74 1470.63 1476.38 1477.75
1481.68 1483.88 1490.76 1503.04 1523.32 1564.75
1638.67 1648.32 1676.48 1686.63 1822.95 2592.95
2653.58 2753.31 3002.67 3005.52 3018.71 3029.16
3029.96 3042.54 3050.50 3059.11 3080.77 3090.35
3102.05 3108.02 3112.62 3121.66 3127.57 3130.47
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3199.90 3211.11 3212.55

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A1'-TS

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356.91 385.13 400.09 445.51 449.28 459.33
505.35 556.30 654.42 671.33 749.40 762.54
805.11 822.18 851.14 852.23 908.13 959.71
998.68 1024.93 1036.65 1055.89 1061.75 1087.57
1112.14 1153.38 1156.74 1164.11 1171.93 1177.02
1178.33 1192.92 1228.05 1248.77 1268.14 1307.55
1362.59 1395.07 1434.96 1442.28 1444.35 1451.78
1452.13 1453.73 1460.69 1461.08 1464.55 1466.22
1471.28 1474.09 1520.86 1594.90 1660.09 3032.84
3044.34 3044.65 3048.52 3122.80 3133.29 3144.03
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3211.25 3218.24 3230.51

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A5

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33.25 46.08 61.45 66.94 80.85 95.24
109.56 118.07 154.83 162.93 196.32 228.65
236.61 265.79 276.65 289.15 321.92 373.42
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572.39 638.72 708.02 745.48 785.09 799.93
827.00 840.93 841.86 871.66 945.08 975.48
998.77 1010.15 1036.81 1068.49 1076.65 1090.36
1118.21 1149.57 1159.49 1160.20 1183.32 1191.65
1209.32 1226.62 1300.61 1324.33 1332.16 1340.44
1358.19 1369.23 1402.16 1429.41 1446.83 1453.71
1456.45 1458.22 1461.69 1464.61 1465.64 1497.47
1507.50 1516.84 1550.33 1561.81 1615.52 2047.73
2100.87 2155.32 3029.91 3043.49 3044.66 3048.09
3122.69 3149.55 3151.99 3161.09 3189.43 3191.58
3198.52 3203.27 3214.33

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A6

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15.24 54.51 55.34 59.30 81.45 90.70
107.31 112.81 133.82 158.27 175.43 189.92
206.50 211.77 256.33 286.69 300.97 325.17
360.41 385.27 408.23 444.07 473.89 506.06
536.36 581.09 639.95 700.39 729.71 754.73
786.92 851.51 898.28 914.77 930.61 993.83
1029.96 1046.73 1076.19 1100.11 1109.05 1130.45
1147.27 1168.90 1172.09 1174.36 1191.60 1193.66
1202.75 1226.25 1266.17 1310.45 1341.91 1391.85

1411.43 1432.34 1437.91 1446.16 1453.76 1454.25
1458.35 1465.21 1466.76 1475.03 1476.85 1478.98
1482.08 1501.23 1658.02 3005.72 3014.58 3019.59
3030.39 3079.18 3100.39 3110.65 3122.58 3128.13
3149.22 3152.71 3157.05 3176.18 3181.41 3207.84
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A2'-TS
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39.28 46.32 54.30 67.58 73.47 76.63
79.89 87.39 89.98 95.09 108.12 112.83
117.95 122.57 124.36 137.81 140.99 152.58
160.71 170.52 177.86 193.17 204.33 225.98
233.66 236.28 249.07 253.35 265.36 302.14
322.43 325.32 356.90 384.96 394.10 398.00
417.73 425.78 427.01 465.37 490.99 497.79
517.34 534.85 548.60 585.06 624.53 642.69
702.22 707.62 739.28 754.52 775.20 780.74
806.96 811.78 817.71 825.67 838.89 856.48
864.35 885.69 923.74 971.05 976.41 987.07
1019.15 1050.85 1068.04 1080.22 1090.11 1109.61
1111.25 1112.22 1119.93 1122.82 1131.09 1135.40
1165.13 1166.24 1167.31 1167.39 1169.33 1171.33
1181.01 1182.40 1183.78 1187.14 1191.63 1195.08
1197.48 1210.43 1240.79 1257.65 1260.80 1293.51
1301.67 1308.95 1313.06 1323.62 1327.48 1328.72
1330.43 1351.31 1395.86 1407.16 1424.56 1432.06
1448.65 1452.02 1454.12 1456.40 1459.20 1459.69
1463.10 1464.85 1465.69 1467.13 1467.24 1471.14
1472.14 1474.81 1475.76 1476.63 1479.00 1481.98
1493.51 1565.25 1650.20 1688.24 1845.06 2989.77
3002.12 3007.08 3014.68 3021.54 3027.64 3028.77
3030.99 3033.80 3035.27 3070.44 3079.59 3090.62
3091.04 3093.36 3106.13 3110.72 3121.12 3127.01
3150.12 3151.30 3156.10 3158.94 3159.69 3195.34
3197.56 3212.08 3213.77
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5a
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15.44 16.86 22.14 35.29 49.80 66.89
75.34 82.97 99.27 101.64 111.04 114.88
122.75 134.27 153.43 164.62 185.09 188.51
214.87 224.82 229.56 253.46 269.70 301.26
325.40 327.08 362.05 387.43 400.51 426.05
463.89 487.95 496.62 517.52 521.71 550.08
623.56 642.54 691.90 702.04 733.09 766.48
778.43 786.87 810.69 826.06 832.93 855.93
861.29 883.18 919.03 969.83 976.73 995.19
1018.53 1043.01 1064.83 1080.22 1101.14 1110.50
1113.53 1114.68 1119.23 1135.54 1165.98 1166.10
1170.37 1172.02 1181.07 1187.52 1193.13 1195.75
1197.36 1204.60 1254.97 1266.77 1291.66 1301.03
1305.39 1319.44 1324.33 1329.82 1345.08 1349.09
1394.64 1403.46 1425.70 1430.06 1453.30 1458.65
1459.72 1465.18 1465.87 1467.05 1467.59 1470.81
1473.57 1475.88 1477.65 1481.91 1484.30 1497.48

1564.91 1649.19 1687.48 1843.46 2997.81 3002.41
3014.04 3020.33 3025.23 3030.59 3032.20 3040.46
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3109.62 3124.77 3150.44 3153.53 3155.82 3195.33
3196.93 3210.96 3213.63
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B1-TS
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86.62 111.08 123.31 127.58 148.15 197.34
225.38 264.58 337.51 350.37 365.55 434.62
475.93 505.87 518.17 669.81 690.50 755.94
798.94 816.40 818.60 860.98 926.85 975.35
992.10 993.11 1041.86 1076.49 1081.83 1097.41
1106.17 1160.41 1173.26 1179.22 1186.87 1214.96
1242.25 1257.50 1320.69 1335.26 1397.52 1415.02
1449.92 1453.20 1459.55 1462.39 1463.07 1463.52
1475.27 1480.76 1511.68 1594.14 1632.83 3021.41
3029.26 3037.93 3114.90 3116.98 3121.07 3122.60
3139.74 3140.50 3151.66 3152.06 3181.28 3182.49
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B2
==========
43.05 50.84 73.59 86.71 102.00 107.15
121.78 128.01 167.48 209.29 227.28 242.44
282.78 301.51 352.10 391.28 437.50 481.53
495.58 515.79 580.52 655.49 714.18 764.30
791.45 806.95 832.00 858.02 904.21 967.91
976.43 1037.54 1041.29 1068.50 1108.05 1126.75
1130.02 1134.65 1168.82 1173.70 1192.80 1193.50
1217.45 1296.87 1319.22 1323.18 1369.85 1398.84
1412.23 1453.47 1456.01 1456.51 1458.94 1464.87
1467.04 1477.45 1482.79 1579.80 1621.94 3000.23
3031.17 3034.07 3036.26 3110.95 3113.42 3123.61
3134.81 3137.57 3155.28 3155.75 3175.38 3182.54
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B2-TS
==========
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43.35 47.64 51.73 68.40 71.74 76.77
84.88 97.58 113.85 126.87 131.16 133.90
141.03 157.11 158.88 165.58 191.29 213.69
223.57 245.50 252.27 258.29 260.60 266.38
305.57 317.87 324.00 353.04 361.08 377.24
385.20 402.29 416.85 426.98 466.94 484.39
499.13 510.59 510.78 520.62 534.78 600.48
630.54 643.51 669.73 697.45 703.35 722.54
735.40 780.69 785.70 788.84 798.48 811.69
818.06 828.50 830.88 856.46 858.41 870.38
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1070.90 1078.35 1088.77 1088.88 1097.76 1106.63
1109.49 1121.21 1136.46 1146.36 1159.23 1167.01
1168.73 1171.60 1176.19 1183.50 1193.52 1196.46
1197.87 1211.86 1227.11 1236.15 1239.87 1288.01
1296.58 1302.06 1304.03 1314.94 1326.70 1328.15

1334.33 1338.65 1345.12 1390.71 1398.43 1407.19
1407.84 1415.57 1424.98 1451.59 1454.86 1455.55
1458.50 1460.22 1461.97 1463.71 1466.19 1466.26
1467.76 1473.15 1478.05 1478.64 1479.85 1482.32
1506.78 1562.44 1588.67 1624.76 1644.13 1684.90
1822.24 2976.47 2994.66 3011.75 3013.58 3020.06
3020.64 3028.52 3038.82 3049.89 3071.78 3088.27
3096.27 3099.50 3103.24 3109.24 3109.56 3118.44
3118.74 3120.89 3143.64 3147.93 3151.13 3154.96
3164.41 3173.03 3183.40 3187.74 3204.62 3207.01
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B3
==========
4.56 12.87 26.50 32.17 38.37 44.18
65.97 67.19 77.34 79.98 90.03 101.62
112.22 127.80 135.67 150.17 164.94 176.27
193.54 198.47 203.84 213.32 234.96 249.13
253.22 265.11 293.55 301.95 307.88 323.44
336.61 357.65 371.46 394.99 407.04 413.79
426.81 444.51 465.71 490.00 504.11 516.05
522.56 531.27 544.83 559.56 611.88 629.80
642.65 666.13 702.47 711.29 731.60 738.53
747.69 780.09 791.61 803.30 816.28 821.43
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C2b

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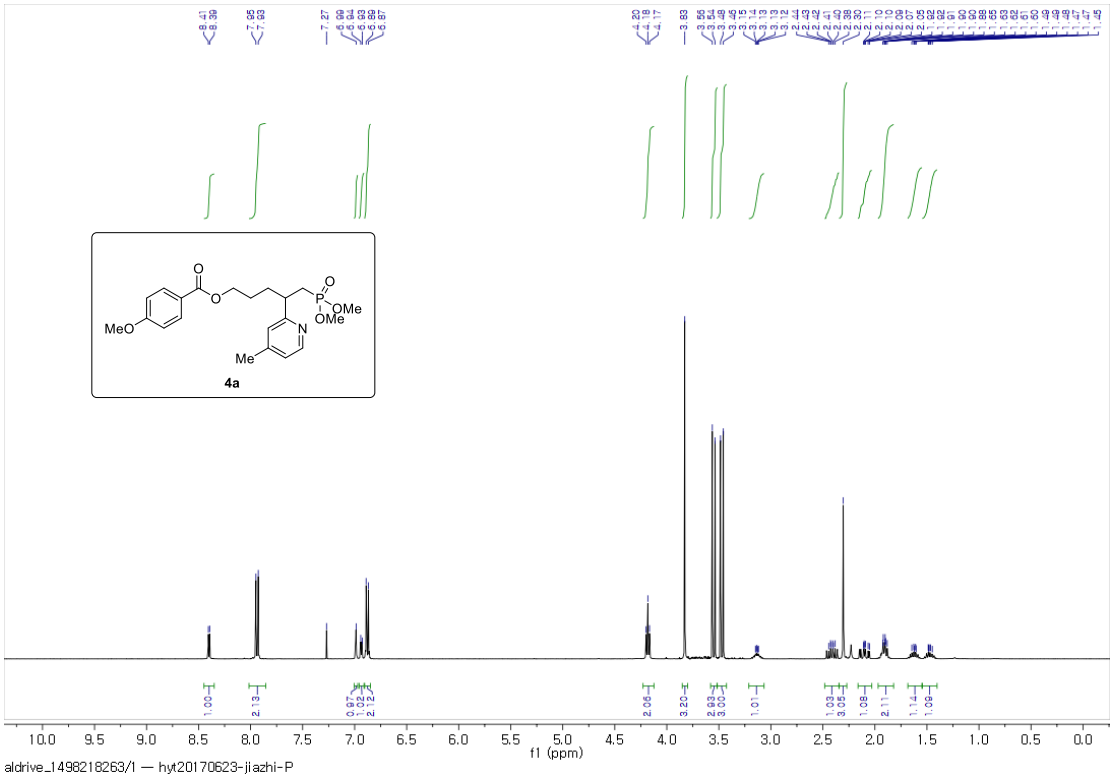
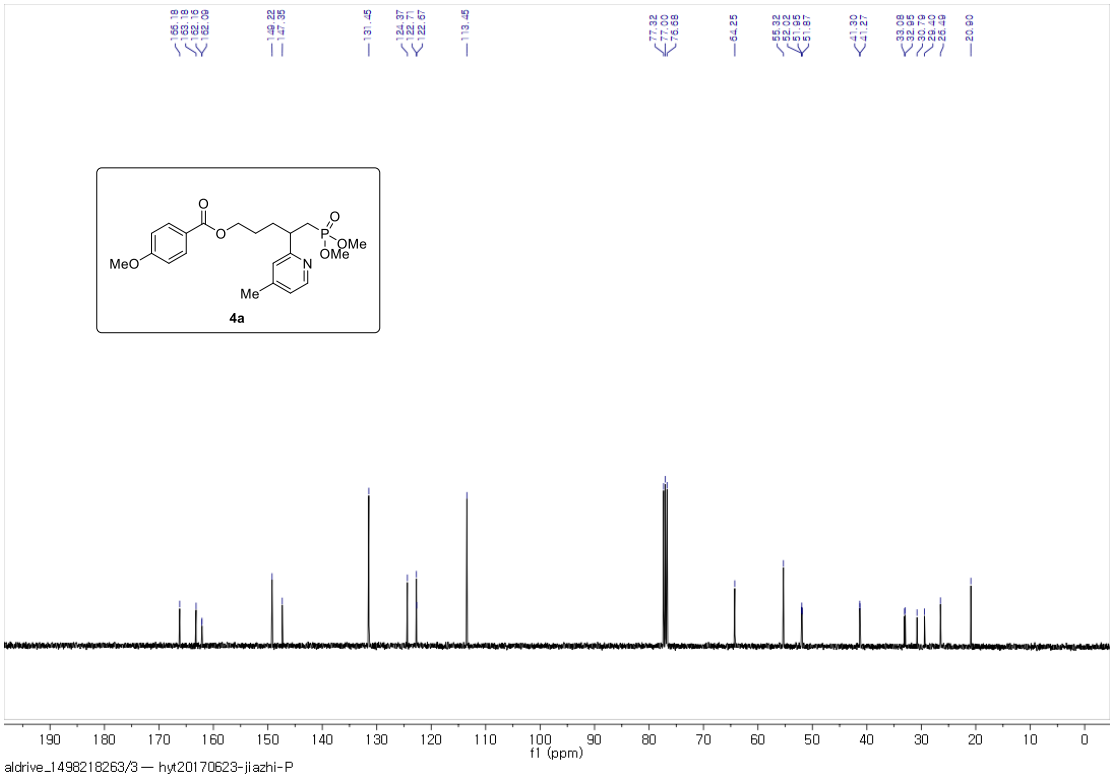
Appendix I

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

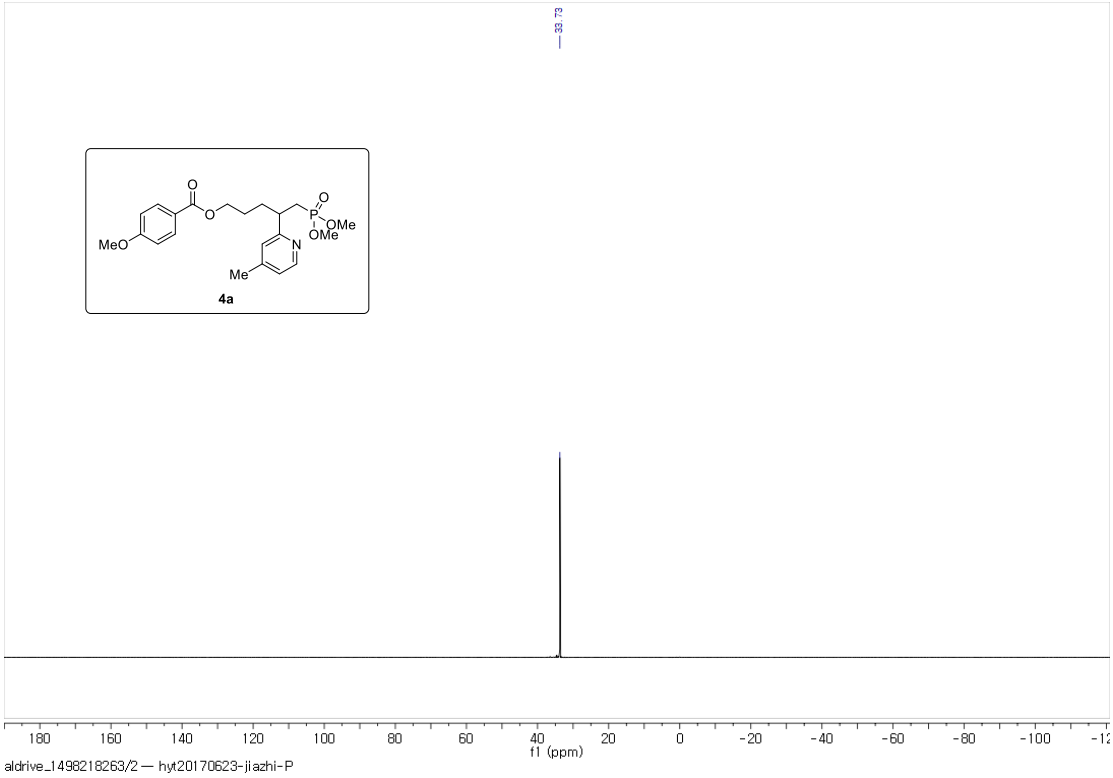
5-(dimethoxyphosphoryl)-4-(4-methylpyridin-2-yl)pentyl 4-methoxybenzoate (4a).



400 MHz, ^{1}H NMR in $CDCl_3$

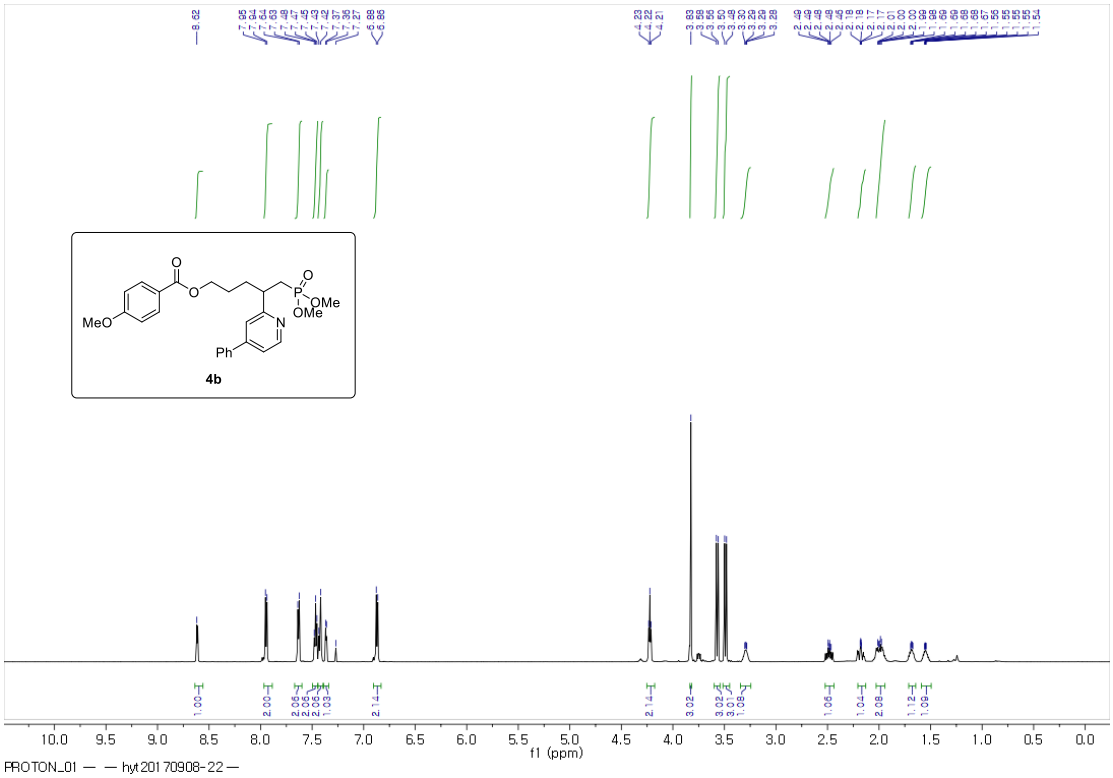


100 MHz, ^{13}C NMR in $CDCl_3$

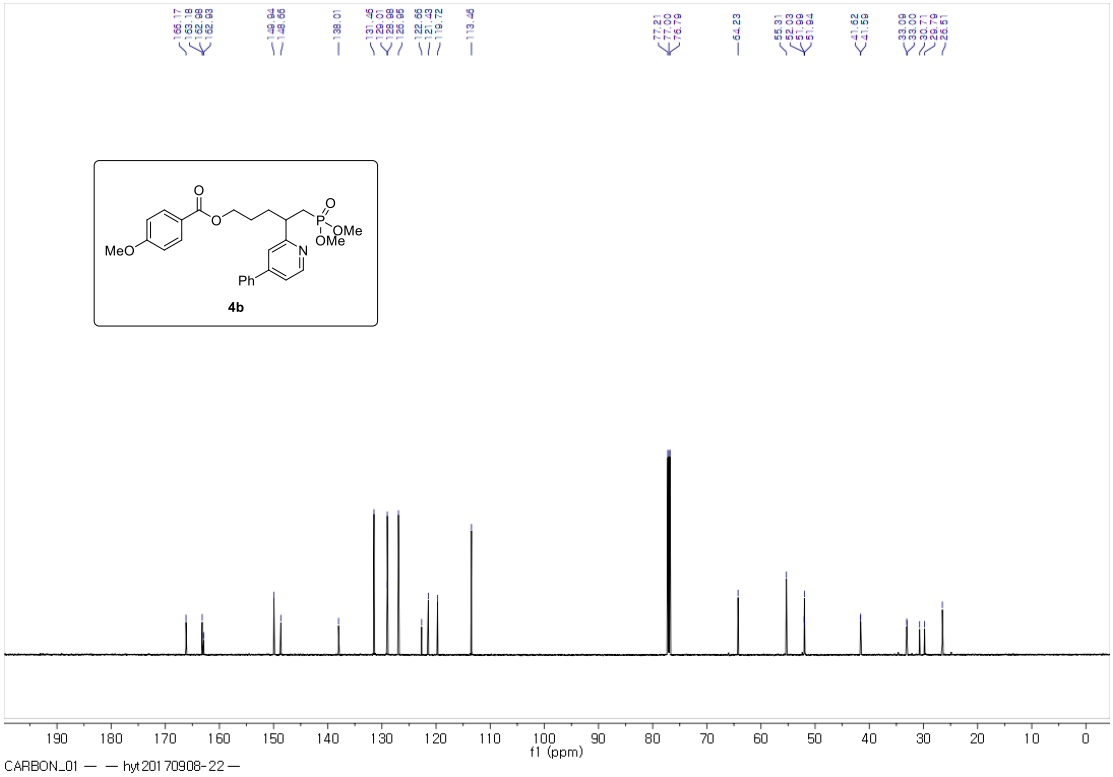


162 MHz, ^{31}P NMR in $CDCl_3$

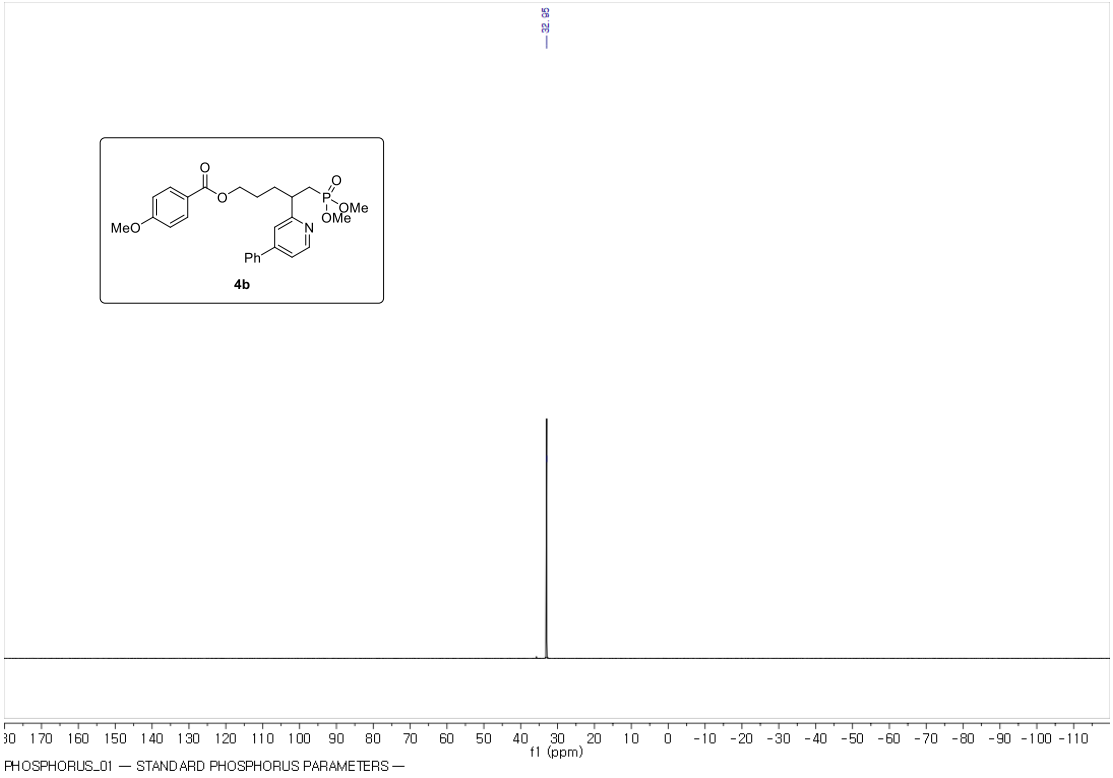
5-(dimethoxyphosphoryl)-4-(4-phenylpyridin-2-yl)pentyl 4-methoxybenzoate (4b)



600 MHz, ^{1}H NMR in $CDCl_3$

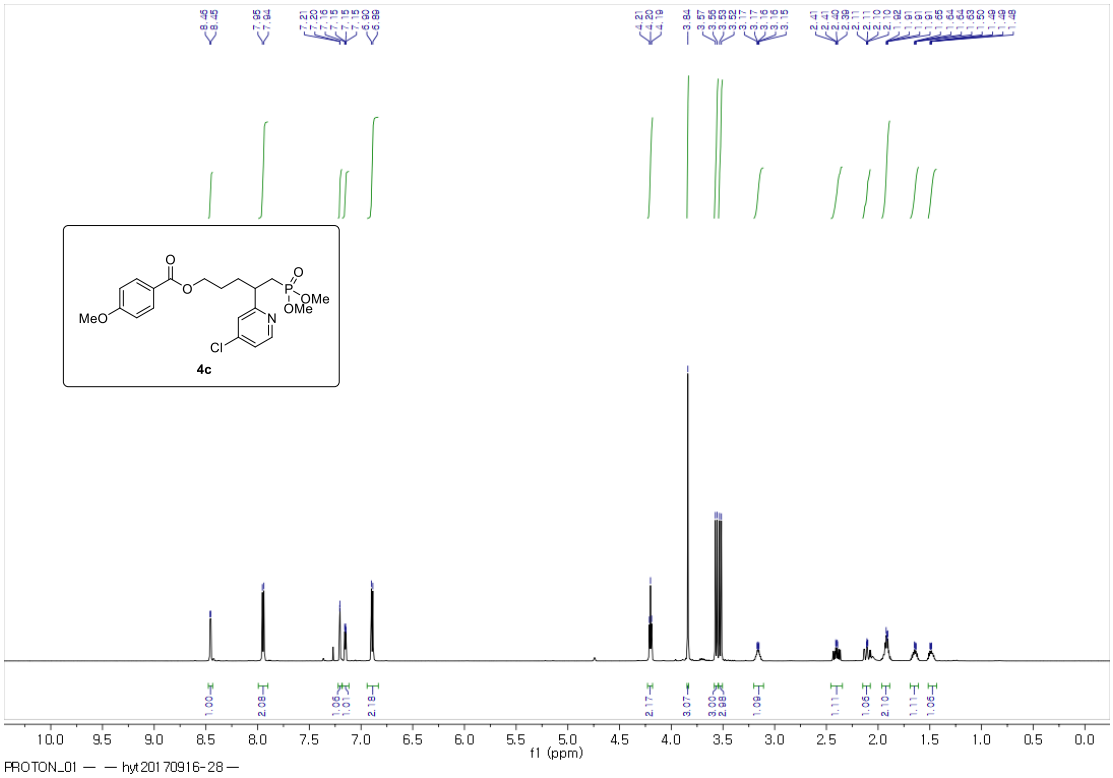


150 MHz, ^{13}C NMR in $CDCl_3$

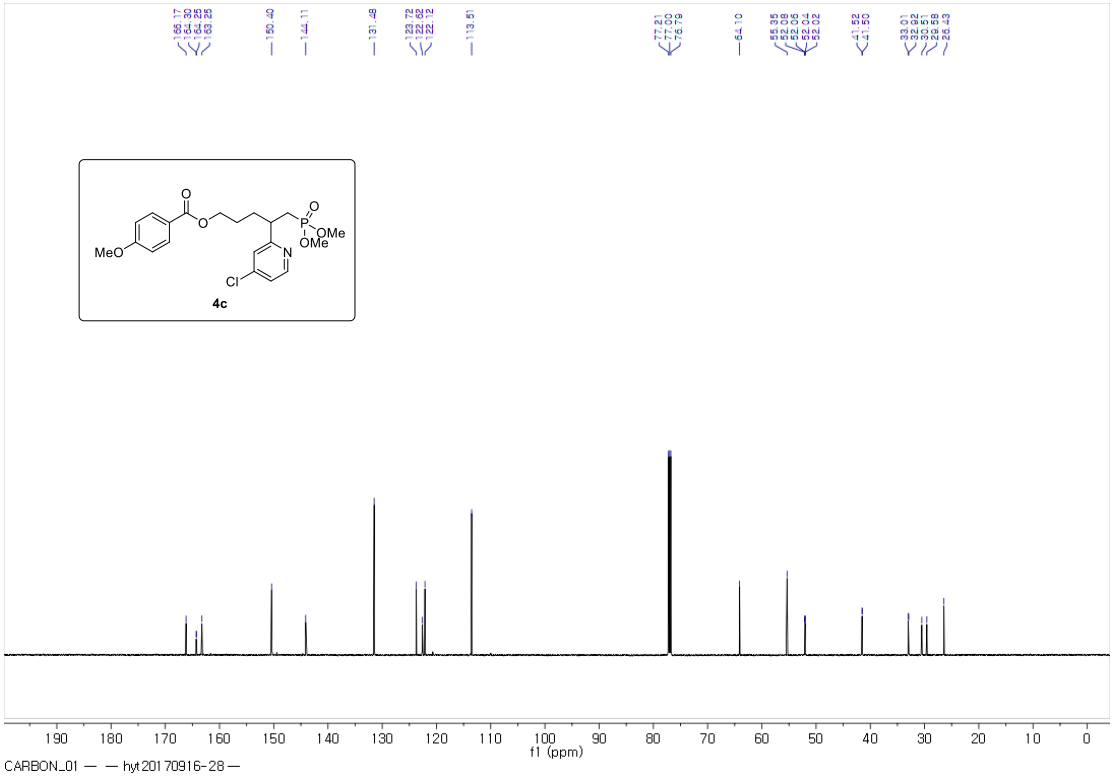


243 MHz, ^{31}P NMR in $CDCl_3$

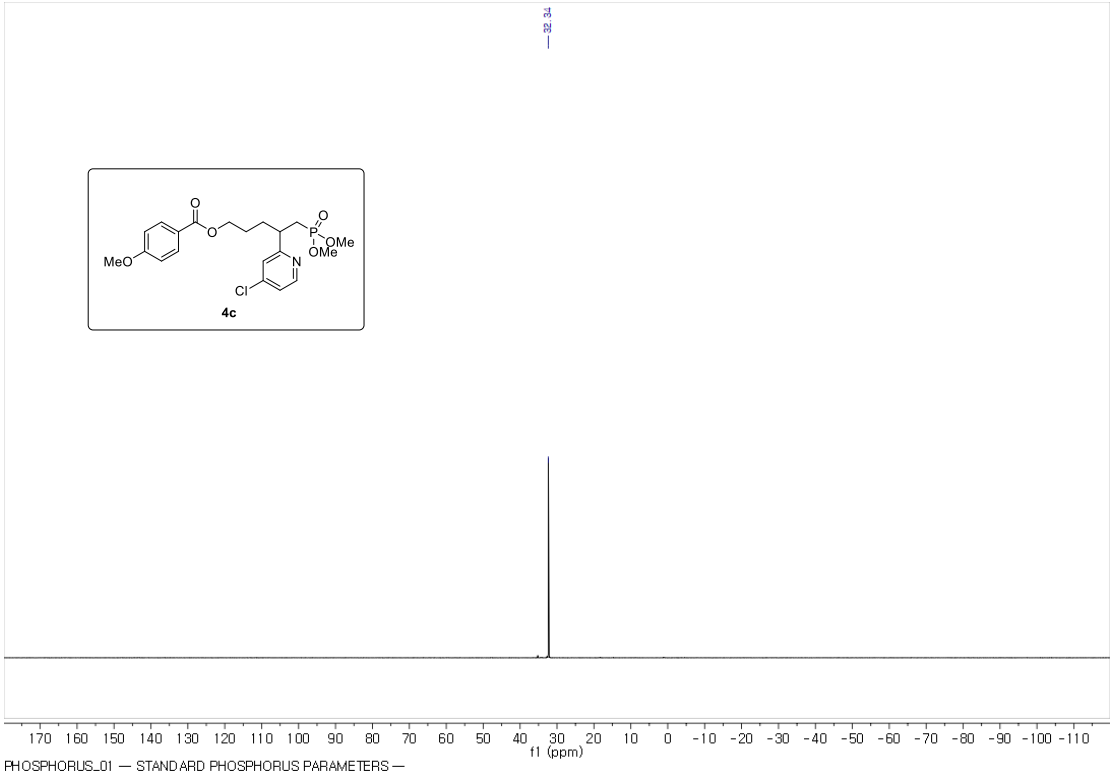
4-(4-chloropyridin-2-yl)-5-(dimethoxyphosphoryl)pentyl 4-methoxybenzoate (4c)



600 MHz, ^{1}H NMR in $CDCl_3$

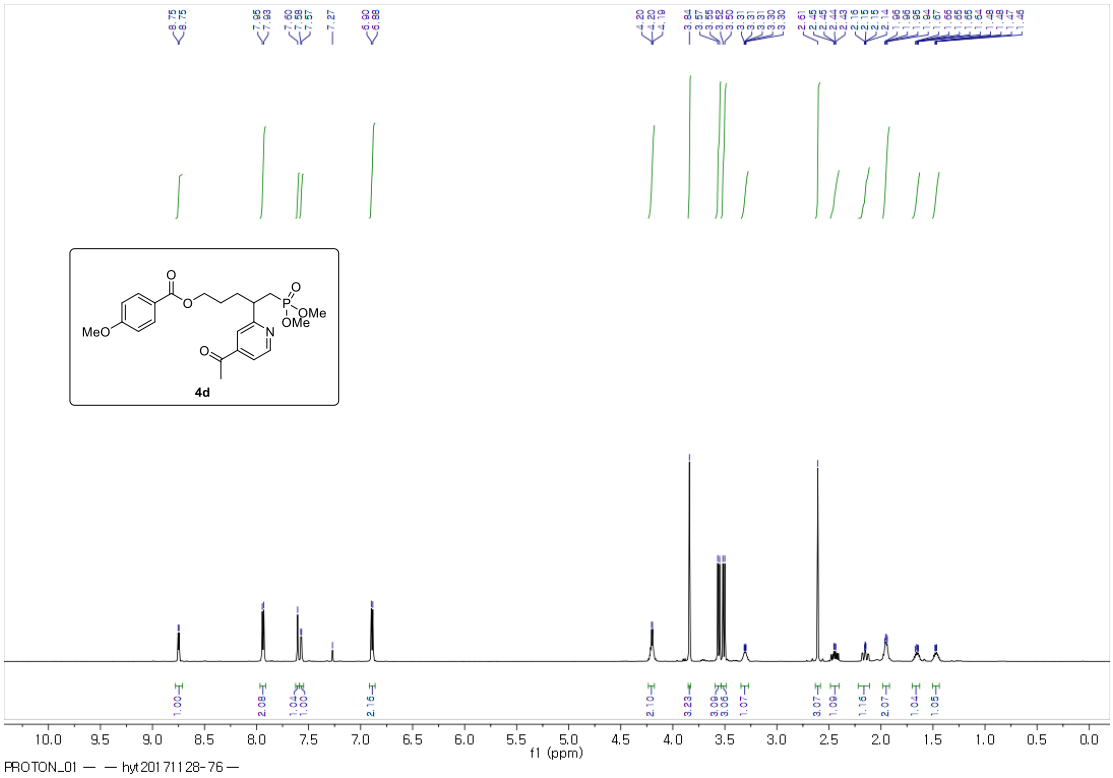


150 MHz, ^{13}C NMR in $CDCl_3$

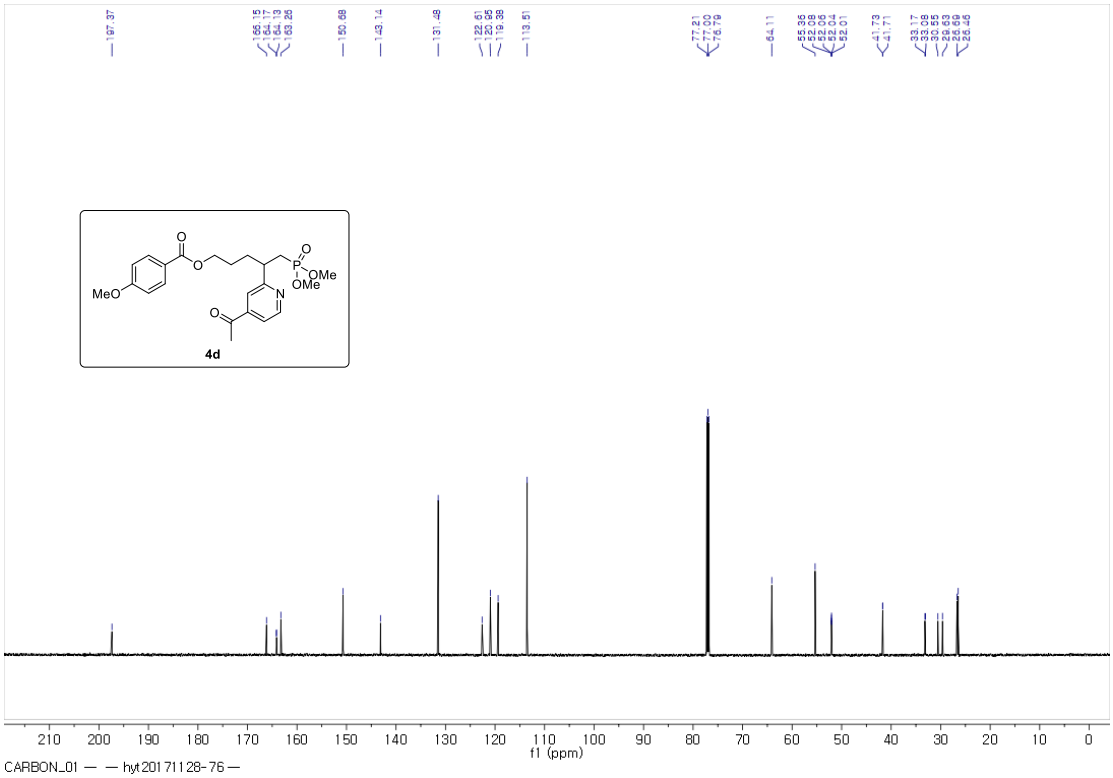


243 MHz, ^{31}P NMR in $CDCl_3$

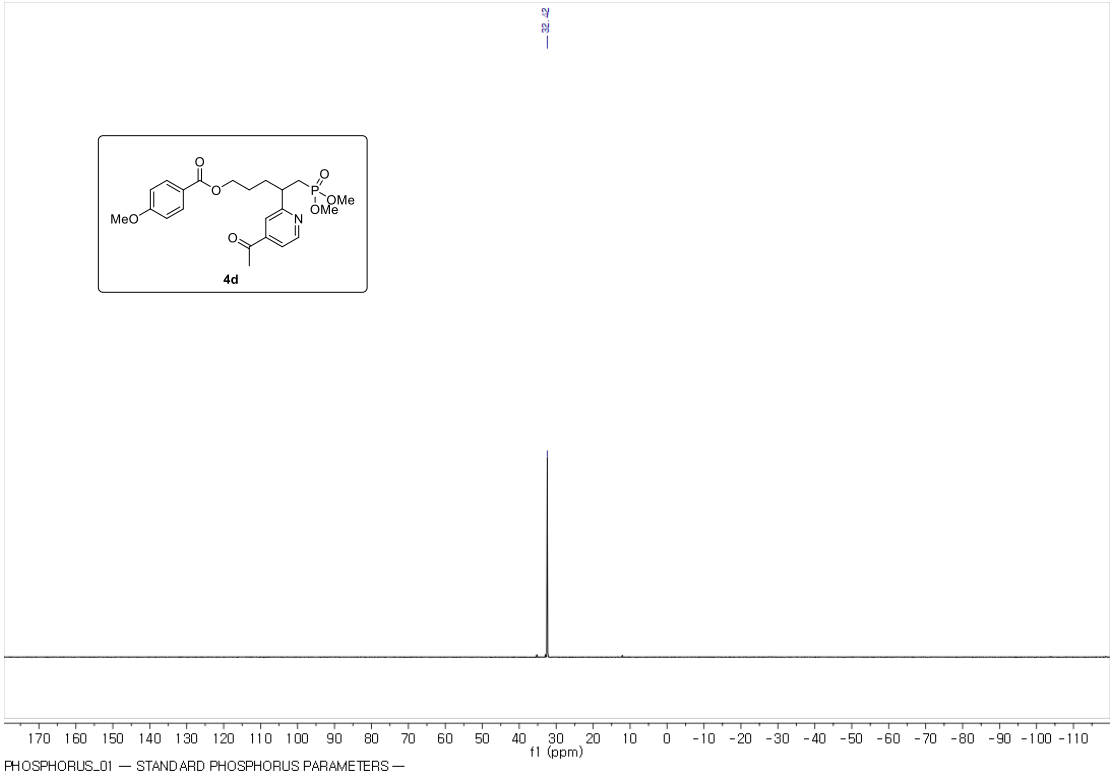
4-(4-acetylpyridin-2-yl)-5-(dimethoxyphosphoryl)pentyl 4-methoxybenzoate (4d)



600 MHz, ^{1}H NMR in $CDCl_3$

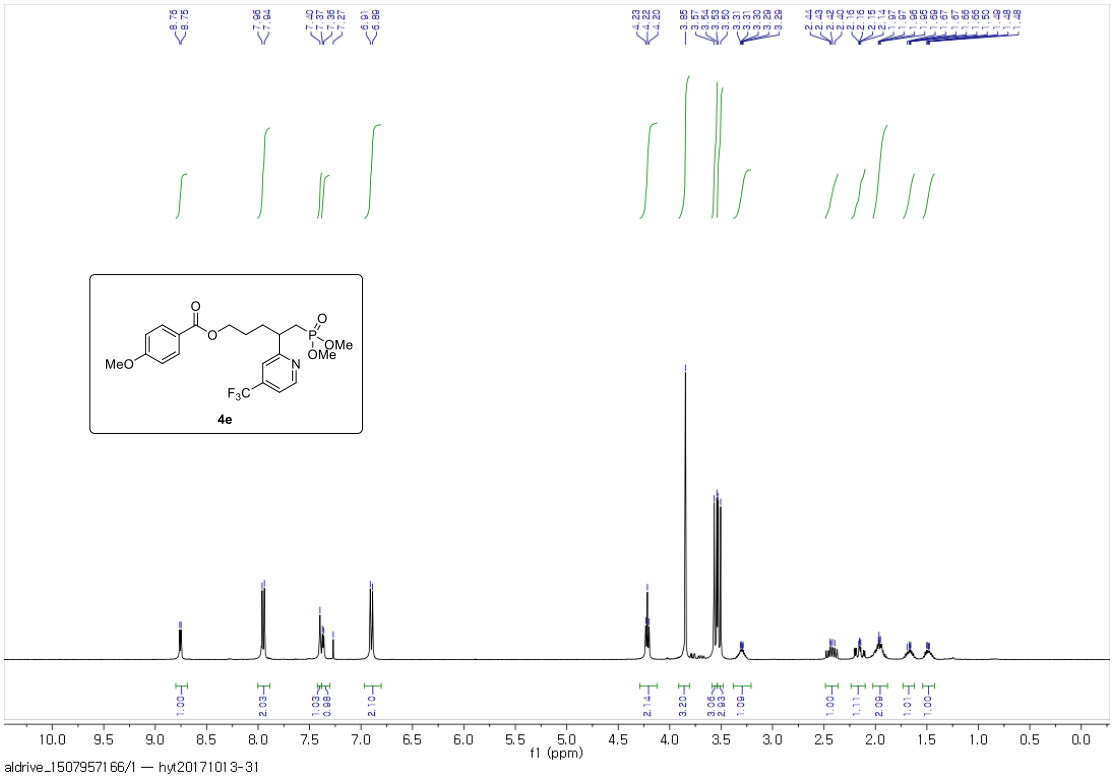


150 MHz, ^{13}C NMR in $CDCl_3$

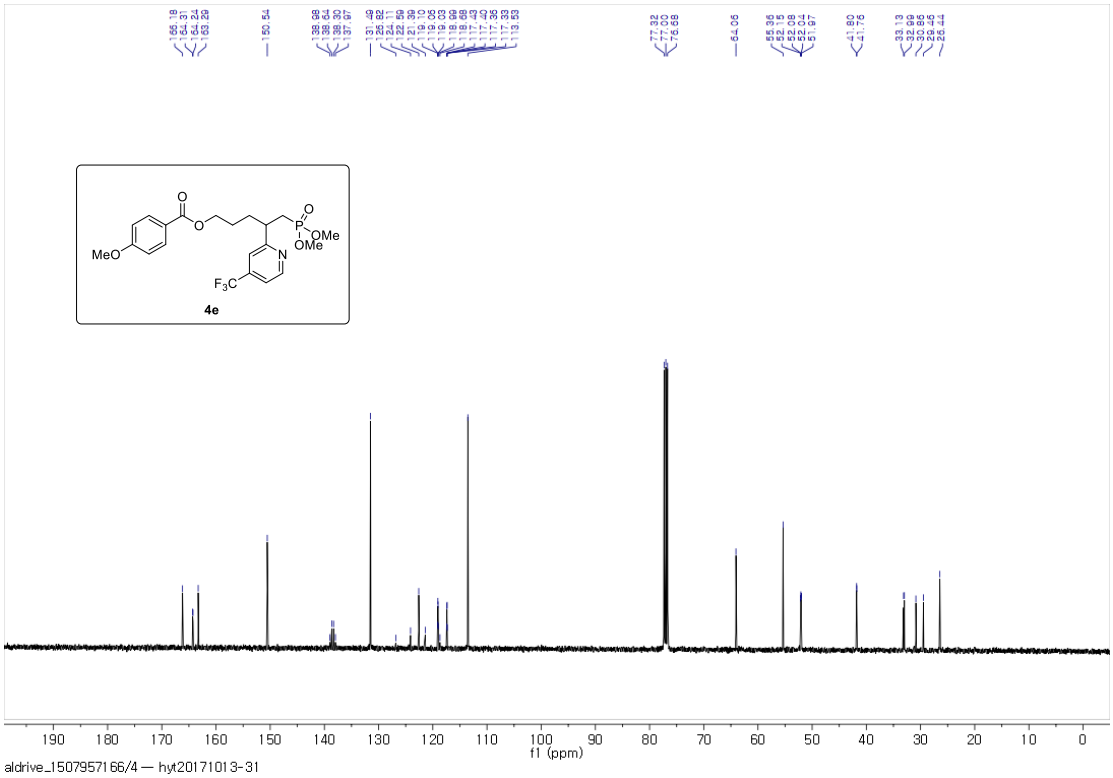


243 MHz, ^{31}P NMR in $CDCl_3$

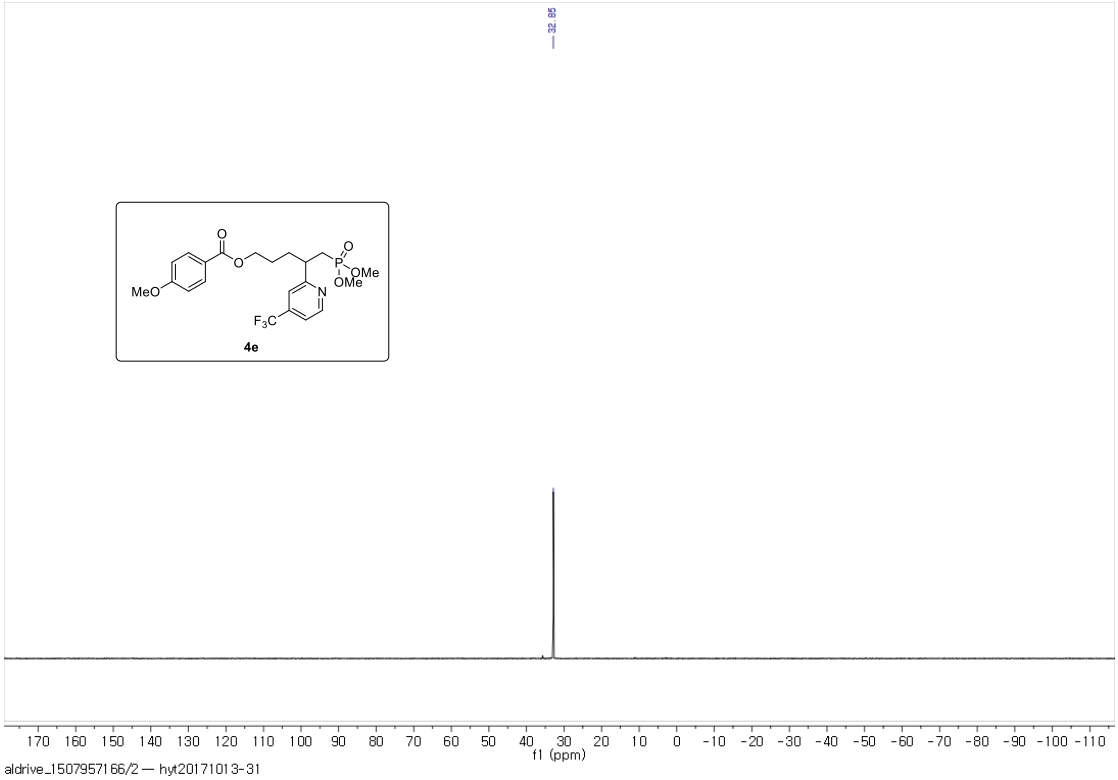
5-(dimethoxyphosphoryl)-4-(4-(trifluoromethyl)pyridin-2-yl)pentyl 4-methoxybenzoate (4e)



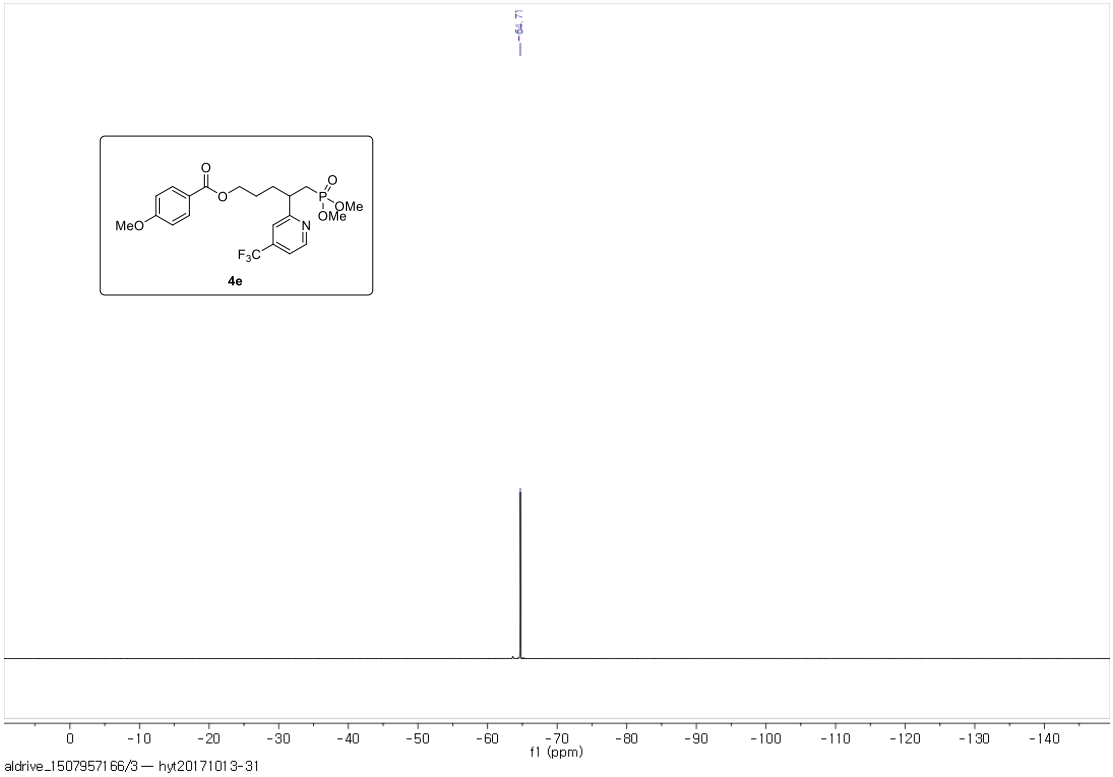
400 MHz, ^{1}H NMR in $CDCl_3$



100 MHz, ^{13}C NMR in $CDCl_3$

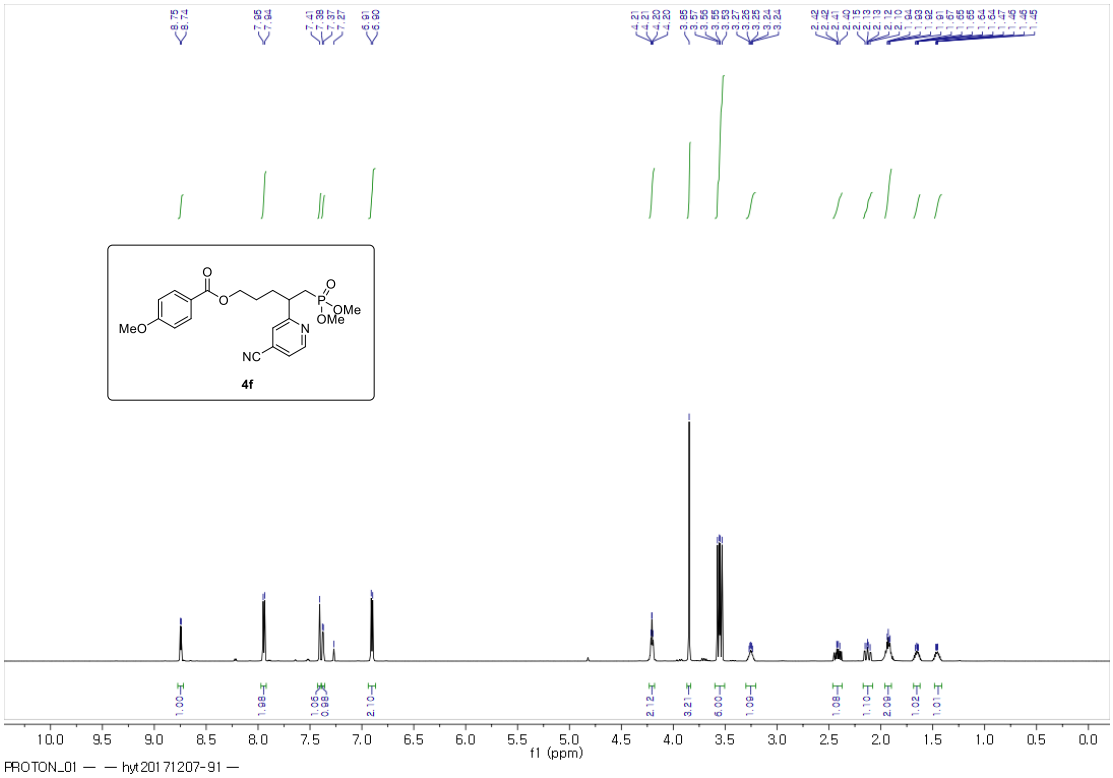


162 MHz, ^{31}P NMR in $CDCl_3$

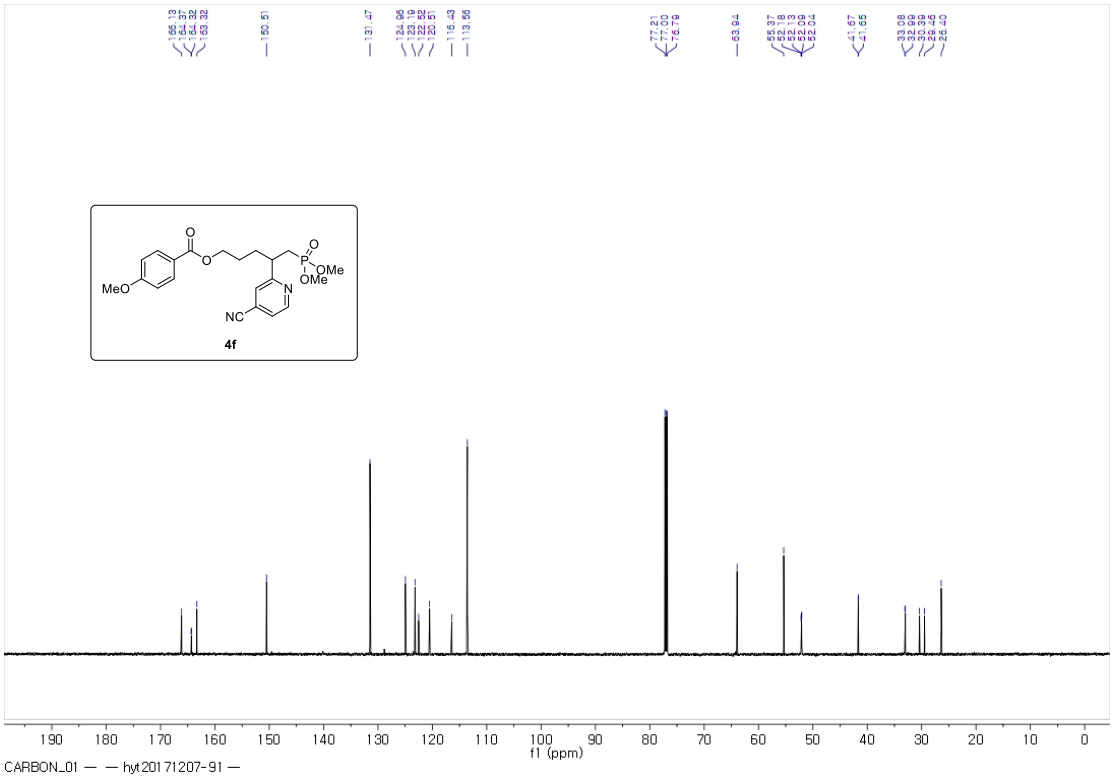


376 MHz, ^{19}F NMR in $CDCl_3$

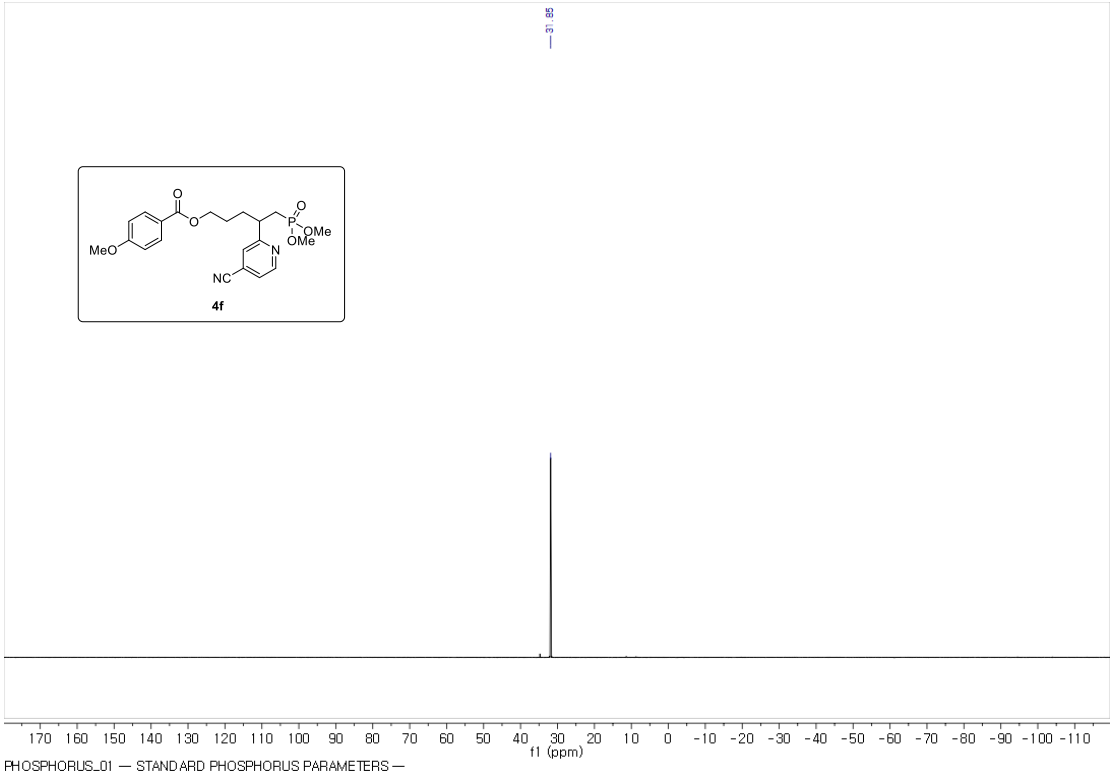
4-(4-cyanopyridin-2-yl)-5-(dimethoxyphosphoryl)pentyl 4-methoxybenzoate (4f)



600 MHz, ^{1}H NMR in $CDCl_3$

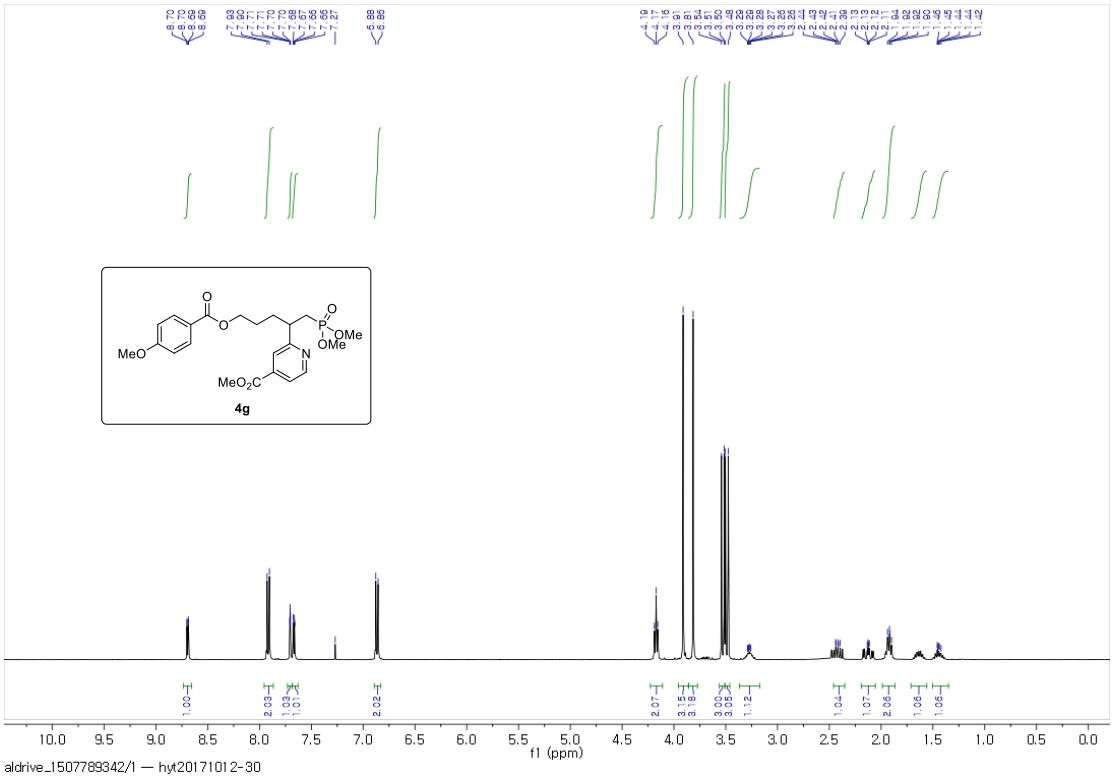


150 MHz, ^{13}C NMR in $CDCl_3$

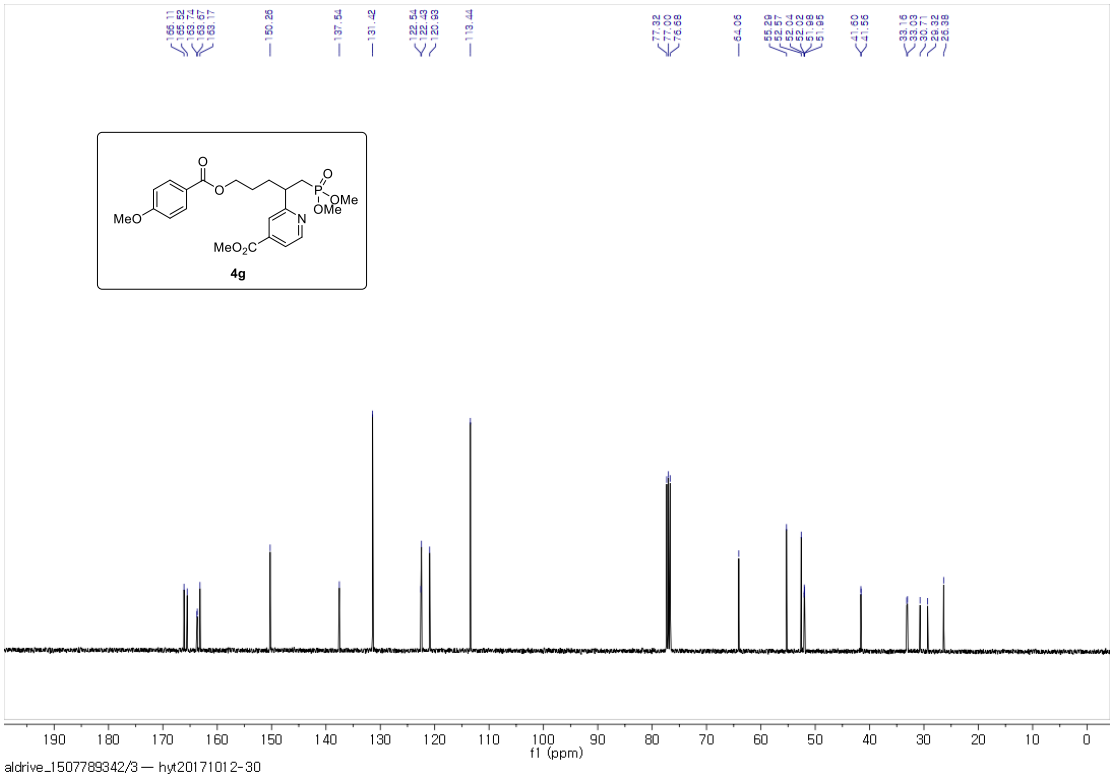


243 MHz, ^{31}P NMR in $CDCl_3$

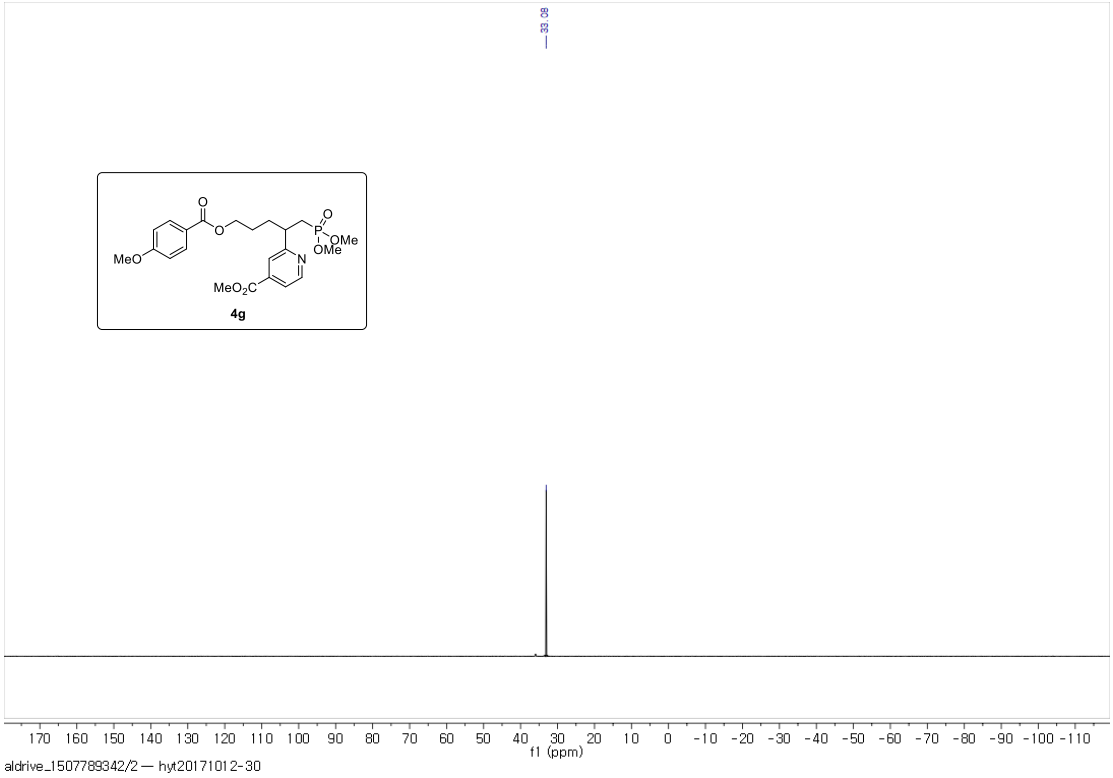
methyl 2-(1-(dimethoxyphosphoryl)-5-((4-methoxybenzoyl)oxy)pentan-2-yl) isonicotinate (4g)



400 MHz, ^{1}H NMR in $CDCl_3$

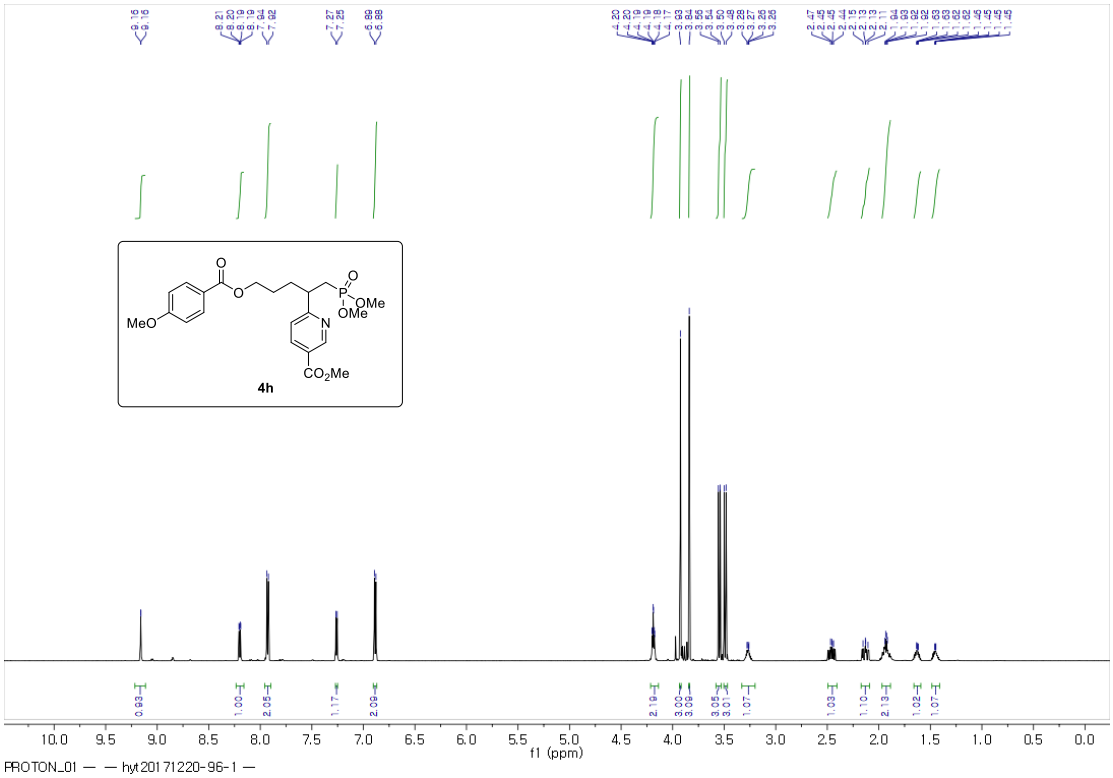


100 MHz, ^{13}C NMR in $CDCl_3$

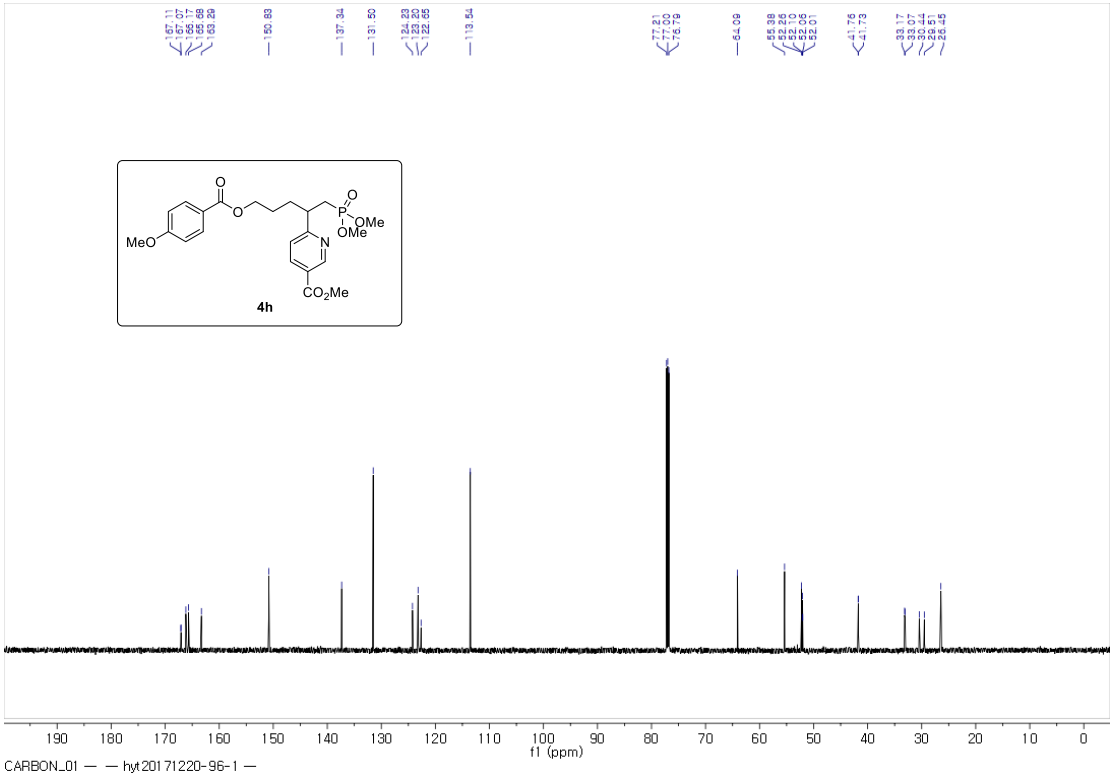


162 MHz, ^{31}P NMR in $CDCl_3$

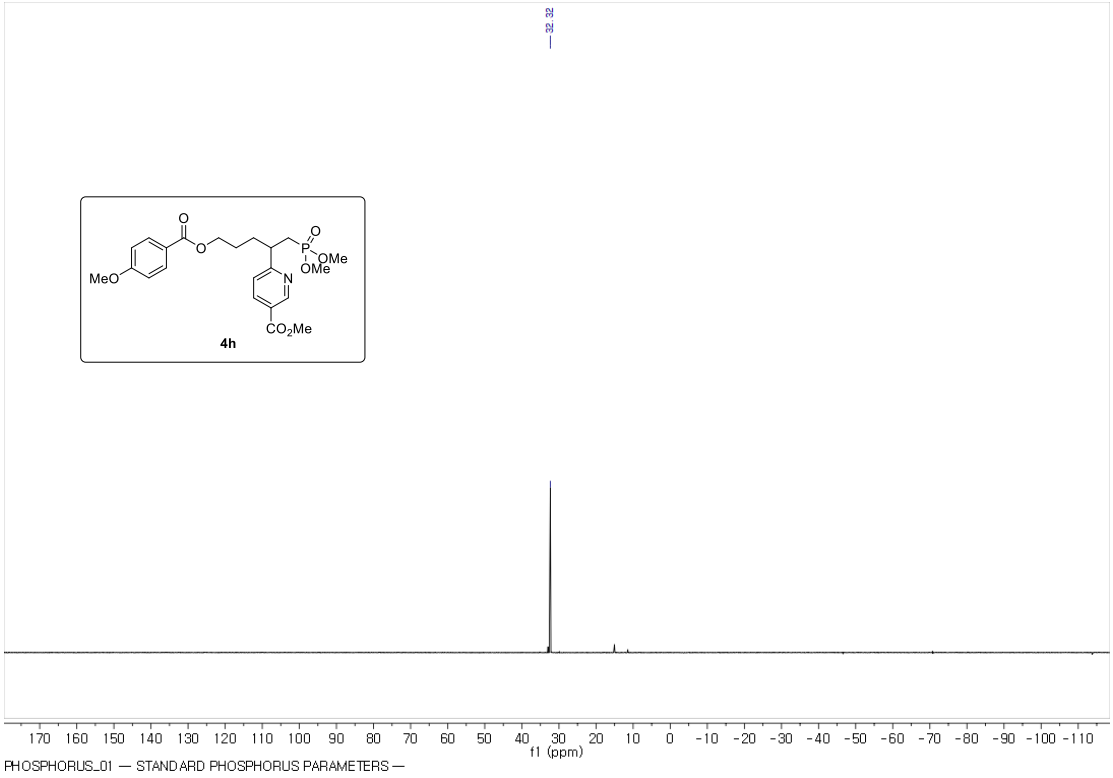
methyl 6-(1-(dimethoxyphosphoryl)-5-((4-methoxybenzoyl)oxy)pentan-2-yl)nicotinate (4h)



600 MHz, ^{1}H NMR in $CDCl_3$

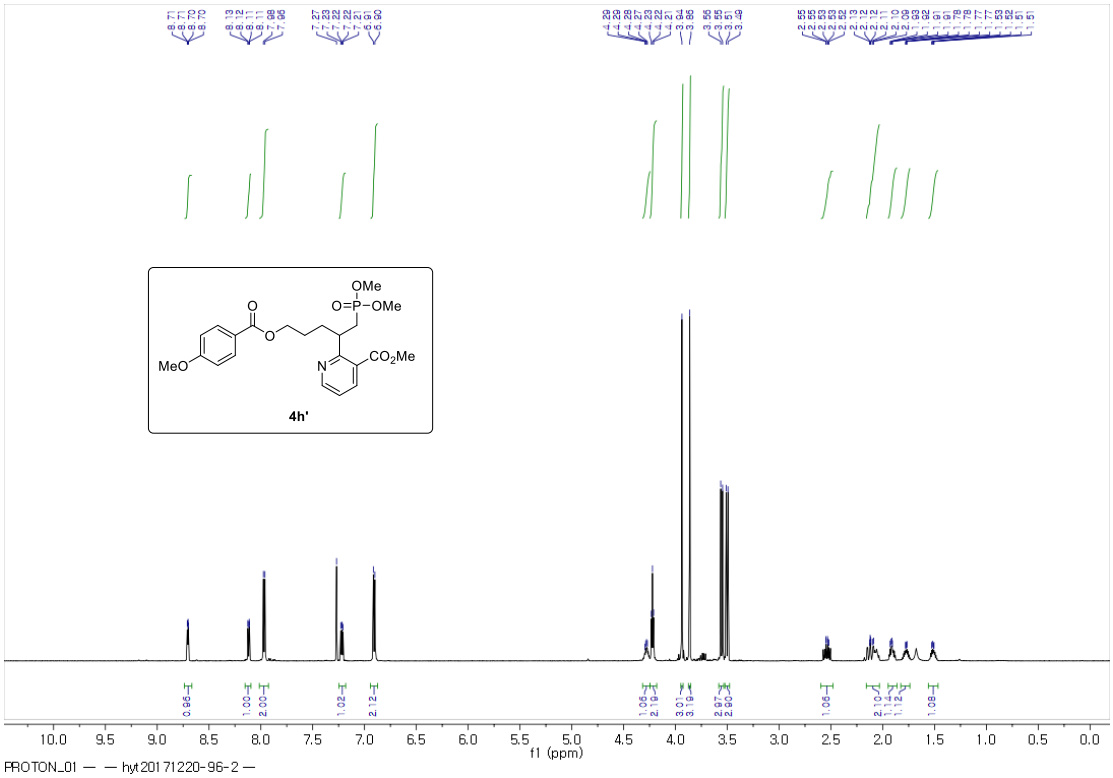


150 MHz, ^{13}C NMR in $CDCl_3$

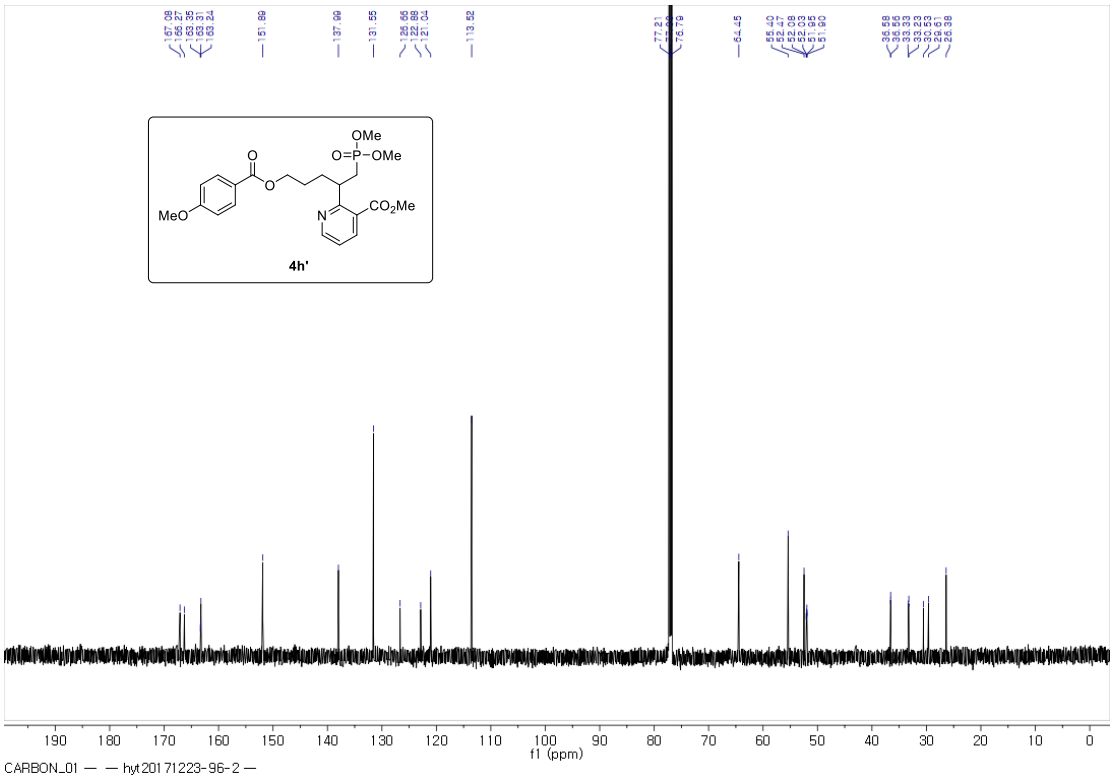


243 MHz, ^{31}P NMR in $CDCl_3$

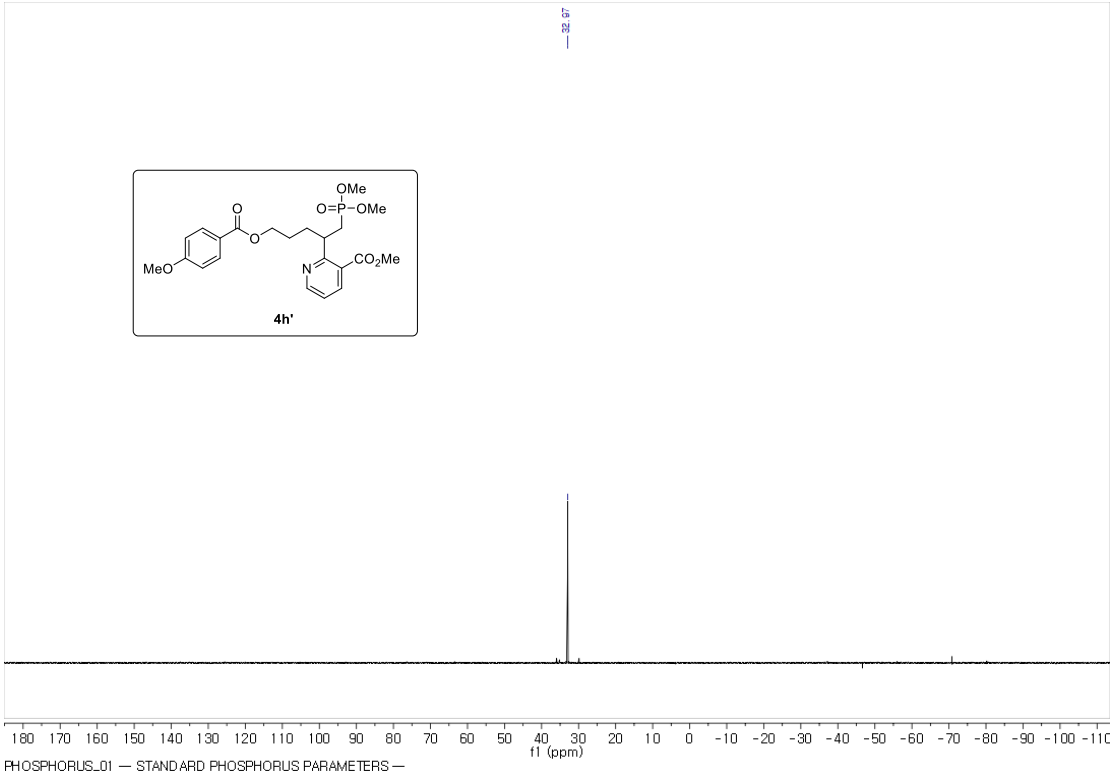
methyl 2-(1-(dimethoxyphosphoryl)-5-((4-methoxybenzoyl)oxy)pentan-2-yl)nicotinate (4h')



600 MHz, ^{1}H NMR in $CDCl_3$

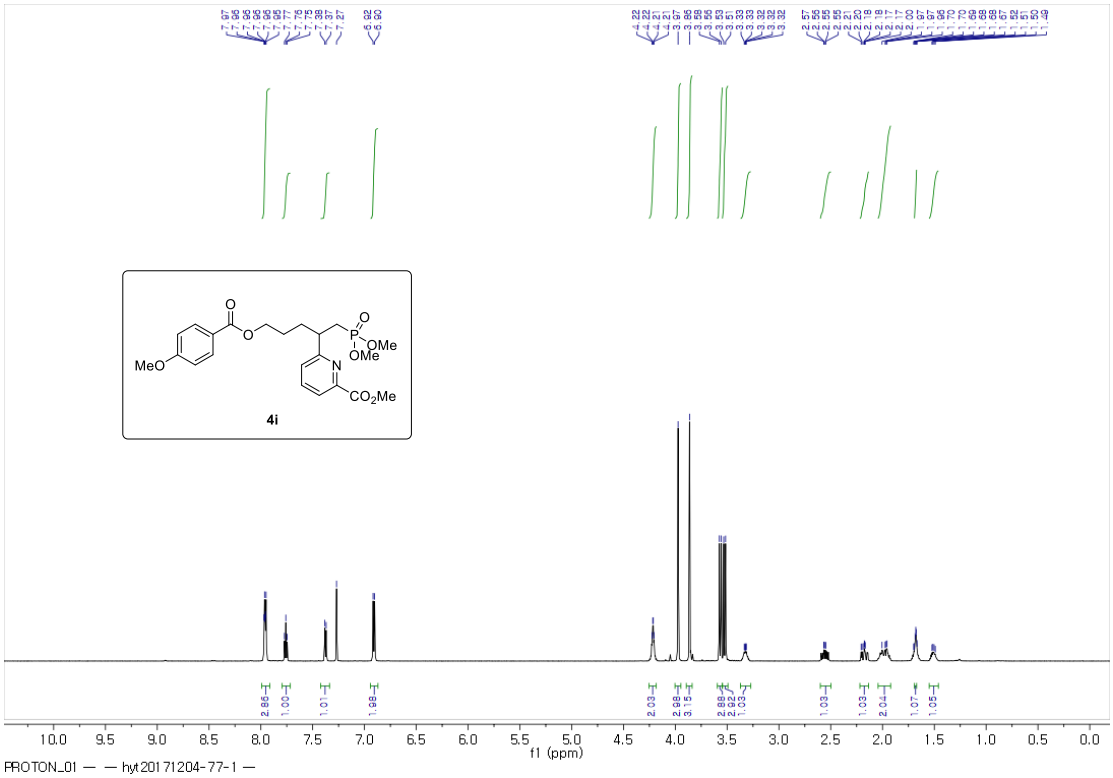


150 MHz, ^{13}C NMR in $CDCl_3$

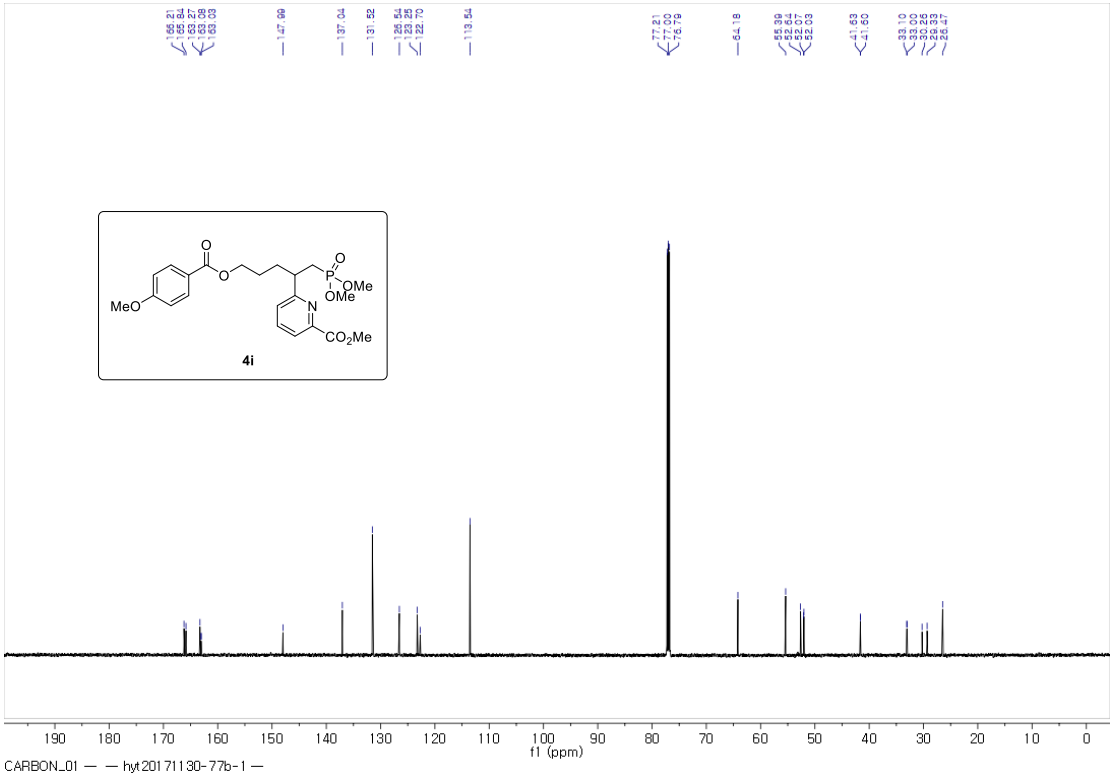


243 MHz, ^{31}P NMR in $CDCl_3$

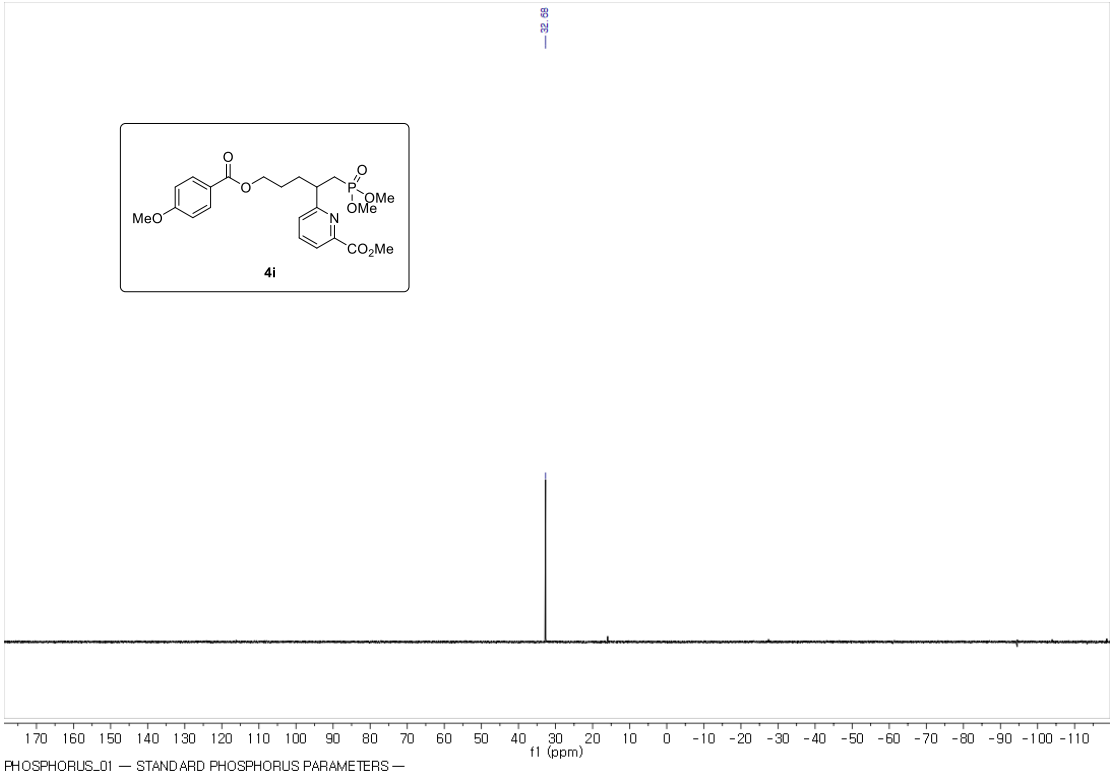
methyl 6-(1-(dimethoxyphosphoryl)-5-((4-methoxybenzoyl)oxy)pentan-2-yl) picolinate (4i)



600 MHz, ^{1}H NMR in $CDCl_3$

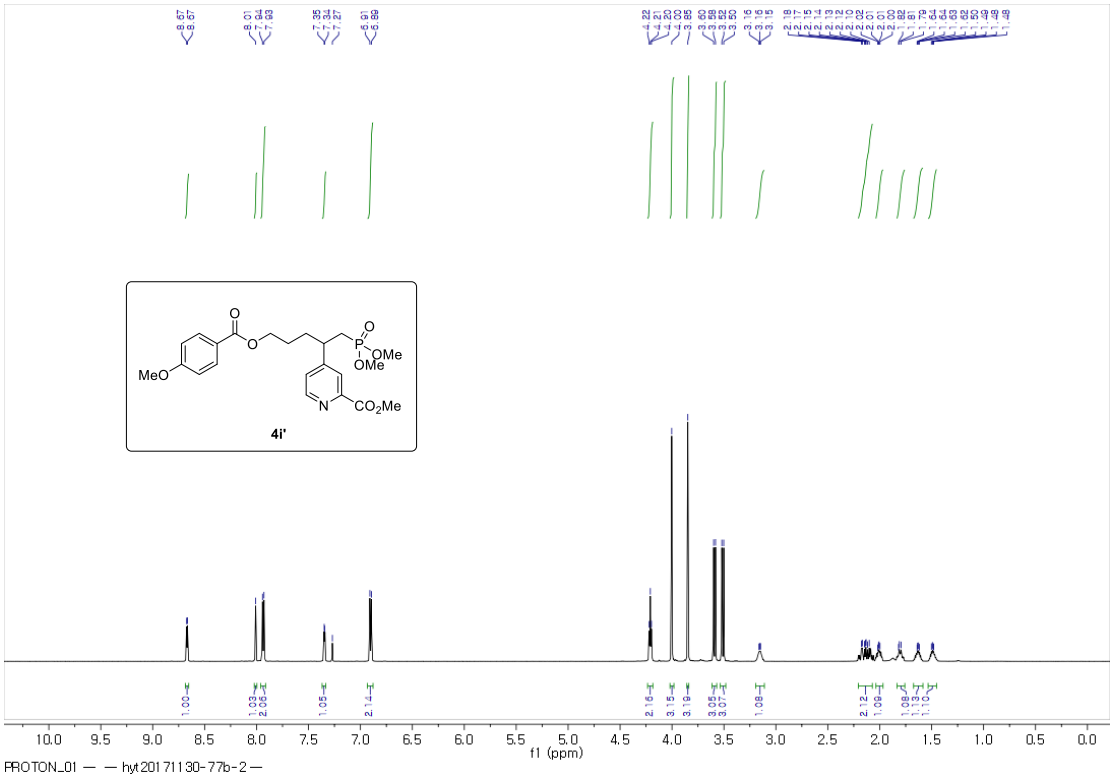


150 MHz, ^{13}C NMR in $CDCl_3$

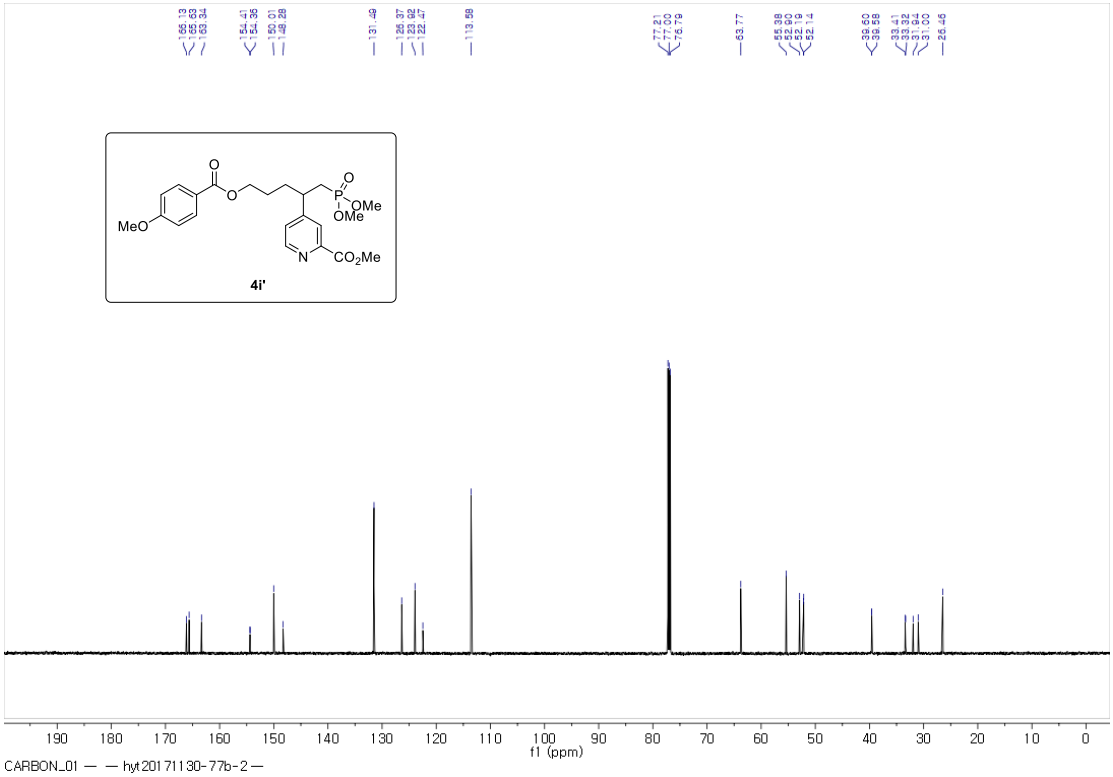


243 MHz, ^{31}P NMR in $CDCl_3$

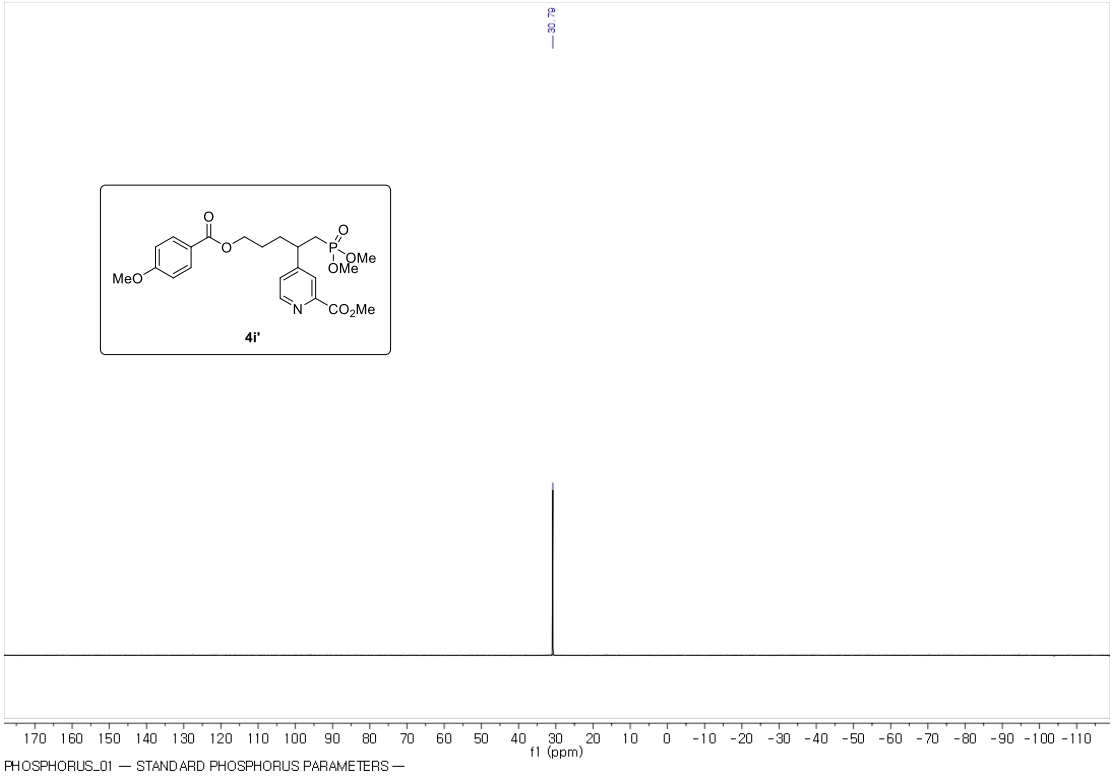
methyl 4-(1-(dimethoxyphosphoryl)-5-((4-methoxybenzoyl)oxy)pentan-2-yl)picolinate (4i')



600 MHz, ^{1}H NMR in $CDCl_3$

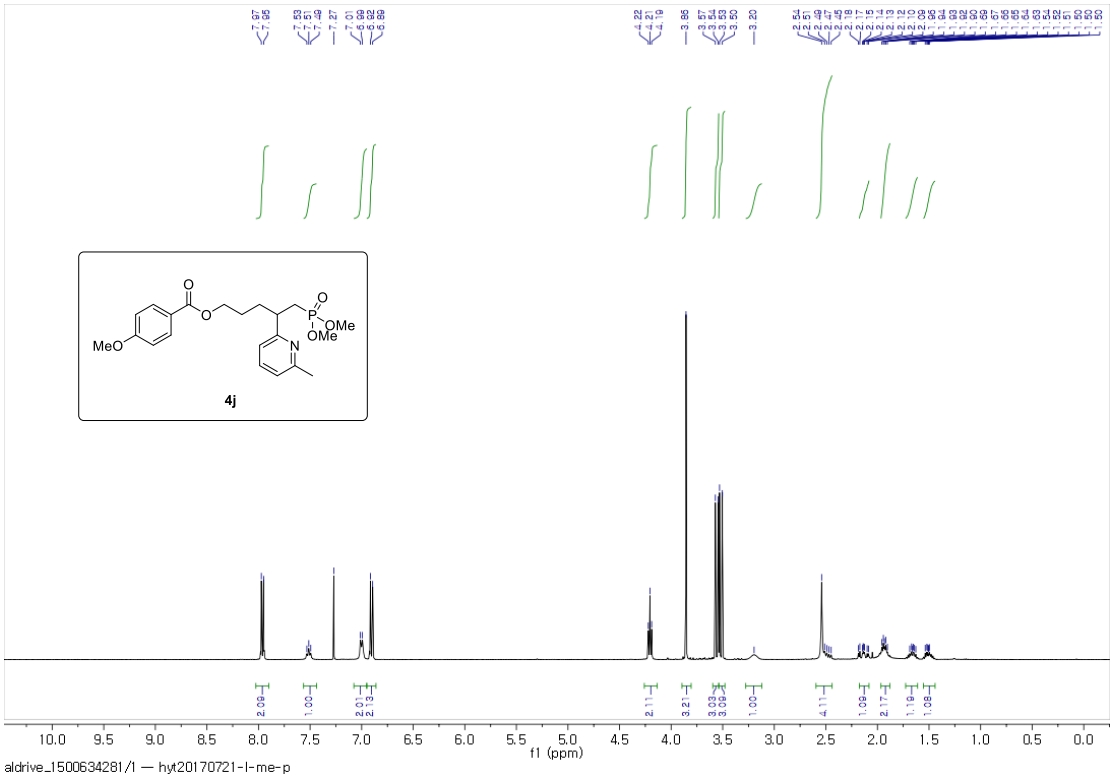


150 MHz, ^{13}C NMR in $CDCl_3$

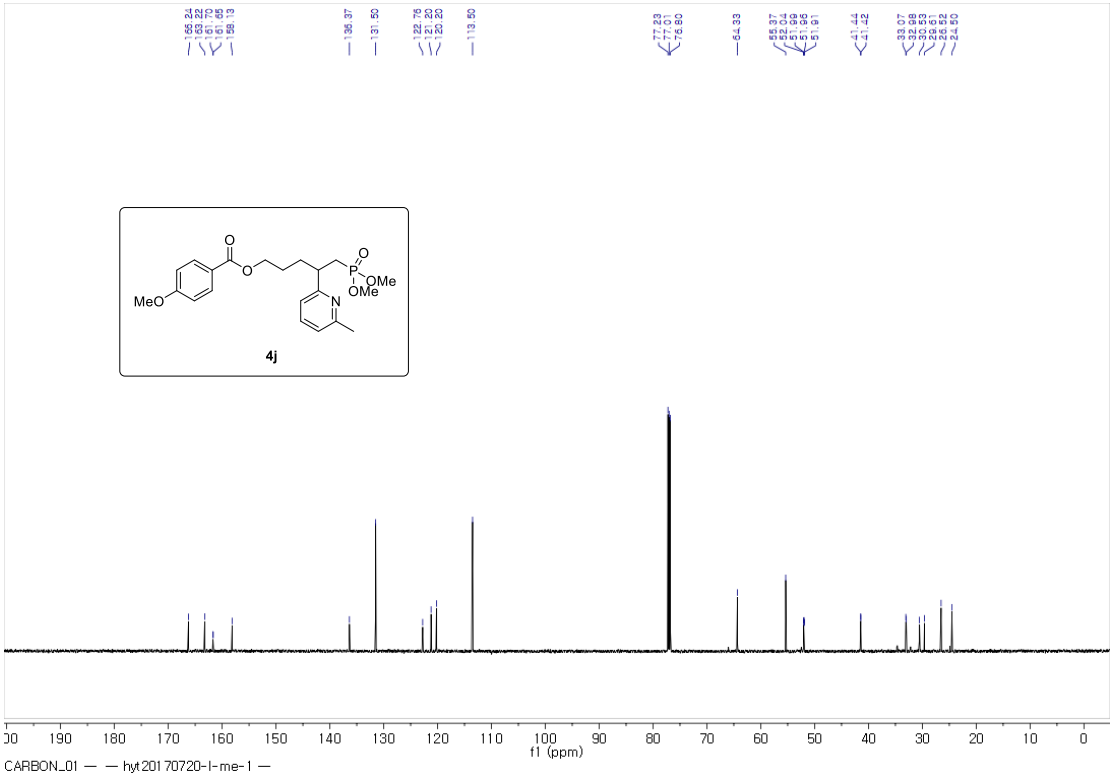


243 MHz, ^{31}P NMR in $CDCl_3$

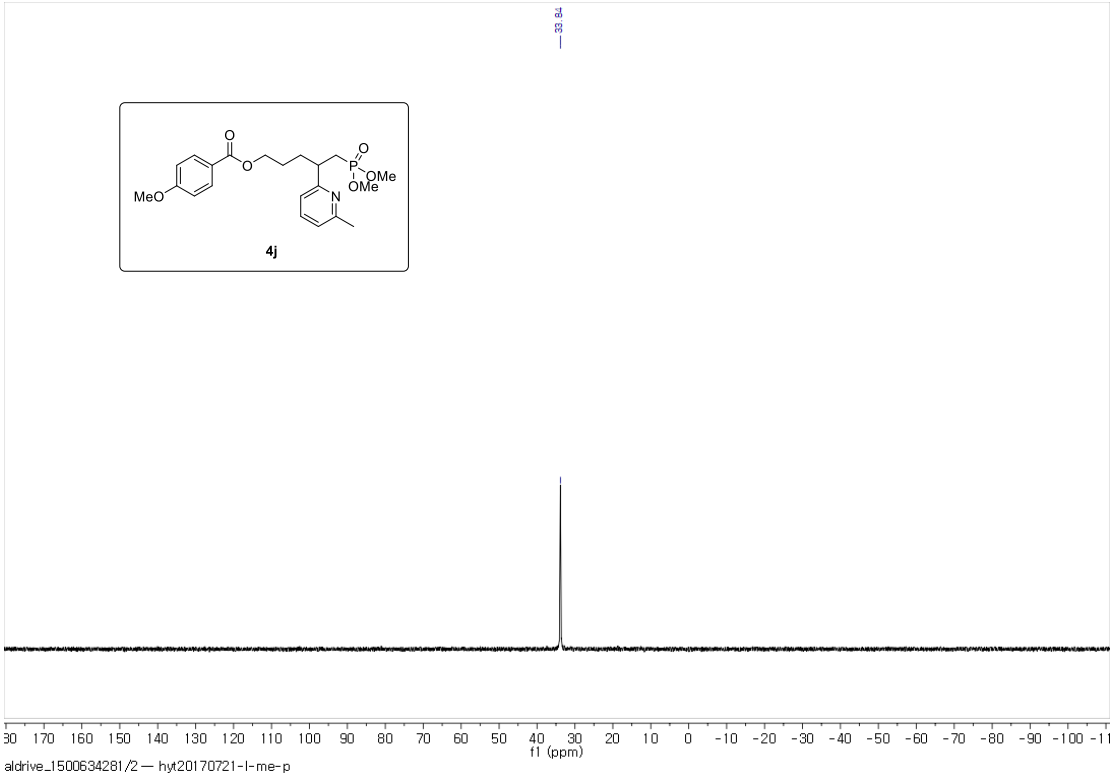
5-(dimethoxyphosphoryl)-4-(6-methylpyridin-2-yl)pentyl 4-methoxybenzoate (4j)



600 MHz, ^{1}H NMR in $CDCl_3$

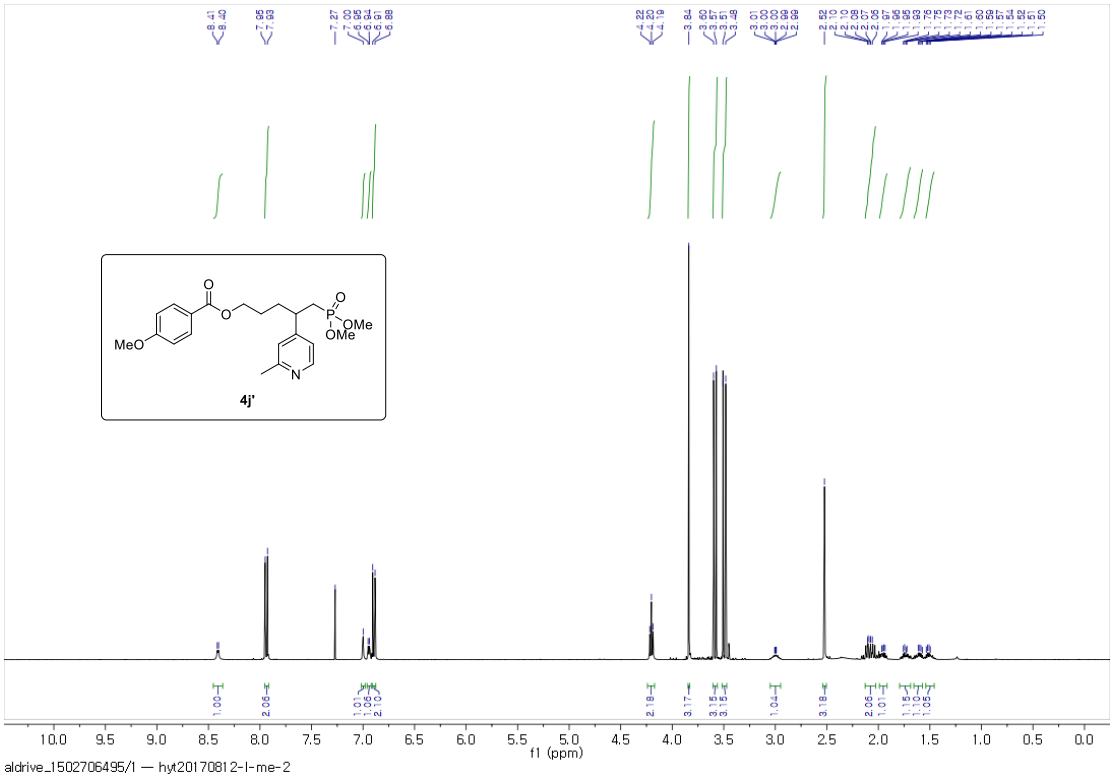


150 MHz, ^{13}C NMR in $CDCl_3$

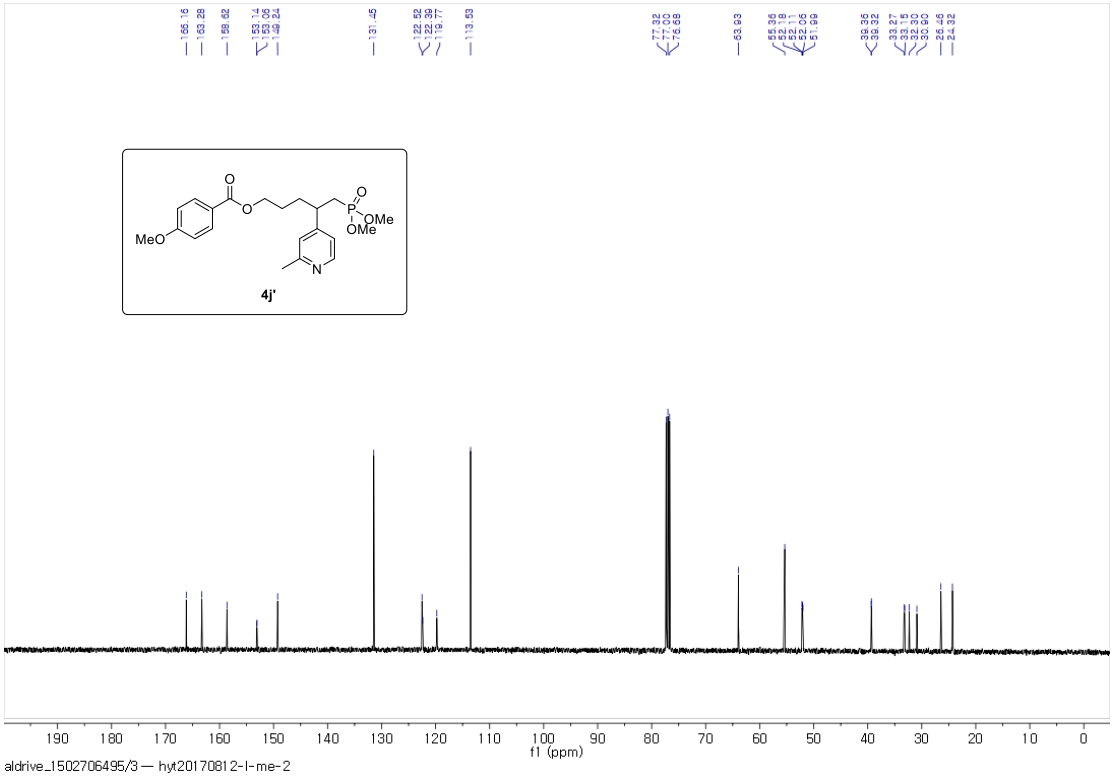


243 MHz, ^{31}P NMR in $CDCl_3$

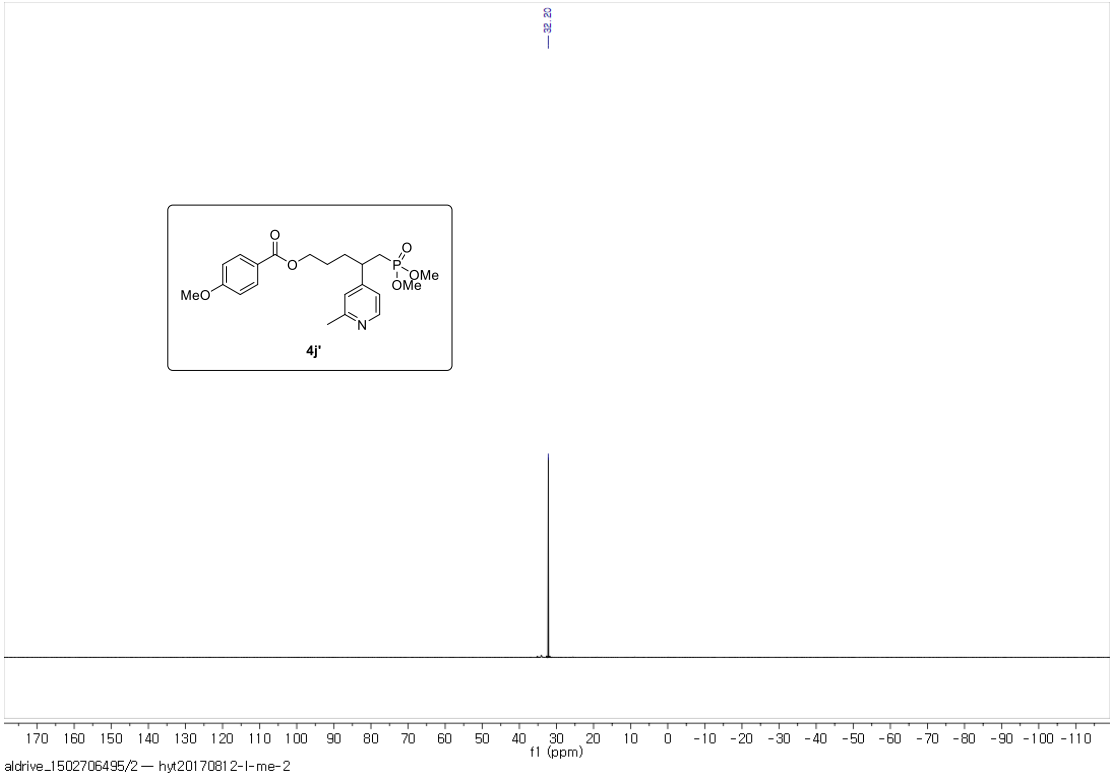
5-(dimethoxyphosphoryl)-4-(2-methylpyridin-4-yl)pentyl 4-methoxybenzoate (4j')



600 MHz, ^{1}H NMR in $CDCl_3$

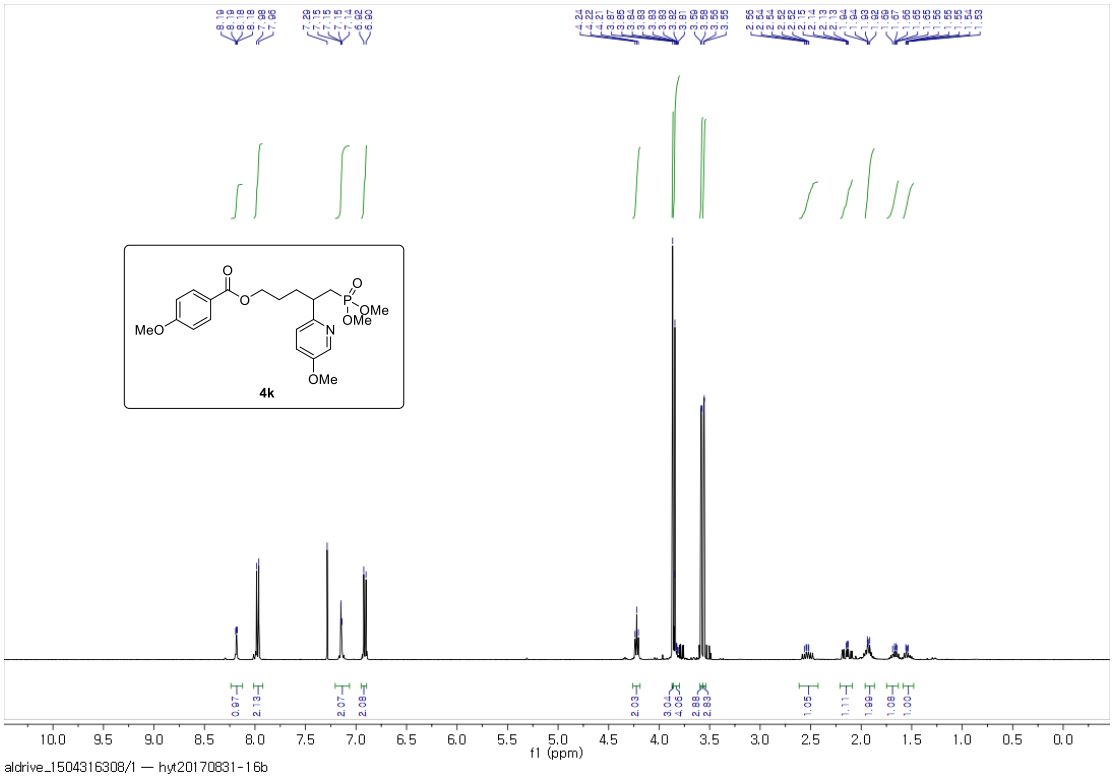


150 MHz, ^{13}C NMR in $CDCl_3$

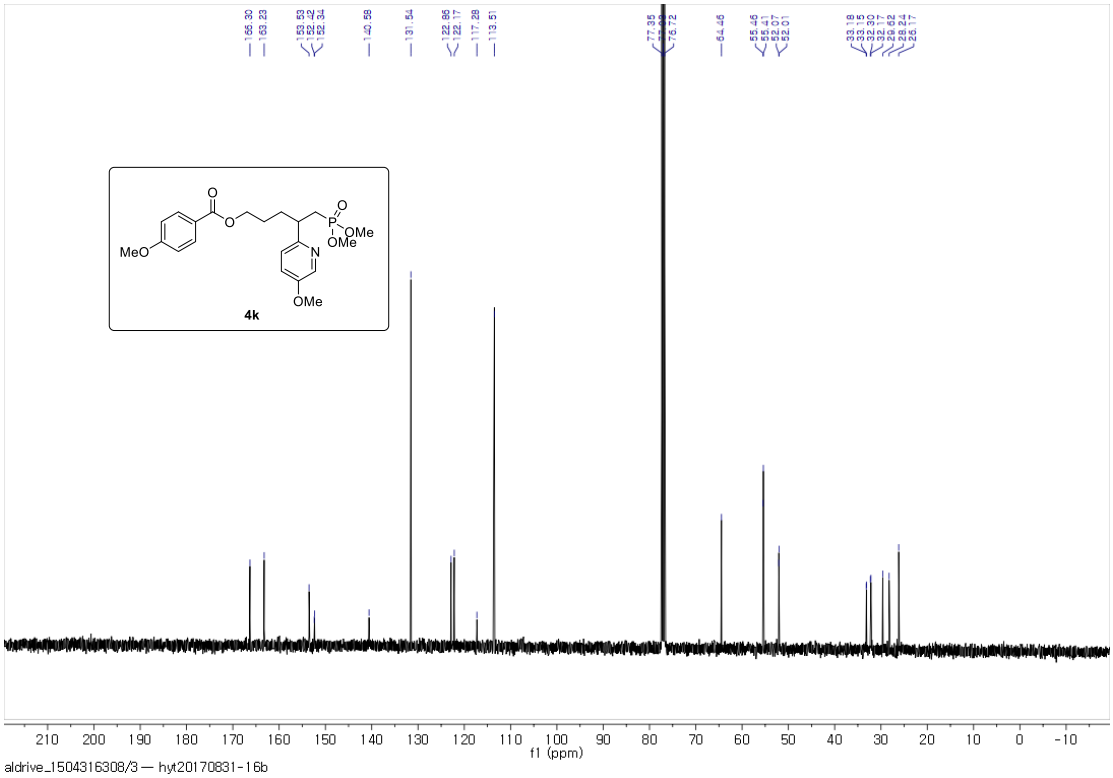


243 MHz, ^{31}P NMR in $CDCl_3$

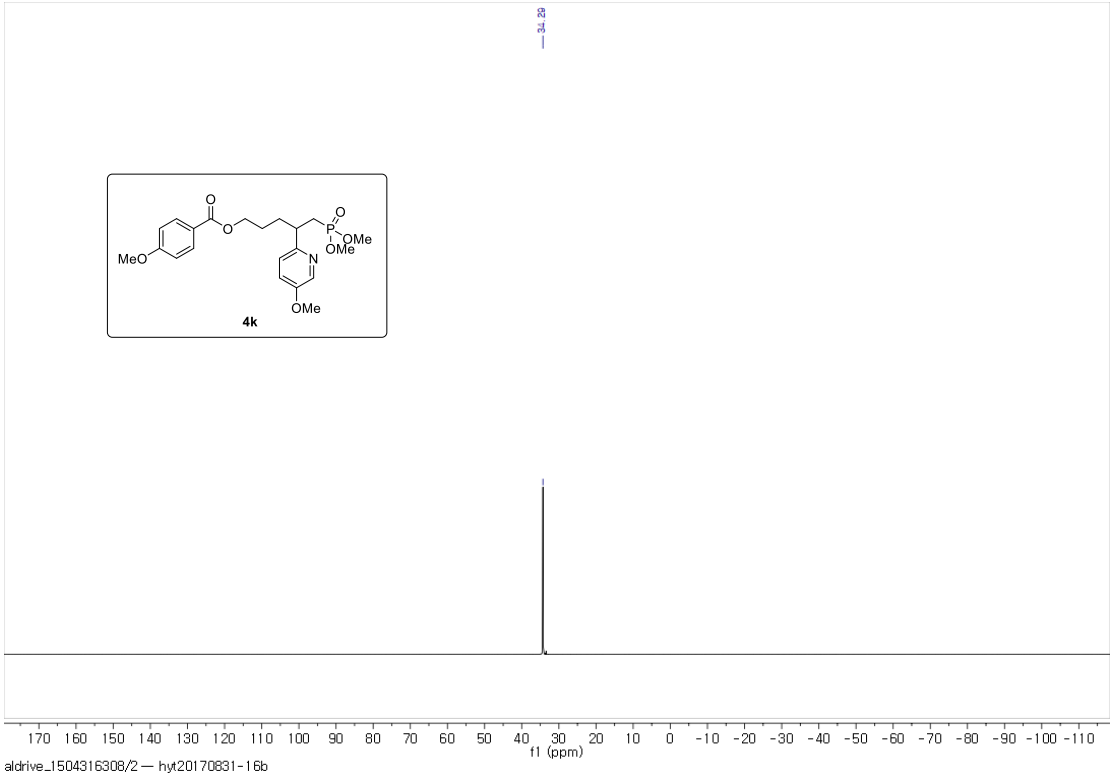
5-(dimethoxyphosphoryl)-4-(5-methoxypyridin-2-yl)pentyl 4-methoxybenzoate (4k)



400 MHz, ^{1}H NMR in $CDCl_3$

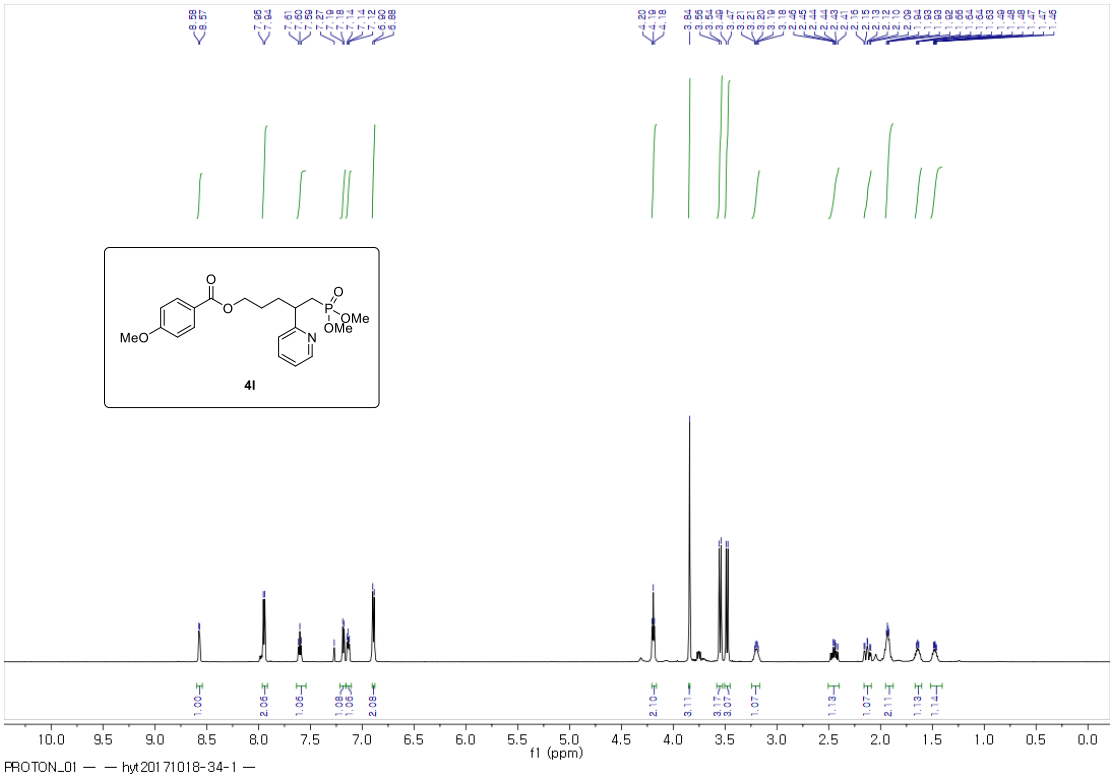


100 MHz, ^{13}C NMR in $CDCl_3$

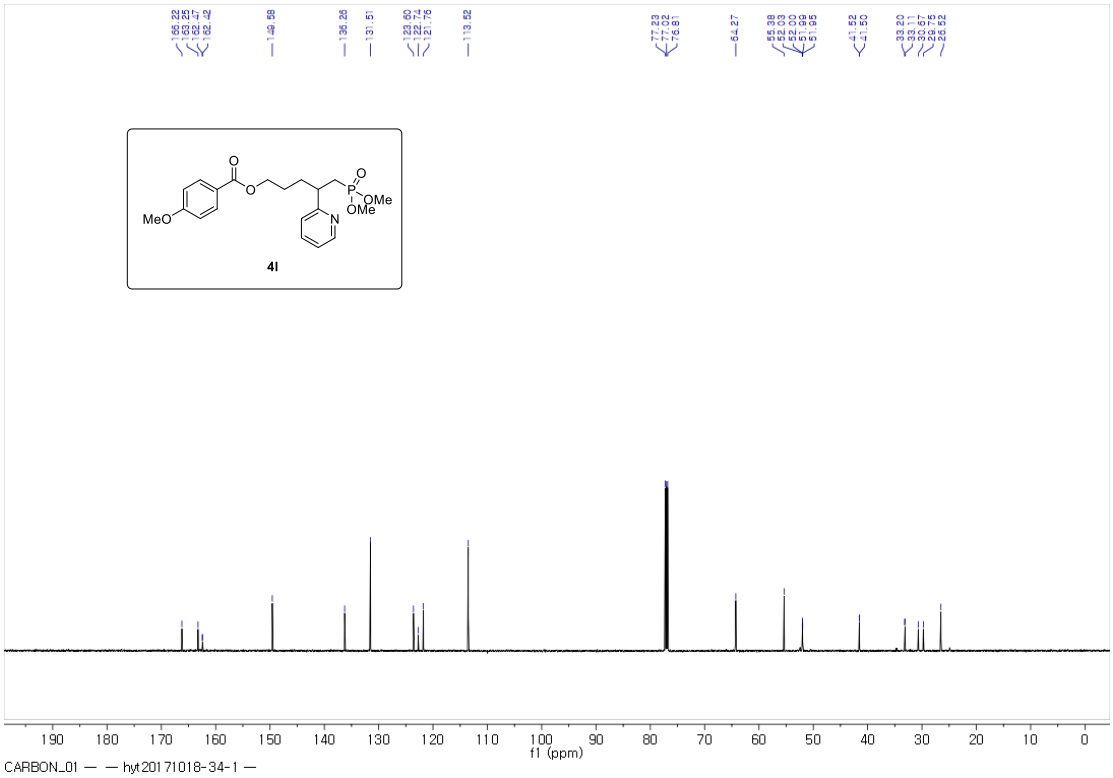


162 MHz, ^{31}P NMR in $CDCl_3$

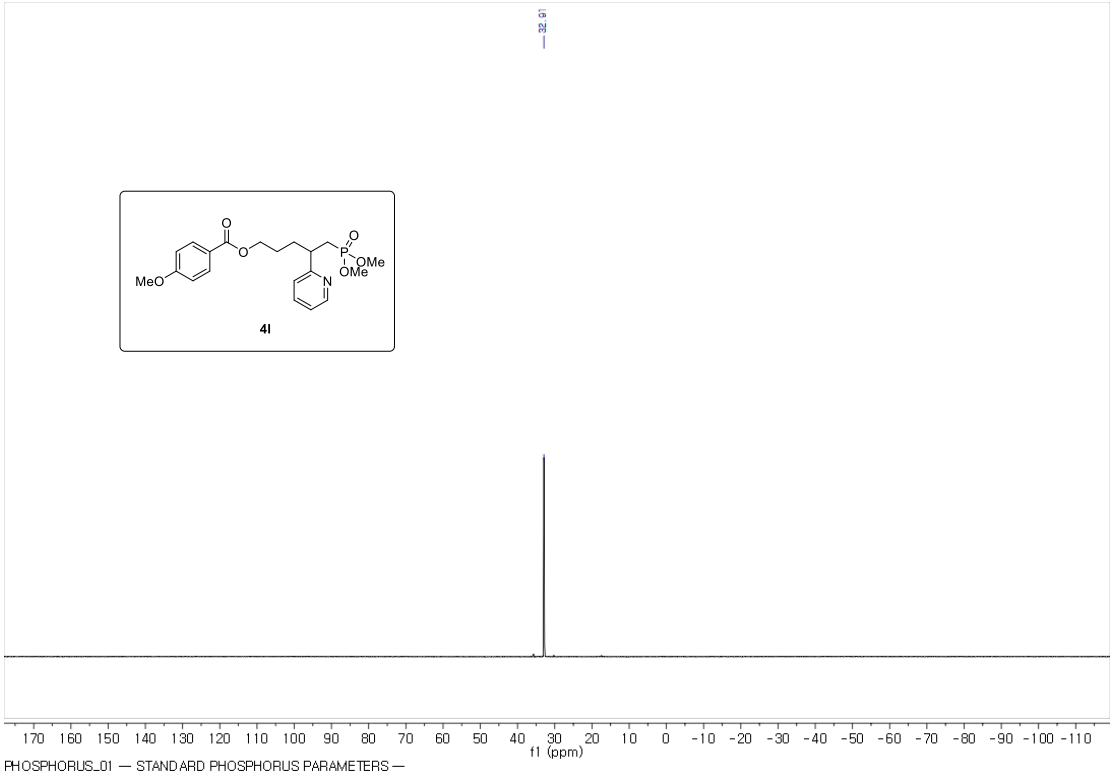
5-(dimethoxyphosphoryl)-4-(pyridin-2-yl)pentyl 4-methoxybenzoate (4l)



600 MHz, ^{1}H NMR in $CDCl_3$

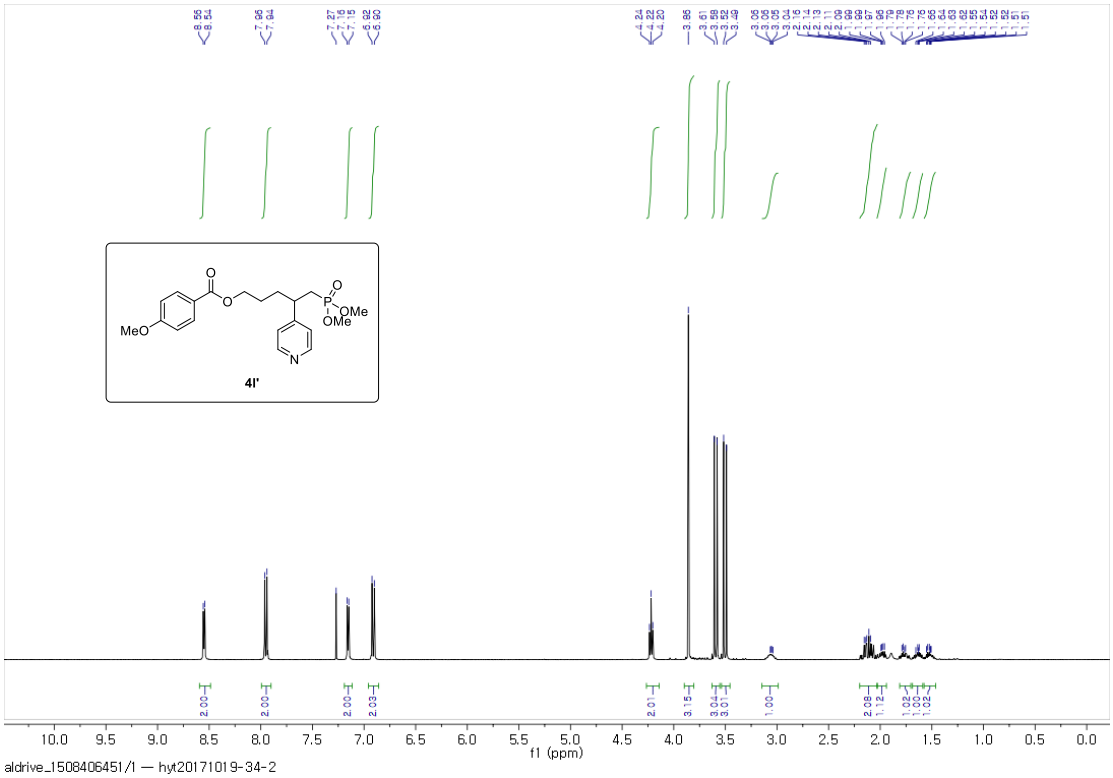


150 MHz, ^{13}C NMR in $CDCl_3$

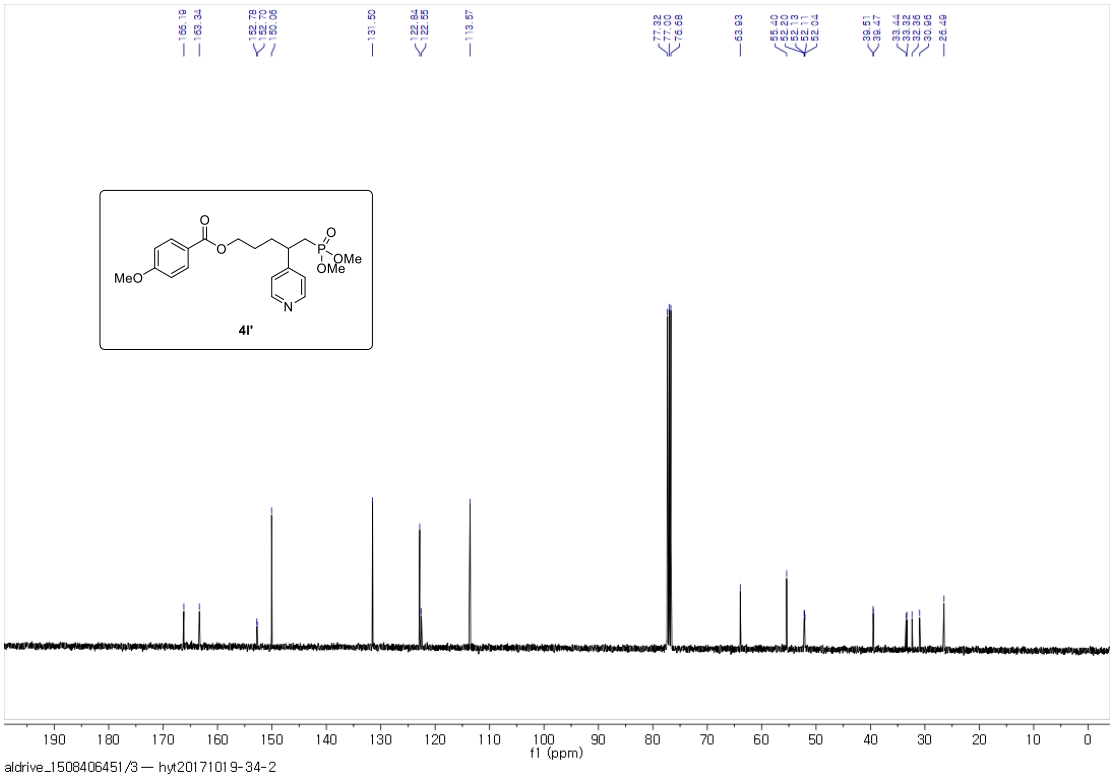


243 MHz, ^{31}P NMR in $CDCl_3$

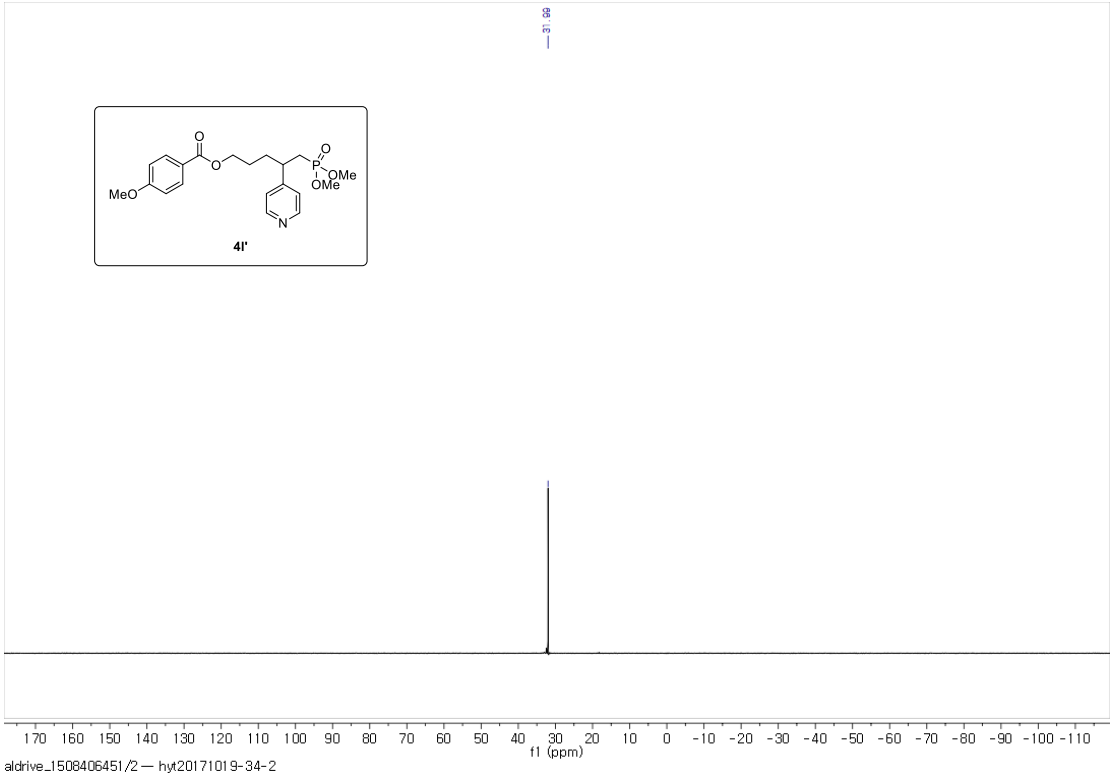
5-(dimethoxyphosphoryl)-4-(pyridin-4-yl)pentyl 4-methoxybenzoate (4l')



400 MHz, ^{1}H NMR in $CDCl_3$

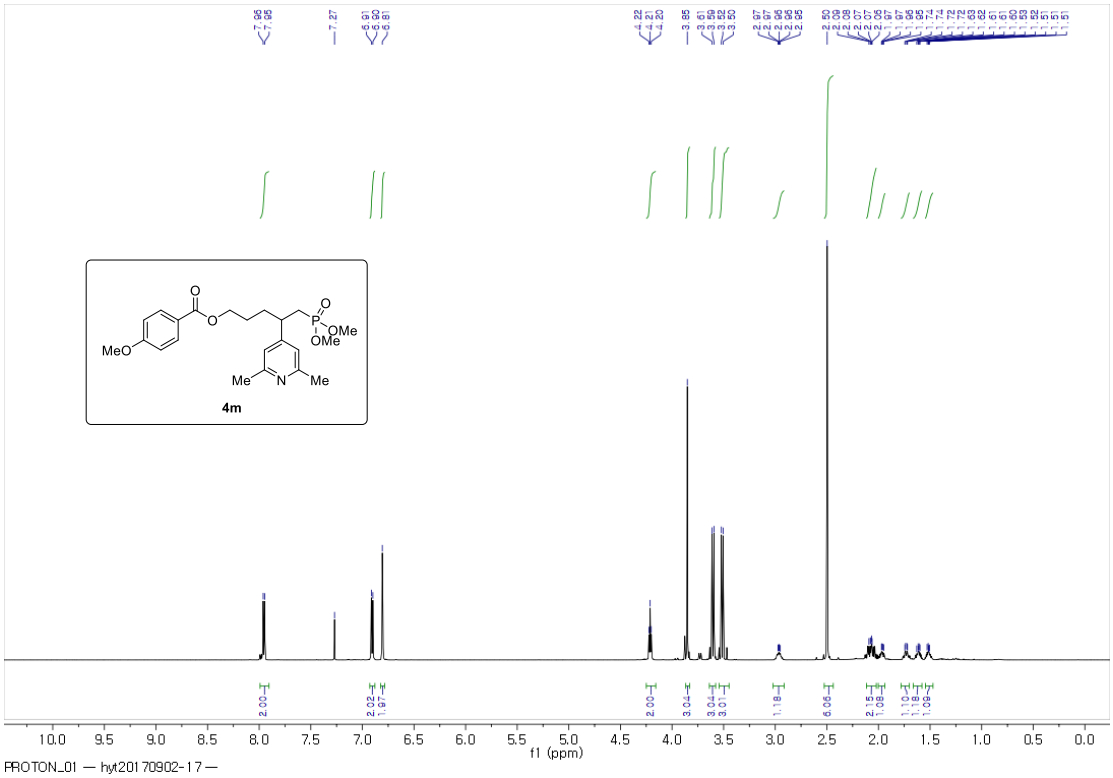


100 MHz, ^{13}C NMR in $CDCl_3$

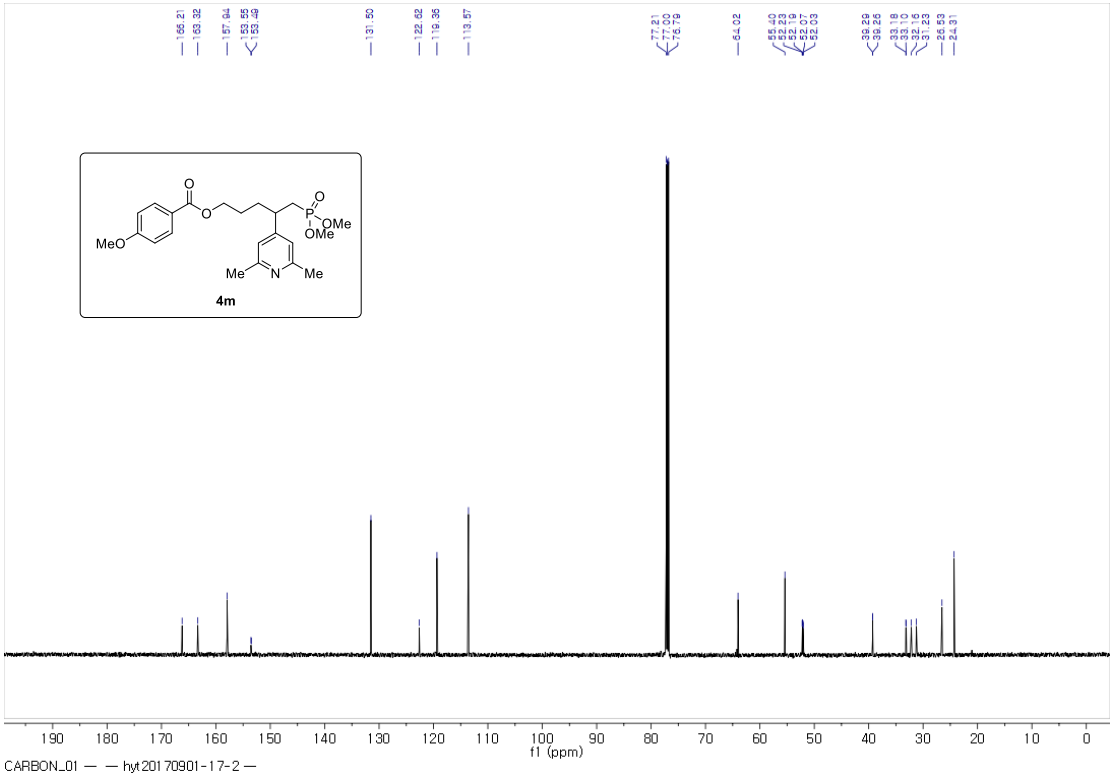


162 MHz, ^{31}P NMR in $CDCl_3$

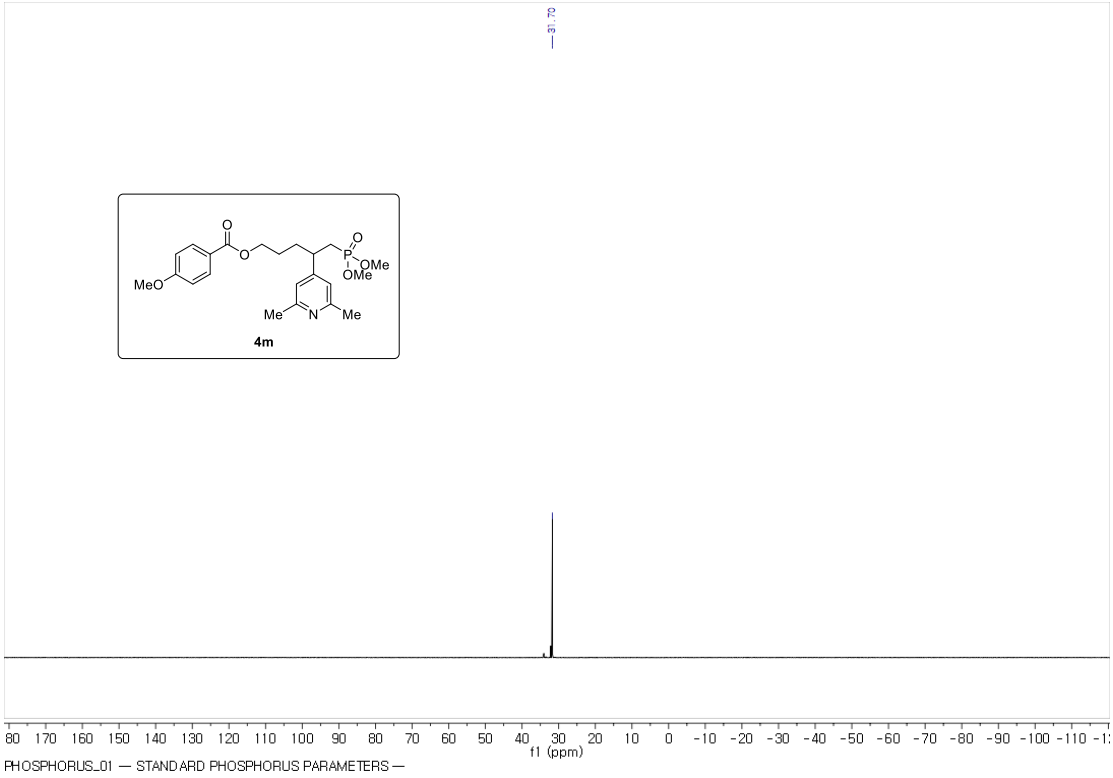
5-(dimethoxyphosphoryl)-4-(2,6-dimethylpyridin-4-yl)pentyl 4-methoxybenzoate (4m)



600 MHz, ^{1}H NMR in $CDCl_3$

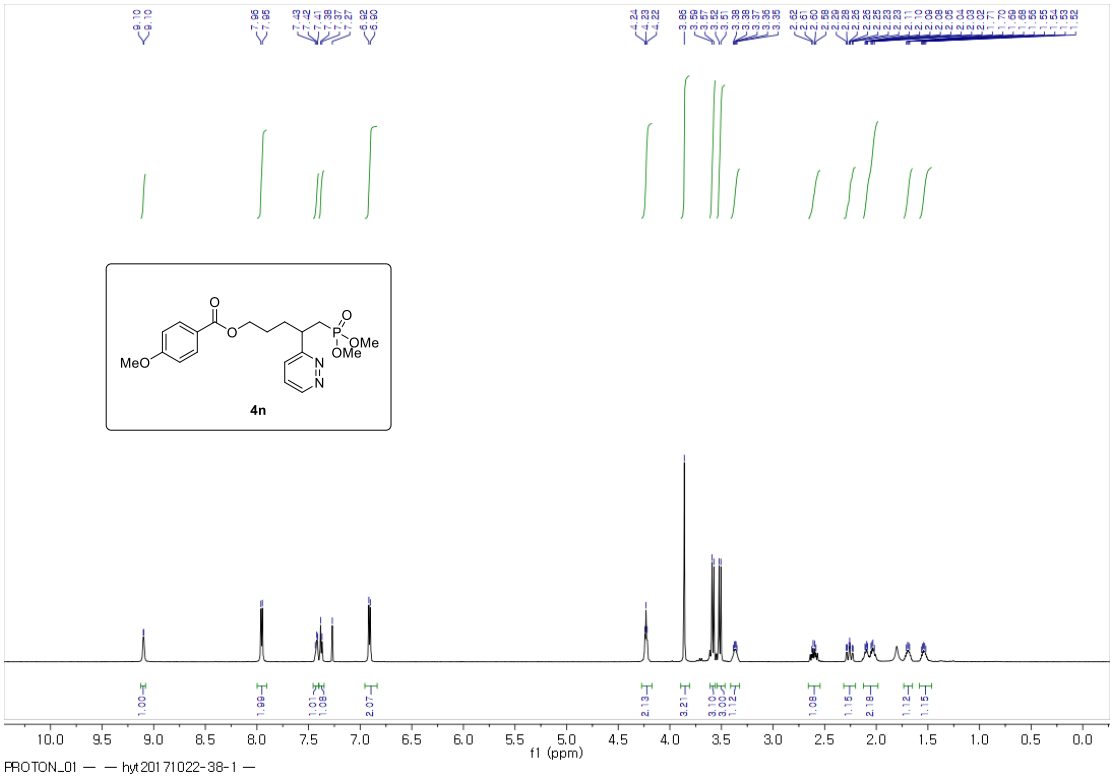


150 MHz, ^{13}C NMR in $CDCl_3$

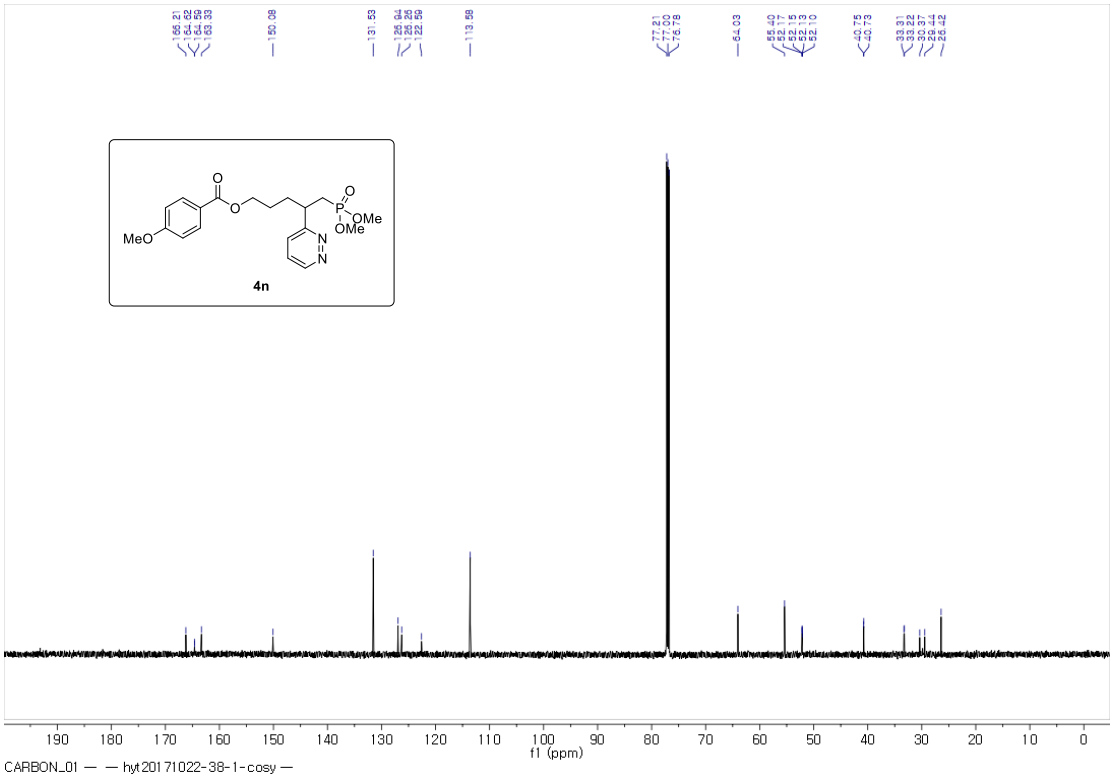


243 MHz, ^{31}P NMR in $CDCl_3$

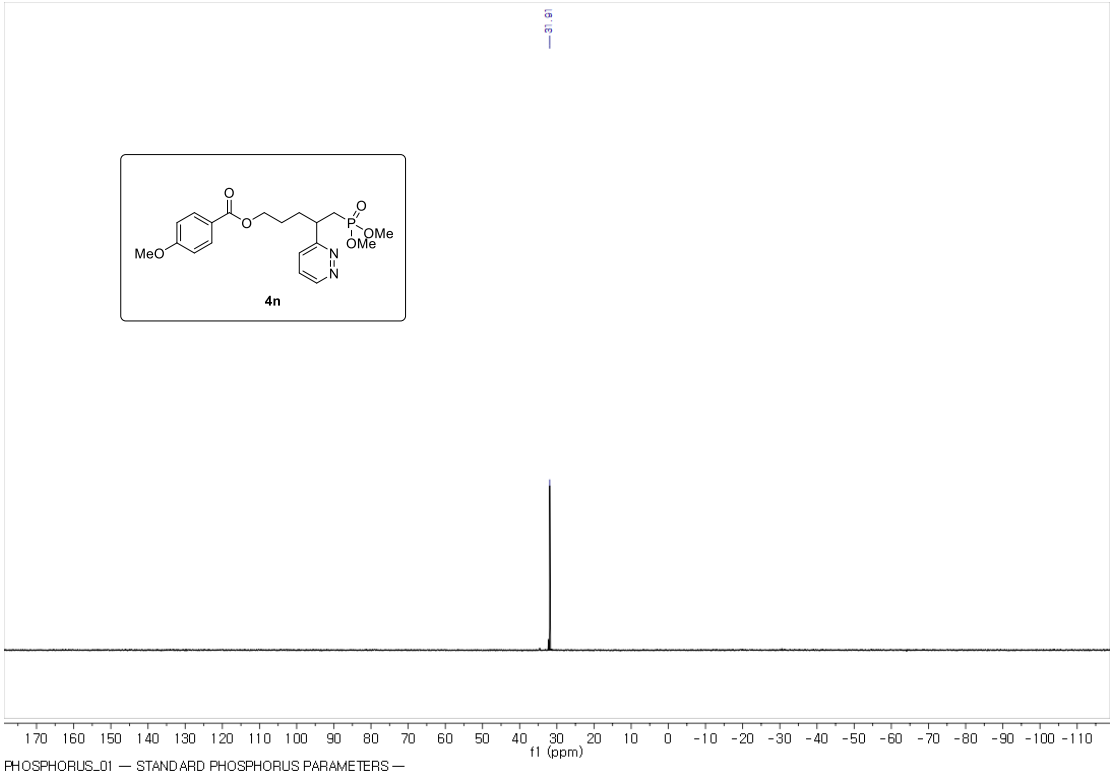
5-(dimethoxyphosphoryl)-4-(pyridazin-3-yl)pentyl 4-methoxybenzoate (4n)



600 MHz, ^{1}H NMR in $CDCl_3$

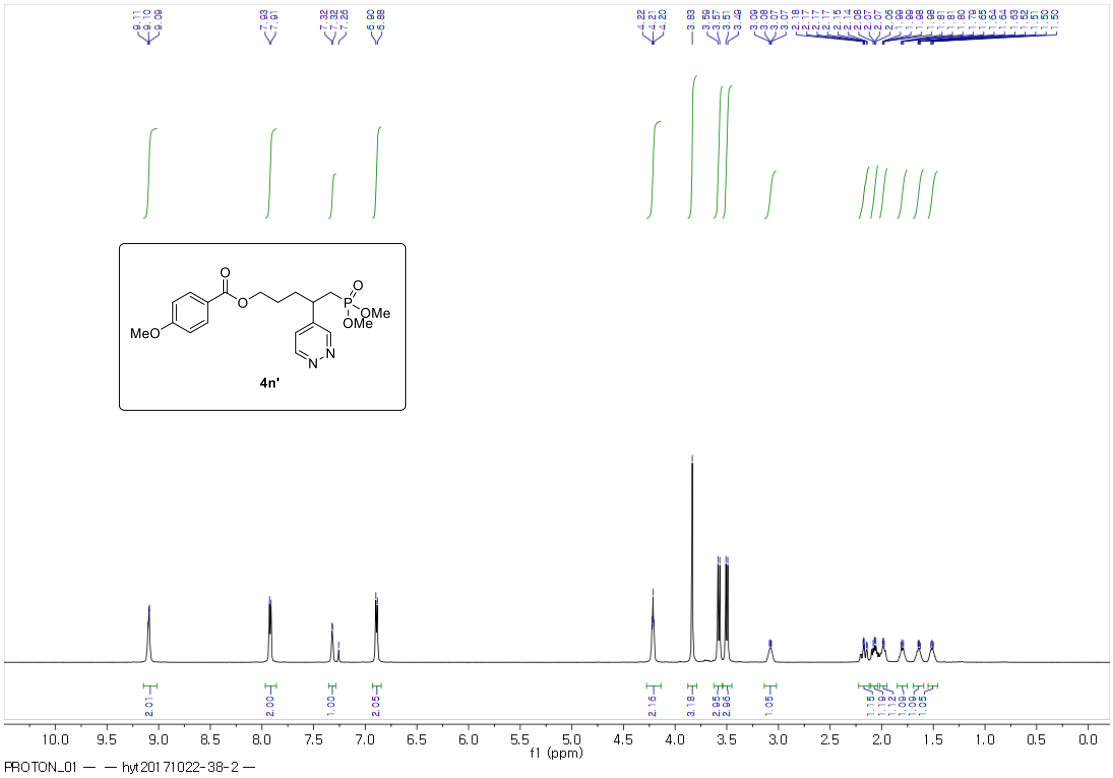


150 MHz, ^{13}C NMR in $CDCl_3$

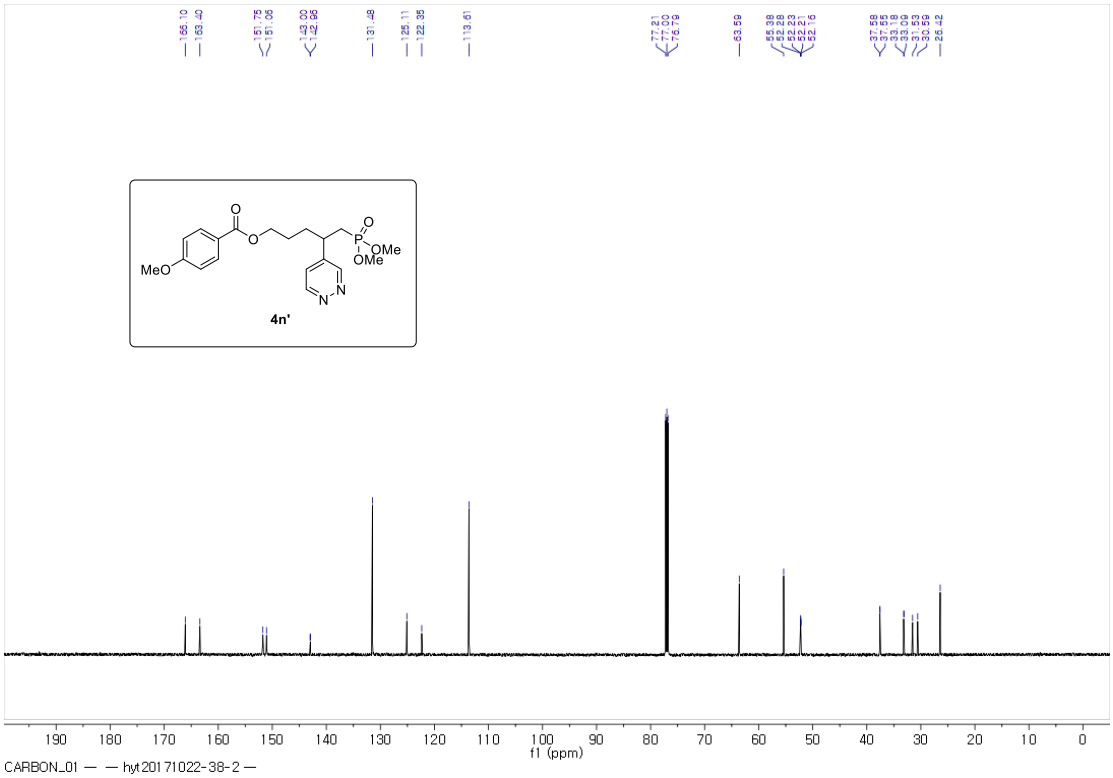


243 MHz, ^{31}P NMR in $CDCl_3$

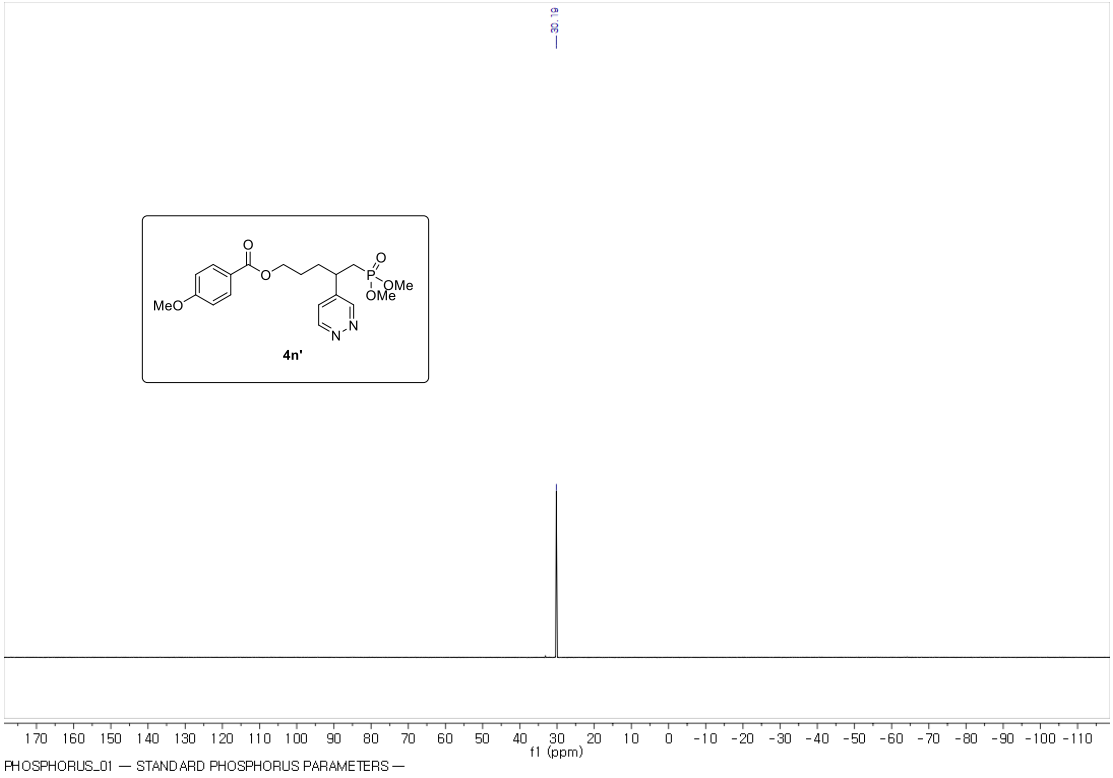
5-(dimethoxyphosphoryl)-4-(pyridazin-4-yl)pentyl 4-methoxybenzoate (4n')



600 MHz, ^{1}H NMR in $CDCl_3$

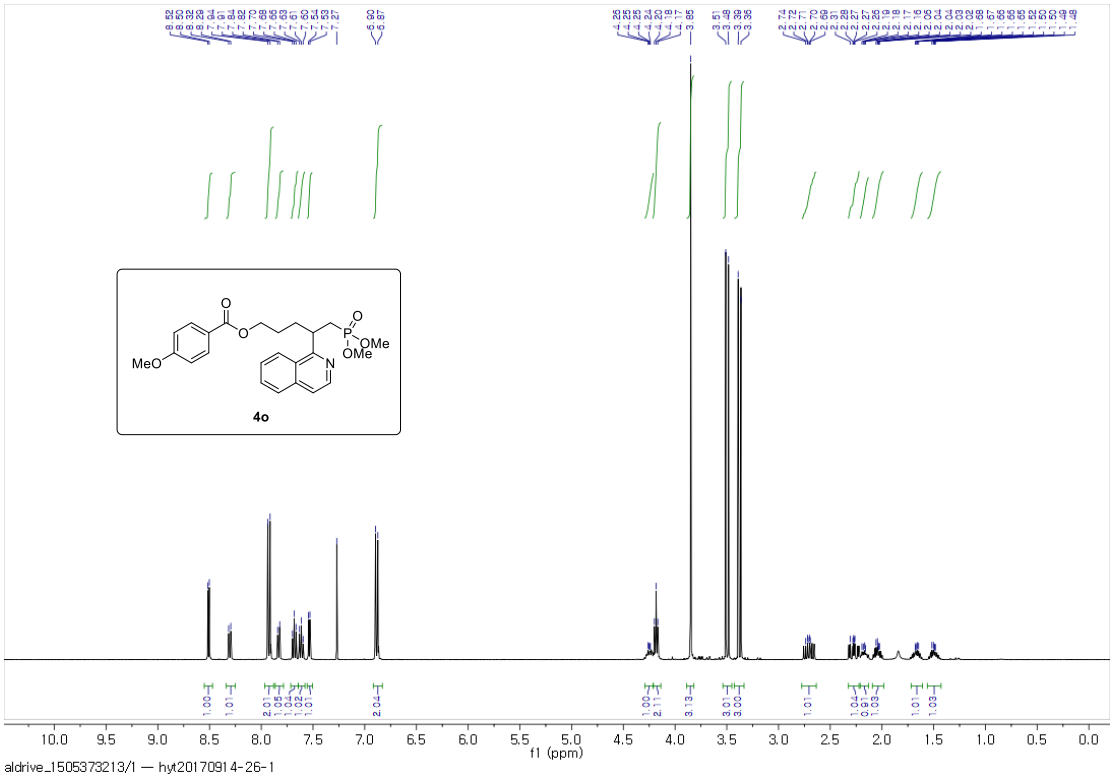


150 MHz, ^{13}C NMR in $CDCl_3$

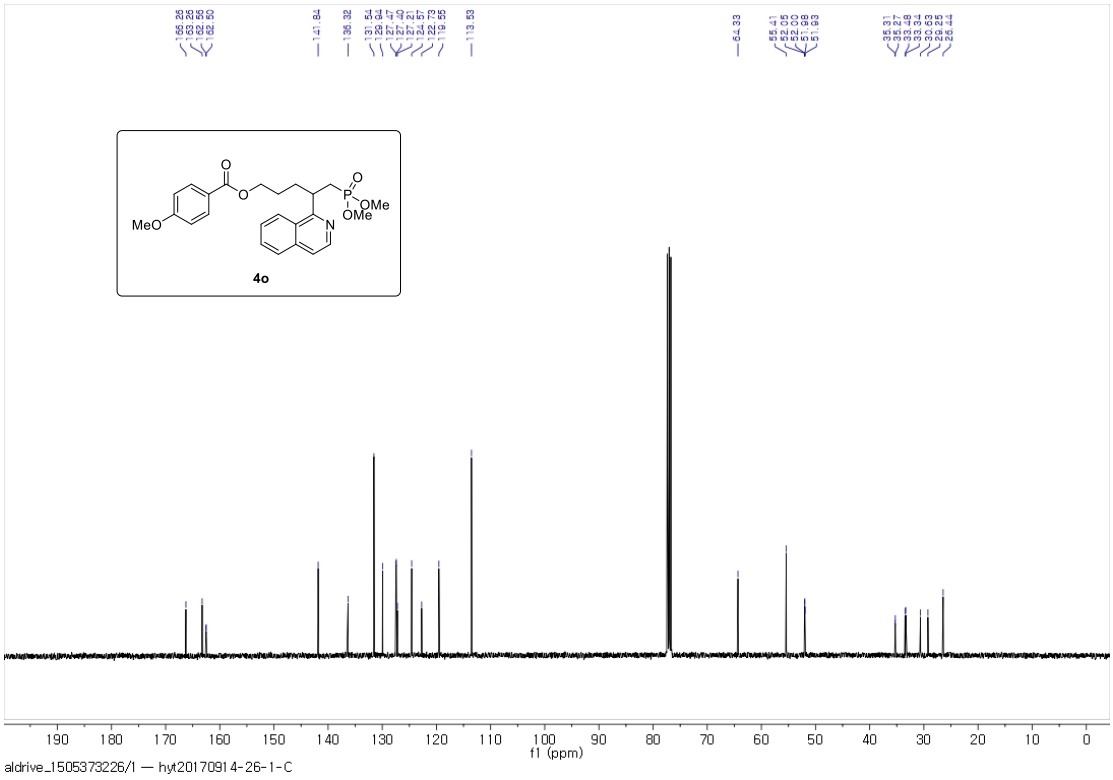


243 MHz, ^{31}P NMR in $CDCl_3$

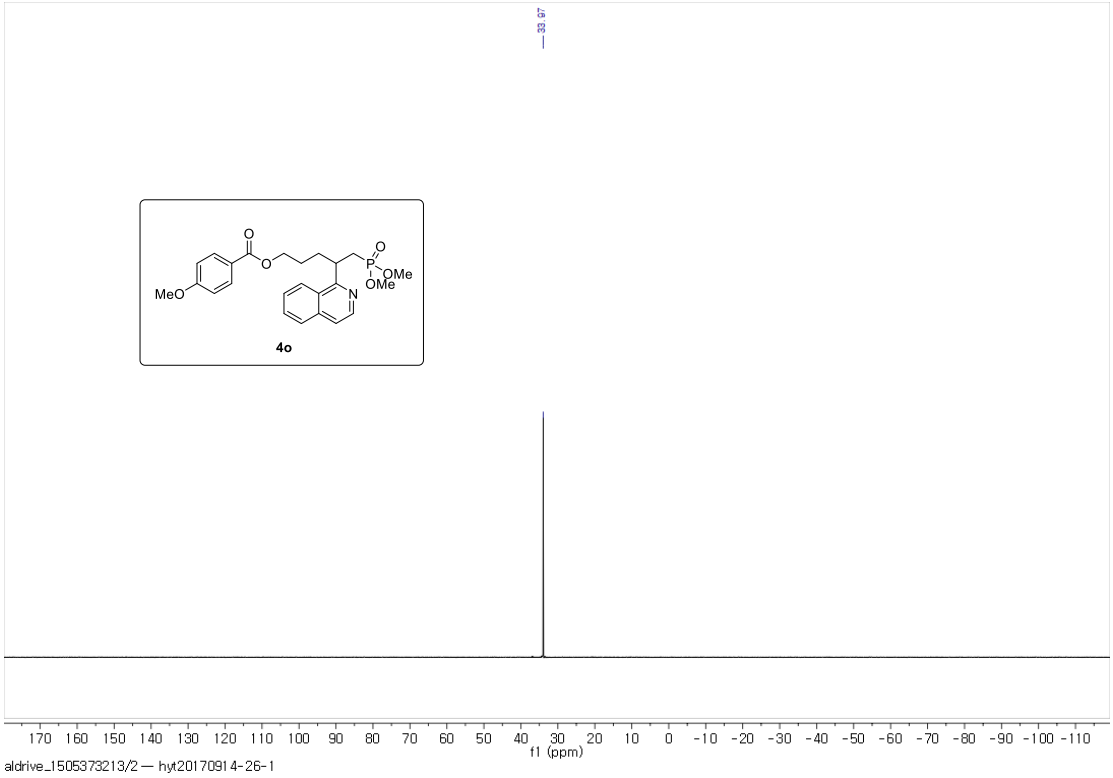
5-(dimethoxyphosphoryl)-4-(isoquinolin-1-yl)pentyl 4-methoxybenzoate (4o).



400 MHz, ^{1}H NMR in $CDCl_3$

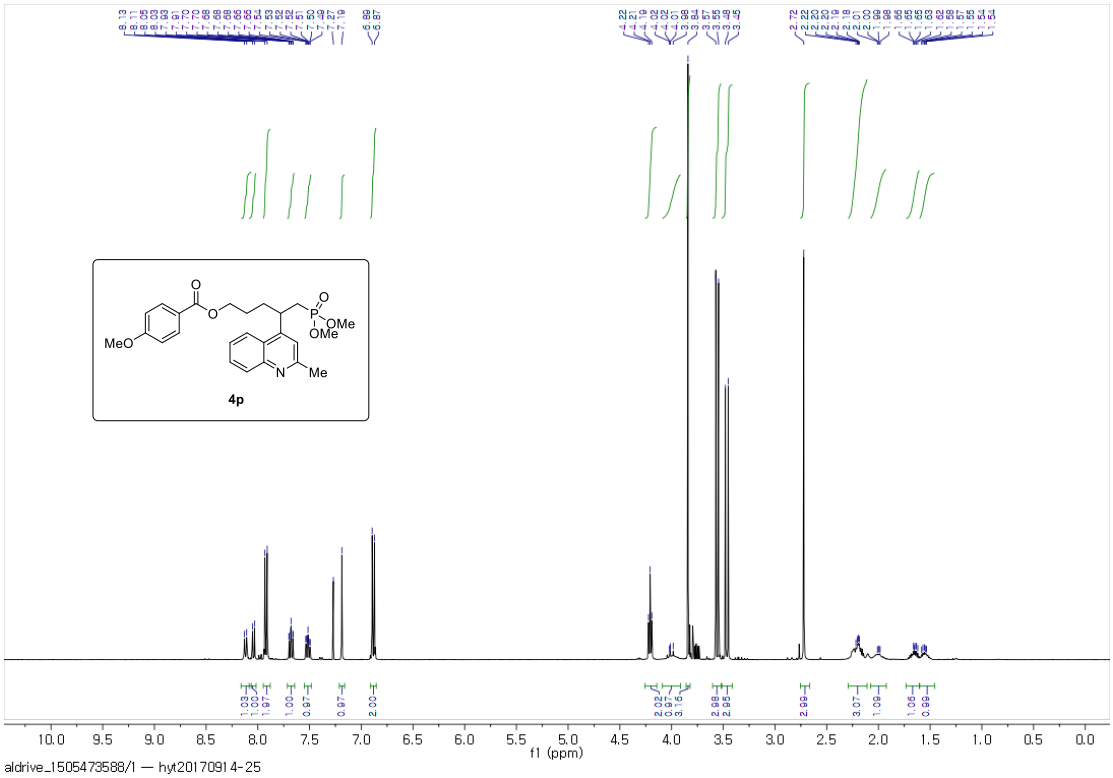


100 MHz, ^{13}C NMR in $CDCl_3$

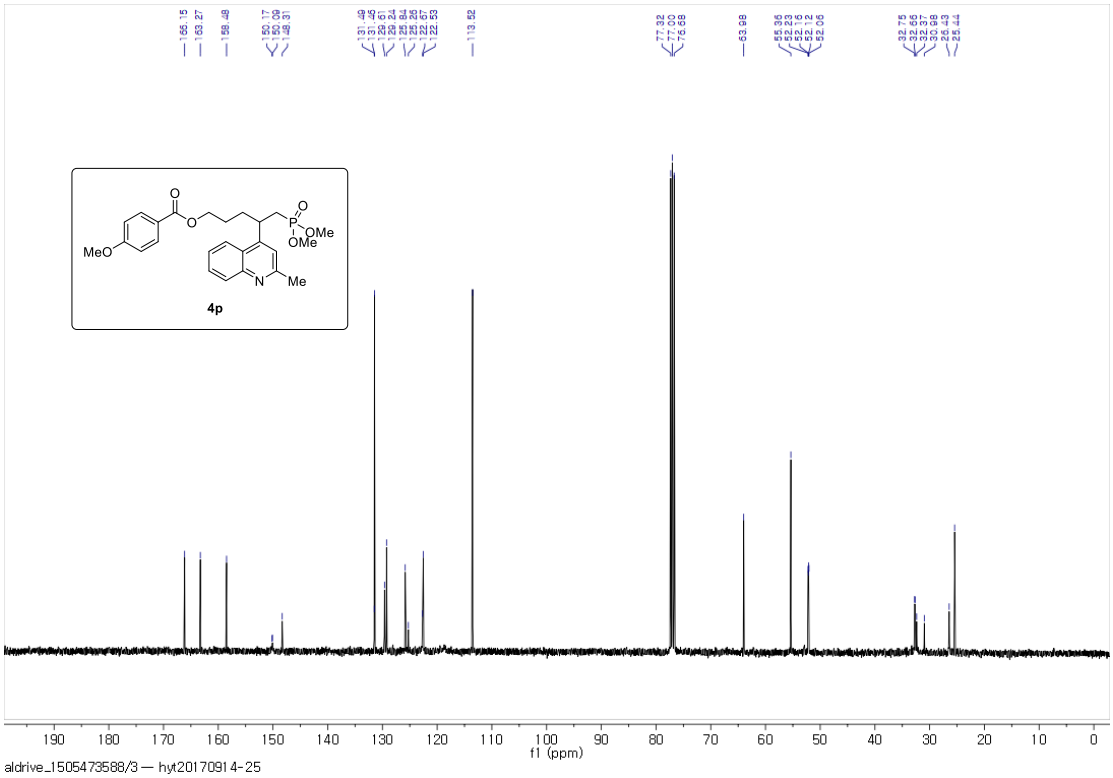


243 MHz, ^{31}P NMR in $CDCl_3$

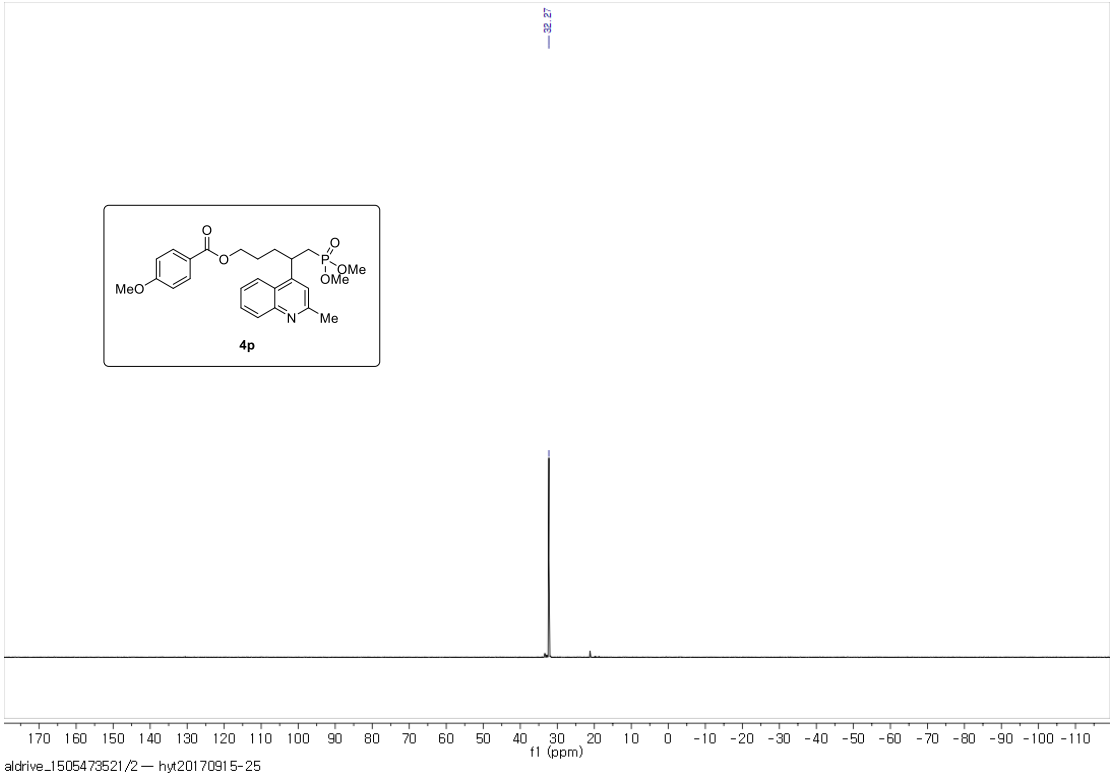
5-(dimethoxyphosphoryl)-4-(2-methylquinolin-4-yl)pentyl 4-methoxybenzoate (4p)



400 MHz, ^{1}H NMR in $CDCl_3$

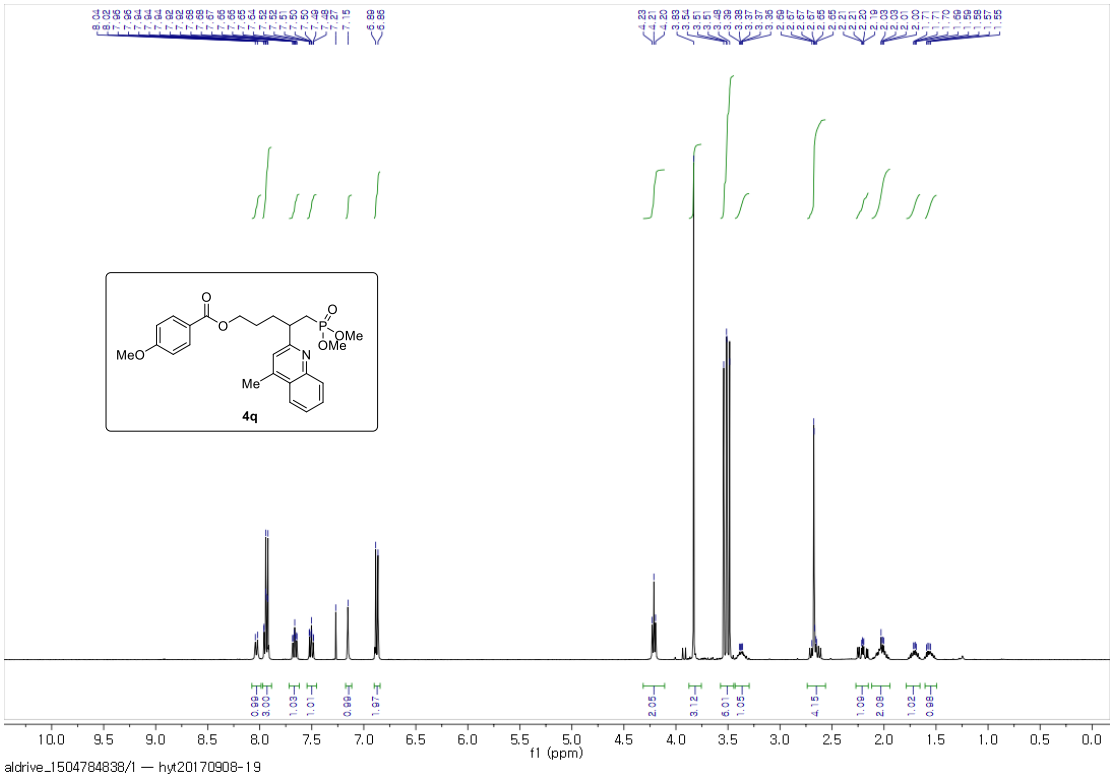


100 MHz, ^{13}C NMR in $CDCl_3$

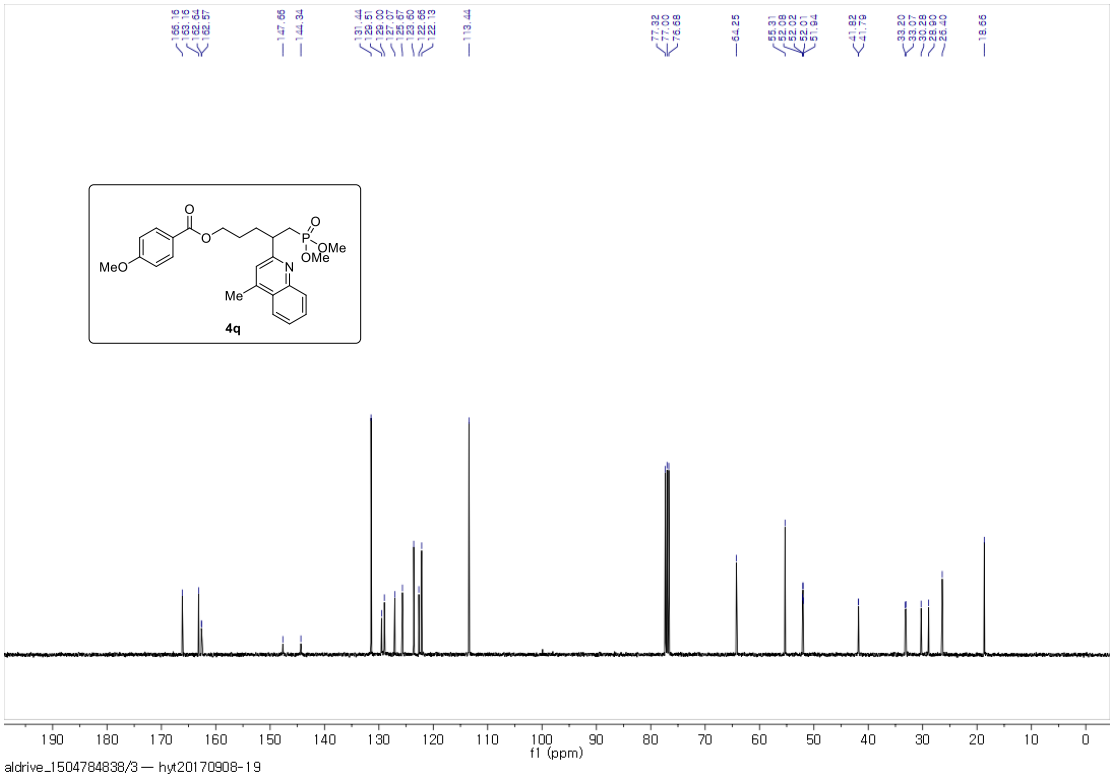


162 MHz, ^{31}P NMR in $CDCl_3$

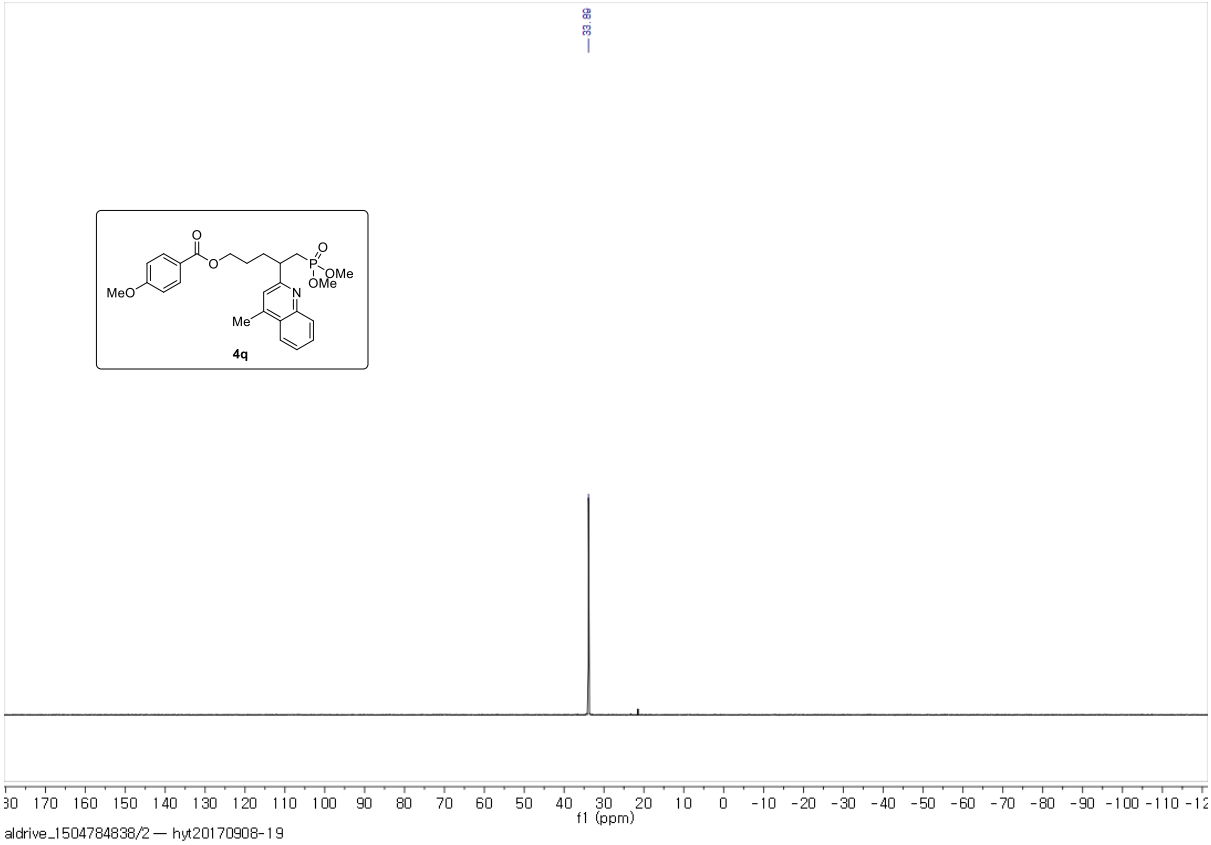
5-(dimethoxyphosphoryl)-4-(4-methylquinolin-2-yl)pentyl 4-methoxybenzoate (4q)



400 MHz, ^{1}H NMR in $CDCl_3$

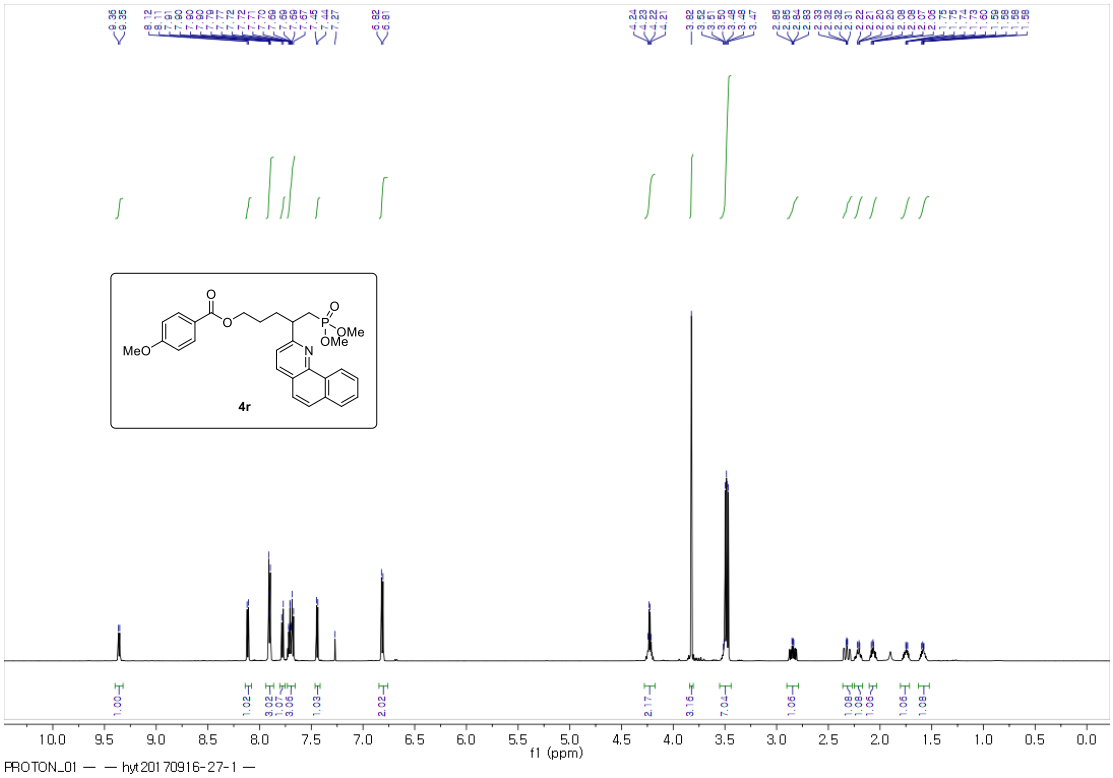


100 MHz, ^{13}C NMR in $CDCl_3$

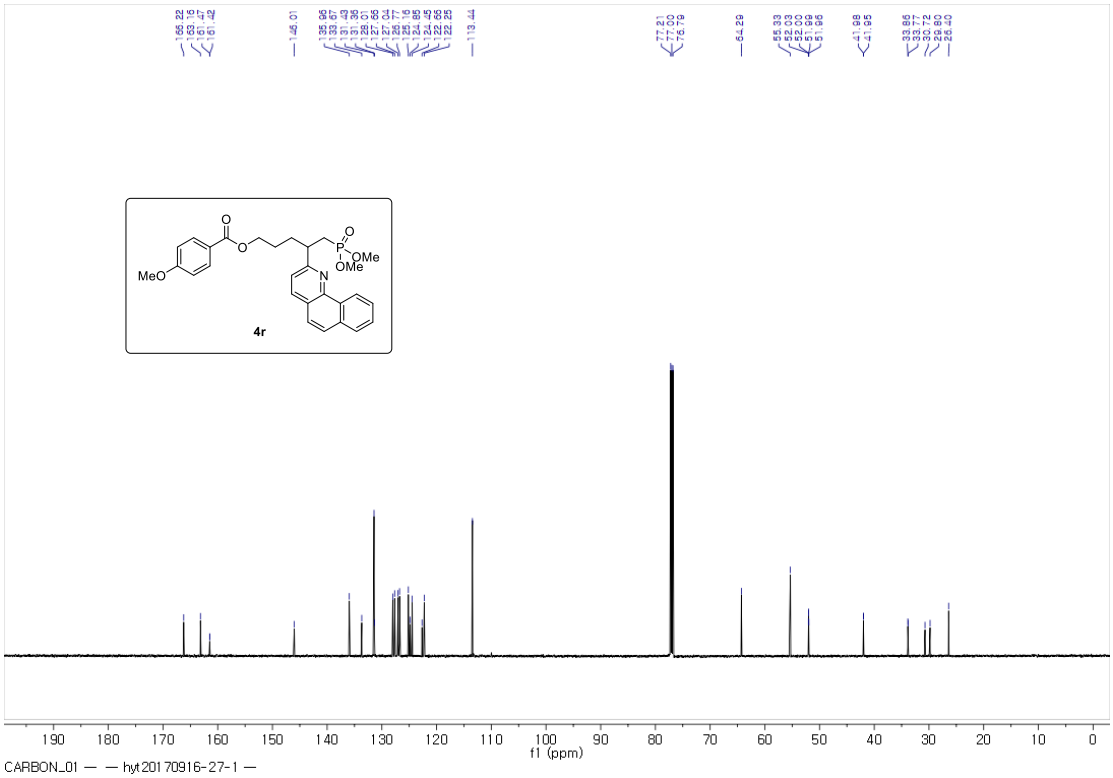


162 MHz, ^{31}P NMR in $CDCl_3$

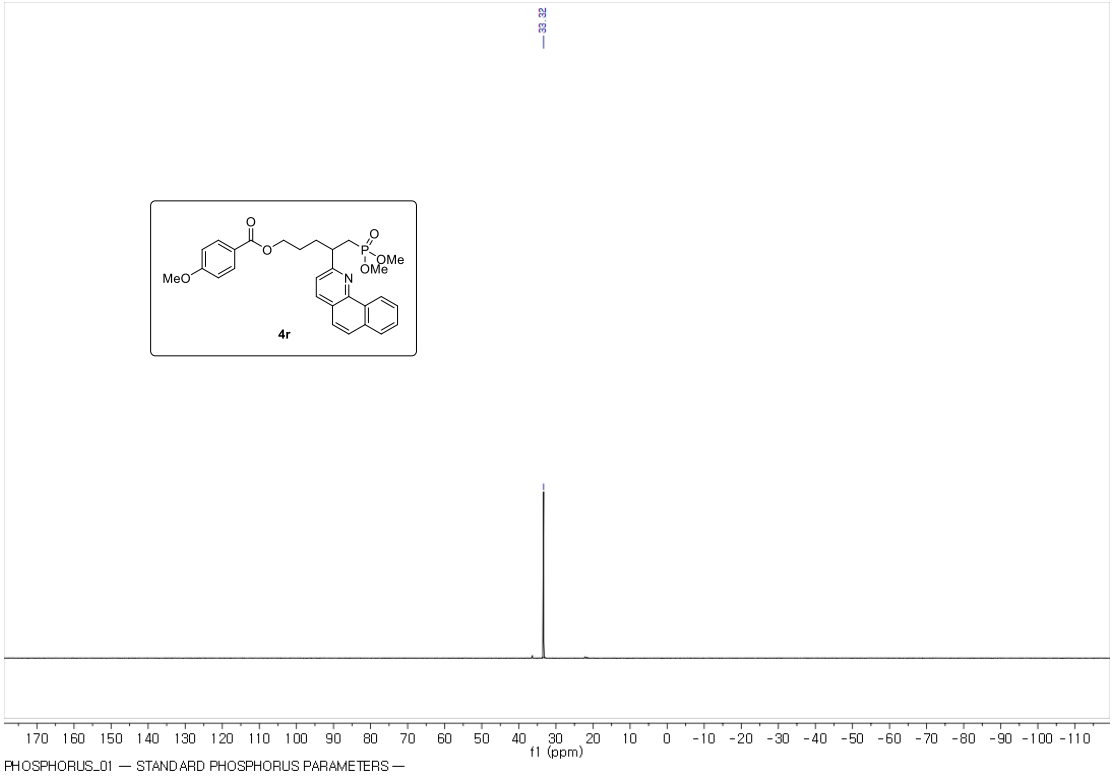
4-(benzo[h]quinolin-2-yl)-5-(dimethoxyphosphoryl)pentyl 4-methoxybenzoate (4r)



600 MHz, ^{1}H NMR in $CDCl_3$

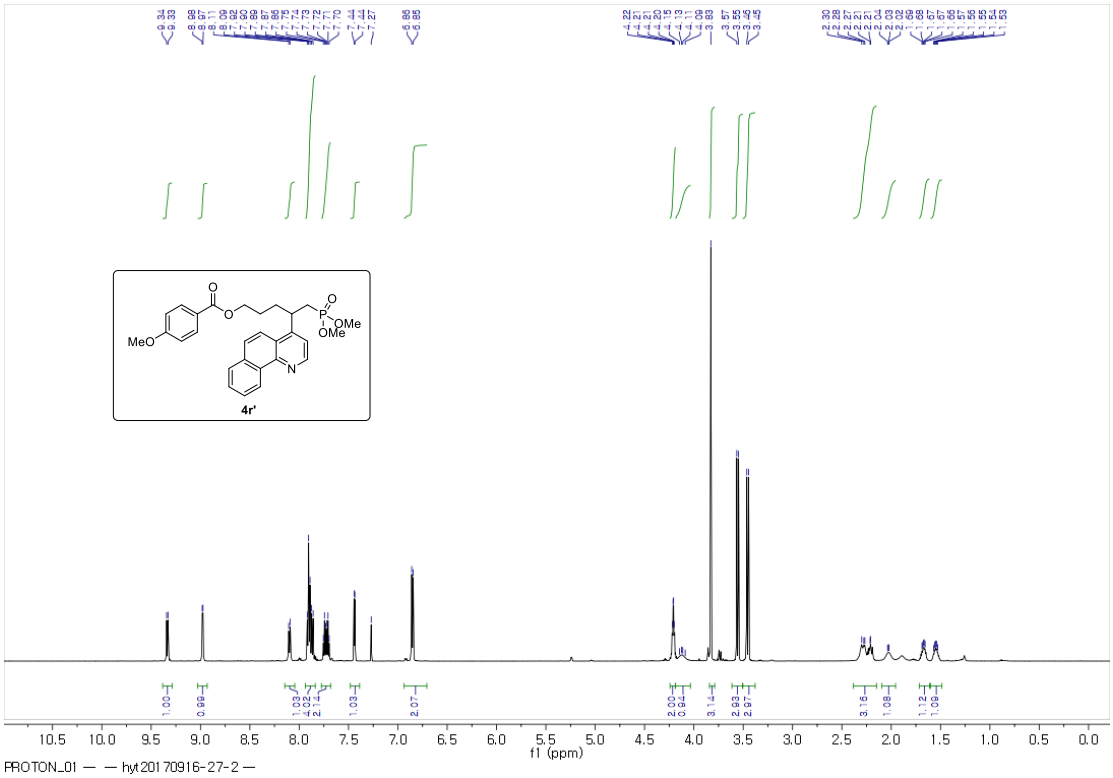


150 MHz, ^{13}C NMR in $CDCl_3$

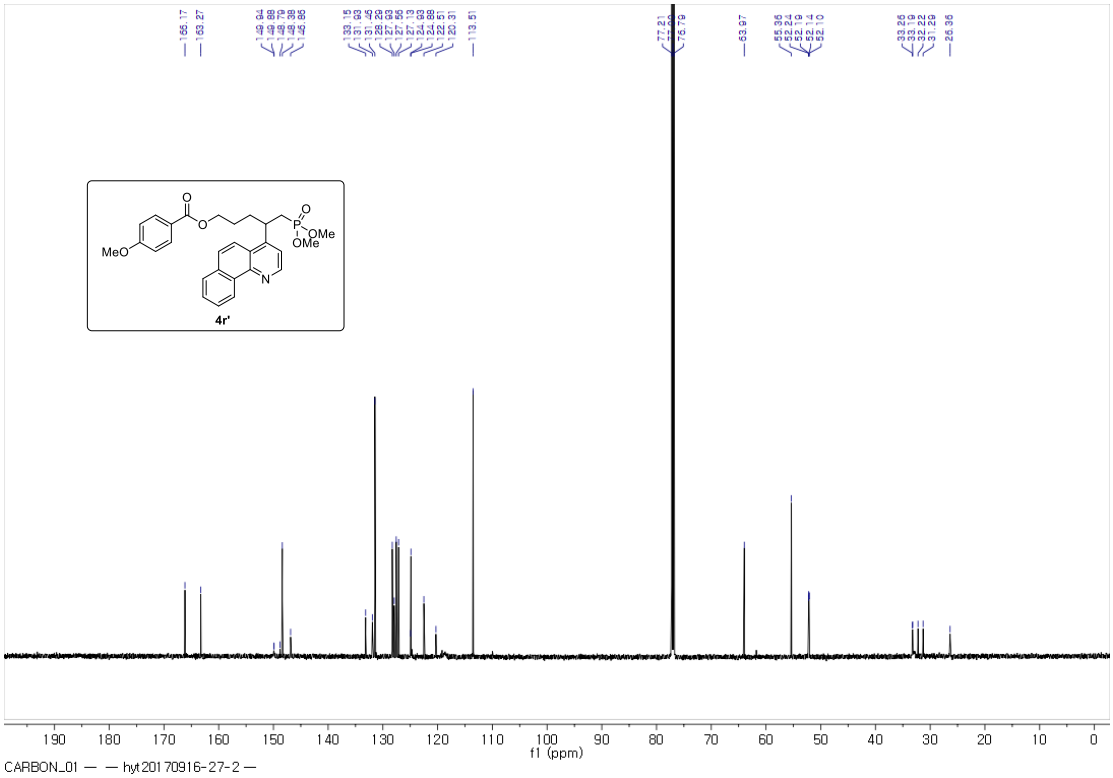


243 MHz, ^{31}P NMR in $CDCl_3$

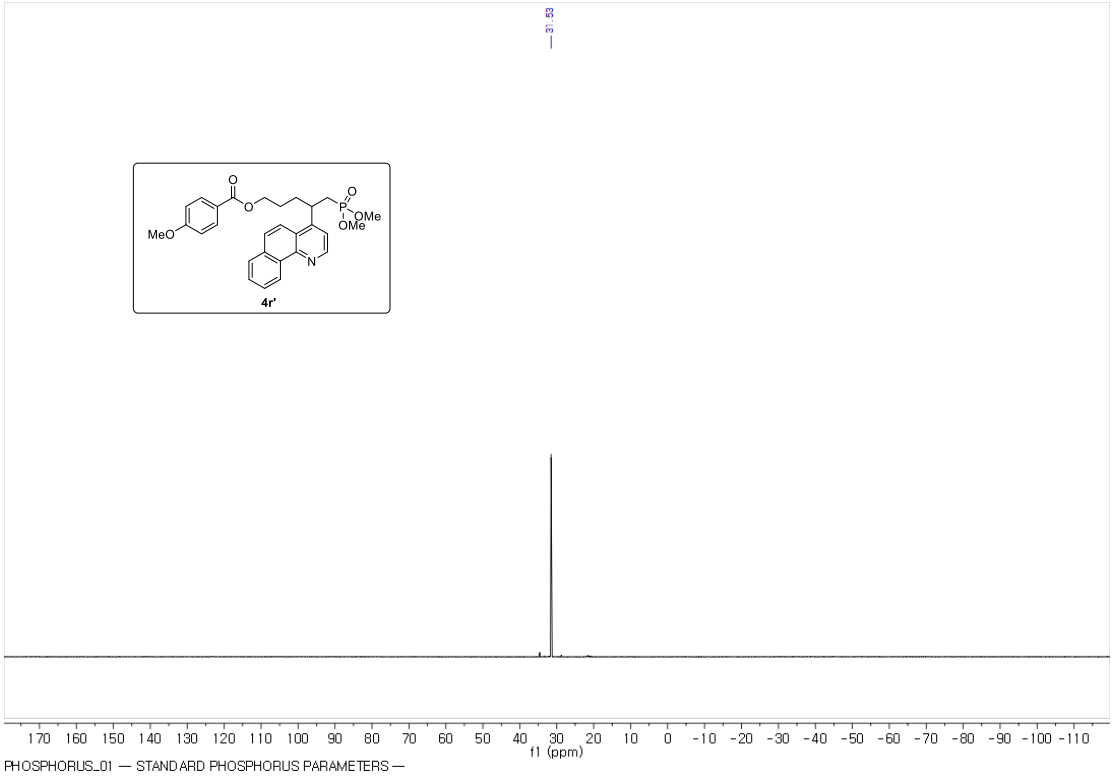
4-(benzo[h]quinolin-4-yl)-5-(dimethoxyphosphoryl)pentyl 4-methoxybenzoate (4r')



600 MHz, ^{1}H NMR in $CDCl_3$

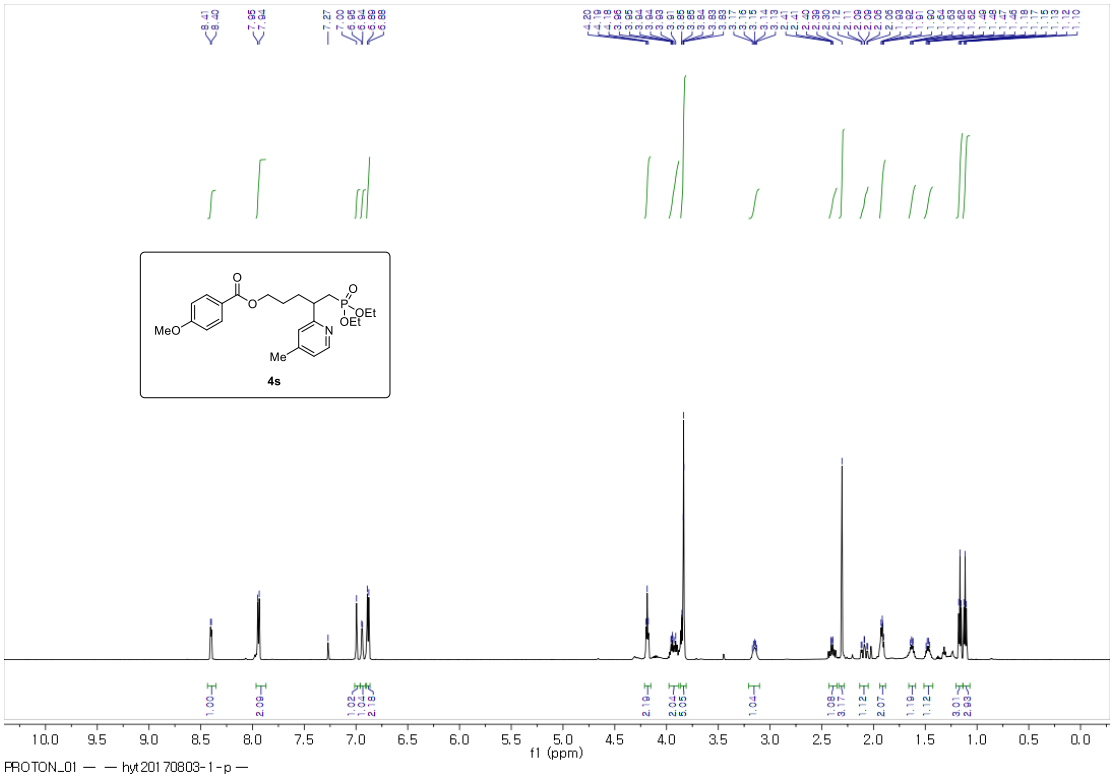


150 MHz, ^{13}C NMR in $CDCl_3$

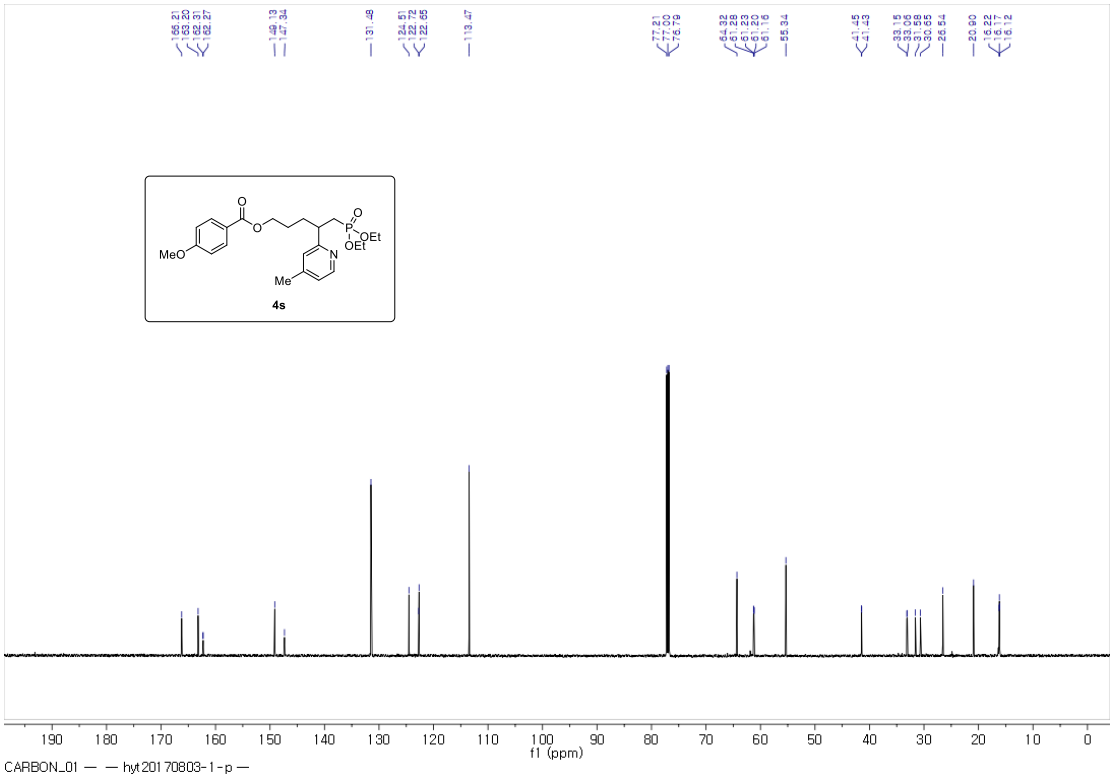


243 MHz, ^{31}P NMR in $CDCl_3$

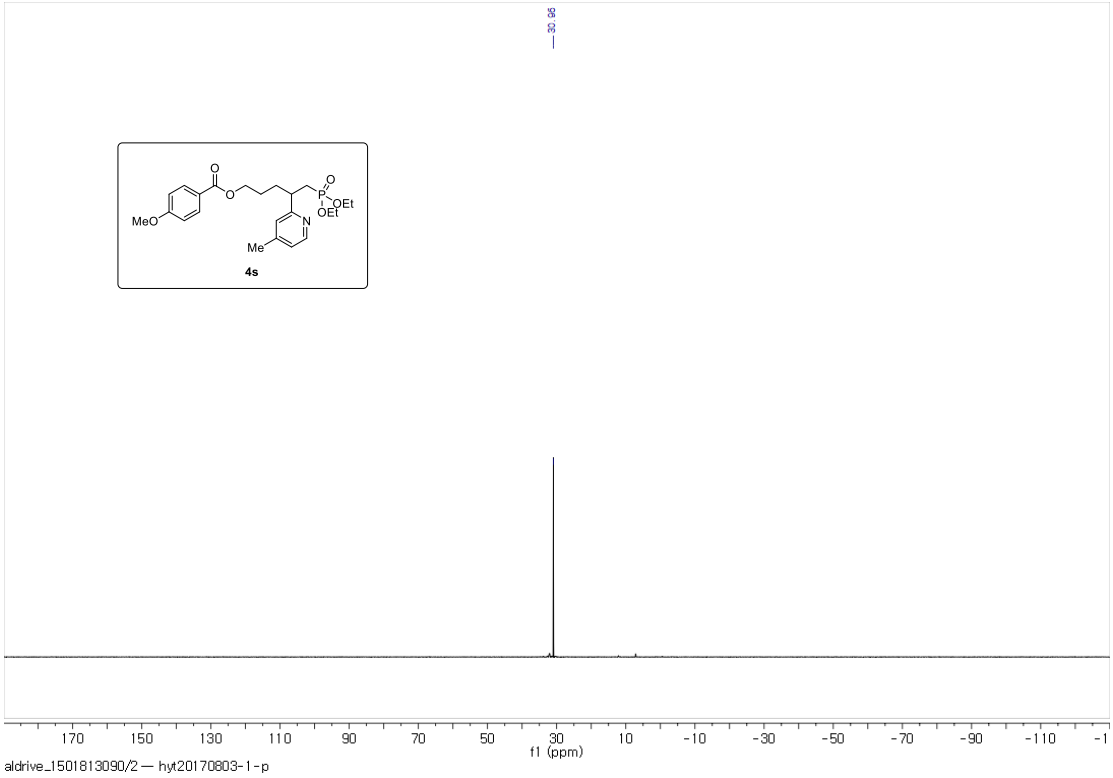
5-(diethoxyphosphoryl)-4-(4-methylpyridin-2-yl)pentyl 4-methoxybenzoate (4s)



600 MHz, ^{1}H NMR in $CDCl_3$

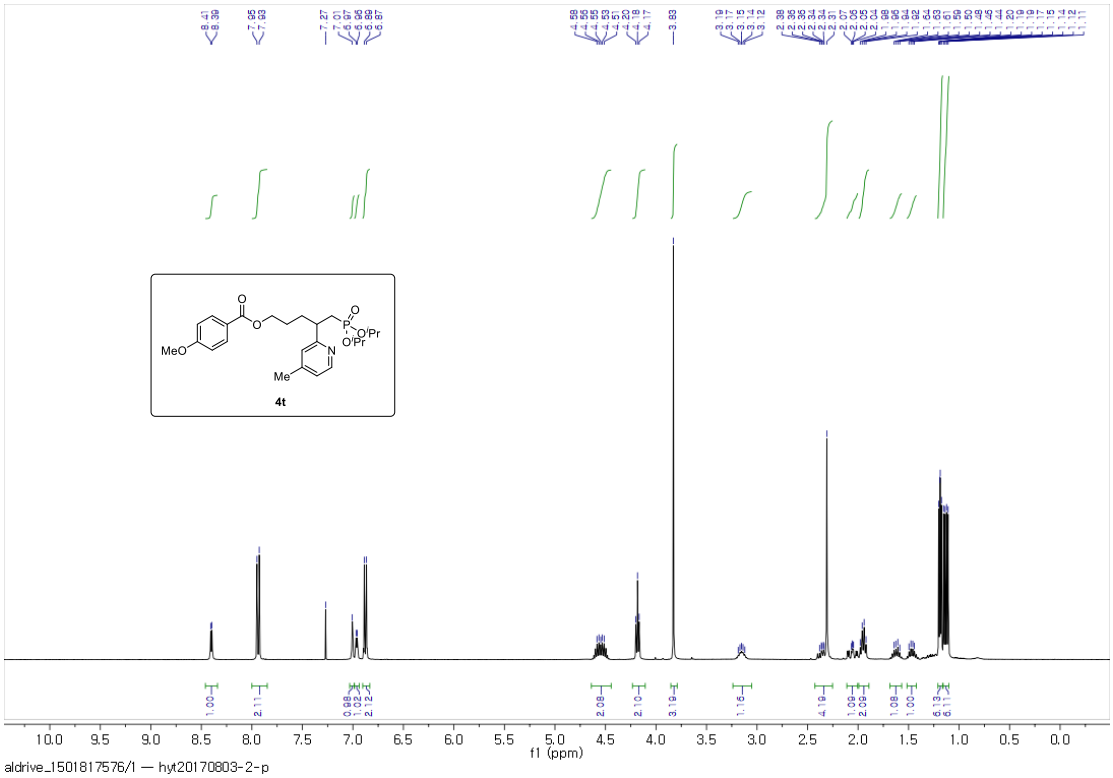


150 MHz, ^{13}C NMR in $CDCl_3$

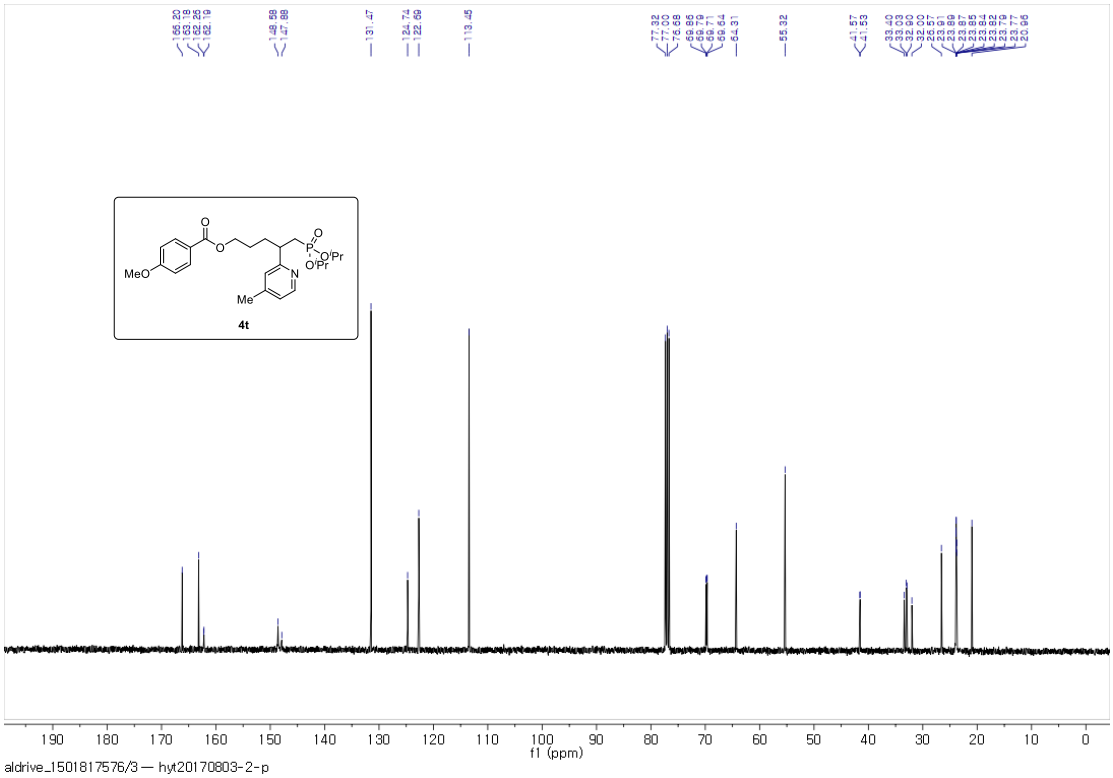


162 MHz, ^{31}P NMR in $CDCl_3$

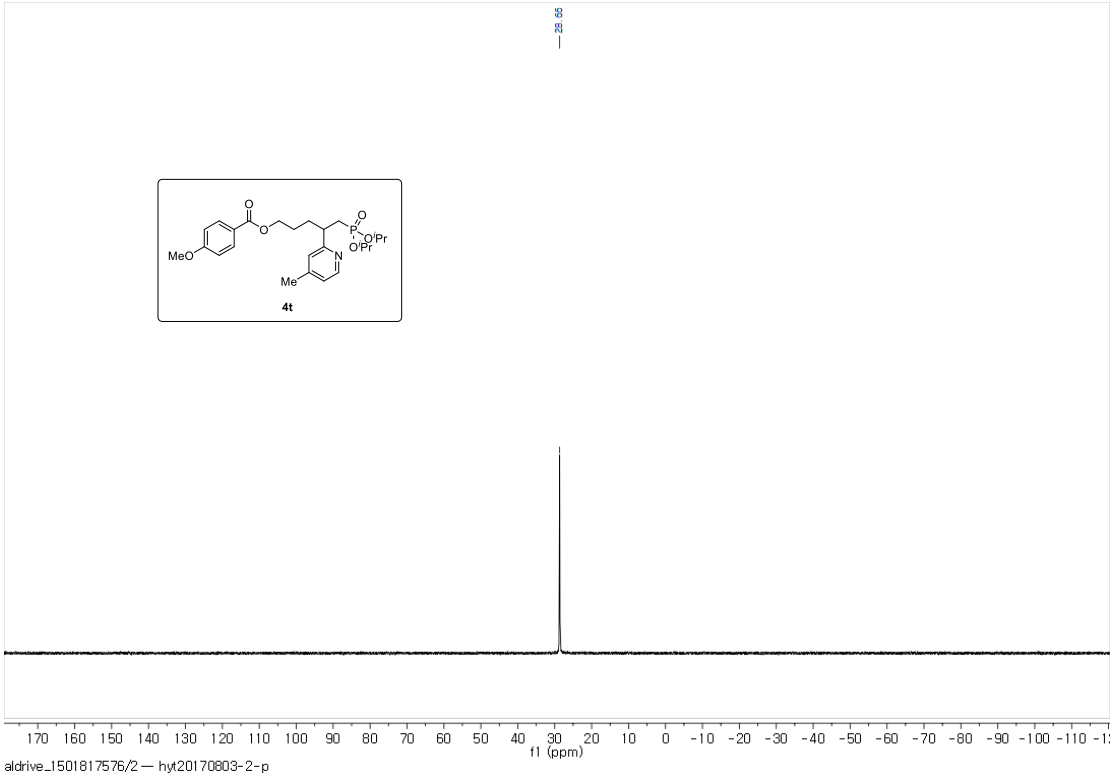
5-(diisopropoxyphosphoryl)-4-(4-methylpyridin-2-yl)pentyl 4-methoxybenzoate (4t)



400 MHz, ^{1}H NMR in $CDCl_3$

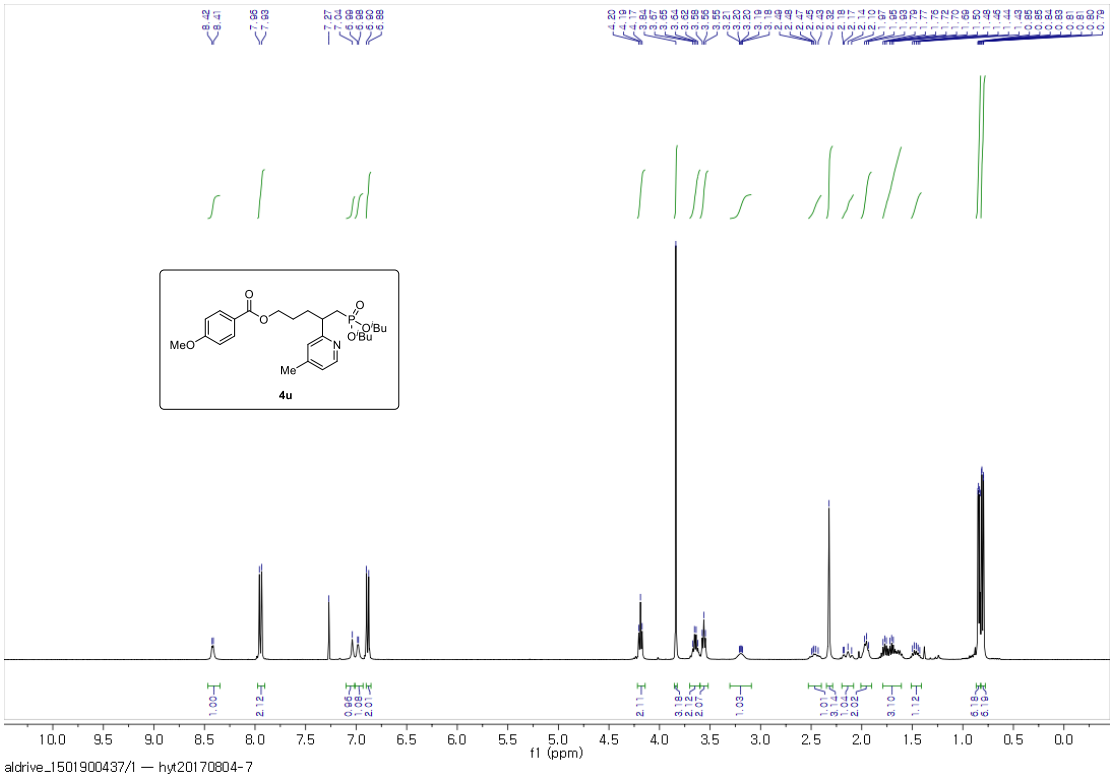


100 MHz, ^{13}C NMR in $CDCl_3$

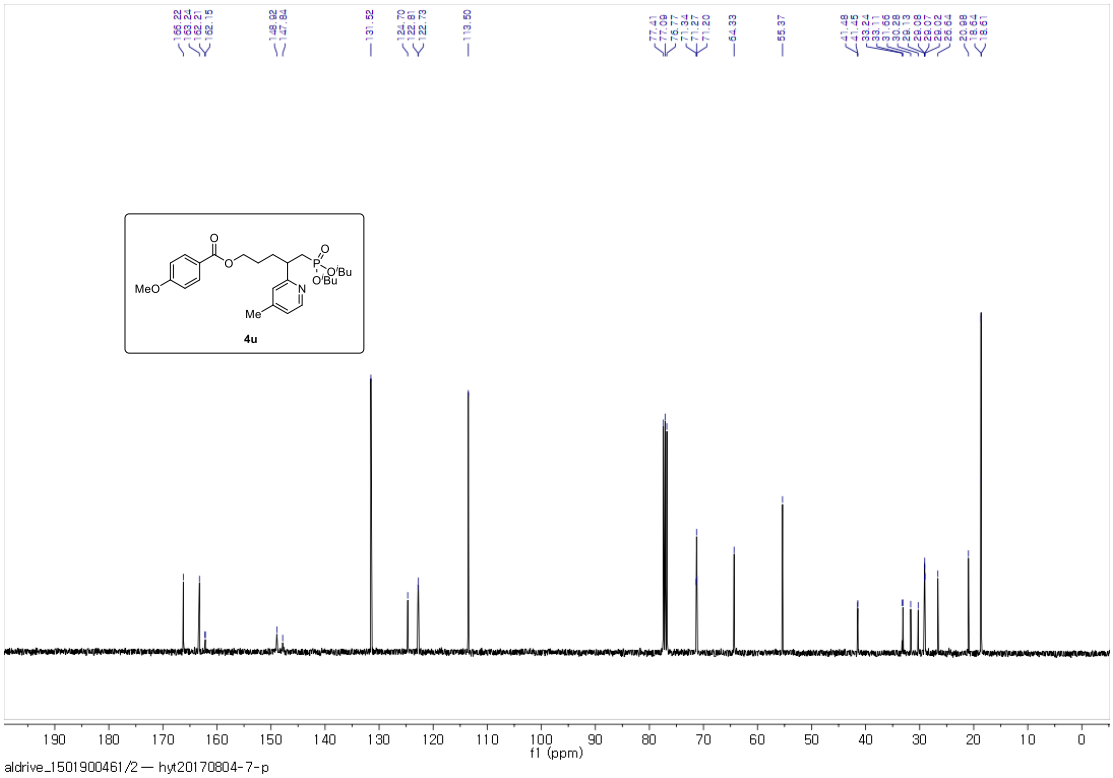


162 MHz, ^{31}P NMR in $CDCl_3$

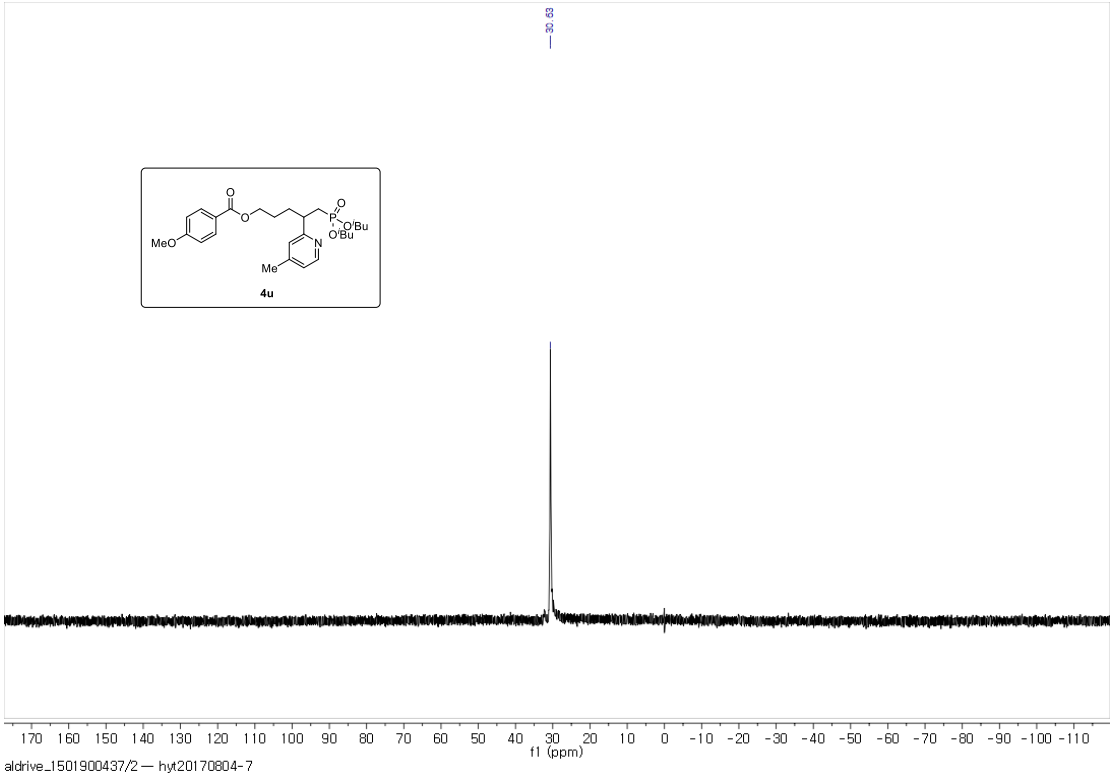
5-(diisobutoxyphosphoryl)-4-(4-methylpyridin-2-yl)pentyl 4-methoxybenzoate (4u)



400 MHz, ^{1}H NMR in $CDCl_3$

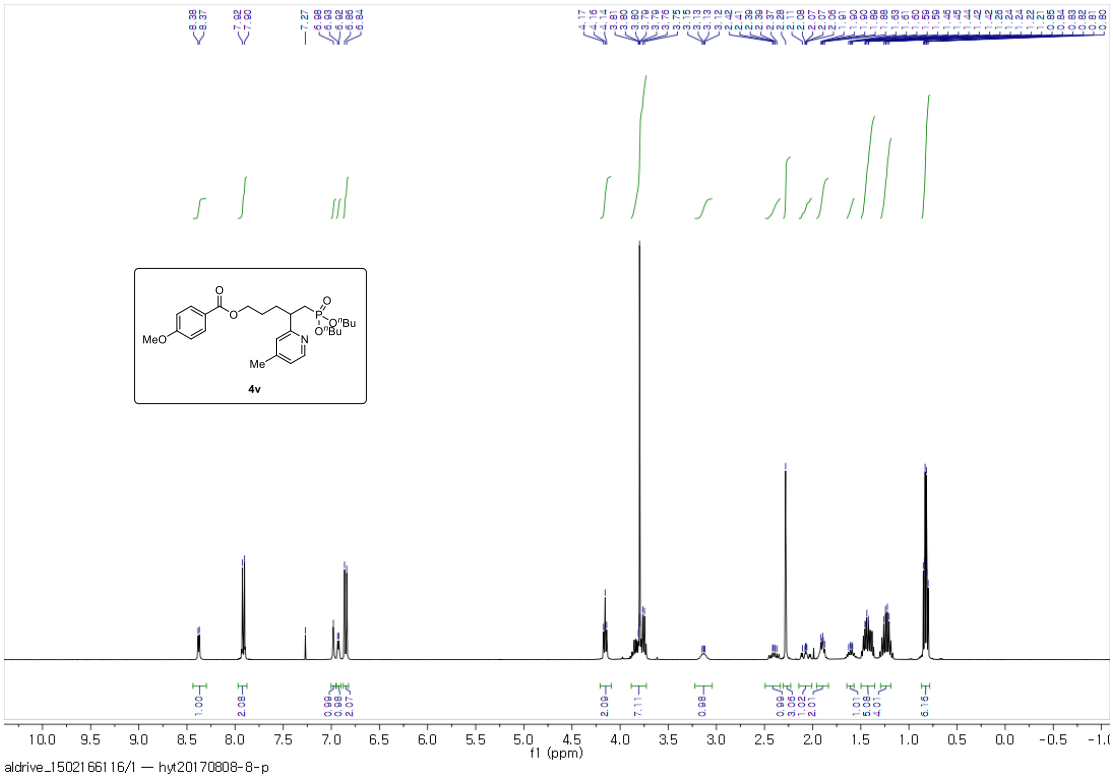


100 MHz, ^{13}C NMR in $CDCl_3$

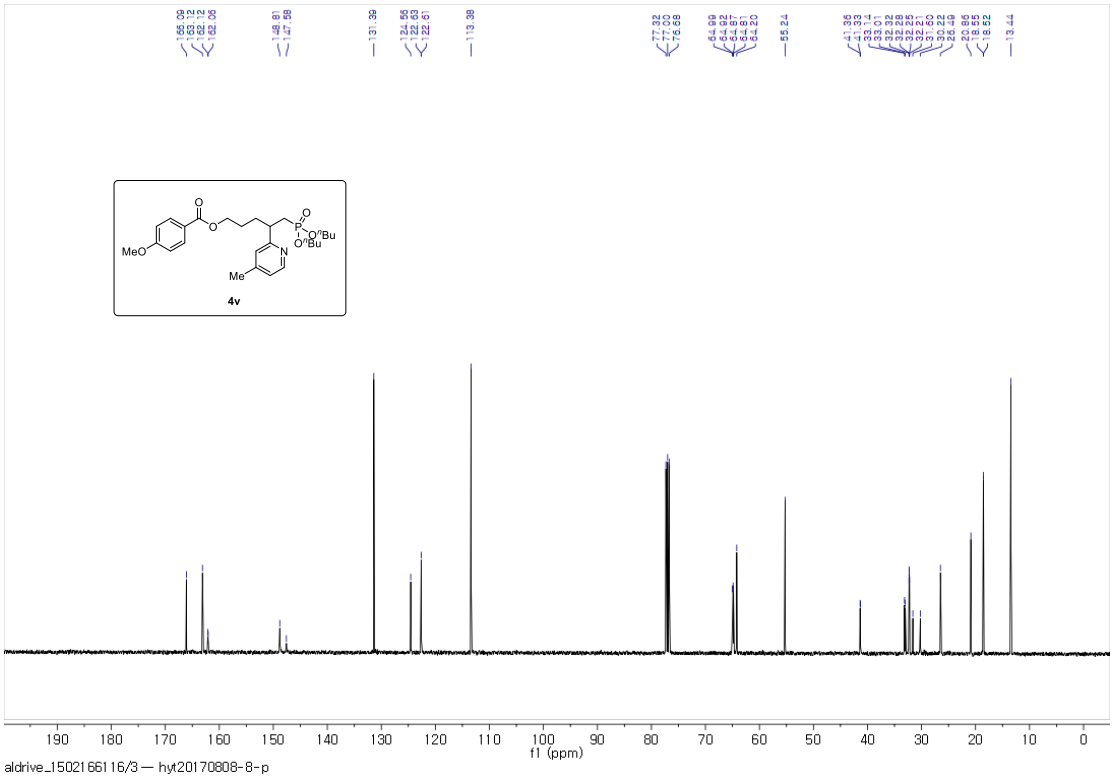


162 MHz, ^{31}P NMR in $CDCl_3$

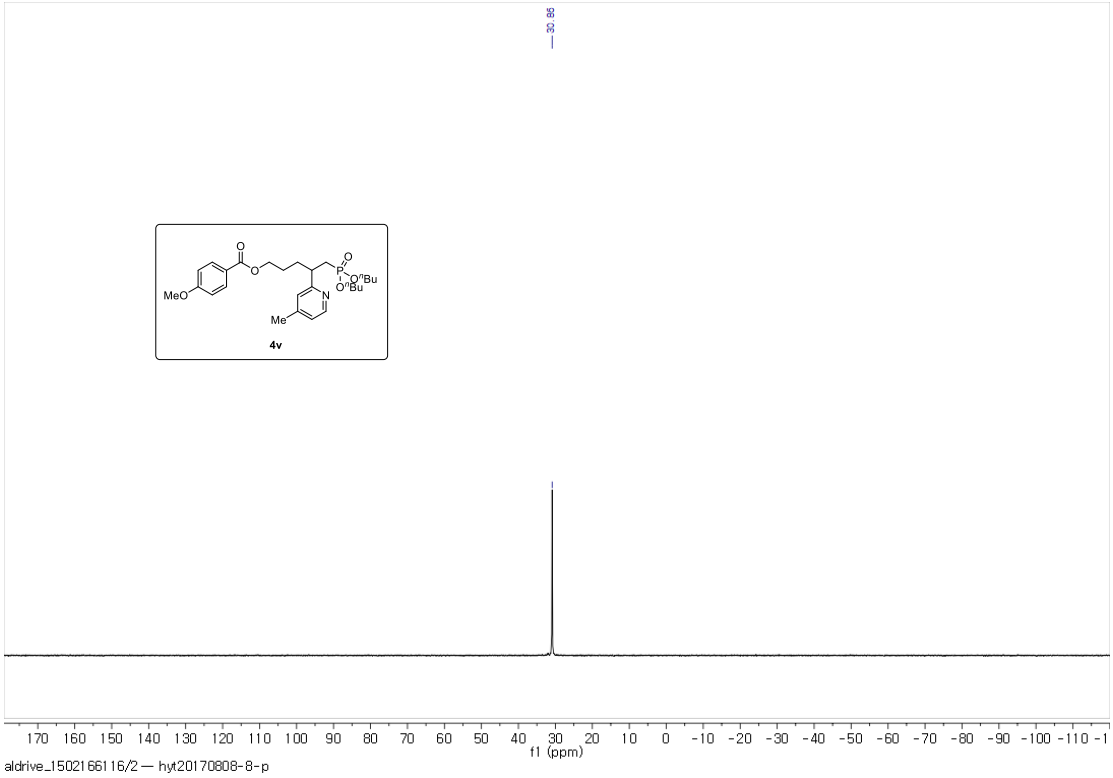
5-(dibutoxyphosphoryl)-4-(4-methylpyridin-2-yl)pentyl 4-methoxybenzoate (4v)



400 MHz, ^{1}H NMR in $CDCl_3$

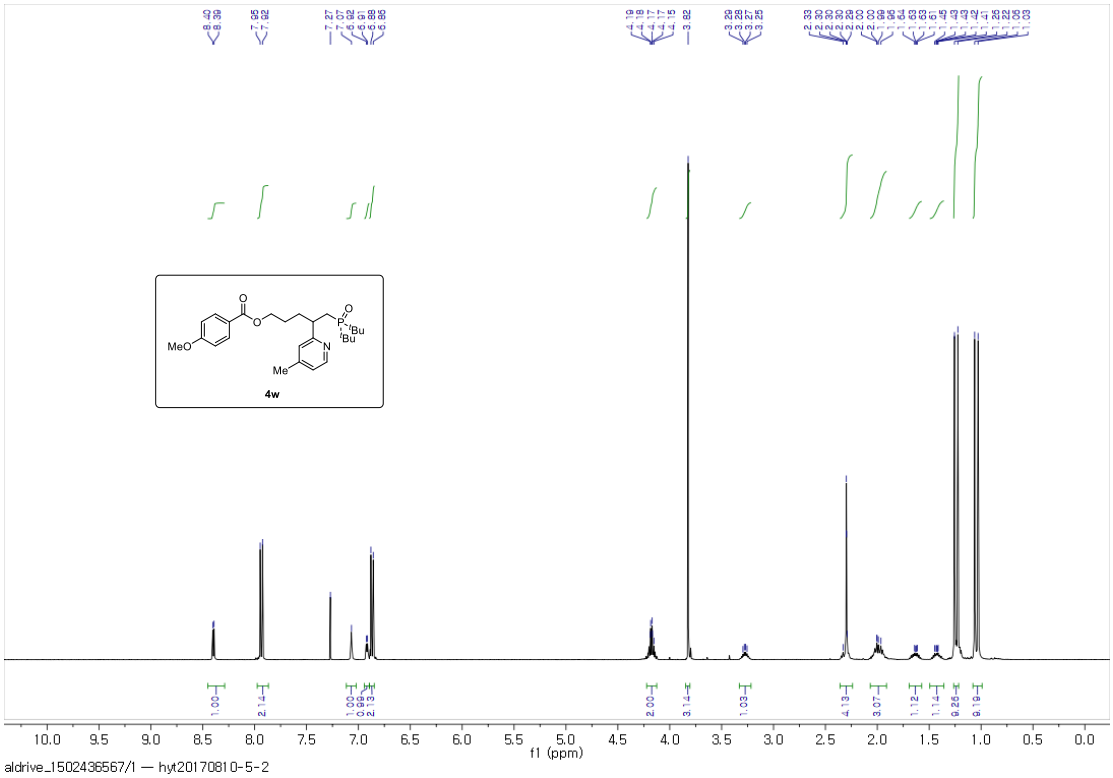


100 MHz, ^{13}C NMR in $CDCl_3$

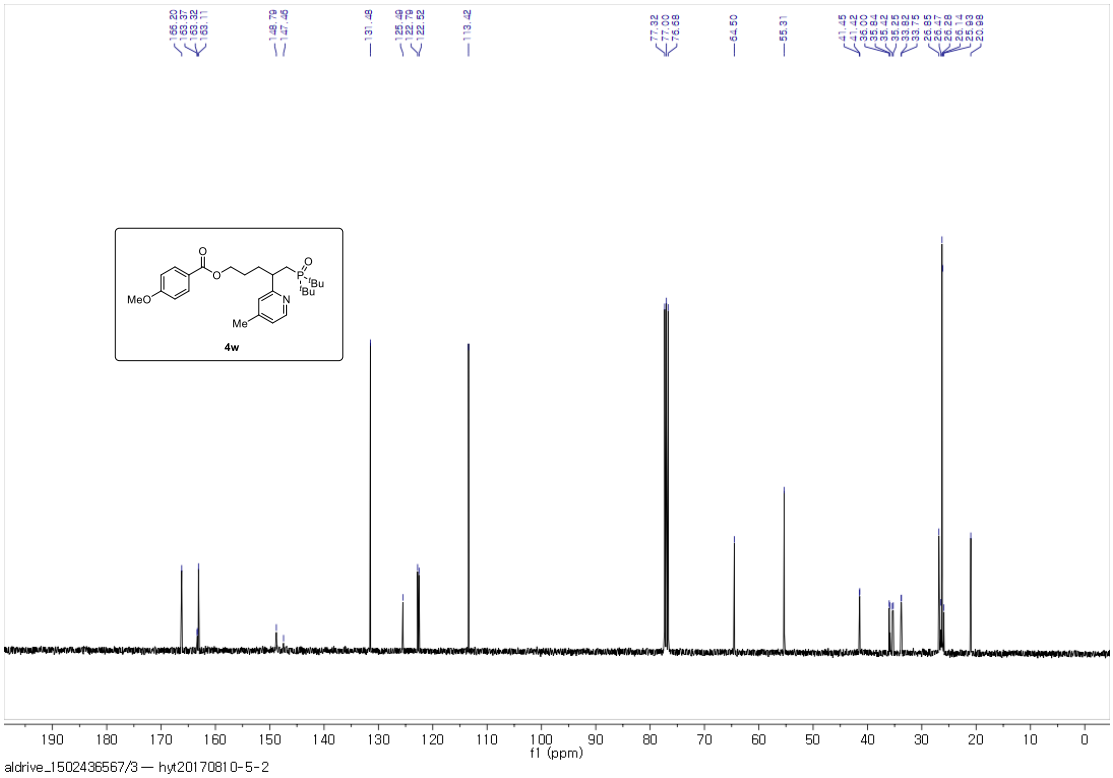


162 MHz, ^{31}P NMR in $CDCl_3$

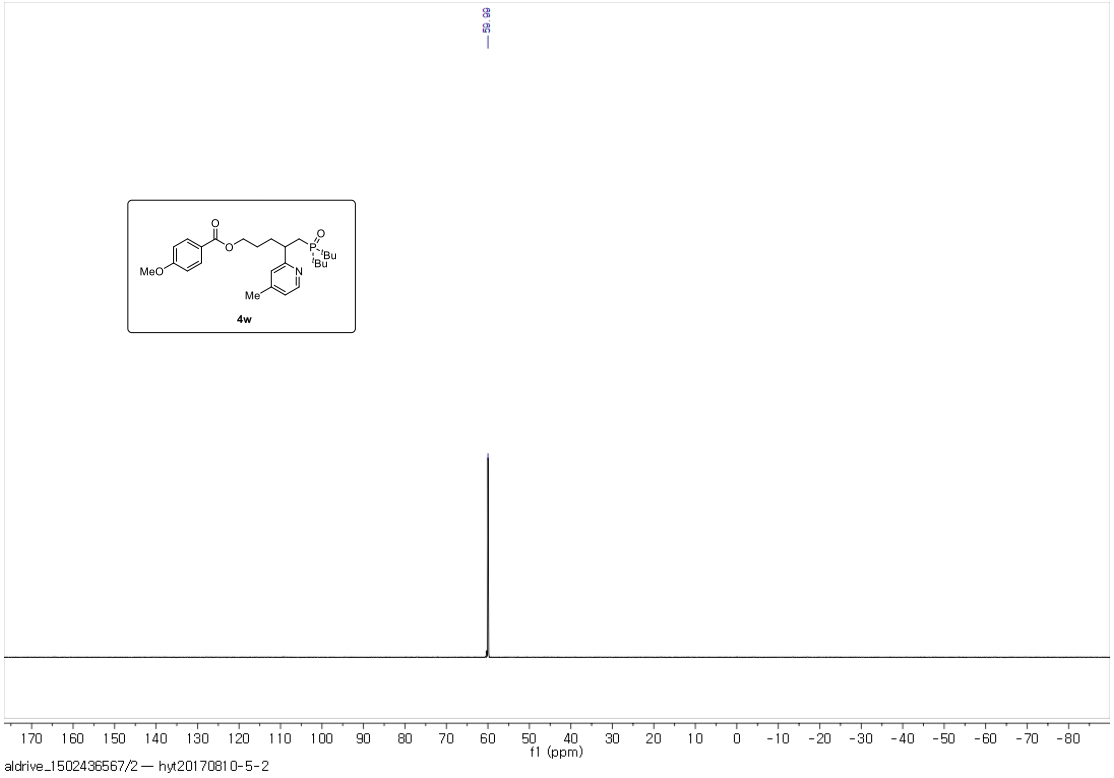
5-(di-tert-butylphosphoryl)-4-(4-methylpyridin-2-yl)pentyl 4-methoxybenzoate (4w)



400 MHz, ^{1}H NMR in $CDCl_3$

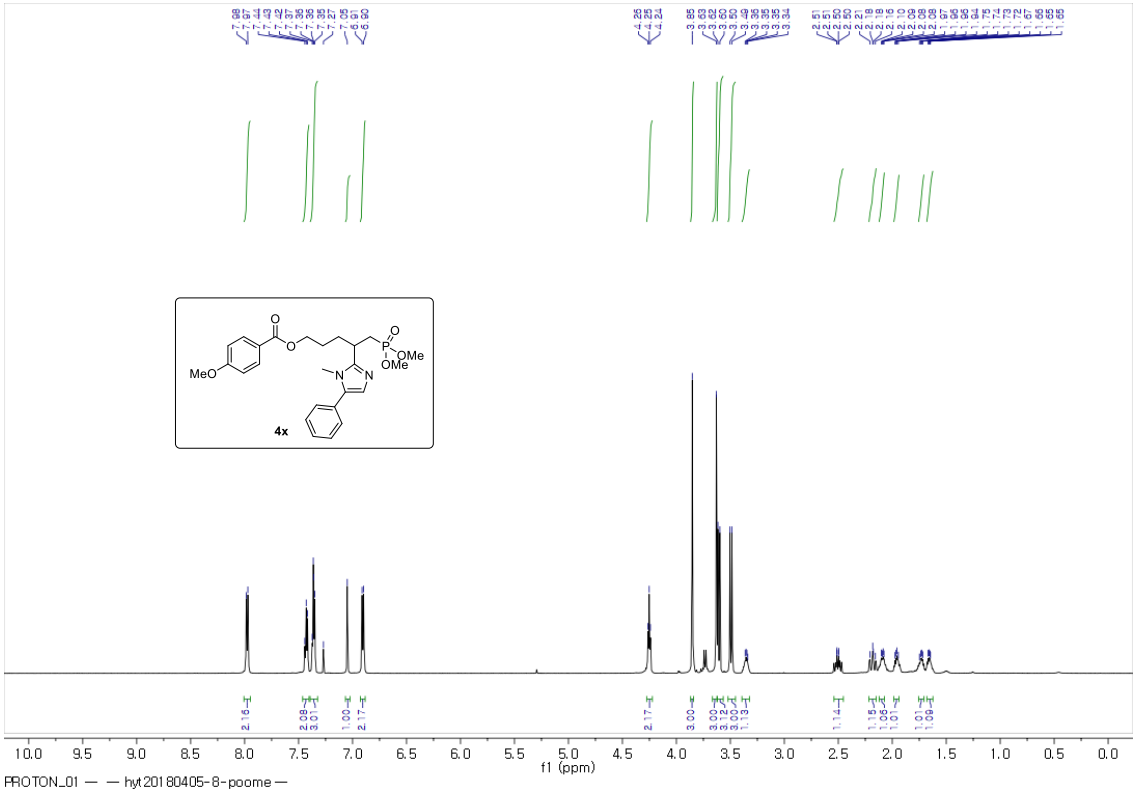


100 MHz, ^{13}C NMR in $CDCl_3$

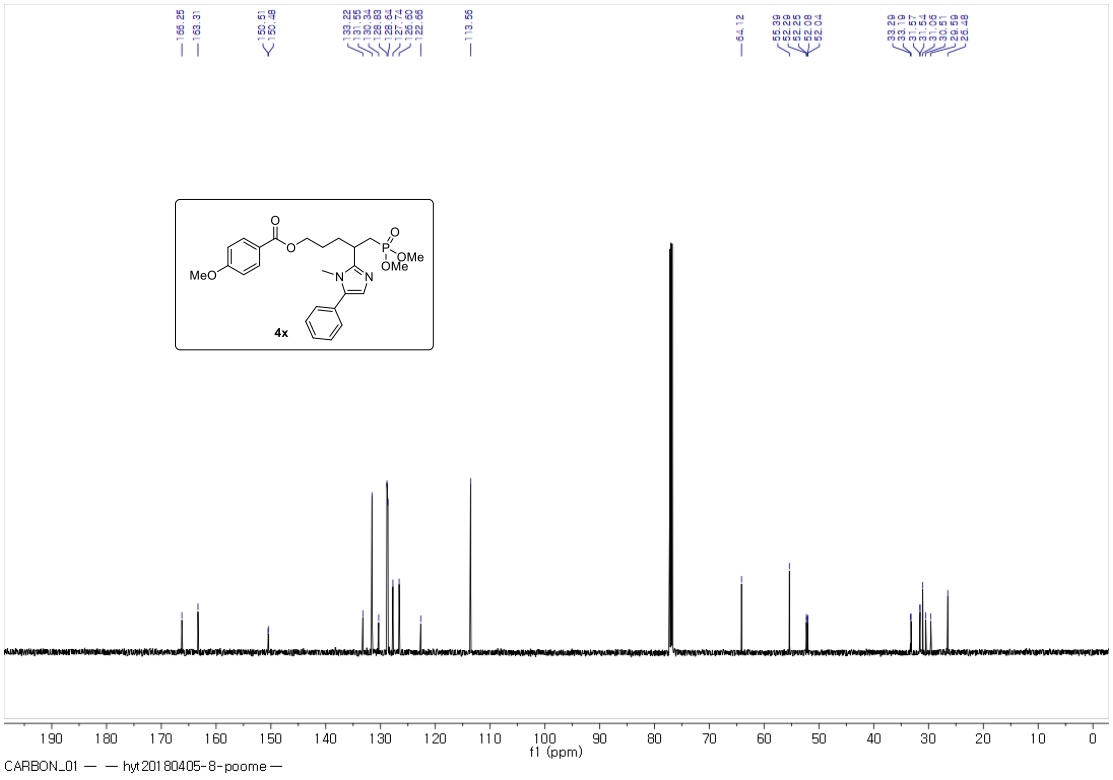


162 MHz, ^{31}P NMR in $CDCl_3$

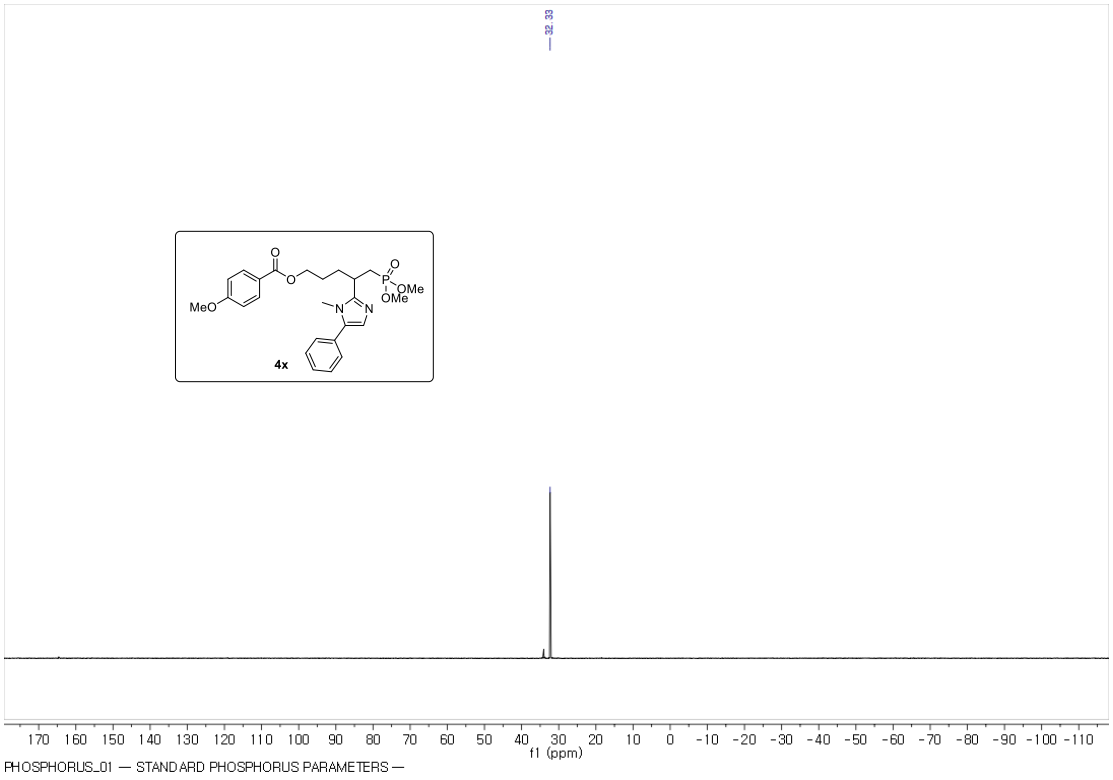
5-(dimethoxyphosphoryl)-4-(1-methyl-5-phenyl-1H-imidazol-2-yl)pentyl 4-methoxybenzoate (4x)



600 MHz, ^{1}H NMR in $CDCl_3$

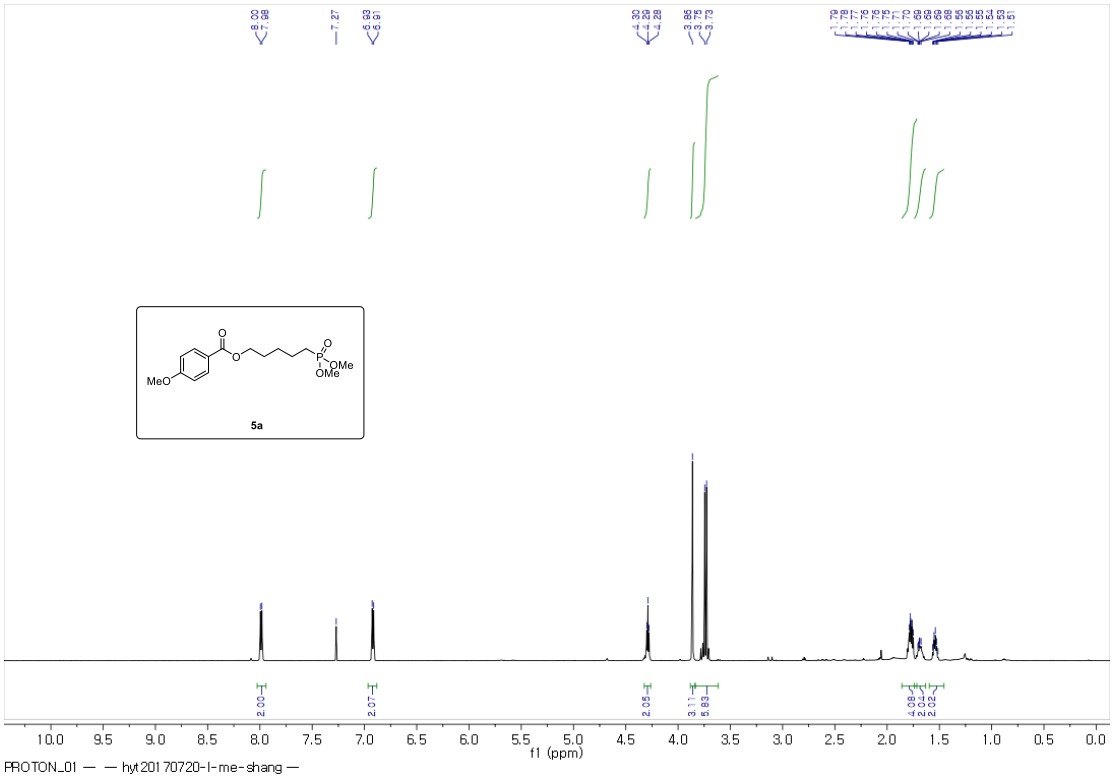


150 MHz, ^{13}C NMR in $CDCl_3$

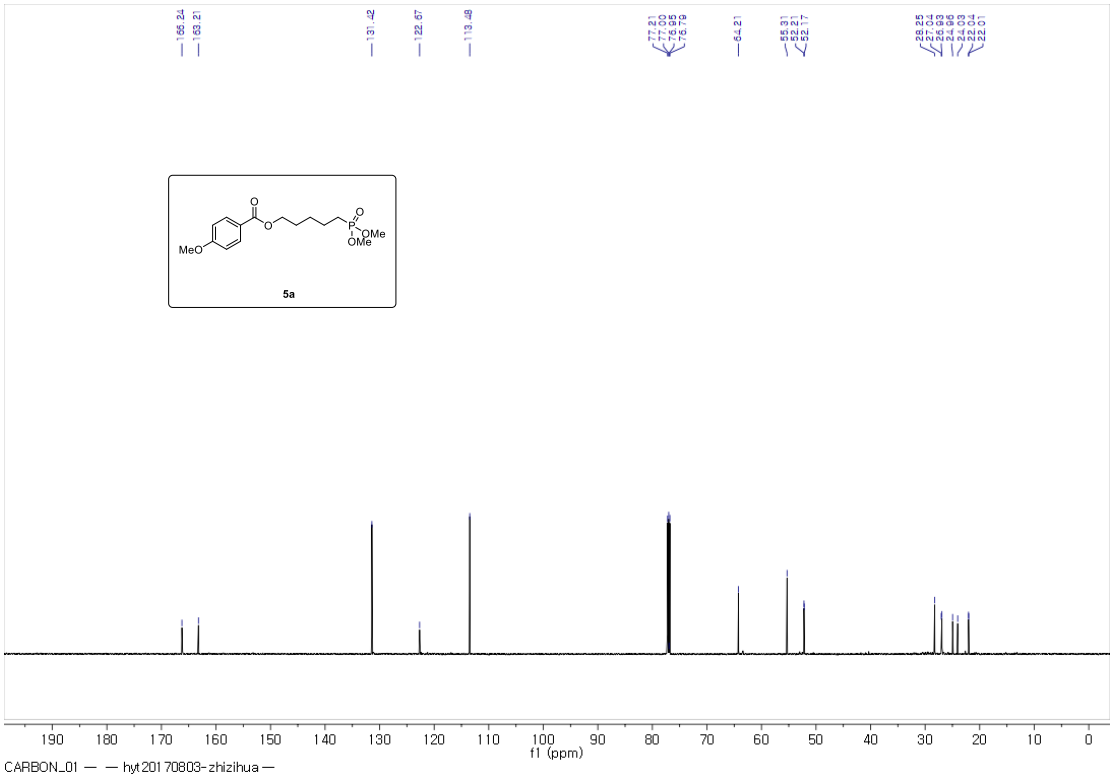


243 MHz, ^{31}P NMR in $CDCl_3$

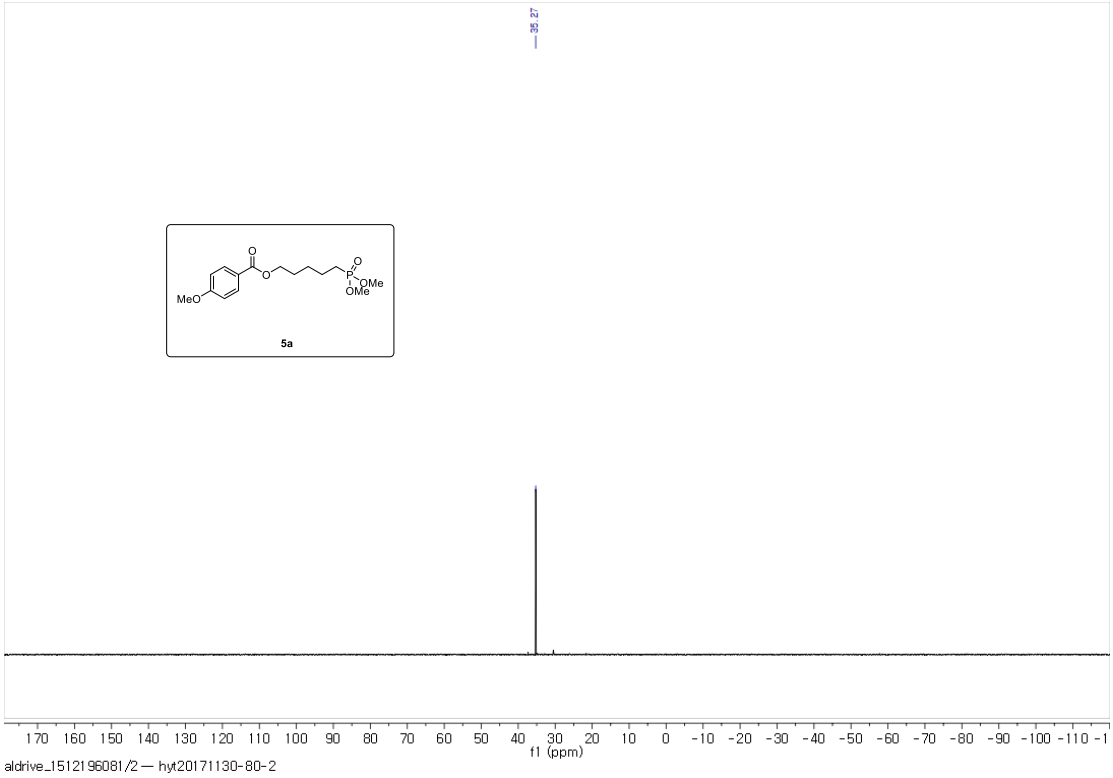
5-(dimethoxyphosphoryl)pentyl 4-methoxybenzoate (5a)



600 MHz, ^{1}H NMR in $CDCl_3$

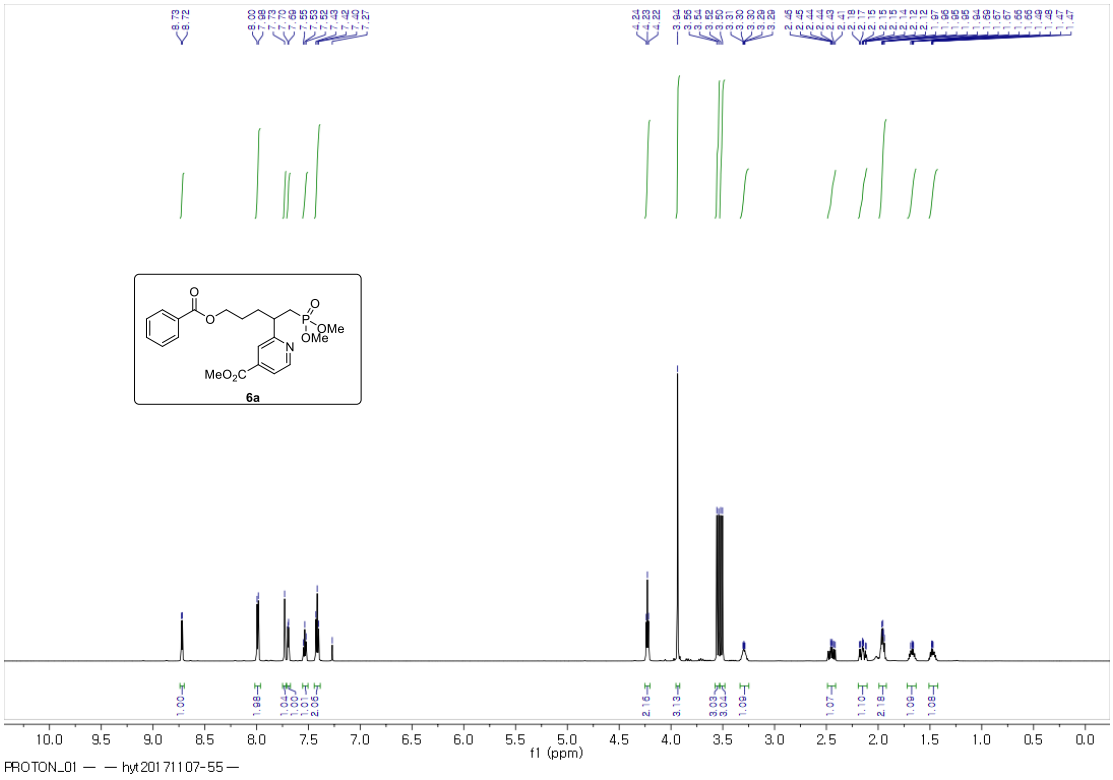


150 MHz, ^{13}C NMR in $CDCl_3$

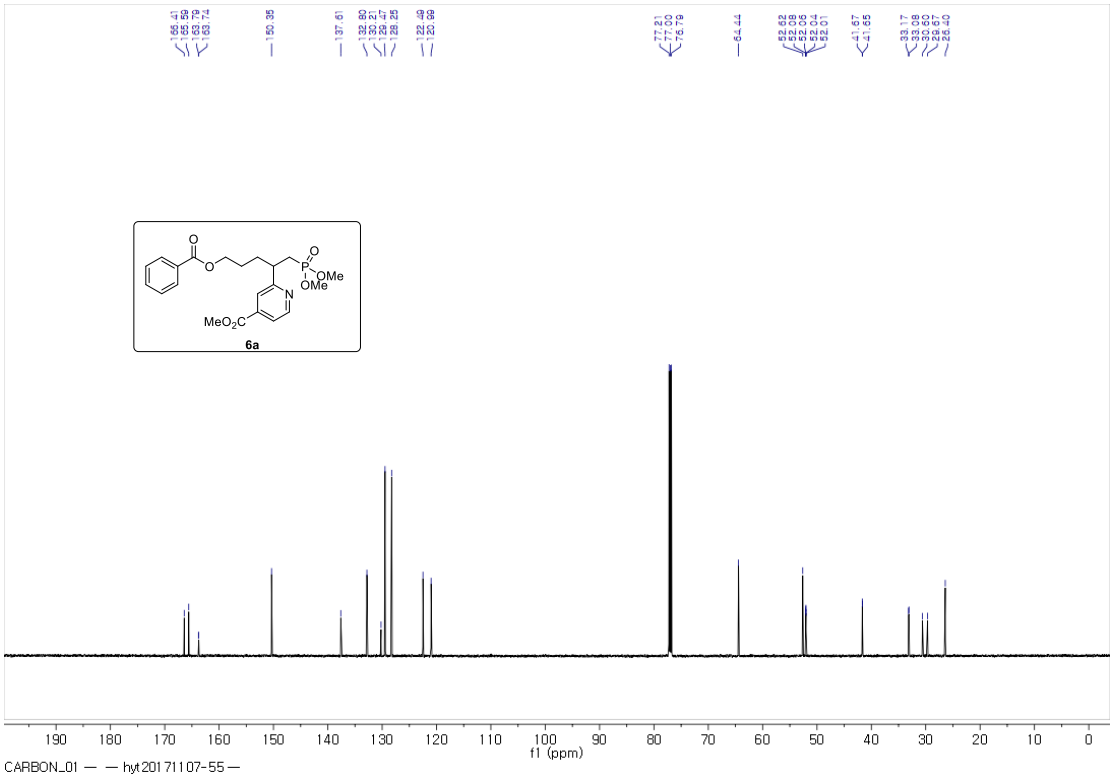


162 MHz, ^{31}P NMR in $CDCl_3$

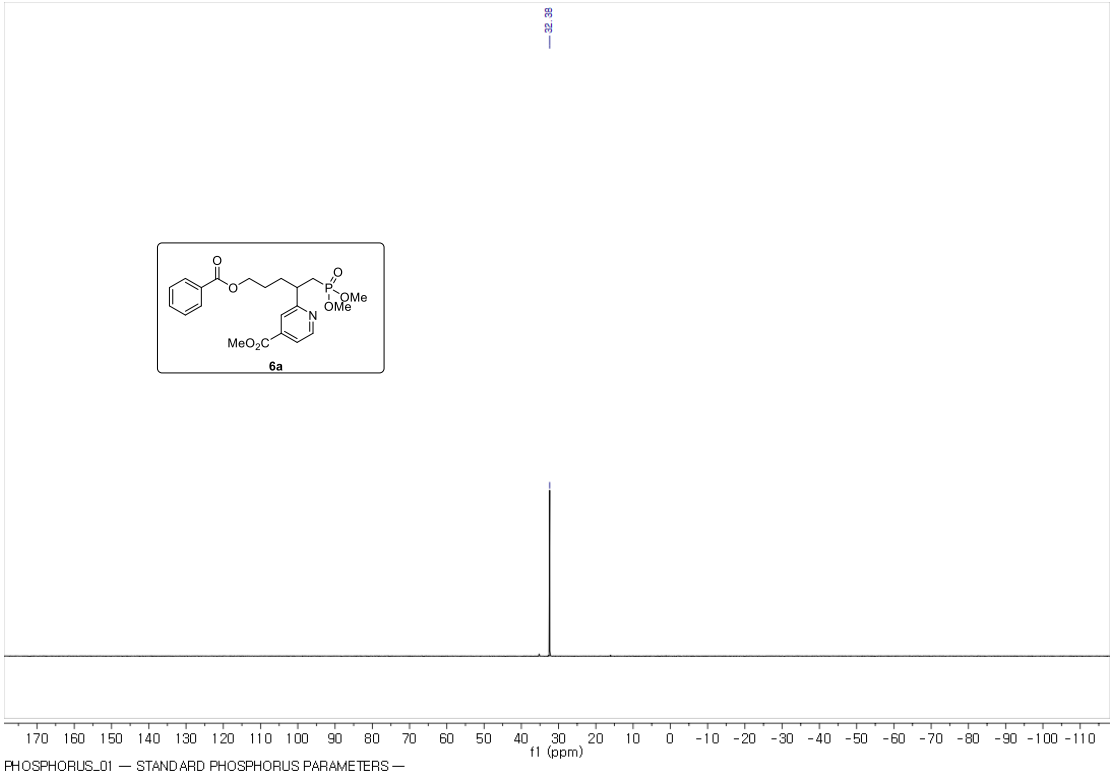
methyl 2-(5-(benzoyloxy)-1-(dimethoxyphosphoryl)pentan-2-yl)isonicotinate (6a)



600 MHz, ^{1}H NMR in $CDCl_3$

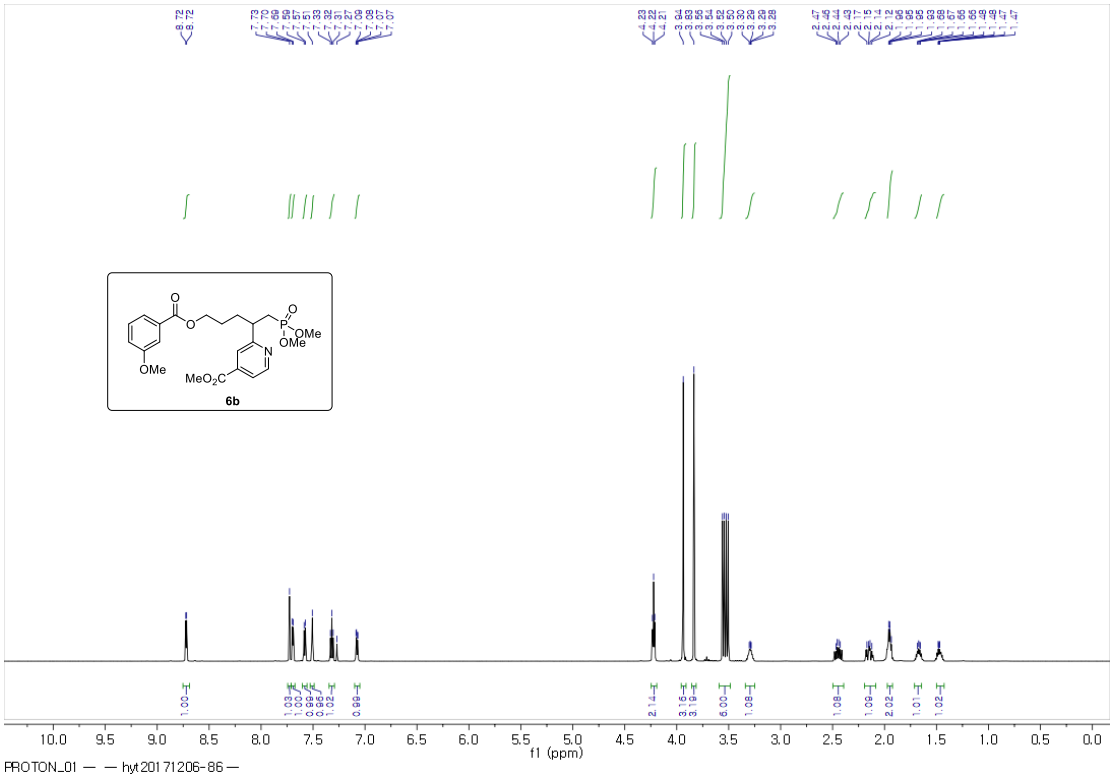


150 MHz, ^{13}C NMR in $CDCl_3$

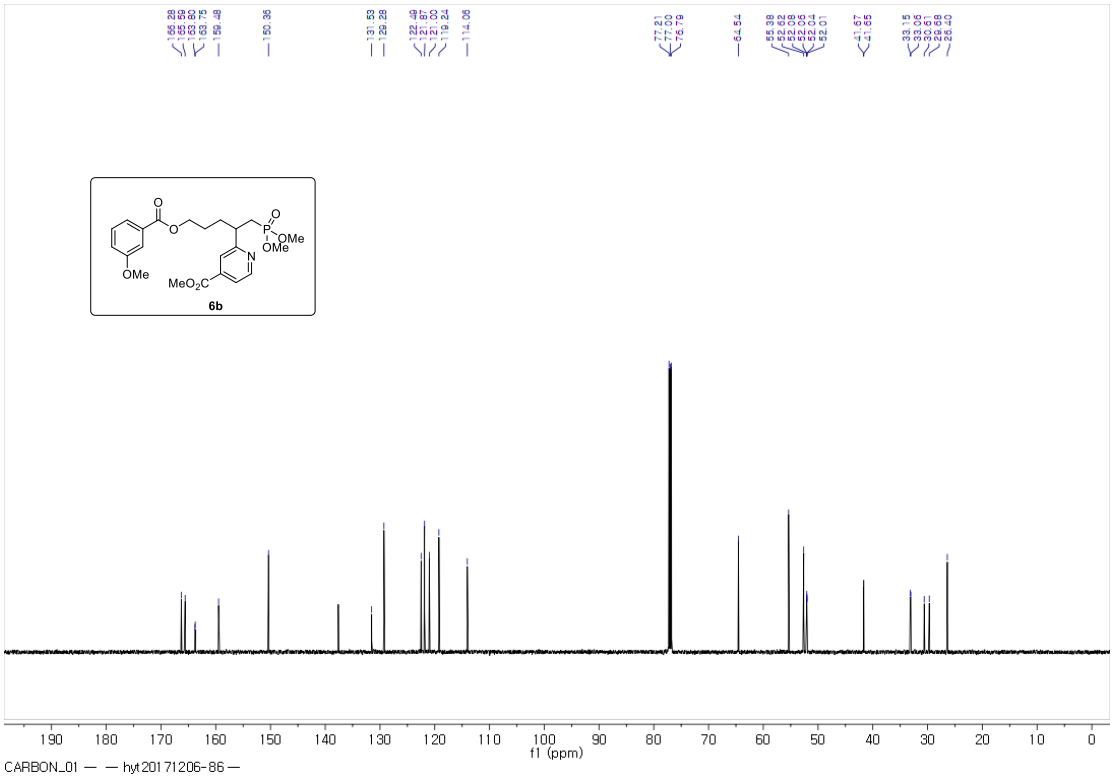


243 MHz, ^{31}P NMR in $CDCl_3$

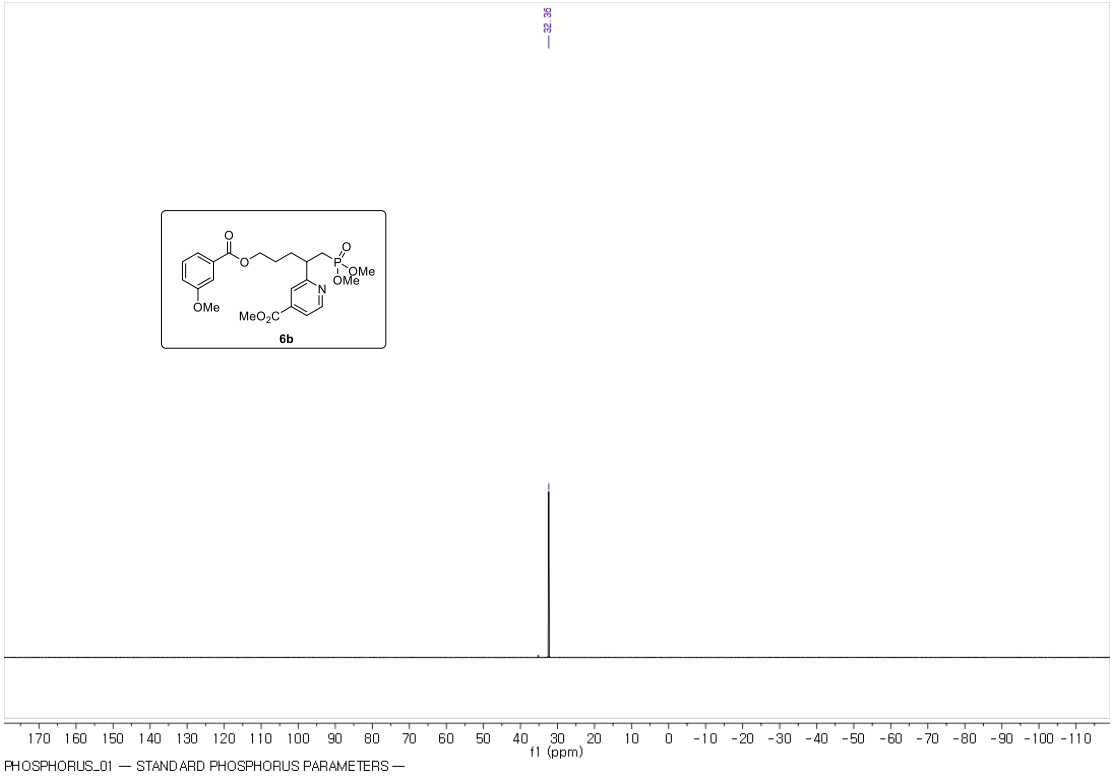
methyl 2-(1-(dimethoxyphosphoryl)-5-((3-methoxybenzoyl)oxy)pentan-2-yl)isonicotinate (6b)



600 MHz, ^{1}H NMR in $CDCl_3$

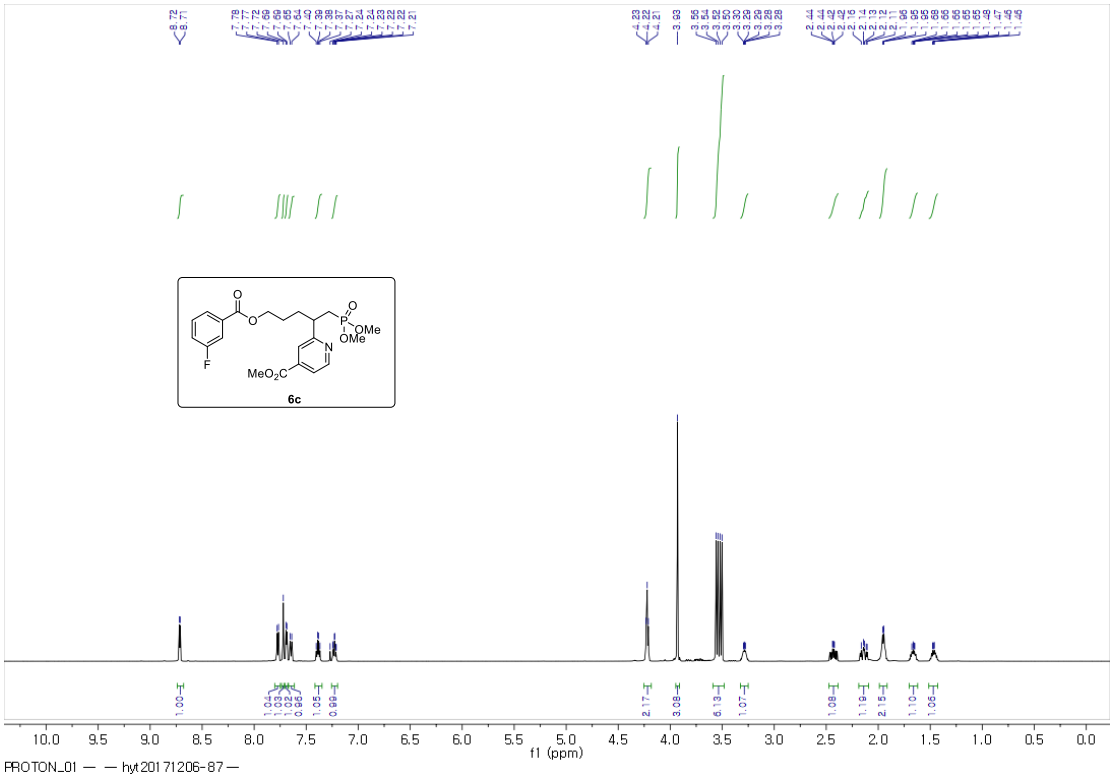


150 MHz, ^{13}C NMR in $CDCl_3$

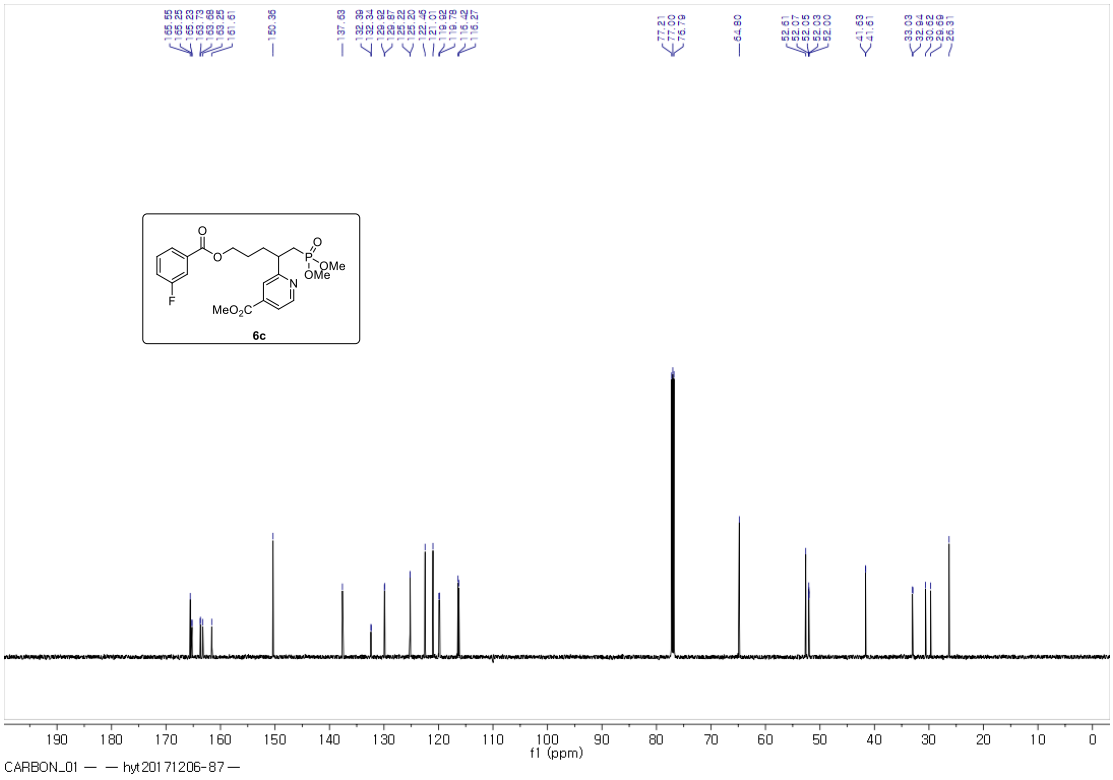


243 MHz, ^{31}P NMR in $CDCl_3$

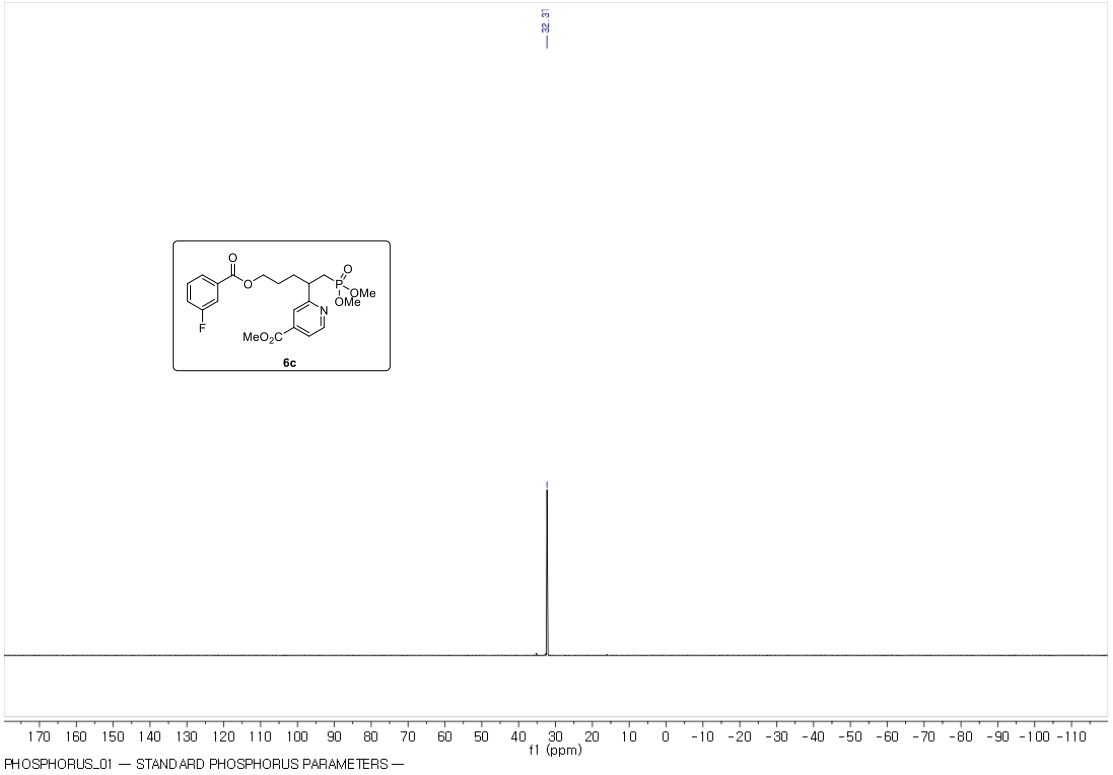
methyl 2-(1-(dimethoxyphosphoryl)-5-((3-fluorobenzoyl)oxy)pentan-2-yl)isonicotinate (6c)



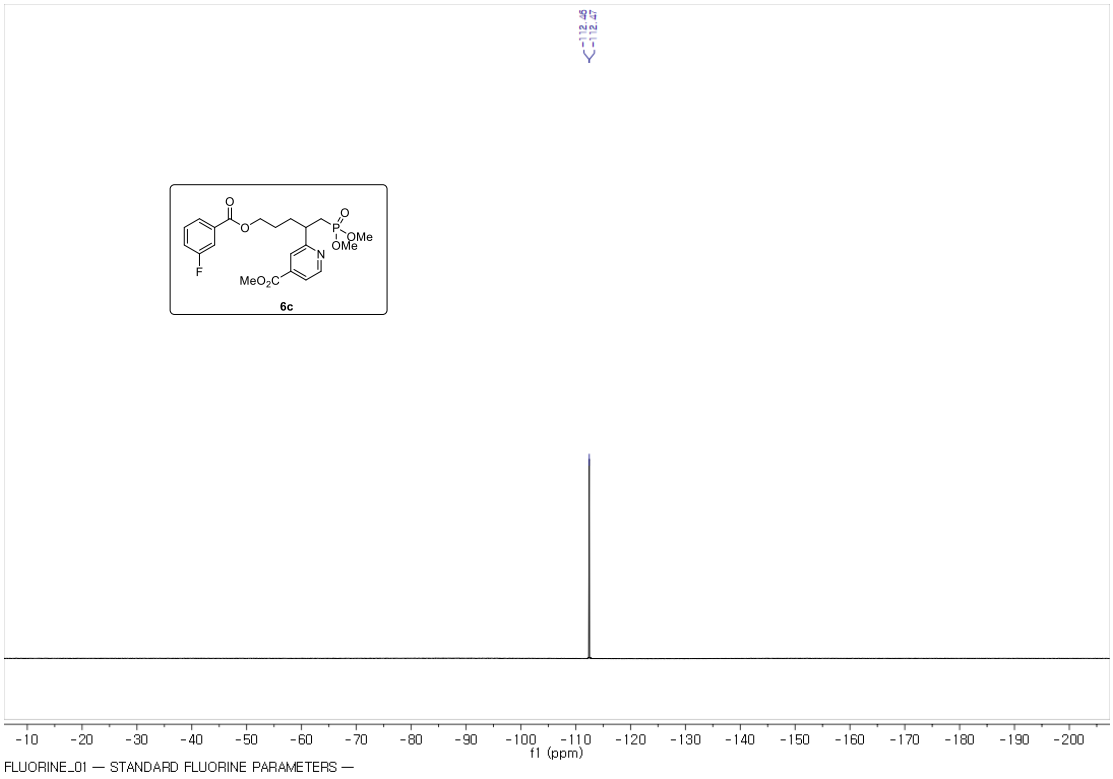
600 MHz, ^{1}H NMR in $CDCl_3$



150 MHz, ^{13}C NMR in $CDCl_3$

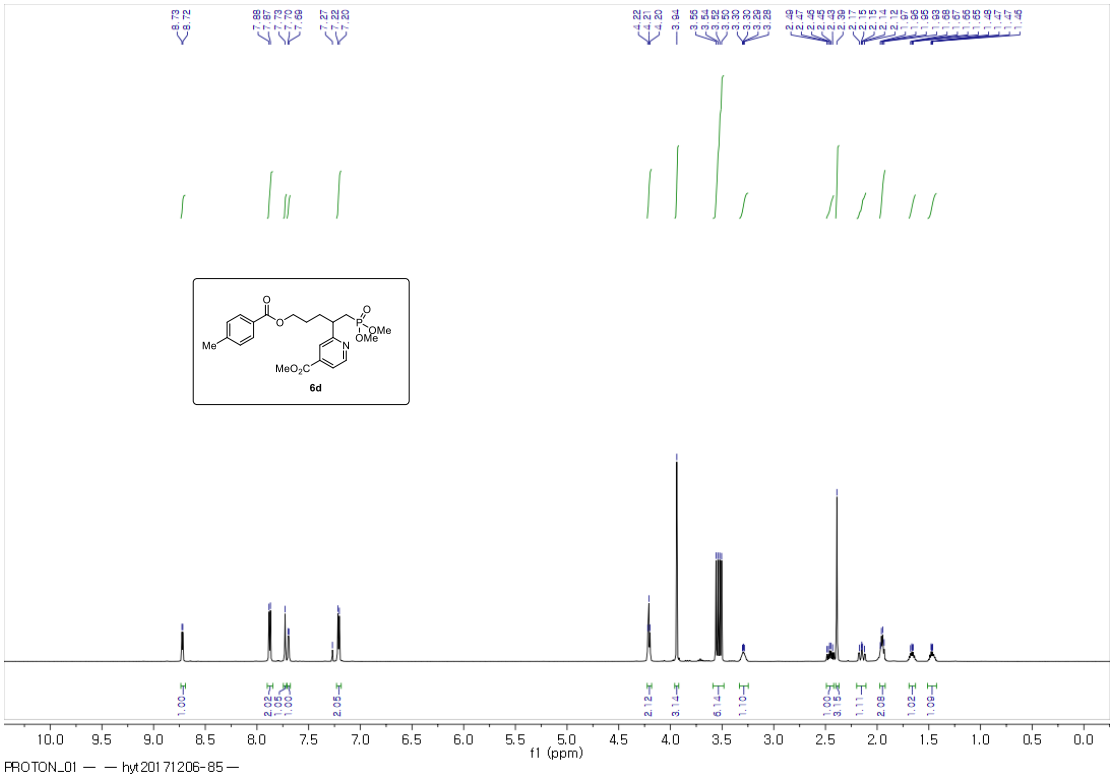


243 MHz, ^{31}P NMR in $CDCl_3$

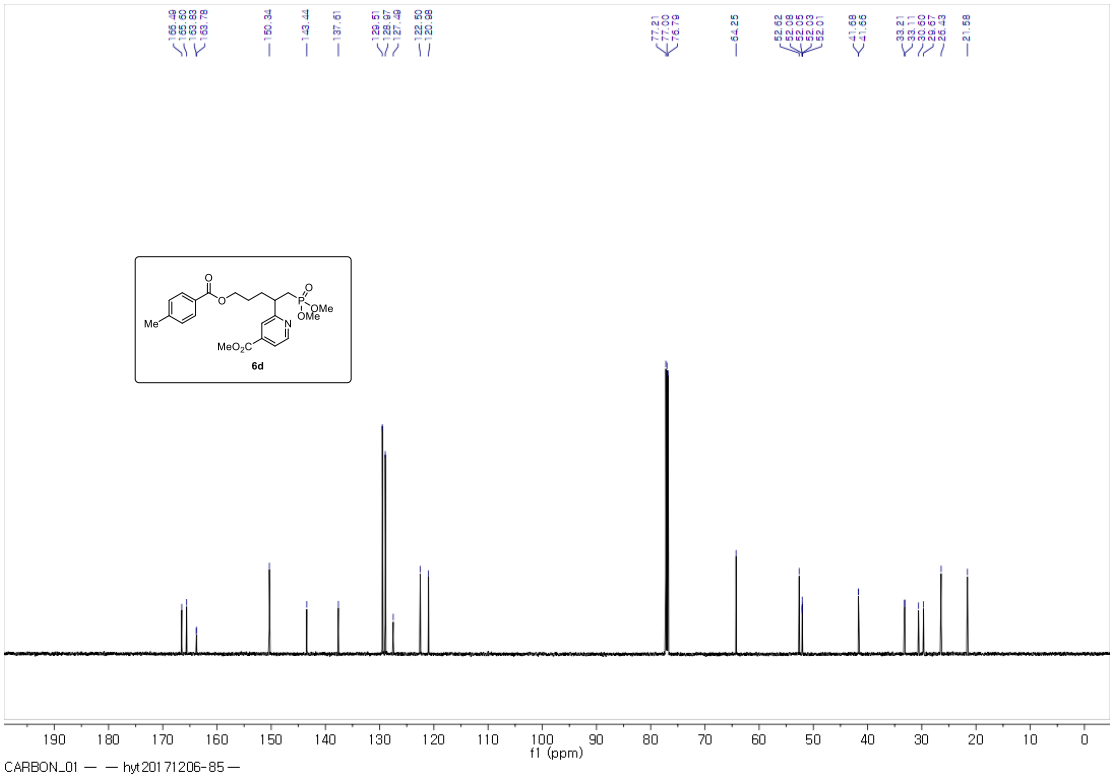


564 MHz, ^{19}F NMR in $CDCl_3$

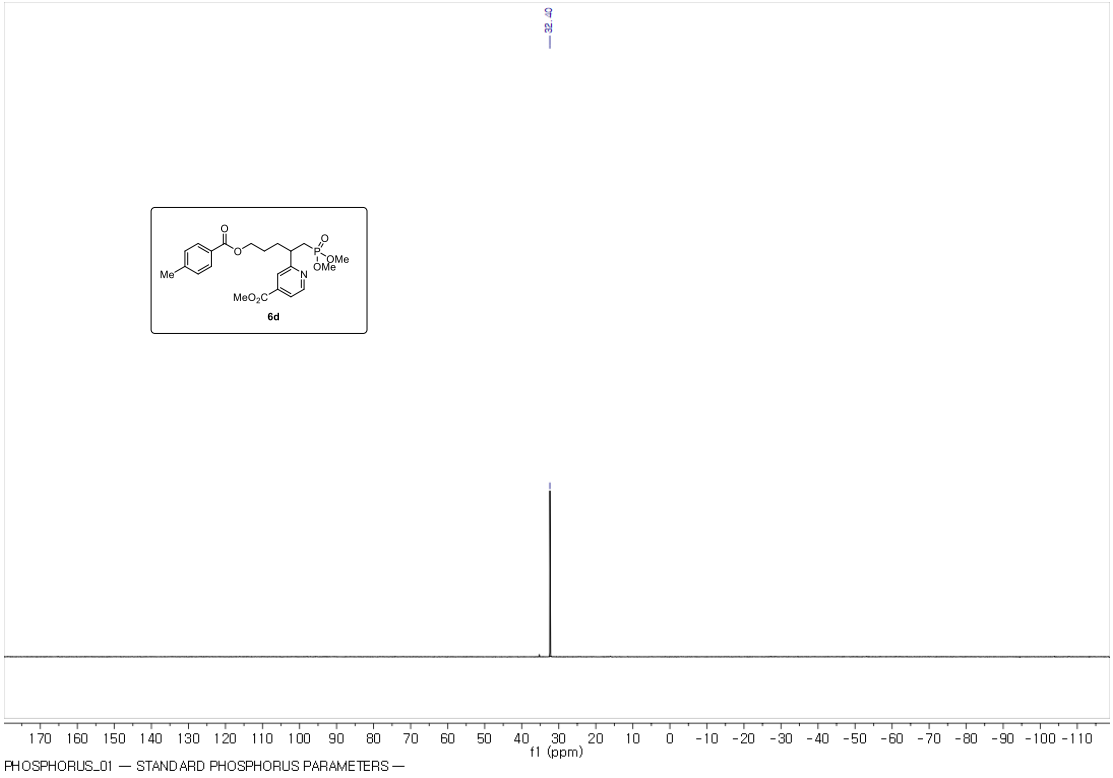
methyl 2-(1-(dimethoxyphosphoryl)-5-((4-methylbenzoyl)oxy)pentan-2-yl)isonicotinate (6d)



600 MHz, ^{1}H NMR in $CDCl_3$

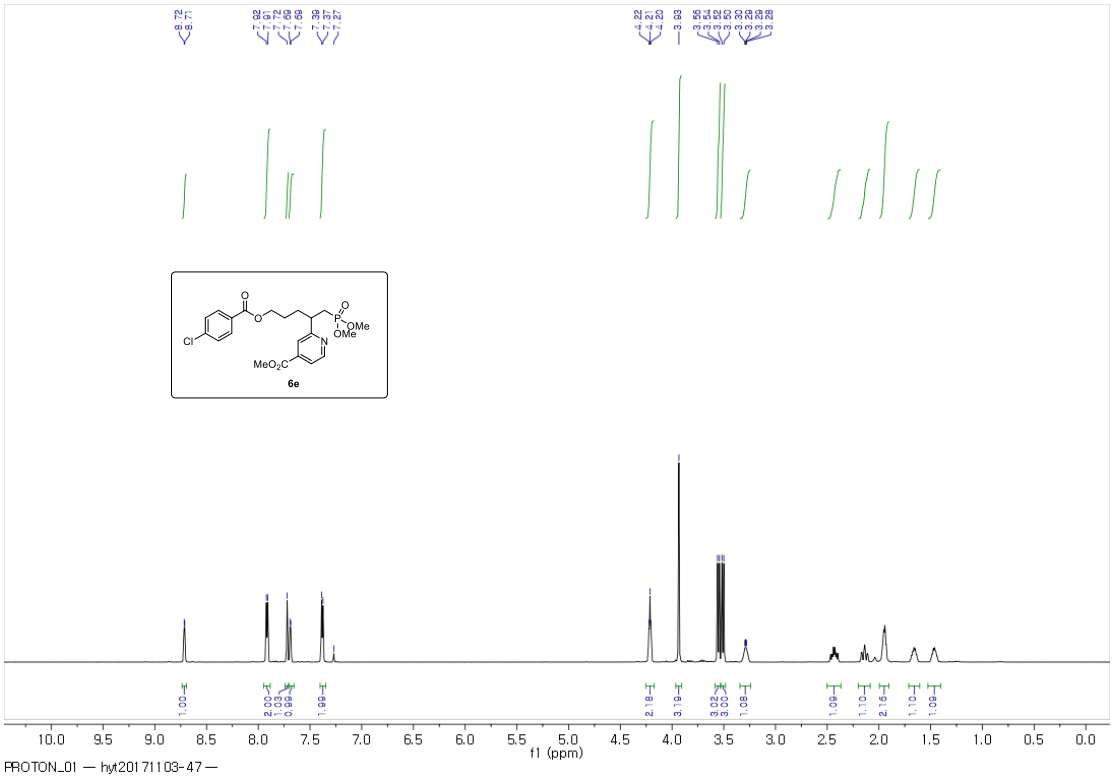


150 MHz, ^{13}C NMR in $CDCl_3$

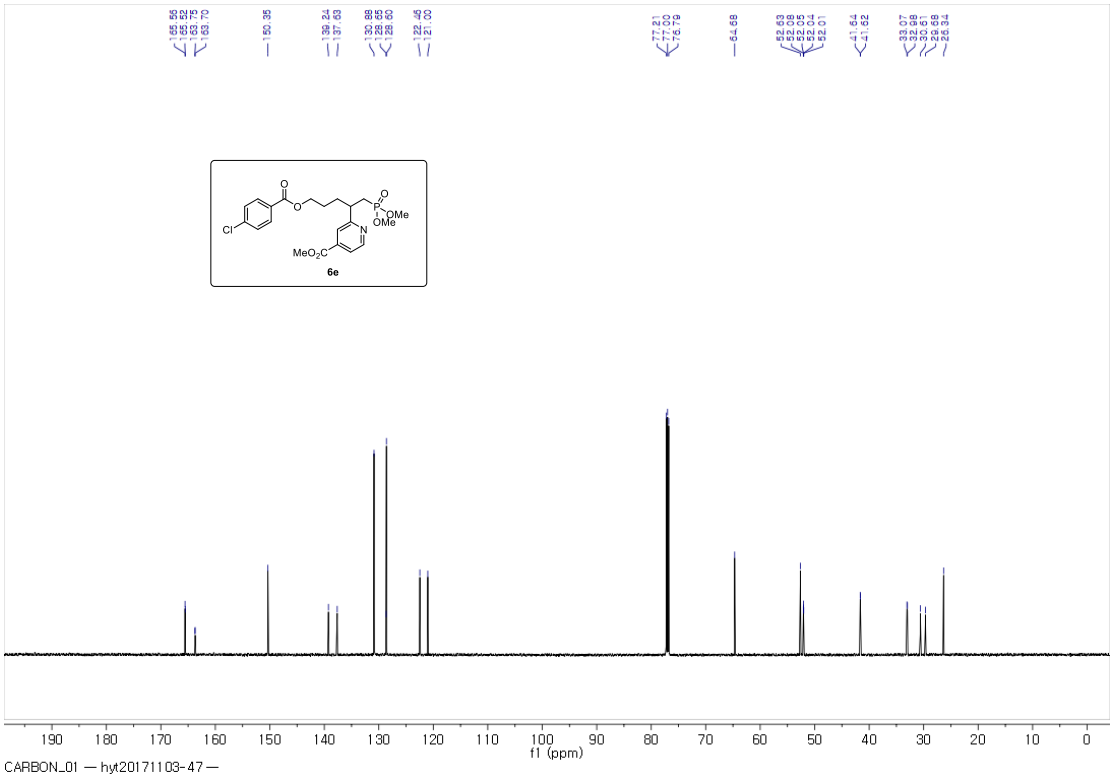


243 MHz, ^{31}P NMR in $CDCl_3$

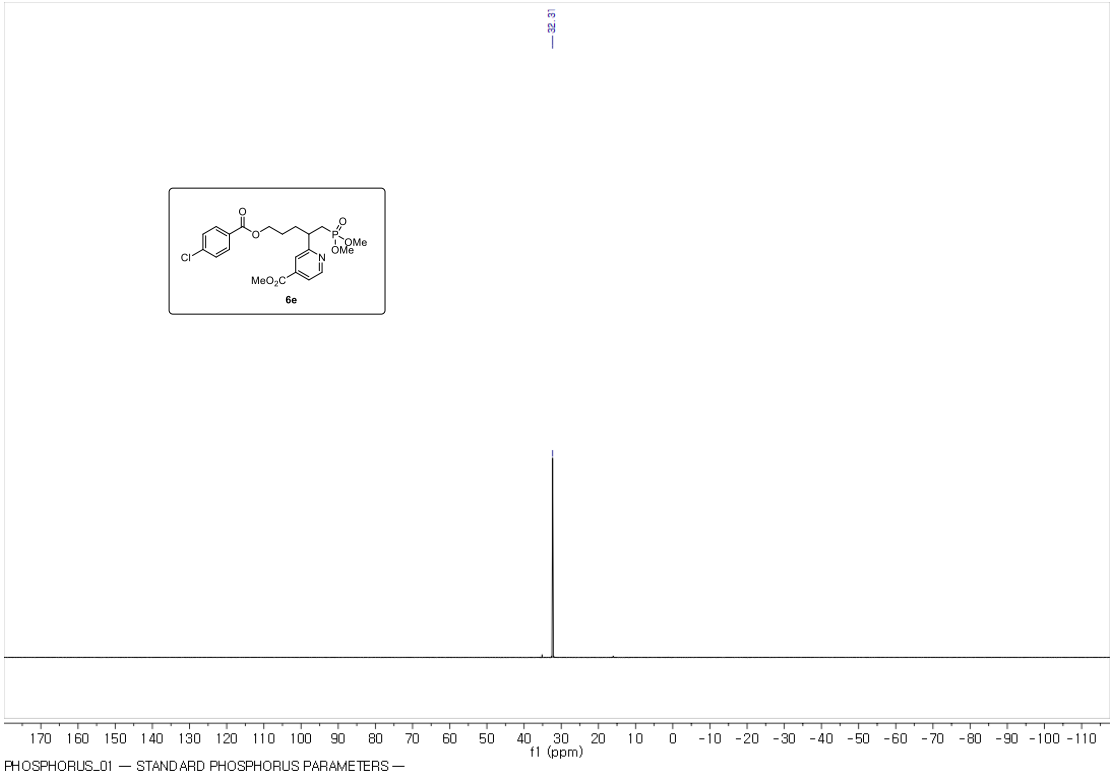
methyl 2-(5-((4-chlorobenzoyl)oxy)-1-(dimethoxyphosphoryl)pentan-2-yl)isonicotinate (6e)



600 MHz, ^{1}H NMR in $CDCl_3$

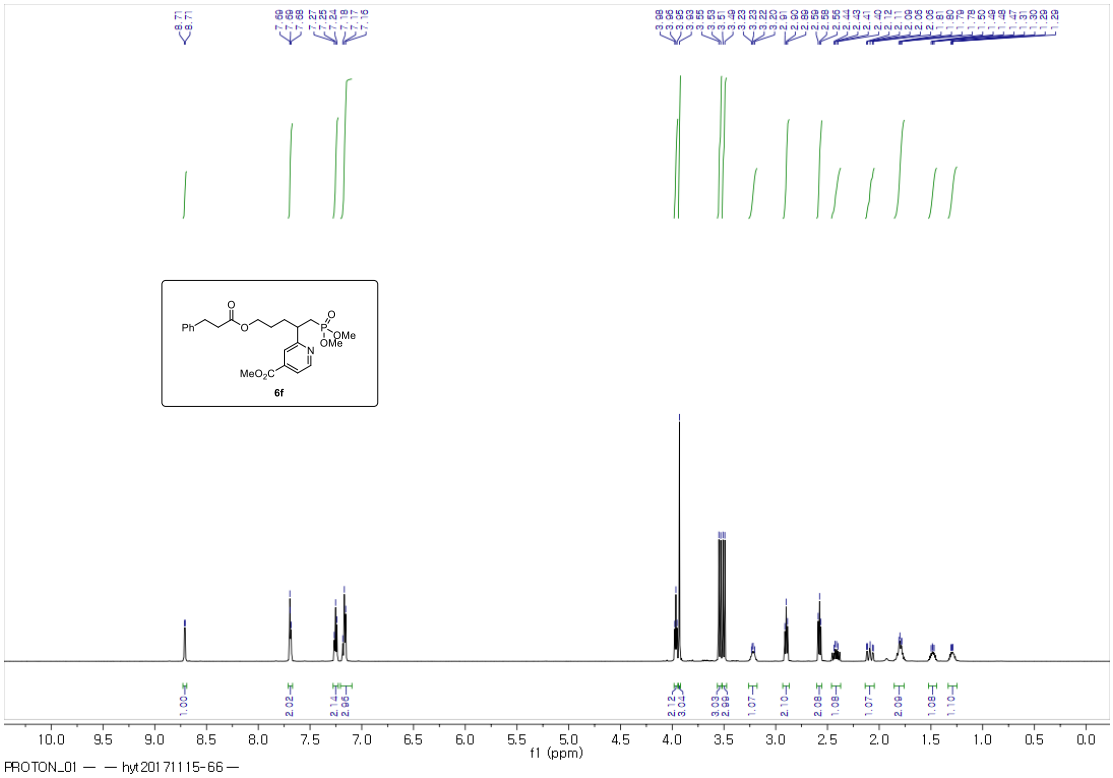


150 MHz, ^{13}C NMR in $CDCl_3$

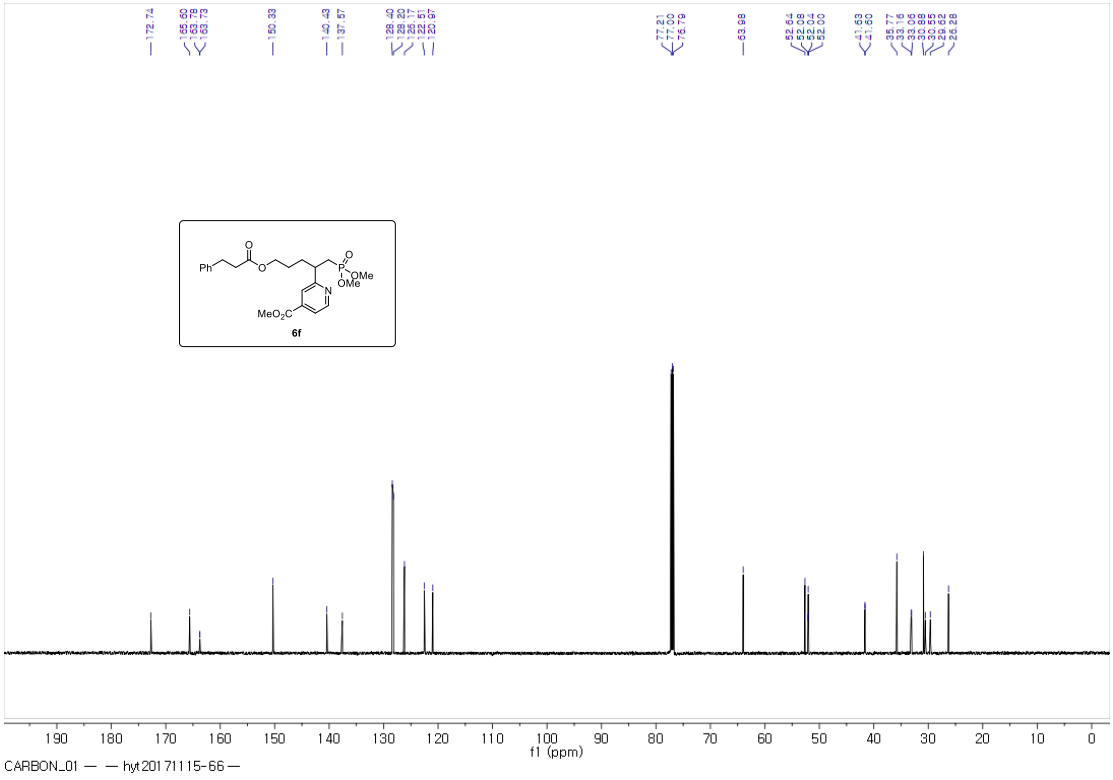


243 MHz, ^{31}P NMR in $CDCl_3$

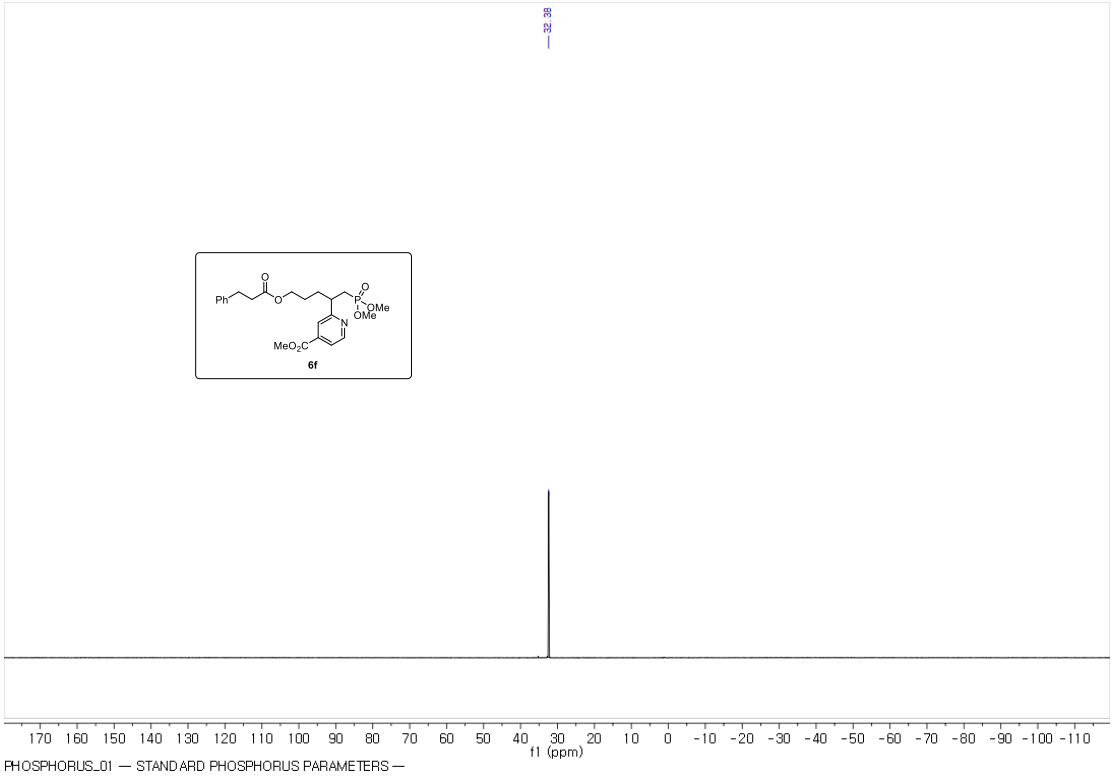
methyl 2-(1-(dimethoxyphosphoryl)-5-((3-phenylpropanoyl)oxy)pentan-2-yl)isonicotinate (6f)



600 MHz, ^{1}H NMR in $CDCl_3$

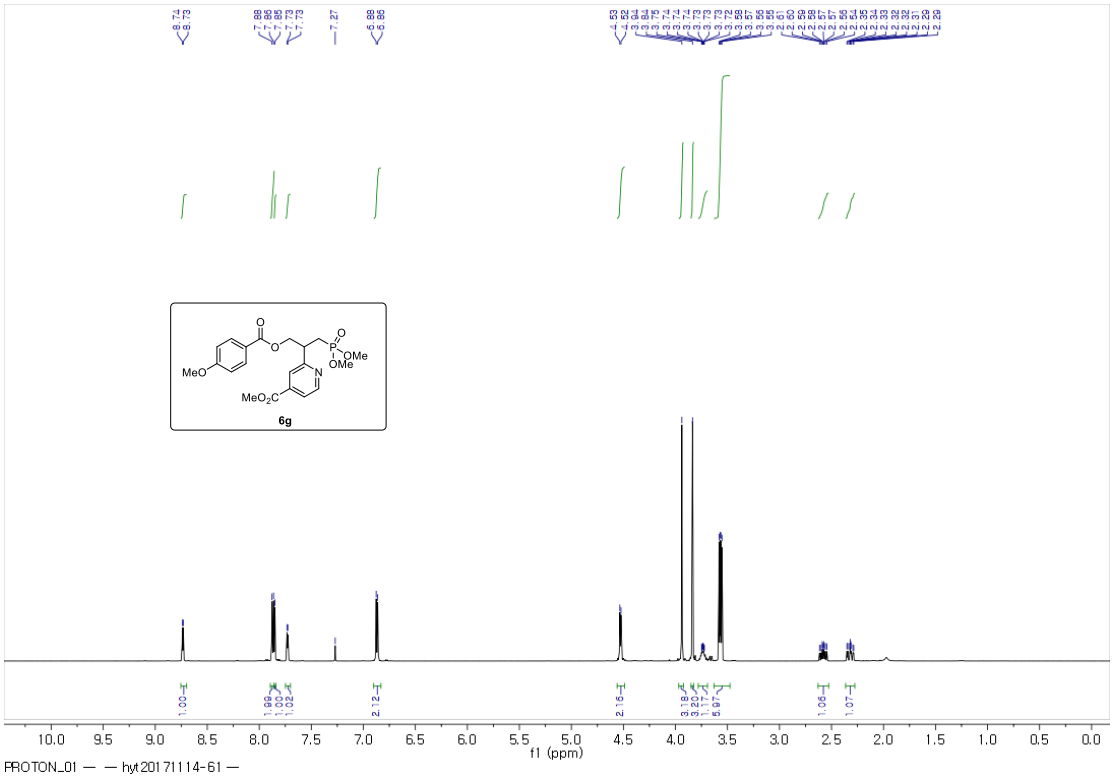


150 MHz, ^{13}C NMR in $CDCl_3$

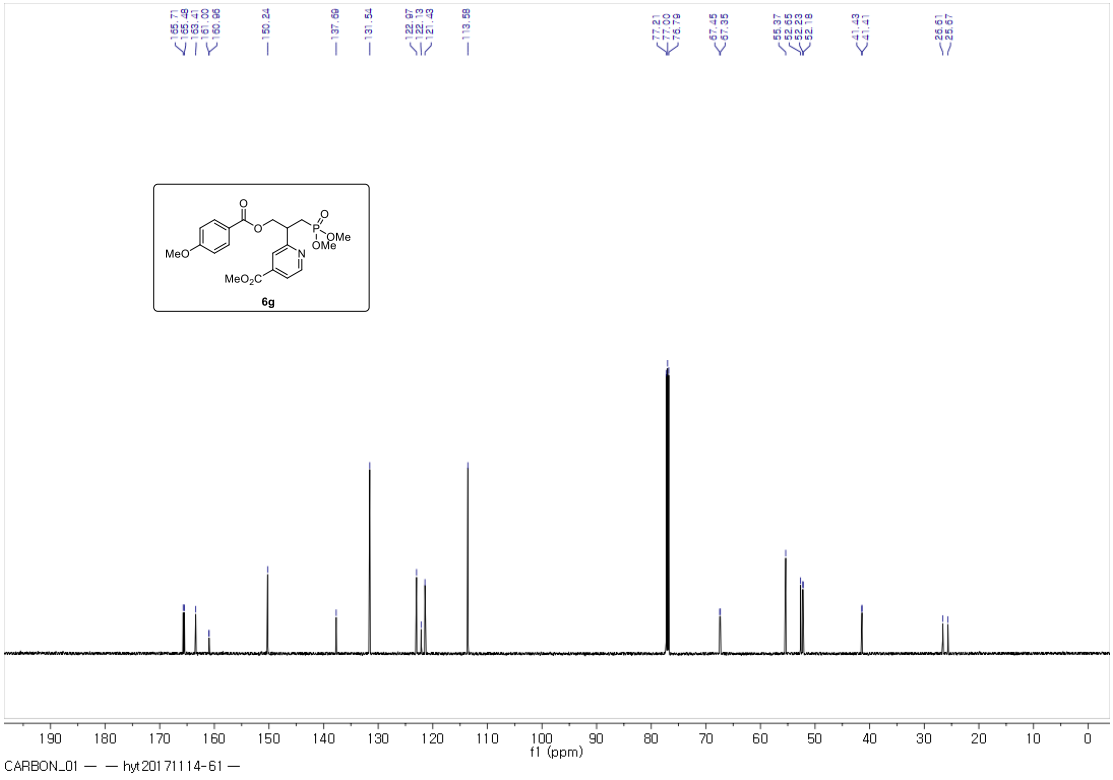


243 MHz, ^{31}P NMR in $CDCl_3$

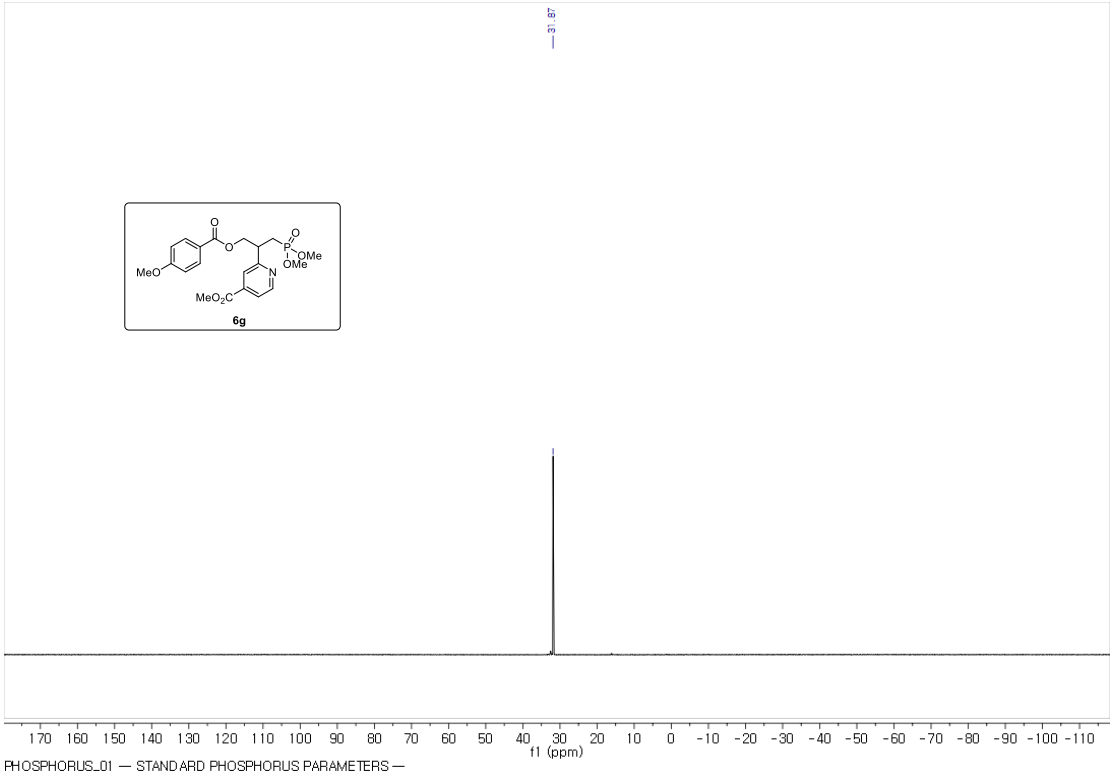
methyl 2-(1-(dimethoxyphosphoryl)-3-((4-methoxybenzoyl)oxy)propan-2-yl)isonicotinate (6g)



600 MHz, ^{1}H NMR in $CDCl_3$

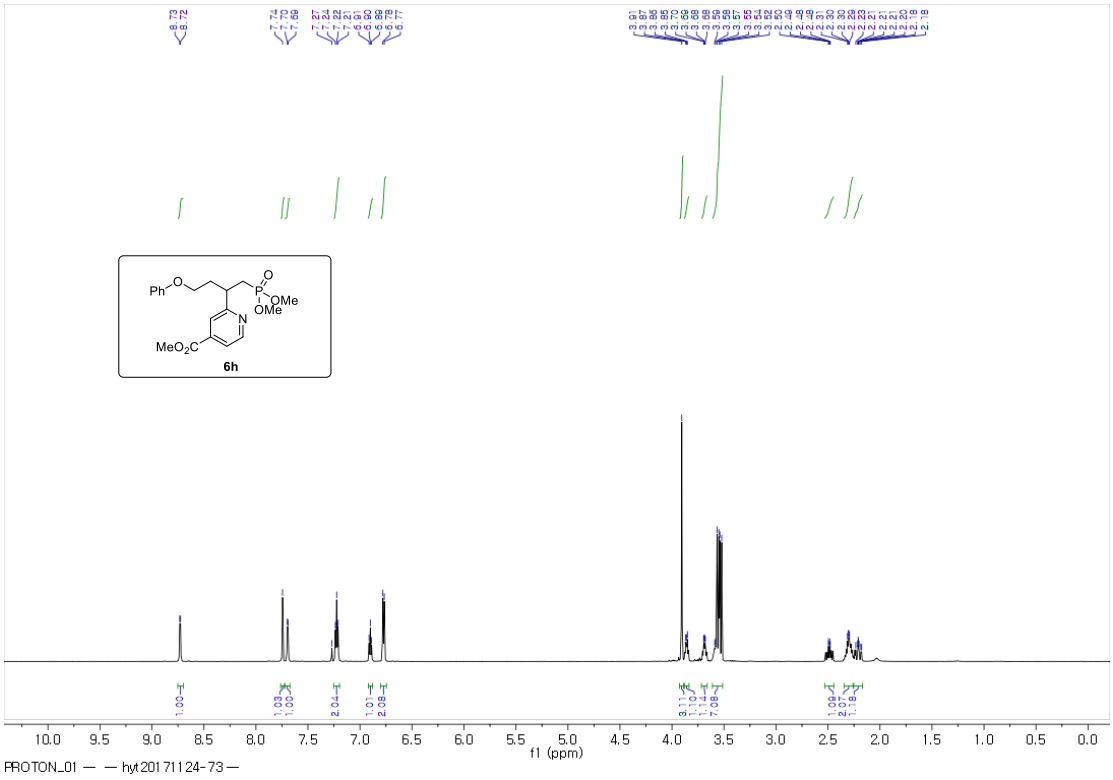


150 MHz, ^{13}C NMR in $CDCl_3$

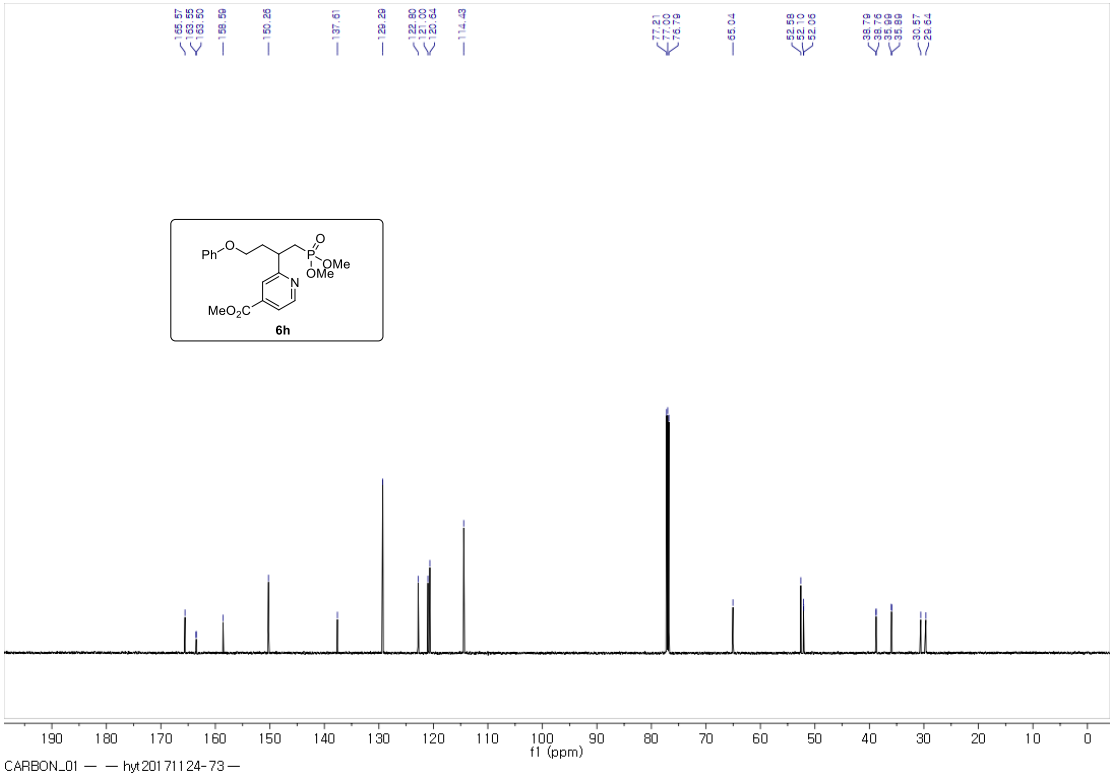


243 MHz, ^{31}P NMR in $CDCl_3$

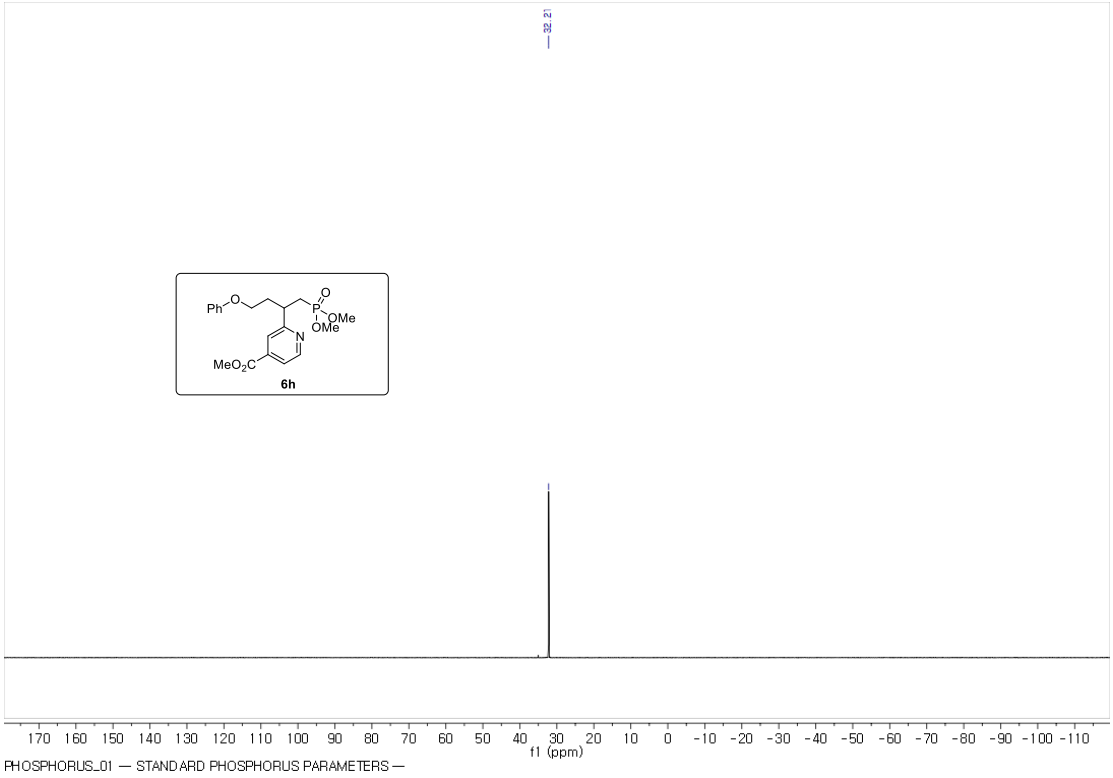
methyl 2-(1-(dimethoxyphosphoryl)-4-phenoxybutan-2-yl)isonicotinate (6h)



600 MHz, ^{1}H NMR in $CDCl_3$

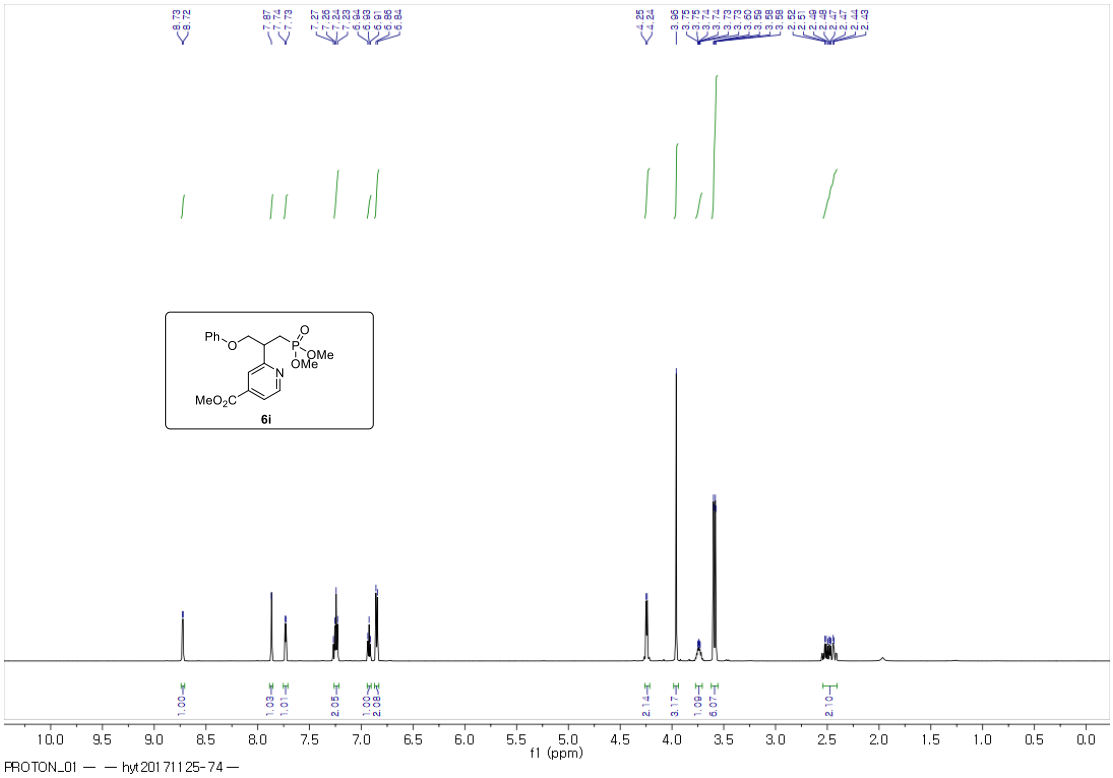


150 MHz, ^{13}C NMR in $CDCl_3$

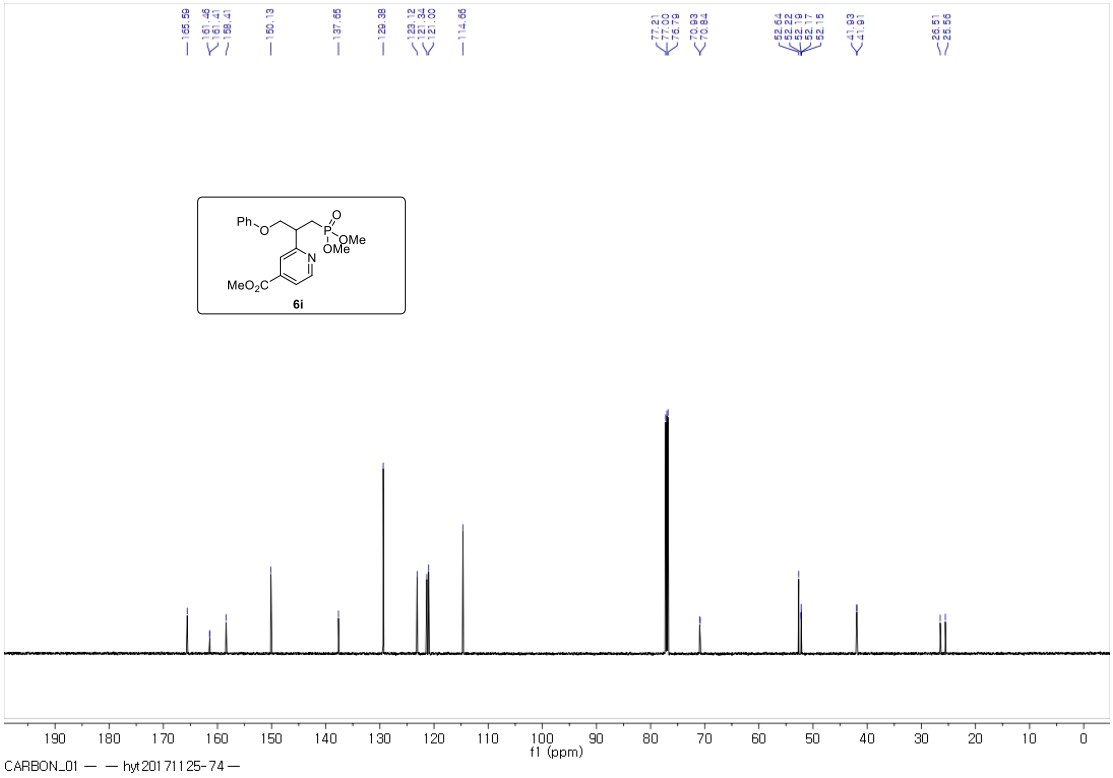


243 MHz, ^{31}P NMR in $CDCl_3$

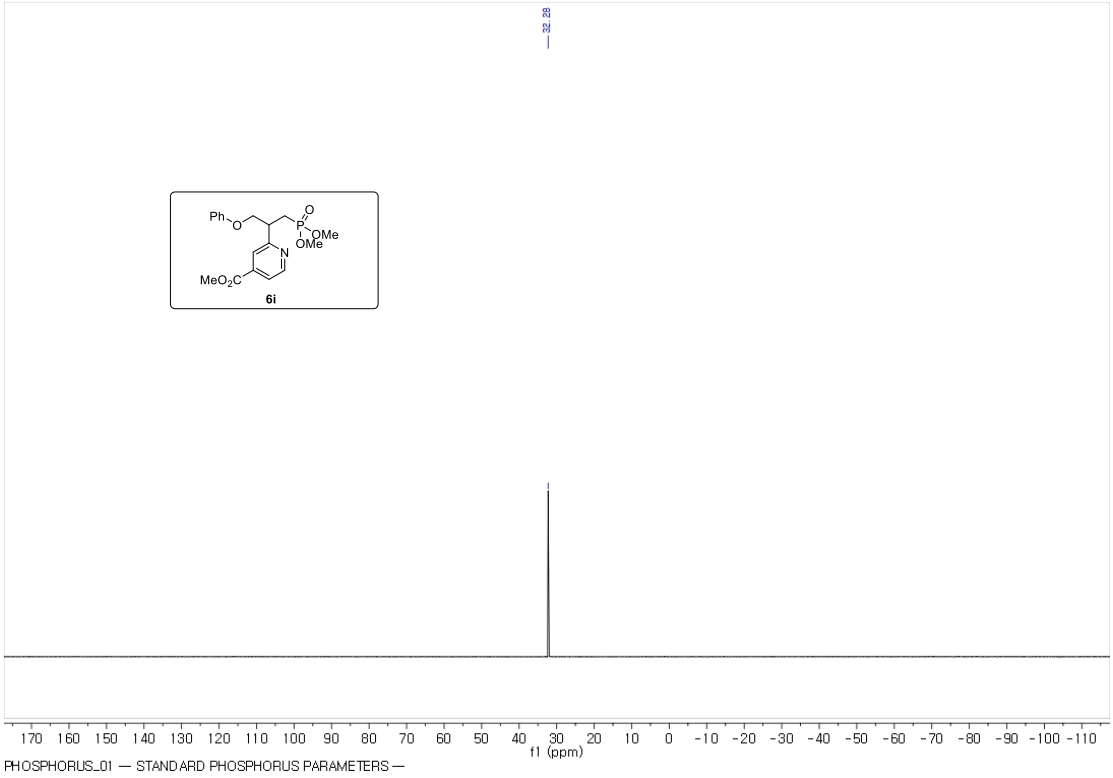
methyl 2-(1-(dimethoxyphosphoryl)-3-phenoxypropan-2-yl)isonicotinate (6i)



600 MHz, ^{1}H NMR in $CDCl_3$

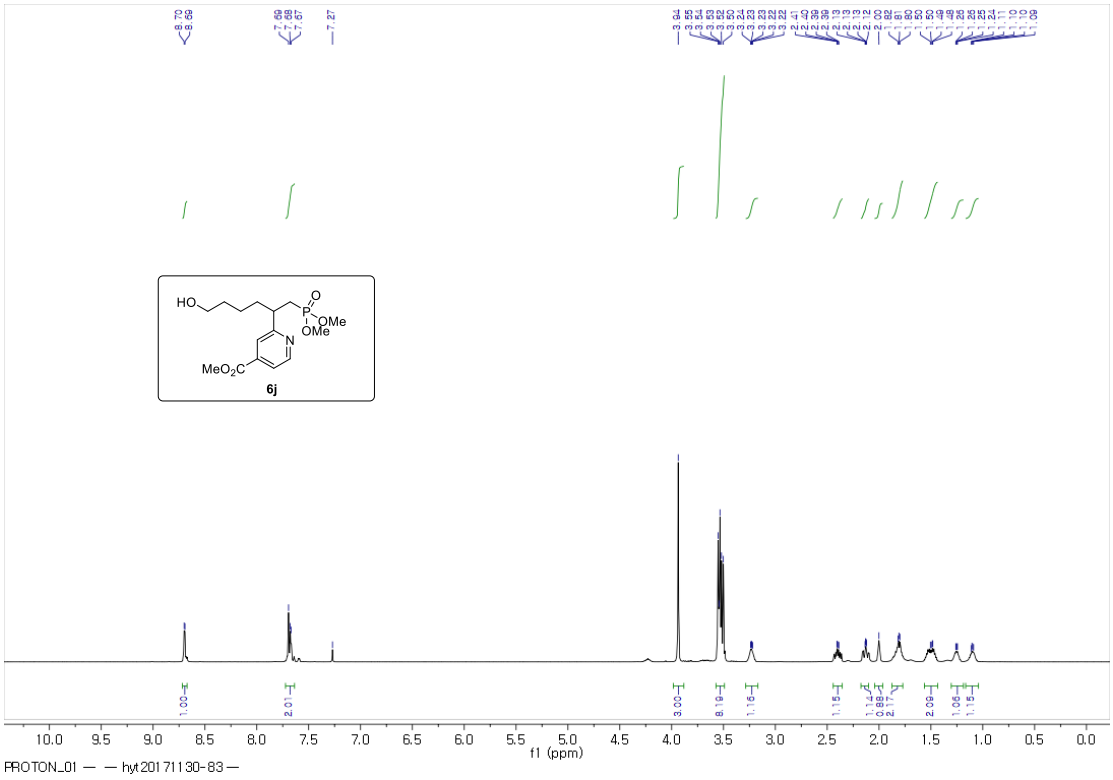


150 MHz, ^{13}C NMR in $CDCl_3$

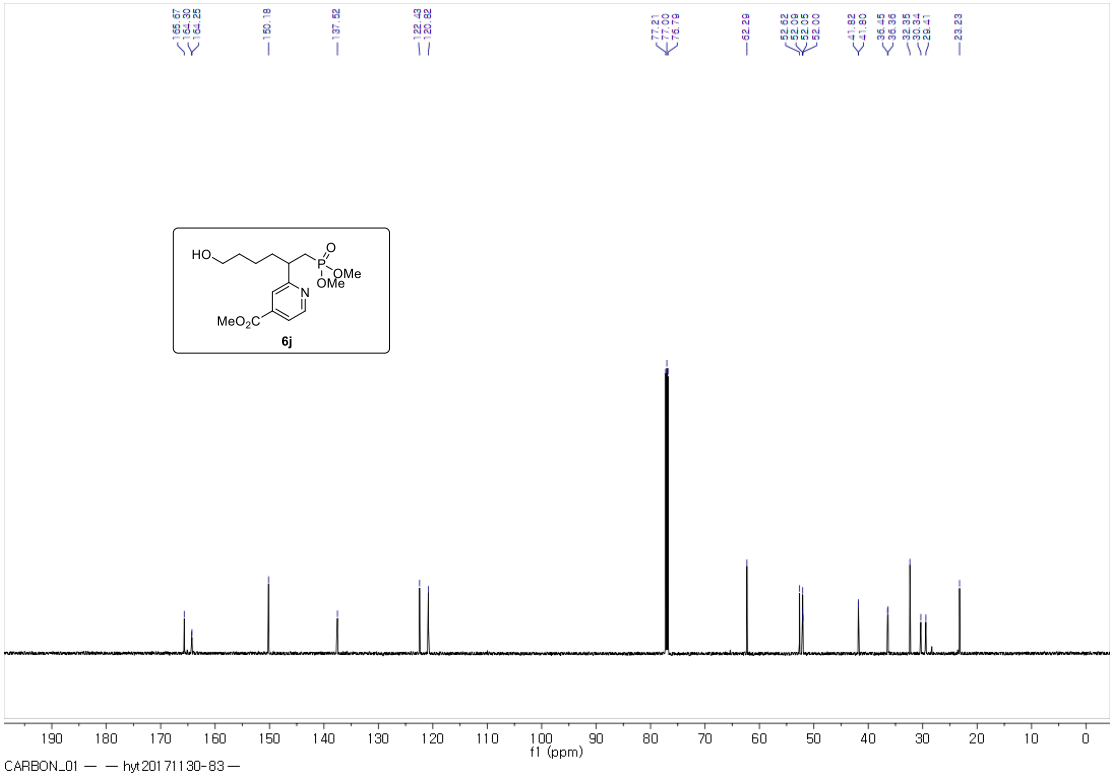


243 MHz, ^{31}P NMR in $CDCl_3$

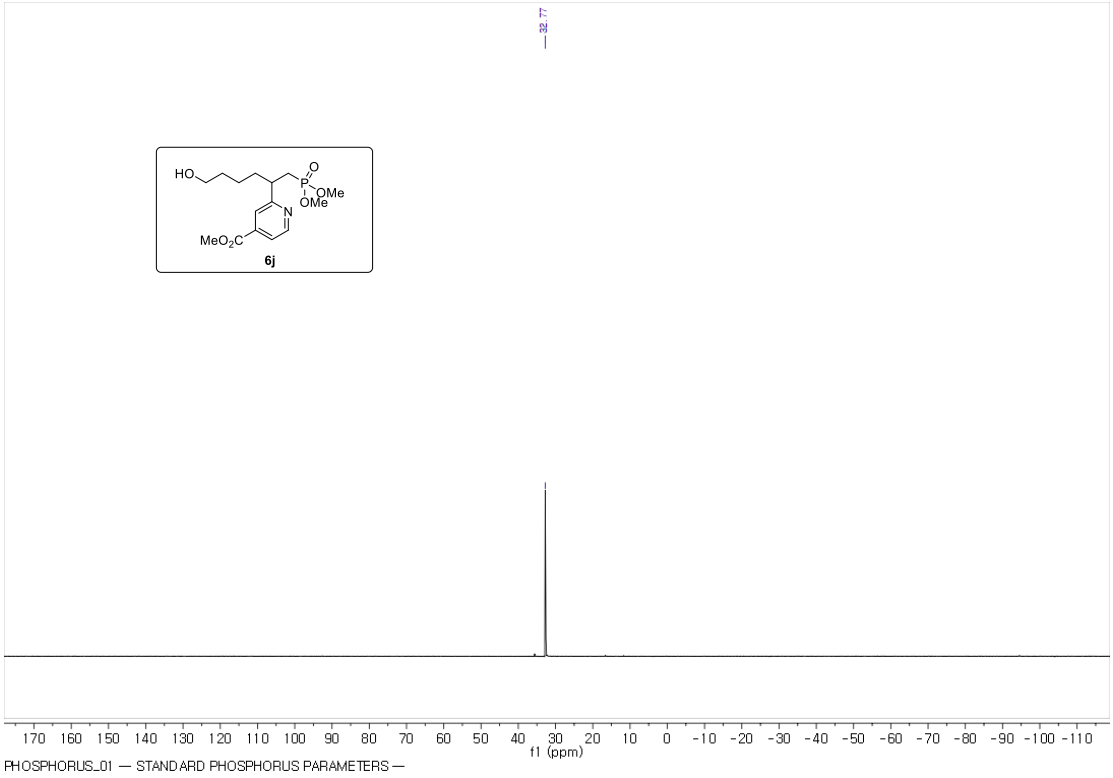
methyl 2-(1-(dimethoxyphosphoryl)-6-hydroxyhexan-2-yl)isonicotinate (6j)



600 MHz, ^{1}H NMR in $CDCl_3$

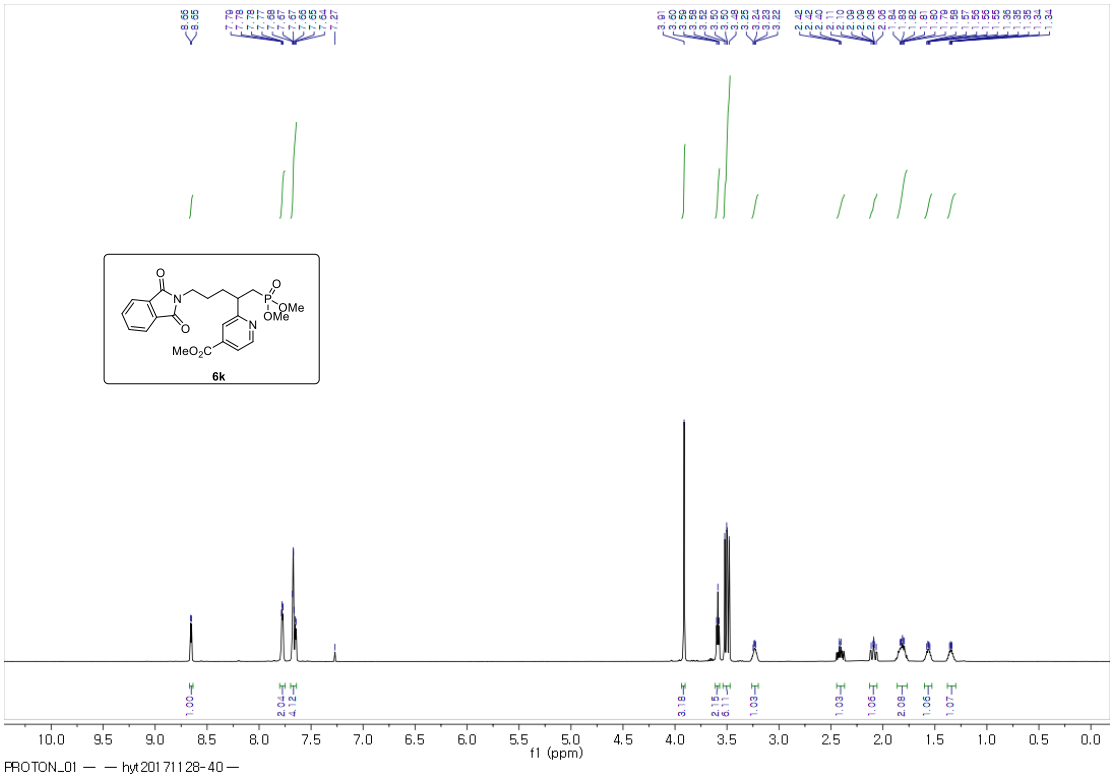


150 MHz, ^{13}C NMR in $CDCl_3$

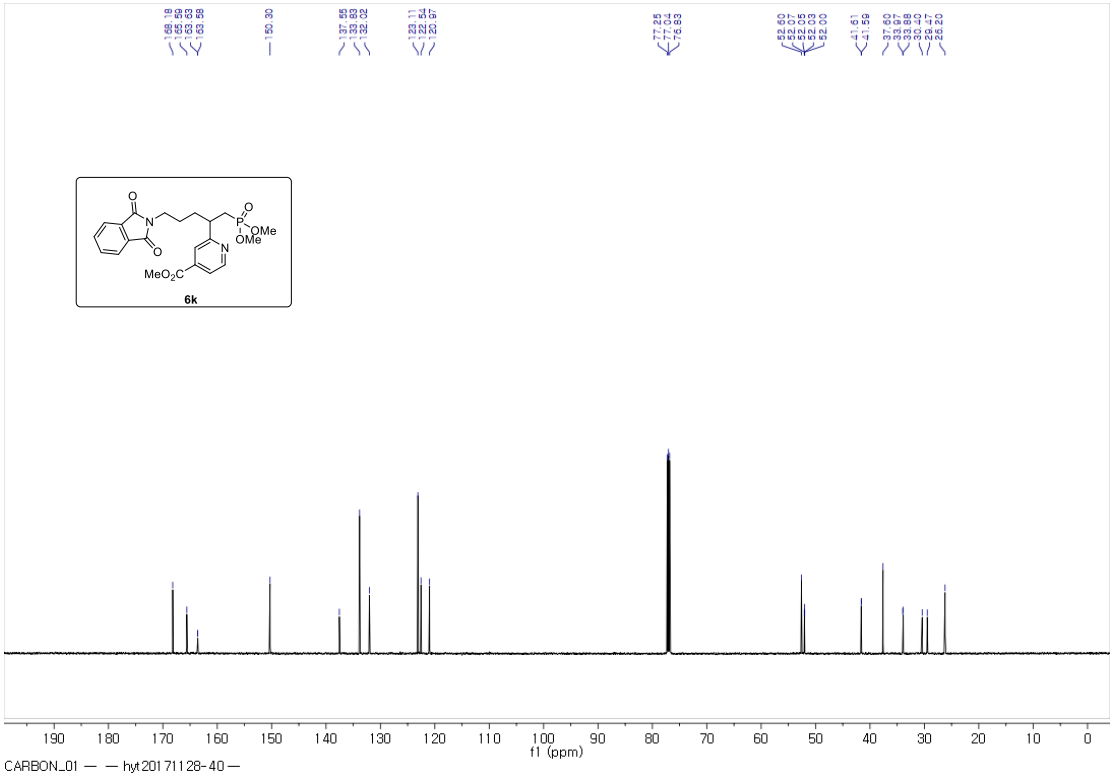


243 MHz, ^{31}P NMR in $CDCl_3$

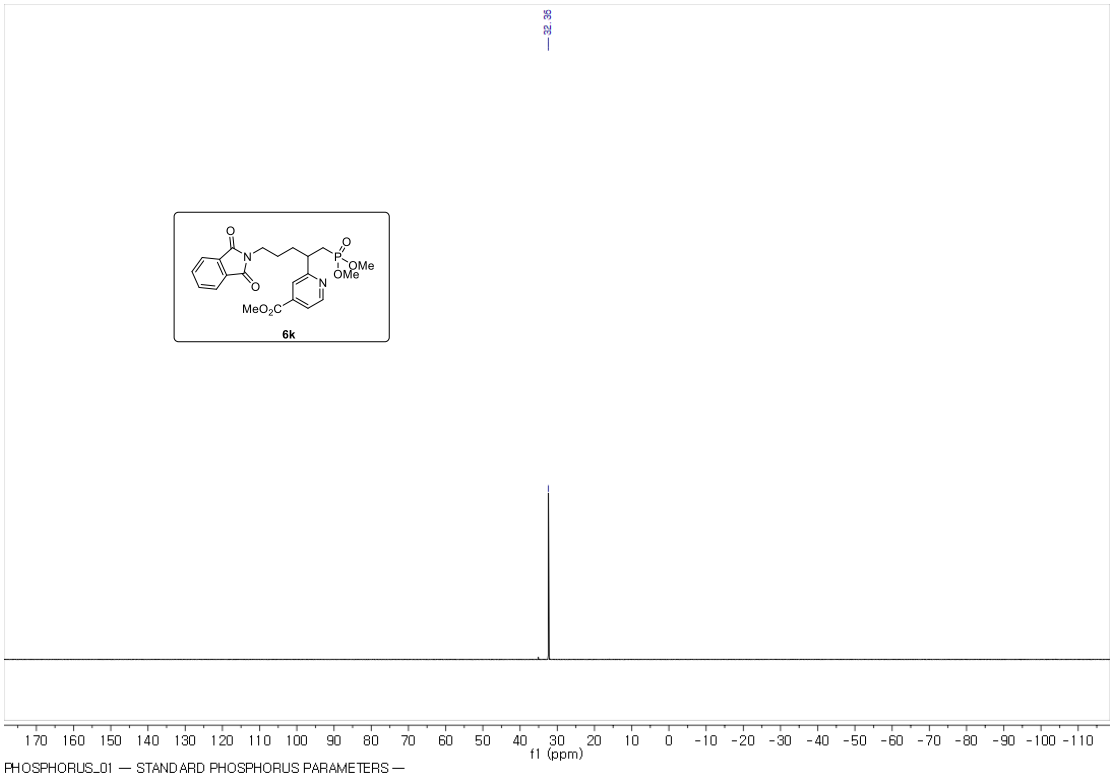
methyl 2-(1-(dimethoxyphosphoryl)-5-(1,3-dioxoisoindolin-2-yl)pentan-2-yl)isonicotinate (6k)



600 MHz, ^{1}H NMR in $CDCl_3$

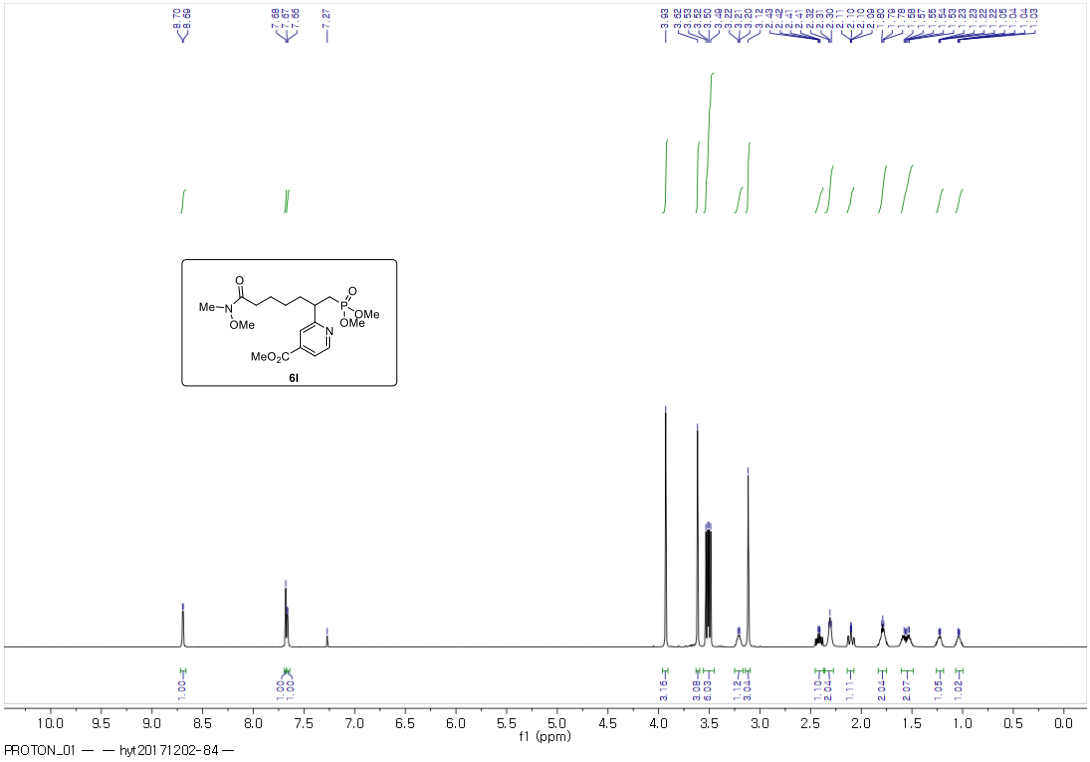


150 MHz, ^{13}C NMR in $CDCl_3$

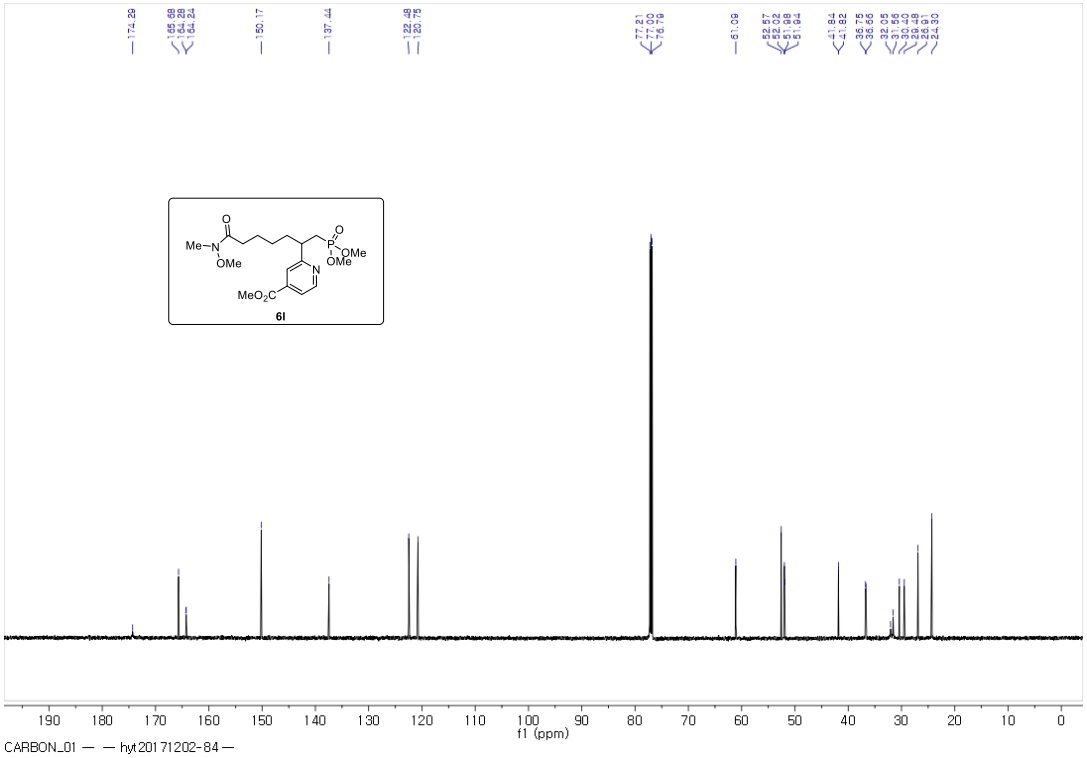


243 MHz, ^{31}P NMR in $CDCl_3$

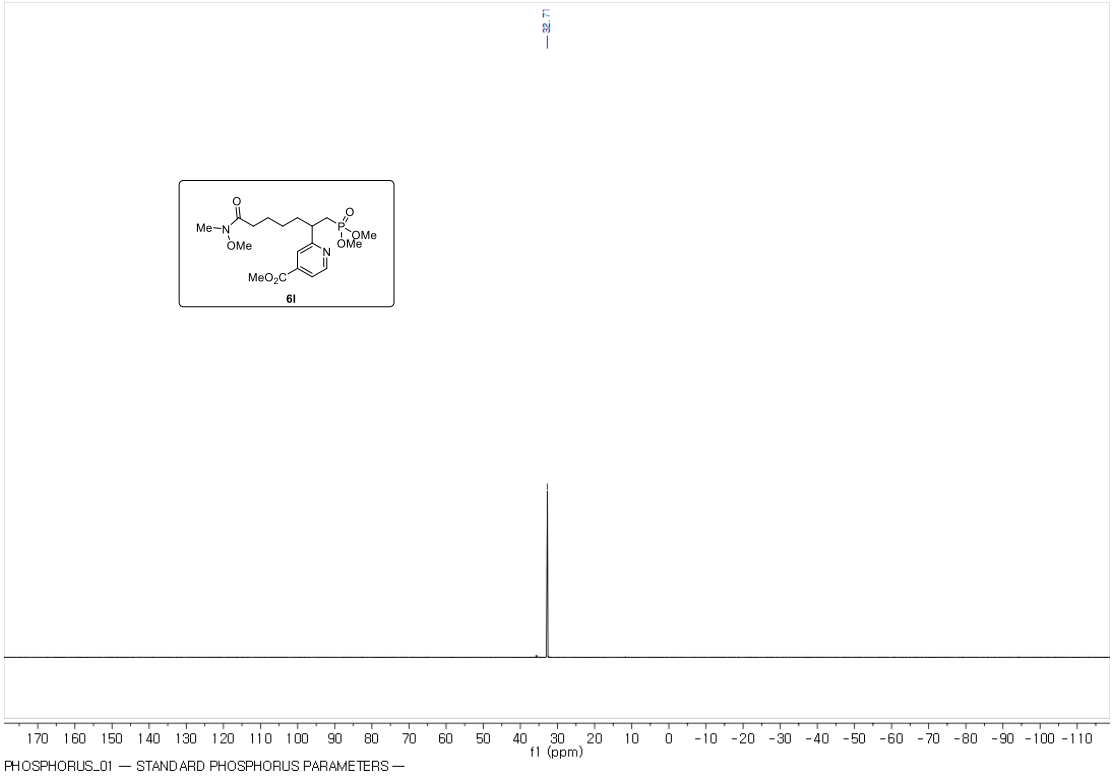
methyl 2-(1-(dimethoxyphosphoryl)-7-(methoxy(methyl)amino)-7-oxoheptan-2-yl)isonicotinate(6l)



600 MHz, ^{1}H NMR in $CDCl_3$

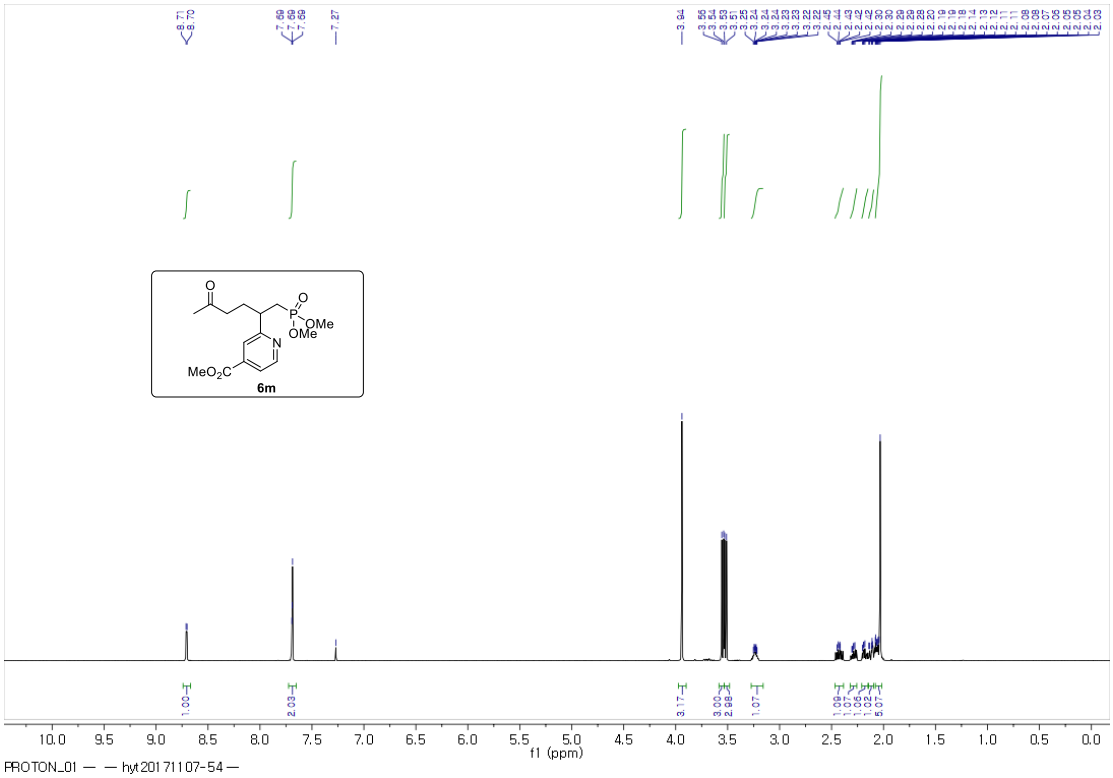


150 MHz, ^{13}C NMR in $CDCl_3$

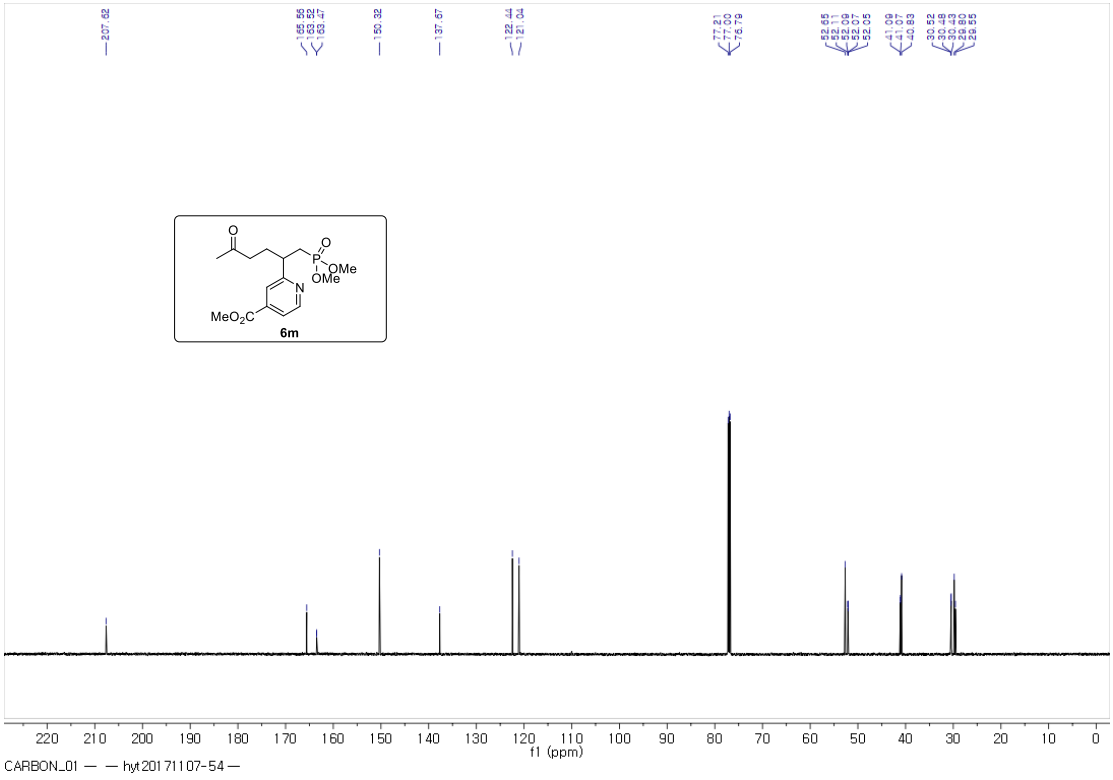


243 MHz, ^{31}P NMR in $CDCl_3$

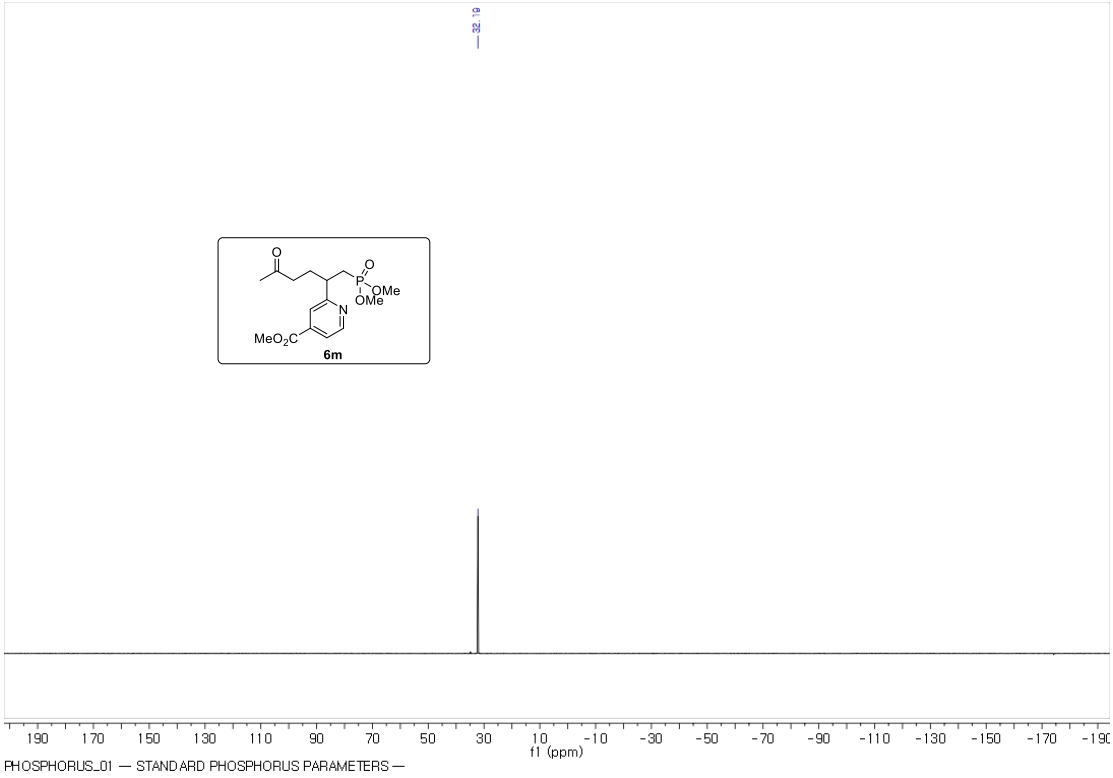
methyl 2-(1-(dimethoxyphosphoryl)-5-oxohexan-2-yl)isonicotinate (6m)



600 MHz, ^{1}H NMR in $CDCl_3$

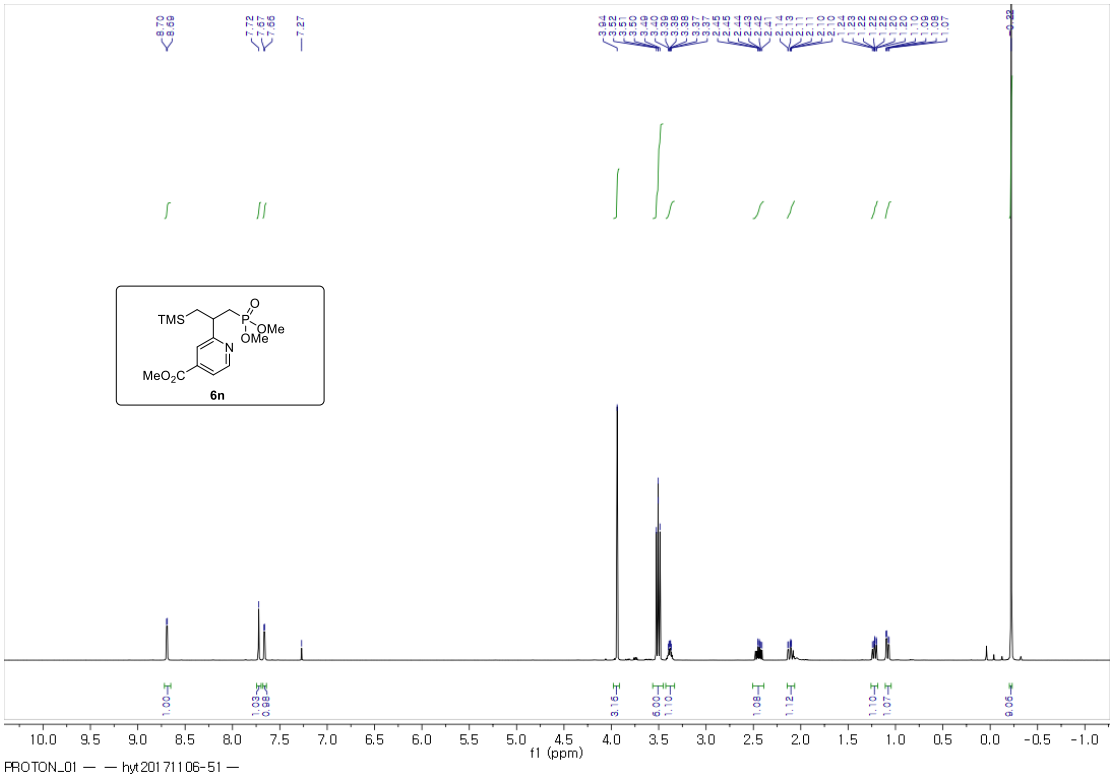


150 MHz, ^{13}C NMR in $CDCl_3$

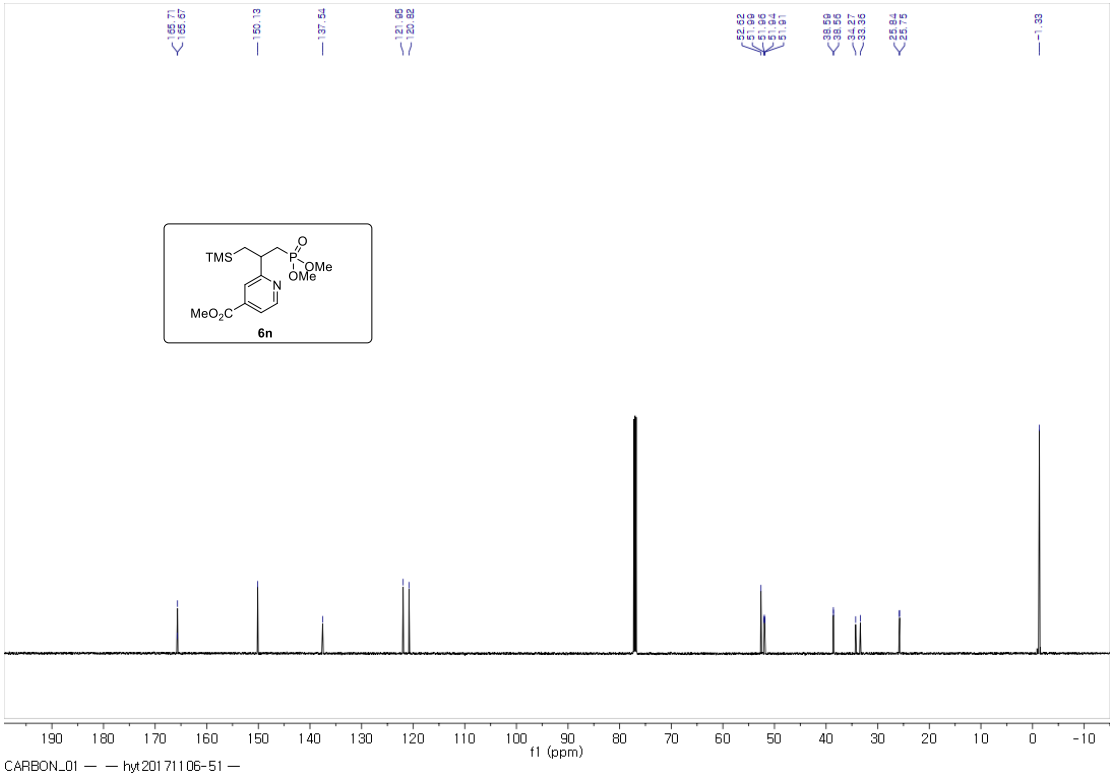


243 MHz, ^{31}P NMR in $CDCl_3$

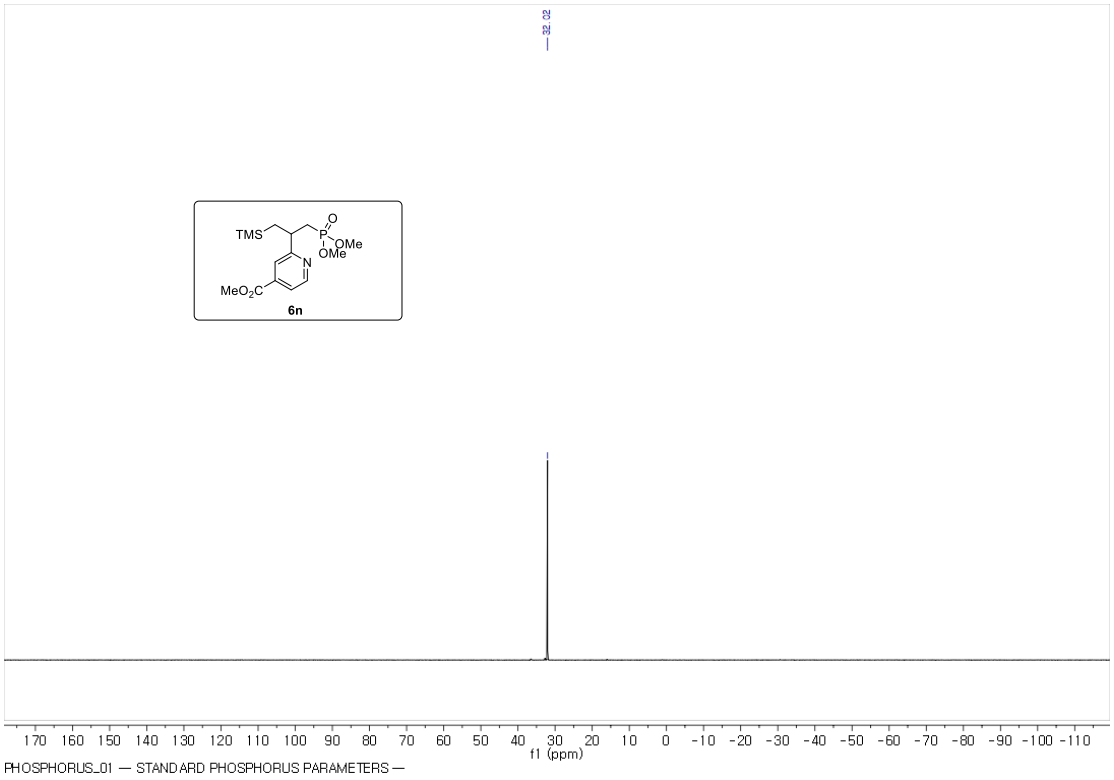
methyl 2-(1-(dimethoxyphosphoryl)-3-(trimethylsilyl)propan-2-yl)isonicotinate (6n)



600 MHz, ^{1}H NMR in $CDCl_3$

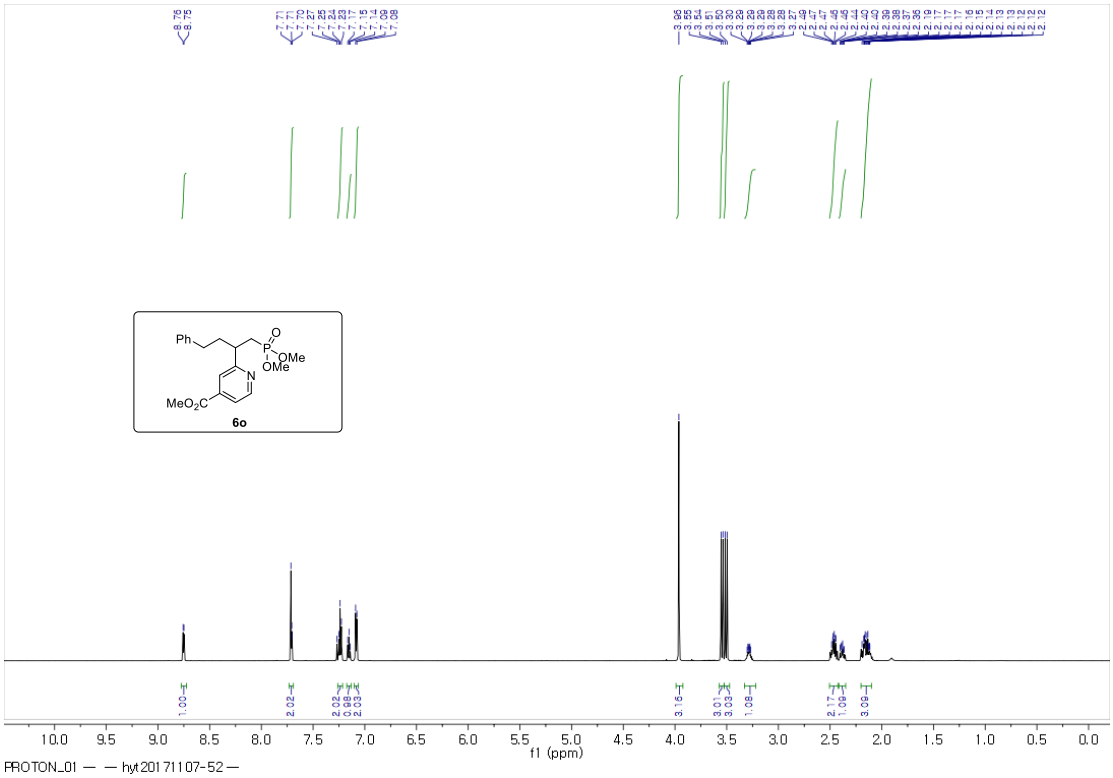


150 MHz, ^{13}C NMR in $CDCl_3$

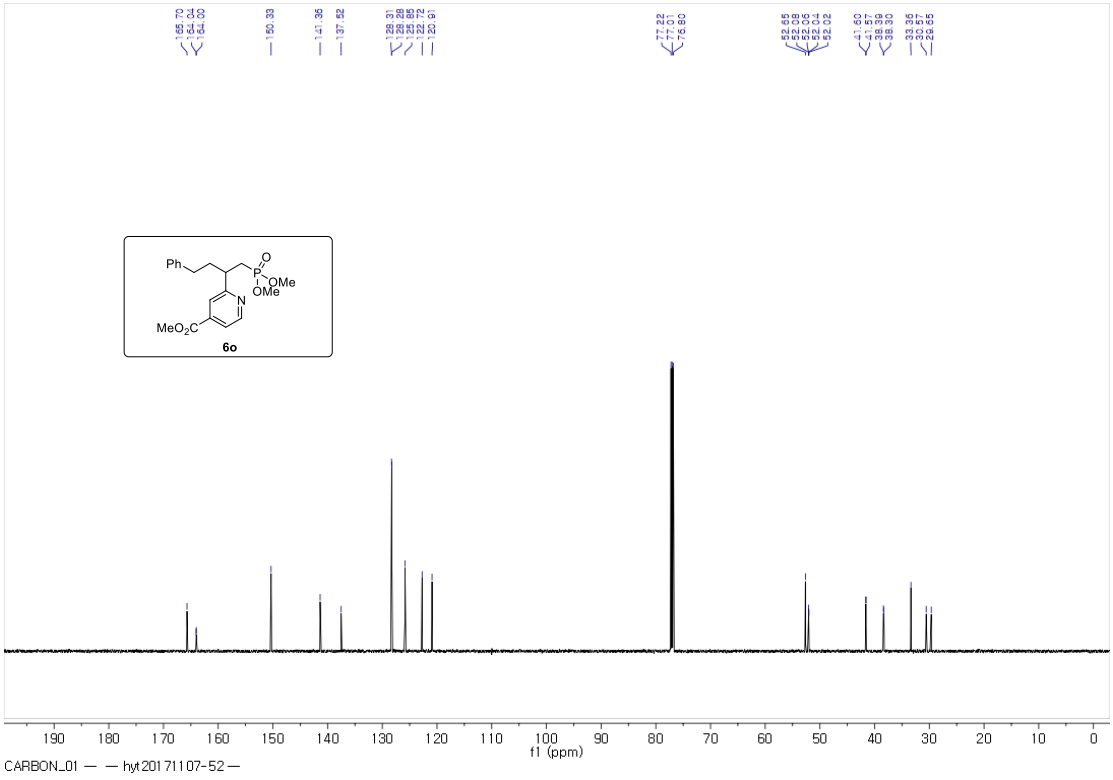


243 MHz, ^{31}P NMR in $CDCl_3$

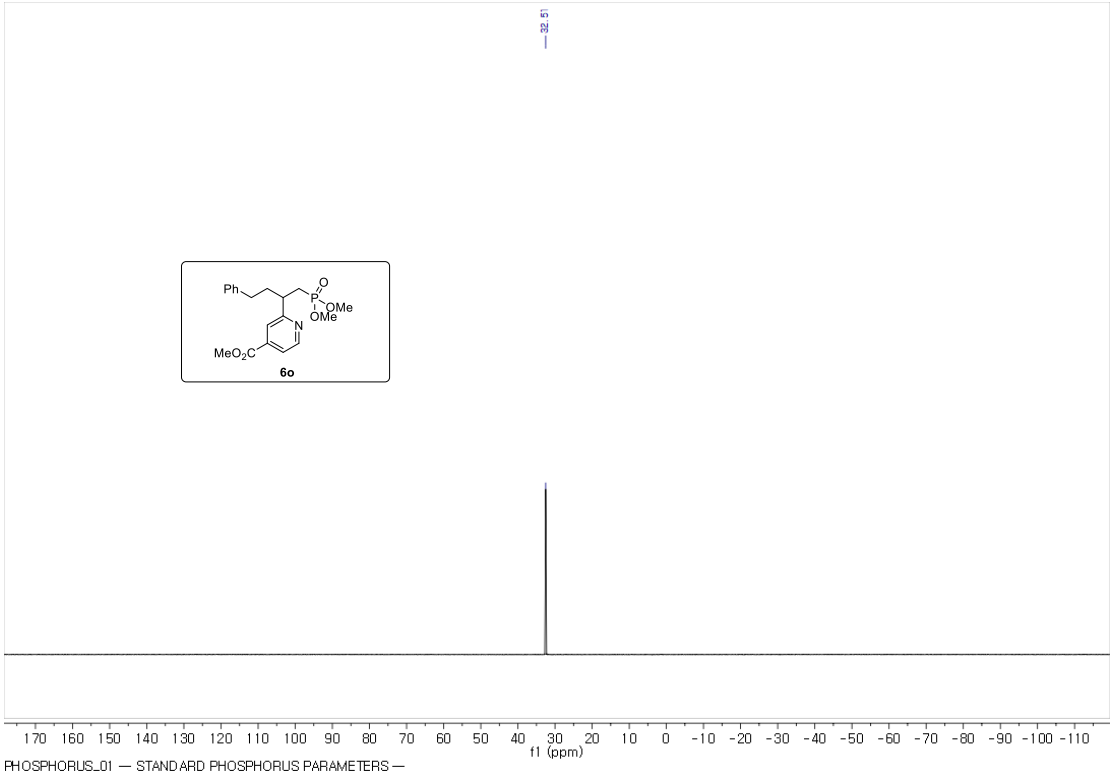
methyl 2-(1-(dimethoxyphosphoryl)-4-phenylbutan-2-yl)isonicotinate (6o)



600 MHz, ^{1}H NMR in $CDCl_3$

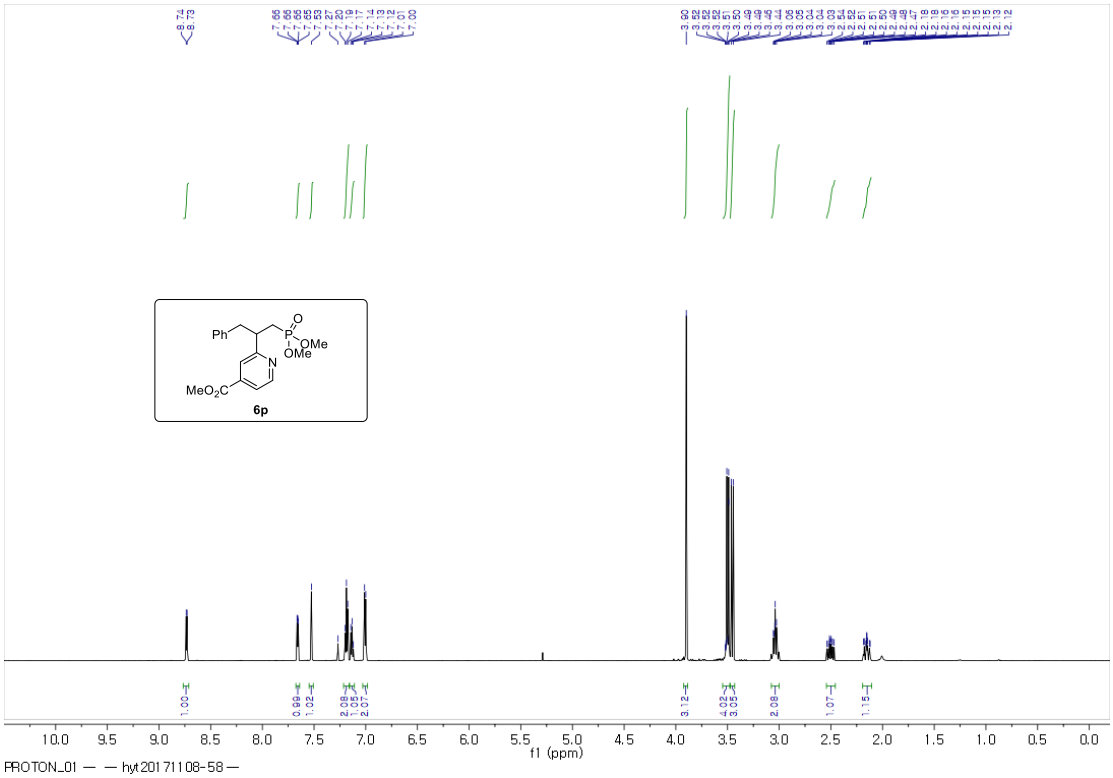


150 MHz, ^{13}C NMR in $CDCl_3$

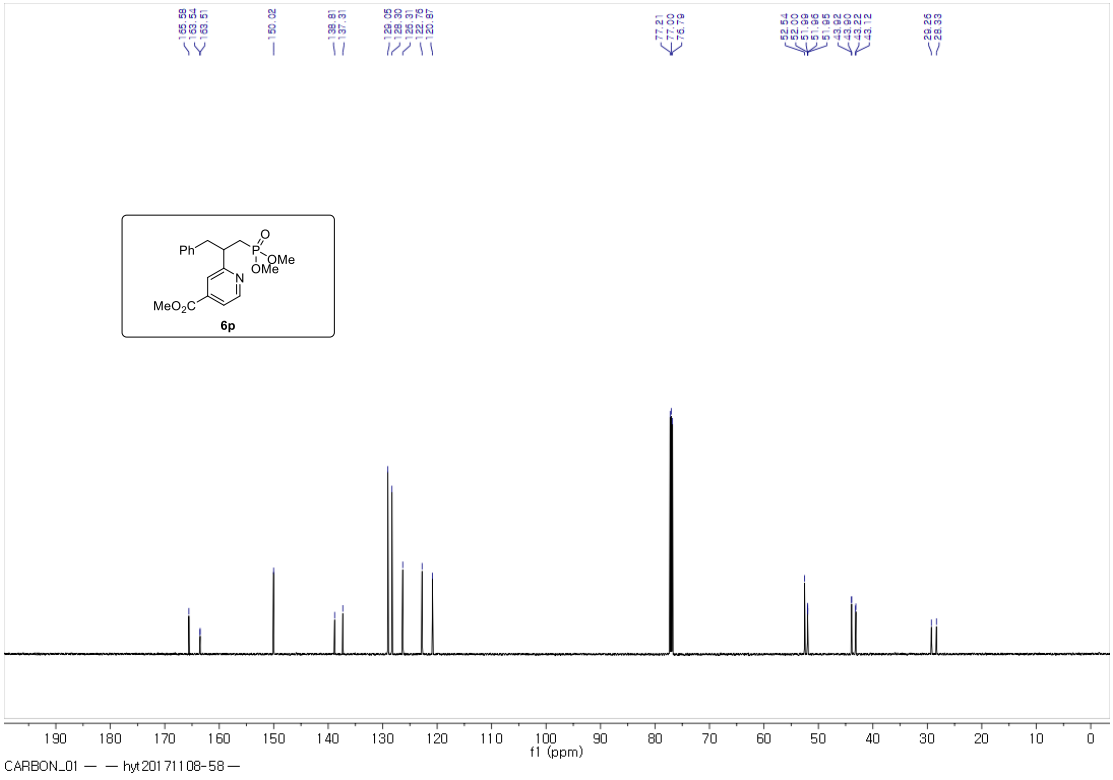


243 MHz, ^{31}P NMR in $CDCl_3$

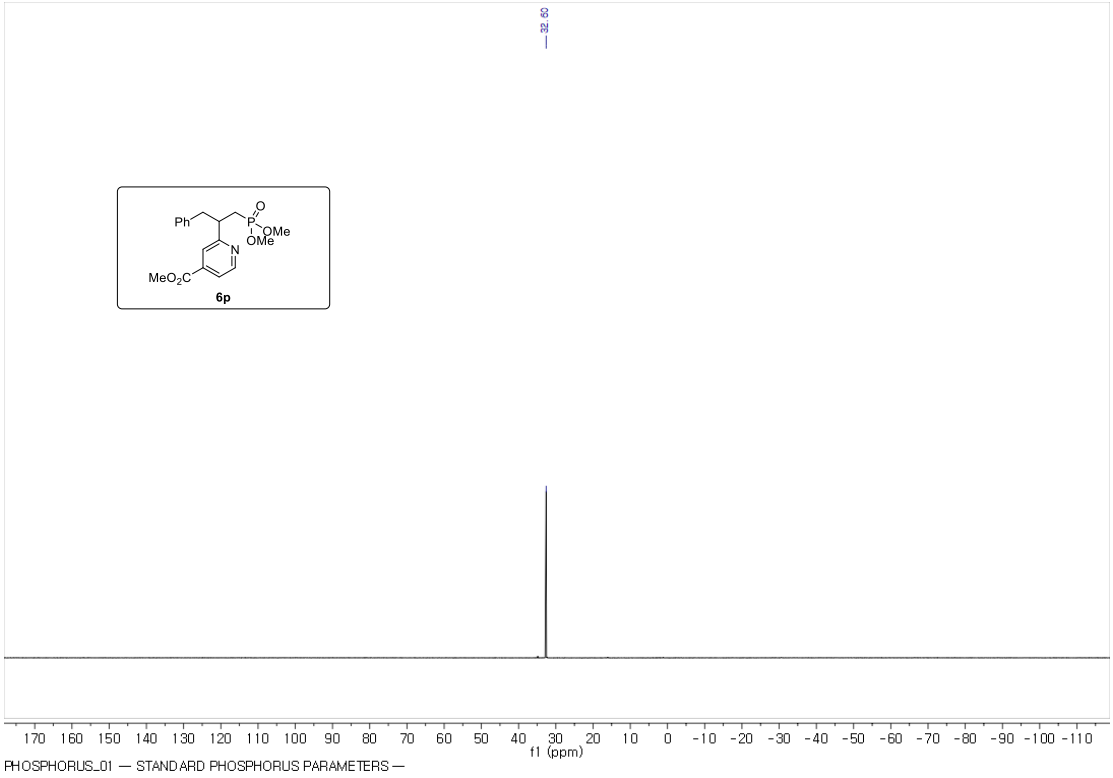
methyl 2-(1-(dimethoxyphosphoryl)-3-phenylpropan-2-yl)isonicotinate (6p)



600 MHz, ^{1}H NMR in $CDCl_3$

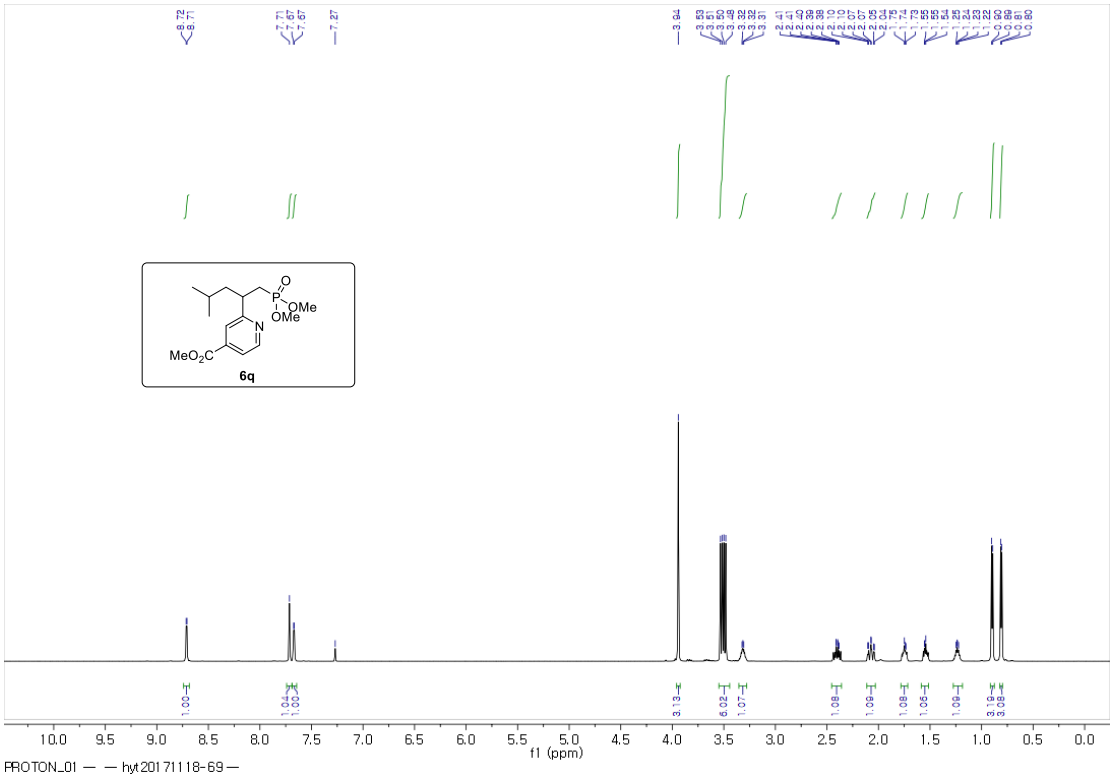


150 MHz, ^{13}C NMR in $CDCl_3$



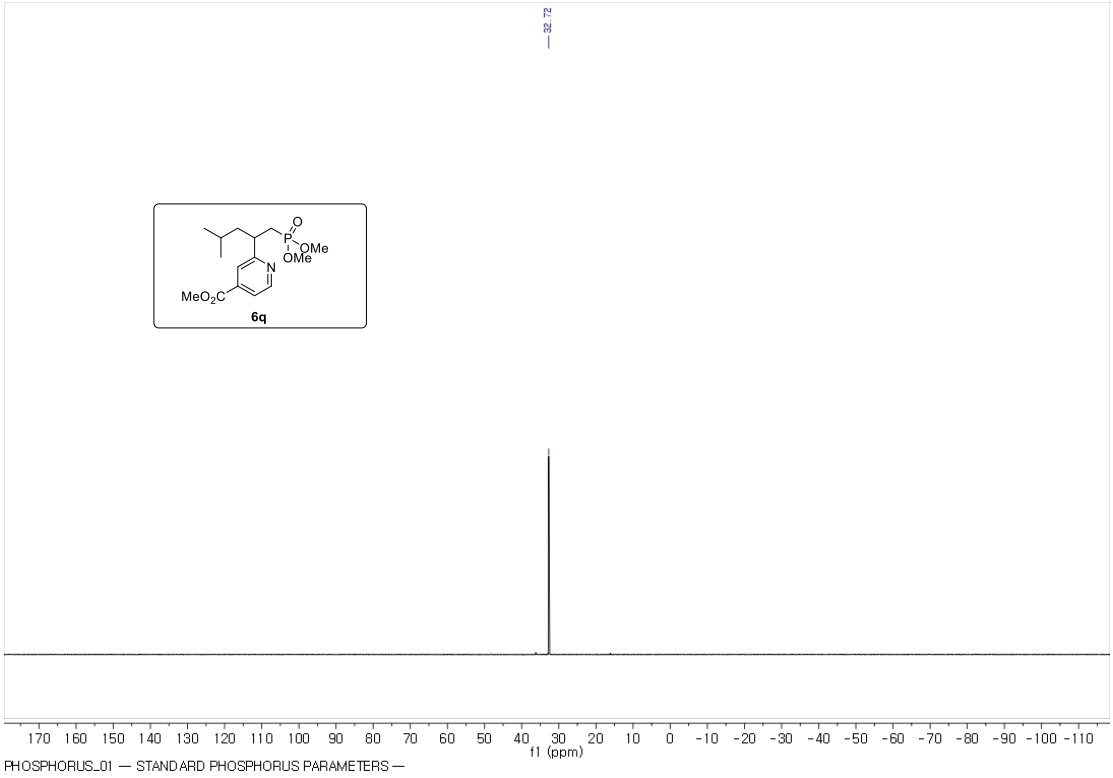
243 MHz, ^{31}P NMR in $CDCl_3$

methyl 2-(1-(dimethoxyphosphoryl)-4-methylpentan-2-yl)isonicotinate (6q)



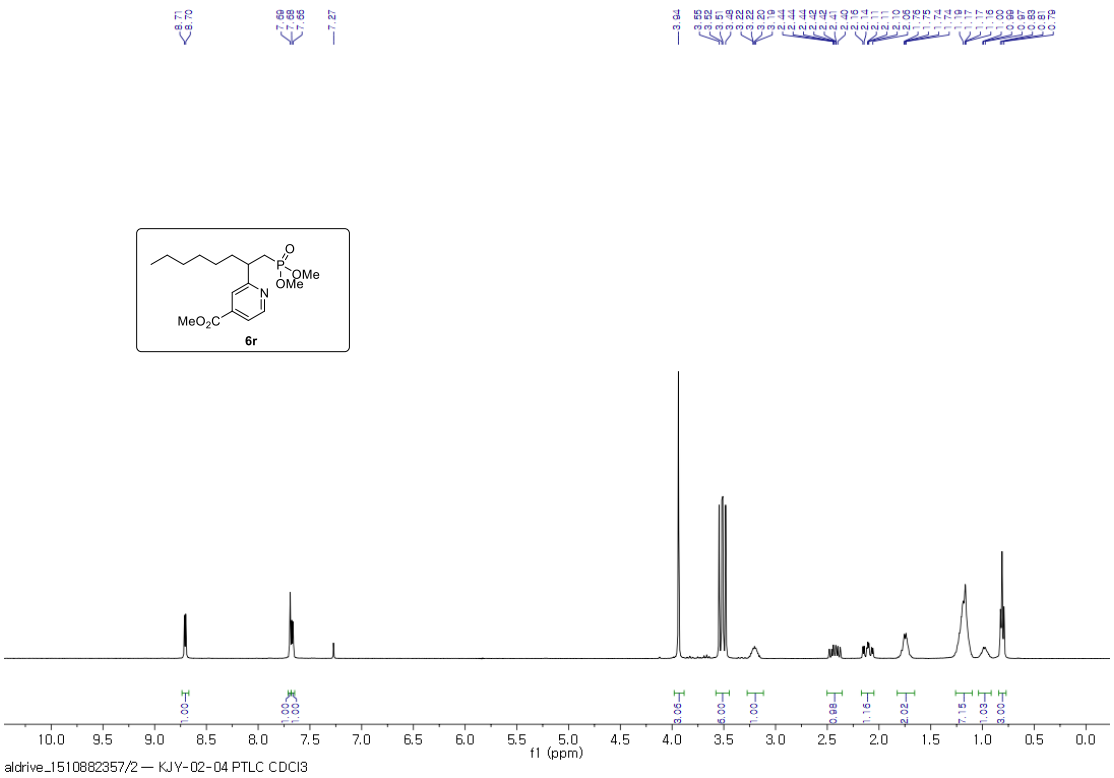
600 MHz, ^{1}H NMR in $CDCl_3$

150 MHz, ^{13}C NMR in $CDCl_3$

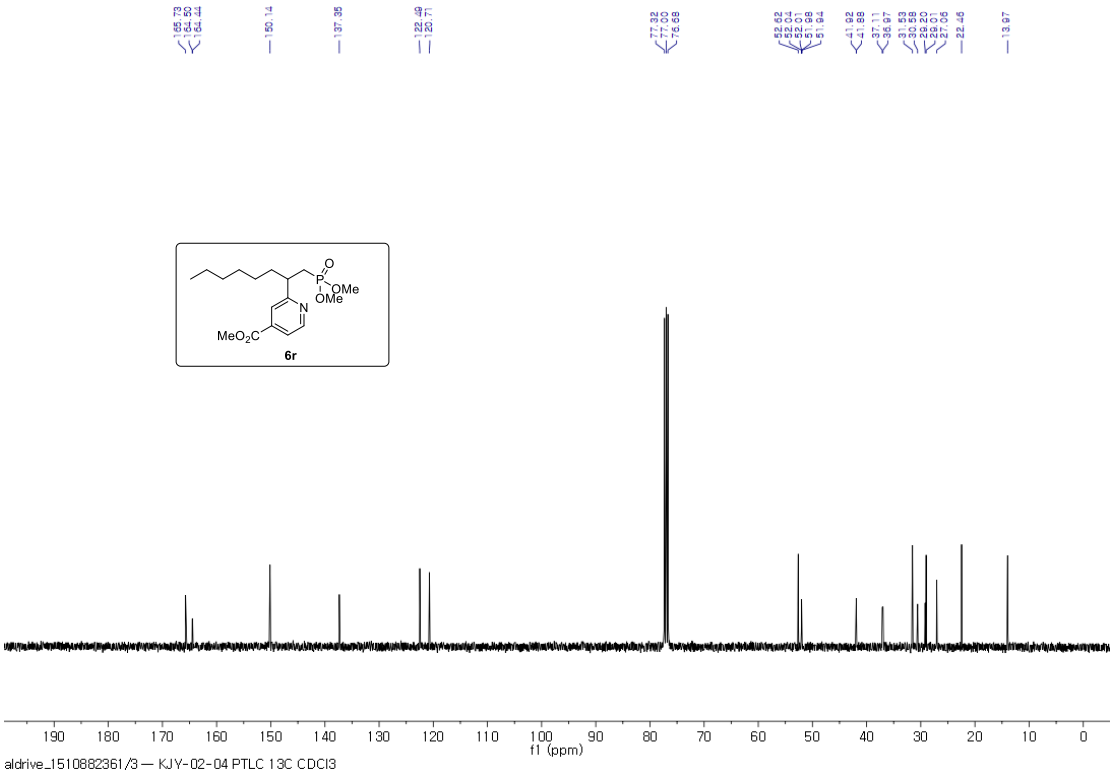


243 MHz, ^{31}P NMR in $CDCl_3$

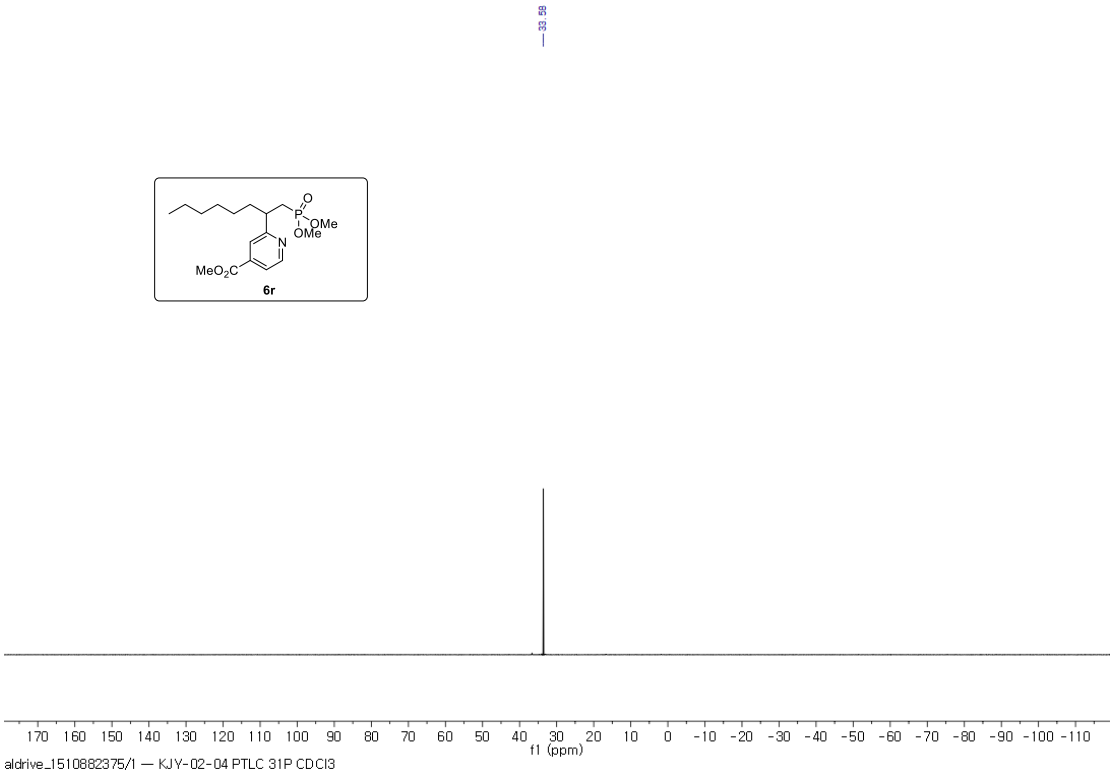
methyl 2-(1-(dimethoxyphosphoryl)octan-2-yl)isonicotinate (6r)



400 MHz, ^{1}H NMR in $CDCl_3$

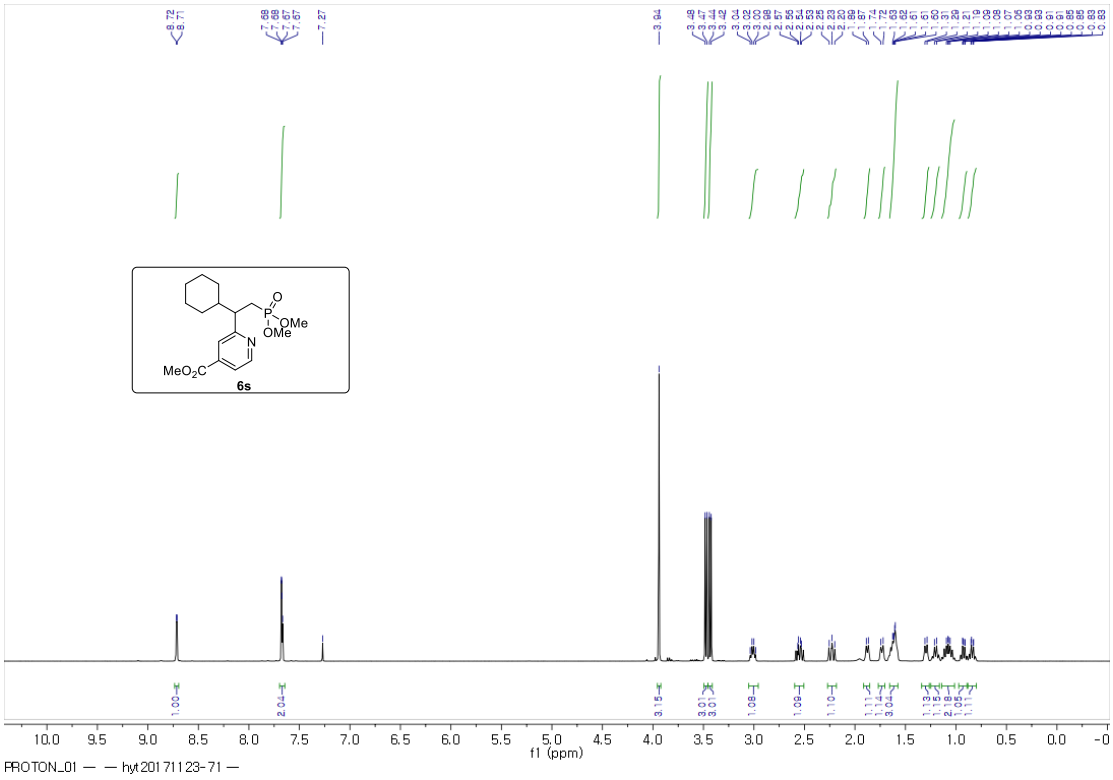


100 MHz, ^{13}C NMR in $CDCl_3$

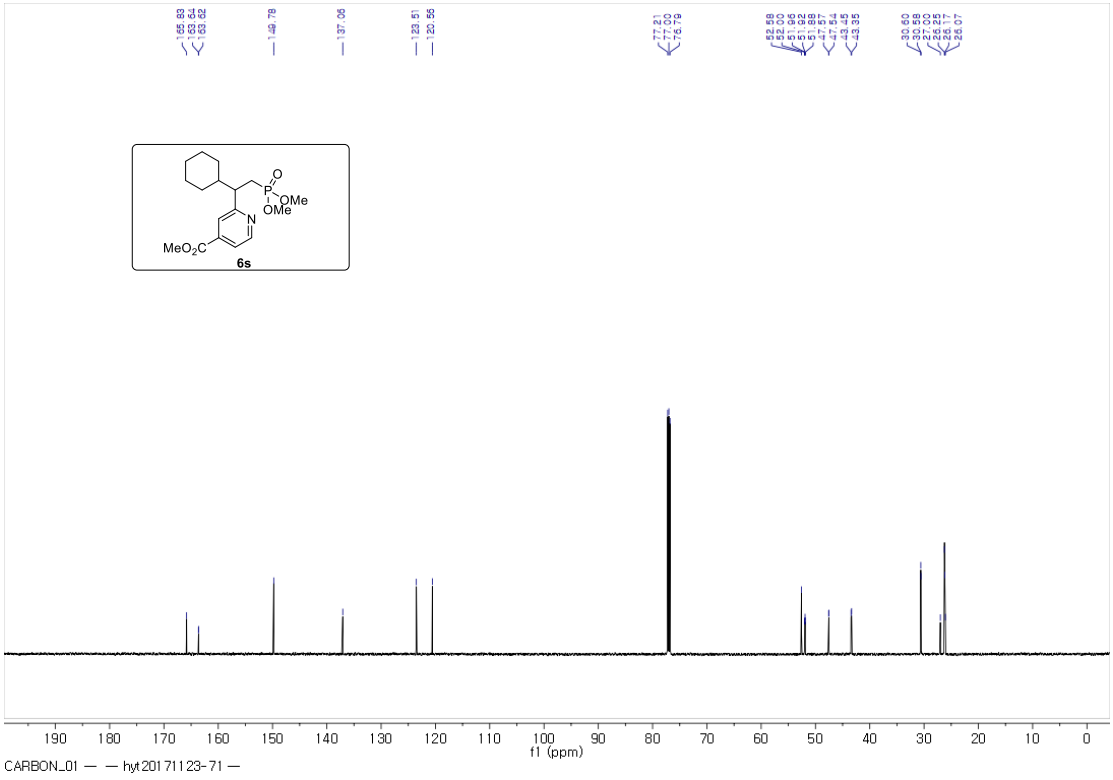


162 MHz, ^{31}P NMR in $CDCl_3$

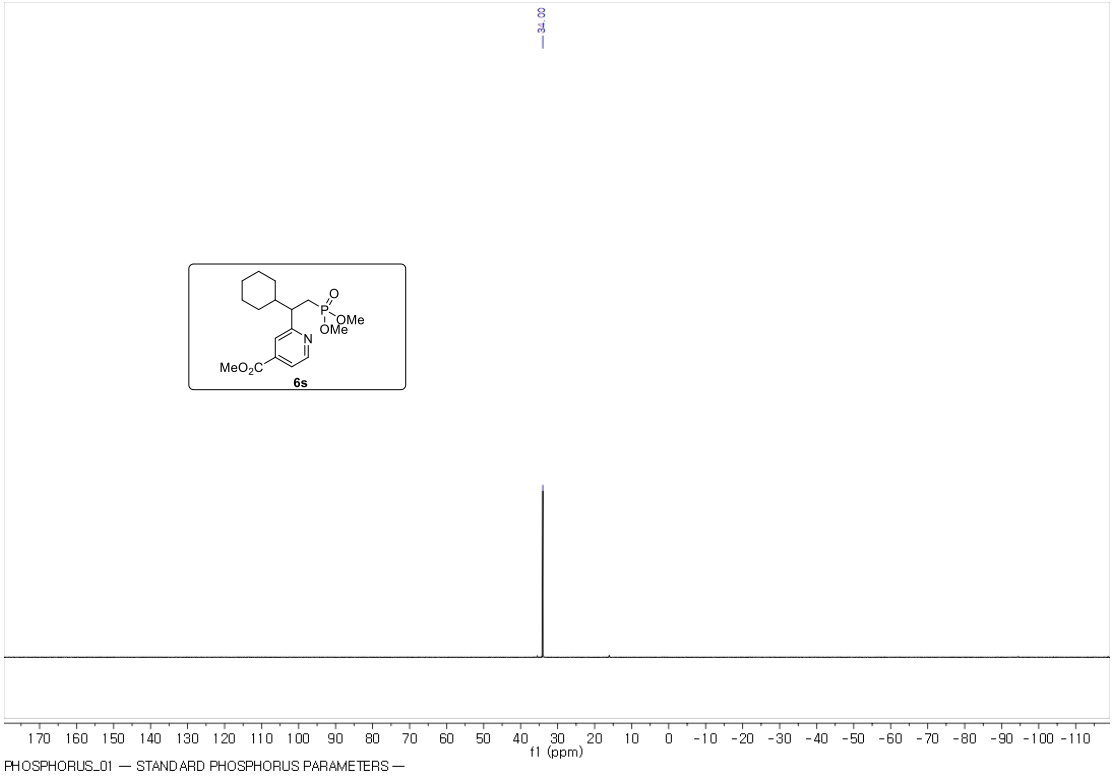
methyl 2-(1-cyclohexyl-2-(dimethoxyphosphoryl)ethyl)isonicotinate (6s)



600 MHz, ^{1}H NMR in $CDCl_3$

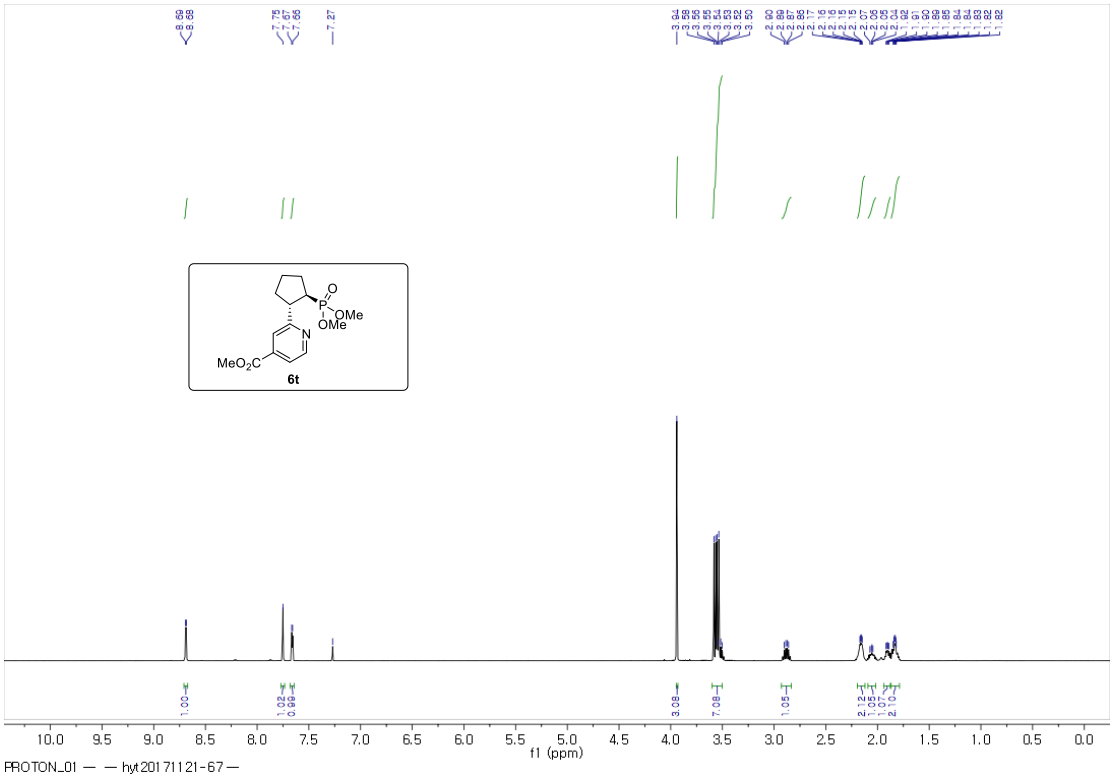


150 MHz, ^{13}C NMR in $CDCl_3$

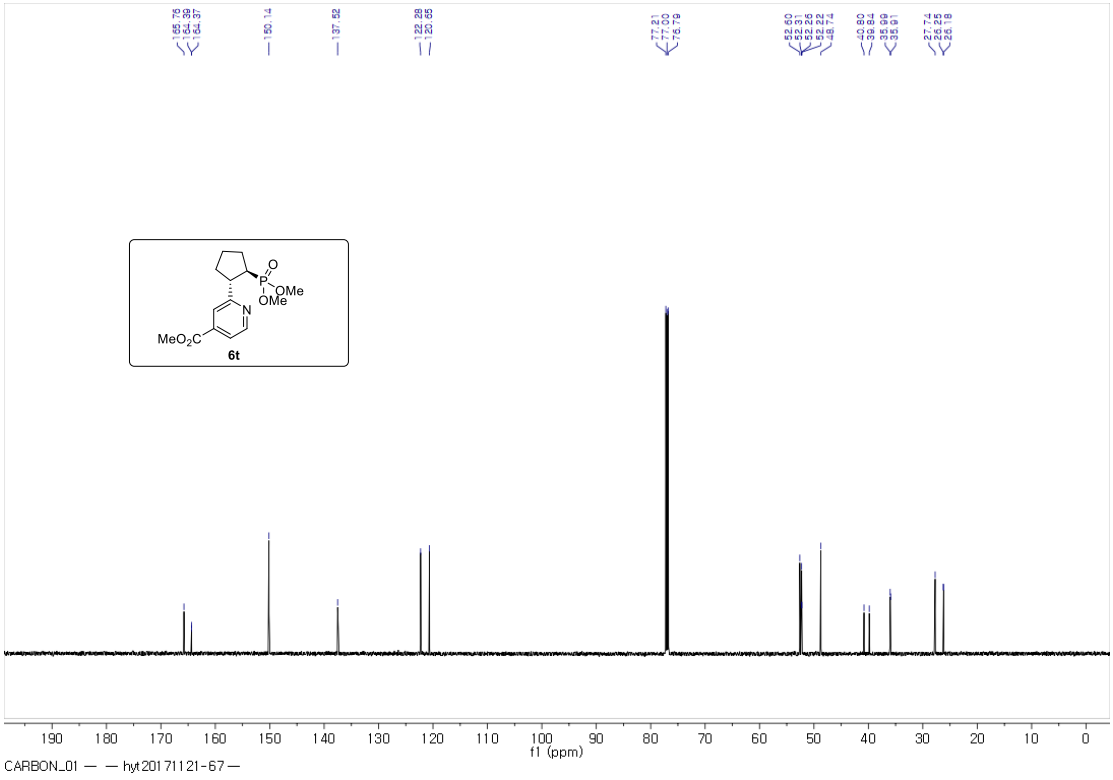


243 MHz, ^{31}P NMR in $CDCl_3$

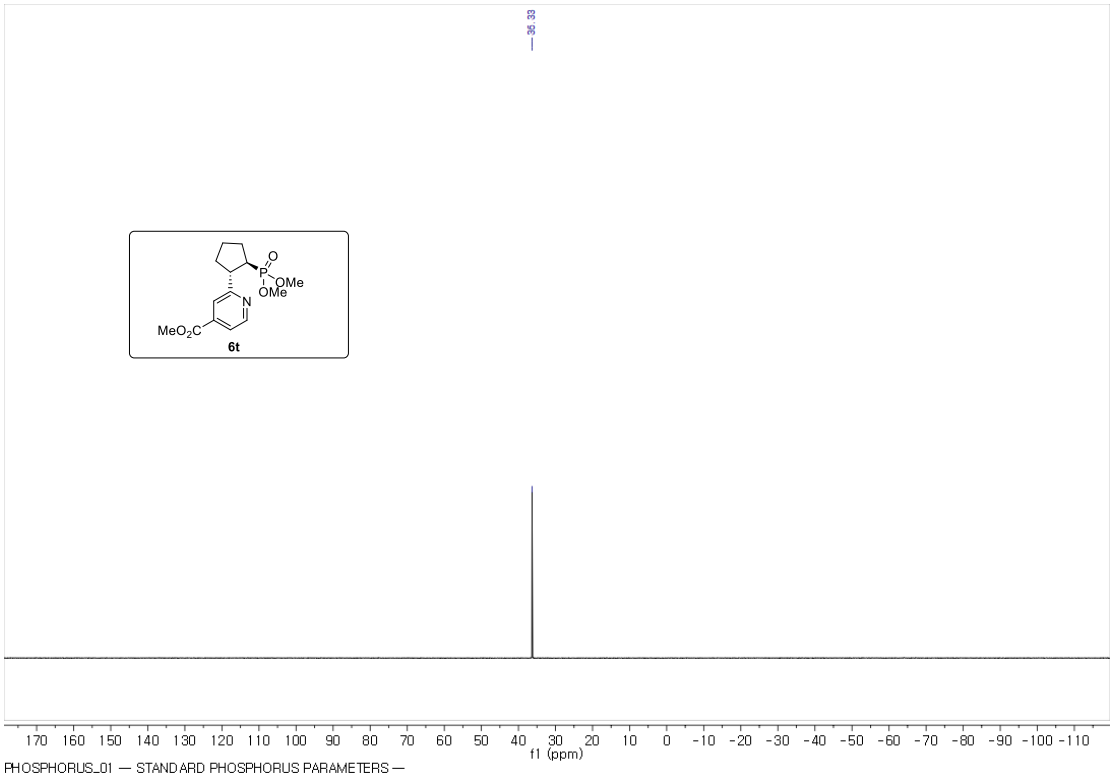
methyl 2-((1S,2R)-2-(dimethoxyphosphoryl)cyclopentyl)isonicotinate (6t).



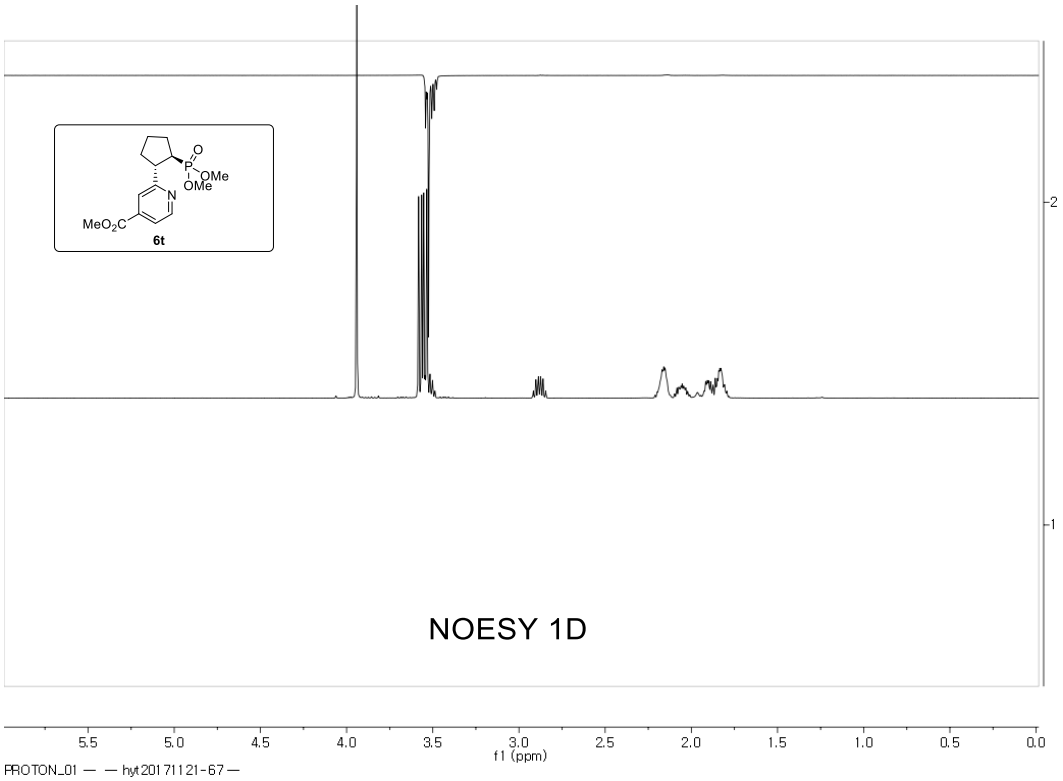
600 MHz, ^{1}H NMR in $CDCl_3$



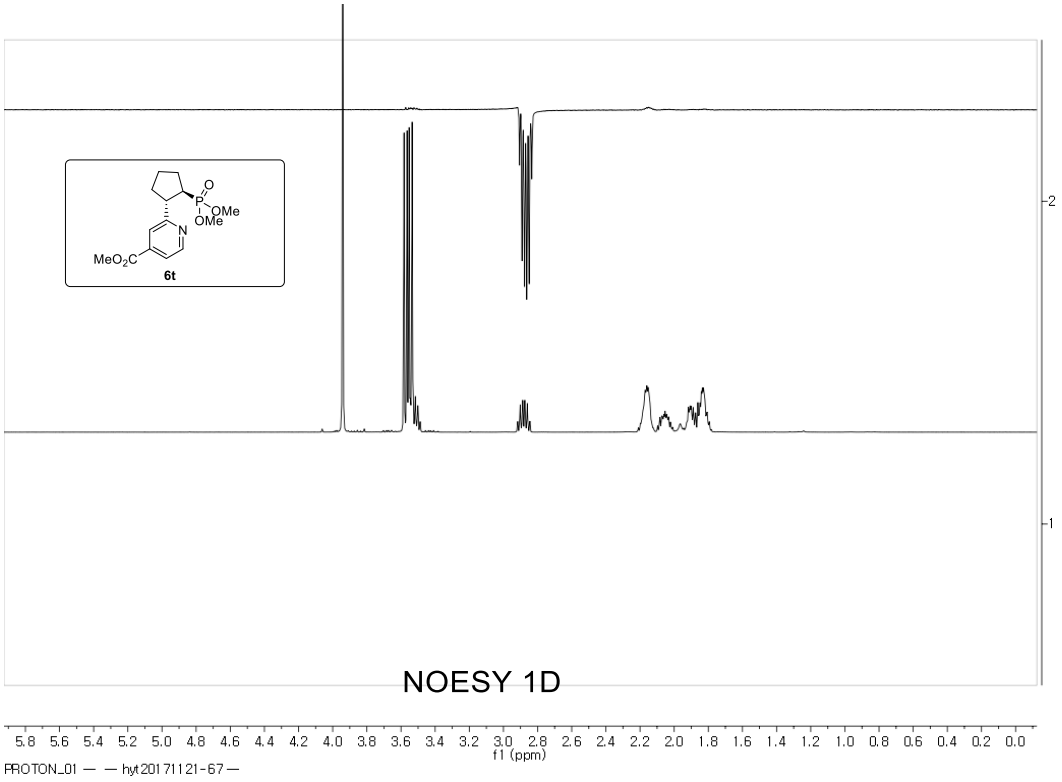
150 MHz, ^{13}C NMR in $CDCl_3$



243 MHz, ^{31}P NMR in $CDCl_3$

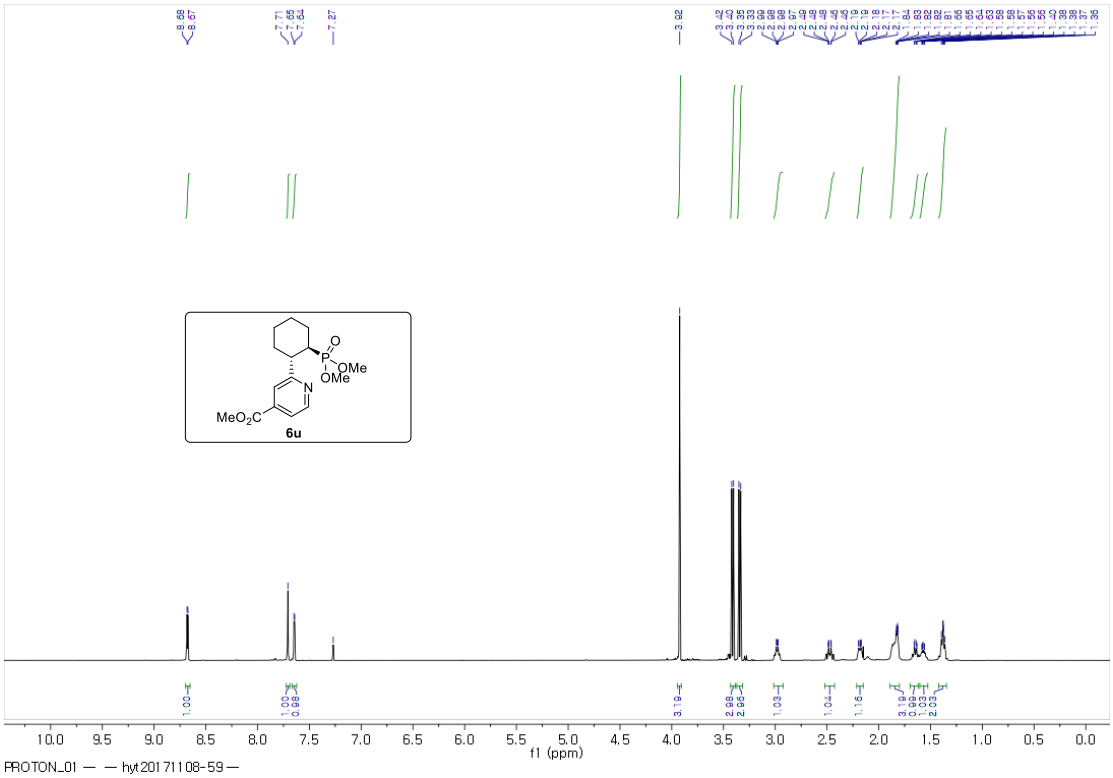


NOESY 1D in $CDCl_3$

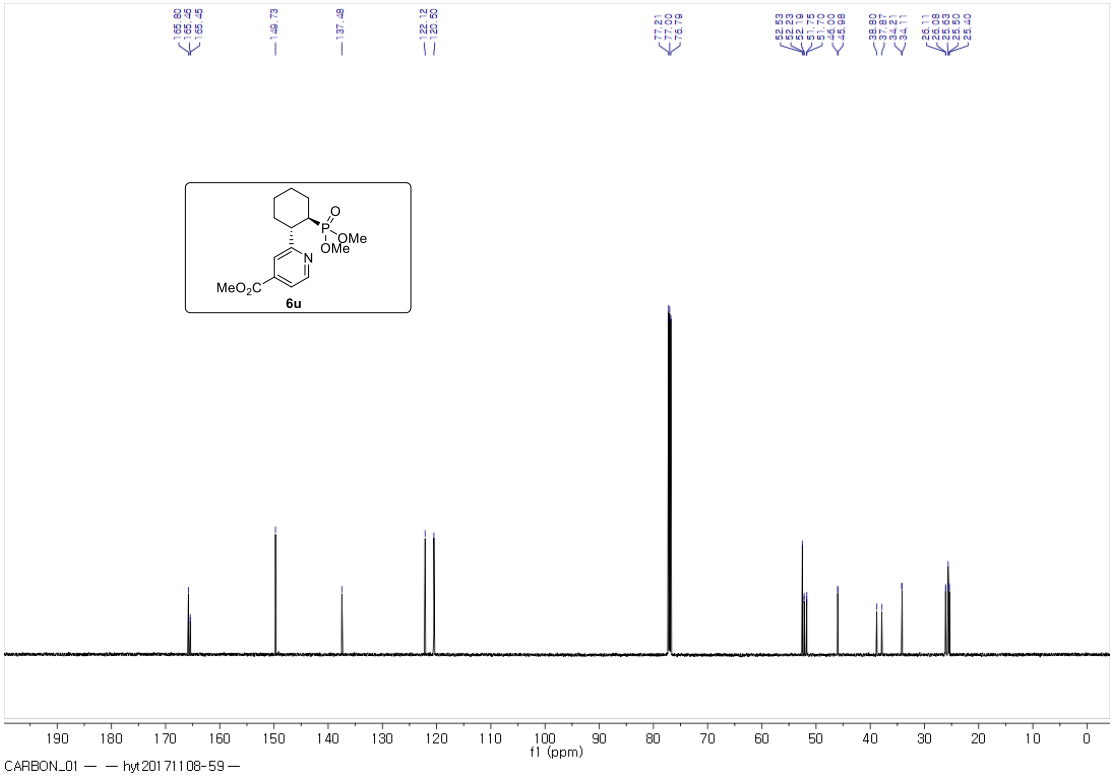


NOESY 1D in $CDCl_3$

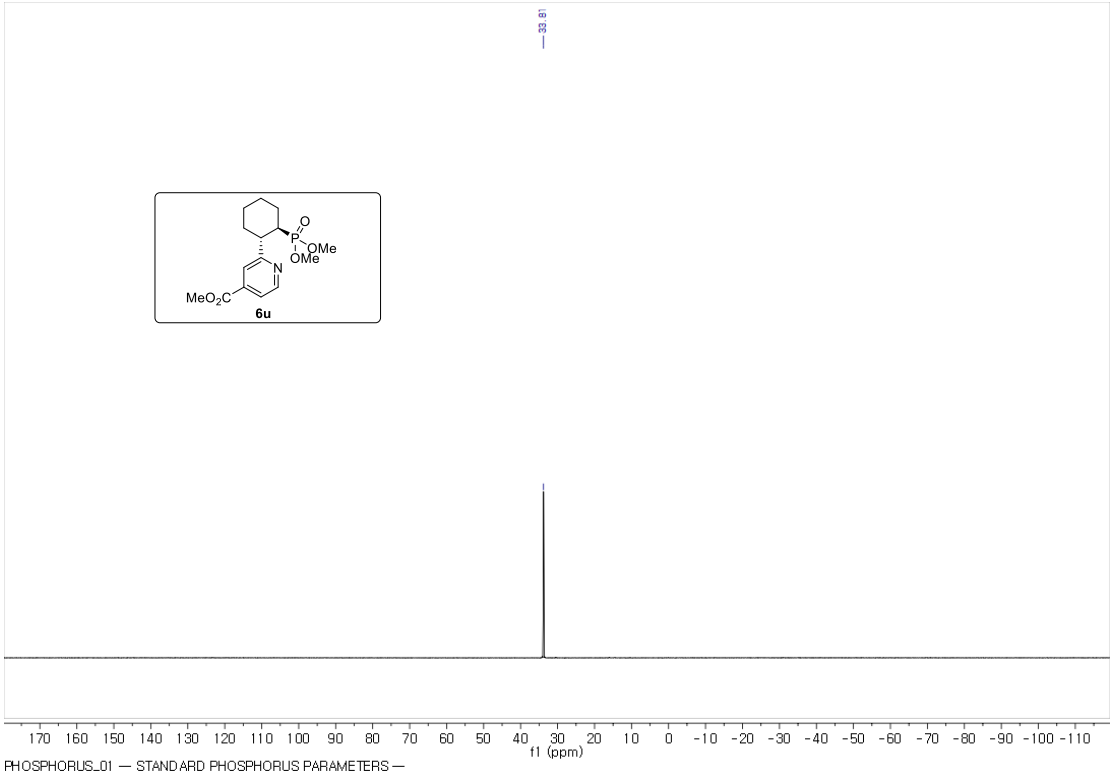
methyl 2-((1S,2R)-2-(dimethoxyphosphoryl)cyclohexyl)isonicotinate (6u)



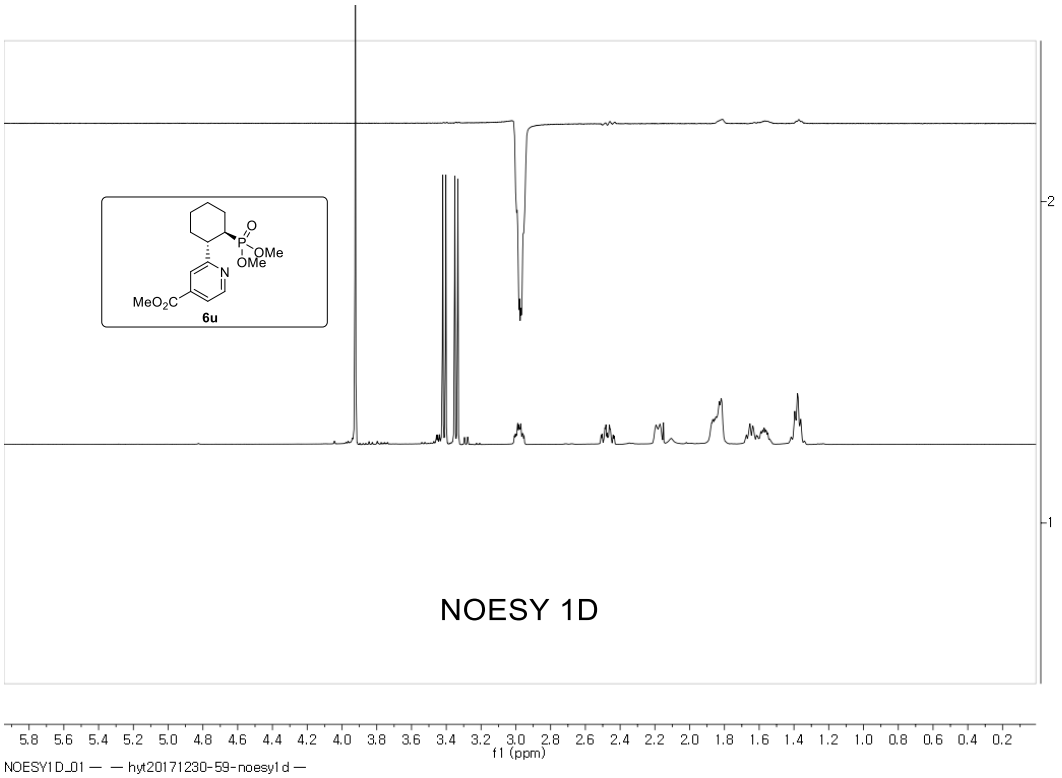
600 MHz, ^{1}H NMR in $CDCl_3$



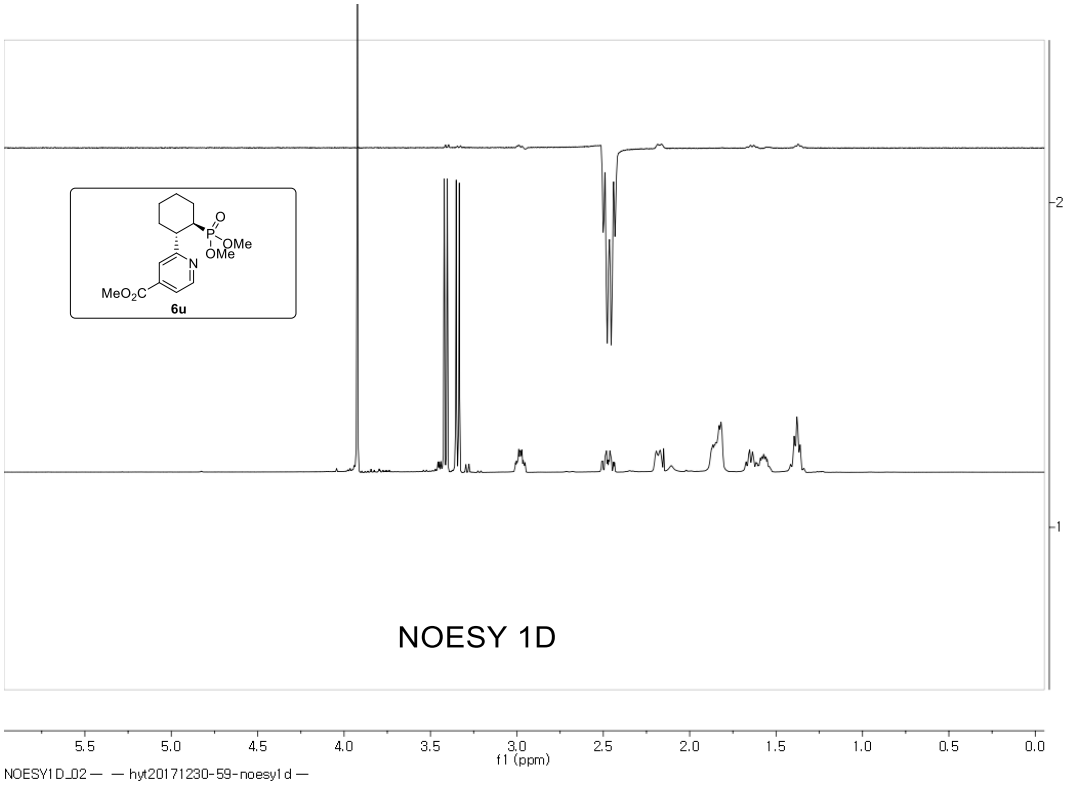
150 MHz, ^{13}C NMR in $CDCl_3$



243 MHz, ^{31}P NMR in $CDCl_3$

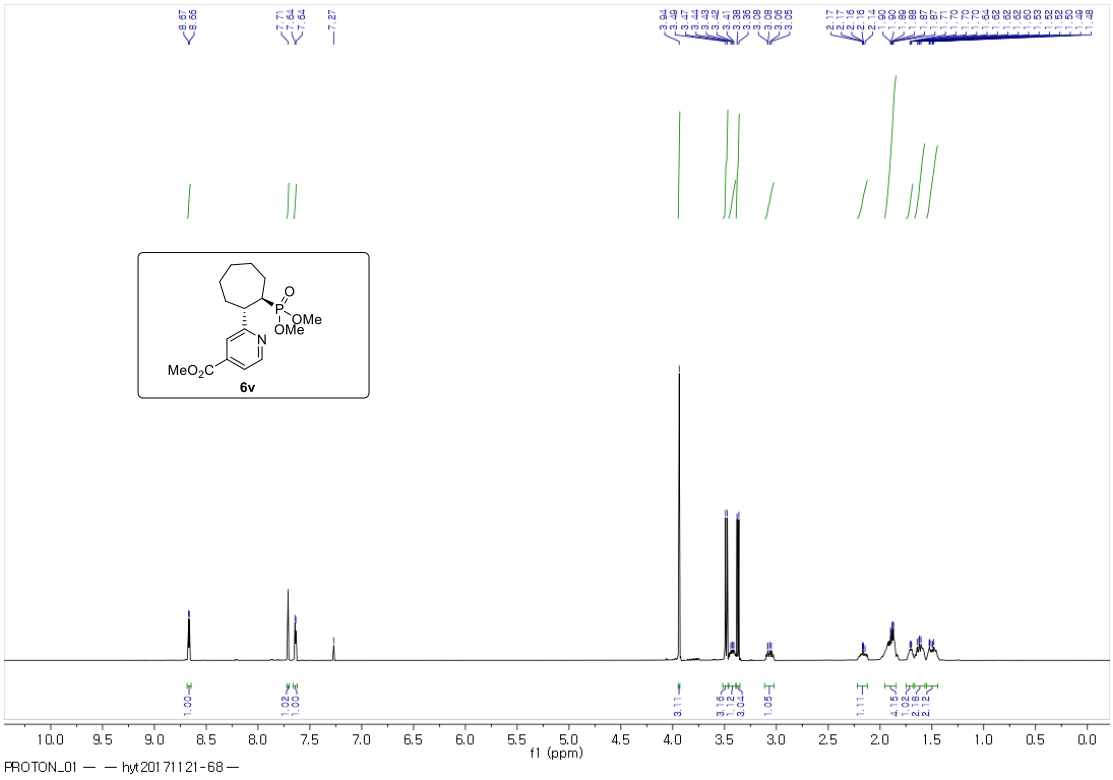


NOESY 1D in $CDCl_3$

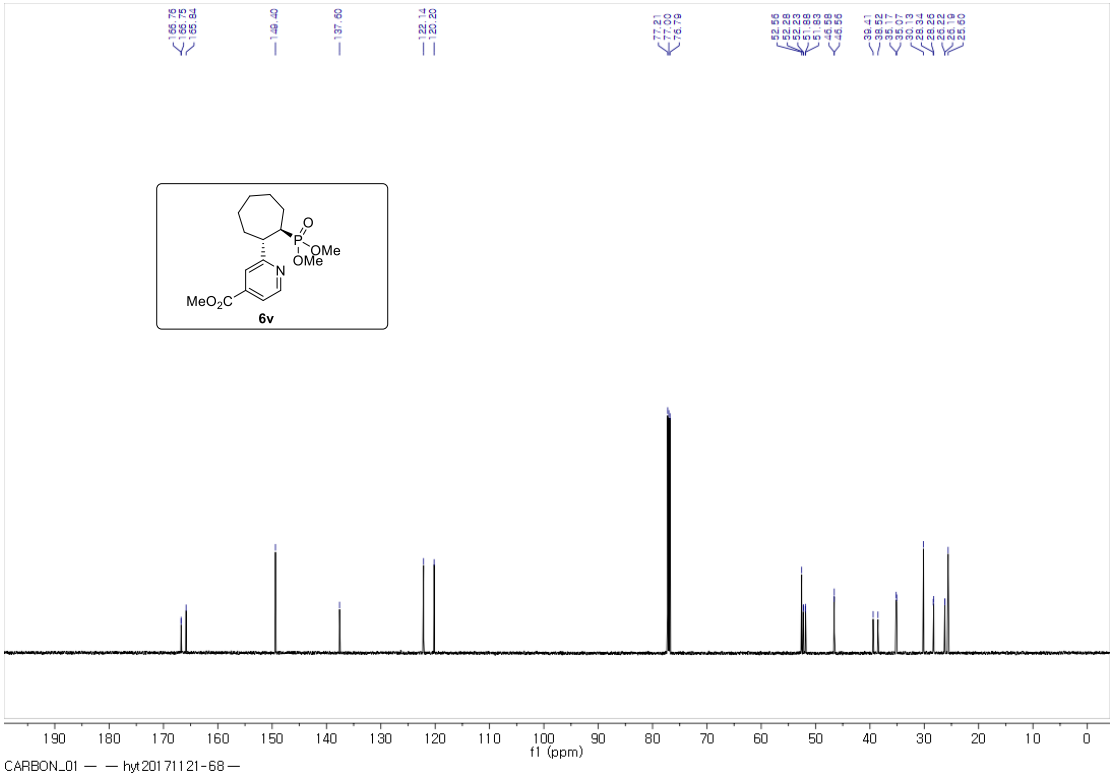


NOESY 1D in $CDCl_3$

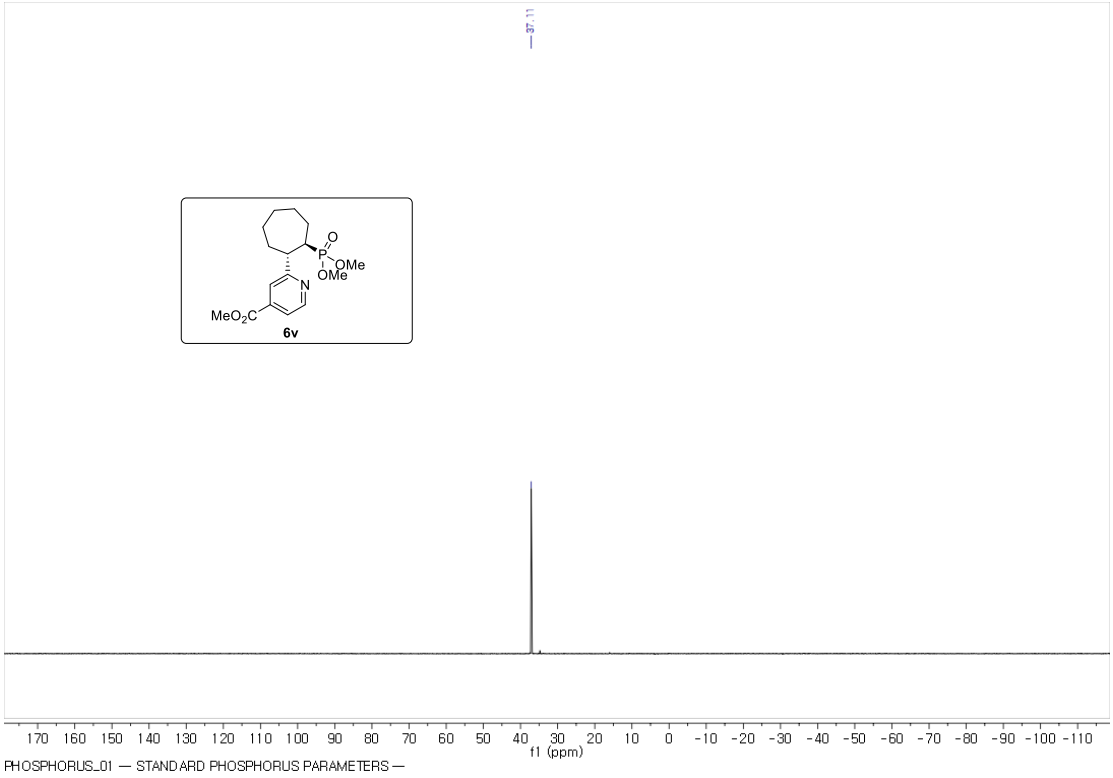
methyl 2-((1S,2R)-2-(dimethoxyphosphoryl)cycloheptyl)isonicotinate (6v)



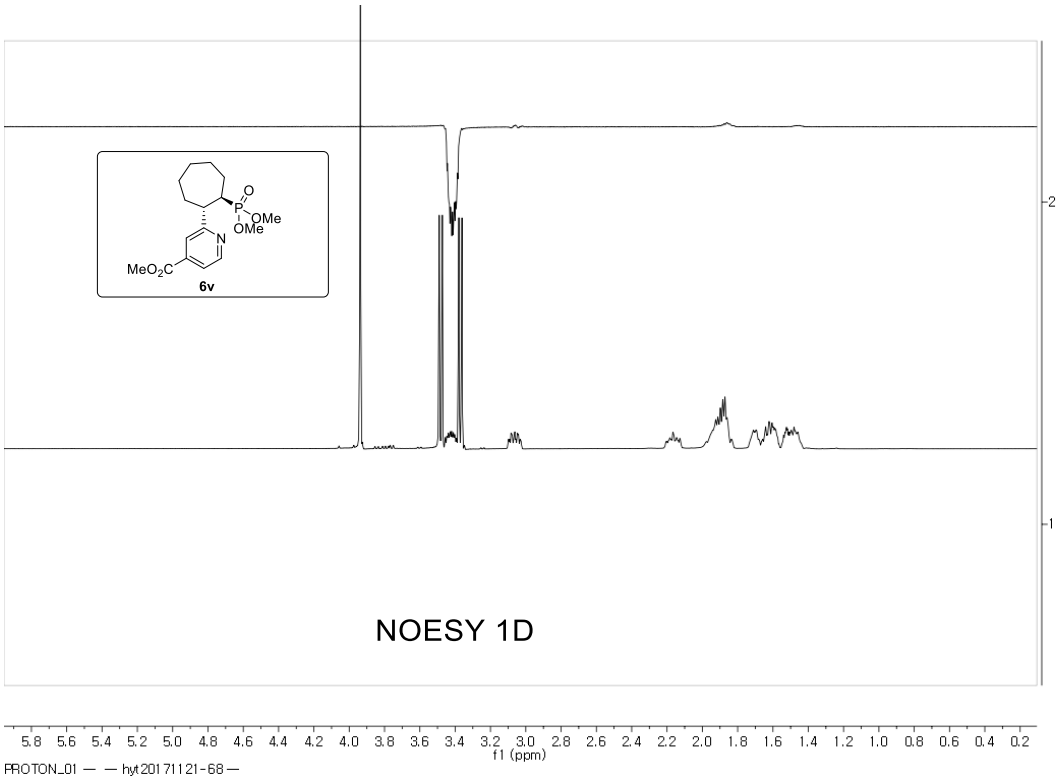
600 MHz, ^{1}H NMR in $CDCl_3$



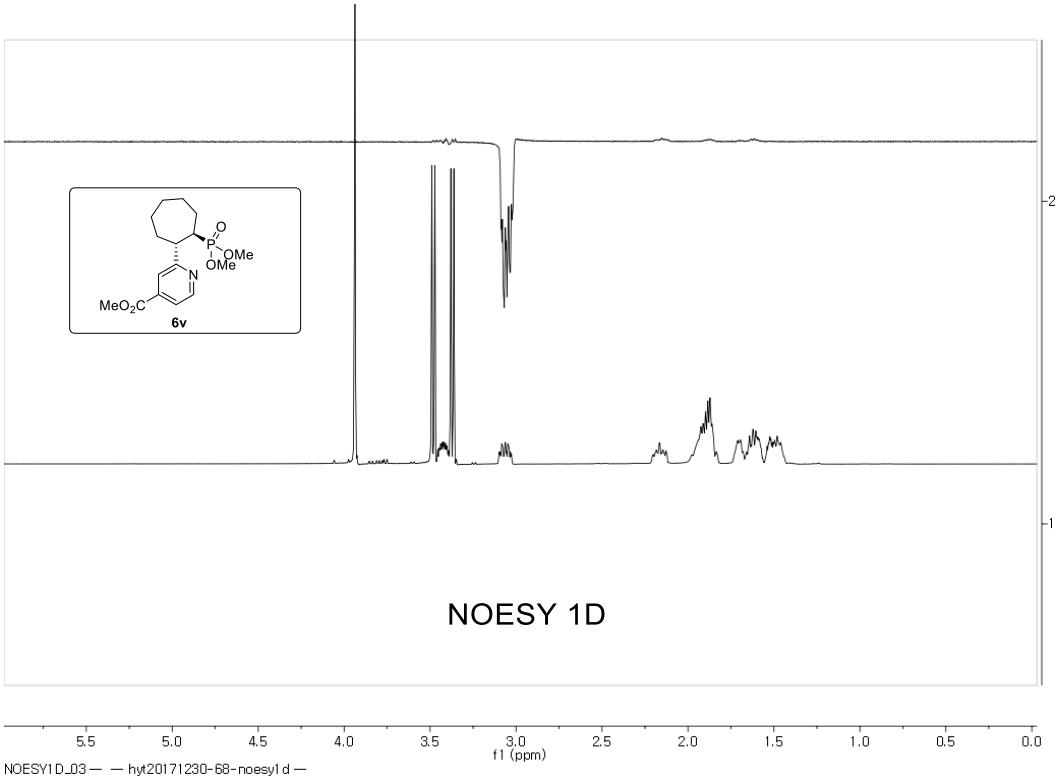
150 MHz, ^{13}C NMR in $CDCl_3$



243 MHz, ^{31}P NMR in $CDCl_3$

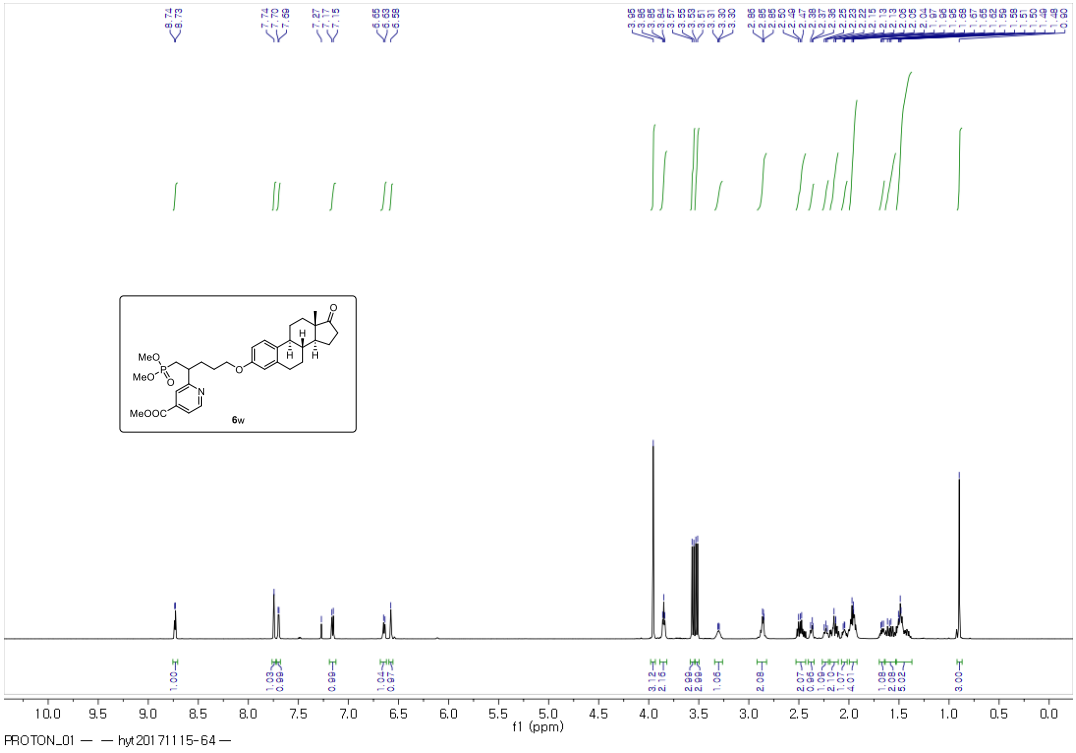


NOESY 1D in $CDCl_3$

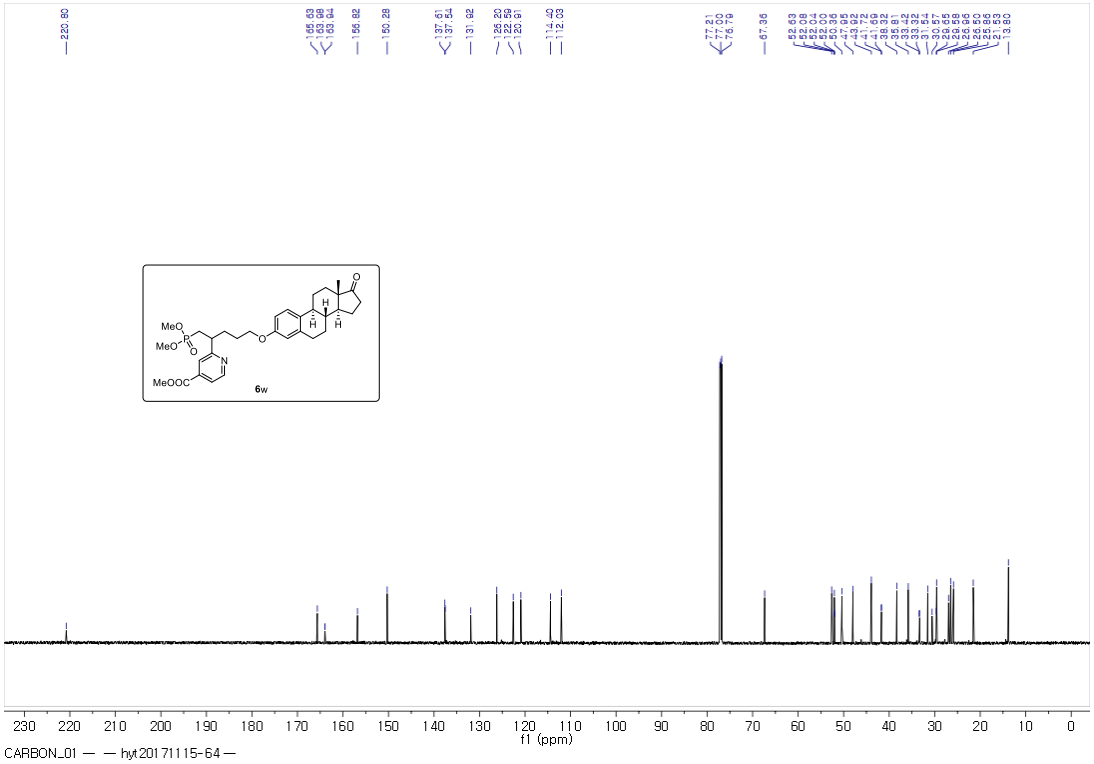


NOESY 1D in $CDCl_3$

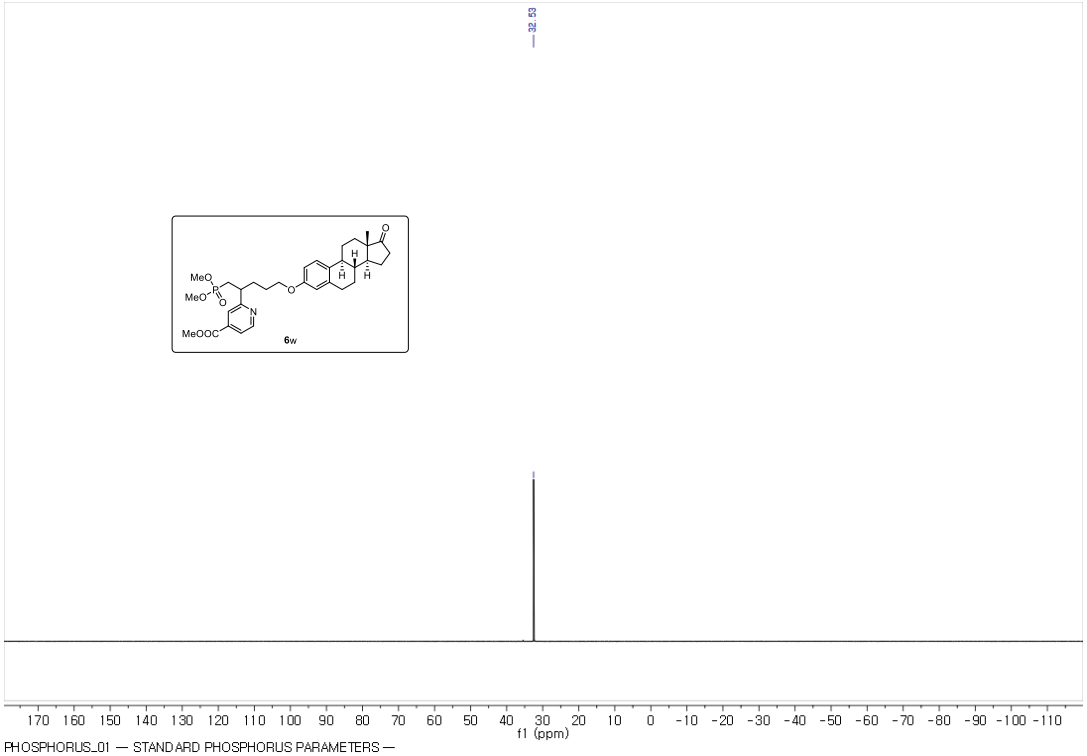
methyl2-(1-(dimethoxyphosphoryl)-5-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)pentan-2-yl)isonicotinate (6w).



600 MHz, ^{1}H NMR in $CDCl_3$

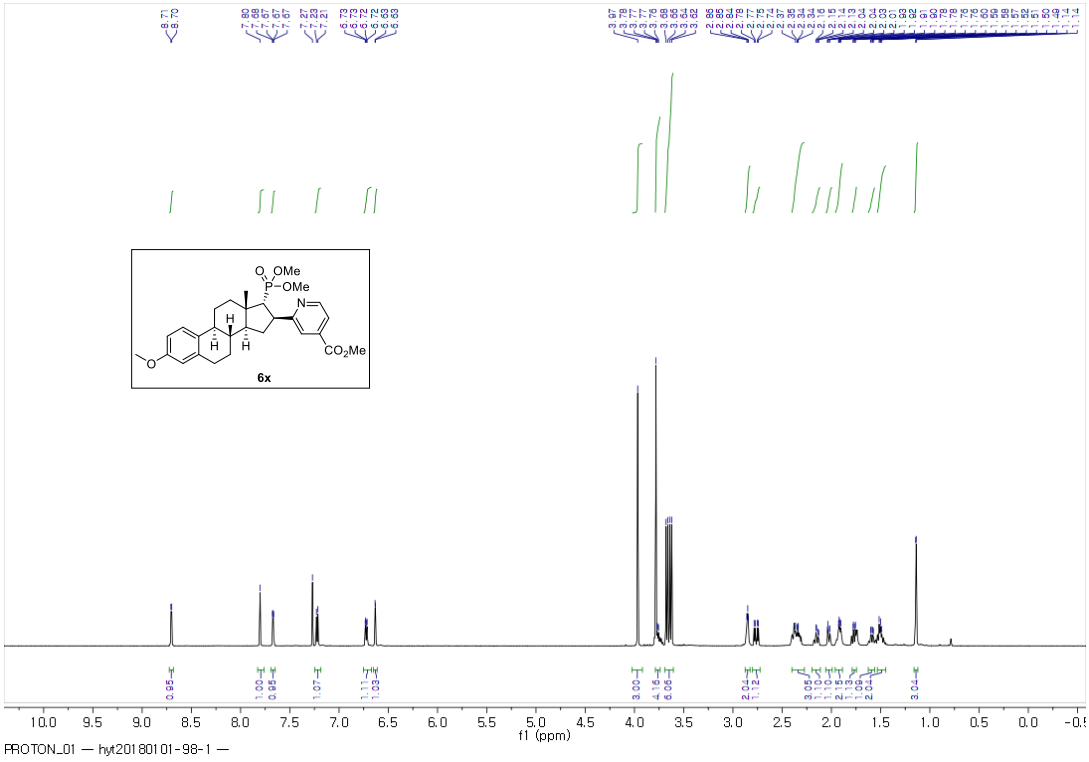


150 MHz, ^{13}C NMR in $CDCl_3$

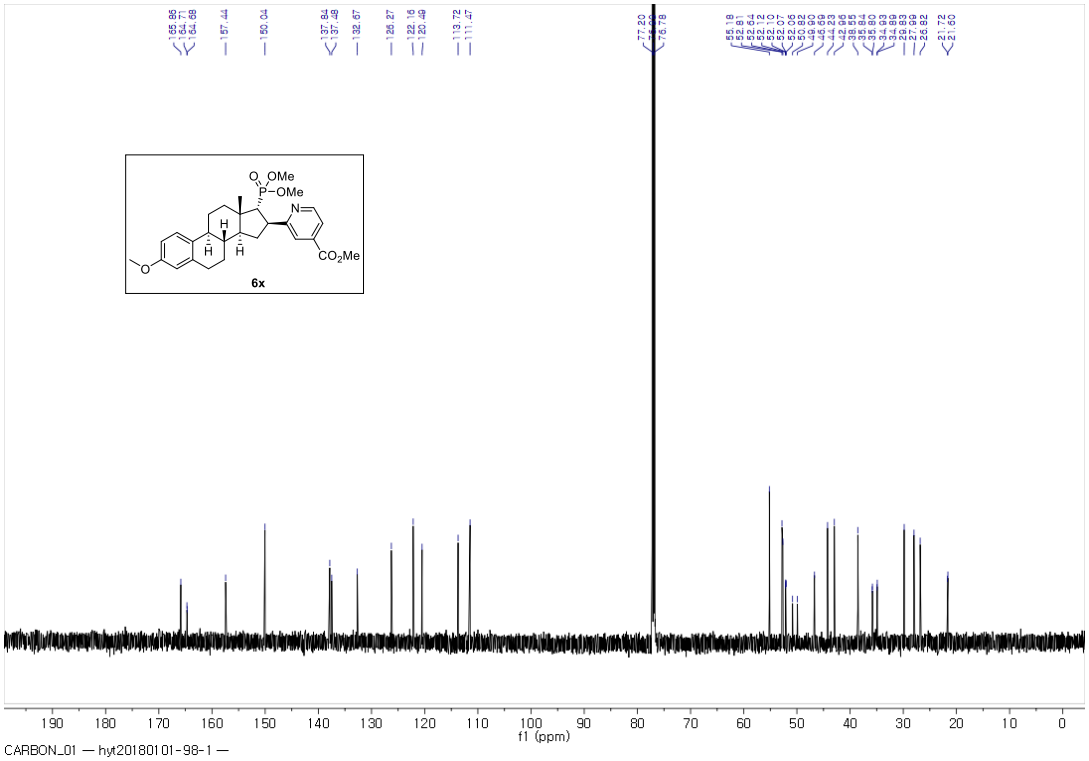


243 MHz, ^{31}P NMR in $CDCl_3$

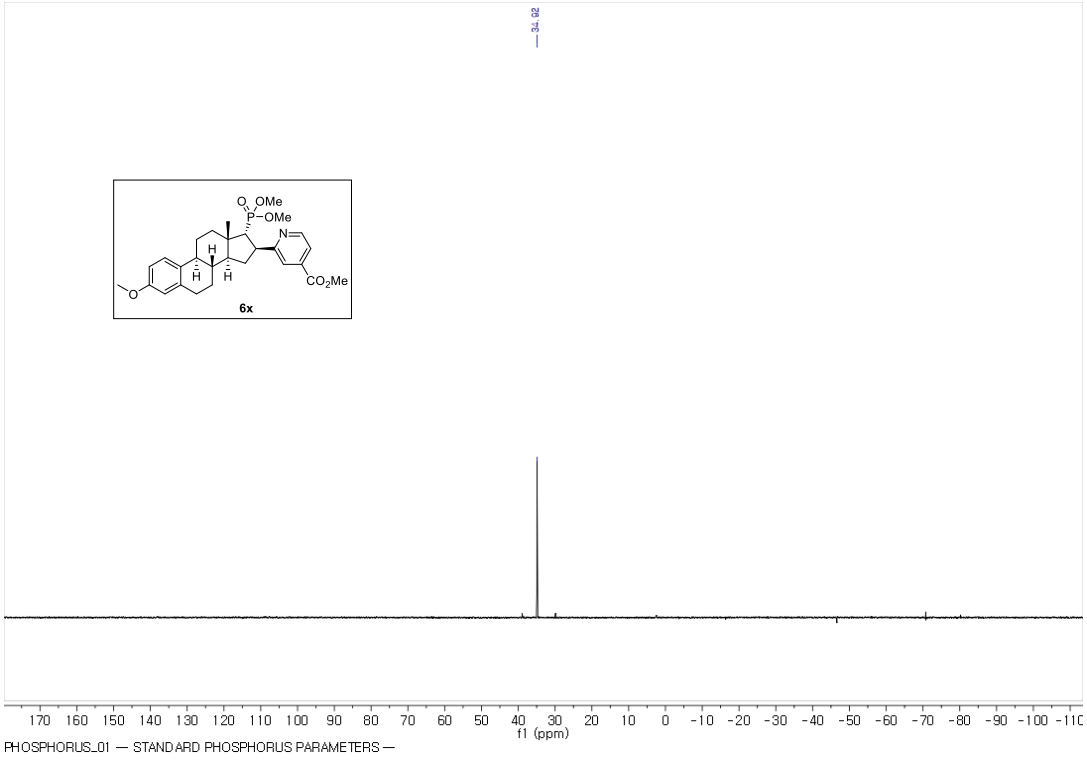
methyl 2-((8R,9S,13S,14S,16R,17R)-17-(dimethoxyphosphoryl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-16-yl)isonicotinate (6x)



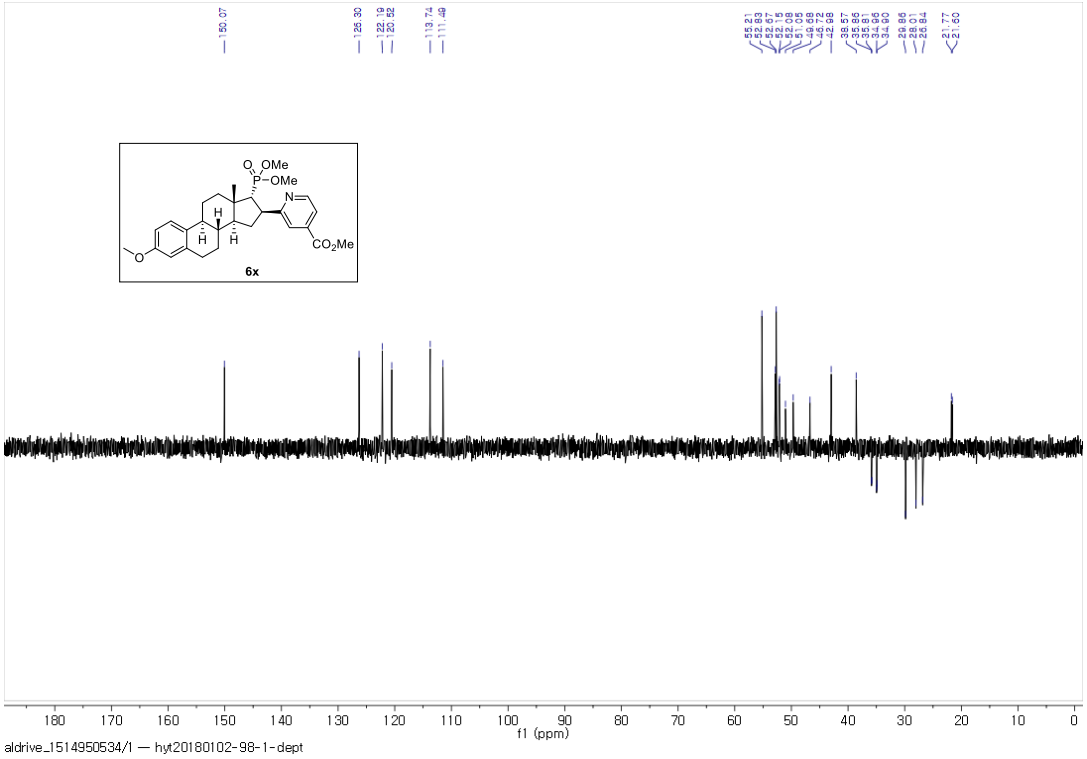
600 MHz, ^{1}H NMR in $CDCl_3$



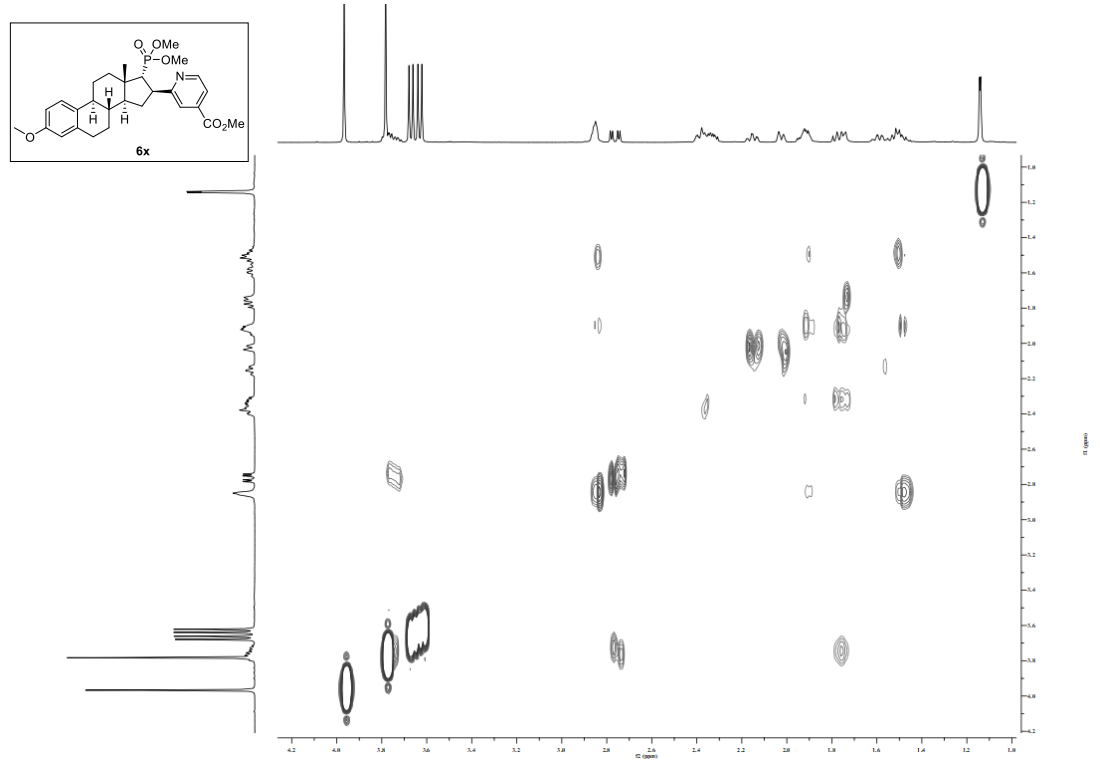
150 MHz, ^{13}C NMR in $CDCl_3$



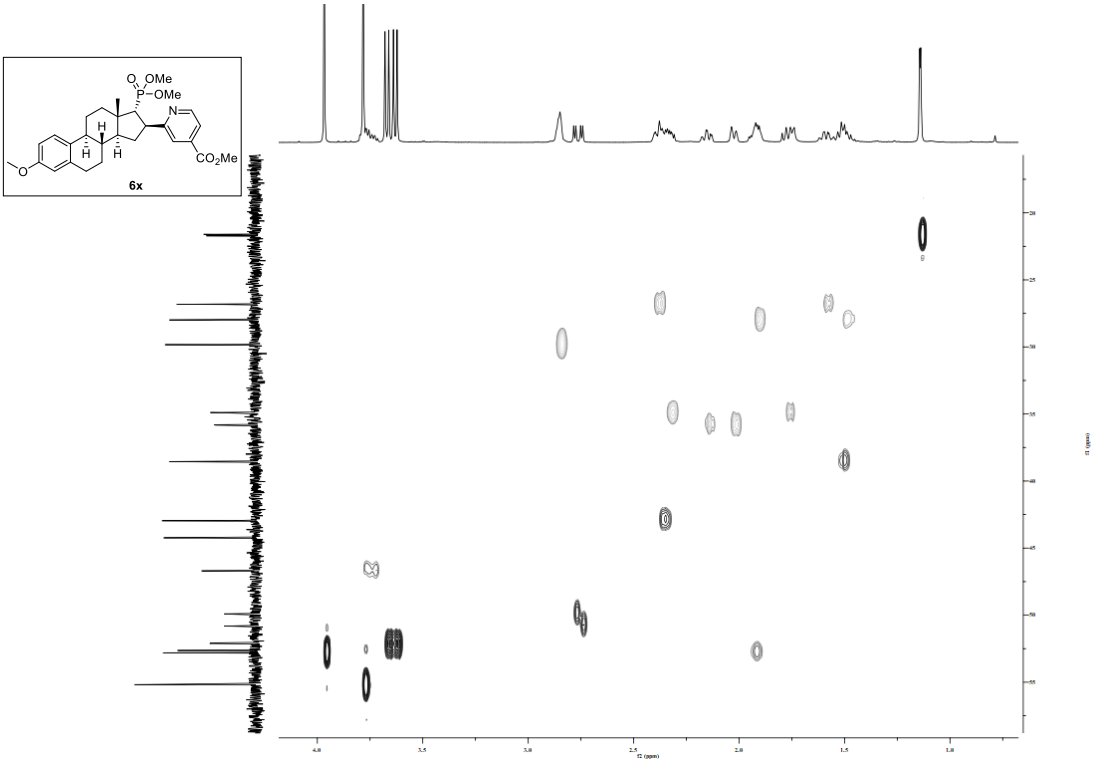
243 MHz, ^{31}P NMR in $CDCl_3$



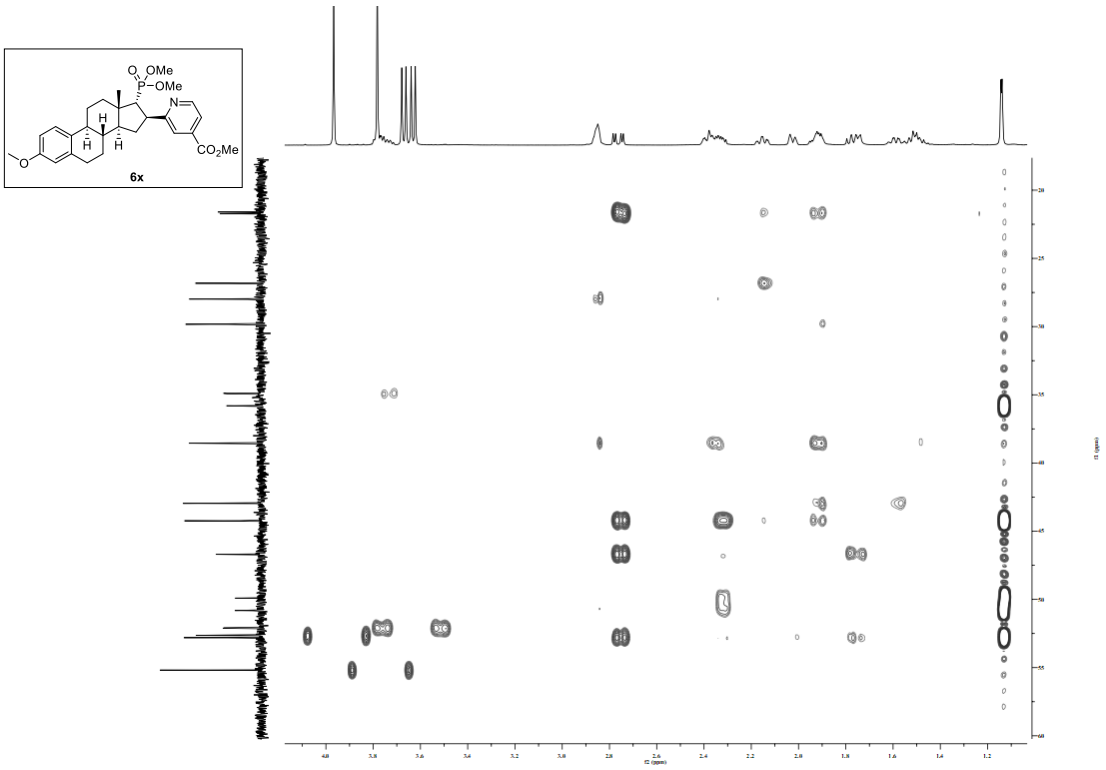
DEPT135 in $CDCl_3$



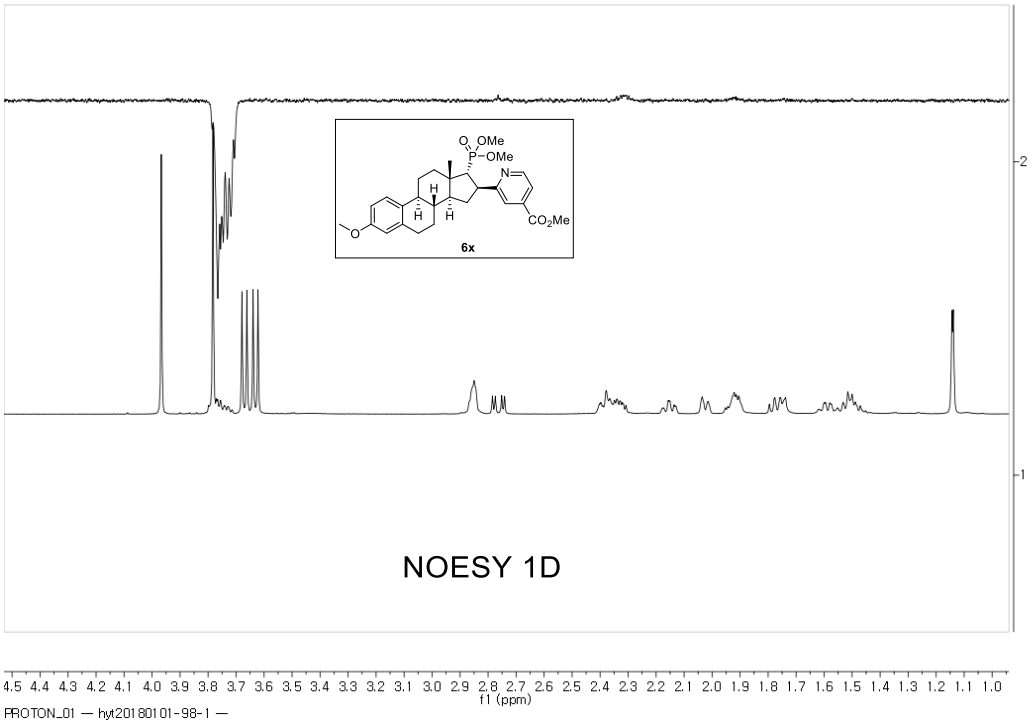
COSY in $CDCl_3$



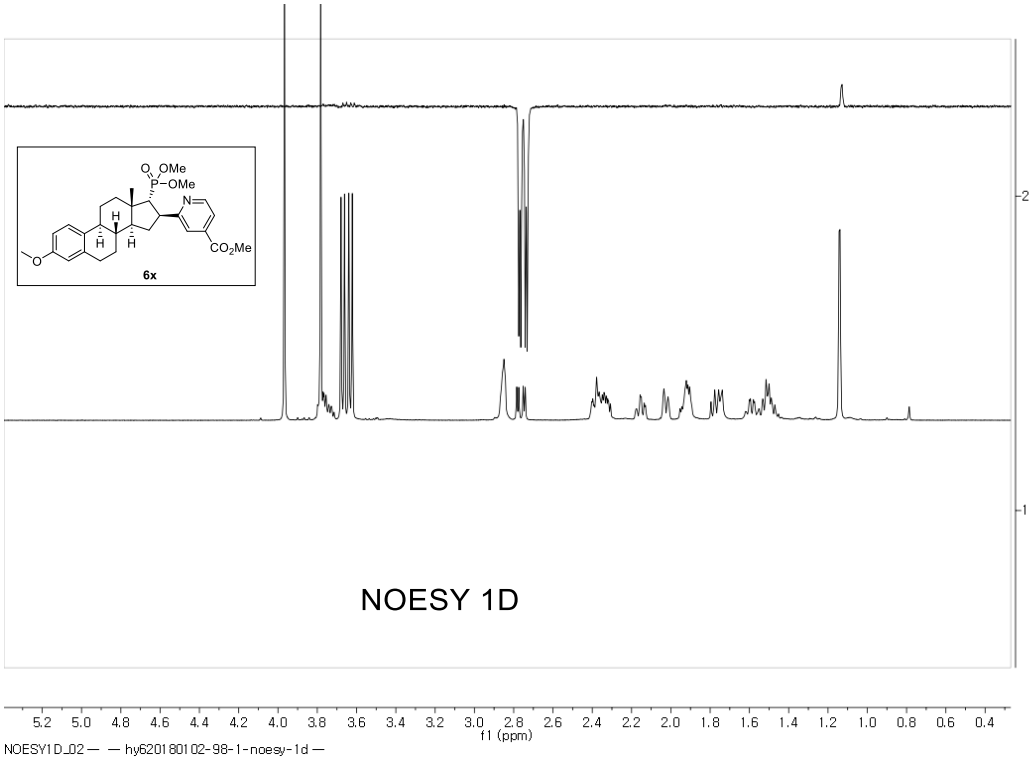
HSQC in $CDCl_3$



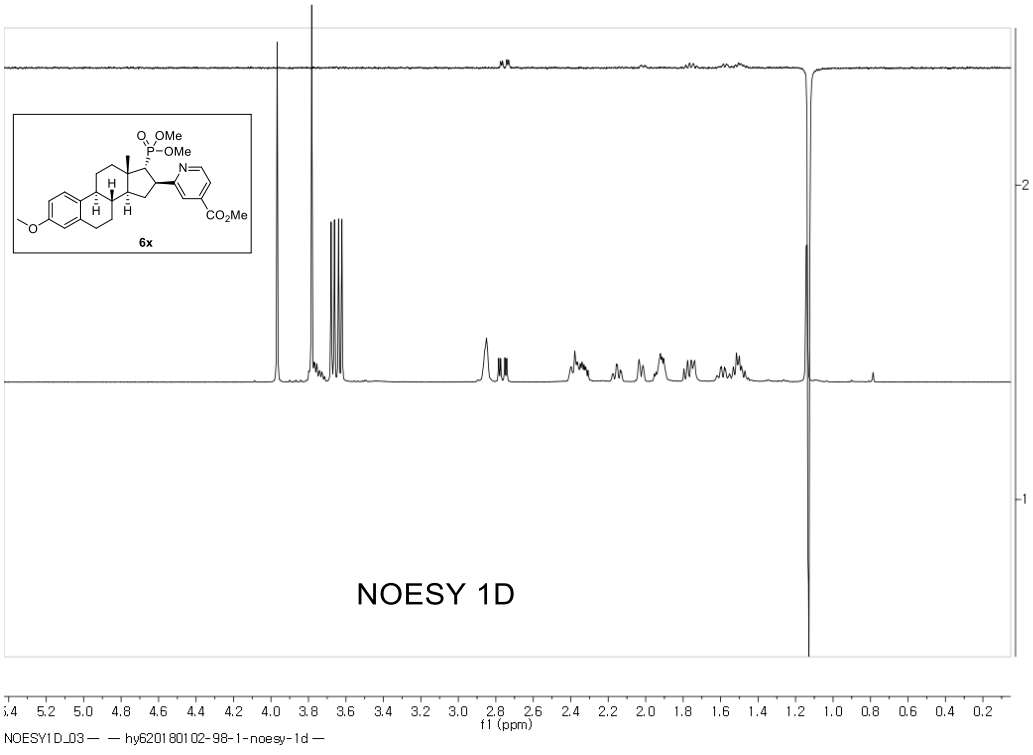
HMBC in $CDCl_3$



NOESY 1D in $CDCl_3$

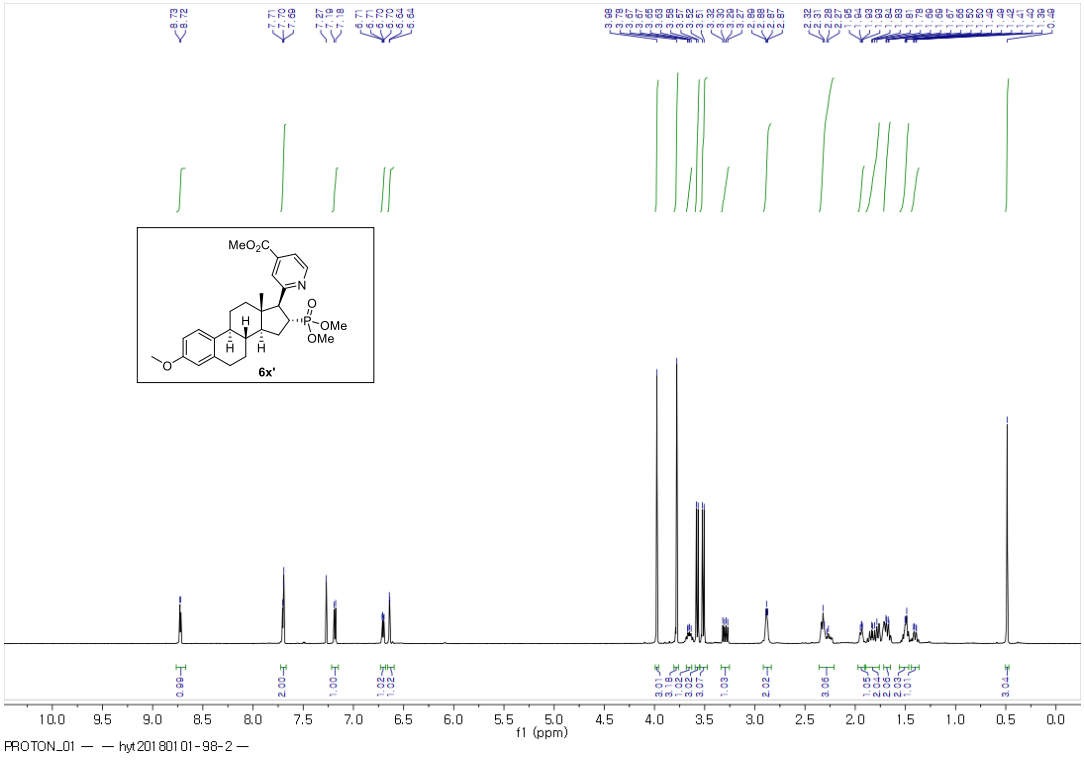


NOESY 1D in $CDCl_3$

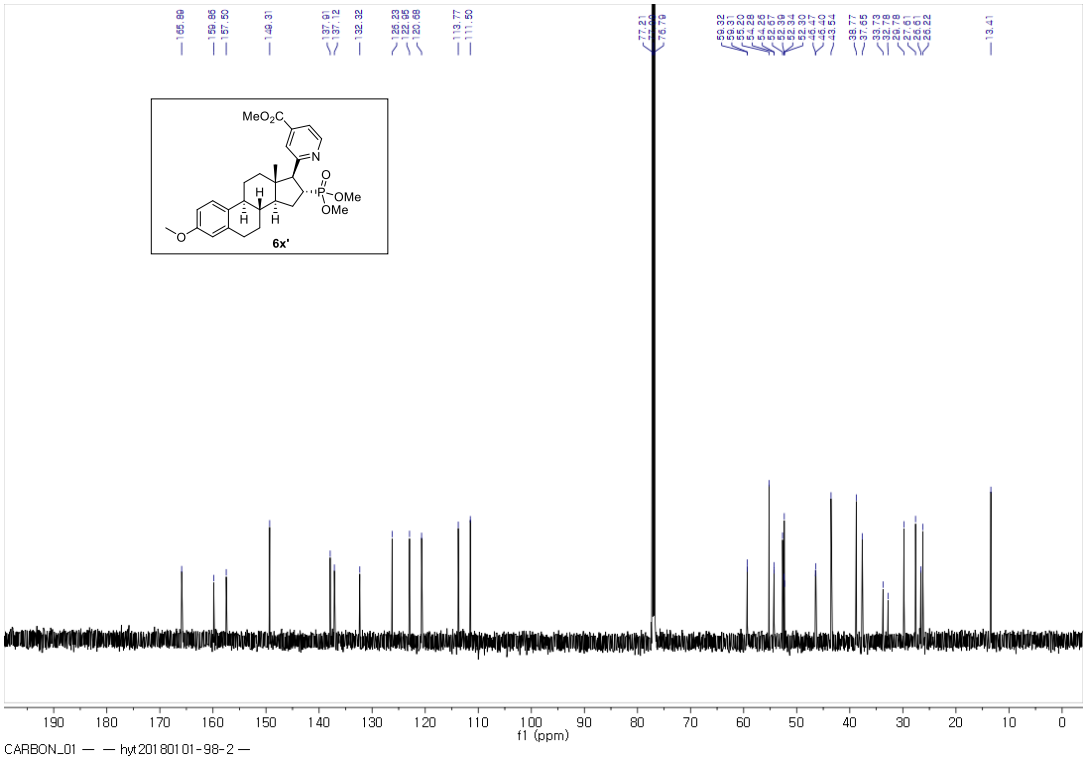


NOESY 1D in $CDCl_3$

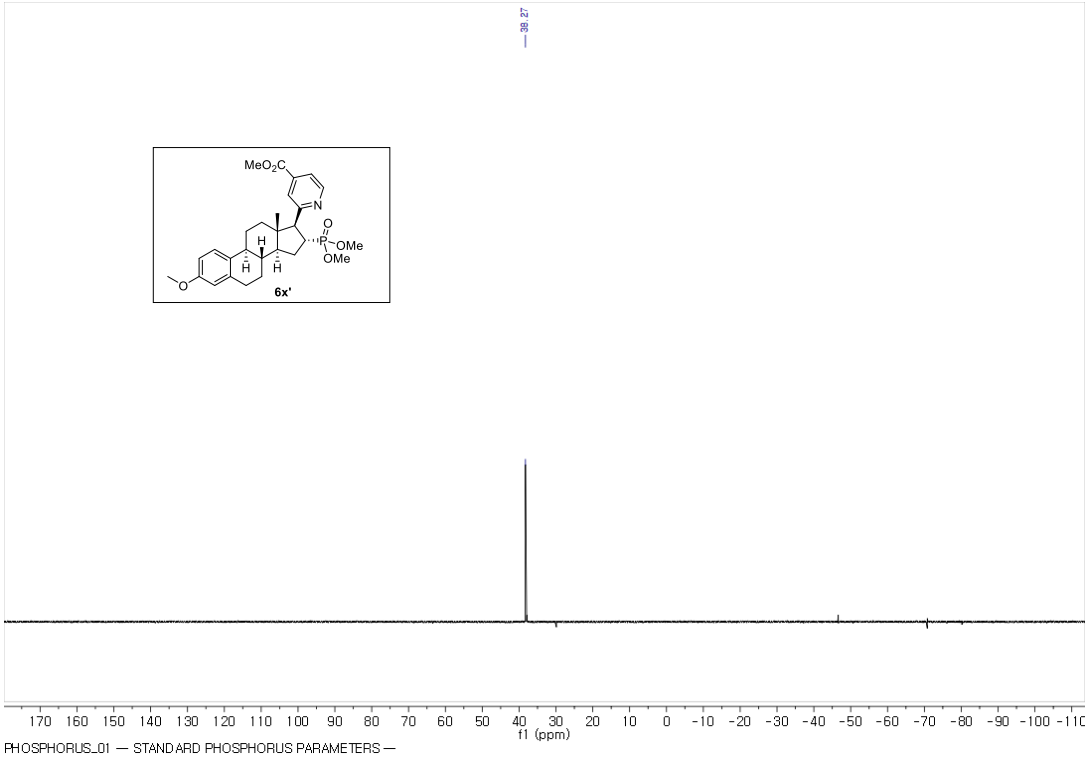
methyl 2-((8S,9S,13S,14S,16R,17S)-16-(dimethoxyphosphoryl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)isonicotinate (6x')



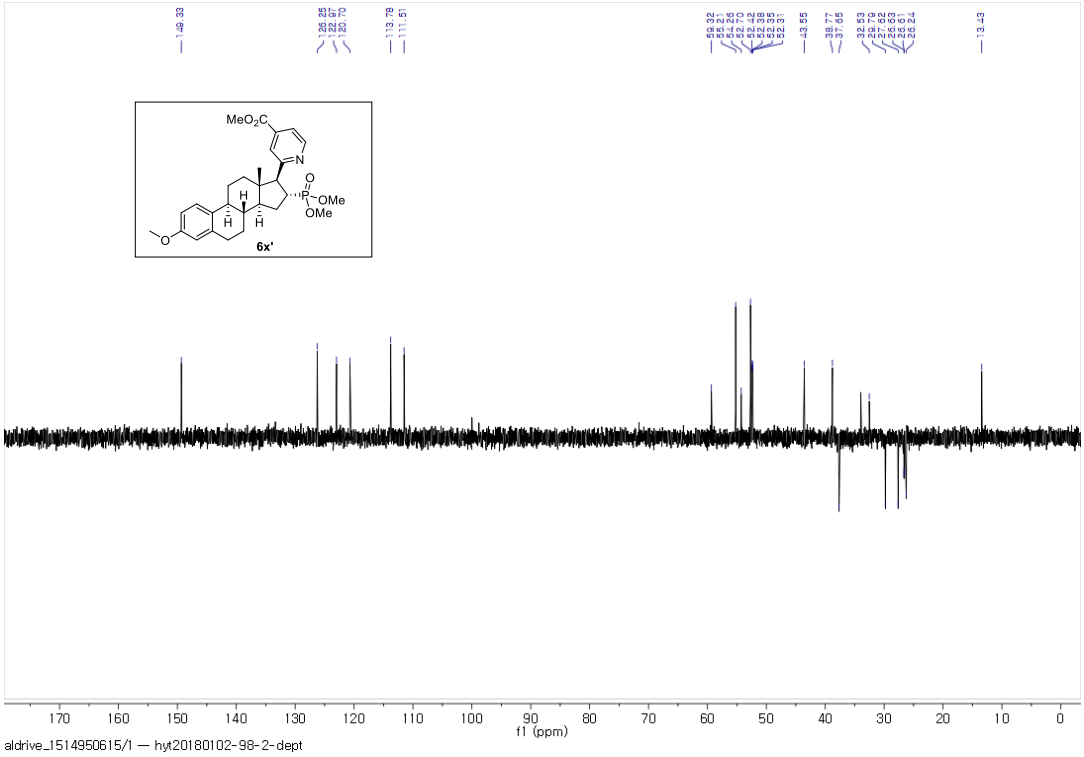
600 MHz, ^{1}H NMR in $CDCl_3$



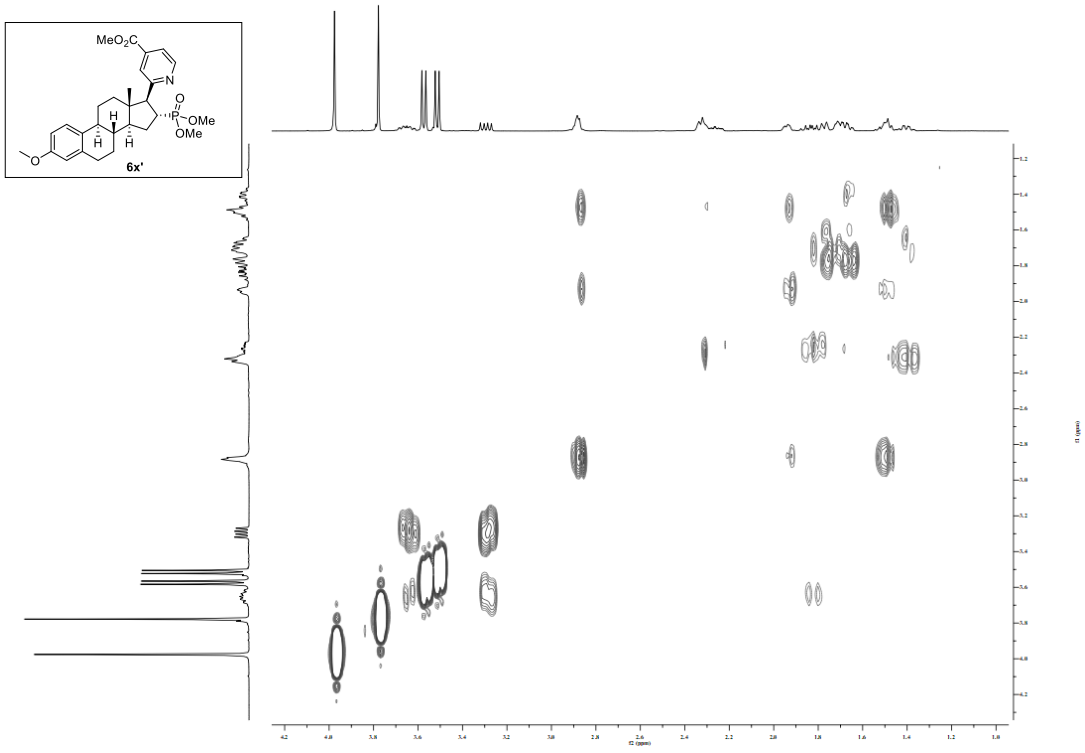
150 MHz, ^{13}C NMR in $CDCl_3$



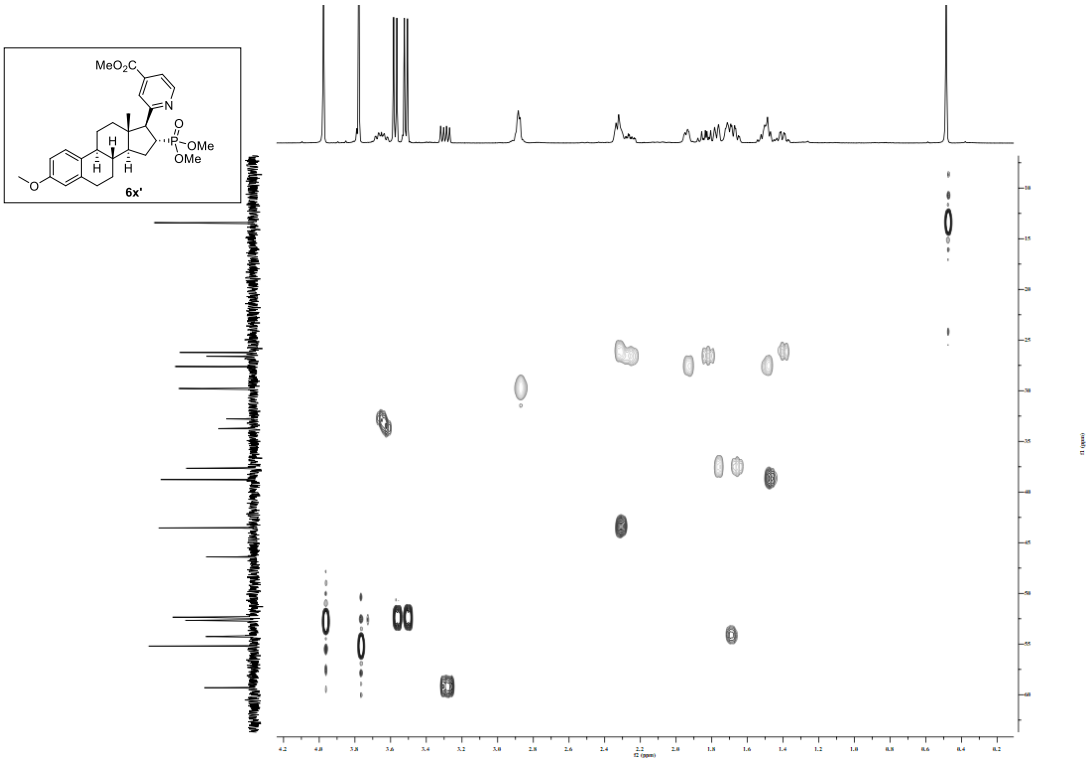
243 MHz, ^{31}P NMR in $CDCl_3$



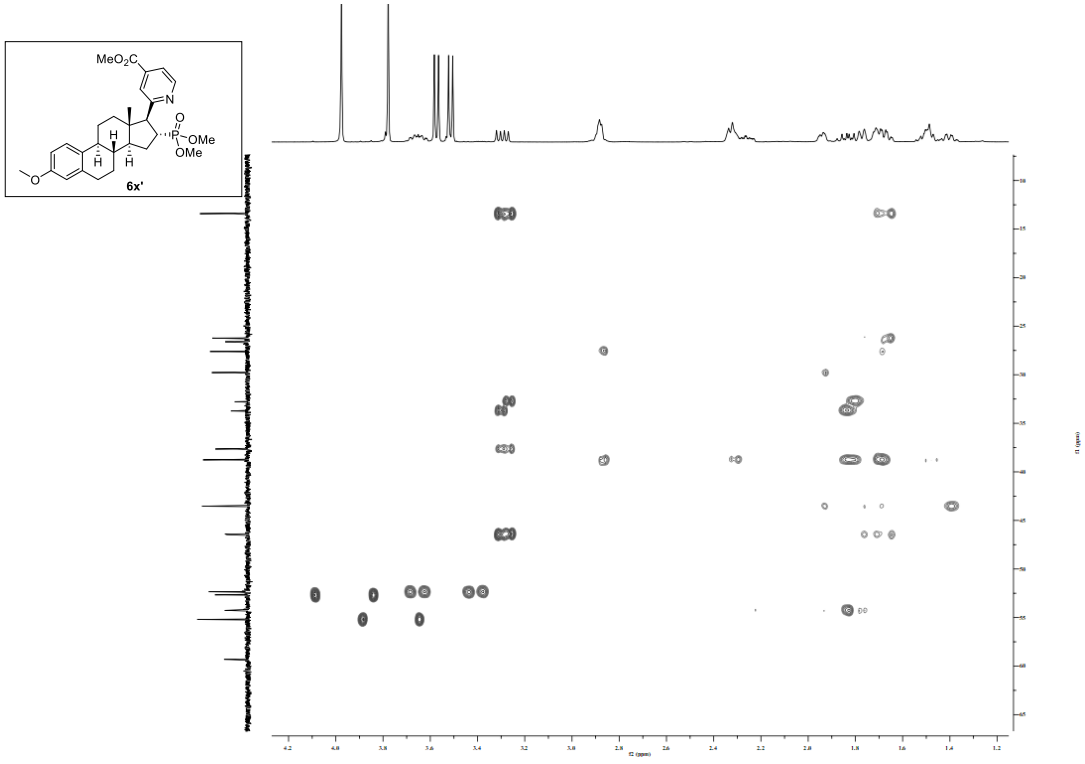
DEPT135 in $CDCl_3$



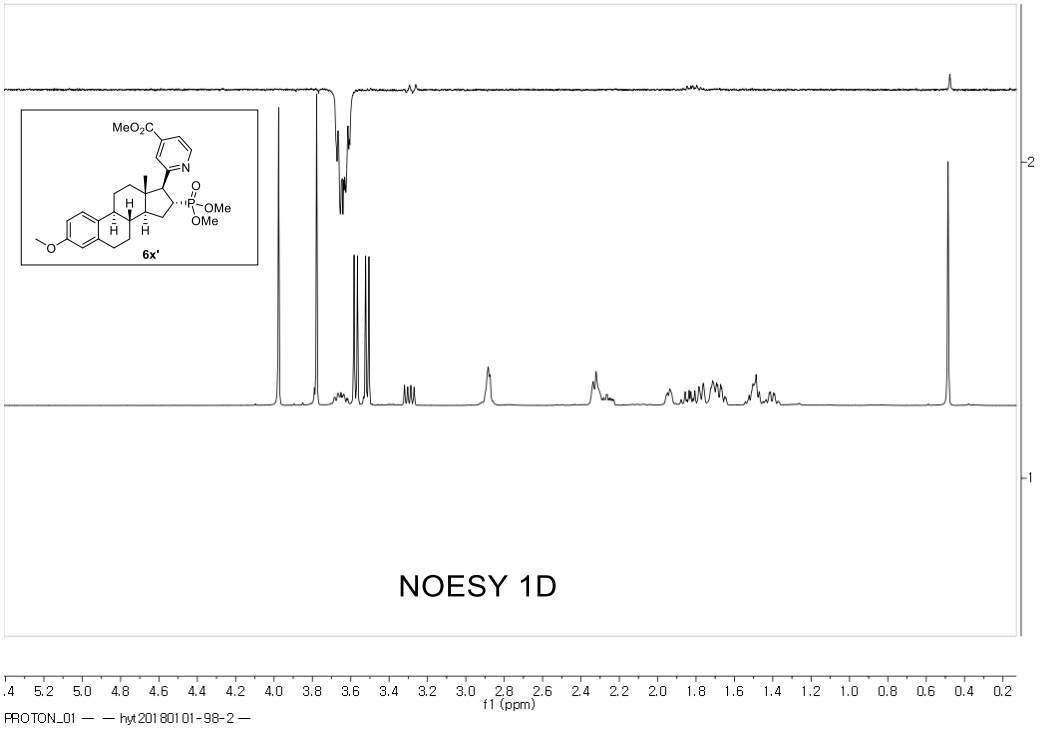
COSY in $CDCl_3$



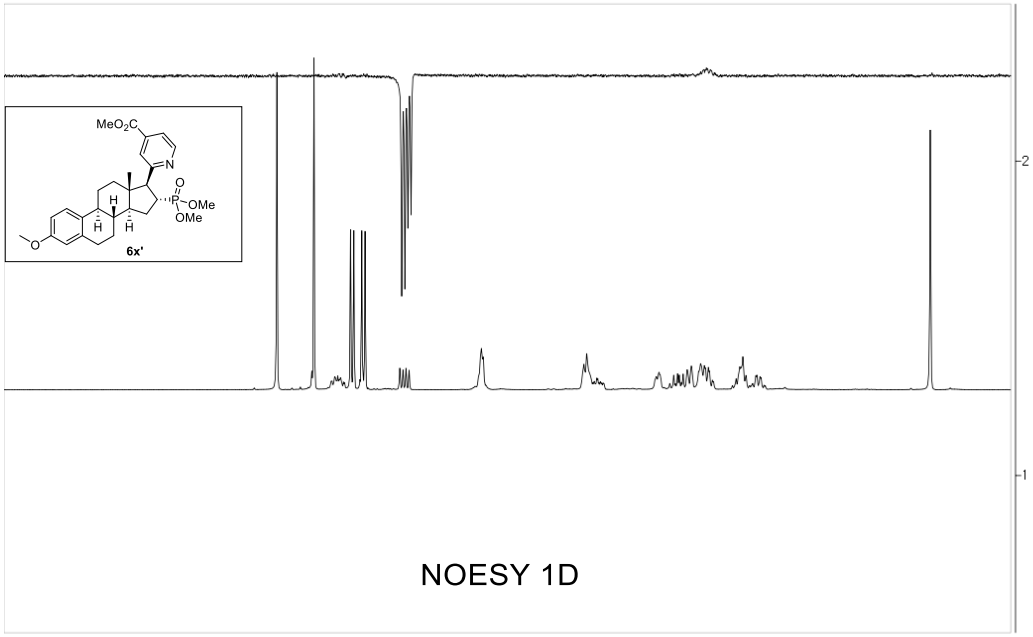
HSQC in $CDCl_3$



HMBC in $CDCl_3$



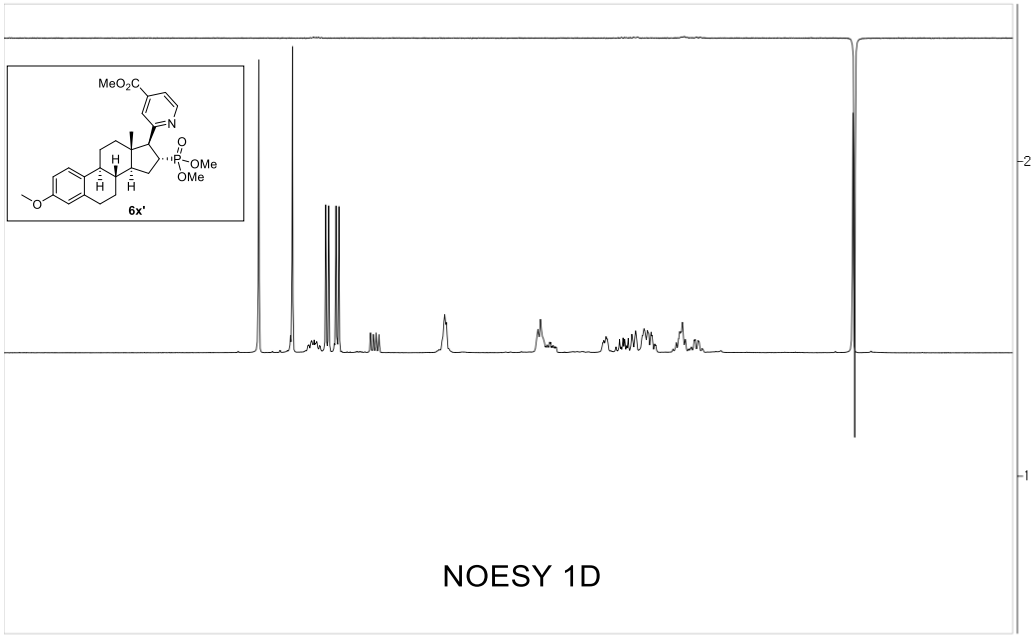
NOSY 1D in $CDCl_3$



5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2
f1 (ppm)

PROTON_01 — — hyt20180101-98-2 —

NOSY 1D in $CDCl_3$

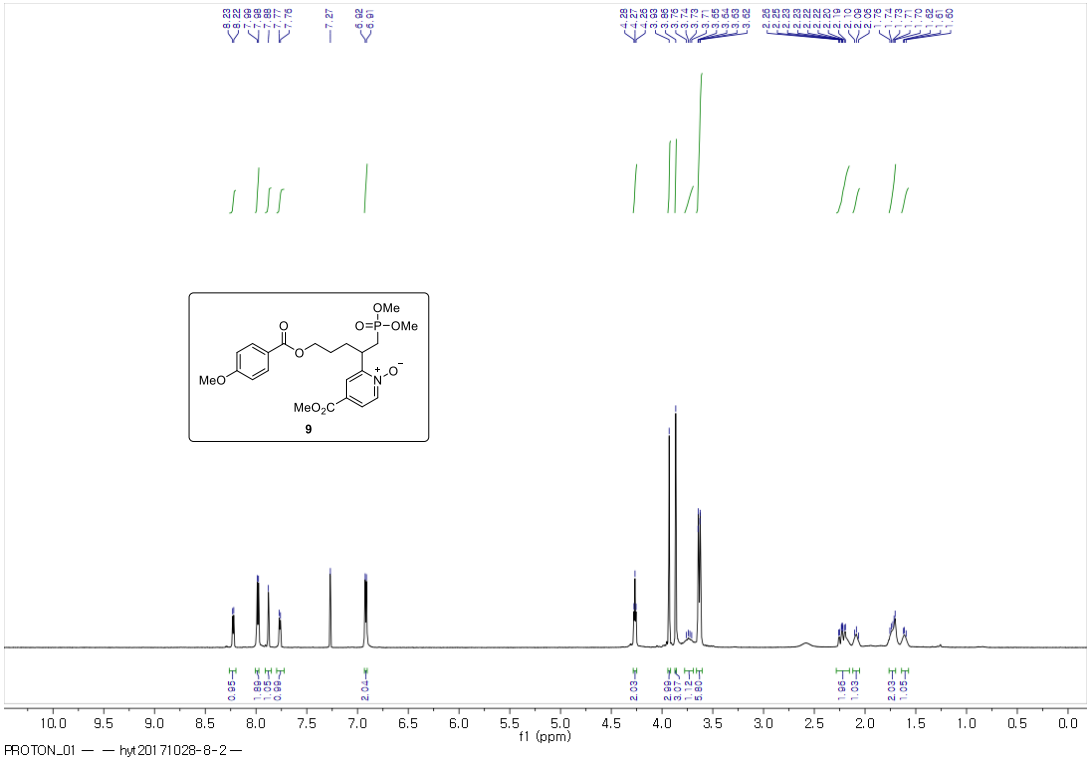


5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 -0.2 -0.4
f1 (ppm)

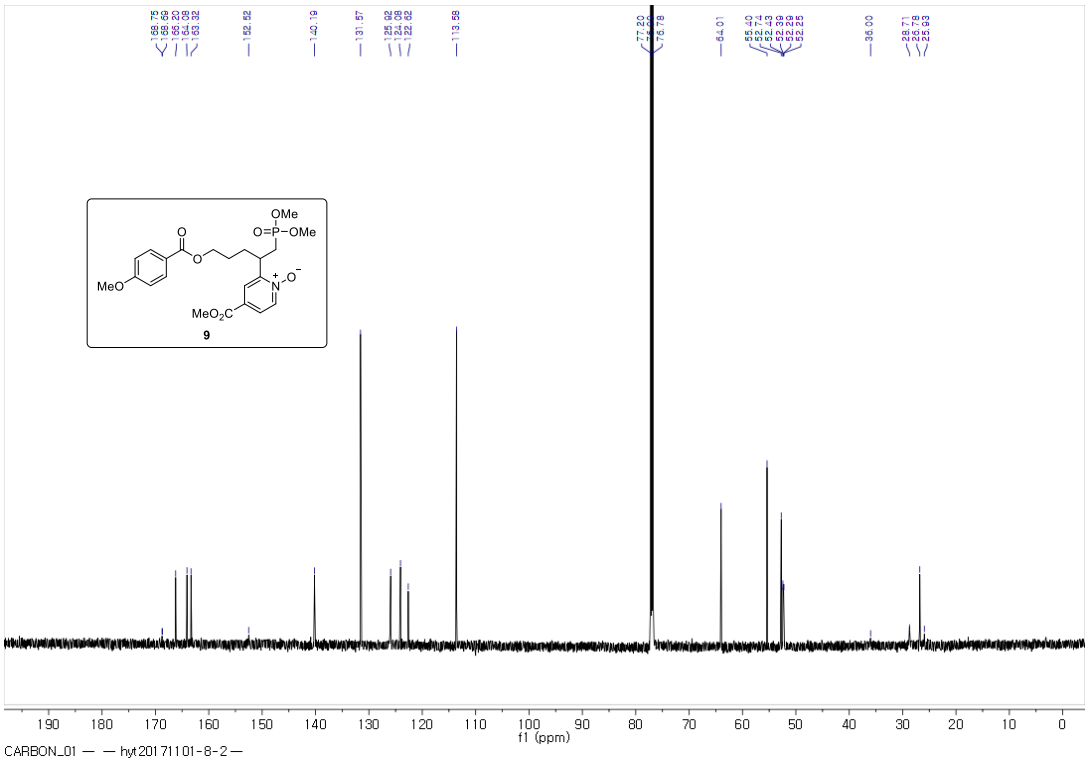
NOESY1D_03 — — hyt20180102-98-2-noesy-2d —

NOSY 1D in $CDCl_3$

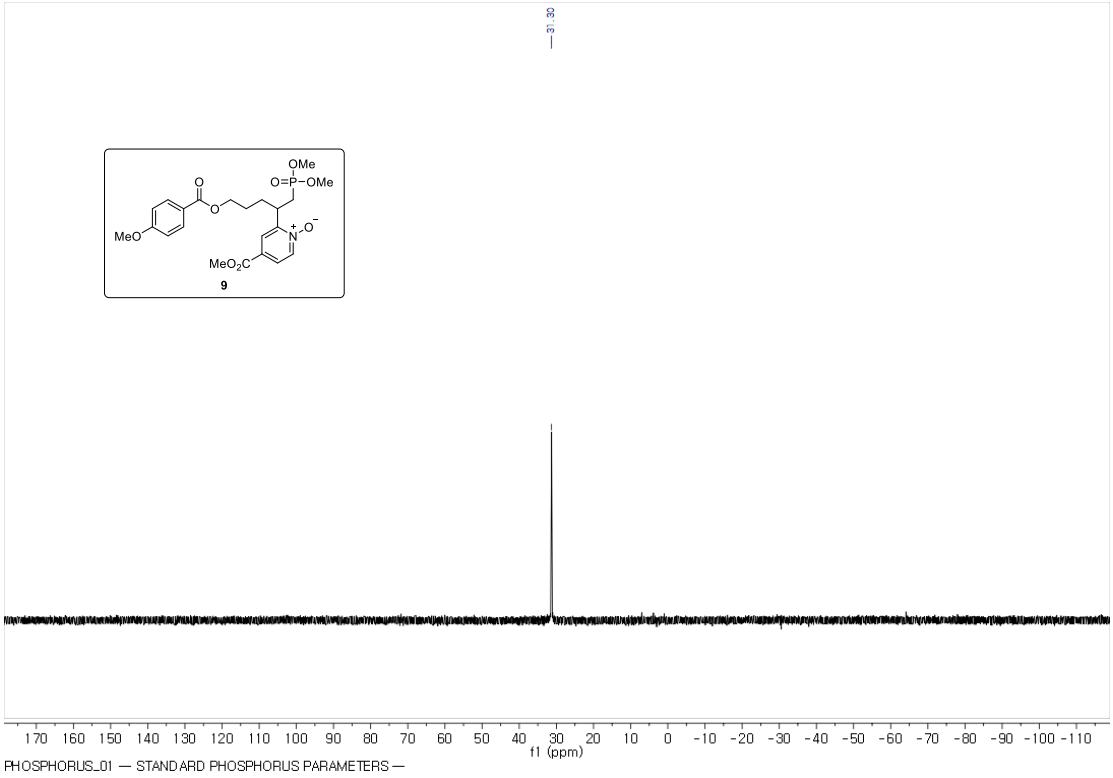
2-(1-(dimethoxyphosphoryl)-5-((4-methoxybenzoyl)oxy)pentan-2-yl)-4-(methoxycarbonyl)pyridine 1-oxide (9)



600 MHz, ^{1}H NMR in $CDCl_3$

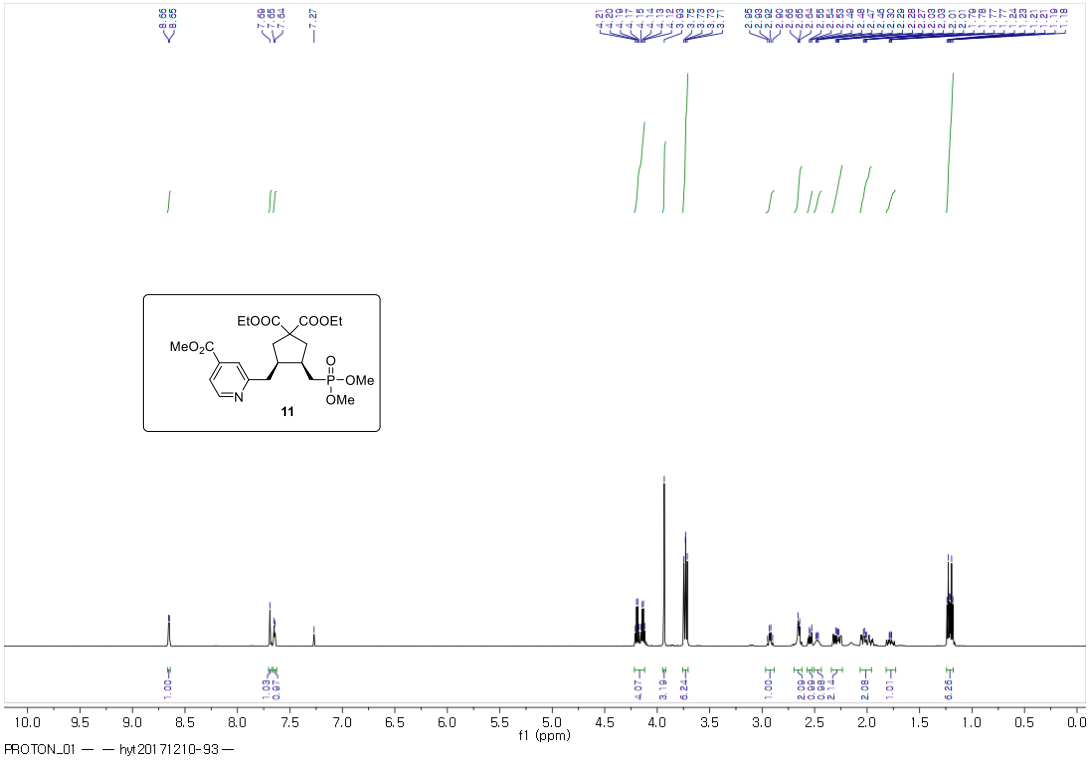


150 MHz, ^{13}C NMR in $CDCl_3$

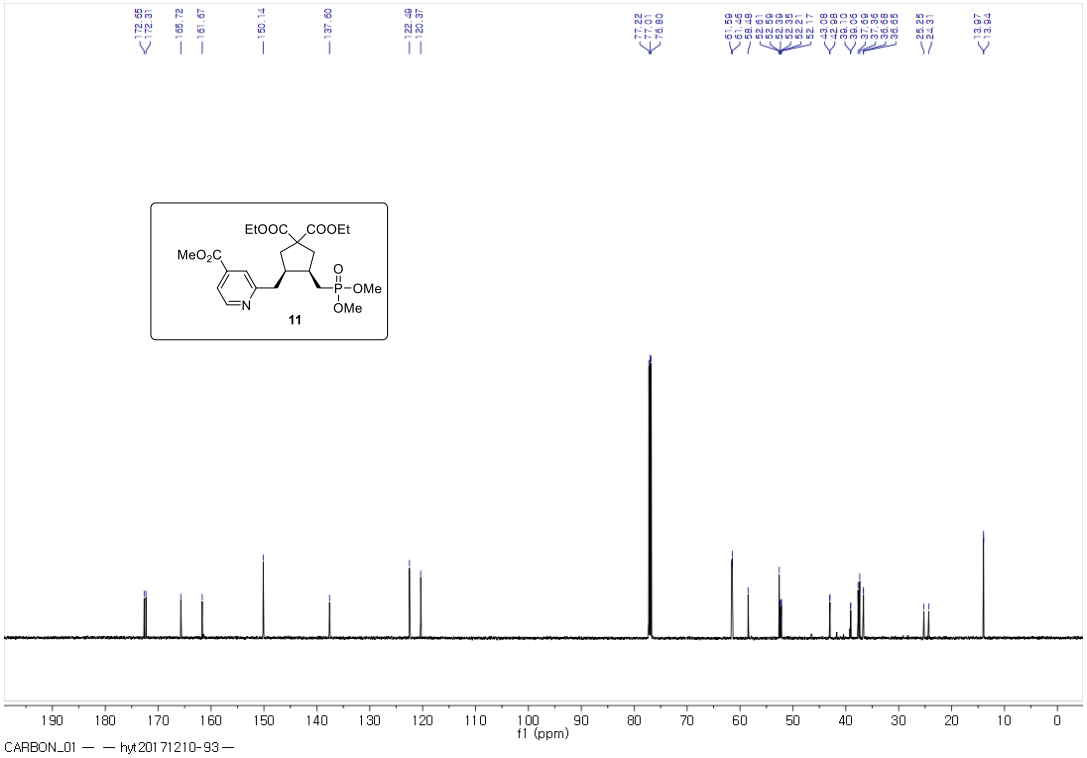


243 MHz, ^{31}P NMR in $CDCl_3$

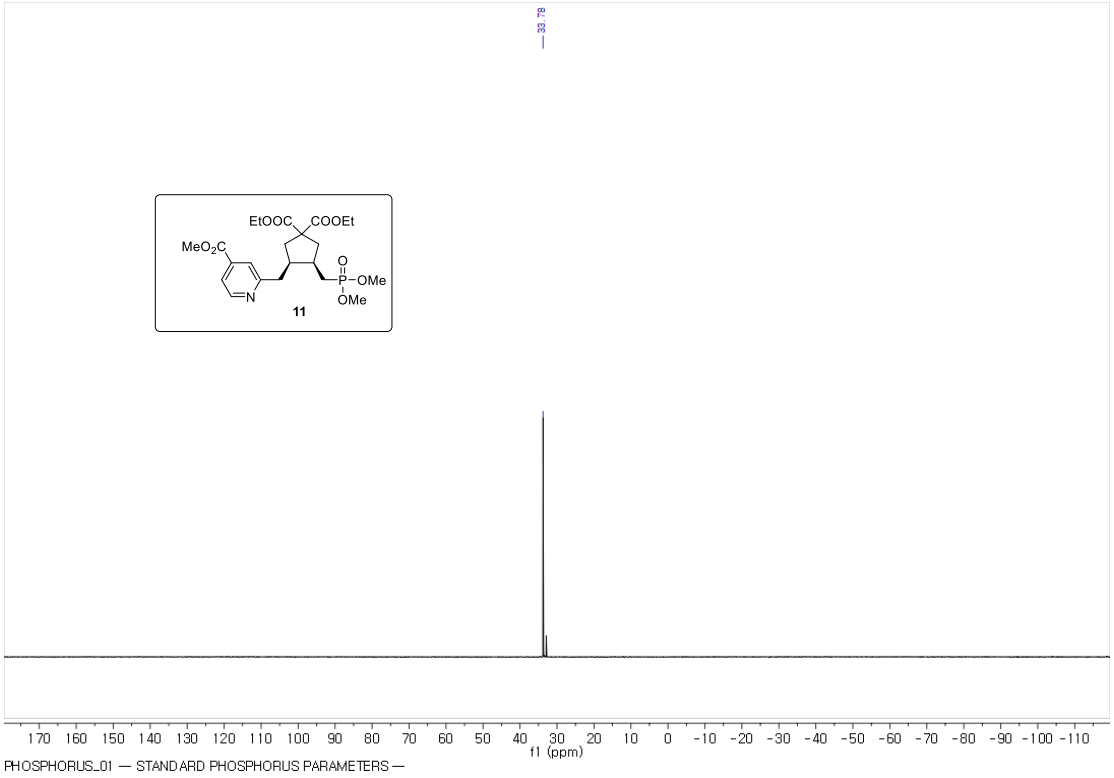
diethyl (3R,4R)-3-((dimethoxyphosphoryl)methyl)-4-((4-(methoxycarbonyl)pyridin-2-yl)methyl)cyclopentane-1,1-dicarboxylate (11)



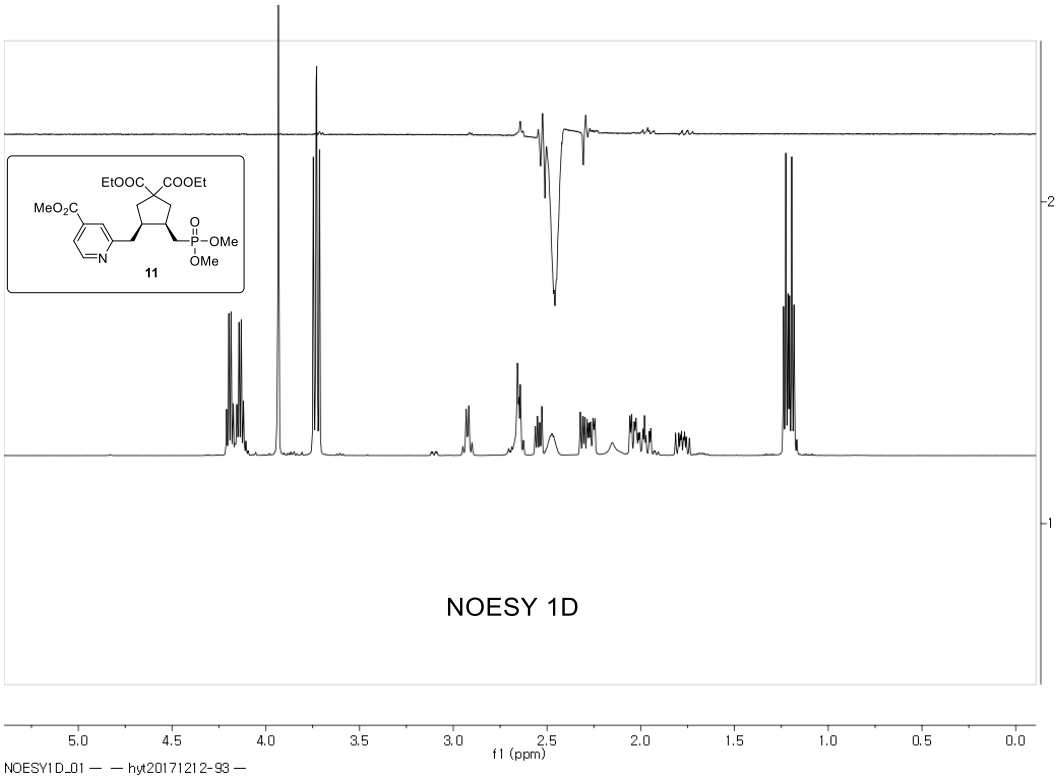
600 MHz, ^{1}H NMR in $CDCl_3$



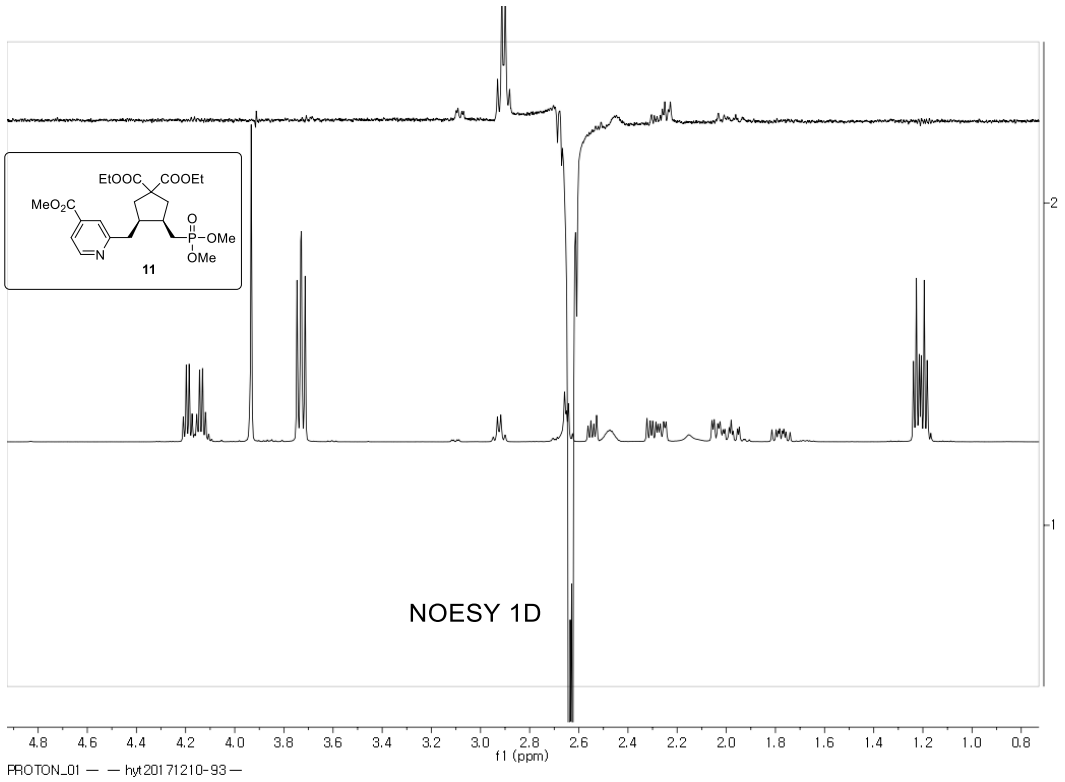
150 MHz, ^{13}C NMR in $CDCl_3$



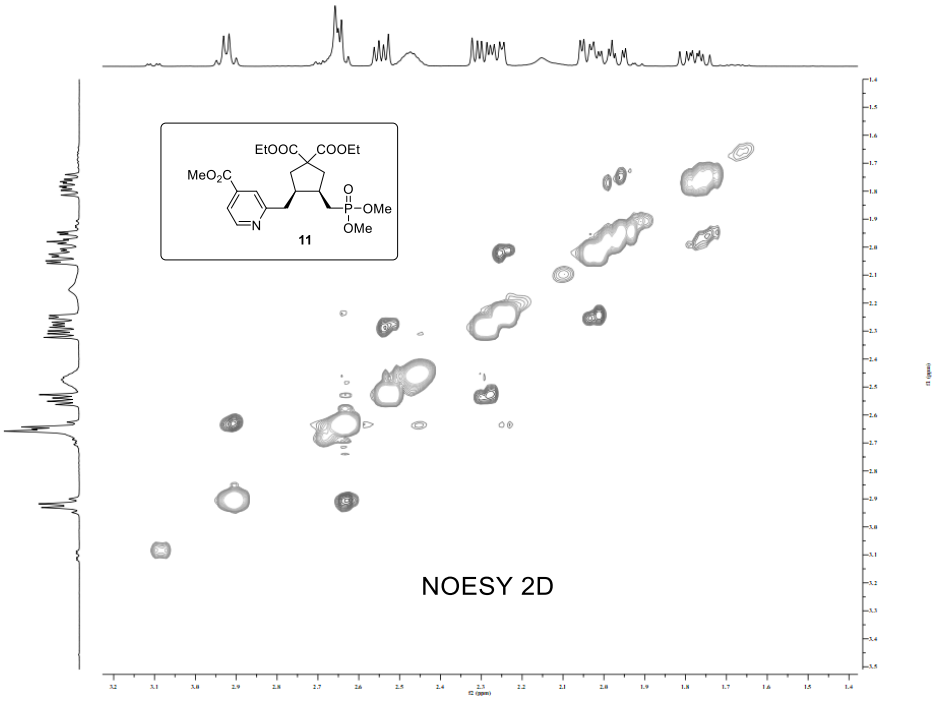
243 MHz, ^{31}P NMR in $CDCl_3$



NOESY 1D in $CDCl_3$

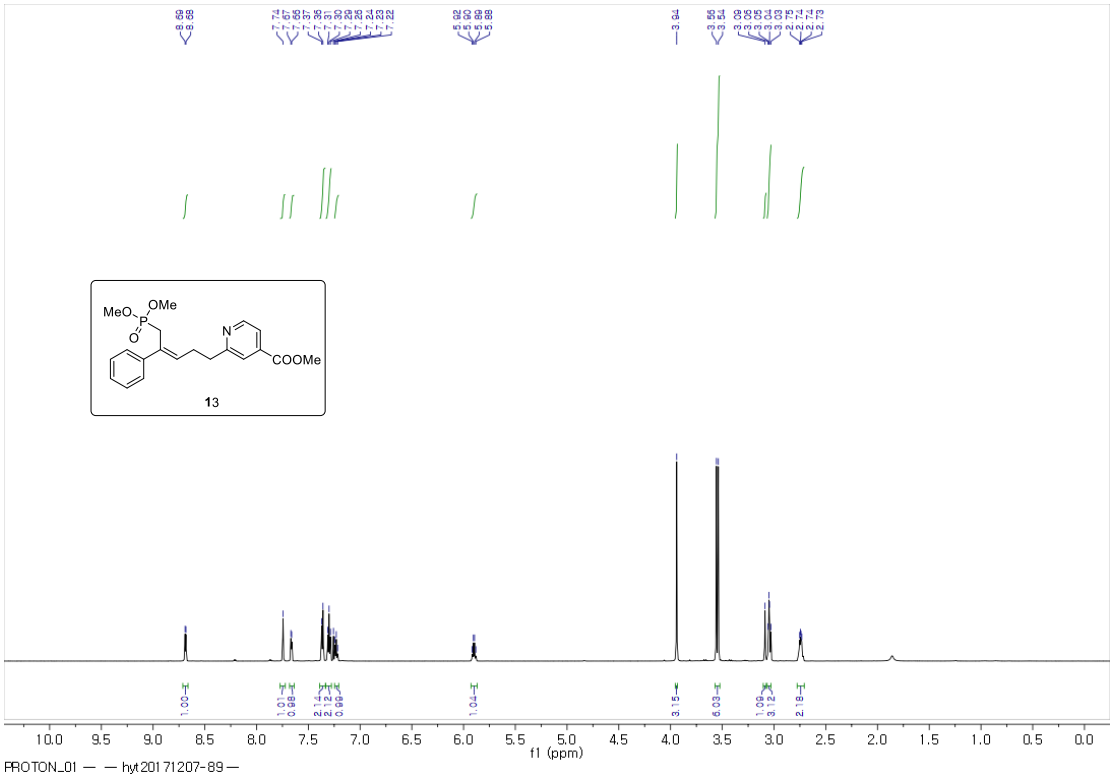


NOESY 1D in $CDCl_3$

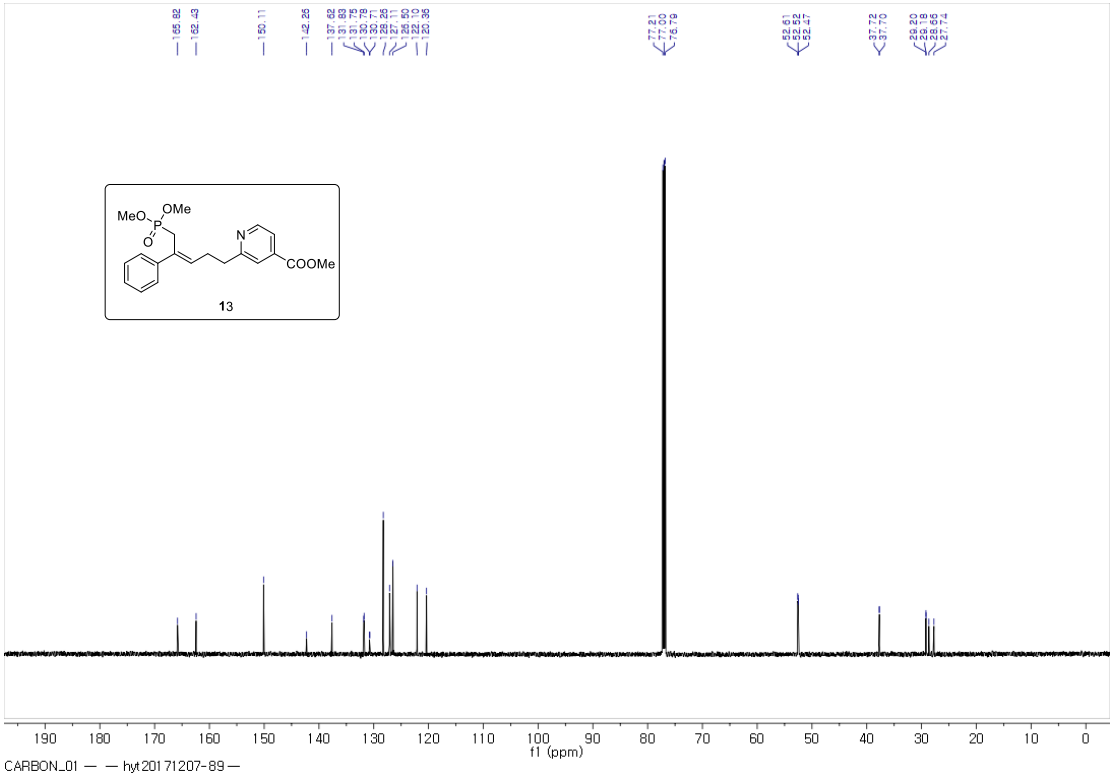


NOESY 2D in $CDCl_3$

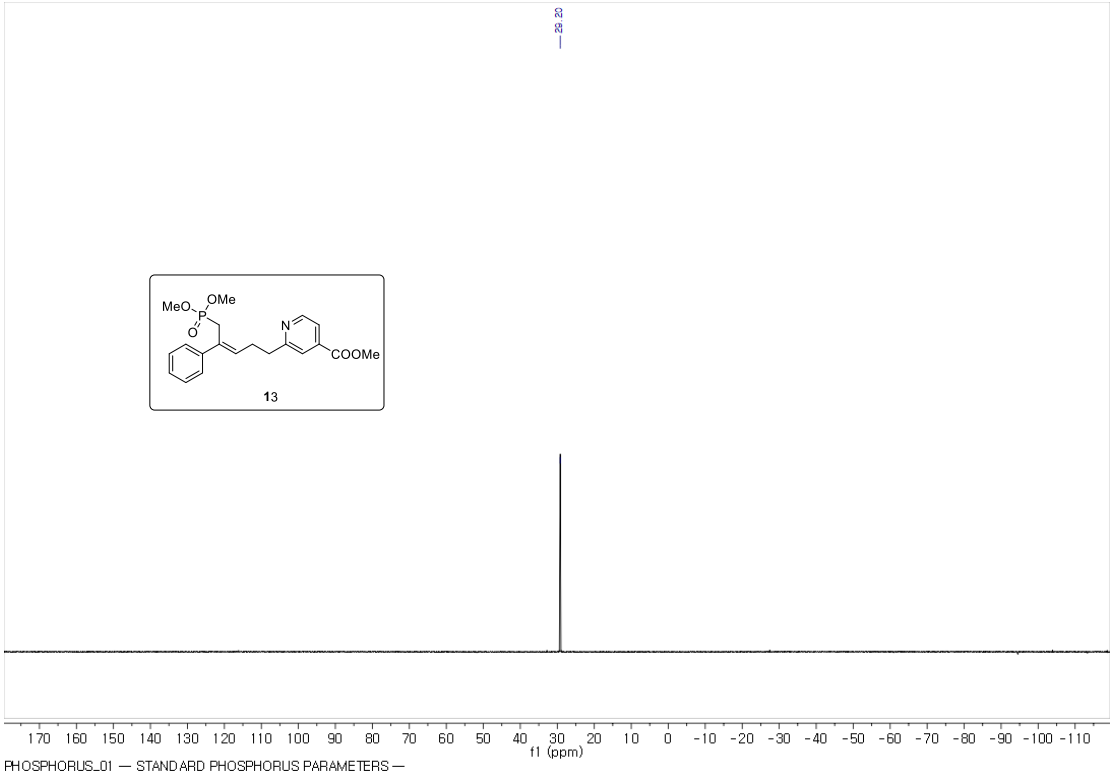
methyl (Z)-2-(5-(dimethoxyphosphoryl)-4-phenylpent-3-en-1-yl)isonicotinate (13)



600 MHz, ^{1}H NMR in $CDCl_3$

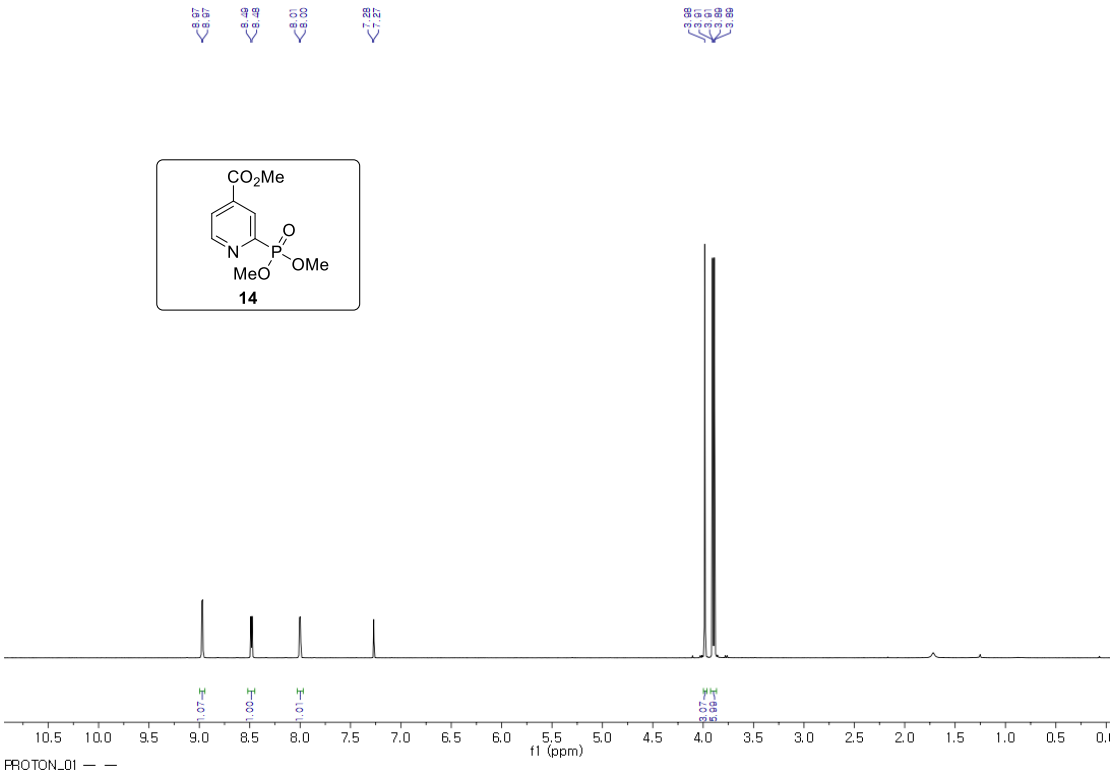


150 MHz, ^{13}C NMR in $CDCl_3$

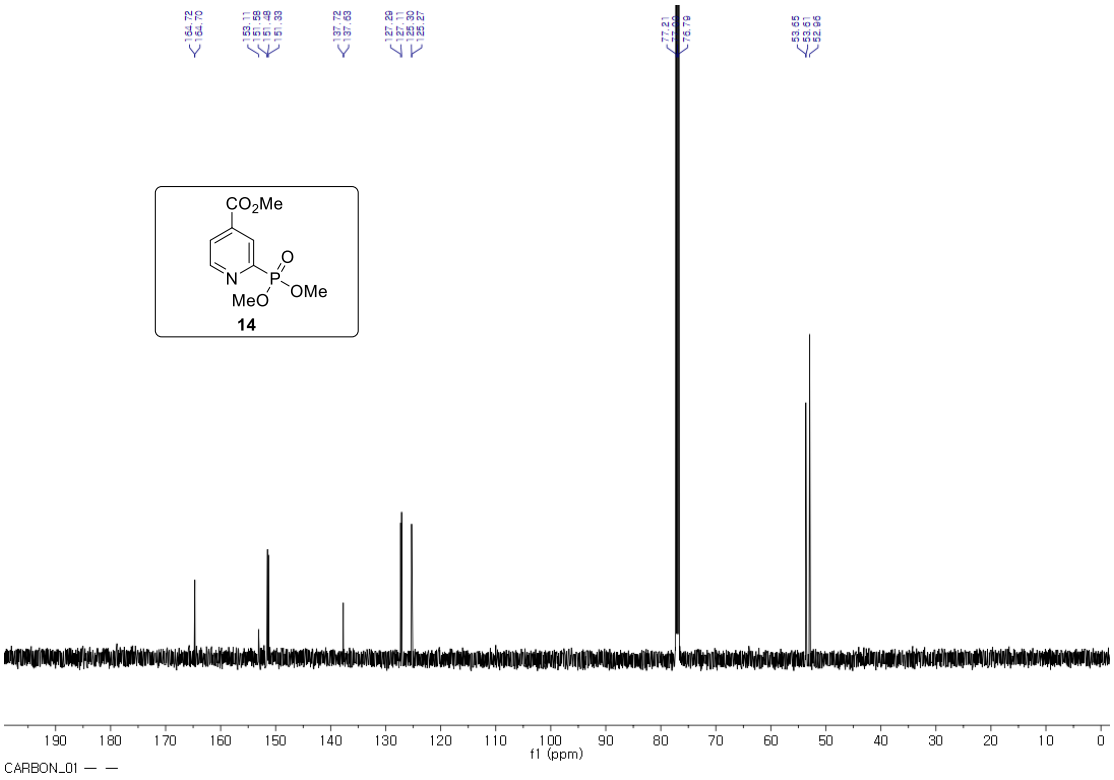


243 MHz, ^{31}P NMR in $CDCl_3$

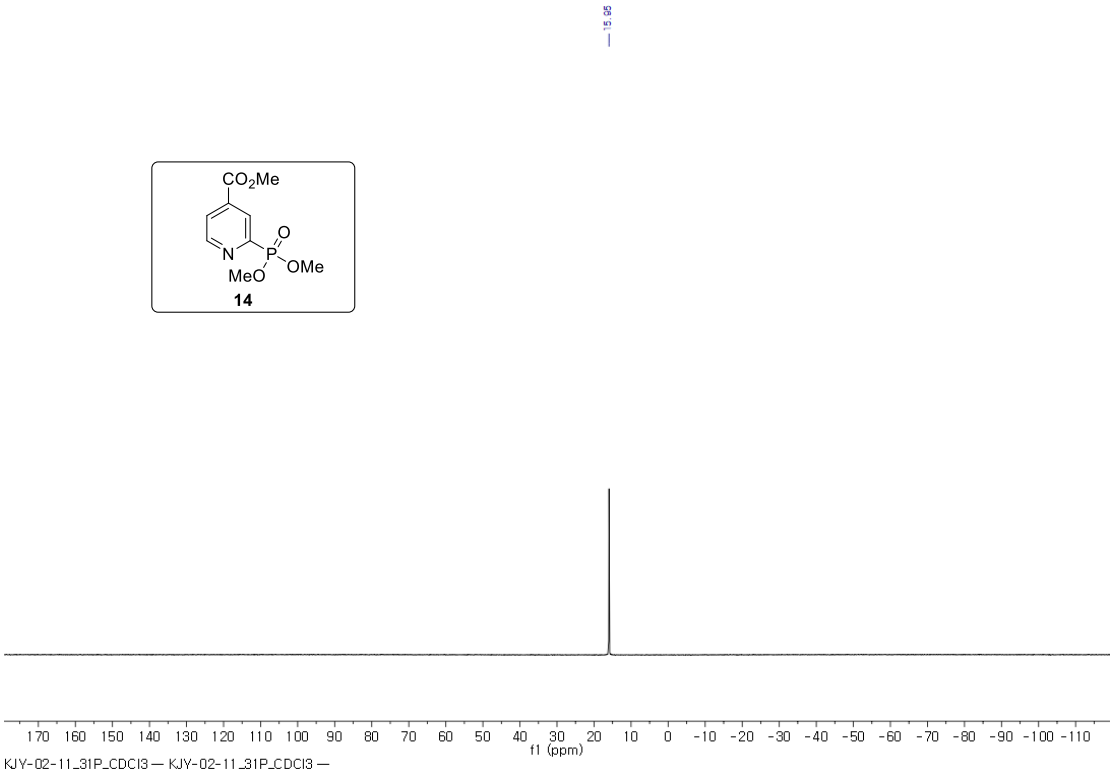
methyl 2-(dimethoxyphosphoryl)isonicotinate (14)



600 MHz, ^{1}H NMR in $CDCl_3$



150 MHz, ^{13}C NMR in $CDCl_3$



243 MHz, ^{31}P NMR in $CDCl_3$