SUPPORTING INFORMATION

Transition Metal-Free and Regioselective Vinylation of Phosphine Oxides and H-Phosphinates with VBX reagents

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Contents

1 General Experimental Procedures

Chemicals

*m*CPBA (<77 wt.%) was purchased from Sigma-Aldrich and dried under high vacuum at rt for three hours. The weight percent active oxidant was then determined by iodometric titration[1] and varied between 84-88% in different batches. The dried *m*CPBA can be stored for prolonged time in the refrigerator. NB: *m*CPBA of 95-100% purity can de can be detonated by shock or sparks, but such high concentrations cannot be achieved with this drying procedure, as commercial *m*CPBA contains up to 15% *m*CBA.
https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Bulletin/al_techbull_al116.pdf

2-iodobenzoic acid was purchased from Sigma-Aldrich and used as received.

Trifluoromethanesulfonic acid (TfOH) and trimethylsilyl trifluoromethanesulfonate (TMSOTf) were purchased from TCI, stored under argon and handled using dry glass Hamilton syringes with oven-dried metal needles. $BF_3.OEt_2$ was purchased from Sigma-Aldrich, stored under argon and handled using dry glass Hamilton syringes with oven-dried metal needles.

The purity of the boronic acids is of high importance for reproducible yields and the quality was determined by ^{1}H-NMR with internal standard. All the boronic acids used were purchased from Sigma-Aldrich and were used without any purification.

Unless otherwise noted, all materials were purchased from commercial suppliers and used as received.

Diphenylphosphine oxide **(1a)** was purchased from Tokyo Chemical Industry, bis(3,5-dimethylphenyl)phosphine oxide **(1c)** and di(2-naphtyl)phosphine oxide **(1f)** were purchased from Fluorochem Ltd. Diethyl phosphonate **(9)** was purchased from Sigma-Aldrich.

Solvents

CH_2Cl_2, Et_2O and MeCN were used as received. Toluene and THF were dried using a VAC-purification system. Anhydrous THF was purified prior to use by passage through a column of neutral alumina under nitrogen.

Procedures and Analysis

TLC analysis was performed on pre-coated silica gel 60 F254 plates using either UV light. The crude products were purified by flash column chromatography using 40-60 µm 60A silica gel as stationary phase or using automated flash system Teledyne ISCO CombiFlash Rf 200 with RediSep Rf columns.

Melting points were measured using a STUART SMP3 and are reported uncorrected. The melting point measurements refer to the solidified materials as the result of the given experimental procedures, no additional recrystallization was done.

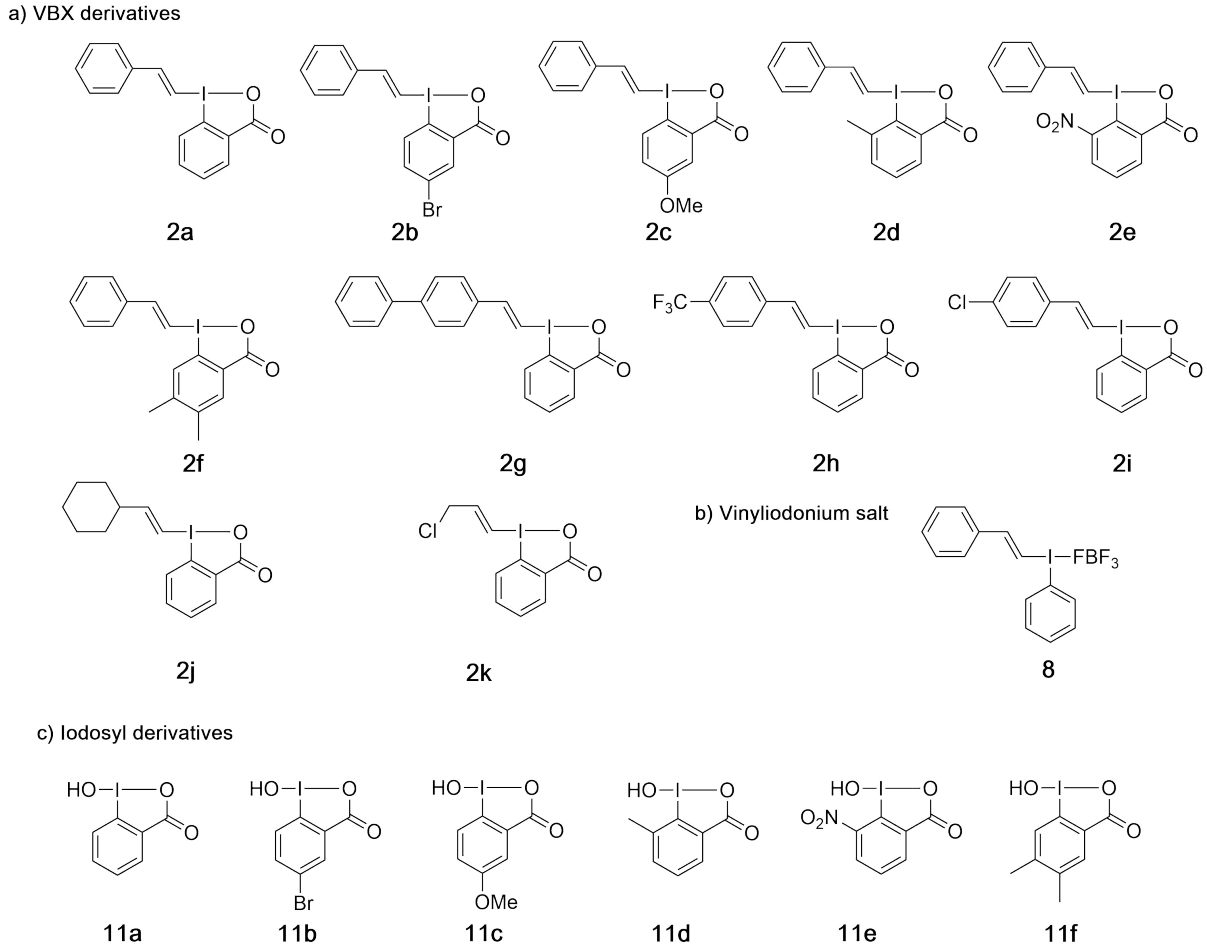
NMR spectra were recorded using a 400 MHz Bruker AVANCE II with a BBO probe at 298 K using $CDCl_3$, MeOD-d_4 or DMSO-d_6 as solvent. Chemical shifts are given in ppm relative to the residual solvent peak (^{1}H NMR: $CDCl_3$ δ 7.26; MeOD-d_4 δ 3.31; DMSO-d_6 δ 2.50; ^{13}C NMR: $CDCl_3$ δ 77.16; MeOD-d_4 δ 49.00; DMSO-d_6 δ 39.52) with multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet, app = apparent), coupling constants (in Hz) and integration. Full analytical data is given for compounds that are novel or not fully characterized in the literature; ^{1}H NMR and ^{13}C NMR are given for literature reported VBX reagents and products. The chemical shifts are reported in ppm relative to solvent peaks.

The *dr* of compounds **6e** and **6f** has been determined by ^{31}P NMR experiment as a ratio between integrals of two diastereomers.

High-resolution mass analyses were obtained using a Bruker microTOF ESI.

2 Synthesis of Iodine(III) Reagents

The synthesized iodine(III) reagents are shown in Figure S1.



The synthesis of VBX **2a** and **2g-2j** were obtained using our reported procedure (Section 2.1).[2] The core-substituted VBX **2b-2f** were synthetized using Nachtsheim's two-step procedure (Section 2.2).[3] Reagent **2k** was prepared according to literature.[4]

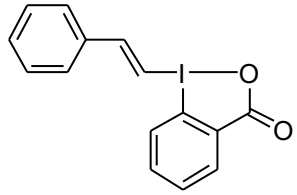
Vinyliodonium salt **8** was synthetized according to the reported procedure.[3] The iodosyl compounds **11** were prepared following literature procedures: **11a**,[3] **11b**,[5] **11b**,[6] **11c**,[7] **11d**,[5] **11e**,[8] **11f**.[9]

2.1 One-Pot Synthesis of VBX Reagents

VBX reagents with unsubstituted benziodoxolone core were prepared by employing our reported one-pot synthesis.[2]

General procedure S1:
2-iodobenzoic acid (1 equiv) was added to a round bottom flask followed by CH_2Cl_2. *m*CPBA (85%, 1.1 equiv) was added, and the mixture was cooled to 0 °C followed by the addition of TfOH (1.5 equiv). The mixture was stirred at RT for 15 minutes and then cooled to 0 °C for 5 minutes. The corresponding boronic acid (1.4 equiv) was added in one portion and rinsed down with CH_2Cl_2 (1-5 mL). The mixture was stirred at room temperature for 1 h. Saturated $NaHCO_3$ was added and the mixture was stirred vigorously at rt for 1 h. The reaction mixture was transferred to a separation funnel, diluted with DCM and H_2O. *Note: dilution helped to avoid emulsions in the separation.* The layers were separated the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were washed with H_2O and brine and then dried over Na_2SO_4. The drying agent was filtered off and the solvent was removed *in vacuo.* Et_2O was added to the white precipitate and the mixture was stirred vigorously at RT for approx. 30 min. The solid was filtered off (glass filter funnel, porosity 3) and washed with Et_2O to obtain VBX reagents.

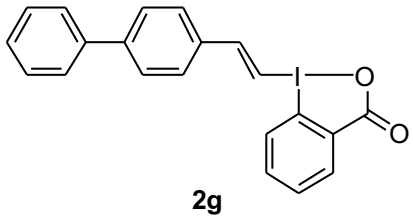
(E)-1-Styryl-1,2-benziodoxol-3-(1H)-one (2a)[2]



2a

Prepared according to General procedure S1[2] (1255 mg, 3.6 mmol, 72%). 1H NMR (400 MHz, MeOD-d4): δ 8.31-8.22 (m, 1H), 7.96 (d, J = 15.5 Hz, 1H), 7.76-7.61 (m, 6H), 7.55-7.42 (m, 3H).13C NMR (101 MHz, MeOD-d4): δ 170.1, 155.8, 136.7, 135.3, 134.5, 133.3, 132.1, 131.8, 130.2, 129.0, 129.0, 115.5, 100.0.

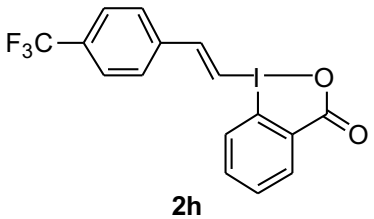
(*E*)-1-(2-([1,1'-biphenyl]-4-yl)vinyl)-1,2-benziodoxol-3-(1*H*)-one (2g)[9]



2g

Prepared according to General procedure S1[2] (109 mg, 0.25 mmol, 64%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.20 – 8.11 (m, 1H), 7.98 (d, *J* = 15.6 Hz, 1H), 7.88 (d, *J* = 15.6 Hz, 1H), 7.81 (s, 4H), 7.78 – 7.72 (m, 2H), 7.71 – 7.60 (m, 3H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.45 – 7.37 (m, 1H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 165.6, 151.4, 142.0, 139.2, 134.6, 134.5, 133.4, 131.4, 130.3, 129.1, 128.3, 128.1, 127.7, 127.2, 126.8, 115.1, 103.1.

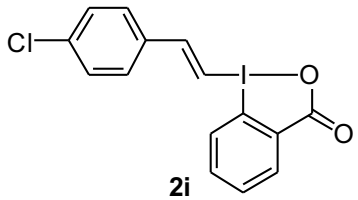
(E)-1-(4-(trifluoromethyl)styryl)-1,2-benziodoxol-3-(1H)-one (2h)[2]



2h

Prepared according to General procedure S1[2] (103.1 mg, 0.25 mmol, 64%). 1H NMR (400 MHz, MeOD-d4): δ 8.32-8.24 (m, 1H), 8.03 (d, J = 15.6 Hz, 1H), 7.93-7.66 (m, 8H). 13C NMR (101 MHz, MeOD-d4) δ 170.0, 153.5, 140.27 (d, J = 1.0 Hz), 135.4, 134.4, 133.3, 133.2 (q, J = 32.7 Hz), 131.9, 129.5, 129.1, 127.1 (q, J = 3.9 Hz), 125.3 (q, J = 272.4 Hz), 115.5, 104.0. 19F-NMR (377 MHz, MeOD-d4): δ - 64.4.

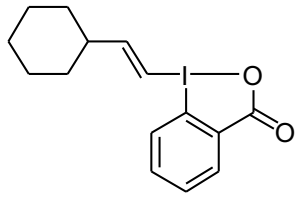
(*E*)-1-(4-chlorostyryl)-1,2-benziodoxol-3-(1*H*)-one (2i)[9]



2i

Prepared according to General procedure S1[2] (433 mg, 1.13 mmol, 56%). ^{1}H NMR (400 MHz, MeOD-*d4*): δ 8.33- 8.25 (m, 1H), 7.95 (d, *J* = 15.5 Hz, 1H), 7.71 (dq, *J* = 9.6, 5.8, 4.7 Hz, 6H), 7.55 – 7.49 (m, 2H). ^{13}C NMR (101 MHz, MeOD-*d4*): δ 170.0, 154.1, 138.0, 135.4, 135.3, 134.5, 133.3, 131.9, 130.4, 130.4, 129.9, 129.0, 115.5, 101.0.

(*E*)-1-(2-cyclohexylvinyl)-1,2-benziodoxol-3-(1H)-one (2j)[2]



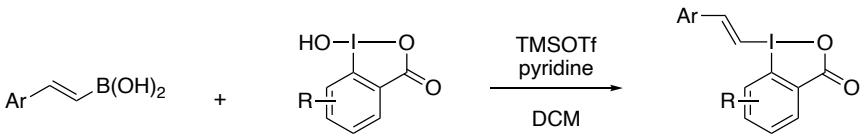
2j

Prepared according to General procedure S1[2] (41.3 mg, 0.12 mmol, 27%). ^{1}H NMR (400 MHz, MeOD-*d4*): δ 8.31-8.23 (m, 1H), 7.88 (d, *J* = 15.4 Hz, 1H), 7.76-7.59 (m, 5H), 7.44 (d, *J* = 15.4 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, MeOD-*d4*): δ 170.1, 163.6, 155.8, 135.2, 134.5, 133.3, 131.8, 130.8, 129.4, 128.8, 115.6, 115.5, 96.0, 56.0.

2.2 Step-Wise Synthesis of Core-Substituted VBX

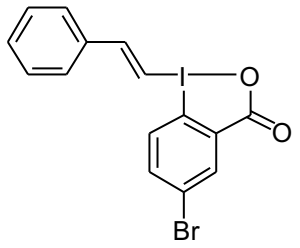
The core-substituted VBX **2b-2f** were synthetized using Nachtsheim's two-step procedure[3] since our one-pot procedure is optimized for 2-iodobenzoic acid and yields of vinylbenziodoxolones with substituted iodobenzoic acids varied considerably.

General procedure S2[3]



To a suspension of 2-iodosylbenzoic acid 11 (0.6-2.0 mmol, 1 equiv) in dry CH_2Cl_2 or MeCN (10-20 mL) was added TMSOTf (0.67-2.30 mmol, 1.15 equiv) dropwise over 10 min and stirred for 30 min at room temperature. Afterwards (*E*)-styrylboronic acid (0.67-2.30 mmol, 1.15 equiv) was added over 5 min and the reaction mixture was stirred for 1.5 h at room temperature. Pyridine (1.15 equiv) was added and after further 10 min stirring the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed with a solution of HCl 1M. The aqueous phase was extracted three times with CH_2Cl_2 and the combined organic phases were washed with a saturated solution of $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated under reduce pressure. The residue was dissolved in a minimum amount of CH_2Cl_2 and precipitate in Et_2O, stirred vigorously for 30 min and stored at 4 °C for 2-16 h. The precipitate was filtered and washed with Et_2O to afford the corresponding core-substituted VBX reagent.

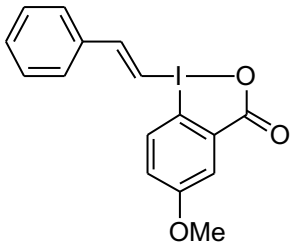
(*E*)-5-bromo-1-styryl-1,2-benziodoxol-3-(1*H*)-one (2b)[9]



2b

Prepared according to General procedure S2,[3] (625 mg, 1.46 mmol, 73 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.02 (d, *J* = 2.4 Hz, 1 H), 8.79 (d, *J* = 15.6 Hz), 8.72-8.65 (m, 2H), 8.56-8.50 (m, 2H), 8.40 (d, *J* = 8.6 Hz, 1H), 8.37-8.28 (m, 3H); ^{13}C NMR (400 MHz, DMSO-d_6) δ 164.1, 152.2, 136.7, 135.7, 135.4, 133.6, 130.6, 129.9, 129.0, 127.7, 124.2, 113.7, 102.7.

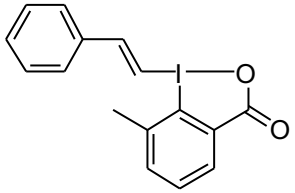
(*E*)-5-methoxy-1-styryl-1,2-benziodoxol-3-(1*H*)-one (2c)[9]



2c

Prepared according to General procedure S2,[3] (330 mg, 0.870 mmol, 60 %). ^{1}H NMR (400 MHz, MeOD-*d4*) δ 7.93 (d, *J*=15.5 Hz, 1H), 7.77 (d, *J* = 3.0 Hz, 1H), 7.72-7.67 (m, 3H), 7.62 (d, *J* = 15.5 Hz, 1H), 7.53-7.45 (m, 3H), 7.20 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.85(s, 3H);^{13}C NMR (400 MHz, MeOD-*d4*) 169.8, 163.6, 155.5, 136.7, 135.9, 132.1, 130.2, 129.6, 129.0, 121.6, 117.8, 103.6, 99.6, 56.4.

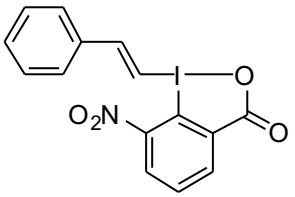
(*E*)-7-methyl-1-styryl-1,2-benziodoxol-3-(1*H*)-one (2d)[9]



2d

Prepared according to General procedure S2,[3] (202 mg, 0.55 mmol, 49 %). ^{1}H NMR (400 MHz, MeOD-*d4*) δ 7.99 (dd, *J* = 6.9, 2.4 Hz, 1H), 7.90 (q, *J* = 15.1 Hz, 2H), 7.61-7.49 (m, 4H), 7.43 (dt, *J* = 5.4, 3.0 Hz, 3H), 2.59 (s, 3H); ^{13}C NMR (400 MHz, MeOD-*d4*) δ 171.2, 151.5, 142.0, 139.8, 136.9, 136.5, 132.0, 131.9, 130.7, 130.2, 128.7, 119.0, 102.9, 25.7.

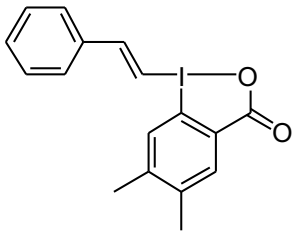
(*E*)-7-nitro-1-styryl-1,2-benziodoxol-3-(1*H*)-one (2e)[9]



2e

Prepared according to General procedure S2,[3] but the reaction was done in MeCN (74 mg, 0.19 mmol, 32 %). ^{1}H NMR (400 MHz, MeOD-*d4*) δ 8.44 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.10 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.88-7.78 (m, 2H), 7.52-7.39 (m, 6H); ^{13}C NMR (400 MHz, MeOD-*d4*) δ 168.6, 153.7, 152.0, 140.8, 136.2, 136.1, 133.2, 132.1, 130.9, 130.0, 128.8, 108.7, 102.1.

(*E*)-5,6-dimethyl-1-styryl-1,2-benziodoxol-3-(1*H*)-one (2f)[9]

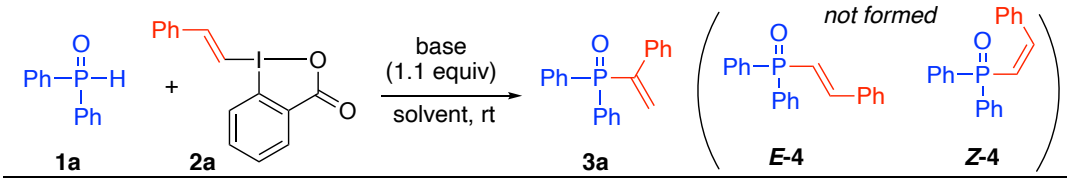


2f

Prepared according to General procedure S2,[3] (326 mg, 0.86 mmol, 58 %). ^{1}H NMR (400 MHz, MeOD-*d4*) δ 8.00 (s, 1H), 7.94 (d, *J* = 15.5 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.65 (d, *J* = 15.5 Hz, 1H), 7.53 – 7.46 (m, 3H), 7.37 (s, 1H), 2.35 (s, 3H), 2.31 (s, 3H);^{13}C NMR (101 MHz, MeOD-*d4*) δ 170.4, 155.5, 145.4, 141.3, 136.8, 134.1, 132.1, 132.0, 130.2, 129.2, 129.0, 112.0, 99.8, 20.2, 19.4.

3 Optimization Studies

3.1 Full Optimization Table of Phosphine Oxides

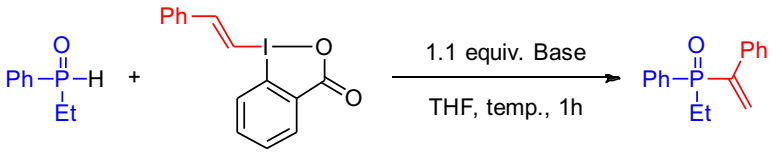


1a **2a** **3a** ***E*-4** ***Z*-4**

Entry	Base	Solvent	Conc. [mol/L]	Time [h]	NMR Yield **3a** [%]
1	Et3N	THF	0.1	20	5
2	DMAP	THF	0.1	20	<5
3[a]	Cs_2CO_3	THF	0.1	20	62
4	-	THF	0.1	20	0
5	DBU	THF	0.1	20	88
6	BTMG	THF	0.1	20	90
7	DBU	Et2O	0.1	20	40
8	DBU	Toluene	0.1	20	64
9	DBU	EtOAc	0.1	20	76
10	DBU	Cyclohexane	0.1	24	6
11	DBU	MeCN	0.1	24	71
12	DBU	Pyridine	0.1	24	96
13	-	Pyridine	0.1	24	0
14	DBU	THF	0.1	1	84
15[b]	DBU	THF	0.1	1	80
16	DBU	THF	0.25	1	78
17	**DBU**	**THF**	**0.05**	**1**	**93 (94)**
18[c]	DBU	THF	0.05	1	90
19[d]	DBU	THF	0.05	1	82
20[e]	DBU	THF	0.05	1	84

[a] At 60 °C. [b] 1.0 equiv of **2a**. [c] Reaction performed adding the reagents at the same time. [d] With addition of 1.0 equiv. TEMPO. [e] With addition of 1.0 equiv. of 1,1–diphenylethylene (DPE).

3.2 Optimization of Alkylaryl Phosphine Oxides

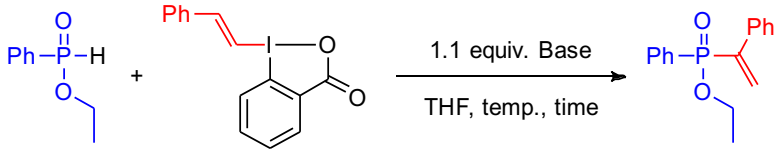


1q **2a** 1.2 equiv. **3q**

Entry	Base	Temp [°C]	Solvent:	NMR yield of **3q** [%]
1[a]	BTMG	RT	THF	40
2[a]	BTMG	60	THF	43
3[a]	DBU	RT	THF	31
4[a]	DBU	60	THF	37
5[b]	BTMG	RT	THF	79
6[b]	BTMG	60	THF	79
7[b]	DBU	RT	THF	51
8[b]	**DBU**	**60**	**THF**	**86**
9[b]	K_2CO_3	60	THF	53
10[b]	Cs_2CO_3	60	THF	65
11[b]	DBU	RT	THF	70
12[b]	DBU	RT	Pyridine	68
13b[a]	DBU	RT	MeCN	66
14[b]	DBU	60	THF	75
15[b,c]	DBU	60	THF	77
16[b,d]	DBU	60	THF	78

[a] Reaction performed under inert conditions, anhydrous THF and followed by acidic work up.
[b] Reaction performed in THF stored over molecular sieves, workup consisted of precipitation with Et_2O and recollection of the organic phase after filtration. [c] Reaction time 2 h. [d] Reaction time 4 h.

3.3 Optimization of Phosphinates

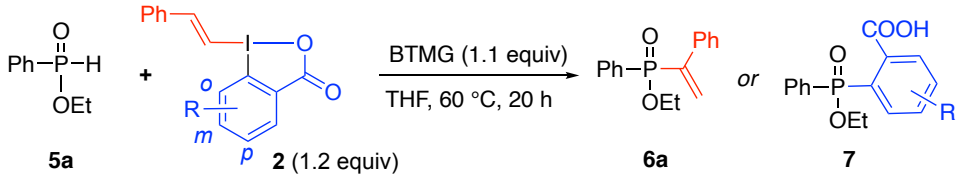


5a **2a** 1.2 equiv. **6a**

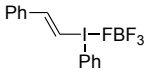
Entry	Solvent	Base	Temp. [°C]	Time [h]	NMR yield of **6a** [%]
1	Pyridine	DBU	RT	18	8
2	THF	K_2CO_3	60	22	46
3	THF	Cs_2CO_3	RT	22	44
4	Dioxane	K_2CO_3	100	22	41
5	Dioxane	Cs_2CO_3	100	22	39
6	THF	P1-*t*Bu	RT	1	<1
7	THF	BTMG	RT	1	<1
8	THF	DBU	RT	1	<1
9	THF	P1-*t*Bu	60	18	79
10	THF	DBU	60	20	70
11	**THF**	**BTMG**	**60**	**20**	**80**
12	THF	Cs_2CO_3	60	24	62
13	Toluene	DBU	100	20	36

3.4 Influence of Core-Substituted VBX with Phosphinates

Phosphinate **5a** was reacted with substituted VBX reagents **2b-f** to investigate electronic and steric effects. The presence of both electron donating and electron withdrawing groups had a negative effect on the reactivity (**2b-c**, entries 1-3). Steric effects were screened with *o*-substituted VBX reagents **2d-e**, and *o*-Me VBX **2d** caused a drastic loss of reactivity (entry 4), while the corresponding *o*-nitro reagent **2e** changed the chemoselectivity to give the arylated product in 60% yield (entry 5). Such arylations were also observed in S-vinylations with nitro-substituted reagents.[9] Me_2-VBX **2f**, which we previously reported to improve the S-vinylation yields,[9] showed comparable reactivity to the unsubstituted VBX (entry 6). A control reaction with the acyclic vinyliodonium salt **8** gave only 10% yield of **6a** (entry 7).

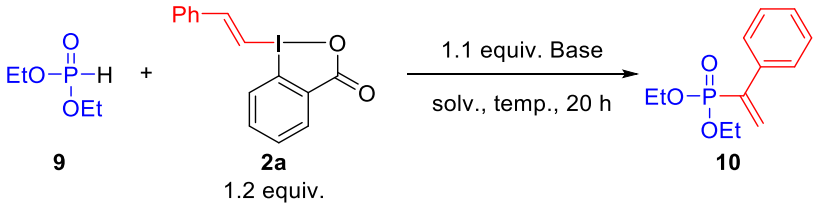


5a **2** (1.2 equiv) **6a** **7**

Entry	**2**	R	Yield **6a** (%)	Yield **7** (%)	Recovered **5a** (%)
1	**2a**	H	79	0	0
2	**2b**	*p*-Br	45	0	30
3	**2c**	*p*-OMe	44	0	34
4	**2d**	*o*-Me	0	0	92
5	**2e**	*o*-NO_2	0	60	0
6	**2f**	*m,p*-Me_2	75	0	0
7	**8**		10	0	0

[a] Reaction conditions as in Table 1 entry 6; NMR yields given.

3.5 Attempts of Phosphonates Optimization

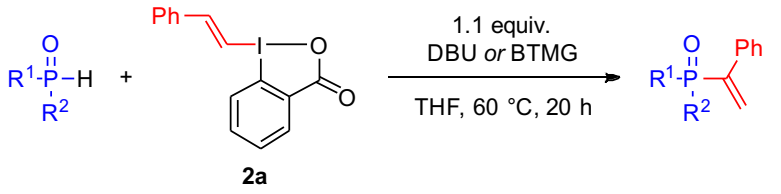


9 **2a** 1.2 equiv. **10**

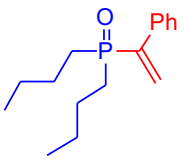
Entry	Solvent	Base	Temperature	Yield **6a** [%][b]
1	THF	DBU	rt	-
2	THF	KOtBu	rt	<5
3	THF	TMG	rt	-
4	THF	K_2CO_3	rt	<5
5	THF	NaH	rt	-
6	THF	DBU	50	12
7	THF	K_2CO_3	50	9
8	THF	Cs_2CO_3	60	17
9	THF	Cs_2CO_3	rt	<5
10	THF	TBD	rt	-
11	Toluene	DBU	100	<5
12	Toluene	Cs_2CO_3	100	10
13	Pyridine	DBU	100	8
14	Pyridine	-	100	-
15	Pyridine	DBU	rt	-
16	Pyridine	DBU	50	5
17	Et_2O	DBU	50	-
18	MeCN	DBU	50	<5
19	AcOEt	DBU	50	-
20	Cyclohexane	DBU	50	-
21	THF	Et_3N	60	-
22	THF	DIPEA	60	-
23	THF	TMEDA	60	-
24	THF	NaOMe	60	-
25	THF	DMAP	60	-
26	THF	DABCO	60	-
27	THF[b]	DBU	60	<5
28	THF[b]	Cs_2CO_3	60	10
29	THF	DBU	60	-
30[a]	THF	-	60	-
31[a]	THF	DBU	100	<5
32	THF	Cs_2CO_3	100	<5

[a] Reaction performed with vinyliodonium salt **8**. [b] Degassed THF was used.

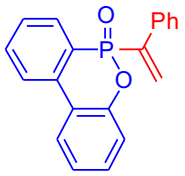
3.6 Limitations



2a



3x 30%[a]
(with DBU as a base)



6g 8%[a]
(with BTMG as a base)

[a] Yields determined by ^{1}H NMR spectroscopy.

4 Preparation of Substrates

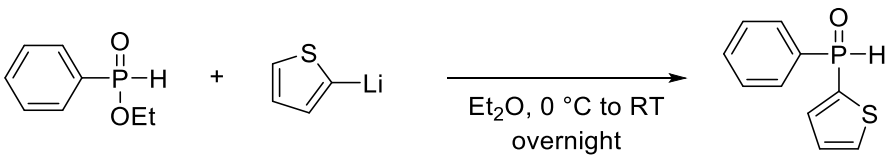
4.1 Preparation of Symmetric H-Phosphine Oxides 1

Symmetric H-phosphine oxides were prepared according to literature: di(4-*tert*-butylphenyl)phosphine oxide (**1b**),[10] di(*o*-tolyl)phosphine oxide (**1d**),[11] di(4-methoxyphenyl)phosphine oxide (**1g**),[10] di(1-naphtyl)phosphine oxide (**1e**),[12] di(4-fluorophenyl)phosphine oxide (**1h**),[12] di(4-trifluoromethylphenyl)phosphine oxide (**1i**),[10] di-n-butylphosphine oxide (**1x**).[13]

4.2 Preparation of Unsymmetric H-Phosphine Oxides 1

Unsymmetric H-phosphine oxides were prepared according to literature: phenyl-(4-methylphenyl)phosphine oxide (**1k**),[14] benzylphenylphosphine oxide (**1s**),[15] allylphenylphosphine oxide (**1u**)[15] and cyclopropylphenylphosphine oxide (**1v**),[16] *t*-butylphenylphosphine oxide (**1w**).[17]

Phenyl(2-thienyl)phosphine oxide (1j)

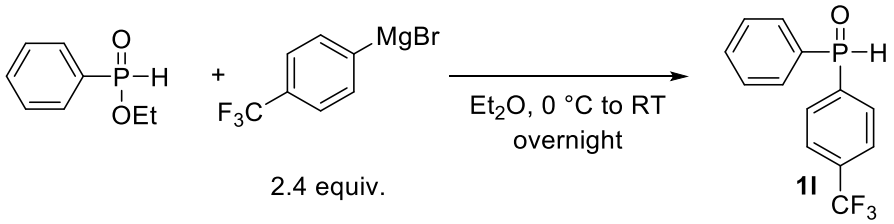


3.0 equiv. **1j**

An oven-dried flask was evacuated and refilled with argon 3 times, then 2-thienyllithium solution (30 mL, 30.0 mmol) was added. The mixture was cooled down to 0 °C and a solution of ethyl phenylphosphate (1.70 g, 10.0 mmol) in anhydrous THF (20 mL) was added dropwise via an addition funnel. The cooling bath was removed and the resulting mixture was stirred at room temperature overnight. Subsequently 1 N HCl (60 mL) was added dropwise over a period of 15 minutes at 0 °C, followed by addition of CH_2Cl_2 (40 mL) and stirring for further 5 minutes. The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL), then the combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography (petroleum ether:ethyl acetate 1:1 to 1:4) and the product was obtained as a yellow oil (1.33 g, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 497.9 Hz, 1H), 7.80 – 7.72 (m, 3H), 7.62 – 7.48 (m, 4H), 7.20 (ddd, J = 5.0, 3.6, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1 (d, $J_{P\text{-}C}$ = 11.3 Hz), 134.2 (d, $J_{P\text{-}C}$ = 5.3 Hz), 133.0 (d, $J_{P\text{-}C}$ = 3.0 Hz), 132.3 (d, $J_{P\text{-}C}$ = 108.9 Hz), 131.3 (d, $J_{P\text{-}C}$ = 107.7 Hz), 130.6 (d, $J_{P\text{-}C}$ = 12.2 Hz), 129.0 (d, $J_{P\text{-}C}$ = 13.4 Hz), 128.6 (d, $J_{P\text{-}C}$

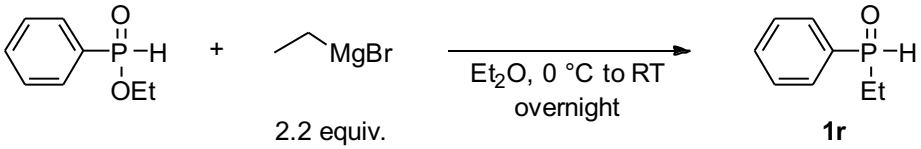
= 14.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.1 (dd, *J* = 497.9, 7.2 Hz). HRMS m/z calcd for $C_{10}H_9NaOPS^+$: 231.0004 [M+Na]$^+$; found: 231.0008.

Phenyl[4-(trifluoromethyl)phenyl]phosphine oxide (1l)



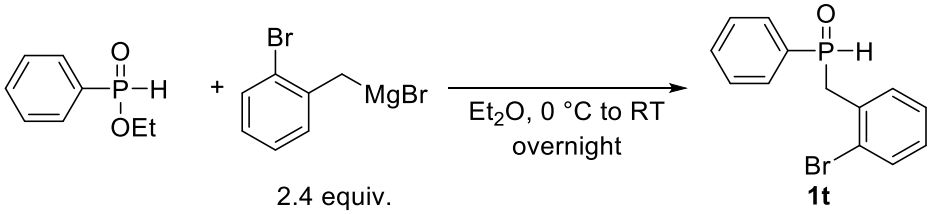
An oven-dried flask was evacuated and refilled with argon 3 times, then a solution of ethyl phenylphosphate (0.85 g, 5.0 mmol) in anhydrous THF (10 mL) was added and cooled down to 0 °C. The Grignard reagent mixture (12 mL, 12.0 mmol) formed from Mg turnings (15 mmol, 360 mg) and 4-trifluoromethylphenylbromide (12 mmol, 1.7 mL) was cooled to 0° and it was added dropwise *via* canula to ethyl phenylphosphate. The cooling bath was removed and the resulting mixture was stirred at room temperature overnight. Subsequently 1 N HCl (30 mL) was added dropwise over a period of 15 minutes at 0 °C, followed by addition of CH_2Cl_2 (20 mL) and stirring for further 5 minutes. The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL), then the combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography (petroleum ether:ethyl acetate 1:1 to 1:3) and product was obtained as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 13.0, 8.0 Hz, 2H), 8.13 (d, *J* = 486.7, 1H), 7.80 – 7.73 (m, 2H), 7.73 – 7.67 (m, 2H), 7.61 (td, *J* = 7.3, 1.7 Hz, 1H), 7.57 – 7.48 (m, 2H). ^{13}C NMR (101 MHz, , $CDCl_3$) δ 135.9 (d, J_{P-C} = 98.5 Hz), 134.5 (dd, J_{F-C} = 32.9 Hz, J_{P-C} = 3.0 Hz), 133.2 (d, J_{P-C} = 2.9 Hz), 131.4 (d, J_{P-C} = 11.6 Hz), 130.8 (d, J_{P-C} = 11.6 Hz), 130.5 (d, J_{P-C} = 103.0 Hz), 129.3 (d, *J* = 13.1 Hz), 125.9 (dq, J_{P-C} = 12.9 Hz, J_{P-C} = 3.8 Hz), 123.6 (q, J_{F-C} = 274.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.6 (dp, *J* = 485.6, 12.8 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.25. HRMS m/z calcd for $C_{13}H_{10}F_3NaOP^+$: 293.0314 [M+Na]$^+$; found: 293.0309.

Ethylphenylphosphine oxide (1r)



An oven-dried flask was evacuated and refilled with argon 3 times, then 1 M solution of EtMgBr (22.0 ml, 22 mmol) in THF was added and cooled to 0 °C. Solution of ethyl phenylphosphinate (1.70 ml, 10.0 mmol) in 20 mL of anh. Et_2O was added dropwise over 30 minutes, then reaction was warmed to RT and stirred overnight. After, resulting mixture was quenched with aq. NH_4Cl solution (20 mL) and 50 ml of water was added. Aqueous phase was extracted with DCM (3 x 80 mL) and combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. Crude was purified by column chromatography (dichloromethane:methanol 97:3) and obtained as a colorless oil (1.15 g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 2H), 7.58 – 7.52 (m, 1H), 7.52 – 7.45 (m, 2H), 7.41 (dt, *J* = 463.2, 3.3 Hz, 1H), 2.10 – 1.90 (m, 2H), 1.14 (dt, *J* = 19.7, 7.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.5 (d, J_{P-C} = 2.9 Hz), 130.8 (d, J_{P-C} = 96.1 Hz), 130.0 (d, J_{P-C} = 10.7 Hz), 129.0 (d, J_{P-C} = 12.3 Hz), 23.4 (d, J_{P-C} = 68.6 Hz), 5.5 (d, J_{P-C} = 4.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.6 – 28.8 (dm, *J* = 464.0 Hz). Obtained spectral data are in accordance with literature.[18]

Phenyl(2-bromobenzyl)phosphine oxide (1t)



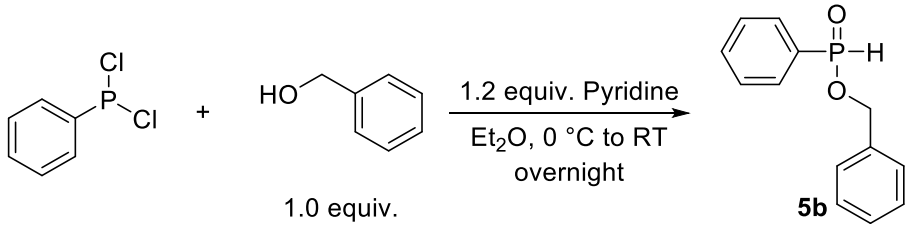
An oven-dried flask was evacuated and refilled with argon 3 times, then a solution of solution of ethyl phenylphosphate (0.85 g, 5.0 mmol) in dry THF (10 mL) was added and cooled down to 0 °C. The

Grignard reagent mixture (12 mL, 12.0 mmol) formed from Mg turnings (15 mmol, 360 mg) and 2-bromobenzylbromide (12 mmol, 1.6 mL) was cooled to 0° and it was added dropwise via canula to ethyl phenylphosphate. After, cooling bath was removed and resulting mixture was stirred at room temperature overnight. Subsequently 1 N HCl (30 mL) were added dropwise over a period of 15 minutes at 0 °C, followed by addition DCM (20 mL) and stirring for further 5 minutes. Organic phase was collected and aqueous phase was extracted with DCM (3 x 30 mL), then combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography (petroleum ether:ethyl acetate 1:1 to 1:3) and product was obtained as an colorless oil (821 mg, 46 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.77 (m, 2H), 7.73 – 7.47 (m, 5H), 7.72 (d, *J* = 566.4 Hz, 1H), 7.34 (td, *J* = 7.5, 1.3 Hz, 1H), 7.21 (td, *J* = 7.7, 1.8 Hz, 1H), 5.33 – 5.10 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1 (d, *J* = 7.5 Hz), 133.3 (d, *J* = 2.9 Hz), 132.9, 131.0 (d, *J* = 12.0 Hz), 130.1 (d, *J* = 2.4 Hz), 129.8, 128.9, 128.8, 127.7, 123.0, 66.8 (d, *J* = 5.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.37 – 23.41 (m).

4.3 Preparation of Phosphinates 5

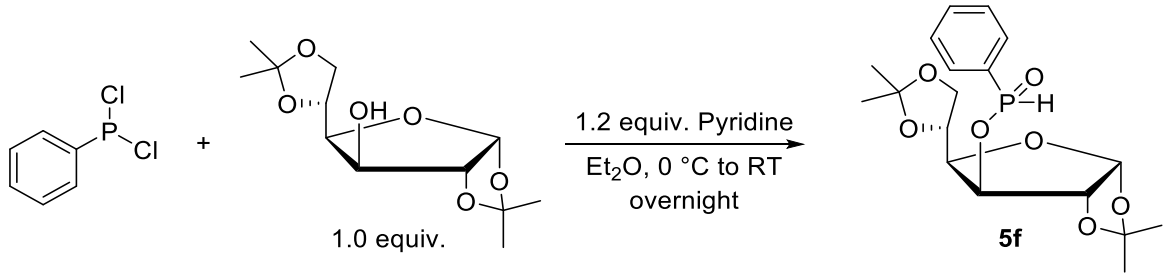
Phosphinates were prepared according to literature: ethyl phenylphosphinate **(5a)**,[19] phenyl phenylphosphinate **(5c)**,[20] allyl phenylphosphinate **(5d)**,[21] and (1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl phenylphosphinate **(5e).**[22]

Benzyl phenylphosphinate (5b)



$PhPCl_2$ (1.36 mL, 10.0 mmol) was dissolved in Et_2O (14 mL) and cooled to 0 °C. A solution of a benzyl alcohol (1.04 mL, 10.0 mmol) and pyridine (0.97 mL, 12.0 mmol) in Et_2O (7 mL) was added dropwise. After addition cooling bath was removed and reaction mixture was left stirred overnight. Water (0.2 mL, 11 mmol) was added, resulting mixture was stirred for 10 minutes and after it was transferred to separatory funnel and washed with $NaHCO_3$ (15 mL), then aqueous phase was extracted with AcOEt (3 x 15 mL). Combined organic phases were dried over Na_2SO_4, filtered and evaporated. Crude was purified by column chromatography (petroleum ether:ethyl acetate 1:1) and product was obtained as a colorless liquid (793 mg, 34% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 2H), 7.65 (d, *J* = 565.9 Hz, 1H), 7.61 (td, *J* = 7.3, 1.4 Hz, 1H), 7.51 (td, *J* = 7.5, 3.6 Hz, 2H), 7.44 – 7.27 (m, 5H), 5.12 (ddd, *J* = 21.2, 11.8, 8.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7 (d, $J_{P\text{-}C}$ = 6.6 Hz), 133.3 (d, $J_{P\text{-}C}$ = 3.0 Hz), 131.1 (d, $J_{P\text{-}C}$ = 12.0 Hz), 128.9 (d, $J_{P\text{-}C}$ = 14.0 Hz), 128.82, 128.76, 128.2, 127.9 (d, $J_{P\text{-}C}$ = 154.4 Hz), 67.4 (d, $J_{P\text{-}C}$ = 6.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.03 (ddd, *J* = 567.2, 11.4, 7.7 Hz). Obtained spectral data are in accordance with literature.[23]

1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose 3-*O*-phenylphosphonite (5f)



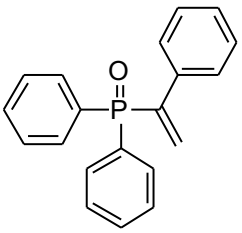
$PhPCl_2$ (1.36 mL, 10.0 mmol) was dissolved in Et_2O (14 mL) and cooled to 0 °C. A solution of a 1,2:5,6-di-*O*-isopropylidene-α-D-glucose (2.60 g, 10.0 mmol) and pyridine (0.97 mL, 12.0 mmol) in Et_2O (7 mL) was added dropwise. After addition cooling bath was removed and reaction mixture was left stirred overnight. Water (0.2 mL, 11 mmol) was added, resulting mixture was stirred for 10 minutes and after it was transferred to separatory funnel and washed with $NaHCO_3$ (15 mL), then aqueous phase was

extracted with AcOEt (3 x 15 mL). Combined organic phases were dried over Na_2SO_4, filtered and evaporated. Crude was purified by column chromatography (petroleum ether:ethyl acetate 1:1) and product was obtained as a colorless sticky liquid (2.71 g, 71% yield). *Both diastereomers*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.75 (m, 2H), 7.70 (dd, *J* = 575.3, 31.6 Hz, 1H), 7.68 – 7.59 (m, 1H), 7.51 (tt, *J* = 12.3, 6.2 Hz, 2H), 6.00 – 4.82 (m, 3H), 4.29 – 3.94 (m, 4H), 1.50 (d, *J* = 7.8 Hz, 3H), 1.45 (d, *J* = 7.8 Hz, 3H), 1.37 (d, *J* = 10.2 Hz, 3H), 1.31 (d, *J* = 5.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.7 (d, J_{P-C} = 2.9 Hz), 133.6 (d, J_{P-C} = 2.9 Hz), 131.8 (d, J_{P-C} = 12.3 Hz), 131.0 (d, J_{P-C} = 12.2 Hz), 129.5 (d, J_{P-C} = 122.6 Hz), 128.91 (d, J_{P-C} = 14.2 Hz), 128.87 (d, J_{P-C} = 14.0 Hz), 128.8 (d, J_{P-C} = 14.7 Hz), 128.2 (d, J_{P-C} = 111.5 Hz), 112.7, 112.5, 111.9, 109.7, 109.4, 105.5, 105.4, 105.3, 85.2, 84.1, 83.9, 81.3, 81.1 (d, J_{P-C} = 6.7 Hz), 80.8 (d, J_{P-C} = 7.7 Hz), 80.1 (d, J_{P-C} = 6.2 Hz), 78.0 (d, J_{P-C} = 6.8 Hz), 75.3, 73.6, 72.6, 72.1, 68.0, 67.7, 67.6, 27.02, 26.97, 26.90, 26.8, 26.4, 26.3, 25.42, 25.38, 25.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.11 (ddd, *J* = 565.7, 26.1, 13.6 Hz), 26.19 (ddd, *J* = 586.1, 23.6, 12.9 Hz). Obtained spectral data are in accordance with literature.[24,25]

5 Analytical data

General Procedure for Vinylation of P-Nuclephiles:
A microwave vial was charged with the phosphorus compound (1.0 equiv) and THF was added, followed by addition of base (1.1 equiv). The vial was capped with a septum and the resulting mixture was stirred at room temperature for 5 minutes. VBX **2** (1.2 equiv.) was added and the vial was rinsed with THF (1.0 mL) to obtain a final concentration as a 0.05M, then the vial was capped with a septum (or metal cap if reaction takes place in elevated temperature). The resulting mixture was stirred (see below for exact conditions). The reaction mixture was then concentrated and the crude was purified by column chromatography.

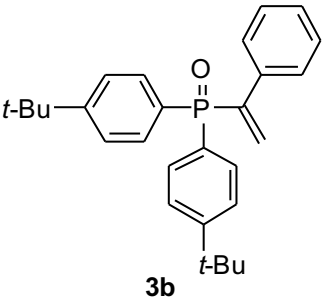
Diphenyl(1-phenylethenyl)phosphine oxide (3a)



3a

The title compound was prepared according to the General Procedure from phosphine oxide **1a** (0.5 mmol) and VBX **2a** (0.6 mmol) at room temperature within 1 h. After purification by column chromatography (petroleum ether:ethyl acetate 1:2), the product was obtained as a yellowish solid (143 mg, 97% yield). R_f = 0.32 (petroleum ether:ethyl acetate 1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 4H), 7.54 – 7.48 (m, 2H), 7.48 – 7.40 (m, 6H), 7.27 – 7.21 (m, 3H), 6.25 (dd, *J* = 40.1, 1.0 Hz, 1H), 5.76 (dd, *J* = 19.7, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5 (d, $J_{P\text{-}C}$ = 92.4 Hz), 137.6 (d, $J_{P\text{-}C}$ = 10.1 Hz), 132.1, 132.0 (d, $J_{P\text{-}C}$ = 2.8 Hz), 132.1 (d, $J_{P\text{-}C}$ = 9.6 Hz), 131.7 (d, $J_{P\text{-}C}$ = 103.6 Hz), 128.6, 128.5, 128.3, 128.2 (d, $J_{P\text{-}C}$ = 4.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.5 – 29.6 (m). Obtained spectral data are in accordance with literature.[26]

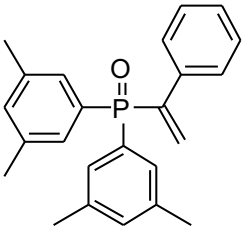
Di(4-*tert*-butylphenyl)(1-phenylethenyl)phosphine oxide (3b)



3b

The title compound was prepared according to the General Procedure from phosphine oxide **1b** (0.5 mmol) and VBX **2a** (0.6 mmol) at room temperature within 1 h. After purification by column chromatography (petroleum ether:ethyl acetate 2:1 to 1:1), the product was obtained as yellowish solid (193 mg, 93% yield). R_f = 0.38 (petroleum ether:ethyl acetate/1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 4H), 7.51 – 7.47 (m, 2H), 7.46 – 7.42 (m, 4H), 7.27 – 7.21 (m, 3H), 6.22 (dd, *J* = 39.9, 1.1 Hz, 1H), 5.74 (dd, *J* = 19.7, 1.1 Hz, 1H), 1.31 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3 (d, $J_{P\text{-}C}$ = 2.8 Hz), 144.7 (d, $J_{P\text{-}C}$ = 92.3 Hz), 138.0 (d, $J_{P\text{-}C}$ = 9.9 Hz), 132.0 (d, $J_{P\text{-}C}$ = 9.9 Hz), 31.8 (d, $J_{P\text{-}C}$ = 9.9 Hz), 128.7 (d, $J_{P\text{-}C}$ = 106.2 Hz), 128.5, 128.2, 128.3 (d, $J_{P\text{-}C}$ = 4.6 Hz), 125.6 (d, $J_{P\text{-}C}$ = 12.3 Hz), 35.1, 31.2. HRMS m/z calcd for $C_{28}H_{33}NaOP^+$: 439.2161 [M+Na]$^+$; found: 439.2164.

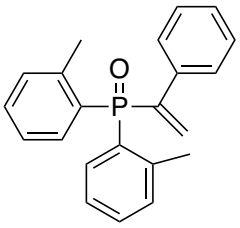
Bis(3,5-dimethylphenyl)(1-phenylethenyl)phosphine oxide (3c)



3c

The title compound was prepared according to the General Procedure from phosphine oxide **1c** (0.5 mmol) and VBX **2a** (0.6 mmol) at room temperature within 1 h. After purification by column chromatography (petroleum ether:ethyl acetate 1:1), the product was obtained as yellowish glassy solid (168 mg, 93% yield). R_f = 0.41 (petroleum ether:ethyl acetate 1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (ddd, *J* = 5.4, 2.7, 1.3 Hz, 2H), 7.33 (d, *J* = 12.2 Hz, 4H), 7.28 – 7.25 (m, 3H), 7.14 (s, 2H), 6.23 (dd, *J* = 39.8, 1.2 Hz, 1H), 5.76 (dd, *J* = 19.6, 1.2 Hz, 1H), 2.32 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7 (d, $J_{P\text{-}C}$ = 91.7 Hz), 138.2 (d, $J_{P\text{-}C}$ = 12.7 Hz), 138.0 (d, $J_{P\text{-}C}$ = 9.7 Hz), 133.7 (d, $J_{P\text{-}C}$ = 2.9 Hz), 131.8 (d, $J_{P\text{-}C}$ = 9.8 Hz), 131.5 (d, $J_{P\text{-}C}$ = 102.6 Hz), 129.7 (d, $J_{P\text{-}C}$ = 9.6 Hz), 128.4, 128.3, 128.1 (d, $J_{P\text{-}C}$ = 4.6 Hz), 21.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.2 – 30.4 (m). HRMS m/z calcd for $C_{24}H_{25}NaOP^+$: 383.1540 [M+Na]$^+$; found: 383.1535.

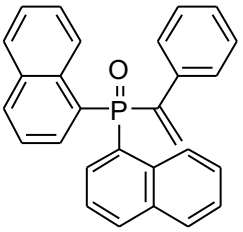
Di(2-tolyl)(1-phenylethynyl)phosphine oxide (3d)



3d

The title compound was prepared according to the General Procedure from phosphine oxide **1d** (0.1 mmol) and VBX **2a** (0.12 mmol) at room temperature within 1 h. After purification by column chromatography (pentane:ethyl acetate 6:4), the product was obtained as colorless oil (22 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 2H), 7.44 – 7.38 (m, 2H), 7.37 – 7.25 (m, 7H), 7.19 – 7.12 (m, 2H), 6.28 (dd, *J* = 40.3, 1.0 Hz, 1H), 5.62 (dd, *J* = 19.9, 1.0 Hz, 1H), 2.58 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9 (d, *J* = 91.3 Hz), 143.7 (d, *J* = 7.7 Hz), 133.1 (d, *J* = 12.7 Hz), 132.2 (d, *J* = 10.4 Hz), 132.0 (d, *J* = 2.6 Hz), 131.3 (d, *J* = 10.2 Hz), 130.4 (d, *J* = 101.5 Hz), 128.6, 128.4, 128.4, 128.3, 125.5 (d, *J* = 12.8 Hz), 22.0 (d, *J* = 4.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.9 (m). HRMS m/z calcd for $C_{22}H_{21}NaOP^+$: 355.1222 [M+Na]$^+$; found: 355.1227.

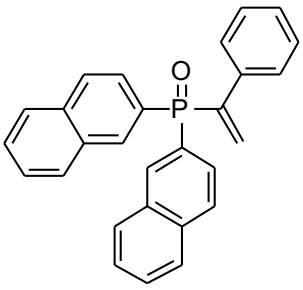
Di(1-naphtyl)(1-phenylethenyl)phosphine oxide (3e)



3e

The title compound was prepared according to the General Procedure from phosphine oxide **1e** (0.5 mmol) and VBX **2a** (0.6 mmol) at room temperature within 1 h. After purification by column chromatography (petroleum ether:ethyl acetate 2:1), the product was obtained as colorless solid (182 mg, 90% yield). R_f = 0.26 (petroleum ether:ethyl acetate 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 – 8.89 (m, 2H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.91 (ddd, *J* = 5.5, 4.6, 2.5 Hz, 2H), 7.72 – 7.64 (m, 2H), 7.62 – 7.57 (m, 2H), 7.56 – 7.50 (m, 4H), 7.35 (ddd, *J* = 8.2, 7.2, 2.5 Hz, 2H), 7.30 – 7.23 (m, 3H), 6.32 (dd, *J* = 41.4, 0.7 Hz, 1H), 5.64 (dd, *J* = 20.4, 0.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8 (d, J_{P-C} = 92.9 Hz), 137.9 (d, J_{P-C} = 9.4 Hz), 134.3 (d, J_{P-C} = 7.9 Hz), 134.1 (d, J_{P-C} = 9.0 Hz), 133.6 (d, J_{P-C} = 11.9 Hz), 133.4 (d, J_{P-C} = 2.9 Hz), 132.2 (d, J_{P-C} = 10.4 Hz), 128.9 (d, J_{P-C} = 1.1 Hz), 128.6, 128.4 (d, J_{P-C} = 4.7 Hz), 128.38, 128.36 (d, J_{P-C} = 101.6 Hz), 128.1 (d, J_{P-C} = 5.1 Hz), 127.5, 126.7, 124.4 (d, J_{P-C} = 14.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.7 (td, *J* = 36.1, 17.2 Hz). HRMS m/z calcd for $C_{28}H_{21}NaOP^+$: 427.1222 [M+Na]$^+$; found: 427.1220.

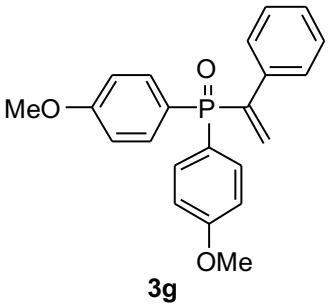
Di(2-naphtyl)(1-phenylethenyl)phosphine oxide (3f)



3f

The title compound was prepared according to the General Procedure from phosphine oxide **1f** (0.3 mmol) and VBX **2a** (0.36 mmol) at room temperature within 1 h. After purification by column chromatography (petroleum ether:ethyl acetate 2:1), the product was obtained as colorless solid 103 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 13.6, 1.5 Hz, 2H), 7.94 – 7.83 (m, 6H), 7.70 (ddd, *J* = 9.9, 8.4, 1.5 Hz, 2H), 7.65 – 7.50 (m, 6H), 7.23 (dd, *J* = 5.0, 1.9 Hz, 3H), 6.32 (dd, *J* = 40.4, 1.1 Hz, 1H), 5.86 (dd, *J* = 19.9, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5 (d, *J* = 92.6 Hz), 137.7 (d, *J* = 9.9 Hz), 134.9 (d, *J* = 2.3 Hz), 134.2 (d, *J* = 8.9 Hz), 132.7 (d, *J* = 13.2 Hz), 132.4 (d, *J* = 10.0 Hz), 129.2, 129.1 (d, *J* = 103.7 Hz), 128.6, 128.4 (d, *J* = 3.3 Hz), 128.31, 128.29, 129.26, 128.3, 128.0, 127.04, 126.98, 126.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.09 (ddd, *J* = 44.3, 19.2, 11.2 Hz). HRMS m/z calcd for $C_{28}H_{21}NaOP^+$: 427.1222 [M+Na]$^+$; found: 427.1223.

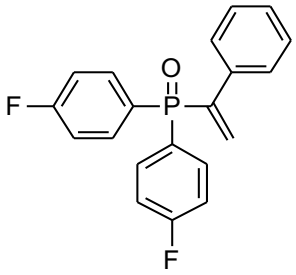
Di(4-methoxyphenyl)(1-phenylethenyl)phosphine oxide (3g)



3g

The title compound was prepared according to the General Procedure from phosphine oxide **1g** (0.5 mmol) and VBX **2a** (0.6 mmol) at room temperature within 1 h. After purification by column chromatography (dichloromethane:methanol 97:3), the product was obtained as yellowish glassy solid (130 mg, 71% yield). R_f = 0.50 (dichloromethane: methanol 19:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.56 (m, 4H), 7.47 – 7.41 (m, 2H), 7.26 – 7.21 (m, 3H), 6.96 – 6.90 (m, 4H), 6.19 (dd, *J* = 39.6, 1.2 Hz, 1H), 5.75 (dd, *J* = 19.6, 1.2 Hz, 1H), 3.82 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, J_{P-C} = 2.9 Hz), 145.1 (d, J_{P-C} = 93.1 Hz), 138.0 (d, J_{P-C} = 10.0 Hz), 133.9 (d, J_{P-C} = 11.0 Hz), 131.5 (d, J_{P-C} = 9.7 Hz), 128.5, 128.3 (d, J_{P-C} = 4.6 Hz), 128.2 (d, J_{P-C} = 0.7 Hz), 123.2 (d, J_{P-C} = 110.2 Hz), 114.1 (d, J_{P-C} = 13.1 Hz), 55.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.8 (ddd, *J* = 29.3, 20.2, 10.2 Hz). Obtained spectral data are in accordance with literature.[10]

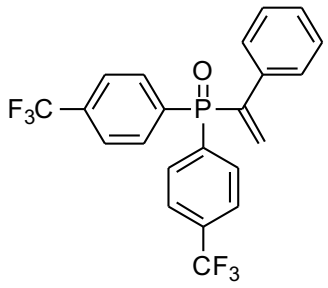
Di(4-fluorophenyl)(1-phenylethenyl)phosphine oxide (3h)



3h

The title compound was prepared according to the General Procedure from phosphine oxide **1h** (0.5 mmol) and VBX **2a** (0.6 mmol) at room temperature within 1 h. After purification by column chromatography (petroleum ether:ethyl acetate 1:1), the product was obtained as yellowish liquid (110 mg, 65% yield). R_f = 0.54 (petroleum ether:ethyl acetate 1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 4H), 7.46 – 7.40 (m, 2H), 7.29 – 7.23 (m, 3H), 7.18 – 7.09 (m, 4H), 6.26 (dd, *J* = 40.7, 0.9 Hz, 1H), 5.77 (dd, *J* = 20.0, 0.9 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -106.3 – -106.4 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2 (dd, J_{F-C} = 253.9, J_{P-C} = 3.3 Hz), 144.3 (d, J_{P-C} = 93.9 Hz), 137.3 (d, J_{P-C} = 10.2 Hz), 134.5 (dd, J_{P-C} = 11.1, J_{F-C} = 8.8 Hz), 132.3 (d, J_{P-C} = 9.8 Hz), 128.7, 128.6 (d, J_{P-C} = 0.9 Hz), 128.2 (d, J_{P-C} = 4.7 Hz), 127.4 (dd, J_{P-C} = 106.9, J_{F-C} = 3.4 Hz), 116.1 (dd, J_{F-C} = 21.4, J_{P-C} = 13.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.8 – 28.1 (m). HRMS m/z calcd for $C_{20}H_{15}F_2NaOP^+$: 363.0721 $[M+Na]^+$; found: 363.0718.

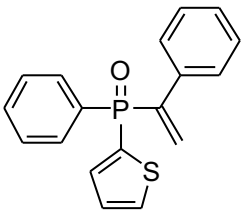
Bis(4-(trifluoromethyl(phenyl)(1-phenylethenyl)phosphine oxide (3i)



3i

The title compound was prepared according to the General Procedure from phosphine oxide **1i** (0.1 mmol) and VBX **2a** (0.12 mmol) at 60° within 20 h. After purification by column chromatography (petroleum ether:ethyl acetate 1:2), the product was obtained as yellowish oil (12 mg, 27% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.80 (m, 4H), 7.78 – 7.67 (m, 4H), 7.55 – 7.43 (m, 2H), 7.34 – 7.27 (m, 3H), 6.34 (dd, *J* = 41.8, 0.7 Hz, 1H), 5.79 (dd, *J* = 20.5, 0.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3 (d, J_{P-C} = 94.1 Hz), 136.7 (d, J_{P-C} = 10.2 Hz), 135.5 (d, J_{P-C} = 101.7 Hz), 134.2 (dd, J_{F-C} = 32.8, J_{P-C} = 2.9 Hz), 133.16 (d, *J* = 10.0 Hz), 132.5 (d, J_{P-C} = 9.9 Hz), 128.9 (d, J_{P-C} = 4.0 Hz), 128.8, 128.1 (d, J_{P-C} = 4.9 Hz), 125.7 (dq, J_{P-C} = 11.8, J_{F-C} = 3.7 Hz), 123.6 (d, J_{F-C} = 272.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.48 (dd, *J* = 32.4, 19.9 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.24. Obtained spectral data are in accordance with literature.[26]

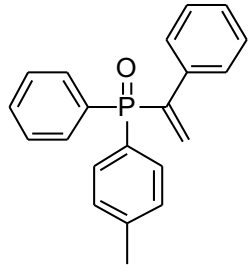
Phenyl(2-thienyl)(1-phenylethenyl)phosphine oxide (3j)



3j

The title compound was prepared according to the General Procedure from phosphine oxide **1j** (0.5 mmol) and VBX **2a** (0.6 mmol) at room temperature within 1 h. After purification by column chromatography (petroleum ether:ethyl acetate 1:1), the product was obtained as yellowish liquid (96 mg, 62% yield). R_f = 0.50 (petroleum ether:ethyl acetate 1:4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 2H), 7.69 (td, *J* = 4.6, 1.1 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.49 – 7.40 (m, 5H), 7.27 – 7.23 (m, 3H), 7.15 (ddd, *J* = 4.8, 3.6, 1.9 Hz, 1H), 6.23 (dd, *J* = 41.3, 1.0 Hz, 1H), 5.93 (dd, *J* = 20.5, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0 (d, J_{P-C} = 97.8 Hz), 137.4 (d, J_{P-C} = 10.8 Hz), 137.0 (d, J_{P-C} = 9.6 Hz), 134.0 (d, J_{P-C} = 4.9 Hz), 133.4, 132.3 (d, J_{P-C} = 2.8 Hz), 132.1 (d, J_{P-C} = 109.1 Hz), 132.0 (d, J_{P-C} = 9.9 Hz), 131.8 (d, J_{P-C} = 10.2 Hz), 128.6 (d, J_{P-C} = 12.7 Hz), 128.5 (d, J_{P-C} = 13.1 Hz), 128.4 (d, J_{P-C} = 1.1 Hz), 128.4, 128.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.2 – 22.6 (m). HRMS m/z calcd for $C_{18}H_{15}NaOPS^+$: 333.0473 $[M+Na]^+$; found: 333.0478.

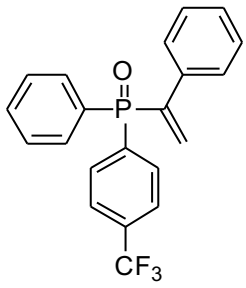
Phenyl(*4*-tolyl)(1-phenylethenyl)phosphine oxide (3k)



3k

The title compound was prepared according to the General Procedure from phosphine oxide **1k** (0.3 mmol) and VBX **2a** (0.36 mmol) at room temperature within 1 h. After purification by column chromatography (petroleum ether:ethyl acetate 1:1), the product was obtained as yellowish colorless oil (82mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (ddd, *J* = 11.8, 8.2, 1.4 Hz, 2H), 7.60 (dd, *J* = 11.7, 8.1 Hz, 2H), 7.54 – 7.37 (m, 5H), 7.34 – 7.17 (m, 5H), 6.23 (dd, *J* = 40.0, 1.1 Hz, 1H), 5.75 (dd, *J* = 19.7, 1.1 Hz, 1H), 2.38 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6 (d, *J* = 92.5 Hz), 142.5 (d, *J* = 2.7 Hz), 137.8 (d, *J* = 9.8 Hz), 132.12 (d, *J* = 14.6 Hz), 132.11 (d, *J* = 4.4 Hz), 131.91 (d, *J* = 9.6 Hz), 131.89 (d, *J* = 2.7 Hz) 129.4 (d, *J* = 12.4 Hz), 128.6, 128.5 (d, *J* = 3.7 Hz), 128.3 (d, *J* = 106.0 Hz),128.26 (d, *J* = 4.5 Hz) 21.7 (d, J_{P-C} = 1.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.3 - 29.3 (m). HRMS m/z calcd for $C_{21}H_{19}NaOP^+$: 341.1066 $[M+Na]^+$; found: 341.1066.

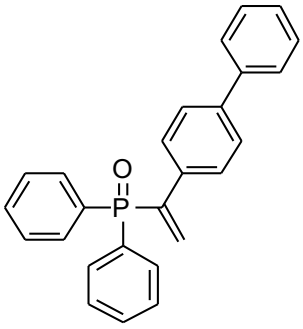
Phenyl(4-(trifluoromethyl)phenyl)(1-phenylethenyl)phosphine oxide (3l)



3l

The title compound was prepared according to the General Procedure from phosphine oxide **1l** (0.1 mmol) and VBX **2a** (0.12 mmol) at room temperature within 1 h. After purification by column chromatography (petroleum ether:ethyl acetate 2:1), the product was obtained as yellowish oil (15 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 11.3, 8.0 Hz, 2H), 7.78 – 7.67 (m, 4H), 7.60 – 7.53 (m, 1H), 7.49 (dtd, *J* = 7.1, 3.9, 3.3, 1.9 Hz, 4H), 7.34 – 7.24 (m, 3H), 6.32 (dd, *J* = 41.0, 0.9 Hz, 1H), 5.80 (dd, *J* = 20.0, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9 (d, J_{P-C} = 93.3 Hz), 137.18 (d, J_{P-C} = 10.1 Hz), 135.8 (d, J_{P-C} = 99.8 Hz), 133.8 (dd, J_{F-C} = 32.8, J_{P-C} = 2.9 Hz), 132.7 (d, J_{P-C} = 10.1 Hz), 132.6 (d, J_{P-C} = 9.9 Hz), 132.44 (d, J_{P-C} = 2.8 Hz), 132.04 (d, J_{P-C} = 9.8 Hz), 130.90 (d, J_{P-C} = 104.6 Hz), 128.83 (d, J_{P-C} = 12.3 Hz), 128.71, 128.6 (J_{P-C} = 0.8 Hz), 128.17 (d, J_{P-C} = 4.6 Hz), 125.42 (dq, J_{P-C} = 11.8 Hz, J_{F-C} = 3.7 Hz), 123.68 (q, J_{F-C} = 273.4 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.16. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.4 – 28.3 (m). HRMS m/z calcd for $C_{21}H_{16}F_3NaOP^+$: 395.0783 $[M+Na]^+$; found: 395.0791.

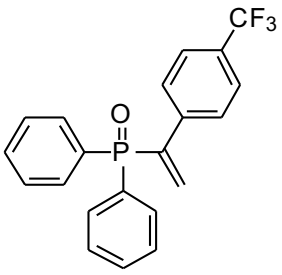
(1-([1,1'-biphenyl]-4-yl)vinyl)diphenylphosphine oxide (3m)



3m

The title compound was prepared according to the General Procedure from phosphine oxide **1a** (0.1 mmol) and VBX **2g** (0.12 mmol) at room temperature within 1 h. After purification by column chromatography (petroleum ether:ethyl acetate 1:2), the product was obtained as white solid (22 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.69 (m, 4H), 7.61 – 7.37 (m, 14H), 7.35 – 7.29 (m, 1H), 6.30 (dd, *J* = 40.3, 1.0 Hz, 1H), 5.74 (dd, *J* = 19.8, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0 (d, J_{P-C} = 92.6 Hz), 141.1, 140.5, 136.6 (d, J_{P-C} = 9.8 Hz), 132.2, 132.1 (d, J_{P-C} = 3.0 Hz), 131.8 (d, J_{P-C} = 10.2 Hz),131.3 (d, J_{P-C} = 103.5 Hz),128.9, 128.7 (d, J_{P-C} = 4.4 Hz), 128.6 (d, J_{P-C} = 2.6 Hz), 127.6, 127.2, 127.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.37 (dq, *J* = 30.9, 13.8, 11.9 Hz). HRMS m/z calcd for $C_{26}H_{21}NaOP^+$: 403.1222 $[M+Na]^+$; found: 403.1214.

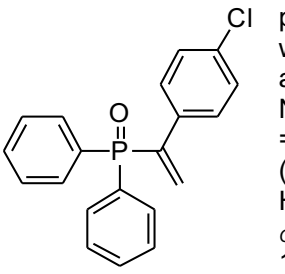
Diphenyl[1-[4-(trifluoromethyl)phenyl]ethenyl]phosphine oxide (3n)



3n

The title compound was prepared according to the General Procedure from phosphine oxide **1a** (0.1 mmol) and VBX **2h** (0.12 mmol) at room temperature within 1 h. After purification by column chromatography (petroleum ether:ethyl acetate 1:2), the product was obtained as white solid (25 mg, 67% yield). ^{1}H NMR (400 MHz $CDCl_3$) δ 7.77 – 7.66 (m, 4H), 7.66 – 7.58 (m, 2H), 7.57 – 7.42 (m, 8H), 6.28 (dd, *J* = 39.6, 0.9 Hz, 1H), 5.77 (dd, *J* = 19.6, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8 (d, J_{P-C} = 92.4 Hz), 141.3 (d, J_{P-C} = 10.0 Hz), 133.3 (d, J_{P-C} = 9.4 Hz), 132.3 (d, J_{P-C} = 2.9 Hz), 132.1 (d, J_{P-C} = 9.6 Hz), 131.2 (d, J_{P-C} = 104.2 Hz), 130.3 (q, J_{F-C} = 32.4 Hz), 128.77 (d, J_{P-C} = 12.2 Hz), 128.60 (d, J_{P-C} = 4.5 Hz), 125.52 (q, J_{F-C} = 3.7 Hz), 124.1 (q, J_{F-C} = 273.3). ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.1 (ddt, *J* = 41.1, 20.1, 12.5 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.72. Obtained spectral data are in accordance with literature.[27]

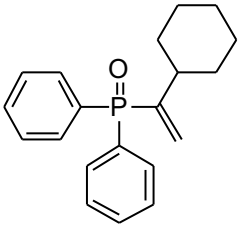
Diphenyl[1-[4-(trifluoromethyl)phenyl]ethenyl]phosphine oxide (3o)



3o

The title compound was prepared according to the General Procedure from phosphine oxide **1a** (0.1 mmol) and VBX **2i** (0.12 mmol) at room temperature within 1 h. After purification by column chromatography (petroleum ether:ethyl acetate 1:2), the product was obtained as white solid (25 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.58 (m, 4H), 7.56 – 7.49 (m, 2H), 7.44 (tdd, *J* = 8.2, 2.9, 1.3 Hz, 6H), 7.24 – 7.18 (m, 2H), 6.22 (dd, *J* = 40.0, 0.9 Hz, 1H), 5.70 (dd, *J* = 19.6, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5 (d, J_{P-C} = 92.6 Hz), 136.1 (d, J_{P-C} = 9.9 Hz), 134.5, 132.3, 132.2 (d, J_{P-C} = 2.8 Hz), 132.0 (d, J_{P-C} = 9.5 Hz), 131.3 (d, J_{P-C} = 103.9 Hz), 129.5 (d, J_{P-C} = 4.8 Hz), 128.8 (d, J_{P-C} = 1.6 Hz), 128.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.27 (ddd, *J* = 43.8, 20.1, 11.3 Hz). Obtained spectral data are in accordance with literature.[28]

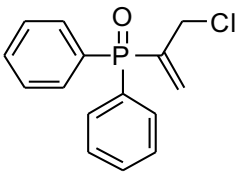
(1-Cyclohexylethenyl)diphenylphosphine oxide (3p)



3p

The title compound was prepared according to the General Procedure from phosphine oxide **1a** (0.1 mmol) and VBX **2j** (0.12 mmol) at room temperature within 1 h. After purification by column chromatography (petroleum ether:ethyl acetate 2:1), the product was obtained as colorless oil (9 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.62 (m, 4H), 7.59 – 7.39 (m, 6H), 5.96 (dt, *J* = 44.5, 0.8 Hz, 1H), 5.53 (dd, *J* = 21.8, 0.8 Hz, 1H), 2.56 – 2.27 (m, 1H), 1.78 (p, *J* = 4.5 Hz, 2H), 1.73 – 1.58 (m, 4H), 1.24 – 1.13 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8 (d, J_{P-C} = 90.5 Hz), 132.2 (d, J_{P-C} = 100.8 Hz), 132.1 (d, J_{P-C} = 9.8 Hz), 131.9 (d, J_{P-C} = 2.7 Hz), 128.5 (d, J_{P-C} = 11.9 Hz), 127.9 (d, J_{P-C} = 10.2 Hz), 33.8 (d, J_{P-C} = 4.1 Hz), 26.8, 26.1.^{31}P NMR (162 MHz, $CDCl_3$) δ 32.57 (ddd, *J* = 33.7, 22.1, 11.5 Hz). Obtained spectral data are in accordance with literature.[29]

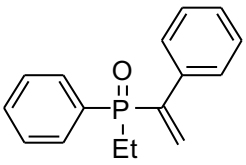
(3-Chloroprop-1-en-2-yl)diphenylphosphine oxide (3q)



3q

The title compound was prepared according to the General Procedure from phosphine oxide **1a** (0.1 mmol) and VBX **2k** (0.12 mmol) at –10 °C within 2 h. After purification by column chromatography (petroleum ether:ethyl acetate 2:1), the product was obtained as colorless oil (8 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.64 (m, 4H), 7.62 – 7.55 (m, 2H), 7.54 – 7.46 (m, 4H), 6.41 (dt, *J* = 38.5, 1.8 Hz, 1H), 5.82 (dd, *J* = 19.1, 1.4 Hz, 1H), 4.34 (dt, *J* = 6.8, 1.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1 (d, J_{P-C} = 92.7 Hz), 132.6 (d, J_{P-C} = 2.9 Hz), 132.3 (d, J_{P-C} = 8.2 Hz), 132.0 (d, J_{P-C} = 10.1 Hz), 130.6 (d, J_{P-C} = 104.3 Hz), 128.9 (d, J_{P-C} = 12.3 Hz), 43.4 (d, J_{P-C} = 19.0 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.19 – 28.46 (m), -138.49. HRMS m/z calcd for $C_{15}H_{14}ClNaOP^+$: 299.0363 [M+Na]$^+$; found: 299.0367.

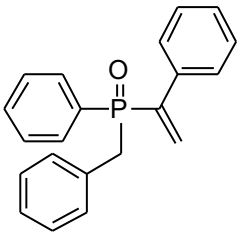
Ethylphenyl(1-phenylethenyl)phosphine oxide (3r)



3r

The title compound was prepared according to the General Procedure from phosphine oxide **1r** (0.5 mmol) and VBX **2a** (0.6 mmol) at 60 °C within 1 h. After purification by column chromatography (dichloromethane:methanol 19:1), the product was obtained a brownish liquid (96 mg, 62% yield). R_f = 0.32 (dichloromethane:methanol 19:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.39 (m, 2H), 7.29 – 7.12 (m, 5H), 6.12 (dd, *J* = 23.2, 1.4 Hz, 1H), 6.05 (dd, *J* = 41.3, 1.4 Hz, 1H), 2.13 – 1.94 (m, 2H), 1.12 (dt, *J* = 17.3, 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2 (d, J_{P-C} = 85.9 Hz), 138.1 (d, J_{P-C} = 10.4 Hz), 131.8 (d, J_{P-C} = 2.7 Hz), 131.6 (d, J_{P-C} = 97.0 Hz), 131.3 (d, J_{P-C} = 9.0 Hz), 130.6 (d, J_{P-C} = 7.3 Hz), 128.6 (d, J_{P-C} = 11.5 Hz), 128.5, 128.2 (d, J_{P-C} = 1.2 Hz), 128.1 (d, J_{P-C} = 4.1 Hz), 21.0 (d, J_{P-C} = 73.4 Hz), 5.5 (d, J_{P-C} = 5.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.0 – 34.2 (m). HRMS m/z calcd for $C_{16}H_{17}NaOP^+$: 279.0909 [M+Na]$^+$; found: 279.0912.

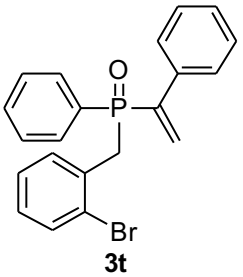
Benzyl(phenyl)(1-phenylethenyl)phosphine oxide (3s)



3s

The title compound was prepared according to the General Procedure from phosphine oxide **1s** (0.3 mmol) and VBX **2a** (0.3 mmol) at 60 °C within 2 h. After purification by column chromatography (petroleum ether:ethyl acetate 1:1), the product was obtained as colorless oil (69 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.55 (m, 2H), 7.53 – 7.44 (m, 1H), 7.44 – 7.35 (m, 2H), 7.30 (s, 5H), 7.21 – 7.14 (m, 3H), 7.06 (dt, *J* = 5.2, 2.3 Hz, 2H), 6.13 (s, 1H), 6.06 (dd, *J* = 18.4, 1.2 Hz, 1H), 3.60 – 3.23 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7 (d, J_{P-C} = 86.8 Hz), 138.0 (d, J_{P-C} = 10.5 Hz), 132.0 (d, J_{P-C} = 2.8 Hz), 131.6 (d, J_{P-C} = 9.0 Hz), 131.2 (dd, J_{P-C} = 7.7, 1.4 Hz), 130.3 (d, J_{P-C} = 5.4 Hz), 128.6, 128.5, 128.44, 128.42, 128.38, 128.35 (d, J_{P-C} = 1.4 Hz), 128.26, 128.24,126.9 (d, J_{P-C} = 2.9 Hz), 36.3 (d, J_{P-C} = 67.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.23 (m). HRMS m/z calcd for $C_{21}H_{19}NaOP^+$: 341.1066 [M+Na]$^+$; found: 341.1062.

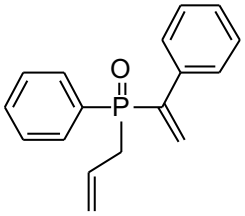
(2-Bromobenzyl)(phenyl)(1-phenylethenyl)phosphine oxide (3t)



3t

The title compound was prepared according to the General Procedure from 2-phenylphosphine oxide **1t** (0.3 mmol) and VBX **2a** (0.36 mmol) at 60 °C within 2 h. After purification by column chromatography (petroleum ether:ethyl acetate 8:2), the product was obtained as colorless oil (79 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.71 (m, 2H), 7.53 (tt, *J* = 8.5, 1.4 Hz, 2H), 7.45 – 7.38 (m, 5H), 7.31 – 7.25 (m, 4H), 7.17 (td, *J* = 7.7, 1.8 Hz, 1H), 6.33 (dd, *J* = 20.3, 1.5 Hz, 1H), 6.17 (dd, *J* = 41.4, 1.4 Hz, 1H), 5.21 (dd, *J* = 12.9, 7.0 Hz, 1H), 5.12 (dd, *J* = 12.9, 6.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1 (d, J_{P-C} = 124.6 Hz), 137.1 (d, J_{P-C} = 11.7 Hz),135.9 (d, J_{P-C} = 7.5 Hz),132.7, 132.5 (d, J_{P-C} = 2.8 Hz), 132.0 (d, J_{P-C} = 10.2 Hz), 131.9 (d, J_{P-C} = 8.6 Hz), 131.3 (d, J_{P-C} = 104.8 Hz), 129.7, 129.5, 128.7, 128.5 (d, J_{P-C} = 6.0 Hz), 128.3 (d, J_{P-C} = 1.5 Hz), 128.1 (d, J_{P-C} = 5.1 Hz), 127.6, 122.7, 65.9 (d, J_{P-C} = 5.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.07 (dd, *J* = 39.9, 19.3 Hz). HRMS m/z calcd for $C_{21}H_{18}NaOPBr^+$: 419.0171 [M+Na]$^+$; found: 419.0176.

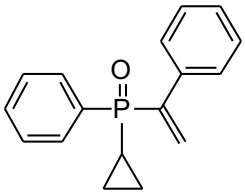
(Allyl)(phenyl)(1-phenylethenyl)phosphine oxide (3u)



3u

The title compound was prepared according to the General Procedure from phosphine oxide **1u** (0.3 mmol) and VBX **2a** (0.36 mmol) at 60 °C within 2 h. After purification by column chromatography (petroleum ether:ethyl acetate 1:2), the product was obtained as colorless oil (41 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (ddd, *J* = 11.4, 8.3, 1.4 Hz, 2H), 7.59 – 7.39 (m, 3H), 7.33 – 7.19 (m, 5H), 6.14 (d, *J* = 3.6 Hz, 1H), 6.07 (dd, *J* = 23.6, 1.3 Hz, 1H), 5.85 – 5.66 (m, 1H), 5.14 (ddd, *J* = 10.2, 3.6, 1.4 Hz, 1H), 5.05 (ddd, *J* = 17.0, 4.6, 1.5 Hz, 1H), 2.97 – 2.92 (m, 1H), 2.90 (dd, *J* = 7.4, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9 (d, J_{P-C} = 86.9 Hz), 137.9 (d, J_{P-C} = 10.3 Hz), 132.0 (d, J_{P-C} = 2.8 Hz), 131.5 (d, J_{P-C} = 9.0 Hz), 131.3 (d, J_{P-C} = 98.2 Hz),131.0 (d, J_{P-C} = 7.5 Hz), 128.6 (d, J_{P-C} = 3.6 Hz), 128.5, 128.3 (d, J_{P-C} = 1.5 Hz), 128.2 (d, J_{P-C} = 4.2 Hz), 127.0 (d, J_{P-C} = 9.0 Hz), 121.0 (d, J_{P-C} = 11.9 Hz), 34.5 (d, J_{P-C} = 69.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.91 – 29.41 (m). HRMS m/z calcd for $C_{17}H_{17}NaOP^+$: 291.0909 [M+Na]$^+$; found: 291.0914.

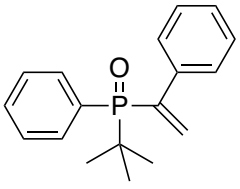
(Cyclopropyl)(phenyl)(1-phenylethenyl)phosphine oxide (3v)



3v

The title compound was prepared according to the General Procedure from phosphine oxide **1v** (0.3 mmol) and VBX **2a** (0.36 mmol) at 60 °C within 2 h. After purification by column chromatography (petroleum ether:ethyl acetate 1:2), the product was obtained as colorless oil (36 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.69 (m, 2H), 7.60 – 7.43 (m, 3H), 7.41 – 7.12 (m, 5H), 6.30 (dd, *J* = 18.6, 1.4 Hz, 1H), 6.15 (dd, *J* = 37.1, 1.5 Hz, 1H), 1.19 – 0.98 (m, 3H), 0.89 (dddd, *J* = 10.6, 5.8, 4.1, 2.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$ δ 145.4 (d, J_{P-C} = 91.7 Hz), 138.0 (d, J_{P-C} = 10.6 Hz), 133.0 (d, J_{P-C} = 102.6 Hz), 131.7 (d, J_{P-C} = 2.8 Hz), 131.1 (d, J_{P-C} = 9.4 Hz), 130.1 (d, J_{P-C} = 7.6 Hz), 128.6, 128.5, 128.4, 128.1 – 128.00 (m), 6.6, 5.6, 3.2 (t, J_{P-C} = 4.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.00 – 30.18 (m). HRMS m/z calcd for $C_{17}H_{17}NaOP^+$: 291.0909 [M+Na]$^+$; found: 291.0906.

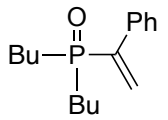
***tert*-Butyl(phenyl)(1-phenylvinyl)phosphine oxide (3w)**



3w

The title compound was prepared according to the General Procedure from phosphine oxide **1w** (0.14 mmol) and VBX **2a** (0.16 mmol) at 60 °C within 2 h. After purification by column chromatography (pentane:ethyl acetate 1:1), the product was obtained as colorless oil (19 mg, 48% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (ddd, *J* = 9.8, 8.3, 1.4 Hz, 2H), 7.58 – 7.39 (m, 6H), 7.34 – 7.27 (m, 2H), 6.09 (dd, *J* = 17.1, 1.4 Hz, 1H), 6.00 (dd, *J* = 36.5, 1.4 Hz, 1H), 1.08 (d, *J* = 14.9 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9 (d, *J* = 79.7 Hz), 139.9 (d, *J* = 9.3 Hz), 132.9 (d, *J* = 7.8 Hz), 132.4 (d, *J* = 7.8 Hz), 131.6 (d, *J* = 2.7 Hz), 129.6 (d, *J* = 89.8 Hz), 128.9 (d, *J* = 3.7 Hz), 128.3, 128.2, 128.09, 128.06, 34.2 (d, *J* = 70.1 Hz), 25.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.6 (m). HRMS m/z calcd for $C_{18}H_{21}NaOP^+$: 307.1222 [M+Na]$^+$; found: 307.1229.

Di(1-butyl)(1-phenylvinyl)phosphine oxide (**3x)**

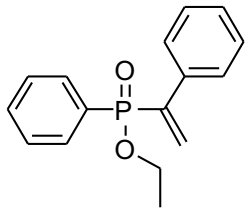


3x

The title compound was prepared according to the General Procedure from phosphine oxide **1x** (0.1 mmol) and VBX **2a** (0.11 mmol) at 60 °C within 24 h. After reaction mixture was filtered through silica pad, and volatiles were evaporated *in vacuo*. The product yield was determined to 30% via ^{1}H NMR with the internal standard 1,3,5-trimethoxybenzene.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 2H), 7.40 – 7.25 (m, 3H), 6.27 (dd, J = 17.1, 1.7 Hz, 1H), 6.04 (dd, J = 33.3, 1.7 Hz, 1H), 1.80-1.40 (m, 12H), 0.86 (t, J = 7.3 Hz, 6H).

This result is added to show the limitations of the method, and the product was hence never isolated and fully characterized.

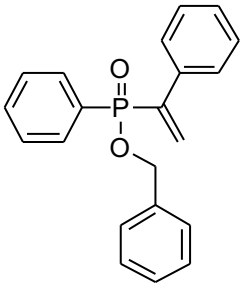
Ethyl phenyl(1-phenylethenyl)phosphinate (6a)



6a

The title compound was prepared according to the General Procedure from phosphinate **5a** (0.5 mmol) and VBX **2a** (0.6 mmol) at 60 °C within 20 h. After purification by column chromatography (petroleum ether:ethyl acetate 1:2), the product was obtained a yellow liquid (107 mg, 79% yield). R_f = 0.45 (petroleum ether:ethyl acetate 1:4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 2H), 7.55 – 7.48 (m, 1H), 7.46 – 7.38 (m, 4H), 7.33 – 7.27 (m, 3H), 6.25 (dd, *J* = 50.8, 1.6 Hz, 1H), 6.18 (dd, *J* = 71.5, 1.6 Hz, 1H), 4.22 – 4.04 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3 (d, *J* = 124.7 Hz), 137.3 (d, *J* = 11.7 Hz), 132.3 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 10.0 Hz), 131.5 (d, *J* = 8.3 Hz), 130.7 (d, *J* = 135.1 Hz), 128.5, 128.4, 128.2 (d, *J* = 1.2 Hz), 128.0 (d, *J* = 4.9 Hz), 61.3 (d, *J* = 6.0 Hz), 16.6 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.0 – 30.3 (m). Obtained spectral data are in accordance with literature.[10]

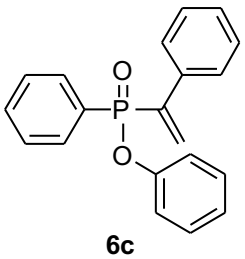
Benzyl phenyl(1-phenylethenyl)phosphinate (6b)



6b

The title compound was prepared according to the General Procedure from phosphinate **5b** (0.3 mmol) and VBX **2a** (0.36 mmol) at 60 °C within 20 h. After purification by column chromatography (petroleum ether:ethyl acetate 7:3), the product was obtained a colorless oil (51 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.55 – 7.48 (m, 1H), 7.44 – 7.39 (m, 4H), 7.36 – 7.32 (m, 4H), 7.31 – 7.25 (m, 4H), 6.33 (dd, *J* = 20.1, 1.5 Hz, 1H), 6.17 (dd, *J* = 41.1, 1.5 Hz, 1H), 5.14 (dd, *J* = 11.8, 6.8 Hz, 1H), 5.05 (dd, *J* = 11.8, 6.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1 (d, J_{P-C} = 124.4 Hz), 137.1 (d, J_{P-C} = 10.1 Hz), 136.5 (d, J_{P-C} = 7.7 Hz), 132.5 (d, J_{P-C} = 2.9 Hz), 132.1 (d, J_{P-C} = 10.1 Hz), 131.9 (d, J_{P-C} = 8.3 Hz), 130.4 (d, J_{P-C} = 134.8 Hz), 128.6, 128.5 (d, J_{P-C} = 3.2 Hz), 128.3 (d, J_{P-C} = 1.4 Hz), 128.1 (d, J_{P-C} = 5.0 Hz), 128.0, 66.5 (d, J_{P-C} = 5.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.73 (dt, *J* = 19.7, 5.0 Hz). HRMS m/z calcd for $C_{21}H_{19}NaO_2P^+$: 357.1015 $[M+Na]^+$; found: 357.1017.

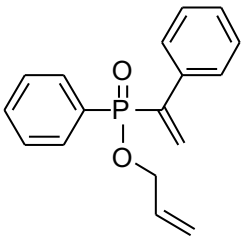
Phenyl phenyl(1-phenylethenyl)phosphinate (6c)



6c

The title compound was prepared according to the General Procedure from phosphinate **5c** (0.3 mmol) and VBX **2a** (0.36 mmol) at 60 °C within 20 h. After purification by column chromatography (petroleum ether:ethyl acetate 1:2), the product was obtained a colorless oil (28 mg, 29% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.74 (m, 2H), 7.57 – 7.48 (m, 1H), 7.46 – 7.34 (m, 4H), 7.33 – 7.18 (m, 5H), 7.14 (dq, *J* = 7.8, 1.2 Hz, 2H), 7.08 (ddt, *J* = 8.1, 5.8, 1.0 Hz, 1H), 6.38 (dd, *J* = 20.6, 1.3 Hz, 1H), 6.19 (dd, *J* = 42.5, 1.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0 (d, J_{P-C} = 8.3 Hz), 143.1 (d, J_{P-C} = 125.4 Hz), 137.0 (d, J_{P-C} = 11.6 Hz), 132.7 (d, J_{P-C} = 2.7 Hz), 132.6, 132.2 (d, J_{P-C} = 10.2 Hz), 130.0 (d, J_{P-C} = 134.3 Hz), 129.7, 128.7, 128.5, 128.4 (d, J_{P-C} = 1.4 Hz), 128.2 (d, J_{P-C} = 5.0 Hz), 124.7, 120.8 (d, J_{P-C} = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.94 – 28.83 (m). HRMS m/z calcd for $C_{20}H_{17}NaO_2P^+$: $[M+Na]^+$ 343.0858; found: 343.0858.

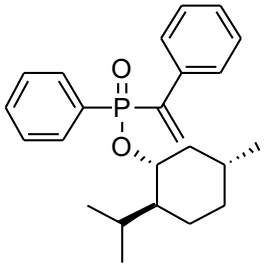
Allyl phenyl (1-phenylethenyl)phosphinate (6d)



6d

The title compound was prepared according to the General Procedure from allyl phosphinate **5d** (0.3 mmol) and VBX **2a** (0.36 mmol) at 60 °C within 20 h. After purification by column chromatography (petroleum ether:ethyl acetate 7:3), the product was obtained a colorless oil (48 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.69 (m, 2H), 7.56 – 7.48 (m, 1H), 7.47 – 7.36 (m, 4H), 7.30 (ddd, *J* = 6.1, 3.2, 1.5 Hz, 3H), 6.31 (dd, *J* = 20.1, 1.5 Hz, 1H), 6.15 (dd, *J* = 41.0, 1.5 Hz, 1H), 6.04 – 5.87 (m, 1H), 5.36 – 5.29 (m, 1H), 5.22 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.69 – 4.41 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0 (d, *J* = 124.7 Hz), 137.1 (d, *J* = 11.6 Hz), 133.0 (d, *J* = 7.1 Hz), 132.5 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 10.2 Hz), 131.9 (d, *J* = 8.5 Hz), 130.2 (d, *J* = 135.1 Hz),128.6, 128.5, 128.5, 128.3 (d, *J* = 1.1 Hz), 128.1 (d, *J* = 4.9 Hz), 118.0, 65.6 (d, *J* = 5.7 Hz).^{31}P NMR (162 MHz, $CDCl_3$) δ 32.81 – 30.30 (m). HRMS m/z calcd for $C_{17}H_{17}NaOP^+$: 307.0858 [M+Na]$^+$; found: 307.0855.

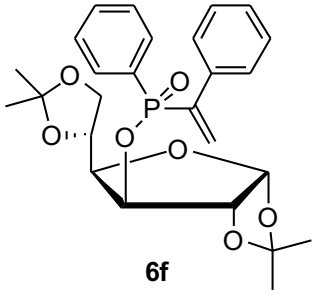
(1*R*,2*S*,5*R*)-5-Methyl-2-(propan-2-yl)cyclohexyl phenyl(1-phenylethenyl)phosphinate (6e)



6e

The title compound was prepared according to the General Procedure from phosphinate **5e** (0.3 mmol) and VBX **2a** (0.36 mmol) at 60 °C within 20 h. After purification by column chromatography (petroleum ether:ethyl acetate 7:3), the product was obtained a colorless oil as a mixture of both diastereoisomers (78 mg, 68% yield, dr: 1: 1.84).
^{1}H NMR (400 MHz, $CDCl_3$) *Major diastereomer* δ 7.81 – 7.76 (m, 2H), 7.52 – 7.36 (m, 5H), 7.29 – 7.25 (m, 3H), 6.12 (m, 1H), 6.04 (dd, *J* = 28.8, 1.6 Hz, 1H), 4.37 (tdd, *J* = 10.7, 7.5, 4.4 Hz, 1H), 1.96 (ddd, *J* = 14.3, 7.2, 2.8 Hz, 2H), 1.90 – 1.81 (m, 1H), 1.68 – 1.59 (m, 2H), 1.45 – 1.27 (m, 2H), 1.07 (td, *J* = 12.1, 10.9 Hz, 1H), 1.02 – 0.91 (m, 1H), 0.82 – 0.74 (m, 6H), 0.71 (d, *J* = 6.9 Hz, 3H). *Minor diastereomer* δ 7.74 – 7.10 (m, 2H), 7.52 – 7.36 (m, 5H), 7.29 – 7.25 (m, 3H), 6.34 (dd, *J* = 19.5, 1.7 Hz, 1H), 6.13 (dd, *J* = 39.9, 1.7 Hz, 1H), 4.25 (tdd, *J* = 10.7, 7.4, 4.4 Hz, 1H), 2.35 – 2.26 (m, 1H), 1.86 (m, 2H), 1.68 – 1.59 (m, 2H), 1.45 – 1.27 (m, 2H), 1.26 – 1.16 (m, 1H), 1.02 – 0.91 (m, 1H), 0.90 – 0.83 (m, 6H), 0.47 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) *Both diastereomers* δ 144.4 (d, J_{P-C} = 127.1 Hz), 144.3 (d, J_{P-C} = 125.4 Hz), 137.6 (d, J_{P-C} = 1.6 Hz), 137.5 (d, J_{P-C} = 2.6 Hz), 133.3, 131.8, 130.9 (d, *J* = 7.3 Hz), 130.5 (d, J_{P-C} *J* = 9.3 Hz), 128.4 (d, J_{P-C} = 2.9 Hz), 128.3 (d, J_{P-C} = 2.9 Hz), 128.2, 128.2, 128.2, 128.1, 128.1 – 128.1 (m), 128.1 – 128.0 (m), 49.0 (dd, J_{P-C} = 6.3, 2.2 Hz), 43.5 (d, J_{P-C} = 13.6 Hz), 34.2, 31.7 (d, J_{P-C} = 9.0 Hz), 25.5 (d, J_{P-C} = 13.6 Hz), 22.8 (d, J_{P-C} = 3.0 Hz), 22.1 (d, J_{P-C} = 1.7 Hz), 21.2, 15.6, 15.3. ^{31}P NMR (162 MHz, $CDCl_3$) *Both diastereomers* δ 29.1, 28.3. Obtained spectral data are in accordance with literature.[30]

1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose phenyl(1-phenylethenyl)phosphinate (6f)



6f

The title compound was prepared according to the General Procedure from phosphinate **5f** (0.3 mmol) and VBX **2a** (0.36 mmol) at 60 °C within 20 h. After purification by column chromatography (petroleum ether:ethyl acetate 7:3), the product was obtained a colorless oil as mixture of both diastereoisomers (99 mg, 68% yield, dr: 1: 1.6).
Analytical data for the diastereomeric mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (ddd, *J* = 12.3, 8.3, 1.4 Hz, 2H), 7.76 – 7.67 (m, 3.2H), 7.57 – 7.49 (m, 2.6H), 7.42 (ddd, *J* = 8.2, 6.7, 3.7 Hz, 5.2H), 7.39 – 7.32 (m, 5.2H), 7.31 – 7.24 (m, 7.8H), 6.42 (dd, *J* = 20.1, 1.3 Hz, 1.6H), 6.22 (dd, *J* = 42.5, 1.3 Hz, 1.6H), 6.18 (dd, *J* = 20.7, 1.4 Hz, 1H), 6.07 (dd, *J* = 42.7, 1.4 Hz, 1H), 5.94 (d, *J* = 3.6 Hz, 1H), 5.85 (d, *J* = 3.5 Hz, 1.6H), 4.97 (d, *J* = 3.5 Hz, 1H), 4.94 (d, *J* = 3.6 Hz, 1.6H), 4.90 (dd, *J* = 6.0, 2.7 Hz, 1.6H), 4.39 – 4.31 (m, 1.6H), 4.23 –3.97 (m, 9.8H), 1.50 (s, 3H), 1.47 (s, 4.8H), 1.44 (s, 3H), 1.41 (s, 3H), 1.36 (s, 3H), 1.32 (s, 4.8H), 1.31 (s, 4.8H), 1.24 (s, 4.8H). ^{3}C NMR (101 MHz, $CDCl_3$) δ 143.7 (d, J_{P-C} = 128.9 Hz), 142.3 (d, J_{P-C} = 120.5 Hz), 137.0 (dd, J_{P-C} = 11.6, 5.0 Hz), 132.8 (d, J_{P-C} = 2.9 Hz), 132.7 (d, J_{P-C} = 2.9 Hz), 131.6 (dd, J_{P-C} = 9.7, 5.3 Hz), 128.7, 128.6, 128.5, 128.4, 128.4 (d, J_{P-C} = 4.9 Hz), 128.3 (d, J_{P-C} = 4.9 Hz), 128.1 (d, J_{P-C} = 5.0 Hz), 112.3 (d, J_{P-C} = 6.5 Hz), 111.9, 109.7, 109.3 (d, J_{P-C} = 1.6 Hz), 105.3, 105.0, 85.2, 83.6 (d, J_{P-C} = 15.3 Hz), 81.1 (d, J_{P-C} = 8.2 Hz), 80.9 (d, J_{P-C} = 7.7 Hz), 78.9 (d, J_{P-C} = 6.6 Hz), 78.4 (d, J_{P-C} = 6.3 Hz), 75.2, 73.5, 72.1, 67.7, 67.1, 27.0, 26.9, 26.8, 26.4, 26.3, 25.4, 25.3, 25.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.1, 32.3. HRMS m/z calcd for $C_{26}H_{31}NaO_7P^+$: 509.1700 [M+Na]$^+$; found: 509.1704.

We have not separated the two diastereomers, but the ^{1}H NMR data should be:

Major diastereomer: 7.76 – 7.67 (m, 2H), 7.57 – 7.49 (m, 1H), 7.42 (ddd, *J* = 8.2, 6.7, 3.7 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.31 – 7.24 (m, 3H), 6.42 (dd, *J* = 20.1, 1.3 Hz, 1H), 6.22 (dd, *J* = 42.5, 1.3 Hz, 1H), 5.85 (d, *J* = 3.5 Hz, 1H), 4.94 (d, *J* = 3.6 Hz, 1H), 4.39 – 4.31 (m, 1H) 4.23 –3.97 (m, 4H), 1.47 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H), 1.24 (s, 3H).
Minor diastereomer: 7.84 (ddd, *J* = 12.3, 8.3, 1.4 Hz, 2H), 7.57 – 7.49 (m, 1H), 7.42 (ddd, *J* = 8.2, 6.7, 3.7 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.31 – 7.24 (m, 3H), 6.18 (dd, *J* = 20.7, 1.4 Hz, 1H), 6.07 (dd, *J* = 42.7, 1.4 Hz, 1H), 5.94 (d, *J* = 3.6 Hz, 1H), 4.97 (d, *J* = 3.5 Hz, 1H), 4.23 –3.97 (m, 5H), 1.50 (s, 3H), 1.44 (s, 3H), 1.41 (s, 3H), 1.36 (s, 3H).

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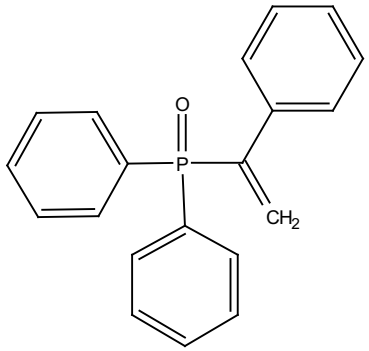
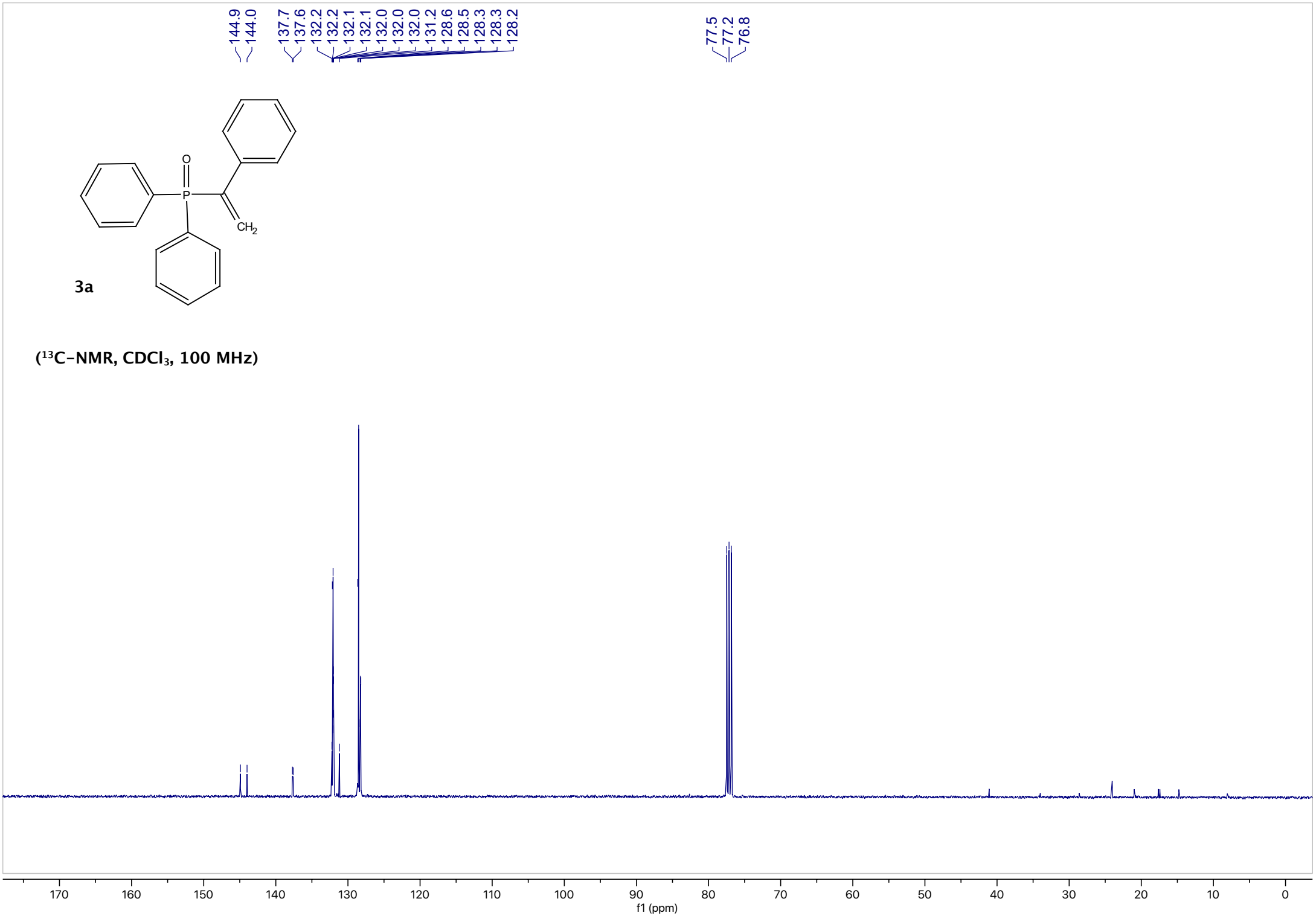
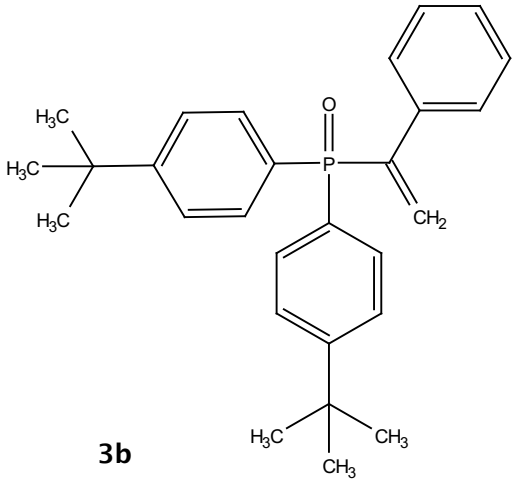
7 NMR Spectra



3a

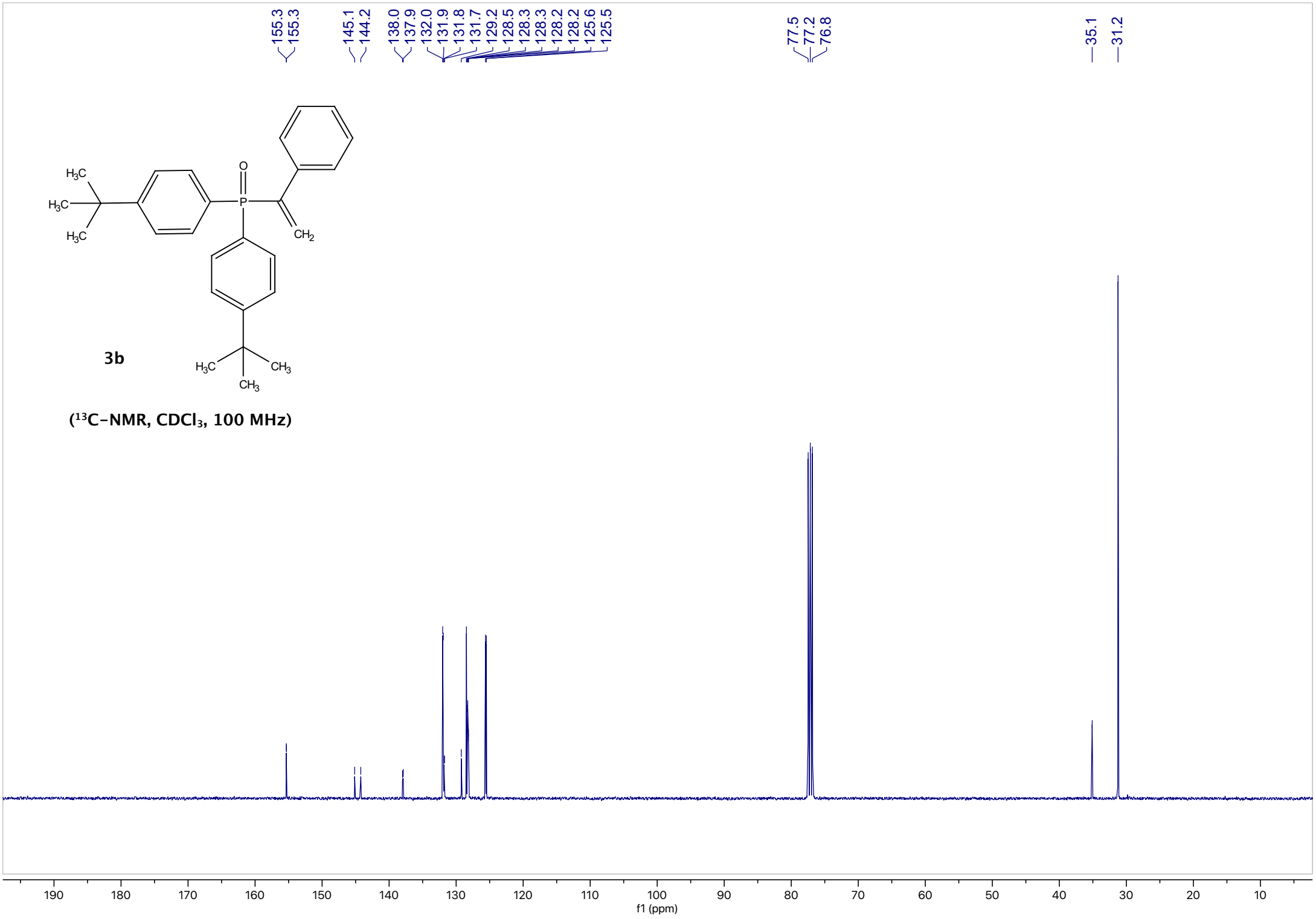
(^{1}H–NMR, $CDCl_3$, 400 MHz)


144.9
144.0
137.7
137.6
132.2
132.2
132.1
132.1
132.0
132.0
132.0
131.2
128.6
128.5
128.3
128.3
128.2
77.5
77.2
76.8
O
P
CH2
3a
(13C-NMR, CDCl3, 100 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

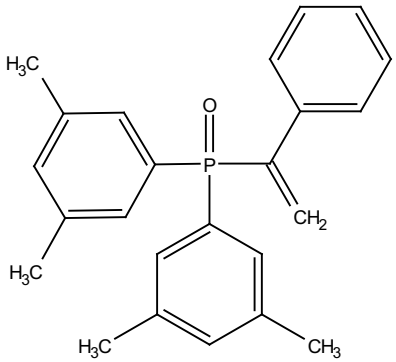


3b

(^{1}H–NMR, $CDCl_3$, 400 MHz)

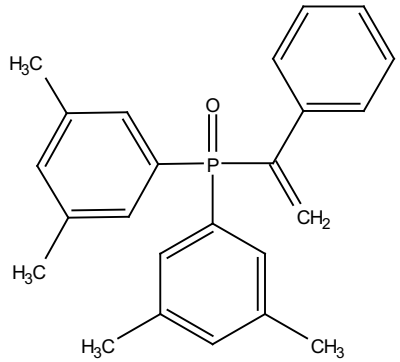


(^{13}C–NMR, $CDCl_3$, 100 MHz)



3c

(^{1}H–NMR, $CDCl_3$, 400 MHz)

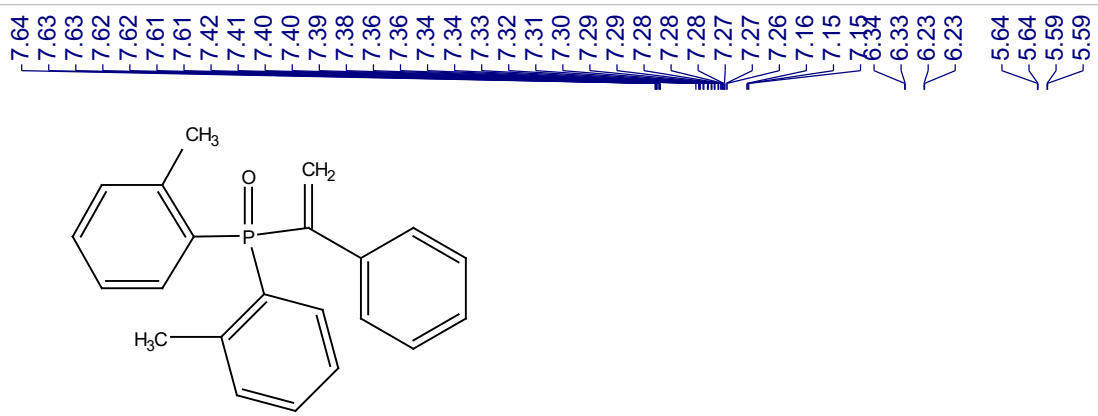


3c

(^{13}C–NMR, $CDCl_3$, 100 MHz)

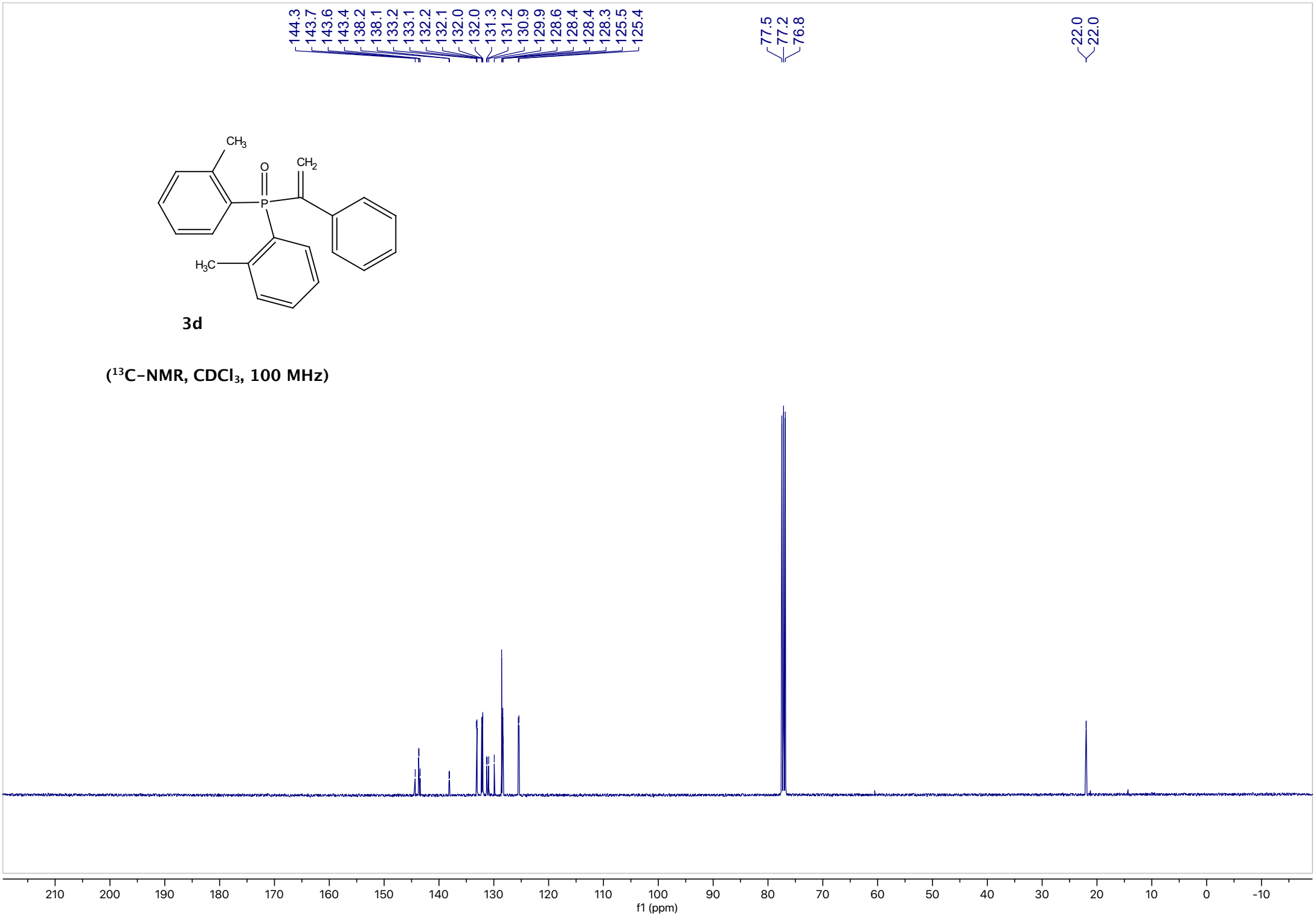
145.1
144.2
138.2
138.1
138.0
137.9
133.7
133.7
132.0
131.8
131.7
131.0
129.7
129.6
128.4
128.3
128.3
128.1
77.5
77.2
76.8
21.4

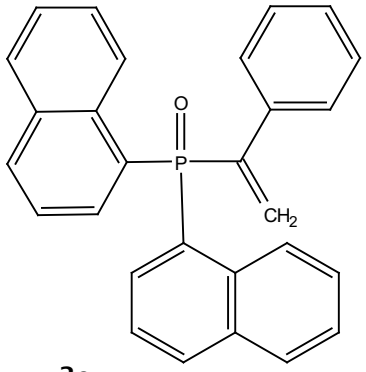
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3d

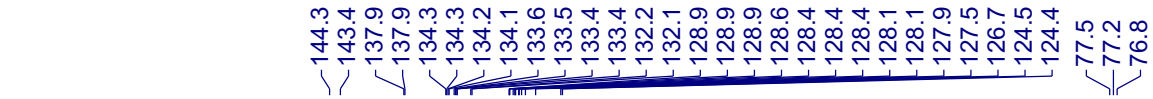
(^{1}H–NMR, $CDCl_3$, 400 MHz)

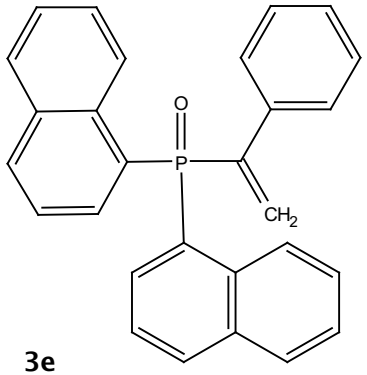

144.3
143.7
143.6
143.4
138.2
138.1
133.2
133.1
132.2
132.1
132.0
132.0
131.3
131.2
130.9
129.9
128.6
128.4
128.4
128.3
125.5
125.4
77.5
77.2
76.8
22.0
22.0
CH3
O
CH2
P
H3C
3d
(13C-NMR, CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3e

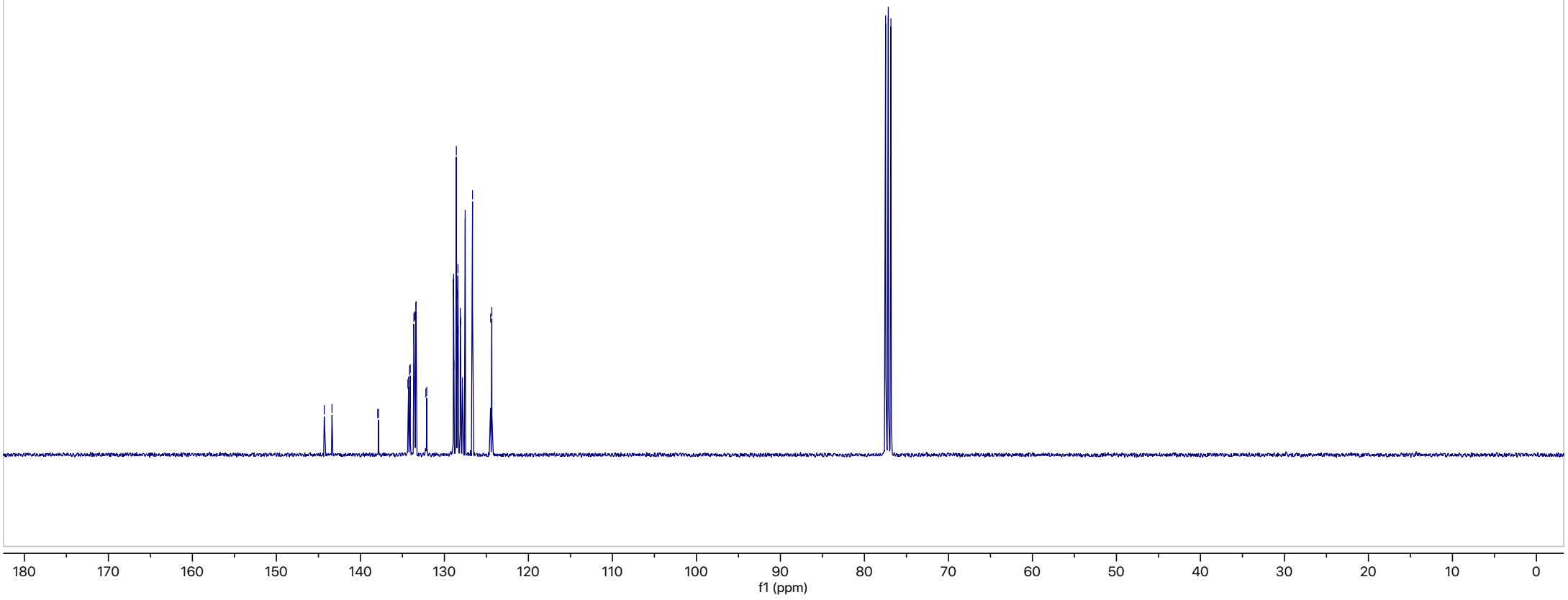
(^{1}H–NMR, $CDCl_3$, 400 MHz)

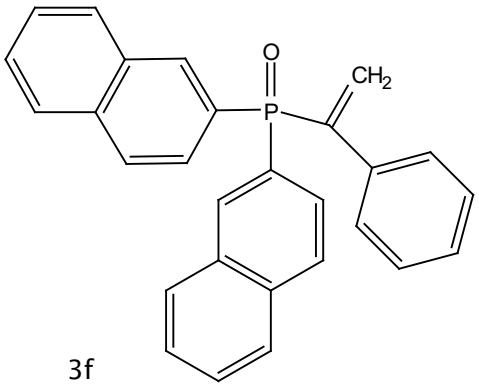




3e

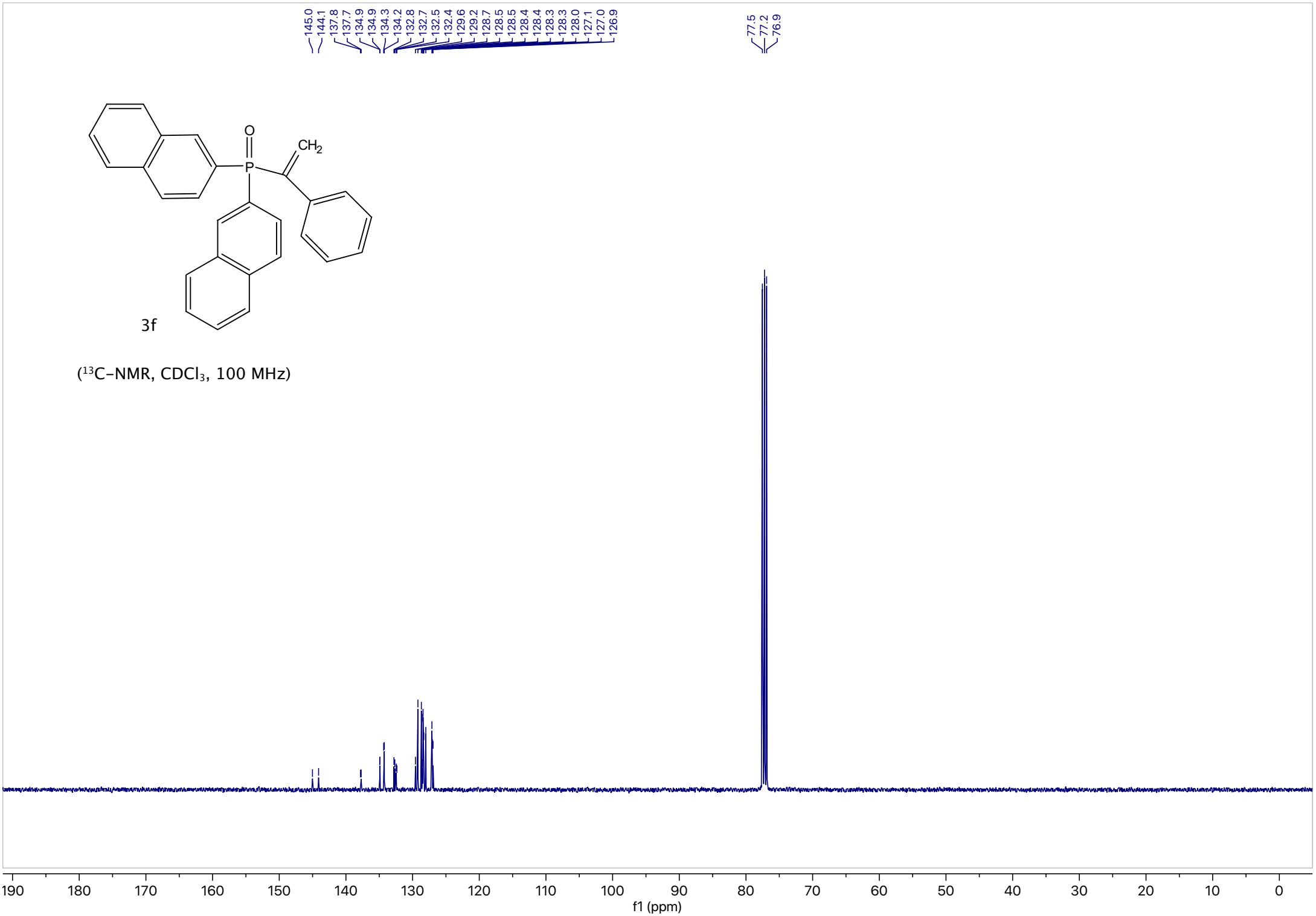
(^{13}C–NMR, $CDCl_3$, 100 MHz)

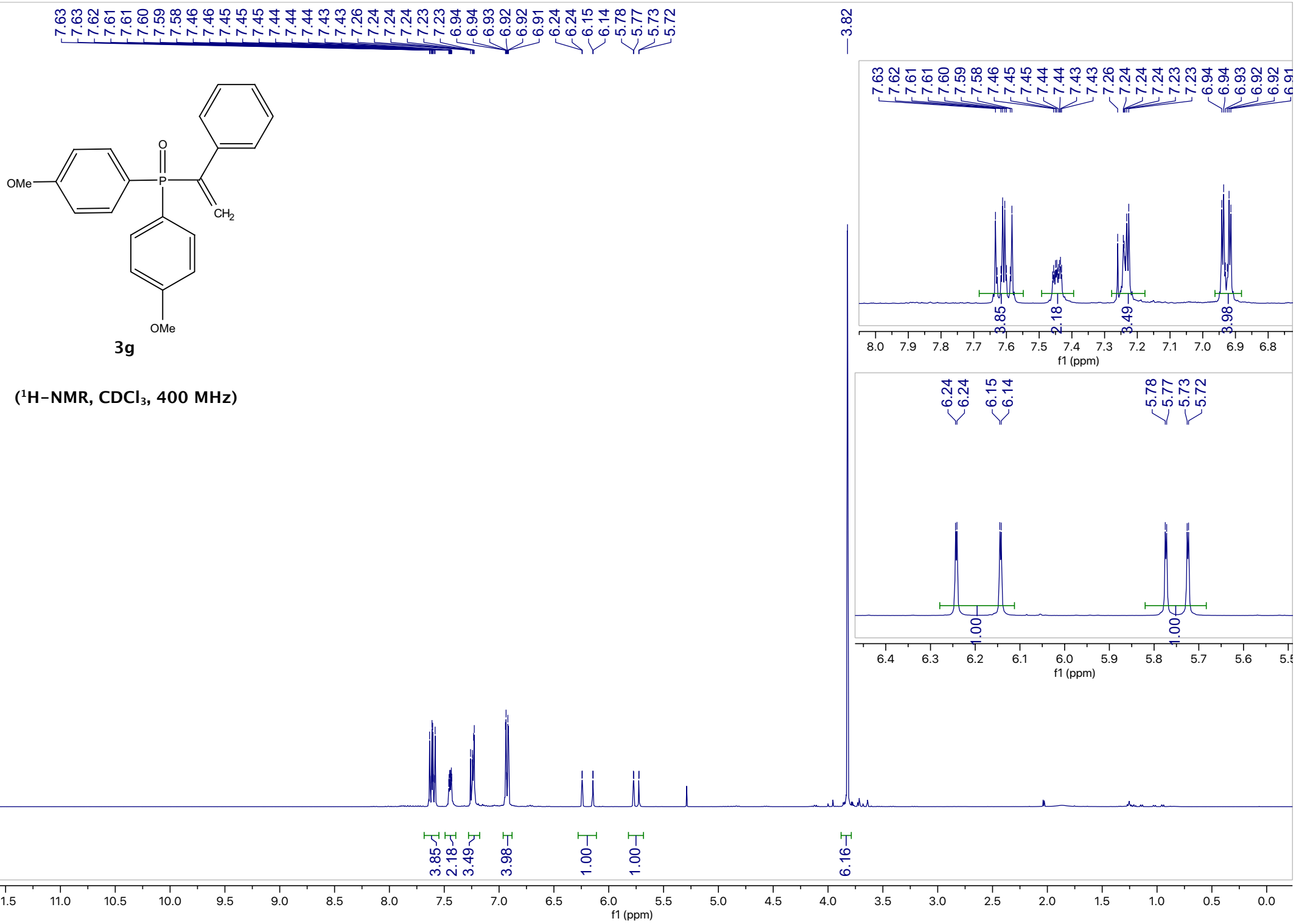


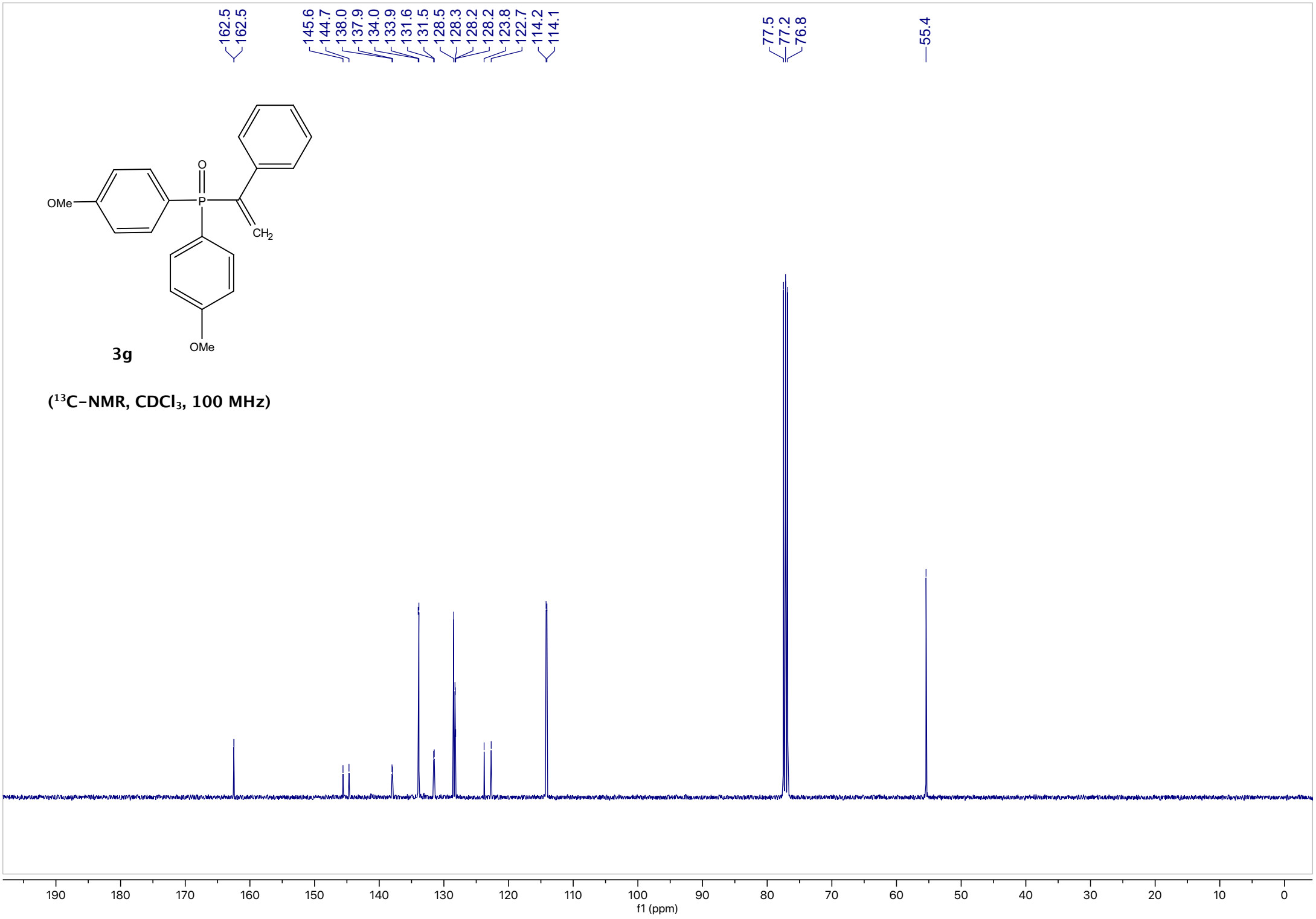


3f

(1H–NMR, $CDCl_3$, 400 MHz)

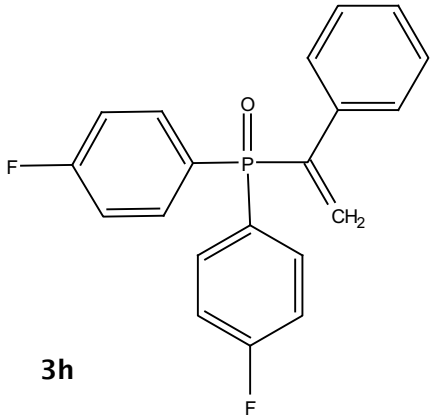

145.0
144.1
137.8
137.7
134.9
134.9
134.3
134.2
132.8
132.7
132.5
132.4
129.6
129.2
128.7
128.5
128.5
128.4
128.4
128.3
128.3
128.0
127.1
127.0
126.9
77.5
77.2
76.9
O
P
CH2
3f
(13C-NMR, CDCl3, 100 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.63 7.63 7.62 7.61 7.61 7.60 7.59 7.58 7.46 7.45 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.26 7.24 7.24 7.24 7.23 7.23 6.94 6.94 6.93 6.92 6.92 6.91 6.24 6.24 6.15 6.14 5.78 5.77 5.73 5.72
3.82
OMe
O
P
CH2
OMe
3g
(1H–NMR, CDCl3, 400 MHz)
3.85 2.18 3.49 3.98
f1 (ppm)
6.24 6.24 6.15 6.14 5.78 5.77 5.73 5.72
1.00 1.00
f1 (ppm)
3.85 2.18 3.49 3.98 1.00 1.00 6.16
f1 (ppm)



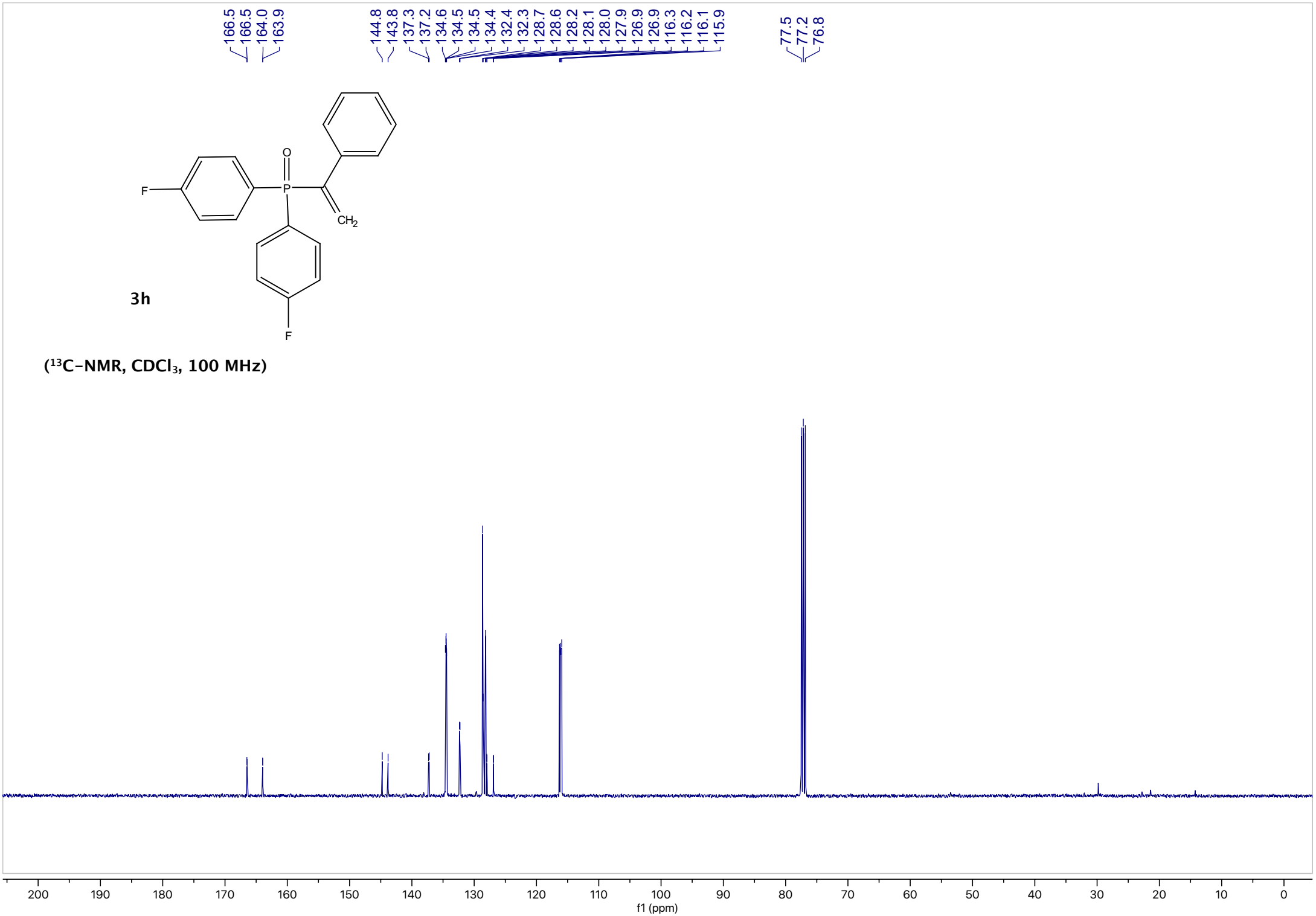
3g

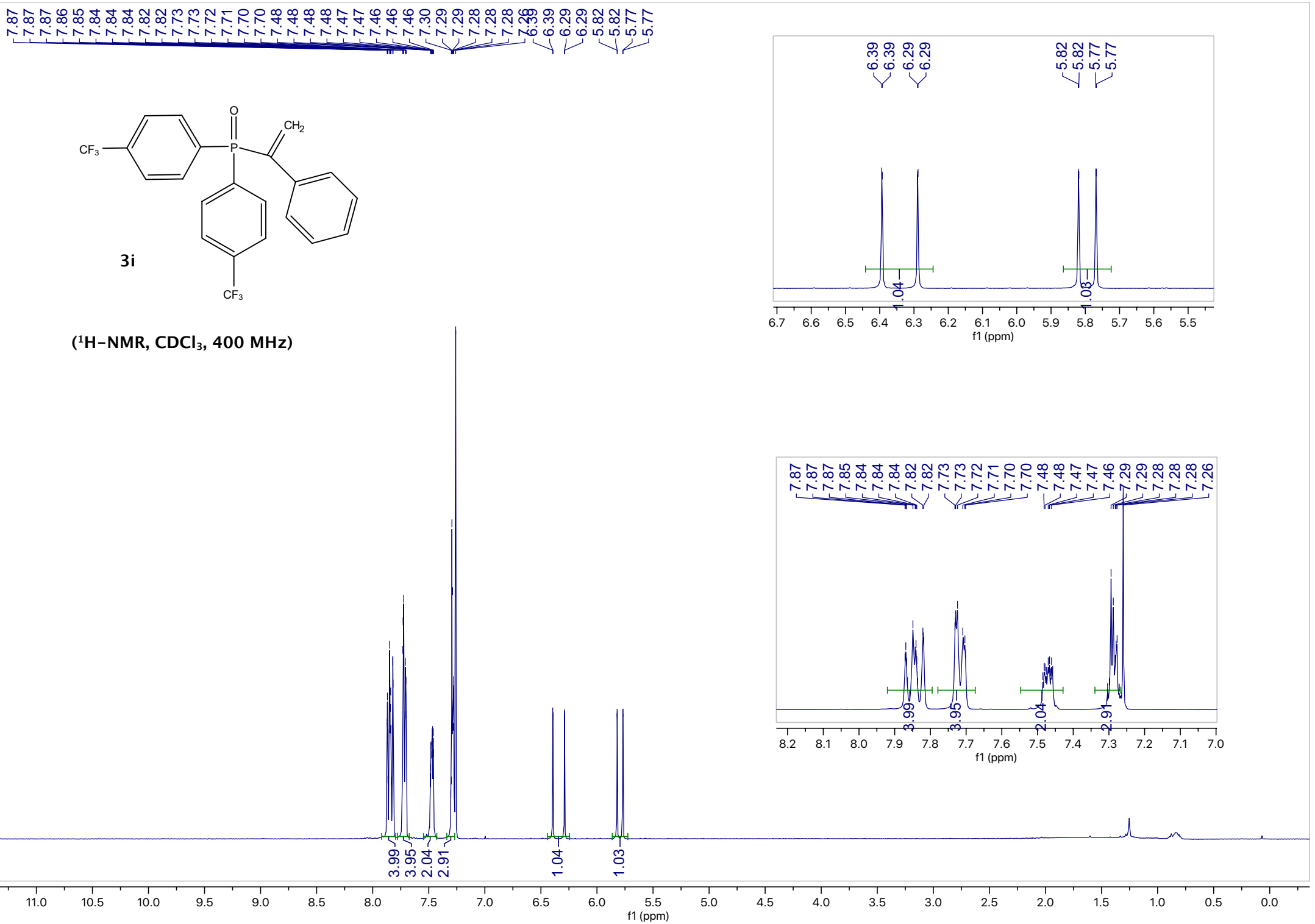
(^{13}C–NMR, $CDCl_3$, 100 MHz)

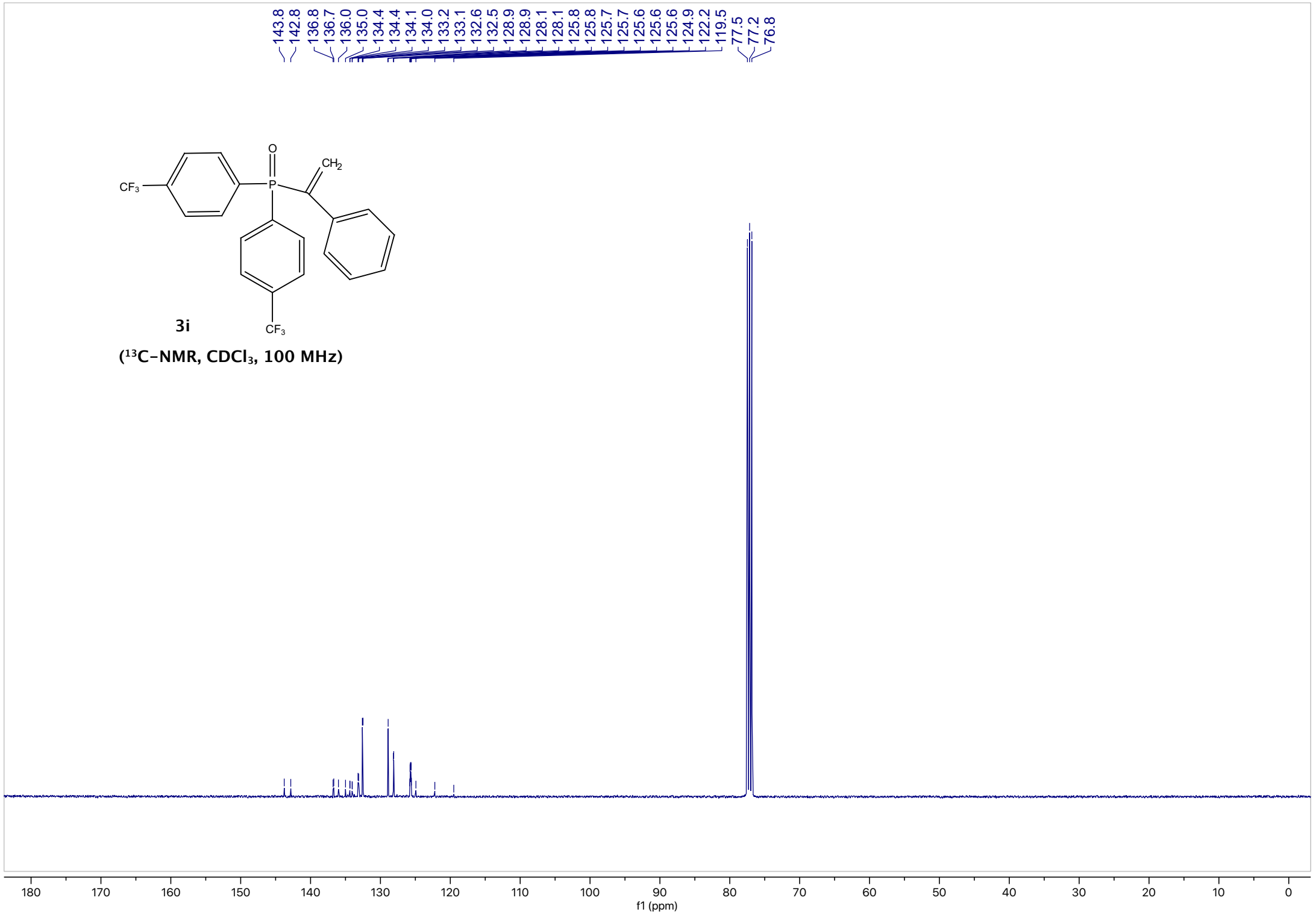


3h

(^{1}H–NMR, $CDCl_3$, 400 MHz)

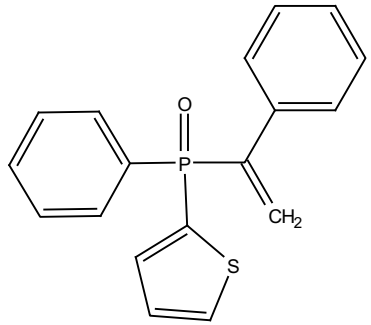

166.5
166.5
164.0
163.9
144.8
143.8
137.3
137.2
134.6
134.5
134.4
132.4
132.3
128.7
128.6
128.2
128.1
128.0
127.9
126.9
126.9
116.3
116.2
116.1
115.9
77.5
77.2
76.8
O
P
F
CH2
F
3h
(13C-NMR, CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.87 7.87 7.87 7.86 7.85 7.84 7.84 7.84 7.82 7.82 7.73 7.73 7.72 7.71 7.70 7.70 7.48 7.48 7.48 7.47 7.47 7.46 7.46 7.46 7.30 7.29 7.29 7.28 7.28 7.28 7.26 6.39 6.39 6.29 6.29 5.82 5.82 5.77 5.77
O
CH2
CF3
P
CF3
3i
(1H–NMR, CDCl3, 400 MHz)
6.39 6.39 6.29 6.29
5.82 5.82 5.77 5.77
1.04
1.08
6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5
f1 (ppm)
7.87 7.87 7.87 7.85 7.84 7.84 7.84 7.82 7.82 7.73 7.73 7.72 7.71 7.70 7.70 7.48 7.48 7.47 7.47 7.46 7.29 7.29 7.28 7.28 7.28 7.26
3.99
3.95
2.04
2.91
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
3.99
3.95
2.04
2.91
1.04
1.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



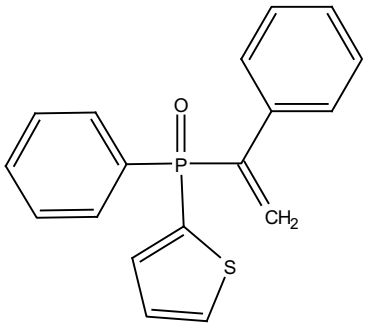
3i

(^{13}C–NMR, $CDCl_3$, 100 MHz)



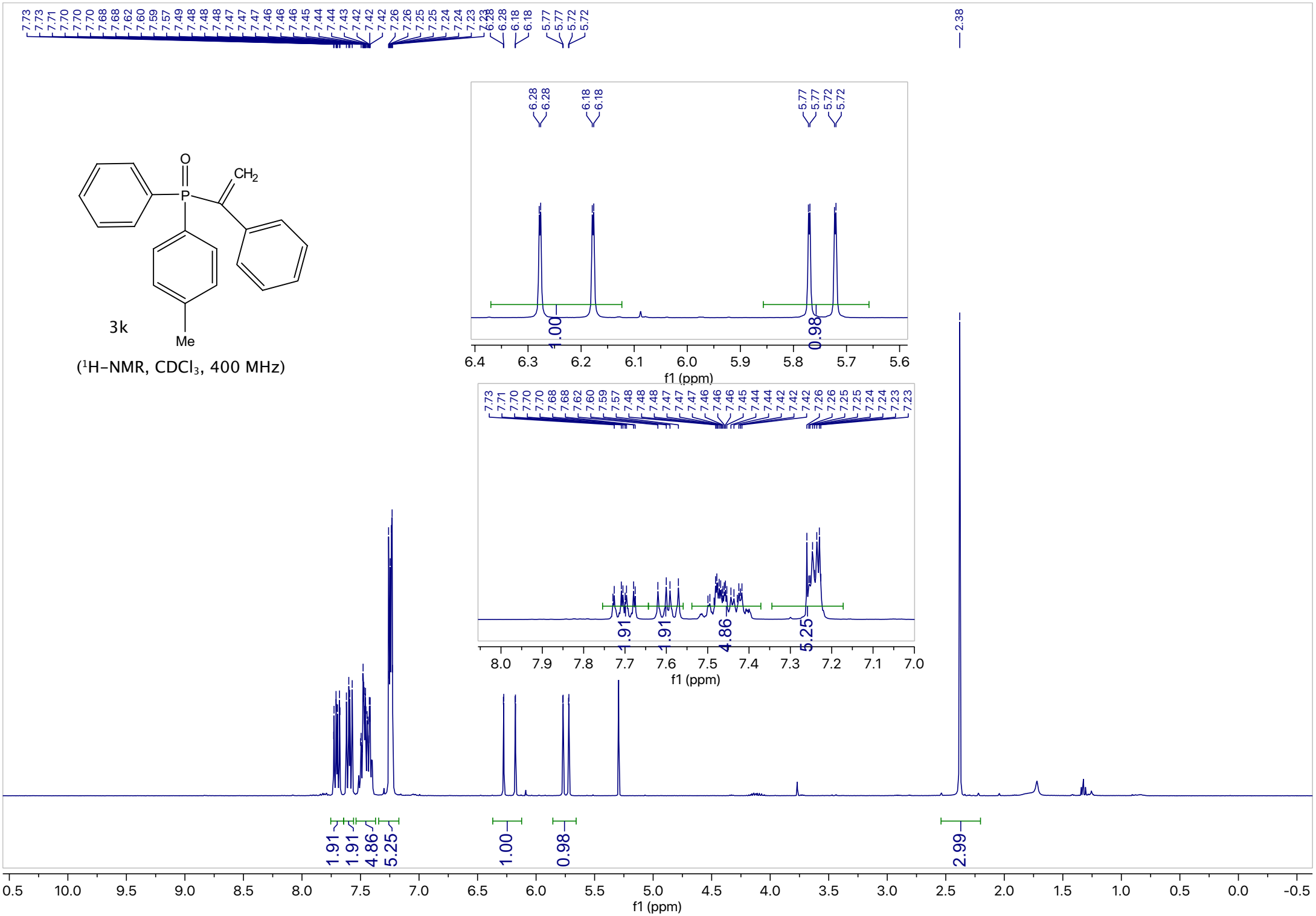
3j

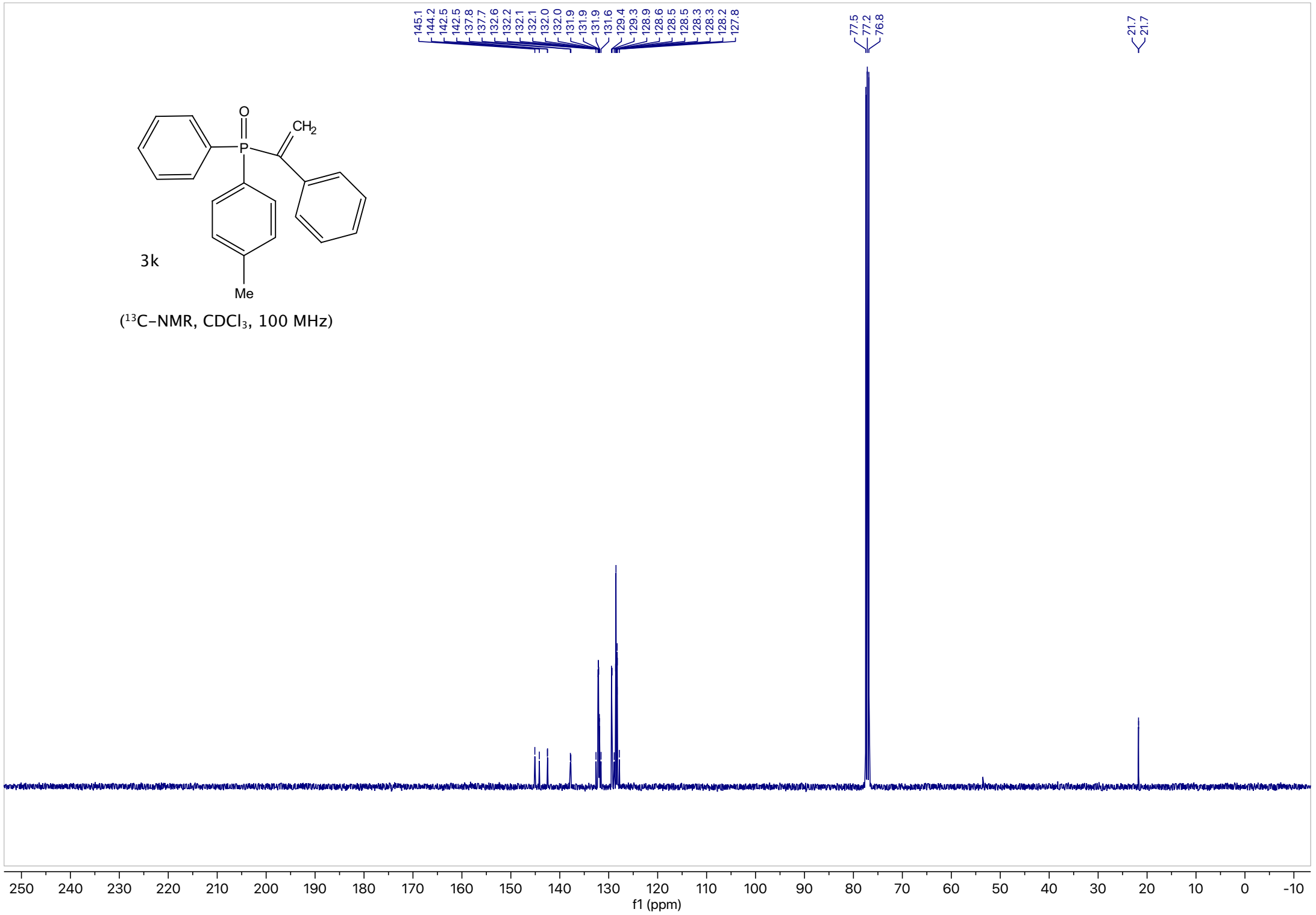
(^{1}H–NMR, $CDCl_3$, 400 MHz)

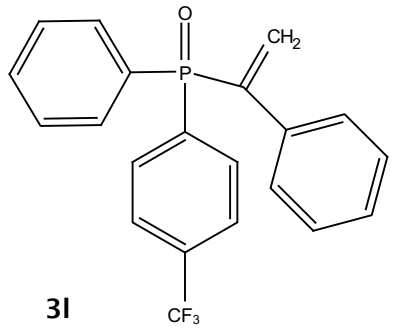


3j

(^{13}C–NMR, $CDCl_3$, 100 MHz)

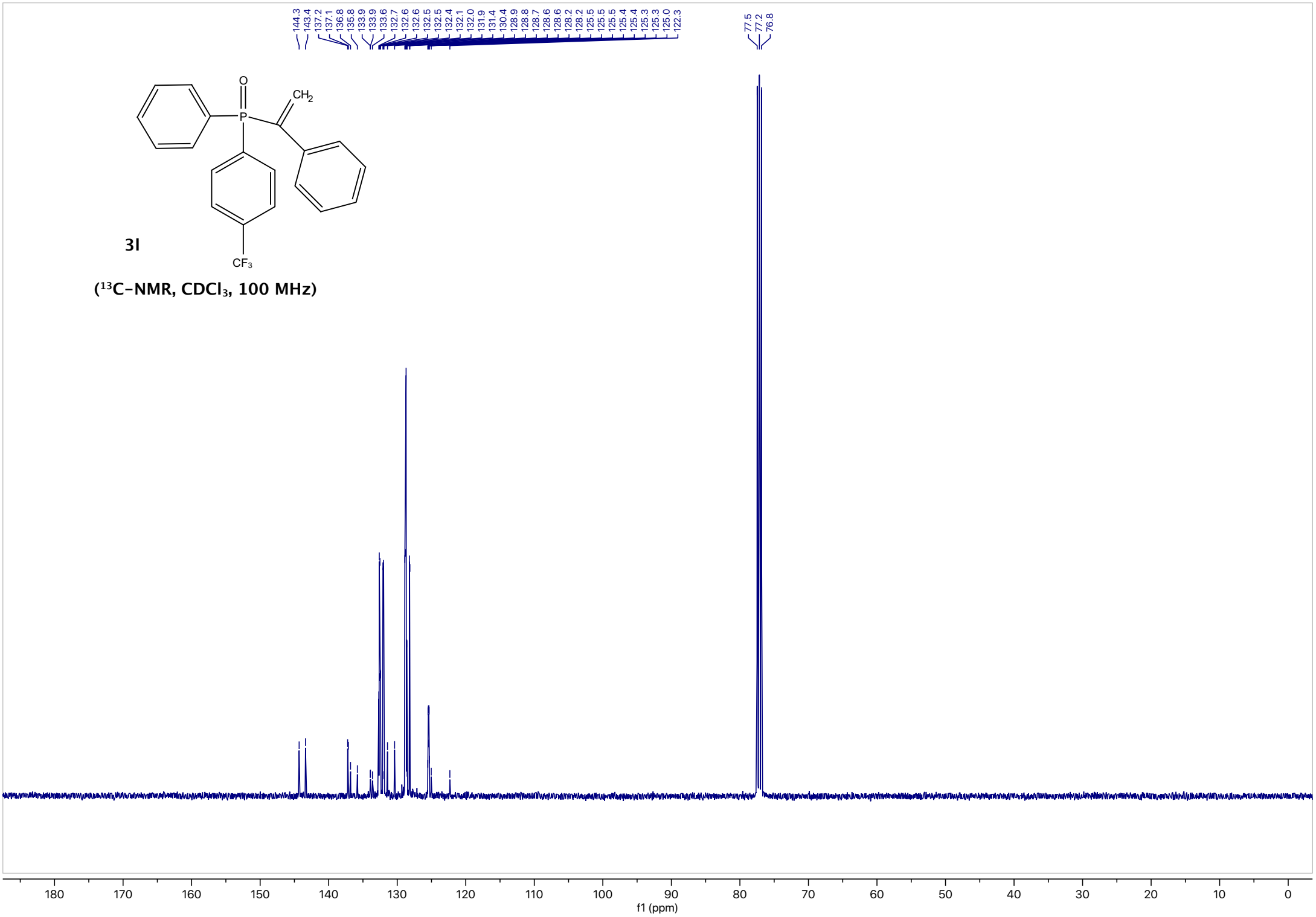

3k
Me
(1H–NMR, CDCl3, 400 MHz)
f1 (ppm)


145.1
144.2
142.5
142.5
137.8
137.7
132.6
132.2
132.1
132.1
132.0
132.0
131.9
131.9
131.9
131.6
129.4
129.3
128.9
128.6
128.5
128.5
128.3
128.3
128.2
127.8
77.5
77.2
76.8
21.7
21.7
O
P
CH2
Me
3k
(13C-NMR, CDCl3, 100 MHz)
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



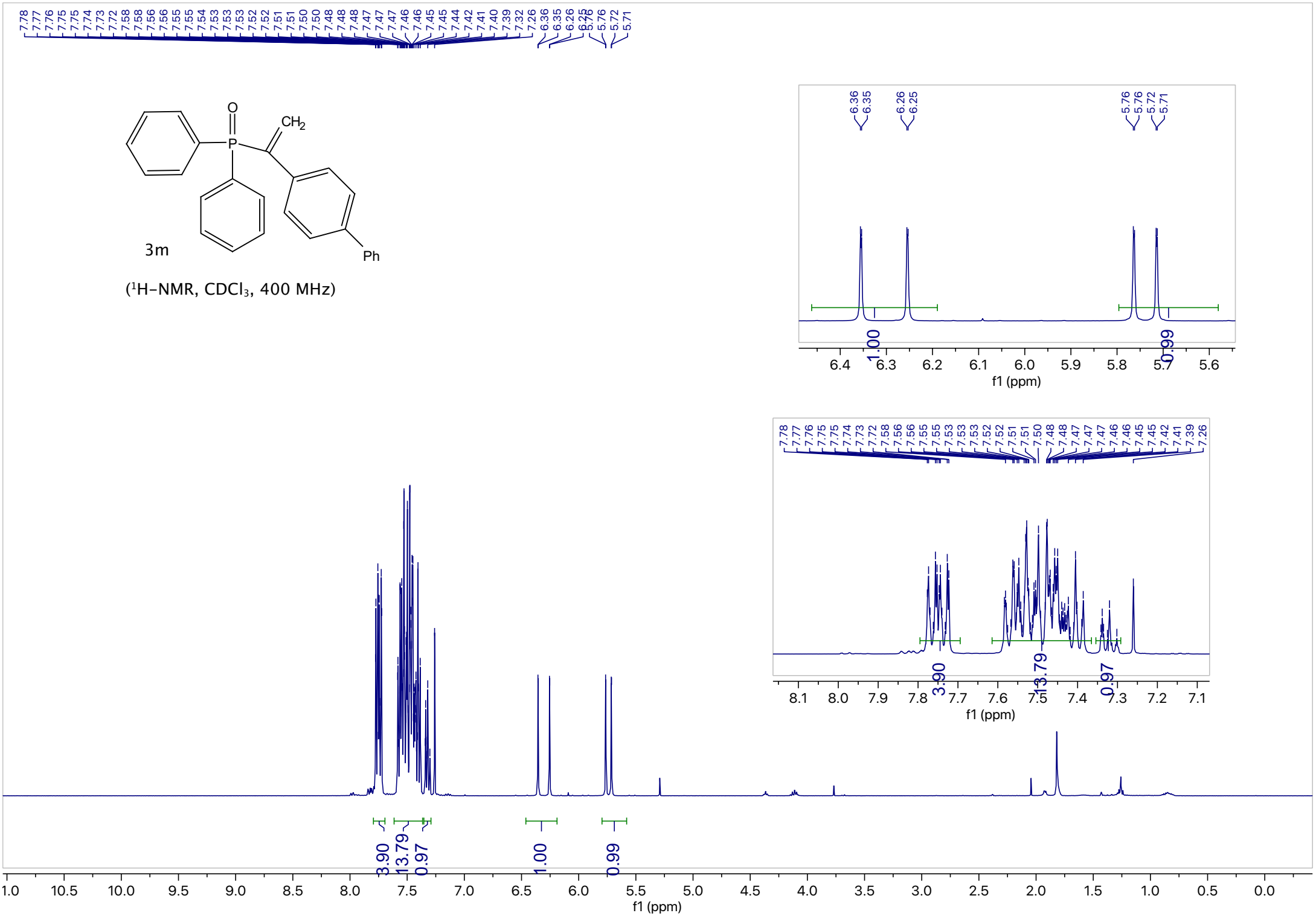
3l

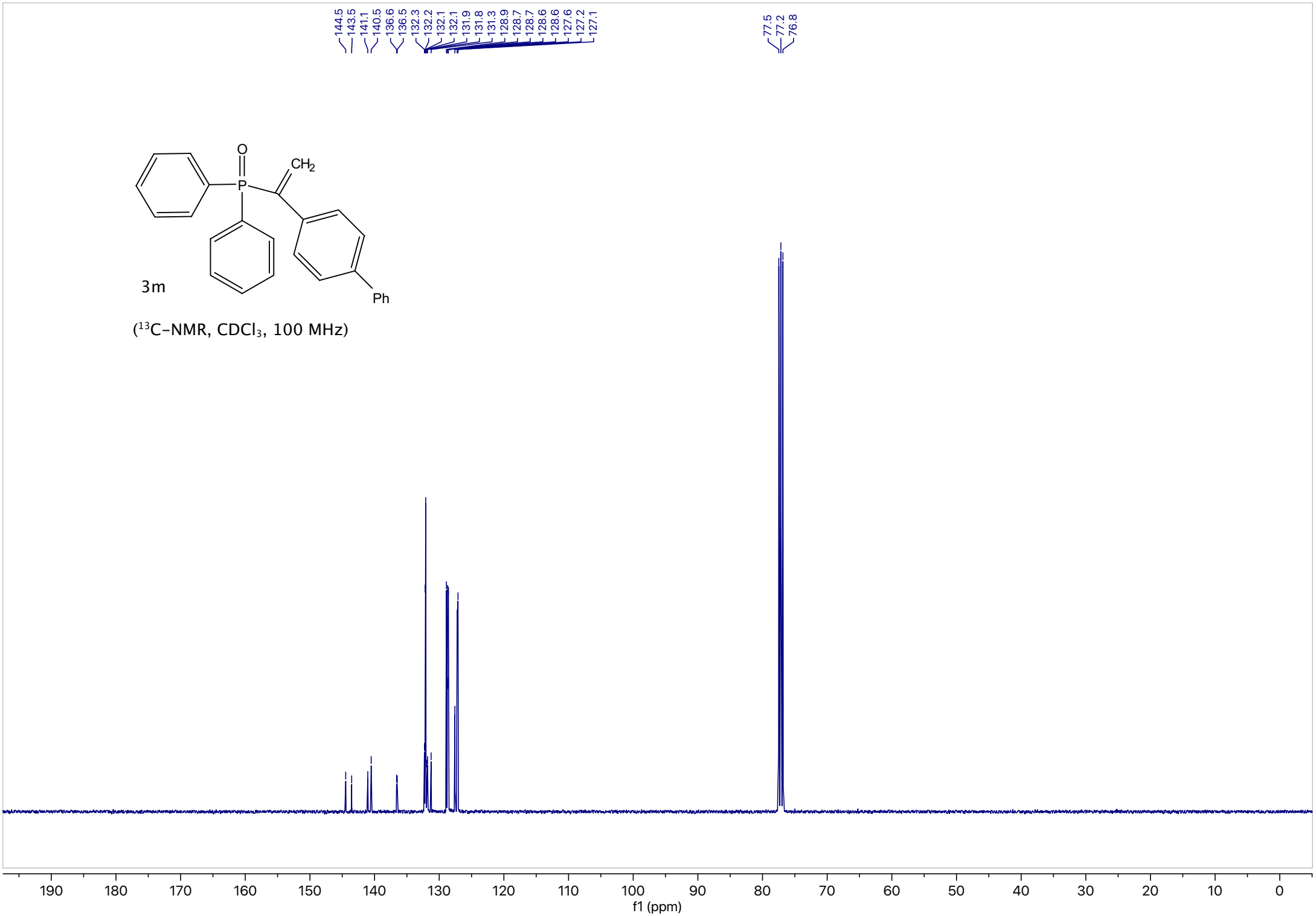
(^{1}H–NMR, $CDCl_3$, 400 MHz)

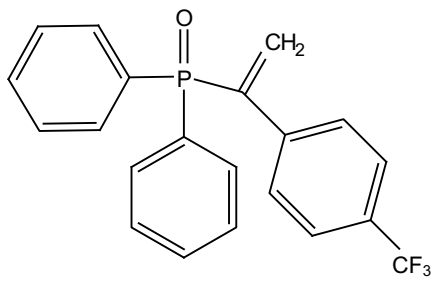


3l

(^{13}C–NMR, $CDCl_3$, 100 MHz)

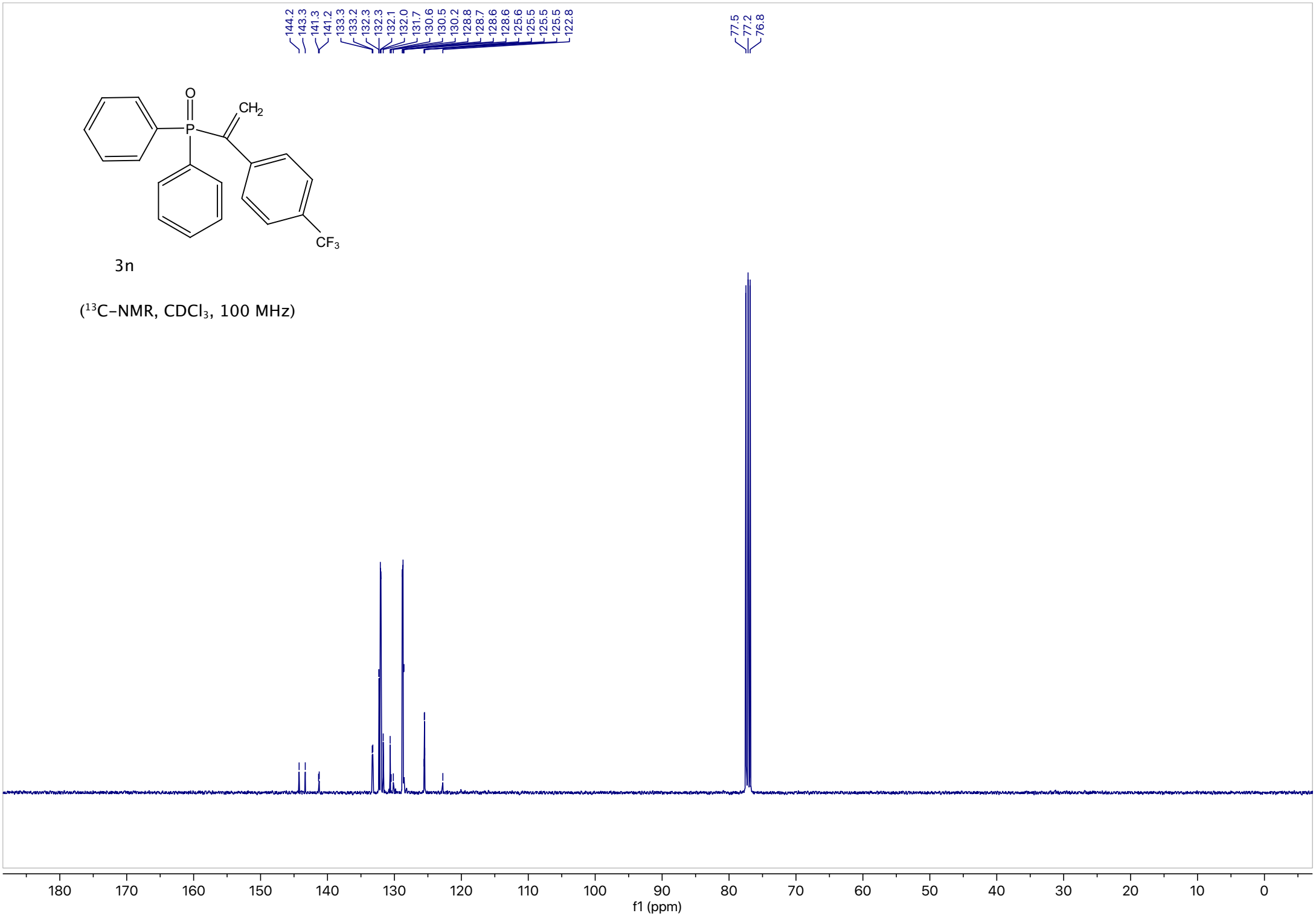

7.78 7.77 7.76 7.75 7.75 7.74 7.73 7.72 7.58 7.58 7.56 7.56 7.55 7.55 7.54 7.53 7.53 7.53 7.52 7.52 7.51 7.51 7.50 7.50 7.48 7.48 7.48 7.47 7.47 7.47 7.46 7.46 7.45 7.45 7.44 7.42 7.41 7.40 7.39 7.32 7.26 6.36 6.35 6.26 6.25 5.76 5.72 5.71
O
P
CH2
Ph
3m
(1H-NMR, CDCl3, 400 MHz)
6.36 6.35 6.26 6.25 5.76 5.76 5.72 5.71
1.00 0.99
6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6
f1 (ppm)
7.78 7.77 7.76 7.75 7.75 7.74 7.73 7.72 7.58 7.56 7.56 7.55 7.55 7.53 7.53 7.52 7.52 7.51 7.51 7.50 7.48 7.48 7.47 7.47 7.47 7.46 7.46 7.45 7.45 7.42 7.41 7.39 7.26
3.90 13.79 0.97
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
3.90 13.79 0.97 1.00 0.99
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

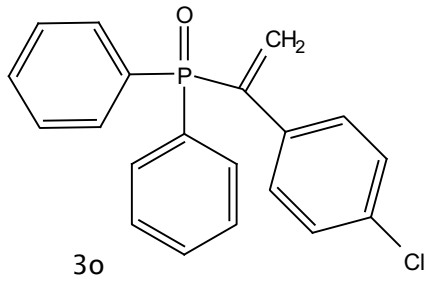

144.5
143.5
141.1
140.5
136.6
136.5
132.3
132.2
132.1
132.1
131.9
131.8
131.3
128.9
128.7
128.7
128.6
128.6
127.6
127.2
127.1
77.5
77.2
76.8
O
P
CH2
Ph
3m
(13C-NMR, CDCl3, 100 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3n

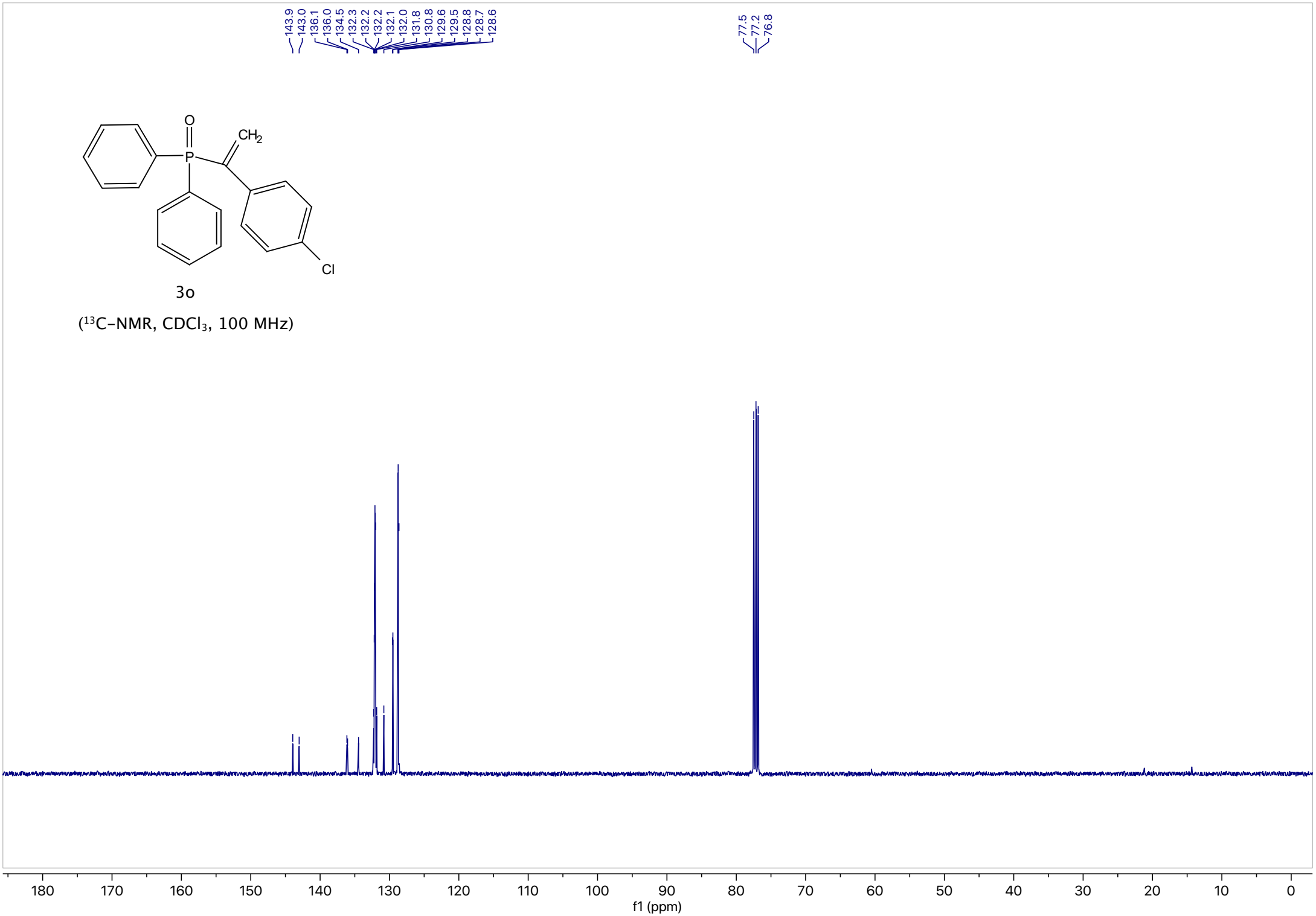
(^{1}H–NMR, $CDCl_3$, 400 MHz)


144.2
143.3
141.3
141.2
133.3
133.2
132.3
132.3
132.1
132.0
131.7
130.6
130.5
130.2
128.8
128.7
128.6
128.6
125.6
125.5
125.5
125.5
122.8
77.5
77.2
76.8
O
P
CH2
CF3
3n
(13C–NMR, CDCl3, 100 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



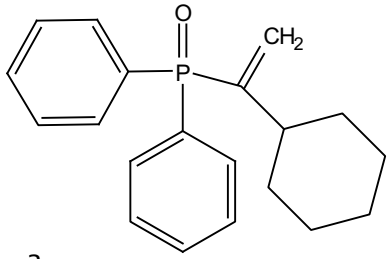
3o

(^{1}H–NMR, $CDCl_3$, 400 MHz)



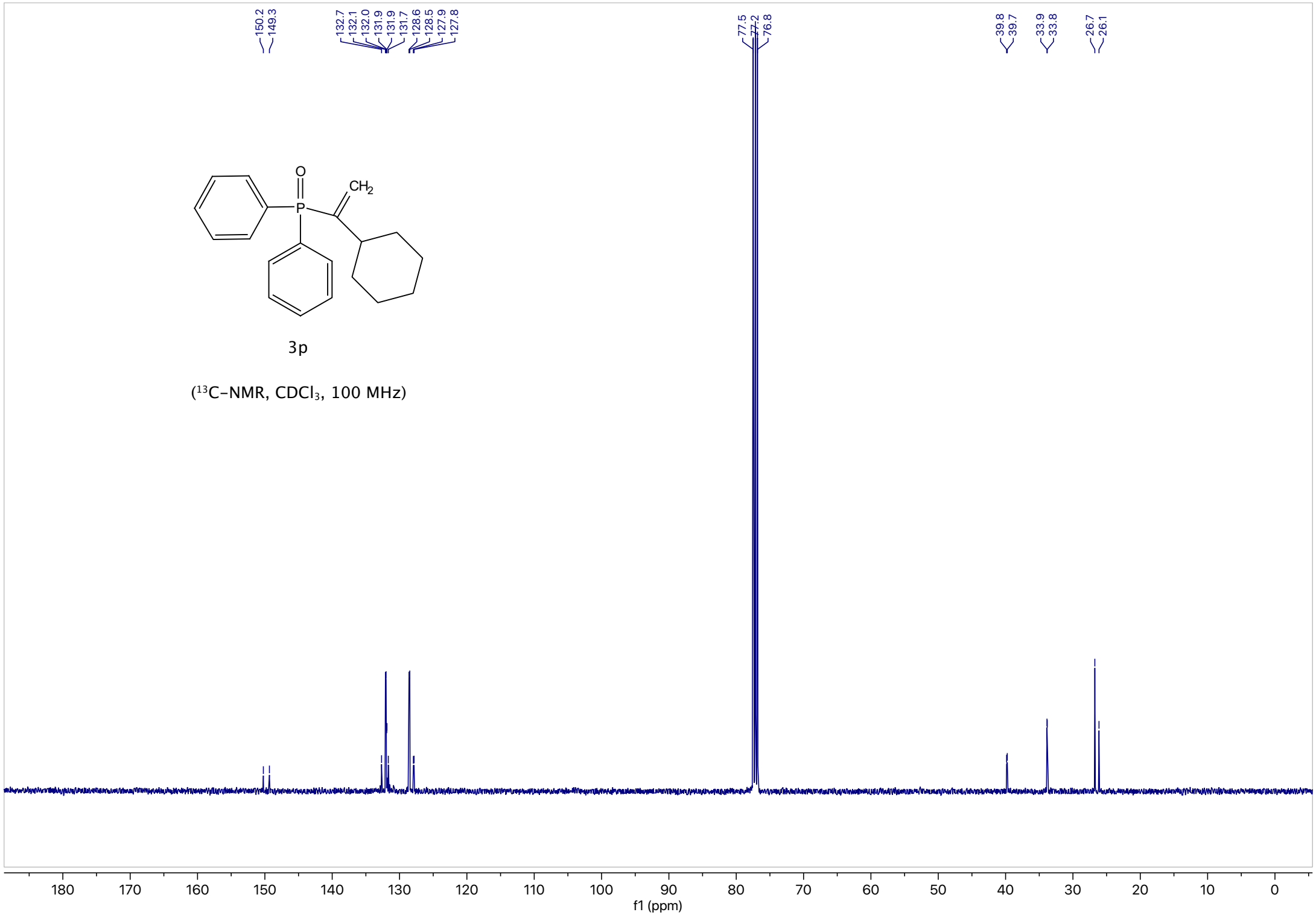
3o

(^{13}C–NMR, $CDCl_3$, 100 MHz)



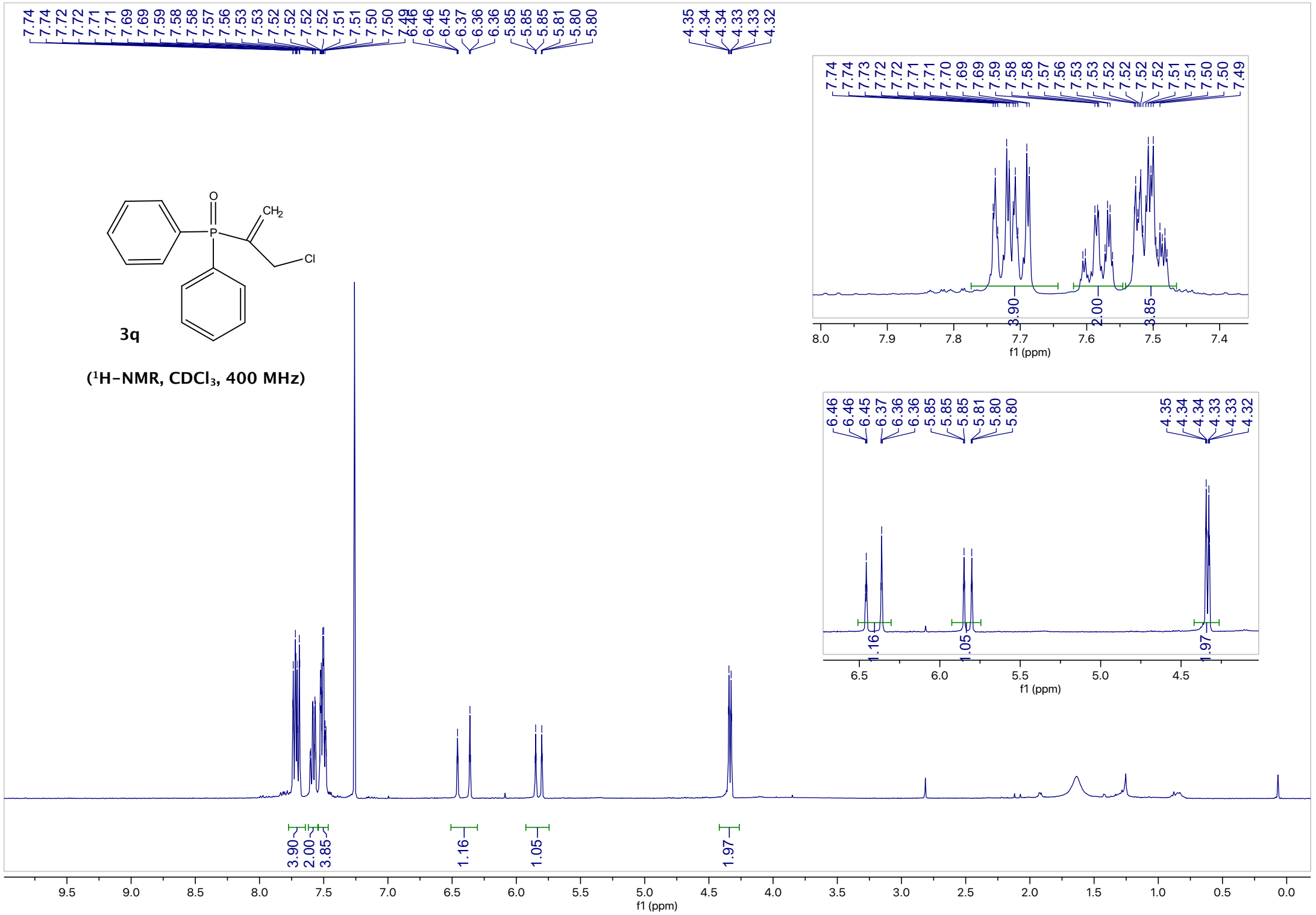
3p

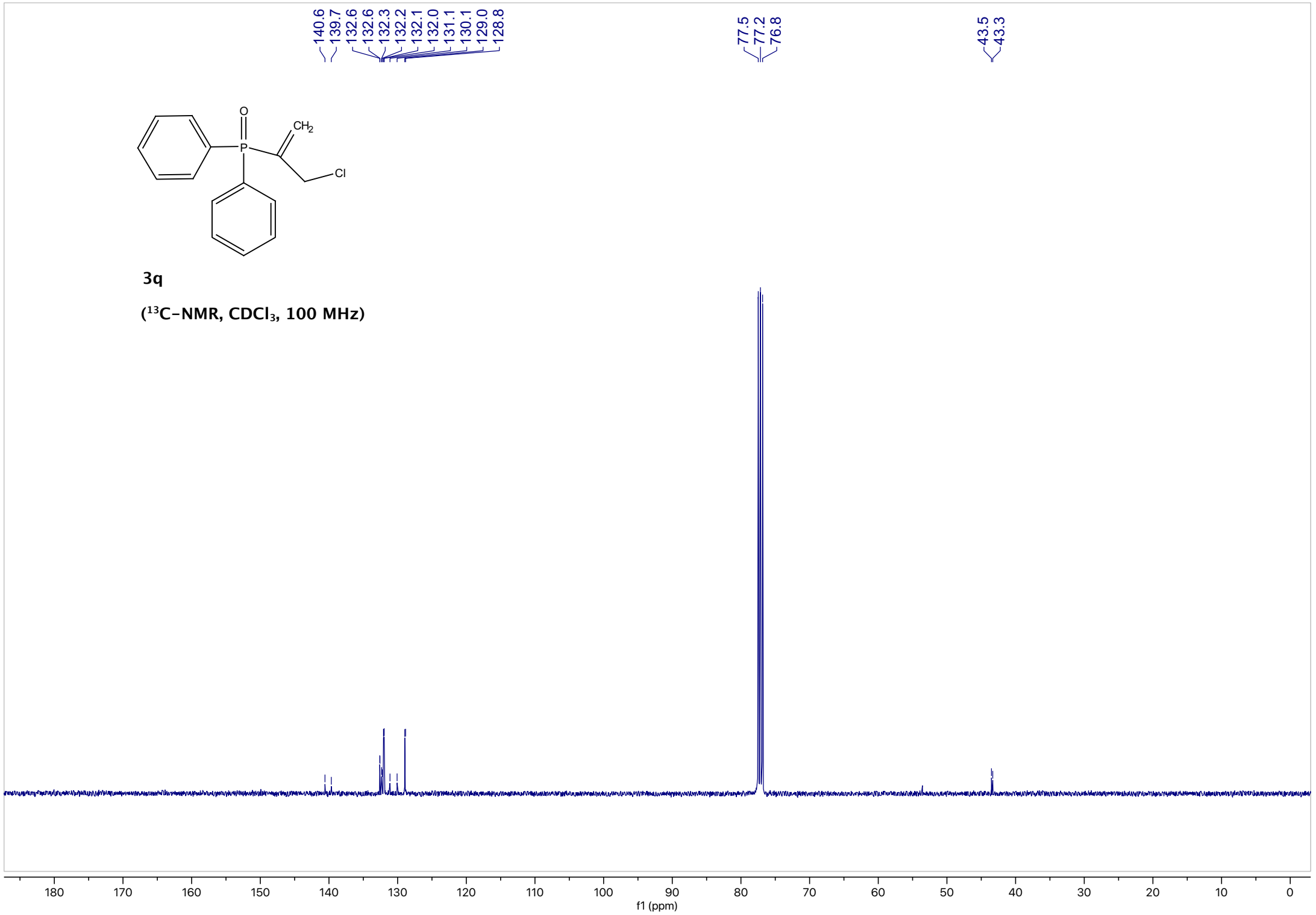
(^{1}H–NMR, $CDCl_3$, 400 MHz)



3p

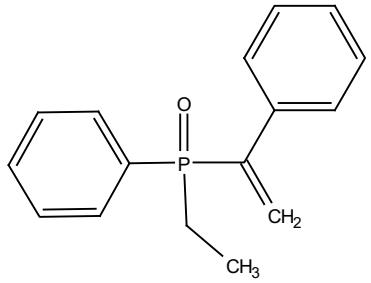
(^{13}C–NMR, $CDCl_3$, 100 MHz)


7.74 7.74 7.72 7.72 7.71 7.71 7.69 7.69 7.59 7.58 7.58 7.57 7.56 7.53 7.53 7.52 7.52 7.52 7.52 7.51 7.51 7.50 7.50 7.49 6.46 6.46 6.45 6.37 6.36 6.36 5.85 5.85 5.85 5.81 5.80 5.80
4.35 4.34 4.34 4.33 4.33 4.32
O
P
CH2
Cl
3q
(1H–NMR, CDCl3, 400 MHz)
3.90 2.00 3.85 1.16 1.05 1.97
f1 (ppm)



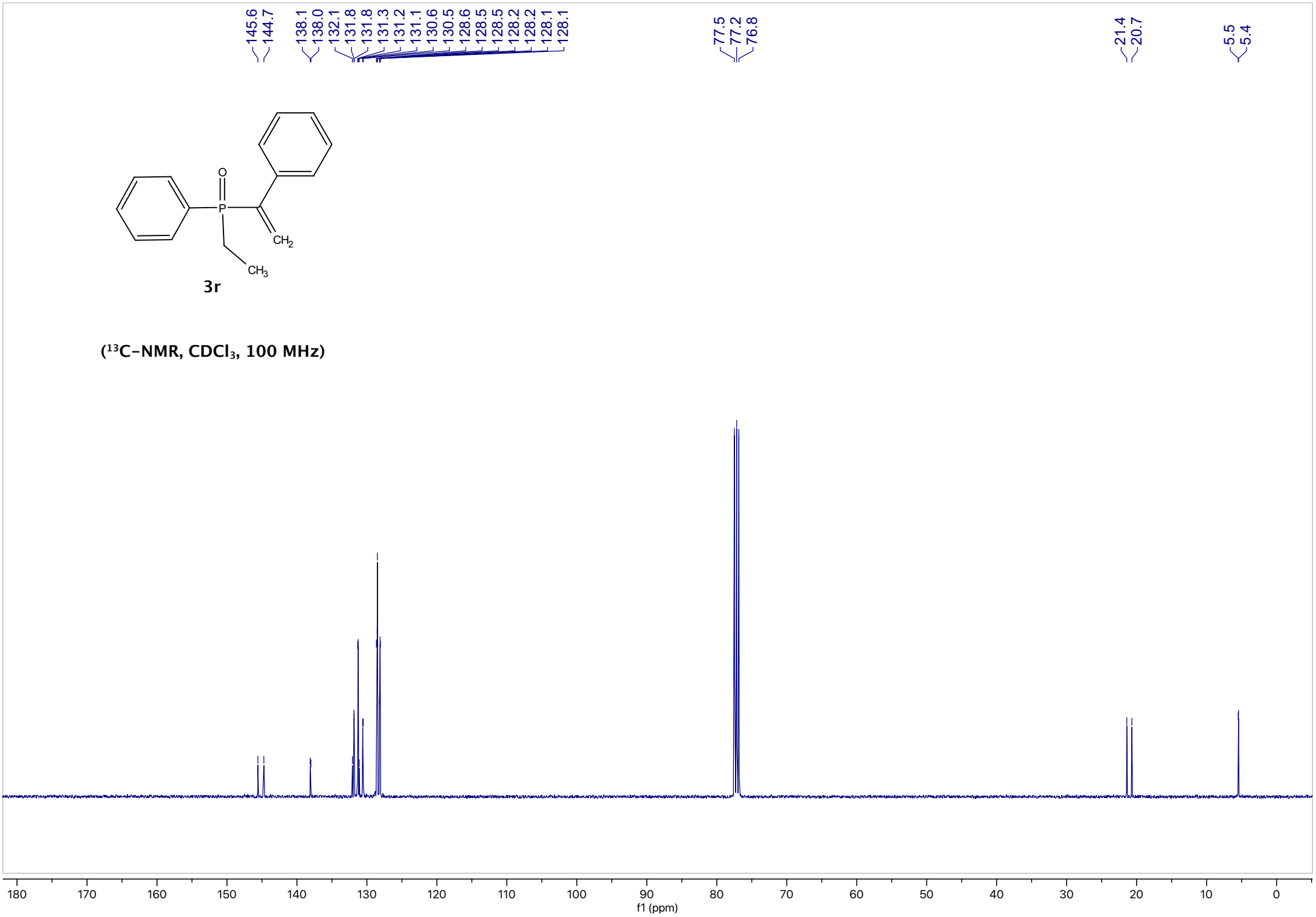
3q

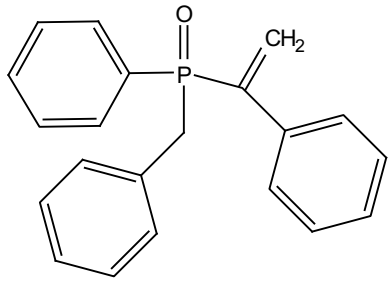
(^{13}C–NMR, $CDCl_3$, 100 MHz)



3r

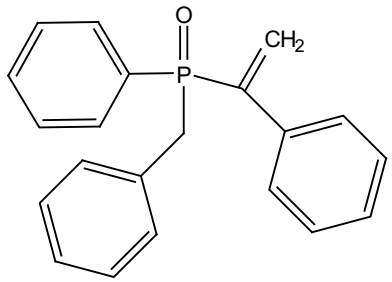
(^{1}H–NMR, $CDCl_3$, 400 MHz)


145.6
144.7
138.1
138.0
132.1
131.8
131.8
131.3
131.2
131.1
130.6
130.5
128.6
128.5
128.5
128.2
128.2
128.1
128.1
77.5
77.2
76.8
21.4
20.7
5.5
5.4
O
P
CH2
CH3
3r
(13C-NMR, CDCl3, 100 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



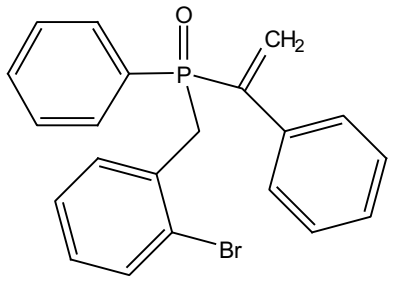
3s

(¹H–NMR, $CDCl_3$, 400 MHz)



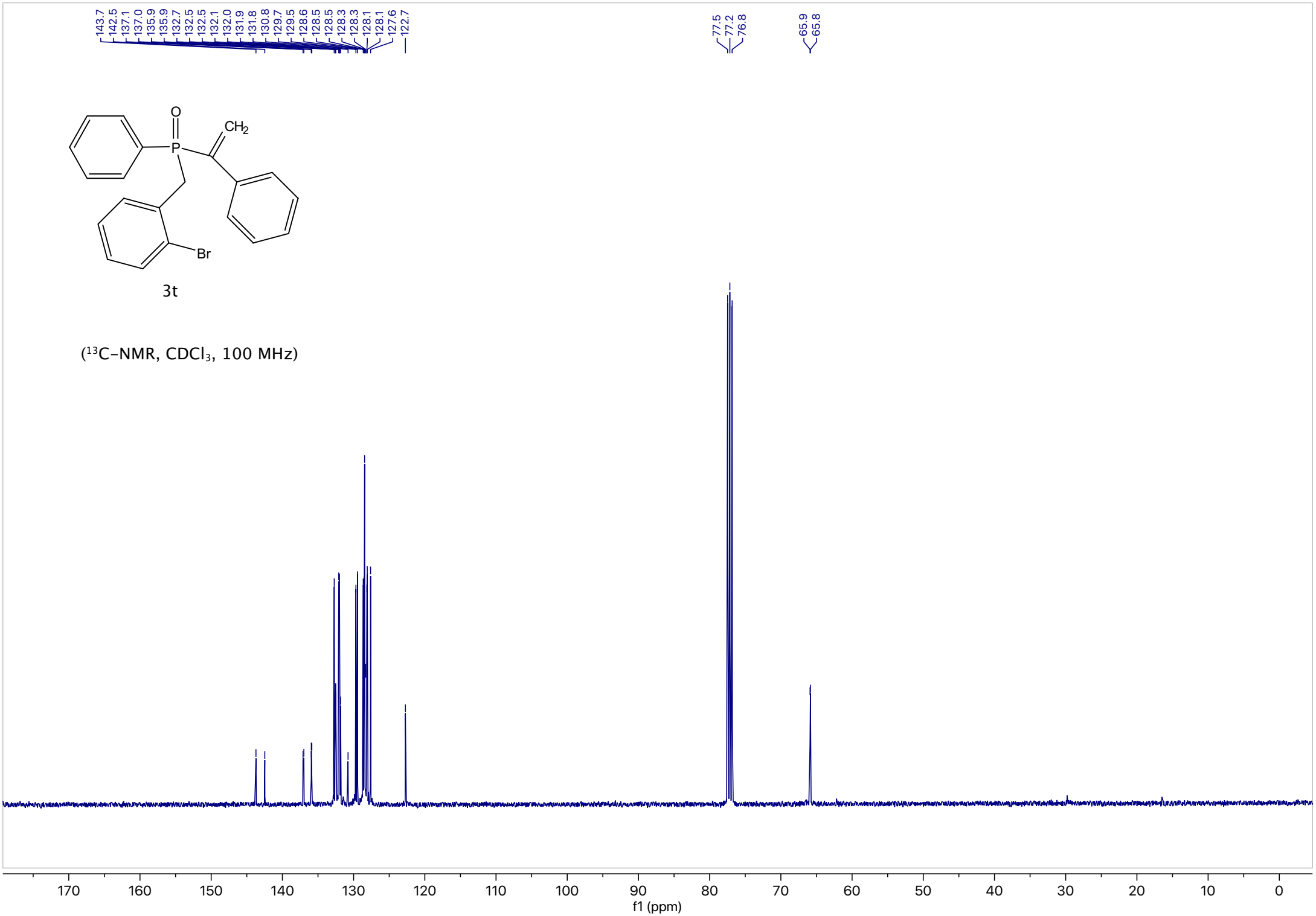
3s

(^{13}C–NMR, $CDCl_3$, 100 MHz)



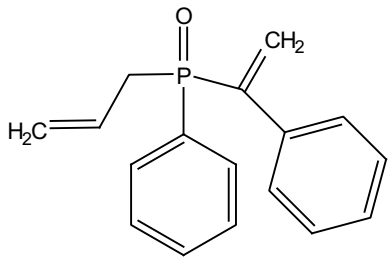
3t

(^{1}H–NMR, $CDCl_3$, 400 MHz)



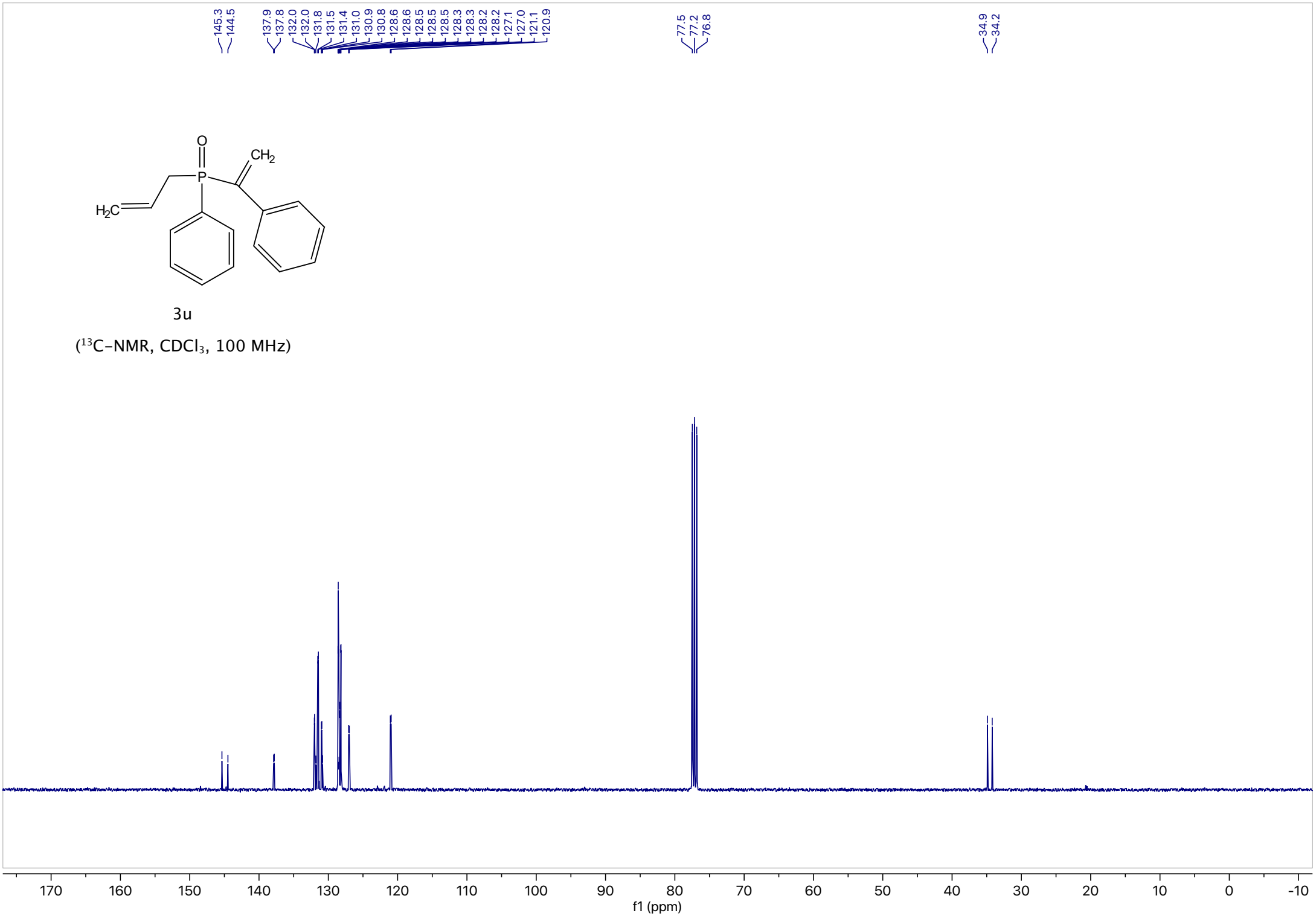
3t

(^{13}C–NMR, $CDCl_3$, 100 MHz)



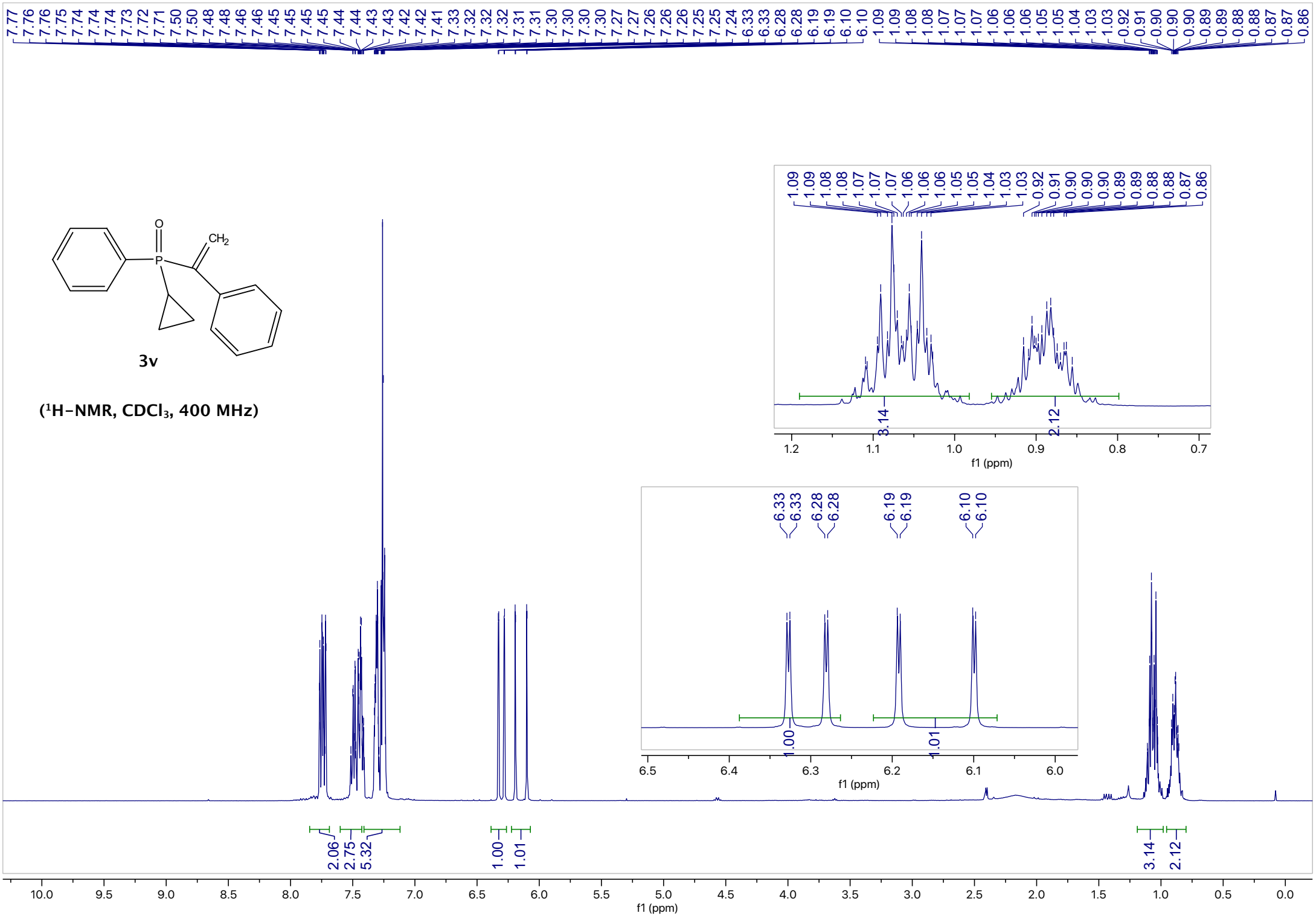
3u

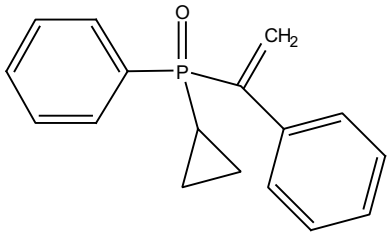
(^{1}H–NMR, $CDCl_3$, 400 MHz)



3u

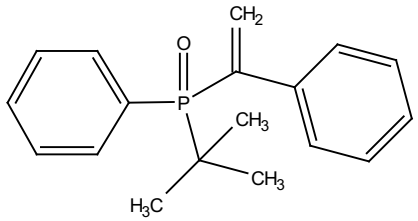
(^{13}C–NMR, $CDCl_3$, 100 MHz)


O
CH2
P
3v
(1H–NMR, CDCl3, 400 MHz)
f1 (ppm)



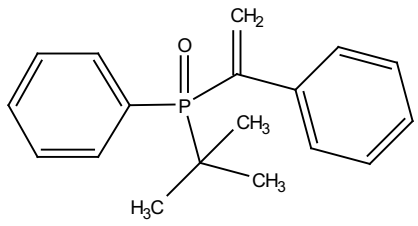
3v

(^{13}C–NMR, $CDCl_3$, 100 MHz)



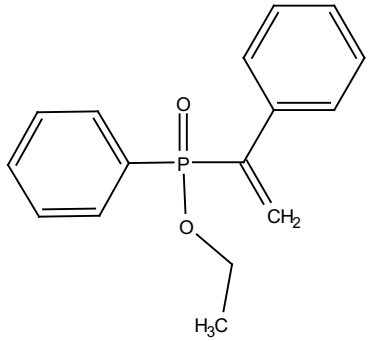
3w

(^{1}H–NMR, $CDCl_3$, 400 MHz)



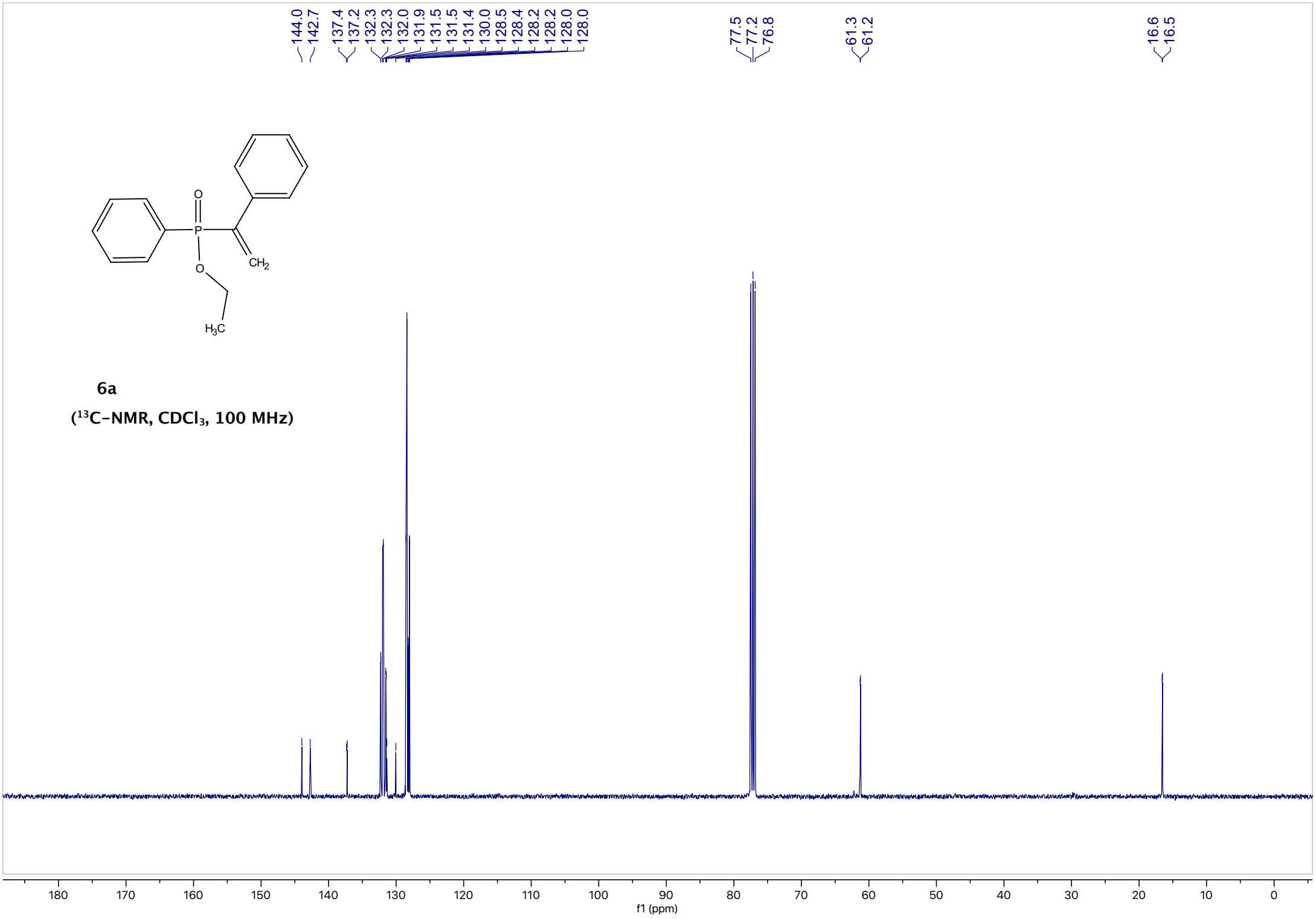
3w

(^{13}C–NMR, $CDCl_3$, 100 MHz)



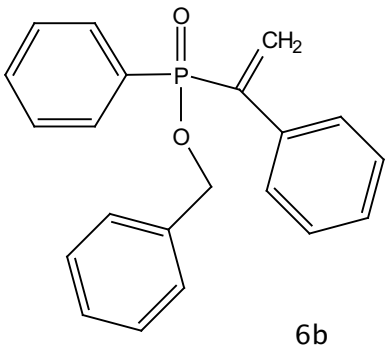
6a

(^{1}H–NMR, $CDCl_3$, 400 MHz)



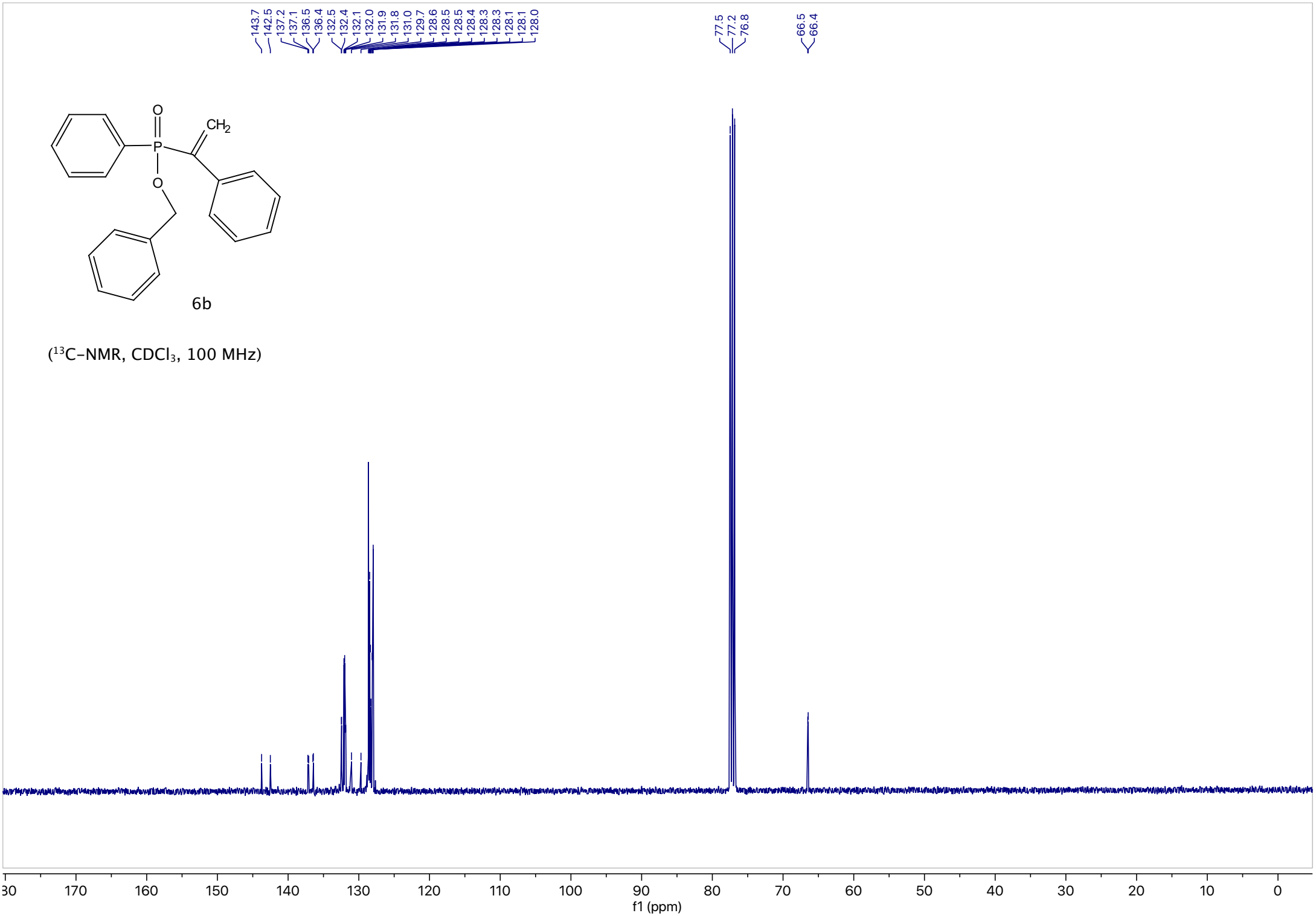
6a

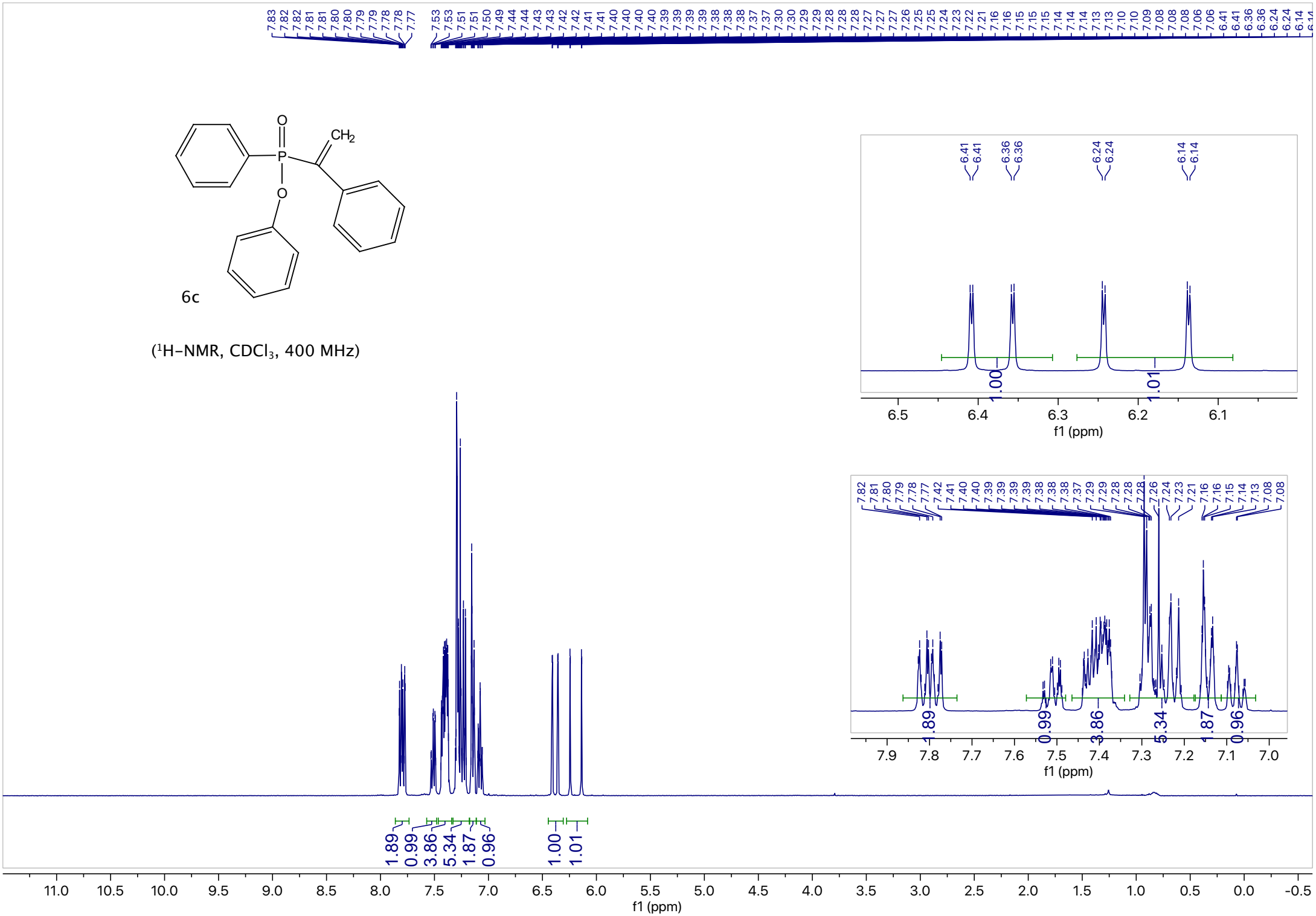
(^{13}C–NMR, $CDCl_3$, 100 MHz)

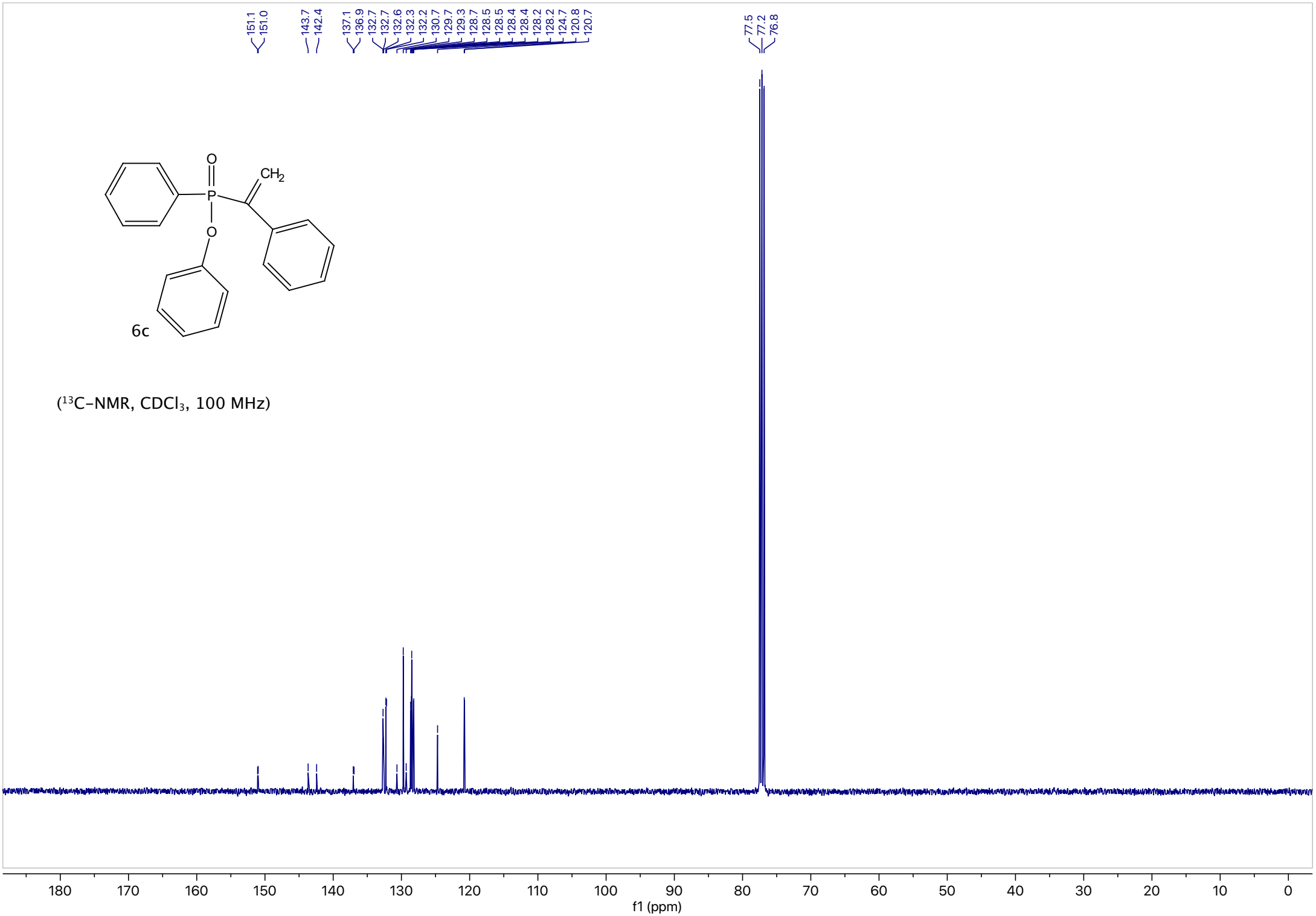


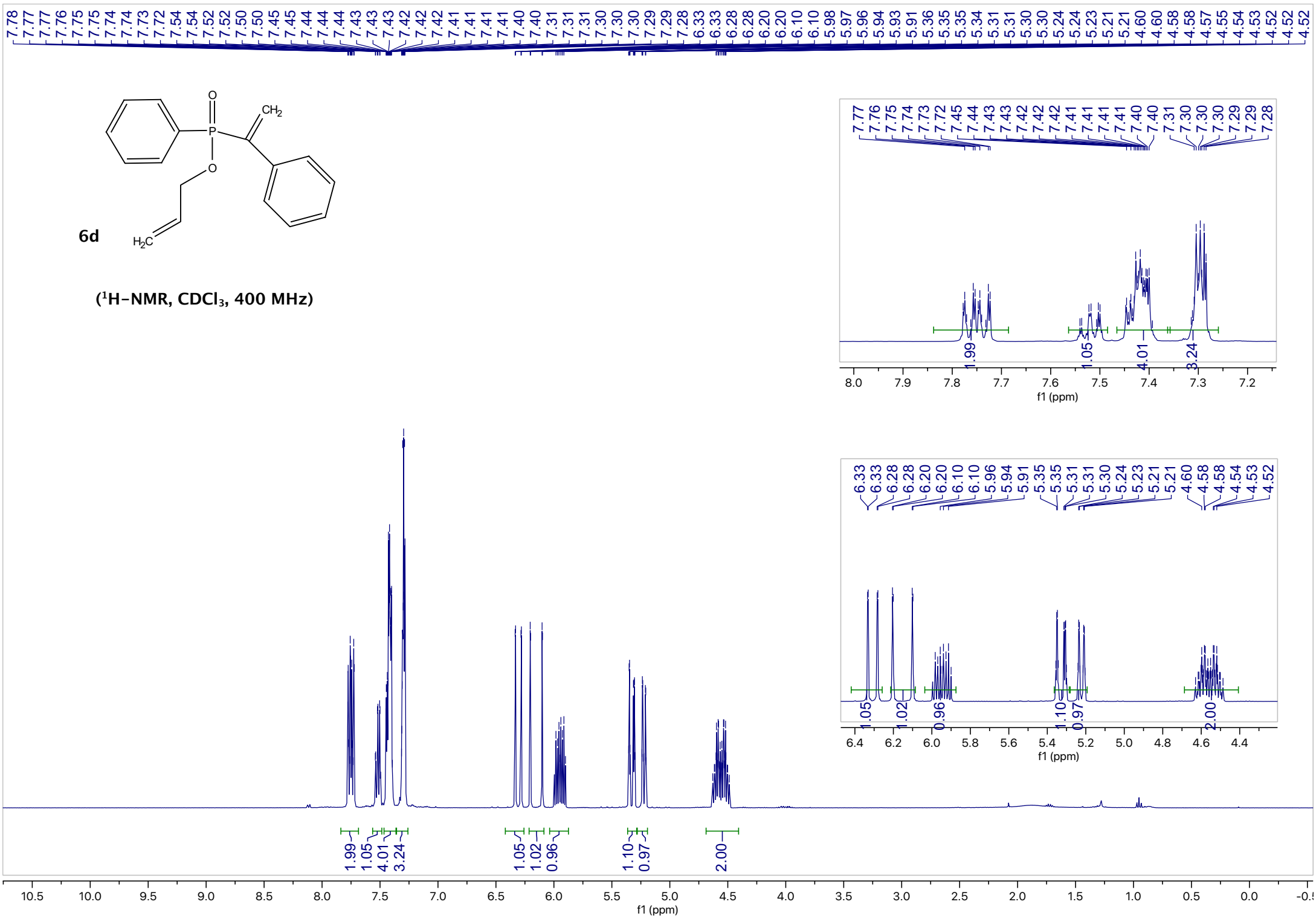
6b

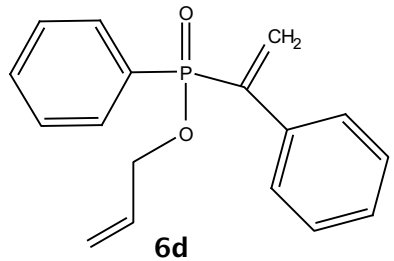
(^{1}H–NMR, $CDCl_3$, 400 MHz)


143.7
142.5
137.2
137.1
136.5
136.4
132.5
132.4
132.1
132.0
131.9
131.8
131.0
129.7
128.6
128.5
128.5
128.4
128.3
128.3
128.1
128.1
128.0
77.5
77.2
76.8
66.5
66.4
O
P
O
CH2
6b
(13C–NMR, CDCl3, 100 MHz)
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6c
(1H–NMR, CDCl3, 400 MHz)
f1 (ppm)


151.1
151.0
143.7
142.4
137.1
136.9
132.7
132.7
132.6
132.3
132.2
130.7
129.7
129.3
128.7
128.5
128.5
128.4
128.4
128.2
128.2
124.7
120.8
120.7
77.5
77.2
76.8
O
P
O
CH2
6c
(13C–NMR, CDCl3, 100 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

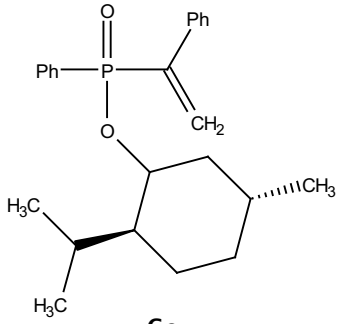

7.78 7.77 7.77 7.76 7.75 7.75 7.74 7.74 7.73 7.72 7.54 7.54 7.52 7.52 7.50 7.50 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.28 6.33 6.33 6.28 6.28 6.20 6.20 6.10 6.10 5.98 5.97 5.96 5.94 5.93 5.91 5.36 5.35 5.35 5.34 5.31 5.31 5.30 5.30 5.24 5.24 5.23 5.21 5.21 4.60 4.60 4.58 4.58 4.57 4.55 4.54 4.53 4.52 4.52 4.52
O
CH2
P
O
H2C
6d
(1H–NMR, CDCl3, 400 MHz)
7.77 7.76 7.75 7.74 7.73 7.72 7.45 7.44 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.41 7.41 7.40 7.40 7.31 7.30 7.30 7.30 7.29 7.29 7.28
1.99 1.05 4.01 3.24
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
6.33 6.33 6.28 6.28 6.20 6.20 6.10 6.10 5.96 5.94 5.91 5.35 5.35 5.31 5.31 5.30 5.24 5.23 5.21 5.21 4.60 4.58 4.58 4.54 4.53 4.52
1.05 1.02 0.96 1.10 0.97 2.00
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4
f1 (ppm)
1.99 1.05 4.01 3.24 1.05 1.02 0.96 1.10 0.97 2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



6d

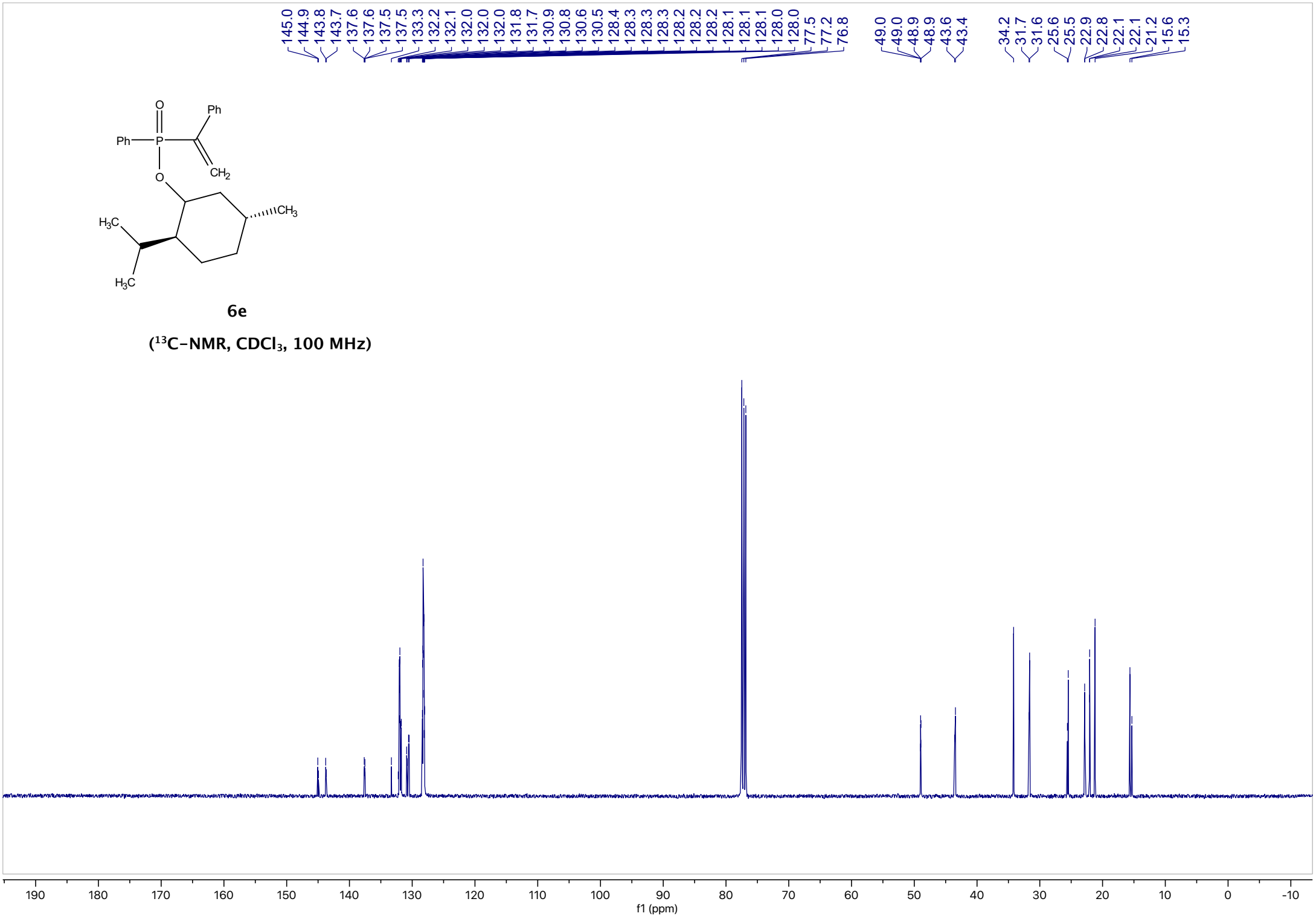
H_2C

(^{13}C–NMR, $CDCl_3$, 100 MHz)



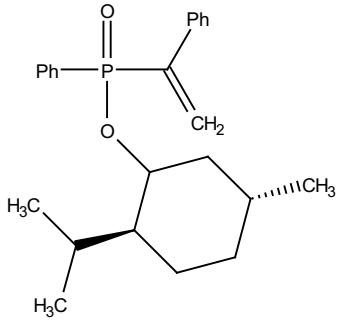
6e

(^{1}H–NMR, $CDCl_3$, 400 MHz)



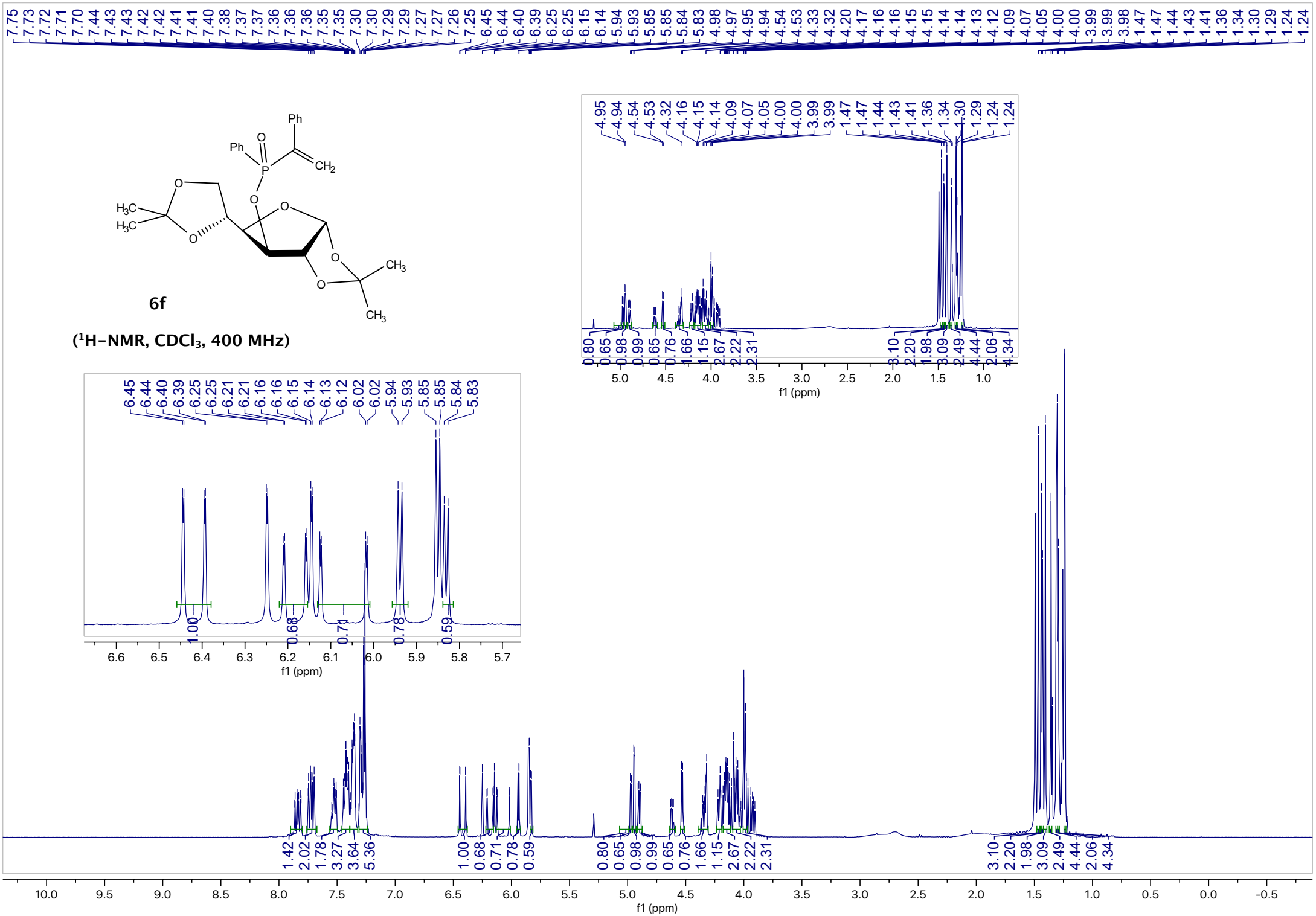
6e

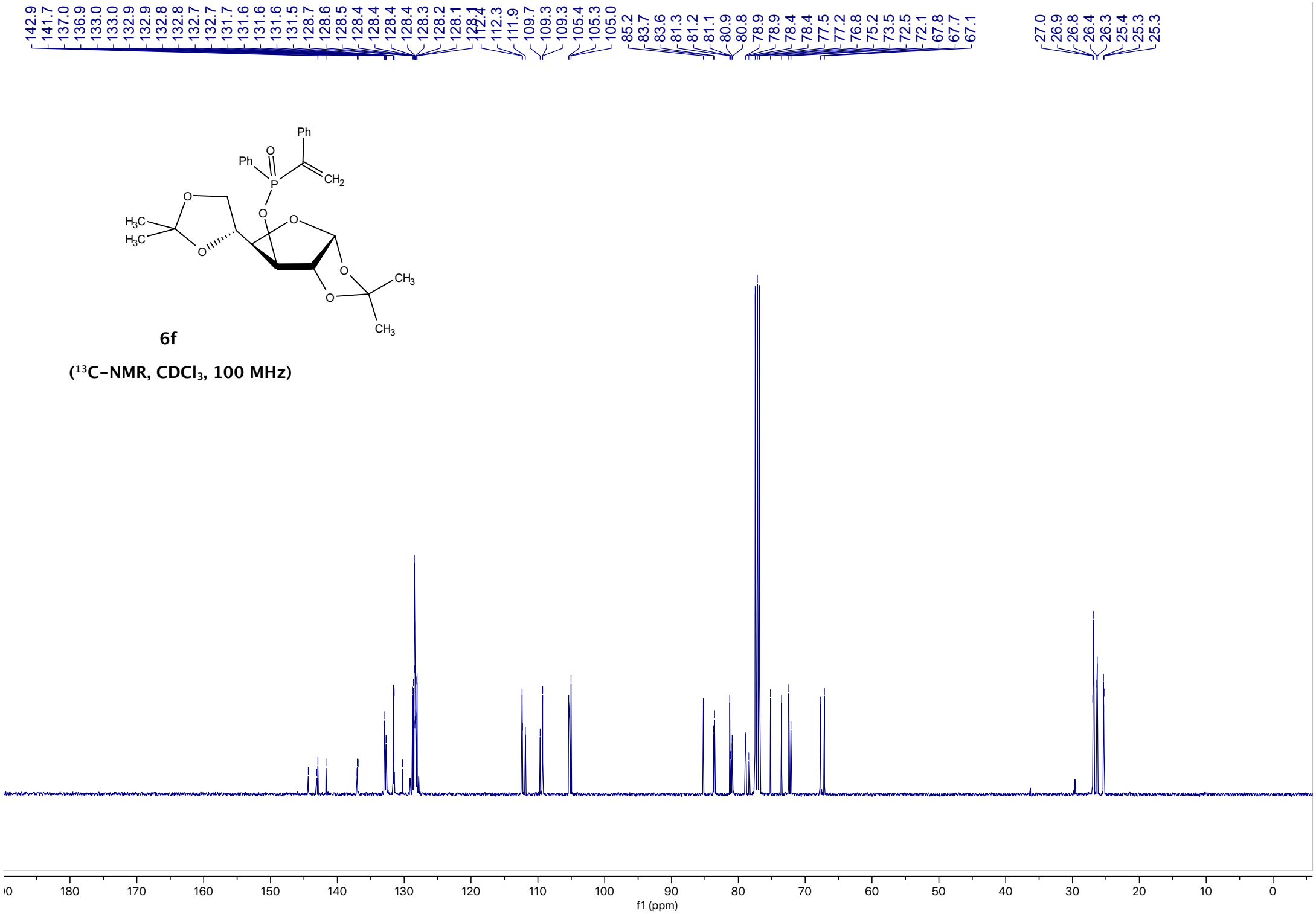
(^{13}C–NMR, $CDCl_3$, 100 MHz)



6e

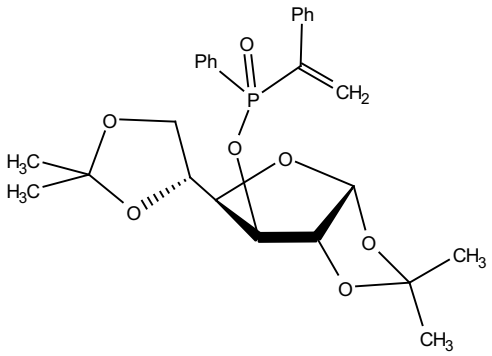
(^{31}P–NMR, $CDCl_3$, 162 MHz)


Ph
Ph
O
P
CH2
O
O
O
H3C
H3C
O
O
O
CH3
O
CH3
6f
(1H-NMR, CDCl3, 400 MHz)
f1 (ppm)
f1 (ppm)
f1 (ppm)



6f

(^{13}C–NMR, $CDCl_3$, 100 MHz)



6f

(^{31}P–NMR, $CDCl_3$, 162 MHz)