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Copper-Catalyzed Stereo- and Regioselective Hydrophosphorylation of Terminal Alkynes: Scope and Mechanistic Study

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1. General experimental

Anhydrous tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), Acetonitrile (MeCN), hexane, methyl *tert*-butyl ether (MTBE), EtOAc, and dichloromehane (DCM) were purchased from J&K. All reagents were purchased at the highest commercial quality and used as received without further purification unless otherwise stated. All experiments were carried out under ambient air with no precautions taken to exclude moisture. Reactions were monitored by thin layer chromatography (TLC), GC-MS, and LC/MS. TLC was performed using 0.25 mm E. Merck silica plates (60F-254), using short-wave UV light as the visualizing agent, or $KMnO_4$ and heat as developing agents. Flash column chromatography was performed using 200-300 mesh silica gel obtained from Qingdao Haiyang Chemical Co., Ltd. NMR spectra were recorded on an Bruker Ultrashield™ 300 MHz instrument and are calibrated using residual undeuterated solvent (TMS @ 0.00 ppm, $CDCl_3$ @ 7.26 ppm, d_6-DMSO @ 2.50 ppm, d_7-DMF @ 2.92 & 2.75 ppm ^{1}H NMR, $CDCl_3$ @ 77.16 ppm, d_6-DMSO @ 39.52 ppm, d_7-DMF @ 163.15 ppm ^{13}C NMR). The ^{31}P NMR chemical shifts are proton decoupled referenced to the deuterium solvent calibrated in 1H NMR. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were recorded on an Agilent 1200 HPLC/6520 Accurate-Mass Q-TOF LC/MS mass spectrometer by electrospray ionization time of flight reflectron experiments. HPLC analyses were conducted on a Agilent 1260 LC/MSC with a MZ PerfectChrom 100 C8 column (4.6 ID x 150 mm, 5 µm). Preparative HPLC were conducted on an Buchi Pure C850 instrument with a MZ PerfectChrom 100 C8 Prep column (30 ID x 150 mm, 5 µm).

2. General procedure

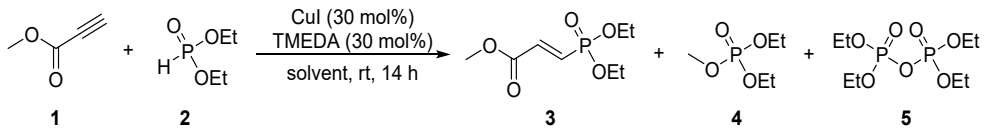
Product synthesis: to a 5 mL vessel, CuCl (0.09 mmol, 30 mol%), TBD (0.09 mmol, 30 mol%), DMF (2 mL), alkyne (0.3 mmol), and P(O)H compound (0.3 mmol) were added in sequence, then the reaction was stirred for 5-24 h at 100 ºC. After cooling down to room temperature, the reaction mixture was filtered through a short pad of celite™ 545, washed with DCM (50 mL), and then extracted with saturated salt water (50 mL × 3 times). The organic layer was then dried over anhydrous Na_2SO_4, and concentrated. The crude product was puried by column chromatography with petroleum ether/EtOAc or MeCN/H_2O as eluents to afford the desired product.

Competitive experiments: similar to above manipulations, 0.3 mmol of each substrate was employed. The yields were determined by GC-MS.

Deuterium-labeling experiments: similar to above manipulations. The deuterium content of **5ak** was determined by ^{1}H NMR.

3. Optimization details

Table S1 Optimization of the solvents [a, b]

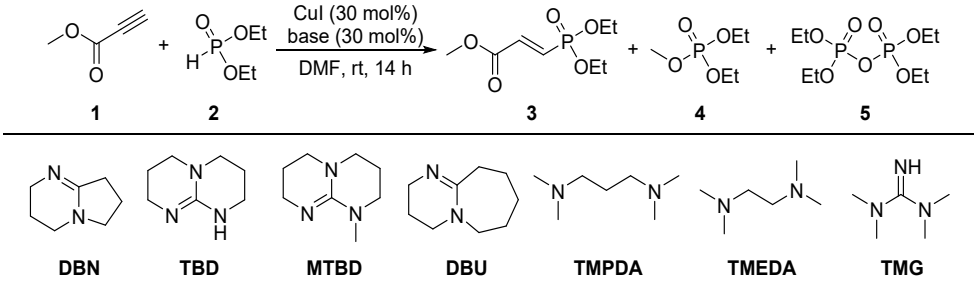


1 2 3 4 5

Entry	Solvent	Yield of 3 (%)	Yield of 4 (%)	Yield of 5 (%)
1	Toluene	22	16	17
2	THF	13	20	28
3	MeCN	17	8	0
4	DCM	6	32	31
5	Hexane	3	10	0
6	MTBE	11	16	25
7	EtOAc	13	19	23
8	PhOMe	25	9	8
9	DMF	29	11	0

[a]Conditions: alkyne **1** (0.3 mmol), diethyl phosphite **2** (0.36 mmol), CuI (30 mol%), TMEDA (30 mol%), solvent (2 mL), air, 14 h. [b]Yields were determined by GC-MS.

Table S2 Optimization of the organic bases [a, b]



1 2 3 4 5

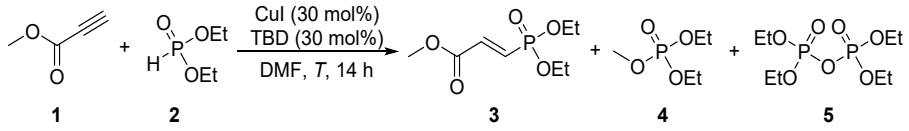
DBN TBD MTBD DBU TMPDA TMEDA TMG

Entry	Base	Yield of 3 (%)	Yield of 4 (%)	Yield of 5 (%)
1	DBN	0	0	0
2	TBD	13	0	0
3	MTBD	0	0	5

Entry	Base	Yield of 3 (%)	Yield of 4 (%)	Yield of 5 (%)
4	DBU	0	0	0
5	DMAP	9	0	0
6	TMPDA	19	7	0
7	TMG	11	0	0
8	DABCO	0	35	21
9	Et_3N	0	0	0

[a]Conditions: alkyne **1** (0.36 mmol), diethyl phosphite **2** (0.3 mmol), CuI (30 mol%), base (30 mol%), DMF (2 mL), air, 14 h. [b]Yields were determined by GC-MS.

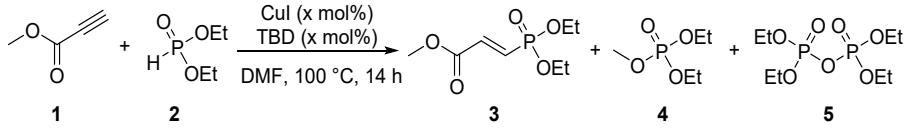
Table S3 Optimization of temperature [a, b]



Entry	Temp (ºC)	Yield of 3 (%)	Yield of 4 (%)	Yield of 5 (%)
1	80	19	0	0
2	100	84	0	0
3	120	67	0	5

[a]Conditions: alkyne **1** (0.36 mmol), diethyl phosphite **2** (0.3 mmol), CuI (30 mol%), TBD (30 mol%), DMF (2 mL), air, 14 h. [b]Yields were determined by GC-MS.

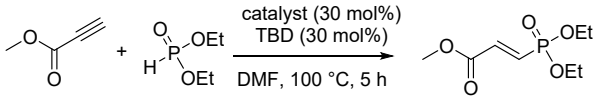
Table S4 Further optimization of catalyst and base loading [a, b]



Entry	CuI (mol%)	TBD (mol%)	Yield of 3 (%)	Yield of 4 (%)	Yield of 5 (%)
1	0	0	0	0	0
2	0	30	10	0	0
3	5	30	12	0	0
4	15	30	32	0	0
5	30	0	0	0	0
6	30	15	55	0	0
7	30	50	58	0	0

[a]Conditions: alkyne **1** (0.36 mmol), diethyl phosphite **2** (0.3 mmol), CuI (x mol%), TBD (x mol%), DMF (2 mL), air, 14 h. [b]Yields were determined by GC-MS.

Table S5 Further optimization of catalyst[a, b]



1 2 3

Entry	Cu catalyst	Yield (%)
1	CuI	57
2	CuBr	83
3	CuCl	88 (81)[c]
4	$CuCl_2$	0
5	CuCN	12
6	CuOTf	6
7	$Cu(MeCN)_4PF_6$	48

[a]Conditions: alkyne **1** (0.36 mmol), diethyl phosphite **2** (0.3 mmol), catalyst (30 mol%), TBD (30 mol%), DMF (2 mL), air, 5 h. [b]Yields were determined by GC-MS. [c]Isolated yield in parentheses.

4. Structure Determination of the *E*-alkenylphosphorus compounds

We selected the compound of **3ap** to demonstrate its absolute configuration. The single ^{31}P peak at 19.66 ppm clearly shows that this compound is a single isomer. From figure S1, we can observe that the chemical shift of COCH=C*H*P(O) is 7.53 ppm, and its H-H coupling constant is calculated as 17.0 Hz. The chemical shift of COC*H*=CHP(O) is 6.90 ppm, and the H-H coupling constant is calculated as 17.0 Hz. As for the *E*-isomers, their coupling constants generally lie in the range of 12 -20 Hz, whereas the coupling constants of *Z*-isomers lie in the range of 3-13 Hz. Consequently, the absolute configuration of **3ap** is precisely examined as *E*-isomer. Similarly, the configuration of the other compounds were determinated as *E*-isomer.

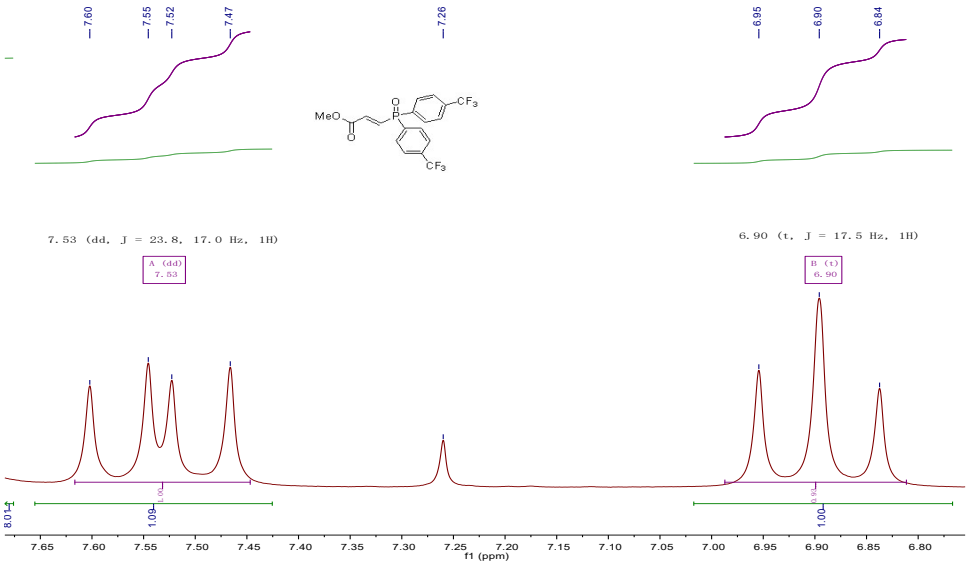


Figure S1 The ^1H NMR of compound **5ap** (7.65-6.60 ppm)

5. Computational details

DFT calculations were performed using the Gaussian 16 package.[1] All of the structures are optimized using the M06 functional[2] with the basis set 6-311G* for Cu[3] and 6-31G* for other elements.[4] Vibrational analyses were performed to ensure intermediates to have no imaginary frequencies and the transition state structures to have only one imaginary frequency. Transition state structures were confirmed to connect appropriate reactants or products by intrinsic reaction coordinate (IRC) calculations.[5] Solvent effects were considered using DMF with the SMD[6] model at the M06/6-311++G** level[7-9] with 6-311G* for Cu.[3]

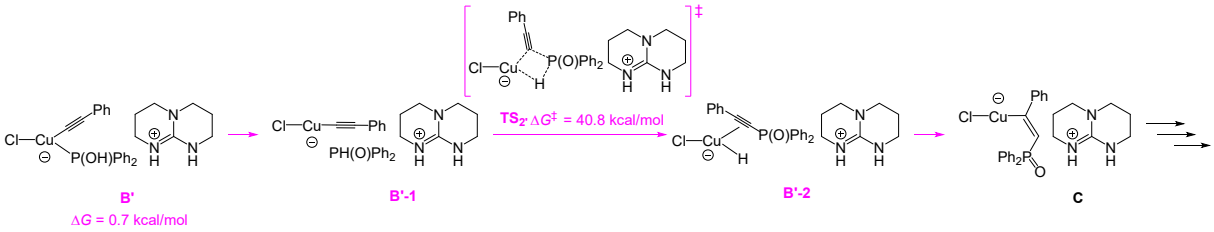


Figure S2. A proposed unfavorable pathway from the the phenylethynyl Cu(I) complex B'.

6. Cartesian coordinates

A E = -3727.366431

C	-0.39465900	0.98561500	-1.74596100
C	-1.42414700	0.27077100	-1.71224500
C	-2.80184300	-0.07525300	-1.94633400
C	-3.70083300	0.94177200	-2.30727400
C	-3.26719900	-1.38815500	-1.81367800
C	-5.04073800	0.64885300	-2.51915900
H	-3.32657500	1.95880100	-2.42215300
C	-4.61017000	-1.67387800	-2.03197200
H	-2.56412100	-2.16965500	-1.52388800
C	-5.49889700	-0.66028600	-2.37984800
H	-5.73049300	1.44356300	-2.79873600
H	-4.96467700	-2.69785700	-1.92680400
H	-6.54998900	-0.88946500	-2.54820600

Cu	0.00956000	-0.50478600	-0.61072600
H	0.28208200	1.77472000	-2.03732300
P	2.02640500	-0.09362900	0.29277800
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C	3.04944800	2.51039500	0.55351000
C	3.16456600	1.54808900	-1.65554800
C	3.60636200	3.68965100	0.06404900
H	2.79544100	2.40968300	1.60858500
C	3.71809400	2.72586400	-2.14300800
H	2.99925000	0.70267200	-2.32806400
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B E = -3727.374125

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C	-1.06054700	3.03424600	0.96338800
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C	-1.70746800	-1.43365800	2.85561300
H	0.38460400	1.57824600	1.70458100
Cl	-0.35849900	-2.81426200	0.04189200

TS_{B-C} E = -3727.3288

C	0.14504800	0.55507000	-1.28216400

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C	-2.77798900	1.78735200	-1.88983800
C	-3.25486900	-0.55748300	-2.16928800
C	-4.05015300	2.09952200	-2.35381000
H	-2.08400400	2.58207600	-1.61179300
C	-4.51217000	-0.24019200	-2.66678800
H	-2.93825600	-1.59874100	-2.08511400
C	-4.92580700	1.08885000	-2.74632500
H	-4.35524400	3.14311800	-2.42654500
H	-5.18278100	-1.03860900	-2.98293400
H	-5.91971500	1.33458100	-3.11615500
Cu	0.21141800	-1.30436500	-0.78165800
H	0.72202400	1.28721200	-1.85141600
P	1.77509200	0.13385400	0.29575400
C	2.28019400	1.88433200	0.18317900
C	1.98972900	2.75040000	1.23738200
C	2.89850100	2.38897800	-0.96546200
C	2.31144300	4.10182000	1.14693300
H	1.53952800	2.34575500	2.14471600
C	3.21071300	3.73988800	-1.06006100
H	3.15598300	1.71244300	-1.78341300
C	2.91559500	4.59894900	-0.00384000
H	2.09649600	4.76913300	1.98070500
H	3.69342200	4.12428800	-1.95737700
H	3.16490800	5.65645300	-0.07607000
C	3.36353500	-0.68546700	-0.09170600
C	3.43645700	-1.62644300	-1.11529300
C	4.51225700	-0.35736400	0.63583200
C	4.64951800	-2.23430500	-1.42284000
H	2.52294800	-1.90320400	-1.64260700

C	5.71973800	-0.97507600	0.33821600
H	4.45301200	0.38044700	1.43688400
C	5.78842500	-1.90937300	-0.69472500
H	4.69956500	-2.97183100	-2.22167700
H	6.61317300	-0.72610900	0.90908800
H	6.73786900	-2.38915400	-0.92839400
O	1.29577300	-0.11613700	1.73544300
N	-1.25095000	0.87367500	2.16414200
N	-3.17773400	-0.35836200	1.66576600
N	-1.18345600	-1.42064200	2.23574400
H	-0.16215200	-1.30933600	2.22140200
C	-1.87691300	-0.30339700	1.99879700
C	-1.84310200	2.10185500	1.66927100
H	-1.68701700	2.19403400	0.58196400
H	-1.33317700	2.94232200	2.15440500
C	-3.31963500	2.08447000	2.00964400
H	-3.43741200	2.09056800	3.10240900
H	-3.82027600	2.97568000	1.61203000
C	-3.96499600	0.84830600	1.41578800
H	-4.96477800	0.68478300	1.84457300
H	-4.08502600	0.96335400	0.32615700
H	-4.37152800	-1.37515100	0.31094500
H	-4.52511800	-1.93319000	1.99478700
C	-2.77336700	-2.68158000	0.94826300
H	-3.26606900	-3.64852000	0.79562100
H	-2.20064200	-2.43503000	0.04154700
H	-2.28096800	-3.02436100	3.03769900
H	-0.98182600	-3.44590400	1.88230200
C	-3.80504500	-1.60912100	1.22563300
C	-1.78718900	-2.73699900	2.09556600
H	-0.22346100	0.77624100	2.15048200

Cl	0.54121500	-3.35954400	-0.27875000

TS'$_{B\text{-}C'}$ E = -3727.317962

C	-1.39995900	-2.47564000	-0.69773000
C	-0.23038400	-2.89361900	-0.91379600
Cu	1.16957500	-1.69819900	-1.31221900
P	-1.09133800	0.37649600	0.02134600
C	-2.71311900	1.07201800	0.54496800
C	-3.69969600	1.35236300	-0.40499300
C	-3.01376800	1.22202400	1.90056300
C	-4.96075900	1.78000900	-0.00908200
H	-3.46990400	1.23103600	-1.46666800
C	-4.27482800	1.65551300	2.30056100
C	-5.25230400	1.92922300	1.34689000
H	-5.72350000	1.99631300	-0.75708900
H	-6.24149600	2.26340100	1.65833900
C	-0.33045200	1.90865500	-0.69890200
C	0.56955200	1.71938600	-1.74843200
C	-0.53722200	3.20620600	-0.21548000
C	1.25856500	2.79090300	-2.30888200
H	0.75905400	0.70388800	-2.09939300
C	0.13904300	4.28469800	-0.77974700
H	-1.24218200	3.37089600	0.60124300
C	1.03871000	4.07784000	-1.82606000
H	1.96823700	2.61359800	-3.11655200
H	-0.03636600	5.29328300	-0.40548000
H	1.56460800	4.92416300	-2.26696900
O	-0.32663900	0.09590100	1.36917400
N	2.05111900	-1.20561000	1.56573100
N	4.12839200	-0.17348900	1.23092900
N	2.17643100	1.07945700	1.45548100

H	1.13854200	1.01421100	1.50613100
C	2.79434700	-0.10022700	1.39551200
C	2.59298400	-2.53472700	1.37245700
H	2.53032000	-2.81906100	0.30604900
H	1.97729700	-3.23985700	1.94388200
C	4.03518200	-2.54972600	1.83509700
H	4.07684900	-2.37779400	2.92038500
H	4.49610200	-3.52358600	1.63153300
C	4.79920600	-1.46377300	1.10585100
H	5.80975800	-1.34829200	1.52312000
H	4.89121000	-1.70455300	0.03344100
H	5.58109600	0.62767000	-0.00884500
H	5.51018500	1.36164100	1.60933400
C	3.99463000	2.06797600	0.21799000
H	4.57522400	2.98066900	0.03819700
H	3.57314900	1.72692100	-0.73810100
H	3.24662300	2.76073500	2.12979600
H	2.13116100	3.03116900	0.77297500
C	4.89684500	0.98540800	0.77387700
C	2.86261900	2.32847200	1.19017800
H	1.02730600	-1.02398000	1.53391200
Cl	3.03129000	-0.81683900	-1.89693000
C	-2.76787200	-2.21150300	-0.46831400
C	-3.24902700	-2.04328000	0.84453500
C	-3.67027200	-2.17755400	-1.54851000
C	-4.60247900	-1.84890200	1.06419800
C	-5.02038900	-1.97729200	-1.31567900
H	-3.28624200	-2.30471700	-2.55895800
C	-5.48710100	-1.81198400	-0.01133500
H	-5.71598500	-1.94598600	-2.15215600
H	-6.54768600	-1.64283200	0.16710500

H	0.05519600	-3.94631100	-0.94842000
H	-2.53459500	-2.02975900	1.66689500
H	-4.96993900	-1.69911600	2.07720300
H	-2.23507800	0.98824100	2.62815900
H	-4.49929100	1.78008900	3.36012000

C E = -3727.396271

C	-0.58362000	0.36594900	1.06574000
C	0.55923100	-0.36456400	1.07618100
C	1.67914200	0.05430900	1.94929700
C	1.79221100	1.32658500	2.53542900
C	2.73976900	-0.84181100	2.15907900
C	2.90315000	1.68117000	3.29195800
H	0.99500200	2.05749500	2.39070300
C	3.84908800	-0.49876300	2.92187100
H	2.66215200	-1.82827700	1.69611700
C	3.94012100	0.77062900	3.48687000
H	2.96355400	2.67613000	3.73267400
H	4.64756800	-1.22424400	3.07181500
H	4.81235600	1.04982900	4.07610100
Cu	0.76453500	-1.93124000	0.05923600
H	-0.78553200	1.21360700	1.73720000
P	-1.82974100	0.09340400	-0.19195800
C	-2.83016400	1.61177800	-0.11439800
C	-3.08866500	2.29184200	-1.30544100
C	-3.30122500	2.13803100	1.09315400
C	-3.80477800	3.48600200	-1.29098100
H	-2.72390800	1.86942900	-2.24192100
C	-4.02123100	3.32701700	1.10630000
H	-3.11111900	1.60924500	2.02888400
C	-4.27033400	4.00283000	-0.08637600

H	-4.00501100	4.01089000	-2.22384000
H	-4.38962000	3.72874600	2.04892300
H	-4.83368800	4.93465200	-0.07480600
C	-2.93656800	-1.27964000	0.23306600
C	-2.42177600	-2.57918100	0.18058300
C	-4.27801200	-1.08675100	0.57258600
C	-3.23580500	-3.66646300	0.46529200
H	-1.37624600	-2.74049900	-0.08626700
C	-5.09001400	-2.17888200	0.86163000
H	-4.69958500	-0.08284400	0.60196600
C	-4.57090000	-3.46806700	0.80817300
H	-2.81981400	-4.67096100	0.41375100
H	-6.13519700	-2.01998200	1.12276700
H	-5.20855900	-4.32193300	1.03253900
O	-1.27440100	-0.07228000	-1.60063600
N	0.76920000	1.79884900	-1.70351800
N	3.00085900	1.23232500	-1.29319200
N	1.57730000	-0.22816700	-2.41980700
H	0.60142800	-0.53490000	-2.45721500
C	1.78760200	0.92844900	-1.78171300
C	0.84246500	2.97439100	-0.85594000
H	0.60877800	2.71331500	0.19039400
H	0.07853900	3.68224500	-1.19911500
C	2.23780600	3.55326200	-0.96852300
H	2.40966000	3.89441800	-1.99924600
H	2.35479900	4.41847100	-0.30560700
C	3.25119900	2.49081800	-0.59321000
H	4.27130800	2.81122700	-0.84961100
H	3.22587100	2.29231200	0.49316100
H	4.48612600	0.31947200	-0.16981100
H	4.87501900	0.52115300	-1.89336300

C	3.57559300	-1.16371500	-1.44709100
H	4.41988700	-1.84918900	-1.58029500
H	2.97958200	-1.52064300	-0.59387200
H	3.19708300	-0.90014000	-3.57281000
H	2.21270500	-2.16744100	-2.77926500
C	4.07552900	0.23986000	-1.18851600
C	2.65939100	-1.17570300	-2.65224800
H	-0.14734500	1.33928500	-1.82861400
Cl	1.04219200	-3.72676800	-1.06092600

$TS_{C\text{-}D}$ E = -3727.360317

C	-1.50754500	-1.11184300	0.21118100
C	-0.28971300	-1.74122000	0.29284700
C	-0.23233400	-3.19838000	0.32322300
C	-1.05201800	-3.96829300	1.16296100
C	0.70036500	-3.86665700	-0.48693100
C	-0.94509600	-5.35400800	1.18368200
H	-1.76184800	-3.45956700	1.81623000
C	0.78393400	-5.25056000	-0.48875300
H	1.34518600	-3.26953100	-1.13592200
C	-0.03467800	-6.00228700	0.35321600
H	-1.58227300	-5.93541700	1.84964100
H	1.49923700	-5.74801600	-1.14252200
H	0.04427600	-7.08824300	0.36848400
Cu	0.04407300	-0.87466300	-1.37354100
H	-2.46708000	-1.65986200	0.17895600
P	-1.64026800	0.62877900	0.68408900
C	-3.40887800	1.01901400	0.54923000
C	-3.94811200	1.90278000	1.48550200
C	-4.23390500	0.47600400	-0.44010200
C	-5.29403000	2.24809200	1.42749500

H	-3.29756400	2.29967900	2.26416800
C	-5.57901800	0.82258500	-0.49762600
H	-3.83104800	-0.23416900	-1.16382000
C	-6.10854100	1.71007100	0.43533300
H	-5.71065300	2.93638500	2.16130100
H	-6.21813000	0.39362800	-1.26763600
H	-7.16311900	1.97808400	0.39223000
C	-0.82147700	1.60354900	-0.62585200
C	-1.16776100	1.48059800	-1.97651600
C	0.14994000	2.53474300	-0.25315300
C	-0.55646300	2.27761500	-2.93618700
H	-1.92991800	0.76318900	-2.28624400
C	0.77257600	3.32277300	-1.21650500
H	0.39340200	2.63767600	0.80472900
C	0.41982000	3.19372300	-2.55773100
H	-0.81955500	2.16000700	-3.98514100
H	1.52539600	4.05345700	-0.91895600
H	0.90601100	3.81061500	-3.31160100
O	-1.08290600	1.01147700	2.02674700
N	1.88092200	-0.34496900	1.68813600
N	3.42451900	1.40093000	1.55430100
N	2.87817300	0.13649000	-0.32614800
H	2.20149700	-0.48967400	-0.76688700
C	2.71461100	0.40522900	0.97973900
C	1.60787500	-0.10459400	3.09518400
H	2.26052700	-0.74059700	3.71432300
H	0.56478400	-0.39074700	3.26758200
C	1.80928300	1.36117400	3.41402100
H	1.01015600	1.92472200	2.91424300
H	1.72079800	1.54039400	4.49220600
C	3.17707100	1.80590800	2.93801500

H	3.26425900	2.90160300	2.97474800
H	3.97317500	1.39490700	3.58125100
H	5.21217500	2.44969200	1.46386100
H	3.88496400	3.17380400	0.53602500
C	4.84473200	1.50402600	-0.45234200
H	5.43298300	2.19465700	-1.06777700
H	5.49482200	0.66120000	-0.17835000
H	3.02008400	1.82147600	-1.58434900
H	3.92124700	0.38756800	-2.08763900
C	4.36874000	2.21581500	0.79817500
C	3.64350100	0.98961400	-1.21627400
H	1.15596900	-0.89315800	1.13684800
Cl	1.28098800	-0.69011800	-3.12280100

D E = -3727.396443

C	-0.29762700	-1.15507600	-0.70063700
C	0.97480300	-1.25946000	-0.16384400
C	2.00486000	-2.22436700	-0.56027300
C	1.70376500	-3.46151200	-1.14266300
C	3.34480600	-1.86112600	-0.35665700
C	2.72657800	-4.32057400	-1.51906400
H	0.66393100	-3.76097400	-1.27422100
C	4.36248800	-2.72284400	-0.74421100
H	3.55367400	-0.88757900	0.09866800
C	4.05622200	-3.95077500	-1.32479900
H	2.48840900	-5.28643800	-1.96122900
H	5.40101600	-2.43467100	-0.59238500
H	4.85581400	-4.62650400	-1.62395800
Cu	0.94156000	0.10489500	-1.61920900
H	-0.65998000	-1.88701100	-1.43221000
P	-1.53602500	-0.15899800	0.17954200

C	-2.47364900	-1.36549000	1.15325700
C	-2.38608500	-1.27852500	2.54326300
C	-3.20707800	-2.39991300	0.56413400
C	-3.03320600	-2.21837800	3.33980100
H	-1.81156800	-0.46389600	2.98476400
C	-3.85182600	-3.33653900	1.36206900
H	-3.28603500	-2.46471100	-0.52256600
C	-3.76315500	-3.24537500	2.74992600
H	-2.96790600	-2.14798600	4.42408400
H	-4.42552400	-4.13964700	0.90274700
H	-4.26851300	-3.98057500	3.37402600
C	-2.65345300	0.45610400	-1.10548500
C	-4.02434400	0.57833100	-0.85754100
C	-2.13199900	0.92081700	-2.31643300
C	-4.85943500	1.14543100	-1.81299500
H	-4.44003000	0.22535600	0.08641000
C	-2.96740000	1.48772100	-3.27016900
H	-1.06098600	0.85144500	-2.51563400
C	-4.33170100	1.59775800	-3.01944700
H	-5.92619000	1.23566300	-1.61569400
H	-2.54753200	1.84578000	-4.20801500
H	-4.98811500	2.04030500	-3.76689800
O	-0.90352600	0.89328600	1.03884100
N	2.78122900	0.84995700	1.44804900
N	1.32893500	2.49973000	2.35998600
N	1.97483200	2.52526800	0.11579400
H	2.49834900	2.06128400	-0.61698500
C	2.03222300	1.90610000	1.33753400
C	2.88443200	0.27604900	2.77038300
H	3.65859300	0.79250300	3.37056400
H	3.22141200	-0.76866200	2.67158900

C	1.55634400	0.33513400	3.51030700
H	0.80466300	-0.23502800	2.94268100
H	1.62447200	-0.10333600	4.51527100
C	1.10929200	1.77927200	3.60575200
H	0.03341500	1.82859600	3.84238700
H	1.64101400	2.29721400	4.42359700
H	0.38611000	4.21891000	3.04250400
H	-0.62333100	3.16331600	2.01964700
C	0.74561000	4.40865200	0.91587900
H	-0.05521900	5.13093200	0.71200000
H	1.67594900	4.96832800	1.08890200
H	-0.01689800	2.95666000	-0.48012800
H	1.26228200	3.98764100	-1.15919300
C	0.38870200	3.58975800	2.13808800
C	0.93982900	3.46391400	-0.25210800
H	1.24850700	-0.60633800	0.67796100
Cl	1.72556500	1.43476200	-3.05804000

$TS_{A\text{-}B'}$ E = -3727.327084

C	0.97205600	1.09263300	0.33134300
C	0.03086100	1.88904800	0.47408200
C	-1.10353700	2.74905400	0.58072600
C	-2.17663900	2.38672800	1.41150400
C	-1.22086100	3.90863800	-0.20180000
C	-3.33622900	3.14865700	1.44077000
H	-2.09307400	1.47937600	2.01020700
C	-2.37756600	4.67668700	-0.15553000
H	-0.39425800	4.18726100	-0.85411400
C	-3.44179300	4.29686600	0.65902200
H	-4.16550300	2.84133300	2.07789300
H	-2.45353100	5.57424600	-0.76808100

H	-4.35215900	4.89370200	0.68222500
Cu	0.17820100	-0.59669900	-0.10205700
Cl	1.41784100	-2.65705700	-0.47997900
H	2.71209800	0.98587500	0.56498200
P	-1.77532200	-1.47950200	-0.46295600
C	-2.88076600	-0.56437300	-1.57277000
C	-4.07694300	-1.10159900	-2.05808500
C	-2.53409200	0.74987300	-1.88667200
C	-4.91555700	-0.32326600	-2.84510200
H	-4.34562900	-2.12872900	-1.80901500
C	-3.38693500	1.53809000	-2.65401600
H	-1.58965600	1.14777100	-1.50968200
C	-4.57528500	0.99857900	-3.13458400
H	-5.84589500	-0.74074400	-3.22796200
H	-3.11906900	2.57172900	-2.87027400
H	-5.24397300	1.60924900	-3.74005400
C	-2.83761000	-1.76872100	0.98499100
C	-2.59555000	-2.89940100	1.76940500
C	-3.78498400	-0.83148400	1.40595300
C	-3.30307700	-3.09741700	2.94959000
H	-1.85378600	-3.62683300	1.43889400
C	-4.48395300	-1.02704500	2.59245800
H	-3.98203900	0.05290300	0.79799500
C	-4.24582100	-2.16046500	3.36491800
H	-3.11519300	-3.98596000	3.55064400
H	-5.22481900	-0.29455600	2.91171100
H	-4.79535400	-2.31421000	4.29251200
O	-1.67443800	-2.97983900	-1.11060600
H	-0.71914300	-3.21022600	-1.13989500
N	3.76568600	1.04610100	0.70788900
N	5.87794900	0.31619900	0.03994500

N	3.96347200	-0.87728200	-0.52969100
H	2.96325800	-1.06895400	-0.38601300
C	4.53212900	0.16523500	0.07665000
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H	4.55281800	1.98622200	2.41889100
H	3.51658800	2.97415900	1.37496200
C	5.54357800	2.68104100	0.62671600
H	5.25930100	3.01419800	-0.38127100
H	6.01916400	3.52627400	1.13830100
C	6.52396500	1.52827500	0.53122200
H	7.34428900	1.76942600	-0.16115500
H	6.98028000	1.32476200	1.51522700
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C	6.06261700	-2.06680300	-0.54121200
H	6.69308200	-2.78317500	-1.08076800
H	5.90107400	-2.45922900	0.47242700
H	4.86976000	-1.60447500	-2.28528500
H	4.11666600	-2.80372400	-1.21365000
C	6.76385900	-0.72454100	-0.47353200
C	4.72508500	-1.89246700	-1.23122800

B' E = -3727.343099

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C	-1.20690800	1.72678800	0.01333000
C	-2.15985600	2.78097500	0.11431500
C	-2.19493500	3.83125500	-0.81970600
C	-3.15032300	2.74789000	1.11358900
C	-3.19104100	4.79753800	-0.76374300
H	-1.42988900	3.86650600	-1.59368600
C	-4.14295300	3.71794400	1.16545800

H	-3.12277400	1.93865200	1.84377300
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H	-3.20245200	5.60143800	-1.49869400
H	-4.89948700	3.67429600	1.94862500
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Cu	0.71094800	-0.68216000	-0.16562600
Cl	0.44028500	-3.01459700	-0.28976200
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P	2.91494500	-0.75556800	-0.01687100
C	3.56606200	0.03702900	1.48542700
C	4.86291500	-0.20498900	1.94742400
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H	3.35090900	1.98699400	-0.80680200
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H	-3.91978000	-4.90512900	1.04453800
H	-3.46789400	-4.26176900	-0.54448000
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C	-2.63911900	-3.16027300	1.09476100

$TS_{B'}$ E = -3727.299332

Cu	0.38873200	-1.61366300	0.67741400
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P	0.11834200	1.27429200	-0.57459600

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C	2.79329800	3.71243700	-2.64137300
H	0.86549300	2.79206800	-2.99247500
C	3.74281200	3.32775500	-0.46394000
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H	2.84783100	4.16814700	-3.62974000
H	4.53741000	3.48886800	0.26418700
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C	4.64296500	-1.33024600	0.11118400
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H	4.72698800	-0.27080100	-0.12822100
C	5.63498200	-3.48954600	0.52434500
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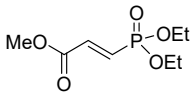
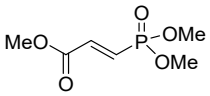
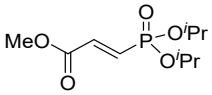
7. Characterization Data



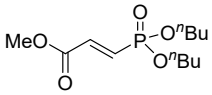
Methyl (E)-3-(diethoxyphosphoryl)acrylate (**3aa**)[10]. 81% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.96-6.65 (m, 2H), 4.18-4.08 (m, 4H), 3.80 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.10 (d, *J* = 28.2 Hz), 136.94 (d, *J* = 7.0 Hz), 132.49 (d, *J* = 184.2 Hz), 62.65 (d, *J* = 5.7 Hz), 52.55, 16.51 (d, *J* = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 14.36. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 223.0730; Found 223.0738.



Methyl (E)-3-(dimethoxyphosphoryl)acrylate (**3ab**)[11]. 49% yield. Light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.93-6.67 (m, 2H), 3.80 (d, $J_{P\text{-}H}$ = 5.3 Hz, 6H), 3.75 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.90 (d, *J* = 28.4 Hz), 137.81 (d, *J* = 7.1 Hz), 130.99 (d, *J* = 184.9 Hz), 53.02 (d, *J* = 5.8 Hz), 52.61. ^{31}P NMR (121 MHz, $CDCl_3$) δ 17.24. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 195.0417; Found 195.0416.

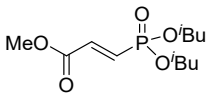


Methyl (E)-3-(diisopropoxyphosphoryl)acrylate (**3ac**)[12]. 82% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 6.95-6.61 (m, 2H), 4.77-4.63 (m, 2H), 3.79 (s, 3H), 1.32 (dd, *J* = 11.4, 6.2 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.27 (d, *J* = 28.2 Hz), 136.03 (d, *J* = 7.0 Hz), 133.99 (d, *J* = 185.0 Hz), 71.57 (d, *J* = 5.9 Hz), 52.46, 24.12 (dd, *J* = 7.3, 4.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 12.06. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 251.1043; Found 251.1047.

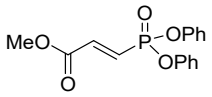


Methyl (E)-3-(dibutoxyphosphoryl)acrylate (**3ad**)[13]. 80% yield. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94-6.63 (m, 2 H), 4.03 (dd, *J* = 6.8 Hz, 4H), 3.79 (s, 3H), 1.64 (dt, *J* = 14.5, 6.7 Hz, 4H), 1.44-1.32 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.08 (d, *J* = 28.1 Hz), 136.86 (d, *J* = 7.0 Hz), 132.38 (d, *J* = 184.4 Hz), 66.30 (d, *J* = 6.0 Hz), 52.51, 32.52 (d, *J* = 6.3 Hz), 18.79, 13.67. ^{31}P NMR (121 MHz, $CDCl_3$) δ 14.44. HRMS (ESI-TOF, m/z): HRMS (ESI)

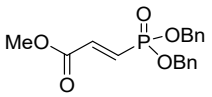
Calcd for $[M+H]^+$ 279.1356; Found 279.1366.



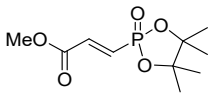
Methyl (E)-3-(diisobutoxyphosphoryl)acrylate (**3ae**). 75% yield. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 – 6.64 (m, 2H), 3.83 – 3.78 (m, 7H), 2.03 – 1.84 (m, 2H), 0.93 (d, *J* = 6.7 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.09 (d, *J* = 28.2 Hz), 136.94 (d, *J* = 7.1 Hz), 132.23 (d, *J* = 185.1 Hz), 72.43 (d, *J* = 6.3 Hz), 52.53, 29.28 (d, *J* = 6.6 Hz), 18.78. ^{31}P NMR (121 MHz, $CDCl_3$) δ 14.32. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 279.1356; Found 279.1359.



Methyl (E)-3-(diphenoxyphosphoryl)acrylate (**3af**). 83% yield. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.32 (m, 4H), 7.22-7.17 (m, 6H), 7.13-6.85 (m, 2H), 3.81 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.52 (d, *J* = 29.9 Hz), 149.83 (d, *J* = 7.8 Hz), 139.36 (d, *J* = 7.7 Hz), 130.69 (d, *J* = 186.8 Hz), 130.03 (d, *J* = 0.7 Hz), 125.68 (d, *J* = 1.2 Hz), 120.57 (d, *J* = 4.6 Hz), 52.70. ^{31}P NMR (121 MHz, $CDCl_3$) δ 7.26. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 319.0730; Found 319.0737.

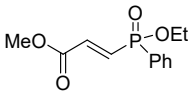


Methyl (E)-3-(bis(benzyloxy)phosphoryl)acrylate (**3ag**). 61% yield. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (m, 10H), 6.92-6.60 (m, 2H), 5.10-4.99 (m, 4H), 3.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.80 (d, *J* = 28.8 Hz), 137.05 (d, *J* = 7.2 Hz), 135.66 (d, *J* = 6.3 Hz), 131.87 (d, *J* = 185.7 Hz), 128.71, 128.14 , 68.01 (d, *J* = 5.7 Hz), 52.45. ^{31}P NMR (121 MHz, $CDCl_3$) δ 15.47. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 347.1043; Found 347.1045.

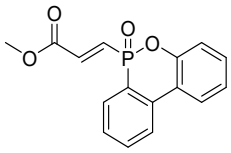


Methyl (E)-3-(4,4,5,5-tetramethyl-2-oxido-1,3,2-dioxaphospholan-2-yl)acrylate (**3ah**)[14]. 91% yield. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.93-6.70 (m, 2H), 3.78 (s, 3H), 1.50 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.90 (d, *J* = 28.8 Hz), 138.12 (d, *J* = 6.9 Hz),

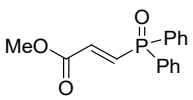
132.57 (d, *J* = 179.4 Hz), 89.37, 52.56, 24.77 (d, *J* = 4.0 Hz), 24.12 (d, *J* = 5.4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 25.44. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 249.0886; Found 249.0893.



Methyl (E)-3-(ethoxy(phenyl)phosphoryl)acrylate (**3ai**)[15]. 81% yield. Light yellow Oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.72 (m, 2H), 7.59-7.53 (m, 1H), 7.50-7.43 (m, 2H), 7.09 (dd, J_{P-H} = 20.0 Hz, J_{H-H} = 17.1 Hz, 1H), 6.67 (dd, J_{P-H} = 18.8 Hz, J_{H-H} = 17.1 Hz, 1H), 4.17-3.95 (m, 2H), 3.74 (s, 3H), 1.32 (t, J = 7.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.03 (d, *J* = 24.2 Hz), 136.31 (d, *J* = 6.4 Hz), 136.08 (d, *J* = 129.4 Hz), 133.07 (d, *J* = 2.8 Hz), 131.68 (d, *J* = 10.4 Hz), 129.18 (d, *J* = 139.2 Hz), 128.91 (d, *J* = 13.4 Hz), 52.44, 61.66 (d, *J* = 5.9 Hz), 16.49 (d, *J* = 6.6 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 28.30. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 255.0781; Found 255.0782.

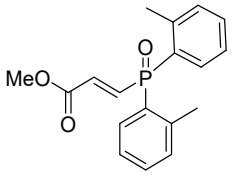


Methyl (E)-3-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)acrylate (**3aj**). 91% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 – 7.92 (m,2H), 7.88 – 7.70 (m, 1H), 7.74 (t, J_{H-H} = 7.8 Hz, 1H), 7.58 – 7.48 (m, 1H), 7.40 (t, J_{H-H} = 7.7 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.13 (dd, J_{P-H} = 20.8 Hz, J_{H-H} = 17.2 Hz, 1H), 6.75 (dd, J_{P-H} = 20.1 Hz, J_{H-H} = 17.2 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.73 (d, *J* = 25.6 Hz), 148.77 (d, *J* = 8.1 Hz), 137.60 (d, *J* = 7.1 Hz), 136.09 (d, *J* = 6.4 Hz), 134.17 (d, *J* = 131.4 Hz), 134.05 (d, *J* = 2.4 Hz), 130.98 , 130.89 (d, *J* = 11.4 Hz), 128.78 (d, *J* = 14.0 Hz), 125.26 , 125.09 , 124.05 (d, *J* = 10.1 Hz), 122.83 (d, *J* = 146.6 Hz), 122.04 (d, *J* = 3.7 Hz), 120.59 (d, *J* = 6.5 Hz), 52.64. ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.16. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 301.0624; Found 301.0631.

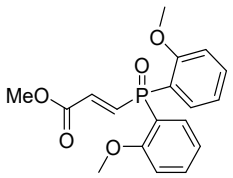


Methyl (E)-3-(diphenylphosphoryl)acrylate (**3ak**)[15]. 92% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.56 (m, 4H), 7.52-7.38 (m, 4H), 6.76 (t, *J* = 17.3 Hz, 1H), 3.71 (s, 3H). ^{13}C

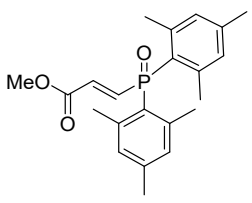
NMR (75 MHz, $CDCl_3$) δ 164.87 (d, *J* = 21.3 Hz), 138.11 (d, *J* = 93.9 Hz), 136.33 (d, *J* = 4.2 Hz), 132.40 (d, *J* = 2.8 Hz), 131.21 (d, *J* = 10.1 Hz), 130.98 (d, *J* = 106.5 Hz), 128.79 (d, *J* = 12.4 Hz), 52.35. ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.06. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 287.0832; Found 287.0834.



Methyl (E)-3-(di-o-tolylphosphoryl)acrylate (**3al**). 63% yield. White solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.52 (m, 3H), 7.45 (dd, J_{H-H} = J_{H-H} = 7.5 Hz, 2H), 7.30 – 7.25 (m, 4H), 6.88 (dd, J_{P-H} = J_{H-H} = 17.2 Hz, 1H), 3.81 (s, 3H), 2.39 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.19 (d, *J* = 21.1 Hz), 142.01 (d, *J* = 9.0 Hz), 138.70 (d, *J* = 93.0 Hz), 136.50 (d, *J* = 4.3 Hz), 132.44 (d, *J* = 5.0 Hz), 132.34 (d, *J* = 14.1 Hz), 131.98 (d, *J* = 10.9 Hz), 129.97 (d, *J* = 104.9 Hz), 125.99 (d, *J* = 12.7 Hz), 52.43 , 21.42 (d, *J* = 4.6 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.70. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 315.1145; Found 315.1153.

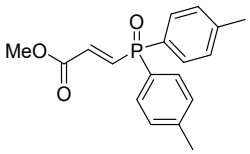


Methyl (E)-3-(bis(2-methoxyphenyl)phosphoryl)acrylate (**3am**). 86% yield. White solid. ^1H NMR (300 MHz, Chloroform-*d*) δ 7.71 (dd, J_{P-H} = 23.9, J_{H-H} =17.2 Hz, 1H), 7.58 (dd, J_{P-H} = 14.2, J_{H-H} =6.8 Hz, 2H), 7.42 (*t*, J_{H-H} = 7.7 Hz, 2H), 6.98 – 6.80 (m, 6H), 3.70 (s, 3H), 3.60 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.75 (d, *J* = 22.8 Hz), 160.50 (d, *J* = 3.2 Hz), 140.33 (d, *J* = 98.7 Hz), 134.44 (d, *J* = 3.9 Hz), 133.95 (d, *J* = 1.8 Hz), 133.51 (d, *J* = 7.7 Hz), 120.75 (d, *J* = 12.4 Hz), 119.78 (d, *J* = 110.4 Hz), 111.05 (d, *J* = 6.7 Hz), 55.47, 52.05. ^{31}P NMR (121 MHz, $CDCl_3$) δ 17.85. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 347.1043; Found 347.1048.

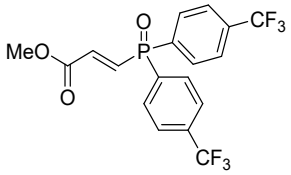


Methyl (E)-3-(dimesitylphosphoryl)acrylate (**3an**)[16]. 55% yield. White solid. ^1H NMR (300

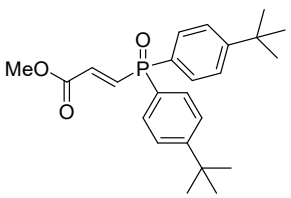
MHz, $CDCl_3$) δ 7.67 (dd, J_{P-H}= 24.5, J_{H-H}=17.0 Hz, 1H), 6.89 (dd, J_{P-H}= J_{H-H} = 17.0 Hz, 1H), 6.80 (d, J_{P-H} = 3.9 Hz, 4H), 3.74 (s, 3H), 2.28 (s, 12H), 2.23 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.91 (d, *J* = 21.0 Hz), 142.95 (d, *J* = 86.2 Hz), 141.46 (d, *J* = 2.7 Hz), 141.05 (d, *J* = 10.4 Hz), 132.18 (d, *J* = 4.0 Hz), 131.07 (d, *J* = 11.5 Hz), 128.42 (d, *J* = 104.4 Hz), 52.21, 22.89 (d, *J* = 4.9 Hz), 21.02 (d, *J* = 1.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.84. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 371.1771; Found 371.1777.



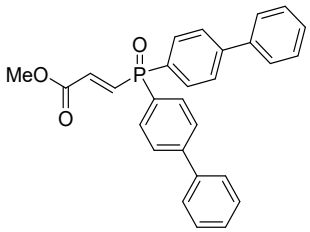
Methyl (E)-3-(di-p-tolylphosphoryl)acrylate (**3ao**). 96% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.46 (m, 5H), 7.29 (dd, J_{H-H} = 7.9, J_{H-H} = 2.5 Hz, 4H), 6.78 (dd, J_{P-H} = J_{H-H} = 17.2 Hz, 1H), 3.79 (s, 3H), 2.40 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.18 (d, *J* = 21.2 Hz), 143.04 (d, *J* = 2.8 Hz), 138.83 (d, *J* = 93.9 Hz), 135.92 (d, *J* = 4.2 Hz), 131.40 (d, *J* = 10.5 Hz), 129.60 (d, *J* = 12.8 Hz), 127.99 (d, *J* = 109.7 Hz), 52.42, 21.71 (d, *J* = 1.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.46. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 315.1145; Found 315.1150.



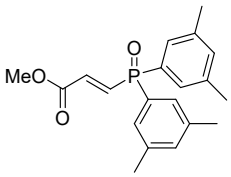
Methyl (E)-3-(bis(4-(trifluoromethyl)phenyl)phosphoryl)acrylate (**3ap**). 79% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.75 (m, 8H), 7.53 (dd, J_{P-H} = 23.8, J_{H-H} =17.5 Hz, 1H), 6.90 (dd, J_{P-H} = J_{H-H} = 17.5 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.59 (d, J_{P-C} = 21.8 Hz), 138.34 (d, J_{P-C} = 4.0 Hz), 136.08 (d, J_{P-C} = 95.5 Hz), 135.03 (d, J_{P-C} = 105.3 Hz), 134.66 (dq, J_{F-C} = 31.0, J_{P-C} = 2.7 Hz), 131.86 (d, *J* = 10.4 Hz), 126.03 (dq, *J* = 12.2, *J* = 3.5 Hz), 123.38 (d, J_{F-C} = 272.7 Hz), 52.75. ^{31}P NMR (121 MHz, $CDCl_3$) δ 19.66. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 423.0579; Found 423.0583.



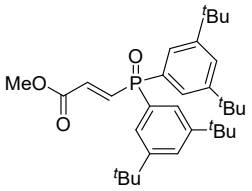
Methyl (E)-3-(bis(4-(tert-butyl)phenyl)phosphoryl)acrylate (**3aq**). 76% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-7.44 (m, 9H), 6.76 (dd, J_{P-H} = J_{H-H} = 17.2 Hz), 3.74 (s, 3H), 1.28 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.09 (d, *J* = 21.2 Hz), 155.85 (d, *J* = 2.6 Hz), 138.90 (d, *J* = 93.5 Hz), 135.68 (d, *J* = 4.1 Hz), 131.20 (d, *J* = 10.4 Hz), 127.89 (d, *J* = 109.6 Hz), 125.79 (d, *J* = 12.6 Hz), 52.33, 35.02, 31.05. ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.86. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 399.2084; Found 399.2085.



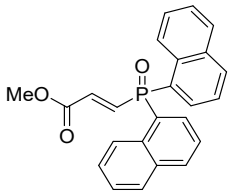
Methyl (E)-3-(di([1,1'-biphenyl]-4-yl)phosphoryl)acrylate (**3ar**). 35% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.56 (m, 13H), 7.49-7.37 (m, 6H), 6.90 (dd, J_{P-H} = J_{H-H} =17.3 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.15 (d, *J* = 21.3 Hz), 145.40 (d, *J* = 2.7 Hz), 139.77, 138.34 (d, *J* = 94.4 Hz), 136.52 (d, *J* = 4.0 Hz), 131.95 (d, *J* = 10.4 Hz), 129.72 (d, *J* = 108.0 Hz), 129.09, 128.41, 127.65 (d, *J* = 12.7 Hz), 127.38, 52.55. ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.97. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 439.1458; Found 439.1463.



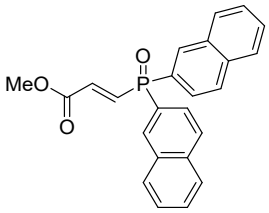
Methyl (E)-3-(bis(3,5-dimethylphenyl)phosphoryl)acrylate (**3as**). 64% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (dd, J_{P-H} = 22.0, J_{H-H} = 17.2 Hz, 1H), 7.26 (d, J_{P-H} = 12.7 Hz, 4H), 7.13 (s, 2H), 6.77 (dd, J_{H-H} = 17.2 Hz, 1H), 3.75 (s, 3H), 2.29 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.19 (d, *J* = 21.1 Hz), 138.78 (d, *J* = 93.0 Hz), 138.58 (d, *J* = 13.0 Hz), 135.87 (d, *J* = 4.2 Hz), 134.10 (d, *J* = 2.8 Hz), 130.96 (d, *J* = 106.3 Hz), 128.75 (d, *J* = 10.1 Hz), 52.36, 21.28. ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.53. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 343.1458; Found 343.1457.



Methyl (E)-3-(bis(3,5-di-tert-butylphenyl)phosphoryl)acrylate (**3at**). 84% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.45 (m, 7H), 6.82 (dd, $J_{P\text{-}H} = J_{H\text{-}H}$ = 17.1 Hz, 1H), 3.77 (s, 3H), 1.29 (s, 36H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.40 (d, *J* = 21.0 Hz), 151.40 (d, *J* = 12.1 Hz), 139.68 (d, *J* = 91.9 Hz), 135.30 (d, *J* = 4.0 Hz), 130.15 (d, *J* = 106.4 Hz), 126.64 (d, *J* = 2.7 Hz), 125.53 (d, *J* = 10.7 Hz), 52.39, 35.16, 31.39. ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.84. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 511.3336; Found 511.3344.

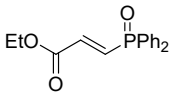


Methyl (E)-3-(di(naphthalen-1-yl)phosphoryl)acrylate (**3au**). 74% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.78 – 7.65 (m, 5H), 7.40 – 7.32 (m, 6H), 6.90 (t, $J_{P\text{-}H} = J_{H\text{-}H}$ = 17.4 Hz, 1H), 3.64 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.01 (d, *J* = 21.5 Hz), 139.24 (d, *J* = 94.7 Hz), 136.84 (d, *J* = 4.5 Hz), 133.83 (d, *J* = 10.1 Hz), 133.74 (d, *J* = 3.3 Hz), 133.17 (d, *J* = 8.8 Hz), 132.82 (d, *J* = 11.2 Hz), 129.07 (d *J* = 0.9 Hz), 127.93 (d, *J* = 105.1 Hz), 127.64, 126.65, 126.51 (d, *J* = 5.6 Hz), 124.66 (d, *J* = 14.4 Hz), 52.37. ^{31}P NMR (121 MHz, $CDCl_3$) δ 26.17. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 387.1145; Found 387.1148.

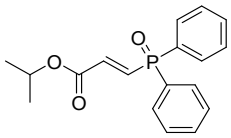


Methyl (E)-3-(di(naphthalen-2-yl)phosphoryl)acrylate (**3av**). 74% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 14.3 Hz, 2H), 7.93 – 7.71 (m, 13H), 6.94 (dd, $J_{P\text{-}H} = J_{H\text{-}H}$ = 17.3 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.06 (d, *J* = 21.4 Hz), 138.07 (d, *J* = 94.4 Hz), 136.74 (d, *J* = 4.2 Hz), 134.91 (d, *J* = 2.4 Hz), 133.49 (d, *J* = 9.6 Hz), 132.51 (d, *J* = 13.6 Hz), 128.93, 128.78, 128.59, 128.13 (d, *J* = 107.8 Hz), 127.93, 127.24, 125.84 (d, *J* = 11.1 Hz),

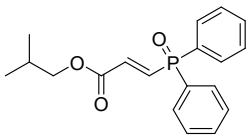
52.49. ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.61. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 387.1145; Found 387.1154.



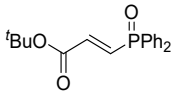
Ethyl (E)-3-(diphenylphosphoryl)acrylate (**3bk**)[17]. 72% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 4H), 7.57 – 7.42 (m, 7H), 6.76 (dd, $J_{P\text{-}H} = J_{H\text{-}H}$ =17.3 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.53 (d, J = 21.4 Hz), 137.79 (d, J = 94.2 Hz), 136.98 (d, J = 4.1 Hz), 132.47 (d, J = 2.8 Hz), 131.33 (d, J = 10.1 Hz), 131.08 (d, J = 107.2 Hz), 128.87 (d, J = 12.4 Hz), 61.53, 14.14. ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.36. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 301.0988; Found 301.0993.



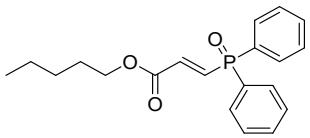
Isopropyl (E)-3-(diphenylphosphoryl)acrylate (**3ck**)[18]. 83% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.62 (m, 4H), 7.60 – 7.39 (m, 7H), 6.74 (dd, $J_{H\text{-}H} = J_{P\text{-}}$= 17.3 Hz, 1H), 5.07 (hept, $J_{H\text{-}H}$ = 6.2 Hz, 1H), 1.25 (d, $J_{H\text{-}H}$ = 6.3 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.10 (d, J = 21.3 Hz), 137.56 (d, J = 4.2 Hz), 137.53 (d, J = 94.3 Hz), 132.46 (d, J = 2.8 Hz), 131.39 (d, J = 10.1 Hz), 131.24 (d, J = 107.1 Hz), 128.89 (d, J = 12.4 Hz), 69.25, 21.80. ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.32. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 315.1145; Found 315.1149.



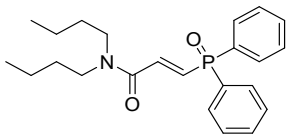
Isobutyl (E)-3-(diphenylphosphoryl)acrylate (**3dk**). 79% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 – 7.64 (m, 4H), 7.60 – 7.42 (m, 7H), 6.83 (dd, $J_{P\text{-}H} = J_{H\text{-}H}$ = 17.3 Hz, 1H), 3.95 (d, $J_{H\text{-}H}$ = 6.6 Hz, 2H), 1.94 (m, 1H), 0.91 (d, J = 6.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.70 (d, J = 21.3 Hz), 137.85 (d, J = 94.1 Hz), 137.03 (d, J = 4.2 Hz), 132.50 (d, J = 2.8 Hz), 131.37 (d, J = 10.1 Hz), 131.17 (d, J = 107.2 Hz), 128.92 (d, J = 12.4 Hz), 71.59, 27.71, 19.10. ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.24. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 329.1301; Found 329.1306.



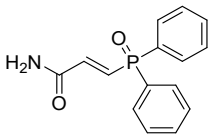
tert-Butyl (E)-3-(diphenylphosphoryl)acrylate (**3ek**). 96% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.68 (m, 4H), 7.59-7.31 (m, 7H), 6.72 (dd, $J_{P-H} = J_{H-H}$ =17.3 Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.69 (d, *J* = 21.3 Hz), 138.99 (d, *J* = 4.1 Hz), 136.48 (d, *J* = 94.8 Hz), 132.38 (d, *J* = 2.8 Hz), 131.33 (d, *J* = 10.1 Hz), 131.27 (d, *J* = 107.0 Hz), 128.83 (d, *J* = 12.4 Hz), 82.08, 27.96. ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.53. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 329.1301; Found 329.1303.



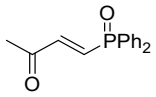
Pentyl (E)-3-(diphenylphosphoryl)acrylate (**3fk**). 85% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.62 (m, 4H), 7.59 – 7.43 (m, 7H), 6.79 (t, *J* = 17.3 Hz, 1H), 4.16 (t, *J* = 6.7 Hz, 1H), 1.74 – 1.55 (m, 2H), 1.39 – 1.20 (m, 4H), 0.87 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 164.70 (d, *J* = 21.3 Hz), 137.82 (d, *J* = 94.2 Hz), 137.04 (d, *J* = 4.2 Hz), 132.48 (d, *J* = 2.8 Hz), 131.37 (d, *J* = 10.1 Hz), 131.18 (d, *J* = 107.2 Hz), 128.90 (d, *J* = 12.4 Hz), 65.71, 28.11 (d, *J* = 14.7 Hz), 22.32, 14.01. ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.26. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 343.1458; Found 343.1465.



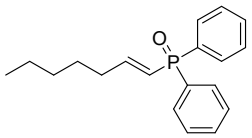
(E)-N,N-Dibutyl-3-(diphenylphosphoryl)acrylamide (**3gk**). 81% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.65 (m, 4H), 7.64 – 7.23 (m, 8H), 3.48 – 3.19 (m, 4H), 1.66 – 1.46 (m, 4H), 1.41 – 1.19 (m, 4H), 0.99 – 0.75 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.62 (d, *J* = 18.3 Hz), 136.84 (d, *J* = 4.4 Hz), 134.70 (d, *J* = 97.0 Hz), 132.25 (d, *J* = 2.7 Hz), 131.96 (d, *J* = 108.7 Hz), 131.31 (d, *J* = 10.1 Hz), 128.80 (d, *J* = 12.3 Hz), 48.08, 46.85, 32.02, 29.86, 20.32, 20.02, 13.94, 13.85. ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.95. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 384.2087; Found 384.2092.



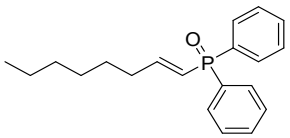
(E)-3-(Diphenylphosphoryl)acrylamide (**3hk**)[19]. 92% yield. White solid. ^{1}H NMR (300 MHz, d_6-DMSO) δ 7.91 (s, 2H), 7.76 – 7.62 (m, 4H), 7.61 – 7.42 (m, 8H), 6.88 (dd, $J_{H\text{-}H}$ = 18.1 Hz, $J_{P\text{-}H}$ =16.9 Hz, 1H). ^{13}C NMR (75 MHz, d_6-DMSO) δ 164.31 (d, *J* = 19.0 Hz), 140.44 (d, *J* = 3.3 Hz), 133.15 (d, *J* = 95.0 Hz), 132.69 (d, *J* = 104.5 Hz), 132.15 (d, *J* = 2.6 Hz), 130.75 (d, *J* = 10.0 Hz), 128.94 (d, *J* = 12.0 Hz). ^{31}P NMR (121 MHz, d_6-DMSO) δ 19.75. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 272.0835; Found 272.0834.



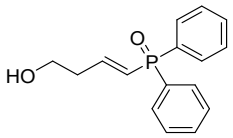
(E)-4-(Diphenylphosphoryl)but-3-en-2-one (**3ik**)[20]. 81% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.67 (m, 4H), 7.61-7.47 (m, 6H), 7.41-7.27 (m, 1H), 7.06 (dd, $J_{P\text{-}H}$ = $J_{H\text{-}H}$ = 17.6 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.47 (d, *J* = 17.2 Hz), 142.88 (d, *J* = 2.2 Hz), 135.34 (d, *J* = 93.5 Hz), 132.62 (d, *J* = 2.8 Hz), 131.43 (d, *J* = 10.1 Hz), 131.19 (d, *J* = 107.1 Hz), 129.02 (d, *J* = 12.4 Hz), 29.11. ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.92. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 271.0882; Found 271.0887.



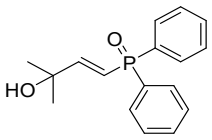
(E)-Hept-1-en-1-yldiphenylphosphine oxide (**3jk**)[21]. 91% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 4H), 7.53 – 7.35 (m, 6H), 6.71 (ddt, $J_{P\text{-}H}$ = 19.6 Hz, $J_{H\text{-}H}$ = 17.0 Hz, $J_{H\text{-}H}$ = 6.5 Hz, 1H), 6.20 (dd, $J_{P\text{-}H}$ = 24.7 Hz, $J_{H\text{-}H}$ = 17.0 Hz, 1H), 2.27 (q, *J* = 6.9 Hz, 2H), 1.45 (p, *J* = 6.9 Hz, 2H), 1.32 – 1.20 (m, 4H), 0.86 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.07 (d, *J* = 2.0 Hz), 133.15 (d, *J* = 104.7 Hz), 131.74 (d, *J* = 2.7 Hz), 131.34 (d, *J* = 9.9 Hz), 128.55 (d, *J* = 12.0 Hz), 121.49 (d, *J* = 103.4 Hz), 34.55 (d, *J* = 16.8 Hz), 31.38, 27.60, 22.46, 14.06. ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.84. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 299.1559; Found 299.1561.



(E)-Oct-1-en-1-yldiphenylphosphine oxide (**3kk**)[22]. 92% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 – 7.61 (m, 4H), 7.55 – 7.36 (m, 6H), 6.72 (ddt, J_{P-H} = 19.6 Hz, J_{H-H} = 17.0 Hz, J_{H-H} = 6.5 Hz, 1H), 6.21 (ddt, J_{P-H} = 24.7 Hz, J_{H-H} = 17.0 Hz, J_{H-H} = 1.4 Hz, 1H), 2.37 – 2.18 (m, 2H), 1.53 – 1.39 (m, 2H), 1.37 – 1.18 (m, 6H), 0.85 (t, J_{H-H} = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.13 (d, *J* = 1.9 Hz), 133.22 (d, *J* = 104.8 Hz), 131.79 (d, *J* = 2.7 Hz), 131.39 (d, *J* = 9.9 Hz), 128.60 (d, *J* = 12.0 Hz), 121.55 (d, *J* = 103.4 Hz), 34.65 (d, *J* = 16.9 Hz), 31.65, 28.92, 27.94 (d, *J* = 1.0 Hz), 22.66, 14.16. ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.85. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 313.1716; Found 313.1718.

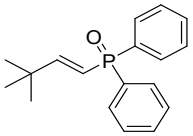


(E)-(4-Hydroxybut-1-en-1-yl)diphenylphosphine oxide (**3lk**)[23]. 75% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 6H), 7.54 – 7.38 (m, 7H), 6.72 (ddt, J_{P-H} = 19.6, J_{H-H} = 17.1 Hz, J_{H-H} = 6.7 Hz, 1H), 6.33 (ddt, J_{P-H} = = 24.7 Hz, J_{H-H} = 17.1 Hz, J_{H-H} = 1.3 Hz, 1H), 3.77 – 3.65 (m, 2H), 3.40 (s, 1H), 2.53 (qt, J_{H-H} = 6.4 Hz, J_{P-H} =1.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.79 (d, *J* = 2.2 Hz), 132.74 (d, *J* = 105.3 Hz), 131.96 (d, *J* = 2.7 Hz), 131.39 (d, *J* = 10.0 Hz), 128.69 (d, *J* = 12.1 Hz), 123.89 (d, *J* = 102.3 Hz), 60.62 , 37.94 (d, *J* = 16.7 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.14. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 273.1039; Found 273.1037.

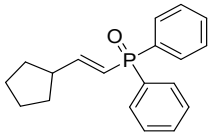


(E)-(3-Hydroxy-3-methylbut-1-en-1-yl)diphenylphosphine oxide (**3mk**)[23]. 87% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 4H), 7.51 – 7.35 (m, 6H), 6.81 (dd, J_{P-H} = 19.9 Hz, J_{H-H} = 16.9 Hz, 1H), 6.50 (dd, J_{P-H} = 24.9 Hz, J_{H-H} = 16.9 Hz, 1H), 3.40 (s, 1H), 1.32 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.89 (d, *J* = 1.8 Hz), 132.95 (d, *J* = 105.4 Hz), 131.84 (d, *J* = 2.7 Hz), 131.34 (d, *J* = 10.0 Hz), 128.62 (d, *J* = 12.1 Hz), 117.58 (d, *J* = 102.6 Hz), 71.72 (d, *J* = 15.5 Hz), 29.34 (d, *J* = 1.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.32. HRMS (ESI-TOF, m/z): HRMS

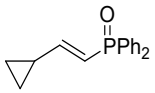
(ESI) Calcd for $[M+H]^+$ 287.1195; Found 287.1199.



(E)-(3,3-Dimethylbut-1-en-1-yl)diphenylphosphine oxide (**3nk**)[24]. 85% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.60 (m, 4H), 7.55 – 7.37 (m, 6H), 6.75 (dd, J_{P-H} = 20.4 Hz, J_{H-H} = 17.3 Hz, 1H), 6.09 (dd, J_{P-H} = 24.5, J_{H-H} = 17.3 Hz, 1H), 1.08 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.38 (d, *J* = 1.2 Hz), 133.36 (d, *J* = 104.6 Hz), 131.73 (d, *J* = 2.7 Hz), 131.35 (d, *J* = 9.8 Hz), 128.58 (d, *J* = 12.0 Hz), 116.40 (d, *J* = 103.4 Hz), 35.37 (d, *J* = 14.9 Hz), 28.71. ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.25. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 285.1403; Found 285.1405.

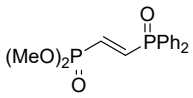


(E)-(2-Cyclopentylvinyl)diphenylphosphine oxide (**3ok**)[24]. 83% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 – 7.63 (m, 4H), 7.55 – 7.38 (m, 6H), 6.72 (ddd, J_{P-H}= 19.5 Hz, J_{H-H} = 17.0 Hz, J_{H-H} = 7.5 Hz, 1H), 6.17 (ddd, *J* = 24.9 Hz, J_{H-H} = 17.0 Hz, J_{H-H} = 1.1 Hz, 1H), 2.75 – 2.58 (m, 1H), 1.91 – 1.77 (m, 2H), 1.73 – 1.50 (m, 4H), 1.48 – 1.33 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.95 (d, *J* = 1.7 Hz), 133.34 (d, *J* = 104.6 Hz), 131.73 (d, *J* = 2.7 Hz), 131.36 (d, *J* = 9.9 Hz), 128.57 (d, *J* = 12.0 Hz), 119.34 (d, *J* = 103.3 Hz), 45.06 (d, *J* = 16.3 Hz), 32.33, 25.28. ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.72. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 297.1403; Found 297.1410.

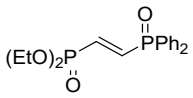


(E)-(2-Cyclopropylvinyl)diphenylphosphine oxide (**3pk**)[24]. 52% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.63 (m, 4H), 7.49-7.37 (m, 6H), 6.30-6.06 (m, 2H), 1.70-1.59 (m, 1H), 0.91-0.85 (m, 2H), 0.62-0.57 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.75 (d, *J* = 3.1 Hz), 133.52 (d, *J* = 105.1 Hz), 131.63 (d, *J* = 2.7 Hz), 131.26 (d, *J* = 9.9 Hz), 128.50 (d, *J* = 12.0 Hz), 117.71 (d, *J* = 106.3 Hz), 16.68, 16.40, 8.55. ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.26. HRMS (ESI-TOF, m/z):

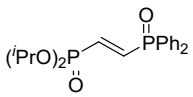
HRMS (ESI) Calcd for $[M+H]^+$ 269.1090; Found 269.1093.



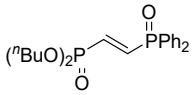
Dimethyl (E)-(2-(diphenylphosphoryl)vinyl)phosphonate (**3qk**). 63% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 4H), 7.60 – 7.34 (m, 7H), 6.98 (ddd, $J_{P\text{-}P}$ = 21.6 Hz, $J_{P\text{-}H}$ = $J_{H\text{-}H}$ = 18.6 Hz, 1H), 3.77 (d, J = 11.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.58 (dd, J = 87.2 Hz, J = 2.1 Hz), 134.34 (d, J = 177.4 Hz), 132.47 (d, J = 2.8 Hz), 131.23 (d, J = 10.1 Hz), 130.80 (d, J = 106.1 Hz), 128.86 (d, J = 12.3 Hz), 52.88 (d, J = 5.9 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 18.93 (dd, $J_{P\text{-}P}$ = 603.5 Hz, $J_{P\text{-}P}$ = 69.1 Hz). HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 337.0753; Found 337.0760.



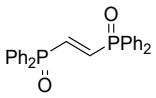
Diethyl (E)-(2-(diphenylphosphoryl)vinyl)phosphonate (**3rk**). 77% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 4H), 7.61 – 7.33 (m, 7H), 6.99 (ddd, $J_{P\text{-}P}$ = 21.5, $J_{P\text{-}H}$ = $J_{H\text{-}H}$ = 18.6 Hz, 1H), 4.12 (dq, $J_{H\text{-}H}$ = 7.1, $J_{P\text{-}H}$ =2.2 Hz, 4H), 1.33 (t, $J_{H\text{-}H}$ = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.47 (dd, J = 87.9 Hz,, J = 1.9 Hz), 135.91 (d, J = 176.8 Hz), 132.42 (d, J = 2.7 Hz), 131.26 (d, J = 10.1 Hz), 130.98 (d, J = 106.1 Hz), 128.84 (d, J = 12.3 Hz), 62.52 (d, J = 5.9 Hz), 16.34 (d, J = 6.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 17.61 (dd, $J_{P\text{-}P}$ = 963.6, $J_{P\text{-}P}$ = 69.0 Hz). HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 365.1066; Found 365.1072.



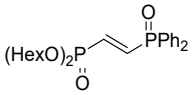
Diisopropyl (E)-(2-(diphenylphosphoryl)vinyl)phosphonate (**3sk**). 55% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72-7.66 (m, 4H), 7.60 – 7.28 (m, 7H), 7.06 – 6.85 (m, 1H), 4.69 (dh, $J_{P\text{-}H}$ = 12.3 Hz, $J_{H\text{-}H}$ = 6.2 Hz, 2H), 2.92 (d, $J_{P\text{-}H}$ = 22.1 Hz, 2H), 1.31 (dd, $J_{P\text{-}H}$ = 16.5 Hz, $J_{H\text{-}H}$ = 6.2 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.38 (dd, J = 86.7 Hz, J = 1.7 Hz), 137.67 (d, J = 177.6 Hz), 132.49 (d, J = 2.6 Hz), 131.41 (d, J = 10.0 Hz), 131.22 (d, J = 106.2 Hz), 128.93 (d, J = 12.3 Hz), 71.58 (d, J = 6.0 Hz), 24.10 (dd, J = 7.6 Hz, J = 4.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 16.66 (dd, $J_{P\text{-}P}$ = 1277.2 Hz, $J_{P\text{-}P}$ = 70.4 Hz). HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 393.1379; Found 393.1380.



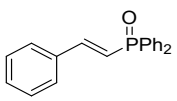
Dibutyl (E)-(2-(diphenylphosphoryl)vinyl)phosphonate (**3tk**). 56% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 4H), 7.52 – 7.22 (m, 7H), 6.91 (ddd, $J_{P\text{-}H}$ = 21.4 Hz, $J_{P\text{-}H}$ = $J_{H\text{-}H}$ = 18.6 Hz, 1H), 4.00 – 3.93 (m, 4H), 1.56 (dt, *J* = 14.6 Hz, *J* = 6.6 Hz, 4H), 1.29 (dq, *J* = 14.5 Hz, *J* = 7.3 Hz, 4H), 0.82 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.49 (dd, *J* = 87.9 Hz, *J* = 2.0 Hz), 135.96 (d, *J* = 176.7 Hz), 132.50 (d, *J* = 2.7 Hz), 131.34 (d, *J* = 10.1 Hz), 131.01 (d, *J* = 106.3 Hz), 128.91 (d, *J* = 12.3 Hz), 66.32 (d, *J* = 6.1 Hz), 32.44 (d, *J* = 6.2 Hz), 18.73, 13.61. ^{31}P NMR (121 MHz, $CDCl_3$) δ 17.77 (dd, $J_{P\text{-}P}$ = 961.6 Hz, $J_{P\text{-}P}$ = 69.4 Hz). HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 421.1692; Found 421.1695.



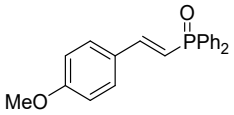
(E)-Ethene-1,2-diylbis(diphenylphosphine oxide) (**3uk**). 67% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.65 (m, 10H), 7.56 – 7.43 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.60 (ddd, $J_{P\text{-}P}$ = 86.7 Hz, $J_{P\text{-}C}$ = $J_{P\text{-}C}$ = 65.9 Hz), 132.37, 131.40 (dd, *J* = 126.3 Hz, *J* = 19.9 Hz), 131.36 (t, *J* = 5.1 Hz), 128.96 (t, *J* = 6.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.61. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 429.1168; Found 429.1170.



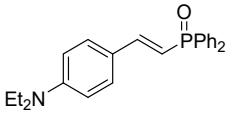
Dihexyl (E)-(2-(diphenylphosphoryl)vinyl)phosphonate (**3vk**). 60% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 4H), 7.60 – 7.32 (m, 7H), 7.00 (ddd, $J_{P\text{-}H}$ = 21.4 Hz, $J_{P\text{-}H}$ = $J_{H\text{-}H}$ = 18.7 Hz, 1H), 4.02 (td, $J_{P\text{-}H}$ = 10.3 Hz, *J* = 8.3 Hz, 4H), 1.65 (p, *J* = 6.6 Hz, 4H), 1.49 – 1.10 (m, 12H), 0.87 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.43 (dd, *J* = 88.1, 1.6 Hz), 135.96 (d, *J* = 176.9 Hz), 132.45 (d, *J* = 2.4 Hz), 131.30 (d, *J* = 10.0 Hz), 131.05 (d, *J* = 106.1 Hz), 128.86 (d, *J* = 12.3 Hz), 66.59 (d, *J* = 6.1 Hz), 31.27, 30.39 (d, *J* = 6.2 Hz), 25.13, 22.50, 14.00. ^{31}P NMR (121 MHz, $CDCl_3$) δ 17.77 (dd, $J_{P\text{-}P}$ = 956.17 Hz, $J_{P\text{-}P}$ = 65.5 Hz). HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 505.1903; Found 505.1906.



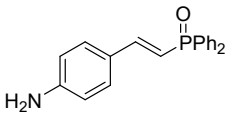
(E)-Diphenyl(styryl)phosphine oxide (**5ak**)[21]. 92% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (ddd, $J_{P\text{-}H}$ = 12.1 Hz, $J_{H\text{-}H}$ = 8.0, $J_{H\text{-}H}$ = 1.4 Hz, 4H), 7.57 – 7.35 (m, 12H), 6.84 (dd, $J_{P\text{-}H}$ = 22.4 Hz, $J_{H\text{-}H}$ = 17.4 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 147.62 (d, *J* = 3.6 Hz), 135.14 (d, *J* = 17.9 Hz), 132.97 (d, *J* = 105.9 Hz), 131.96 (d, *J* = 2.7 Hz), 131.44 (d, *J* = 10.0 Hz), 130.19, 128.92, 128.70 (d, *J* = 12.1 Hz), 127.83, 119.24 (d, *J* = 104.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.60. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 305.1090; Found 305.1093.



(E)-(4-Methoxystyryl)diphenylphosphine oxide (**5bk**)[21]. 95% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 4H), 7.55 – 7.28 (m, 9H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.67 (dd, $J_{P\text{-}H}$ = 22.3 Hz, $J_{H\text{-}H}$ = 17.4 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.20, 147.10, 133.26 (d, *J* = 105.7 Hz), 131.82 (d, *J* = 2.7 Hz), 131.41 (d, *J* = 9.9 Hz), 129.41, 128.61 (d, *J* = 12.1 Hz), 127.95 (d, *J* = 18.3 Hz), 116.13 (d, *J* = 106.4 Hz), 114.25, 55.43. ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.92. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 335.1195; Found 335.1196.

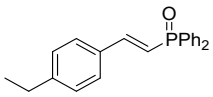


(E)-(4-(Diethylamino)styryl)diphenylphosphine oxide (**5ck**). 73% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 4H), 7.51 – 7.34 (m, 9H), 6.60 (d, *J* = 8.8 Hz, 2H), 6.49 (dd, $J_{P\text{-}H}$ = 22.4 Hz, $J_{P\text{-}H}$ = 17.3 Hz, 1H), 3.35 (q, *J* = 7.0 Hz, 4H), 1.14 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.01, 147.80 (d, *J* = 4.2 Hz), 133.68 (d, *J* = 105.2 Hz), 131.49 (d, *J* = 2.7 Hz), 131.33 (d, *J* = 9.9 Hz), 129.54, 128.39 (d, *J* = 12.0 Hz), 122.08 (d, *J* = 18.5 Hz), 111.31 (d, *J* = 109.7 Hz), 111.02, 44.36, 12.49. ^{31}P NMR (121 MHz, $CDCl_3$) δ 26.01. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 376.1825; Found 376.1831.

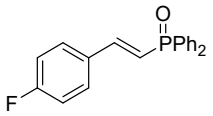


(E)-(4-Aminostyryl)diphenylphosphine oxide (**5dk**). 89% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 4H), 7.53 – 7.26 (m, 9H), 6.60 (d, *J* = 8.4 Hz, 2H), 6.53 (dd, $J_{P\text{-}H}$ = 22.3 Hz, $J_{H\text{-}H}$ = 17.3 Hz, 1H), 4.13 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.86, 147.78 (d, *J* = 4.0

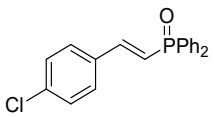
Hz), 133.48 (d, *J* = 105.4 Hz), 131.70 (d, *J* = 2.7 Hz), 131.40 (d, *J* = 9.9 Hz), 129.49, 128.54 (d, *J* = 12.1 Hz), 125.17 (d, *J* = 18.5 Hz), 114.73, 113.26 (d, *J* = 108.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 25.64. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 320.1199; Found 320.1200.



(E)-(4-Ethylstyryl)diphenylphosphine oxide (**5ek**)[25]. 86% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 4H), 7.53 – 7.42 (m, 9H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.78 (dd, J_{P-H} = 22.4 Hz, J_{P-H} = 17.4 Hz, 1H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.54 (d, *J* = 3.6 Hz), 146.81, 133.09 (d, *J* = 105.7 Hz), 132.63 (d, *J* = 18.0 Hz), 131.84 (d, *J* = 2.5 Hz), 131.39 (d, *J* = 9.9 Hz), 128.60 (d, *J* = 12.1 Hz), 128.40, 127.86, 117.88 (d, *J* = 105.3 Hz), 28.78, 15.46. ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.93. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 333.1403; Found 333.1408.

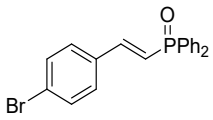


(E)-(4-Fluorostyryl)diphenylphosphine oxide (**5fk**)[21]. 90% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (ddd, *J* = 12.1 Hz, *J* = 8.0 Hz, *J* = 1.5 Hz, 4H), 7.56 – 7.30 (m, 9H), 7.09 – 7.01 (m, 2H), 6.78 (dd, *J* = 22.2 Hz, *J* = 17.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.72 (d, *J* = 251.0 Hz), 146.18 (d, *J* = 3.6 Hz), 132.87 (d, *J* = 106.0 Hz), 131.94 (d, *J* = 2.5 Hz), 131.50 (d, *J* = 3.3 Hz), 131.32 (dd, *J* = 10.0, 1.5 Hz), 129.64 (d, *J* = 8.5 Hz), 128.64 (dd, *J* = 12.1, 1.6 Hz), 118.96 (d, *J* = 103.9 Hz), 115.94 (d, *J* = 21.9 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.34. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 323.0996; Found 323.1002.

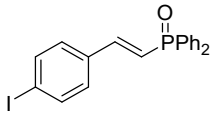


(E)-(4-Chlorostyryl)diphenylphosphine oxide (**5gk**)[21]. 73% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 4H), 7.57 – 7.29 (m, 11H), 6.83 (dd, J_{P-H} = 22.1 Hz, J_{H-H} = 17.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.09 (d, *J* = 3.7 Hz), 135.99, 133.61 (d, *J* = 18.1 Hz), 132.73 (d, *J* = 109.9 Hz), 132.04, 131.37 (d, *J* = 10.0 Hz), 129.12, 129.00, 128.71 (d, *J* = 12.2 Hz), 120.05 (d, *J* = 103.6 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.22. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd

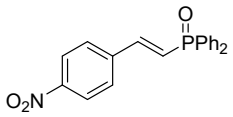
for $[M+H]^+$ 339.0700; Found 339.0707.



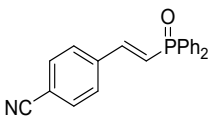
(E)-(4-Bromostyryl)diphenylphosphine oxide (**5hk**)[21]. 47% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 4H), 7.57 – 7.27 (m, 11H), 6.84 (dd, *J* = 22.1 Hz, *J* = 17.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.25 (d, *J* = 3.7 Hz), 134.08 (d, *J* = 18.0 Hz), 132.74 (d, *J* = 106.3 Hz), 132.16, 132.11 (d, *J* = 2.7 Hz), 131.45 (d, *J* = 10.0 Hz), 129.30, 128.79 (d, *J* = 12.2 Hz), 124.43, 120.20 (d, *J* = 103.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.36. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 383.0195; Found 383.0199.



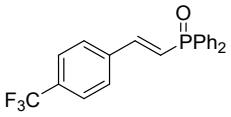
(E)-(4-Iodostyryl)diphenylphosphine oxide (**5ik**)[21]. 68% yield. Light yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.67 (m, 6H), 7.60 – 7.36 (m, 7H), 7.28 – 7.22 (m, 2H), 6.85 (dd, J_{P-H} = 22.1 Hz, J_{H-H} = 17.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.42 (d, *J* = 3.8 Hz), 138.16, 134.67 (d, *J* = 18.0 Hz), 132.76 (d, *J* = 106.1 Hz), 132.13 (d, *J* = 2.8 Hz), 131.47 (d, *J* = 10.0 Hz), 129.40 (d, *J* = 0.6 Hz), 128.81 (d, *J* = 12.2 Hz), 120.33 (d, *J* = 103.4 Hz), 96.44. ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.27. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 431.0056; Found 431.0058.



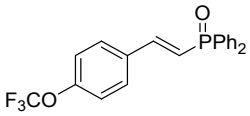
(E)-(4-Nitrostyryl)diphenylphosphine oxide (**5jk**)[21]. 57% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.77 – 7.70 (m, 4H), 7.67 – 7.44 (m, 9H), 7.04 (dd, *J* = 21.7, *J* = 17.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.38, 144.63 (d, *J* = 3.6 Hz), 141.09 (d, *J* = 17.8 Hz), 132.30 (d, *J* = 2.7 Hz), 132.21 (d, *J* = 106.7 Hz), 131.38 (d, *J* = 10.1 Hz), 128.87 (d, *J* = 12.3 Hz), 124.88 (d, *J* = 102.1 Hz), 124.20. ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.38. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 350.0941; Found 350.0942.



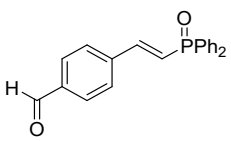
(E)-4-(2-(Diphenylphosphoryl)vinyl)benzonitrile (**5kk**)[21]. 89% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 4H), 7.65 – 7.43 (m, 11H), 6.98 (dd, *J* = 21.8, 17.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.11 (d, *J* = 3.6 Hz), 139.22 (d, *J* = 17.8 Hz), 132.66, 132.24 (d, *J* = 2.7 Hz), 132.22 (d, *J* = 106.5 Hz), 131.34 (d, *J* = 10.0 Hz), 128.82 (d, *J* = 12.3 Hz), 128.23, 123.86 (d, *J* = 100.9 Hz), 118.43, 113.18. ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.59. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 330.1042; Found 330.1047.



(E)-Diphenyl(4-(trifluoromethyl)styryl)phosphine oxide (**5lk**)[21]. 78% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (ddd, *J* = 12.2 Hz, *J* = 8.0 Hz, *J* = 1.4 Hz, 4H), 7.59 (s, 4H), 7.55 – 7.42 (m, 7H), 6.95 (dd, *J* = 22.0 Hz, *J* = 17.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.72 (d, *J* = 3.6 Hz), 138.41 (d, *J* = 16.8 Hz), 132.48 (d, *J* = 106.3 Hz), 132.14 (d, *J* = 2.7 Hz), 131.36 (d, *J* = 10.0 Hz), 131.36 , 128.77 (d, *J* = 12.2 Hz), 127.99 , 125.84 (q, *J* = 3.8 Hz), 123.85 (d, J_{F-C} = 272.3 Hz), 122.56 (d, *J* = 102.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.84. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 373.0964; Found 373.0969.

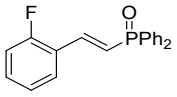


(E)-Diphenyl(4-(trifluoromethoxy)styryl)phosphine oxide (**5mk**)[21]. 60% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.64 (m, 4H), 7.54 – 7.40 (m, 9H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.82 (dd, J_{P-H} = 22.1 Hz, J_{H-H} = 17.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.21 (d, *J* = 1.7 Hz), 145.74 (d, *J* = 3.7 Hz), 133.73 (d, *J* = 18.1 Hz), 132.67 (d, *J* = 106.1 Hz), 132.02 (d, *J* = 2.7 Hz), 131.32 (d, *J* = 10.0 Hz), 129.23, 128.69 (d, *J* = 12.2 Hz), 121.13, 120.52 (d, *J* = 103.3 Hz), 120.34 (d, *J* = 257.9 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.09. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 389.0913; Found 389.0918.

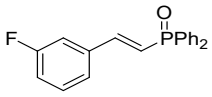


(E)-4-(2-(Diphenylphosphoryl)vinyl)benzaldehyde (**5nk**)[26]. 76% yield. White solid. ^{1}H NMR

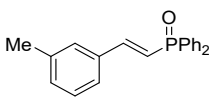
(300 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.78 – 7.63 (m, 6H), 7.58 – 7.42 (m, 7H), 7.00 (dd, J_{P-H} = 22.0 Hz, J_{H-H} = 17.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.59, 145.89 (d, *J* = 3.5 Hz), 140.66 (d, *J* = 17.6 Hz), 137.07, 132.43 (d, *J* = 106.5 Hz), 132.23 (d, *J* = 2.7 Hz), 131.43 (d, *J* = 10.0 Hz), 130.26, 128.84 (d, *J* = 12.2 Hz), 128.37, 123.37 (d, *J* = 101.6 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.85. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 333.1039; Found 333.1044.



(E)-(2-Fluorostyryl)diphenylphosphine oxide (**5ok**)[26]. 92% yield. White solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.29 (m, 13H), 7.17 - 6.94 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.16 (d, *J* = 253.2 Hz), 140.32 (dd, *J* = 4.2 Hz, *J* = 2.7 Hz), 132.73 (d, *J* = 105.9 Hz), 131.96 (d, *J* = 2.7 Hz), 131.57, 131.38 (d, *J* = 10.0 Hz), 129.28 (d, *J* = 2.3 Hz), 128.67 (d, *J* = 12.1 Hz), 124.44 (d, *J* = 3.6 Hz), 123.13 (dd, *J* = 18.1 Hz, *J* = 11.2 Hz), 122.65 (dd, *J* = 102.7, 6.9 Hz), 116.21 (d, *J* = 21.9 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.23. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 323.0996; Found 323.0998.

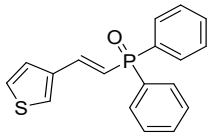


(E)-(3-Fluorostyryl)diphenylphosphine oxide (**5pk**). 84% yield. White solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 7.72(m, 4), 7.57 7.44(m, 7H), 7.37 – 7.21 (m, 3H), 7.08 – 7.01 (m, 1H), 6.87 (dd, J_{P-H} = 22.1 Hz, J_{H-H} = 17.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.01 (d, J_{F-C} = 247.2 Hz), 146.09 (dd, *J* = 3.3 Hz, *J* = 2.9 Hz), 137.36 (dd, *J* = 18.2, 7.5 Hz), 133.39, 132.03 (d, *J* = 2.7 Hz), 131.35 (d, *J* = 10.0 Hz), 130.46 (d, *J* = 8.3 Hz), 128.71 (d, *J* = 12.2 Hz), 123.88 (d, *J* = 2.4 Hz), 121.05 (d, *J* = 102.9 Hz), 116.95 (d, *J* = 21.4 Hz), 113.98 (d, *J* = 22.4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.92. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 323.0996; Found 323.0995.

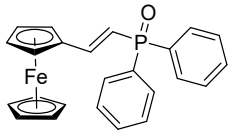


(E)-(3-Methylstyryl)diphenylphosphine oxide (**5qk**)[21]. 80% yield. White solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 4H), 7.56 - 7.42 (m, 7H), 7.34 – 7.16 (m, 4H), 6.83 (dd, J_{P-H} = 22.5 Hz, J_{P-H} = 17.4 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.74 (d, *J* = 3.6 Hz),

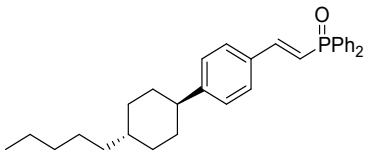
138.54, 135.06 (d, *J* = 17.8 Hz), 133.01 (d, *J* = 105.8 Hz), 131.90 (d, *J* = 2.7 Hz), 131.41 (d, *J* = 10.0 Hz), 130.98, 128.79, 128.64 (d, *J* = 12.1 Hz), 128.33, 125.09, 118.91 (d, *J* = 104.6 Hz), 21.38. ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.67. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 319.1246; Found 319.1251.



(E)-Diphenyl(2-(thiophen-3-yl)vinyl)phosphine oxide (**5rk**)[21]. 87% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.67 (m, 4H), 7.56 – 7.37 (m, 8H), 7.32 – 7.27 (m, 2H), 6.61 (dd, J_{P-H} = 22.4 Hz, J_{H-H} = 17.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.09 (d, *J* = 3.9 Hz), 138.50 (d, *J* = 19.2 Hz), 132.88 (d, *J* = 105.9 Hz), 131.93 (d, *J* = 2.8 Hz), 131.40 (d, *J* = 10.0 Hz), 128.66 (d, *J* = 12.1 Hz), 127.55, 126.96, 125.04, 118.52 (d, *J* = 105.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.88. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 311.0654; Found 311.0657.

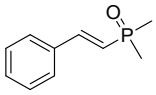


(E)-2-(Diphenylphosphoryl)ethenyl ferrocene (**5sk**)[25]. 91% yield. Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.68 (m, 4H), 7.60 – 7.24 (m, 7H), 6.37 (dd, J_{P-H} = 23.2 Hz, J_{H-H} = 17.1 Hz, 1H), 4.51 – 4.45 (m, 2H), 4.41 – 4.33 (m, 2H), 4.13 (s, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.16 (d, *J* = 4.0 Hz), 133.54 (d, *J* = 105.4 Hz), 131.79 (d, *J* = 2.7 Hz), 131.41 (d, *J* = 9.9 Hz), 128.63 (d, *J* = 12.0 Hz), 115.14 (d, *J* = 107.3 Hz), 80.25, 79.98, 70.67, 69.62, 68.31. ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.73. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 413.0758; Found 413.0766.

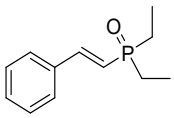


((E)-4-((1s,4r)-4-Pentylcyclohexyl)styryl)diphenylphosphine oxide (**5tk**). 87% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 4H), 7.54 – 7.41 (m, 9H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.77 (dd, *J* = 22.5, 17.4 Hz, 1H), 2.46 (t, *J* = 12.2 Hz, 1H), 1.86 (d, *J* = 11.3 Hz, 4H), 1.49 – 1.17 (m, 11H), 1.03 (dd, *J* = 11.4, 10.9 Hz, 2H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$)

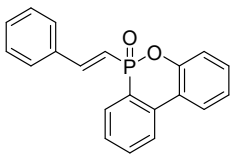
δ 150.45, 147.54 (d, *J* = 3.8 Hz), 133.12 (d, *J* = 105.7 Hz), 132.81 (d, *J* = 17.9 Hz), 131.83 (d, *J* = 2.7 Hz), 131.40 (d, *J* = 10.0 Hz), 128.60 (d, *J* = 12.1 Hz), 127.85, 127.39, 117.89 (d, *J* = 105.4 Hz), 44.56, 37.36, 37.24, 34.16, 32.22, 26.67, 22.76, 14.20. ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.78. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 457.2655; Found 457.2661.



(E)-Dimethyl(styryl)phosphine oxide (**5aw**)[27]. 58% yield. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.19 (m, 6H), 6.42 (dd, J_{P-H} = 24.8, J_{H-H} = 17.4 Hz, 1H), 1.61 (d, *J* = 13.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.90 (d, *J* = 2.8 Hz), 135.06 (d, *J* = 17.4 Hz), 130.04, 128.96, 127.62, 121.17 (d, *J* = 98.4 Hz), 17.91 (d, *J* = 73.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.82. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 181.0777; Found 181.0778.

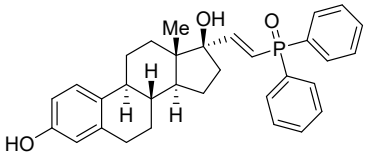


(E)-Diethyl(styryl)phosphine oxide (**5ax**)[28]. 92% yield. Corlorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.17 (m, 6H), 6.30 (dd, J_{P-H} = 24.9 Hz, J_{H-H} = 17.5 Hz, 1H), 1.99 – 1.62 (m, 4H), 1.18 (dt, J_{P-H} = 16.9 Hz, J_{H-H} = 7.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.82 (d, *J* = 2.0 Hz), 135.28 (d, *J* = 16.3 Hz), 129.96, 128.93, 127.62, 117.92 (d, *J* = 92.5 Hz), 22.15 (d, *J* = 71.1 Hz), 5.85 (d, *J* = 4.9 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 42.00. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 209.1090; Found 209.1097.

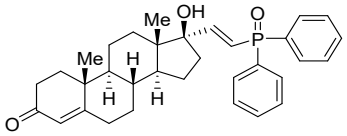


(E)-6-Styryldibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5ay**)[21]. 87% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 – 7.95 (m, 2H), 7.88 – 7.66 (m, 3H), 7.58 – 7.45 (m, 3H), 7.43 – 7.35 (m, 4H), 7.31 – 7.21 (m, 2H), 6.50 (dd, J_{P-H} = 21.8 Hz, J_{H-H} = 17.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.53 (d, *J* = 6.4 Hz), 149.11 (d, *J* = 8.2 Hz), 135.66 (d, *J* = 5.8 Hz), 134.69, 134.41, 133.18 (d, *J* = 2.3 Hz), 130.73 (d, *J* = 16.7 Hz), 130.64 (d, *J* = 12.3 Hz), 129.03, 128.43 (d, J = 14.1 Hz), 128.23, 125.97, 125.19 (d, *J* = 0.7 Hz), 124.70, 123.97, 123.84, 123.23 (d, *J* = 152.2 Hz),

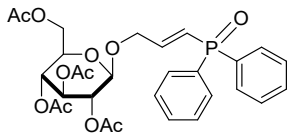
122.37, 120.77 (d, *J* = 6.1 Hz), 115.21 (d, *J* = 144.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.90. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 319.0882; Found 319.0887.



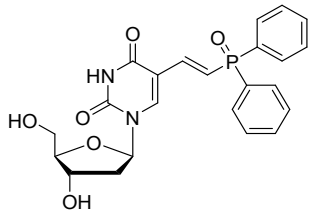
((E)-2-((8R,9S,13S,14S,17R)-3,17-Dihydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)vinyl)diphenylphosphine oxide (**5uk**)[29]. 75% yield. White solid. ^{1}H NMR (300 MHz, d_6-DMSO) δ 9.08 (s, 1H), 7.72 – 7.54 (m, 4H), 7.51 – 7.37 (m, 6H), 7.00 – 6.78 (m, 2H), 6.57 (dd, *J* = 28.0, 16.8 Hz, 1H), 6.46 – 6.39 (m, 1H), 6.36 – 6.32 (m, 1H), 5.01 (s, 1H), 2.65 – 2.53 (m, 2H), 2.14 – 2.00 (m, 1H), 1.83 – 1.56 (m, 5H), 1.51 – 1.44 (m, 1H), 1.36 – 1.01 (m, 6H), 0.77 (s, 3H). ^{13}C NMR (75 MHz, d_6-DMSO) δ 156.79, 155.02, 137.11, 134.98, 134.74, 133.62, 133.37, 131.87 – 131.64 (m), 130.81, 130.69, 130.56, 130.27, 128.75 (d, *J* = 11.5 Hz), 126.04, 117.84 (d, *J* = 100.6 Hz), 114.92, 112.66, 83.75 (d, *J* = 14.6 Hz), 49.25, 47.35, 43.24, 36.13, 32.35, 29.21, 27.22, 25.97, 23.19, 14.28. ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.44. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 499.2397; Found 499.2403.



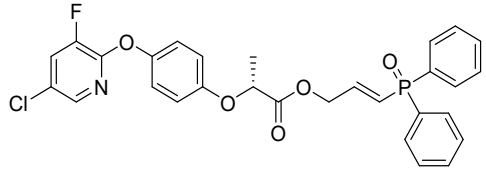
(8R,9S,10R,13S,14S,17R)-17-((E)-2-(Diphenylphosphoryl)vinyl)-17-hydroxy-10,13-dimethyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one (**5vk**)[29]. 81% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 – 7.61 (m, 4H), 7.55 – 7.33 (m, 6H), 7.04 (dd, *J* = 19.9, 16.8 Hz, 1H), 6.50 (dd, *J* = 27.3, 16.8 Hz, 1H), 5.72 (s, 1H), 2.48 – 2.20 (m, 6H), 2.10 – 1.78 (m, 6H), 1.74 – 1.33 (m, 10H), 1.16 (s, 3H), 0.96 (s, 3H), 0.92 – 0.80 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.64 , 171.06, 155.72, 134.10 (d, *J* = 3.9 Hz), 132.70 (d, *J* = 3.7 Hz), 132.01 – 131.74 (m), 131.31 (d, *J* = 10.1 Hz), 128.67 (d, *J* = 12.5 Hz), 124.09, 118.08 (d, *J* = 102.1 Hz), 85.00 (d, *J* = 14.4 Hz), 53.33, 50.18, 47.41, 38.65, 37.42, 36.40, 35.75, 34.03, 32.83, 32.48, 31.68, 23.93, 20.73, 17.48, 14.35. ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.76. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 515.2710; Found 515.2715.



(2R,3R,4S,5R,6R)-2-(Acetoxymethyl)-6-(((E)-3-(diphenylphosphoryl)allyl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**5wk**). 57% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.58 (m, 4H), 7.57 – 7.34 (m, 6H), 6.77 (ddt, *J* = 20.1, 17.0, 3.2 Hz, 1H), 6.54 (ddt, *J* = 24.8, 16.9, 1.7 Hz, 1H), 5.26 – 5.00 (m, 3H), 4.68 – 4.51 (m, 2H), 4.32 – 4.19 (m, 2H), 4.13 – 4.02 (m, 1H), 3.73 – 3.60 (m, 1H), 2.05 (s, 3H), 2.01 (s, 2H), 1.99 (s, 2H), 1.88 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.74, 170.30, 169.50, 169.39, 145.73 (d, *J* = 3.2 Hz), 133.48 (d, *J* = 6.3 Hz), 132.16 – 131.88 (m), 131.31 (d, *J* = 10.0 Hz), 131.22 (d, *J* = 9.9 Hz), 128.70 (d, *J* = 12.1 Hz), 122.07 (d, *J* = 101.9 Hz), 100.52, 72.59, 71.99, 71.21, 69.22 (d, *J* = 16.7 Hz), 68.24, 61.82, 20.85, 20.72, 20.70, 20.66. ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.02. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 589.1833; Found 589.1842.



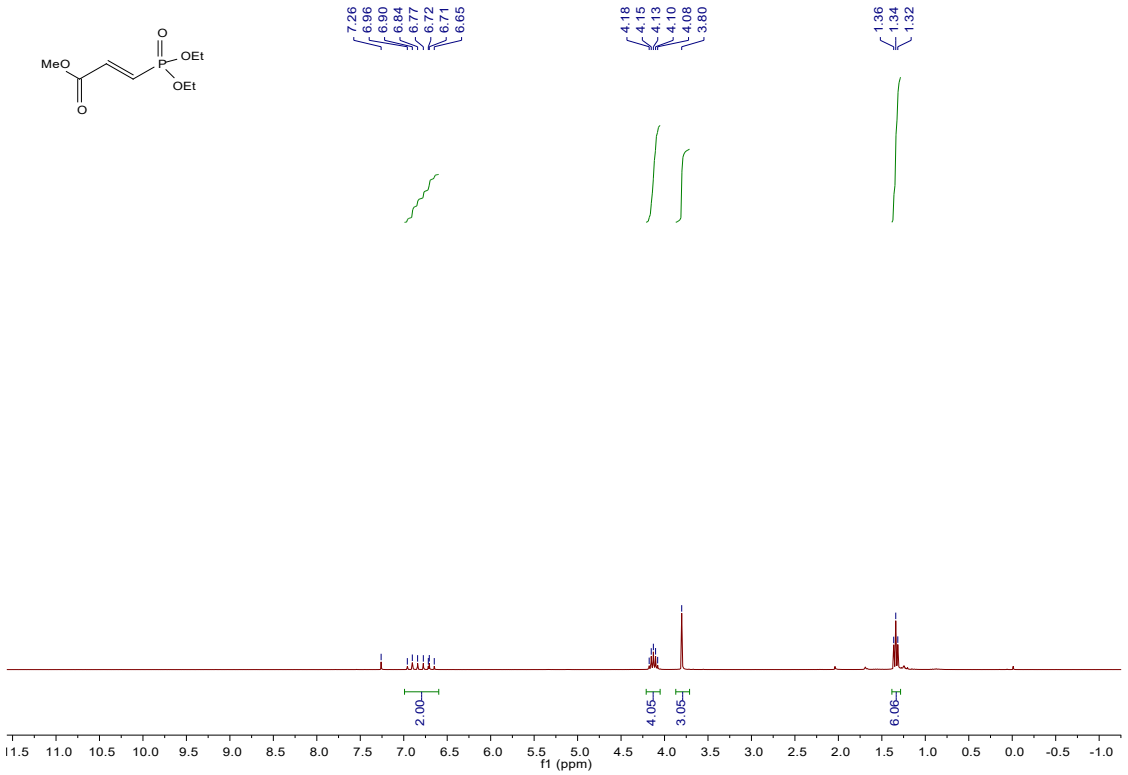
5-((E)-2-(Diphenylphosphoryl)vinyl)-1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)pyrimidine-2,4(1H,3H)-dione (**5xk**). 62% yield. White solid. ^{1}H NMR (300 MHz, d_7-DMF) δ 11.74 (s, 1H), 7.88 – 7.72 (m, 4H), 7.59 (s, 7H), 7.43 – 7.20 (m, 1H), 6.42 – 6.23 (m, 1H), 5.61 – 5.42 (m, 2H), 4.62 – 4.41 (m, 1H), 3.97 (s, 1H), 3.91 – 3.73 (m, 5H), 2.47 – 2.23 (m, 2H), 2.22 – 2.05 (m, 2H). ^{13}C NMR (75 MHz, d_7-DMF) δ 163.24, 150.71, 145.82, 144.38, 140.60 (d, *J* = 3.9 Hz), 135.79 (d, *J* = 103.7 Hz), 132.71, 131.85 (d, *J* = 9.7 Hz), 129.83 (d, *J* = 11.7 Hz), 119.57 (d, *J* = 102.9 Hz), 118.69, 110.47 (d, *J* = 17.1 Hz), 89.35, 86.38, 71.49, 62.50. ^{31}P NMR (121 MHz, d_7-DMF) δ 20.86. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 455.1366; Found 455.1371.



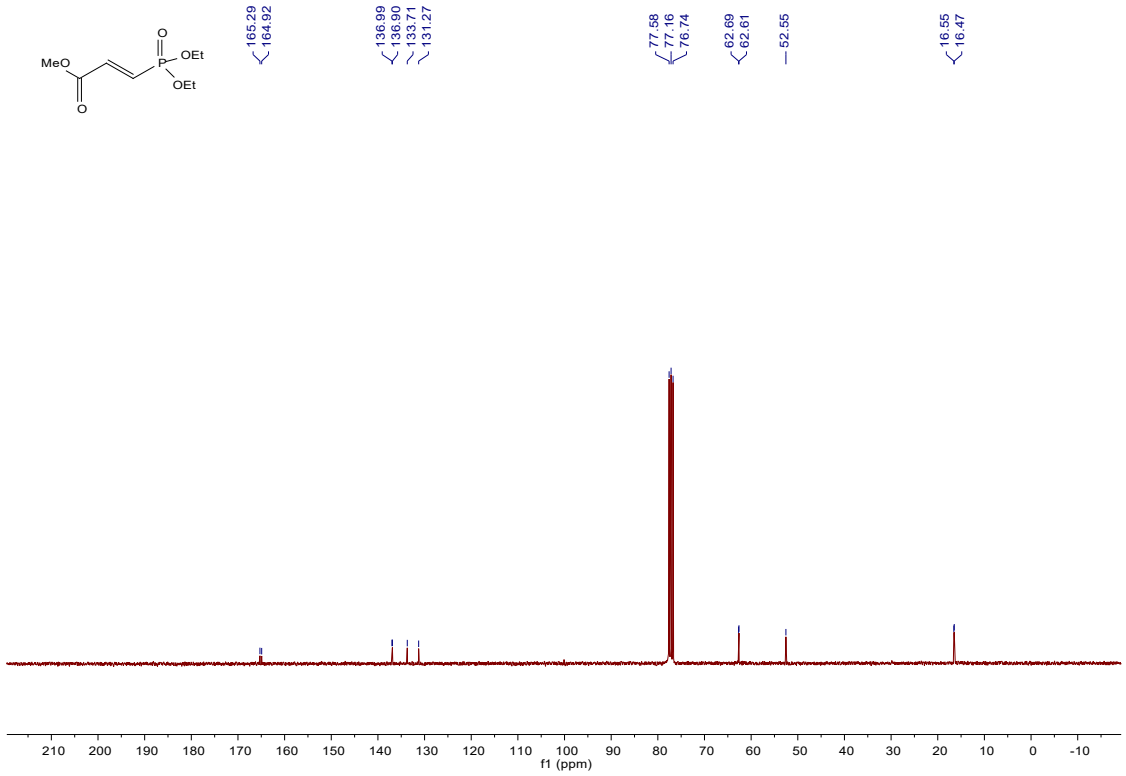
(E)-3-(Diphenylphosphoryl)allyl (R)-2-(4-((5-chloro-3-fluoropyridin-2-yl)oxy)-phenoxy)propanoate (**5yk**). 61% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, $J_{H\text{-}H}$ =

2.2 Hz, 1H), 7.67 – 7.55 (m, 4H), 7.54 – 7.41 (m, 7H), 7.08 – 6.85 (m, 4H), 6.75 (ddt, J_{P-H} = 20.9 Hz, J_{H-H} = 17.1 Hz, J_{H-H} = 3.9 Hz, 1H), 6.33 (ddt, J_{P-H} = 23.0 Hz, J_{H-H} = 17.1, 1.7 Hz, 1H), 5.19 – 4.57 (m, 3H), 1.64 (d, J_{H-H} = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.53, 154.85, 151.26 (d, *J* = 11.2 Hz), 147.04, 146.97 (d, J_{P-C} = 265.9 Hz), 143.82 (d, *J* = 3.4 Hz), 140.17 (d, *J* = 6.1 Hz), 132.87 (d, *J* = 4.7 Hz), 132.13 (d, *J* = 2.7 Hz), 131.49, 131.34 (d, *J* = 10.1 Hz), 128.74 (d, *J* = 12.3 Hz), 125.06 (d, *J* = 1.4 Hz), 125.04 (d, *J* = 18.1 Hz), 123.30 (d, J_{P-C} = 101.0 Hz), 122.49, 115.92, 73.01, 64.48 (d, *J* = 17.7 Hz), 18.84. ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.26. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 552.1137; Found 552.1144.

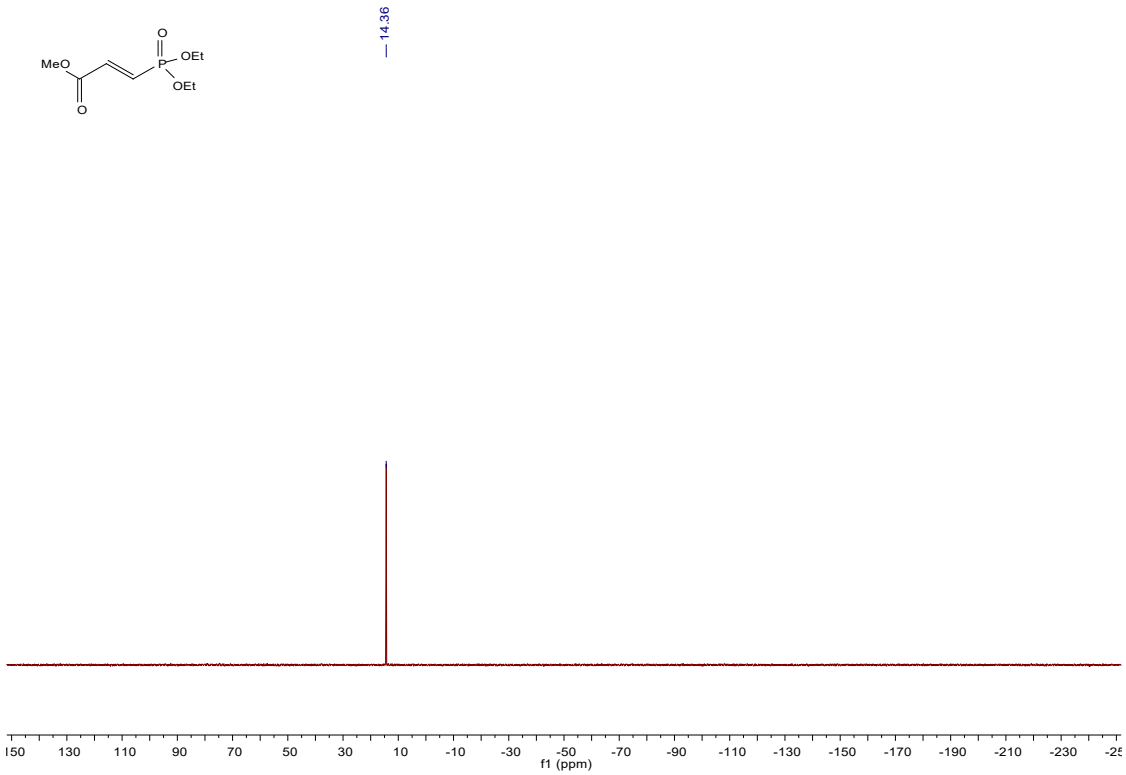
8. NMR spectra



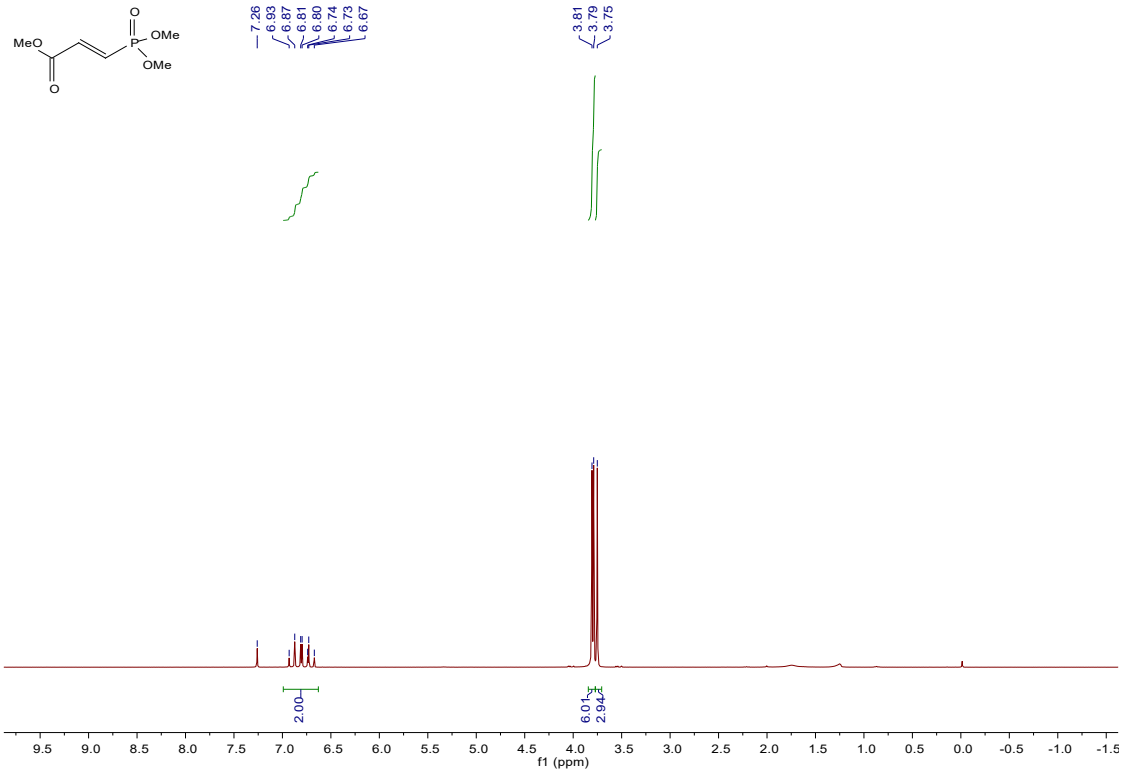
^{1}H NMR of compound **3aa**



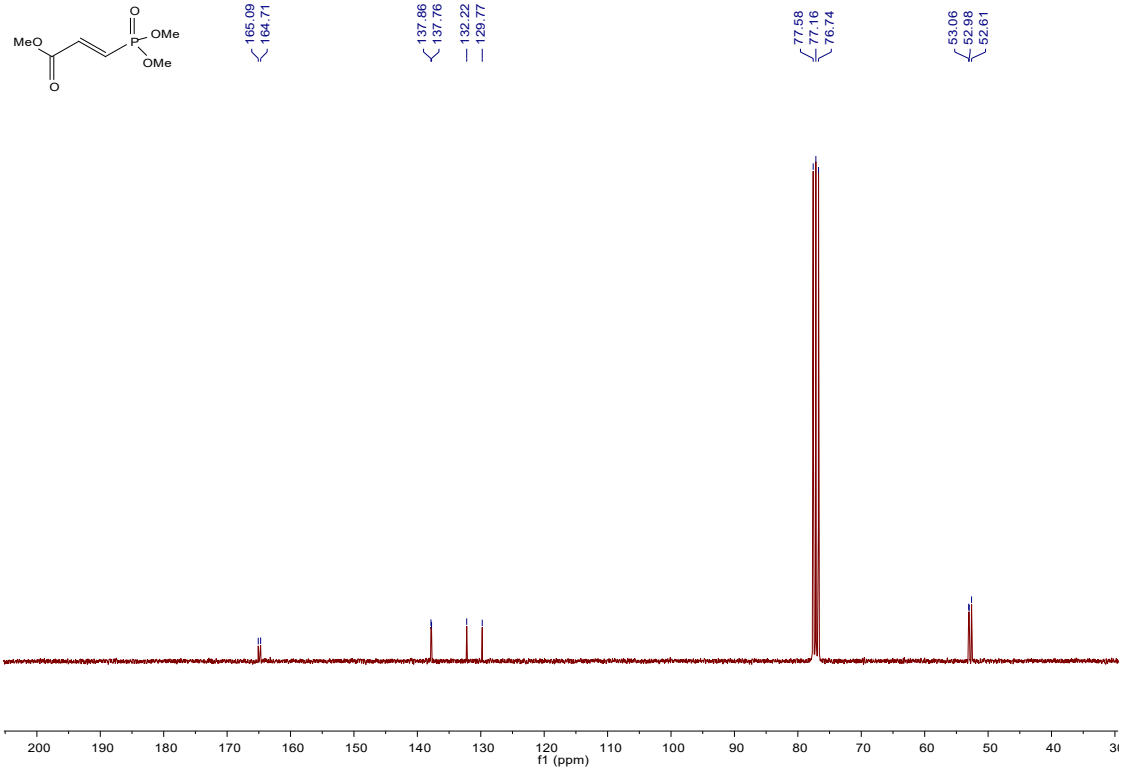
^{13}C NMR of compound **3aa**



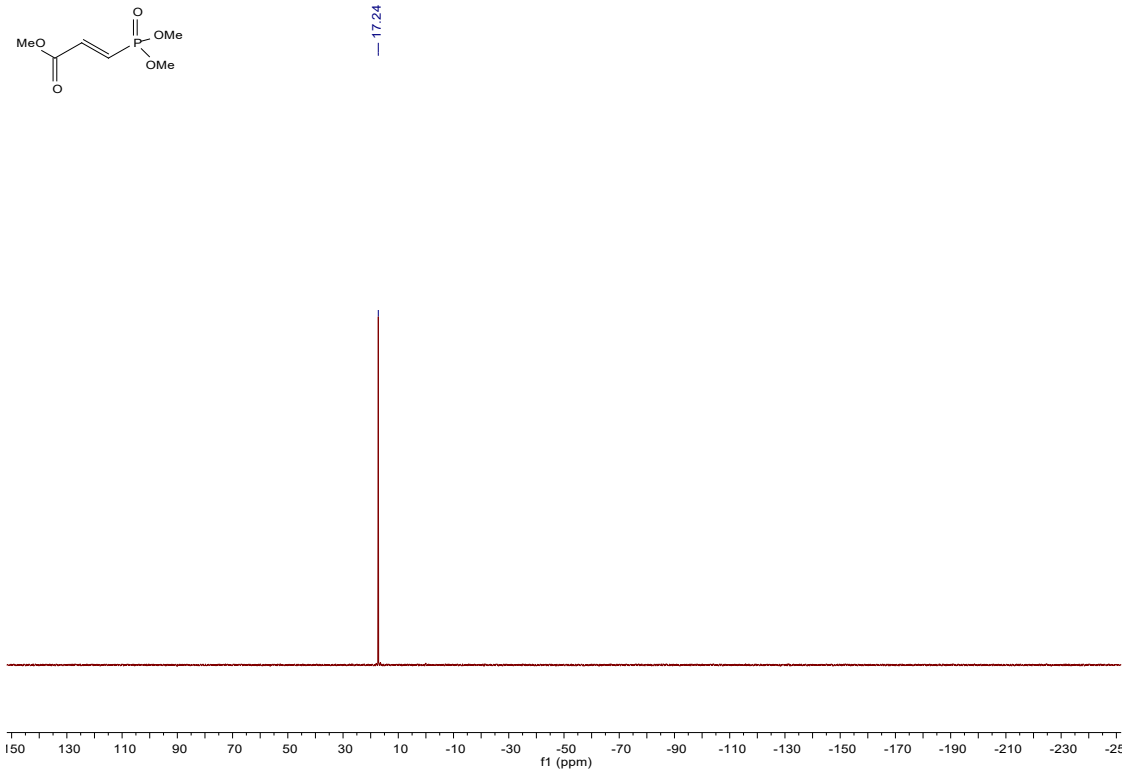
^{31}P NMR of compound **3aa**



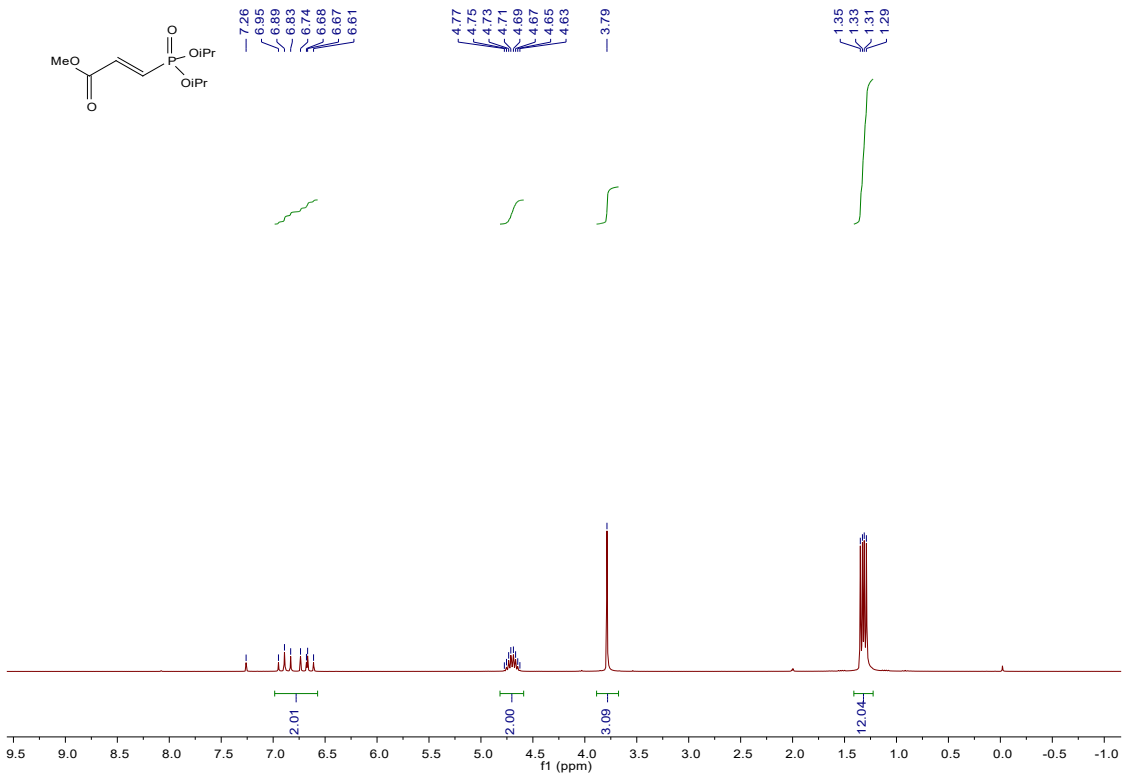
^{1}H NMR of compound **3ab**



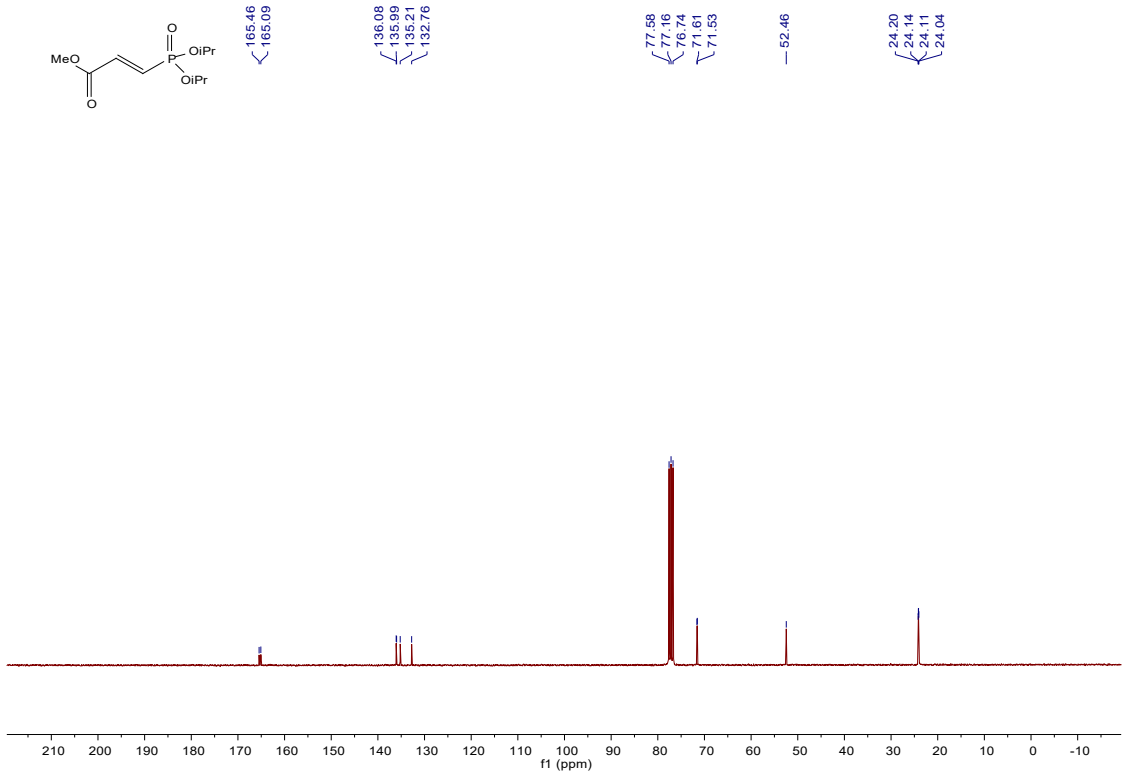
^{13}C NMR of compound **3ab**



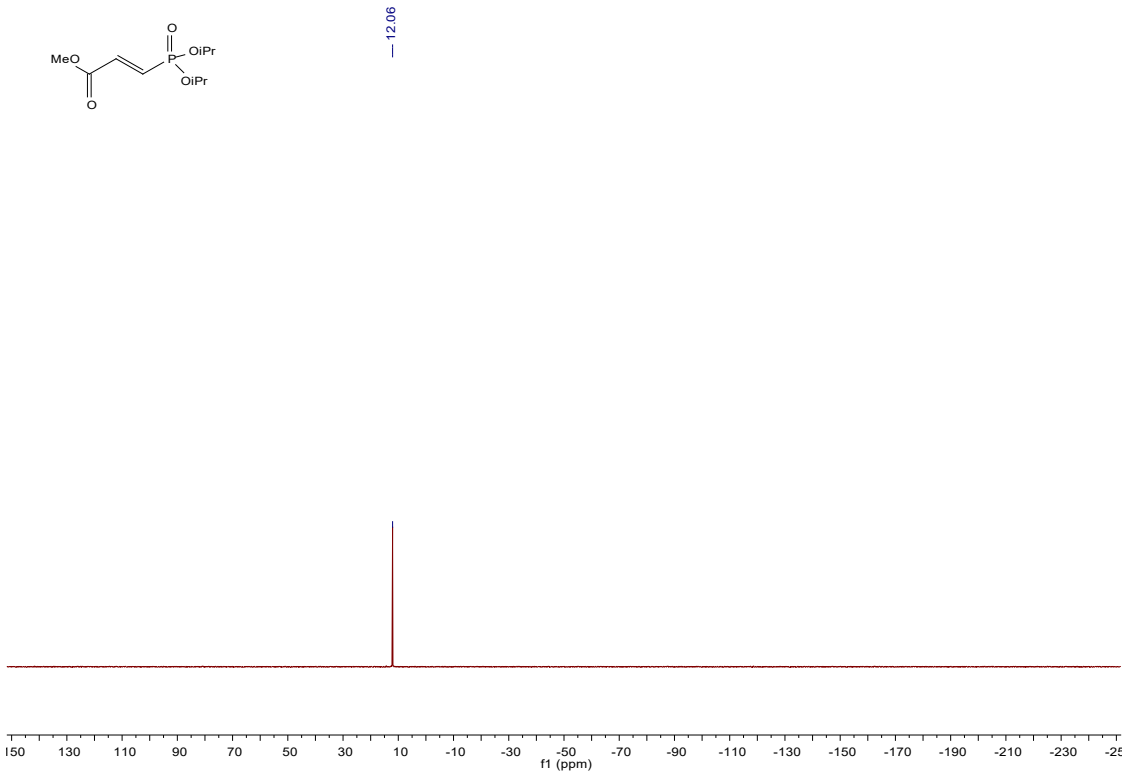
^{31}P NMR of compound **3ab**



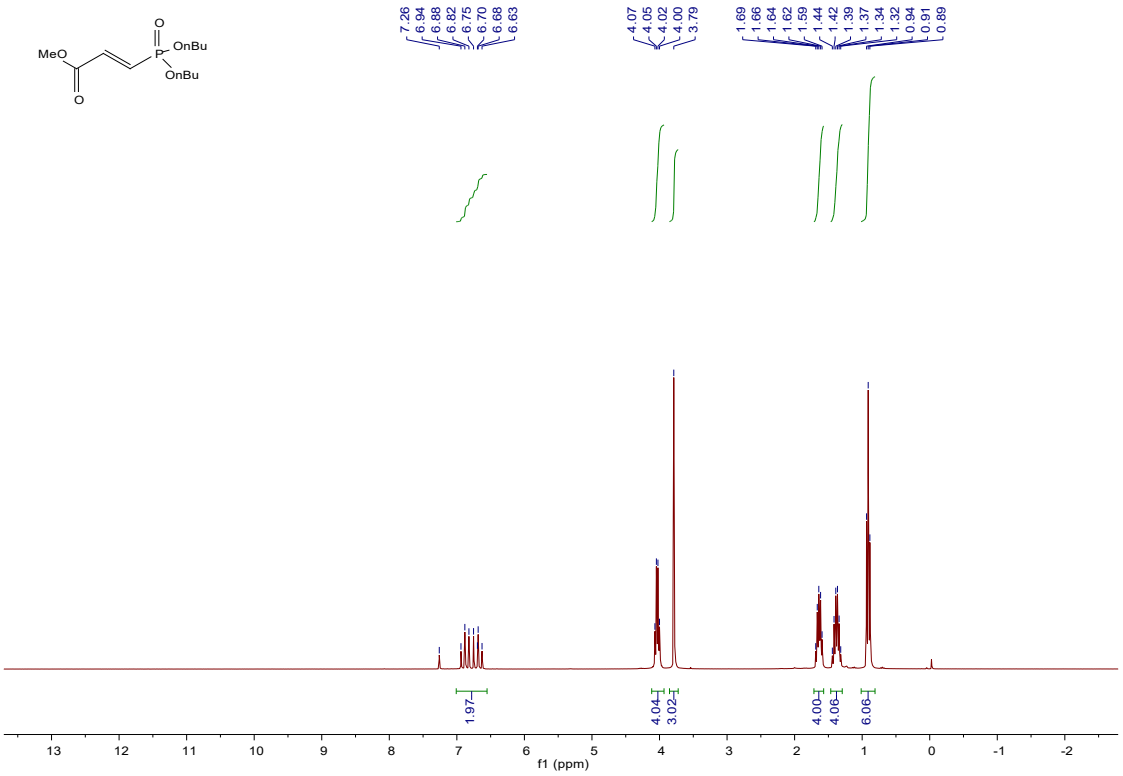
^{1}H NMR of compound **3ac**



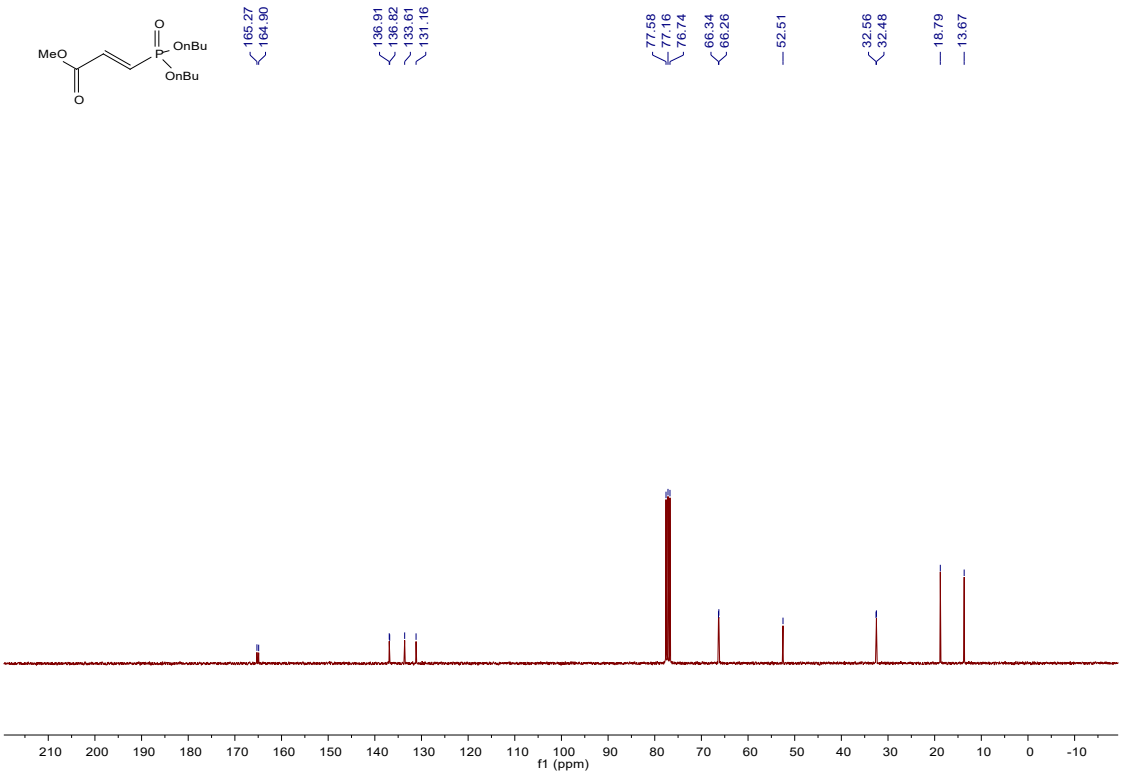
^{13}C NMR of compound **3ac**



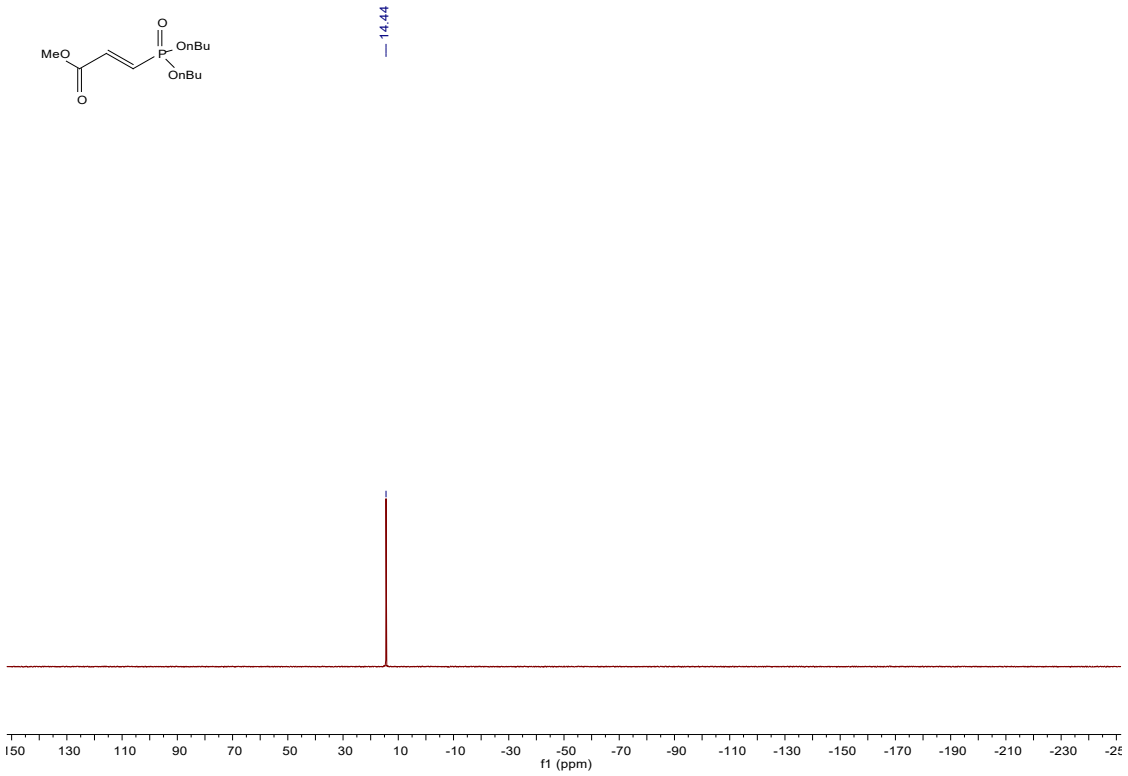
^{31}P NMR of compound **3ac**



^{1}H NMR of compound **3ad**



^{13}C NMR of compound **3ad**



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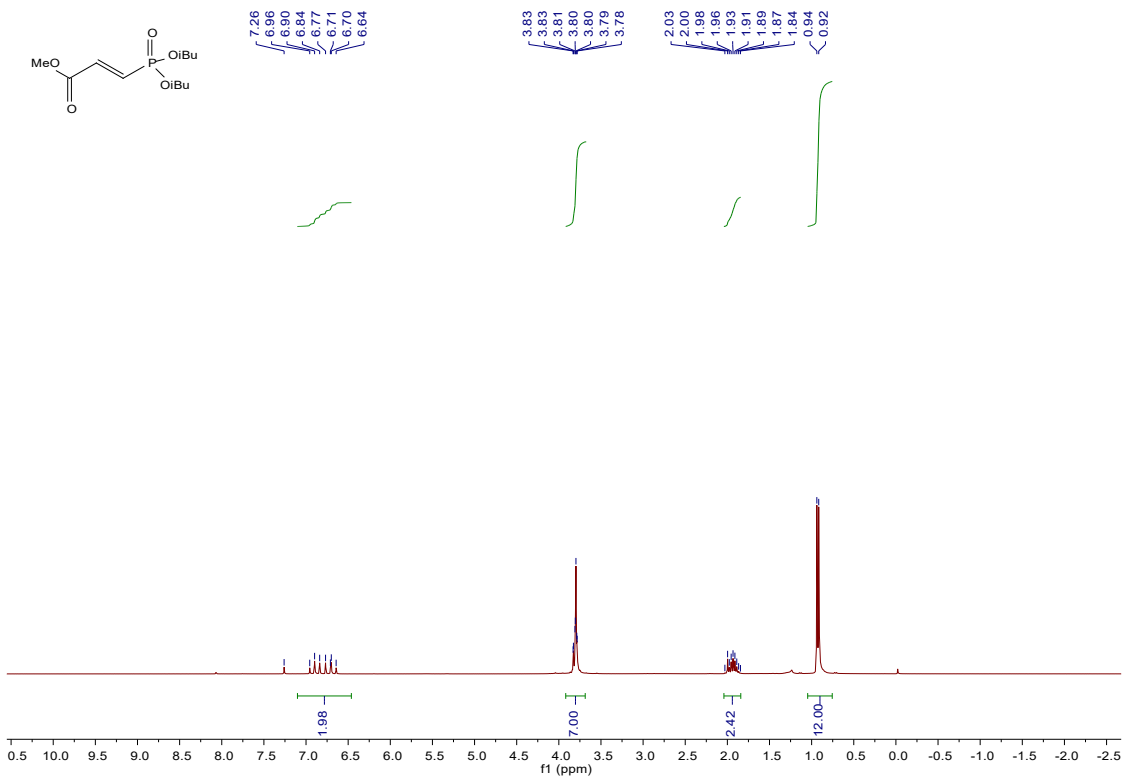
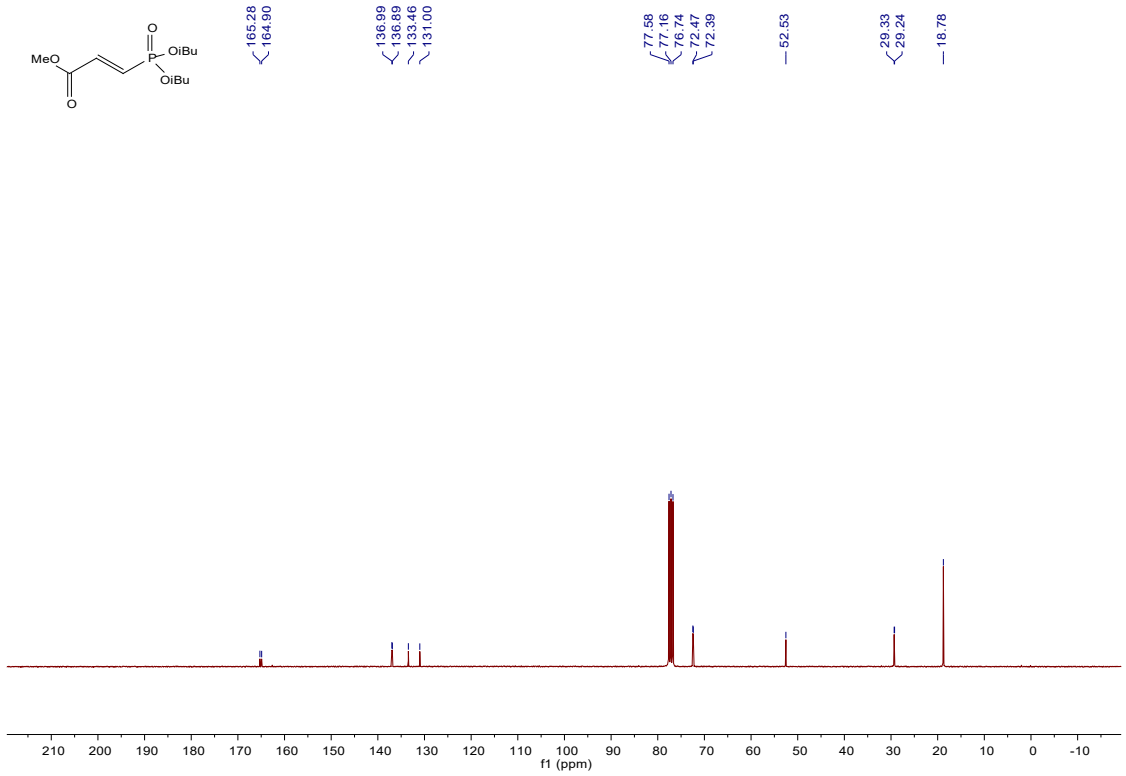
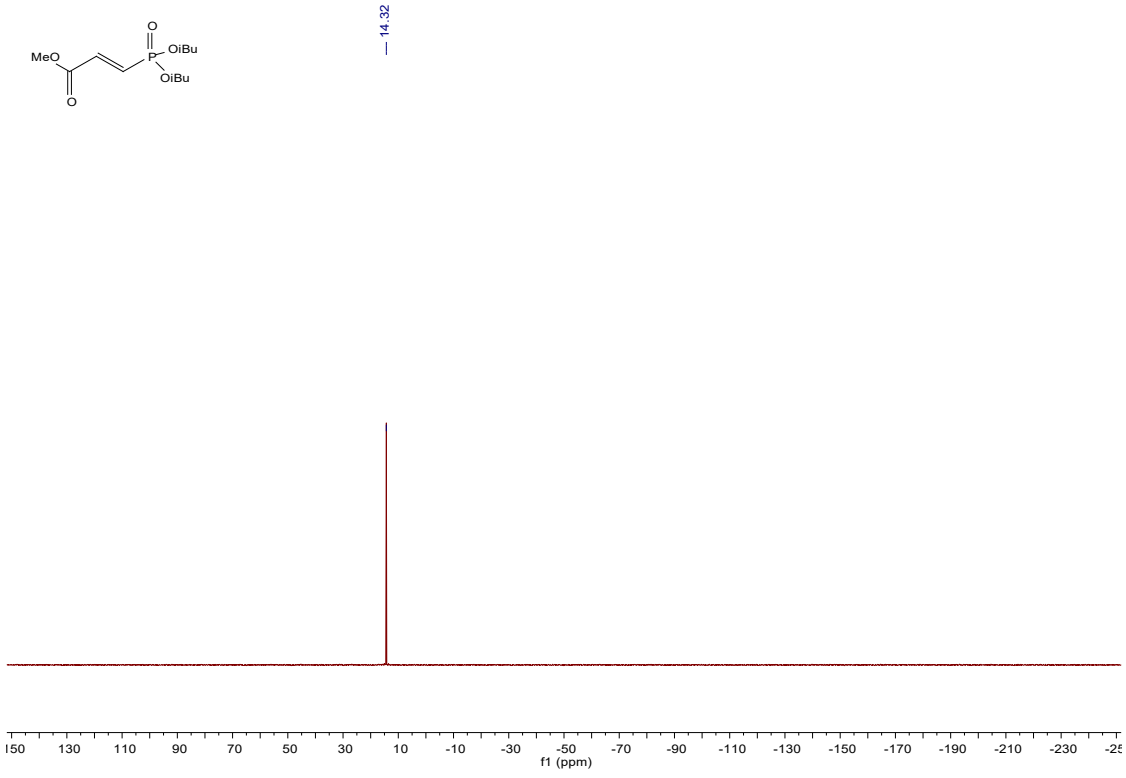


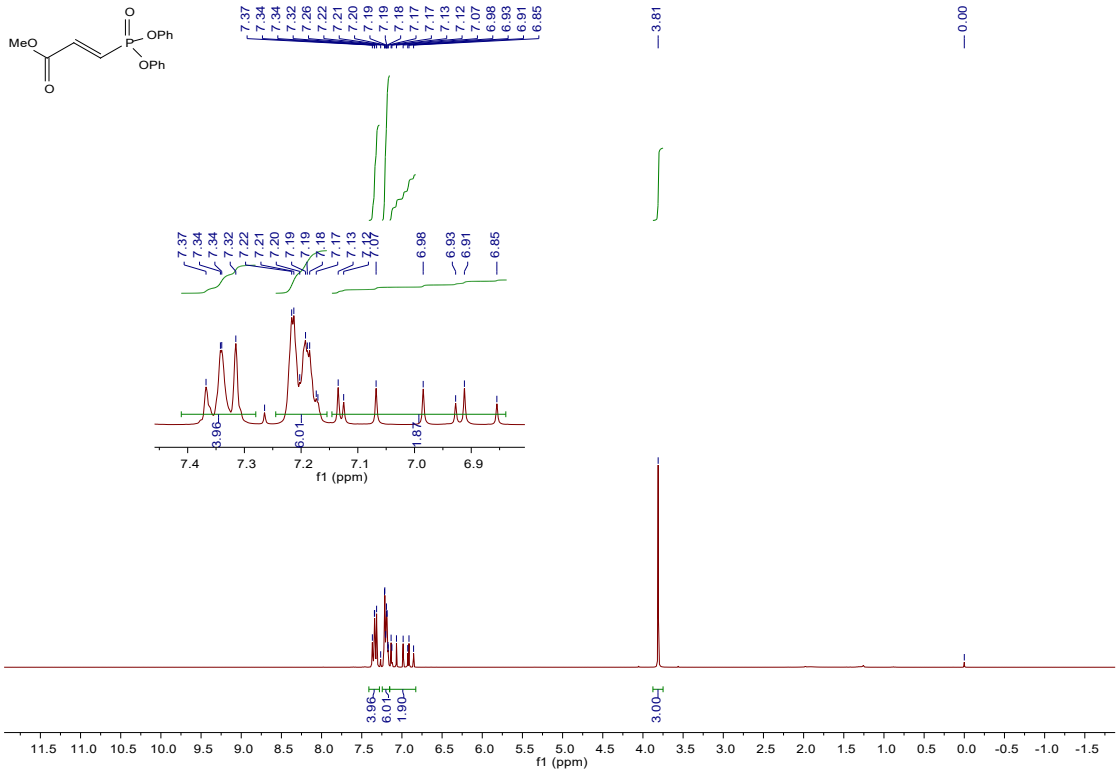
^{1}H NMR of compound **3ae**



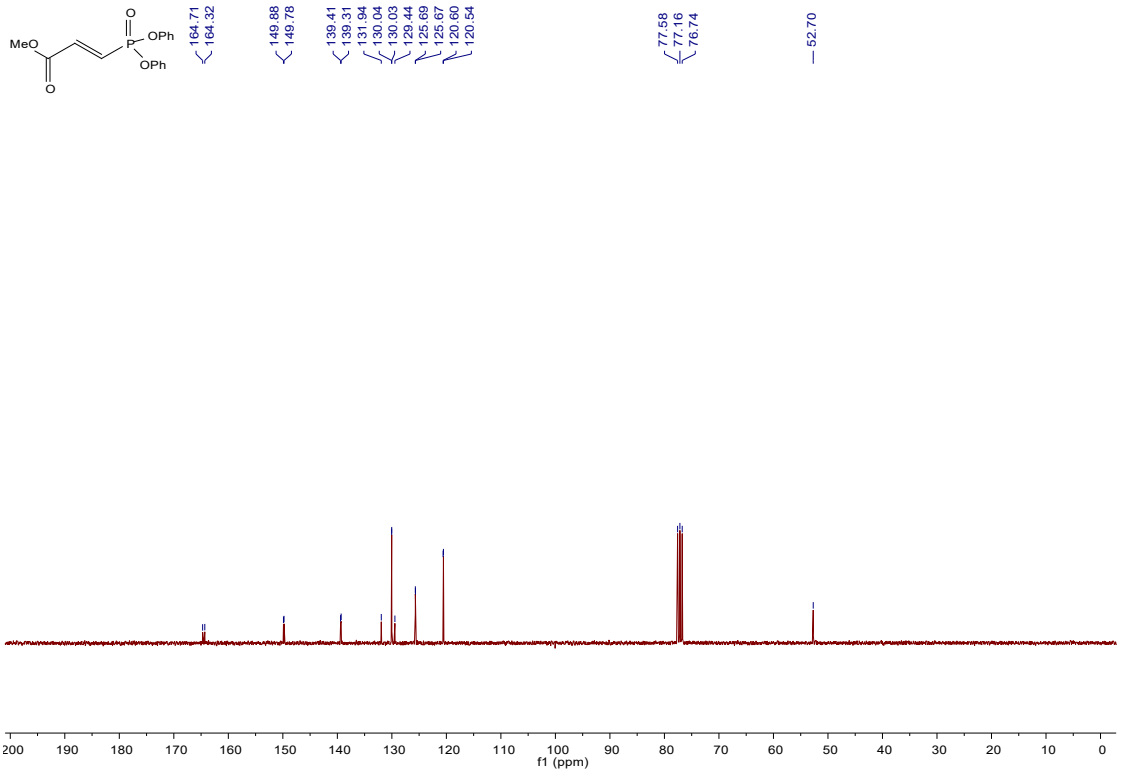
^{13}C NMR of compound **3ae**



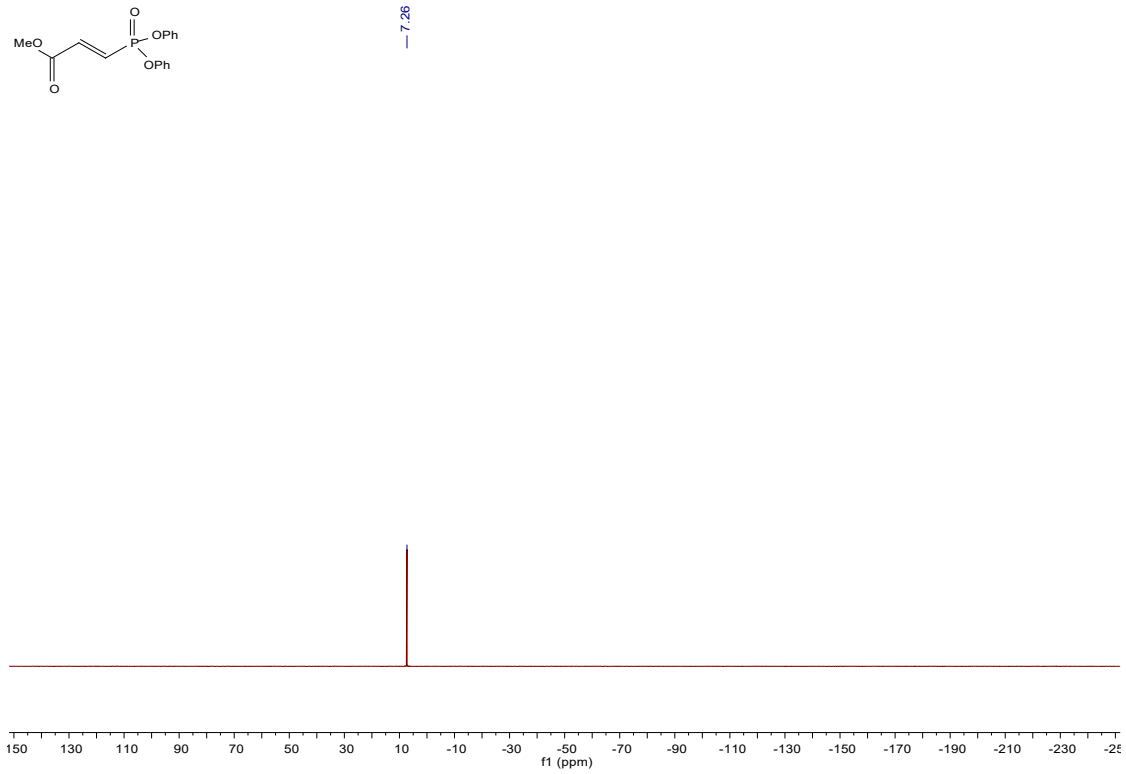
^{31}P NMR of compound **3ae**



^{1}H NMR of compound **3af**



^{13}C NMR of compound **3af**



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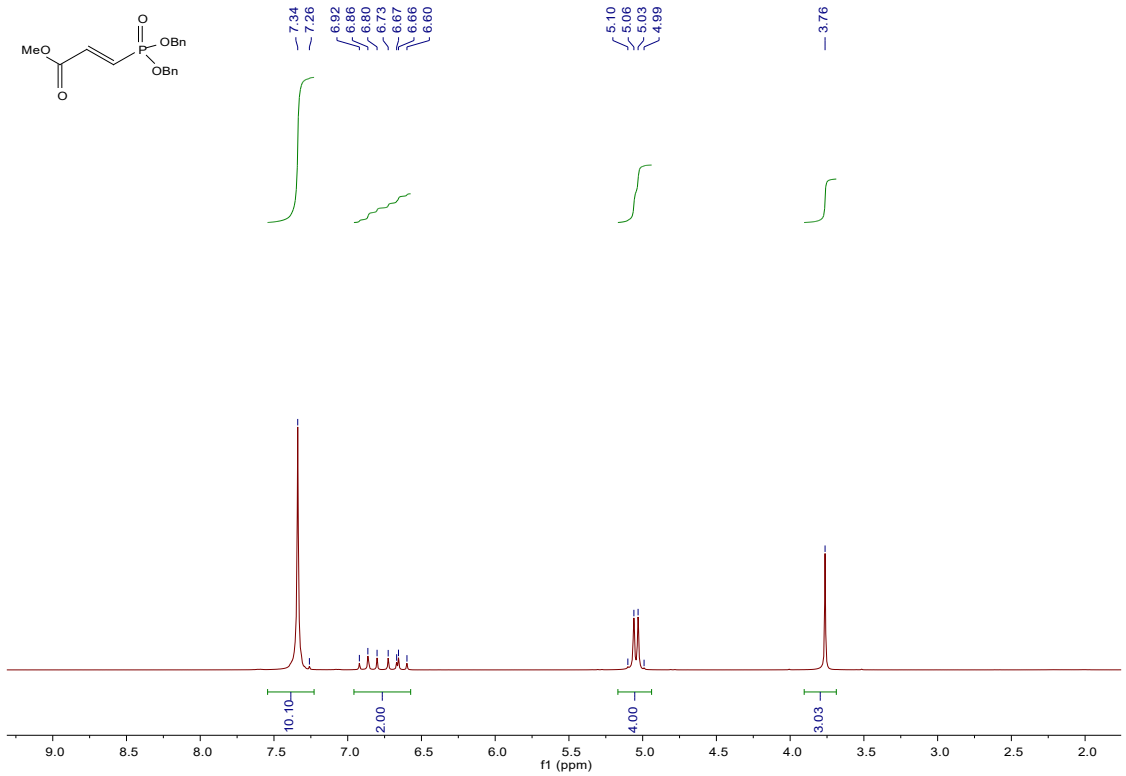
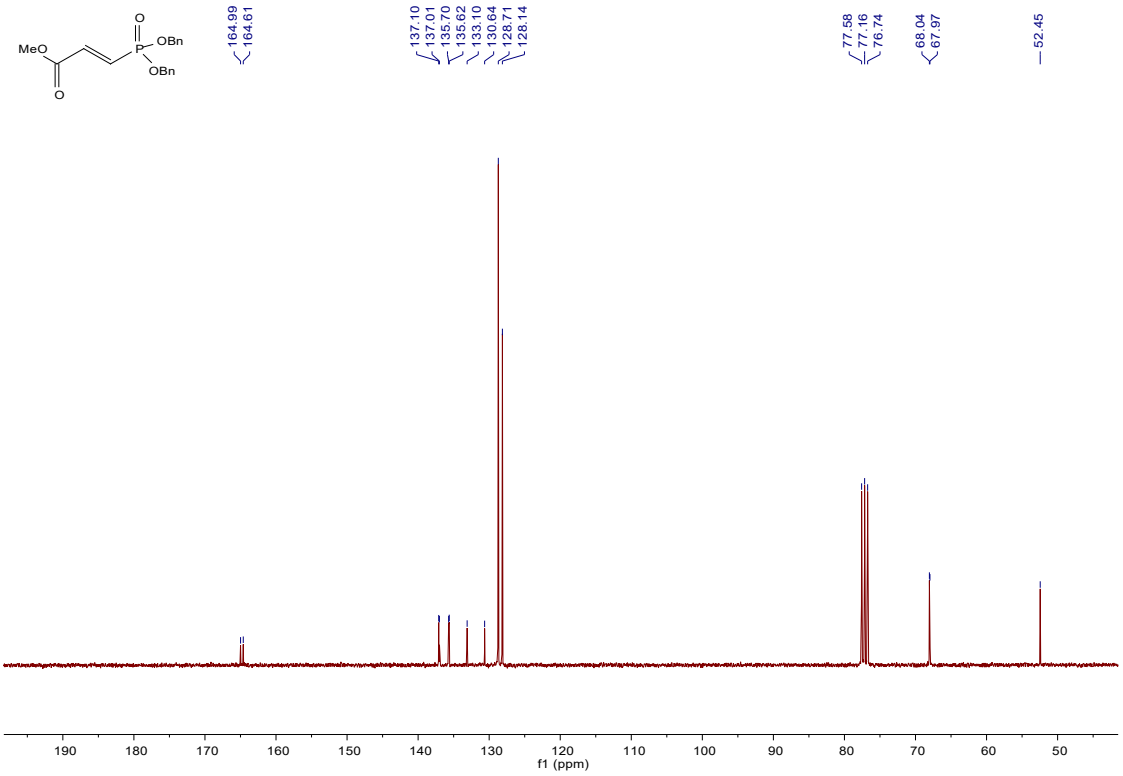
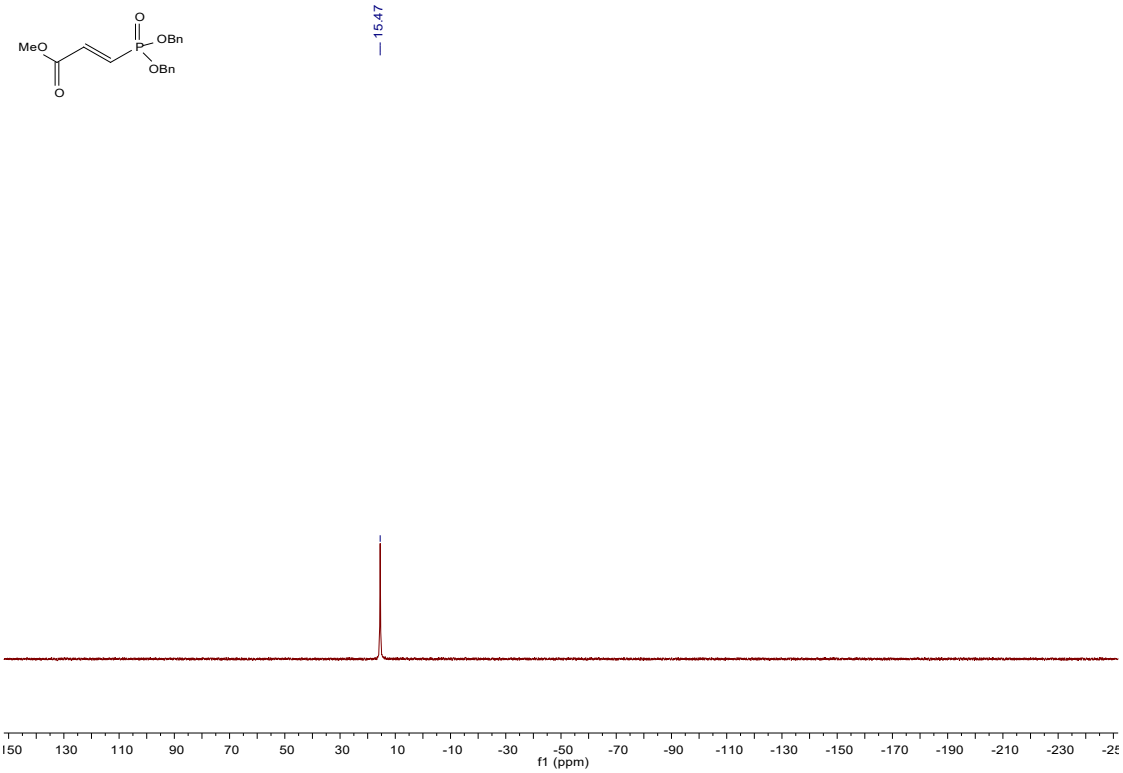


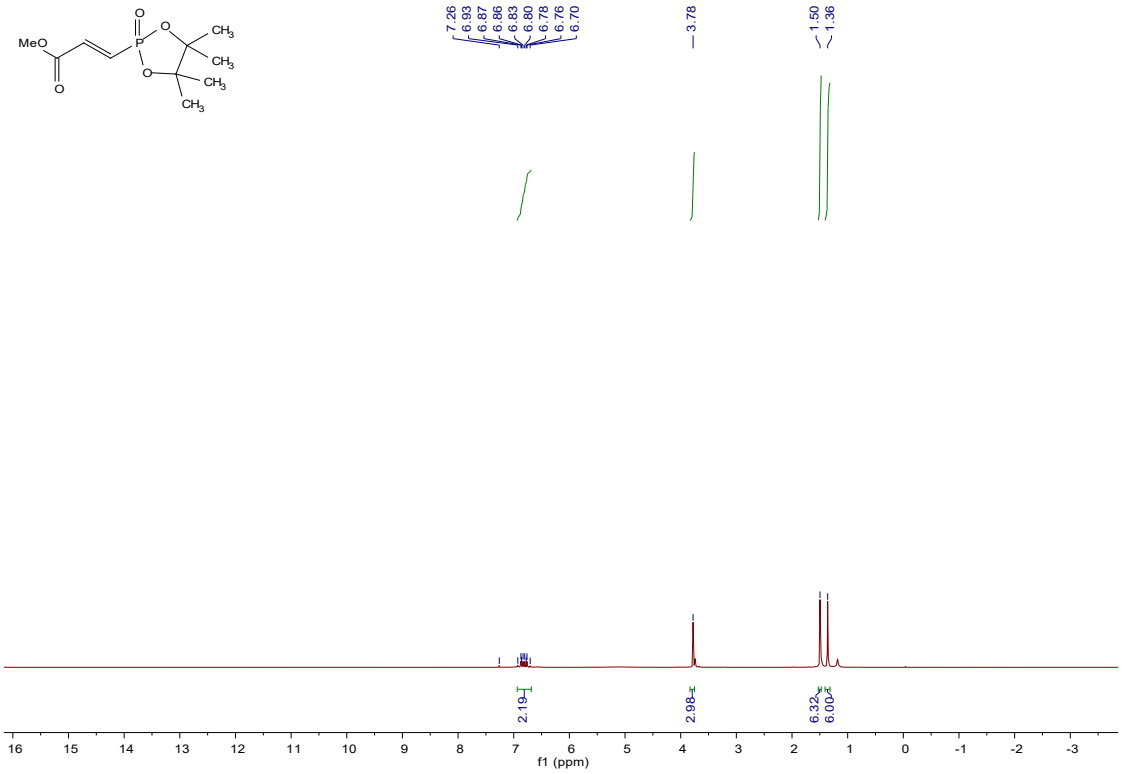
^{1}H NMR of compound **3ag**



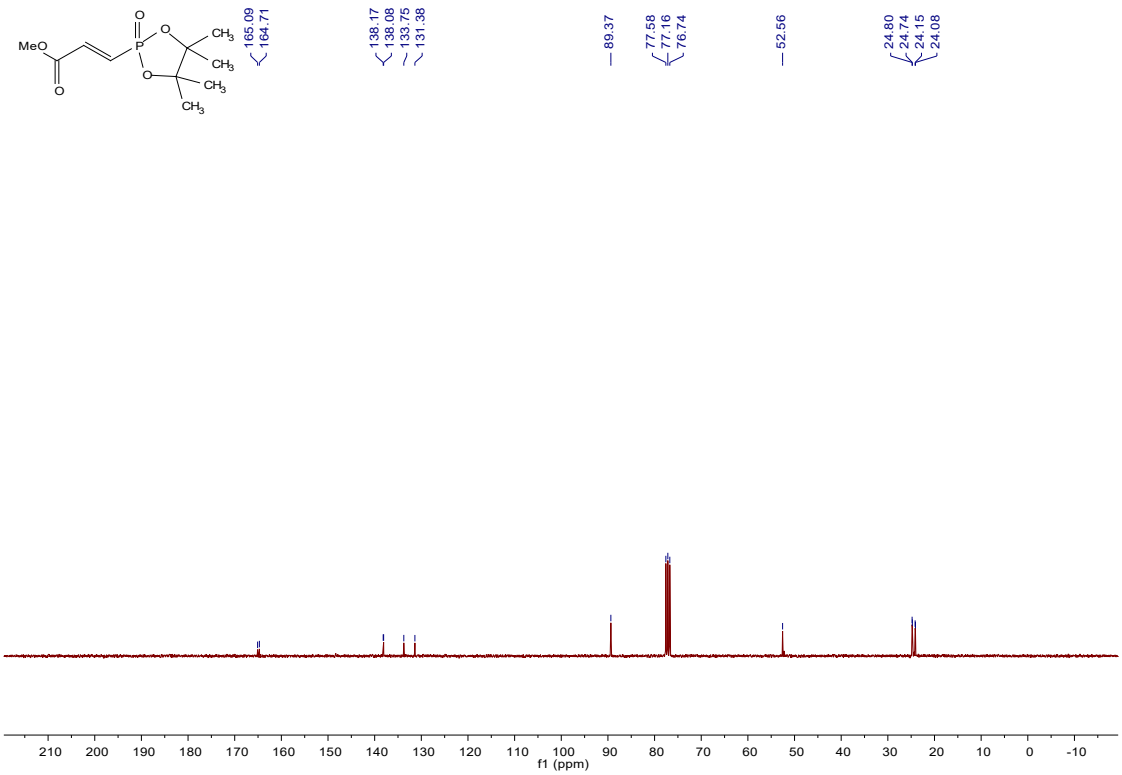
^{13}C NMR of compound **3ag**



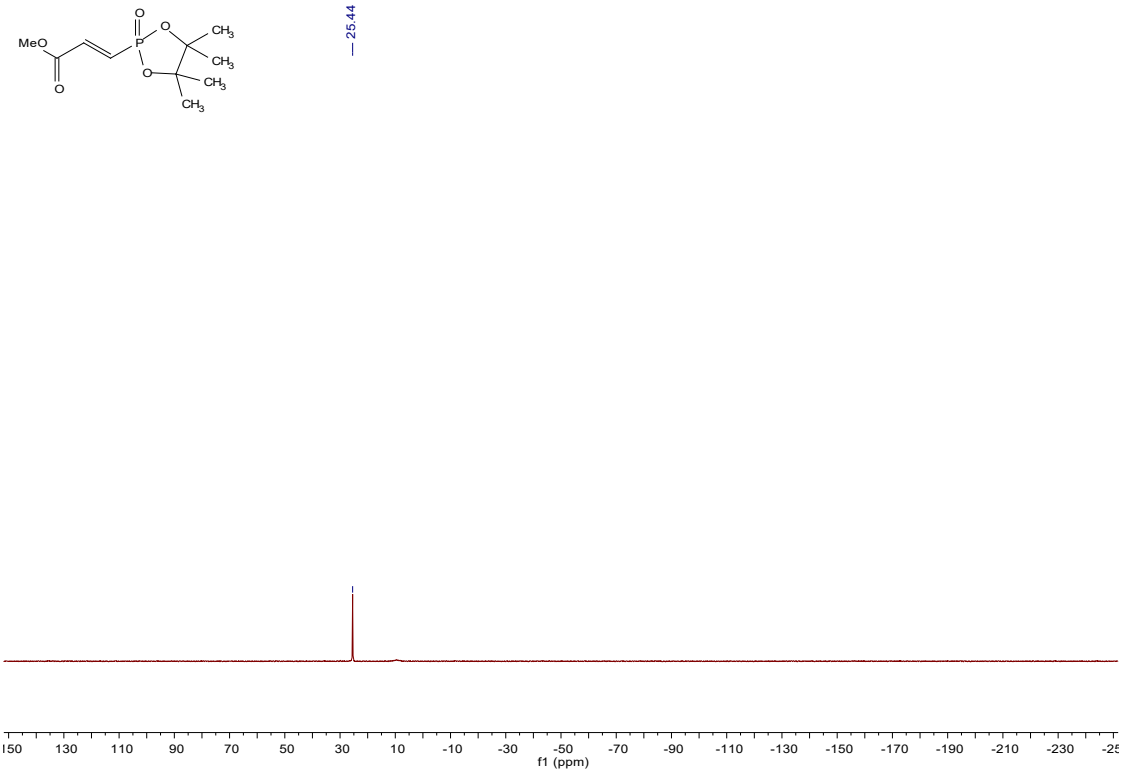
^{31}P NMR of compound **3ag**



^{1}H NMR of compound **3ah**



^{13}C NMR of compound **3ah**



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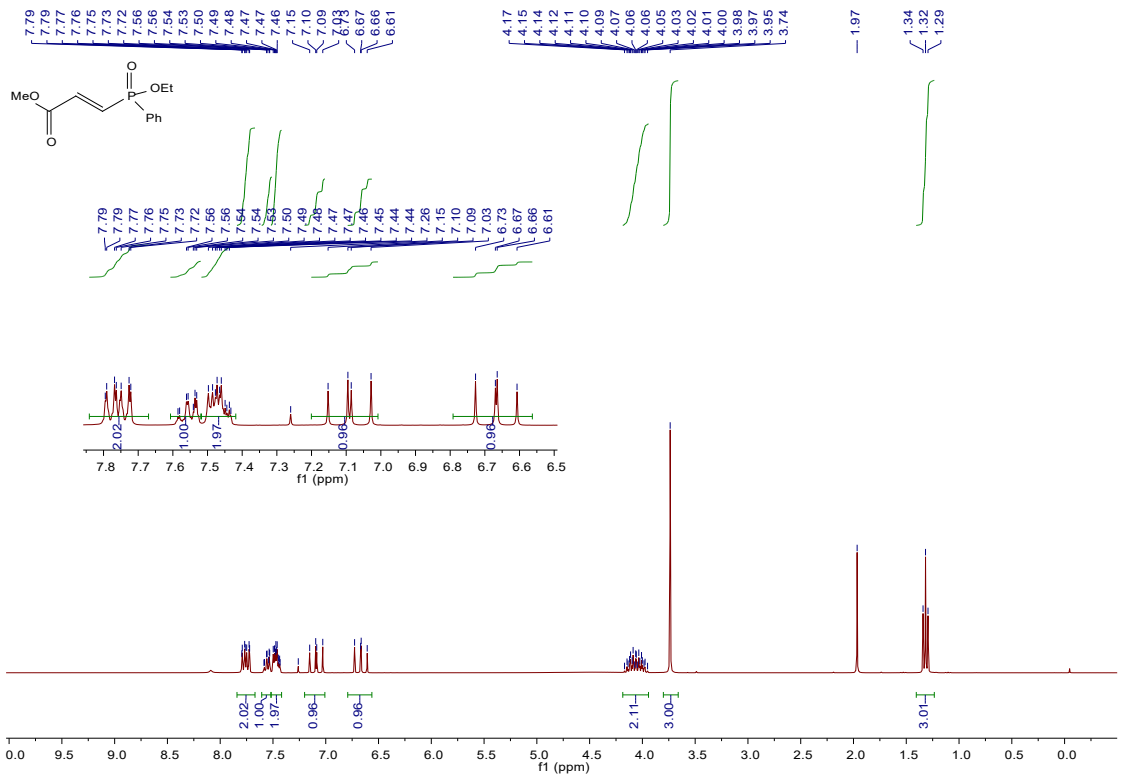
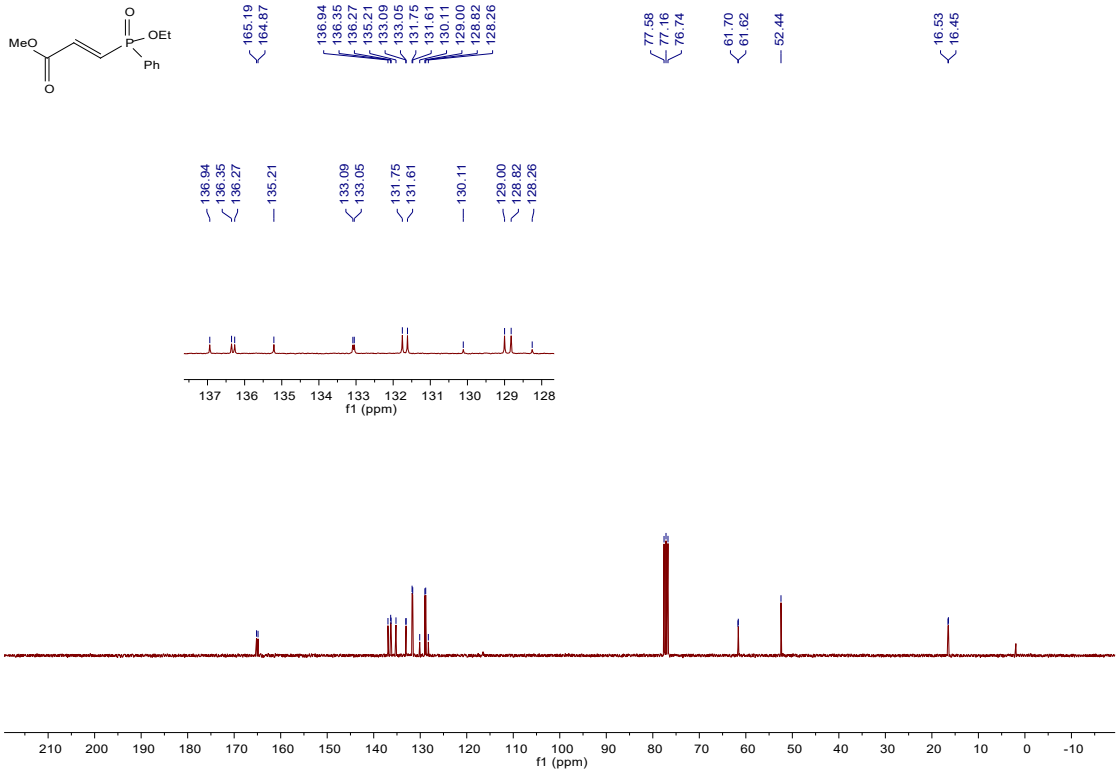


^{1}H NMR of compound **3ai**



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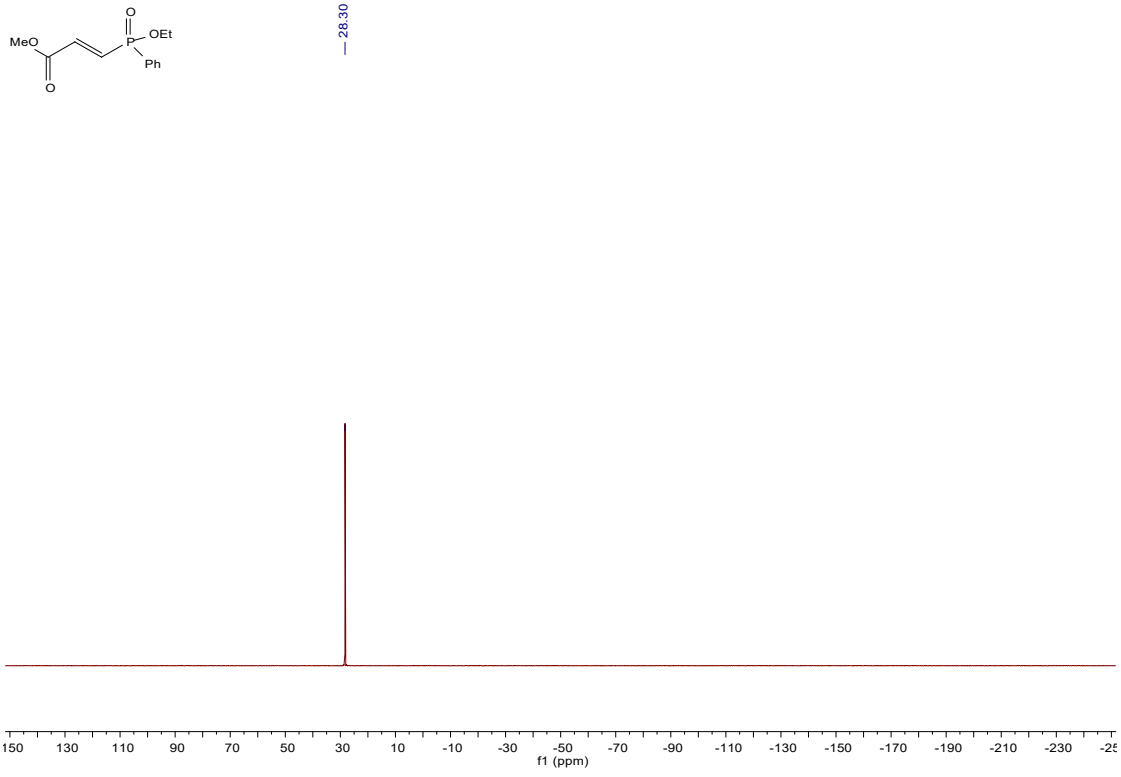

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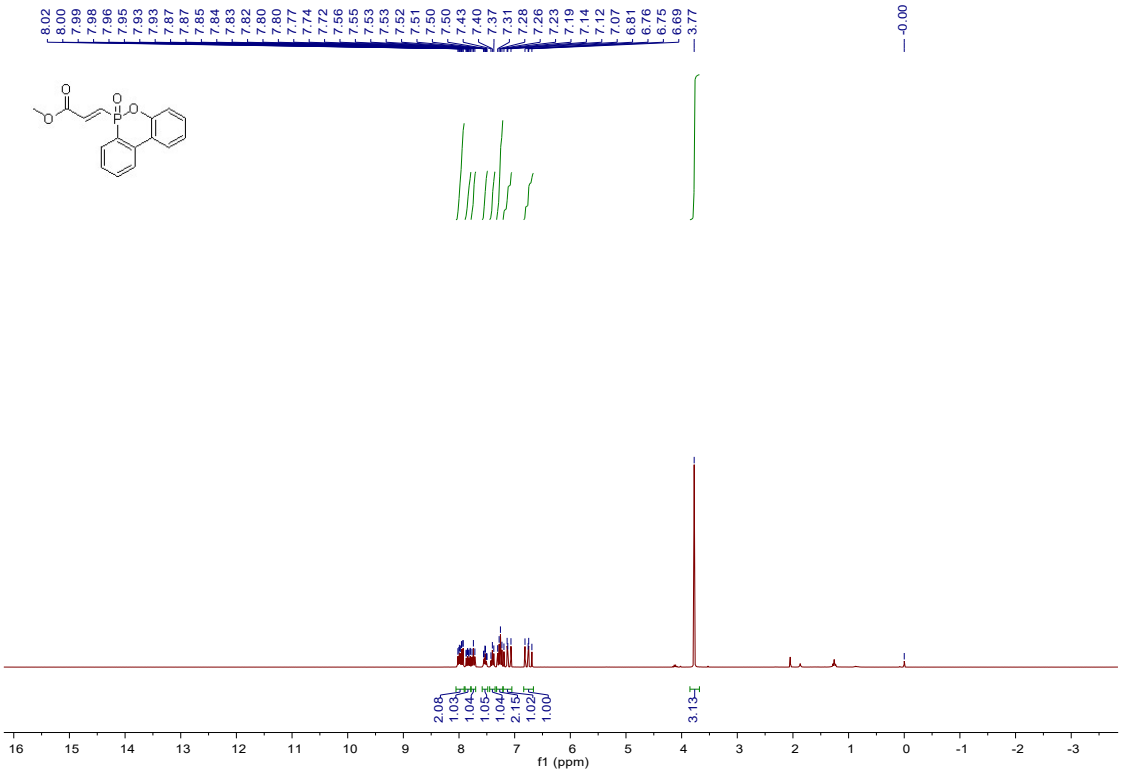

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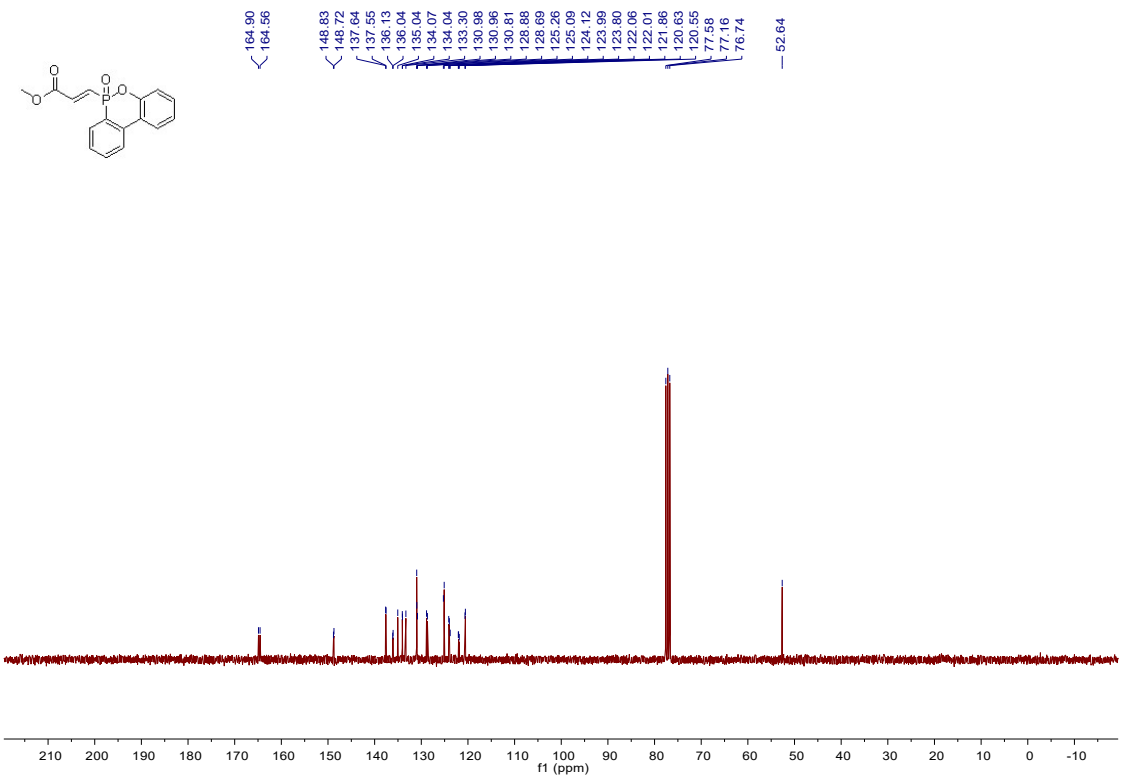

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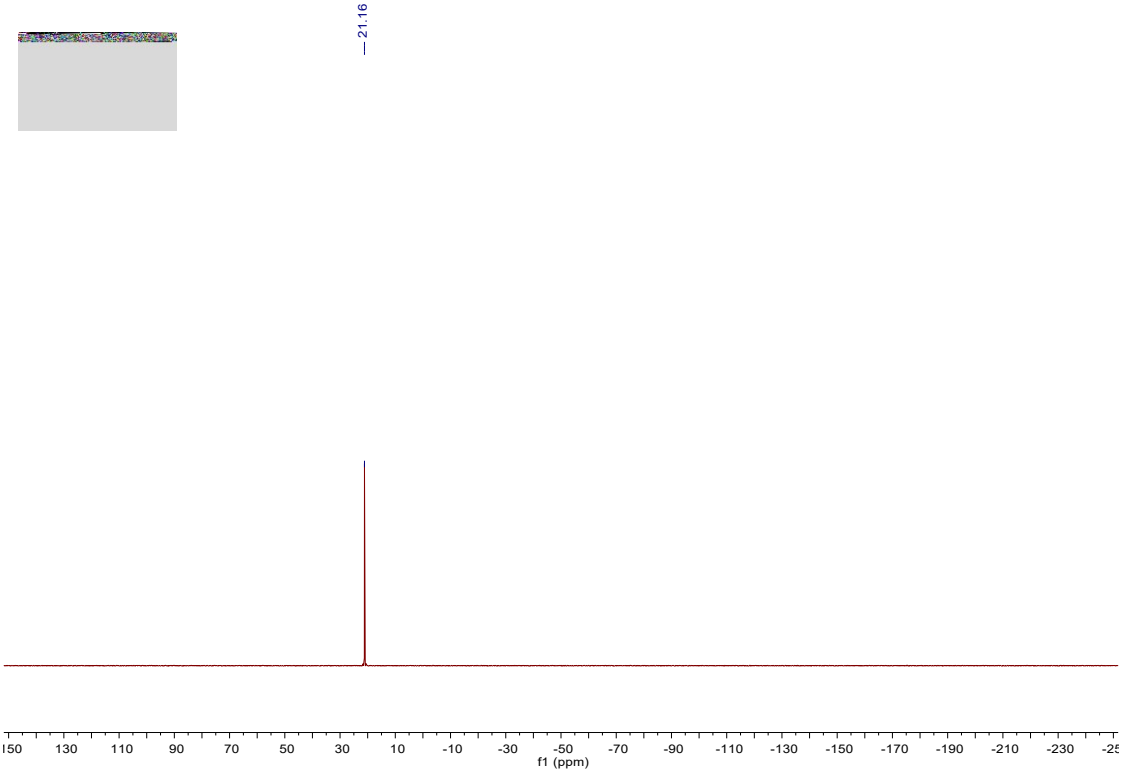

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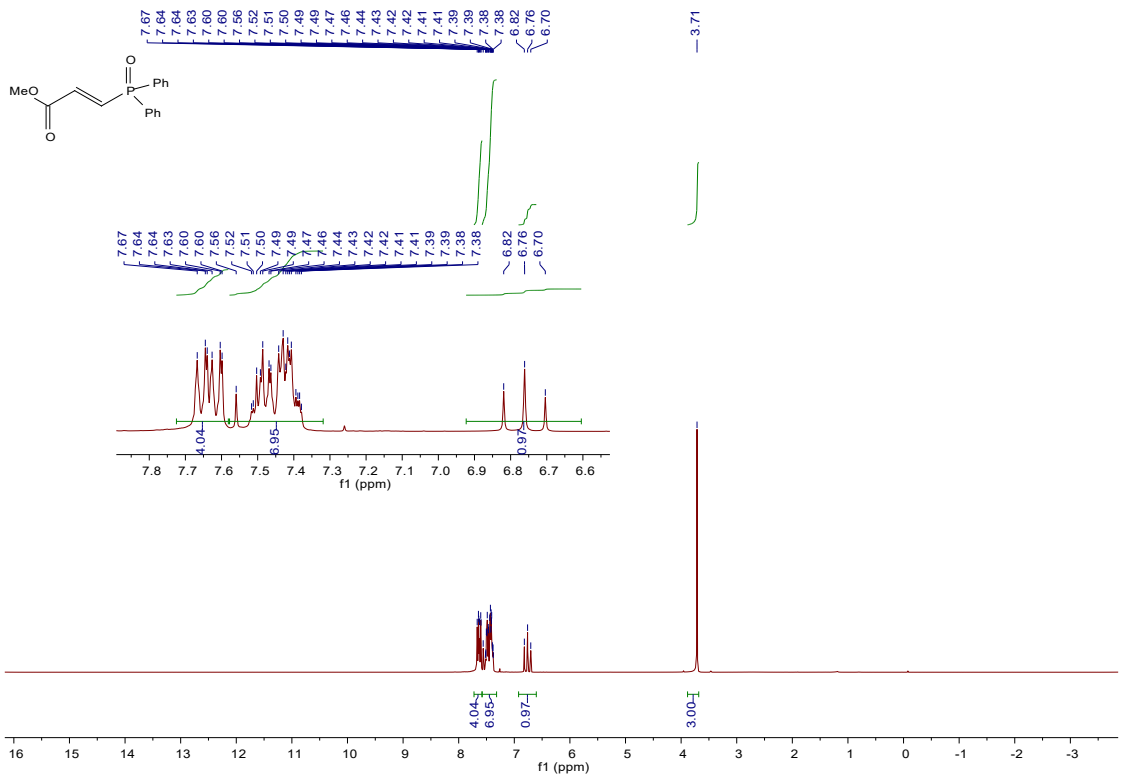

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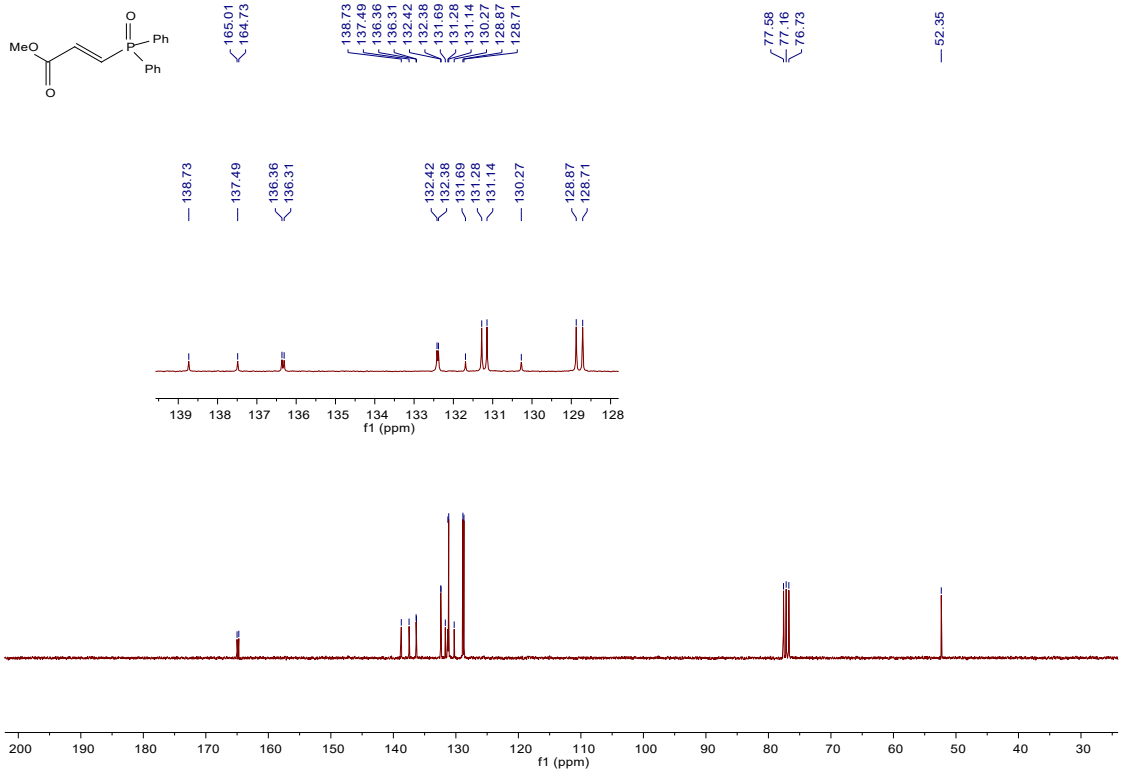

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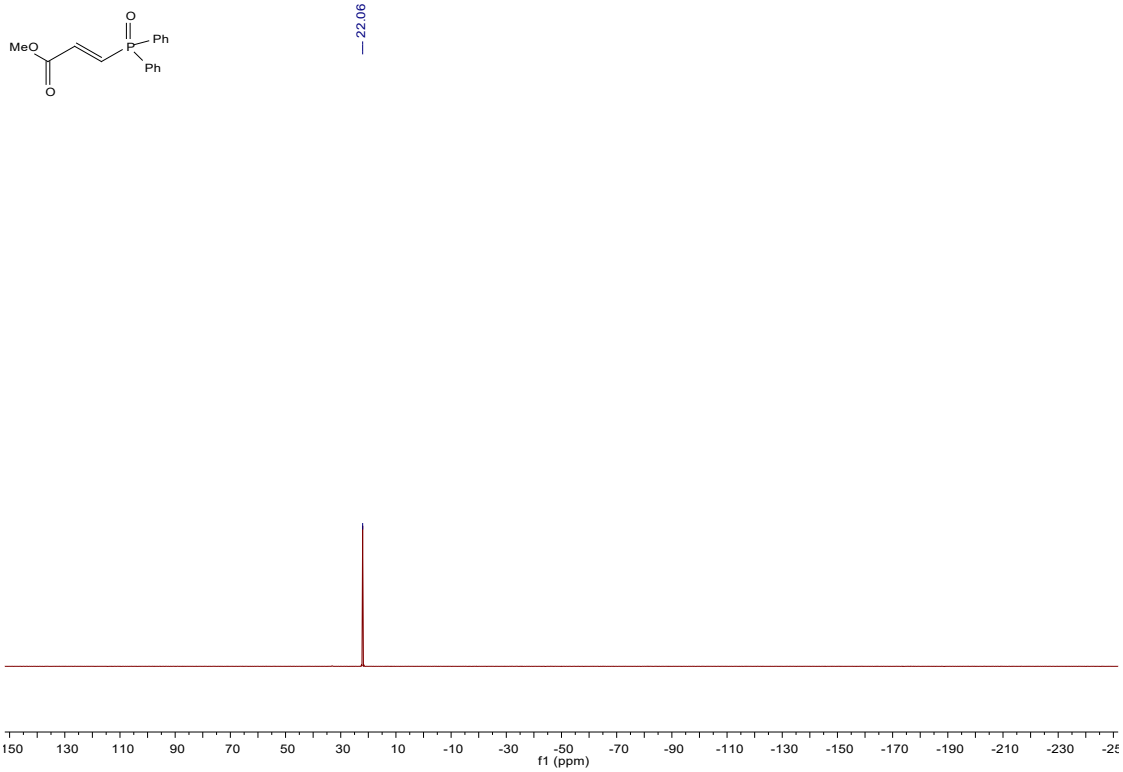

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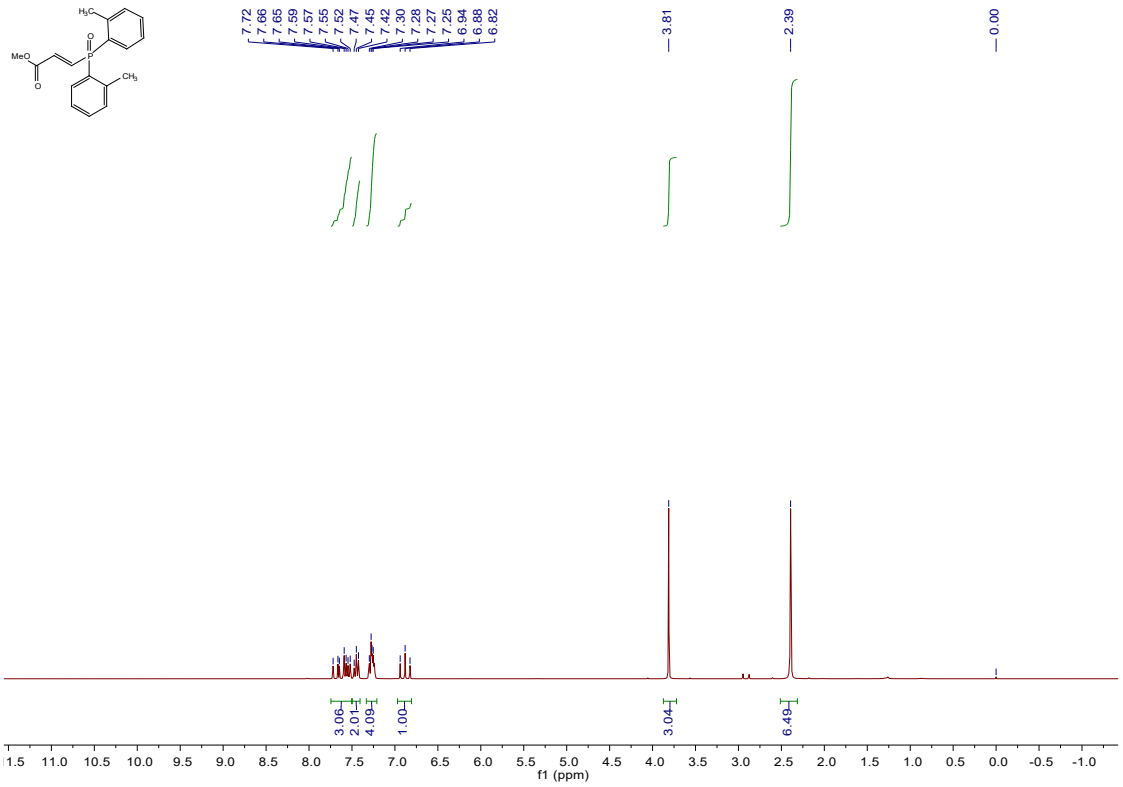
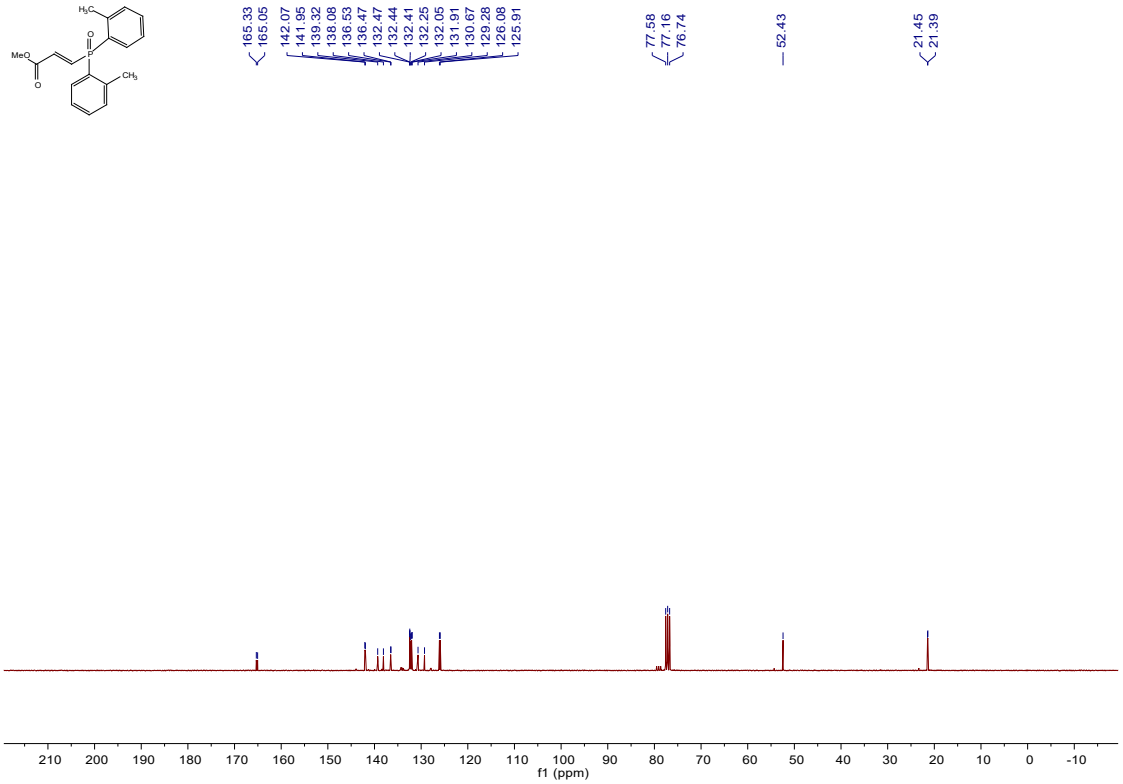
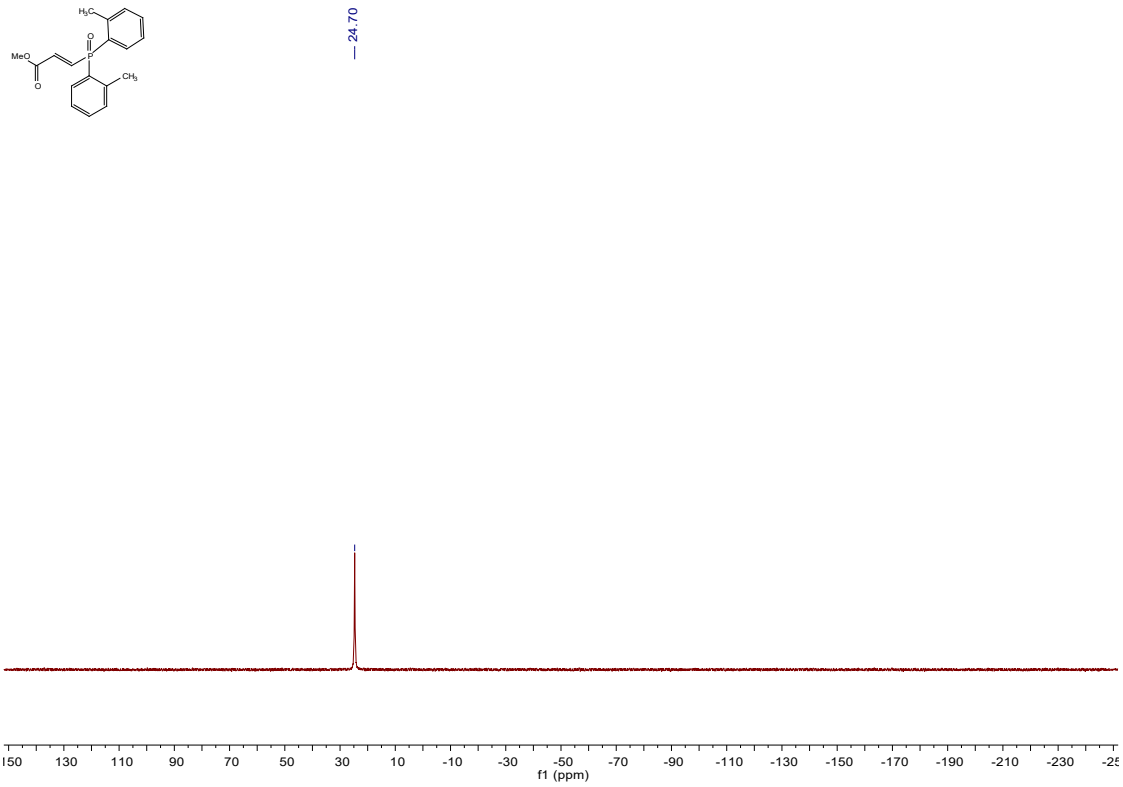


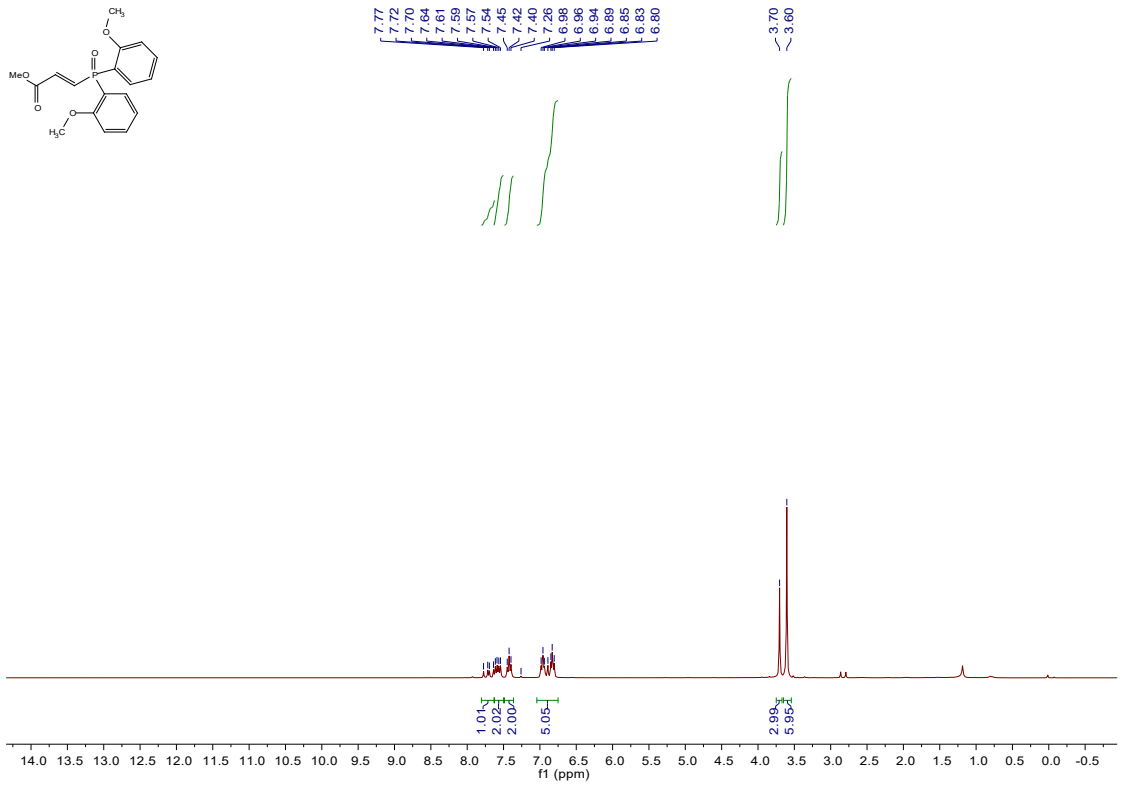
^{1}H NMR of compound **3al**



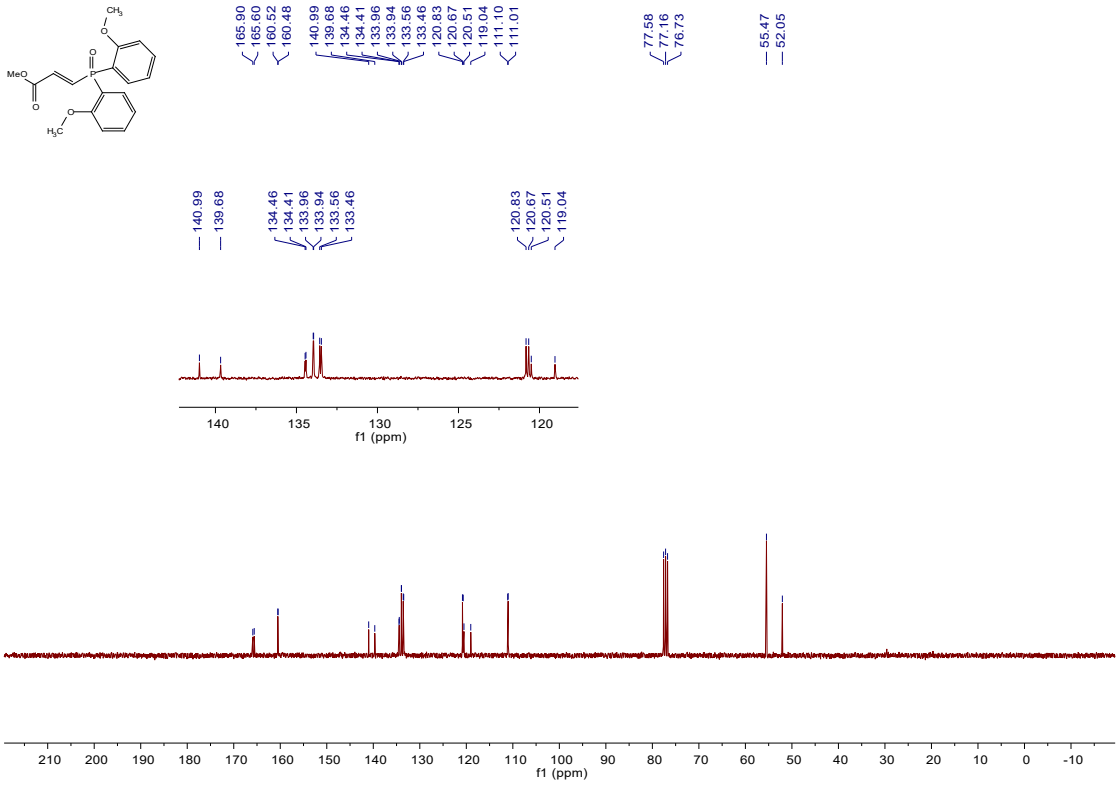
^{13}C NMR of compound **3al**



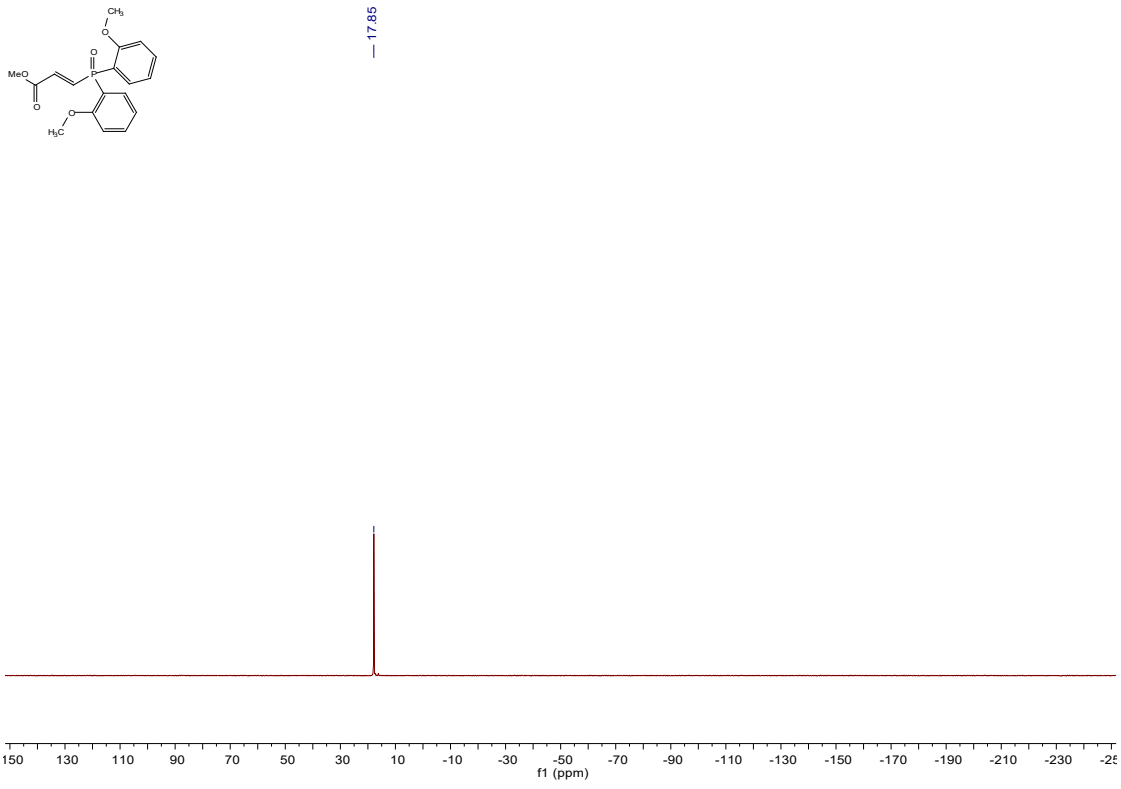
^{31}P NMR of compound **3al**



^{1}H NMR of compound **3am**



^{13}C NMR of compound **3am**



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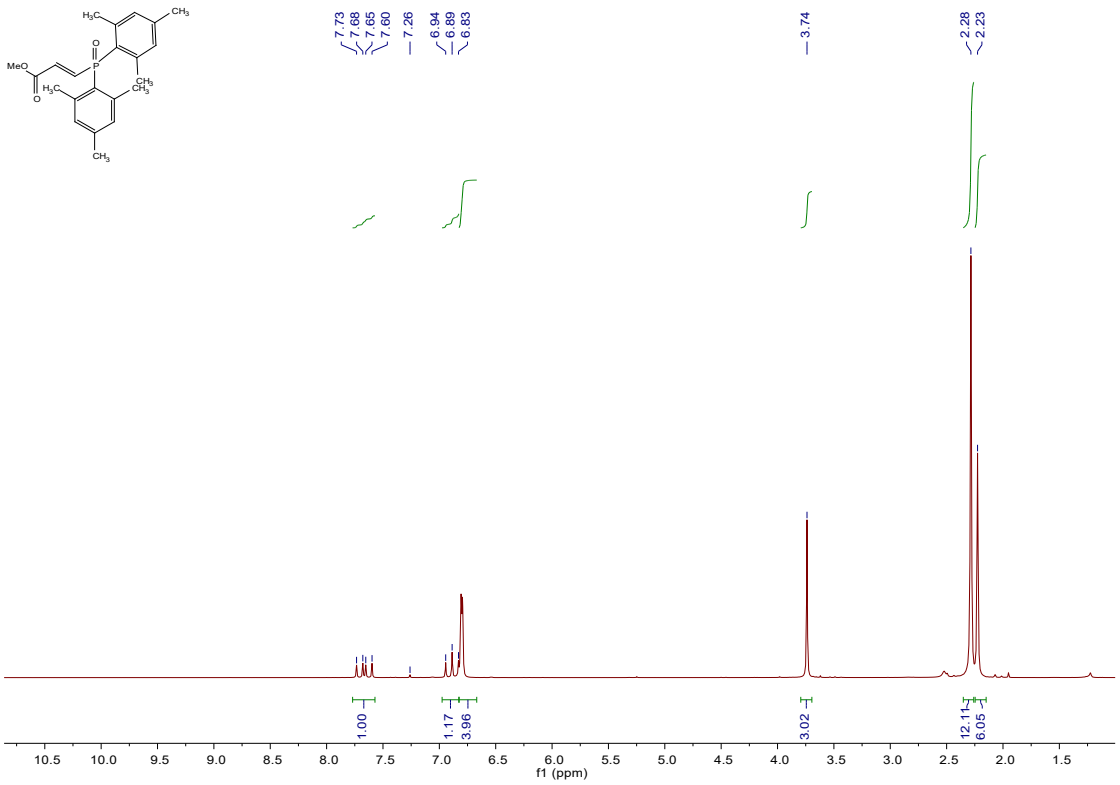
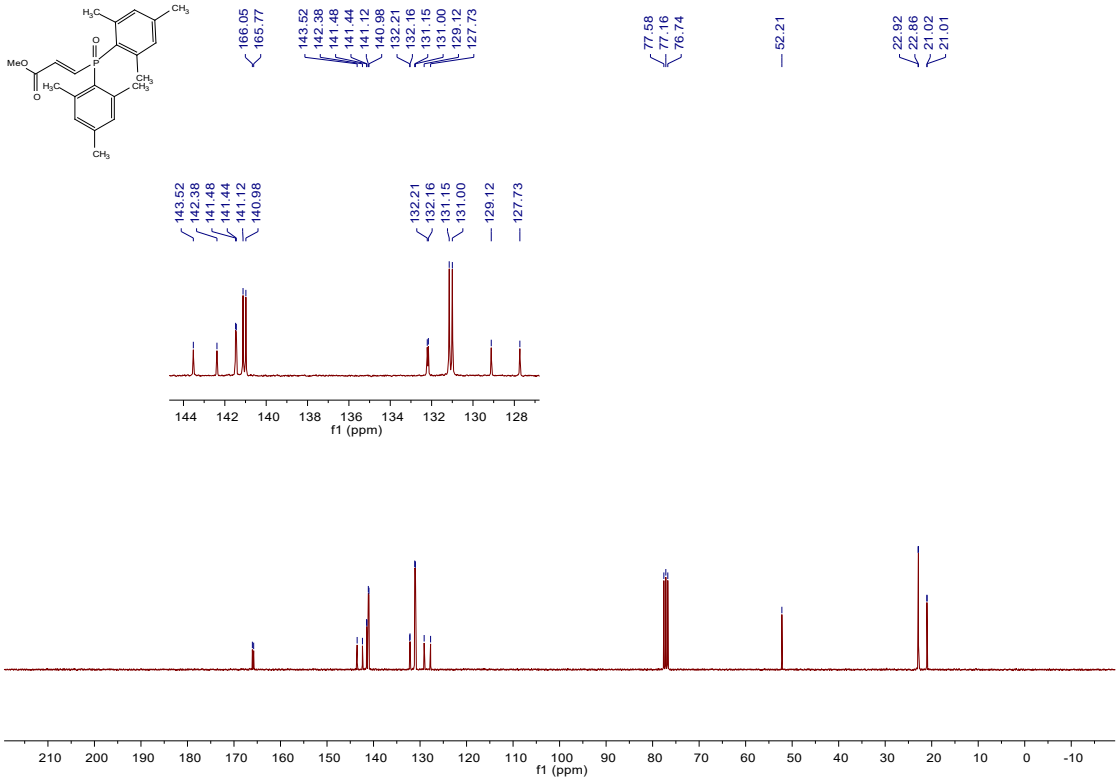
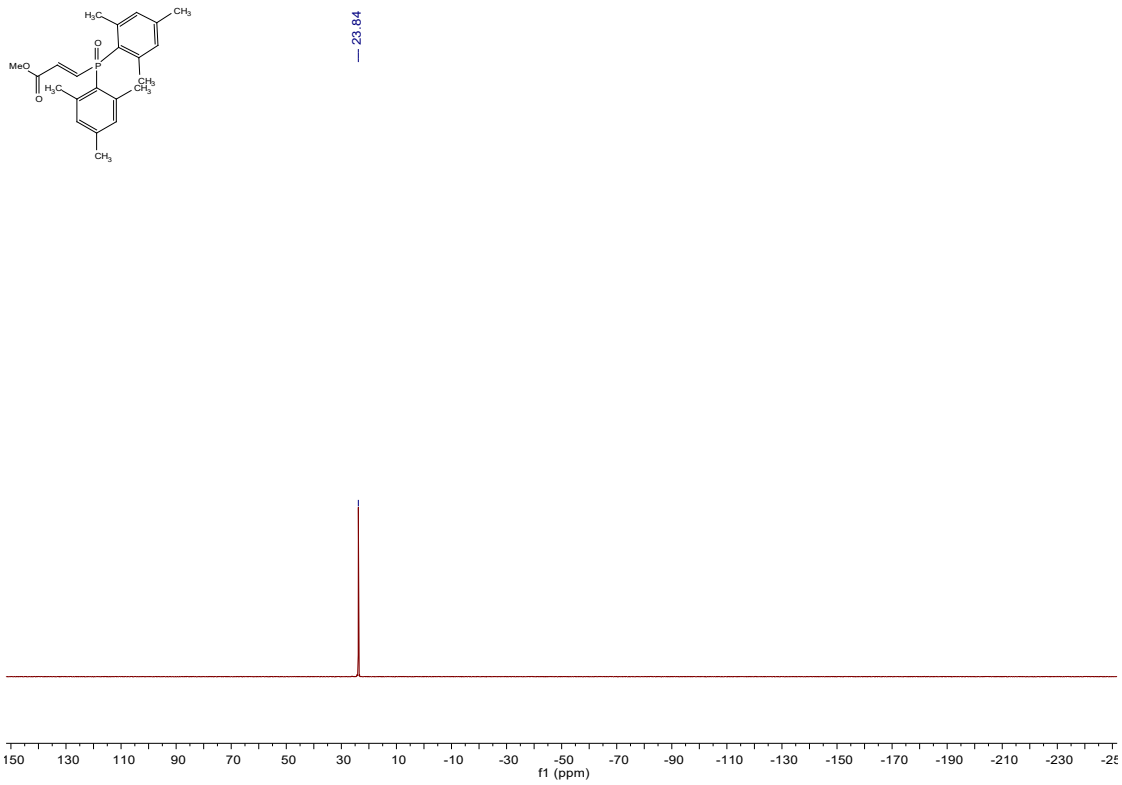


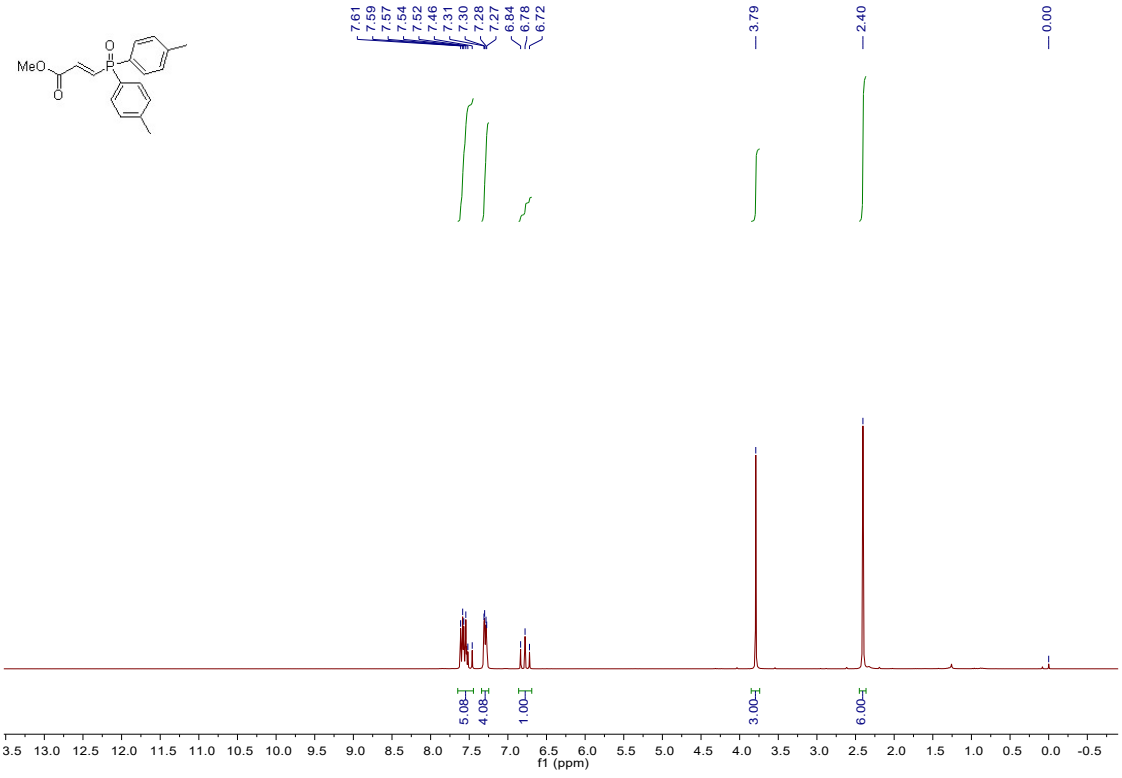
^{1}H NMR of compound **3an**



^{13}C NMR of compound **3an**



^{31}P NMR of compound **3an**



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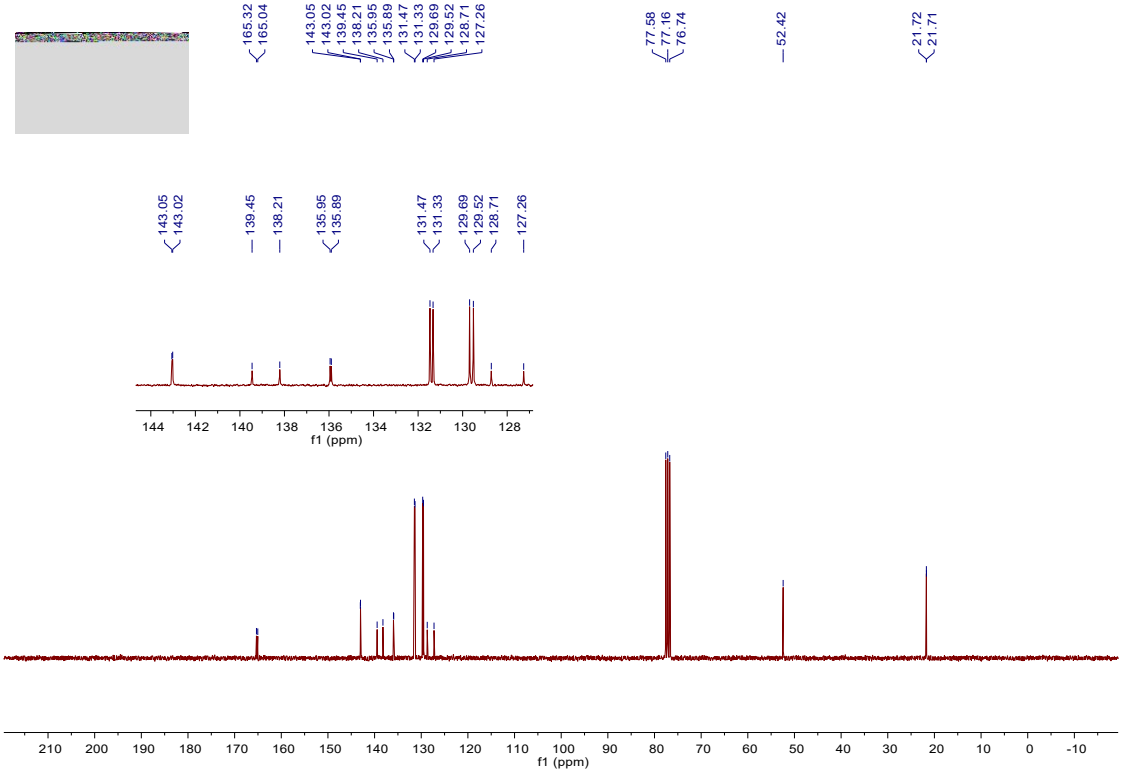

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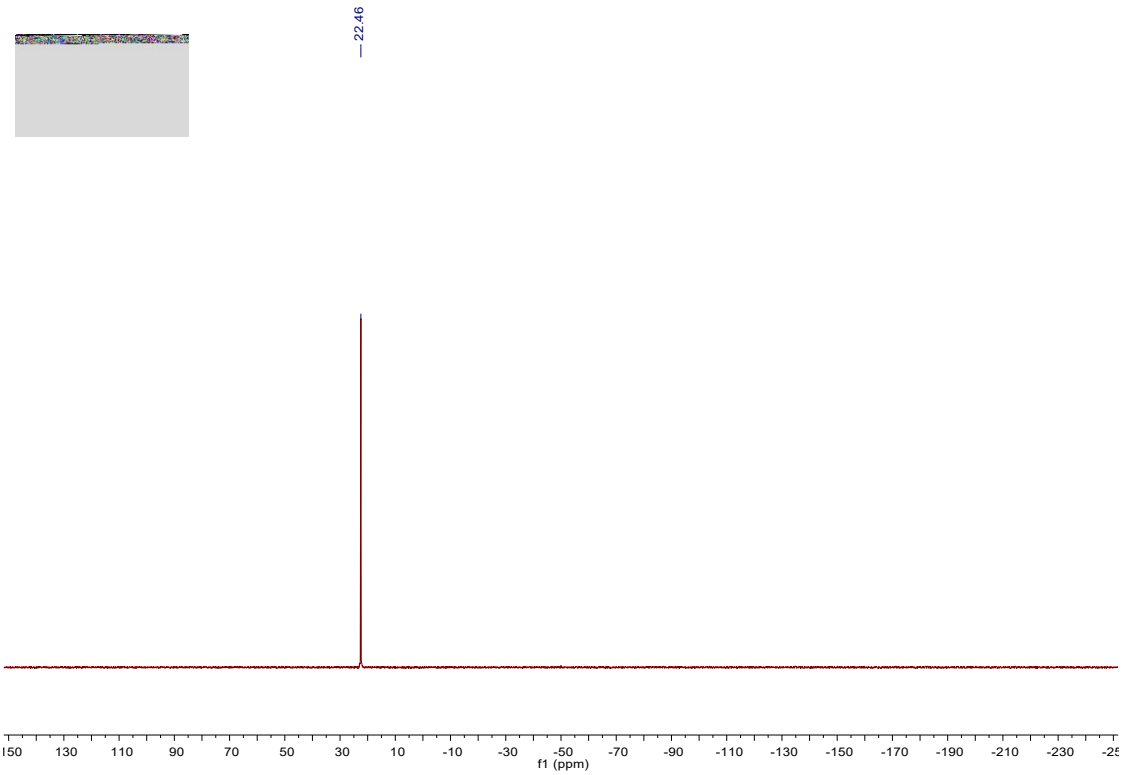
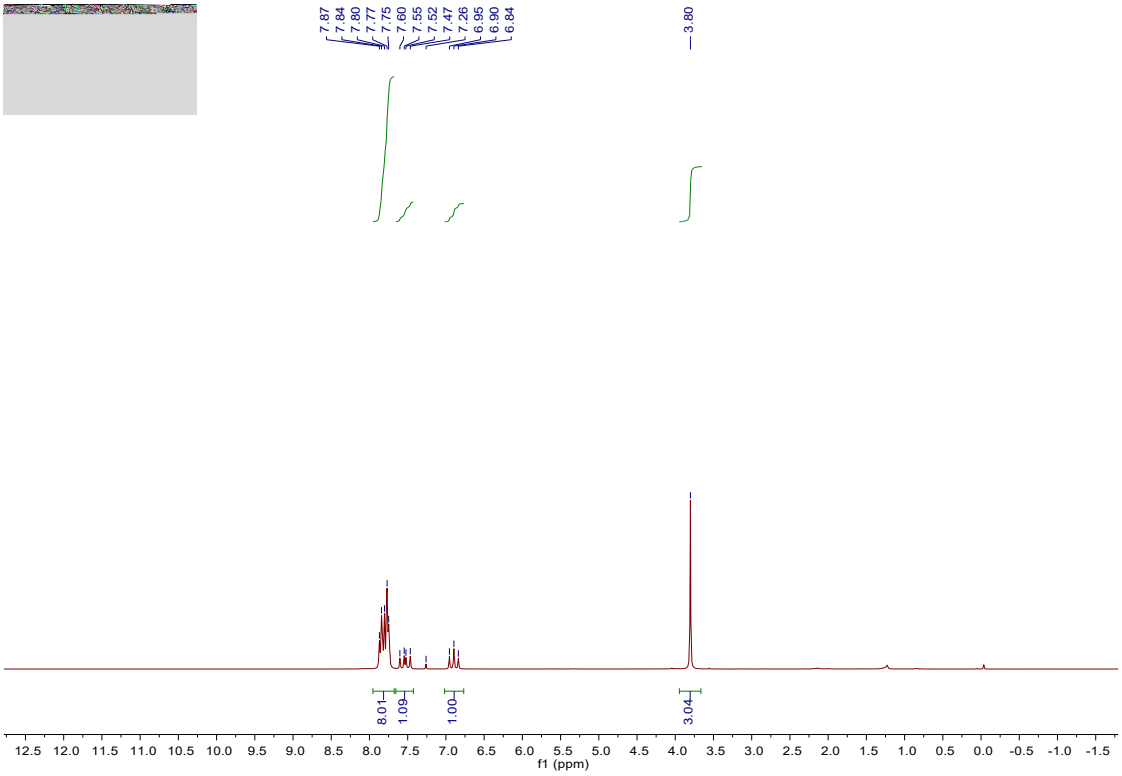


^{31}P NMR of compound **3ao**



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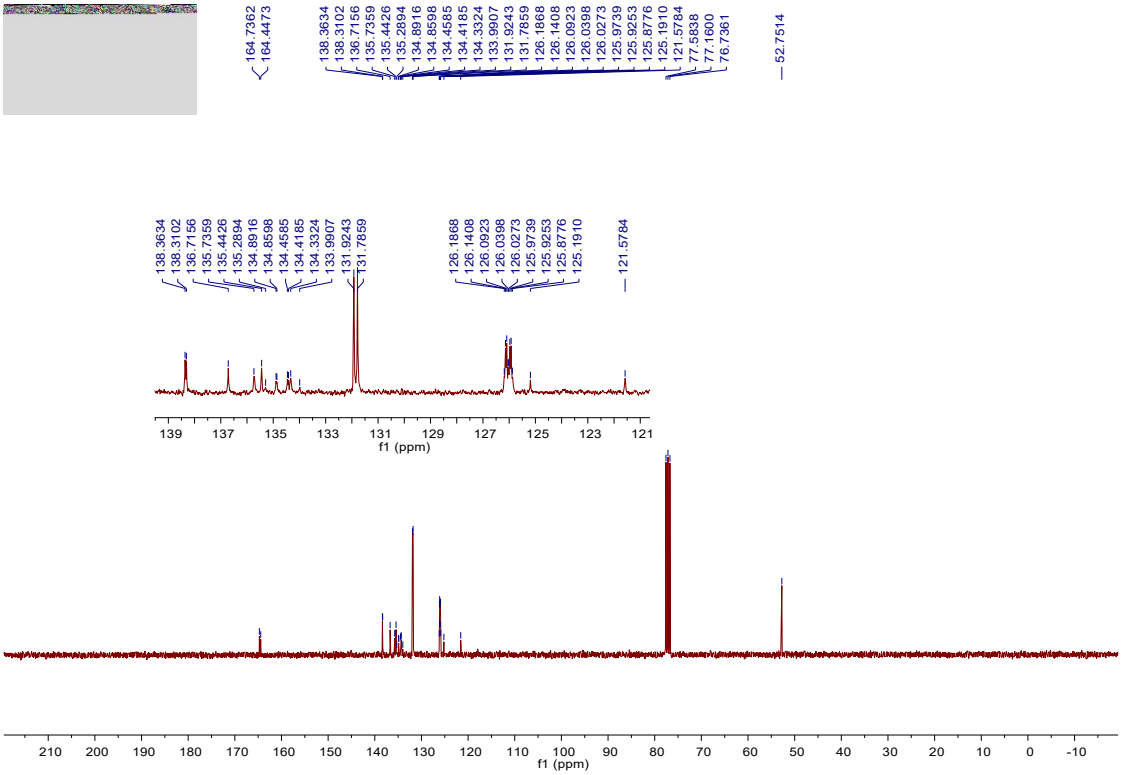

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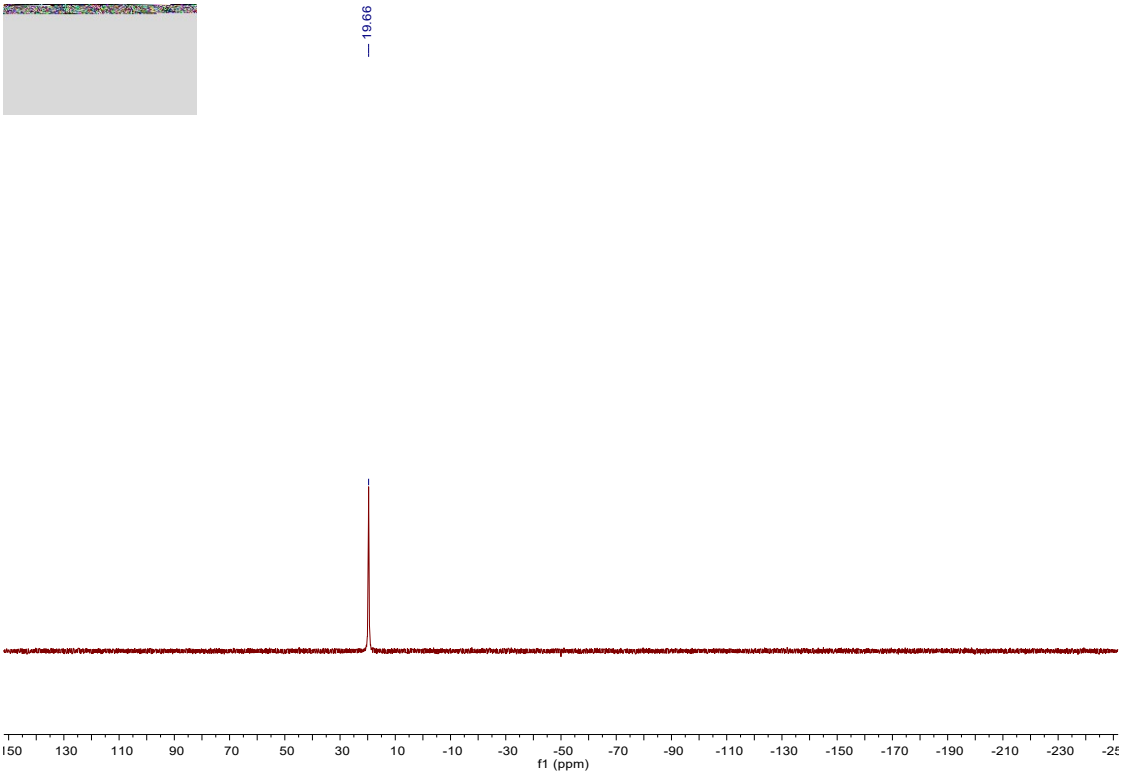
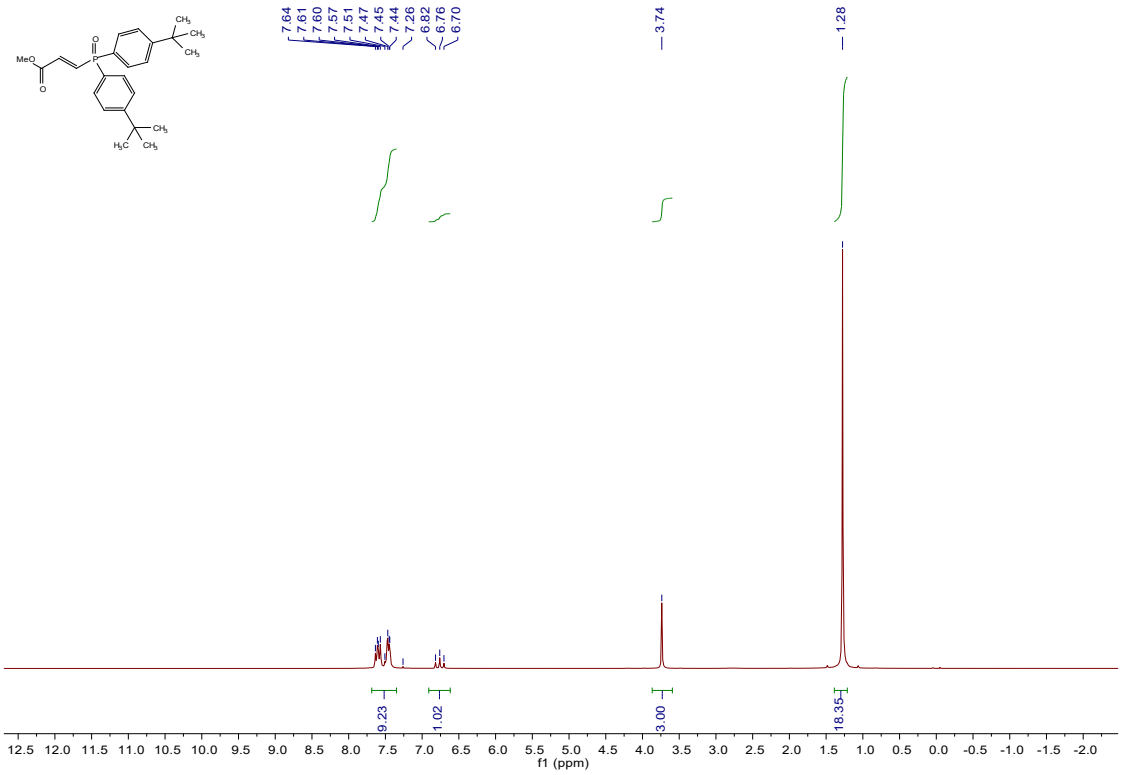


^{31}P NMR of compound **3ap**



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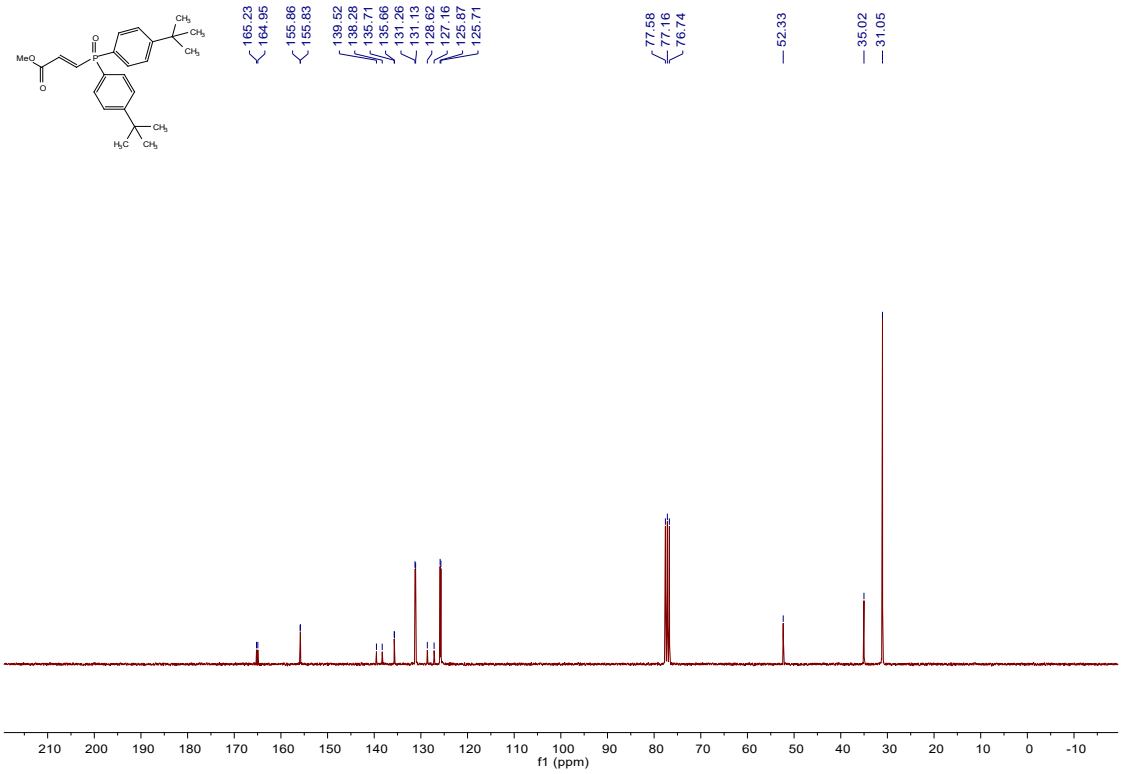

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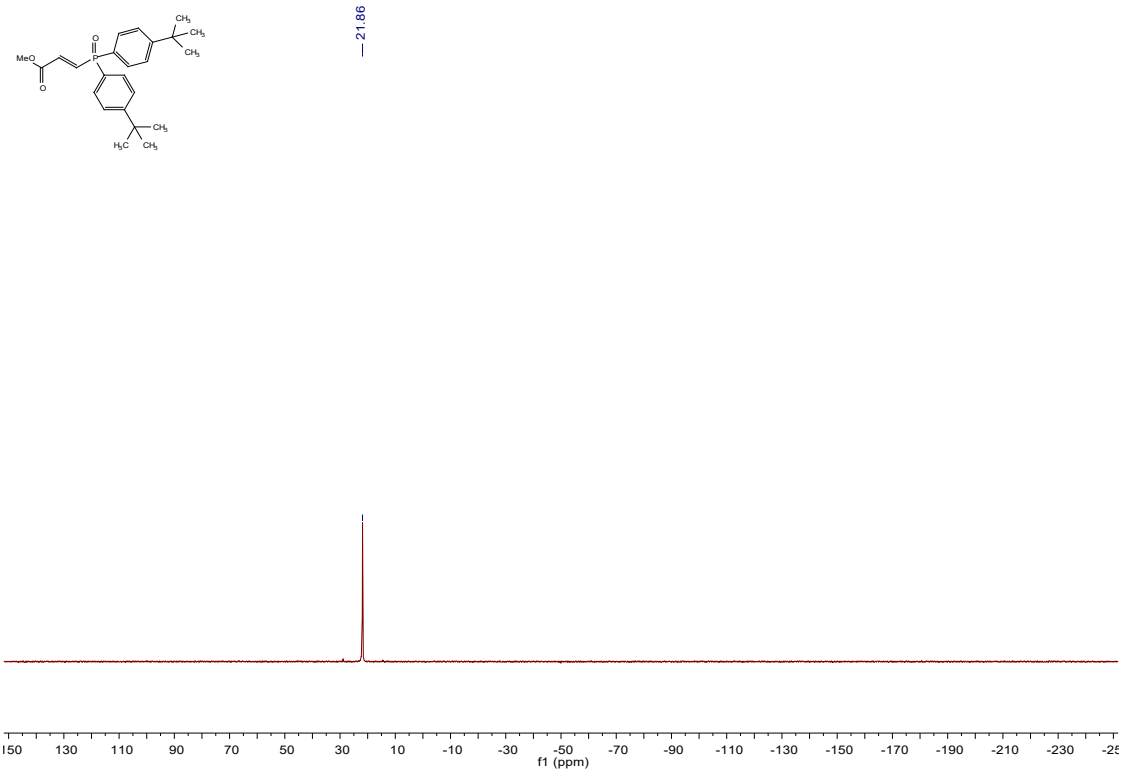

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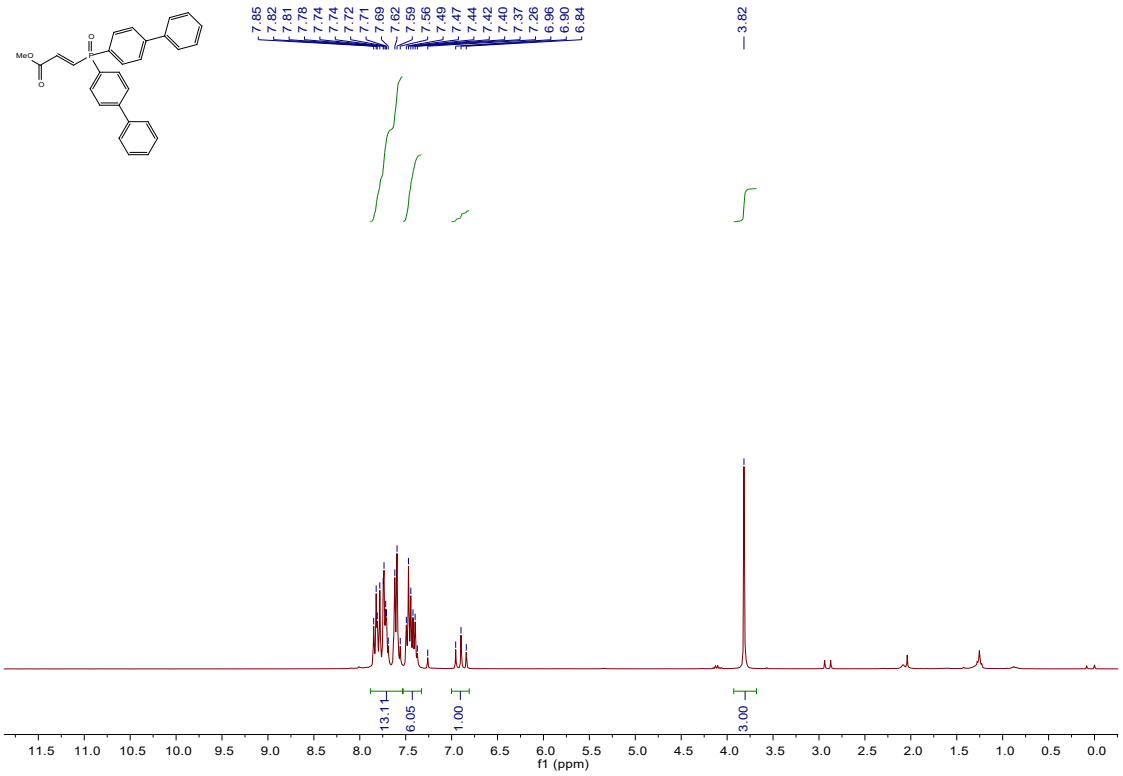
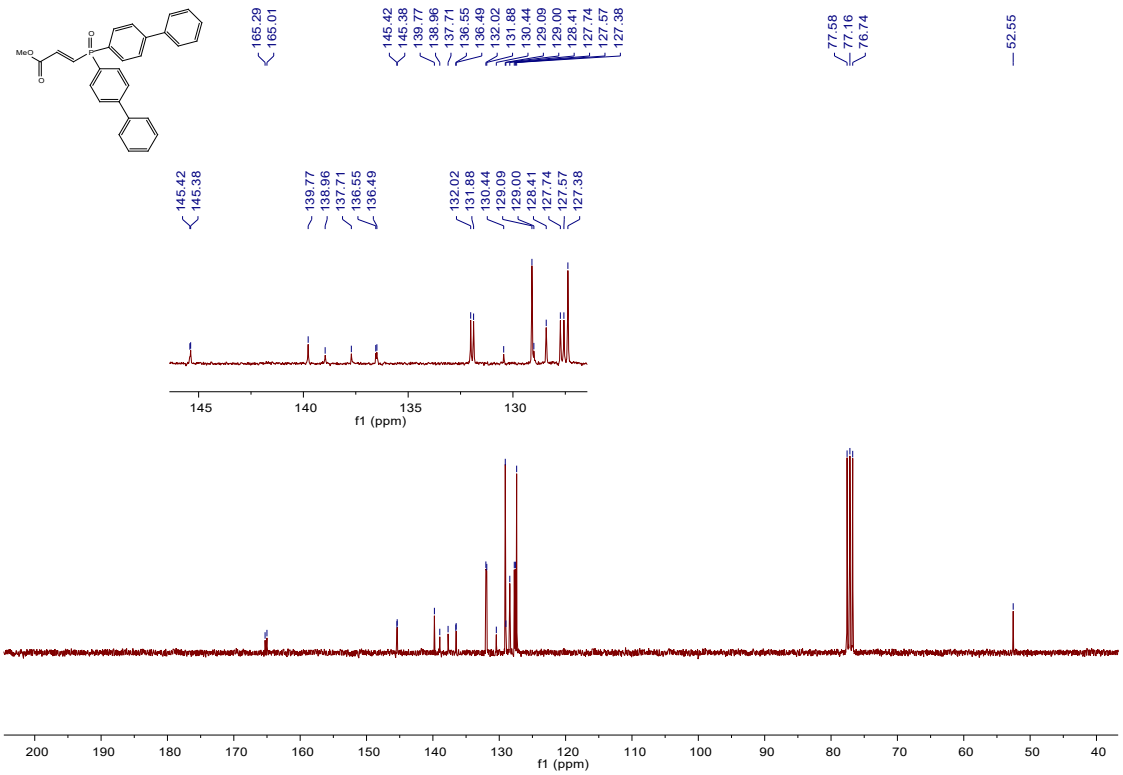
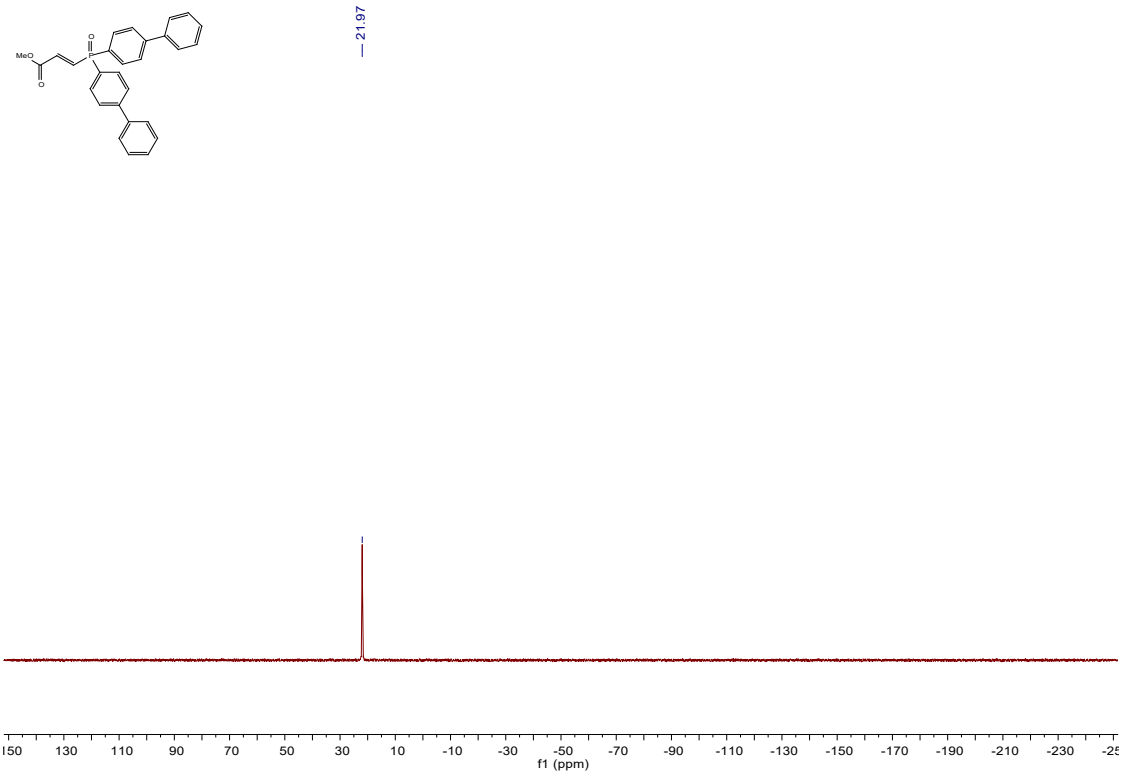


^{1}H NMR of compound **3ar**



^{13}C NMR of compound **3ar**



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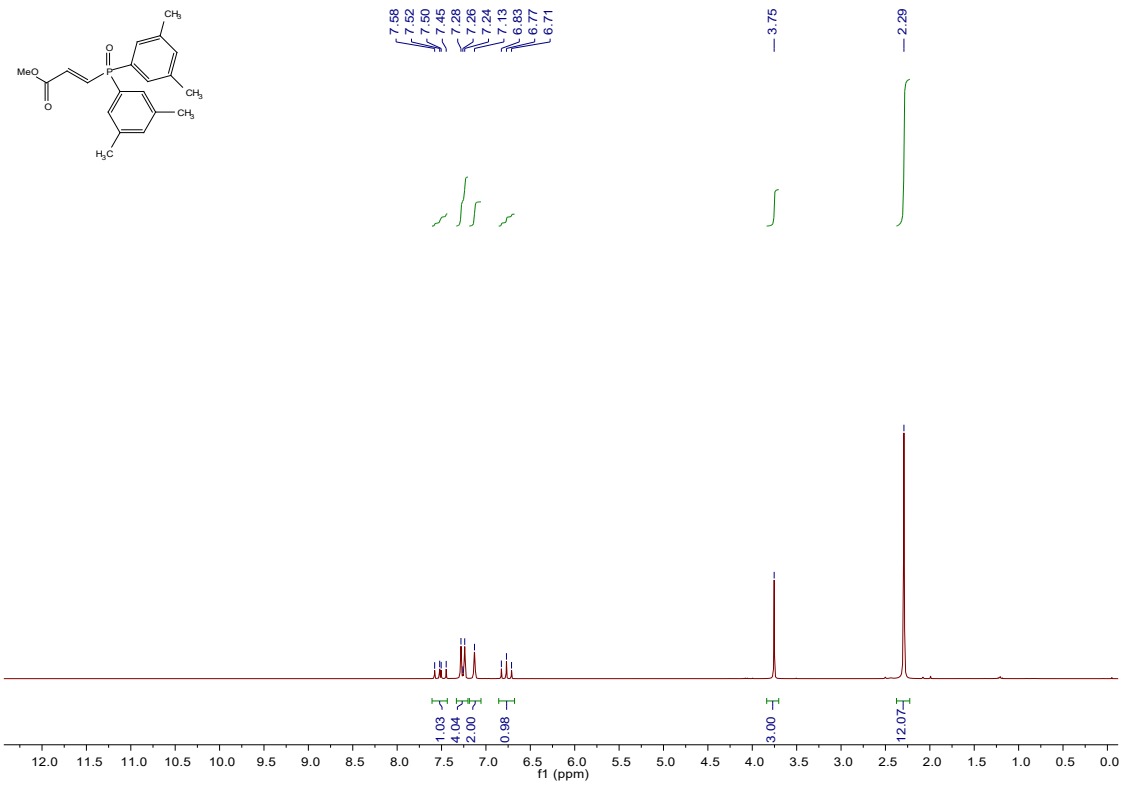

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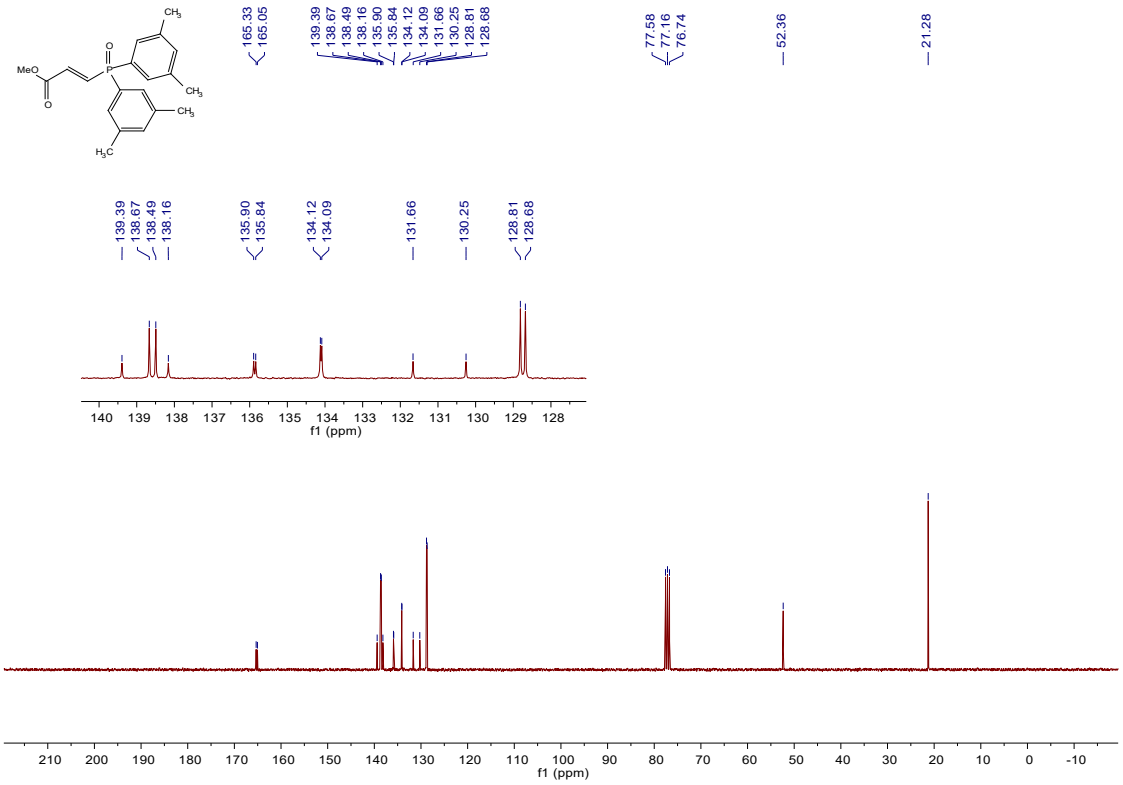

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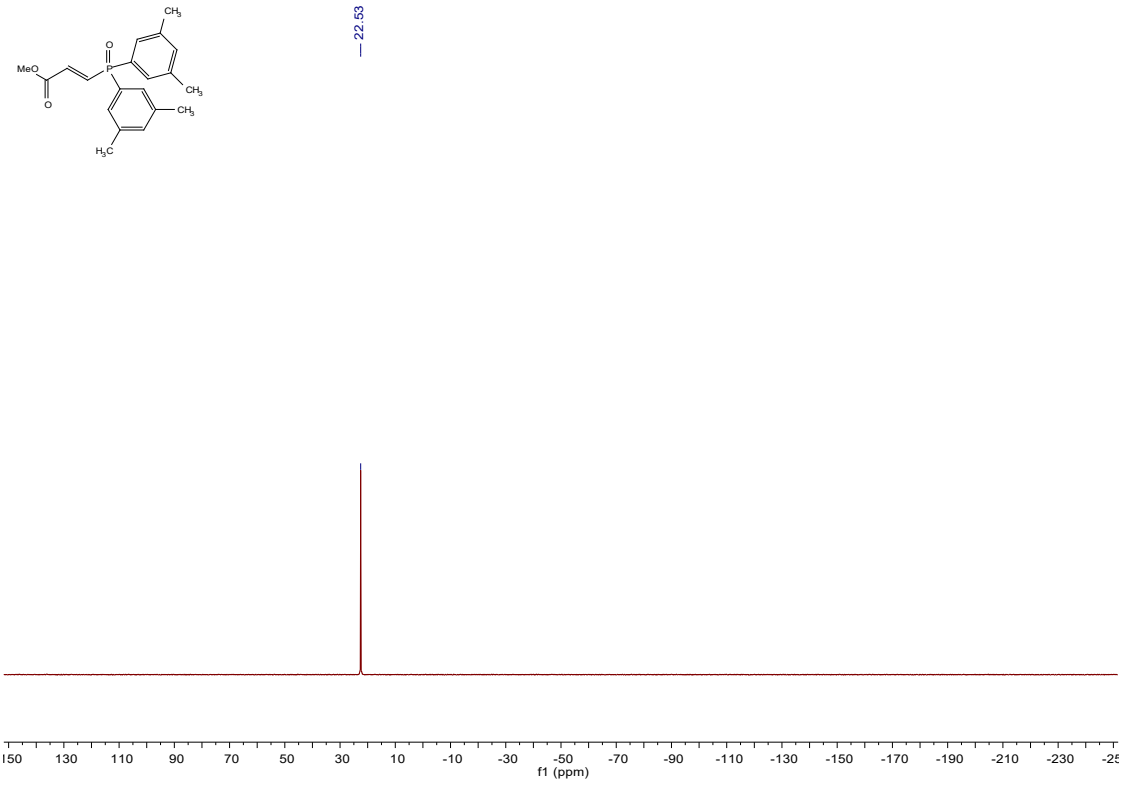

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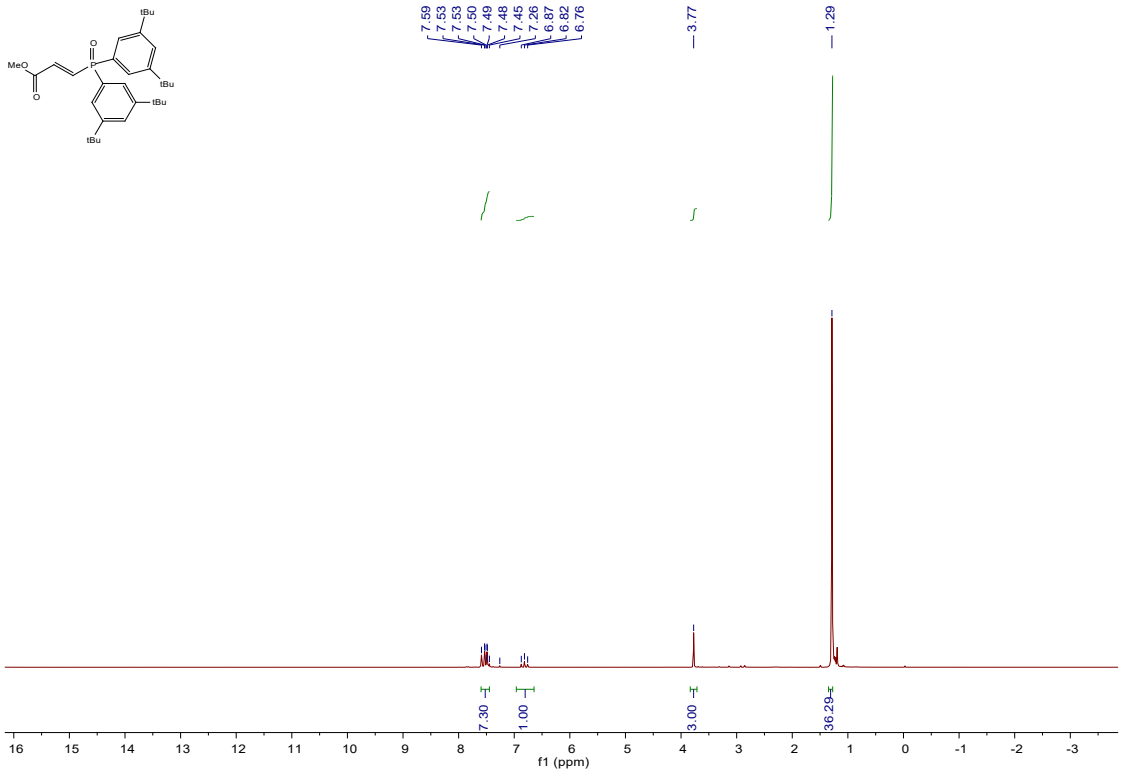

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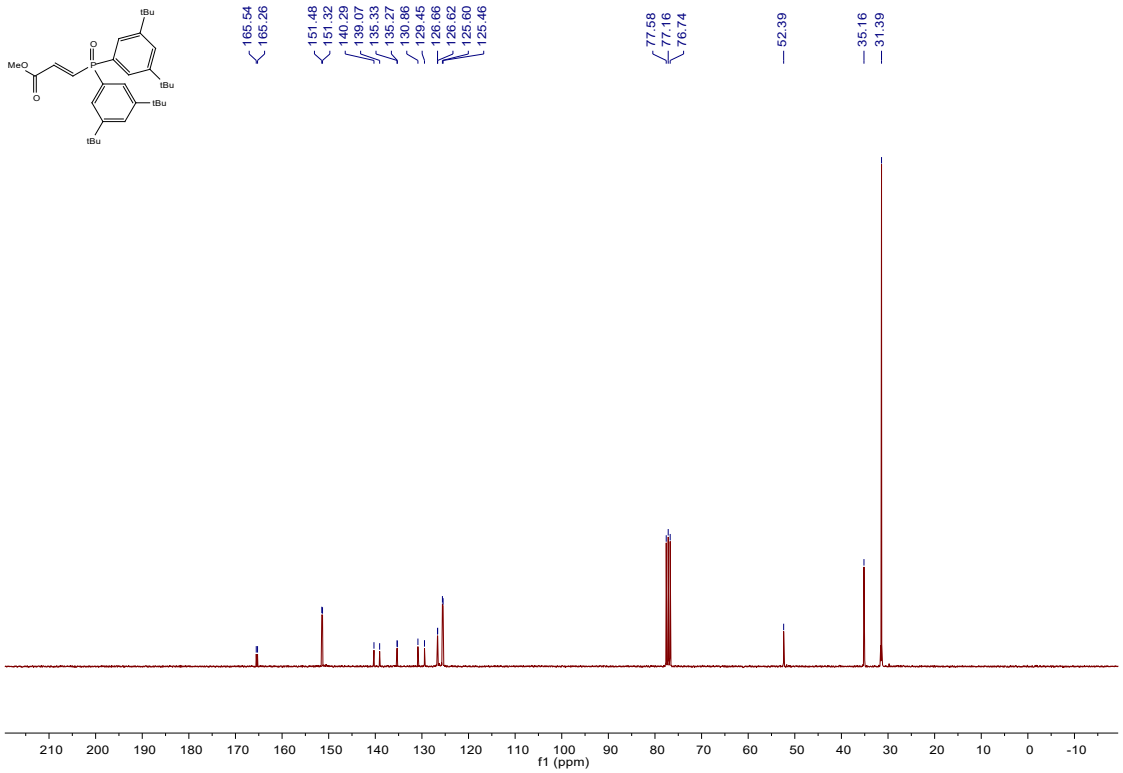
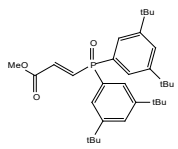
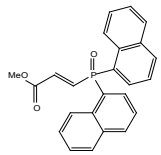


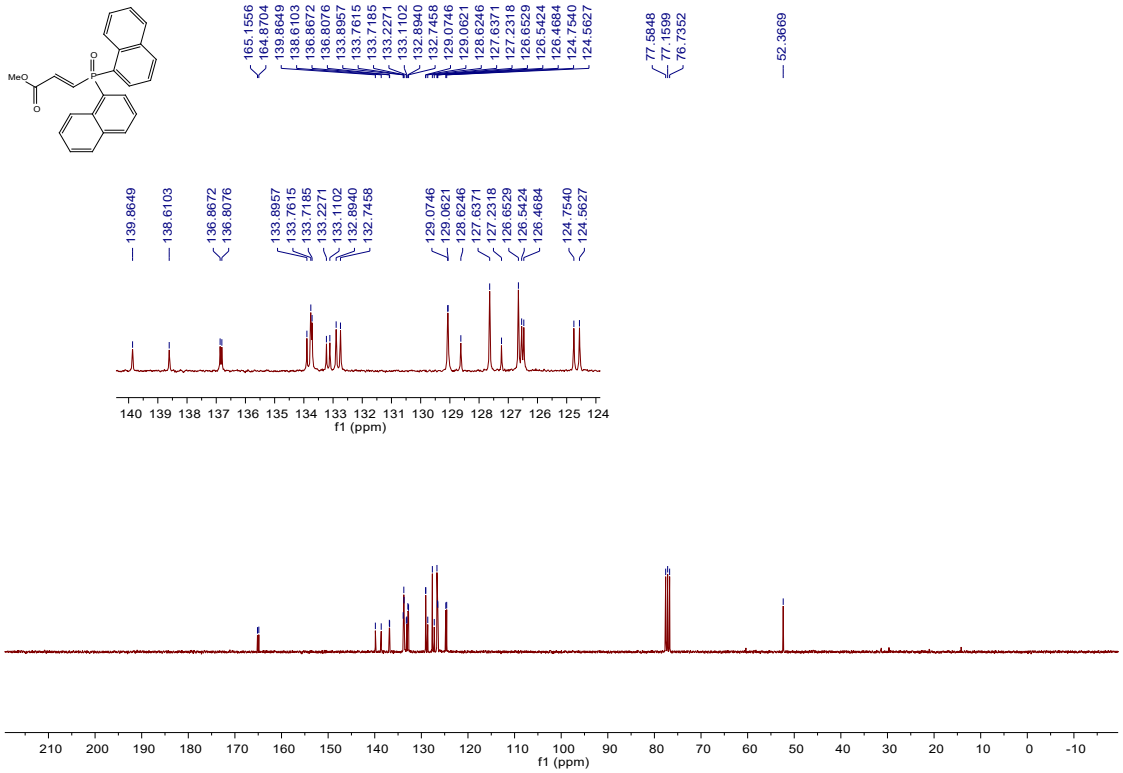
^{13}C NMR of compound **3at**



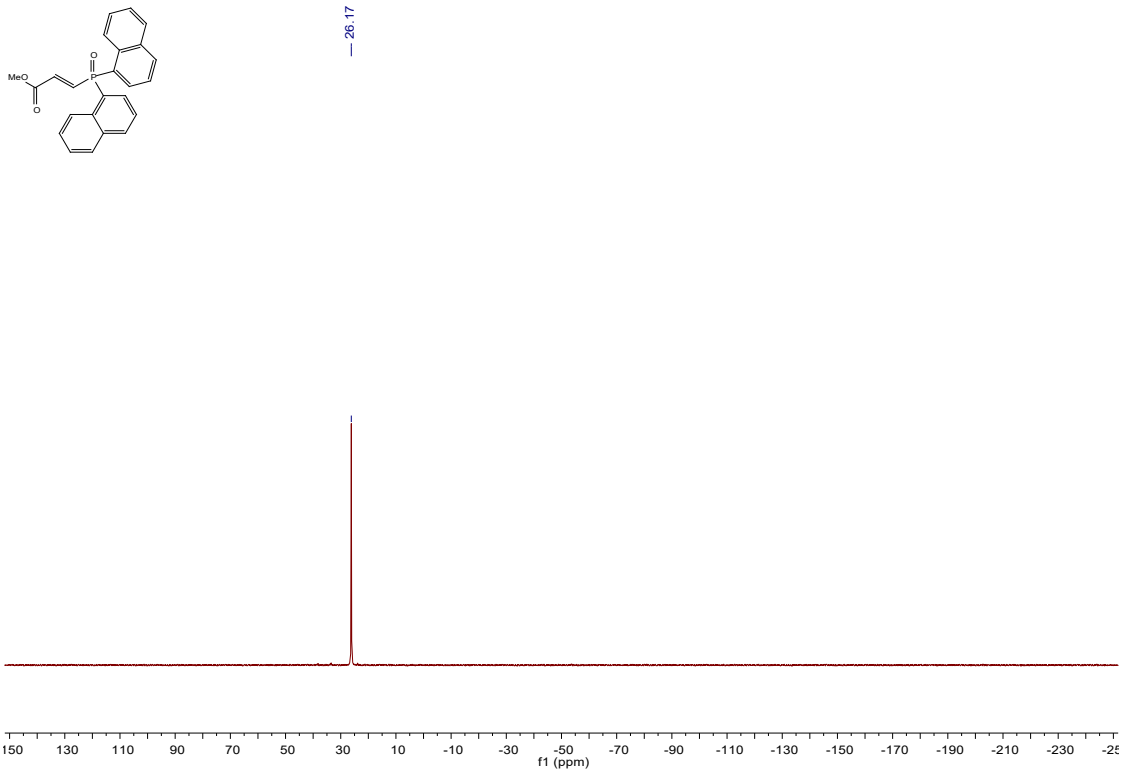
^{31}P NMR of compound **3at**



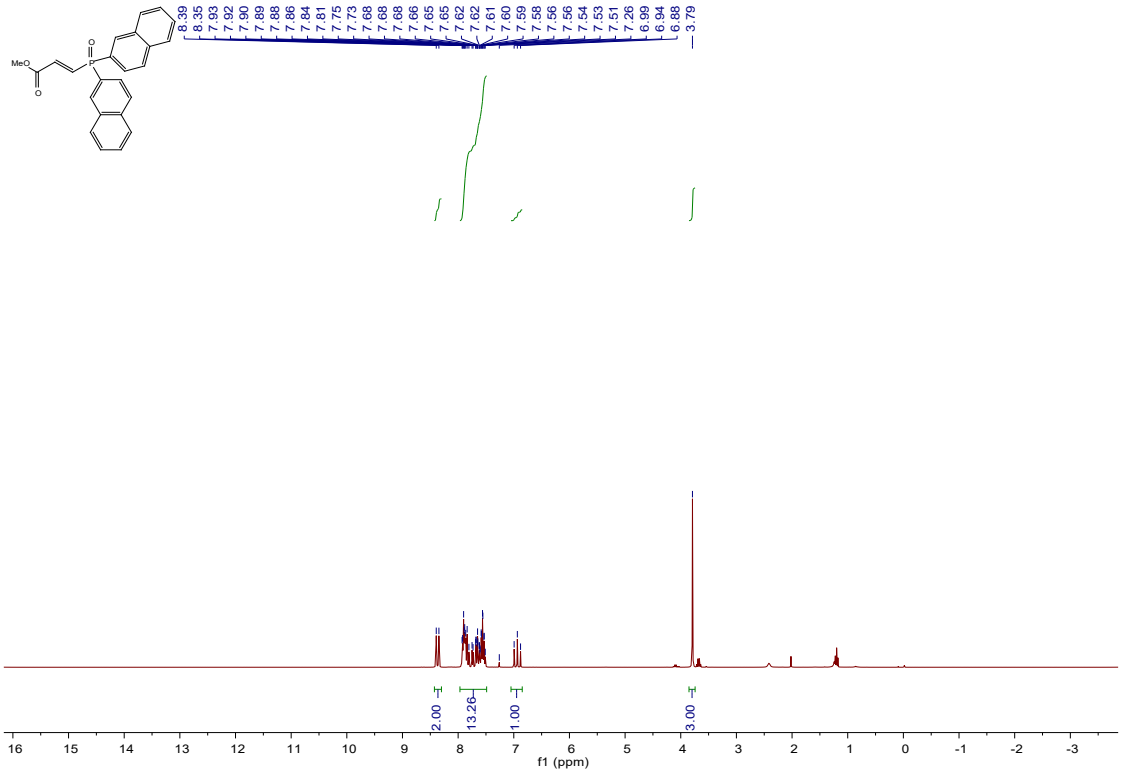
^{1}H NMR of compound **3au**



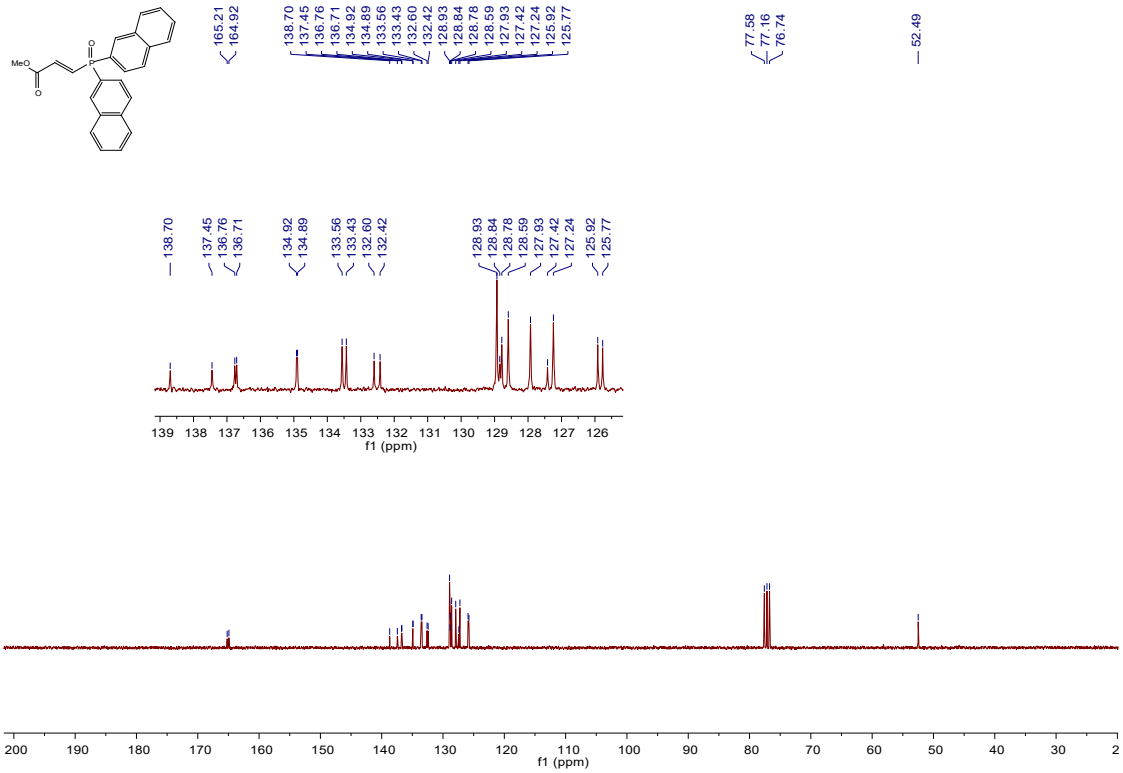
^{13}CNMR of compound **3au**



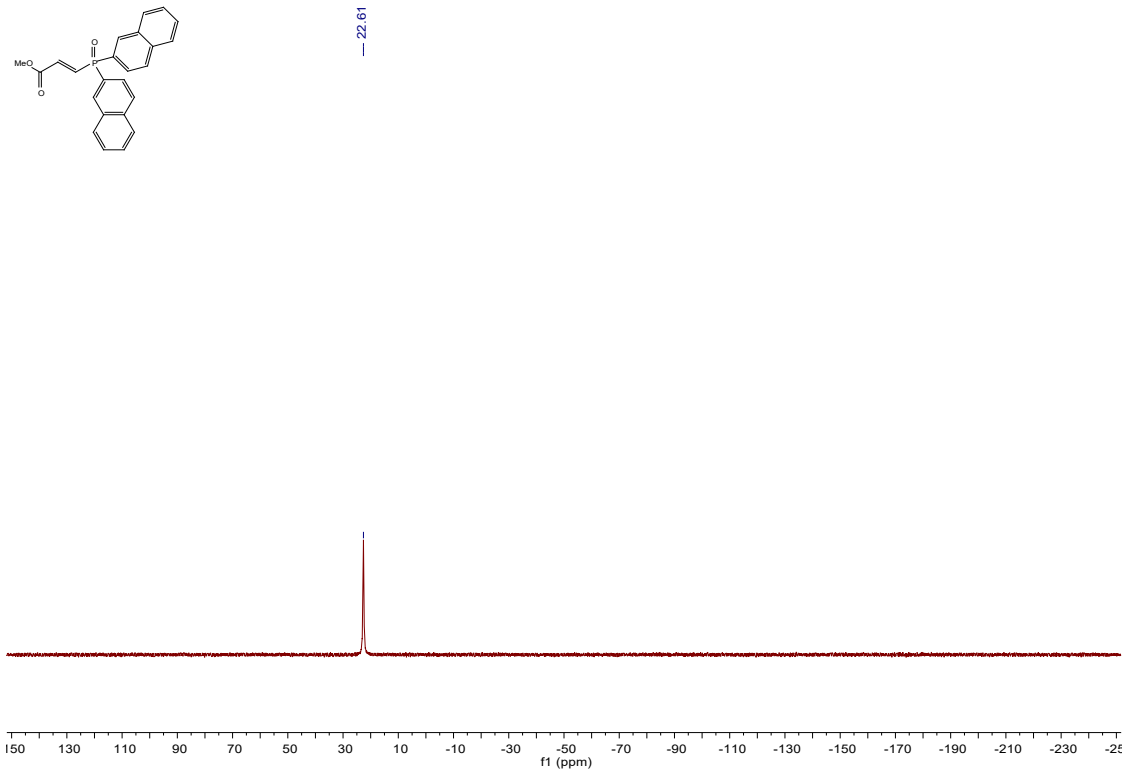
^{31}P NMR of compound **3au**



^{1}H NMR of compound **3av**



^{13}C NMR of compound **3av**



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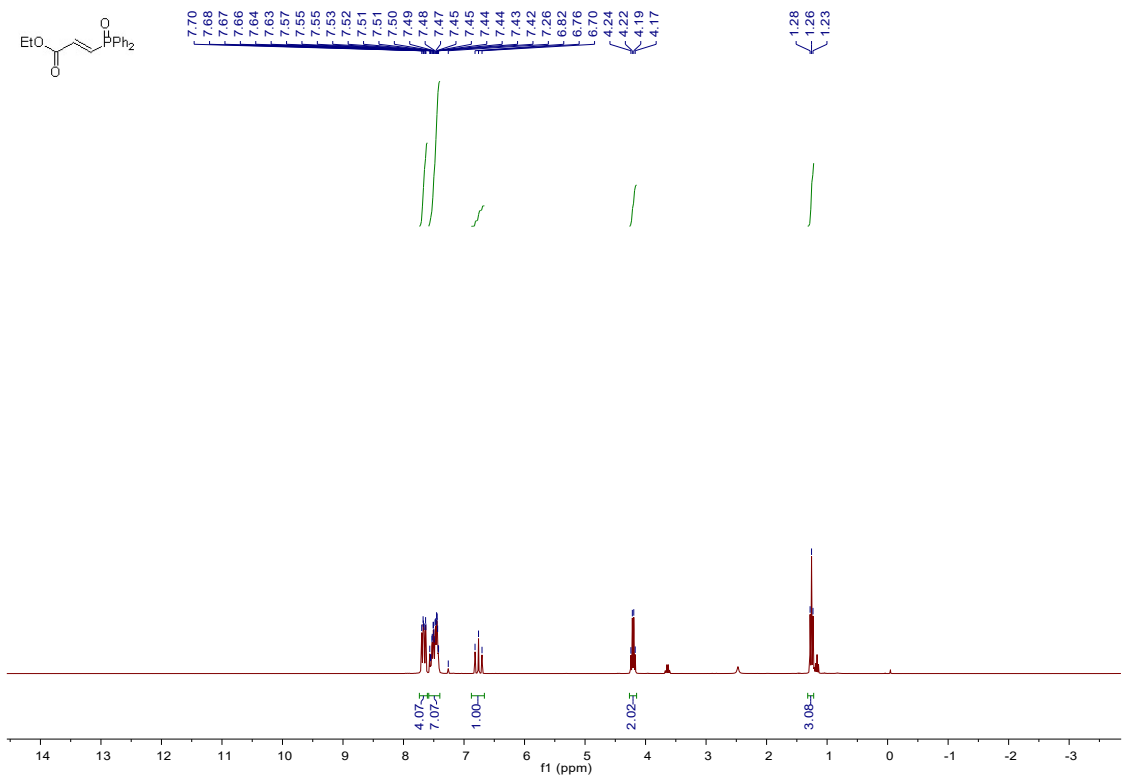

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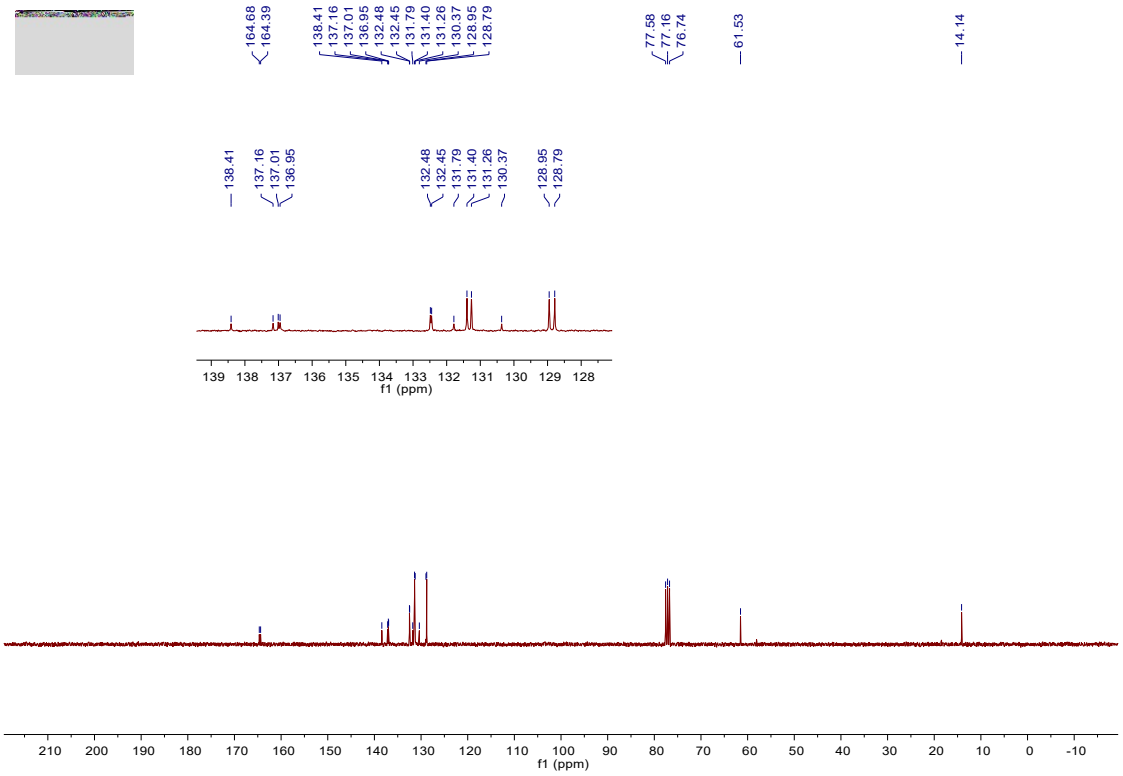

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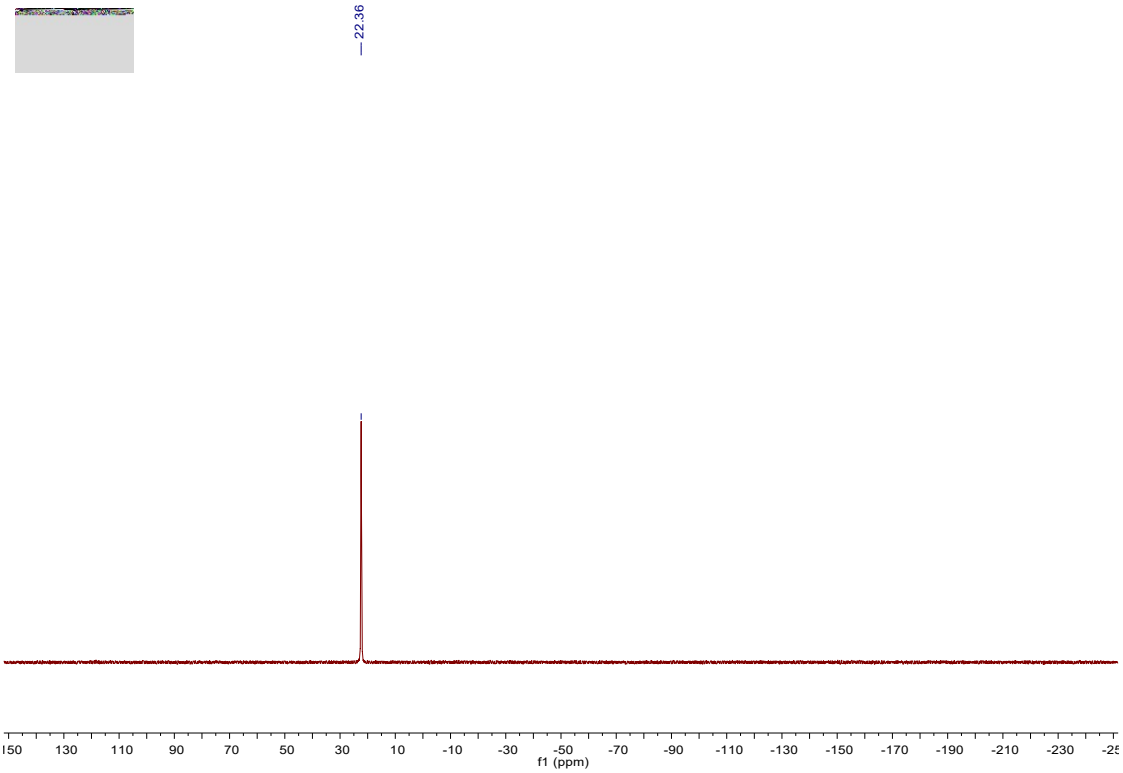

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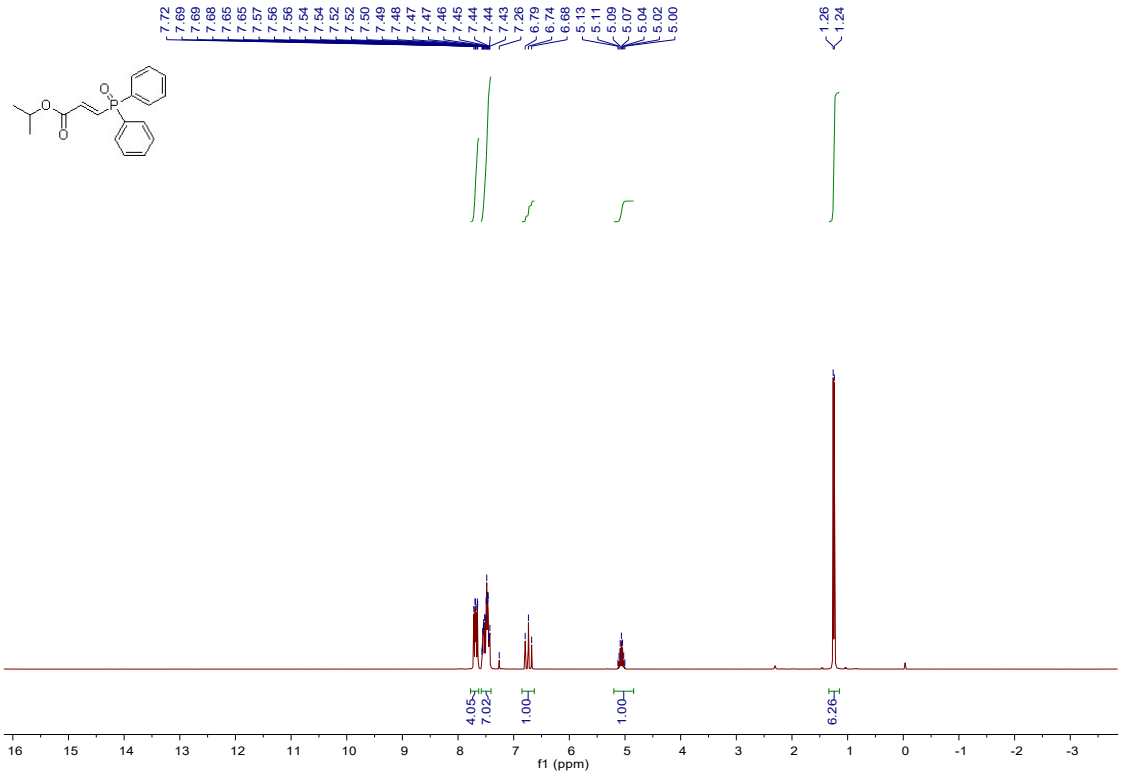

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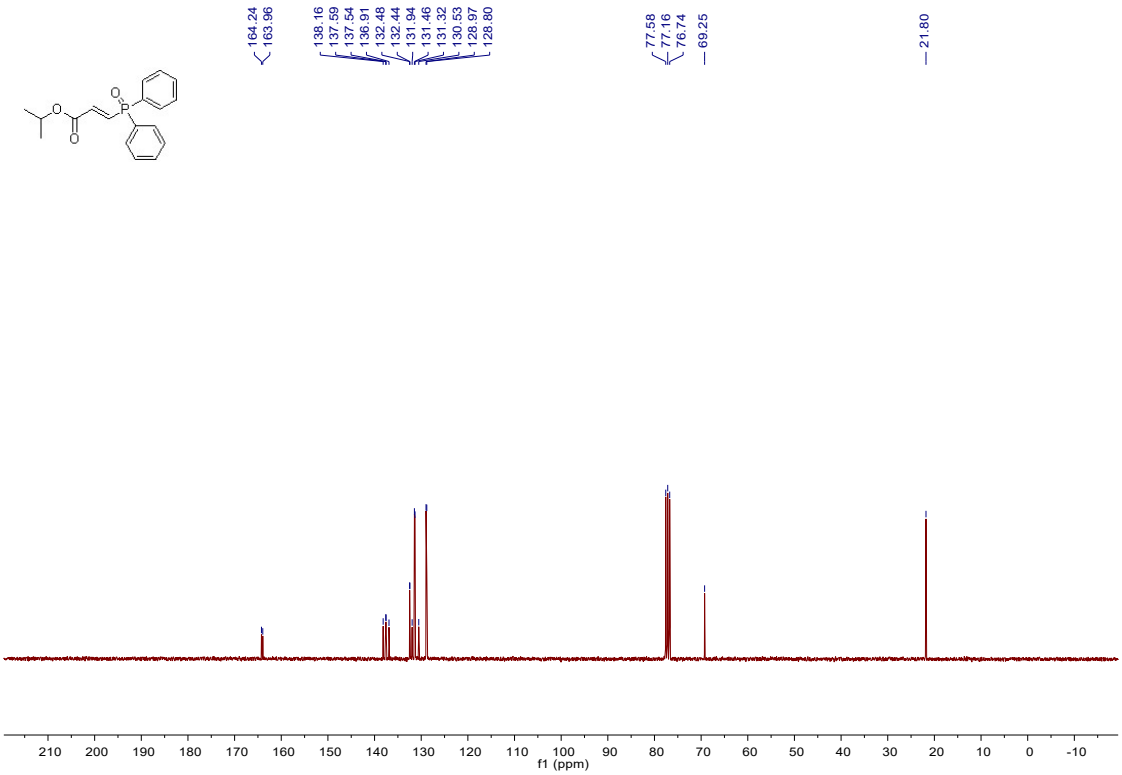

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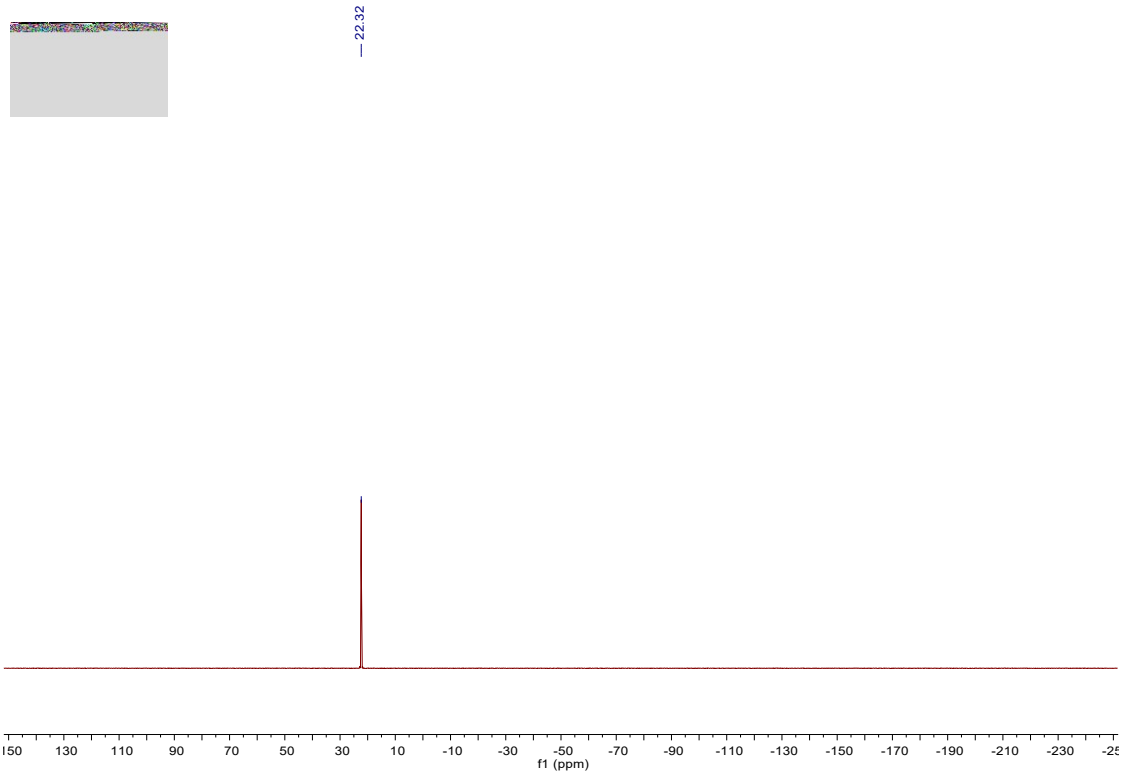

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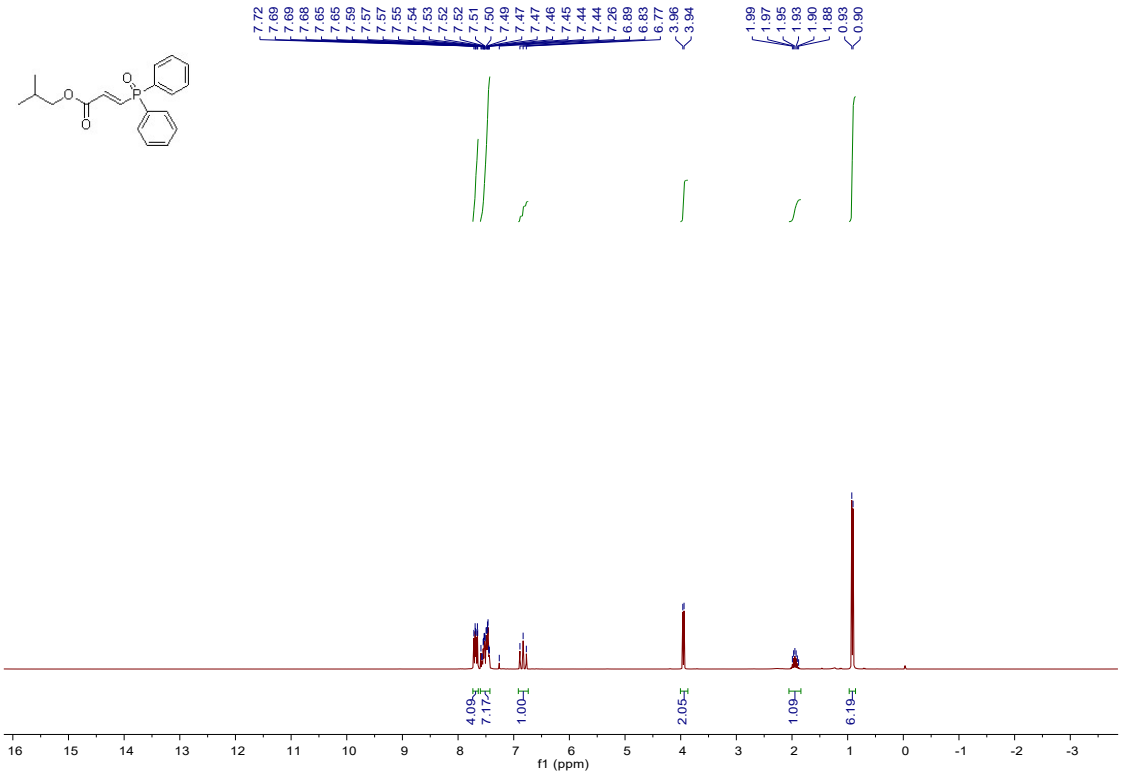

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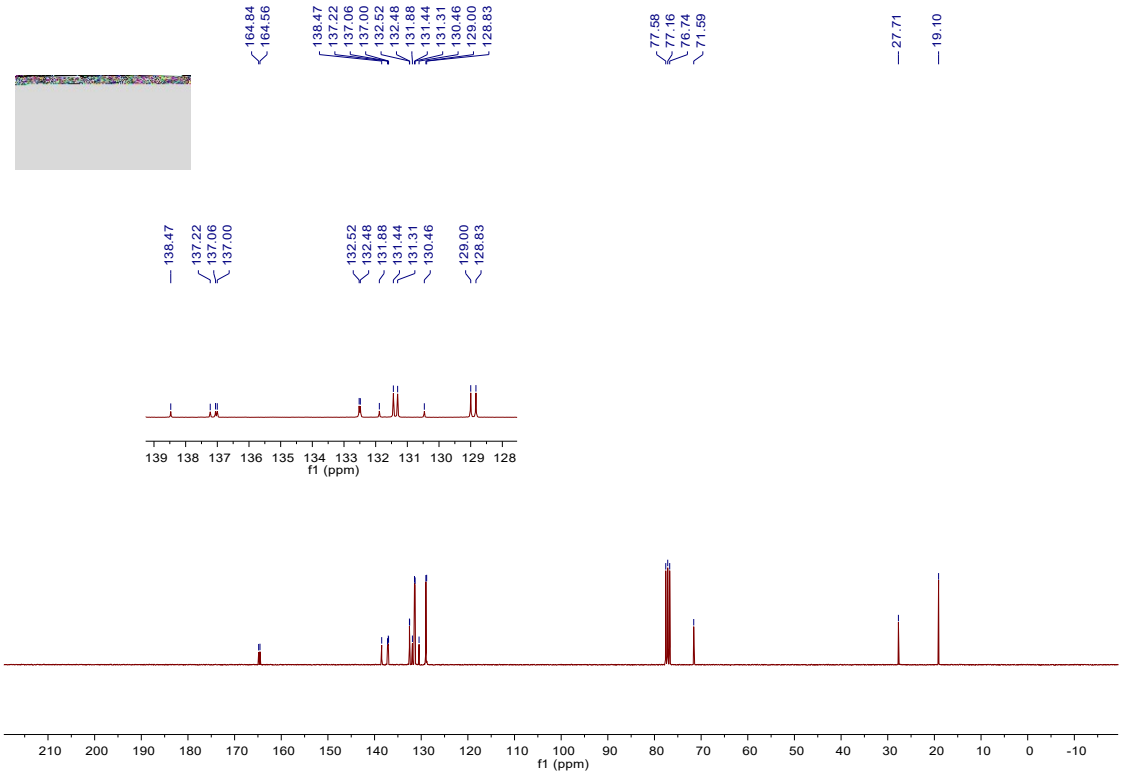
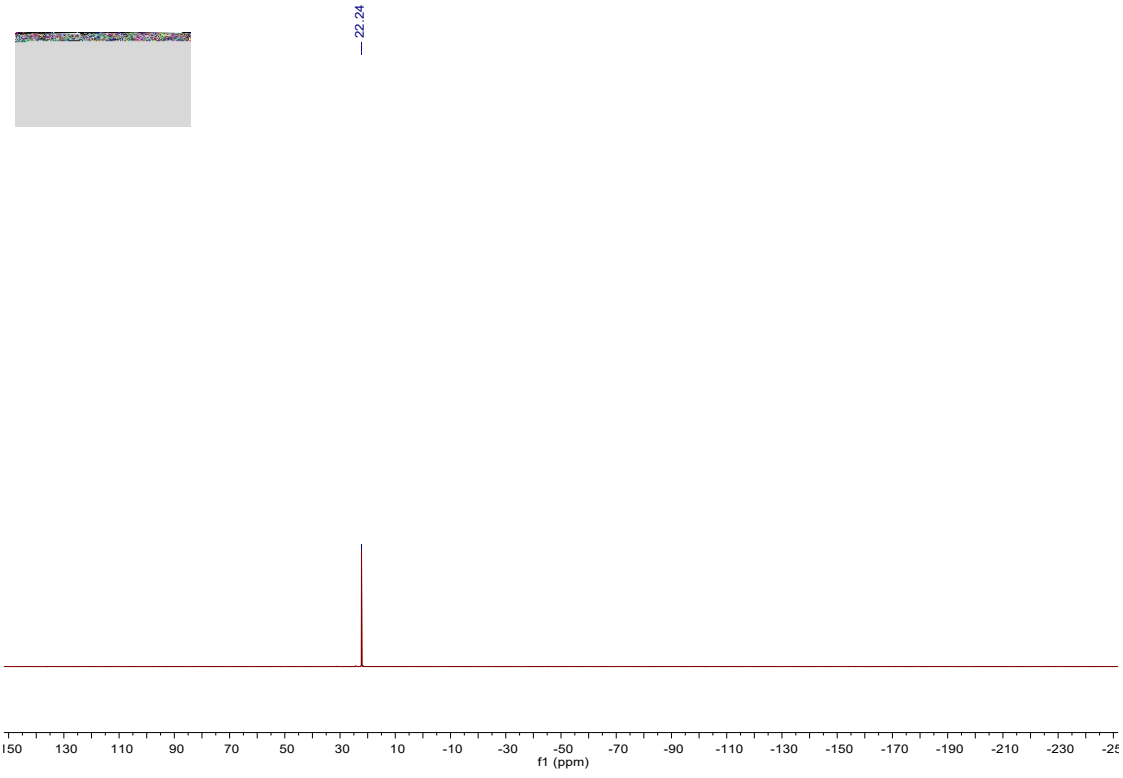
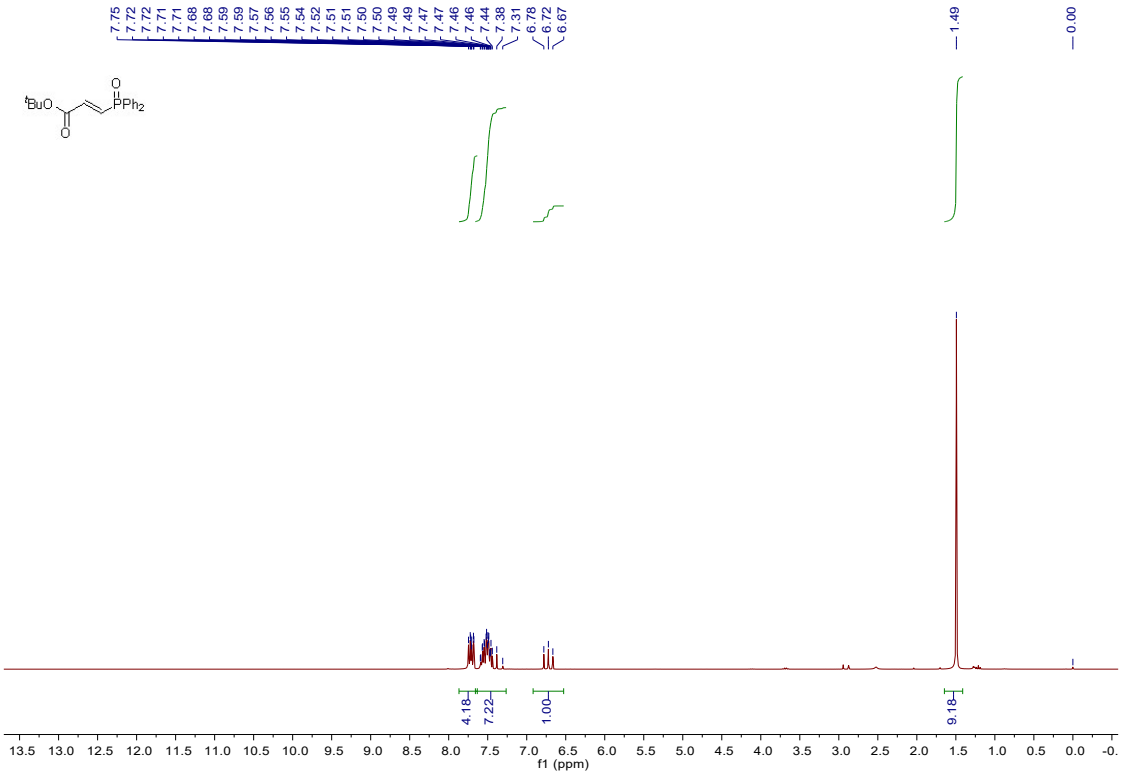


^{13}C NMR of compound **3dk**



^{31}P NMR of compound **3dk**



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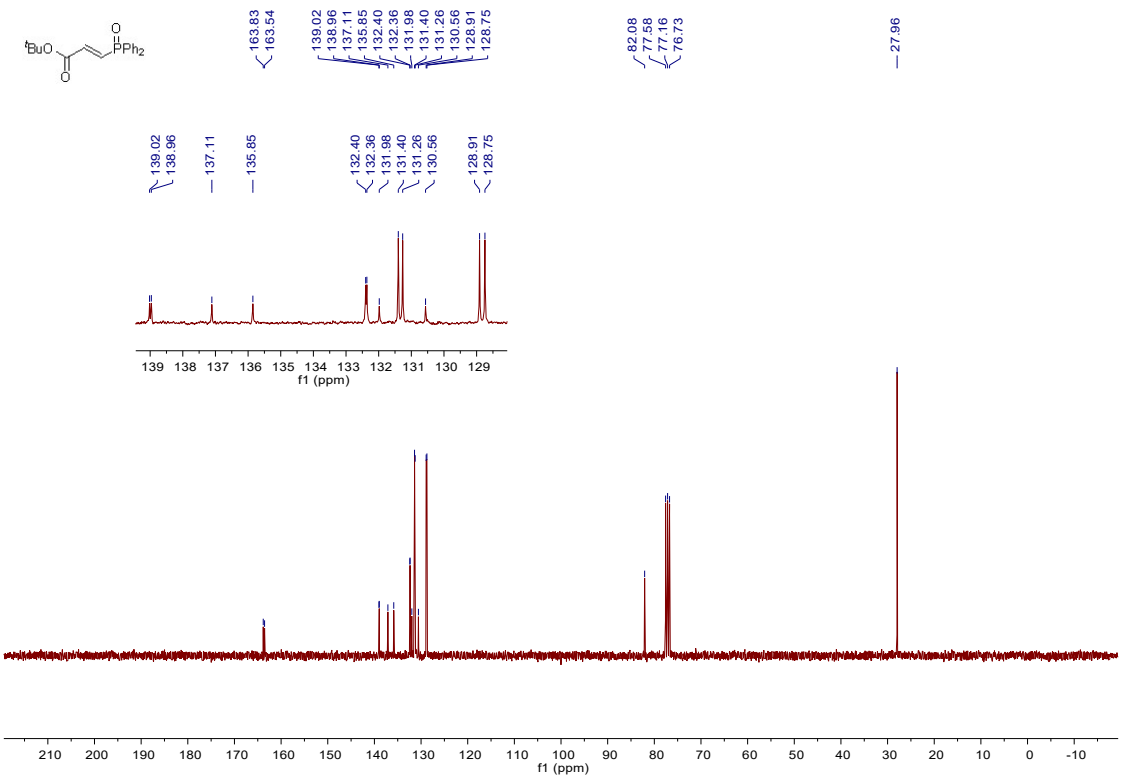
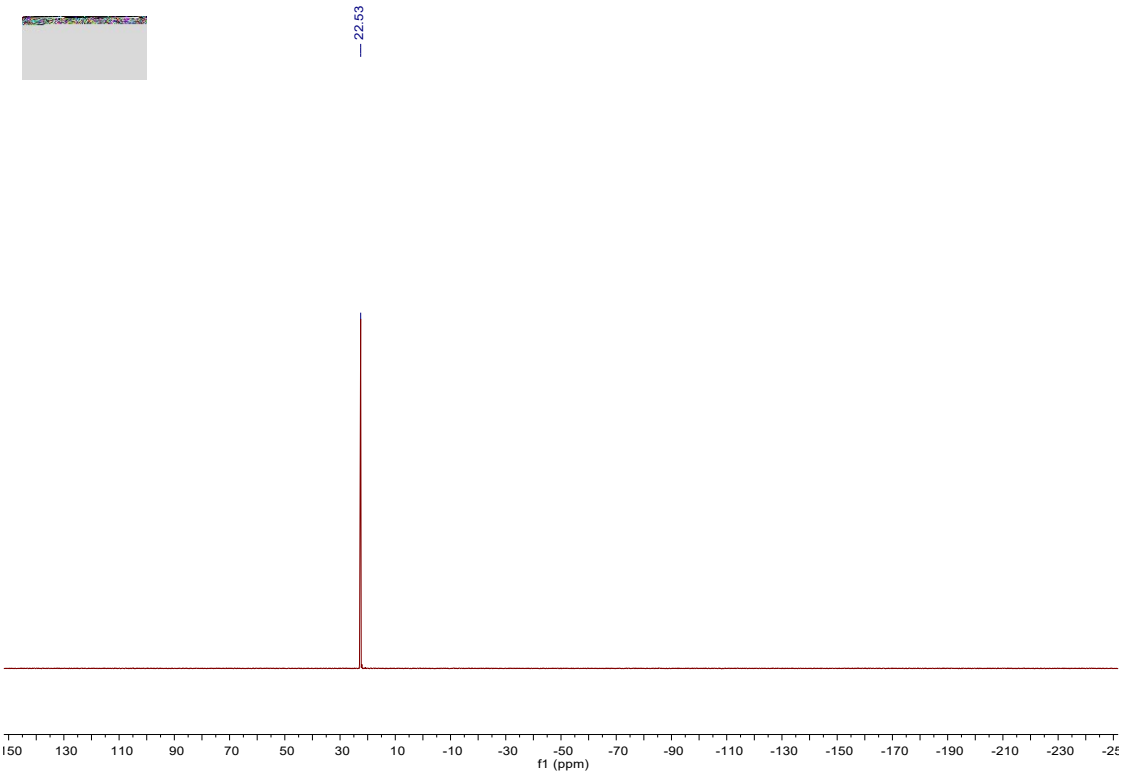
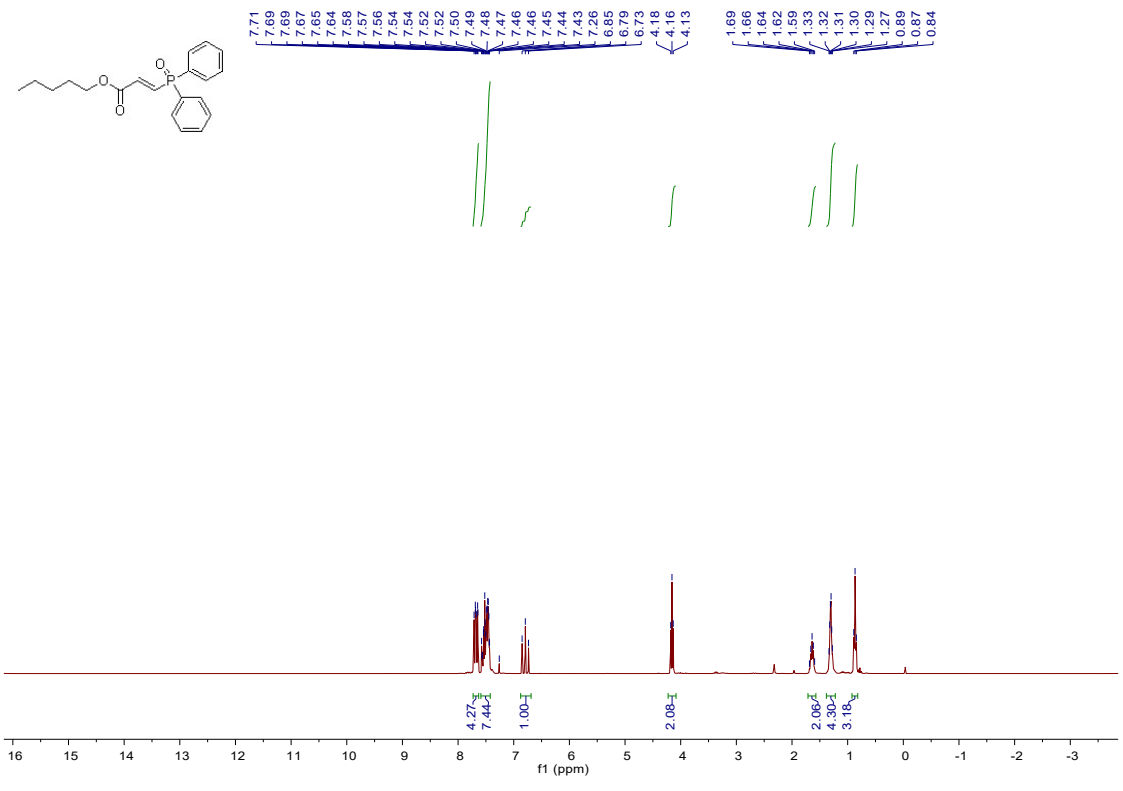


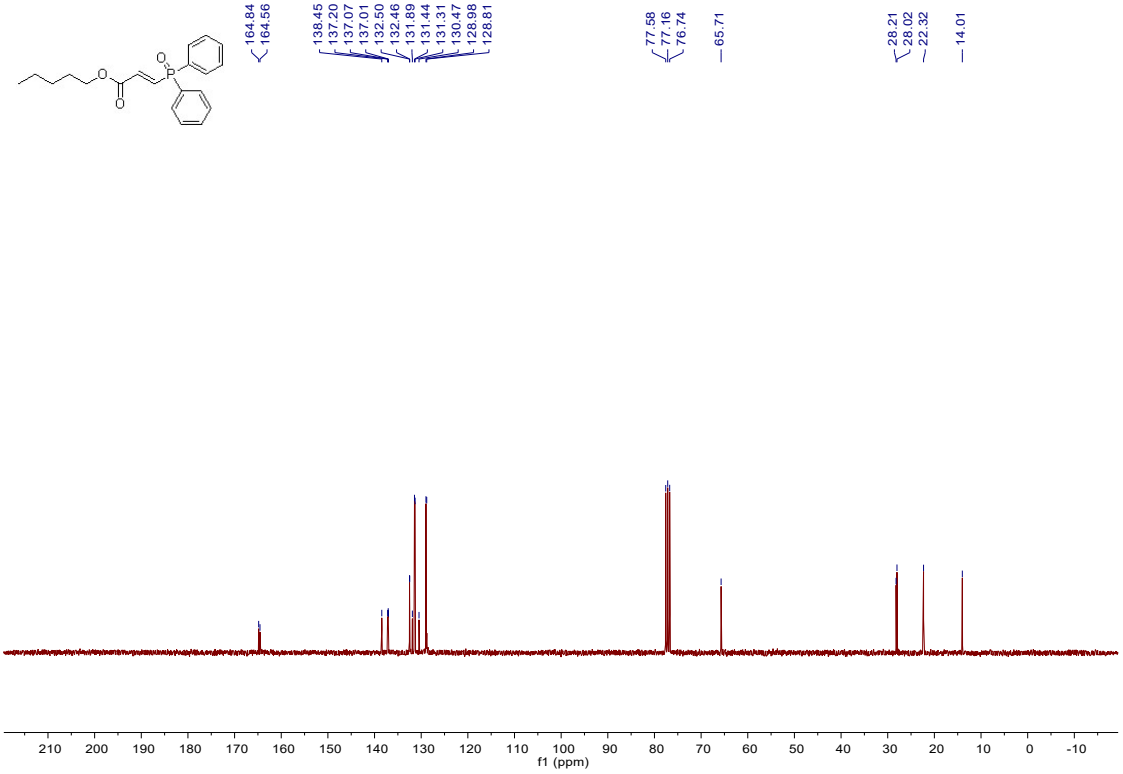
^{13}C NMR of compound **3ek**



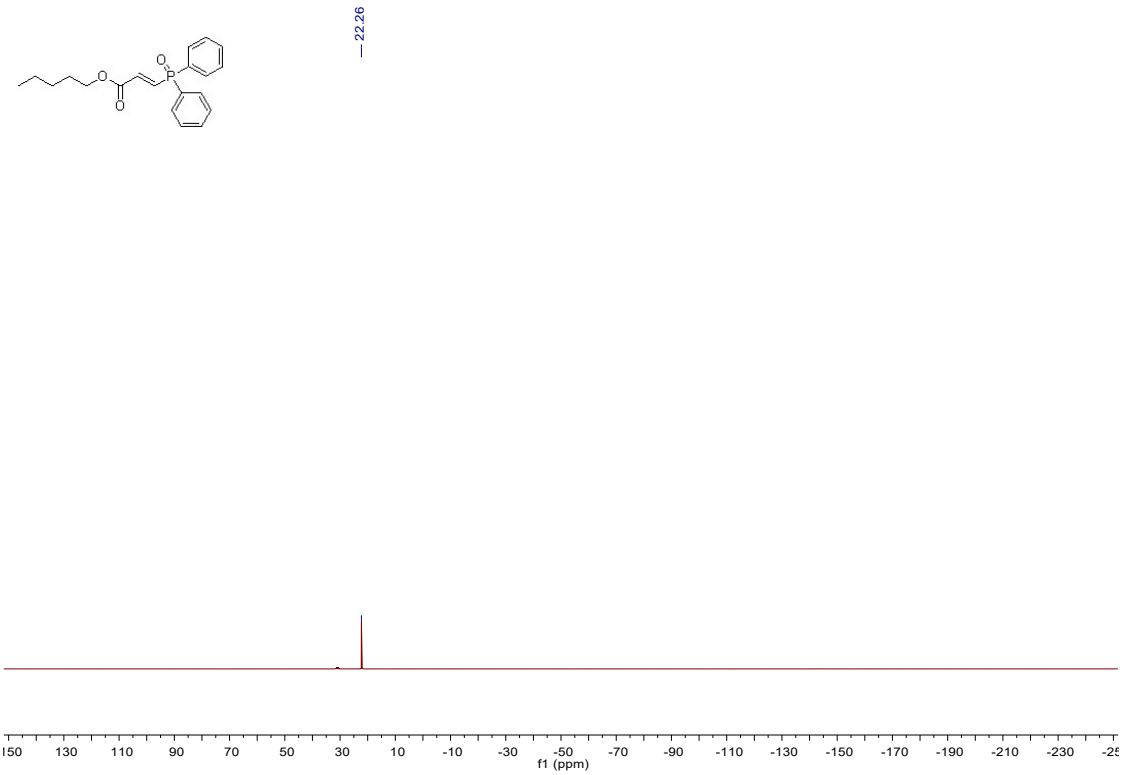
^{31}P NMR of compound **3ek**



^{1}H NMR of compound **3fk**



^{13}C NMR of compound **3fk**



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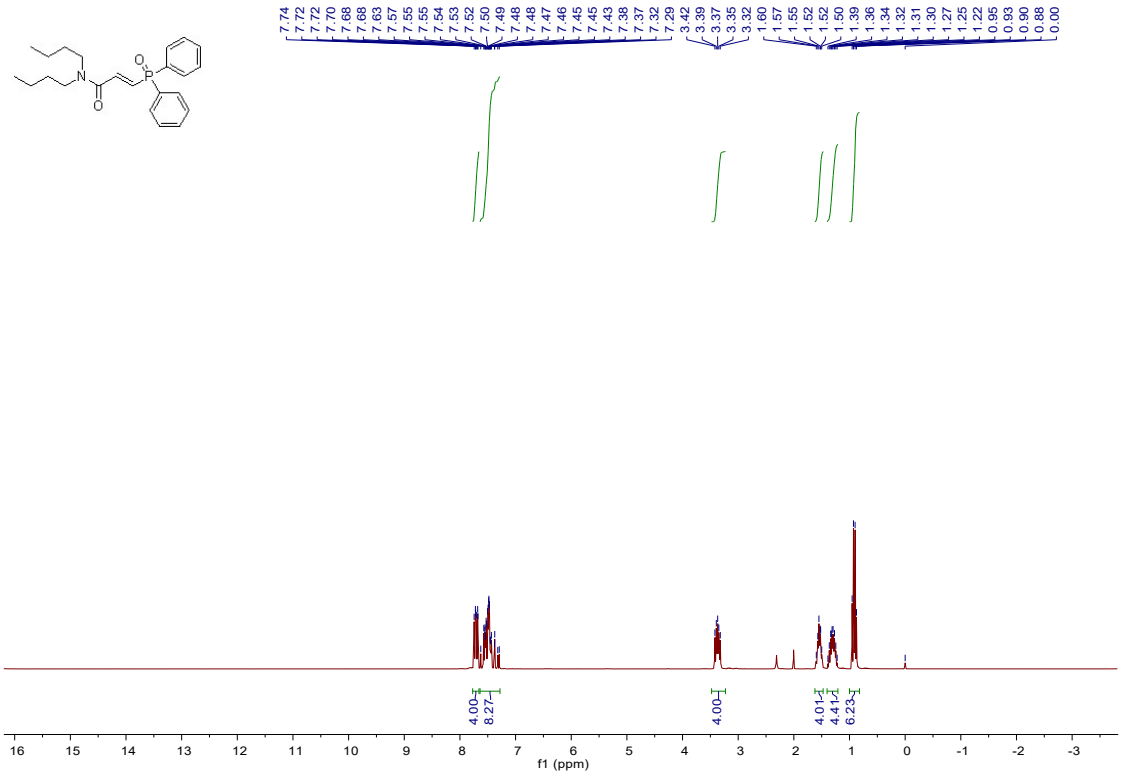
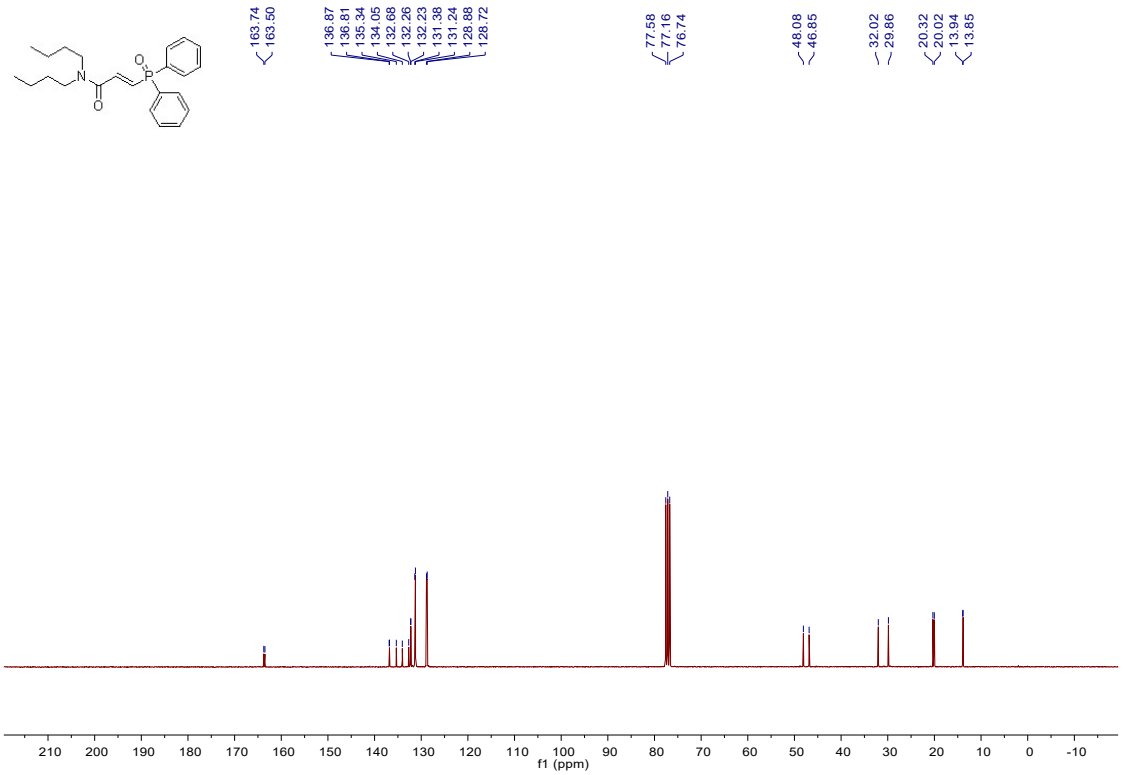
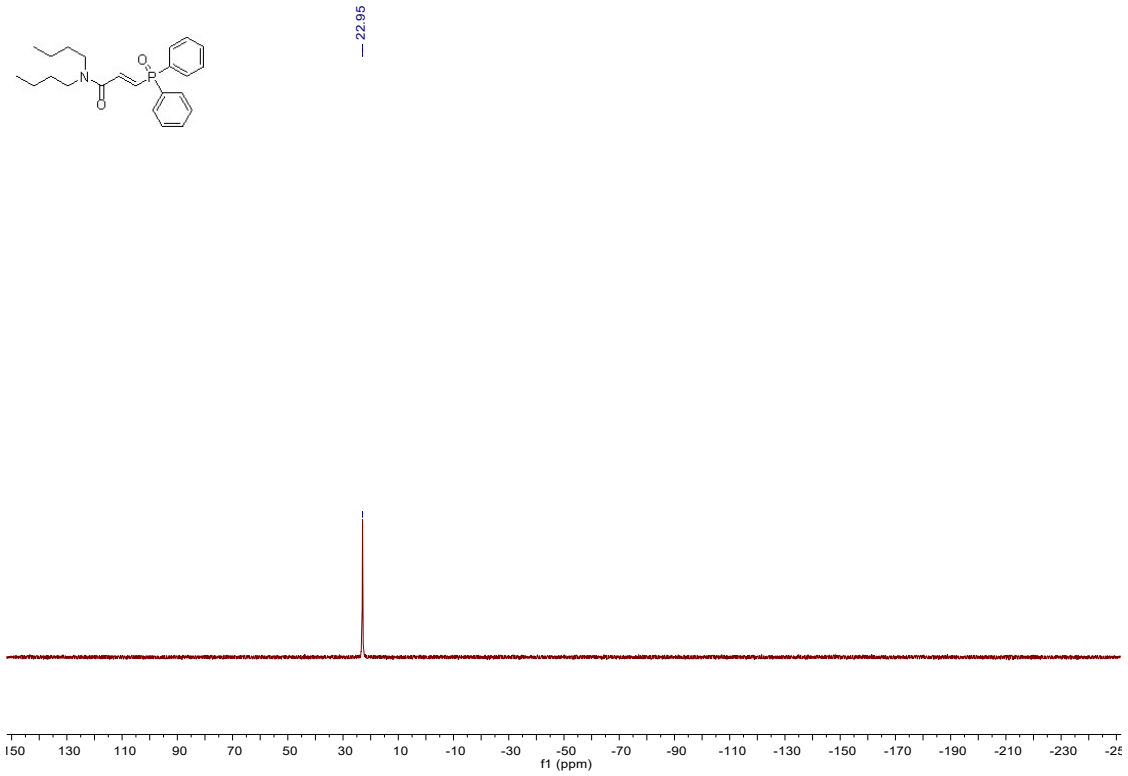


^{1}H NMR of compound **3gk**



^{13}C NMR of compound **3gk**



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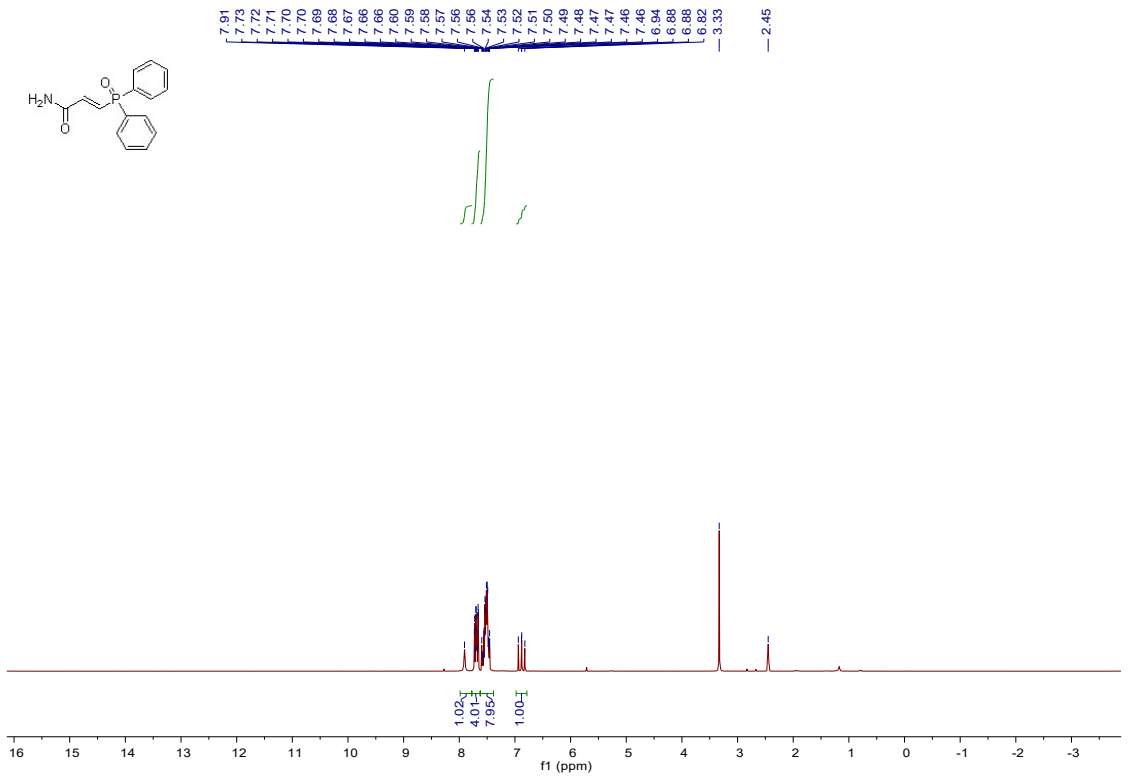
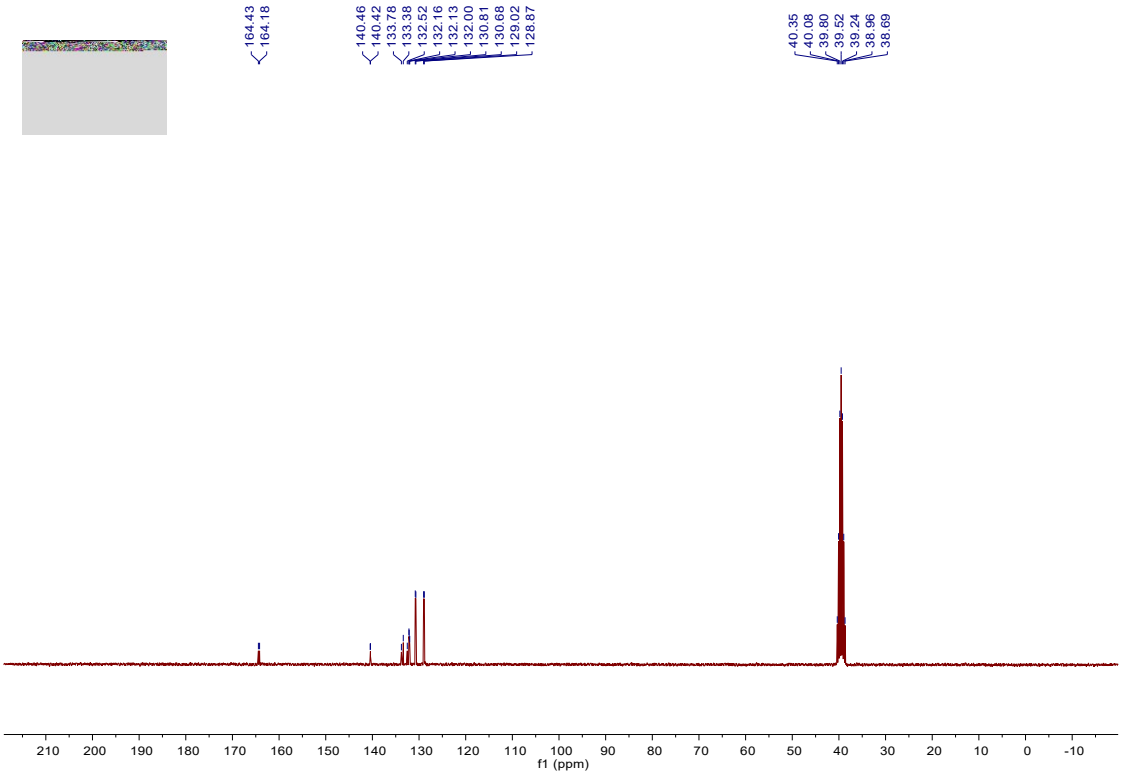
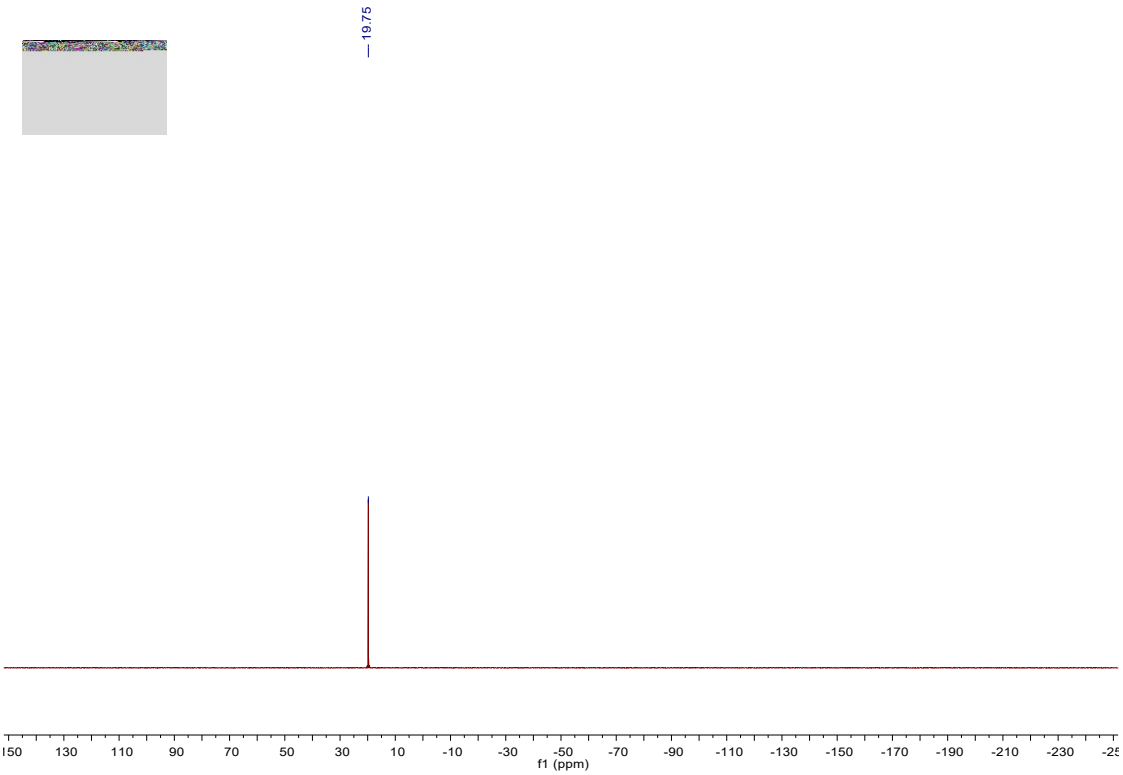


^{1}H NMR of compound **3hk**



^{13}C NMR of compound **3hk**



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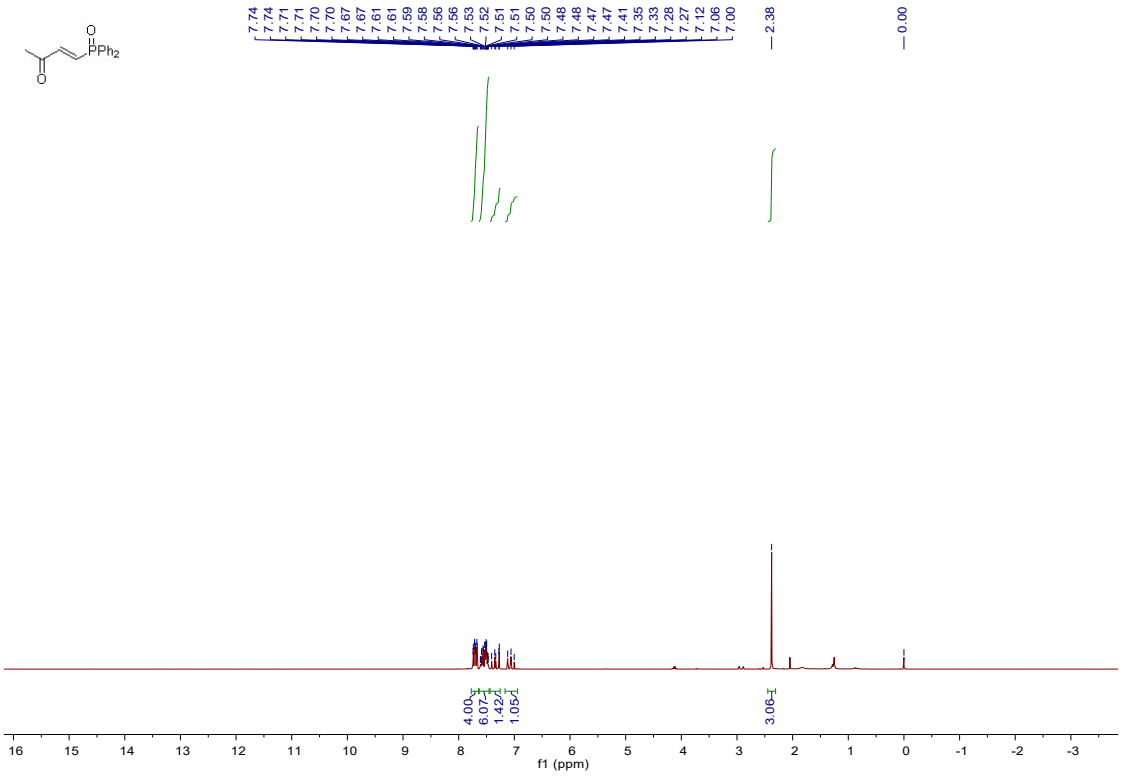

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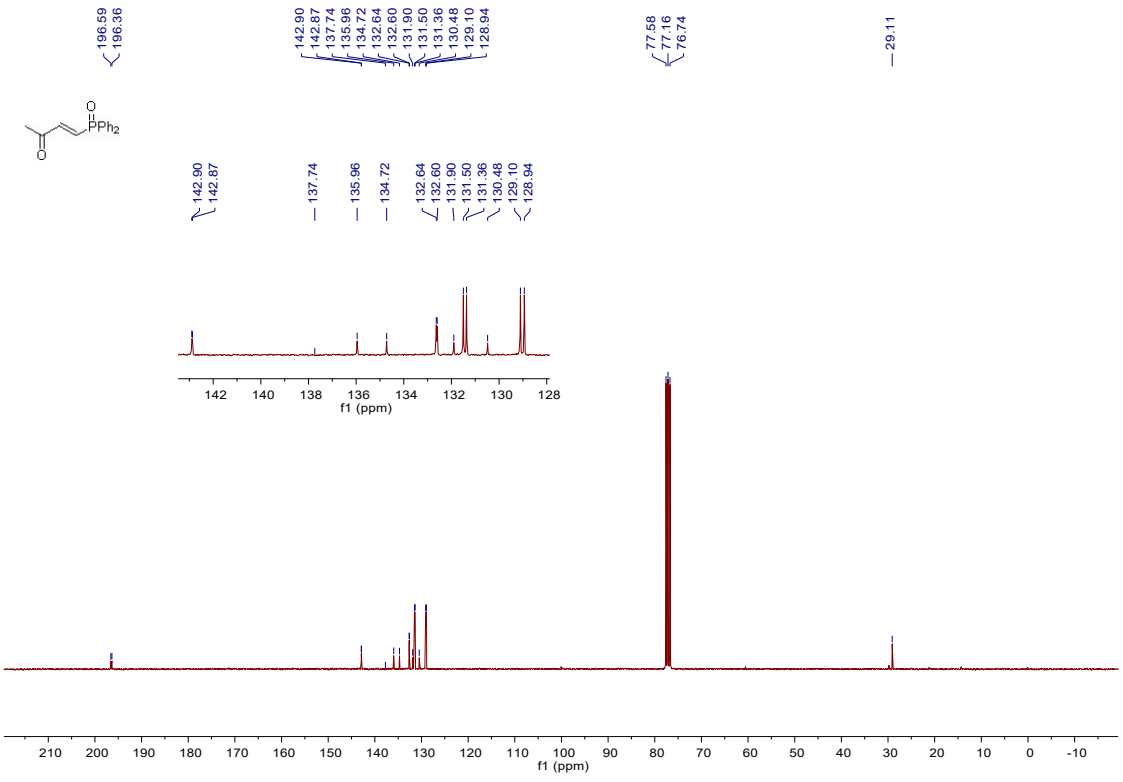

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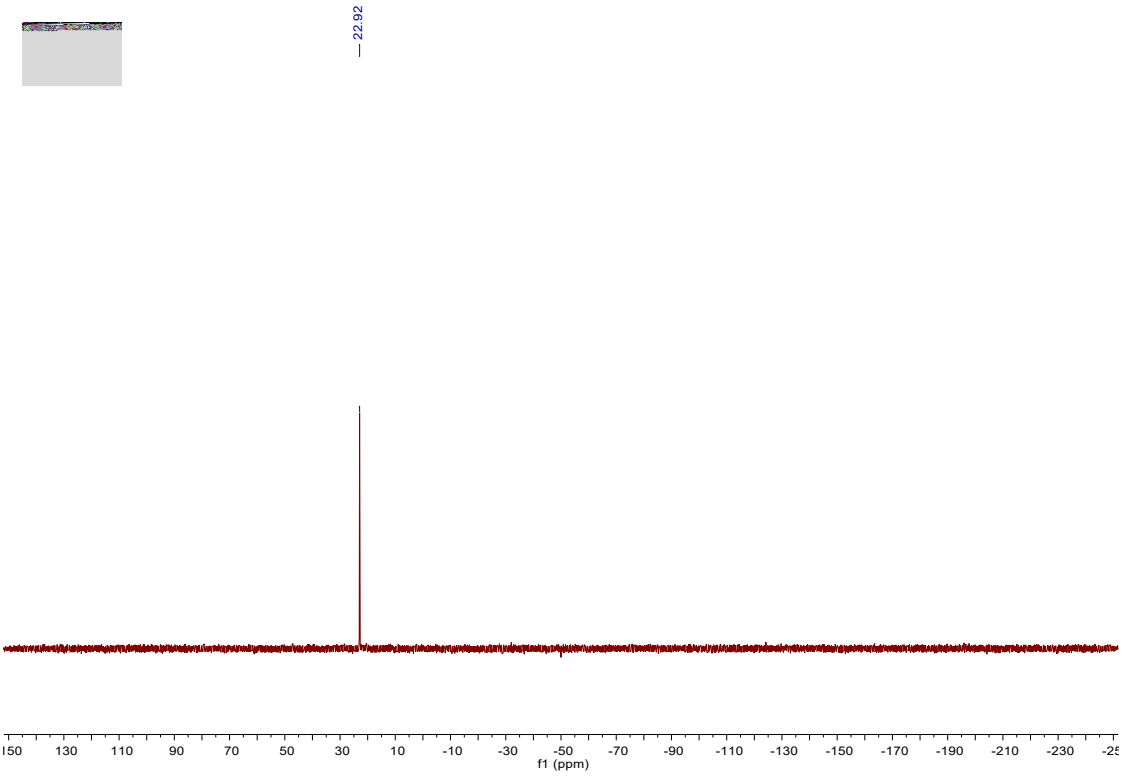

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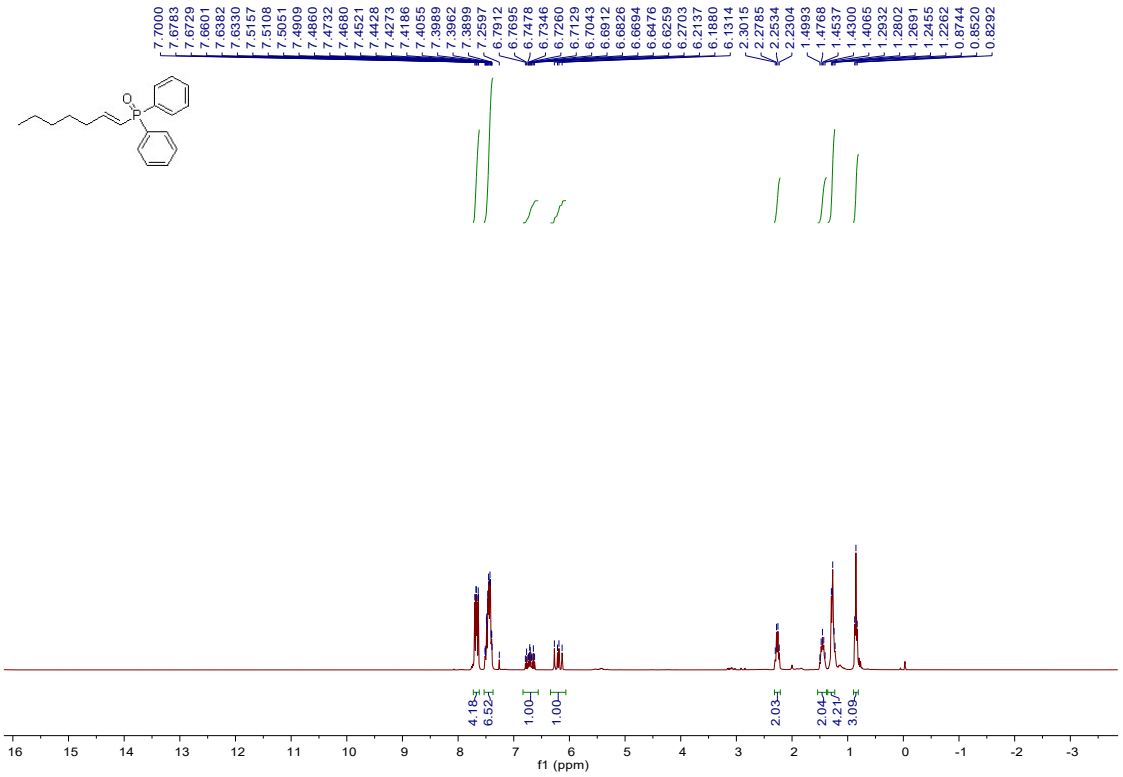

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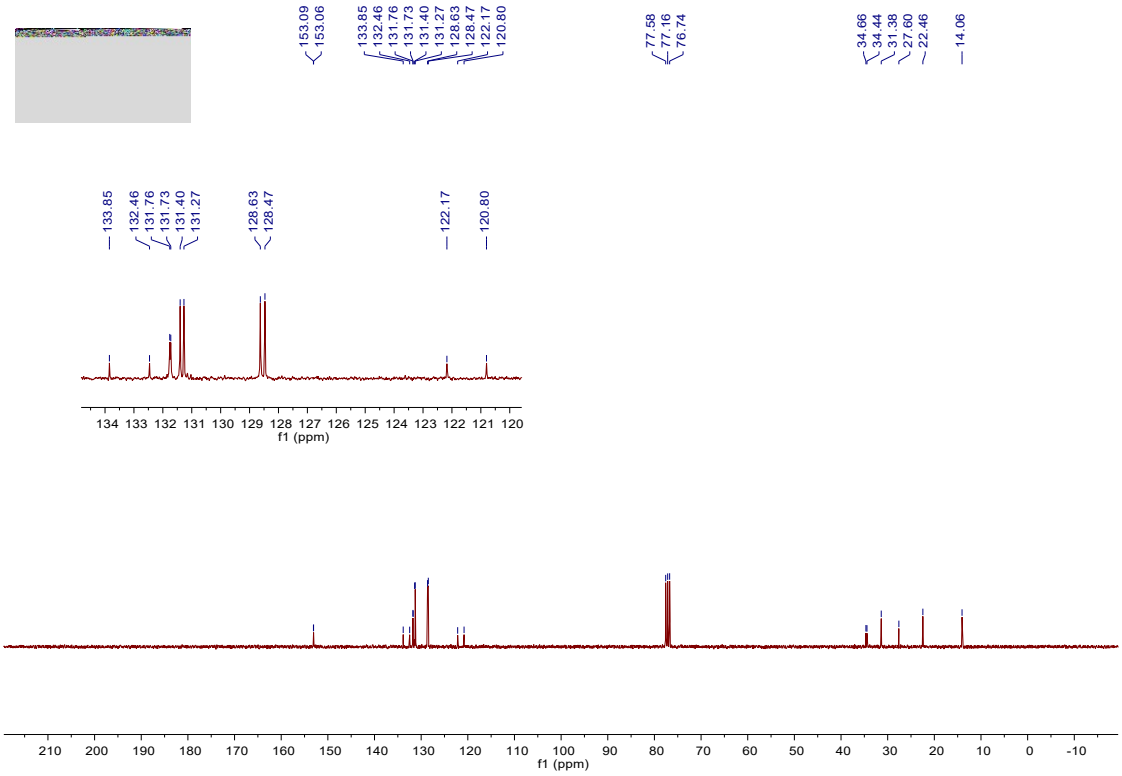

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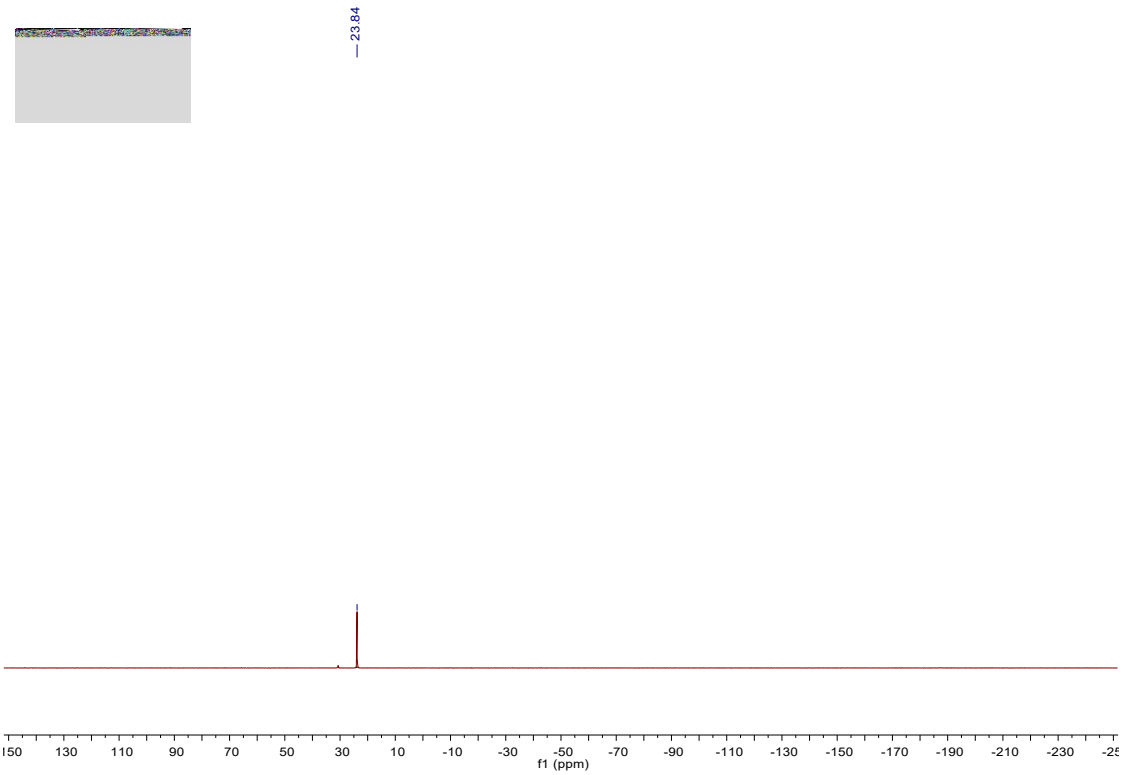

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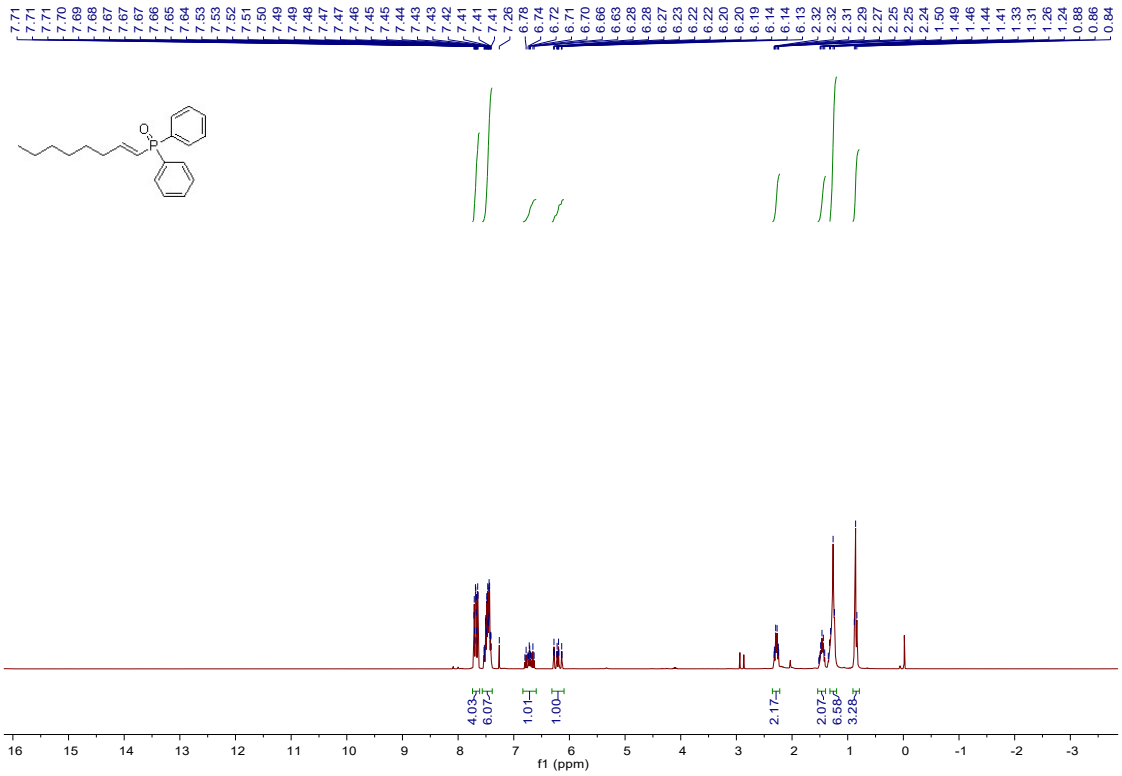
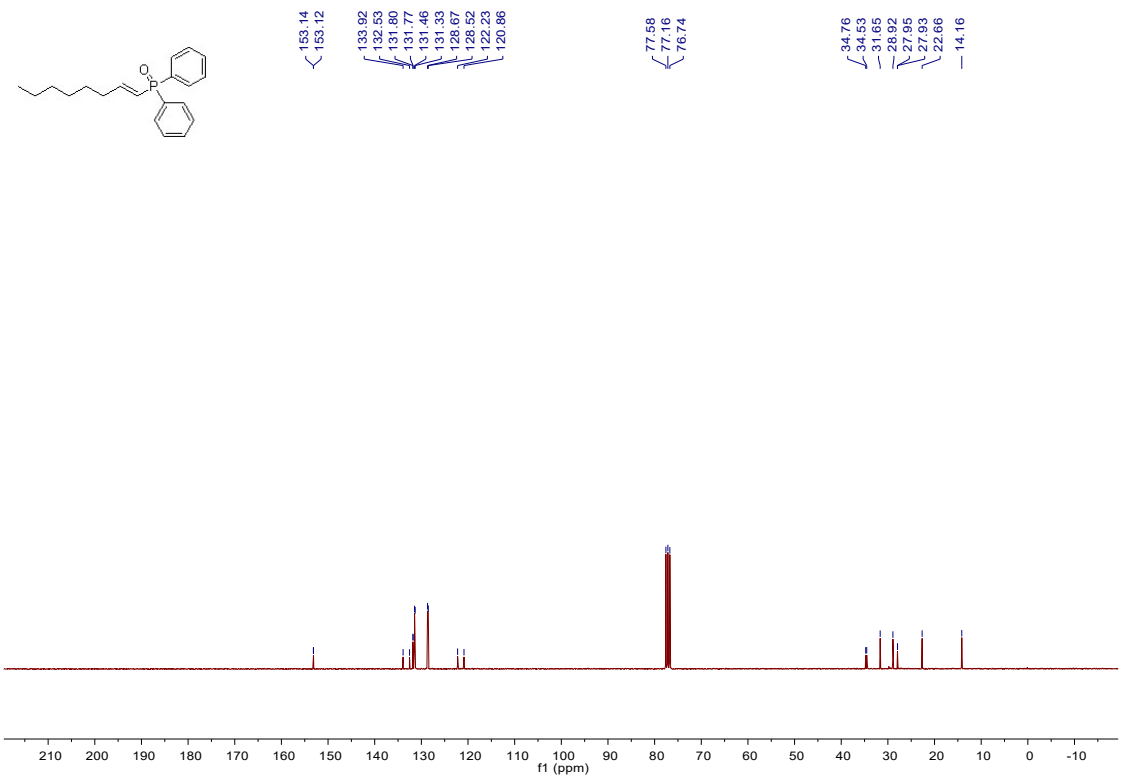


^{1}H NMR of compound **3kk**



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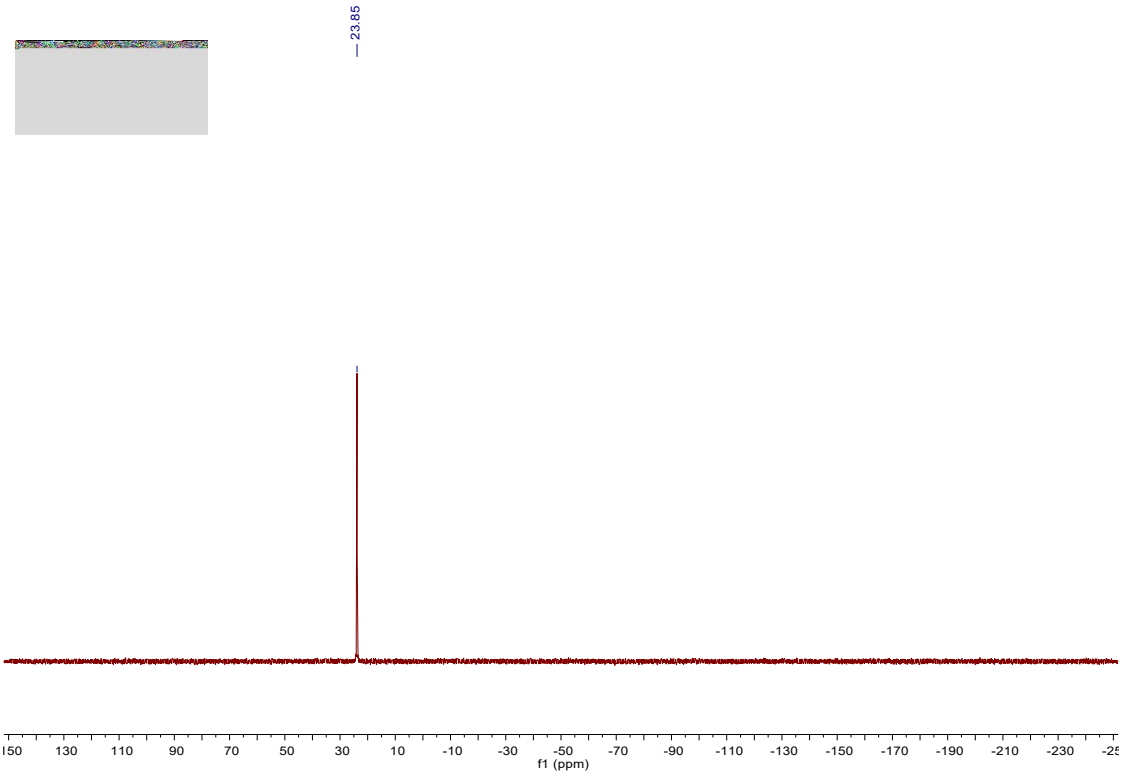

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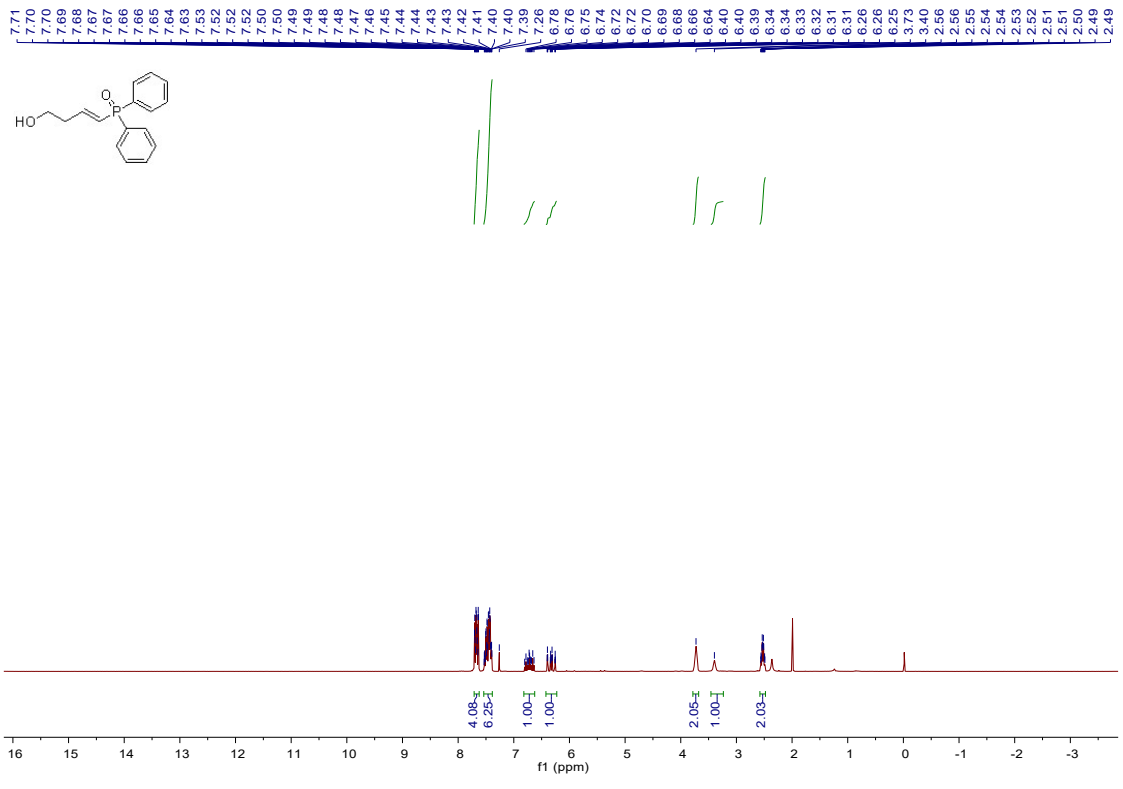

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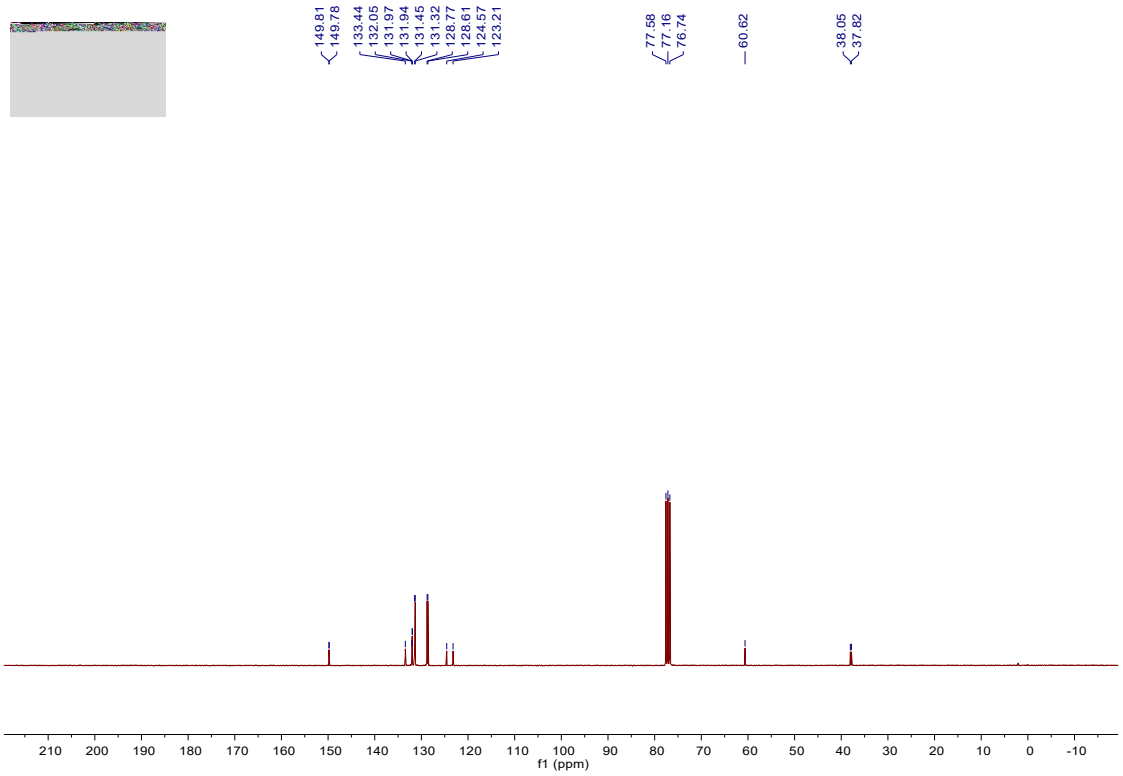

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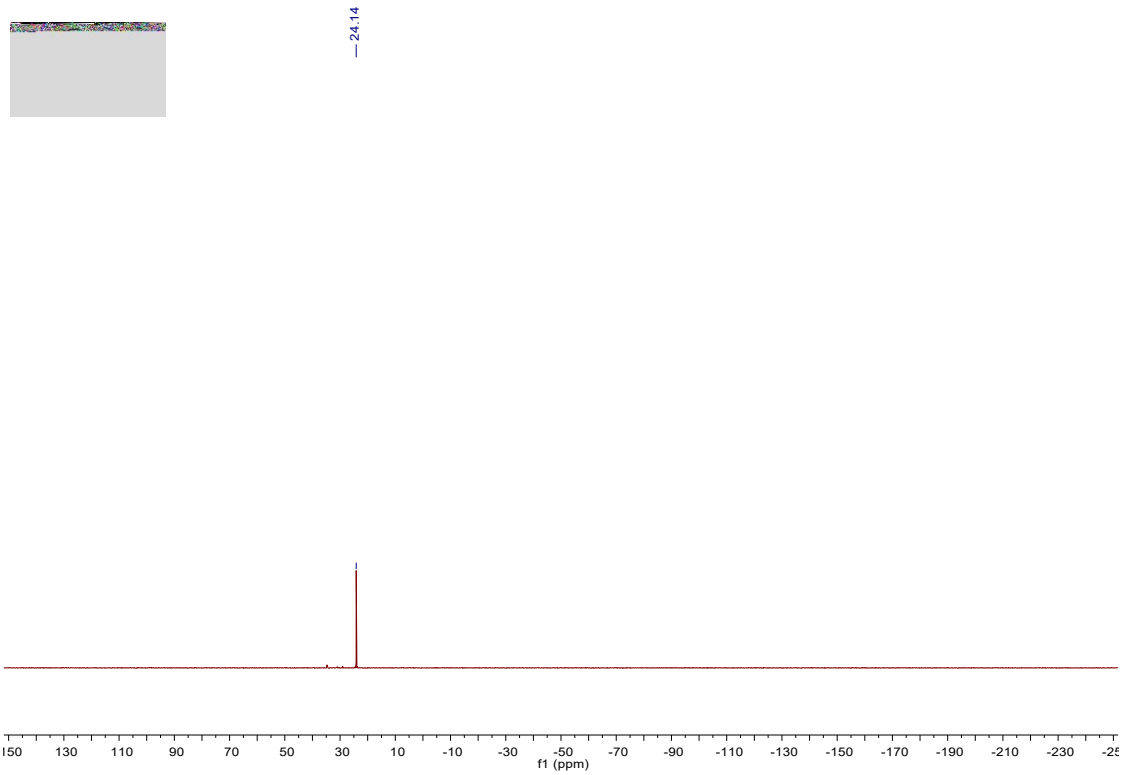

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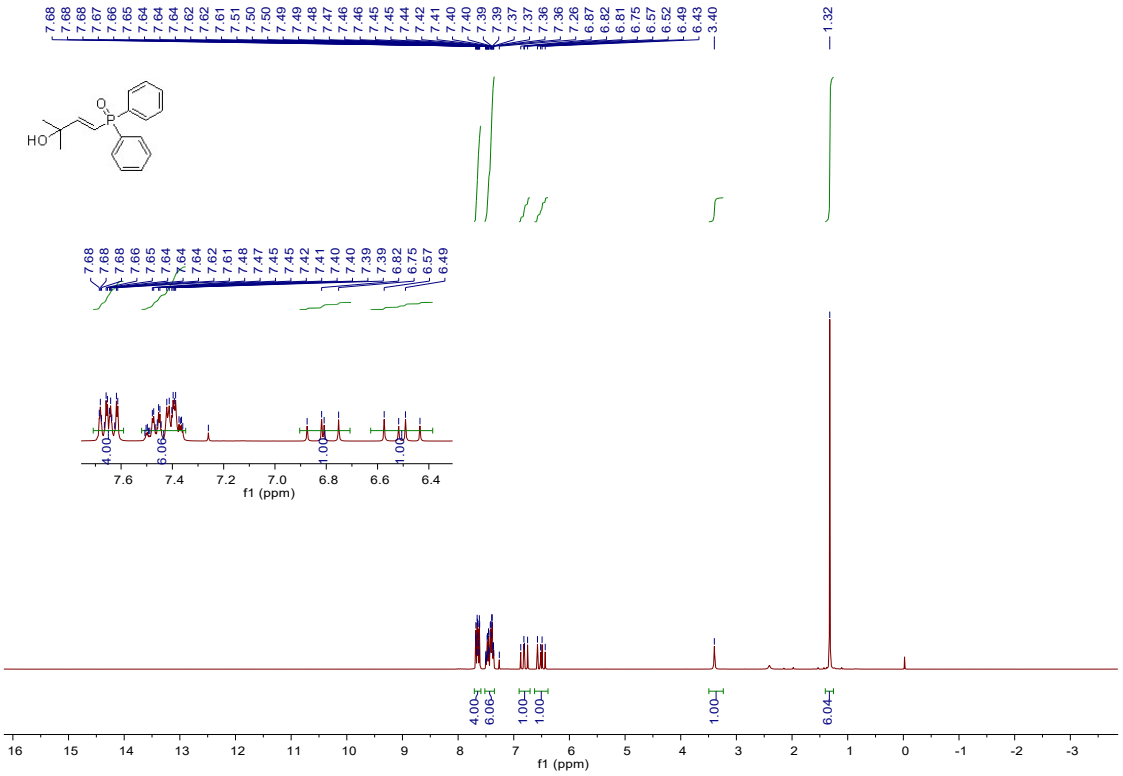

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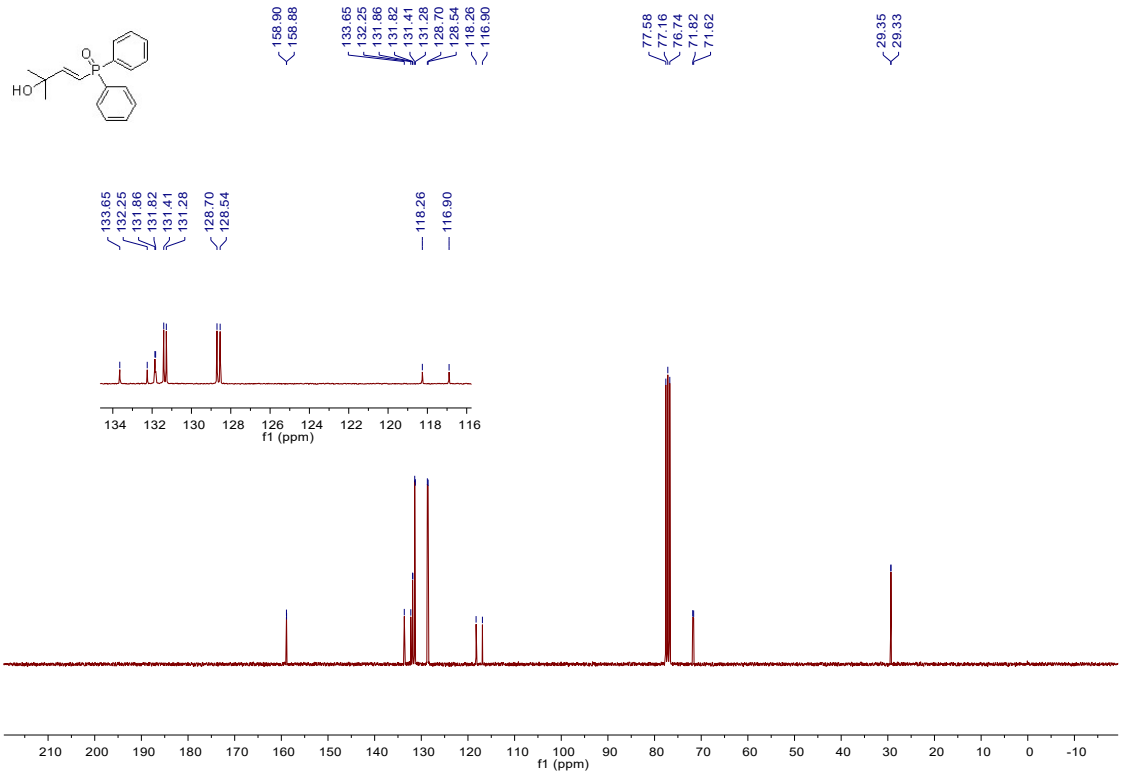

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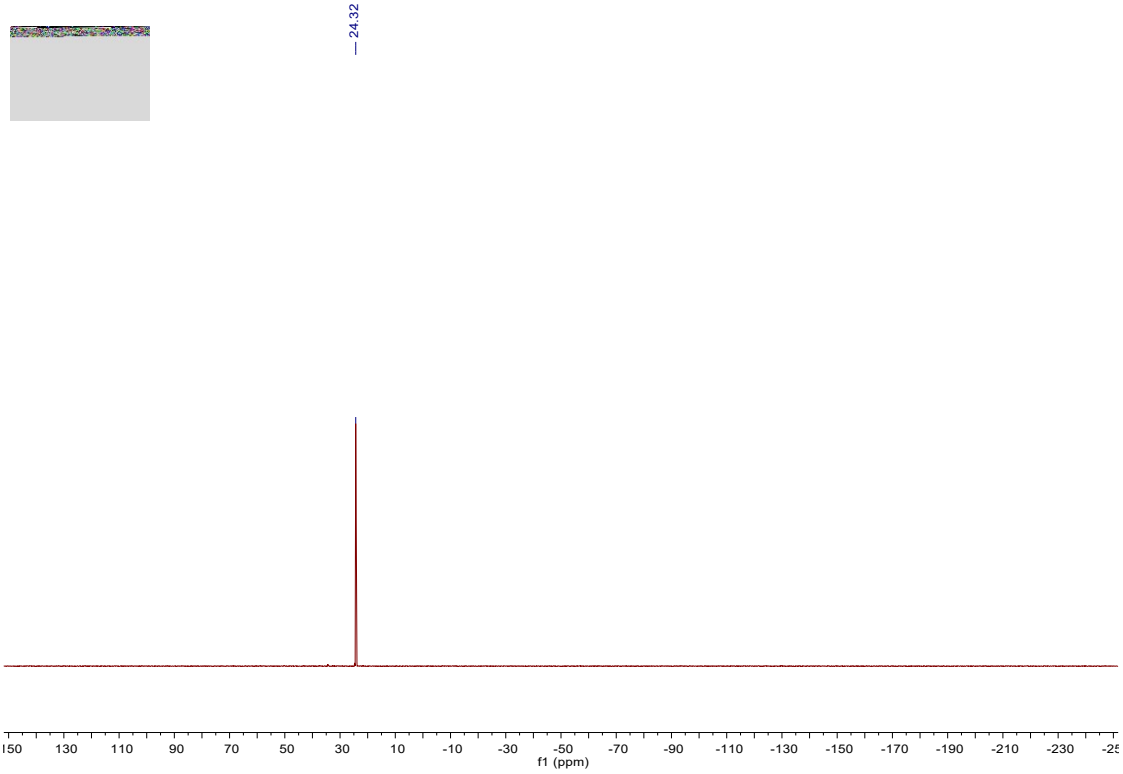

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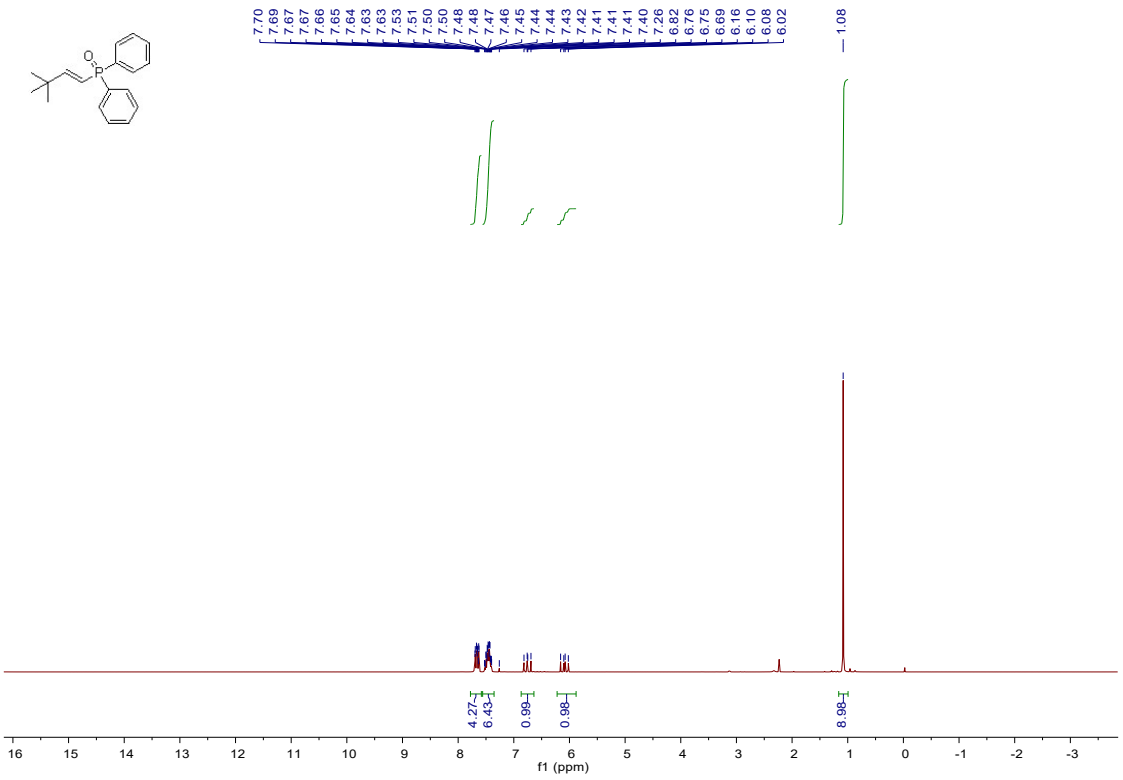

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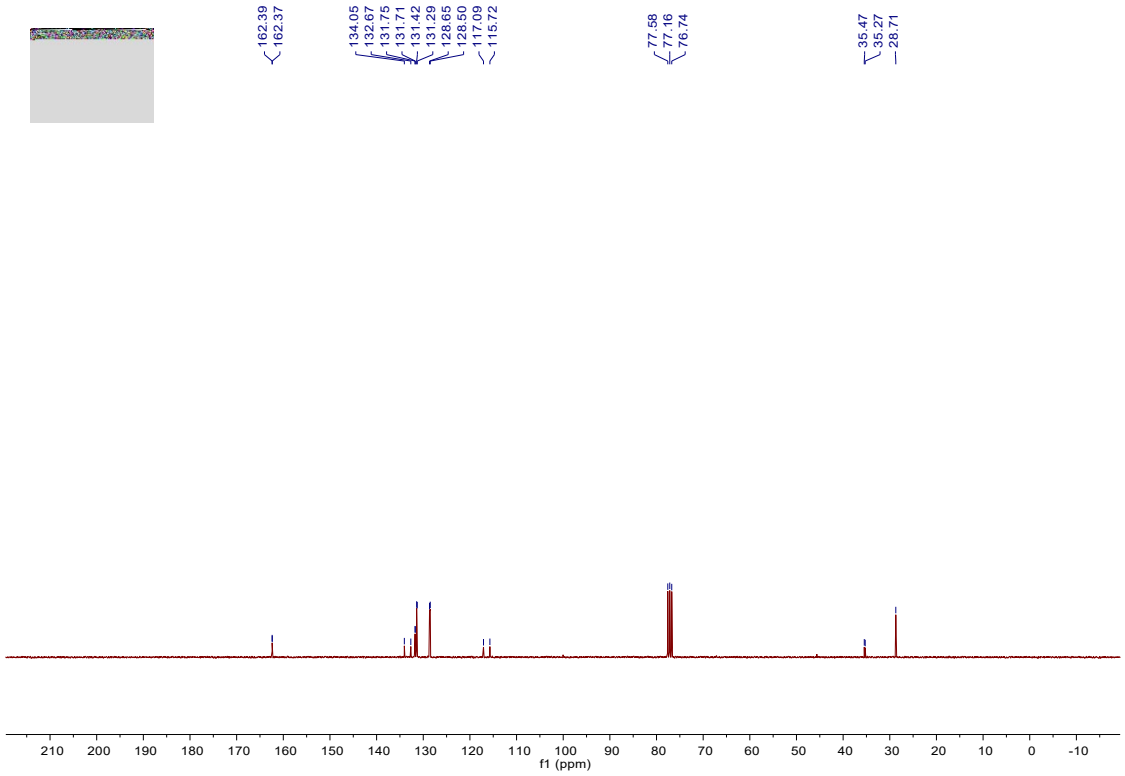

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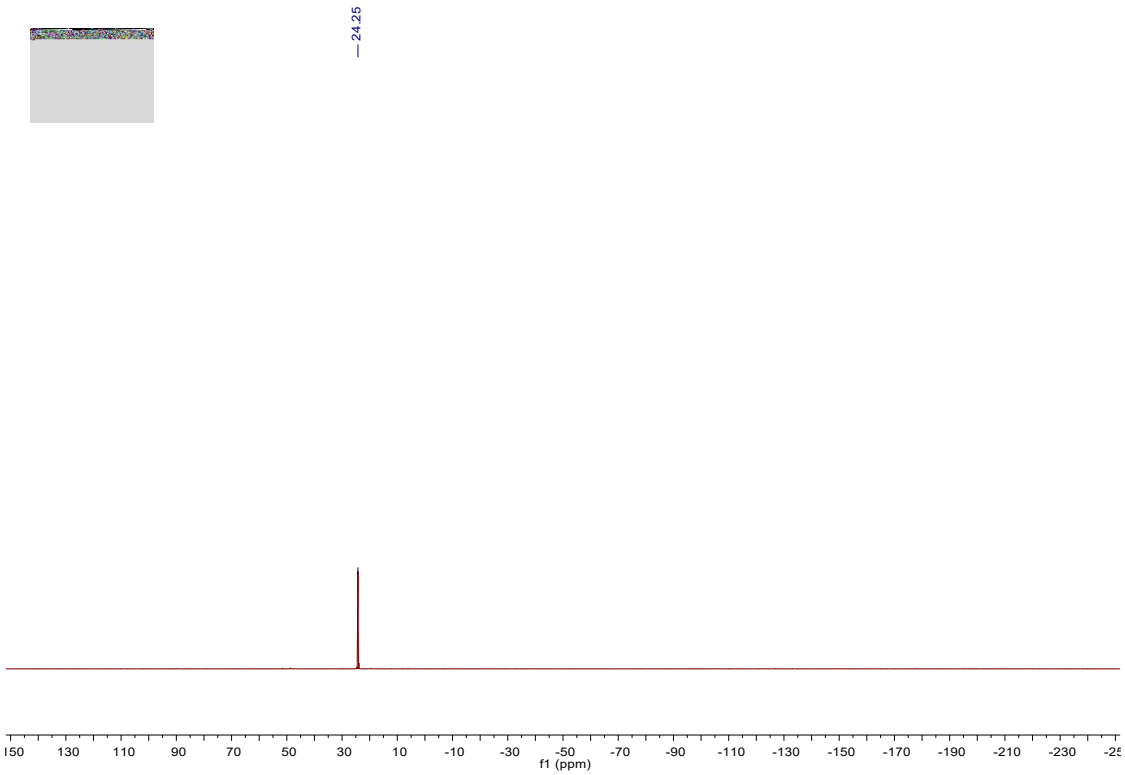

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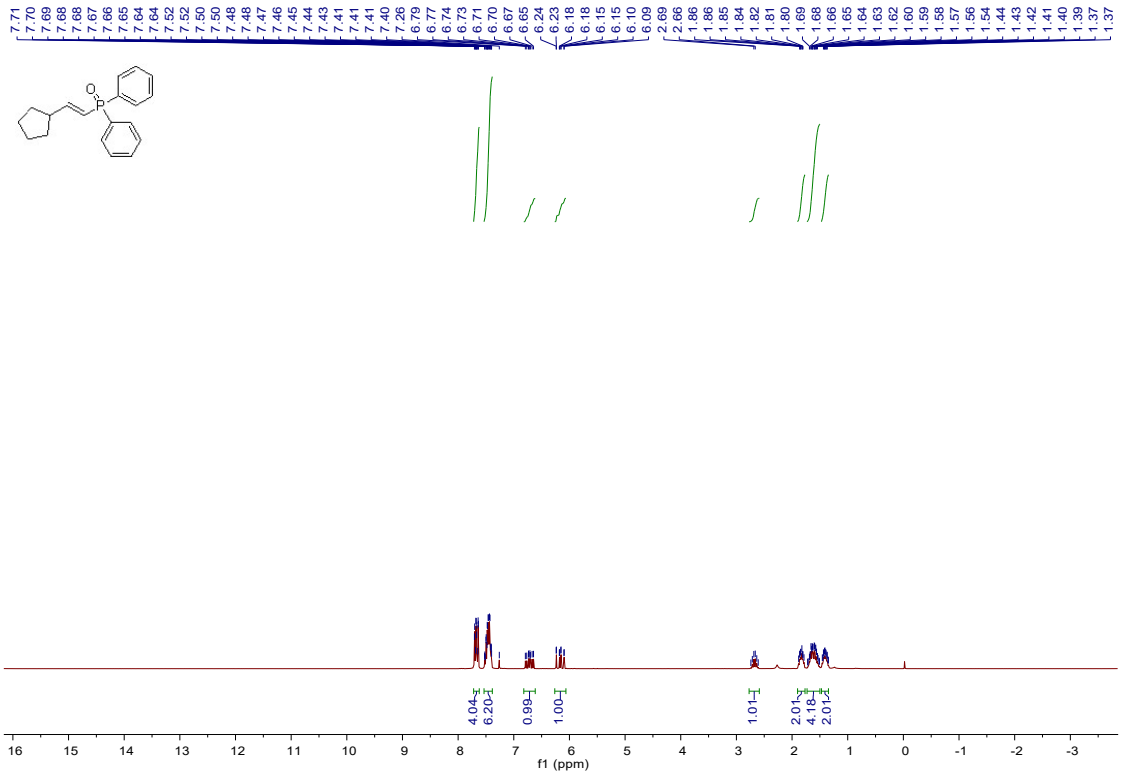

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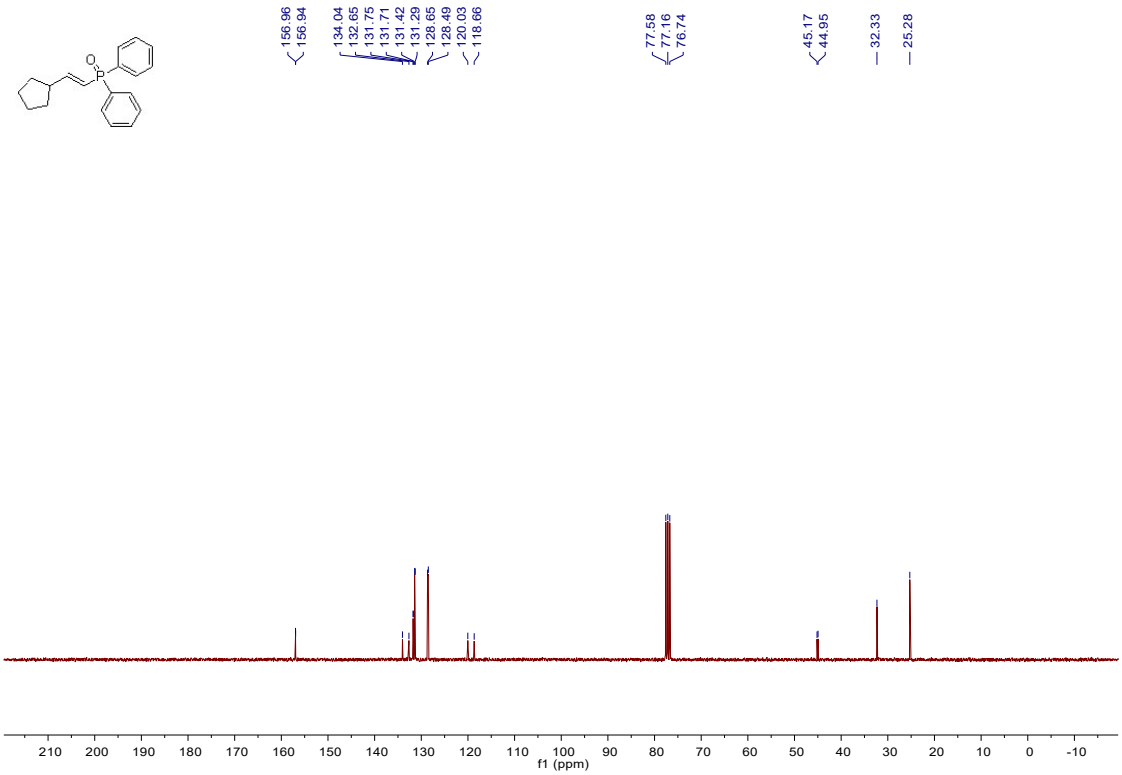

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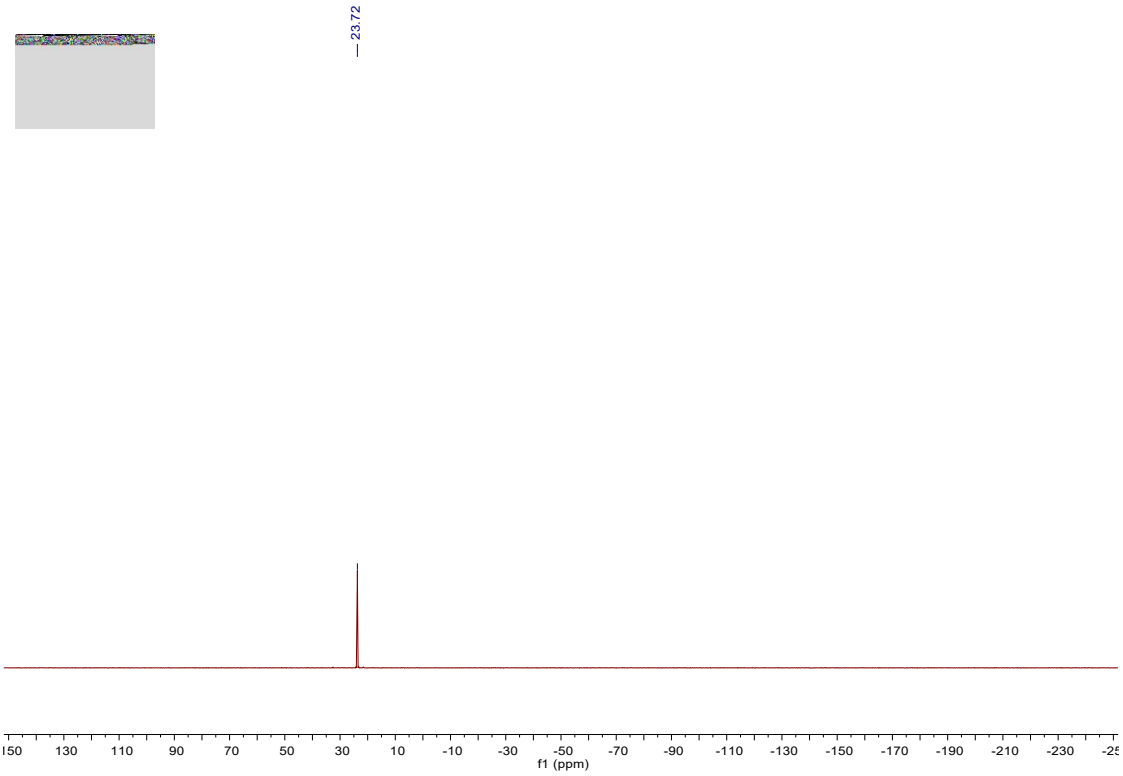

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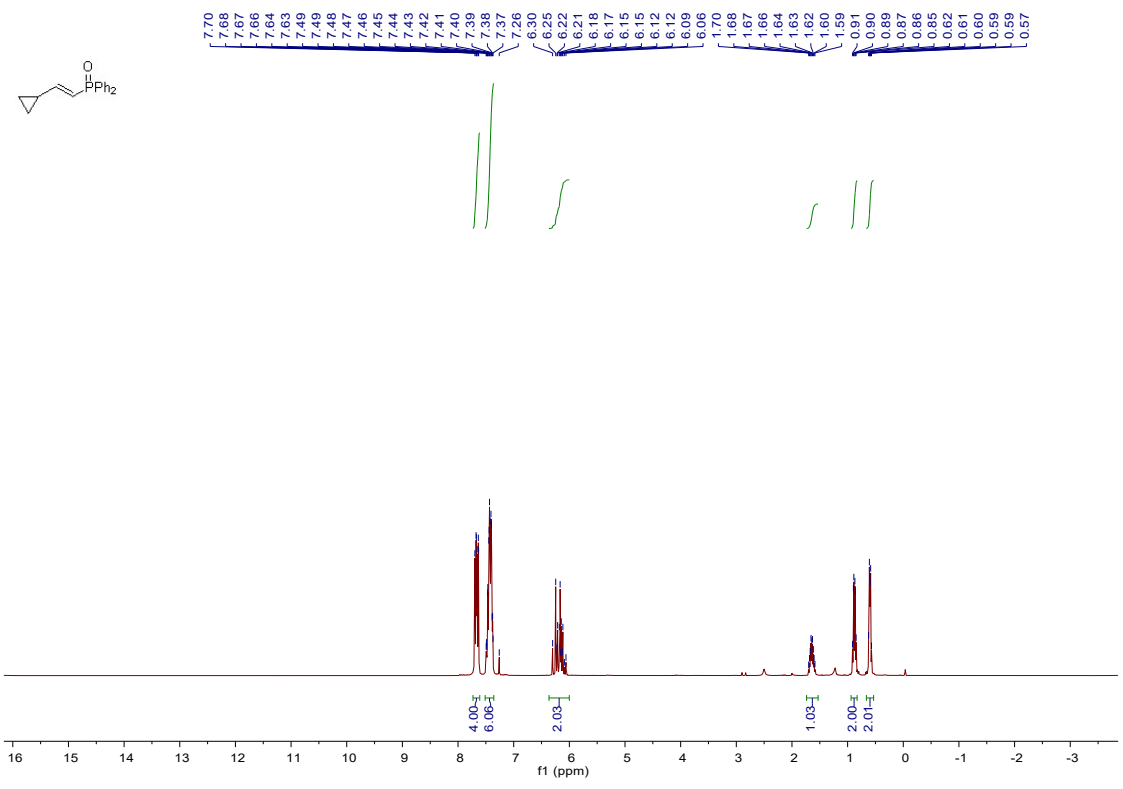

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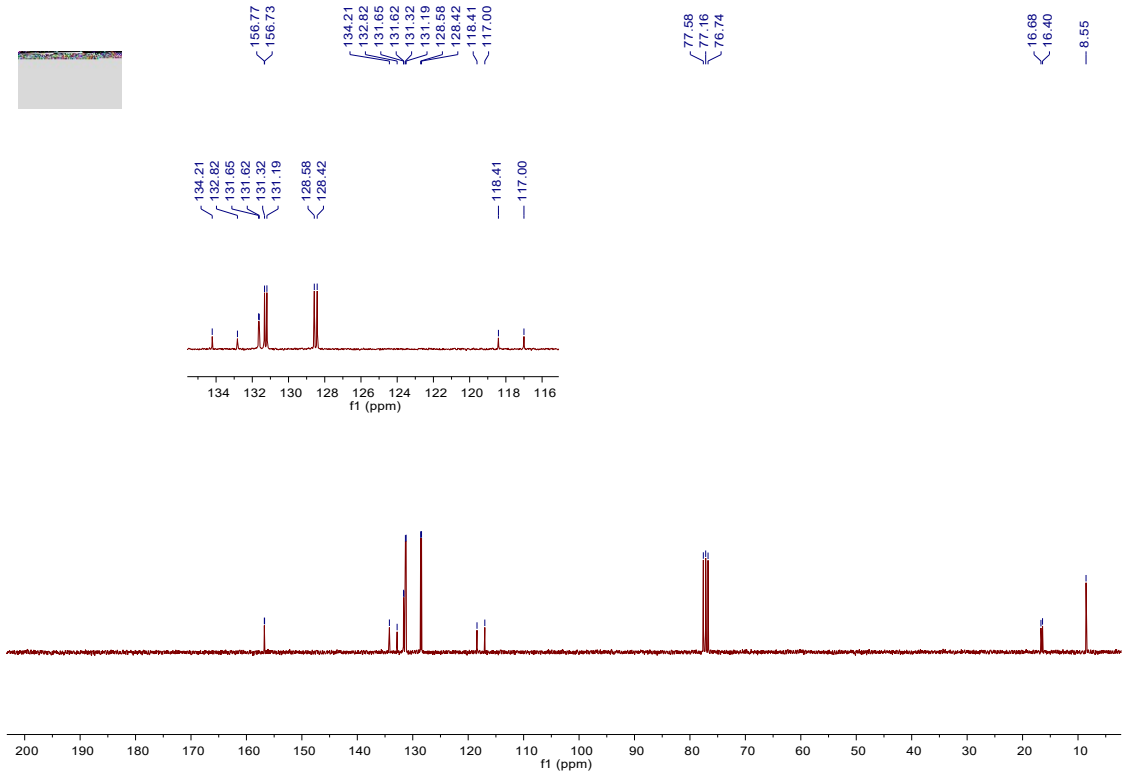

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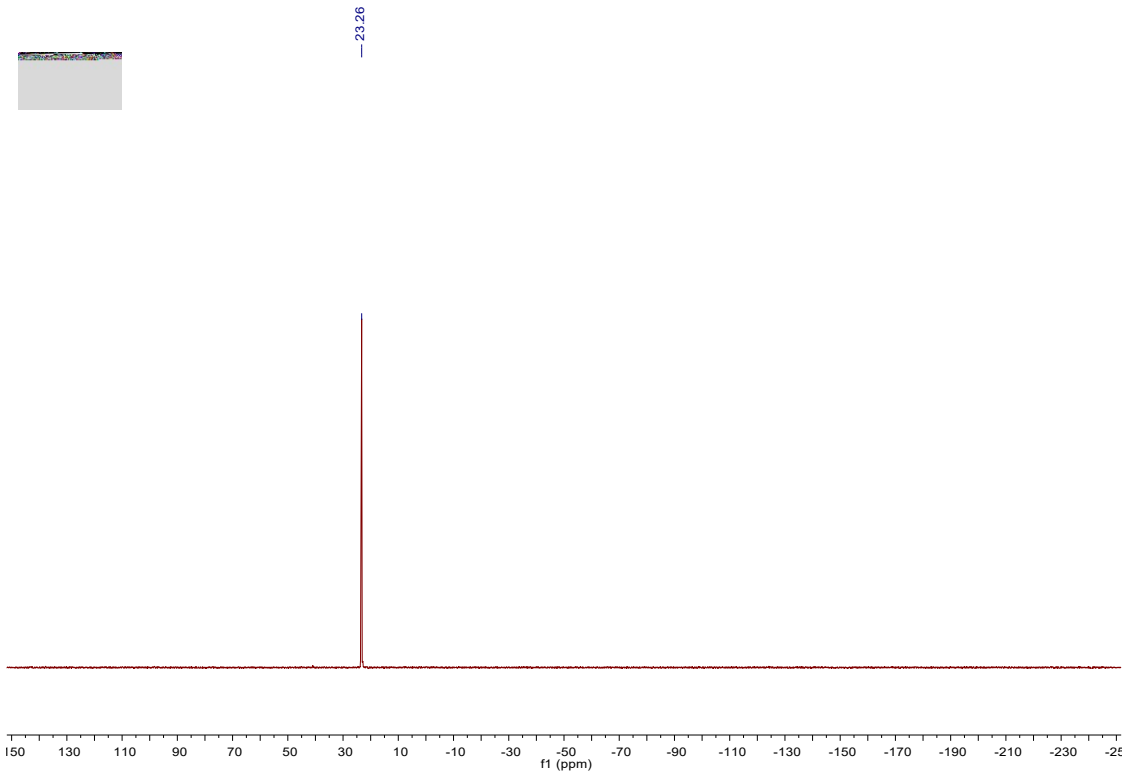

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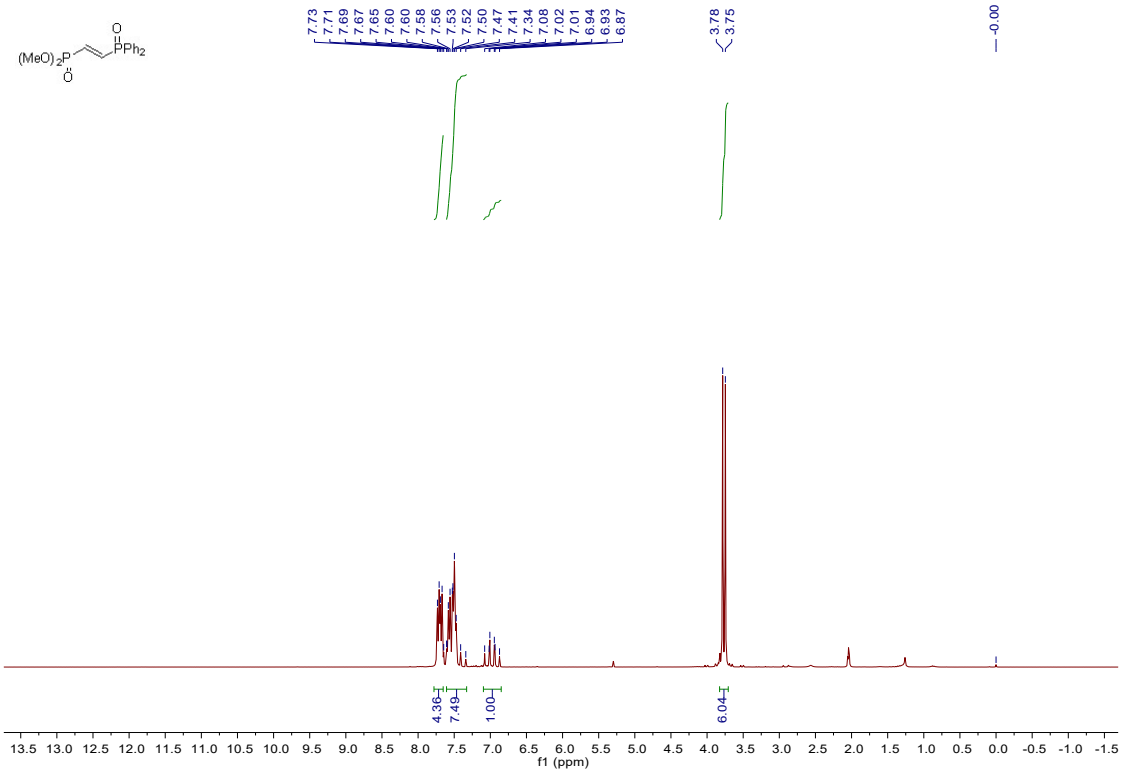

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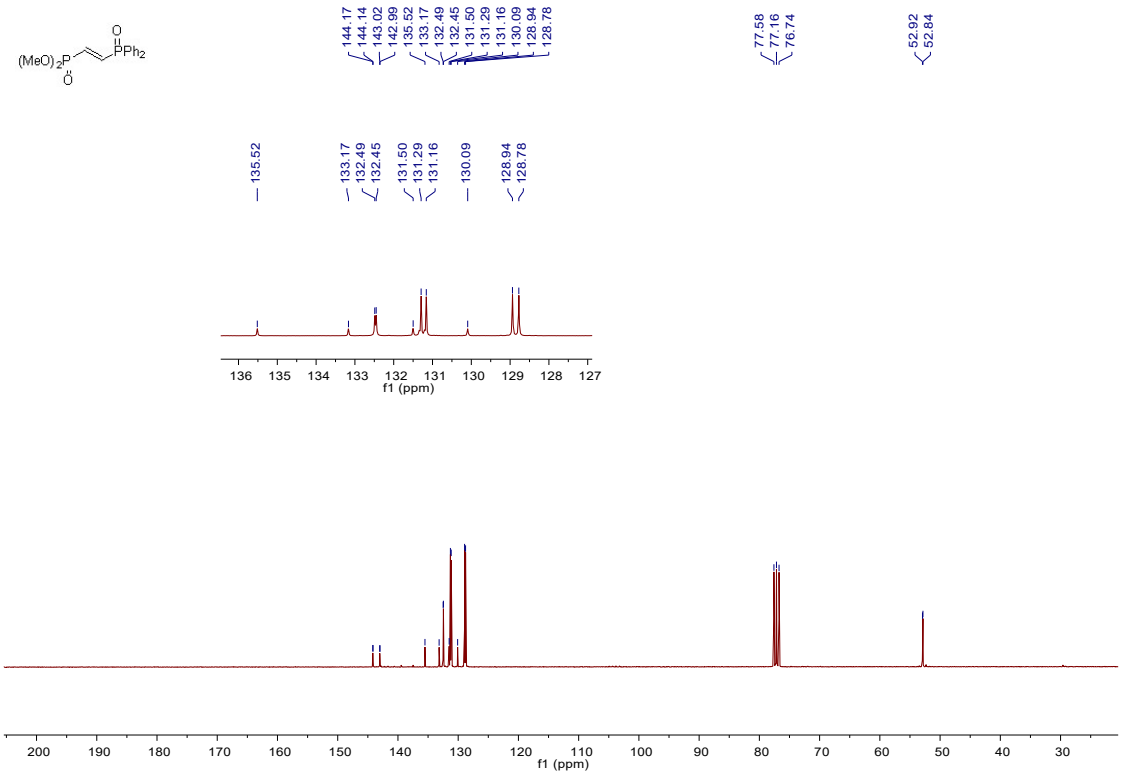

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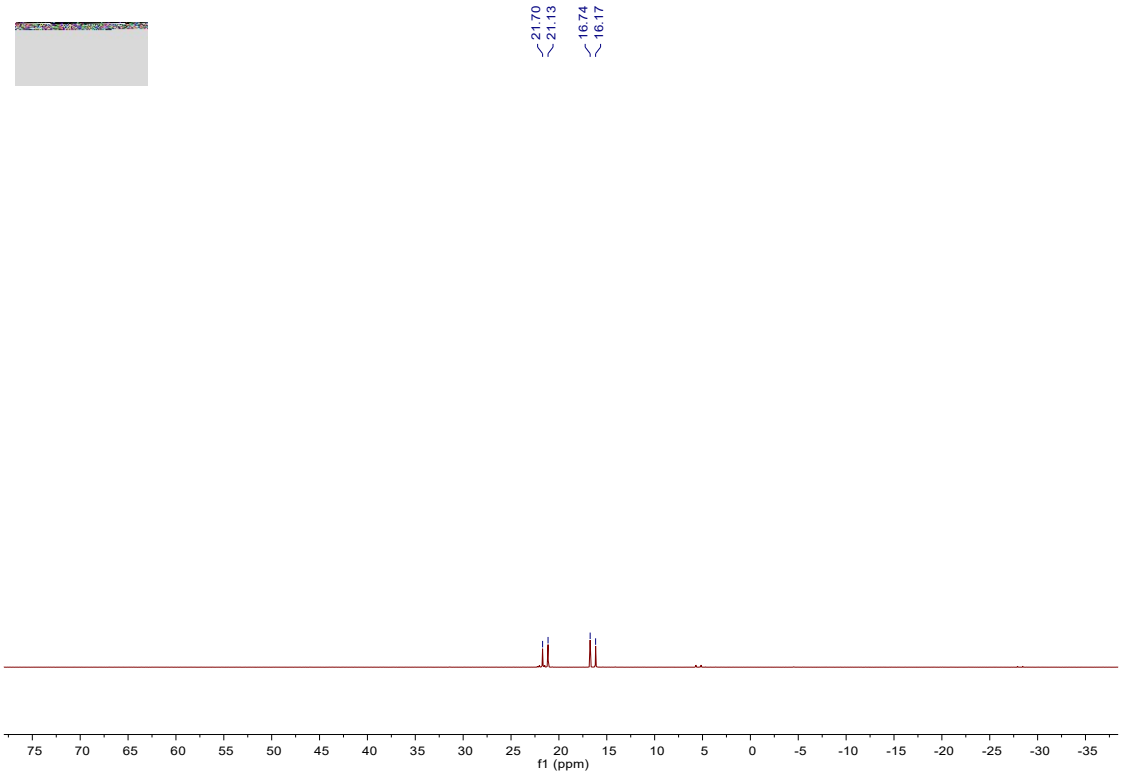

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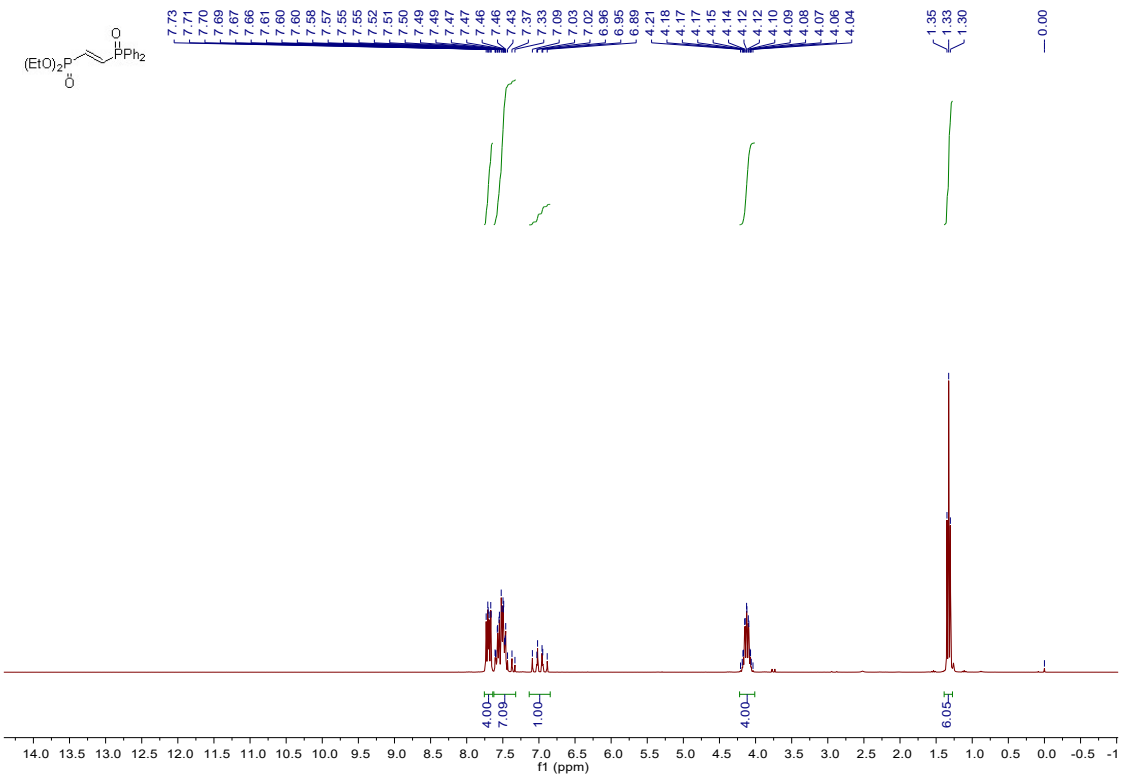
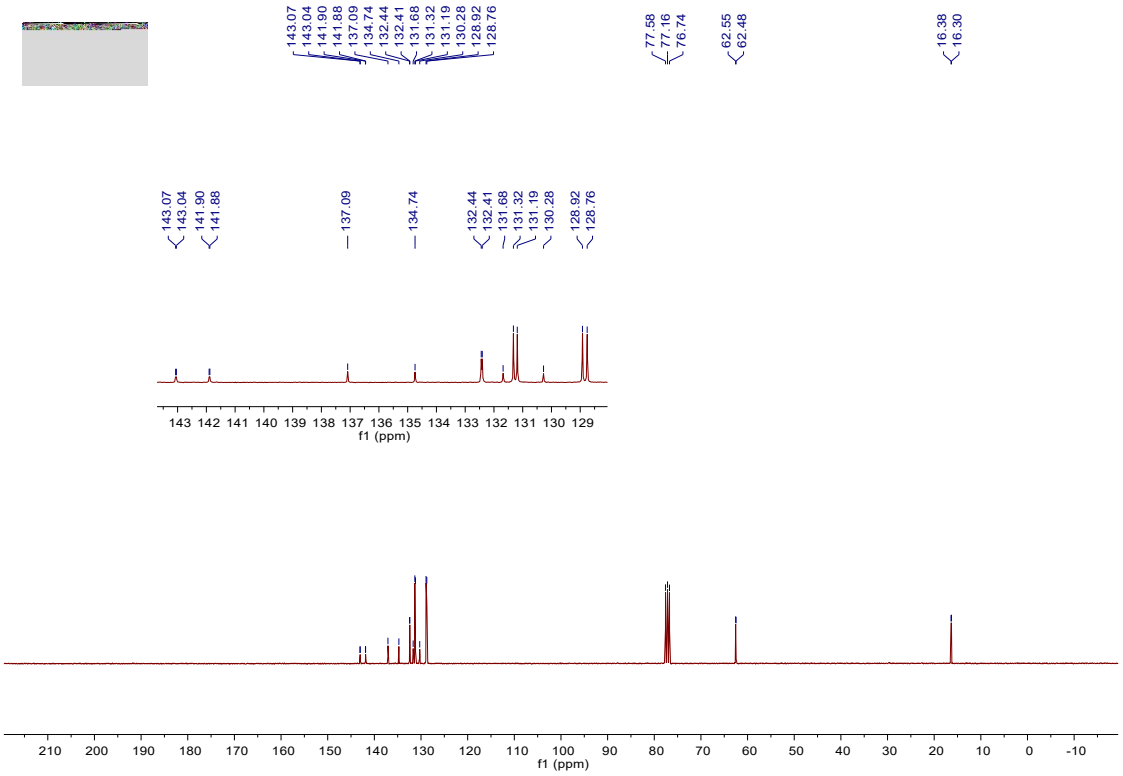
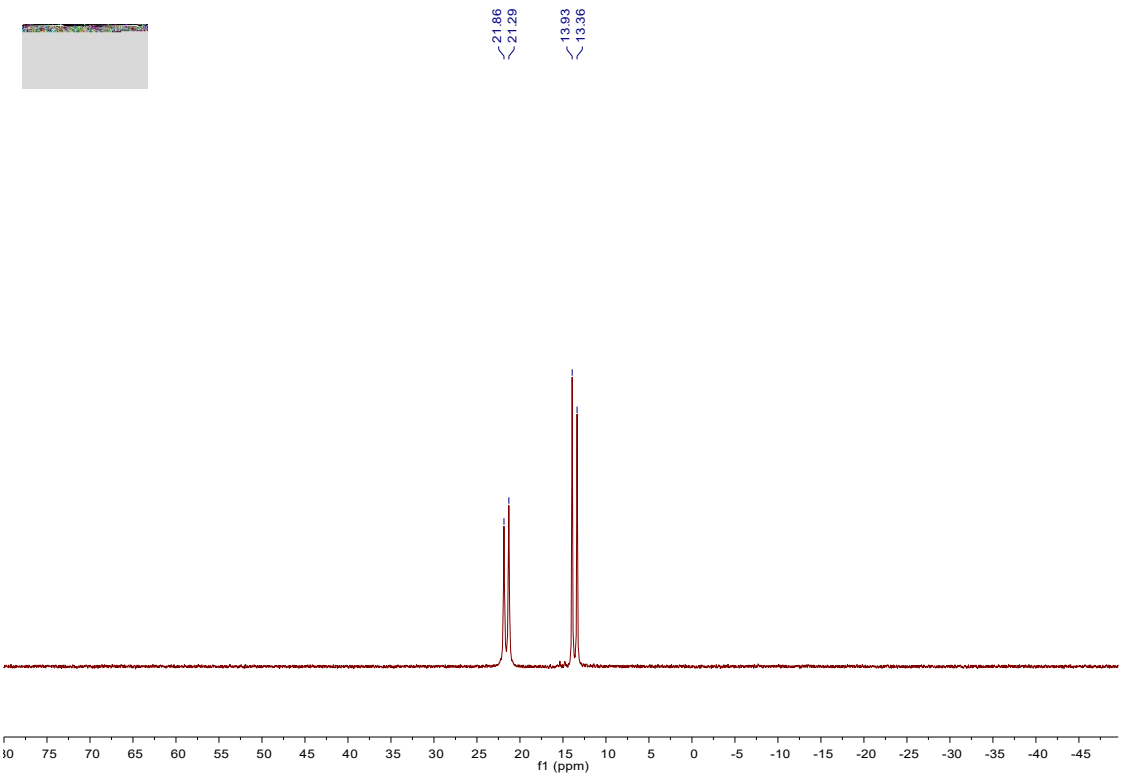


^{1}H NMR of compound **3rk**



^{13}C NMR of compound **3rk**



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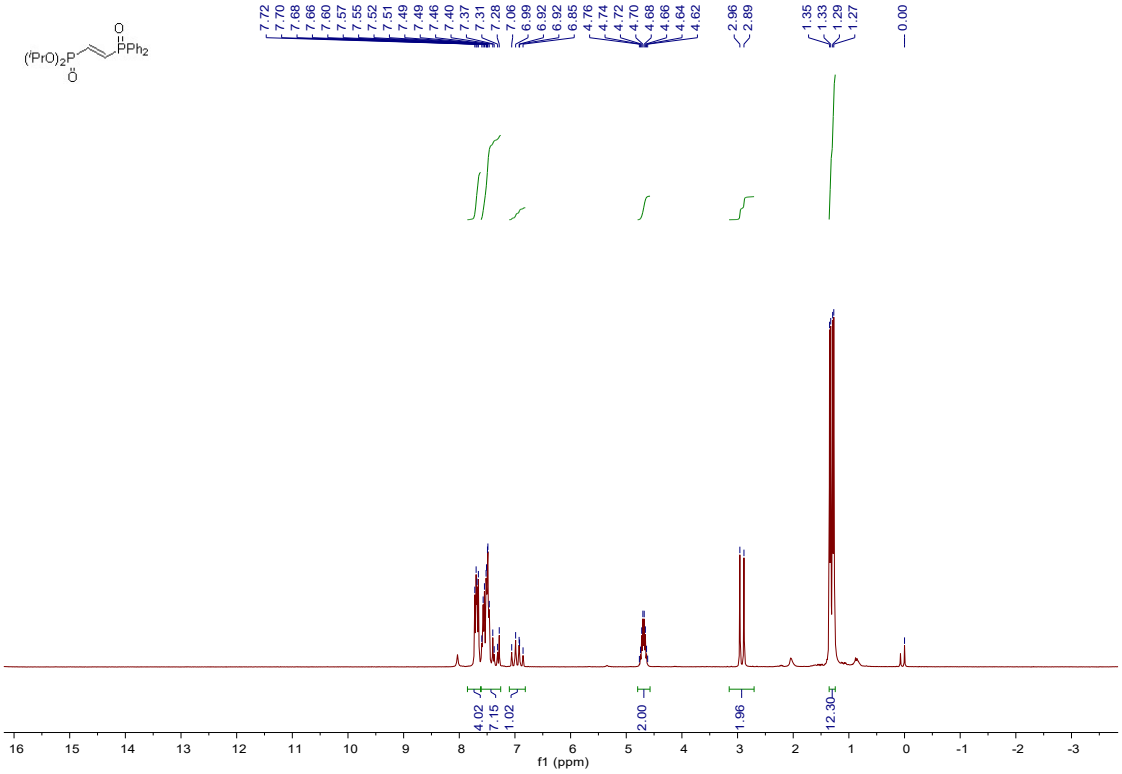

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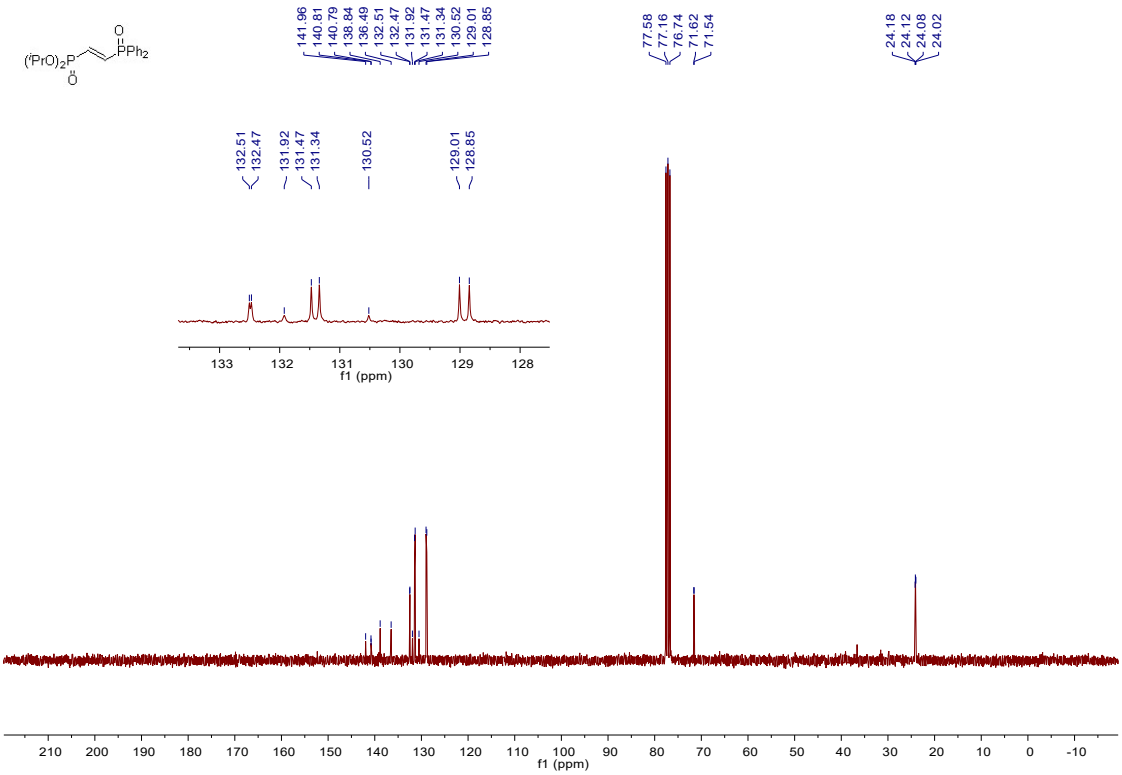

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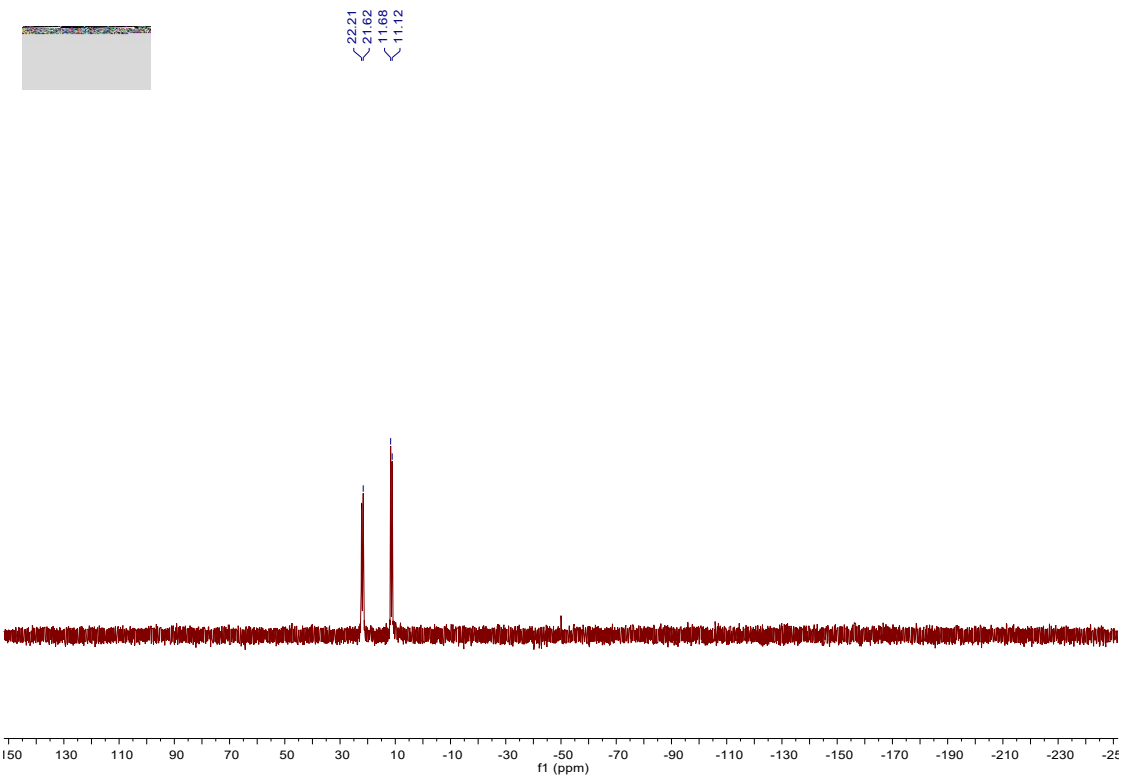

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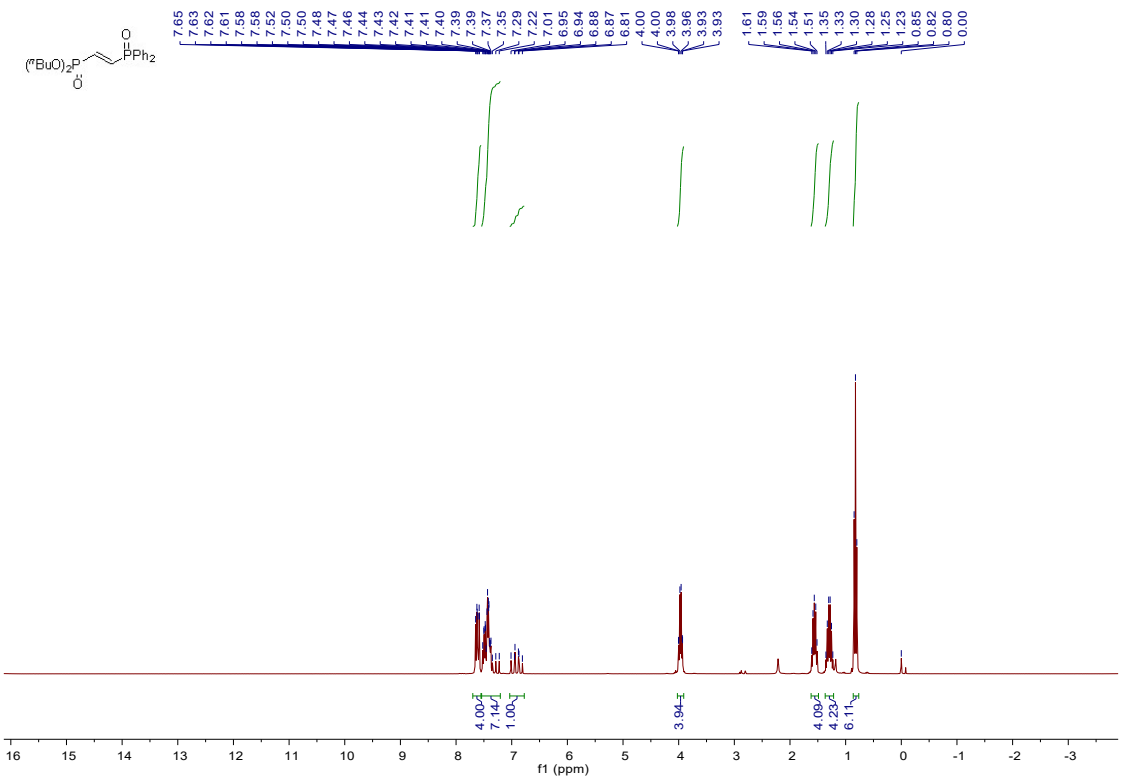

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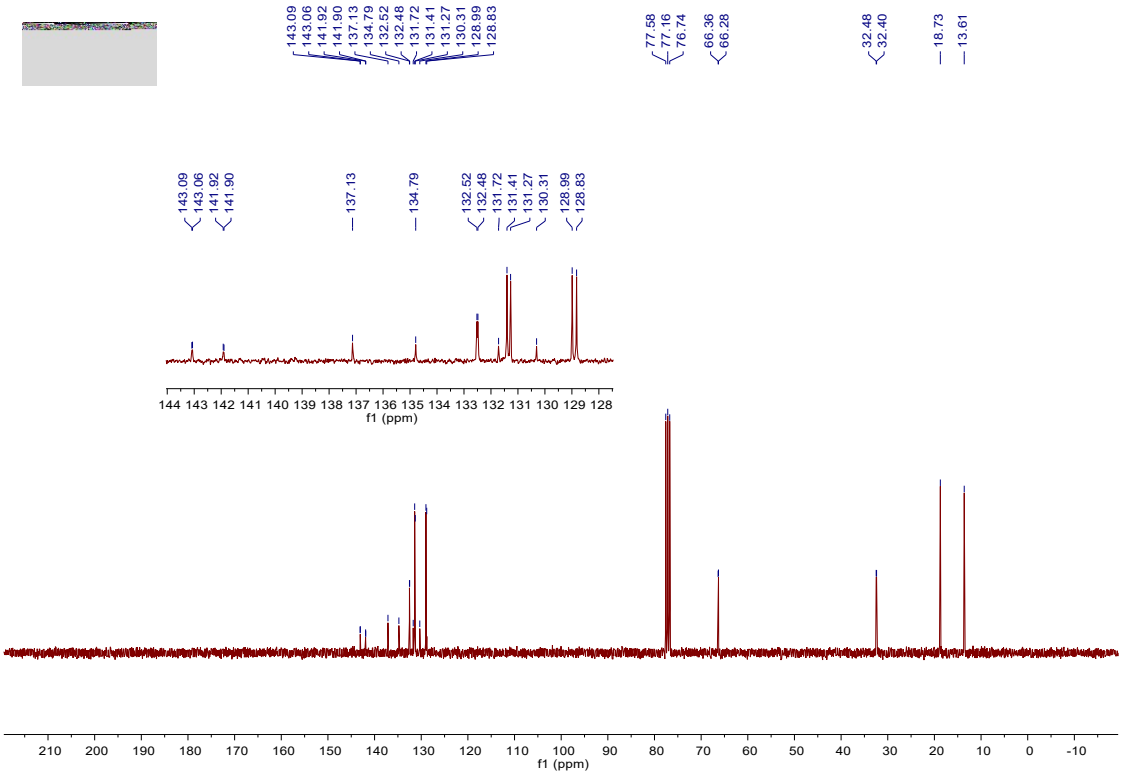

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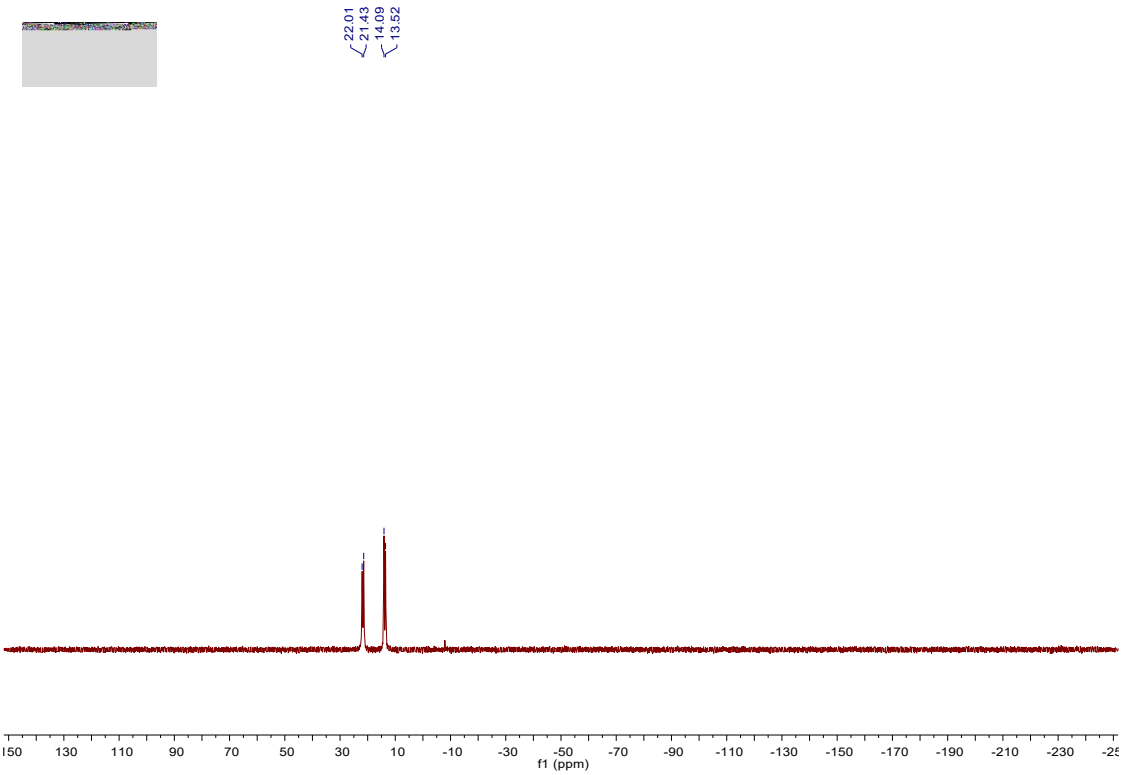

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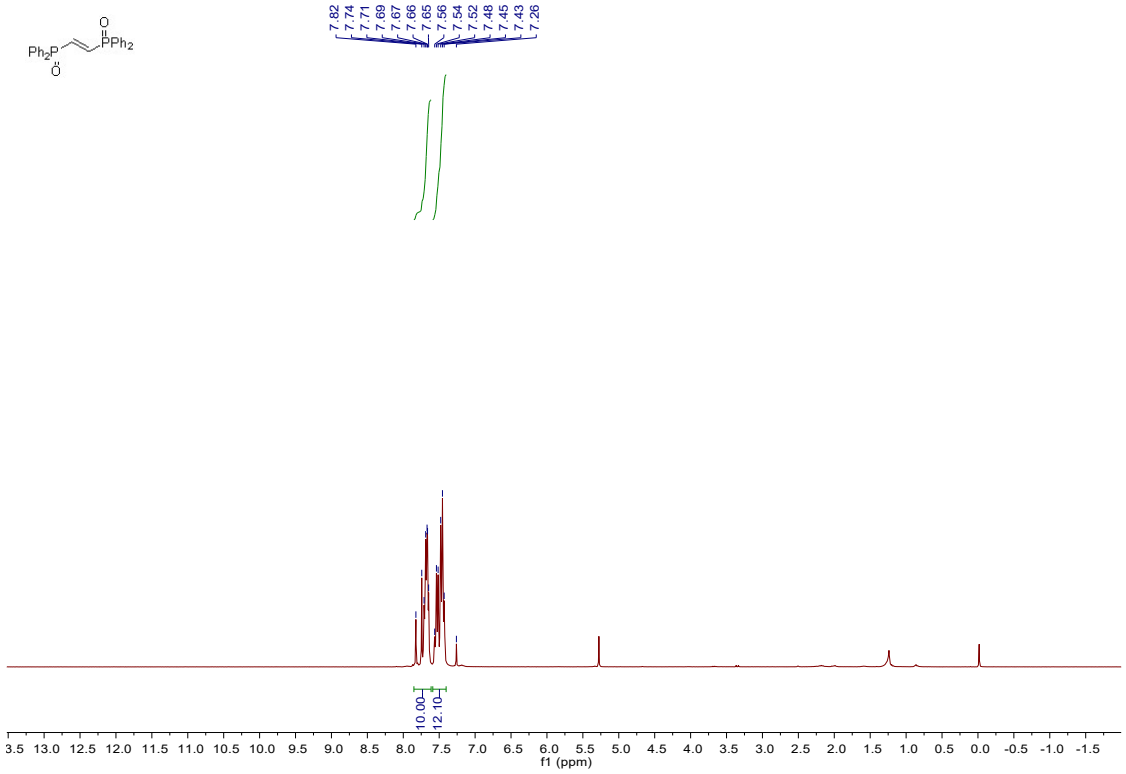

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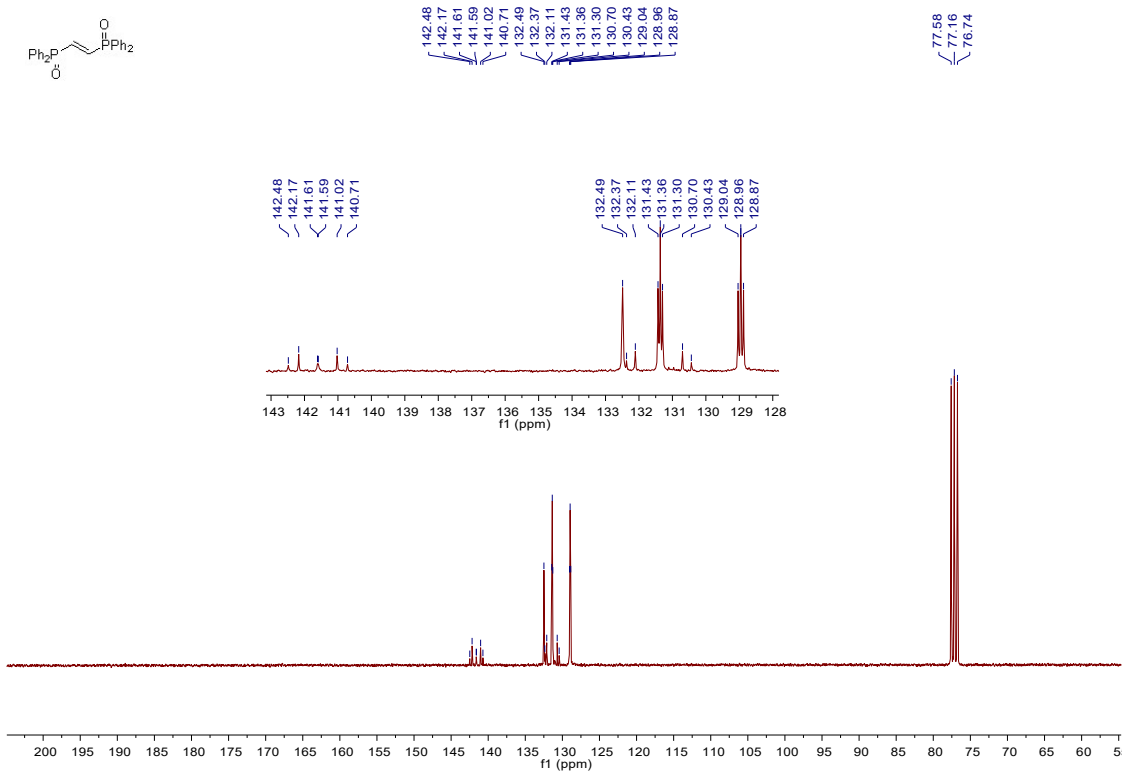

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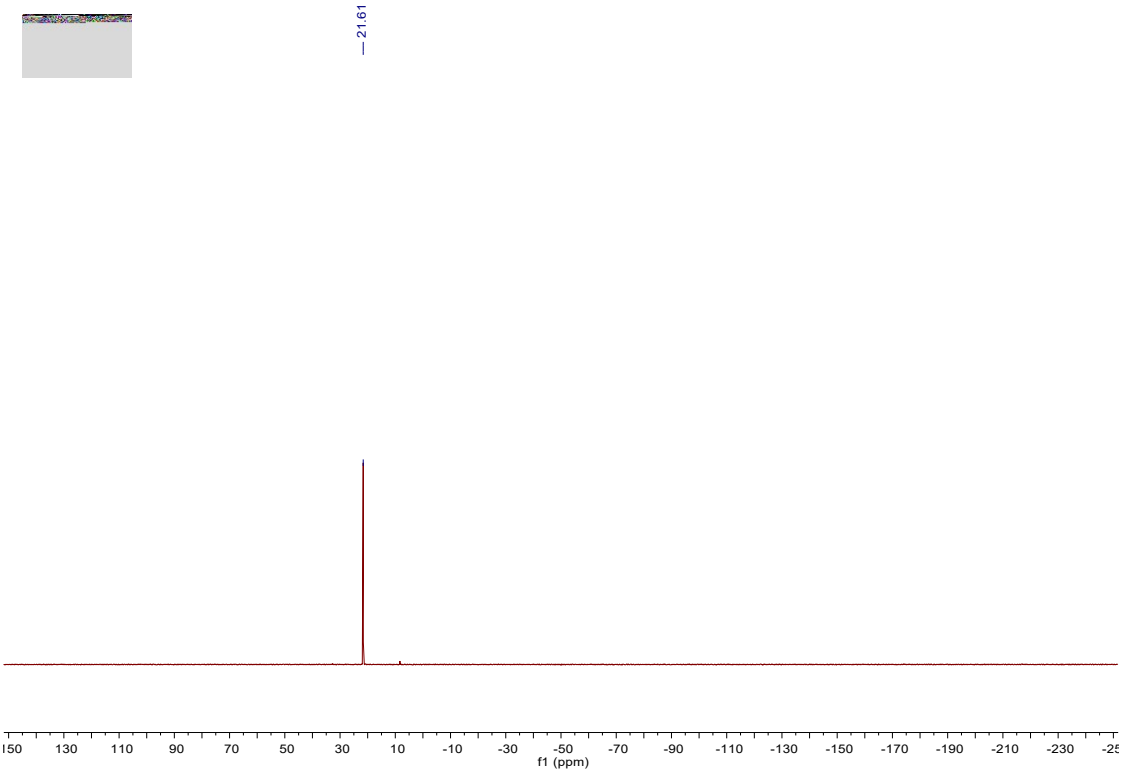

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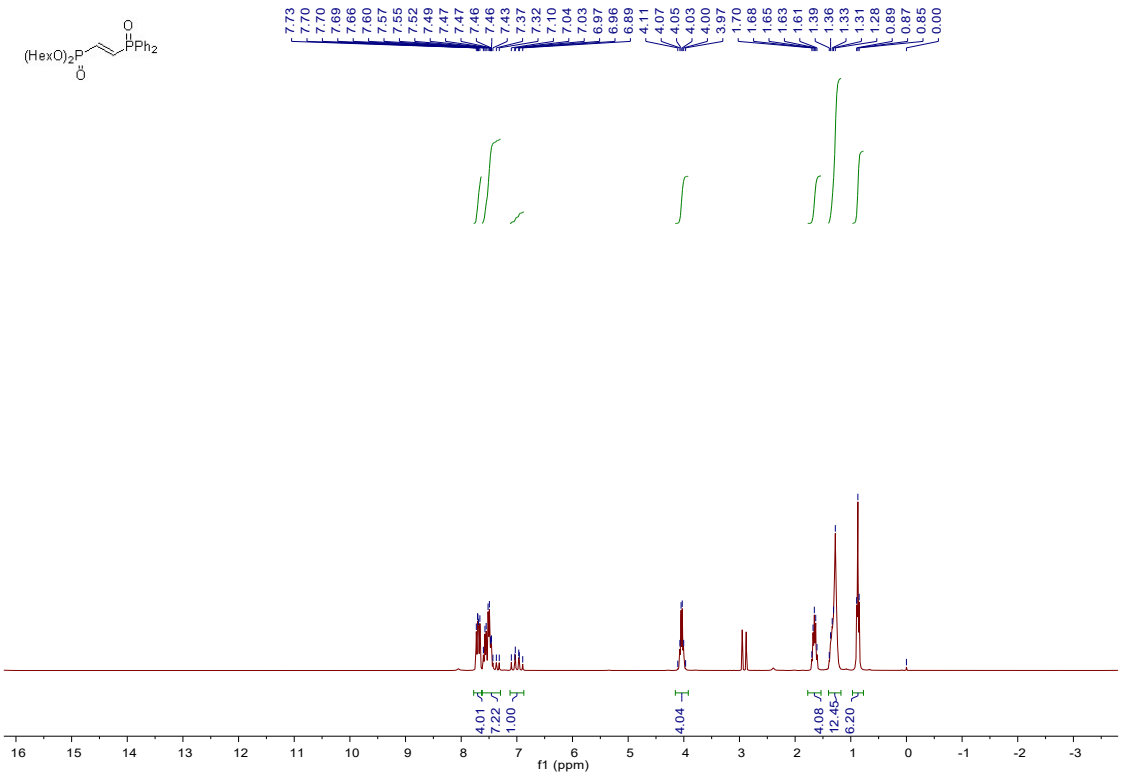

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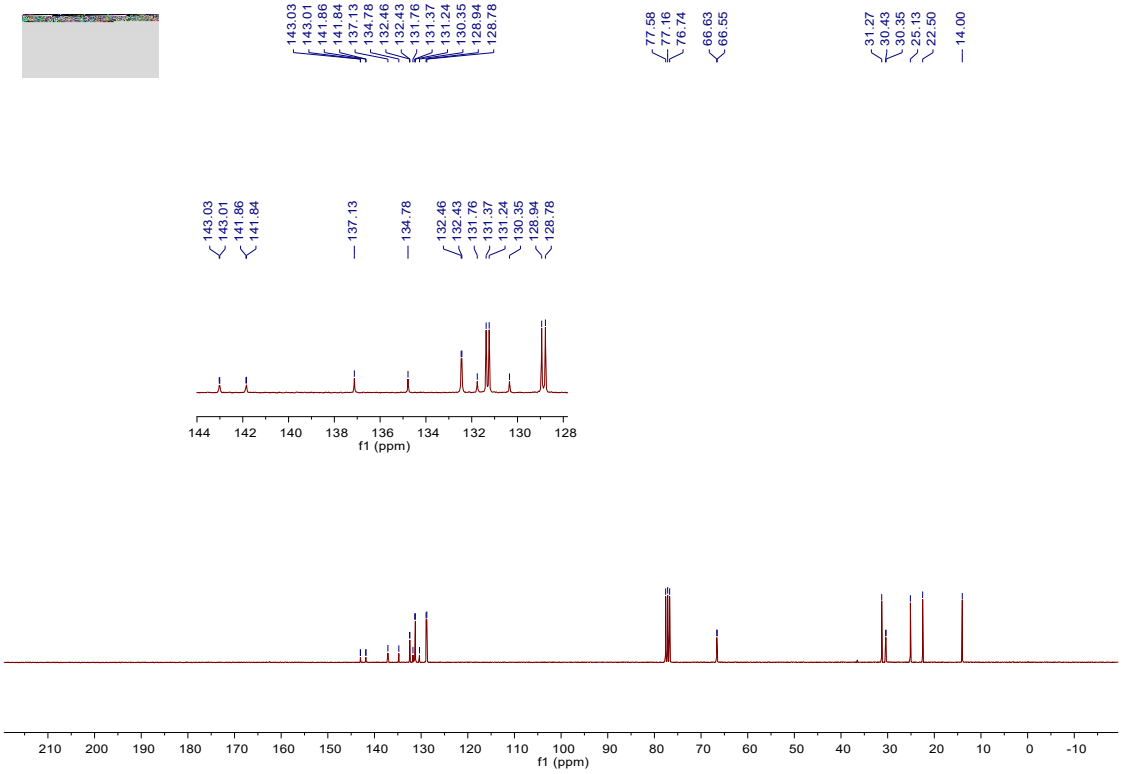

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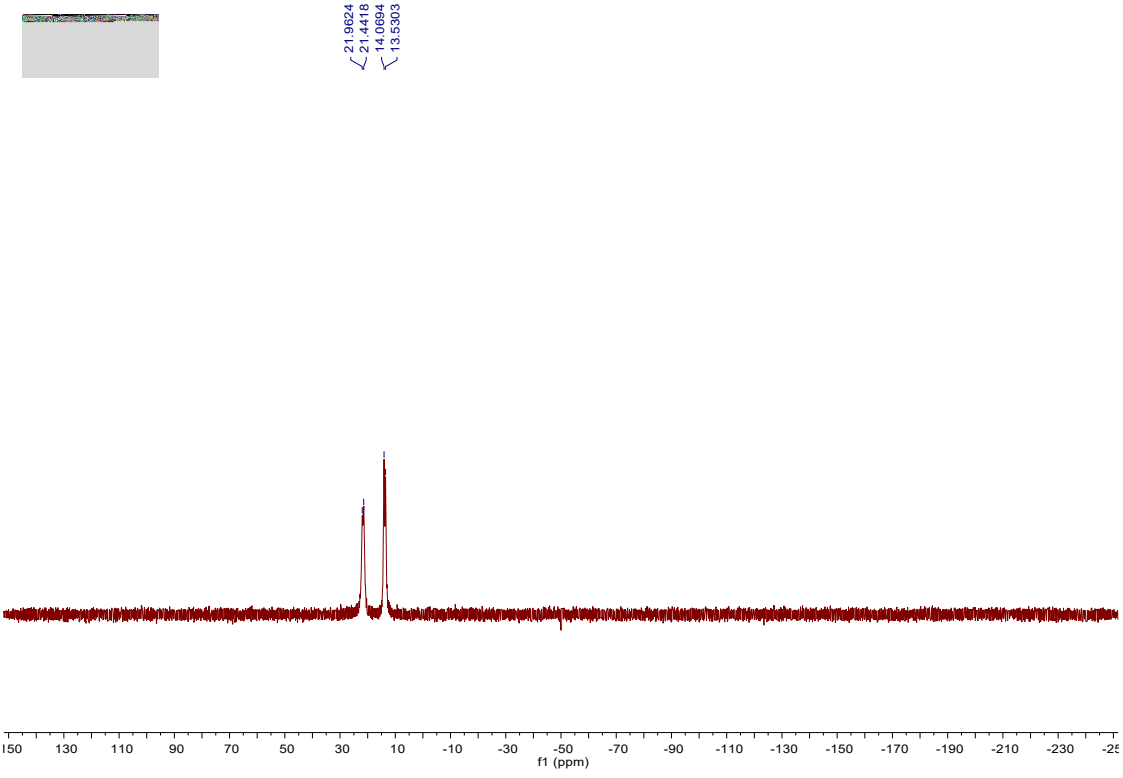

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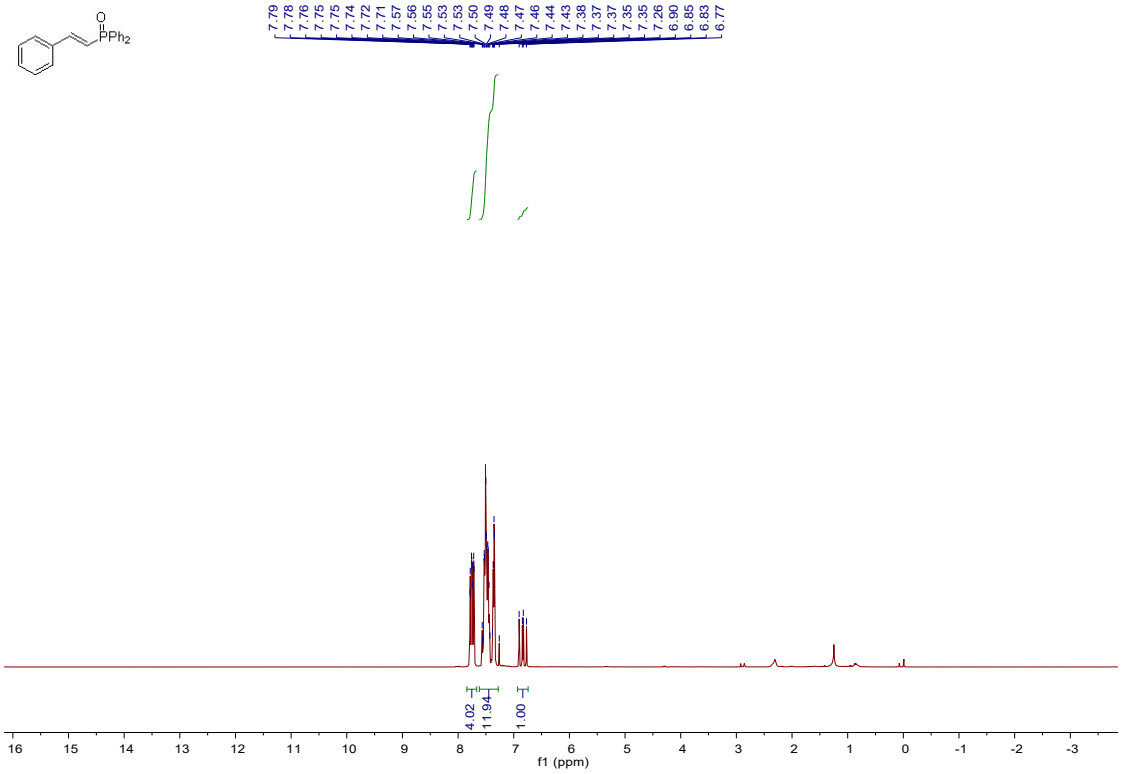
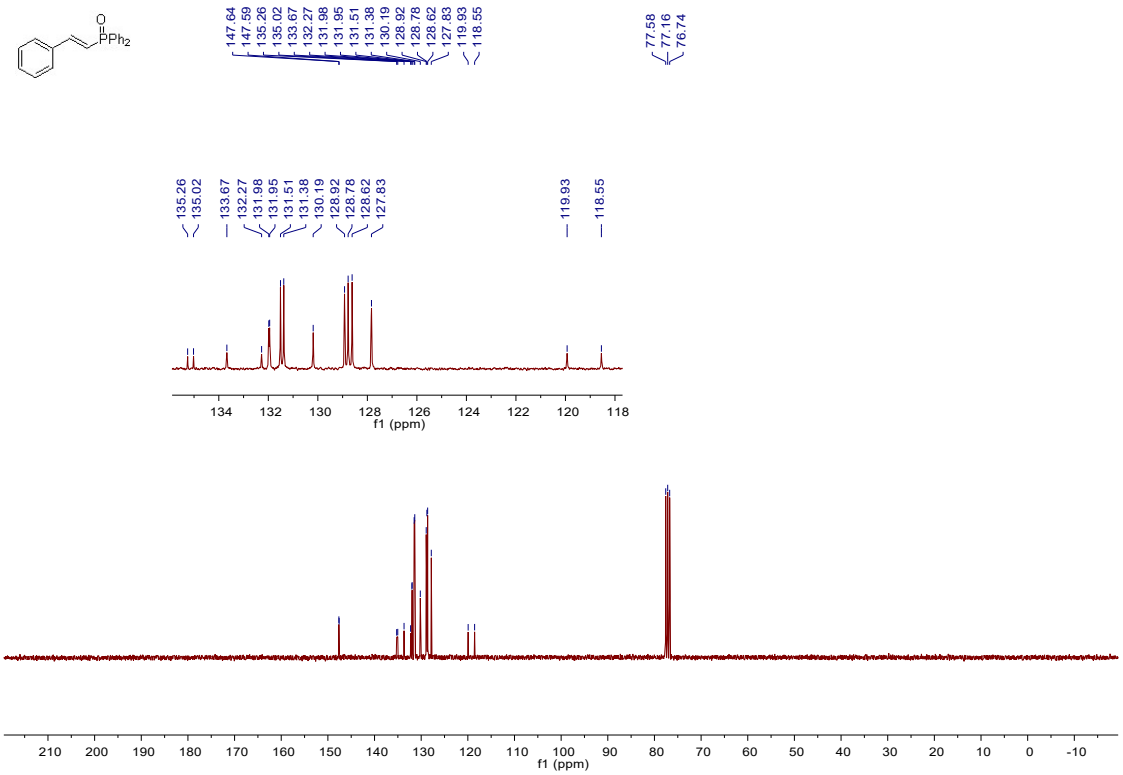


^{1}H NMR of compound **5ak**



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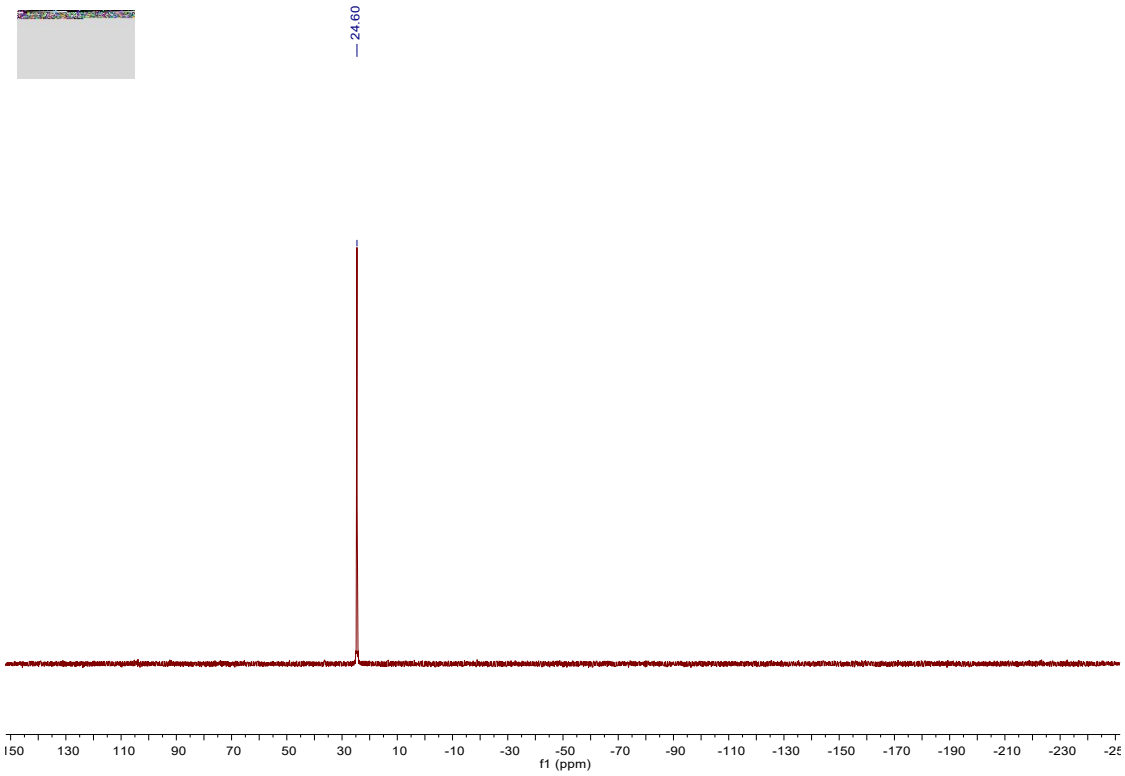

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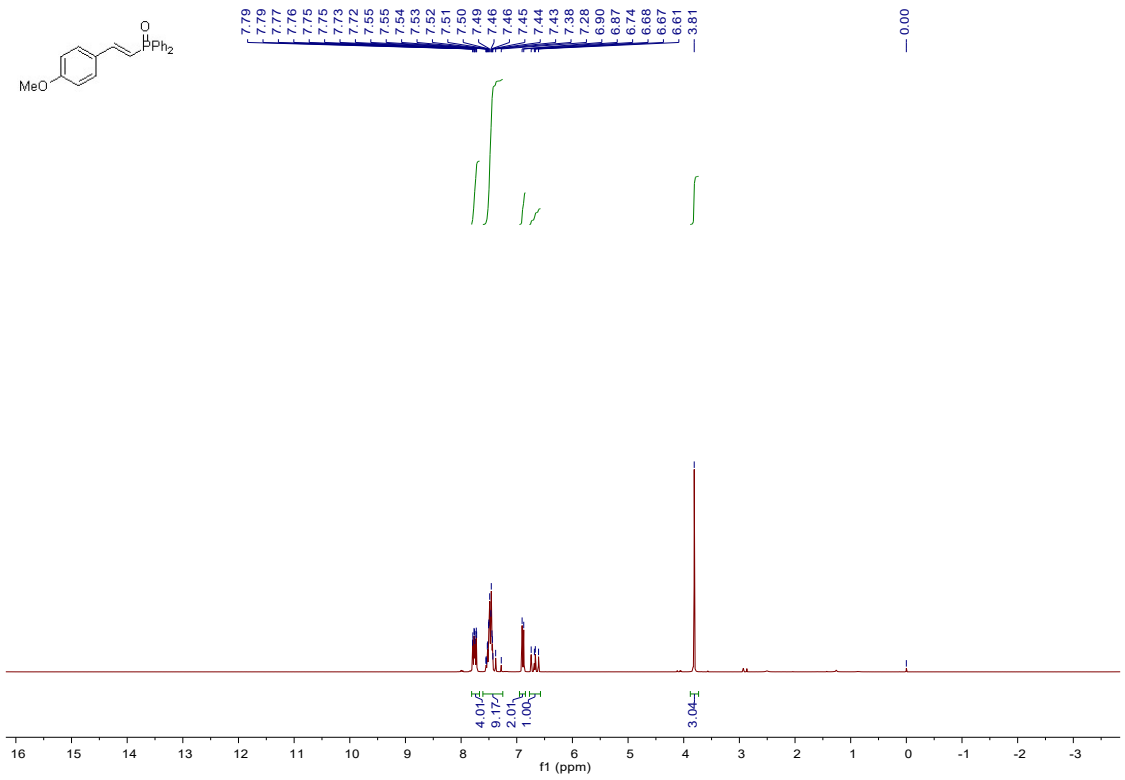
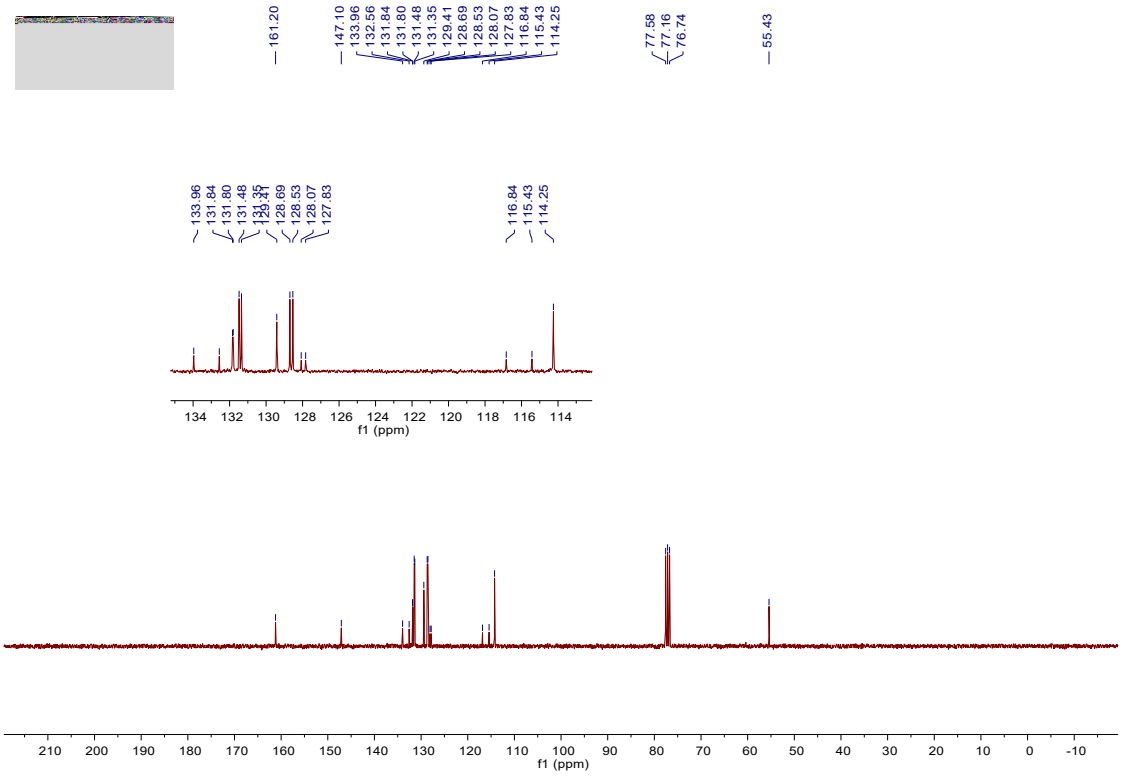


^{1}H NMR of compound **5bk**



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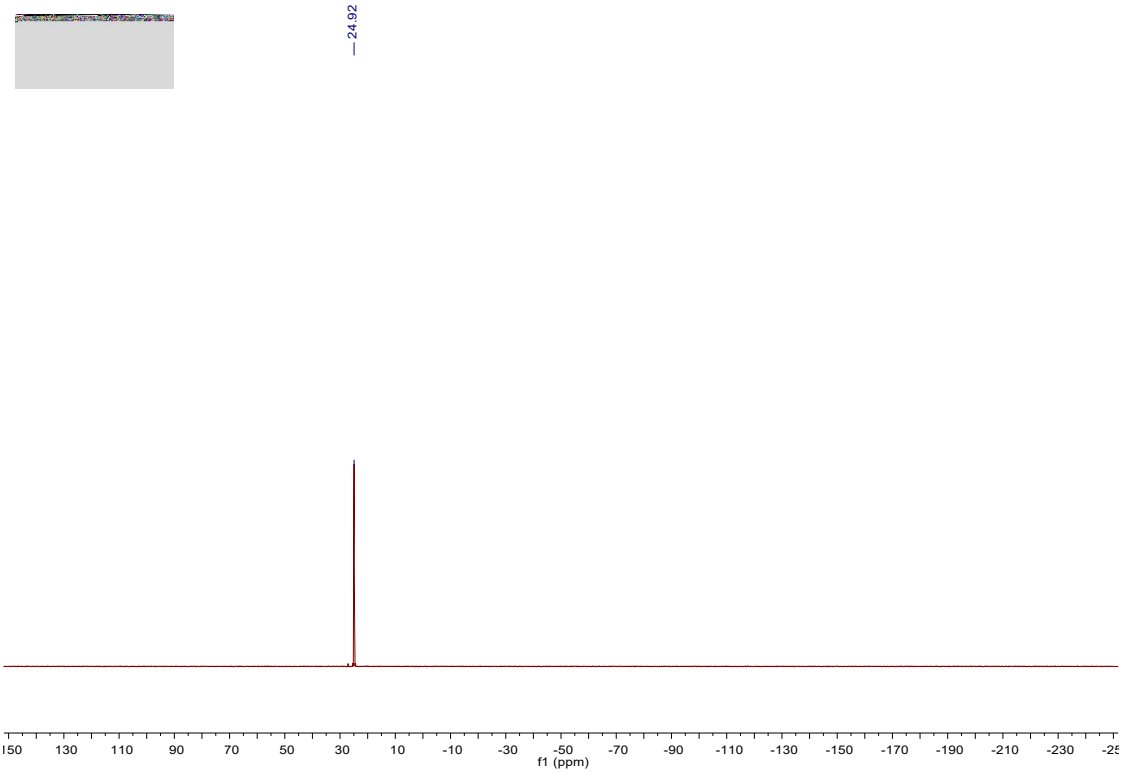

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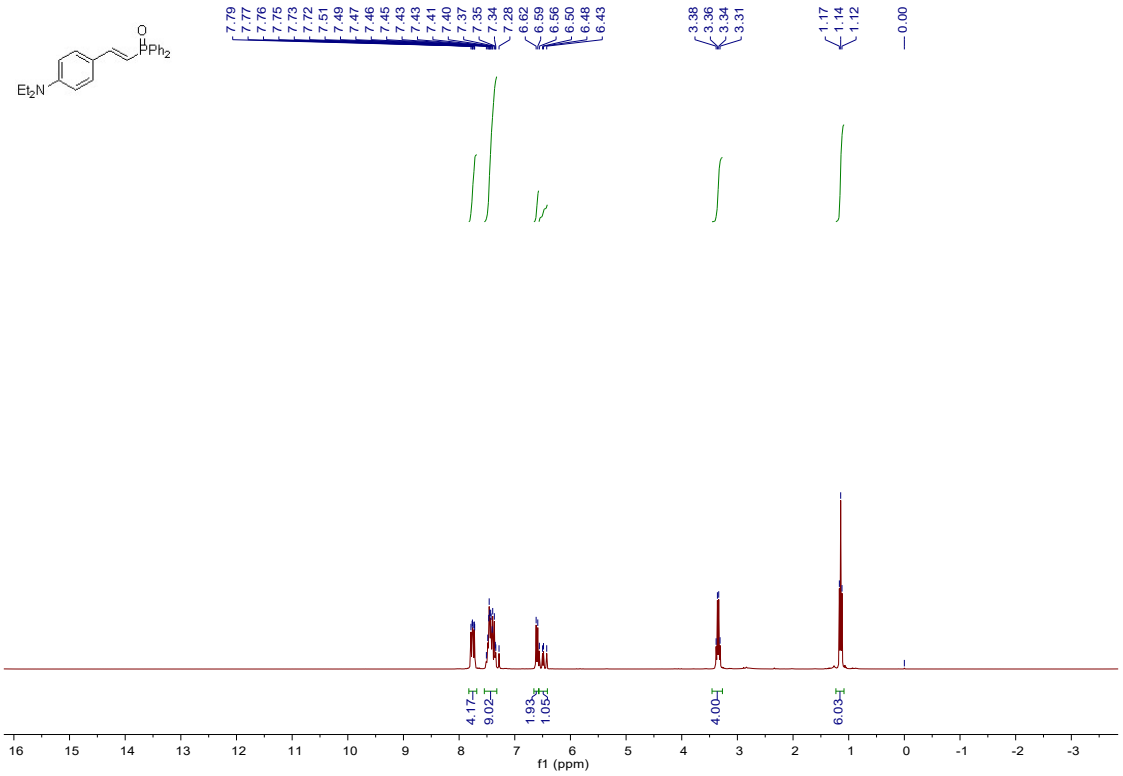

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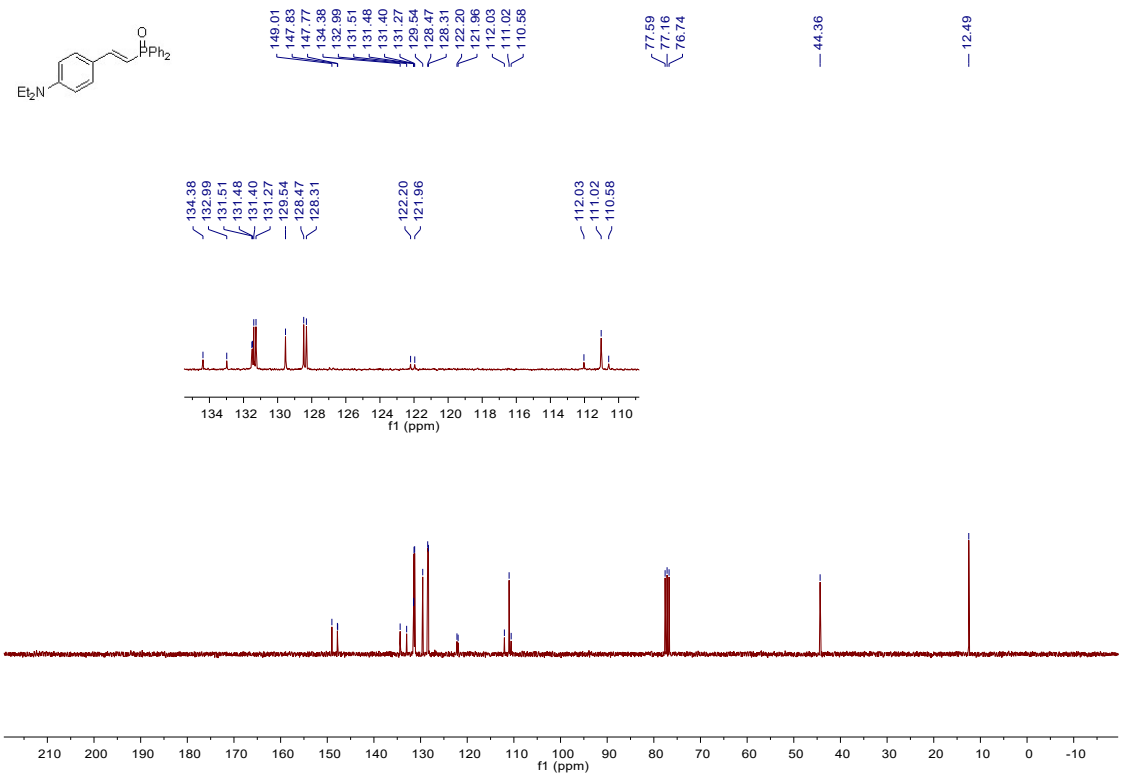

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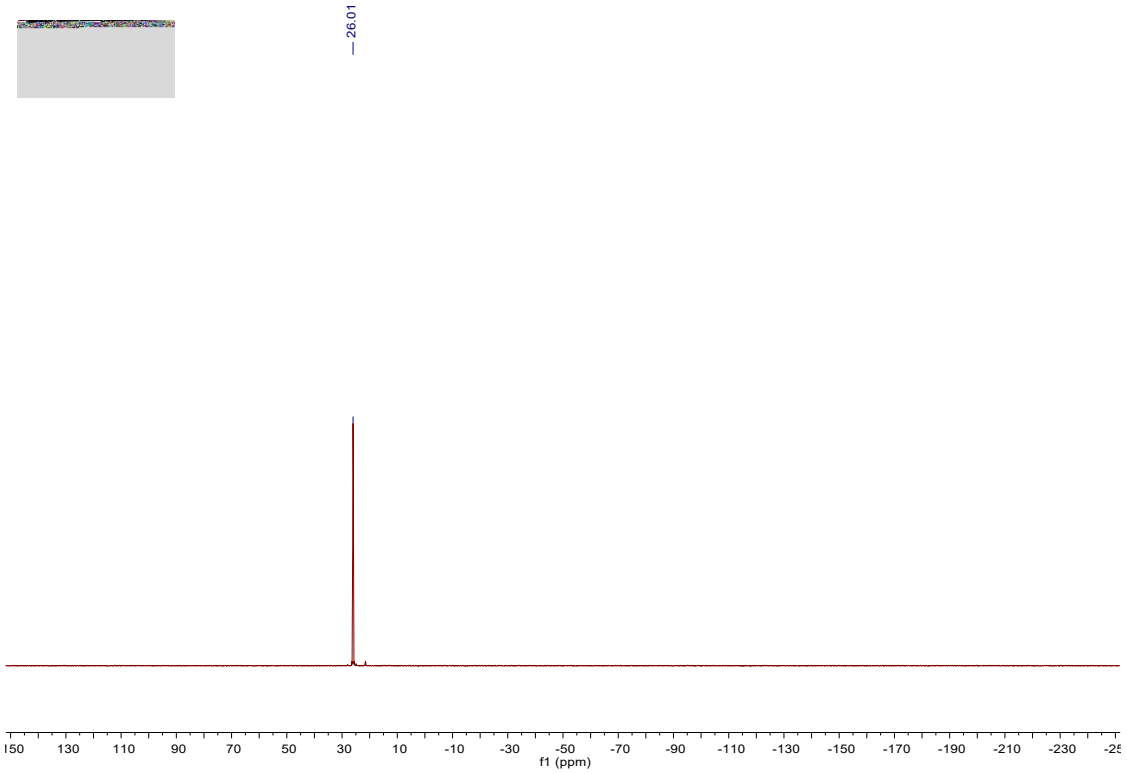

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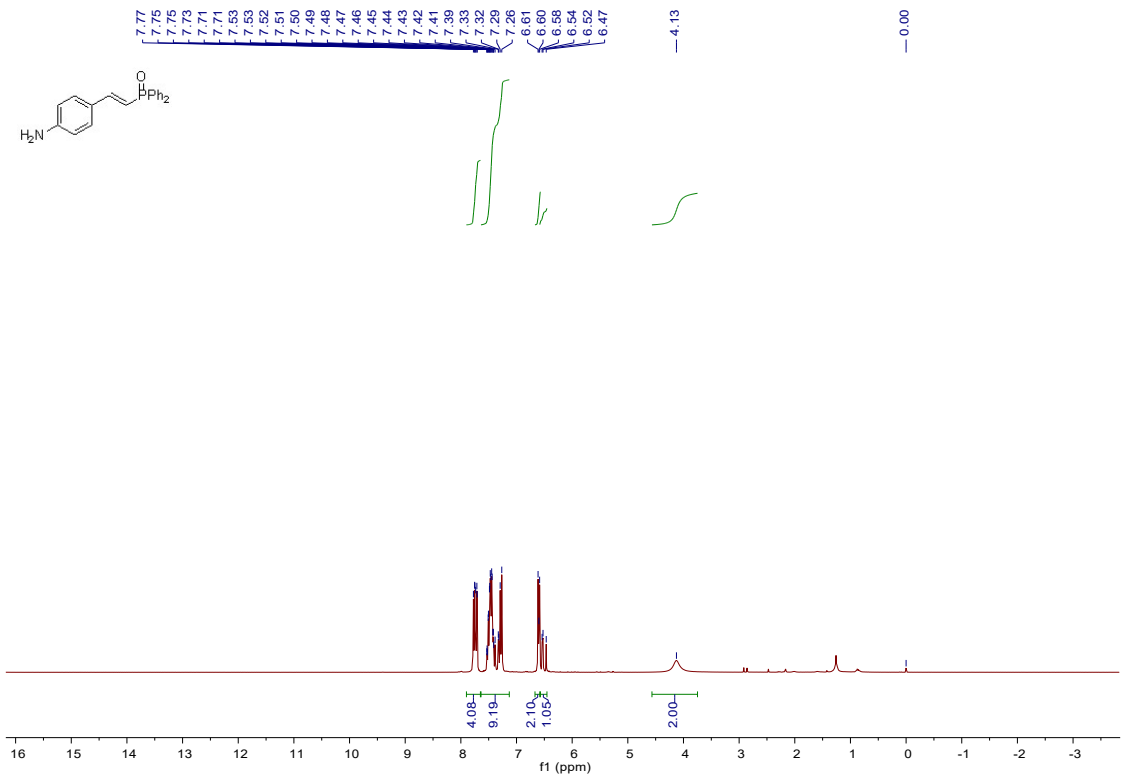

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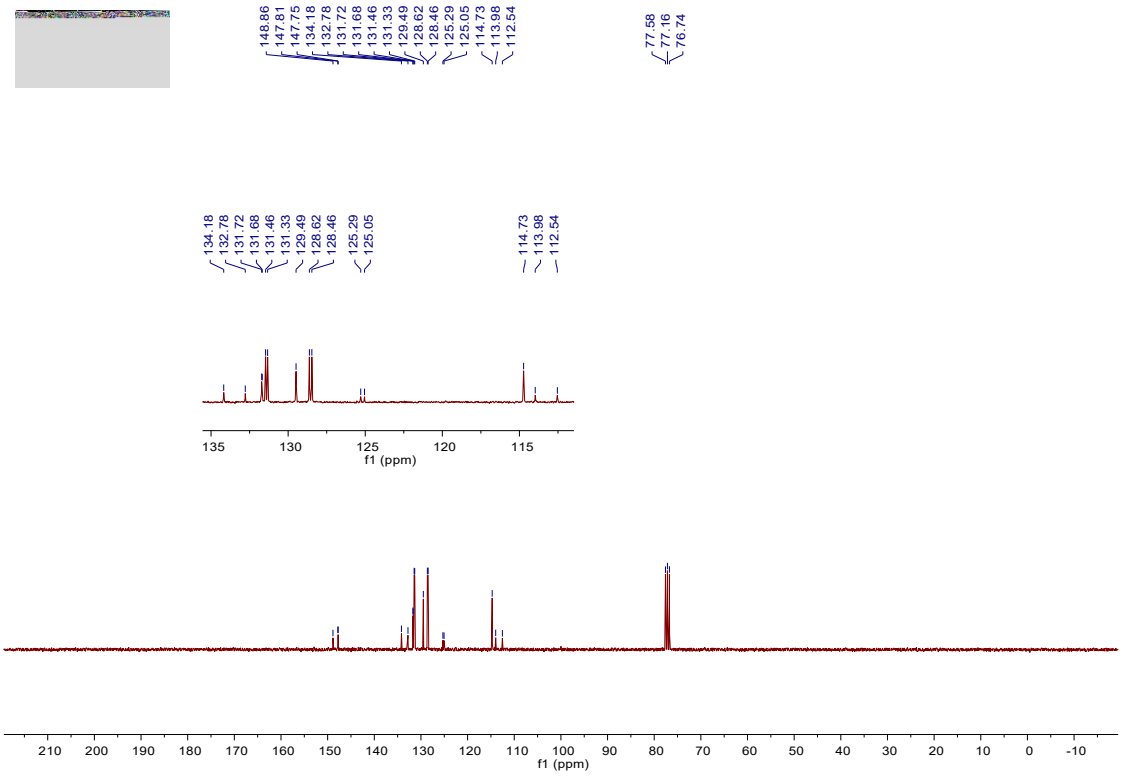

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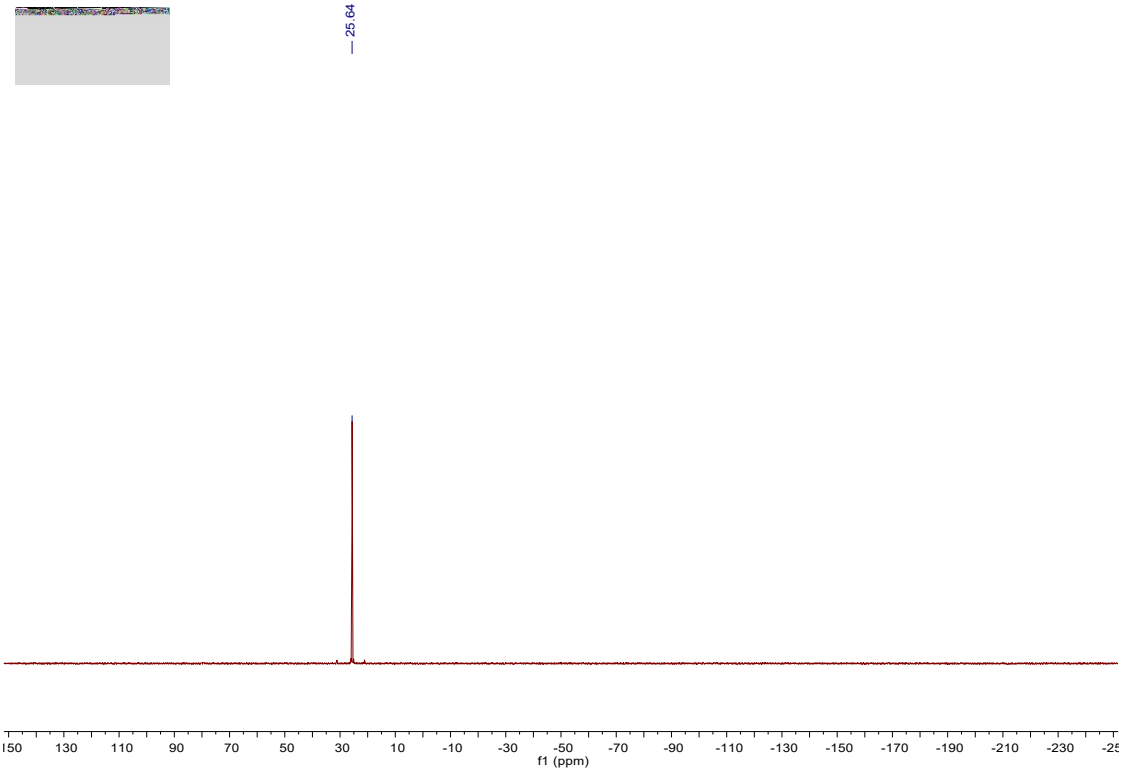

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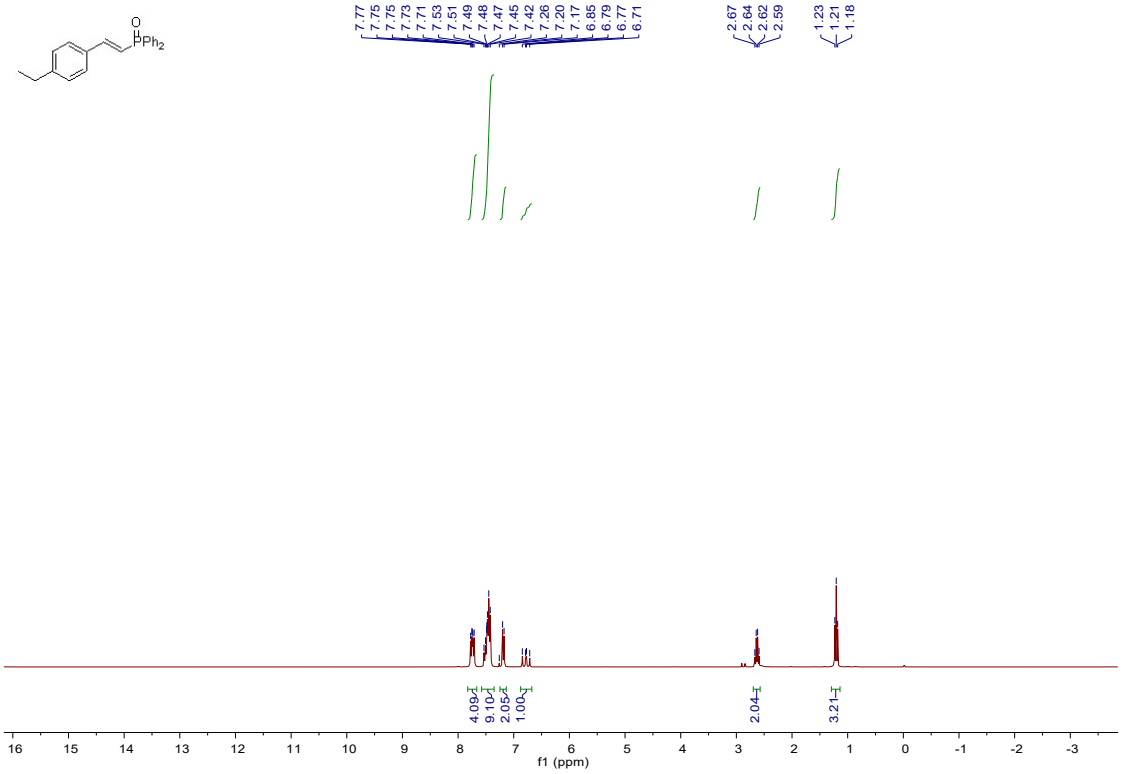

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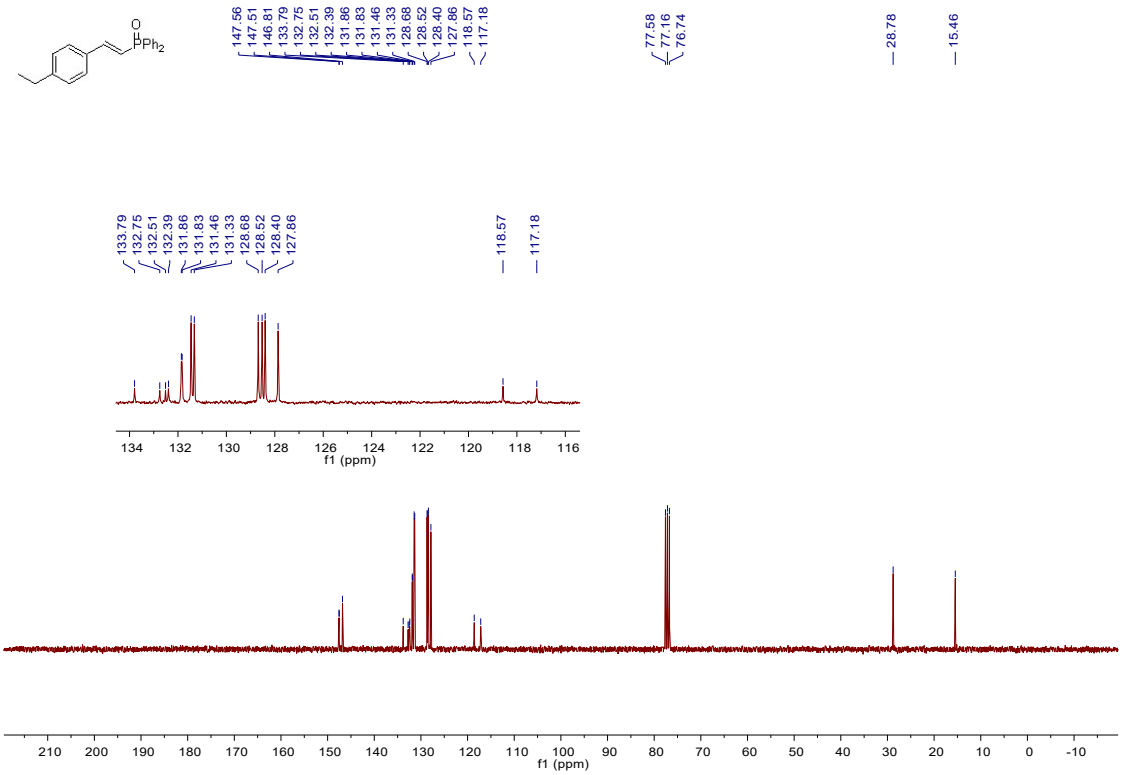

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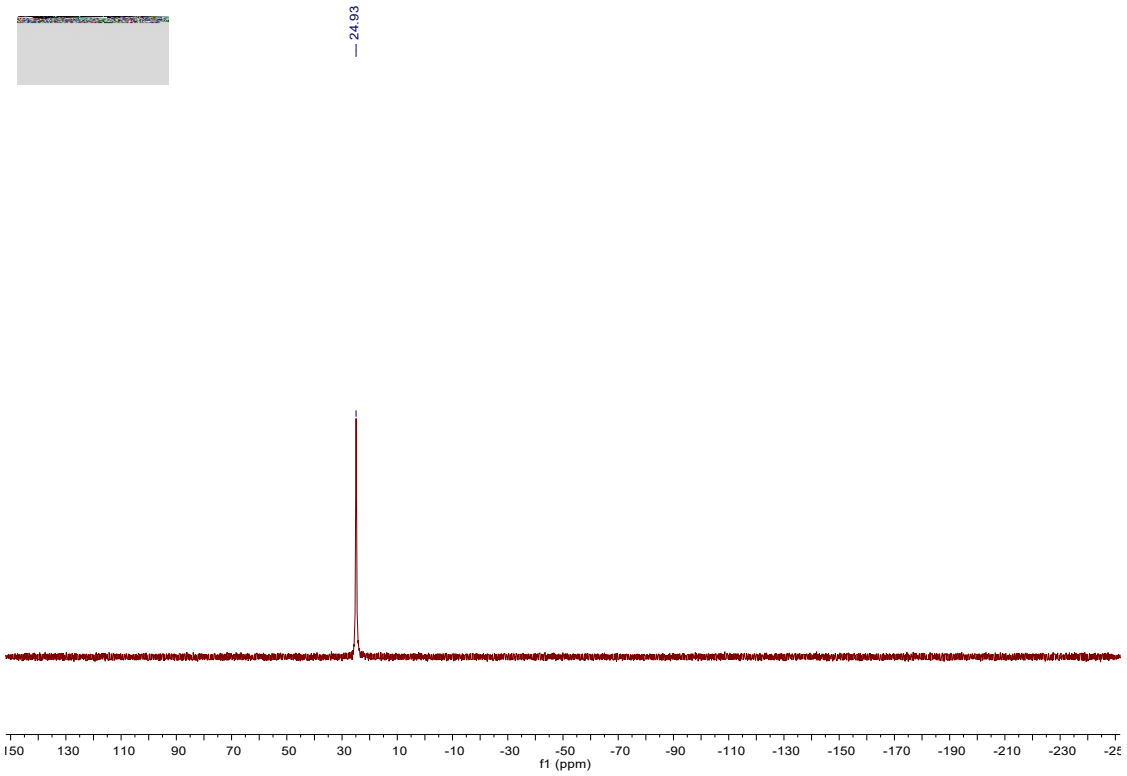

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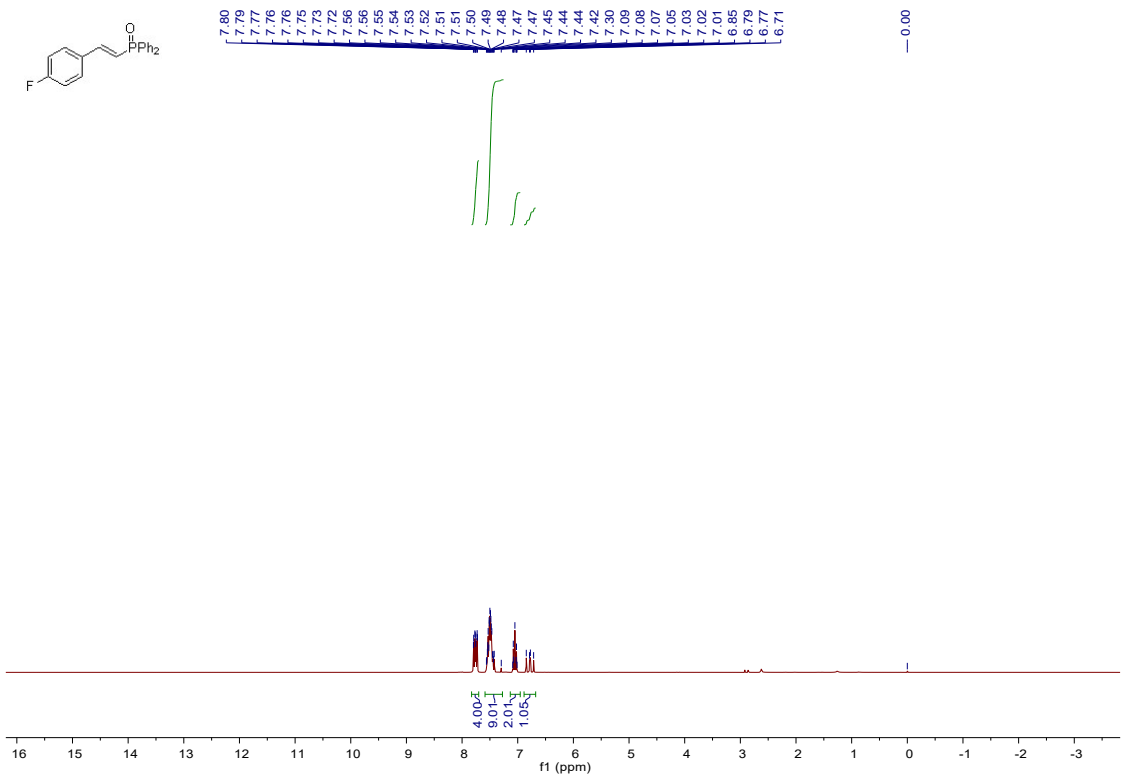

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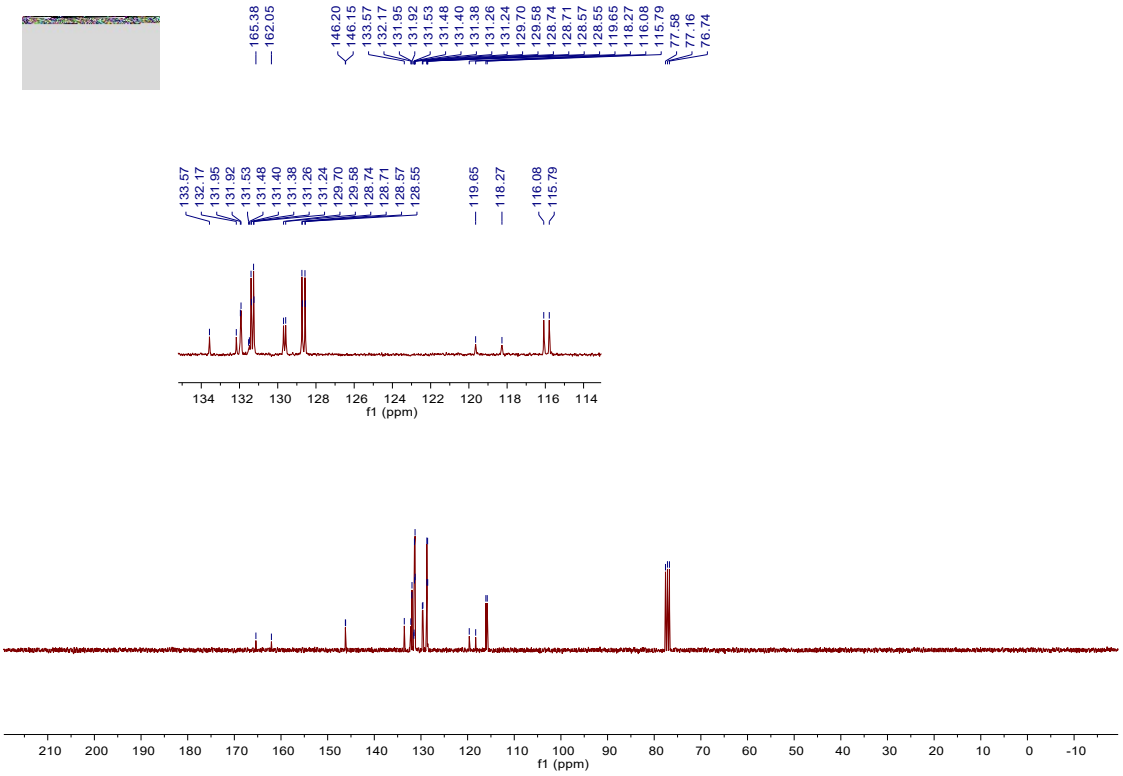

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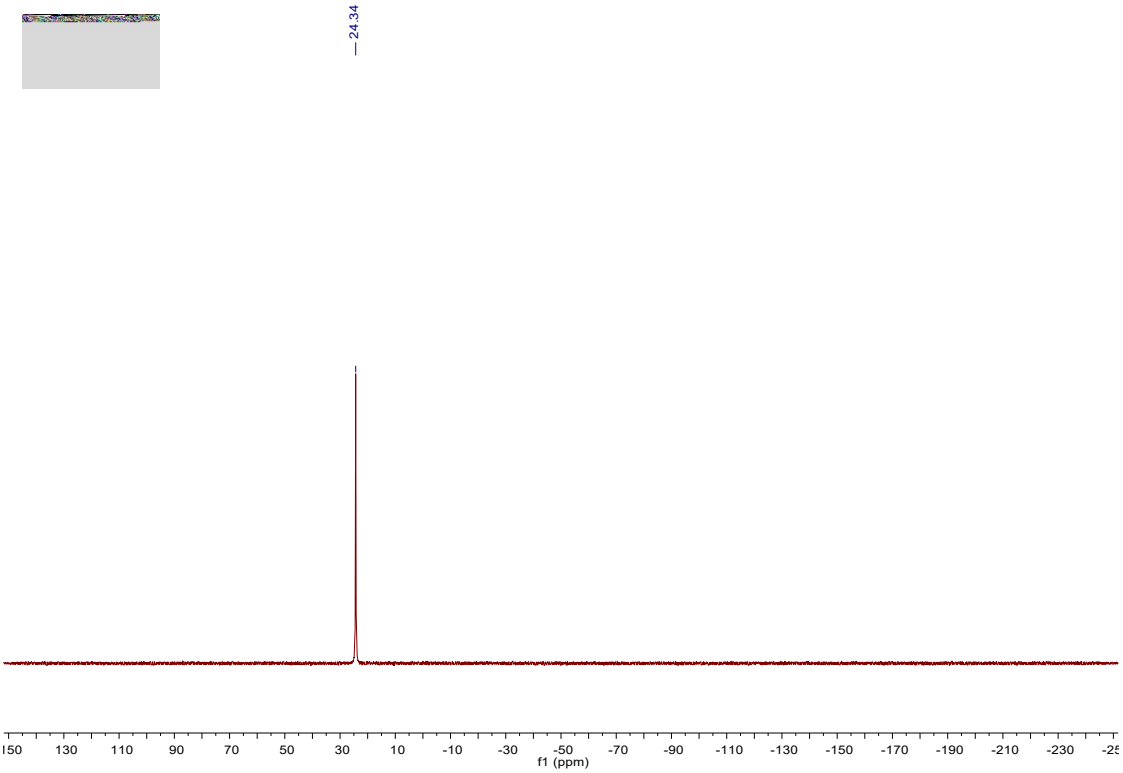

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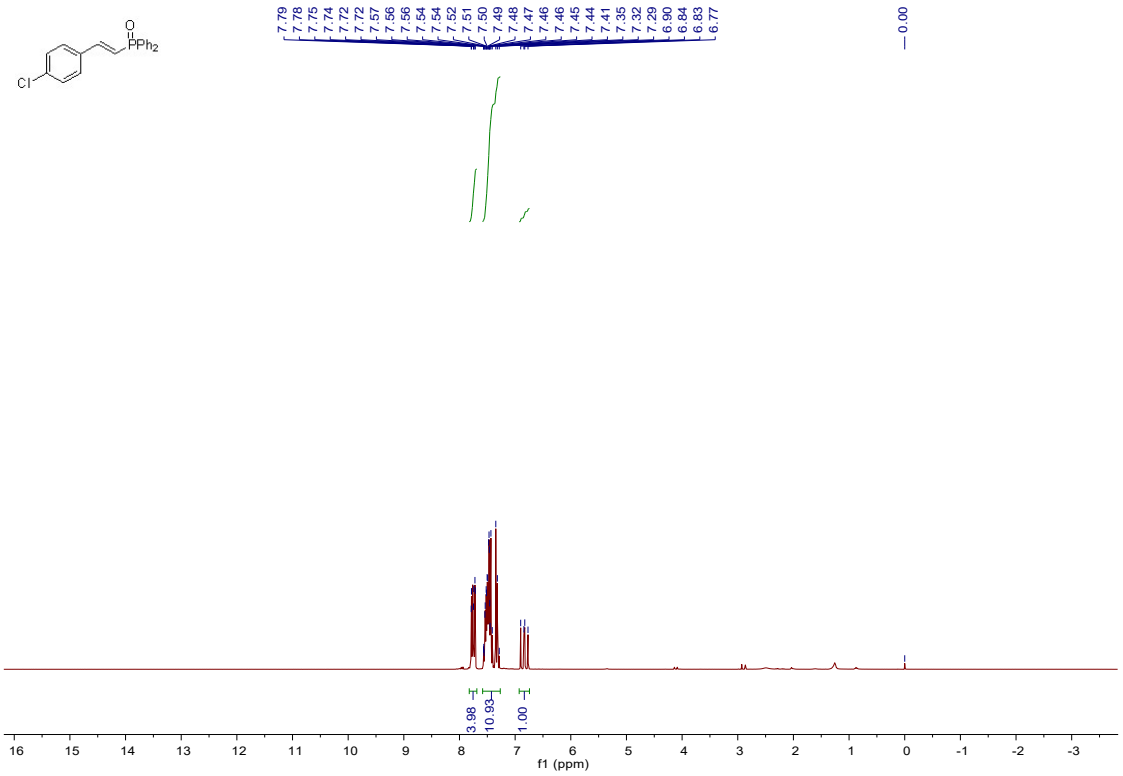

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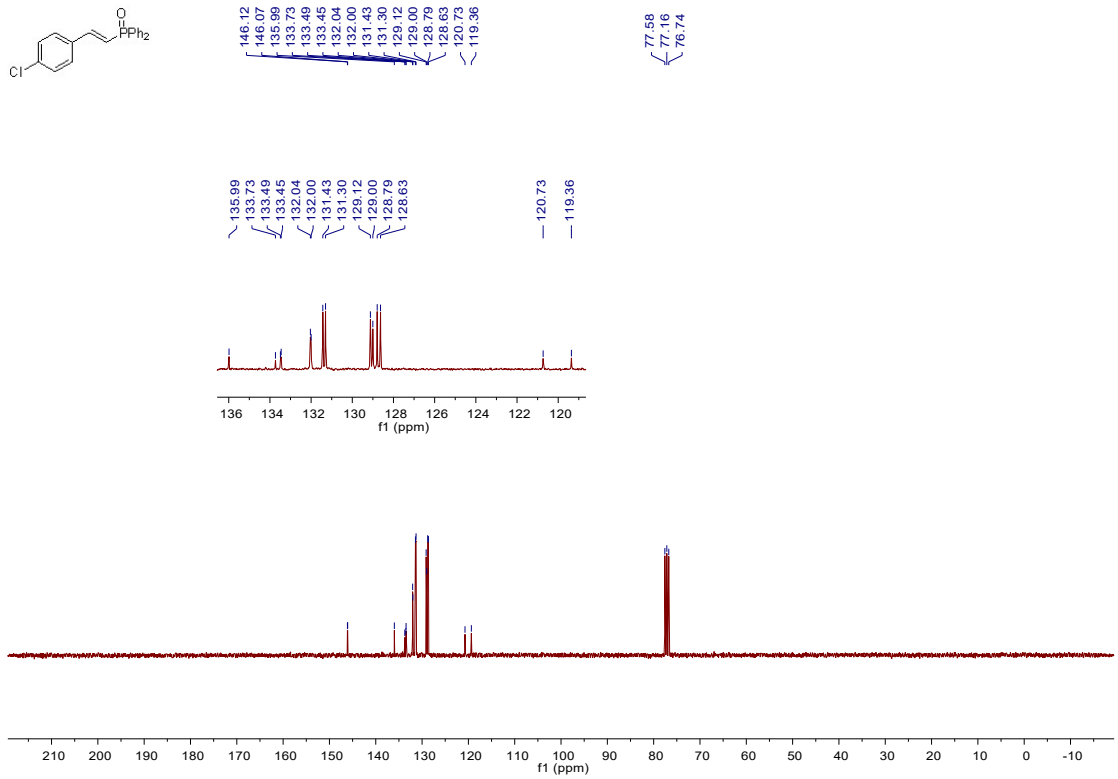

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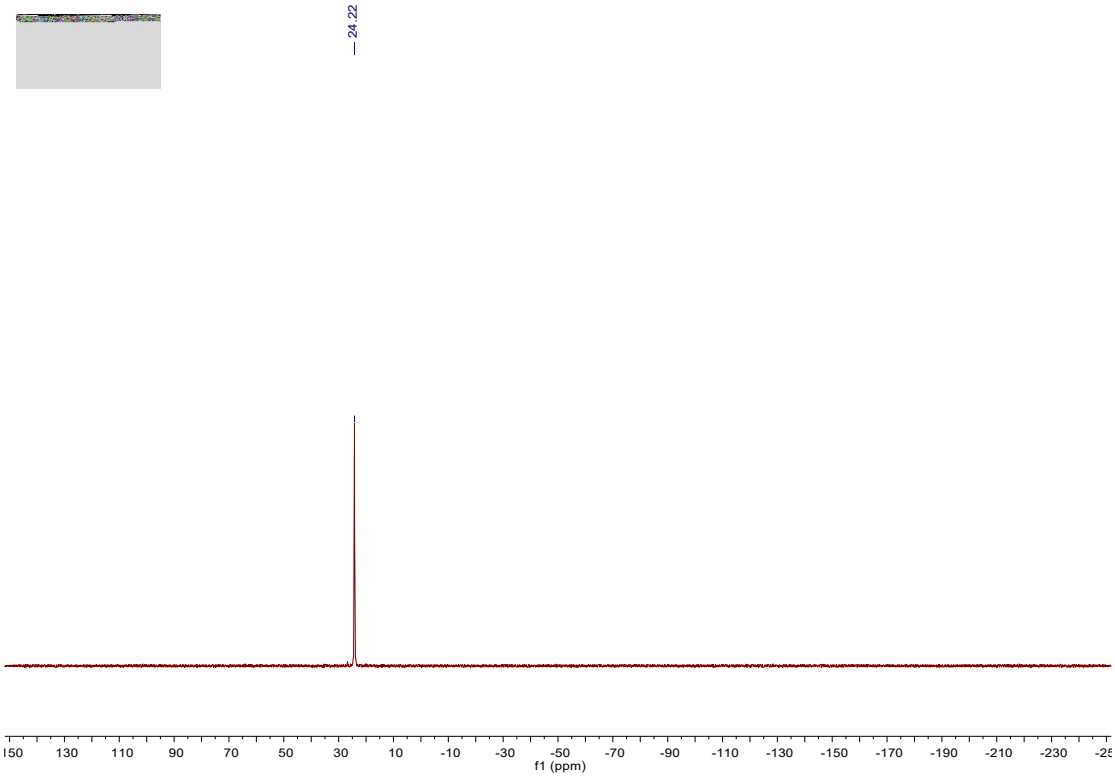

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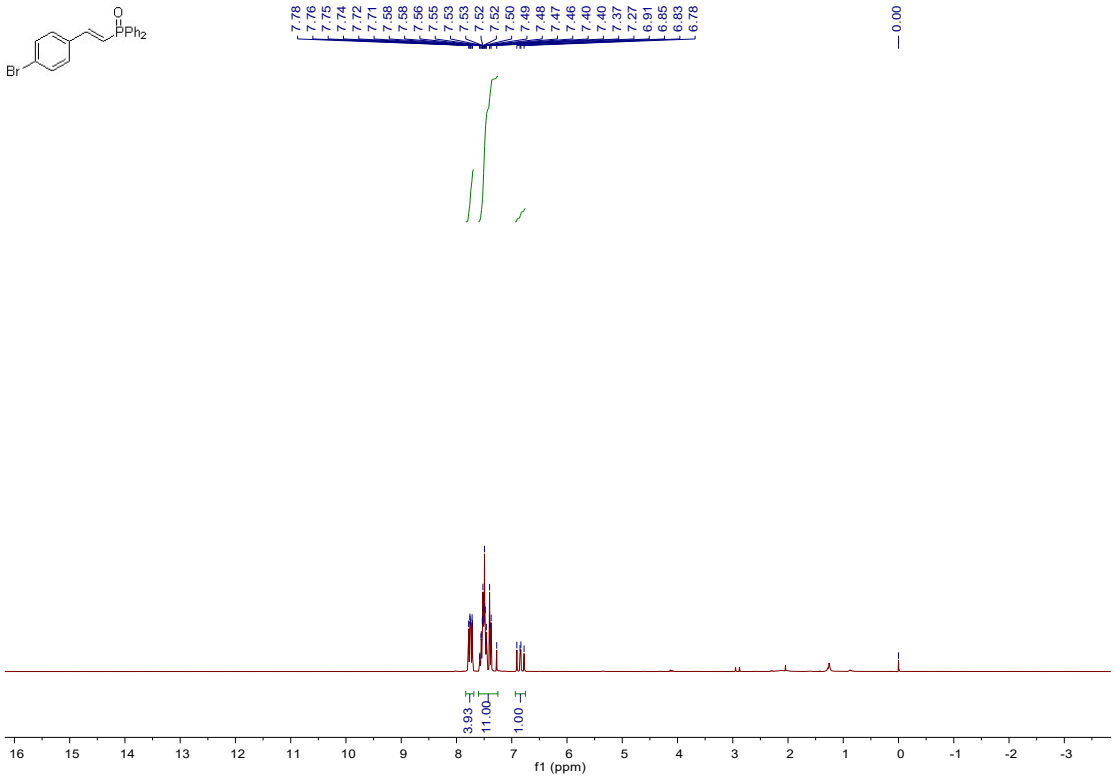

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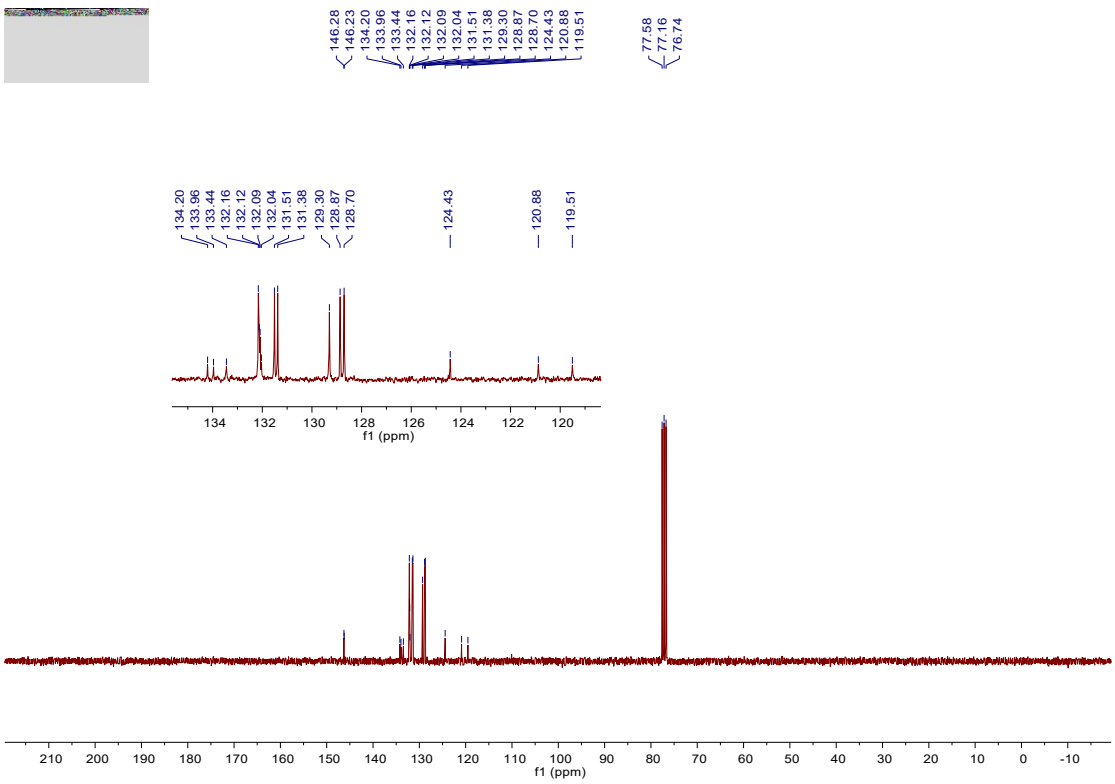

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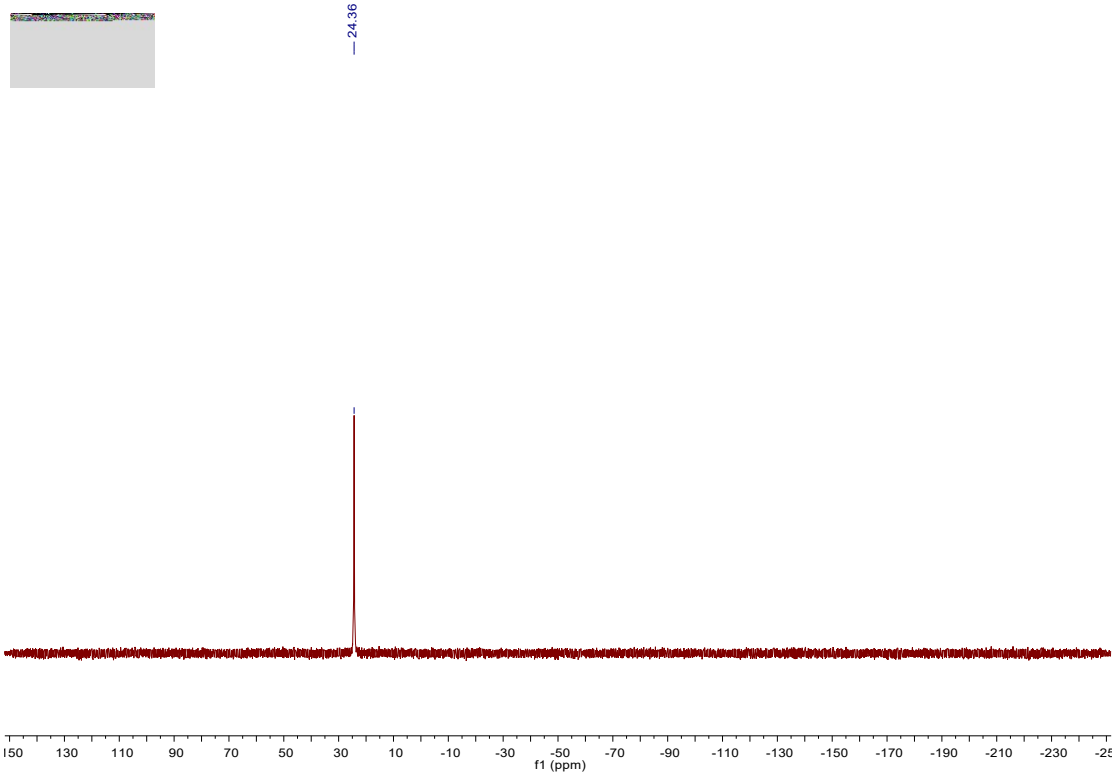

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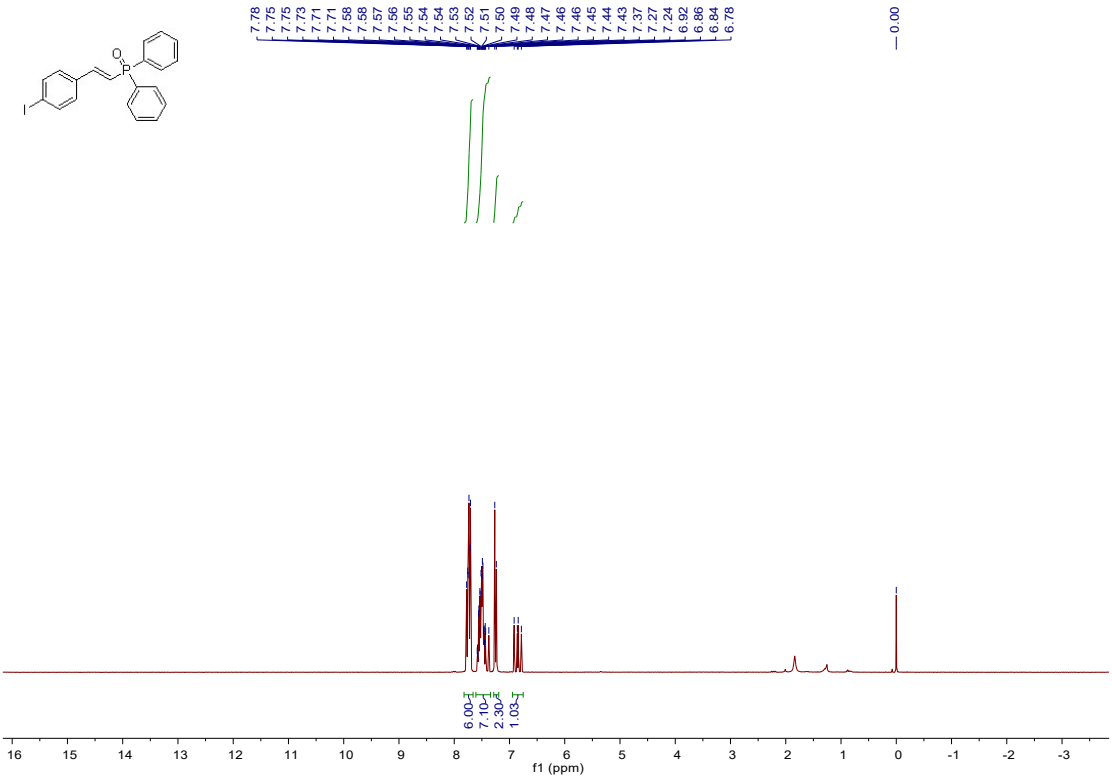

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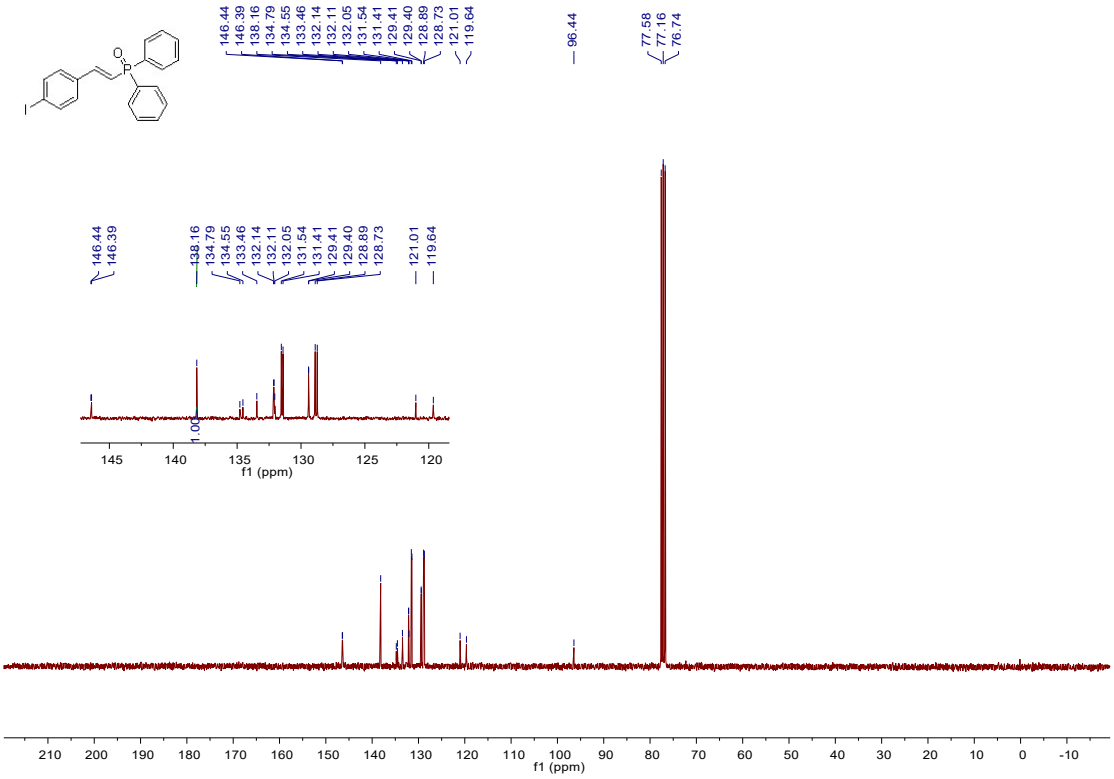

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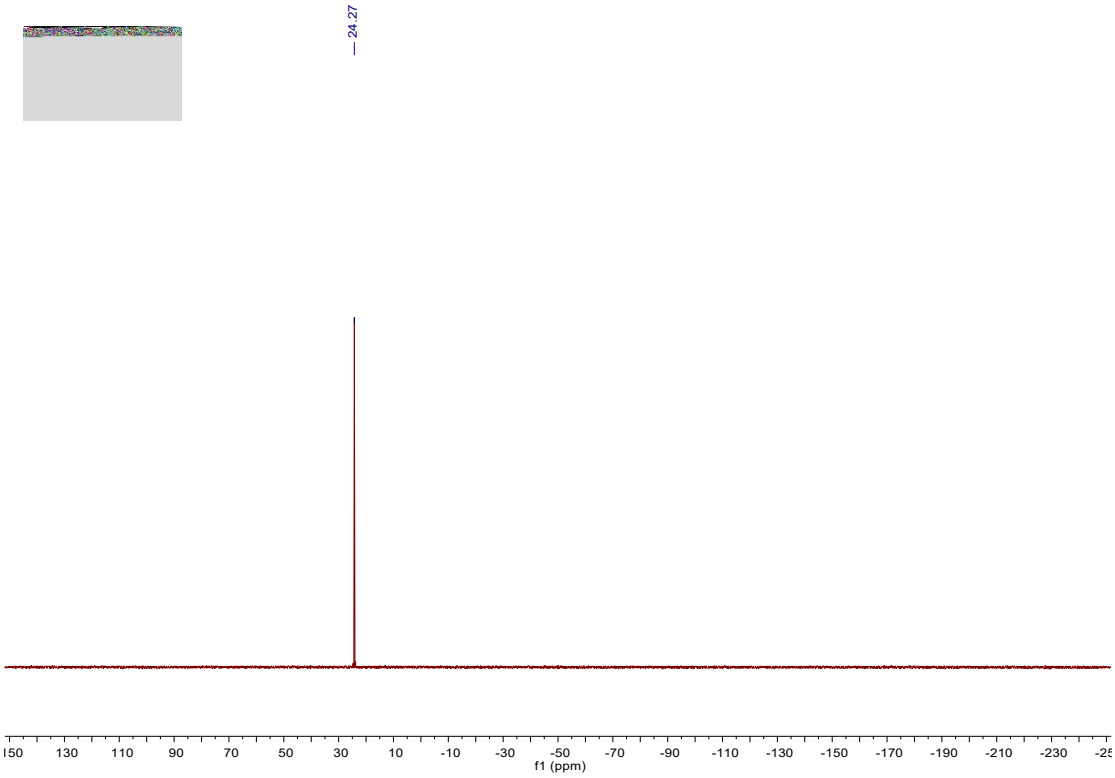

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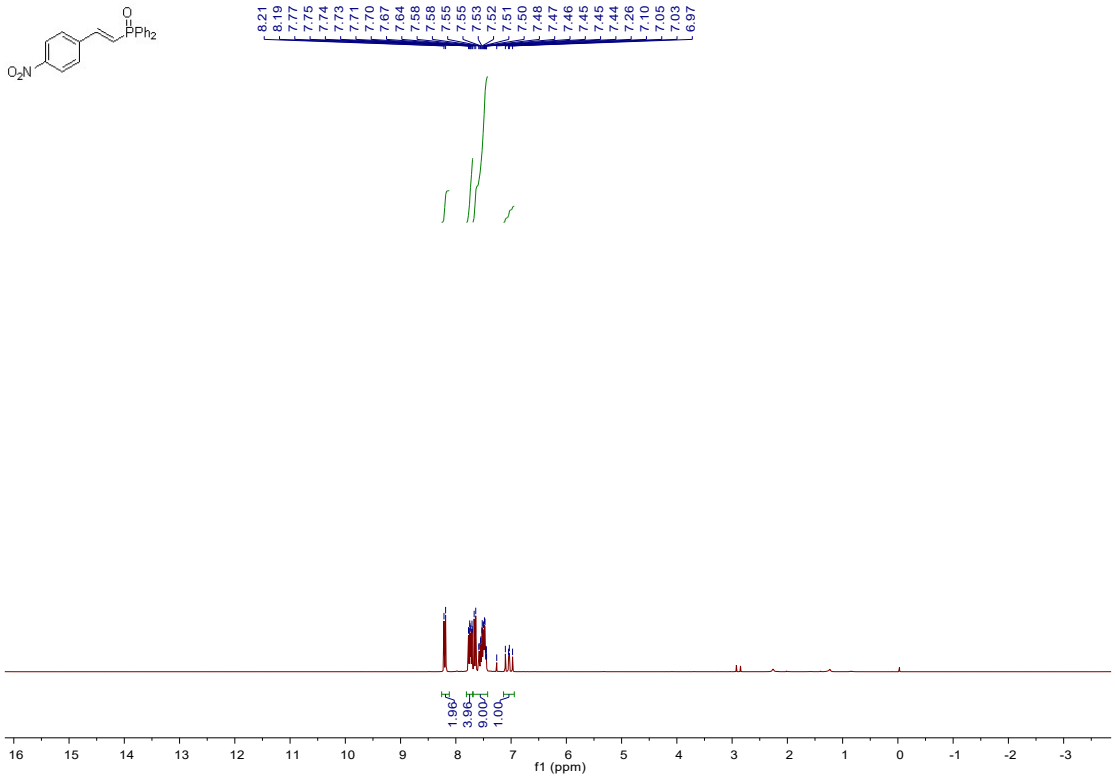

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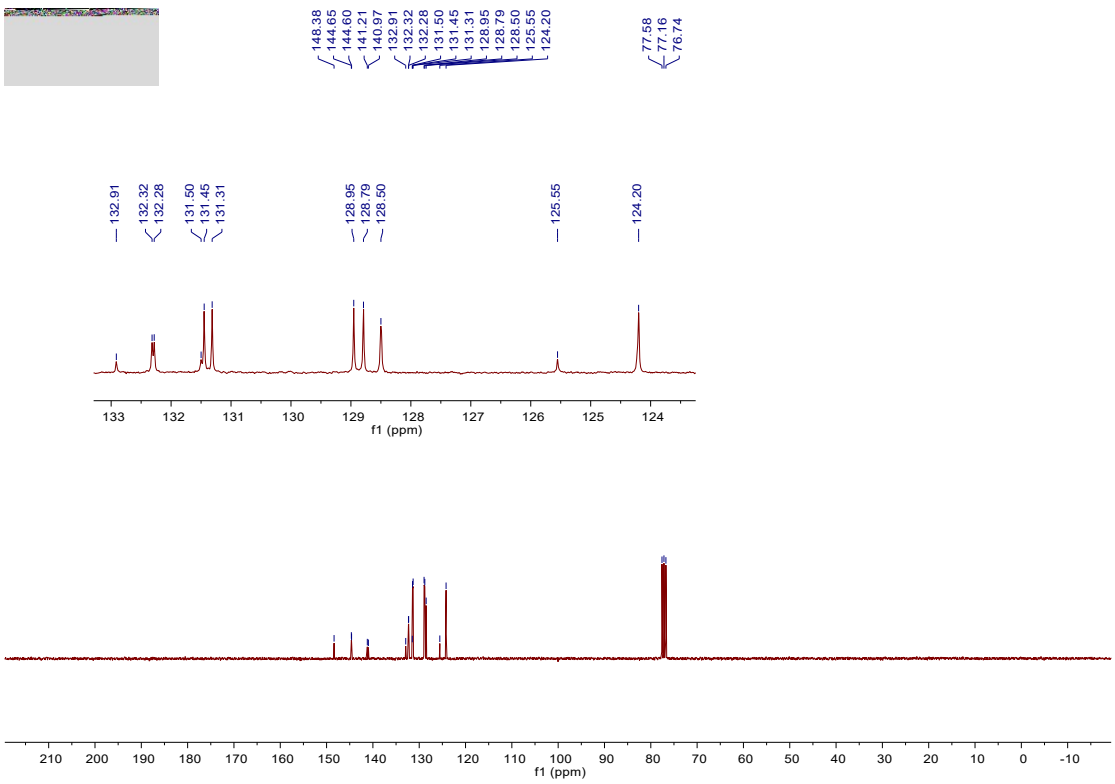

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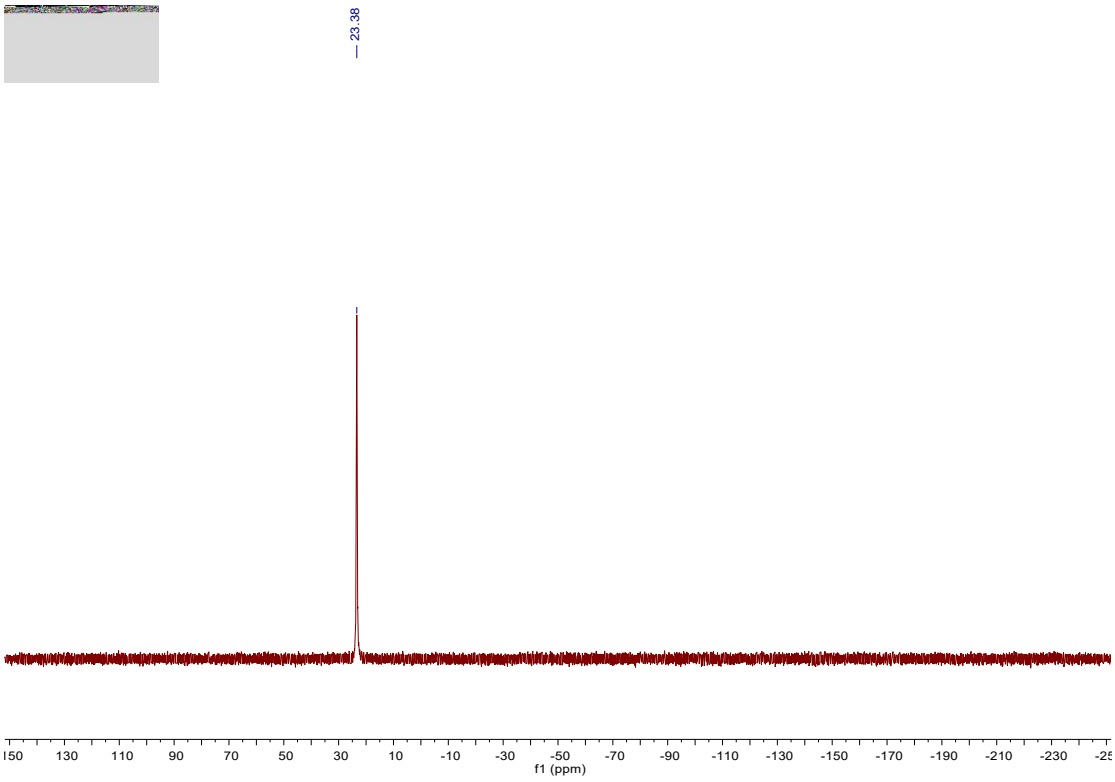

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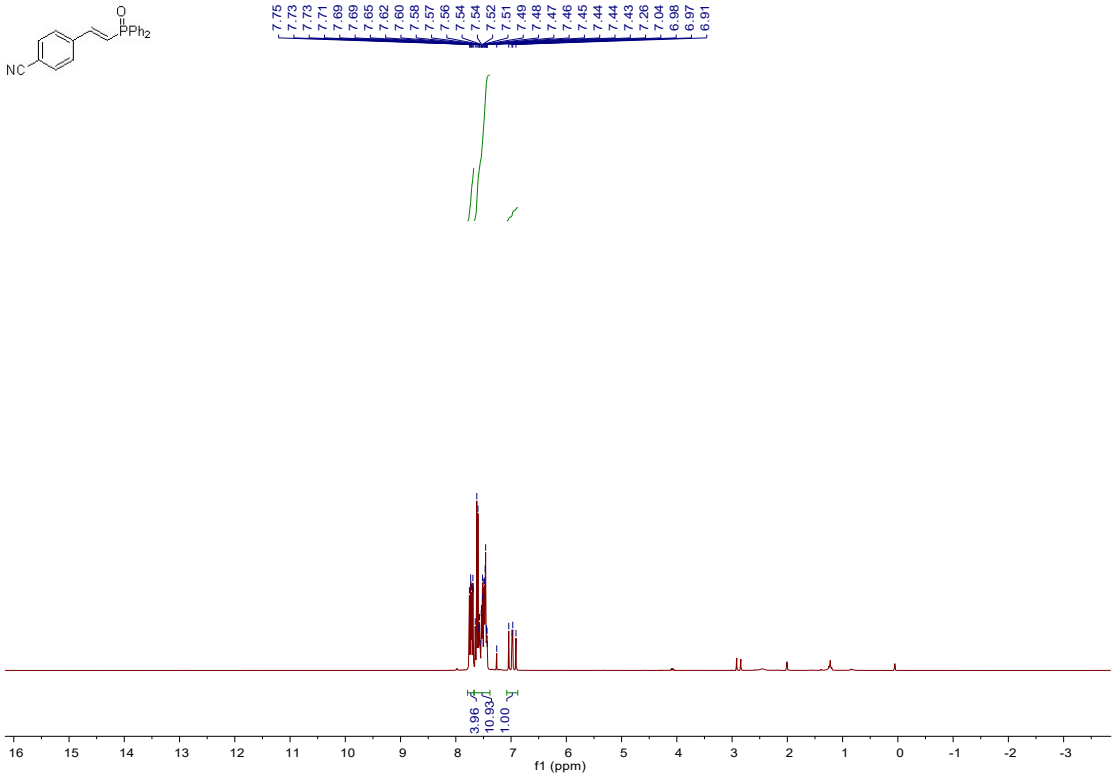

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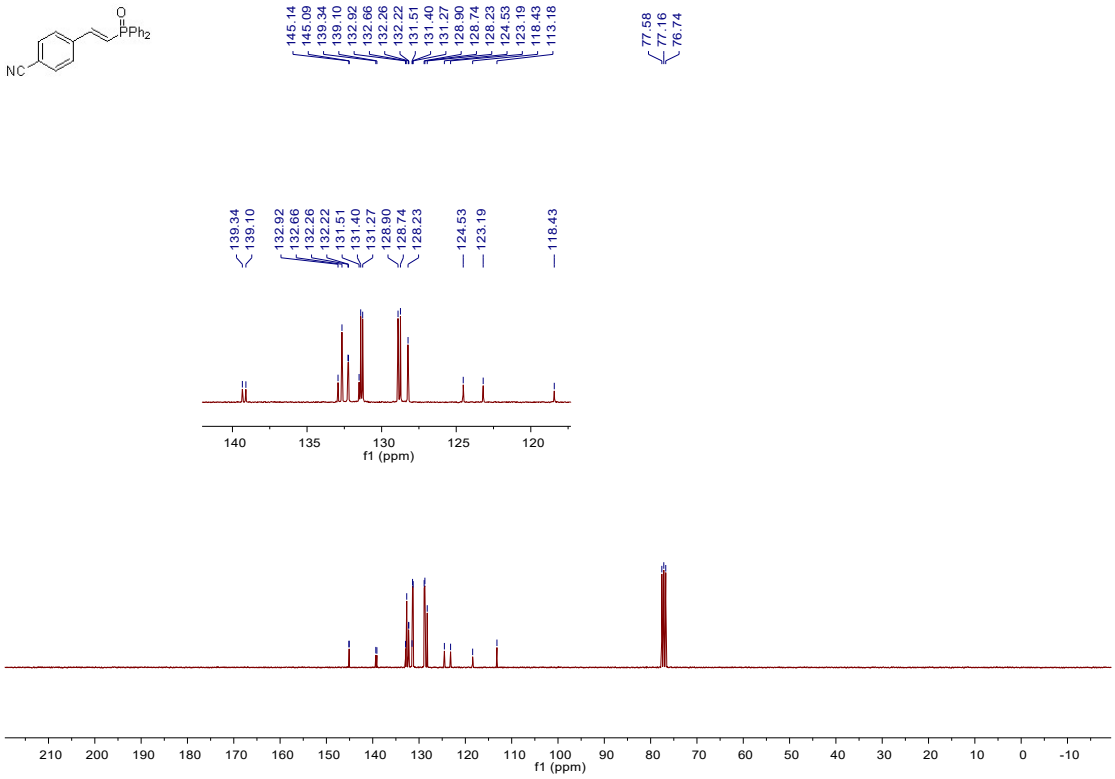

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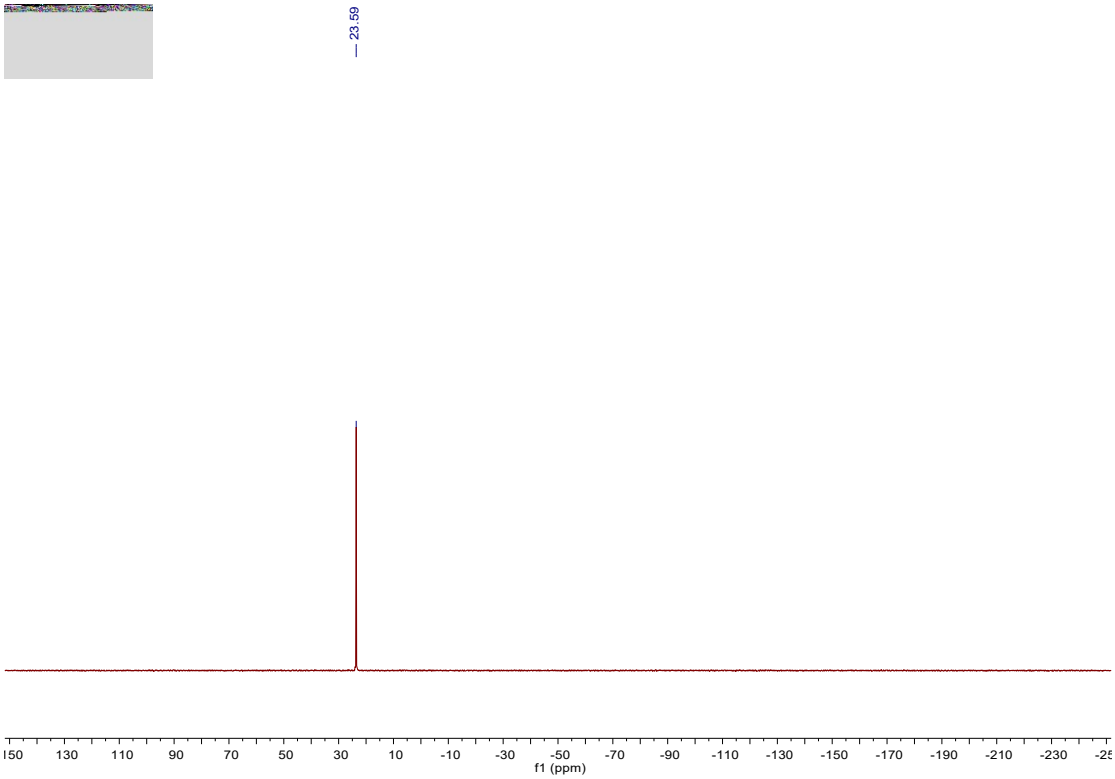

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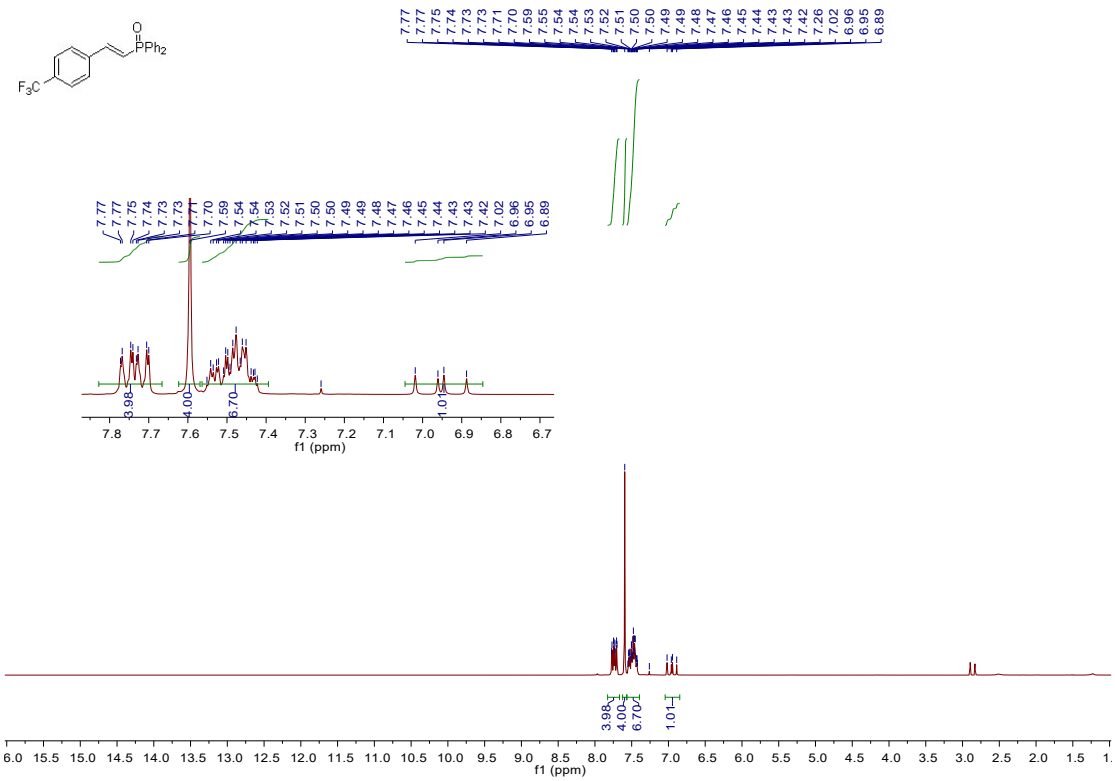

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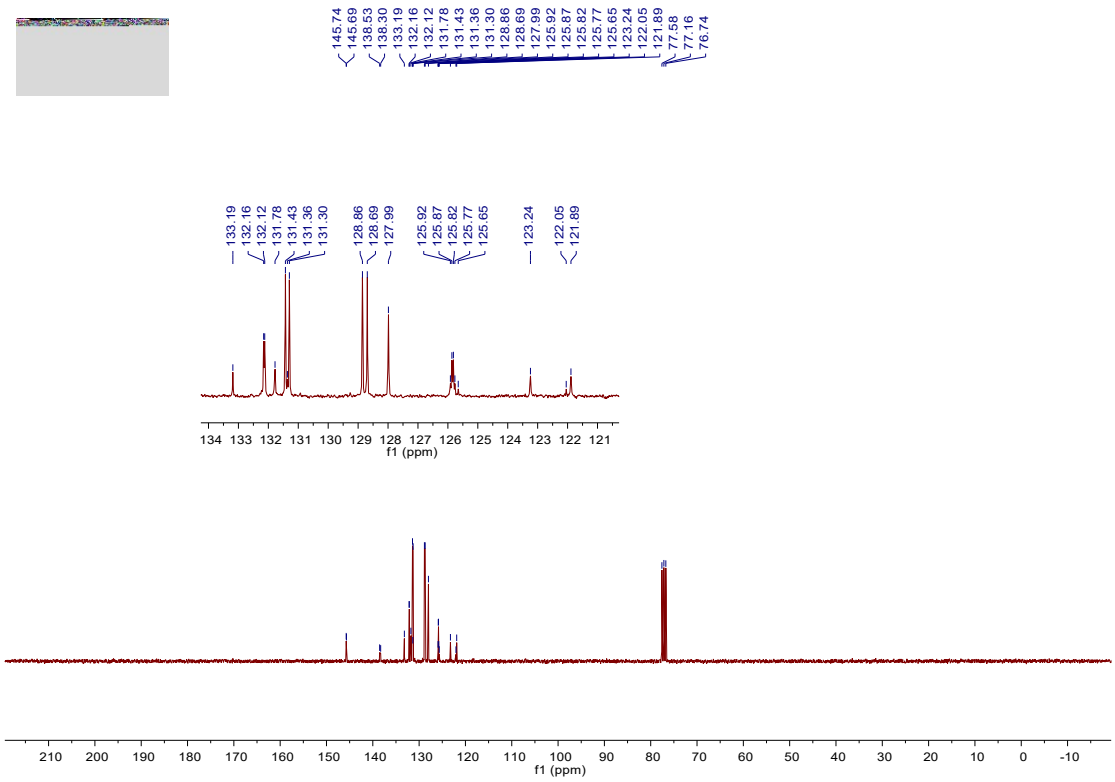

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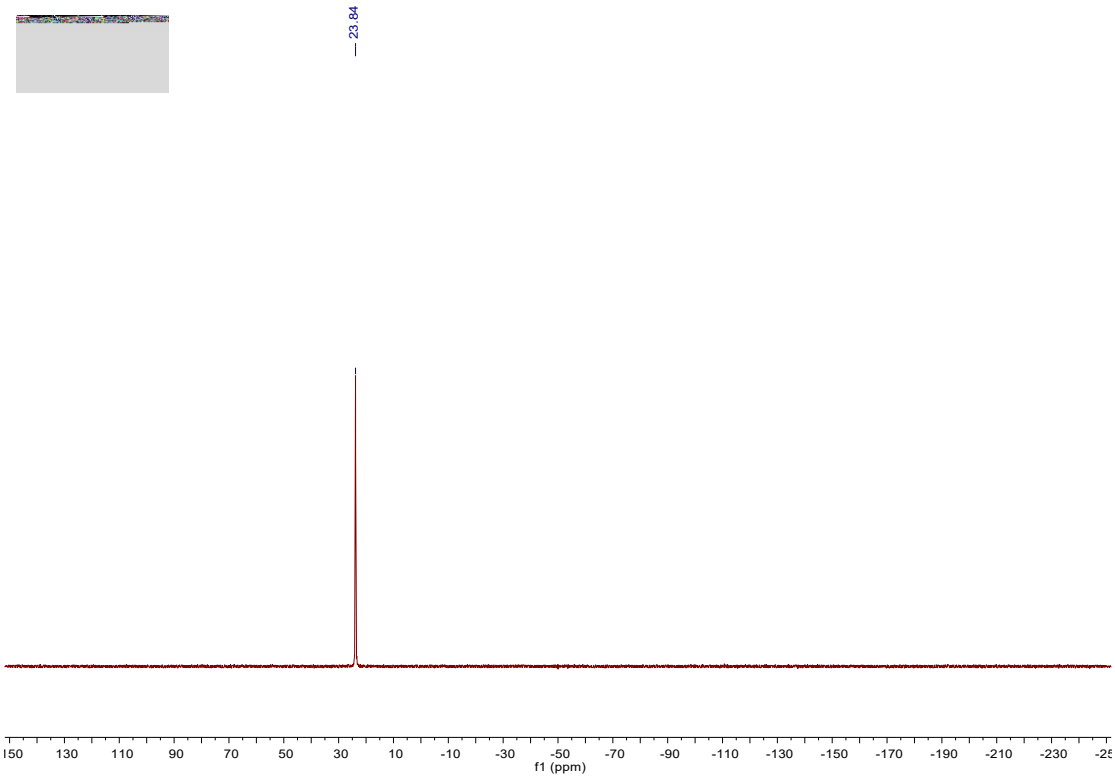

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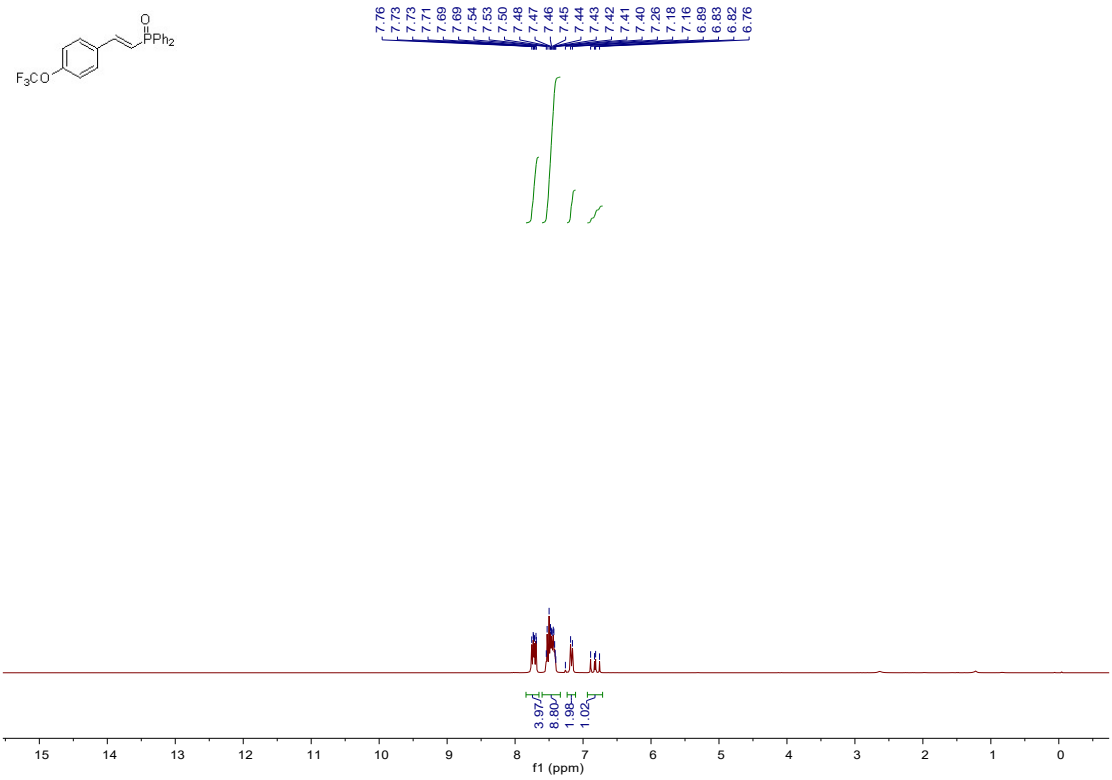

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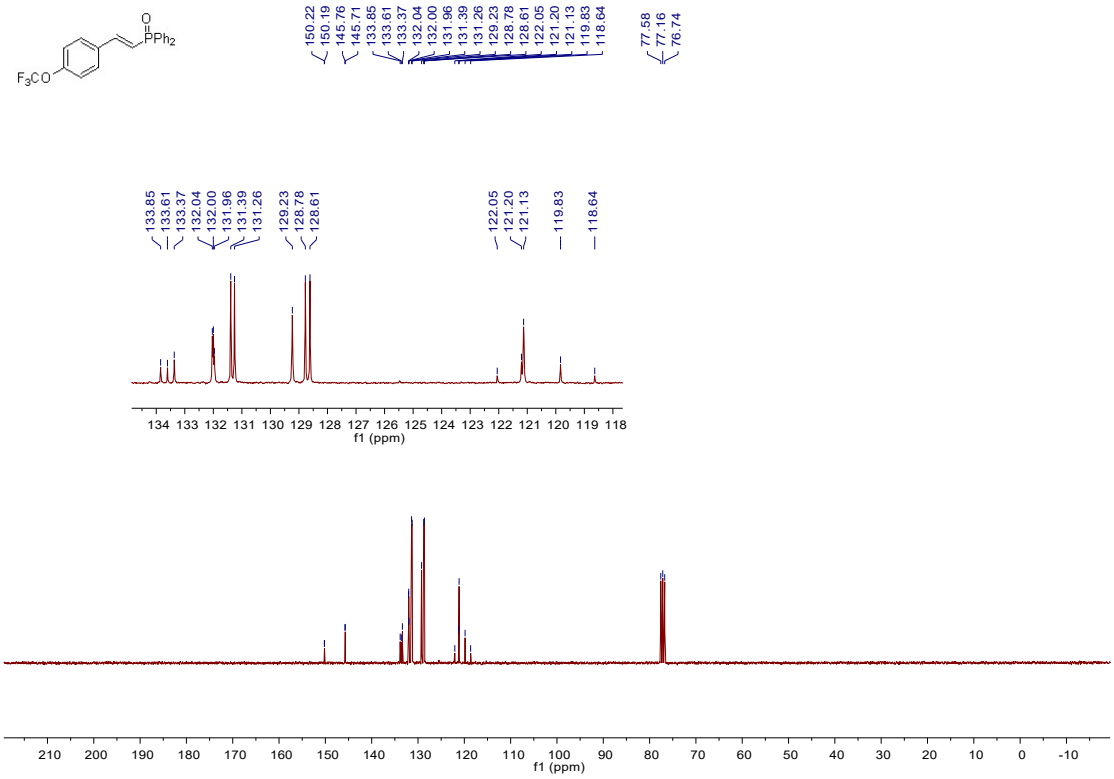

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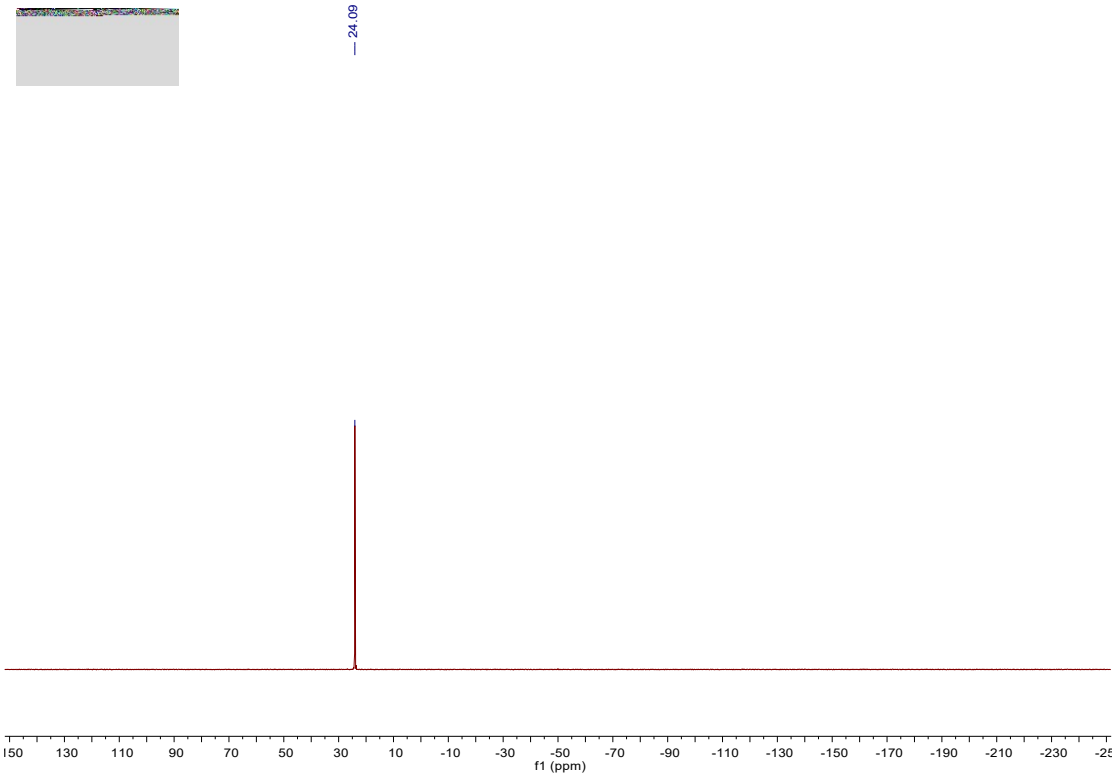

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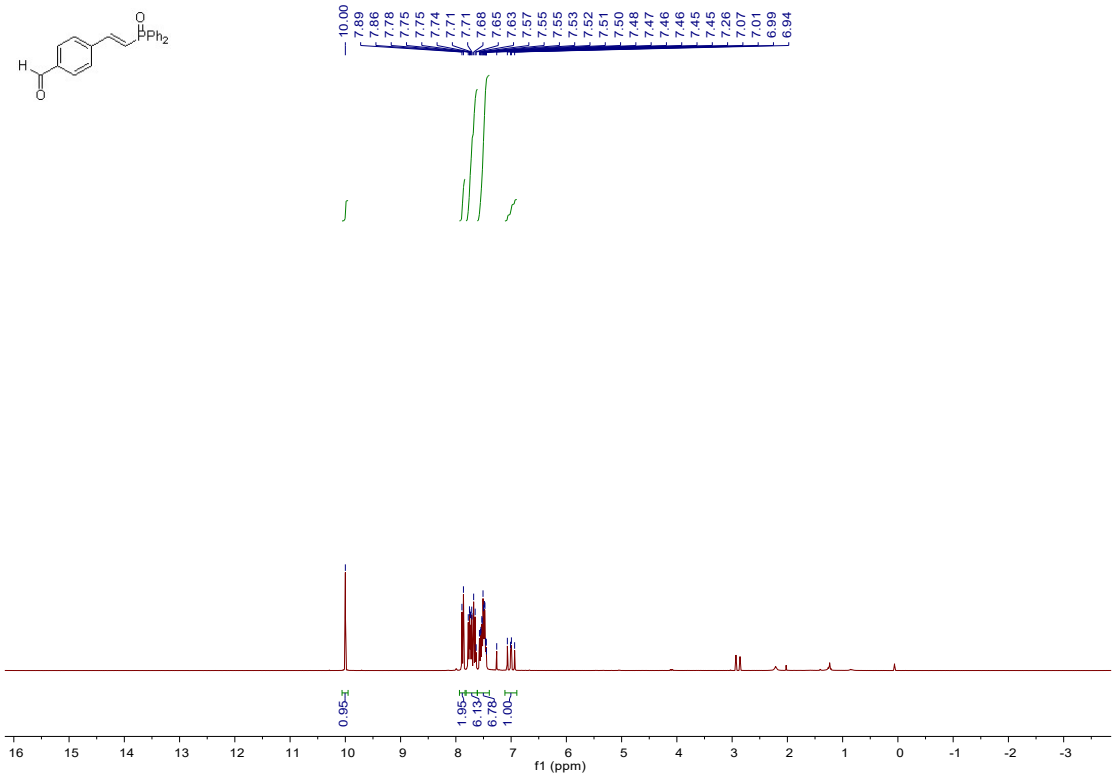

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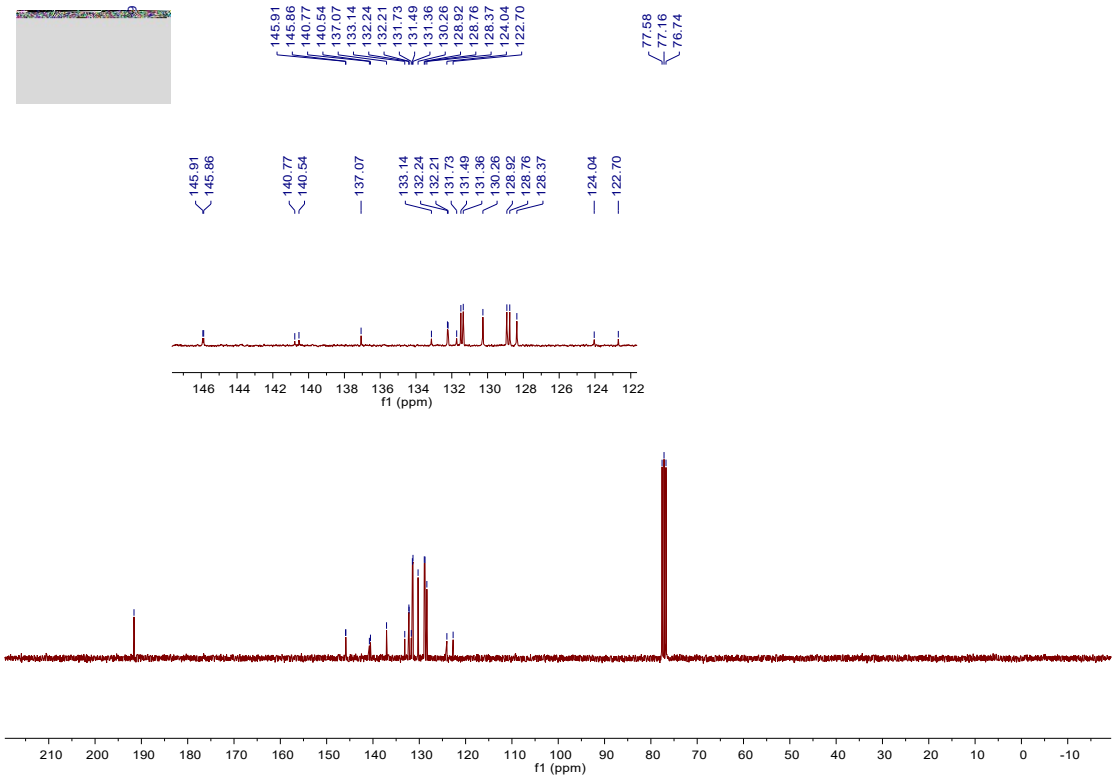

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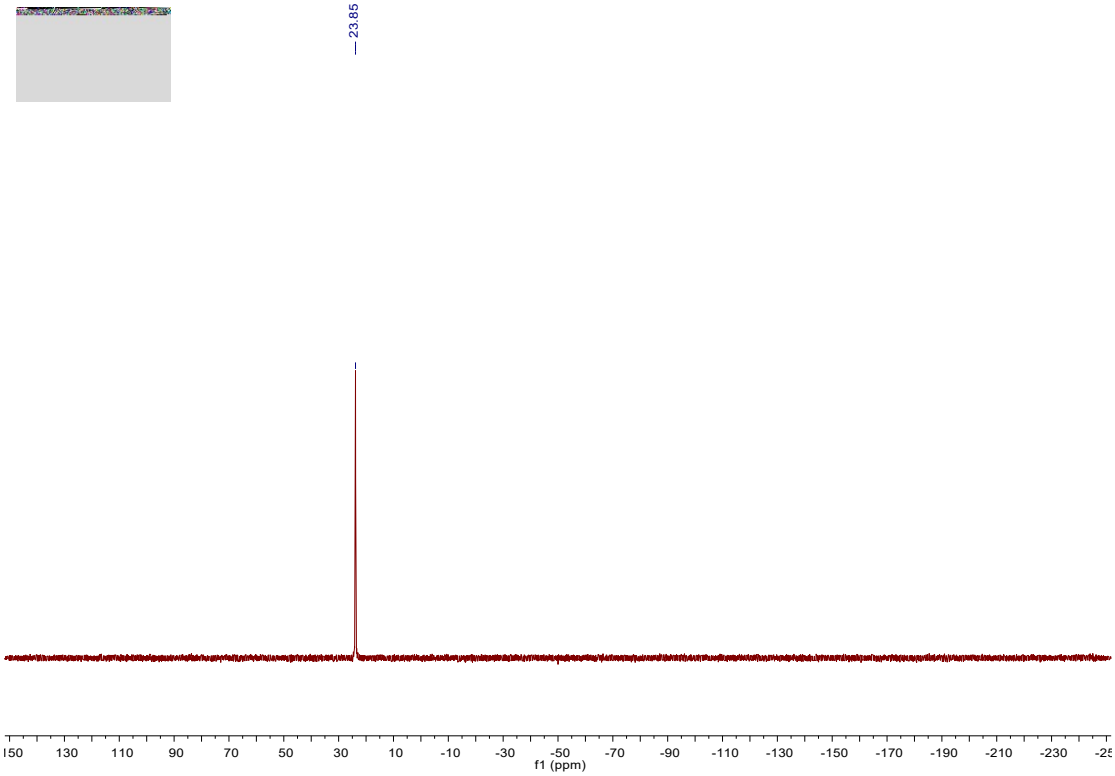

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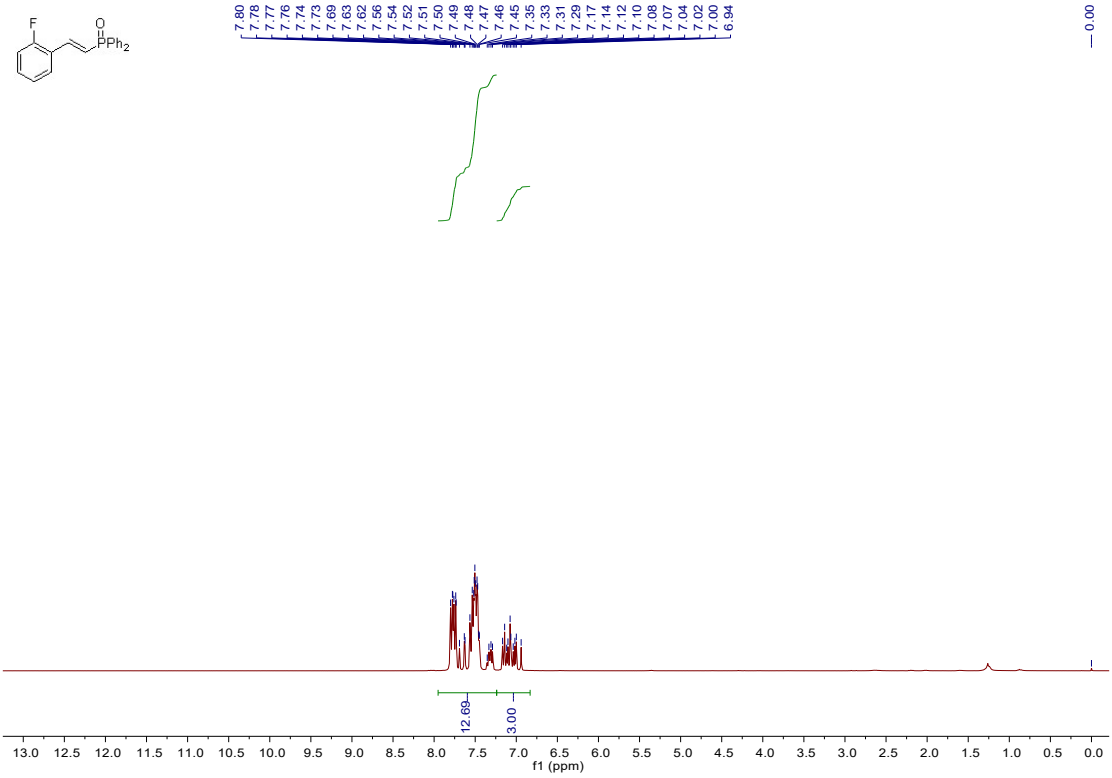

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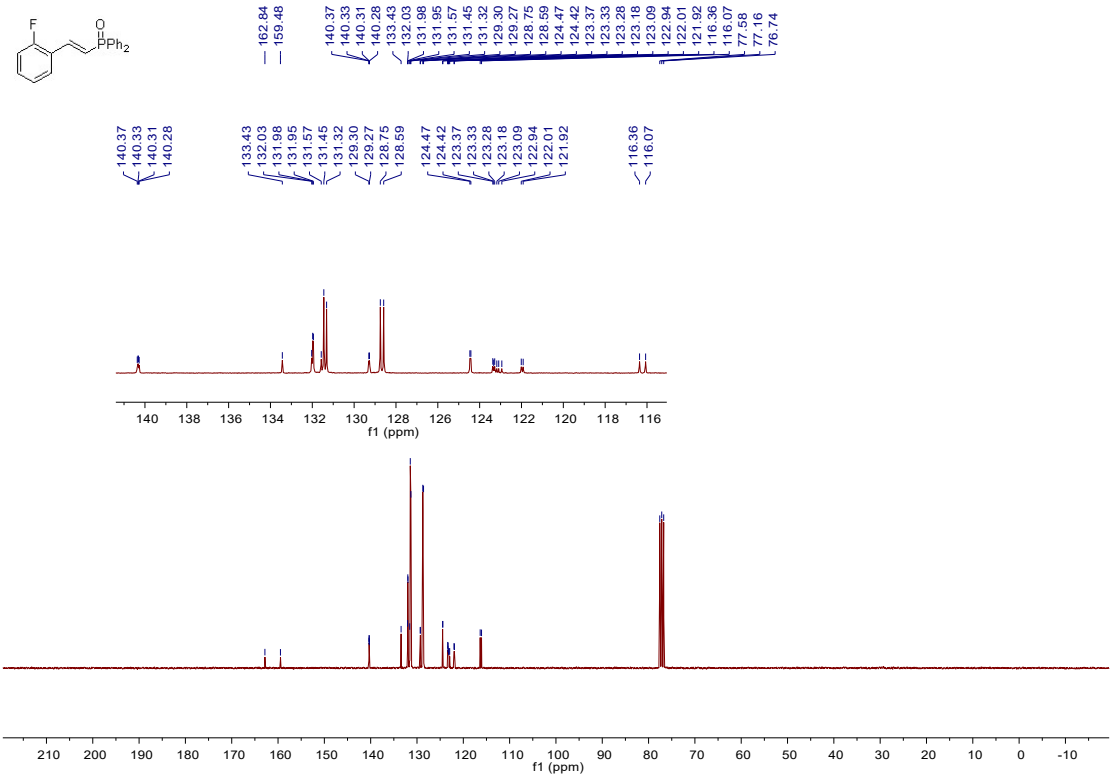

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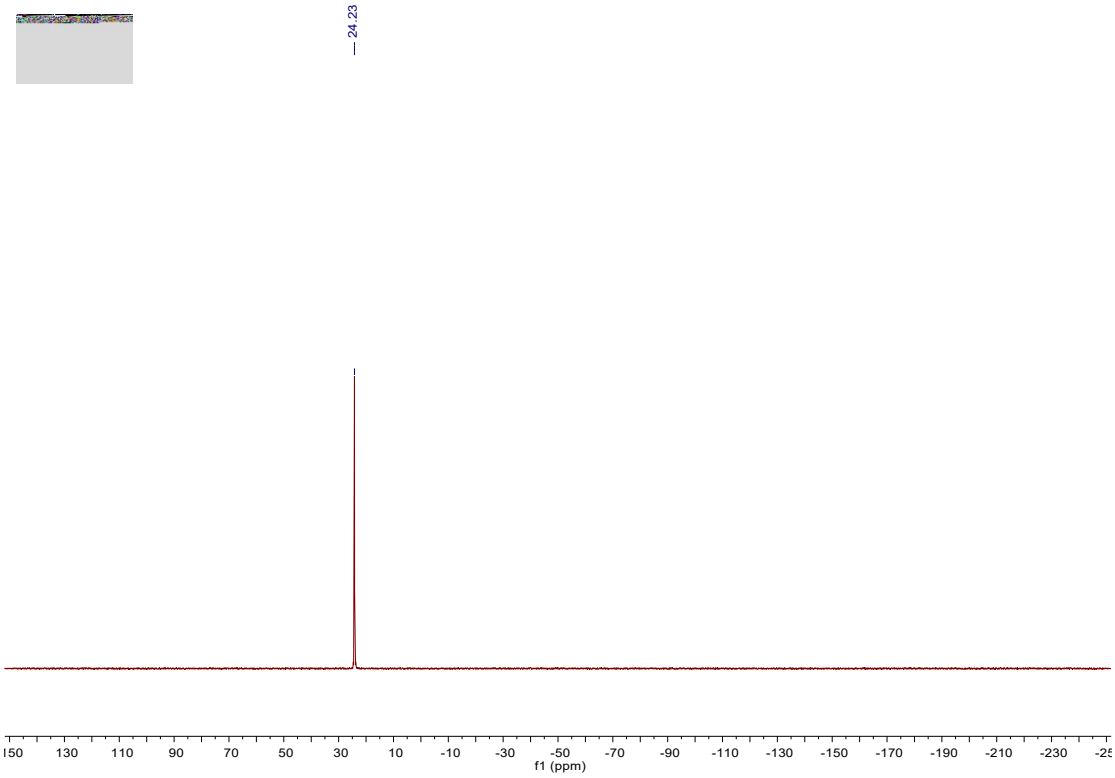

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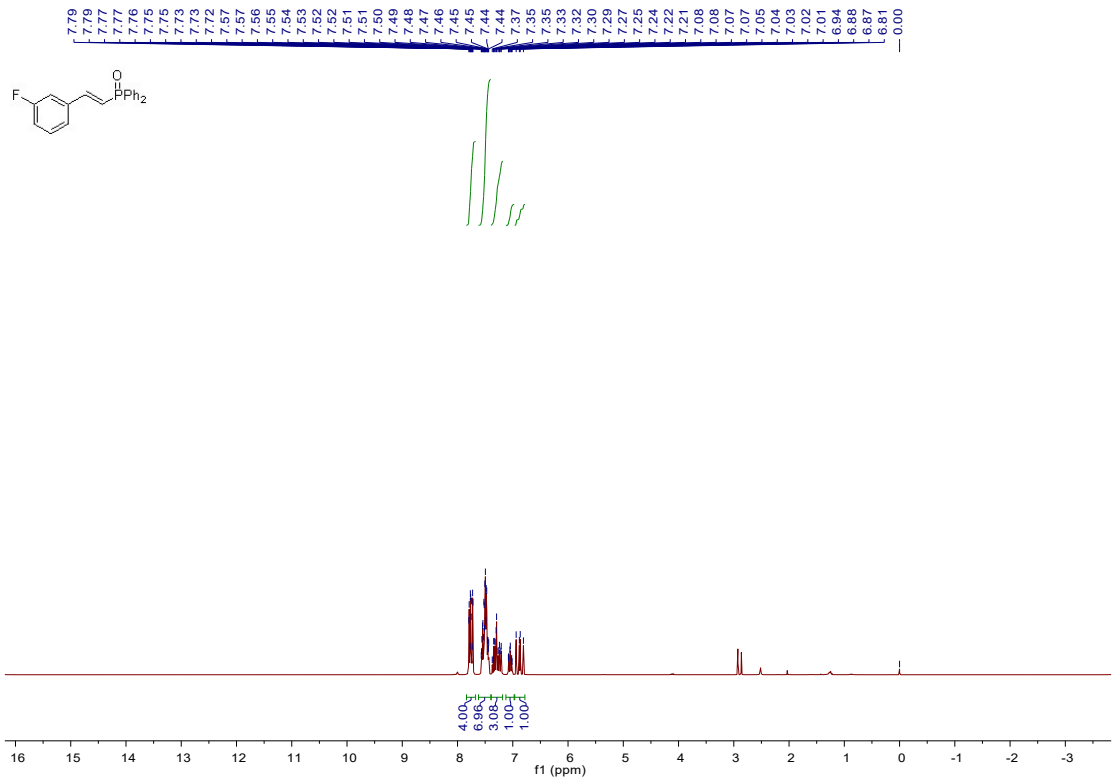

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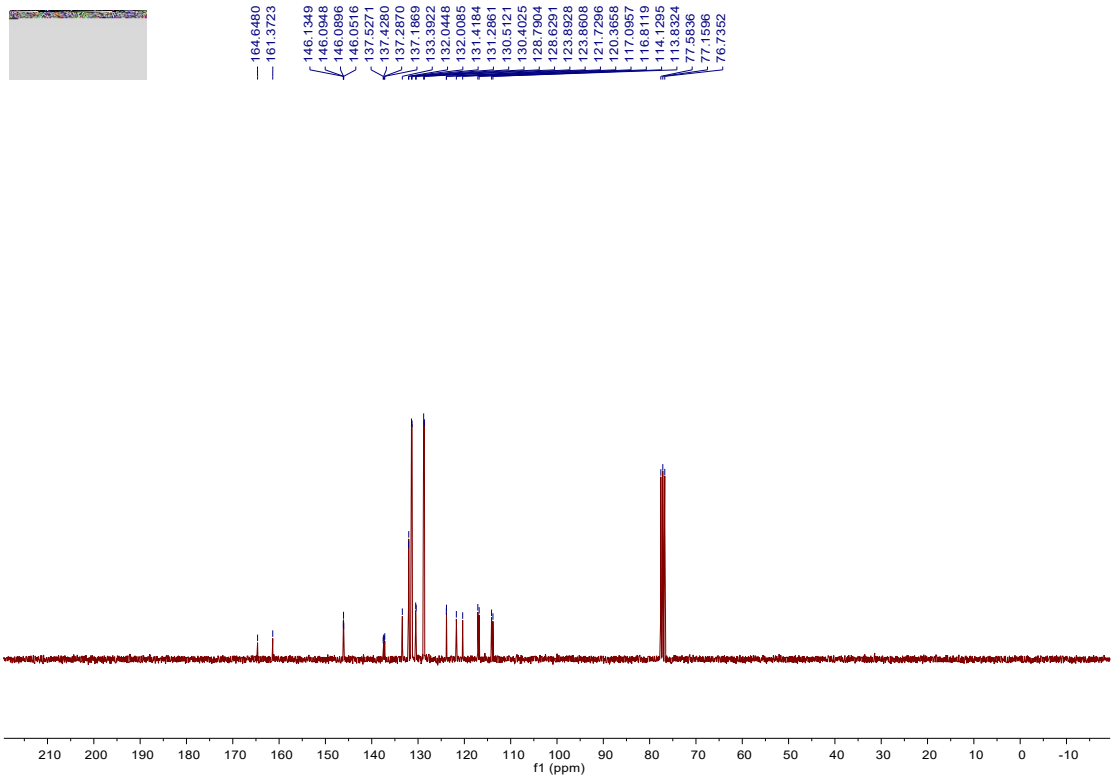

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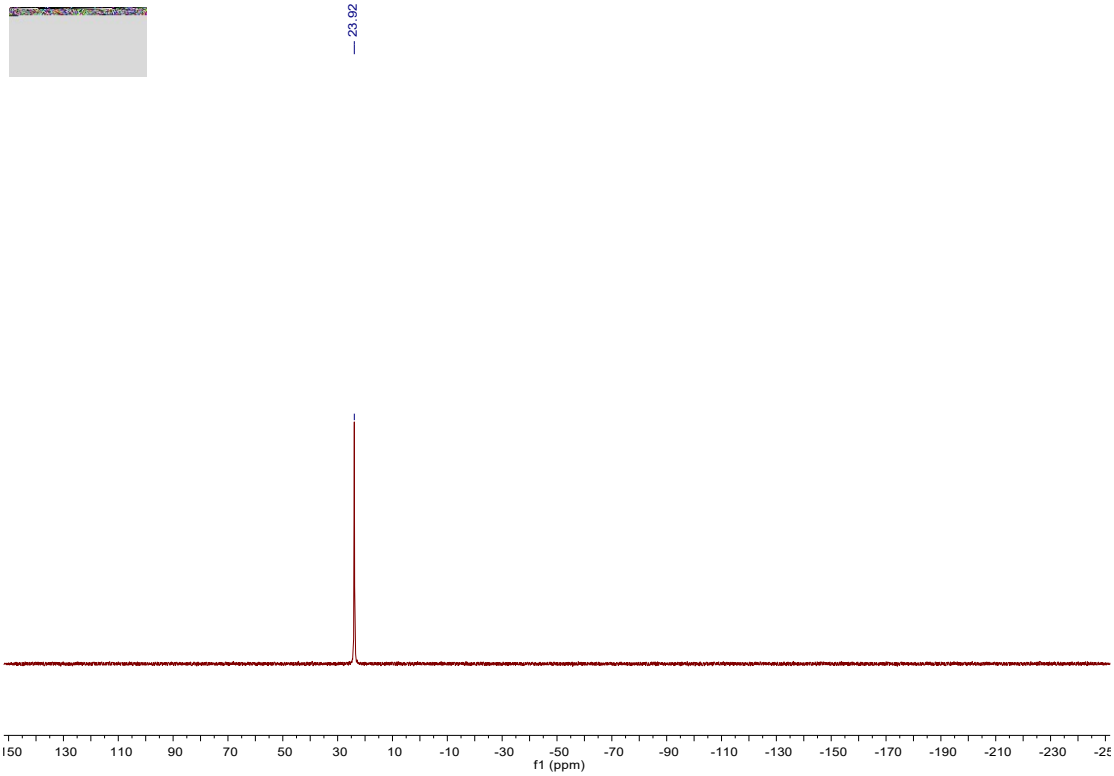

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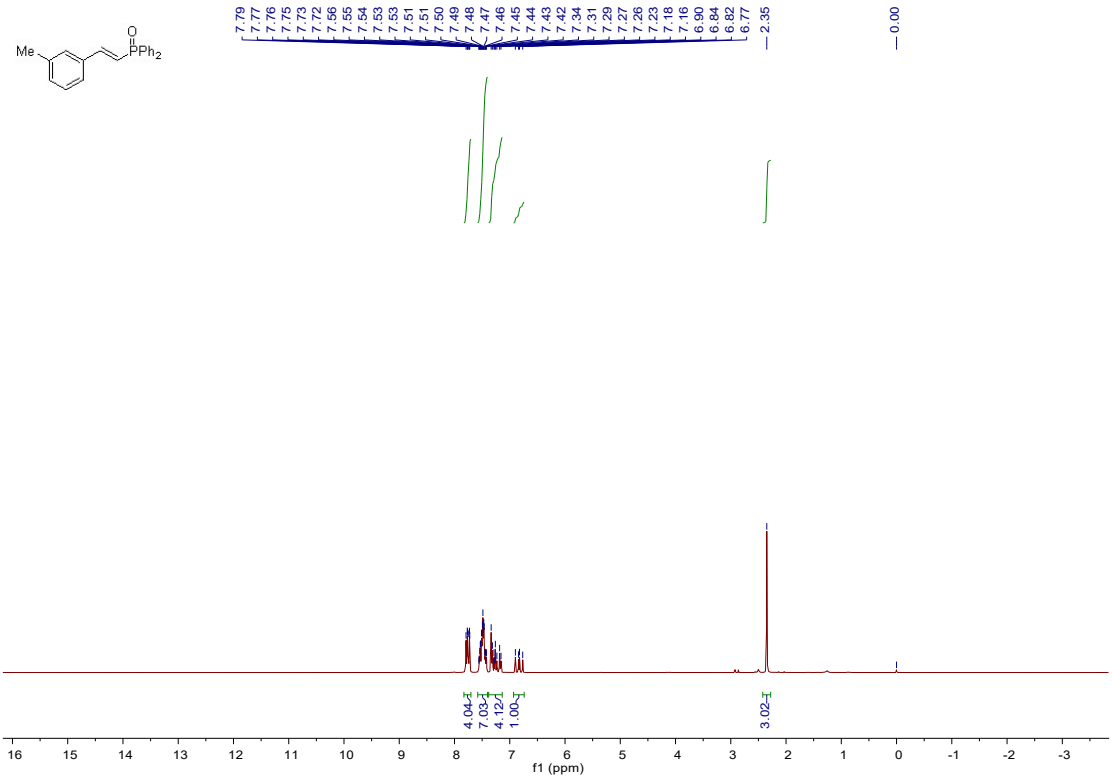

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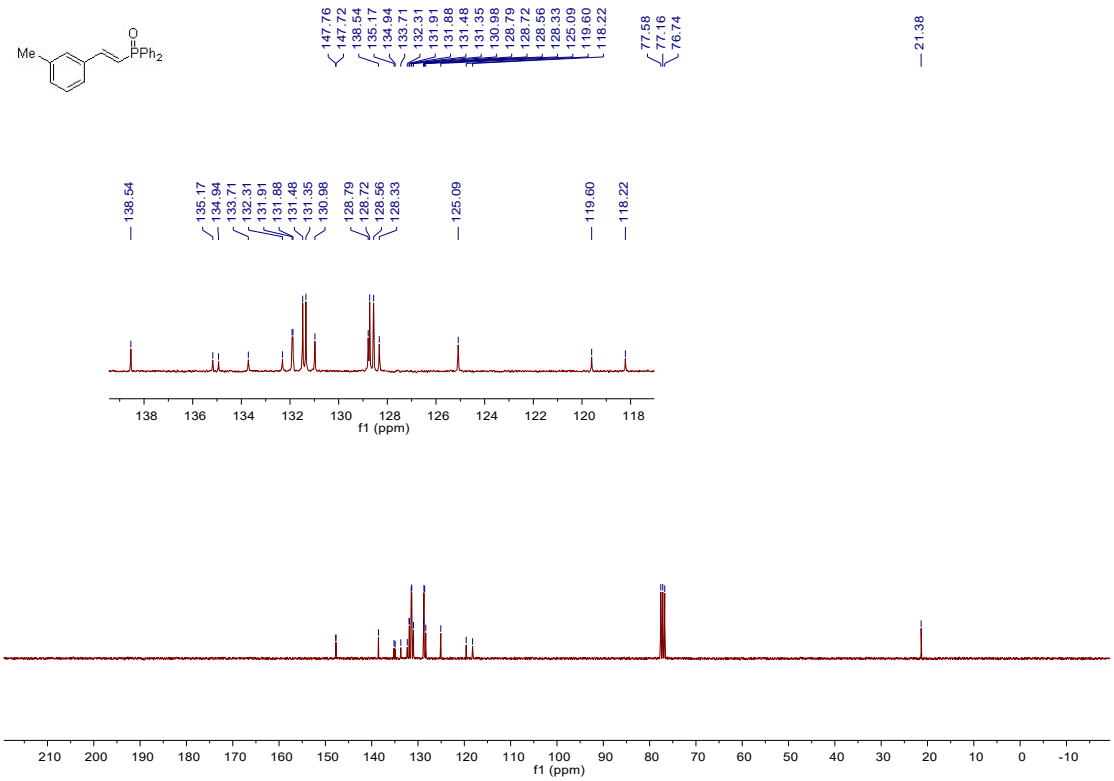

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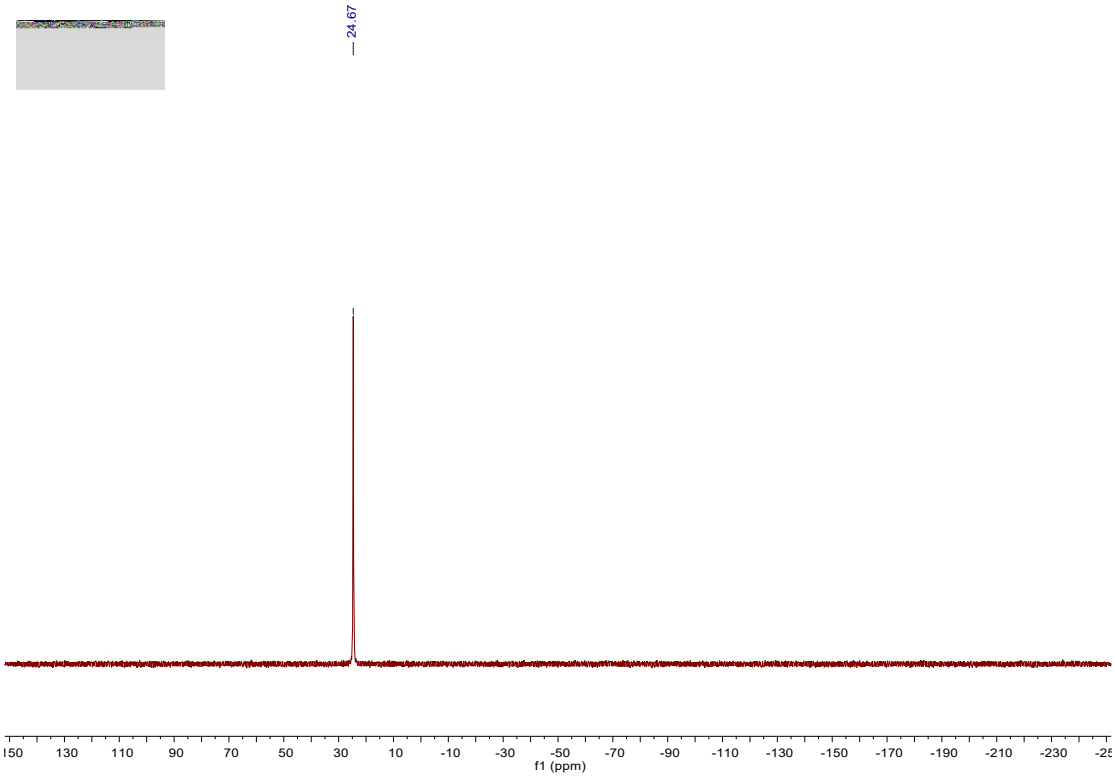

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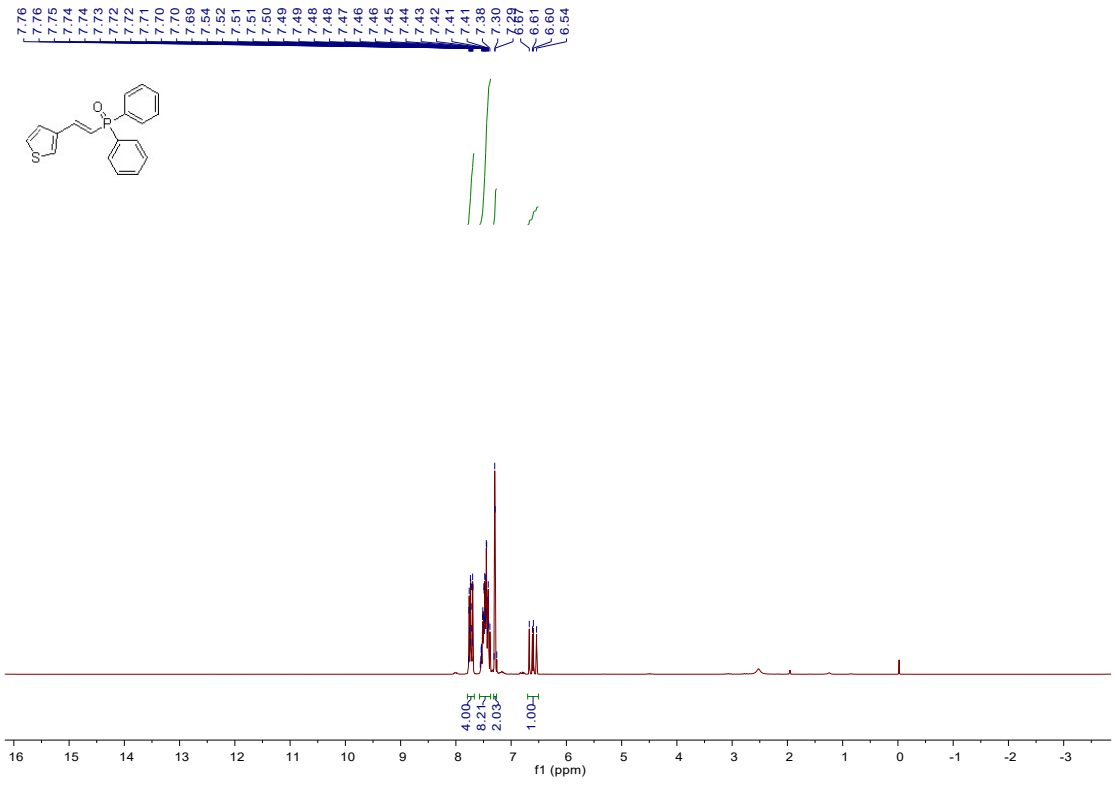

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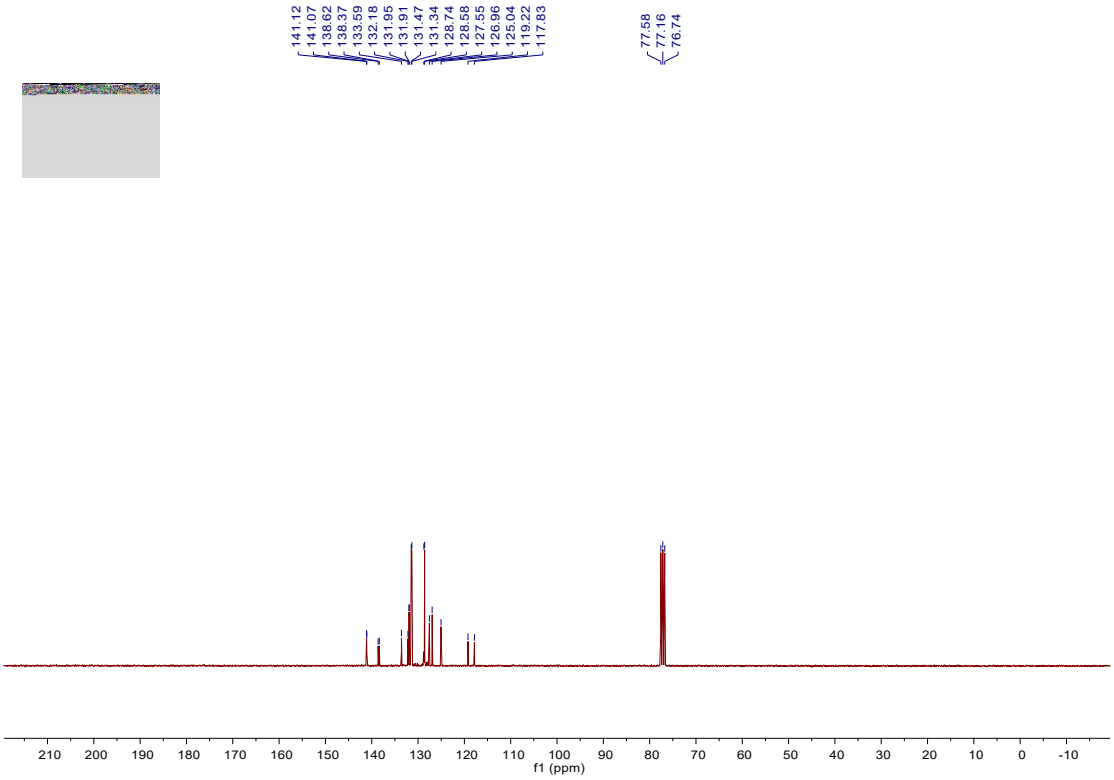

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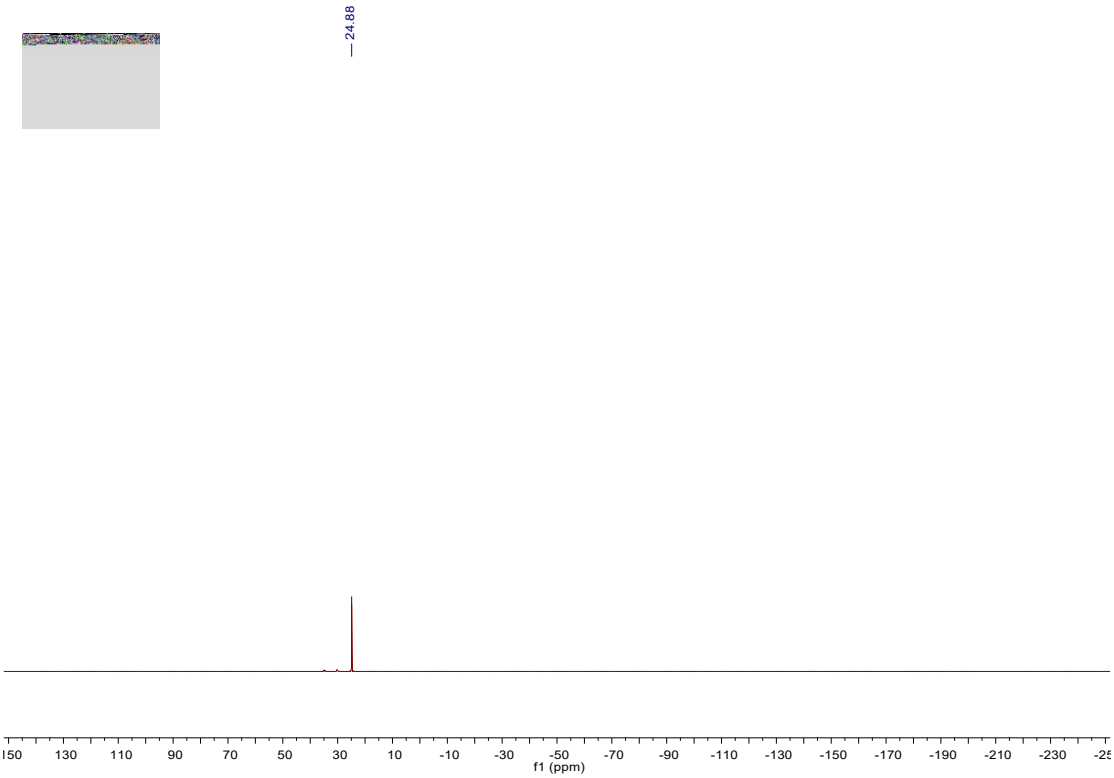

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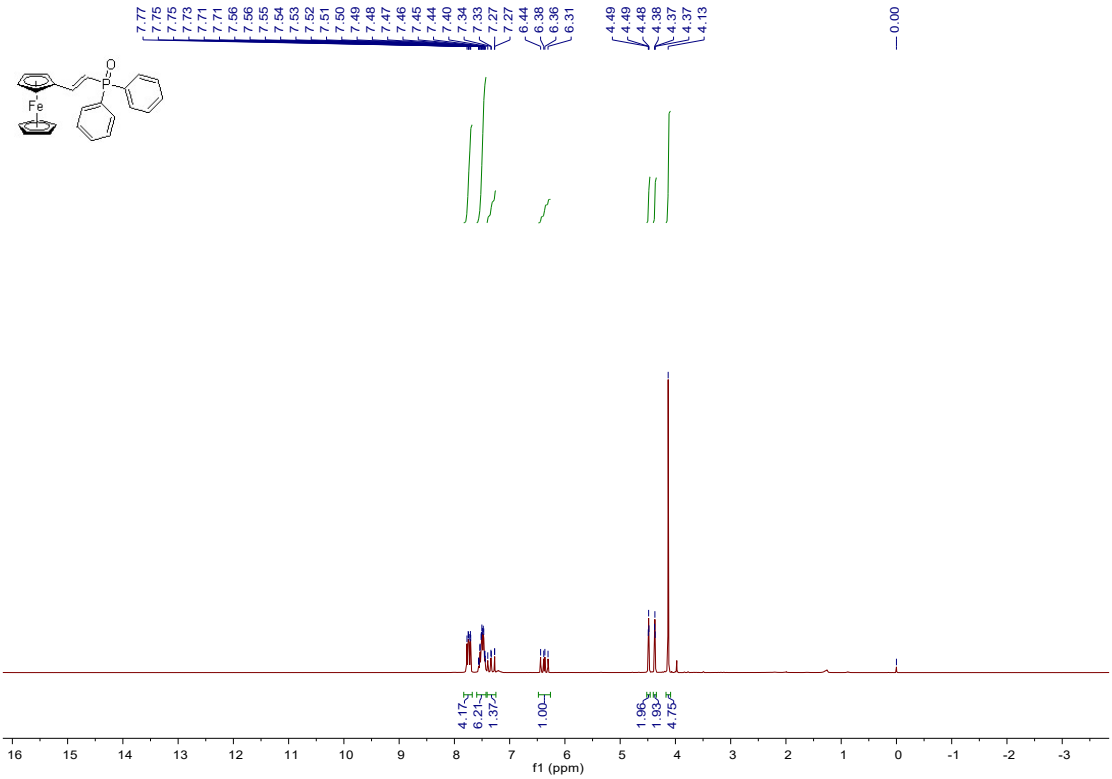

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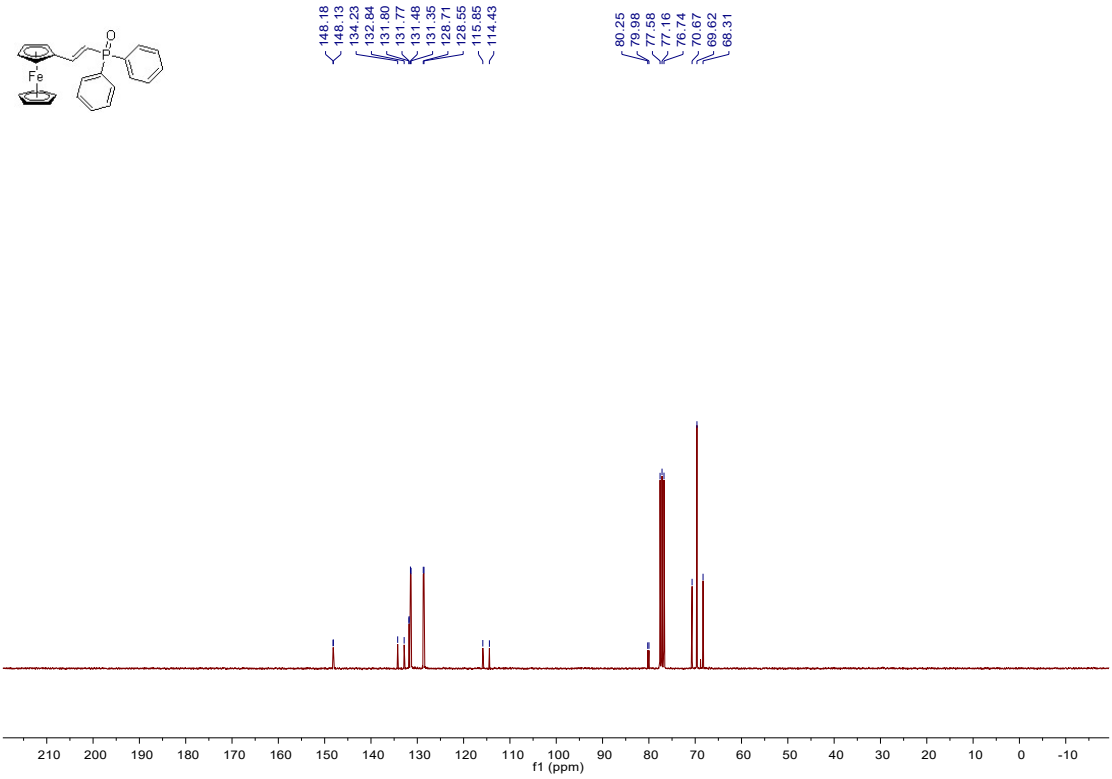

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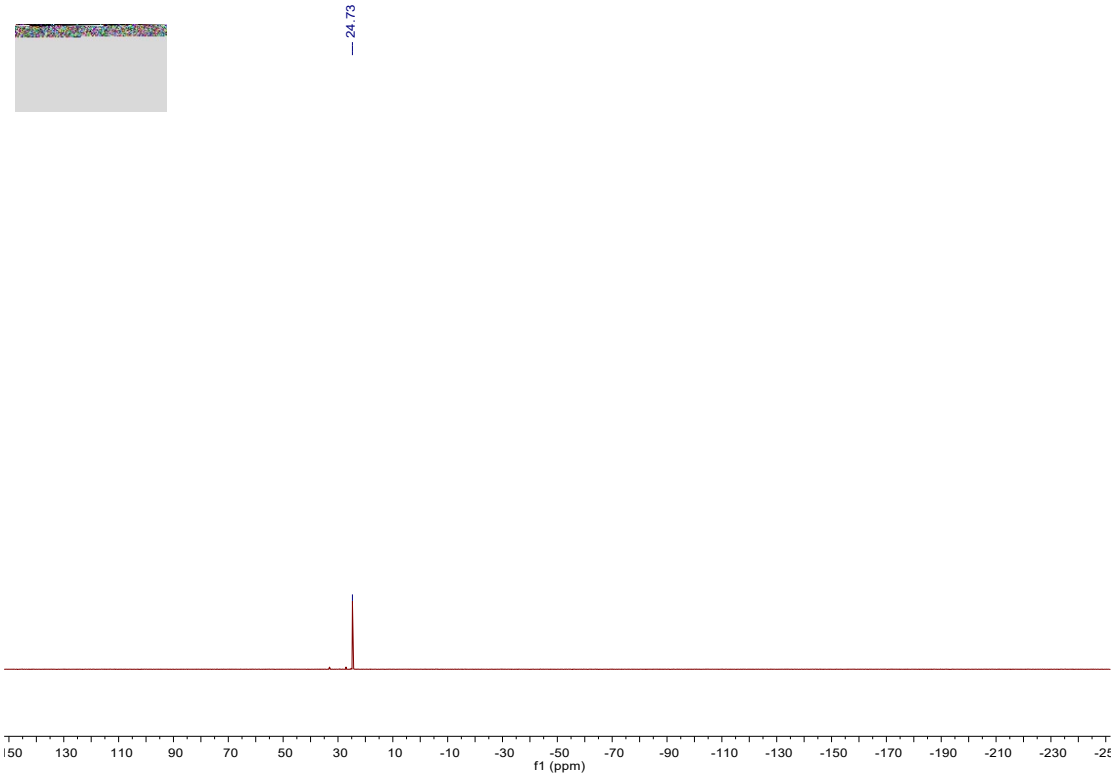

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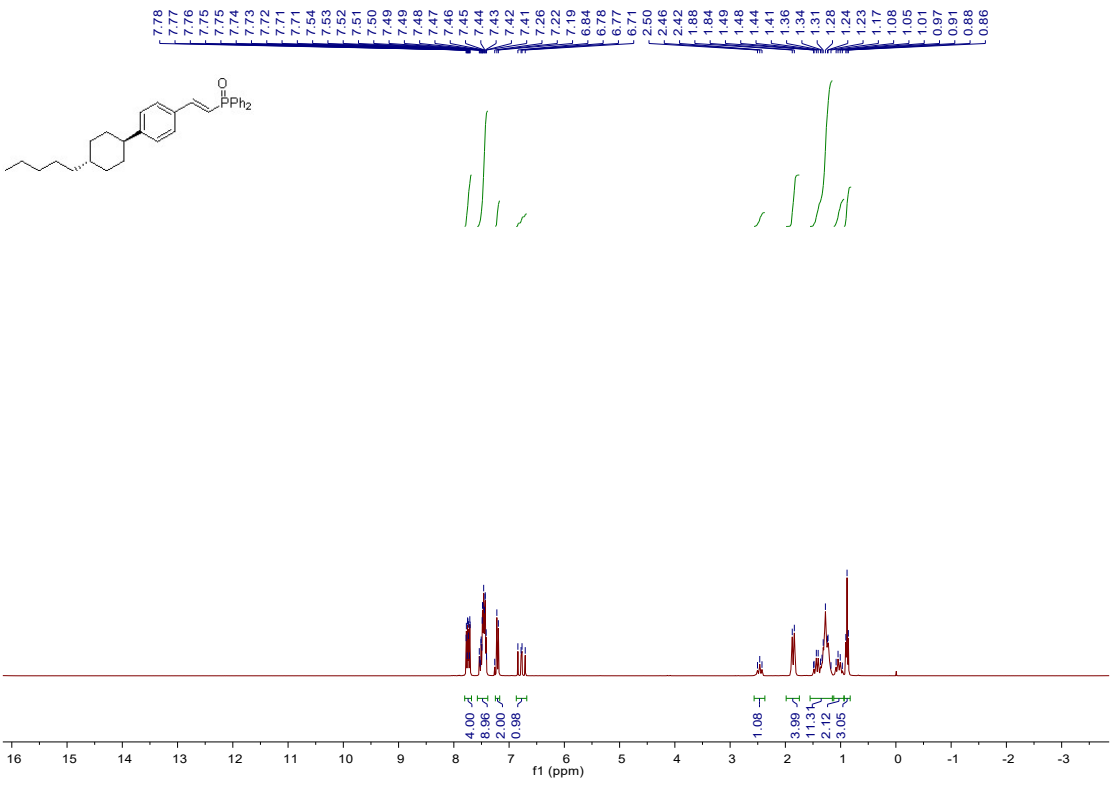

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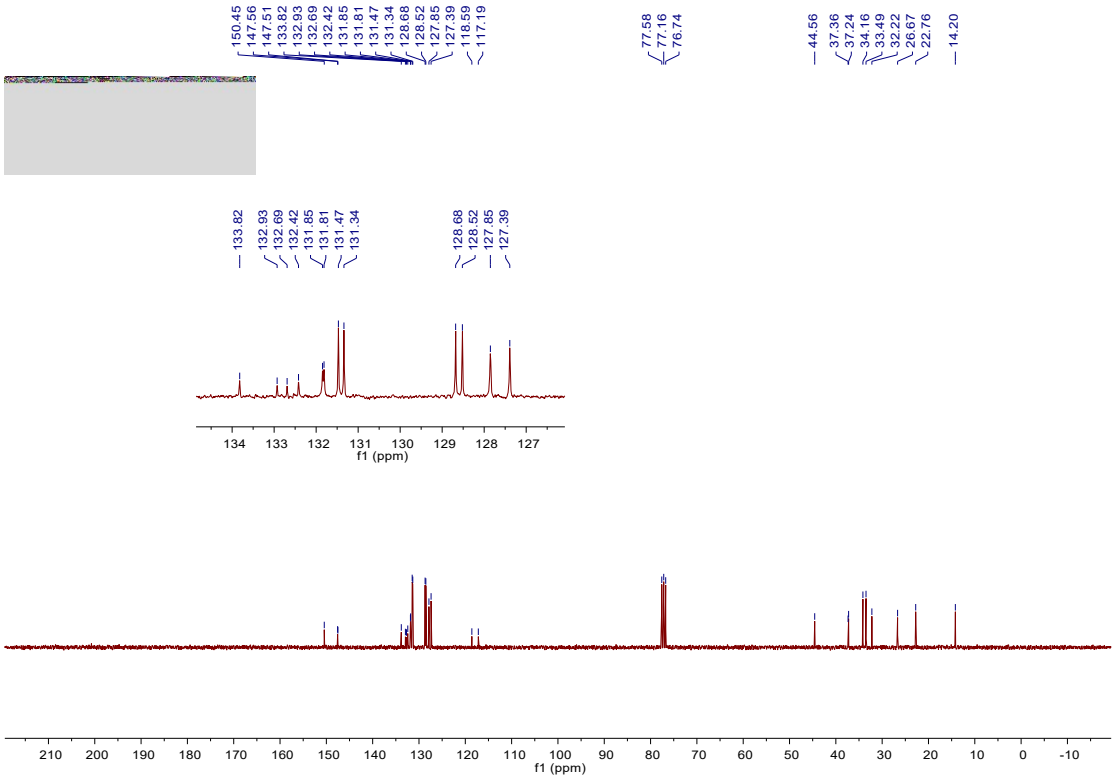

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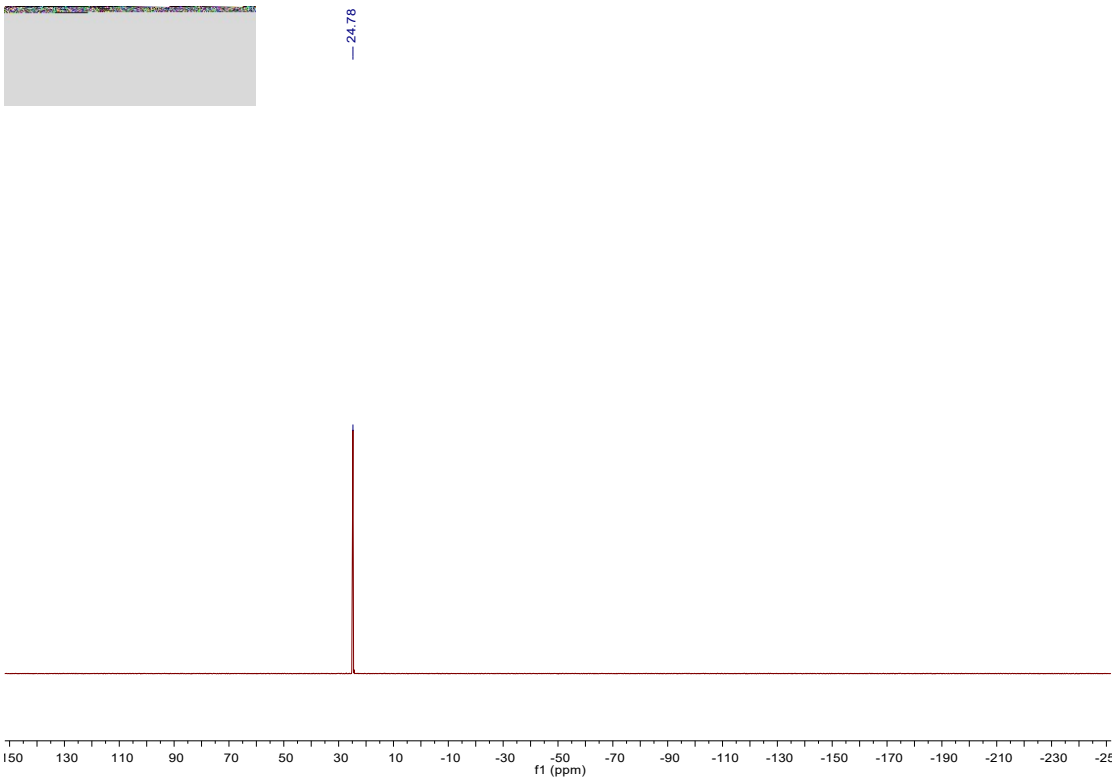

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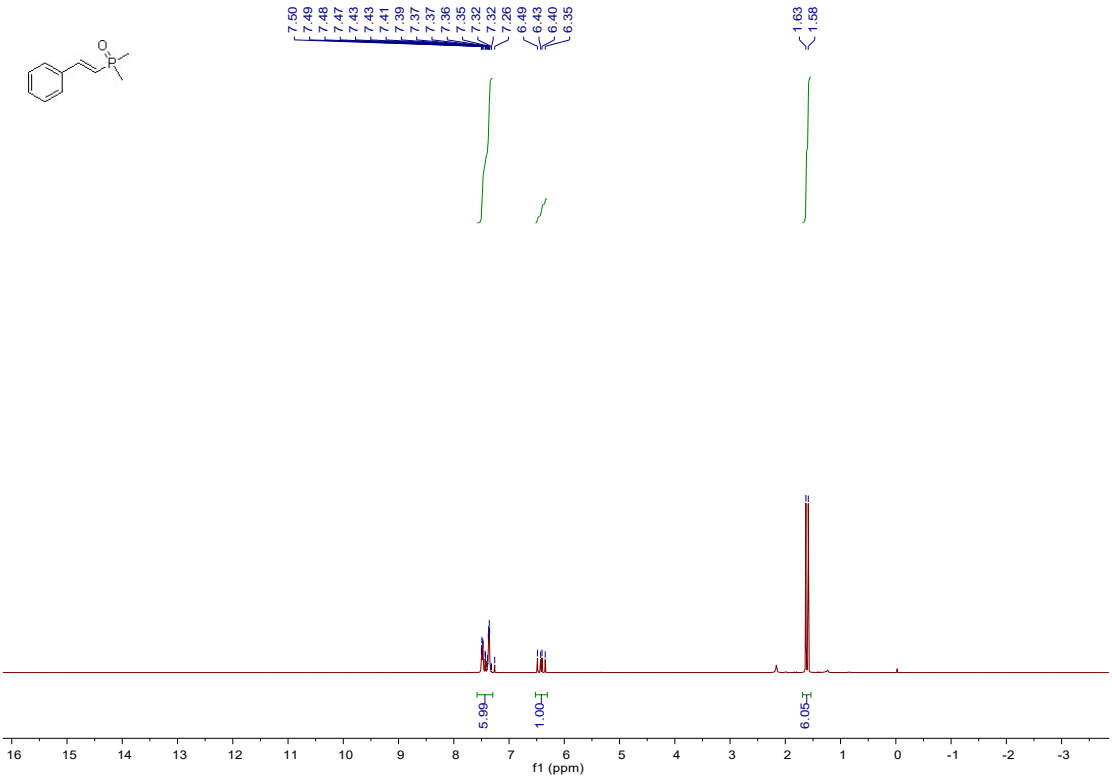

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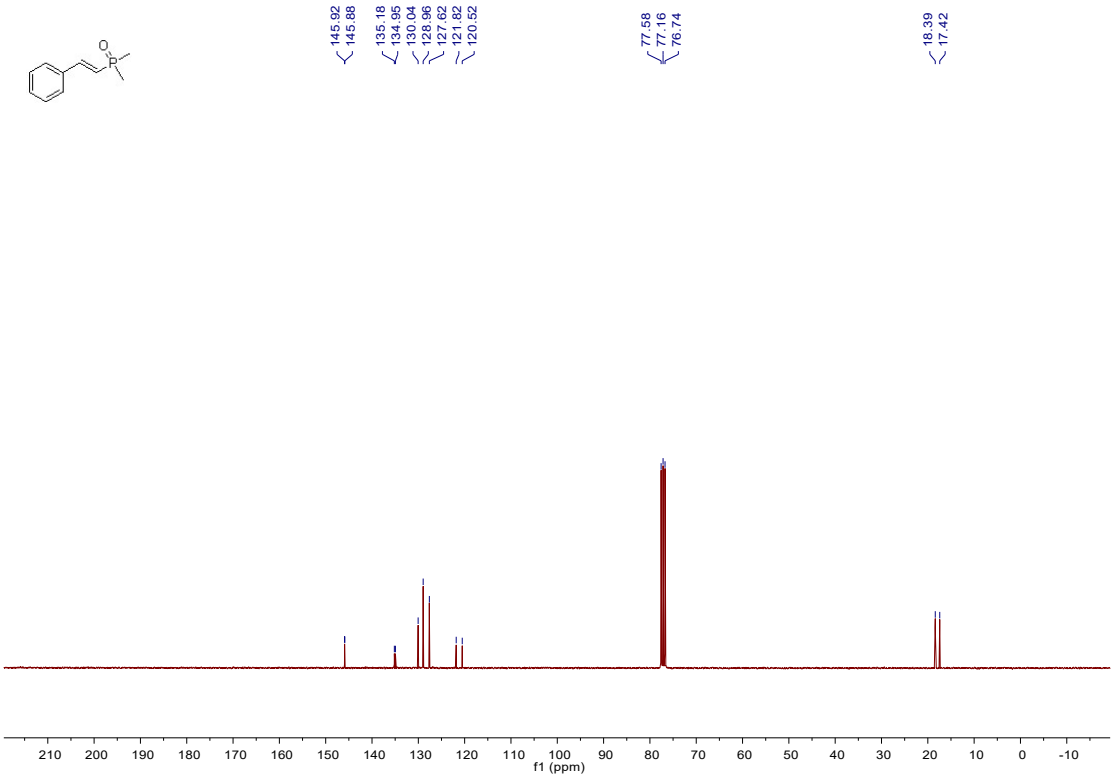

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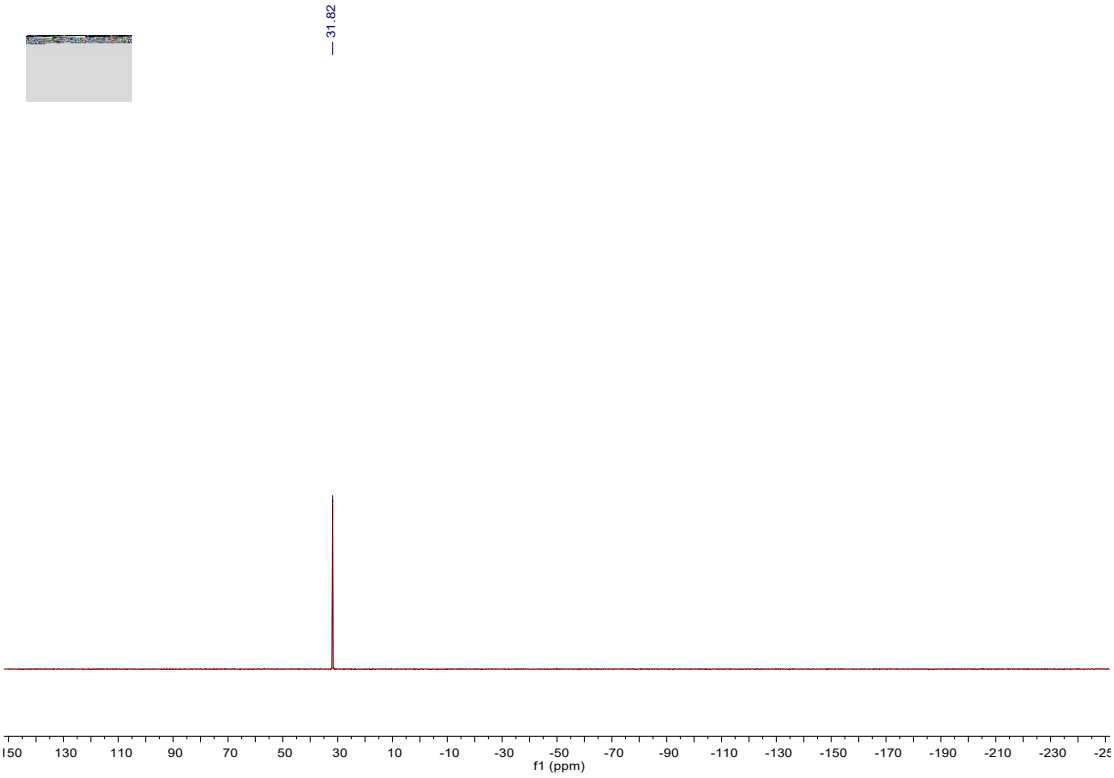

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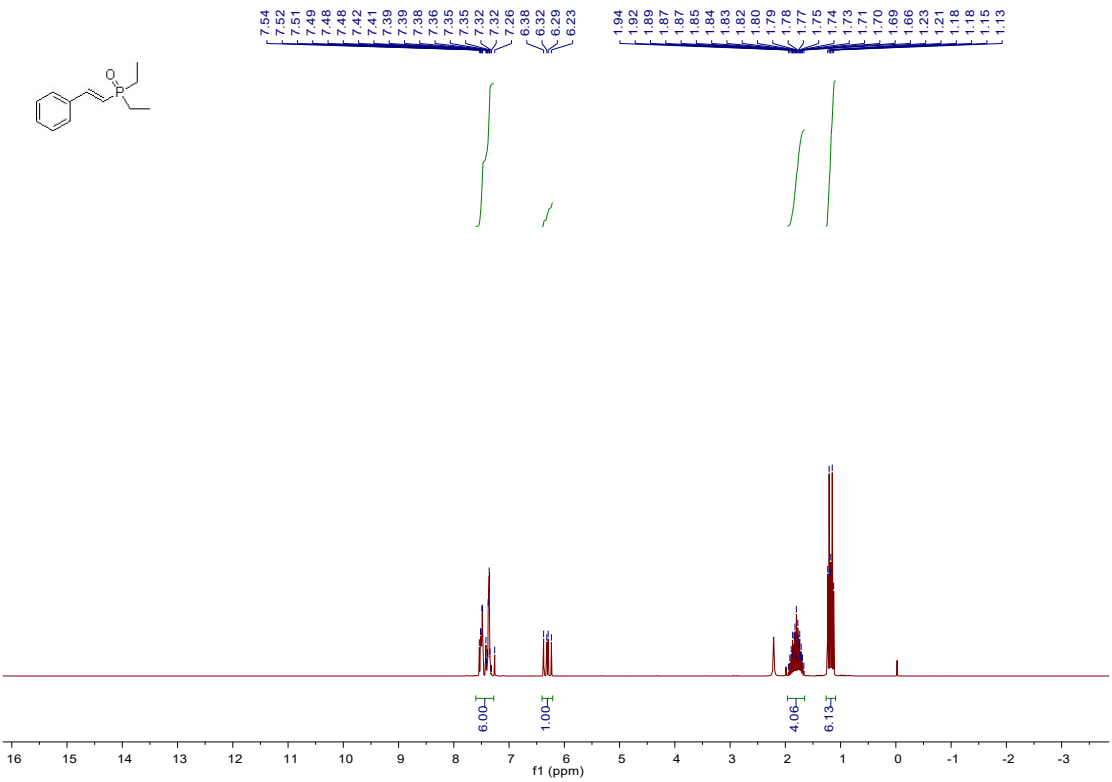

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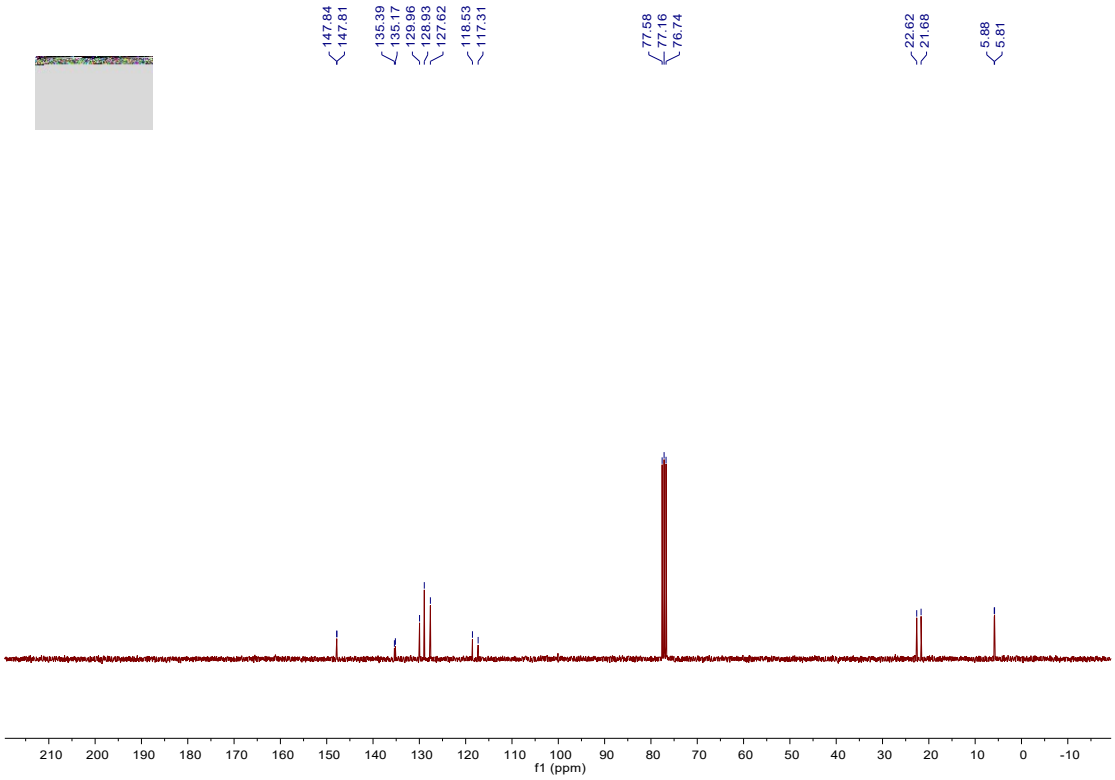

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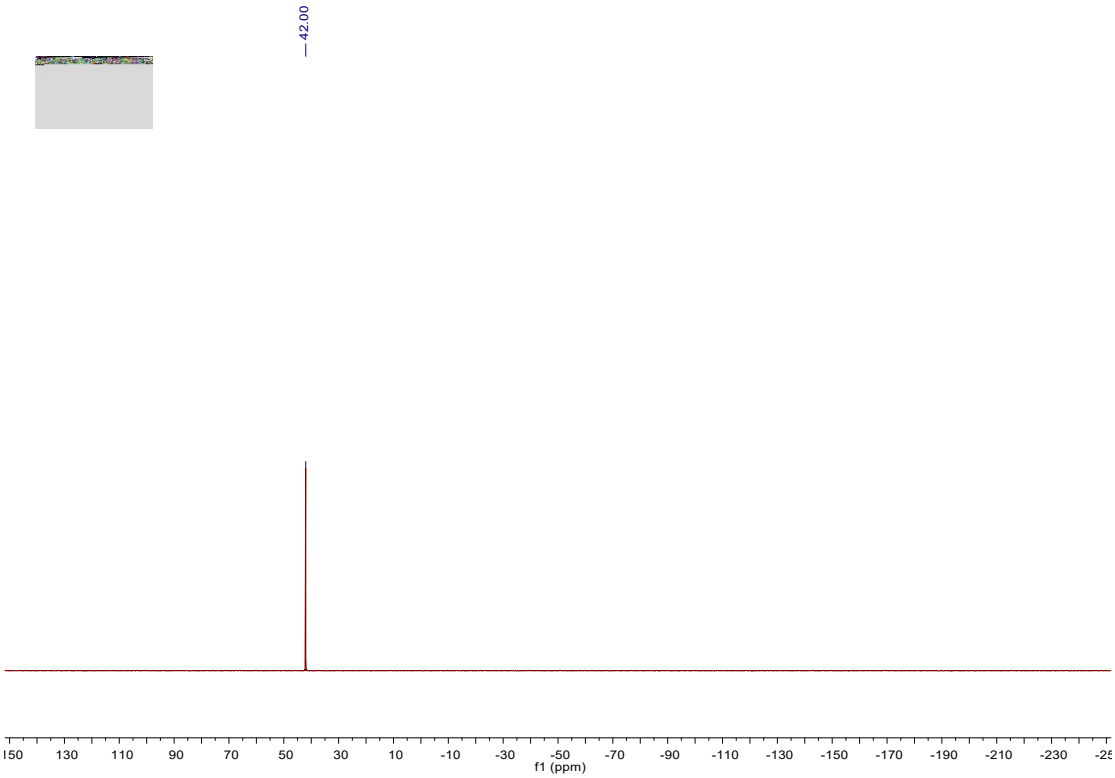

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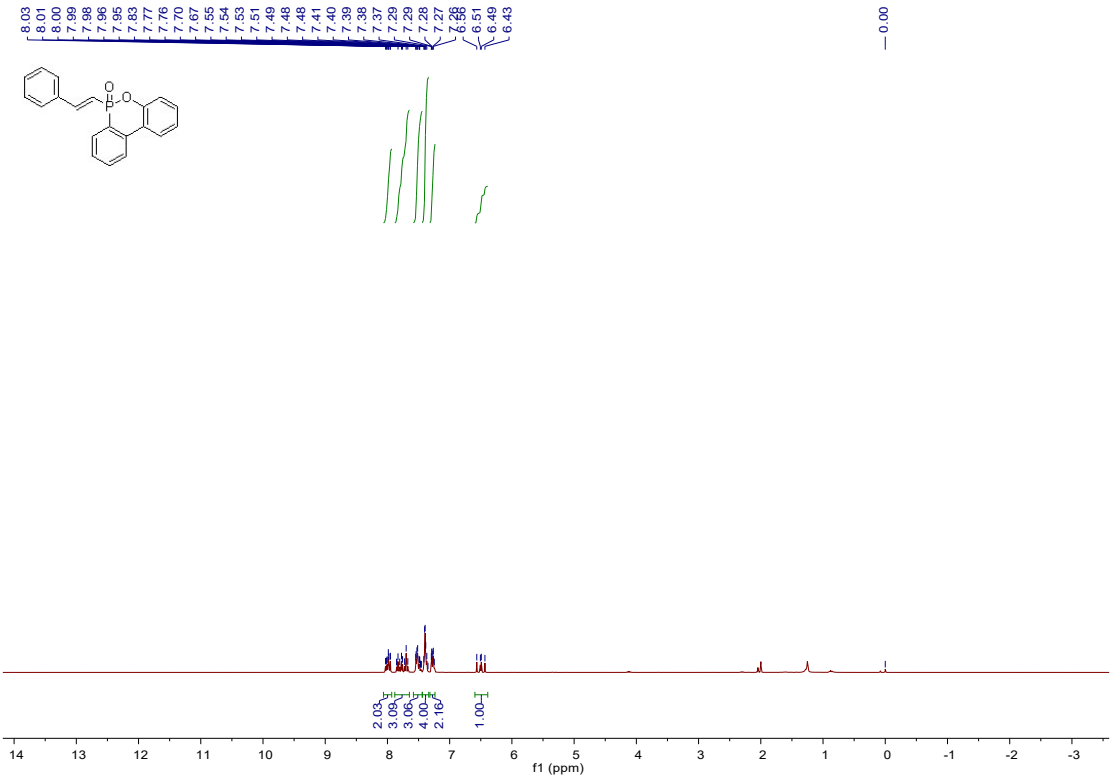

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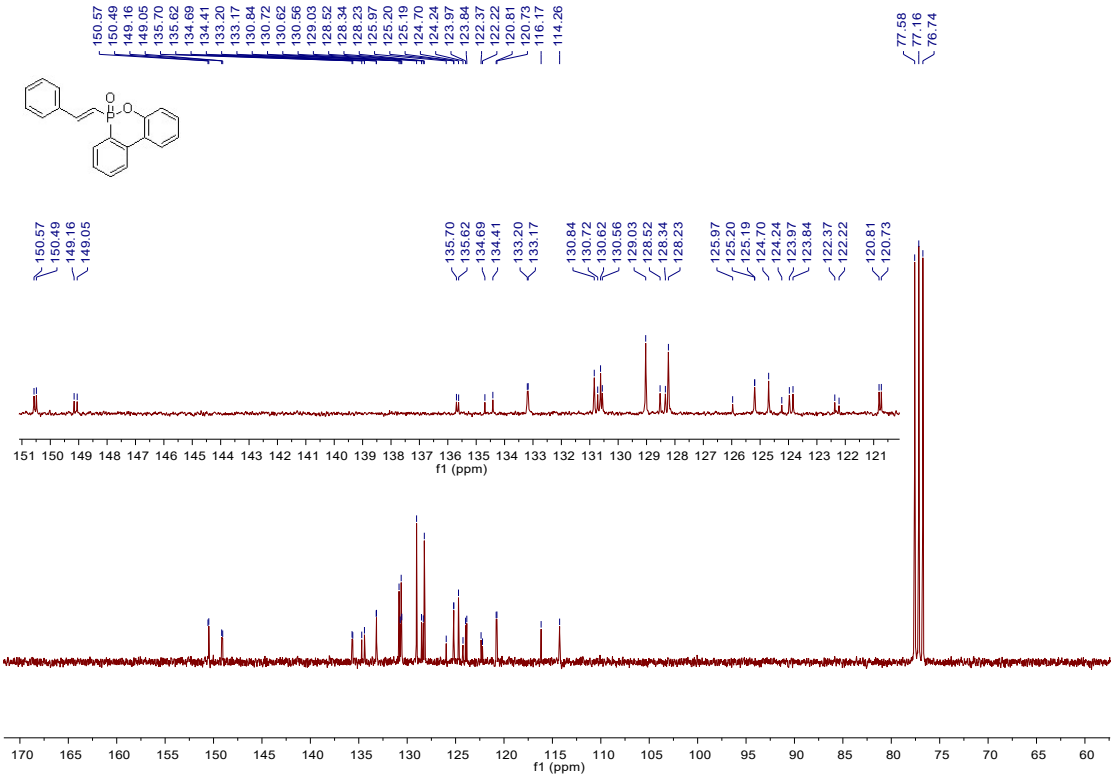

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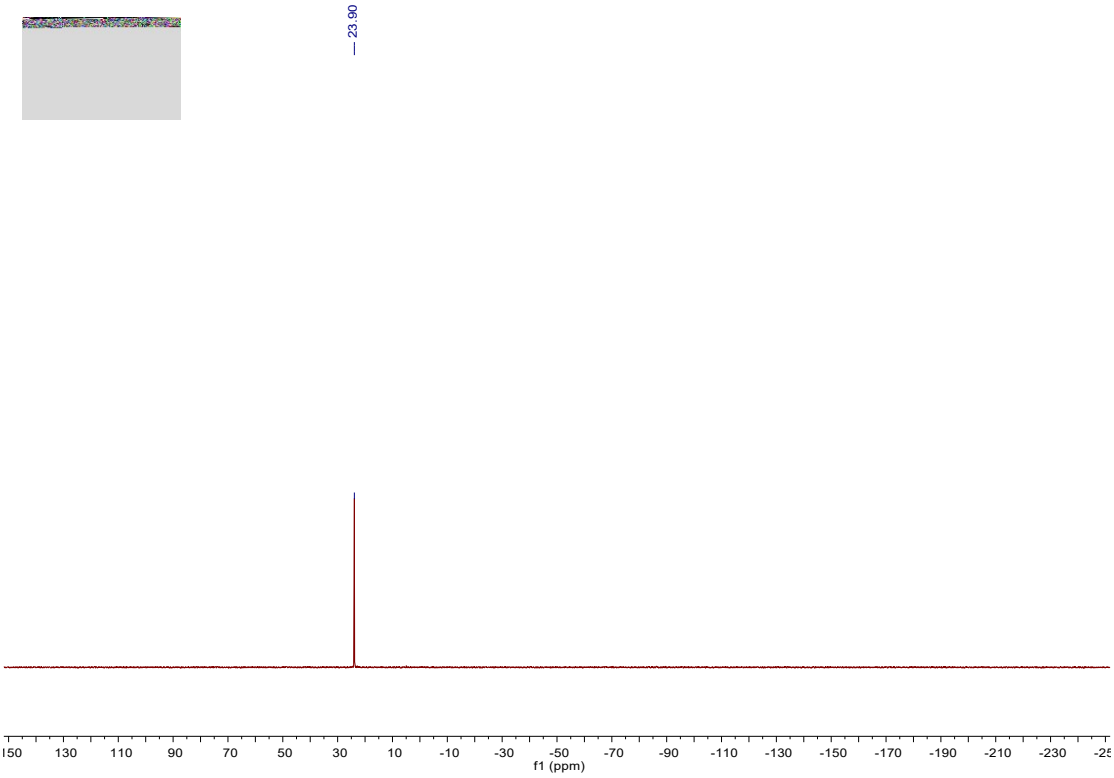

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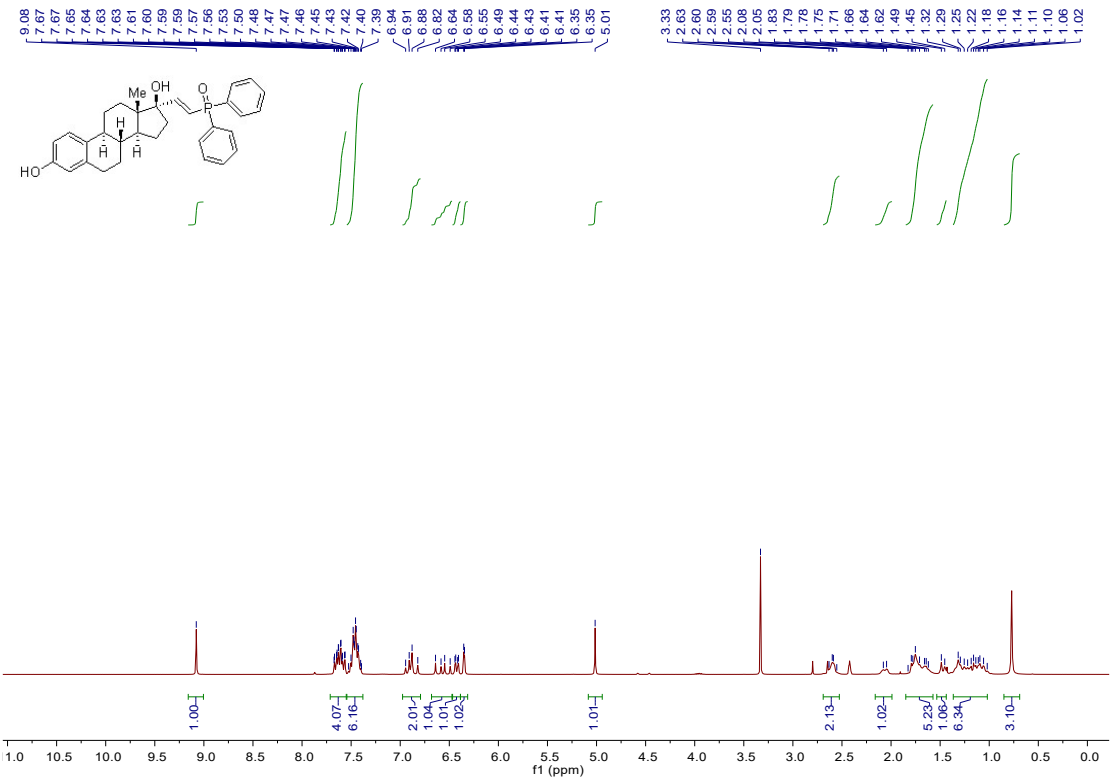

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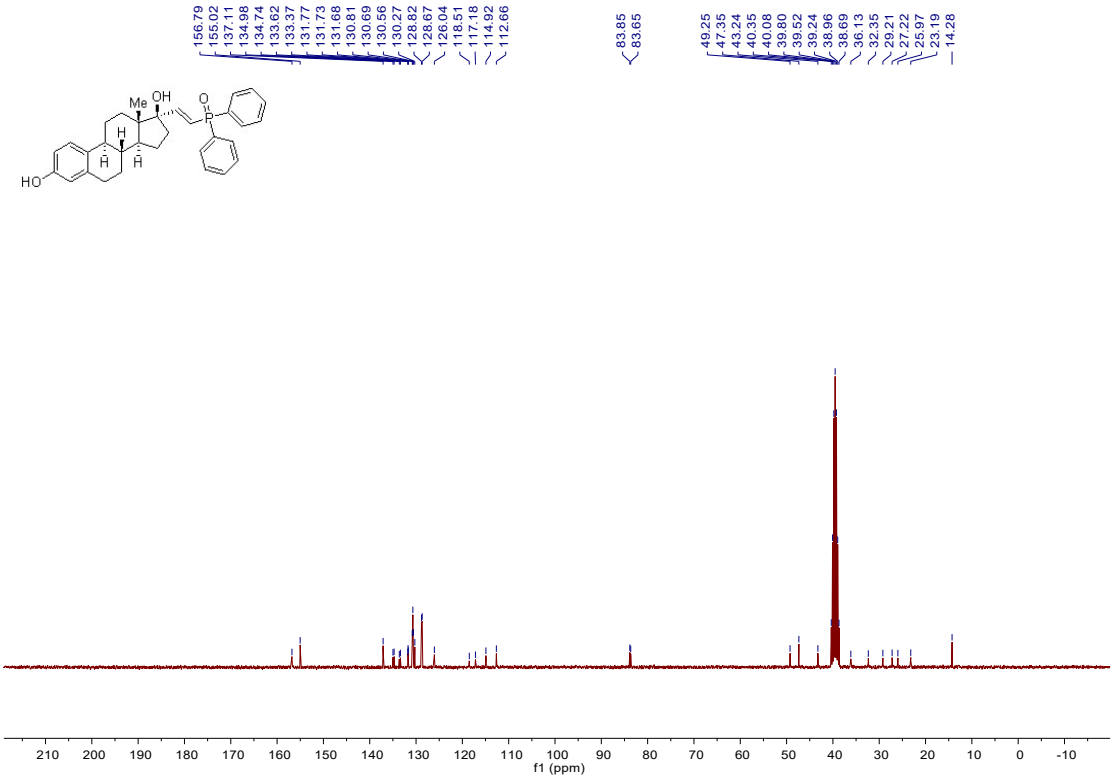

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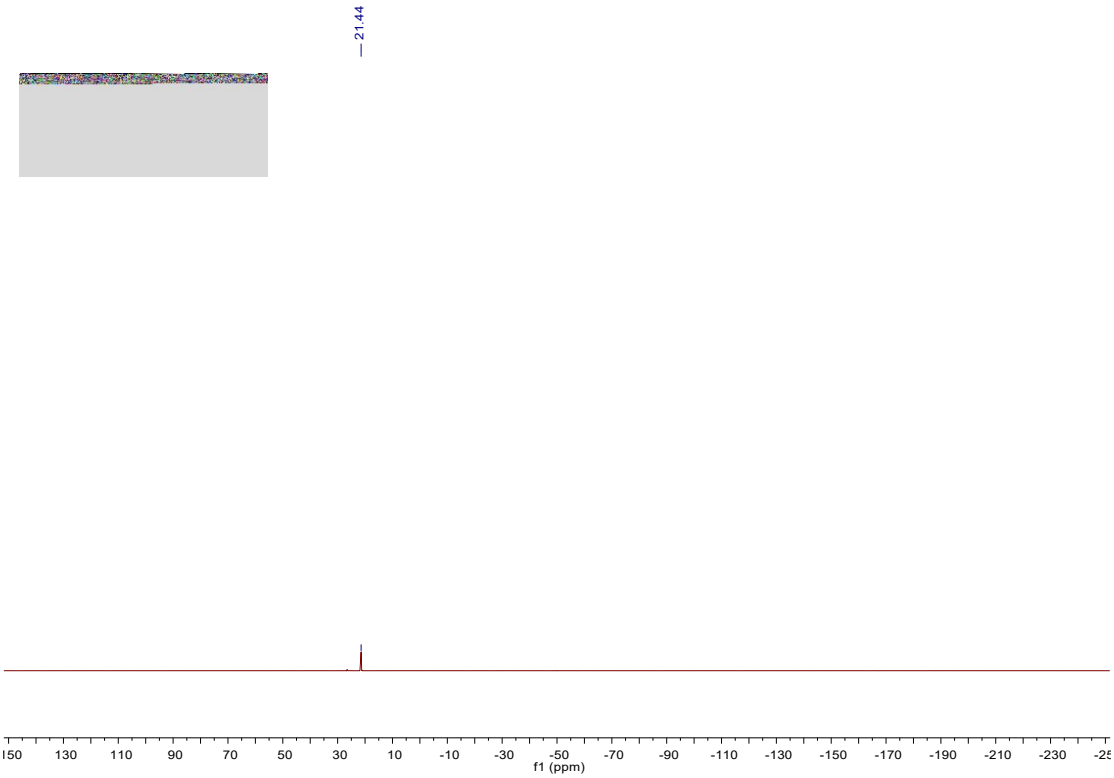

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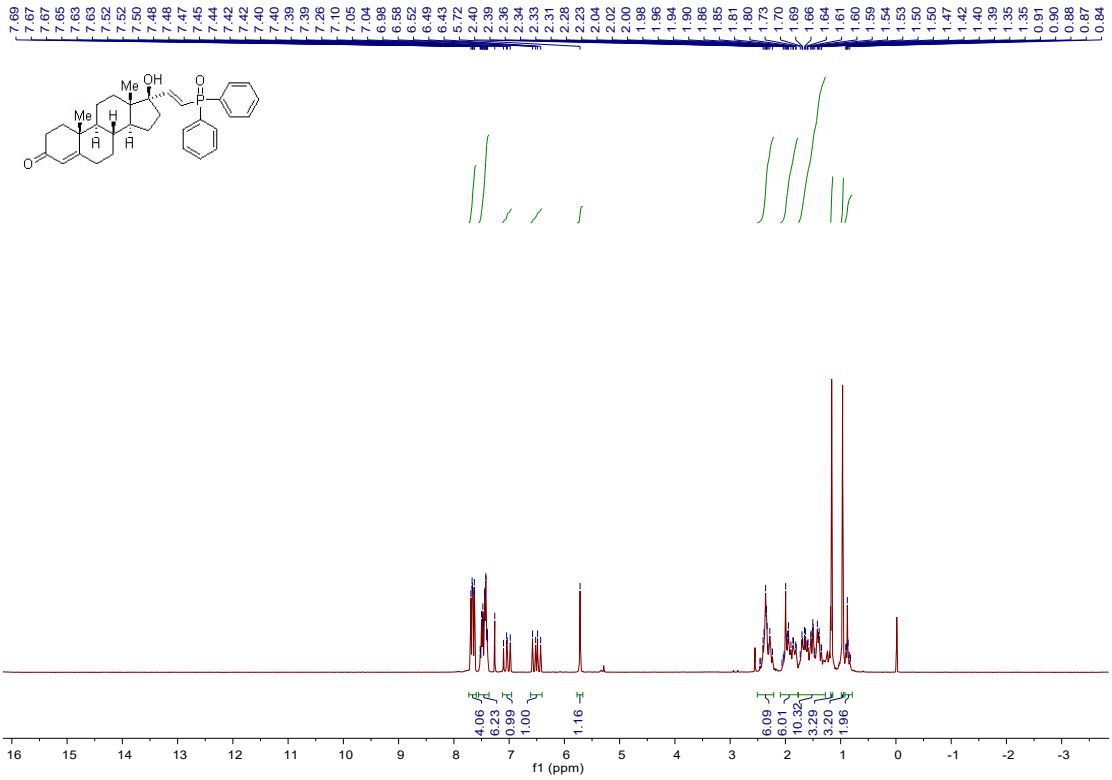

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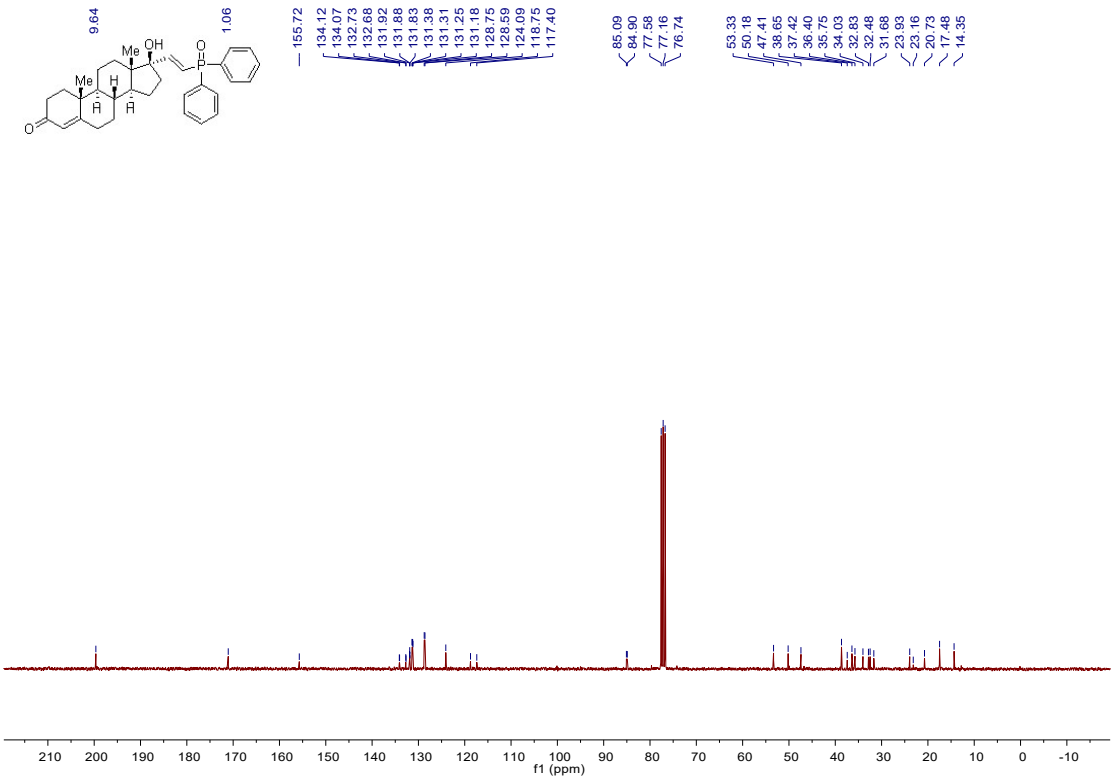

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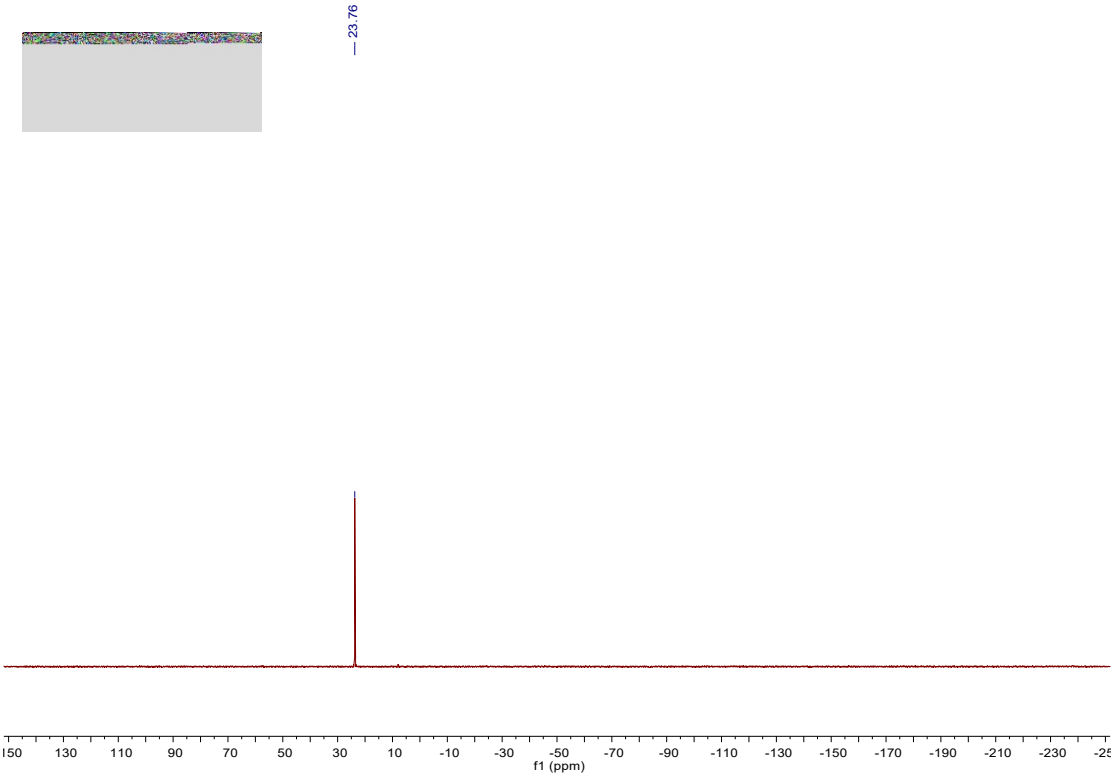

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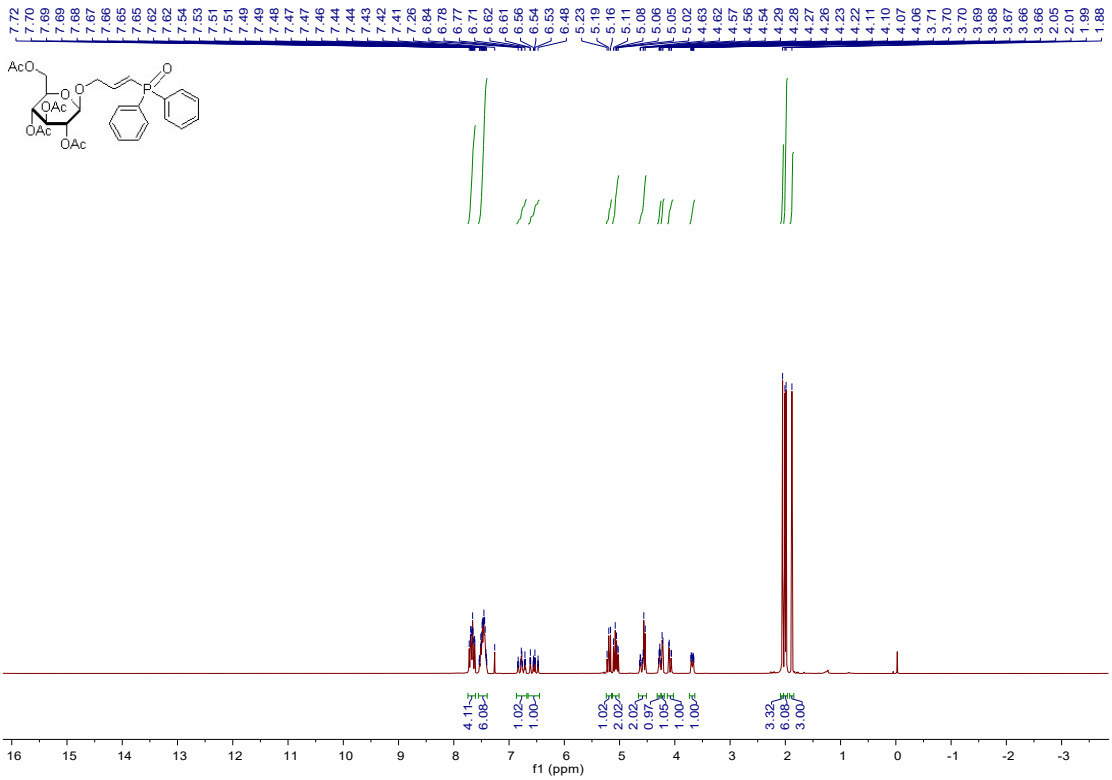

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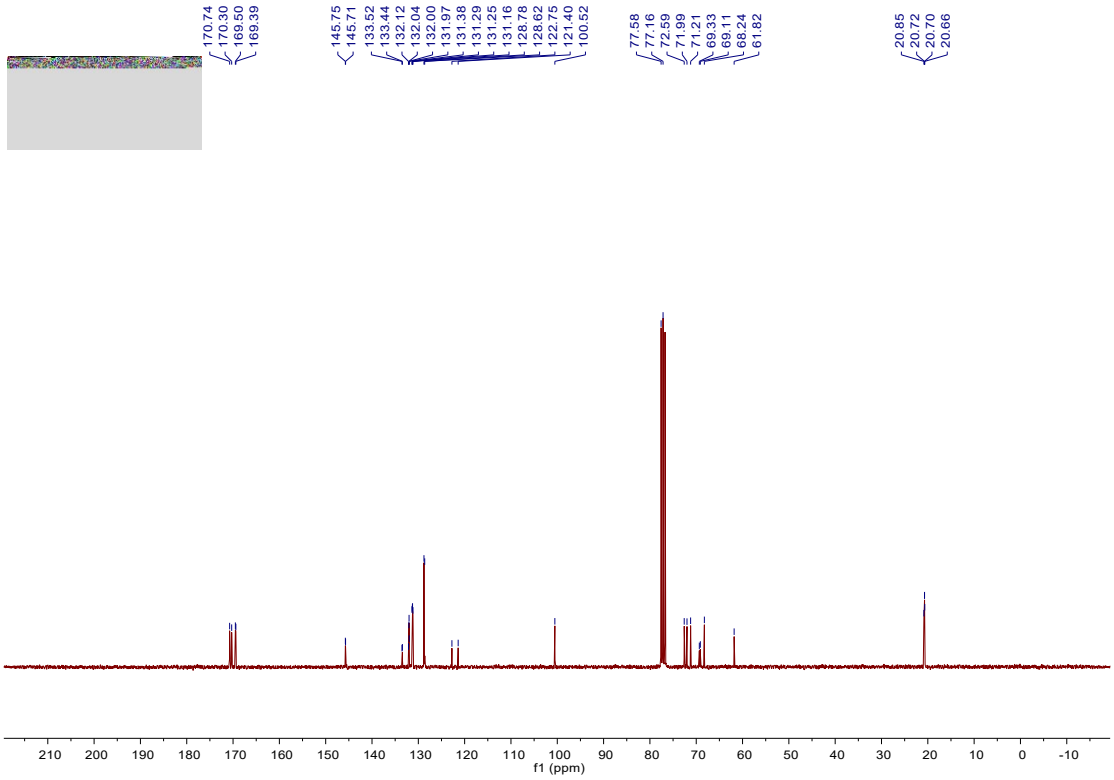

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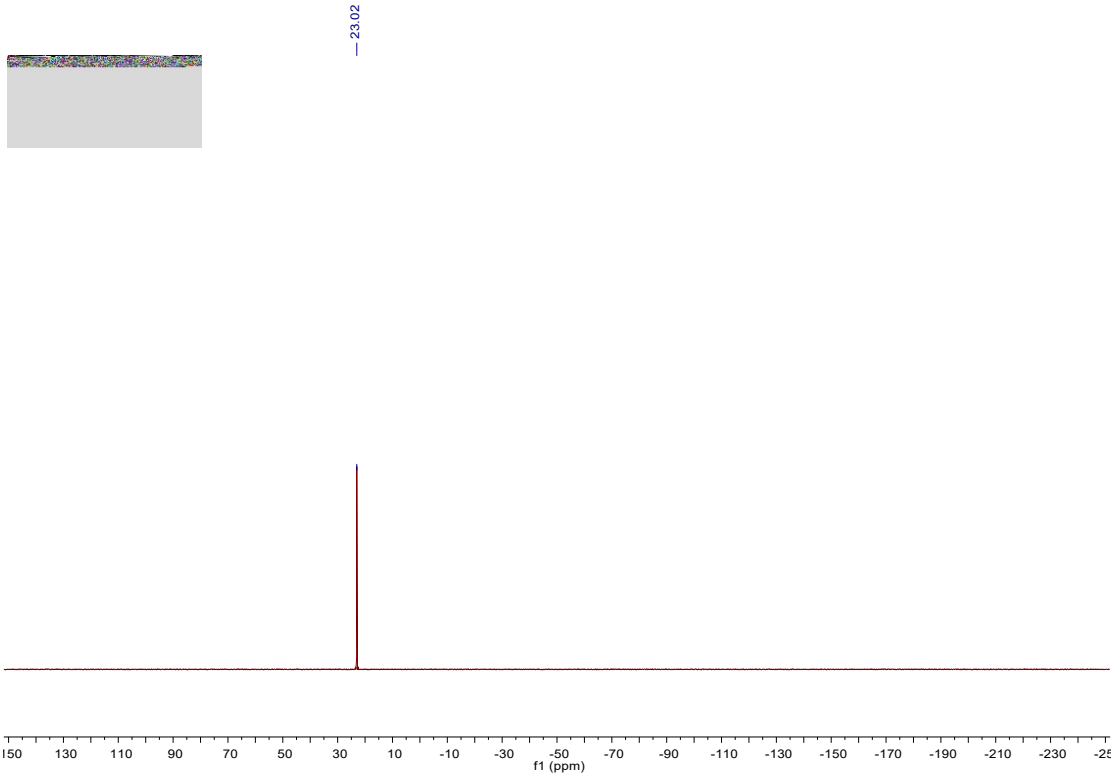

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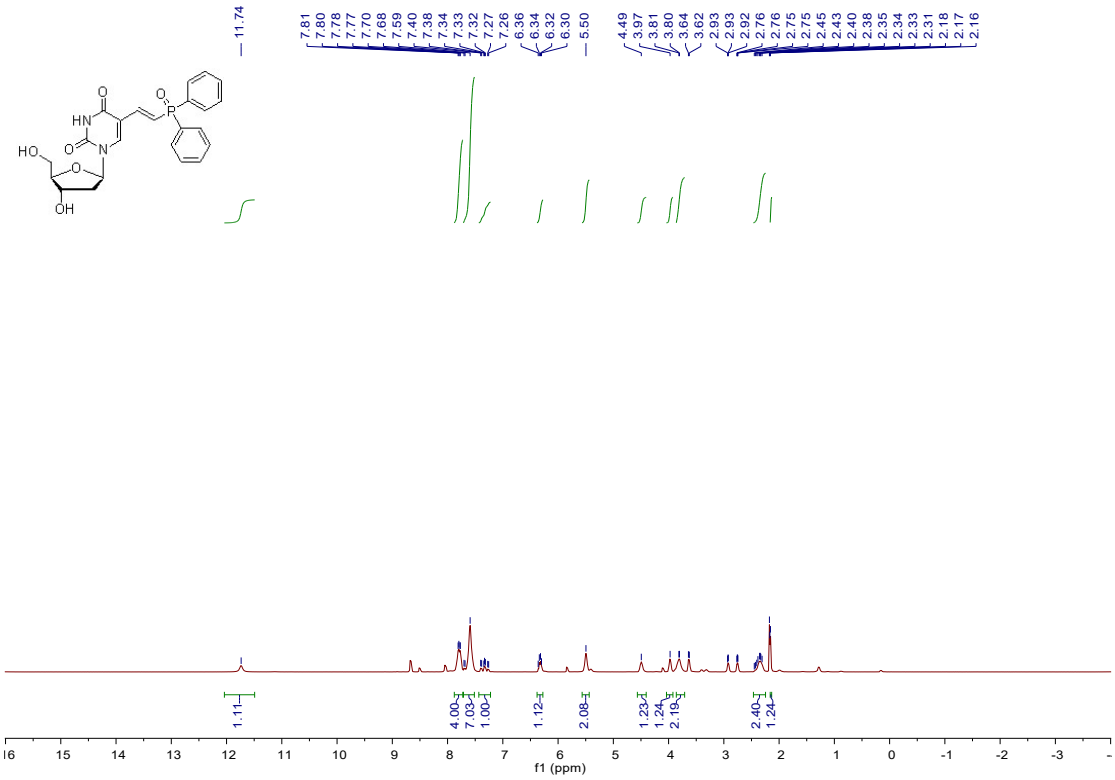

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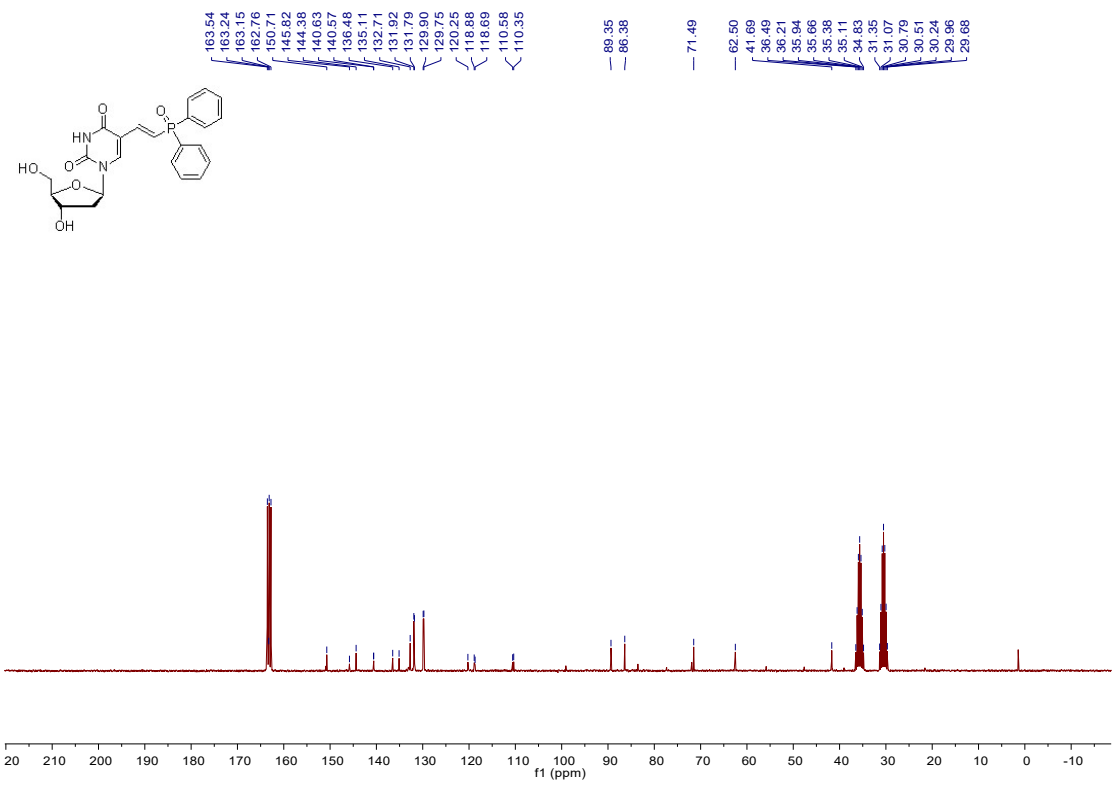

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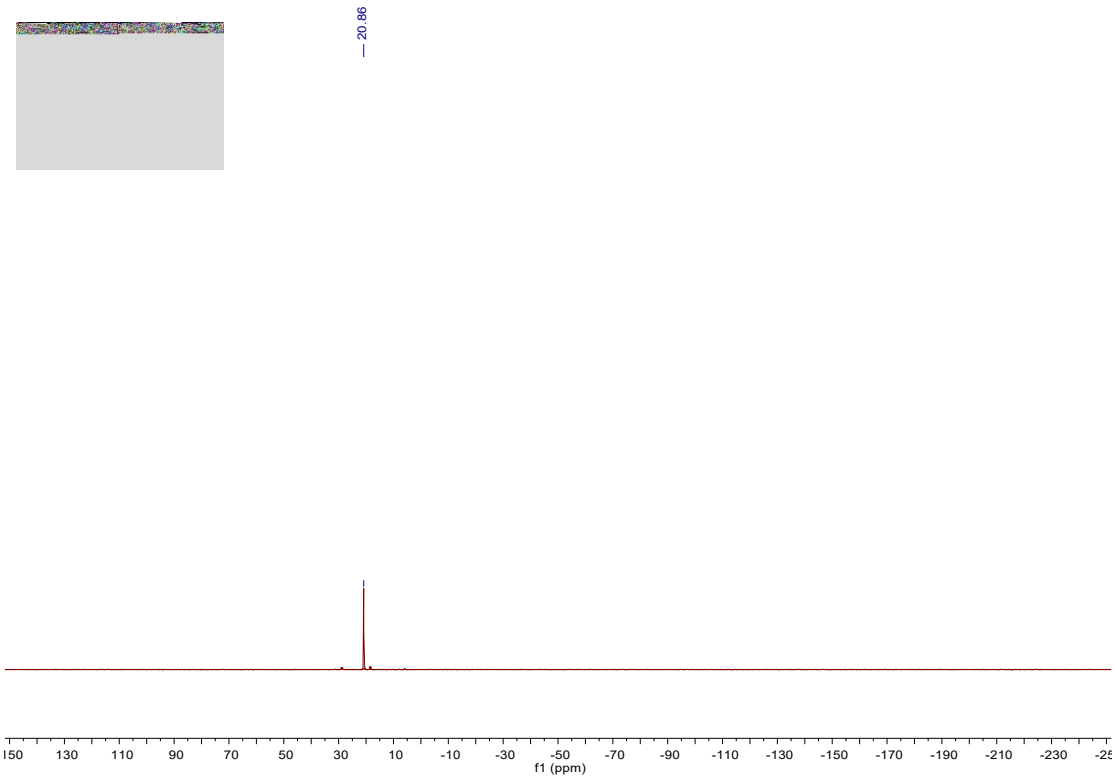

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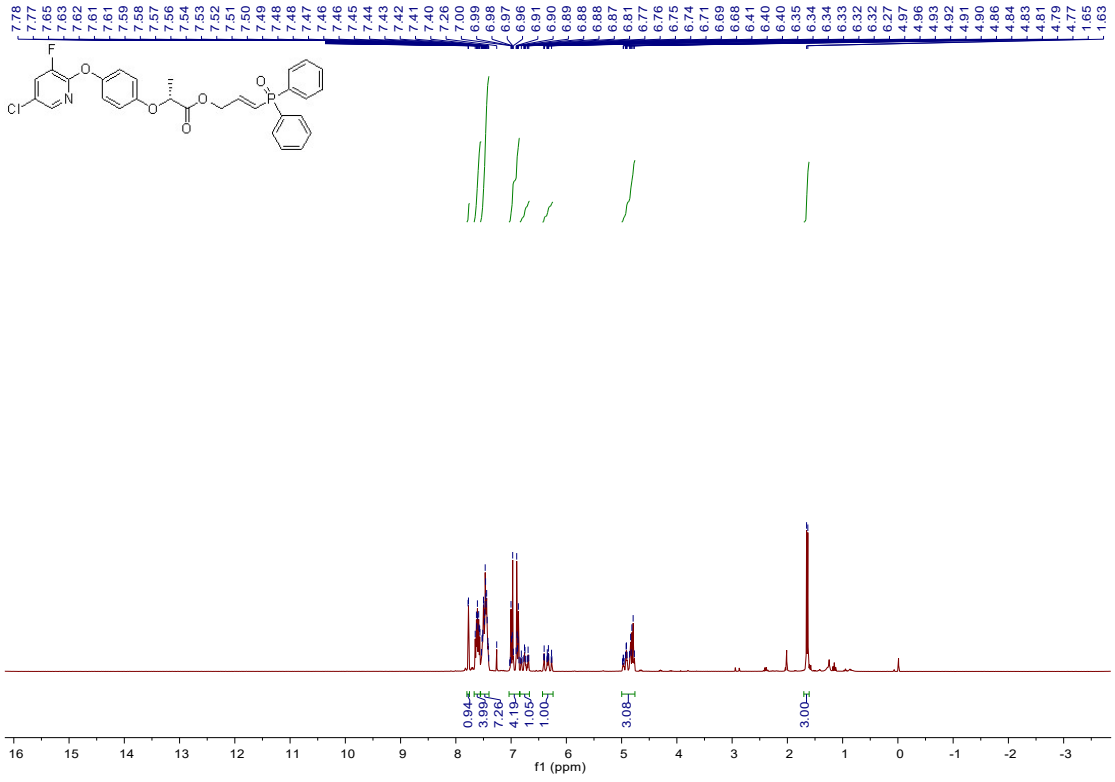

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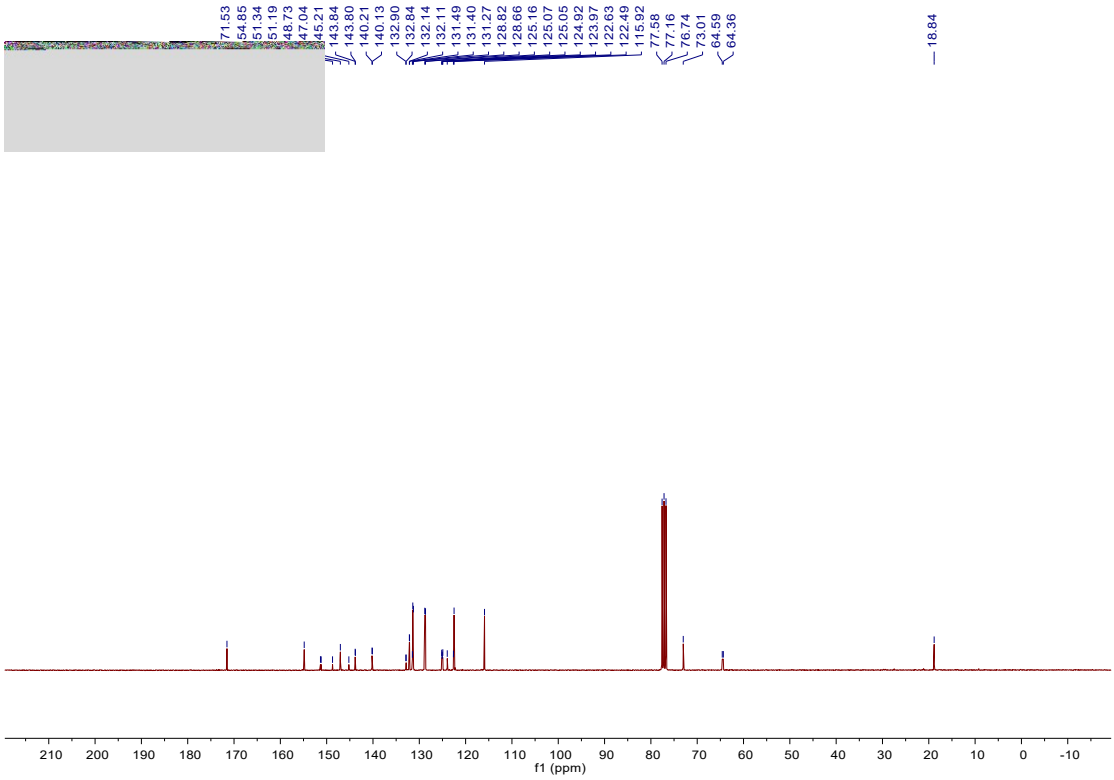

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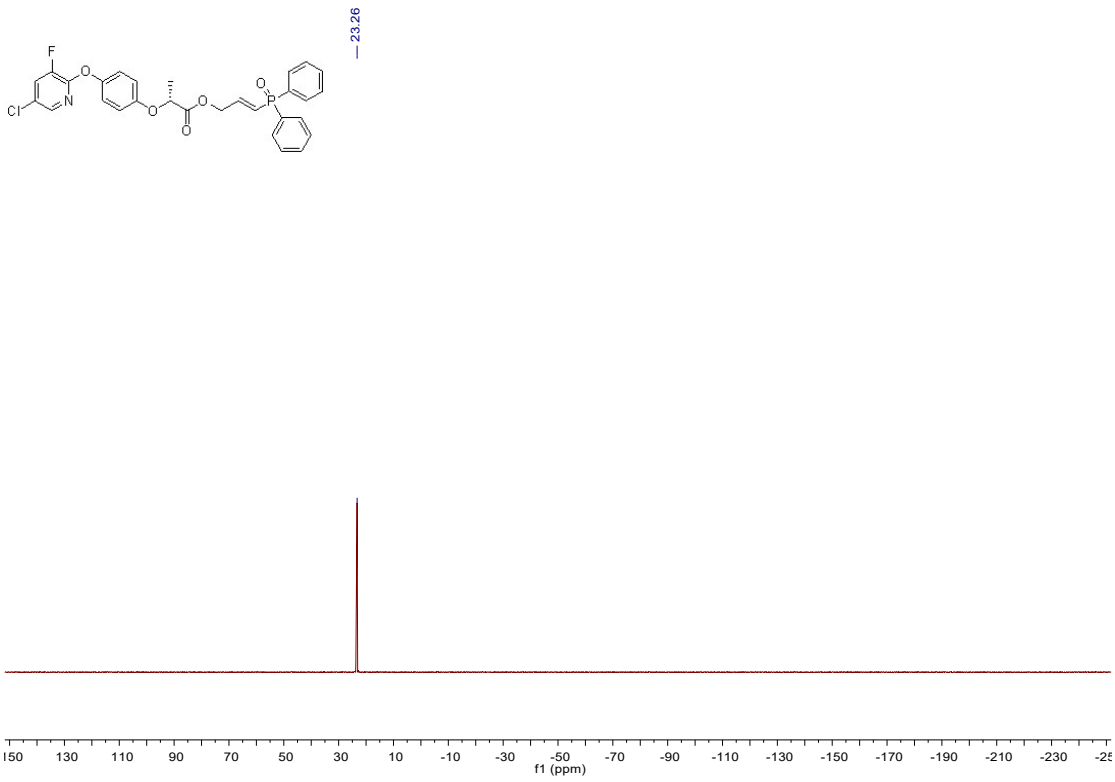

^{31}P NMR of compound **5yk**

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