Supporting Information
For

Chemodivergent Phosphonylation of Diazocarboxylates: Light-On Vs Light-Off Reaction

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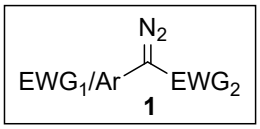
1. General Information

Unless mentioned otherwise, all reactions were carried out under nitrogen atmosphere in flame-dried glassware. All reactions were monitored by TLC, visualization was effected with UV and/or by developing in iodine. The NMR Chemical shifts are reported in δ (ppm) relative to TMS as the internal standard for ^{1}H and $^{13}C\{H\}$, TFA as the internal standard for $^{19}F\{H\}$ and phosphoric acid as the external standard for $^{31}P\{H\}$. To describe spin multiplicity, standard abbreviations such as s, d, t, q, m, dd referring to singlet, doublet, triplet, quartet, multiplet and doublet of doublet respectively, are used.

The aryldiazoacetates (**1a-1q**)[1] as well as other diazo substrates **(1r-1u)** [2-4] were synthesized following reported literature protocols. All the trialkyl phosphites (**2a-2d**) were commercially available. All other chemicals and catalysts were purchased from commercial sources and used as received. The structure of substrates **1a-1u** and **2a-2d** have been provided in Table S1 and S2, respectively.

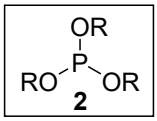
Table S1. Substitutions in diazo substrates **1**



1

Compound	Ar/EWG_1	EWG_2	Compound	Ar/EWG_1	EWG_2
1a	Ph	CO_2Me	**1l**	2-NO_2-Ph	CO_2Me
1b	2-OMe-Ph	-do-	**1m**	1-naphthyl	-do-
1c	4-OMe-Ph	-do-	**1n**	3,4-(OCH_2O)-Ph	CO_2Et
1d	4-OCF_3-Ph	-do-	**1o**	3-thienyl	-do-
1e	4-Ph-Ph	-do-	**1p**	Ph	CO_2allyl
1f	4-Cl-Ph	-do-	**1q**	Ph	CO_2propargyl
1g	4-Br-Ph	-do-	**1r**	Ph	COPh
1h	4-F-Ph	-do-	**1s**	Ph	CF_3
1i	3-CF_3-Ph	-do-	**1t**	CO_2Et	CO_2Et
1j	4-CF_3-Ph	-do-	**1u**	COPh	COPh
1k	2-NO_2-Ph	-do-			

Table S2. Substitutions in alkyl phosphites **2**



2

Compound	R	Compound	R
2a	Me	**2c**	^{i}-propyl
2b	Et	**2d**	allyl

2. Instrumentation Details

Melting points were recorded on a Precision melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker Avance spectrometer at 400/500 MHz (^{1}H), 100/125 MHz (^{13}C{H}), 162 MHz (^{31}P{H}) and 376 MHz (^{19}F{H}). The ESI-HRMS spectra were recorded on Agilent 6520-Q-Tof LC/MS system. The reactions were irradiated using high power blue LEDs (make: Original Opulant America, power = 3 W, λ_{max} = 455 nm, luminous flux/radiant flux = 687 mW at 700 mA) fitted in an aluminum block. The block contains 6 holes to hold vials and water inlet-outlet nozzles. The vials placed in holes on the block were irradiated from bottom at a distance of ≈ 2 cm. The reaction temperature can be maintained by circulating water through the aluminum block via inlet-outlet nozzles (Figure S1).

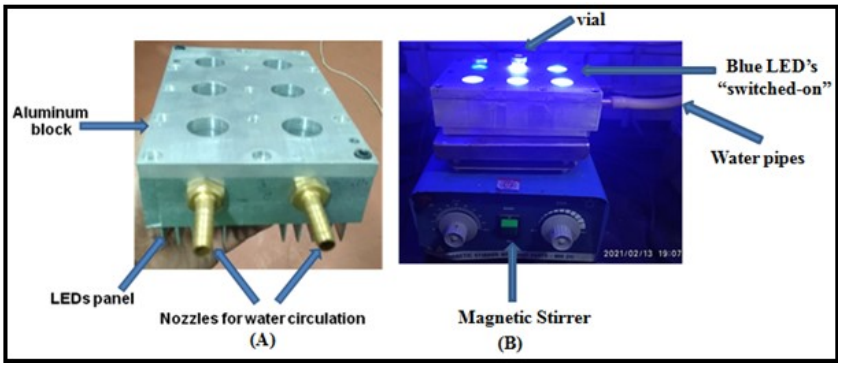


Figure S1. (A) Picture of the visible light photoreactor; (B) Experimental set-up

3. General Procedures

3.1. General procedure for thermal phosphonylation

In an oven dried 5 mL snap vial equipped with a magnetic stir bar, diazo compound **1** (0.2 mmol) and trialkyl phosphite **2** (0.6 mmol) were dissolved in anhydrous acetonitrile (2.0 mL). The solution was purged with nitrogen and stirred at room temperature (25-30 ^{o}C) for 12 h. Upon completion of the reaction (TLC monitoring), the reaction mixture was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (100-200 mesh) with hexane/ethyl acetate as eluent, furnishing the pure product **3**.

3.2. General procedure for photocatalytic phosphonylation

In an oven dried 5 mL snap vial equipped with a magnetic stir bar, diazo compound **1** (0.4 mmol) and trialkyl phosphite (0.2 mmol) were dissolved in dichloromethane (2.0 mL). The resulting reaction mixture was degassed by three "pump-freeze-thaw" cycles via a syringe needle and stirred at room temperature (25-30 ^{o}C) under the irradiation of 455 nm, 3W blue LEDs for 6 h. Upon completion of the reaction (TLC monitoring), the reaction mixture was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (100-200 mesh) with hexane/ethyl acetate as eluent, furnishing the pure product **4**.

4. Details of X-ray Analysis of 3k

A good quality single crystal of size 0.39 x 0.15 x 0.15 mm, was selected under a polarizing microscope and mounted on a glass fiber for data collection. Single crystal X-ray data for compound **3k** were collected on the Rigaku XtaLAB Synergy-S single crystal X-ray diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector, dual Mo and Cu microfocus sealed X-ray source with kappa goiniometer at 294 (2) K. Data collection cell determination, and data reduction was performed using the CrysAlisPro[5] software. Structure solution and refinement were performed by using SHELX-97.[6] Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbons were generated with idealized geometries and isotropically refined using a riding model.

Crystallization: Crystals of compound **3k** were grown from the solvent chloroform by slow evaporation method (Figure S2, Table S3).

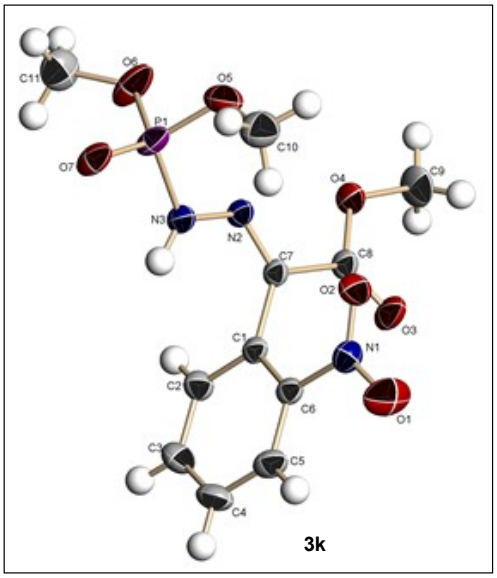


Figure S2. ORTEP diagram drawn with 30% ellipsoid probability for non-H atoms of the crystal structure of compound **3k** determined at 294K.

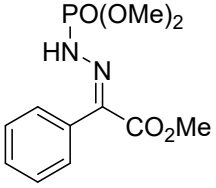
Table S3. Crystal data and structure refinement details for compound **3k**

Compound	**3k**
Empirical formula	$C_{11}\ H_{14}\ N_3\ O_7\ P$
Formula weight	331.22
Crystal System	Monoclinic
Space group	P $2_1/c$
a (Å)	9.6313(2)
b (Å)	8.3277(2)
c (Å)	18.8433(3)

α (°)	90.00
β (°)	95.670(2)
γ (°)	90.00
V (Å^3)	1503.96(5)
Z	4
D_c (g/cm^3)	1.463
F_{000}	688
μ (mm^{-1})	2.001
θ_{max} (°)	77.58
Total reflections	10723
Unique reflections	3050
Reflections [$I > 2\sigma(I)$]	2716
Parameters	203
R_{int}	0.0372
Goodness-of-fit	1.065
R [$F^2 > 2\sigma(F^2)$]	0.0649
wR (F^2, all data)	0.1805
CCDC No.	2342436

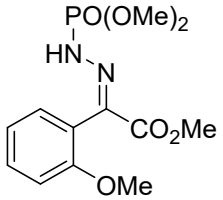
5. Characterization Data

Methyl (*E*)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)-2-phenylacetate (3a)[7]



White solid; isolated yield 78% (45 mg). R_f 0.50 (50% EtOAc/hexane); Mp 93-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.54 (m, 3H), 7.26 (d, J = 7.8 Hz, 2H merged with solvent peak), 7.08 (d, $^2J_{H\text{-}P}$ = 30.5 Hz, 1H), 3.87 (d, $^3J_{H\text{-}P}$ = 12.2 Hz, 6H merged with s at 3.84), 3.84 (s, 3H merged with d at 3.87); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 163.95, 143.66 (d, $^3J_{C\text{-}P}$ = 16.9 Hz), 130.39, 129.70, 128.40, 128.29, 54.42 (d, $^2J_{C\text{-}P}$ = 5.9 Hz), 52.77; ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ 1.62; HRMS for $C_{11}H_{16}N_2O_5P^+$: calcd. $[M+H]^+$: 287.0791, found: 287.0792

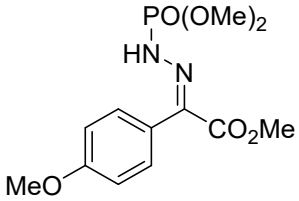
Methyl (*E*)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)-2-(2-methoxyphenyl)acetate (3b)



White solid; isolated yield 76% (51 mg). R_f 0.50 (60% EtOAc/hexane); Mp 144-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.48 (m, 1H), 7.13 (dd, J = 7.4 Hz, 1.5 Hz, 1H), 7.07 (t, J = 7.3 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.91 (d, $^2J_{H\text{-}P}$ = 30.5 Hz, 1H), 3.85 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 6H), 3.82 (s, 3H), 3.80 (s, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 164.06, 156.70, 141.61

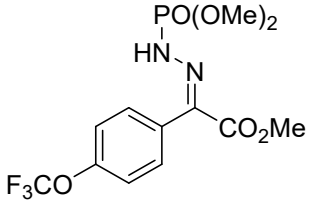
(d, $^{3}J_{C\text{-}P}$ = 17.4 Hz), 132.08, 129.84, 121.46, 117.08, 111.78, 55.64, 54.28 (d, $^{2}J_{C\text{-}P}$ = 5.8 Hz), 52.63; $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 1.81; HRMS for $C_{12}H_{17}N_2O_6PNa^+$: calcd. $[M+Na]^+$: 339.0722, found: 339.0718

Methyl (*E*)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)-2-(4-methoxyphenyl)acetate (3c)[7]



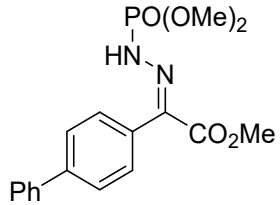
White solid; isolated yield 70% (47 mg). R_f 0.50 (60% EtOAc/hexane); Mp 158-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.22 (m, 2H), 7.13 (d, $^{2}J_{H\text{-}P}$ = 30.4 Hz, 1H), 7.01-7.04 (m, 2H), 3.86 (s, 3H), 3.85 (d, $^{3}J_{H\text{-}P}$ = 11.4 Hz, 6H), 3.83 (s, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 164.21, 160.95, 143.57 (d, $^{3}J_{C\text{-}P}$ = 17.2 Hz), 129.88, 120.11, 115.15, 55.43, 54.39 (d, $^{2}J_{C\text{-}P}$ = 5.9 Hz), 52.74; $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 1.82; HRMS for $C_{12}H_{17}N_2O_6PNa^+$: calcd. $[M+Na]^+$: 339.0722, found: 339.0719

Methyl (*E*)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)-2-(4-(trifluoromethoxy)phenyl)acetate (3d)



White solid; isolated yield 69% (51 mg). R_f 0.50 (40% EtOAc/hexane); Mp 135-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.31-7.33 (m, 2H), 7.05 (d, $^{2}J_{H\text{-}P}$ = 30.1 Hz, 1H), 3.86 (d, $^{3}J_{H\text{-}P}$ = 11.5 Hz, 6H), 3.85 (s, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 163.71, 150.43, 142.03 (d, $^{3}J_{C\text{-}P}$ = 16.8 Hz), 130.38, 126.81, 122.00, 120.34 (q, $^{1}J_{C\text{-}F}$ = 257.2 Hz), 54.51 (d, $^{2}J_{C\text{-}P}$ = 5.9 Hz), 52.87; $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 1.27; $^{19}F\{H\}$ NMR (376 MHz, $CDCl_3$) δ -57.70; HRMS for $C_{12}H_{15}F_3N_2O_6P^+$: calcd. $[M+H]^+$: 371.0614, found: 371.0619

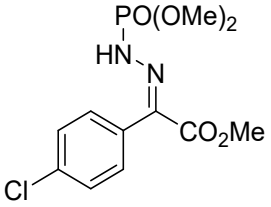
Methyl (*E*)-2-([1,1'-biphenyl]-4-yl)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)acetate (3e)



White solid; isolated yield 65% (47 mg). R_f 0.50 (50% EtOAc/hexane); Mp 133-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.16 (d, $^{2}J_{H\text{-}P}$ = 30.4 Hz, 1H), 3.87 (d, $^{3}J_{H\text{-}P}$ = 11.4 Hz, 6H), 3.86 (s, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 164.02, 143.44, 143.43 (d, $^{3}J_{C\text{-}P}$ = 16.9 Hz), 140.03, 128.98, 128.79, 128.46, 128.04, 127.26, 127.03, 54.46 (d,

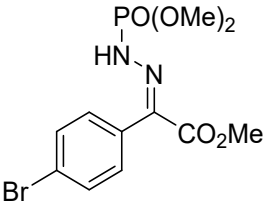
$^{2}J_{C\text{-}P}$ = 5.9 Hz), 52.83; $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 1.64; HRMS for $C_{17}H_{20}N_2O_5P^+$: calcd. $[M+H]^+$: 363.1104, found: 363.1109

Methyl (*E*)-2-(4-chlorophenyl)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)acetate (3f)[7]



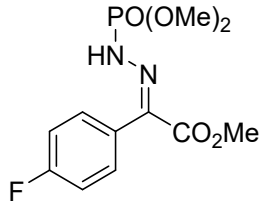
White solid; isolated yield 75% (51 mg). R_f 0.50 (50% EtOAc/hexane); Mp 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.52 (m, 2H), 7.20-7.22 (m, 2H), 7.03 (d, $^{2}J_{H\text{-}P}$ = 30.1 Hz, 1H), 3.86 (d, $^{3}J_{H\text{-}P}$ = 11.4 Hz, 6H), 3.84 (s, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 163.70, 142.31 (d, $^{3}J_{C\text{-}P}$ = 16.9 Hz), 136.67, 130.04, 129.89, 126.66, 54.49 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz), 52.85; $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 1.33; HRMS for $C_{11}H_{14}ClN_2O_5PNa^+$: calcd. $[M+Na]^+$: 343.0227, found: 343.0217

Methyl (*E*)-2-(4-bromophenyl)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)acetate (3g)[7]



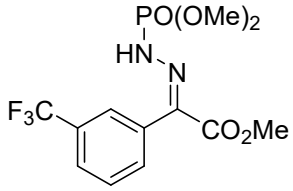
White solid; isolated yield 70% (54 mg). R_f 0.50 (50% EtOAc/hexane); Mp 150-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.66 (m, 2H), 7.12-7.14 (m, 2H), 7.08 (d, $^{2}J_{H\text{-}P}$ = 31.2 Hz, 1H), 3.84 (d, $^{3}J_{H\text{-}P}$ = 11.4 Hz, 6H merged with s at 3.82), 3.82 (s, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 163.62, 142.33 (d, $^{3}J_{C\text{-}P}$ = 16.6 Hz), 133.00, 130.06, 127.14, 124.92, 54.50 (d, $^{2}J_{C\text{-}P}$ = 5.9 Hz), 52.85; $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 1.30; HRMS for $C_{11}H_{14}BrN_2O_5PNa^+$: calcd. $[M+Na]^+$: 386.9721, found: 386.9711

Methyl (*E*)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)-2-(4-fluorophenyl)acetate (3h)[7]



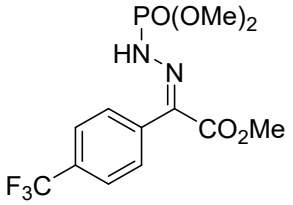
White solid; isolated yield 85% (55 mg). R_f 0.50 (60% EtOAc/hexane); Mp 144-146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.29 (m, 4H), 7.06 (d, $^{2}J_{H\text{-}P}$ = 30.2 Hz, 1H), 3.86 (d, $^{3}J_{H\text{-}P}$ = 11.4 Hz, 6H), 3.84 (s, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 163.86, 163.58 (d, $^{1}J_{C\text{-}F}$ = 250.0 Hz), 142.50, (d, $^{3}J_{C\text{-}P}$ = 16.8 Hz), 130.65 (d, $^{3}J_{C\text{-}F}$ = 8.5 Hz), 124.24 (d, $^{4}J_{C\text{-}F}$ = 3.5 Hz), 116.98 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 54.46 (d, $^{2}J_{C\text{-}P}$ = 5.9 Hz), 52.81; $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 1.41; $^{19}F\{H\}$ NMR (376 MHz, $CDCl_3$) δ -108.96; HRMS for $C_{11}H_{14}FN_2O_5PNa^+$: calcd. $[M+Na]^+$: 327.0522, found: 327.0528

Methyl (*E*)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)-2-(3-(trifluoromethyl)phenyl)acetate (3i)



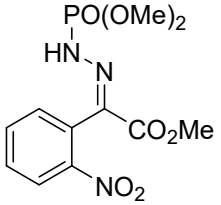
White solid; isolated yield 62% (44 mg). R_f 0.50 (40% EtOAc/hexane); Mp 159-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.9 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.51 (s, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.12 (d, $^2J_{H\text{-}P}$ = 29.9 Hz, 1H), 3.83 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 6H), 3.82 (s, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 163.56, 141.67 (d, $^3J_{C\text{-}P}$ = 17.0 Hz), 132.15 (q, $^2J_{C\text{-}F}$ = 32.8 Hz), 131.90, 130.19, 129.52, 127.12 (q, $J_{C\text{-}F}$ = 3.6 Hz), 125.55 (q, $J_{C\text{-}F}$ = 3.6 Hz), 123.49 (q, $^1J_{C\text{-}F}$ = 271.0 Hz), 54.47 (d, $^2J_{C\text{-}P}$ = 5.9 Hz), 52.86; ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ 1.09; ^{19}F{H} NMR (376 MHz, $CDCl_3$) δ -62.84; HRMS for $C_{12}H_{14}F_3N_2O_5PNa^+$: calcd. $[M+Na]^+$: 377.0490, found: 377.0487

Methyl (*E*)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)-2-(4-(trifluoromethyl)phenyl)acetate (3j)



White solid; isolated yield 76% (54 mg). R_f 0.50 (40% EtOAc/hexane); Mp 156-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.01 (d, $^2J_{H\text{-}P}$ = 29.9 Hz, 1H), 3.86 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 6H), 3.85 (s, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 163.49, 141.86 (d, $^3J_{C\text{-}P}$ = 16.9 Hz), 132.41 (q, $J_{C\text{-}F}$ = 32.5 Hz), 132.23, 129.11, 126.65 (q, $J_{C\text{-}F}$ = 3.6 Hz), 123.52 (q, $^1J_{C\text{-}F}$ = 271.1 Hz), 54.52 (d, $^2J_{C\text{-}P}$ = 6.0 Hz), 52.90; ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ 1.09; ^{19}F{H} NMR (376 MHz, $CDCl_3$) δ -63.18; HRMS for $C_{12}H_{14}F_3N_2O_5PNa^+$: calcd. $[M+Na]^+$: 377.0490, found: 377.0498

Methyl (*E*)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)-2-(2-nitrophenyl)acetate (3k)

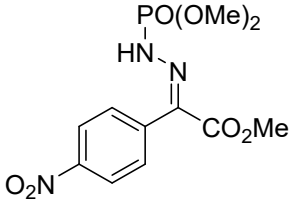


White solid; isolated yield 33% (22 mg). R_f 0.50 (40% EtOAc/hexane); Mp 186-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, J = 8.2 Hz, 1.2 Hz, 1H), 7.78-7.82 (m, 1H), 7.70-7.74 (m, 1H), 7.34 (dd, J = 7.5 Hz, 1.4 Hz, 1H), 7.03 (d, $^2J_{H\text{-}P}$ = 29.1 Hz, 1H), 3.86 (d, $^3J_{H\text{-}P}$ = 11.3 Hz, 3H), 3.81 (s, 3H), 3.78 (d, $^3J_{H\text{-}P}$ = 11.6 Hz, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 162.92, 147.66, 140.34 (d, $^3J_{C\text{-}P}$ = 17.4 Hz), 134.85, 131.48, 130.56, 125.75, 125.26, 54.57 (d, $^2J_{C\text{-}P}$ = 6.0 Hz), 54.21 (d, $^2J_{C\text{-}P}$ = 5.7 Hz), 52.93; ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ 1.10; HRMS for $C_{11}H_{14}N_3O_7PNa^+$: calcd. $[M+Na]^+$: 354.0467, found: 354.0467

Selected X-ray crystallographic data for 3k, $C_{11}H_{14}N_3O_7P$, M = 331.22, Monoclinic, P $2_1/c$, a = 9.6313 (2) Å, b = 8.3277 (2) Å, c = 18.8433 (3) Å, V = 1503.96 (5) Å^3, α = 90.00°, β

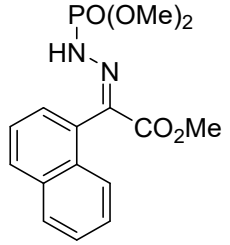
= 95.670° (2), γ = 90.00°, Z = 4, D_c = 1.463 g cm^{-3}, μ (Mo-Kα) = 2.001 mm^{-1}, F(000) = 688, Reflections collected/unique 10723/3050, [R(int) = 0.0372]. Final R indices [$I > 2\sigma$ (I)], $R1$ = 0.0649, wR = 0.1805

Methyl (*E*)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)-2-(4-nitrophenyl)acetate (3l)



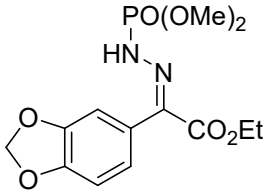
Yellow solid; isolated yield 55% (36 mg). R_f 0.50 (40% EtOAc/hexane); Mp 82-83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.7 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 6.96 (d, $^2J_{H\text{-}P}$ = 29.6 Hz, 1H), 3.87 (d, $^3J_{H\text{-}P}$ = 11.1 Hz, 6H merged with s at 3.86), 3.86 (s, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 158.49, 144.06, 136.19, 130.29, 125.26, 119.95, 49.87 (d, $^2J_{C\text{-}P}$ = 6.1 Hz), 48.26; ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ 0.76; HRMS for $C_{11}H_{14}N_3O_7PK^+$: calcd. $[M+K]^+$: 370.0206, found: 370.0197

Methyl (*E*)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)-2-(naphthalen-1-yl)acetate (3m)



White solid; isolated yield 63% (45 mg). R_f 0.50 (50% EtOAc/hexane); Mp 176-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.51-7.61 (m, 4H), 7.38 (dd, J = 7.0 Hz, 1.1 Hz, 1H), 6.75 (d, $^2J_{H\text{-}P}$ = 30.7 Hz, 1H), 3.86 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 3H), 3.83 (s, 3H), 3.82 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 164.11, 143.23 (d, $^3J_{C\text{-}P}$ = 17.2 Hz), 133.89, 130.86, 129.71, 129.14, 127.65, 127.27, 126.96, 126.23, 125.72, 123.74, 54.47 (d, $^2J_{C\text{-}P}$ = 6.0 Hz), 54.26 (d, $^2J_{C\text{-}P}$ = 5.8 Hz), 52.83; ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ 1.45; HRMS for $C_{15}H_{17}N_2O_5PNa^+$: calcd. $[M+Na]^+$: 359.0773, found: 359.0780

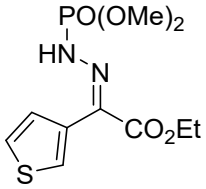
Ethyl (*E*)-2-(benzo[d][1,3]dioxol-5-yl)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)acetate (3n)



White solid; isolated yield 70% (48 mg). R_f 0.50 (40% EtOAc/hexane); Mp 104-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, $^2J_{H\text{-}P}$ = 30.4 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.73 (d appearing as s, 1H, merged with s at 6.70), 6.70 (s, 1H), 6.03 (s, 2H), 4.29 (q, J = 7.0 Hz, 2 H), 3.85 (d, $^3J_{H\text{-}P}$ = 11.3 Hz, 6H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 163.51, 149.15, 148.76, 143.33 (d, $^3J_{C\text{-}P}$ = 16.9 Hz), 122.34, 121.54, 109.40, 108.68, 101.69,

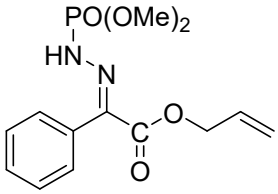
61.83, 54.47 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz), 14.17; $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 1.53; HRMS for $C_{13}H_{18}N_2O_7P^+$: calcd. $[M+H]^+$: 345.0846, found: 345.0854

Ethyl (*E*)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)-2-(thiophen-3-yl)acetate (3o)



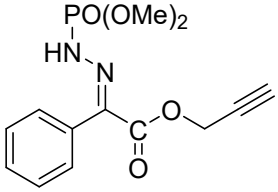
Yellow liquid; isolated yield 55% (34 mg). R_f 0.50 (40% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.53 (m, 2H), 7.34 (d, $^{2}J_{H\text{-}P}$ = 30.2 Hz, 1H), 7.12 (dd, J = 4.4 Hz, 1.8 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2 H), 3.87 (d, $^{3}J_{H\text{-}P}$ = 11.3 Hz, 6H), 1.33 (t, J = 7.1 Hz, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 163.39, 139.38 (d, $^{3}J_{C\text{-}P}$ = 17.1 Hz), 127.95, 127.65, 127.28, 126.91, 61.83, 54.53 (d, $^{2}J_{C\text{-}P}$ = 6.1 Hz), 14.15; $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 1.51; HRMS for $C_{10}H_{16}N_2O_5PS^+$: calcd. $[M+H]^+$: 307.0512, found: 307.0504

Allyl (*E*)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)-2-phenylacetate (3p)



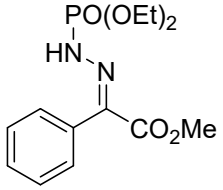
White solid; isolated yield 63% (39 mg). R_f 0.50 (40% EtOAc/hexane); Mp 44-46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.54 (m, 3H), 7.25-7.27 (m, 2H), 7.10 (d, $^{2}J_{H\text{-}P}$ = 30.5 Hz, 1H), 5.90-5.99 (m, 1H), 5.29-5.33 (m, 1H), 5.22-5.25 (m, 1H), 4.72-4.74 (m, 2H), 3.86 (d, $^{3}J_{H\text{-}P}$ = 11.3 Hz, 6H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 163.10, 143.56 (d, $^{3}J_{C\text{-}P}$ = 16.9 Hz), 131.70, 130.35, 129.67, 128.40, 128.29, 118.44, 66.18, 54.50 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz); $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 1.33; HRMS for $C_{13}H_{18}N_2O_5P^+$: calcd. $[M+H]^+$: 313.0948, found: 313.0947

Prop-2-yn-1-yl (*E*)-2-(2-(dimethoxyphosphoryl)hydrazineylidene)-2-phenylacetate (3q)



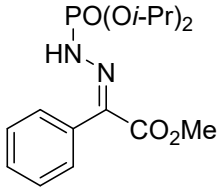
White solid; isolated yield 60% (37 mg). R_f 0.50 (40% EtOAc/hexane); Mp 54-56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.55 (m, 3H), 7.26-7.28 (m, 2H), 7.16 (d, $^{2}J_{H\text{-}P}$ = 30.5 Hz, 1H), 4.83 (d, J = 2.32 Hz, 2H), 3.87 (d, $^{3}J_{H\text{-}P}$ = 11.3 Hz, 6H), 2.48 (s, 1H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 162.71, 142.82 (d, $^{3}J_{C\text{-}P}$ = 16.9 Hz), 130.48, 129.71, 128.36, 128.00, 77.30, 75.24, 54.56 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz), 53.00; $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 1.16; HRMS for $C_{13}H_{15}N_2O_5PNa^+$: calcd. $[M+Na]^+$: 333.0616, found: 333.0613

Methyl (*E*)-2-(2-(diethoxyphosphoryl)hydrazineylidene)-2-phenylacetate (3r)[7]



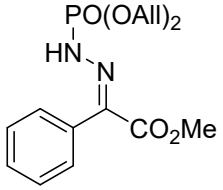
White solid; isolated yield 72% (45 mg). R_f 0.50 (40% EtOAc/hexane); Mp 60-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.54 (m, 3H), 7.23-7.26 (m, 2H), 7.07 (d, $^2J_{H\text{-}P}$ = 30.4 Hz, 1H), 4.13-4.28 (m, 4H), 3.83 (s, 3H), 1.39 (td, J = 7.1 Hz, 0.8 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 164.09, 143.05 (d, $^3J_{C\text{-}P}$ = 17.0 Hz), 130.29, 129.67, 128.56, 128.34, 64.13 (d, $^2J_{C\text{-}P}$ = 5.8 Hz), 52.67, 16.11 (d, $^3J_{C\text{-}P}$ = 6.5 Hz); ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ -0.93; HRMS for $C_{13}H_{20}N_2O_5P^+$: calcd. $[M+H]^+$: 315.1104, found: 315.1102

Methyl (*E*)-2-(2-(diisopropoxyphosphoryl)hydrazineylidene)-2-phenylacetate (3s)[7]



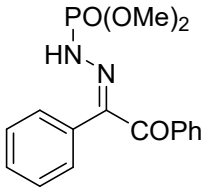
White solid; isolated yield 65% (44 mg). R_f 0.50 (40% EtOAc/hexane); Mp 70-72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.53 (m, 3H), 7.23 (d, J = 6.6 Hz, 2H), 7.05 (d, $^2J_{H\text{-}P}$ = 30.4 Hz, 1H), 4.67-4.75 (m, 2H), 3.83 (s, 3H), 1.39 (d, J = 6.2 Hz, 6H), 1.36 (d, 6.2 Hz, 6H); ^{13}C{H} NMR (125 MHz, $CDCl_3$) δ 164.22, 142.37 (d, $^3J_{C\text{-}P}$ = 17.0 Hz), 130.17, 129.64, 128.76, 128.36, 73.05 (d, $^2J_{C\text{-}P}$ = 5.8 Hz), 52.53, 23.77 (d, $^3J_{C\text{-}P}$ = 4.6 Hz), 23.54 (d, $^3J_{C\text{-}P}$ = 5.0 Hz); ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ -2.94; HRMS for $C_{15}H_{23}N_2O_5PNa^+$: calcd. $[M+Na]^+$: 365.1237, found: 365.1239

Methyl (*E*)-2-(2-(bis(allyloxy)phosphoryl)hydrazineylidene)-2-phenylacetate (3t)



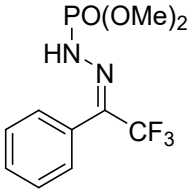
White solid; isolated yield 68% (46 mg). R_f 0.50 (40% EtOAc/hexane); Mp 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.53 (m, 3H), 7.23 (d, J = 6.4 Hz, 2H), 7.09 (d, $^2J_{H\text{-}P}$ = 30.8 Hz, 1H), 5.94-6.03 (m, 2H), 5.40 (d, J = 17.0 Hz, 2H), 5.27 (d, J = 10.2 Hz, 2H), 4.62-4.67 (m, 4H), 3.83 (s, 3H); ^{13}C{H} NMR (125 MHz, $CDCl_3$) δ 164.01, 143.29 (d, $^3J_{C\text{-}P}$ = 16.9 Hz), 132.33 (d, $^3J_{C\text{-}P}$ = 5.6 Hz), 130.32, 129.65, 128.45, 128.32, 118.60, 68.49 (d, $^2J_{C\text{-}P}$ = 5.7 Hz), 52.68; ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ -0.77; HRMS for $C_{15}H_{20}N_2O_5P^+$: calcd. $[M+H]^+$: 339.1104, found: 339.1091

Dimethyl (*E*)-(2-(2-oxo-1,2-diphenylethylidene)hydrazineyl)phosphonate (3u)



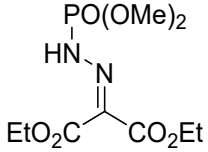
White solid; isolated yield 70% (46 mg). R_f 0.50 (50% EtOAc/hexane); Mp 150-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.4 Hz, 2H), 7.37-7.50 (m, 6H), 7.25 (d, J = 6.8 Hz, 2H), 7.10 (d, $^2J_{H\text{-}P}$ = 30.5 Hz, 1H), 3.73 (d, $^3J_{H\text{-}P}$ = 11.2 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 190.61, 150.25 (d, $^3J_{C\text{-}P}$ = 16.5 Hz), 136.62, 132.68, 130.63, 130.30, 129.69, 128.61, 128.43, 127.99, 54.44 (d, $^2J_{C\text{-}P}$ = 6.1 Hz); ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ 1.40; HRMS for $C_{16}H_{18}N_2O_4P^+$: calcd. $[M+H]^+$: 333.0999, found: 333.0999

Dimethyl (*E*)-(2-(2,2,2-trifluoro-1-phenylethylidene)hydrazineyl)phosphonate (3v)



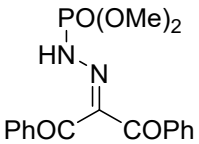
White solid; isolated yield 65% (51 mg). R_f 0.50 (40% EtOAc/hexane); Mp 90-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (br s, 3H), 7.32 (br s, 2H), 6.93 (d, $^2J_{H\text{-}P}$ = 29.4 Hz, 1H), 3.85 (d, $^3J_{H\text{-}P}$ = 11.3 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 140.78 (dd, $^2J_{C\text{-}F}$ = 34.9 Hz, $^3J_{C\text{-}P}$ = 17.7 Hz), 131.26, 130.03, 128.40, 125.52, 120.38 (q, $^1J_{C\text{-}F}$ = 272.4 Hz), 54.47 (d, $^2J_{C\text{-}P}$ = 5.9 Hz); ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ 1.36; ^{19}F{H} NMR (376 MHz, $CDCl_3$) δ -68.06; HRMS for $C_{10}H_{13}F_3N_2O_3P^+$: calcd. $[M+H]^+$: 297.0610, found: 297.0604

Diethyl 2-(2-(dimethoxyphosphoryl)hydrazineylidene)malonate (3w)



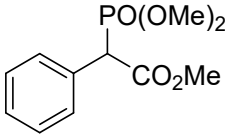
Colorless viscous liquid; isolated yield 56% (33 mg). R_f 0.50 (40% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.87 (d, $^2J_{H\text{-}P}$ = 34.6 Hz, 1H), 4.31-4.37 (m, 4), 3.86 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 6H), 1.35 (t, J = 7.0 Hz, 3H), 1.34 (t, J = 7.0 Hz, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 162.26, 160.43, 130.80 (d, $^3J_{C\text{-}P}$ = 14.8 Hz), 62.22, 61.93, 54.62 (d, $^2J_{C\text{-}P}$ = 5.9 Hz), 13.99, 13.88; ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ -0.13; HRMS for $C_9H_{18}N_2O_7P^+$: calcd. $[M+H]^+$: 297.0846, found: 297.0830

Dimethyl (2-(1,3-dioxo-1,3-diphenylpropan-2-ylidene)hydrazineyl)phosphonate (3x)



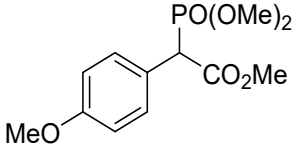
White solid; isolated yield 80% (57 mg). R_f 0.50 (40% EtOAc/hexane); Mp 102-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (d, $^2J_{H\text{-}P}$ = 33.1 Hz, 1H), 8.10-8.12 (m, 2H), 7.72-7.74 (m, 2H), 7.62-7.65 (m, 1H), 7.55-7.59 (m, 1H), 7.51 (t, J = 7.7 Hz, 2H), 7.42 (t, J = 7.8 Hz, 2H), 3.83 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 191.42, 190.06, 143.18 (d, $^3J_{C\text{-}P}$ = 13.8 Hz), 135.93, 135.12, 134.19, 133.65, 130.67, 128.88, 128.69, 128.45, 54.67 (d, $^2J_{C\text{-}P}$ = 5.9 Hz); ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ 0.26; HRMS for $C_{17}H_{18}N_2O_5P^+$: calcd. $[M+H]^+$: 361.0948, found: 361.0944

Methyl 2-(dimethoxyphosphoryl)-2-phenylacetate (4a)[8]



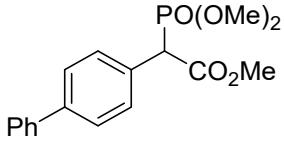
Colorless viscous liquid; isolated yield 55% (40 mg). R_f 0.50 (40% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.51 (m, 2H), 7.32-7.39 (m, 3H), 4.29 (d, $^2J_{H\text{-}P}$ = 23.5 Hz, 1H), 3.77 (s, 3H), 3.73 (d, $^3J_{H\text{-}P}$ = 11.0 Hz, 3H), 3.67 (d, $^3J_{H\text{-}P}$ = 10.9 Hz, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 168.01 (d, $^2J_{C\text{-}P}$ = 3.0 Hz), 130.57 (d, $J_{C\text{-}P}$ = 8.6 Hz), 129.56 (d, $J_{C\text{-}P}$ = 6.2 Hz), 128.71 (d, $J_{C\text{-}P}$ = 2.3 Hz), 128.18 (d, $J_{C\text{-}P}$ = 2.9 Hz), 54.08 (d, $^2J_{C\text{-}P}$ = 6.7 Hz), 53.70 (d, $^2J_{C\text{-}P}$ = 7.1 Hz), 52.95, 51.65 (d, $^1J_{C\text{-}P}$ = 135.2 Hz); ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ 21.11; HRMS for $C_{11}H_{16}O_5P^+$: calcd. $[M+H]^+$: 259.0730, found: 259.0730

Methyl 2-(dimethoxyphosphoryl)-2-(4-methoxyphenyl)acetate (4b)



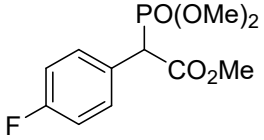
Colorless viscous liquid; isolated yield 60% (35 mg). R_f 0.50 (40% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.43 (m, 2H), 6.89 (d, J = 8.5 Hz, 2H), 4.23 (d, $^2J_{H\text{-}P}$ = 23.5 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.73 (d, $^3J_{H\text{-}P}$ = 11.0 Hz, 3H), 3.67 (d, $^3J_{H\text{-}P}$ = 10.8 Hz, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 168.23 (d, $^2J_{C\text{-}P}$ = 2.5 Hz), 159.51 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.68 ($J_{C\text{-}P}$ = 6.2 Hz), 122.38 ($J_{C\text{-}P}$ = 8.7 Hz), 114.16 ($J_{C\text{-}P}$ = 2.2 Hz), 55.26, 54.08 (d, $^2J_{C\text{-}P}$ = 6.6 Hz), 53.69 (d, $^2J_{C\text{-}P}$ = 7.2 Hz), 52.91, 50.69 (d, $^1J_{C\text{-}P}$ = 136.3 Hz); ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ 21.43; HRMS for $C_{12}H_{18}O_6P^+$: calcd. $[M+H]^+$: 289.0836, found: 289.0814

Methyl 2-([1,1'-biphenyl]-4-yl)-2-(dimethoxyphosphoryl)acetate (4c)



Colorless viscous liquid; isolated yield 52% (35 mg). R_f 0.50 (40% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.61 (m, 6H), 7.42-7.46 (m, 2H), 7.33-7.37 (m, 1H), 4.34 (d, $^2J_{H\text{-}P}$ = 23.5 Hz, 1H), 3.79 (s, 3H), 3.76 (d, $^3J_{H\text{-}P}$ = 11.0 Hz, 3H), 3.72 (d, $^3J_{H\text{-}P}$ = 10.9 Hz, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 168.01 (d, $^2J_{C\text{-}P}$ = 3.3 Hz), 141.07 (d, $J_{C\text{-}P}$ = 2.9 Hz), 140.40, 129.94 (d, $J_{C\text{-}P}$ = 6.4 Hz), 129.53 (d, $J_{C\text{-}P}$ = 8.7 Hz), 128.81, 127.51, 127.41 (d, $J_{C\text{-}P}$ = 2.2 Hz), 127.08, 54.13 (d, $^2J_{C\text{-}P}$ = 6.6 Hz), 53.78 (d, $^2J_{C\text{-}P}$ = 7.0 Hz), 53.02, 51.32 (d, $^1J_{C\text{-}P}$ = 135.2 Hz); ^{31}P{H} NMR (162 MHz, $CDCl_3$) δ 21.08; HRMS for $C_{17}H_{20}O_5P^+$: calcd. $[M+H]^+$: 335.1043, found: 335.1029

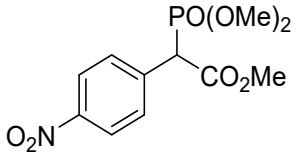
Methyl 2-(dimethoxyphosphoryl)-2-(4-fluorophenyl)acetate (4d)



Colorless viscous liquid; isolated yield 48% (26 mg). R_f 0.50 (40% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.51 (m, 2H), 7.05 (t, J = 8.5 Hz, 2H), 4.27 (d, $^2J_{H\text{-}P}$ = 23.8 Hz, 1H), 3.77 (s, 3H), 3.74 (d, $^3J_{H\text{-}P}$ = 11.0 Hz, 3H), 3.68 (d, $^3J_{H\text{-}P}$ = 10.9 Hz, 3H); ^{13}C{H} NMR

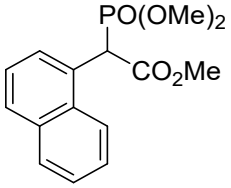
(100 MHz, $CDCl_3$) δ 167.89 (d, $^2J_{C\text{-}P}$ = 4.0 Hz), 162.64 (d, $^1J_{C\text{-}F}$ = 249.2 Hz), 131.30 (dd, $^3J_{C\text{-}F}$ = 7.9 Hz, $J_{C\text{-}P}$ = 6.7 Hz), 126.39 (dd, $^4J_{C\text{-}F}$ = 3.0 Hz, $J_{C\text{-}P}$ = 8.5 Hz), 115.66 (dd, $^2J_{C\text{-}F}$ = 21.3 Hz, $J_{C\text{-}P}$ = 2.2 Hz), 54.06 (d, $^2J_{C\text{-}P}$ = 6.6 Hz), 53.74 (d, $^2J_{C\text{-}P}$ = 7.0 Hz), 53.02, 50.75 (d, $^1J_{C\text{-}P}$ = 135.4 Hz); $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 20.84 (d, $J_{P\text{-}F}$ = 5.0 Hz); $^{19}F\{H\}$ NMR (376 MHz, $CDCl_3$) δ -113.96 (d, $J_{F\text{-}P}$ = 4.4 Hz); HRMS for $C_{11}H_{15}FO_5P^+$: calcd. $[M+H]^+$: 277.0636, found: 277.0627

Methyl 2-(dimethoxyphosphoryl)-2-(4-nitrophenyl)acetate (4e)[8]



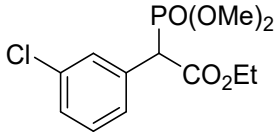
Colorless viscous liquid; isolated yield 45% (27 mg). R_f 0.50 (40% EtOAc/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.6 Hz, 2H), 7.70 (dd, J = 8.9 Hz, 2.2 Hz, 2H), 4.41 (d, $^2J_{H\text{-}P}$ = 24.1 Hz, 1H), 3.81 (s, 3H), 3.77 (d, $^3J_{H\text{-}P}$ = 11.1 Hz, 3H), 3.73 (d, $^3J_{H\text{-}P}$ = 11.0 Hz, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 166.98 (d, $^2J_{C\text{-}P}$ = 4.4 Hz), 147.73 (d, $J_{C\text{-}P}$ = 3.2 Hz), 138.04 ($J_{C\text{-}P}$ = 8.5 Hz), 130.62 ($J_{C\text{-}P}$ = 6.3 Hz), 123.72 ($J_{C\text{-}P}$ = 2.2 Hz), 54.19 (d, $^2J_{C\text{-}P}$ = 6.6 Hz), 53.99 (d, $^2J_{C\text{-}P}$ = 6.9 Hz), 53.33, 51.44 (d, $^1J_{C\text{-}P}$ = 133.4 Hz); $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 19.43; HRMS for $C_{11}H_{15}NO_7P^+$: calcd. $[M+H]^+$: 304.0581, found: 304.0576

Methyl 2-(dimethoxyphosphoryl)-2-(naphthalen-1-yl)acetate (4f)



Colorless viscous liquid; isolated yield 50% (31 mg). R_f 0.50 (40% EtOAc/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.5 Hz, 1H), 8.00 (dd, J = 7.1 Hz, 2.5 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.49-7.53 (m, 2H), 5.17 (d, $^2J_{H\text{-}P}$ = 24.1 Hz, 1H), 3.74 (s, 3H), 3.73 (d, $^3J_{H\text{-}P}$ = 11.0 Hz, 3H), 3.58 (d, $^3J_{H\text{-}P}$ = 10.8, Hz, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 168.44 (d, $^2J_{C\text{-}P}$ = 2.4 Hz), 134.03, 131.51 ($J_{C\text{-}P}$ = 6.8 Hz), 129.10, 128.89 (d, $J_{C\text{-}P}$ = 2.9 Hz), 127.95 ($J_{C\text{-}P}$ = 6.3 Hz), 126.81, 126.68 (d, $J_{C\text{-}P}$ = 7.9 Hz), 125.81, 125.40 (d, $J_{C\text{-}P}$ = 3.0 Hz), 122.77, 54.01 (d, $^2J_{C\text{-}P}$ = 6.6 Hz), 53.69 (d, $^2J_{C\text{-}P}$ = 7.0 Hz), 53.04, 46.25 (d, $^1J_{C\text{-}P}$ = 139.3 Hz); $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 21.67; HRMS for $C_{15}H_{18}O_5P^+$: calcd. $[M+H]^+$: 309.0886, found: 309.0889

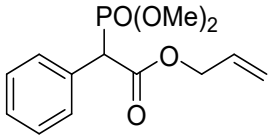
Ethyl 2-(3-chlorophenyl)-2-(dimethoxyphosphoryl)acetate (4g)



Colorless viscous liquid; isolated yield 45% (28 mg). R_f 0.50 (40% EtOAc/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.31-7.34 (m, 1H), 7.20-7.21 (m, 2H), 4.08-4.20 (m, 3H), 3.66 (d, $^3J_{H\text{-}P}$ = 11.0 Hz, 3H), 3.63 (d, $^3J_{H\text{-}P}$ = 11.0 Hz, 3H), 1.19 (t, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 166.70 (d, $^2J_{C\text{-}P}$ = 3.6 Hz), 134.09 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.45 (d, $J_{C\text{-}P}$ = 8.5 Hz), 129.55 ($J_{C\text{-}P}$ = 2.3 Hz), 129.34 ($J_{C\text{-}P}$ = 6.4 Hz), 128.03 ($J_{C\text{-}P}$ = 2.8 Hz), 127.59 ($J_{C\text{-}P}$ = 6.3 Hz), 61.90, 53.79 (d, $^2J_{C\text{-}P}$ = 6.6 Hz), 53.51 (d, $^2J_{C\text{-}P}$ = 7.1 Hz), 51.05 (d, $^1J_{C\text{-}P}$ = 134.4 Hz),

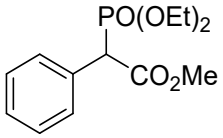
13.71; $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 20.59; HRMS for $C_{12}H_{17}ClO_5P^+$: calcd. $[M+H]^+$: 307.0497, found: 307.0491

Allyl 2-(dimethoxyphosphoryl)-2-phenylacetate (4h)[8]



Colorless viscous liquid; isolated yield 66% (38 mg). R_f 0.50 (50% EtOAc/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.44 (m, 2H), 7.23-7.30 (m, 3H), 5.77-5.87 (m, 1H), 5.24 (dd, J = 17.2 Hz, 1.4 Hz, 1H), 5.15 (dd, J = 10.4 Hz, 1.1 Hz, 1H), 4.53-4.63 (m, 2H), 4.24 (d, $^2J_{H\text{-}P}$ = 23.5 Hz, 1H), 3.64 (d, $^3J_{H\text{-}P}$ = 11.0 Hz, 3H), 3.59 (d, $^3J_{H\text{-}P}$ = 10.9 Hz, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 167.18 (d, $^2J_{C\text{-}P}$ = 3.1 Hz), 131.41, 130.55 ($J_{C\text{-}P}$ = 8.6 Hz), 129.58 ($J_{C\text{-}P}$ = 6.5 Hz), 128.68 ($J_{C\text{-}P}$ = 2.2 Hz), 128.15 ($J_{C\text{-}P}$ = 3.0 Hz), 118.76, 66.38, 54.03 (d, $^2J_{C\text{-}P}$ = 6.6 Hz), 53.69 (d, $^2J_{C\text{-}P}$ = 6.8 Hz), 51.75 (d, $^1J_{C\text{-}P}$ = 134.9 Hz); $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 21.14; HRMS for $C_{13}H_{18}O_5P^+$: calcd. $[M+H]^+$: 285.0886 found: 285.0882

Methyl 2-(diethoxyphosphoryl)-2-phenylacetate (4i)[8]



Colorless viscous liquid; isolated yield 60% (35 mg). R_f 0.50 (40% EtOAc/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.46 (m, 2H), 7.24-7.30 (m, 3H), 4.19 (d, $^2J_{H\text{-}P}$ = 23.6 Hz, 1H), 3.87-4.06 (m, 4H), 3.69 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 168.16 (d, $^2J_{C\text{-}P}$ = 3.4 Hz), 130.86 (d, $J_{C\text{-}P}$ = 8.3 Hz), 129.64 ($J_{C\text{-}P}$ = 6.5 Hz), 128.56 ($J_{C\text{-}P}$ = 2.3 Hz), 128.02 ($J_{C\text{-}P}$ = 2.9 Hz), 63.49 (d, $^2J_{C\text{-}P}$ = 6.8 Hz), 63.16 (d, $^2J_{C\text{-}P}$ = 7.0 Hz), 52.80, 52.13 (d, $^1J_{C\text{-}P}$ = 133.6 Hz), 16.29 (d, $^3J_{C\text{-}P}$ = 6.4 Hz), 16.23 (d, $^3J_{C\text{-}P}$ = 6.4 Hz); $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$) δ 18.54; HRMS for $C_{13}H_{20}O_5P^+$: calcd. $[M+H]^+$: 287.1043 found: 287.1043

6. References

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7. Copies of ^{1}H, $^{13}C\{H\}$, $^{31}P\{H\}$, $^{19}F\{H\}$ NMR Spectra & ESMS of crude 4a

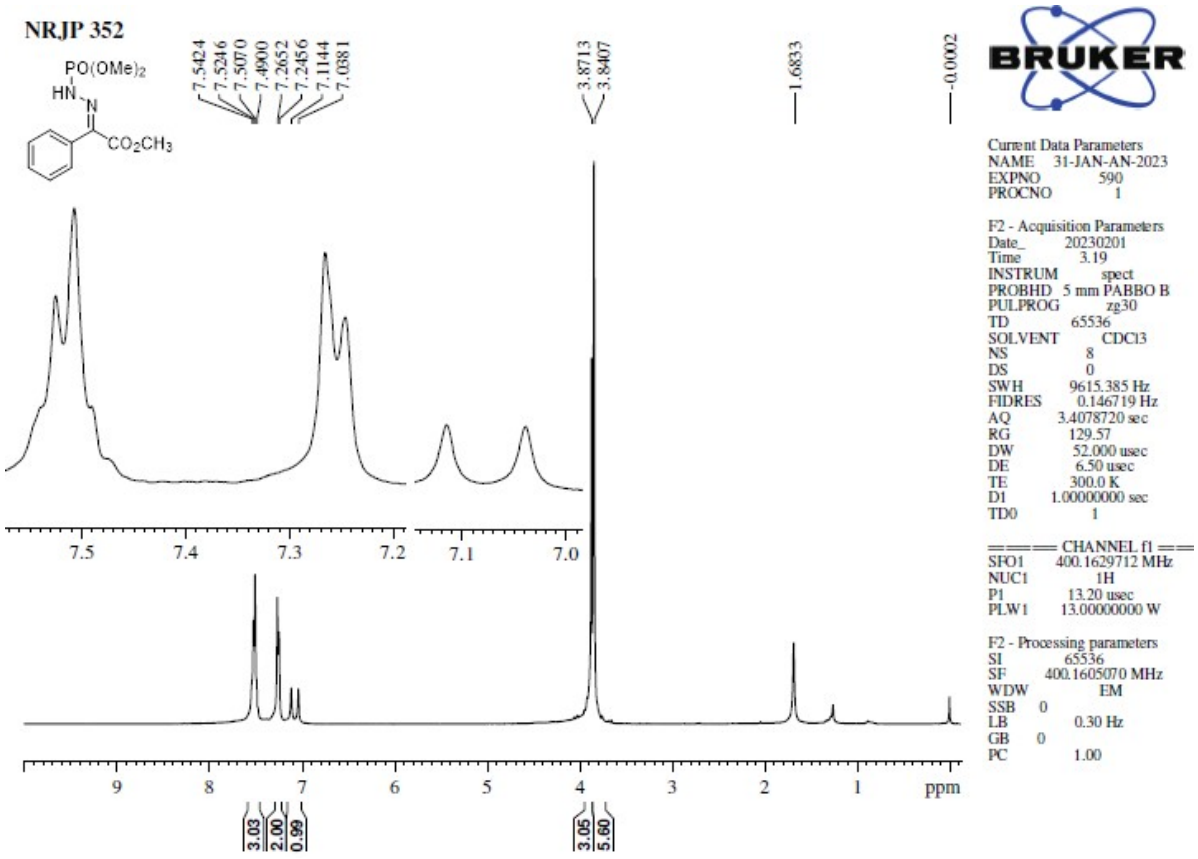


Figure S3: ^{1}H NMR spectrum of 3a

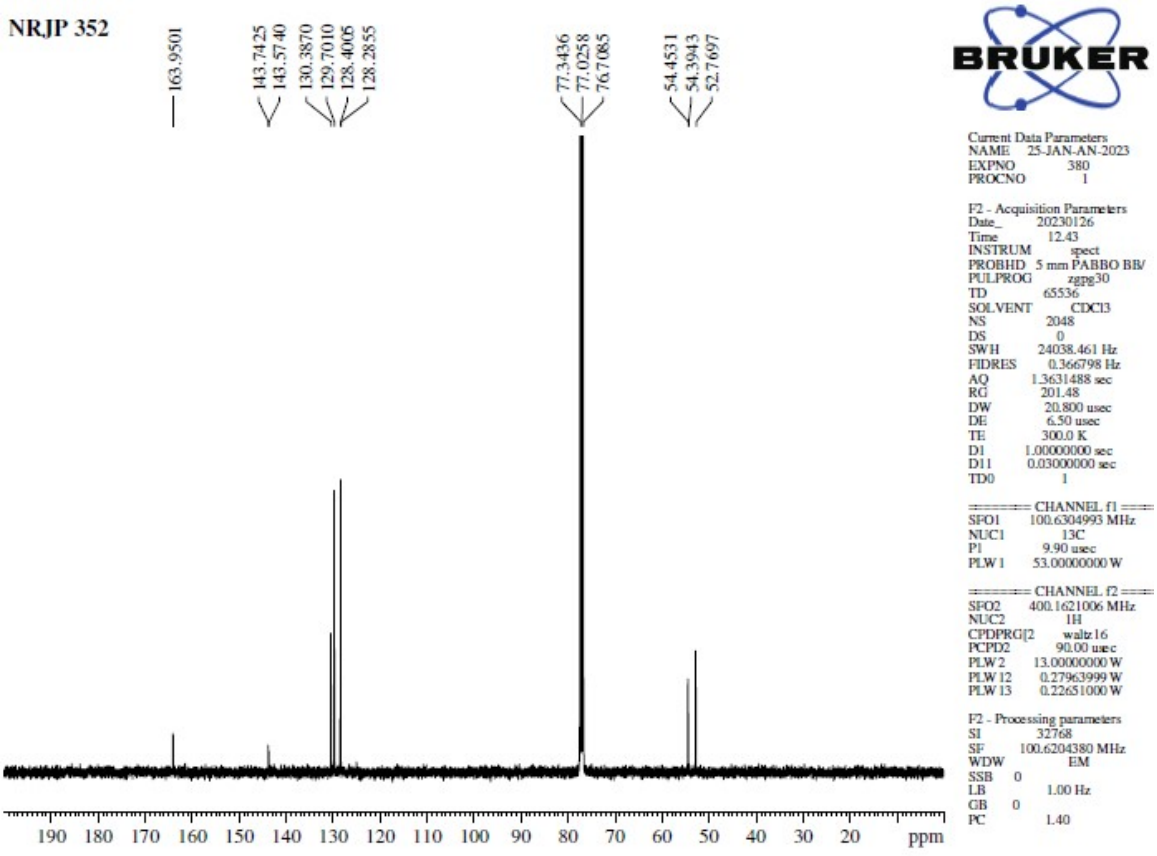


Figure S4: $^{13}C\{H\}$ NMR spectrum of 3a

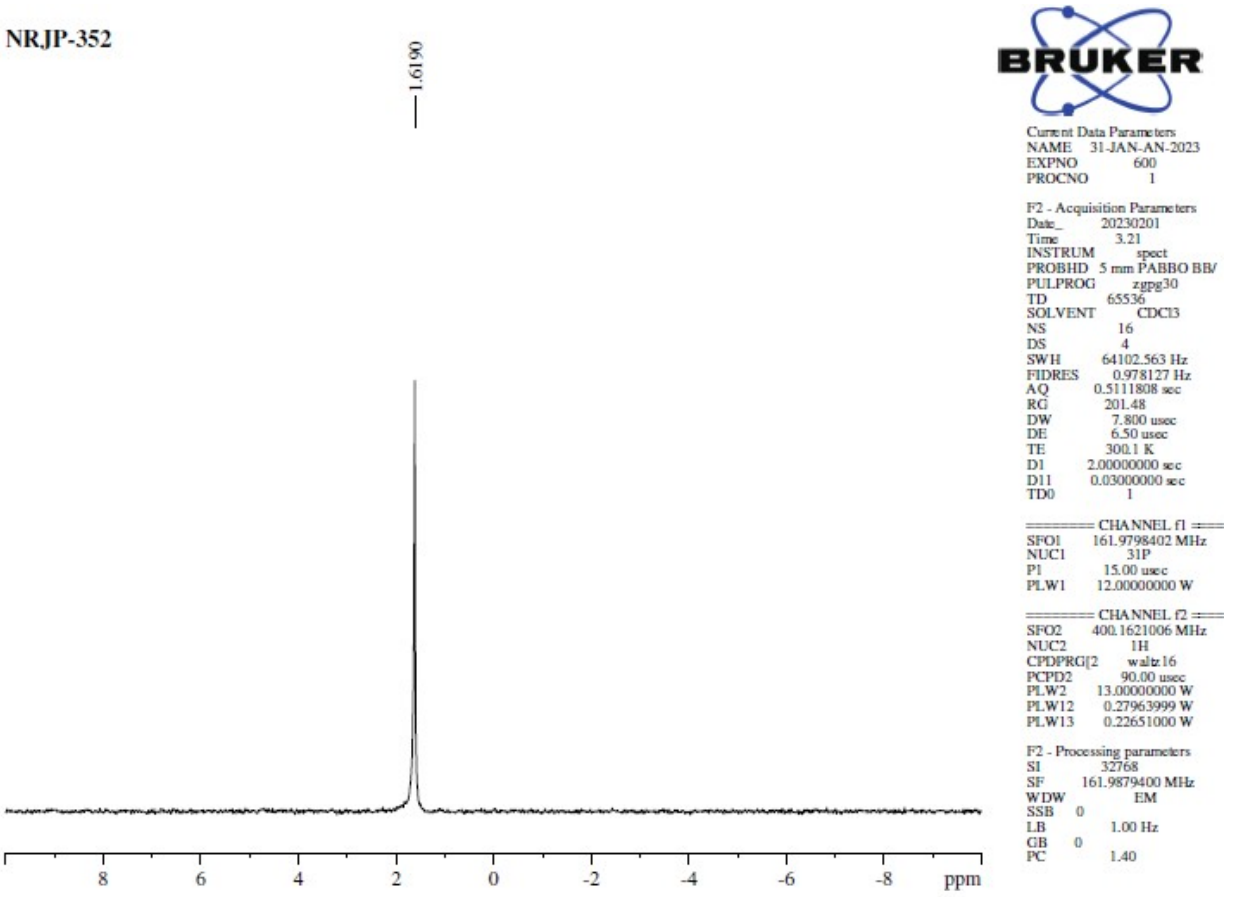


Figure S5: $^{31}P\{H\}$ NMR spectrum of 3a

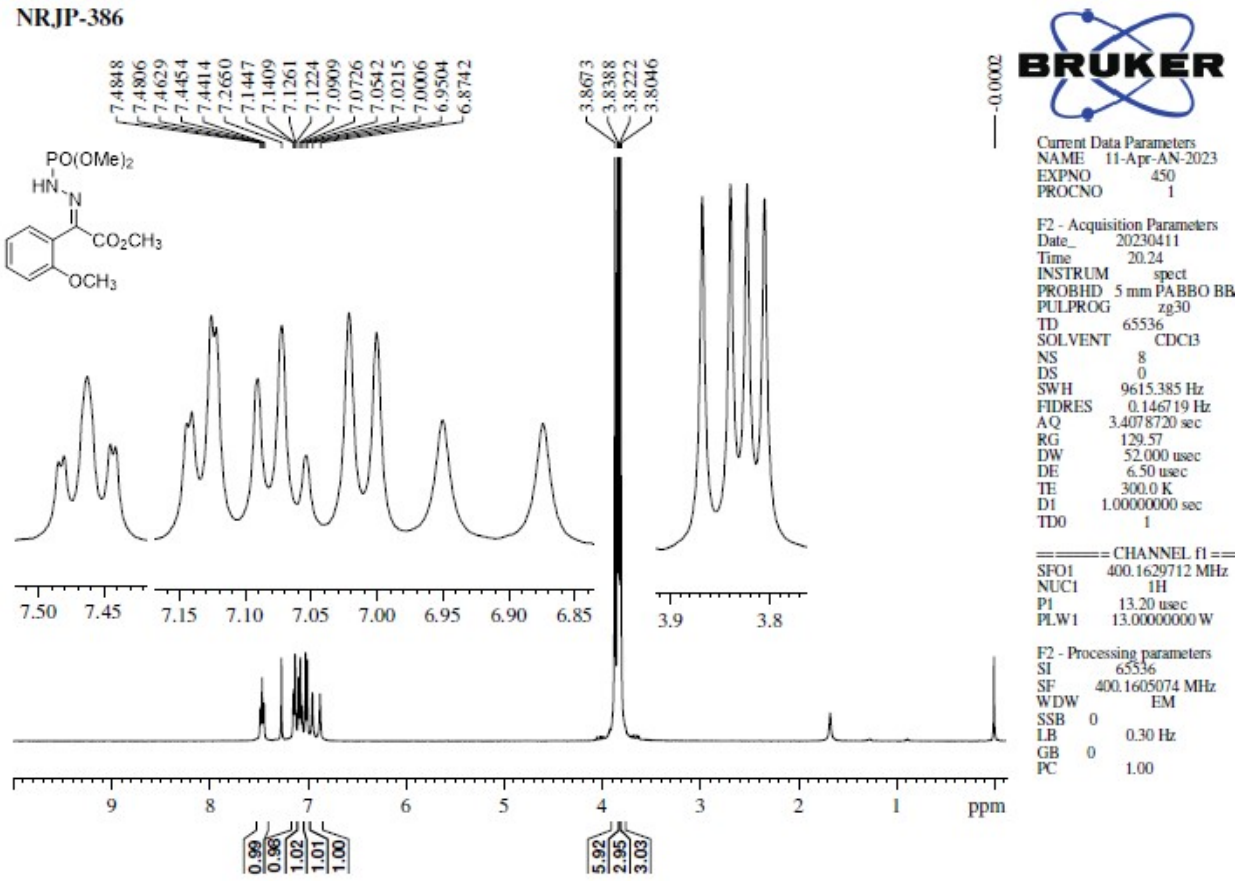


Figure S6: ^{1}H NMR spectrum of 3b

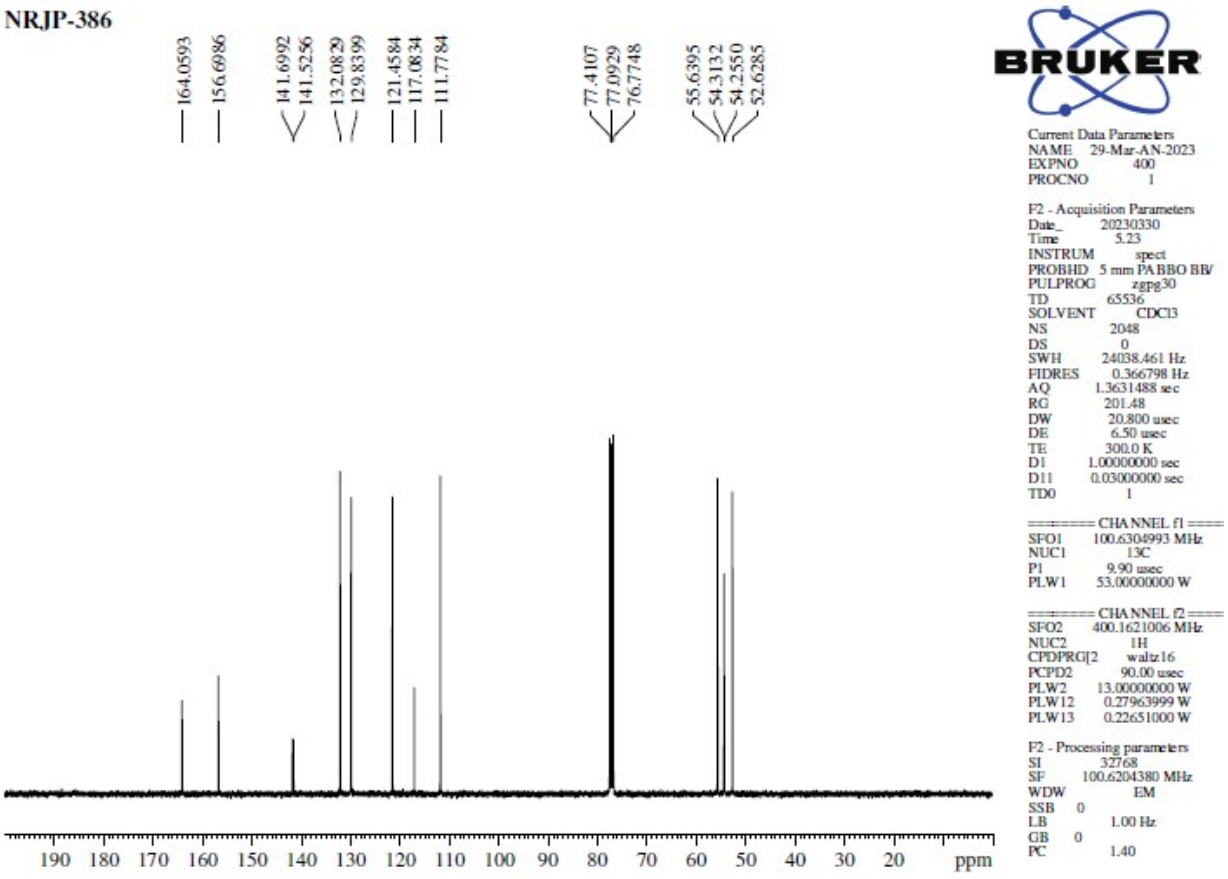


Figure S7: $^{13}C\{H\}$ NMR spectrum of 3b

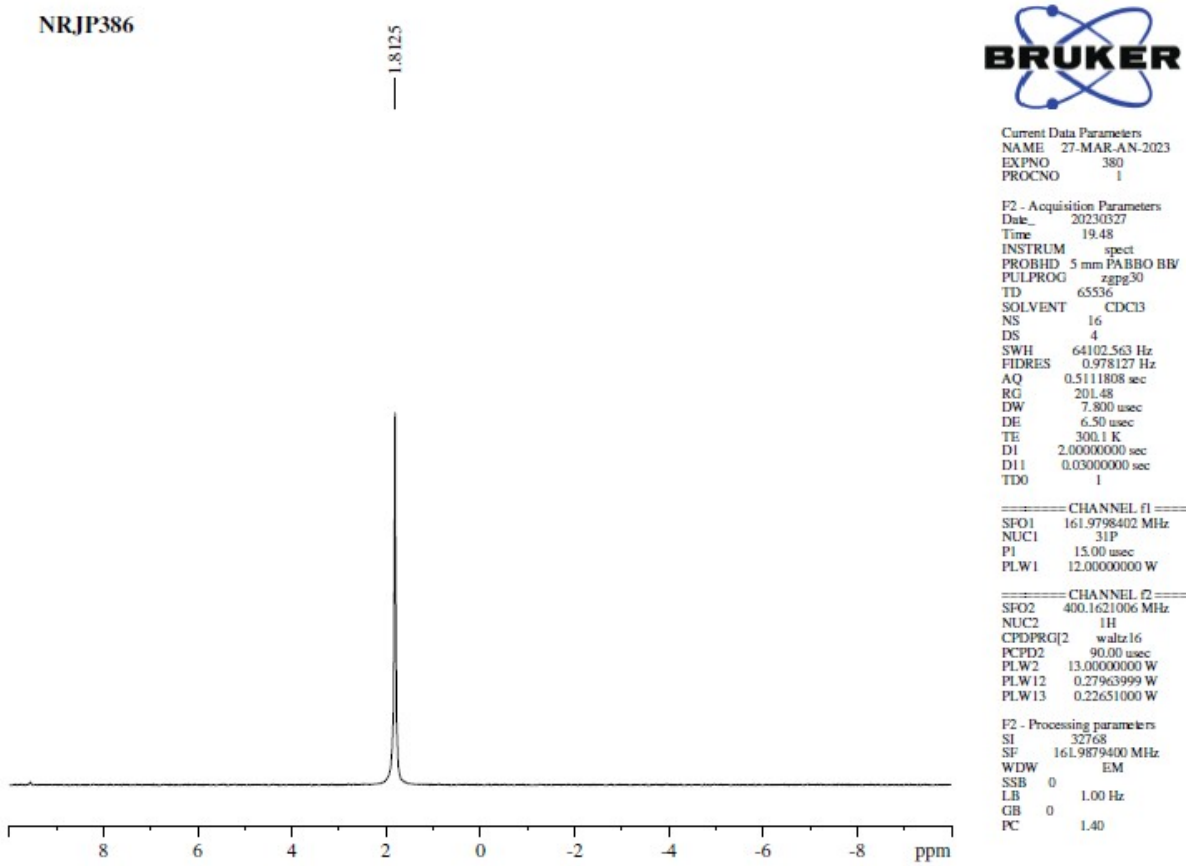


Figure S8: $^{31}P\{H\}$ NMR spectrum of 3b

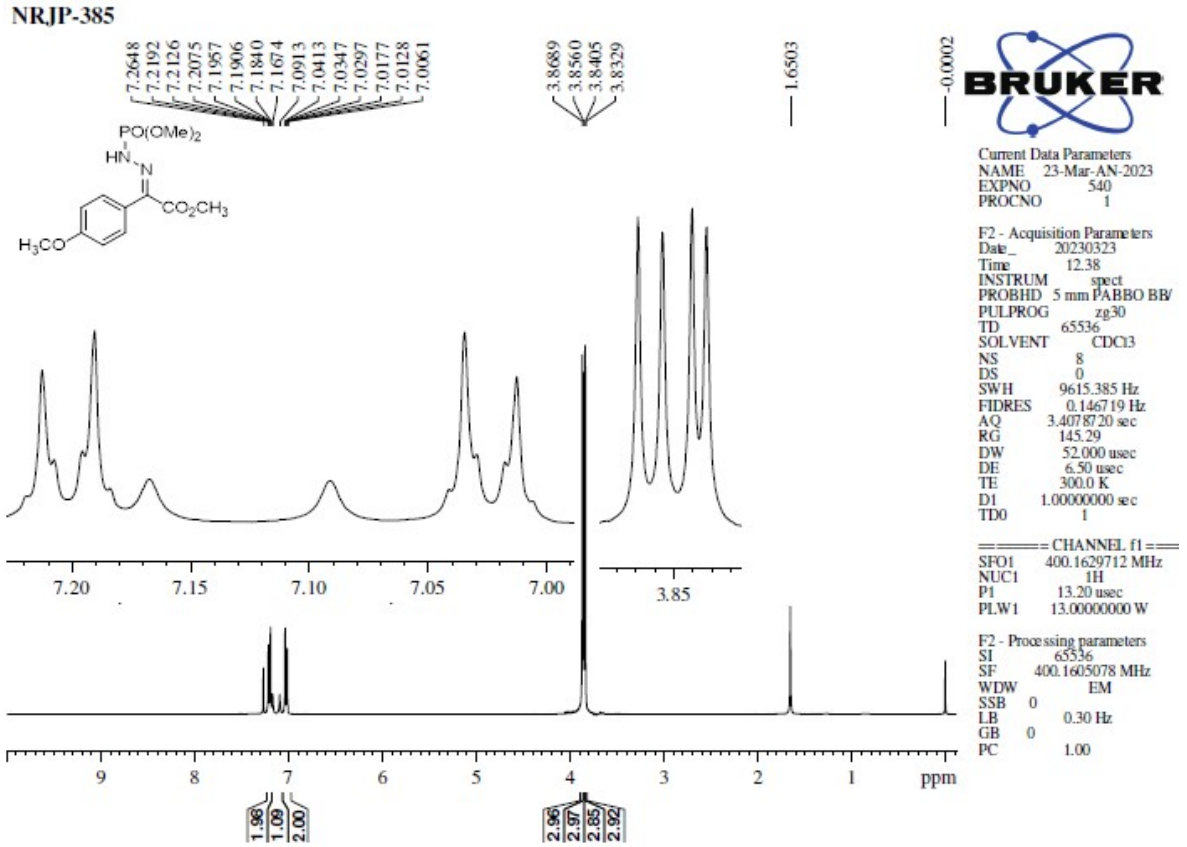


Figure S9: ^{1}H NMR spectrum of 3c

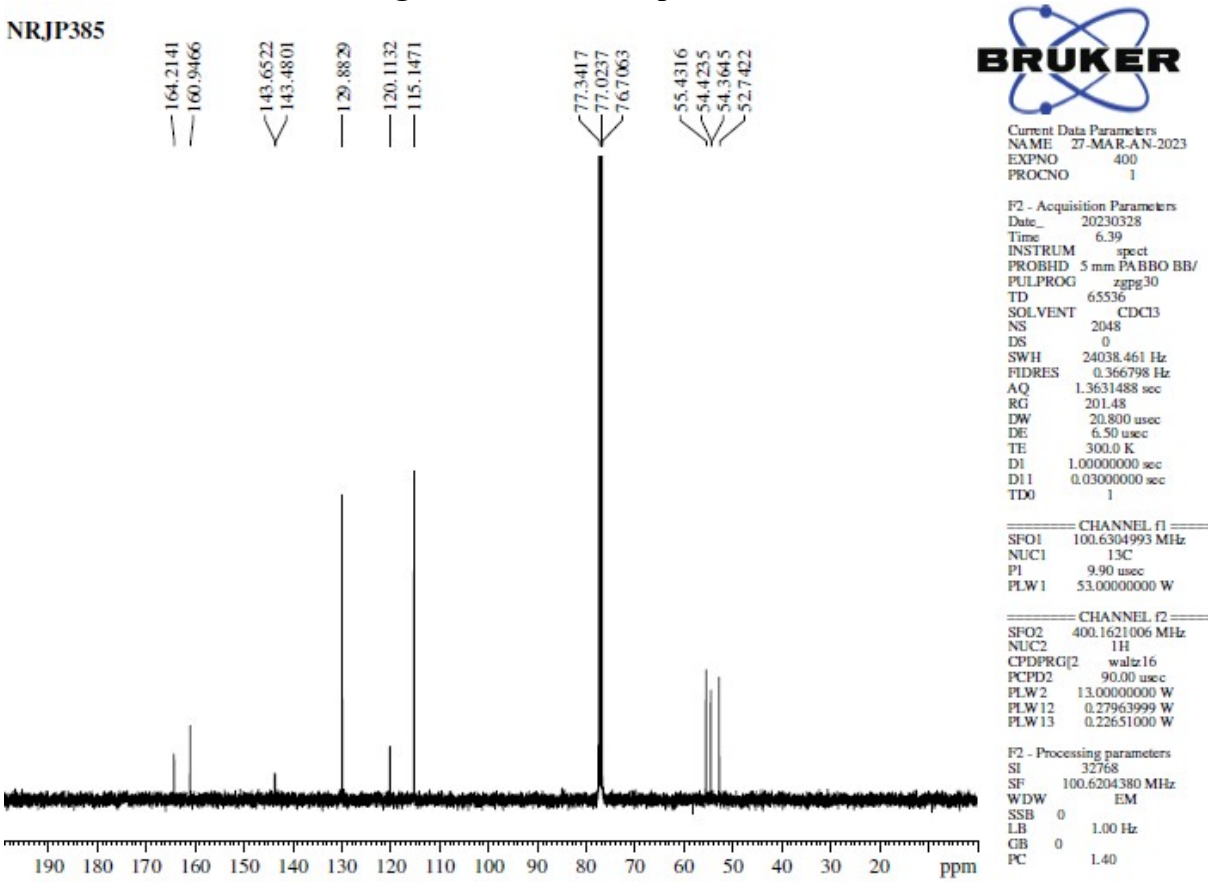


Figure S10: ^{13}C{H} NMR spectrum of 3c

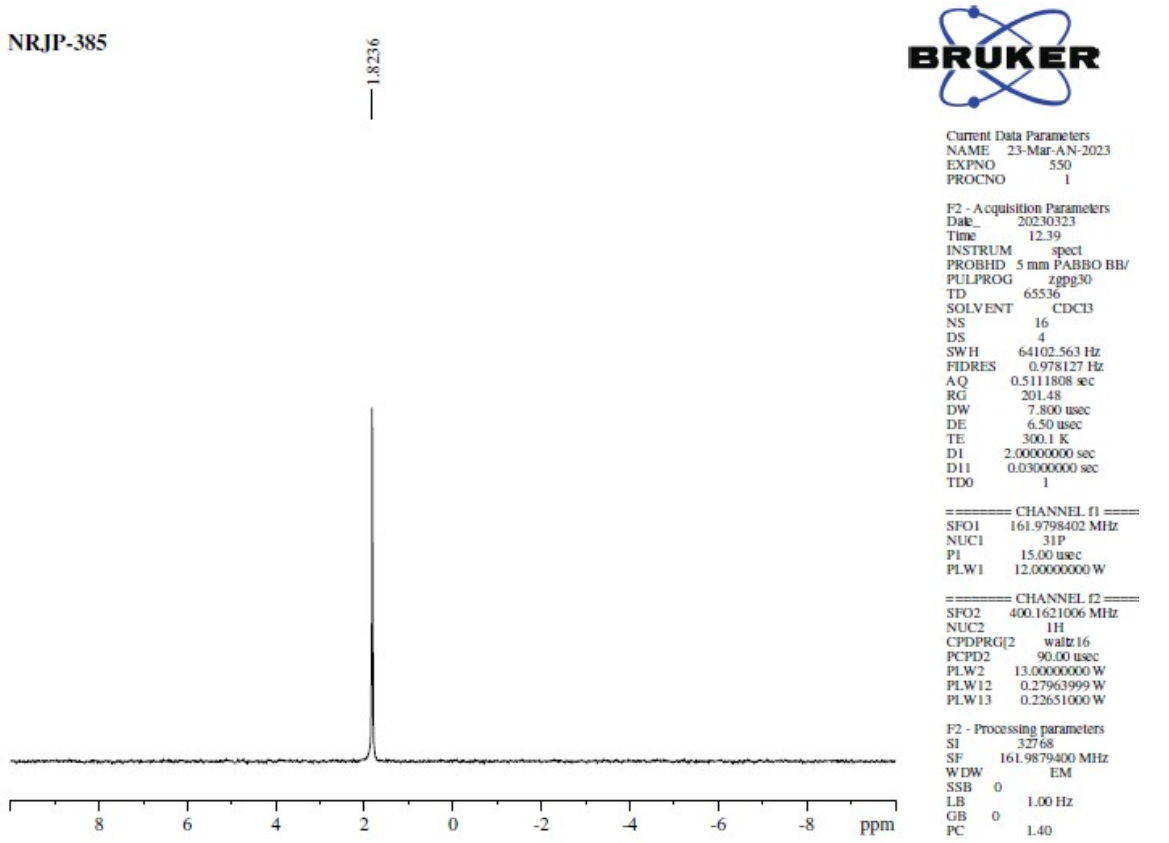


Figure S11: $^{31}P\{H\}$ NMR spectrum of 3c

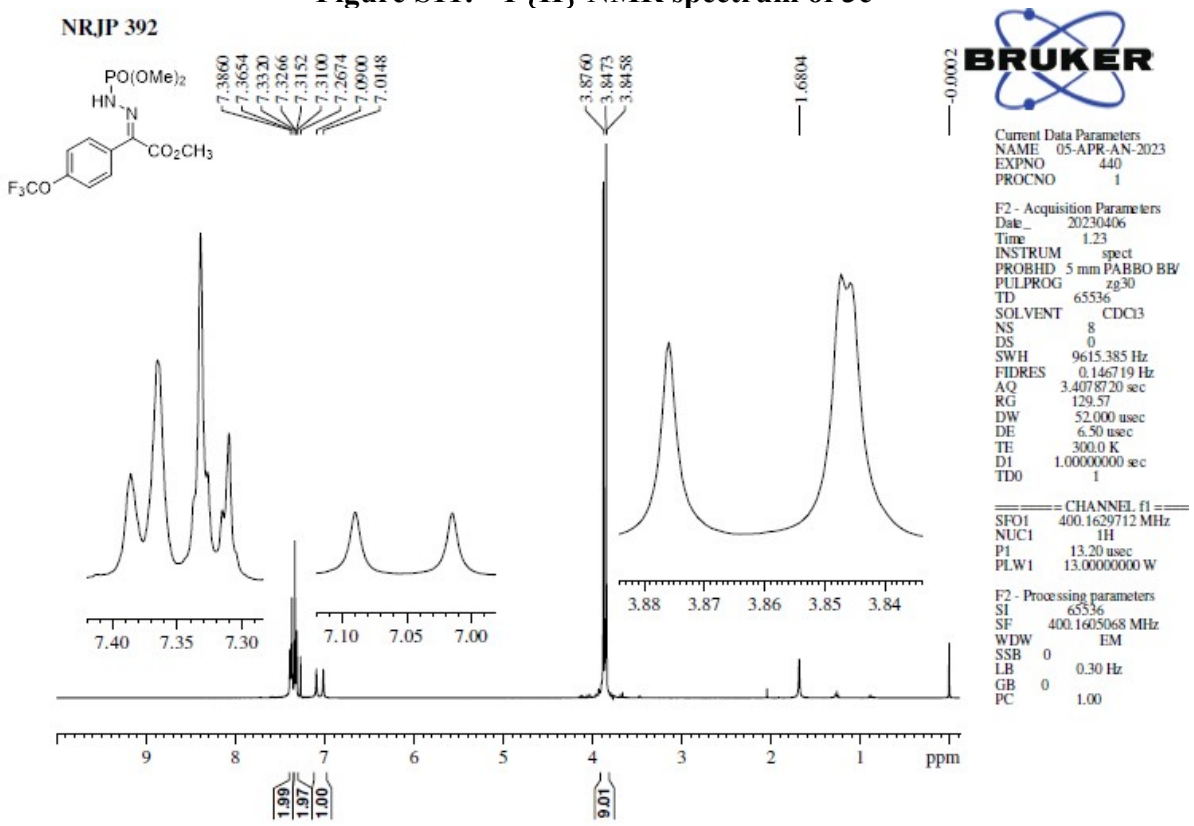


Figure S12: ^{1}H NMR spectrum of 3d

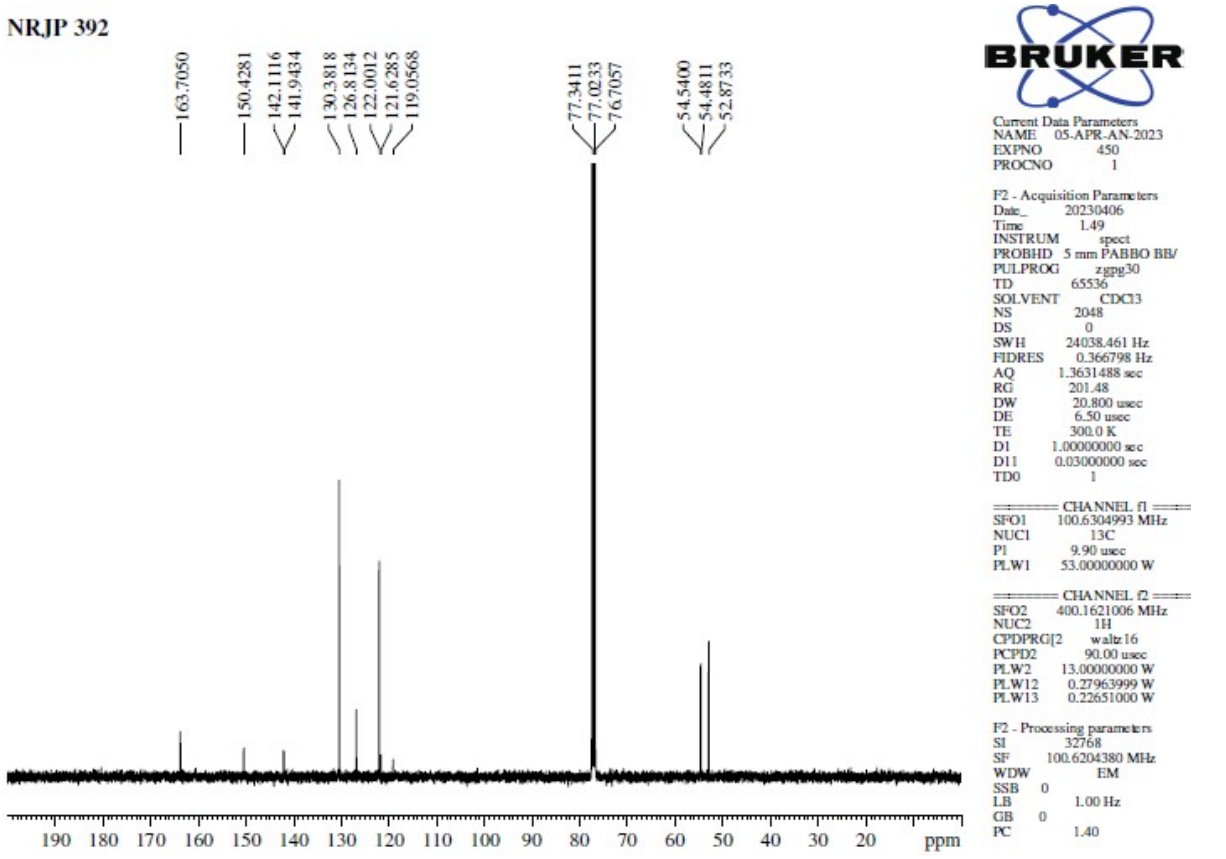


Figure S13: $^{13}C\{H\}$ NMR spectrum of 3d

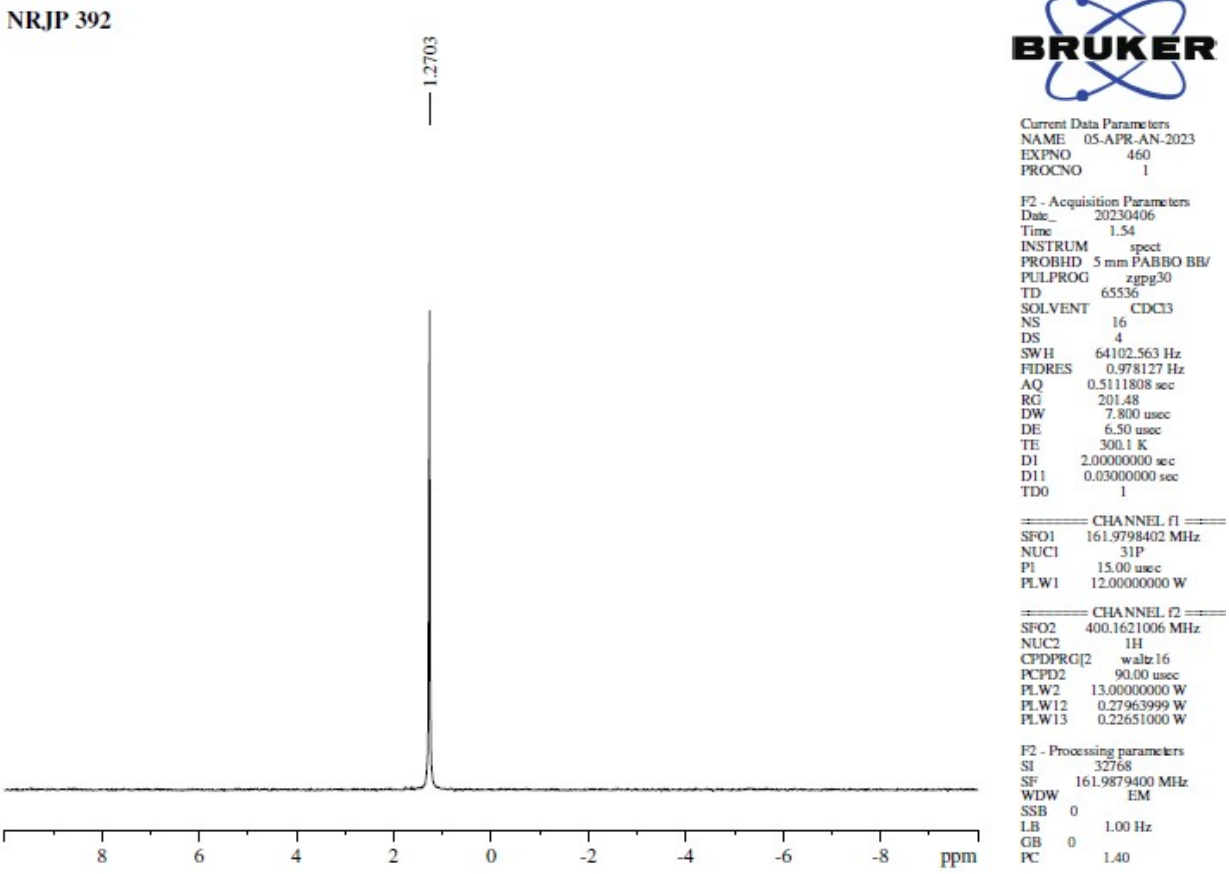


Figure S14: $^{31}P\{H\}$ NMR spectrum of 3d

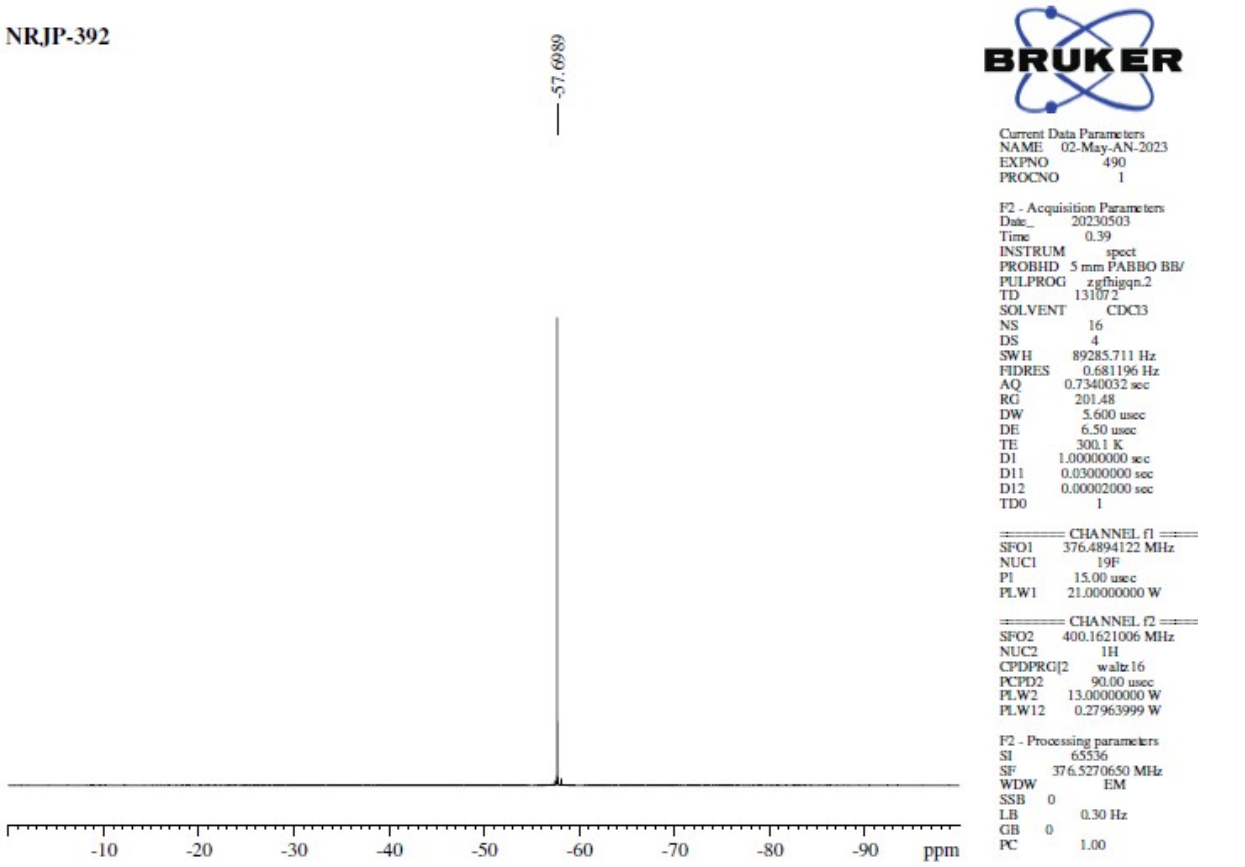


Figure S15: $^{19}F\{H\}$ NMR spectrum of 3d

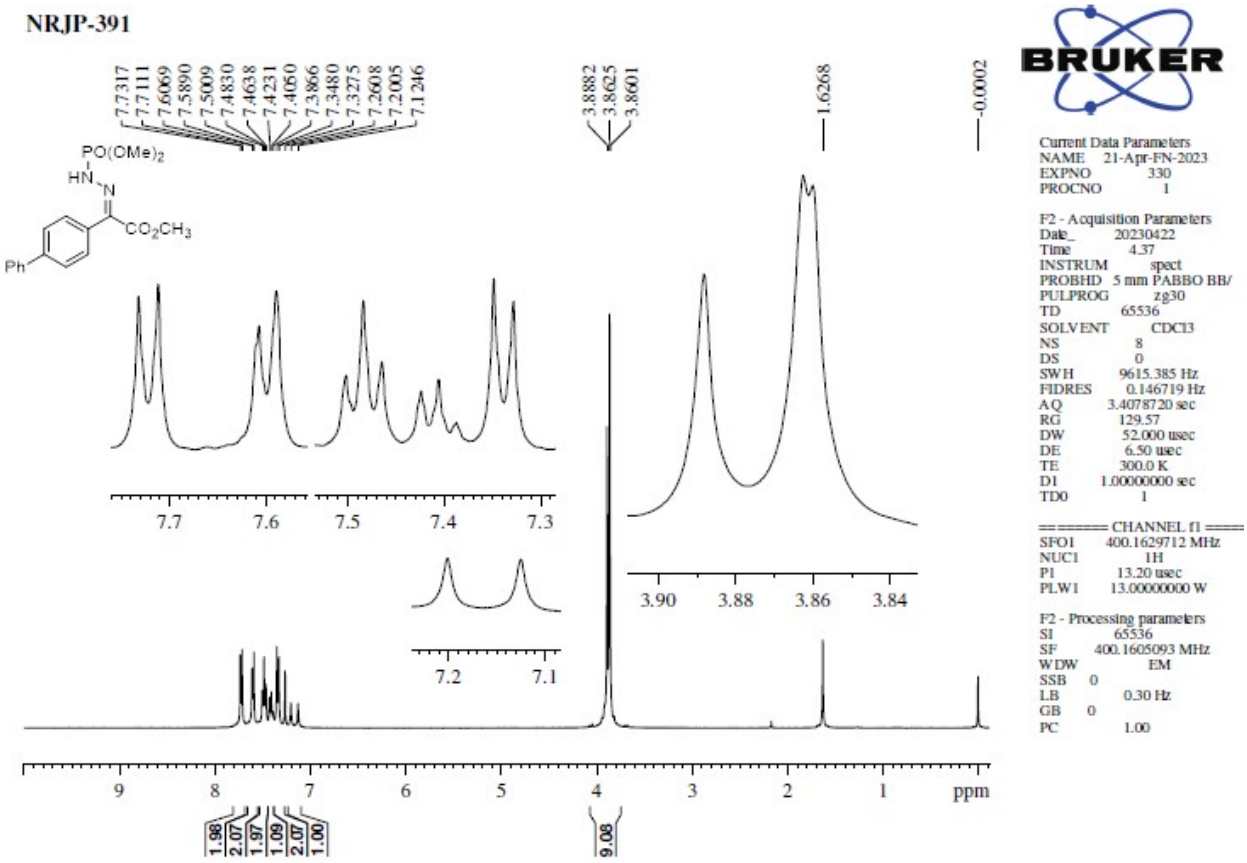


Figure S16: ^{1}H NMR spectrum of 3e

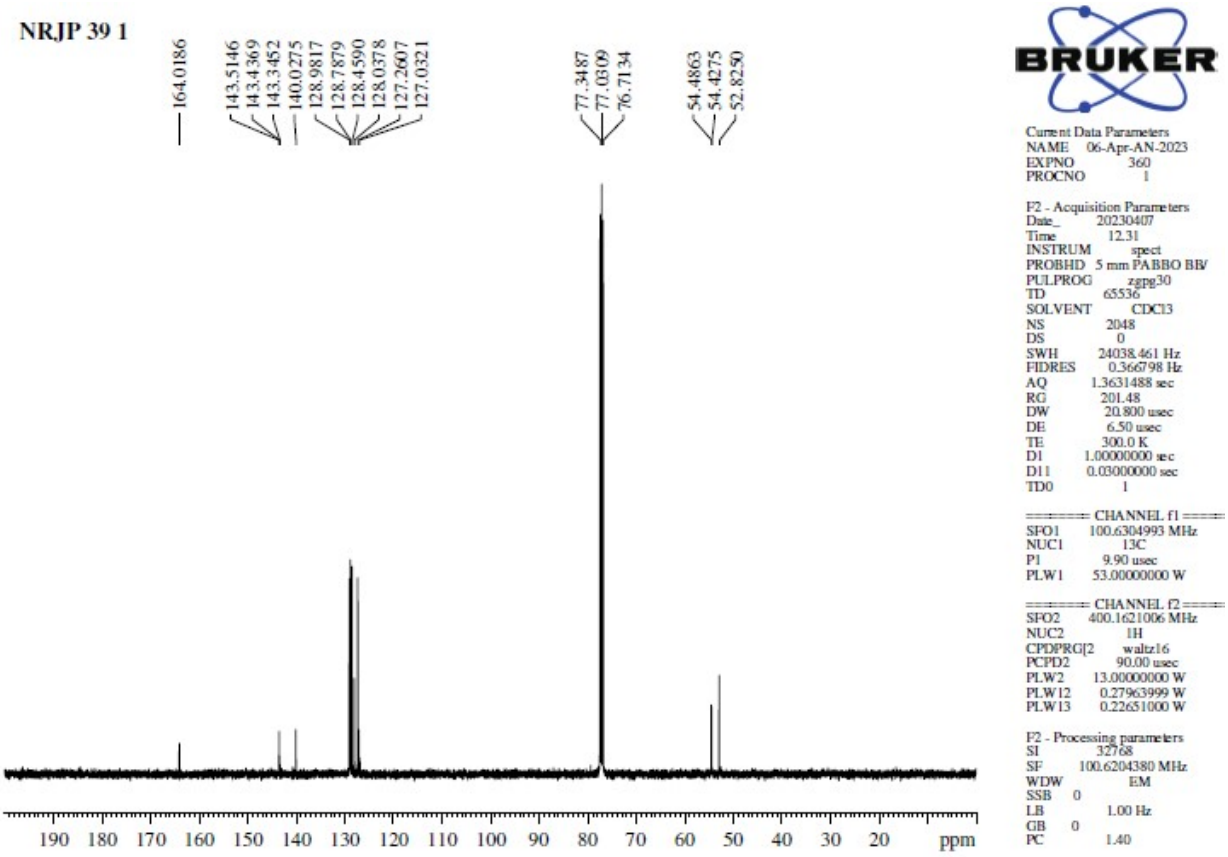


Figure S17: $^{13}C\{H\}$ NMR spectrum of 3e

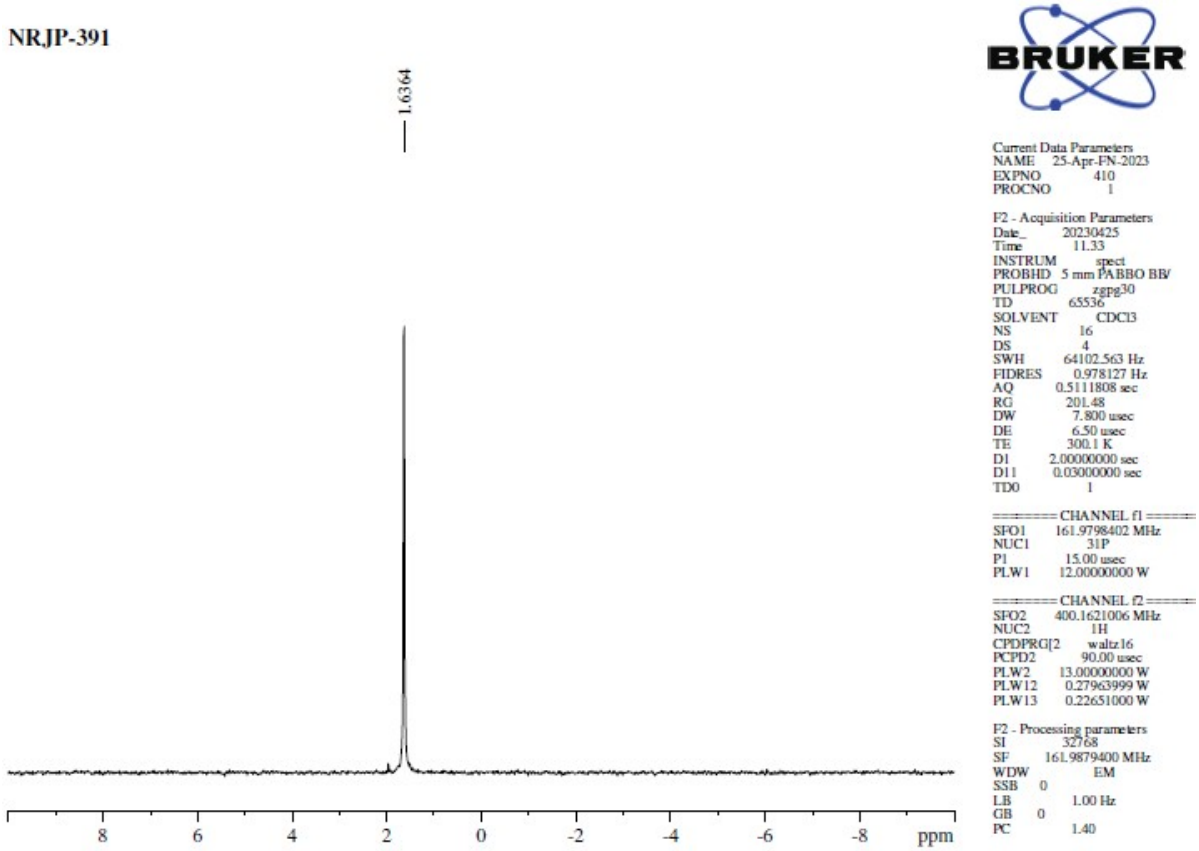


Figure S18: $^{31}P\{H\}$ NMR spectrum of 3e

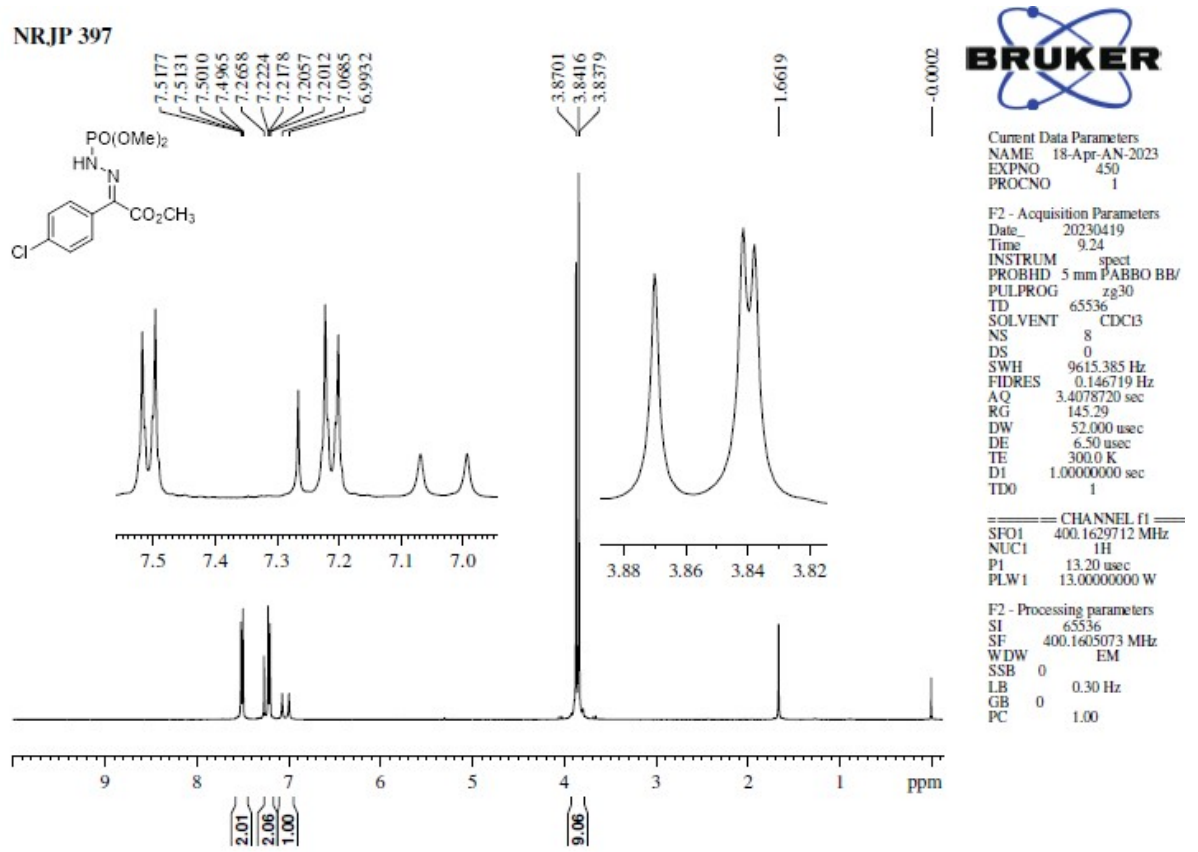


Figure S19: ^{1}H NMR spectrum of 3f

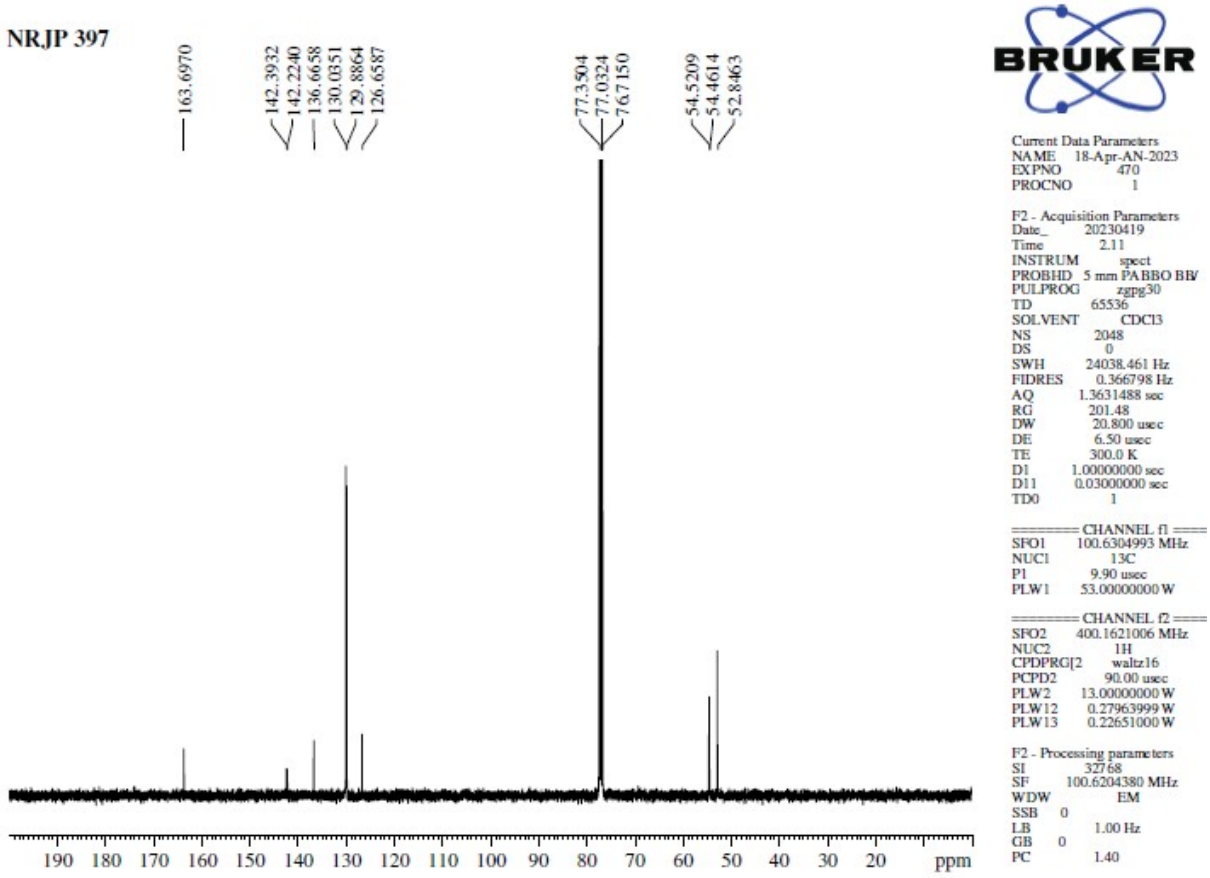


Figure S20: ^{13}C{H} NMR spectrum of 3f

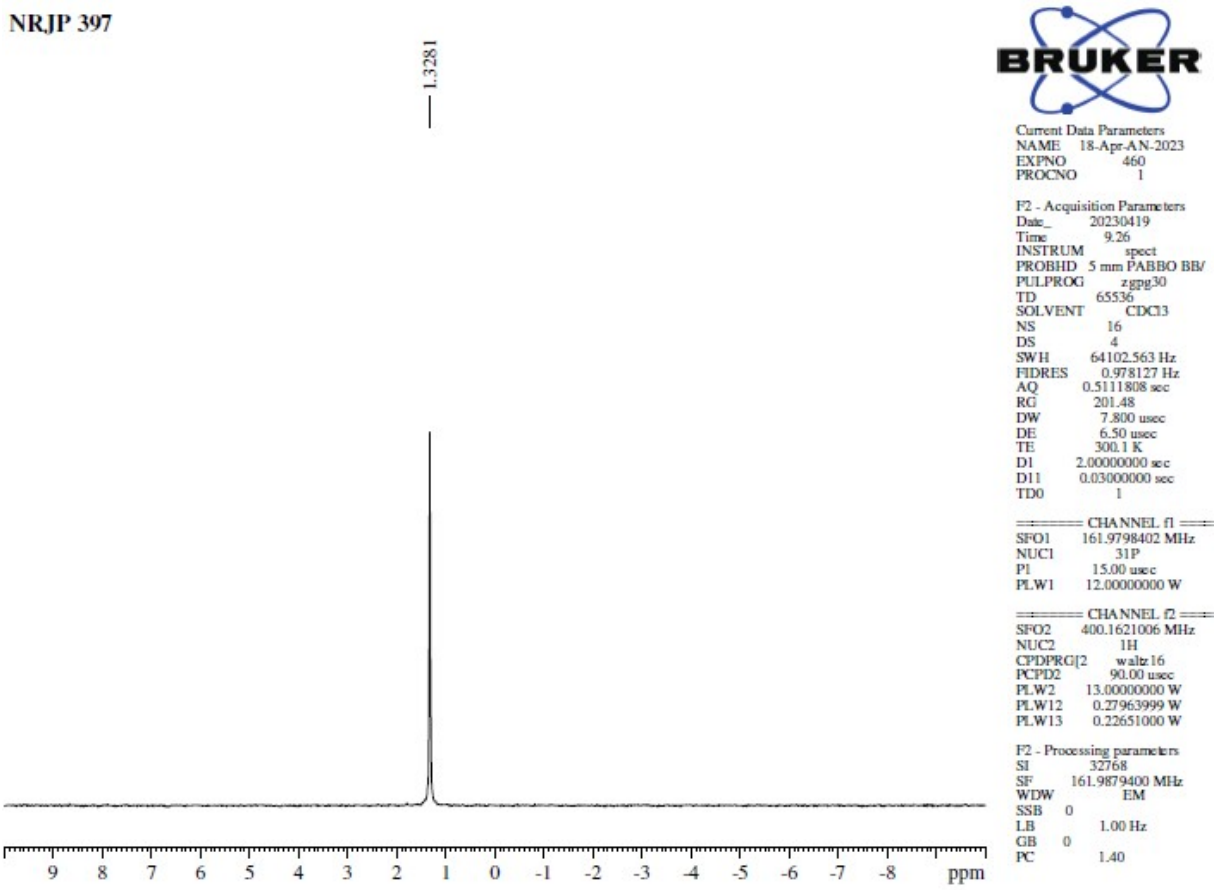


Figure S21: $^{31}P\{H\}$ NMR spectrum of 3f

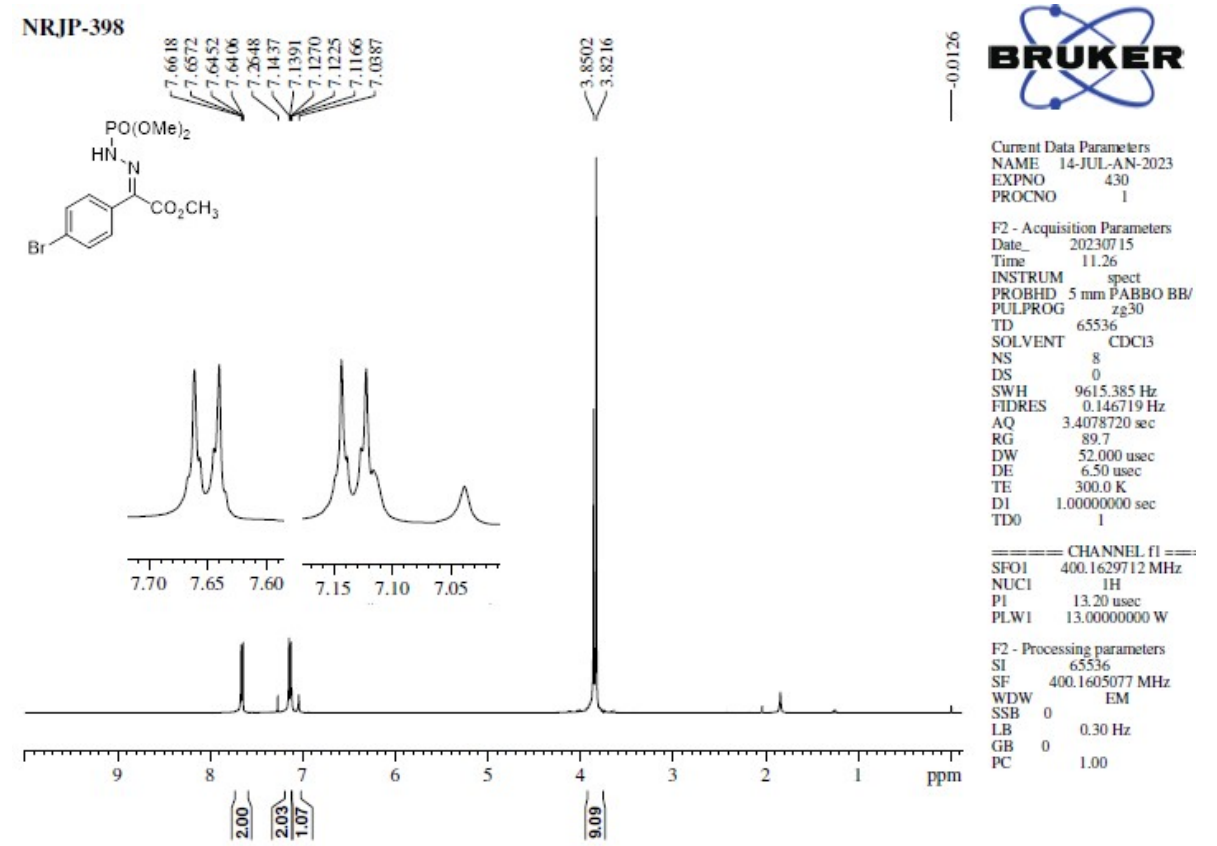


Figure S22: ^{1}H NMR spectrum of 3g

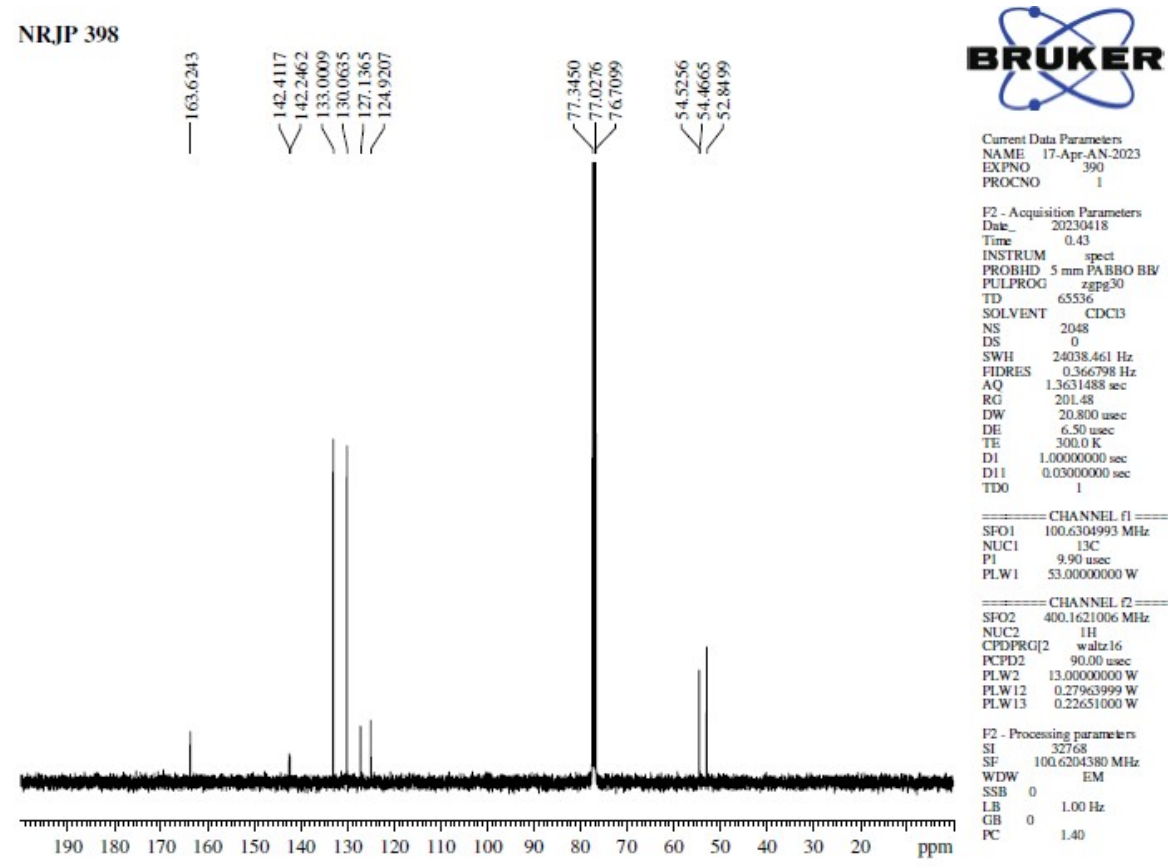


Figure S23: $^{13}C\{H\}$ NMR spectrum of 3g

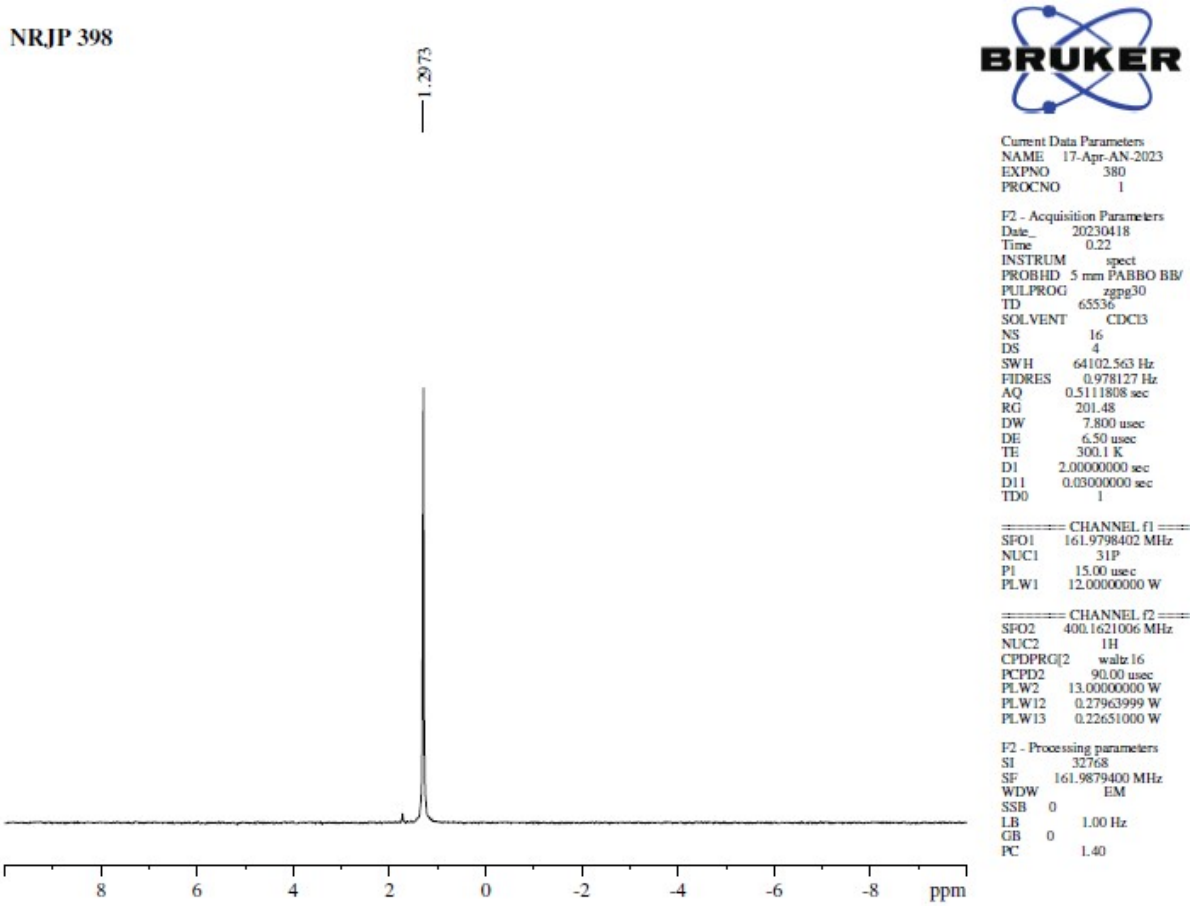


Figure S24: $^{31}P\{H\}$ NMR spectrum of 3g

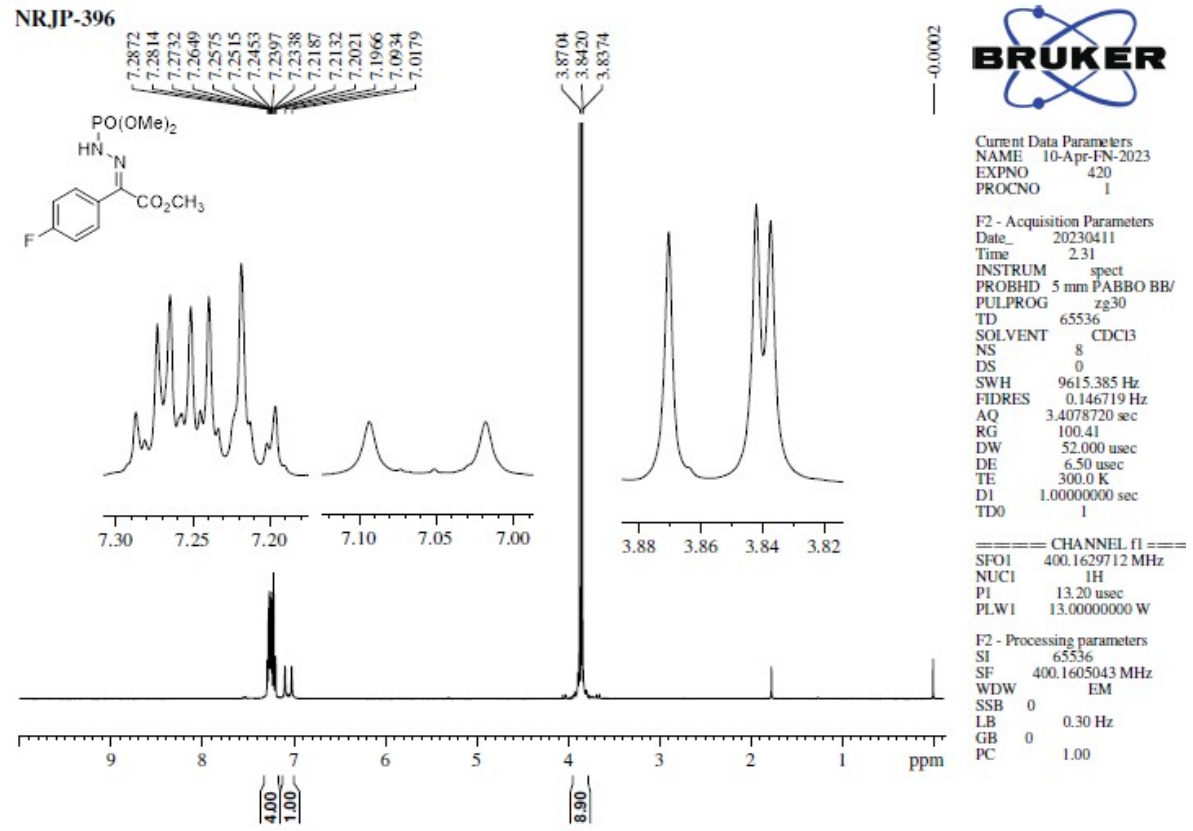


Figure S25: ^{1}H NMR spectrum of 3h

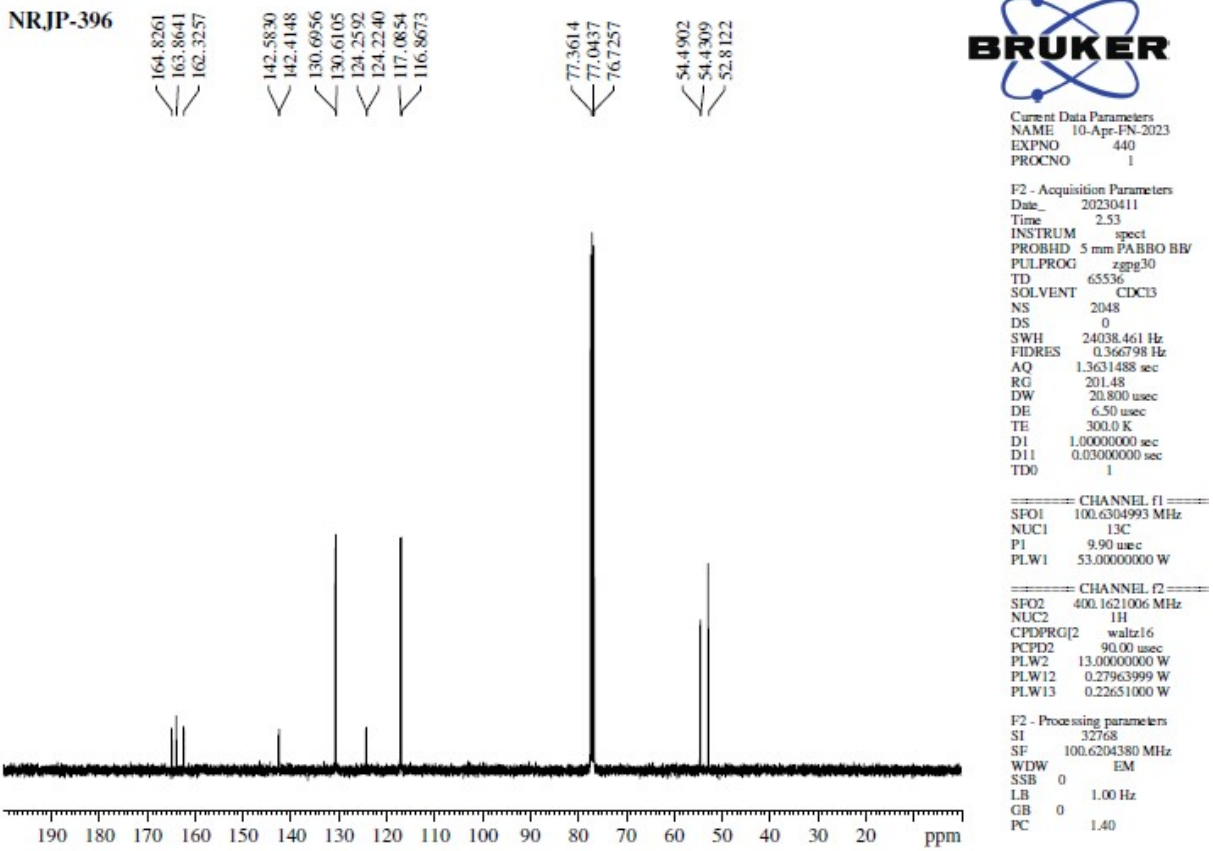


Figure S26: ^{13}C{H} NMR spectrum of 3h

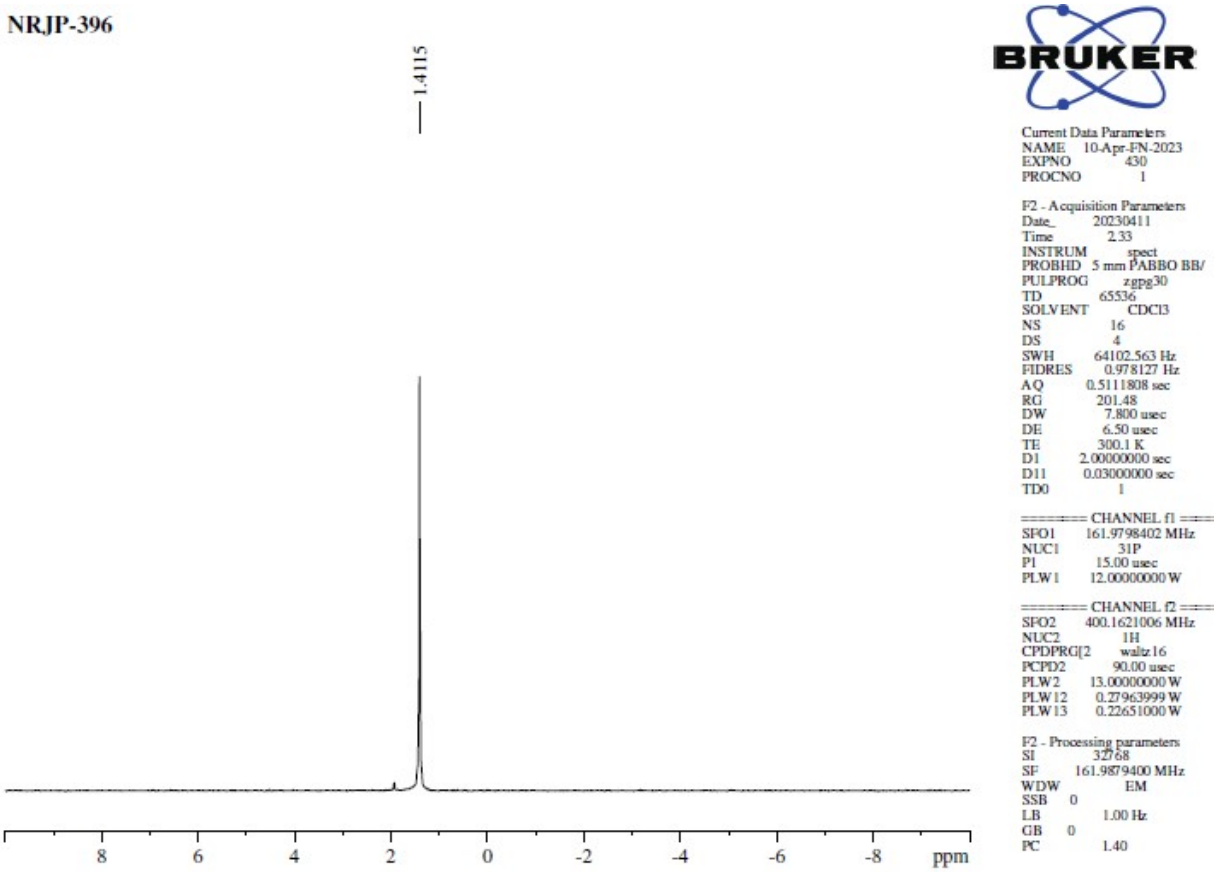


Figure S27: $^{31}P\{H\}$ NMR spectrum of 3h

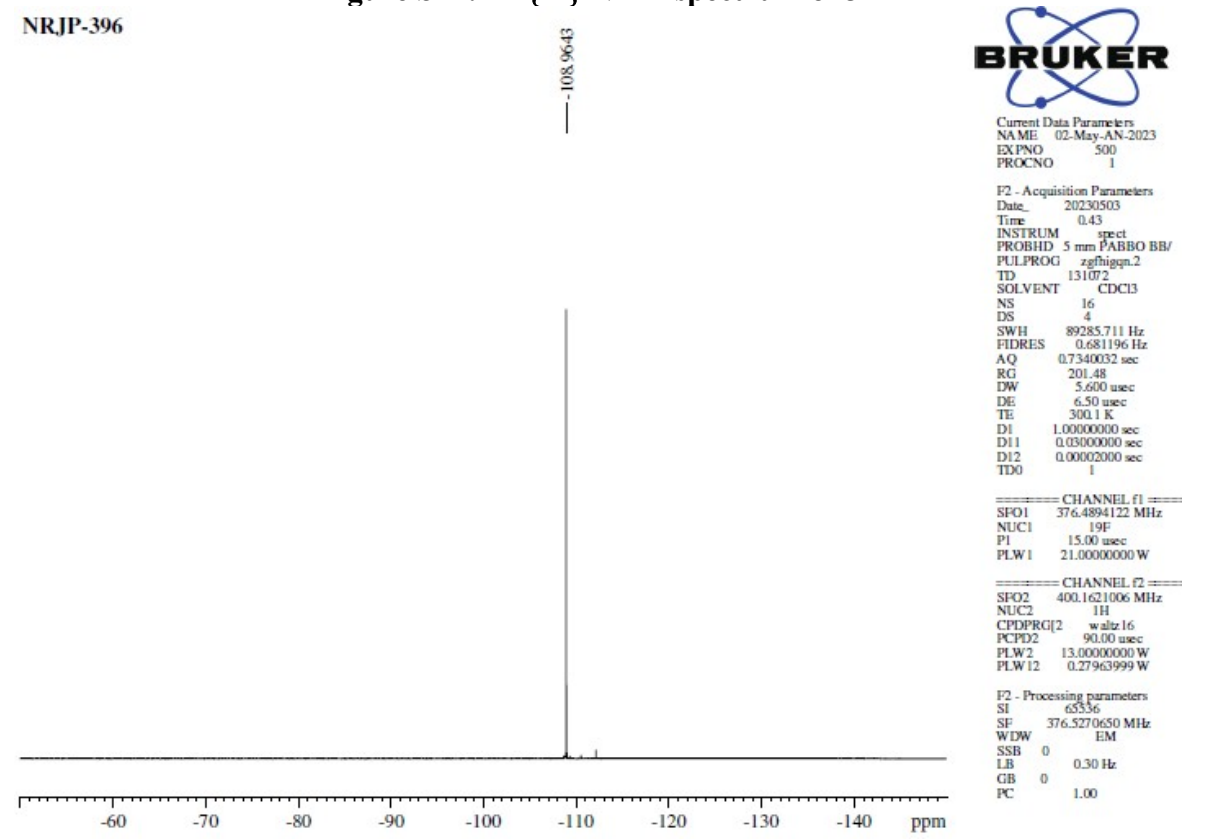


Figure S28: $^{19}F\{H\}$ NMR spectrum of 3h

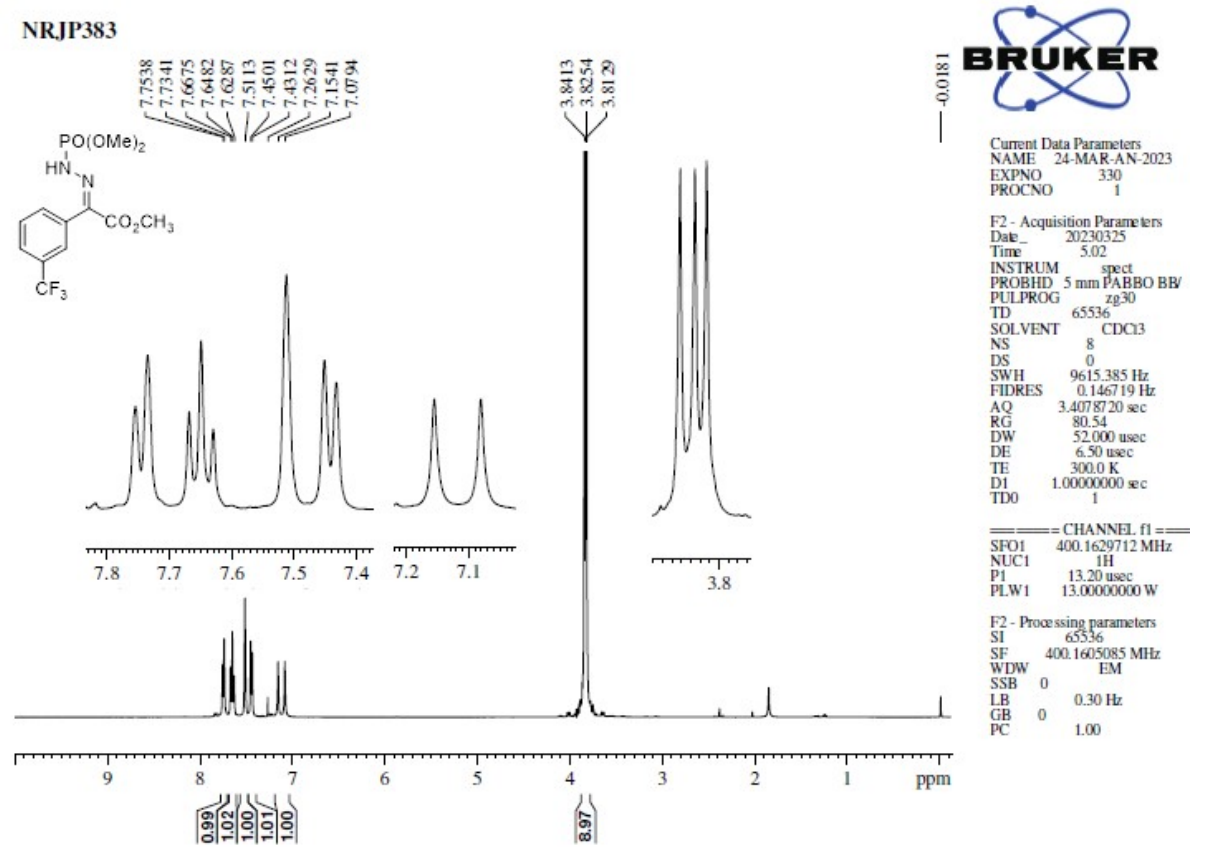


Figure S29: ^{1}H NMR spectrum of 3i

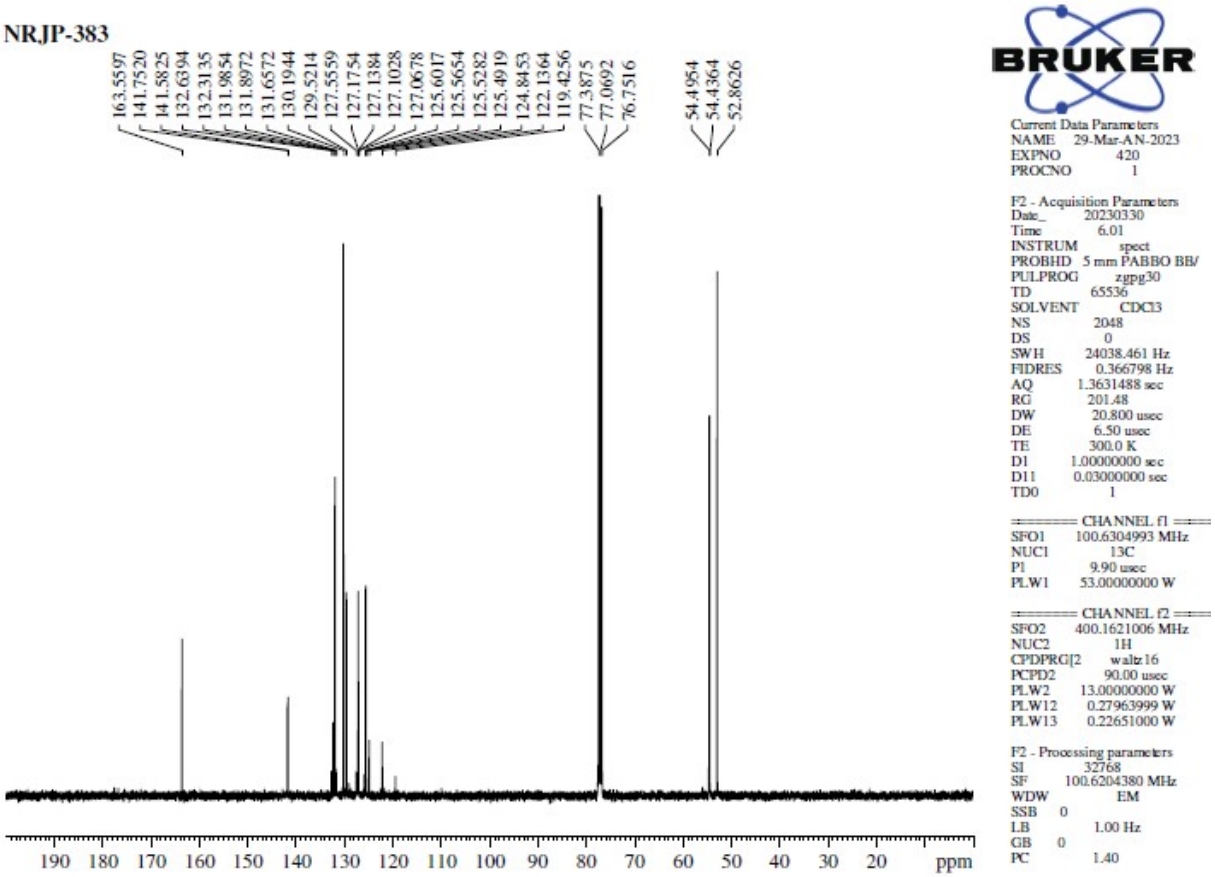


Figure S30: ^{13}C{H} NMR spectrum of 3i

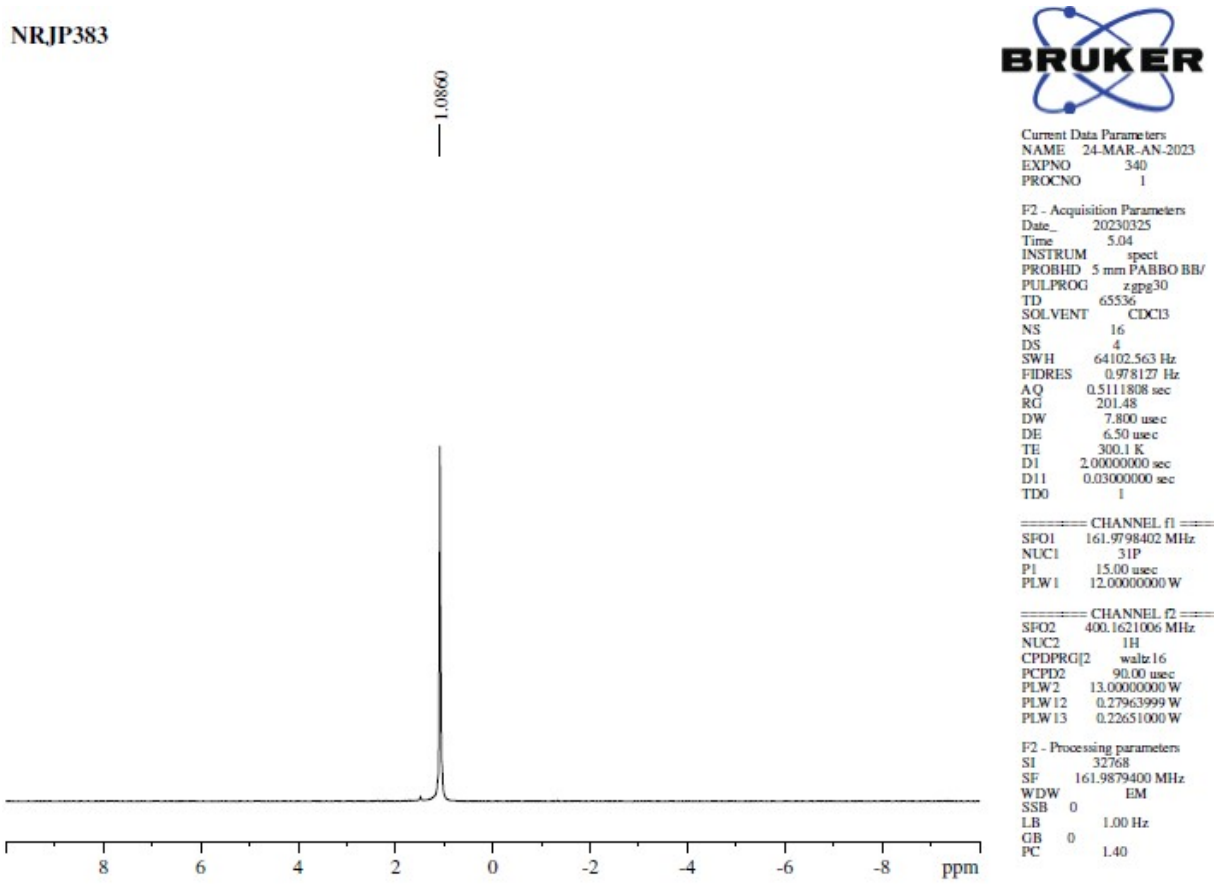


Figure S31: $^{31}P\{H\}$ NMR spectrum of 3i

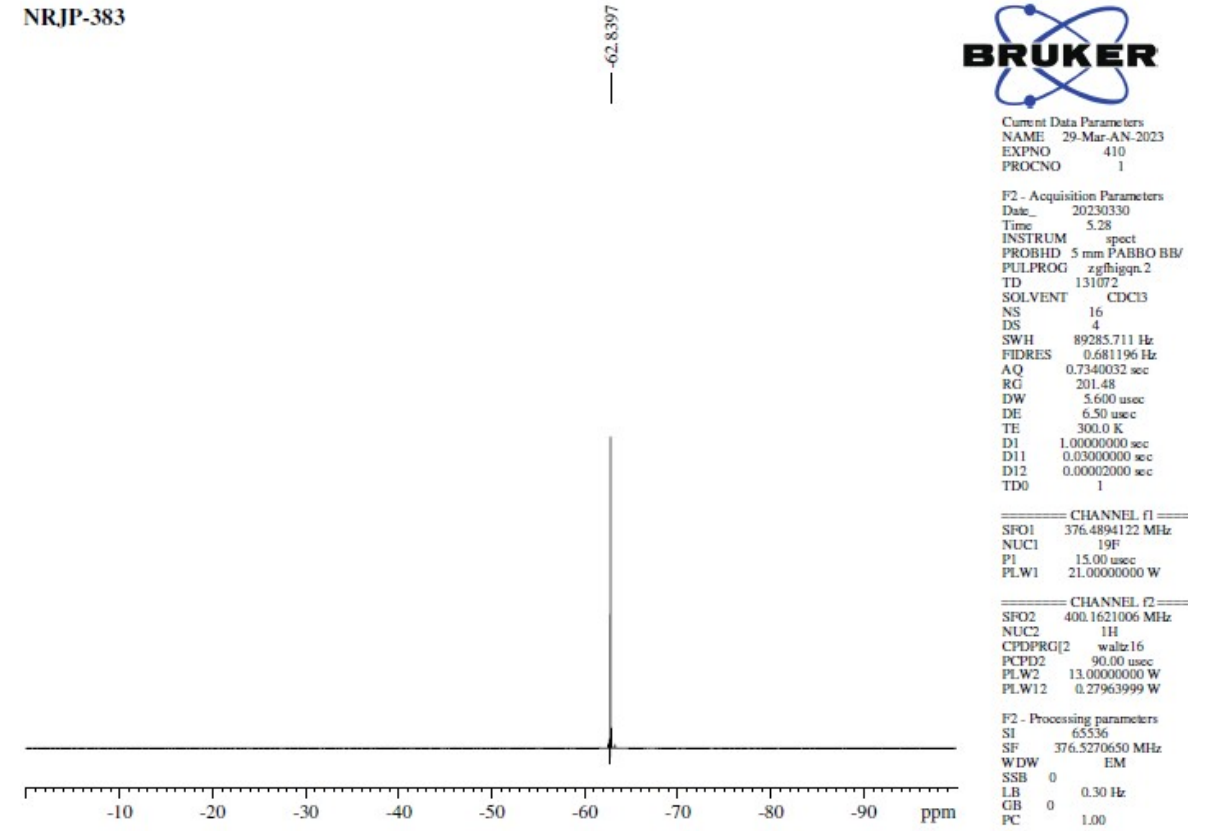


Figure S32: $^{19}F\{H\}$ NMR spectrum of 3i

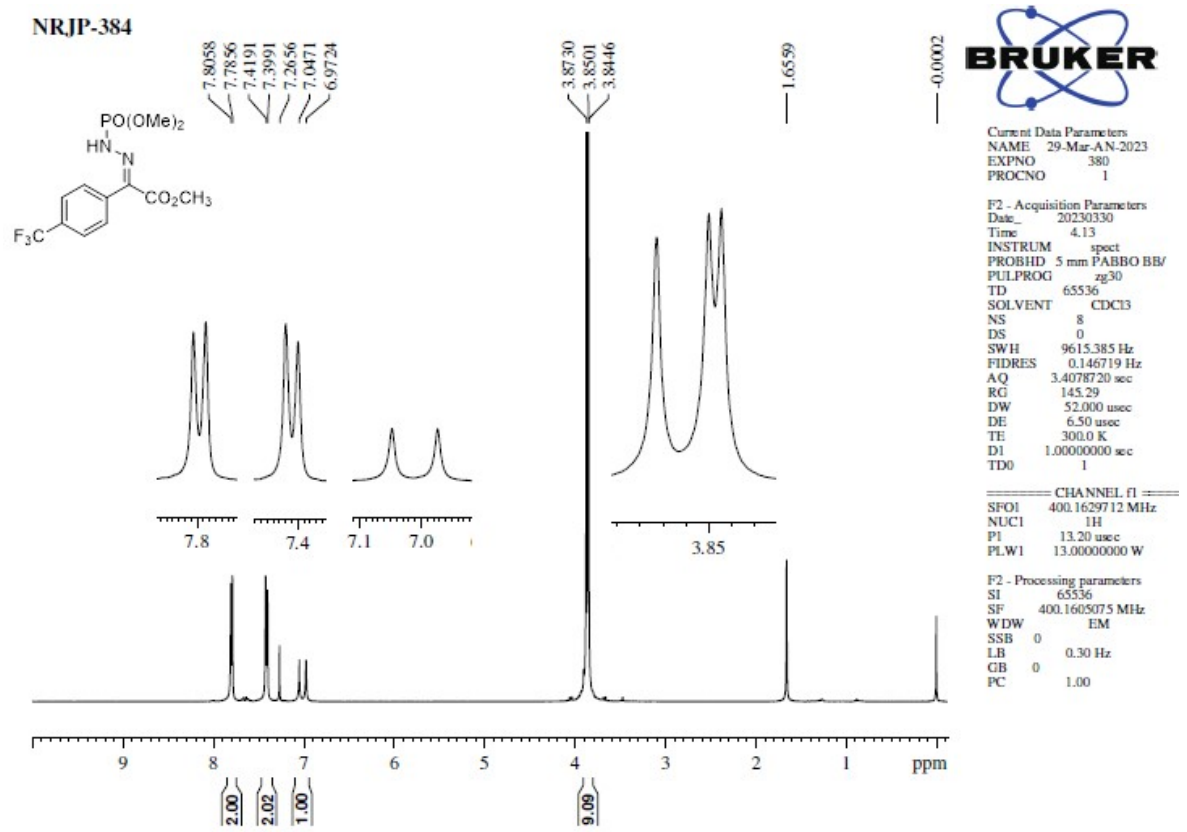


Figure S33: ^{1}H NMR spectrum of 3j

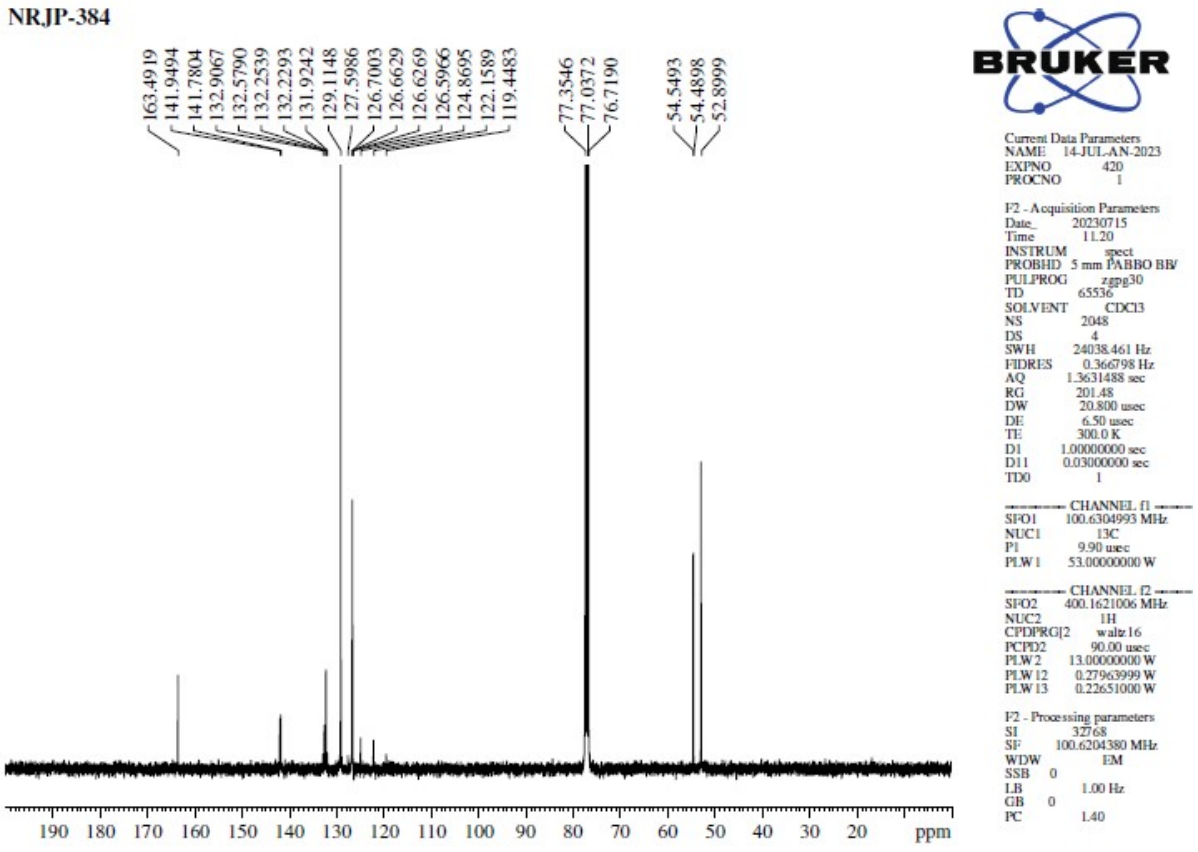


Figure S34: ^{13}C{H} NMR spectrum of 3j

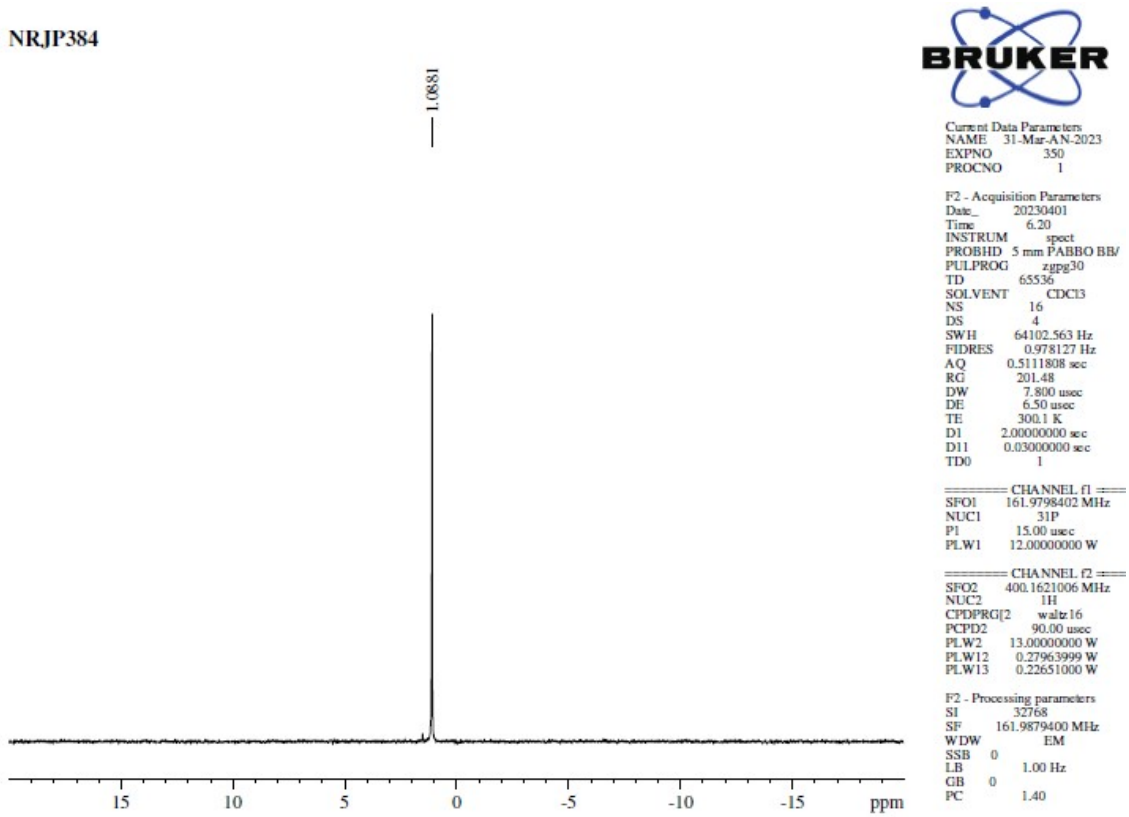


Figure S35: $^{31}P\{H\}$ NMR spectrum of 3j

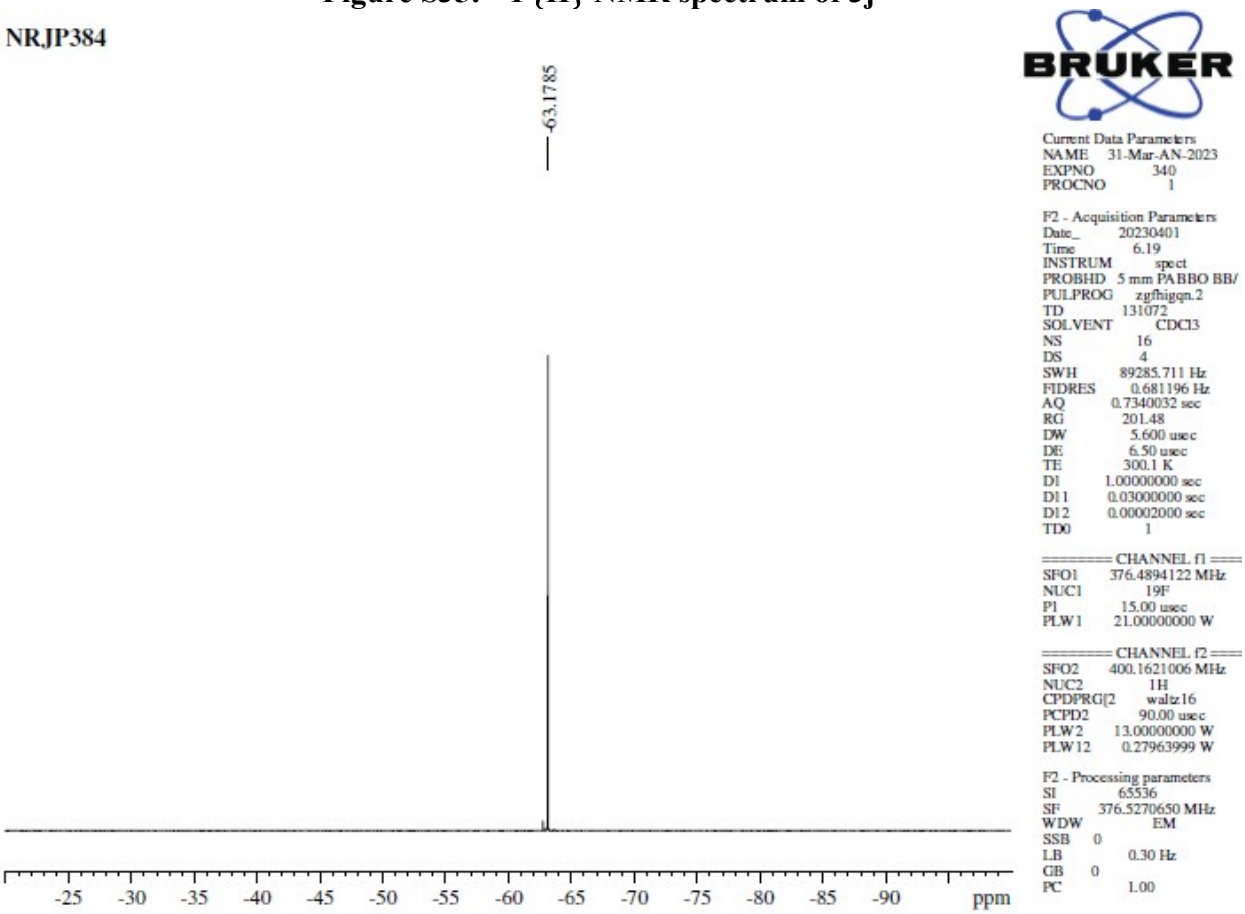


Figure S36: $^{19}F\{H\}$ NMR spectrum of 3j

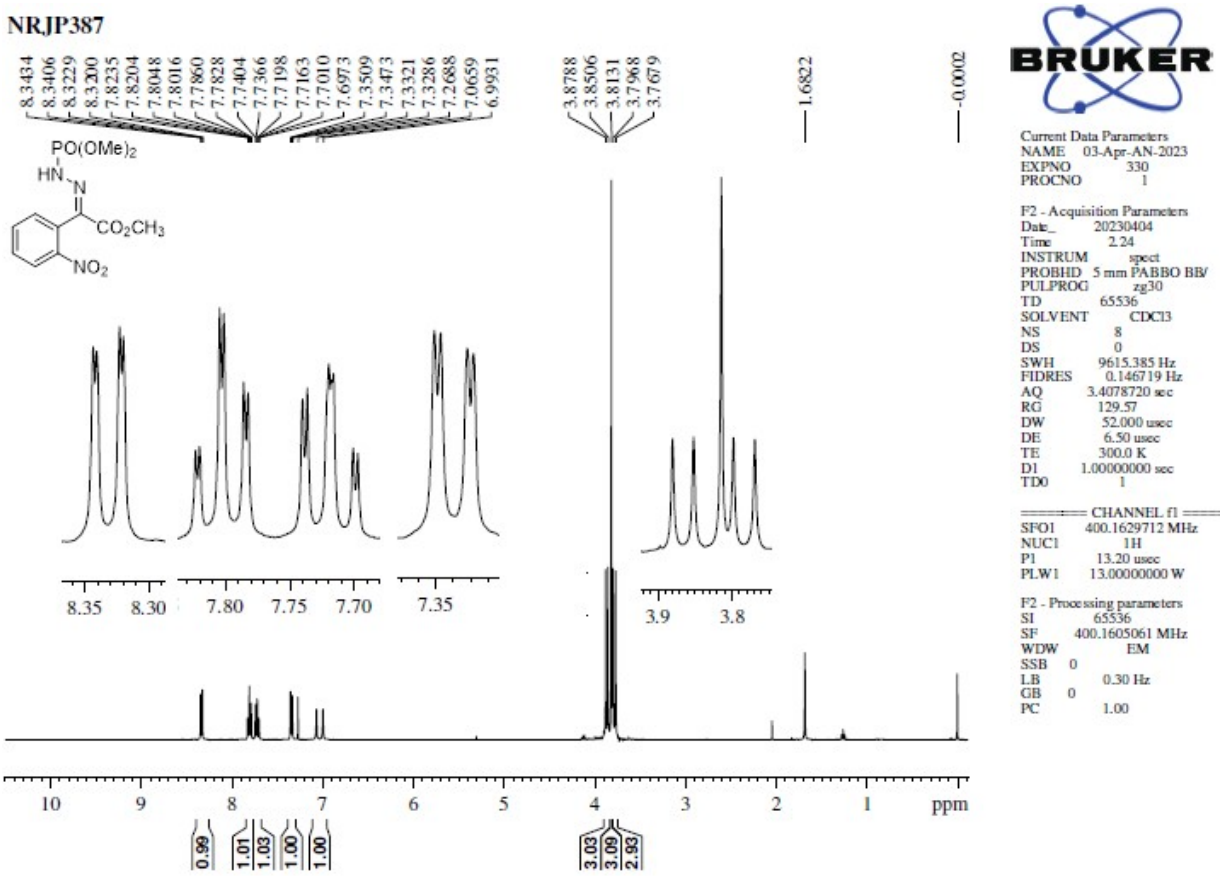


Figure S37: ^{1}H NMR spectrum of 3k

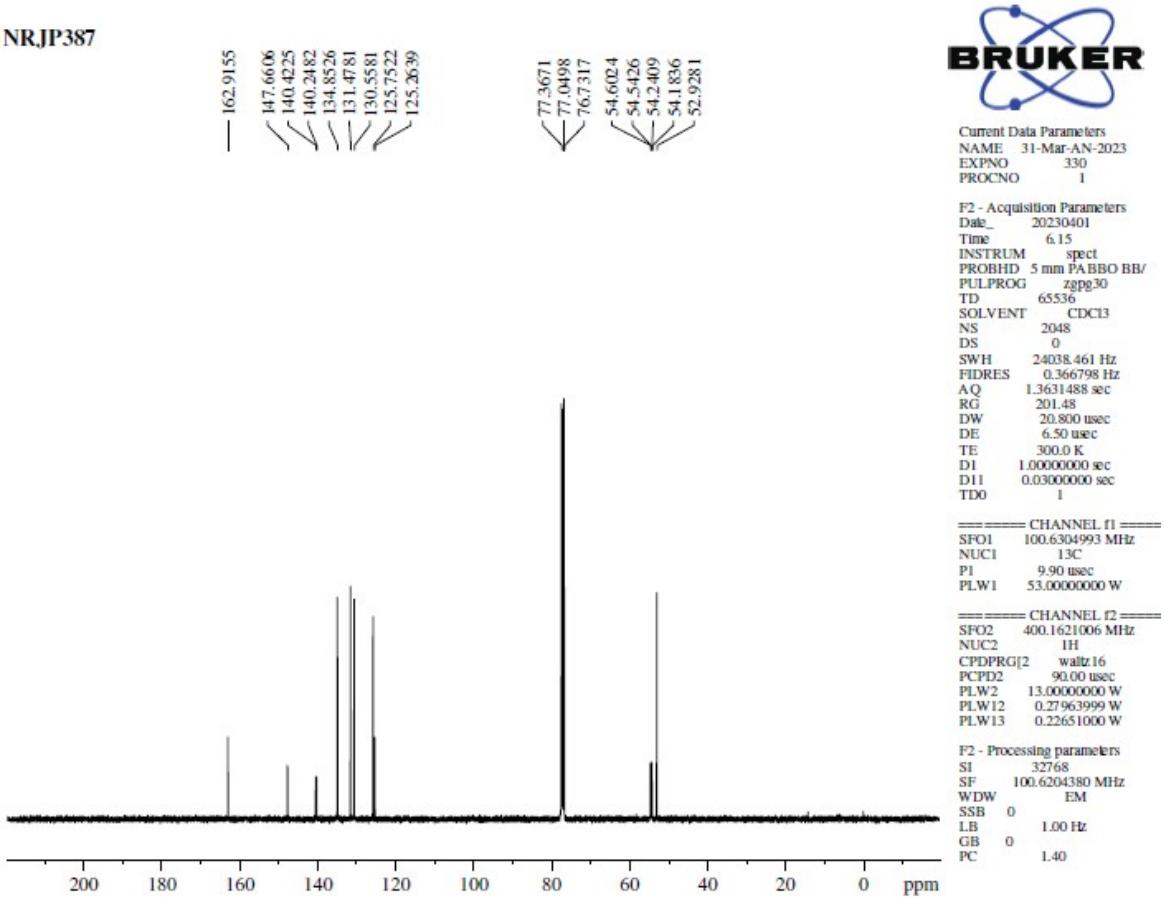


Figure S38: ^{13}C{H} NMR spectrum of 3k

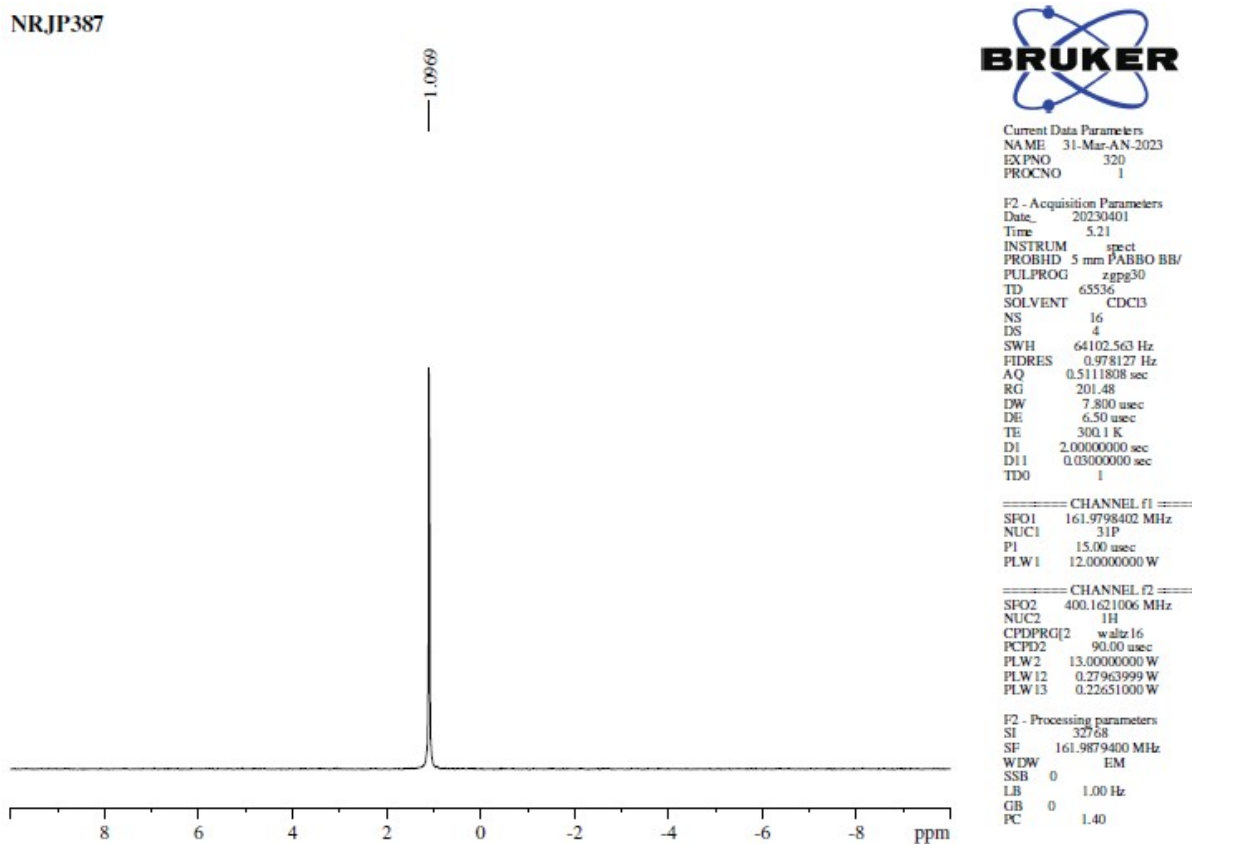


Figure S39: $^{31}P\{H\}$ NMR spectrum of 3k

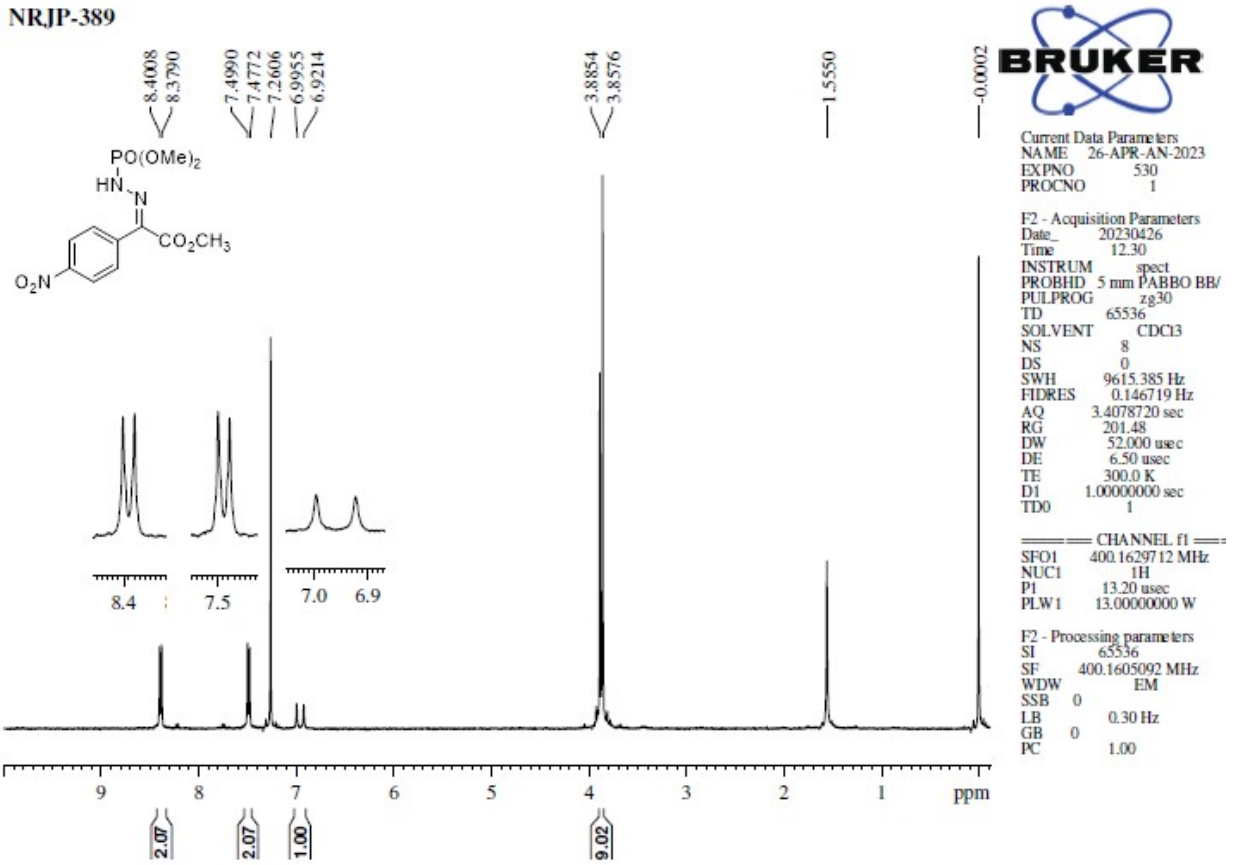


Figure S40: ^{1}H NMR spectrum of 3l

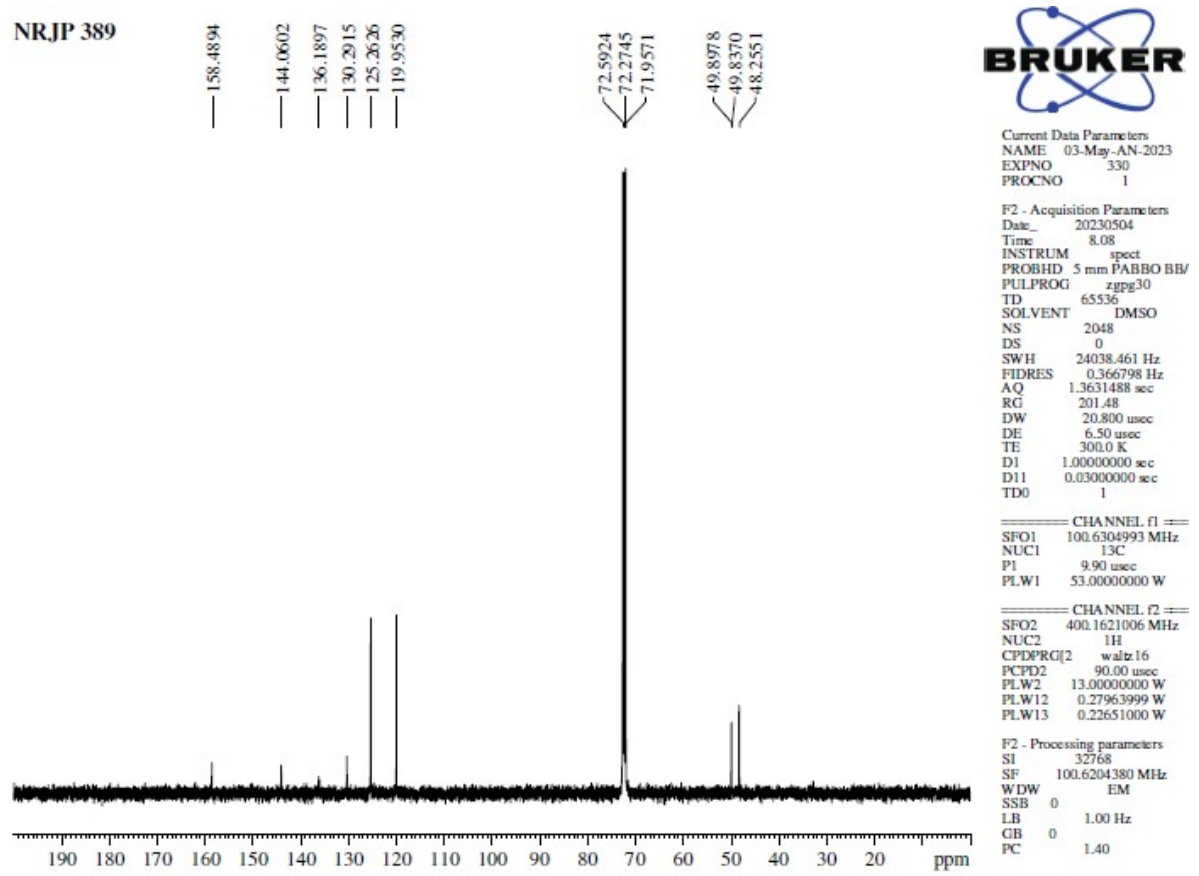


Figure S41: $^{13}C\{H\}$ NMR spectrum of 3l

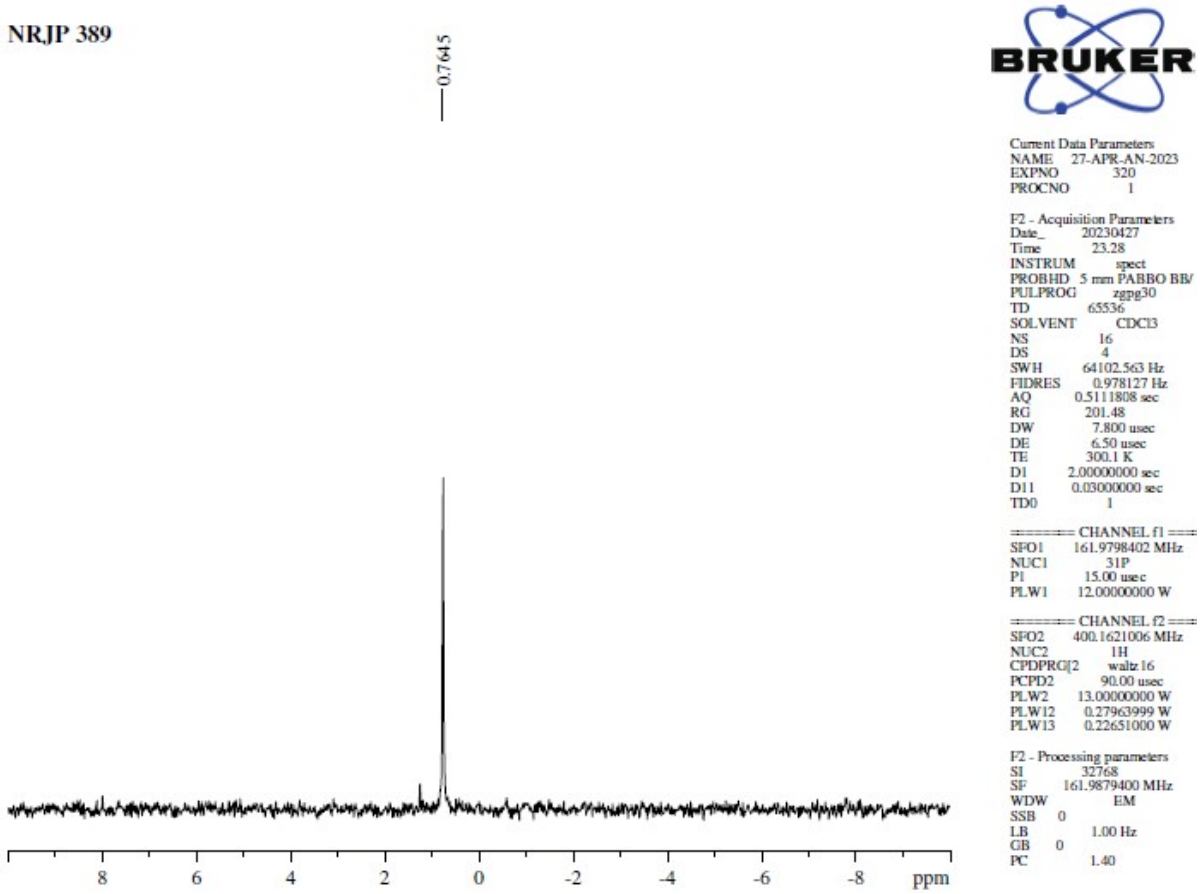


Figure S42: $^{31}P\{H\}$ NMR spectrum of 3l

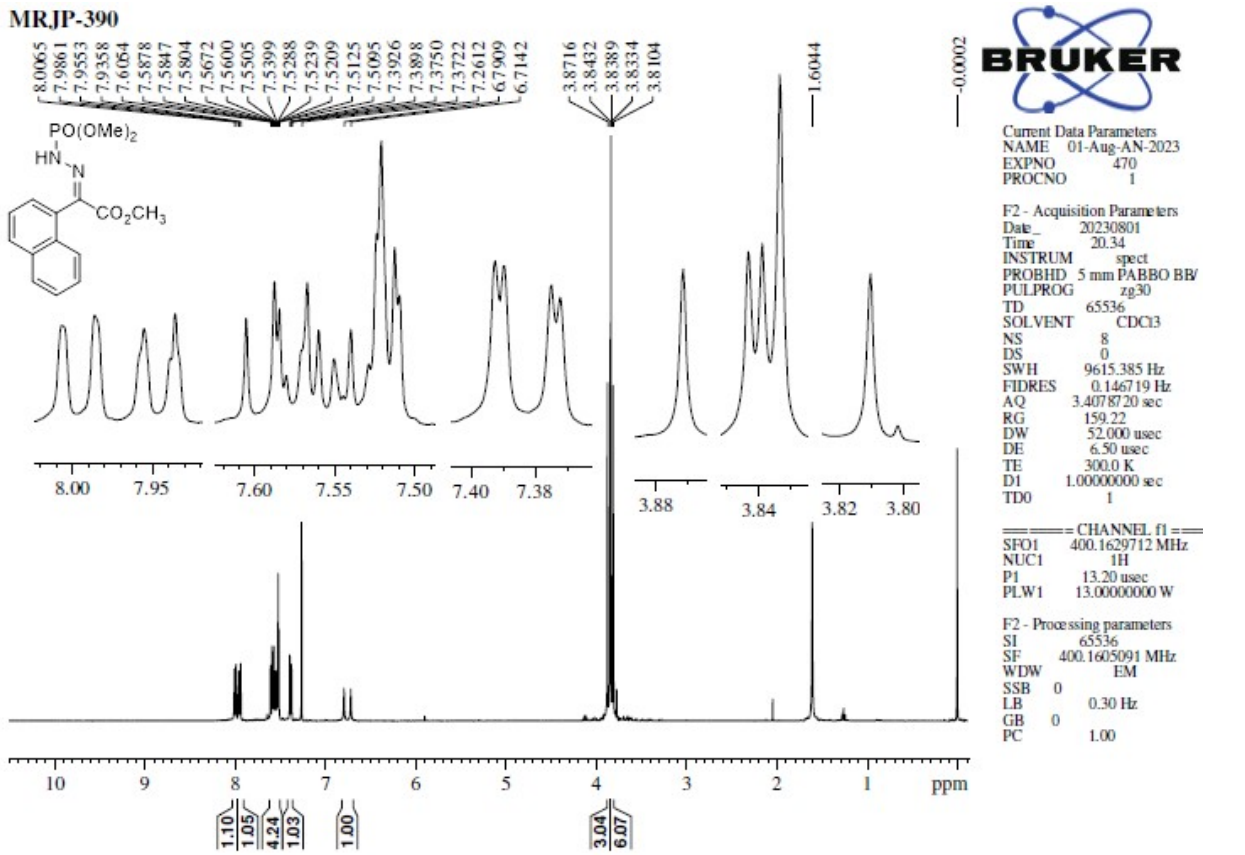


Figure S43: ^{1}H NMR spectrum of 3m

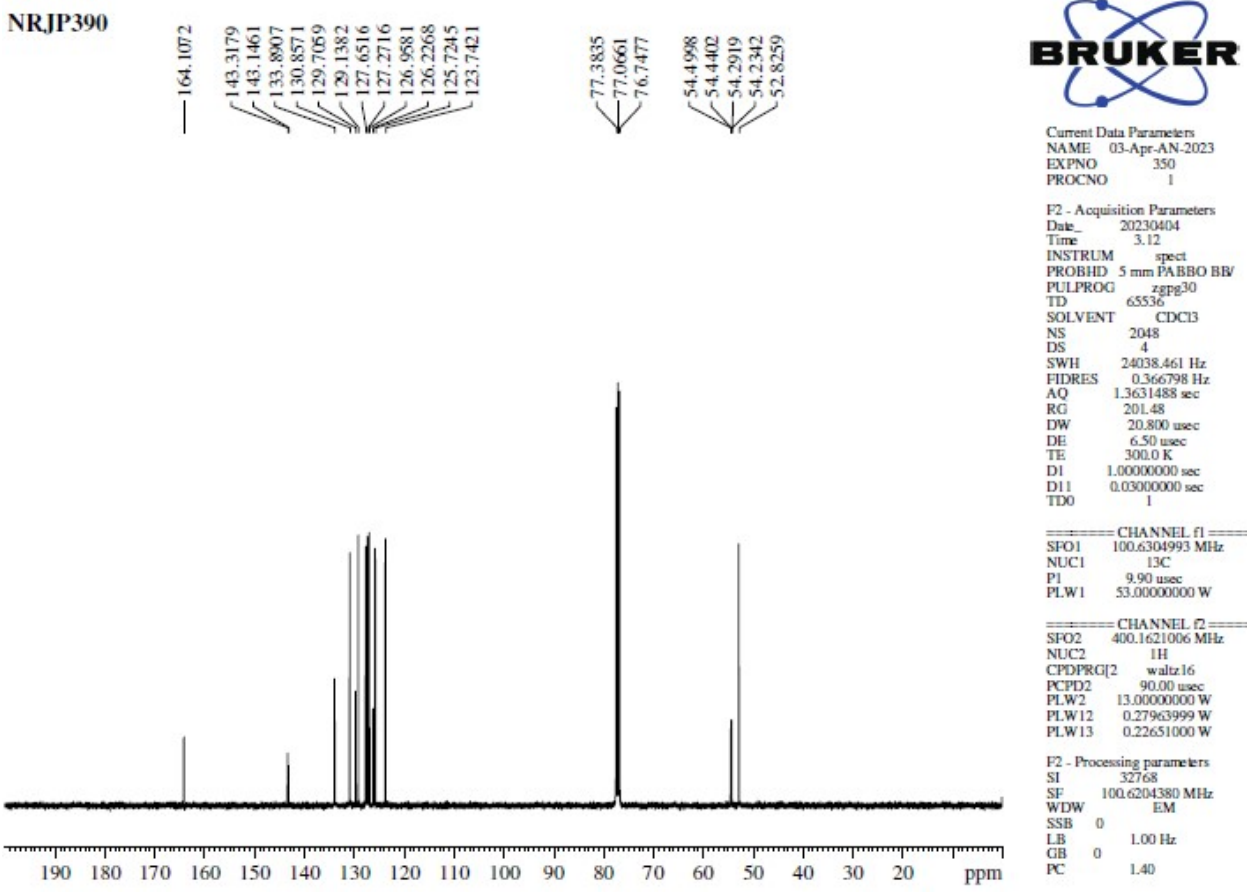


Figure S44: ^{13}C{H} NMR spectrum of 3m

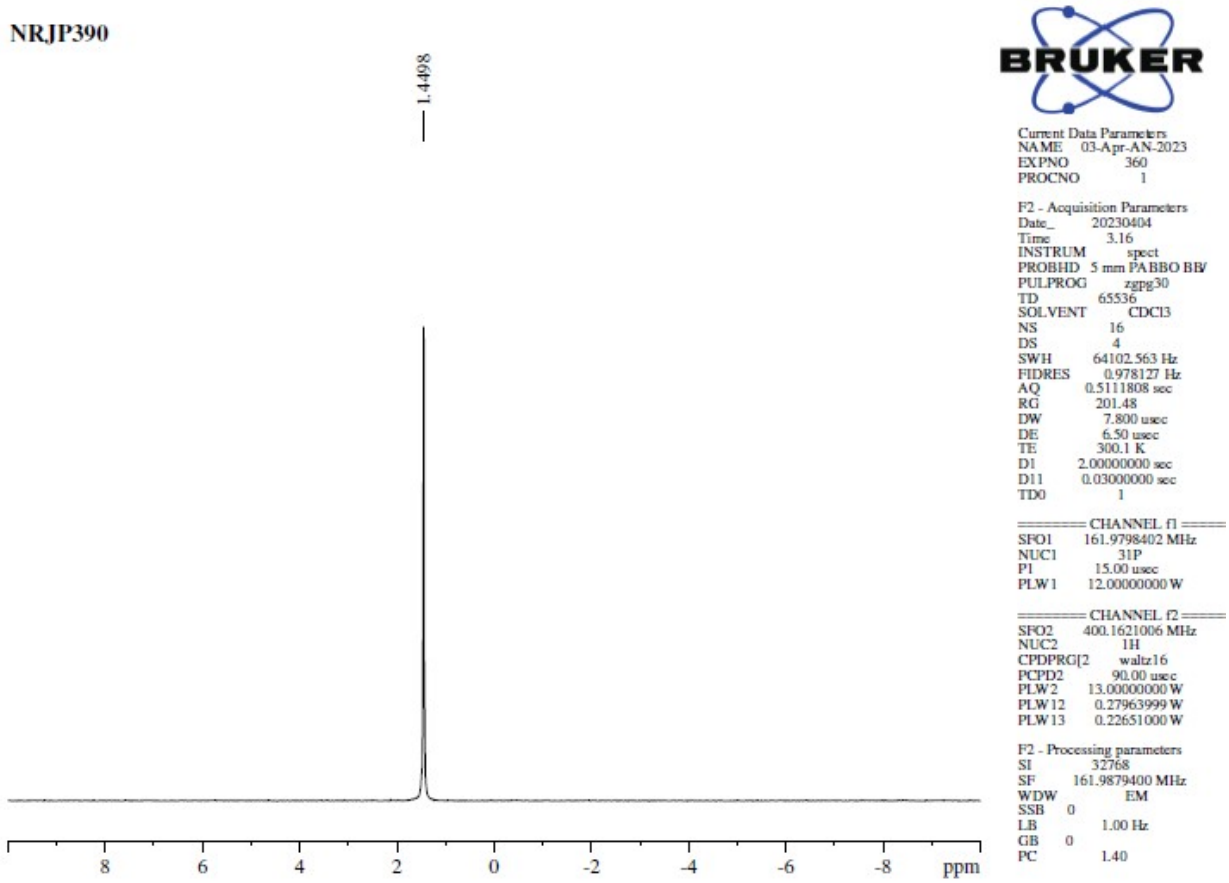


Figure S45: $^{31}P\{H\}$ NMR spectrum of 3m

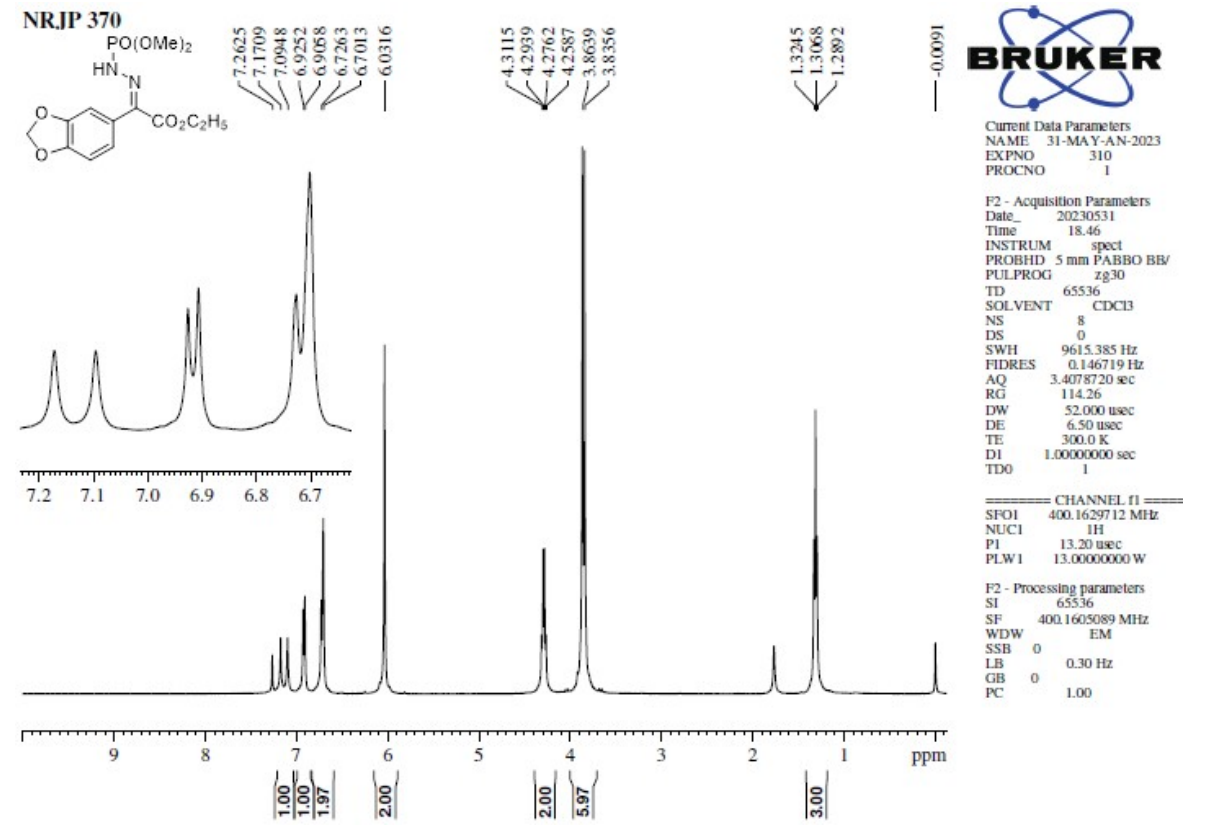


Figure S46: ^{1}H NMR spectrum of 3n

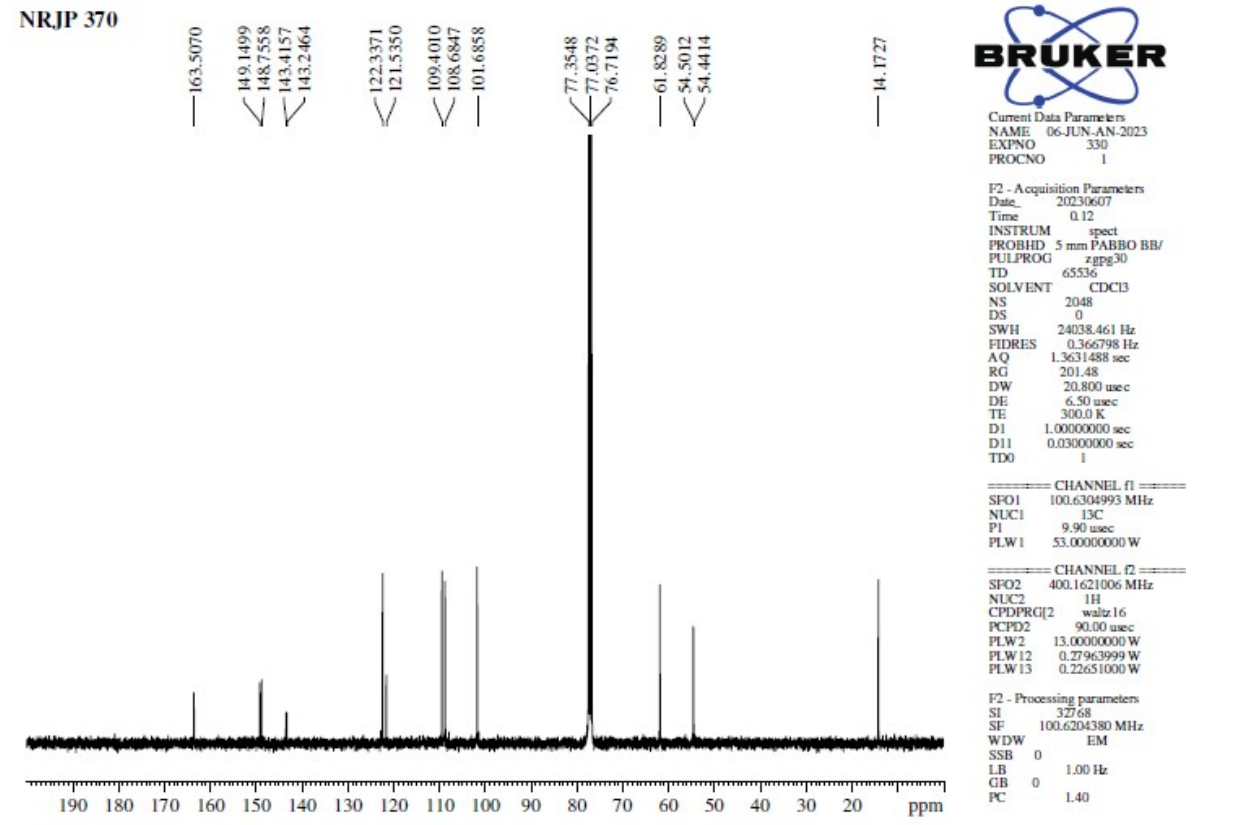


Figure S47: $^{13}C\{H\}$ NMR spectrum of 3n

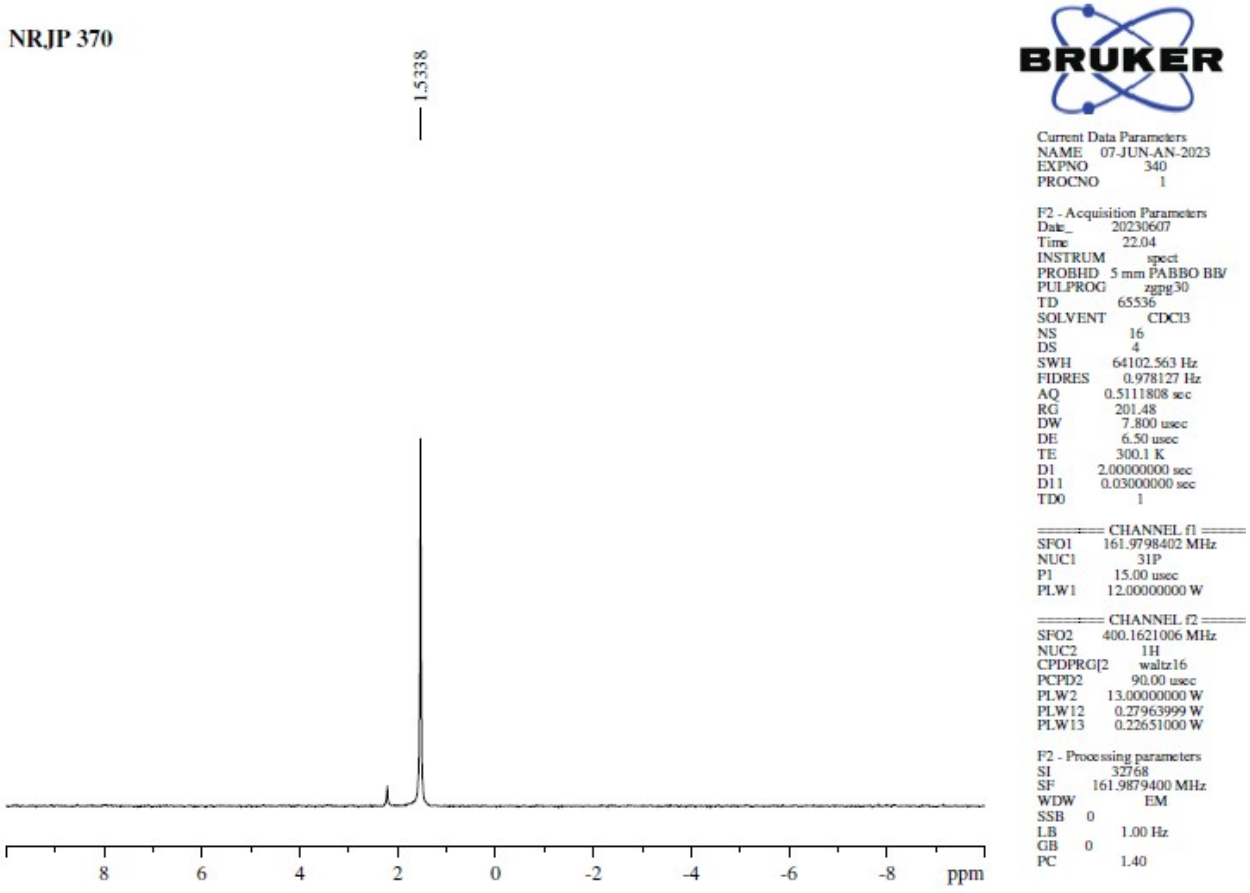


Figure S48: $^{31}P\{H\}$ NMR spectrum of 3n

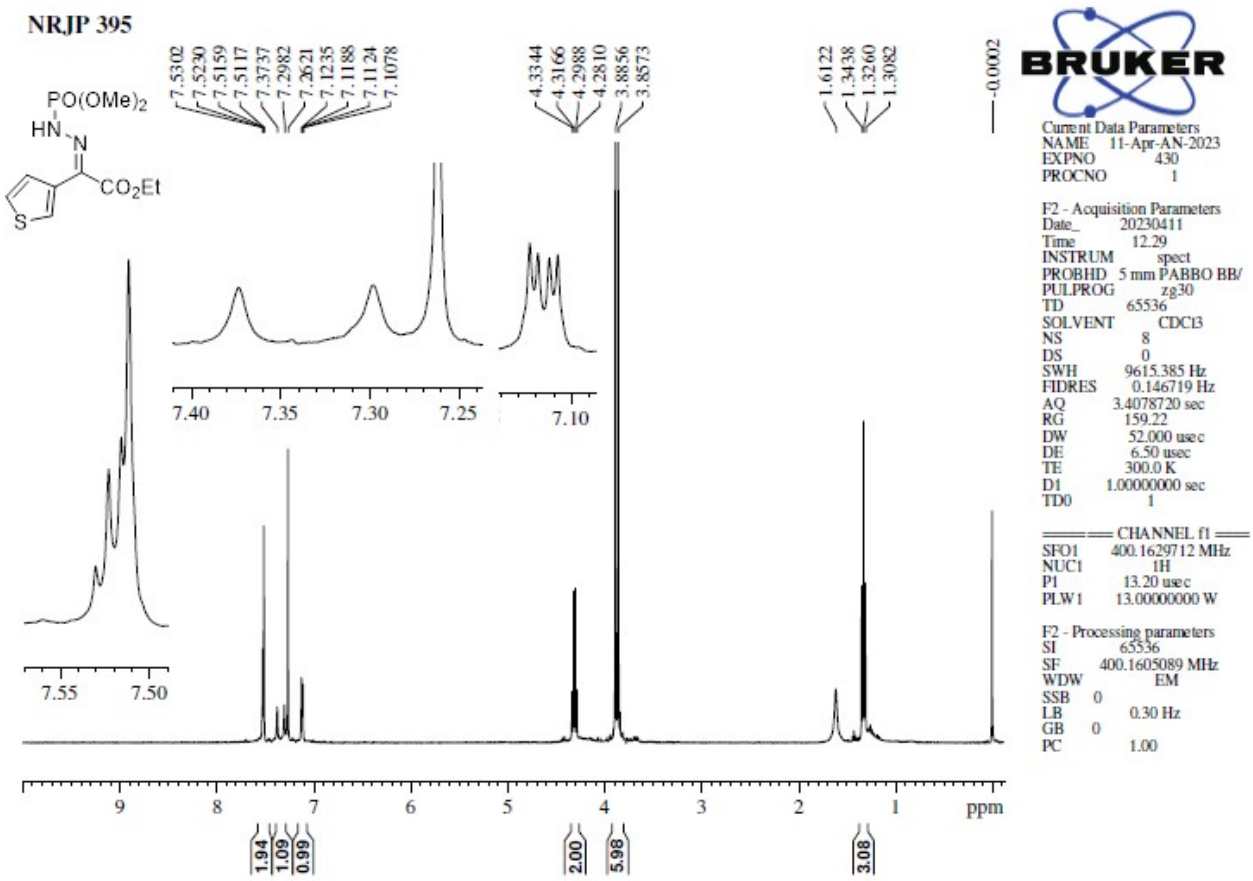


Figure S49: ^{1}H NMR spectrum of 3o

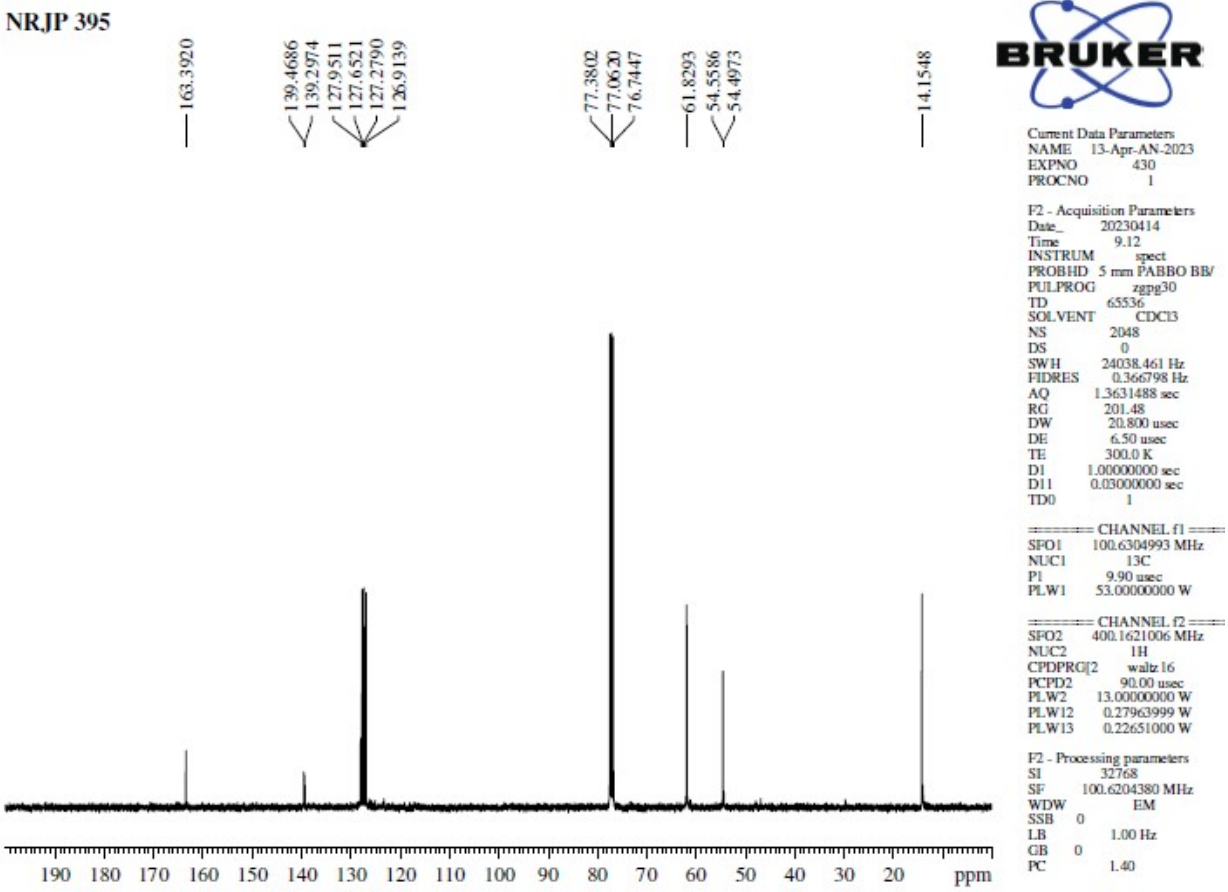


Figure S50: ^{13}C{H} NMR spectrum of 3o

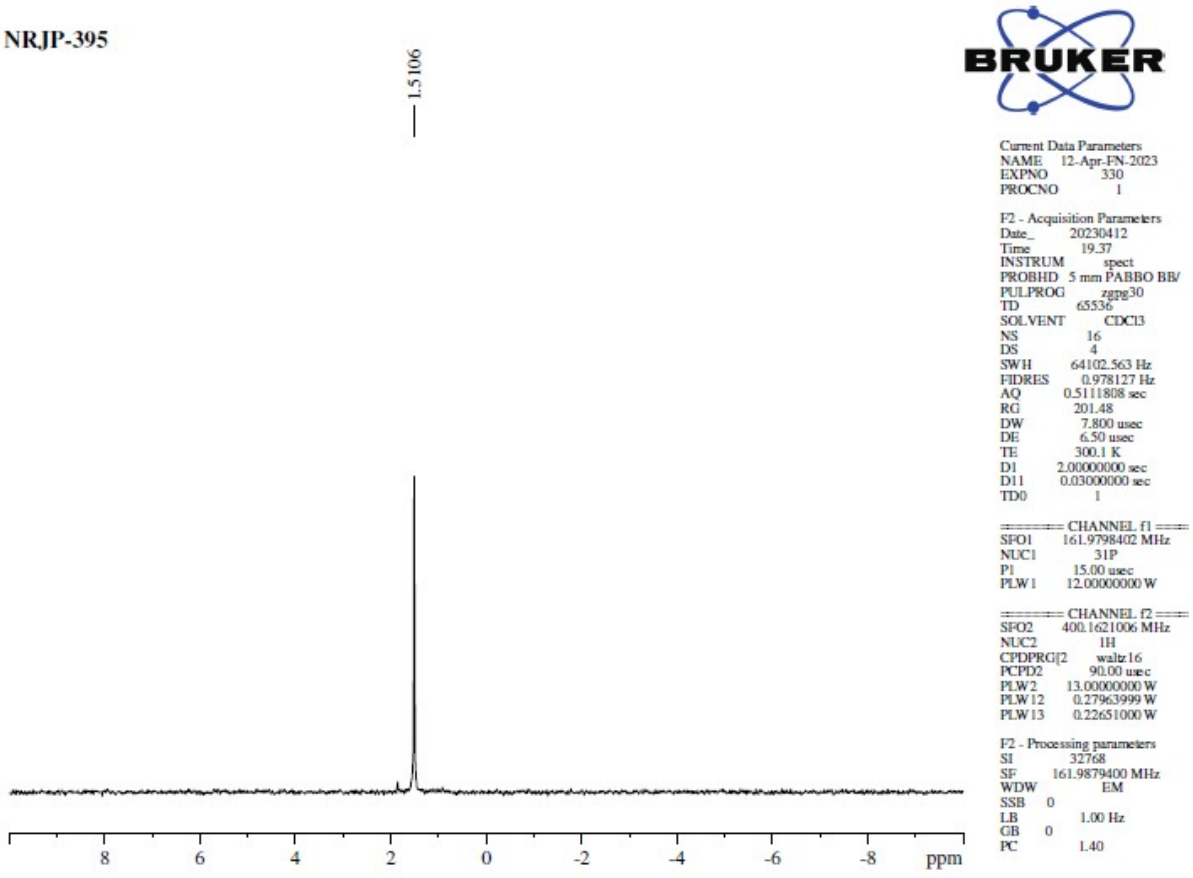


Figure S51: $^{31}P\{H\}$ NMR spectrum of 3o

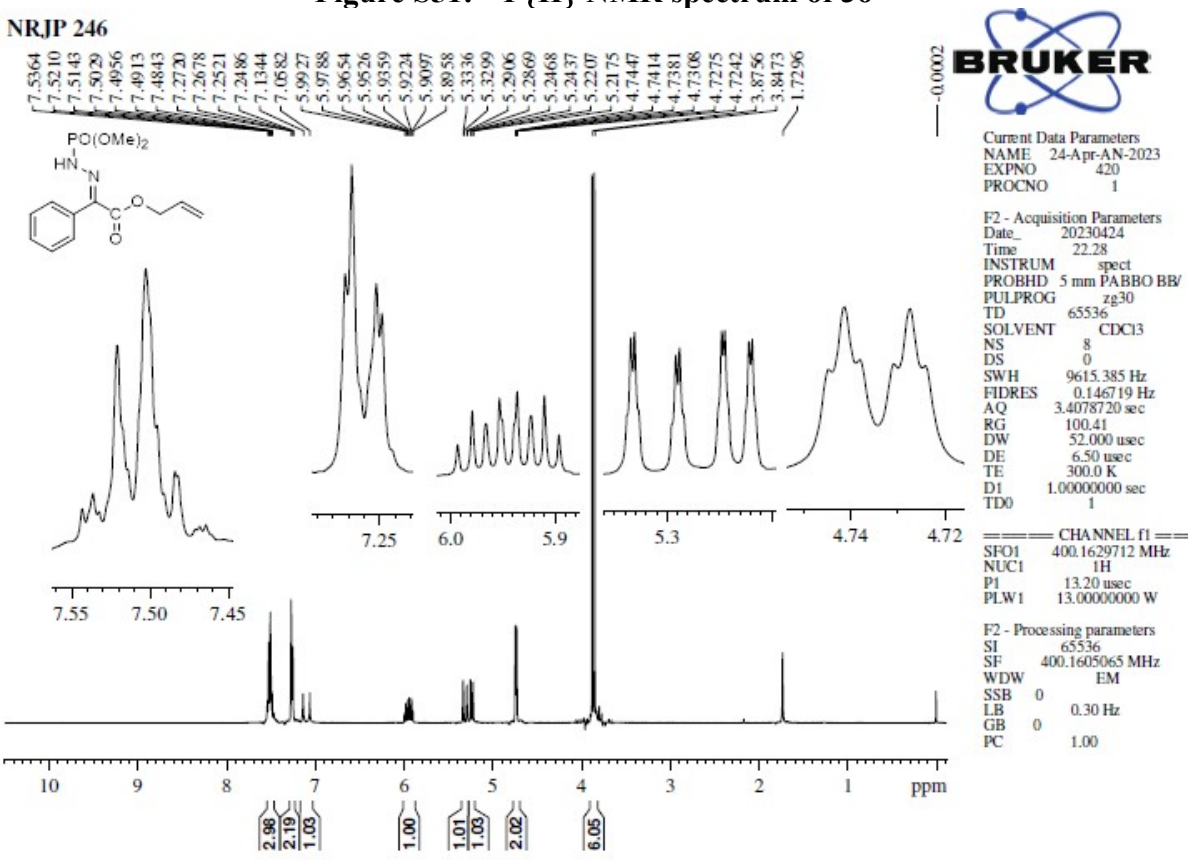


Figure S52: ^{1}H NMR spectrum of 3p

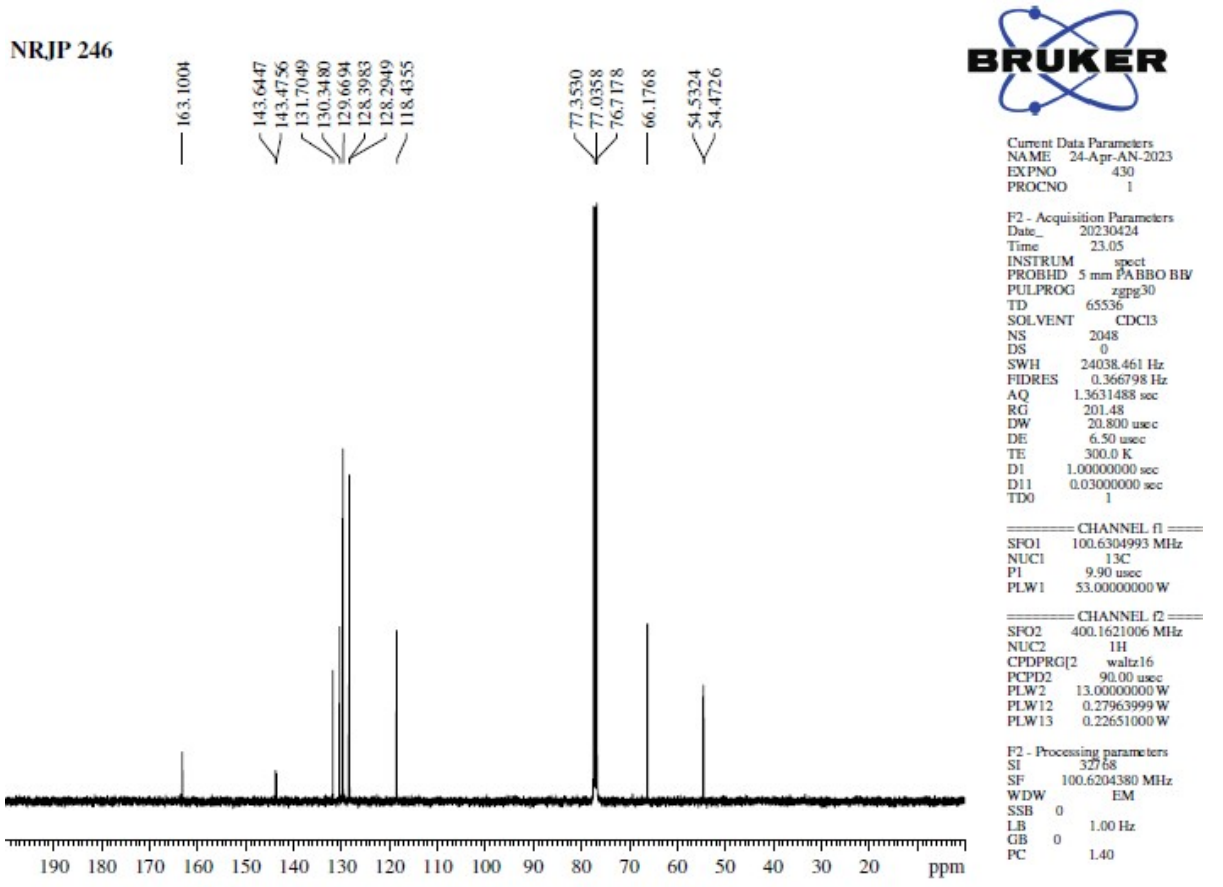


Figure S53: $^{13}C\{H\}$ NMR spectrum of 3p

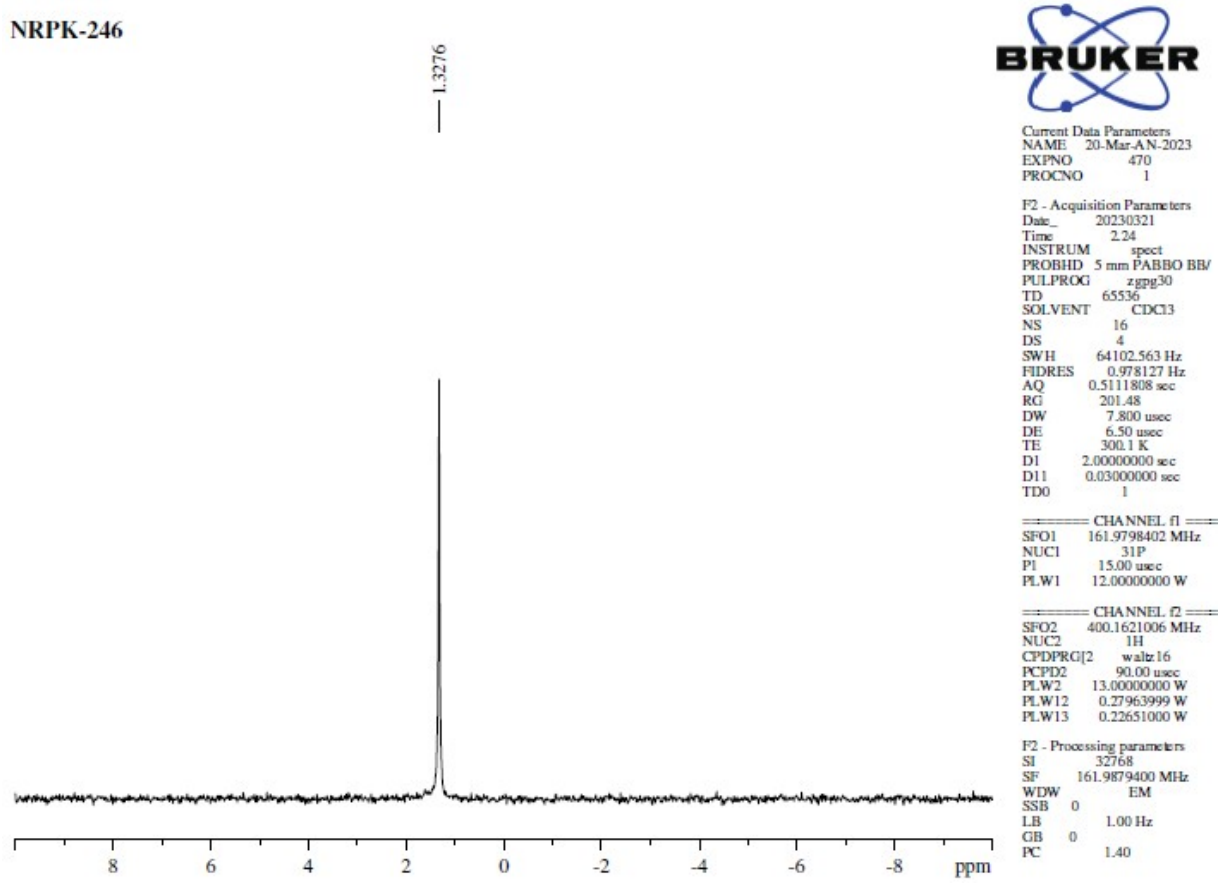


Figure S54: $^{31}P\{H\}$ NMR spectrum of 3p

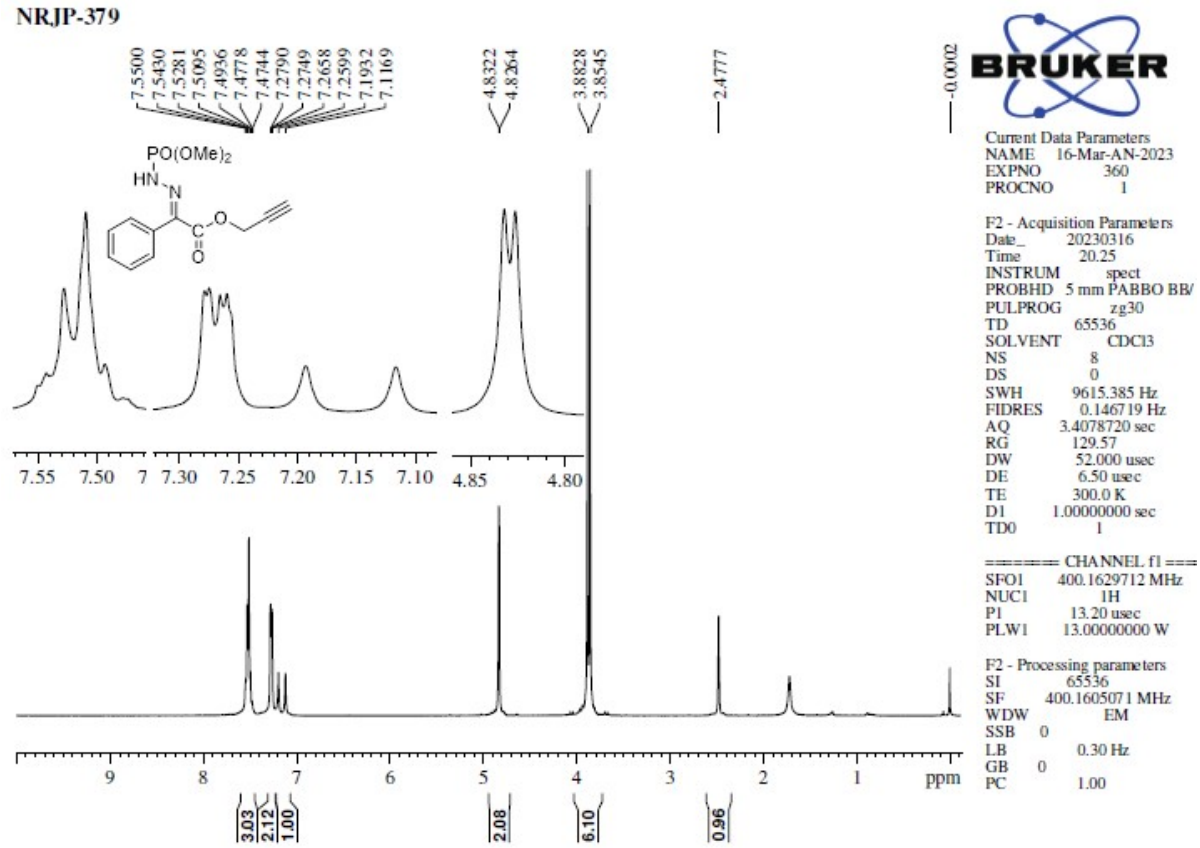


Figure S55: ^{1}H NMR spectrum of 3q

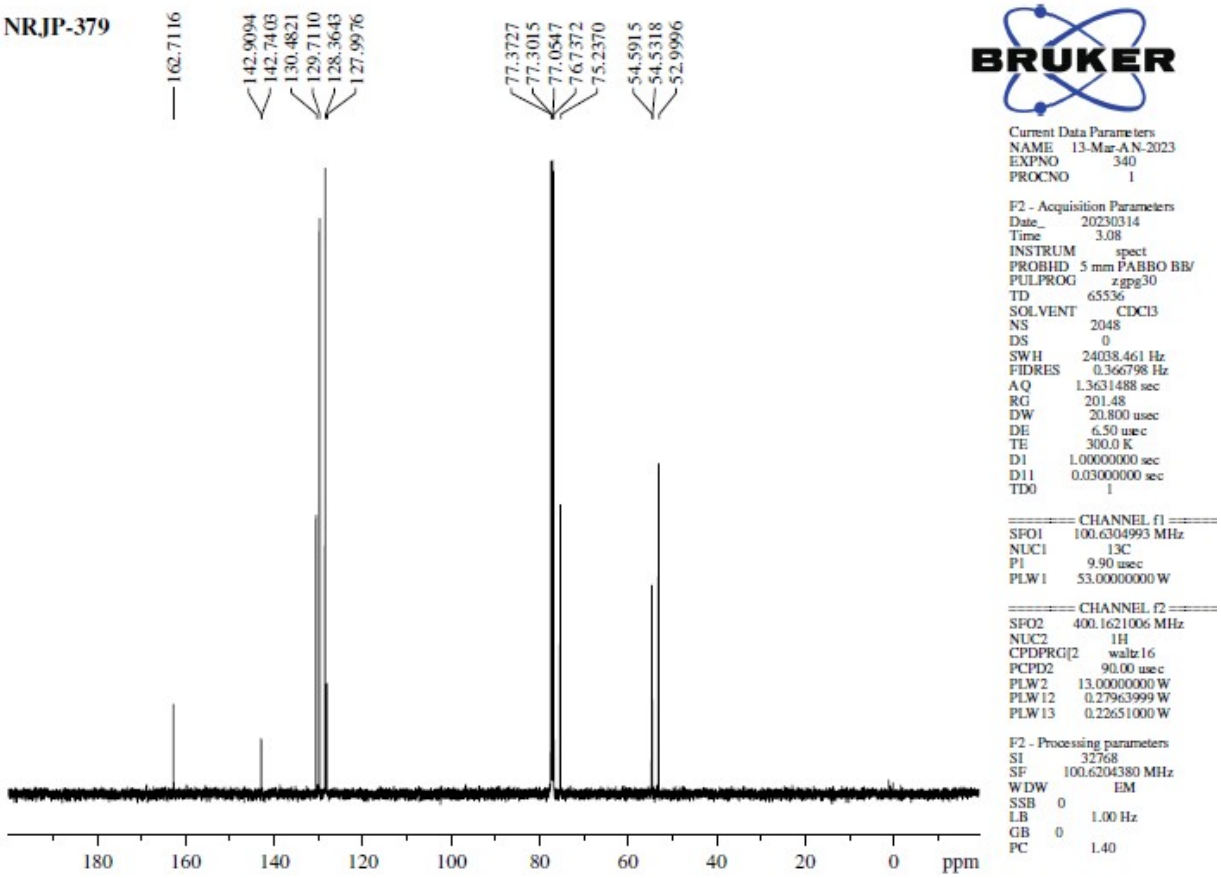


Figure S56: ^{13}C{H} NMR spectrum of 3q

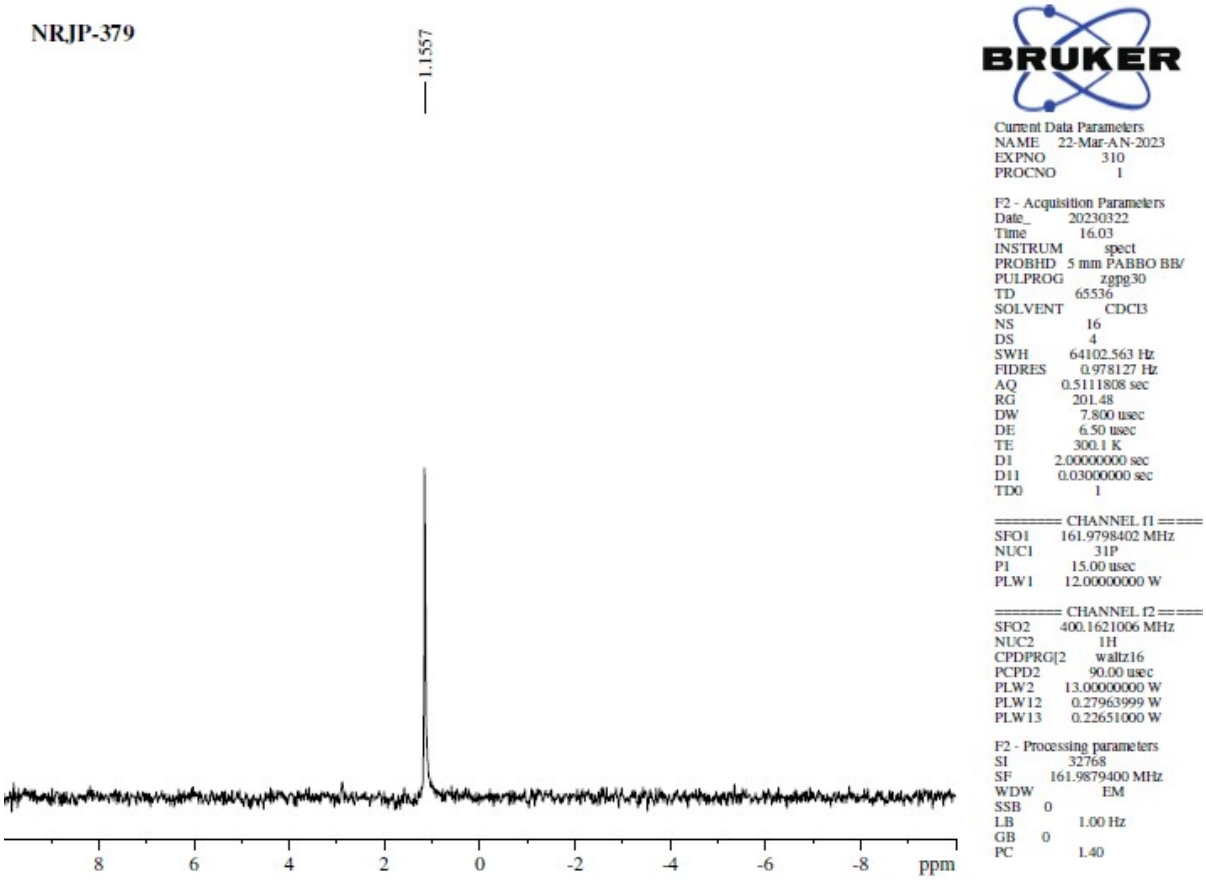


Figure S57: $^{31}P\{H\}$ NMR spectrum of 3q

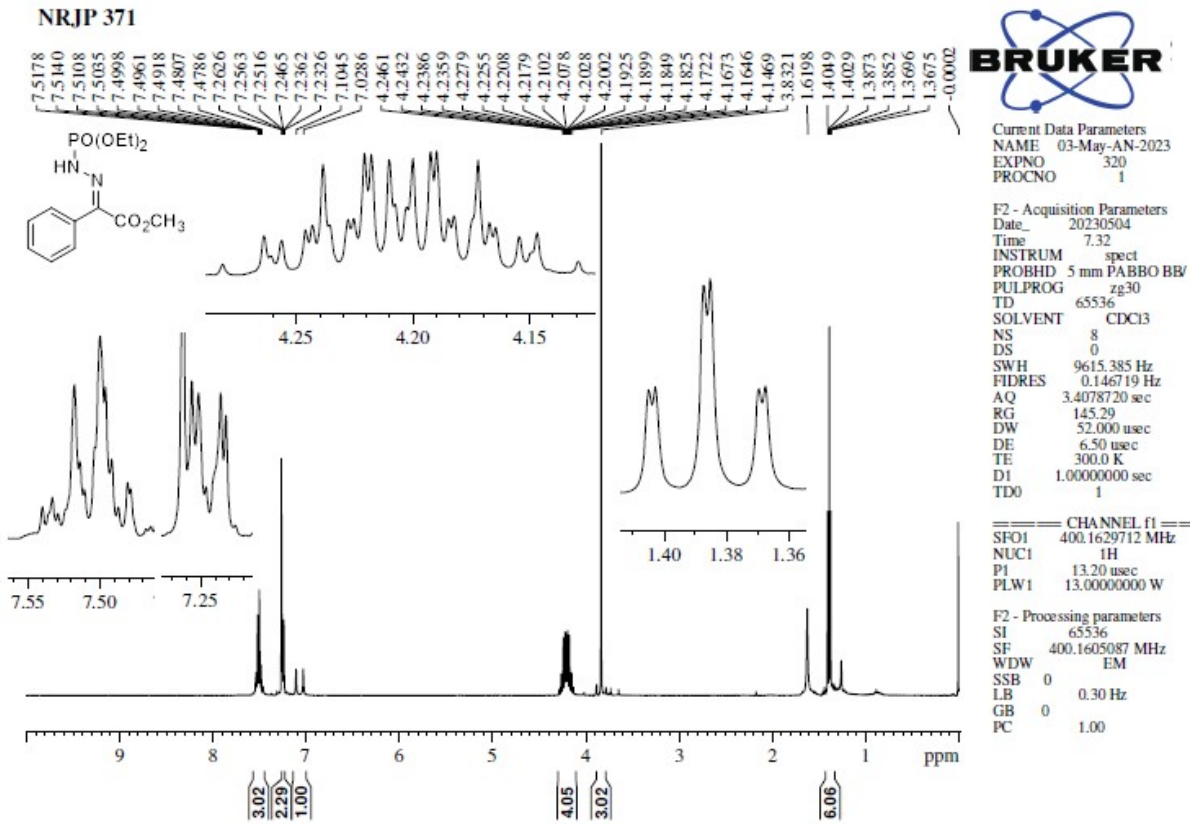


Figure S58: ^{1}H NMR spectrum of 3r

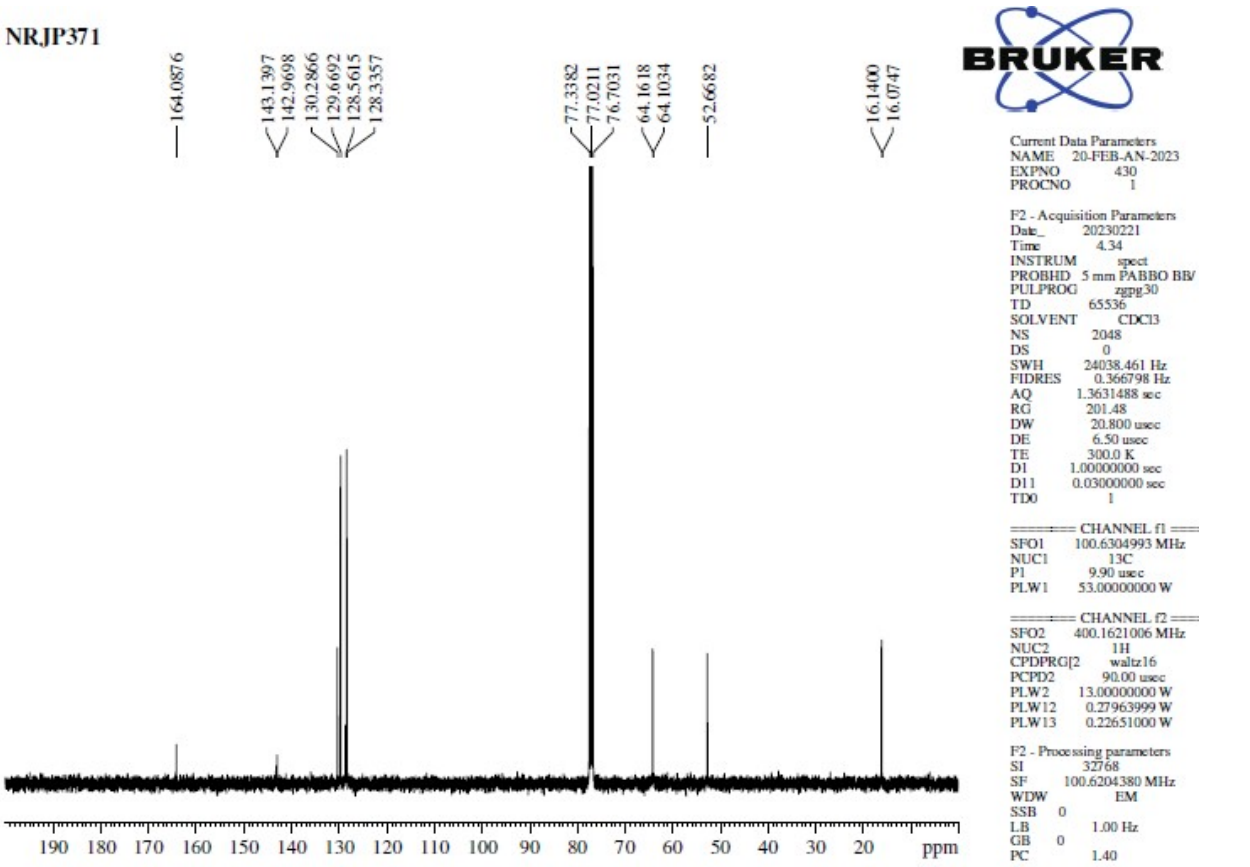


Figure S59: $^{13}C\{H\}$ NMR spectrum of 3r

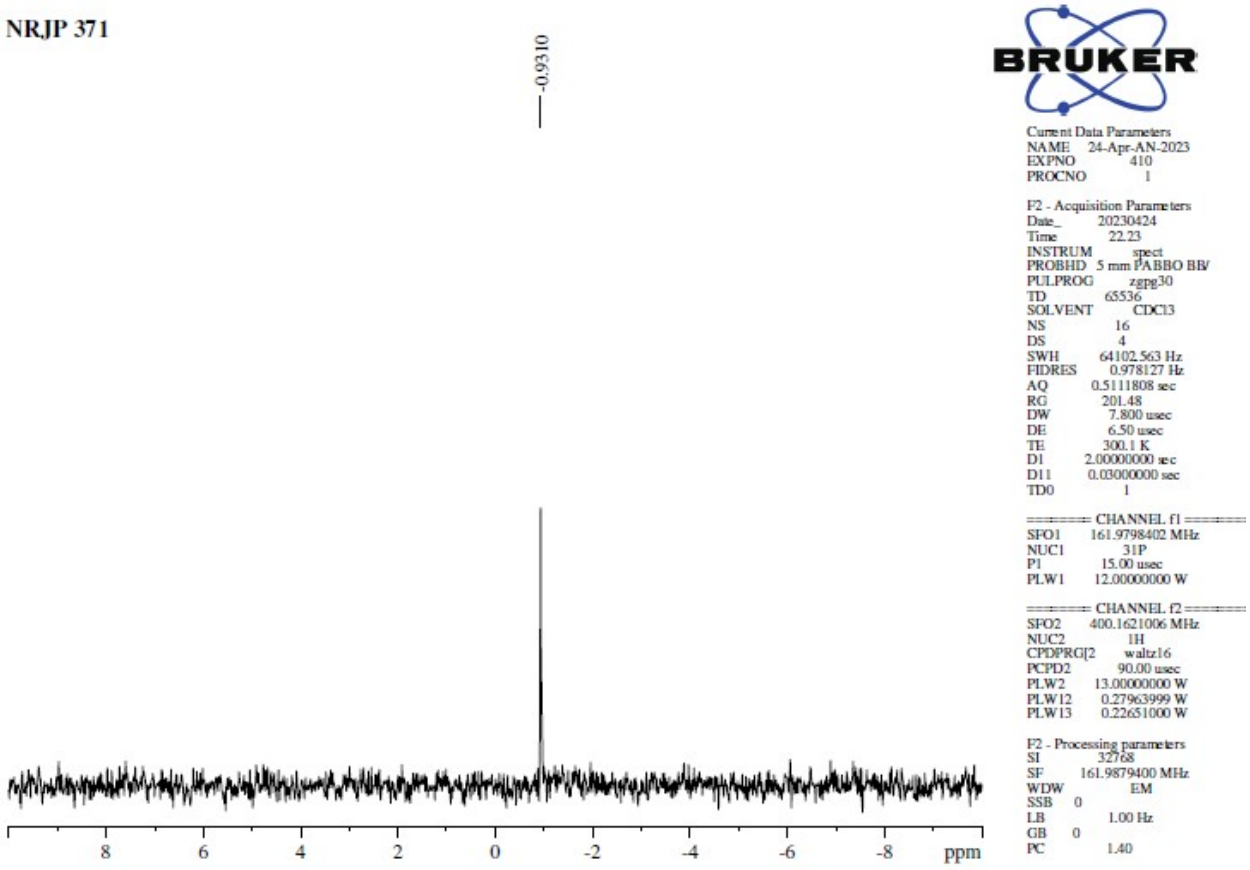


Figure S60: $^{31}P\{H\}$ NMR spectrum of 3r

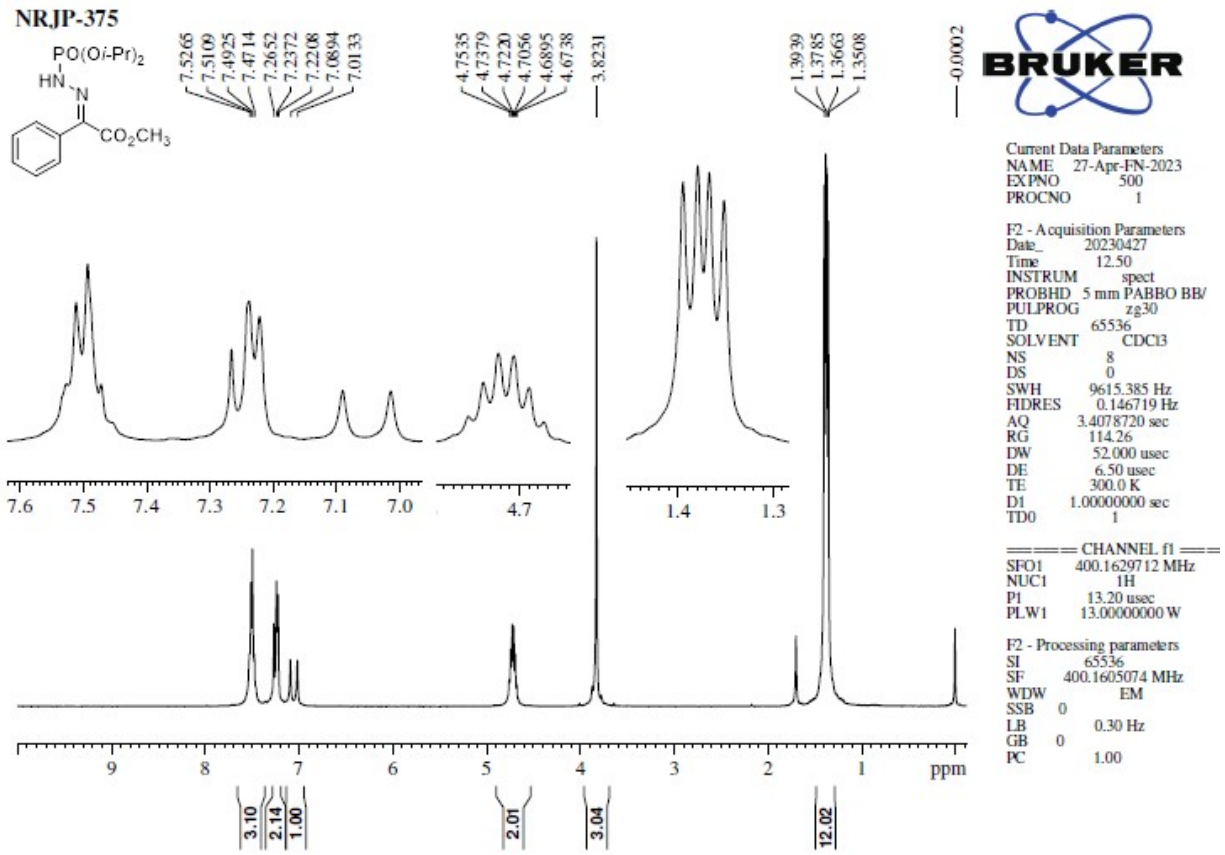


Figure S61: ^{1}H NMR spectrum of 3s

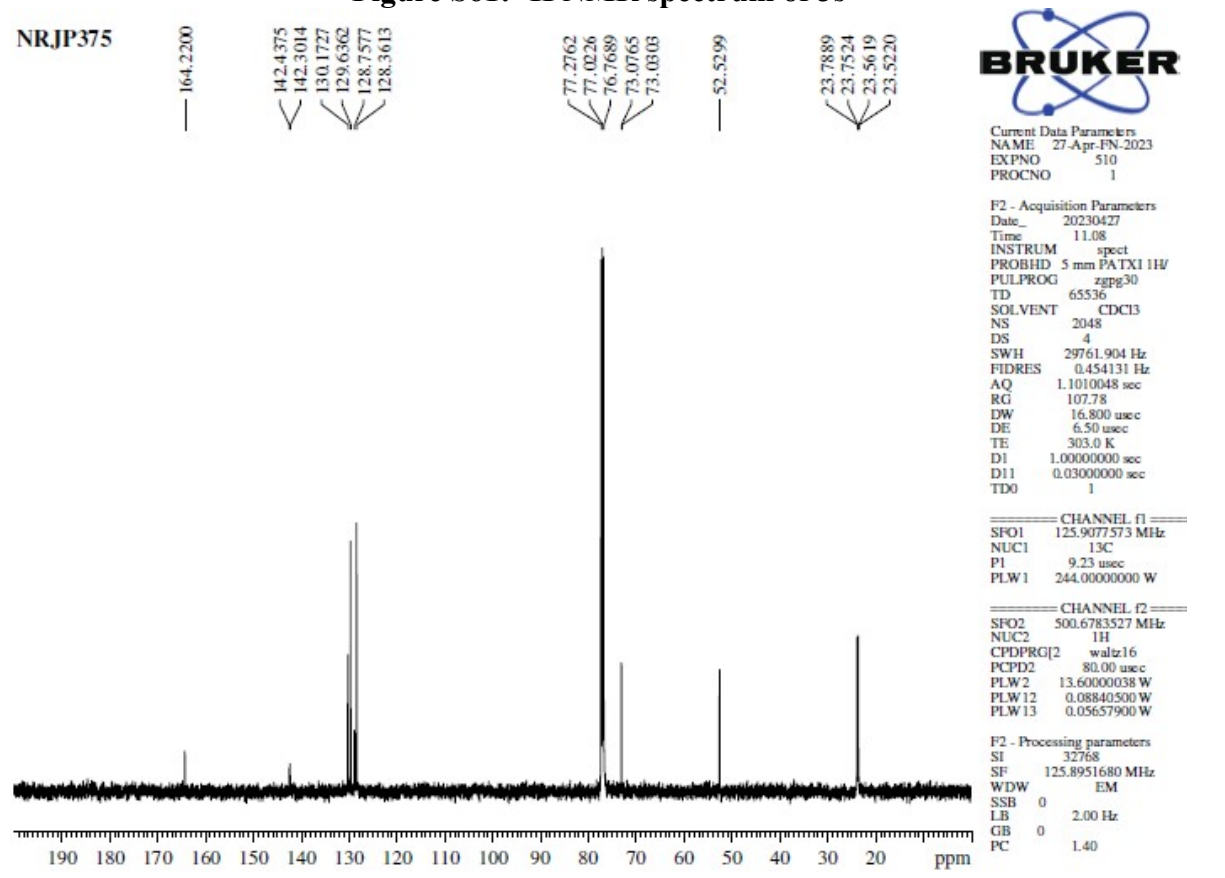


Figure S62: ^{13}C{H} NMR spectrum of 3s

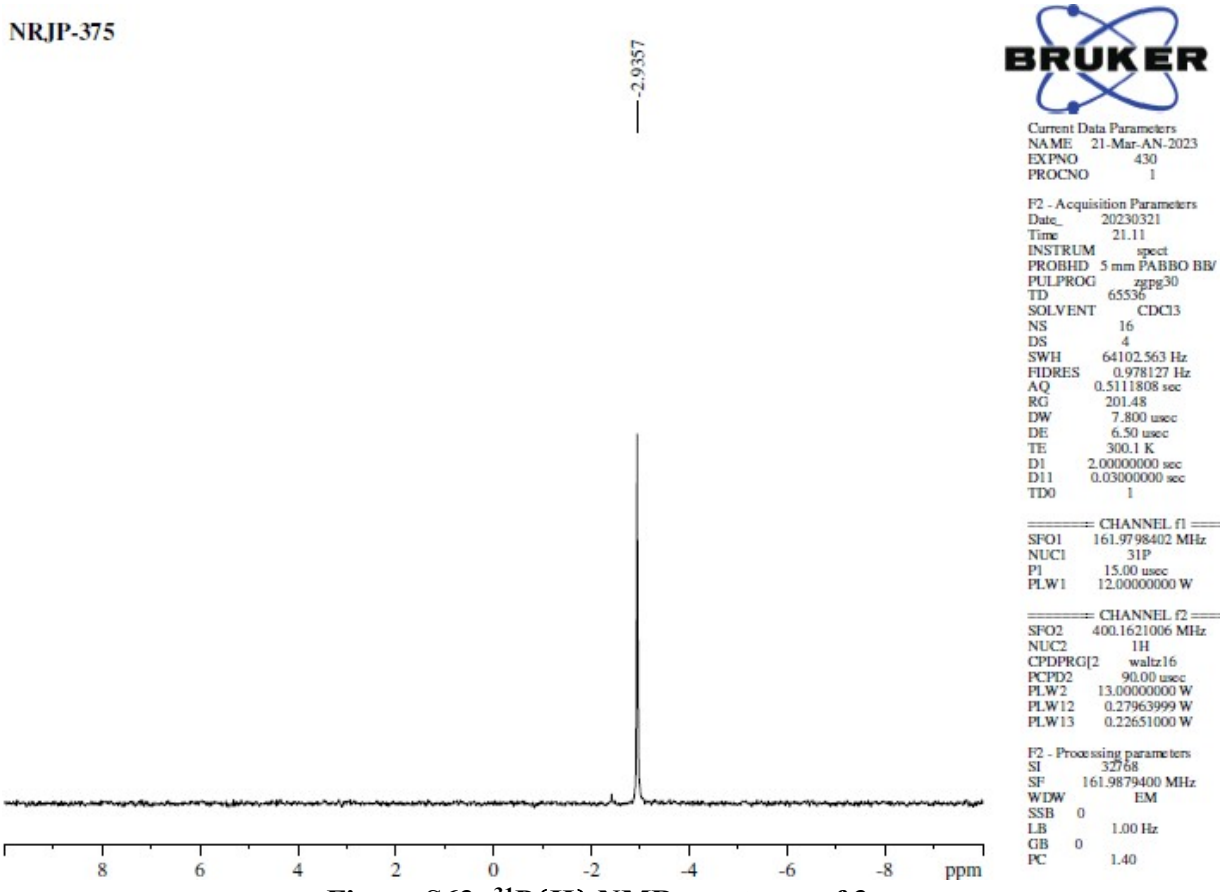


Figure S63: $^{31}P\{H\}$ NMR spectrum of 3s

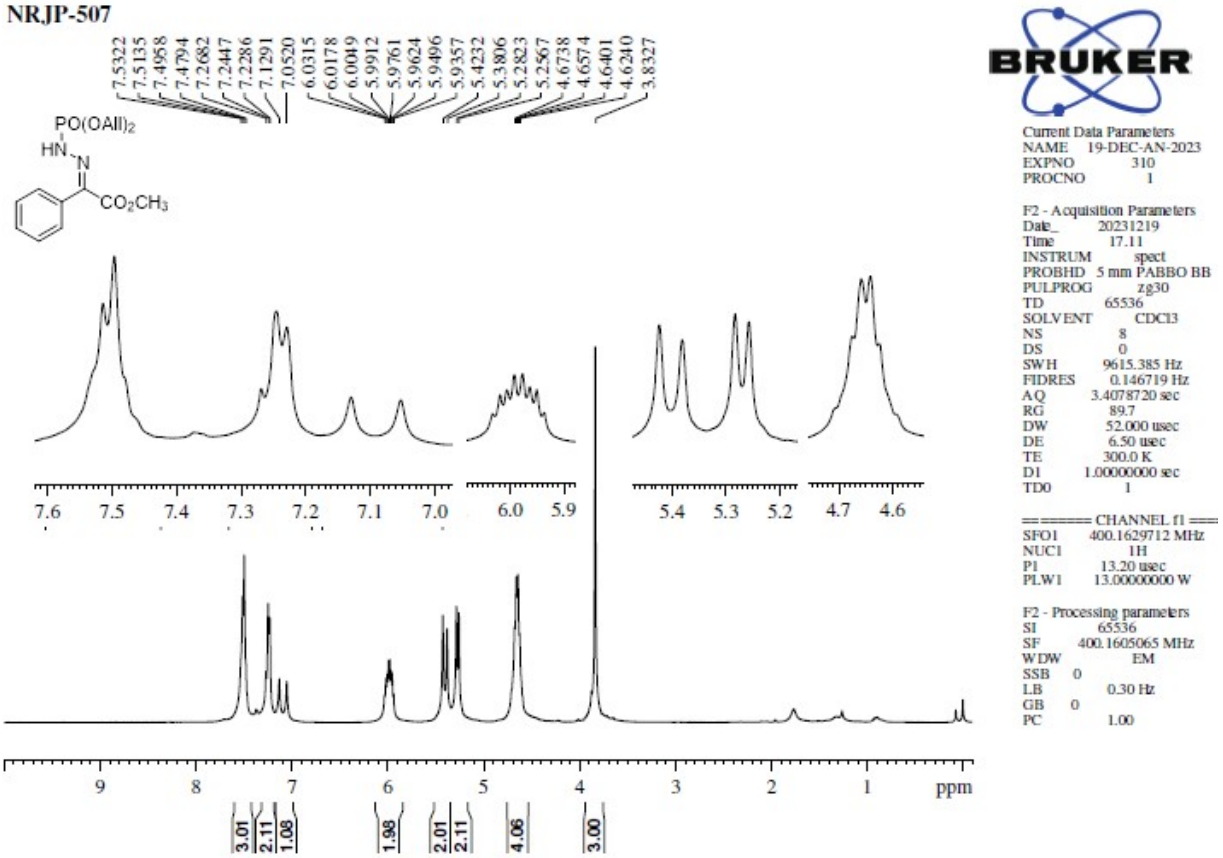


Figure S64: ^{1}H NMR spectrum of 3t

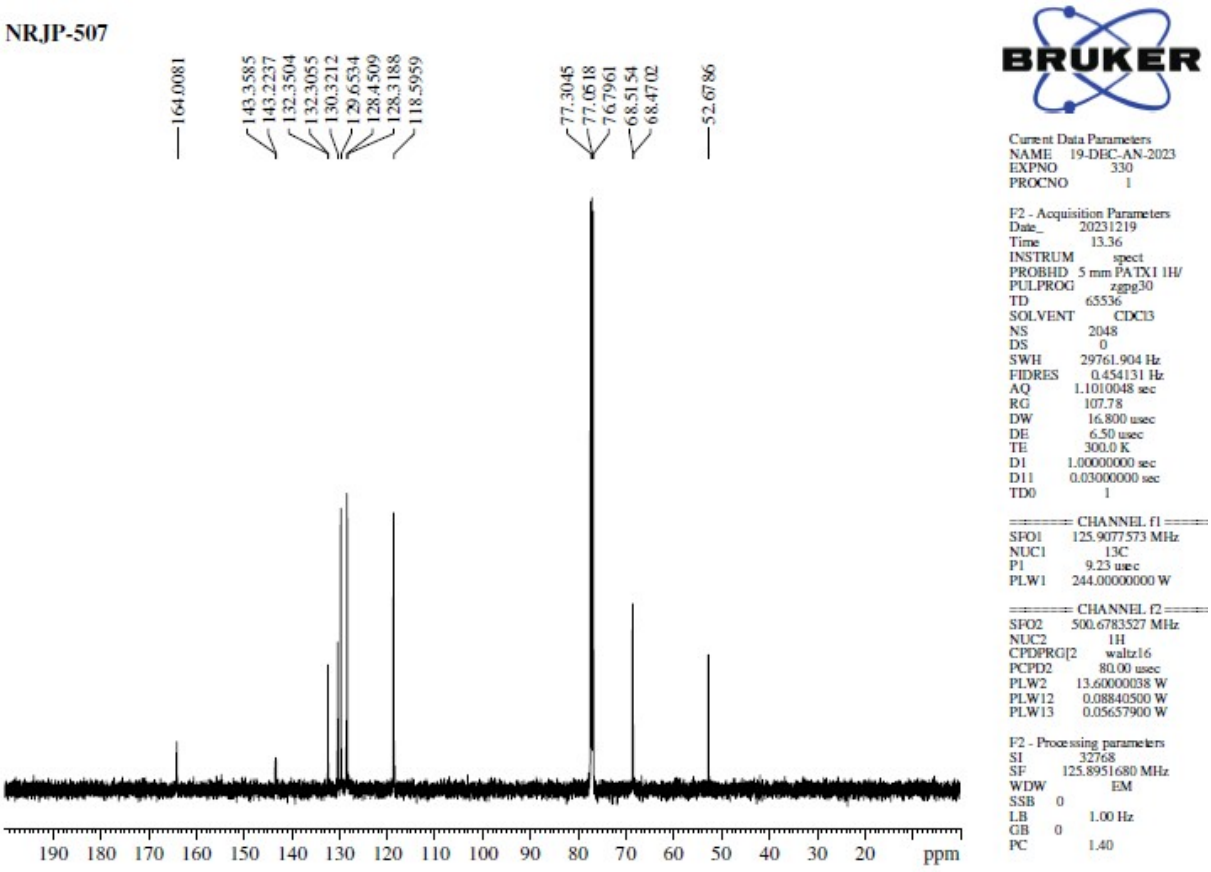


Figure S65: $^{13}C\{H\}$ NMR spectrum of 3t

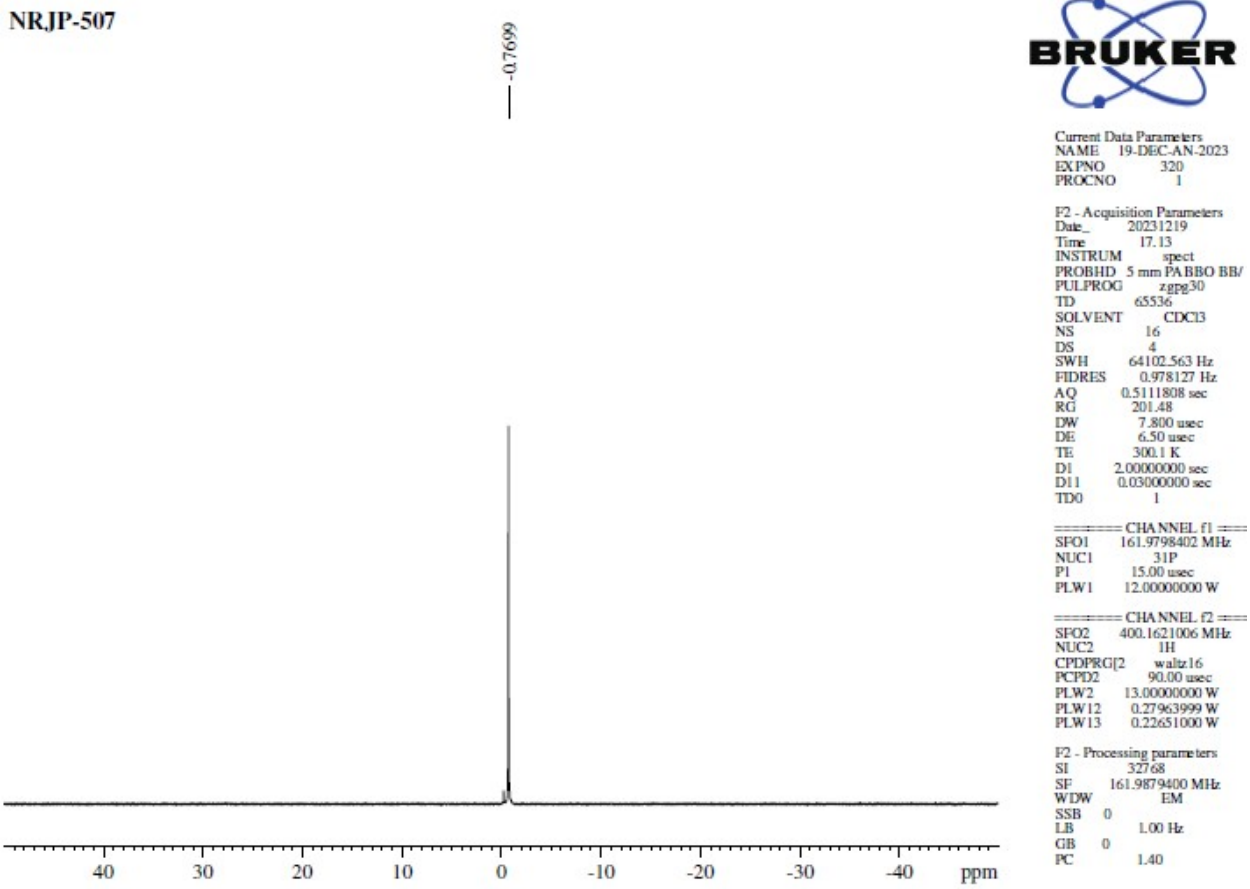


Figure S66: $^{31}P\{H\}$ NMR spectrum of 3t

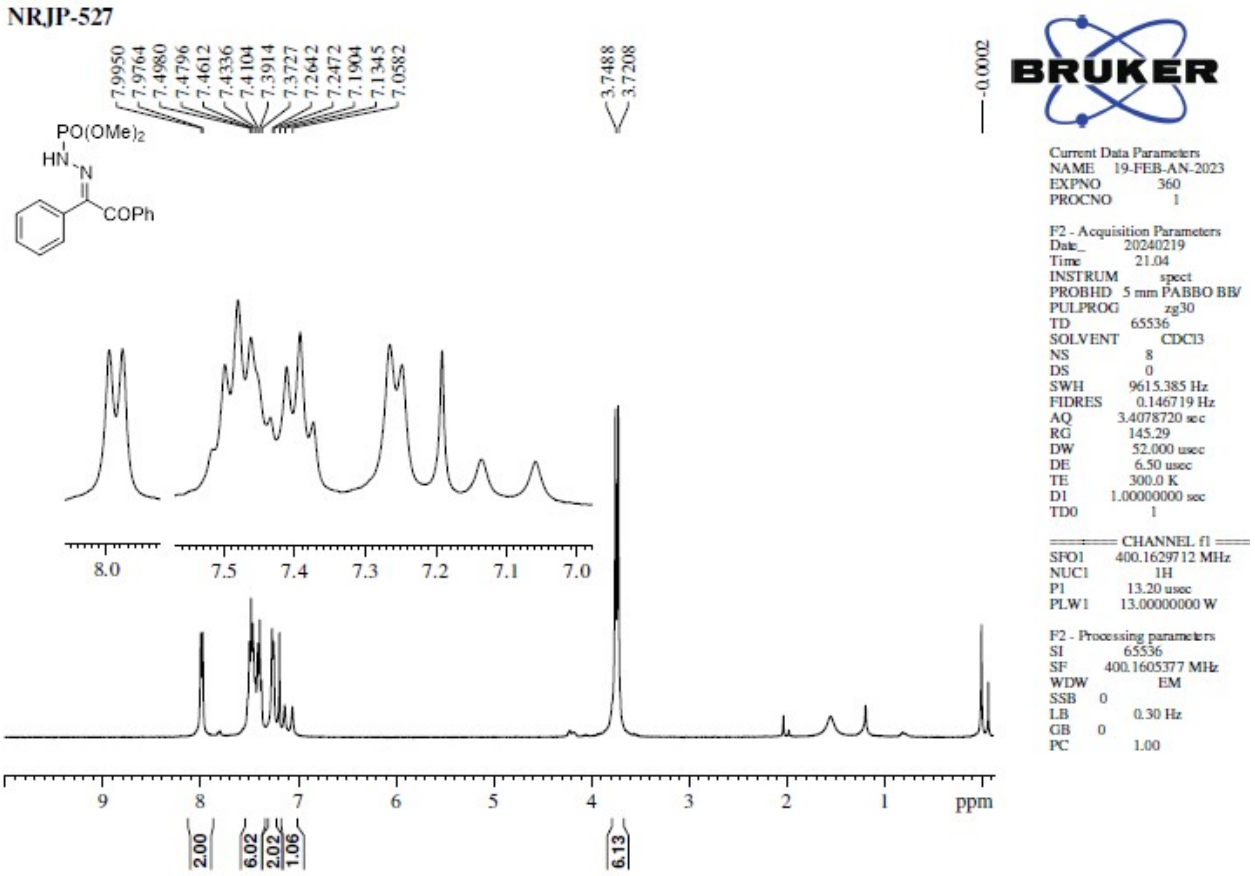


Figure S67: ^{1}H NMR spectrum of 3u

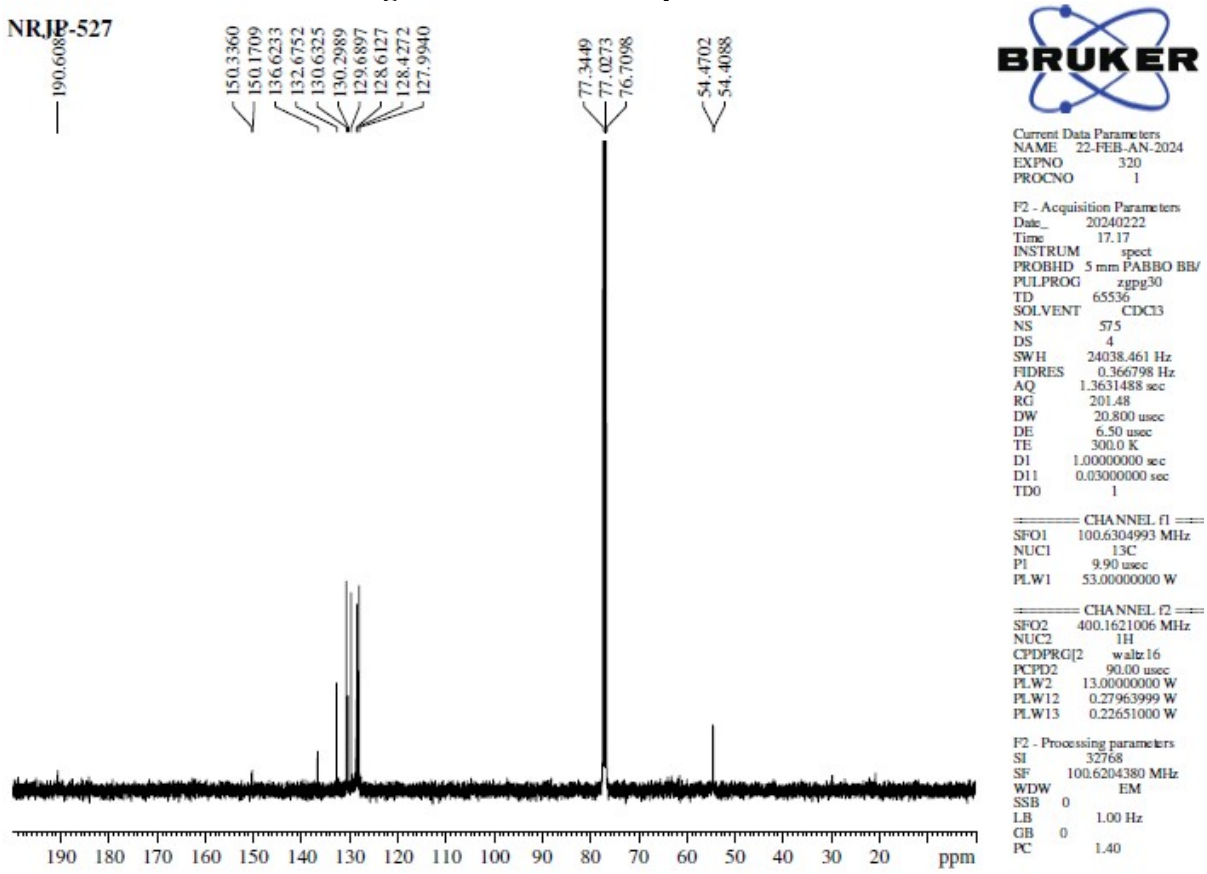


Figure S68: ^{13}C{H} NMR spectrum of 3u

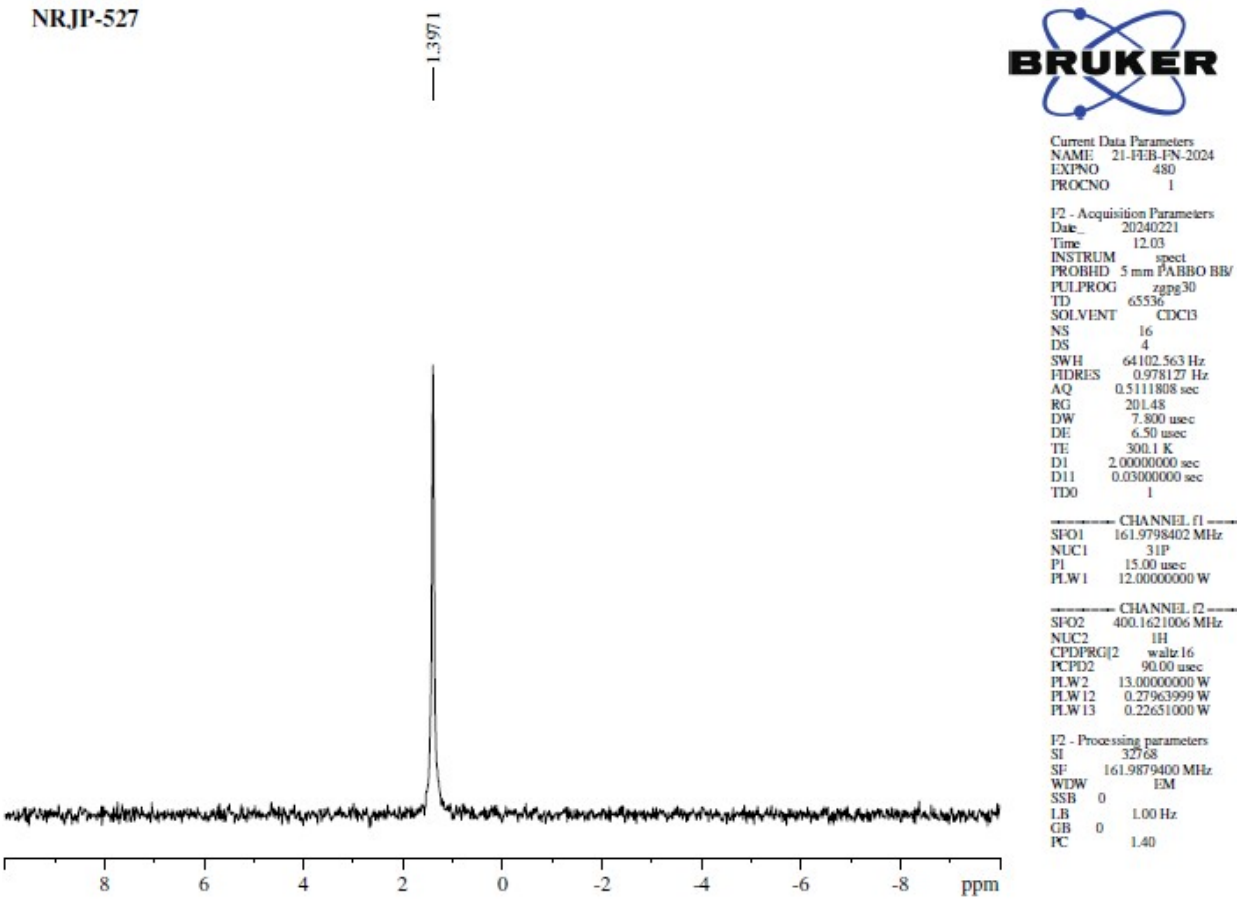


Figure S69: $^{31}P\{H\}$ NMR spectrum of 3u

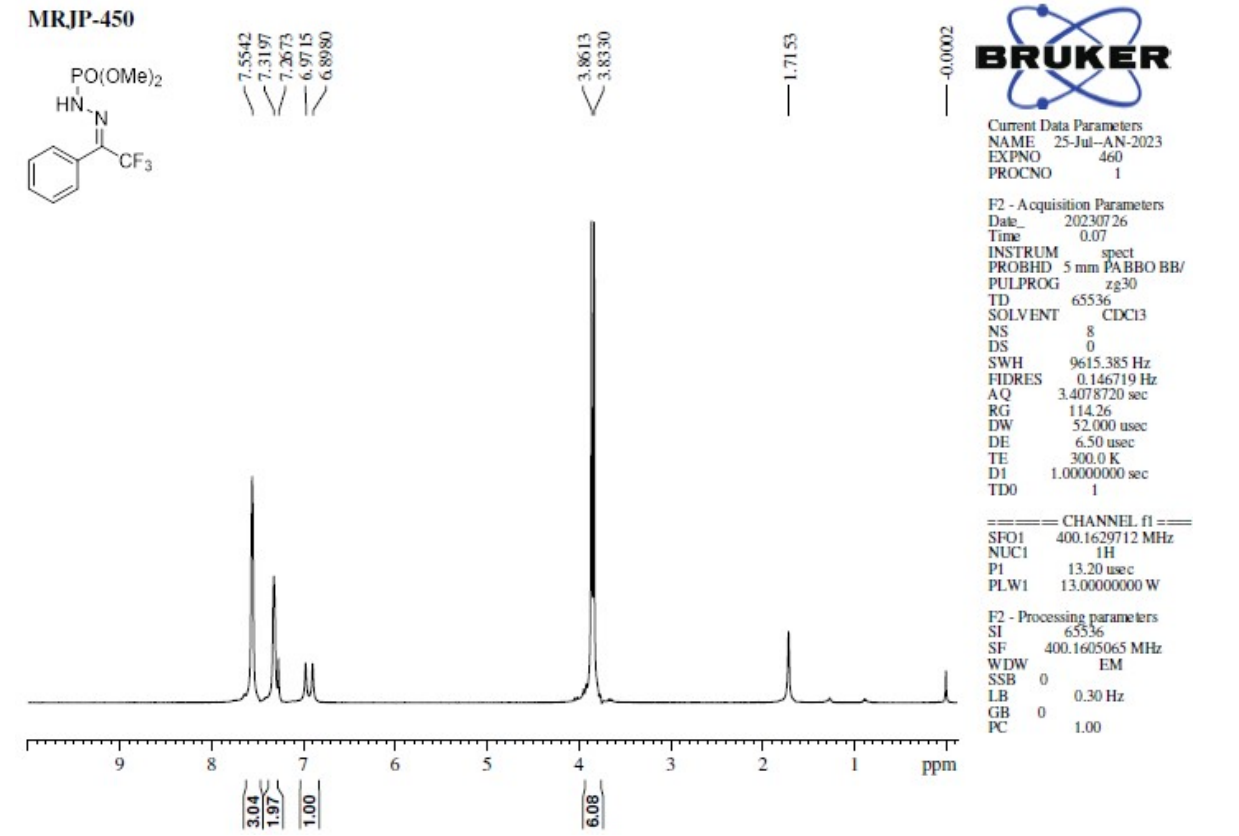


Figure S70: ^{1}H NMR spectrum of 3v

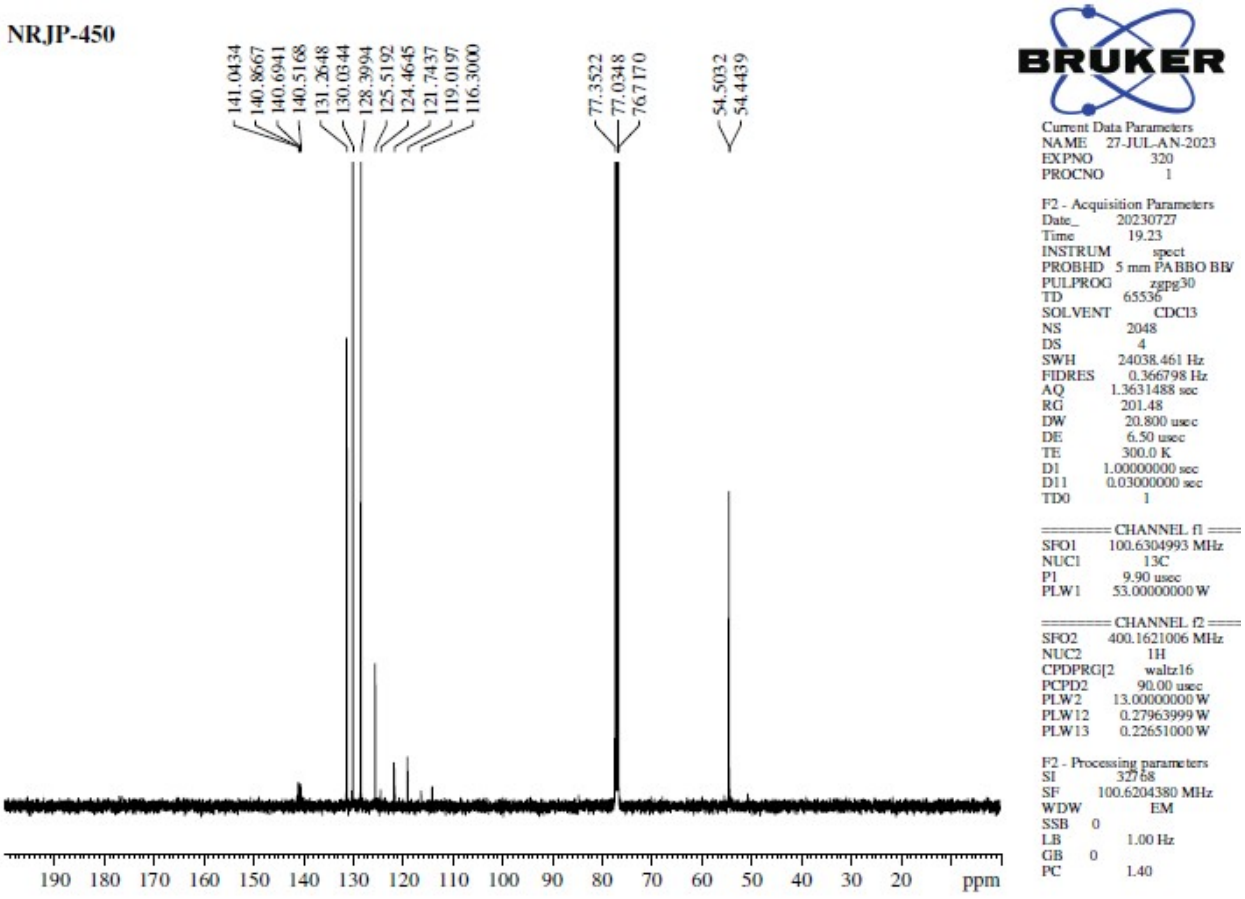


Figure S71: $^{13}C\{H\}$ NMR spectrum of 3v

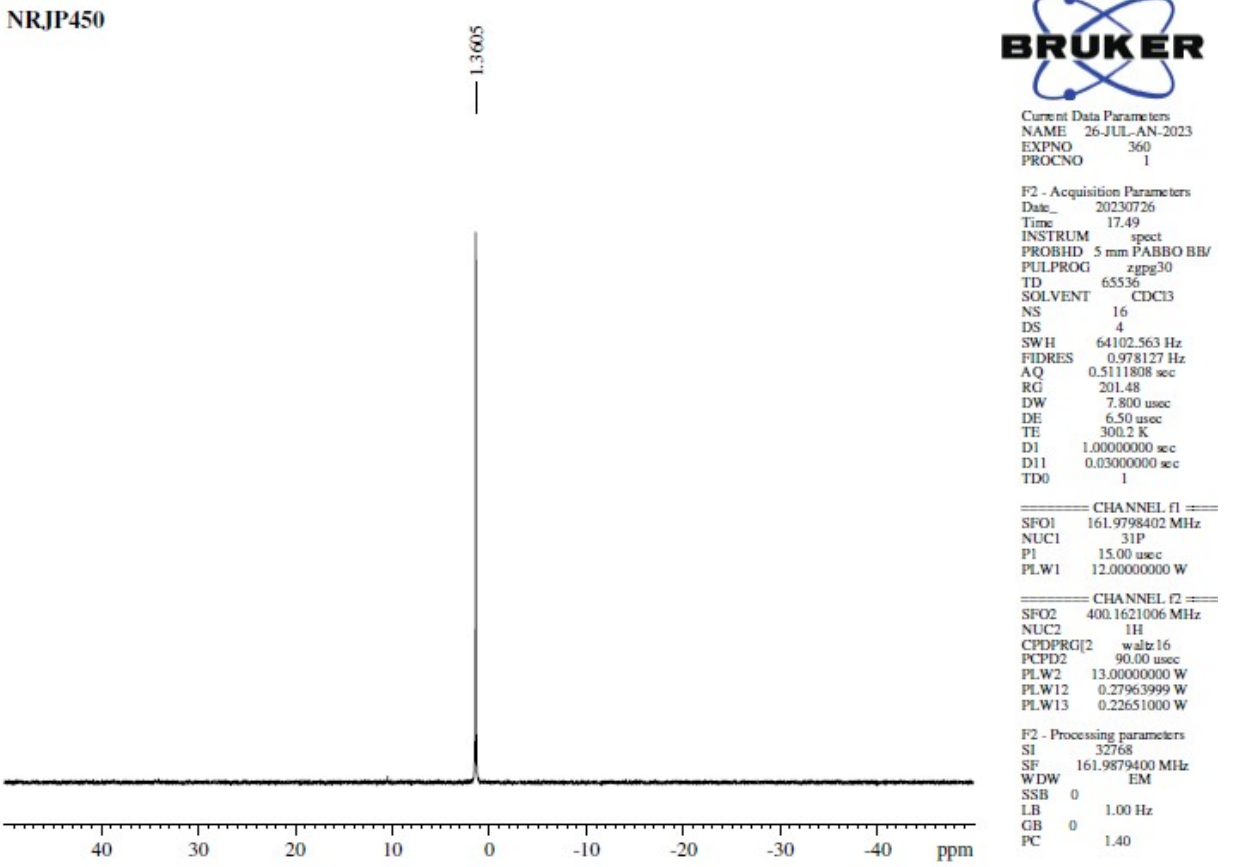


Figure S72: $^{31}P\{H\}$ NMR spectrum of 3v

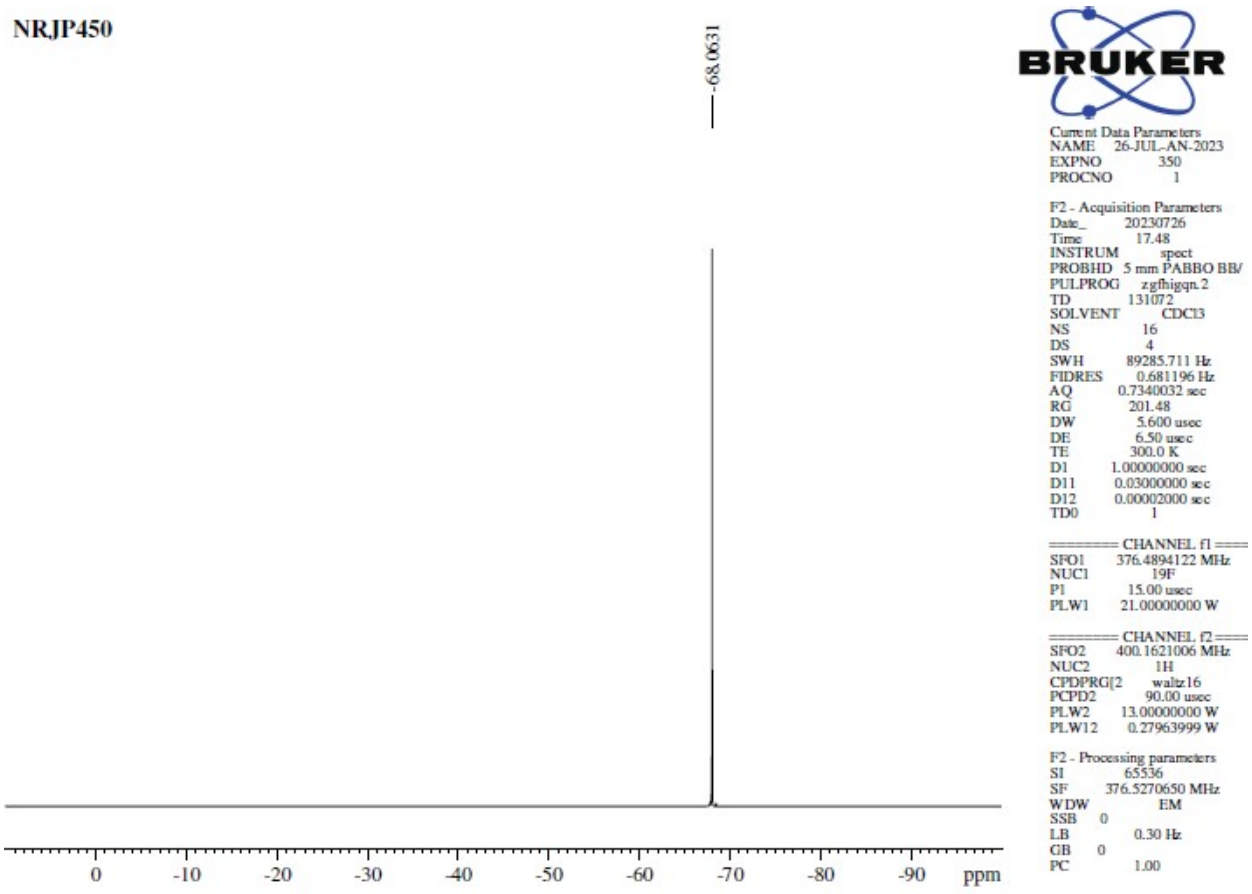


Figure S73: $^{19}F\{H\}$ NMR spectrum of 3v

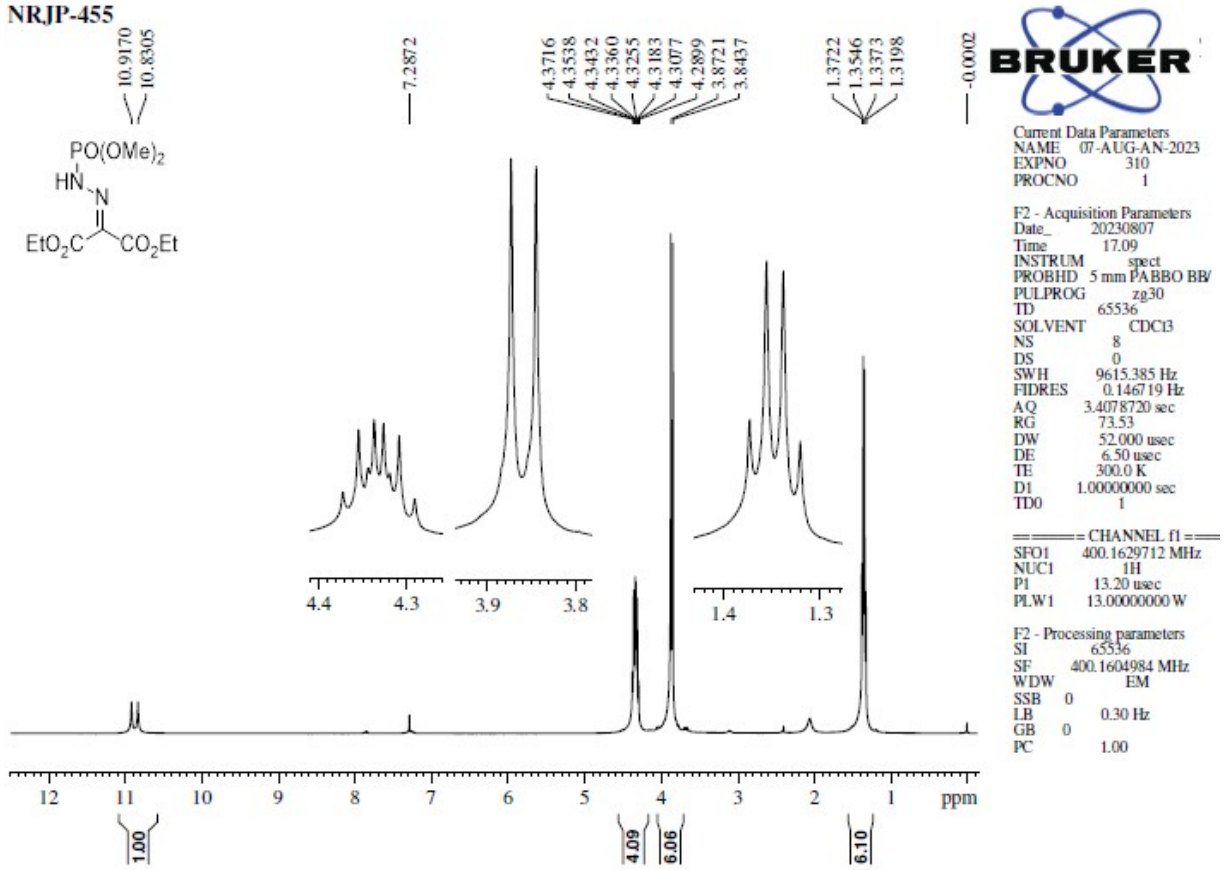


Figure S74: ^{1}H NMR spectrum of 3w

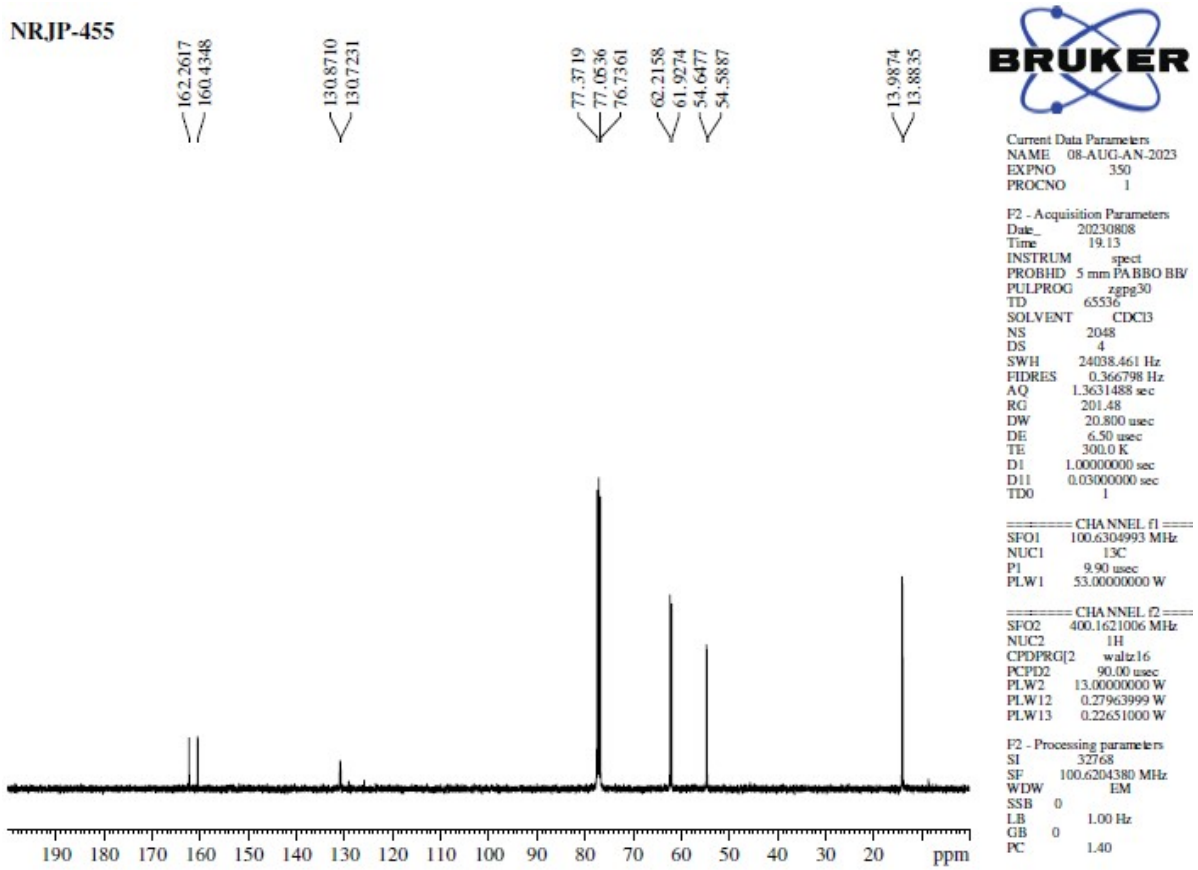


Figure S75: $^{13}C\{H\}$ NMR spectrum of 3w

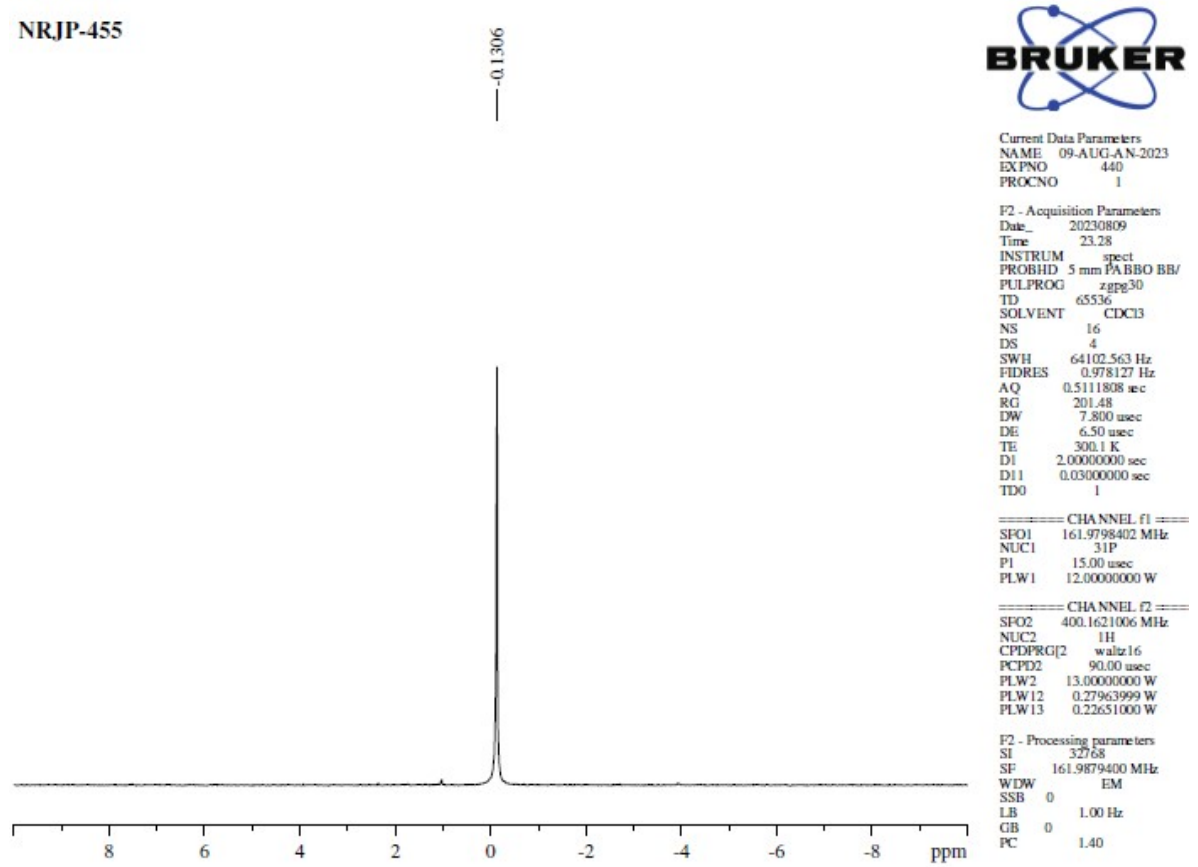


Figure S76: $^{31}P\{H\}$ NMR spectrum of 3w

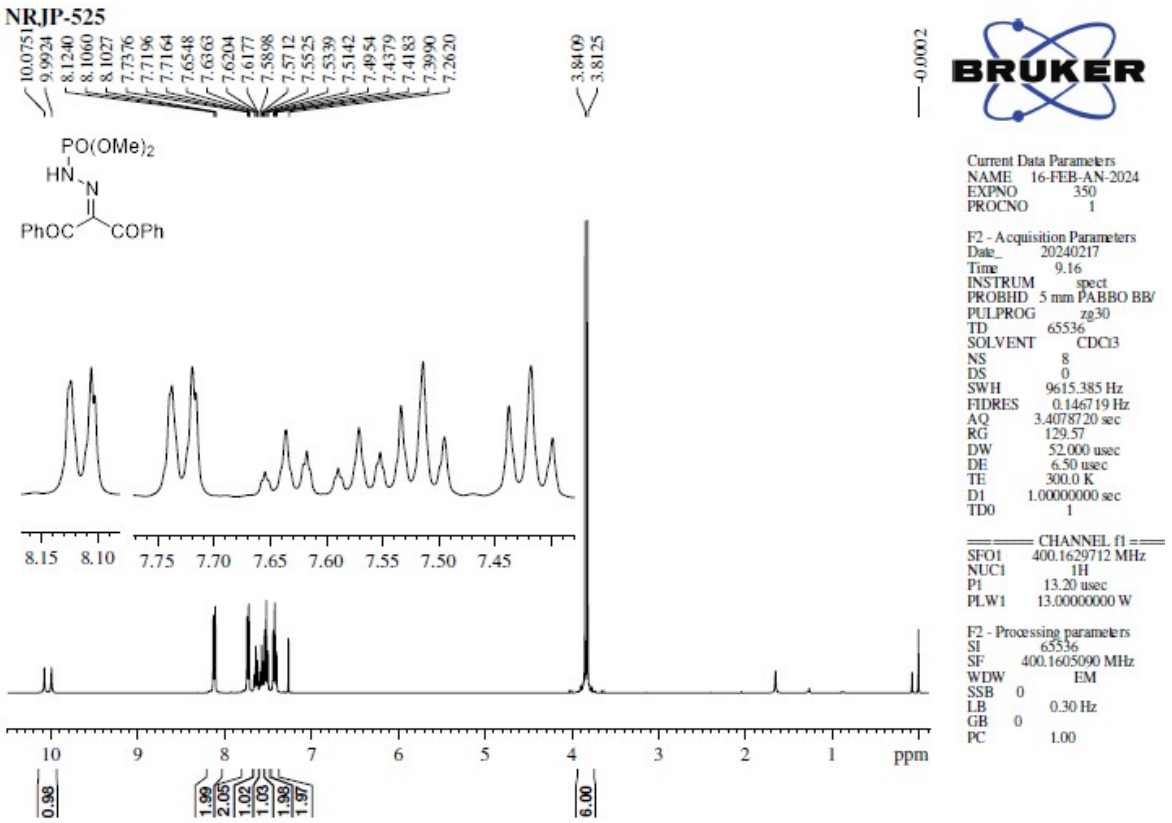


Figure S77: ^{1}H NMR spectrum of 3x

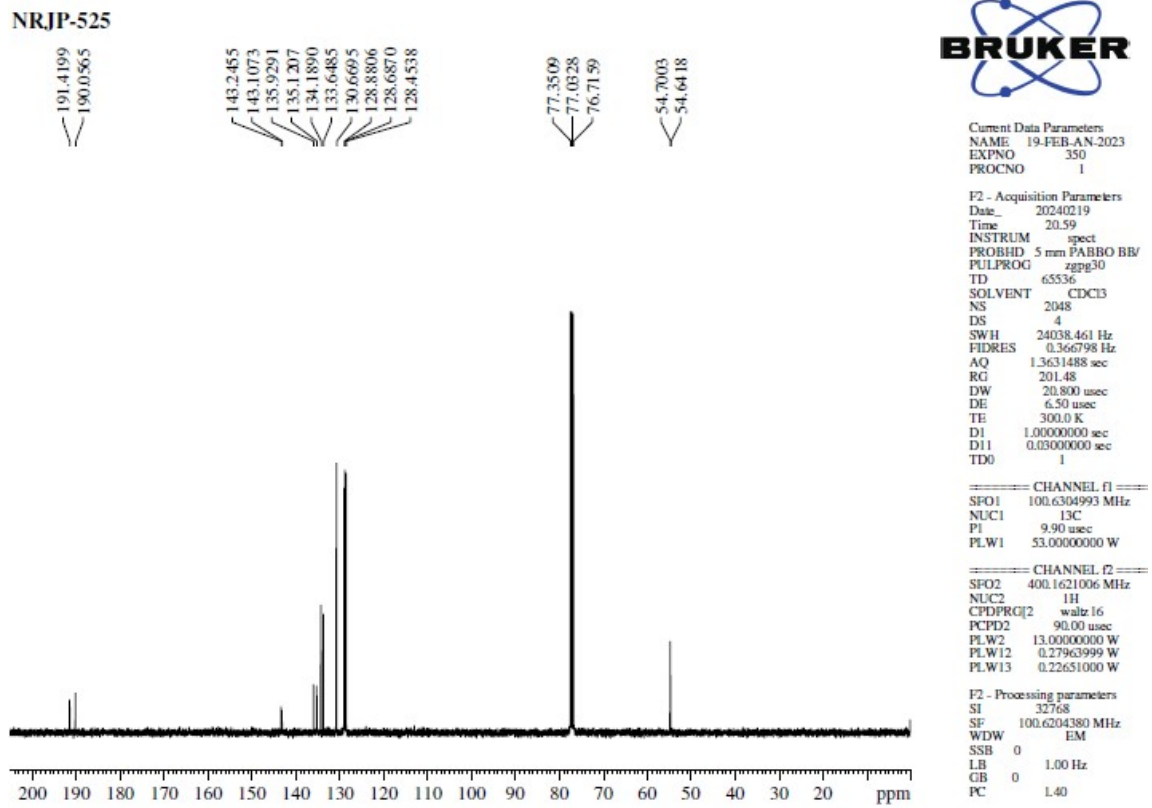


Figure S78: ^{13}C{H} NMR spectrum of 3x

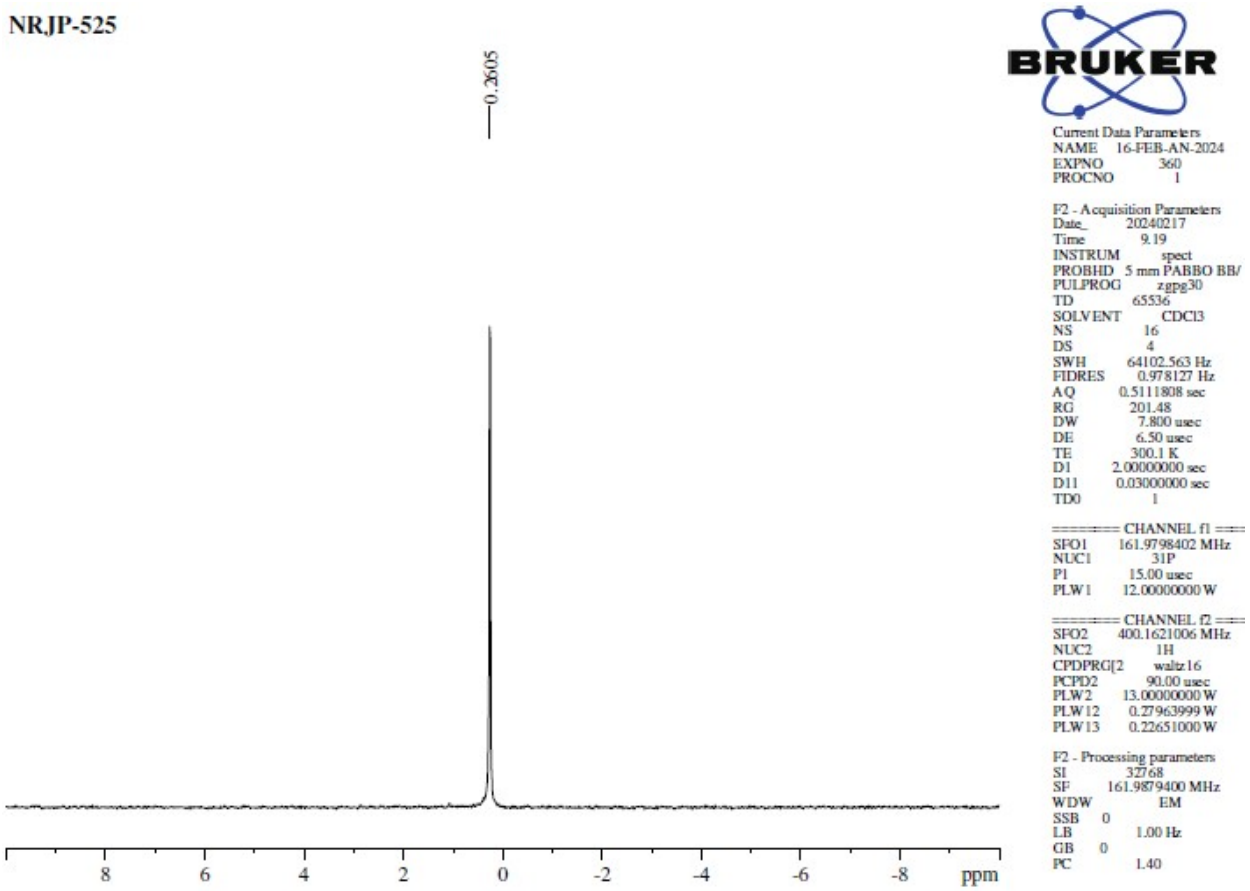


Figure S79: $^{31}P\{H\}$ NMR spectrum of 3x

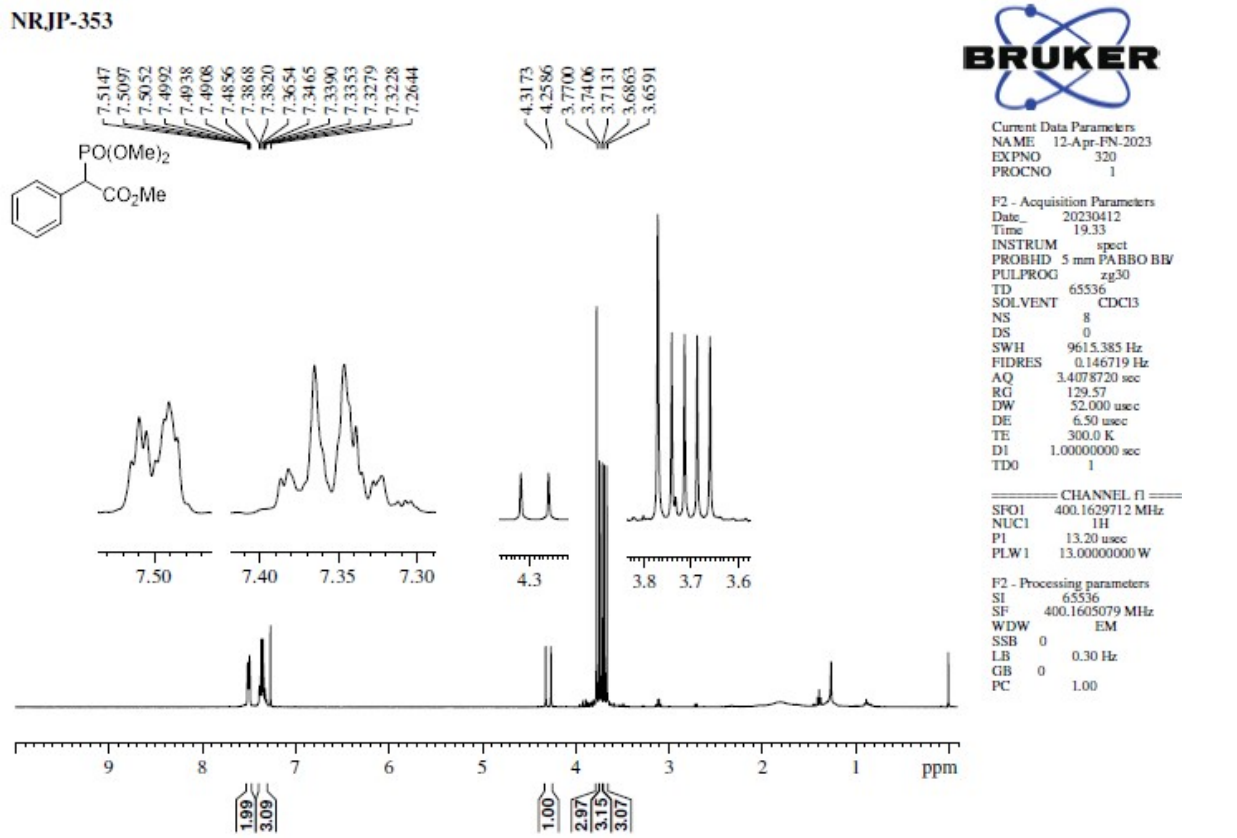


Figure S80: ^{1}H NMR spectrum of 4a

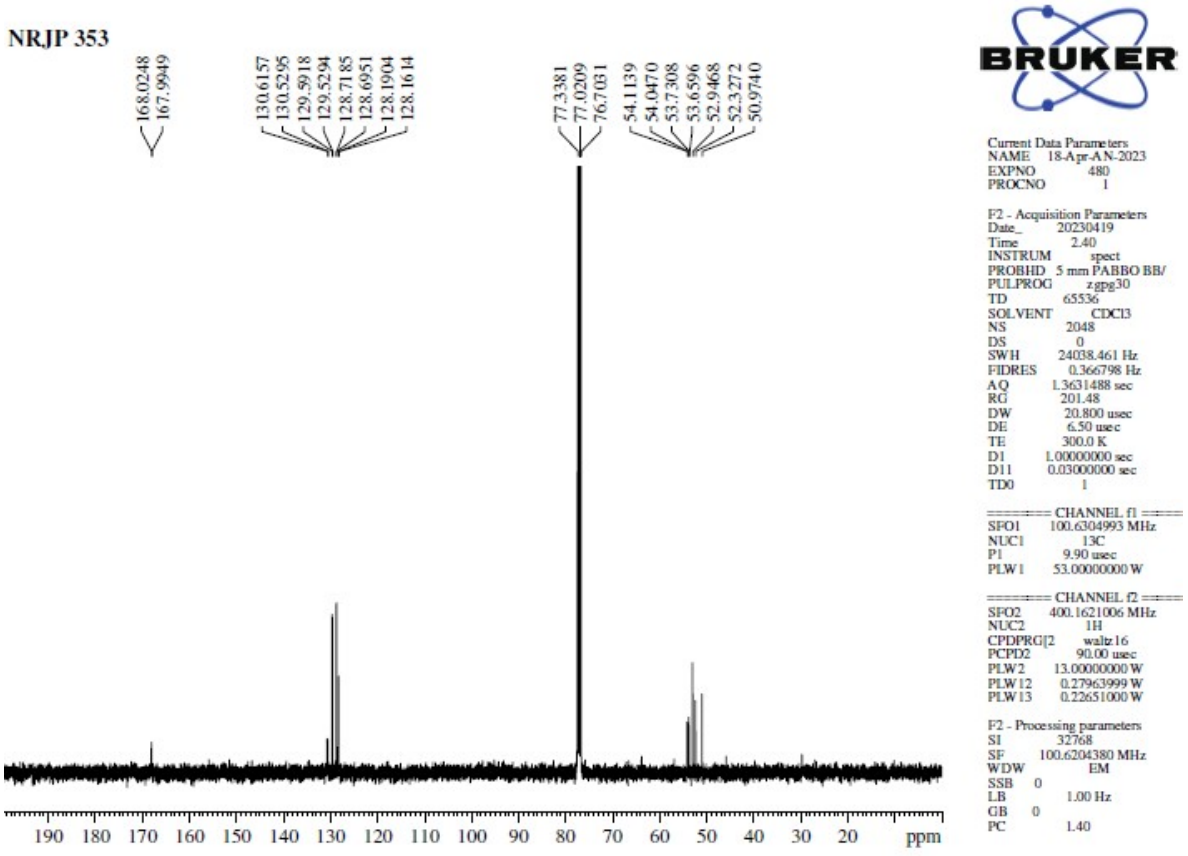


Figure S81: $^{13}C\{H\}$ NMR spectrum of 4a

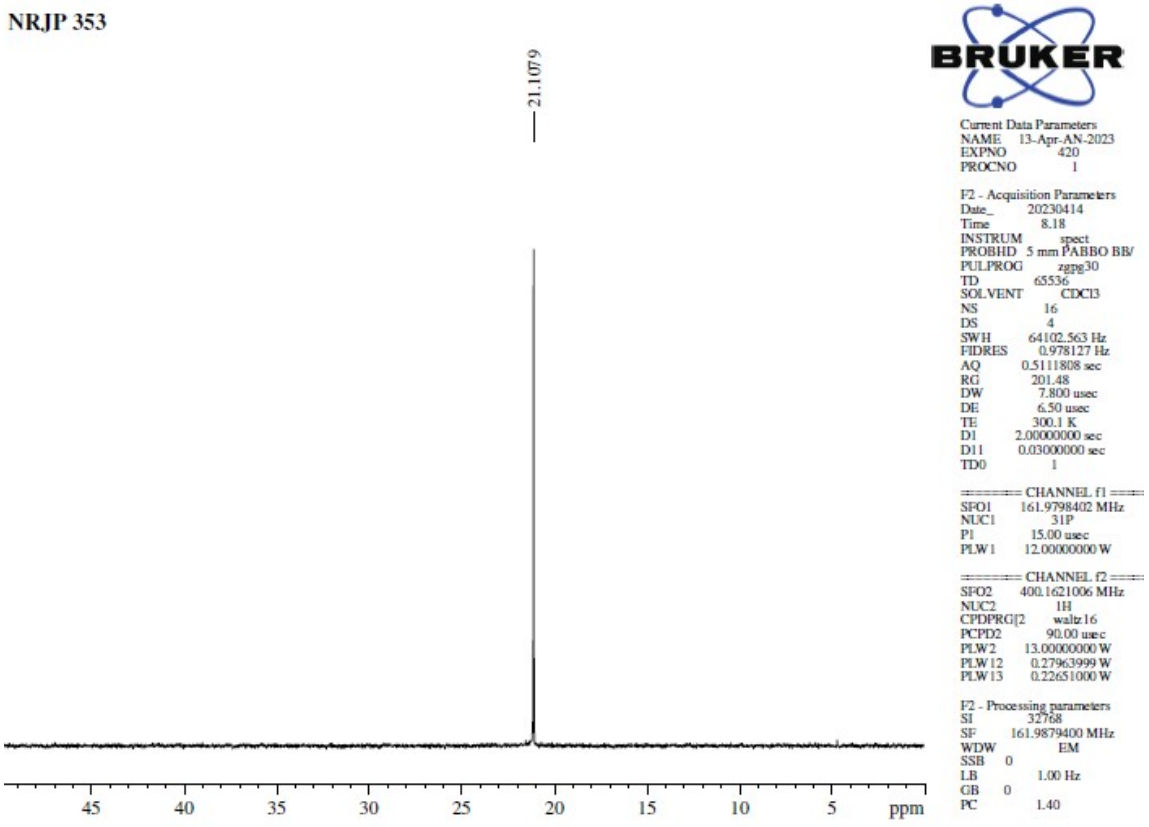


Figure S82: $^{31}P\{H\}$ NMR spectrum of 4a

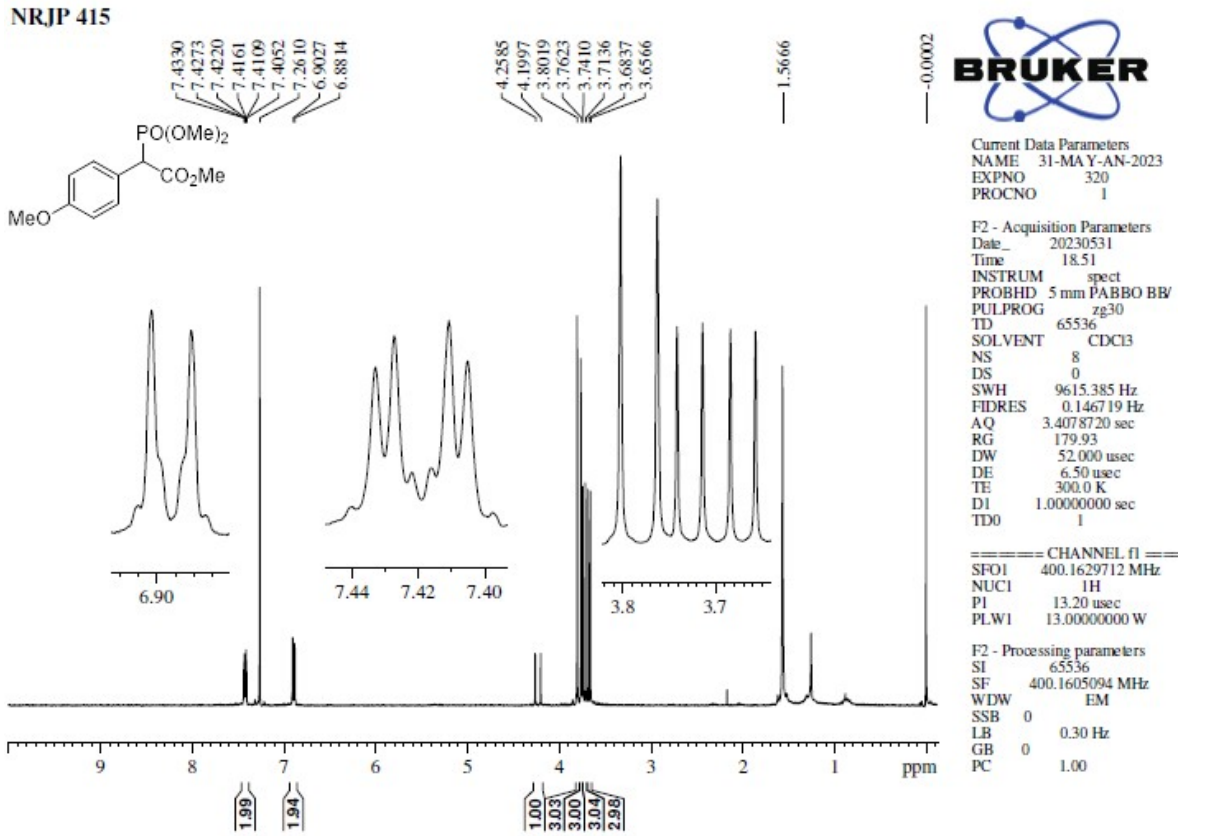


Figure S83: ^{1}H NMR spectrum of 4b

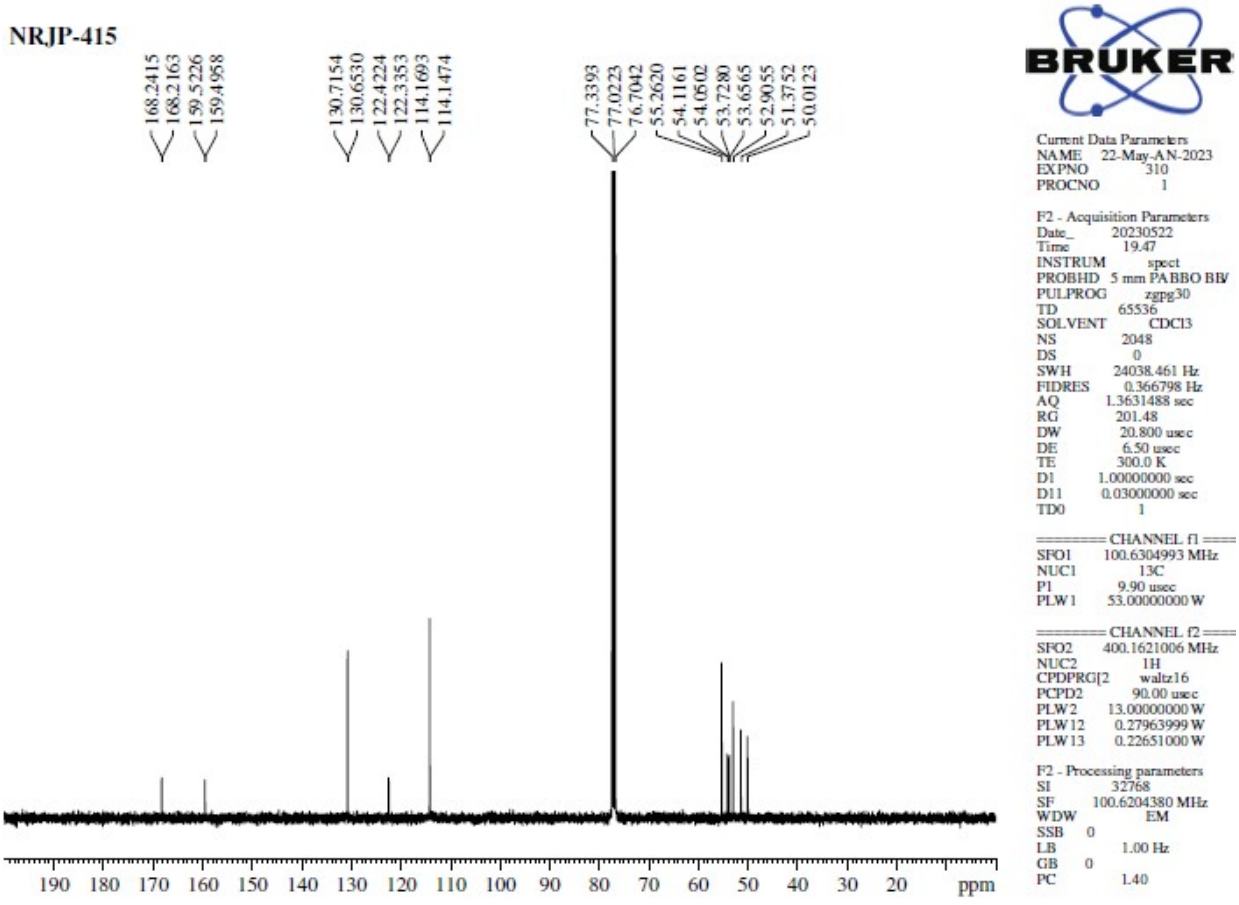


Figure S84: ^{13}C{H} NMR spectrum of 4b

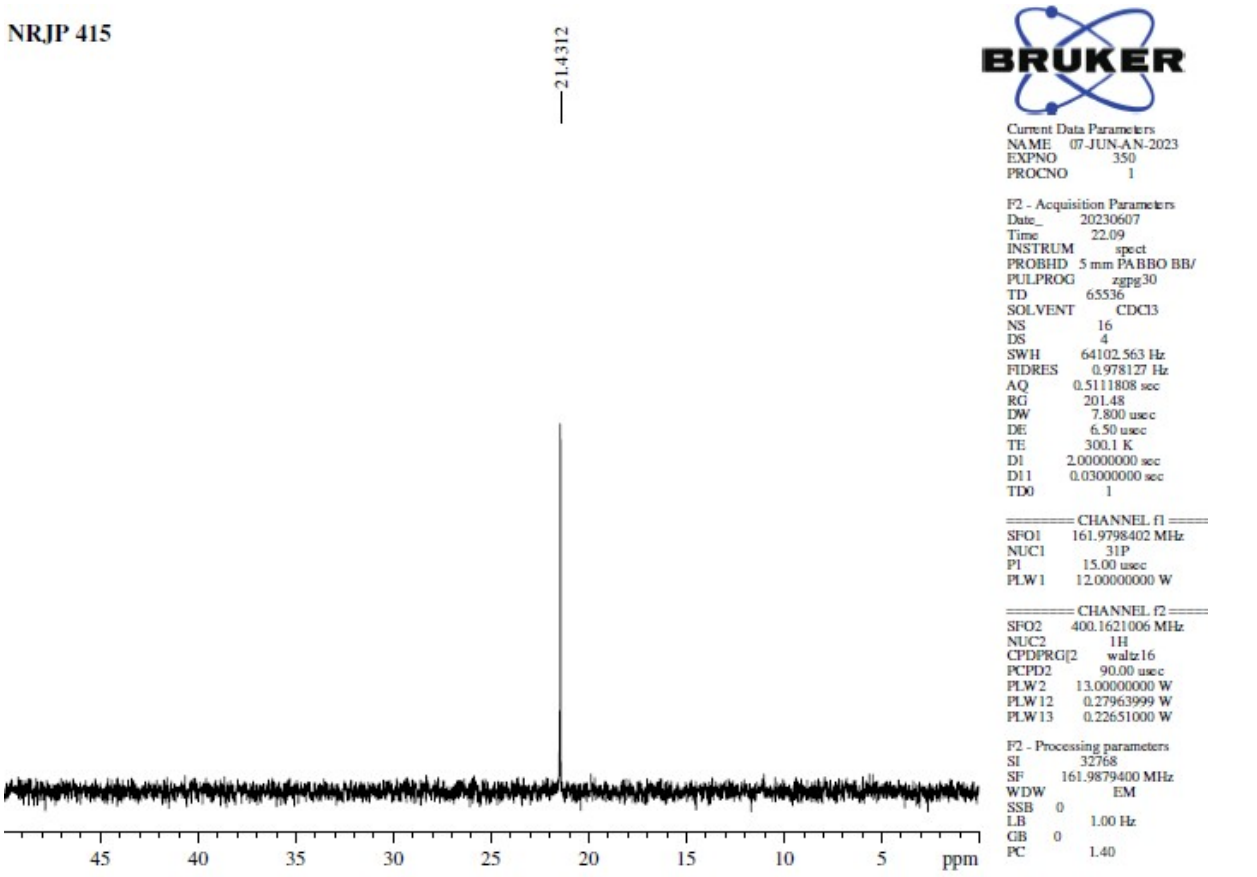


Figure S85: $^{31}P\{H\}$ NMR spectrum of 4b

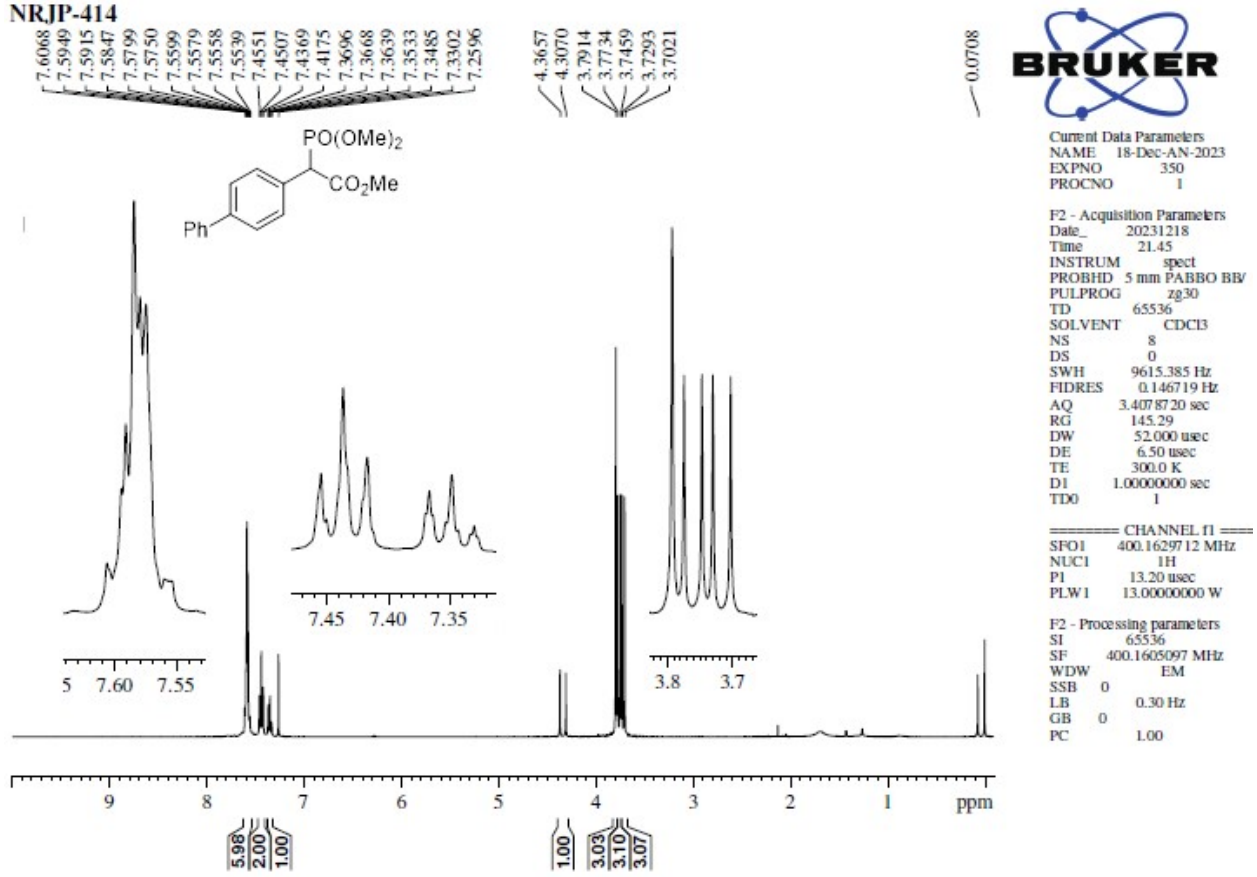


Figure S86: ^{1}H NMR spectrum of 4c

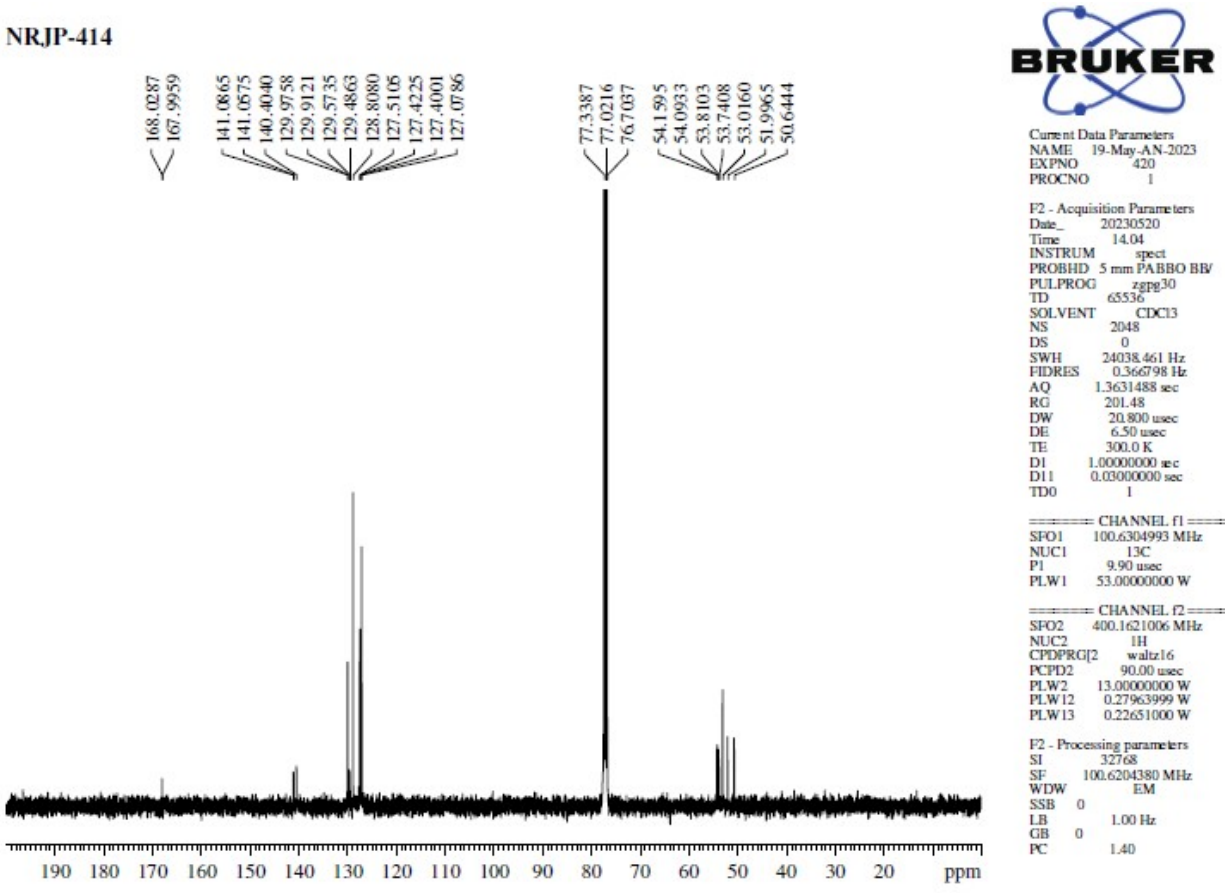


Figure S87: $^{13}C\{H\}$ NMR spectrum of 4c

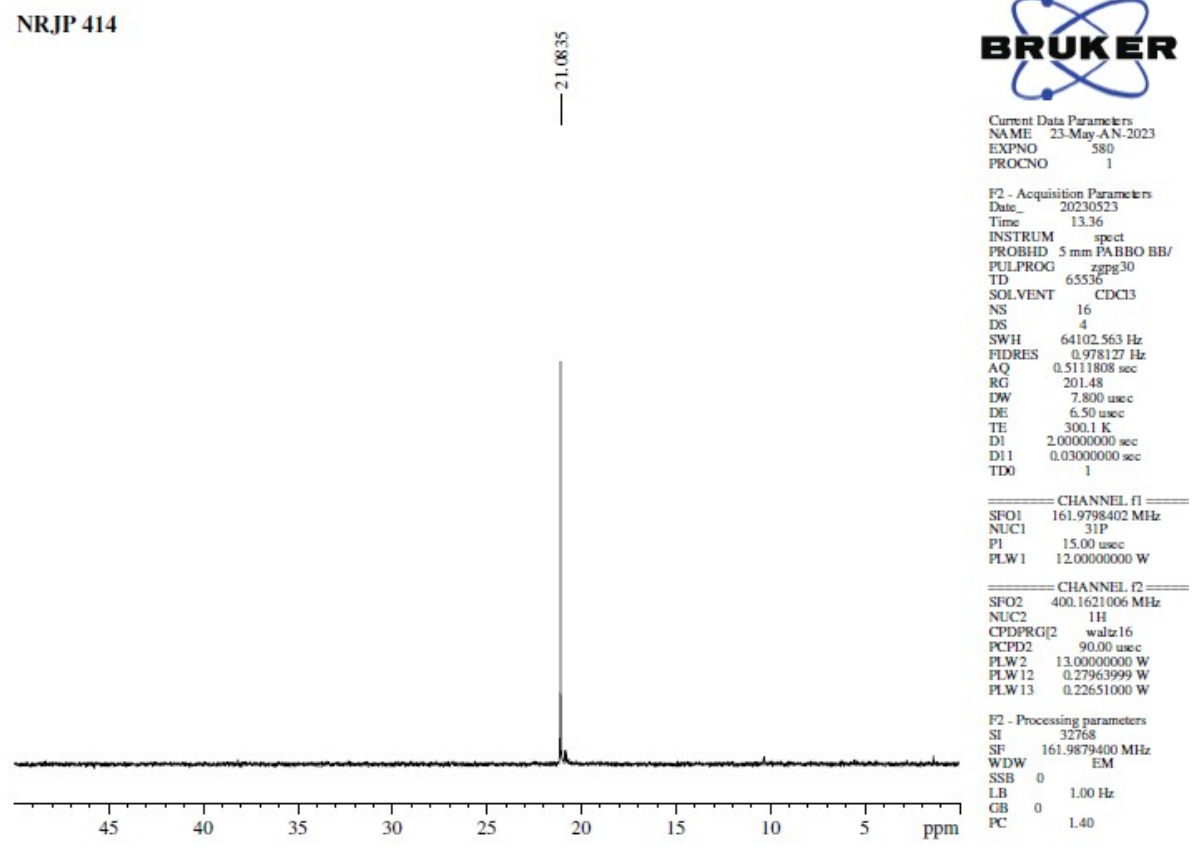


Figure S88: $^{31}P\{H\}$ NMR spectrum of 4c

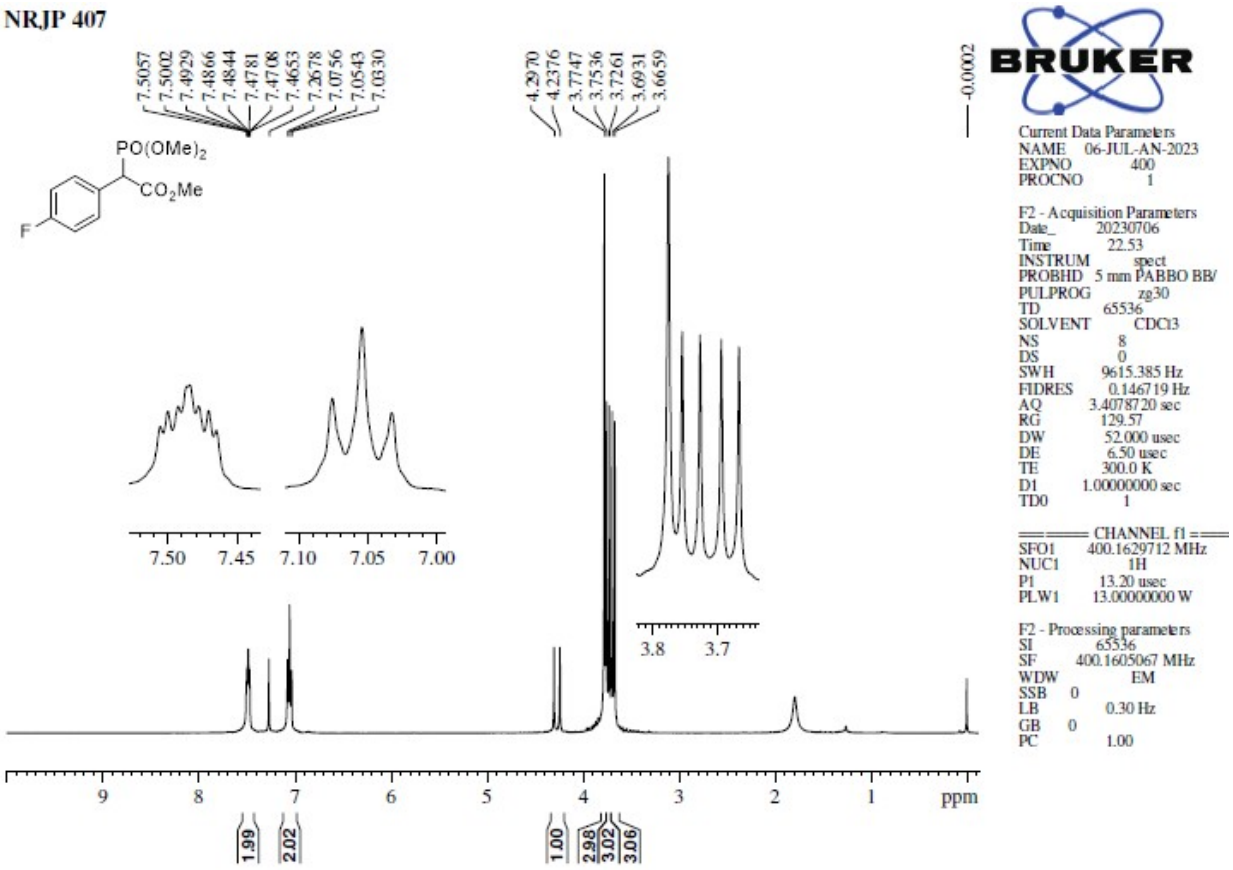


Figure S89: ^{1}H NMR spectrum of 4d

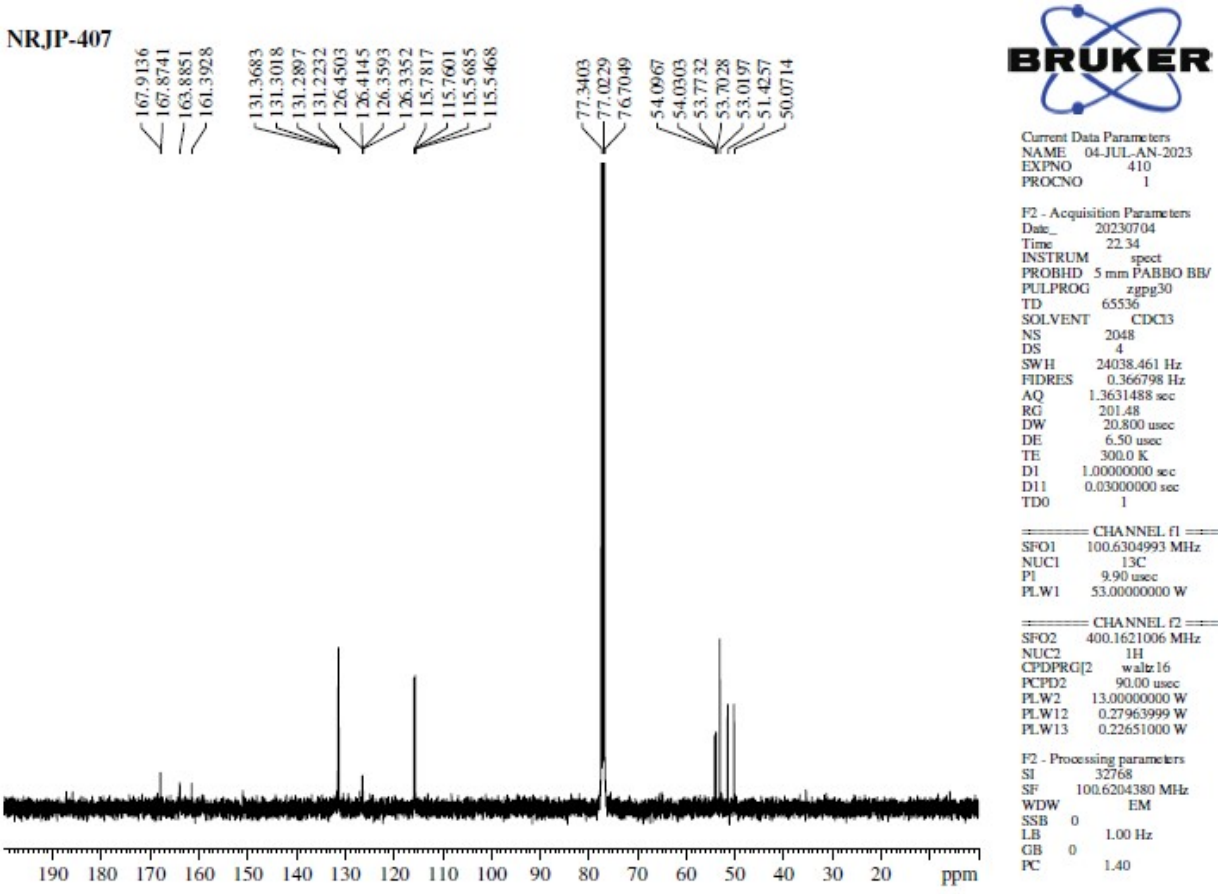


Figure S90: ^{13}C{H} NMR spectrum of 4d

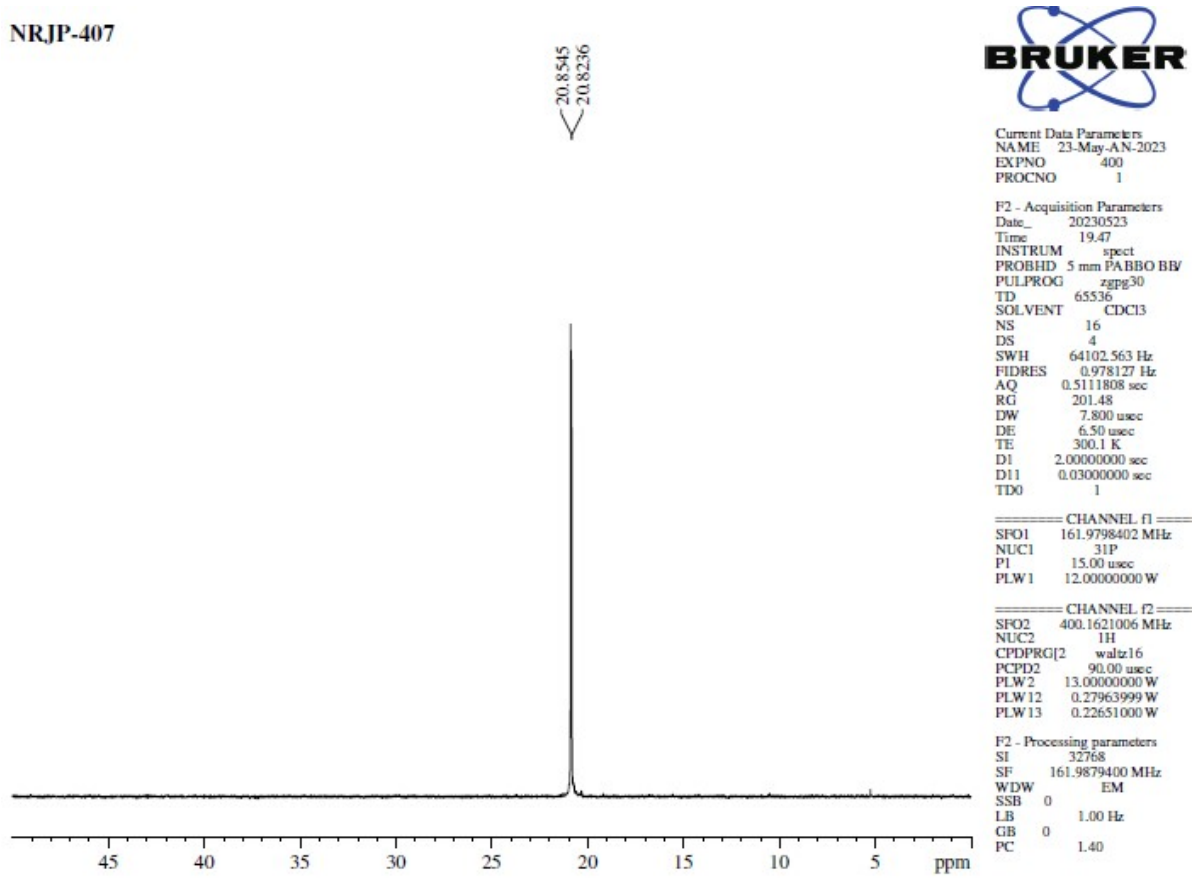


Figure S91: $^{31}P\{H\}$ NMR spectrum of 4d

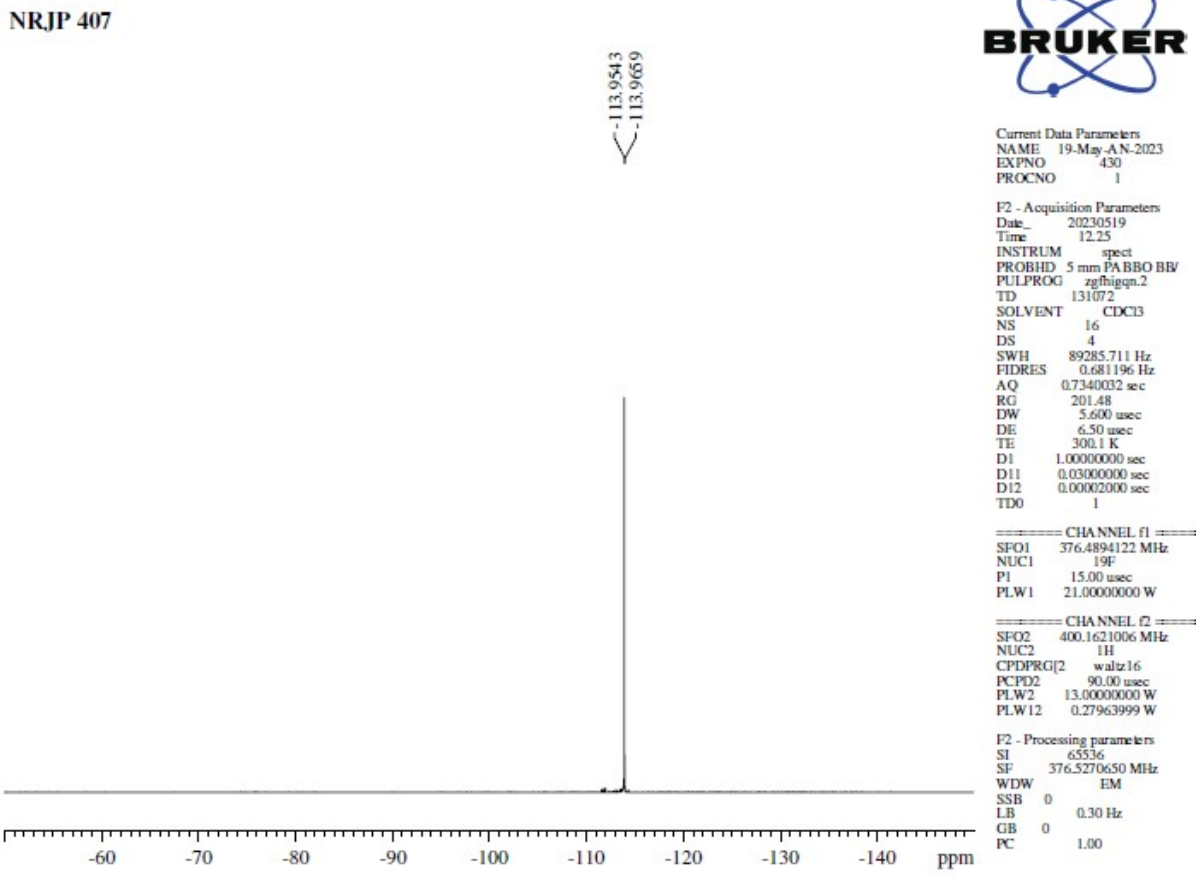


Figure S92: $^{19}F\{H\}$ NMR spectrum of 4d

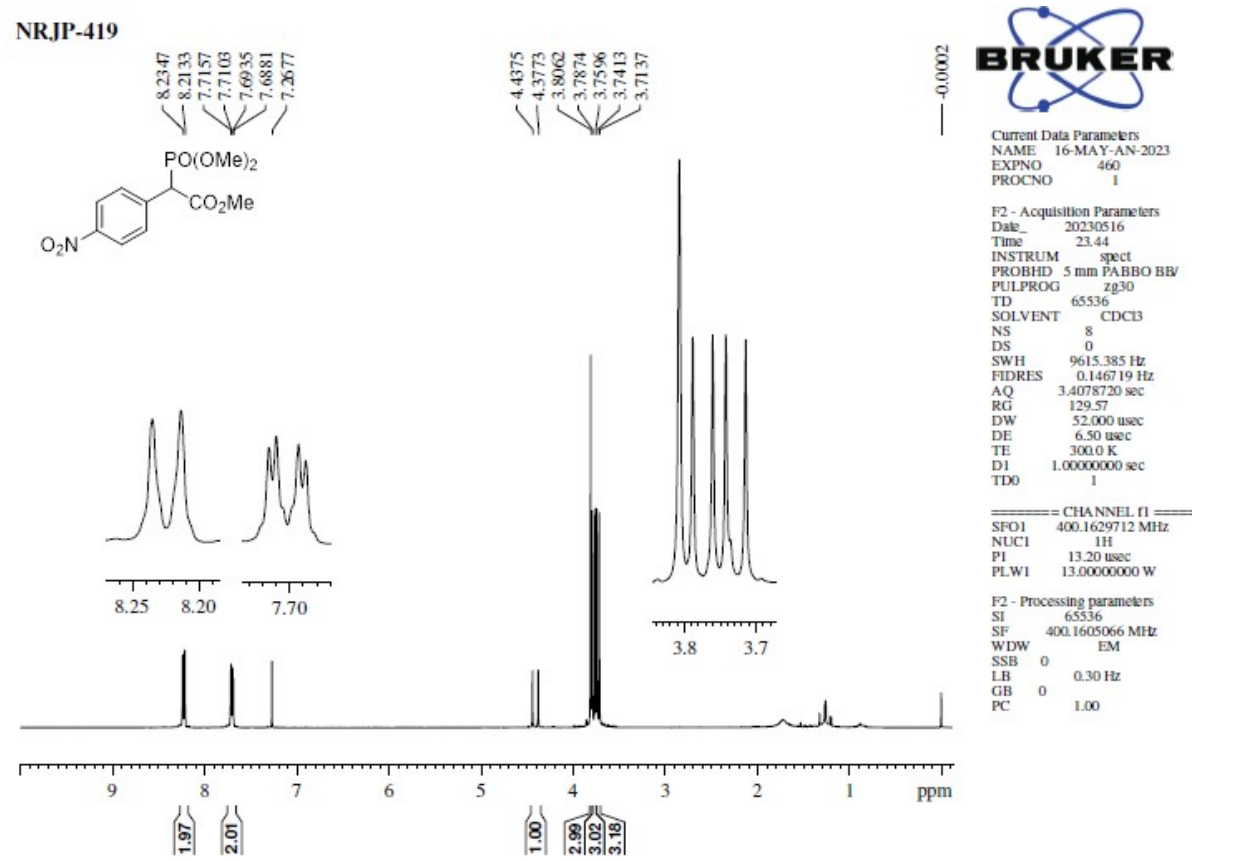


Figure S93: ^{1}H NMR spectrum of 4e

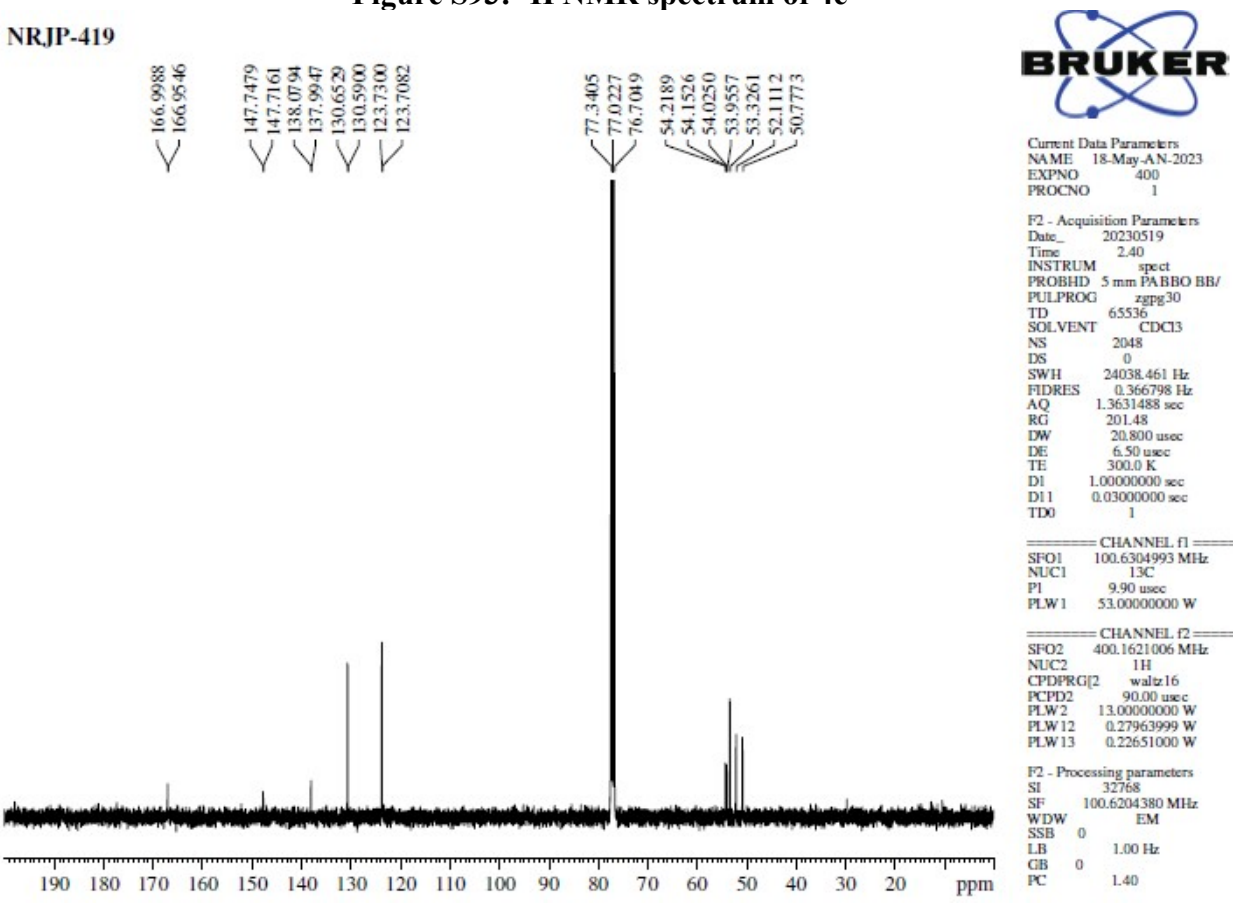


Figure S94: ^{13}C{H} NMR spectrum of 4e

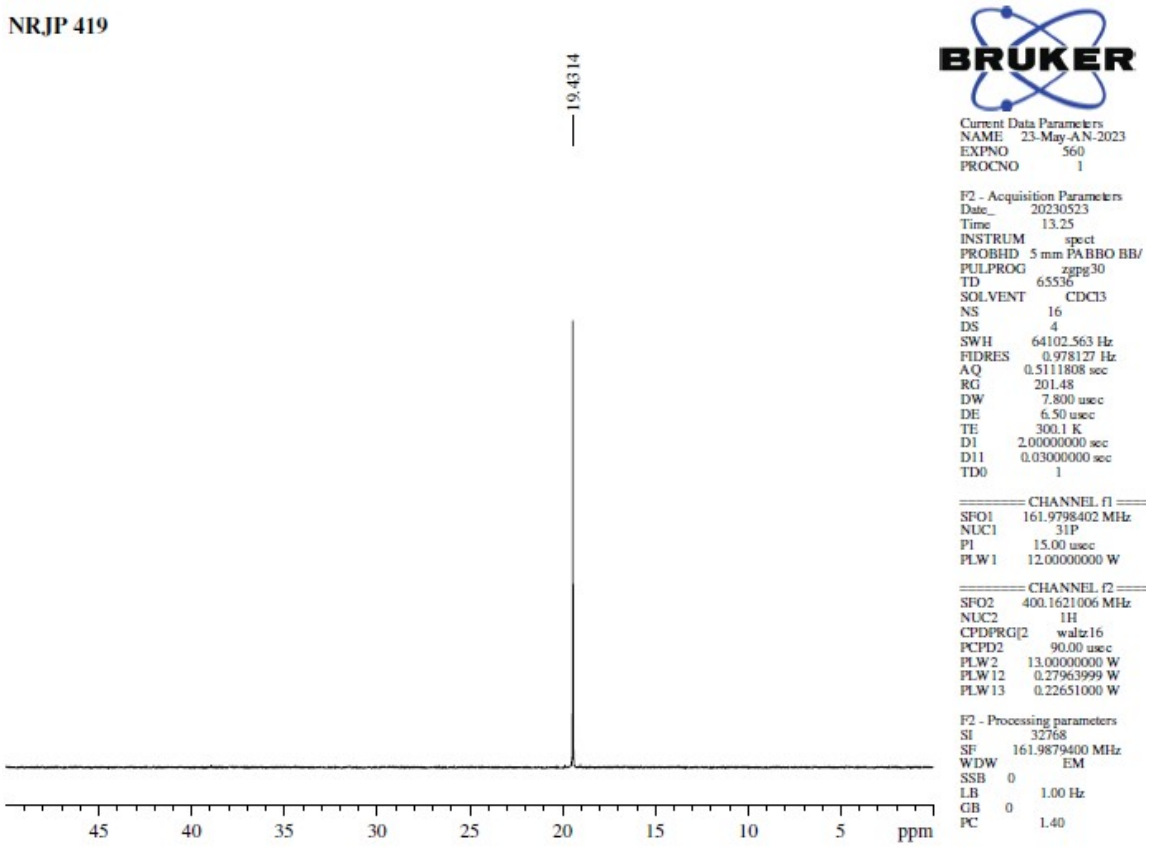


Figure S95: $^{31}P\{H\}$ NMR spectrum of 4e

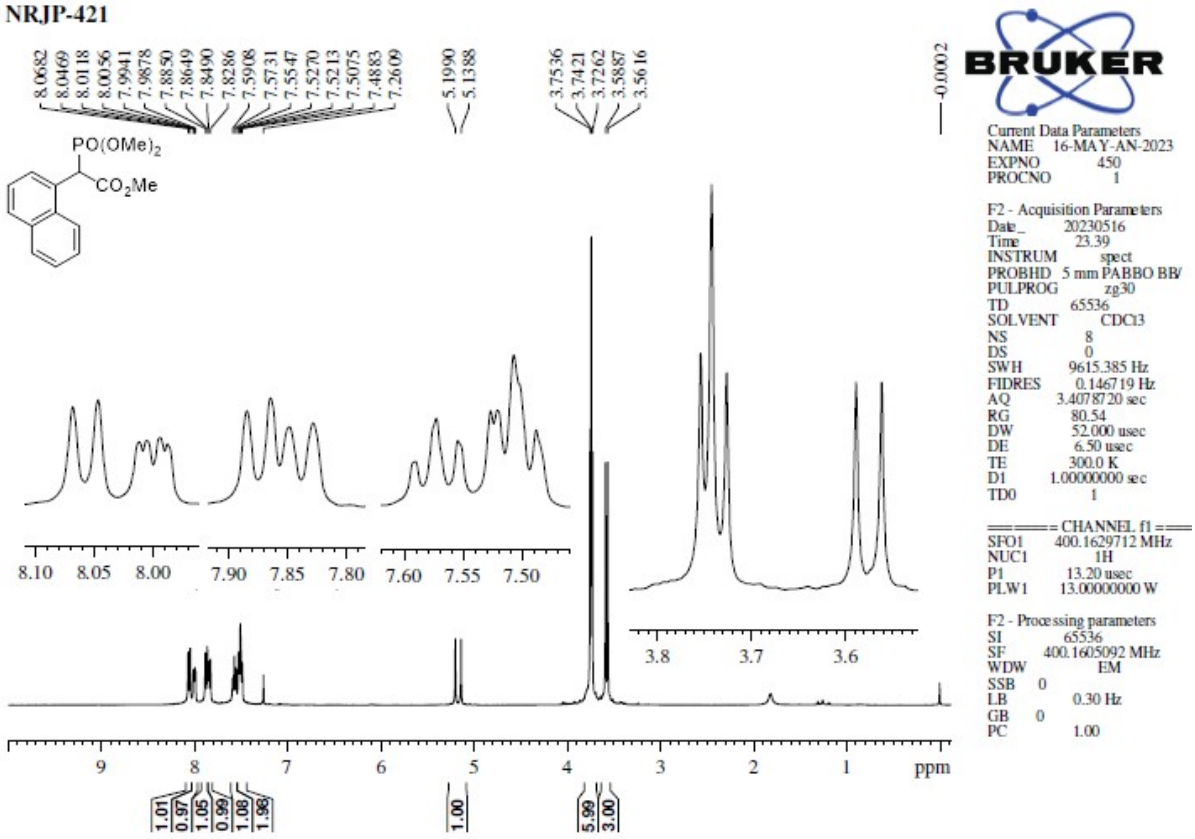


Figure S96: ^{1}H NMR spectrum of 4f

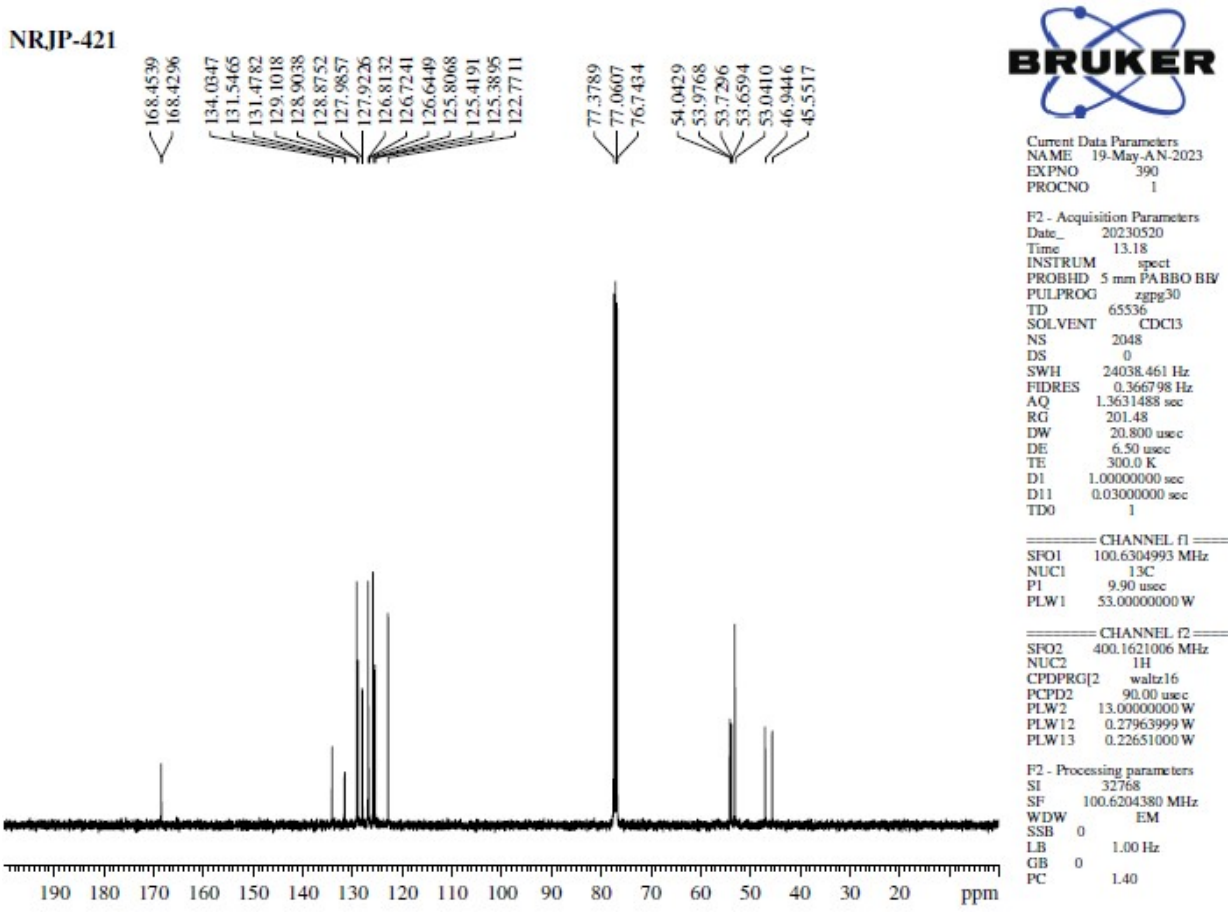


Figure S97: $^{13}C\{H\}$ NMR spectrum of 4f

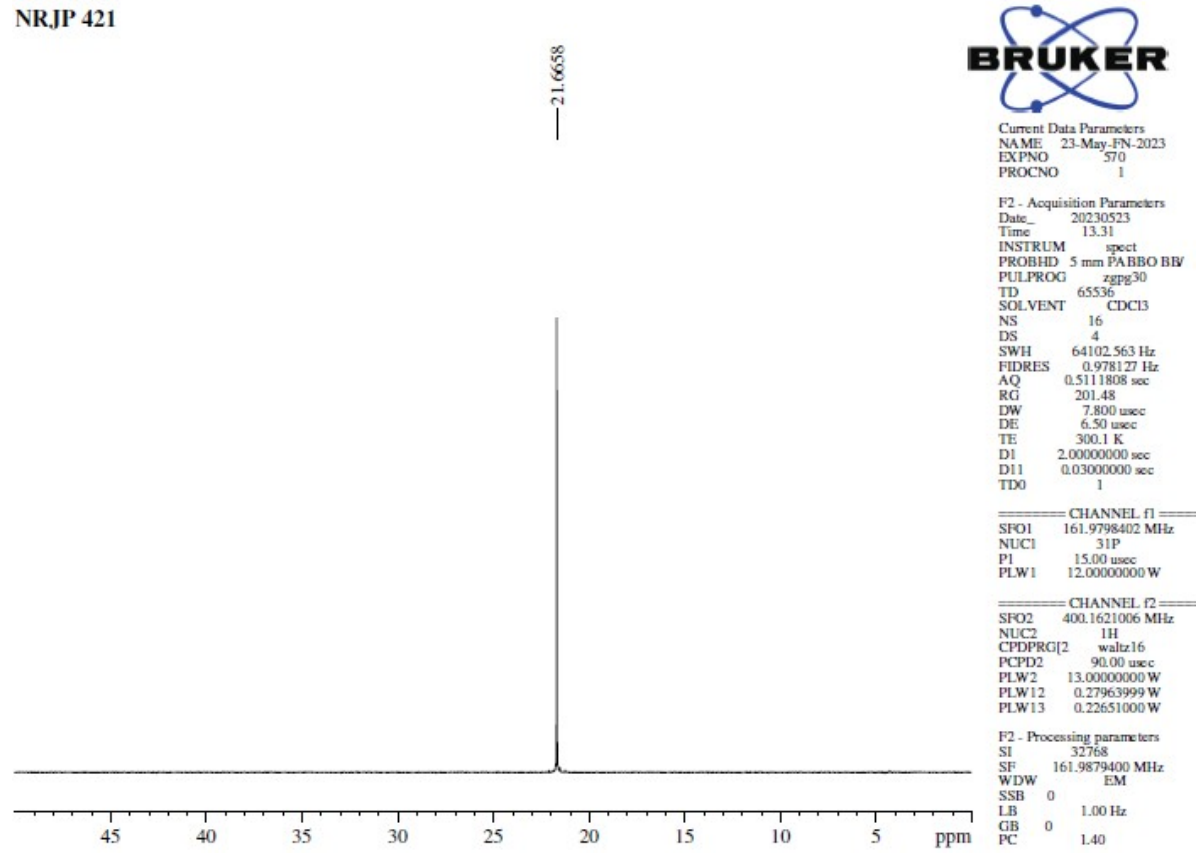
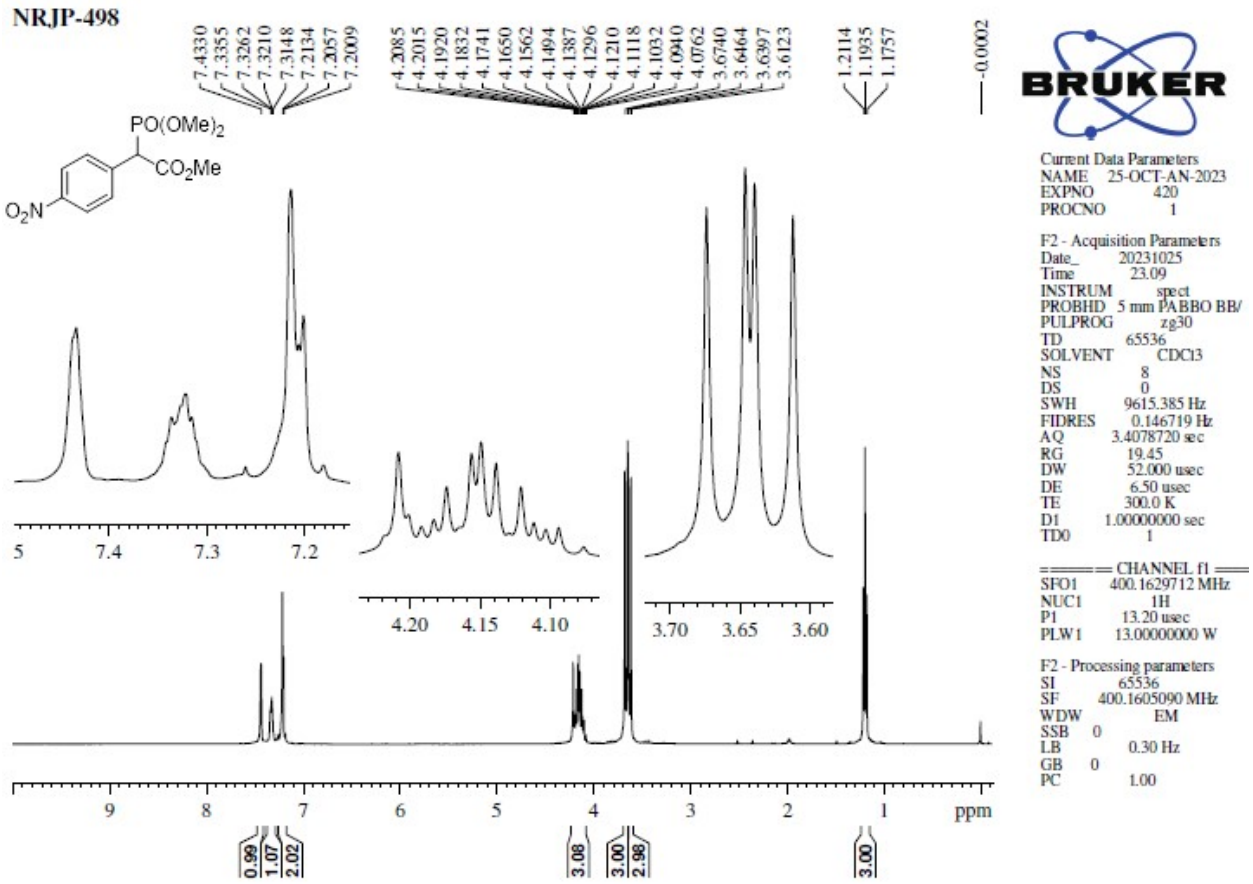


Figure S98: $^{31}P\{H\}$ NMR spectrum of 4f



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EXPNO 420
PROCNO 1

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Time 23.09
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PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 9615.385 Hz
FIDRES 0.146719 Hz
AQ 3.4078720 sec
RG 19.45
DW 52.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

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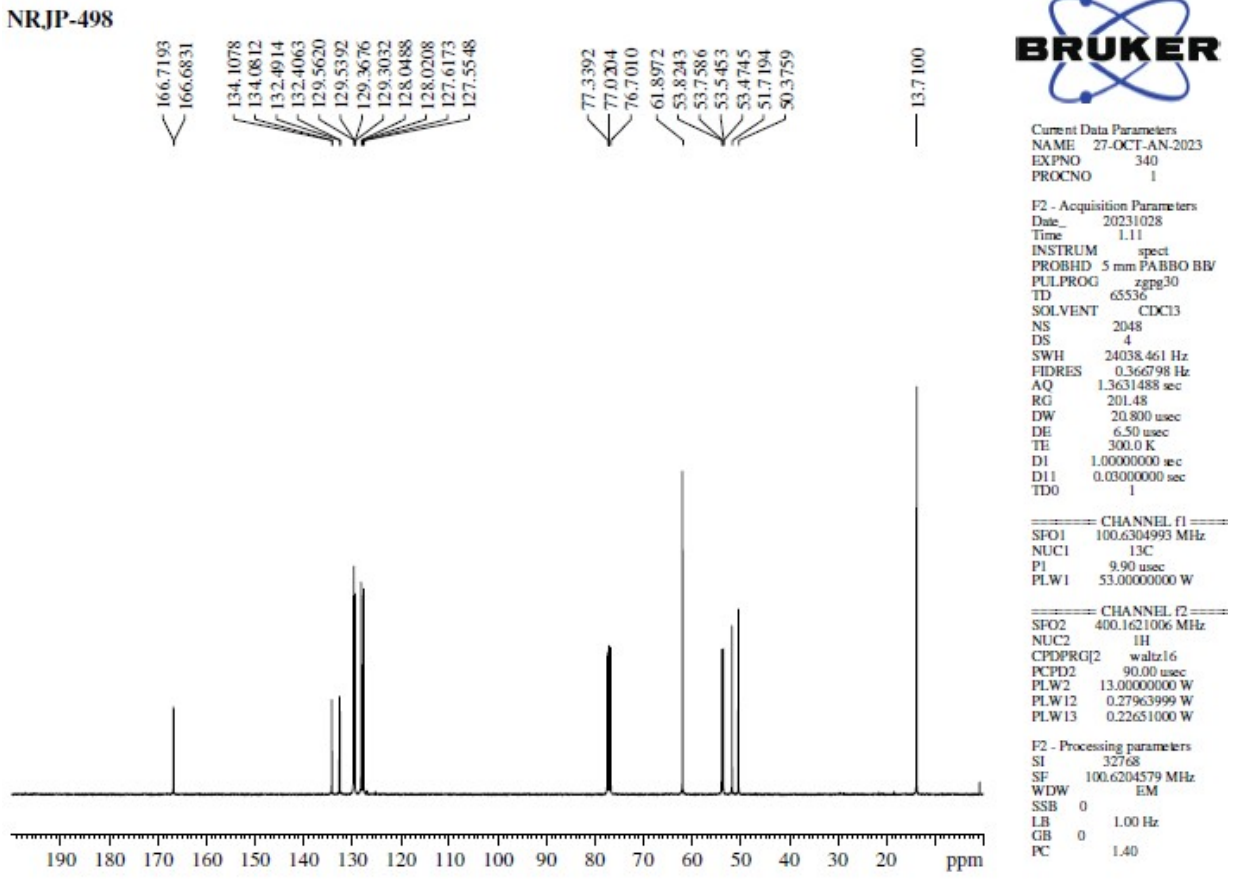
SFO1 400.1629712 MHz
NUC1 1H
P1 13.20 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1605090 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure S99: ^{1}H NMR spectrum of 4g



Current Data Parameters
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EXPNO 340
PROCNO 1

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TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 201.48
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 100.6304993 MHz
NUC1 13C
P1 9.90 usec
PLW1 53.00000000 W

======== CHANNEL f2 ========
SFO2 400.1621006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.27963999 W
PLW13 0.22651000 W

F2 - Processing parameters
SI 32768
SF 100.6204579 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure S100: ^{13}C{H} NMR spectrum of 4g

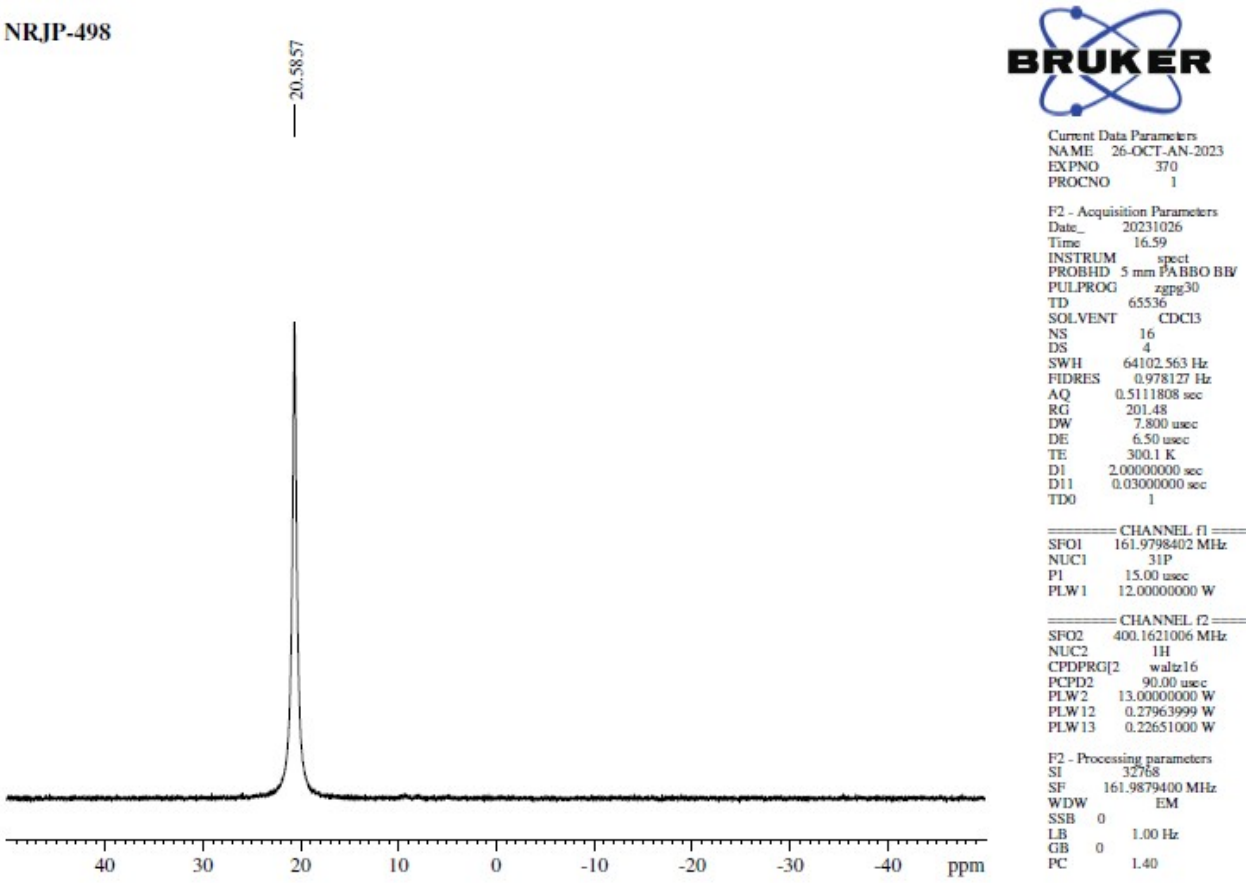

Figure S101: $^{31}P\{H\}$ NMR spectrum of 4g

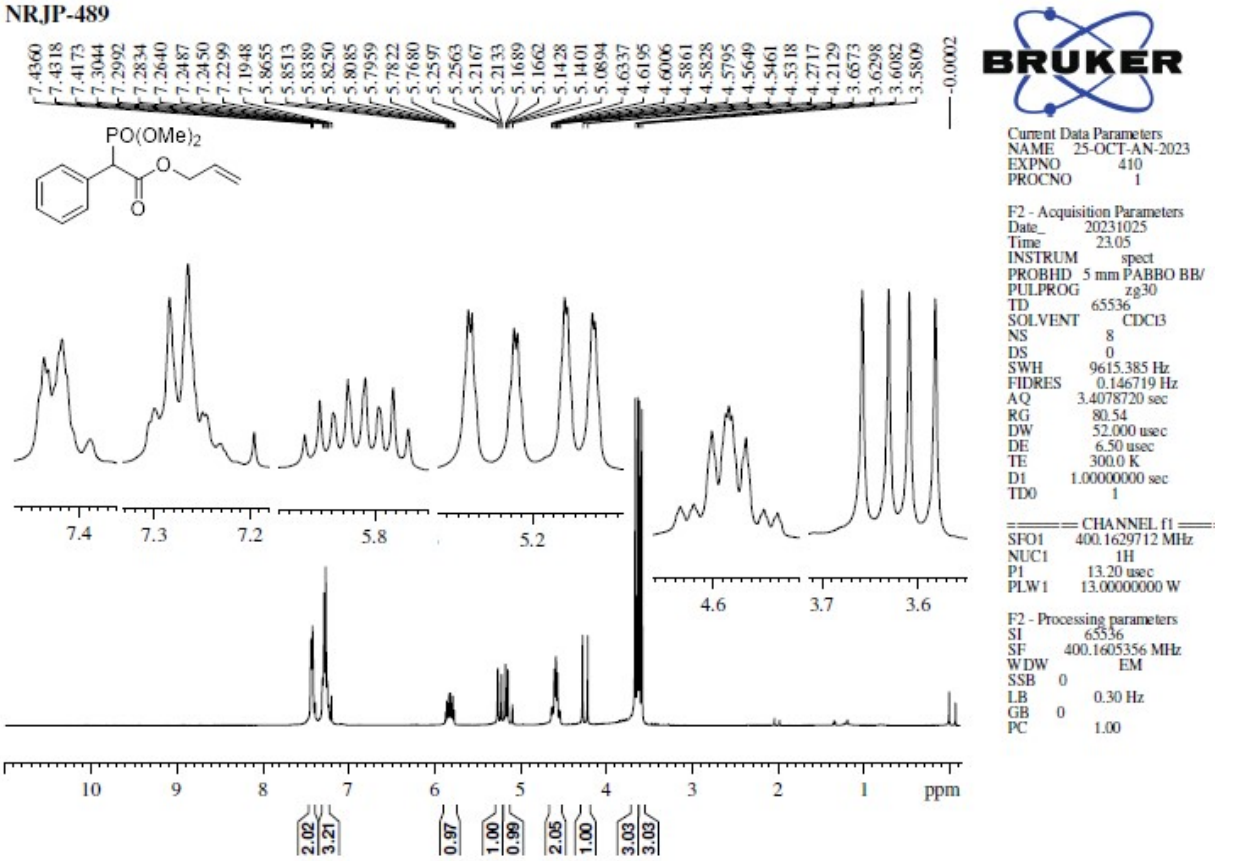

Figure S102: ^{1}H NMR spectrum of 4h

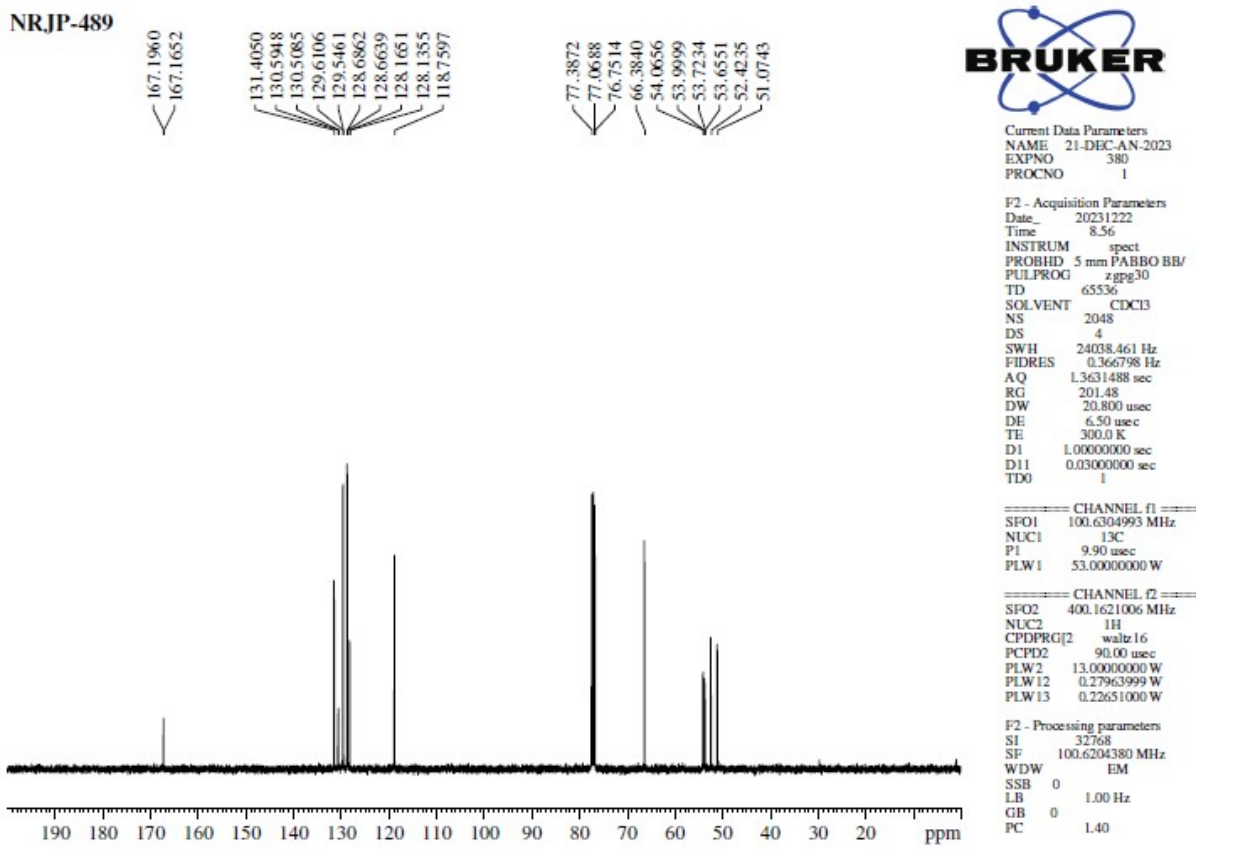

Figure S103: $^{13}C\{H\}$ NMR spectrum of 4h

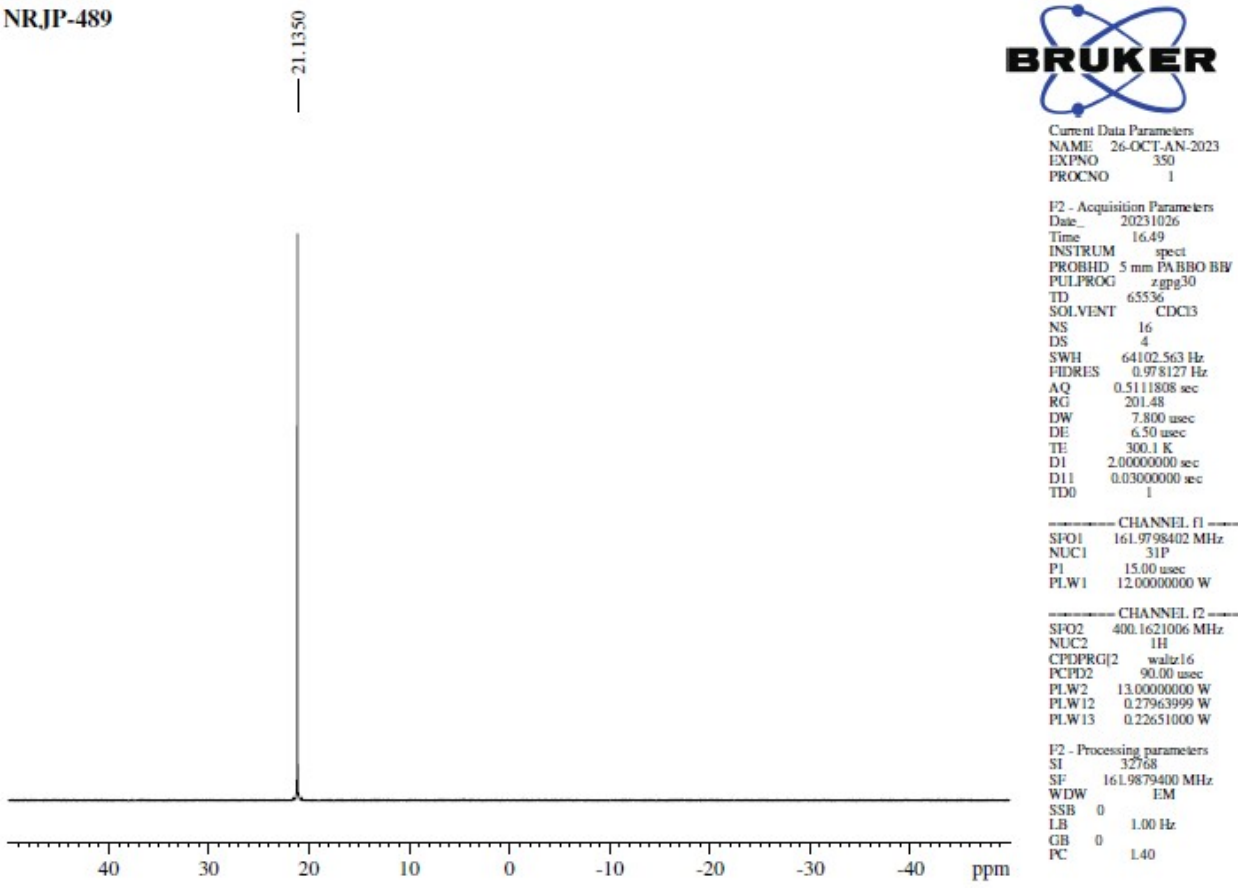

Figure S104: $^{31}P\{H\}$ NMR spectrum of 4h

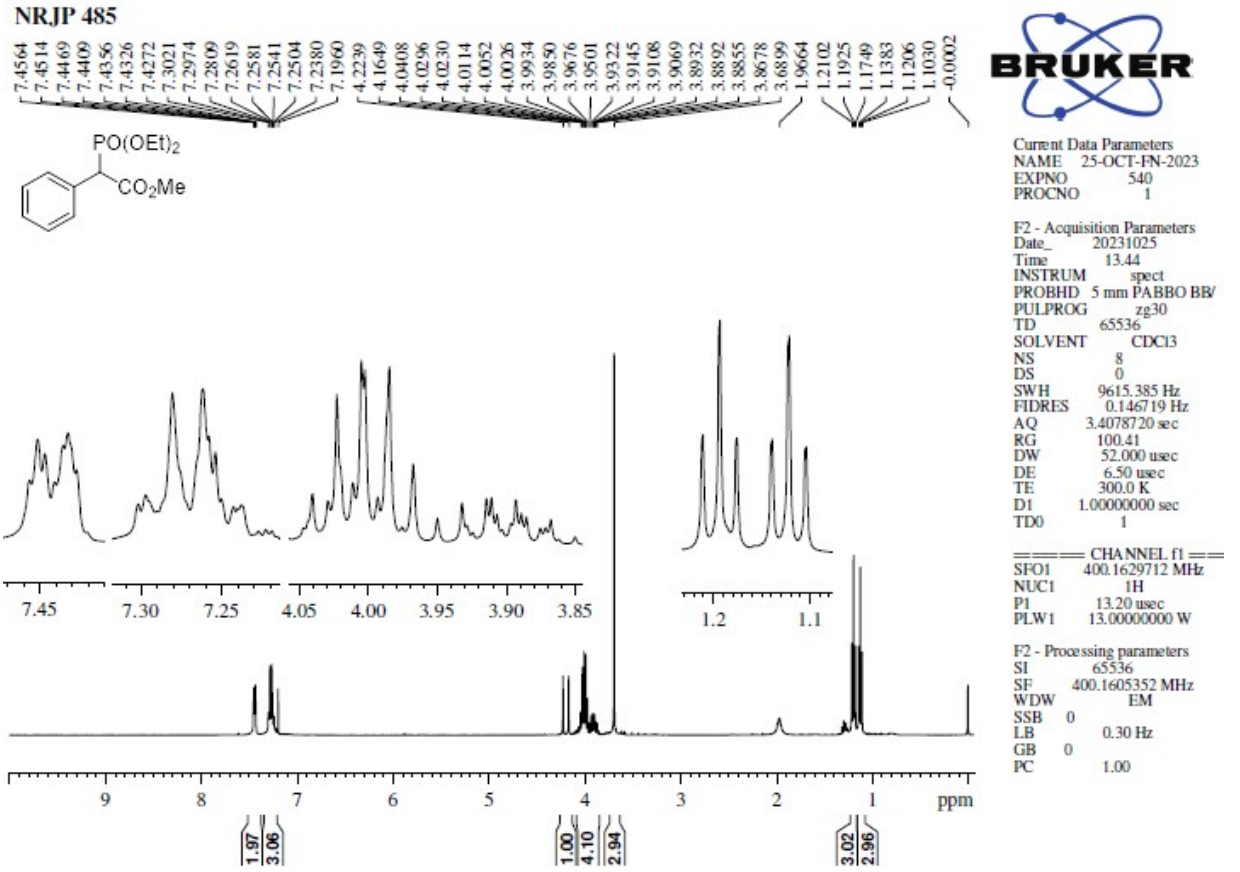

Figure S105: ^{1}H NMR spectrum of 4i

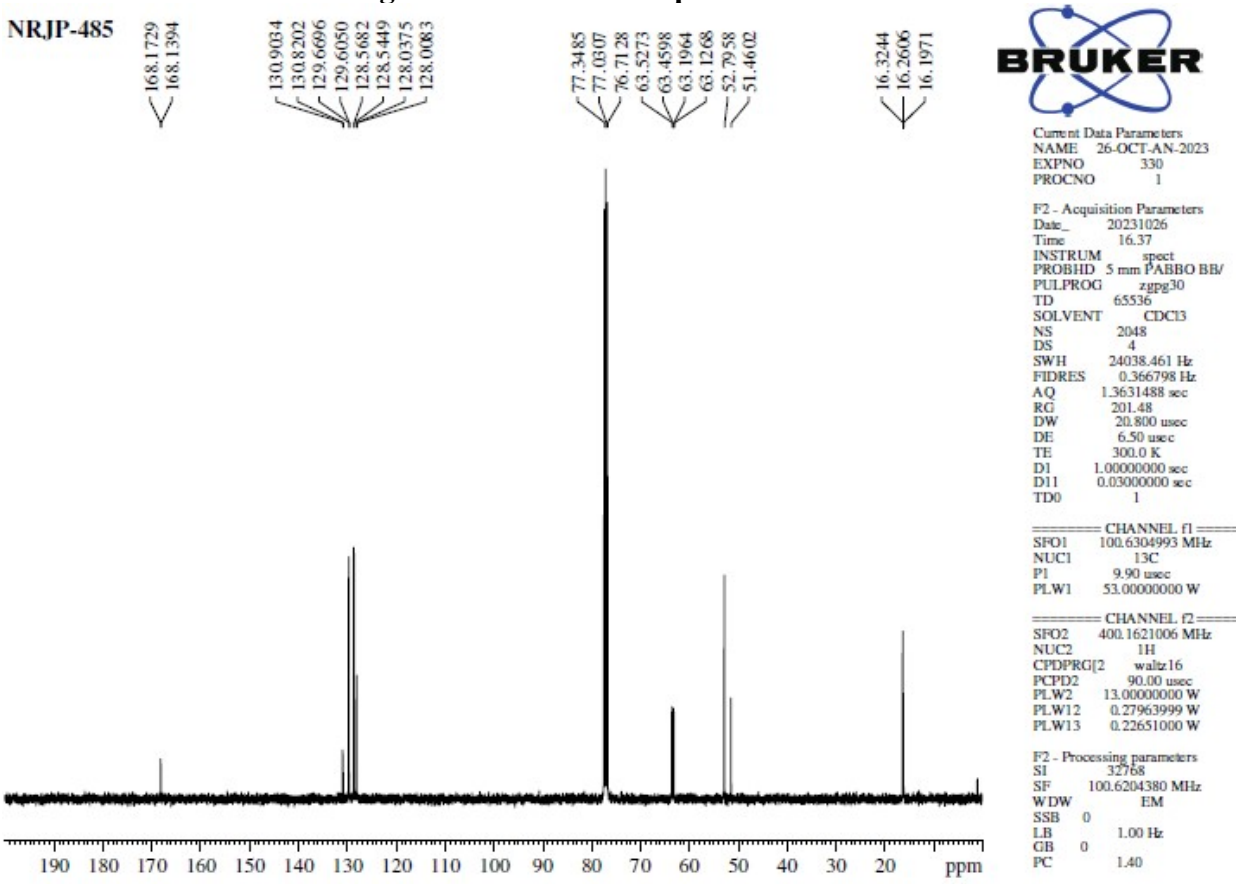

Figure S106: ^{13}C{H} NMR spectrum of 4i

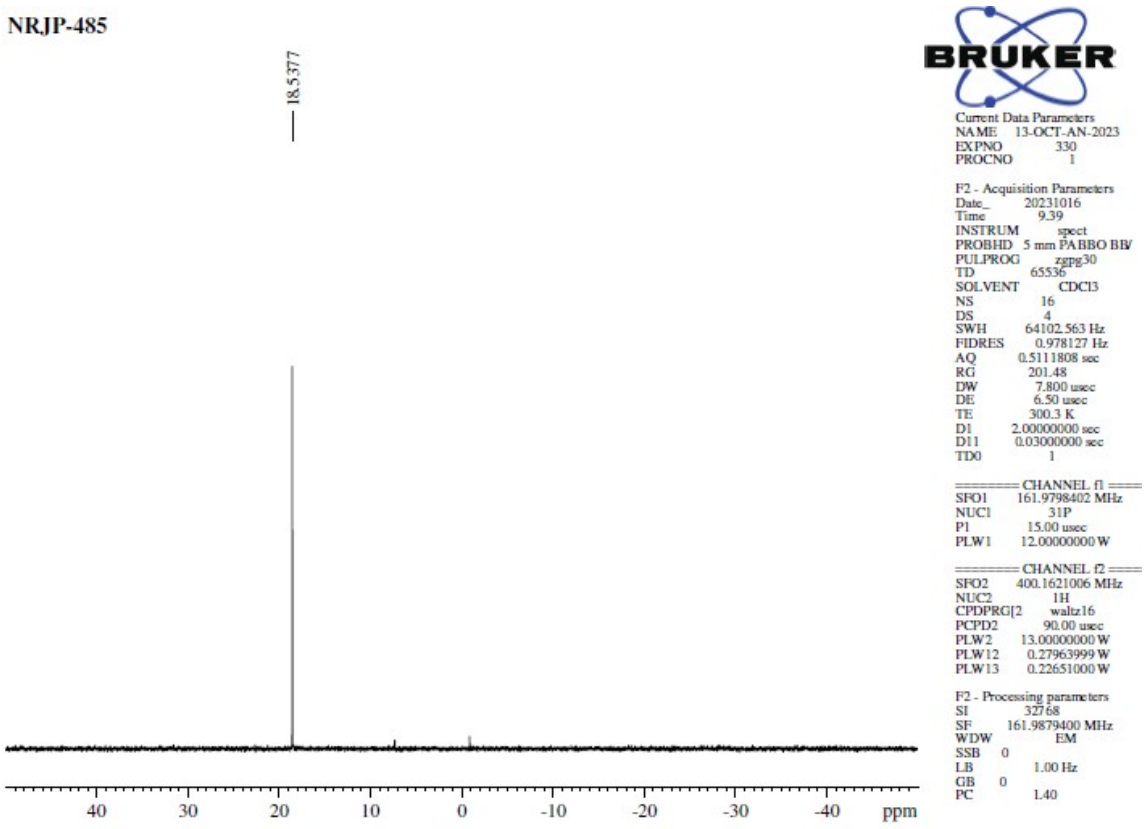

Figure S107: $^{31}P\{H\}$ NMR spectrum of 4i

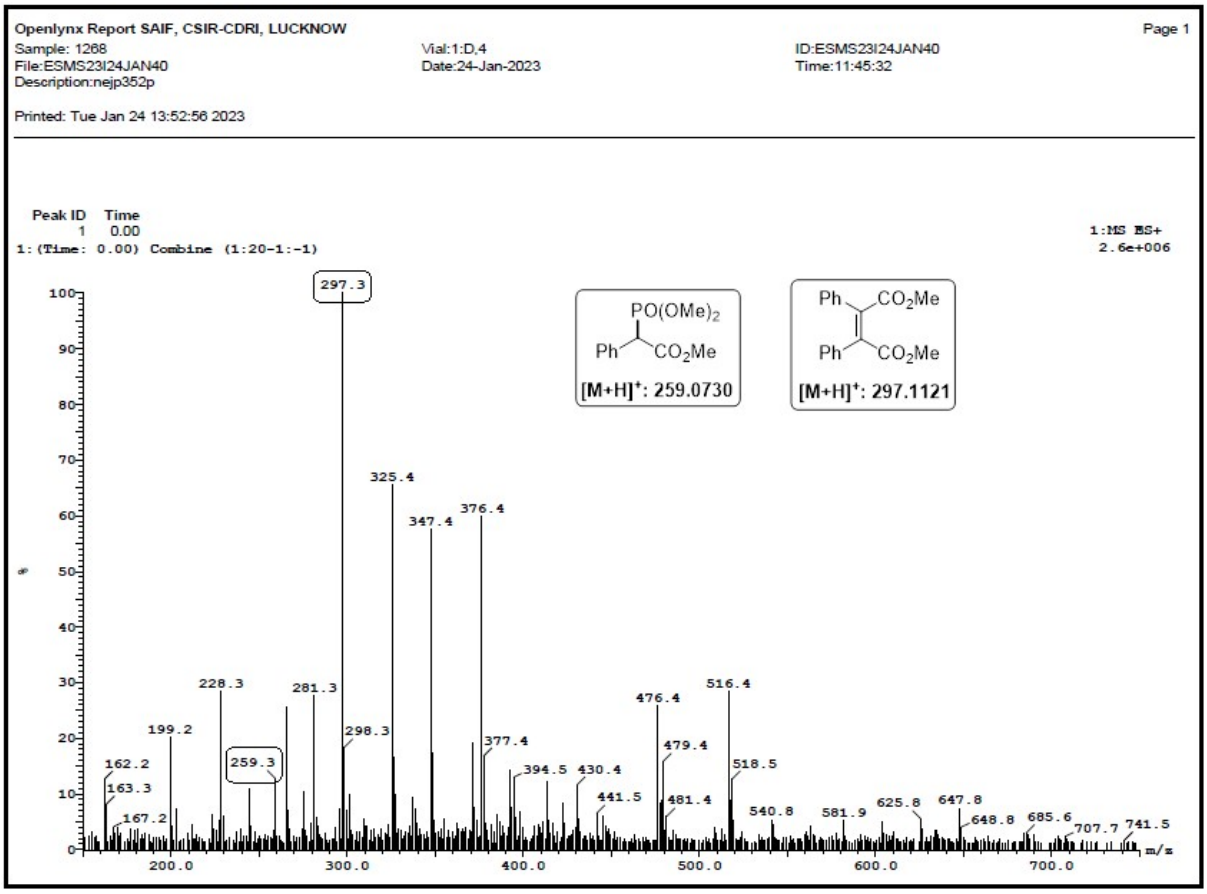

Figure S108: ESMS of crude 4a