Supplementary Information

Visible Light-Induced Cobalt-Catalyzed 1, 3-Diphosphination of Alkenes

Wenlong Shan,[a] Zemin Wang,[a] Chenxia Gao,[a] Xiaowei Li,[a] Wenli Zhuang,[a] Ruihua Liu,[a] Cong Shi,[a] Hongyun Qin,[a] Xiangqian Li,[a] and Dayong Shi[*a,b]

[a] State Key Laboratory of Microbial Technology, Shandong University, Qingdao 266237, Shandong, P. R. China.
[b] Laboratory for Marine Drugs and Bioproducts, Qingdao Marine Science and Technology Center, Qingdao, 266237, Shandong, P. R. China.

* Corresponding author: shidayong@sdu.edu.cn

Contents

1. General information.....1
2. Optimization of the reaction conditions.....1
3. General procedure.....4
4. Procedure for Synthetic applications.....7
5. Exploration of reaction mechanism.....9
6. Biological experiments.....12
7. Characterization data.....16
8. References.....56
9. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of compounds.....57

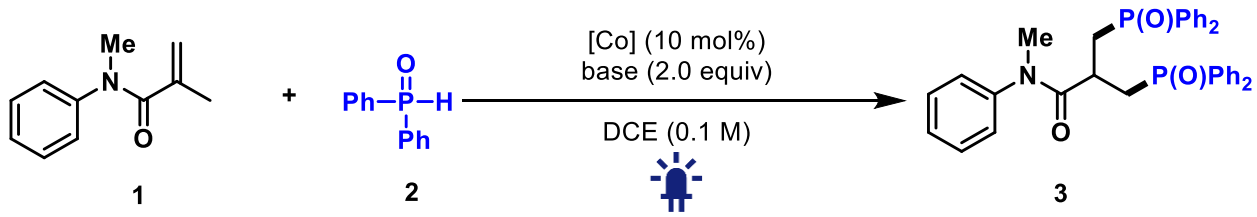
1. General information

All reactions involving air- and/or moisture-sensitive compounds were carried out in the argon-filled glove box or by standard Schlenk techniques under argon atmosphere. Unless otherwise noted, chemicals and solvents were purchased from commercial suppliers (Alfa, Aldrich, Energy Chemical, Bidepharm, Innochem, Sinopharm, Stream, and so on) and used without further purification. All new compounds were fully characterized. Reactions were monitored by thin layer chromatography (TLC) using glass 0.25 mm silica gel plates. Column chromatography was performed on 200-300 mesh silica gel.

^{1}H, ^{13}C, ^{19}F, ^{31}P NMR data were recorded on a Bruker AVANCE NEO (400, 600 MHz) spectrometer and Agilent DD2 600 (600 MHz). All chemical shifts (δ) were given in ppm and coupling constants (*J*) were provided in Hz. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), broad (br), doublet of doublet (dd), doublet of triplet (dt), triplet of doublet (td), doublet of triplet of doublet (dtd), doublet of doublet of doublet (ddd), and multiplet (m). GC-MS analysis results were obtained by Thermo TRACE-1300-ISQ-7000. Melting points were determined with melting point apparatus SGW X-4A and were not corrected. Fourier transform mass spectra (FTMS) analysis was performed on a Thermo Fisher Q-Exactive instrument.

2. Optimization of the reaction conditions

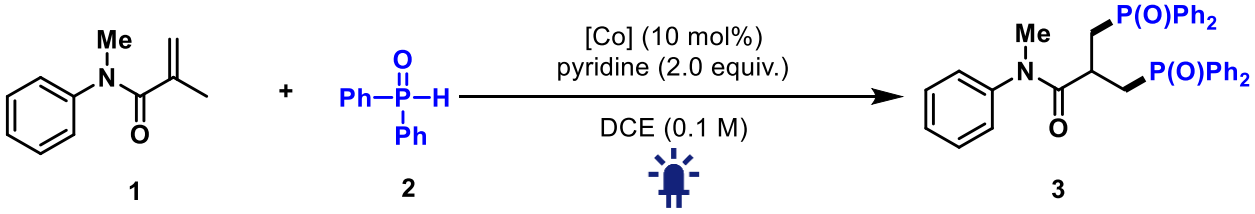
Table S1: Screening of Bases [a]



Entry	Bases	Yield (%)
1	none	17
2	**pyridine**	**90**
3	HCOONa	41
4	$CsCO_3$	46
5	DBU	32
6	DABCO	23
7	DMAP	48
8	pyridine (1.0 eq)	49
9	pyridine (4.0 eq)	56

[a]Reaction conditions: **1** (0.1 mmol), **2** (0.25 mmol), Co(dmgH)$_2$(DMAP)Cl (0.01 mmol), base (0.2 mmol), DCE (1 mL), 6 W LED (420–430 nm), 25 °C for 24 h under Ar atmosphere. Yields were determined by ^{1}H NMR analysis (with CH_2Br_2 as the internal standard).

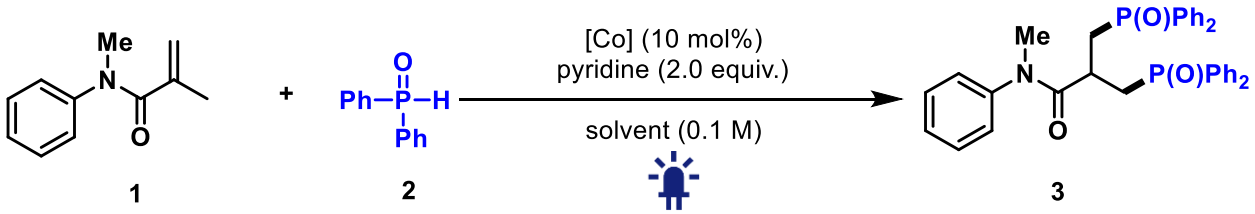
Table S2: Screening of Light sources [a]



Entry	Light sources (nm)	Yield (%)
1	380–385	46
2	400–410	59
3	**420–430**	**90**
4	460–465	70
5	520–525	n.d.

[a]Reaction conditions: **1** (0.1 mmol), **2** (0.25 mmol), Co(dmgH)$_2$(DMAP)Cl (0.01 mmol), pyridine (0.2 mmol), DCE (1 mL), 6 W LED, 25 °C for 24 h under Ar atmosphere. Yields were determined by ^{1}H NMR analysis (with CH_2Br_2 as the internal standard).

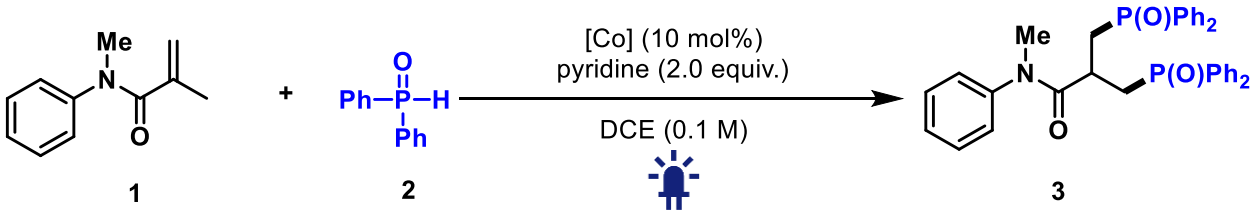
Table S3: Screening of Solvents [a]



Entry	Solvents	Yield (%)
1	**DCE**	**90**
2	DCM	78
3	MeCN	27
4	THF	n.d.
5	DMSO	n.d.
6	DMF	n.d.
7	MeOH	n.d.
8	EA	n.d.

[a]Reaction conditions: **1** (0.1 mmol), **2** (0.25 mmol), Co(dmgH)$_2$(DMAP)Cl (0.01 mmol), pyridine (0.2 mmol), solvent (1 mL), 6 W LED (420–430 nm), 25 °C for 24 h under Ar atmosphere. Yields were determined by ^{1}H NMR analysis (with CH_2Br_2 as the internal standard). n.d. = not detected.

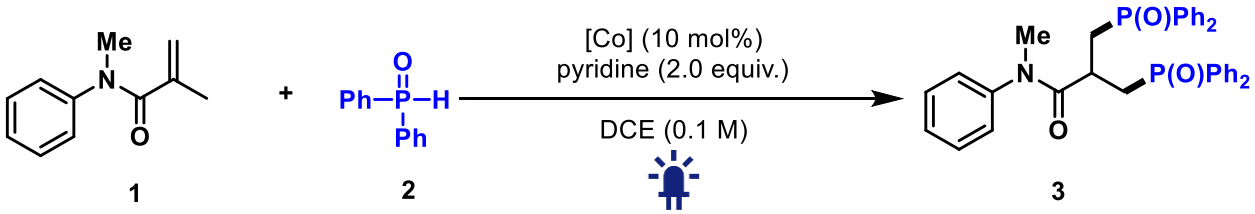
Table S4: Screening of Co Catalysts [a]



Entry	Catalysts	Yield (%)
1	**$Co(dmgH)_2(DMAP)Cl$**	**90**
2	$Co(dmgH)_2pyCl$	34
3	$Co(dmgH)(dmgH_2)Cl_2$	n.d.
4	$Co(dmgH)_2(DMAP)Cl$ [5 mol%]	14
5	$Co(dmgH)_2(DMAP)Cl$ [15 mol%]	88

[a]Reaction conditions: **1** (0.1 mmol), **2** (0.25 mmol), [Co] (0.01 mmol), pyridine (0.2 mmol), DCE (1 mL), 6 W LED (420–430 nm), 25 °C for 24 h under Ar atmosphere. Yields were determined by ^1H NMR analysis (with CH_2Br_2 as the internal standard). n.d. = not detected.

Table S5: Screening of the amount of **2**[a]

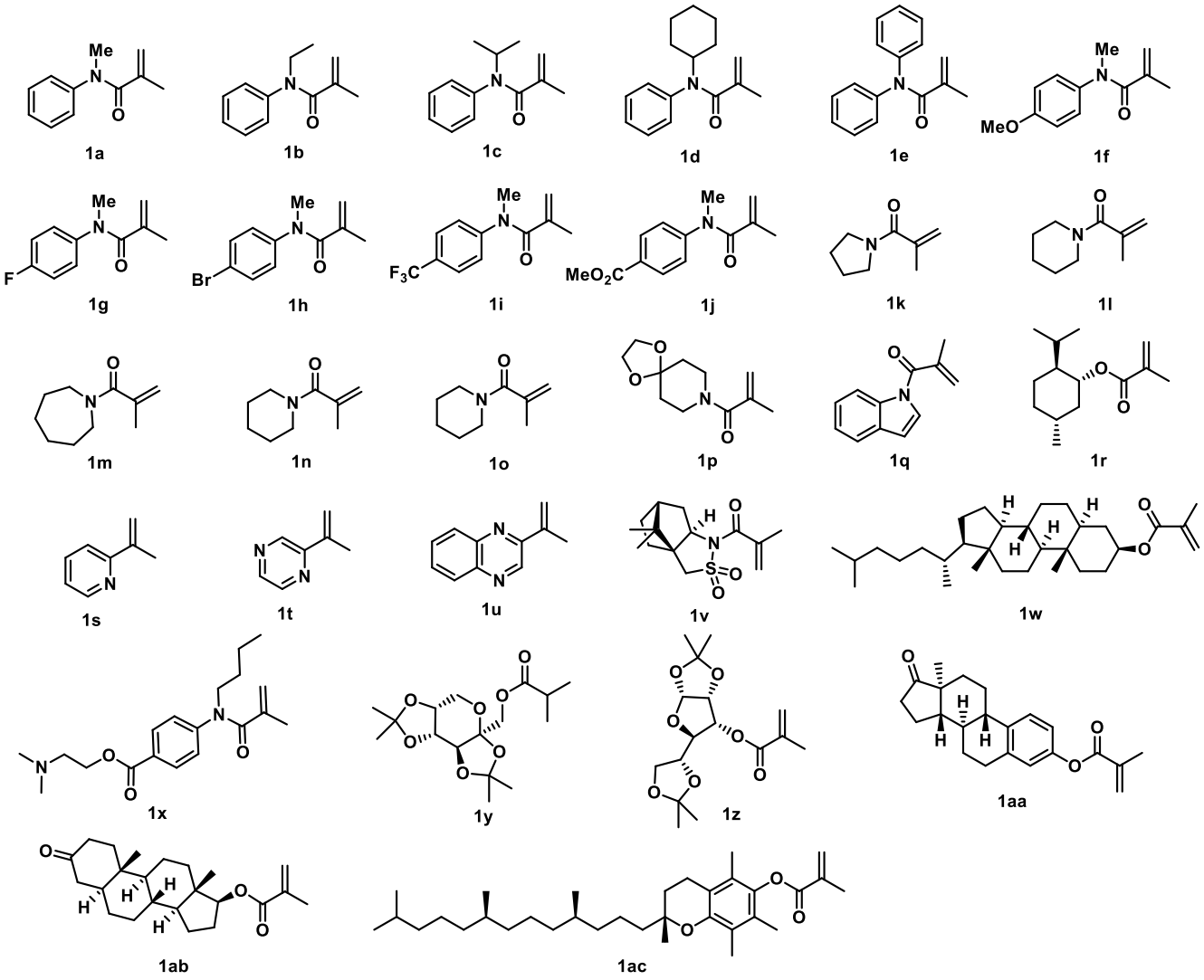


Entry	The amount of **2** (equiv.)	Yield (%)
1	2.0	70
2	**2.5**	**90**
3	3.0	82
4	4.0	61

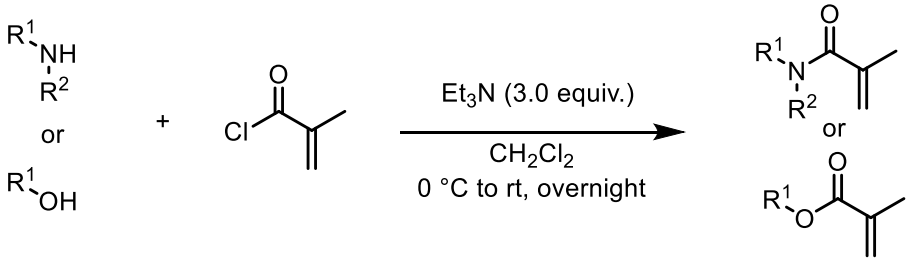
[a]Reaction conditions: **1** (0.1 mmol), **2**, $Co(dmgH)_2(DMAP)Cl$ (0.01 mmol), pyridine (0.2 mmol), DCE (1 mL), 6 W LED (420–430 nm), 25 °C for 24 h under Ar atmosphere. Yields were determined by ^1H NMR analysis (with CH_2Br_2 as the internal standard).

3. General procedure

3.1 Preparation of starting materials 1:



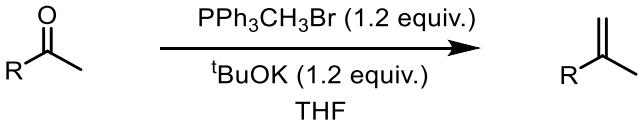
(a) General procedure for the synthesis of α,β-unsaturated amides and methacrylates



Amine or alcohol (10 mmol, 1.0 equiv.), Et_3N (4.2 mL, 30 mmol, 3 equiv.), and dry CH_2Cl_2 (20 mL) were added to a 100 mL dry round-bottom flask with a stir bar under argon. The reaction mixture was cooled to 0 °C using an ice bath, and then acid chloride (10.0 mmol) in 10 mL CH_2Cl_2 were added dropwise. The reaction was allowed to stir overnight at rt. The mixture was poured into brine and extracted with CH_2Cl_2 (3 x 20 mL). The organic phase was dried over Na_2SO_4, filtered, and evaporated

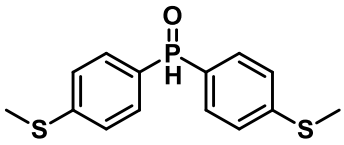
in vacuo. The corresponding pure product was obtained after purification of the resulting crude mixture by flash column chromatography on silica gel with petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 20:1-5:1) as the eluent.

(b) General procedure for the synthesis of heterocyclic aromatic alkenes

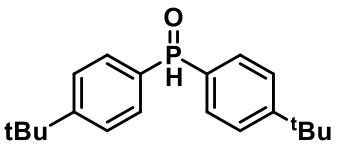


An oven-dried 50 mL round-bottom flask equipped with a magnetic stir bar was charged with methyl triphenyl phosphonium bromide (6 mmol) and potassium tert-butoxide (6 mmol). Next, anhydrous THF (10 mL) was added to the vessel under Ar, and the reaction mixture was stirred at room temperature for 15 min. Then, this suspension was cooled to 0 °C with an ice bath and ketone (5.0 mmol) in THF (5 mL) was added via syringe to the cooled suspension. The reaction mixture continued to stir overnight at room temperature, and then was quenched with water (20 mL) and extracted with methyl EtOAc (3×30 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 50:1-20:1) as the eluent to give the corresponding alkenes.[1]

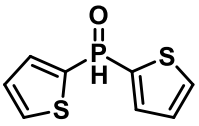
3.2 Preparation of phosphine oxides 2.



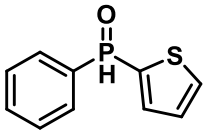
2a



2b

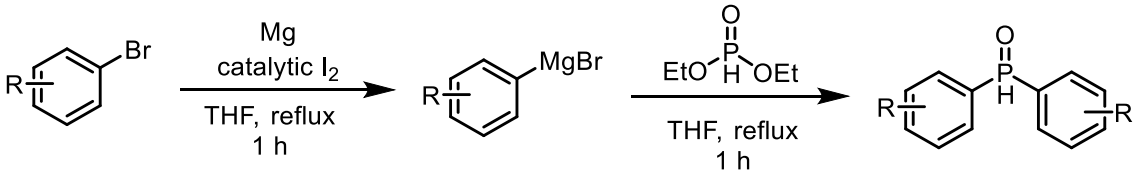


2c



2d

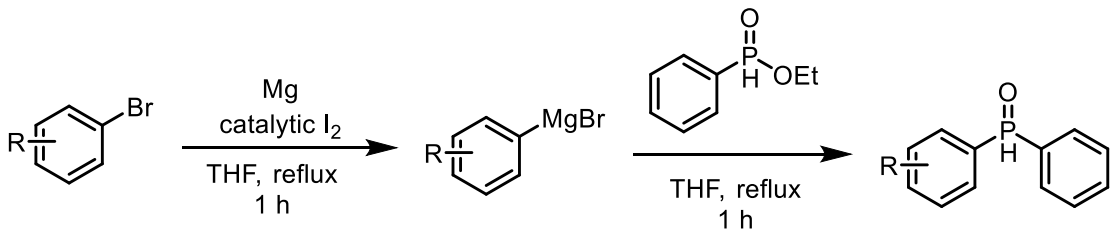
(a) General procedure for the synthesis of symmetrical phosphine oxide[2]



To a 50 mL round bottom flask, aryl bromide (15 mmol) was added along with Mg turnings (389 mg, 16 mmol), I_2 (catalytic) and THF (5 mL). The reaction was heated to reflux for 1 hour at which time, the reaction was cooled to room temperature and diethyl phosphite (690 mg, 5 mmol) was added with THF (5 mL). The reaction was once again heated to reflux for one hour. After this time, the mixture was cooled to 0 ˚C , and NH_4Cl (5 mL) was added to quench the reaction. The crude mixture was then extracted with chloroform and washed with water (3 x 100 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification was performed via

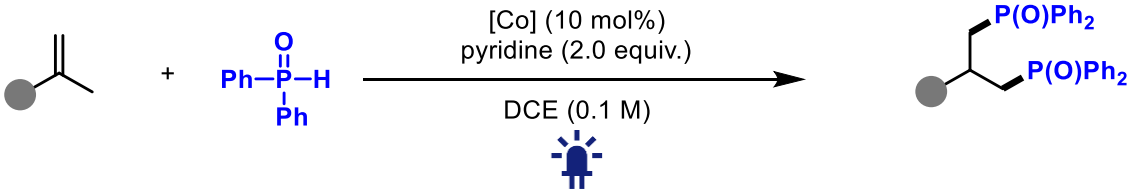
silica gel chromatography using petroleum ether /ethyl acetate (petroleum ether /ethyl acetate = 5:1-1:1) as the eluent.

b) General procedure for the synthesis of unsymmetrical phosphine oxides:



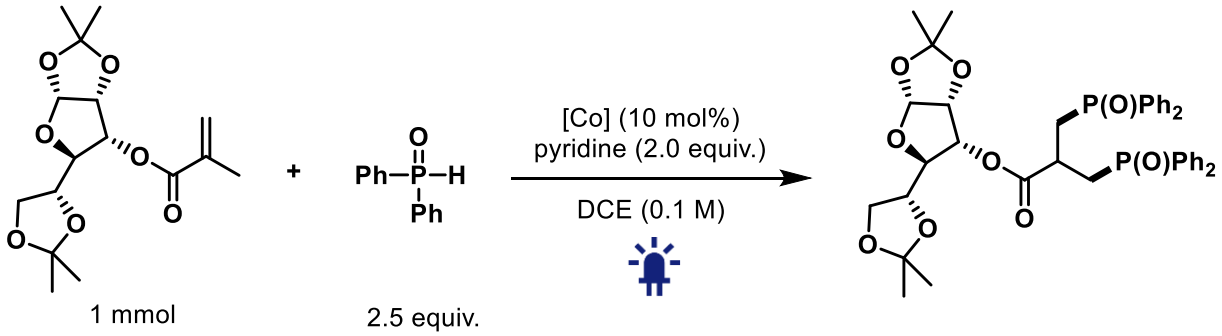
To a 50 mL round bottom flask, aryl bromide (11.0 mmol) was added along with Mg turnings (305 mg, 12.5 mmol), I_2 (catalytic) , and THF (5 mL). The reaction was heated to reflux for 1 hour at which time, the reaction was cooled to room temperature and ethyl phenylphosphinate (850mg, 5 mmol) was added with THF (2.5 mL). The reaction was once again heated to reflux for one hour. After this time, the mixture was cooled to 0 ˚C and NH_4Cl was added to quench the reaction. The crude mixture was then extracted with chloroform and dried over Na_2SO_4 followed by purification via silica gel chromatography using petroleum ether /ethyl acetate (petroleum ether /ethyl acetate = 5:1-1:1) as the eluent.

3.3 General procedure for visible light–initiated cobalt-catalysed 1, 3-diphosphination of alkenes



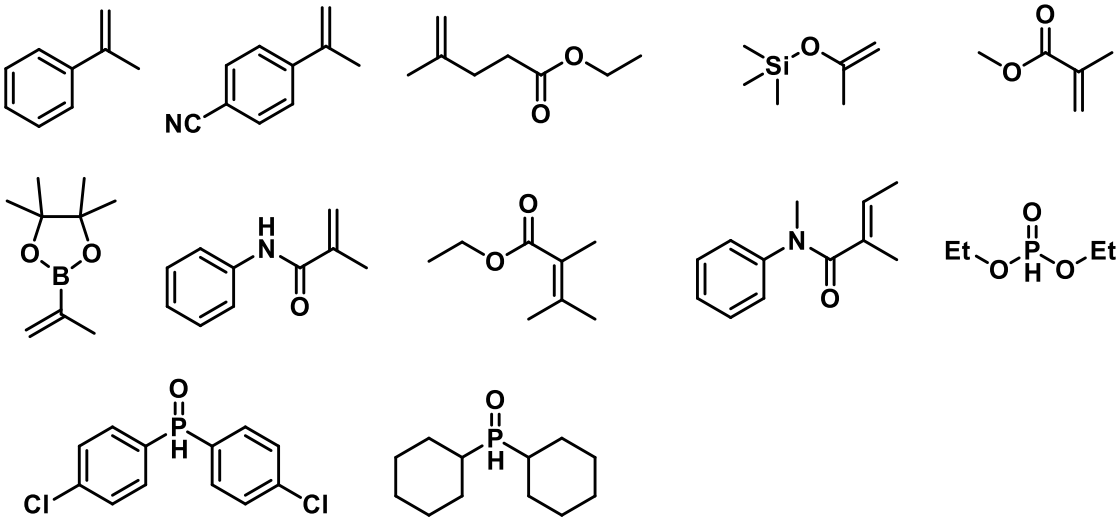
To an oven-dried 10 mL tube equipped with a magnetic stir bar was charged with alkene (0.1 mmol), diphenylphosphine oxide (0.25 mmol), pyridine (0.2 mmol) , and $Co(dmgH)_2(DMAP)Cl$ (0.01 mmol) in anhydrous 1,2-dichloroethane (1 mL). The mixture was irradiated with a 6 W LED lamp (420–430 nm) for 24 hours under argon at room temperature. After the reaction, upon removal of the solvent under vacuum, the residue was purified by chromatography on silica gel to get the product.

3.4 Gram-scale synthesis



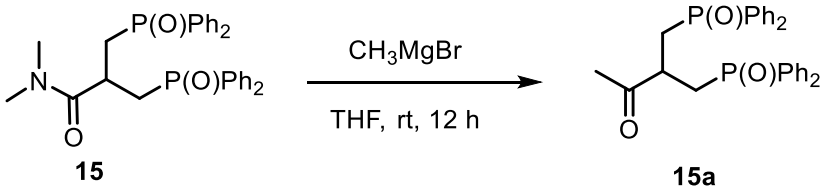
A solution of diphenylphosphine oxide (2.5 mmol), alkene (1 mmol), $Co(dmgH)_2(DMAP)Cl$ (0.1 mmol), pyridine (2 mmol) in anhydrous 1,2-dichloroethane (10 mL) was irradiated with 6 W LEDs (420–430 nm) for 48 hours under argon atmosphere at room temperature. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel to afford the desired product with 80% yield.

3.5 Unsuccessful substrates



4. Procedure for Synthetic applications

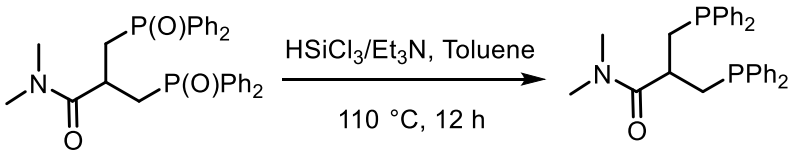
4.1 Procedure for conversion of acylamide to ketone



15 **15a**

To a solution of product **15** (0.1 mmol) in anhydrous THF (1 mL), CH_3MgBr (6.0 equiv.) was added under Ar atmosphere. Then this mixture reacted at room temperature for 12 h. After the reaction, H_2O was added carefully. The resulting solution was diluted with water and subsequently extracted with ethyl acetate. The organic phase was dried over Na_2SO_4. After the solvent had been removed under reduced pressure, the residue was purified by column chromatography on silica gel using ethyl acetate as eluent to give the target **15a** with 75% yield.

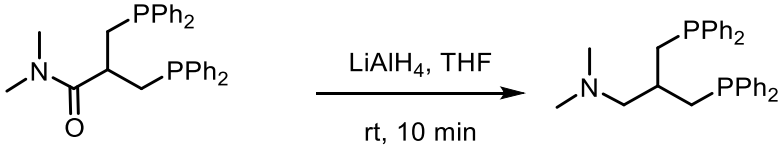
4.2 Procedure for P=O reduction of product



15 **15b**

To a solution of product **15** (0.05 mmol) in toluene (1 mL), excess $HSiCl_3$ (20 equiv.), Et_3N (20 equiv.) was added under Ar atmosphere. Then this mixture reacted at 110 ℃ for 12 h. After the reaction, 10% aq. NaOH was added carefully to quench unreacted $HSiCl_3$. The resulting solution was diluted with water and subsequently extracted with ethyl acetate. The organic phase was dried over Na_2SO_4. After the solvent had been removed under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 1/1 as eluent to give the target **15b** with 82% yield.[3]

4.3 Procedure for C=O reduction of product

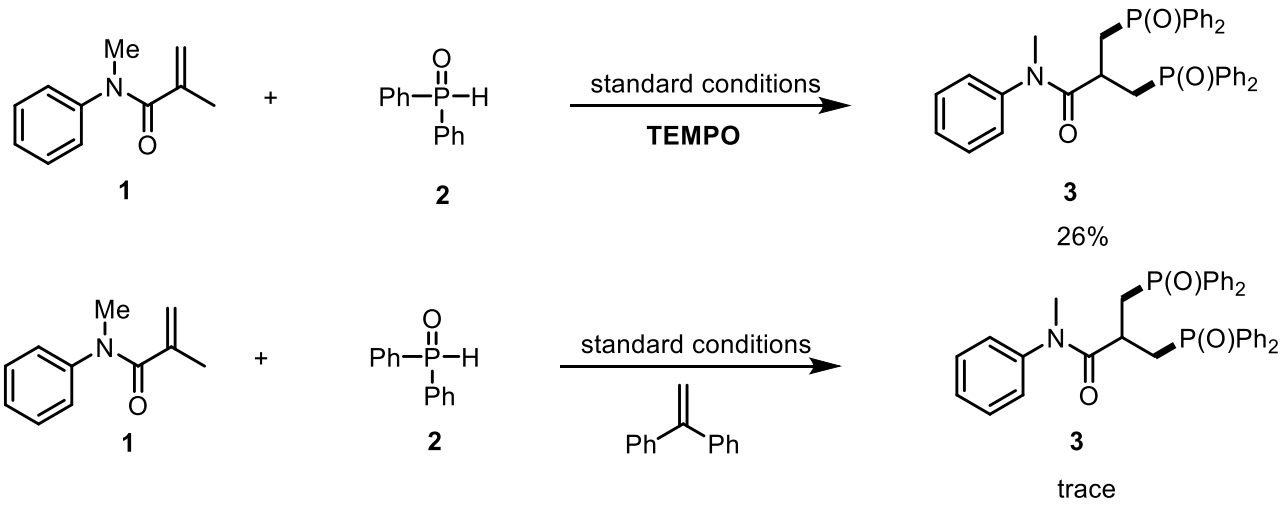


15b **15c**

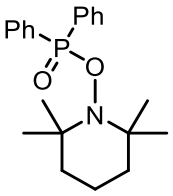
To a solution of $LiAlH_4$ (2 equiv) in THF (0.5 mL) under N_2 at 0 ºC, was added dropwise the desired amide **15b** (0.04 mmol) in THF (0.25mL). The resultant mixture stirred for 10 min. After reaction, 10% aq. NaOH was added carefully. The resulting solution was diluted with water and subsequently extracted with ethyl acetate. The organic phase was dried over Na_2SO_4. After the solvent had been removed under reduced pressure, the residue was purified by column chromatography on silica gel using ethyl acetate as eluent to give the target **15c** with 55% yield.[4]

5. Exploration of reaction mechanism

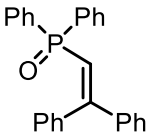
5.1 Radical trapping experiment



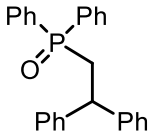
A solution of alkene **1** (0.1 mmol), diphenylphosphine oxide **2** (0.25 mmol), pyridine (0.2 mmol), $Co(dmgH)_2(DMAP)Cl$ (0.01 mmol), TEMPO or 1,1-diphenylethylene (0.3 mmol) in anhydrous DCE (1 mL) was irradiated with 6 W LEDs (420–430 nm) for 24 hours under argon atmosphere at ambient temperature. In the reaction of TEMPO, a coupling product of phosphinoyl radical and TEMPO was detected by HRMS. In the reaction of 1,1-diphenylethylene, a coupling product of phosphinoyl radical and 1,1-diphenylethylene was detected by ^{1}HNMR and HRMS.



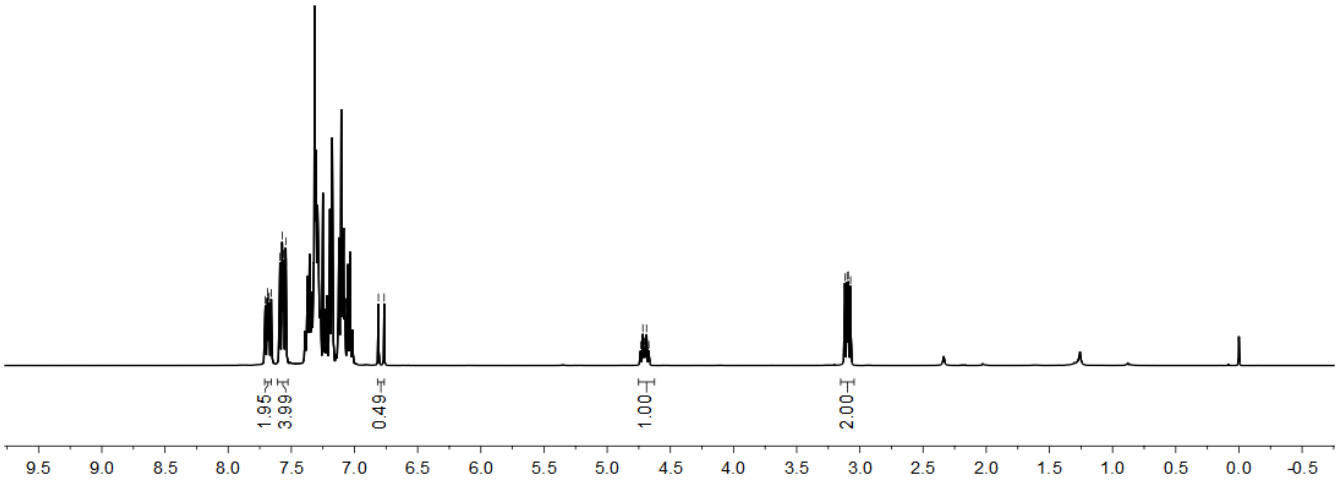
HRMS (ESI): Calcd for $C_{21}H_{29}NO_2P$ $(M+H)^+$: 358.1930; Found: 358.1927.



HRMS (ESI): Calcd for $C_{26}H_{22}OP (M+H)^+$: 381.1403; Found: 381.1397.

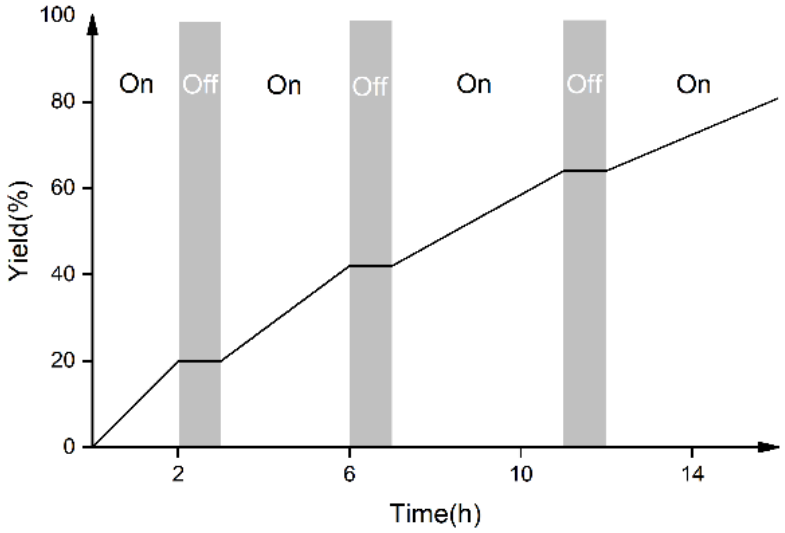


HRMS (ESI): Calcd for $C_{26}H_{24}OP (M+H)^+$: 383.1559; Found: 383.1556.



5.2 Light on/off experiment

From the profile of the reaction with the light ON/OFF over time, it was observed that the transformation progressed smoothly under light, but no further conversion was observed when the light was turned off, which suggested that the transformation requires the constant participation of light.



5.3 Quantum yield measurement

The quantum yield of the reaction was determined using the procedure reported previously[5]. The following solutions were prepared in the dark (flasks were wrapped in aluminum foil) and stored in the dark at room temperature:

− Ferrioxalate solution (0.15 M): Potassium ferrioxalate hydrate (1.474 g) was added to a flask wrapped in aluminum foil containing H_2SO_4 (20 mL, 0.05 M). The flask was stirred for complete solvation of the green solid in complete darkness. It is noteworthy that the solution should not be exposed to any incident light.

− Developer solution: 1,10-Phenanthroline (20 mg) and NaOAc (4.50 g) was added to a flask containing H_2SO_4 (20 mL, 0.5 M) and sonicated until completely solvated.

The absorbance of the non-irradiated sample. The buffered solution of phen (350 µL) was added to a ferrioxalate solution (2.0 mL) in a vial that had been covered with aluminum foil and with the lights of the laboratory switched off. The vial was capped and allowed to rest for 1 h and then transferred to a cuvette. The absorbance of the non-irradiated solution was measured at 510 nm to be 0.416 (average of three determinations).

The absorbance of the irradiated sample. In a cuvette equipped with a stir bar was added the ferrioxalate solution (2.0 mL), and the stirred solution was irradiated for 90 s at λ = 425 nm with an excitation slit width = 10.0 nm. After irradiation, the buffered phen solution (350 µL) was added to the cuvette and allowed to rest for 1 h in the dark to allow the ferrous ions to coordinate completely to phen. The absorbance was measured at 510 nm to be 3.653 (average of three determinations).

Photon flux calculation.

$$\text{mol}\,(Fe^{2+}) = \frac{V \cdot \Delta A}{1 \cdot \varepsilon} = \frac{0.00235\ \text{L} \cdot (3.653 - 0.416)}{1.000\ \text{cm} \cdot 11100\ \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}} = 6.85 \times 10^{-7}\ \text{mol}$$

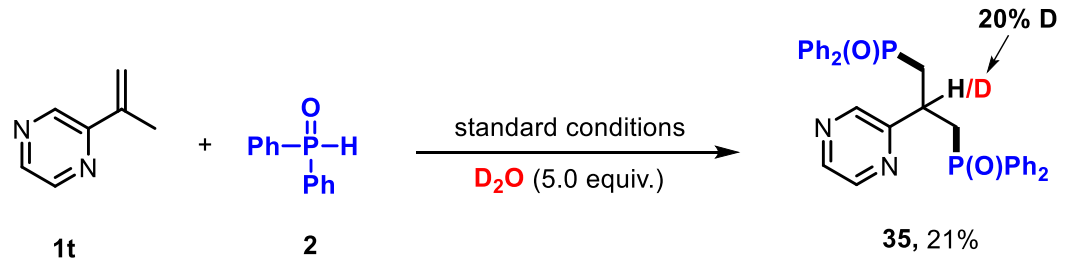
$$\text{photon flux} = \frac{6.85 \times 10^{-7}\text{mol}}{1.01 \cdot 90.0\ \text{s} \cdot 1} = 7.54 \times 10^{-9}\ \text{einstein}\ \text{s}^{-1}$$

The reaction mixture was stirred and irradiated by LEDs (λ max = 425 nm) for 3600 s. The yield of product **3** was determined by ^{1}H NMR analysis using CH_2Br_2 as an internal standard. The yield of **3** was determined to be 5% (5×10^{-6} mol of **3**). Therefore, the quantum yield of the reaction was determined to be:

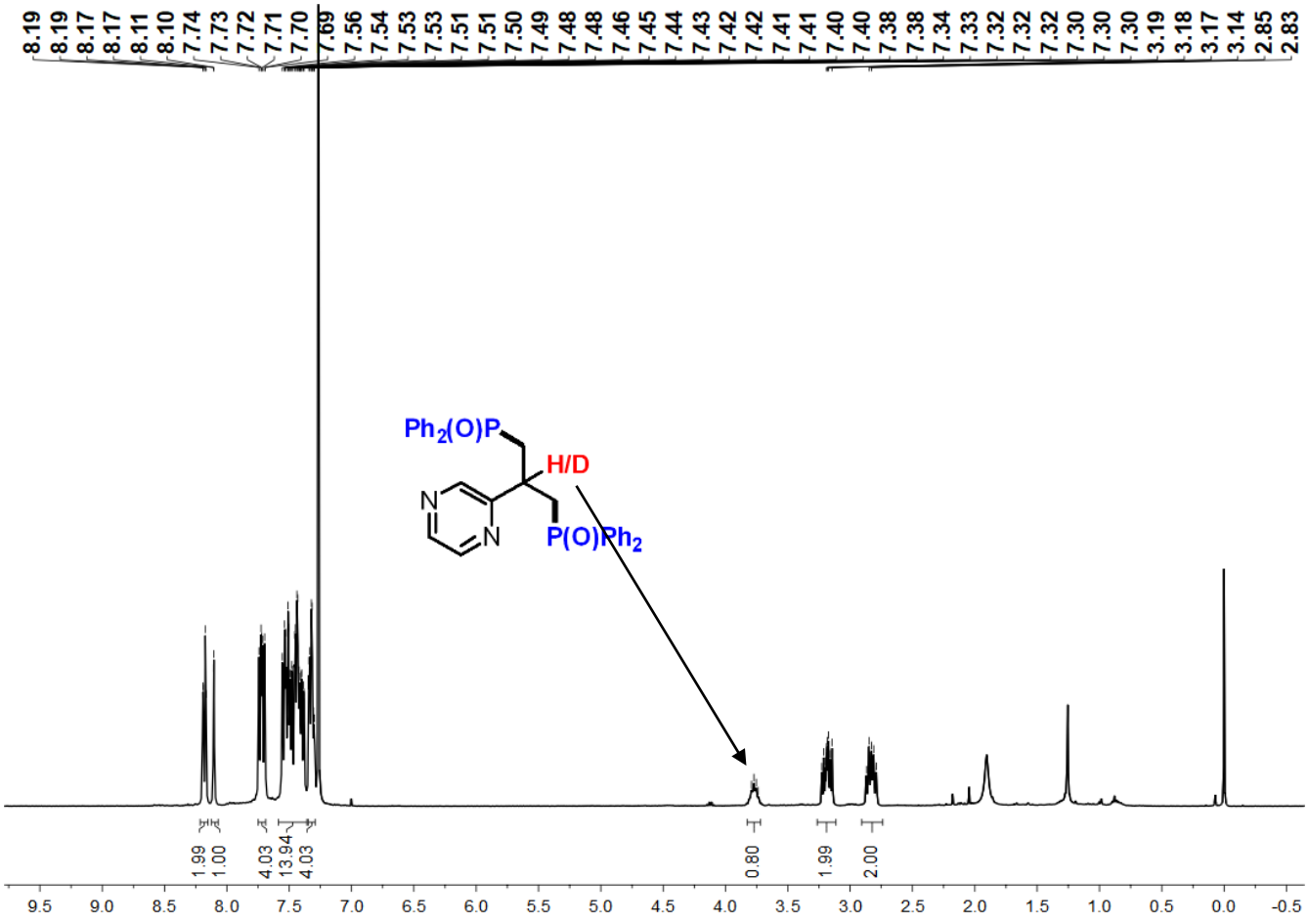
$$\Phi(\text{reaction at 425nm}) = \frac{\text{mol of product}}{\text{mol of photon flux} \cdot \text{t} \cdot \text{f}} = \frac{5 \times 10^{-6}\ \text{mol}}{7.54 \times 10^{-9} \cdot 3600\ \text{s} \cdot 1} = 0.18$$

The reaction quantum yield (Φ) was calculated to be 0.18.

5.4 Deuterium-labeling experiment



A solution of alkene 1t (0.1 mmol), diphenylphosphine oxide 2 (0.25 mmol), pyridine (0.2 mmol), $Co(dmgH)_2(DMAP)Cl$ (0.01 mmol), D_2O (5.0 equiv) in anhydrous DCE (1 mL) was irradiated with 6 W LEDs (420–430 nm) for 24 hours under argon atmosphere at ambient temperature. After reaction, upon removal of solvent under vacuum, the residue was purified by chromatography on silica gel to get the product.



6. Biological experiments

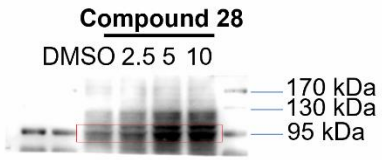
Cell Culture. Human colon cancer cell line HCT116, human pulmonary epithelial cell line A549, colon epithelial cell line NCM460, and immortalized human normal cervical epithelial cell line H8 were purchased from the Institute of Biochemistry and Cell Biology, Chinese Academy of Sciences

(Shanghai, China). Human cervical cancer cell line Hela, and human ovarian cancer cell line SK-OV-3 were purchased from Wuhan Procell Life Science&Technology Co. Ltd. (Wuhan, China). SK-OV-3 and HCT116 cell lines were cultured in McCoy's 5A medium (Hyclone, Logan, UT, USA). Hela, A549, NCM460, and H8 cell lines were cultured in DMEM-high glucose medium (Hyclone, Logan, UT, USA). All cells were cultured in the medium with 10% fetal calf serum and 1% penicillin-streptomycin under a humidified atmosphere of 5% CO_2 at 37 °C.

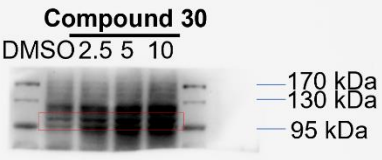
Cell Viability Assay. Inhibition of cell viability was assayed by Cell Counting Kit-8 (CCK-8, Cat.HY-K0301-30, MCE). In CCK-8 assay, adherent cells were seeded in 96-well plates (5000 cells per well). After treatment with compounds for 72 h, cells were fixed with CCK-8 assay solution and incubated at 37 °C for 1−4 h. The absorbance at 450 nm was detected in a multimode reader (Berthold Technologies, Germany), and the IC_{50} value was calculated using GraphPad Prism 8.0 software. 5-FU is an antimetabolite drug that is widely used for the treatment of cancer.

Western Blot Analysis. HCT116 cells were lysed with RIPA lysis buffer (Beyotime Institute of Biotechnology, Shanghai,China) on ice for 5 min, and the total protein concentrations of the lysates were determined by the BSA assay (Beyotime Institute of Biotechnology, Shanghai, China). Total proteins (10 μg) were electrophoresed on SDS polyacrylamide gels and then transferred to PVDF membranes (Pall, New York, NY, USA). After blocking with blocking buffer, the membrane was incubated with primary antibodies overnight at 4 °C, followed by three washes with TBST for 5 min each time. Membranes were then incubated with the appropriate secondary antibody for 1 h at room temperature, followed by three washes with TBST for 5 min each time. Finally, the chemiluminescence method was employed to detect the signals using the Pierce ECL Western Blotting Substrate (Thermo Scientific, Waltham, MA, USA)

C- PARP 89 kDa



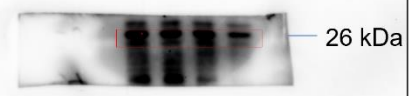
C- PARP 89 kDa



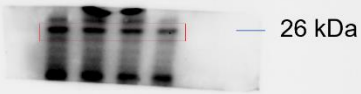
β-Tubulin 52 kDa

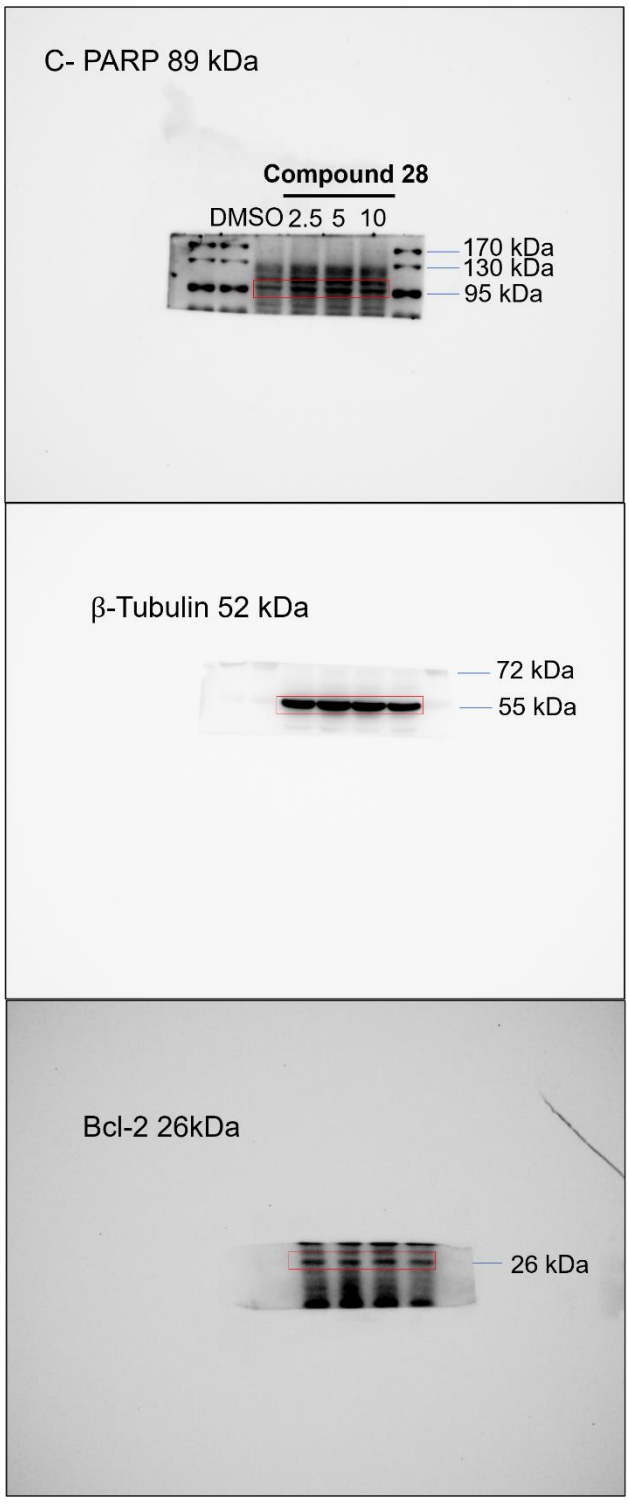
β-Tubulin 52 kDa

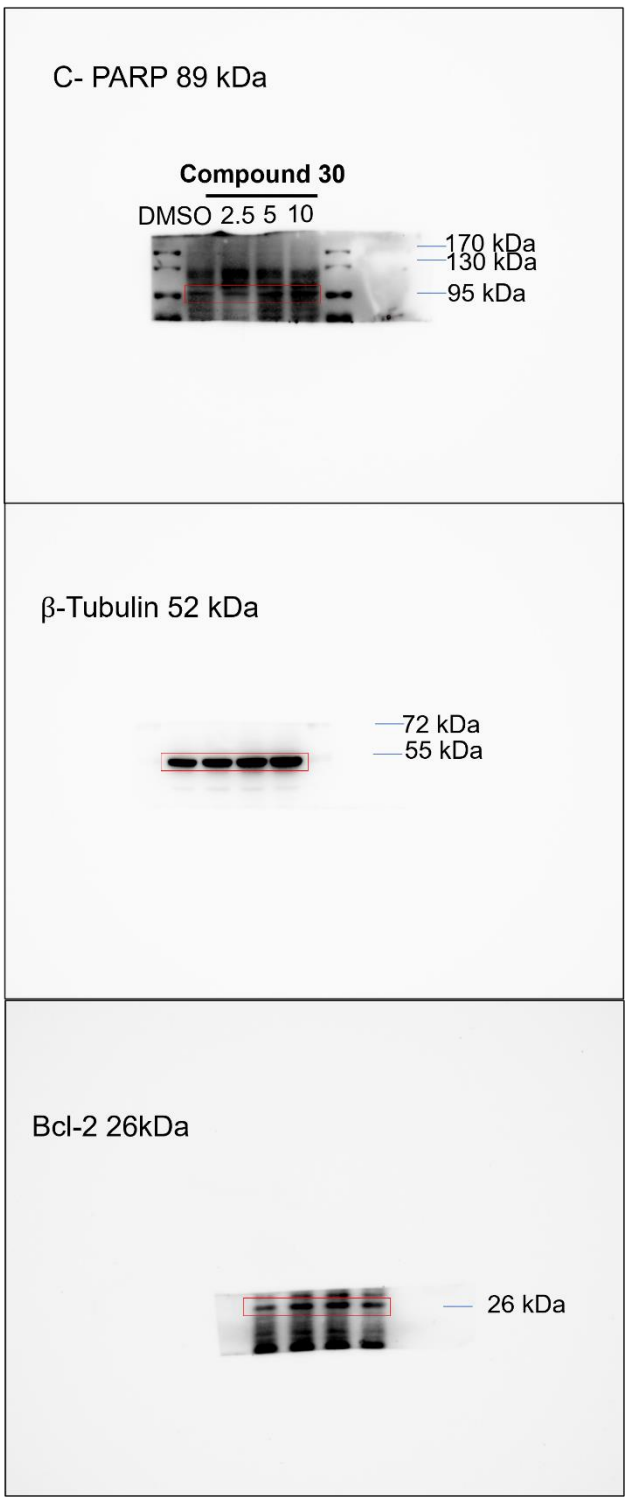
Bcl-2 26kDa



Bcl-2 26kDa



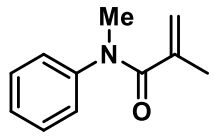

C- PARP 89 kDa
Compound 28
DMSO 2.5 5 10
170 kDa
130 kDa
95 kDa
β-Tubulin 52 kDa
72 kDa
55 kDa
Bcl-2 26kDa
26 kDa


C- PARP 89 kDa
Compound 30
DMSO 2.5 5 10
170 kDa
130 kDa
95 kDa
β-Tubulin 52 kDa
72 kDa
55 kDa
Bcl-2 26kDa
26 kDa

7. Characterization data

7.1 Characterization data for starting materials

N-methyl-N-phenylmethacrylamide (1a)



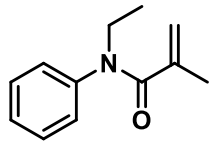
1a

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.27 – 7.23 (m, 1H), 7.17 – 7.11 (m, 2H), 5.05 – 5.01 (m, 1H), 5.00 – 4.96 (m, 1H), 3.35 (s, 3H), 1.76 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 144.6, 140.7, 129.2, 126.9, 126.5, 119.4, 37.7, 20.3.

N-ethyl-N-phenylmethacrylamide (1b)



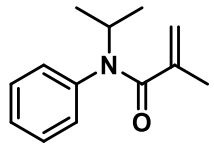
1b

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, J = 7.4 Hz, 2H), 7.30 – 7.23 (m, 1H), 7.11 (d, J = 7.8 Hz, 2H), 5.00 (s, 1H), 4.97 (s, 1H), 3.83 (q, J = 7.1 Hz, 2H), 1.75 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 142.9, 141.1, 129.2, 127.6, 127.1, 119.0, 44.6, 20.4, 12.9.

N-isopropyl-N-phenylmethacrylamide (1c)



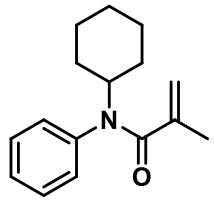
1c

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 3H), 7.10 – 7.05 (m, 2H), 4.97 (dt, J = 13.5, 6.6 Hz, 1H), 4.90 (s, 1H), 4.86 (s, 1H), 1.73 (s, 3H), 1.15 – 1.11 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 141.5, 139.1, 130.3, 128.7, 127.7, 117.7, 46.8, 21.0, 20.7.

N-cyclohexyl-N-phenylmethacrylamide (1d)



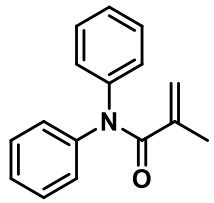
1d

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 3H), 7.08 – 7.04 (m, 2H), 4.89 (s, 1H), 4.83 (s, 1H), 4.61 – 4.49 (m, 1H), 1.90 – 1.84 (m, 2H), 1.77 – 1.71 (m, 5H), 1.61 – 1.56 (m, 1H), 1.46 – 1.36 (m, 2H), 1.18 – 1.08 (m, 2H), 0.97 – 0.87 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 141.5, 139.5, 130.4, 128.6, 127.8, 117.6, 54.8, 31.6, 25.8, 25.4, 20.8.

N, N-diphenylmethacrylamide (1e)



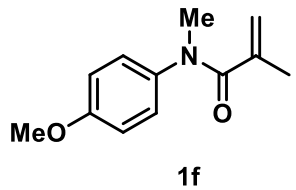
1e

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, J = 7.7 Hz, 4H), 7.22 (t, J = 7.4 Hz, 2H), 7.17 (d, J = 7.5 Hz, 4H), 5.23 (s, 1H), 5.17 (s, 1H), 1.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 143.5, 141.2, 129.1, 127.2, 126.5, 120.9, 19.9.

N-(4-methoxyphenyl)-N-methylmethacrylamide (1f)



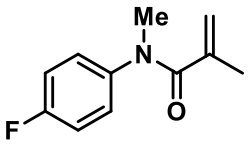
1f

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 7.7 Hz, 2H), 6.87 – 6.82 (m, 2H), 5.02 (s, 1H), 4.99 (s, 1H), 3.81 (d, J = 1.9 Hz, 3H), 3.30 (d, J = 1.8 Hz, 3H), 1.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 158.3, 140.9, 137.4, 127.8, 119.0, 114.4, 55.4, 37.8, 20.4.

N-(4-fluorophenyl)-N-methylmethacrylamide (1g)



1g

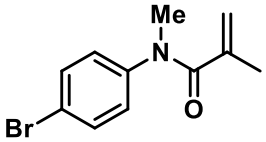
The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.09 (m, 2H), 7.09 – 6.99 (m, 2H), 5.06 (s, 1H), 4.99 (s, 1H), 3.33 (s, 3H), 1.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 161.2 (d, J = 247.0 Hz), 140.5, 128.2 (d, J = 8.6 Hz), 119.4, 116.1 (d, J = 22.7 Hz), 37.8, 20.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.57.

N-(4-bromophenyl)-N-methylmethacrylamide (1h)



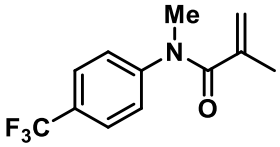
1h

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 2H), 7.02 (dd, J = 8.6, 1.3 Hz, 2H), 5.08 (d, J = 1.1 Hz, 1H), 4.99 (s, 1H), 3.33 (d, J = 1.6 Hz, 3H), 1.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 143.7, 140.4, 132.4, 128.1, 120.4, 119.8, 37.6, 20.3

N-methyl-N-(4-(trifluoromethyl)phenyl)methacrylamide (1i)



1i

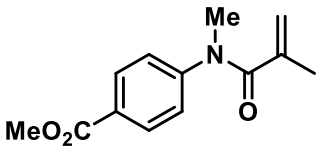
The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 5.12 (s, 1H), 5.00 (d, J = 0.6 Hz, 1H), 3.39 (s, 3H), 1.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 147.8, 140.2, 128.7 (q, J = 32.9 Hz), 126.6 – 126.2 (m), 123.8 (q, J = 272.2 Hz), 120.2, 37.5, 20.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.46.

methyl 4-(N-methylmethacrylamido) benzoate (1j)



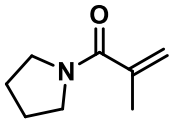
1j

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 2H), 7.24 – 7.17 (m, 2H), 5.10 – 5.07 (m, 1H), 5.01 – 4.98 (m, 1H), 3.92 (s, 3H), 3.38 (s, 3H), 1.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 166.3, 148.8, 140.4, 130.7, 128.3, 125.9, 120.2, 52.3, 37.4, 20.2.

2-methyl-1-(pyrrolidin-1-yl) prop-2-en-1-one (1k)



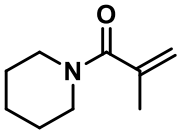
1k

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (d, J = 1.6 Hz, 1H), 5.19 – 5.08 (m, 1H), 3.54 – 3.43 (m, 4H), 1.98 – 1.94 (m, 3H), 1.94 – 1.84 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 141.7, 116.1, 48.7, 45.5, 26.1, 24.3, 19.9.

2-methyl-1-(piperidin-1-yl) prop-2-en-1-one (1l)



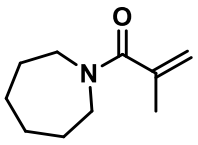
1l

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (s, 1H), 5.03 – 4.94 (m, 1H), 3.64 – 3.37 (m, 4H), 1.95 (s, 3H), 1.69 – 1.51 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 141.0, 114.5, 47.9, 42.3, 26.7, 25.5, 24.6, 20.5.

1-(azepan-1-yl)-2-methylprop-2-en-1-one (1m)



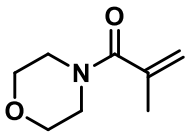
1m

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (d, J = 1.1 Hz, 1H), 5.00 (d, J = 1.0 Hz, 1H), 3.64 – 3.38 (m, 4H), 1.97 (s, 3H), 1.82 – 1.65 (m, 4H), 1.65 – 1.52 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 141.5, 114.3, 48.9, 45.7, 29.7, 27.7, 27.1, 26.4, 20.7.

2-methyl-1-morpholinoprop-2-en-1-one (1n)



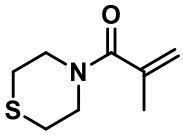
1n

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 – 5.16 (m, 1H), 5.04 (s, 1H), 3.64 (d, J = 24.5 Hz, 3H), 1.96 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 140.0, 115.8, 66.9, 47.4, 41.8, 20.4.

2-methyl-1-thiomorpholinoprop-2-en-1-one (1o)



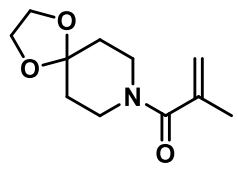
1o

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18 (s, 1H), 5.02 (s, 1H), 4.01 – 3.64 (m, 4H), 2.74 – 2.49 (m, 4H), 1.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 140.3, 115.1, 49.2, 43.7, 27.9, 27.4, 20.4.

2-methyl-1-(1,4-dioxa-8-azaspiro [4.5] decan-8-yl) prop-2-en-1-one (1p)



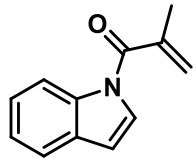
1p

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 – 5.12 (m, 1H), 5.03 (d, J = 1.0 Hz, 1H), 3.98 (s, 4H), 3.76 – 3.46 (m, 4H), 1.95 (s, 3H), 1.74 – 1.61 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 114.8, 106.7, 64.3, 44.7, 39.3, 35.6, 34.5, 20.3.

1-(1H-indol-1-yl)-2-methylprop-2-en-1-one (1q)



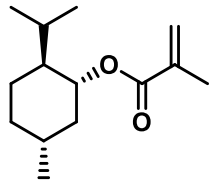
1q

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, J = 8.3 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 3.8 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.28 (td, J = 7.7, 1.0 Hz, 1H), 6.62 – 6.55 (m, 1H), 5.66 (dd, J = 1.5, 0.5 Hz, 1H), 5.45 (d, J = 0.7 Hz, 1H), 2.19 – 2.10 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.7, 139.9, 135.7, 131.1, 127.1, 124.9, 123.9, 121.9, 120.9, 116.5, 108.5, 20.0.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl methacrylate (1r)



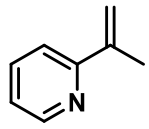
1r

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (s, 1H), 5.52 (d, J = 0.7 Hz, 1H), 4.74 (td, J = 10.9, 4.4 Hz, 1H), 2.06 – 2.01 (m, 1H), 1.94 (s, 3H), 1.91 – 1.82 (m, 1H), 1.73 – 1.66 (m, 2H), 1.55 – 1.40 (m, 2H), 1.15 – 0.93 (m, 3H), 0.90 (dd, J = 6.7, 4.3 Hz, 6H), 0.77 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 136.9, 124.9, 74.4, 47.2, 40.9, 34.3, 31.4, 26.4, 23.6, 22.0, 20.8, 18.4, 16.5.

2-(prop-1-en-2-yl) pyridine (1s)



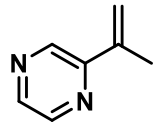
1s

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 50:1 - 20:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.1 Hz, 1H), 7.64 (td, *J* = 7.9, 1.6 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.09 (m, 1H), 5.86 (s, 1H), 5.37 – 5.19 (m, 1H), 2.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 148.9, 143.2, 136.3, 122.1, 119.8, 115.6, 20.5.

2-(prop-1-en-2-yl) pyrazine (1t)



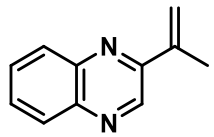
1t

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 50:1 - 20:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.0 Hz, 1H), 8.58 – 8.48 (m, 1H), 8.47 – 8.33 (m, 1H), 5.99 – 5.85 (m, 1H), 5.43 (d, *J* = 4.7 Hz, 1H), 2.29 – 2.16 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 143.4, 142.8, 141.6, 140.8, 117.6, 19.9.

2-(prop-1-en-2-yl) quinoxaline (1u)



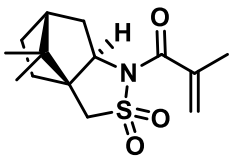
1u

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 50:1 - 20:1, v/v)

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.07 (s, 1H), 7.99 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.68 – 7.60 (m, 2H), 5.96 (s, 1H), 5.54 (dd, *J* = 1.4, 0.6 Hz, 1H), 2.29 (dd, *J* = 1.3, 0.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.9, 141.8, 141.3, 140.8, 140.2, 129.0, 128.6, 128.3, 128.0, 117.7, 19.1.

1-((3aS,6R,7aR)-8,8-dimethyl-2,2-dioxidotetrahydro-3H-3a,6-methanobenzo[c]isothiazol-1(4H)-yl)-2-methylprop-2-en-1-one (1v)



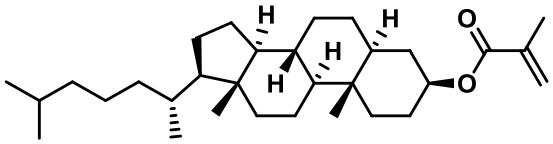
1v

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 (s, 1H), 5.65 (d, J = 1.5 Hz, 1H), 4.04 (dd, J = 7.6, 4.8 Hz, 1H), 3.51 (d, J = 13.6 Hz, 1H), 3.40 (d, J = 13.7 Hz, 1H), 2.09 – 1.88 (m, 8H), 1.46 – 1.34 (m, 2H), 1.23 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 139.0, 124.4, 65.5, 53.6, 48.0, 47.7, 45.3, 38.4, 33.3, 26.5, 21.3, 19.9, 18.7.

(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl) hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl methacrylate (1w)



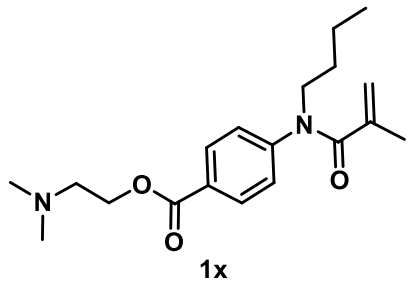
1w

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.00 (d, *J* = 0.4 Hz, 1H), 5.47 – 5.41 (m, 1H), 4.74 – 4.64 (m, 1H), 1.89 (dt, *J* = 12.6, 3.3 Hz, 1H), 1.85 (s, 3H), 1.80 – 1.71 (m, 2H), 1.67 (dt, *J* = 13.3, 3.6 Hz, 1H), 1.60 – 1.54 (m, 2H), 1.51 – 1.40 (m, 4H), 1.38 – 0.87 (m, 20H), 0.83 (d, *J* = 6.5 Hz, 3H), 0.79 (dd, *J* = 6.6, 2.7 Hz, 6H), 0.77 (s, 3H), 0.58 (s, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 137.0, 124.8, 74.0, 56.4, 56.3, 54.3, 44.7, 42.6, 40.0, 39.5, 36.8, 36.2, 35.8, 35.5, 34.1, 32.0, 28.7, 28.3, 28.0, 27.5, 24.2, 23.9, 22.8, 22.6, 21.2, 18.7, 18.4, 12.3, 12.1.

2-(dimethylamino) ethyl 4-(N-butylmethacrylamido) benzoate (1x)



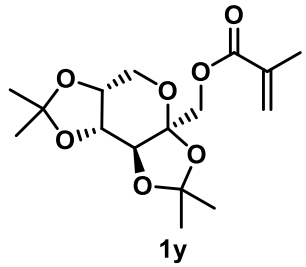
1x

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 5.04 (d, *J* = 0.8 Hz, 1H), 4.96 (d, *J* = 0.7 Hz, 1H), 4.43 (t, *J* = 5.7 Hz, 2H), 3.83 – 3.77 (m, 2H), 2.72 (t, *J* = 5.7 Hz, 2H), 2.34 (s, 6H), 1.78 (d, *J* = 0.5 Hz, 3H), 1.55 – 1.47 (m, 2H), 1.36 – 1.27 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 165.8, 147.6, 140.7, 130.7, 128.5, 126.9, 119.8, 63.1, 57.9, 49.4, 45.8, 29.9, 20.3, 20.1, 13.8.

((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis ([1,3] dioxolo) [4,5-b:4',5'-d] pyran-3a-yl) methyl isobutyrate (1y)



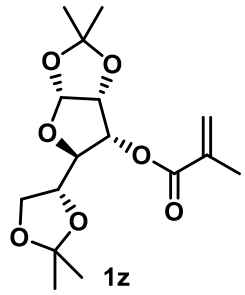
1y

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (s, 1H), 5.64 – 5.57 (m, 1H), 4.63 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.49 (d, *J* = 11.9 Hz, 1H), 4.38 (d, *J* = 2.7 Hz, 1H), 4.25 (dd, *J* = 7.9, 1.2 Hz, 1H), 4.15 (d, *J* = 11.9 Hz, 1H), 3.94 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.78 (d, *J* = 13.0 Hz, 1H), 1.97 (s, 3H), 1.55 (s, 3H), 1.49 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 136.0, 126.0, 109.2, 108.8, 101.6, 70.8, 70.4, 70.1, 65.0, 61.3, 26.6, 25.9, 25.5, 24.0, 18.5.

(3aR,5R,6R,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d] [1,3] dioxol-6-yl methacrylate (1z)



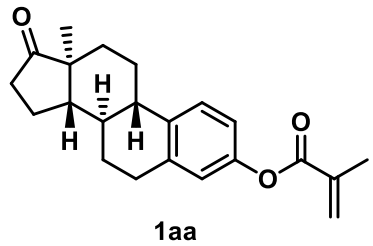
1z

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (s, 1H), 5.90 (d, J = 3.7 Hz, 1H), 5.68 – 5.59 (m, 1H), 5.30 (d, J = 2.0 Hz, 1H), 4.54 (d, J = 3.7 Hz, 1H), 4.30 – 4.21 (m, 2H), 4.13 – 3.99 (m, 2H), 1.96 (s, 3H), 1.53 (s, 3H), 1.41 (s, 3H), 1.31 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 135.8, 126.5, 112.3, 109.3, 105.1, 83.3, 79.9, 76.4, 72.5, 67.2, 26.8, 26.7, 26.2, 25.2, 18.2.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl methacrylate (1aa)



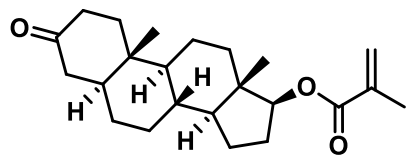
1aa

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.4 Hz, 1H), 6.89 (dd, J = 8.4, 2.5 Hz, 1H), 6.85 (d, J = 2.4 Hz, 1H), 6.33 (s, 1H), 5.76 – 5.71 (m, 1H), 2.95 – 2.88 (m, 2H), 2.55 – 2.46 (m, 1H), 2.45 – 2.39 (m, 1H), 2.34 – 2.26 (m, 1H), 2.19 – 1.95 (m, 7H), 1.71 (d, J = 14.1 Hz, 1H), 1.63 – 1.46 (m, 5H), 0.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.9, 166.2, 148.8, 138.0, 137.3, 136.0, 127.1, 126.4, 121.6, 118.8, 50.5, 48.0, 44.2, 38.0, 35.9, 31.6, 29.4, 26.4, 25.8, 21.6, 18.4, 13.9.

(5S,8R,9S,10S,13S,14S,17S)-10,13-dimethyl-3-oxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl methacrylate (1ab)



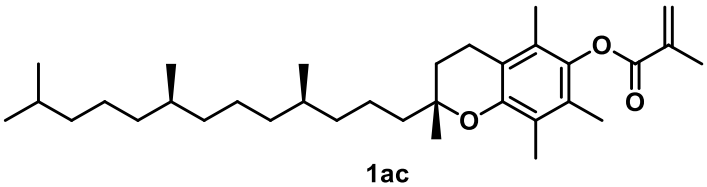
1ab

The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (s, 1H), 5.56 – 5.51 (m, 1H), 4.65 (dd, *J* = 9.0, 7.9 Hz, 1H), 2.43 – 2.17 (m, 4H), 2.13 – 2.06 (m, 1H), 2.04 (s, 1H), 1.94 (s, 3H), 1.81 – 1.58 (m, 4H), 1.57 – 1.46 (m, 3H), 1.42 – 1.28 (m, 5H), 1.23 – 1.16 (m, 1H), 1.13 – 1.06 (m, 1H), 1.02 (s, 3H), 0.93 (dt, *J* = 12.0, 6.8 Hz, 1H), 0.85 (s, 3H), 0.81 – 0.73 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 211.9, 167.4, 136.8, 125.0, 82.9, 53.8, 50.6, 46.6, 44.7, 42.9, 38.5, 38.1, 36.9, 35.7, 35.2, 31.3, 28.8, 27.6, 23.6, 20.9, 18.3, 12.2, 11.5.

(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl) chroman-6-yl methacrylate (1ac)



1ac

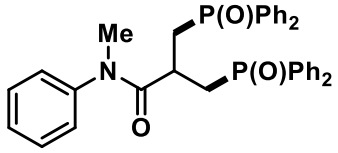
The compound was prepared according to the general procedure, obtained after silica gel chromatography (petroleum ether/ethyl acetate = 20:1 - 5:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (s, 1H), 5.76 – 5.70 (m, 1H), 2.59 (t, *J* = 6.7 Hz, 2H), 2.09 (d, *J* = 1.6 Hz, 6H), 2.01 (s, 3H), 1.97 (s, 3H), 1.84 – 1.73 (m, 2H), 1.60 – 1.45 (m, 4H), 1.44 – 1.33 (m, 4H), 1.31 – 1.21 (m, 10H), 1.16 – 1.03 (m, 6H), 0.88 – 0.83 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 149.4, 140.6, 135.9, 126.8, 126.6, 125.0, 123.1, 117.4, 75.0, 39.4, 37.5, 37.3, 32.8, 28.0, 24.8, 24.5, 22.8, 22.7, 21.1, 20.6, 19.8, 19.7, 18.6, 13.0, 12.1, 11.8.

6.2 Characterization data for products

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-N-methyl-N-phenylpropanamide (3)



3

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 51.3 mg, 89% yield.

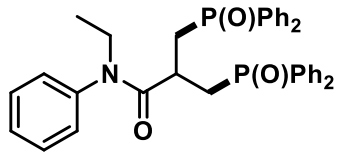
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 4H), 7.47 – 7.35 (m, 12H), 7.28 – 7.26 (m, 4H), 7.17 – 7.12 (m, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.8 Hz, 2H), 3.23 (s, 3H), 3.21 – 3.12 (m, 3H), 2.74 – 2.65 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0 (t, *J* = 8.6 Hz), 142.9, 133.2 (d, *J* = 98.6 Hz), 132.7 (d, *J* = 99.2 Hz), 131.6, 131.5, 130.7 (d, *J* = 9.6 Hz), 130.5 (d, *J* = 9.6 Hz), 129.3, 128.5 (d, *J* = 11.9 Hz), 128.5 (d, *J* = 11.9 Hz), 127.3, 127.3, 38.1, 32.4 (dd, *J* = 70.6, 7.9 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.42.

HRMS (ESI): Calcd for $C35H34NO3P2(M+H)^+$: 578.2008; Found: 578.2004.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-N-ethyl-N-phenylpropanamide (4)



4

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 54.1 mg, 91% yield.

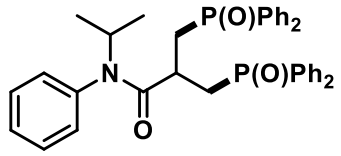
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 4H), 7.47 – 7.34 (m, 12H), 7.28 – 7.23 (m, 4H), 7.17 – 7.12 (m, 2H), 7.08 – 7.02 (m, 1H), 6.94 (t, *J* = 7.6 Hz, 2H), 3.70 (q, *J* = 7.1 Hz, 2H), 3.22 – 3.12 (m, 2H), 3.11 – 3.01 (m, 1H), 2.76 – 2.63 (m, 2H), 1.07 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4 (t, *J* = 8.6 Hz), 141.1, 133.3 (d, *J* = 98.6 Hz), 132.7 (d, *J* = 99.1 Hz), 131.6, 131.5, 130.7 (d, *J* = 9.7 Hz), 130.6 (d, *J* = 10.2 Hz), 129.2, 128.5 (d, *J* = 11.8 Hz), 128.5 (d, *J* = 12.5 Hz), 128.4, 127.5, 44.8, 32.3 (dd, *J* = 69.7, 7.0 Hz), 31.9, 12.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.58.

HRMS (ESI): Calcd for $C36H36NO3P2(M+H)^+$: 592.2165; Found: 592.2166.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-N-isopropyl-N-phenylpropanamide (5)



5

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 44.0 mg, 73% yield.

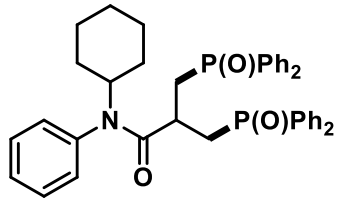
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 4H), 7.49 – 7.35 (m, 12H), 7.30 – 7.27 (m, 4H), 7.05 (dd, *J* = 16.2, 7.4 Hz, 3H), 6.89 (t, *J* = 7.7 Hz, 2H), 5.02 – 4.91 (m, 1H), 3.23 – 3.10 (m, 2H), 2.92 – 2.82 (m, 1H), 2.75 – 2.64 (m, 2H), 1.00 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3 (t, *J* = 8.5 Hz), 137.1, 133.2 (d, *J* = 98.6 Hz), 132.7 (d, *J* = 99.3 Hz), 131.6, 131.5, 130.7 (d, *J* = 9.3 Hz), 130.6 (d, *J* = 9.5 Hz), 130.2, 128.7, 128.5 (d, *J* = 11.8 Hz), 128.5 (d, *J* = 12.1 Hz), 127.8, 46.6, 32.6, 32.3 (dd, *J* = 70.7, 8.2 Hz), 20.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.75.

HRMS (ESI): Calcd for C37H38NO3P2 $(M+H)^+$: 606.2321; Found: 606.2319.

N-cyclohexyl-3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-N-phenylpropanamide (6)



6

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. White solid; 51.2 mg, 80% yield.

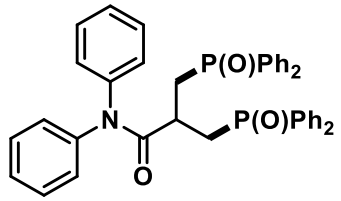
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 4H), 7.47 – 7.34 (m, 12H), 7.30 – 7.27 (m, 4H), 7.09 – 6.99 (m, 3H), 6.87 (t, *J* = 7.7 Hz, 2H), 4.62 – 4.50 (m, 1H), 3.24 – 3.08 (m, 2H), 2.92 – 2.79 (m, 1H), 2.77 – 2.61 (m, 2H), 1.86 (d, *J* = 11.3 Hz, 2H), 1.68 (d, *J* = 13.4 Hz, 2H), 1.51 (d, *J* = 12.9 Hz, 1H), 1.40 – 1.28 (m, 2H), 0.99 – 0.79 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4 (t, *J* = 8.5 Hz), 137.70 (s), 133.4 (d, *J* = 98.4 Hz), 132.9 (d, *J* = 98.9 Hz), 131.5, 131.4, 130.7 (d, *J* = 9.4 Hz), 130.6 (d, *J* = 9.7 Hz), 130.2, 128.6, 128.5 (d, *J* = 11.2 Hz), 128.5 (d, *J* = 12.1 Hz), 127.7, 54.7, 32.6, 32.4 (dd, *J* = 70.7, 8.0 Hz), 31.2, 25.8, 25.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.52.

HRMS (ESI): Calcd for C40H42NO3P2 $(M+H)^+$: 646.2634; Found: 646.2632.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-N, N-diphenylpropanamide (7)



7

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. White solid; 48.5 mg, 76% yield.

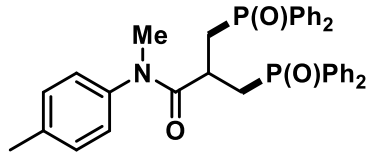
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 4H), 7.52 – 7.36 (m, 14H), 7.32 – 7.26 (m, 6H), 7.22 (d, *J* = 7.4 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.86 (t, *J* = 7.7 Hz, 2H), 3.34 – 3.19 (m, 3H), 2.88 – 2.74 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4 (t, *J* = 8.7 Hz), 143.0, 141.8, 133.1 (d, *J* = 98.7 Hz), 132.8 (d, *J* = 99.2 Hz), 131.7, 131.6, 130.7 (d, *J* = 9.5 Hz), 130.6 (d, *J* = 9.7 Hz), 129.2, 128.9, 128.6 (d, *J* = 12.0 Hz), 128.6 (d, *J* = 12.3 Hz), 128.5, 127.4, 127.2, 126.4, 32.7 (dd, *J* = 70.3, 8.4 Hz), 32.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.52.

HRMS (ESI): Calcd for C40H36NO3P2 $(M+H)^+$: 640.2165; Found: 640.2163.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-N-methyl-N-(p-tolyl) propenamide (8)



8

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 45.1 mg, 76% yield.

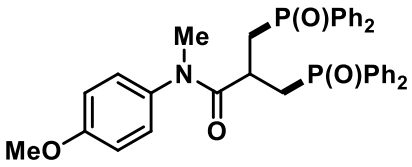
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 4H), 7.48 – 7.36 (m, 12H), 7.28 (d, *J* = 3.5 Hz, 4H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.69 (d, *J* = 8.1 Hz, 2H), 3.25 – 3.09 (m, 6H), 2.76 – 2.63 (m, 2H), 2.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1 (t, *J* = 8.6 Hz), 140.3, 136.9, 133.2 (d, *J* = 98.7 Hz), 132.7 (d, *J* = 99.2 Hz), 131.6, 131.3, 130.7 (d, *J* = 9.9 Hz), 130.6 (d, *J* = 10.1 Hz), 129.9, 128.5 (d, *J* = 12.1 Hz), 128.4 (d, *J* = 12.0 Hz), 127.0, 38.0, 32.4 (dd, *J* = 70.7, 7.9 Hz), 31.3, 21.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.48.

HRMS (ESI): Calcd for C36H36NO3P2 $(M+H)^+$: 592.2165; Found: 592.2164.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-N-(4-methoxyphenyl)-N-methylpropanamide (9)



9

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 40.3 mg, 66% yield.

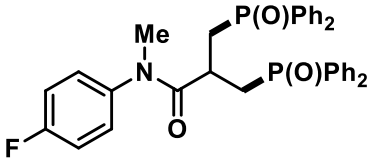
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 4H), 7.49 – 7.36 (m, 12H), 7.28 (d, *J* = 2.4 Hz, 4H), 7.08 – 7.00 (m, 2H), 6.46 – 6.34 (m, 2H), 3.72 (s, 3H), 3.25 – 3.08 (m, 6H), 2.76 – 2.61 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3 (t, *J* = 8.5 Hz), 158.3, 135.7, 133.2 (d, *J* = 98.7 Hz), 132.7 (d, *J* = 99.2 Hz), 131.6, 131.5, 130.7 (d, *J* = 9.6 Hz), 130.6 (d, *J* = 9.9 Hz), 128.5 (d, *J* = 11.6 Hz), 128.4 (d, *J* = 11.7 Hz), 128.3, 114.3, 55.2, 38.1, 32.3 (dd, *J* = 70.6, 8.0 Hz), 31.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.61.

HRMS (ESI): Calcd for $C_{36}H_{36}NO_4P_2$ $(M+H)^+$: 608.2114; Found: 608.2111.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-N-(4-fluorophenyl)-N-methylpropanamide (10)



10

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 47.3 mg, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 10.7, 7.9 Hz, 4H), 7.53 – 7.41 (m, 12H), 7.30 – 7.27 (m, 4H), 7.10 (dd, *J* = 8.6, 4.9 Hz, 2H), 6.52 (t, *J* = 8.5 Hz, 2H), 3.30 – 3.12 (m, 5H), 3.12 – 3.02 (m, 1H), 2.75 – 2.55 (m, 2H).

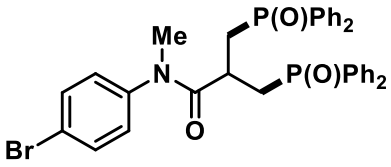
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2 (t, *J* = 8.5 Hz), 161.2 (d, *J* = 247.3 Hz), 138.8 (d, *J* = 3.0 Hz), 133.0 (d, *J* = 98.7 Hz), 132.6 (d, *J* = 99.4 Hz), 131.8, 131.6, 130.7 (d, *J* = 9.5 Hz), 130.6 (d, *J* = 9.7 Hz), 129.0 (d, *J* = 8.6 Hz), 128.6 (d, *J* = 12.1 Hz), 128.5 (d, *J* = 12.4 Hz), 116.0 (d, *J* = 22.6 Hz), 38.1, 32.5 (dd, *J* = 70.5, 8.0 Hz), 31.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.54.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.94.

HRMS (ESI): Calcd for $C_{35}H_{33}FNO_3P_2$ $(M+H)^+$: 596.1914; Found: 596.1914.

N-(4-bromophenyl)-3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-N-methylpropanamide (11)



11

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 52.8 mg, 81% yield.

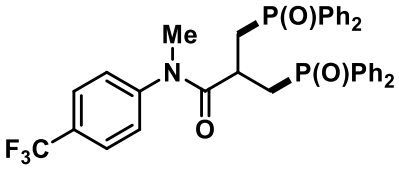
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 4H), 7.53 – 7.41 (m, 12H), 7.34 – 7.28 (m, 4H), 7.01 – 6.96 (m, 2H), 6.96 – 6.90 (m, 2H), 3.27 – 3.13 (m, 5H), 3.11 – 3.00 (m, 1H), 2.77 – 2.54 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0 (t, *J* = 8.4 Hz), 141.8, 132.9 (d, *J* = 98.8 Hz), 132.5 (d, *J* = 99.4 Hz), 132.3, 131.8, 131.7, 130.7 (d, *J* = 9.5 Hz), 130.5 (d, *J* = 9.7 Hz), 128.9, 128.7 (d, *J* = 12.0 Hz), 128.5 (d, *J* = 12.0 Hz), 121.1, 37.9, 32.6 (dd, *J* = 70.5, 7.9 Hz), 31.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.55.

HRMS (ESI): Calcd for C35H33BrNO3P2 $(M+H)^+$: 656.1114; Found: 656.1112.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-N-methyl-N-(4-(trifluoromethyl)phenyl) propenamide (12)



12

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 62.6 mg, 97% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 4H), 7.53 – 7.41 (m, 12H), 7.31 (dd, *J* = 7.6, 2.5 Hz, 4H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 3.34 – 3.16 (m, 5H), 3.00 – 2.91 (m, 1H), 2.76 – 2.57 (m, 2H).

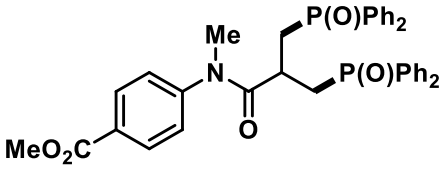
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1 (t, *J* = 8.4 Hz), 145.8, 132.8 (d, *J* = 98.9 Hz), 132.6 (d, *J* = 99.3 Hz), 131.9, 131.8, 130.7 (d, *J* = 9.5 Hz), 130.5 (d, *J* = 9.7 Hz), 129.0 (q, *J* = 32.6 Hz), 128.7 (d, *J* = 11.9 Hz), 128.5 (d, *J* = 12.2 Hz), 127.6, 126.19 (q, *J* = 7.0 Hz), 123.6 (q, *J* = 272.4 Hz), 37.9, 32.9 (dd, *J* = 70.5, 8.0 Hz), 31.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.41.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.58.

HRMS (ESI): Calcd for C36H33F3NO3P2 $(M+H)^+$: 646.1882; Found: 646.1881.

methyl 4-(3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-N-methylpropanamido) benzoate (13)



13

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 60.3 mg, 95% yield.

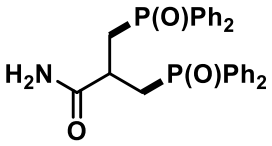
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 4H), 7.53 – 7.37 (m, 15H), 7.25 (dd, *J* = 7.6, 2.7 Hz, 3H), 7.15 (d, *J* = 8.5 Hz, 2H), 3.97 (s, 3H), 3.28 – 3.15 (m, 5H), 3.11 – 3.03 (m, 1H), 2.73 – 2.60 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0 (t, *J* = 8.5 Hz), 166.0, 146.8, 132.8 (d, *J* = 98.8 Hz), 132.5 (d, *J* = 99.4 Hz), 131.8, 131.6, 130.7 (d, *J* = 9.8 Hz), 130.7, 130.5 (d, *J* = 9.8 Hz), 128.7 (d, *J* = 11.7 Hz), 128.5 (d, *J* = 12.1 Hz), 127.1, 52.3, 37.8, 32.6 (dd, *J* = 70.5, 8.0 Hz), 31.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.44.

HRMS (ESI): Calcd for C37H36NO5P2 $(M+H)^+$: 636.2063; Found: 636.2059.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) propenamide (14)



14

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 33.9 mg, 70% yield.

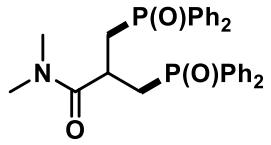
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.86 – 7.75 (m, 4H), 7.70 – 7.59 (m, 4H), 7.52 – 7.32 (m, 12H), 5.52 (s, 1H), 3.14 – 3.00 (m, 2H), 2.99 – 2.75 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6 (t, *J* = 7.4 Hz), 132.0 (d, *J* = 100.4 Hz), 132.0, 131.9, 131.7 (d, *J* = 100.4 Hz), 131.0 (d, *J* = 9.7 Hz), 130.7 (d, *J* = 9.4 Hz), 128.8 (d, *J* = 11.9 Hz), 128.7 (d, *J* = 11.8 Hz), 34.4, 31.9 (dd, *J* = 70.2, 7.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 33.16.

HRMS (ESI): Calcd for C28H28NO3P2 $(M+H)^+$: 488.1539; Found: 488.1537.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-N, N-dimethylpropanamide (15)



15

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 36.0 mg, 70% yield.

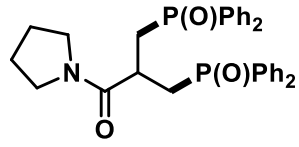
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.63 (m, 8H), 7.53 – 7.36 (m, 12H), 3.74 – 3.60 (m, 1H), 2.89 – 2.79 (m, 2H), 2.76 – 2.68 (m, 2H), 2.63 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5 (t, *J* = 5.1 Hz), 133.5 (d, *J* = 99.2 Hz), 131.9 (d, *J* = 98.3 Hz), 131.8, 131.8, 130.9 (d, *J* = 9.6 Hz), 130.5 (d, *J* = 9.5 Hz), 128.7 (d, *J* = 11.8 Hz), 128.4 (d, *J* = 12.0 Hz), 37.3, 35.5, 34.5 (dd, *J* = 70.0, 10.7 Hz), 29.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.37.

HRMS (ESI): Calcd for $C_{30}H_{32}NO_3P_2$ $(M+H)^+$: 516.1852; Found: 516.1848.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-1-(pyrrolidin-1-yl) propan-1-one (16)



16

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 50.3 mg, 93% yield.

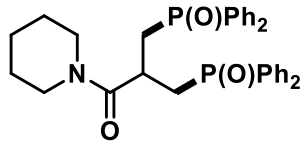
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.66 (m, 8H), 7.51 – 7.36 (m, 12H), 3.67 – 3.55 (m, 1H), 3.27 (t, *J* = 6.9 Hz, 2H), 3.00 – 2.86 (m, 2H), 2.63 – 2.55 (m, 2H), 2.47 (t, *J* = 6.9 Hz, 2H), 1.55 (p, *J* = 6.8 Hz, 2H), 1.36 (p, *J* = 6.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3 (t, *J* = 4.5 Hz), 134.0 (d, *J* = 99.3 Hz), 131.8 (d, *J* = 97.9 Hz), 131.7, 131.7, 131.0 (d, *J* = 9.7 Hz), 130.3 (d, *J* = 9.6 Hz), 128.7 (d, *J* = 11.9 Hz), 128.3 (d, *J* = 12.0 Hz), 46.2, 45.3, 34.7 (dd, *J* = 69.9, 11.7 Hz), 31.4, 25.5, 23.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.82.

HRMS (ESI): Calcd for $C_{32}H_{34}NO_3P_2$ $(M+H)^+$: 542.2008; Found: 542.2009.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-1-(piperidin-1-yl) propan-1-one (17)



17

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 37.7 mg, 68% yield.

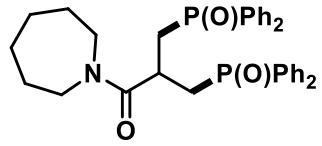
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.62 (m, 8H), 7.53 – 7.36 (m, 12H), 3.66 – 3.52 (m, 1H), 3.13 – 3.02 (m, 2H), 2.95 – 2.87 (m, 2H), 2.86 – 2.72 (m, 4H), 1.45 – 1.35 (m, 2H), 1.28 – 1.17 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2 (t, *J* = 6.1 Hz), 133.6 (d, *J* = 98.7 Hz), 132.4 (d, *J* = 98.6 Hz), 131.7 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 2.7 Hz), 130.9 (d, *J* = 9.4 Hz), 130.6 (d, *J* = 9.4 Hz), 128.7 (d, *J* = 11.7 Hz), 128.4 (d, *J* = 11.7 Hz), 46.8, 42.9, 34.1 (dd, *J* = 70.1, 9.8 Hz), 28.6, 26.0, 24.9, 24.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.64.

HRMS (ESI): Calcd for $C_{33}H_{36}NO_3P_2$ $(M+H)^+$: 556.2165; Found: 556.2166.

1-(azepan-1-yl)-3-(diphenylphosphoryl)-2-((diphenylphosphoryl) methyl) propan-1-one (18)



18

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 50.6 mg, 89% yield.

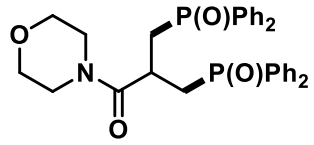
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.73 (m, 4H), 7.73 – 7.63 (m, 4H), 7.55 – 7.35 (m, 12H), 3.56 – 3.44 (m, 1H), 3.09 – 2.87 (m, 6H), 2.79 – 2.68 (m, 2H), 1.44 – 1.37 (m, 2H), 1.33 (d, *J* = 2.3 Hz, 4H), 1.15 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5 (t, *J* = 6.7 Hz), 133.6 (d, *J* = 98.8 Hz), 132.4 (d, *J* = 98.5 Hz), 131.8 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 2.5 Hz), 131.0 (d, *J* = 9.4 Hz), 130.7 (d, *J* = 9.4 Hz), 128.7 (d, *J* = 11.7 Hz), 128.4 (d, *J* = 11.8 Hz), 47.5, 45.8, 33.9 (dd, *J* = 70.3, 9.1 Hz), 29.4, 28.2, 27.4, 26.8, 26.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.69.

HRMS (ESI): Calcd for $C_{34}H_{38}NO_3P_2$ $(M+H)^+$: 570.2321; Found: 570.2320.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-1-morpholinopropan-1-one (19)



19

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 44.6 mg, 80% yield.

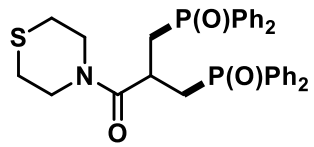
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.66 (m, 8H), 7.53 – 7.38 (m, 12H), 3.75 – 3.65 (m, 1H), 3.40 – 3.31 (m, 2H), 3.23 – 3.15 (m, 2H), 3.12 – 3.04 (m, 2H), 3.03 – 2.95 (m, 2H), 2.94 – 2.84 (m, 2H), 2.73 – 2.61 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5 (t, *J* = 5.0 Hz), 133.5 (d, *J* = 99.3 Hz), 132.0 (d, *J* = 98.5 Hz), 131.9, 130.9 (d, *J* = 9.7 Hz), 130.4 (d, *J* = 9.8 Hz), 128.8 (d, *J* = 12.1 Hz), 128.5 (d, *J* = 12.1 Hz), 66.1, 66.0, 46.3, 41.9, 34.5 (dd, *J* = 69.7, 10.8 Hz), 28.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.43.

HRMS (ESI): Calcd for $C_{32}H_{34}NO_4P_2$ $(M+H)^+$: 558.1958; Found: 558.1953.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-1-thiomorpholinopropan-1-one



20

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 42.6 mg, 74% yield.

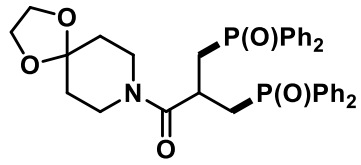
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 8H), 7.52 – 7.40 (m, 12H), 3.72 – 3.62 (m, 1H), 3.36 – 3.29 (m, 2H), 3.30 – 3.22 (m, 2H), 2.86 (dt, *J* = 15.8, 8.1 Hz, 2H), 2.77 – 2.65 (m, 2H), 2.38 (dd, *J* = 6.3, 3.8 Hz, 2H), 2.19 – 2.09 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3 (t, *J* = 5.2 Hz), 133.5 (d, *J* = 99.2 Hz), 132.1 (d, *J* = 98.4 Hz), 131.9, 130.9 (d, *J* = 9.7 Hz), 130.5 (d, *J* = 9.8 Hz), 128.8 (d, *J* = 11.8 Hz), 128.5 (d, *J* = 12.0 Hz), 48.8, 44.5, 34.4 (dd, *J* = 69.8, 10.7 Hz), 28.7, 27.1, 26.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.27.

HRMS (ESI): Calcd for $C_{32}H_{34}NO_3P_2S$ $(M+H)^+$: 574.1729; Found: 574.1728.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-1-(1,4-dioxa-8-azaspiro [4.5] decan-8-yl) propan-1-one (21)



21

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 43.3 mg, 71% yield.

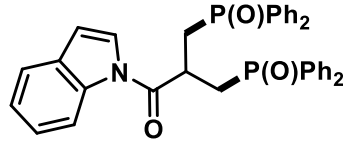
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.65 (m, 8H), 7.51 – 7.38 (m, 12H), 3.88 (s, 4H), 3.70 – 3.58 (m, 1H), 3.22 – 3.15 (m, 2H), 3.10 – 3.01 (m, 2H), 2.80 (dd, *J* = 10.3, 6.6 Hz, 4H), 1.46 – 1.38 (m, 2H), 1.33 – 1.26 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1 (t, *J* = 5.9 Hz), 133.5 (d, *J* = 99.0 Hz), 132.1 (d, *J* = 98.4 Hz), 131.8, 130.9 (d, *J* = 9.5 Hz), 130.6 (d, *J* = 9.4 Hz), 128.7 (d, *J* = 11.7 Hz), 128.5 (d, *J* = 11.9 Hz), 106.8, 64.3, 43.8, 40.0, 34.9, 34.1 (dd, *J* = 70.1, 9.8 Hz), 34.0, 28.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.53.

HRMS (ESI): Calcd for $C_{35}H_{38}NO_5P_2$ $(M+H)^+$: 614.2220; Found: 614.2219.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-1-(1H-indol-1-yl) propan-1-one (22)



22

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 54.1 mg, 92% yield.

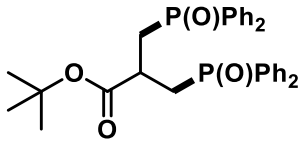
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.77 – 7.72 (m, 4H), 7.59 – 7.54 (m, 4H), 7.53 – 7.49 (m, 2H), 7.48 – 7.42 (m, 5H), 7.36 – 7.31 (m, 2H), 7.27 – 7.24 (m, 4H), 7.21 – 7.16 (m, 2H), 6.74 (s, 1H), 6.38 (d, *J* = 3.7 Hz, 1H), 3.95 – 3.83 (m, 1H), 3.12 – 3.02 (m, 2H), 2.94 – 2.85 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8 (t, *J* = 7.1 Hz), 135.6, 132.7 (d, *J* = 99.6 Hz), 132.1 (d, *J* = 2.1 Hz), 131.8 (d, *J* = 2.6 Hz), 131.5 (d, *J* = 99.4 Hz), 130.8 (d, *J* = 9.9 Hz), 128.8 (d, *J* = 11.9 Hz), 128.5 (d, *J* = 11.9 Hz), 124.8, 124.5, 123.8, 120.4, 117.1, 109.5, 33.5 (dd, *J* = 69.4, 8.3 Hz), 33.1.

^{31}P NMR (243 MHz, $CDCl_3$) δ 29.40.

HRMS (ESI): Calcd for $C_{36}H_{32}NO_3P_2$ $(M+H)^+$: 588.1852; Found: 588.1841.

tert-butyl 3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) propanoate (23)



23

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 39.1 mg, 73% yield.

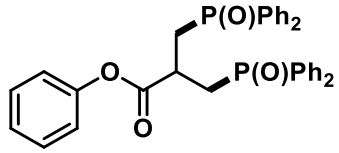
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 8H), 7.50 – 7.45 (m, 4H), 7.44 – 7.36 (m, 8H), 3.00 – 2.87 (m, 3H), 2.74 – 2.65 (m, 2H), 1.42 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4 (t, *J* = 8.8 Hz), 133.1 (d, *J* = 99.2 Hz), 132.5 (d, *J* = 99.6 Hz), 131.7 (d, *J* = 1.7 Hz), 131.7 (d, *J* = 1.6 Hz), 130.9 (d, *J* = 9.6 Hz), 130.8 (d, *J* = 9.9 Hz), 128.6 (d, *J* = 12.0 Hz), 81.6, 35.6, 31.9 (dd, *J* = 70.8, 7.1 Hz), 27.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.54.

HRMS (ESI): Calcd for C32H35O4P2 $(M+H)^+$: 545.2005; Found: 545.2003.

phenyl 3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) propanoate (24)



24

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. White solid; 28.8 mg, 51% yield.

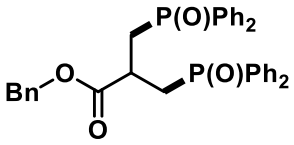
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 – 7.68 (m, 8H), 7.51 – 7.38 (m, 12H), 7.33 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.19 (t, *J* = 8.3 Hz, 3H), 3.27 – 3.17 (m, 1H), 3.17 – 3.09 (m, 2H), 2.94 – 2.84 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.2 (t, *J* = 8.9 Hz), 150.8, 132.7 (d, *J* = 99.6 Hz), 132.1 (d, *J* = 100.0 Hz), 132.0 (d, *J* = 1.9 Hz), 131.9 (d, *J* = 1.8 Hz), 130.9 (d, *J* = 10.6 Hz), 130.8 (d, *J* = 10.2 Hz), 129.3, 128.8 (d, *J* = 11.9 Hz), 128.7 (d, *J* = 11.9 Hz), 125.8, 121.7, 35.0, 32.0 (dd, *J* = 70.3, 7.1 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.55.

HRMS (ESI): Calcd for C34H31O4P2 $(M+H)^+$: 565.1692; Found: 565.1690.

benzyl 3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) propanoate (25)



25

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 42.4 mg, 74% yield.

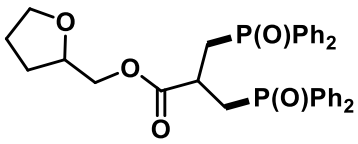
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.60 (m, 8H), 7.50 – 7.44 (m, 4H), 7.43 – 7.35 (m, 8H), 7.35 – 7.27 (m, 5H), 4.98 (s, 2H), 3.14 – 3.06 (m, 1H), 3.05 – 2.94 (m, 2H), 2.82 – 2.71 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.2 (t, *J* = 8.8 Hz), 135.7, 132.8 (d, *J* = 99.8 Hz), 132.3 (d, *J* = 99.5 Hz), 131.9 (d, *J* = 2.0 Hz), 131.8 (d, *J* = 2.6 Hz), 130.9 (d, *J* = 9.7 Hz), 130.8 (d, *J* = 9.9 Hz), 128.7 (d, *J* = 12.0 Hz), 128.7 (d, *J* = 11.9 Hz), 128.4, 128.3, 128.1, 67.1, 34.7, 31.9 (dd, *J* = 70.5, 7.1 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.31.

HRMS (ESI): Calcd for $C_{35}H_{33}O_4P_2$ $(M+H)^+$: 579.1849; Found: 579.1846.

(tetrahydrofuran-2-yl) methyl 3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) propanoate (26)



26

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 47.2 mg, 83% yield.

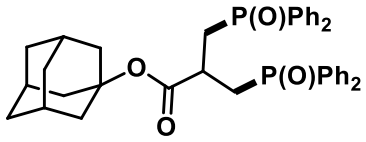
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 – 7.64 (m, 8H), 7.51 – 7.38 (m, 12H), 4.11 – 4.05 (m, 1H), 4.04 (dd, *J* = 11.3, 3.8 Hz, 1H), 3.94 (dd, *J* = 11.3, 6.5 Hz, 1H), 3.81 – 3.72 (m, 2H), 3.10 – 2.98 (m, 3H), 2.82 – 2.72 (m, 2H), 1.98 – 1.91 (m, 1H), 1.86 – 1.79 (m, 2H), 1.65 – 1.58 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.38, 173.32, 173.26, 133.16, 133.12, 132.66, 132.56, 132.50, 132.46, 132.00, 131.90, 131.84, 131.82, 131.80, 131.78, 130.89, 130.82, 130.80, 130.76, 130.73, 128.69, 128.64, 128.61, 76.30, 68.37, 67.36, 34.66, 32.08, 32.04, 31.99, 31.62, 31.57, 31.52, 27.93, 25.70.

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.42, 30.36.

HRMS (ESI): Calcd for $C_{33}H_{35}O_5P_2$ $(M+H)^+$: 573.1954; Found: 573.1954.

adamantan-1-yl 3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) propanoate (27)



27

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 54.0 mg, 87% yield.

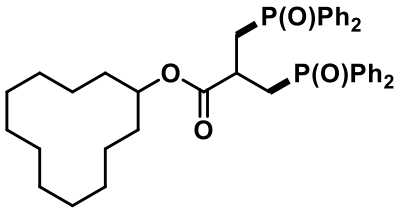
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 8H), 7.48 – 7.36 (m, 12H), 2.99 – 2.85 (m, 3H), 2.75 – 2.66 (m, 2H), 2.15 – 2.07 (m, 9H), 1.67 – 1.59 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.2 (t, *J* = 8.9 Hz), 133.1 (d, *J* = 98.8 Hz), 132.5 (d, *J* = 99.6 Hz), 131.7, 131.7, 130.9 (d, *J* = 10.2 Hz), 130.8 (d, *J* = 10.0 Hz), 128.6 (d, *J* = 11.8 Hz), 128.6 (d, *J* = 11.8 Hz), 81.6, 41.0, 36.2, 35.7, 31.9 (dd, *J* = 70.8, 7.2 Hz), 30.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.62.

HRMS (ESI): Calcd for $C_{38}H_{41}O_4P_2$ $(M+H)^+$: 623.2475; Found: 623.2474.

cyclododecyl 3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) propanoate (28)



28

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Colorless oil; 50.6 mg, 80% yield.

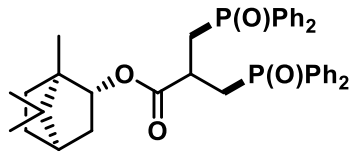
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 8H), 7.49 – 7.38 (m, 12H), 4.97 – 4.89 (m, 1H), 3.06 – 2.92 (m, 3H), 2.81 – 2.68 (m, 2H), 1.68 – 1.59 (m, 2H), 1.53 – 1.45 (m, 2H), 1.39 – 1.27 (m, 18H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0 (t, *J* = 8.7 Hz), 133.0 (d, *J* = 97.9 Hz), 132.4 (d, *J* = 98.4 Hz), 131.8, 131.7, 130.9 (d, *J* = 13.0 Hz), 130.8 (d, *J* = 13.0 Hz), 128.6 (d, *J* = 12.0 Hz), 73.8, 34.9, 31.9 (dd, *J* = 70.7, 7.2 Hz), 28.5, 24.4, 24.2, 23.2, 23.1, 20.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.51.

HRMS (ESI): Calcd for $C_{40}H_{49}O_4P_2$ $(M+H)^+$: 655.3101; Found: 655.3099.

(1R,2R,4R)-1,7,7-trimethylbicyclo [2.2.1] heptan-2-yl 3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) propanoate (29)



29

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. White solid; 48.4 mg, 78% yield.

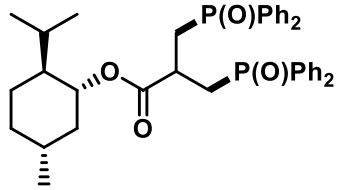
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.60 (m, 8H), 7.49 – 7.44 (m, 4H), 7.43 – 7.36 (m, 8H), 4.52 (dd, *J* = 7.9, 3.4 Hz, 1H), 3.08 – 3.02 (m, 1H), 2.99 – 2.93 (m, 1H), 2.87 (qt, *J* = 13.2, 6.8 Hz, 1H), 2.75 – 2.69 (m, 1H), 2.68 – 2.61 (m, 1H), 1.94 – 1.88 (m, 1H), 1.81 (dd, *J* = 14.0, 7.9 Hz, 1H), 1.72 (t, *J* = 4.2 Hz, 1H), 1.69 – 1.63 (m, 1H), 1.54 – 1.48 (m, 1H), 1.14 – 1.04 (m, 2H), 0.85 (s, 3H), 0.80 (d, *J* = 3.4 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.8, 172.7, 172.7, 133.2, 133.0, 132.7, 132.6, 132.4, 132.4, 132.1, 131.8, 131.8, 131.7, 131.7, 130.9, 130.8, 130.8, 130.7, 128.7, 128.6, 128.6, 128.6, 128.6, 128.5, 82.4, 48.5, 46.9, 45.0, 38.6, 34.9, 33.7, 32.3, 32.2, 32.1, 31.8, 31.7, 31.7, 27.1, 20.1, 20.0, 11.6.

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.52, 30.34.

HRMS (ESI): Calcd for $C38H43O4P2$ $(M+H)^+$: 625.2631; Found: 625.2625.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) propanoate (30)



30

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 48.0 mg, 77% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 – 7.62 (m, 8H), 7.50 – 7.38 (m, 12H), 4.60 (td, *J* = 10.9, 4.3 Hz, 1H), 3.13 – 3.05 (m, 1H), 3.03 – 2.95 (m, 1H), 2.95 – 2.88 (m, 1H), 2.81 – 2.72 (m, 1H), 2.72 – 2.63 (m, 1H), 2.08 – 2.00 (m, 1H), 1.83 – 1.75 (m, 1H), 1.66 – 1.59 (m, 2H), 1.48 – 1.38 (m, 1H), 1.31 – 1.26 (m, 1H), 1.06 – 0.98 (m, 1H), 0.91 – 0.87 (m, 4H), 0.87 – 0.81 (m, 4H), 0.73 (d, *J* = 6.9 Hz, 3H).

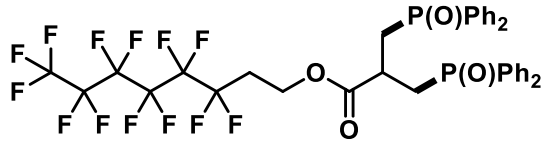
^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0, 173.0, 173.0, 172.9, 133.4, 133.3, 132.9, 132.8, 132.6, 132.4, 132.3, 132.1, 131.8, 131.8, 131.8, 131.7, 131.7, 131.0, 130.9, 130.8, 130.7, 130.6, 128.7, 128.7, 128.6,

128.6, 128.6, 75.5, 46.9, 40.1, 34.9, 34.3, 32.3, 32.2, 32.0, 32.0, 31.8, 31.7, 31.5, 31.5, 31.4, 26.3, 23.4, 22.0, 20.8, 16.4.

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.41, 30.35.

HRMS (ESI): Calcd for C38H45O4P2 $(M+H)^+$: 627.2788; Found: 627.2785.

3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) propanoate (31)



31

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. White solid; 54.1 mg, 65% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.63 (m, 8H), 7.55 – 7.33 (m, 12H), 4.27 (t, *J* = 6.4 Hz, 2H), 3.11 – 2.92 (m, 3H), 2.85 – 2.65 (m, 2H), 2.52 – 2.32 (m, 1H).

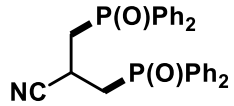
^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0 (t, *J* = 8.6 Hz), 132.7 (d, *J* = 99.8 Hz), 132.1 (d, *J* = 99.8 Hz), 131.9, 130.8 (d, *J* = 9.9 Hz), 130.7 (d, *J* = 9.6 Hz), 128.7 (d, *J* = 11.8 Hz), 128.7 (d, *J* = 11.9 Hz), 57.1, 31.9 (dd, *J* = 70.3, 7.0 Hz), 30.2 (t, *J* = 21.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.27.

^{19}F NMR (565 MHz, $CDCl_3$) δ -80.77 (t, *J* = 11.3 Hz), -113.13 – -113.53 (m), -121.66 – -122.03 (m), -122.40 – -122.91 (m), -123.28 – -123.85 (m), -125.71 – -126.50 (m).

HRMS (ESI): Calcd for C36H30F13O4P2 $(M+H)^+$: 835.1406; Found: 835.1404.

3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) propanenitrile (32)



32

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. White solid; 18.8 mg, 40% yield.

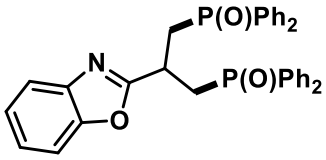
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 4H), 7.72 – 7.64 (m, 4H), 7.56 – 7.43 (m, 12H), 3.35 – 3.15 (m, 3H), 2.78 – 2.65 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 132.4 (d, *J* = 2.2 Hz), 132.3 (d, *J* = 2.4 Hz), 131.8 (d, *J* = 101.3 Hz), 131.2 (d, *J* = 101.4 Hz), 130.8 (d, *J* = 9.9 Hz), 128.9 (d, *J* = 12.1 Hz), 119.8 (t, *J* = 10.0 Hz), 32.6 (dd, *J* = 68.9, 5.7 Hz), 20.5.

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.82.

HRMS (ESI): Calcd for C28H26NO2P2 $(M+H)^+$: 470.1433; Found: 470.1433.

(2-(benzo[d]oxazol-2-yl) propane-1,3-diyl) bis (diphenylphosphine oxide) (33)



33

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. White solid; 23.6 mg, 42% yield.

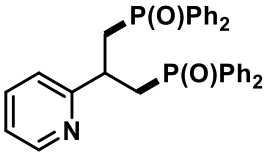
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 4H), 7.67 – 7.58 (m, 4H), 7.48 – 7.27 (m, 13H), 7.23 – 7.14 (m, 3H), 4.06 – 3.93 (m, 1H), 3.43 – 3.30 (m, 2H), 3.08 – 2.96 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4 (t, *J* = 8.1 Hz), 150.0, 140.7, 132.6 (d, *J* = 99.8 Hz), 131.7 (d, *J* = 99.7 Hz), 131.7 (d, *J* = 2.6 Hz), 131.6 (d, *J* = 2.2 Hz), 130.8 (d, *J* = 9.6 Hz), 130.7 (d, *J* = 9.6 Hz), 128.6 (d, *J* = 12.0 Hz), 128.5 (d, *J* = 12.0 Hz), 124.6, 124.0, 119.8, 110.6, 33.8 (dd, *J* = 69.6, 7.0 Hz), 29.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.74.

HRMS (ESI): Calcd for C34H30NO3P2 $(M+H)^+$: 562.1695; Found: 562.1698.

(2-(pyridin-2-yl) propane-1,3-diyl) bis (diphenylphosphine oxide) (34)



34

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. White solid; 17.1 mg, 34% yield.

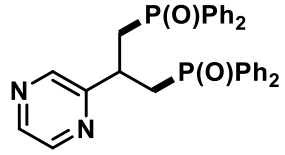
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 3.9 Hz, 1H), 7.74 – 7.68 (m, 4H), 7.56 – 7.51 (m, 4H), 7.46 (td, *J* = 7.4, 1.2 Hz, 2H), 7.43 – 7.39 (m, 4H), 7.36 (td, *J* = 7.5, 1.2 Hz, 2H), 7.31 – 7.27 (m, 4H), 7.26 – 7.25 (m, 1H), 6.91 – 6.82 (m, 2H), 3.81 – 3.72 (m, 1H), 3.20 – 3.10 (m, 2H), 2.93 – 2.83 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.3 (t, *J* = 6.3 Hz), 149.3, 136.2, 133.8 (d, *J* = 98.5 Hz), 132.7 (d, *J* = 98.5 Hz), 131.6 (d, *J* = 2.4 Hz), 131.3 (d, *J* = 2.7 Hz), 130.7 (d, *J* = 9.3 Hz), 130.6 (d, *J* = 9.7 Hz), 128.6 (d, *J* = 11.8 Hz), 128.3 (d, *J* = 11.9 Hz), 123.7, 122.07, 36.2, 35.9 (dd, *J* = 70.3, 9.4 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ 29.78.

HRMS (ESI): Calcd for C32H30NO2P2 $(M+H)^+$: 522.1746; Found: 522.1742.

(2-(pyrazin-2-yl) propane-1,3-diyl) bis (diphenylphosphine oxide) (35)



35

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. White solid; 22.7 mg, 38% yield.

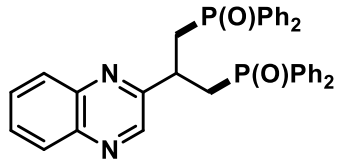
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 – 8.18 (m, 1H), 8.17 (d, *J* = 2.4 Hz, 1H), 8.10 (d, *J* = 1.1 Hz, 1H), 7.74 – 7.69 (m, 4H), 7.55 – 7.51 (m, 4H), 7.50 – 7.48 (m, 2H), 7.45 – 7.42 (m, 4H), 7.39 (dd, *J* = 7.4, 1.1 Hz, 2H), 7.32 (td, *J* = 7.6, 2.8 Hz, 4H), 3.81 – 3.73 (m, 1H), 3.23 – 3.13 (m, 2H), 2.87 – 2.79 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0 (t, *J* = 6.0 Hz), 144.7, 144.0, 143.1, 133.3 (d, *J* = 98.8 Hz), 132.4 (d, *J* = 98.6 Hz), 131.8 (d, *J* = 2.6 Hz), 131.5 (d, *J* = 2.7 Hz), 130.7 (d, *J* = 9.0 Hz), 130.6 (d, *J* = 9.5 Hz), 128.7 (d, *J* = 11.8 Hz), 128.5 (d, *J* = 11.8 Hz), 35.82 (dd, *J* = 70.0, 9.2 Hz), 33.8.

^{31}P NMR (243 MHz, $CDCl_3$) δ 29.31.

HRMS (ESI): Calcd for $C31H29N2O2P2$ $(M+H)^+$: 523.1699; Found: 523.1701.

(2-(quinoxalin-2-yl) propane-1,3-diyl) bis (diphenylphosphine oxide) (36)



36

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. White solid; 16.0 mg, 28% yield.

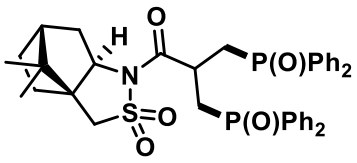
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.93 – 7.86 (m, 1H), 7.77 – 7.68 (m, 5H), 7.65 – 7.60 (m, 2H), 7.49 – 7.38 (m, 10H), 7.21 – 7.07 (m, 6H), 4.14 – 4.01 (m, 1H), 3.31 – 3.16 (m, 2H), 3.10 – 2.95 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 (t, *J* = 5.7 Hz), 145.9, 141.8, 141.5, 133.4 (d, *J* = 99.2 Hz), 132.0 (d, *J* = 98.8 Hz), 131.8 (d, *J* = 2.3 Hz), 131.2 (d, *J* = 2.5 Hz), 130.6 (d, *J* = 9.5 Hz), 130.6 (d, *J* = 9.5 Hz), 129.4, 129.2, 129.1, 128.8, 128.7 (d, *J* = 11.7 Hz), 128.2 (d, *J* = 11.7 Hz), 36.5 (dd, *J* = 69.8, 9.8 Hz), 34.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.29.

HRMS (ESI): Calcd for $C35H31N2O2P2$ $(M+H)^+$: 573.1855; Found: 573.1850.

1-((3aS,6R,7aR)-8,8-dimethyl-2,2-dioxidotetrahydro-3H-3a,6-methanobenzo[c]isothiazol-1(4H)-yl)-3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) propan-1-one (37)



37

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 54.5 mg, 80% yield.

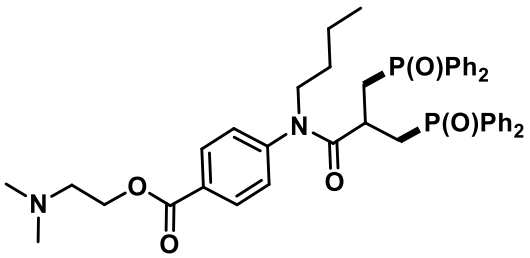
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.61 (m, 8H), 7.51 – 7.28 (m, 12H), 3.85 (dd, *J* = 7.7, 4.7 Hz, 1H), 3.75 – 3.65 (m, 1H), 3.55 – 3.42 (m, 1H), 3.40 – 3.24 (m, 2H), 3.12 – 2.99 (m, 1H), 2.99 – 2.89 (m, 1H), 2.67 – 2.47 (m, 2H), 2.00 – 1.77 (m, 4H), 1.37 – 1.25 (m, 5H), 0.91 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 171.9, 171.8, 171.8, 134.1, 133.8, 133.4, 133.2, 131.9, 131.6, 131.6, 131.6, 131.5, 131.5, 131.4, 131.4, 131.4, 130.8, 130.7, 130.3, 130.3, 128.7, 128.7, 128.5, 128.4, 128.3, 128.3, 65.6, 53.2, 48.6, 47.9, 44.6, 37.5, 34.8, 32.9, 32.8, 32.5, 32.4, 32.4, 32.1, 26.7, 20.9, 20.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ 31.28, 30.23.

HRMS (ESI): Calcd for $C_{38}H_{42}NO_5P_2S$ $(M+H)^+$: 686.2253; Found: 686.2252.

2-(dimethylamino) ethyl 4-(N-butyl-3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)propanamido) benzoate (38)



38

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 40.0 mg, 55% yield.

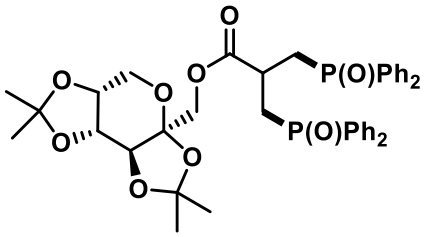
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 10.8, 7.8 Hz, 4H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.47 – 7.34 (m, 10H), 7.26 (td, *J* = 7.7, 2.3 Hz, 4H), 7.18 (d, *J* = 8.3 Hz, 2H), 4.49 (t, *J* = 5.8 Hz, 2H), 3.69 – 3.61 (m, 2H), 3.25 – 3.15 (m, 2H), 3.03 – 2.94 (m, 1H), 2.79 (t, *J* = 5.7 Hz, 2H), 2.72 – 2.62 (m, 2H), 2.41 (s, 6H), 1.46 – 1.39 (m, 2H), 1.27 – 1.23 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.5 (t, *J* = 8.5 Hz), 165.5, 145.6, 133.0 (d, *J* = 98.5 Hz), 132.5 (d, *J* = 99.3 Hz), 131.7, 131.6, 130.8 (d, *J* = 9.2 Hz), 130.7, 130.5 (d, *J* = 9.7 Hz), 128.9, 128.6 (d, *J* = 11.7 Hz), 128.5 (d, *J* = 12.0 Hz), 128.1, 62.9, 57.9, 49.9, 45.8, 32.5 (dd, *J* = 70.5, 7.7 Hz), 31.9, 29.3, 20.0, 13.7.

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.51.

HRMS (ESI): Calcd for C43H49N2O5P2 $(M+H)^+$: 735.3111; Found: 735.3101.

((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)propanoate (39)



39

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 67.1 mg, 91% yield.

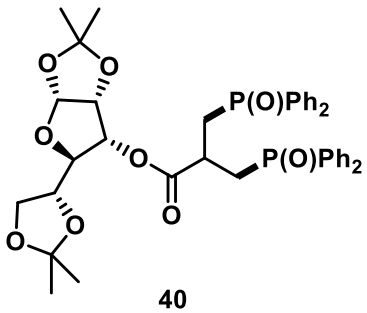
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.66 (m, 8H), 7.50 – 7.38 (m, 12H), 4.55 (dd, *J* = 7.8, 2.6 Hz, 1H), 4.24 (d, *J* = 2.6 Hz, 1H), 4.19 (dd, *J* = 7.9, 1.4 Hz, 1H), 4.16 (d, *J* = 11.6 Hz, 1H), 4.09 (d, *J* = 11.6 Hz, 1H), 3.86 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.70 (d, *J* = 13.0 Hz, 1H), 3.17 – 3.11 (m, 1H), 3.11 – 3.03 (m, 1H), 3.03 – 2.96 (m, 1H), 2.88 – 2.81 (m, 1H), 2.80 – 2.74 (m, 1H), 1.47 (s, 3H), 1.43 (s, 3H), 1.31 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9, 172.8, 172.8, 172.7, 133.3, 133.0, 132.8, 132.6, 132.4, 132.4, 132.2, 131.9, 131.8, 131.8, 131.0, 130.9, 130.9, 130.9, 130.8, 130.7, 130.7, 128.7, 128.7, 128.6, 128.6, 109.1, 108.5, 101.6, 70.7, 70.5, 70.2, 66.2, 61.3, 34.6, 32.1, 32.0, 31.9, 31.8, 31.6, 31.5, 31.4, 31.4, 26.4, 26.0, 25.1, 24.2.

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.20, 30.18.

HRMS (ESI): Calcd for C40H45O9P2 $(M+H)^+$: 731.2534; Found: 731.2533.

(3aR,5R,6R,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)propanoate (40)



40

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 67.6 mg, 93% yield.

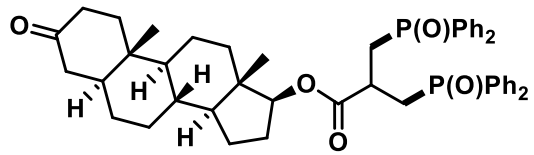
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.58 (m, 8H), 7.51 – 7.37 (m, 12H), 5.91 (d, *J* = 3.6 Hz, 1H), 5.13 (d, *J* = 3.2 Hz, 1H), 4.87 (d, *J* = 3.6 Hz, 1H), 4.20 (dd, *J* = 7.9, 3.2 Hz, 1H), 4.05 – 4.00 (m, 1H), 3.99 – 3.92 (m, 2H), 3.30 – 3.19 (m, 1H), 2.94 – 2.75 (m, 3H), 2.72 – 2.62 (m, 1H), 1.50 (s, 3H), 1.38 (s, 3H), 1.32 (s, 3H), 1.22 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.5, 172.4, 172.4, 172.4, 133.1, 132.9, 132.4, 132.4, 132.2, 132.1, 131.9, 131.9, 131.9, 131.8, 131.8, 131.2, 131.0, 130.9, 130.8, 130.8, 130.7, 130.7, 130.5, 130.4, 128.8, 128.8, 128.7, 128.7, 128.6, 112.2, 109.2, 105.6, 82.6, 79.8, 72.8, 67.5, 34.8, 32.4, 32.3, 32.08, 32.1, 31.9, 31.9, 31.6, 31.6, 26.9, 26.9, 26.5, 25.5.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.89, 30.74.

HRMS (ESI): Calcd for $C_{40}H_{45}O_9P_2$ $(M+H)^+$: 731.2533; Found: 731.2531.

(5S,8R,9S,10S,13S,14S,17S)-10,13-dimethyl-3-oxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl 3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) propanoate (41)



41

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 73.7 mg, 97% yield.

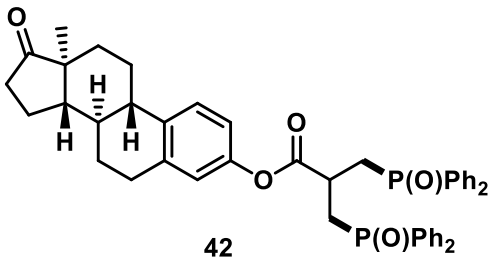
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.63 (m, 8H), 7.49 – 7.37 (m, 12H), 4.51 (t, *J* = 8.3 Hz, 1H), 3.03 – 2.92 (m, 3H), 2.76 – 2.67 (m, 2H), 2.40 – 2.34 (m, 1H), 2.31 – 2.22 (m, 2H), 2.21 – 2.13 (m, 1H), 2.11 – 2.05 (m, 1H), 2.00 (dd, *J* = 13.1, 6.4 Hz, 1H), 1.77 (d, *J* = 12.7 Hz, 1H), 1.73 – 1.67 (m, 1H), 1.63 – 1.50 (m, 4H), 1.44 (qd, *J* = 11.1, 3.2 Hz, 1H), 1.36 – 1.24 (m, 5H), 1.16 (td, *J* = 12.9, 3.6 Hz, 1H), 1.04 – 0.97 (m, 4H), 0.93 – 0.86 (m, 1H), 0.77 – 0.70 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.9, 173.4, 173.3, 173.2, 133.2, 133.2, 132.7, 132.6, 132.6, 132.5, 132.1, 132.0, 131.8, 131.8, 131.7, 131.7, 130.8, 130.8, 130.7, 128.7, 128.6, 128.6, 128.6, 83.9, 53.7, 50.5, 46.6, 44.7, 42.8, 38.5, 38.1, 36.9, 35.7, 35.2, 34.8, 32.4, 32.3, 32.3, 32.2, 31.9, 31.9, 31.8, 31.8, 31.2, 28.8, 27.3, 23.6, 21.0, 12.2, 11.5.

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.35, 30.21.

HRMS (ESI): Calcd for $C_{47}H_{55}O_5P_2$ $(M+H)^+$: 761.3519; Found: 761.3520.

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



42

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 48.0 mg, 65% yield.

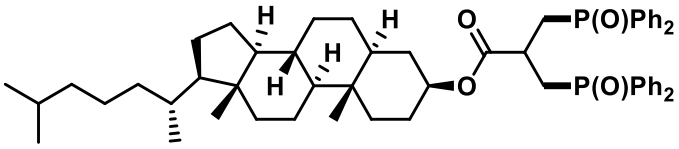
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 8H), 7.52 – 7.38 (m, 12H), 7.24 (d, *J* = 8.5 Hz, 1H), 6.94 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.86 (d, *J* = 2.2 Hz, 1H), 3.26 – 3.18 (m, 1H), 3.17 – 3.04 (m, 2H), 2.97 – 2.79 (m, 4H), 2.50 (dd, *J* = 19.1, 8.6 Hz, 1H), 2.42 – 2.35 (m, 1H), 2.27 (td, *J* = 10.8, 3.8 Hz, 1H), 2.18 – 2.11 (m, 1H), 2.06 – 2.03 (m, 1H), 2.01 – 1.93 (m, 2H), 1.64 – 1.39 (m, 6H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.9, 172.5 (t, *J* = 8.9 Hz), 148.7, 137.8, 137.4, 132.7 (d, *J* = 99.6 Hz), 132.1 (d, *J* = 99.2 Hz), 132.0 (d, *J* = 2.7 Hz), 131.9 (d, *J* = 2.4 Hz), 130.9 (d, *J* = 8.9 Hz), 130.8 (d, *J* = 8.9 Hz), 128.8 (d, *J* = 11.9 Hz), 128.7 (d, *J* = 11.9 Hz), 126.3, 121.5, 118.8, 50.5, 48.0, 44.2, 38.1, 35.9, 34.9, 32.0 (dd, *J* = 70.5, 6.9 Hz), 31.6, 29.4, 26.4, 25.8, 21.6, 13.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.54.

HRMS (ESI): Calcd for $C_{46}H_{47}O_5P_2$ $(M+H)^+$: 741.2893; Found: 741.2889.

(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl) hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) propanoate (43)



43

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 71.6 mg, 84% yield.

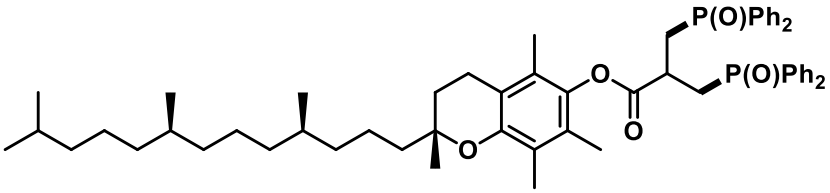
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 8H), 7.47 (t, *J* = 7.4 Hz, 4H), 7.43 – 7.37 (m, 8H), 4.60 – 4.52 (m, 1H), 3.05 – 2.93 (m, 3H), 2.78 – 2.70 (m, 2H), 1.98 – 1.91 (m, 1H), 1.84 – 1.76 (m, 2H), 1.70 – 1.61 (m, 2H), 1.58 – 1.49 (m, 3H), 1.48 – 0.93 (m, 22H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 2.7 Hz, 6H), 0.77 (s, 3H), 0.64 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9, 172.9, 172.8, 133.3, 133.3, 132.7, 132.6, 132.6, 132.0, 132.0, 131.8, 131.8, 130.9, 130.9, 130.8, 130.8, 128.7, 128.7, 128.6, 128.6, 75.1, 56.4, 56.3, 54.2, 44.7, 42.6, 40.0, 39.5, 36.7, 36.2, 35.8, 35.5, 35.5, 34.9, 33.6, 32.1, 32.0, 31.7, 28.6, 28.3, 28.0, 27.2, 24.2, 23.9, 22.8, 22.6, 21.2, 18.7, 12.3, 12.1.

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.58, 30.54.

HRMS (ESI): Calcd for $C_{55}H_{73}O_4P_2$ $(M+H)^+$: 859.4979; Found: 859.4974.

(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)propanoate (44)



44

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. White solid; 67.1 mg, 74% yield.

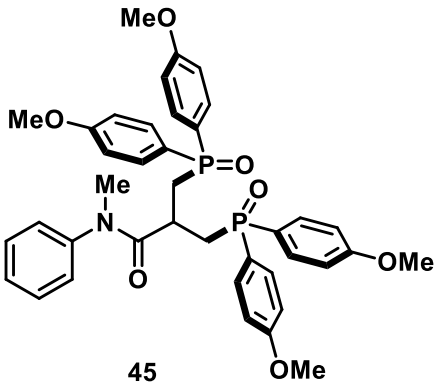
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.68 (m, 8H), 7.50 – 7.38 (m, 12H), 3.39 – 3.31 (m, 1H), 3.26 – 3.09 (m, 2H), 3.06 – 2.98 (m, 2H), 2.57 (t, *J* = 6.7 Hz, 2H), 2.07 (s, 3H), 2.05 (s, 6H), 1.80 (dt, *J* = 13.8, 7.1 Hz, 1H), 1.73 (dt, *J* = 13.2, 6.5 Hz, 1H), 1.57 – 1.49 (m, 3H), 1.42 – 1.06 (m, 21H), 0.88 – 0.84 (m, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0 (t, *J* = 9.1 Hz), 149.5, 140.6, 133.1 (d, *J* = 99.9 Hz), 131.8, 131.8, 130.9 (d, *J* = 9.1 Hz), 130.9 (d, *J* = 10.3 Hz), 128.7 (d, *J* = 11.8 Hz), 128.7 (d, *J* = 11.6 Hz), 126.9, 125.6, 122.9, 117.4, 75.0, 39.4, 37.5, 37.3, 34.8, 32.8, 32.7, 31.7 (d, *J* = 69.7 Hz), 28.0, 24.8, 24.5, 22.8, 22.7, 21.1, 20.6, 19.8, 19.7, 13.2, 12.4, 11.8.

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.44.

HRMS (ESI): Calcd for $C_{57}H_{75}O_5P_2$ $(M+H)^+$: 901.5084; Found: 901.5081.

3-(bis(4-methoxyphenyl)phosphoryl)-2-((bis(4-methoxyphenyl)phosphoryl)methyl)-N-methyl-N-phenylpropanamide (45)



45

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 55.8 mg, 80% yield.

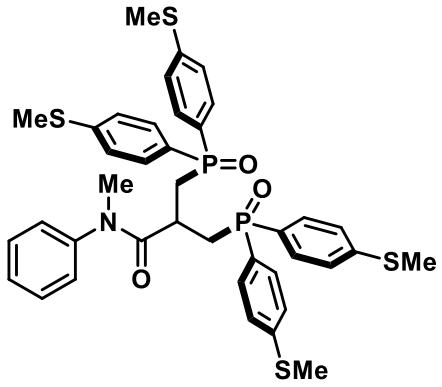
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 10.9, 8.7 Hz, 4H), 7.31 (dd, *J* = 11.1, 8.7 Hz, 4H), 7.18 (d, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.87 (dd, *J* = 8.8, 2.1 Hz, 4H), 6.75 (dd, *J* = 8.8, 2.1 Hz, 4H), 3.81 (d, *J* = 2.9 Hz, 12H), 3.22 (s, 3H), 3.13 – 3.00 (m, 3H), 2.69 – 2.54 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.4 (t, *J* = 8.3 Hz), 162.1 (d, *J* = 1.5 Hz), 162.0 (d, *J* = 1.7 Hz), 143.1, 132.5 (d, *J* = 10.7 Hz), 132.4 (d, *J* = 11.0 Hz), 129.3, 127.5, 127.1, 124.8 (d, *J* = 105.1 Hz), 124.2 (d, *J* = 105.7 Hz), 114.0 (d, *J* = 12.9 Hz), 114.0 (d, *J* = 13.1 Hz), 55.3, 55.2, 38.1, 32.8 (dd, *J* = 71.5, 7.9 Hz), 31.5.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.62.

HRMS (ESI): Calcd for $C_{39}H_{42}NO_7P_2$ $(M+H)^+$: 698.2431; Found: 698.2429.

3-(bis(4-(methylthio)phenyl) phosphoryl)-2-((bis(4-(methylthio)phenyl)phosphoryl)methyl)-N-methyl-N-phenylpropanamide (46)



46

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 37.6 mg, 49% yield.

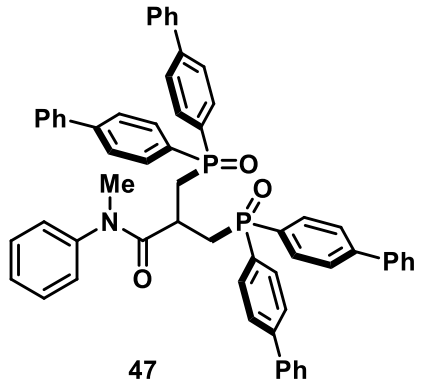
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 11.0, 8.4 Hz, 4H), 7.27 – 7.17 (m, 8H), 7.17 – 7.11 (m, 3H), 7.07 (dd, *J* = 8.4, 2.1 Hz, 4H), 7.01 (t, *J* = 7.7 Hz, 2H), 3.23 (s, 3H), 3.14 – 3.03 (m, 3H), 2.69 – 2.59 (m, 2H), 2.49 (d, *J* = 2.1 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1 (t, *J* = 8.6 Hz), 144.0, 143.9, 142.9, 131.0 (d, *J* = 10.1 Hz), 130.8 (d, *J* = 10.3 Hz), 129.4, 128.7 (d, *J* = 102.3 Hz), 128.0 (d, *J* = 103.0 Hz), 127.4, 127.2, 125.3 (d, *J* = 12.2 Hz), 125.3 (d, *J* = 12.4 Hz), 38.2, 32.4 (dd, *J* = 71.1, 8.0 Hz), 31.3, 14.8 (d, *J* = 4.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.46.

HRMS (ESI): Calcd for $C_{39}H_{42}NO_3P_2S_4$ $(M+H)^+$: 762.1517; Found: 762.1509.

3-(di([1,1'-biphenyl]-4-yl)phosphoryl)-2-((di([1,1'-biphenyl]-4-yl)phosphoryl)methyl)-N-methyl-N-phenylpropanamide (47)



47

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 60.7 mg, 70% yield.

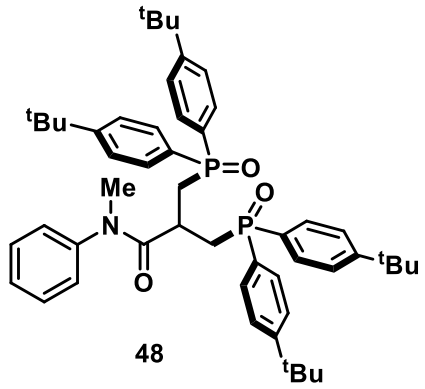
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 10.9, 8.3 Hz, 4H), 7.54 – 7.39 (m, 20H), 7.36 – 7.27 (m, 12H), 7.16 – 7.13 (m, 2H), 6.91 – 6.83 (m, 3H), 3.28 – 3.10 (m, 6H), 2.80 – 2.65 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1 (t, *J* = 8.6 Hz), 144.5, 144.3, 143.1, 139.8, 131.8 (d, *J* = 98.9 Hz), 131.3 (d, *J* = 9.7 Hz), 131.2 (d, *J* = 100.4 Hz), 131.1 (d, *J* = 10.0 Hz), 129.4, 129.0, 128.2, 128.1, 127.5, 127.3 (d, *J* = 12.1 Hz), 127.2 (d, *J* = 12.6 Hz), 127.2, 127.2, 38.2, 32.6 (dd, *J* = 70.9, 8.0 Hz), 31.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.49.

HRMS (ESI): Calcd for $C_{59}H_{50}NO_3P_2$ $(M+H)^+$: 882.3260; Found: 882.3249.

3-(bis(4-(tert-butyl)phenyl)phosphoryl)-2-((bis(4-(tert-butyl)phenyl)phosphoryl)methyl)-N-methyl-N-phenylpropanamide (48)



48

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. White solid; 50.7 mg, 63% yield.

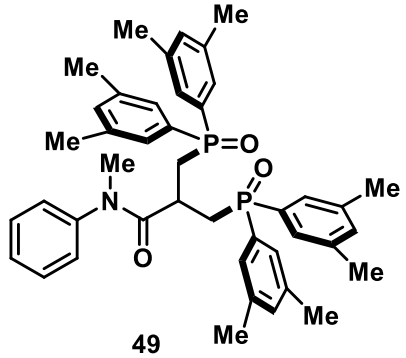
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 10.9, 8.4 Hz, 4H), 7.49 – 7.39 (m, 8H), 7.31 (dd, *J* = 8.3, 2.3 Hz, 4H), 7.06 (d, *J* = 7.4 Hz, 2H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 2H), 3.20 (s, 3H), 3.18 – 3.08 (m, 3H), 2.69 – 2.57 (m, 2H), 1.31 (d, *J* = 7.8 Hz, 36H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3 (t, *J* = 8.4 Hz), 154.8, 154.5, 142.8, 130.6 (d, *J* = 6.9 Hz), 130.5 (d, *J* = 7.3 Hz), 130.2 (d, *J* = 100.8 Hz), 129.9 (d, *J* = 101.5 Hz), 129.0, 127.2, 126.9, 125.5 (d, *J* = 11.3 Hz), 125.4 (d, *J* = 11.7 Hz), 37.9, 34.9 (d, *J* = 5.2 Hz), 33.0 (dd, *J* = 70.6, 8.0 Hz), 31.5, 31.2 (d, *J* = 2.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.07.

HRMS (ESI): Calcd for $C_{51}H_{65}NO_3P_2$ $(M+H)^+$: 802.4512; Found: 802.4501.

3-(bis(3,5-dimethylphenyl)phosphoryl)-2-((bis(3,5-dimethylphenyl)phosphoryl)methyl)-N-methyl-N-phenylpropanamide (49)



49

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 48.1 mg, 70% yield.

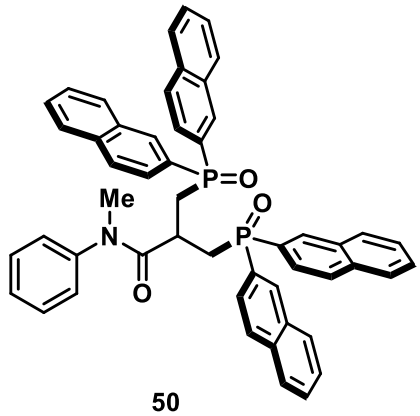
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 11.6 Hz, 4H), 7.09 (d, *J* = 11.0 Hz, 6H), 7.04 – 6.95 (m, 4H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.74 (t, *J* = 7.7 Hz, 2H), 3.24 (d, *J* = 16.2 Hz, 3H), 3.18 – 3.03 (m, 3H), 2.64 – 2.53 (m, 2H), 2.34 (s, 12H), 2.22 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.7 (t, *J* = 8.1 Hz), 142.8, 138.1 (d, *J* = 12.7 Hz), 137.9 (d, *J* = 12.8 Hz), 133.4 (d, *J* = 98.3 Hz), 133.3, 133.2, 133.1 (d, *J* = 97.4 Hz), 128.5, 128.4 (d, *J* = 9.2 Hz), 128.0 (d, *J* = 9.7 Hz), 127.2, 126.8, 38.0, 33.3 (dd, *J* = 70.2, 7.9 Hz), 31.0, 21.3, 21.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.11.

HRMS (ESI): Calcd for $C_{43}H_{50}NO_3P_2$ $(M+H)^+$: 690.3260; Found: 690.3258.

3-(di(naphthalen-2-yl)phosphoryl)-2-((di(naphthalen-2-yl)phosphoryl)methyl)-N-methyl-N-phenylpropanamide (50)



50

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. White solid; 32.7 mg, 42% yield.

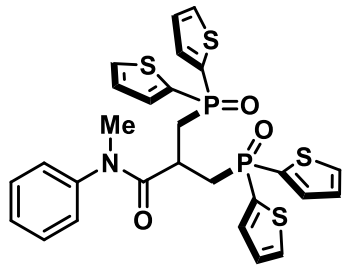
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 13.1 Hz, 2H), 8.09 (d, *J* = 13.4 Hz, 2H), 7.98 (d, *J* = 7.7 Hz, 2H), 7.91 – 7.85 (m, 4H), 7.82 – 7.73 (m, 4H), 7.65 – 7.52 (m, 8H), 7.41 (d, *J* = 3.7 Hz, 4H), 7.36 – 7.28 (m, 2H), 6.97 (d, 2H), 6.23 (t, *J* = 7.6 Hz, 2H), 6.13 (t, *J* = 7.4 Hz, 1H), 3.54 – 3.42 (m, 2H), 3.29 – 3.16 (m, 4H), 2.95 – 2.84 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.4 (t, *J* = 8.4 Hz), 142.5, 134.7, 134.6, 132.8 (d, *J* = 8.7 Hz), 132.7 (d, *J* = 8.7 Hz), 132.6 (d, *J* = 13.0 Hz), 132.4 (d, *J* = 12.9 Hz), 130.1 (d, *J* = 98.5 Hz), 130.0 (d, *J* = 99.6 Hz), 129.0, 128.8, 128.6 (d, *J* = 11.2 Hz), 128.6, 128.3 (d, *J* = 11.9 Hz), 128.2, 128.0, 127.9, 127.6, 126.9 (d, *J* = 15.4 Hz), 126.7, 126.0 (d, *J* = 10.2 Hz), 125.3 (d, *J* = 11.3 Hz), 38.1, 32.8 (dd, *J* = 70.8, 7.9 Hz), 31.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.77.

HRMS (ESI): Calcd for $C_{51}H_{42}NO_3P_2$ $(M+H)^+$: 778.2634; Found: 778.2629.

3-(di(thiophen-2-yl)phosphoryl)-2-((di(thiophen-2-yl)phosphoryl)methyl)-N-methyl-N-phenylpropanamide (51)



51

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 24.0 mg, 40% yield.

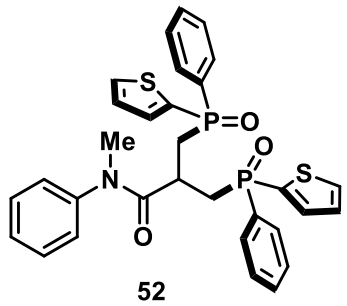
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 2H), 7.61 – 7.55 (m, 4H), 7.27 – 7.24 (m, 2H), 7.21 – 7.17 (m, 2H), 7.15 – 7.07 (m, 5H), 7.04 – 7.00 (m, 2H), 3.41 – 3.31 (m, 1H), 3.24 (s, 3H), 3.18 – 3.09 (m, 2H), 2.84 – 2.72 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5 (t, *J* = 8.8 Hz), 142.9, 135.2 (d, *J* = 6.6 Hz), 135.1 (d, *J* = 6.5 Hz), 134.6 (d, *J* = 57.8 Hz), 133.5 (d, *J* = 59.3 Hz), 133.4, 133.3, 128.4 (d, *J* = 10.0 Hz), 128.2 (d, *J* = 10.2 Hz), 127.5, 127.5, 38.2, 36.3 (dd, *J* = 78.8, 8.7 Hz), 31.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 20.39.

HRMS (ESI): Calcd for $C_{27}H_{26}NO_3P_2S_4$ $(M+H)^+$: 602.0266; Found: 602.0259.

N-methyl-N-phenyl-3-(phenyl(thiophen-2-yl)phosphoryl)-2-((phenyl(thiophen-2-yl)phosphoryl)methyl)propenamide (52)



52

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 57.1 mg, 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 2H), 7.66 – 7.61 (m, 1H), 7.59 – 7.39 (m, 8H), 7.35 – 7.28 (m, 2H), 7.27 – 7.15 (m, 3H), 7.10 – 6.95 (m, 5H), 3.32 – 3.20 (m, 4H), 3.19 – 3.03 (m, 2H), 2.86 – 2.61 (m, 2H).

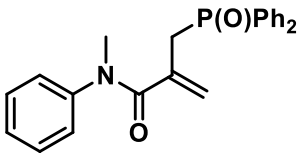
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 172.8, 172.7, 172.7, 143.0, 142.9, 135.1, 135.0, 134.9, 134.7, 134.3, 134.2, 133.2, 133.7, 133.5, 133.1, 133.0, 132.5, 131.9, 131.8, 131.8, 131.7, 130.6, 130.5, 130.5,

130.4, 130.4, 129.5, 129.4, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 127.5, 127.4, 77.4, 77.3, 77.1, 76.8, 38.1, 38.1, 35.5, 34.8, 34.8, 34.7, 34.6, 34.1, 34.0, 33.9, 33.9, 31.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.73 (d, *J* = 50.5 Hz), 25.68 (d, *J* = 36.8 Hz).

HRMS (ESI): Calcd for C31H30NO3P2S2 $(M+H)^+$: 590.1137; Found:590.1134.

2-((diphenylphosphoryl)methyl)-N-methyl-N-phenylacrylamide



3a

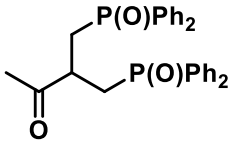
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 4H), 7.54 – 7.50 (m, 2H), 7.49 – 7.44 (m, 4H), 7.27 – 7.23 (m, 2H), 7.21 – 7.15 (m, 1H), 7.06 – 7.00 (m, 2H), 5.44 (d, *J* = 3.8 Hz, 1H), 5.07 (d, *J* = 2.4 Hz, 1H), 3.43 (d, *J* = 13.6 Hz, 2H), 3.24 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 144.5, 133.9 (d, *J* = 7.6 Hz), 132.8 (d, *J* = 99.2 Hz), 131.9 (d, *J* = 2.9 Hz), 131.0 (d, *J* = 9.5 Hz), 129.3, 128.6 (d, *J* = 11.6 Hz), 126.8, 126.6, 38.9, 34.7 (d, *J* = 68.8 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ 28.78.

HRMS (ESI): Calcd for C31H30NO3P2S2 $(M+H)^+$: 376.1461; Found:376.1454.

4-(diphenylphosphoryl)-3-((diphenylphosphoryl)methyl)butan-2-one (15a)



15a

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 36.2 mg, 75% yield.

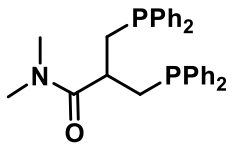
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 4H), 7.67 – 7.59 (m, 4H), 7.55 – 7.38 (m, 12H), 3.15 – 3.03 (m, 1H), 2.92 – 2.84 (m, 2H), 2.69 – 2.57 (m, 2H), 2.15 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.4 (t, *J* = 7.2 Hz), 132.7 (d, *J* = 99.1 Hz), 132.3 (d, *J* = 99.6 Hz), 131.9, 130.8 (d, *J* = 9.4 Hz), 130.7 (d, *J* = 9.3 Hz), 128.8 (d, *J* = 11.7 Hz), 128.7 (d, *J* = 11.8 Hz), 40.1, 31.8 (dd, *J* = 70.3, 7.8 Hz), 29.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.61.

HRMS (ESI): Calcd for C29H29O3P2 $(M+H)^+$: 487.1586; Found:487.1577.

3-(diphenylphosphaneyl)-2-((diphenylphosphaneyl)methyl)-N,N-dimethylpropanamide (15b)



15b

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate =1:1. Pale yellow oil; 19.6 mg, 82% yield.

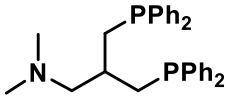
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 4H), 7.35 – 7.31 (m, 6H), 7.29 – 7.24 (m, 10H), 2.78 (s, 3H), 2.57 – 2.46 (m, 5H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.5 (t, *J* = 4.5 Hz), 138.5 (d, *J* = 13.2 Hz), 138.1 (d, *J* = 12.6 Hz), 133.0 (d, *J* = 20.1 Hz), 132.8 (d, *J* = 19.2 Hz), 128.8, 128.6, 128.5 (d, *J* = 6.6 Hz), 128.3 (d, *J* = 6.7 Hz), 36.6, 35.8, 35.0 (t, *J* = 16.9 Hz), 33.6 (dd, *J* = 13.2, 9.9 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ -20.12.

HRMS (ESI): Calcd for C30H32NOP2 $(M+H)^+$: 484.1954; Found:484.1949.

3-(diphenylphosphaneyl)-2-((diphenylphosphaneyl)methyl)-N,N-dimethylpropan-1-amine



15c

According to the general procedure, the product was purified by chromatography on petroleum ether/ethyl acetate/methanol=10:10:1. Pale yellow oil; 10.3 mg, 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 4H), 7.34 – 7.25 (m, 16H), 2.61 (d, *J* = 7.0 Hz, 2H), 2.39 – 2.25 (m, 4H), 2.02 (s, 6H), 1.64 – 1.54 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7 (d, *J* = 12.8 Hz), 138.5 (d, *J* = 12.4 Hz), 133.1 (d, *J* = 3.5 Hz), 132.9 (d, *J* = 3.2 Hz), 128.6, 128.4 (d, *J* = 3.4 Hz), 128.4 (d, *J* = 3.5 Hz), 64.9, 44.8, 33.2, 30.8, 22.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ -20.21.

HRMS (ESI): Calcd for C30H34NP2 $(M+H)^+$: 470.2161; Found:470.2156.

8. References

(1) Yang, H.; Wang, E.; Yang, P.; Lv, H.; Zhang, X. Pyridine-Directed Asymmetric Hydrogenation of 1,1-Diarylalkenes. *Org. Lett.* **2017**, *19* (19), 5062-5065.

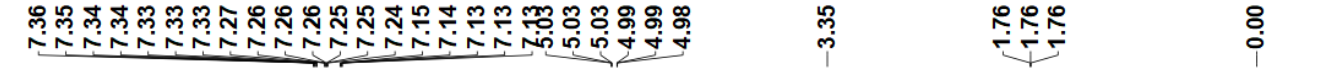
(2) Miller, L. P.; Vogel, J. A.; Harel, S.; Krussman, J. M.; Melvin, P. R. Rapid Generation of P(V)–F Bonds Through the Use of Sulfone Iminium Fluoride Reagents. *Org. Lett.* **2023**, *25* (11), 1834-1838.

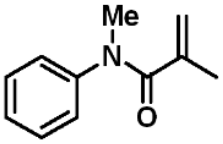
(3) Bergbreiter, D. E.; Yang, Y. C.; Hobbs, C. E. Polyisobutylene-supported phosphines as recyclable and regenerable catalysts and reagents. *J. Org. Chem.* **2011**, *76* (16), 6912-6917.

(4) Rodrigalvarez, J.; Nappi, M.; Azuma, H.; Floden, N. J.; Burns, M. E.; Gaunt, M. J. Catalytic C(sp(3))-H bond activation in tertiary alkylamines. *Nat. Chem.* **2020**, *12* (1), 76-81.

(5) Wang, Z.; Yan, C. X.; Liu, R.; Li, X.; Dai, J.; Li, X.; Shi, D. Photo-induced versatile aliphatic C-H functionalization via electron donor-acceptor complex. *Sci Bull (Beijing)* **2024**, *69* (3), 345-353.

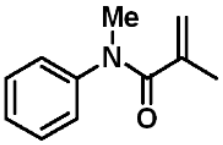
9. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of compounds





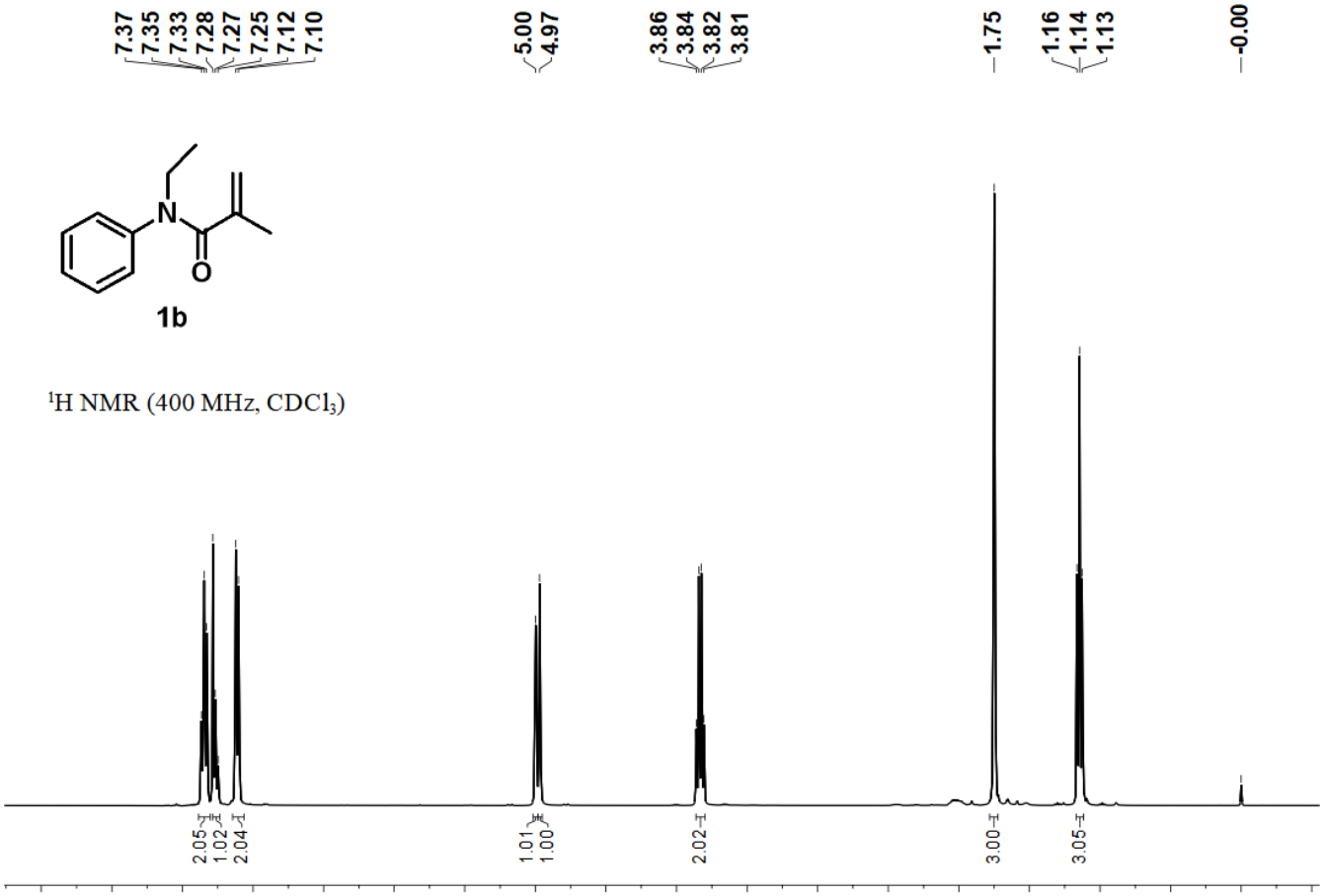
1a

^{1}H NMR (600 MHz, $CDCl_3$)

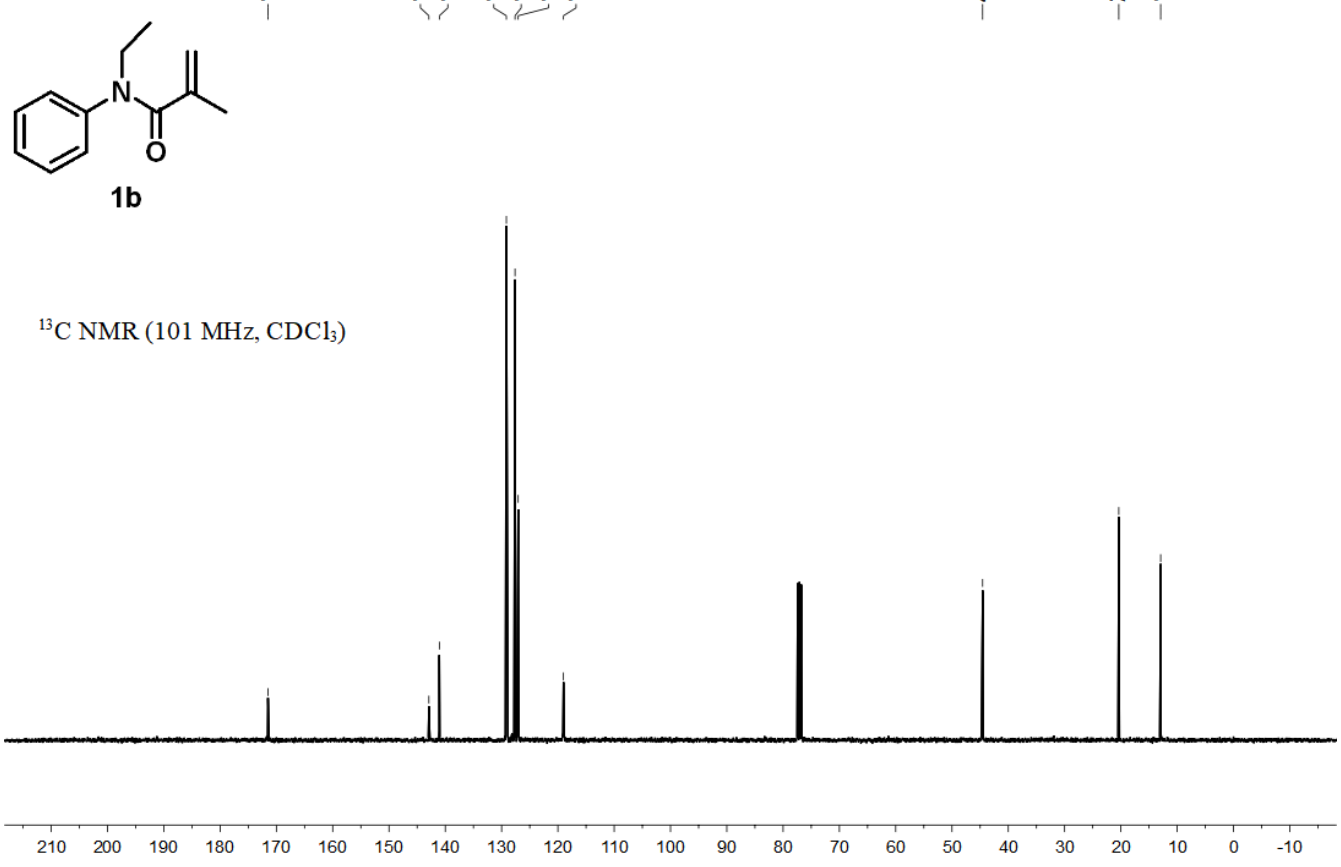


1a

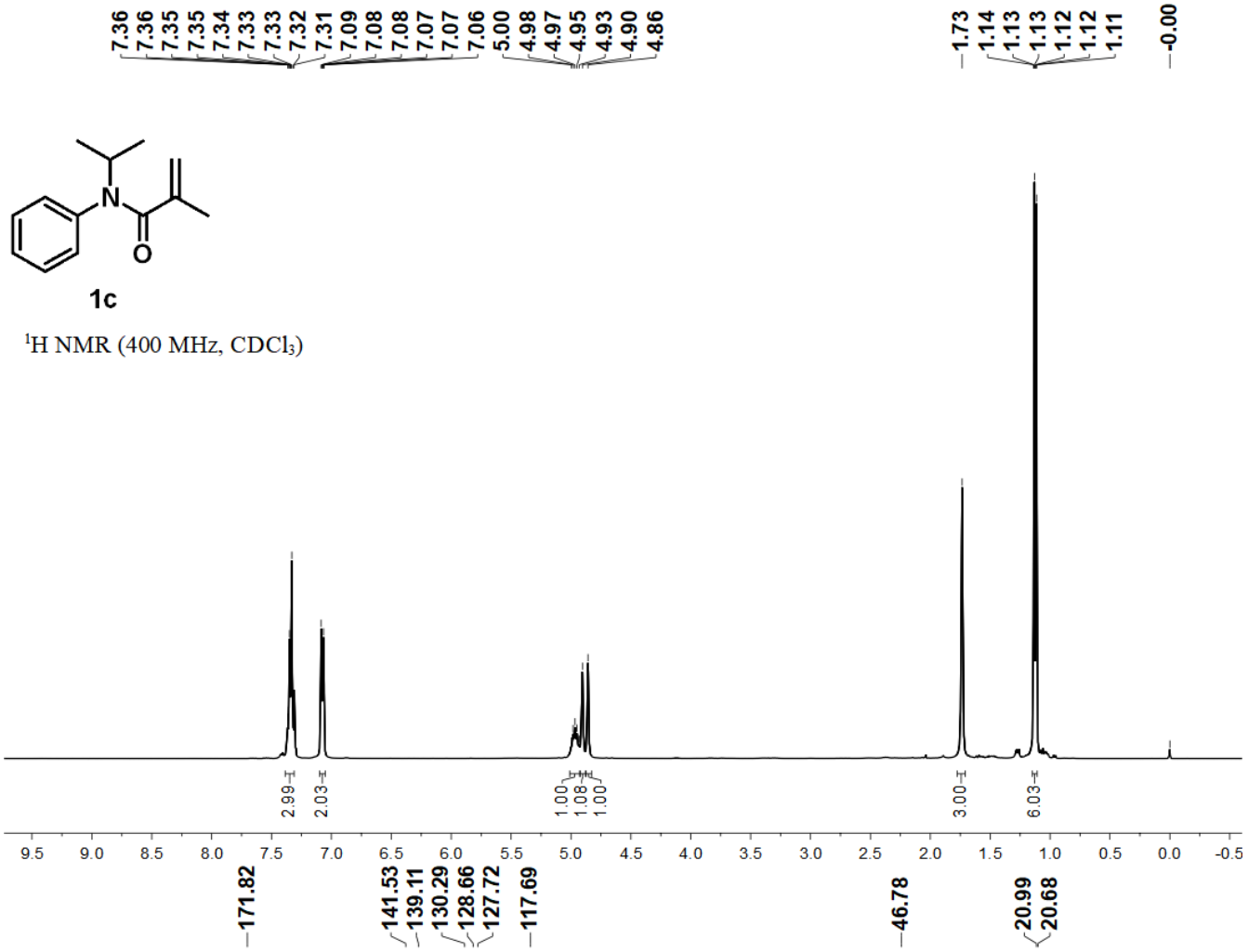
^{13}C NMR (151 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

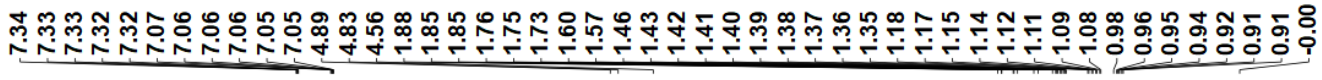


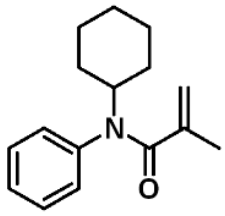
1c

^{1}H NMR (400 MHz, $CDCl_3$)

1c

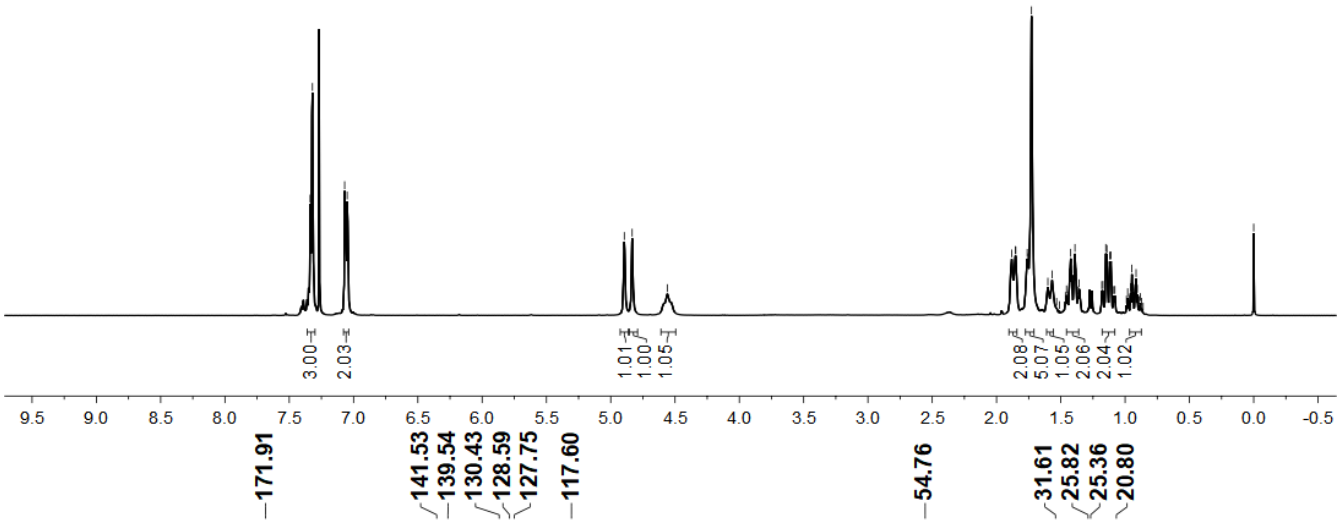
^{13}C NMR (101 MHz, $CDCl_3$)

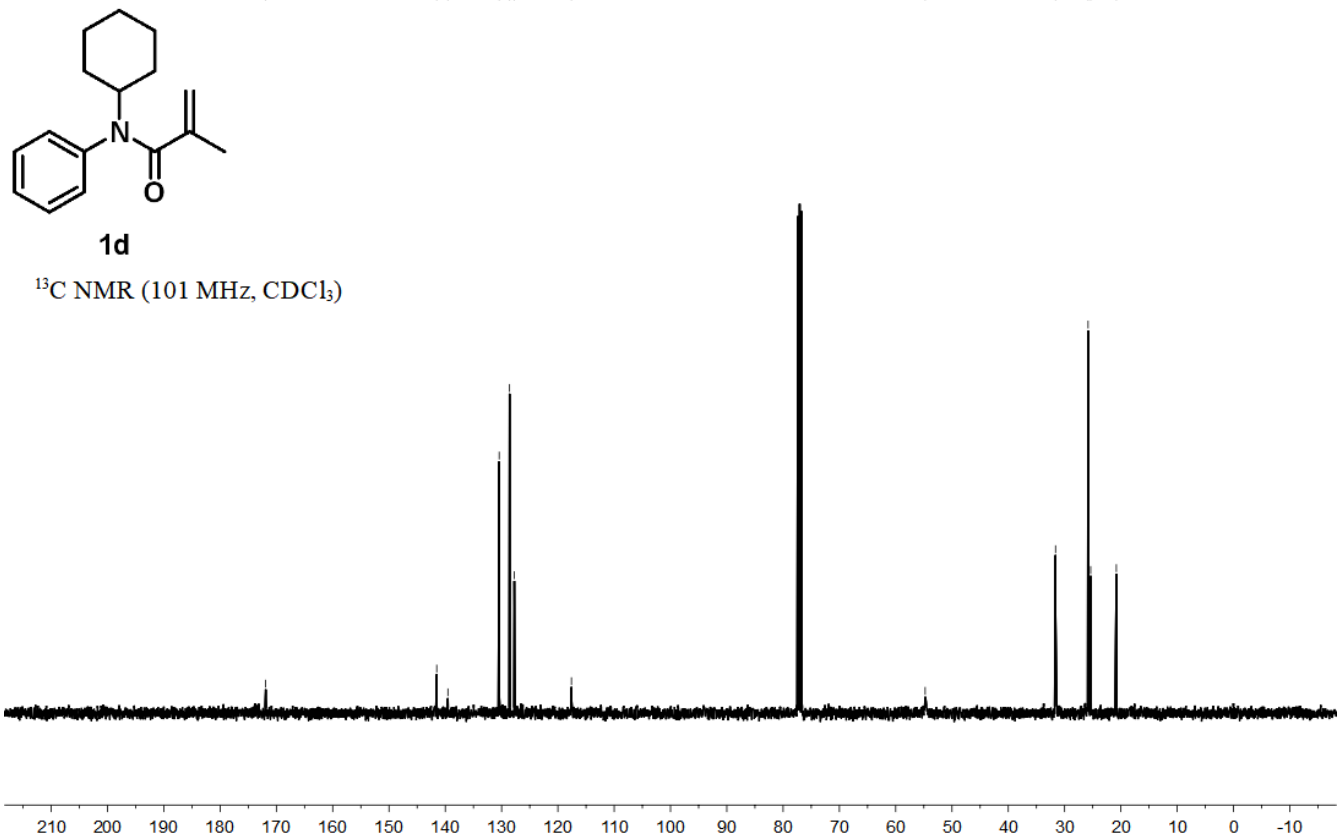




1d

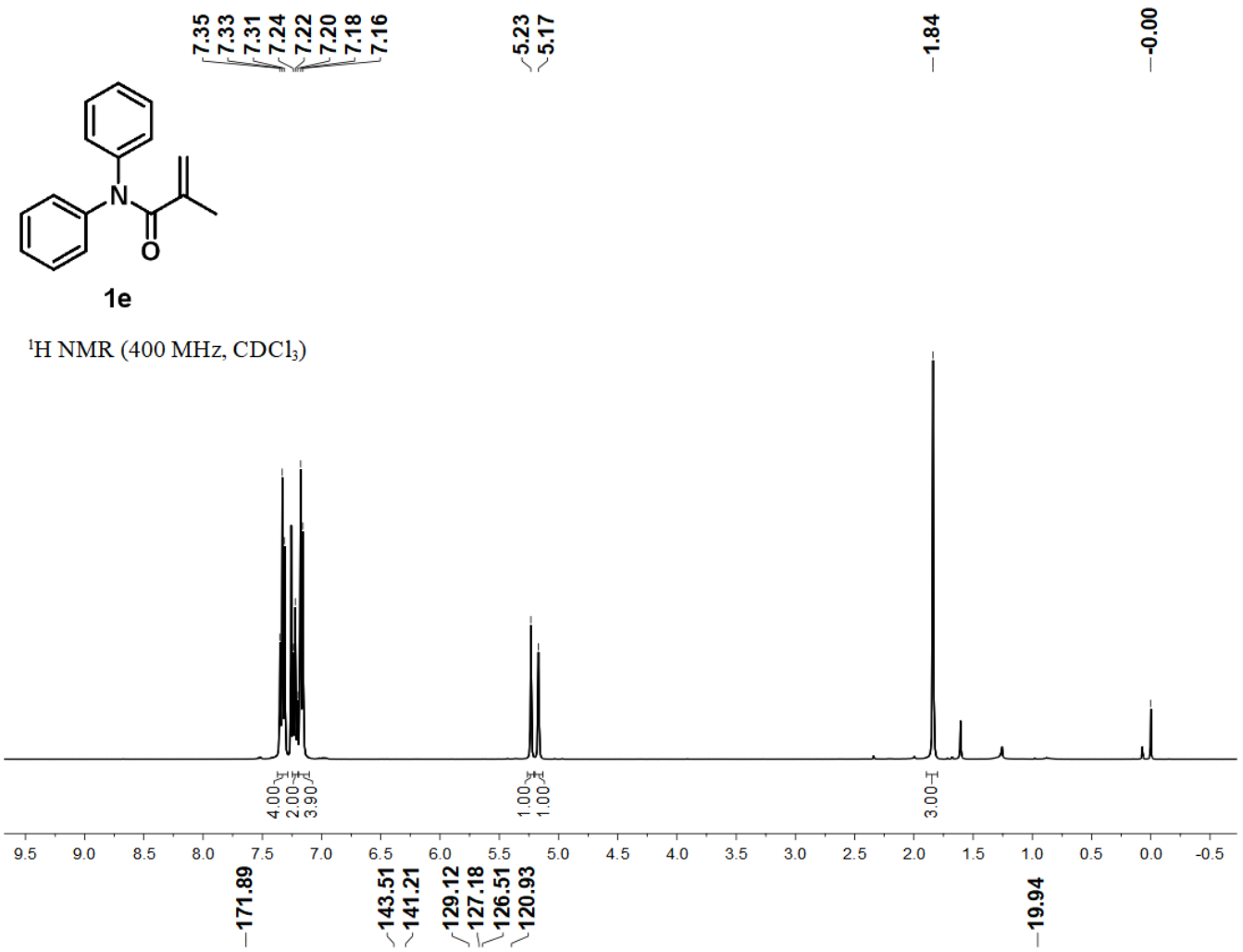
^{1}H NMR (400 MHz, $CDCl_3$)





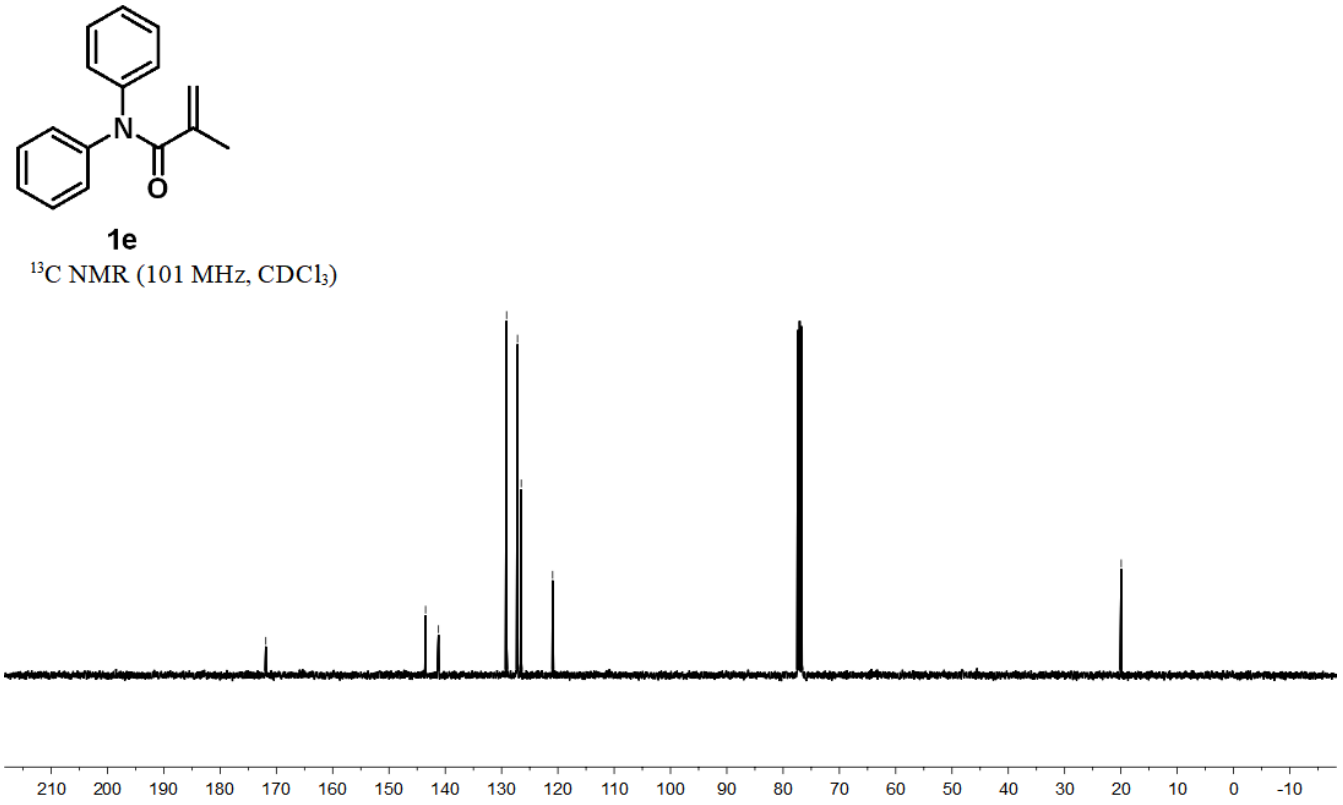
1d

^{13}C NMR (101 MHz, $CDCl_3$)



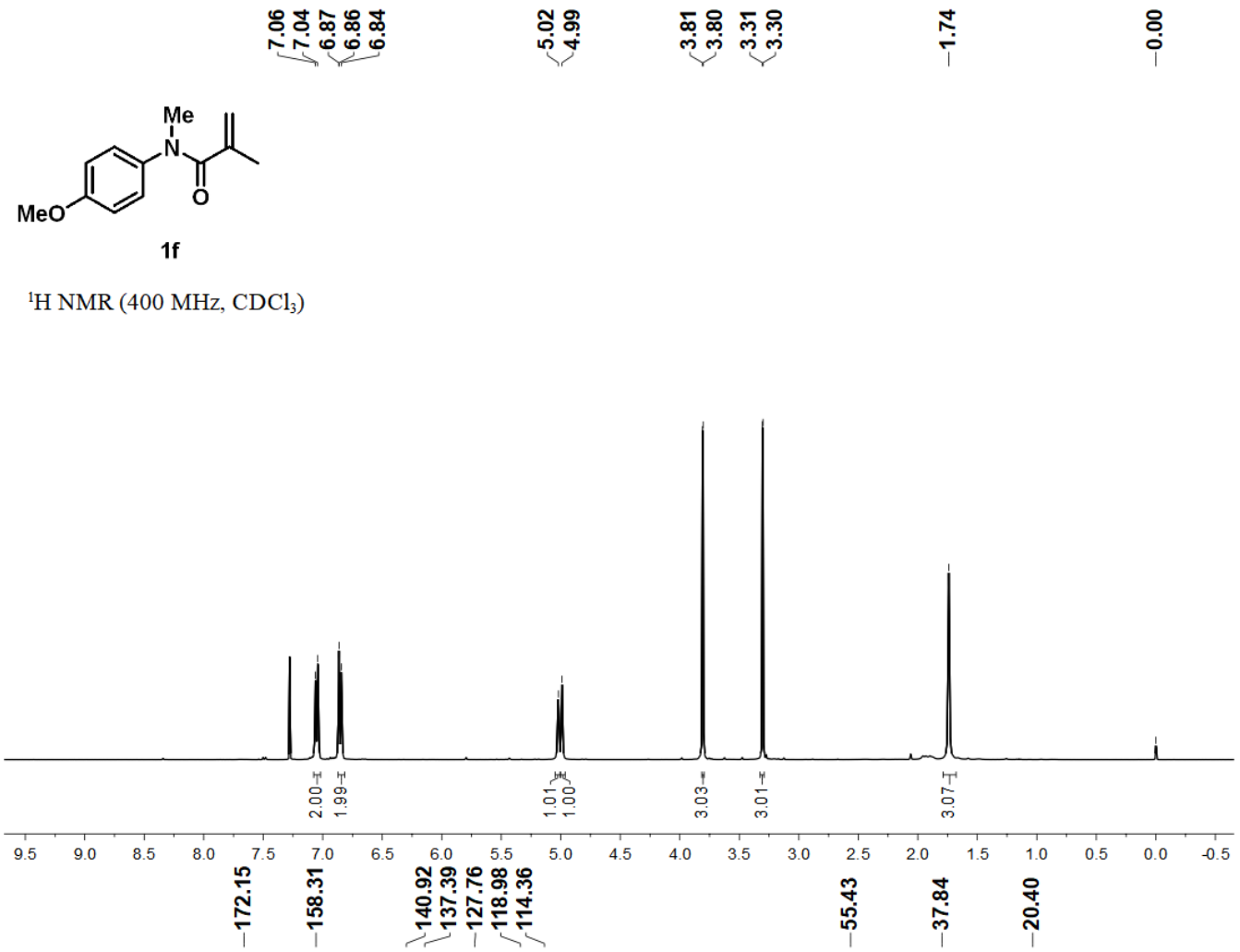
1e

^{1}H NMR (400 MHz, $CDCl_3$)



1e

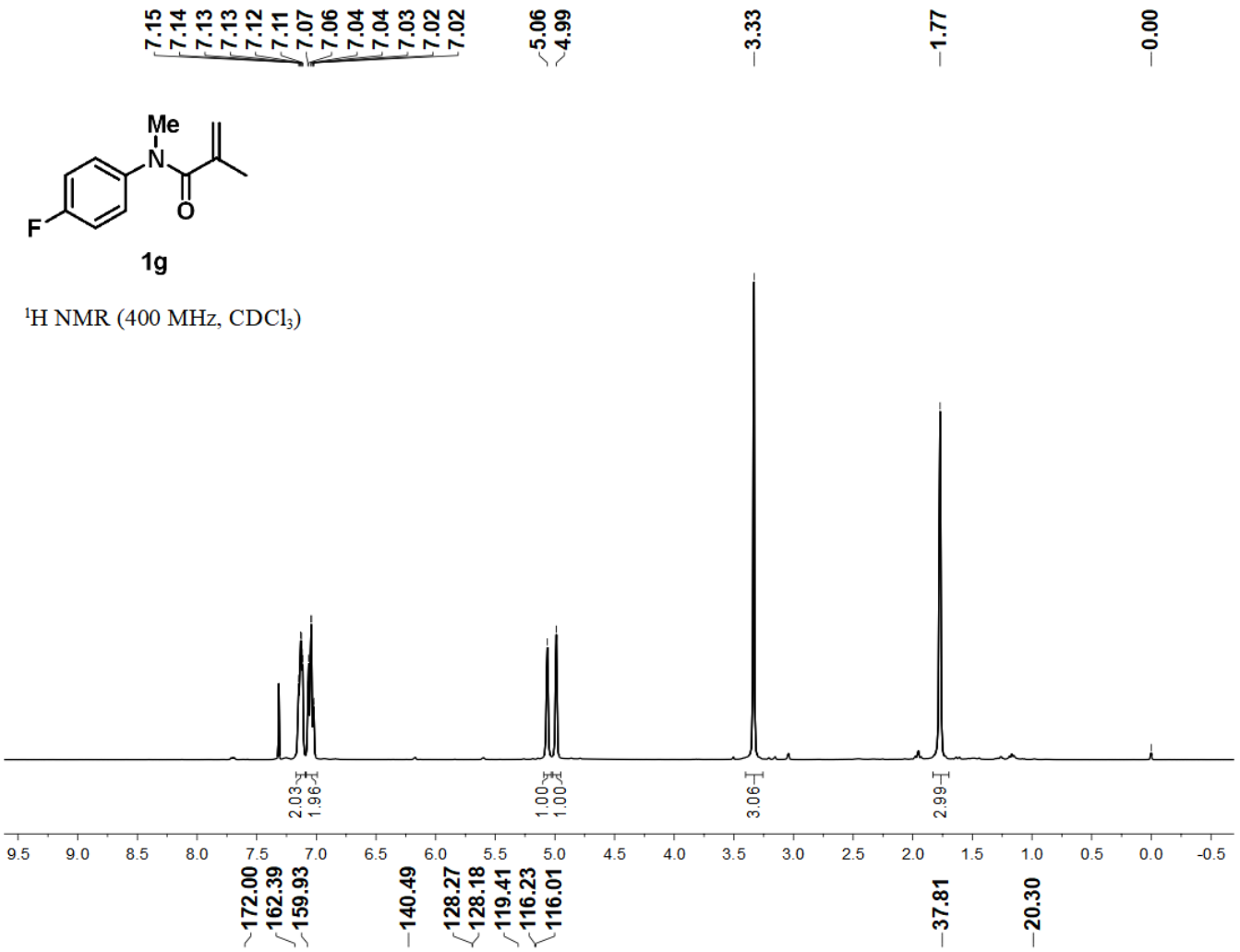
^{13}C NMR (101 MHz, $CDCl_3$)



1f

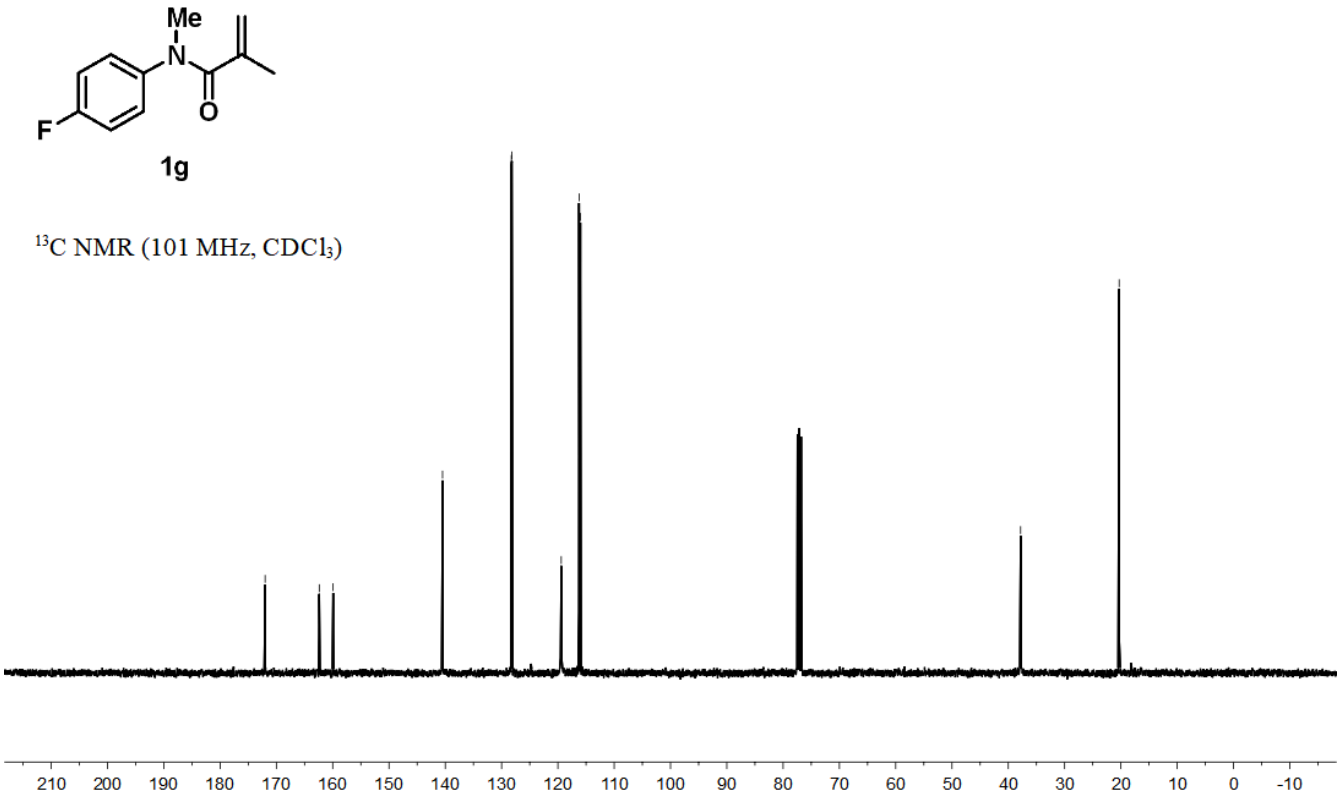
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$)



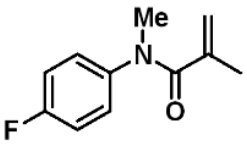
1g

^{1}H NMR (400 MHz, $CDCl_3$)



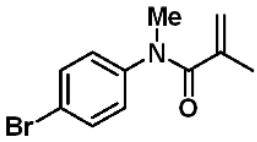
1g

^{13}C NMR (101 MHz, $CDCl_3$)



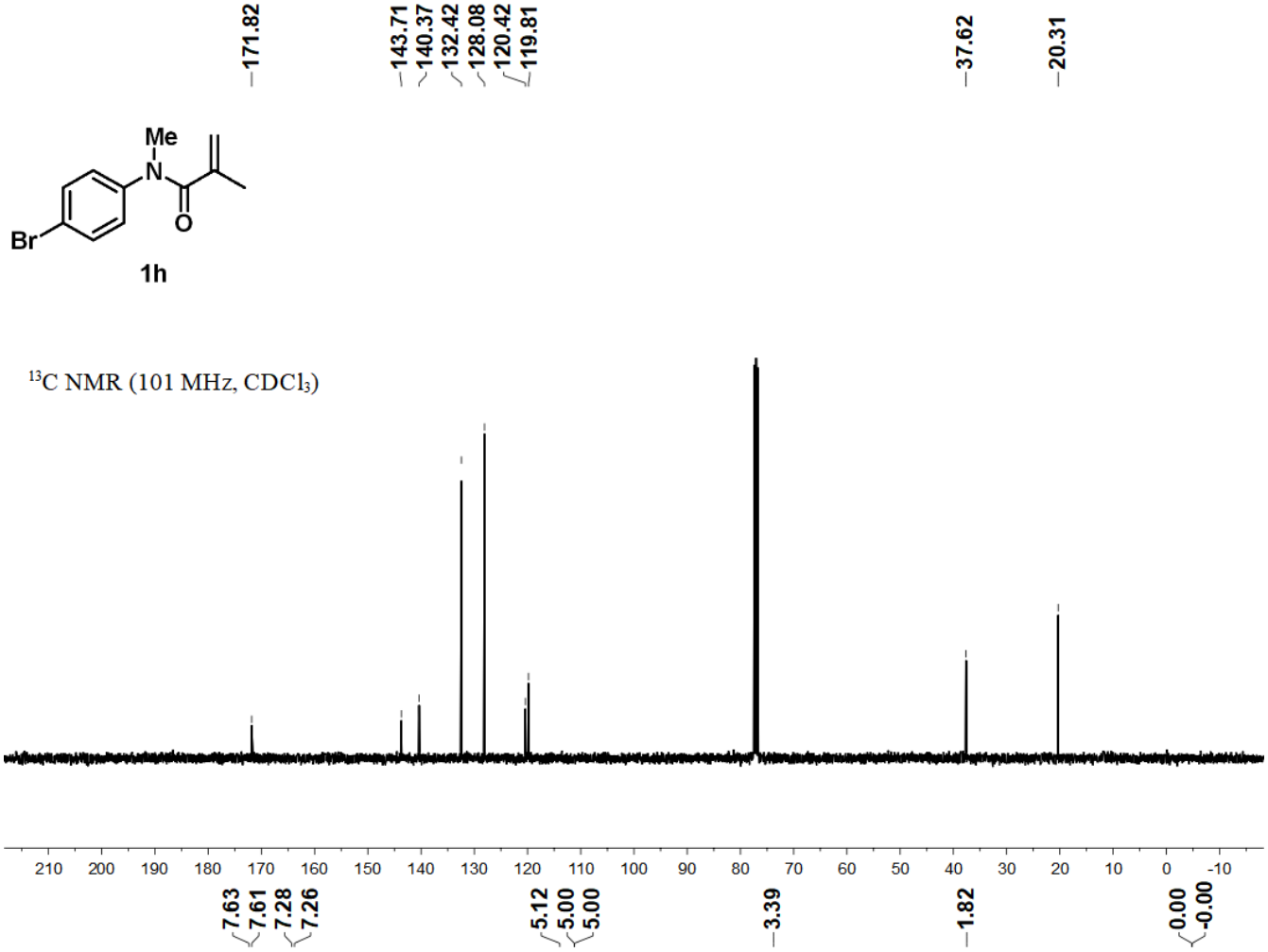
1g

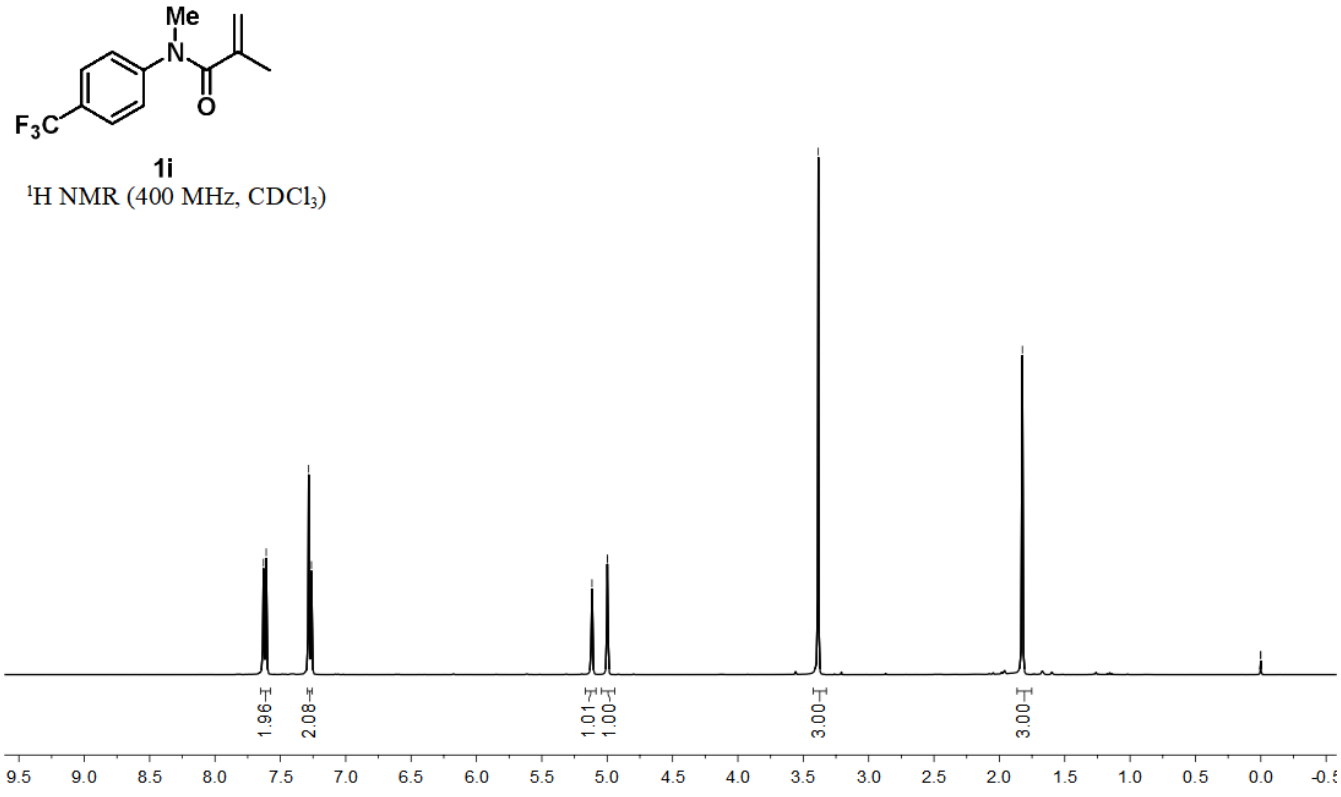
^{19}F NMR (376 MHz, $CDCl_3$)

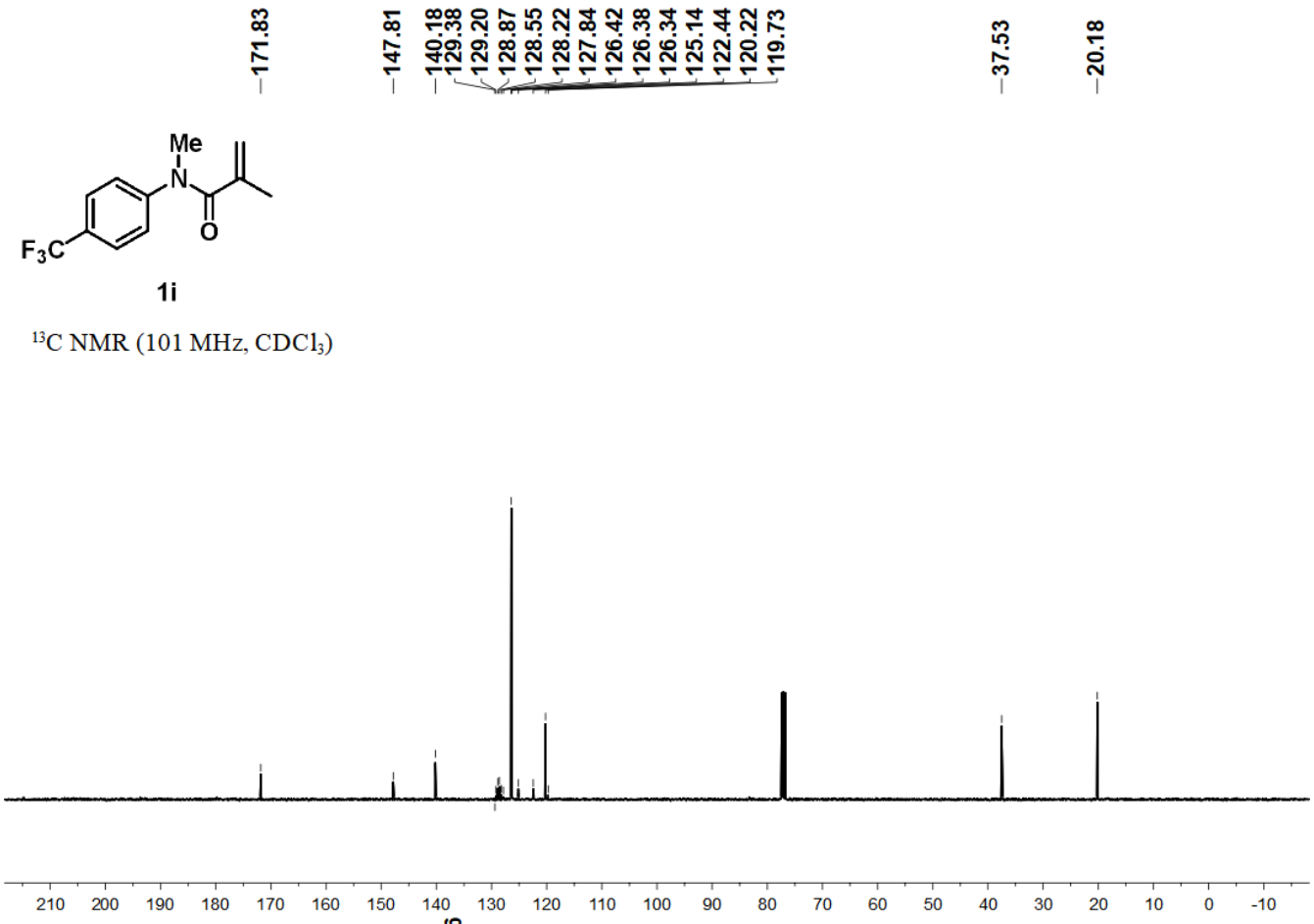


1h

^{1}H NMR (400 MHz, $CDCl_3$)

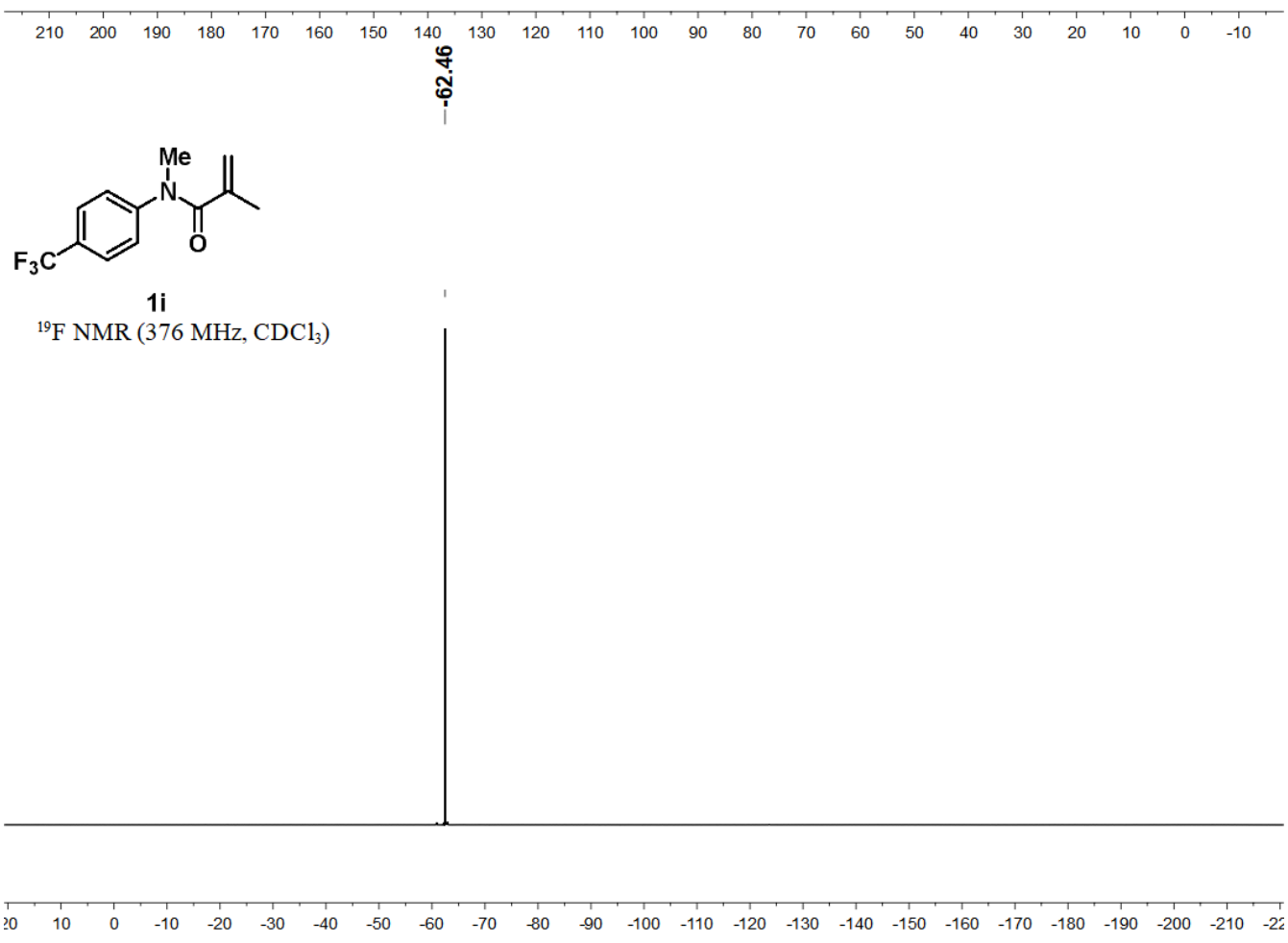

171.82
143.71
140.37
132.42
128.08
120.42
119.81
37.62
20.31
Me
N
O
Br
1h
13C NMR (101 MHz, CDCl3)
7.63
7.61
7.28
7.26
5.12
5.00
5.00
3.39
1.82
0.00
-0.00


Me
N
O
F3C
1i
1H NMR (400 MHz, CDCl3)
1.96
2.08
1.01
1.00
3.00
3.00



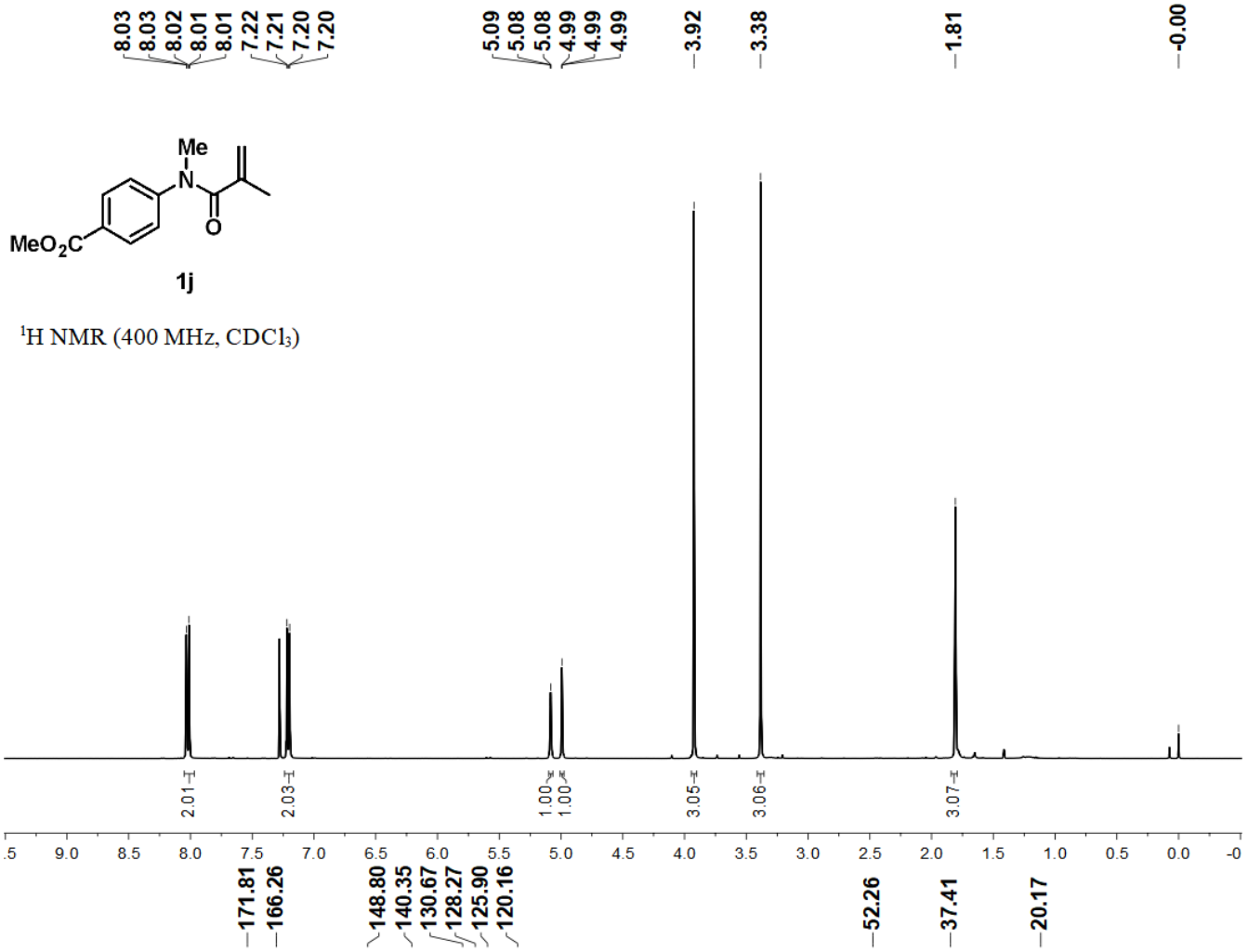
1i

^{13}C NMR (101 MHz, $CDCl_3$)



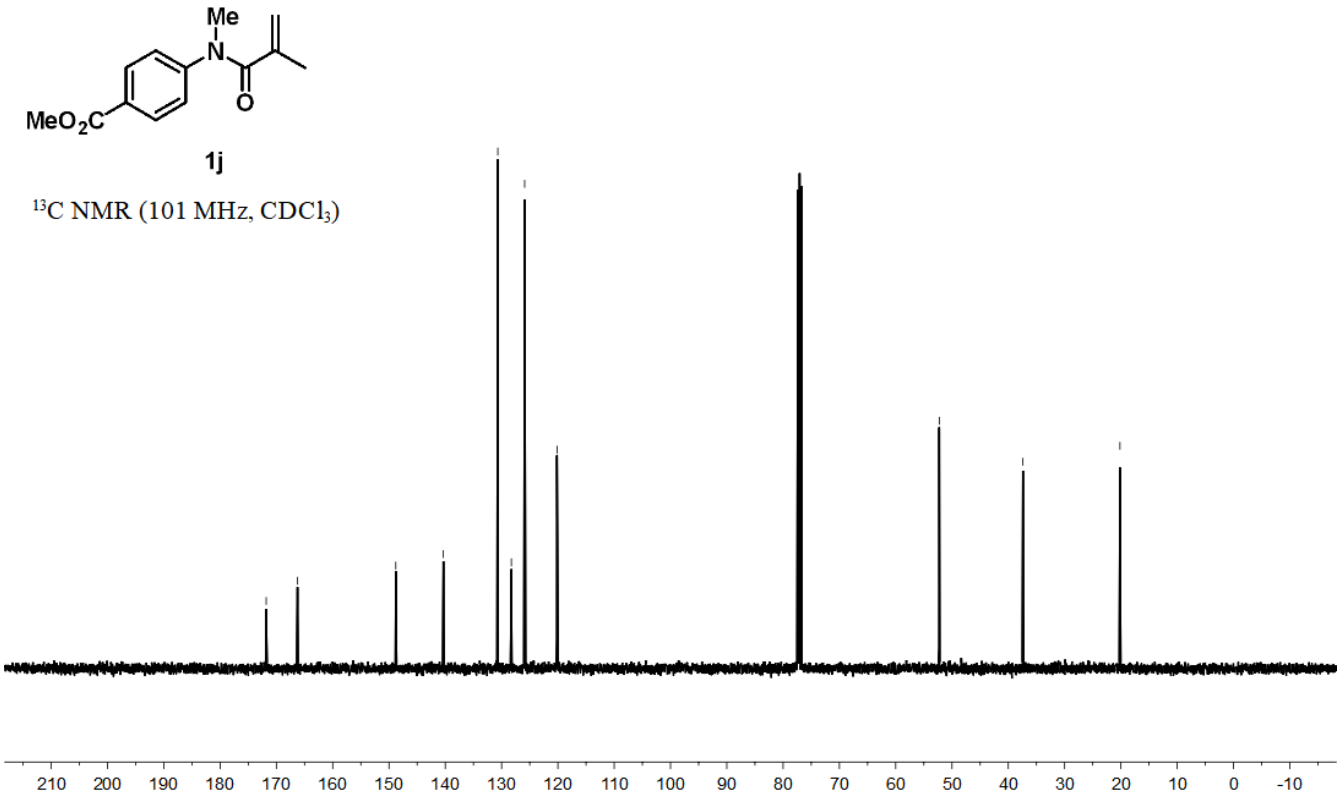
1i

^{19}F NMR (376 MHz, $CDCl_3$)



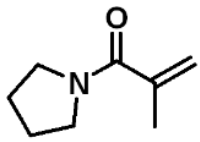
1j

^{1}H NMR (400 MHz, $CDCl_3$)



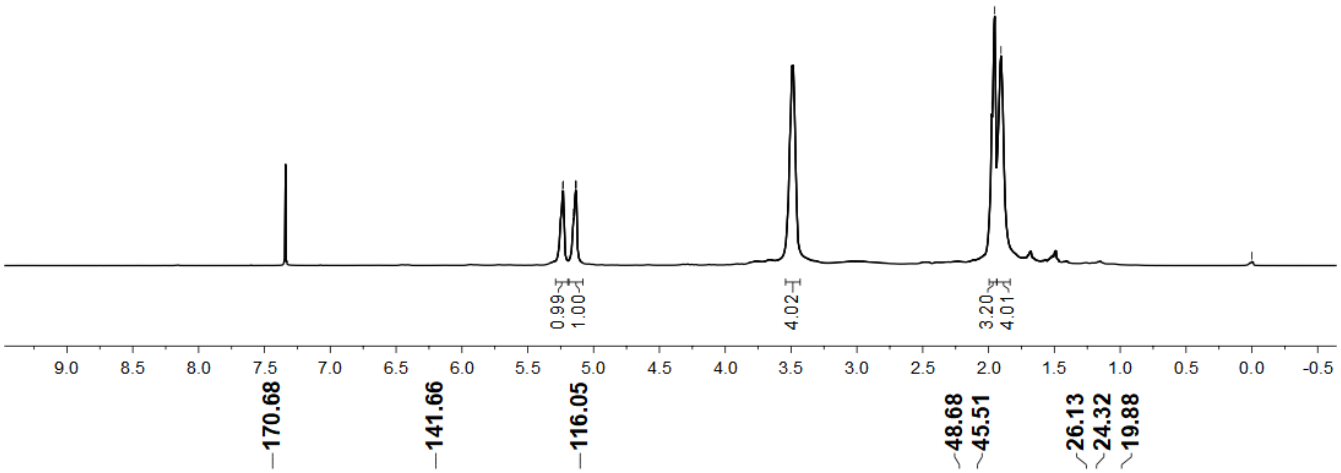
1j

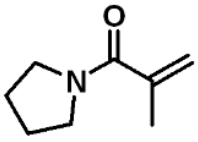
^{13}C NMR (101 MHz, $CDCl_3$)



1k

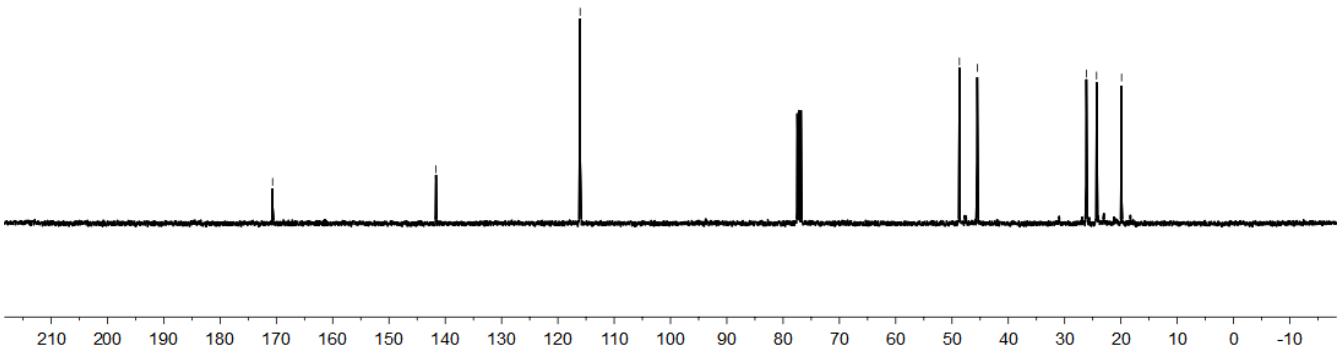
^{1}H NMR (400 MHz, $CDCl_3$)

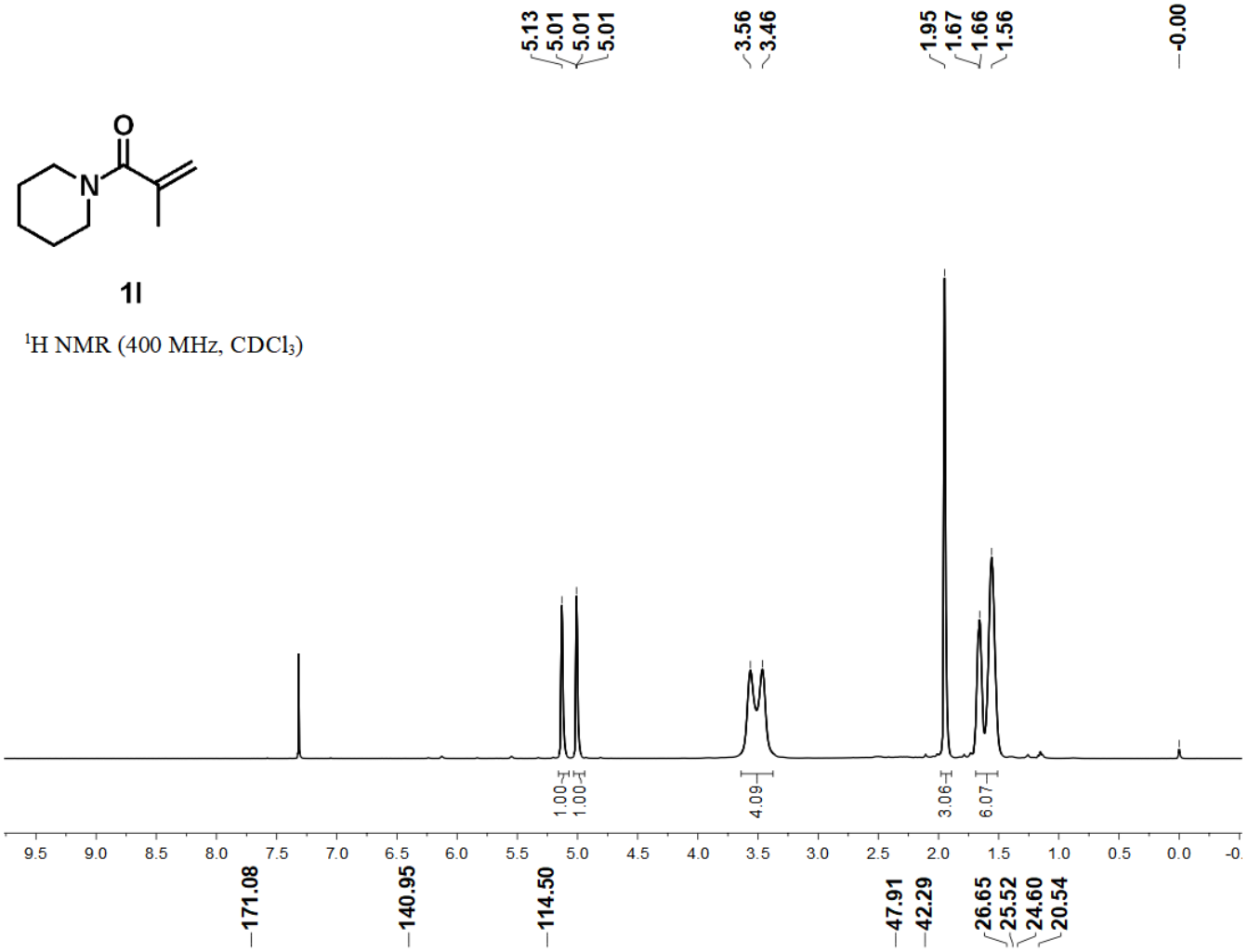




1k

^{13}C NMR (101 MHz, $CDCl_3$)



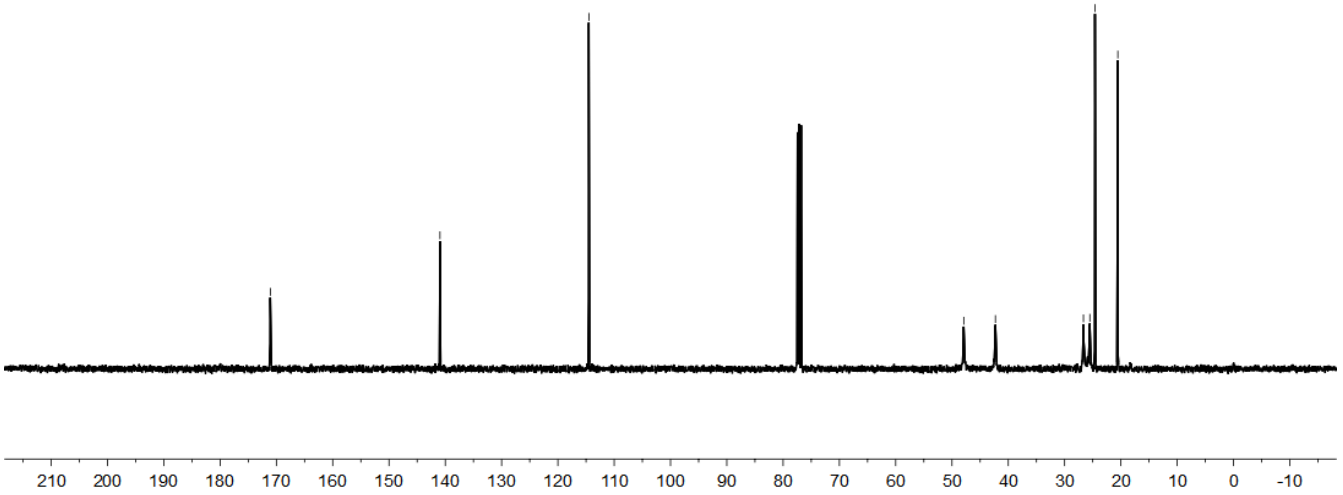


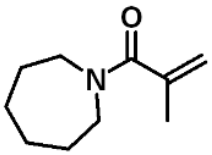
1l

^{1}H NMR (400 MHz, $CDCl_3$)

1l

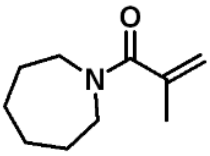
^{13}C NMR (101 MHz, $CDCl_3$)





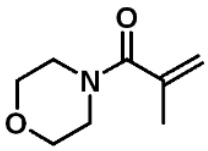
1m

^{1}H NMR (400 MHz, $CDCl_3$)



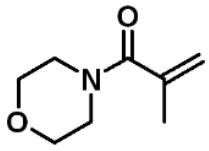
1m

^{13}C NMR (101 MHz, $CDCl_3$)



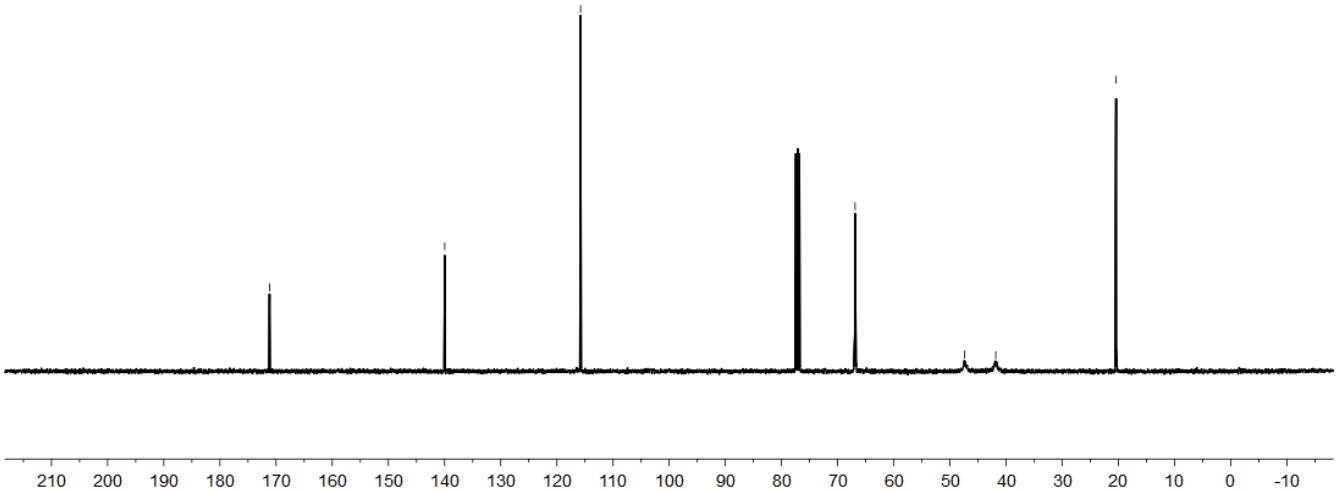
1n

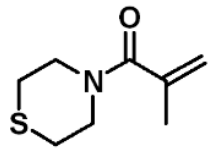
^{1}H NMR (400 MHz, $CDCl_3$)



1n

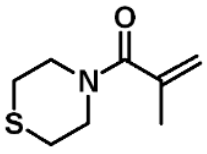
^{13}C NMR (101 MHz, $CDCl_3$)





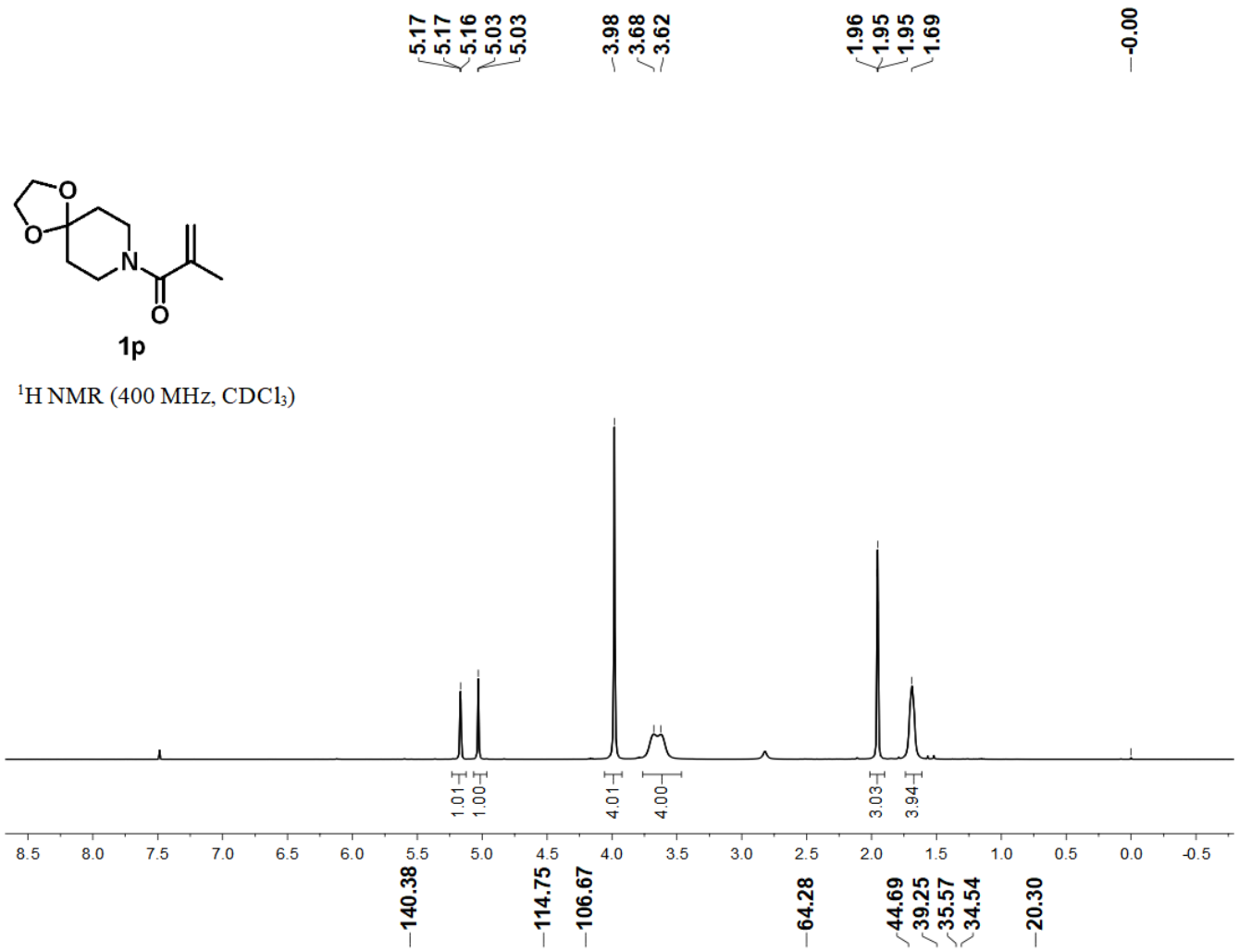
1o

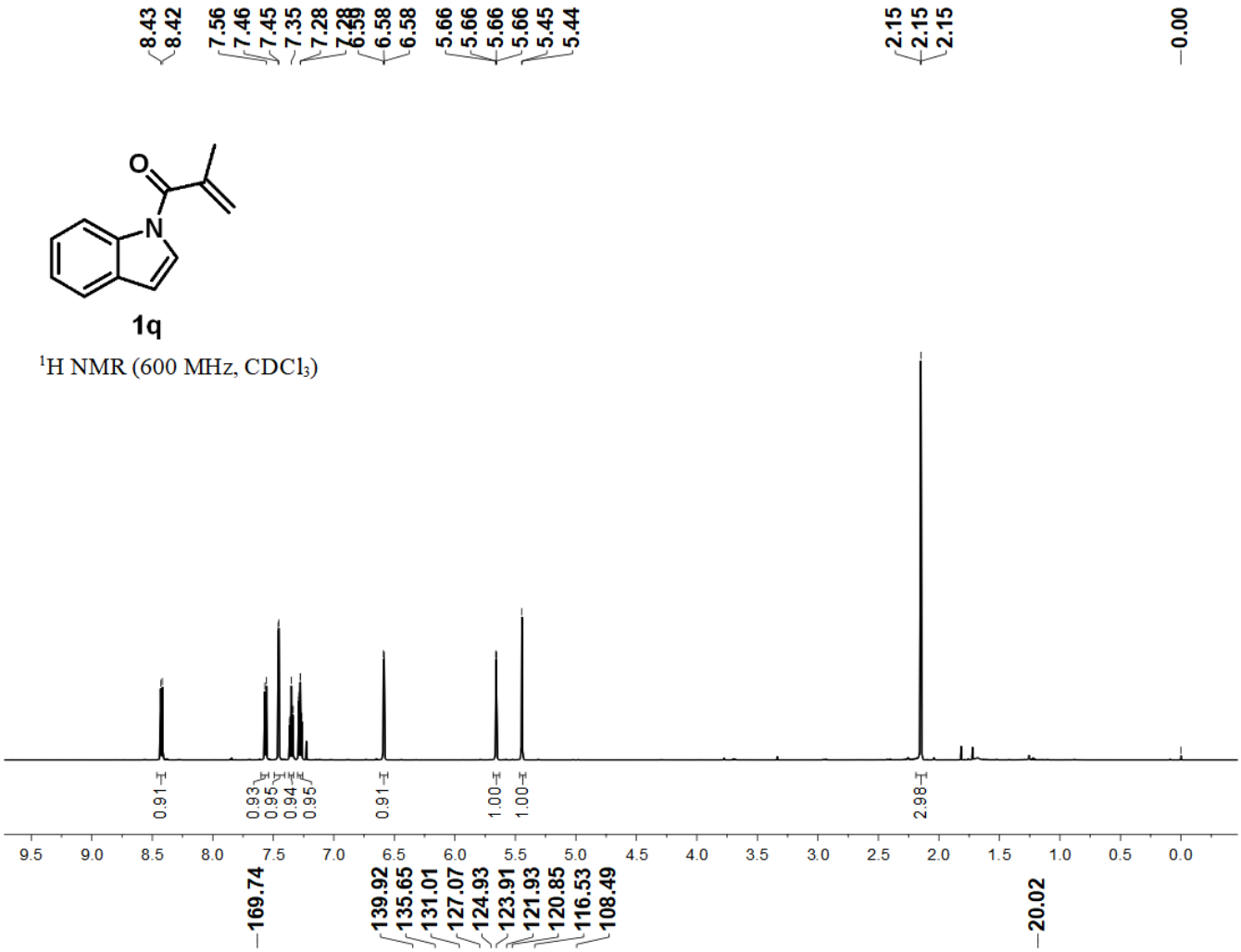
^{1}H NMR (400 MHz, $CDCl_3$)



1o

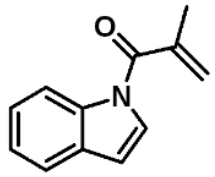
^{13}C NMR (101 MHz, $CDCl_3$)


5.17
5.17
5.16
5.03
5.03
3.98
3.68
3.62
1.96
1.95
1.95
1.69
0.00
1p
1H NMR (400 MHz, CDCl3)
1.01
1.00
4.01
4.00
3.03
3.94
140.38
114.75
106.67
64.28
44.69
39.25
35.57
34.54
20.30
1p
13C NMR (101 MHz, CDCl3)



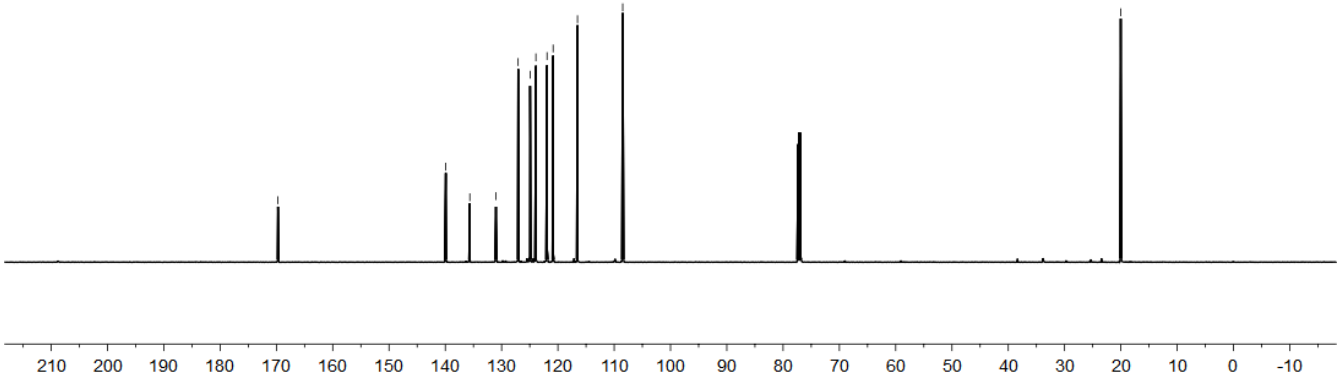
1q

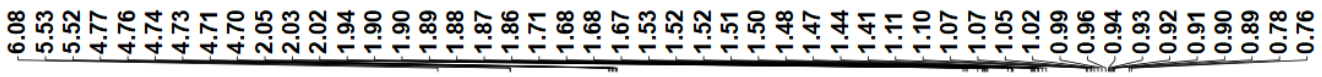
^{1}H NMR (600 MHz, $CDCl_3$)

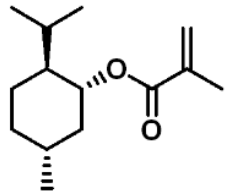


1q

^{13}C NMR (151 MHz, $CDCl_3$)

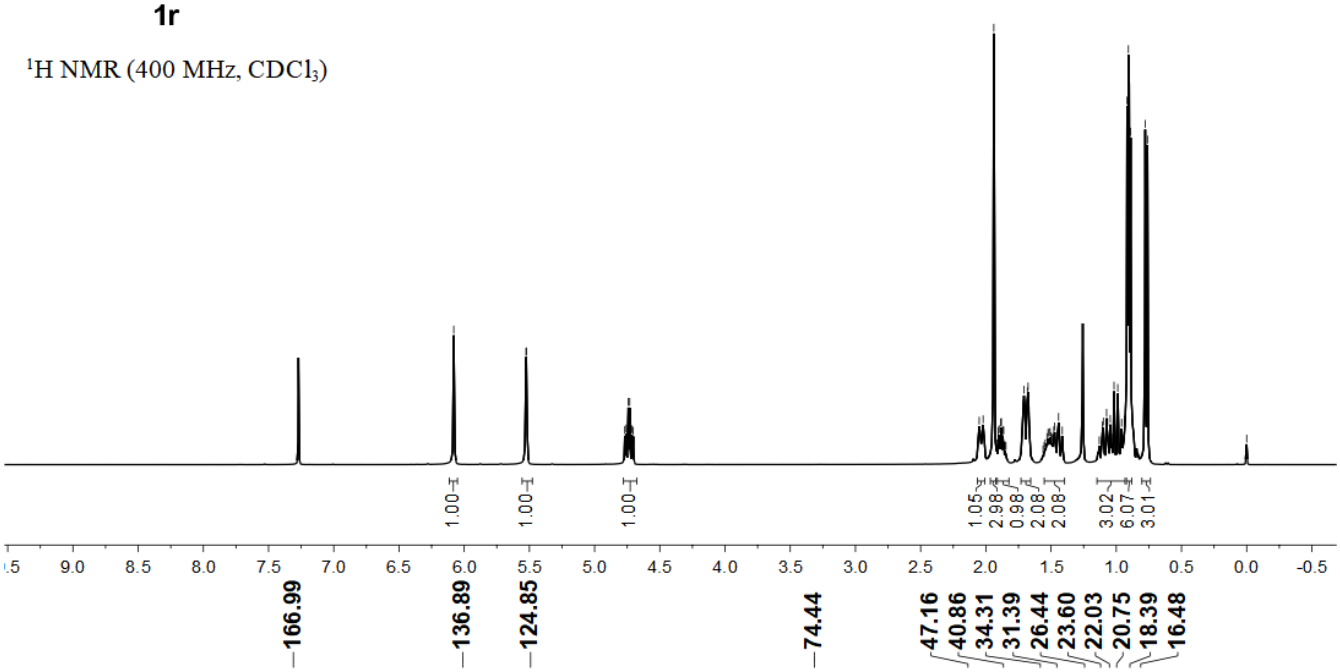


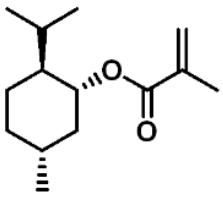




1r

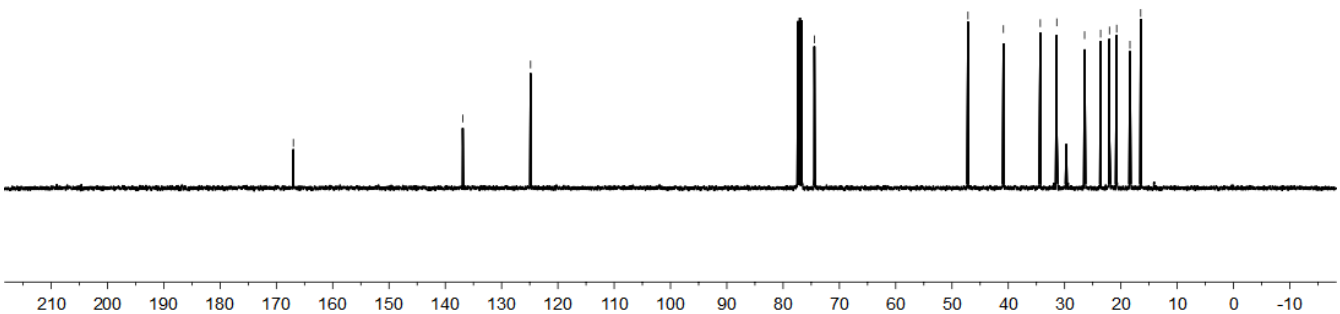
^{1}H NMR (400 MHz, $CDCl_3$)

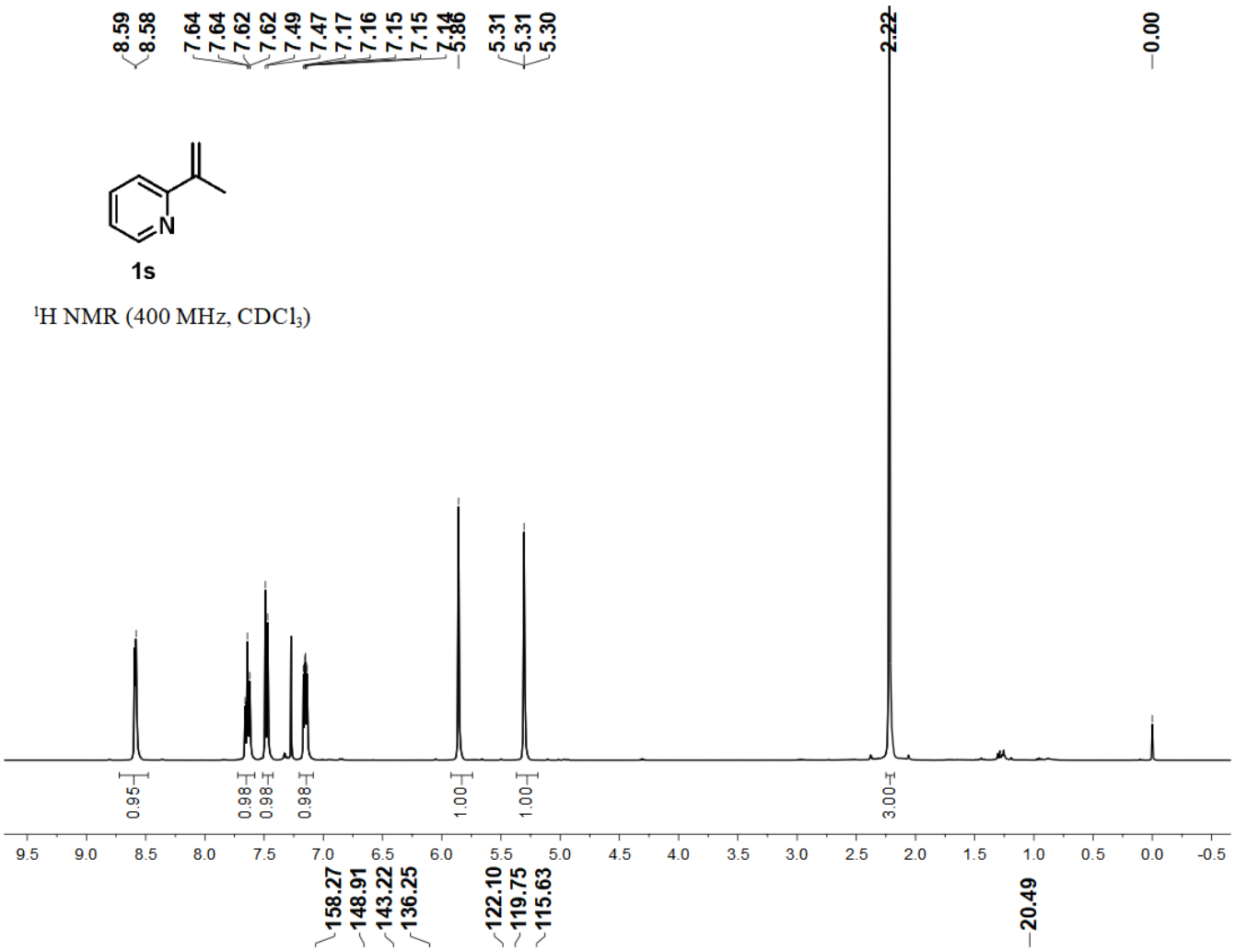




1r

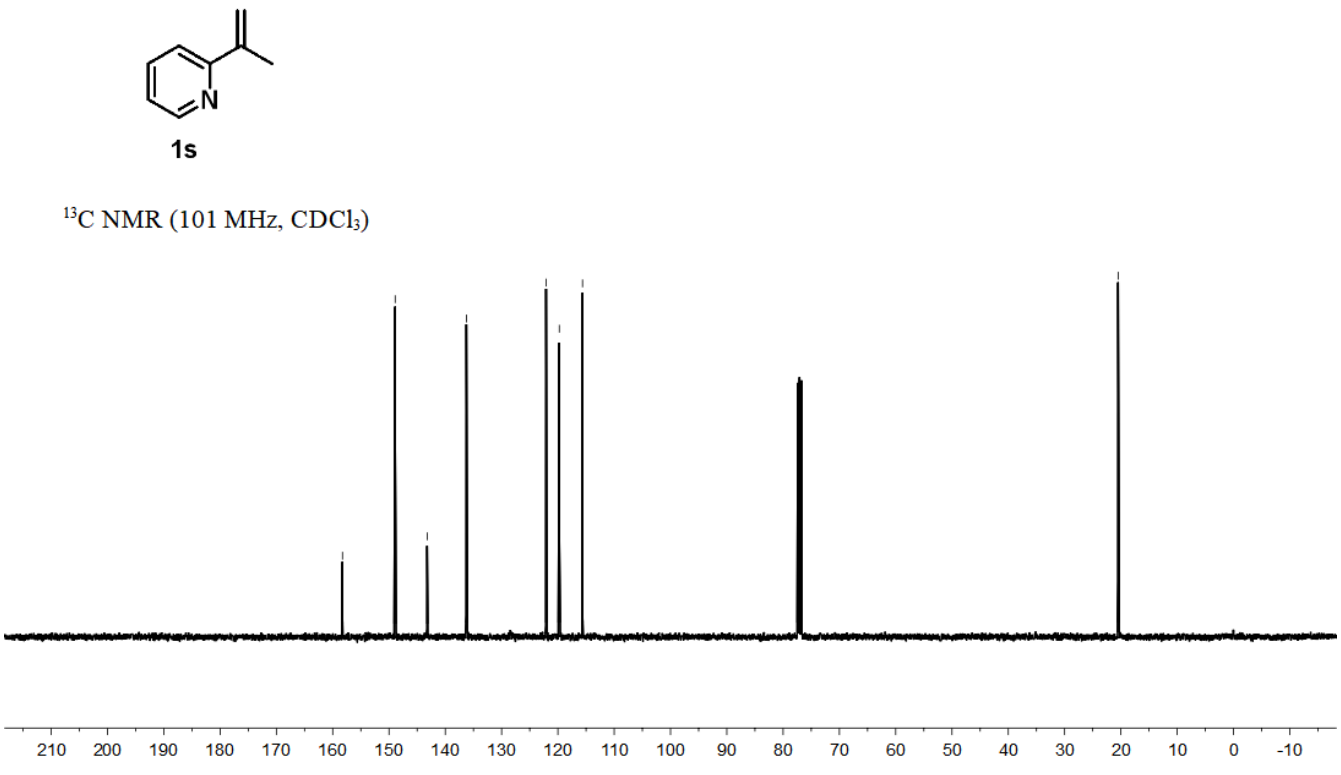
^{13}C NMR (101 MHz, $CDCl_3$)





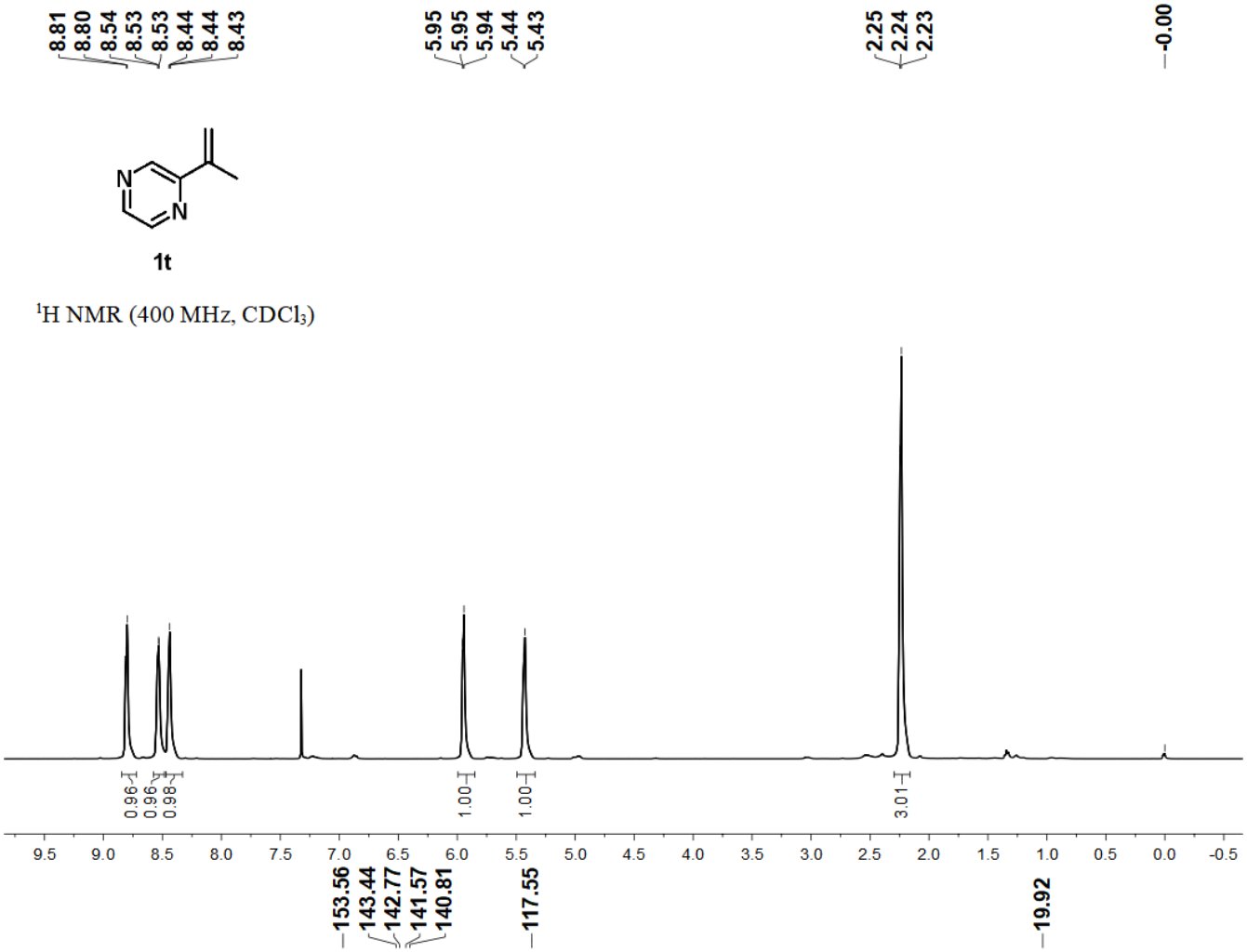
1s

^{1}H NMR (400 MHz, $CDCl_3$)



1s

^{13}C NMR (101 MHz, $CDCl_3$)

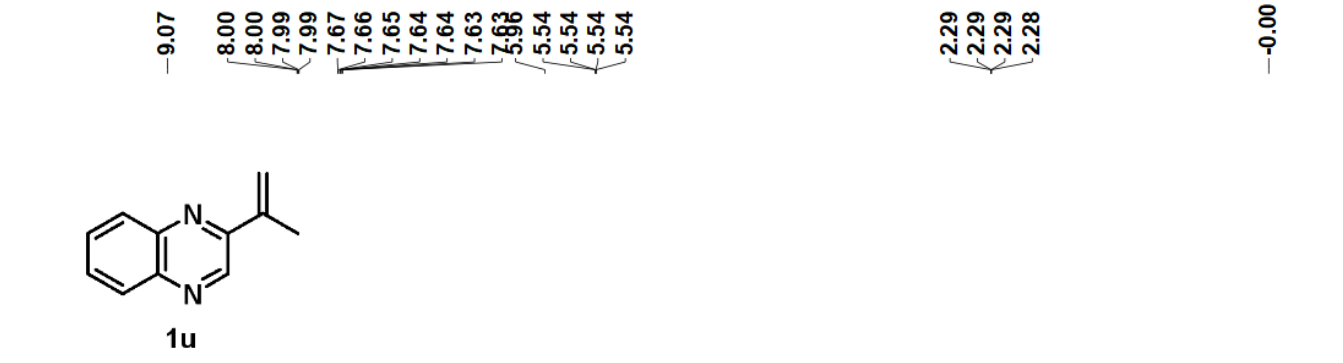


1t

^{1}H NMR (400 MHz, $CDCl_3$)

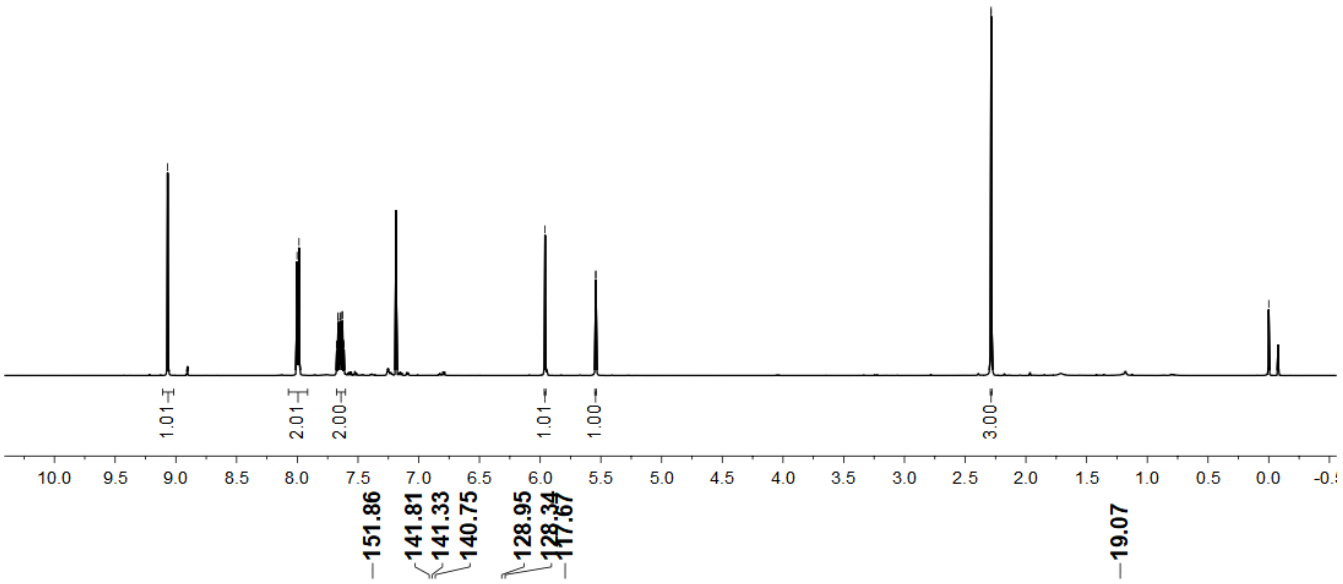
1t

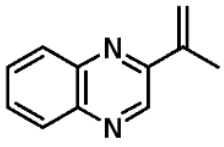
^{13}C NMR (101 MHz, $CDCl_3$)



1u

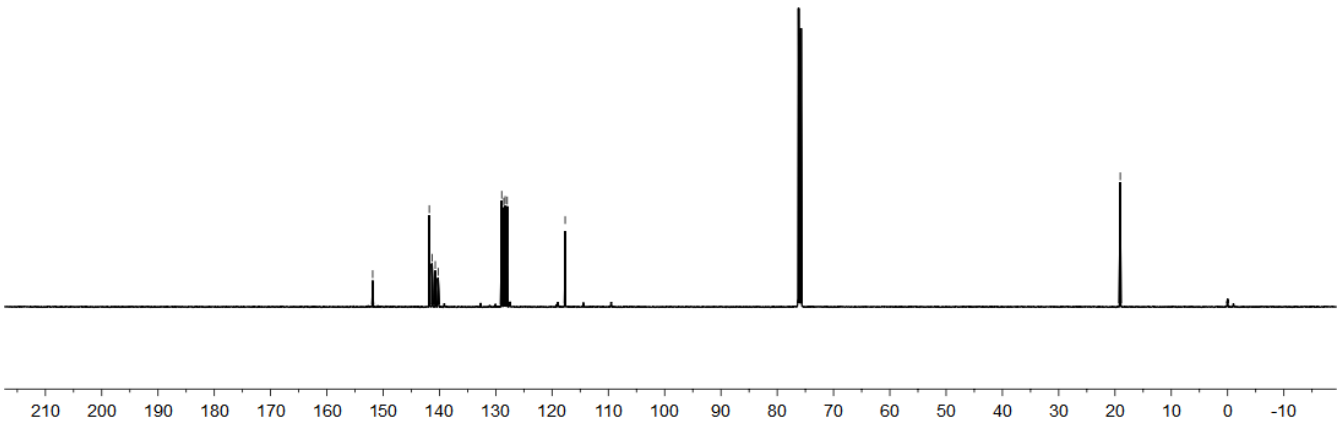
^{1}H NMR (600 MHz, $CDCl_3$)

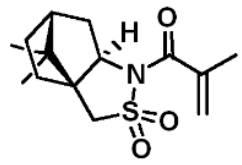




1u

^{13}C NMR (151 MHz, $CDCl_3$)



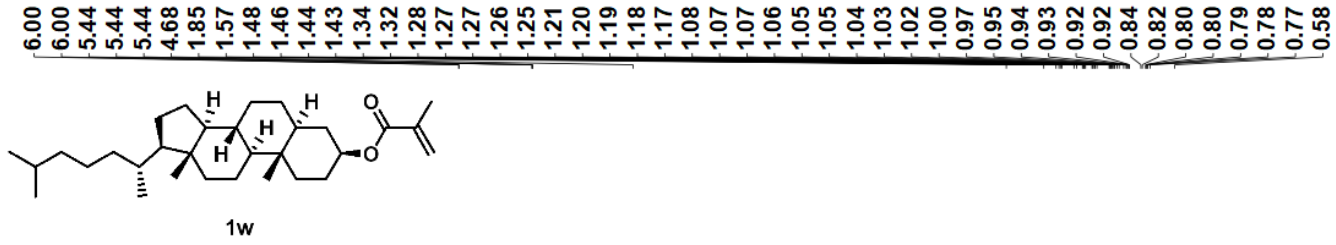


1v

^{1}H NMR (400 MHz, $CDCl_3$)

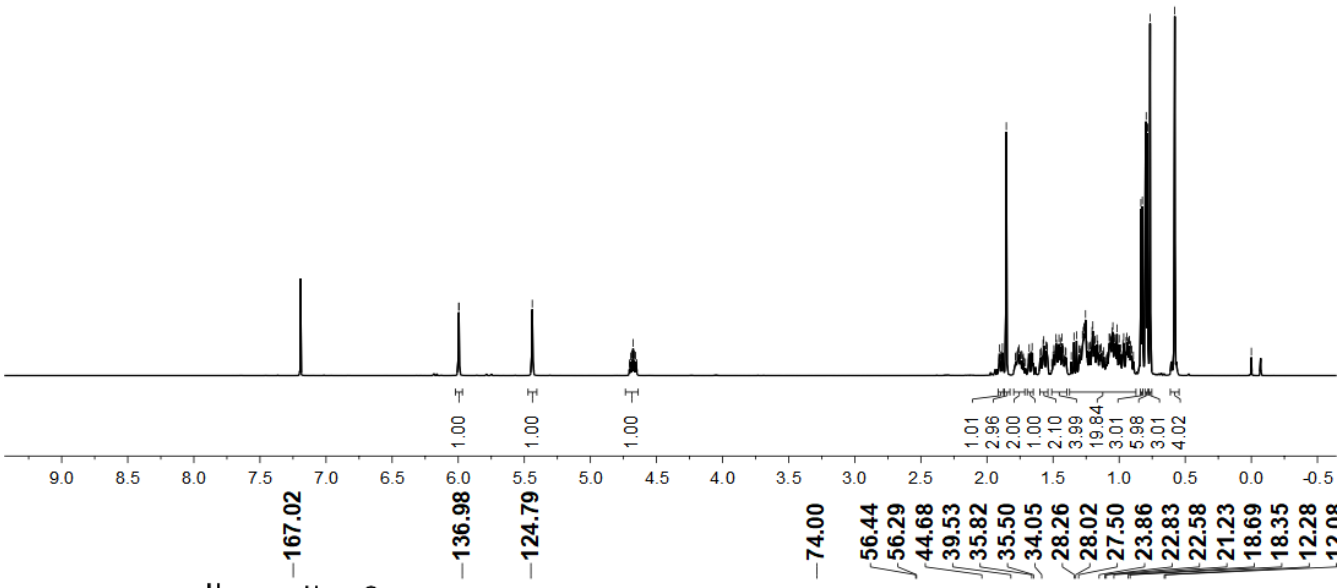
1v

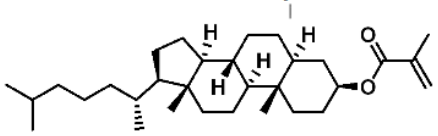
^{13}C NMR (101 MHz, $CDCl_3$)



1w

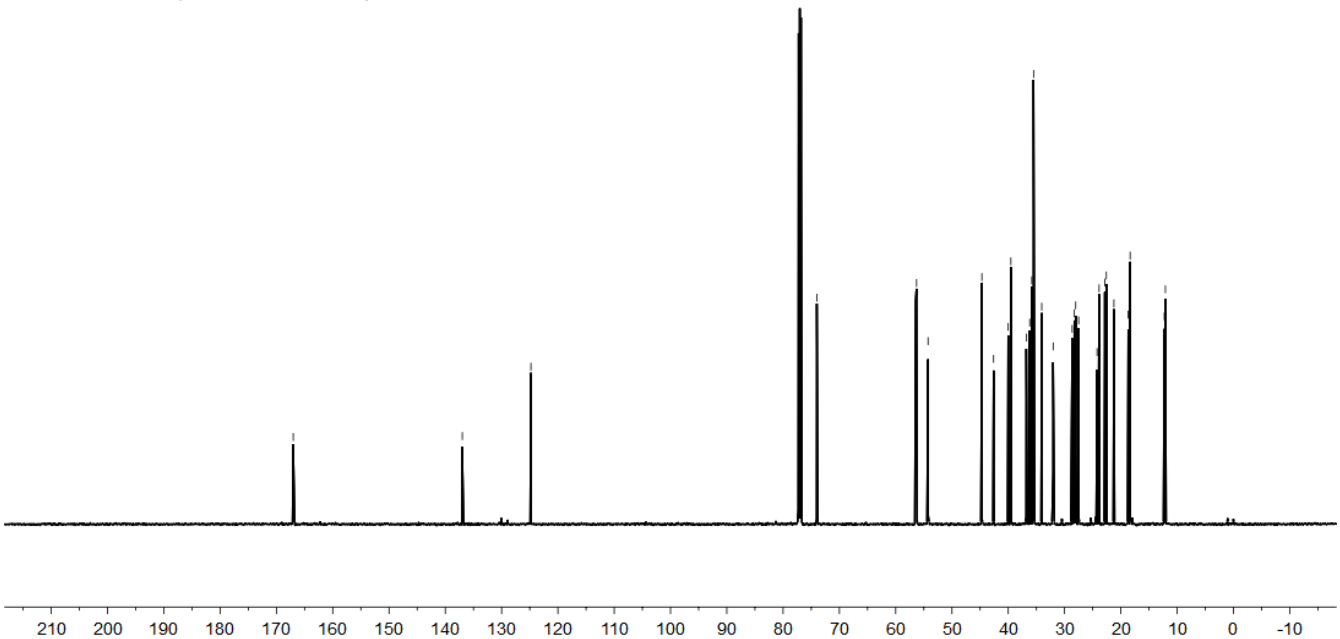
^{1}H NMR (400 MHz, $CDCl_3$)

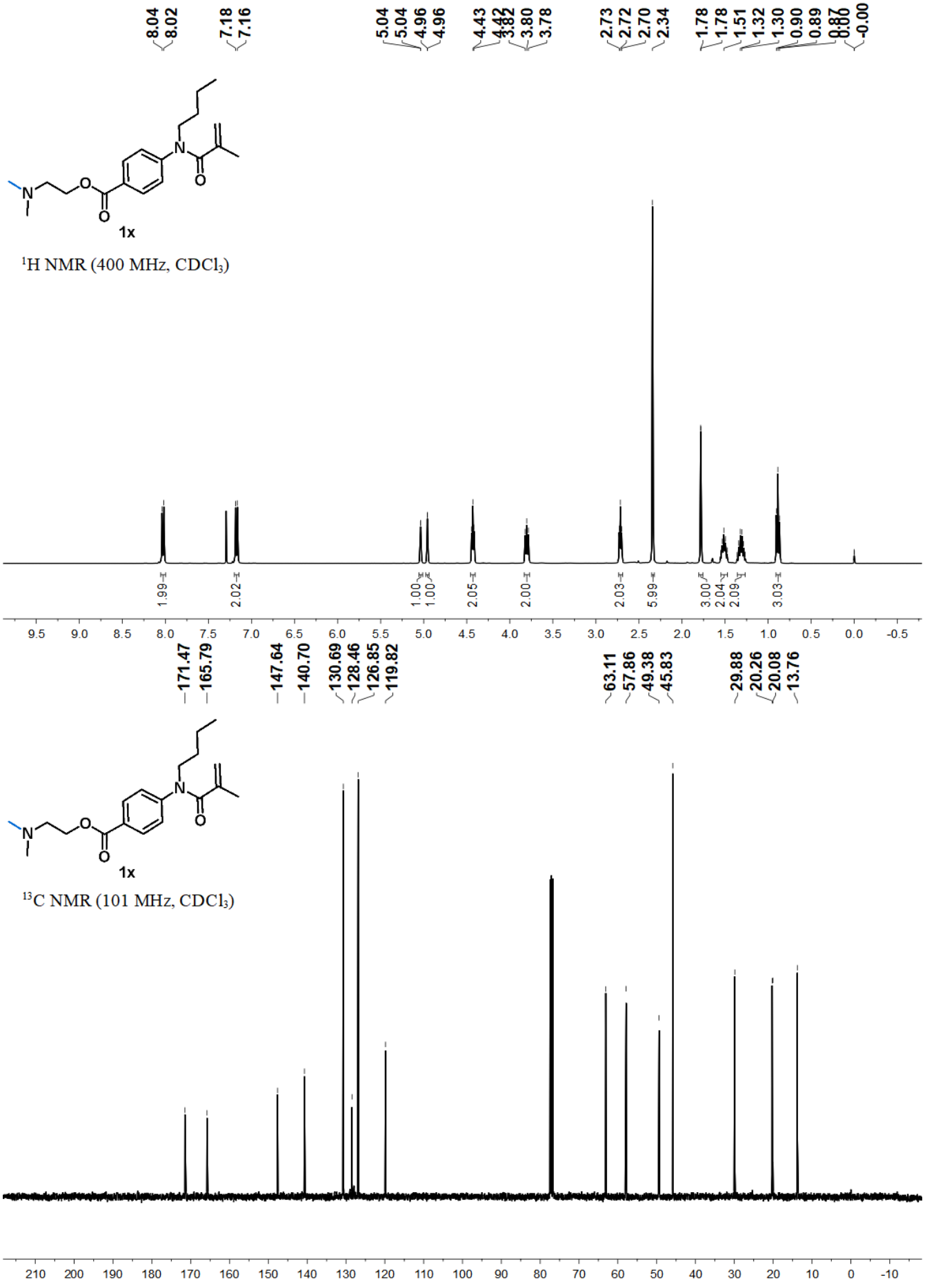


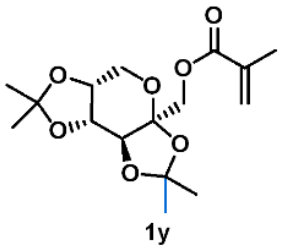


1w

^{13}C NMR (151 MHz, $CDCl_3$)

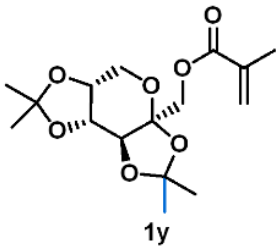



8.04
8.02
7.18
7.16
5.04
5.04
4.96
4.96
4.43
4.42
3.82
3.80
3.78
2.73
2.72
2.70
2.34
1.78
1.78
1.51
1.32
1.30
0.90
0.89
0.87
0.86
-0.00
1x
1H NMR (400 MHz, CDCl3)
1.99
2.02
1.00
1.00
2.05
2.00
2.03
5.99
3.00
2.04
2.09
3.03
171.47
165.79
147.64
140.70
130.69
128.46
126.85
119.82
63.11
57.86
49.38
45.83
29.88
20.26
20.08
13.76
1x
13C NMR (101 MHz, CDCl3)



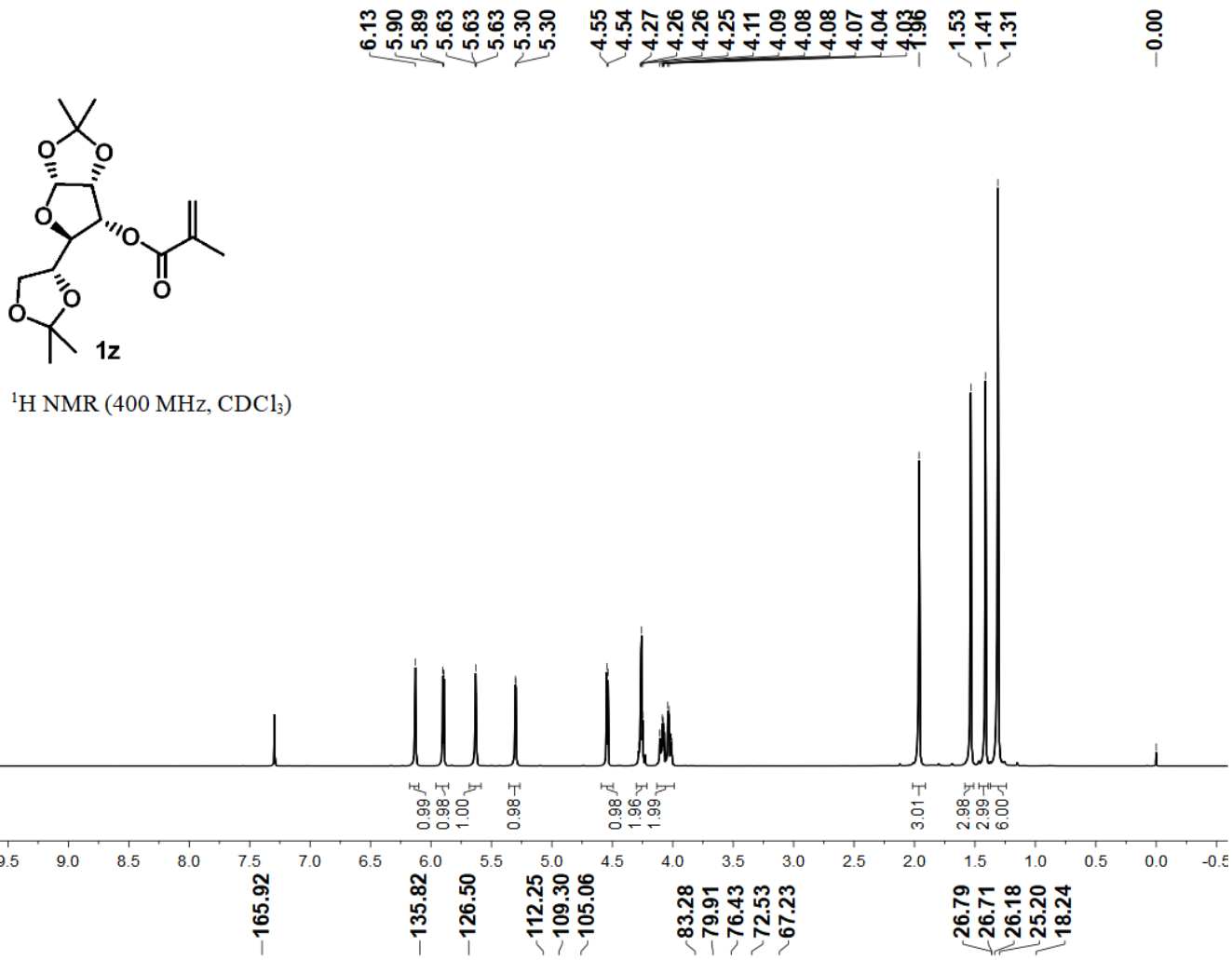
1y

^{1}H NMR (400 MHz, $CDCl_3$)

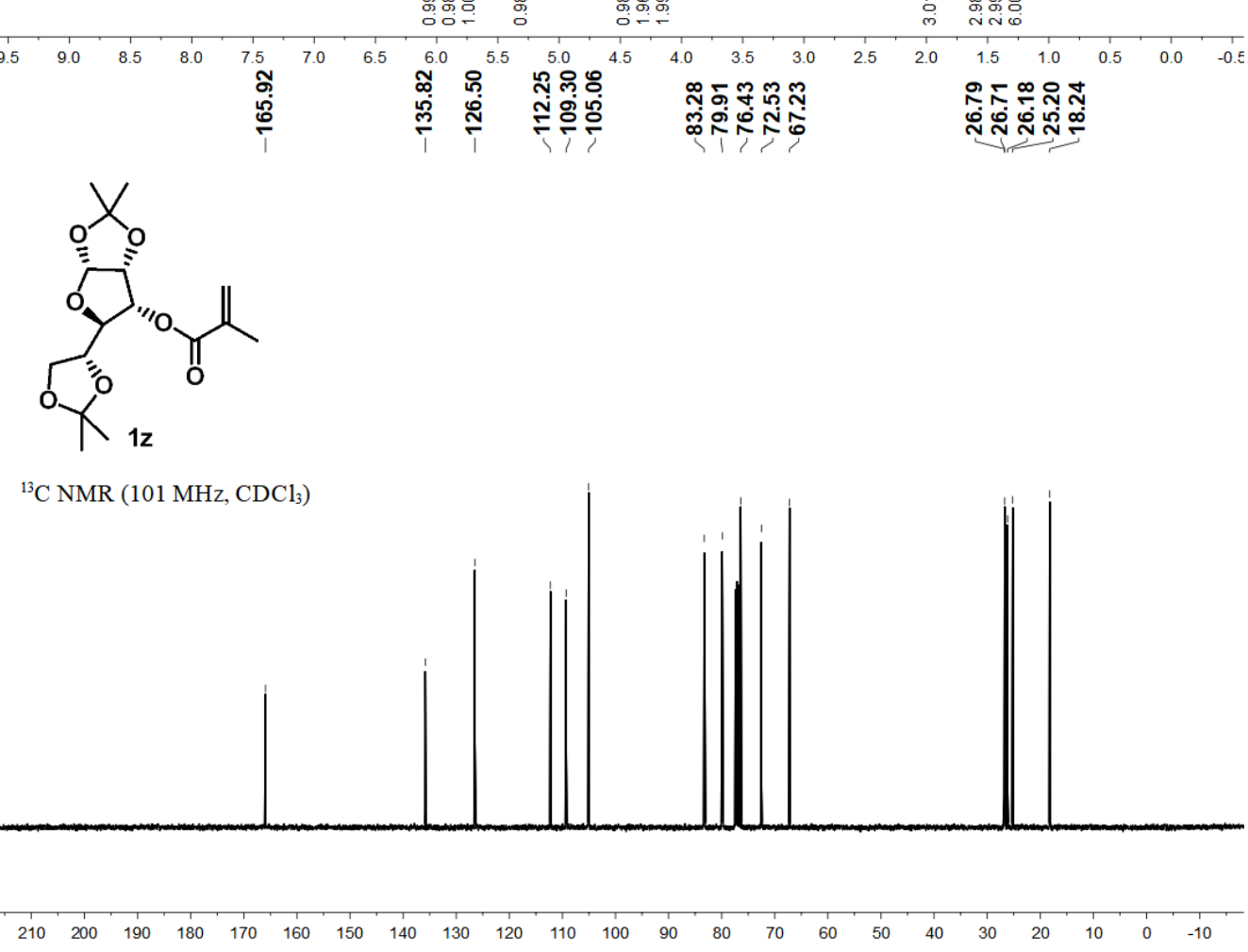


1y

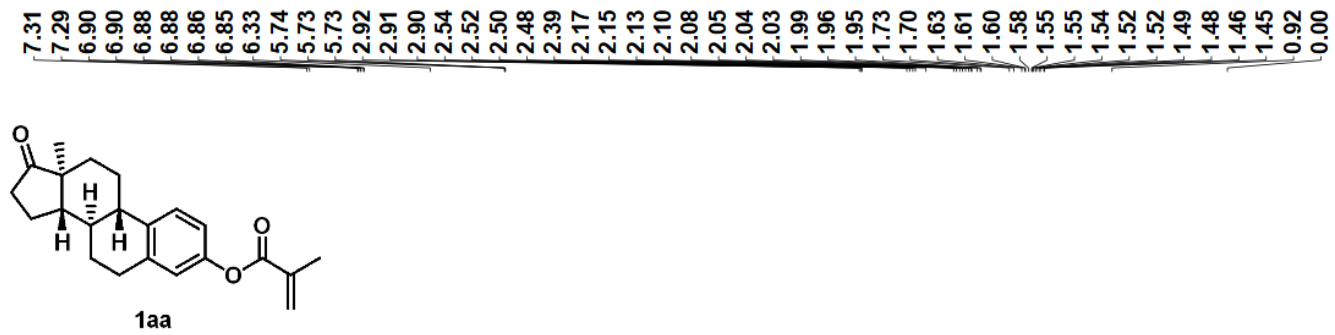
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

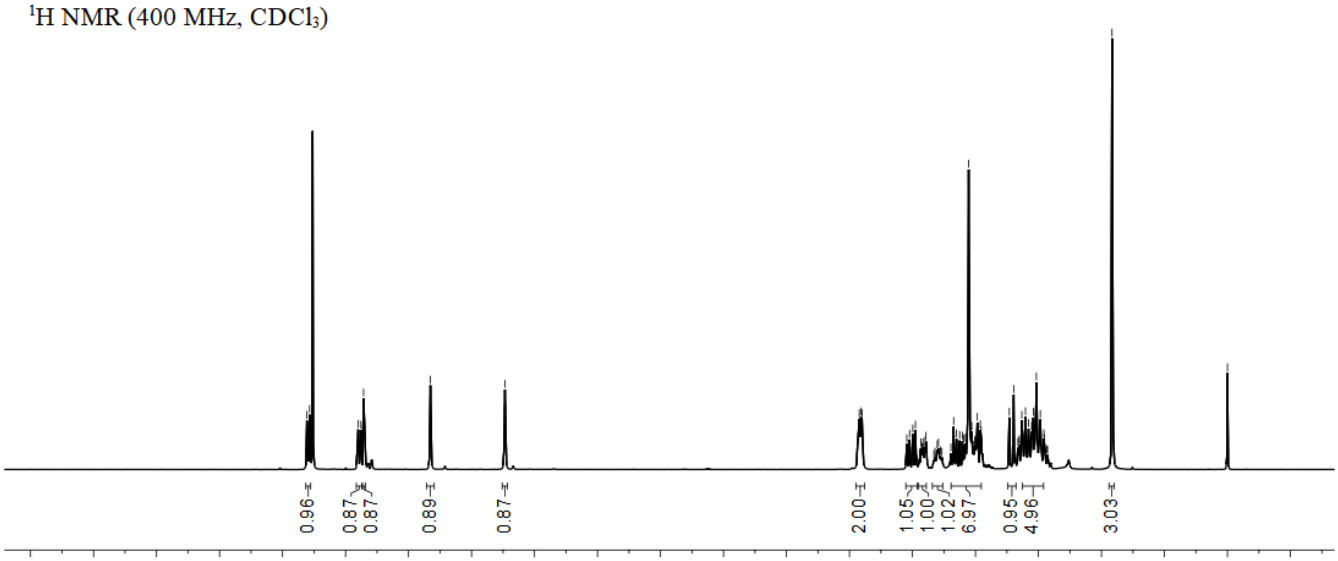


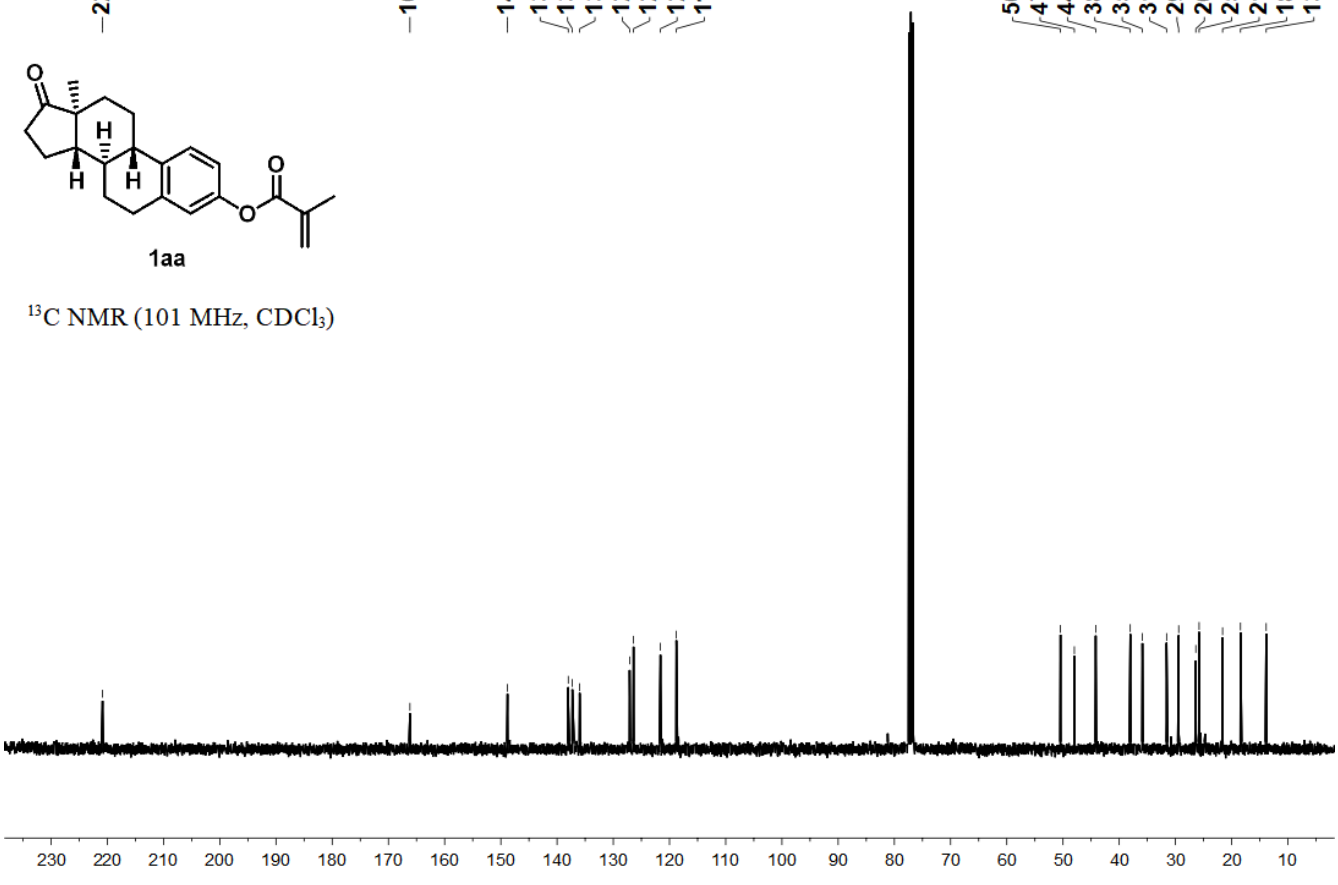
^{13}C NMR (101 MHz, $CDCl_3$)



1aa

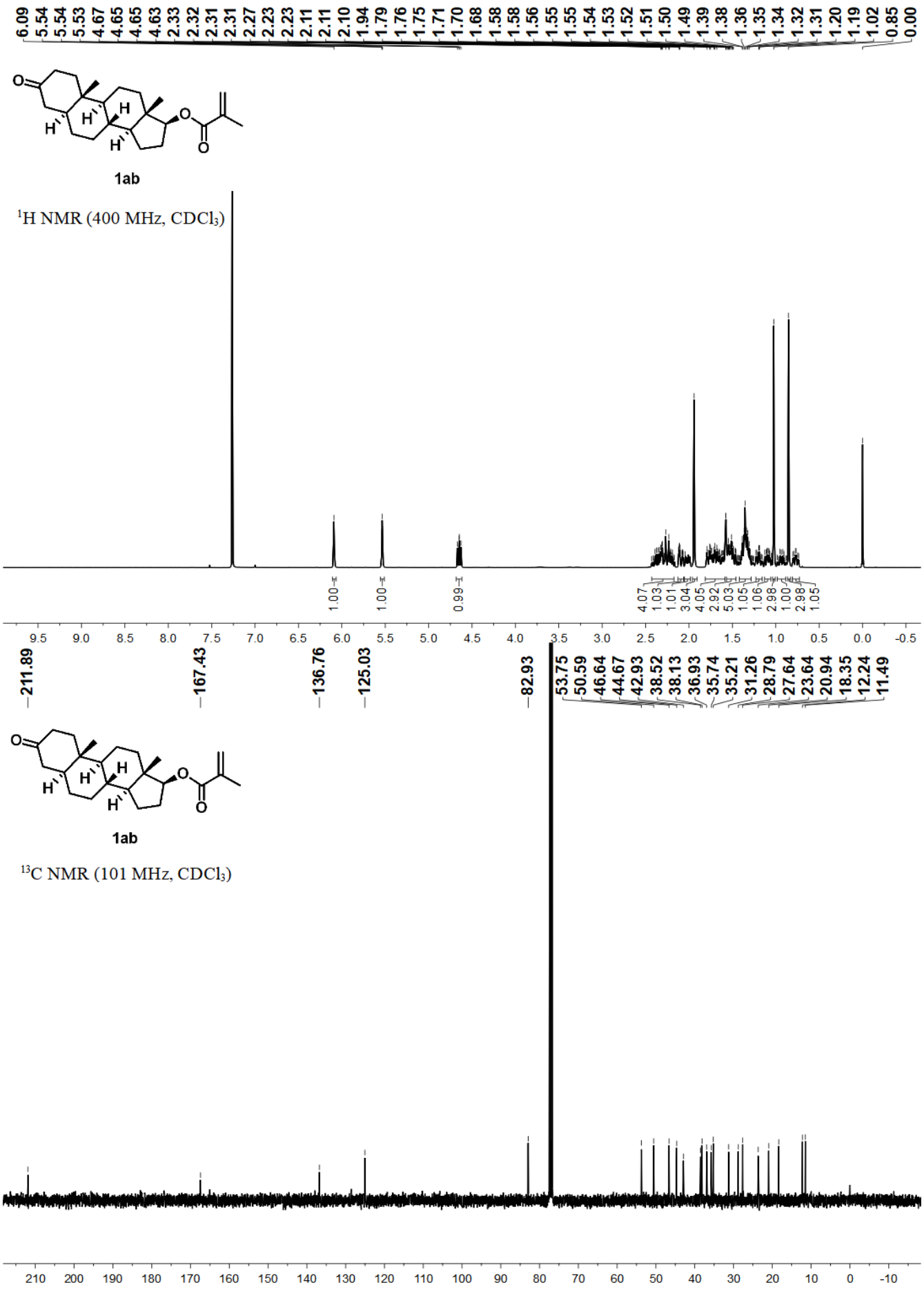
^{1}H NMR (400 MHz, $CDCl_3$)

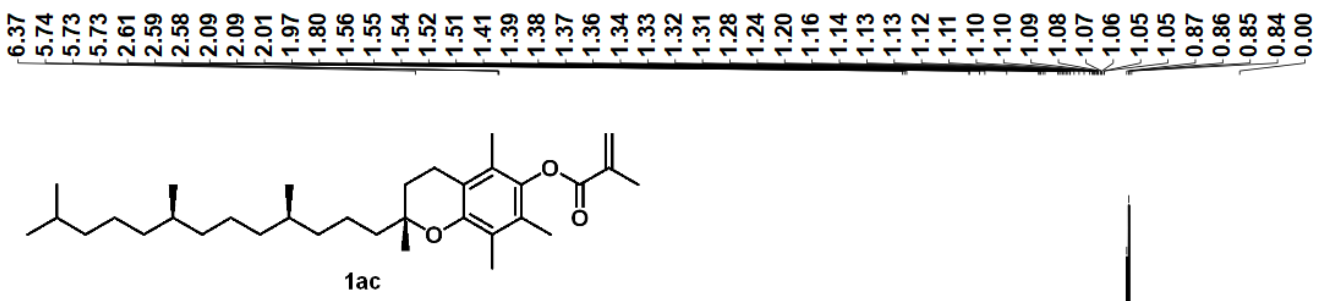




1aa

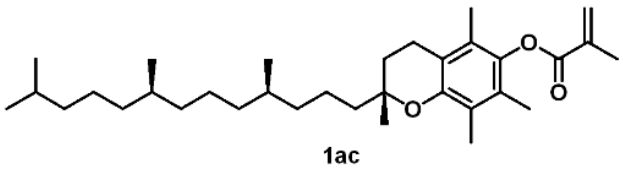
^{13}C NMR (101 MHz, $CDCl_3$)


6.09 5.54 5.54 5.53 4.67 4.65 4.65 4.63 2.33 2.32 2.31 2.31 2.27 2.23 2.23 2.11 2.11 2.10 1.94 1.79 1.76 1.75 1.71 1.70 1.68 1.58 1.58 1.56 1.55 1.55 1.54 1.53 1.52 1.51 1.50 1.49 1.39 1.38 1.36 1.35 1.34 1.32 1.31 1.20 1.19 1.02 0.85 0.00
1ab
1H NMR (400 MHz, CDCl3)
1.00 1.00 0.99 4.07 1.03 1.01 3.04 4.05 2.92 5.03 1.05 1.06 2.98 1.00 2.98 1.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
211.89 167.43 136.76 125.03 82.93 53.75 50.59 46.64 44.67 42.93 38.52 38.13 36.93 35.74 35.21 31.26 28.79 27.64 23.64 20.94 18.35 12.24 11.49
1ab
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



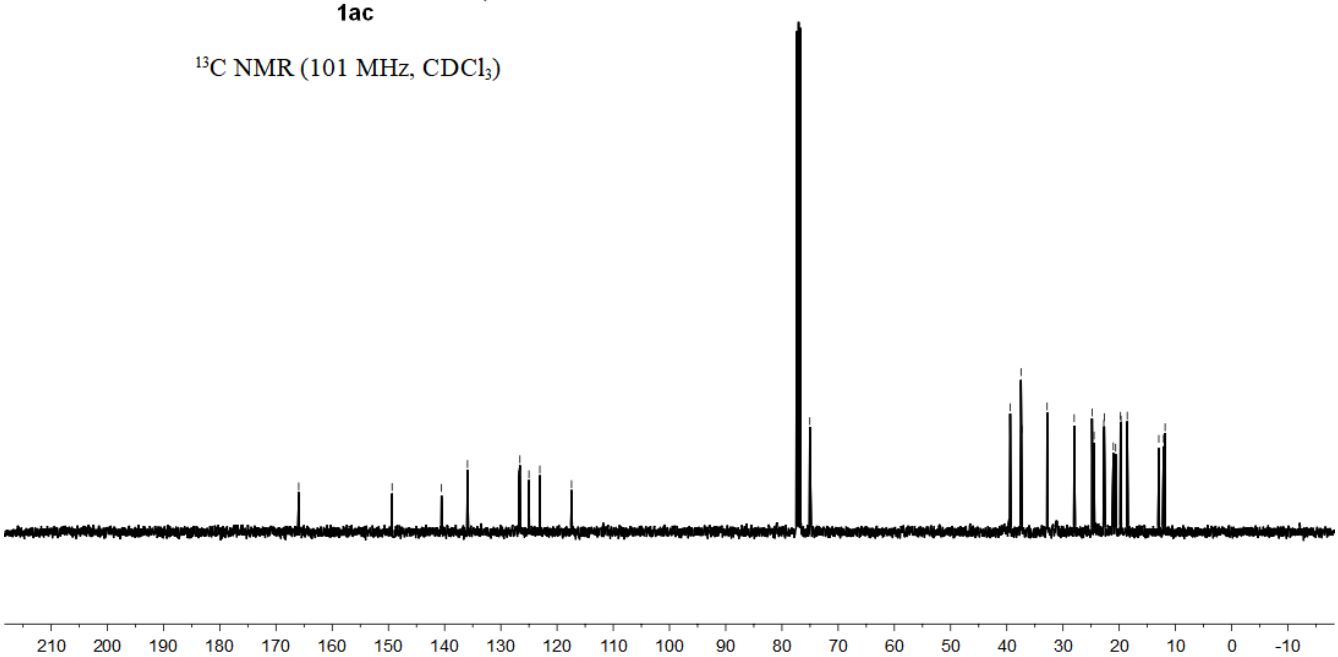
1ac

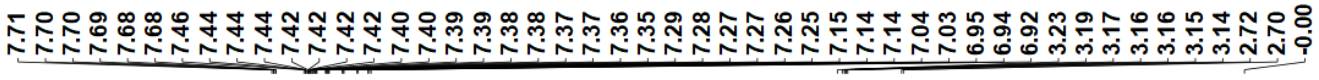
^{1}H NMR (400 MHz, $CDCl_3$)

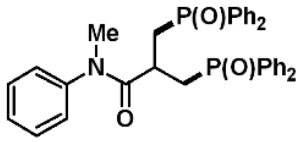


1ac

^{13}C NMR (101 MHz, $CDCl_3$)

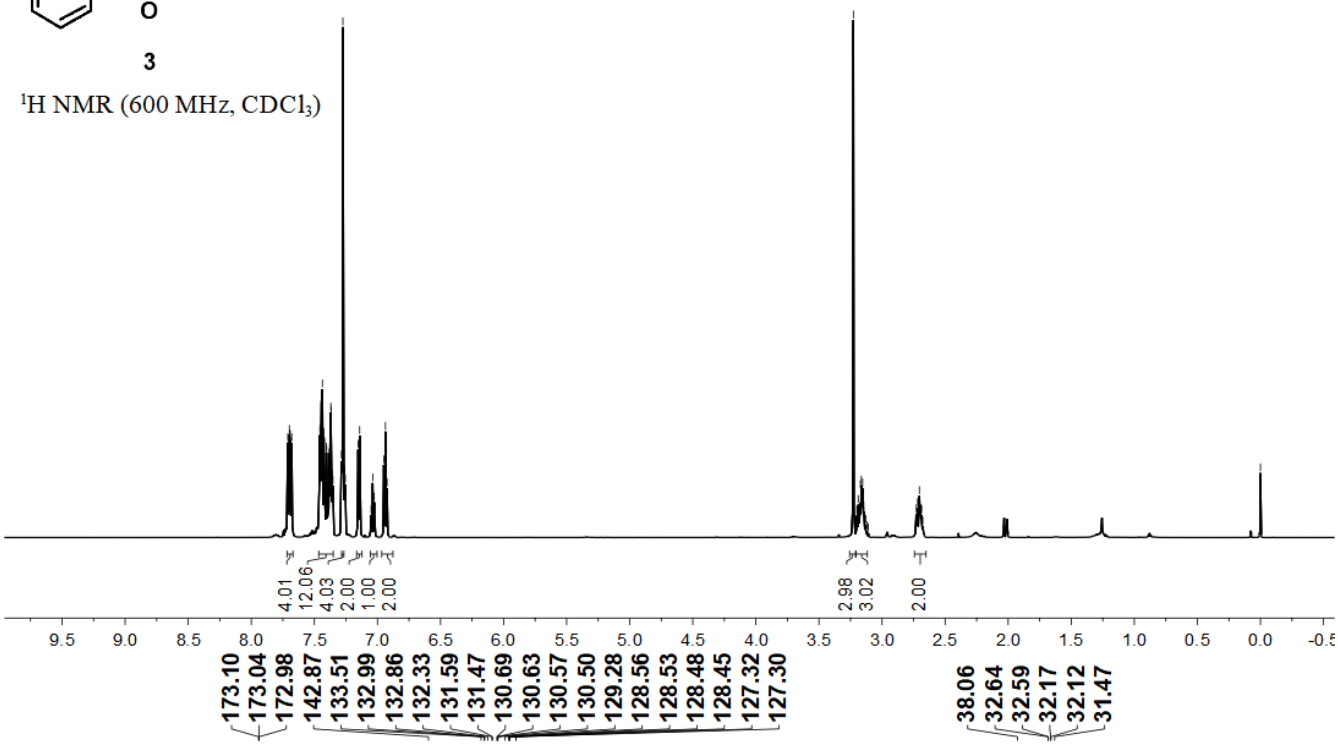


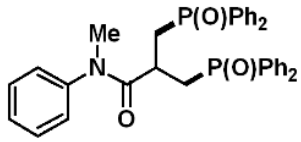




3

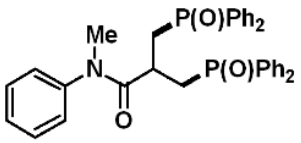
^{1}H NMR (600 MHz, $CDCl_3$)





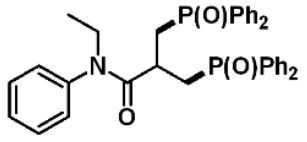
3

^{13}C NMR (151 MHz, $CDCl_3$)



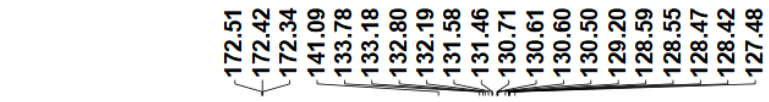
3

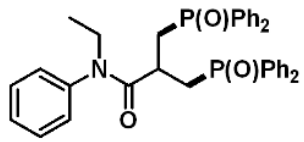
^{31}P NMR (243 MHz, $CDCl_3$)



4

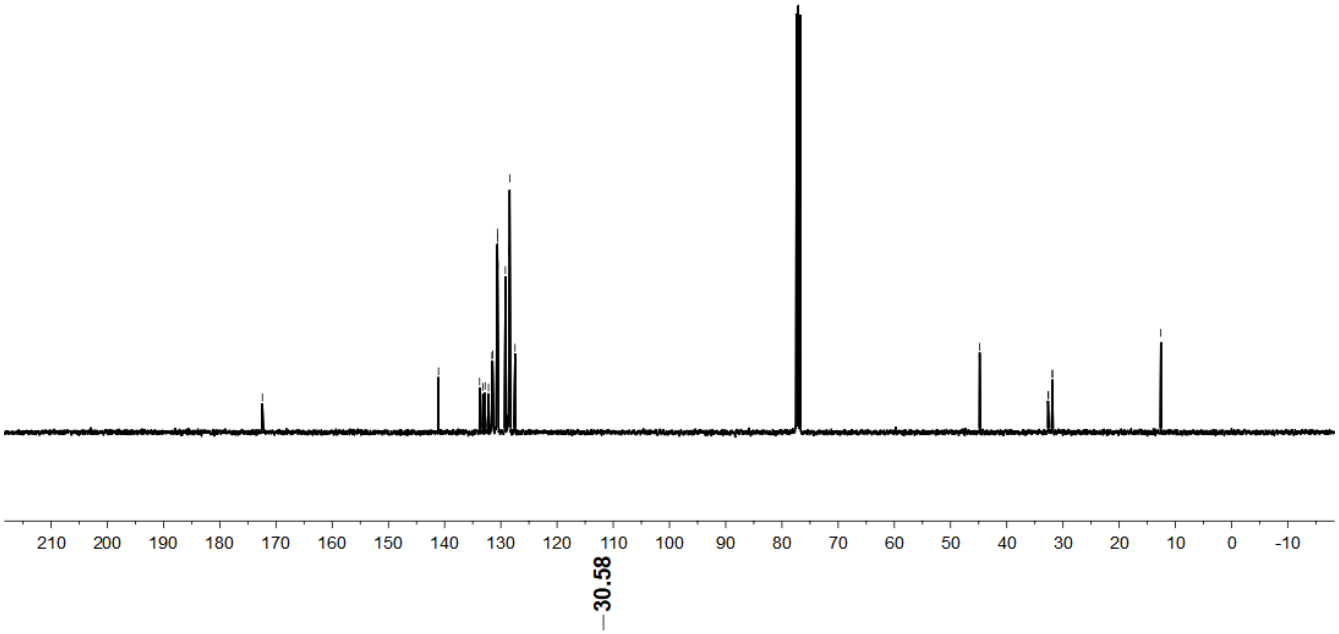
^{1}H NMR (400 MHz, $CDCl_3$)

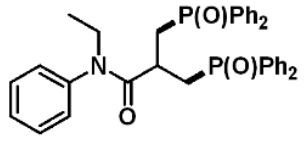




4

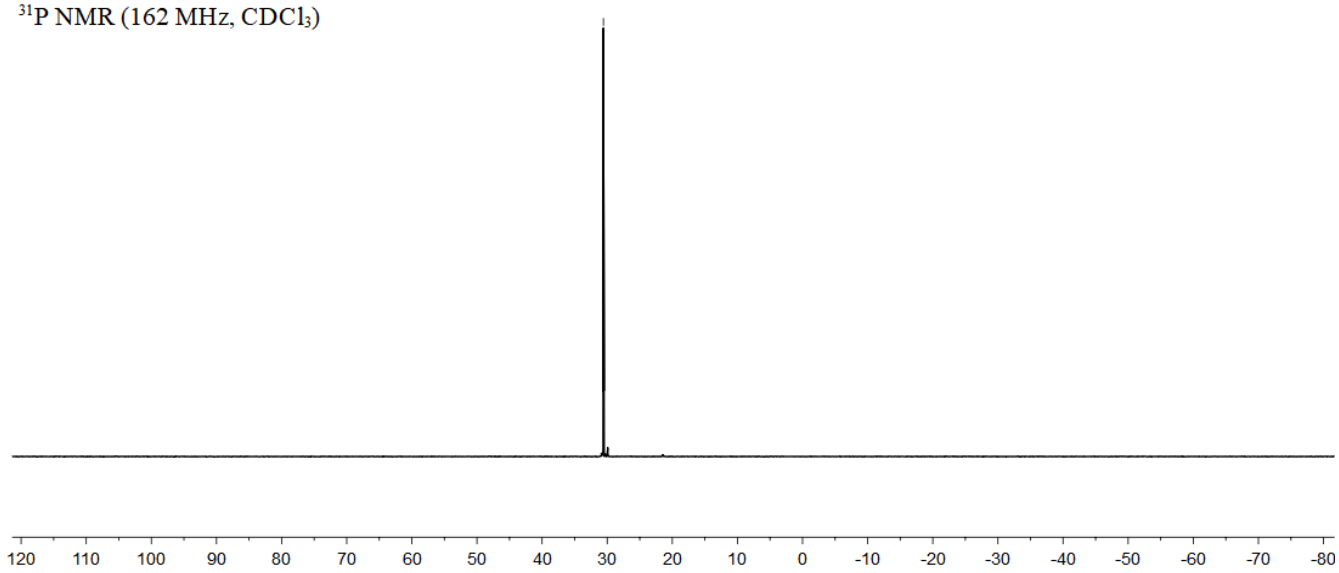
^{13}C NMR (101 MHz, $CDCl_3$)

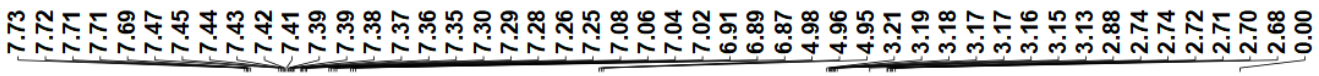


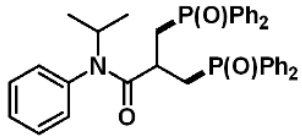


4

^{31}P NMR (162 MHz, $CDCl_3$)

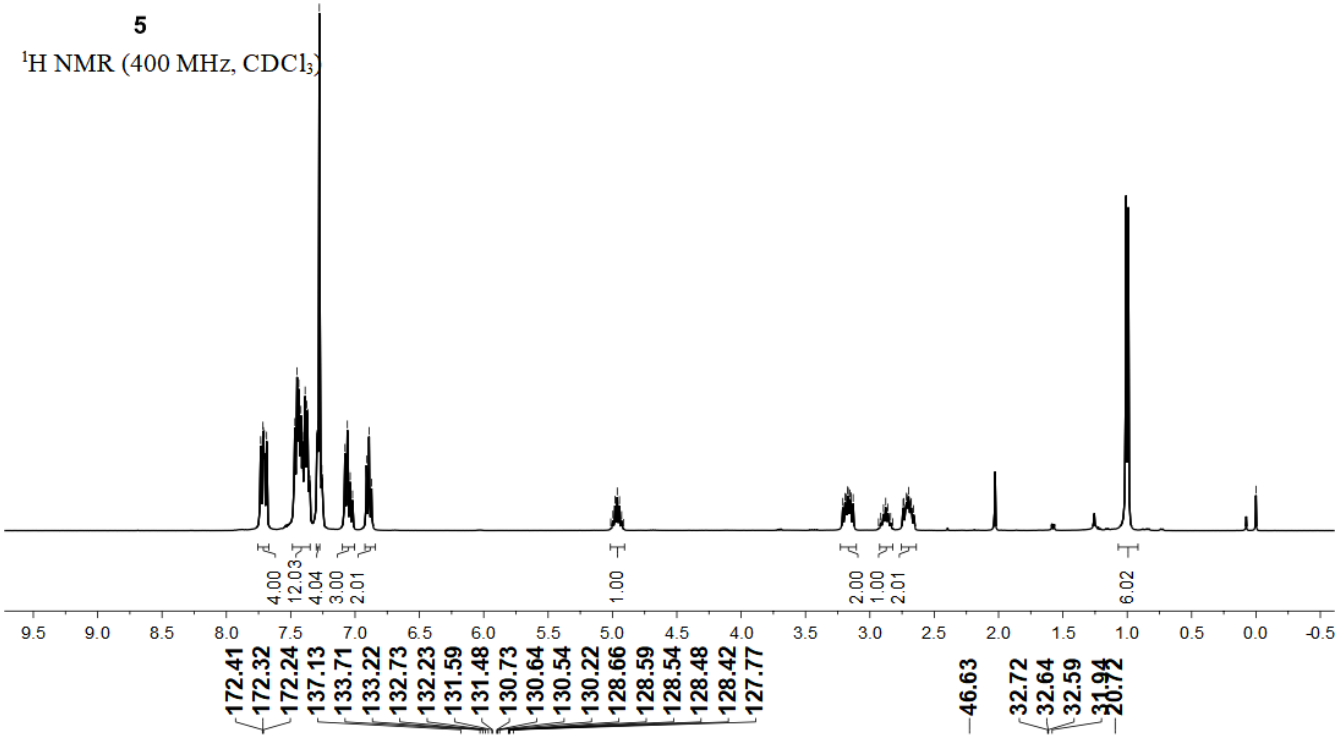


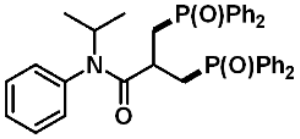




5

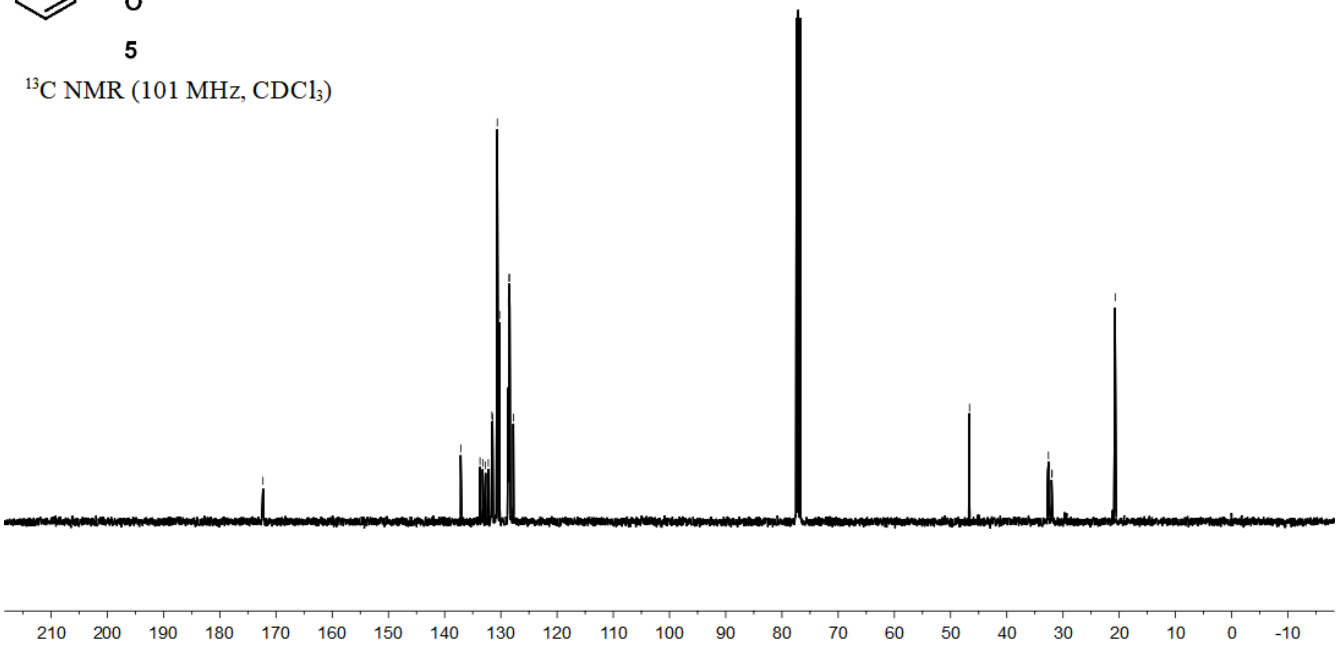
^{1}H NMR (400 MHz, $CDCl_3$)

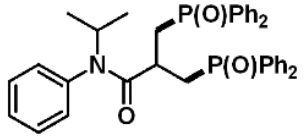




5

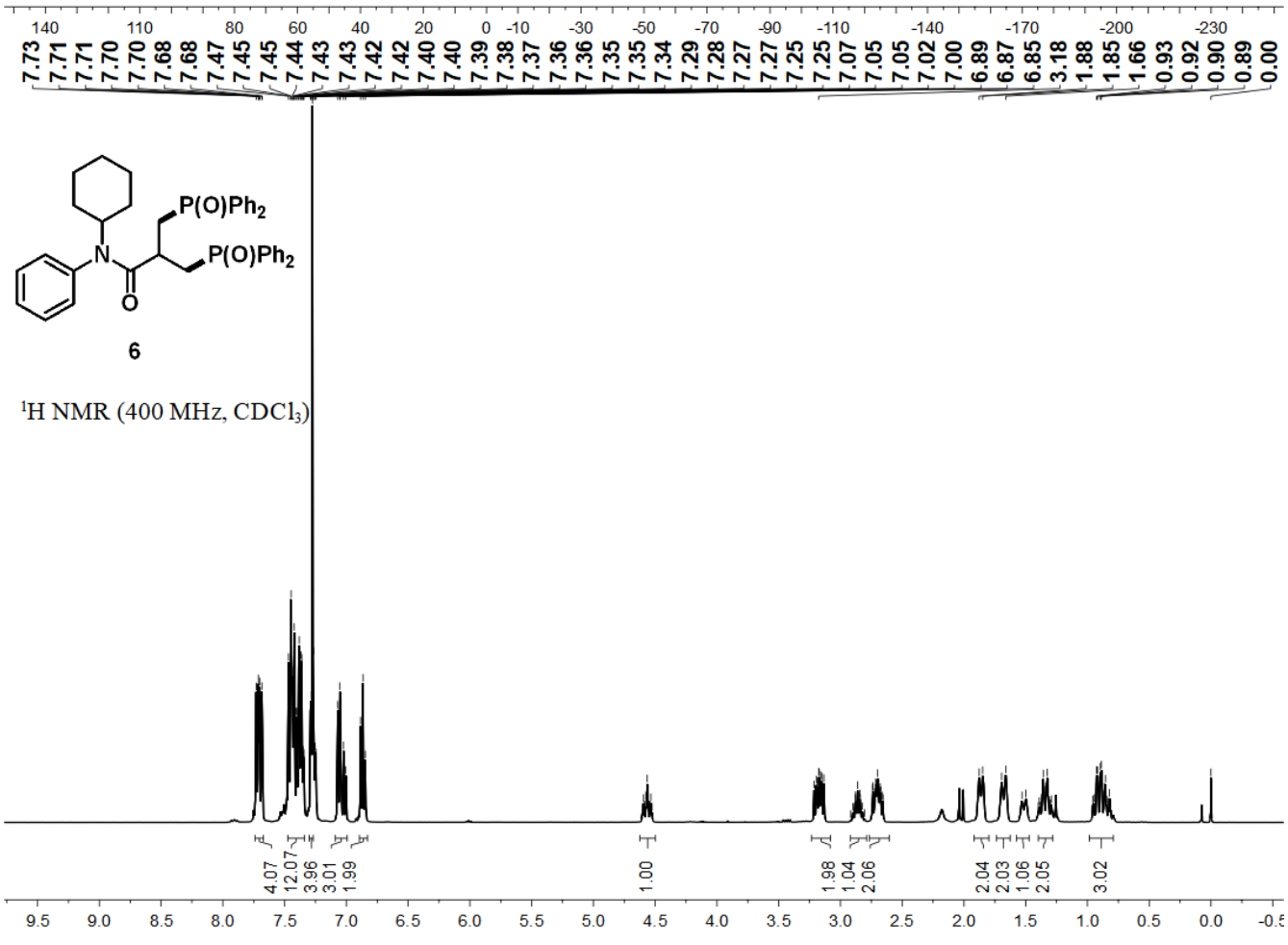
^{13}C NMR (101 MHz, $CDCl_3$)





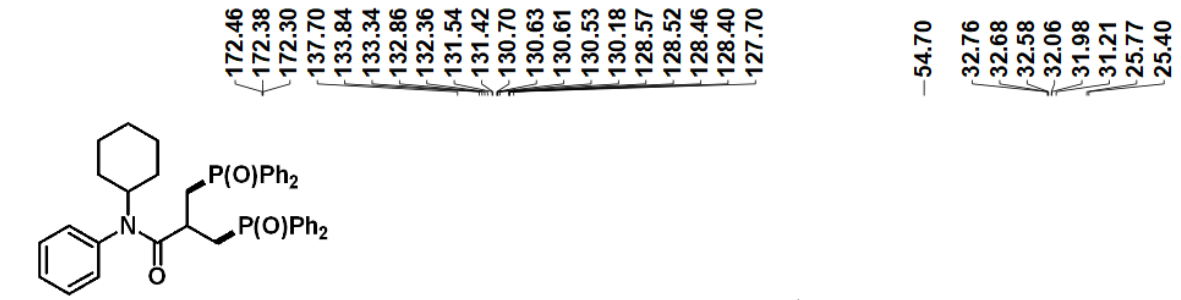
5

^{31}P NMR (162 MHz, $CDCl_3$)



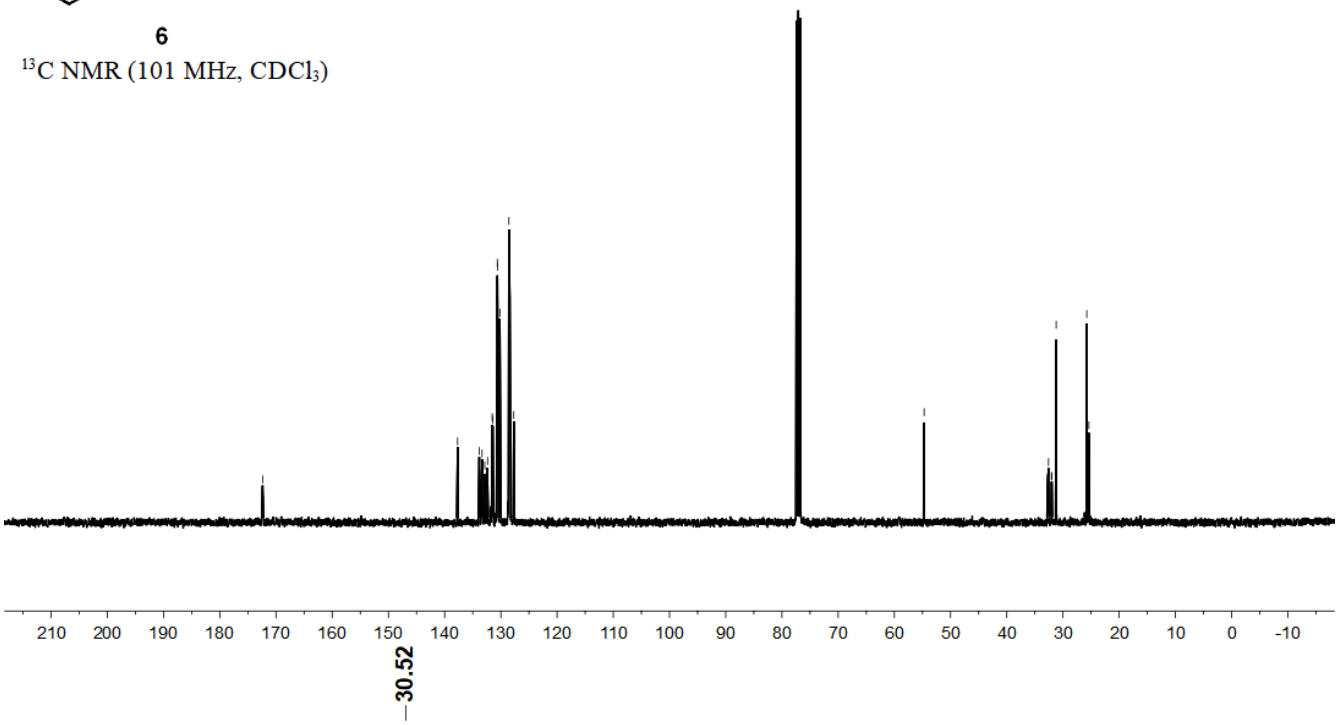
6

^{1}H NMR (400 MHz, $CDCl_3$)

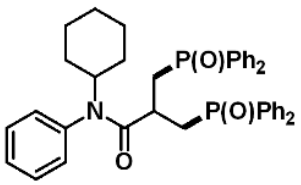


6

^{13}C NMR (101 MHz, $CDCl_3$)

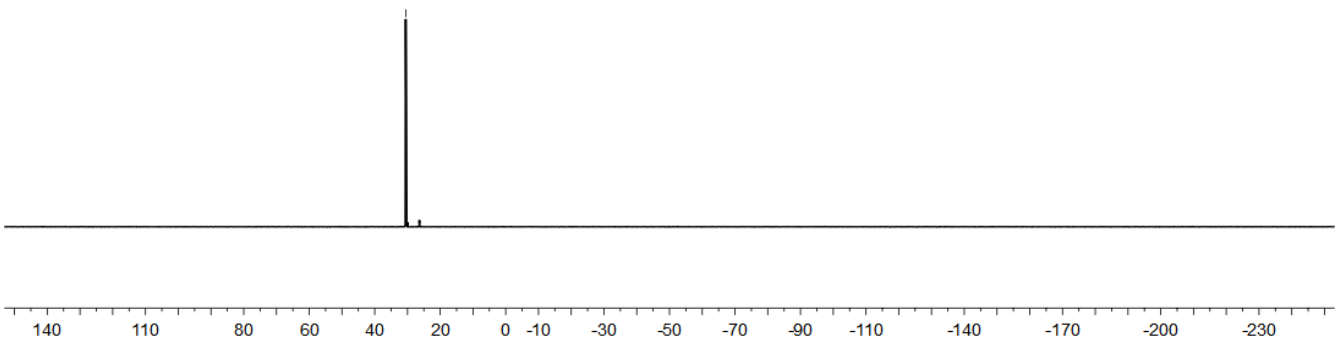


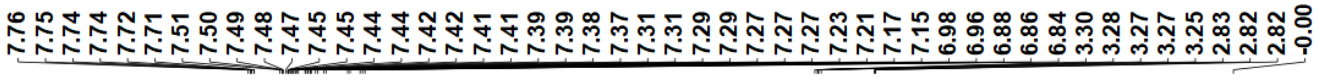
30.52

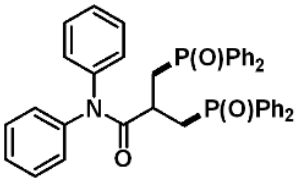


6

^{31}P NMR (162 MHz, $CDCl_3$)

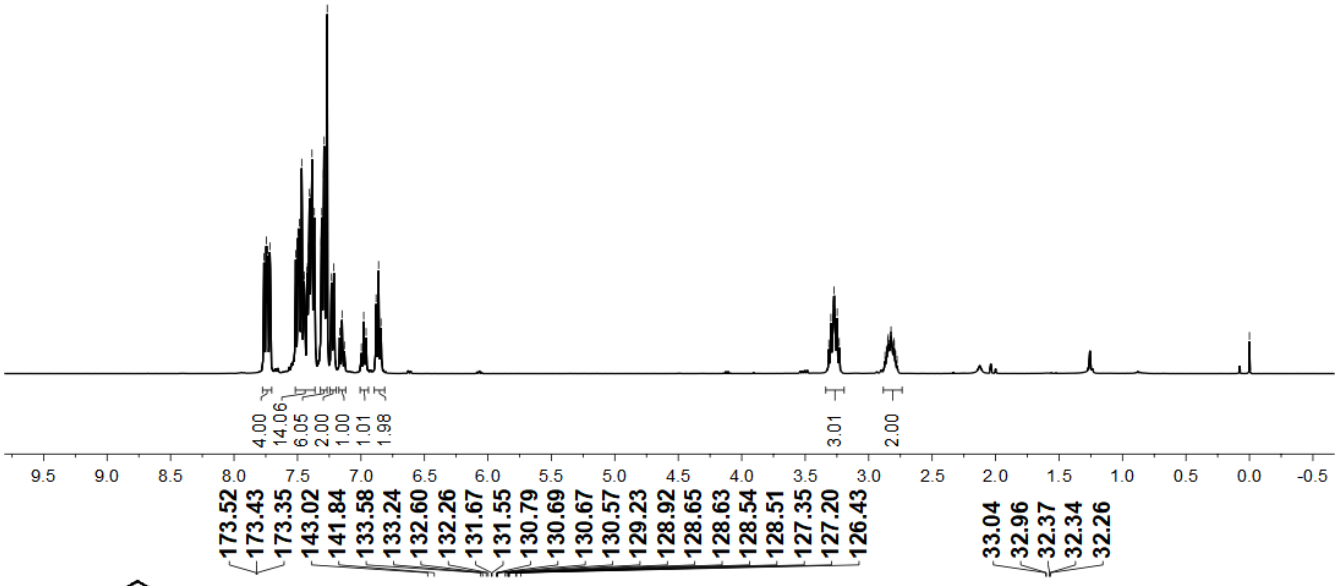


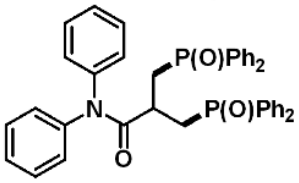




7

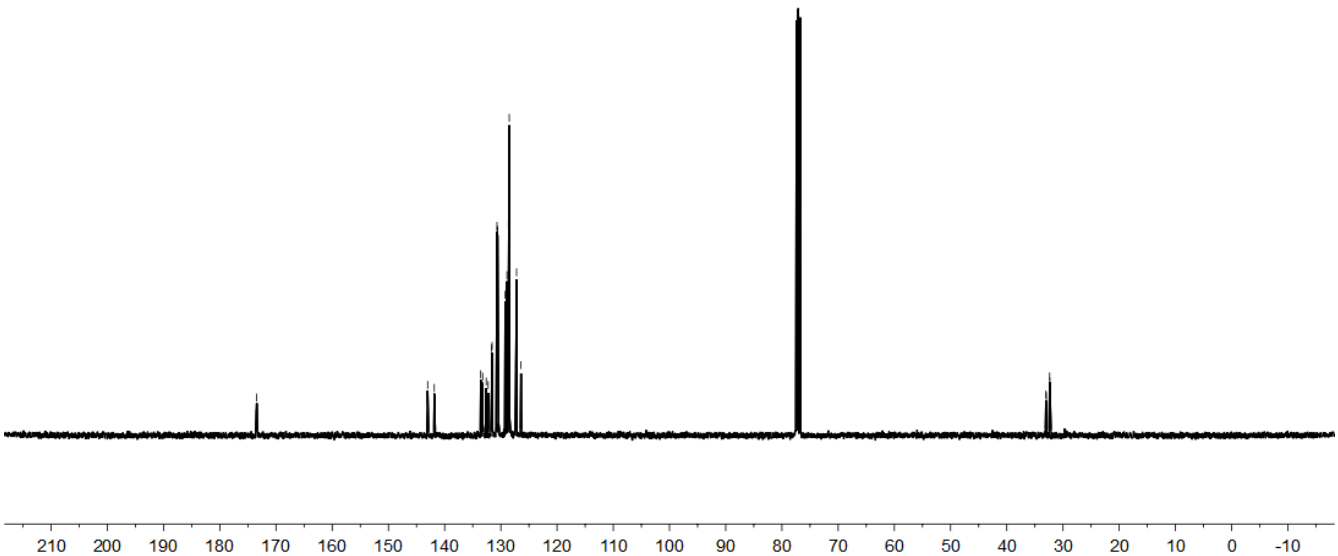
^{1}H NMR (400 MHz, $CDCl_3$)

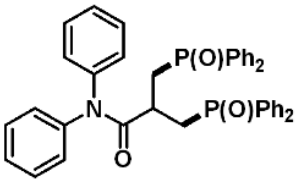




7

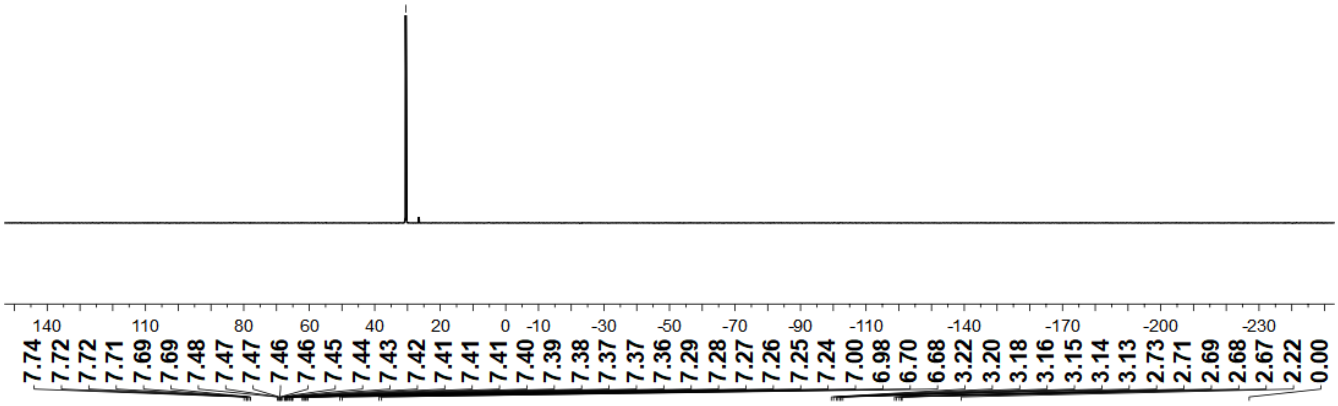
^{13}C NMR (101 MHz, $CDCl_3$)

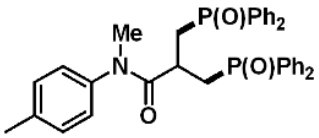




7

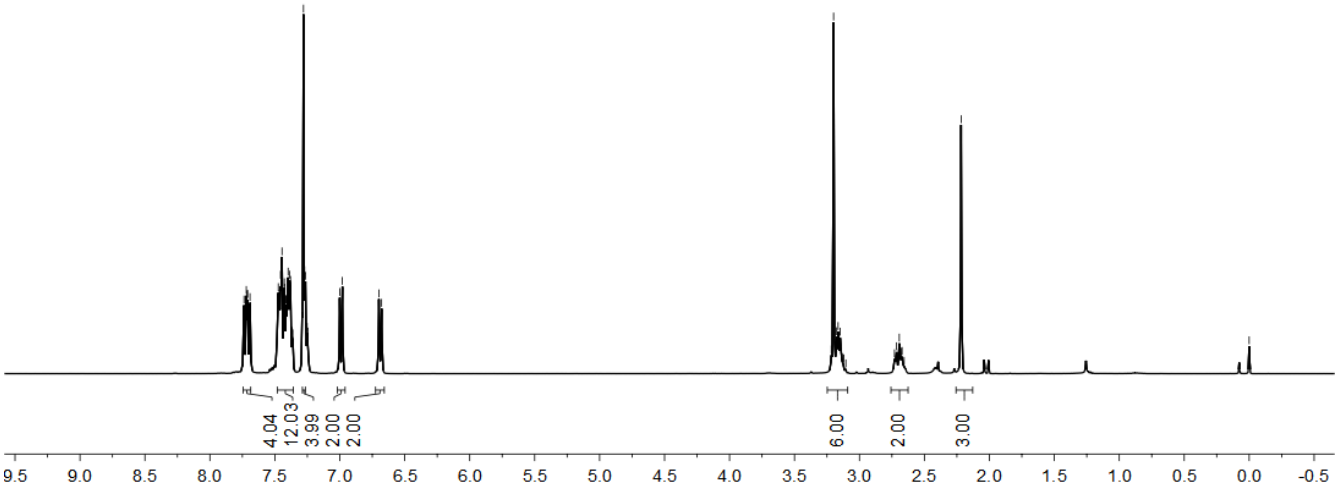
^{31}P NMR (162 MHz, $CDCl_3$)

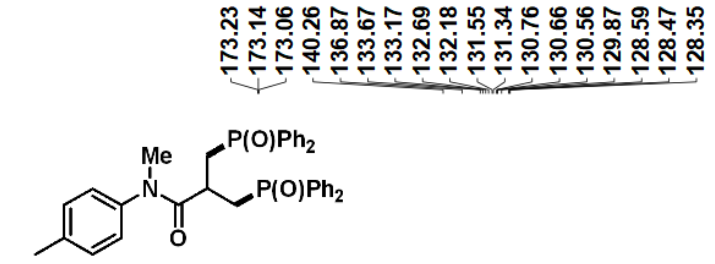




8

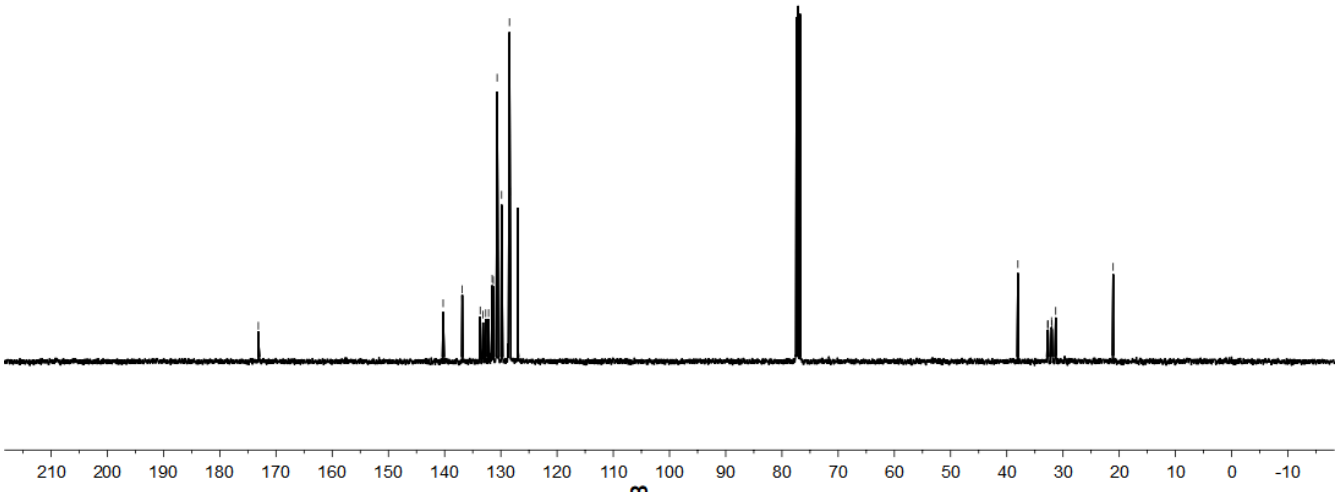
^{1}H NMR (400 MHz, $CDCl_3$)

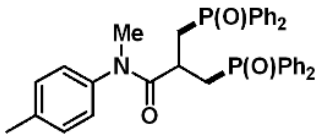




8

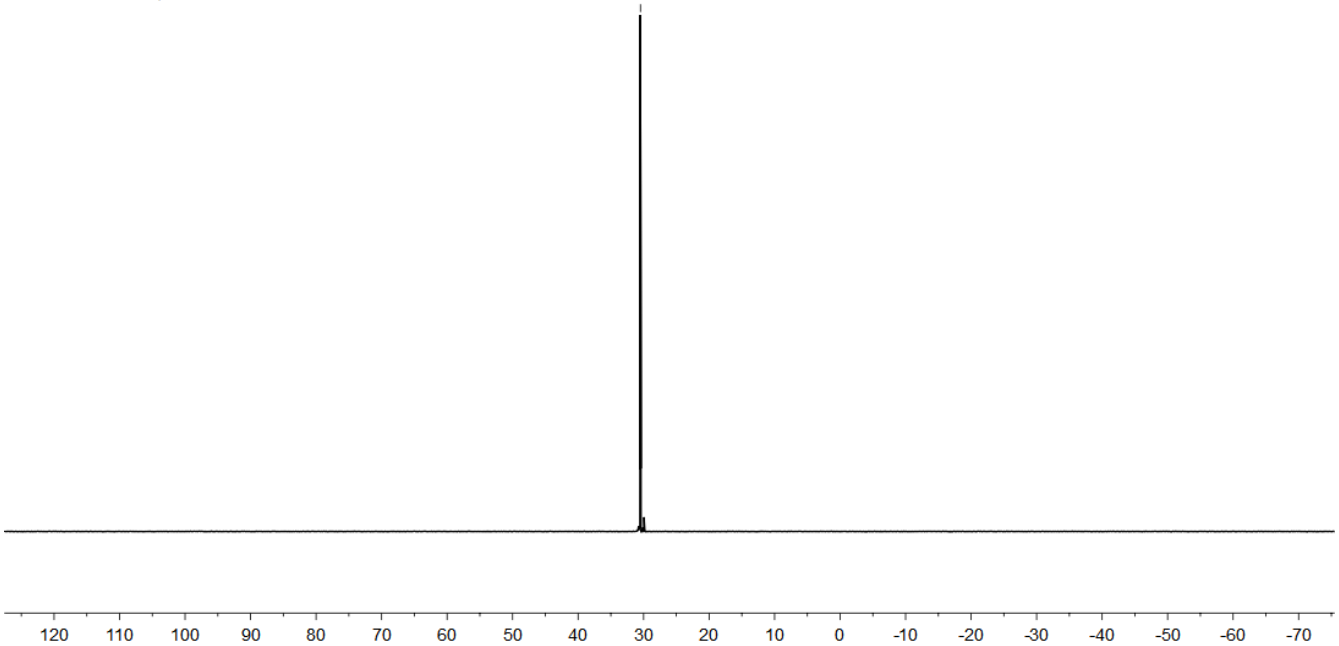
^{13}C NMR (101 MHz, $CDCl_3$)

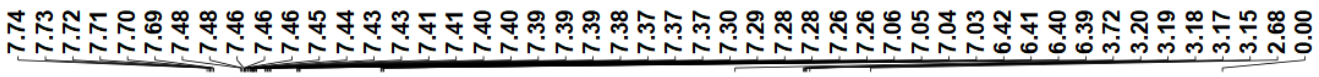


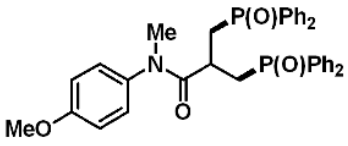


8

^{31}P NMR (162 MHz, $CDCl_3$)

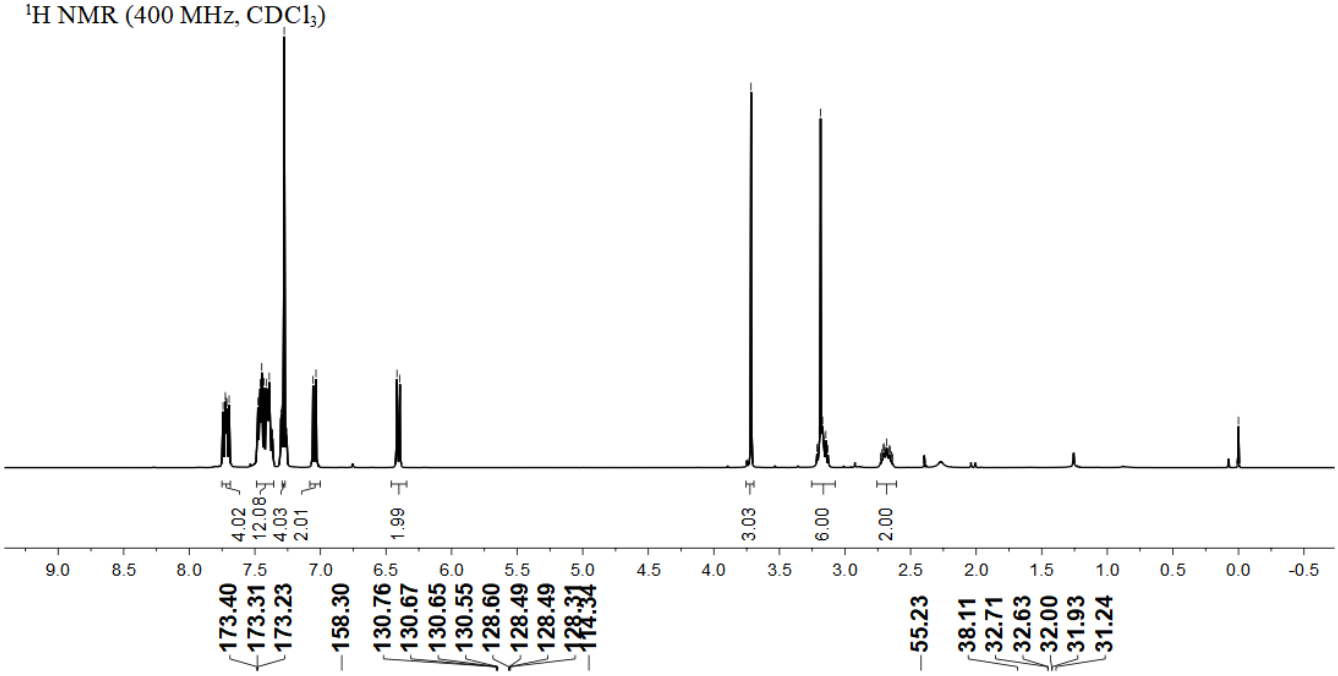


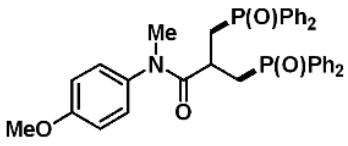




9

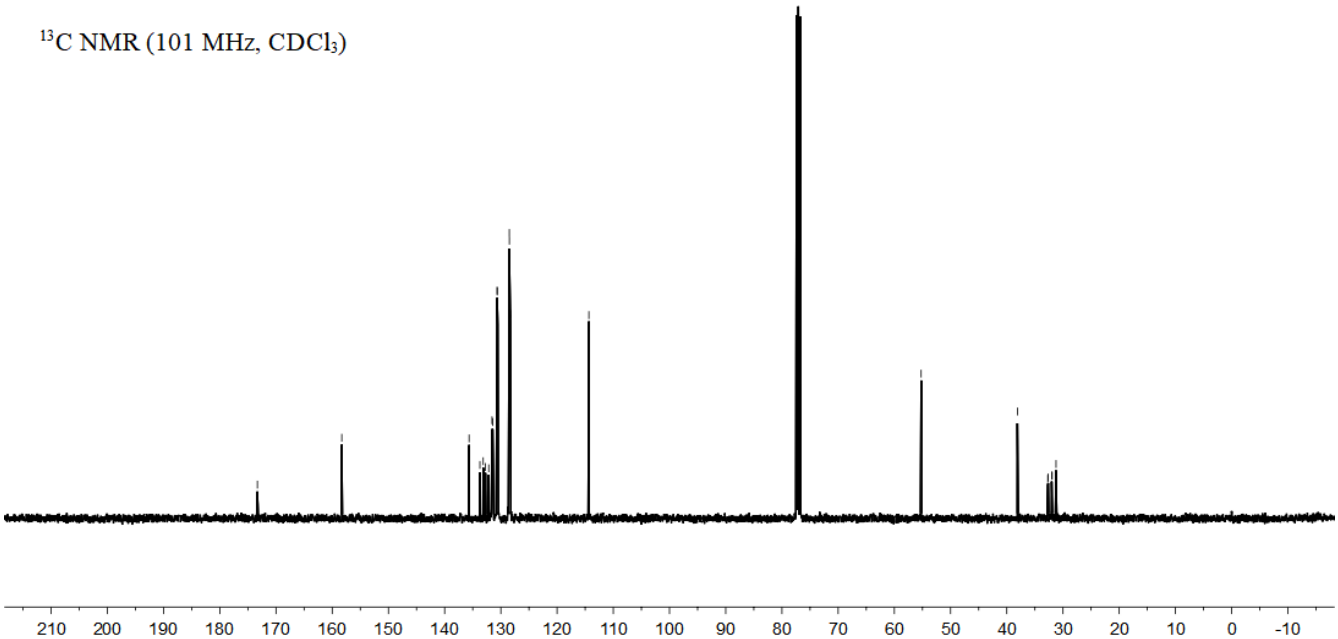
^{1}H NMR (400 MHz, $CDCl_3$)

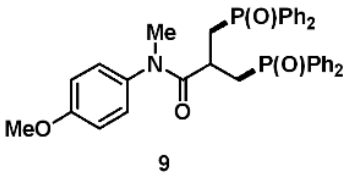




9

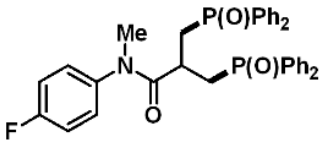
^{13}C NMR (101 MHz, $CDCl_3$)





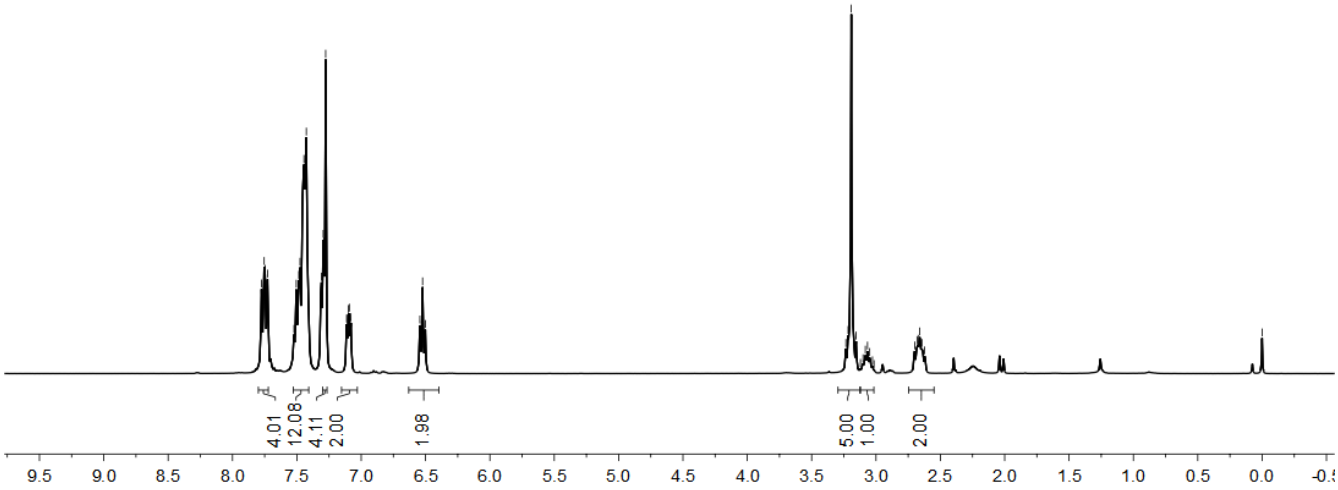
9

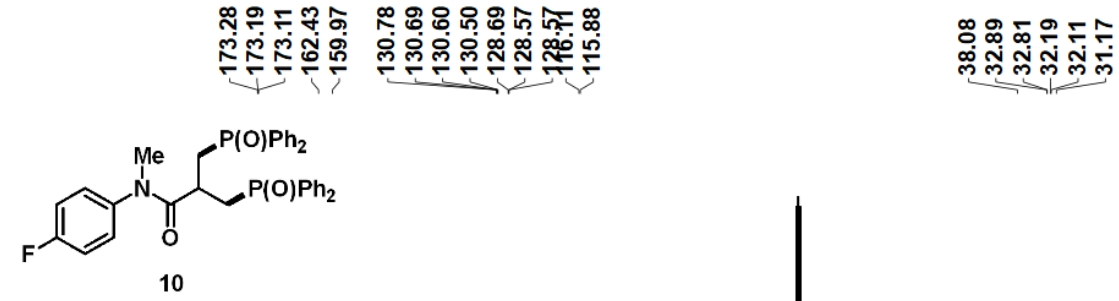
^{31}P NMR (162 MHz, $CDCl_3$)



10

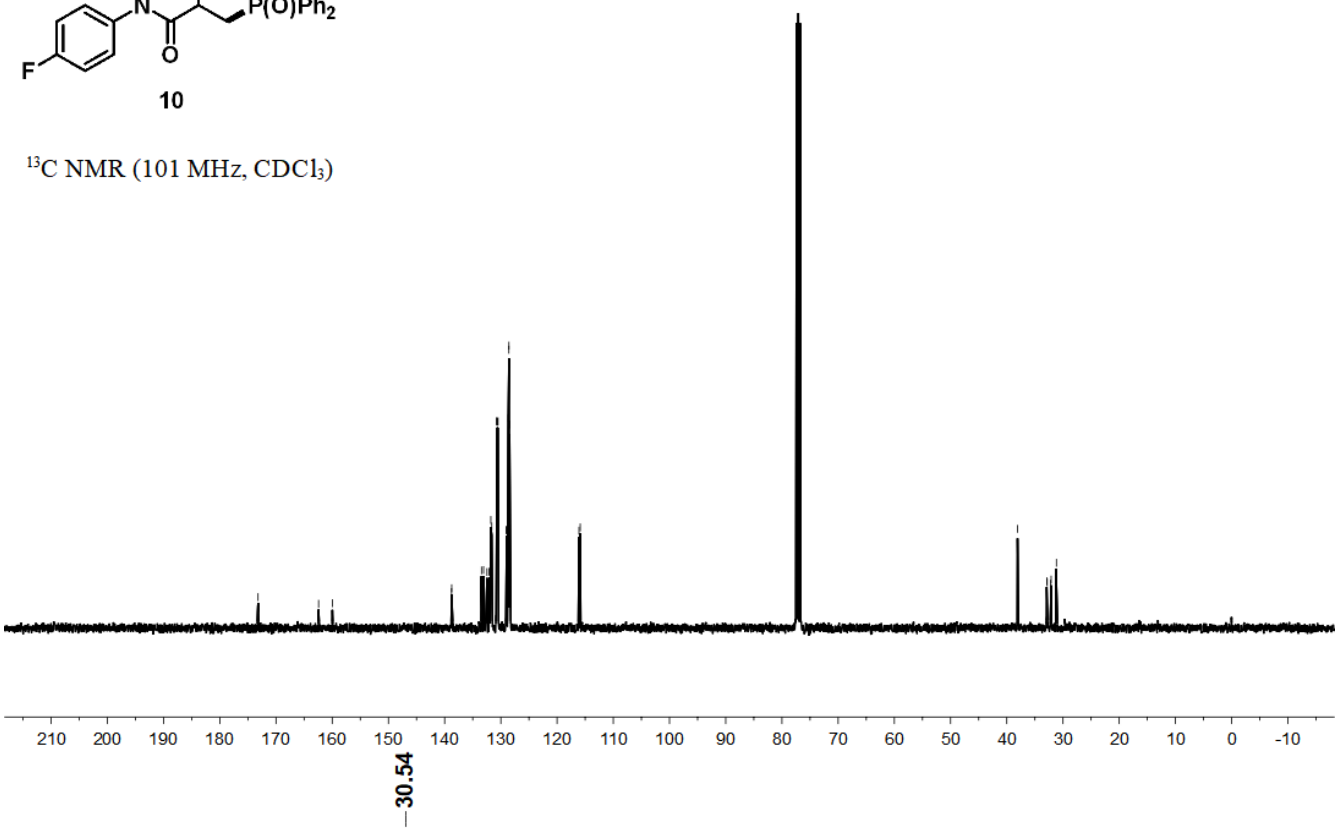
^{1}H NMR (400 MHz, $CDCl_3$)

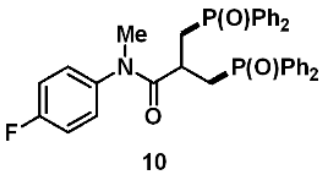




10

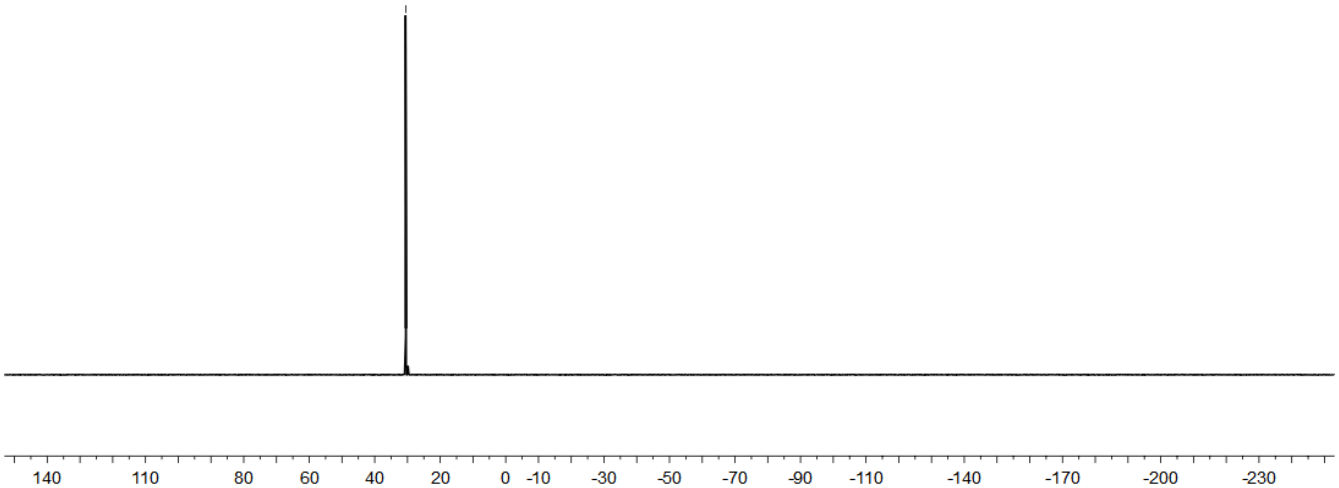
^{13}C NMR (101 MHz, $CDCl_3$)

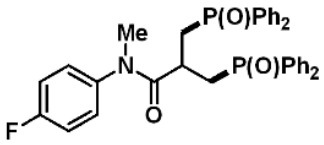




10

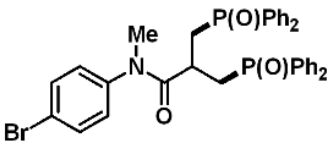
^{31}P NMR (162 MHz, $CDCl_3$)





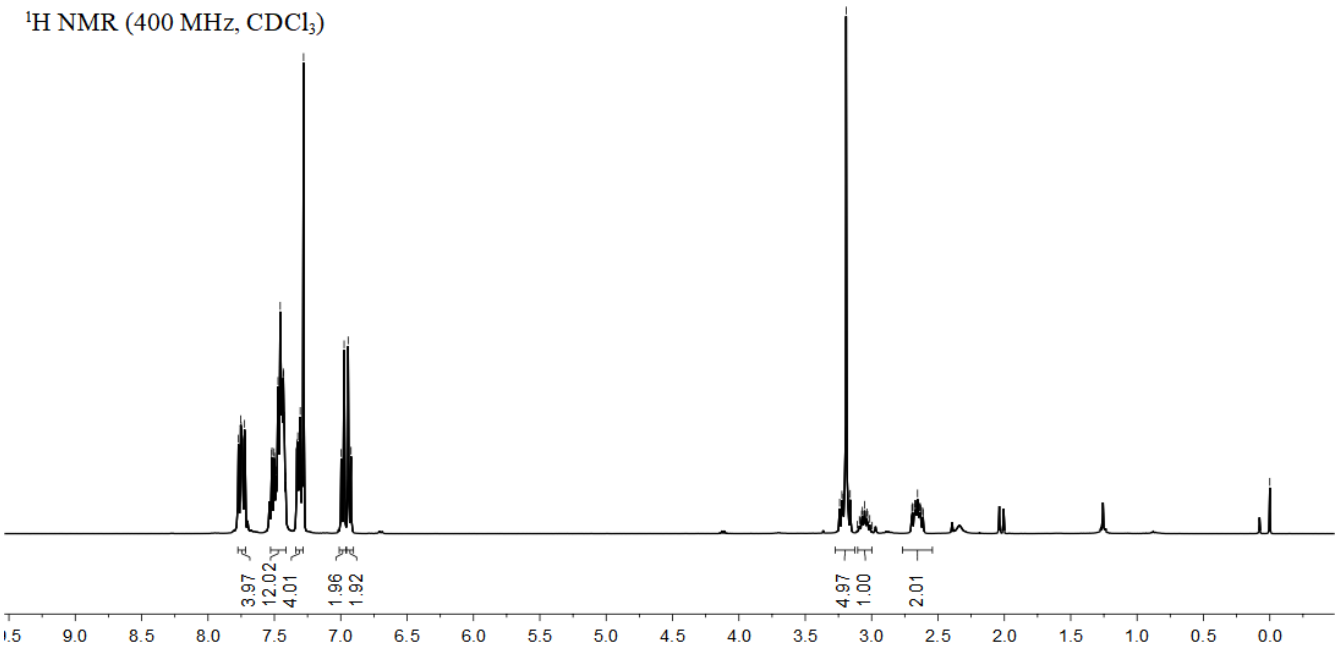
10

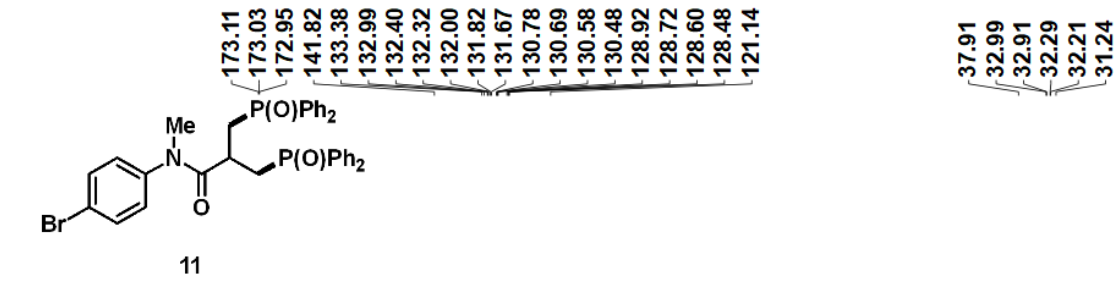
^{19}F NMR (376 MHz, $CDCl_3$)



11

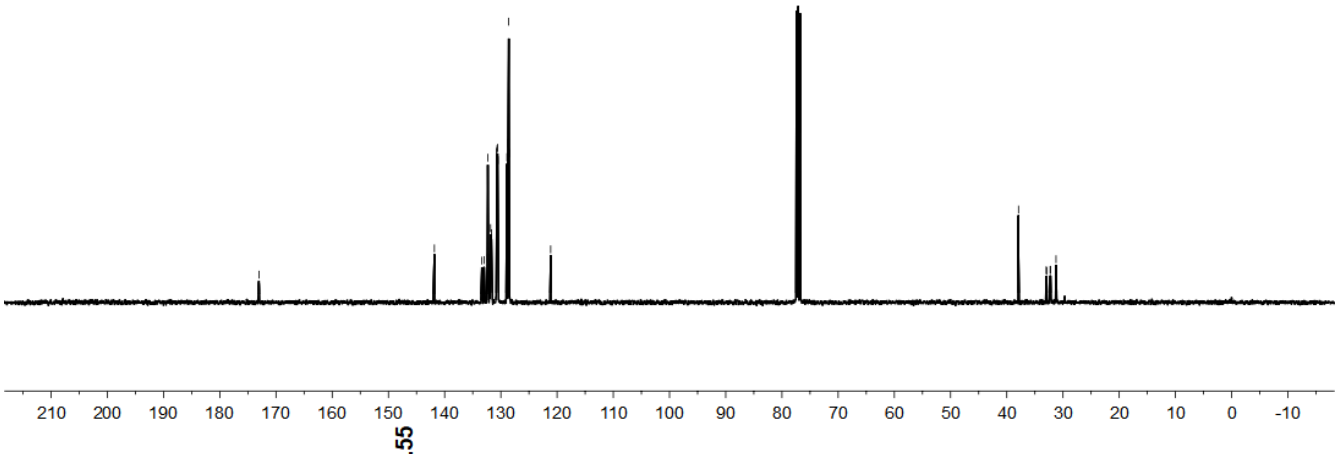
^{1}H NMR (400 MHz, $CDCl_3$)



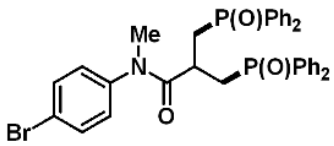


11

^{13}C NMR (101 MHz,$CDCl_3$)

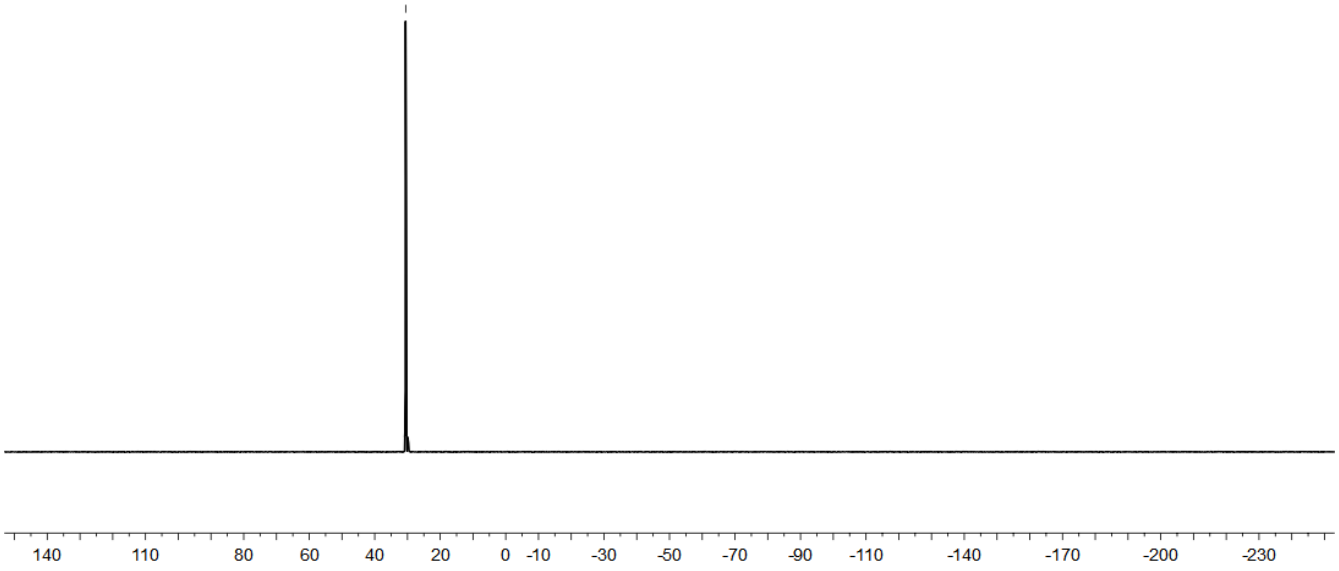


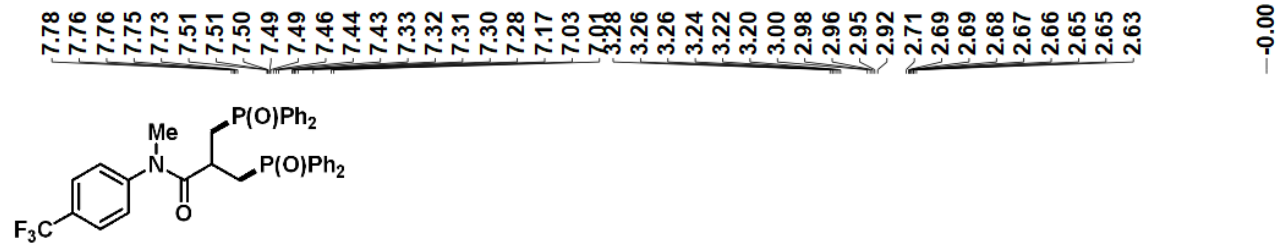
30.55



11

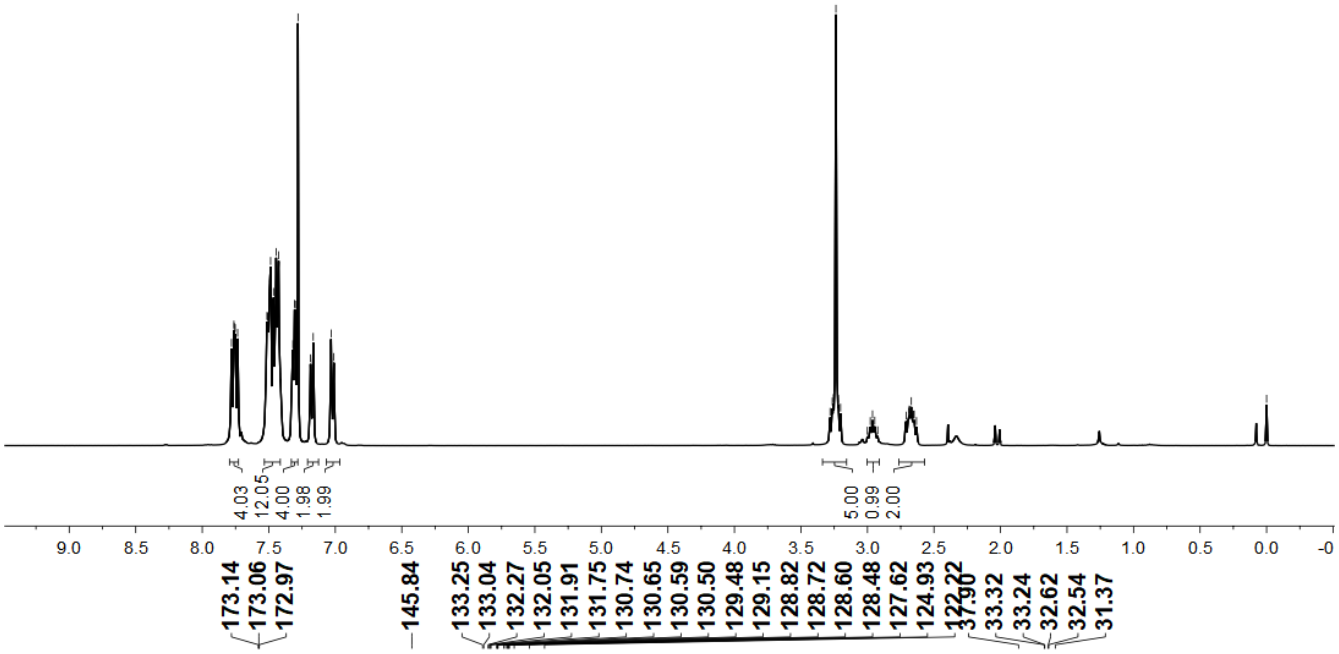
^{31}P NMR (162 MHz, $CDCl_3$)

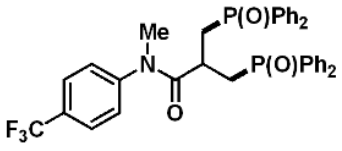




12

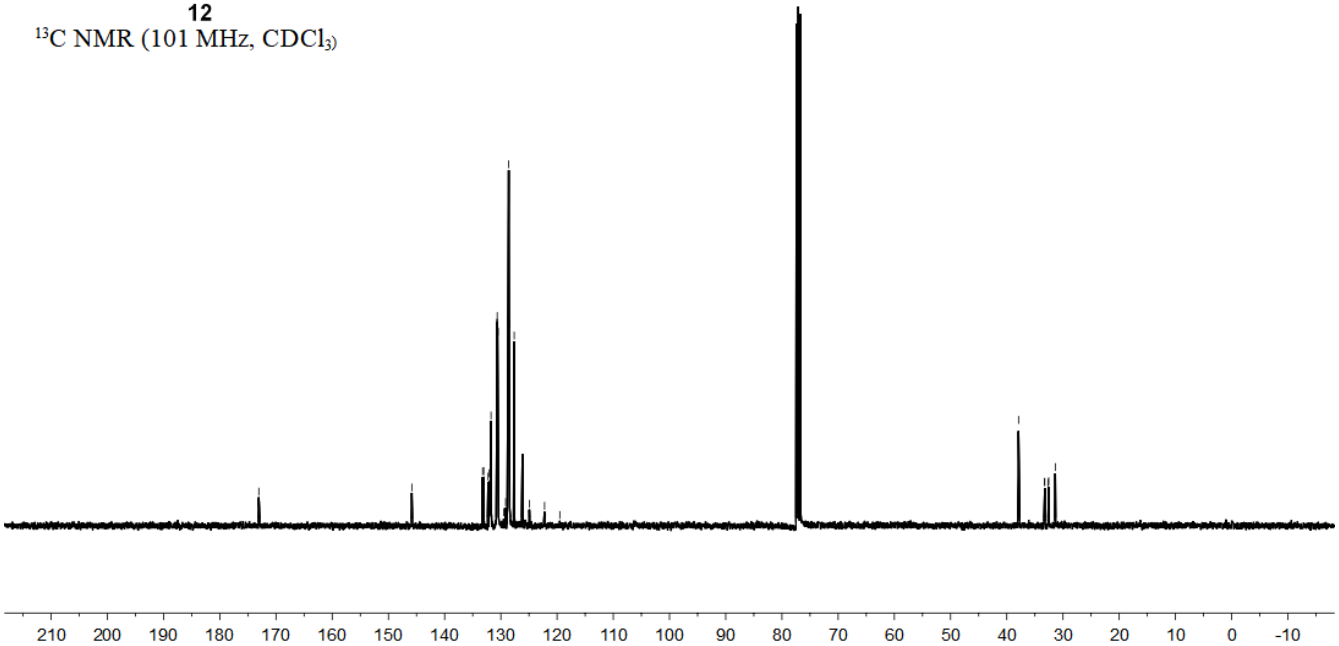
^{1}H NMR (400 MHz, $CDCl_3$)

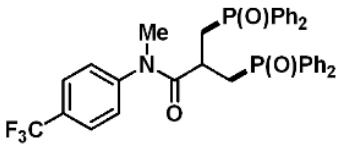




12

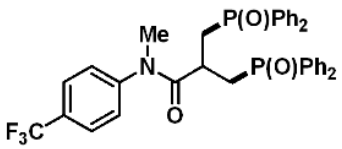
^{13}C NMR (101 MHz, $CDCl_3$)





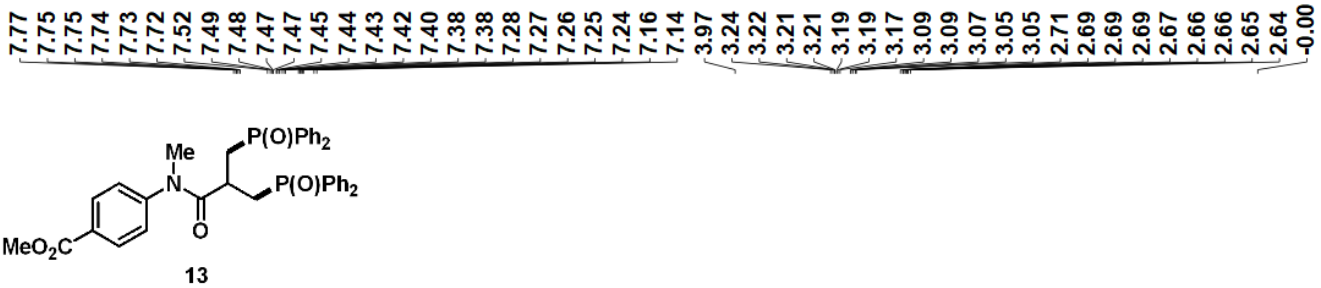
12

^{31}P NMR (162 MHz, $CDCl_3$)



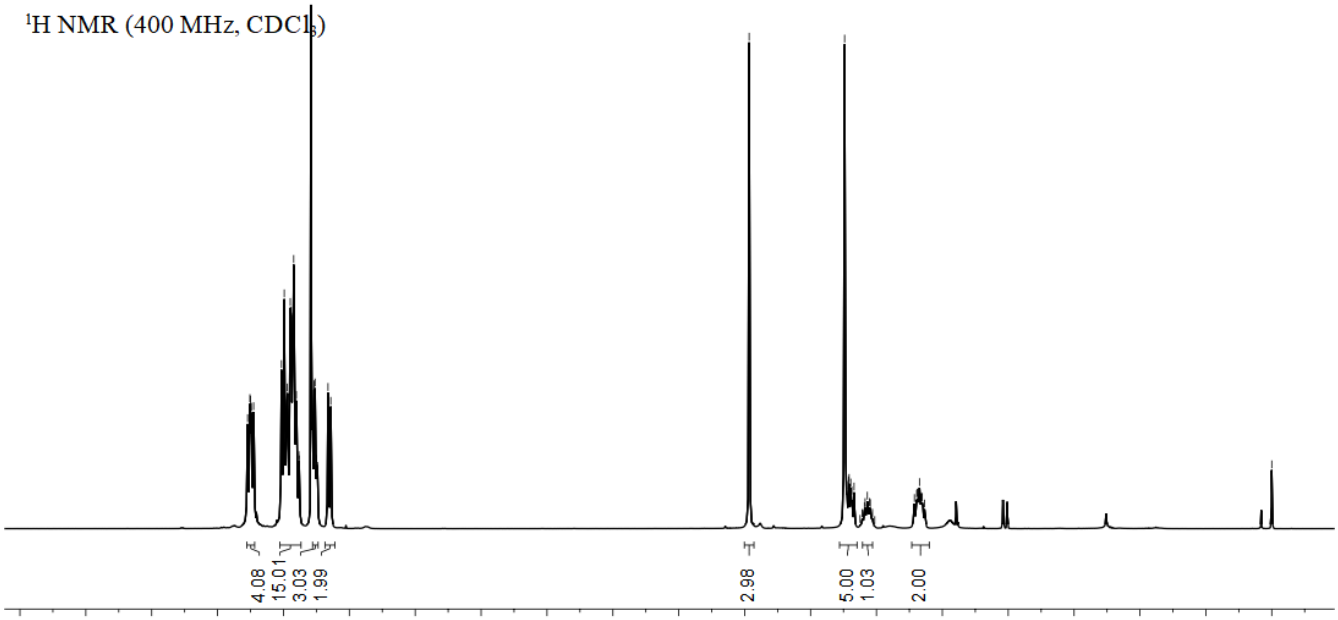
12

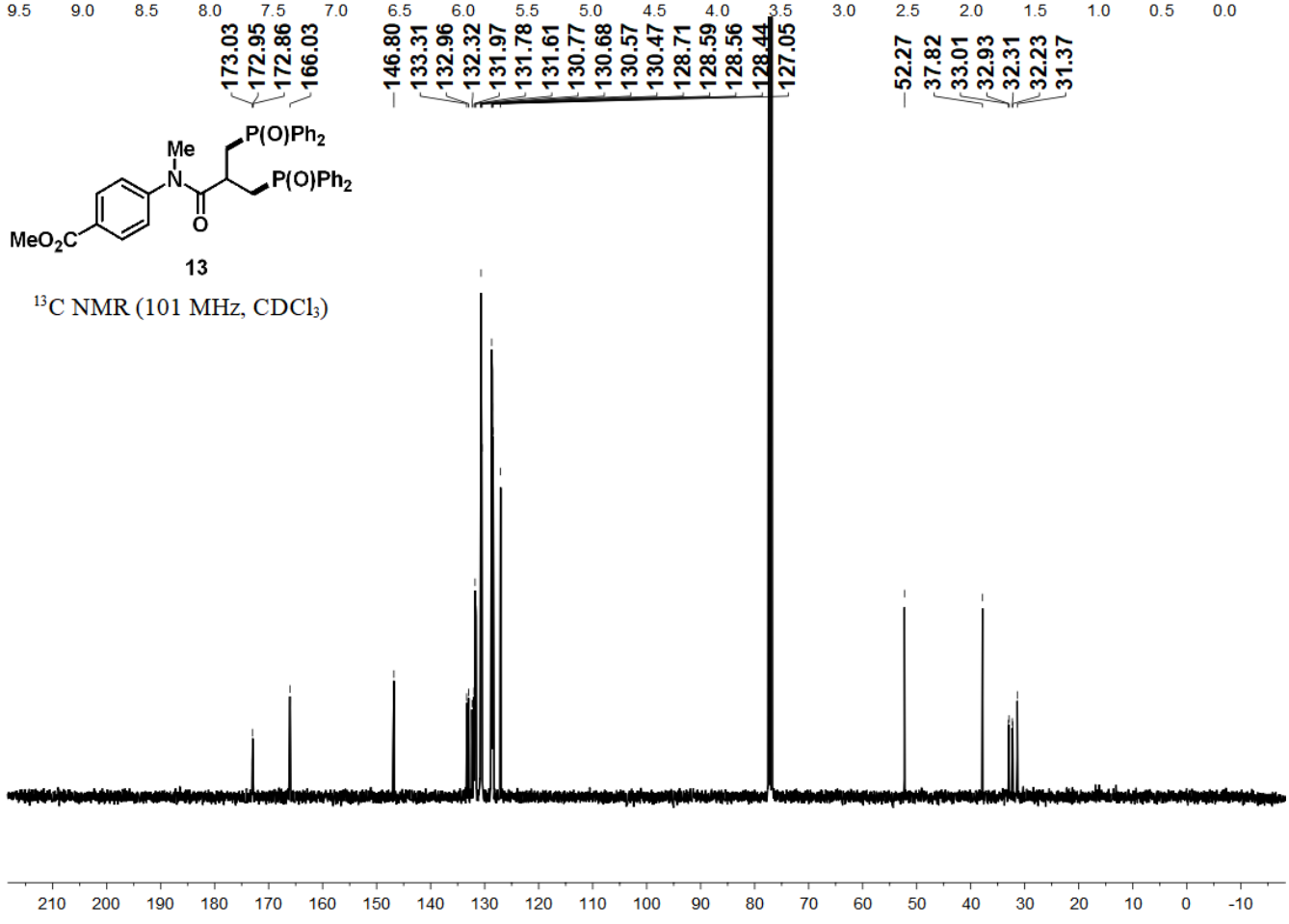
^{19}F NMR (376 MHz, $CDCl_3$)



13

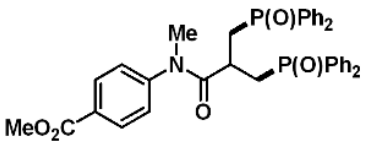
^{1}H NMR (400 MHz, $CDCl_3$)





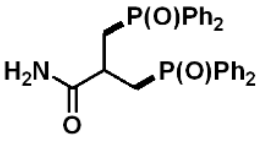
13

^{13}C NMR (101 MHz, $CDCl_3$)



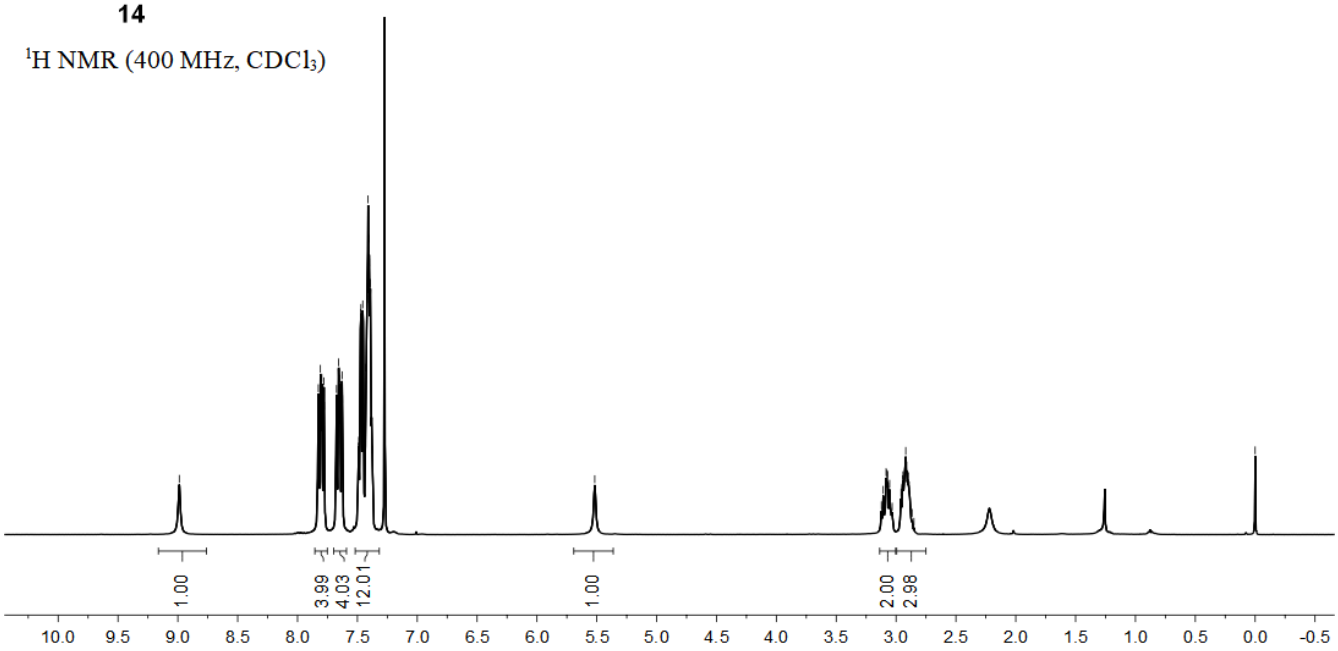
13

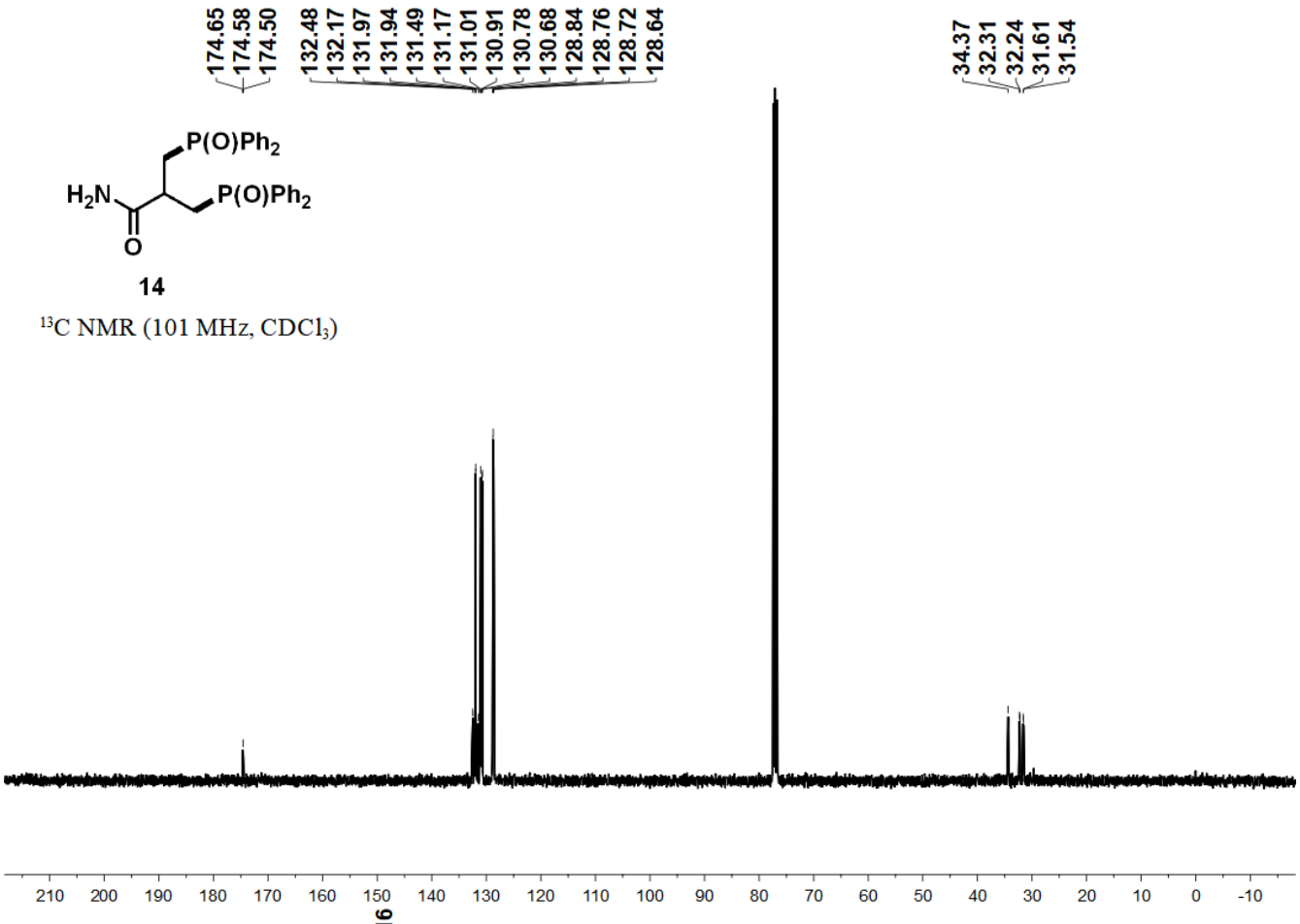
^{31}P NMR (162 MHz, $CDCl_3$)



14

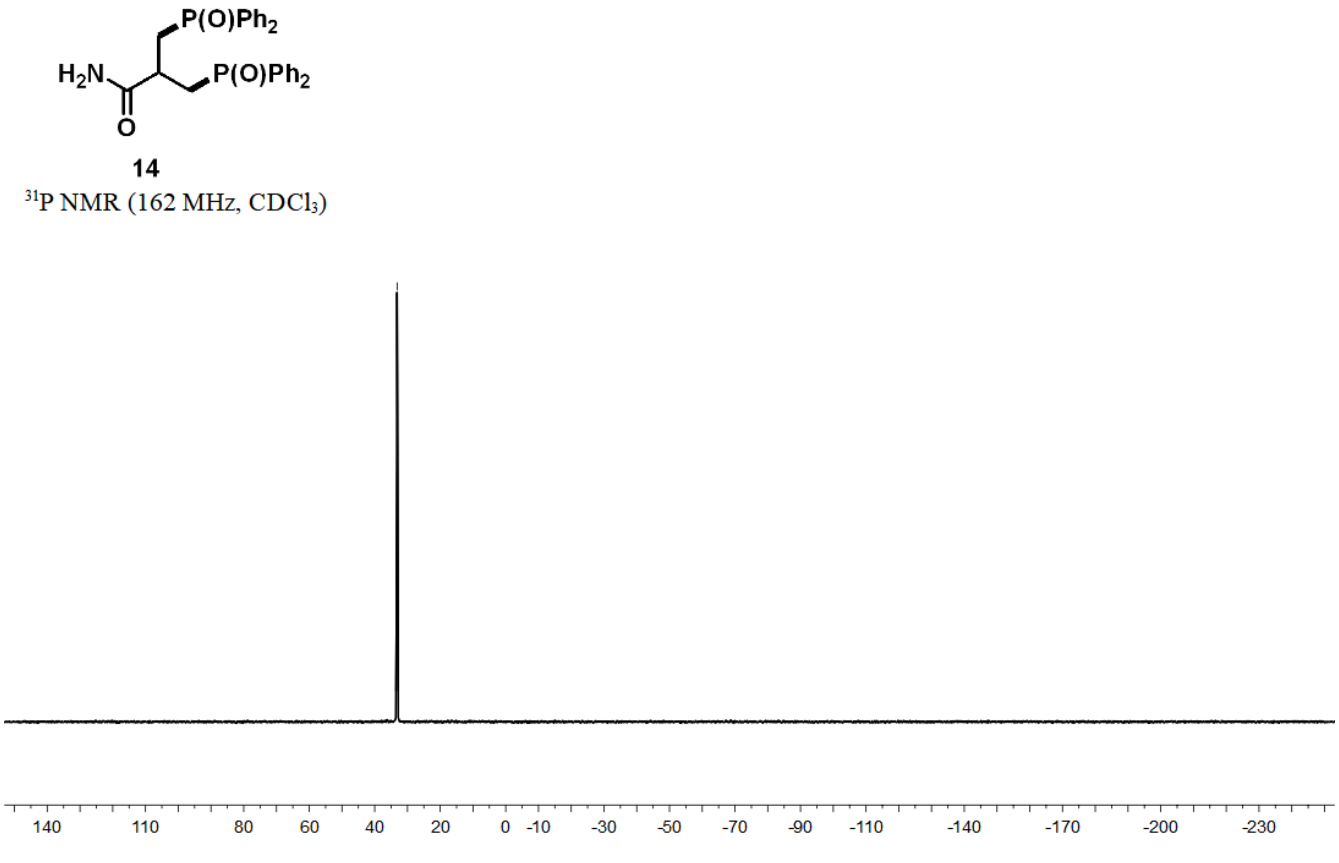
^{1}H NMR (400 MHz, $CDCl_3$)





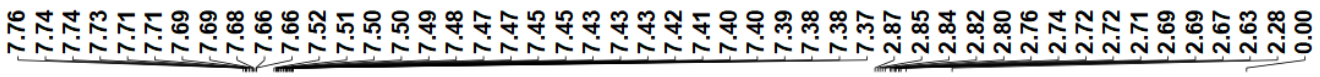
14

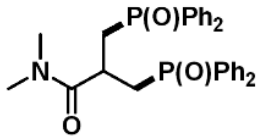
^{13}C NMR (101 MHz, $CDCl_3$)



14

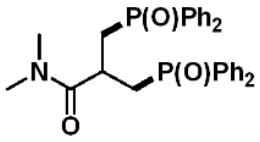
^{31}P NMR (162 MHz, $CDCl_3$)





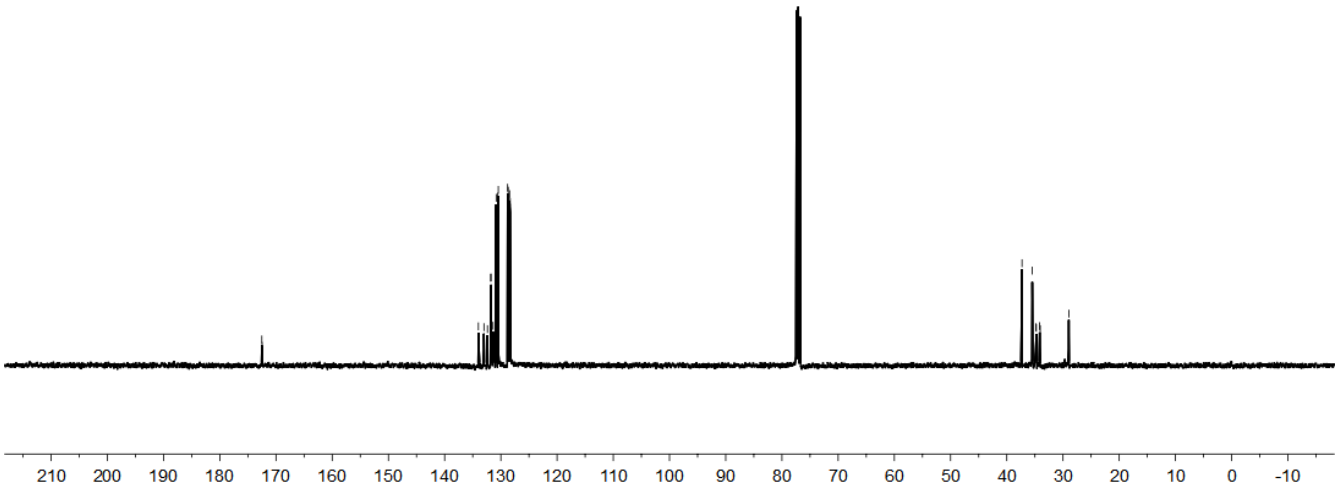
15

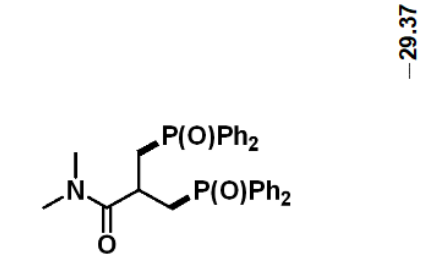
^{1}H NMR (400 MHz, $CDCl_3$)



15

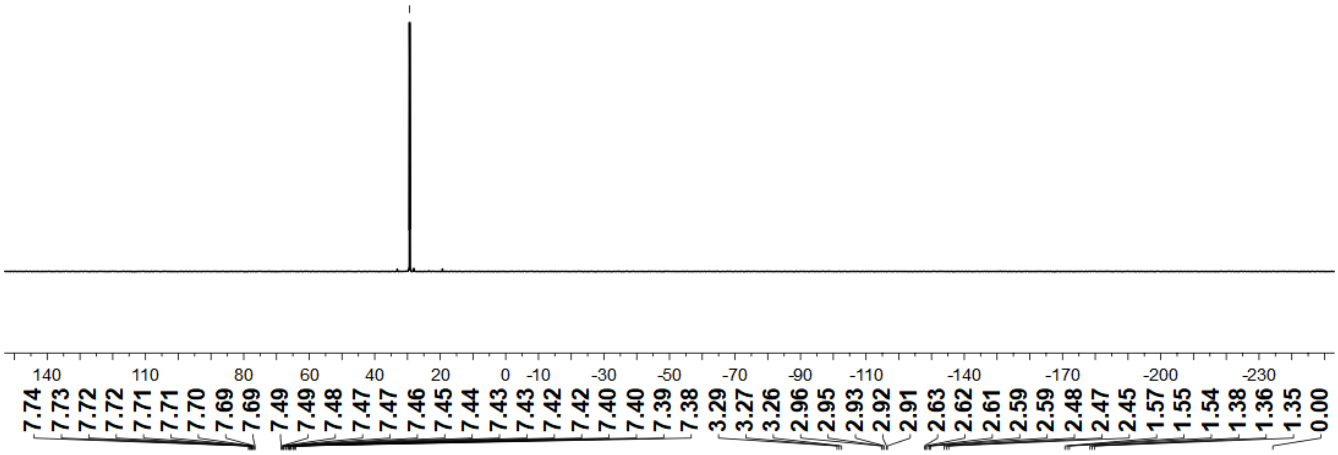
^{13}C NMR (101 MHz, $CDCl_3$)

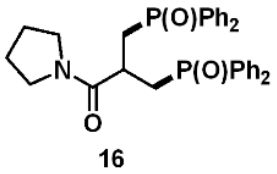




15

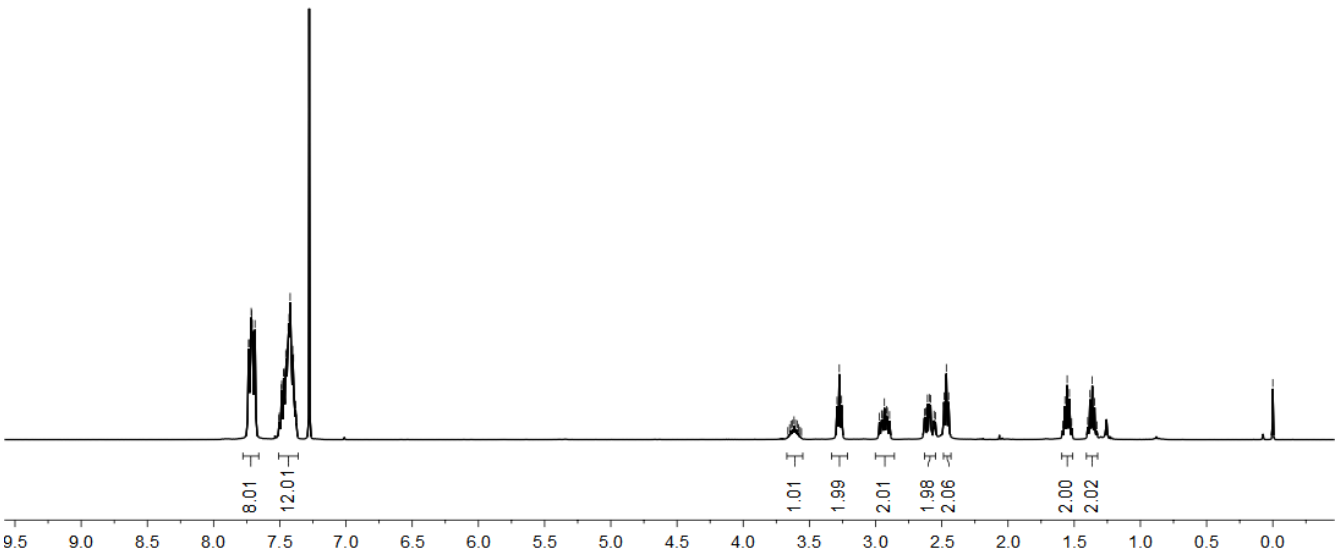
^{31}P NMR (162 MHz, $CDCl_3$)

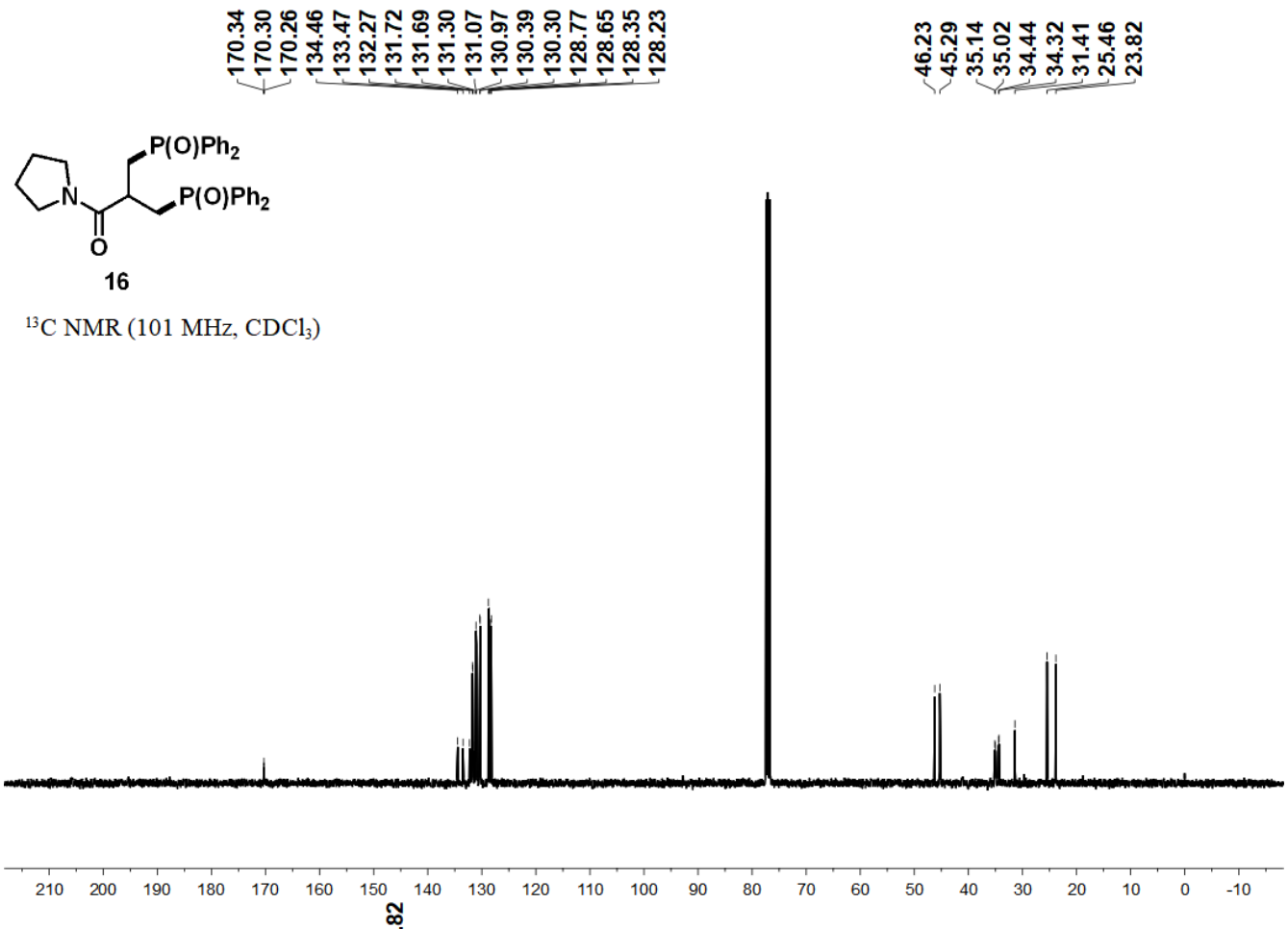




16

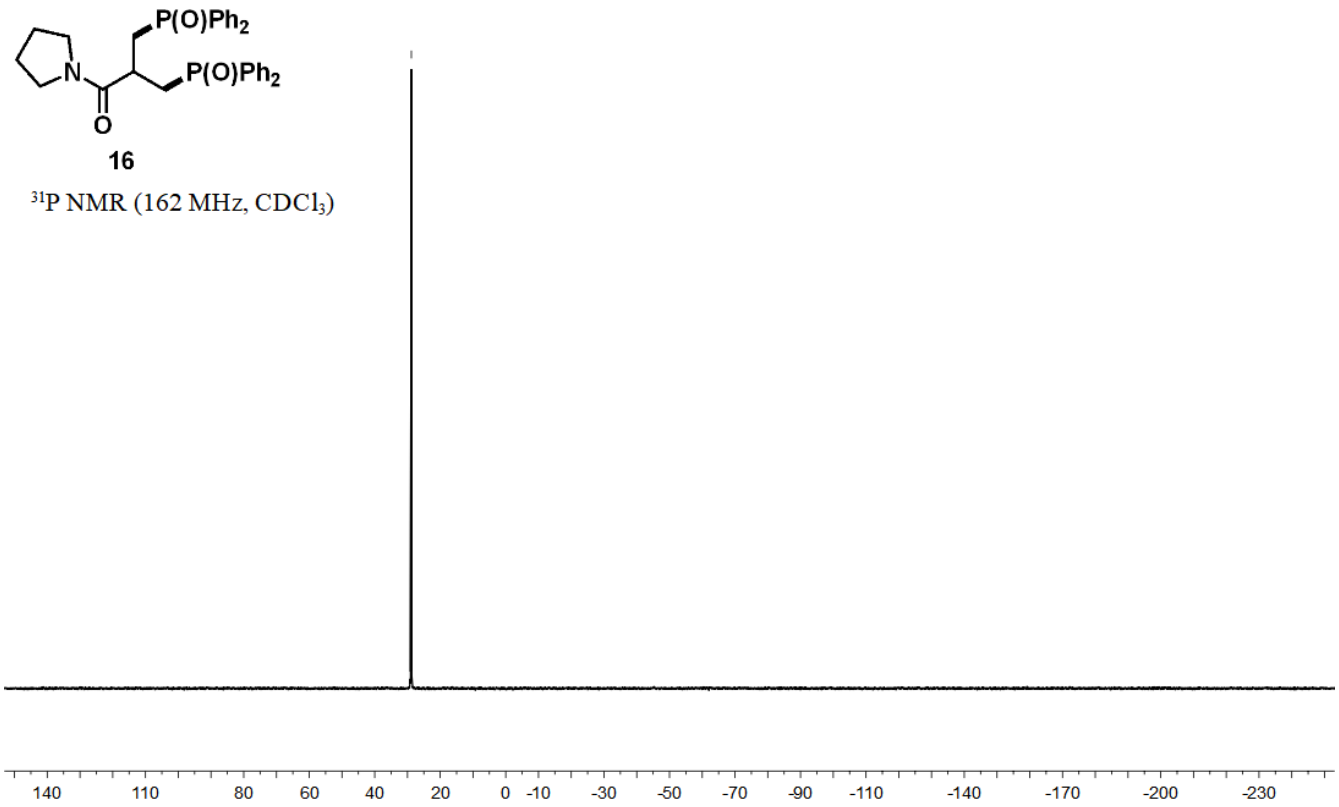
^{1}H NMR (400 MHz, $CDCl_3$)





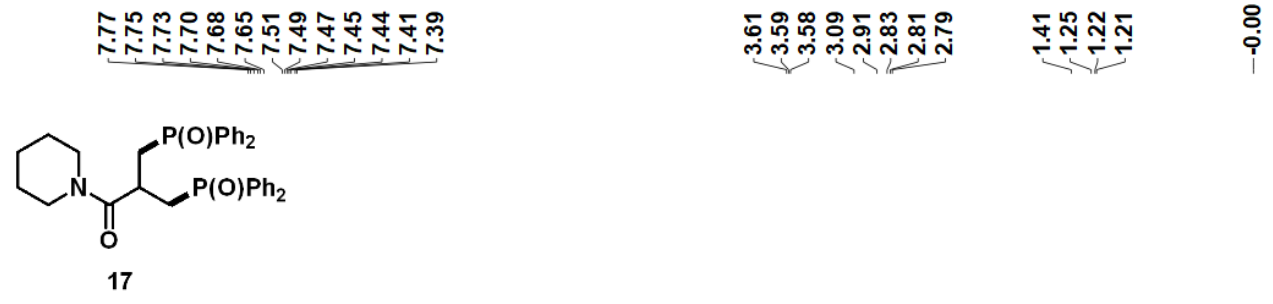
16

^{13}C NMR (101 MHz, $CDCl_3$)



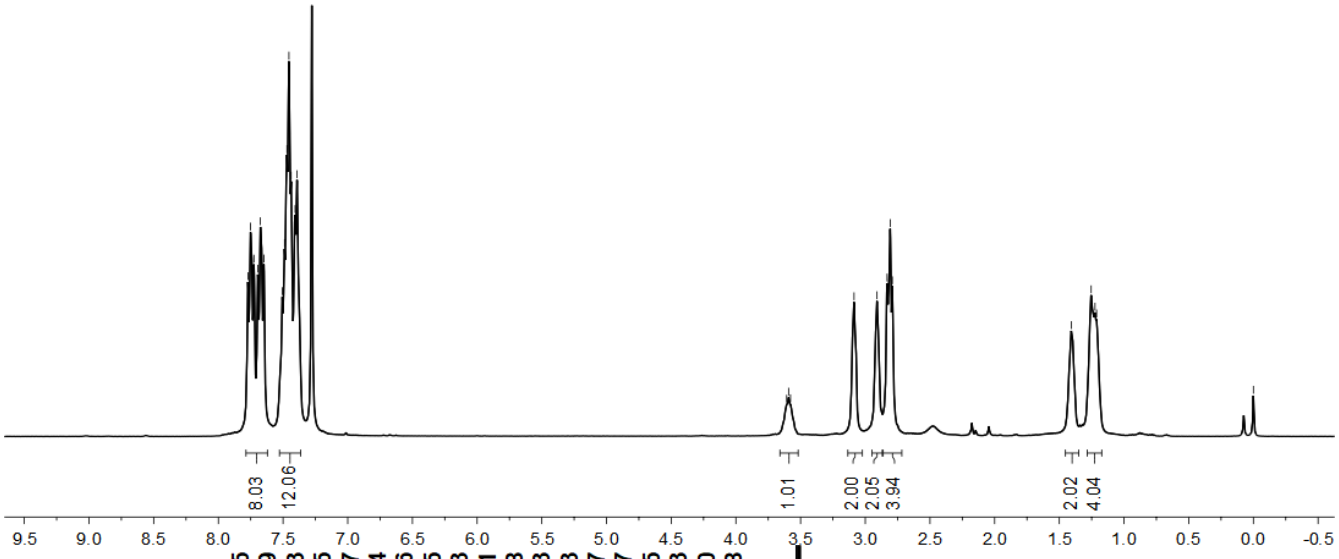
16

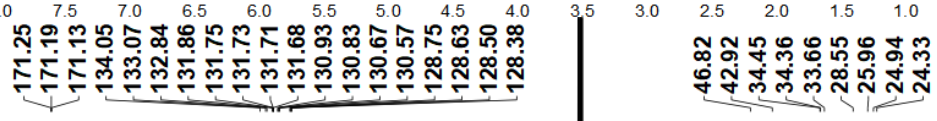
^{31}P NMR (162 MHz, $CDCl_3$)

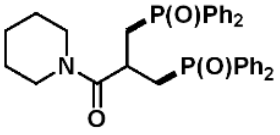


17

^{1}H NMR (400 MHz, $CDCl_3$)

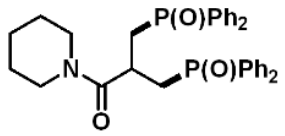






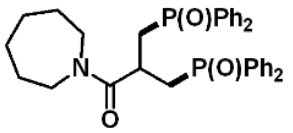
17

^{13}C NMR (101 MHz, $CDCl_3$)



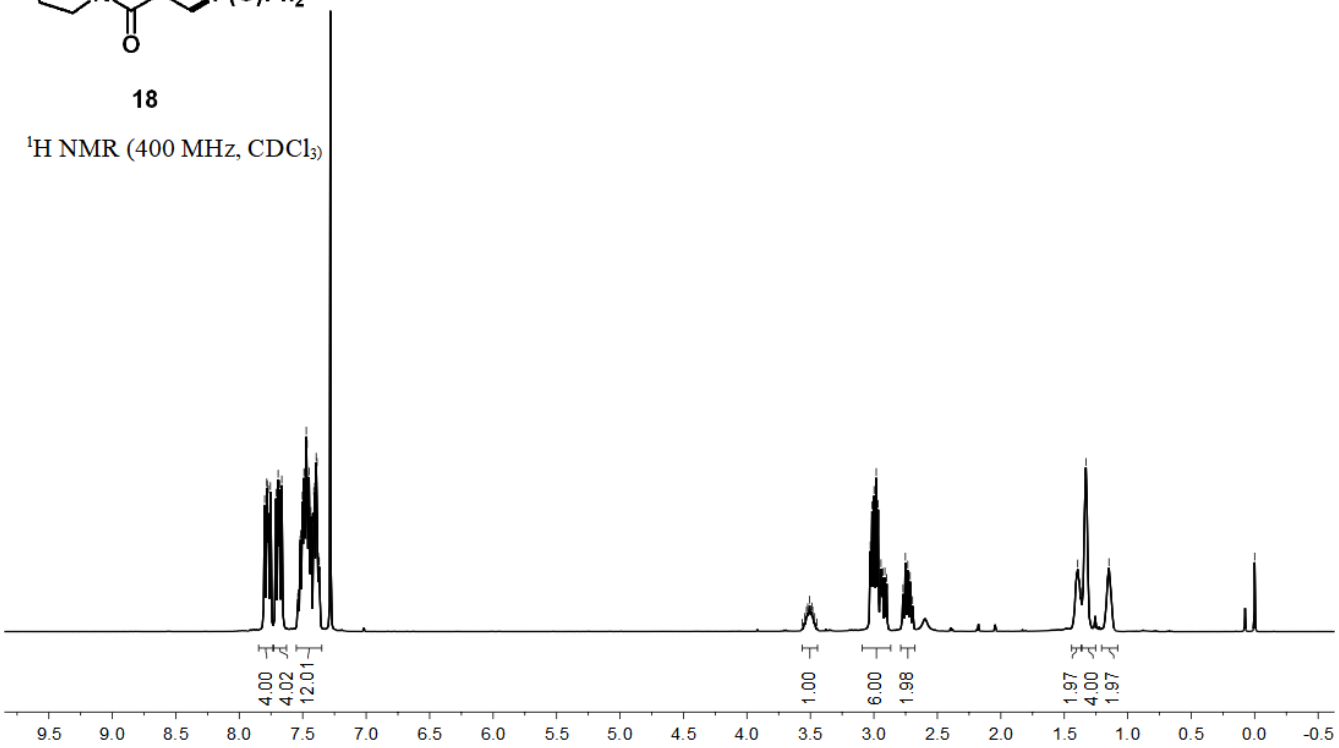
17

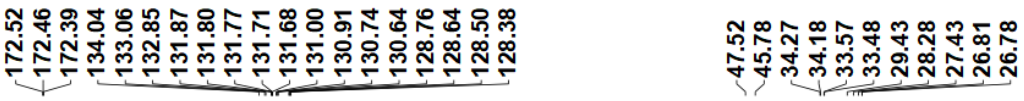
^{31}P NMR (162 MHz, $CDCl_3$)

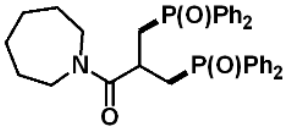


18

^{1}H NMR (400 MHz, $CDCl_3$)

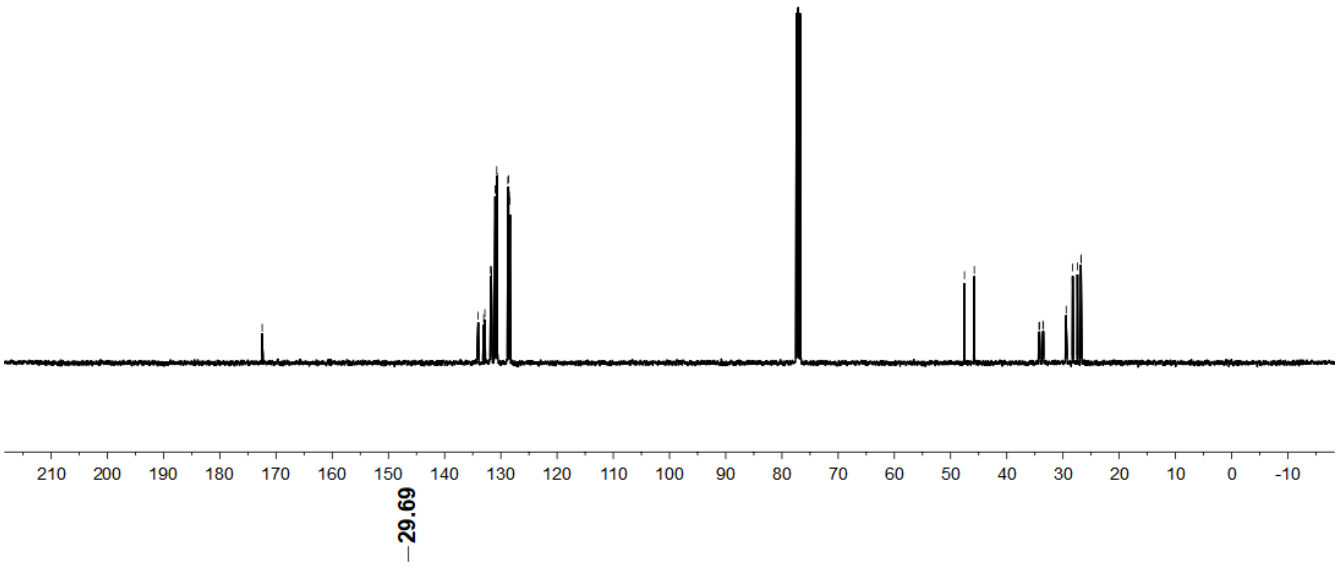


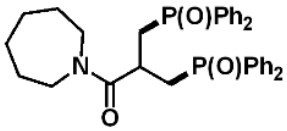




18

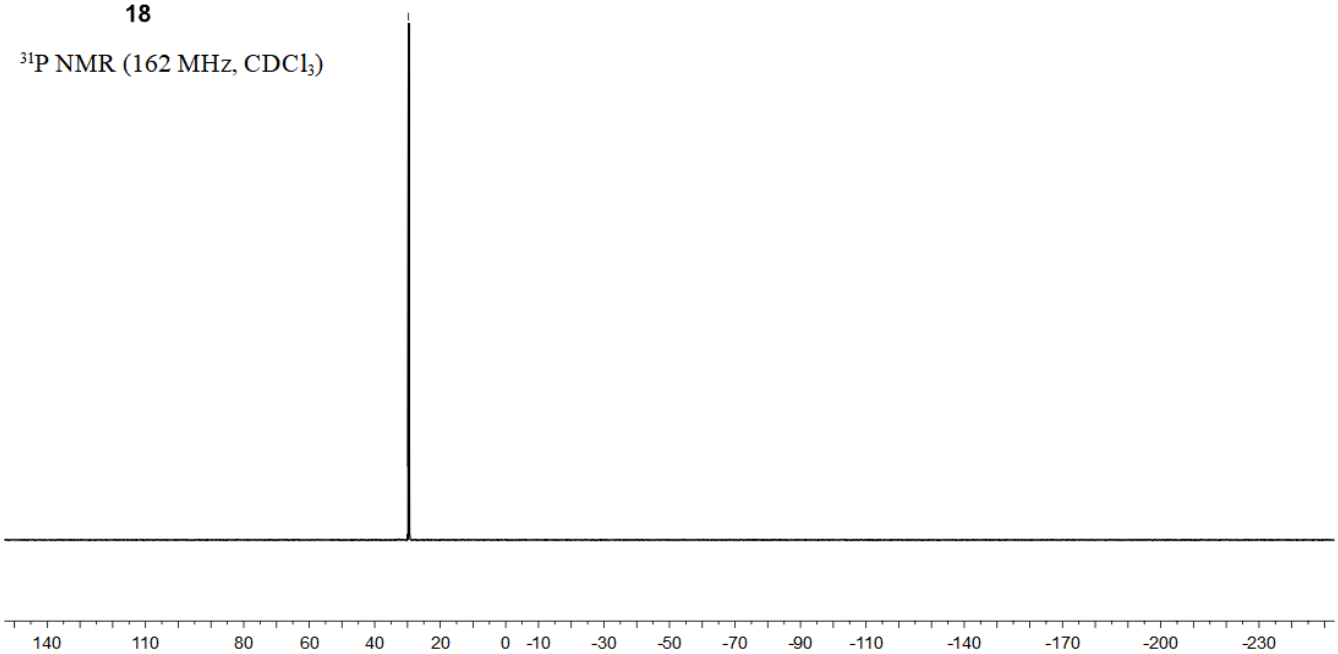
^{13}C NMR (101 MHz, $CDCl_3$)

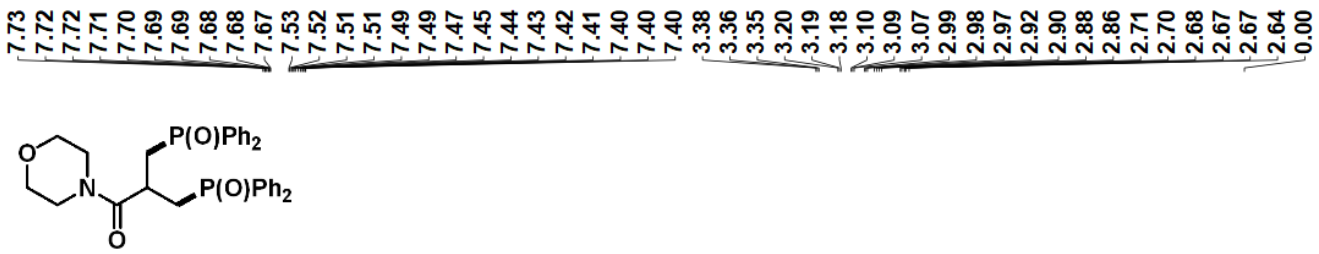




18

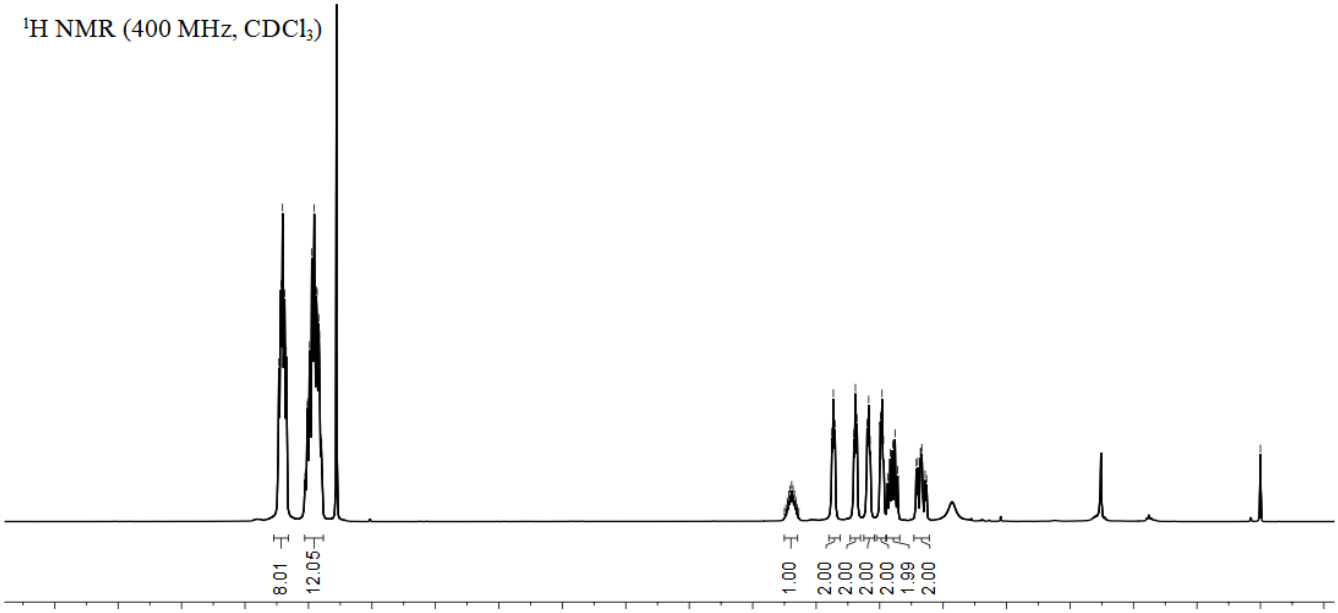
^{31}P NMR (162 MHz, $CDCl_3$)

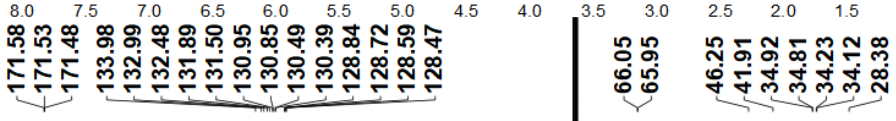


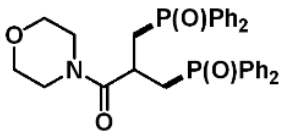


19

^{1}H NMR (400 MHz, $CDCl_3$)

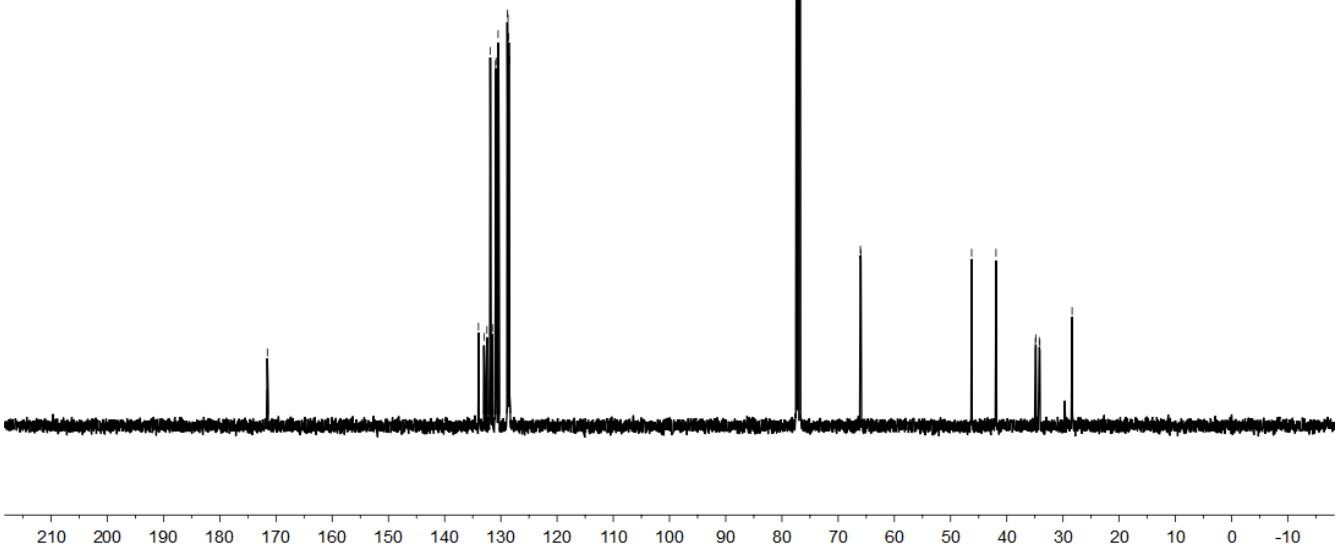


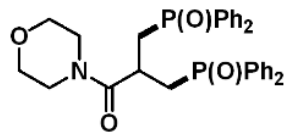




19

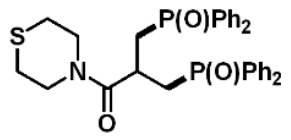
^{13}C NMR (101 MHz, $CDCl_3$)





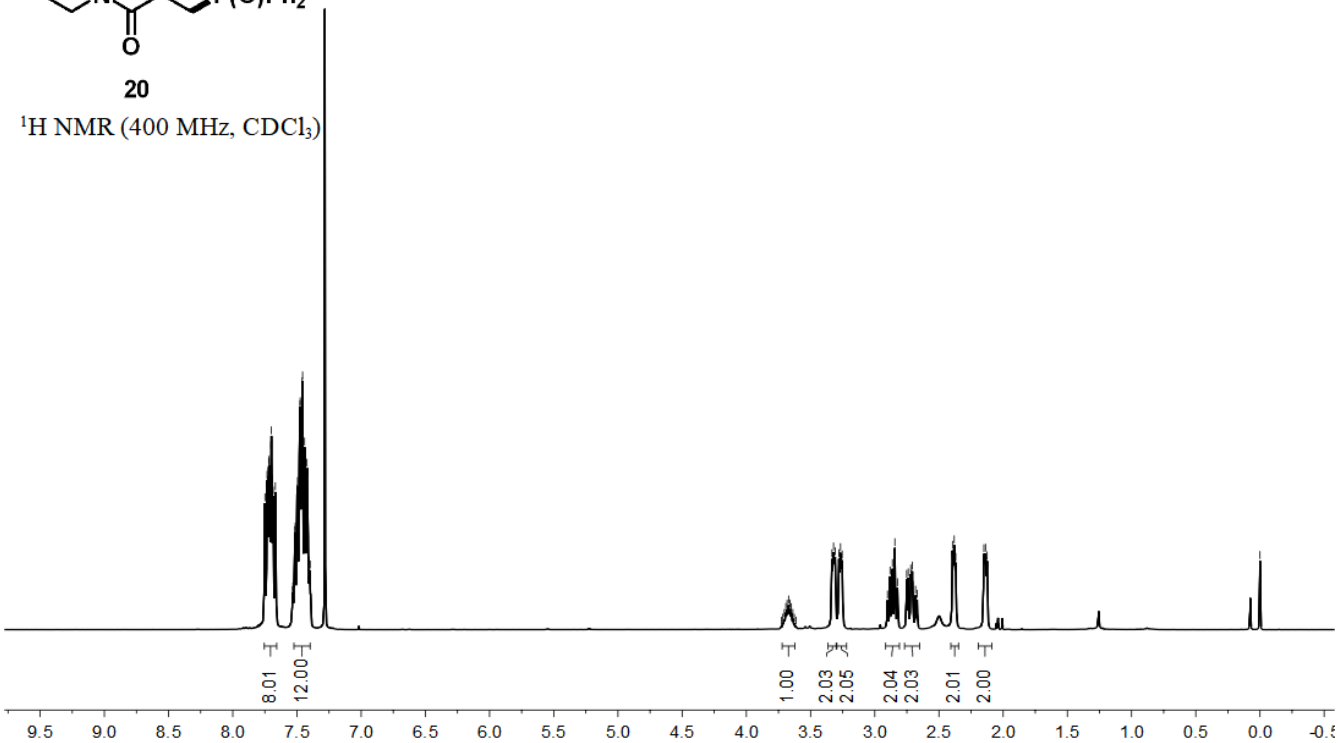
19

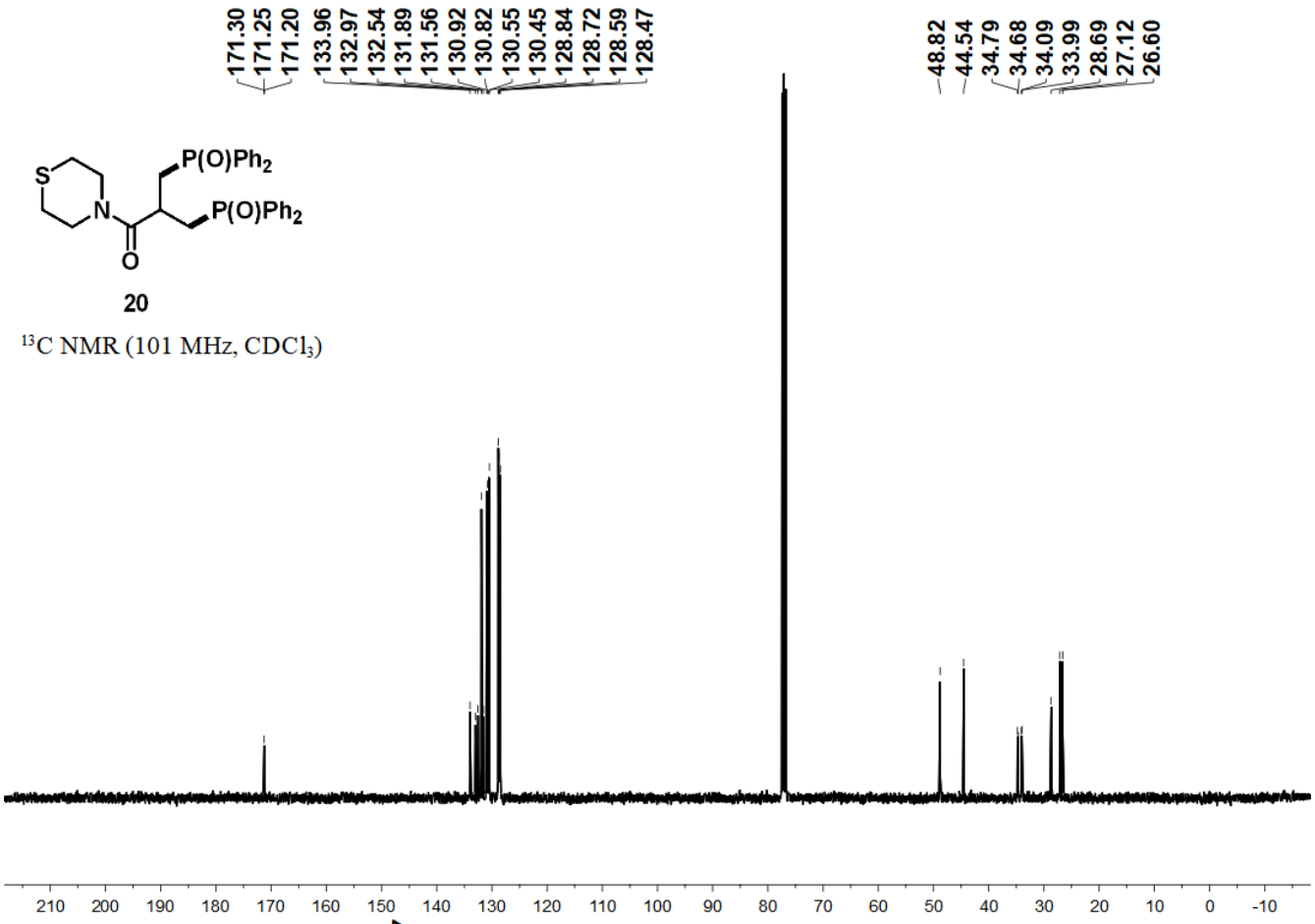
^{31}P NMR (162 MHz, $CDCl_3$)



20

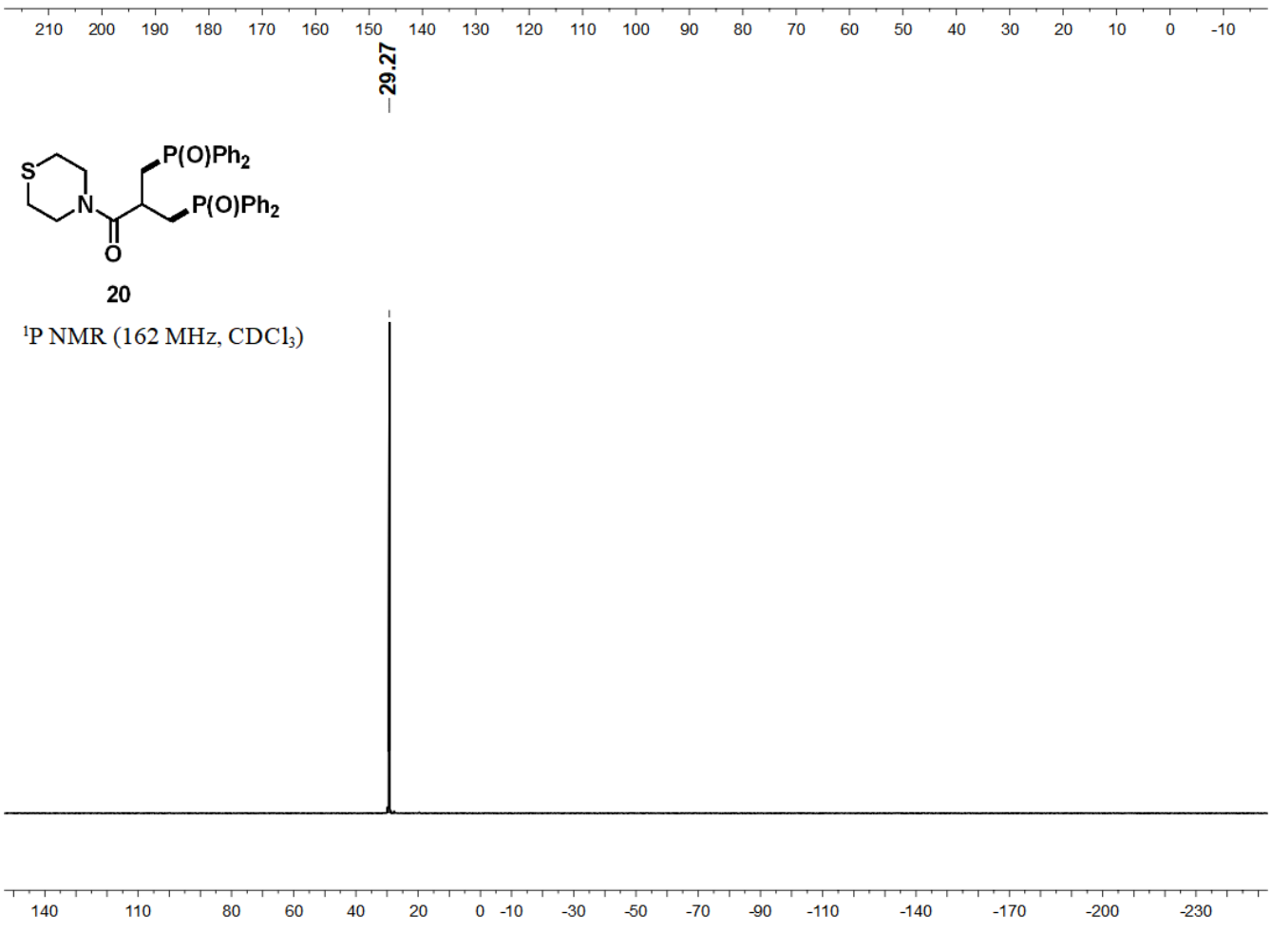
^{1}H NMR (400 MHz, $CDCl_3$)





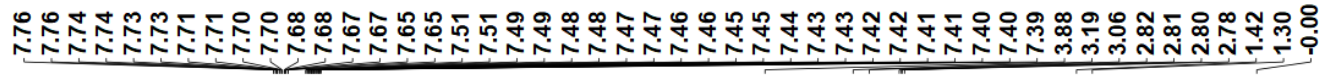
20

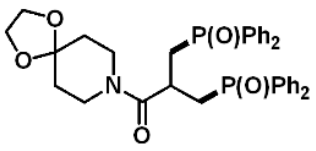
^{13}C NMR (101 MHz, $CDCl_3$)



20

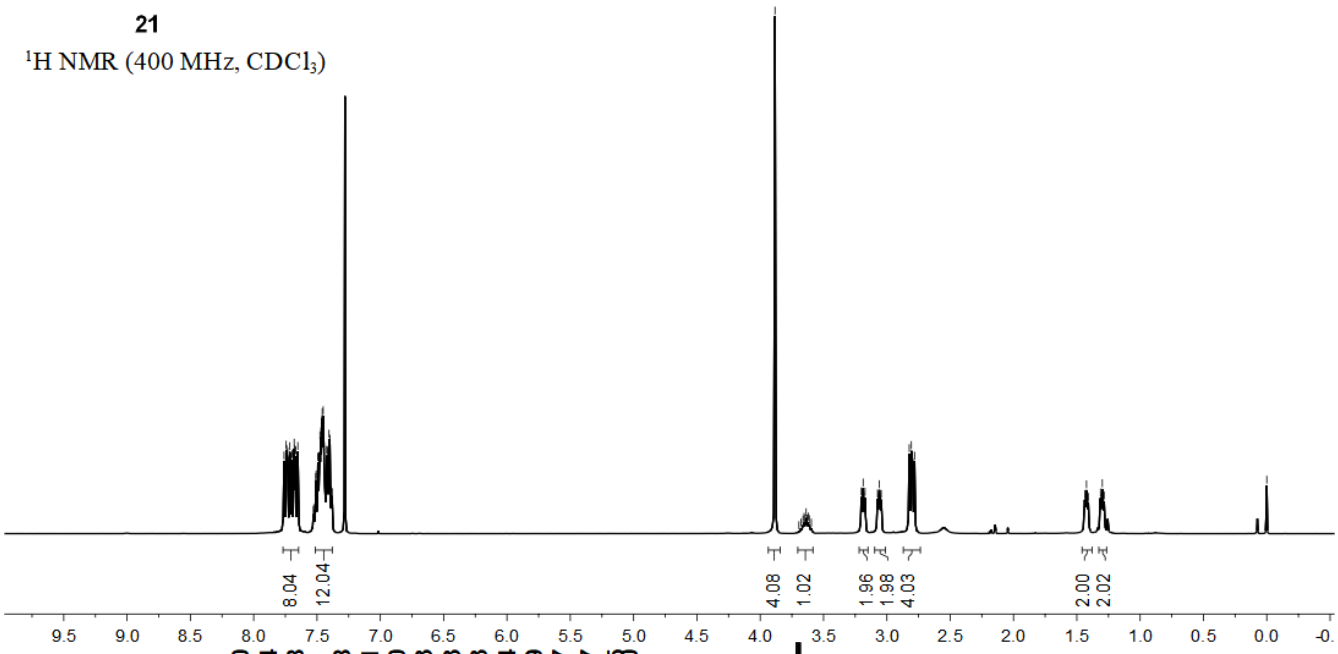
^{1}P NMR (162 MHz, $CDCl_3$)

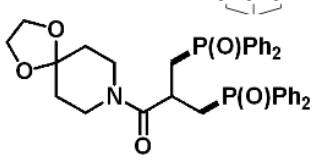




21

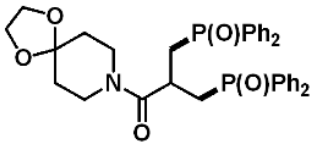
^{1}H NMR (400 MHz, $CDCl_3$)





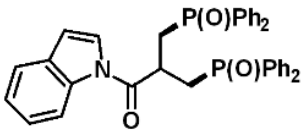
21

^{13}C NMR (101 MHz, $CDCl_3$)



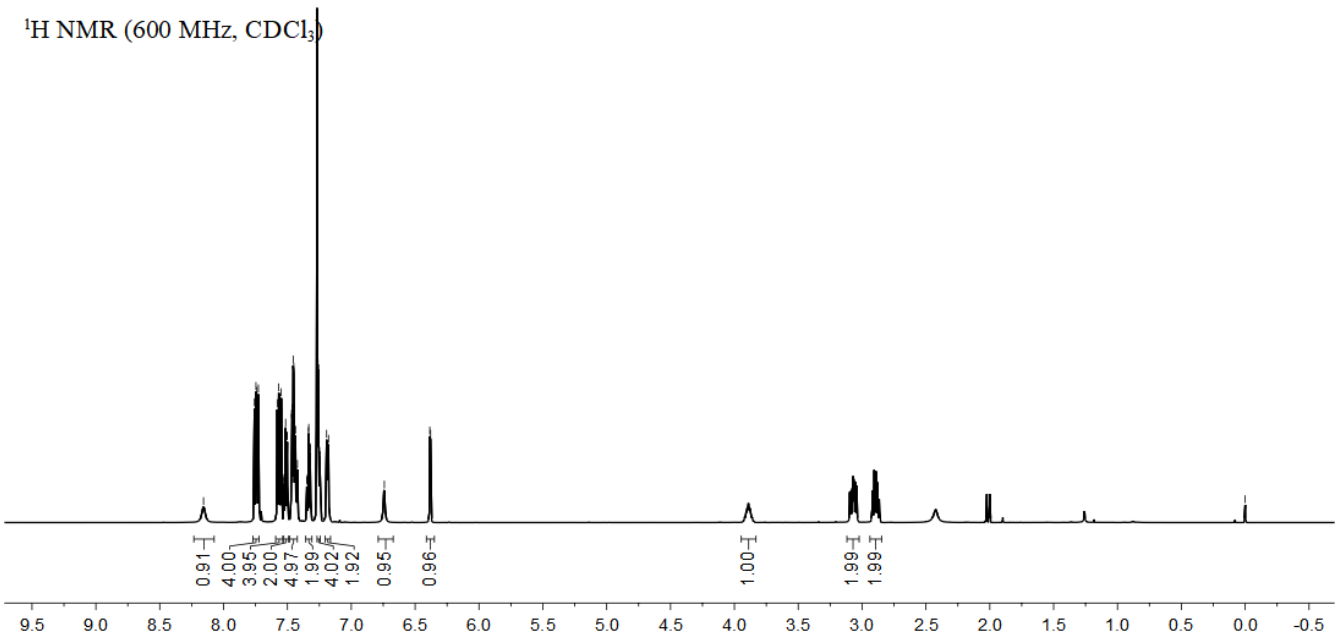
21

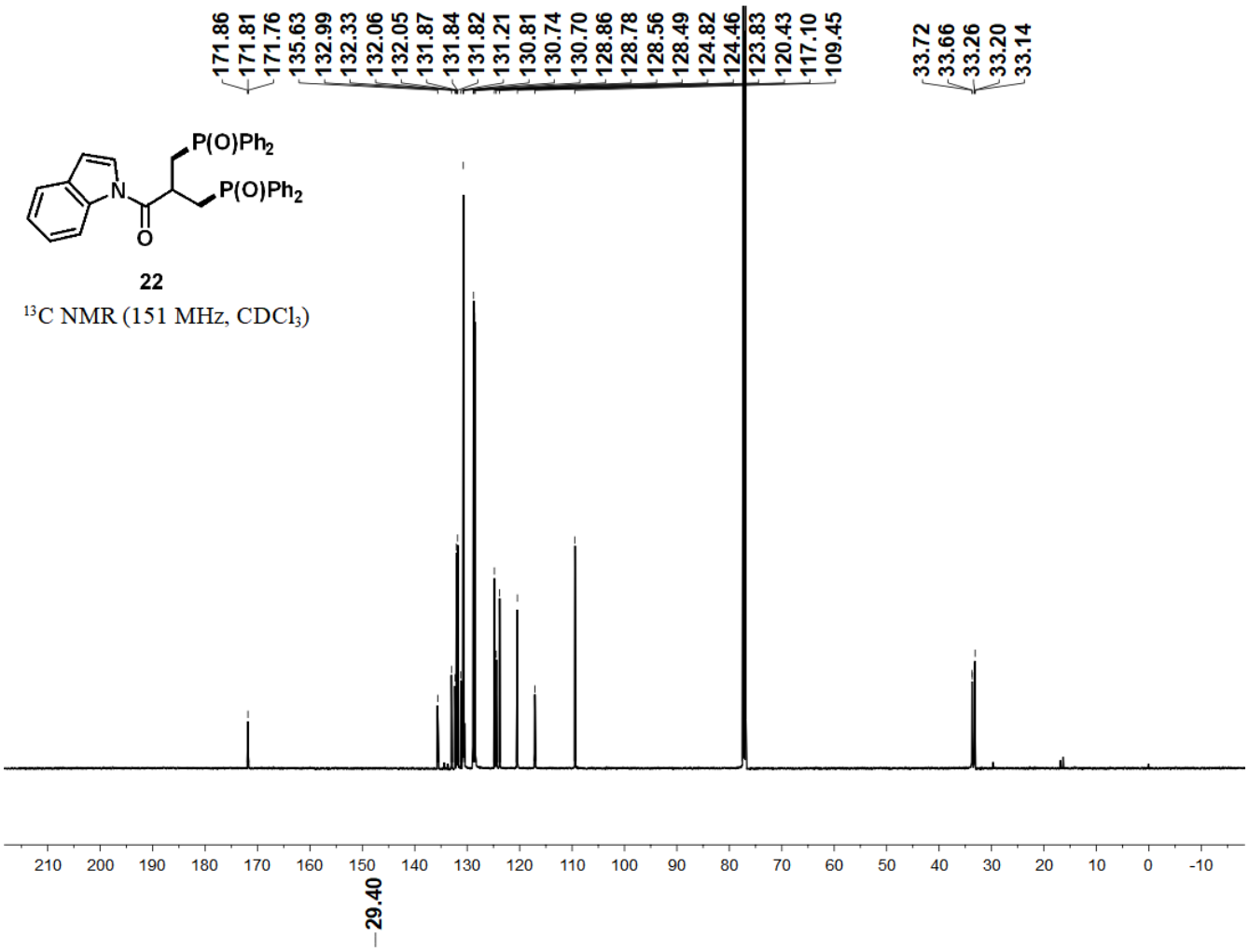
^{31}P NMR (162 MHz, $CDCl_3$)



22

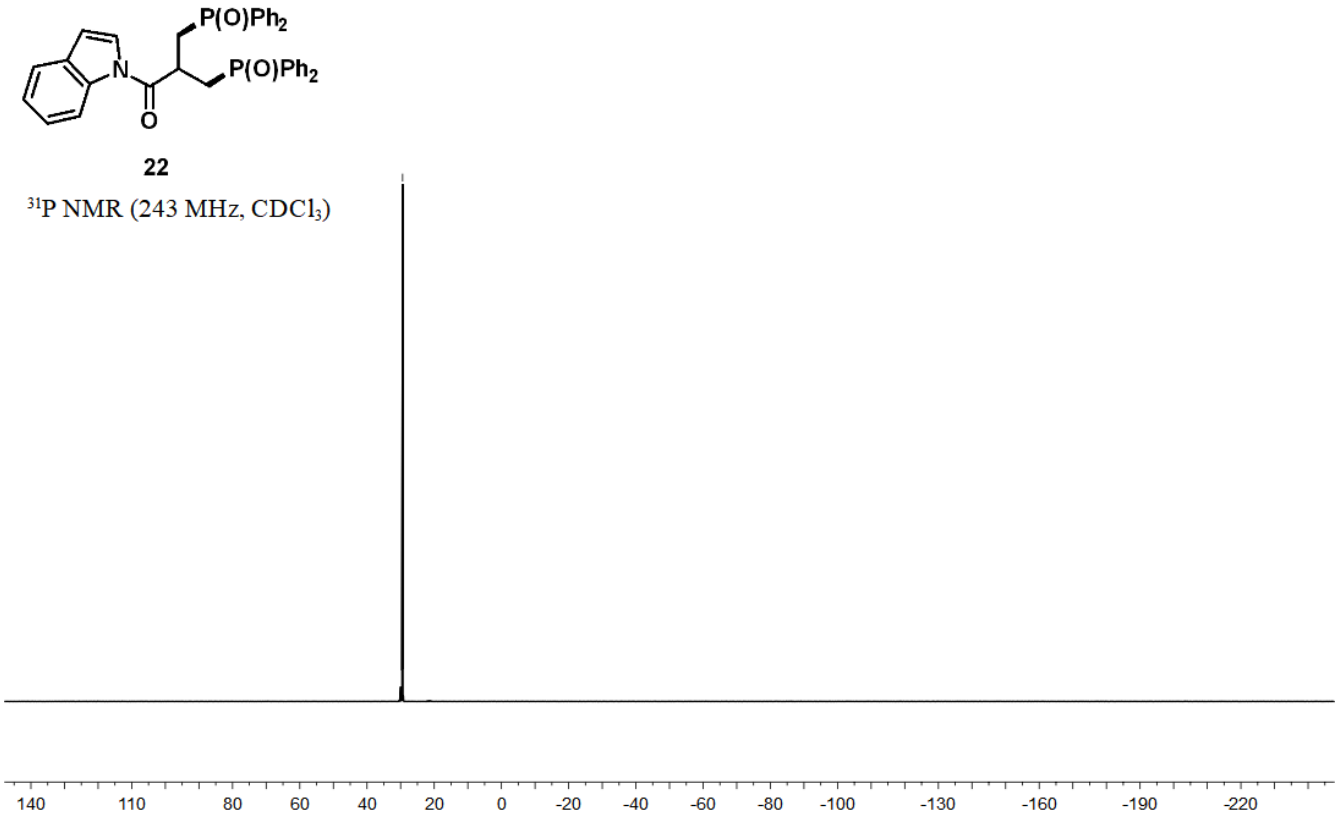
^{1}H NMR (600 MHz, $CDCl_3$)





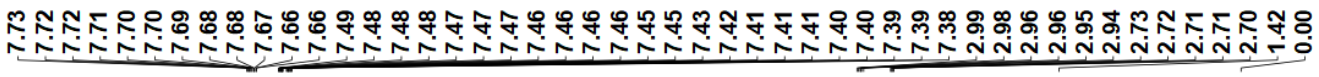
22

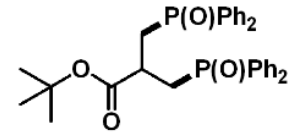
^{13}C NMR (151 MHz, $CDCl_3$)



22

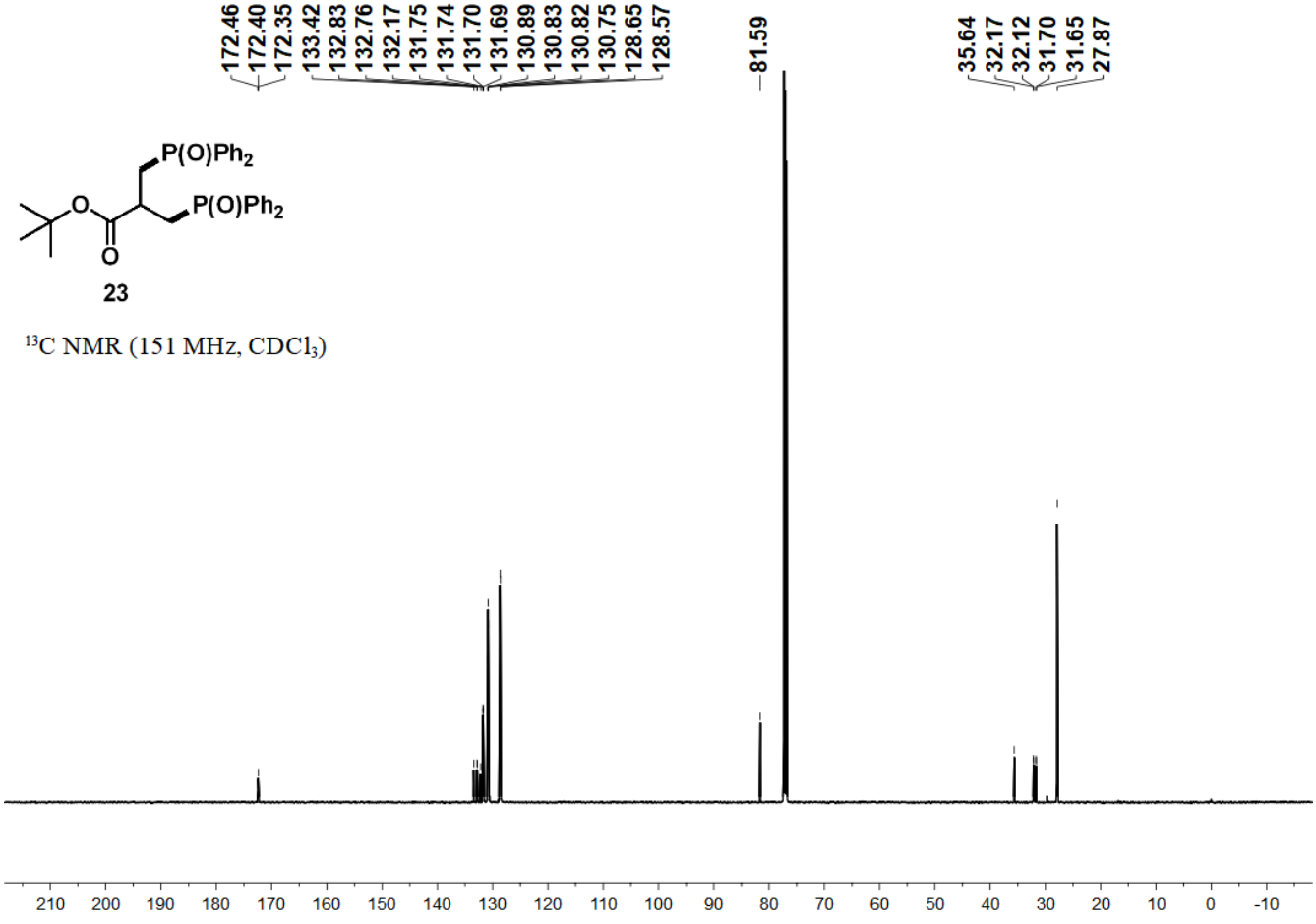
^{31}P NMR (243 MHz, $CDCl_3$)





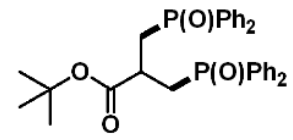
23

^{1}H NMR (600 MHz, $CDCl_3$)



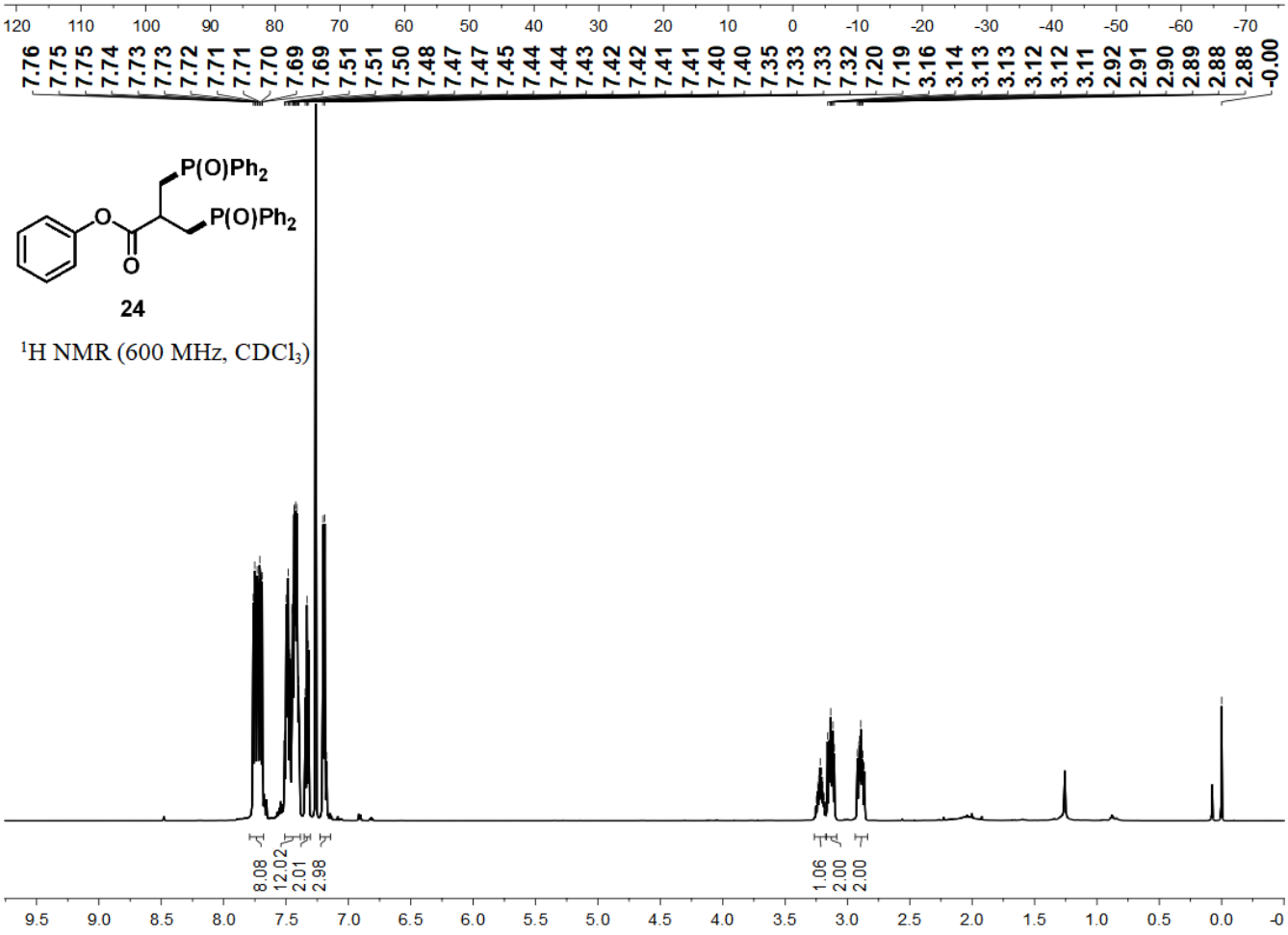
23

^{13}C NMR (151 MHz, $CDCl_3$)



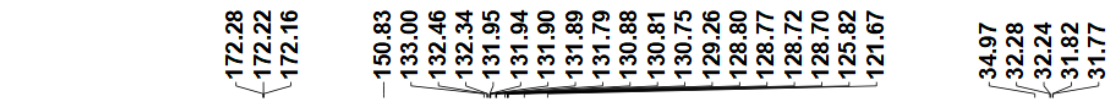
23

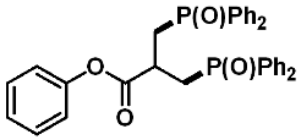
^{31}P NMR (243 MHz, $CDCl_3$)



24

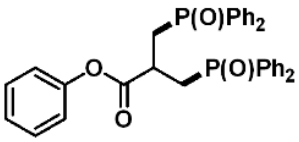
^{1}H NMR (600 MHz, $CDCl_3$)





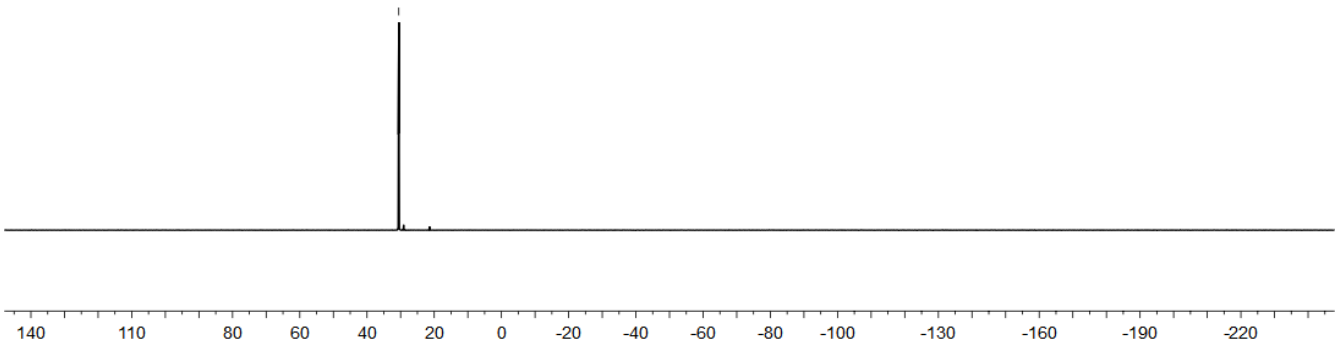
24

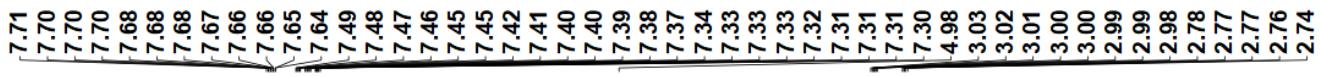
^{13}C NMR (151 MHz, $CDCl_3$)

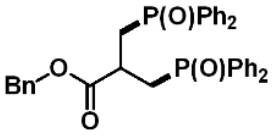


24

^{31}P NMR (243 MHz, $CDCl_3$)

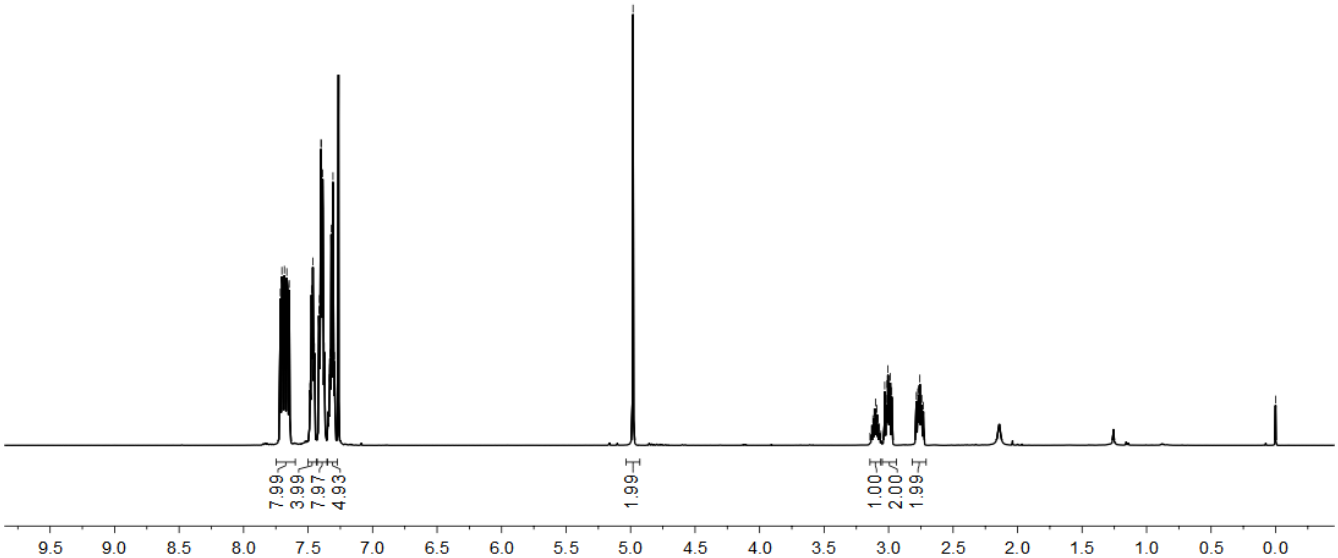


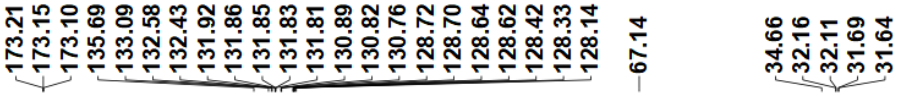


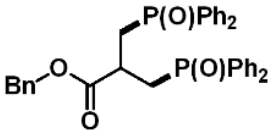


25

^{1}H NMR (600 MHz, $CDCl_3$)

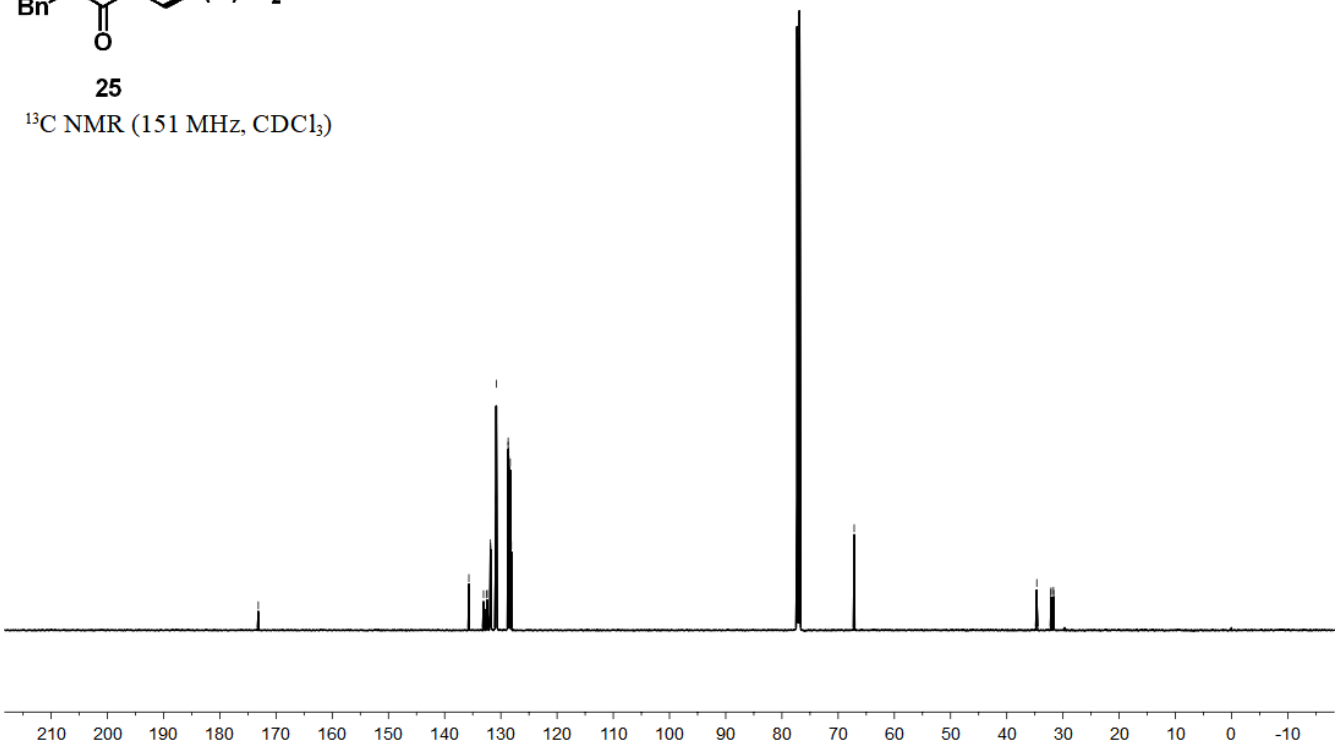


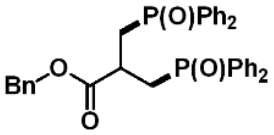




25

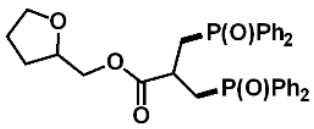
^{13}C NMR (151 MHz, $CDCl_3$)





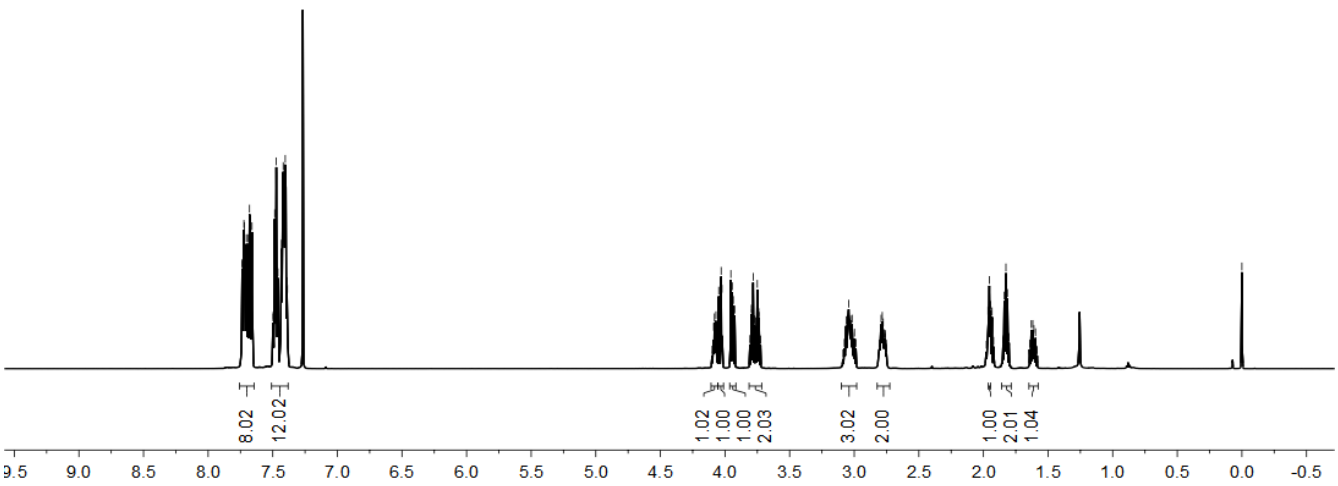
25

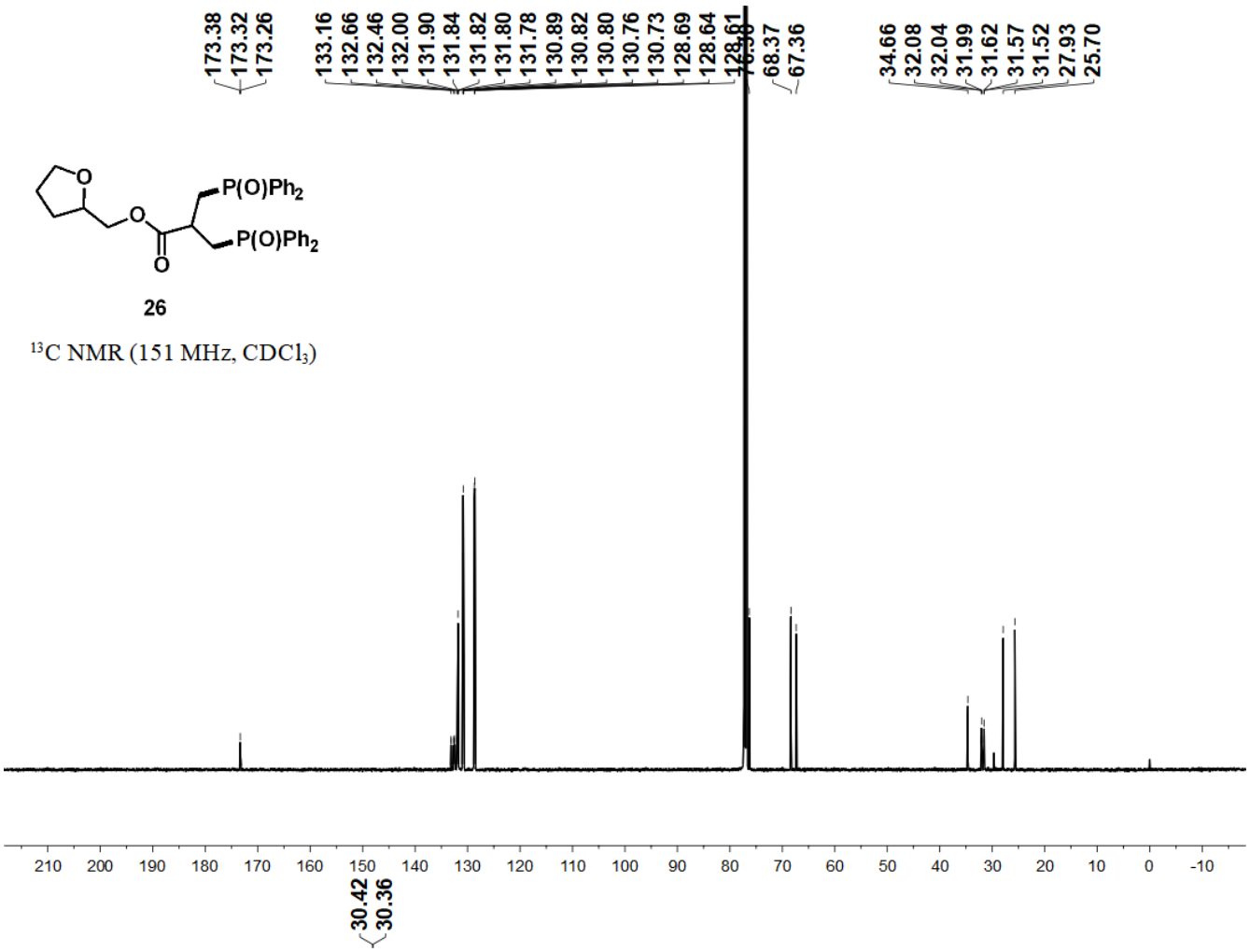
^{31}P NMR (243 MHz, $CDCl_3$)



26

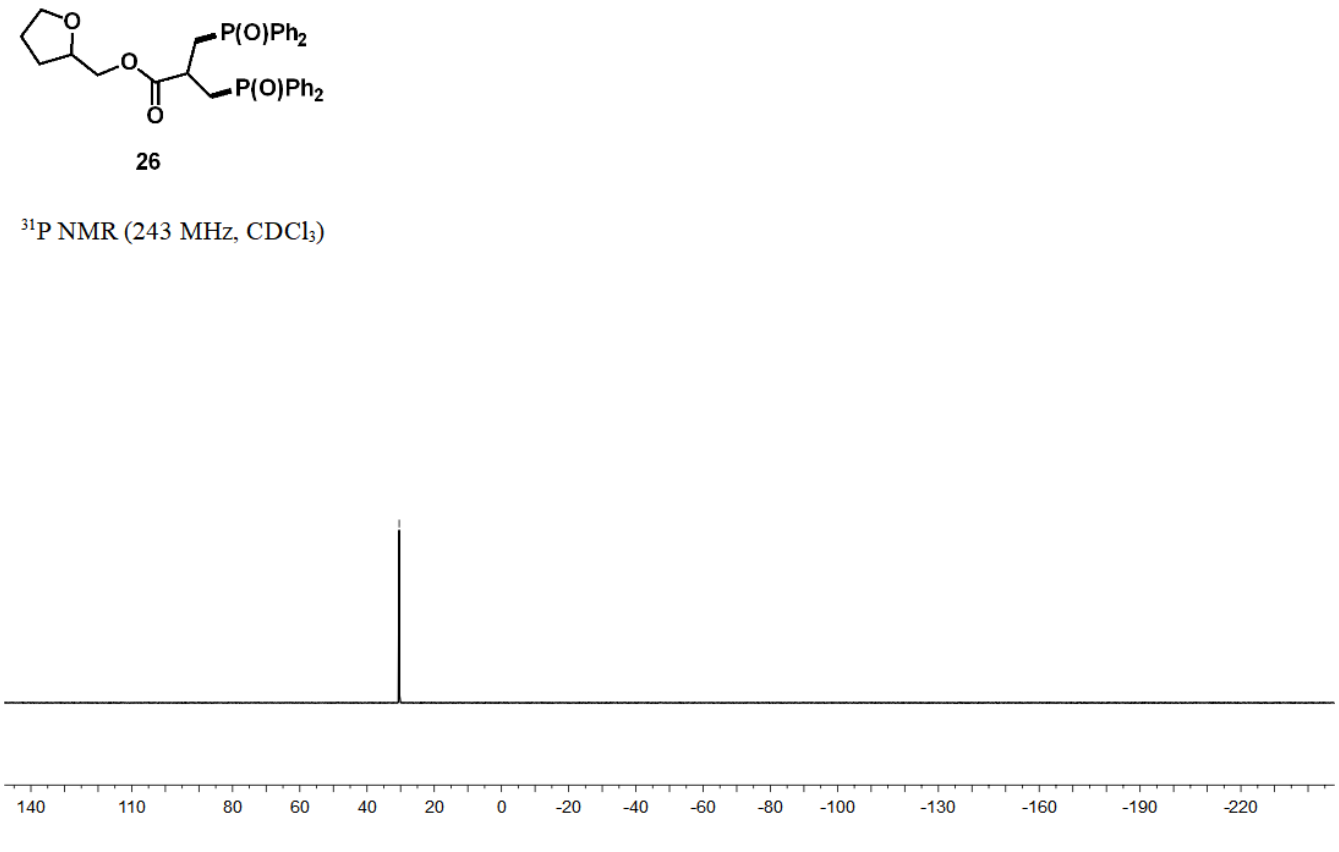
^{1}H NMR (600 MHz, $CDCl_3$)





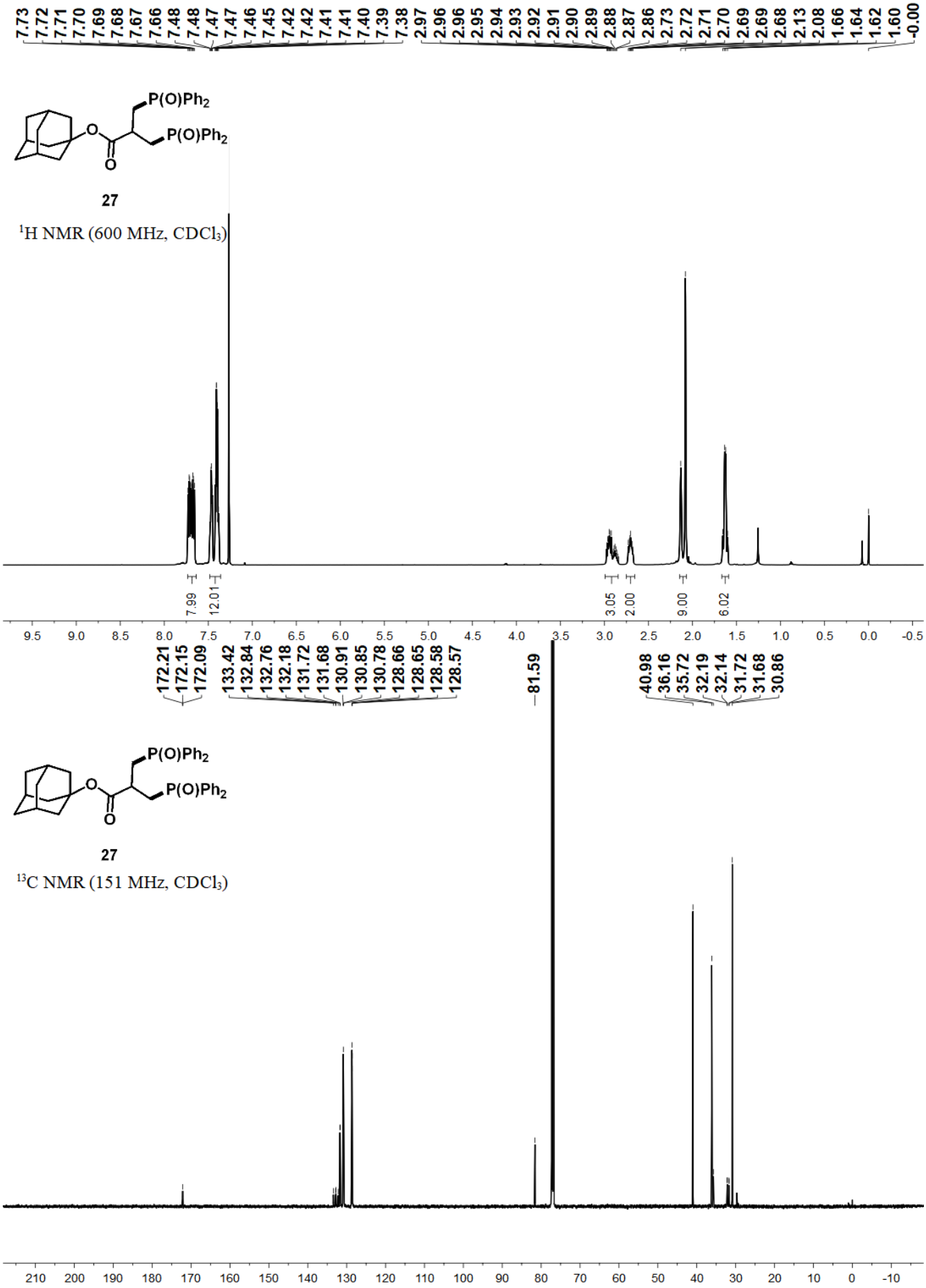
26

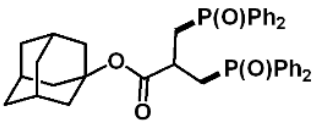
^{13}C NMR (151 MHz, $CDCl_3$)



26

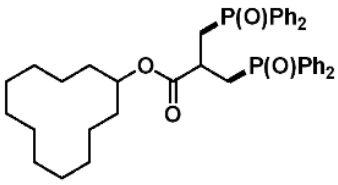
^{31}P NMR (243 MHz, $CDCl_3$)


7.73 7.72 7.71 7.70 7.69 7.68 7.67 7.66 7.48 7.48 7.47 7.47 7.46 7.45 7.42 7.42 7.41 7.41 7.40 7.39 7.38
2.97 2.96 2.96 2.95 2.94 2.93 2.92 2.91 2.90 2.89 2.88 2.87 2.86 2.73 2.72 2.71 2.70 2.69 2.69 2.68 2.13 2.08 1.66 1.64 1.62 1.60 -0.00
P(O)Ph2
P(O)Ph2
O
O
27
1H NMR (600 MHz, CDCl3)
7.99
12.01
3.05
2.00
9.00
6.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
172.21 172.15 172.09 133.42 132.84 132.76 132.18 131.72 131.68 130.91 130.85 130.78 128.66 128.65 128.58 128.57 81.59 40.98 36.16 35.72 32.19 32.14 31.72 31.68 30.86
P(O)Ph2
P(O)Ph2
O
O
27
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



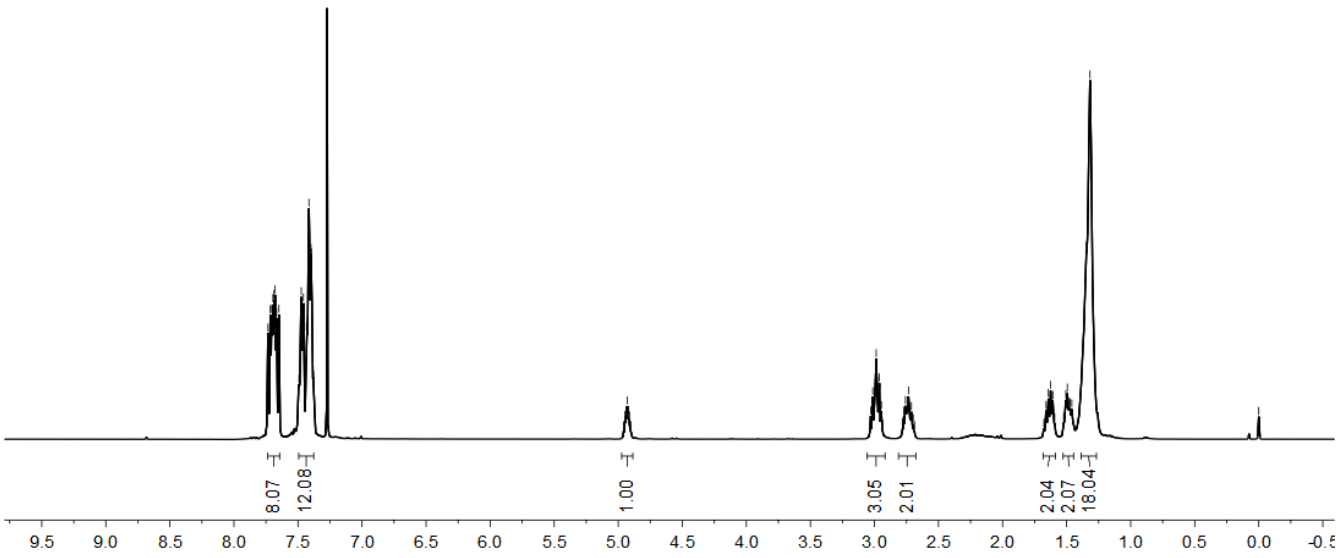
27

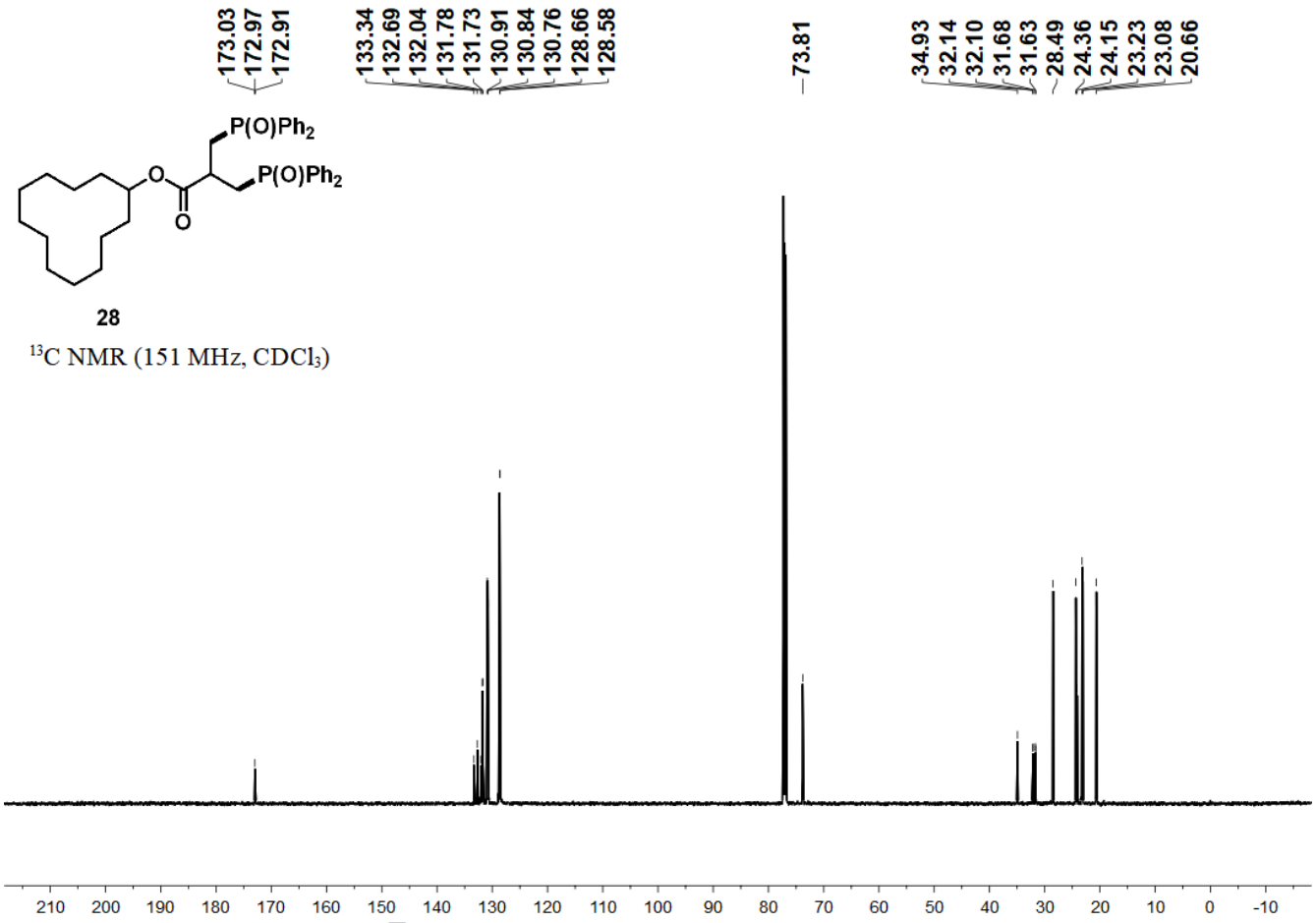
^{31}P NMR (243 MHz, $CDCl_3$)



28

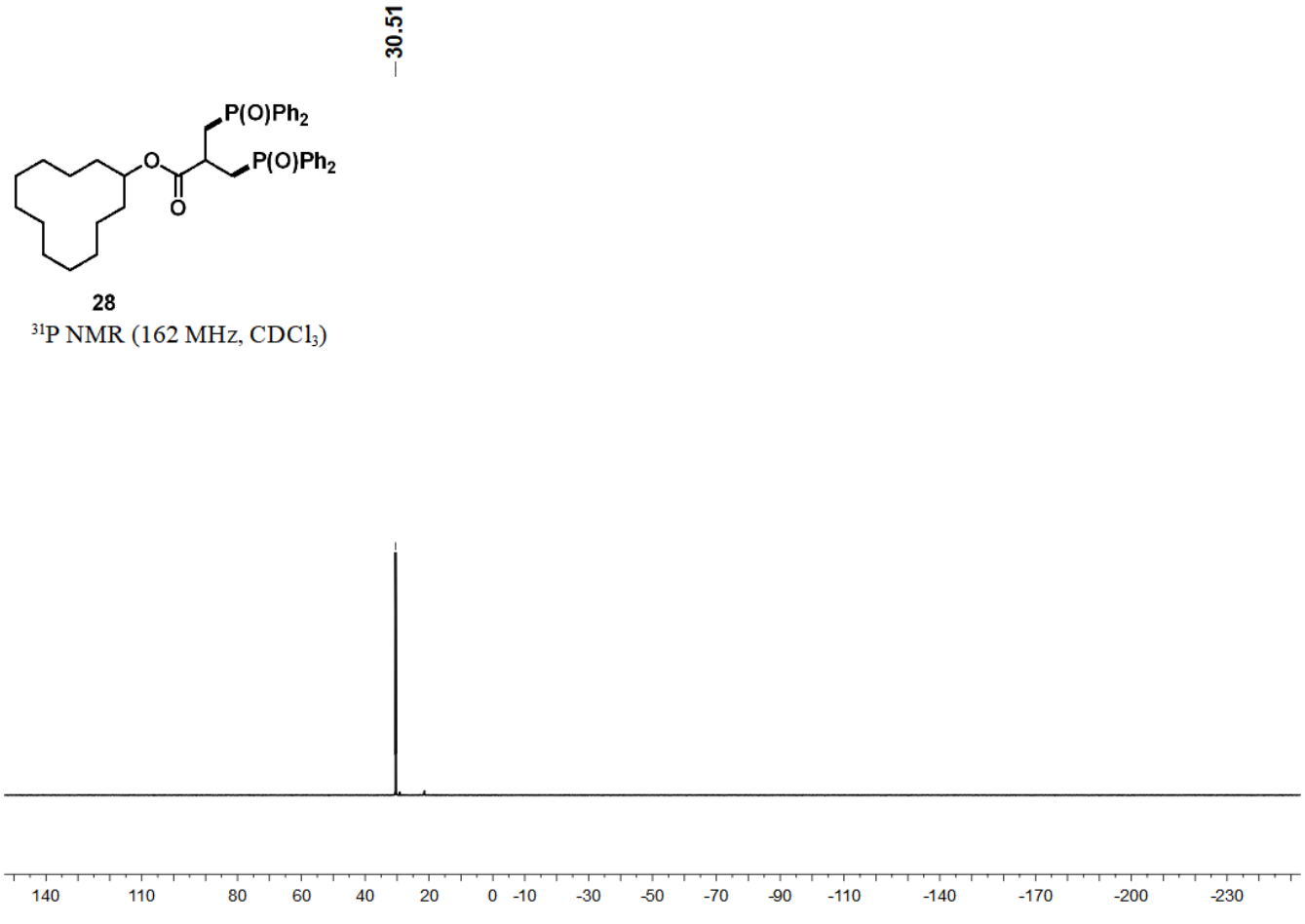
^{1}H NMR (400 MHz, $CDCl_3$)





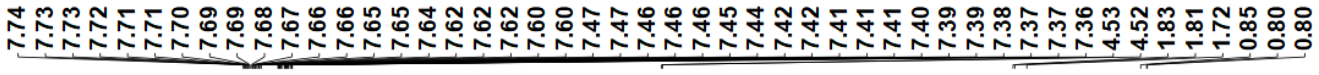
28

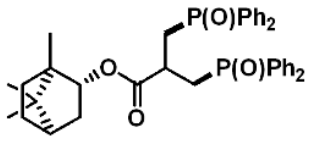
^{13}C NMR (151 MHz, $CDCl_3$)



28

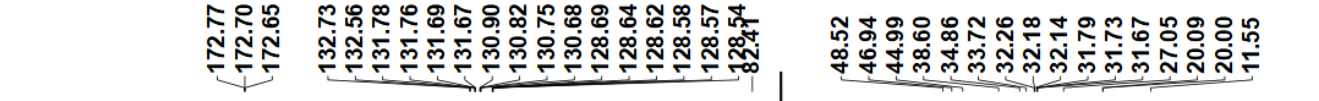
^{31}P NMR (162 MHz, $CDCl_3$)

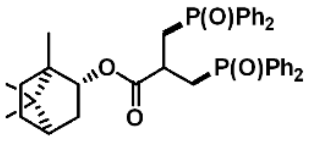




29

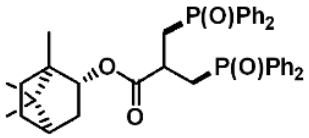
^{1}H NMR (600 MHz, $CDCl_3$)





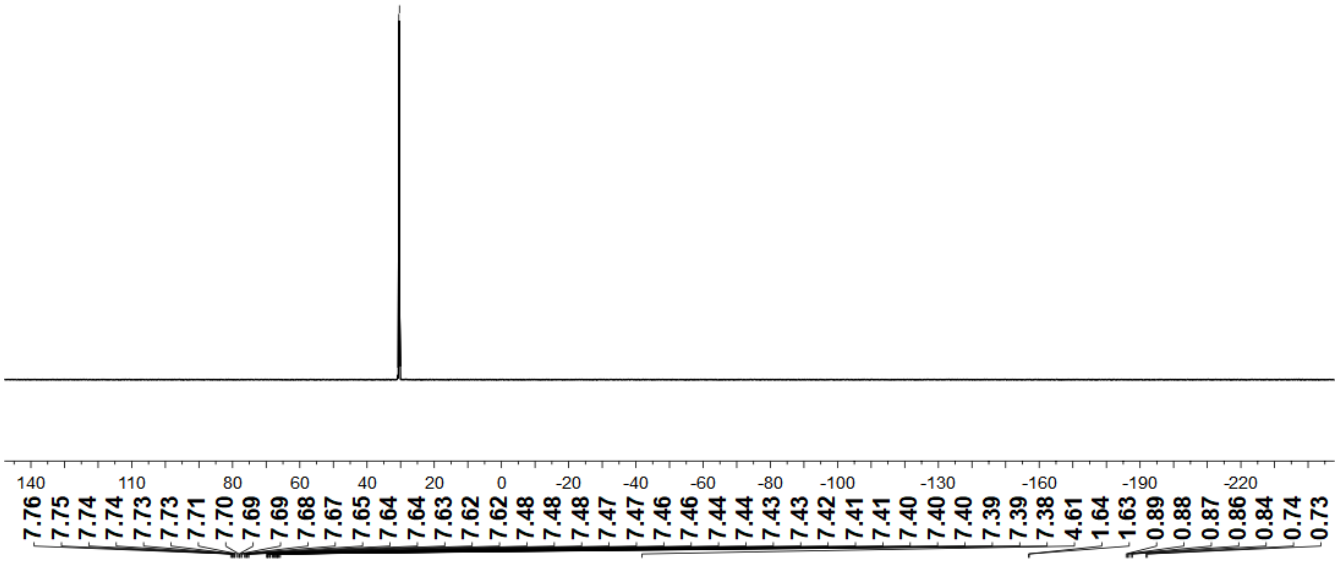
29

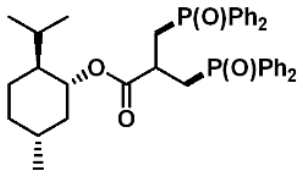
^{13}C NMR (151 MHz, $CDCl_3$)



29

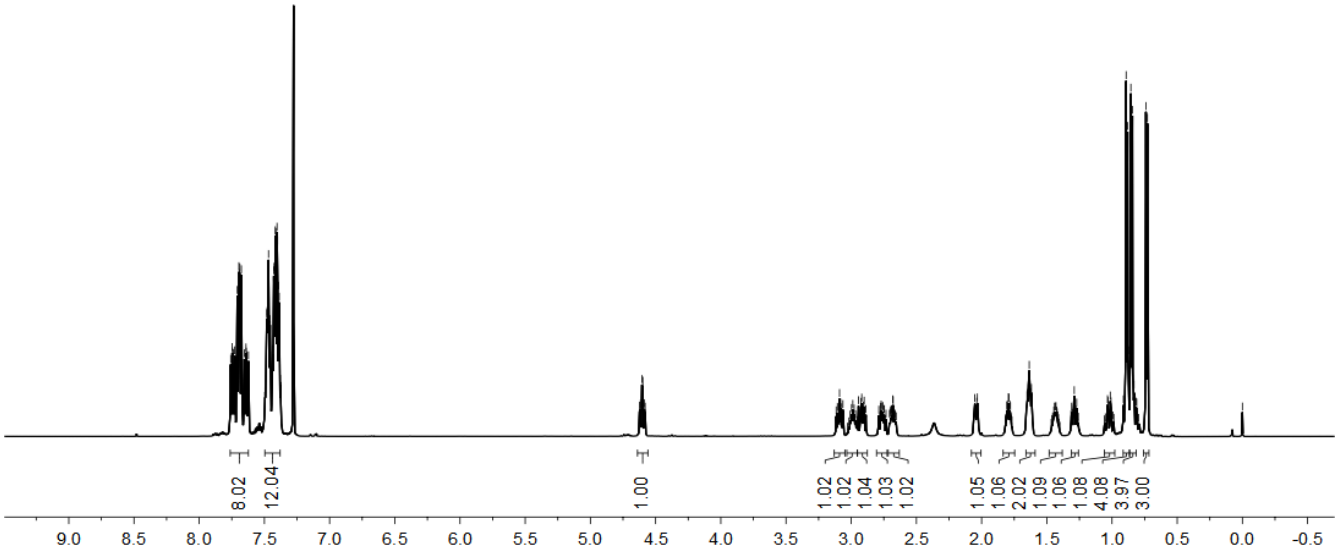
^{31}P NMR (243 MHz, $CDCl_3$)

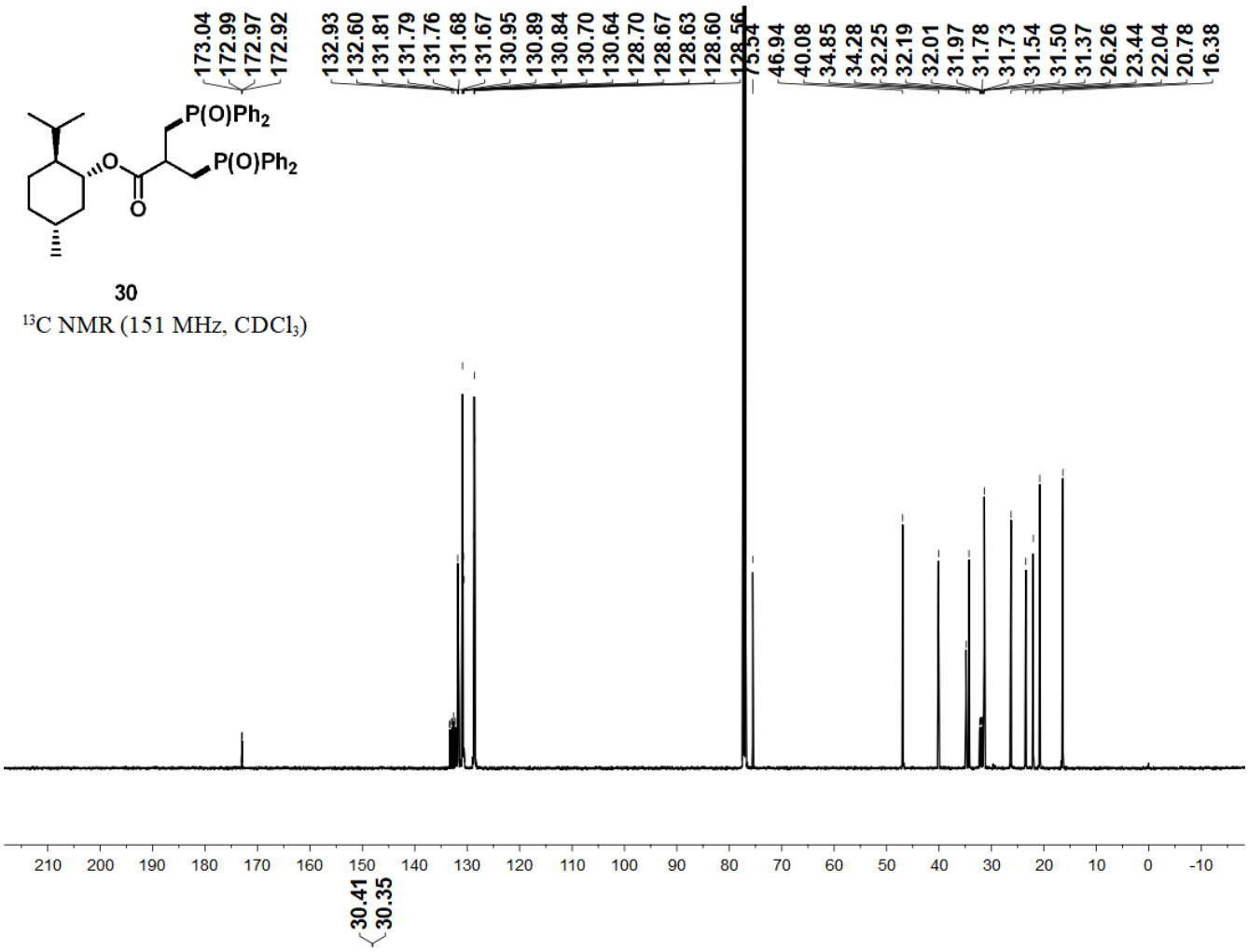




30

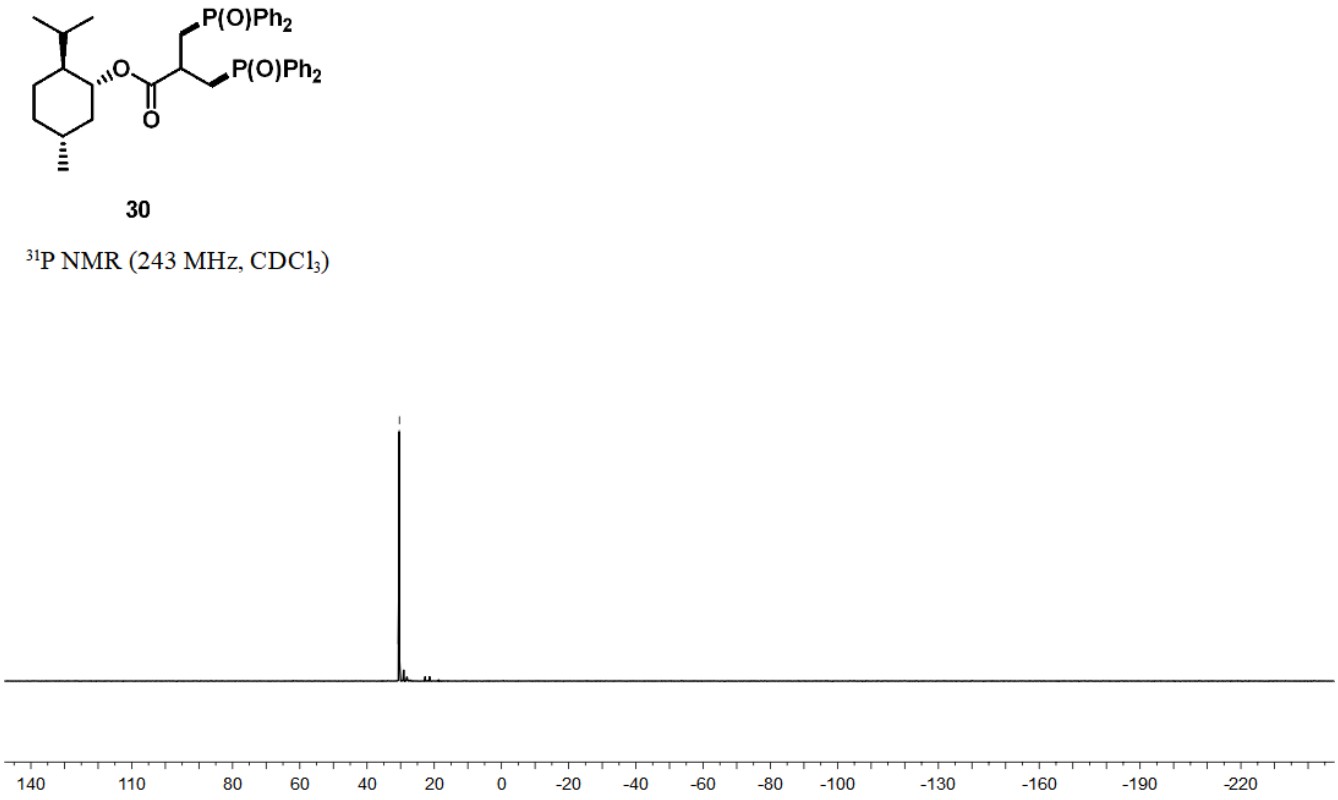
^{1}H NMR (600 MHz, $CDCl_3$)





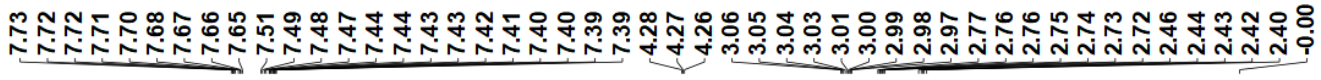
30

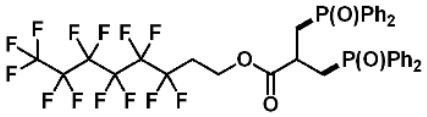
^{13}C NMR (151 MHz, $CDCl_3$)



30

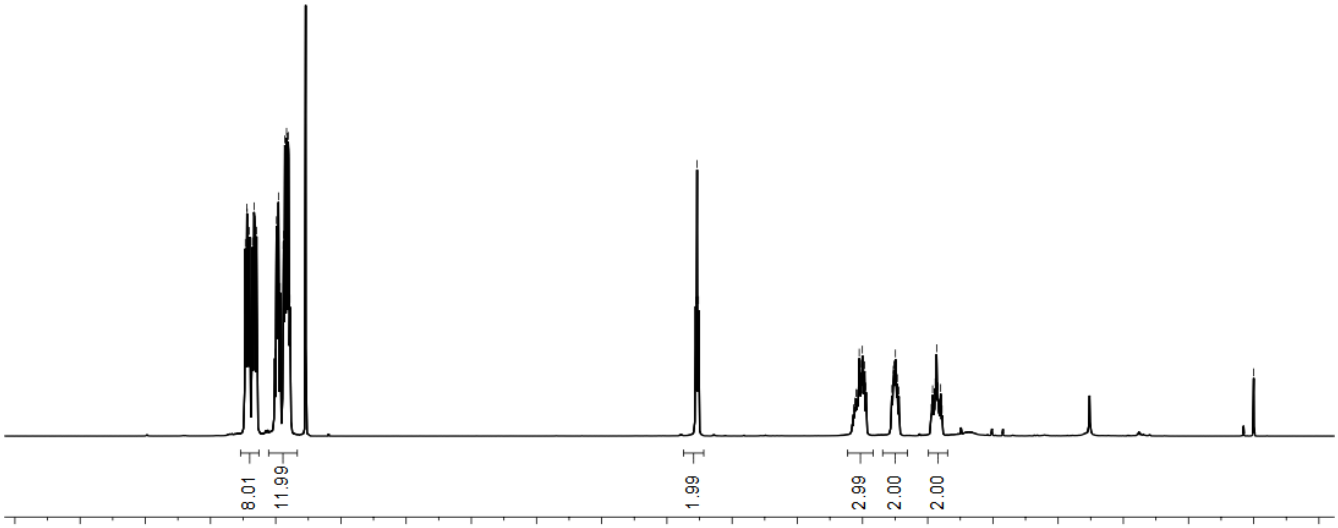
^{31}P NMR (243 MHz, $CDCl_3$)

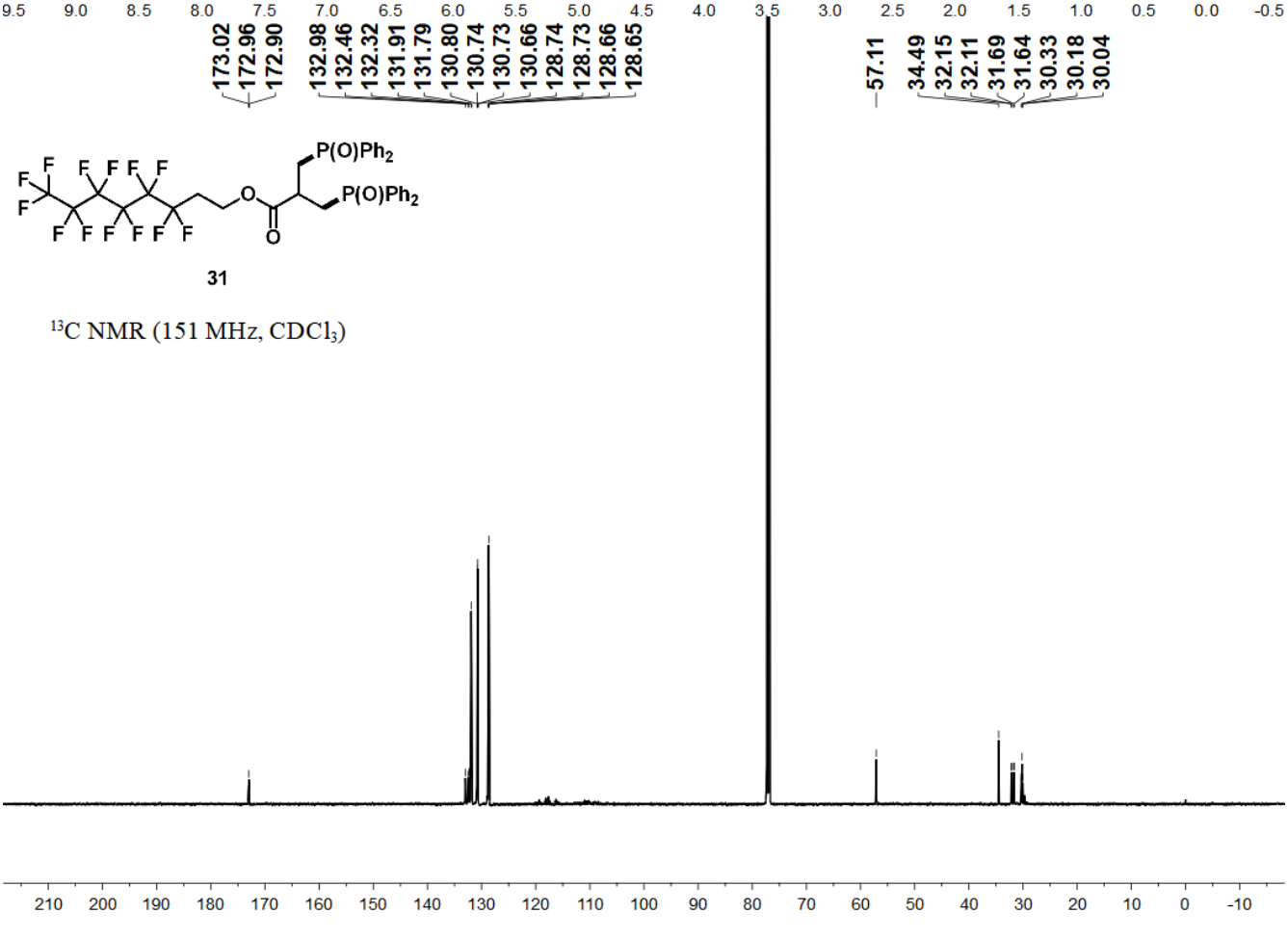




31

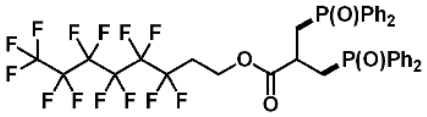
^{1}H NMR (600 MHz, $CDCl_3$)





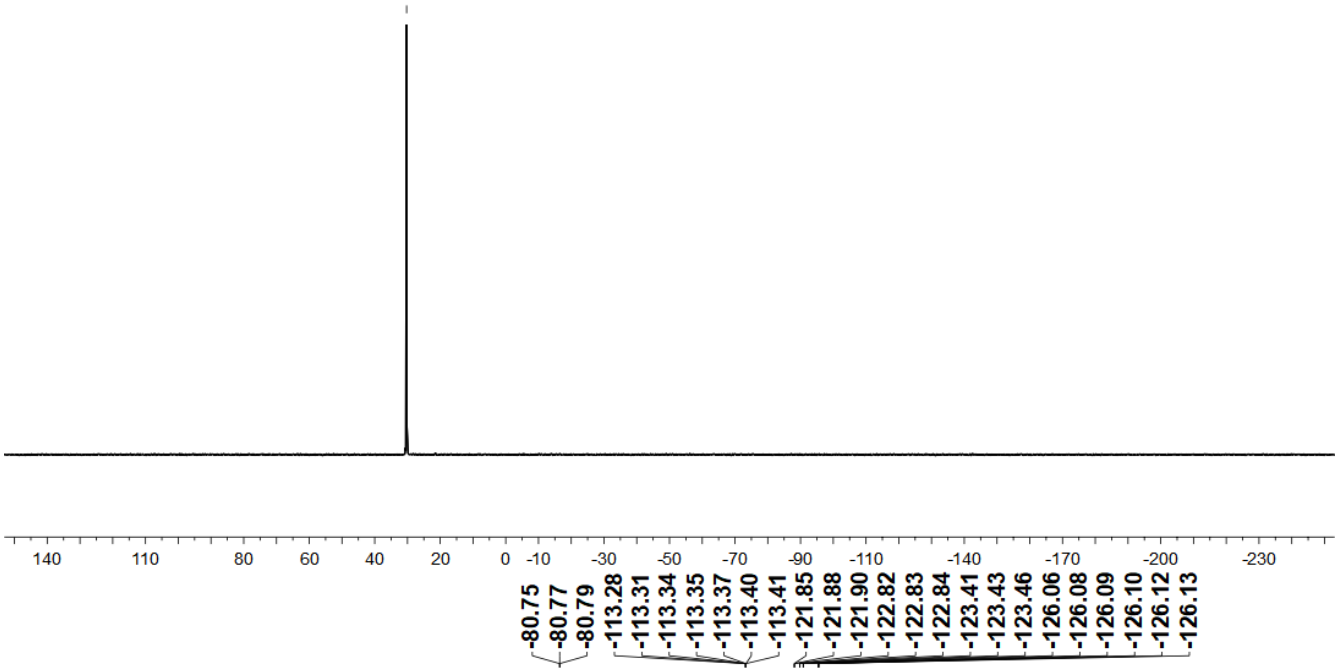
31

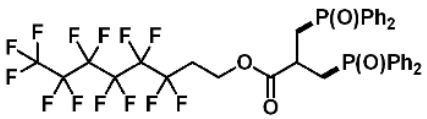
^{13}C NMR (151 MHz, $CDCl_3$)



31

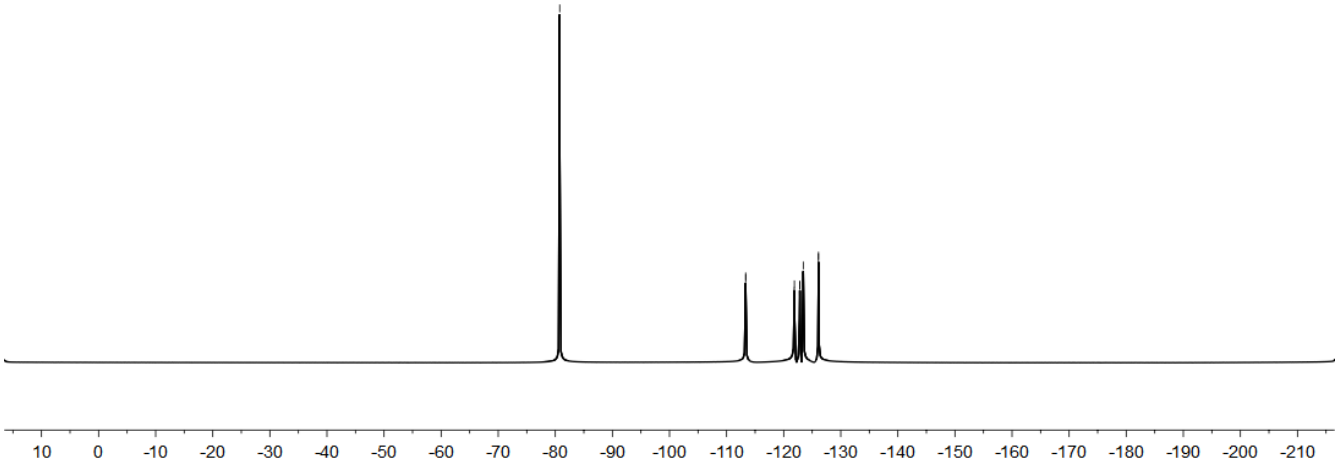
^{31}P NMR (162 MHz, $CDCl_3$)

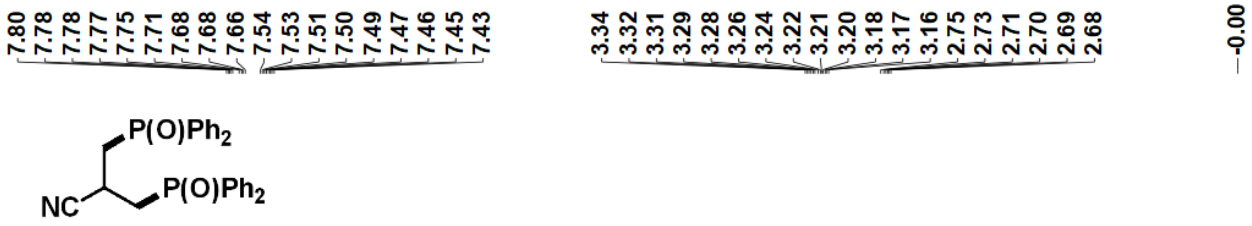




31

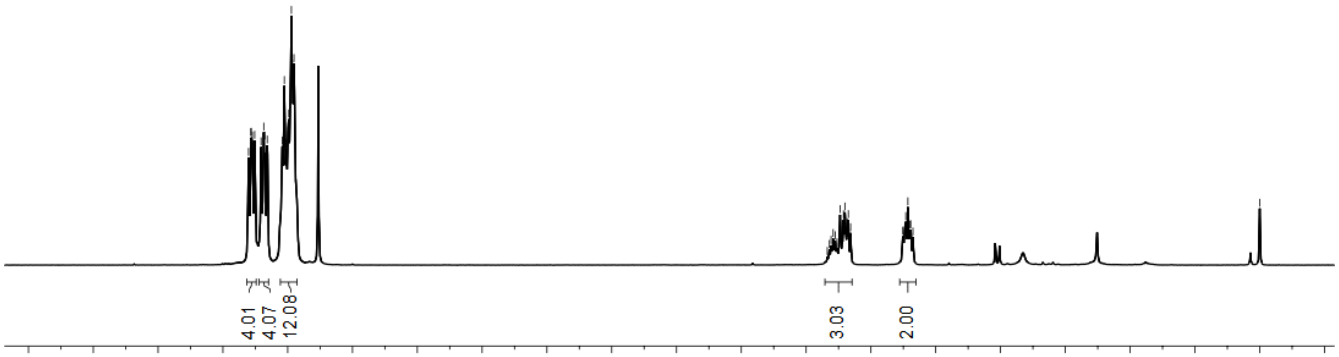
^{19}F NMR (565 MHz, $CDCl_3$)

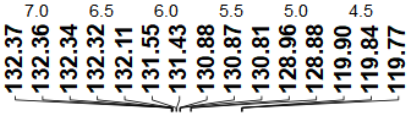


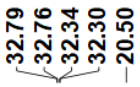


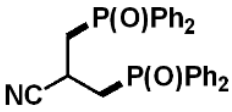
32

^{1}H NMR (400 MHz, $CDCl_3$)



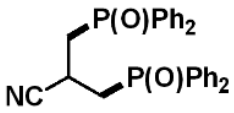






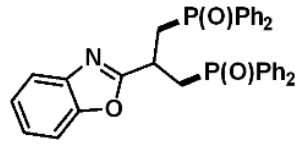
32

^{13}C NMR (151 MHz, $CDCl_3$)



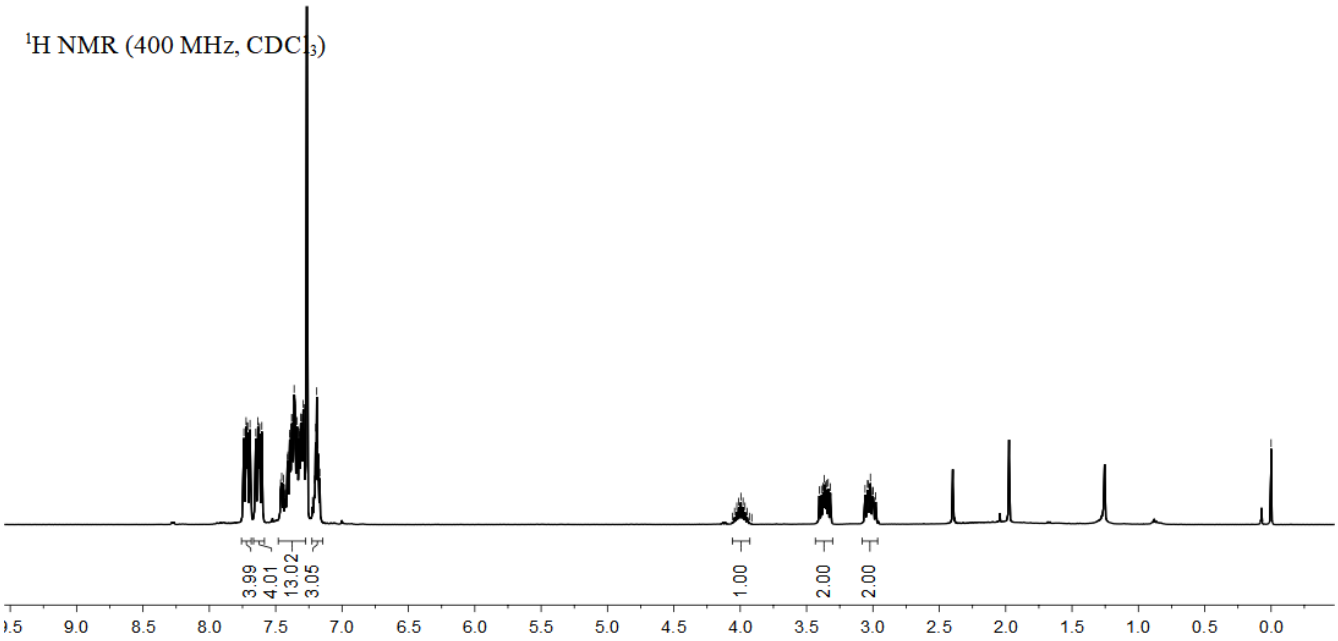
32

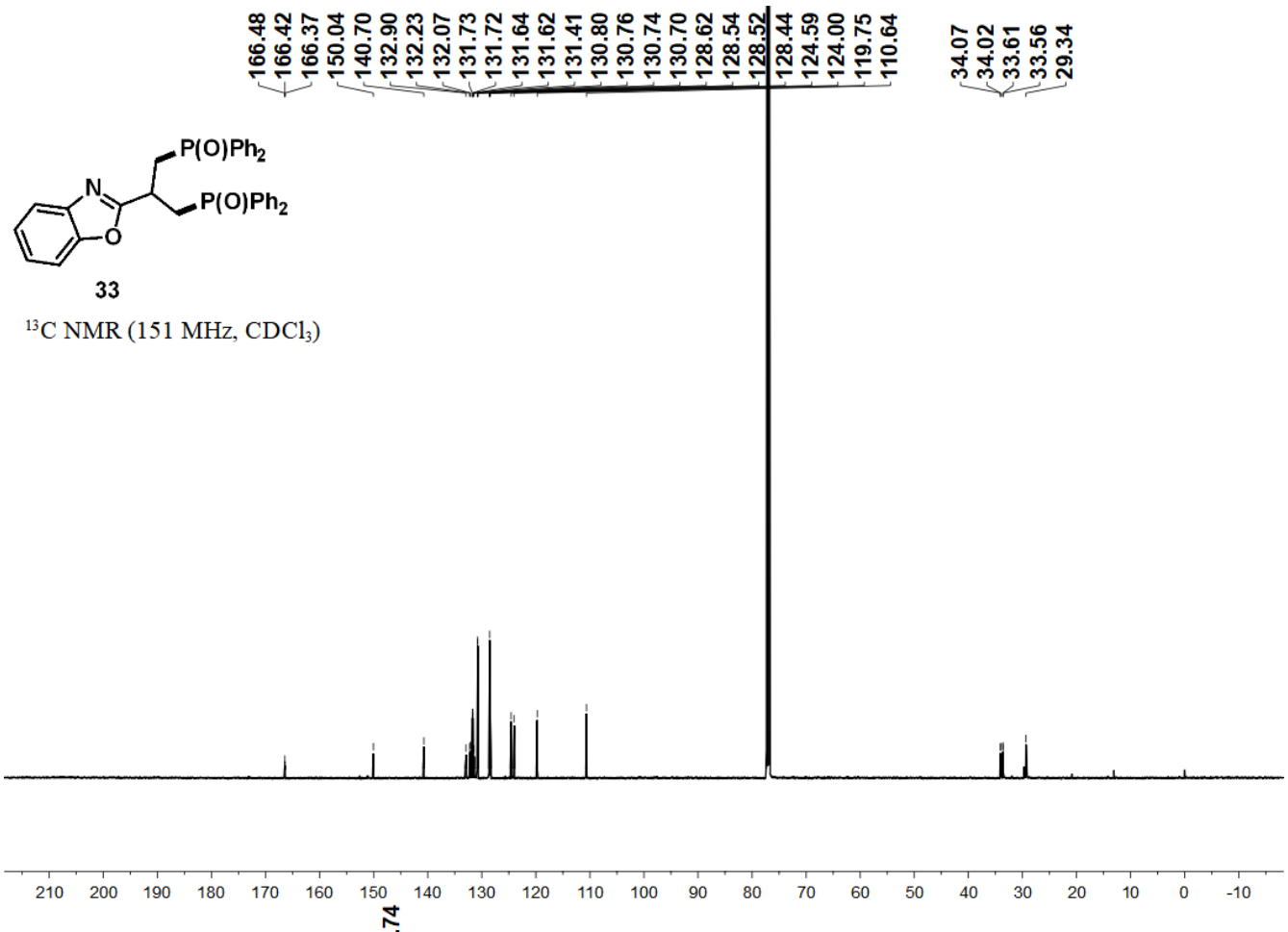
^{31}P NMR (162 MHz, $CDCl_3$)



33

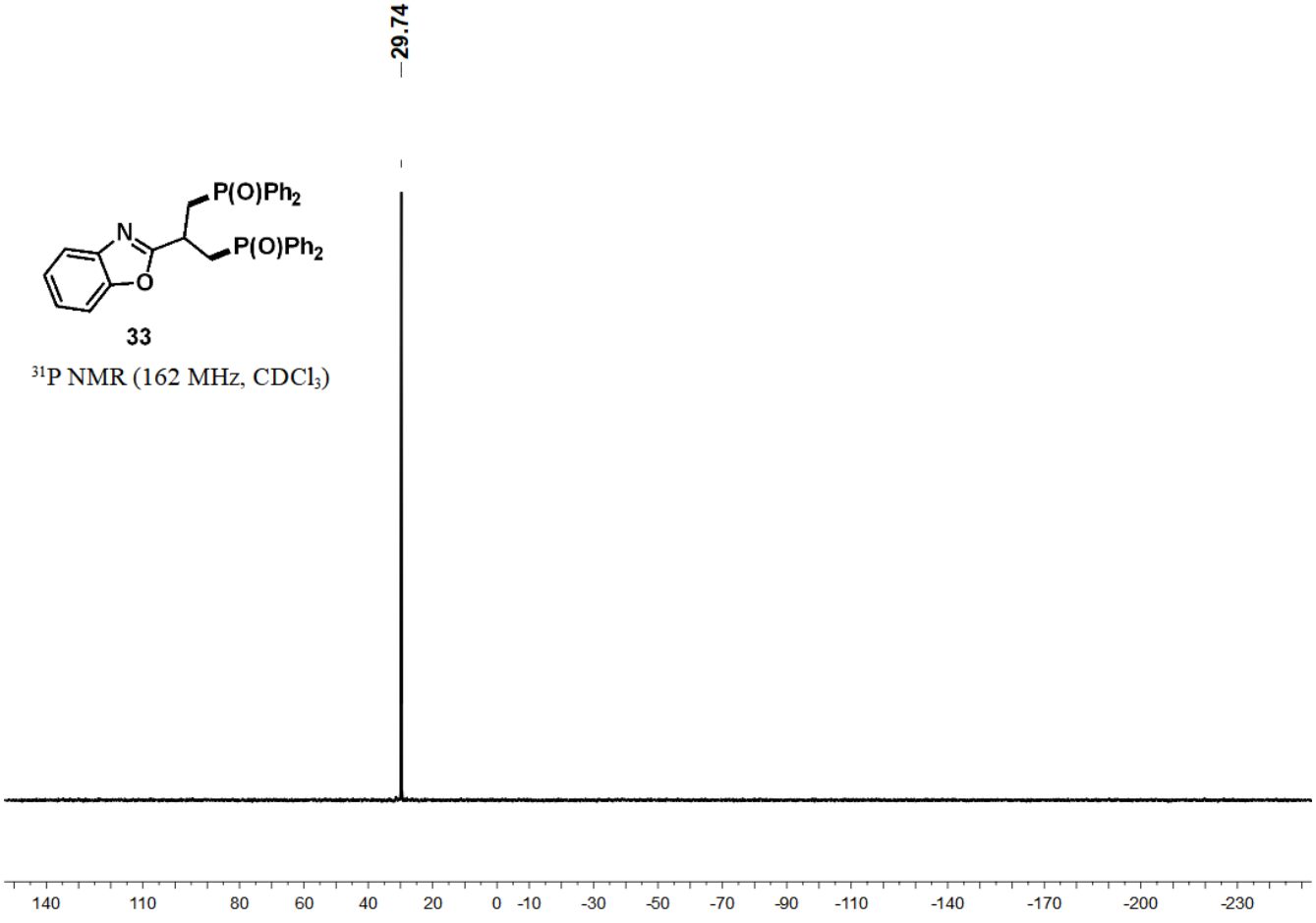
^{1}H NMR (400 MHz, $CDCl_3$)





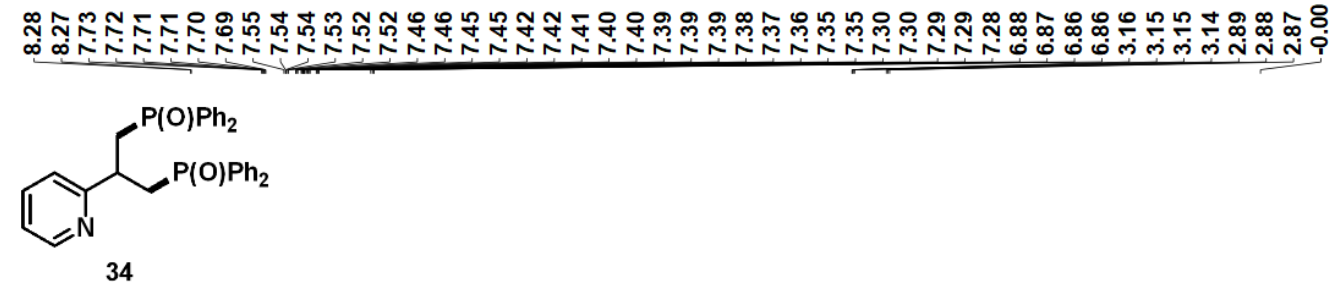
33

^{13}C NMR (151 MHz, $CDCl_3$)



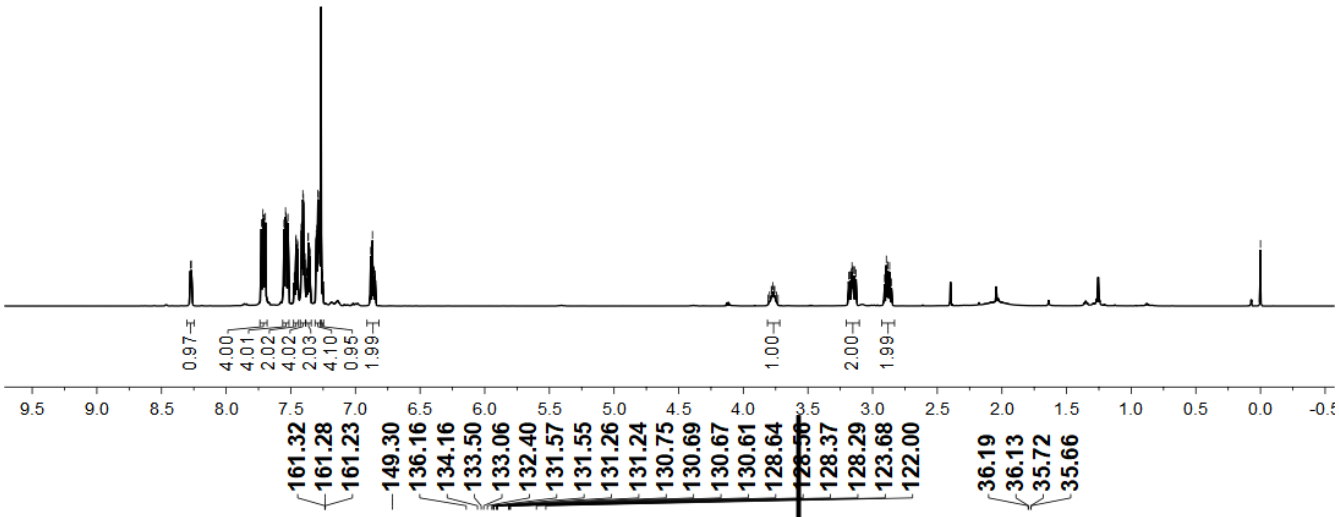
33

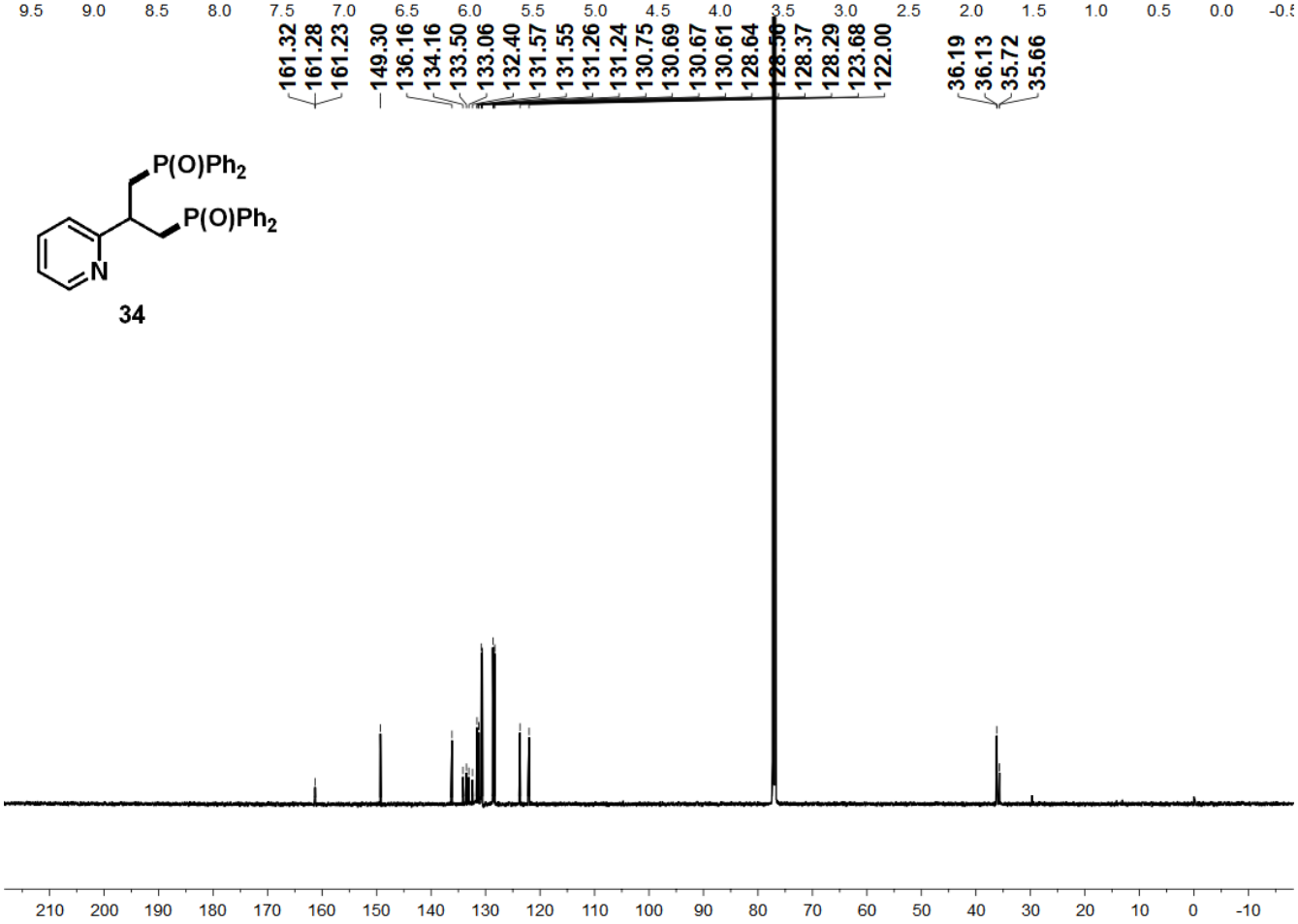
^{31}P NMR (162 MHz, $CDCl_3$)


8.28
8.27
7.73
7.72
7.71
7.71
7.70
7.69
7.55
7.54
7.54
7.53
7.52
7.52
7.46
7.46
7.45
7.45
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.37
7.36
7.35
7.35
7.30
7.30
7.29
7.29
7.28
6.88
6.87
6.86
6.86
3.16
3.15
3.15
3.14
2.89
2.88
2.87
-0.00

P(O)Ph2
P(O)Ph2
N

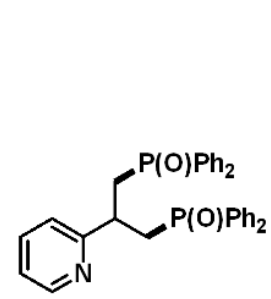
34


0.97
4.00
4.01
2.02
4.02
2.03
4.10
0.95
1.99
1.00
2.00
1.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


161.32
161.28
161.23
149.30
136.16
134.16
133.50
133.06
132.40
131.57
131.55
131.26
131.24
130.75
130.69
130.67
130.61
128.64
128.50
128.37
128.29
123.68
122.00
36.19
36.13
35.72
35.66
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

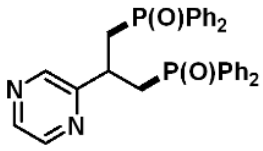
P(O)Ph2
P(O)Ph2
N

34



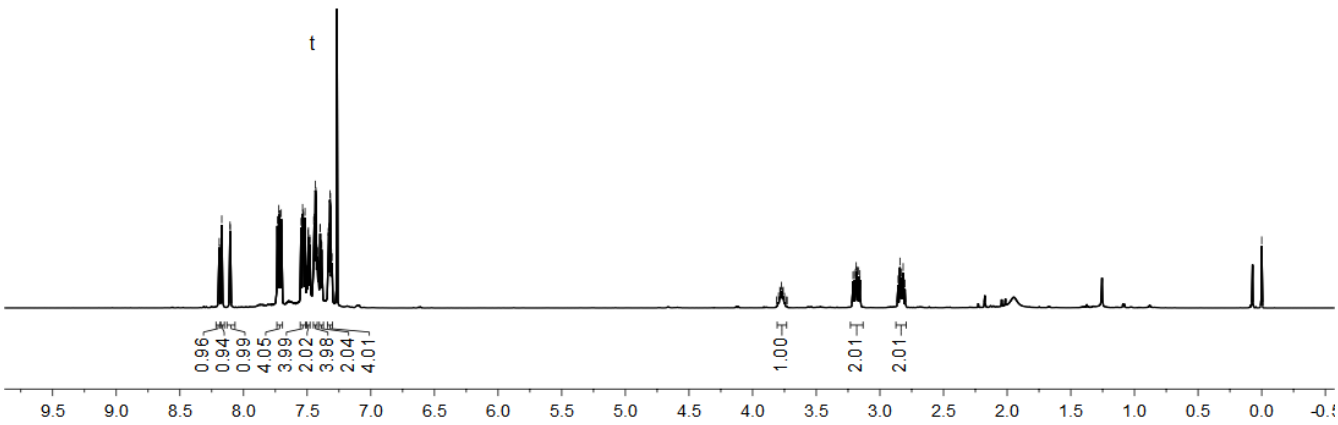
34

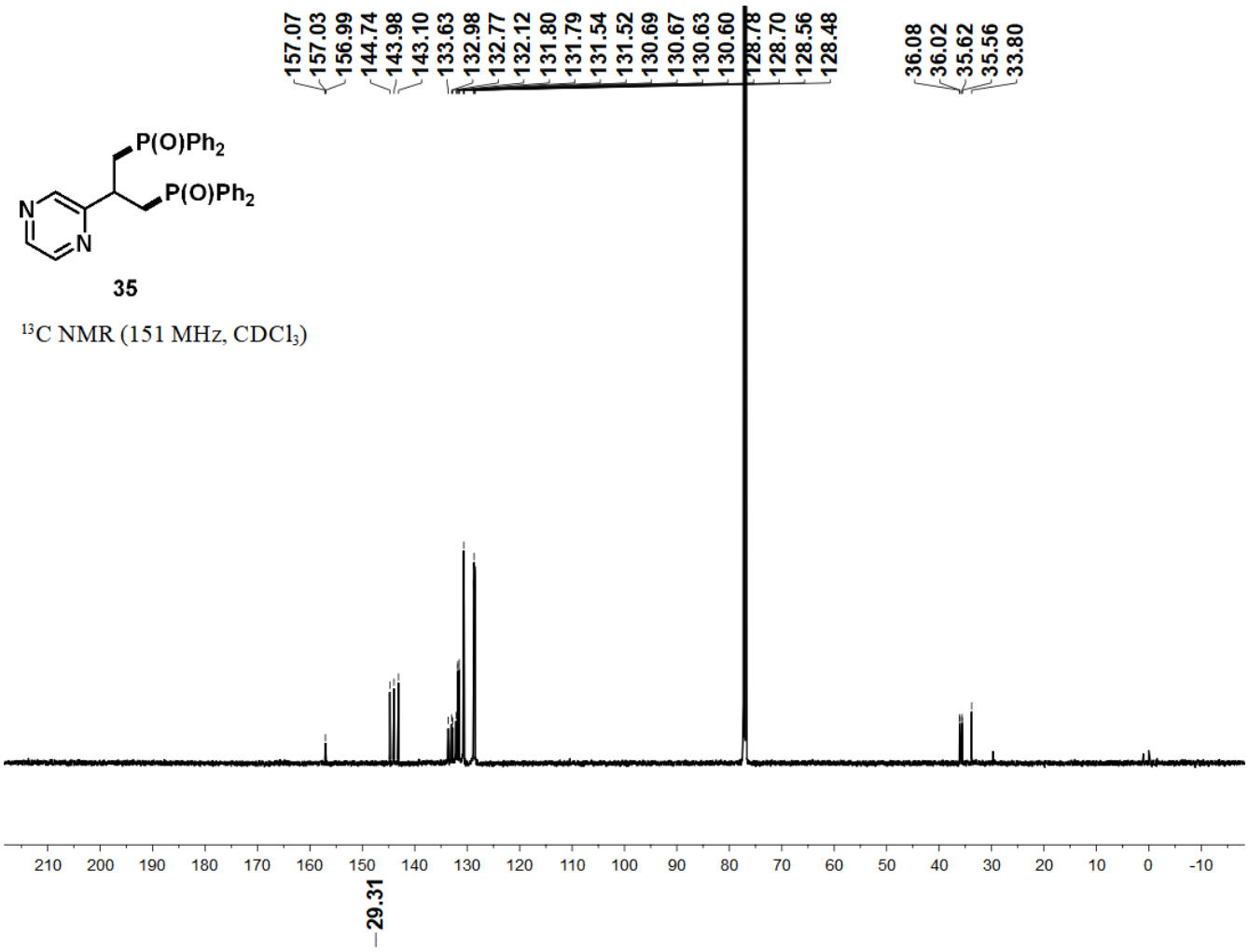
^{31}P NMR (243 MHz, $CDCl_3$)



35

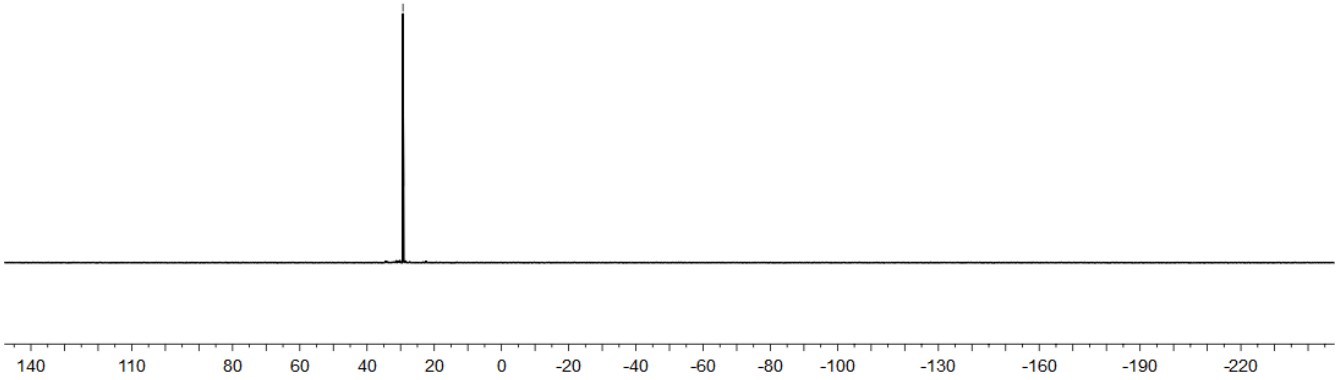
^{1}H NMR (600 MHz, $CDCl_3$)





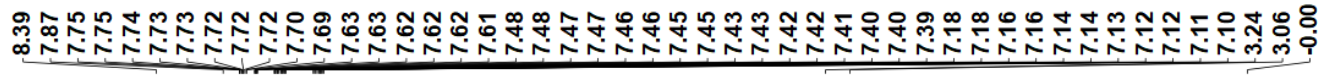
35

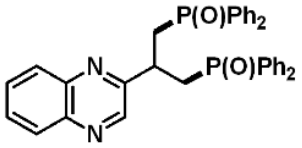
^{13}C NMR (151 MHz, $CDCl_3$)



35

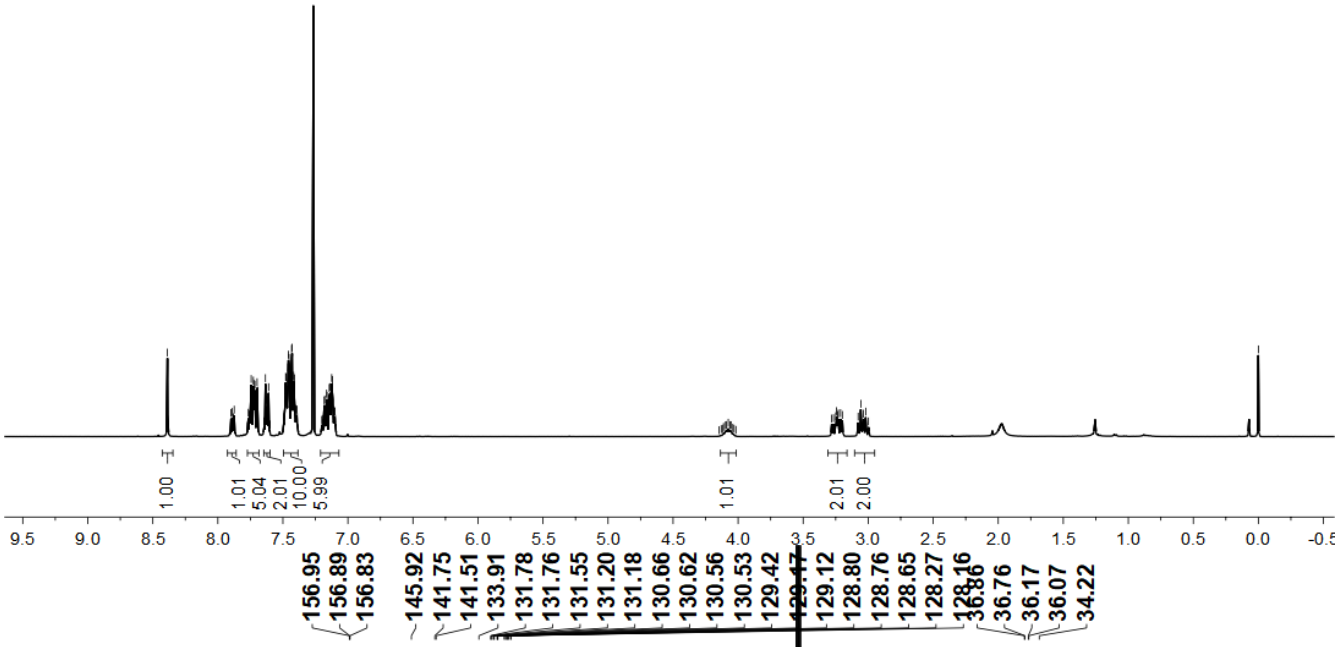
^{31}P NMR (243 MHz, $CDCl_3$)

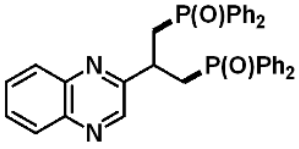




36

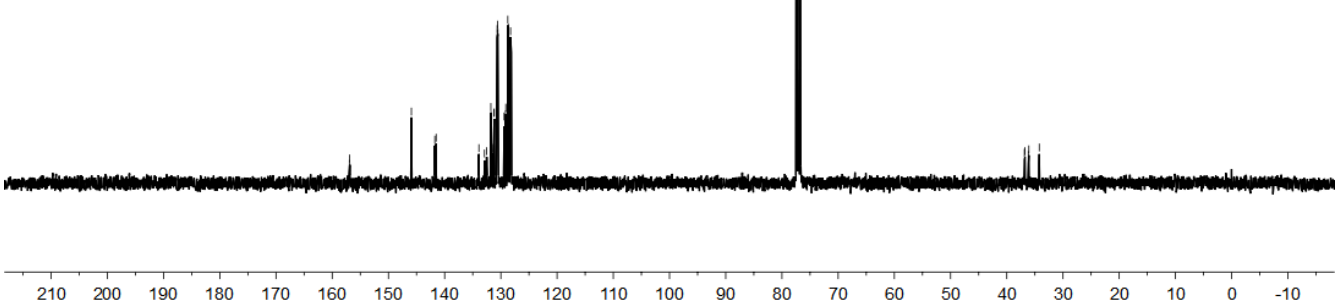
^{1}H NMR (400 MHz, $CDCl_3$)

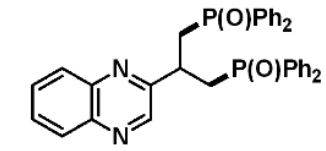




36

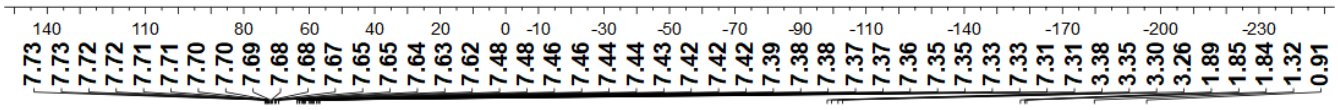
^{13}C NMR (101 MHz, $CDCl_3$)

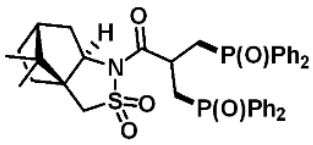




36

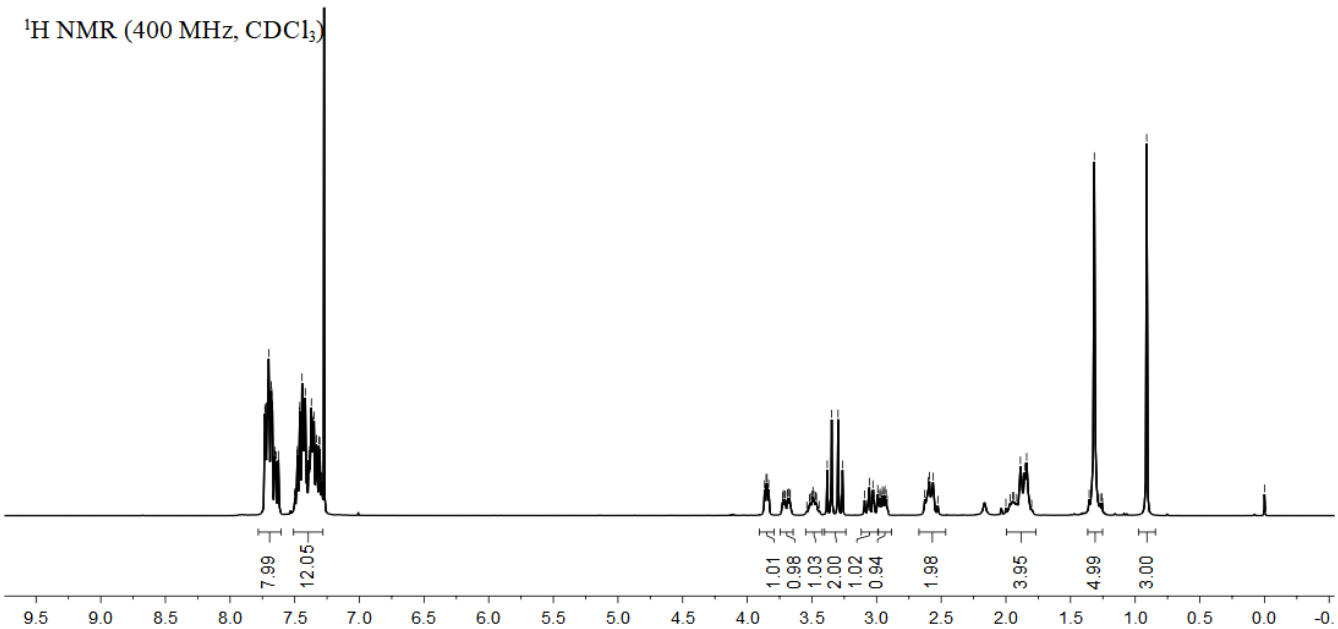
^{31}P NMR (162 MHz, $CDCl_3$)

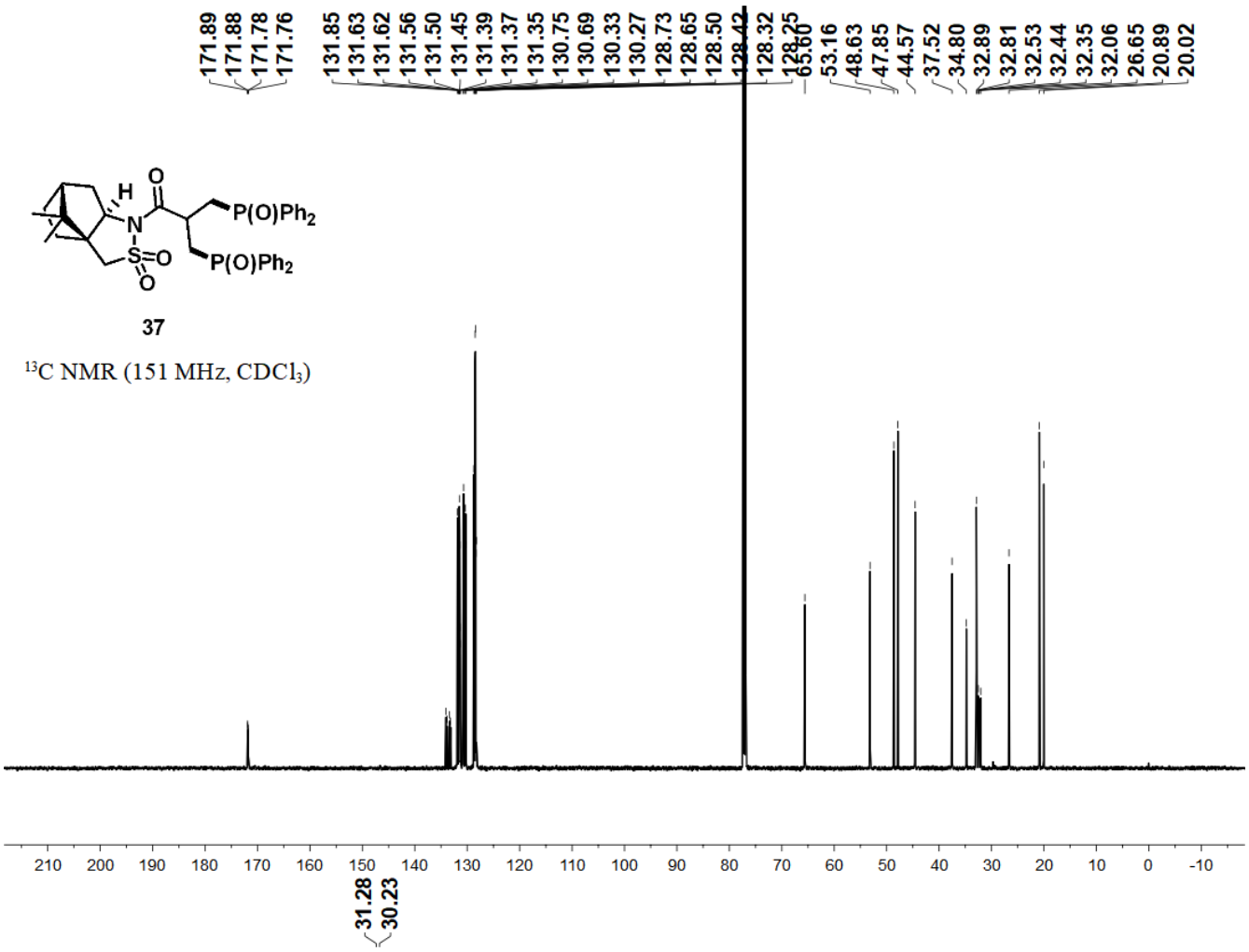




37

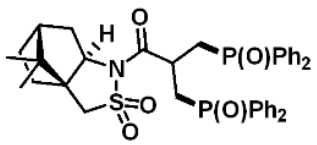
^{1}H NMR (400 MHz, $CDCl_3$)





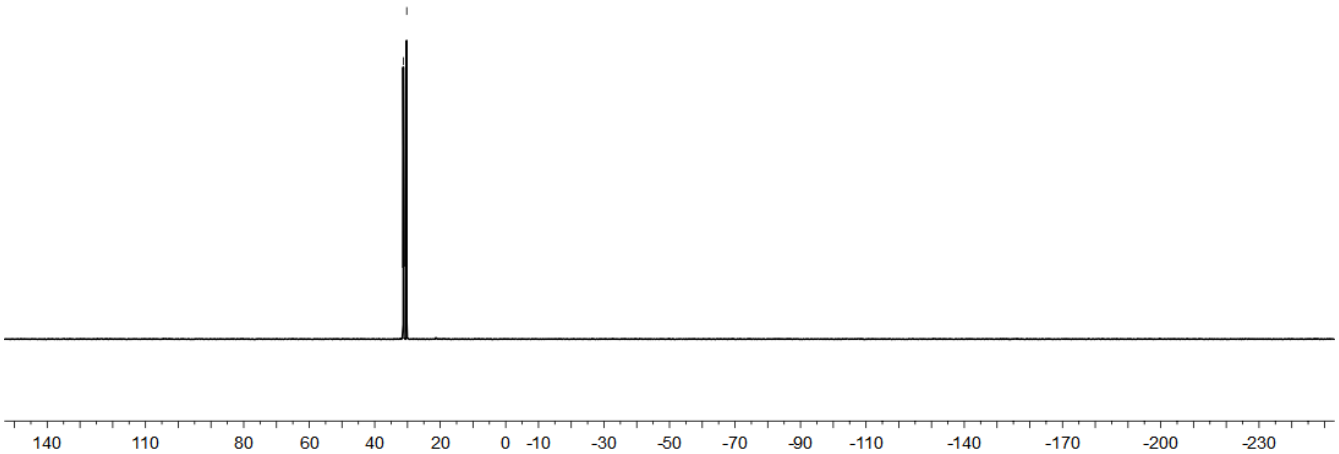
37

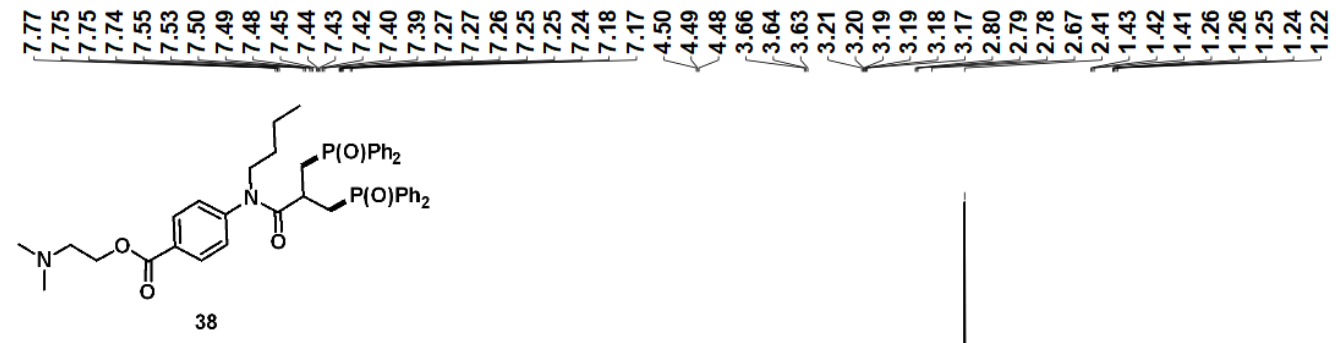
^{13}C NMR (151 MHz, $CDCl_3$)



37

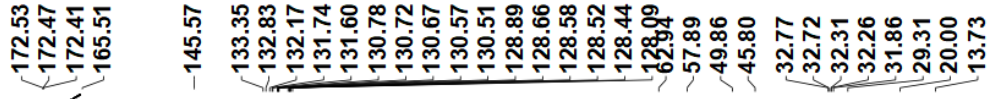
^{31}P NMR (162 MHz, $CDCl_3$)

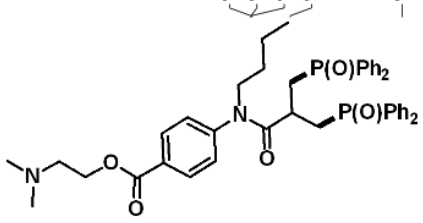




38

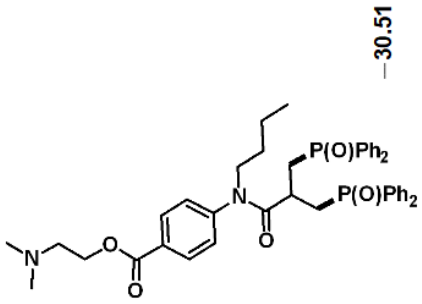
^{1}H NMR (600 MHz, $CDCl_3$)





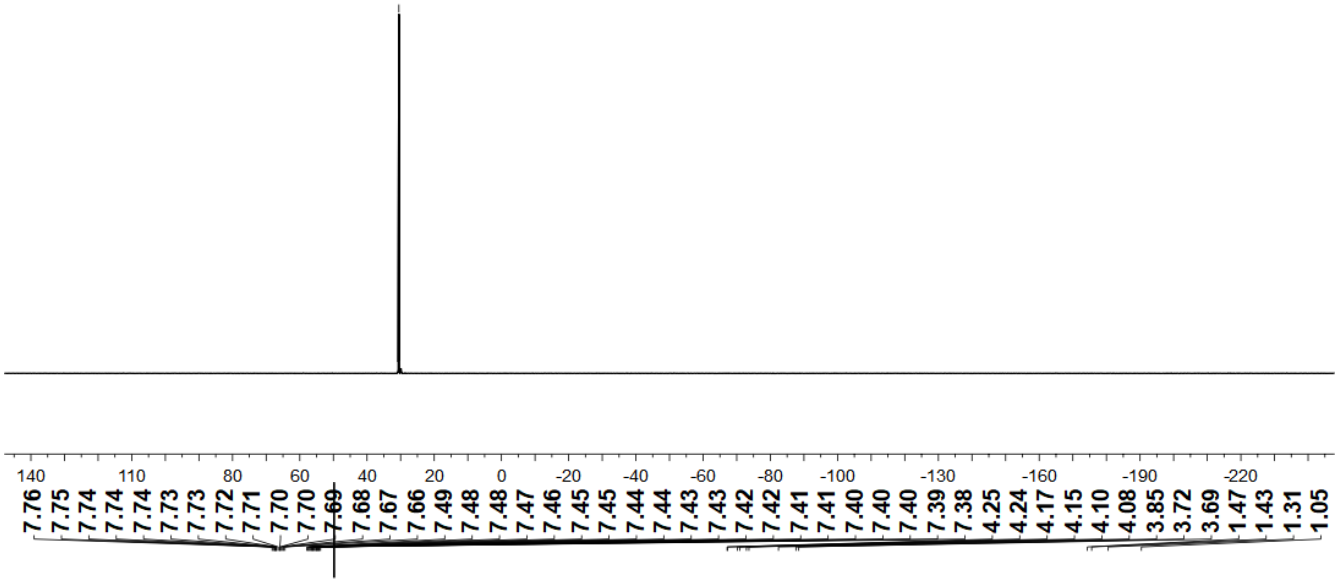
38

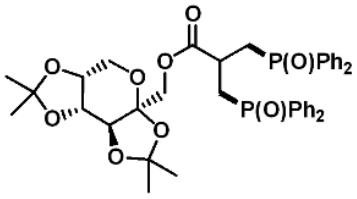
^{13}C NMR (151 MHz, $CDCl_3$)



38

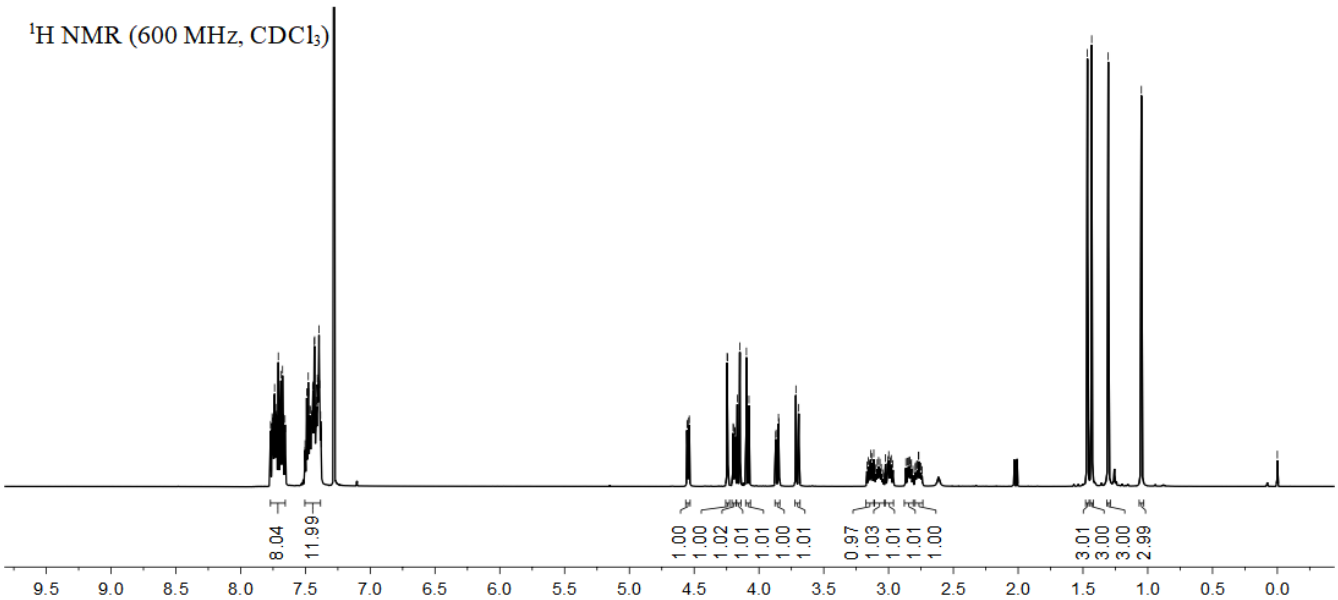
^{31}P NMR (243 MHz, $CDCl_3$)

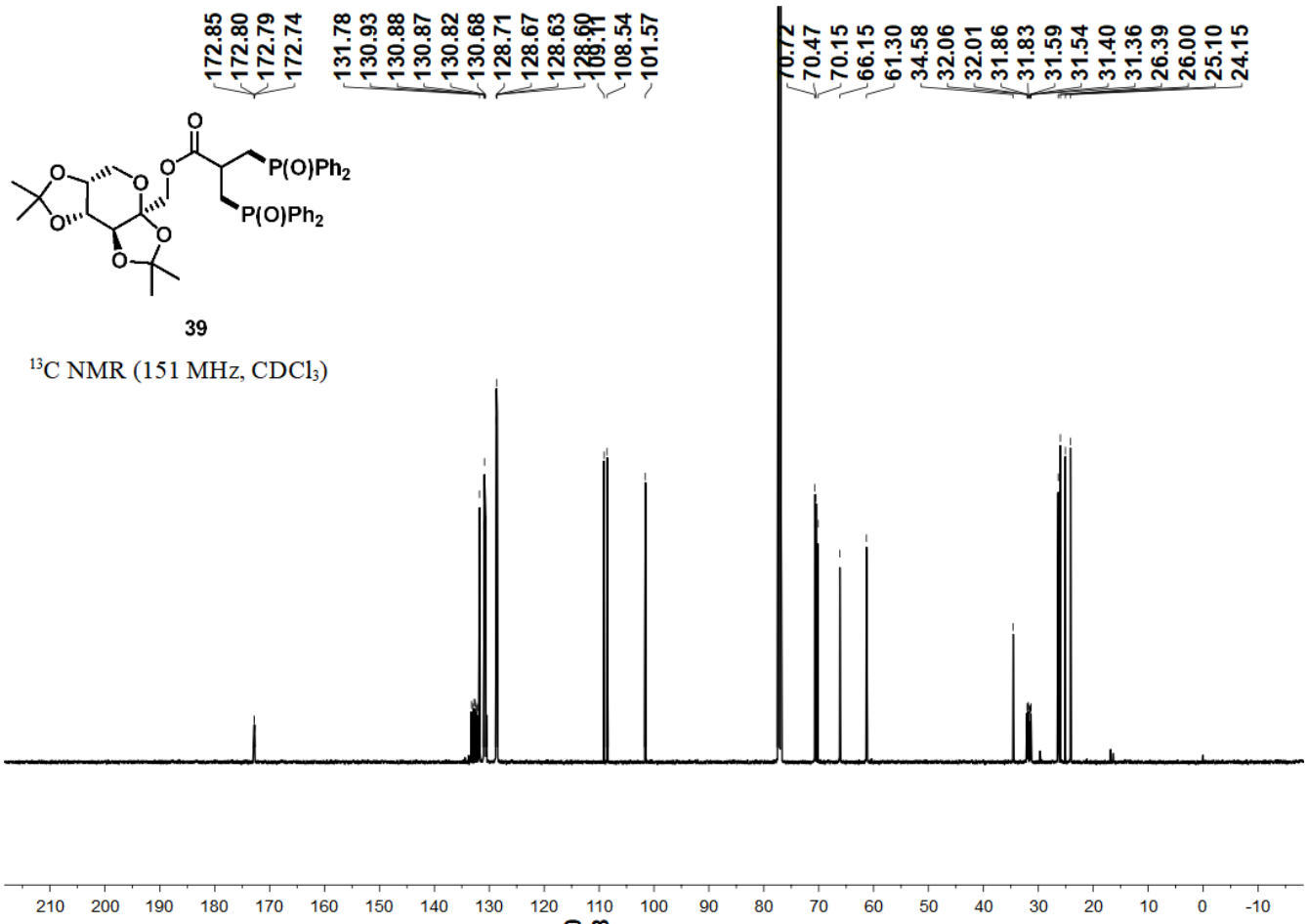




39

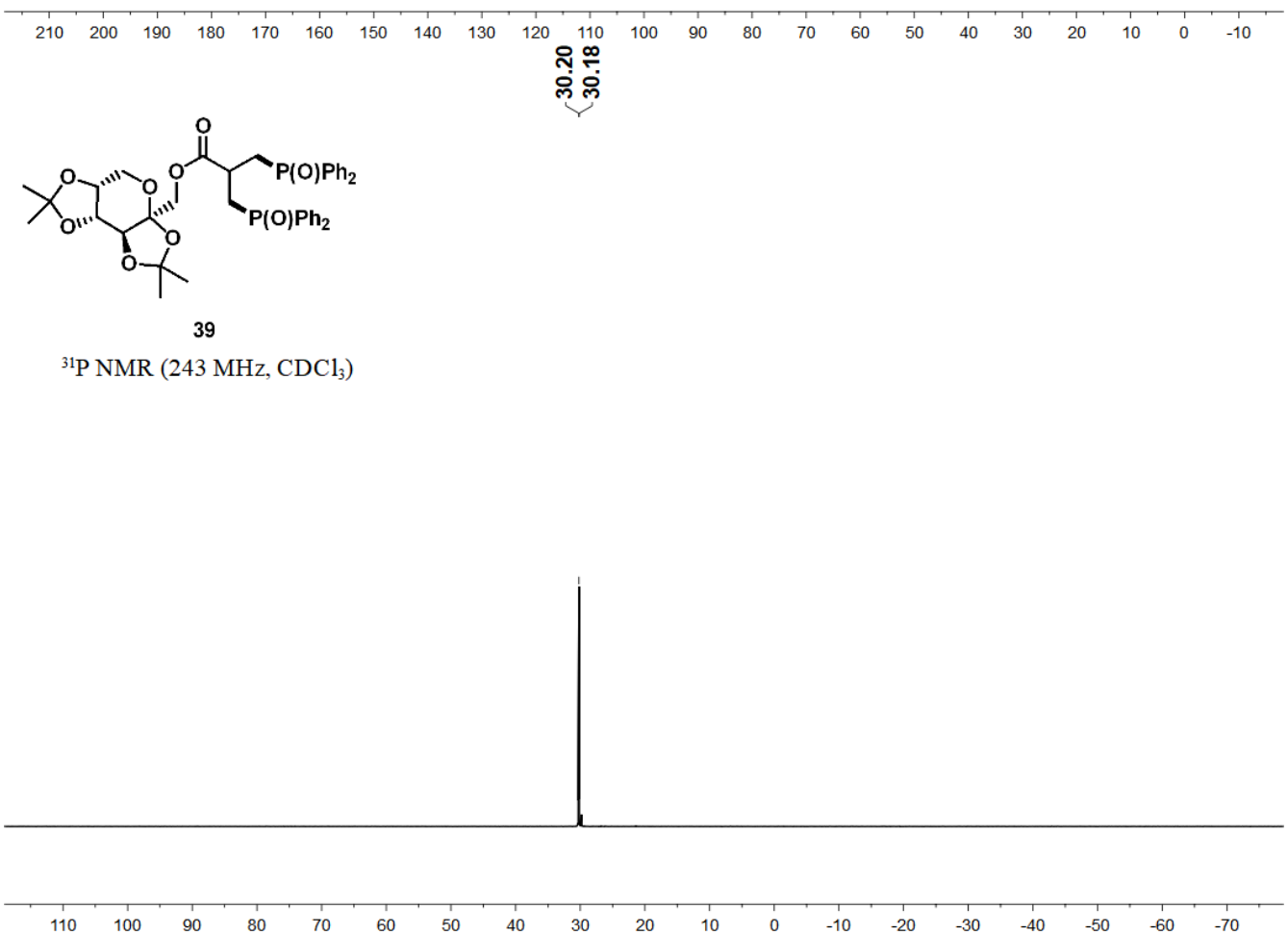
^{1}H NMR (600 MHz, $CDCl_3$)





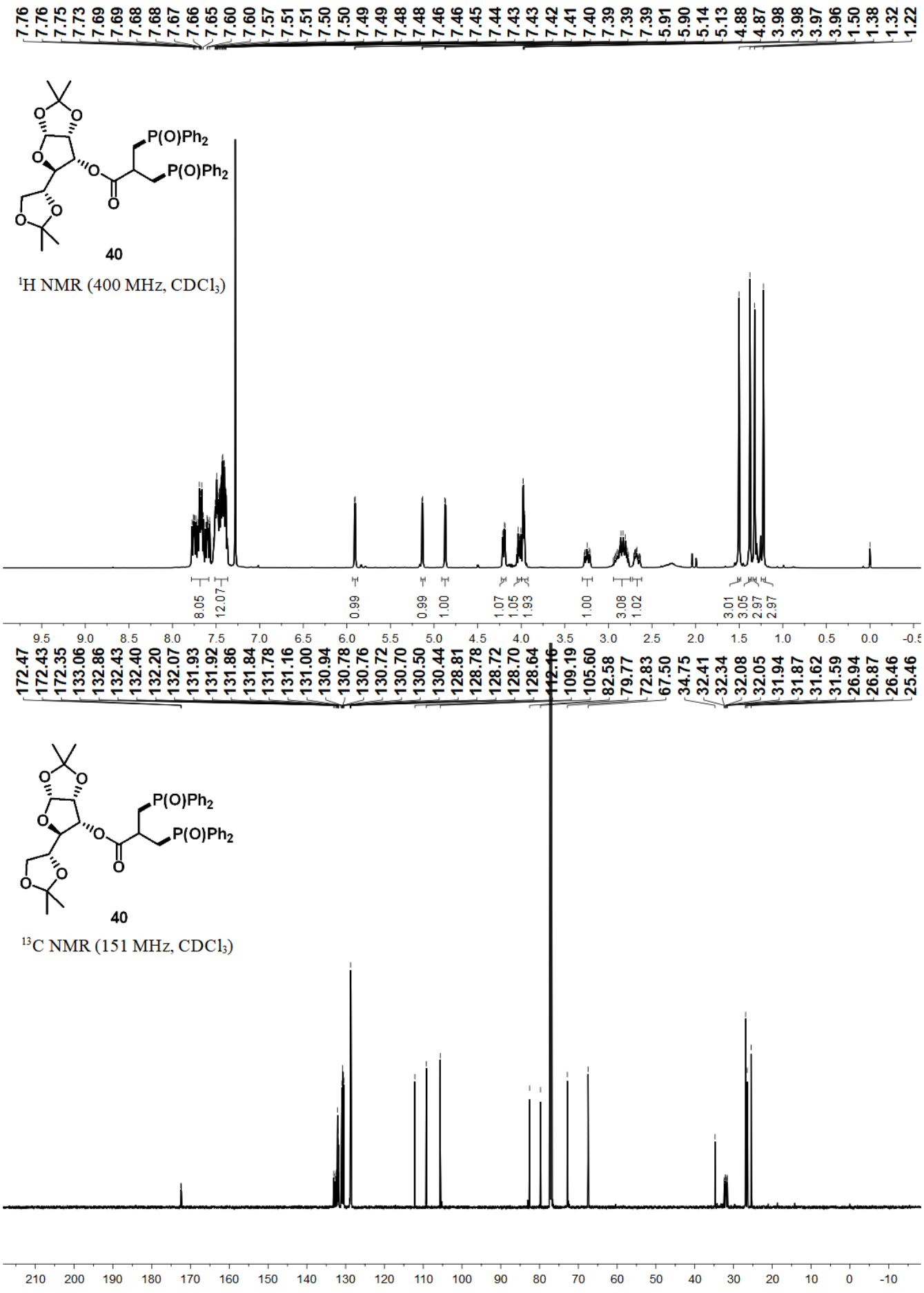
39

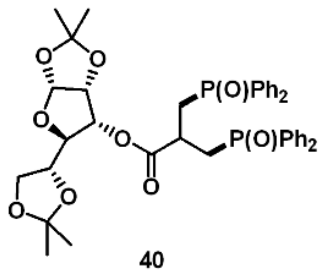
^{13}C NMR (151 MHz, $CDCl_3$)



39

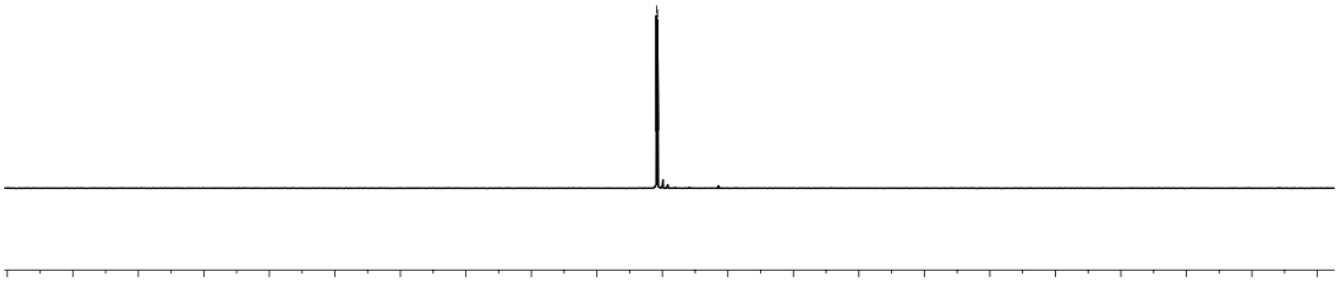
^{31}P NMR (243 MHz, $CDCl_3$)

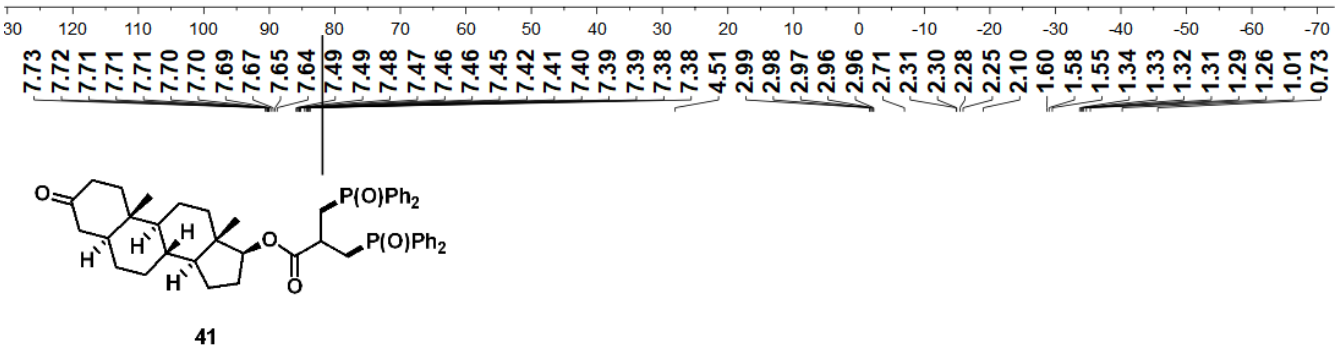

P(O)Ph2
P(O)Ph2
40
1H NMR (400 MHz, CDCl3)
13C NMR (151 MHz, CDCl3)



40

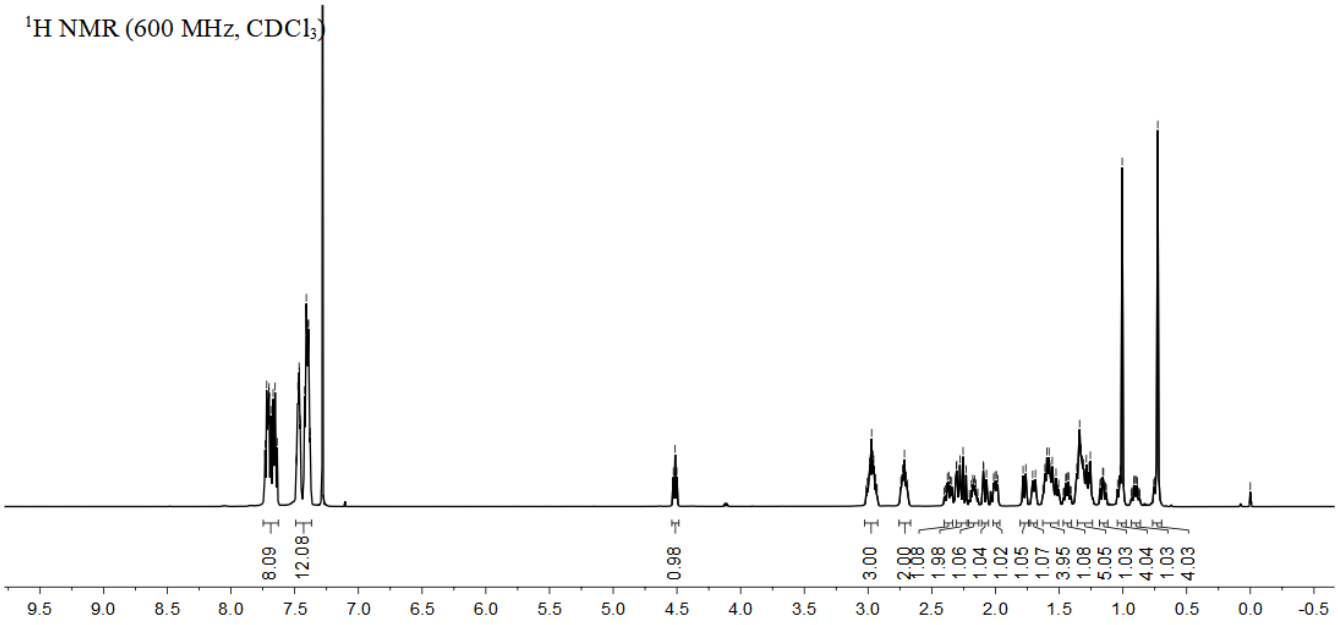
^{31}P NMR (162 MHz, $CDCl_3$)

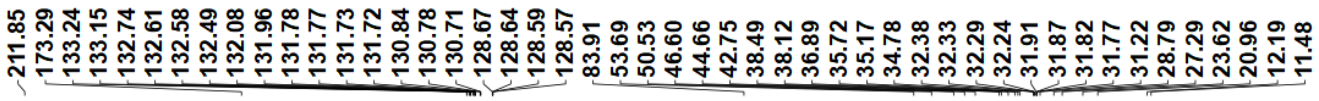


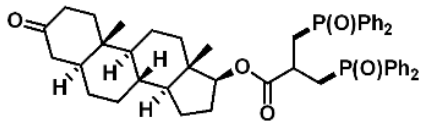


41

^{1}H NMR (600 MHz, $CDCl_3$)

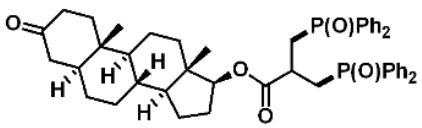






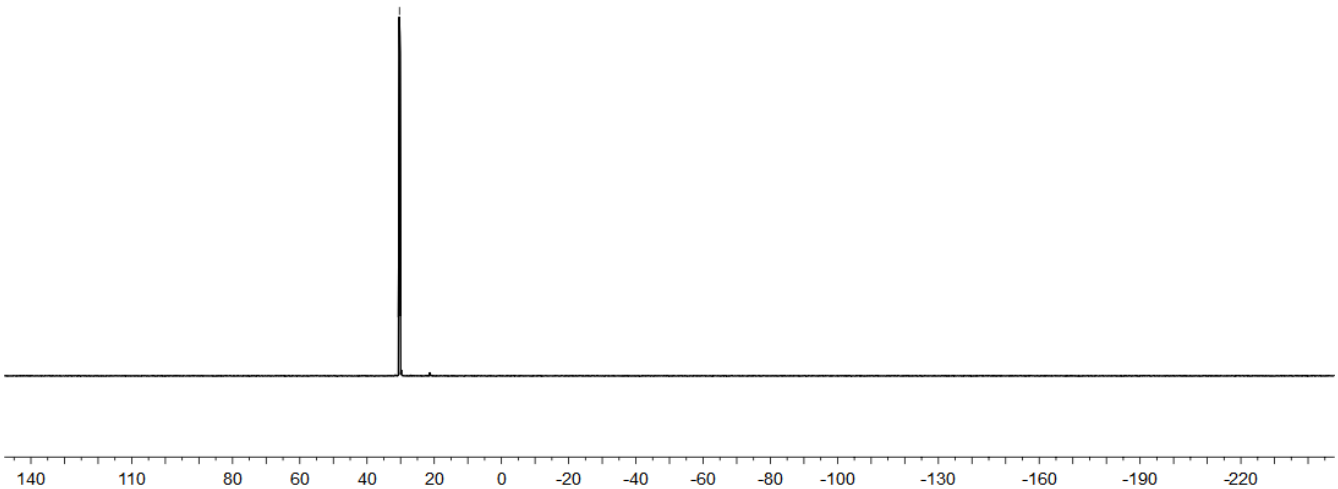
41

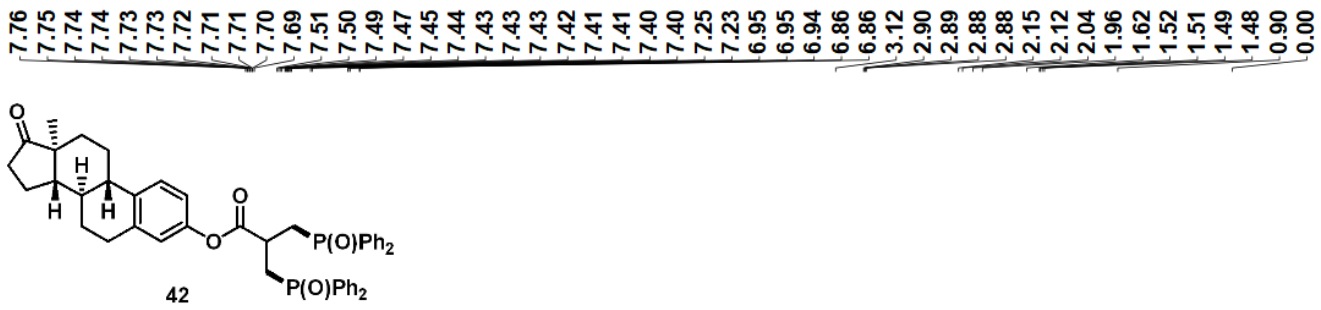
^{13}C NMR (151 MHz, $CDCl_3$)



41

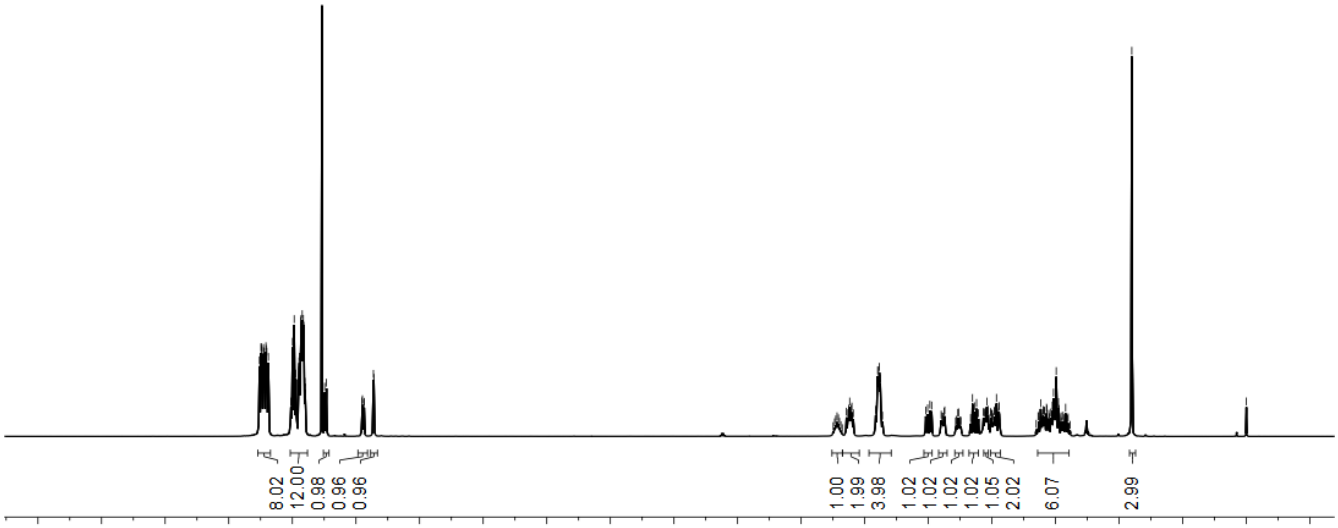
^{31}P NMR (243 MHz, $CDCl_3$)

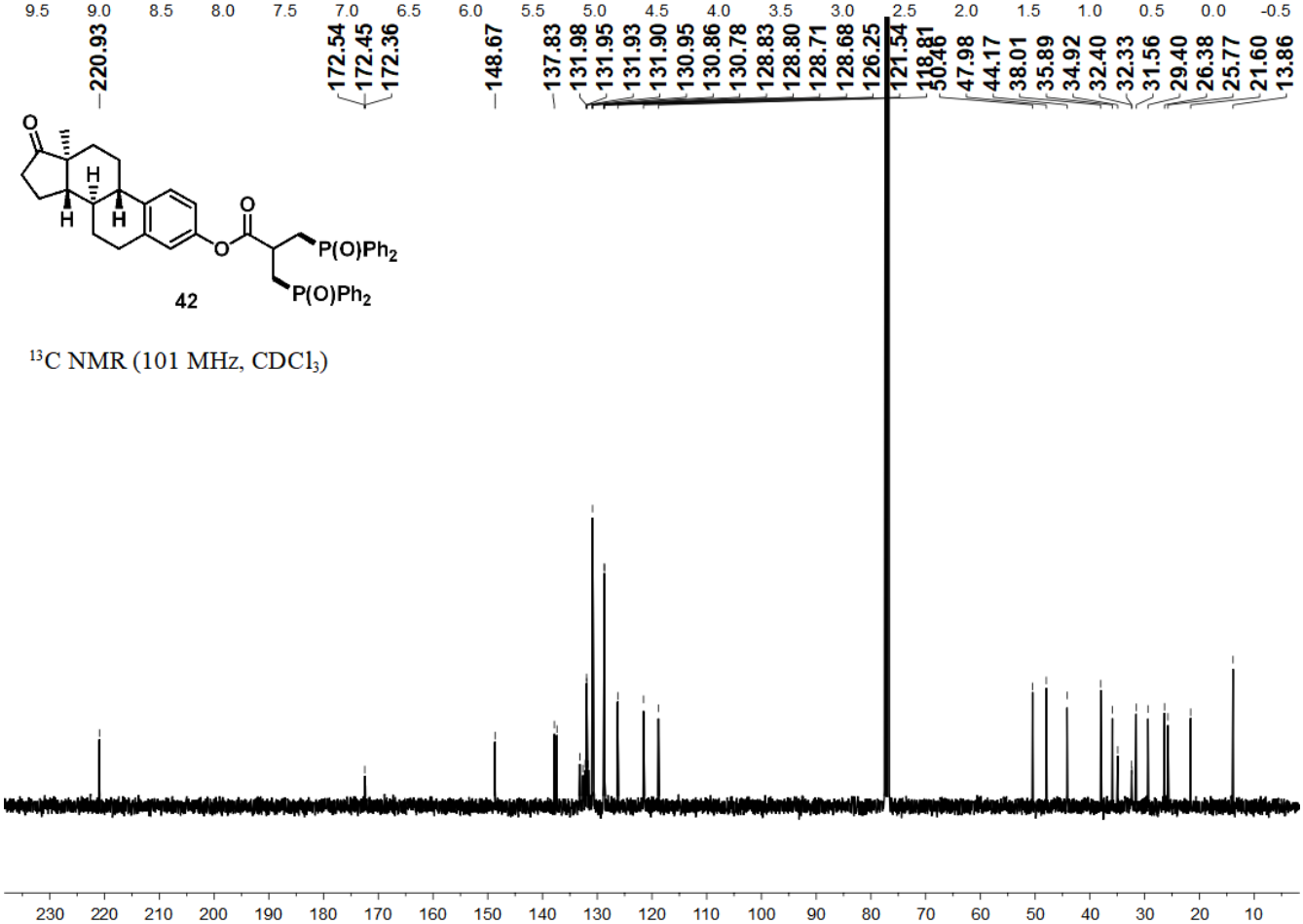




42

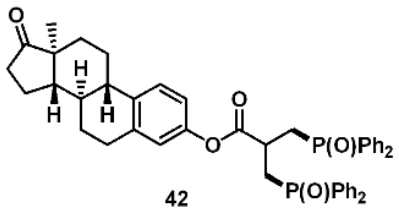
^{1}H NMR (600 MHz, $CDCl_3$)





42

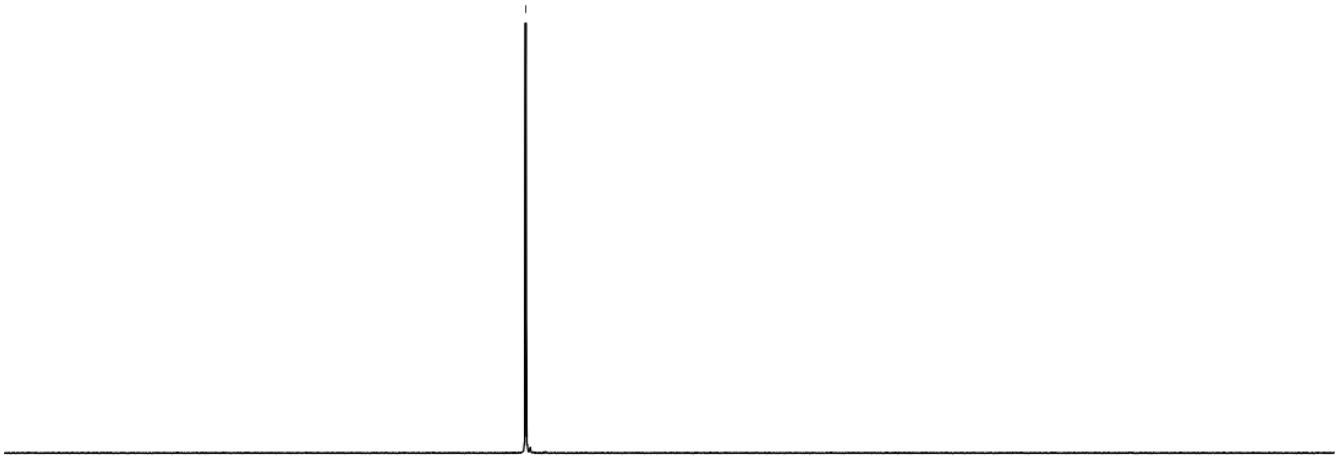
^{13}C NMR (101 MHz, $CDCl_3$)

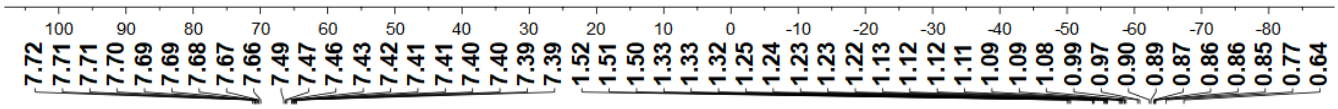


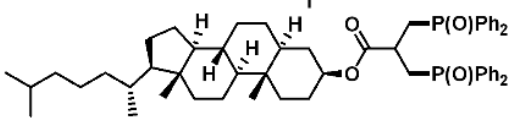
42

30.54

^{31}P NMR (243 MHz, $CDCl_3$)

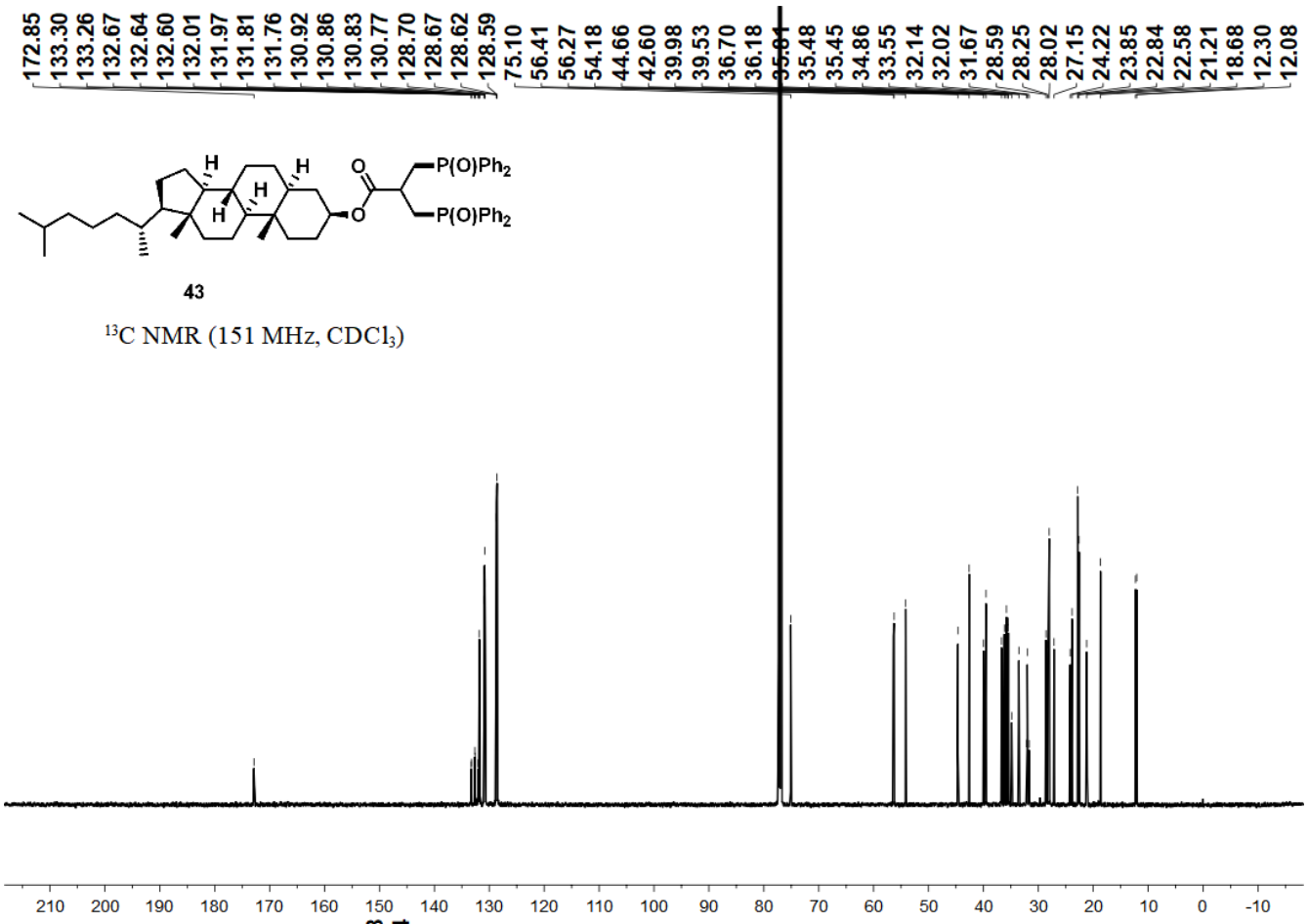






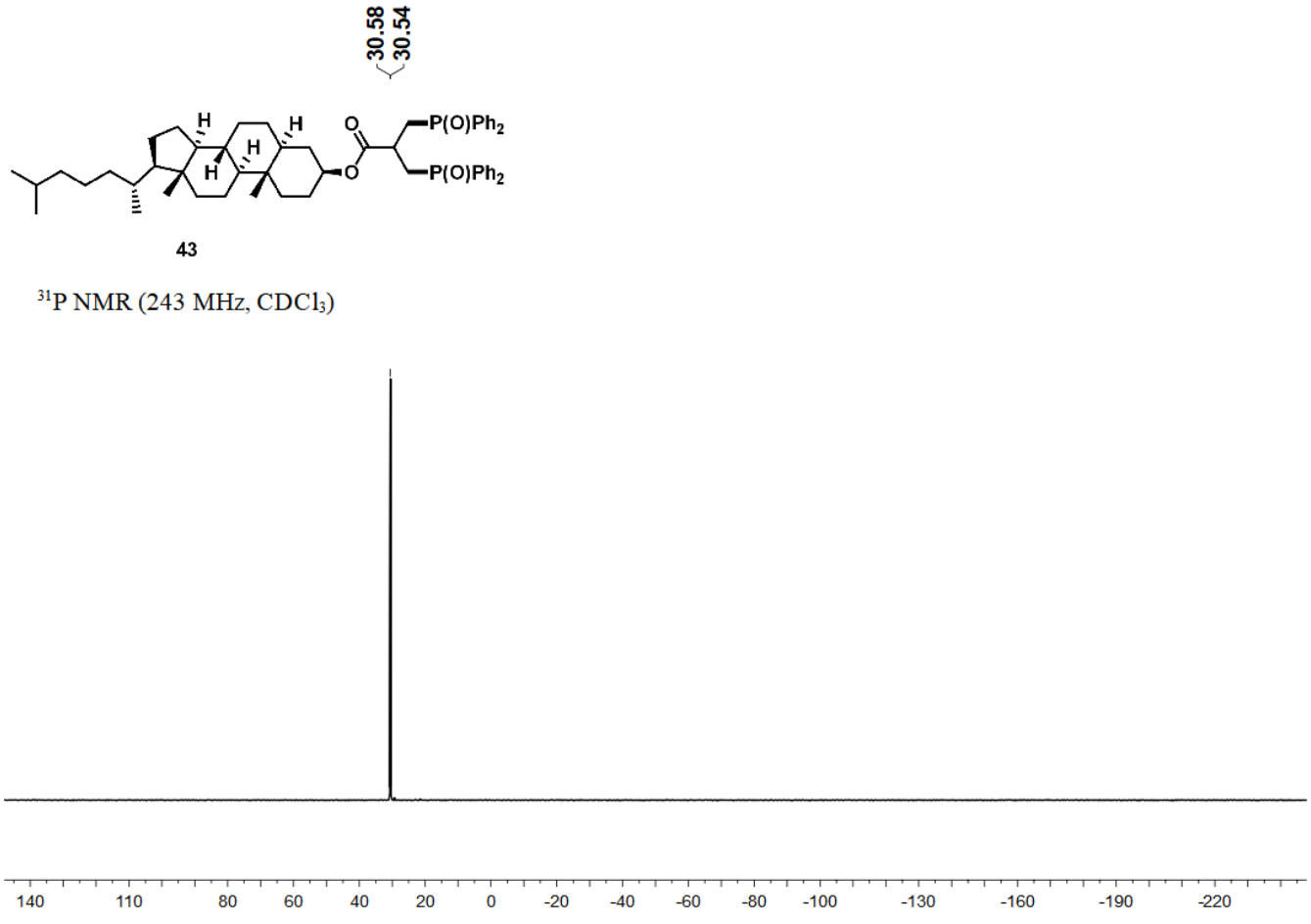
43

^{1}H NMR (600 MHz, $CDCl_3$)



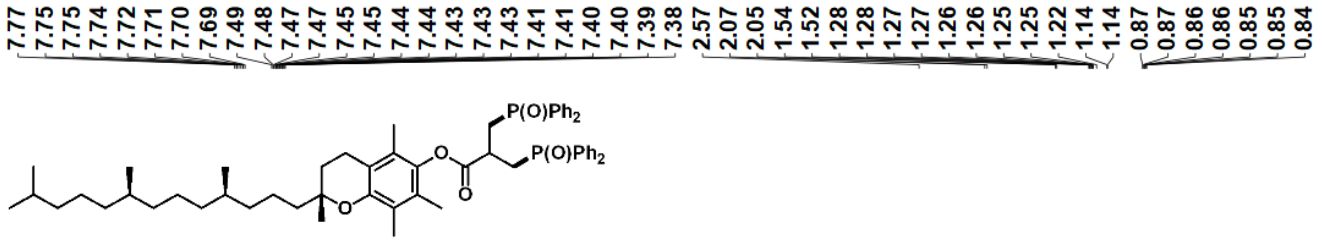
43

^{13}C NMR (151 MHz, $CDCl_3$)



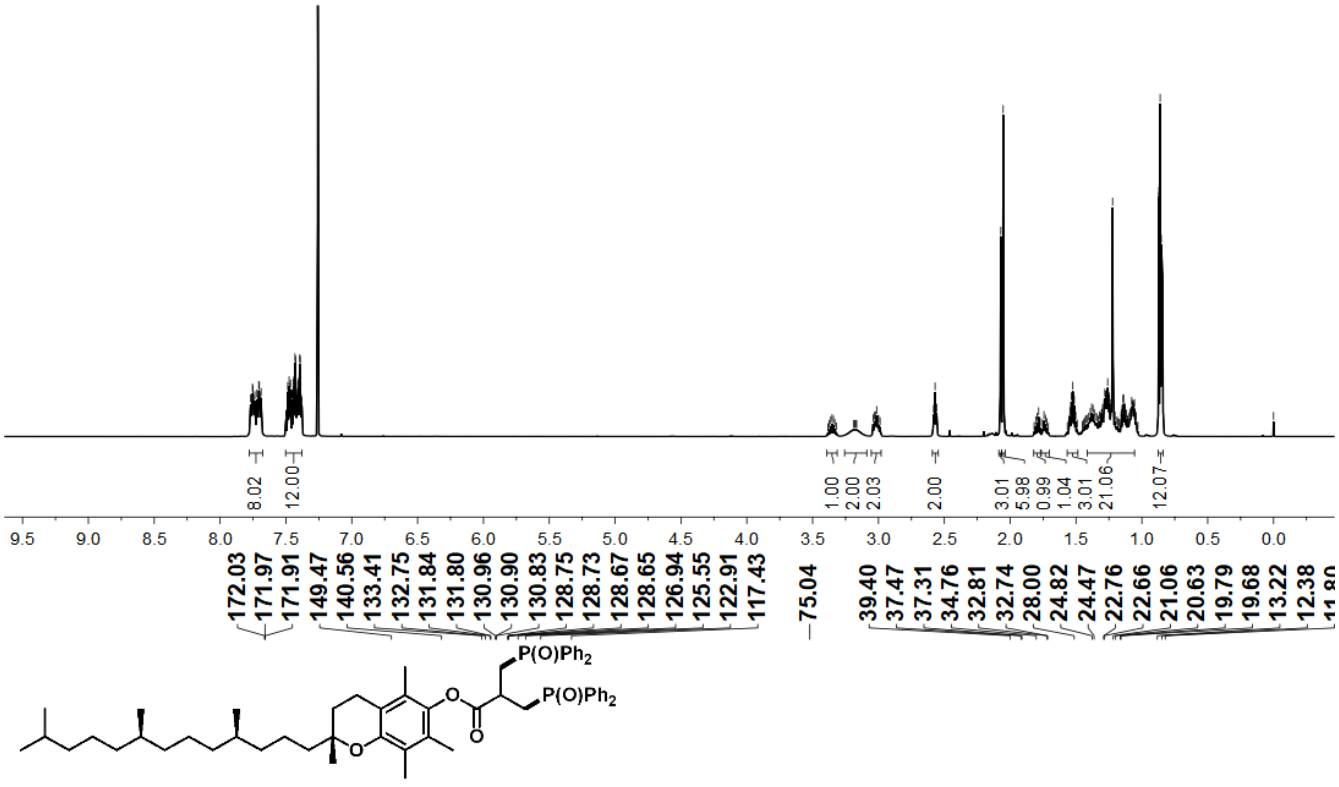
43

^{31}P NMR (243 MHz, $CDCl_3$)



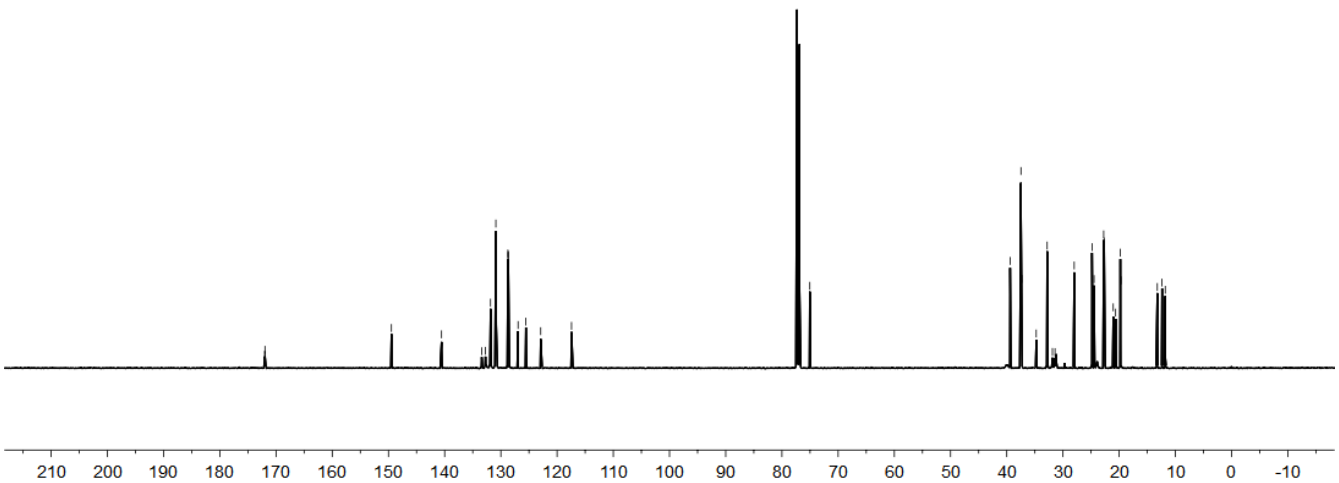
44

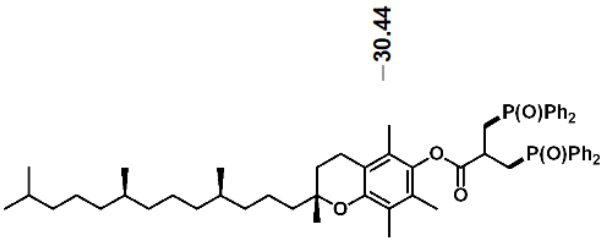
^{1}H NMR (600 MHz, $CDCl_3$)



44

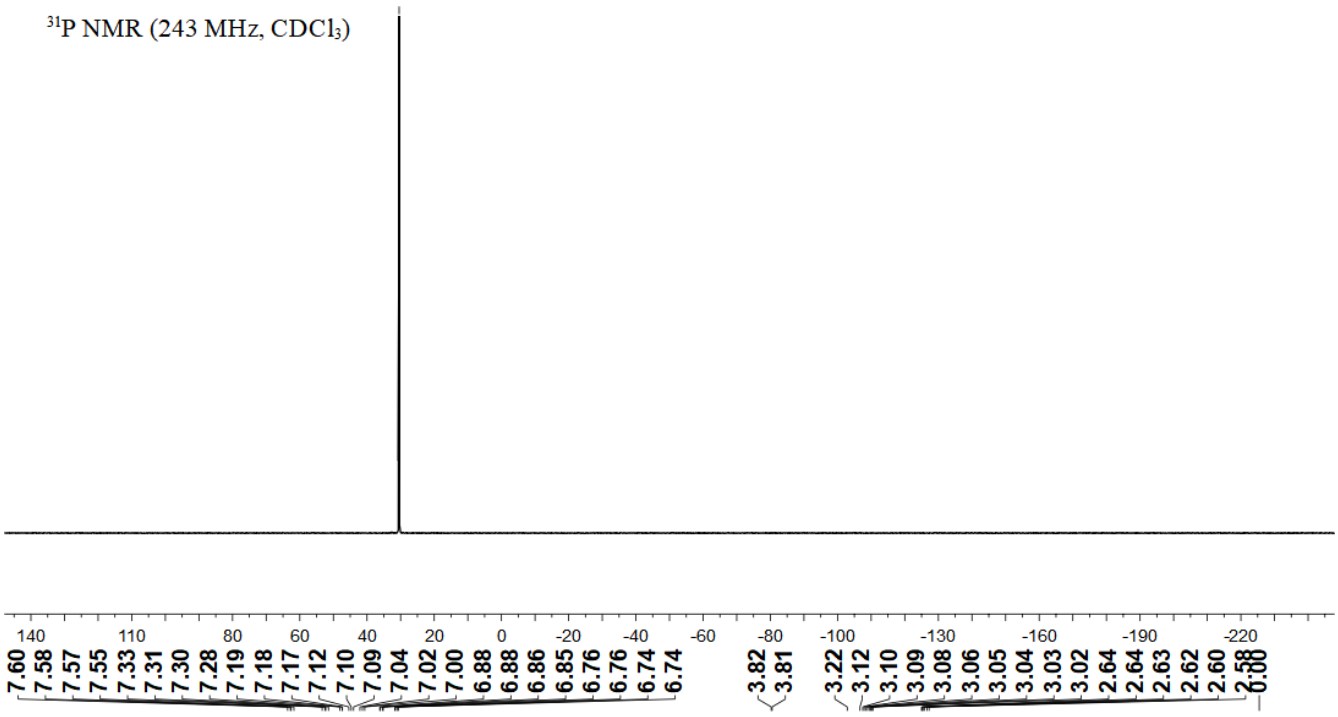
^{13}C NMR (151 MHz, $CDCl_3$)

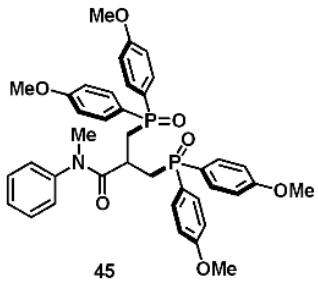




44

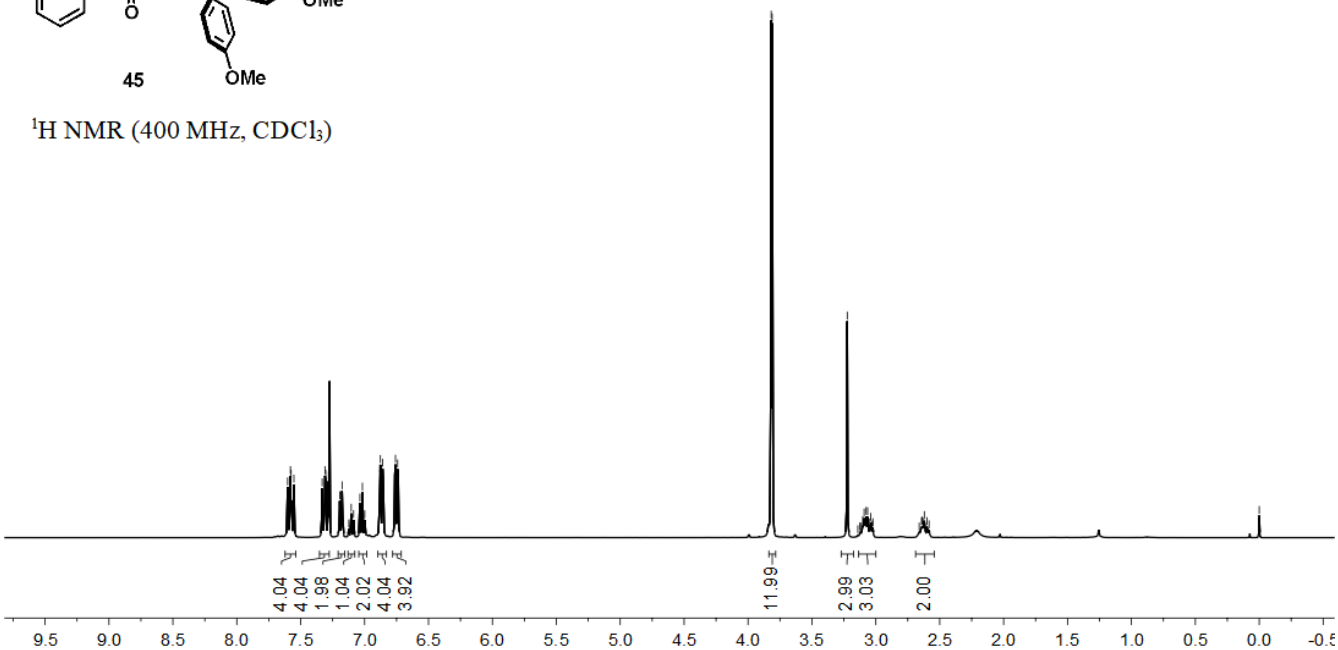
^{31}P NMR (243 MHz, $CDCl_3$)

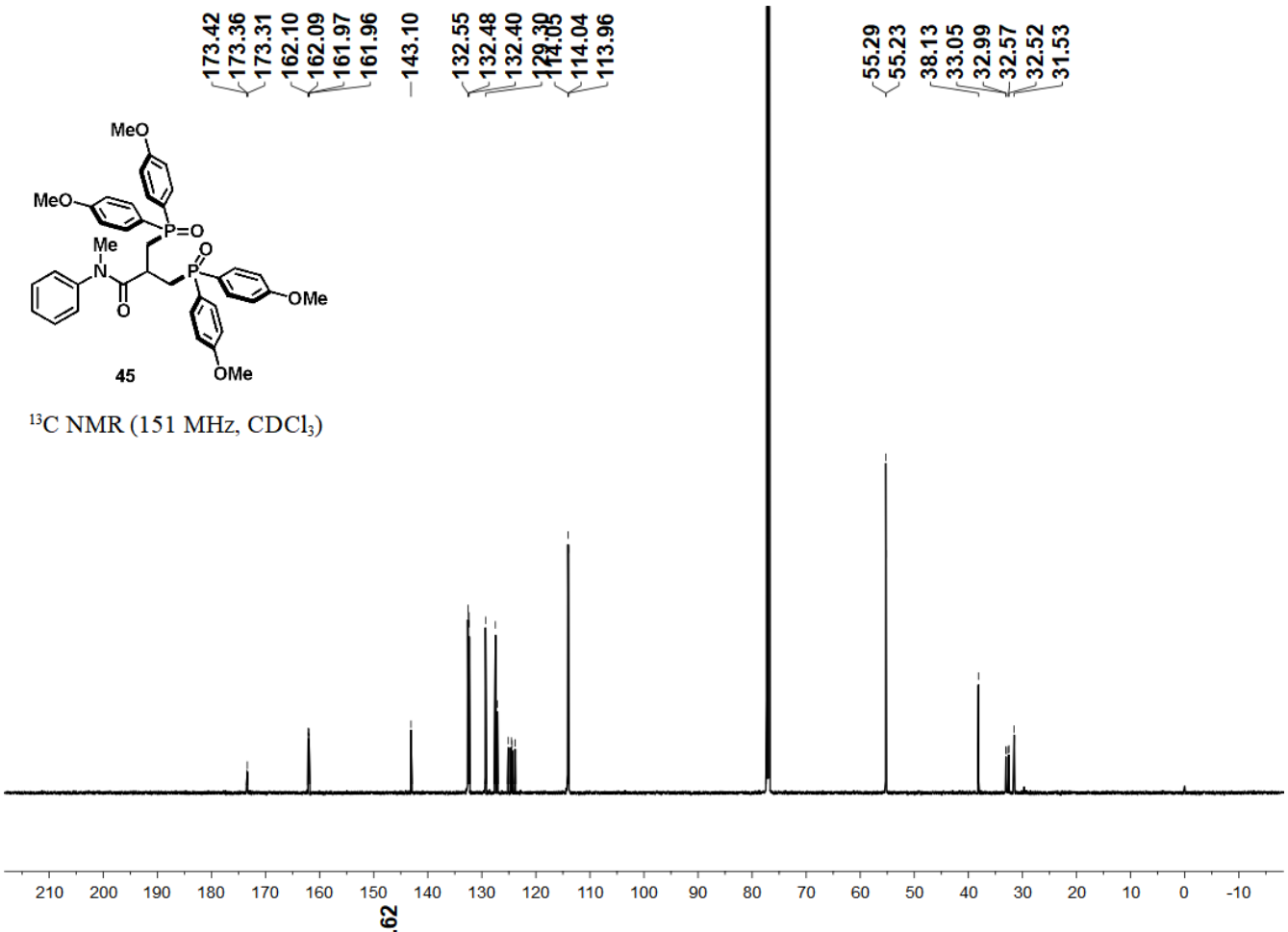




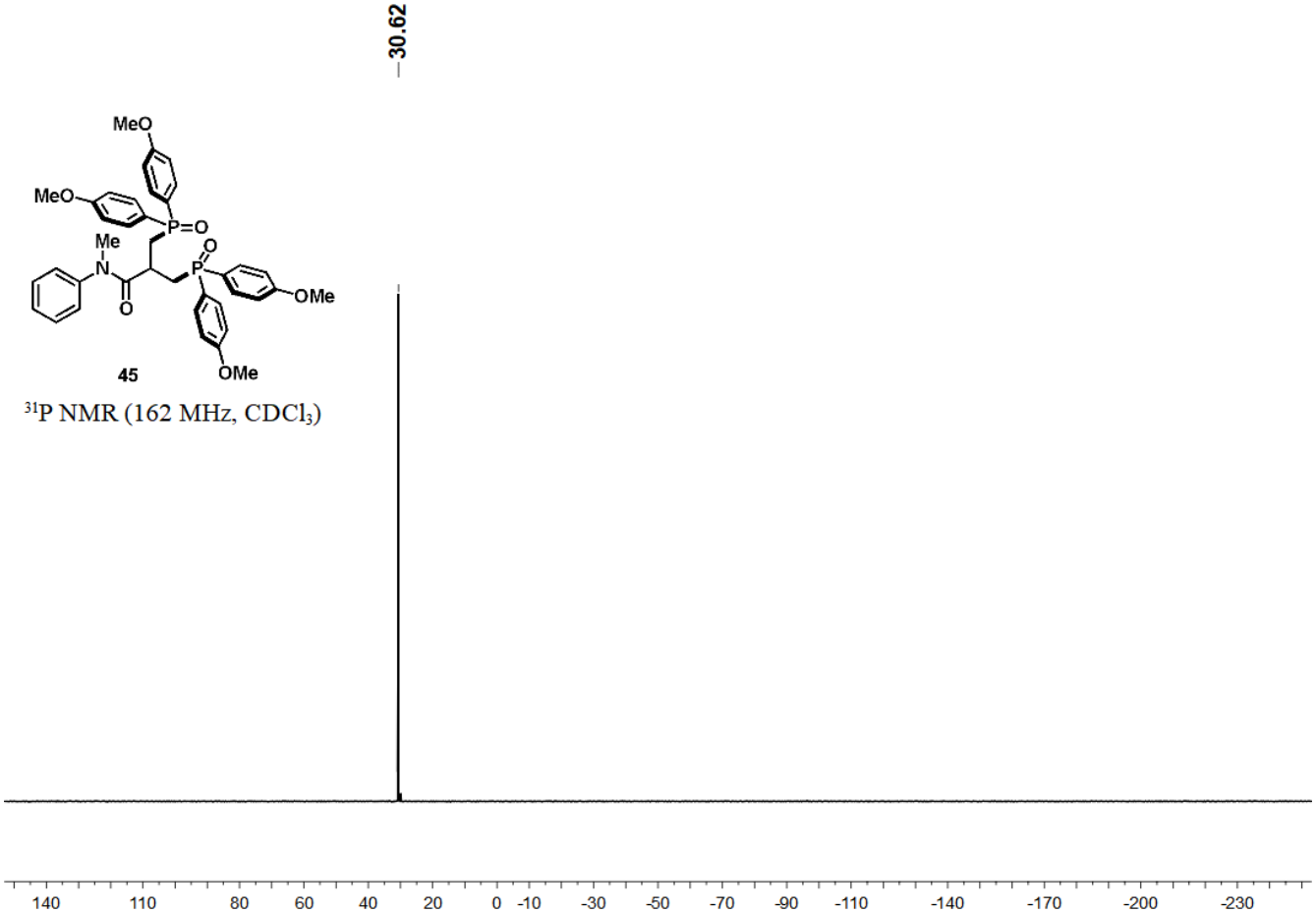
45

^{1}H NMR (400 MHz, $CDCl_3$)

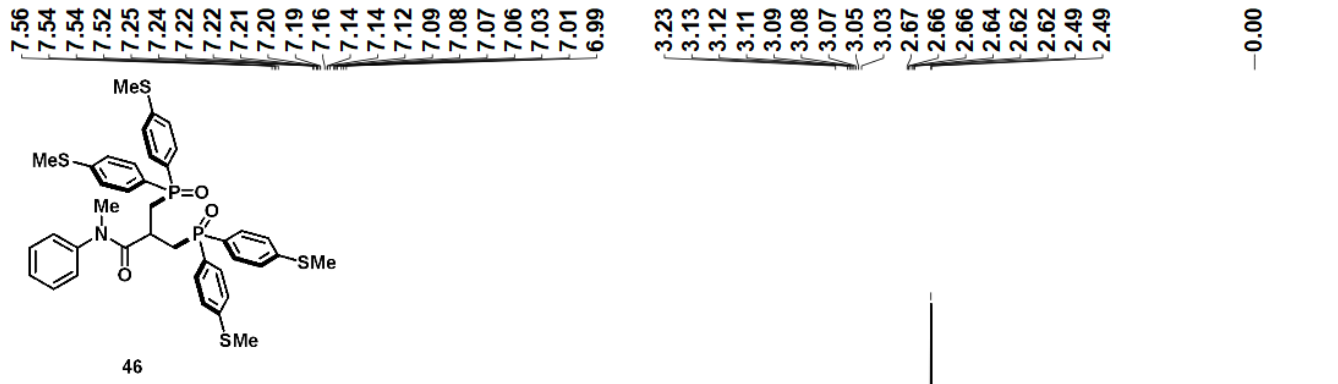




^{13}C NMR (151 MHz, $CDCl_3$)

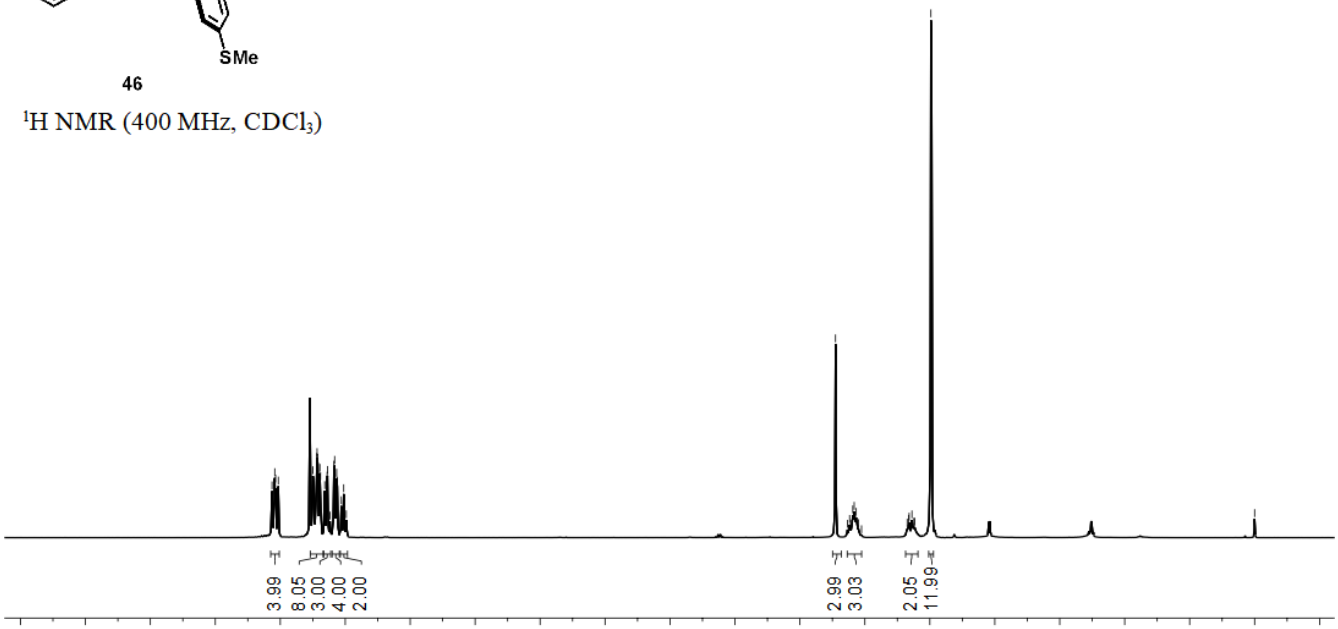


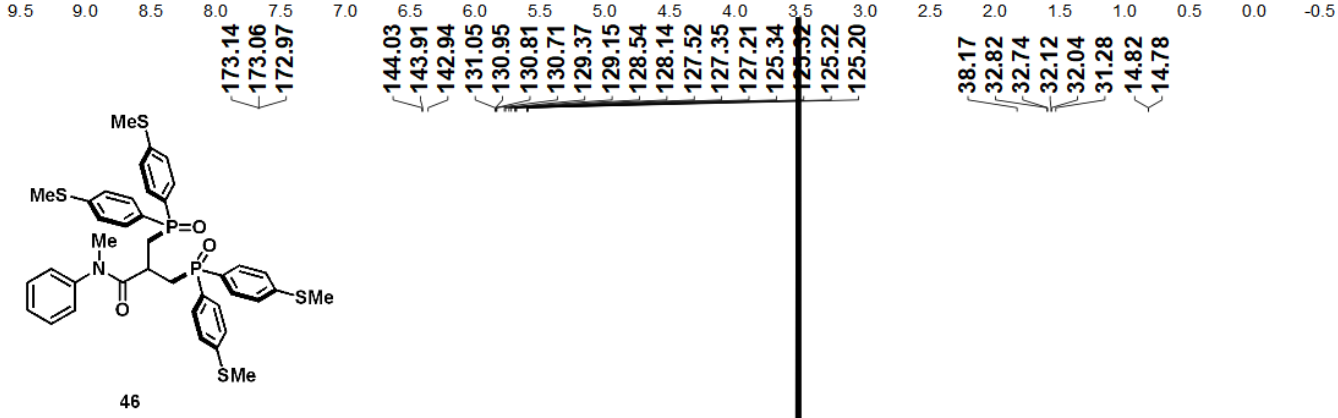
^{31}P NMR (162 MHz, $CDCl_3$)



46

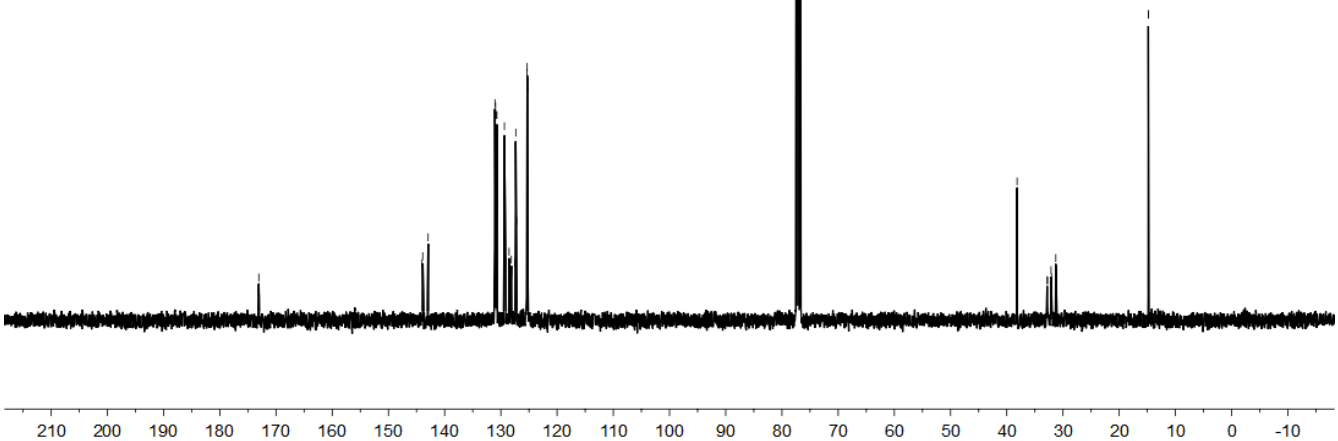
^{1}H NMR (400 MHz, $CDCl_3$)

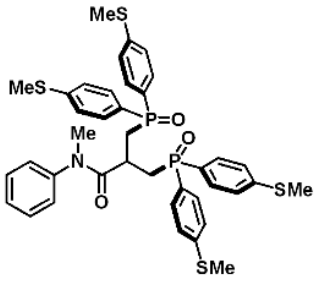




46

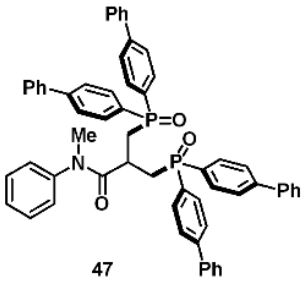
^{13}C NMR (101 MHz, $CDCl_3$)





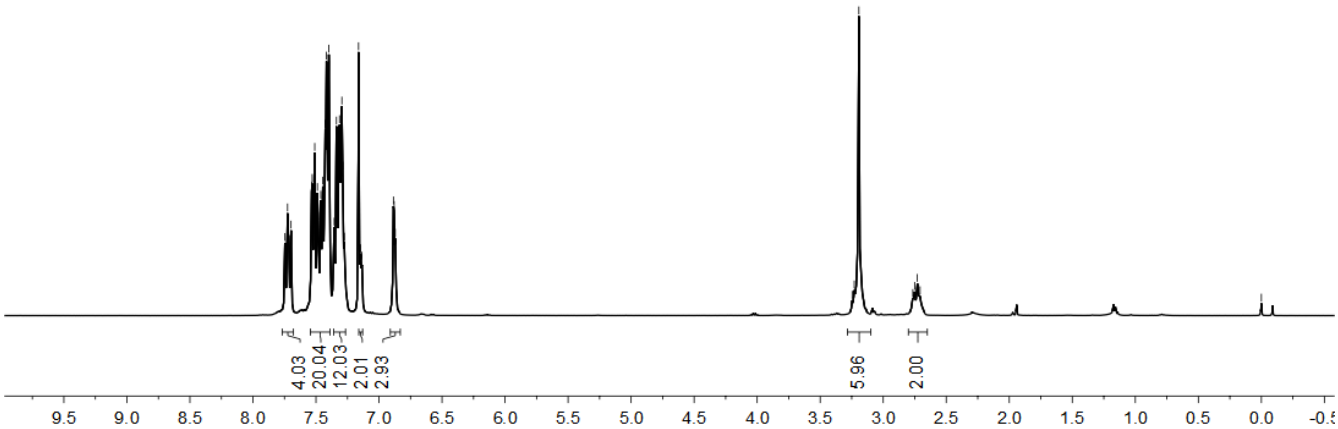
46

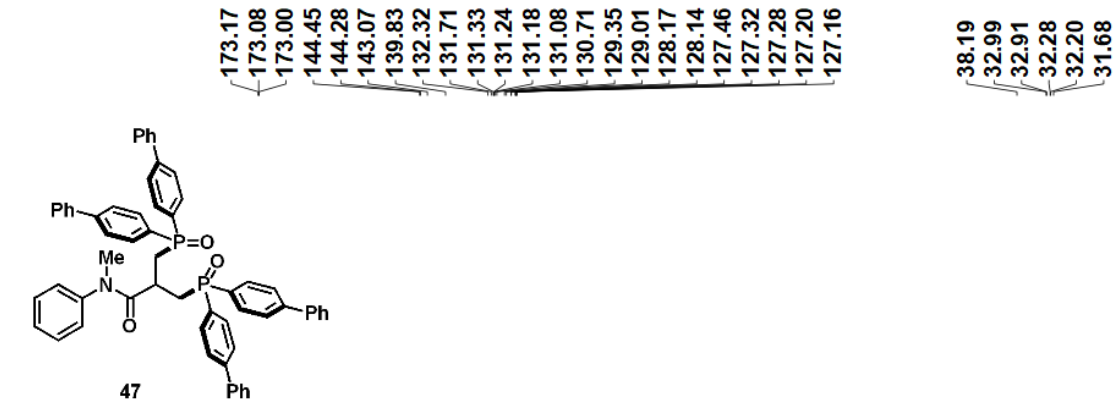
^{31}P NMR (162 MHz, $CDCl_3$)



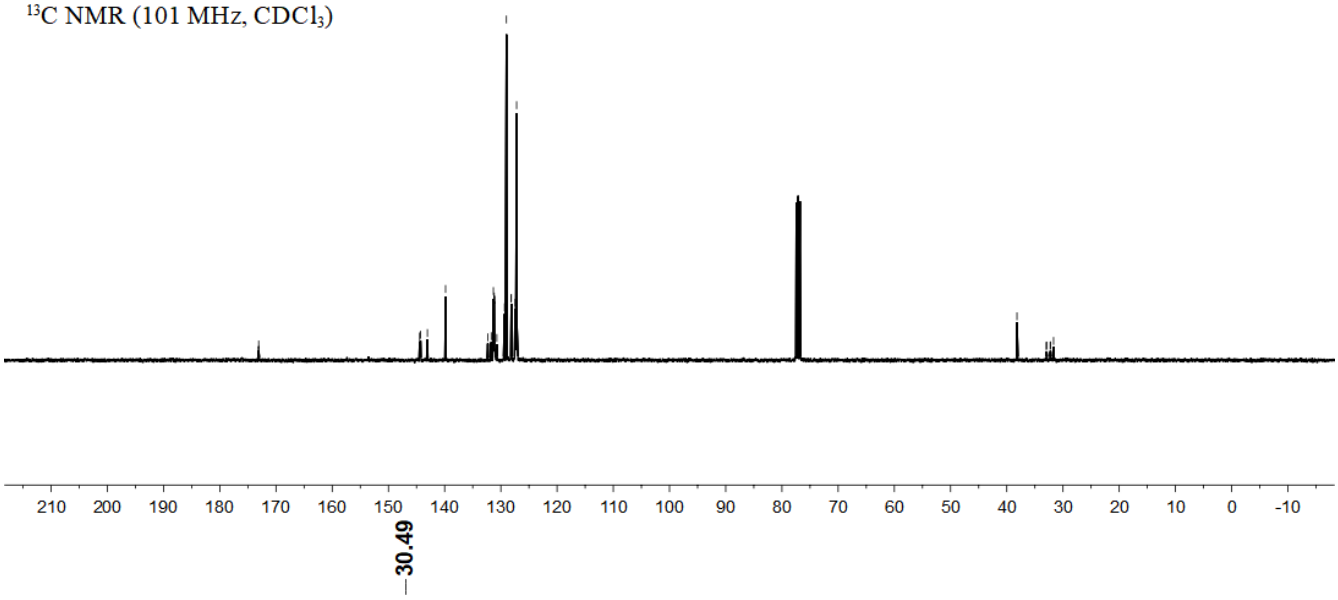
47

^{1}H NMR (400 MHz, $CDCl_3$)

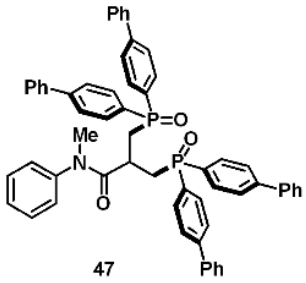




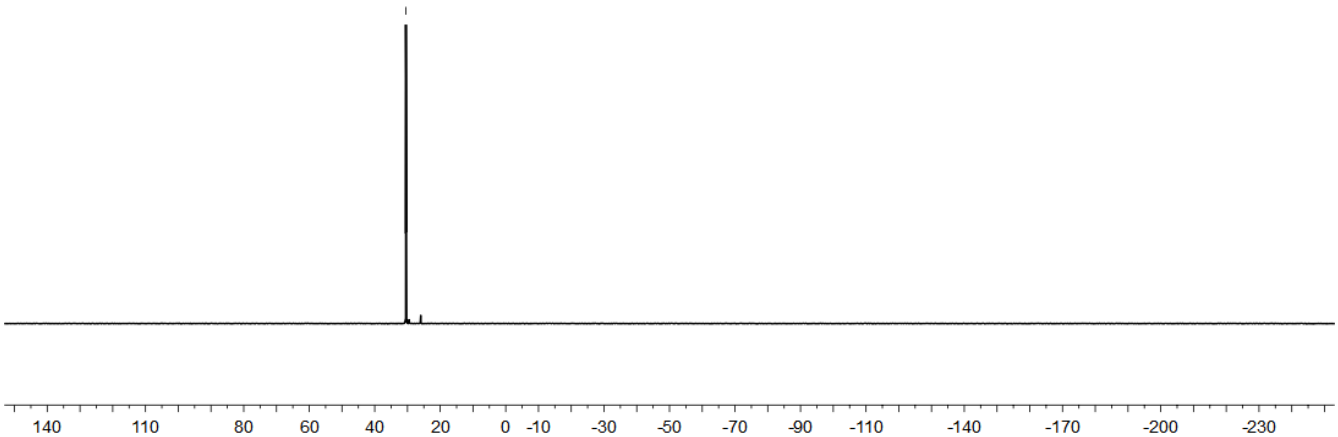
^{13}C NMR (101 MHz, $CDCl_3$)

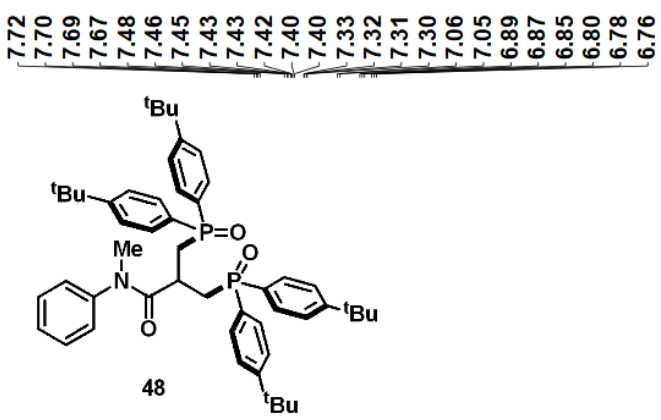


30.49

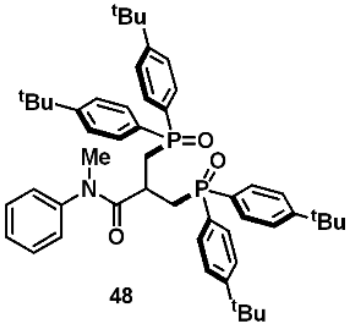


^{31}P NMR (162 MHz, $CDCl_3$)

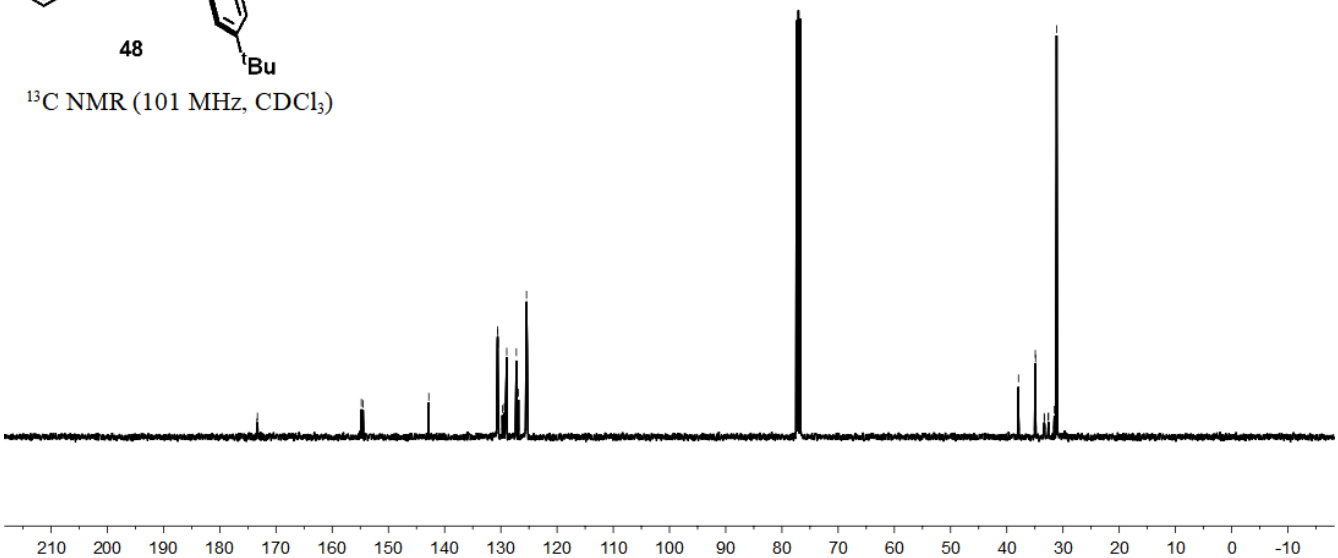


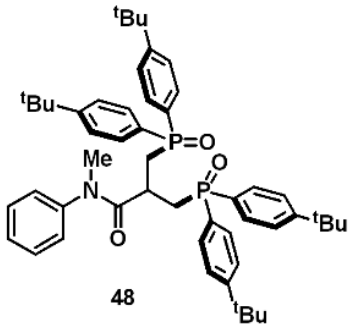


^{1}H NMR (400 MHz, $CDCl_3$)



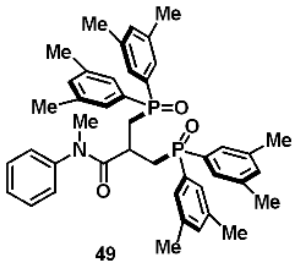
^{13}C NMR (101 MHz, $CDCl_3$)





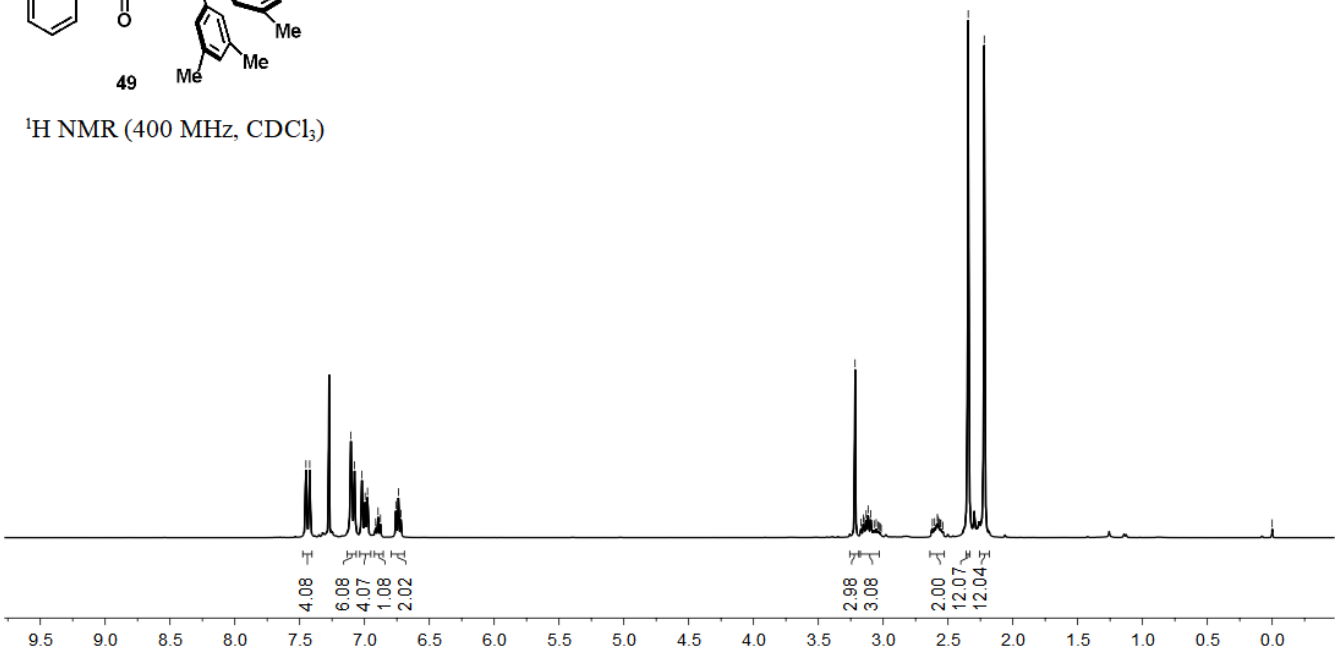
48

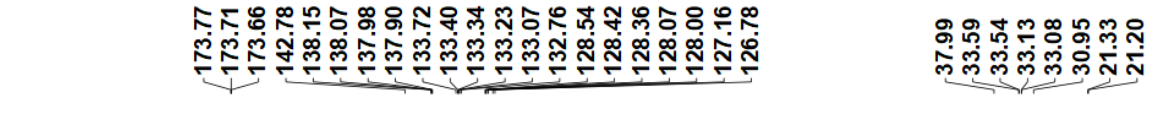
^{31}P NMR (162 MHz, $CDCl_3$)

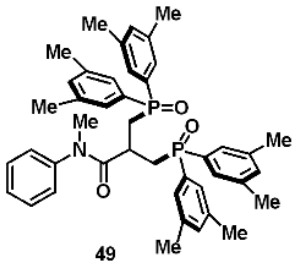


49

^{1}H NMR (400 MHz, $CDCl_3$)

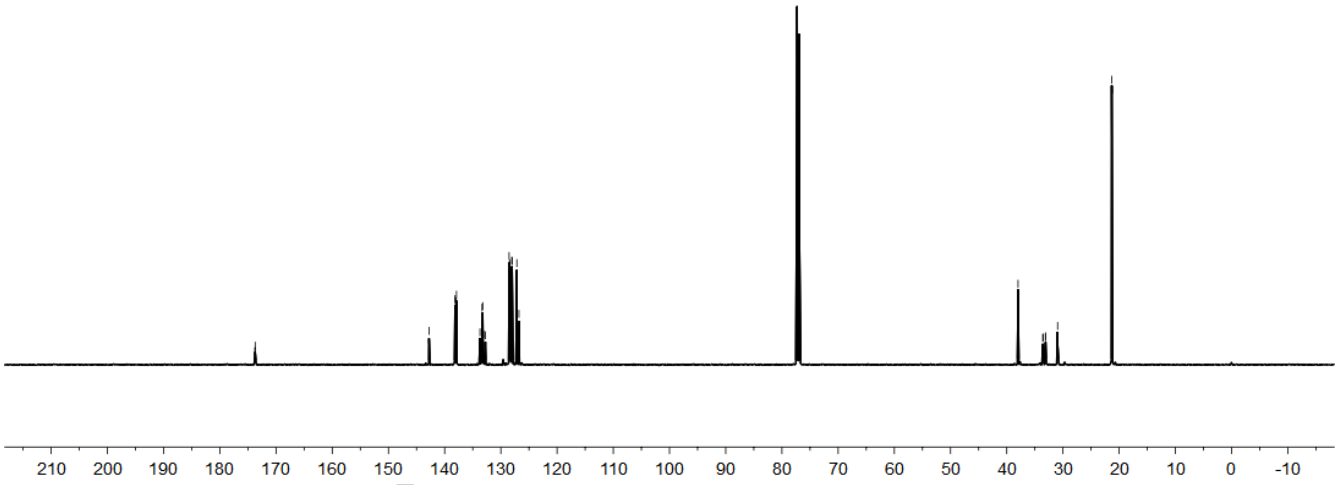




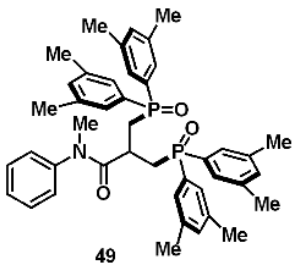


49

^{13}C NMR (151 MHz, $CDCl_3$)

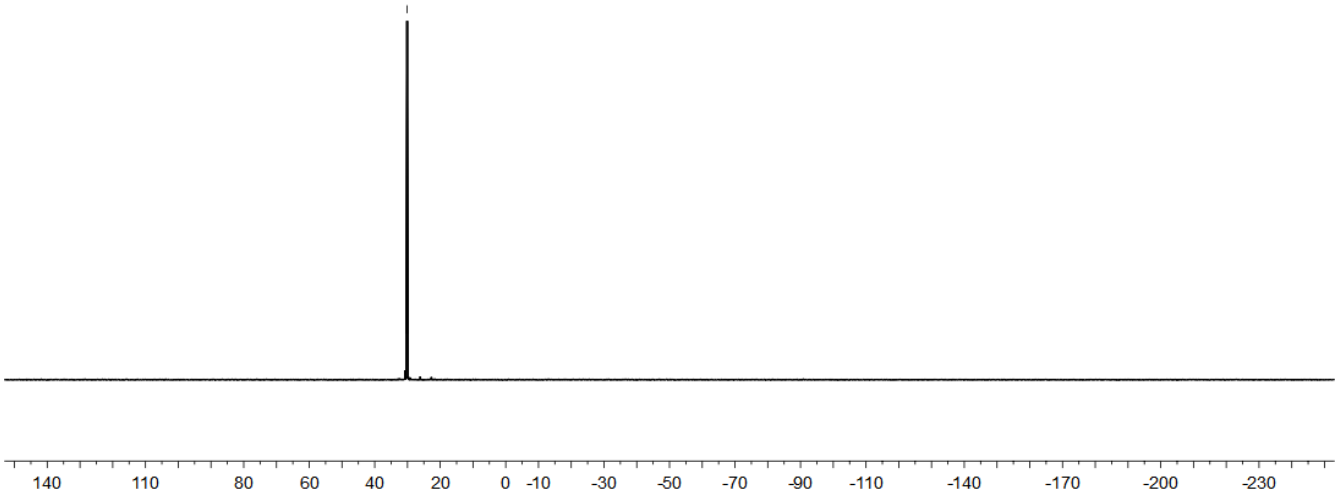


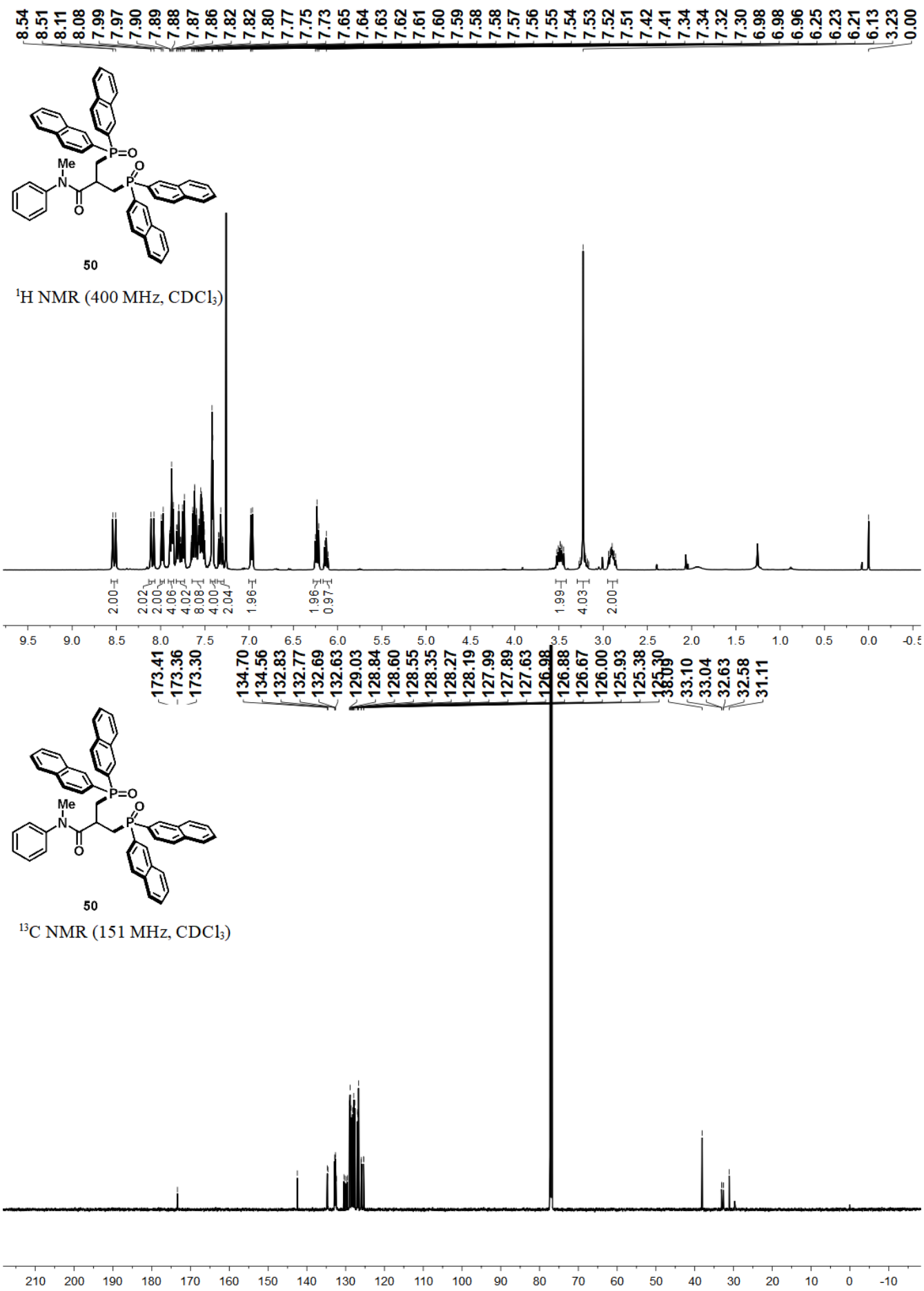
30.11



49

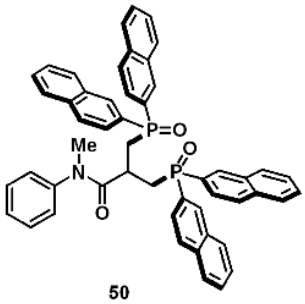
^{31}P NMR (162 MHz, $CDCl_3$)





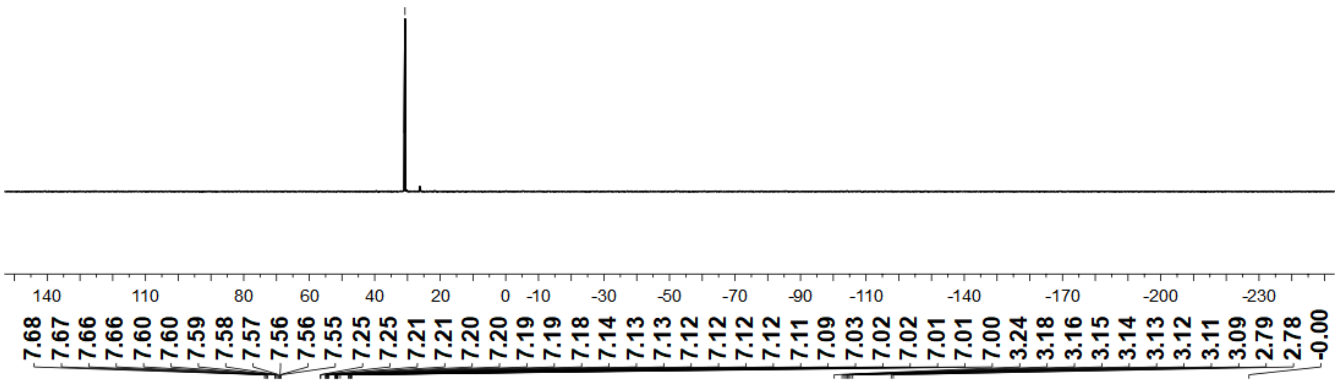
^{1}H NMR (400 MHz, $CDCl_3$)

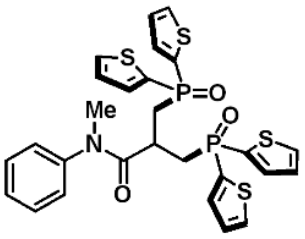
^{13}C NMR (151 MHz, $CDCl_3$)



50

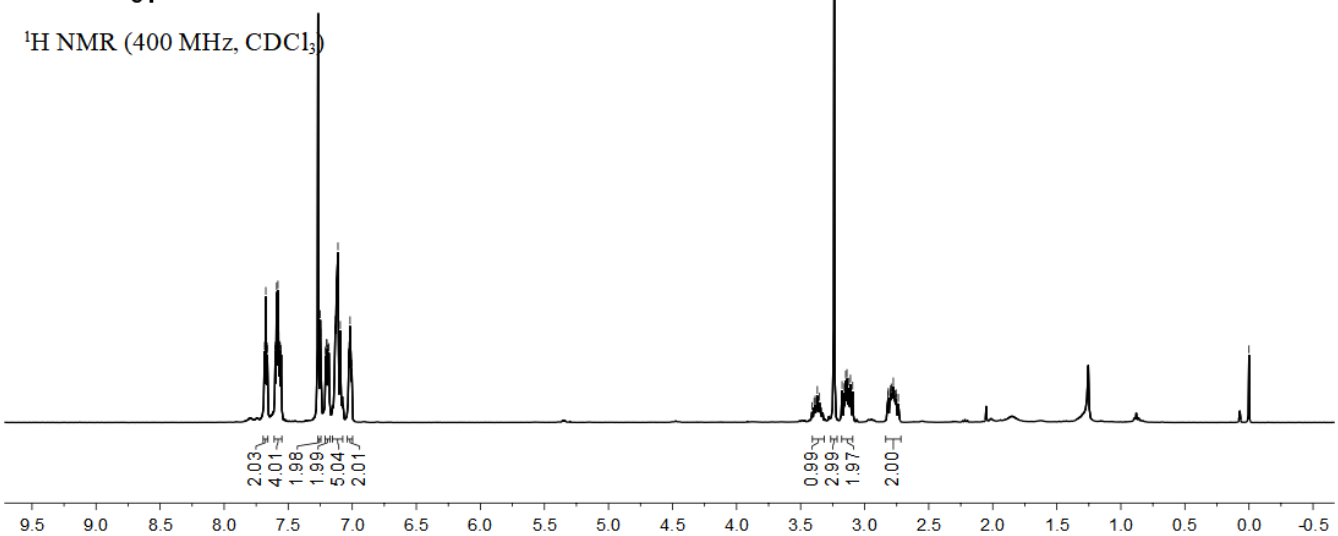
^{31}P NMR (162 MHz, $CDCl_3$)

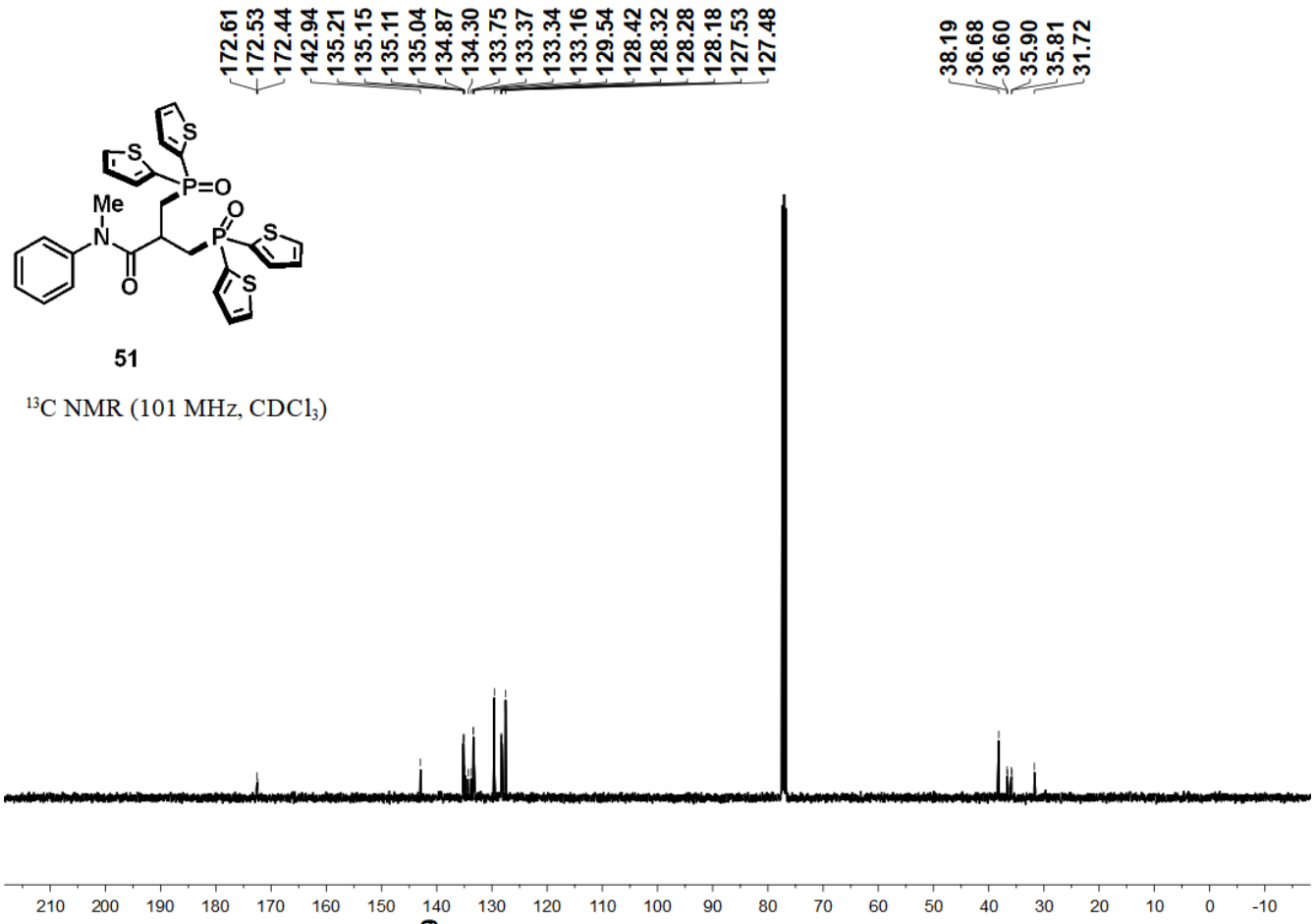




51

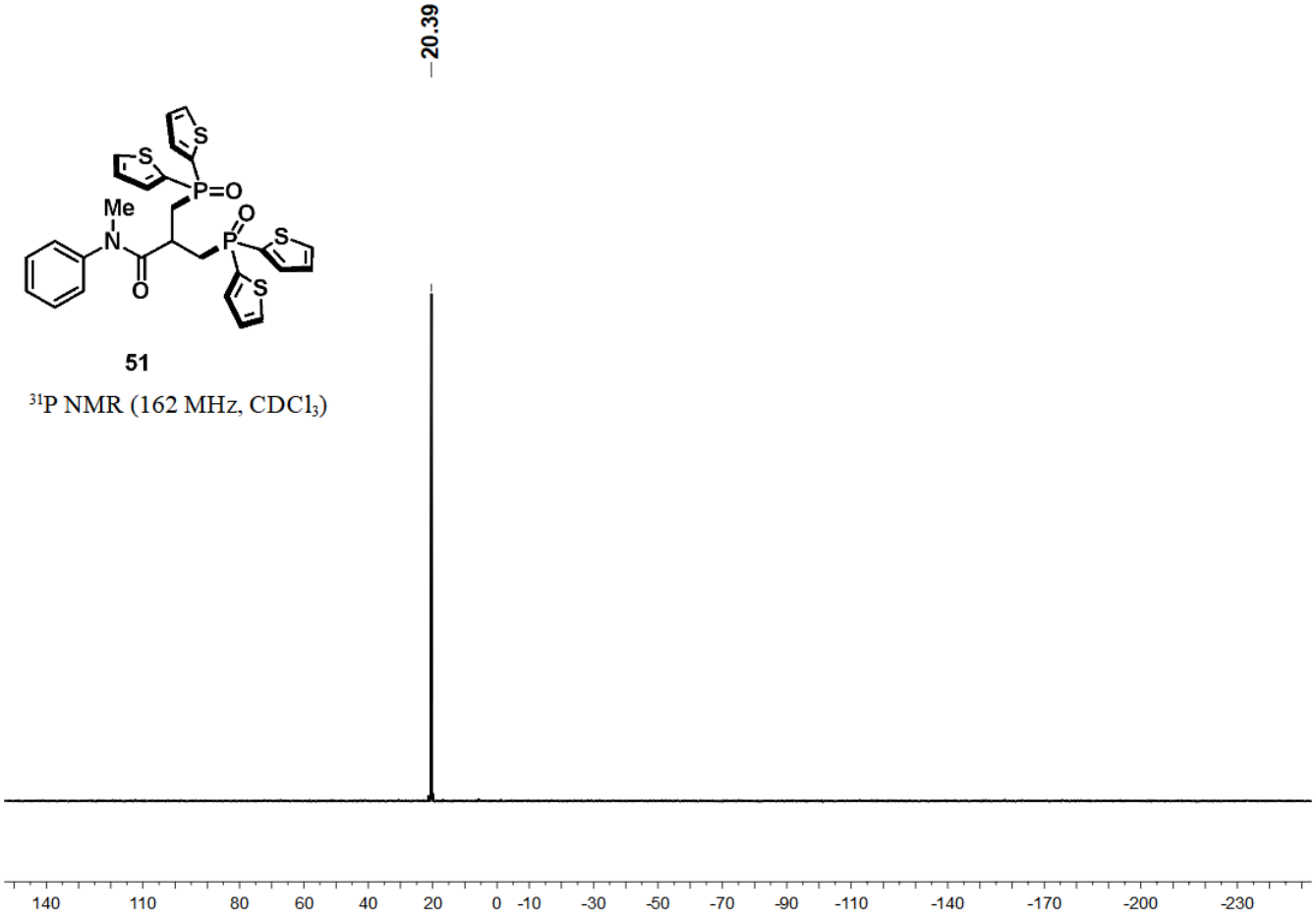
^{1}H NMR (400 MHz, $CDCl_3$)





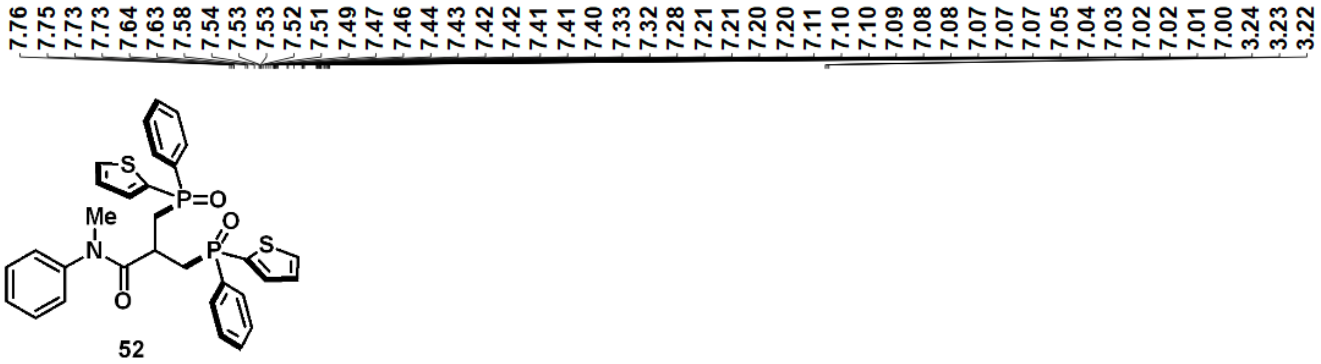
51

^{13}C NMR (101 MHz, $CDCl_3$)



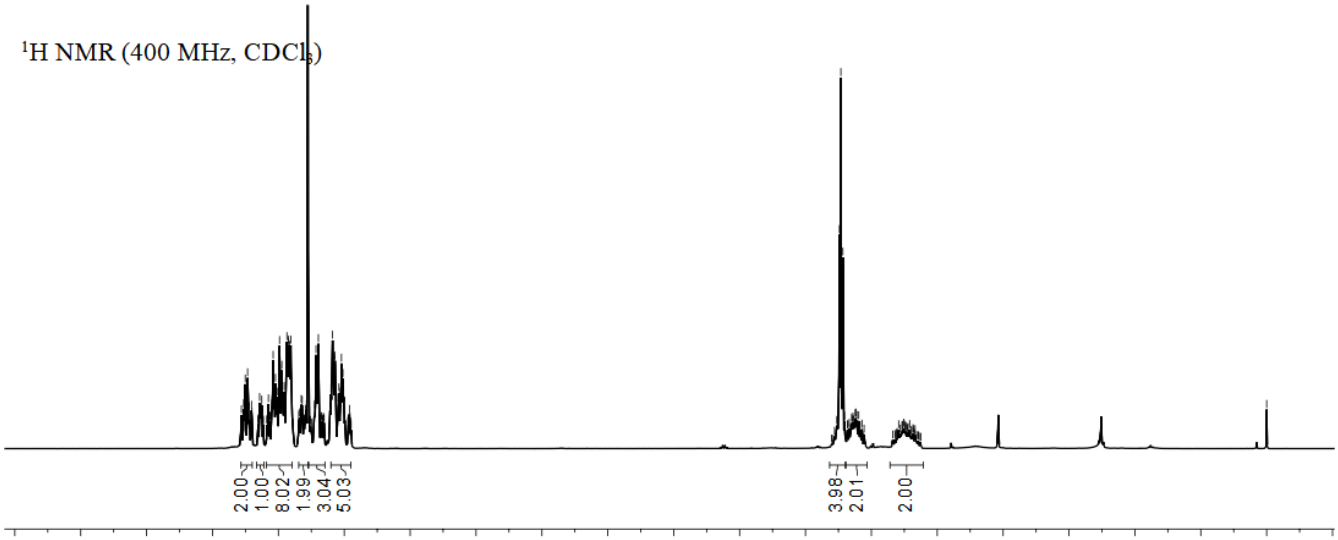
51

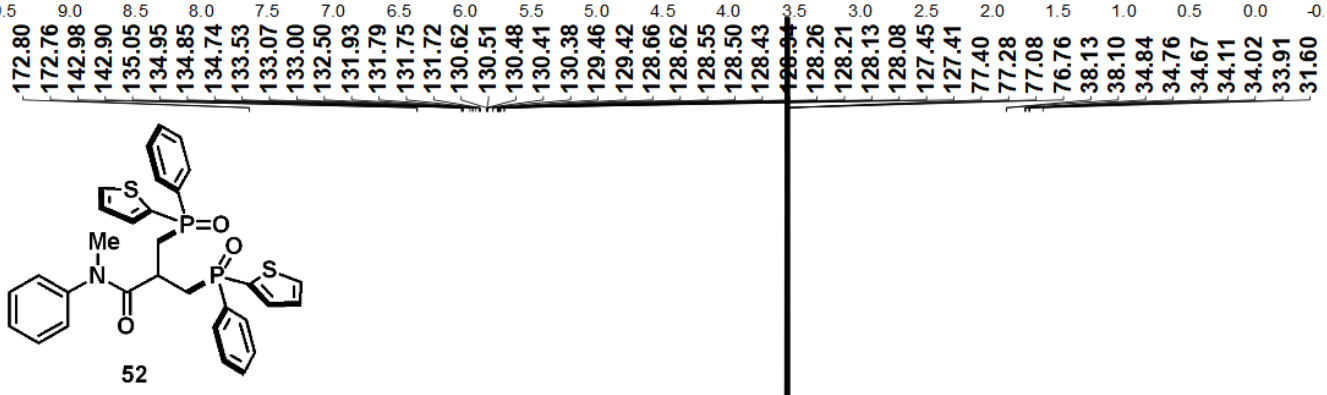
^{31}P NMR (162 MHz, $CDCl_3$)



52

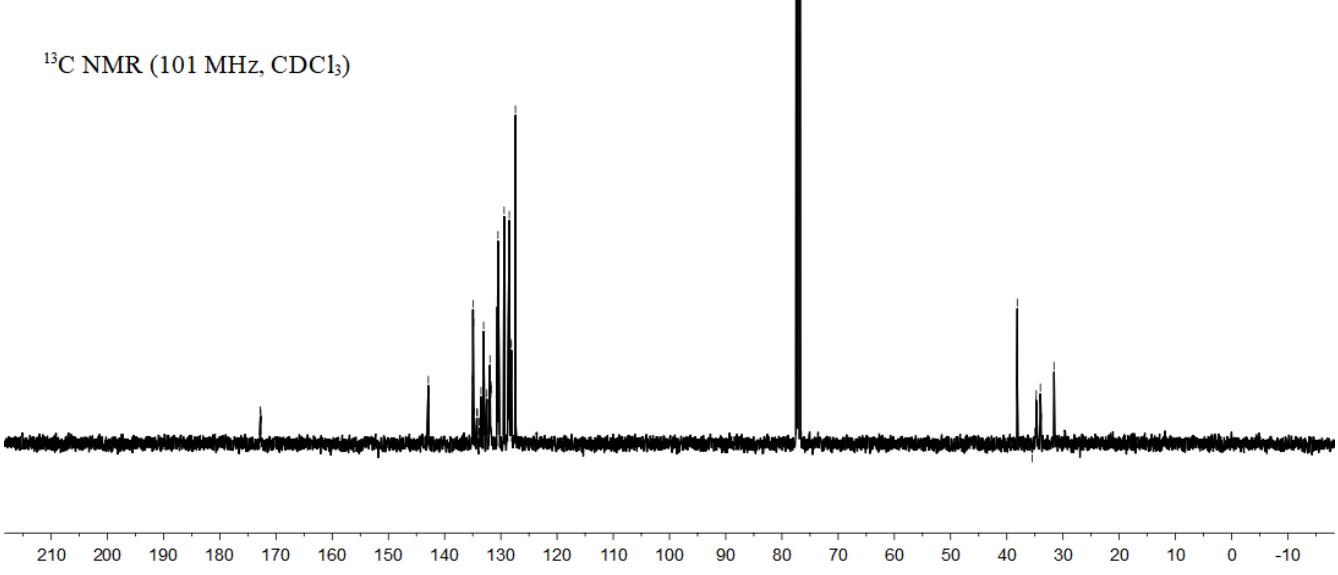
^{1}H NMR (400 MHz, $CDCl_3$)

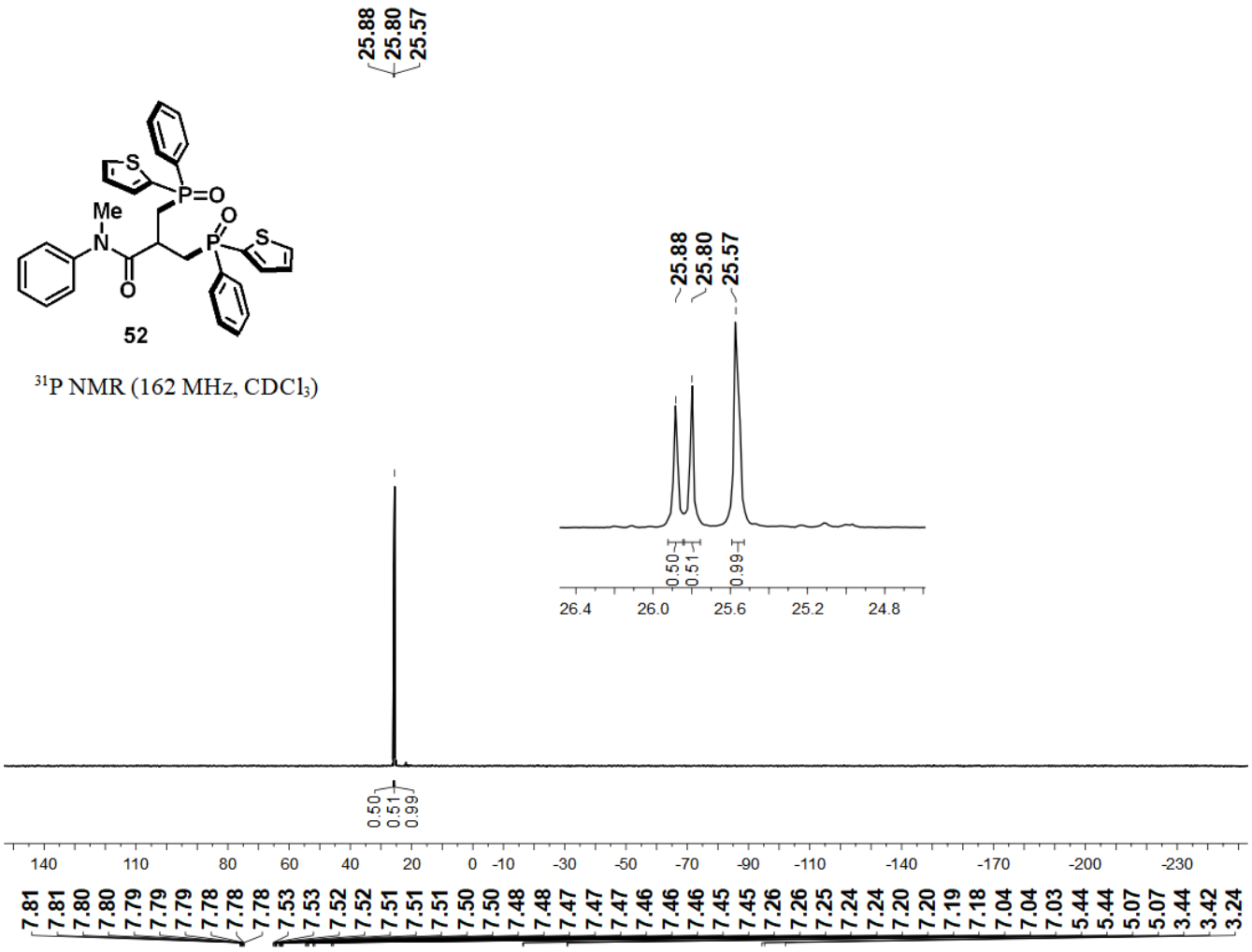


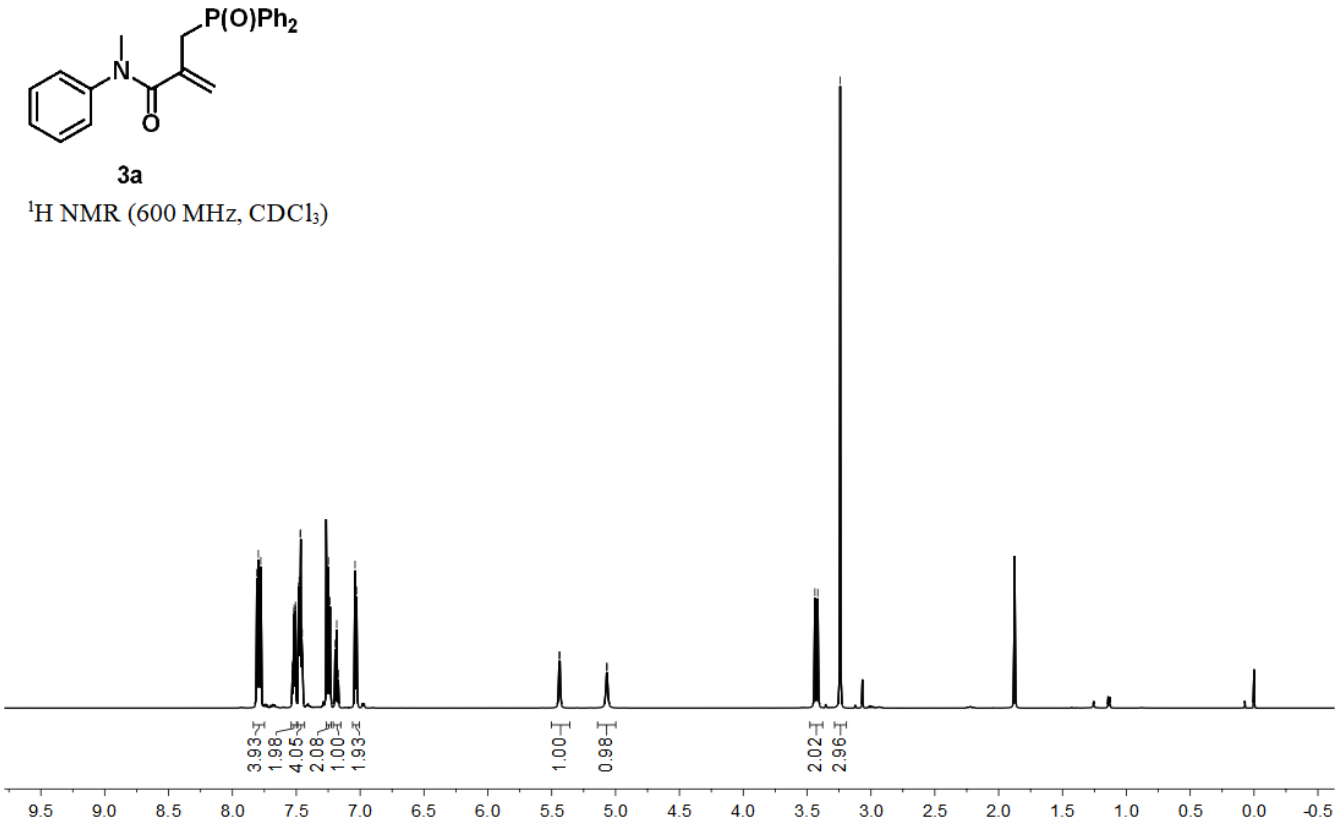


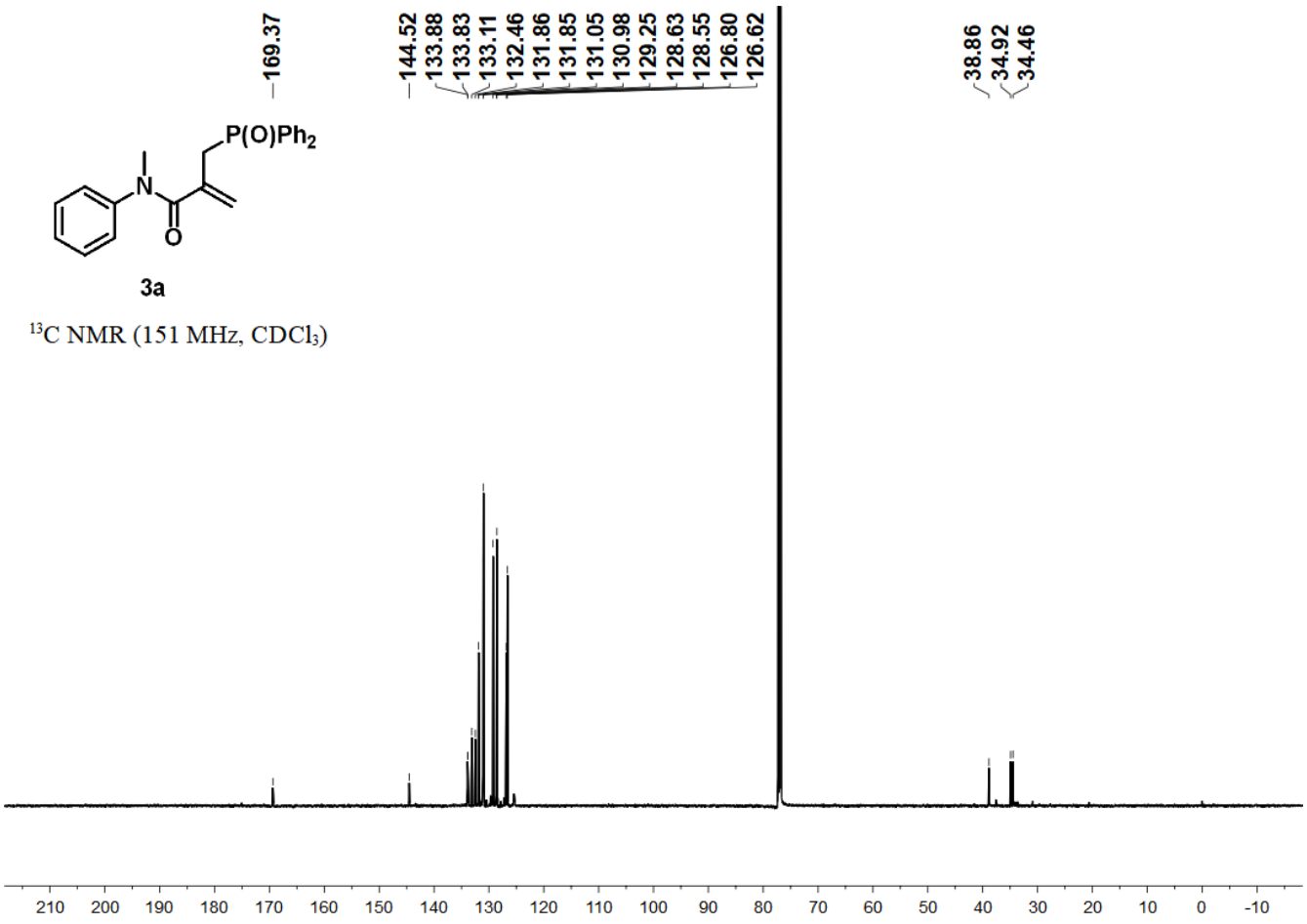
52

^{13}C NMR (101 MHz, $CDCl_3$)



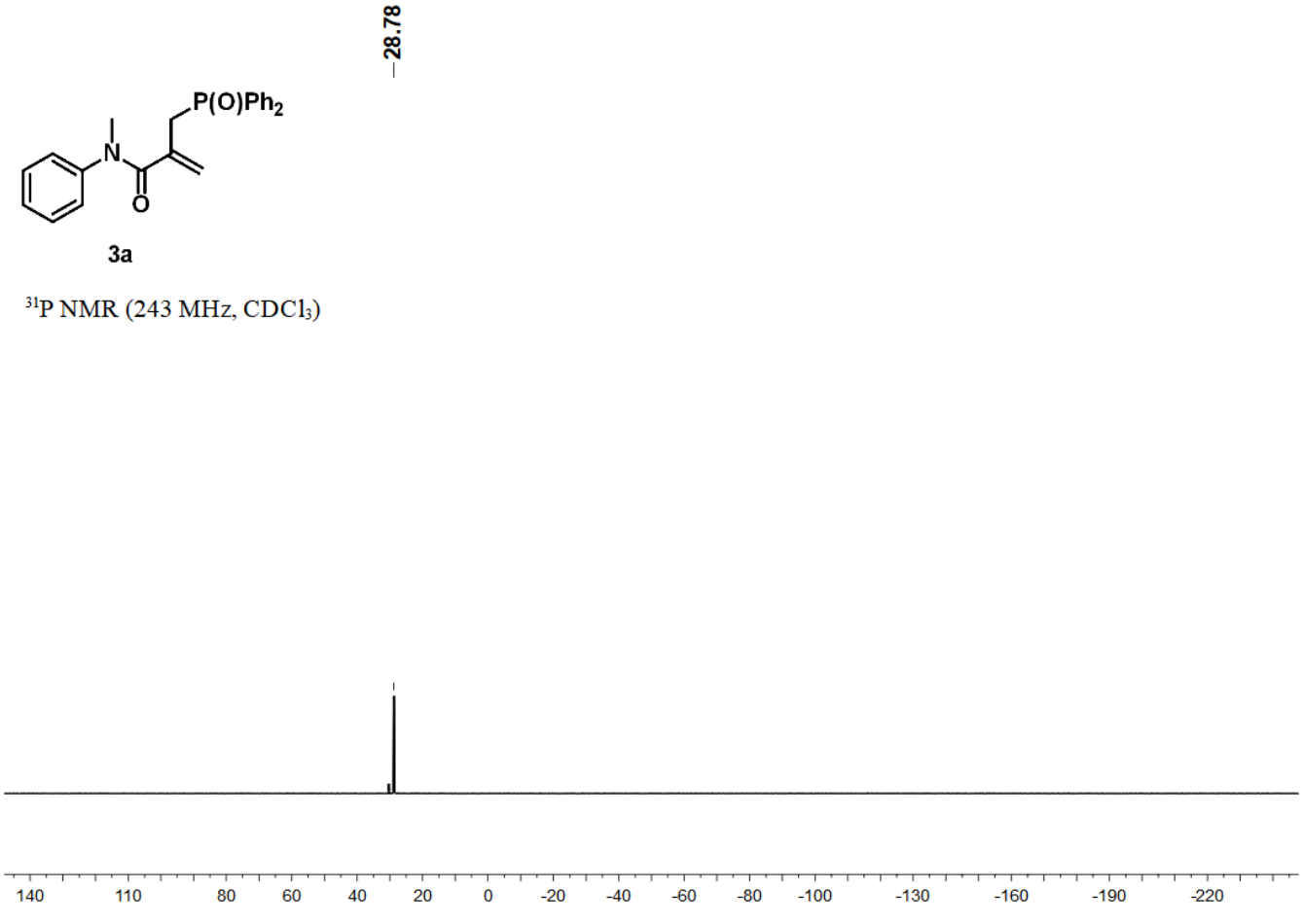

25.88
25.80
25.57
Me
N
O
S
P=O
P=O
S
52
31P NMR (162 MHz, CDCl3)
25.88
25.80
25.57
0.50
0.51
0.99
26.4
26.0
25.6
25.2
24.8
0.50
0.51
0.99
140
110
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-140
-170
-200
-230
7.81 7.81 7.80 7.80 7.79 7.79 7.79 7.78 7.78 7.78 7.53 7.53 7.52 7.52 7.51 7.51 7.51 7.50 7.50 7.48 7.48 7.47 7.47 7.47 7.46 7.46 7.46 7.45 7.45 7.26 7.26 7.25 7.24 7.24 7.20 7.20 7.19 7.18 7.04 7.04 7.03 5.44 5.44 5.07 5.07 3.44 3.42 3.24


P(O)Ph2
N
O
3a
1H NMR (600 MHz, CDCl3)
3.93
1.98
4.05
2.08
1.00
1.93
1.00
0.98
2.02
2.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5



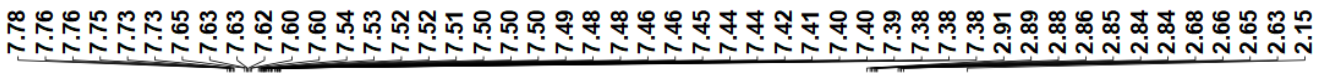
3a

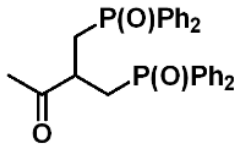
^{13}C NMR (151 MHz, $CDCl_3$)



3a

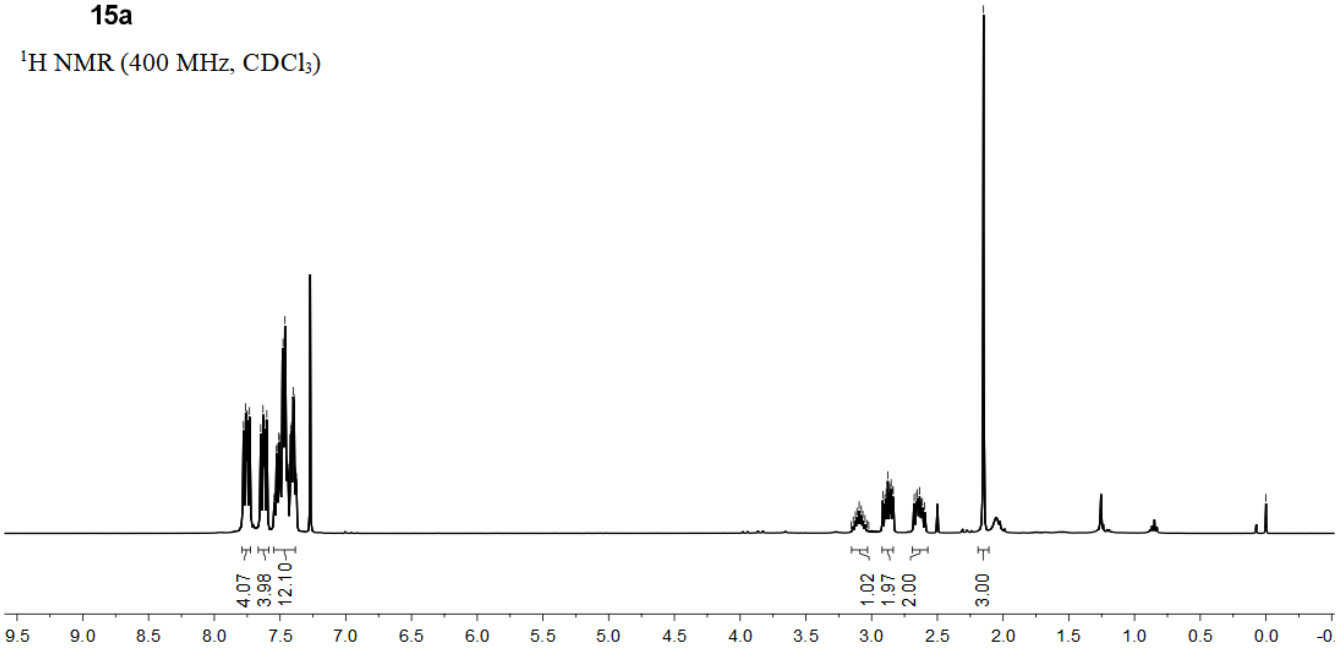
^{31}P NMR (243 MHz, $CDCl_3$)

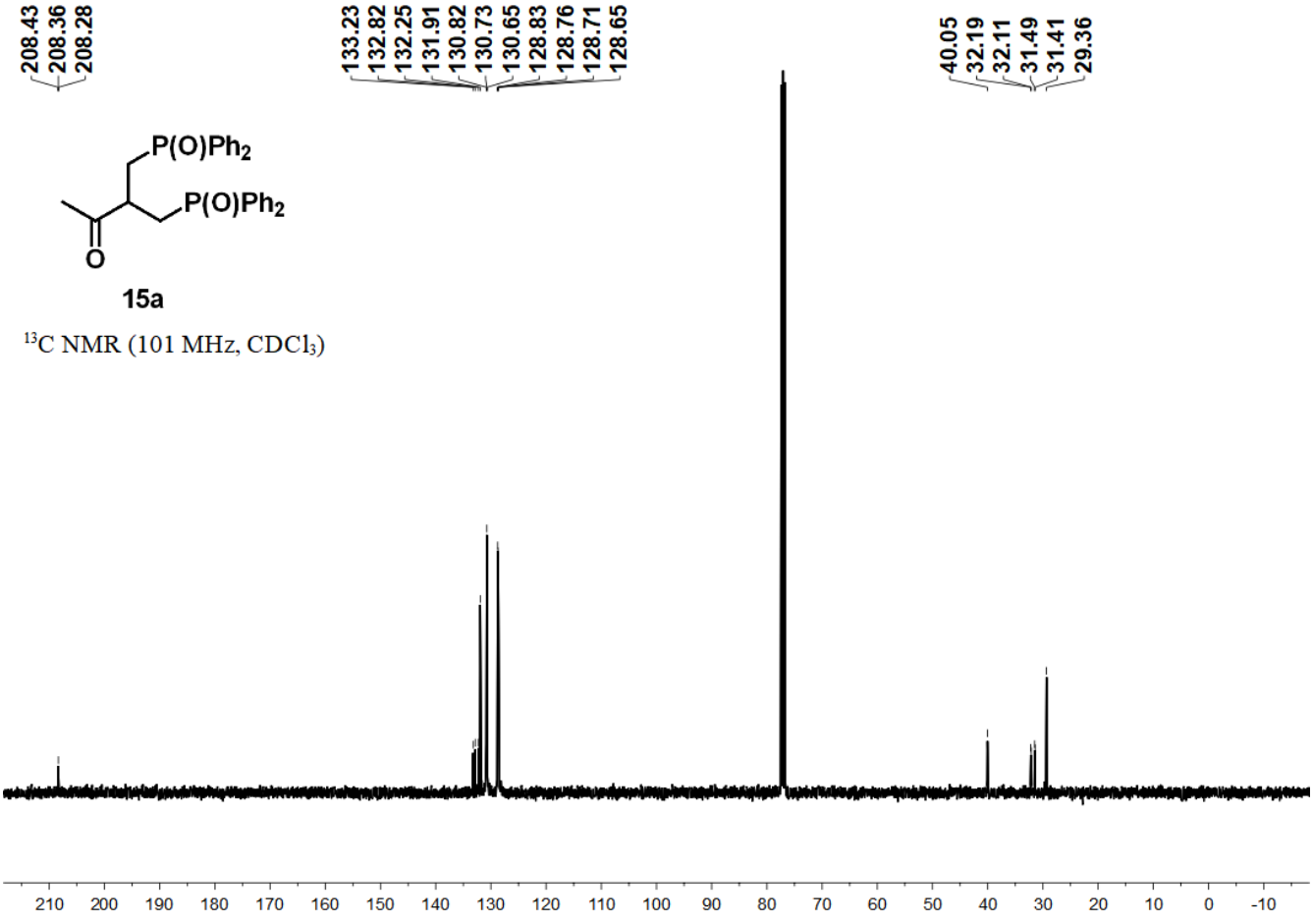




15a

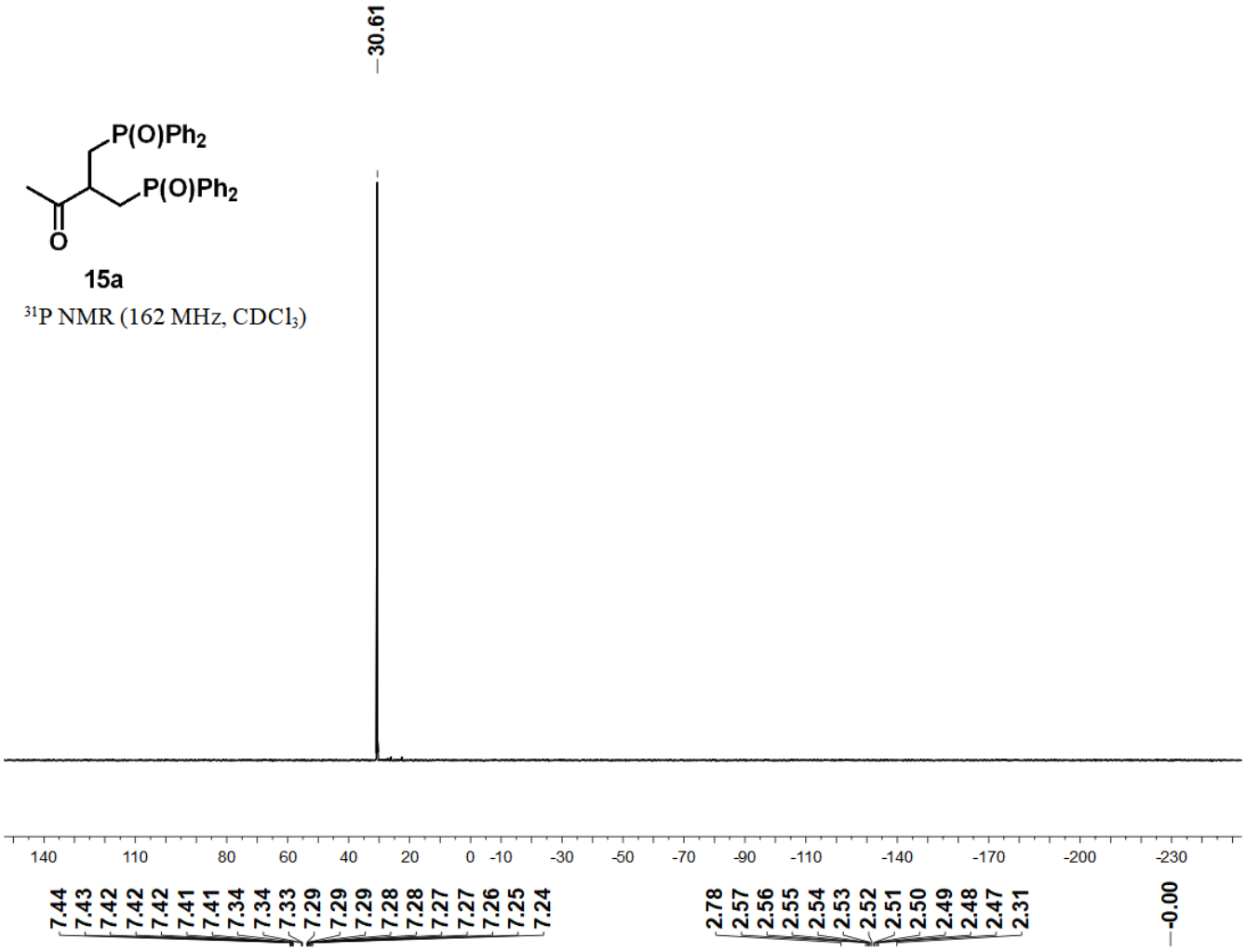
^{1}H NMR (400 MHz, $CDCl_3$)





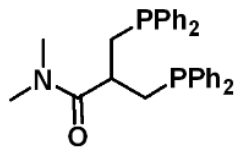
15a

^{13}C NMR (101 MHz, $CDCl_3$)



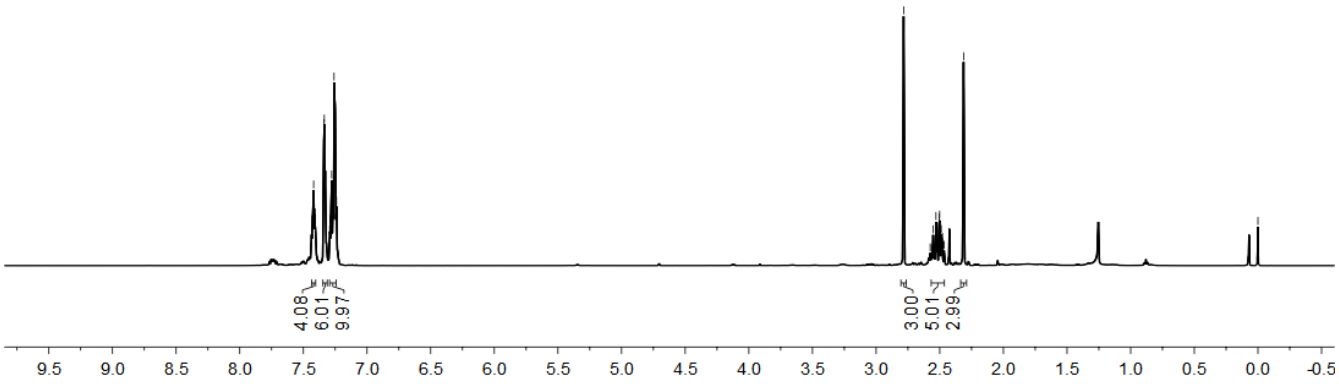
15a

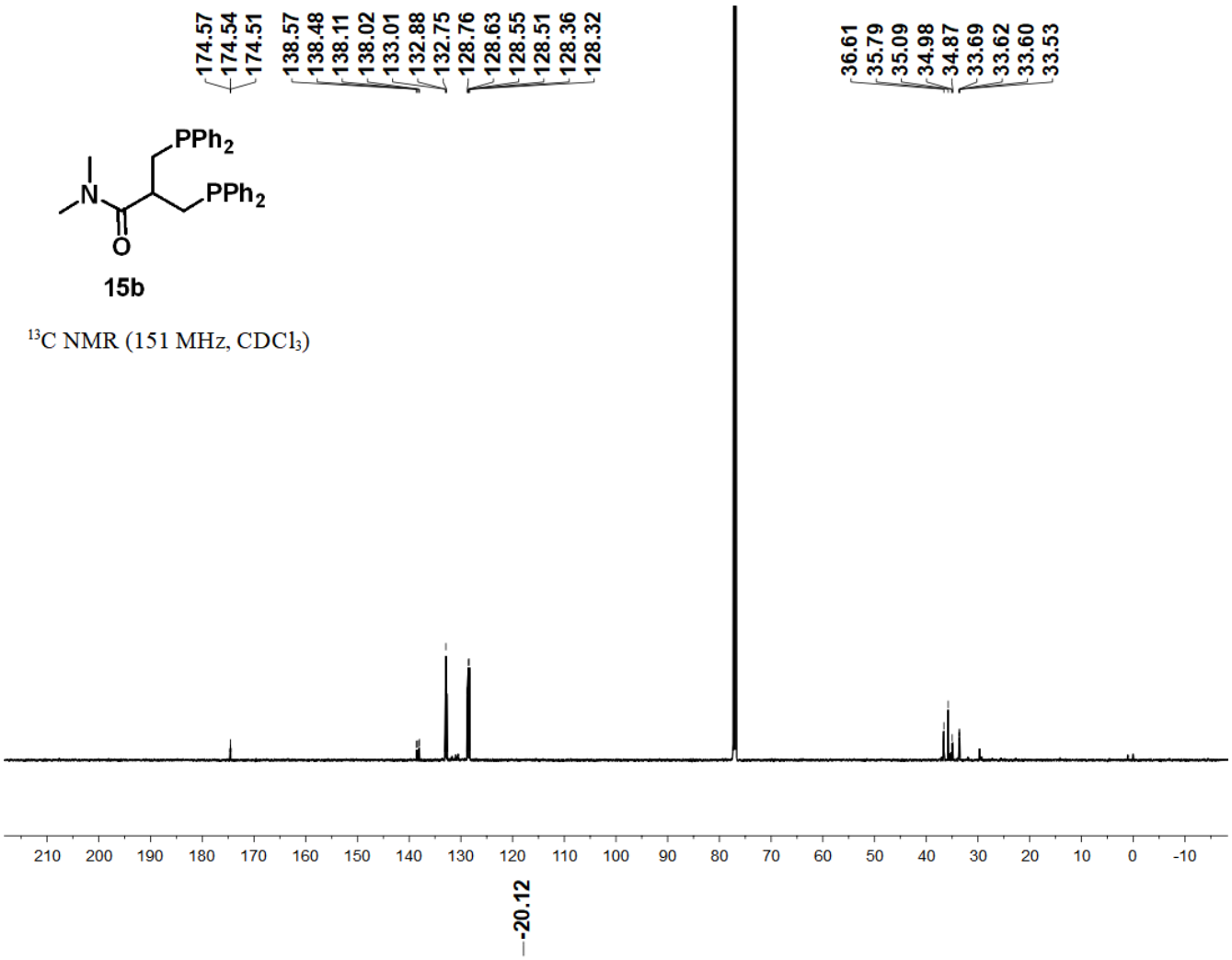
^{31}P NMR (162 MHz, $CDCl_3$)



15b

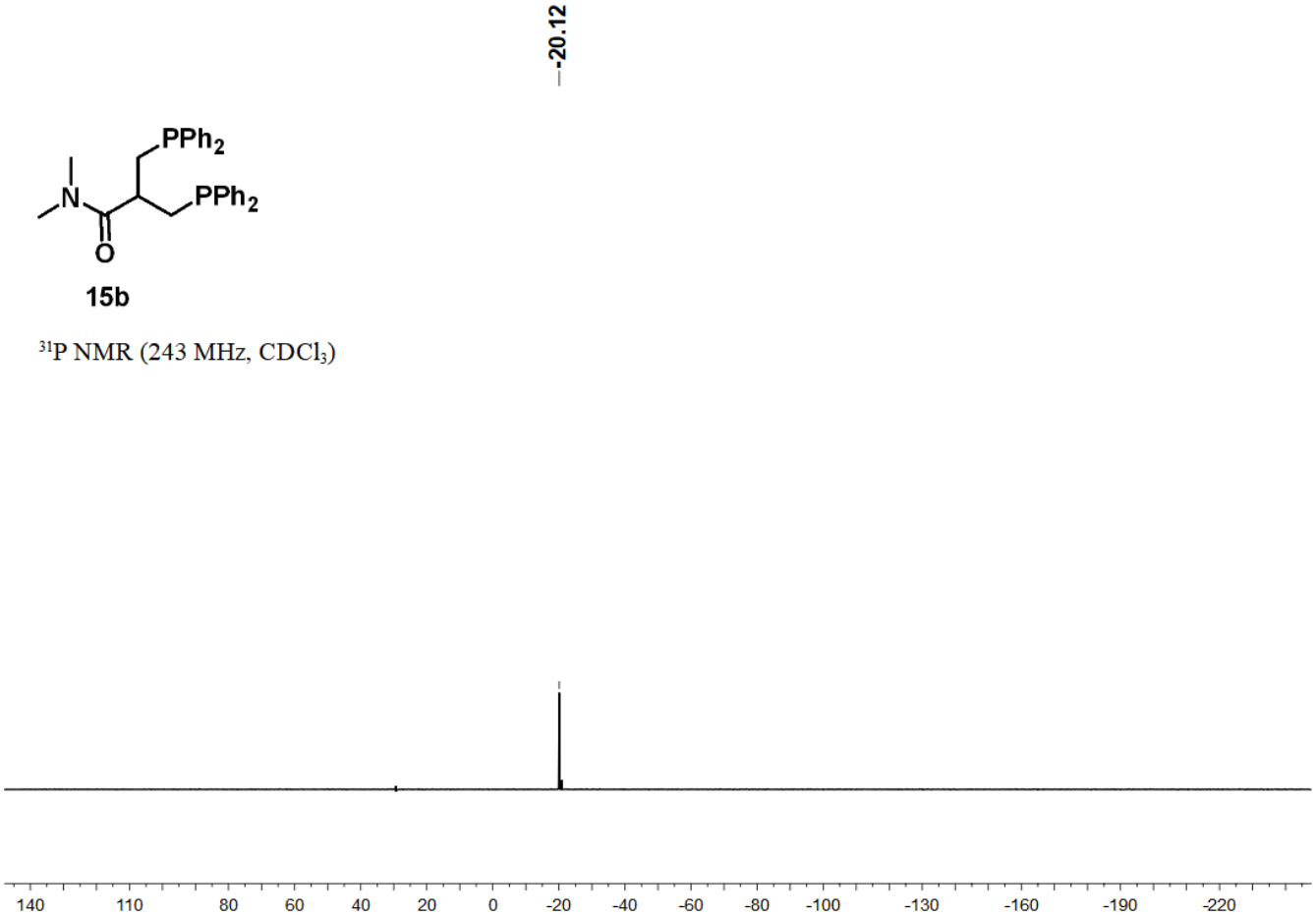
^{1}H NMR (600 MHz, $CDCl_3$)





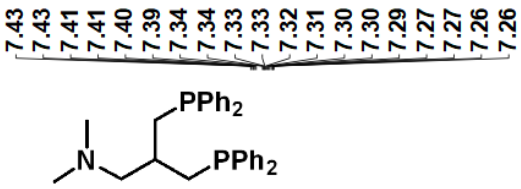
15b

^{13}C NMR (151 MHz, $CDCl_3$)



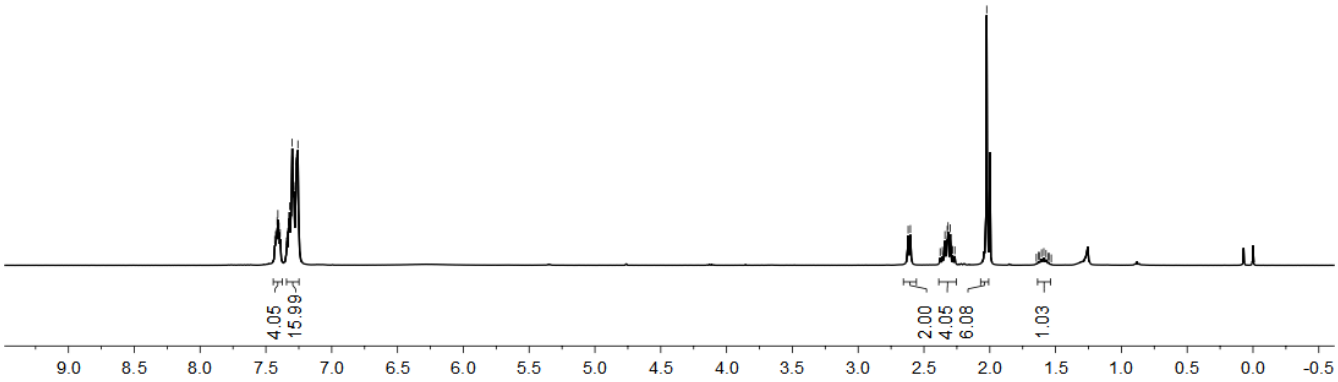
15b

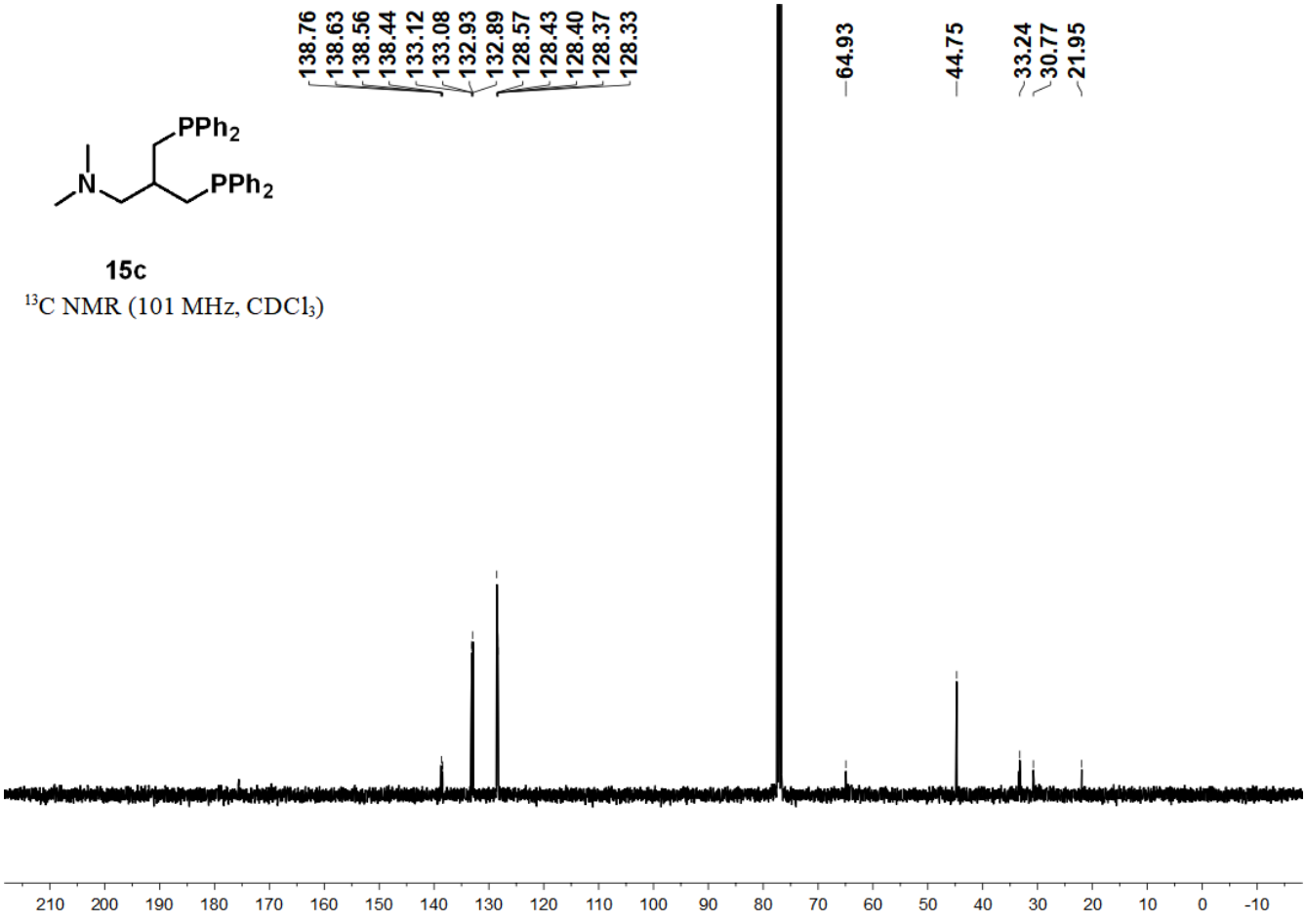
^{31}P NMR (243 MHz, $CDCl_3$)



15c

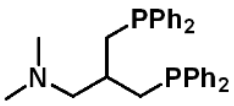
^{1}H NMR (400 MHz, $CDCl_3$)





15c

^{13}C NMR (101 MHz, $CDCl_3$)


PPh2
N
PPh2

15c

-20.21
140
110
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-140
-170
-200
-230