Supplementary Information

# Palladium Catalyzed Asymmetric Hydrophosphination of Internal Alkynes: Access to Phosphine-Functionalized Axially Chiral Olefins

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## 1. General Information:

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon. The $^{1}H$ NMR spectra were recorded on 400 MHz or 600 MHz NMR spectrometer. The $^{13}C$ NMR spectra were recorded at 100 MHz or 150 MHz. The $^{19}F$ NMR spectra were recorded at 376 MHz or 565 MHz. The $^{31}P$ NMR spectra were recorded at 162 MHz or 243 MHz. Chemical shifts were expressed in parts per million ($\delta$) downfield from the internal standard tetramethylsilane (TMS), and were reported as s (singlet), d (doublet), t (triplet), dd (doublets of doublet), dt (doublets of triplet), and m (multiplet). The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: $\delta$ H = 7.26 ppm, $\delta$ C = 77.16 ppm). The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained via ESI mode by using a MicroTOF mass spectrometer. Column chromatography was performed on silica gel 200-300 mesh. The enantiomeric excess (ee) of the products were determined by high-performance liquid chromatography (HPLC) with a chiral stationary phase in comparison with the authentic racemate sample with $^{n}$hexane and $^{i}$PrOH as solvents. All the chiral stationary phases including Chiralcel AD-H, IA, IE, OD-H, OZ-H, OX-3 used in this study were purchased from Daicel Chirsal Technologies. Optical rotations were reported as follows: $[\alpha]_D^T$ = (c: mg/ mL, in $CDCl_3$).

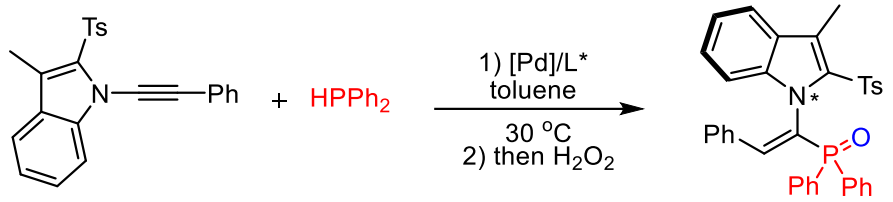
Chiral palladium catalysts and phosphine ligands were purchased from J&K and stored under argon. Anhydrous toluene, THF (Tetrahydrofuran) and dioxane were distilled before use.

The diarylphosphine[1] and racemic secondary phosphines,[2] and 1-indoyl substituted alkynes[3] were synthesized according to reported procedures.

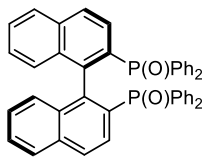
# 2. Experimental Section

## 2.1 Detailed screening of the reaction conditions

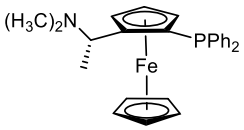
### Table S1. Screening of detailed Ligands [a]



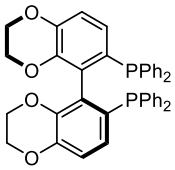

**1** **2a** **3, (*S*)-product**



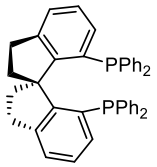

(*R*)-BINAP
59%, <5% ee



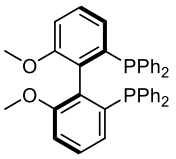

(*S*)-(*Rp*)-PPFA
47%, <5% ee



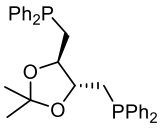

(*S*)-SYNPHOS
43%, -30% ee



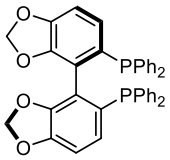

(*R*)-SDP
9%, <5% ee



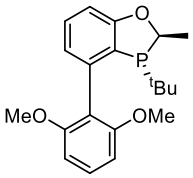

(*R*)-MeO-BIPHEP
56%, 33% ee



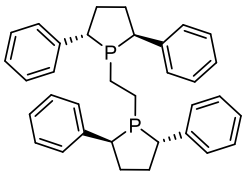

(*R*,*R*)-DIOP
74%, <5% ee



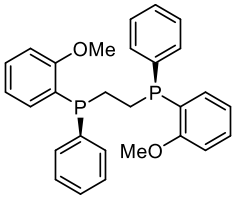

(*R*)-SEGPHOS
63%, 57% ee



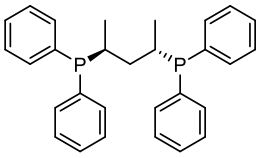

(2*R*,3*R*)-Me-BIDIME
41%, -6% ee



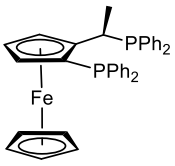

(*R*,*R*)-Ph-BPE
82%, 79% ee



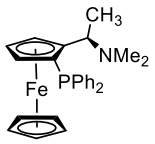

(*S*,*S*)-DIPAMP
58%, 46% ee



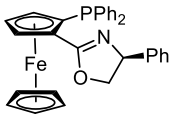

(*S*,*S*)-BDPP
61%, 81% ee



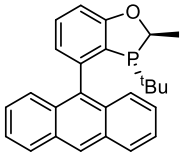

**L1**
46%, 62% ee



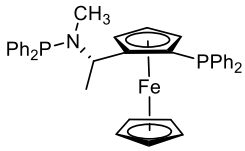

**L2**
45%, -6% ee



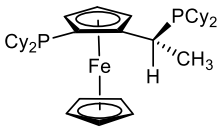

**L3**
52%, <5% ee



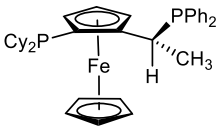

**L4**
51%, <5% ee



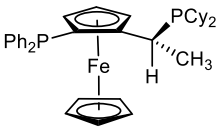

(*S*)-Me-Bophoz
46%, 38% ee



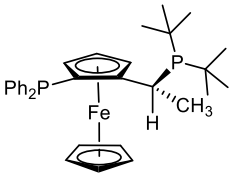

Josiphos SL-J003-1
**88%, 92% ee**



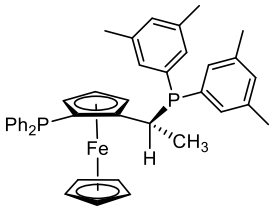

Josiphos SL-J004-1
89%, 85% ee



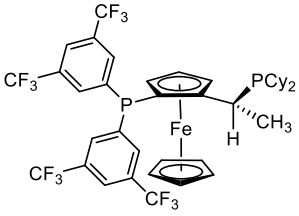

Josiphos SL-J001-1
54%, 18% ee



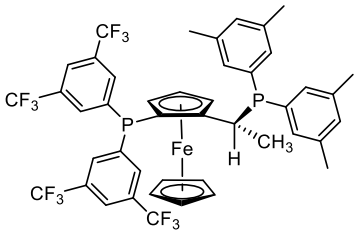

Josiphos SL-J002-1
61%, 39% ee



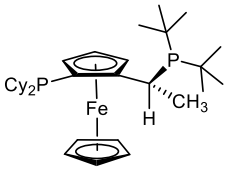
Josiphos SL-J005-1
73%, 44% ee



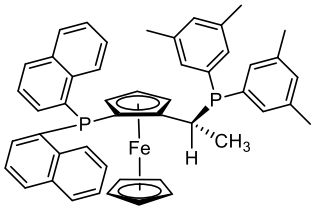
Josiphos SL-J006-1
71%, 62% ee



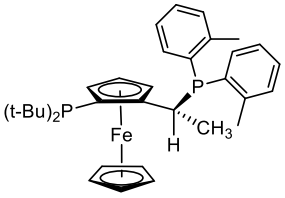
Josiphos SL-J008-1
52%, 30% ee



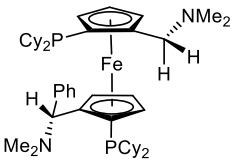
Josiphos SL-J009-1
56%, 20% ee



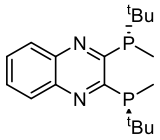
Josiphos SL-J404-1
66%, 58% ee



Josiphos SL-J505-1
50%, <5% ee



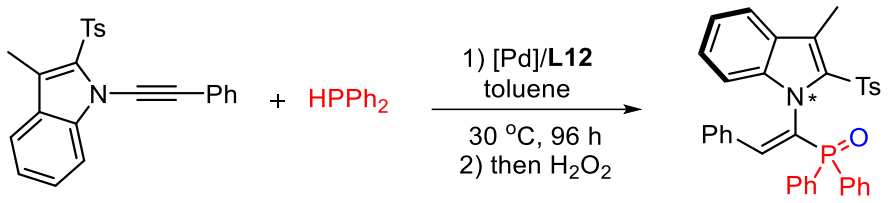
Mandyphos SL-M002-1
42%, <5% ee



(*S*,*S*)-QuinoxP
85%, 91% ee

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(acac)_2$ (6 mol%), L* (9 mol%) in toluene (2.0 mL), 30 °C, 96 h, then $H_2O_2$ at 0 °C for 20 min. Isolated yield. The ee was determined by HPLC analysis using a chiral stationary phase.

**Table S2. Screening of Pd catalysts[a]**

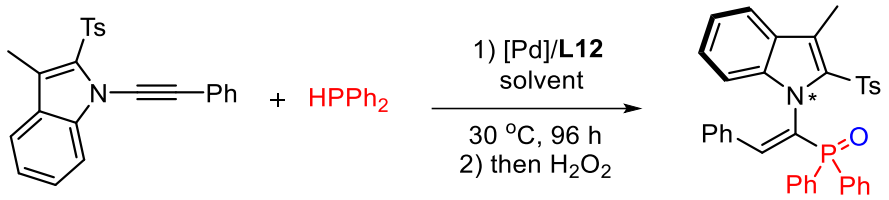



**1** **2a** **3, (*S*)-product**

| Entry | [Pd] | Ligand | Solvent | Yield (%) | ee (%) |
|---|---|---|---|---|---|
| 1 | $Pd(hfac)_2$ | **L12** | toluene | 53 | 14 |
| 2 | $Pd(NO_3)_2{\cdot}H_2O$ | **L12** | toluene | 80 | 87 |
| 3 | $Pd(OH)_2$ | **L12** | toluene | 71 | 88 |
| 4 | $[Pd(allyl)Cl]_2$ | **L12** | toluene | 52 | <5 |
| 5 | $Pd(OAc)_2$ | **L12** | toluene | 81 | 92 |
| 6 | $Pd(TFA)_2$ | **L12** | toluene | 54 | <5 |
| 7 | $PdCl_2$ | **L12** | toluene | - | - |

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), Pd catalysts (6 mol%), **L12** (9 mol%) in toluene (2.0 mL), 30 °C, 96 h, then $H_2O_2$ at 0 °C for 20 min. Isolated yield. The ee was determined by HPLC analysis using a chiral stationary phase.

**Table S3. Screening of Solvents[a]**

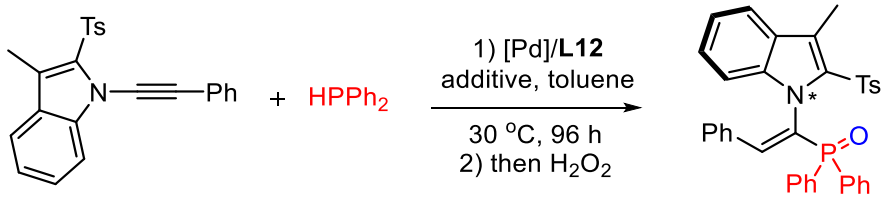



**1** **2a** **3, (*S*)-product**

| Entry | [Pd] | Ligand | Solvent | Yield (%) | ee (%) |
|---|---|---|---|---|---|
| 1 | $Pd(acac)_2$ | **L12** | DCE | - | - |
| 2 | $Pd(acac)_2$ | **L12** | MeCN | 67 | 79 |
| 3 | $Pd(acac)_2$ | **L12** | THF | 64 | 75 |
| 4 | $Pd(acac)_2$ | **L12** | MeOH | 41 | <5 |
| 5 | $Pd(acac)_2$ | **L12** | EA | 75 | 92 |
| 6 | $Pd(acac)_2$ | **L12** | Hexane | 79 | 79 |
| 7 | $Pd(acac)_2$ | **L12** | PhCl | 63 | 92 |
| 8 | $Pd(acac)_2$ | **L12** | Acetone | 56 | 88 |
| 9 | $Pd(acac)_2$ | **L12** | $PhCF_3$ | 43 | 9 |
| 10 | $Pd(acac)_2$ | **L12** | Ph | 82 | 93 |
| 11 | $Pd(acac)_2$ | **L12** | m-xylene | 85 | 92 |

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(acac)_2$ (6 mol%), **L12** (9 mol%) in a solvent (2.0 mL), 30 °C, 96 h, then $H_2O_2$ at 0 °C for 20 min. Isolated yield. The ee was determined by HPLC analysis using a chiral stationary phase.

**Table S4. Screening of additives[a]**

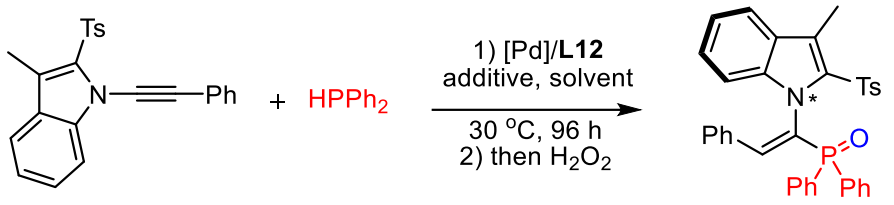



**1** **2a** **3, (*S*)-product**

| Entry | [Pd] | Ligand | Additive | Solvent | Yield (%) | ee (%) |
|---|---|---|---|---|---|---|
| 1 | $Pd(acac)_2$ | **L12** | $Fe(OAc)_2$ | toluene | - | - |
| 2 | $Pd(acac)_2$ | **L12** | $Zn(OAc)_2$ | toluene | 77 | 93 |
| 3 | $Pd(acac)_2$ | **L12** | AgOAc | toluene | 89 | 88 |
| 4 | $Pd(acac)_2$ | **L12** | HOAc | toluene | 85 | 93 |
| 5 | $Pd(acac)_2$ | **L12** | $K_2CO_3$ | toluene | 46 | 74 |
| 6 | $Pd(acac)_2$ | **L12** | CsOAc | toluene | 93 | 94 |
| 7 | $Pd(acac)_2$ | **L12** | LiOAc | toluene | 86 | 93 |
| 8 | $Pd(acac)_2$ | **L12** | NaOAc | toluene | 84 | 92 |
| 9 | $Pd(acac)_2$ | **L12** | KOAc | toluene | 89 | 92 |

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(acac)_2$ (6 mol%), **L12,** and additive (0.3 equiv) in toluene (2.0 mL), 30 °C, 96 h; then $H_2O_2$ at 0 °C for 20 min. Isolated yield. The ee was determined by HPLC analysis using a chiral stationary phase.

**Table S5. Screening of temperature[a]**



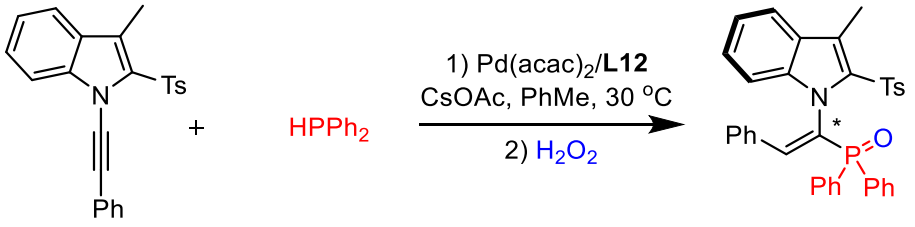

**1a** **2a** **3, (*S*)-product**

| Entry | [Pd] | Ligand | Additive | T(℃) | Yield (%) | ee (%) |
|---|---|---|---|---|---|---|
| 1 | $Pd(acac)_2$ | **L12** | CsOAc | 10 | 56 | 98 |
| 2 | $Pd(acac)_2$ | **L12** | CsOAc | 40 | 87 | 93 |
| 3 | $Pd(acac)_2$ | **L12** | CsOAc | 60 | 91 | 89 |
| 4 | $Pd(acac)_2$ | **L12** | CsOAc | 80 | 89 | 76 |

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(acac)_2$ (6 mol%), **L12** (9 mol%), and CsOAc (0.3 equiv) in toluene (2.0 mL), 96 h; then $H_2O_2$ at 0 °C for 20 min. Isolated yield. The ee was determined by HPLC analysis using a chiral stationary phase.

## 2.2. Typical Procedure for the Asymmetric Catalysis

### General procedure for the synthesis of 3-29 and 31-44

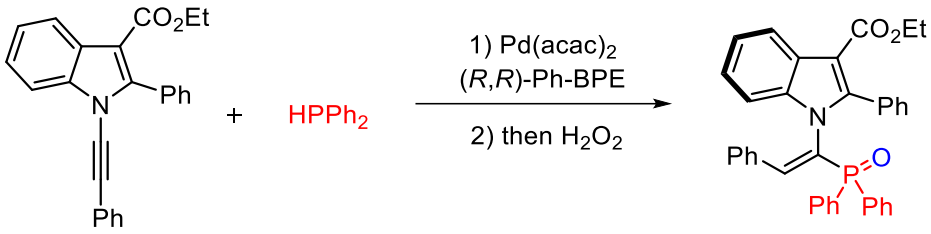



**1** **2a** **3, (*S*)-product**

To a sealable tube (15 mL) were charged with 1-indolylalkyne **1** (38.5 mg, 0.1 mmol), $Pd(acac)_2$ (1.8 mg, 6 mol%), **L12** (5.4 mg, 9 mol%), CsOAc (5.8 mg, 0.3 equiv) and anhydrous toluene (2.0 mL) under argon. Then symmetrical diarylphosphine **2a** (37.2 mg, 0.2 mmol) was addeded and the mixture was stirred at 30 °C for 96 h. After that, $H_2O_2$ (30%, 0.5 mL) was added at 0 °C and the resulting solution was stirred for another 20 min. The reaction mixture was quenched with $H_2O$ and the mixture

was concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 5/1 to 1/1) to afford the desired product. The enantiomeric excess was determined by chiral HPLC analysis.

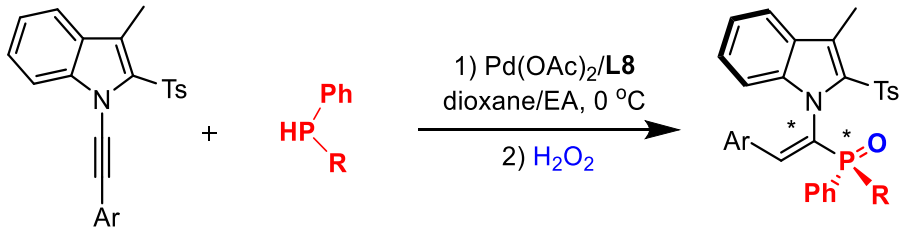
**General procedure for the synthesis of 30**




**30**

To a sealable tube (15 mL) were charged with the above 1-indolylalkyne (36.5 mg, 0.1 mmol), $Pd(acac)_2$ (1.8 mg, 6 mol %), (*R*, *R*)-Ph-BPE (4.6 mg, 9 mol%) and anhydrous toluene (2.0 mL) under argon, then diphenylphosphine **2a** (37.2 mg, 0.2 mmol) was addeded and the mixture was stirred at 0 °C for 96 h. After that, $H_2O_2$ (30%, 0.5 mL) was added at 0 °C and the resulting solution was stirred for another 20 min. The reaction mixture was quenched with $H_2O$ and the mixture was concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 3/1 to 1/1) to afford the desired products **30** (68% yield). The enantiomeric excess was determined by chiral HPLC analysis (82% ee).

**General procedure for the synthesis of 45-54**

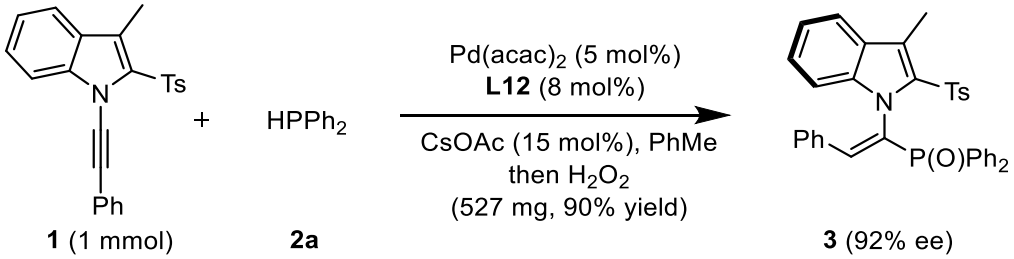



**1a** **2** **(*S*,*S*)-45-54**

To a sealable tube (15 mL) were charged with 1-indolylalkyne (38.5 mg, 0.1 mmol), $Pd(OAc)_2$ (1.3 mg, 6 mol%), **L8** (5.5 mg, 9 mol%) and dioxane (1.0 mL)/EtOAc (1.0 mL) under argon. Then secondary phosphine **2** (0.2 mmol) was addeded at 0 °C and the mixture was stirred for 96 h. After that, $H_2O_2$ (30%, 0.5 mL) was added at 0 °C and the resulting solution was stirred for another 20 min. The reaction mixture was quenched with $H_2O$ and the mixture was concentrated under vacuum. The residue

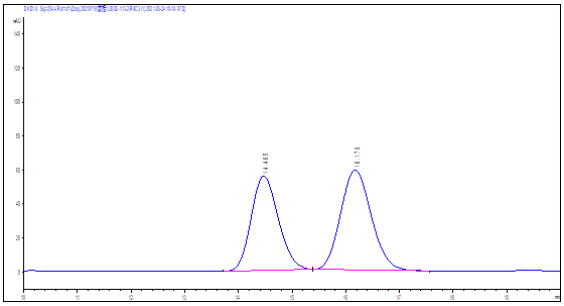
was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 3/1 to 1/1) to afford the desired products **45-54**. The enantiomeric excess was determined by chiral HPLC analysis.

**1 mmol scale synthesis of 3**

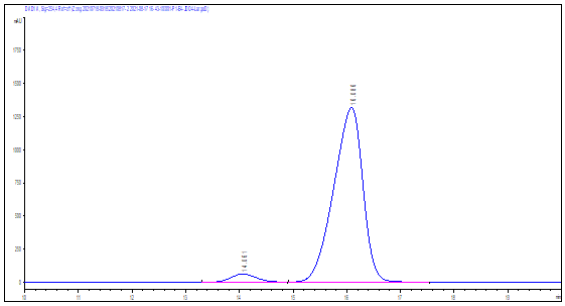



To a sealable tube (50 mL) were charged with 1-indolylalkyne **1** (385 mg, 1 mmol), $Pd(acac)_2$ (15.2 mg, 5 mol%), chiral **L12** (48.4 mg, 8 mol%), CsOAc (28.8 mg, 0.15 equiv) and anhydrous toluene (20.0 mL) under argon, then diarylphosphines **2a** (372 mg, 0.2 mmol) was addeded and the mixture was stirred at 30 ºC for 96 h. After that, $H_2O_2$ was added and the resulting solution was stirred for another 20 min. The reaction mixture was quenched with $H_2O$ and the mixture was concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 3/1 to 1/1) to afford the desired products **3** (90% yield).

**HPLC analysis**: Daicel Chiralpak OZ-H column (hexane:2-propanol = 95:5, v = 1.0 mL/min, 40 ºC, 254 nm; tr (minor) = 14.061 min, tr (major) = 16.086 min, 4:96 er (direct hydrosphosphination product **3'** was analyzed).

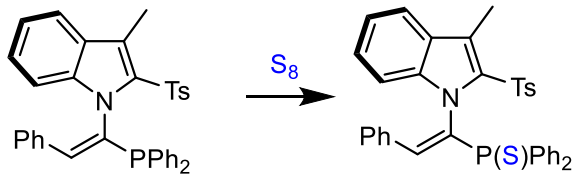


| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 14.465 | 1958.9 | 45.65 |
| 2 | 16.17 | 2332.4 | 54.35 |



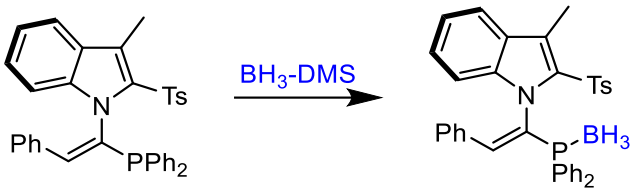
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 14.061 | 2001.9 | 3.89 |
| 2 | 16.086 | 49541.1 | 96.12 |

**2.3 Transformations and application**



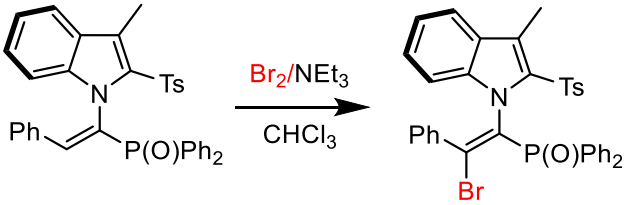

**3'** (92% ee) **55** 95% (92% ee)

The product **3'** was treated with elemental sulphur (12.8 mg, 0.05 mmol, 1.0 equiv) and stirred for 0.5 hour.[4] Crude product was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford **55**.



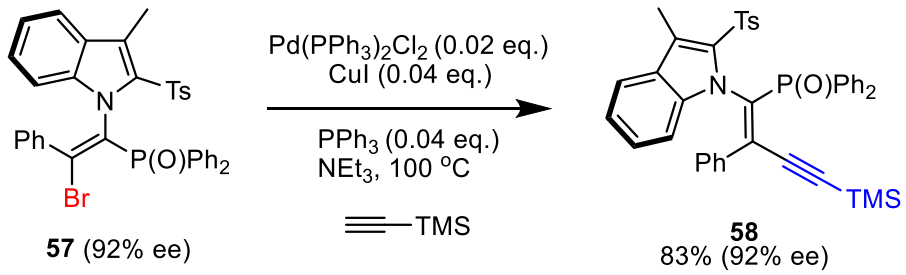

**3'** (92% ee) **56** 91% (93% ee)

$BH_3$-DMS (5.0 μl, 1.0 equiv) was added into the toluene of **3'** (28.6 mg, 0.05 mmol, 1.0 equiv) and the resulting solution was stirred for 15 min.[5] The excess borane was quenched with $H_2O$ and the mixture was extracted with ethyl acetate, washed with saturated NaCl (aq) solution. The organic phase was dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with petroleum ether/EtOAc = 20/1 to afford product **56** as a white solid.




**3** (92% ee) **57** 74% (92% ee)

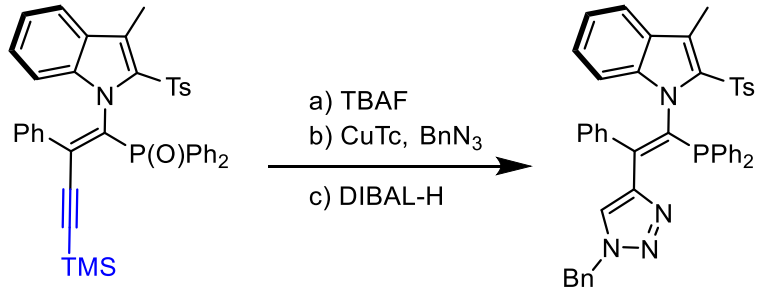
To a solution of **3** (35.2 mg, 0.06 mmol) in chloroform (1.0 mL) was added a solution of bromine (10.6 mg, 0.066 mmol) in chloroform (1.0 mL) slowly. Then $NEt_3$ (9.1 mg, 0.09 mmol) was added dropwisely to the solution. The solvent was washed with saturated $Na_2S_2O_3$ (aq) solution. The organic phase was concentrated and the residue was purified by silica gel flash chromatography to afford the desired bromo derivative **57.**[6]




**57** (92% ee)

**58**
83% (92% ee)

In an oven-dried round bottom flask, CuI (0.4 mg, 0.04 eq.), $PdCl_2(PPh_3)_2$ (0.7 mg, 0.02 eq.) and triphenylphosphine (0.6 mg, 0.04 eq.) were dissolved in 2.0 mL of fresh distilled trimethylamine.[7] The mixture was heated at 40 °C under inert atmosphere for 20 min. Then **57** (0.05 mmol, 33.3 g, 1.0 eq.) and ethynyltrimethylsilane (0.075 mmol, 7.4 mg, 1.5 eq.) were added and the reaction mixture was heated to reflux and allowed to react overnight. The solvent was removed under reduced pressure, and 10.0 mL of EtOAc were added. The crude was filtered with celite, and the filtrate was washed with water (3 x 20.0 mL), brine (5.0 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel using petroleum ether/EtOAc = 20/1. The product was obtained as a pale yellow solid.

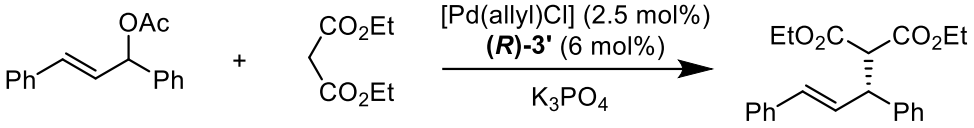



**58** (92% ee)

**59**
73% ( 92% ee)

Under argon atmosphere, alkynylation product of **58** (68 mg, 0.1 mmol, 92% ee) was charged into a dry 10 mL flask along with anhydrous THF, the flask was then cooled to -78 ºC and TBAF (1.0 mL, 1.0 mmol) was added dropwise and stirred for 5 min. Then the desiliconized product from previous step was treated with copper (I) thiophene-2-carboxylate (CuTc, 1.4 mg, 0.0075 mmol, 10 mol%) and anhydrous toluene (2.0 mL). Subsequently, $BnN_3$ (12.0 mg, 0.09 mmol, 1.2 equiv) was added slowly, then the reaction mixture was stirred until completed (monitored by TLC). The reaction was quenched by saturated $NH_4Cl$ aqueous solution (10 mL) and extracted with EtOAc (3× 5 mL). The combined organic layers were dried over $Na_2SO_4$, filtrated and concentrated under vacuum.

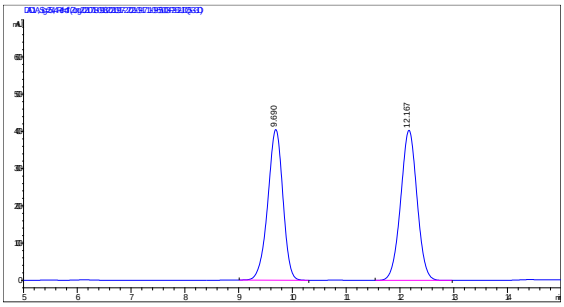
**The application of chiral phosphine 3' in the reaction**

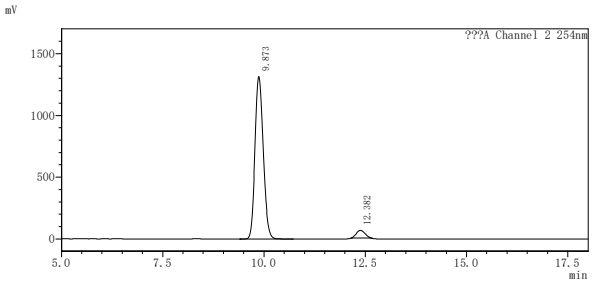



**60**
78%, 90% ee

To a suspension of the desired chiral ligand **(*R*)-3'** (0.006 mmol), $[Pd(C_3H_5)Cl]_2$ (0.9 mg, 0.0025 mmol) and $K_3PO_4$ (42.4 mg, 0.2 mmol) in $CHCl_3$ (2.0 mL) were stirred at 0 °C. 1,3-diphenyl-2-propenyl acetate (37.8 mg, 0.15 mmol) and dimethyl malonate (16.0 mg, 0.1 mmol) were subsequently added. After the reaction time the reaction mixture was diluted with EtOAc (5 mL). Saturated $NH_4Cl$ (aq) (10 mL) was then added, the mixture was extracted with EtOAc (3 × 10 mL), and the extract was dried over $MgSO_4$. The residue was purified by flash column chromatography on silica gel (PE:EtOAc = 20:1) to afford the product **60** as a light yellow oil (27.3 mg, 78% yield, 90% ee). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.33 – 7.29 (m, 6H), 7.28 – 7.25 (m, 2H), 7.24 – 7.18 (m, 2H), 6.47 (d, *J* = 15.7 Hz, 1H), 6.34 (dd, *J* = 15.7, 8.6 Hz, 1H), 4.26 (dd, *J* = 11.0, 8.6 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.00 – 3.94 (m, 2H), 3.92 (d, *J* = 11.0 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H).

**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 95:5, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 9.87 min, tr (minor) = 12.38 min, 95:5 er.



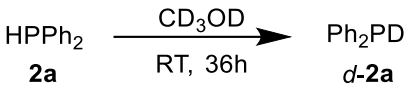




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.69 | 7889.7 | 48.03 |
| 2 | 12.167 | 8537.5 | 52.00 |

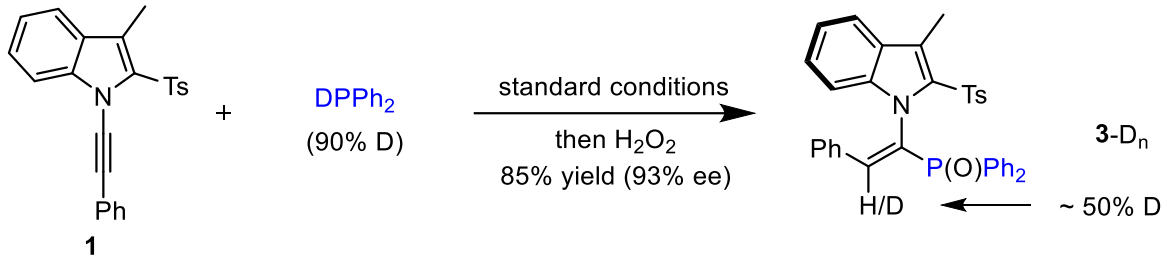
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.873 | 18616925 | 95.13 |
| 2 | 12.382 | 953155 | 4.87 |

## 2.4 Mechanistic Studies

### (a) H/D Exchange experiment

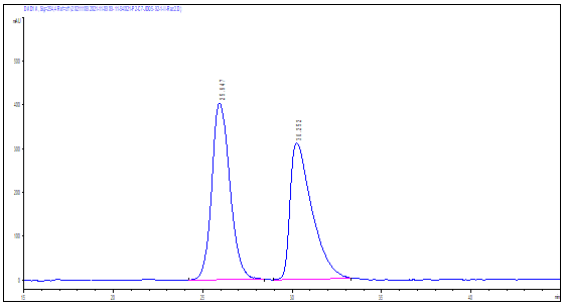



To an oven dried vial was charged with diarylphosphine **2a** (2 mmol) and a magnetic stir bar, **2a** was then dissolved in $d_4$-MeOH (2 mL) and the resulting solution was stirred at 30 °C for 36 hours in a glove box under argon. The clear solution was concentrated in vacuo and resulted in 90% D of the title compound *d*-**2a**. The deuterium incorporation in **2a** was determined by $^1$H NMR spectroscopy. $^1$H NMR analysis indicated 90% deuteration of the **2a**.

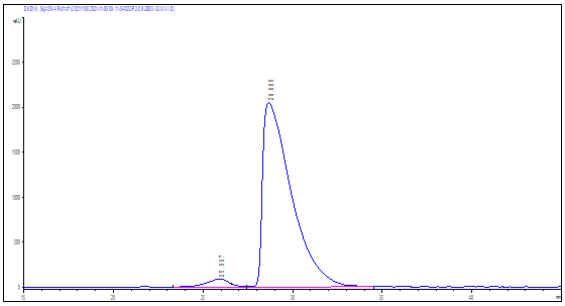



To a 15 mL tube were charged with 1-indolylalkyne **1** (38.5 mg, 0.1 mmol), $Pd(acac)_2$ (1.8 mg, 6 mol %), **L12** (5.4 mg, 9 mol%), CsOAc (5.8 mg, 0.3 equiv) and anhydrous toluene (2.0 mL) under argon, then deuterated diarylphosphine ***d*-2a** (37.4 mg, 0.2 mmol) was addeded and the mixture was stirred at 30 °C for 96 h. After that, $H_2O_2$ was added and the resulting solution was stirred for another 20 min. The reaction mixture was quenched with $H_2O$ and the mixture was concentrated under vacuum.

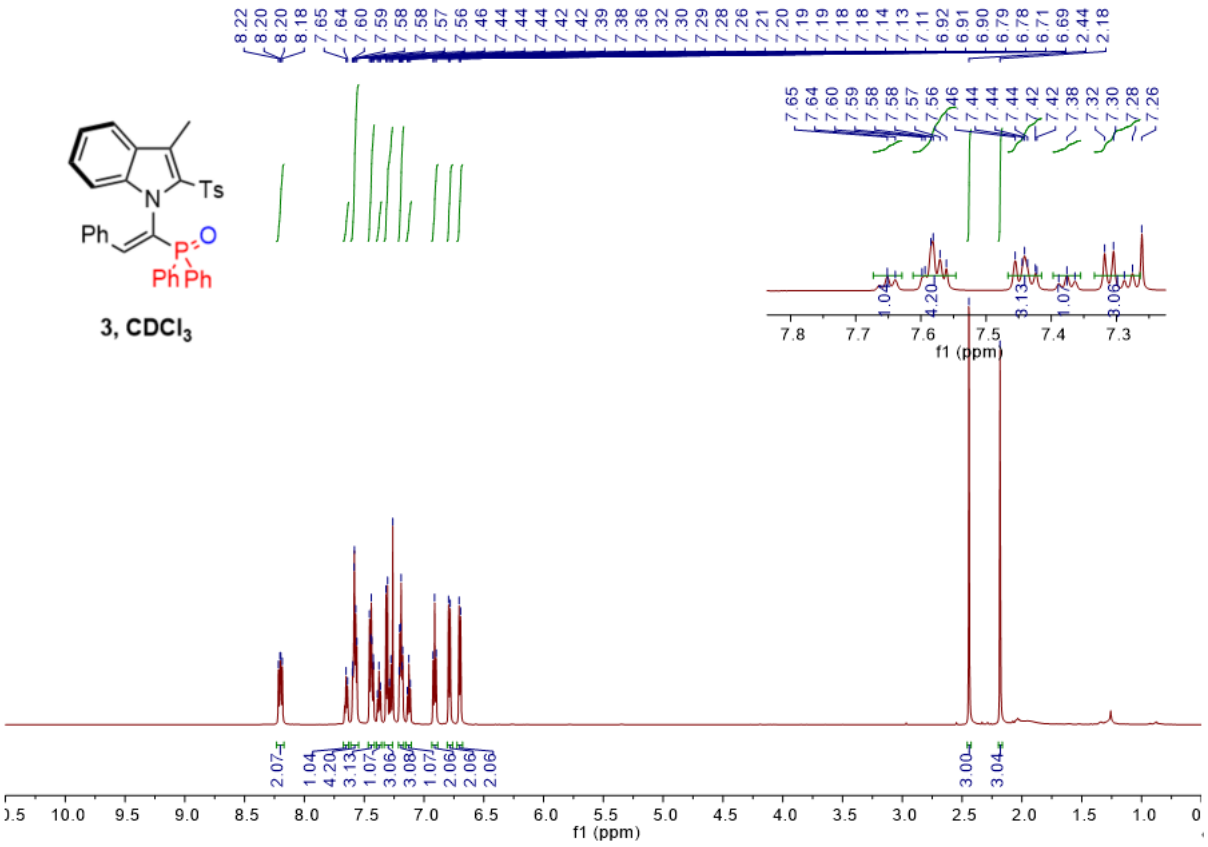
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 98:2, v = 0.5 mL/min, 40 °C, 254 nm); tr (minor) = 25.907 min, tr (major) = 28.669 min, 3.3:96.7 er.

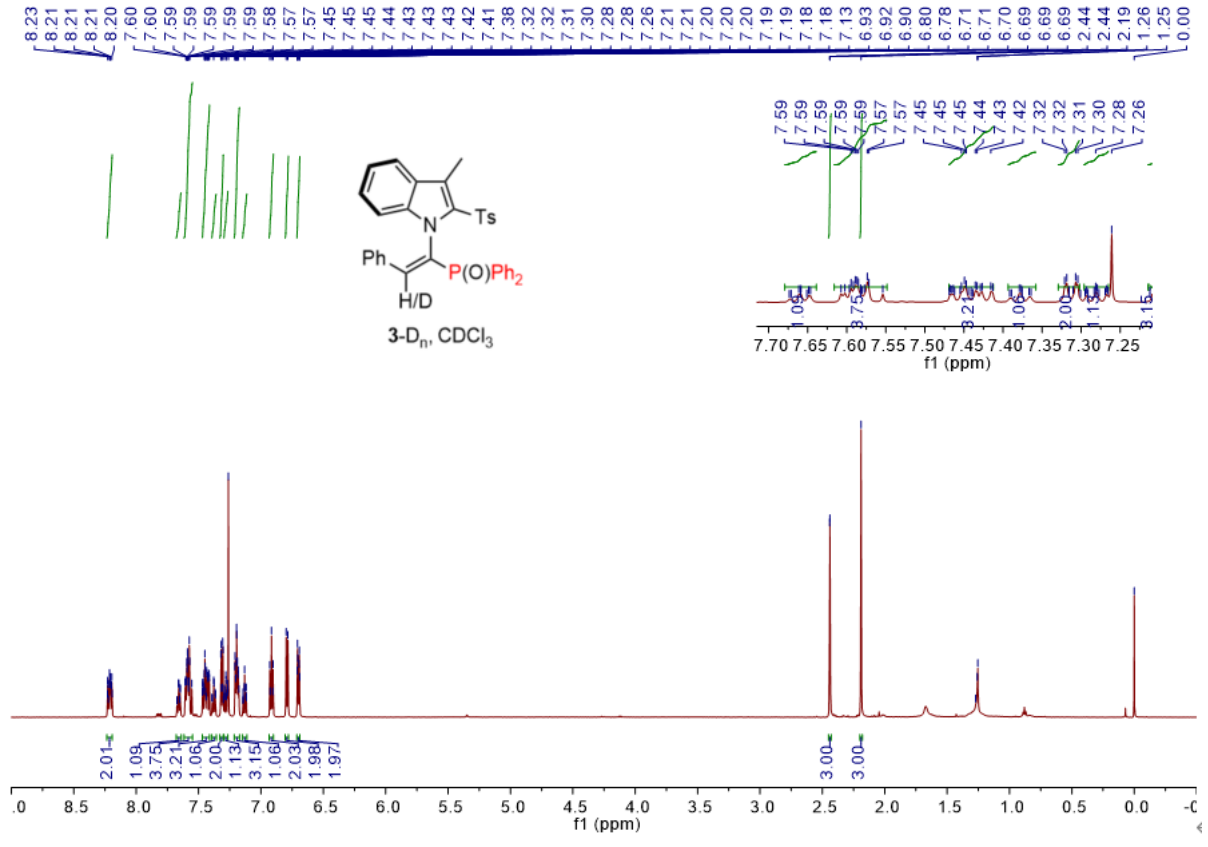


| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 25.947 | 28582.8 | 51.96 |
| 2 | 30.252 | 26421.9 | 48.04 |

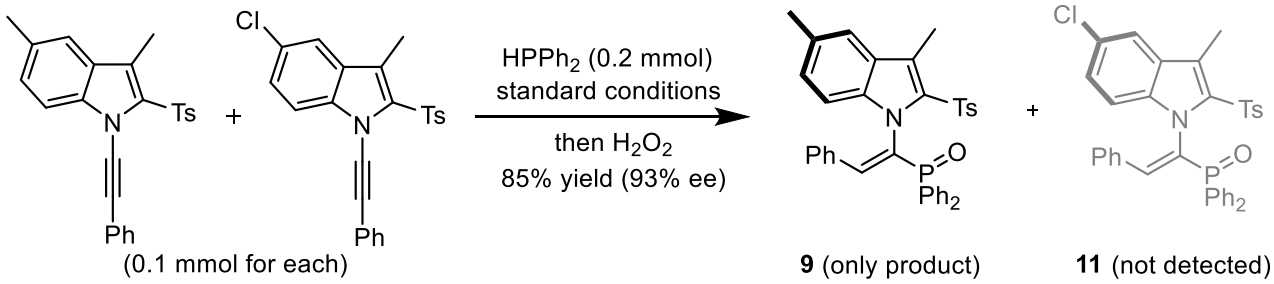


| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 25.907 | 7772 | 3.31 |
| 2 | 28.669 | 227363.7 | 96.70 |


Ts
N
Ph
P
O
Ph
Ph
3, CDCl3
f1 (ppm)

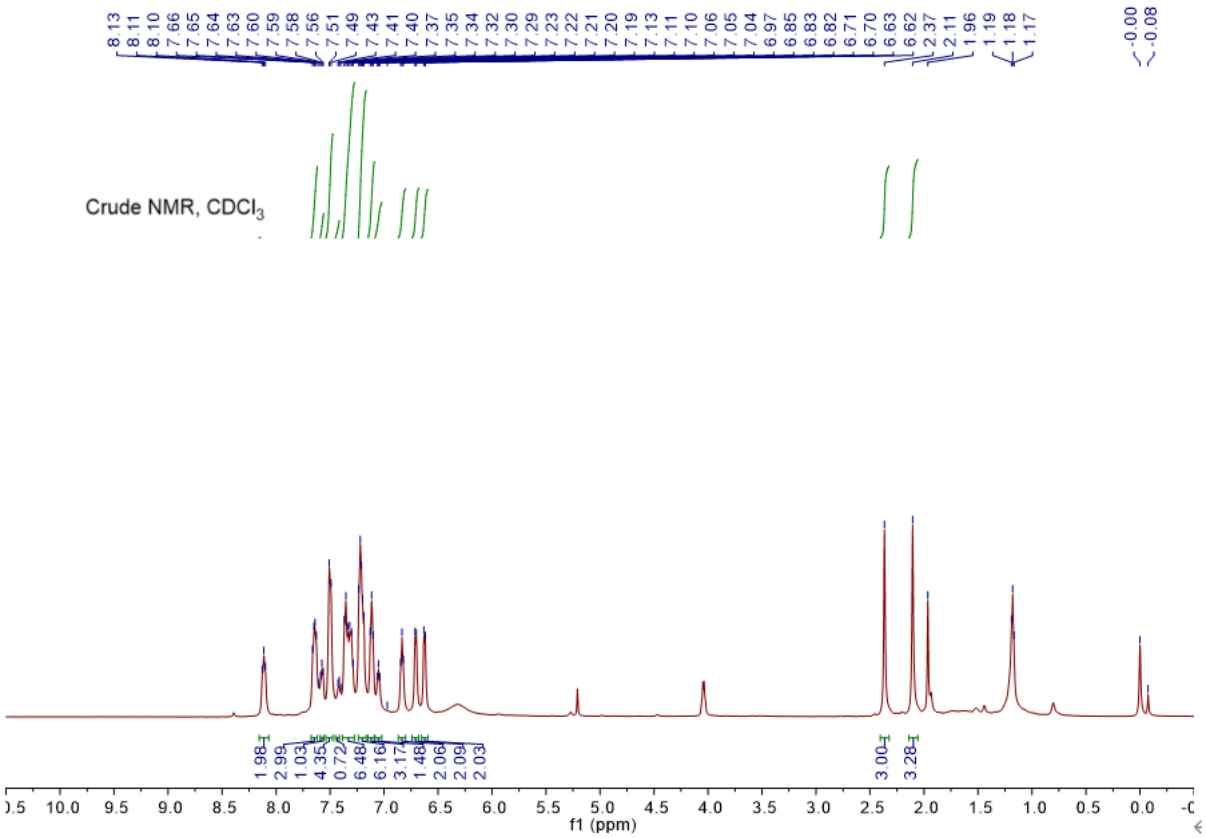

Ts
N
Ph
P(O)Ph2
H/D
3-Dn, CDCl3
f1 (ppm)

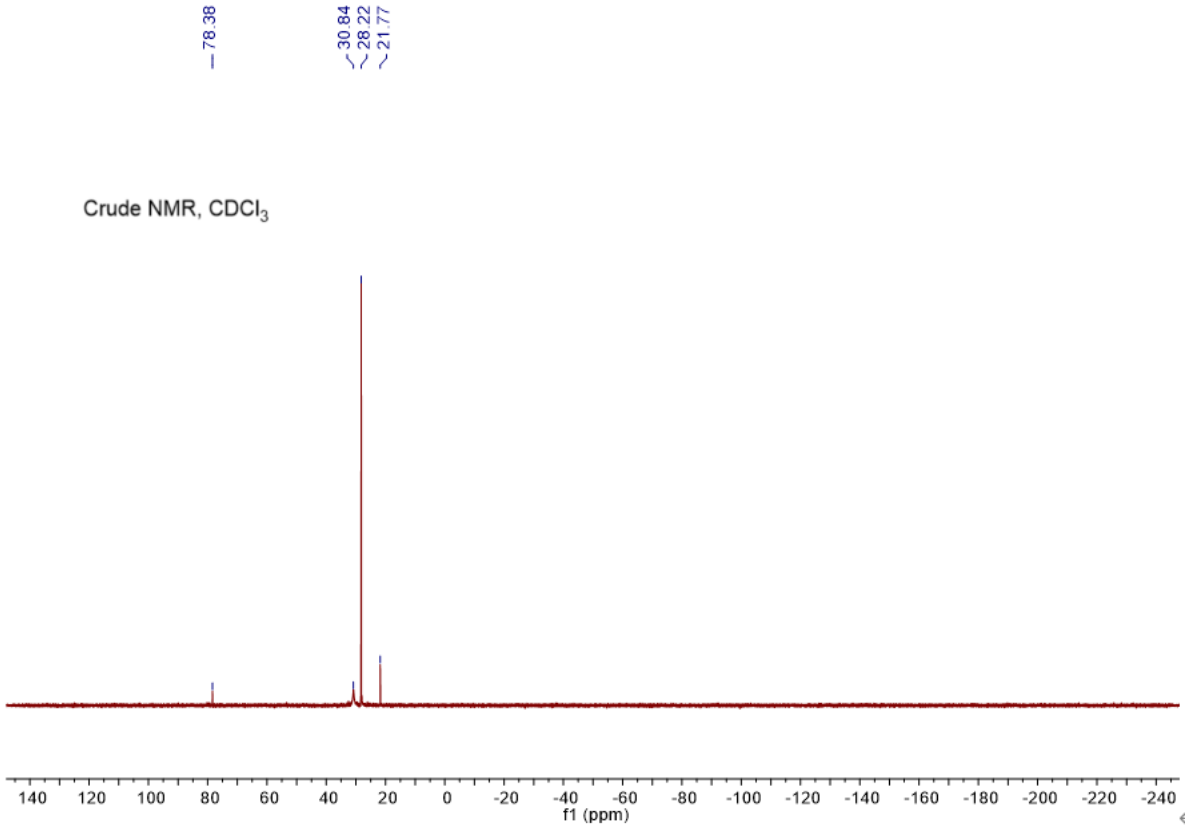
**(b) Competition Reaction**



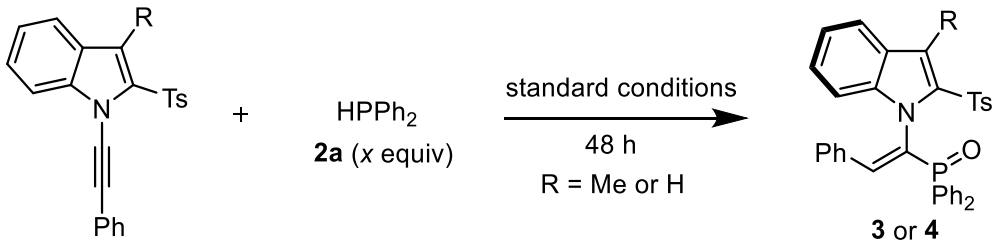

(0.1 mmol for each) **9** (only product) **11** (not detected)

A pressure tube was charged with 5-methyl substrate (39.9 mg, 0.1 mmol) and 5-chlorine substituted indolylalkynes (41.9 mg, 0.1 mmol), $Pd(acac)_2$ (1.8 mg, 6 mol%), **L12** (5.4 mg, 9 mol%), CsOAc (5.8 mg, 0.3 equiv) and anhydrous toluene (2.0 mL) under argon. Then diarylphosphine **2a** (37.2 mg, 0.2 mmol) was addeded and the mixture was stirred at 30 °C for 96 h. After that, $H_2O_2$ (30%, 0.5 mL) was added and the resulting solution was stirred for another 20 min. The reaction mixture was quenched with $H_2O$ and the mixture was concentrated under vacuum. Only **9** was detected.

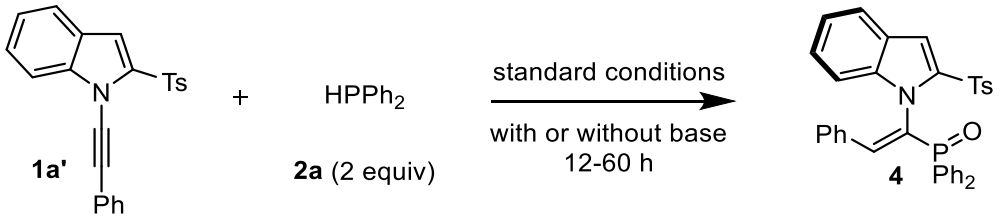





**(c) Control experiments**

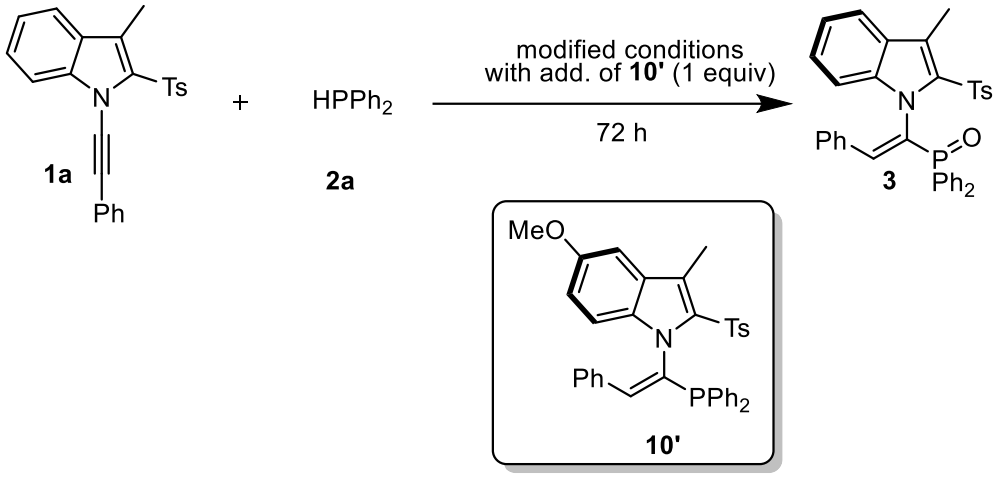



General procedure was used with a 3-susbtituted indole (**1a)** and 3-unsusbtituted indole (**1a'**) respectively reacted with different equivalents of **2a** at the standard conditions.




To a sealable tube (15 mL) were charged with 3-unsusbtituted indole **1a'** (19.3 mg, 0.05 mmol), $Pd(acac)_2$ (0.9 mg, 6 mol%), **L12** (2.7 mg, 9 mol%), w/o CsOAc (2.9 mg, 0.3 equiv) and anhydrous toluene (1.0 mL) under argon. Then diarylphosphine **2a** (18.6 mg, 0.2 mmol) was addeded and the

mixture was stirred at 30 °C. The enantiomeric excess was determined by chiral HPLC analysis with the direct hydrosphosphination product **4'** at more than one time point. After that, $H_2O_2$ (30%, 0.3 mL) was added at 0 °C and the resulting solution was stirred for another 20 min. The reaction mixture was quenched with $H_2O$ and the mixture was concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 5/1 to 1/1) to afford the desired product.



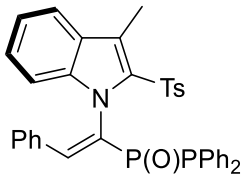

To a 15 mL tube were charged with 1-indolylalkyne **1a** (19.3 mg, 0.05 mmol), $Pd(acac)_2$ (0.9 mg, 6 mol%), **L12** (2.7 mg, 9 mol%), CsOAc (2.9 mg, 0.3 equiv), a chiral or racemic phosphine product **10'** (30.1 mg, 1.0 equiv) and anhydrous toluene (1.0 mL) under argon, then diarylphosphine **2a** (18.6 mg, 0.2 mmol) was addeded and the mixture was stirred at 30 °C for 72 h. The enantiomeric excess was determined by chiral HPLC analysis with the direct hydrosphosphination product **3'**. After that, $H_2O_2$ was added and the resulting solution was stirred for another 20 min. The reaction mixture was quenched with $H_2O$ and the mixture was concentrated under vacuum. The residue was purified by flash chromatography on silica gel to afford the desired products **3**.

**(d) Determination of $t_{1/2}^{rac}$ and Rotational Barrier for 3**

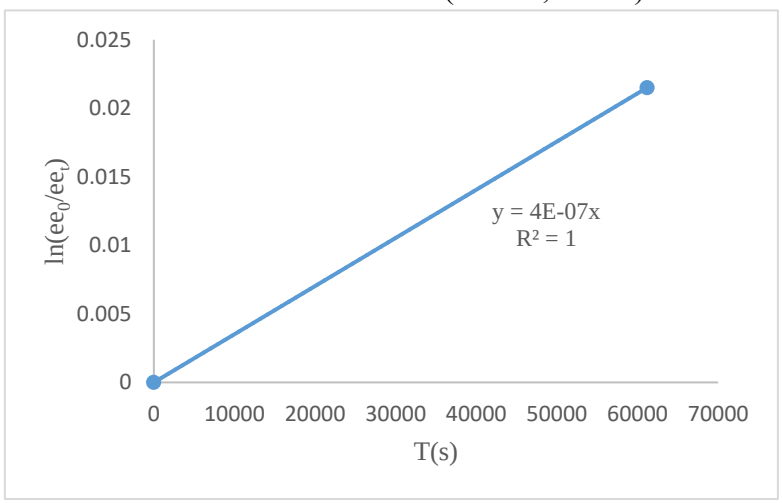
The enantiomerisation barrier, corresponding to the barrier to rotation for the following atropisomers, was obtained by kinetic of racemisation of an enantiomer. The slope of the first order kinetic line gives the racemisation constant ($k_{racemisation} = 2 \times k_{enantiomerisation}$). Eyring equation gives the enantiomerisation barrier ($\Delta G^{\ddagger}_{enaniomerization}$) from enantiomerisation constant ($k_{enantiomerisation}$), R = 8.31451 $J \bullet K^{-1} \bullet mol^{-1}$, $h$ = 6.62608 × $10^{-34}$ Js and $k_B$ = 1.38066 × $10^{-23}$ J/K. Reactions were conducted at 1 mg/mL concentration. Enantiomeric excess values were determined by HPLC.

$$\Delta G^{\ddagger}_{enantiomerization} = RT \times \ln \frac{k_B \times T}{h \times k_{enantiomerisation}}$$

Racemization of **3** in PhMe at 100 °C.




**3**. $\Delta G^{\ddagger}$ = 33.4 kcal/mol (100 °C, PhMe)




| T/s | ee | ln ($ee_0/ee_t$) |
|---|---|---|
| 0 | 94 | 0 |
| 61200 | 92 | 0.021506 |

$k_{racemization}$ (100 °C) = $4.0\times10^{-7}$ $s^{-1}$

$k_{enantiomerization}$ (100 °C) = $2.0\times10^{-7}$ $s^{-1}$

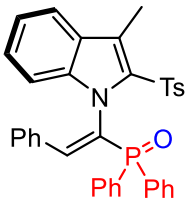
$t_{1/2}^{rac}$ (100 °C) = ln (2)/$k_{racemization}$ = 962.7 h

Employing the Eyring equation: $\Delta G^{\ddagger}_{enantiomerization} = RT\times \ln\frac{k_B\times T}{hk_{enantiomerisation}}$

$$\Delta G^{\neq} = 8.314\ J\bullet K^{-1}\bullet mol^{-1} \times 373.15\ K \times \ln\frac{1.381\times10^{-23}\ J\bullet K^{-1}\times 373.15\ K}{2.0\times10^{-7}\ S^{-1}\times 6.626\times10^{-34}\ J\bullet s}$$

$$\Delta G^{\neq} = 140\ kJ\bullet mol^{-1} = 33.4\ kcal\bullet mol^{-1}$$

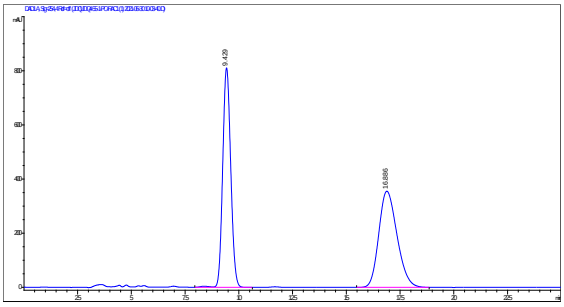
## 3. Characterization Data and HPLC Chromatograms



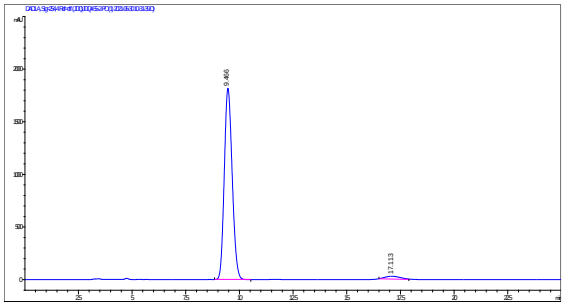

**(*S*,*E*)-(1-(3-Methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine oxide (3)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 54.6 mg, 93%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.23 – 8.17 (m, 2H), 7.67 – 7.63 (m, 1H), 7.61 – 7.55 (m, 4H), 7.47 – 7.41 (m, 3H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.27 (m,

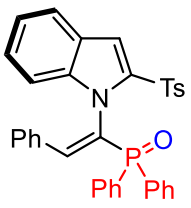
3H), 7.22 – 7.17 (m, 3H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.91 (t, *J* = 7.7 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.70 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H), 2.18 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.5, 143.2 (d, *J* = 23.0 Hz), 138.9, 137.6, 134.1 (d, *J* = 113.3 Hz), 133.1 (d, *J* = 9.5 Hz), 132.6 (d, *J* = 13.1 Hz), 132.4 (d, *J* = 2.7 Hz), 132.0 (d, *J* = 10.1 Hz), 131.8 (d, *J* = 2.7 Hz), 130.6, 130.5 (d, *J* = 105.0 Hz), 129.9, 129.8 (d, *J* = 102.1 Hz), 129.7, 129.1, 128.6, 128.5 (d, *J* = 12.0 Hz), 127.9, 127.8 (d, *J* =12.1 Hz), 127.0, 126.9, 122.3, 121.7, 120.3, 113.5, 21.4, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.9; **HRMS (ESI) :** calcd. for $C_{36}H_{30}NNaO_3PS^+$ $[M+Na]^+$ : 610.1576; found : 610.1580; **$[\alpha]_D^{20}$** = +80 (c = 0.1, $CHCl_3$). **HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 9.466 min, tr (minor) = 17.113 min, 97:3 er.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.429 | 21054.7 | 50.17 |
| 2 | 16.886 | 20912.8 | 49.83 |



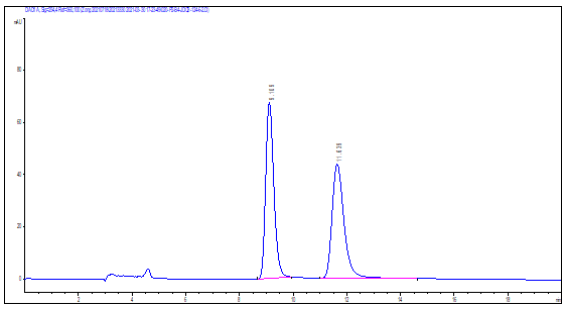
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.466 | 46401.3 | 97.14 |
| 2 | 17.113 | 1368.4 | 2.87 |

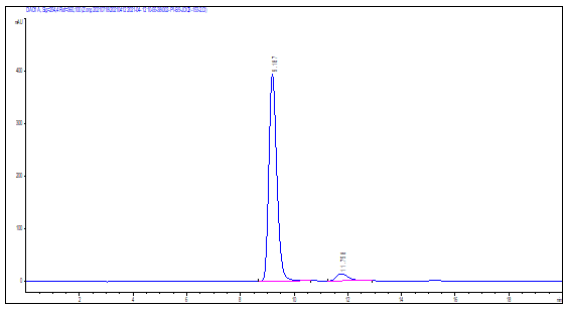



**(*S*,*E*)-Diphenyl(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl) phosphine oxide (4)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 41.8 mg, 73%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.21 – 8.14 (m, 2H), 7.68 – 7.64 (m, 1H), 7.63 – 7.57 (m, 4H), 7.51 – 7.44 (m, 3H), 7.40 – 7.34 (m, 3H), 7.29 – 7.23 (m, 2H), 7.21 – 7.14 (m, 3H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.79 (t, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.44 (d, *J* = 7.9 Hz, 2H), 2.14 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 144.5 (d, *J* = 21.7 Hz), 143.7, 138.4, 137.4, 135.5, 133.1 (d, *J* = 113.2 Hz), 133.0 (d, *J* = 9.5 Hz), 132.5 (d, *J* = 2.8 Hz), 132.2 (d, *J* = 12.9 Hz), 131.93 (d, *J* = 2.7 Hz), 131.86 (d, *J* = 10.0 Hz), 130.2 (d, *J* = 95.0 Hz), 129.8, 129.5 (d, *J* = 91.9 Hz), 129.1, 128.5 (d, *J* = 12.1 Hz), 128.4, 127.8 (d, *J* = 12.1 Hz), 127.7, 126.5, 126.0, 122.3 (d, *J* = 13.9 Hz), 113.4, 113.0, 21.4; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.6; **HRMS (ESI):** calcd. for $C_{35}H_{28}NNaO_3PS^+$ $[M+Na]^+$ : 596.1420; found: 596.1412; **$[\alpha]_D^{20}$** = +110 (c = 0.1, $CHCl_3$).

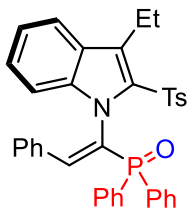
**HPLC analysis**: Daicel Chiralpak OZ-H column (hexane:2-propanol = 80:20, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 9.187 min, tr (minor) = 11.758 min, 95:5 er. (The direct hydrosphosphination product **4'** was analyzed).





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.109 | 1427.5 | 51.169 |
| 2 | 11.639 | 1362.3 | 48.831 |

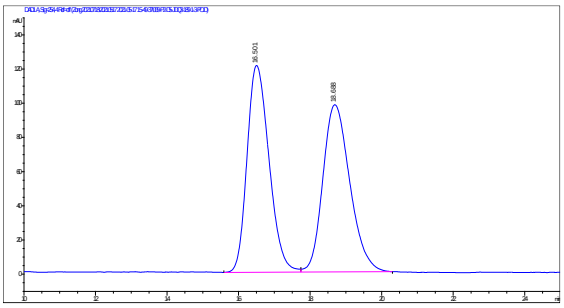
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.187 | 8147.3 | 95.173 |
| 2 | 11.758 | 413.2 | 4.827 |

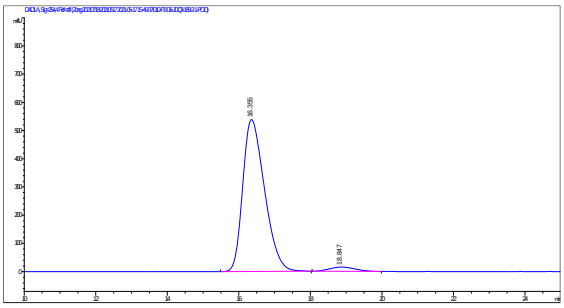



**(*S*,*E*)-(1-(3-Ethyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine oxide (5)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 54.7 mg, 91%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.28 – 8.17 (m, 2H), 7.70 – 7.50 (m, 6H), 7.46 – 7.27 (m, 6H), 7.23 – 7.06 (m, 4H), 6.87 (t, *J* = 7.8 Hz, 2H), 6.75 (d, *J* = 7.9 Hz, 2H), 6.61 (d, *J* = 7.7 Hz, 2H), 3.13 – 3.02 (m, 1H), 2.93 – 2.82 (m, 1H), 2.16 (s, 3H), 1.08 (t, *J* = 7.8 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ143.5, 143.3, 138.9, 137.6, 134.3 (d, *J* = 114.1 Hz), 133.1 (d, *J* = 9.4 Hz), 132.6 (d, *J* = 13.0 Hz), 132.4, 131.9 (d, *J* = 10.1 Hz), 131.8 (d, *J* = 1.4 Hz), 130.6 (d, *J* = 105.9 Hz), 129.9, 129.7, 129.669, 129.668 (d, *J* = 102.3 Hz), 129.1, 128.7, 128.6, 128.51, 128.49, 127.8 (d, *J* = 12.1 Hz), 126.94, 126.85, 126.8, 121.7, 120.4, 113.7, 21.4, 18.4, 16.0; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 28.3; **HRMS (ESI):** calcd. for $C_{37}H_{32}NNaO_3PS^+[M+Na]^+$ : 624.1733; found : 624.1727; **$[\alpha]_D^{20}$** = +52 (c = 0.1, $CHCl_3$).

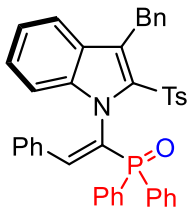
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 70:30, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 16.355min, tr (minor) = 18.847 min, 97:3 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 16.501 | 5169.7 | 50.22 |
| 2 | 18.688 | 5125.3 | 49.78 |

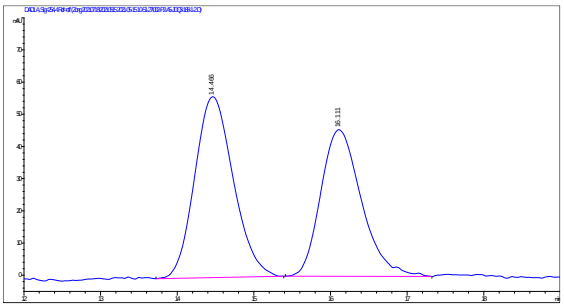
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 16.355 | 22746.7 | 96.79 |
| 2 | 18.847 | 754.1 | 3.21 |

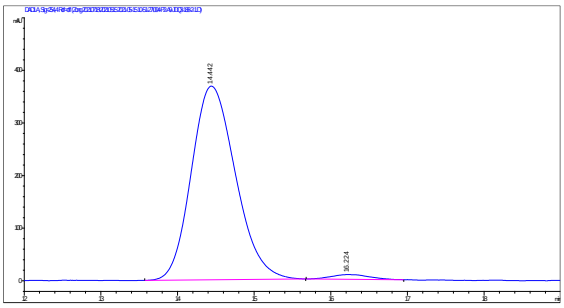



**(*S*,*E*)-(1-(3-Benzyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine oxide (6)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 61.0 mg, 92%). **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.24 – 8.16 (m, 2H), 7.67 – 7.54 (m, 4H), 7.54 – 7.43 (m, 4H), 7.40 – 7.34 (m, 1H), 7.24 – 7.13 (m, 8H), 7.12 – 7.04 (m, 2H), 7.03 – 6.97 (m, 2H), 6.85 (t, *J* = 7.7 Hz, 2H), 6.62 (d, *J* = 8.1 Hz, 2H), 6.47 (d, *J* = 7.8 Hz, 2H), 4.50 (d, *J* = 15.7 Hz, 1H), 4.36 (d, *J* = 15.8 Hz, 1H), 2.08 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.7 (d, *J* = 22.2 Hz), 143.6, 139.5, 138.3, 137.3, 134.2 (d, *J* = 115.2 Hz), 133.0 (d, *J* = 9.4 Hz), 132.5 (d, *J* = 12.8 Hz), 132.4 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 9.9 Hz), 131.8 (d, *J* = 2.7 Hz), 131.3 (d, *J* = 105.4 Hz), 131.0, 129.81, 129.78, 129.77 (d, *J* = 102.0 Hz), 129.0, 128.61, 128.60, 128.52, 128.49, 128.2, 128.0 (d, *J* = 12.2 Hz), 127.24, 127.20, 126.9, 126.0, 124.2, 122.0, 121.1, 113.4, 30.4, 21.3; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.7; **HRMS (ESI):** calcd. for $C_{42}H_{35}NO_3PS^+$ $[M+H]^+$ : 664.2070; found: 664.2062; **$[\alpha]_D^{20}$** = -32(c = 0.1, $CHCl_3$).

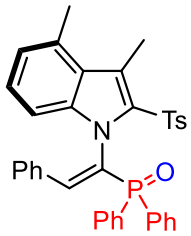
**HPLC analysis**: Daicel Chiralpak OZ-H column (hexane:2-propanol = 95:5, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 14.442 min, tr (minor) = 16.224 min, 98:2 er. (The direct hydrosphosphination product **6'** was analyzed).





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 14.466 | 1968.8 | 53.95 |
| 2 | 16.111 | 1680.8 | 46.05 |

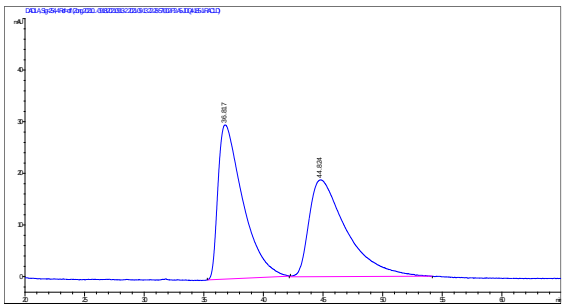
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 14.442 | 14741.5 | 97.98 |
| 2 | 16.224 | 303.7 | 2.02 |

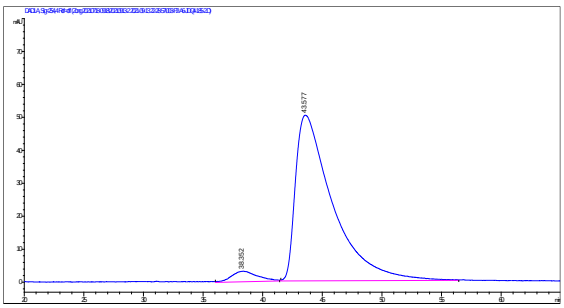


**(*S*,*E*)-(1-(3,4-Dimethyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine oxide (7)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 38.5 mg, 64%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.22 – 8.15 (m, 2H), 7.67 – 7.62 (m, 1H), 7.60 – 7.53 (m, 3H), 7.49 – 7.44 (m, 2H), 7.42 – 7.38 (m, 1H), 7.33 – 7.29 (m, 2H), 7.26 – 7.20 (m, 3H), 7.18 – 7.14 (m, 1H), 7.11 – 7.06 (m, 1H), 6.97 (t, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 7.1 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 2H), 6.78 (d, *J* = 7.8 Hz, 2H), 2.67 (s, 3H), 2.60 (s, 3H), 2.21 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.4, 142.8 (d, *J* = 22.7 Hz), 139.3, 138.2, 134.3 (d, *J* = 113.3 Hz), 133.1 (d, *J* = 9.6 Hz), 133.0, 132.7 (d, *J* = 13.2 Hz), 132.3 (d, *J* = 2.8 Hz), 132.1 (d, *J* = 10.2 Hz), 131.8 (d, *J* = 2.8 Hz), 130.7 (d, *J* = 104.7 Hz), 130.5, 129.93, 129.92 (d, *J* = 101.9 Hz), 129.7, 129.1, 128.6, 128.5 (d, *J* = 12.1 Hz), 127.8 (d, *J* = 12.1 Hz), 126.9, 126.5, 123.6, 123.2, 111.5, 21.4, 20.9, 12.5; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.8; **HRMS (ESI):** calcd. for $C_{36}H_{30}NO_3PS^+$ $[M+H]^+$ : 602.1913; found : 602.1906; **$[\alpha]_D^{20}$** = +40 (c = 0.1, $CHCl_3$).

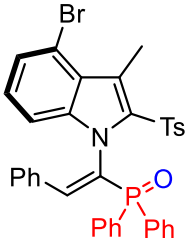
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 95:5, v = 1.0 mL/min, 40 °C, 254 nm); tr (minor) = 38.352 min, tr (major) = 43.577 min, 4:96 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 36.817 | 4325.7 | 51.40 |
| 2 | 44.824 | 4090.8 | 48.61 |

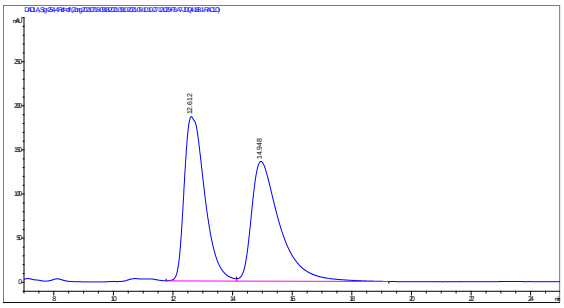
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 38.352 | 482.3 | 4.23 |
| 2 | 43.577 | 10919.2 | 95.77 |

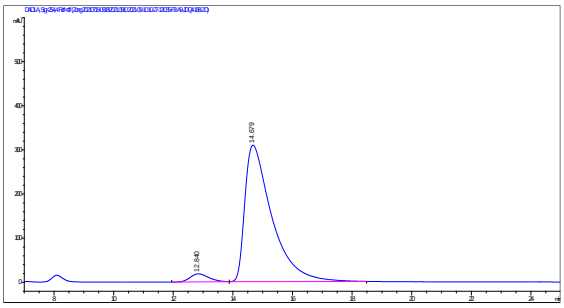



**(*S*,*E*)-(1-(4-Bromo-3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine oxide (8)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 39.2 mg, 59%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.23 – 8.17 (m, 2H), 7.68 – 7.63 (m, 1H), 7.61 – 7.58 (m, 2H), 7.58 – 7.54 (m, 1H), 7.47 – 7.41 (m, 3H), 7.40 – 7.36 (m, 1H), 7.33 – 7.30 (m, 2H), 7.29 – 7.26 (m, 1H), 7.22 – 7.17 (m, 3H), 7.15 – 7.11 (m, 1H), 6.91 (t, *J* = 7.7 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.70 (d, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 2.19 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.5, 143.2(d, *J* = 22.6 Hz), 138.9, 137.6, 134.2(d, *J* = 113.2 Hz), 133.1(d, *J* = 9.4 Hz), 132.6(d, *J* = 13.2 Hz), 132.4(d, *J* = 2.8 Hz), 132.0(d, *J* = 10.4 Hz), 131.8(d, *J* = 3.0 Hz), 130.6, 130.5 (d, *J* = 105.0 Hz), 129.9, 129.8(d, *J* = 100.0 Hz), 129.7, 129.1, 128.6, 128.5 (d, *J* = 12.1 Hz), 127.9, 127.8(d, *J* = 12.2 Hz), 127.0, 126.9, 122.3, 121.7, 120.3, 113.5, 21.4, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.8; **HRMS (ESI):** calcd. for $C_{36}H_{29}BrNNaO_3PS^+$ $[M+Na]^+$ : 688.0681; found: 688.0677; **$[\alpha]_D^{20}$** = +98 (c = 0.1, $CHCl_3$).

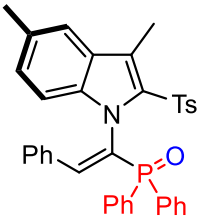
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 90:10, v = 1.0 mL/min, 40 ºC, 254 nm); tr (minor) = 12.84 min, tr (major) = 14.679 min, 4:96 er.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.612 | 8907.6 | 49.99 |
| 2 | 14.948 | 8912.4 | 50.01 |

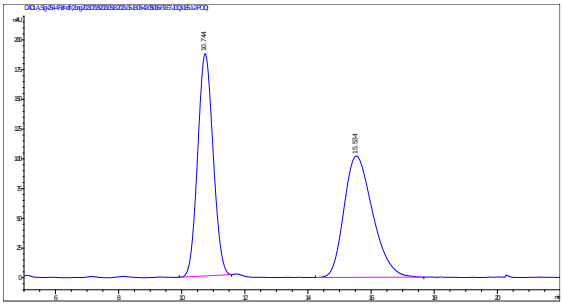
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.84 | 776.3 | 3.84 |
| 2 | 14.679 | 19435 | 96.16 |

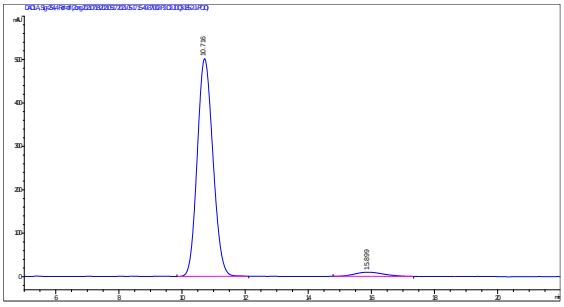



**(*S*,*E*)-(1-(3,5-Dimethyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine oxide (9)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 57.1 mg, 95%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.23 – 8.15 (m, 2H), 7.67 – 7.62 (m, 1H), 7.61 – 7.52 (m, 3H), 7.47 – 7.41 (m, 2H), 7.40 – 7.32 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.14 – 7.07 (m, 2H), 6.90 (t, *J* = 7.6 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 2.42 (d, *J* = 11.7 Hz, 6H), 2.17 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.4, 143.1 (d, *J* = 23.0 Hz), 139.0, 136.0, 134.3 (d, *J* = 112.8 Hz), 133.1 (d, *J* = 9.4 Hz), 132.7 (d, *J* = 13.3 Hz), 132.3 (d, *J* = 3.0 Hz), 132.0 (d, *J* = 10.0 Hz), 131.8 (d, *J* = 2.7 Hz), 131.2, 130.7 (d, *J* = 104.7 Hz), 130.5, 129.9, 129.7 (d, *J* = 102.3 Hz), 129.7, 129.1, 128.8, 128.54, 128.45 (d, *J* = 11.9 Hz), 128.1, 127.8 (d, *J* = 12.0 Hz), 126.9, 121.8, 119.6, 113.2, 21.5, 21.4, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.8; **HRMS (ESI):** calcd. for $C_{37}H_{32}NNaO_3PS^+$ $[M+Na]^+$ : 624.1733; found: 624.1723; **$[\alpha]_D^{20}$** = +62 (c = 0.1, $CHCl_3$).

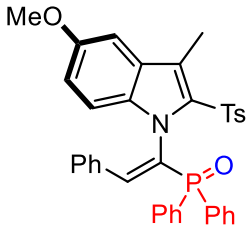
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 10.716 min, tr (minor) = 15.899 min, 96.6:3.4 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.744 | 6336.3 | 49.59 |
| 2 | 15.534 | 6441 | 50.41 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.716 | 17281.2 | 96.59 |
| 2 | 15.899 | 609.6 | 3.41 |

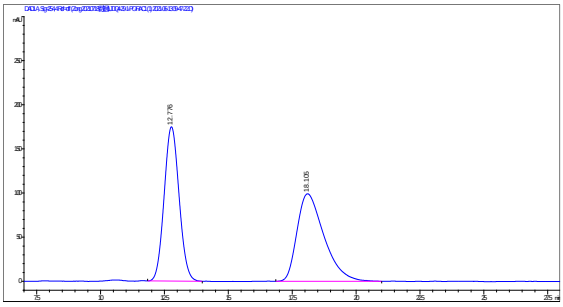



**(*S*,*E*)-(1-(5-Methoxy-3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine oxide (10)**

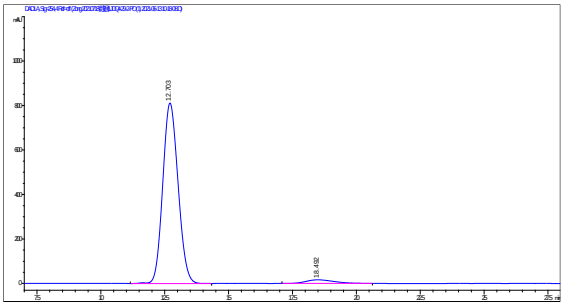
The title compound was isolated as a pale-yellow solid (eluent : petroleum ether/ethyl acetate = 3/1, 53.1 mg, 86%). **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.21 – 8.13 (m, 2H), 7.67-7.61 (m, 1H), 7.60 – 7.51 (m, 3H), 7.48 – 7.41 (m, 2H), 7.40

– 7.34 (m, 1H), 7.33 – 7.26 (m, 3H), 7.23 – 7.17 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.95 – 6.87 (m, 4H), 6.77 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 7.8 Hz, 2H), 3.84 (s, 3H), 2.39 (s, 3H), 2.17 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ155.4, 143.5, 143.2 (d, *J* = 23.0 Hz), 139.0, 134.2 (d, *J* = 113.3 Hz), 133.2 (d, *J* = 9.6 Hz), 132.7, 132.6, 132.5 (d, *J* = 1.7 Hz), 132.1 (d, *J* = 10.0 Hz), 132.0 (d, *J* = 1.8 Hz), 131.1, 130.9, 129.6 (d, *J* = 101.8 Hz), 130.0, 129.9, 129.2, 128.7, 128.5, 128.4, 127.9 (d, *J* = 12.2 Hz), 127.0, 121.6, 118.1, 114.6, 100.7, 55.8, 21.5, 10.1; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 27.8; **HRMS (ESI) :** calcd. for $C_{37}H_{33}NO_4PS^+$ $[M+H]^+$ : 618.1862; found : 618.1852; **$[\alpha]_D^{20}$** = +40 (c = 0.1, $CHCl_3$).

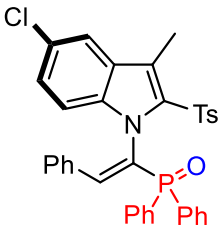
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 12.703 min, tr (minor) = 18.492 min, 96.4:3.6 er.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.776 | 7115.5 | 49.44 |
| 2 | 18.105 | 7277.2 | 50.56 |




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.703 | 33738.3 | 96.42 |
| 2 | 18.492 | 1251.3 | 3.58 |

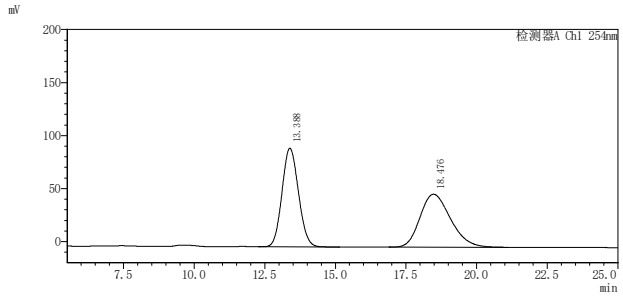


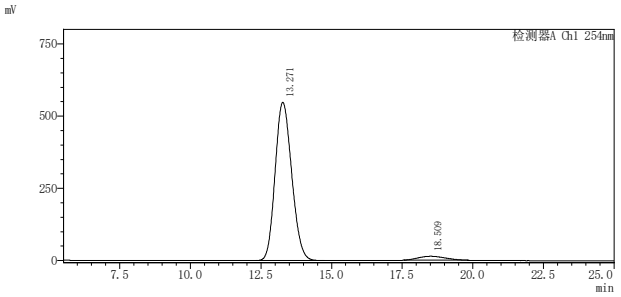

**(*S*,*E*)-(1-(5-Chloro-3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine oxide (11)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 55.3 mg, 89%). **$^{1}$H NMR (600 MHz, $CDCl_3$)** δ 8.24 – 8.16 (m, 2H), 7.69 – 7.64(m, 1H), 7.63 – 7.52 (m, 4H), 7.51 – 7.45 (m, 2H), 7.43 – 7.36 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.19 (m, 3H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.7 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 7.8 Hz, 2H), 2.40 (s, 3H), 2.19 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.8, 143.4 (d, *J* = 22.3 Hz), 138.6, 135.7, 133.7 (d, *J* = 113.4 Hz), 133.0 (d, *J* = 9.6 Hz), 132.5 (d, *J* = 2.1 Hz), 132.4 (d, *J* = 13.1 Hz), 132.1, 132.02, 132.00, 130.6, 130.0, 129.9, 129.8, 129.2, 128.71, 128.66, 128.63, 128.55, 128.0 (d, *J* = 12.2 Hz), 127.5, 127.3, 127.1, 121.3, 119.7, 114.7, 21.4, 9.8; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.9; **HRMS (ESI) :** calcd. for $C_{36}H_{30}ClNO_3PS^+$ $[M+H]^+$ : 622.1367; found :

622.1368; $[\alpha]_D^{20}$ = +38(c = 0.1, $CHCl_3$).

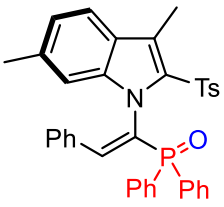
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 13.271 min, tr (minor) = 18.509 min, 96:4 er.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 13.388 | 3781792 | 50.164 |
| 2 | 18.476 | 3757065 | 49.84 |

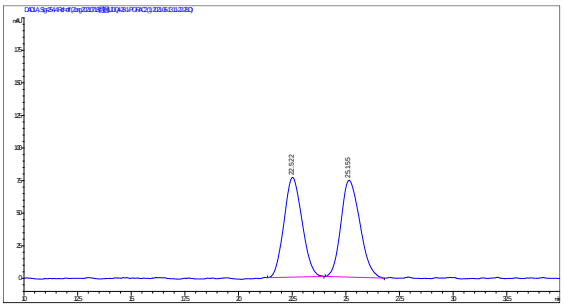
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 13.271 | 22395814 | 96.07 |
| 2 | 18.509 | 917053 | 3.93 |



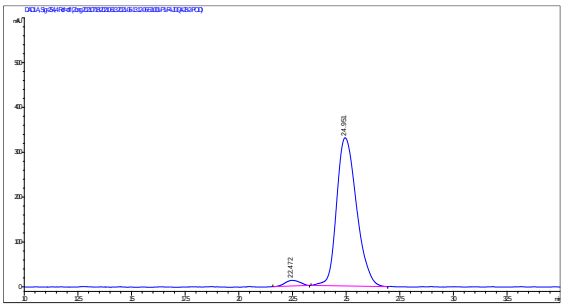

**(*S*,*E*)-(1-(3,6-Dimethyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine oxide (12)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 49.9 mg, 83%). **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.15 – 8.06 (m, 2H), 7.67 – 7.53 (m, 4H), 7.51 – 7.53 (m, 3H), 7.50 – 7.43 (m, 1H), 7.32 – 7.27 (m, 2H), 7.24 – 7.18 (m, 2H), 7.14 – 7.09 (m, 1H), 7.08 (s, 1H), 6.99 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.93 – 6.87 (m, 2H), 6.76 (d, *J* = 8.1 Hz, 2H), 6.69 (d, *J* = 7.4 Hz, 2H), 2.42 (s, 3H), 2.28 (s, 3H), 2.16 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 143.4, 143.2 (d, *J* = 22.5 Hz), 139.0, 137.9, 137.4, 134.0 (d, *J* = 114.3 Hz), 133.2 (d, *J* = 9.6 Hz), 132.7 (d, *J* = 13.4 Hz), 132.5 (d, *J* = 1.7 Hz), 132.1 (d, *J* = 10.2 Hz), 132.0 (d, *J* = 1.7 Hz), 131.5 (d, *J* = 104.6 Hz), 130.1, 130.0, 129.8, 129.1, 129.0, 128.7, 128.5 (d, *J* = 12.0 Hz), 128.0 (d, *J* = 9.6 Hz), 127.0, 125.9, 123.9, 122.5, 120.0, 113.0, 22.1, 21.5, 10.1; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.4; **HRMS (ESI) :** calcd. for $C_{37}H_{32}NNaO_3PS^+$ $[M+Na]^+$ : 624.1733; found : 624.1723; $[\alpha]_D^{20}$ = +118 (c = 0.1, $CHCl_3$).

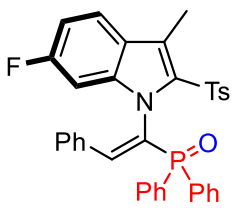
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 80:20, v = 1.0 mL/min, 40 ºC, 254 nm); tr (minor) = 22.472 min, tr (major) = 24.951 min, 3:97 er.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 22.522 | 4495.7 | 49.49 |
| 2 | 25.155 | 4587.6 | 50.51 |



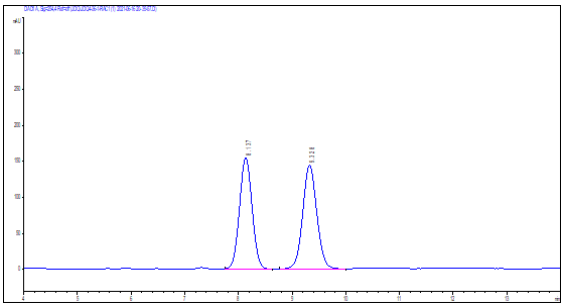
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 22.472 | 607.7 | 2.78 |
| 2 | 24.951 | 21288.5 | 97.23 |

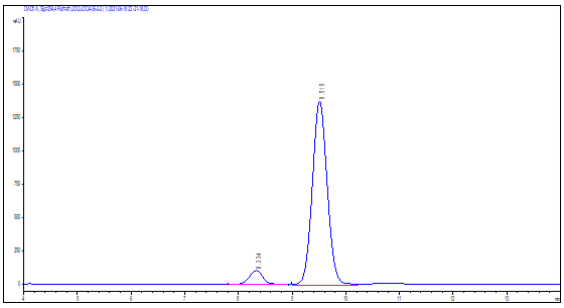



**(*S*,*E*)-(1-(6-Fluoro-3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine oxide (13)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 50.2 mg, 83%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.20 – 8.15 (m, 2H), 7.68 – 7.64 (m, 1H), 7.62 – 7.57 (m, 2H), 7.57 – 7.50 (m, 4H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.27 – 7.23 (m, 2H), 7.17 – 7.13 (m, 1H), 7.02 (dd, *J* = 9.6, 2.2 Hz, 1H), 6.96 – 6.91 (m, 3H), 6.82 (d, *J* = 8.1 Hz, 2H), 6.67 (d, *J* = 7.7 Hz, 2H), 2.44 (s, 3H), 2.20 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 162.5 (d, *J* = 244.1 Hz), 143.7, 143.4 (d, *J* = 22.3 Hz), 138.8, 137.7 (d, *J* = 12.5 Hz), 134.3, 133.1 (d, *J* = 9.3 Hz), 132.6 (d, *J* = 2.2 Hz), 132.4 (d, *J* = 12.8 Hz), 132.3, 132.2, 132.1, 131.3 (d, *J* = 3.9 Hz), 131.1, 130.1, 130.0, 129.7 (d, *J* = 102.1 Hz), 129.3, 128.8, 128.7, 128.6, 128.1 (d, *J* = 12.0 Hz), 127.2, 124.4, 122.4, 121.8 (d, *J* = 10.2 Hz), 111.4 (d, *J* = 25.3 Hz), 99.5 (d, *J* = 27.3 Hz), 21.5, 10.1; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.5; **$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -112.53; **HRMS (ESI) :** calcd. for $C_{36}H_{30}FNO_3PS^+$ $[M+H]^+$ : 606.1663; found : 606.1654; **$[\alpha]_D^{20}$** = +64 (c = 0.1, $CHCl_3$).

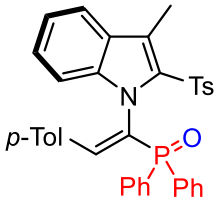
**HPLC analysis** : Daicel Chiralpak AD-H column (hexane:2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (minor) = 8.334 min, tr (major) = 9.515 min, 6:94 er. (The direct hydrosphosphination product **13'** was analyzed).





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.137 | 2519.3 | 48.997 |
| 2 | 9.328 | 2622.4 | 51.003 |

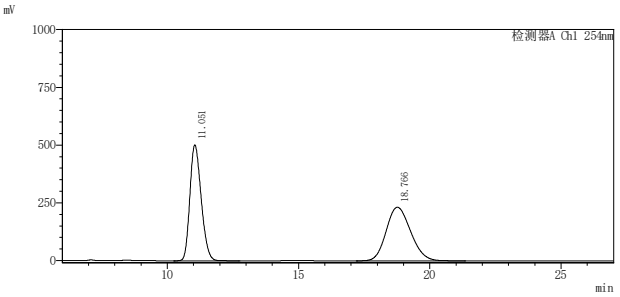
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.334 | 1732.4 | 6.148 |
| 2 | 9.515 | 26447.6 | 93.852 |

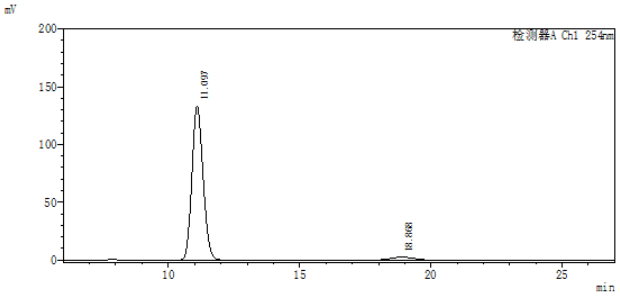



**(*S*,*E*)-(1-(3-Methyl-2-tosyl-1H-indol-1-yl)-2-(*p*-tolyl)vinyl)diphenylphosphine oxide (14)**

The title compound was isolated as pale-yellow oil (eluent: petroleum ether/ethyl acetate = 3/1, 55.9 mg, 93%). **$^{1}$H NMR (600 MHz, $CDCl_3$)** δ 8.23 – 8.17 (m, 2H), 7.66 – 7.63 (m, 1H), 7.60 – 7.56 (m, 3H), 7.53 (d, *J* = 11.9 Hz, 1H), 7.47 – 7.42 (m, 3H), 7.38-7.34 (m, 3H), 7.28 – 7.24 (m, 1H), 7.21-7.16 (m, 3H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H), 2.19 (s, 3H), 2.18 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.4, 143.2 (d, *J* = 22.8 Hz), 140.3, 138.9, 137.5, 133.1 (d, *J* = 9.5 Hz), 132.9 (d, *J* = 115.2 Hz), 132.3 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 10.0 Hz), 131.7 (d, *J* = 2.7 Hz), 130.7 (d, *J* = 105.1 Hz), 130.6, 130.0, 129.94 (d, *J* = 101.6 Hz), 129.90, 129.3, 129.0, 128.5 (d, *J* = 12.0 Hz), 127.80, 127.76 (d, *J* = 11.9 Hz), 127.0, 126.8, 122.2, 121.6, 120.2, 113.5, 21.4, 21.3, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.8; **HRMS (ESI) :** calcd. for $C_{37}H_{33}NO_3PS^+$ $[M+H]^+$ : 602.1913; found : 602.1907; **$[\alpha]_D^{20}$** = +60 (c = 0.1, $CHCl_3$).

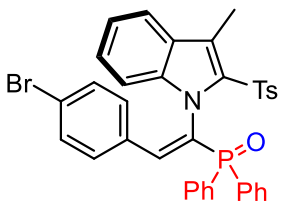
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 11.097 min, tr (minor) = 18.868 min, 96:4 er.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.051 | 15038781 | 50.08 |
| 2 | 18.766 | 14989347 | 49.92 |

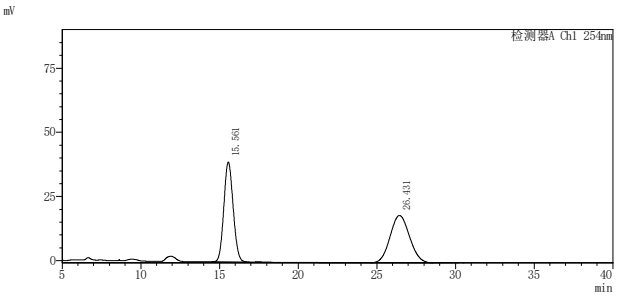
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.097 | 3956677 | 95.99 |
| 2 | 18.868 | 165297 | 4.01 |

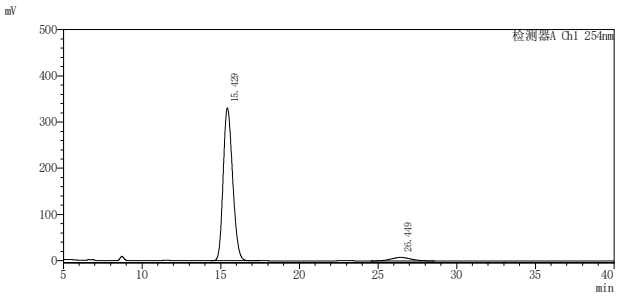



**(*S,E*)-(2-(4-Bromophenyl)-1-(3-methyl-2-tosyl-1H-indol-1-yl)vinyl)diphenylphosphine oxide (15)**

The title compound was isolated as a pale-yellow oil (eluent: petroleum ether/ethyl acetate = 3/1, 50.5 mg, 76%). **$^{1}$H NMR (600 MHz, $CDCl_3$)** δ 8.25 – 8.17 (m, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.62 – 7.56 (m, 3H), 7.50 (d, *J* = 11.7 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.23 – 7.14 (m, 3H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.50 (d, *J* = 8.3 Hz, 2H), 2.49 (s, 3H), 2.26 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 144.0, 141.8 (d, *J* = 22.9 Hz), 138.7, 137.5, 135.3 (d, *J* = 111.3 Hz), 133.1 (d, *J* = 9.7 Hz), 132.5, 132.0, 131.9, 131.7, 131.5 (d, *J* = 13.1 Hz), 131.1, 130.5, 129.5 (d, *J* = 100.1 Hz), 129.2, 129.1, 128.5 (d, *J* = 12.0 Hz), 127.9, 127.8 (d, *J* = 12.0 Hz), 127.1, 126.8, 124.4, 122.7, 121.9, 120.4, 113.4, 21.5, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.8; **HRMS (ESI):** calcd. for $C_{36}H_{30}BrNO_3PS^+$ $[M+H]^+$ : 666.0862; found : 666.0851; **$[\alpha]_D^{20}$** = +78 (c = 0.1, $CHCl_3$).

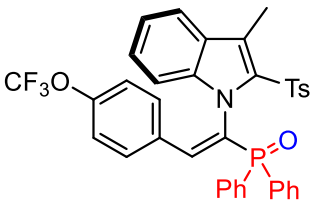
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 15.429 min, tr (minor) = 26.449 min, 95.5:4.5 er.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 15.561 | 1603203 | 50.19 |
| 2 | 26.431 | 1591340 | 49.81 |

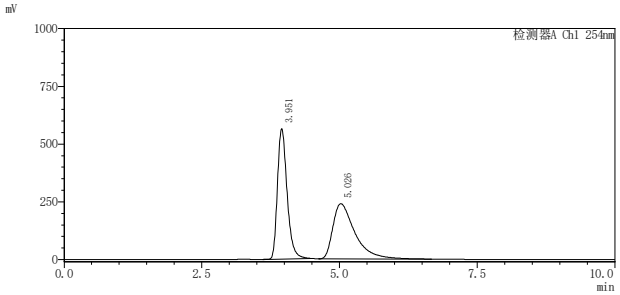
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 15.429 | 13807475 | 95.52 |
| 2 | 26.449 | 647632 | 4.48 |

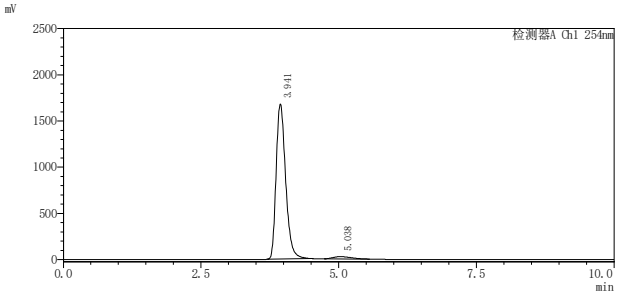


**(*S,E*)-(1-(3-Methyl-2-tosyl-1H-indol-1-yl)-2-(4-(trifluoromethoxy)phenyl)vinyl)diphenylphosphine oxide (16)**

The title compound was isolated as a pale-yellow solid (eluent : petroleum ether/ethyl acetate = 3/1, 50.3 mg, 75%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.22 – 8.16 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.62 – 7.57 (m, 3H), 7.55 (d, *J* = 11.7 Hz, 1H), 7.45 – 7.41 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.23 – 7.16 (m, 3H), 6.84 (d, *J* = 8.1 Hz, 2H), 6.76 – 6.70 (m, 4H), 2.48 (s, 3H), 2.21 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 150.0, 143.9, 141.3 (d, *J* = 22.8 Hz), 138.8, 137.3, 135.3 (d, *J* = 112.3 Hz), 133.1 (d, *J* = 9.4 Hz), 132.5 (d, *J* = 2.8 Hz), 132.03, 131.96, 131.9, 131.5, 131.0 (d, *J* = 13.3 Hz), 130.6, 129.9, 129.8, 129.1, 128.5 (d, *J* = 12.1 Hz), 128.0, 127.8 (d, *J* = 12.1 Hz), 127.1, 126.9, 122.7, 121.9, 120.4, 120.3, 120.2 (d, *J* = 256.8 Hz), 113.3, 21.2, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.8; **$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -57.73; **HRMS (ESI) :** calcd. for $C_{37}H_{30}F_3NO_4PS^+$ $[M+H]^+$ : 672.1580; found : 672.1577; **$[\alpha]_D^{20}$** = +74 (c = 0.1, $CHCl_3$).

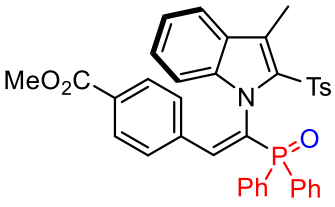
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 95:5, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 3.941 min, tr (minor) = 5.038 min, 97:3 er.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 3.951 | 6879671 | 50.86 |
| 2 | 5.026 | 6648085 | 49.14 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 3.941 | 20207236 | 97.21 |
| 2 | 5.038 | 579750 | 2.79 |

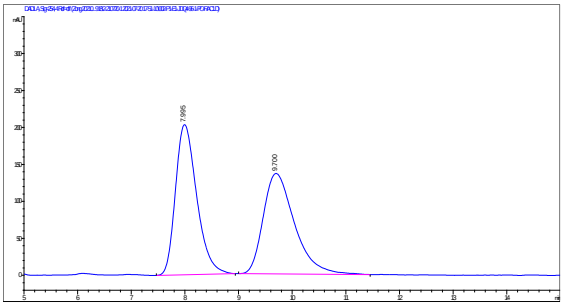


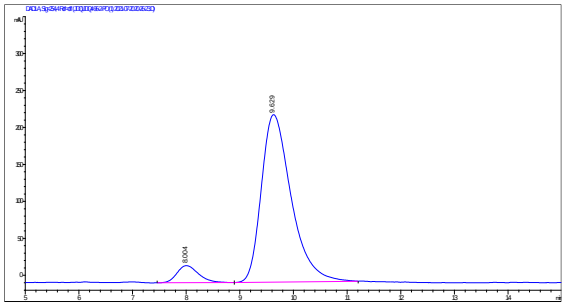
**(*S,E*)-*Methyl (E)*-4-(2-(diphenylphosphoryl)-2-(3-methyl-2-tosyl-1H-indol-1-yl)vinyl)benzoate (17)**

The title compound was isolated as a pale-yellow solid (eluent : petroleum ether/ethyl acetate = 3/1, 54.8 mg, 85%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.24 – 8.18 (m, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.63 – 7.57 (m, 4H), 7.55 – 7.51 (m, 2H), 7.47 – 7.42 (m,

3H), 7.38 (t, $J$ = 7.2 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.24 – 7.17 (m, 3H), 6.77 (d, $J$ = 8.1 Hz, 2H), 6.71 (d, $J$ = 8.3 Hz, 2H), 3.83 (s, 3H), 2.49 (s, 3H), 2.13 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 166.1, 143.7, 141.8 (d, $J$ = 22.8 Hz), 138.8, 137.4, 137.3, 136.7, 136.6, 133.0 (d, $J$ = 9.7 Hz), 132.5 (d, $J$ =2.8 Hz), 132.1, 132.0, 130.7, 130.5, 130.1 (d, $J$ = 105.5 Hz), 129.8, 129.6 (d, $J$ = 2.1 Hz), 129.1, 128.6 (d, $J$ = 12.1 Hz), 127.9, 127.8 (d, $J$ = 12.2 Hz), 127.1, 126.8, 122.8, 121.9, 120.5, 113.3, 52.2, 21.2, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.8; **HRMS (ESI) :** calcd. for $C_{38}H_{33}NO_5PS^+$ $[M+H]^+$ : 646.1812; found : 646.1809; **$[\alpha]_D^{20}$** = 100 (c = 0.1, $CHCl_3$).

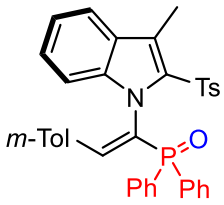
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (minor) = 8.004 min, tr (major) = 9.629 min, 7:93 er.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 7.995 | 5586.6 | 50.35 |
| 2 | 9.7 | 5507.9 | 49.65 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.004 | 645.2 | 6.86 |
| 2 | 9.629 | 8764.6 | 93.14 |

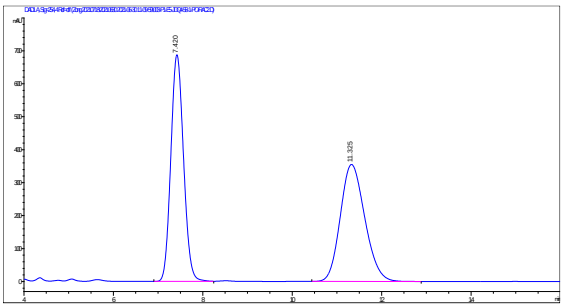


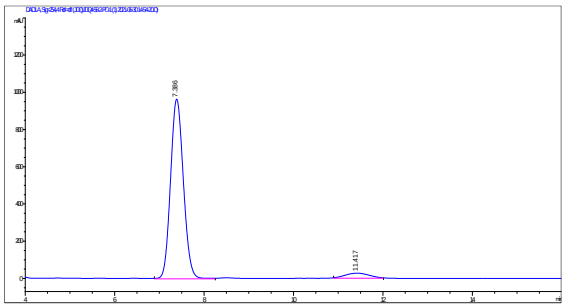

**(*S*,*E*)-(1-(3-Methyl-2-tosyl-1H-indol-1-yl)-2-(*m*-tolyl)vinyl)diphenylphosphine oxide (18)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 55.9 mg, 93%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.21 (dd, $J$ = 11.5, 7.6 Hz, 2H), 7.65 (t, $J$ = 7.5 Hz, 1H), 7.61 – 7.56 (m, 3H), 7.52 (d, $J$ = 12.0 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.37 (t, $J$ = 7.5 Hz, 1H), 7.34 (d, $J$ = 8.0 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.22 – 7.15 (m, 3H), 6.93 (d, $J$ = 7.6 Hz, 1H), 6.80 (d, $J$ = 8.1 Hz, 2H), 6.75 (t, $J$ = 7.7 Hz, 1H), 6.47 (s, 1H), 6.43 (d, $J$ = 7.9 Hz, 1H), 2.46 (s, 3H), 2.19 (s, 3H), 1.96 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.5 (d, $J$ = 22.7 Hz), 143.4, 139.0, 138.0, 137.5, 133.8 (d, $J$ = 114.1 Hz), 133.1 (d, $J$ = 9.7 Hz), 132.5 (d, $J$ = 13.2 Hz), 132.3 (d, $J$ = 2.7 Hz), 132.0 (d, $J$ = 10.0 Hz), 131.8 (d, $J$ = 2.8 Hz), 130.9, 130.598 (d, $J$ = 105.0 Hz), 130.596, 130.56, 130.2, 129.8 (d, $J$ = 102.0 Hz), 128.474 (d, $J$ = 12.1 Hz), 128.465, 127.80 (d, $J$

= 12.1 Hz), 127.78, 127.0, 126.8, 122.2, 121.6, 120.2, 113.5, 21.4, 21.1, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.9; **HRMS (ESI) :** calcd. For $C_{37}H_{33}NO_3PS^+$ $[M+H]^+$ : 602.1913; found : 602.1911; **$[\alpha]_D^{20}$** = +172 (c = 0.1, $CHCl_3$).

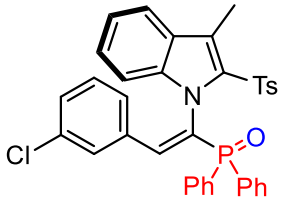
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 7.386 min, tr (minor) = 11.417 min, 95:5 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 7.42 | 13544.1 | 50.08 |
| 2 | 11.325 | 13503 | 49.92 |

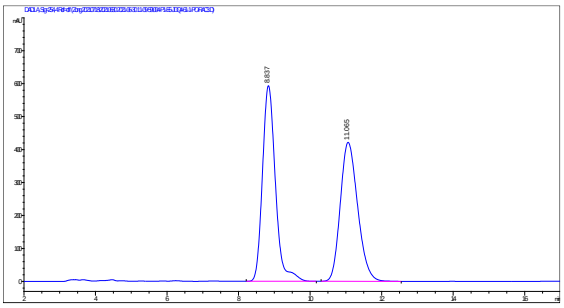
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 7.386 | 19305.1 | 94.82 |
| 2 | 11.417 | 1054.3 | 5.18 |



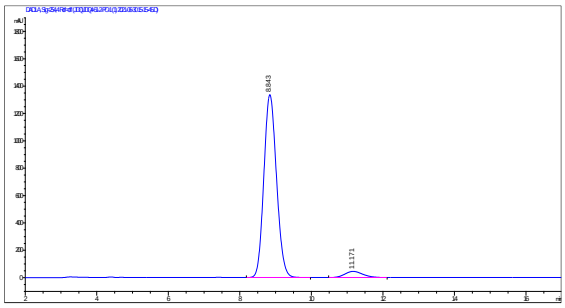

**(*S,E*)-(2-(3-Chlorophenyl)-1-(3-methyl-2-tosyl-1H-indol-1-yl)vinyl)diphenylphosphine oxide (19)**

The title compound was isolated as a pale-yellow solid (eluent : petroleum ether/ethyl acetate = 3/1, 55.3 mg, 89%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.20 (dd, *J* = 11.5, 7.3 Hz, 2H), 7.66 (t, *J* = 7.1 Hz, 1H), 7.63 – 7.57 (m, 3H), 7.48 – 7.41 (m, 4H), 7.40 – 7.33(m, 3H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.23 – 7.17 (m, 3H), 7.05 (d, *J* = 7.1 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 2H), 6.79 (t, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 1.9 Hz, 1H), 6.51 (d, *J* = 7.9 Hz, 1H), 2.49 (s, 3H), 2.20 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.6, 141.6 (d, *J* = 22.9 Hz), 138.7, 137.4, 136.1 (d, *J* = 11.5 Hz), 134.4, 134.2 (d, *J* = 13.4 Hz), 133.0 (d, *J* = 9.6 Hz), 132.5 (d, *J* = 2.8 Hz), 132.04 (d, *J* = 10.2 Hz), 131.96 (d, *J* = 2.7 Hz), 130.5, 130.4, 129.8, 129.7, 129.6, 129.2, 129.1, 128.6 (d, *J* = 12.2 Hz), 127.9, 127.8 (d, *J* = 12.1 Hz), 127.7, 127.1, 126.8, 122.8, 121.9, 120.4, 113.3, 21.4, 9.9; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 27.8; **HRMS (ESI) :** calcd. for $C_{36}H_{30}ClNO_3PS^+$ $[M+H]^+$ : 622.1367; found : 622.1362; **$[\alpha]_D^{20}$** = +72 (c = 0.1, $CHCl_3$).

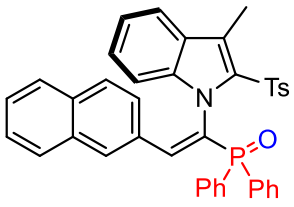
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 8.843 min, tr (minor) = 11.171 min, 95.5:4.5 er.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.837 | 14972 | 51.29 |
| 2 | 11.065 | 14220.2 | 48.71 |



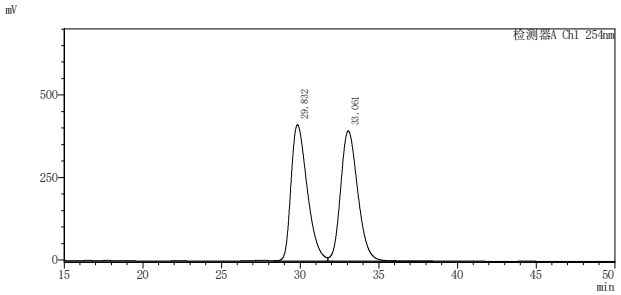
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.843 | 32787.7 | 95.45 |
| 2 | 11.171 | 1564.7 | 4.56 |

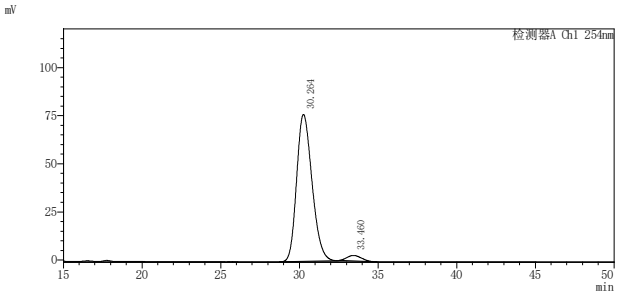



***(S,E)*-(1-(3-Methyl-2-tosyl-1H-indol-1-yl)-2-(naphthalen-2-yl)vinyl)diphenylphosphine oxide (20)**

The title compound was isolated as a pale-yellow oil (eluent: petroleum ether/ethyl acetate = 3/1, 56.7 mg, 89%). **$^{1}$H NMR (600 MHz, $CDCl_3$)** δ 8.29 – 8.24 (m, 2H), 7.72 (d, *J* = 11.8 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.64 – 7.60 (m, 3H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.43 – 7.33 (m, 4H), 7.32 – 7.28 (m, 2H), 7.25 – 7.15 (m, 6H), 6.48 (dd, *J* = 8.8, 1.8 Hz, 1H), 6.42 (d, *J* = 8.1 Hz, 2H), 2.54 (s, 3H), 1.78 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.4, 143.3 (d, *J* = 22.6 Hz), 138.6, 137.8, 134.4 (d, *J* = 113.6 Hz), 133.7, 133.1 (d, *J* = 9.6 Hz), 132.7, 132.4 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 10.1 Hz), 131.8 (d, *J* = 2.8 Hz), 131.2, 130.7, 130.4 (d, *J* = 105.2 Hz), 130.3 (d, *J* = 13.2 Hz), 129.8 (d, *J* = 101.7 Hz), 128.8, 128.7, 128.5 (d, *J* = 12.1 Hz), 128.2, 127.9, 127.8 (d, *J* = 12.1 Hz), 127.4, 127.2, 127.0, 126.7, 126.3, 125.5, 122.5, 121.8, 120.3, 113.6, 21.0, 10.0; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.9; **HRMS (ESI) :** calcd. for $C_{40}H_{33}NO_3PS^+$ $[M+H]^+$ : 638.1913; found : 638.1907; **$[\alpha]_D^{20}$** = +166 (c = 0.1, $CHCl_3$).

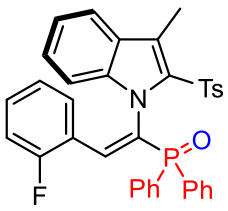
**HPLC analysis**: Daicel Chiralpak IA column (hexane:2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 30.264 min, tr (minor) = 33.460 min, 96.5:3.4 er.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 29.832 | 29624796 | 49.67 |
| 2 | 33.061 | 30016339 | 50.33 |

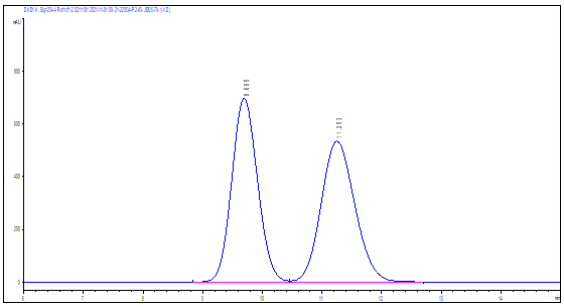
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 30.264 | 5203182 | 96.58 |
| 2 | 33.460 | 184343 | 3.42 |

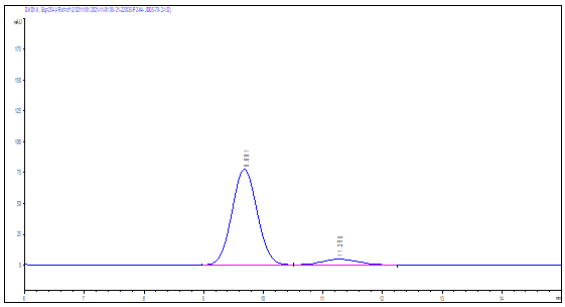



***(S,E)*-(2-(2-Fluorophenyl)-1-(3-methyl-2-tosyl-1H-indol-1-yl)vinyl)(phenyl)phosphine oxide (21)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 43.6 mg, 72%). **$^{1}$H NMR (600 MHz, $CDCl_3$)** δ 8.27 – 8.22 (m, 2H), 7.82 (d, *J* = 12.1 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.62 – 7.56 (m, 3H), 7.51 – 7.46 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.37 (m, 3H), 7.31 – 7.7.27 (m, 1H), 7.23 – 7.18 (m, 3H), 7.13 – 7.08 (m, 1H), 6.98 – 6.93 (m, 1H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.38 (t, *J* = 7.6 Hz, 1H), 6.21 (t, *J* = 7.4 Hz, 1H), 2.42 (s, 3H), 2.20 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 160.9 (d, *J* = 252.0 Hz), 143.5, 139.0, 137.7, 136.0 (d, *J* = 112.3 Hz), 134.5 (d, *J* = 7.0 Hz), 134.4 (d, *J* = 7.1 Hz), 133.1 (d, *J* = 9.5 Hz), 132.5 (d, *J* = 2.9 Hz), 132.2 (d, *J* = 10.3 Hz), 131.9 (d, *J* = 2.8 Hz), 131.4 (d, *J* = 8.7 Hz), 130.6, 130.2 (d, *J* = 105.2 Hz), 129.8 (d, *J* = 101.5 Hz), 129.2, 128.8, 128.5 (d, *J* = 12.1 Hz), 127.9, 127.8 (d, *J* = 13.5 Hz), 127.0, 126.9, 124.2 (d, *J* = 3.6 Hz), 122.6, 121.8, 120.9 (d, *J* = 10.6 Hz), 120.8 (d, *J* = 10.5 Hz), 120.3, 115.4 (d, *J* = 21.9 Hz), 113.4, 21.4, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 28.2; **$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -113.87; **HRMS (ESI) :** calcd. for $C_{36}H_{30}FNO_3PS^+$ $[M+H]^+$ : 606.1663; found : 606.1656; **$[\alpha]_D^{20}$** = +12 (c = 0.1, $CHCl_3$).

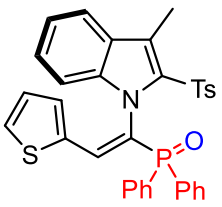
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 9.681 min, tr (minor) = 11.25 min, 92.5:7.5 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.722 | 4508.8 | 49.99 |
| 2 | 11.138 | 4511.4 | 50.01 |

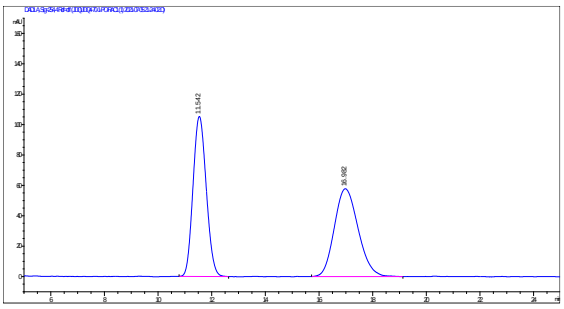
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.681 | 2275.6 | 92.27 |
| 2 | 11.25 | 190.6 | 7.73 |



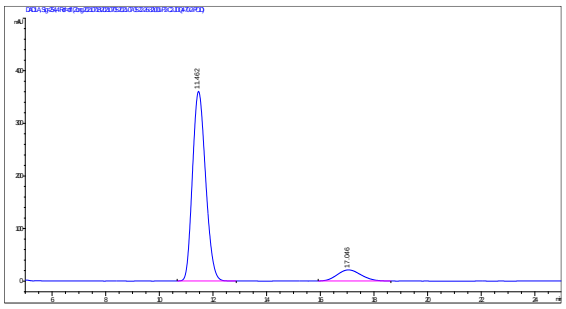
***(S,E)*-(1-(3-Methyl-2-tosyl-1H-indol-1-yl)-2-(thiophen-2-yl)vinyl)diphenylphosphine oxide (22)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 51.6 mg, 87%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.12 (dd, *J* = 11.3, 7.6 Hz, 2H), 7.82 (d, *J* = 10.2 Hz, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.61 – 7.55 (m, 3H), 7.54 – 7.46 (m, 4H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.25 – 7.14 (m, 5H), 6.96 (d, *J* = 3.7 Hz, 1H), 6.90 (d, *J* = 5.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.78 (dd, *J* = 5.0, 3.7 Hz, 1H), 2.53 (s, 3H), 2.22 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.6, 138.7, 136.9, 136.5 (d, *J* = 24.6 Hz), 135.5 (d, *J* = 13.8 Hz), 133.0 (d, *J* = 9.3 Hz), 132.7, 132.4 (d, *J* = 2.6 Hz), 132.5 (d, *J* = 10.1 Hz), 131.9 (d, *J* = 2.5 Hz), 131.0 (d, *J* = 105.6 Hz), 131.2, 130.4, 130.3, 129.5 (d, *J* = 102.9 Hz), 129.0, 128.5 (d, *J* = 12.1 Hz), 128.1, 127.9 (d, *J* = 12.2 Hz), 127.3, 126.7, 126.3, 122.7, 121.6, 120.3, 113.0, 21.4, 10.0; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 26.7; **HRMS (ESI) :** calcd. for $C_{34}H_{29}NO_3PS_2^+$ $[M+H]^+$ : 594.1321; found : 594.1314; **$[\alpha]_D^{20}$** = +42 (c = 0.1, $CHCl_3$).

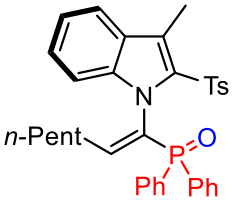
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 11.462 min, tr (minor) = 17.046 min, 90.5:9.5 er.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.542 | 3606.1 | 50.33 |
| 2 | 16.982 | 3559.2 | 49.67 |



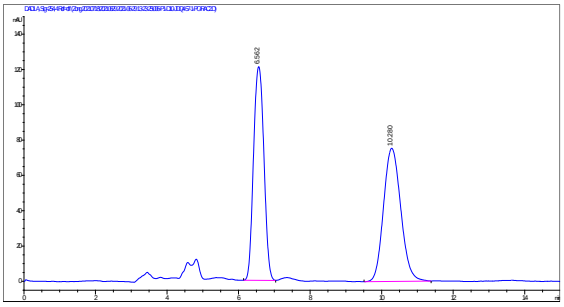
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.462 | 12207.8 | 90.39 |
| 2 | 17.046 | 1298 | 9.61 |

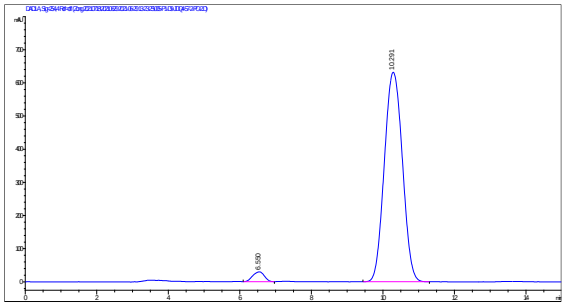


***(S,E)*-(1-(3-Methyl-2-tosyl-1H-indol-1-yl)hept-1-en-1-yl)diphenylphosphine oxide (23)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 52.3 mg, 90%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.16 – 8.08 (m, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 6.8 Hz, 1H), 7.60 – 7.53 (m, 3H), 7.51 – 7.44 (m,

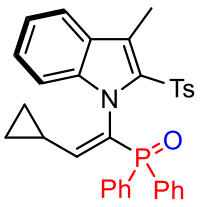
2H), 7.40 (t, $J$ = 7.1 Hz, 1H), 7.30 – 7.12 (m, 7H), 6.80 – 6.71 (m, 1H), 2.35 (s, 3H), 2.35 (s, 3H), 1.78 – 1.60 (m, 2H), 1.35-1.20 (m, 2H), 1.13 – 0.94 (m, 4H), 0.74 (t, $J$ = 7.0 Hz, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 150.0 (d, $J$ = 20.1 Hz), 143.8, 139.9, 138.2, 135.1 (d, $J$ = 116.1 Hz), 133.0 (d, $J$ = 9.5 Hz), 132.3 (d, $J$ = 2.8 Hz), 132.1 (d, $J$ = 101.6 Hz), 131.8 (d, $J$ = 2.7 Hz), 130.7 (d, $J$ = 7.0 Hz), 130.4, 129.6, 129.5, 128.4 (d, $J$ = 12.0 Hz), 127.9 (d, $J$ = 12.1 Hz), 127.2, 127.1, 126.6, 122.0, 121.3, 120.1, 112.9, 31.5, 28.5 (d, $J$ = 9.4 Hz), 27.6, 22.1, 21.5, 13.8, 9.8; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 26.0; **HRMS (ESI) :** calcd. for $C_{35}H_{37}NO_3PS^+$ $[M+H]^+$ : 582.2226; found : 582.2222; **$[\alpha]_D^{20}$** = -60 (c = 0.1, $CHCl_3$). **HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 60:40, v = 1.0 mL/min, 40 °C, 254 nm); tr (minor) = 6.55 min, tr (major) = 10.291 min, 3:97 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 6.562 | 2439.9 | 49.09 |
| 2 | 10.28 | 2530.1 | 50.91 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 6.55 | 661.5 | 2.90 |
| 2 | 10.291 | 22168.3 | 97.10 |

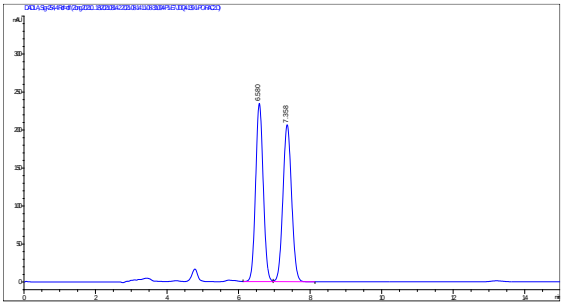


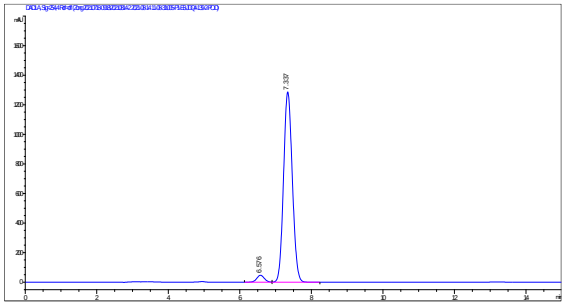

***(S,E)*-(2-Cyclopropyl-1-(3-methyl-2-tosyl-1H-indol-1-yl)vinyl)diphenylphosphine oxide (24)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 50.7 mg, 92%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.16 – 8.10 (m, 2H), 7.73 (d, $J$ = 8.1 Hz, 2H), 7.64 – 7.60 (m, 1H), 7.58 – 7.53 (m, 3H), 7.46 (d, $J$ = 8.4 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.32 (t, $J$ = 7.7 Hz, 1H), 7.22 – 7.15 (m, 5H), 6.13 (t, $J$ = 10.4 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 1.02 – 0.94 (m, 1H), 0.75 – 0.69 (m, 1H), 0.68 – 0.58 (m, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 153.1 (d, $J$ = 21.3 Hz), 143.7, 140.0, 138.3, 133.4 (d, $J$ = 117.9 Hz), 133.1 (d, $J$ = 9.4 Hz), 132.2 (d, $J$ = 2.7 Hz), 131.9 (d, $J$ = 10.0 Hz), 131.7 (d, $J$ = 2.8 Hz), 131.2 (d, $J$ = 106.1 Hz), 130.8, 129.9 (d, $J$ = 103.1 Hz), 129.5, 128.4 (d, $J$ = 12.0 Hz), 127.8 (d, $J$ = 12.1 Hz), 127.3, 127.1, 126.7, 121.8, 121.4, 120.1, 113.2, 21.5, 12.3, 12.2, 9.8, 8.9 (d, $J$ = 1.0 Hz); **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 25.6; **HRMS**

**(ESI) :** calcd. for $C_{33}H_{31}NO_3PS^+$ $[M+H]^+$ : 552.1757; found : 552.1751; $[\alpha]_D^{20}$ = +36 (c = 0.1, $CHCl_3$).

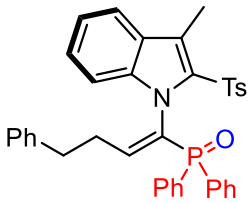
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 60:40, v = 1.0 mL/min, 40 ºC, 254 nm); tr (minor) = 6.576 min, tr (major) = 7.337 min, 3:97 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 6.58 | 3475.1 | 49.93 |
| 2 | 7.358 | 3485.4 | 50.07 |

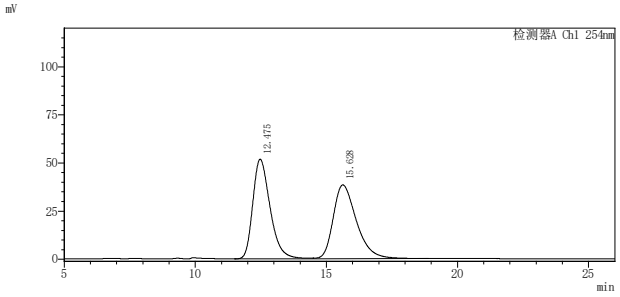
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 6.576 | 686.3 | 3.04 |
| 2 | 7.337 | 21888.1 | 96.96 |

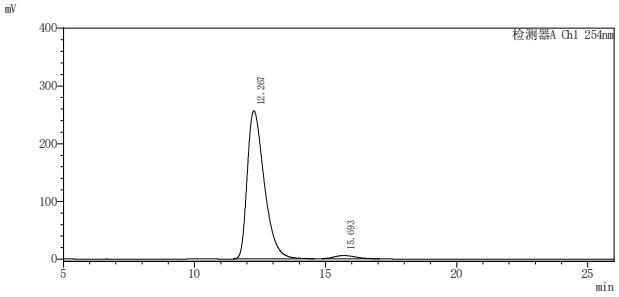



***(S,E)*-(1-(3-Methyl-2-tosyl-1H-indol-1-yl)-4-phenylbut-1-en-1-yl)diphenylphosphine oxide (25)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 49.8 mg, 81%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.01 – 7.96 (M, 2H), 7.76 – 7.72 (m, 2H), 7.61 (t, *J* = 7.0 Hz, 1H), 7.56 – 7.50 (m, 5H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.28-7.23 (m, 2H), 7.19 – 7.09 (m, 7H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.90 – 6.86 (m, 2H), 6.79 – 6.73 (m, 1H), 2.70 – 2.63 (m, 1H), 2.60 – 2.53 (m, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 2.15 – 2.07 (m, 1H), 2.04 – 1.95 (m, 1H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 148.8 (d, *J* = 20.9 Hz), 143.9, 140.2, 139.9, 138.0, 135.6 (d, *J* = 115.5 Hz), 132.9 (d, *J* = 9.6 Hz), 132.3, 132.23, 132.20, 131.9 (d, *J* = 2.7 Hz), 131.4 (d, *J* = 104.7 Hz), 130.6, 130.1 (d, *J* = 102.3 Hz), 129.5, 128.5, 128.4, 128.3, 128.0 (d, *J* = 12.2 Hz), 127.3, 127.2, 126.5, 126.2, 122.0, 121.3, 120.2, 112.7, 33.9, 30.0 (d, *J* = 9.6 Hz), 21.5, 9.8; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 25.6; **HRMS (ESI) :** calcd. for $C_{38}H_{34}NNaO_3PS^+$ $[M+Na]^+$ :638.1889; found : 638.1878; $[\alpha]_D^{20}$ = -50 (c = 0.1, $CHCl_3$).

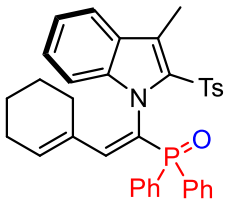
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 90:10, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 12.267 min, tr (minor) = 15.693 min, 97.5:2.5 er.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.475 | 2376291 | 50.21 |
| 2 | 15.628 | 2356258 | 49.79 |

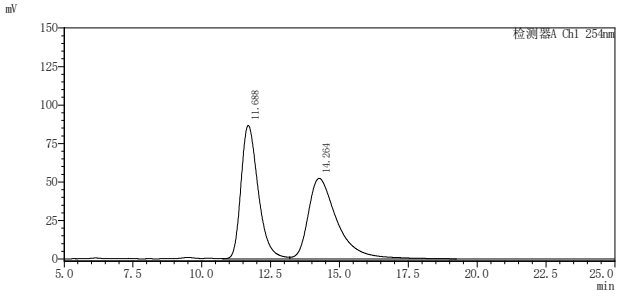
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.267 | 11555524 | 97.33 |
| 2 | 15.693 | 316450 | 2.67 |

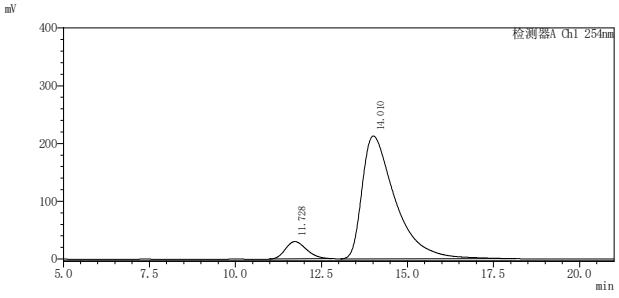



***(S,E)*-(2-(Cyclohex-1-en-1-yl)-1-(3-methyl-2-tosyl-1H-indol-1-yl)vinyl)diphenylphosphine oxide (26)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 37.8 mg, 64%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.06 – 8.01 (m, 2H), 7.84 – 7.80 (m, 2H), 7.63 – 7.58 (m, 1H), 7.55 – 7.46 (m, 5H), 7.40 – 7.36 (m, 1H), 7.24 – 7.18 (m, 6H), 7.14 – 7.10 (m, 1H), 7.07 (d, *J* = 12.3 Hz, 1H), 6.04 – 6.01 (m, 1H), 2.45 – 2.42 (m, 3H), 2.36 (s, 3H), 2.06 – 2.01 (m, 2H), 1.26 – 1.19 (m, 2H), 1.16 – 1.09 (m, 1H), 1.05 – 1.00 (m, 1H), 0.98 – 0.88 (m, 2H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 147.4 (d, *J* = 22.6 Hz), 143.9, 141.1, 139.8, 139.0, 134.4 (d, *J* = 13.6 Hz), 132.9 (d, *J* = 9.4 Hz), 132.14 (d, *J* = 10.3 Hz), 132.07 (d, *J* = 2.8 Hz), 131.7 (d, *J* = 2.7 Hz), 131.5 (d, *J* = 104.2 Hz), 131.6, 130.4 (d, *J* = 101.5 Hz), 129.5, 129.4, 129.1, 128.3 (d, *J* = 12.0 Hz), 127.8 (d, *J* = 12.1 Hz), 127.6, 127.0, 126.5, 121.6 (d, *J* = 0.9 Hz), 121.1, 120.1, 113.3, 26.5, 23.9, 21.8, 21.5, 20.9, 10.0; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.6; **HRMS (ESI):** calcd. for $C_{36}H_{35}NO_3PS^+$ $[M+H]^+$ : 592.2070; found : 592.2062; **$[\alpha]_D^{20}$** = +22 (c = 0.1, $CHCl_3$).

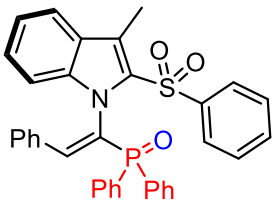
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 90:10, v = 1.0 mL/min, 40 ºC, 254 nm); tr (minor) = 11.728 min, tr (major) = 14.010 min, 8:92 er.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.688 | 3773692 | 49.74 |
| 2 | 14.264 | 3813882 | 50.27 |

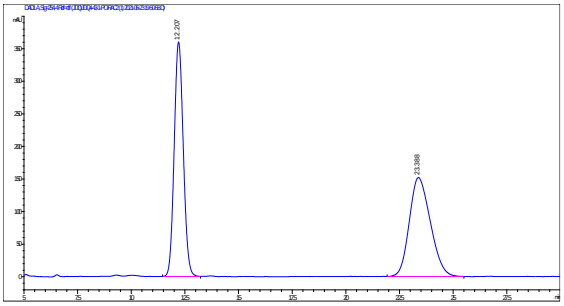
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.728 | 1279533 | 8.23 |
| 2 | 14.010 | 14272453 | 91.77 |

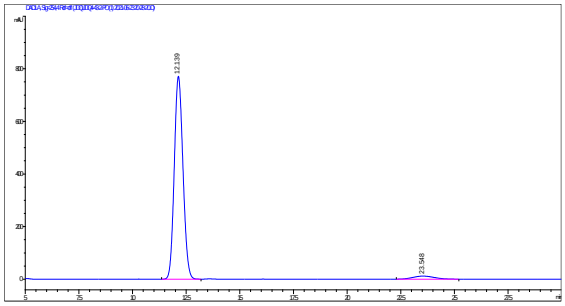


***(S,E)*-(1-(3-Methyl-2-(phenylsulfonyl)-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine oxide (27)**

The title compound was isolated as a white solid (eluent : petroleum ether/ethyl acetate = 3/1, 47.0 mg, 82%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.23 – 8.18 (m, 2H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.62 – 7.56 (m, 4H), 7.48 – 7.43 (m, 5H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.26 – 7.18 (m, 4H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 2H), 6.93 (t, *J* = 7.8 Hz, 2H), 6.74 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.3 (d, *J* = 22.8 Hz), 141.8, 137.7, 134.1 (d, *J* = 113.3 Hz), 133.1 (d, *J* = 9.5 Hz), 132.7, 132.6, 132.4 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 10.2 Hz), 131.9 (d, *J* = 2.7 Hz), 130.5 (d, *J* = 105.0 Hz), 130.4, 130.1, 129.9, 129.4, 128.7, 128.5 (d, *J* = 12.1 Hz), 128.5, 127.871, 127.865 (d, *J* = 12.2 Hz), 127.0, 126.9, 122.6, 121.8, 120.3, 113.5, 9.9; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 27.9; **HRMS (ESI) :** calcd. for $C_{35}H_{28}NNaO_3PS^+$ $[M+Na]^+$ :596.1420; found : 596.1411; **$[\alpha]_D^{20}$** = +88 (c = 0.1, $CHCl_3$).

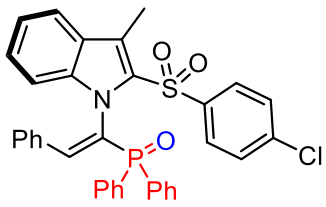
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 60:40, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 12.139 min, tr (minor) = 23.548 min, 96.5:3.5 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.207 | 10588.4 | 50.59 |
| 2 | 23.388 | 10339.7 | 49.41 |

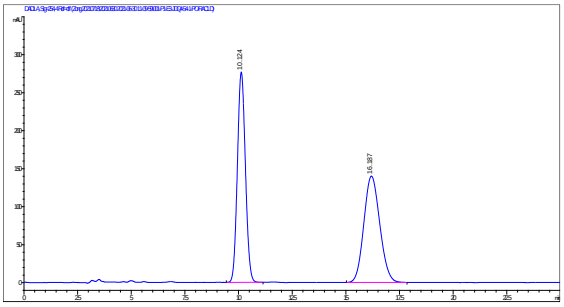
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.139 | 21702.2 | 96.41 |
| 2 | 23.548 | 808 | 3.59 |

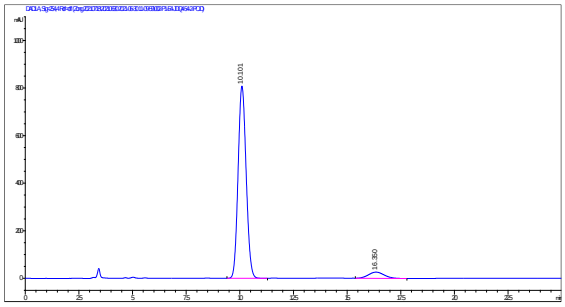


***(S,E)*-(1-(2-((4-Chlorophenyl)sulfonyl)-3-methyl-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine oxide (28)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 54.6 mg, 90%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.15 (dd, *J* = 11.4, 7.4 Hz, 2H), 7.65 (t, *J* = 7.1 Hz, 1H), 7.62 – 7.55 (m, 4H), 7.47 (dd, *J* = 12.1, 7.2 Hz, 2H), 7.43 – 7.36 (m, 4H), 7.28 (t *J* = 7.4 Hz, 1H), 7.24 – 7.16 (m, 4H), 6.98 – 6.91 (m, 4H), 6.69 (d, *J* = 7.8 Hz, 2H), 2.47 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 143.3 (d, *J* = 22.4 Hz), 140.1, 139.2, 137.8, 133.9 (d, *J* = 112.7 Hz), 133.0 (d, *J* = 9.5 Hz), 132.46 (d, *J* = 13.4 Hz), 132.45, 132.1, 132.0, 130.6 (d, *J* = 104.3 Hz), 130.2, 130.1, 129.8, 129.1, 128.7, 128.5 (d, *J* = 12.2 Hz), 128.3, 127.9 (d, *J* = 12.2 Hz), 127.8, 127.2, 123.0, 121.9, 120.5, 113.4, 10.0; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.4; **HRMS (ESI) :** calcd. for $C_{35}H_{28}ClNO_3PS^+$ $[M+H]^+$ : 608.1211; found : 608.1205; **$[\alpha]_D^{20}$** = +96 (c = 0.1, $CHCl_3$).

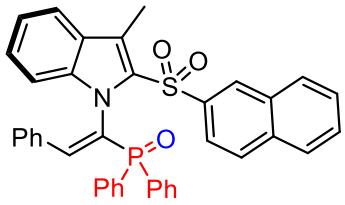
**HPLC analysis** : Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 10.101 min, tr (minor) = 16.35 min, 94:6 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.124 | 7184.5 | 49.87 |
| 2 | 16.187 | 7221.2 | 50.13 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.101 | 21076.4 | 94.11 |
| 2 | 16.35 | 1319.1 | 5.89 |

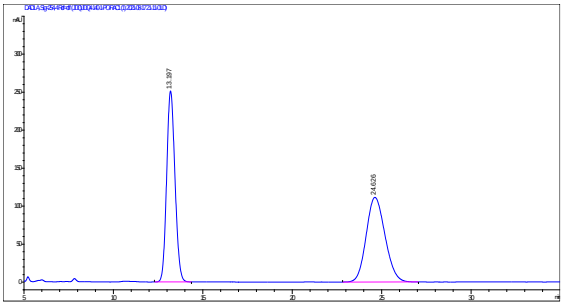


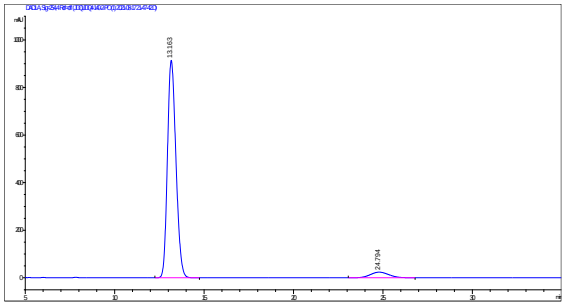
***(S,E)*-(1-(3-Methyl-2-(naphthalen-2-ylsulfonyl)-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine oxide (29)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 51.7 mg, 83%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.21 – 8.15 (m, 2H), 8.06 (s, 1H), 7.68 – 7.64 (m, 2H), 7.63 – 7.58 (m, 4H), 7.52 – 7.47 (m, 5H), 7.43 – 7.37 (m, 4H), 7.27 – 7.17 (m, 4H), 6.75 – 6.71 (m, 1H), 6.65 – 6.58 (m, 4H), 2.54 (s, 3H); **$^{13}$C NMR**

**(150 MHz, $CDCl_3$)** δ 143.3 (d, *J* = 22.6 Hz), 138.5, 137.6, 134.7, 133.9 (d, *J* = 113.3 Hz), 133.1 (d, *J* = 9.4 Hz), 132.4 (d, *J* = 2.8 Hz), 132.2 (d, *J* = 13.1 Hz), 132.0 (d, *J* = 10.0 Hz), 131.9 (d, *J* = 2.7 Hz), 131.6, 130.72 (d, *J* = 104.8 Hz), 130.67 (d, *J* = 102.1 Hz), 130.2, 129.7, 129.6, 129.5, 129.0, 128.74, 128.65, 128.5 (d, *J* = 12.1 Hz), 128.4, 127.89, 127.87 (d, *J* = 12.0 Hz), 127.5, 127.00, 126.95, 122.9, 122.0, 121.8, 120.4, 113.4, 10.0; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.6; **HRMS (ESI):** calcd. for $C_{39}H_{31}NO_3PS^+$ $[M+H]^+$ : 624.1757; found : 624.1751; **$[\alpha]_D^{20}$** = -12(c = 0.1, $CHCl_3$).

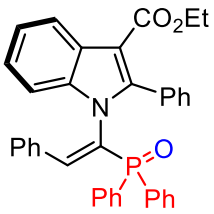
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 60:40, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 13.163 min, tr (minor) = 24.794 min, 94.6:5.4 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 13.197 | 8128.6 | 49.93 |
| 2 | 24.626 | 8151 | 50.07 |

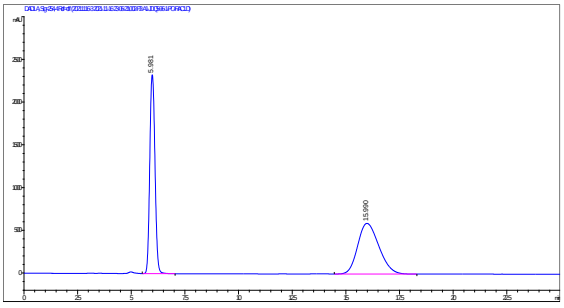
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 13.163 | 30170.8 | 94.63 |
| 2 | 24.794 | 1713.5 | 5.37 |

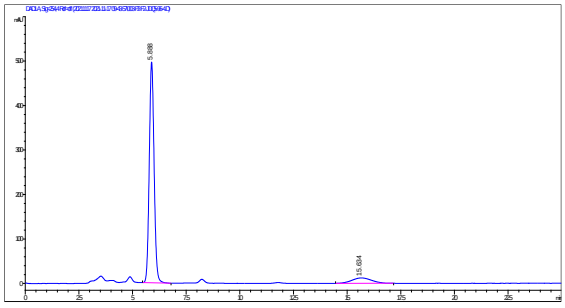



***(S,E)*-Ethyl *(E)*-1-(1-(Diphenylphosphoryl)-2-phenylvinyl)-2-phenyl-1H-indole-3-carboxylate (30)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 38.6 mg, 68%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 11.9 Hz, 1H), 7.51 (t, *J* = 7.0 Hz, 1H), 7.36 – 7.28 (m, 7H), 7.24 – 7.15 (m, 5H), 7.14 – 7.08 (m, 4H), 7.03 – 6.98 (m, 2H), 6.92 (d, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 7.2 Hz, 2H), 4.22 – 4.10 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ166.1, 143.7, 141.9 (d, *J* = 21.7 Hz), 138.8, 137.4, 137.3, 136.7, 136.6, 133.0 (d, *J* = 9.7 Hz), 132.5 (d, *J* =2.8 Hz), 132.1, 132.0, 130.7, 130.5, 130.1 (d, *J* = 105.5 Hz), 129.8, 129.6 (d, *J* = 2.1 Hz), 129.1, 128.6 (d, *J* = 12.1 Hz), 127.9, 127.8 (d, *J* = 12.2 Hz), 127.1, 126.8, 122.8, 121.9, 120.5, 113.3, 52.2, 21.2, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.8; **HRMS (ESI):** calcd. for $C_{37}H_{31}NO_3P^+$ $[M+H]^+$ : 568.2036; found : 568.2034; **$[\alpha]_D^{20}$** = +60 (c = 0.1, $CHCl_3$).

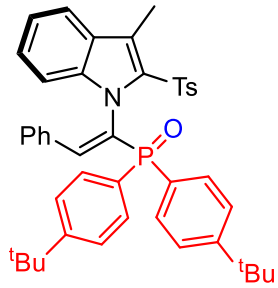
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 5.888 min, tr (minor) = 15.634 min, 91:9 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 5.981 | 39182.6 | 49.11 |
| 2 | 15.99 | 40596.6 | 50.89 |

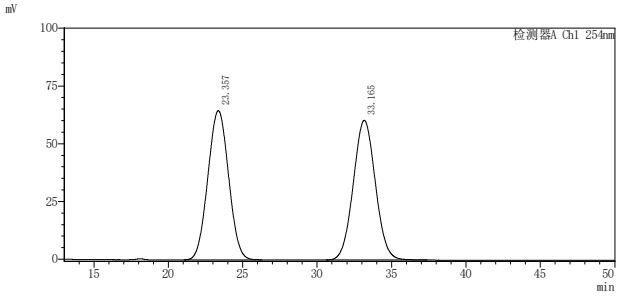
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 5.888 | 7759.9 | 91.02 |
| 2 | 15.634 | 765.9 | 8.98 |



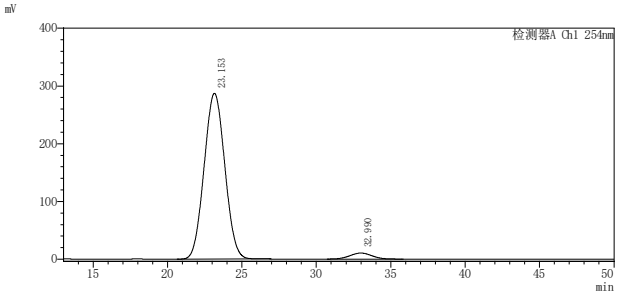

***(S,E)*-Bis(4-(tert-butyl)phenyl)(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)phosphine oxide (31)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 63.6 mg, 91%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.11 (dd, *J* = 11.4, 8.3 Hz, 2H), 7.59 – 7.56 (m, 3H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.33 (m, 5H), 7.26 – 7.22 (m, 1H), 7.21 – 7.16 (m, 3H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.91 (t, *J* = 7.8 Hz, 2H), 6.78 (dd, *J* = 12.1, 8.0 Hz, 4H), 2.43 (s, 3H), 2.19 (s, 3H), 1.39 (s, 9H), 1.25 (s, 9H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 155.7 (d, *J* = 2.8 Hz), 155.2 (d, *J* = 2.7 Hz), 143.3, 142.8 (d, *J* = 22.5 Hz), 139.1, 137.7, 135.6 (d, *J* = 112.2 Hz), 132.9 (d, *J* = 9.7 Hz), 132.8, 131.9 (d, *J* = 10.6 Hz), 130.8, 129.9, 129.6, 129.1, 128.5, 127.9, 127.0 (d, *J* = 107.3 Hz), 126.7 (d, *J* = 104.0 Hz), 127.0, 126.7, 125.4 (d, *J* = 12.3 Hz), 124.7 (d, *J* = 12.3 Hz), 122.1, 121.6, 120.1, 113.6, 35.1, 34.8, 31.2, 31.1, 21.4, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 28.3; **HRMS (ESI) :** calcd. for $C_{44}H_{46}NNaO_3PS^+$ $[M+Na]^+$ : 722.2828; found :722.2825; **$[\alpha]_D^{20}$** = +66 (c = 0.1, $CHCl_3$).

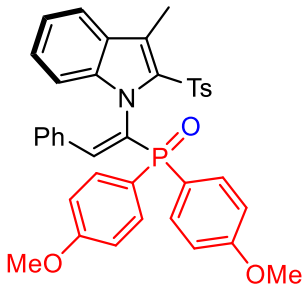
**HPLC analysis**: Daicel Chiralpak IA column (hexane:2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 23.153 min, tr (minor) = 32.990 min, 96.5:3.5 er.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 23.357 | 6258822 | 50.04 |
| 2 | 33.165 | 6247806 | 49.96 |



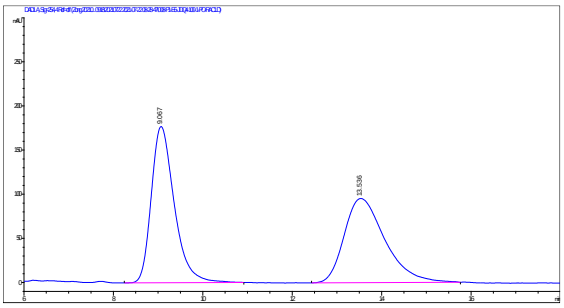

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 23.153 | 27799771 | 96.26 |
| 2 | 32.990 | 1079932 | 3.74 |

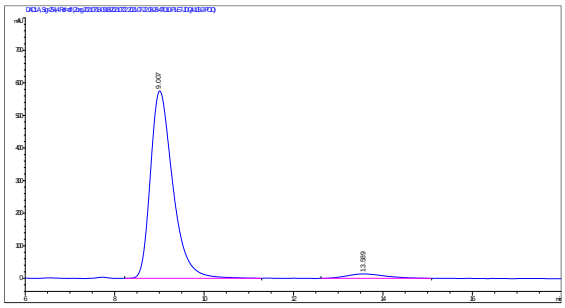



***(S,E)*-Bis(4-methoxyphenyl)(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)phosphine oxide (32)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 53.1 mg, 82%). **$^{1}$H NMR (600 MHz, $CDCl_3$)** δ 8.06 (dd, *J* = 11.4, 7.8 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 11.9 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.37 (dd, *J* = 8.1, 2.7 Hz, 2H), 7.35 – 7.30 (m, 4H), 7.27 – 7.24 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.00 (dd, *J* = 8.2, 2.7 Hz, 2H), 6.90 (t, *J* = 7.8 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 7.8 Hz, 2H), 2.47 (s, 3H), 2.45 (s, 3H), 2.30 (s, 3H), 2.18 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 162.9 (d, *J* = 2.7 Hz), 162.5 (d, *J* = 2.5 Hz), 143.4, 142.6 (d, *J* = 22.6 Hz), 139.0, 137.6, 134.8 (d, *J* = 113.6 Hz), 134.9 (d, *J* = 10.9 Hz), 133.9 (d, *J* = 11.6 Hz), 132.8 (d, *J* = 13.3 Hz), 130.6, 129.8, 129.6, 129.1, 128.5, 127.9, 127.0, 126.8, 122.4, 122.2, 121.6, 121.9 (d, *J* = 108.2 Hz), 120.2, 114.1 (d, *J* = 13.1 Hz), 113.6, 113.4 (d, *J* = 13.1 Hz), 55.4, 55.3, 21.4, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 28.4; **HRMS (ESI) :** calcd. for $C_{38}H_{35}NO_5PS^+$ $[M+H]^+$ : 648.1968; found : 648.1959; **$[\alpha]_D^{20}$** = +68 (c = 0.1, $CHCl_3$).

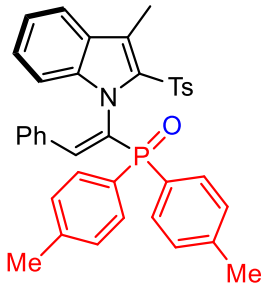
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 80:20, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 9.007 min, tr (minor) = 13.589 min, 96:4 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.067 | 6326.2 | 51.20 |
| 2 | 13.536 | 6030.6 | 48.80 |

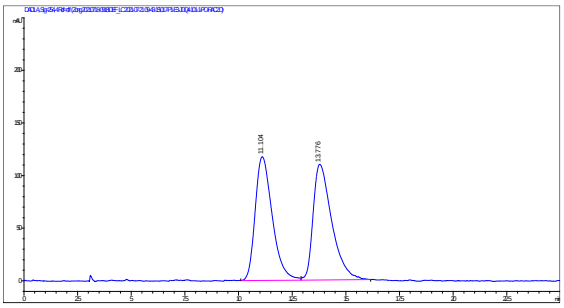
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.007 | 19919.4 | 96.07 |
| 2 | 13.589 | 815.3 | 3.93 |

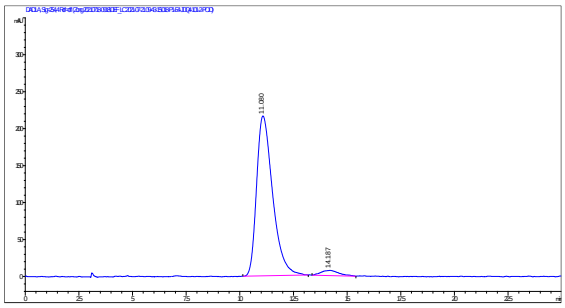



***(S,E)*-(1-(3-Methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)di-*p*-tolylphosphine oxide (33)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 55.4 mg, 90%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.06 (dd, *J* = 11.4, 7.8 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 11.9 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.37 (dd, *J* = 8.1, 2.7 Hz, 2H), 7.35 – 7.30 (m, 4H), 7.27 – 7.24 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.00 (dd, *J* = 8.2, 2.7 Hz, 2H), 6.90 (t, *J* = 7.8 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 7.8 Hz, 2H), 2.47 (s, 3H), 2.45 (s, 3H), 2.30 (s, 3H), 2.18 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.4, 142.9 (d, *J* = 22.6 Hz), 142.7 (d, *J* = 2.8 Hz), 142.2 (d, *J* = 2.6 Hz), 139.0, 137.6, 134.6 (d, *J* = 113.1 Hz), 133.0 (d, *J* = 9.9 Hz), 132.7 (d, *J* = 13.2 Hz), 132.1 (d, *J* = 10.4 Hz), 130.6, 129.9, 129.6, 129.2 (d, *J* = 12.5 Hz), 129.1, 128.5 (d, *J* = 12.6 Hz), 128.5, 127.9, 127.5 (d, *J* = 107.5 Hz), 126.7 (d, *J* = 104.7 Hz), 127.0, 126.8,122.1, 121.6, 120.2, 113.5, 21.7, 21.5, 21.4, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 28.4; **HRMS (ESI) :** calcd. for $C_{38}H_{35}NO_3PS^+$ $[M+H]^+$ : 616.2070; found : 616.2066; **$[\alpha]_D^{20}$** = +82 (c = 0.1, $CHCl_3$).

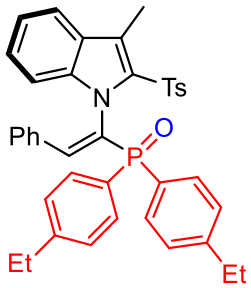
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 90:10, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 11.08 min, tr (minor) = 14.187 min, 96.5:3.5 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.104 | 6515.7 | 49.48 |
| 2 | 13.776 | 6653.1 | 50.52 |

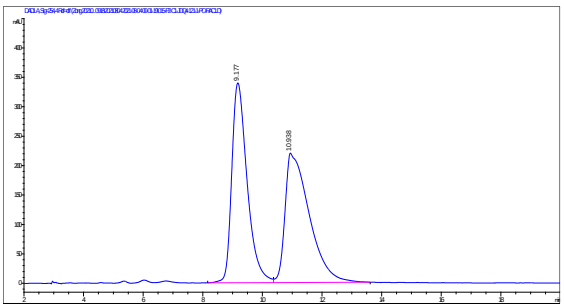
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.08 | 11232.5 | 96.49 |
| 2 | 14.187 | 408.4 | 3.51 |

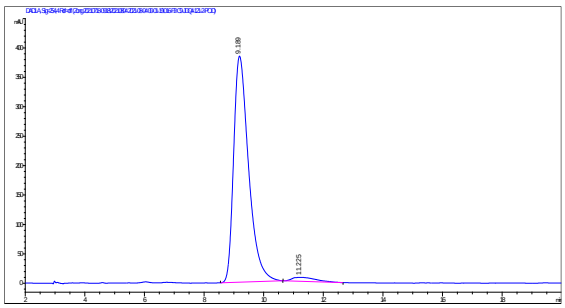



***(S,E)*-Bis(4-ethylphenyl)(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)phosphine oxide (34)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 52.1 mg, 81%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.09 (t, *J* = 9.5 Hz, 2H), 7.56 (dd, *J* = 9.8, 5.3 Hz, 2H), 7.43 – 7.30 (m, 7H), 7.28 – 7.22 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 2H), 6.91 (t, *J* = 7.7 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 7.8 Hz, 2H), 2.81 – 2.74 (m, 2H), 2.62 – 2.55 (m, 2H), 2.44 (s, 3H), 2.19 (s, 3H), 1.32 (t, *J* = 7.6 Hz, 3H), 1.17 (t, *J* = 7.7 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 148.9 (d, *J* = 2.1 Hz), 148.5 (d, *J* = 2.2 Hz), 143.4, 142.8 (d, *J* = 22.5 Hz), 139.0, 137.6, 135.0, 134.2, 133.1 (d, *J* = 9.9 Hz), 132.8 (d, *J* = 13.2 Hz), 132.2 (d, *J* = 10.5 Hz), 130.7, 129.9, 129.6, 129.1, 128.5, 128.0 (d, *J* = 12.3 Hz), 127.93, 127.88, 127.3 (d, *J* = 12.6 Hz), 127.1, 127.0, 126.7, 126.6, 122.1, 121.6, 120.1, 113.6, 29.0 ,28.9, 21.4, 15.4, 15.2, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 28.4; **HRMS (ESI):** calcd. for $C_{40}H_{39}NO_3PS^+$ $[M+H]^+$ : 644.2383; found : 644.2376; **$[\alpha]_D^{20}$** = +44 (c = 0.1, $CHCl_3$).

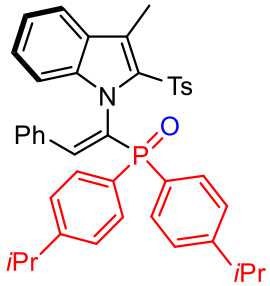
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 90:10, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 9.189 min, tr (minor) = 11.225 min, 97:3 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.177 | 12186.3 | 49.58 |
| 2 | 10.938 | 12391.5 | 50.42 |

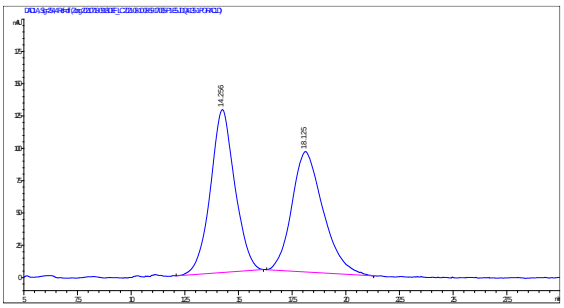
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.189 | 13403.1 | 97.22 |
| 2 | 11.225 | 383.3 | 2.78 |

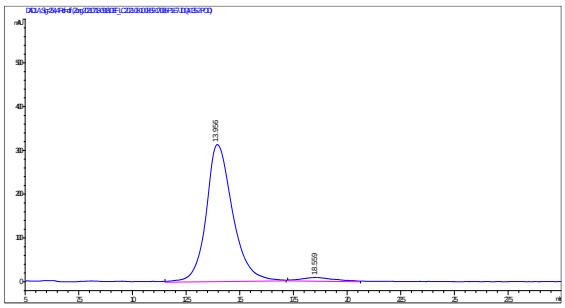



***(S,E)*-Bis(4-isopropylphenyl)(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)phosphine oxide (35)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 52.4 mg, 78%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.10 (dd, *J* = 11.4, 8.0 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.44 – 7.32 (m, 7H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.03 (dd, *J* = 8.2, 2.7 Hz, 2H), 6.91 (t, *J* = 7.8 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.75 (d, *J* = 7.7 Hz, 2H), 3.02 (p, *J* = 6.9 Hz, 1H), 2.87 – 2.80 (m, 1H), 2.43 (s, 3H), 2.19 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H), 1.19 (d, *J* = 1.6 Hz, 3H), 1.18 (d, *J* = 1.7 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 153.4 (d, *J* = 2.7 Hz), 153.0 (d, *J* = 2.8 Hz), 143.3, 142.8 (d, *J* = 22.7 Hz), 139.1, 137.7, 134.7 (d, *J* = 112.1 Hz), 133.1 (d, *J* = 9.9 Hz), 132.9 (d, *J* = 13.1 Hz), 132.2 (d, *J* = 10.5 Hz), 130.8, 129.9, 129.6, 129.1, 128.5, 127.9, 127.2, 127.1 (d, *J* = 103.8 Hz), 127.0,126.7, 126.6, 125.9 (d, *J* = 12.4 Hz), 122.1, 121.6, 120.1, 113.6, 34.2 (d, *J* = 21.9 Hz), 23.80, 23.76, 23.6, 21.4, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 28.3; **HRMS (ESI) :** calcd. for $C_{42}H_{43}NO_3PS^+$ $[M+H]^+$ : 672.2696; found : 672.2687; **$[\alpha]_D^{20}$** = +76 (c = 0.1, $CHCl_3$).

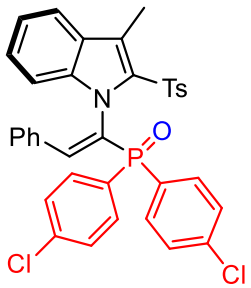
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 95:5, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 13.956 min, tr (minor) = 18.559 min, 96.5:3.5 er.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 14.256 | 9963.5 | 51.30 |
| 2 | 18.125 | 9457.8 | 48.70 |

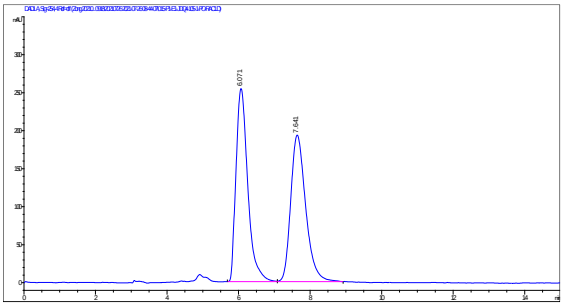
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 13.956 | 26835.2 | 96.64 |
| 2 | 18.559 | 934.5 | 3.37 |



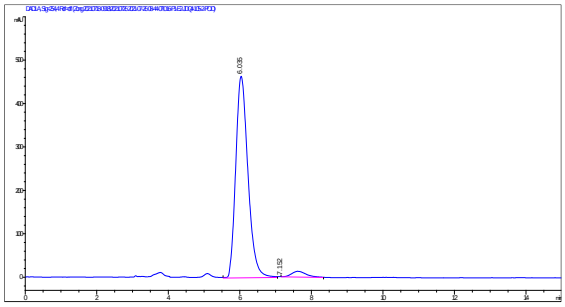

**_(S,E)_-Bis(4-chlorophenyl)(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)phosphine oxide (36)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 40.0 mg, 61%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.25 – 8.18 (m, 2H), 7.62 – 7.57 (m, 3H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 12.2 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.31 – 7.22 (m, 5H), 7.18 – 7.12 (m, 3H), 6.93 (t, *J* = 7.9 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 2H), 6.73 (d, *J* = 7.7 Hz, 2H), 2.45 (s, 3H), 2.20 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.71(d, *J* = 23.4 Hz), 143.68, 139.4 (d, *J* = 3.7 Hz), 138.68, 138.66, 137.7, 134.5 (d, *J* = 10.7 Hz), 134.1 , 133.4, 133.3 (d, *J* = 11.1 Hz), 132.4 (d, *J* = 13.6 Hz), 130.5, 130.02, 129.99, 129.2, 129.1 (d, *J* = 12.7 Hz), 128.64, 128.58, 128.1 (d, *J* = 12.8 Hz), 128.0, 127.88, 127.87, 127.2, 126.9, 122.8, 122.0, 120.4, 113.4, 21.4, 9.8; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.3; **HRMS (ESI) :** calcd. for $C_{36}H_{28}Cl_2NNaO_3PS^+$ $[M+Na]^+$ : 678.0797; found : 678.0800; **$[\alpha]_D^{20}$** = +70(c = 0.1, $CHCl_3$).

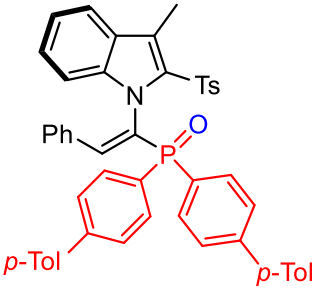
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 80:20, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 6.035 min, tr (minor) = 7.152 min, 96.5:3.5 er.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 6.071 | 5805.3 | 50.90 |
| 2 | 7.641 | 5599.7 | 49.10 |




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 6.035 | 11004.6 | 96.75 |
| 2 | 7.152 | 369.6 | 3.25 |

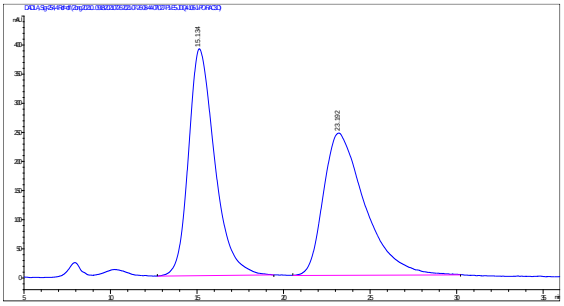



**_(S,E)_-(1-(3-Methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)bis(4'-methyl-[1,1'-biphenyl]-4-yl)phosphine oxide (37)**

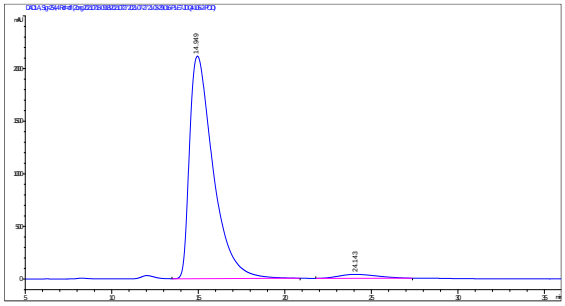
The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 64.5 mg, 84%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.31 (dd, *J* = 11.3, 7.9 Hz, 2H), 7.84 – 7.79 (m, 2H), 7.65 – 7.59 (m, 3H), 7.57 – 7.49 (m, 4H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.41 – 7.38 (m, 2H), 7.31 (t,

$J$ = 8.6 Hz, 5H), 7.25 – 7.22 (m, 2H), 7.19 (t, $J$ = 7.5 Hz, 1H), 7.13 (t, $J$ = 7.4 Hz, 1H), 6.92 (t, $J$ = 7.7 Hz, 2H), 6.78 (d, $J$ = 7.9 Hz, 4H), 2.42 (s, 3H), 2.39 (s, 3H), 2.38 (s, 3H), 2.17 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 145.0 (d, $J$ = 2.9 Hz), 144.6 (d, $J$ = 2.9 Hz), 143.5, 143.3 (d, $J$ = 22.9 Hz), 139.0, 138.1, 137.9, 137.3 (d, $J$ = 28.0 Hz), 134.5 (d, $J$ = 113.4 Hz), 133.6 (d, $J$ = 9.9 Hz), 132.8 (d, $J$ = 13.2 Hz), 132.5 (d, $J$ = 10.4 Hz), 130.7, 130.0, 129.8, 129.7, 129.6, 129.1, 128.6, 128.5 (d, $J$ = 107.0 Hz), 128.1, 127.9, 127.2, 127.1, 127.01, 126.96, 126.95, 126.9, 126.3 (d, $J$ = 12.3 Hz), 122.5, 121.8, 120.3, 113.7, 21.4, 21.21, 21.16, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 28.5; **HRMS (ESI) :** calcd. for $C_{50}H_{43}NO_3PS^+$ $[M+H]^+$ : 768.2696; found : 768.2685; **$[\alpha]_D^{20}$** = +14 (c = 0.1, $CHCl_3$).

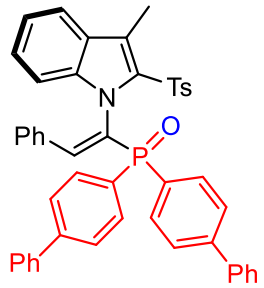
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 14.949 min, tr (minor) = 24.143 min, 97:3 er.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 15.487 | 8160.7 | 49.90 |
| 2 | 23.899 | 8192 | 50.10 |



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 14.949 | 200062.9 | 97.23 |
| 2 | 24.143 | 5705.9 | 2.77 |

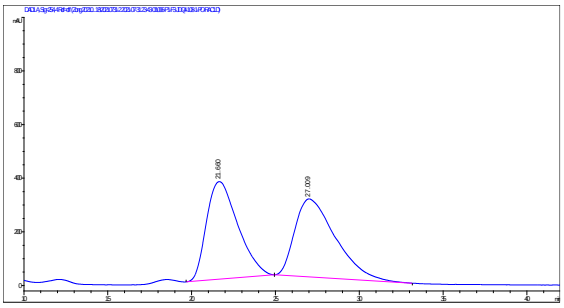


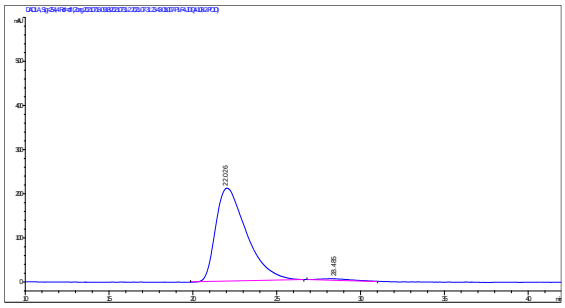

***(S,E)*-Di([1,1'-biphenyl]-4-yl)(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)phosphine oxide (38)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 59.9 mg, 81%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.34 (dd, $J$ = 11.3, 8.0 Hz, 2H), 7.84 (dd, $J$ = 8.3, 2.6 Hz, 2H), 7.73 – 7.69 (m, 2H), 7.63 (d, $J$ = 12.0 Hz, 1H), 7.57 – 7.48 (m, 8H), 7.44 – 7.39 (m, 5H), 7.38 – 7.34 (m, 1H), 7.33 – 7.29 (m, 3H), 7.20 (t, $J$ = 7.5 Hz, 1H), 7.14 (t, $J$ = 7.4 Hz, 1H), 6.93 (t, $J$ = 7.8 Hz, 2H), 6.79 (dd, $J$ = 8.4, 2.6 Hz, 4H), 2.40 (s, 3H), 2.18 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 145.1 (d, $J$ = 2.8 Hz), 144.6 (d, $J$ = 2.8 Hz), 143.5, 143.3 (d, $J$ = 22.7 Hz), 140.2 (d, $J$ = 27.1 Hz), 139.0, 137.9, 134.5 (d, $J$ = 113.2 Hz), 133.6 (d, $J$ = 9.9 Hz), 132.7 (d, $J$ = 13.2 Hz), 132.5 (d, $J$ = 10.4 Hz), 130.7, 130.0, 129.8, 129.3,

129.1, 129.0, 128.9, 128.6, 128.3, 128.2, 128.1, 127.9, 127.4, 127.3, 127.2 (d, $J$ = 12.2 Hz), 127.0, 126.5 (d, $J$ = 12.5 Hz), 122.5, 121.8, 120.3, 113.7, 21.4, 9.9; **$^{31}$P NMR (243 MHz, CDCl$_3$)** δ 28.1; **HRMS (ESI) :** calcd. for $C_{48}H_{39}NO_3PS^+$ $[M+H]^+$ : 740.2383; found :740.2372; **$[\alpha]_D^{20}$** = +26(c = 0.1, $CHCl_3$).

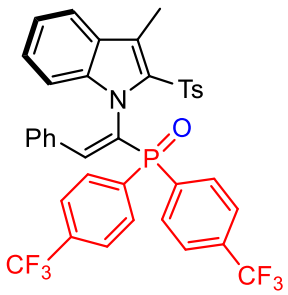
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 90:10, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 22.026 min, tr (minor) = 28.485 min, 98:2 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 21.66 | 47440 | 49.12 |
| 2 | 27.009 | 49133.7 | 50.88 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 22.026 | 26976.6 | 98.22 |
| 2 | 28.485 | 488.6 | 1.78 |

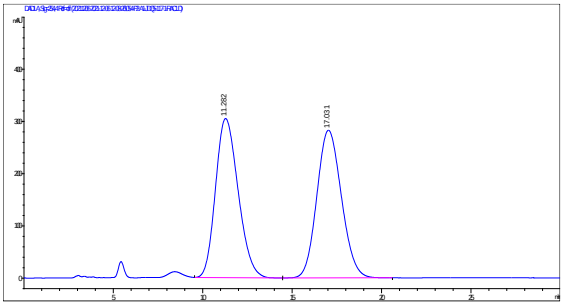


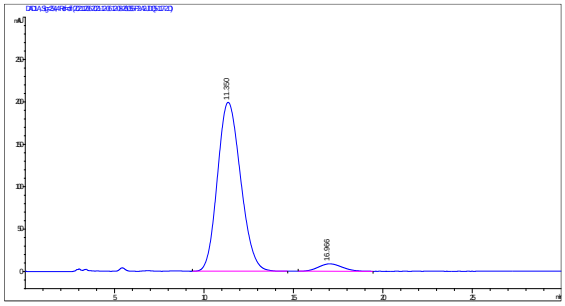

***(S,E)*-(1-(3-Methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (39)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 58.6 mg, 81%). **$^1$H NMR (600 MHz, CDCl$_3$)** δ 8.49 (dd, $J$ = 11.3, 8.0 Hz, 2H), 7.90 (dd, $J$ = 8.4, 2.4 Hz, 2H), 7.60 – 7.52 (m, 3H), 7.52 – 7.48 (m, 2H), 7.42 – 7.37 (m, 3H), 7.27 – 7.23 (m, 3H), 7.21 – 7.16 (m, 1H), 6.98 – 6.93 (m, 2H), 6.83 – 6.78 (m, 4H), 2.40 (s, 3H), 2.20 (s, 3H); **$^{13}$C NMR (150 MHz, CDCl$_3$)** δ 144.4 (d, $J$ = 23.3 Hz), 143.8, 138.5, 137.8, 134.8, 134.6 (d, $J$ = 2.9 Hz), 134.5, 134.3 (d, $J$ = 3.0 Hz), 134.12 (d, $J$ = 2.6 Hz), 134.05 (d, $J$ = 2.4 Hz), 133.9, 133.8, 133.7 (d, $J$ = 10.2 Hz), 133.6, 133.6, 133.41, 133.40, 133.2, 132.8, 132.4 (d, $J$ = 10.4 Hz), 132.3, 132.2, 130.6, 130.3, 130.1, 129.2, 128.7, 128.0, 127.4, 126.8, 126.3 (d, $J$ = 22.0 Hz), 125.63, 125.60, 125.58, 125.55, 125.52, 125.50, 125.47, 124.54, 124.53, 124.51, 124.48, 124.45, 124.42, 124.40, 124.37, 123.1 (d, $J$ = 0.7 Hz), 122.7 (d, $J$ = 21.6 Hz), 122.2, 120.9 (d, $J$ = 21.6 Hz), 120.5, 113.4, 21.4, 9.6; **$^{31}$P NMR (243 MHz, CDCl$_3$)** δ 26.1; **$^{19}$F NMR (376 MHz, CDCl$_3$)** δ -63.02, -63.18; **HRMS (ESI) :** calcd. for $C_{38}H_{28}F_6NNaO_3PS^+$

$[M+Na]^+$ : 746.1324; found :746.1333; $[\alpha]_D^{20}$ = +42 (c = 0.1, $CHCl_3$).

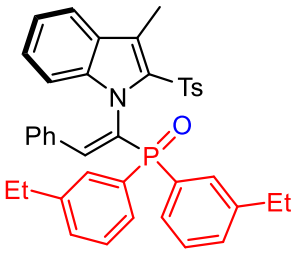
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 11.35 min, tr (minor) = 16.966 min, 95.5:4.5 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.282 | 26767.7 | 49.80 |
| 2 | 17.031 | 26982.2 | 50.20 |

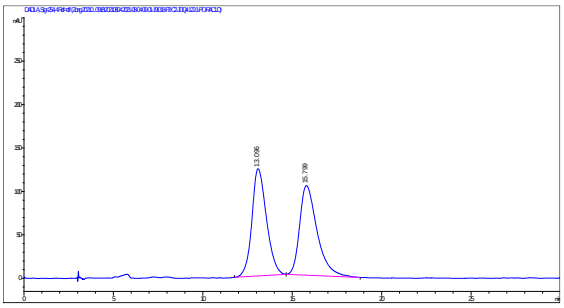
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.35 | 17916.8 | 95.68 |
| 2 | 16.966 | 808.8 | 4.32 |

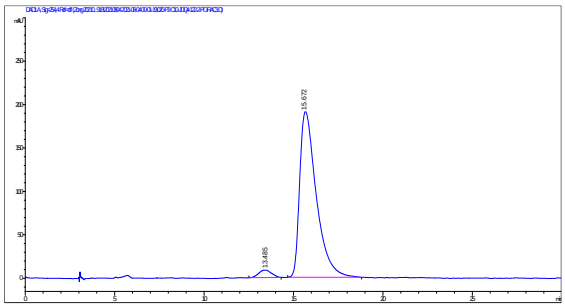



***(S,E)*-Bis(3-ethylphenyl)(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)phosphine oxide (40)**

The title compound was isolated as pale-yellow oil (eluent: petroleum ether/ethyl acetate = 3/1, 55.3 mg, 86%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.11 (dd, *J* = 11.3, 7.6 Hz, 1H), 8.02 (d, *J* = 12.1 Hz, 1H), 7.59 – 7.46 (m, 5H), 7.36 – 7.27 (m, 4H), 7.22 – 7.17 (m, 2H), 7.17 – 7.09 (m, 3H), 6.89 (t, *J* = 7.7 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 7.8 Hz, 2H), 2.77 – 2.70 (m, 2H), 2.44 (s, 3H), 2.42 – 2.35 (m, 2H), 2.17 (s, 3H), 1.28 (t, *J* = 7.6 Hz, 3H), 1.00 (t, *J* = 7.6 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 144.5 (d, *J* = 11.5 Hz), 143.7 (d, *J* = 11.4 Hz), 143.4, 143.1 (d, *J* = 22.7 Hz), 139.0, 137.7, 134.6 (d, *J* = 112.4 Hz), 132.8 (d, *J* = 13.1 Hz), 132.6 (d, *J* = 9.4 Hz), 132.0 (d, *J* = 3.2 Hz), 131.4 (d, *J* = 2.9 Hz), 131.1 (d, *J* = 9.3 Hz), 130.64, 130.57, 130.4 (d, *J* = 9.9 Hz), 130.0, 129.9, 129.8, 129.7, 129.6, 129.3, 129.0, 128.5, 128.4 (d, *J* = 12.9 Hz), 127.8, 127.7 (d, *J* = 13.1 Hz), 126.94, 126.85, 122.1, 121.6, 120.2, 113.6, 28.9, 28.5, 21.4, 15.4, 15.0, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 28.7; **HRMS (ESI) :** calcd. for $C_{40}H_{39}NO_3PS^+$ $[M+H]^+$ : 644,2383; found : 644.2364; $[\alpha]_D^{20}$ = +50 (c = 0.1, $CHCl_3$).

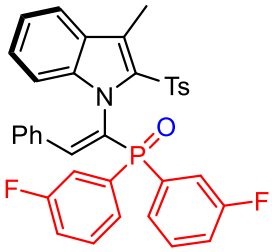
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 95:5, v = 1.0 mL/min, 40 ºC, 254 nm); tr (minor) = 13.485 min, tr (major) = 15.672 min, 3.5:96.5 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 13.096 | 6987.9 | 49.93 |
| 2 | 15.799 | 7006.3 | 50.07 |

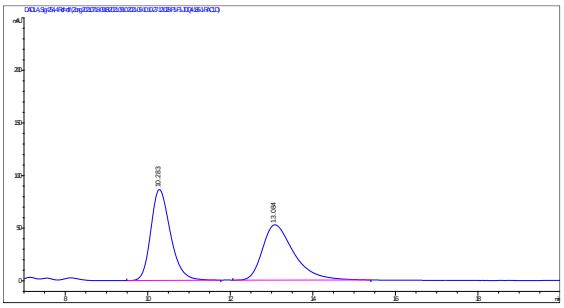
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 13.485 | 426.3 | 3.35 |
| 2 | 15.672 | 12299.4 | 96.65 |



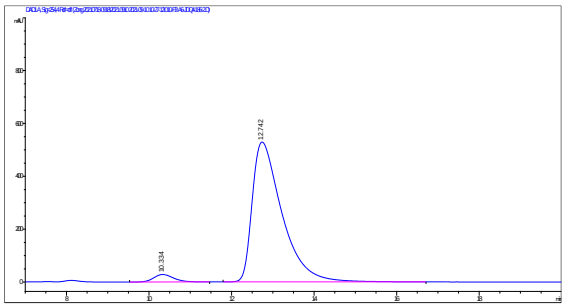

***(S,E)*-Bis(3-fluorophenyl)(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)phosphine oxide (41)**

The title compound was isolated as a white solid (eluent: petroleum ether/ ethyl acetate = 3/1, 52.3 mg, 84%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.04 (dd, *J* = 11.1, 7.6 Hz, 1H), 7.95 – 7.89 (m, 1H), 7.63 – 7.59 (m, 2H), 7.56 (d, *J* = 12.3 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.30 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 7.18 – 7.14 (m, 1H), 7.10 – 7.06 (m, 1H), 7.05 – 6.99 (m, 1H), 6.94 (t, *J* = 7.8 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.75 (d, *J* = 7.8 Hz, 2H), 2.47 (s, 3H), 2.19 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 163.4 (d, *J* = 17.3 Hz), 162.8 (d, *J* = 17.2 Hz), 161.8 (d, *J* = 17.4 Hz), 161.1 (d, *J* = 17.1 Hz), 143. 8 (d, *J* = 23.2 Hz), 143.7, 138.7, 137.5, 133.7, 132.9, 132.4, 132.3, 132.2 (d, *J* = 4.9 Hz), 131.7 (d, *J* = 6.5 Hz), 130.7, 130.6, 130.5 (d, *J* = 7.3 Hz), 130.1, 130.0, 129.8 (d, *J* = 7.2 Hz), 129.7 (d, *J* = 7.5 Hz), 129.2, 128.91 (d, *J* = 3.2 Hz), 128.85 (d, *J* = 3.3 Hz), 128.7, 128.0, 127.73 (d, *J* = 3.3 Hz), 127.67 (d, *J* =3.1 Hz), 127.2, 127.0, 126.9, 122.7, 122.1, 120.5, 120.1, 120.0, 119.92, 119.85, 119.8, 119.2, 119.1 (d, *J* = 2.5 Hz), 118.8 (d, *J* = 10.8 Hz), 118.7 (d, *J* = 10.9 Hz), 113.2, 21.4, 9.8; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 26.8, 26.74, 26.70; **$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -110.53, -110.55, -111.73, -111.74; **HRMS (ESI) :** calcd. for $C_{36}H_{29}F_2NO_3PS^+$ $[M+H]^+$ : 624.1568; found : 624.1564; **$[\alpha]_D^{20}$** = +86 (c = 0.1, $CHCl_3$).

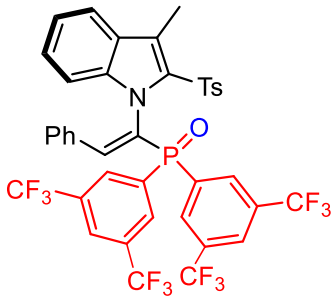
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 90:10, v = 1.0 mL/min, 40 ºC, 254 nm); tr (minor) = 10.334 min, tr (major) = 12.742 min, 3.5:96.5 er.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.283 | 2859.3 | 50.76 |
| 2 | 13.084 | 2773.7 | 49.24 |



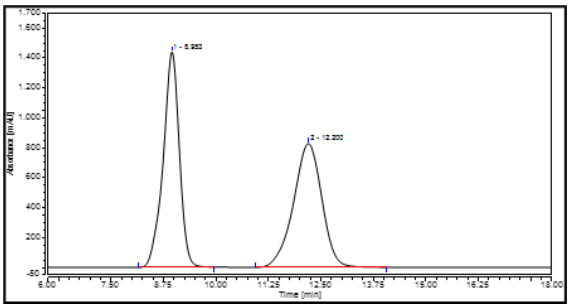
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.334 | 946.6 | 3.45 |
| 2 | 12.742 | 26530.6 | 96.56 |



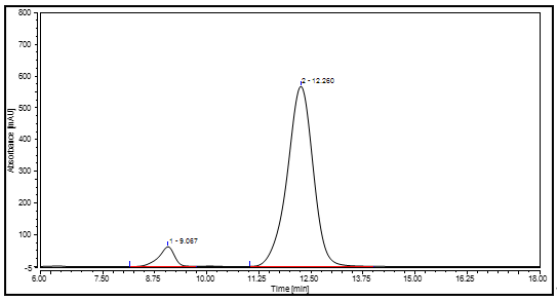

***(S,E)*-Bis(3,5-bis(trifluoromethyl)phenyl)(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)phosphine oxide (42)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 58.4 mg, 68%). **$^{1}$H NMR (600 MHz, $CDCl_3$)** δ 8.81 (d, *J* = 11.4 Hz, 2H), 8.24 (s, 1H), 7.85 (s, 1H), 7.76 (d, *J* = 11.7 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.47 – 7.42 (m, 1H), 7.31 – 7.28 (m, 1H), 7.27 – 7.24 (m, 2H), 7.18 – 7.14 (m, 1H), 6.93 – 6.88 (m, 2H), 6.76 (d, *J* = 8.2 Hz, 2H), 6.66 (d, *J* = 7.7 Hz, 2H), 2.48 (s, 3H), 2.16 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 145.6 (d, *J* = 23.8 Hz), 144.0, 137.8, 137.0, 133.5, 132.9, 132.7, 132.6, 132.44, 132.36, 132.2, 132.13, 132.07, 131.72, 131.66, 131.6, 131.54, 131.46, 131.31, 131.27, 131.2, 130.7, 130.2, 130.1, 129.3, 128.8, 128.0, 127.7, 126.84, 126.79, 126.1, 125.6, 125.2, 123.8, 123.68, 123.67, 123.4, 122.6, 122.0, 121.6, 121.1, 112.6, 21.4, 9.6; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 24.2; **$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -110.53, -110.55, -111.73, -111.74; **HRMS (ESI) :** calcd. for $C_{40}H_{26}F_{12}NNaO_3PS^+$ $[M+Na]^+$ : 882.1072; found : 882.1076; **$[\alpha]_D^{20}$** = +46 (c = 0.1, $CHCl_3$).

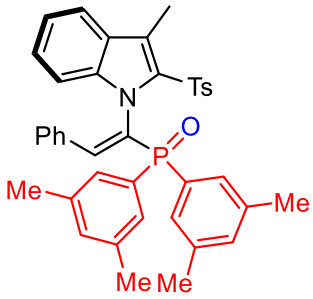
**HPLC analysis**: Daicel Chiralpak IE column (hexane:2-propanol = 95:5, v = 1.0 mL/min, 40 °C, 254 nm); tr (minor) = 9.067 min, tr (major) = 12.260 min, 6.5:93.5 er.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.953 | 642.684 | 49.82 |
| 2 | 12.200 | 647.384 | 50.18 |



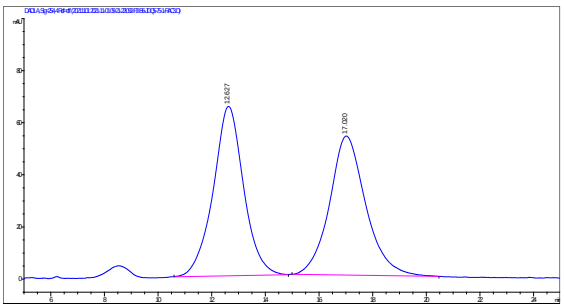
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.067 | 27.744 | 6.36 |
| 2 | 12.260 | 408.424 | 93.64 |

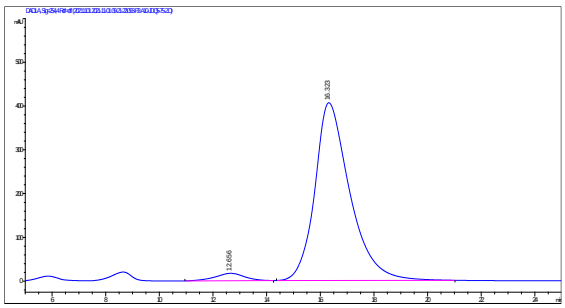



***(S,E)*-Bis(3,5-bis(trifluoromethyl)phenyl)(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)phosphine oxide (43)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 57.3 mg, 89%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 11.8 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.28 – 7.24 (m, 3H), 7.22 – 7.17 (m, 1H), 7.15 – 7.10 (m, 1H), 6.98 – 6.90 (m, 5H), 6.77 (t, *J* = 7.2 Hz, 4H), 2.44 (s, 3H), 2.41 (s, 6H), 2.18 (s, 3H), 2.11 (s, 6H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.3, 142.9 (d, *J* = 24.6 Hz), 139.1, 138.3 (d, *J* = 12.6 Hz), 137.9, 137.4 (d, *J* = 12.7 Hz), 134.8 (d, *J* = 110.9 Hz), 134.0 (d, *J* = 2.9 Hz), 133.3 (d, *J* = 2.8 Hz), 132.9 (d, *J* = 13.0 Hz), 130.9, 130.7 (d, *J* = 9.7 Hz), 130.1 (d, *J* = 104.3 Hz), 129.9, 129.4 (d, *J* = 102.0 Hz), 129.5 (d, *J* = 6.0 Hz), 129.4, 129.0, 128.5, 128.0, 126.9, 126.8, 122.1, 121.6, 120.0, 113.8, 21.5, 21.4, 21.1, 9.8; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 28.6; **HRMS (ESI) :** calcd. for $C_{40}H_{38}NNaO_3PS^+$ $[M+Na]^+$ : 666.2202; found: 666.2196; **$[\alpha]_D^{20}$** = +74 (c = 0.1, $CHCl_3$).

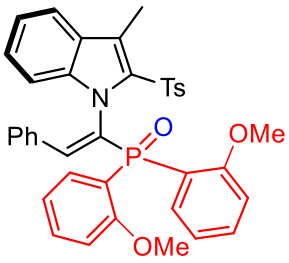
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane:2-propanol = 95:5, v = 1.0 mL/min, 40 °C, 254 nm); tr (minor) = 12.656 min, tr (major) = 16.323 min, 3.5:96.5 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.627 | 5117.8 | 50.48 |
| 2 | 17.02 | 5020 | 49.52 |

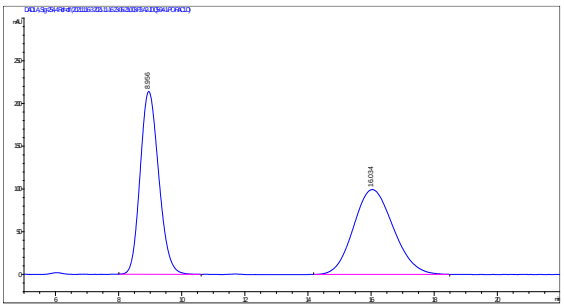
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.656 | 1274.9 | 3.35 |
| 2 | 16.323 | 36762.1 | 96.65 |

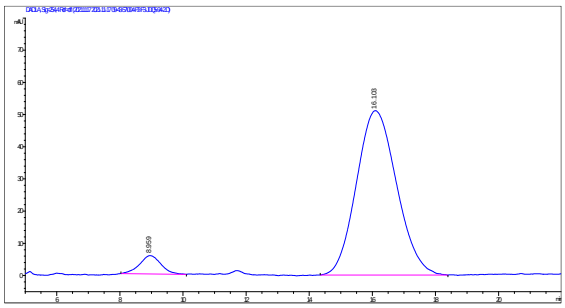



***(S,E)*-Bis(2-methoxyphenyl)(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)phosphine oxide (44)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 23.3 mg, 36%). **$^{1}$H NMR (600 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 12.3 Hz, 1H), 7.79 (dd, *J* = 14.4, 7.7 Hz, 1H), 7.72 (dd, *J* = 14.5, 7.6 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.32 (d, *J* = 7.7 Hz, 3H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.97 – 6.91 (m, 3H), 6.90 – 6.84 (m, 4H), 6.78 – 6.73 (m, 3H), 6.69 – 6.64 (m, 1H), 6.54 (d, *J* = 7.8 Hz, 2H), 3.48 (s, 3H), 3.24 (s, 3H), 2.42 (s, 3H), 2.11 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 161.6 (d, *J* = 2.8 Hz), 160.9 (d, *J* = 3.1 Hz),145.2 (d, *J* = 22.7 Hz), 143.1, 139.3, 138.0, 135.5 (d, *J* = 7.5 Hz), 134.9 (d, *J* = 8.6 Hz), 133.7 (d, *J* = 11.4 Hz), 133.3 (d, *J* = 13.6 Hz), 131.3 , 131.2, 130.5, 129.7, 129.3, 128.9, 128.5, 127.42, 127.37, 125.7, 120.9 (d, *J* = 1.1 Hz), 120.8, 120.6 (d, *J* = 12.2 Hz), 120.4 (d, *J* = 12.1 Hz), 119.7 (d, *J* = 105.1 Hz), 119.7, 112.7, 110.8 (d, *J* = 6.5 Hz), 110.3 (d, *J* = 6.7 Hz), 55.3, 54.8, 21.4, 10.1; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 23.8; **HRMS (ESI) :** calcd. for $C_{38}H_{35}NO_5PS^+$ $[M+H]^+$ : 648.1968; found : 648.1959; **$[\alpha]_D^{20}$** = +40 (c = 0.1, $CHCl_3$).

**HPLC analysis** : Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 ºC, 254 nm); tr (minor) = 8.959 min, tr (major) = 16.103 min, 5.5:94.5 er.

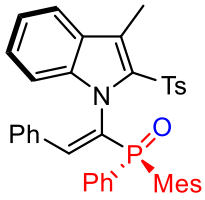




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.956 | 8736.6 | 50.10 |
| 2 | 16.034 | 8702.3 | 49.90 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.959 | 268 | 5.60 |
| 2 | 16.103 | 4515.1 | 94.40 |

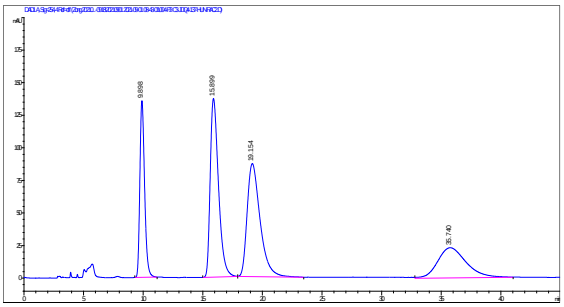
**Two regiomers (d.r. determined by crude NMR) (45-54)**



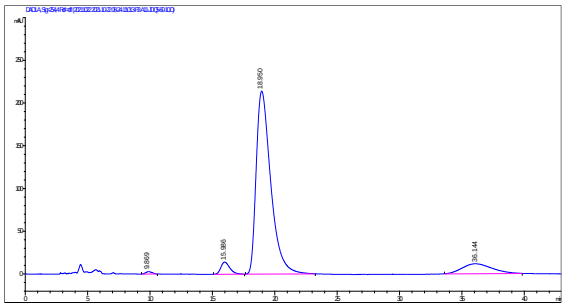

***(S,S,E)*-Mesityl(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)(phenyl)phosphine oxide (45)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 44.7 mg, 71%). **$^{1}$H NMR (600 MHz, $CDCl_3$)** δ 7.96 – 7.91 (m, 2H), 7.70 – 7.64 (m, 3H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.48 – 7.44 (m, 2H), 7.22 – 7.18 (m, 1H), 7.07 – 7.02 (m, 3H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.9 – 6.88 (m, 1H), 6.87 – 6.82 (m, 4H), 6.69 (d, *J* = 8.5 Hz, 1H), 2.46 (s, 3H), 2.31 (s, 3H), 2.24 (s, 3H), 2.22 (s, 6H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 144.9 (d, *J* = 10.4 Hz), 143.3, 142.1 (d, *J* = 22.1 Hz), 141.9 (d, *J* = 2.6 Hz), 139.9, 137.3, 134.9 (d, *J* = 100.9 Hz), 132.7 (d, *J* = 13.0 Hz), 132.4, 132.1, 131.7 (d, *J* = 2.7 Hz), 131.44 (d, *J* = 10.7 Hz), 131.40 (d, *J* = 11.6 Hz), 130.0, 129.8, 129.1, 128.8, 128.7, 128.0, 127.6, 125.7, 122.2 (d, *J* = 99.2 Hz), 121.2, 121.1, 120.0, 112.4, 23.99, 23.97, 21.5, 21.1, 10.1; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 30.1; **HRMS (ESI) :** calcd. for $C_{39}H_{36}NNaO_3PS^+$ $[M+Na]^+$ : 652.2046; found : 610.2036; **$[\alpha]_D^{20}$** = +76 (c = 0.1, $CHCl_3$).

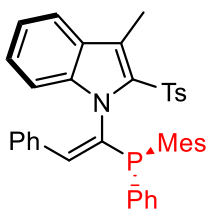
**HPLC analysis**: Daicel Chiralpak OX-3 column (hexane:2-propanol = 70:30, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 18.95 min, tr (minor) = 15.986 min, 96:4 er. tr (major) = 36.144 min, tr (minor) = 9.869 min, 95:5 er. 8.5:1 d.r. determined by crude NMR.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.898 | 3738.8 | 18.00 |
| 2 | 15.899 | 6599.6 | 31.77 |
| 3 | 19.154 | 6546 | 31.51 |
| 4 | 35.74 | 3890.9 | 18.73 |

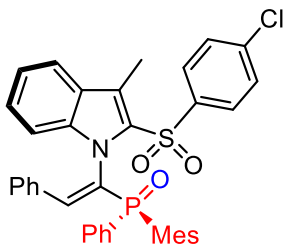


| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.869 | 102 | 0.51 |
| 2 | 15.986 | 718.5 | 3.57 |
| 3 | 18.95 | 17348.3 | 86.13 |
| 4 | 36.144 | 1972.7 | 9.79 |




***(S,S,E)*-1-(1-(Mesityl(phenyl)phosphaneyl)-2-phenylvinyl)-3-methyl-2-tosyl-1H-indole (45')**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 10/1, 44.0 mg, 70%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.62 (t, *J* = 6.8 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.10 – 7.05 (d, *J* = 7.1 (m, 1H), 6.99 – 6.90 (m, 6H), 6.84 – 6.80 (m, 2H), 6.76 – 6.71 (m, 1H), 6.66 – 6.62 (m, 1H), 6.46 (d, *J* = 8.4 Hz, 1H), 2.66 (s, 3H), 2.23 (s, 3H), 2.30 – 2.05 (m, 12H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 146.5, 146.4, 143.4, 143.3, 140.9, 140.3, 140.0, 137.9, 137.7, 137.1, 137.0, 135.9, 135.8, 135.6, 135.5, 135.4, 134.7, 134.3, 134.23, 134.17, 131.2, 130.9, 130.8, 130.5, 130.4, 130.23, 130.20, 129.7, 129.5, 129.2, 129.1, 128.8, 128.7, 128.6, 128.53, 128.51, 128.34, 128.29, 128.2, 127.9, 127.64, 127.62, 127.59, 127.5, 127.38, 127.36, 127.2, 127.124, 127.119, 126.6, 126.5, 125.72, 125.65, 125.5, 123.3, 122.8, 121.2, 120.8, 120.5, 119.9, 113.0, 112.0, 24.5, 24.4, 23.7, 23.5, 21.5, 21.3, 21.0, 10.7, 10.3; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ -7.27, -8.93; **HRMS (ESI) :** calcd. for $C_{39}H_{37}NO_2PS^+$ $[M+H]^+$ : 614.2277; found : 614.2270; **$[\alpha]_D^{20}$** = 86 (c = 0.1, $CHCl_3$).

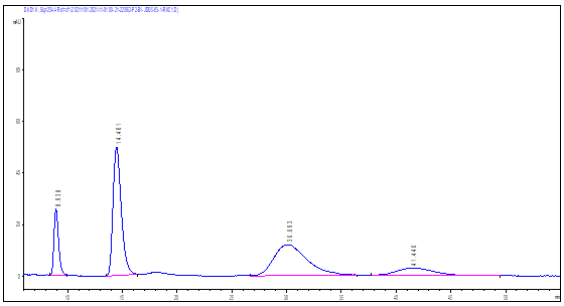


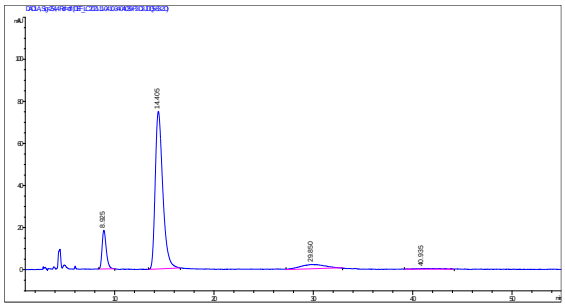

***(S,S,E)*-(1-(2-((4-Chlorophenyl)sulfonyl)-3-methyl-1H-indol-1-yl)-2-phenylvinyl)(mesityl)(phenyl)phosphine oxide (46)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 50.6 mg, 78%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.99 – 7.94 (m, 2H), 7.81 – 7.78 (m, 2H), 7.64 (d, *J* = 11.6 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.51 – 7.46 (m, 2H), 7.25 – 7.22 (m, 1H), 7.16 – 7.13 (m, 2H), 7.10 – 7.04 (m, 3H), 6.86 – 6.82 (m, 1H), 6.85 – 6.82 (m, 4H), 6.61 (d, *J* = 8.5 Hz, 1H), 2.46 (s, 3H), 2.32 (s, 3H), 2.22 (s, 6H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 144.8 (d, *J* = 10.8 Hz), 143.0, 142.9, 142.0, 141.2, 139.0, 137.5, 134.6 (d, *J* = 100.9 Hz), 132.6 (d, *J* = 12.8 Hz), 131.8, 131.4 (d, *J* = 110.8 Hz), 131.6, 131.54, 131.47, 130.1, 129.8, 129.2, 128.9, 128.8 (d, *J* = 10.7 Hz), 127.8, 125.9, 121.7, 121.2, 120.1, 112.3, 23.97, 23.95, 21.1, 10.1; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 29.8; **HRMS (ESI) :** calcd. for $C_{38}H_{34}ClNO_3PS^+$ $[M+H]^+$ : 650.1680 found : 610.1674; **$[\alpha]_D^{20}$** = +70 (c = 0.1, $CHCl_3$).

**HPLC analysis**: Daicel Chiralpak OX-3 column (hexane:2-propanol = 70:30, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 14.405 min, tr (minor) = 29.85 min, 92:8 er. tr (major) = 8.925 min, tr (minor) =

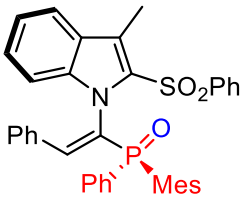
40.935 min, 91:9 er. 6.5:1 d.r. determined by crude NMR.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.938 | 748.6 | 11.39 |
| 2 | 14.461 | 2622.7 | 39.90 |
| 3 | 30.093 | 2521.2 | 38.35 |
| 4 | 41.44 | 682.3 | 10.38 |

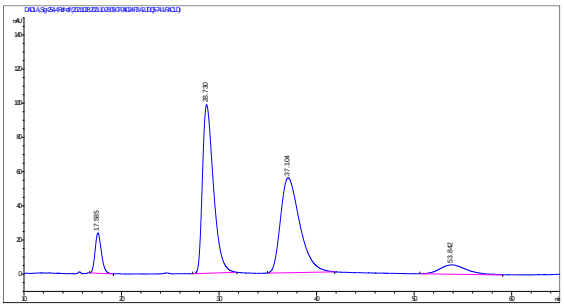
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.925 | 535 | 10.96 |
| 2 | 14.405 | 3951.3 | 80.94 |
| 3 | 29.85 | 344.5 | 7.06 |
| 4 | 40.935 | 51.3 | 1.05 |

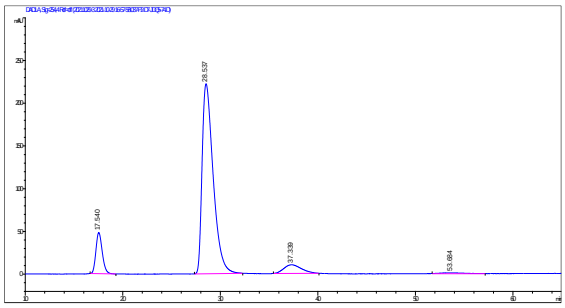



***(S,S,E)*-Mesityl(1-(3-methyl-2-(phenylsulfonyl)-1H-indol-1-yl)-2-phenylvinyl)(phenyl)phosphine oxide (47)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 36.9 mg, 60%). **$^{1}$H NMR (600 MHz, $CDCl_3$)** δ 7.99 – 7.94 (m, 2H), 7.84 –7.80 (m, 2H), 7.67 (d, *J* = 11.6 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.49 – 7.45 (m, 2H), 7.36 – 7.32 (m, 1H), 7.23 – 7.16 (m, 3H), 7.08 – 7.03 (m, 3H), 6.91 – 6.86 (m, 3H), 6.84 (d, *J* = 3.6 Hz, 2H), 6.66 (d, *J* = 8.5 Hz, 1H), 2.44 (s, 3H), 2.32 (s, 3H), 2.22 (s, 6H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 144.8 (d, *J* = 10.4 Hz), 142.8 (d, *J* = 22.1 Hz), 142.7, 141.9 (d, *J* = 21.7 Hz), 137.4, 134.8 (d, *J* = 100.8 Hz), 132.7 (d, *J* = 12.9 Hz), 132.5, 132.2, 131.7 (d, *J* = 2.7 Hz), 131.6 (d, *J* = 110.1 Hz), 131.53, 131.48, 131.5, 131.4, 129.98, 129.95, 128.78 (d, *J* = 27.4 Hz), 128.77, 128.5, 128.0, 127.6, 125.8, 122.6 (d, *J* = 99.1 Hz), 121.4, 121.2, 120.1, 112.3, 23.99, 23.96, 21.1, 10.0; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 29.9; **HRMS (ESI) :** calcd. for $C_{38}H_{34}NNaO_3PS^+$ $[M+Na]^+$ : 638.1889; found : 638.1884; **$[\alpha]_D^{20}$** = +80 (c = 0.1, $CHCl_3$).

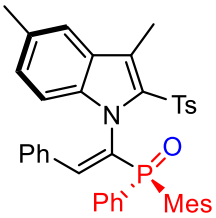
**HPLC analysis**: Daicel Chiralpak OX-3 column (hexane:2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 28.537 min, tr (minor) = 37.339 min, 93:7 er. tr (major) = 17.54 min, tr (minor) = 53.684 min, 91.5:8.5 er. 8.3:1 d.r. determined by crude NMR.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 17.585 | 1050.3 | 6.03 |
| 2 | 28.73 | 7730.6 | 44.35 |
| 3 | 37.104 | 7590.3 | 43.55 |
| 4 | 53.842 | 1059.7 | 6.08 |

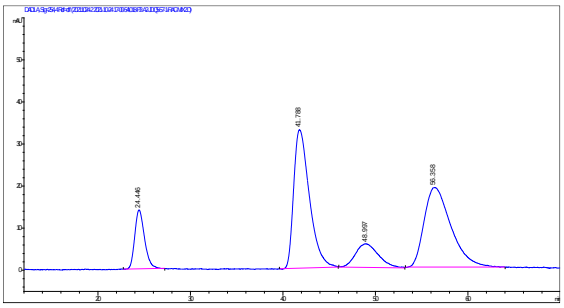
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 17.54 | 2179.3 | 10.29 |
| 2 | 28.537 | 17535.1 | 82.80 |
| 3 | 37.339 | 1262.8 | 5.96 |
| 4 | 53.684 | 201.8 | 0.95 |

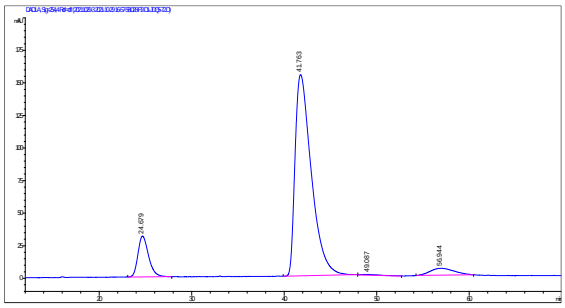



***(S,S,E)*-(1-(3,5-Dimethyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)(mesityl)(phenyl)phosphine oxide (48)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 46.3mg, total 72%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.90 – 7.85 (m, 2H), 7.69 (d, *J* = 11.6 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.51 – 7.48 (m, 1H), 7.46 – 7.42 (m, 2H), 7.32 (s, 1H), 7.20 – 7.17 (m, 1H), 7.05 – 7.01 (m, 2H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.87 – 6.84 (m 2H), 6.82 (d, *J* = 7.4 Hz, 2H), 6.78 – 6.75 (m, 1H), 6.67 (d, *J* = 8.7 Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H), 2.23 (s, 9H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 145.6, 145.4, 145.00, 144.98, 144.94, 144.91, 143.18, 143.15, 142.8, 142.6, 141.89, 141.87, 141.7, 141.6, 139.9, 139.6, 138.2, 136.7, 135.9, 135.5, 134.8, 133.4, 133.3, 132.8, 132.7, 132.4, 132.0, 131.61, 131.59, 131.40, 131.37, 131.33, 131.29, 131.26, 130.84, 130.76, 130.7, 130.5, 130.3, 130.0, 129.9, 129.7, 129.6, 129.5, 129.02, 129.00, 128.9, 128.71, 128.65, 128.6, 128.53, 128.45, 128.4, 128.2, 127.8, 127.7, 127.5, 126.8, 122.4, 121.8, 120.9, 119.4, 112.8, 112.2, 24.30, 24.27, 24.03, 24.01, 21.44, 21.42, 21.39, 21.1, 10.2, 10.0; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 32.9, 30.4; **HRMS (ESI):** calcd. for $C_{40}H_{38}NNaO_3PS^+$ $[M+Na]^+$ : 666.2202; found: 666.2205; **$[\alpha]_D^{20}$** = +90 (c = 0.1, $CHCl_3$).

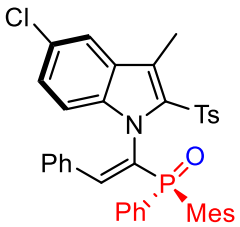
**HPLC analysis**: Daicel Chiralpak OX-3 column (hexane:2-propanol = 85:15, v = 0.8 mL/min, 40 ºC, 254 nm); tr (major) = 41.763 min, tr (minor) = 56.944 min, 95.3:4.7 er. tr (major) = 3.987 min, tr (minor) = 4.667 min, 96.5:3.5 er. 7.7:1 d.r. determined by crude NMR.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 24.446 | 1025.6 | 10.58 |
| 2 | 41.788 | 3883.5 | 40.06 |
| 3 | 48.997 | 970.1 | 10.00 |
| 4 | 56.358 | 3815.1 | 39.35 |

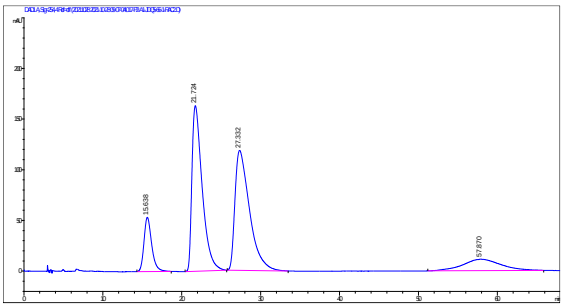
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 24.679 | 2484.7 | 11.11 |
| 2 | 41.763 | 18854.3 | 84.31 |
| 3 | 49.087 | 87.5 | 0.39 |
| 4 | 56.944 | 937.8 | 4.19 |

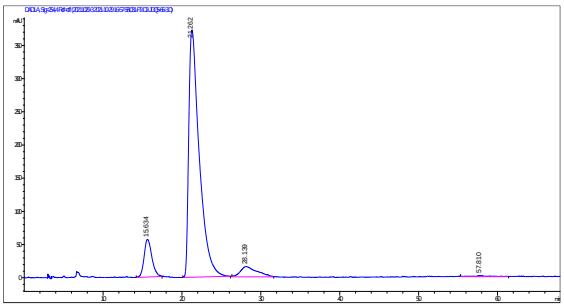



***(S,S,E)*-(1-(5-Chloro-3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)(mesityl)(phenyl)phosphine oxide (49)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 49.7 mg, 75%). **$^{1}$H NMR (600 MHz, $CDCl_3$)** δ 7.94 – 7.88 (m, 2H), 7.72 – 7.68 (m, 2H), 7.61 (d, *J* = 11.6 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.50 – 7.44 (m, 2H), 7.24 – 7.20 (m, 1H), 7.08 – 7.04 (m, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 3.6 Hz, 2H), 6.84 (dd, *J* = 8.9, 2.0 Hz, 1H), 6.79 (d, *J* = 7.4 Hz, 2H), 6.60 (d, *J* = 8.9 Hz, 1H), 2.41 (s, 3H), 2.33 (s, 3H), 2.28 (s, 6H), 2.26 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 144.8 (d, *J* = 10.4 Hz), 143.6, 142.8 (d, *J* = 21.8 Hz), 142.2 (d, *J* = 2.6 Hz), 139.5, 135.6, 134.4 (d, *J* = 101.5 Hz), 133.8, 132.4 (d, *J* = 12.6 Hz), 131.9 (d, *J* = 2.7 Hz), 131.4 (d, *J* = 110.8 Hz), 131.62, 131.56, 131.55, 131.5, 130.0, 129.8, 129.2, 128.84, 128.82, 128.80, 128.77, 127.7, 126.8, 126.1, 122.0 (d, *J* = 98.5 Hz), 120.3, 119.5, 113.7, 24.07, 24.05, 21.5, 21.1, 10.0; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 30.0; **HRMS (ESI):** calcd. for $C_{39}H_{36}ClNO_3PS^+$ $[M+H]^+$ : 664.1837; found : 664.1838; **$[\alpha]_D^{20}$** = +72 (c = 0.1, $CHCl_3$).

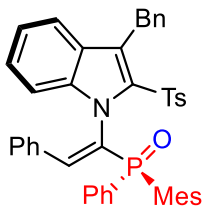
**HPLC analysis**: Daicel Chiralpak OZ-H column (hexane:2-propanol = 90:10, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 21.262 min, tr (minor) = 28.139 min, 94:6 er. tr (major) = 15.634 min, tr (minor) = 57.81 min, 93:7 er. 9.0:1 d.r. determined by crude NMR.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 15.638 | 3628.5 | 9.74 |
| 2 | 21.724 | 14773.9 | 39.64 |
| 3 | 27.332 | 15114.2 | 40.56 |
| 4 | 57.87 | 3750.1 | 10.06 |

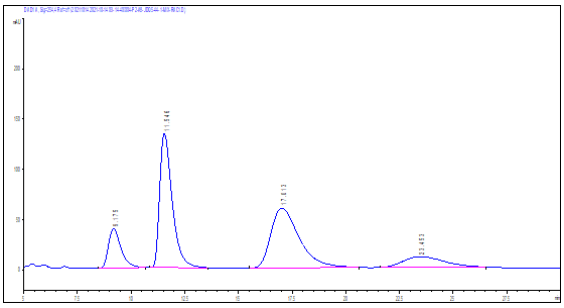
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 15.634 | 3862.5 | 9.44 |
| 2 | 21.262 | 34523.2 | 84.39 |
| 3 | 28.139 | 2238 | 5.47 |
| 4 | 57.81 | 284 | 0.69 |



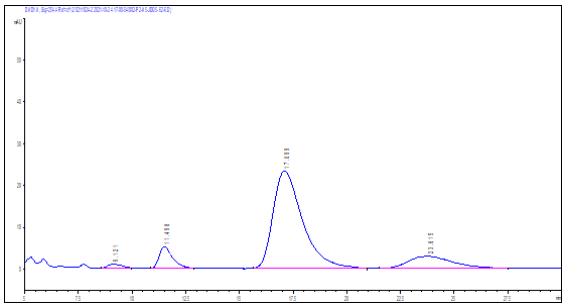

***(S,S,E)*-(1-(3-Benzyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)(mesityl)(phenyl)phosphine oxide (50)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 39.5 mg, 60%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.99 – 7.93 (m, 2H), 7.72 (d, *J* = 11.5 Hz, 1H), 7.54 – 7.51 (m, 3H), 7.49 – 7.45 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.16 (m, 4H), 7.15 – 7.11 (m, 1H), 7.08 – 7.04 (m, 2H), 6.95 – 6.92 (m, 1H), 6.90 (d, *J* = 7.7 Hz, 2H), 6.85 – 6.82 (m, 1H), 6.82 – 6.79 (m, 4H), 6.71 (d, *J* = 8.4 Hz, 1H), 4.55 (d, *J* = 15.6 Hz, 1H), 4.24 (d, *J* = 15.6 Hz, 1H), 2.31 (s, 3H), 2.18 (s, 3H), 2.18 (s, 6H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ144.9 (d, *J* = 10.3 Hz), 143.3, 142.6 (d, *J* = 21.8 Hz), 141.9 (d, *J* = 2.7 Hz), 139.9, 139.4, 137.8, 135.8 (d, *J* = 100.7 Hz), 133.6, 132.7 (d, *J* = 12.7 Hz), 132.3, 131.7 (d, *J* = 2.6 Hz), 131.52, 131.45 (d, *J* = 12.9 Hz), 131.44, 131.37, 131.3, 130.0, 129.8, 129.04, 129.01, 128.8 (d, *J* = 21.7 Hz), 128.7, 128.6, 128.1, 127.7, 127.5, 125.8, 125.6, 123.4, 122.8 (d, *J* = 100.2 Hz), 121.4, 120.9, 112.4, 30.7, 23.90, 23.87, 21.4, 21.1; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 30.2; **HRMS (ESI) :** calcd. for $C_{45}H_{41}NO_3PS^+$ $[M+H]^+$ : 706.2539; found : 706.2532; **$[\alpha]_D^{20}$** = 20 (c = 0.1, $CHCl_3$).

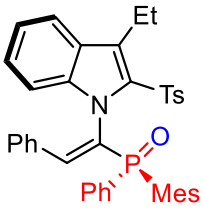
**HPLC analysis**: Daicel Chiralpak OX-3 column (hexane:2-propanol = 70:30, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 17.099 min, tr (minor) = 11.498 min, 91:9 er. tr (major) = 23.815 min, tr (minor) = 9.121 min, 92:8 er. 6.6:1 d.r. determined by crude NMR.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.175 | 1599.3 | 11.49 |
| 2 | 11.546 | 5419.8 | 38.94 |
| 3 | 17.013 | 5457.5 | 39.21 |
| 4 | 23.453 | 1441 | 10.35 |



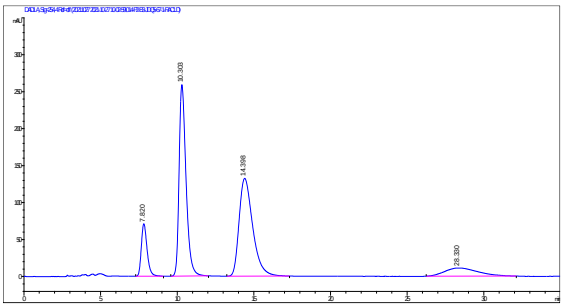
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.121 | 38.4 | 1.323 |
| 2 | 11.498 | 222.1 | 7.643 |
| 3 | 17.099 | 2218.1 | 76.321 |
| 4 | 23.815 | 427.6 | 14.713 |

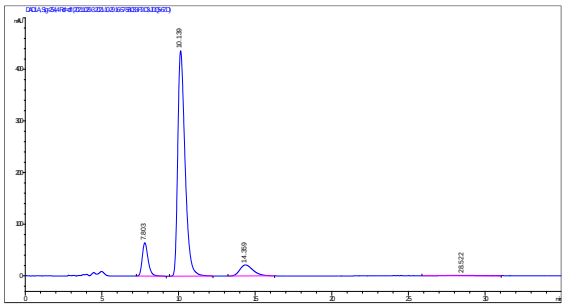



***(S,S,E)*-(1-(3-Ethyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)(mesityl)(phenyl)phosphine oxide (51)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 36.0 mg, 56%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.91 – 7.86 (m, 2H), 7.74 (d, *J* = 11.5 Hz, 1H), 7.67 – 7.64 (m, 2H), 7.60 – 7.57 (m, 1H), 7.52 – 7.47 (m, 1H), 7.46 – 7.41 (m, 2H), 7.21 – 7.17 (m, 1H), 7.07 – 7.01 (m, 3H), 6.95 – 6.90 (m, 3H), 6.86 – 6.82 (m, 4H), 6.80 (d, *J* = 8.4 Hz, 1H), 3.08 – 3.01 (m, 1H), 2.92 – 2.84 (m, 1H), 2.31 (s, 3H), 2.23 (s, 3H), 2.20 (s, 6H), 1.13 (t, *J* = 7.5 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 145.0 (d, *J* = 10.3 Hz), 143.3, 142.6 (d, *J* = 21.7 Hz), 141.9 (d, *J* = 2.6 Hz), 140.3, 137.7, 135.6, 134.9, 132.7 (d, *J* = 12.7 Hz), 132.0 (d, *J* = 110.8 Hz), 131.7, 131.6 (d, *J* = 2.8 Hz), 131.3 (d, *J* = 11.5 Hz), 131.2 (d, *J* = 10.6 Hz), 130.3 (d, *J* = 1.6 Hz), 130.04, 129.77, 129.1, 128.9 (d, *J* = 3.9 Hz), 128.74, 128.66, 128.6, 127.8, 127.5, 127.2, 125.7, 122.8 (d, *J* = 100.1 Hz), 121.1, 120.2, 112.6, 23.92, 23.89, 21.4, 21.1, 18.4, 15.2; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 30.7; **HRMS (ESI) :** calcd. for $C_{40}H_{39}NO_3PS^+$ $[M+H]^+$ : 644.2383; found : 644.2380; **$[\alpha]_D^{20}$** = +44 (c = 0.1, $CHCl_3$).

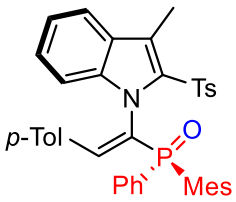
**HPLC analysis**: Daicel Chiralpak OX-3 column (hexane:2-propanol = 70:30, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 10.139 min, tr (minor) = 14.359 min, 91.7:8.3 er. tr (major) = 7.803 min, tr (minor) = 28.522 min, 92:8 er. 8.0:1 d.r. determined by crude NMR.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 7.82 | 1860.3 | 9.39 |
| 2 | 10.303 | 8146.6 | 41.12 |
| 3 | 14.398 | 8151.5 | 41.14 |
| 4 | 28.33 | 1654.7 | 8.35 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 7.803 | 1706.4 | 9.73 |
| 2 | 10.139 | 14375.4 | 81.98 |
| 3 | 14.359 | 1306.6 | 7.45 |
| 4 | 28.522 | 146.7 | 0.84 |



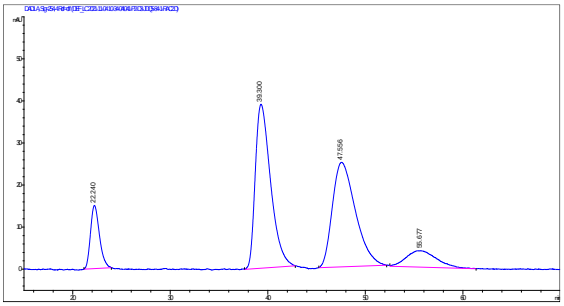

***(S,S,E)*-Mesityl(1-(3-methyl-2-(phenylsulfonyl)-1H-indol-1-yl)-2-(*p*-tolyl)vinyl)(phenyl)phosphine oxide (52)**

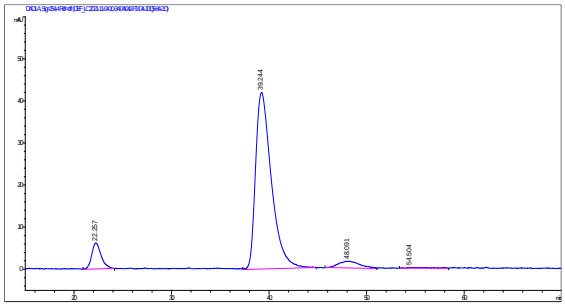
The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 51.5 mg, 80%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.92 (dd, *J* = 12.3, 7.6 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 11.5 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.48-7.43 (m, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.89 (t, *J* = 7.7 Hz, 1H), 6.86 – 6.81 (m, 4H), 6.72 –6.66 (m, 3H), 2.47 (s, 3H), 2.32 (s, 3H), 2.26 (s, 3H), 2.23 (s, 3H), 2.22 (s, 6H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 144.9 (d, *J* = 10.3 Hz), 143.2, 142.8 (d, *J* = 22.1 Hz), 141.8 (d, *J* = 2.7 Hz), 140.3, 139.9, 137.3, 135.1 (d, *J* = 100.9 Hz), 132.3, 131.6 (d, *J* = 2.8 Hz), 131.5, 131.4 (d, *J* = 2.5 Hz), 131.3, 130.5 (d, *J* = 112.2 Hz), 130.0, 129.9 (d, *J* = 13.0 Hz), 129.4, 129.0, 128.7 (d, *J* = 12.2 Hz), 127.9, 127.7, 125.7, 122.3 (d, *J* = 99.7 Hz), 121.1, 121.0, 120.0, 112.4, 23.99, 23.96, 21.5, 21.4, 21.1, 10.1; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 30.1; **HRMS (ESI) :** calcd. for $C_{40}H_{38}NNaO_3PS^+$ $[M+Na]^+$ : 666.2202; found : 666.2197; **$[\alpha]_D^{20}$** = +192 (c = 0.1, $CHCl_3$).

Another diastereomer: the title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 4.5 mg, 7%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.90 (dd, *J* = 12.1, 7.9 Hz, 3H), 7.52 – 7.48 (m, 2H), 7.47 – 7.43 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.16 – 7.12 (m, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 3.7 Hz, 2H), 2.52 (s, 3H), 2.31 (s, 6H), 2.26 (s, 3H), 2.24 (s, 3H), 2.16 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 146.0 (d, *J* = 21.5 Hz), 144.8 (d, *J* = 10.4 Hz), 143.1, 141.5 (d, *J* = 2.7 Hz), 140.1,

139.5, 139.3, 136.9, 136.2, 132.0, 131.3, 131.2 (d, $J$ = 10.7 Hz), 130.7 (d, $J$ = 11.6 Hz), 130.5 (d, $J$ = 12.7 Hz), 130.3, 130.0, 129.3, 128.9, 128.4 (d, $J$ = 12.2 Hz), 127.4, 126.9, 126.3, 123.1, 121.2, 120.0, 113.1, 24.28, 24.25, 21.43, 21.36, 20.9, 10.3; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 33.0; **HRMS (ESI) :** calcd. for $C_{40}H_{39}NO_3PS^+$ $[M+H]^+$ : 644.2383; found : 644.2378; **$[\alpha]_D^{20}$** = +24 (c = 0.1, $CHCl_3$).

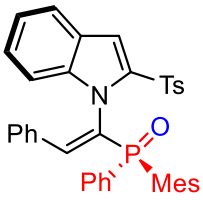
**HPLC analysis**: Daicel Chiralpak OX-3 column (hexane:2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 39.244 min, tr (minor) = 48.091 min, 95 : 5 er. tr (major) = 22.257 min, tr (minor) = 54.504 min, 93.2:6.8 er. 8.5:1 d.r. determined by crude NMR.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 22.24 | 959.3 | 9.46 |
| 2 | 39.3 | 4255.4 | 41.98 |
| 3 | 47.556 | 4069.7 | 40.15 |
| 4 | 55.677 | 852.9 | 8.41 |

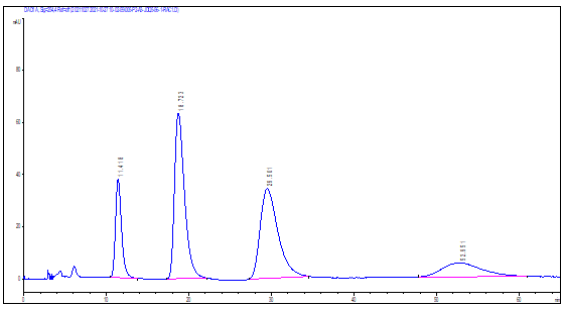
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 22.257 | 416.1 | 7.67 |
| 2 | 39.244 | 4726.7 | 87.17 |
| 3 | 48.091 | 249.3 | 4.60 |
| 4 | 54.504 | 30.4 | 0.56 |

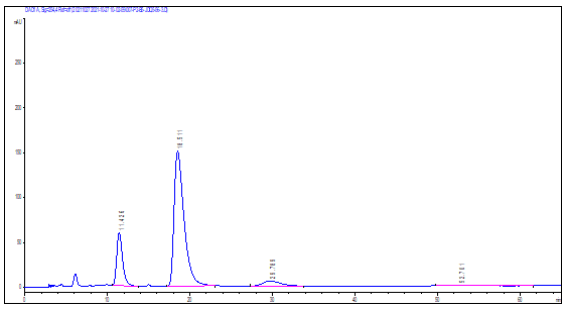



***(S,S,E)*-Mesityl(phenyl)(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phosphine oxide (53)**

The title compound was isolated as a pale-yellow solid (eluent: petroleum ether/ethyl acetate = 3/1, 33.8 mg, 55%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.75 – 7.70 (m, 2H), 7.64 – 7.58 (m, 2H), 7.58 – 7.54 (m, 2H), 7.54 – 7.49 (m, 1H), 7.46 – 7.41 (m, 2H), 7.31 (s, 1H), 7.13 – 7.08 (m, 2H), 7.02 – 6.97 (m, 2H), 6.92 – 6.86 (m, 6H), 6.55 (d, $J$ = 7.7 Hz, 2H), 2.35 (s, 3H), 2.33 (s, 6H), 2.20 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 145.1 (d, $J$ = 10.3 Hz), 143.5, 143.4 (d, $J$ = 21.8 Hz), 142.1 (d, $J$ = 2.7 Hz), 139.0, 138.6, 137.1, 134.3 (d, $J$ = 101.7 Hz), 132.3 (d, $J$ = 12.8 Hz), 131.8 (d, $J$ = 2.9 Hz), 131.379 (d, $J$ = 22.7 Hz), 131.375, 131.0, 129.9, 129.8, 129.1, 128.6 (d, $J$ = 12.2 Hz), 128.5, 127.9, 126.4, 125.7, 122.0 (d, $J$ = 14.4 Hz), 121.5 (d, $J$ = 100.0 Hz), 113.1, 24.08, 24.06, 21.4, 21.1; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 30.9; **HRMS (ESI):** calcd. for $C_{38}H_{35}NO_3PS^+$ $[M+H]^+$ : 616.2070; found : 610.2066; **$[\alpha]_D^{20}$** = +66 (c = 0.1, $CHCl_3$).

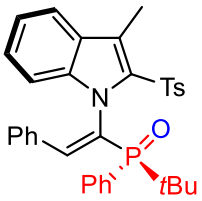
**HPLC analysis**: Daicel Chiralpak OZ-H column (hexane:2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 18.511 min, tr (minor) = 29.789 min, 94:6 er. tr (major) = 11.426 min, tr (minor) = 52.701 min, 96:4 er. 5.2:1 d.r. determined by crude NMR.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.418 | 1933.6 | 13.56 |
| 2 | 18.723 | 5340.1 | 37.46 |
| 3 | 29.501 | 5174.4 | 36.30 |
| 4 | 52.951 | 1807.9 | 12.68 |

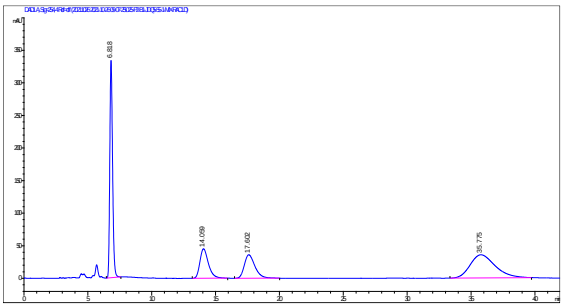
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.426 | 2912.1 | 17.633 |
| 2 | 18.511 | 12642.7 | 76.553 |
| 3 | 29.789 | 837.6 | 5.072 |
| 4 | 52.701 | 122.5 | 0.742 |

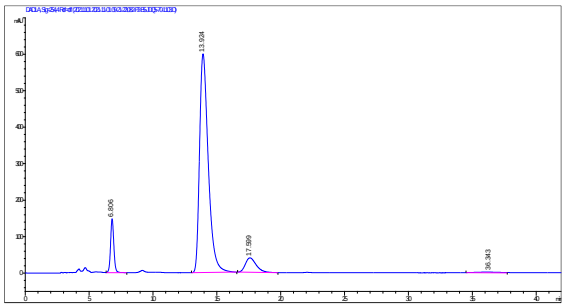



***(S,S,E)*-Tert-butyl(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)(phenyl)phosphine oxide (54)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 44.2 mg, 78%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.73 – 7.70 (m, 2H), 7.61 (t, *J* = 8.9 Hz, 2H), 7.58 – 7.54 (m, 2H), 7.44 – 7.40 (m, 2H), 7.38 – 7.34 (m, 1H), 7.29 – 7.27 (m, 2H), 7.26 – 7.23 (m, 1H), 7.12 – 7.08 (m, 1H), 6.89 – 6.85 (m, 2H), 6.75 (d, *J* = 8.2 Hz, 2H), 6.53 (d, *J* = 7.7 Hz, 2H), 2.62 (s, 3H), 2.16 (s, 3H), 1.07 (d, *J* = 15.0 Hz, 9H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 145.6 (d, *J* = 19.8 Hz), 143.5, 138.9, 136.5, 132.8 (d, *J* = 8.4 Hz), 132.7 (d, *J* = 11.8 Hz), 132.3, 131.7 (d, *J* = 2.6 Hz), 131.2, 130.0, 129.6, 129.2, 129.0, 128.5, 127.2, 126.7, 122.0, 121.7, 120.7, 113.7, 34.9, 34.5, 25.3, 21.3, 10.2; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 42.9; **HRMS (ESI) :** calcd. for $C_{34}H_{35}NO_3PS^+$ $[M+H]^+$ : 568.2070; found: 568.2065; **$[\alpha]_D^{20}$** = +116 (c = 0.1, $CHCl_3$).

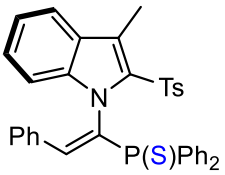
**HPLC analysis**: Daicel Chiralpak OX-3 column (hexane:2-propanol = 70:30, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 13.924 min, tr (minor) = 17.599 min, 92.5:7.5 er. tr (major) = 6.806 min, tr (minor) = 36.343 min, 92:8 er. 10.0:1 d.r. determined by crude NMR.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 6.818 | 5039.7 | 35.87 |
| 2 | 14.059 | 2093.8 | 14.90 |
| 3 | 17.602 | 2083.2 | 14.83 |
| 4 | 35.775 | 4835 | 34.41 |

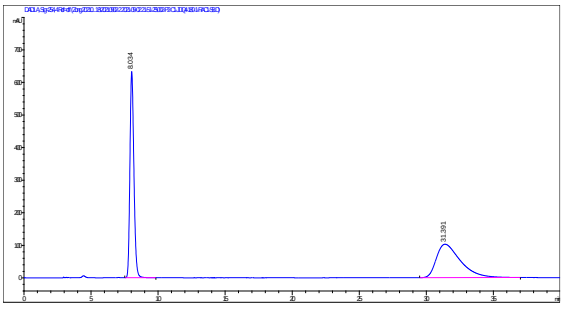
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 6.806 | 2603 | 7.75 |
| 2 | 13.924 | 28436.4 | 84.67 |
| 3 | 17.599 | 2319.4 | 6.91 |
| 4 | 36.343 | 227.2 | 0.68 |

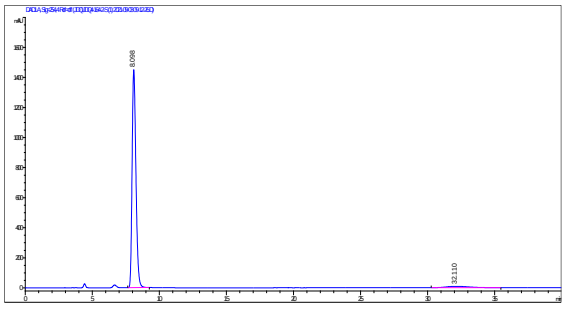



**_(S,E)_-(1-(3-Methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine sulfide (55)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 28.6 mg, 95%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.34 – 8.27 (m, 2H), 7.74 (d, *J* = 12.7 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.59 – 7.54 (m, 3H), 7.53 – 7.45 (m, 3H), 7.39 – 7.34 (m, 1H), 7.25 – 7.13 (m, 7H), 6.95 – 6.91 (m, 2H), 6.77 (d, *J* = 8.1 Hz, 2H), 6.72 (d, *J* = 7.6 Hz, 2H), 2.44 (d, *J* = 1.1 Hz, 3H), 2.18 (s, 3H) ; **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.5, 143.2 (d, *J* = 24.6 Hz), 139.0, 137.8, 134.5, 133.9, 133.7 (d, *J* = 10.8 Hz), 132.8 (d, *J* = 13.8 Hz), 132.2 (d, *J* = 10.7 Hz), 132.1, 132.0, 131.5, 131.42, 131.40, 130.7, 130.2, 129.8, 129.73, 129.66, 129.0, 128.6, 128.3 (d, *J* = 12.5 Hz), 128.0, 127.8 (d, *J* = 12.5 Hz), 126.9, 126.5, 122.3, 121.8, 120.2, 114.5, 21.4, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 45.1; **HRMS (ESI) :** calcd. for $C_{36}H_{31}NO_2PS_2^+$ $[M+H]^+$ : 604.1528; found : 604.1529; **$[\alpha]_D^{20}$** = +160 (c = 0.1, $CHCl_3$).

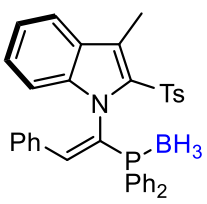
**HPLC analysis**: Daicel Chiralpak OZ-H column (hexane:2-propanol = 80:20, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 8.098 min, tr (minor) = 32.11 min, 96:4 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.034 | 13017.3 | 50.44 |
| 2 | 31.391 | 12787.9 | 49.56 |

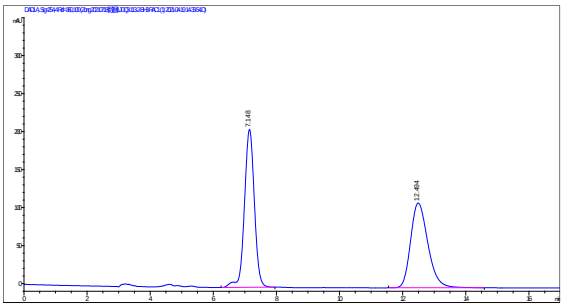
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.098 | 28702 | 96.25 |
| 2 | 32.11 | 1119.6 | 3.75 |

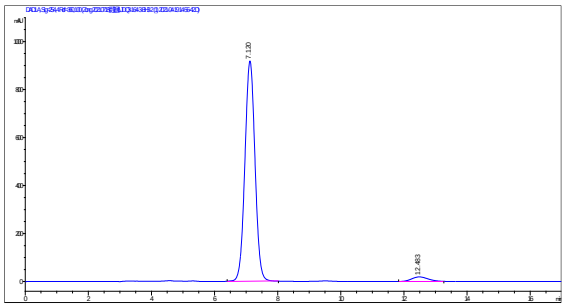



***(S,E)-1*-(1-(Diphenylphosphaneyl)-2-phenylvinyl)-3-methyl-2-tosyl-1H-indole borane (56)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 26.6 mg, 91%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.03 – 7.98 (m, 2H), 7.63 (d, *J* = 11.2 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.52 – 7.47 (m, 2H), 7.37 – 7.31 (m, 3H), 7.30 – 7.26 (m, 2H), 7.25 – 7.16 (m, 5H), 7.15 – 7.11 (m, 1H), 6.93 – 6.88 (m, 2H), 6.75 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 7.7 Hz, 2H), 2.45 (s, 3H), 2.16 (s, 3H), 1.26 (br, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 144.2 (d, *J* = 23.7 Hz), 143.5, 138.9, 137.3, 134.6 (d, *J* = 9.9 Hz), 133.0 (d, *J* = 9.8 Hz), 132.8 (d, *J* = 11.9 Hz), 131.8 (d, *J* = 2.6 Hz), 131.1 (d, *J* = 2.4 Hz), 130.6, 129.9, 129.81, 129.75, 129.5, 129.4, 129.09, 129.06, 128.5 (d, *J* = 10.4 Hz), 128.5, 128.0 (d, *J* = 10.2 Hz), 127.9, 127.5, 127.2, 126.99, 126.96, 126.62, 126.56, 126.2, 122.3, 121.8, 120.4, 113.8, 21.4, 9.9; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.6; **HRMS (ESI) :** calcd. for $C_{36}H_{33}BNNaO_2PS^+$ $[M+Na]^+$ : 608.1955; found : 608.1959; **$[\alpha]_D^{20}$** = +60 (c = 0.1, $CHCl_3$).

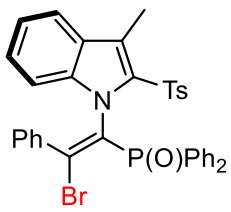
**HPLC analysis**: Daicel Chiralpak OZ-H column (hexane:2-propanol = 80:20, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 7.12 min, tr (minor) = 12.483 min, 96.6:3.4 er.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 7.148 | 4555.9 | 51.82 |
| 2 | 12.494 | 4235.3 | 48.18 |

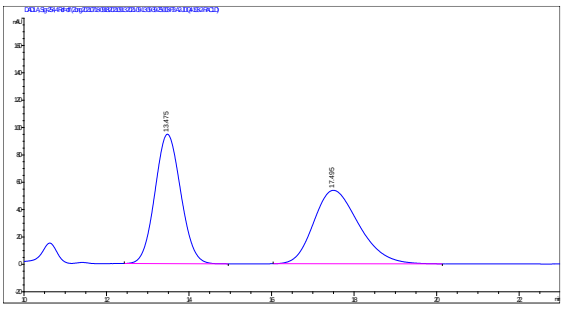
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 7.12 | 20338.2 | 96.64 |
| 2 | 12.483 | 708.2 | 3.37 |

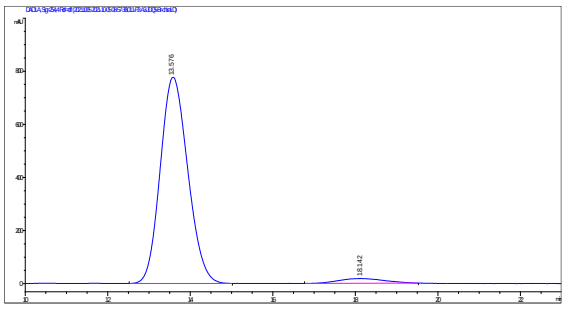



***(S,Z)*-(2-Bromo-1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)diphenylphosphine oxide (57)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 29.5 mg, 74%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.22 – 8.17 (m, 2H), 7.73 – 7.71 (m, 1H), 7.69 – 7.66 (m, 1H), 7.62 – 7.59 (m, 2H), 7.53 (d, *J* = 12.0 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.43 – 7.39 (m, 1H), 7.34 – 7.31 (m, 4H), 7.26 – 7.22 (m, 2H), 7.17 – 7.13 (m, 1H), 6.96 – 6.92 (m, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.64 (d, *J* = 7.7 Hz, 2H), 2.39 (s, 3H), 2.20 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.8, 143.3 (d, *J* = 22.3 Hz), 138.5, 135.9, 133.7 (d, *J* = 114.4 Hz), 133.1 (d, *J* = 9.5 Hz), 132.5 (d, *J* = 2.4 Hz), 132.4 (d, *J* = 13.0 Hz), 132.023 (d, *J* = 10.0 Hz), 132.020 (d, *J* = 2.4 Hz), 131.9, 130.3 (d, *J* = 105.4 Hz), 130.0, 129.83, 129.76, 129.3, 129.2, 128.7, 128.6 (d, *J* =12.0 Hz), 127.9 (d, *J* = 12.3 Hz), 127.1, 122.9, 121.1, 115.1, 115.0, 21.4, 9.8; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.8; **HRMS (ESI) :** calcd. for $C_{36}H_{29}BrNNaO_3PS^+$ $[M+Na]^+$ : 688.0681; found : 688.0674; **$[\alpha]_D^{20}$** = +18 (c = 0.1, $CHCl_3$).

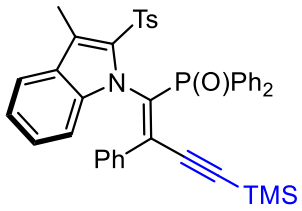
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 13.576 min, tr (minor) = 18.142 min, 96:4 er.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 13.475 | 4105 | 50.10 |
| 2 | 17.495 | 4089 | 49.90 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 13.576 | 36012.2 | 96.27 |
| 2 | 18.142 | 1394.2 | 3.73 |

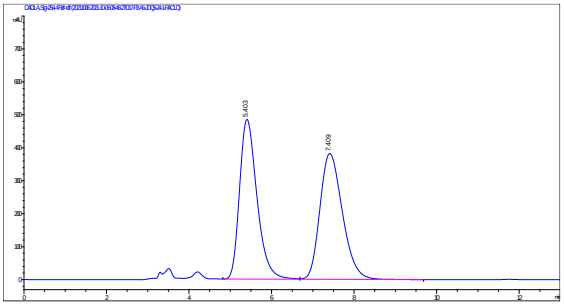


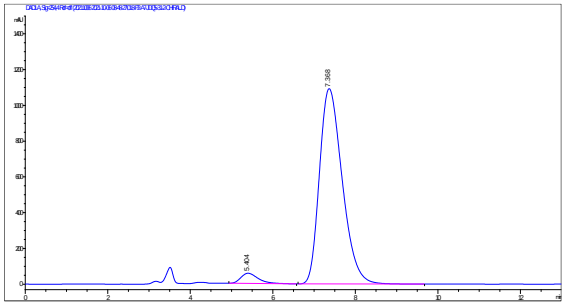

***(S,Z)*-(1-(3-Methyl-2-tosyl-1H-indol-1-yl)-2-phenyl-4-(trimethylsilyl)but-1-en-3-yn-1-yl)diphenylphosphine oxide (58)**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 3/1, 28.4 mg, 83%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.18 – 8.13 (m, 2H), 7.76 – 7.74 (m, 1H), 7.68 – 7.64 (m, 1H), 7.61 – 7.54 (m, 3H), 7.52 – 7.46 (m,

2H), 7.43 – 7.38 (m, 1H), 7.34 – 7.31 (m, 4H), 7.25 –7.21 (m, 2H), 7.15 – 7.11 (m, 1H), 6.93 – 6.88 (m, 2H), 6.81 (d, $J$ = 8.2 Hz, 2H), 6.61 (d, $J$ = 7.7 Hz, 2H), 2.41 (s, 3H), 2.20 (s, 3H), 0.26 (s, 9H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 143.7, 143.3 (d, $J$ = 22.1 Hz), 138.6, 136.8, 133.7 (d, $J$ = 113.5 Hz), 133.0 (d, $J$ = 9.4 Hz), 132.41, 132.39, 132.3, 132.0 (d, $J$ = 10.1 Hz), 131.9 (d, $J$ = 2.7 Hz), 131.6, 130.5 (d, $J$ = 104.9 Hz), 130.3, 129.84, 129.78, 129.7, 129.4, 129.1, 128.6, 128.5, 128.4, 127.9 (d, $J$ = 12.1 Hz), 127.4, 127.0, 124.6, 121.9, 116.3, 113.3, 105.5, 93.0, 21.4, 9.8; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.6; **HRMS (ESI) :** calcd. for $C_{41}H_{38}NNaO_3PSSi^+$ $[M+Na]^+$ : 706.1971; found :706.1967; **$[\alpha]_D^{20}$** = -10 (c = 0.1, $CHCl_3$).

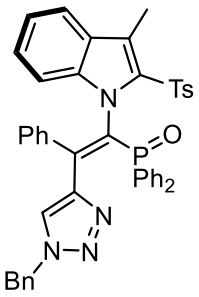
**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 50:50, v = 1.0 mL/min, 40 °C, 254 nm); tr (minor) = 5.404 min, tr (major) = 7.368 min, 4:96 er.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 5.403 | 14246 | 49.60 |
| 2 | 7.409 | 14477.8 | 50.40 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 5.404 | 1644.3 | 3.78 |
| 2 | 7.368 | 41822.6 | 96.22 |

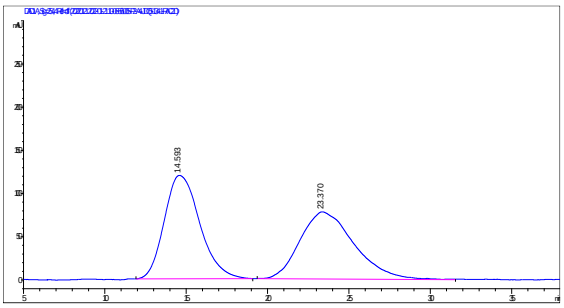


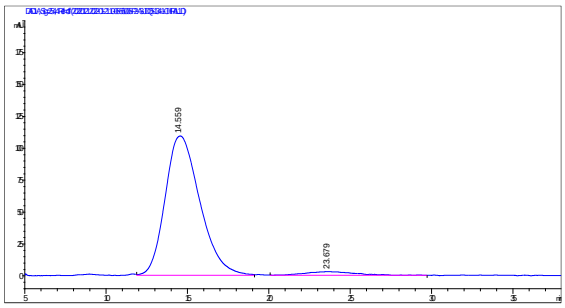

***(S,Z)*-1-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-1-(diphenylphosphaneyl)-2-phenylvinyl)-3-methyl-2-tosyl-1H-indole (59')**

The title compound was isolated as a white solid (eluent: petroleum ether/ethyl acetate = 1/1, 41.7 mg, 73%). **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.23 – 8.17 (m, 3H), 7.69 (s, 1H), 7.68 – 7.64 (m, 1H), 7.61 – 7.55 (m, 4H), 7.49 – 7.44 (m, 3H), 7.41 – 7.36 (m, 4H), 7.34 – 7.30 (m, 4H), 7.20 (td, $J$ = 7.8, 2.9 Hz, 2H), 7.12 (t, $J$ = 7.4 Hz, 1H), 6.90 (t, $J$ = 7.7 Hz, 2H), 6.80 (d, $J$ = 8.1 Hz, 2H), 6.66 (d, $J$ = 7.9 Hz, 2H), 5.58 (s, 2H), 2.46 (s, 3H), 2.19 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 148.5, 143.6, 143.2 (d, $J$ = 22.4 Hz), 138.7, 137.2, 134.7, 134.0(d, $J$ = 113.5 Hz), 133.1(d, $J$ = 9.4 Hz), 132.53, 132.47(d, $J$ = 2.7 Hz), 132.4, 132.02, 131.95, 131.4, 130.5 (d, $J$ = 105.5 Hz), 129.9, 129.8, 129.2, 129.1, 128.8, 128.6, 128.5 (d, $J$ = 12.0 Hz), 128.2, 128.1, 127.9

(d, $J$ = 12.1 Hz), 127.0, 125.1, 124.4, 122.5, 119.3, 117.5, 113.8, 54.3, 21.4, 10.0; **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 27.8; **HRMS (ESI) :** calcd. for $C_{45}H_{37}N_4NaO_3PS^+$ $[M+Na]^+$: 767.2216; found: 767.2218; **$[\alpha]_D^{20}$** = +28 (c = 0.1, $CHCl_3$).

**HPLC analysis**: Daicel Chiralpak AD-H column (hexane:2-propanol = 40:60, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 14.559 min, tr (minor) = 23.679 min, 96:4 er.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 14.593 | 18201.3 | 50.32 |
| 2 | 23.37 | 17972.7 | 49.68 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 14.559 | 16209.6 | 96.21 |
| 2 | 23.679 | 637.8 | 3.79 |

## 4. X-Ray crystallographic data

### (1) X-ray crystal structure of (S)-12 (CCDC 2126532)

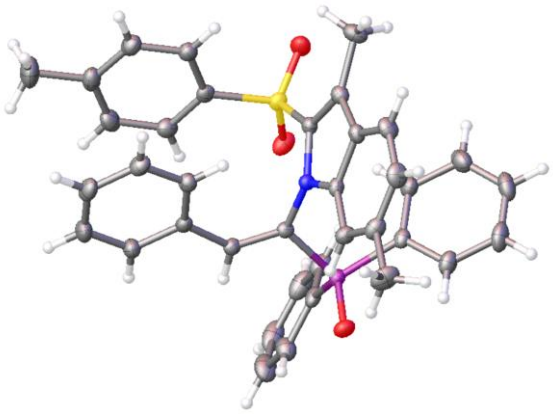


**Table S6 Crystal data and structure refinement for 12.**

| | |
|---|---|
| Identification code | **12** |
| Empirical formula | C37H32NO3PS |
| Formula weight | 601.66 |
| Temperature/K | 153.0 |
| Crystal system | orthorhombic |

| | |
|---|---|
| Space group | P212121 |
| a/Å | 8.4640(3) |
| b/Å | 16.0033(6) |
| c/Å | 22.5434(8) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å3 | 3053.55(19) |
| Z | 4 |
| ρcalcg/cm3 | 1.309 |
| μ/mm-1 | 1.740 |
| F (000) | 1264.0 |
| Crystal size/mm3 | 0.5 × 0.4 × 0.3 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 6.774 to 136.37 |
| Index ranges | -10 ≤ h ≤ 10, -19 ≤ k ≤ 19, -27 ≤ l ≤ 27 |
| Reflections collected | 49484 |
| Independent reflections | 5571 [Rint = 0.0473, Rsigma = 0.0221] |
| Data/restraints/parameters | 5571/0/391 |
| Goodness-of-fit on F2 | 1.038 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0228, wR2 = 0.0583 |
| Final R indexes [all data] | R1 = 0.0239, wR2 = 0.0589 |
| Largest diff. peak/hole / e Å-3 | 0.18/-0.26 |
| Flack parameter | 0.013(4) |

**(2) X-ray crystal structure of 47 (CCDC 2126528)**

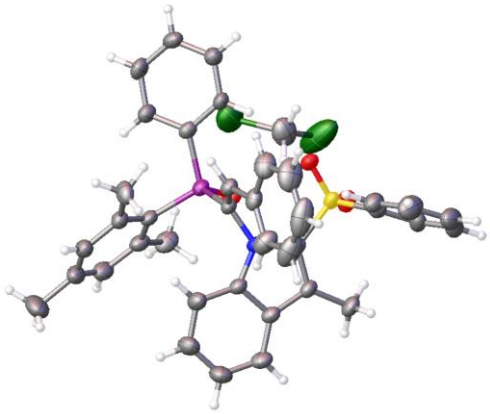
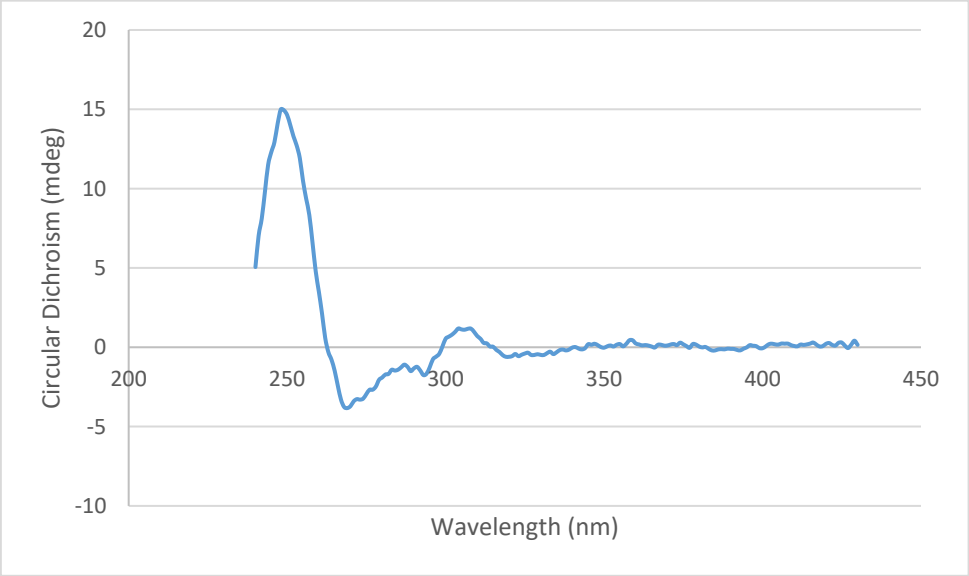


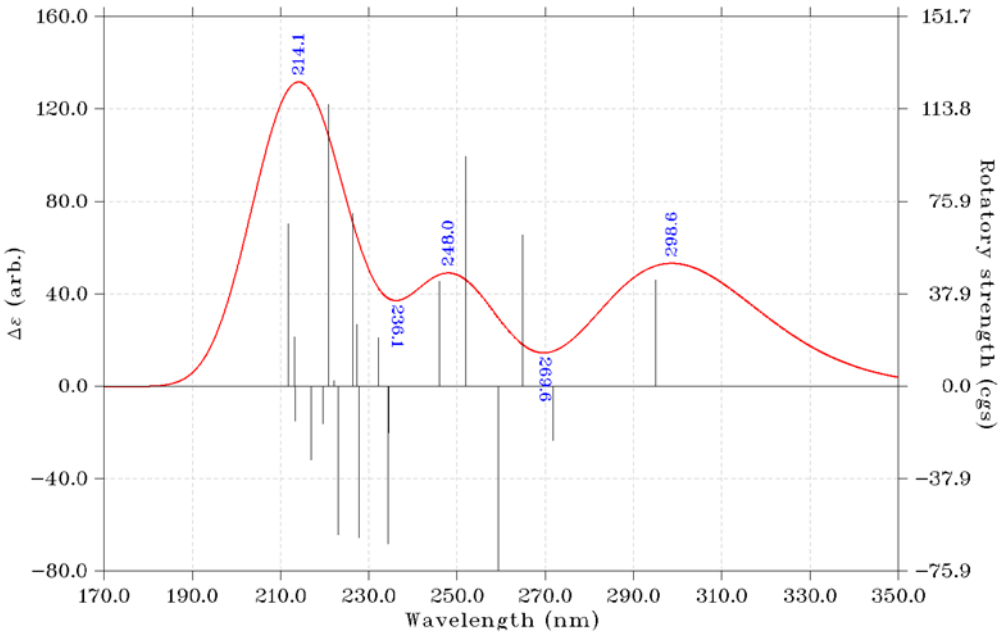
**Table S7 Crystal data and structure refinement for 47.**

| | |
|---|---|
| Identification code | **47** |
| Empirical formula | $C_{39}H_{36}Cl_2NO_3PS$ |
| Formula weight | 700.62 |
| Temperature/K | 153.0 |
| Crystal system | trigonal |
| Space group | $P3_221$ |
| a/Å | 12.421(2) |
| b/Å | 12.421(2) |
| c/Å | 39.695(10) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 120 |
| Volume/Å$^3$ | 5303(2) |
| Z | 6 |
| $\rho_{calc}$g/cm$^3$ | 1.316 |
| μ/mm$^{-1}$ | 2.935 |
| F(000) | 2196.0 |
| Crystal size/mm$^3$ | 0.5 × 0.4 × 0.3 |

| | |
|---|---|
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 6.68 to 139.352 |
| Index ranges | $-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-48 \leq l \leq 47$ |
| Reflections collected | 90054 |
| Independent reflections | 6494 [$R_{int}$ = 0.0680, $R_{sigma}$ = 0.0262] |
| Data/restraints/parameters | 6494/0/428 |
| Goodness-of-fit on $F^2$ | 1.064 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0578, $wR_2$ = 0.1704 |
| Final R indexes [all data] | $R_1$ = 0.0605, $wR_2$ = 0.1752 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.81/-0.82 |
| Flack parameter | 0.079(5) |

## 5. ECD spectrum of (*S*)-30 and Density functional calculations.






**Supplementary Figure 1.** Comparison of experimental (blue line) and calculated (red) ECD spectra of product **30**

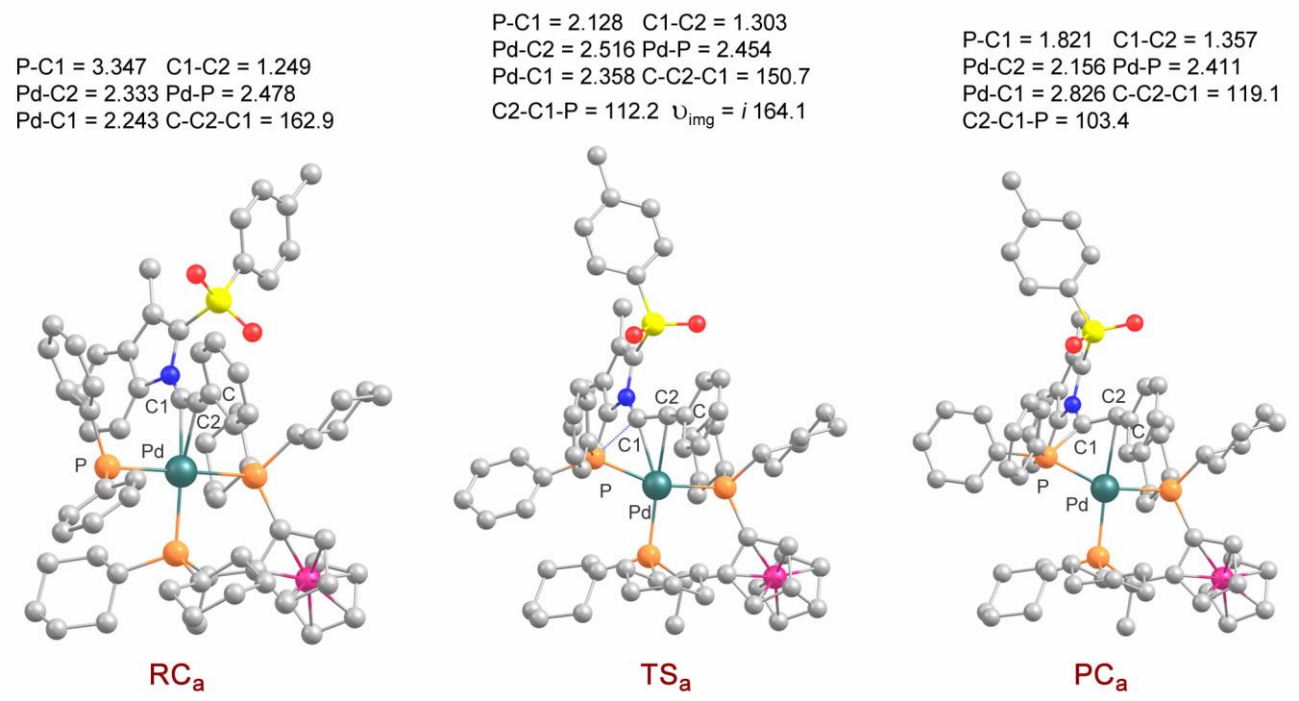
## Computational Methodology

Density functional theory (DFT) calculations were carried out using the Gaussian 16 suite of programs.[8] The spin-unrestricted B3LYP functional[9] was employed. Geometry optimizations and frequency calculations were performed at the UB3LYP/Lanl2dz(Fe, Pd), 6-31G*(the rest atoms) level of theory. Single point energy (SPE) calculations were done with the basis set of Lanl2tz[10] (Fe, Pd), 6-31+G**(the rest atoms). Solvent effects (toluene, ε = 2.3741) were included in all calculations using the conductor-like polarizable continuum model (CPCM)[11] as implemented in Gaussian 16. The experimental reaction temperature 303.15 K was adopted in the free energy calculations. Transition states were ascertained by vibrational frequency analysis to possess a single mode along the reaction coordinate with a sole imaginary frequency. Mulliken spin densities and charges were analyzed to gain insights into the electronic properties of the key reaction species. Based on the crystal structure, the effects of different DFT functionals and basis sets were systematically investigated. The energy values in the text quote the electronic energies (in solvent) plus zero-point vibrational energies.

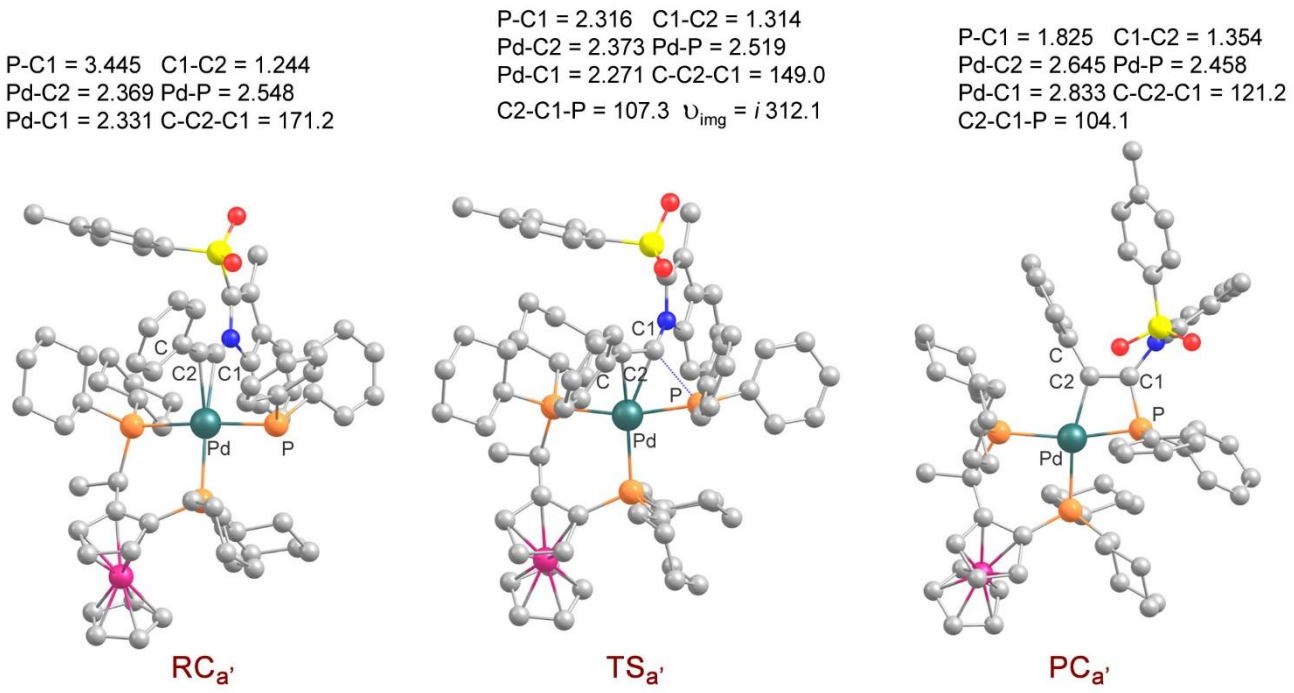
**Table S8**. Various SCF and free energies of the reaction intermediates in the major Route E and in the

minor Route E'. Calculations were done at the UB3LYP/Lanl2tz(Pd,Fe)-6-31+G**(the rest atoms)//Lanl2dz(Pd,Fe)-6-31G*(the rest atoms) level.

| | OPT/B1 | ΔE | OPT +ZPE | ΔE | SPE/B2 | ΔE | SPE+ZPE | ΔE | G | ΔG |
|---|---|---|---|---|---|---|---|---|---|---|
| **$RC_a$** | -4672.234667 | **0.0** | -4670.822885 | **0.0** | -4672.462935 | **0.0** | -4671.051152 | **0.0** | -4670.947707 | **0.0** |
| **$TS_a$** | -4672.200131 | **21.7** | -4670.788405 | **21.6** | -4672.429255 | **21.1** | -4671.017529 | **21.1** | -4670.909829 | **23.8** |
| **$PC_a$** | -4672.294072 | **-37.3** | -4670.880139 | **-35.9** | -4672.524241 | **-38.5** | -4671.110307 | **-37.1** | -4671.004501 | **-35.6** |
| **$RC_{a'}$** | -4672.225888 | **5.5** | -4670.813717 | **5.8** | -4672.452927 | **6.3** | -4671.040756 | **6.5** | -4670.937736 | **6.3** |
| **$TS_{a'}$** | -4672.188160 | **29.2** | -4670.777542 | **28.5** | -4672.416164 | **29.3** | -4671.005546 | **28.6** | -4670.899252 | **30.4** |
| **$PC_{a'}$** | -4672.298729 | **-40.2** | -4670.884686 | **-38.8** | -4672.528285 | **-41.0** | -4671.114242 | **-39.6** | -4671.004262 | **-35.5** |




**Supplementary Figure 2.** The geometries of the reaction intermediates in the major Route E. Hydrogen atoms wre omitted for clarity. Lengths are in Å units, angles are in degree units, and the imaginary frequency is in $cm^{-1}$ units.

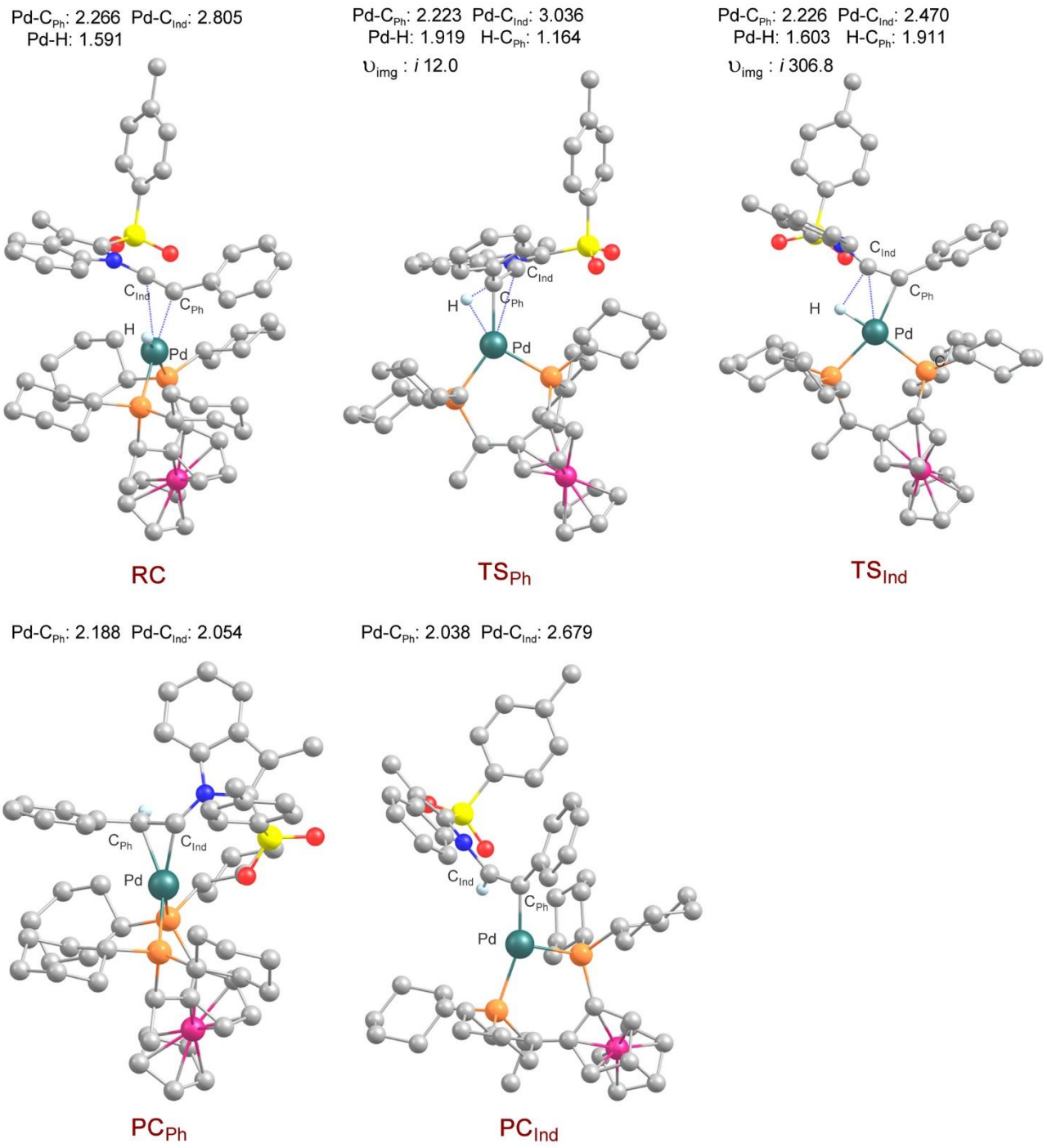



**Supplementary Figure 3.** The geometries of the reaction intermediates in the minor Route E'. Hydrogen atoms wre omitted for clarity. Lengths are in Å units, angles are in degree units, and the imaginary frequency is in $cm^{-1}$ units.

**Table S9**. Various SCF and free energies of the reaction intermediates of the Pd-H addition process in the major Route E. Calculations were done at the UB3LYP/Lanl2tz(Pd,Fe)-6-31+G**(the rest atoms)//Lanl2dz(Pd,Fe)-6-31G*(the rest atoms) level.

| | OPT/B1 | ΔE | OPT +ZPE | ΔE | SPE/B2 | ΔE | SPE+ZPE | ΔE | G | ΔG |
|---|---|---|---|---|---|---|---|---|---|---|
| **RC** | -3868.212190 | **0.0** | -3866.978342 | **0.0** | -3868.412336 | **0.0** | -3867.178488 | **0.0** | -3867.091166 | **0.0** |
| **TS**$_{Ph}$[a] | -3868.187806 | **15.3** | -3866.952425 | **16.3** | -3868.386754 | **16.1** | -3867.151374 | **17.0** | -3867.062813 | **17.8** |
| **TS**$_{Ind}$ | -3868.204146 | **5.0** | -3866.971630 | **4.2** | -3868.406726 | **3.5** | -3867.174209 | **2.7** | -3867.085128 | **3.8** |
| **PC**$_{Ph}$ | -3868.221220 | **-5.7** | -3866.982801 | **-2.8** | -3868.419696 | **-4.6** | -3867.181277 | **-1.8** | -3867.093657 | **-1.6** |
| **PC**$_{Ind}$ | -3868.246938 | **-21.8** | -3867.008233 | **-18.8** | -3868.447352 | **-22.0** | -3867.208647 | **-18.9** | -3867.120597 | **-18.5** |

a. The subscript symbols "Ph" and "Ind" denotes the direction of hydrogen addition to the phenyl or the indole bonded alkynyl carbons.

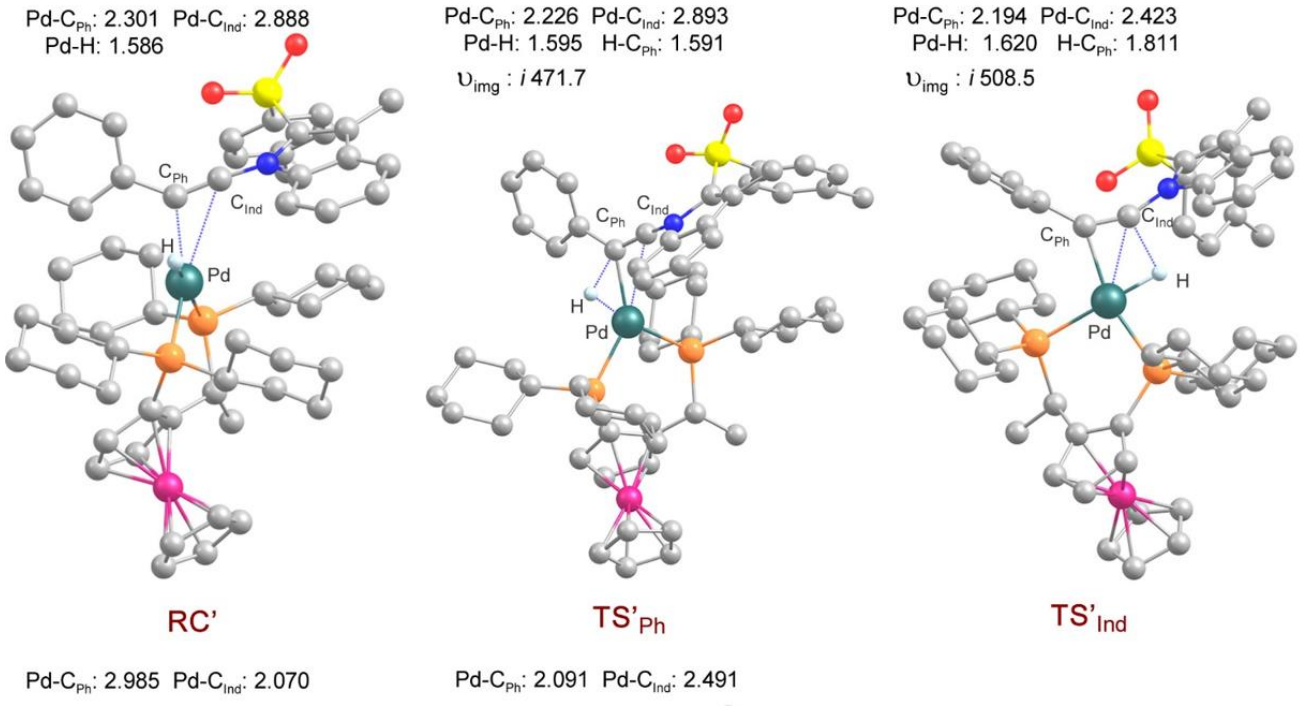


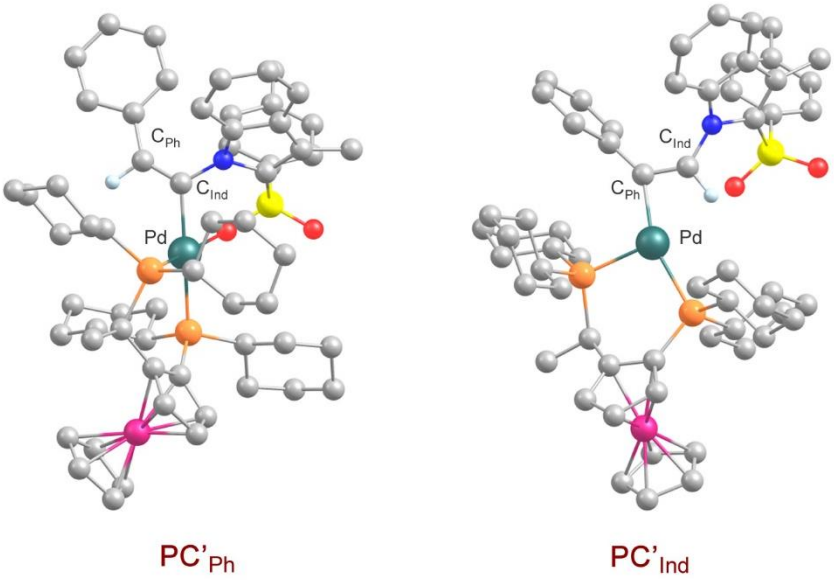

**Supplementary Figure 4.** The geometries of the reaction intermediates of the Pd-H addition process in the major Route E. Hydrogen atoms were omitted for clarity. Lengths are in Å units, angles are in degree units, and the imaginary frequency is in $cm^{-1}$ units. The subscript symbols "Ph" and "Ind" denotes the direction of hydrogen addition to the phenyl or the indole bonded alkynyl carbons.

**Table S10**. Various SCF and free energies of the reaction intermediates of the Pd-H addition process in the major Route E'. Calculations were done at the UB3LYP/Lanl2tz(Pd,Fe)-6-31+G**(the rest atoms)//Lanl2dz(Pd,Fe)-6-31G*(the rest atoms) level.

| | OPT/B1 | ΔE | OPT +ZPE | ΔE | SPE/B2 | ΔE | SPE+ZPE | ΔE | G | ΔG |
|---|---|---|---|---|---|---|---|---|---|---|
| **RC'** | -3868.200596 | **0.0** | -3866.966441 | **0.0** | -3868.401224 | **0.0** | -3867.167069 | **0.0** | -3867.077909 | **0.0** |
| **TS'$_{Ph}$**[a] | -3868.178604 | **13.8** | -3866.946768 | **12.3** | -3868.380451 | **13.0** | -3867.148615 | **11.6** | -3867.056492 | **13.4** |
| **TS'$_{Ind}$** | -3868.196286 | **2.7** | -3866.964337 | **1.3** | -3868.398971 | **1.4** | -3867.167022 | **0.0** | -3867.077546 | **0.2** |
| **PC'$_{Ph}$** | -3868.270064 | **-43.6** | -3867.030293 | **-40.1** | -3868.469346 | **-42.7** | -3867.229575 | **-39.2** | -3867.137168 | **-37.2** |
| **PC'$_{Ind}$** | -3868.238180 | **-23.6** | -3866.999855 | **-21.0** | -3868.438100 | **-23.1** | -3867.199775 | **-20.5** | -3867.112995 | **-22.0** |

a. The subscript symbols "Ph" and "Ind" denotes the direction of hydrogen addition to the phenyl or the indole bonded alkynyl carbons.






**Supplementary Figure 5.** The geometries of the reaction intermediates of the Pd-H addition process in the major Route E'. Hydrogen atoms were omitted for clarity. Lengths are in Å units, angles are in degree units, and the imaginary frequency is in $cm^{-1}$ units. The subscript symbols "Ph" and "Ind" denotes the direction of hydrogen addition to the phenyl or the indole bonded alkynyl carbons.

**DFT calculated Cartesian coordinates of the intermediates**

**1. The Pd-$PPh_2$ addition**

$RC_a$

| | | | |
|---|---|---|---|
| Pd | 0.682972 | -0.154134 | -0.216867 |
| P | 0.691995 | -0.868383 | 2.458024 |
| P | 3.189885 | 0.039939 | -0.213606 |
| P | 0.642182 | 0.929723 | -2.445018 |
| C | -0.548307 | -2.245117 | 2.839378 |
| C | -0.307038 | -3.516710 | 1.998572 |
| C | -0.752274 | -2.611498 | 4.330123 |
| H | -1.488841 | -1.812418 | 2.473263 |
| C | -1.455158 | -4.526924 | 2.171012 |
| H | 0.636784 | -3.992935 | 2.287228 |
| H | -0.213156 | -3.248071 | 0.945312 |
| C | -1.901458 | -3.625323 | 4.490102 |
| H | 0.164234 | -3.044590 | 4.747407 |
| H | -0.971738 | -1.725050 | 4.932554 |
| C | -1.673521 | -4.886993 | 3.646799 |
| H | -1.235730 | -5.428867 | 1.585558 |
| H | -2.375874 | -4.094746 | 1.759103 |
| H | -2.009567 | -3.885614 | 5.550797 |
| H | -2.844550 | -3.150566 | 4.183689 |
| H | -2.525779 | -5.570095 | 3.750083 |
| H | -0.792462 | -5.424629 | 4.028466 |

| | | | |
|---|---|---|---|
| C | 0.290041 | 0.414017 | 3.802483 |
| C | 1.173838 | 1.674860 | 3.728035 |
| C | -1.200714 | 0.813589 | 3.814751 |
| H | 0.518501 | -0.104733 | 4.741968 |
| C | 0.848363 | 2.673794 | 4.855214 |
| H | 1.023326 | 2.168448 | 2.758254 |
| H | 2.229192 | 1.395413 | 3.795260 |
| C | -1.511754 | 1.787773 | 4.965140 |
| H | -1.452462 | 1.297822 | 2.867187 |
| H | -1.844907 | -0.066788 | 3.900436 |
| C | -0.639090 | 3.046633 | 4.886581 |
| H | 1.467895 | 3.571287 | 4.733413 |
| H | 1.128154 | 2.233064 | 5.823071 |
| H | -2.575281 | 2.056194 | 4.935179 |
| H | -1.342283 | 1.282731 | 5.927560 |
| H | -0.845506 | 3.708623 | 5.736677 |
| H | -0.895127 | 3.609320 | 3.977747 |
| C | 4.161408 | -1.459169 | -0.838047 |
| C | 3.428884 | -2.778161 | -0.497028 |
| C | 4.498593 | -1.465782 | -2.345723 |
| H | 5.105292 | -1.429559 | -0.273806 |
| C | 4.295097 | -4.002219 | -0.840273 |
| H | 2.503429 | -2.811204 | -1.086716 |
| H | 3.138448 | -2.816598 | 0.554306 |
| C | 5.387057 | -2.673867 | -2.696348 |
| H | 3.571300 | -1.525723 | -2.921537 |
| H | 5.001227 | -0.549261 | -2.658327 |
| C | 4.720242 | -4.002068 | -2.314563 |
| H | 3.741376 | -4.918892 | -0.600718 |
| H | 5.188311 | -4.000524 | -0.198722 |
| H | 5.611136 | -2.654824 | -3.770054 |
| H | 6.350167 | -2.581713 | -2.172910 |
| H | 5.396669 | -4.841605 | -2.517425 |
| H | 3.832941 | -4.152340 | -2.946487 |
| C | 3.788541 | 1.573883 | -1.140392 |
| C | 3.164811 | 2.858289 | -0.545978 |
| C | 5.303725 | 1.801671 | -1.377001 |
| H | 3.331671 | 1.426661 | -2.128806 |
| C | 3.392827 | 4.063869 | -1.475677 |
| H | 3.610091 | 3.066833 | 0.436507 |
| H | 2.091086 | 2.721530 | -0.390629 |
| C | 5.509813 | 2.977711 | -2.350129 |
| H | 5.804645 | 2.045674 | -0.437373 |

| | | | |
|---|---|---|---|
| H | 5.797369 | 0.908408 | -1.765997 |
| C | 4.877873 | 4.267234 | -1.807460 |
| H | 2.978792 | 4.967593 | -1.010650 |
| H | 2.828074 | 3.901598 | -2.404424 |
| H | 6.583799 | 3.122619 | -2.520789 |
| H | 5.067118 | 2.728997 | -3.325436 |
| H | 4.994669 | 5.083534 | -2.530785 |
| H | 5.415137 | 4.574751 | -0.898269 |
| C | -1.072415 | 1.081037 | -3.118763 |
| C | -1.755767 | 2.271809 | -2.795572 |
| C | -1.687514 | 0.192141 | -4.020654 |
| C | -3.012244 | 2.552141 | -3.332602 |
| H | -1.288988 | 2.995633 | -2.134958 |
| C | -2.941797 | 0.475785 | -4.561977 |
| H | -1.182693 | -0.719508 | -4.317535 |
| C | -3.611909 | 1.651957 | -4.216308 |
| H | -3.514899 | 3.479342 | -3.071288 |
| H | -3.394983 | -0.224246 | -5.258758 |
| H | -4.587208 | 1.870421 | -4.642207 |
| C | 1.435769 | -0.089601 | -3.777611 |
| C | 2.270663 | 0.613573 | -4.665844 |
| C | 1.232884 | -1.461282 | -4.003344 |
| C | 2.878327 | -0.031679 | -5.746175 |
| H | 2.439110 | 1.677535 | -4.518620 |
| C | 1.837073 | -2.106522 | -5.084777 |
| H | 0.601456 | -2.033420 | -3.334322 |
| C | 2.663111 | -1.394535 | -5.958575 |
| H | 3.516727 | 0.532522 | -6.420560 |
| H | 1.661133 | -3.167388 | -5.242588 |
| H | 3.133193 | -1.897813 | -6.798814 |
| C | 3.772413 | 0.261193 | 1.597127 |
| H | 3.073272 | 1.009415 | 1.976429 |
| C | 5.196883 | 0.821482 | 1.768304 |
| H | 5.946780 | 0.263944 | 1.198910 |
| H | 5.250342 | 1.868440 | 1.469379 |
| H | 5.471608 | 0.764129 | 2.825950 |
| Fe | 3.777269 | -1.391790 | 4.446377 |
| C | 4.050288 | -3.090331 | 3.303258 |
| C | 4.626696 | -1.967593 | 2.645316 |
| C | 2.660287 | -2.834839 | 3.465338 |
| C | 3.590693 | -1.017777 | 2.371746 |
| C | 2.346811 | -1.555499 | 2.877395 |
| H | 4.582431 | -3.957652 | 3.671098 |

| | | | |
|---|---|---|---|
| H | 5.676777 | -1.841571 | 2.420428 |
| H | 1.969697 | -3.495269 | 3.964251 |
| C | 3.116473 | -0.311956 | 6.123277 |
| C | 3.477201 | -1.639245 | 6.498861 |
| C | 4.265455 | 0.318486 | 5.556626 |
| C | 4.853137 | -1.829640 | 6.168971 |
| C | 5.340305 | -0.620070 | 5.588058 |
| H | 2.140944 | 0.135767 | 6.244682 |
| H | 2.818232 | -2.379784 | 6.932628 |
| H | 4.313448 | 1.328096 | 5.170781 |
| H | 5.417729 | -2.743517 | 6.299166 |
| H | 6.340822 | -0.456993 | 5.209268 |
| C | -1.355548 | -1.181666 | -0.701067 |
| C | -1.558512 | -0.085761 | -0.136017 |
| C | -1.512239 | -2.363593 | -1.500538 |
| C | -0.528573 | -3.367958 | -1.585774 |
| C | -2.726399 | -2.536743 | -2.201889 |
| C | -0.751401 | -4.514421 | -2.345640 |
| H | 0.411671 | -3.237093 | -1.063675 |
| C | -2.944474 | -3.693827 | -2.945692 |
| H | -3.495478 | -1.776436 | -2.139764 |
| C | -1.960966 | -4.683715 | -3.024487 |
| H | 0.019742 | -5.277055 | -2.403759 |
| H | -3.887347 | -3.818657 | -3.470090 |
| H | -2.136040 | -5.581105 | -3.610706 |
| C | -3.220892 | 2.907939 | 0.943761 |
| C | -2.034457 | 2.215393 | 0.622099 |
| C | -0.807302 | 2.875311 | 0.521473 |
| C | -0.789851 | 4.248659 | 0.745183 |
| C | -1.966039 | 4.956591 | 1.065334 |
| C | -3.182118 | 4.295329 | 1.168469 |
| C | -4.304098 | 1.958231 | 0.979732 |
| C | -3.749657 | 0.729058 | 0.720854 |
| H | 0.101723 | 2.338254 | 0.278956 |
| H | 0.152482 | 4.783646 | 0.671407 |
| H | -1.916214 | 6.027848 | 1.234698 |
| H | -4.087605 | 4.838882 | 1.420196 |
| N | -2.349585 | 0.852435 | 0.467461 |
| C | -5.731244 | 2.323872 | 1.265450 |
| H | -5.967128 | 2.234296 | 2.332564 |
| H | -5.910214 | 3.362790 | 0.973195 |
| H | -6.435579 | 1.698347 | 0.714198 |
| S | -4.581917 | -0.856436 | 0.704156 |

| | | | |
|---|---|---|---|
| O | -5.296264 | -1.006592 | -0.576997 |
| O | -3.581498 | -1.865466 | 1.101866 |
| C | -5.803614 | -0.766995 | 2.009631 |
| C | -5.391336 | -0.657321 | 3.341594 |
| C | -7.151699 | -0.908981 | 1.679947 |
| C | -6.352656 | -0.667864 | 4.347819 |
| H | -4.339177 | -0.560018 | 3.589752 |
| C | -8.098904 | -0.927293 | 2.703616 |
| H | -7.448765 | -1.003039 | 0.641115 |
| C | -7.718878 | -0.806777 | 4.047607 |
| H | -6.039511 | -0.573209 | 5.384171 |
| H | -9.150194 | -1.036442 | 2.451715 |
| C | -8.746564 | -0.851256 | 5.151687 |
| H | -8.810436 | -1.859662 | 5.580904 |
| H | -8.487153 | -0.168192 | 5.967167 |
| H | -9.742263 | -0.587216 | 4.783368 |

$TS_a$

| | | | |
|---|---|---|---|
| Pd | 0.736644 | -0.534736 | 0.255381 |
| P | 1.128758 | -1.288132 | 2.624108 |
| P | 3.081203 | -0.311621 | -0.218528 |
| P | -0.467599 | 0.318213 | -1.706287 |
| C | 0.033674 | -2.742725 | 3.146466 |
| C | 0.408603 | -4.066195 | 2.438770 |
| C | -0.109387 | -2.950591 | 4.676174 |
| H | -0.948079 | -2.437664 | 2.759966 |
| C | -0.586097 | -5.189518 | 2.784039 |
| H | 1.412335 | -4.384610 | 2.735890 |
| H | 0.432086 | -3.919139 | 1.356412 |
| C | -1.107635 | -4.081200 | 4.987494 |
| H | 0.858472 | -3.200598 | 5.125718 |
| H | -0.447979 | -2.034954 | 5.167992 |
| C | -0.715893 | -5.393640 | 4.298254 |
| H | -0.261281 | -6.117146 | 2.296457 |
| H | -1.568814 | -4.942608 | 2.364185 |
| H | -1.167749 | -4.216653 | 6.074687 |
| H | -2.109863 | -3.778486 | 4.652000 |
| H | -1.458210 | -6.171790 | 4.514880 |
| H | 0.241290 | -5.750085 | 4.707844 |
| C | 0.714197 | 0.058206 | 3.876734 |
| C | 1.530777 | 1.348875 | 3.672657 |
| C | -0.792510 | 0.389438 | 3.916110 |
| H | 1.005770 | -0.380605 | 4.840462 |
| C | 1.221739 | 2.385316 | 4.770087 |

| | | | |
|---|---|---|---|
| H | 1.287517 | 1.778736 | 2.692362 |
| H | 2.601496 | 1.123329 | 3.677113 |
| C | -1.097761 | 1.402534 | 5.034040 |
| H | -1.089823 | 0.814385 | 2.953047 |
| H | -1.400507 | -0.508446 | 4.060055 |
| C | -0.278819 | 2.690353 | 4.872529 |
| H | 1.786416 | 3.304809 | 4.570439 |
| H | 1.578753 | 2.006794 | 5.738773 |
| H | -2.170704 | 1.630144 | 5.032515 |
| H | -0.876067 | 0.943770 | 6.008987 |
| H | -0.467236 | 3.367973 | 5.714734 |
| H | -0.605401 | 3.216008 | 3.966078 |
| C | 3.774398 | -1.749748 | -1.212752 |
| C | 3.593233 | -3.124874 | -0.530174 |
| C | 3.165909 | -1.810603 | -2.629867 |
| H | 4.851249 | -1.544853 | -1.301355 |
| C | 4.243076 | -4.244139 | -1.364220 |
| H | 2.519732 | -3.328138 | -0.416806 |
| H | 4.023586 | -3.127223 | 0.471781 |
| C | 3.822400 | -2.916022 | -3.474986 |
| H | 2.095043 | -2.022478 | -2.530655 |
| H | 3.252583 | -0.850640 | -3.149115 |
| C | 3.699656 | -4.287418 | -2.798011 |
| H | 4.080358 | -5.206736 | -0.864040 |
| H | 5.331123 | -4.085772 | -1.390559 |
| H | 3.360143 | -2.936337 | -4.469733 |
| H | 4.883751 | -2.672632 | -3.627744 |
| H | 4.227670 | -5.049748 | -3.383549 |
| H | 2.641028 | -4.585326 | -2.776124 |
| C | 3.465026 | 1.253033 | -1.210785 |
| C | 3.346949 | 2.528547 | -0.342509 |
| C | 4.779001 | 1.279392 | -2.032546 |
| H | 2.638888 | 1.285340 | -1.929242 |
| C | 3.420758 | 3.797283 | -1.210758 |
| H | 4.160023 | 2.562531 | 0.392728 |
| H | 2.414633 | 2.519954 | 0.230571 |
| C | 4.848420 | 2.556060 | -2.893290 |
| H | 5.650931 | 1.252192 | -1.372356 |
| H | 4.855758 | 0.403532 | -2.683378 |
| C | 4.707787 | 3.828509 | -2.046888 |
| H | 3.365409 | 4.682643 | -0.564679 |
| H | 2.547875 | 3.834536 | -1.876234 |
| H | 5.797267 | 2.565709 | -3.443800 |

| | | | |
|---|---|---|---|
| H | 4.047360 | 2.530087 | -3.644159 |
| H | 4.718216 | 4.714925 | -2.692641 |
| H | 5.575095 | 3.918505 | -1.376365 |
| C | -1.174852 | -0.872800 | -2.925282 |
| C | -2.568604 | -1.048262 | -2.955167 |
| C | -0.394902 | -1.521784 | -3.897537 |
| C | -3.160076 | -1.855392 | -3.929356 |
| H | -3.194845 | -0.572789 | -2.210401 |
| C | -0.989662 | -2.321655 | -4.873538 |
| H | 0.681860 | -1.407811 | -3.904589 |
| C | -2.375615 | -2.493186 | -4.891116 |
| H | -4.239125 | -1.981733 | -3.932274 |
| H | -0.367965 | -2.811823 | -5.617844 |
| H | -2.838836 | -3.118577 | -5.649134 |
| C | 0.044587 | 1.727255 | -2.821951 |
| C | -0.621187 | 2.957808 | -2.692097 |
| C | 0.981041 | 1.579410 | -3.861827 |
| C | -0.352880 | 4.011979 | -3.569326 |
| H | -1.365741 | 3.090634 | -1.915228 |
| C | 1.241304 | 2.630567 | -4.742631 |
| H | 1.502742 | 0.639271 | -4.003163 |
| C | 0.578801 | 3.852323 | -4.595900 |
| H | -0.883430 | 4.953028 | -3.454099 |
| H | 1.959396 | 2.491751 | -5.546304 |
| H | 0.782008 | 4.669107 | -5.282554 |
| C | 4.137288 | -0.145311 | 1.362542 |
| H | 3.659463 | 0.708607 | 1.852861 |
| C | 5.612226 | 0.221980 | 1.107787 |
| H | 6.123484 | -0.507886 | 0.472893 |
| H | 5.712506 | 1.203207 | 0.646953 |
| H | 6.137405 | 0.257430 | 2.067582 |
| Fe | 4.417922 | -1.436095 | 4.344939 |
| C | 4.629585 | -3.271950 | 3.418651 |
| C | 5.111111 | -2.241188 | 2.565425 |
| C | 3.257934 | -3.013471 | 3.680938 |
| C | 4.032337 | -1.344563 | 2.272617 |
| C | 2.852813 | -1.833824 | 2.953565 |
| H | 5.217195 | -4.073899 | 3.845314 |
| H | 6.131252 | -2.137619 | 2.224957 |
| H | 2.637145 | -3.607374 | 4.330972 |
| C | 3.876895 | -0.187483 | 5.941156 |
| C | 4.364102 | -1.433403 | 6.432965 |
| C | 4.912556 | 0.423595 | 5.170166 |

| | | | |
|---|---|---|---|
| C | 5.704671 | -1.593846 | 5.968910 |
| C | 6.043921 | -0.445973 | 5.190930 |
| H | 2.890492 | 0.216532 | 6.115904 |
| H | 3.806703 | -2.144815 | 7.027918 |
| H | 4.851635 | 1.374804 | 4.658072 |
| H | 6.339087 | -2.453017 | 6.142657 |
| H | 6.984156 | -0.281335 | 4.681068 |
| C | -1.637859 | -1.363714 | 0.326130 |
| C | -1.571257 | -0.087382 | 0.067788 |
| C | -1.692436 | -2.737817 | -0.114864 |
| C | -0.695278 | -3.369631 | -0.893719 |
| C | -2.825288 | -3.505745 | 0.245334 |
| C | -0.829933 | -4.694197 | -1.302215 |
| H | 0.185731 | -2.806410 | -1.180180 |
| C | -2.973813 | -4.816541 | -0.205201 |
| H | -3.587017 | -3.056468 | 0.869203 |
| C | -1.977620 | -5.421585 | -0.974952 |
| H | -0.044330 | -5.152665 | -1.897294 |
| H | -3.866073 | -5.374155 | 0.066569 |
| H | -2.090770 | -6.447975 | -1.312366 |
| C | -2.603654 | 3.102740 | 1.536166 |
| C | -1.641065 | 2.299289 | 0.878369 |
| C | -0.363028 | 2.801105 | 0.599212 |
| C | -0.086363 | 4.121907 | 0.936979 |
| C | -1.047858 | 4.939864 | 1.561956 |
| C | -2.302109 | 4.434380 | 1.872848 |
| C | -3.781913 | 2.308633 | 1.751696 |
| C | -3.514704 | 1.077585 | 1.192393 |
| H | 0.392350 | 2.186350 | 0.130642 |
| H | 0.894468 | 4.529644 | 0.710097 |
| H | -0.800221 | 5.968103 | 1.807839 |
| H | -3.040851 | 5.057796 | 2.367461 |
| N | -2.197603 | 1.036398 | 0.663171 |
| C | -4.997380 | 2.825187 | 2.468981 |
| H | -5.457011 | 2.070270 | 3.108730 |
| H | -4.711833 | 3.666862 | 3.106707 |
| H | -5.766205 | 3.183010 | 1.774644 |
| S | -4.642067 | -0.304772 | 1.008512 |
| O | -4.463587 | -0.824600 | -0.361506 |
| O | -4.499672 | -1.215376 | 2.161636 |
| C | -6.292779 | 0.385677 | 1.066664 |
| C | -7.116478 | 0.084613 | 2.151528 |
| C | -6.768514 | 1.123368 | -0.022187 |

| | | | |
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| C | -8.431309 | 0.549898 | 2.150690 |
| H | -6.732143 | -0.506111 | 2.975931 |
| C | -8.080780 | 1.586445 | 0.000008 |
| H | -6.125769 | 1.328691 | -0.872040 |
| C | -8.932907 | 1.306973 | 1.082476 |
| H | -9.077419 | 0.318634 | 2.993177 |
| H | -8.454889 | 2.166486 | -0.839501 |
| C | -10.363854 | 1.786334 | 1.074904 |
| H | -10.991006 | 1.124630 | 0.463275 |
| H | -10.787272 | 1.801530 | 2.083482 |
| H | -10.445923 | 2.792300 | 0.650119 |

$PC_a$

| | | | |
|---|---|---|---|
| Pd | 0.788409 | -0.454453 | 0.973482 |
| P | 1.828022 | -1.500523 | 2.939248 |
| P | 2.955324 | -0.185553 | -0.192822 |
| P | -0.721997 | 0.373742 | -0.714125 |
| C | 0.701685 | -2.825413 | 3.659173 |
| C | 0.355856 | -3.912253 | 2.611654 |
| C | 1.146549 | -3.419427 | 5.017931 |
| H | -0.224460 | -2.268173 | 3.842613 |
| C | -0.614251 | -4.967725 | 3.173262 |
| H | 1.263499 | -4.417044 | 2.265020 |
| H | -0.087819 | -3.432337 | 1.730537 |
| C | 0.135254 | -4.462606 | 5.527386 |
| H | 2.133614 | -3.888124 | 4.940134 |
| H | 1.243345 | -2.623002 | 5.763502 |
| C | -0.112128 | -5.567722 | 4.492921 |
| H | -0.761517 | -5.754363 | 2.422662 |
| H | -1.594536 | -4.505969 | 3.344166 |
| H | 0.501647 | -4.888417 | 6.469770 |
| H | -0.816127 | -3.961535 | 5.756191 |
| H | -0.840018 | -6.291907 | 4.878821 |
| H | 0.821096 | -6.124243 | 4.318597 |
| C | 2.222981 | -0.382925 | 4.413620 |
| C | 3.245139 | 0.728333 | 4.108136 |
| C | 0.946065 | 0.236330 | 5.010121 |
| H | 2.669102 | -1.062180 | 5.151260 |
| C | 3.545868 | 1.586201 | 5.352007 |
| H | 2.848207 | 1.376585 | 3.314748 |
| H | 4.177941 | 0.290568 | 3.744386 |
| C | 1.250840 | 1.075606 | 6.262720 |
| H | 0.486987 | 0.882111 | 4.251275 |
| H | 0.207149 | -0.530836 | 5.256503 |

| | | | |
|---|---|---|---|
| C | 2.271806 | 2.179997 | 5.964721 |
| H | 4.250225 | 2.381977 | 5.079122 |
| H | 4.053400 | 0.967432 | 6.106209 |
| H | 0.317275 | 1.506413 | 6.645212 |
| H | 1.639991 | 0.419133 | 7.054562 |
| H | 2.512830 | 2.737234 | 6.878098 |
| H | 1.831142 | 2.902267 | 5.261676 |
| C | 3.296730 | -1.253249 | -1.710174 |
| C | 3.025463 | -2.753444 | -1.447780 |
| C | 2.516011 | -0.815669 | -2.968847 |
| H | 4.369013 | -1.126441 | -1.918240 |
| C | 3.424937 | -3.610481 | -2.662388 |
| H | 1.955226 | -2.886456 | -1.243635 |
| H | 3.561900 | -3.103635 | -0.564424 |
| C | 2.925168 | -1.657885 | -4.191310 |
| H | 1.443329 | -0.953561 | -2.787047 |
| H | 2.672251 | 0.243773 | -3.190564 |
| C | 2.712689 | -3.157315 | -3.943719 |
| H | 3.201227 | -4.663944 | -2.452577 |
| H | 4.513625 | -3.545058 | -2.805615 |
| H | 2.351387 | -1.329862 | -5.067093 |
| H | 3.983838 | -1.468125 | -4.421170 |
| H | 3.068209 | -3.738450 | -4.803541 |
| H | 1.635903 | -3.357623 | -3.850252 |
| C | 3.065018 | 1.611476 | -0.760196 |
| C | 2.968099 | 2.574276 | 0.446010 |
| C | 4.220208 | 2.039457 | -1.695765 |
| H | 2.134686 | 1.726372 | -1.331220 |
| C | 2.801539 | 4.033786 | -0.014116 |
| H | 3.878366 | 2.493811 | 1.056983 |
| H | 2.125660 | 2.289091 | 1.089409 |
| C | 4.010562 | 3.488559 | -2.173796 |
| H | 5.177387 | 1.989093 | -1.169139 |
| H | 4.304746 | 1.371091 | -2.558533 |
| C | 3.910335 | 4.458274 | -0.987608 |
| H | 2.790487 | 4.693277 | 0.862898 |
| H | 1.824669 | 4.144475 | -0.504247 |
| H | 4.838294 | 3.776924 | -2.833594 |
| H | 3.091919 | 3.546354 | -2.774616 |
| H | 3.727902 | 5.479228 | -1.344882 |
| H | 4.873508 | 4.479562 | -0.456673 |
| C | -1.236431 | -0.908958 | -1.925048 |
| C | -0.903491 | -2.243994 | -1.651532 |

| | | | |
|---|---|---|---|
| C | -1.967982 | -0.613281 | -3.085296 |
| C | -1.294442 | -3.264758 | -2.517585 |
| H | -0.344683 | -2.482920 | -0.751022 |
| C | -2.352521 | -1.635289 | -3.954346 |
| H | -2.242471 | 0.409617 | -3.317418 |
| C | -2.017126 | -2.961353 | -3.674014 |
| H | -1.032811 | -4.294351 | -2.290552 |
| H | -2.921183 | -1.392786 | -4.847458 |
| H | -2.318293 | -3.754540 | -4.352345 |
| C | -0.602017 | 1.928117 | -1.689604 |
| C | -1.042036 | 3.153970 | -1.165795 |
| C | -0.029030 | 1.914230 | -2.976141 |
| C | -0.923297 | 4.330112 | -1.910274 |
| H | -1.486914 | 3.204953 | -0.181118 |
| C | 0.090084 | 3.091085 | -3.715789 |
| H | 0.310843 | 0.982835 | -3.413873 |
| C | -0.357929 | 4.303939 | -3.185832 |
| H | -1.281308 | 5.265134 | -1.489053 |
| H | 0.527207 | 3.056405 | -4.709595 |
| H | -0.269378 | 5.218879 | -3.764346 |
| C | 4.440805 | -0.459500 | 0.969555 |
| H | 4.235117 | 0.268448 | 1.756471 |
| C | 5.834180 | -0.138943 | 0.398112 |
| H | 6.041389 | -0.656702 | -0.543203 |
| H | 5.958937 | 0.930904 | 0.232151 |
| H | 6.595143 | -0.448268 | 1.122209 |
| Fe | 5.329486 | -2.627792 | 3.287910 |
| C | 4.848585 | -4.090791 | 1.909043 |
| C | 5.278726 | -2.913461 | 1.236038 |
| C | 3.702850 | -3.757463 | 2.680377 |
| C | 4.386491 | -1.843778 | 1.565456 |
| C | 3.383626 | -2.365228 | 2.469906 |
| H | 5.339499 | -5.054688 | 1.888003 |
| H | 6.150046 | -2.834939 | 0.601113 |
| H | 3.178613 | -4.445453 | 3.322777 |
| C | 5.594168 | -1.808465 | 5.202489 |
| C | 5.838031 | -3.213123 | 5.227773 |
| C | 6.510954 | -1.213279 | 4.283520 |
| C | 6.910284 | -3.487911 | 4.326165 |
| C | 7.326124 | -2.252925 | 3.743498 |
| H | 4.842634 | -1.287738 | 5.778276 |
| H | 5.291283 | -3.944171 | 5.808591 |
| H | 6.576860 | -0.161873 | 4.036982 |

| | | | |
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| H | 7.310964 | -4.465874 | 4.094044 |
| H | 8.102200 | -2.132438 | 2.999024 |
| C | -1.248582 | -0.269595 | 1.656671 |
| C | -1.871486 | 0.460482 | 0.696566 |
| C | -2.016998 | -0.696470 | 2.855403 |
| C | -2.695929 | -1.928904 | 2.801995 |
| C | -2.190910 | 0.110696 | 3.992077 |
| C | -3.504980 | -2.345288 | 3.860160 |
| H | -2.610541 | -2.542845 | 1.911709 |
| C | -2.994809 | -0.312460 | 5.052371 |
| H | -1.715849 | 1.083618 | 4.040542 |
| C | -3.650468 | -1.543960 | 4.995116 |
| H | -4.032256 | -3.292556 | 3.789028 |
| H | -3.118080 | 0.331539 | 5.918992 |
| H | -4.280907 | -1.868146 | 5.818137 |
| C | -4.559195 | 2.736374 | 1.644404 |
| C | -3.202133 | 2.341155 | 1.557633 |
| C | -2.177995 | 3.112171 | 2.131733 |
| C | -2.538287 | 4.296538 | 2.764136 |
| C | -3.885068 | 4.713521 | 2.840223 |
| C | -4.896851 | 3.941256 | 2.289719 |
| C | -5.351616 | 1.710945 | 1.029382 |
| C | -4.460854 | 0.759161 | 0.578188 |
| H | -1.142298 | 2.790483 | 2.097036 |
| H | -1.764601 | 4.910651 | 3.216328 |
| H | -4.127378 | 5.644734 | 3.343593 |
| H | -5.934308 | 4.255239 | 2.359587 |
| N | -3.128782 | 1.133614 | 0.865601 |
| C | -6.847956 | 1.729093 | 0.920779 |
| H | -7.261085 | 0.729262 | 0.780110 |
| H | -7.287667 | 2.150247 | 1.831229 |
| H | -7.174330 | 2.356468 | 0.081166 |
| S | -4.937599 | -0.797915 | -0.140878 |
| O | -3.708578 | -1.558810 | -0.426242 |
| O | -5.964493 | -1.417770 | 0.716495 |
| C | -5.745370 | -0.348262 | -1.682786 |
| C | -6.844942 | -1.108514 | -2.088105 |
| C | -5.260454 | 0.690153 | -2.481053 |
| C | -7.454891 | -0.824654 | -3.308757 |
| H | -7.224937 | -1.897355 | -1.447949 |
| C | -5.888211 | 0.964874 | -3.694974 |
| H | -4.421736 | 1.296040 | -2.152911 |
| C | -6.987881 | 0.210497 | -4.132323 |

| | | | |
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| H | -8.314775 | -1.411396 | -3.621105 |
| H | -5.522517 | 1.783700 | -4.309119 |
| C | -7.644110 | 0.496442 | -5.461488 |
| H | -7.215699 | -0.134591 | -6.251356 |
| H | -8.718712 | 0.290267 | -5.429381 |
| H | -7.502387 | 1.538972 | -5.762928 |

$RC_{a'}$

| | | | |
|---|---|---|---|
| Pd | -0.075062 | 0.462493 | -0.054718 |
| P | -0.154413 | -0.290712 | 2.345938 |
| P | 2.675771 | 0.629472 | 0.100652 |
| P | -2.623104 | 0.483035 | -0.046107 |
| C | -1.493727 | -1.595403 | 2.612965 |
| C | -1.190953 | -2.932870 | 1.898206 |
| C | -1.966570 | -1.837429 | 4.067428 |
| H | -2.338835 | -1.136257 | 2.081045 |
| C | -2.414759 | -3.865162 | 1.932391 |
| H | -0.350741 | -3.444285 | 2.375850 |
| H | -0.878413 | -2.747534 | 0.864614 |
| C | -3.183039 | -2.782818 | 4.086898 |
| H | -1.164296 | -2.274013 | 4.673545 |
| H | -2.240556 | -0.895818 | 4.552479 |
| C | -2.893588 | -4.108499 | 3.370478 |
| H | -2.159920 | -4.816498 | 1.448483 |
| H | -3.230331 | -3.421901 | 1.345393 |
| H | -3.482120 | -2.965002 | 5.126548 |
| H | -4.032433 | -2.283657 | 3.598696 |
| H | -3.789817 | -4.740705 | 3.369279 |
| H | -2.120515 | -4.661252 | 3.924698 |
| C | -0.612061 | 1.078917 | 3.567737 |
| C | 0.409108 | 2.232149 | 3.609527 |
| C | -2.028496 | 1.648439 | 3.345917 |
| H | -0.586781 | 0.570579 | 4.540365 |
| C | 0.042079 | 3.280453 | 4.678637 |
| H | 0.448855 | 2.717542 | 2.625348 |
| H | 1.408695 | 1.842448 | 3.819440 |
| C | -2.397346 | 2.651367 | 4.452999 |
| H | -2.058891 | 2.159402 | 2.376907 |
| H | -2.779918 | 0.855141 | 3.298304 |
| C | -1.390578 | 3.806311 | 4.519881 |
| H | 0.762050 | 4.107278 | 4.635847 |
| H | 0.146824 | 2.831865 | 5.676403 |
| H | -3.409295 | 3.035507 | 4.274605 |
| H | -2.427021 | 2.130584 | 5.421222 |

| | | | |
|---|---|---|---|
| H | -1.637176 | 4.483838 | 5.346280 |
| H | -1.465276 | 4.400299 | 3.597488 |
| C | 3.789302 | -0.572579 | -0.849369 |
| C | 3.739563 | -2.031943 | -0.347835 |
| C | 3.531996 | -0.531564 | -2.372888 |
| H | 4.809447 | -0.205323 | -0.672584 |
| C | 4.744458 | -2.916026 | -1.109408 |
| H | 2.728733 | -2.438510 | -0.477795 |
| H | 3.956179 | -2.083672 | 0.719903 |
| C | 4.553923 | -1.402558 | -3.125144 |
| H | 2.525565 | -0.906977 | -2.581479 |
| H | 3.564624 | 0.492137 | -2.760083 |
| C | 4.533761 | -2.853710 | -2.627187 |
| H | 4.662611 | -3.950007 | -0.751260 |
| H | 5.765185 | -2.582801 | -0.870377 |
| H | 4.339303 | -1.364246 | -4.198887 |
| H | 5.561548 | -0.981980 | -2.989037 |
| H | 5.301452 | -3.444623 | -3.142162 |
| H | 3.564633 | -3.307842 | -2.879469 |
| C | 3.297512 | 2.339889 | -0.492679 |
| C | 3.055330 | 3.441229 | 0.566129 |
| C | 4.748817 | 2.440202 | -1.025541 |
| H | 2.631934 | 2.553548 | -1.340258 |
| C | 3.350556 | 4.843757 | 0.006358 |
| H | 3.708053 | 3.272412 | 1.431482 |
| H | 2.025187 | 3.404924 | 0.931631 |
| C | 5.030703 | 3.845128 | -1.590765 |
| H | 5.465848 | 2.233517 | -0.222673 |
| H | 4.937717 | 1.702698 | -1.809244 |
| C | 4.776232 | 4.942451 | -0.550333 |
| H | 3.193866 | 5.589021 | 0.796060 |
| H | 2.630398 | 5.074909 | -0.788816 |
| H | 6.066530 | 3.888194 | -1.950280 |
| H | 4.387281 | 4.015592 | -2.466670 |
| H | 4.945220 | 5.932703 | -0.991237 |
| H | 5.499501 | 4.837584 | 0.271829 |
| C | -3.192521 | 2.072676 | -0.798402 |
| C | -3.772955 | 3.009450 | 0.077366 |
| C | -3.159285 | 2.381365 | -2.172963 |
| C | -4.296152 | 4.214071 | -0.397252 |
| H | -3.838923 | 2.783740 | 1.137982 |
| C | -3.676935 | 3.586294 | -2.646887 |
| H | -2.738995 | 1.674436 | -2.880271 |

| | | | |
|---|---|---|---|
| C | -4.244522 | 4.507538 | -1.760598 |
| H | -4.749109 | 4.916805 | 0.296708 |
| H | -3.642253 | 3.803174 | -3.711084 |
| H | -4.651511 | 5.443307 | -2.133636 |
| C | -3.366568 | -0.742952 | -1.208920 |
| C | -4.548539 | -0.448407 | -1.923573 |
| C | -2.930670 | -2.081767 | -1.206035 |
| C | -5.247010 | -1.446003 | -2.604811 |
| H | -4.941266 | 0.561030 | -1.936451 |
| C | -3.626181 | -3.077369 | -1.889918 |
| H | -2.026083 | -2.348315 | -0.676515 |
| C | -4.790296 | -2.764945 | -2.595598 |
| H | -6.154704 | -1.186354 | -3.143071 |
| H | -3.252938 | -4.097431 | -1.874133 |
| H | -5.335816 | -3.539417 | -3.127345 |
| C | 3.272797 | 0.545046 | 1.911947 |
| H | 2.775111 | 1.418948 | 2.341385 |
| C | 4.789397 | 0.732951 | 2.103577 |
| H | 5.374738 | -0.040594 | 1.597650 |
| H | 5.122529 | 1.700585 | 1.728555 |
| H | 5.031403 | 0.691368 | 3.170965 |
| Fe | 2.596646 | -0.957053 | 4.736431 |
| C | 2.831582 | -2.740913 | 3.724837 |
| C | 3.626447 | -1.731644 | 3.117454 |
| C | 1.478531 | -2.318212 | 3.660853 |
| C | 2.773044 | -0.683526 | 2.641498 |
| C | 1.407346 | -1.053340 | 2.964630 |
| H | 3.195411 | -3.637468 | 4.208800 |
| H | 4.705313 | -1.738915 | 3.059877 |
| H | 0.650198 | -2.858516 | 4.086114 |
| C | 1.828822 | 0.254735 | 6.269898 |
| C | 2.019861 | -1.076363 | 6.742279 |
| C | 3.091553 | 0.759130 | 5.832042 |
| C | 3.403665 | -1.396947 | 6.599878 |
| C | 4.065469 | -0.262753 | 6.040148 |
| H | 0.888402 | 0.785239 | 6.246842 |
| H | 1.248423 | -1.736033 | 7.117167 |
| H | 3.279311 | 1.739770 | 5.415181 |
| H | 3.864074 | -2.346963 | 6.837206 |
| H | 5.116077 | -0.203009 | 5.787928 |
| C | -0.127583 | 0.213946 | -2.410783 |
| C | -0.086402 | 1.435410 | -2.173806 |
| C | -0.250421 | -1.139121 | -2.882933 |

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| C | 0.324415 | -2.214611 | -2.176066 |
| C | -0.944198 | -1.408855 | -4.081952 |
| C | 0.229004 | -3.516510 | -2.661025 |
| H | 0.828823 | -2.018566 | -1.237403 |
| C | -1.019077 | -2.712901 | -4.566706 |
| H | -1.400456 | -0.593217 | -4.625227 |
| C | -0.434255 | -3.769939 | -3.864565 |
| H | 0.675575 | -4.332141 | -2.099478 |
| H | -1.549724 | -2.903669 | -5.495057 |
| H | -0.501151 | -4.783999 | -4.247946 |
| C | 0.062599 | 5.041256 | -2.218688 |
| C | -0.092965 | 3.825180 | -1.519557 |
| C | -0.343125 | 3.807068 | -0.146492 |
| C | -0.430410 | 5.029149 | 0.512294 |
| C | -0.269786 | 6.250970 | -0.169259 |
| C | -0.023735 | 6.265852 | -1.534051 |
| C | 0.254675 | 4.745945 | -3.613827 |
| C | 0.206198 | 3.375301 | -3.729649 |
| H | -0.484952 | 2.873767 | 0.386961 |
| H | -0.633929 | 5.039096 | 1.578576 |
| H | -0.347862 | 7.184700 | 0.379186 |
| H | 0.088300 | 7.204358 | -2.067801 |
| N | 0.019067 | 2.769615 | -2.443511 |
| C | 0.425746 | 5.810019 | -4.659127 |
| H | -0.544693 | 6.108552 | -5.072148 |
| H | 0.883873 | 6.696061 | -4.209271 |
| H | 1.040438 | 5.481736 | -5.496416 |
| S | 0.103511 | 2.498757 | -5.275214 |
| O | -0.913173 | 1.442118 | -5.129720 |
| O | -0.088259 | 3.528242 | -6.308002 |
| C | 1.696346 | 1.735318 | -5.570431 |
| C | 2.863058 | 2.501644 | -5.465436 |
| C | 1.733745 | 0.434149 | -6.070864 |
| C | 4.075432 | 1.947340 | -5.863229 |
| H | 2.826986 | 3.516947 | -5.082263 |
| C | 2.958342 | -0.099753 | -6.476612 |
| H | 0.821966 | -0.147015 | -6.149938 |
| C | 4.142184 | 0.644472 | -6.387856 |
| H | 4.983192 | 2.539450 | -5.781451 |
| H | 2.989447 | -1.109791 | -6.876008 |
| C | 5.459939 | 0.076492 | -6.856137 |
| H | 5.818839 | 0.608331 | -7.746064 |
| H | 6.233464 | 0.179039 | -6.086555 |

| | | | |
|---|---|---|---|
| H | 5.371903 | -0.982966 | -7.112906 |

$TS_{a'}$

| | | | |
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| Pd | 0.169747 | 0.389362 | -0.051738 |
| P | -0.043224 | -0.101891 | 2.393011 |
| P | 2.747991 | 0.420276 | 0.060252 |
| P | -2.258376 | 0.611387 | -0.685975 |
| C | -1.524073 | -1.254330 | 2.604208 |
| C | -1.369630 | -2.566550 | 1.801401 |
| C | -1.978395 | -1.519581 | 4.060721 |
| H | -2.319519 | -0.681384 | 2.105915 |
| C | -2.641355 | -3.430962 | 1.882971 |
| H | -0.523374 | -3.149990 | 2.179664 |
| H | -1.140952 | -2.334628 | 0.754454 |
| C | -3.244782 | -2.394793 | 4.100140 |
| H | -1.186329 | -2.018672 | 4.629579 |
| H | -2.179901 | -0.578130 | 4.581013 |
| C | -3.052897 | -3.709229 | 3.334170 |
| H | -2.475773 | -4.370037 | 1.340537 |
| H | -3.469389 | -2.915548 | 1.375989 |
| H | -3.514035 | -2.591227 | 5.145261 |
| H | -4.083908 | -1.837425 | 3.659046 |
| H | -3.975429 | -4.301766 | 3.359488 |
| H | -2.277457 | -4.312938 | 3.828495 |
| C | -0.400678 | 1.288610 | 3.623544 |
| C | 0.701992 | 2.362492 | 3.682454 |
| C | -1.769900 | 1.955951 | 3.377203 |
| H | -0.429972 | 0.780110 | 4.595911 |
| C | 0.397764 | 3.425766 | 4.755426 |
| H | 0.787164 | 2.851652 | 2.703121 |
| H | 1.668313 | 1.898607 | 3.898820 |
| C | -2.080717 | 3.000576 | 4.464798 |
| H | -1.768297 | 2.446357 | 2.395720 |
| H | -2.573865 | 1.213766 | 3.352531 |
| C | -0.982620 | 4.066894 | 4.563272 |
| H | 1.182321 | 4.192365 | 4.739471 |
| H | 0.440203 | 2.959798 | 5.750078 |
| H | -3.050089 | 3.467869 | 4.252803 |
| H | -2.183689 | 2.490497 | 5.433470 |
| H | -1.196574 | 4.758316 | 5.387201 |
| H | -0.980128 | 4.670690 | 3.644790 |
| C | 3.916739 | -0.760708 | -0.851151 |
| C | 3.939507 | -2.210010 | -0.321344 |
| C | 3.695746 | -0.767968 | -2.381322 |

| | | | |
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| H | 4.909118 | -0.329789 | -0.657407 |
| C | 5.026980 | -3.037649 | -1.032214 |
| H | 2.963720 | -2.681127 | -0.487352 |
| H | 4.118007 | -2.230912 | 0.754403 |
| C | 4.795181 | -1.582321 | -3.086510 |
| H | 2.725756 | -1.221321 | -2.601720 |
| H | 3.665283 | 0.245756 | -2.792572 |
| C | 4.857562 | -3.021160 | -2.556732 |
| H | 5.002698 | -4.067359 | -0.654099 |
| H | 6.015417 | -2.631766 | -0.770698 |
| H | 4.605564 | -1.581481 | -4.166420 |
| H | 5.769216 | -1.092886 | -2.935603 |
| H | 5.677528 | -3.569897 | -3.036418 |
| H | 3.928109 | -3.543795 | -2.824279 |
| C | 3.255677 | 2.124528 | -0.622312 |
| C | 2.900246 | 3.262844 | 0.360066 |
| C | 4.714461 | 2.300303 | -1.113812 |
| H | 2.600770 | 2.229295 | -1.499909 |
| C | 3.109217 | 4.648234 | -0.275006 |
| H | 3.536425 | 3.190433 | 1.252192 |
| H | 1.863292 | 3.169730 | 0.695364 |
| C | 4.914180 | 3.686678 | -1.754672 |
| H | 5.412253 | 2.197147 | -0.274572 |
| H | 4.986619 | 1.533815 | -1.842898 |
| C | 4.541908 | 4.822106 | -0.793708 |
| H | 2.869679 | 5.424263 | 0.462155 |
| H | 2.400104 | 4.775421 | -1.103543 |
| H | 5.957045 | 3.785133 | -2.081244 |
| H | 4.293795 | 3.755180 | -2.660174 |
| H | 4.652073 | 5.793783 | -1.290798 |
| H | 5.241330 | 4.822732 | 0.055278 |
| C | -3.318922 | 2.122364 | -0.637800 |
| C | -4.045131 | 2.326809 | 0.549245 |
| C | -3.542689 | 2.998225 | -1.715613 |
| C | -4.960452 | 3.375813 | 0.661188 |
| H | -3.908841 | 1.647941 | 1.384551 |
| C | -4.459536 | 4.042939 | -1.604150 |
| H | -2.998914 | 2.879480 | -2.644877 |
| C | -5.168497 | 4.237927 | -0.415631 |
| H | -5.515017 | 3.509742 | 1.585808 |
| H | -4.619040 | 4.706809 | -2.449146 |
| H | -5.881478 | 5.053397 | -0.333635 |
| C | -3.043592 | -0.452014 | -1.971745 |

| | | | |
|---|---|---|---|
| C | -3.442785 | -0.023590 | -3.249057 |
| C | -3.365533 | -1.760801 | -1.572615 |
| C | -4.158806 | -0.875932 | -4.089291 |
| H | -3.184695 | 0.963293 | -3.607746 |
| C | -4.075089 | -2.616101 | -2.417265 |
| H | -3.069065 | -2.108209 | -0.589401 |
| C | -4.478650 | -2.172462 | -3.677200 |
| H | -4.460172 | -0.526063 | -5.072717 |
| H | -4.318098 | -3.621707 | -2.085417 |
| H | -5.038095 | -2.831325 | -4.335514 |
| C | 3.325578 | 0.435869 | 1.880572 |
| H | 2.822971 | 1.331147 | 2.255849 |
| C | 4.839242 | 0.631491 | 2.080213 |
| H | 5.431228 | -0.162203 | 1.615041 |
| H | 5.175580 | 1.584767 | 1.669604 |
| H | 5.066348 | 0.632424 | 3.151635 |
| Fe | 2.641771 | -1.036144 | 4.746200 |
| C | 2.738189 | -2.819665 | 3.709330 |
| C | 3.591050 | -1.857181 | 3.101184 |
| C | 1.413144 | -2.309792 | 3.672573 |
| C | 2.799119 | -0.754052 | 2.649012 |
| C | 1.421109 | -1.029495 | 3.004514 |
| H | 3.049021 | -3.745723 | 4.174420 |
| H | 4.666666 | -1.933711 | 3.026933 |
| H | 0.554023 | -2.807878 | 4.091026 |
| C | 1.987739 | 0.222192 | 6.294972 |
| C | 2.072997 | -1.124511 | 6.754656 |
| C | 3.284024 | 0.624751 | 5.850546 |
| C | 3.425010 | -1.555807 | 6.599143 |
| C | 4.172936 | -0.475196 | 6.042037 |
| H | 1.093971 | 0.828773 | 6.284121 |
| H | 1.253259 | -1.722236 | 7.130912 |
| H | 3.547947 | 1.590589 | 5.440581 |
| H | 3.807754 | -2.542180 | 6.825857 |
| H | 5.222717 | -0.499325 | 5.780578 |
| C | 0.124902 | 0.095379 | -2.406324 |
| C | -0.494718 | 1.203349 | -2.066012 |
| C | 0.061620 | -1.296269 | -2.723164 |
| C | 0.548191 | -2.286996 | -1.829862 |
| C | -0.465523 | -1.743850 | -3.965899 |
| C | 0.508722 | -3.640065 | -2.156682 |
| H | 0.927987 | -1.981553 | -0.862434 |
| C | -0.478668 | -3.095451 | -4.285828 |

| | | | |
|---|---|---|---|
| H | -0.865050 | -1.016141 | -4.656133 |
| C | 0.005506 | -4.056940 | -3.390612 |
| H | 0.874123 | -4.370607 | -1.439833 |
| H | -0.886651 | -3.404542 | -5.244440 |
| H | -0.018826 | -5.111645 | -3.648086 |
| C | -0.342463 | 4.833679 | -2.339406 |
| C | -0.445403 | 3.648739 | -1.577100 |
| C | -0.575637 | 3.706442 | -0.184299 |
| C | -0.636419 | 4.959539 | 0.414098 |
| C | -0.556000 | 6.147544 | -0.338489 |
| C | -0.401929 | 6.092142 | -1.714252 |
| C | -0.189049 | 4.472115 | -3.720752 |
| C | -0.212734 | 3.093692 | -3.762104 |
| H | -0.630200 | 2.807124 | 0.416328 |
| H | -0.750294 | 5.022522 | 1.491649 |
| H | -0.610220 | 7.107405 | 0.165969 |
| H | -0.330897 | 7.002325 | -2.301418 |
| N | -0.375668 | 2.549224 | -2.449183 |
| C | -0.061921 | 5.486105 | -4.822182 |
| H | -1.037716 | 5.693039 | -5.275979 |
| H | 0.324522 | 6.425095 | -4.415356 |
| H | 0.595334 | 5.156256 | -5.626308 |
| S | -0.177672 | 2.160817 | -5.275973 |
| O | -1.068517 | 0.995946 | -5.130790 |
| O | -0.460857 | 3.123315 | -6.352343 |
| C | 1.508592 | 1.588940 | -5.498579 |
| C | 2.578584 | 2.463918 | -5.280472 |
| C | 1.717424 | 0.329898 | -6.062152 |
| C | 3.865822 | 2.062236 | -5.625434 |
| H | 2.411659 | 3.447418 | -4.852539 |
| C | 3.014570 | -0.052144 | -6.408159 |
| H | 0.881440 | -0.337091 | -6.237930 |
| C | 4.105485 | 0.802883 | -6.201487 |
| H | 4.696604 | 2.743532 | -5.460925 |
| H | 3.176430 | -1.028130 | -6.857586 |
| C | 5.506781 | 0.386737 | -6.578232 |
| H | 6.043575 | 1.203420 | -7.072935 |
| H | 6.086842 | 0.110299 | -5.688492 |
| H | 5.500777 | -0.476078 | -7.250616 |

$PC_{a'}$

| | | | |
|---|---|---|---|
| Pd | 0.807359 | 0.550560 | 0.375894 |
| P | 0.048416 | -0.065300 | 2.645772 |
| P | 3.109324 | -0.161189 | 0.822597 |

| | | | |
|---|---|---|---|
| P | -1.281747 | 0.868312 | -0.780223 |
| C | -1.709308 | -0.749240 | 2.735985 |
| C | -1.843636 | -2.142017 | 2.078027 |
| C | -2.394051 | -0.704425 | 4.123507 |
| H | -2.253149 | -0.042731 | 2.095286 |
| C | -3.312119 | -2.597517 | 2.014288 |
| H | -1.270565 | -2.885901 | 2.640150 |
| H | -1.420662 | -2.121273 | 1.069759 |
| C | -3.859022 | -1.171433 | 4.028812 |
| H | -1.862170 | -1.339651 | 4.840700 |
| H | -2.368820 | 0.310256 | 4.533690 |
| C | -3.978433 | -2.564145 | 3.396046 |
| H | -3.358523 | -3.607256 | 1.588376 |
| H | -3.869898 | -1.945730 | 1.327135 |
| H | -4.305872 | -1.163783 | 5.030685 |
| H | -4.427804 | -0.448096 | 3.426695 |
| H | -5.033104 | -2.854946 | 3.316894 |
| H | -3.497285 | -3.305165 | 4.051483 |
| C | -0.044275 | 1.521175 | 3.665226 |
| C | 1.317032 | 2.229562 | 3.805093 |
| C | -1.084976 | 2.498214 | 3.077822 |
| H | -0.371221 | 1.207188 | 4.665050 |
| C | 1.206863 | 3.517575 | 4.641101 |
| H | 1.695289 | 2.481012 | 2.804445 |
| H | 2.043165 | 1.557354 | 4.270737 |
| C | -1.198773 | 3.779579 | 3.921341 |
| H | -0.781993 | 2.765541 | 2.057302 |
| H | -2.071068 | 2.030411 | 2.996620 |
| C | 0.157129 | 4.480405 | 4.071871 |
| H | 2.189391 | 4.003368 | 4.690298 |
| H | 0.935635 | 3.258259 | 5.675021 |
| H | -1.931142 | 4.451482 | 3.457284 |
| H | -1.592170 | 3.525727 | 4.916478 |
| H | 0.062398 | 5.363735 | 4.715058 |
| H | 0.490804 | 4.841579 | 3.087648 |
| C | 3.431742 | -1.772727 | -0.095516 |
| C | 2.520085 | -2.935327 | 0.356023 |
| C | 3.308418 | -1.579186 | -1.623470 |
| H | 4.470938 | -2.044274 | 0.138491 |
| C | 2.851087 | -4.231038 | -0.406782 |
| H | 1.471599 | -2.661305 | 0.175138 |
| H | 2.616341 | -3.114088 | 1.428768 |
| C | 3.651405 | -2.872547 | -2.382287 |

| | | | |
|---|---|---|---|
| H | 2.277883 | -1.283024 | -1.858907 |
| H | 3.951196 | -0.766449 | -1.974449 |
| C | 2.771331 | -4.043925 | -1.927352 |
| H | 2.169416 | -5.026694 | -0.080851 |
| H | 3.865111 | -4.557725 | -0.133127 |
| H | 3.535742 | -2.702382 | -3.459771 |
| H | 4.709530 | -3.122027 | -2.215093 |
| H | 3.068770 | -4.966734 | -2.440409 |
| H | 1.728936 | -3.845371 | -2.216771 |
| C | 4.472108 | 1.022940 | 0.256007 |
| C | 4.603030 | 2.228784 | 1.218839 |
| C | 5.852530 | 0.406019 | -0.082908 |
| H | 4.067076 | 1.413024 | -0.683362 |
| C | 5.618033 | 3.269242 | 0.711225 |
| H | 4.925712 | 1.891443 | 2.211492 |
| H | 3.623486 | 2.705652 | 1.352538 |
| C | 6.820617 | 1.483051 | -0.606607 |
| H | 6.302073 | -0.068436 | 0.794254 |
| H | 5.745788 | -0.377564 | -0.839224 |
| C | 6.978597 | 2.635561 | 0.393500 |
| H | 5.727513 | 4.060442 | 1.463700 |
| H | 5.224880 | 3.745109 | -0.195043 |
| H | 7.792869 | 1.019895 | -0.816321 |
| H | 6.444786 | 1.876559 | -1.561368 |
| H | 7.663658 | 3.394222 | -0.004585 |
| H | 7.435170 | 2.255667 | 1.319652 |
| C | -2.703943 | 1.862654 | -0.174403 |
| C | -3.869074 | 1.233163 | 0.301636 |
| C | -2.612957 | 3.260082 | -0.083267 |
| C | -4.916119 | 1.985470 | 0.836884 |
| H | -3.974041 | 0.155899 | 0.241933 |
| C | -3.664475 | 4.010386 | 0.444717 |
| H | -1.726681 | 3.774784 | -0.430345 |
| C | -4.819316 | 3.376650 | 0.907577 |
| H | -5.810162 | 1.480211 | 1.190968 |
| H | -3.578486 | 5.092362 | 0.487928 |
| H | -5.637684 | 3.961385 | 1.317480 |
| C | -2.012274 | -0.627172 | -1.550023 |
| C | -3.249025 | -0.604865 | -2.214781 |
| C | -1.282279 | -1.825396 | -1.506904 |
| C | -3.752478 | -1.767772 | -2.799247 |
| H | -3.820852 | 0.314225 | -2.284993 |
| C | -1.785558 | -2.983966 | -2.096749 |

| | | | |
|---|---|---|---|
| H | -0.313916 | -1.844289 | -1.016404 |
| C | -3.026581 | -2.958143 | -2.737654 |
| H | -4.708035 | -1.736656 | -3.314024 |
| H | -1.210833 | -3.904793 | -2.053647 |
| H | -3.422622 | -3.860865 | -3.193911 |
| C | 3.497914 | -0.473755 | 2.668599 |
| H | 3.342369 | 0.524927 | 3.084590 |
| C | 4.958459 | -0.869796 | 2.958323 |
| H | 5.256082 | -1.787106 | 2.441038 |
| H | 5.652890 | -0.079850 | 2.676662 |
| H | 5.077606 | -1.036379 | 4.033887 |
| Fe | 2.059264 | -1.474739 | 5.407915 |
| C | 1.760465 | -3.300998 | 4.477623 |
| C | 2.918139 | -2.671712 | 3.943584 |
| C | 0.653658 | -2.443121 | 4.244221 |
| C | 2.538351 | -1.422316 | 3.353137 |
| C | 1.106908 | -1.275994 | 3.525044 |
| H | 1.735580 | -4.236889 | 5.019813 |
| H | 3.923488 | -3.062045 | 4.006235 |
| H | -0.354367 | -2.641214 | 4.568855 |
| C | 1.651027 | 0.095055 | 6.737366 |
| C | 1.230425 | -1.147676 | 7.296744 |
| C | 3.054450 | 0.017555 | 6.484468 |
| C | 2.376044 | -1.994261 | 7.394691 |
| C | 3.502552 | -1.274331 | 6.894222 |
| H | 1.013747 | 0.943653 | 6.532902 |
| H | 0.218372 | -1.411217 | 7.574245 |
| H | 3.670140 | 0.797107 | 6.055201 |
| H | 2.382574 | -3.016983 | 7.748051 |
| H | 4.512209 | -1.654617 | 6.810338 |
| C | 1.034443 | 1.564742 | -1.505440 |
| C | -0.223090 | 1.762787 | -1.968962 |
| C | 2.211632 | 2.108873 | -2.221391 |
| C | 2.746653 | 1.434495 | -3.335086 |
| C | 2.785363 | 3.336422 | -1.845091 |
| C | 3.819100 | 1.976452 | -4.046798 |
| H | 2.298811 | 0.499217 | -3.651688 |
| C | 3.839233 | 3.887883 | -2.576153 |
| H | 2.401520 | 3.864504 | -0.977321 |
| C | 4.365819 | 3.208299 | -3.676897 |
| H | 4.216785 | 1.439164 | -4.903751 |
| H | 4.248995 | 4.850459 | -2.282685 |
| H | 5.189415 | 3.635311 | -4.241869 |

| | | | |
|---|---|---|---|
| C | -1.615988 | 4.315275 | -4.146678 |
| C | -0.812834 | 3.920821 | -3.049145 |
| C | -0.351287 | 4.855115 | -2.111550 |
| C | -0.697493 | 6.188221 | -2.301235 |
| C | -1.492526 | 6.596746 | -3.393481 |
| C | -1.954233 | 5.670800 | -4.317276 |
| C | -1.909271 | 3.140298 | -4.918648 |
| C | -1.283588 | 2.093981 | -4.273894 |
| H | 0.269768 | 4.555022 | -1.276008 |
| H | -0.339143 | 6.932696 | -1.595888 |
| H | -1.738725 | 7.647907 | -3.510469 |
| H | -2.562368 | 5.984376 | -5.160853 |
| N | -0.603273 | 2.540526 | -3.117331 |
| C | -2.682204 | 3.126407 | -6.203238 |
| H | -3.560460 | 3.776064 | -6.118050 |
| H | -2.076942 | 3.505933 | -7.036432 |
| H | -3.028064 | 2.124104 | -6.460630 |
| S | -1.011282 | 0.492206 | -5.016561 |
| O | -0.055394 | -0.242876 | -4.166799 |
| O | -2.320000 | -0.105532 | -5.336993 |
| C | -0.204990 | 0.854153 | -6.584351 |
| C | 0.990705 | 1.578775 | -6.613833 |
| C | -0.760687 | 0.338074 | -7.754634 |
| C | 1.623152 | 1.790552 | -7.835046 |
| H | 1.423141 | 1.973732 | -5.700333 |
| C | -0.107147 | 0.554407 | -8.969181 |
| H | -1.687497 | -0.223238 | -7.711973 |
| C | 1.087210 | 1.283452 | -9.031580 |
| H | 2.550621 | 2.357044 | -7.861528 |
| H | -0.536702 | 0.150105 | -9.881872 |
| C | 1.777789 | 1.538491 | -10.349551 |
| H | 1.639303 | 2.579360 | -10.669261 |
| H | 2.857183 | 1.366440 | -10.273424 |
| H | 1.383259 | 0.893536 | -11.140122 |

## 2. The Pd-H addition

2.1 The A route

RC

| | | | |
|---|---|---|---|
| Pd | 0.813920 | -0.566780 | 0.537476 |
| H | 0.772287 | -0.160768 | -1.000610 |
| P | 1.082745 | -1.240831 | 2.910830 |
| P | 3.044267 | -0.044122 | 0.102388 |
| C | -0.124601 | -2.611863 | 3.370471 |

| | | | |
|---|---|---|---|
| C | 0.034300 | -3.863127 | 2.476278 |
| C | -0.214479 | -2.995521 | 4.865337 |
| H | -1.084554 | -2.152658 | 3.095463 |
| C | -1.097640 | -4.873250 | 2.734425 |
| H | 0.996423 | -4.350273 | 2.671029 |
| H | 0.039090 | -3.572205 | 1.420173 |
| C | -1.348293 | -4.011294 | 5.099344 |
| H | 0.732354 | -3.428668 | 5.210334 |
| H | -0.392871 | -2.109879 | 5.484135 |
| C | -1.189067 | -5.257284 | 4.217748 |
| H | -0.937546 | -5.765105 | 2.115618 |
| H | -2.052385 | -4.435006 | 2.412847 |
| H | -1.373773 | -4.290898 | 6.160037 |
| H | -2.310630 | -3.528832 | 4.876665 |
| H | -2.027619 | -5.945707 | 4.380653 |
| H | -0.277374 | -5.798429 | 4.512189 |
| C | 0.804430 | 0.069814 | 4.236696 |
| C | 1.735526 | 1.287962 | 4.085238 |
| C | -0.666411 | 0.535326 | 4.255446 |
| H | 1.032769 | -0.421306 | 5.191854 |
| C | 1.484877 | 2.338662 | 5.182470 |
| H | 1.565152 | 1.749815 | 3.103019 |
| H | 2.781244 | 0.968928 | 4.120183 |
| C | -0.916166 | 1.576810 | 5.359449 |
| H | -0.908042 | 0.982443 | 3.280597 |
| H | -1.349664 | -0.306888 | 4.392906 |
| C | 0.017564 | 2.785304 | 5.219933 |
| H | 2.146456 | 3.199047 | 5.020343 |
| H | 1.757933 | 1.915824 | 6.160445 |
| H | -1.966649 | 1.886477 | 5.325663 |
| H | -0.759136 | 1.105603 | 6.340757 |
| H | -0.143771 | 3.491588 | 6.043674 |
| H | -0.221460 | 3.324707 | 4.291201 |
| C | 3.833420 | -1.159894 | -1.182772 |
| C | 3.669370 | -2.654485 | -0.821207 |
| C | 3.298825 | -0.896599 | -2.609263 |
| H | 4.905193 | -0.914057 | -1.170814 |
| C | 4.355398 | -3.561777 | -1.857086 |
| H | 2.597208 | -2.891676 | -0.778817 |
| H | 4.075281 | -2.860113 | 0.172687 |
| C | 3.988993 | -1.807882 | -3.640263 |
| H | 2.216290 | -1.080403 | -2.626638 |
| H | 3.443446 | 0.148980 | -2.899281 |

| | | | |
|---|---|---|---|
| C | 3.845412 | -3.291884 | -3.278478 |
| H | 4.192622 | -4.611458 | -1.583145 |
| H | 5.441749 | -3.393870 | -1.821452 |
| H | 3.567656 | -1.611877 | -4.633926 |
| H | 5.055864 | -1.547214 | -3.695657 |
| H | 4.386501 | -3.913240 | -4.002481 |
| H | 2.786167 | -3.581336 | -3.345567 |
| C | 3.129322 | 1.706092 | -0.594633 |
| C | 2.549219 | 2.745527 | 0.388480 |
| C | 4.466636 | 2.207011 | -1.184260 |
| H | 2.417028 | 1.625709 | -1.426858 |
| C | 2.370555 | 4.112163 | -0.297334 |
| H | 3.222796 | 2.858331 | 1.249766 |
| H | 1.584197 | 2.397316 | 0.776801 |
| C | 4.255317 | 3.553784 | -1.900873 |
| H | 5.202598 | 2.356693 | -0.387870 |
| H | 4.896456 | 1.476586 | -1.878225 |
| C | 3.670937 | 4.606197 | -0.947673 |
| H | 2.007858 | 4.843732 | 0.435315 |
| H | 1.588054 | 4.023530 | -1.064405 |
| H | 5.210383 | 3.900767 | -2.313781 |
| H | 3.576779 | 3.410474 | -2.754362 |
| H | 3.491373 | 5.546338 | -1.483365 |
| H | 4.408121 | 4.829042 | -0.162454 |
| C | 4.120015 | -0.108140 | 1.673803 |
| H | 3.671342 | 0.692928 | 2.267887 |
| C | 5.603028 | 0.245125 | 1.453615 |
| H | 6.091029 | -0.415578 | 0.730740 |
| H | 5.722912 | 1.271538 | 1.108374 |
| H | 6.137332 | 0.152663 | 2.404619 |
| Fe | 4.403128 | -1.786585 | 4.460025 |
| C | 4.479708 | -3.501338 | 3.303313 |
| C | 4.993325 | -2.398180 | 2.566376 |
| C | 3.133839 | -3.204181 | 3.649308 |
| C | 3.963229 | -1.411197 | 2.430649 |
| C | 2.780475 | -1.917840 | 3.103212 |
| H | 5.032372 | -4.383179 | 3.599121 |
| H | 6.007459 | -2.307224 | 2.203685 |
| H | 2.492836 | -3.841451 | 4.237428 |
| C | 3.981906 | -0.646626 | 6.169229 |
| C | 4.339021 | -1.977106 | 6.538456 |
| C | 5.077949 | -0.073795 | 5.455119 |
| C | 5.659385 | -2.226978 | 6.056391 |

| | | | |
|---|---|---|---|
| C | 6.116254 | -1.051244 | 5.387859 |
| H | 3.040360 | -0.162480 | 6.385468 |
| H | 3.710430 | -2.681723 | 7.066853 |
| H | 5.114759 | 0.922127 | 5.033549 |
| H | 6.203570 | -3.157888 | 6.146862 |
| H | 7.070698 | -0.934309 | 4.891357 |
| C | -1.308351 | -1.194787 | 0.049928 |
| C | -1.968849 | -0.218268 | 0.466805 |
| C | -1.512973 | -2.469699 | -0.636344 |
| C | -0.592070 | -2.967381 | -1.573332 |
| C | -2.675976 | -3.214934 | -0.356407 |
| C | -0.841825 | -4.169704 | -2.235076 |
| H | 0.307297 | -2.400102 | -1.783572 |
| C | -2.908668 | -4.423454 | -1.009820 |
| H | -3.373593 | -2.848157 | 0.389627 |
| C | -1.996970 | -4.902936 | -1.955000 |
| H | -0.127145 | -4.536297 | -2.966653 |
| H | -3.806756 | -4.990503 | -0.781670 |
| H | -2.184339 | -5.843052 | -2.465633 |
| C | -3.041275 | 3.153001 | 0.682788 |
| C | -2.368459 | 2.115384 | 0.014681 |
| C | -1.627952 | 2.309377 | -1.147034 |
| C | -1.588311 | 3.610196 | -1.650635 |
| C | -2.255194 | 4.668667 | -1.004881 |
| C | -2.982437 | 4.454311 | 0.162341 |
| C | -3.712100 | 2.589916 | 1.839453 |
| C | -3.418407 | 1.252224 | 1.860883 |
| H | -1.117634 | 1.488055 | -1.638242 |
| H | -1.037254 | 3.806717 | -2.565357 |
| H | -2.201828 | 5.667007 | -1.428049 |
| H | -3.495281 | 5.274139 | 0.655654 |
| N | -2.579314 | 0.917614 | 0.746666 |
| C | -4.592654 | 3.374168 | 2.761396 |
| H | -4.823261 | 2.824478 | 3.673692 |
| H | -4.101205 | 4.313182 | 3.039004 |
| H | -5.532981 | 3.637581 | 2.260539 |
| S | -4.169348 | -0.003210 | 2.891013 |
| O | -3.466048 | -1.268293 | 2.609584 |
| O | -4.215178 | 0.532422 | 4.261065 |
| C | -5.851472 | -0.148035 | 2.294543 |
| C | -6.891112 | 0.397859 | 3.050194 |
| C | -6.105141 | -0.820896 | 1.094349 |
| C | -8.200678 | 0.268147 | 2.589065 |

| | | | |
|---|---|---|---|
| H | -6.678457 | 0.900047 | 3.987258 |
| C | -7.418843 | -0.934068 | 0.649754 |
| H | -5.294740 | -1.255378 | 0.518515 |
| C | -8.486496 | -0.395135 | 1.387255 |
| H | -9.013132 | 0.687913 | 3.175856 |
| H | -7.620997 | -1.453758 | -0.282938 |
| C | -9.908675 | -0.553950 | 0.908671 |
| H | -10.315895 | -1.524778 | 1.219975 |
| H | -10.559599 | 0.222341 | 1.321814 |
| H | -9.969900 | -0.511737 | -0.183561 |

$TS_{Ph}$

| | | | |
|---|---|---|---|
| Pd | 0.749081 | -0.560634 | 0.707474 |
| H | -0.500325 | -0.048564 | -0.656160 |
| P | 1.102283 | -1.195402 | 2.963051 |
| P | 3.038827 | -0.122533 | 0.172666 |
| C | -0.172758 | -2.486576 | 3.449453 |
| C | -0.094024 | -3.756135 | 2.570562 |
| C | -0.254963 | -2.831549 | 4.955885 |
| H | -1.108554 | -1.976667 | 3.182327 |
| C | -1.259916 | -4.712433 | 2.878809 |
| H | 0.851817 | -4.283005 | 2.740161 |
| H | -0.112846 | -3.475668 | 1.510997 |
| C | -1.425160 | -3.795159 | 5.227853 |
| H | 0.679344 | -3.292087 | 5.299434 |
| H | -0.392876 | -1.923757 | 5.552429 |
| C | -1.329416 | -5.064362 | 4.371092 |
| H | -1.153957 | -5.620760 | 2.272624 |
| H | -2.205182 | -4.240022 | 2.577763 |
| H | -1.442578 | -4.050547 | 6.294718 |
| H | -2.369392 | -3.277430 | 5.009608 |
| H | -2.188404 | -5.718087 | 4.566283 |
| H | -0.431250 | -5.632457 | 4.656127 |
| C | 0.880503 | 0.186553 | 4.223227 |
| C | 1.886073 | 1.342635 | 4.069396 |
| C | -0.561361 | 0.733686 | 4.195000 |
| H | 1.060324 | -0.296743 | 5.193510 |
| C | 1.669446 | 2.425065 | 5.143511 |
| H | 1.763594 | 1.795653 | 3.077038 |
| H | 2.910269 | 0.964850 | 4.135158 |
| C | -0.775858 | 1.808712 | 5.274036 |
| H | -0.750939 | 1.172175 | 3.205113 |
| H | -1.294516 | -0.065041 | 4.326708 |
| C | 0.230428 | 2.957861 | 5.137395 |

| | | | |
|---|---|---|---|
| H | 2.384148 | 3.242095 | 4.983418 |
| H | 1.894293 | 2.004481 | 6.134627 |
| H | -1.805399 | 2.180459 | 5.209328 |
| H | -0.672819 | 1.348438 | 6.267507 |
| H | 0.092602 | 3.686918 | 5.945232 |
| H | 0.045654 | 3.493380 | 4.194324 |
| C | 3.745637 | -1.286704 | -1.124340 |
| C | 3.551188 | -2.767387 | -0.722848 |
| C | 3.134764 | -1.035282 | -2.522037 |
| H | 4.823667 | -1.076848 | -1.178976 |
| C | 4.140379 | -3.720350 | -1.776951 |
| H | 2.475182 | -2.964318 | -0.613436 |
| H | 4.007911 | -2.968274 | 0.249772 |
| C | 3.723421 | -1.993100 | -3.573378 |
| H | 2.047920 | -1.183824 | -2.467410 |
| H | 3.297697 | -0.002511 | -2.846033 |
| C | 3.549626 | -3.462809 | -3.168934 |
| H | 3.959634 | -4.757592 | -1.468947 |
| H | 5.231871 | -3.590010 | -1.813358 |
| H | 3.247865 | -1.801725 | -4.543355 |
| H | 4.793270 | -1.773129 | -3.700861 |
| H | 4.020371 | -4.118782 | -3.911338 |
| H | 2.478703 | -3.713539 | -3.160080 |
| C | 3.139088 | 1.603464 | -0.581953 |
| C | 2.614943 | 2.689481 | 0.382336 |
| C | 4.466273 | 2.057310 | -1.231238 |
| H | 2.397244 | 1.516068 | -1.390098 |
| C | 2.440217 | 4.035405 | -0.344256 |
| H | 3.321016 | 2.817029 | 1.215080 |
| H | 1.657788 | 2.376709 | 0.817336 |
| C | 4.264075 | 3.385356 | -1.984019 |
| H | 5.226855 | 2.212917 | -0.458593 |
| H | 4.859594 | 1.295346 | -1.912800 |
| C | 3.729249 | 4.480631 | -1.050125 |
| H | 2.114619 | 4.798664 | 0.373280 |
| H | 1.632442 | 3.936926 | -1.083904 |
| H | 5.214061 | 3.698086 | -2.434433 |
| H | 3.558851 | 3.230135 | -2.813592 |
| H | 3.551815 | 5.405875 | -1.611764 |
| H | 4.493992 | 4.714406 | -0.295056 |
| C | 4.183280 | -0.188427 | 1.689392 |
| H | 3.807268 | 0.650367 | 2.282487 |
| C | 5.673368 | 0.070571 | 1.403715 |

| | | | |
|---|---|---|---|
| H | 6.097677 | -0.653420 | 0.701623 |
| H | 5.833791 | 1.068766 | 0.996713 |
| H | 6.238593 | 0.000186 | 2.339151 |
| Fe | 4.379713 | -1.847259 | 4.513988 |
| C | 4.403818 | -3.572448 | 3.367836 |
| C | 4.964550 | -2.493942 | 2.628433 |
| C | 3.067455 | -3.224835 | 3.699469 |
| C | 3.976757 | -1.468156 | 2.477220 |
| C | 2.770250 | -1.927252 | 3.144182 |
| H | 4.920606 | -4.472323 | 3.673795 |
| H | 5.983848 | -2.445009 | 2.272755 |
| H | 2.397071 | -3.833642 | 4.285019 |
| C | 3.998692 | -0.669576 | 6.207305 |
| C | 4.280562 | -2.013240 | 6.593430 |
| C | 5.131450 | -0.162129 | 5.501232 |
| C | 5.591580 | -2.336784 | 6.130088 |
| C | 6.117326 | -1.193681 | 5.455860 |
| H | 3.081511 | -0.134387 | 6.408079 |
| H | 3.609586 | -2.678162 | 7.121106 |
| H | 5.226159 | 0.826301 | 5.071146 |
| H | 6.084642 | -3.294208 | 6.235371 |
| H | 7.081740 | -1.132430 | 4.968833 |
| C | -1.300475 | -0.718361 | -0.140013 |
| C | -2.268339 | -0.222373 | 0.677937 |
| C | -1.475523 | -1.997635 | -0.860405 |
| C | -0.810461 | -2.211432 | -2.082401 |
| C | -2.322750 | -3.012338 | -0.369507 |
| C | -0.983077 | -3.401173 | -2.791102 |
| H | -0.180455 | -1.426369 | -2.490862 |
| C | -2.485023 | -4.200503 | -1.075165 |
| H | -2.821787 | -2.861441 | 0.581734 |
| C | -1.817457 | -4.401860 | -2.289465 |
| H | -0.470793 | -3.541348 | -3.738881 |
| H | -3.132083 | -4.976644 | -0.676063 |
| H | -1.950414 | -5.329479 | -2.838536 |
| C | -3.083078 | 3.271112 | 0.838550 |
| C | -2.492380 | 2.200275 | 0.145456 |
| C | -1.860446 | 2.374348 | -1.084071 |
| C | -1.797092 | 3.673608 | -1.592475 |
| C | -2.353397 | 4.760697 | -0.897220 |
| C | -3.006384 | 4.569326 | 0.317776 |
| C | -3.736548 | 2.750172 | 2.028279 |
| C | -3.516195 | 1.398827 | 2.033561 |

| | | | |
|---|---|---|---|
| H | -1.461043 | 1.542714 | -1.650026 |
| H | -1.319840 | 3.840815 | -2.553408 |
| H | -2.287113 | 5.757434 | -1.322486 |
| H | -3.456203 | 5.405549 | 0.844045 |
| N | -2.720801 | 1.009788 | 0.901286 |
| C | -4.503720 | 3.626041 | 2.969323 |
| H | -4.957725 | 3.064885 | 3.782835 |
| H | -3.836291 | 4.382956 | 3.400163 |
| H | -5.285323 | 4.166494 | 2.421214 |
| S | -4.249071 | 0.193927 | 3.148996 |
| O | -3.378610 | -0.988878 | 3.251893 |
| O | -4.595753 | 0.935439 | 4.373943 |
| C | -5.770782 | -0.287093 | 2.336423 |
| C | -6.981346 | 0.227899 | 2.805223 |
| C | -5.731053 | -1.174774 | 1.256772 |
| C | -8.165624 | -0.157050 | 2.178838 |
| H | -6.993048 | 0.906497 | 3.650915 |
| C | -6.925150 | -1.540374 | 0.641056 |
| H | -4.783647 | -1.567697 | 0.903695 |
| C | -8.158940 | -1.043370 | 1.091657 |
| H | -9.110675 | 0.237474 | 2.542328 |
| H | -6.900250 | -2.227069 | -0.200985 |
| C | -9.448809 | -1.475810 | 0.438186 |
| H | -9.819657 | -2.405513 | 0.889374 |
| H | -10.231249 | -0.720110 | 0.557434 |
| H | -9.311715 | -1.665741 | -0.631150 |

$TS_{ind}$

| | | | |
|---|---|---|---|
| Pd | 0.502437 | -0.627821 | 1.275399 |
| H | 0.070192 | 0.348746 | 0.079693 |
| P | 1.365720 | -2.102876 | 3.021158 |
| P | 2.453757 | 0.659524 | 0.980781 |
| C | 0.746360 | -3.868744 | 2.818415 |
| C | 1.143123 | -4.467393 | 1.448008 |
| C | 1.032625 | -4.839029 | 3.988777 |
| H | -0.341157 | -3.719192 | 2.788107 |
| C | 0.527729 | -5.862683 | 1.235882 |
| H | 2.232825 | -4.546629 | 1.367720 |
| H | 0.822575 | -3.789540 | 0.646075 |
| C | 0.395758 | -6.217174 | 3.733519 |
| H | 2.110348 | -4.969045 | 4.136037 |
| H | 0.642931 | -4.428849 | 4.926568 |
| C | 0.852201 | -6.813975 | 2.395719 |
| H | 0.888003 | -6.276665 | 0.285834 |

| | | | |
|---|---|---|---|
| H | -0.563452 | -5.772348 | 1.146182 |
| H | 0.645697 | -6.891295 | 4.562073 |
| H | -0.699052 | -6.114582 | 3.730689 |
| H | 0.373996 | -7.787326 | 2.231166 |
| H | 1.936276 | -6.998407 | 2.428102 |
| C | 0.876144 | -1.635029 | 4.778013 |
| C | 1.321265 | -0.206968 | 5.150974 |
| C | -0.646949 | -1.778568 | 4.984576 |
| H | 1.396134 | -2.345352 | 5.434302 |
| C | 0.903637 | 0.165823 | 6.584974 |
| H | 0.864864 | 0.503371 | 4.447602 |
| H | 2.406917 | -0.113530 | 5.052714 |
| C | -1.058620 | -1.415371 | 6.421925 |
| H | -1.163991 | -1.111287 | 4.283452 |
| H | -0.985673 | -2.794344 | 4.756859 |
| C | -0.606321 | 0.000793 | 6.799657 |
| H | 1.212090 | 1.197245 | 6.796274 |
| H | 1.442580 | -0.473519 | 7.299643 |
| H | -2.147010 | -1.510425 | 6.520644 |
| H | -0.615858 | -2.140289 | 7.120491 |
| H | -0.868471 | 0.220444 | 7.841792 |
| H | -1.143762 | 0.731759 | 6.178108 |
| C | 3.287342 | 0.337340 | -0.669373 |
| C | 3.575662 | -1.166584 | -0.884648 |
| C | 2.447088 | 0.880776 | -1.849375 |
| H | 4.243254 | 0.880698 | -0.645167 |
| C | 4.266227 | -1.421043 | -2.235771 |
| H | 2.622203 | -1.713113 | -0.850831 |
| H | 4.195438 | -1.563362 | -0.076988 |
| C | 3.145994 | 0.629328 | -3.197398 |
| H | 1.469759 | 0.379113 | -1.851217 |
| H | 2.251150 | 1.951741 | -1.738394 |
| C | 3.453354 | -0.858620 | -3.408805 |
| H | 4.427887 | -2.498843 | -2.361989 |
| H | 5.262277 | -0.954753 | -2.225391 |
| H | 2.512070 | 1.009482 | -4.007907 |
| H | 4.081598 | 1.205960 | -3.233817 |
| H | 3.993219 | -1.005554 | -4.352306 |
| H | 2.507995 | -1.414137 | -3.496370 |
| C | 1.984925 | 2.486653 | 0.995885 |
| C | 1.392351 | 2.908022 | 2.359185 |
| C | 3.032557 | 3.514407 | 0.511054 |
| H | 1.158052 | 2.502225 | 0.273015 |

| | | | |
|---|---|---|---|
| C | 0.790679 | 4.323322 | 2.287060 |
| H | 2.178810 | 2.889070 | 3.127150 |
| H | 0.619037 | 2.194738 | 2.669749 |
| C | 2.396535 | 4.914004 | 0.416669 |
| H | 3.874444 | 3.564244 | 1.208344 |
| H | 3.448252 | 3.228873 | -0.461185 |
| C | 1.803657 | 5.351557 | 1.763583 |
| H | 0.430670 | 4.614589 | 3.281588 |
| H | -0.088651 | 4.305404 | 1.629373 |
| H | 3.151641 | 5.634015 | 0.077799 |
| H | 1.605511 | 4.903661 | -0.347091 |
| H | 1.326520 | 6.334340 | 1.666213 |
| H | 2.617715 | 5.468916 | 2.494206 |
| C | 3.704637 | 0.384542 | 2.383211 |
| H | 3.111242 | 0.681464 | 3.252899 |
| C | 4.951150 | 1.287340 | 2.337927 |
| H | 5.495003 | 1.210805 | 1.391222 |
| H | 4.687065 | 2.333202 | 2.495394 |
| H | 5.634674 | 0.997480 | 3.142501 |
| Fe | 4.867430 | -2.064671 | 4.207622 |
| C | 5.320241 | -3.028429 | 2.430988 |
| C | 5.361241 | -1.619585 | 2.240558 |
| C | 4.008304 | -3.371975 | 2.853959 |
| C | 4.067760 | -1.076071 | 2.526655 |
| C | 3.201055 | -2.177026 | 2.905802 |
| H | 6.153664 | -3.710912 | 2.329872 |
| H | 6.236480 | -1.050360 | 1.960930 |
| H | 3.686957 | -4.370109 | 3.103160 |
| C | 4.348405 | -1.919789 | 6.234860 |
| C | 5.144514 | -3.081686 | 6.010686 |
| C | 5.107493 | -0.776782 | 5.839455 |
| C | 6.400174 | -2.657295 | 5.480090 |
| C | 6.377677 | -1.233790 | 5.375065 |
| H | 3.341761 | -1.909808 | 6.627523 |
| H | 4.841232 | -4.105240 | 6.187152 |
| H | 4.777949 | 0.253171 | 5.878052 |
| H | 7.212061 | -3.303627 | 5.173509 |
| H | 7.173197 | -0.614165 | 4.982232 |
| C | -1.608506 | -1.294409 | 1.037588 |
| C | -1.693585 | -0.382186 | 0.170689 |
| C | -2.528108 | -2.219783 | 1.702470 |
| C | -2.599007 | -3.568601 | 1.319878 |
| C | -3.398279 | -1.739334 | 2.697999 |

| | | | |
|---|---|---|---|
| C | -3.525750 | -4.421386 | 1.922484 |
| H | -1.940633 | -3.940549 | 0.541127 |
| C | -4.314942 | -2.601414 | 3.300361 |
| H | -3.351816 | -0.693717 | 2.986305 |
| C | -4.381638 | -3.944048 | 2.917741 |
| H | -3.578729 | -5.460299 | 1.609272 |
| H | -4.983220 | -2.219087 | 4.066915 |
| H | -5.098420 | -4.611137 | 3.387485 |
| C | -2.242589 | 1.097264 | -3.004181 |
| C | -1.967534 | -0.023605 | -2.198985 |
| C | -1.552884 | -1.247532 | -2.719105 |
| C | -1.441679 | -1.334211 | -4.106256 |
| C | -1.730006 | -0.233501 | -4.936318 |
| C | -2.129940 | 0.985664 | -4.398627 |
| C | -2.608451 | 2.198492 | -2.135541 |
| C | -2.534702 | 1.727850 | -0.849078 |
| H | -1.338424 | -2.094766 | -2.076307 |
| H | -1.131818 | -2.273224 | -4.554867 |
| H | -1.637174 | -0.341298 | -6.012635 |
| H | -2.347965 | 1.831809 | -5.042949 |
| N | -2.170344 | 0.347861 | -0.851346 |
| C | -3.031186 | 3.548050 | -2.627324 |
| H | -3.041389 | 4.289708 | -1.829123 |
| H | -2.346824 | 3.892218 | -3.410699 |
| H | -4.032485 | 3.496244 | -3.073956 |
| S | -3.047221 | 2.565070 | 0.645745 |
| O | -2.576727 | 1.757073 | 1.784282 |
| O | -2.625222 | 3.969647 | 0.512085 |
| C | -4.836441 | 2.514483 | 0.618991 |
| C | -5.547862 | 3.662394 | 0.263302 |
| C | -5.497427 | 1.330355 | 0.962466 |
| C | -6.941225 | 3.616185 | 0.251532 |
| H | -5.019502 | 4.576515 | 0.016546 |
| C | -6.888933 | 1.304893 | 0.939124 |
| H | -4.938633 | 0.446228 | 1.251580 |
| C | -7.632906 | 2.442964 | 0.586246 |
| H | -7.499214 | 4.508160 | -0.020184 |
| H | -7.407621 | 0.387269 | 1.203500 |
| C | -9.141610 | 2.409745 | 0.596112 |
| H | -9.527806 | 2.631978 | 1.599499 |
| H | -9.563205 | 3.152031 | -0.088460 |
| H | -9.521756 | 1.423035 | 0.312805 |

$PC_{Ph}$

| | | | |
|---|---|---|---|
| Pd | 0.035886 | 0.005033 | 1.489614 |
| H | -1.637894 | 1.974113 | 2.685608 |
| P | 1.388263 | 0.185910 | 3.490187 |
| P | 1.799456 | -1.192129 | 0.153316 |
| C | 0.128276 | 0.077913 | 4.889786 |
| C | -0.732422 | -1.203692 | 4.816866 |
| C | 0.641504 | 0.325751 | 6.327269 |
| H | -0.539281 | 0.916578 | 4.640875 |
| C | -1.899655 | -1.137819 | 5.816765 |
| H | -0.117413 | -2.082254 | 5.042587 |
| H | -1.111568 | -1.347927 | 3.799187 |
| C | -0.535364 | 0.378108 | 7.320185 |
| H | 1.330374 | -0.471088 | 6.630713 |
| H | 1.206363 | 1.261974 | 6.386622 |
| C | -1.404716 | -0.885036 | 7.248067 |
| H | -2.472862 | -2.071796 | 5.769160 |
| H | -2.586867 | -0.331158 | 5.520745 |
| H | -0.147243 | 0.519669 | 8.336425 |
| H | -1.154410 | 1.259308 | 7.096012 |
| H | -2.255090 | -0.797569 | 7.935424 |
| H | -0.816360 | -1.750762 | 7.585820 |
| C | 2.377323 | 1.738043 | 3.898622 |
| C | 3.498506 | 2.023165 | 2.881402 |
| C | 1.458586 | 2.972239 | 4.026175 |
| H | 2.838756 | 1.532060 | 4.873892 |
| C | 4.296307 | 3.286618 | 3.252183 |
| H | 3.053844 | 2.163109 | 1.888126 |
| H | 4.175517 | 1.166408 | 2.818051 |
| C | 2.257267 | 4.232801 | 4.403713 |
| H | 0.960947 | 3.138861 | 3.062963 |
| H | 0.671129 | 2.807919 | 4.769407 |
| C | 3.383825 | 4.510953 | 3.400643 |
| H | 5.063033 | 3.468623 | 2.488941 |
| H | 4.831777 | 3.118018 | 4.197872 |
| H | 1.575400 | 5.090281 | 4.463263 |
| H | 2.684573 | 4.102820 | 5.408540 |
| H | 3.967187 | 5.384793 | 3.715240 |
| H | 2.946078 | 4.758990 | 2.422598 |
| C | 1.578995 | -2.879766 | -0.650437 |
| C | 1.428654 | -4.037854 | 0.358710 |
| C | 0.390449 | -2.872310 | -1.636998 |
| H | 2.501158 | -3.049476 | -1.224221 |
| C | 1.294991 | -5.388147 | -0.369314 |

| | | | |
|---|---|---|---|
| H | 0.542000 | -3.863591 | 0.977200 |
| H | 2.288449 | -4.075877 | 1.032386 |
| C | 0.257816 | -4.223581 | -2.361362 |
| H | -0.525933 | -2.669918 | -1.075123 |
| H | 0.495916 | -2.072719 | -2.379127 |
| C | 0.131190 | -5.388024 | -1.369634 |
| H | 1.162571 | -6.187556 | 0.370529 |
| H | 2.232069 | -5.607509 | -0.902824 |
| H | -0.612448 | -4.192914 | -3.029138 |
| H | 1.138831 | -4.381980 | -3.000964 |
| H | 0.092493 | -6.343145 | -1.908435 |
| H | -0.817493 | -5.295506 | -0.822502 |
| C | 2.144446 | -0.049356 | -1.330003 |
| C | 2.691201 | 1.325303 | -0.888296 |
| C | 2.990883 | -0.612221 | -2.495967 |
| H | 1.129932 | 0.120847 | -1.718831 |
| C | 2.771830 | 2.312860 | -2.066293 |
| H | 3.697023 | 1.203163 | -0.462936 |
| H | 2.056207 | 1.746174 | -0.099912 |
| C | 3.034909 | 0.380577 | -3.672198 |
| H | 4.017843 | -0.798333 | -2.162511 |
| H | 2.596286 | -1.570394 | -2.846459 |
| C | 3.584179 | 1.745101 | -3.237195 |
| H | 3.207246 | 3.258233 | -1.718720 |
| H | 1.753850 | 2.544578 | -2.407088 |
| H | 3.646572 | -0.040565 | -4.479730 |
| H | 2.020847 | 0.506134 | -4.079457 |
| H | 3.575650 | 2.446831 | -4.080389 |
| H | 4.635321 | 1.632280 | -2.933337 |
| C | 3.433815 | -1.270933 | 1.142473 |
| H | 3.666691 | -0.209014 | 1.262011 |
| C | 4.617804 | -1.929433 | 0.412254 |
| H | 4.412502 | -2.966116 | 0.129404 |
| H | 4.881597 | -1.381328 | -0.493125 |
| H | 5.495250 | -1.929840 | 1.067787 |
| Fe | 4.455476 | -1.705310 | 4.238252 |
| C | 3.238900 | -3.378100 | 4.280228 |
| C | 3.688709 | -3.142138 | 2.950799 |
| C | 2.510544 | -2.234378 | 4.702663 |
| C | 3.221733 | -1.860206 | 2.520787 |
| C | 2.476471 | -1.279318 | 3.621727 |
| H | 3.461309 | -4.247976 | 4.883851 |
| H | 4.313915 | -3.810607 | 2.375818 |

| | | | |
|---|---|---|---|
| H | 2.070425 | -2.108332 | 5.679076 |
| C | 5.477135 | -0.066988 | 5.060447 |
| C | 5.410277 | -1.132728 | 6.005480 |
| C | 6.163285 | -0.541882 | 3.901289 |
| C | 6.059977 | -2.267910 | 5.432970 |
| C | 6.525690 | -1.902765 | 4.134005 |
| H | 5.072209 | 0.925390 | 5.198610 |
| H | 4.929690 | -1.095797 | 6.974250 |
| H | 6.369282 | 0.025279 | 3.003185 |
| H | 6.148114 | -3.246121 | 5.887031 |
| H | 7.034617 | -2.554851 | 3.436311 |
| C | -1.444608 | 1.605980 | 1.675445 |
| C | -1.984467 | 0.344591 | 1.329811 |
| C | -1.092595 | 2.658272 | 0.698596 |
| C | -0.840784 | 3.965841 | 1.158967 |
| C | -1.101963 | 2.431783 | -0.693459 |
| C | -0.588609 | 5.005406 | 0.264758 |
| H | -0.866379 | 4.169828 | 2.225988 |
| C | -0.855629 | 3.474505 | -1.584132 |
| H | -1.314181 | 1.436050 | -1.069406 |
| C | -0.592014 | 4.764207 | -1.111175 |
| H | -0.400321 | 6.006106 | 0.643128 |
| H | -0.880075 | 3.282895 | -2.653277 |
| H | -0.403498 | 5.574535 | -1.809198 |
| C | -5.267153 | 0.005036 | 2.767195 |
| C | -4.219384 | 0.802943 | 2.278296 |
| C | -4.314329 | 2.195567 | 2.266914 |
| C | -5.466090 | 2.768158 | 2.809608 |
| C | -6.500738 | 1.981591 | 3.340855 |
| C | -6.414051 | 0.593310 | 3.315415 |
| C | -4.932697 | -1.386010 | 2.538809 |
| C | -3.702597 | -1.403190 | 1.935740 |
| H | -3.553297 | 2.828979 | 1.832778 |
| H | -5.562172 | 3.849637 | 2.808507 |
| H | -7.380869 | 2.461932 | 3.756947 |
| H | -7.221442 | -0.022107 | 3.699536 |
| N | -3.190350 | -0.065213 | 1.781208 |
| C | -5.865636 | -2.496862 | 2.909536 |
| H | -5.493466 | -3.475900 | 2.618967 |
| H | -6.025446 | -2.496275 | 3.995063 |
| H | -6.844008 | -2.327227 | 2.443762 |
| S | -2.905186 | -2.860416 | 1.279485 |
| O | -1.452823 | -2.624324 | 1.251376 |

| | | | |
|---|---|---|---|
| O | -3.420501 | -4.016304 | 2.030792 |
| C | -3.531333 | -2.972023 | -0.397252 |
| C | -4.336792 | -4.058204 | -0.743729 |
| C | -3.204377 | -1.985757 | -1.333965 |
| C | -4.815153 | -4.154517 | -2.050283 |
| H | -4.574444 | -4.815058 | -0.004545 |
| C | -3.698901 | -2.097079 | -2.630701 |
| H | -2.566731 | -1.151551 | -1.057608 |
| C | -4.511644 | -3.178599 | -3.010218 |
| H | -5.434613 | -5.003421 | -2.326772 |
| H | -3.446929 | -1.334842 | -3.363369 |
| C | -5.063357 | -3.272979 | -4.411766 |
| H | -5.268563 | -4.310593 | -4.692008 |
| H | -6.006925 | -2.717909 | -4.495625 |
| H | -4.370152 | -2.847857 | -5.144605 |

$PC_{ind}$

| | | | |
|---|---|---|---|
| Pd | 0.953848 | -0.454278 | 0.837632 |
| H | -1.049966 | 1.333754 | 1.095125 |
| P | 1.190632 | -1.613250 | 2.834378 |
| P | 3.222188 | 0.366606 | 0.655368 |
| C | 0.326104 | -3.281504 | 2.765505 |
| C | 0.955229 | -4.236141 | 1.725147 |
| C | 0.097243 | -3.986457 | 4.125597 |
| H | -0.660779 | -2.996017 | 2.376371 |
| C | 0.120942 | -5.520741 | 1.574786 |
| H | 1.974041 | -4.504754 | 2.023922 |
| H | 1.035193 | -3.727347 | 0.758175 |
| C | -0.742032 | -5.263889 | 3.936973 |
| H | 1.051208 | -4.257028 | 4.590998 |
| H | -0.409975 | -3.319589 | 4.829649 |
| C | -0.101009 | -6.219989 | 2.922788 |
| H | 0.624134 | -6.195984 | 0.871490 |
| H | -0.850884 | -5.270810 | 1.129200 |
| H | -0.867842 | -5.758048 | 4.908114 |
| H | -1.748528 | -4.986757 | 3.591720 |
| H | -0.731478 | -7.107378 | 2.789002 |
| H | 0.862488 | -6.576066 | 3.316487 |
| C | 0.402021 | -0.693801 | 4.268498 |
| C | 0.975439 | 0.725938 | 4.446593 |
| C | -1.137025 | -0.635280 | 4.168856 |
| H | 0.679198 | -1.295750 | 5.145352 |
| C | 0.365890 | 1.429966 | 5.672911 |
| H | 0.752733 | 1.312132 | 3.545038 |

| | | | |
|---|---|---|---|
| H | 2.064412 | 0.685060 | 4.548909 |
| C | -1.736445 | 0.048703 | 5.412350 |
| H | -1.419188 | -0.068087 | 3.274517 |
| H | -1.566154 | -1.637136 | 4.061525 |
| C | -1.166854 | 1.459167 | 5.613219 |
| H | 0.767536 | 2.448594 | 5.740370 |
| H | 0.684455 | 0.909027 | 6.587714 |
| H | -2.827339 | 0.092491 | 5.308510 |
| H | -1.530218 | -0.566572 | 6.300592 |
| H | -1.570164 | 1.902986 | 6.531696 |
| H | -1.491608 | 2.095500 | 4.780513 |
| C | 4.233365 | -0.457491 | -0.692326 |
| C | 4.477603 | -1.959179 | -0.423460 |
| C | 3.513745 | -0.277407 | -2.052443 |
| H | 5.206307 | 0.051400 | -0.739797 |
| C | 5.258929 | -2.617425 | -1.574169 |
| H | 3.507891 | -2.464200 | -0.305499 |
| H | 5.020968 | -2.100841 | 0.514138 |
| C | 4.296098 | -0.939289 | -3.199733 |
| H | 2.513864 | -0.732989 | -1.985669 |
| H | 3.360460 | 0.782382 | -2.282201 |
| C | 4.558480 | -2.425594 | -2.925357 |
| H | 5.390952 | -3.684851 | -1.358138 |
| H | 6.267181 | -2.180834 | -1.621095 |
| H | 3.741277 | -0.812464 | -4.137455 |
| H | 5.254503 | -0.416145 | -3.329376 |
| H | 5.160627 | -2.860389 | -3.732322 |
| H | 3.601633 | -2.968525 | -2.919537 |
| C | 3.083292 | 2.176874 | 0.141621 |
| C | 2.468485 | 3.043348 | 1.263437 |
| C | 4.336939 | 2.859068 | -0.452106 |
| H | 2.333941 | 2.124061 | -0.663186 |
| C | 2.137931 | 4.456667 | 0.752479 |
| H | 3.175959 | 3.123152 | 2.100667 |
| H | 1.560844 | 2.569293 | 1.657301 |
| C | 3.991738 | 4.269519 | -0.965432 |
| H | 5.119596 | 2.941002 | 0.310584 |
| H | 4.757598 | 2.264868 | -1.270229 |
| C | 3.367270 | 5.138423 | 0.135463 |
| H | 1.738148 | 5.059315 | 1.576999 |
| H | 1.340608 | 4.387746 | -0.001645 |
| H | 4.898097 | 4.744548 | -1.360422 |
| H | 3.289430 | 4.184939 | -1.807473 |

| | | | |
|---|---|---|---|
| H | 3.092239 | 6.120585 | -0.267481 |
| H | 4.114722 | 5.319996 | 0.921681 |
| C | 4.135719 | 0.305537 | 2.307526 |
| H | 3.491765 | 0.935456 | 2.930705 |
| C | 5.544420 | 0.922676 | 2.313152 |
| H | 6.212824 | 0.444732 | 1.590050 |
| H | 5.504534 | 1.988603 | 2.082639 |
| H | 5.991483 | 0.818011 | 3.307537 |
| Fe | 4.252989 | -1.718772 | 4.875631 |
| C | 4.902423 | -3.177840 | 3.554246 |
| C | 5.286121 | -1.892649 | 3.083260 |
| C | 3.487352 | -3.200079 | 3.650297 |
| C | 4.113336 | -1.102077 | 2.867736 |
| C | 2.963248 | -1.927765 | 3.208146 |
| H | 5.570500 | -3.977677 | 3.844519 |
| H | 6.303696 | -1.554486 | 2.949508 |
| H | 2.910890 | -4.036621 | 4.009166 |
| C | 3.323890 | -1.000846 | 6.614609 |
| C | 3.926137 | -2.268443 | 6.865561 |
| C | 4.345314 | -0.096137 | 6.193824 |
| C | 5.324454 | -2.148021 | 6.603942 |
| C | 5.583396 | -0.806421 | 6.190760 |
| H | 2.274176 | -0.768588 | 6.720534 |
| H | 3.411332 | -3.168336 | 7.175190 |
| H | 4.206826 | 0.941752 | 5.921073 |
| H | 6.054329 | -2.944206 | 6.668600 |
| H | 6.545361 | -0.408789 | 5.894969 |
| C | -1.037574 | -0.701476 | 0.478059 |
| C | -1.489892 | 0.576133 | 0.454767 |
| C | -1.728537 | -1.896372 | -0.013318 |
| C | -1.086594 | -2.832933 | -0.850375 |
| C | -3.069112 | -2.144042 | 0.352477 |
| C | -1.762013 | -3.956508 | -1.321378 |
| H | -0.055606 | -2.657164 | -1.146400 |
| C | -3.738734 | -3.276794 | -0.107369 |
| H | -3.584086 | -1.436153 | 0.994157 |
| C | -3.090845 | -4.185159 | -0.948900 |
| H | -1.253174 | -4.655534 | -1.979258 |
| H | -4.771034 | -3.446825 | 0.185686 |
| H | -3.616304 | -5.063300 | -1.313002 |
| C | -3.609502 | 1.795282 | -2.251967 |
| C | -2.607256 | 0.925256 | -1.757197 |
| C | -1.833447 | 0.140470 | -2.624204 |

| | | | |
|---|---|---|---|
| C | -2.122812 | 0.203610 | -3.982552 |
| C | -3.149221 | 1.030991 | -4.485166 |
| C | -3.890081 | 1.832923 | -3.630294 |
| C | -4.139411 | 2.543062 | -1.145489 |
| C | -3.442720 | 2.114916 | -0.032664 |
| H | -1.043590 | -0.500964 | -2.257411 |
| H | -1.543632 | -0.403423 | -4.672782 |
| H | -3.349957 | 1.045132 | -5.552278 |
| H | -4.665777 | 2.487849 | -4.016124 |
| N | -2.526380 | 1.092549 | -0.373884 |
| C | -5.254180 | 3.539174 | -1.266698 |
| H | -5.295835 | 4.214872 | -0.413167 |
| H | -5.122327 | 4.139857 | -2.173371 |
| H | -6.223035 | 3.030232 | -1.357872 |
| S | -3.762015 | 2.623454 | 1.647865 |
| O | -2.609212 | 2.218660 | 2.478767 |
| O | -4.158257 | 4.039935 | 1.602032 |
| C | -5.182891 | 1.675810 | 2.193665 |
| C | -6.467046 | 2.198911 | 2.016403 |
| C | -4.992435 | 0.433458 | 2.803549 |
| C | -7.565422 | 1.458038 | 2.446298 |
| H | -6.601773 | 3.176177 | 1.566558 |
| C | -6.104533 | -0.293492 | 3.226419 |
| H | -3.990106 | 0.051023 | 2.962151 |
| C | -7.405217 | 0.203182 | 3.055090 |
| H | -8.564523 | 1.864229 | 2.312155 |
| H | -5.959015 | -1.258577 | 3.704520 |
| C | -8.604465 | -0.574376 | 3.540161 |
| H | -8.959949 | -0.181506 | 4.501569 |
| H | -9.438481 | -0.502447 | 2.834108 |
| H | -8.365555 | -1.632289 | 3.684342 |

2.2 The A' route

RC'

| | | | |
|---|---|---|---|
| Pd | 0.404662 | 0.132729 | 0.130468 |
| H | -1.174948 | 0.140625 | 0.282718 |
| P | 0.129214 | -0.364501 | 2.401737 |
| P | 2.876929 | 0.224401 | 0.099085 |
| C | -1.311931 | -1.554788 | 2.639100 |
| C | -1.130396 | -2.873435 | 1.857738 |
| C | -1.777813 | -1.805027 | 4.092055 |
| H | -2.115701 | -1.004585 | 2.132347 |
| C | -2.414102 | -3.720850 | 1.902178 |
| H | -0.299834 | -3.453476 | 2.277289 |

| | | | |
|---|---|---|---|
| H | -0.870639 | -2.649388 | 0.817637 |
| C | -3.060077 | -2.659399 | 4.106657 |
| H | -1.002685 | -2.319711 | 4.669953 |
| H | -1.968409 | -0.857428 | 4.607444 |
| C | -2.877636 | -3.977908 | 3.342624 |
| H | -2.242103 | -4.669514 | 1.379071 |
| H | -3.209804 | -3.198470 | 1.351512 |
| H | -3.353382 | -2.853549 | 5.145591 |
| H | -3.879961 | -2.085501 | 3.650983 |
| H | -3.814902 | -4.547457 | 3.343731 |
| H | -2.132244 | -4.599198 | 3.860799 |
| C | -0.330033 | 1.119529 | 3.463039 |
| C | 0.725327 | 2.240937 | 3.410093 |
| C | -1.722585 | 1.677671 | 3.095681 |
| H | -0.366865 | 0.724428 | 4.487121 |
| C | 0.335800 | 3.434124 | 4.301235 |
| H | 0.828742 | 2.584265 | 2.371978 |
| H | 1.699419 | 1.854642 | 3.724939 |
| C | -2.105348 | 2.865575 | 3.997135 |
| H | -1.707554 | 2.004669 | 2.048712 |
| H | -2.492857 | 0.903882 | 3.174543 |
| C | -1.052971 | 3.980431 | 3.947242 |
| H | 1.095072 | 4.220186 | 4.205952 |
| H | 0.342921 | 3.120473 | 5.355364 |
| H | -3.087047 | 3.248551 | 3.691600 |
| H | -2.217189 | 2.513484 | 5.032796 |
| H | -1.326873 | 4.793503 | 4.630425 |
| H | -1.027513 | 4.411885 | 2.936123 |
| C | 3.817967 | -1.135496 | -0.796975 |
| C | 3.508728 | -2.544303 | -0.242795 |
| C | 3.517278 | -1.091247 | -2.313232 |
| H | 4.889091 | -0.935328 | -0.650789 |
| C | 4.277907 | -3.634432 | -1.009900 |
| H | 2.429787 | -2.734962 | -0.326914 |
| H | 3.753812 | -2.606445 | 0.819577 |
| C | 4.292465 | -2.180820 | -3.074687 |
| H | 2.440484 | -1.238451 | -2.469858 |
| H | 3.763572 | -0.111018 | -2.732090 |
| C | 3.999272 | -3.579730 | -2.517307 |
| H | 4.011434 | -4.618881 | -0.605405 |
| H | 5.355990 | -3.505569 | -0.833888 |
| H | 4.035331 | -2.133973 | -4.140639 |
| H | 5.370874 | -1.976784 | -3.001170 |

| | | | |
|---|---|---|---|
| H | 4.598097 | -4.333032 | -3.043732 |
| H | 2.944372 | -3.829048 | -2.702662 |
| C | 3.427053 | 1.831316 | -0.729874 |
| C | 2.913773 | 3.060339 | 0.054440 |
| C | 4.919790 | 1.996774 | -1.095819 |
| H | 2.863913 | 1.799093 | -1.674422 |
| C | 3.169899 | 4.368701 | -0.713220 |
| H | 3.421369 | 3.118827 | 1.027406 |
| H | 1.841468 | 2.952848 | 0.260308 |
| C | 5.155706 | 3.309613 | -1.864774 |
| H | 5.535395 | 2.009477 | -0.190945 |
| H | 5.269629 | 1.152201 | -1.698806 |
| C | 4.651736 | 4.527813 | -1.079241 |
| H | 2.828492 | 5.219295 | -0.110121 |
| H | 2.566460 | 4.370734 | -1.632075 |
| H | 6.225926 | 3.412637 | -2.084798 |
| H | 4.639607 | 3.262137 | -2.832603 |
| H | 4.802052 | 5.444633 | -1.662686 |
| H | 5.244112 | 4.640896 | -0.159284 |
| C | 3.519277 | 0.304684 | 1.893855 |
| H | 3.030000 | 1.215844 | 2.250245 |
| C | 5.037115 | 0.496441 | 2.060284 |
| H | 5.618533 | -0.277835 | 1.549927 |
| H | 5.355134 | 1.466027 | 1.675816 |
| H | 5.296955 | 0.465092 | 3.123744 |
| Fe | 2.816748 | -1.029507 | 4.811698 |
| C | 3.006751 | -2.870709 | 3.880200 |
| C | 3.829637 | -1.910561 | 3.228928 |
| C | 1.663679 | -2.419208 | 3.798269 |
| C | 3.005824 | -0.859455 | 2.714442 |
| C | 1.632556 | -1.173212 | 3.069303 |
| H | 3.347235 | -3.758248 | 4.396731 |
| H | 4.907554 | -1.953694 | 3.162175 |
| H | 0.816646 | -2.929242 | 4.227173 |
| C | 2.108007 | 0.356824 | 6.218291 |
| C | 2.161490 | -0.946569 | 6.794513 |
| C | 3.424984 | 0.712869 | 5.797151 |
| C | 3.514960 | -1.396640 | 6.734693 |
| C | 4.295392 | -0.371807 | 6.119547 |
| H | 1.221750 | 0.966447 | 6.116464 |
| H | 1.321433 | -1.505045 | 7.185849 |
| H | 3.712754 | 1.636998 | 5.313480 |
| H | 3.879061 | -2.361780 | 7.061454 |

| | | | |
|---|---|---|---|
| H | 5.354926 | -0.423891 | 5.905845 |
| C | -0.206062 | 0.146133 | -2.088224 |
| C | -0.237918 | 1.358265 | -2.405296 |
| C | -0.706116 | -1.127289 | -2.606698 |
| C | -0.346649 | -2.355381 | -2.026239 |
| C | -1.551407 | -1.131235 | -3.735108 |
| C | -0.824873 | -3.556667 | -2.549708 |
| H | 0.314063 | -2.359970 | -1.166018 |
| C | -2.026817 | -2.333046 | -4.253698 |
| H | -1.813173 | -0.190540 | -4.206931 |
| C | -1.668338 | -3.548717 | -3.662623 |
| H | -0.536672 | -4.497251 | -2.088929 |
| H | -2.676948 | -2.320648 | -5.123766 |
| H | -2.041082 | -4.483732 | -4.070932 |
| C | -0.775775 | 4.863173 | -2.247381 |
| C | -1.008140 | 3.561210 | -1.771989 |
| C | -1.790864 | 3.288889 | -0.654610 |
| C | -2.353145 | 4.387033 | -0.002740 |
| C | -2.126185 | 5.702806 | -0.448740 |
| C | -1.340032 | 5.953834 | -1.569144 |
| C | 0.004475 | 4.771002 | -3.466206 |
| C | 0.274236 | 3.441762 | -3.672363 |
| H | -1.964950 | 2.271383 | -0.322831 |
| H | -2.990570 | 4.220595 | 0.860326 |
| H | -2.580341 | 6.531474 | 0.085701 |
| H | -1.174368 | 6.969304 | -1.915186 |
| N | -0.318096 | 2.659159 | -2.619722 |
| C | 0.363575 | 5.960881 | -4.301117 |
| H | -0.500022 | 6.628126 | -4.394908 |
| H | 1.163253 | 6.534131 | -3.814783 |
| H | 0.686039 | 5.681373 | -5.303033 |
| S | 0.757555 | 2.662630 | -5.218283 |
| O | 0.227946 | 1.289622 | -5.159496 |
| O | 0.328799 | 3.580869 | -6.283886 |
| C | 2.543239 | 2.566175 | -5.297570 |
| C | 3.286875 | 3.709055 | -5.615561 |
| C | 3.156856 | 1.319184 | -5.178555 |
| C | 4.661447 | 3.593063 | -5.793565 |
| H | 2.799573 | 4.668952 | -5.746445 |
| C | 4.536645 | 1.222707 | -5.369248 |
| H | 2.558592 | 0.438686 | -4.973041 |
| C | 5.309255 | 2.350703 | -5.675543 |
| H | 5.240726 | 4.477436 | -6.045463 |

| | | | |
|---|---|---|---|
| H | 5.015738 | 0.250393 | -5.293601 |
| C | 6.800639 | 2.244773 | -5.879959 |
| H | 7.102129 | 2.697009 | -6.831631 |
| H | 7.343123 | 2.774073 | -5.086633 |
| H | 7.133321 | 1.202956 | -5.877356 |

$TS'_{Ph}$

| | | | |
|---|---|---|---|
| Pd | 0.605853 | 0.089338 | 0.026768 |
| H | -0.942424 | 0.031012 | -0.355941 |
| P | 0.235564 | -0.433506 | 2.323087 |
| P | 3.039122 | 0.264569 | 0.146048 |
| C | -1.166206 | -1.679862 | 2.528215 |
| C | -0.882607 | -3.026594 | 1.828859 |
| C | -1.714861 | -1.897634 | 3.957667 |
| H | -1.960429 | -1.189889 | 1.947319 |
| C | -2.139557 | -3.913695 | 1.810916 |
| H | -0.074405 | -3.558739 | 2.343420 |
| H | -0.539283 | -2.847269 | 0.805445 |
| C | -2.968161 | -2.793199 | 3.925064 |
| H | -0.957290 | -2.367468 | 4.595279 |
| H | -1.966328 | -0.942709 | 4.430781 |
| C | -2.698799 | -4.131705 | 3.223851 |
| H | -1.900619 | -4.875997 | 1.341444 |
| H | -2.907408 | -3.439540 | 1.182543 |
| H | -3.321387 | -2.960710 | 4.950002 |
| H | -3.774533 | -2.262409 | 3.398302 |
| H | -3.618680 | -4.727448 | 3.180605 |
| H | -1.976042 | -4.713038 | 3.815206 |
| C | -0.325629 | 1.031272 | 3.364992 |
| C | 0.689238 | 2.190791 | 3.354037 |
| C | -1.715908 | 1.540123 | 2.925657 |
| H | -0.397478 | 0.643745 | 4.389996 |
| C | 0.217311 | 3.369484 | 4.224136 |
| H | 0.826058 | 2.536489 | 2.320027 |
| H | 1.662017 | 1.840461 | 3.711721 |
| C | -2.186285 | 2.715065 | 3.802021 |
| H | -1.656418 | 1.866465 | 1.879614 |
| H | -2.462668 | 0.740555 | 2.964528 |
| C | -1.172142 | 3.866296 | 3.805311 |
| H | 0.950966 | 4.182986 | 4.163779 |
| H | 0.186374 | 3.055761 | 5.277833 |
| H | -3.164006 | 3.064242 | 3.446571 |
| H | -2.339027 | 2.359037 | 4.831113 |
| H | -1.507660 | 4.666948 | 4.475729 |

| | | | |
|---|---|---|---|
| H | -1.113145 | 4.302048 | 2.797537 |
| C | 3.963492 | -1.130063 | -0.710032 |
| C | 3.565351 | -2.519482 | -0.162402 |
| C | 3.705132 | -1.082213 | -2.233930 |
| H | 5.037735 | -0.977535 | -0.532147 |
| C | 4.303655 | -3.650735 | -0.899046 |
| H | 2.480635 | -2.650784 | -0.286641 |
| H | 3.769066 | -2.588766 | 0.908360 |
| C | 4.445524 | -2.212379 | -2.970225 |
| H | 2.624713 | -1.179713 | -2.413588 |
| H | 4.006709 | -0.117846 | -2.653422 |
| C | 4.073017 | -3.592868 | -2.414385 |
| H | 3.977462 | -4.618559 | -0.498105 |
| H | 5.380936 | -3.573385 | -0.690867 |
| H | 4.218190 | -2.159664 | -4.042753 |
| H | 5.530060 | -2.058725 | -2.870367 |
| H | 4.651836 | -4.375807 | -2.919537 |
| H | 3.013631 | -3.795794 | -2.629350 |
| C | 3.624002 | 1.851586 | -0.693688 |
| C | 3.082870 | 3.096579 | 0.044782 |
| C | 5.127684 | 2.010229 | -1.013982 |
| H | 3.092990 | 1.799869 | -1.656070 |
| C | 3.357365 | 4.384525 | -0.750600 |
| H | 3.560639 | 3.181597 | 1.030933 |
| H | 2.004992 | 2.989137 | 0.221251 |
| C | 5.384738 | 3.302696 | -1.810678 |
| H | 5.713089 | 2.048806 | -0.090097 |
| H | 5.497916 | 1.149331 | -1.581213 |
| C | 4.849328 | 4.539894 | -1.076526 |
| H | 2.995704 | 5.250720 | -0.182460 |
| H | 2.780969 | 4.357743 | -1.686778 |
| H | 6.461387 | 3.405864 | -1.996931 |
| H | 4.901521 | 3.226003 | -2.793896 |
| H | 5.013660 | 5.440573 | -1.680972 |
| H | 5.412267 | 4.682424 | -0.142336 |
| C | 3.621438 | 0.360308 | 1.957683 |
| H | 3.096505 | 1.258739 | 2.296312 |
| C | 5.127342 | 0.594680 | 2.171209 |
| H | 5.745615 | -0.163829 | 1.680511 |
| H | 5.429344 | 1.572664 | 1.794709 |
| H | 5.354576 | 0.572263 | 3.242295 |
| Fe | 2.863869 | -0.956943 | 4.860804 |
| C | 3.140835 | -2.805274 | 3.969761 |

| | | | |
|---|---|---|---|
| C | 3.953653 | -1.830916 | 3.326627 |
| C | 1.787267 | -2.397074 | 3.836726 |
| C | 3.113061 | -0.815156 | 2.768113 |
| C | 1.738670 | -1.169223 | 3.079892 |
| H | 3.492594 | -3.671836 | 4.513731 |
| H | 5.034000 | -1.840440 | 3.295378 |
| H | 0.942256 | -2.922560 | 4.251522 |
| C | 2.049438 | 0.410335 | 6.227738 |
| C | 2.156440 | -0.880158 | 6.825222 |
| C | 3.356568 | 0.828933 | 5.833590 |
| C | 3.532653 | -1.259352 | 6.805720 |
| C | 4.273886 | -0.203715 | 6.194206 |
| H | 1.134784 | 0.969520 | 6.092506 |
| H | 1.336995 | -1.476683 | 7.203955 |
| H | 3.608515 | 1.759824 | 5.342848 |
| H | 3.938302 | -2.199127 | 7.156626 |
| H | 5.339929 | -0.202672 | 6.008204 |
| C | -0.531904 | 0.203028 | -1.883699 |
| C | -0.376893 | 1.374316 | -2.372114 |
| C | -1.173258 | -0.983259 | -2.492938 |
| C | -0.879358 | -2.273787 | -2.027123 |
| C | -2.066108 | -0.835006 | -3.570395 |
| C | -1.463445 | -3.393299 | -2.619564 |
| H | -0.174353 | -2.389502 | -1.210667 |
| C | -2.656643 | -1.954109 | -4.152854 |
| H | -2.282421 | 0.156065 | -3.955477 |
| C | -2.358784 | -3.235837 | -3.679760 |
| H | -1.218899 | -4.386346 | -2.253322 |
| H | -3.346222 | -1.825616 | -4.982132 |
| H | -2.818666 | -4.106178 | -4.138980 |
| C | -0.816557 | 4.892480 | -2.258860 |
| C | -1.084777 | 3.607306 | -1.761920 |
| C | -1.879759 | 3.373481 | -0.646664 |
| C | -2.418447 | 4.496214 | -0.015604 |
| C | -2.153104 | 5.796767 | -0.481817 |
| C | -1.354481 | 6.008481 | -1.602703 |
| C | -0.033439 | 4.757554 | -3.474973 |
| C | 0.197050 | 3.419623 | -3.660617 |
| H | -2.088710 | 2.367422 | -0.301482 |
| H | -3.064397 | 4.360358 | 0.846269 |
| H | -2.586954 | 6.646284 | 0.036405 |
| H | -1.161267 | 7.013517 | -1.964391 |
| N | -0.417384 | 2.667373 | -2.595609 |

| | | | |
|---|---|---|---|
| C | 0.364354 | 5.923194 | -4.325609 |
| H | -0.466338 | 6.632744 | -4.402164 |
| H | 1.204316 | 6.457749 | -3.863606 |
| H | 0.646810 | 5.620899 | -5.333165 |
| S | 0.685661 | 2.602025 | -5.185822 |
| O | 0.152502 | 1.232367 | -5.101882 |
| O | 0.263602 | 3.500238 | -6.271276 |
| C | 2.471834 | 2.503110 | -5.252434 |
| C | 3.217027 | 3.638904 | -5.590975 |
| C | 3.084190 | 1.257850 | -5.108464 |
| C | 4.591798 | 3.518546 | -5.765505 |
| H | 2.730930 | 4.596143 | -5.742989 |
| C | 4.463481 | 1.156429 | -5.298908 |
| H | 2.485677 | 0.381698 | -4.885432 |
| C | 5.237890 | 2.277829 | -5.625261 |
| H | 5.171842 | 4.397275 | -6.034635 |
| H | 4.941329 | 0.184853 | -5.208005 |
| C | 6.729973 | 2.166101 | -5.820744 |
| H | 7.052618 | 2.695568 | -6.723852 |
| H | 7.268266 | 2.613494 | -4.975351 |
| H | 7.046982 | 1.122594 | -5.903541 |

$TS'_{ind}$

| | | | |
|---|---|---|---|
| Pd | 1.103140 | -0.014341 | -0.289793 |
| H | -0.186283 | 0.953381 | -0.455010 |
| P | 0.681255 | 0.331225 | 2.026340 |
| P | 3.230504 | -1.168490 | -0.050202 |
| C | -1.102567 | -0.184006 | 2.336695 |
| C | -1.344653 | -1.668239 | 1.982971 |
| C | -1.715821 | 0.178543 | 3.708410 |
| H | -1.631645 | 0.410814 | 1.579345 |
| C | -2.843151 | -2.013521 | 2.040740 |
| H | -0.796824 | -2.313019 | 2.681268 |
| H | -0.949274 | -1.881032 | 0.981557 |
| C | -3.216271 | -0.168716 | 3.735512 |
| H | -1.215888 | -0.369051 | 4.514179 |
| H | -1.581335 | 1.243199 | 3.927835 |
| C | -3.462357 | -1.645545 | 3.396550 |
| H | -2.979962 | -3.082101 | 1.834001 |
| H | -3.369902 | -1.469302 | 1.243135 |
| H | -3.627152 | 0.072087 | 4.723560 |
| H | -3.747147 | 0.466195 | 3.011323 |
| H | -4.538202 | -1.858767 | 3.391700 |
| H | -3.021093 | -2.276976 | 4.181606 |

| | | | |
|---|---|---|---|
| C | 0.775482 | 2.124046 | 2.575013 |
| C | 2.158055 | 2.737360 | 2.272281 |
| C | -0.334922 | 2.988947 | 1.938838 |
| H | 0.627438 | 2.104515 | 3.663314 |
| C | 2.246337 | 4.199265 | 2.746212 |
| H | 2.332687 | 2.693628 | 1.187545 |
| H | 2.947471 | 2.147065 | 2.748351 |
| C | -0.252573 | 4.445008 | 2.432008 |
| H | -0.225769 | 2.968089 | 0.845469 |
| H | -1.328471 | 2.588842 | 2.163745 |
| C | 1.123727 | 5.062111 | 2.154179 |
| H | 3.228520 | 4.609758 | 2.479935 |
| H | 2.184600 | 4.230885 | 3.843744 |
| H | -1.041236 | 5.035516 | 1.949950 |
| H | -0.456584 | 4.472220 | 3.512164 |
| H | 1.173496 | 6.079403 | 2.561469 |
| H | 1.265522 | 5.151017 | 1.067987 |
| C | 3.306380 | -3.047971 | -0.107457 |
| C | 2.181878 | -3.691435 | 0.738251 |
| C | 3.224615 | -3.596663 | -1.550830 |
| H | 4.277759 | -3.334420 | 0.322148 |
| C | 2.278781 | -5.227055 | 0.725563 |
| H | 1.212614 | -3.383564 | 0.320692 |
| H | 2.210147 | -3.333955 | 1.769315 |
| C | 3.332344 | -5.131632 | -1.570240 |
| H | 2.266317 | -3.299415 | -1.991566 |
| H | 4.004555 | -3.173251 | -2.189007 |
| C | 2.252244 | -5.789114 | -0.701452 |
| H | 1.457199 | -5.647615 | 1.319031 |
| H | 3.211285 | -5.532853 | 1.222276 |
| H | 3.257892 | -5.484486 | -2.606286 |
| H | 4.326934 | -5.430107 | -1.207686 |
| H | 2.385103 | -6.877920 | -0.685895 |
| H | 1.264814 | -5.598814 | -1.147090 |
| C | 4.397582 | -0.523116 | -1.380836 |
| C | 4.518792 | 1.017181 | -1.305225 |
| C | 5.796418 | -1.165408 | -1.535220 |
| H | 3.834401 | -0.756249 | -2.295379 |
| C | 5.256632 | 1.580441 | -2.533051 |
| H | 5.067463 | 1.299902 | -0.395423 |
| H | 3.522648 | 1.471360 | -1.234524 |
| C | 6.495307 | -0.616924 | -2.793233 |
| H | 6.420708 | -0.937086 | -0.666441 |

| | | | |
|---|---|---|---|
| H | 5.731472 | -2.256320 | -1.592196 |
| C | 6.623313 | 0.912239 | -2.739901 |
| H | 5.374435 | 2.665519 | -2.420811 |
| H | 4.632813 | 1.427983 | -3.423948 |
| H | 7.485122 | -1.079730 | -2.891141 |
| H | 5.922007 | -0.908229 | -3.685137 |
| H | 7.091048 | 1.287213 | -3.658478 |
| H | 7.293140 | 1.188163 | -1.911964 |
| C | 3.954141 | -0.612758 | 1.626378 |
| H | 3.844964 | 0.474650 | 1.559755 |
| C | 5.445009 | -0.922198 | 1.851443 |
| H | 5.686261 | -1.978748 | 1.697569 |
| H | 6.073970 | -0.329964 | 1.186200 |
| H | 5.718231 | -0.662016 | 2.879356 |
| Fe | 3.012446 | -0.442507 | 4.767301 |
| C | 2.382283 | -2.404523 | 4.556674 |
| C | 3.472348 | -2.149061 | 3.677669 |
| C | 1.328267 | -1.514881 | 4.215946 |
| C | 3.099229 | -1.110354 | 2.767598 |
| C | 1.745420 | -0.706626 | 3.095463 |
| H | 2.376054 | -3.109732 | 5.377164 |
| H | 4.435027 | -2.639510 | 3.713203 |
| H | 0.381904 | -1.455987 | 4.729248 |
| C | 2.969629 | 1.490120 | 5.581216 |
| C | 2.605357 | 0.530461 | 6.570853 |
| C | 4.285852 | 1.179574 | 5.121966 |
| C | 3.698939 | -0.373759 | 6.728091 |
| C | 4.737062 | 0.027971 | 5.834551 |
| H | 2.351067 | 2.305865 | 5.235686 |
| H | 1.657949 | 0.480320 | 7.091147 |
| H | 4.841948 | 1.716508 | 4.364878 |
| H | 3.722024 | -1.236295 | 7.381004 |
| H | 5.686147 | -0.473894 | 5.699140 |
| C | 0.724277 | -0.180283 | -2.445272 |
| C | -0.064841 | 0.788348 | -2.255156 |
| C | 1.104143 | -1.129542 | -3.489311 |
| C | 0.419436 | -2.353569 | -3.596128 |
| C | 2.111720 | -0.818351 | -4.418311 |
| C | 0.739634 | -3.248714 | -4.616364 |
| H | -0.363687 | -2.594902 | -2.883234 |
| C | 2.428753 | -1.725724 | -5.430432 |
| H | 2.609174 | 0.142871 | -4.362582 |
| C | 1.749687 | -2.942057 | -5.532405 |

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| H | 0.197198 | -4.186660 | -4.694991 |
| H | 3.203266 | -1.472332 | -6.148915 |
| H | 1.998979 | -3.642141 | -6.324418 |
| C | -2.878859 | 2.957788 | -2.577236 |
| C | -2.280154 | 1.751905 | -2.162169 |
| C | -2.973844 | 0.761284 | -1.466495 |
| C | -4.315173 | 1.013704 | -1.183953 |
| C | -4.937716 | 2.211024 | -1.587985 |
| C | -4.233299 | 3.185760 | -2.286410 |
| C | -1.881768 | 3.731963 | -3.281913 |
| C | -0.715370 | 3.008040 | -3.243189 |
| H | -2.496467 | -0.168010 | -1.175361 |
| H | -4.894152 | 0.266201 | -0.649716 |
| H | -5.985949 | 2.370070 | -1.354153 |
| H | -4.721695 | 4.103719 | -2.598744 |
| N | -0.939108 | 1.764183 | -2.577799 |
| C | -2.133133 | 5.060195 | -3.930522 |
| H | -3.197864 | 5.179094 | -4.149729 |
| H | -1.836171 | 5.887182 | -3.273511 |
| H | -1.581001 | 5.157139 | -4.867710 |
| S | 0.823518 | 3.443973 | -4.052946 |
| O | 1.799977 | 2.383126 | -3.752881 |
| O | 0.496823 | 3.777016 | -5.448082 |
| C | 1.389101 | 4.943631 | -3.252524 |
| C | 2.079392 | 4.856178 | -2.039117 |
| C | 1.217879 | 6.171080 | -3.895446 |
| C | 2.583805 | 6.019253 | -1.463721 |
| H | 2.239460 | 3.892522 | -1.566660 |
| C | 1.727810 | 7.325040 | -3.300833 |
| H | 0.718351 | 6.217470 | -4.856432 |
| C | 2.411302 | 7.271146 | -2.078253 |
| H | 3.134250 | 5.955016 | -0.528928 |
| H | 1.602192 | 8.280189 | -3.803333 |
| C | 2.941152 | 8.526444 | -1.429644 |
| H | 2.227029 | 8.912732 | -0.690486 |
| H | 3.882551 | 8.338049 | -0.903436 |
| H | 3.110033 | 9.317395 | -2.166380 |

$PC'_{Ph}$

| | | | |
|---|---|---|---|
| Pd | 1.378460 | 0.581856 | 0.060577 |
| H | -0.208241 | 3.098949 | -0.226412 |
| P | 1.195543 | -1.301228 | 1.630390 |
| P | 2.777790 | 1.872466 | 1.397821 |
| C | 1.326846 | -2.941424 | 0.721174 |

| | | | |
|---|---|---|---|
| C | 2.731971 | -3.163178 | 0.116228 |
| C | 0.827198 | -4.191469 | 1.482124 |
| H | 0.646089 | -2.777880 | -0.124564 |
| C | 2.765492 | -4.426089 | -0.762744 |
| H | 3.476479 | -3.259138 | 0.915538 |
| H | 3.019194 | -2.291388 | -0.483251 |
| C | 0.870291 | -5.435199 | 0.575474 |
| H | 1.446038 | -4.378515 | 2.367323 |
| H | -0.194692 | -4.041272 | 1.846621 |
| C | 2.272707 | -5.665708 | -0.003551 |
| H | 3.787557 | -4.584017 | -1.129616 |
| H | 2.135890 | -4.260267 | -1.646364 |
| H | 0.538942 | -6.312145 | 1.145457 |
| H | 0.153057 | -5.305696 | -0.248008 |
| H | 2.268861 | -6.539304 | -0.667050 |
| H | 2.970121 | -5.897252 | 0.815377 |
| C | -0.531149 | -1.292900 | 2.379053 |
| C | -0.818684 | 0.023678 | 3.129985 |
| C | -1.610335 | -1.526279 | 1.295811 |
| H | -0.564007 | -2.121925 | 3.099012 |
| C | -2.234354 | 0.039702 | 3.732798 |
| H | -0.717996 | 0.862528 | 2.425856 |
| H | -0.078611 | 0.175124 | 3.921819 |
| C | -3.024001 | -1.515330 | 1.903864 |
| H | -1.534885 | -0.737197 | 0.535688 |
| H | -1.447649 | -2.475491 | 0.775289 |
| C | -3.306931 | -0.213884 | 2.665269 |
| H | -2.407626 | 1.001198 | 4.232168 |
| H | -2.308250 | -0.733911 | 4.511260 |
| H | -3.762649 | -1.661133 | 1.106064 |
| H | -3.129820 | -2.369309 | 2.588663 |
| H | -4.301429 | -0.250124 | 3.126352 |
| H | -3.318991 | 0.626817 | 1.955847 |
| C | 4.558134 | 1.752166 | 0.815485 |
| C | 5.093342 | 0.303228 | 0.768101 |
| C | 4.740820 | 2.405761 | -0.571947 |
| H | 5.145245 | 2.317341 | 1.554391 |
| C | 6.568027 | 0.271991 | 0.326829 |
| H | 4.484749 | -0.273605 | 0.057890 |
| H | 4.996141 | -0.184337 | 1.739796 |
| C | 6.215799 | 2.390914 | -1.007402 |
| H | 4.146368 | 1.843201 | -1.301120 |
| H | 4.363809 | 3.432392 | -0.590627 |

| | | | |
|---|---|---|---|
| C | 6.781502 | 0.964911 | -1.025326 |
| H | 6.908255 | -0.769994 | 0.281729 |
| H | 7.182130 | 0.768059 | 1.092700 |
| H | 6.301726 | 2.851480 | -1.999026 |
| H | 6.805472 | 3.013112 | -0.318392 |
| H | 7.848021 | 0.980207 | -1.281175 |
| H | 6.276691 | 0.386755 | -1.813058 |
| C | 2.341726 | 3.709947 | 1.398935 |
| C | 1.035776 | 3.992291 | 2.178892 |
| C | 3.448472 | 4.715685 | 1.800749 |
| H | 2.122442 | 3.881285 | 0.338792 |
| C | 0.567086 | 5.441930 | 1.958979 |
| H | 1.195403 | 3.834614 | 3.252978 |
| H | 0.246742 | 3.292011 | 1.878220 |
| C | 2.963715 | 6.159379 | 1.567359 |
| H | 3.716908 | 4.601689 | 2.855235 |
| H | 4.363247 | 4.544015 | 1.225597 |
| C | 1.662301 | 6.453063 | 2.326039 |
| H | -0.339061 | 5.626174 | 2.549167 |
| H | 0.290248 | 5.576078 | 0.903798 |
| H | 3.751397 | 6.858577 | 1.873533 |
| H | 2.803683 | 6.318360 | 0.491066 |
| H | 1.320839 | 7.473162 | 2.112747 |
| H | 1.853714 | 6.405891 | 3.408058 |
| C | 2.706058 | 1.327225 | 3.228963 |
| H | 1.636455 | 1.426235 | 3.438607 |
| C | 3.460343 | 2.267233 | 4.189259 |
| H | 4.521456 | 2.360865 | 3.938627 |
| H | 3.023635 | 3.264865 | 4.202680 |
| H | 3.389206 | 1.867357 | 5.205753 |
| Fe | 2.553543 | -1.365699 | 5.060046 |
| C | 4.331323 | -1.954757 | 4.170793 |
| C | 4.255089 | -0.534263 | 4.205329 |
| C | 3.225489 | -2.433314 | 3.418674 |
| C | 3.107955 | -0.114056 | 3.457018 |
| C | 2.457876 | -1.306372 | 2.950180 |
| H | 5.067418 | -2.565291 | 4.676701 |
| H | 4.935373 | 0.113398 | 4.739514 |
| H | 3.002120 | -3.473276 | 3.240794 |
| C | 0.692508 | -1.662460 | 5.978188 |
| C | 1.598667 | -2.697251 | 6.354645 |
| C | 1.249218 | -0.412590 | 6.387977 |
| C | 2.715885 | -2.088205 | 7.002210 |

| | | | |
|---|---|---|---|
| C | 2.499512 | -0.677368 | 7.024038 |
| H | -0.247008 | -1.802570 | 5.462665 |
| H | 1.474537 | -3.754268 | 6.159545 |
| H | 0.806999 | 0.563662 | 6.238045 |
| H | 3.591985 | -2.601937 | 7.375538 |
| H | 3.179981 | 0.062350 | 7.425062 |
| C | 0.111705 | 2.943852 | -1.254065 |
| C | 1.080906 | 2.013284 | -1.406046 |
| C | -0.645604 | 3.781045 | -2.208547 |
| C | -1.490449 | 4.769922 | -1.662187 |
| C | -0.628280 | 3.641178 | -3.611681 |
| C | -2.267509 | 5.595146 | -2.472712 |
| H | -1.537268 | 4.886664 | -0.582091 |
| C | -1.412266 | 4.461755 | -4.421345 |
| H | -0.010650 | 2.883774 | -4.076934 |
| C | -2.230562 | 5.446163 | -3.860647 |
| H | -2.903725 | 6.350603 | -2.019832 |
| H | -1.381490 | 4.330588 | -5.499633 |
| H | -2.834571 | 6.085690 | -4.497949 |
| C | 3.197431 | 1.925766 | -4.378562 |
| C | 2.532998 | 2.638867 | -3.348617 |
| C | 2.768940 | 4.003354 | -3.125173 |
| C | 3.673951 | 4.639917 | -3.963935 |
| C | 4.338802 | 3.947759 | -5.002544 |
| C | 4.108768 | 2.597981 | -5.216938 |
| C | 2.755843 | 0.560101 | -4.332636 |
| C | 1.868473 | 0.499530 | -3.271484 |
| H | 2.252330 | 4.543035 | -2.340080 |
| H | 3.870159 | 5.698979 | -3.823228 |
| H | 5.034886 | 4.485673 | -5.639103 |
| H | 4.619264 | 2.066778 | -6.014885 |
| N | 1.691538 | 1.760060 | -2.672726 |
| C | 3.172810 | -0.501094 | -5.305926 |
| H | 4.258898 | -0.473520 | -5.449525 |
| H | 2.899316 | -1.500826 | -4.969259 |
| H | 2.715636 | -0.327223 | -6.288798 |
| S | 0.824627 | -0.867776 | -2.861677 |
| O | 1.572313 | -2.110384 | -3.104907 |
| O | 0.271161 | -0.630399 | -1.483484 |
| C | -0.591785 | -0.828740 | -3.948876 |
| C | -1.637794 | 0.063248 | -3.697476 |
| C | -0.618600 | -1.694500 | -5.046875 |
| C | -2.725617 | 0.081382 | -4.568340 |

| | | | |
|---|---|---|---|
| H | -1.609931 | 0.723650 | -2.837607 |
| C | -1.717820 | -1.660233 | -5.900154 |
| H | 0.194858 | -2.391500 | -5.214719 |
| C | -2.784349 | -0.773175 | -5.679517 |
| H | -3.543894 | 0.769957 | -4.377825 |
| H | -1.750230 | -2.337114 | -6.749697 |
| C | -3.961233 | -0.744083 | -6.623453 |
| H | -4.751412 | -0.081206 | -6.260181 |
| H | -3.656618 | -0.392785 | -7.617060 |
| H | -4.387602 | -1.745331 | -6.753850 |

$PC'_{ind}$

| | | | |
|---|---|---|---|
| Pd | 1.228507 | 0.020604 | 0.184650 |
| H | -0.211995 | 1.576524 | -0.461008 |
| P | 1.035134 | 0.224858 | 2.600751 |
| P | 3.043160 | -1.403414 | 0.161888 |
| C | -0.780427 | 0.039789 | 3.050963 |
| C | -1.332239 | -1.353795 | 2.678158 |
| C | -1.192935 | 0.448940 | 4.483101 |
| H | -1.250753 | 0.758870 | 2.363589 |
| C | -2.858722 | -1.410648 | 2.863216 |
| H | -0.860698 | -2.121315 | 3.304990 |
| H | -1.072872 | -1.591020 | 1.638715 |
| C | -2.723160 | 0.385938 | 4.644737 |
| H | -0.732080 | -0.220908 | 5.217880 |
| H | -0.838559 | 1.458757 | 4.716804 |
| C | -3.276133 | -0.999702 | 4.282357 |
| H | -3.216575 | -2.422458 | 2.636372 |
| H | -3.335199 | -0.738303 | 2.134855 |
| H | -2.990943 | 0.648800 | 5.675385 |
| H | -3.185476 | 1.144889 | 3.997086 |
| H | -4.369175 | -1.005639 | 4.371629 |
| H | -2.898460 | -1.741112 | 5.001789 |
| C | 1.508167 | 1.959727 | 3.149667 |
| C | 2.955627 | 2.301529 | 2.737654 |
| C | 0.534294 | 3.013047 | 2.572357 |
| H | 1.437427 | 1.968785 | 4.246024 |
| C | 3.346946 | 3.726901 | 3.165434 |
| H | 3.040282 | 2.218833 | 1.644649 |
| H | 3.652894 | 1.578714 | 3.172944 |
| C | 0.926624 | 4.439045 | 2.999375 |
| H | 0.553414 | 2.962959 | 1.475419 |
| H | -0.495477 | 2.814428 | 2.887441 |
| C | 2.371813 | 4.771385 | 2.606560 |

| | | | |
|---|---|---|---|
| H | 4.370548 | 3.937670 | 2.831383 |
| H | 3.357842 | 3.788646 | 4.263846 |
| H | 0.233049 | 5.150743 | 2.536518 |
| H | 0.807011 | 4.538144 | 4.088188 |
| H | 2.641928 | 5.772344 | 2.964544 |
| H | 2.449451 | 4.793011 | 1.510748 |
| C | 2.584008 | -3.210356 | -0.062515 |
| C | 1.558626 | -3.729221 | 0.970777 |
| C | 2.048926 | -3.494253 | -1.483183 |
| H | 3.529675 | -3.756133 | 0.076559 |
| C | 1.288387 | -5.232088 | 0.773720 |
| H | 0.622652 | -3.168005 | 0.846041 |
| H | 1.901099 | -3.555949 | 1.991406 |
| C | 1.794761 | -4.997340 | -1.691390 |
| H | 1.104174 | -2.949652 | -1.605162 |
| H | 2.727333 | -3.124924 | -2.257217 |
| C | 0.814978 | -5.552406 | -0.649632 |
| H | 0.544096 | -5.562316 | 1.508774 |
| H | 2.209498 | -5.793309 | 0.988401 |
| H | 1.410802 | -5.161605 | -2.705736 |
| H | 2.749674 | -5.538640 | -1.626512 |
| H | 0.695229 | -6.635041 | -0.777309 |
| H | -0.176438 | -5.104630 | -0.811625 |
| C | 4.226032 | -0.954091 | -1.227665 |
| C | 4.859110 | 0.438395 | -0.996881 |
| C | 5.293237 | -2.006364 | -1.617775 |
| H | 3.544475 | -0.857061 | -2.082182 |
| C | 5.686263 | 0.884243 | -2.216492 |
| H | 5.513681 | 0.414422 | -0.115713 |
| H | 4.073887 | 1.176424 | -0.790892 |
| C | 6.079553 | -1.531856 | -2.854286 |
| H | 5.997802 | -2.170677 | -0.797388 |
| H | 4.828603 | -2.974447 | -1.830071 |
| C | 6.733658 | -0.164451 | -2.614822 |
| H | 6.167757 | 1.844316 | -1.993661 |
| H | 5.009120 | 1.058079 | -3.062786 |
| H | 6.838546 | -2.282408 | -3.106859 |
| H | 5.399082 | -1.467794 | -3.715363 |
| H | 7.269972 | 0.161796 | -3.514154 |
| H | 7.485542 | -0.255847 | -1.817063 |
| C | 4.003052 | -1.210989 | 1.805053 |
| H | 4.144516 | -0.126655 | 1.844124 |
| C | 5.396961 | -1.866907 | 1.796744 |

| | | | |
|---|---|---|---|
| H | 5.359201 | -2.937329 | 1.572816 |
| H | 6.060029 | -1.388350 | 1.076364 |
| H | 5.847585 | -1.746654 | 2.787126 |
| Fe | 3.459181 | -1.087946 | 5.030548 |
| C | 2.466322 | -2.895836 | 4.821724 |
| C | 3.480476 | -2.781031 | 3.828889 |
| C | 1.556811 | -1.817927 | 4.647089 |
| C | 3.199093 | -1.638932 | 3.012366 |
| C | 1.986015 | -1.029093 | 3.519964 |
| H | 2.426768 | -3.638036 | 5.607889 |
| H | 4.336292 | -3.433957 | 3.731552 |
| H | 0.697664 | -1.623871 | 5.270277 |
| C | 3.854189 | 0.777824 | 5.904554 |
| C | 3.428077 | -0.152587 | 6.897572 |
| C | 5.036163 | 0.262865 | 5.290436 |
| C | 4.349733 | -1.242940 | 6.901917 |
| C | 5.343516 | -0.985919 | 5.910008 |
| H | 3.360357 | 1.706304 | 5.655522 |
| H | 2.547209 | -0.061272 | 7.519282 |
| H | 5.597356 | 0.731516 | 4.492781 |
| H | 4.284154 | -2.128368 | 7.520415 |
| H | 6.166907 | -1.639456 | 5.653210 |
| C | 0.885938 | 0.407607 | -1.842207 |
| C | -0.024296 | 1.328882 | -1.526751 |
| C | 1.423714 | 0.141596 | -3.180384 |
| C | 1.199090 | -1.058342 | -3.879836 |
| C | 2.193332 | 1.145163 | -3.806546 |
| C | 1.716229 | -1.245379 | -5.161980 |
| H | 0.600684 | -1.839809 | -3.424169 |
| C | 2.715023 | 0.952151 | -5.085615 |
| H | 2.378780 | 2.072793 | -3.273060 |
| C | 2.479383 | -0.244334 | -5.768778 |
| H | 1.518903 | -2.174437 | -5.689513 |
| H | 3.303551 | 1.738557 | -5.550299 |
| H | 2.883352 | -0.393805 | -6.765861 |
| C | -2.856593 | 2.535210 | -3.442497 |
| C | -1.955985 | 1.502806 | -3.080447 |
| C | -2.213806 | 0.160362 | -3.383424 |
| C | -3.369209 | -0.122896 | -4.102461 |
| C | -4.258204 | 0.896611 | -4.506757 |
| C | -4.014008 | 2.222348 | -4.179593 |
| C | -2.348913 | 3.770845 | -2.909998 |
| C | -1.177056 | 3.447330 | -2.260620 |

| | | | |
|---|---|---|---|
| H | -1.536186 | -0.627098 | -3.076360 |
| H | -3.591418 | -1.154393 | -4.360719 |
| H | -5.146449 | 0.634476 | -5.073843 |
| H | -4.705819 | 3.004641 | -4.478167 |
| N | -0.890191 | 2.072988 | -2.382308 |
| C | -2.976554 | 5.119006 | -3.096783 |
| H | -4.064644 | 5.045844 | -2.992938 |
| H | -2.616710 | 5.841776 | -2.362485 |
| H | -2.772075 | 5.516550 | -4.099234 |
| S | -0.032333 | 4.601656 | -1.531652 |
| O | -0.763686 | 5.427913 | -0.553063 |
| O | 1.144933 | 3.828927 | -1.079471 |
| C | 0.477382 | 5.671467 | -2.878447 |
| C | 0.320433 | 7.050099 | -2.739248 |
| C | 1.078887 | 5.123799 | -4.016648 |
| C | 0.774022 | 7.889002 | -3.758347 |
| H | -0.145225 | 7.455279 | -1.847560 |
| C | 1.518318 | 5.976396 | -5.024193 |
| H | 1.195317 | 4.049415 | -4.120411 |
| C | 1.374157 | 7.370432 | -4.913158 |
| H | 0.657156 | 8.964052 | -3.651866 |
| H | 1.983093 | 5.555683 | -5.912089 |
| C | 1.837851 | 8.279811 | -6.025032 |
| H | 1.130830 | 8.261816 | -6.864514 |
| H | 1.922105 | 9.316343 | -5.685762 |
| H | 2.811427 | 7.965941 | -6.416866 |

## 6. References


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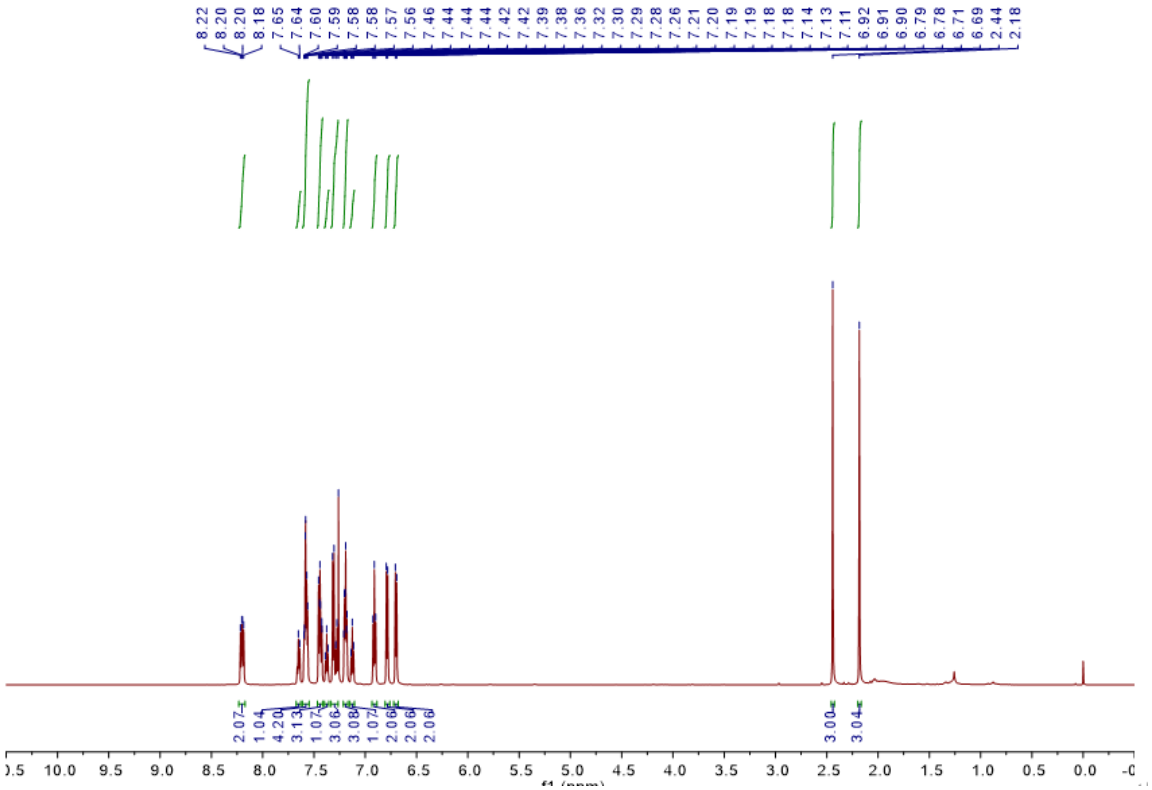
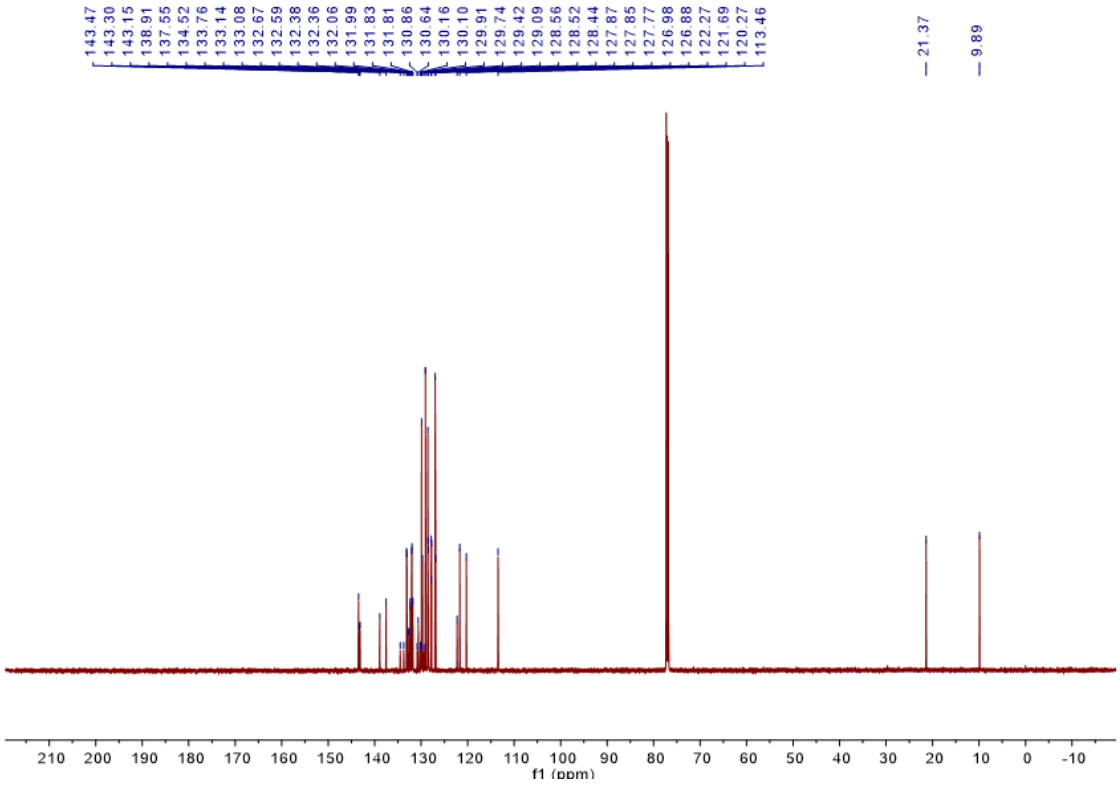
## 7. NMR spectra



$^1$H NMR of 3 ($CDCl_3$)



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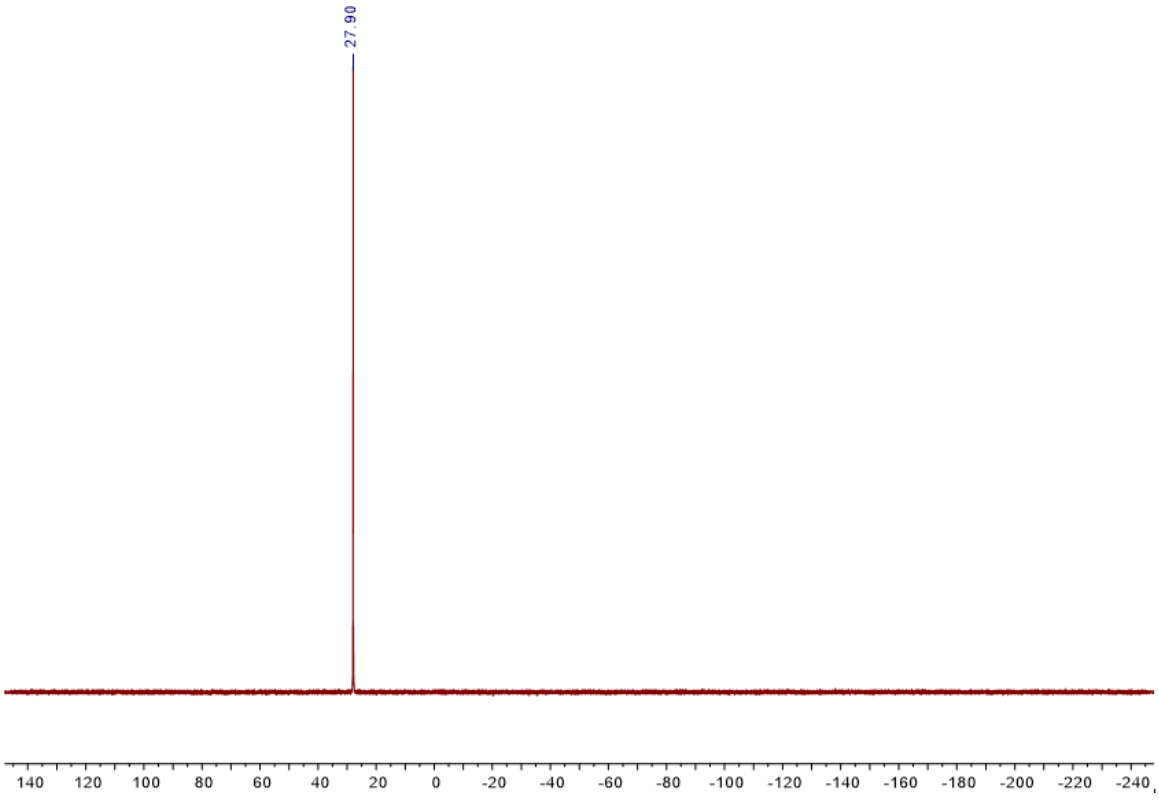


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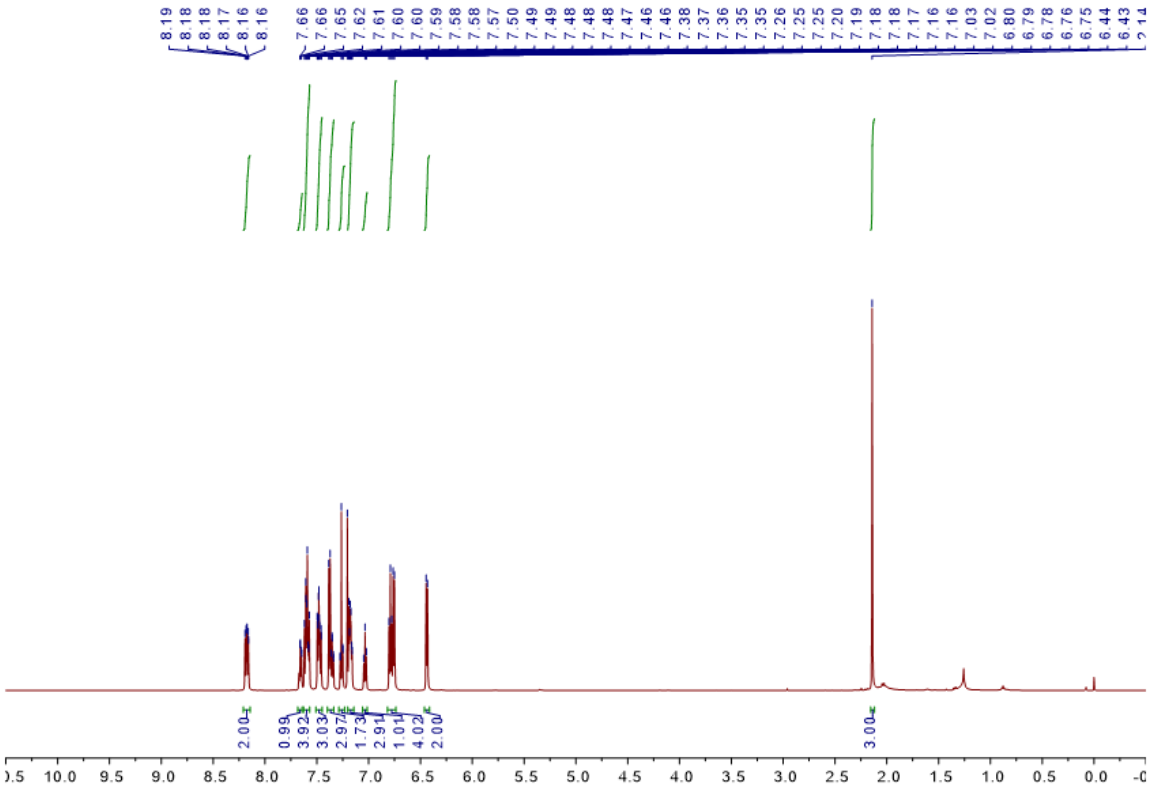

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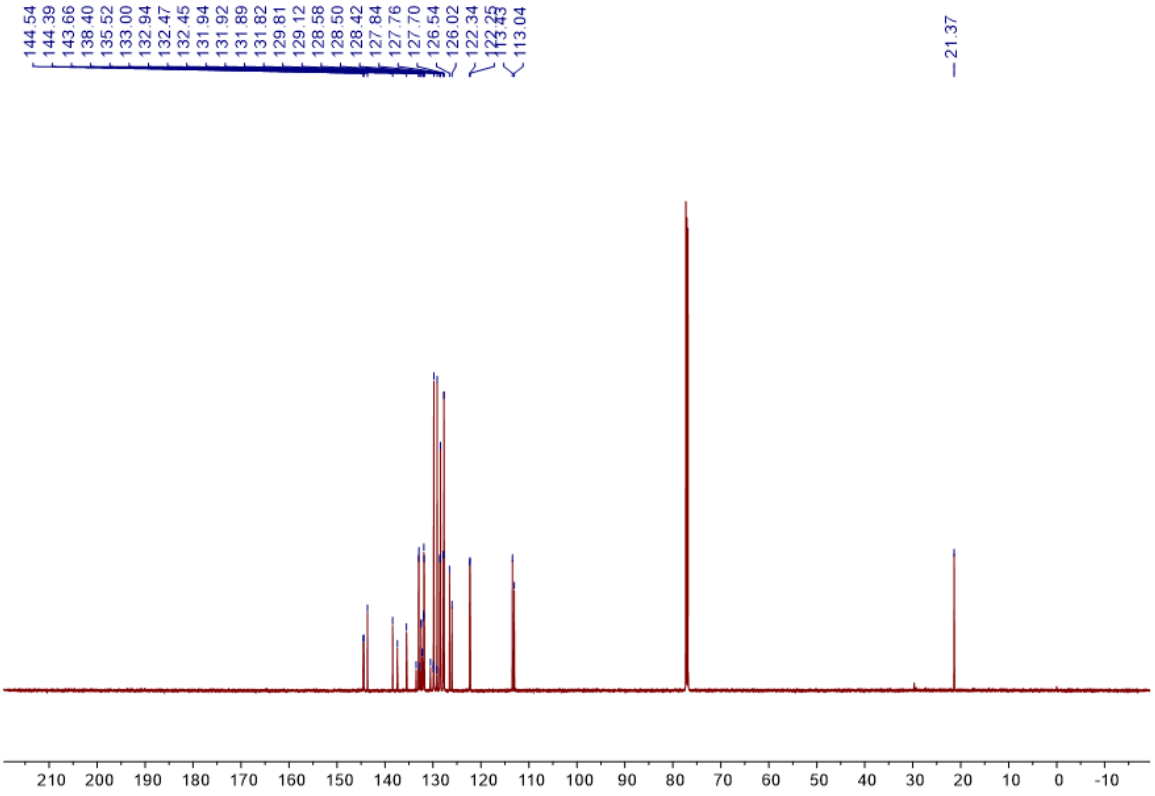


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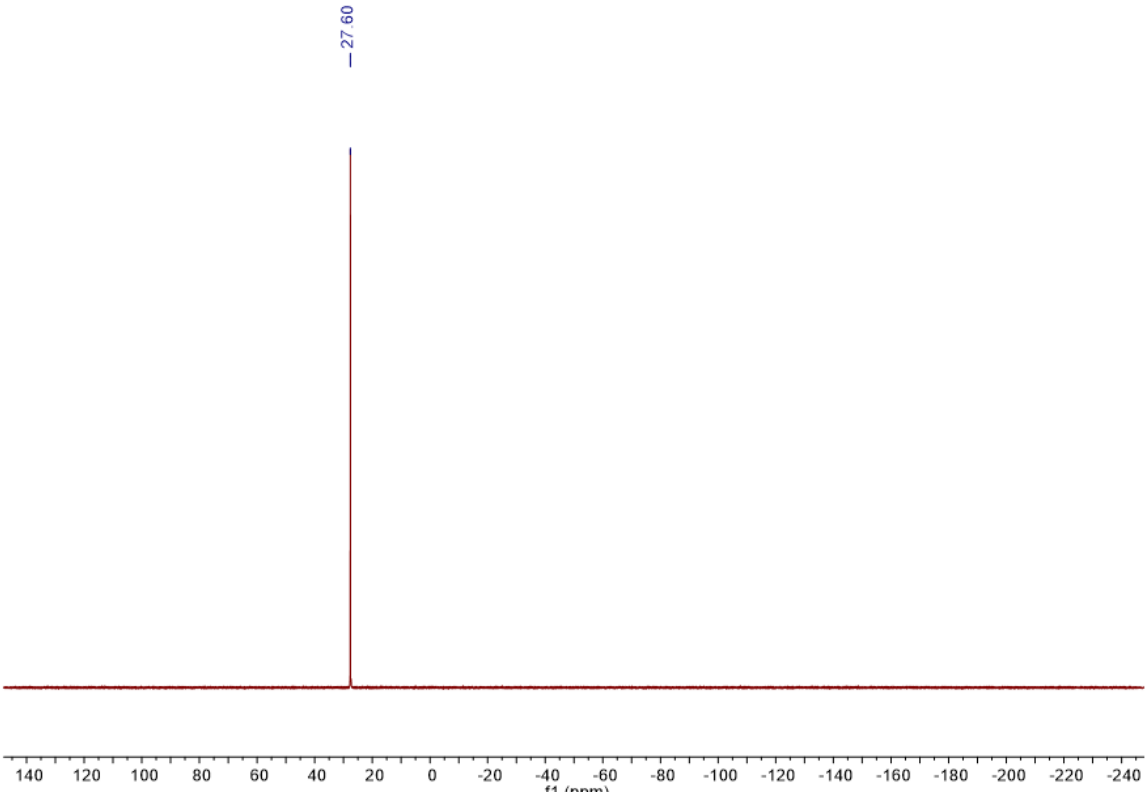

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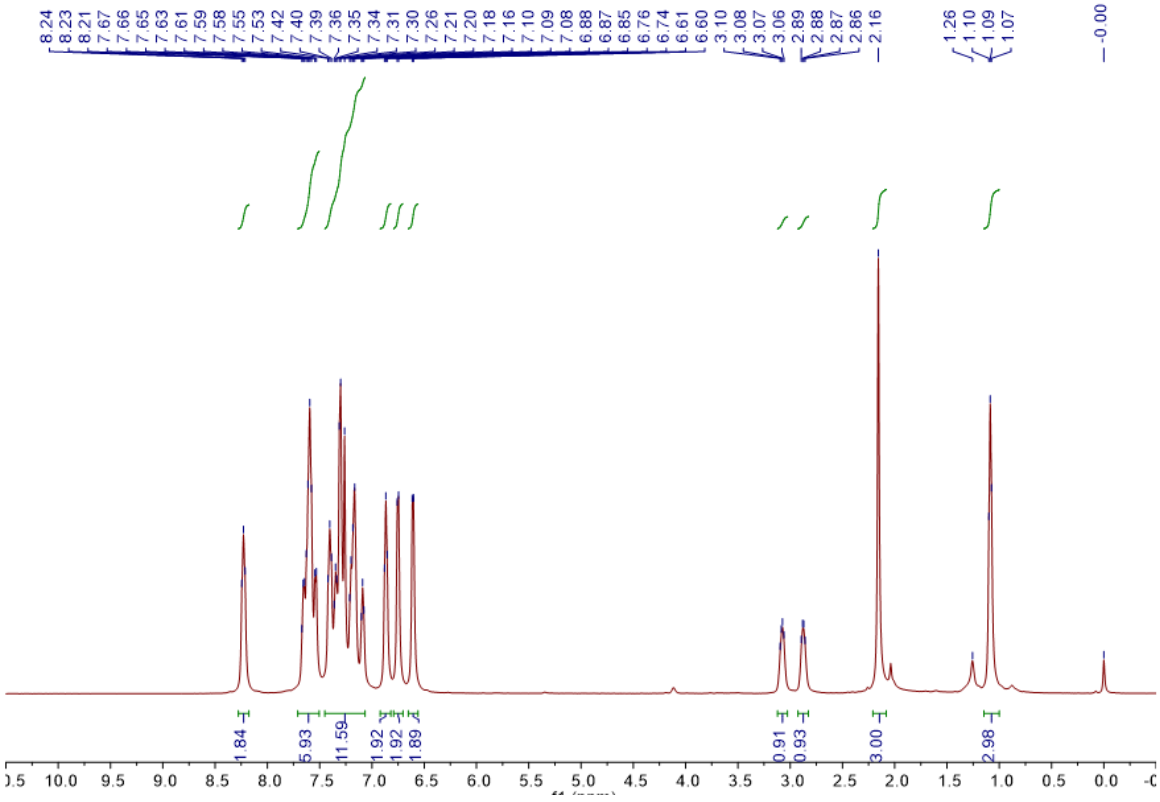

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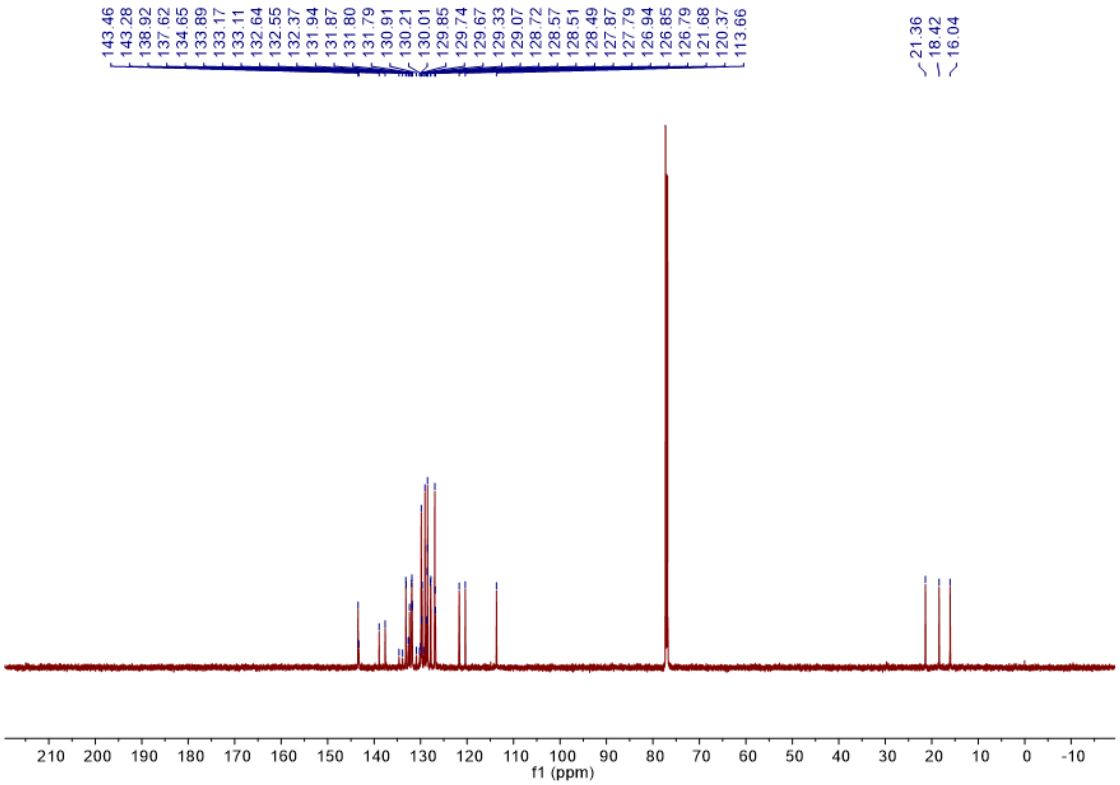

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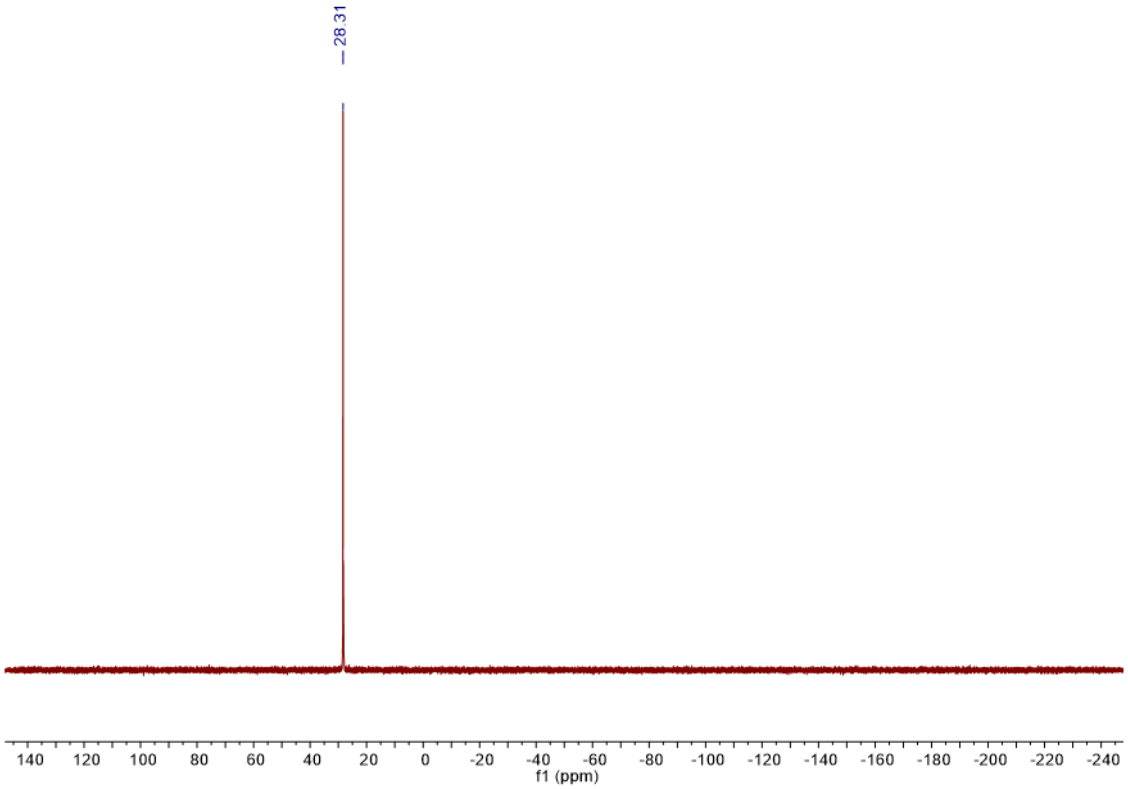


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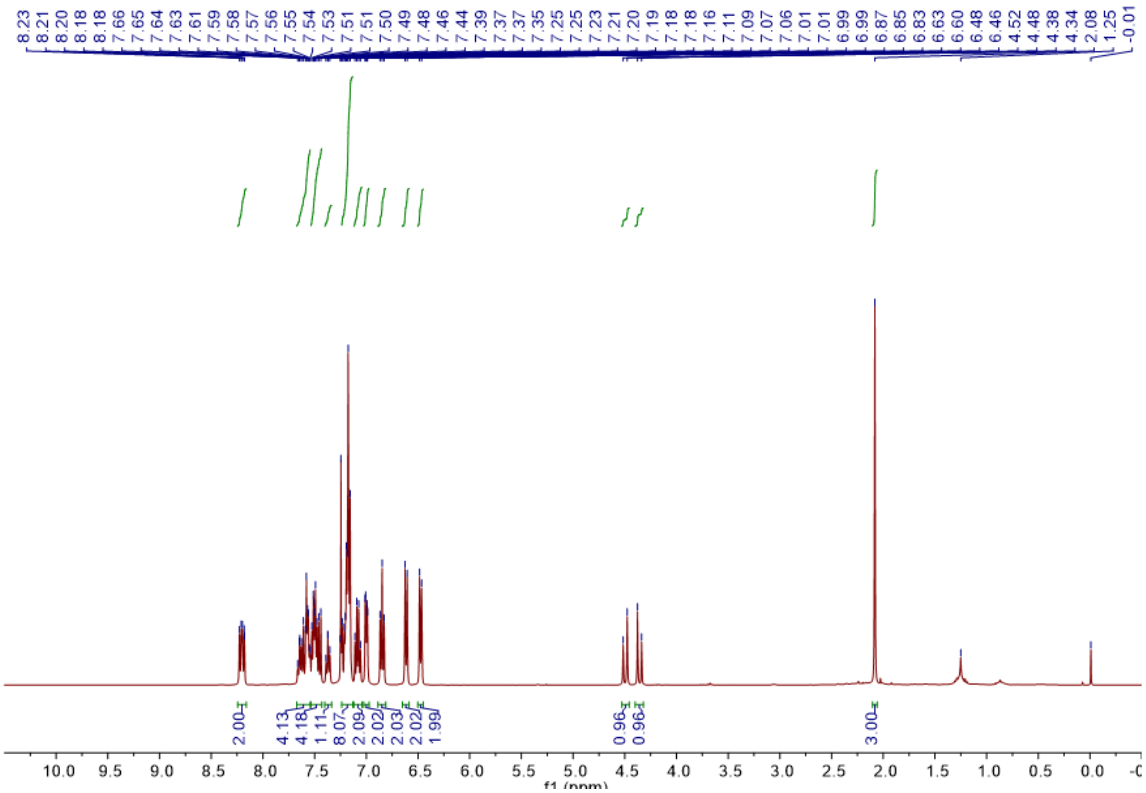

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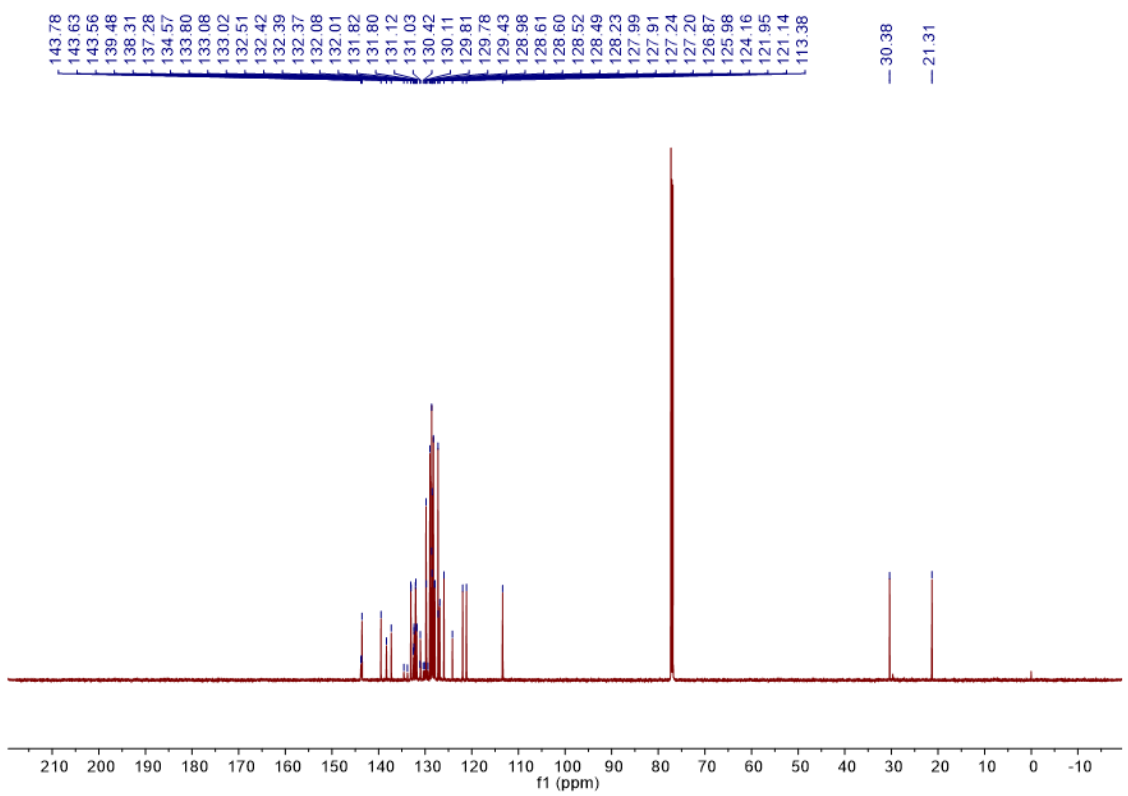


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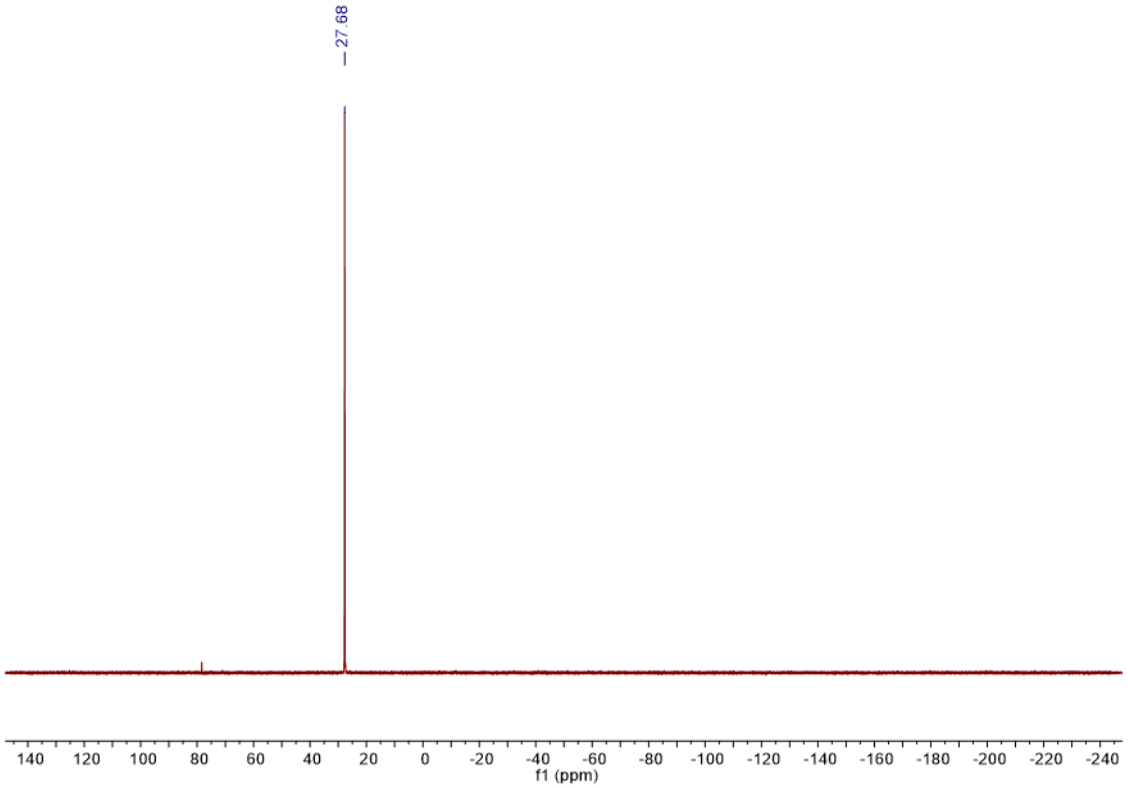

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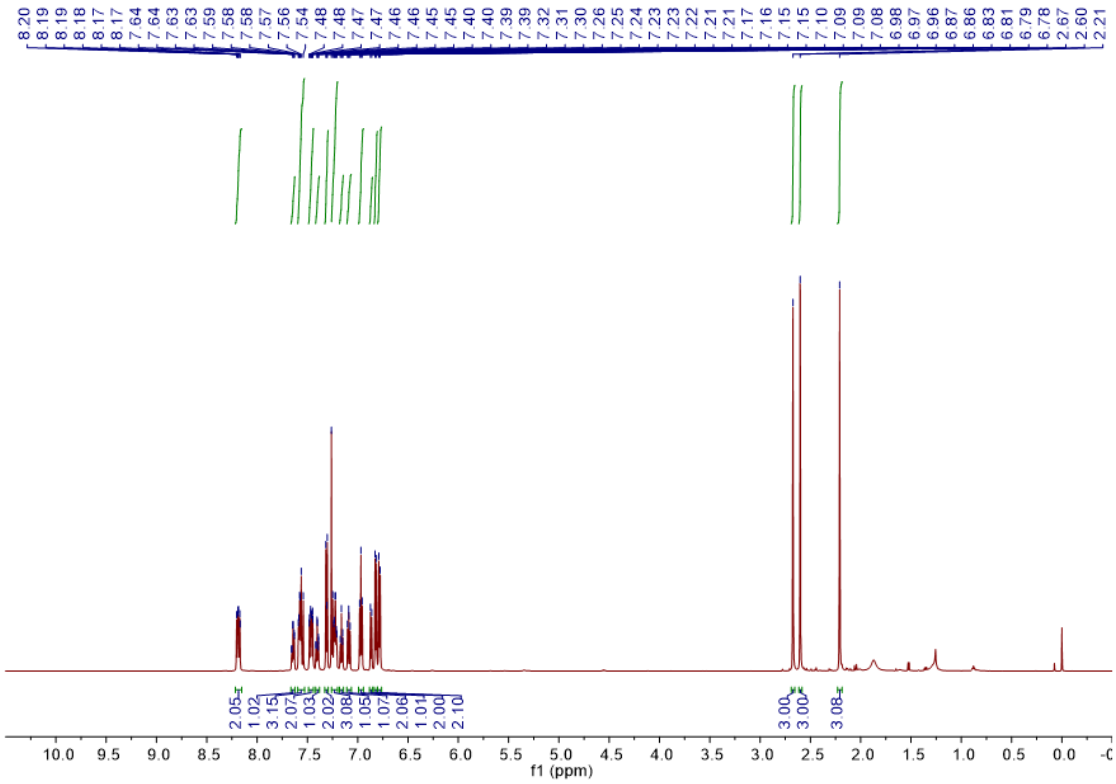


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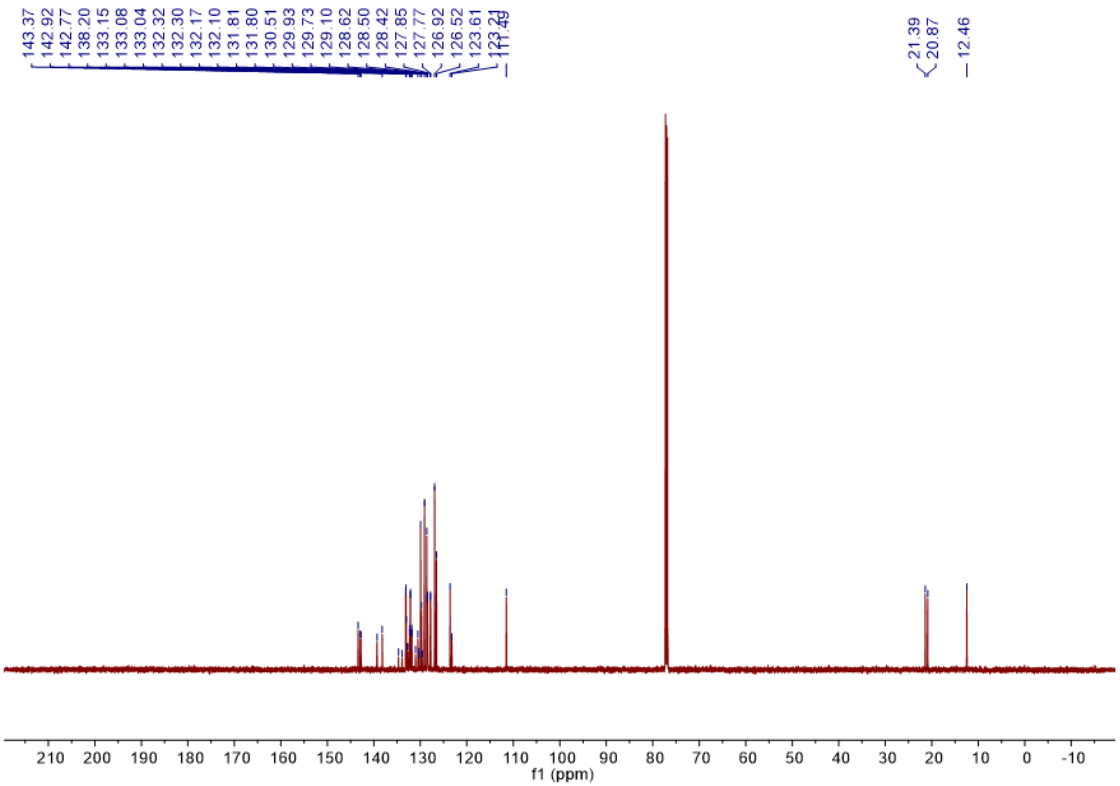

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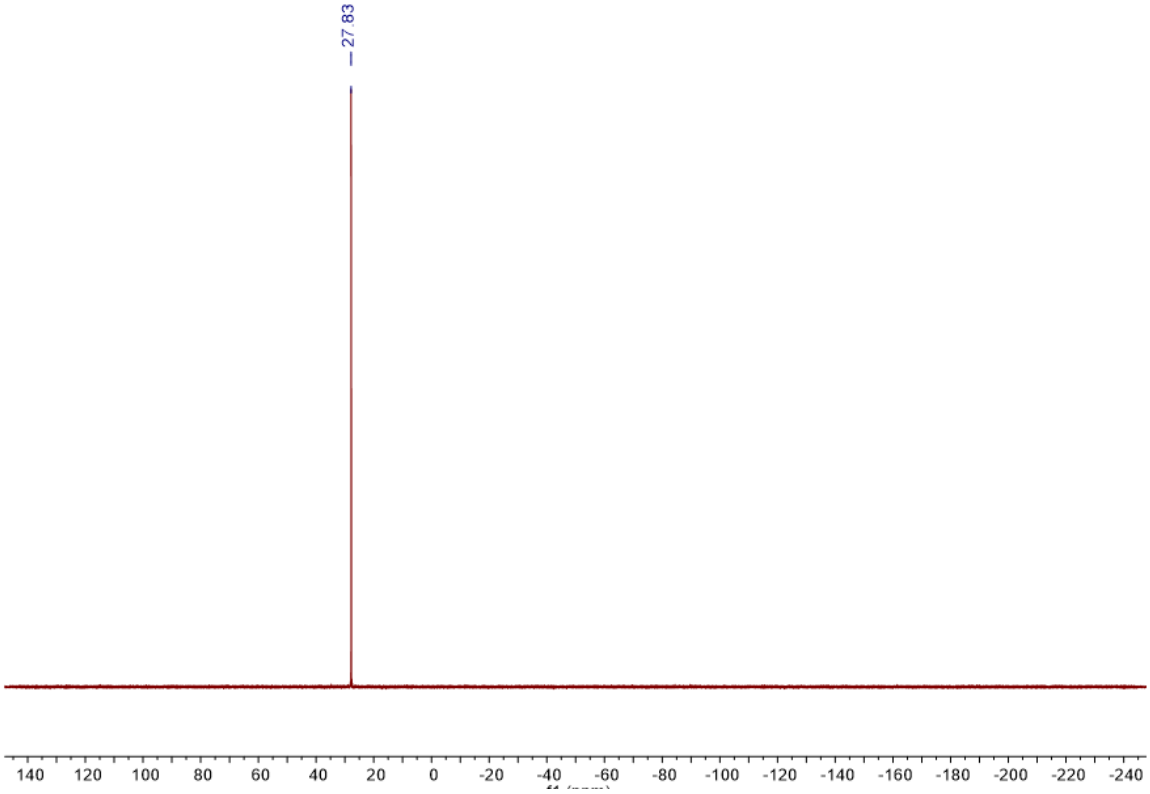


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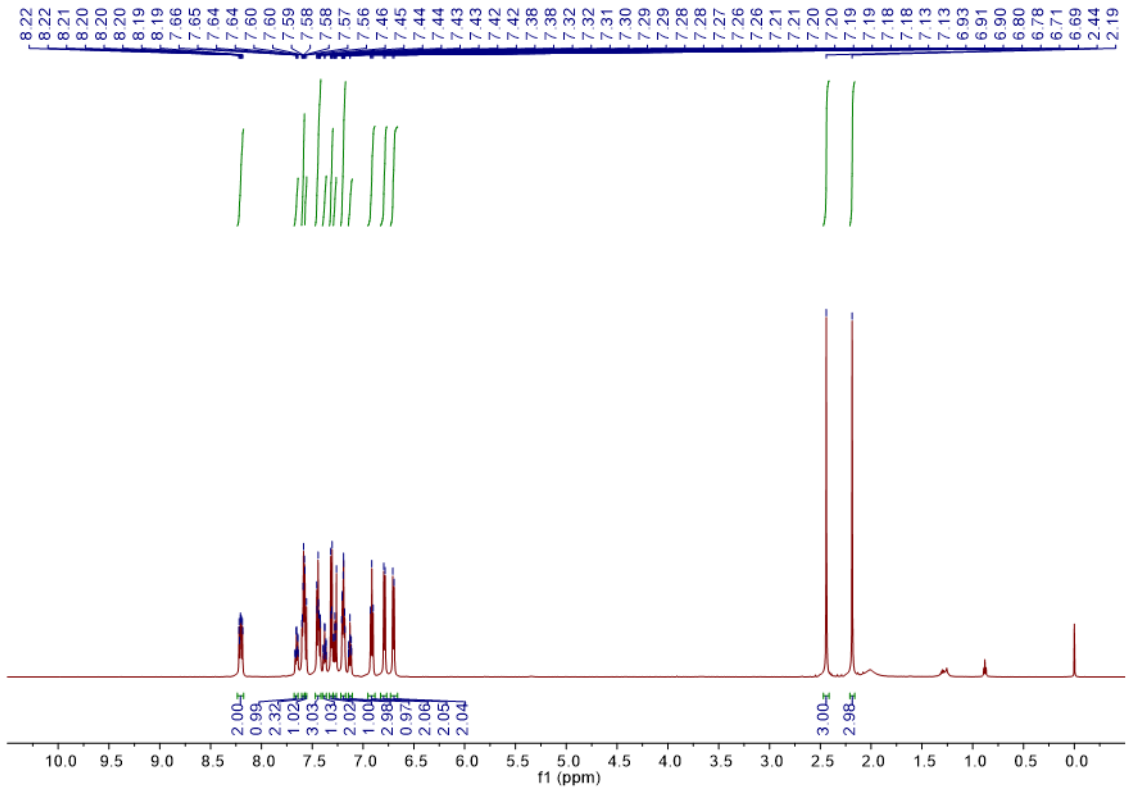

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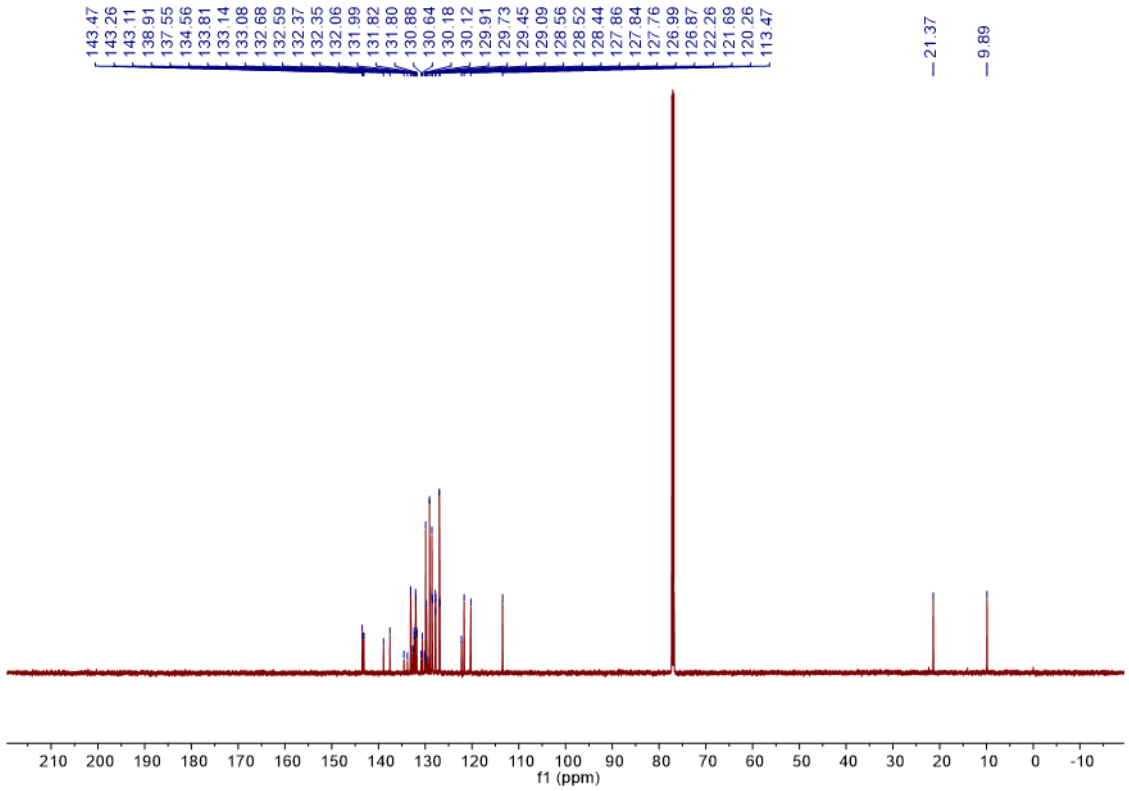


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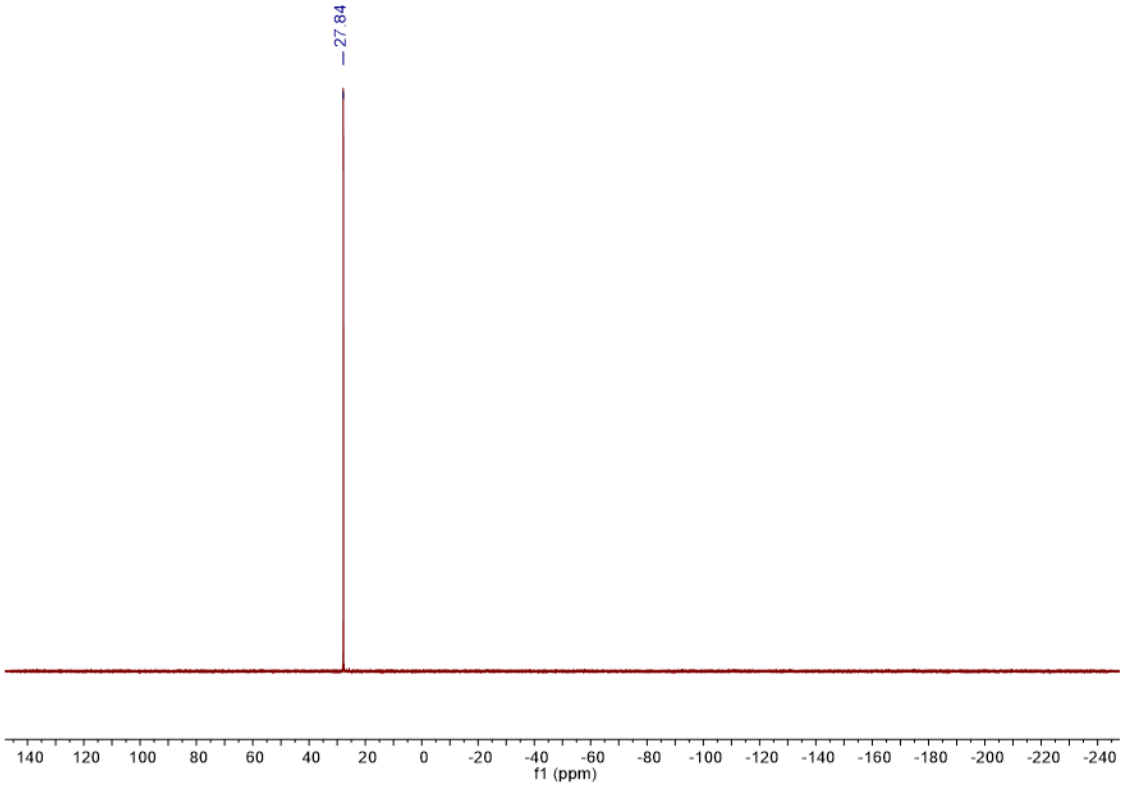

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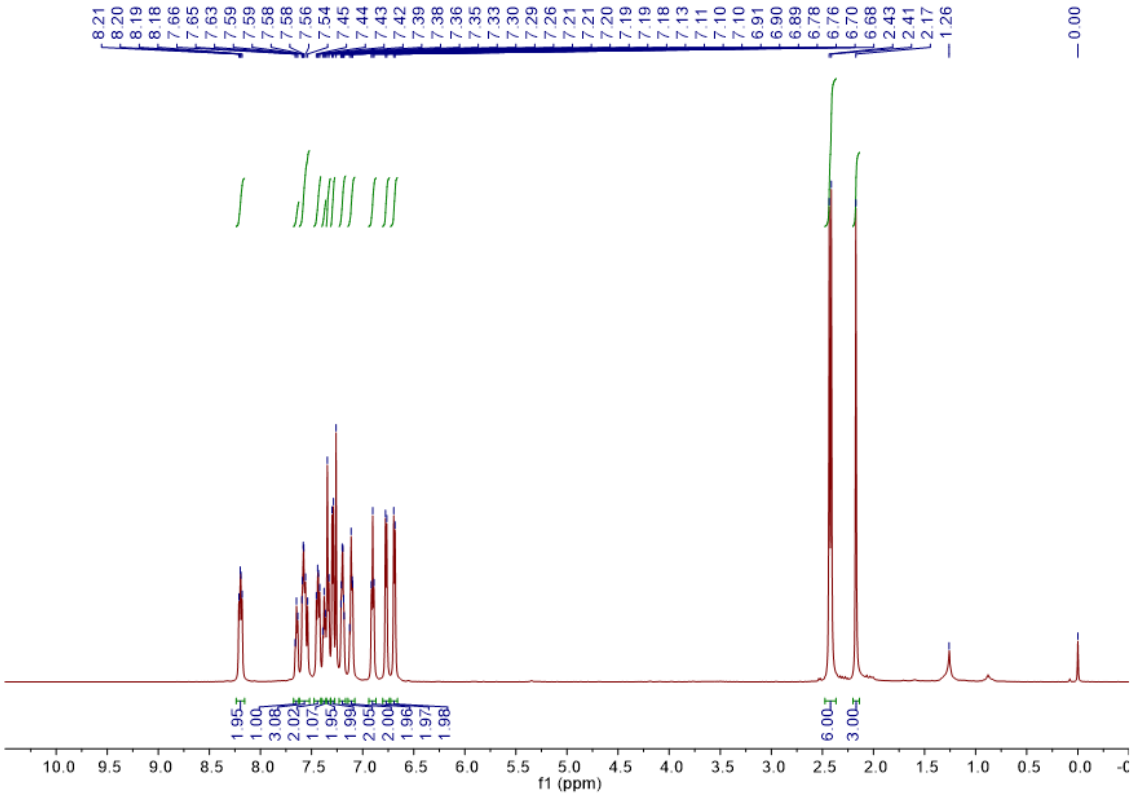


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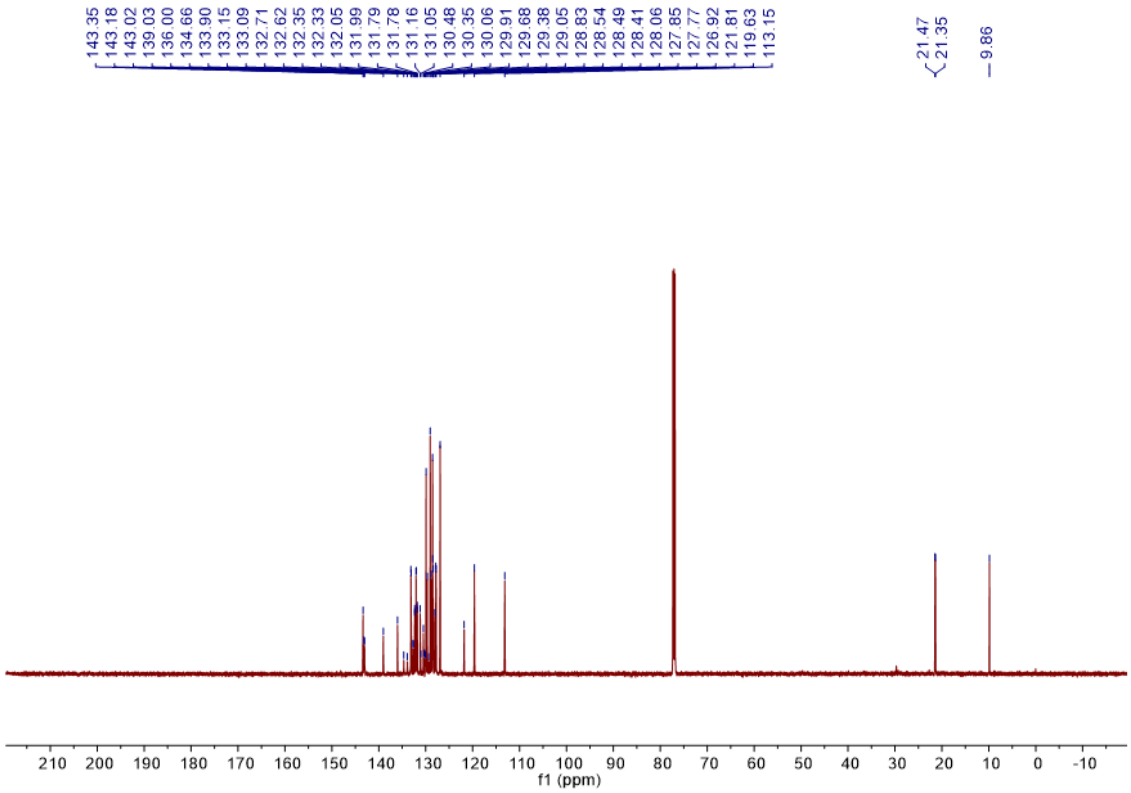

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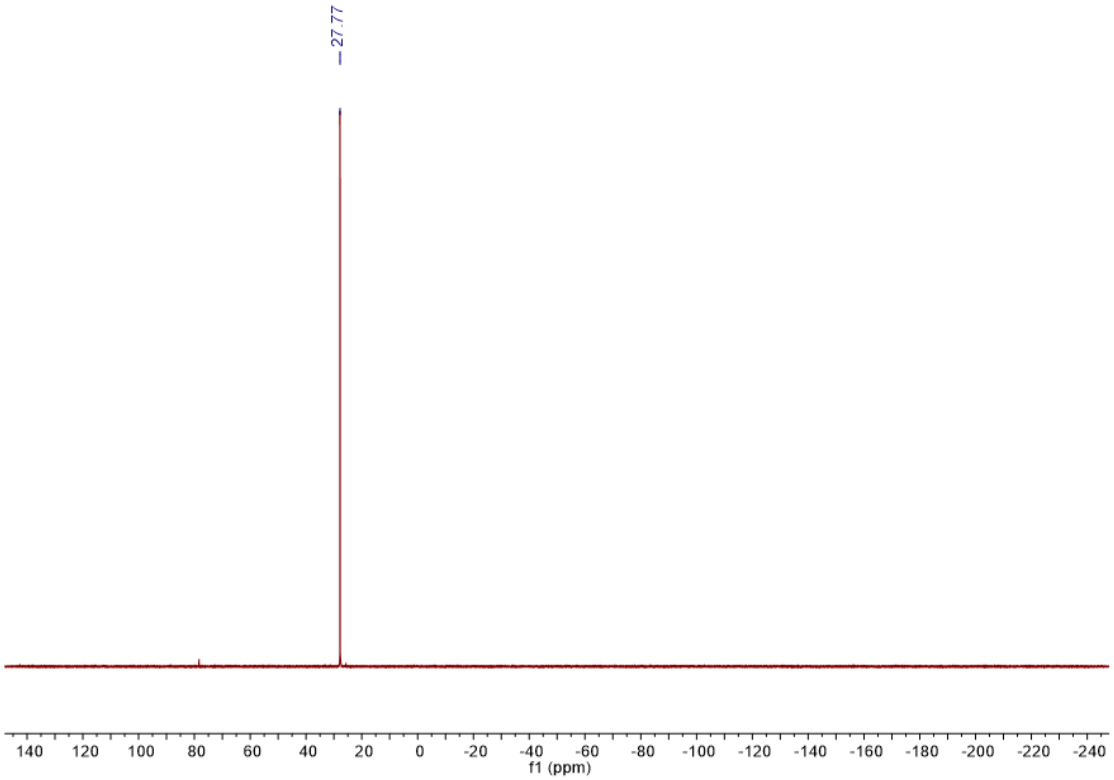


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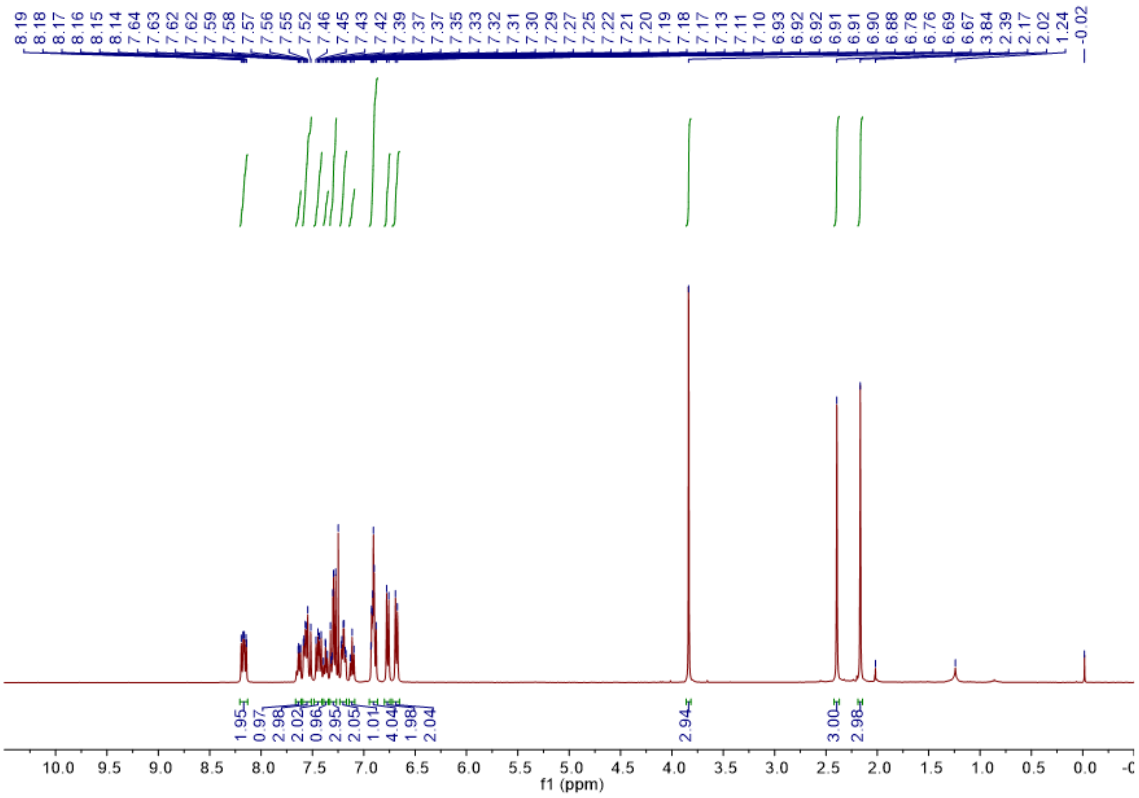

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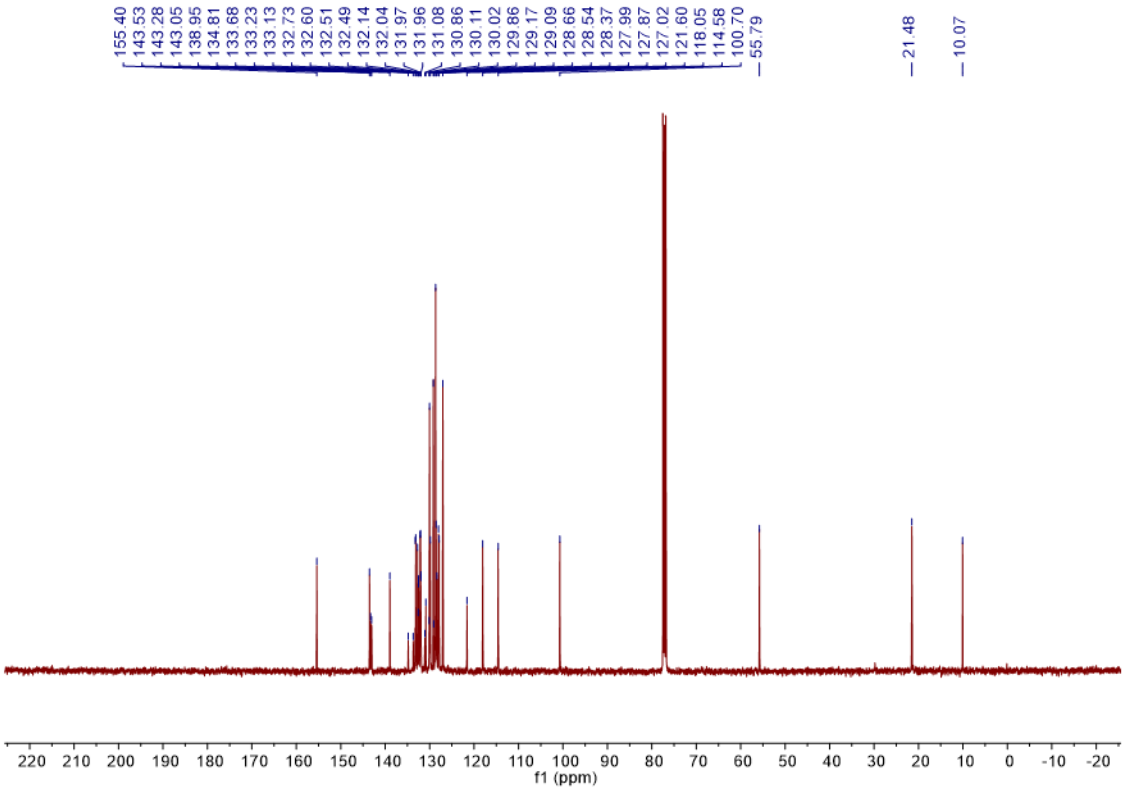


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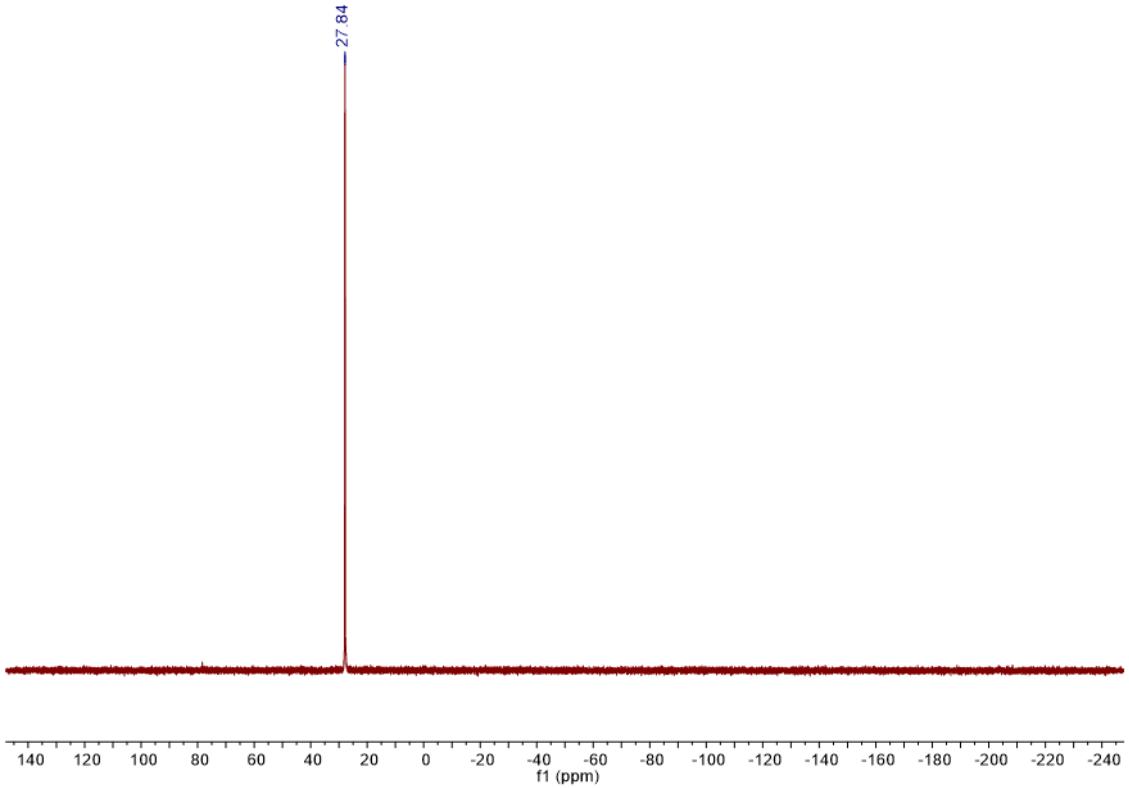

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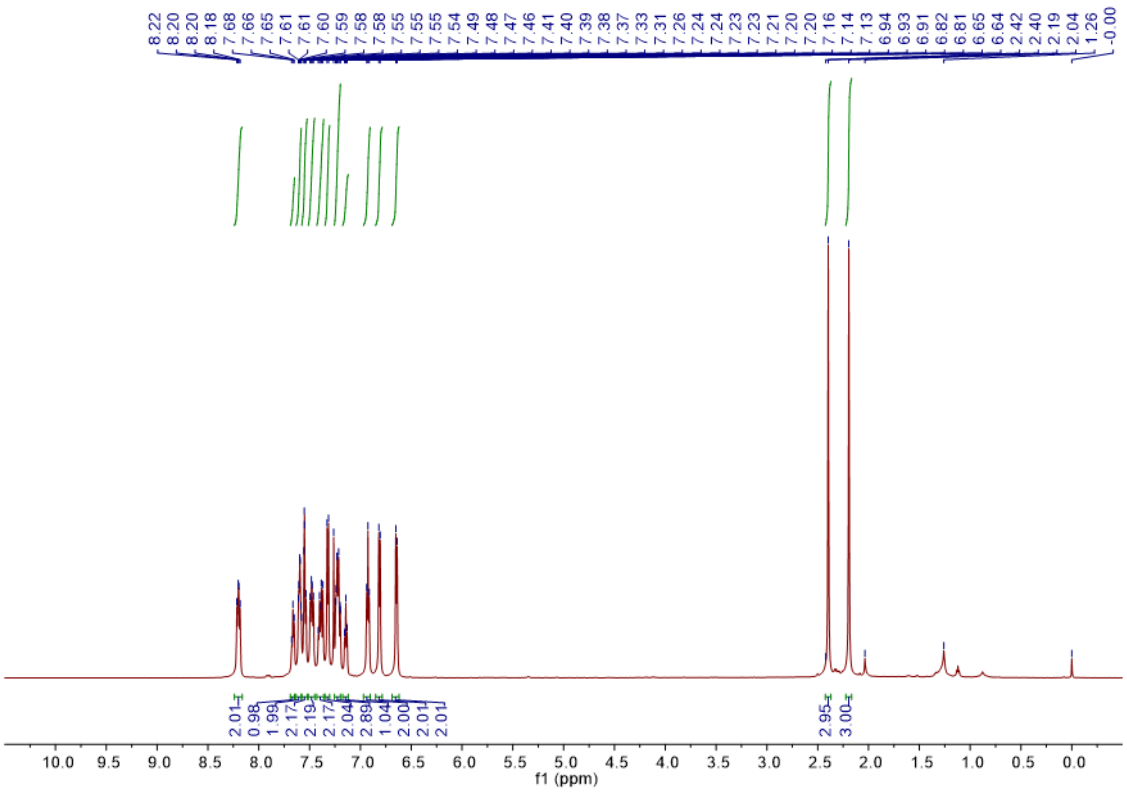


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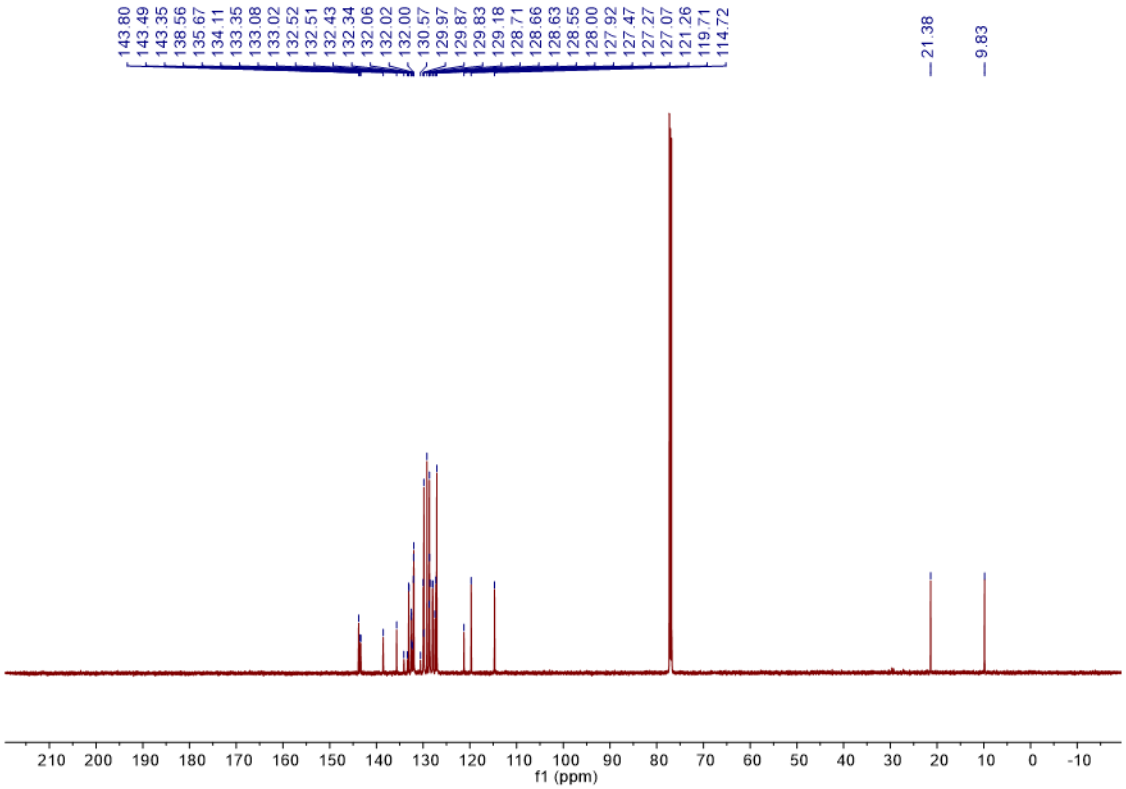

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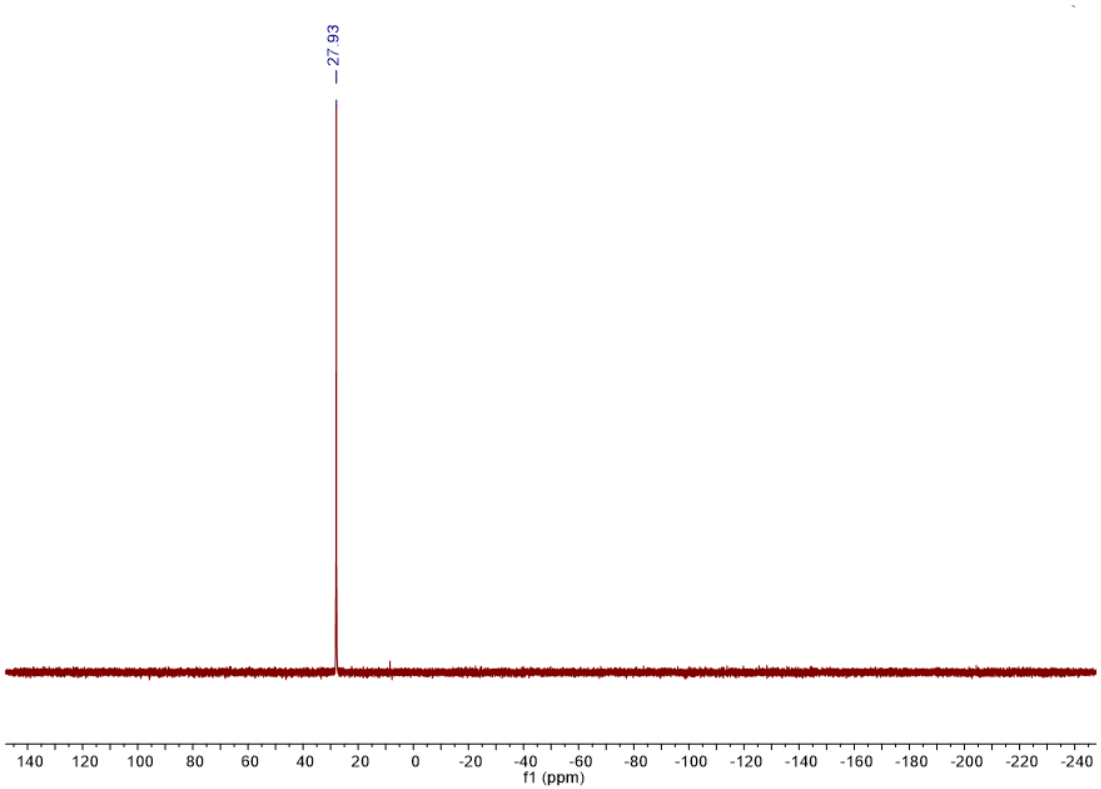


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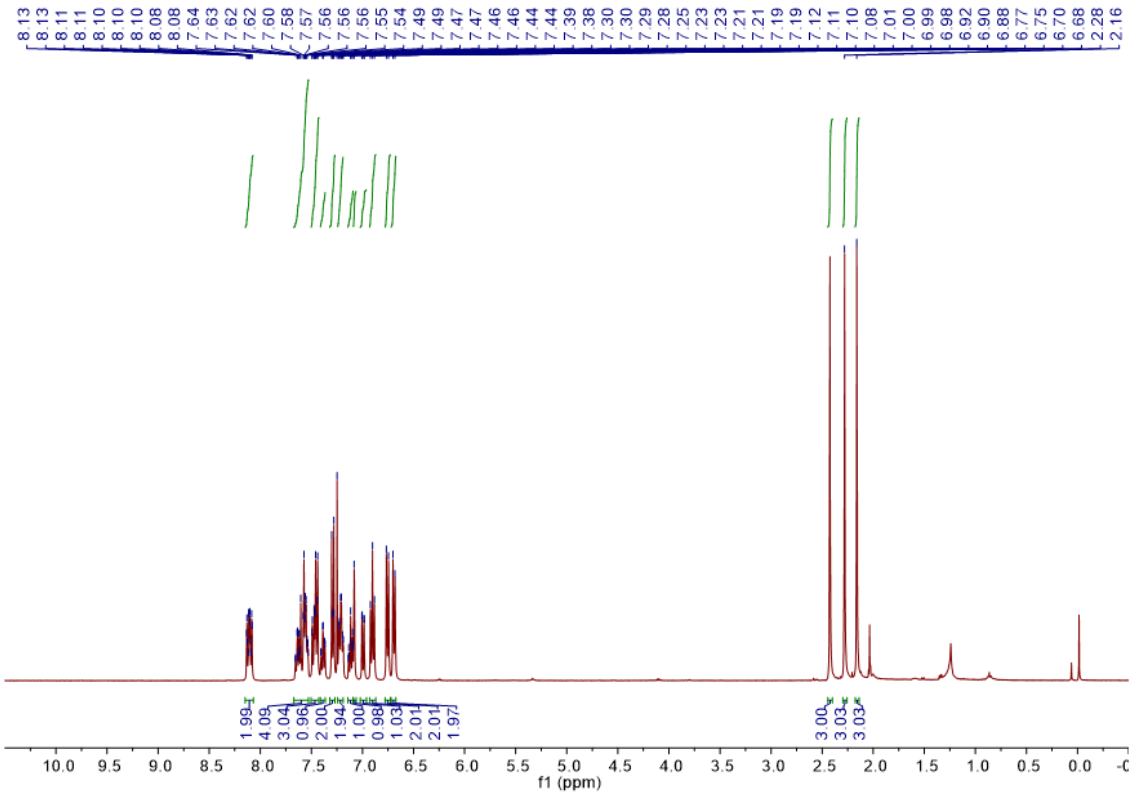

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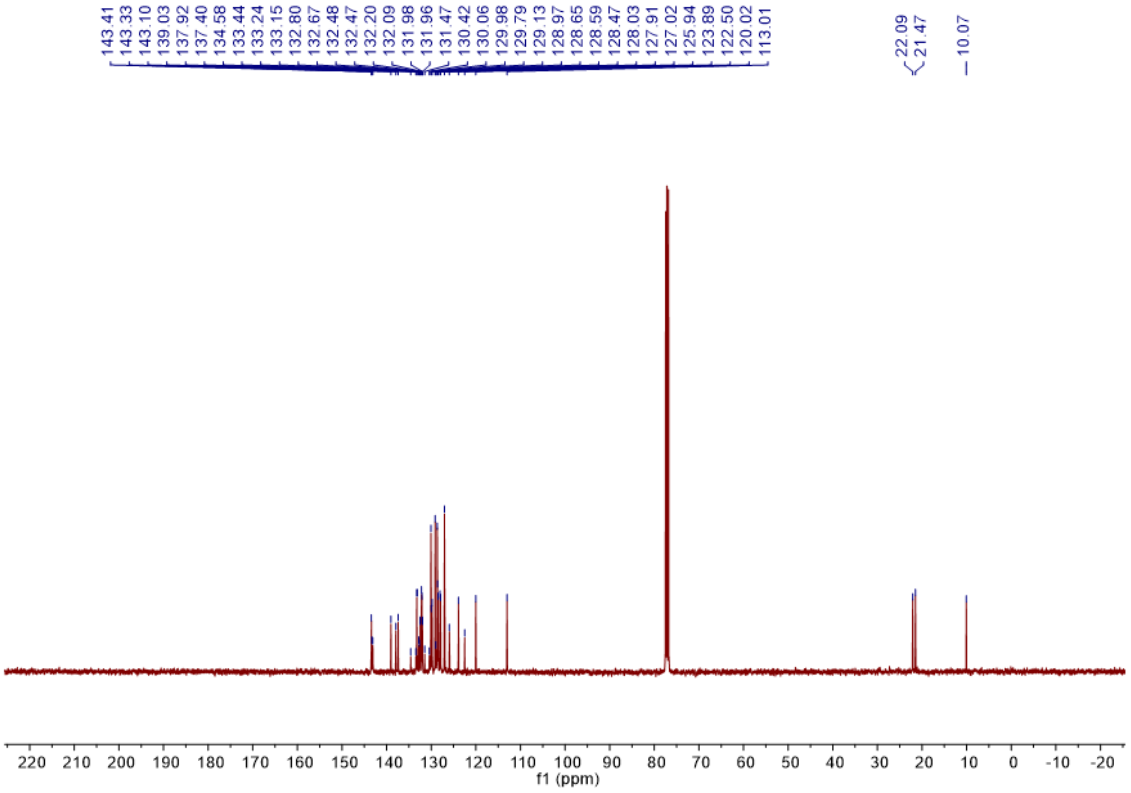


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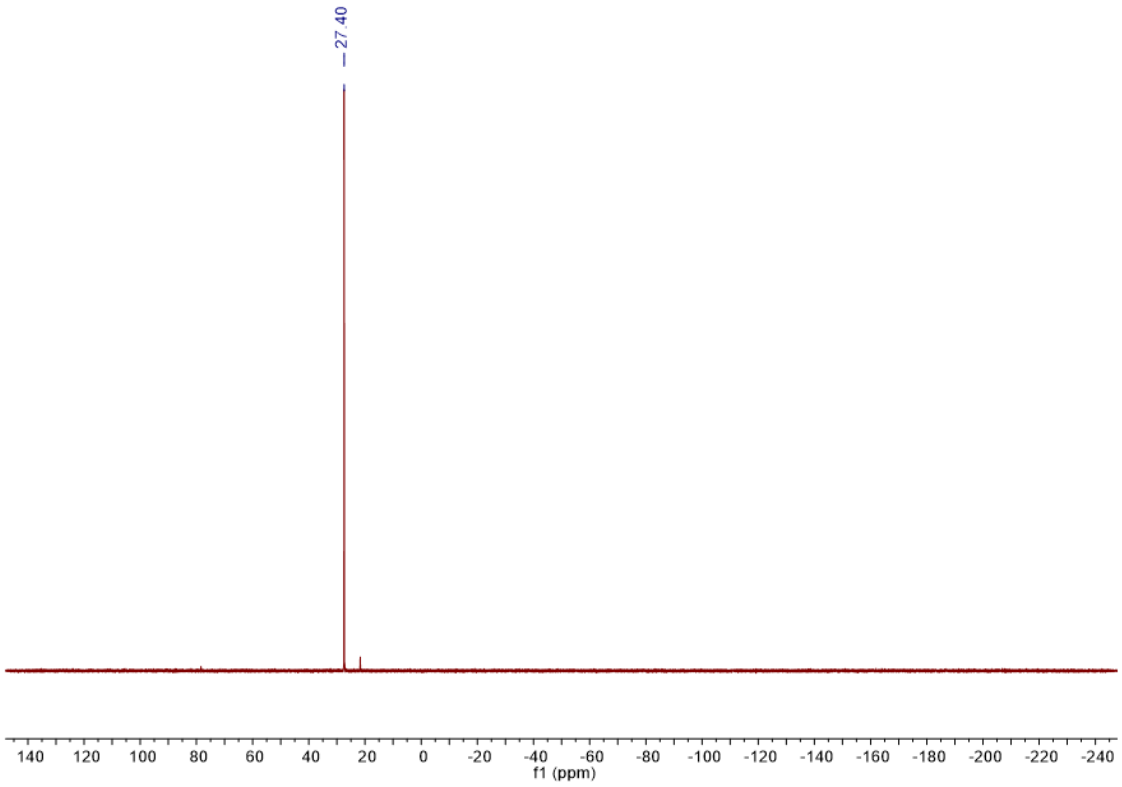

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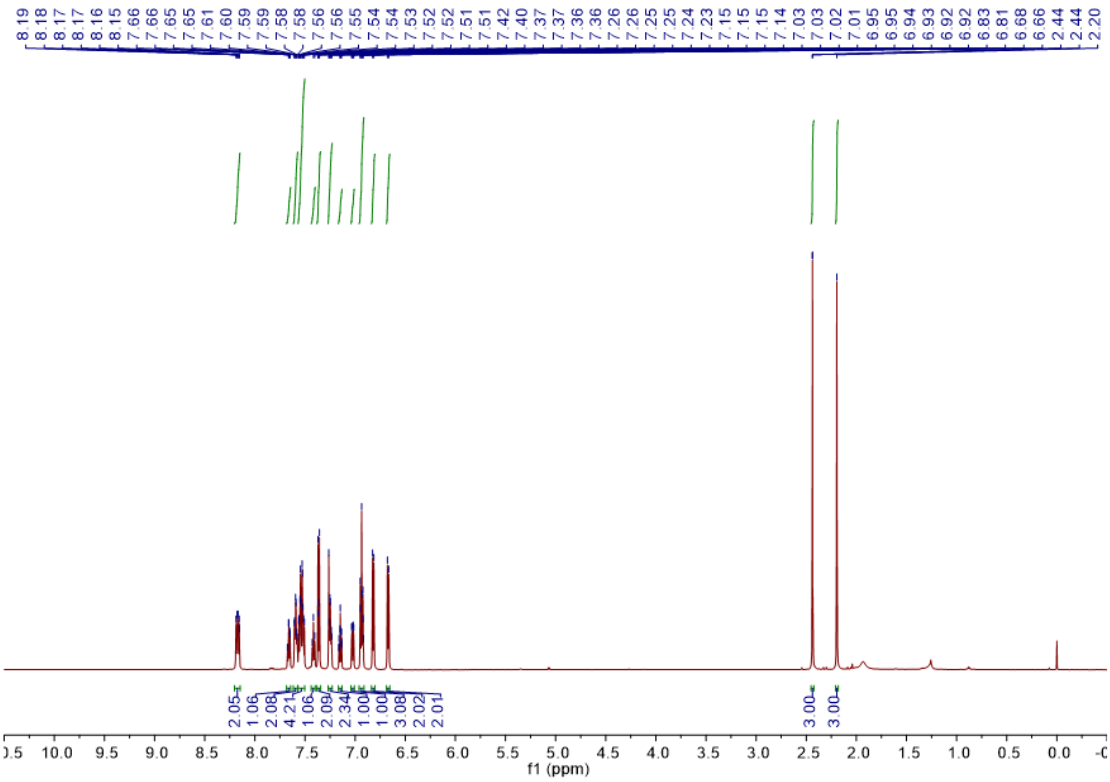

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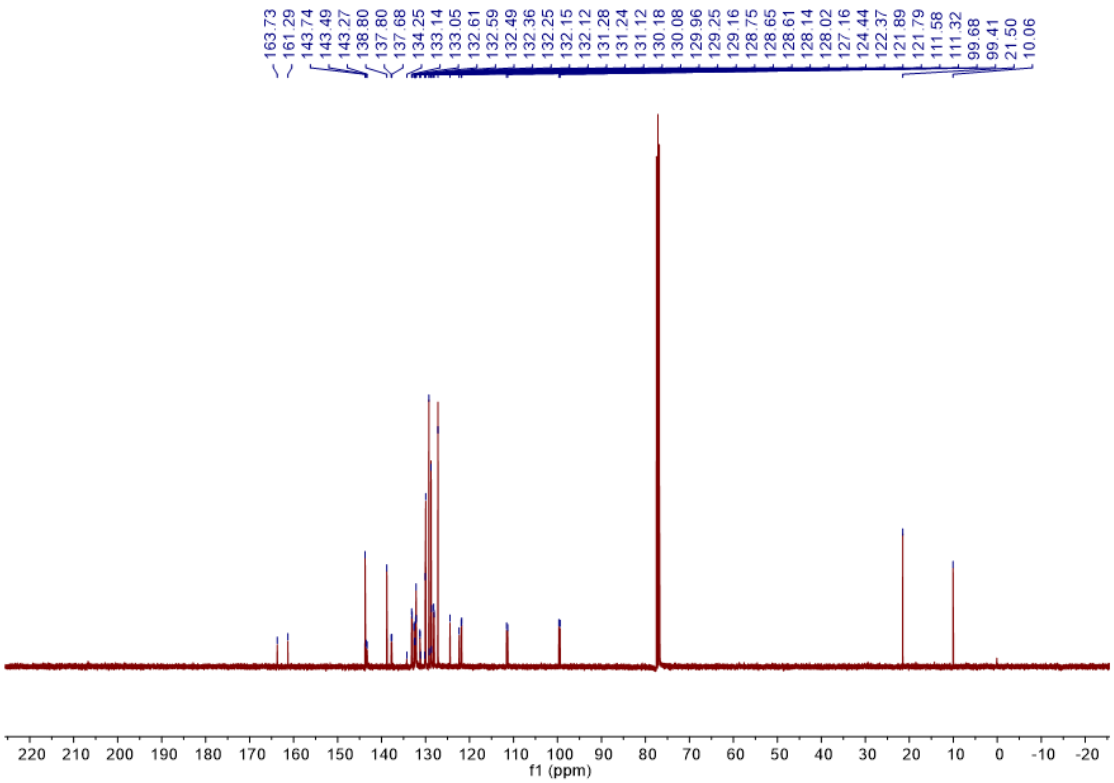

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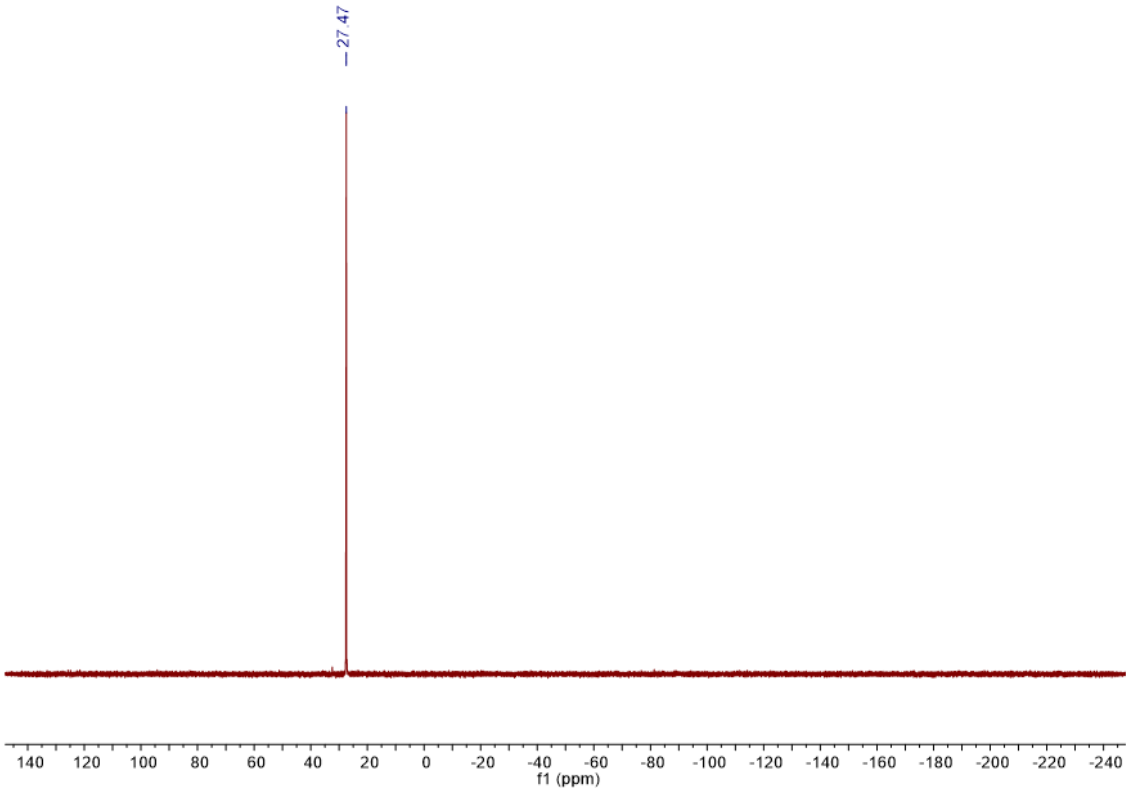


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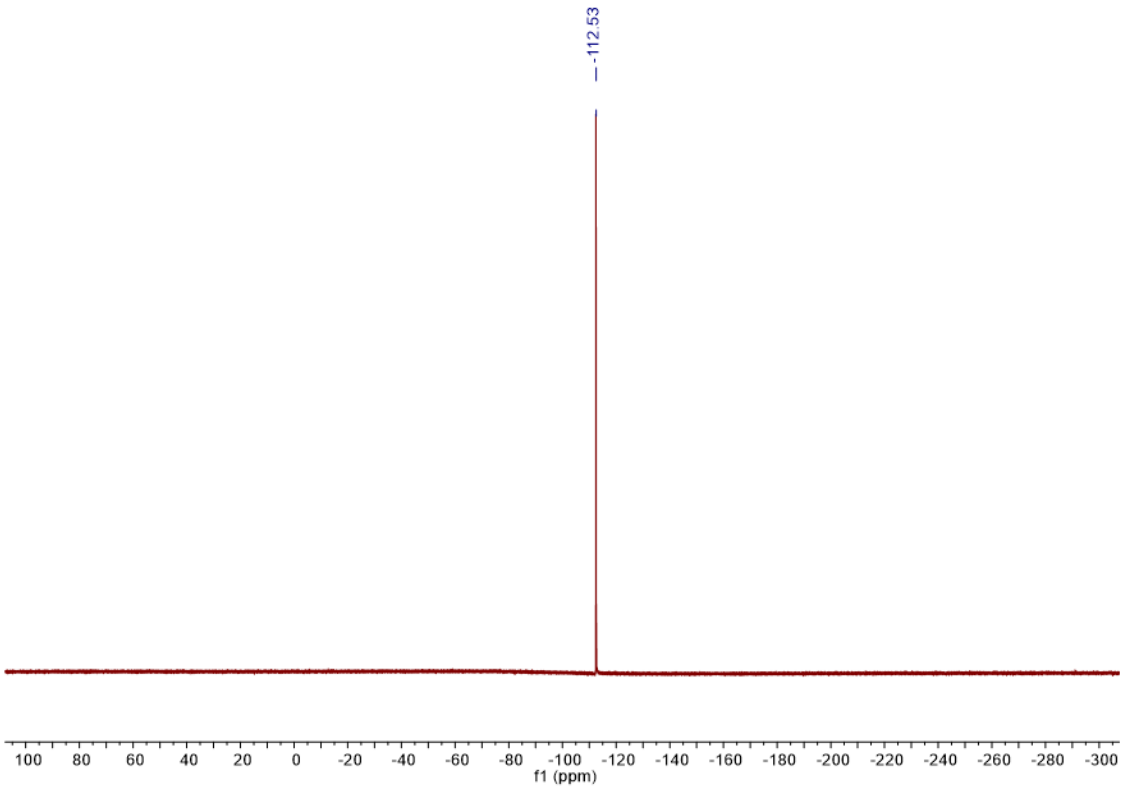

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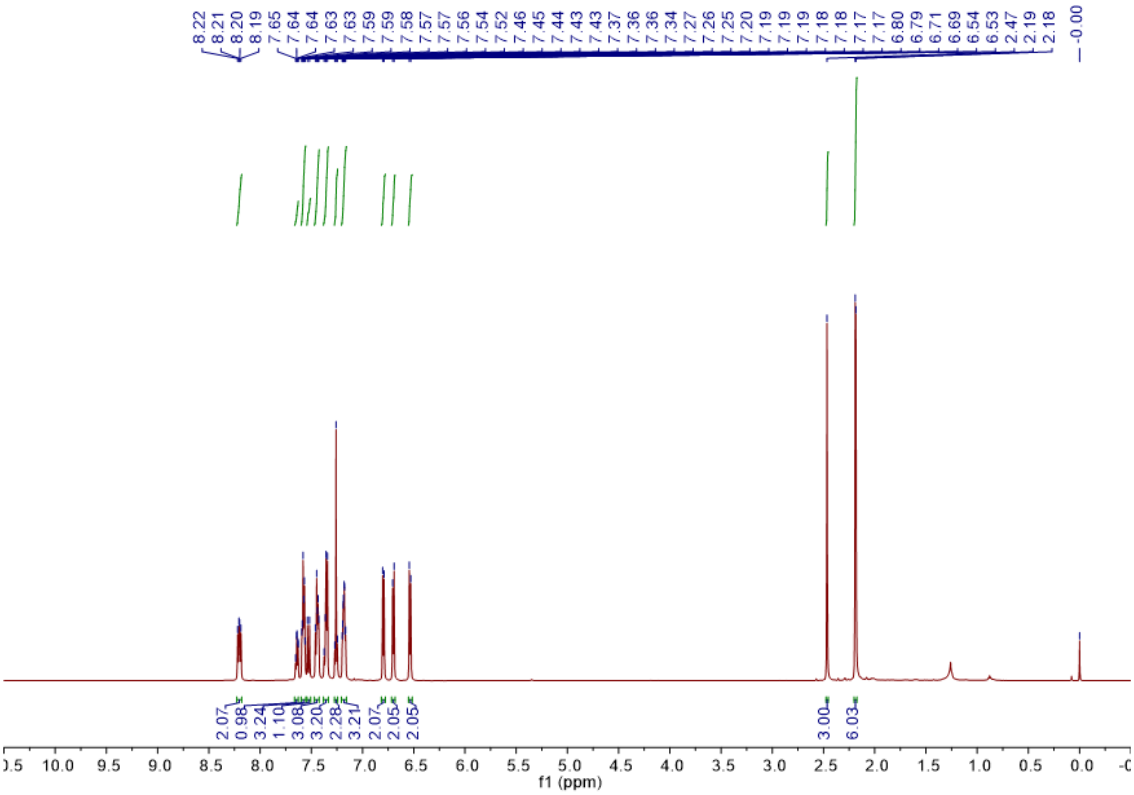


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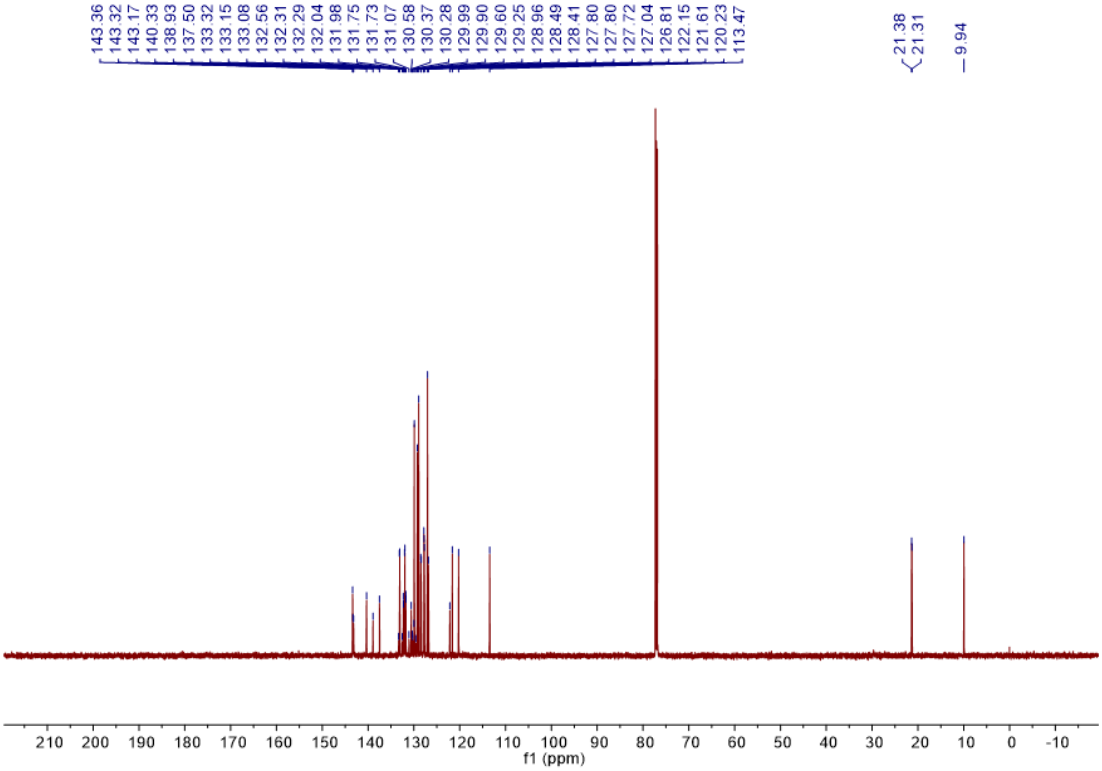

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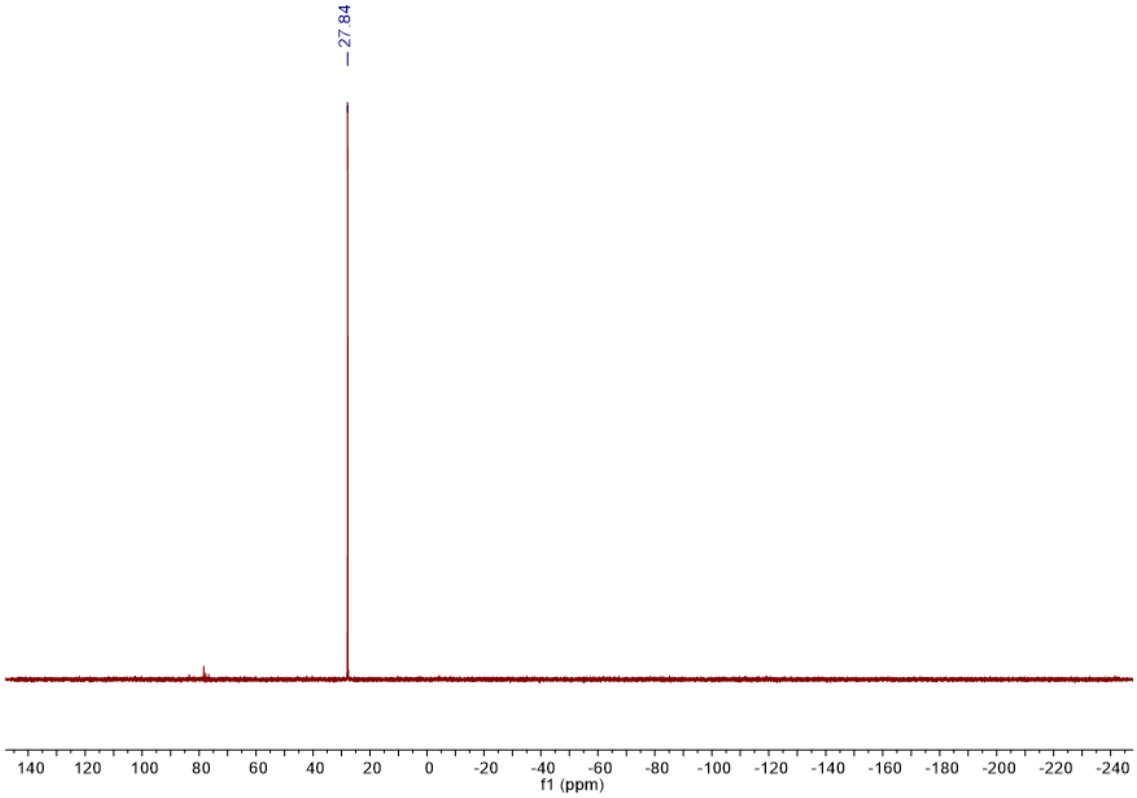


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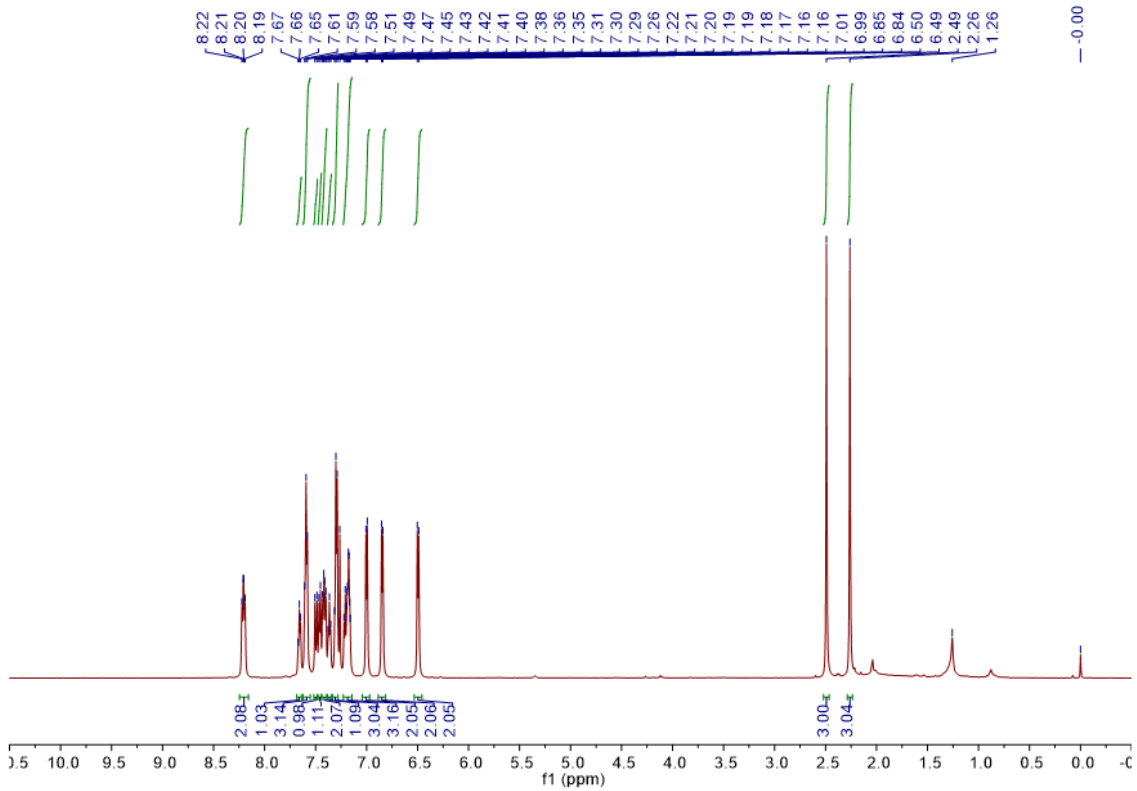

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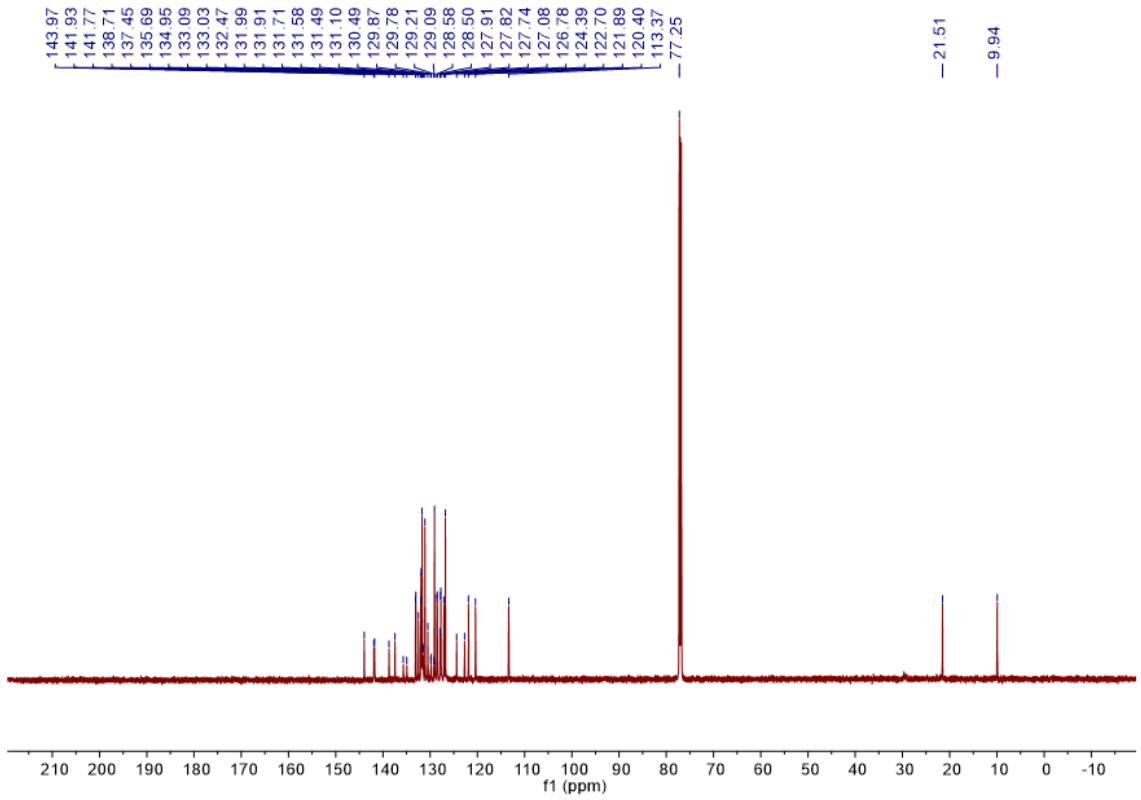


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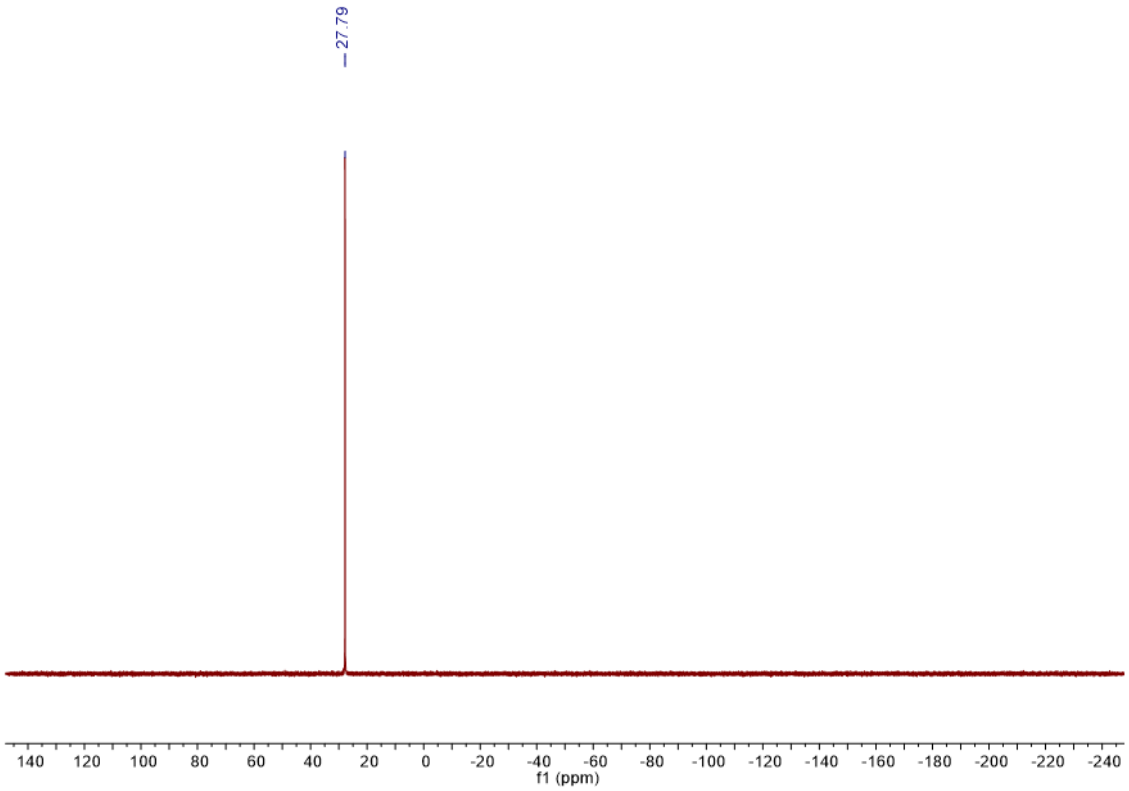

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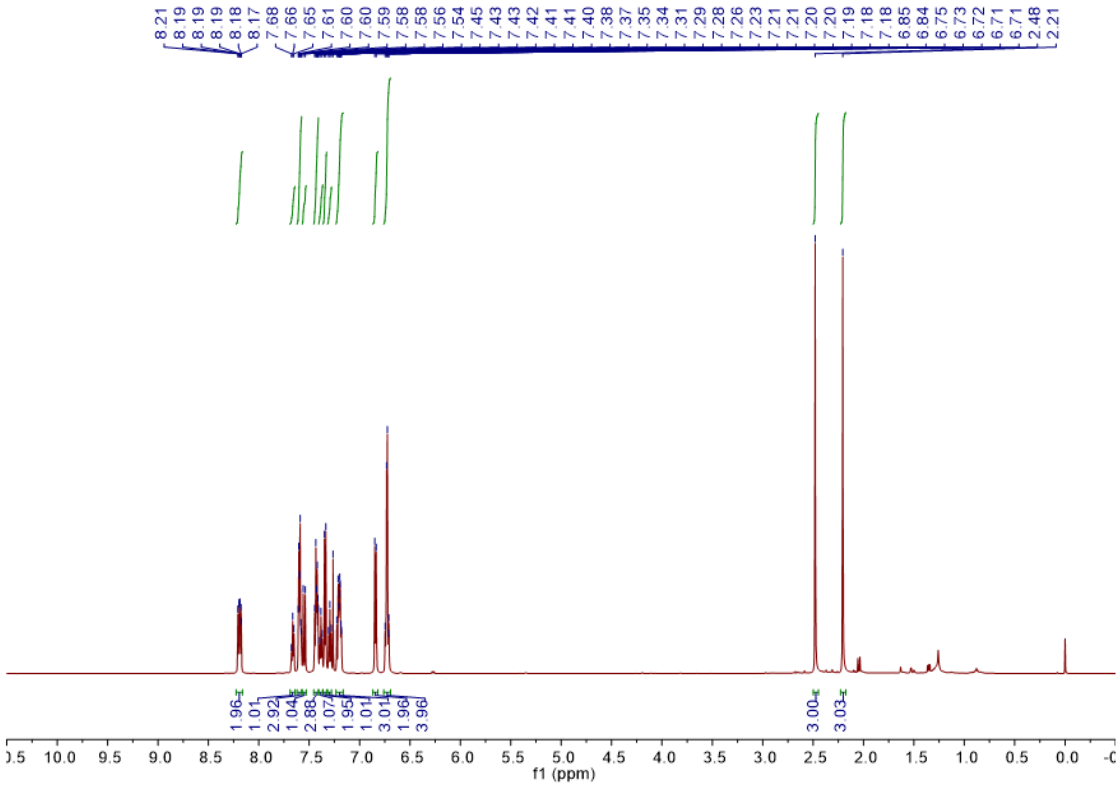


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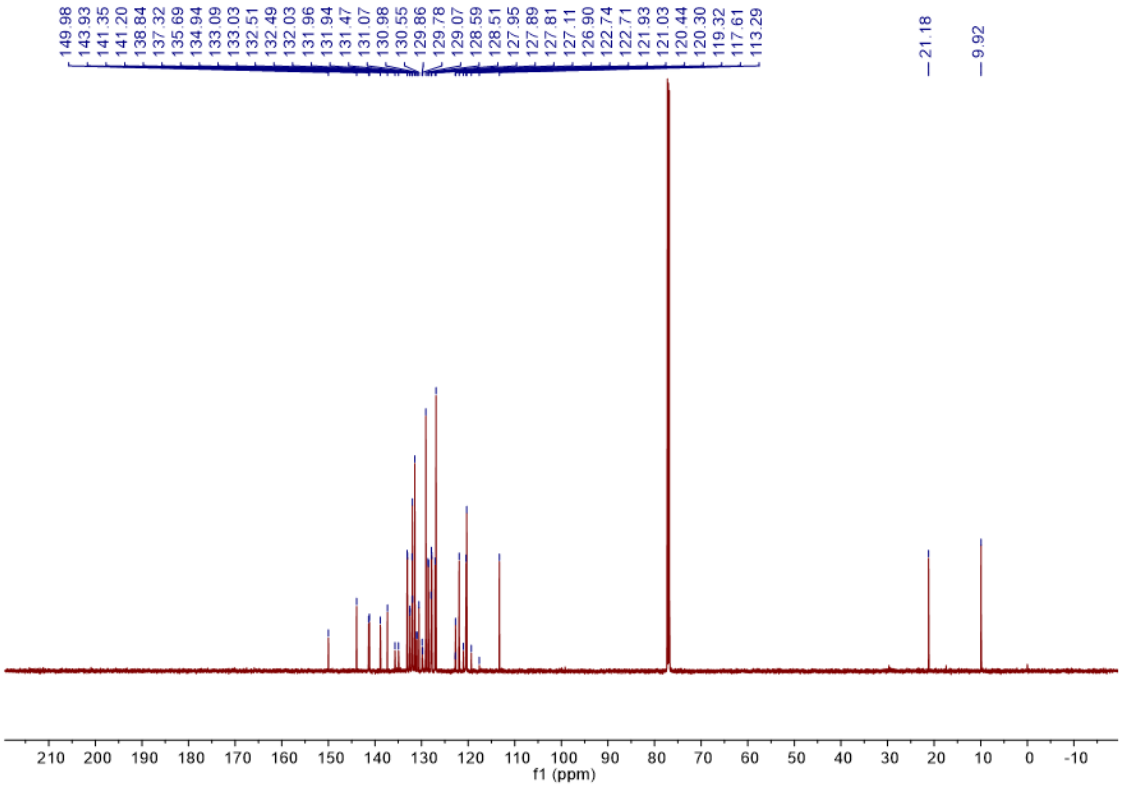

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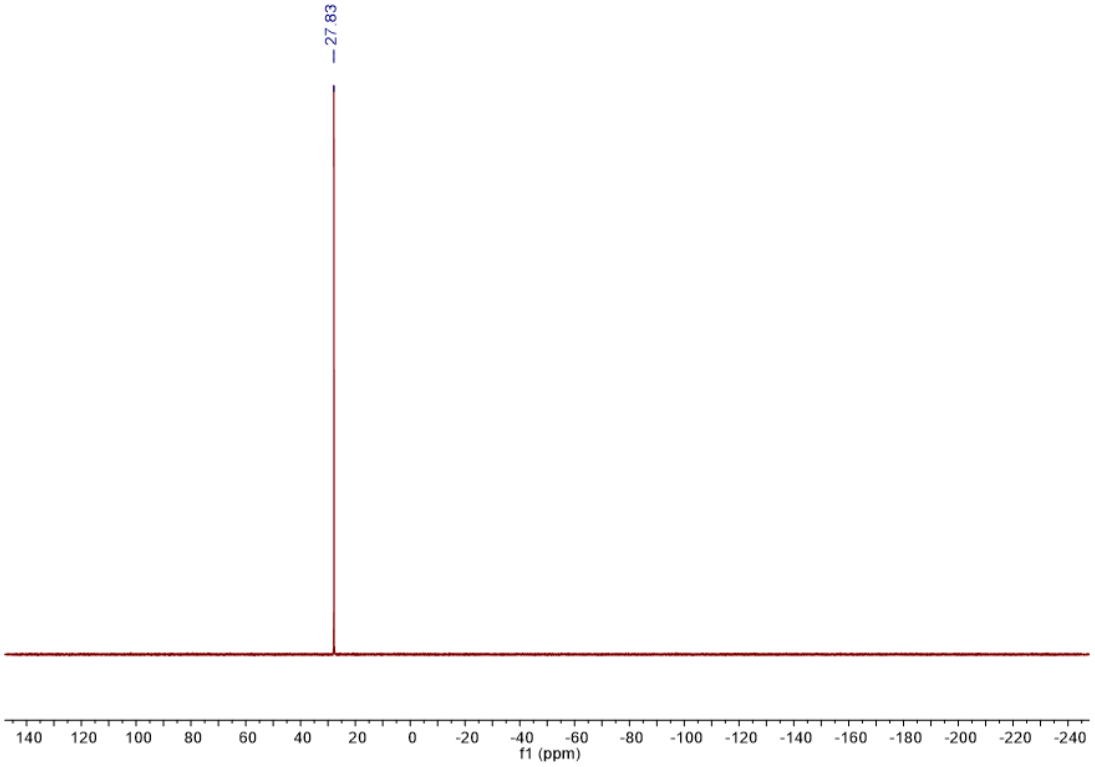


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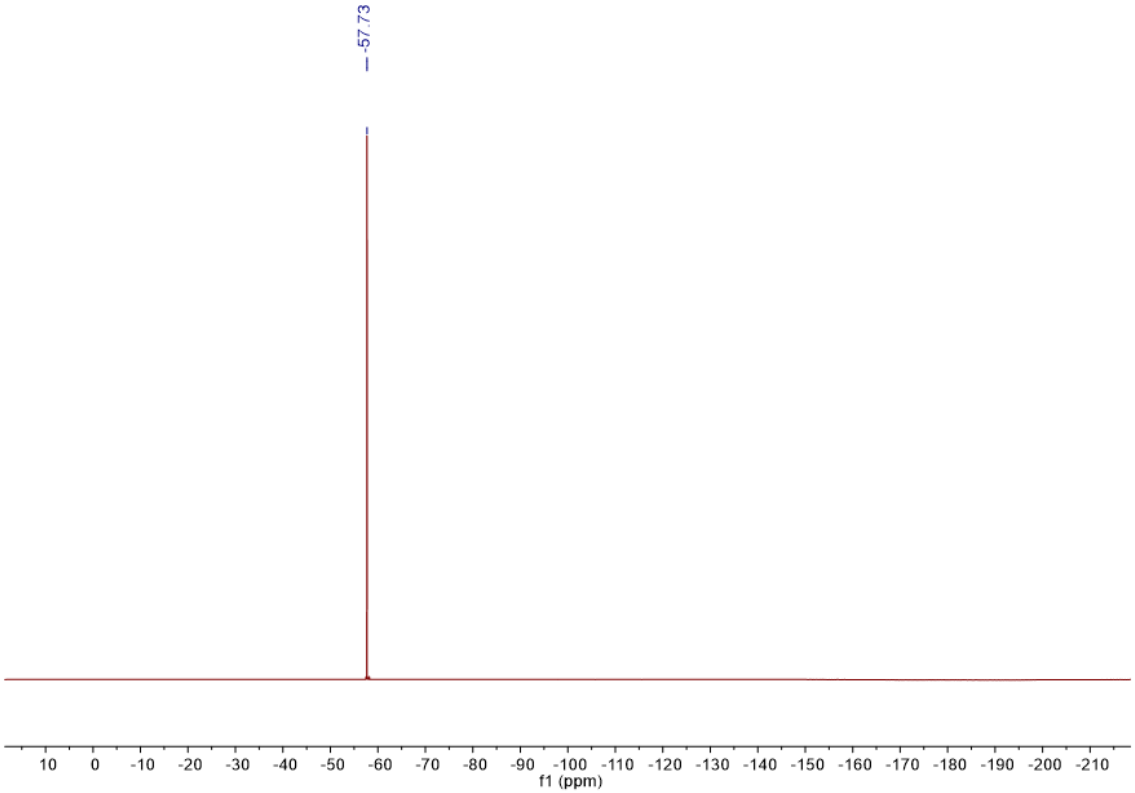
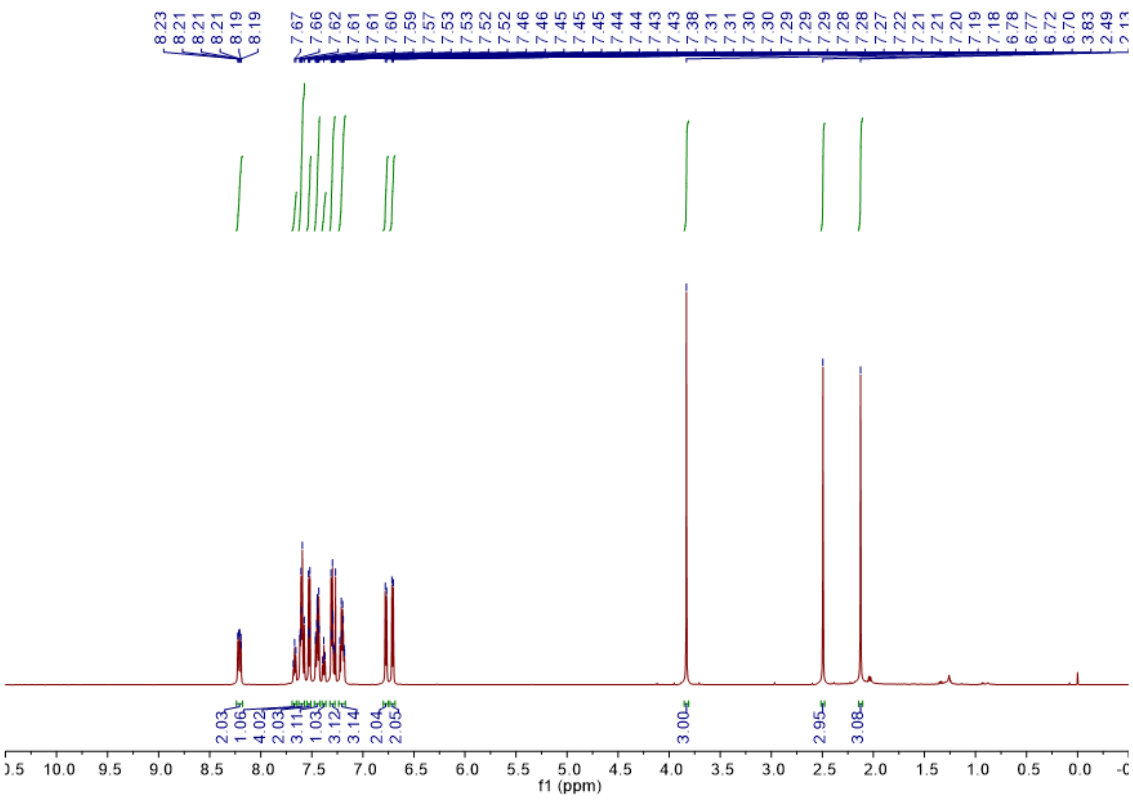
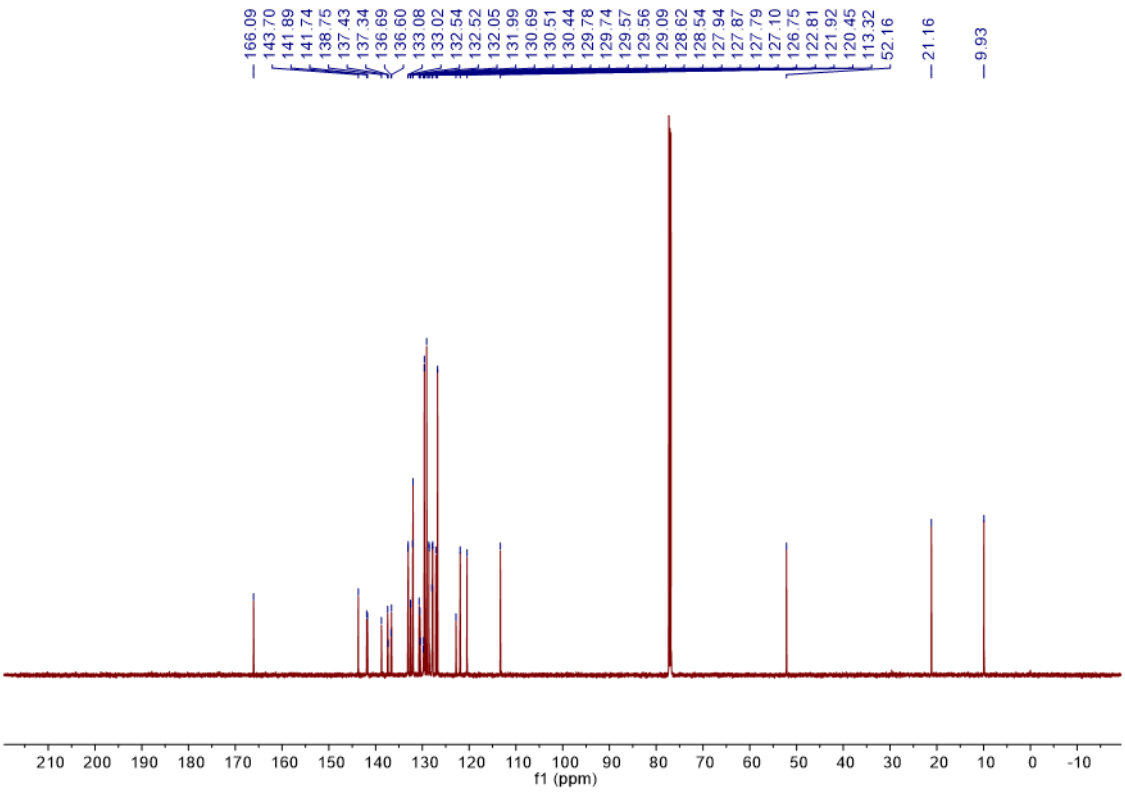


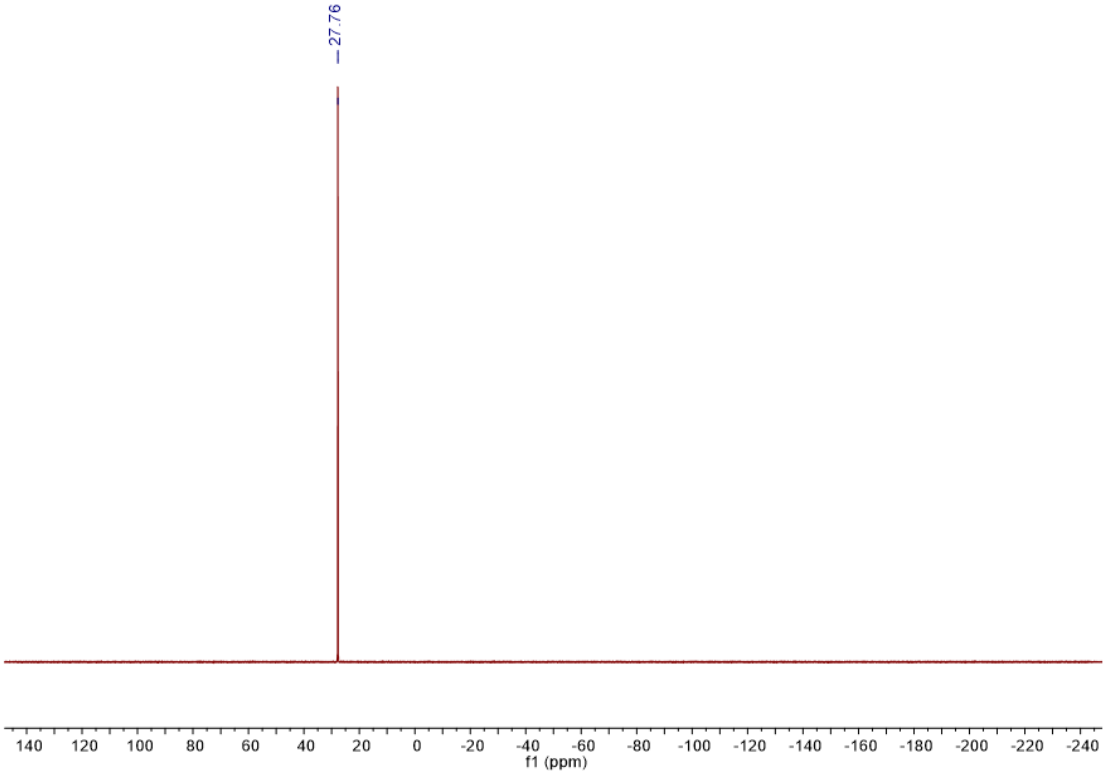
## $^{19}$F NMR of 16 ($CDCl_3$)



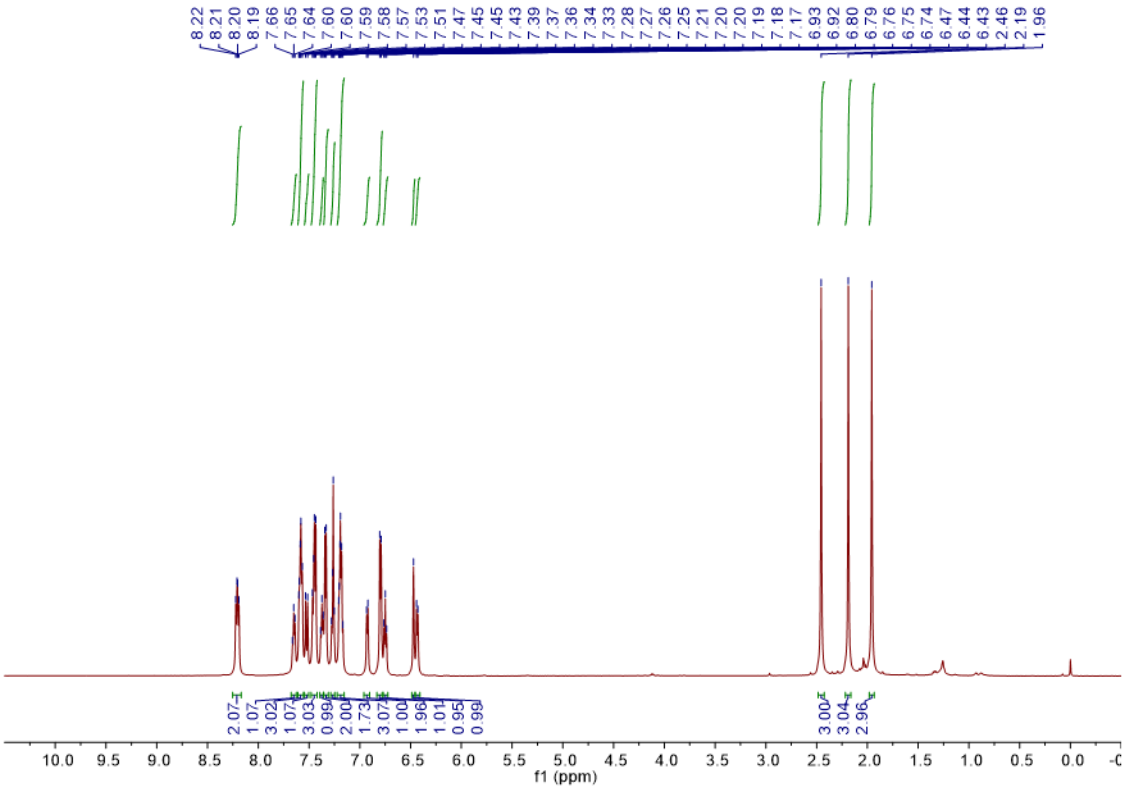

## $^{1}$H NMR of 17 ($CDCl_3$)



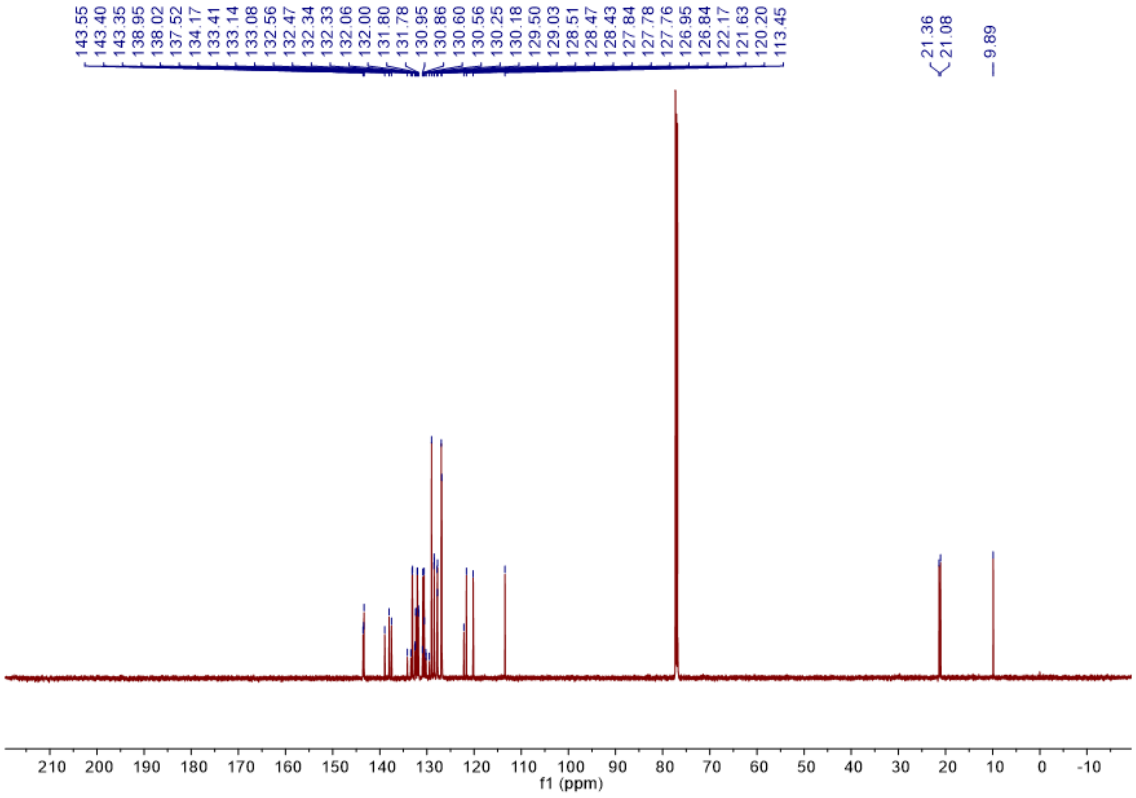
## $^{13}C$ NMR of 17 ($CDCl_3$)



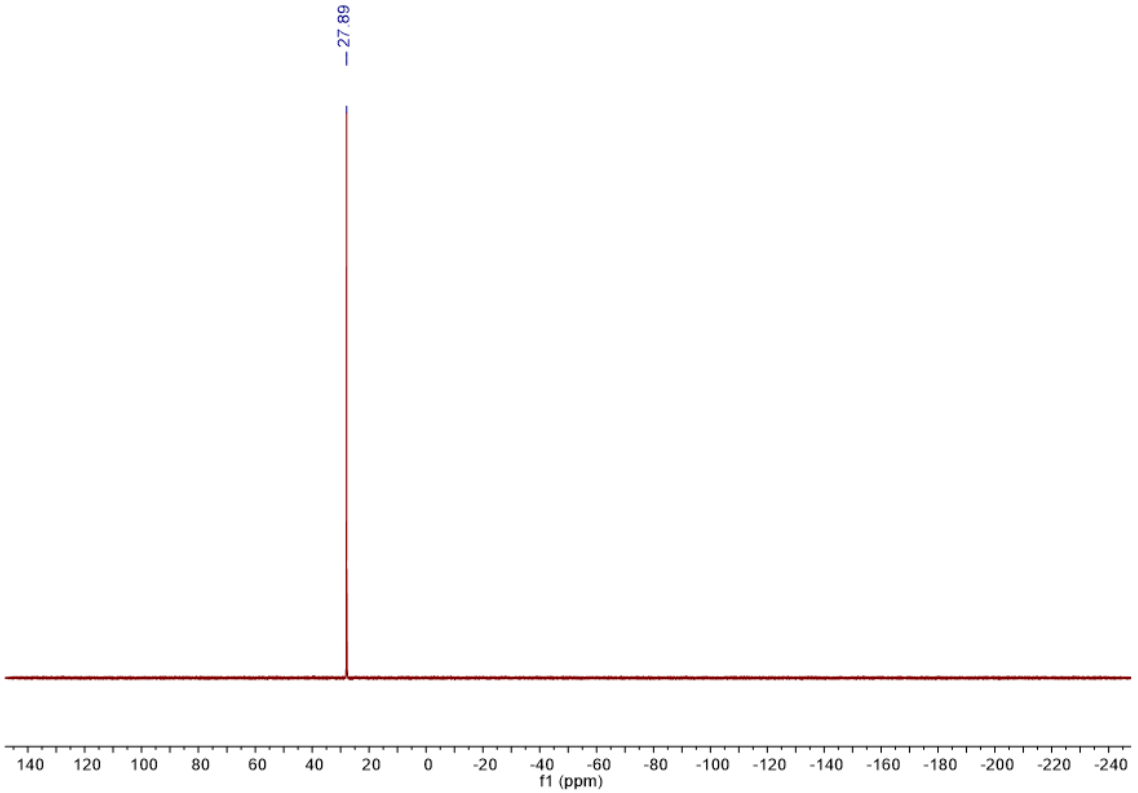

## $^{31}P$ NMR of 17 ($CDCl_3$)



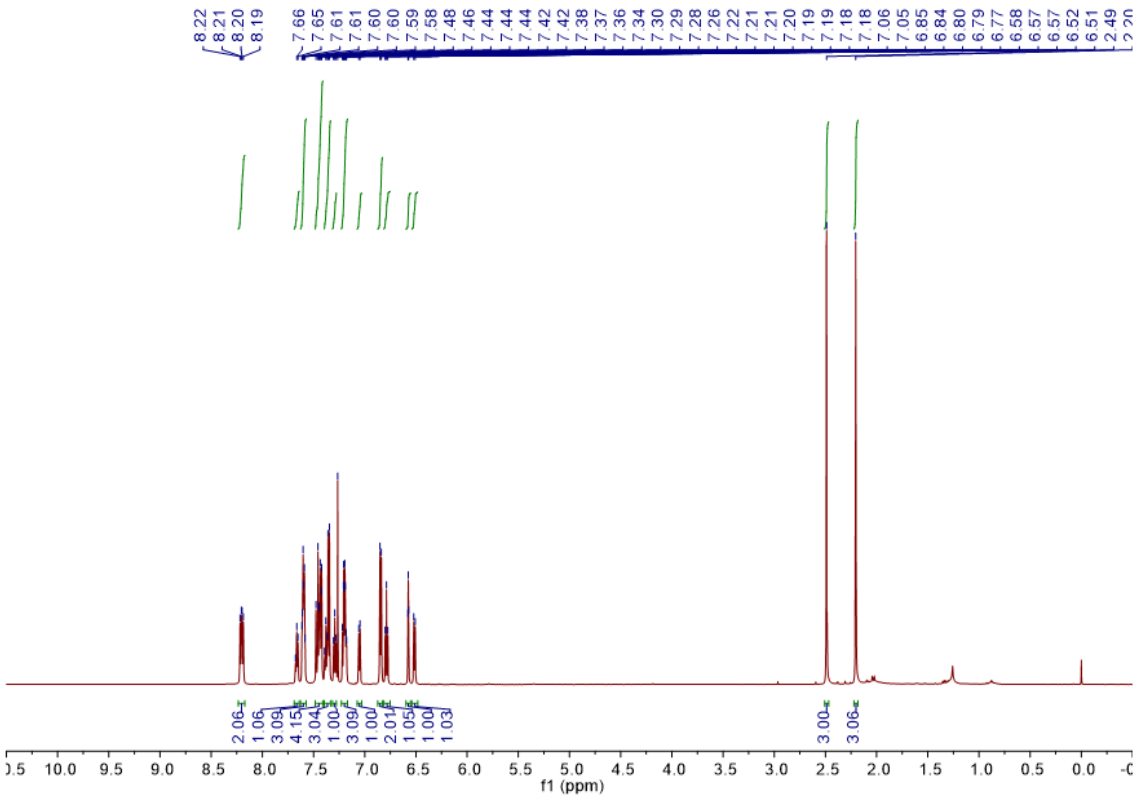
## $^{1}$H NMR of 18 ($CDCl_3$)



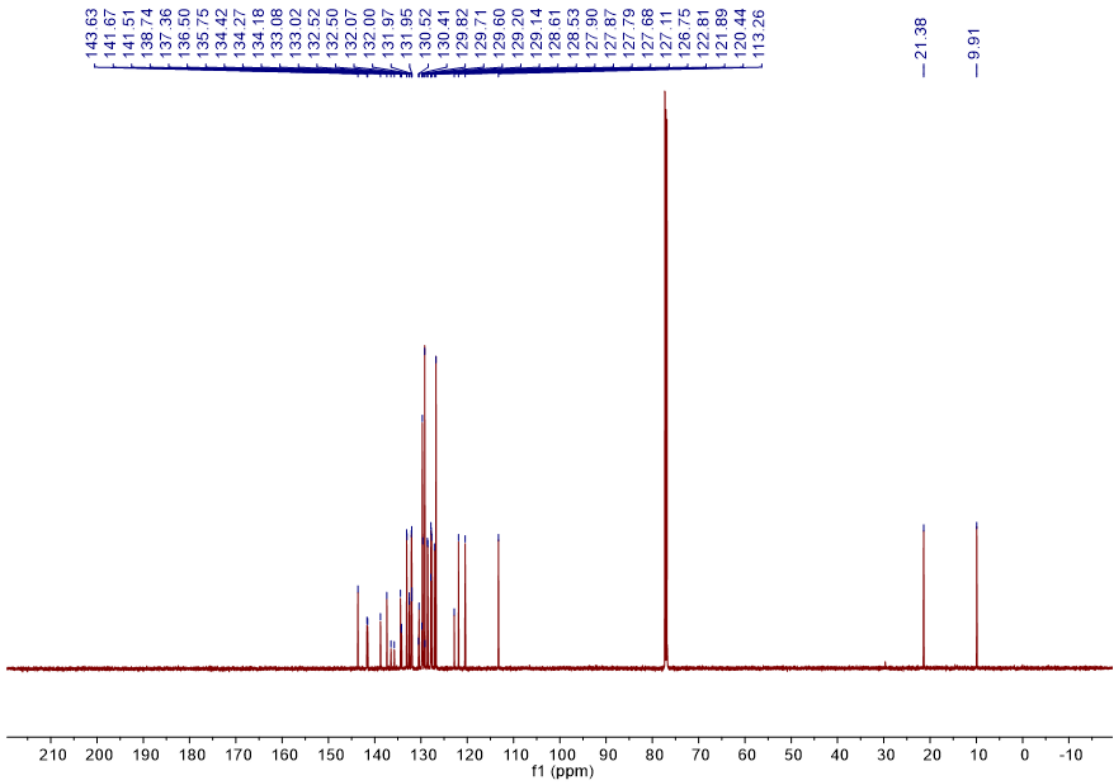

## $^{13}$C NMR of 18 ($CDCl_3$)



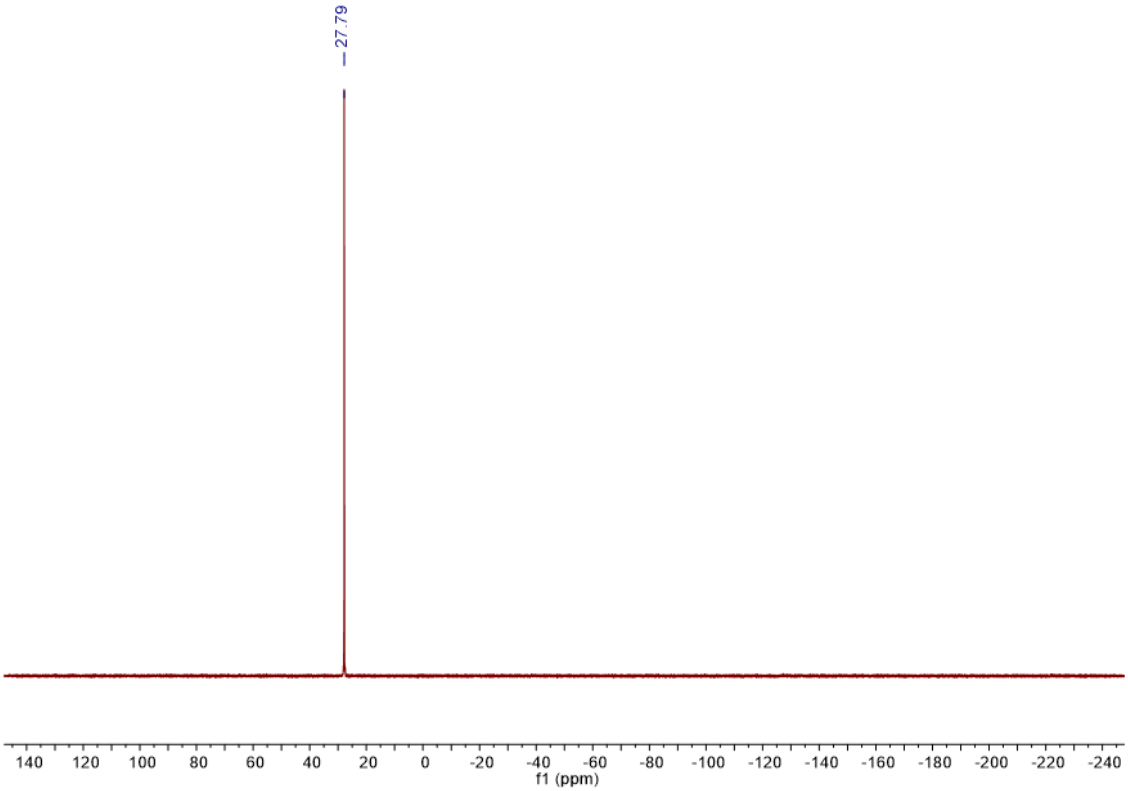
## $^{31}$P NMR of 18 ($CDCl_3$)



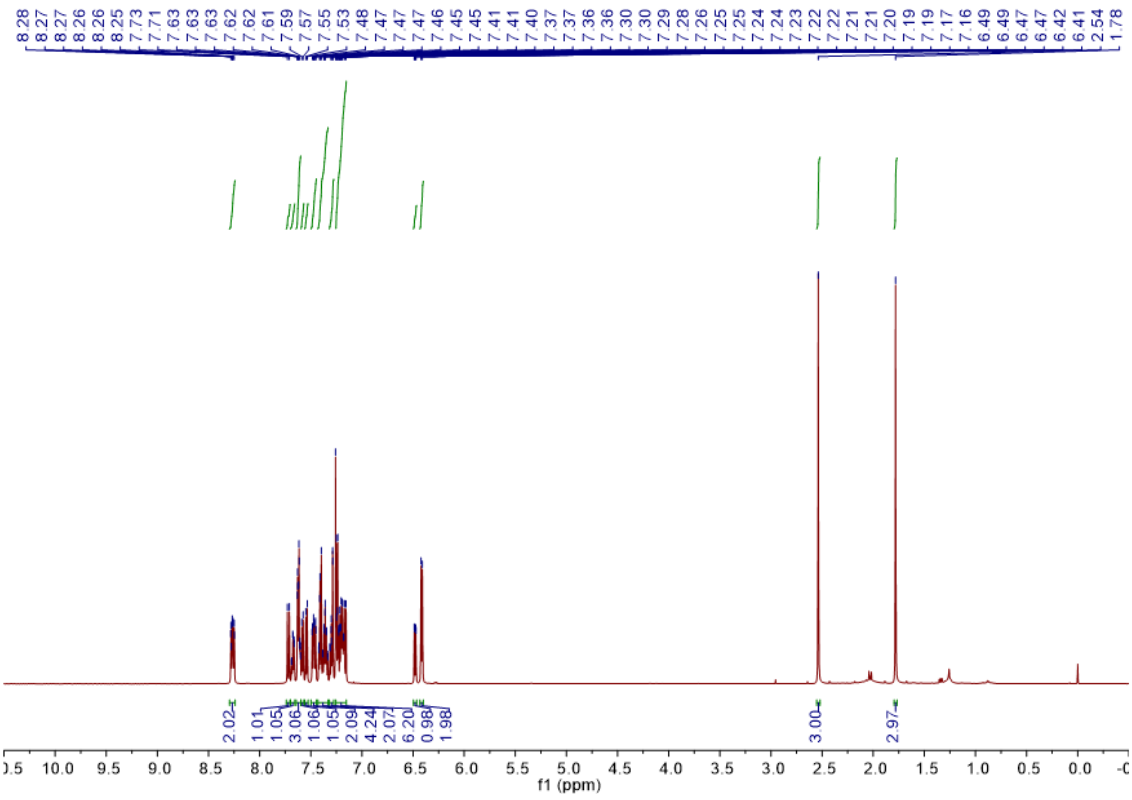

## $^{1}$H NMR of 19 ($CDCl_3$)



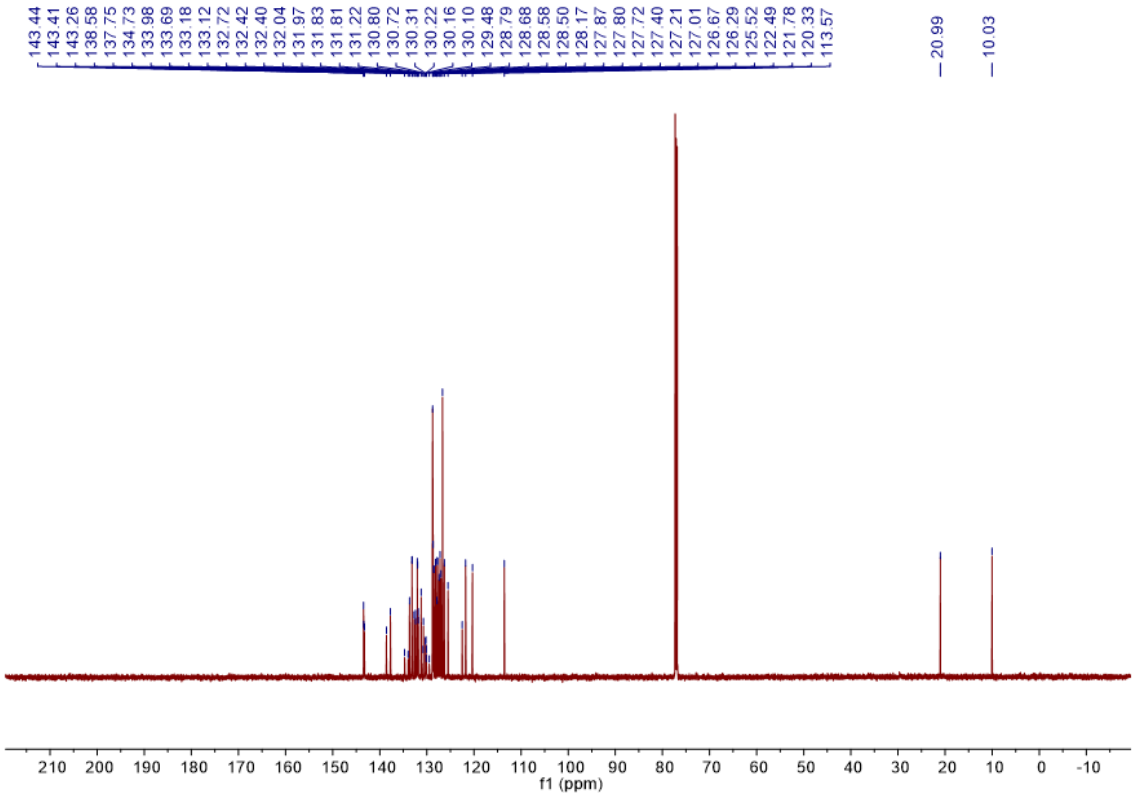
## $^{13}C$ NMR of 19 ($CDCl_3$)



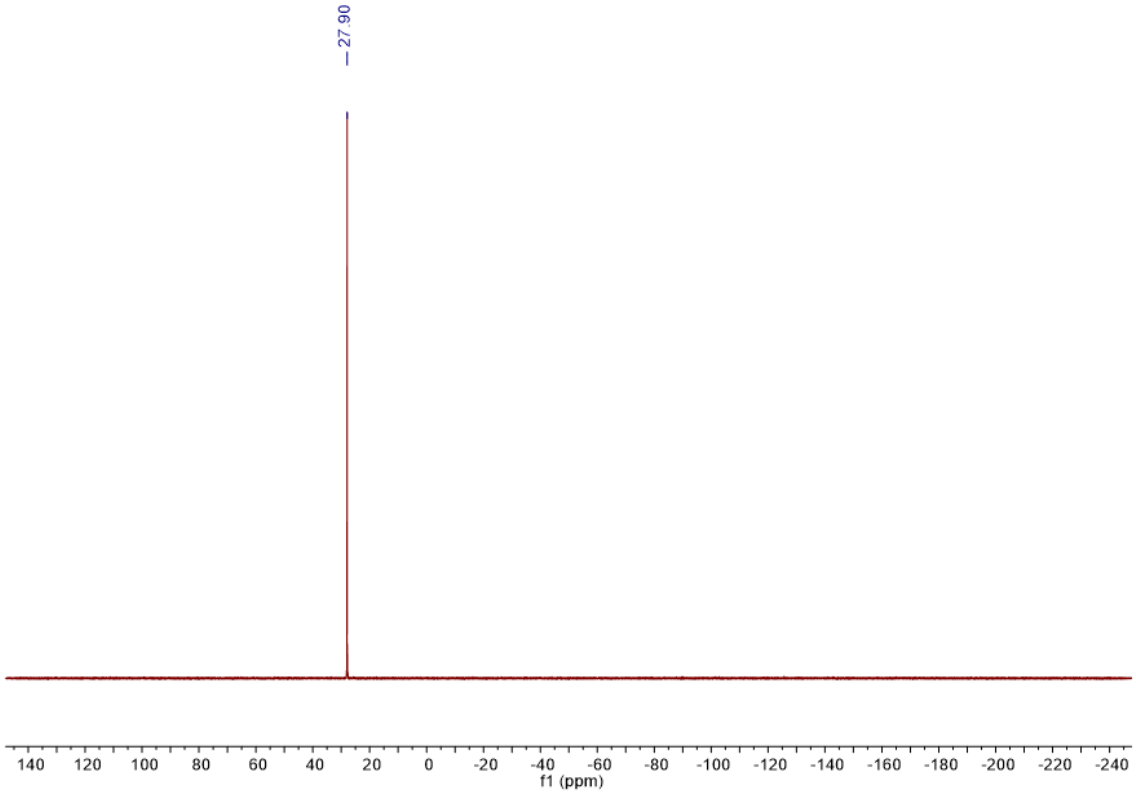

## $^{31}P$ NMR of 19 ($CDCl_3$)



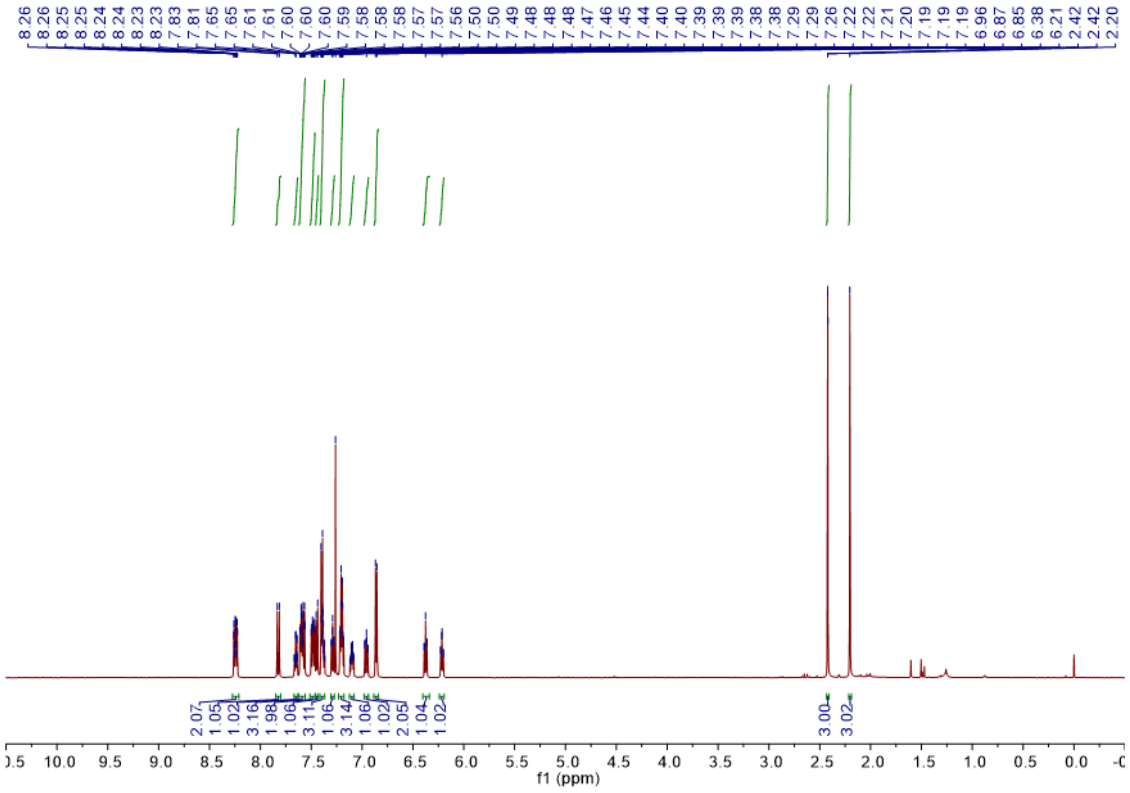
## $^{1}$H NMR of 20 ($CDCl_3$)



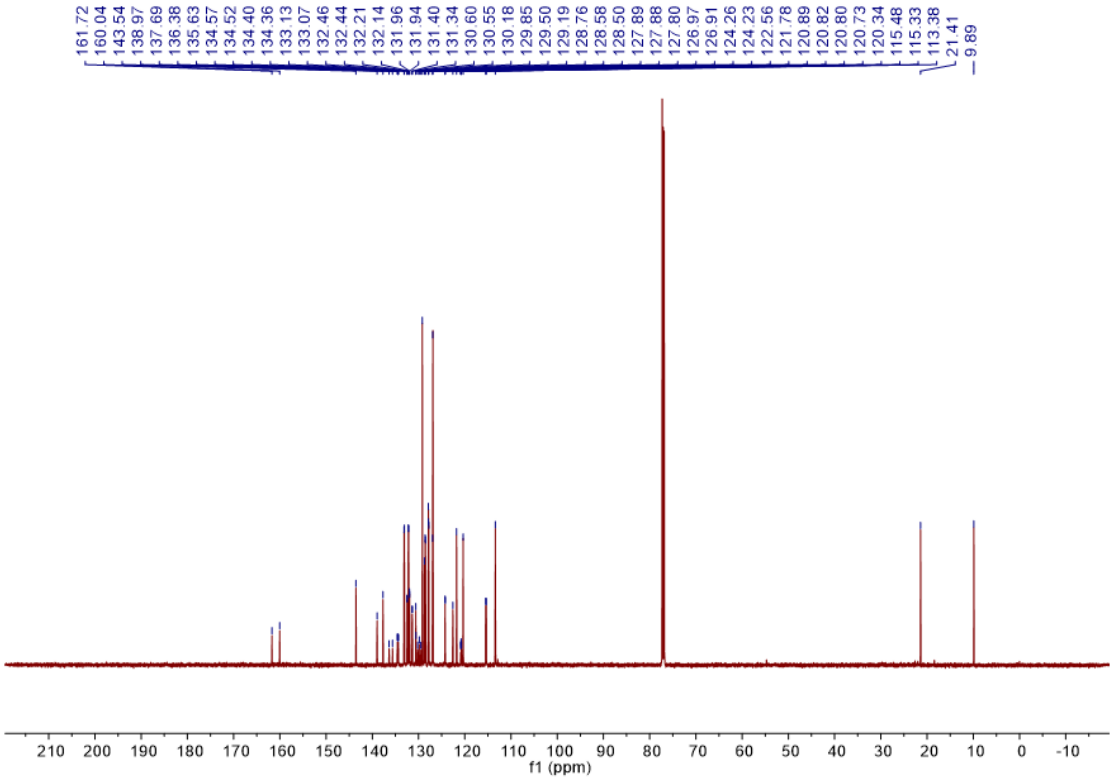

## $^{13}$C NMR of 20 ($CDCl_3$)



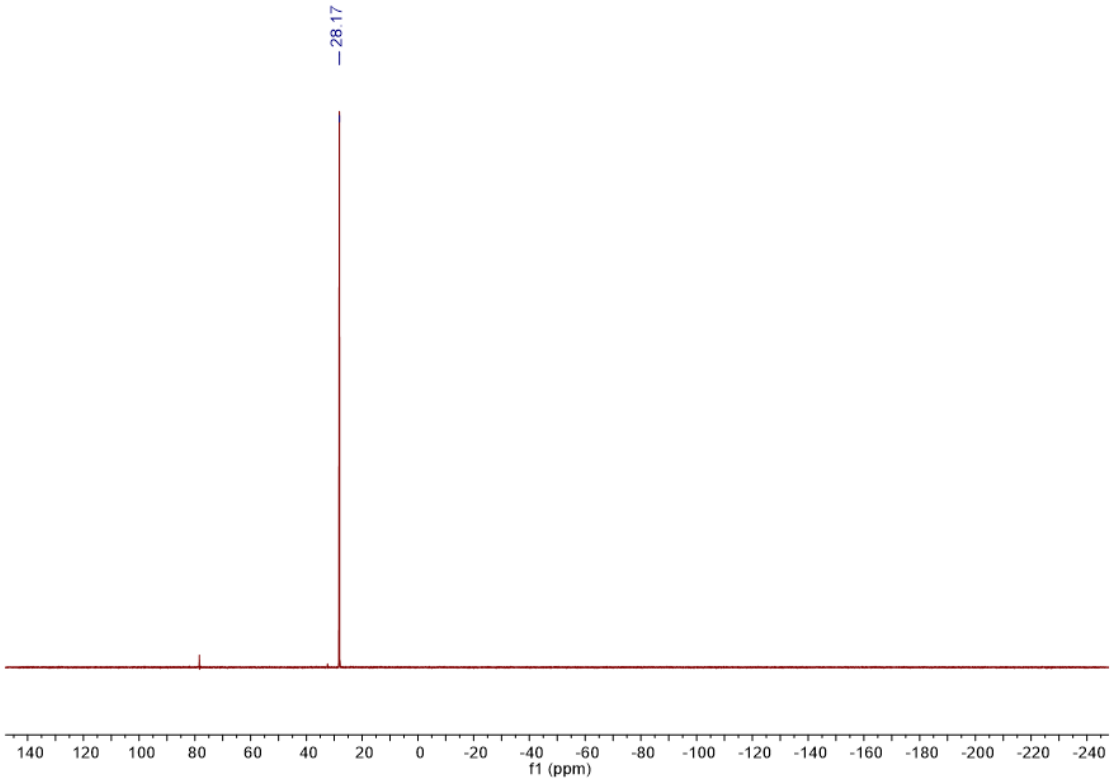
## $^{31}P$ NMR of 20 ($CDCl_3$)



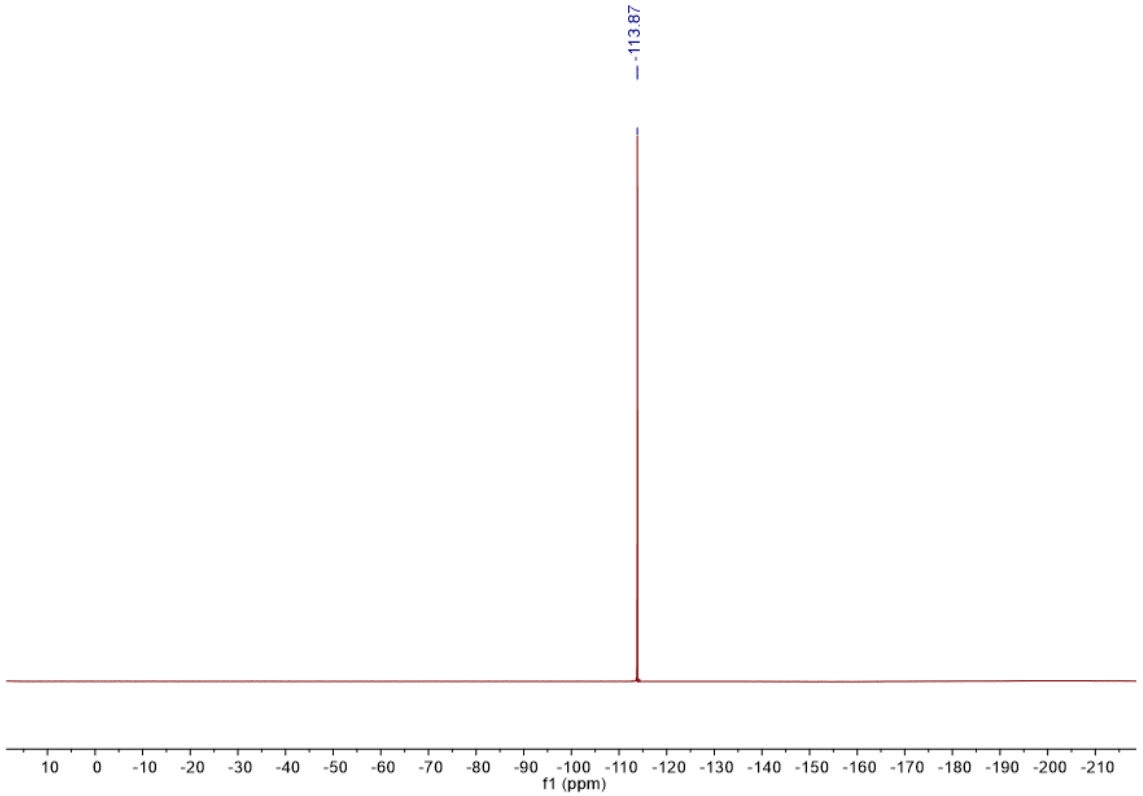

## $^{1}H$ NMR of 21 ($CDCl_3$)



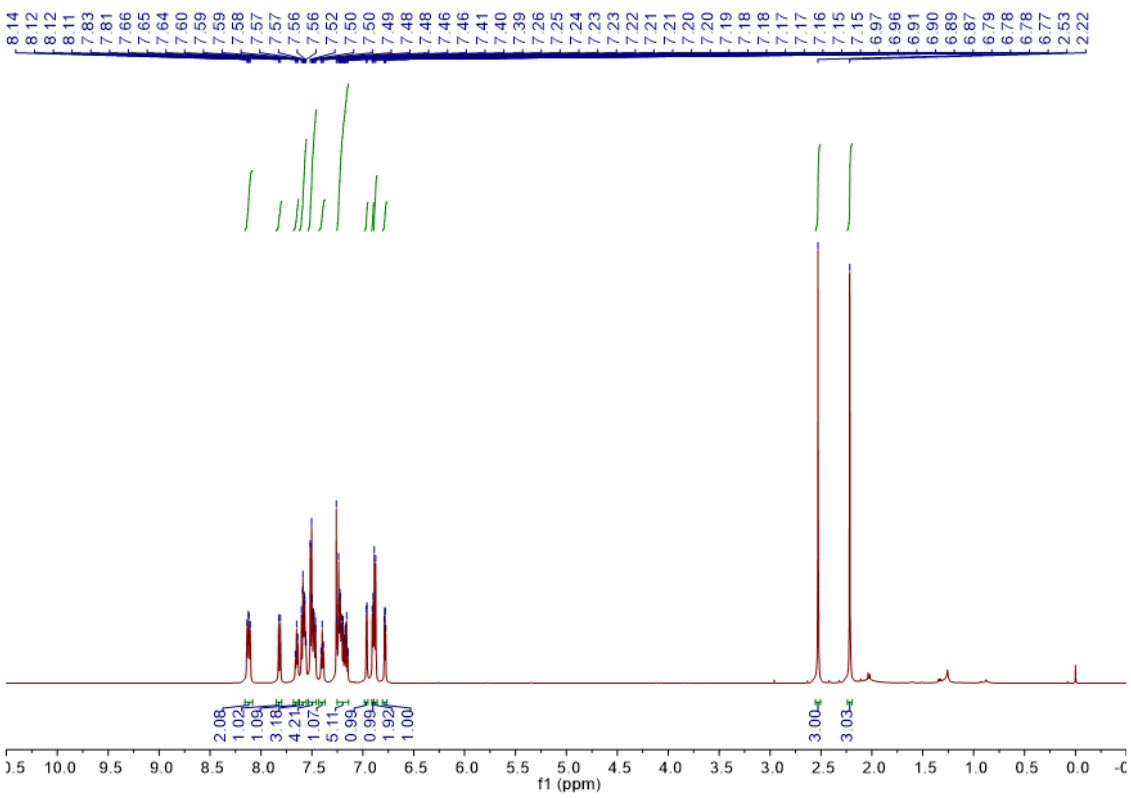
## $^{13}C$ NMR of 21 ($CDCl_3$)



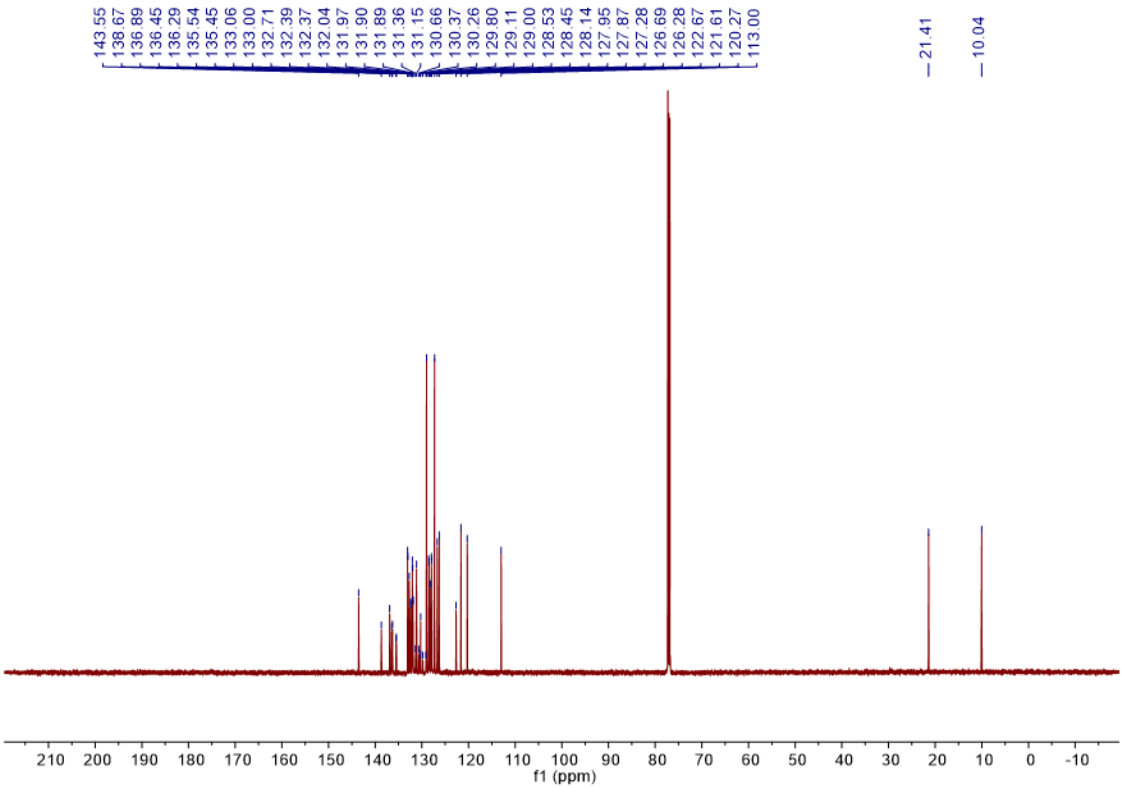

## $^{31}P$ NMR of 21 ($CDCl_3$)



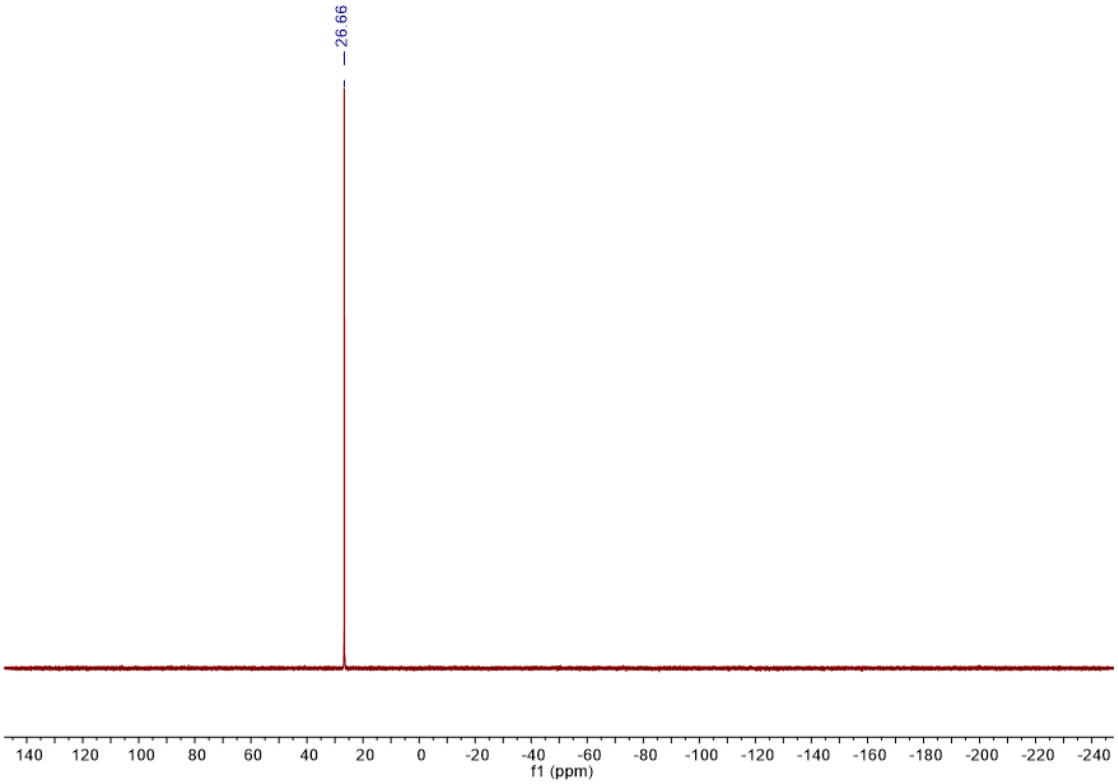
## $^{19}$F NMR of 21 ($CDCl_3$)



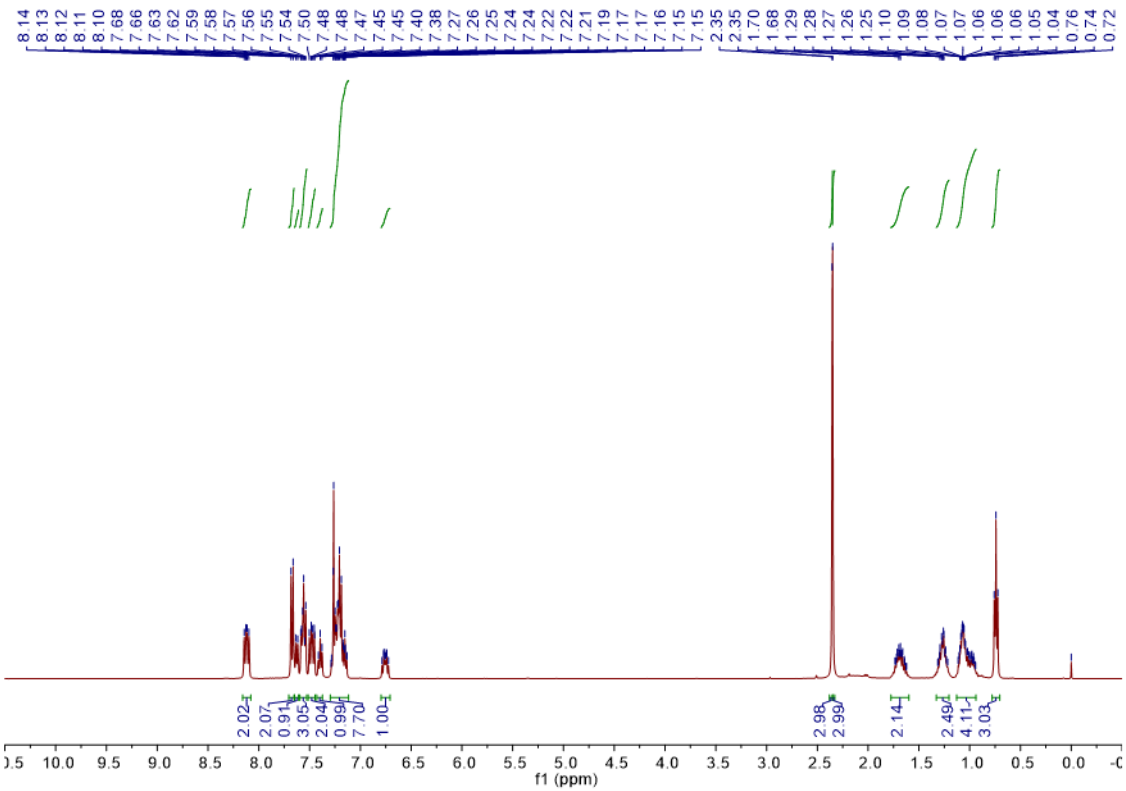

## $^{1}$H NMR of 22 ($CDCl_3$)



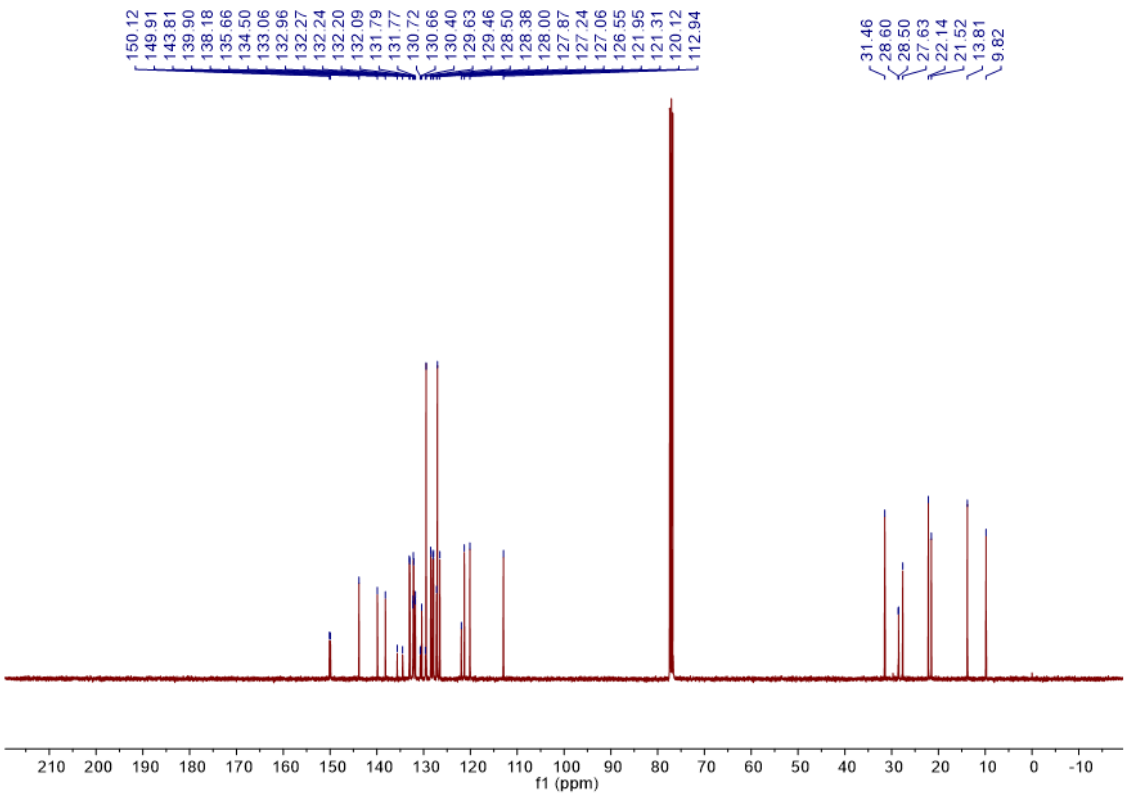
## $^{13}C$ NMR of 22 ($CDCl_3$)



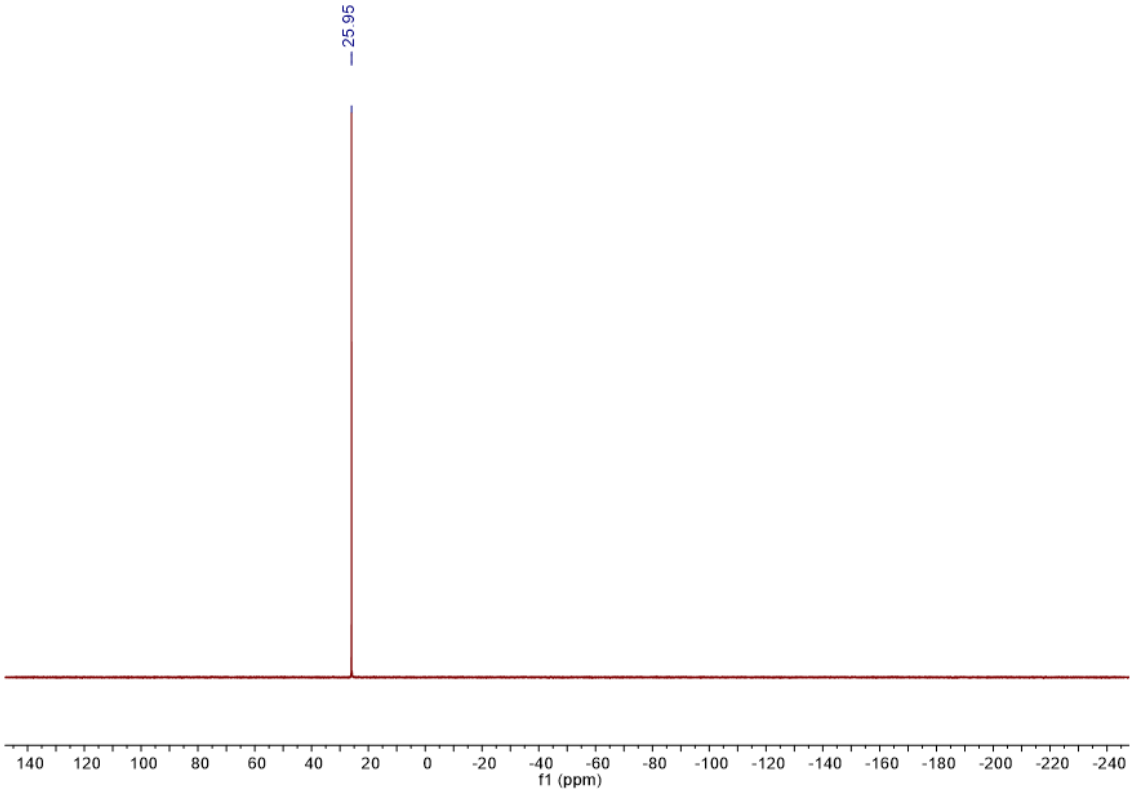

## $^{31}P$ NMR of 22 ($CDCl_3$)



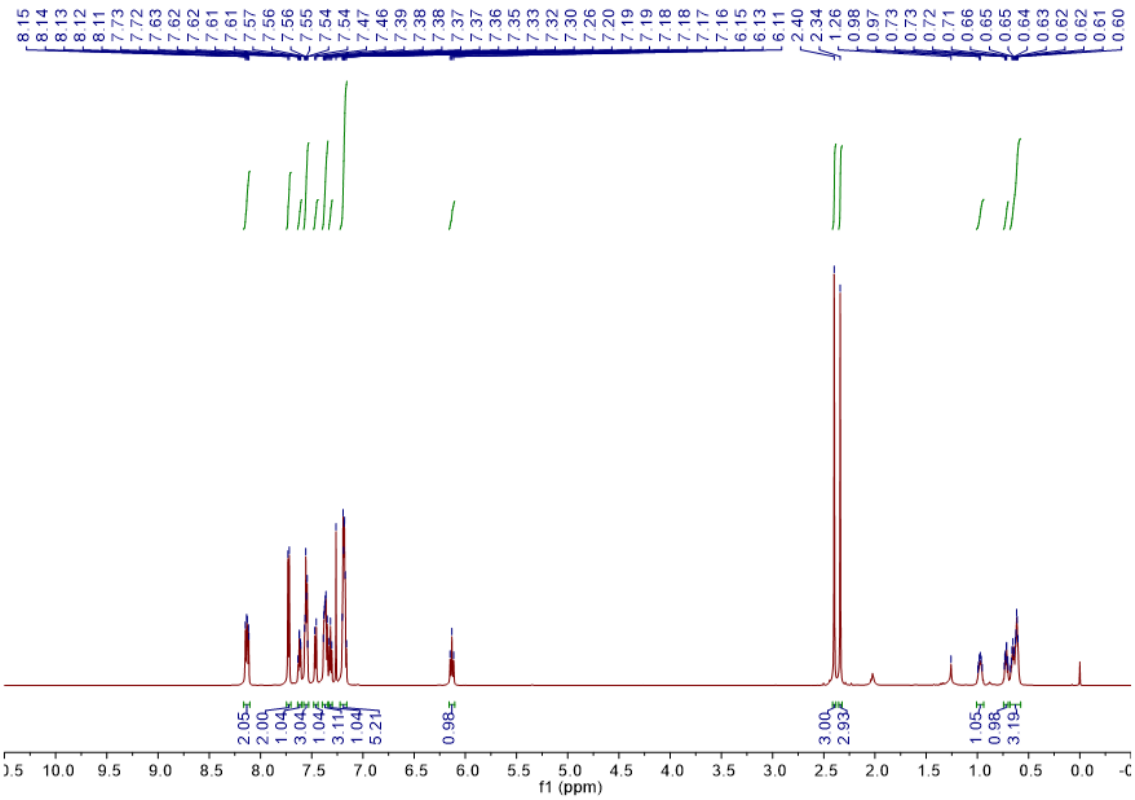
## $^{1}$H NMR of 23 ($CDCl_3$)



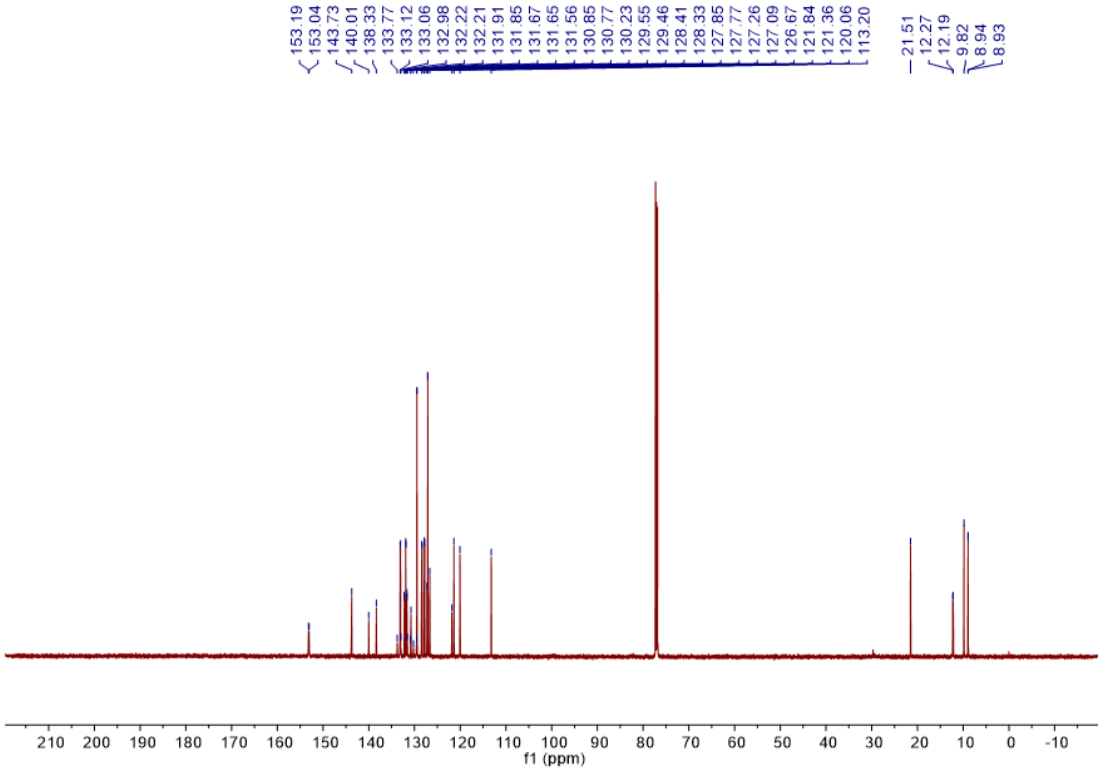

## $^{13}$C NMR of 23 ($CDCl_3$)



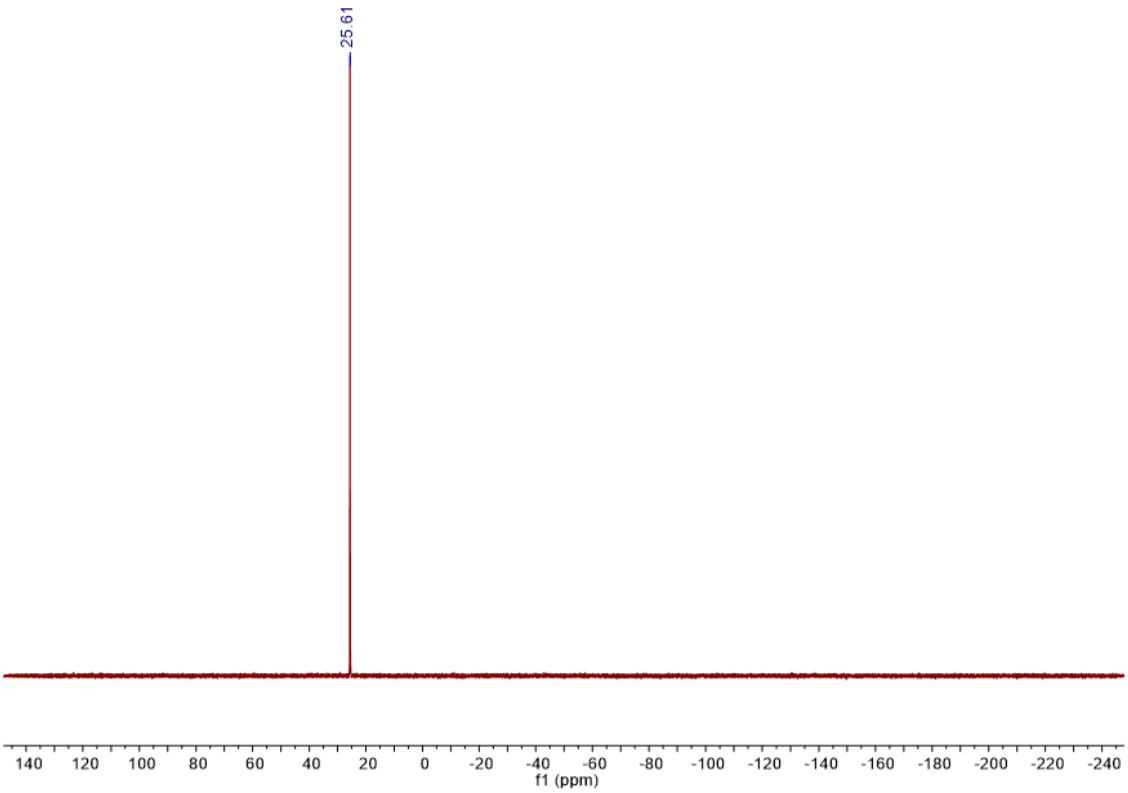
## $^{31}$P NMR of 23 ($CDCl_3$)



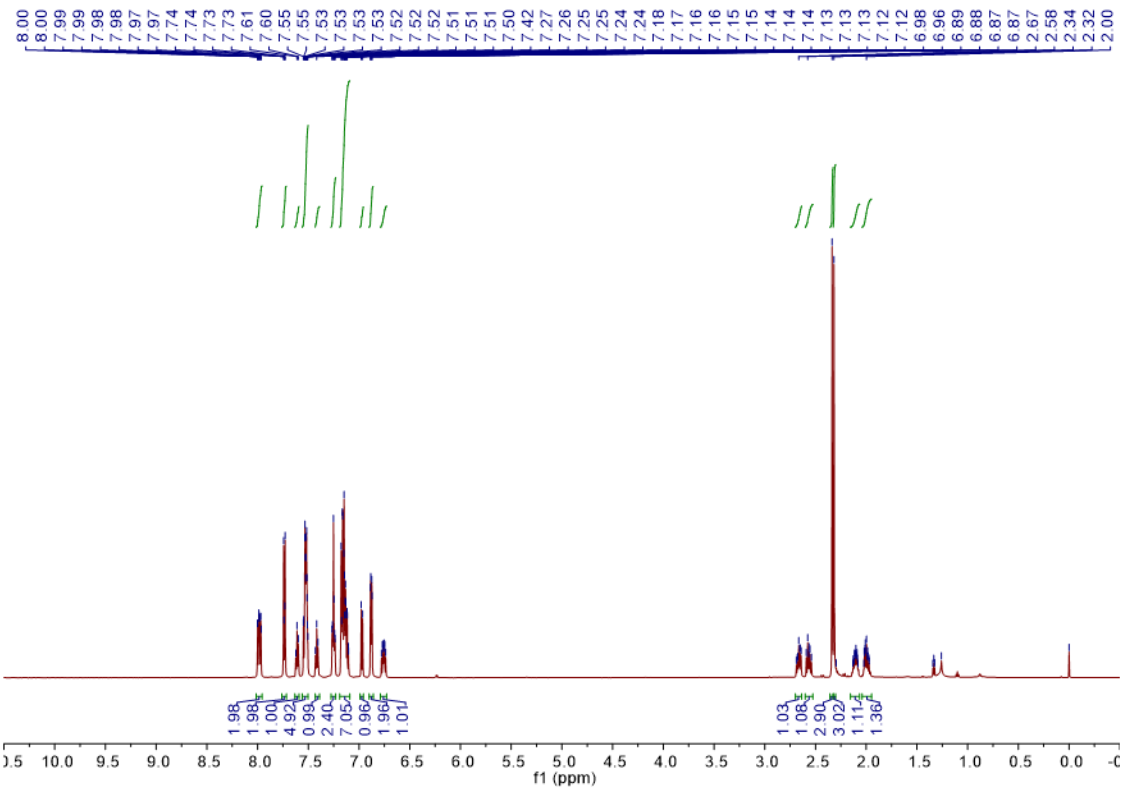

## $^{1}$H NMR of 24 ($CDCl_3$)



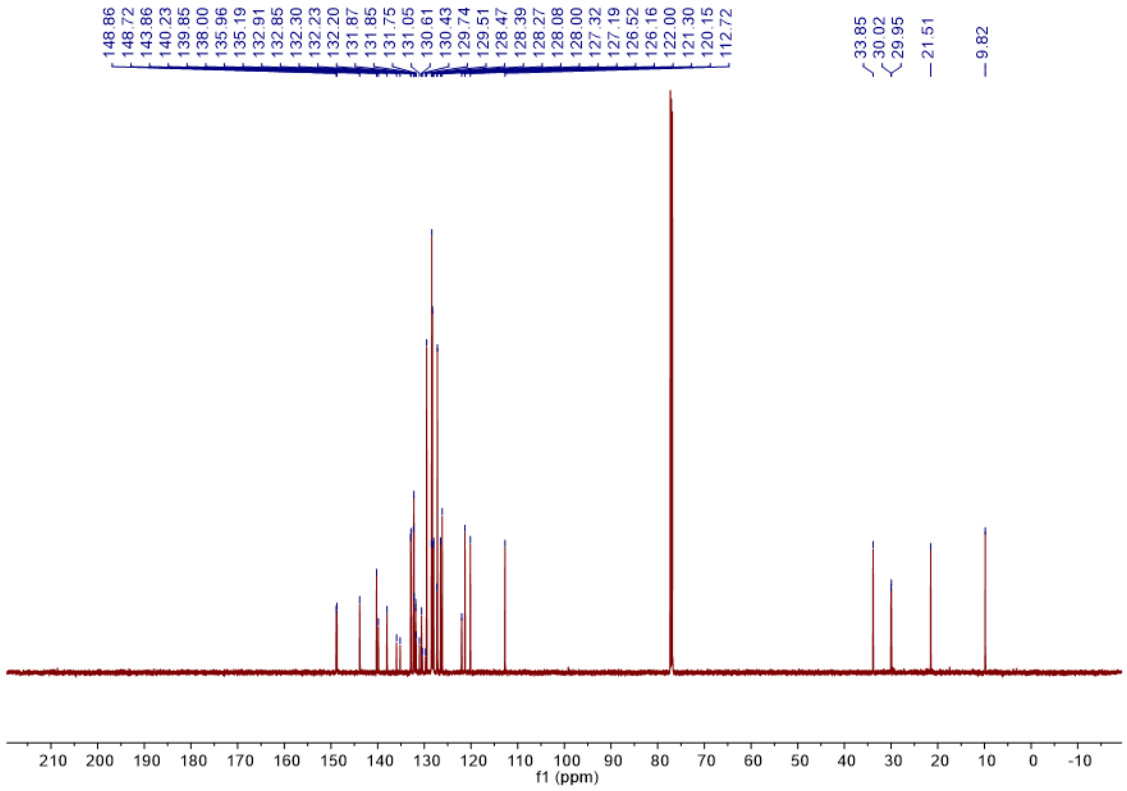
## $^{13}C$ NMR of 24 ($CDCl_3$)



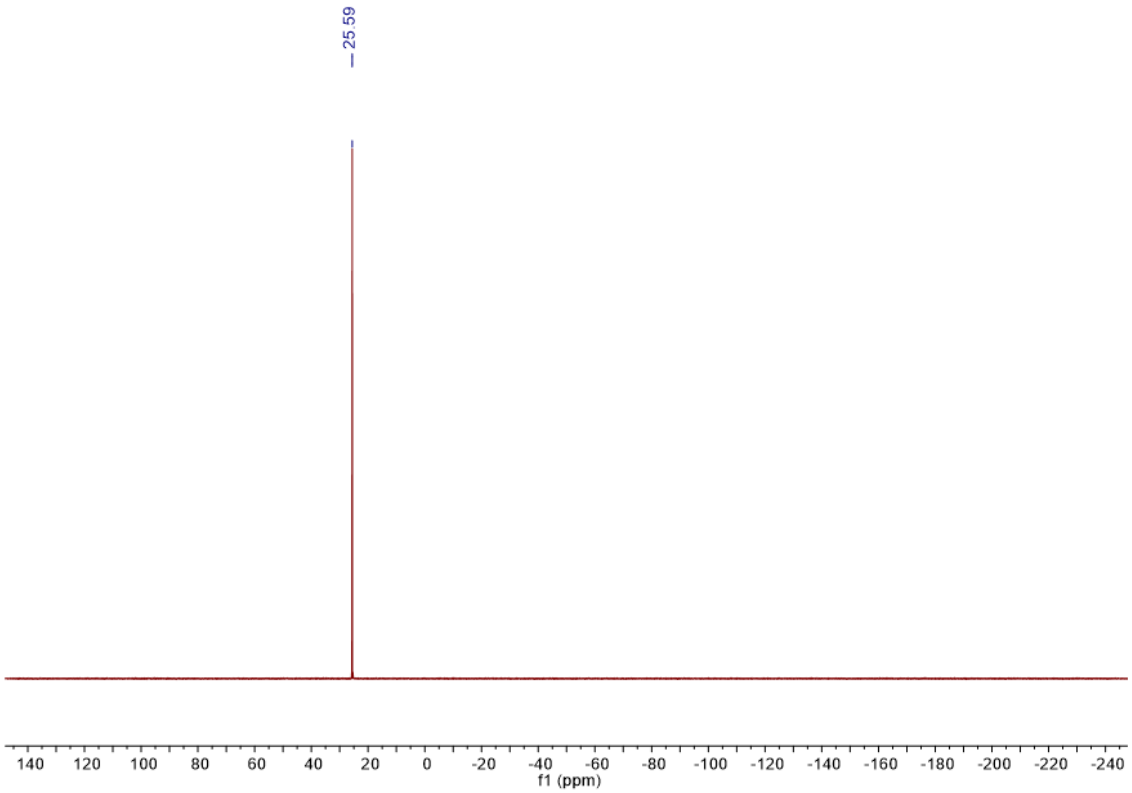

## $^{31}P$ NMR of 24 ($CDCl_3$)



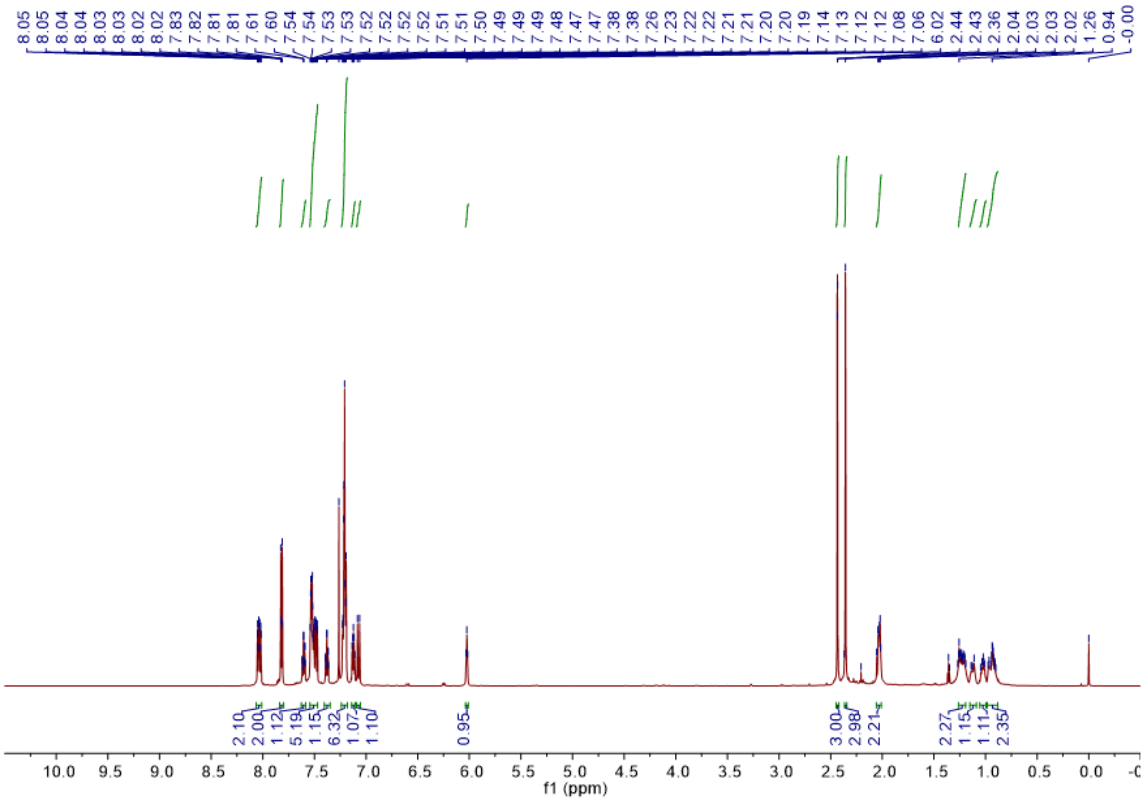
## $^{1}$H NMR of 25 ($CDCl_3$)



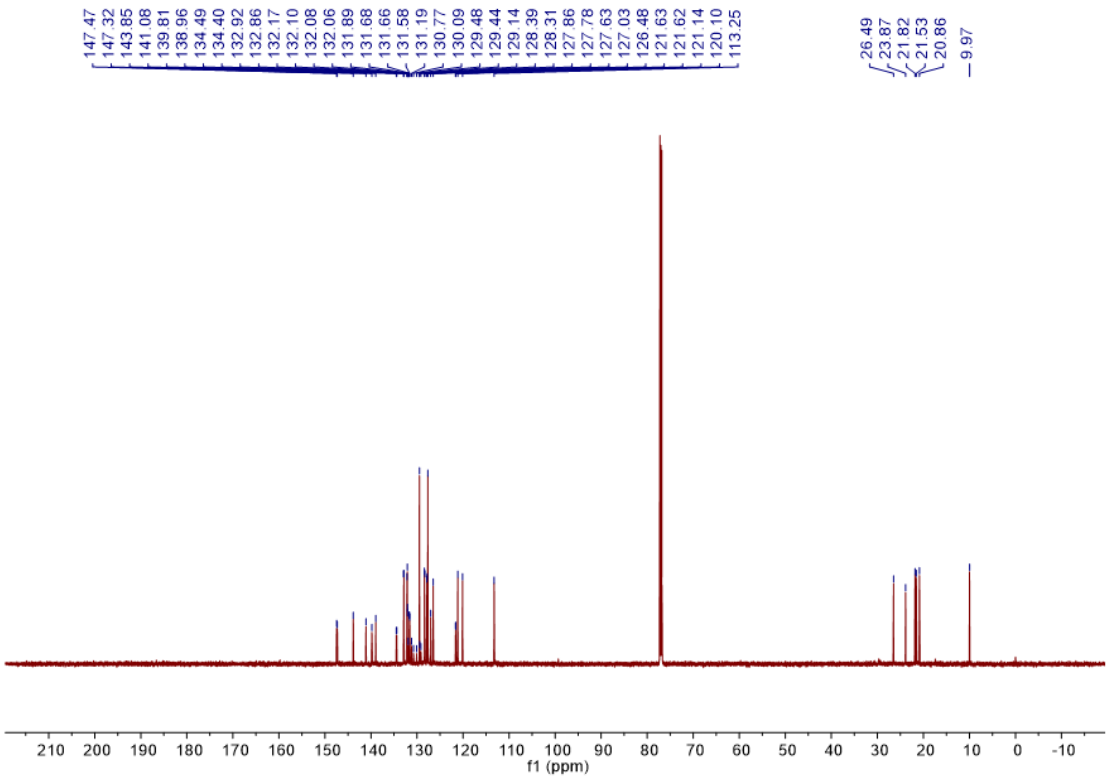

## $^{13}$C NMR of 25 ($CDCl_3$)



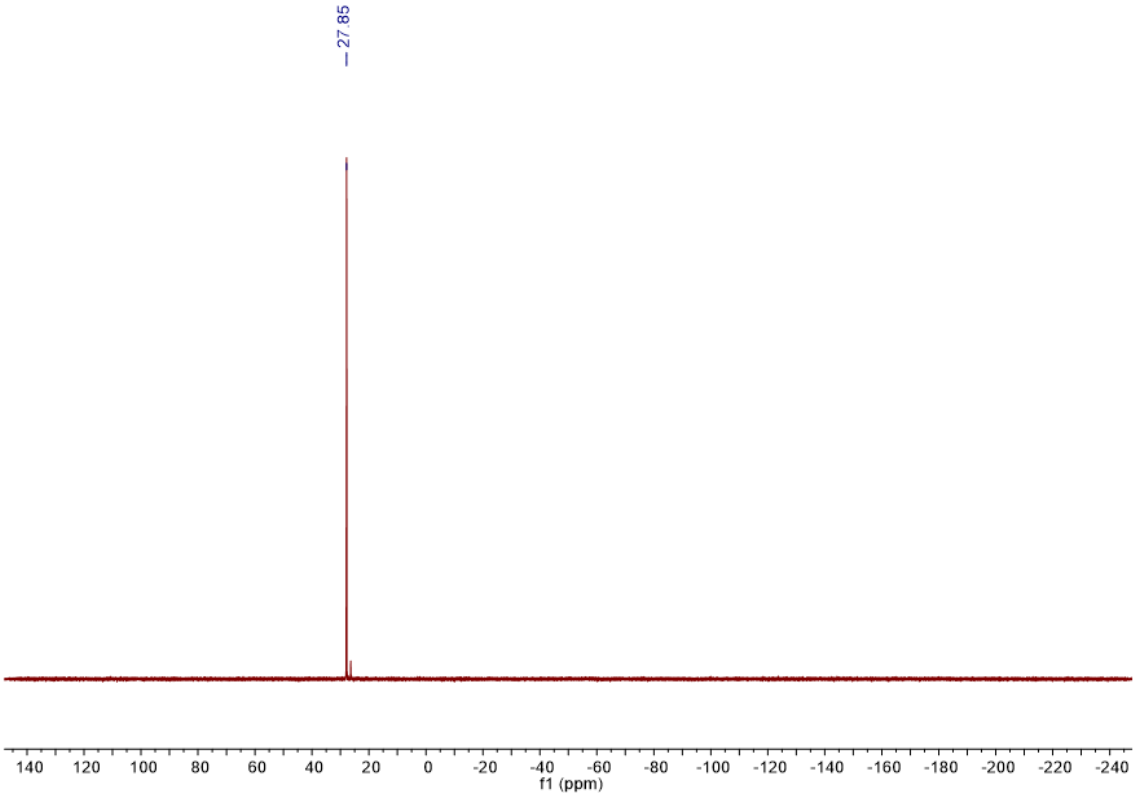
## $^{31}$P NMR of 25 ($CDCl_3$)



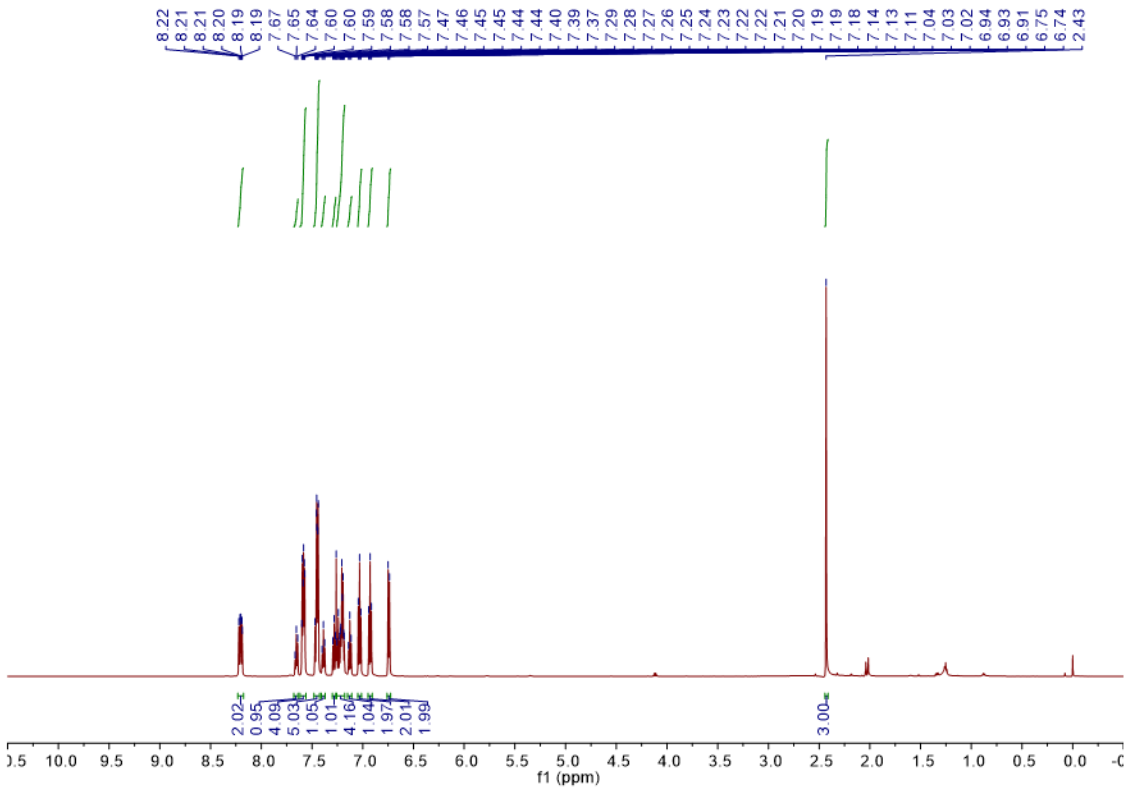
## $^{1}$H NMR of 26 ($CDCl_3$)



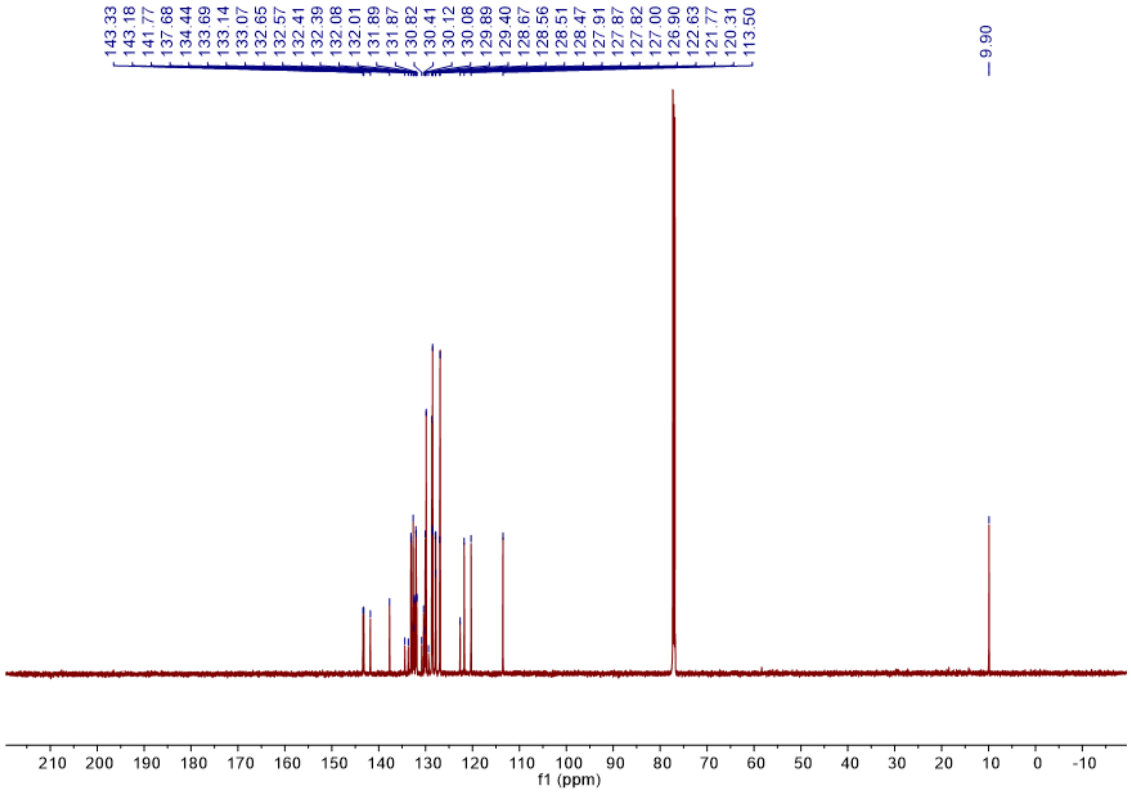
## $^{13}C$ NMR of 26 ($CDCl_3$)



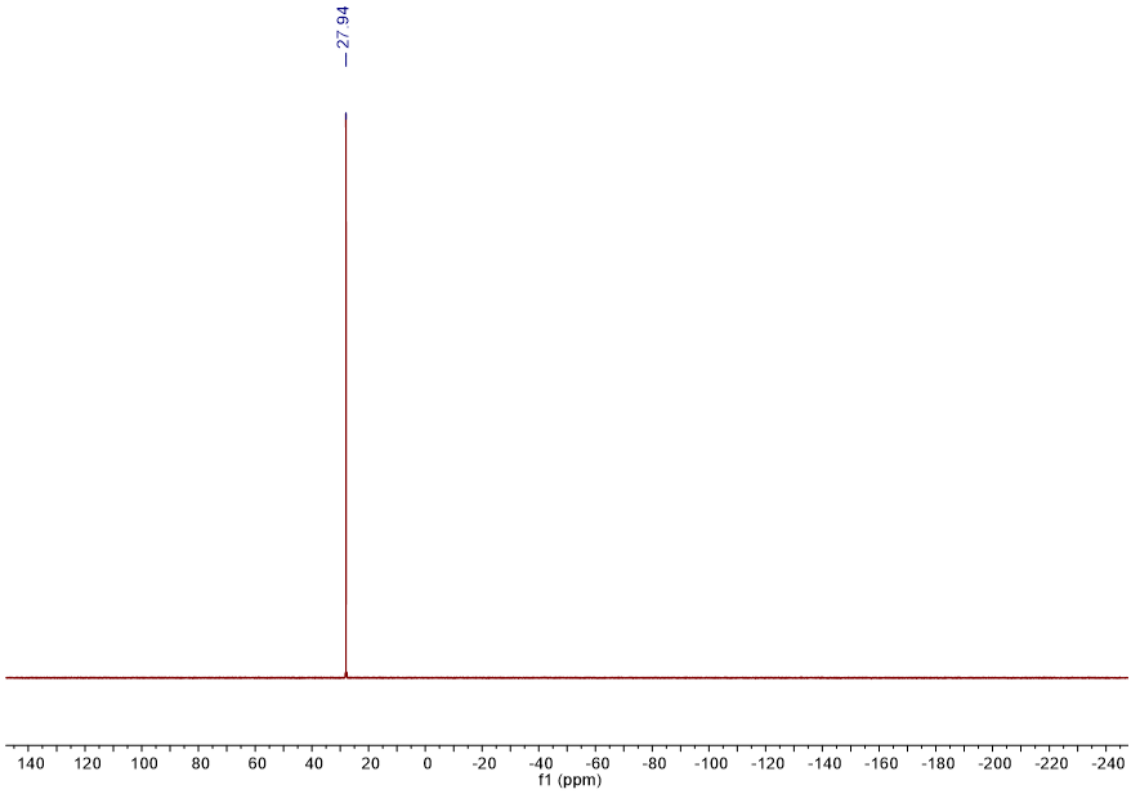

## $^{31}P$ NMR of 26 ($CDCl_3$)



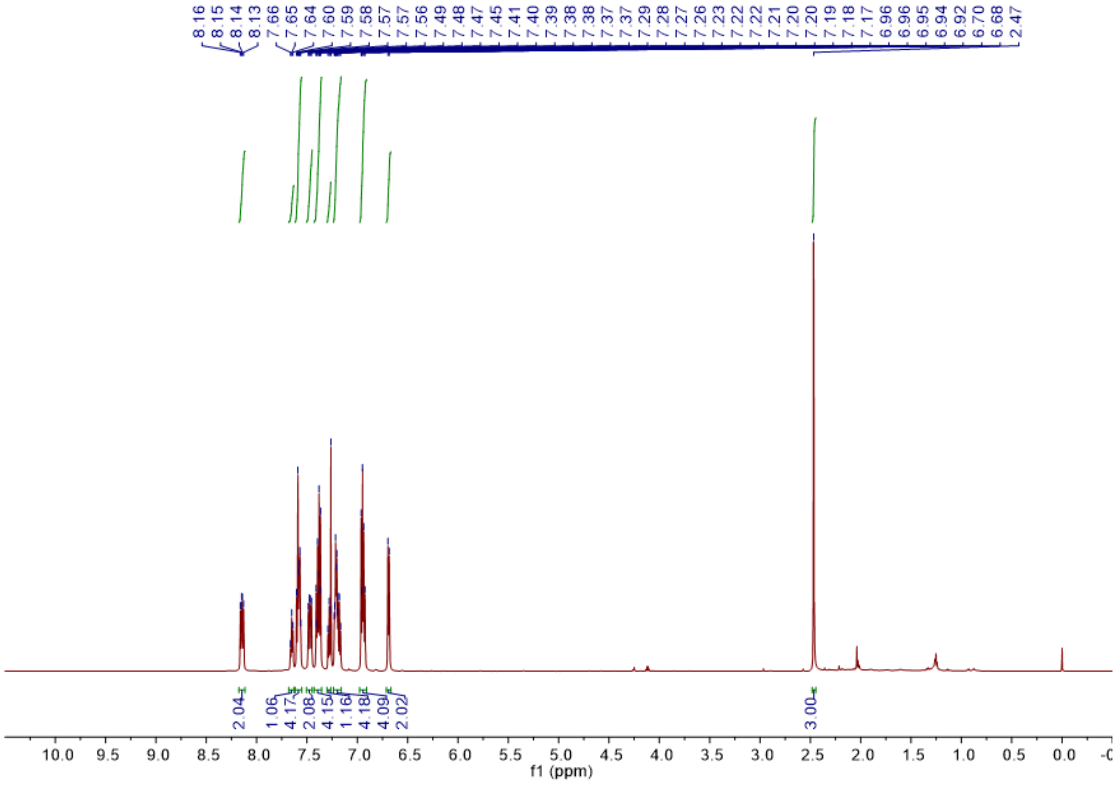
## $^{1}$H NMR of 27 ($CDCl_3$)



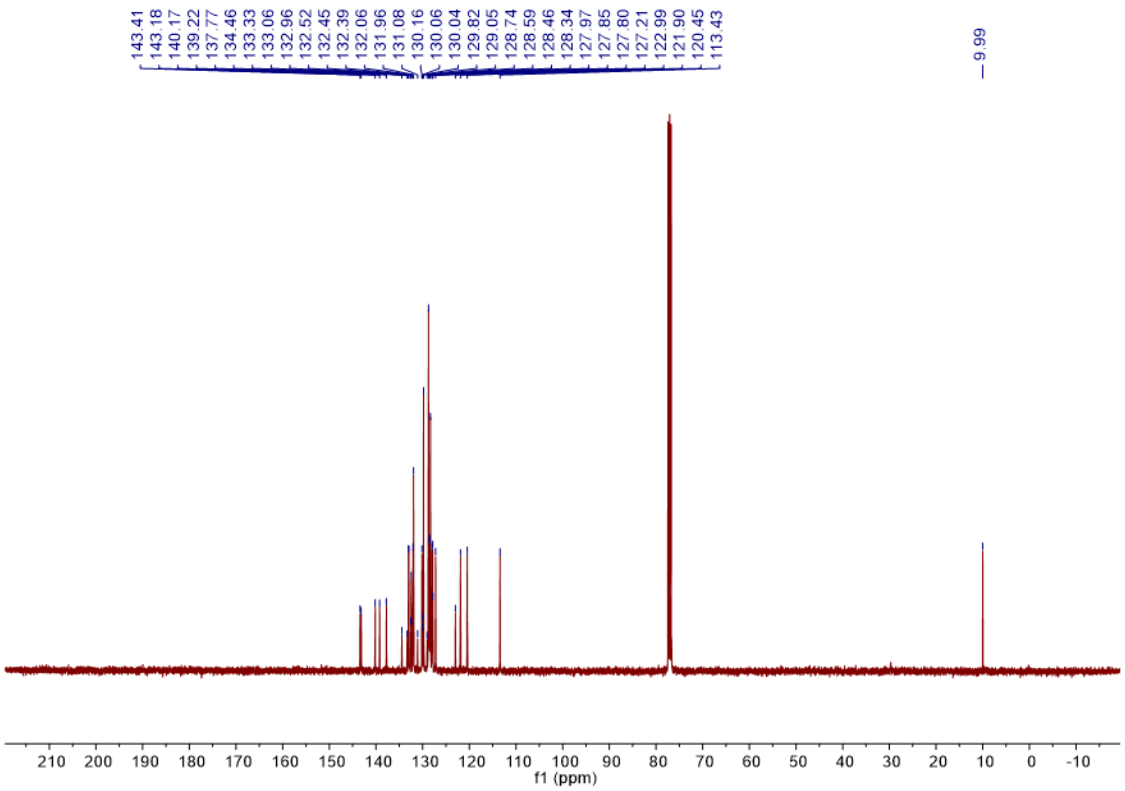

## $^{13}$C NMR of 27 ($CDCl_3$)



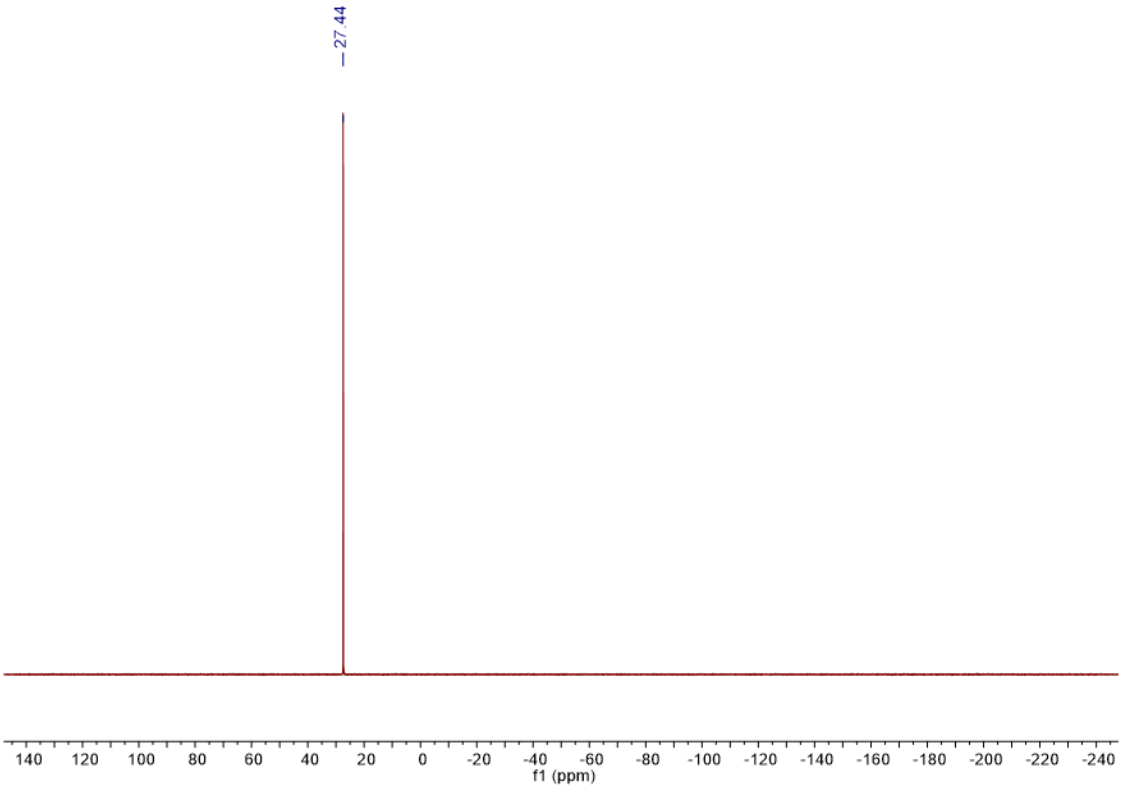
## $^{31}P$ NMR of 27 ($CDCl_3$)



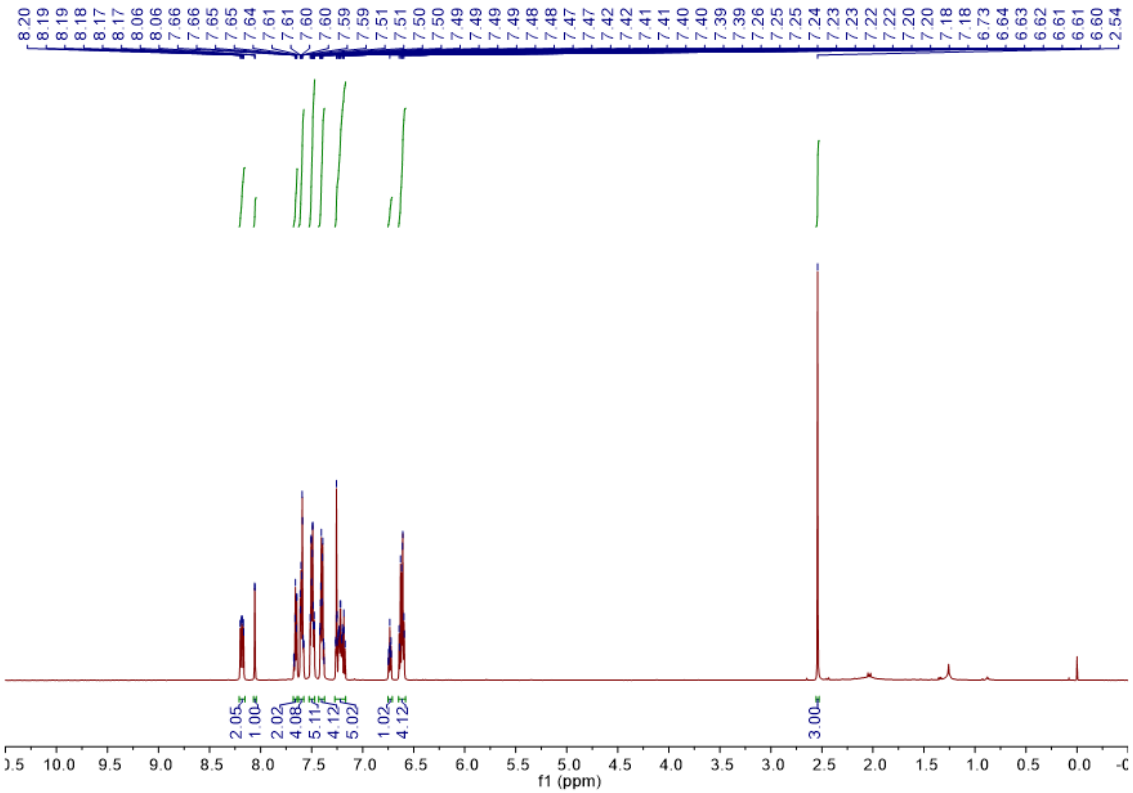
## $^{1}H$ NMR of 28 ($CDCl_3$)



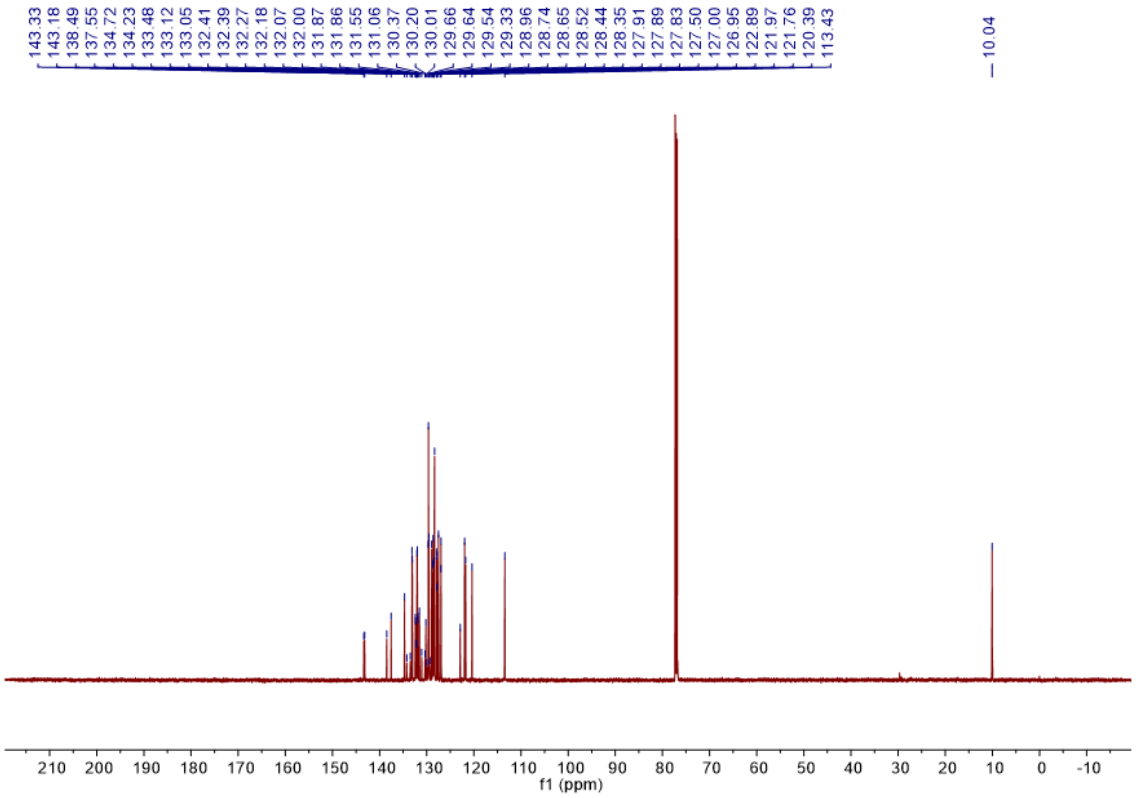
## $^{13}C$ NMR of 28 ($CDCl_3$)



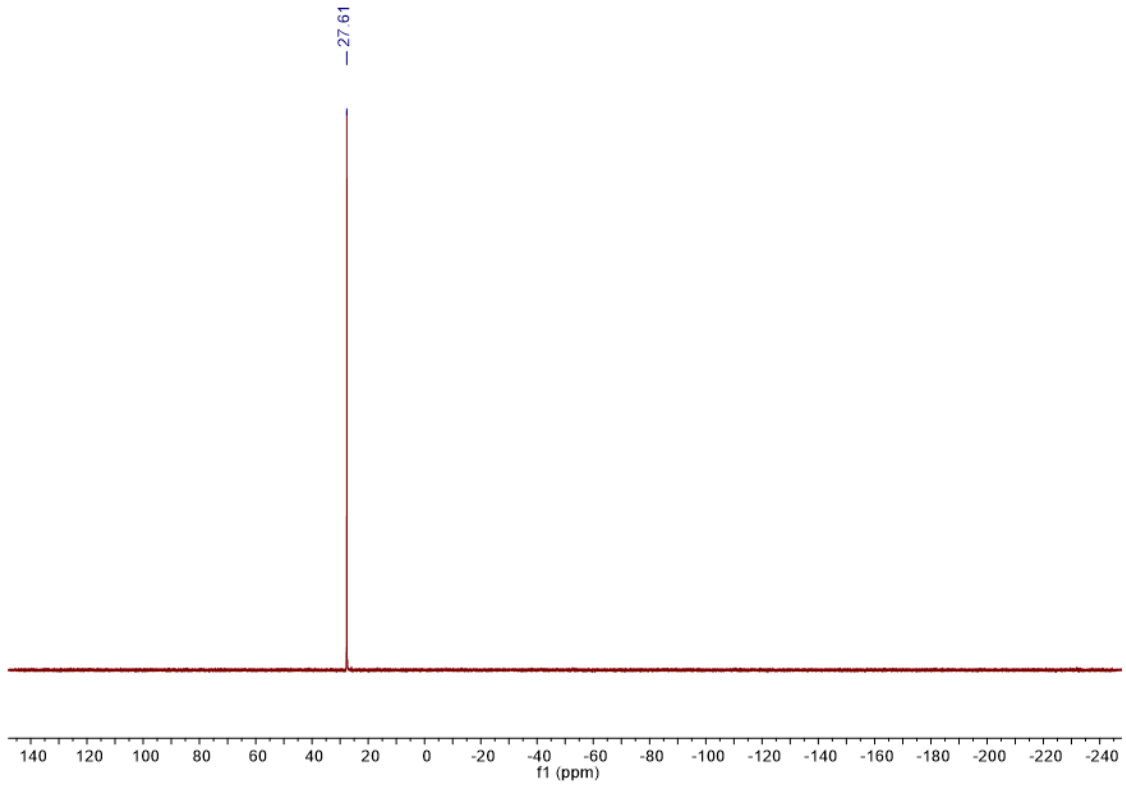

## $^{31}P$ NMR of 28 ($CDCl_3$)



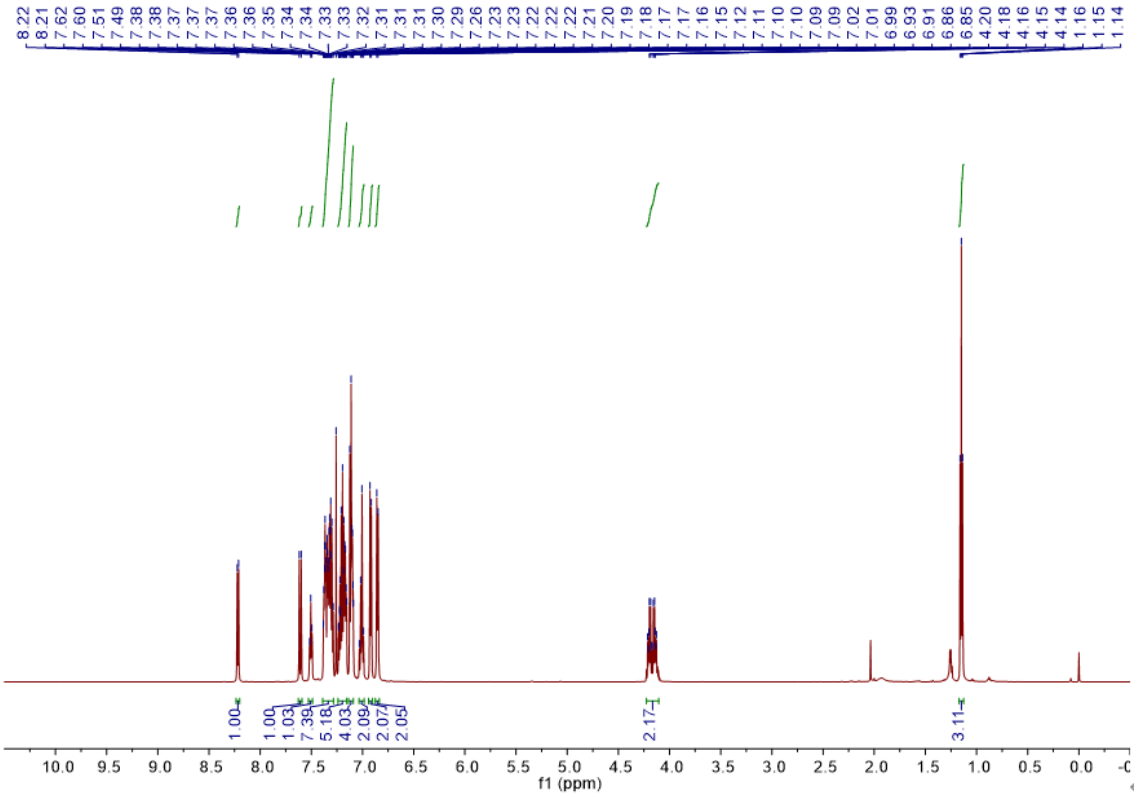
## $^{1}$H NMR of 29 ($CDCl_3$)



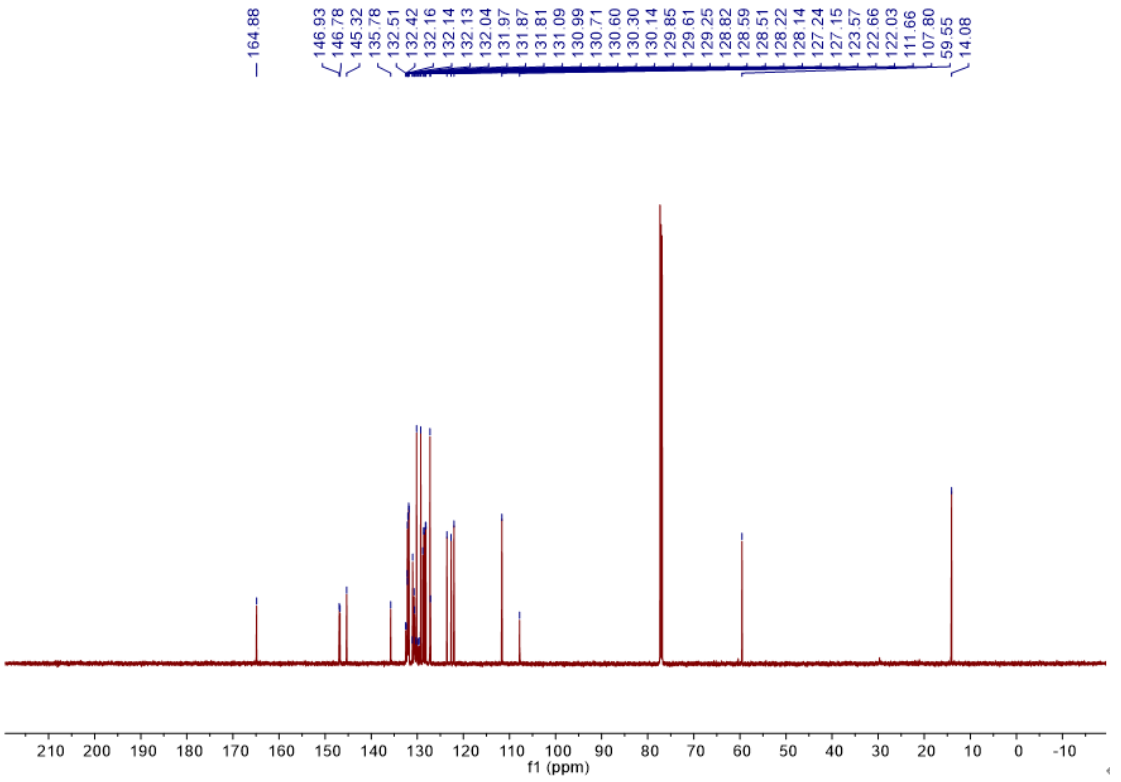

## $^{13}$C NMR of 29 ($CDCl_3$)



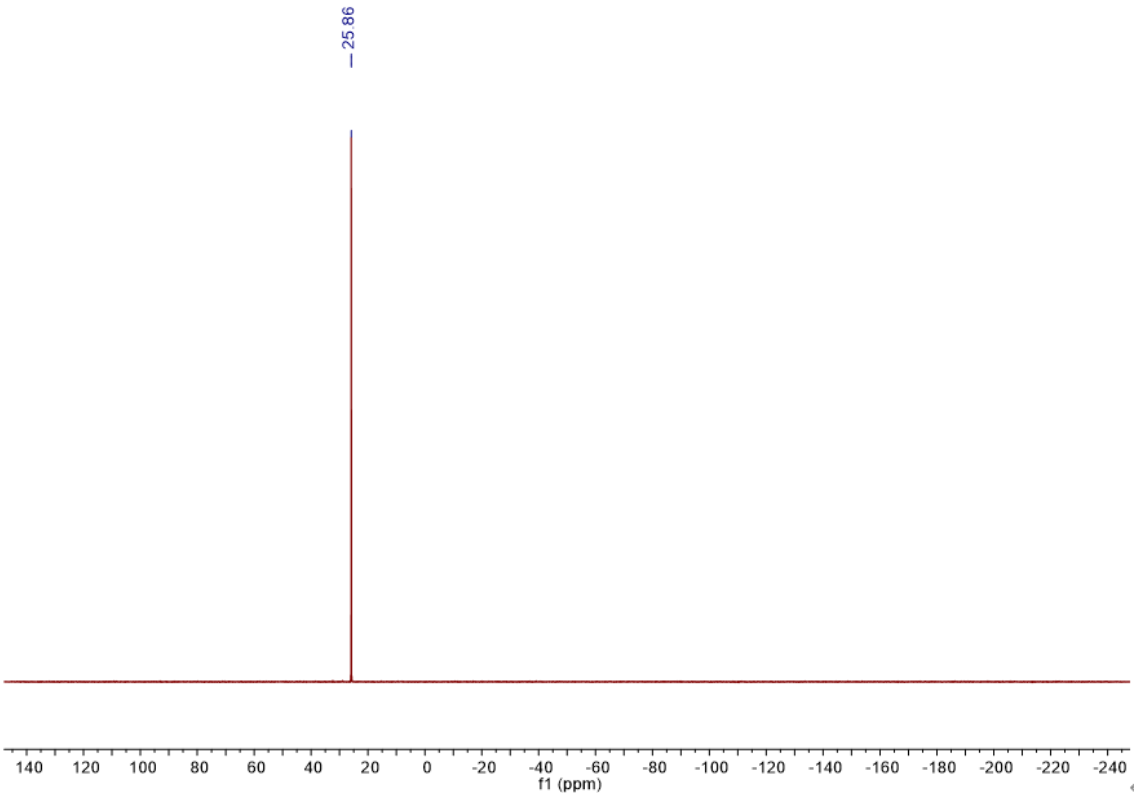
## $^{31}P$ NMR of 29 ($CDCl_3$)



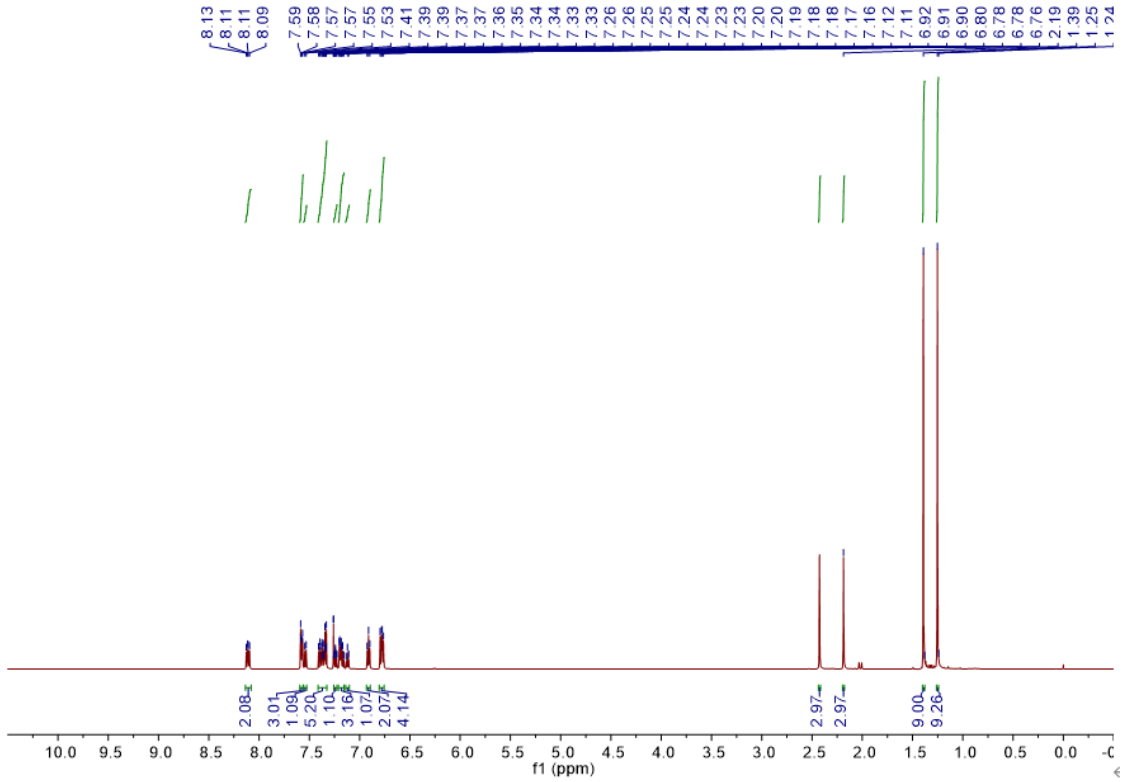

## $^{1}H$ NMR of 30 ($CDCl_3$)



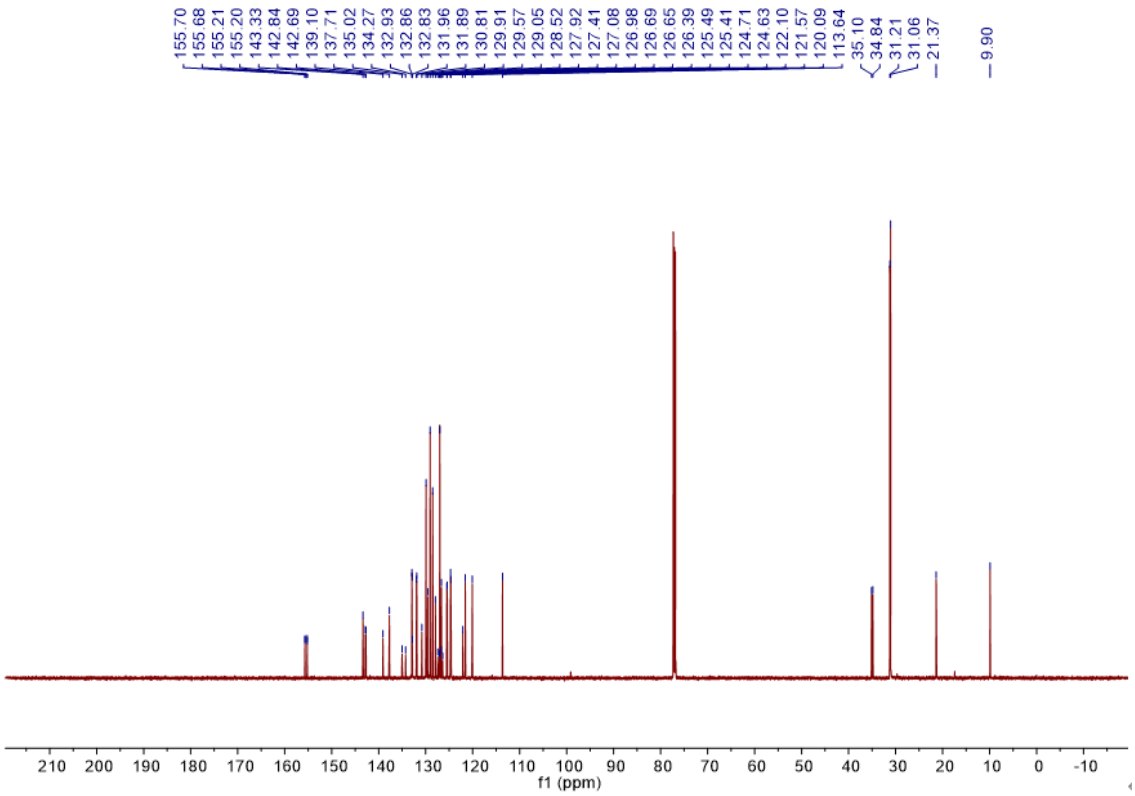
## $^{13}C$ NMR of 30 ($CDCl_3$)



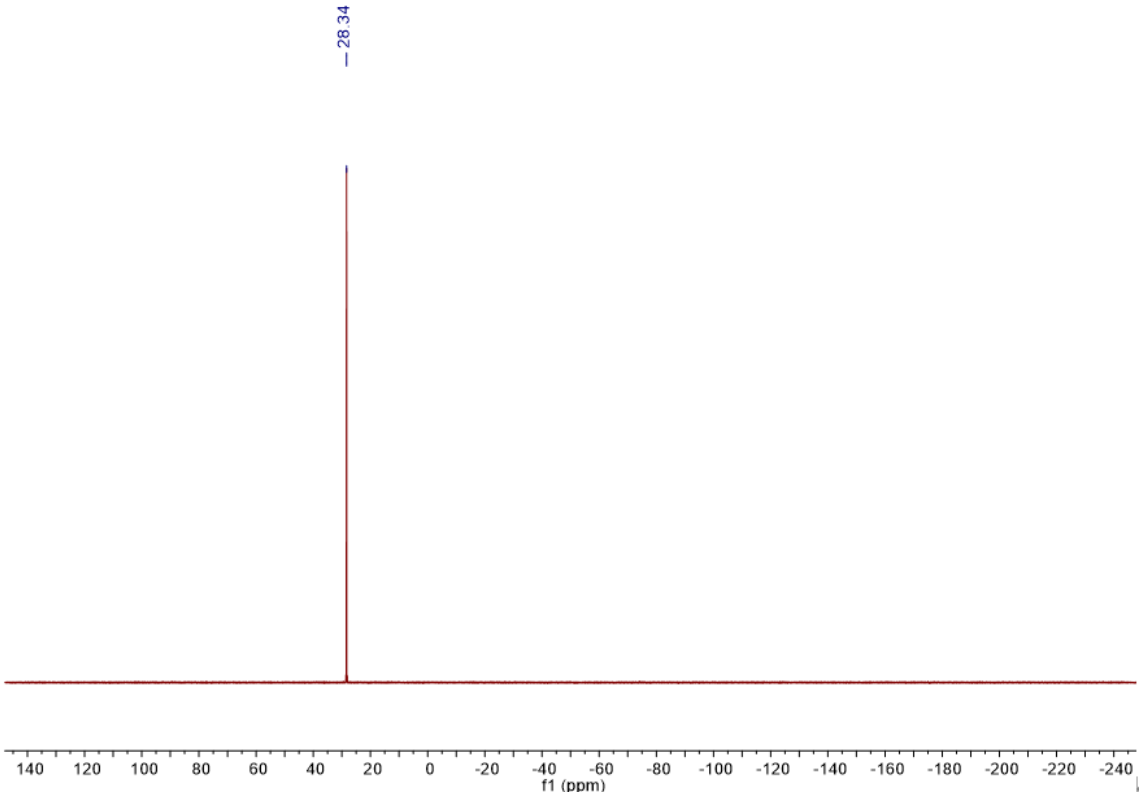

## $^{31}P$ NMR of 30 ($CDCl_3$)



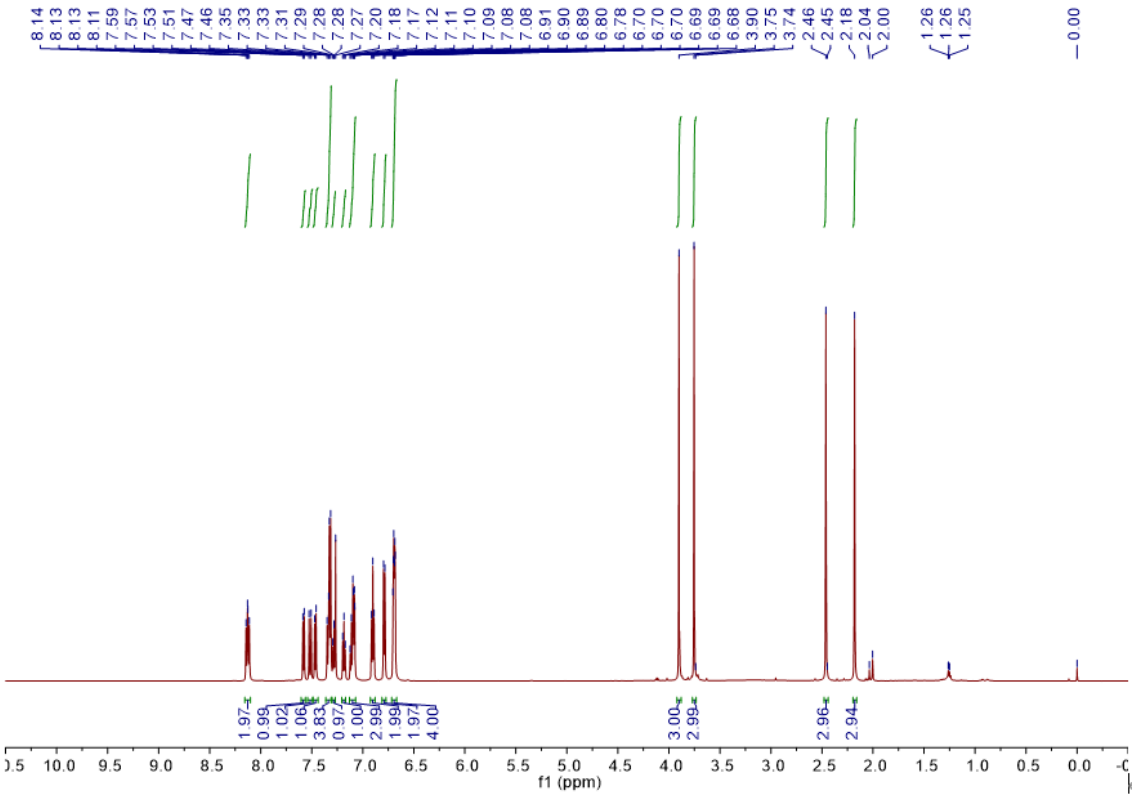
## $^{1}$H NMR of 31 ($CDCl_3$)



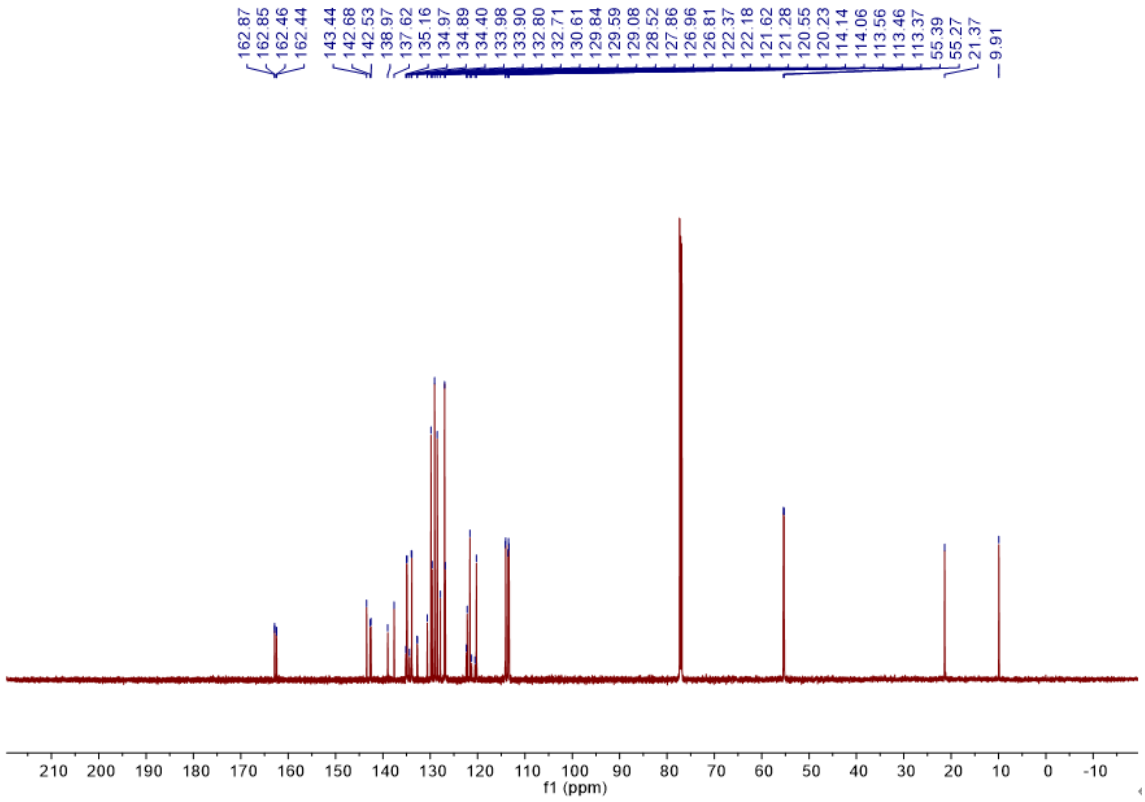

## $^{13}$C NMR of 31 ($CDCl_3$)



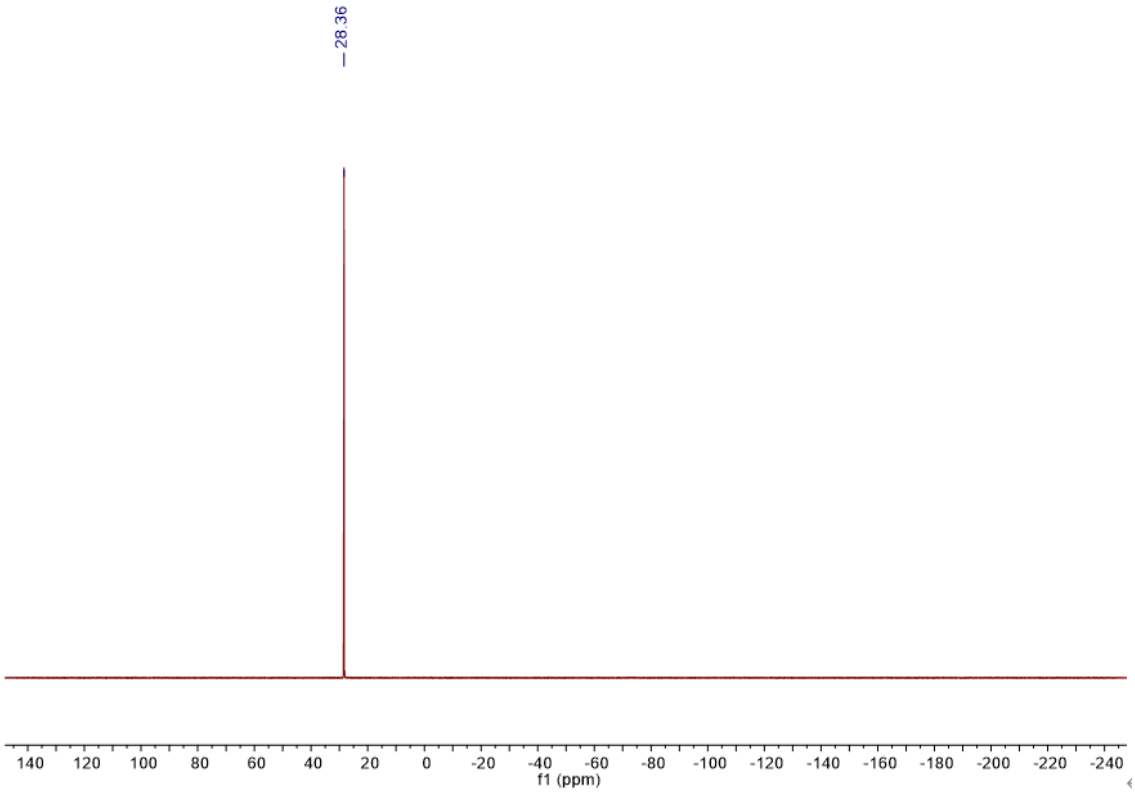
## $^{31}P$ NMR of 31 ($CDCl_3$)



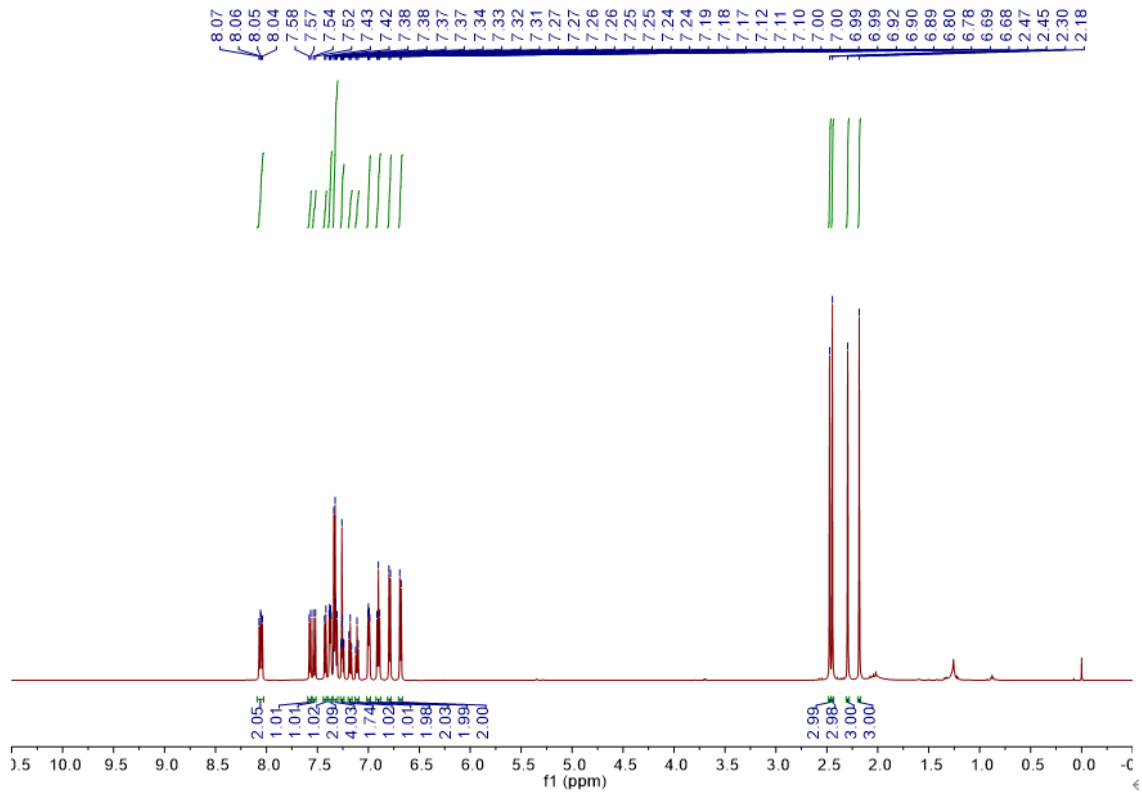

## $^{1}H$ NMR of 32 ($CDCl_3$)



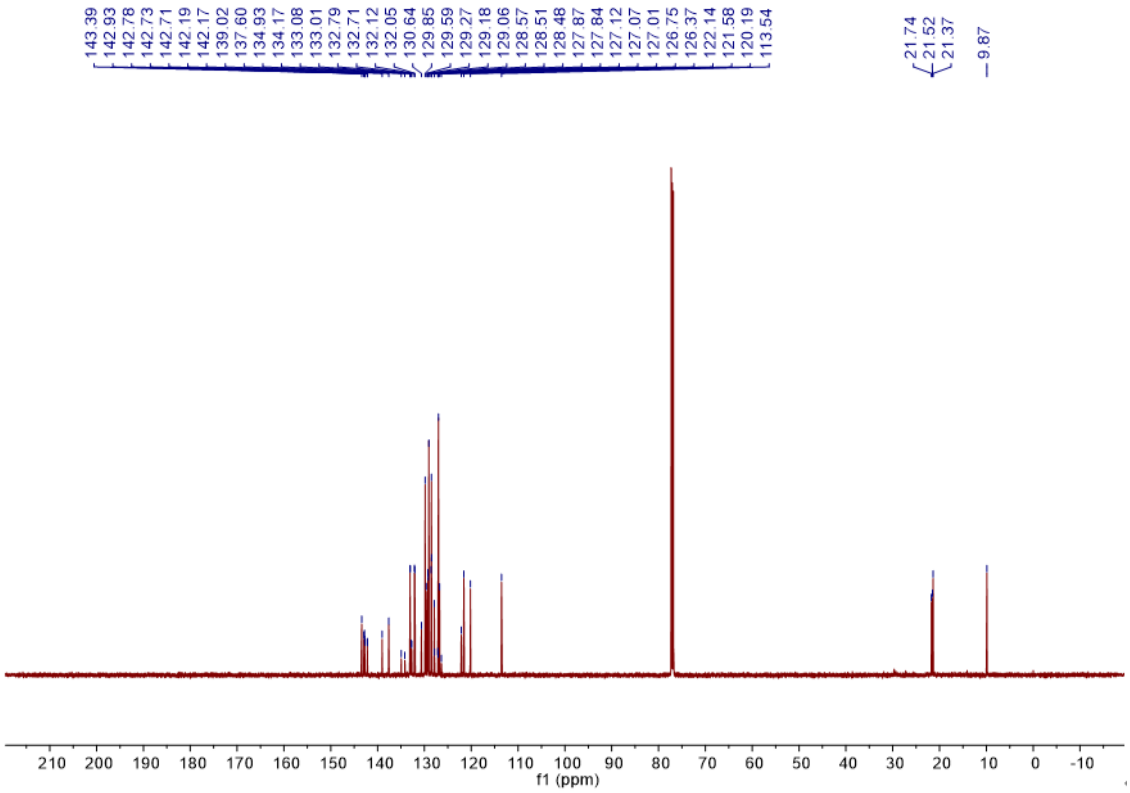
## $^{13}C$ NMR of 32 ($CDCl_3$)



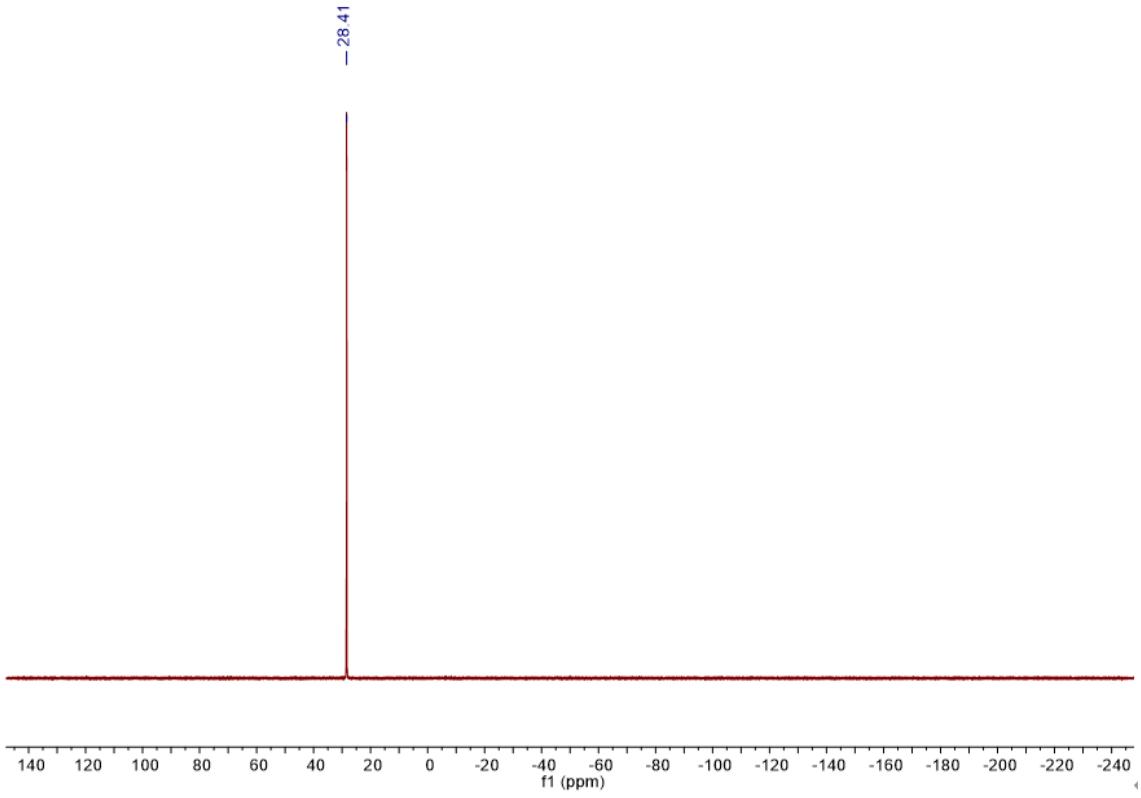

## $^{31}P$ NMR of 32 ($CDCl_3$)



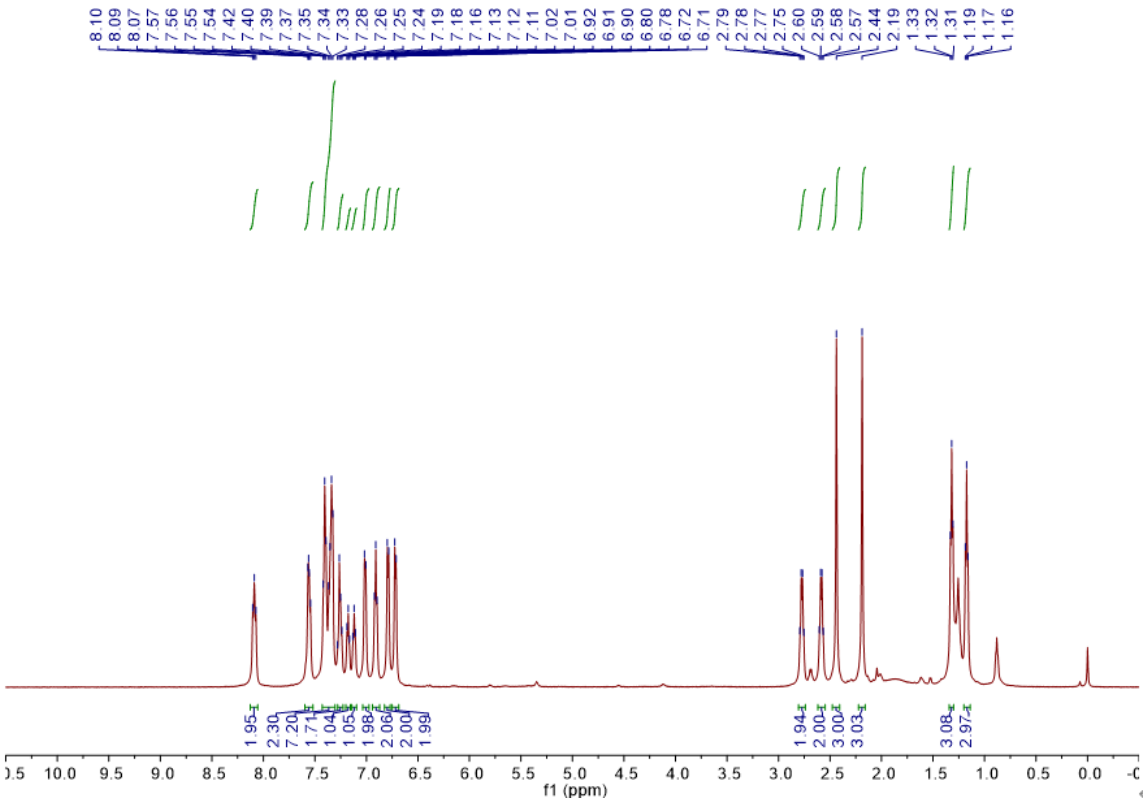
## $^{1}$H NMR of 33 ($CDCl_3$)



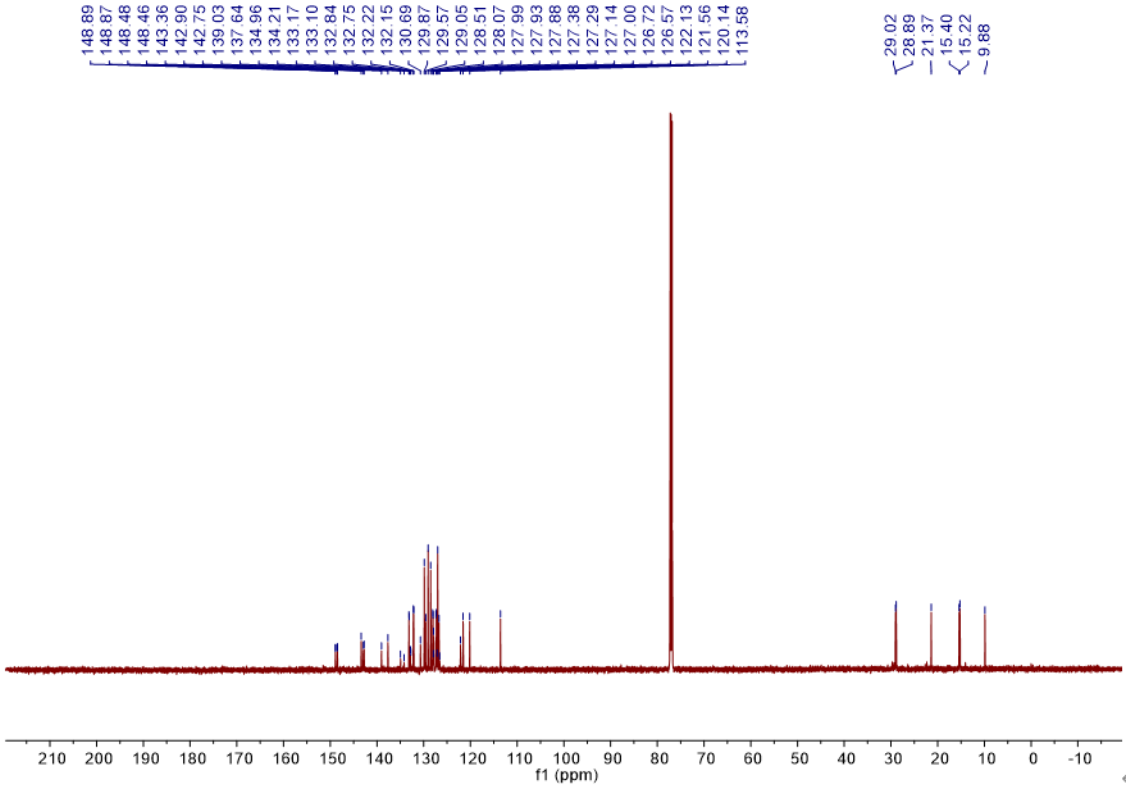

## $^{13}$C NMR of 33 ($CDCl_3$)



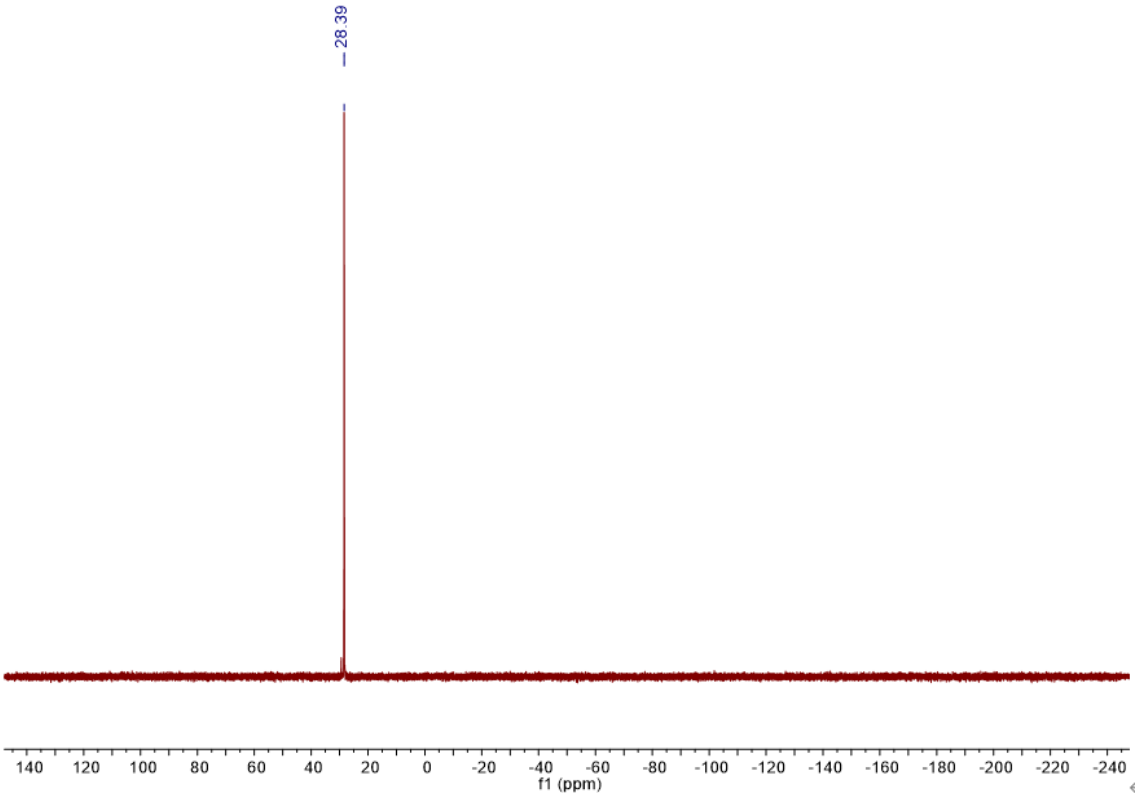
## $^{31}P$ NMR of 33 ($CDCl_3$)



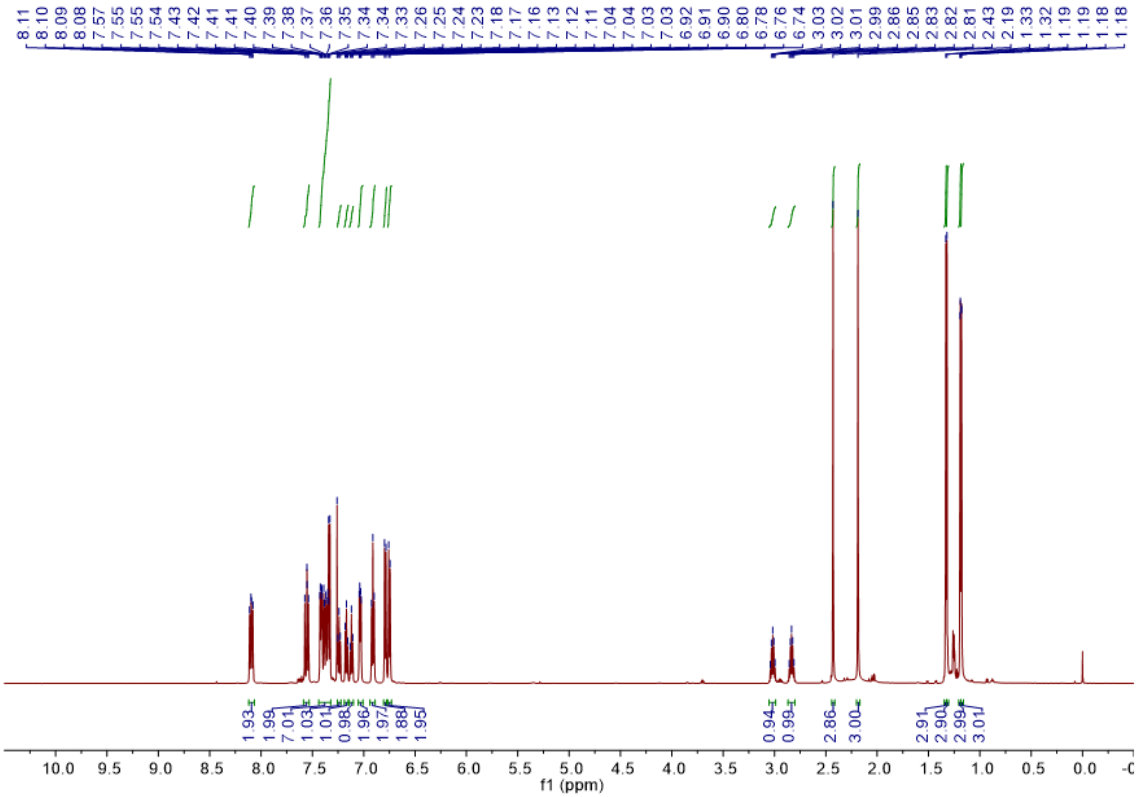

## $^{1}H$ NMR of 34 ($CDCl_3$)



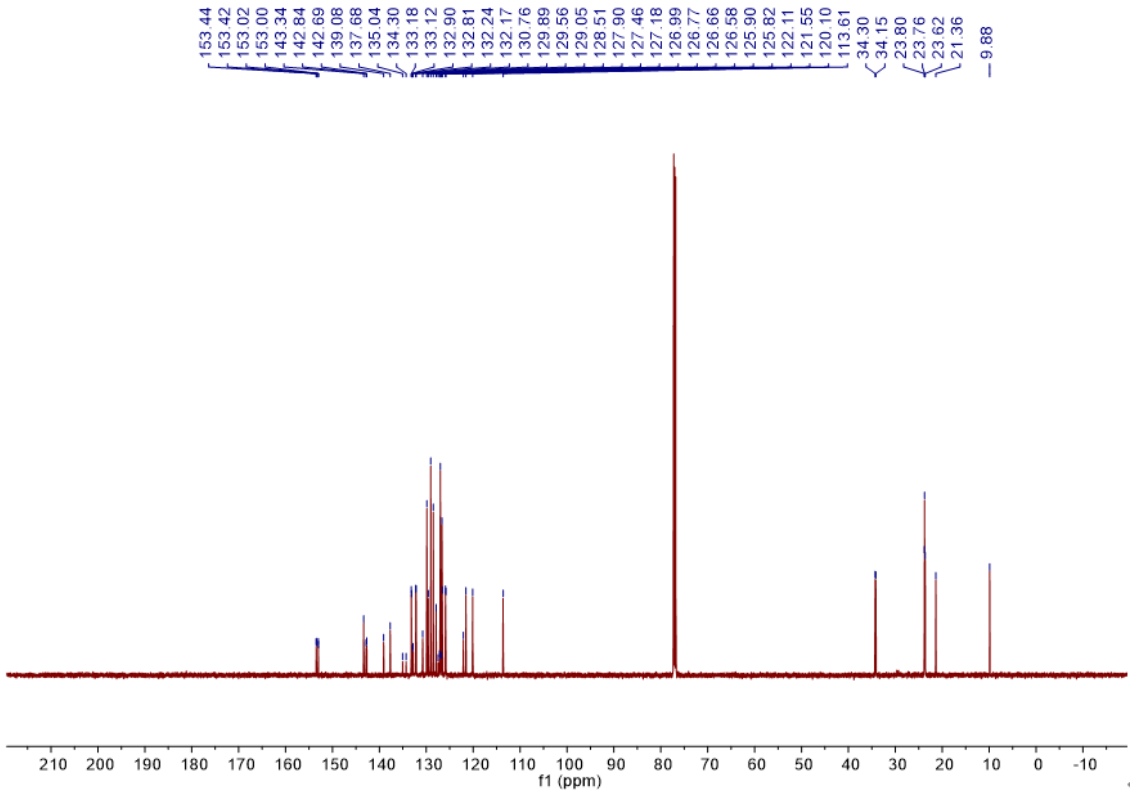
## $^{13}C$ NMR of 34 ($CDCl_3$)



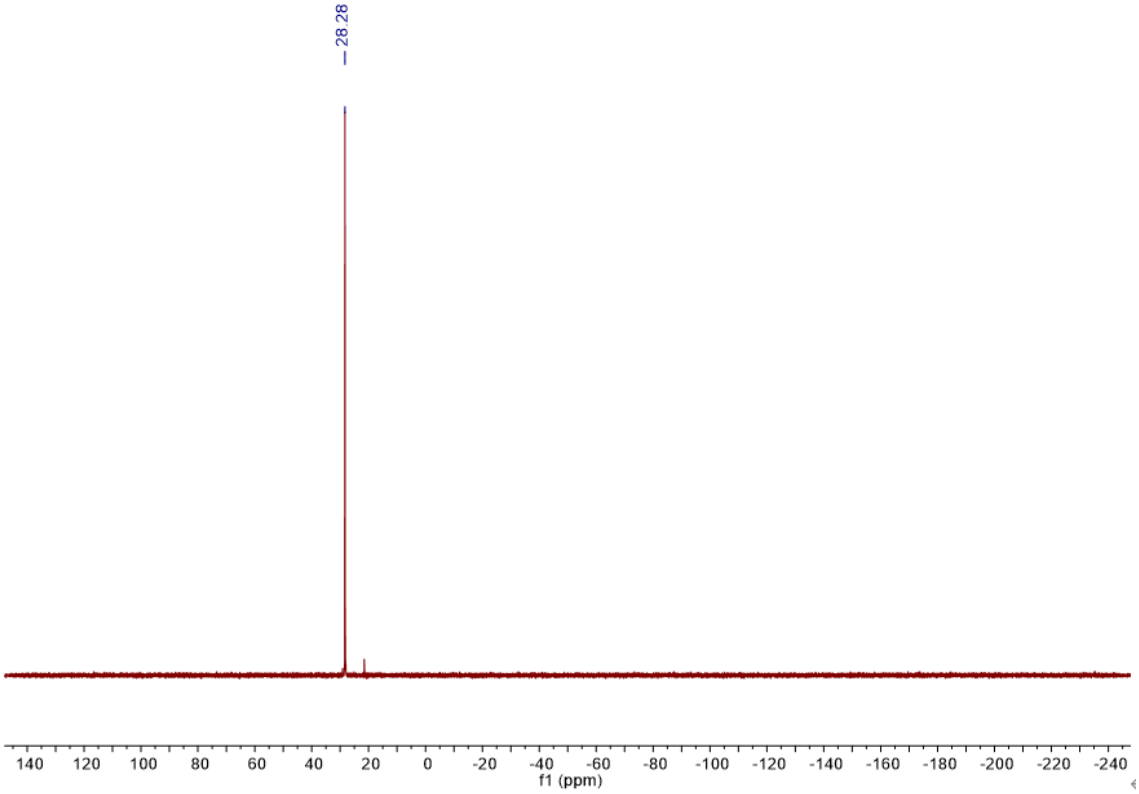

## $^{31}P$ NMR of 34 ($CDCl_3$)



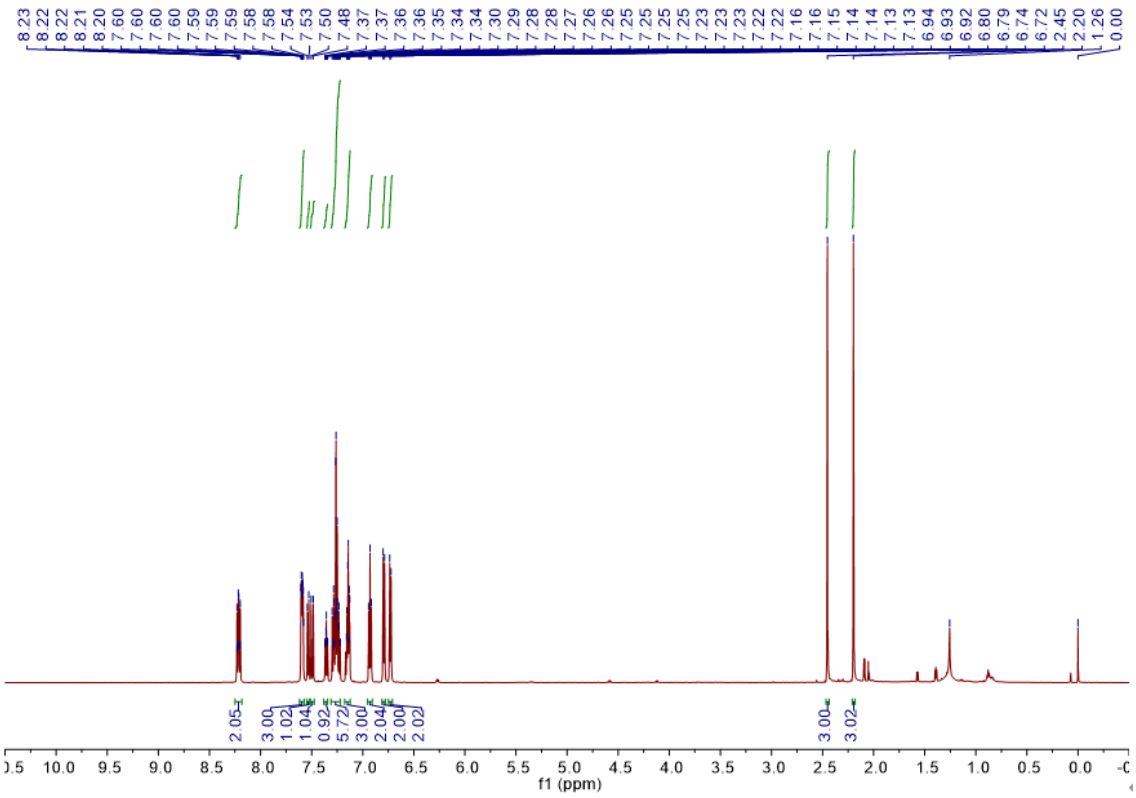
## $^{1}$H NMR of 35 ($CDCl_3$)



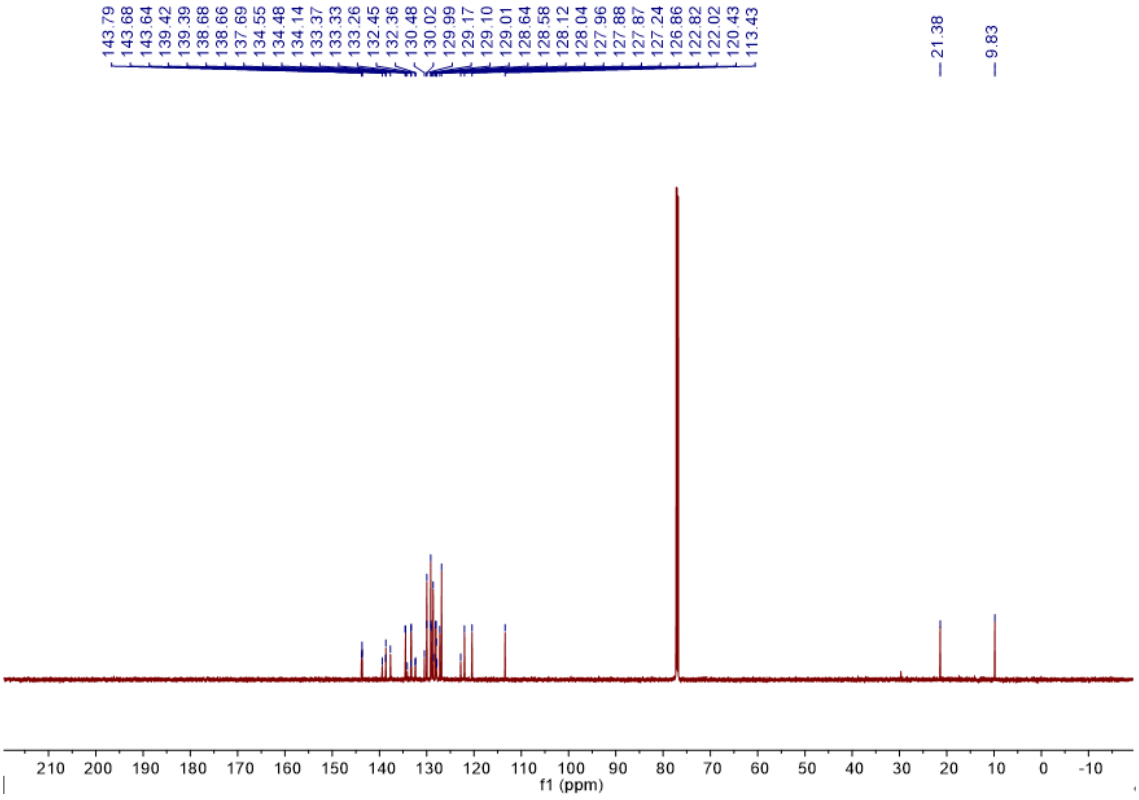

## $^{13}$C NMR of 35 ($CDCl_3$)



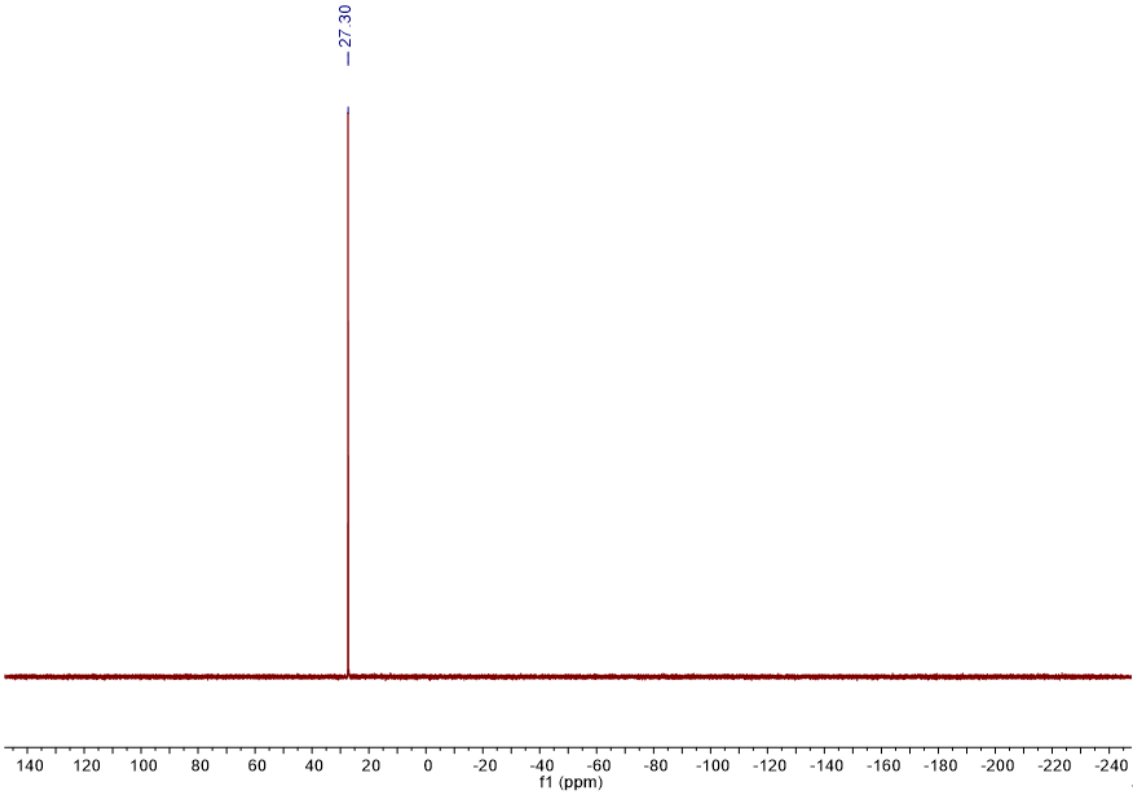
## $^{31}P$ NMR of 35 ($CDCl_3$)



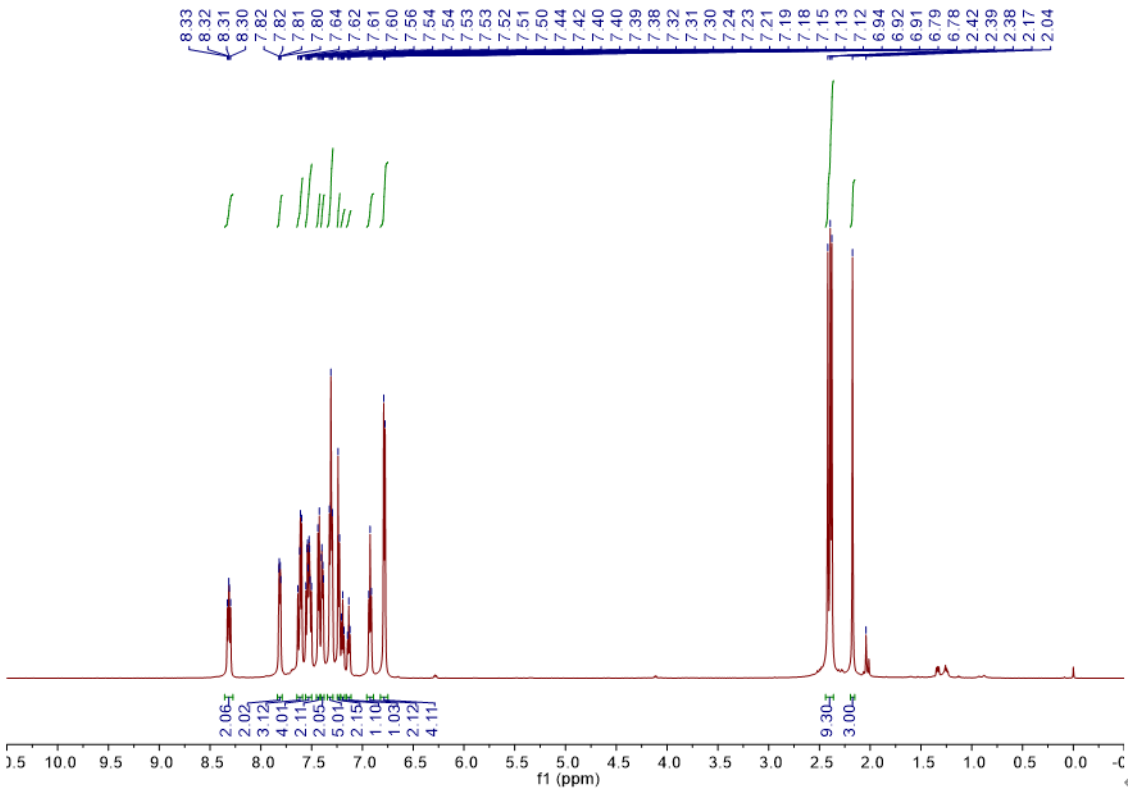

## $^{1}H$ NMR of 36 ($CDCl_3$)



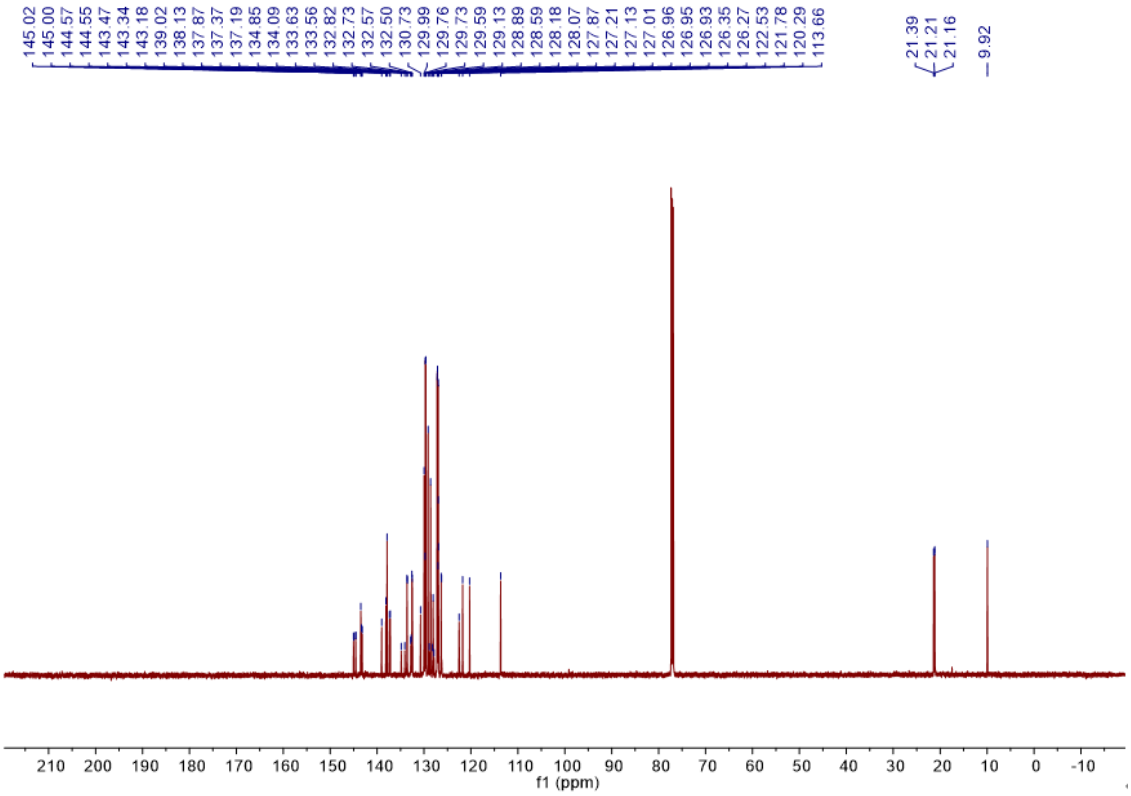
## $^{13}C$ NMR of 36 ($CDCl_3$)



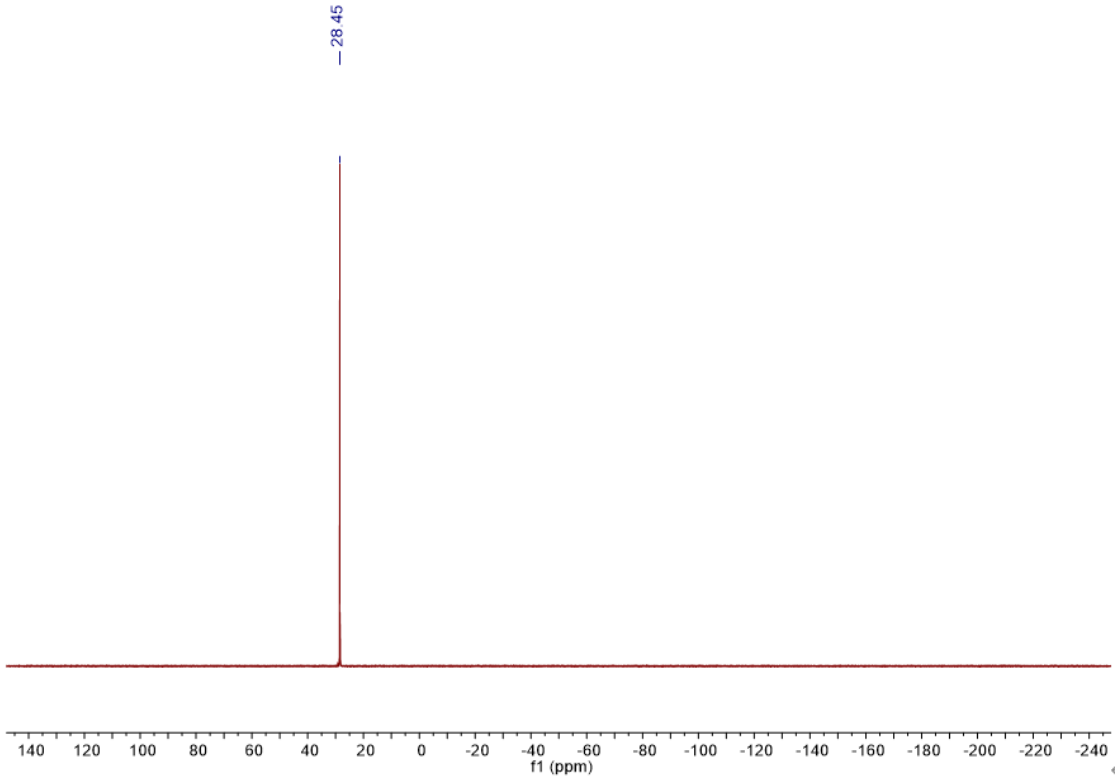

## $^{31}P$ NMR of 36 ($CDCl_3$)



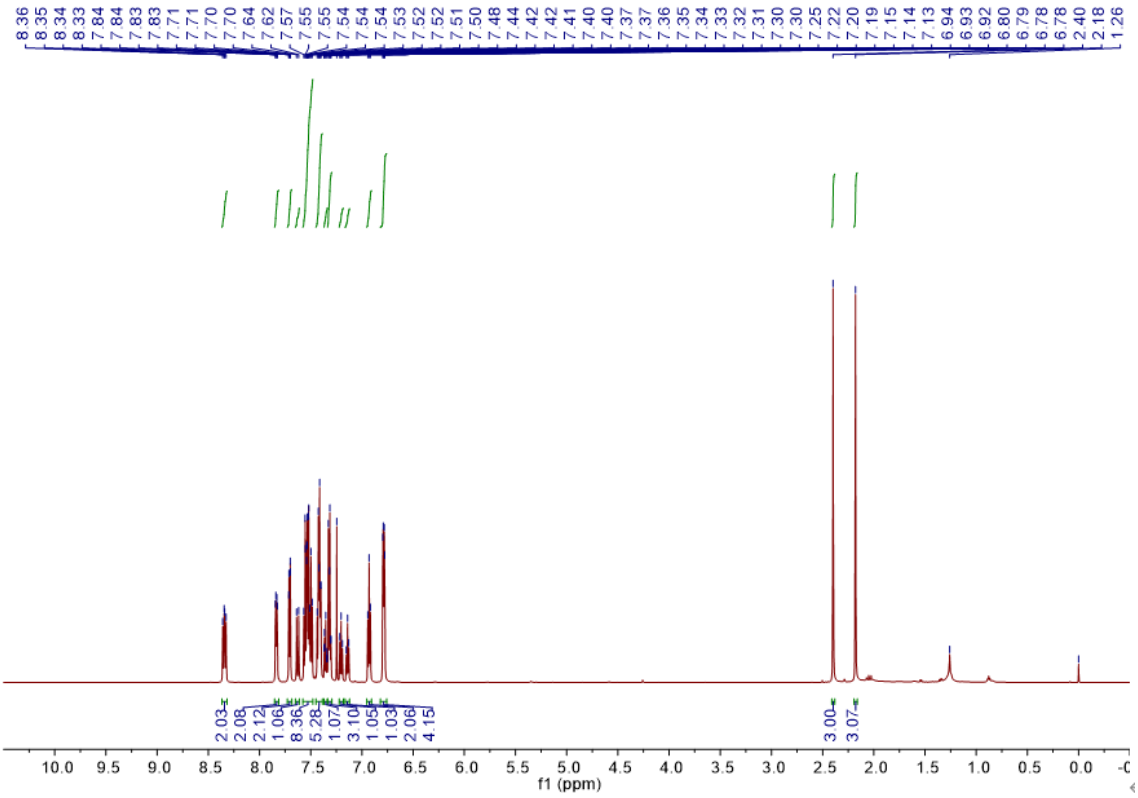
## $^{1}$H NMR of 37 ($CDCl_3$)



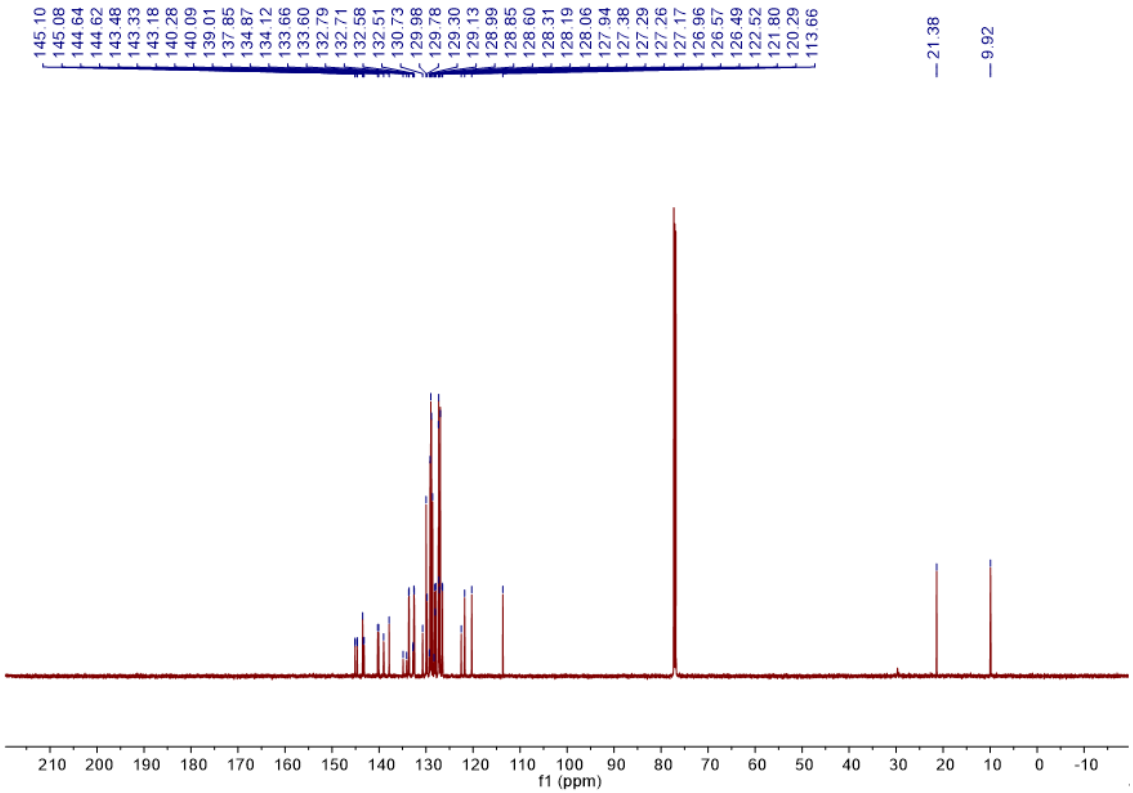

## $^{13}$C NMR of 37 ($CDCl_3$)



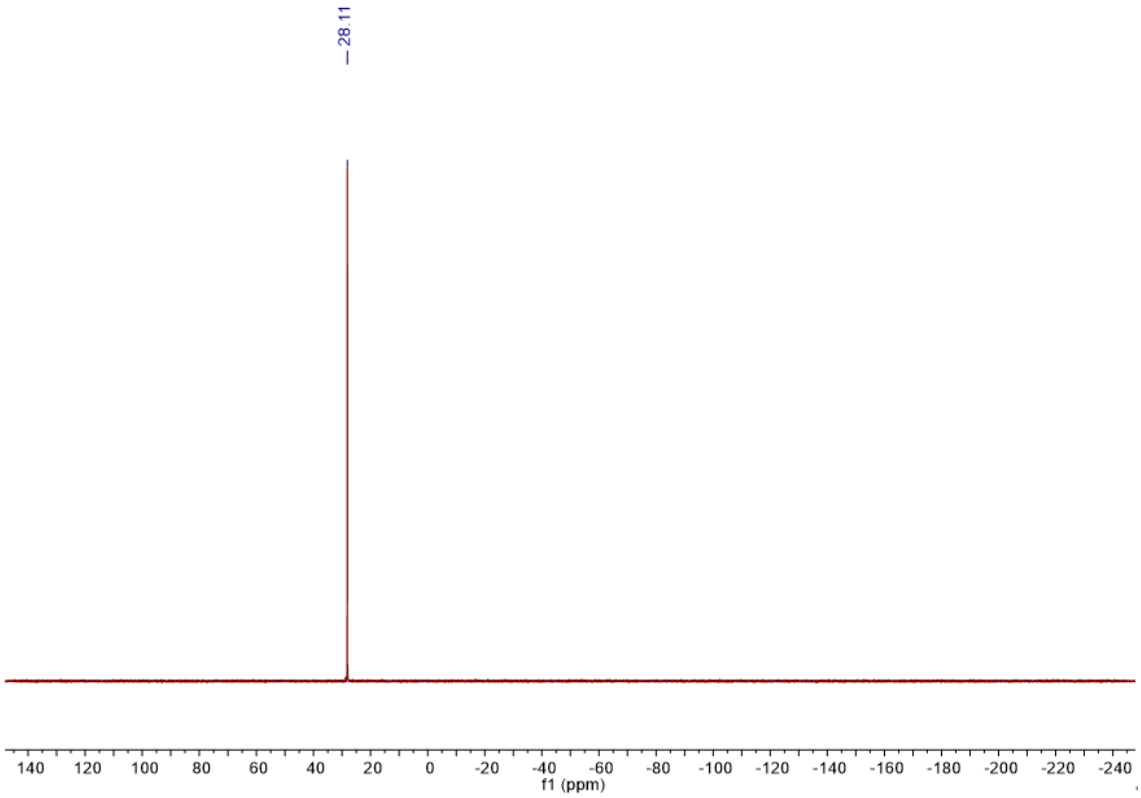
## $^{31}$P NMR of 37 ($CDCl_3$)



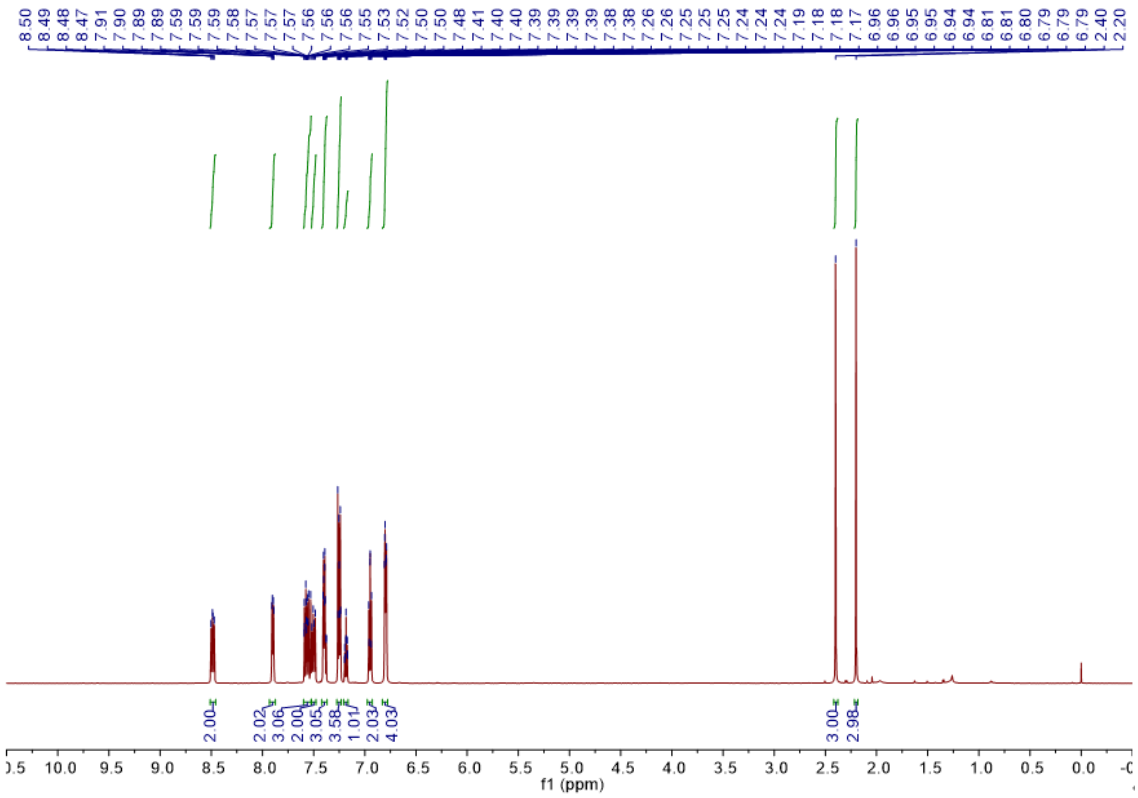
## $^{1}$H NMR of 38 ($CDCl_3$)



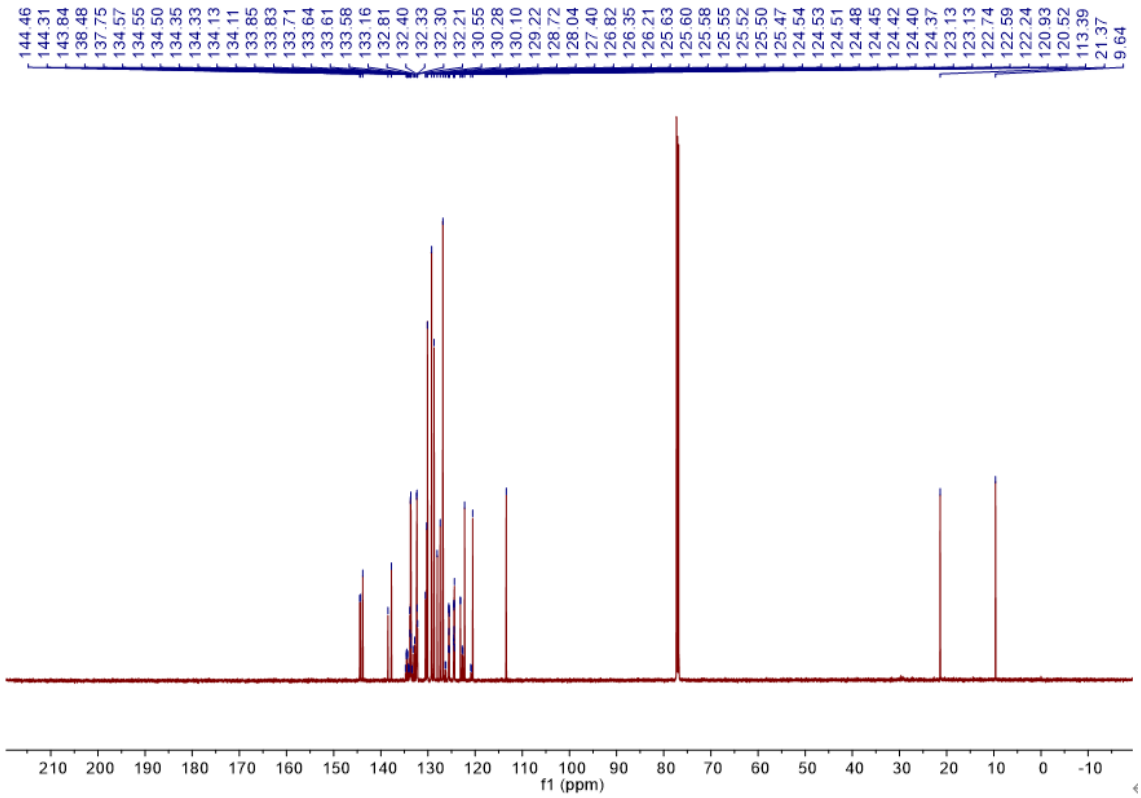
## $^{13}C$ NMR of 38 ($CDCl_3$)



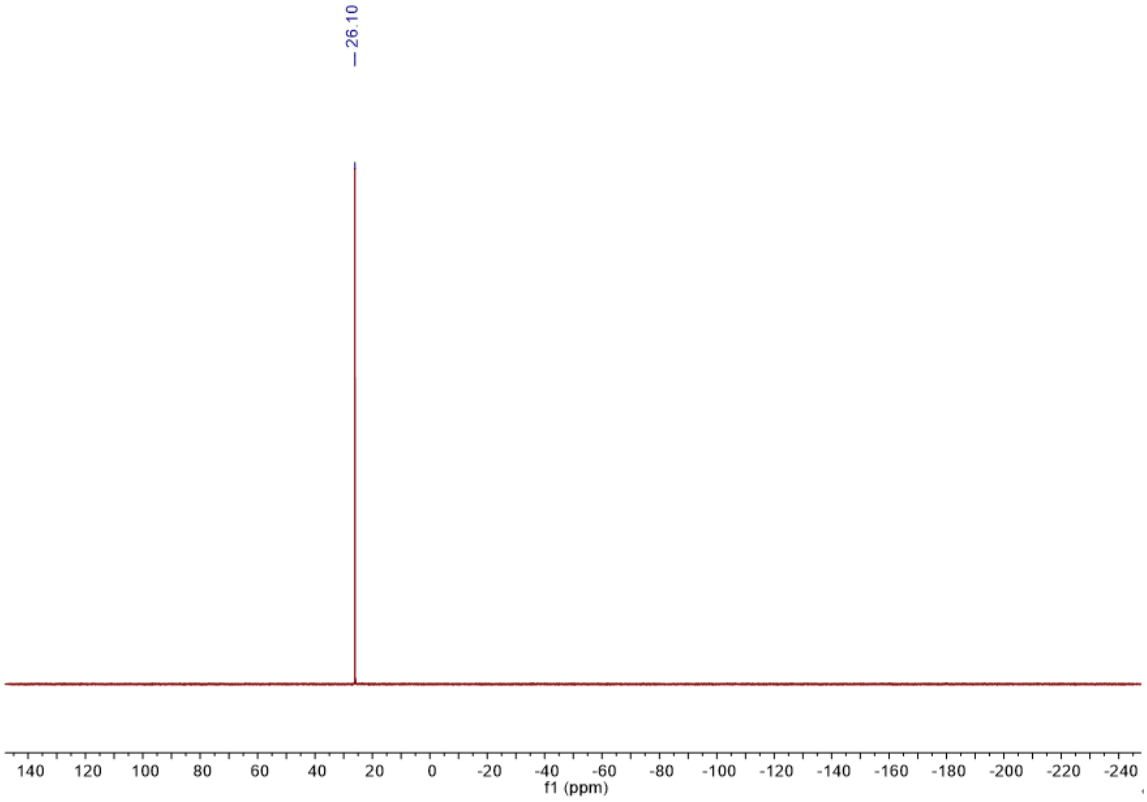

## $^{31}P$ NMR of 38 ($CDCl_3$)



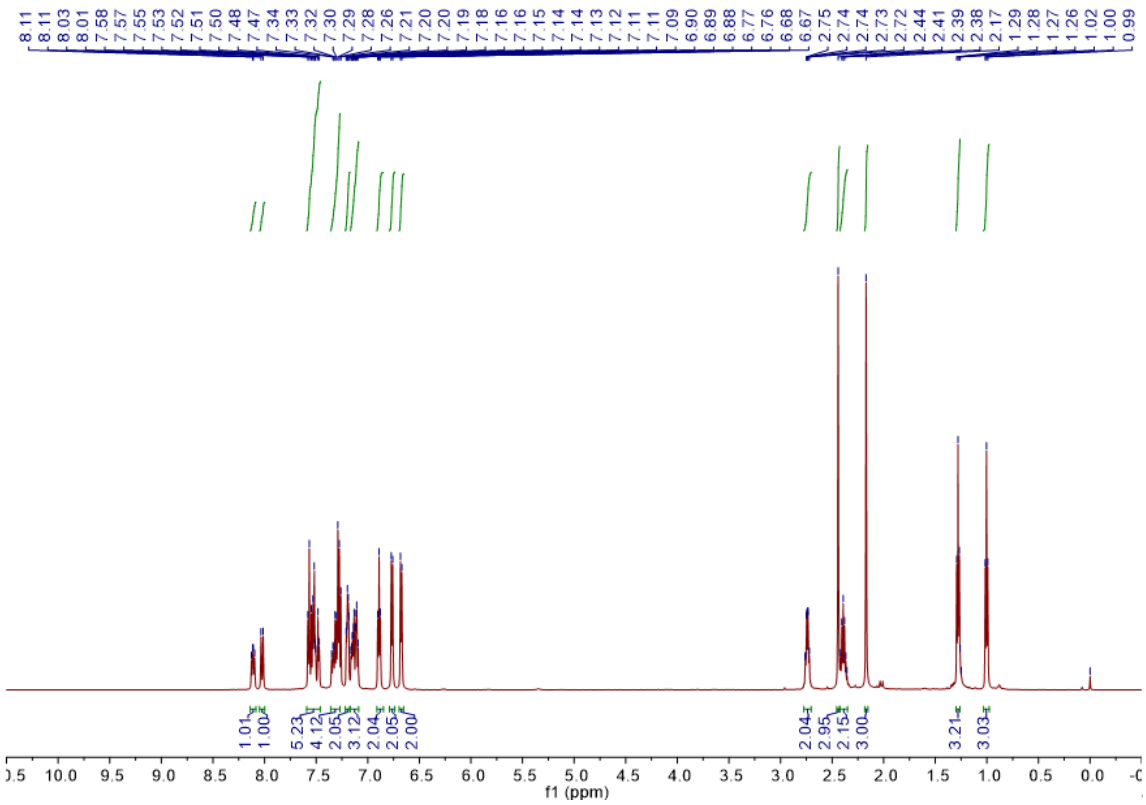
## $^{1}$H NMR of 39 ($CDCl_3$)



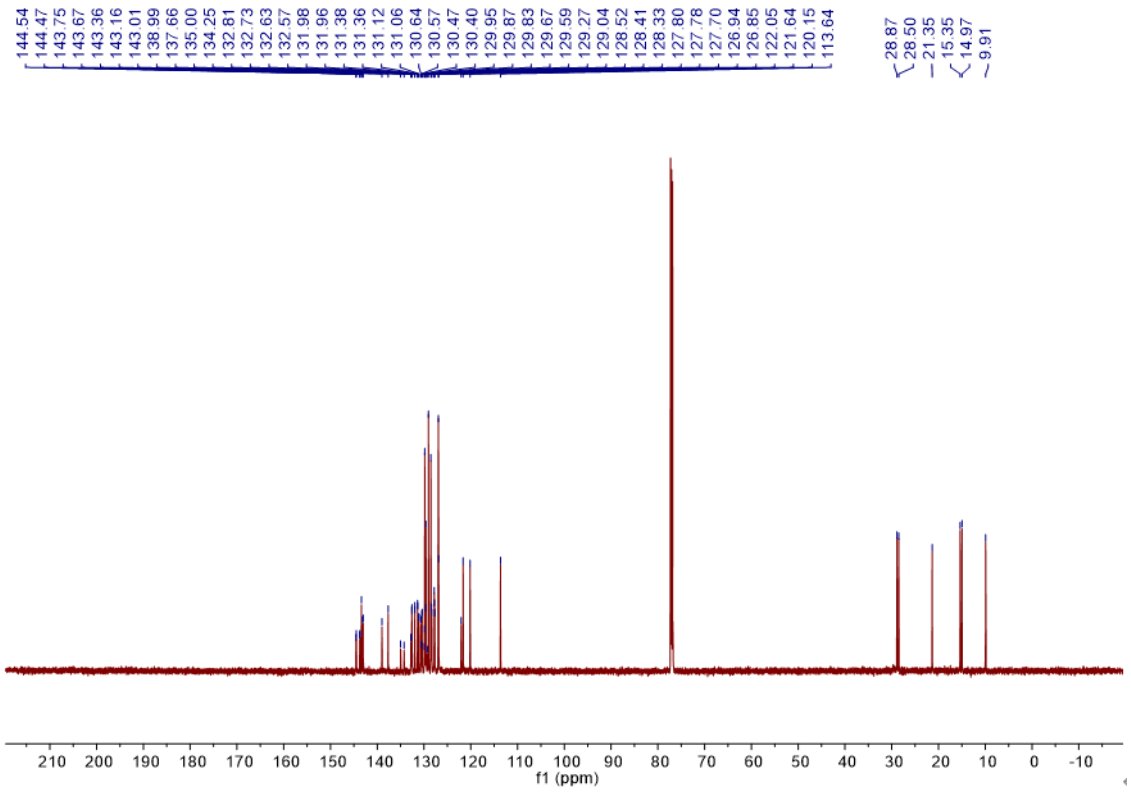

## $^{13}$C NMR of 39 ($CDCl_3$)



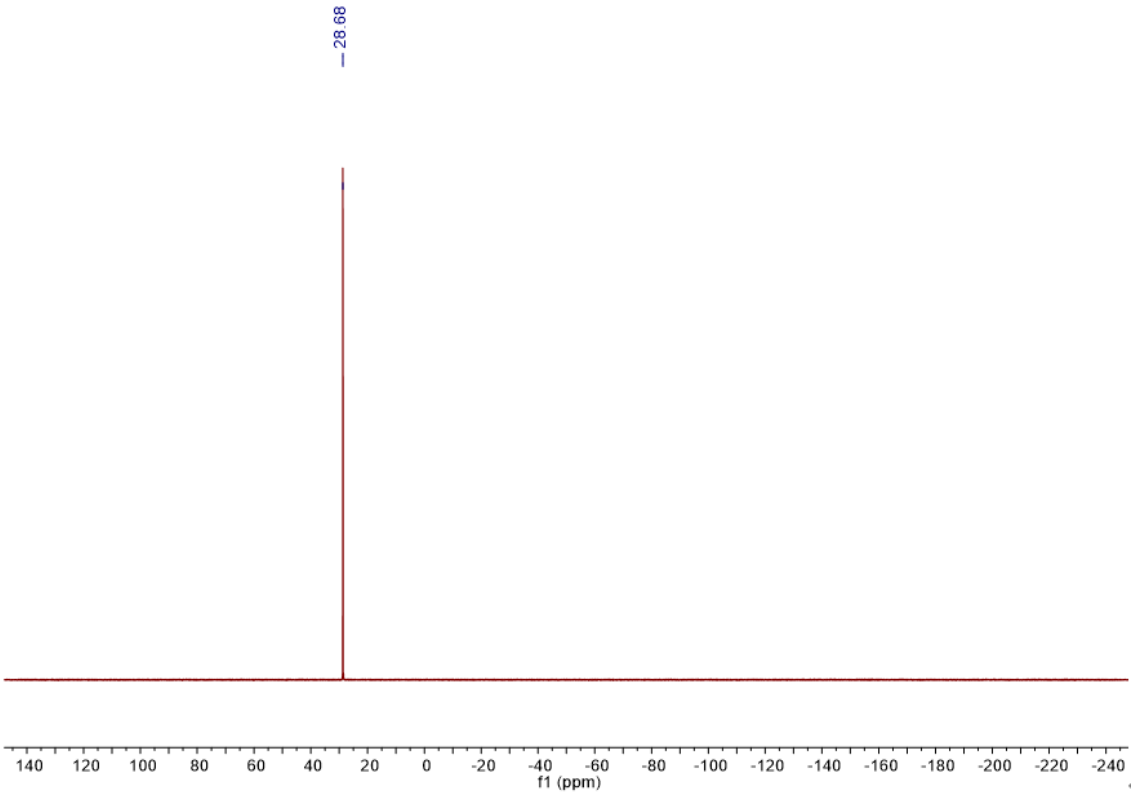
## $^{31}P$ NMR of 39 ($CDCl_3$)



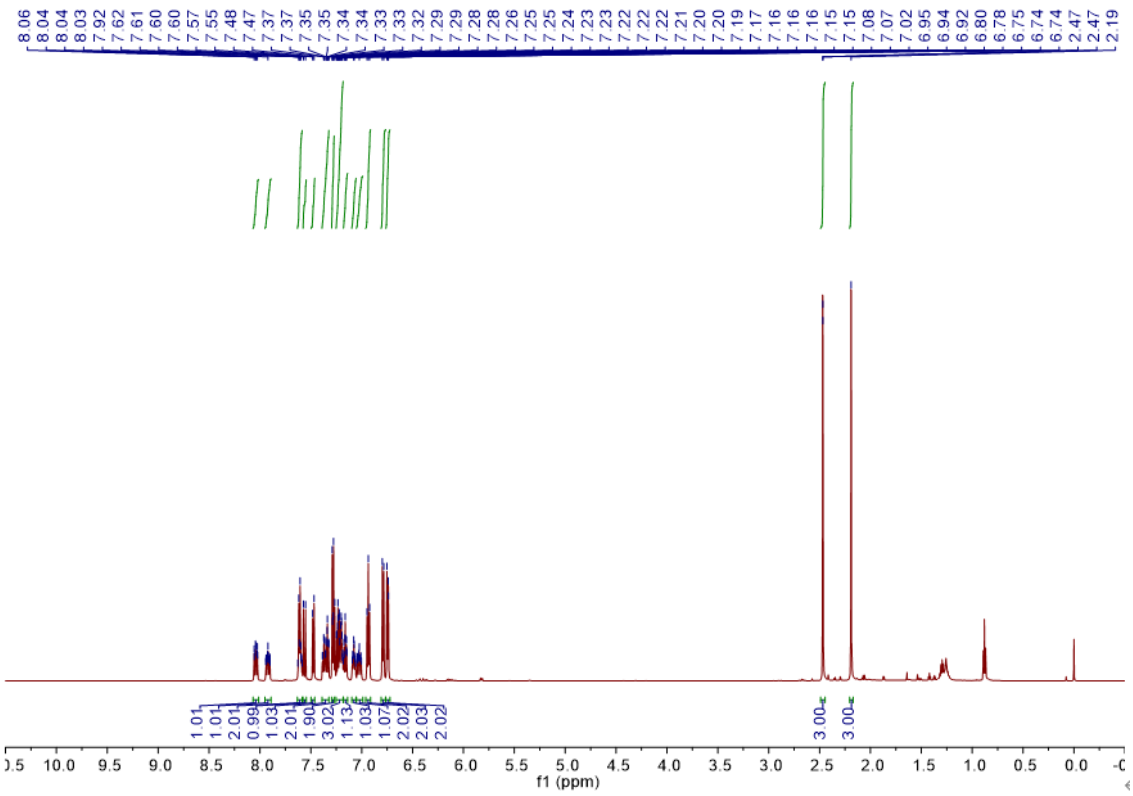

## $^{1}H$ NMR of 40 ($CDCl_3$)



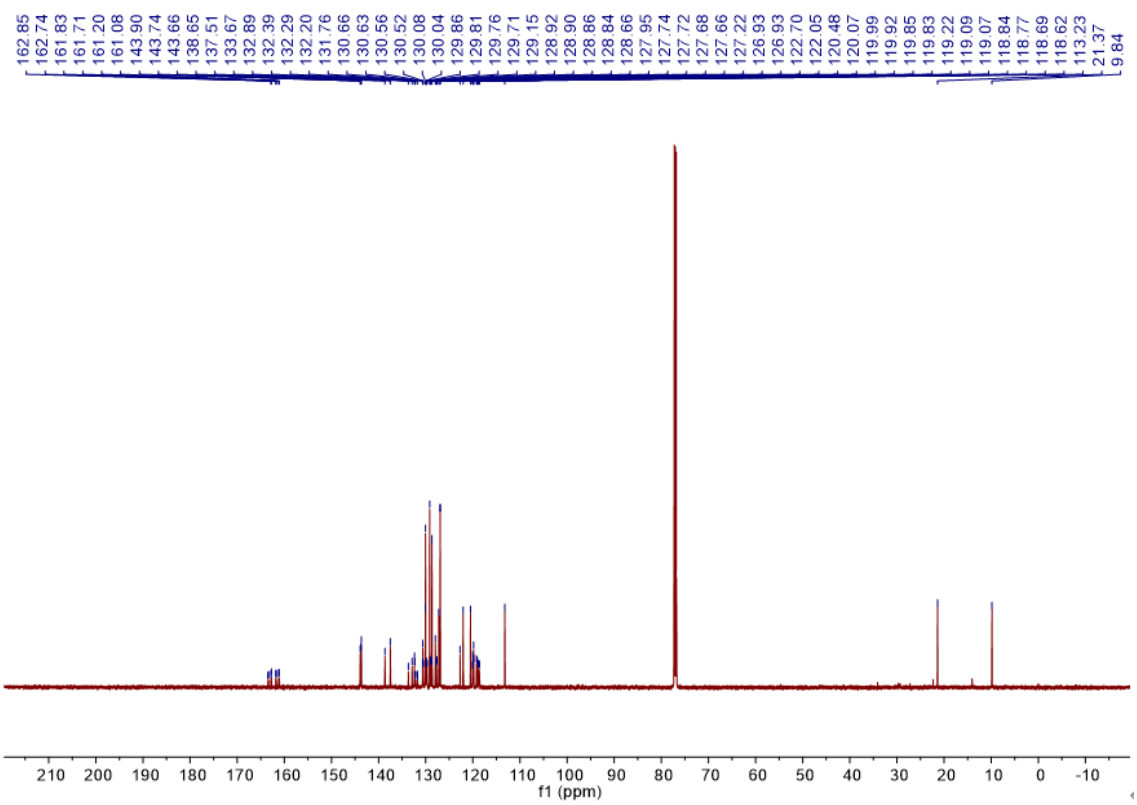
## $^{13}C$ NMR of 40 ($CDCl_3$)



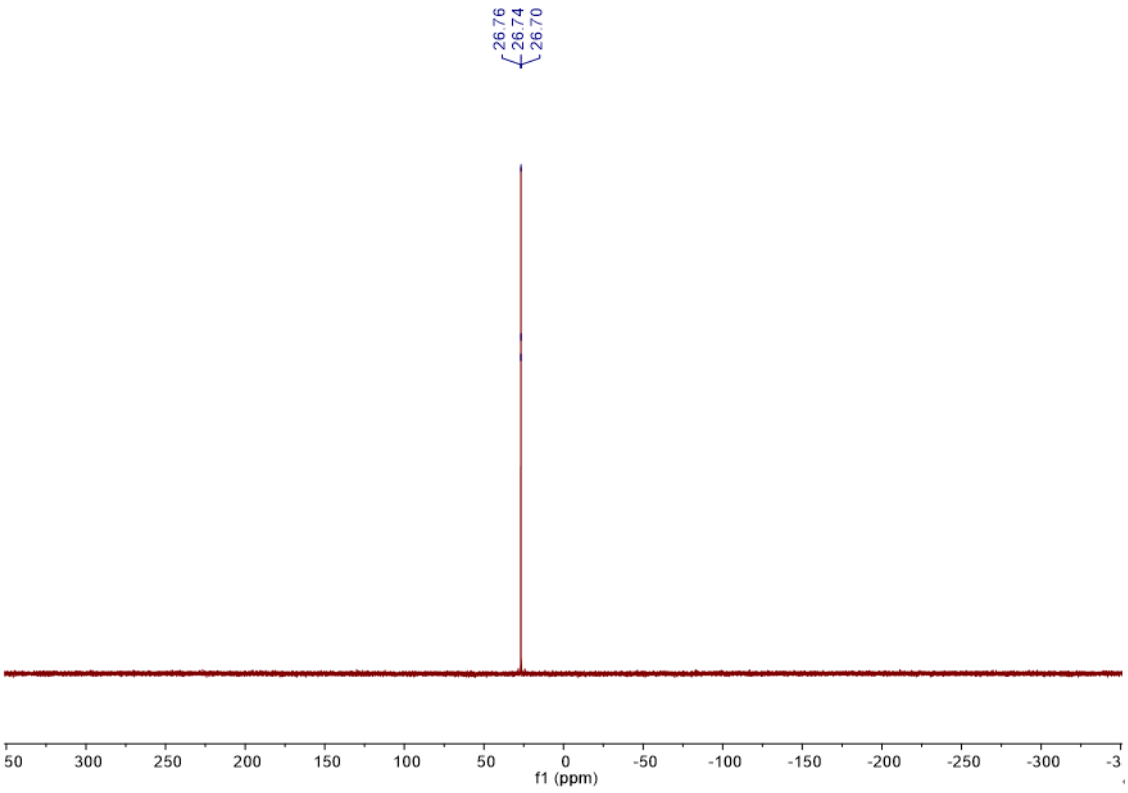

## $^{31}P$ NMR of 40 ($CDCl_3$)



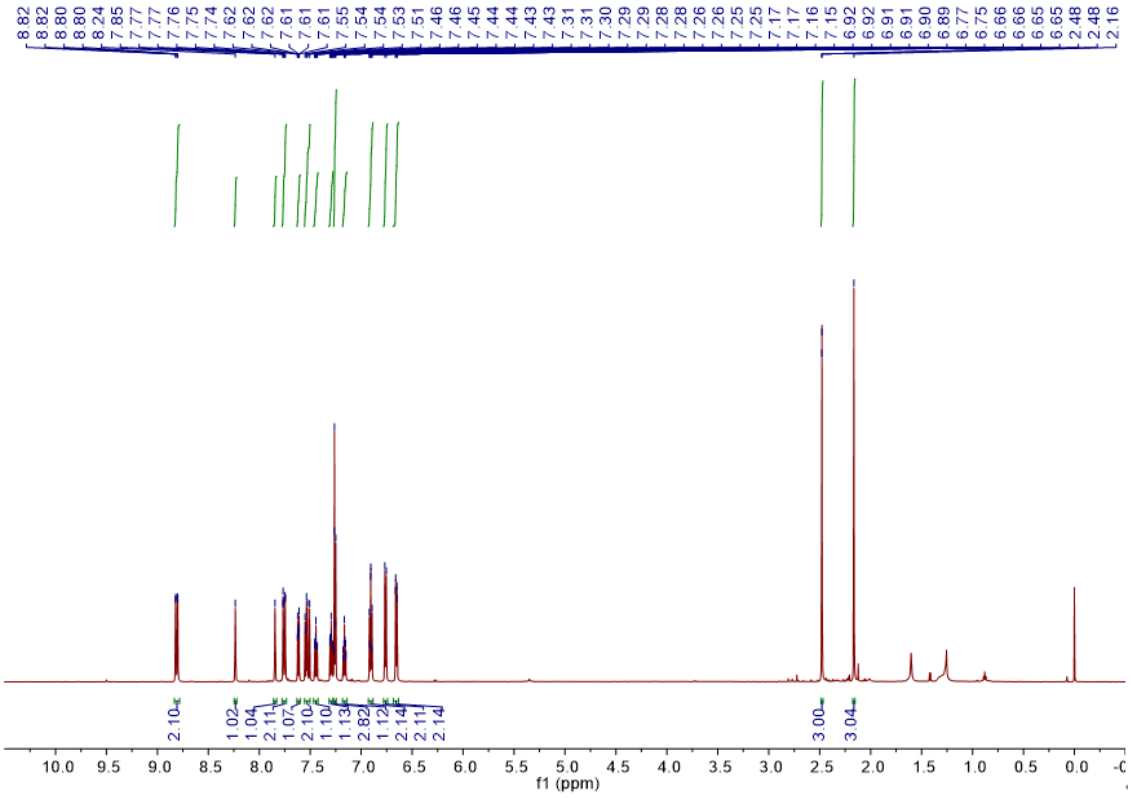
## $^{1}$H NMR of 41 ($CDCl_3$)



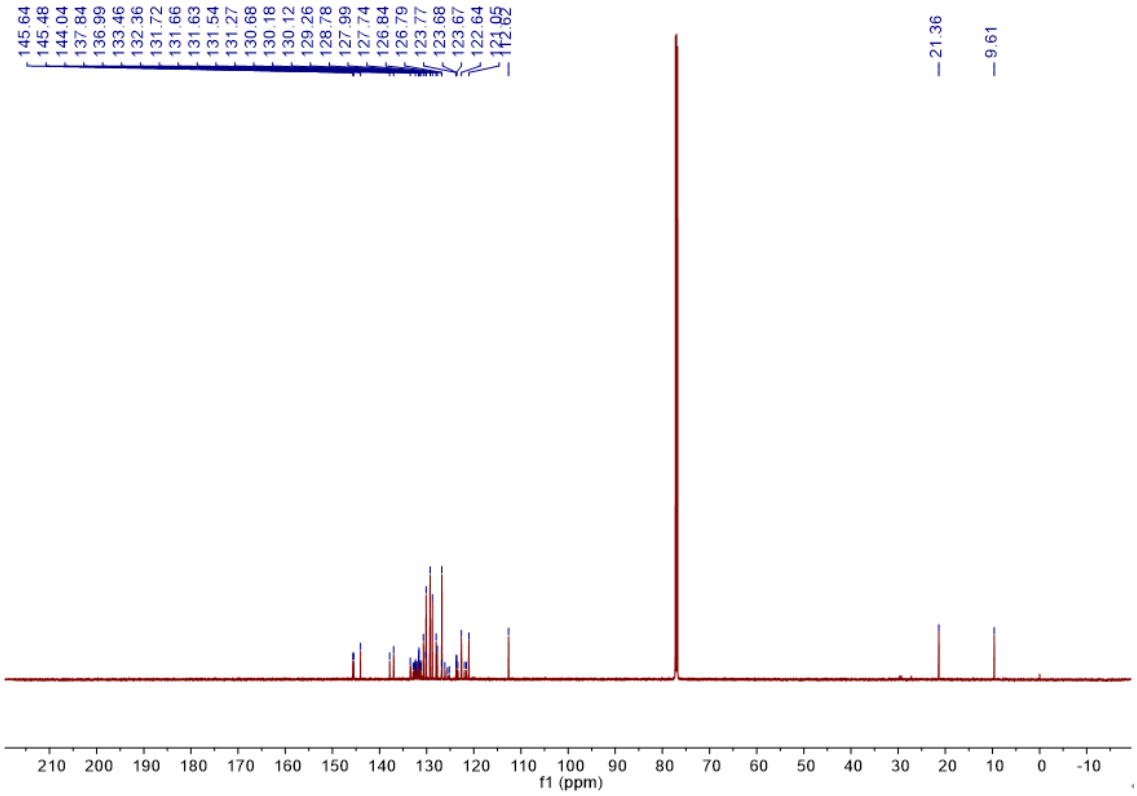

## $^{13}$C NMR of 41 ($CDCl_3$)



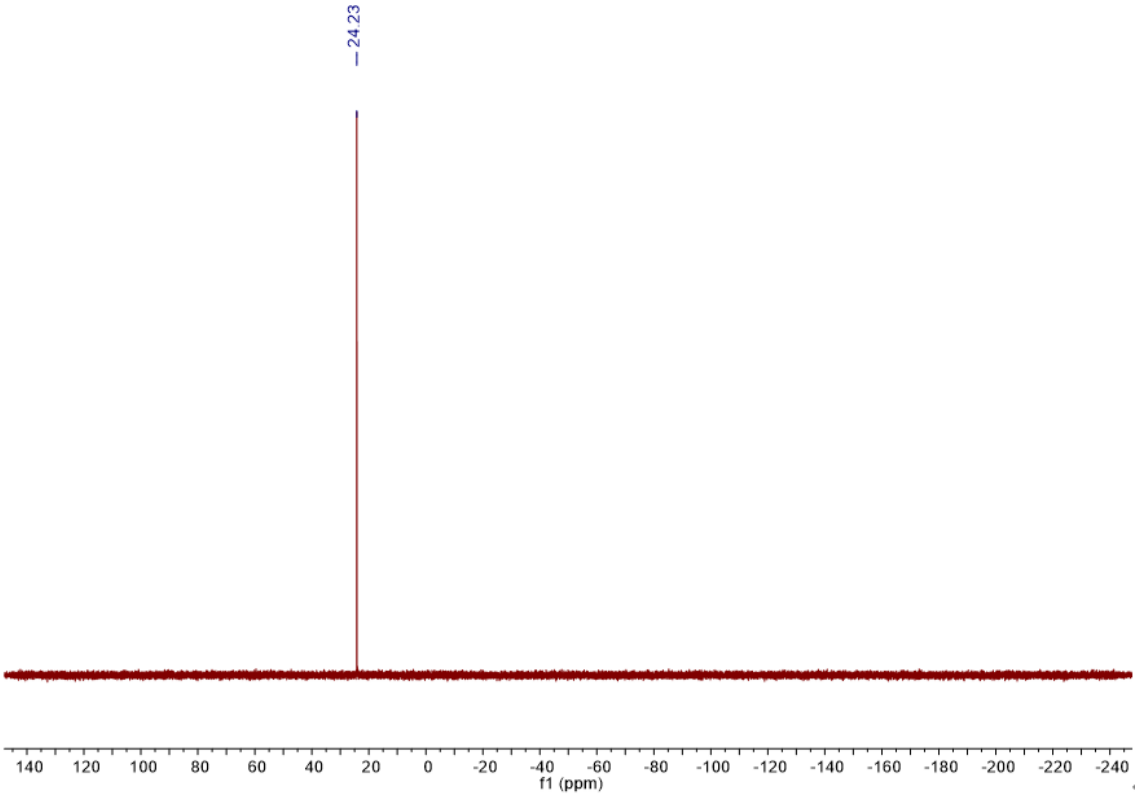
## $^{31}$P NMR of 41 ($CDCl_3$)



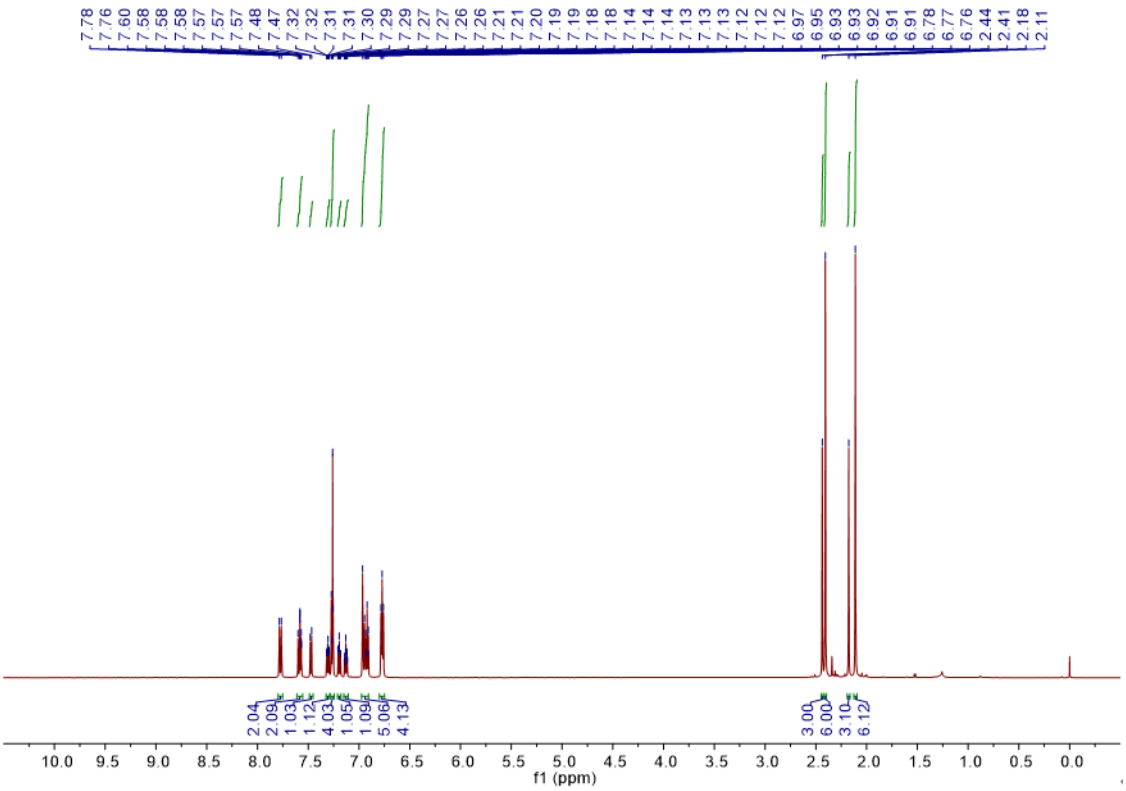
## $^{1}$H NMR of 42 ($CDCl_3$)



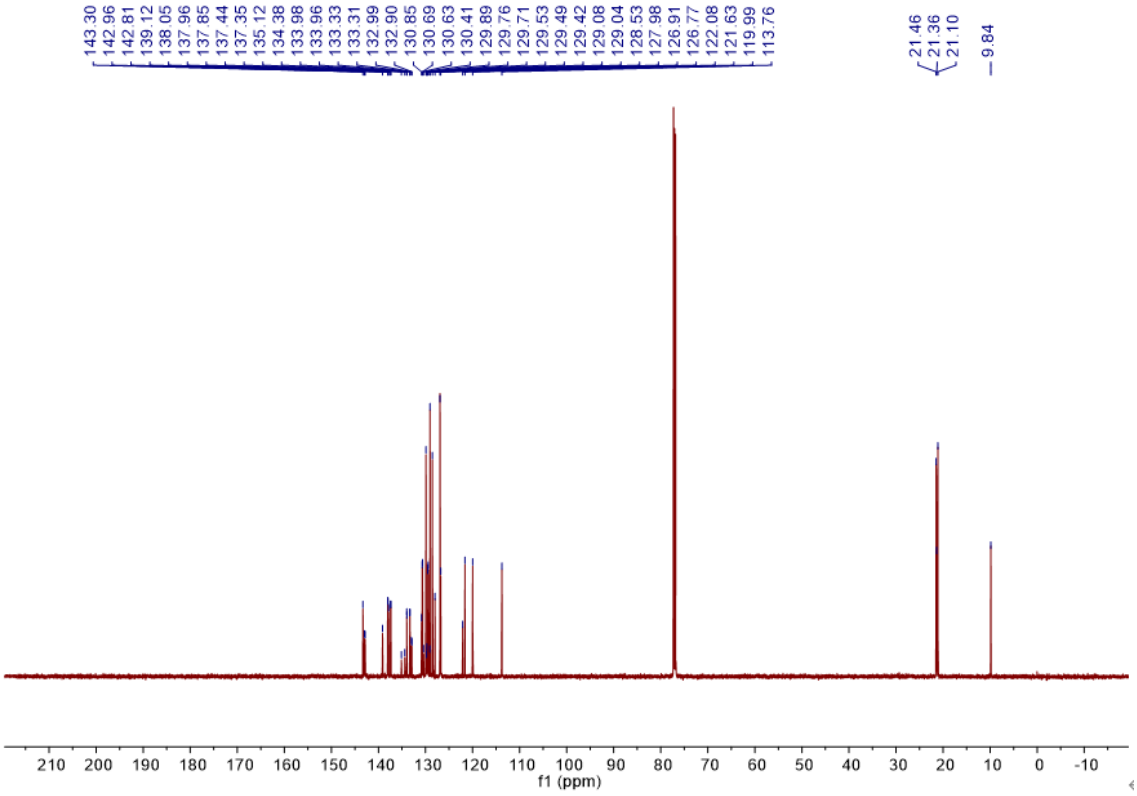
## $^{13}C$ NMR of 42 ($CDCl_3$)



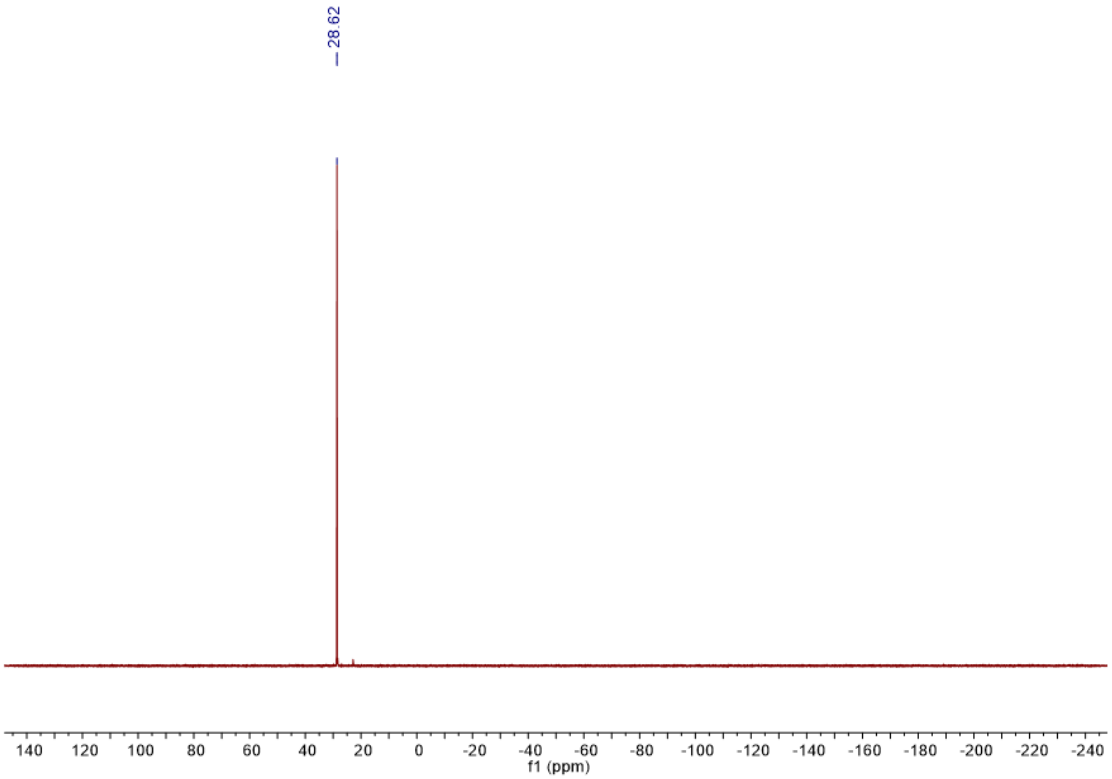

## $^{31}P$ NMR of 42 ($CDCl_3$)



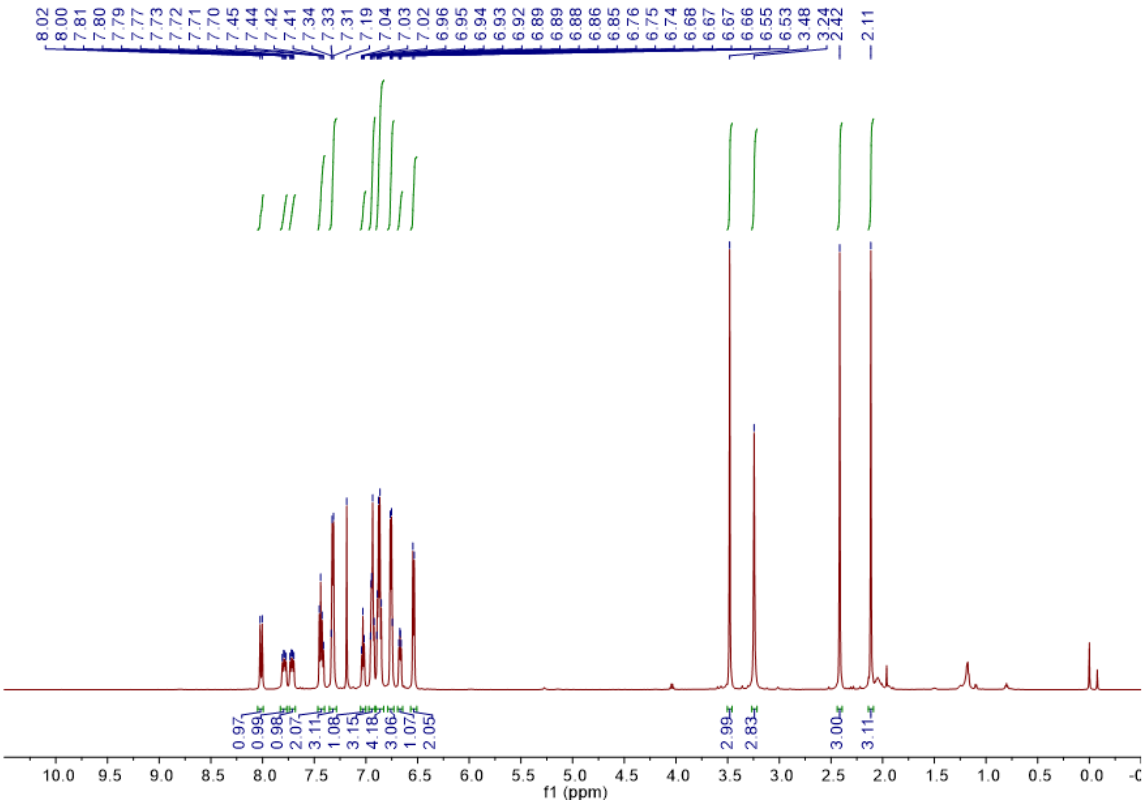
## $^{1}$H NMR of 43 ($CDCl_3$)




## $^{13}$C NMR of 43 ($CDCl_3$)



## $^{31}$P NMR of 43 ($CDCl_3$)

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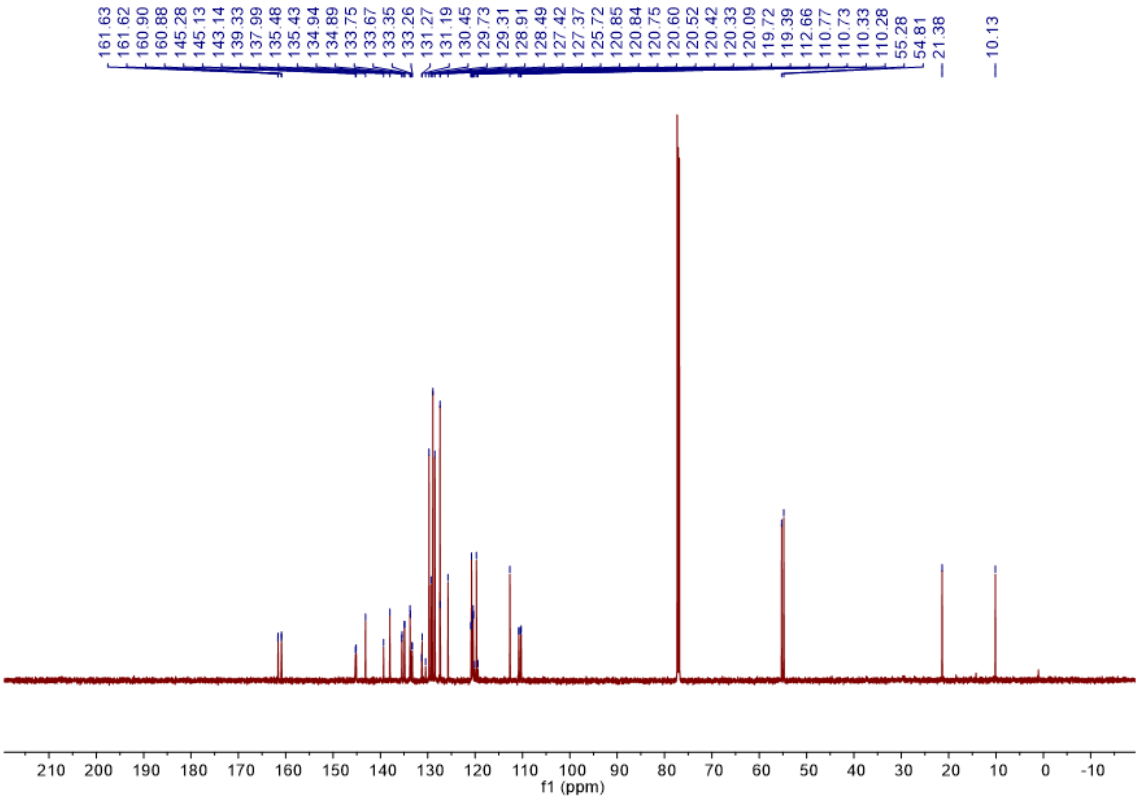
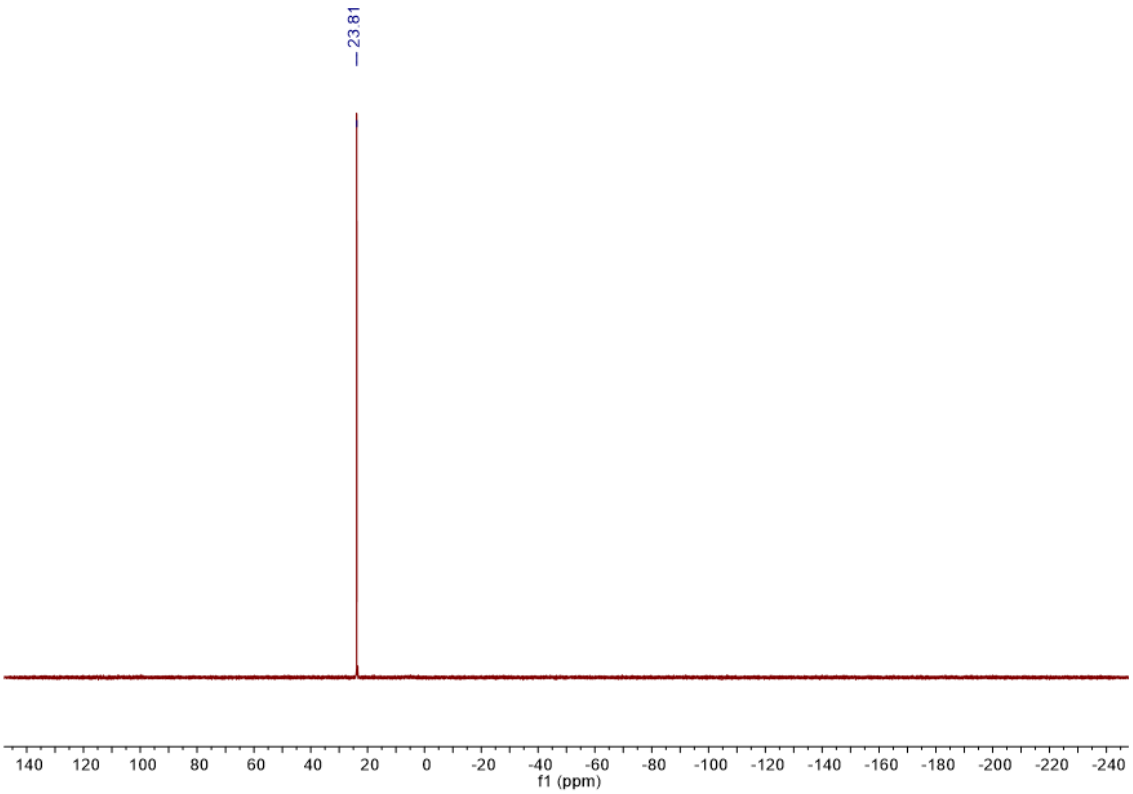
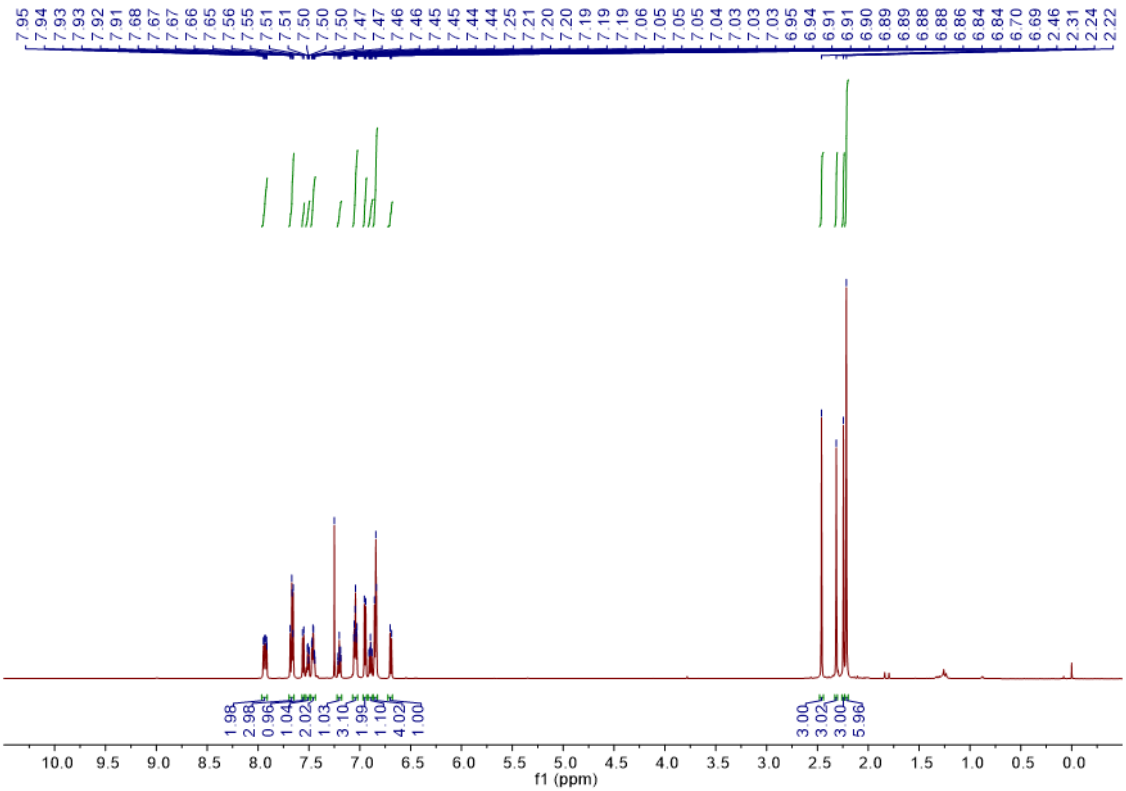


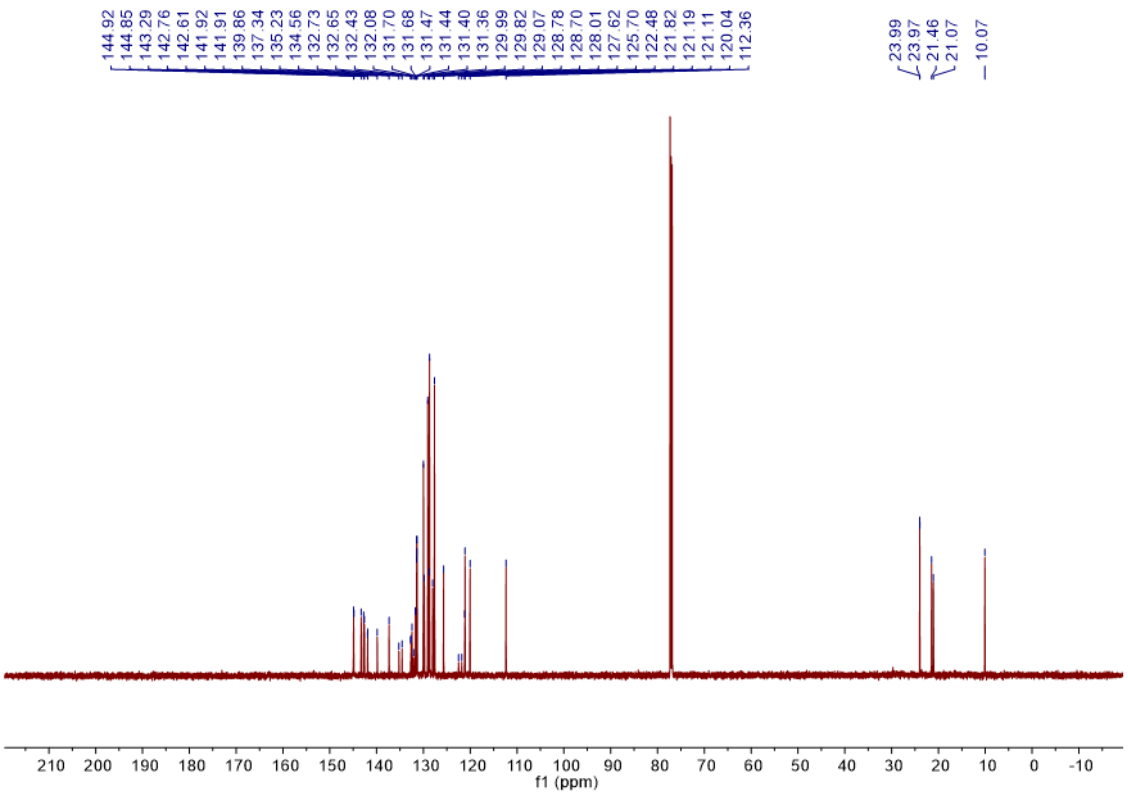
## $^{13}C$ NMR of 44 ($CDCl_3$)



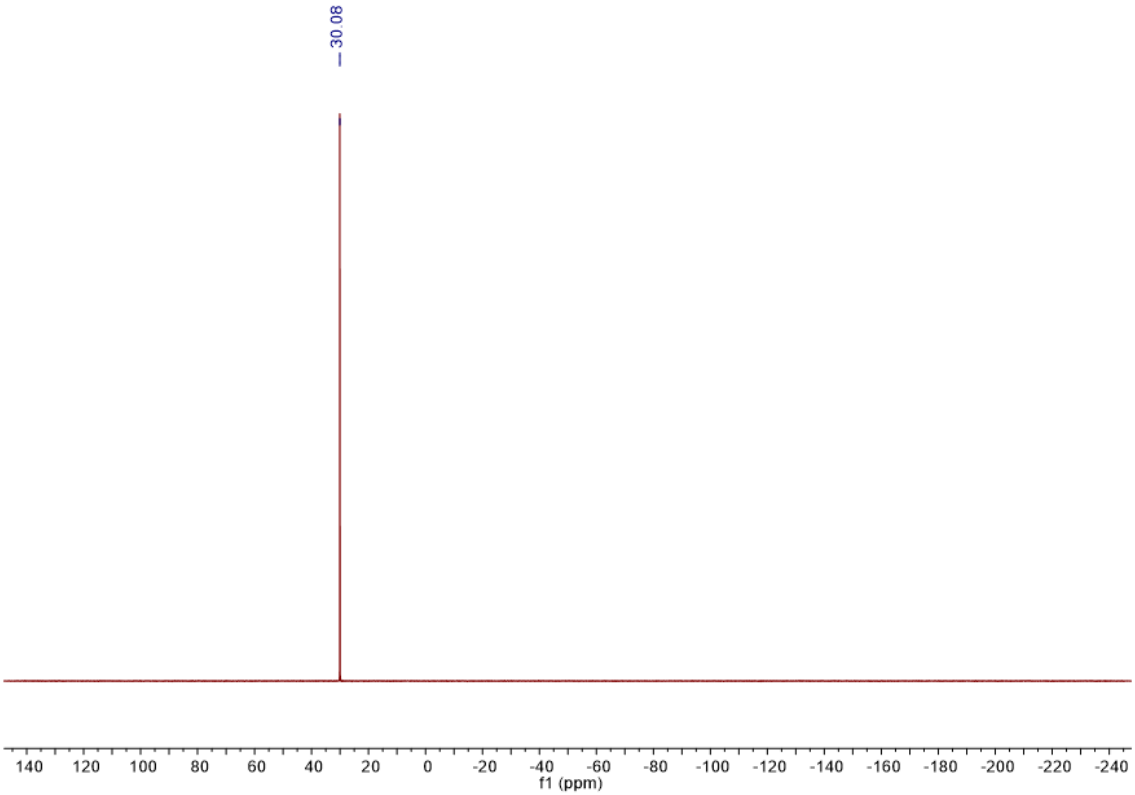

## $^{31}P$ NMR of 44 ($CDCl_3$)



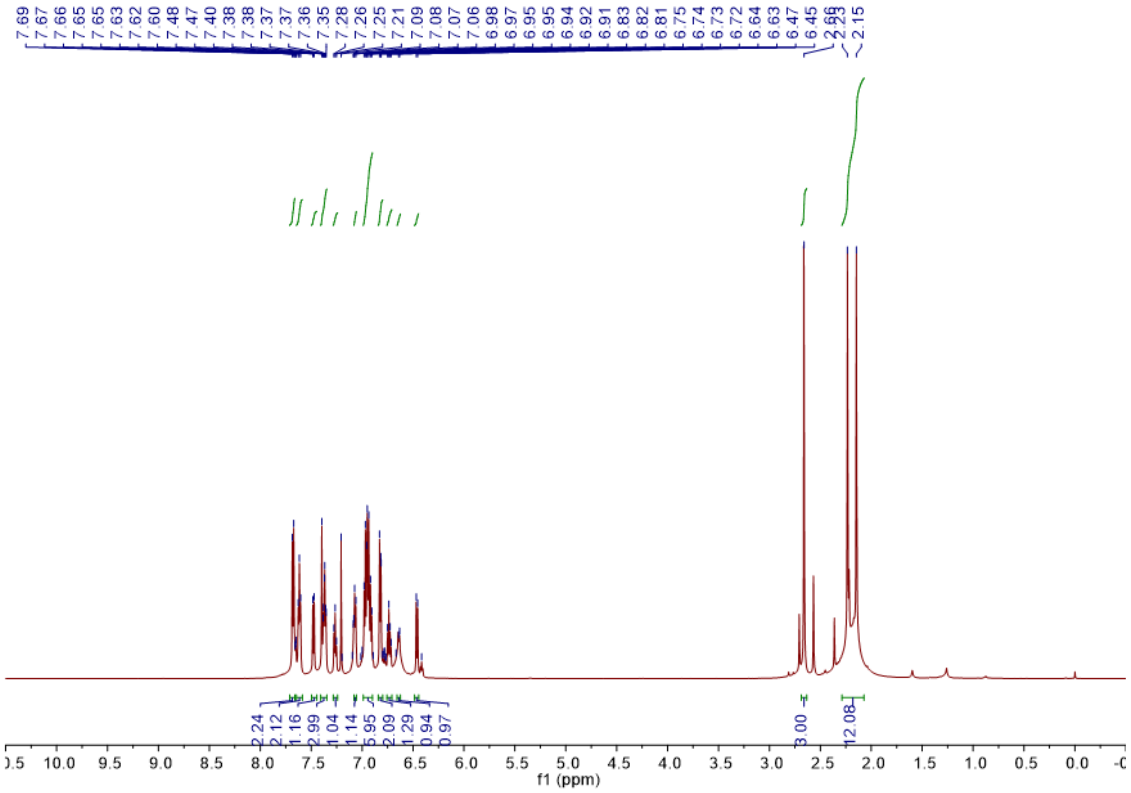
## $^{1}$H NMR of 45 ($CDCl_3$)



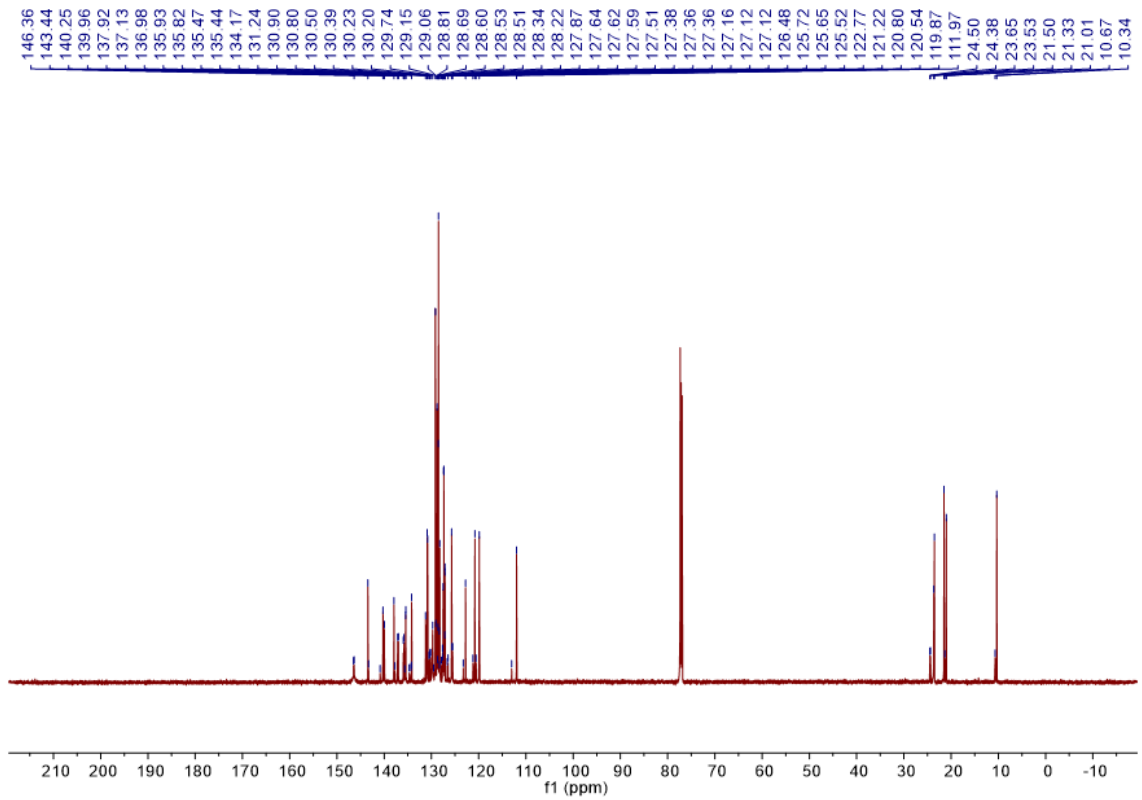

## $^{13}$C NMR of 45 ($CDCl_3$)



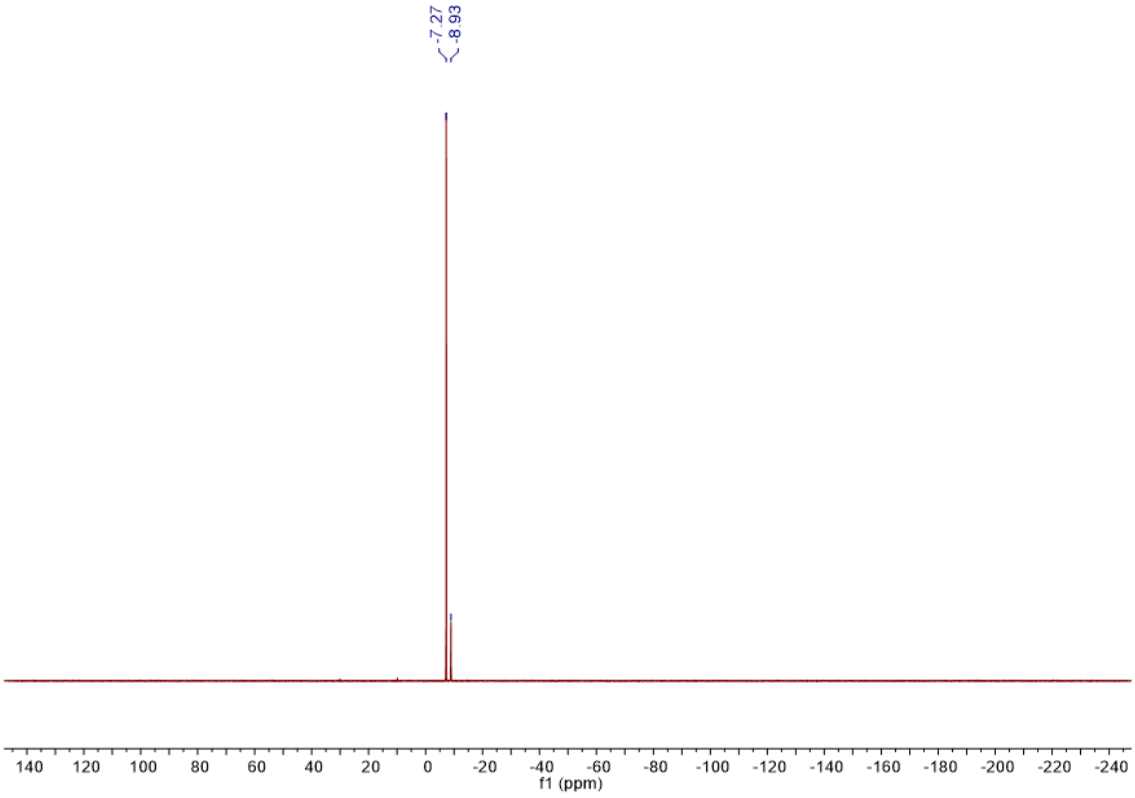
## $^{31}P$ NMR of 45 ($CDCl_3$)



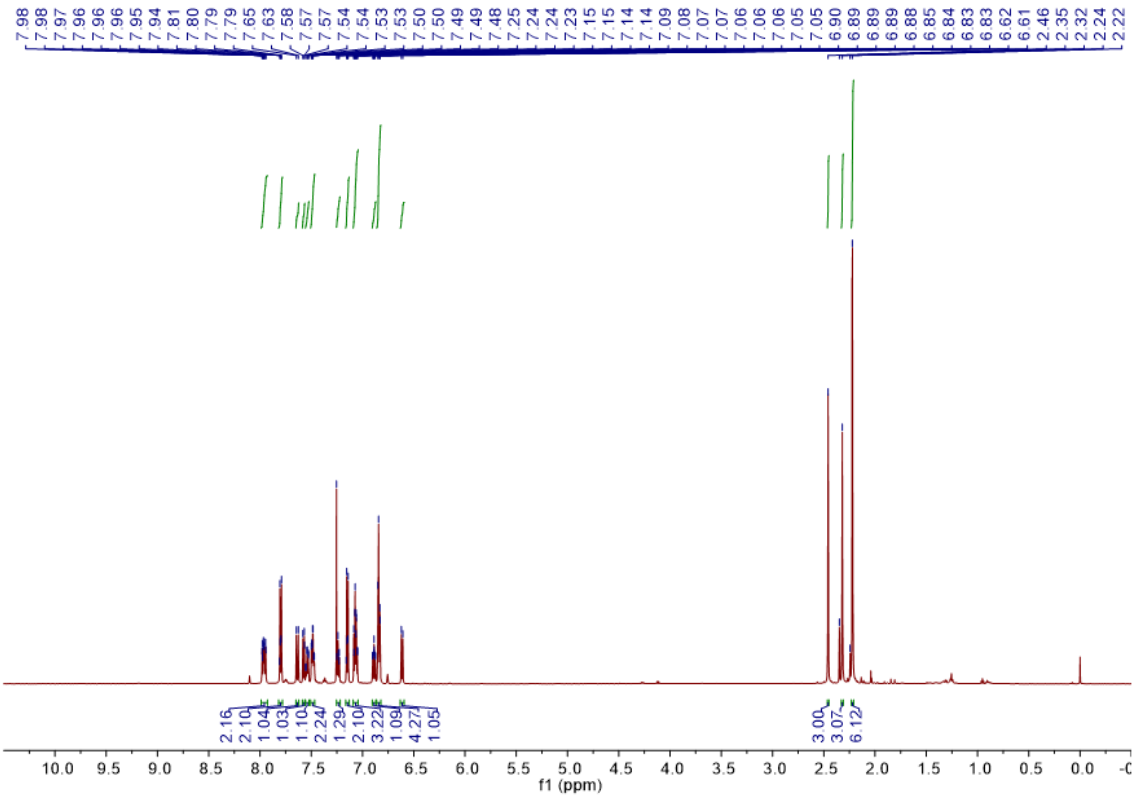

## $^{1}H$ NMR of 45' ($CDCl_3$)



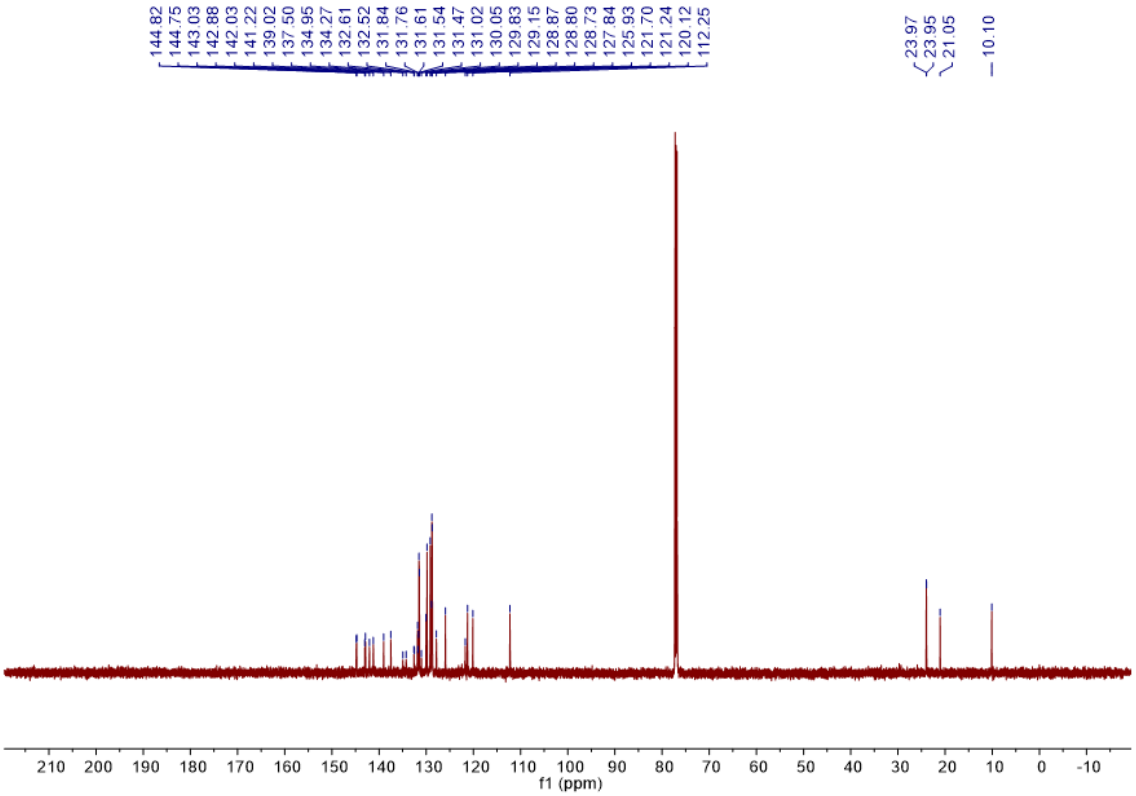
## $^{13}C$ NMR of 45' ($CDCl_3$)



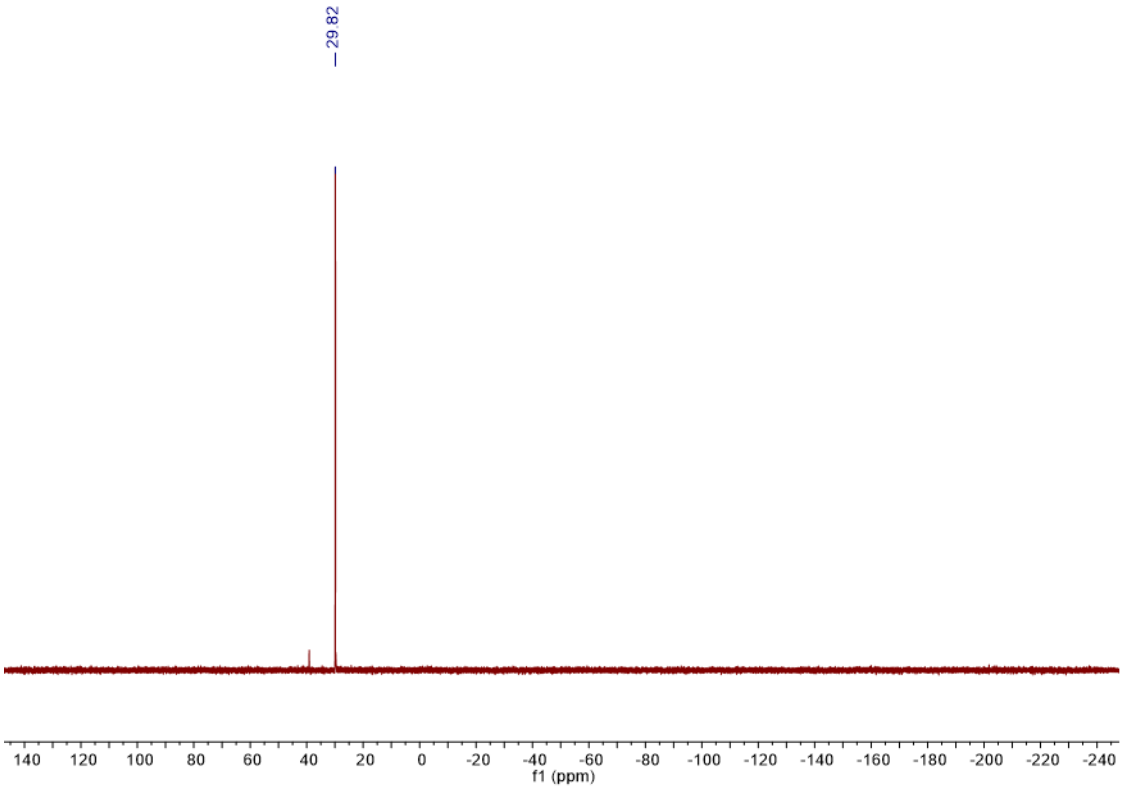

## $^{31}P$ NMR of 45' ($CDCl_3$)



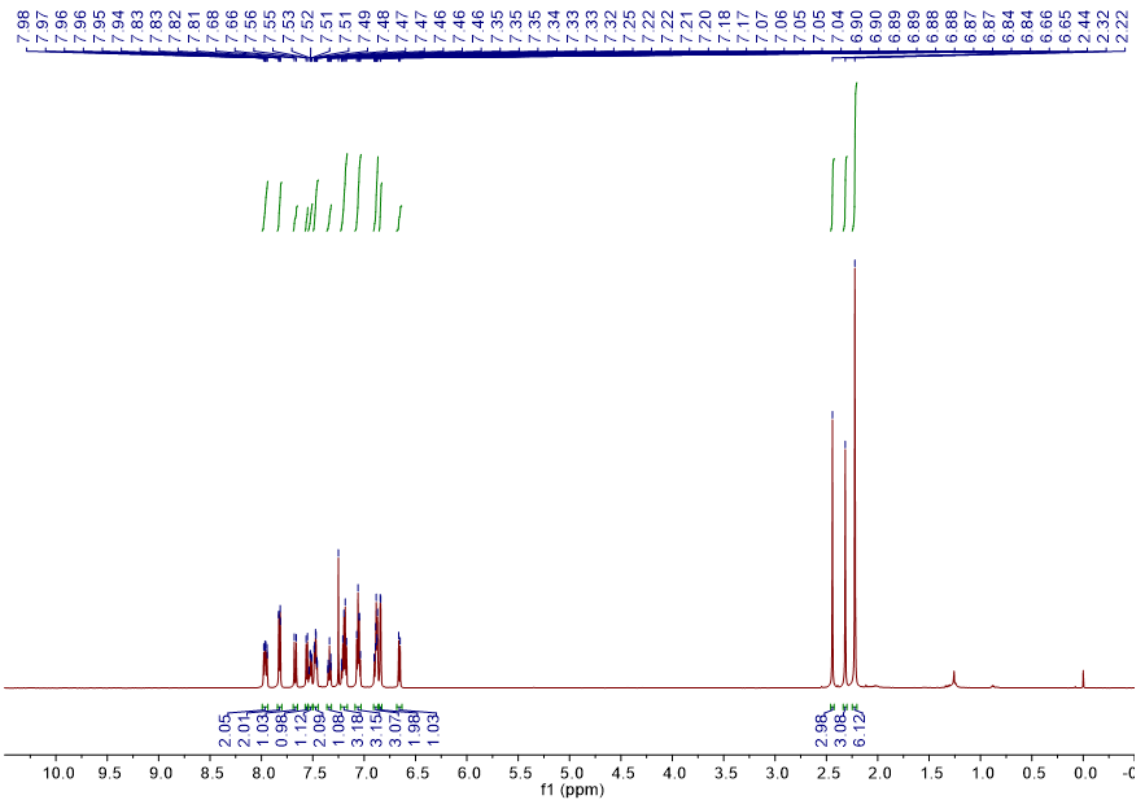
## $^{1}$H NMR of 46 ($CDCl_3$)



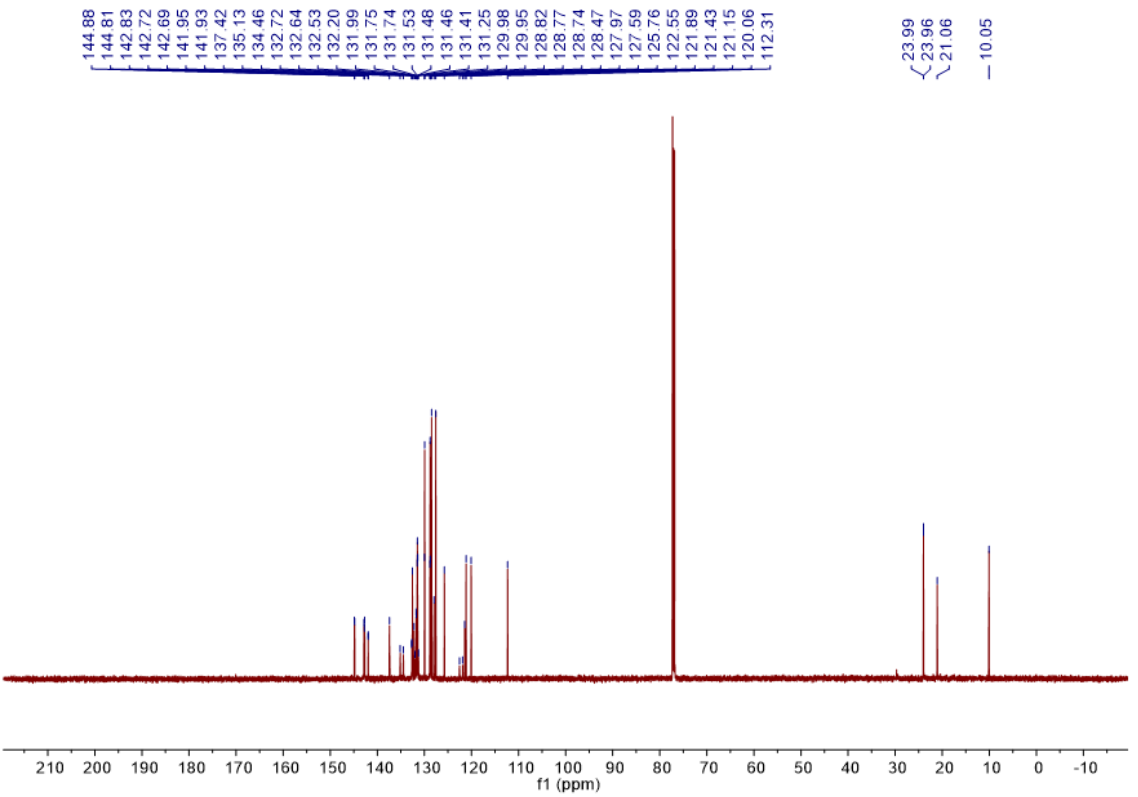

## $^{13}$C NMR of 46 ($CDCl_3$)



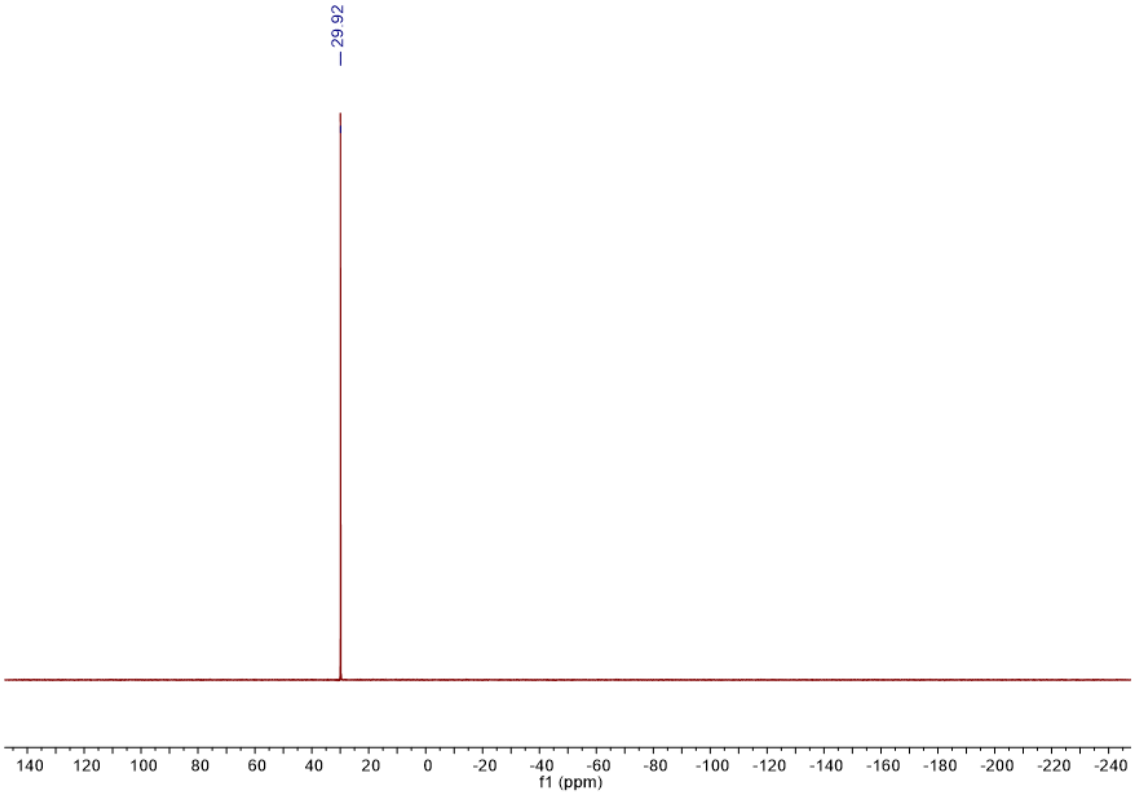
## $^{31}P$ NMR of 46 ($CDCl_3$)



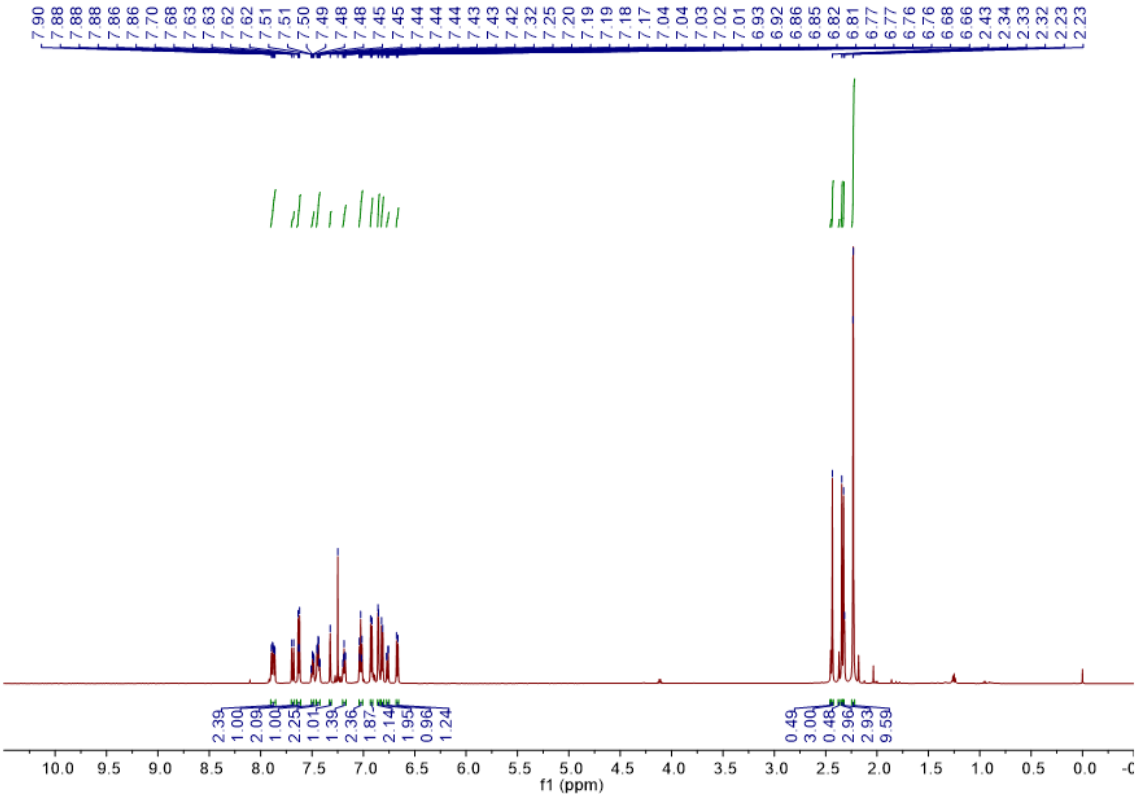

## $^{1}H$ NMR of 47 ($CDCl_3$)



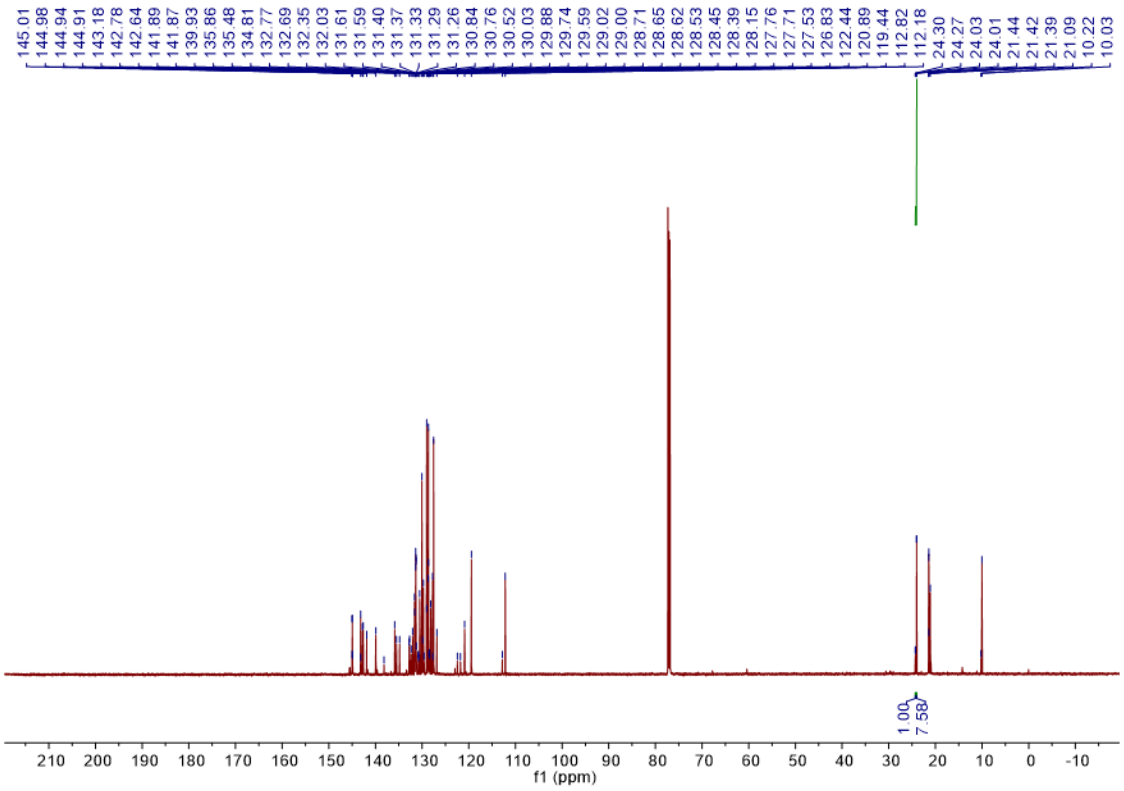
## $^{13}C$ NMR of 47 ($CDCl_3$)



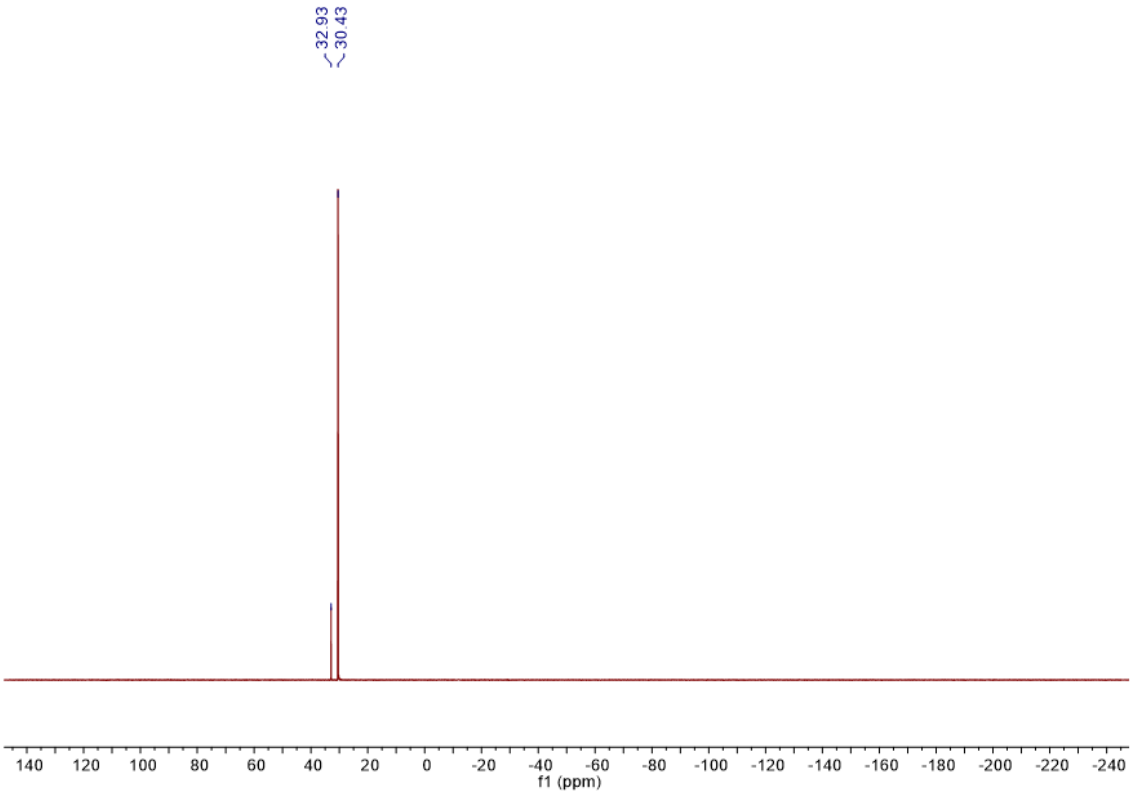

## $^{31}P$ NMR of 47 ($CDCl_3$)



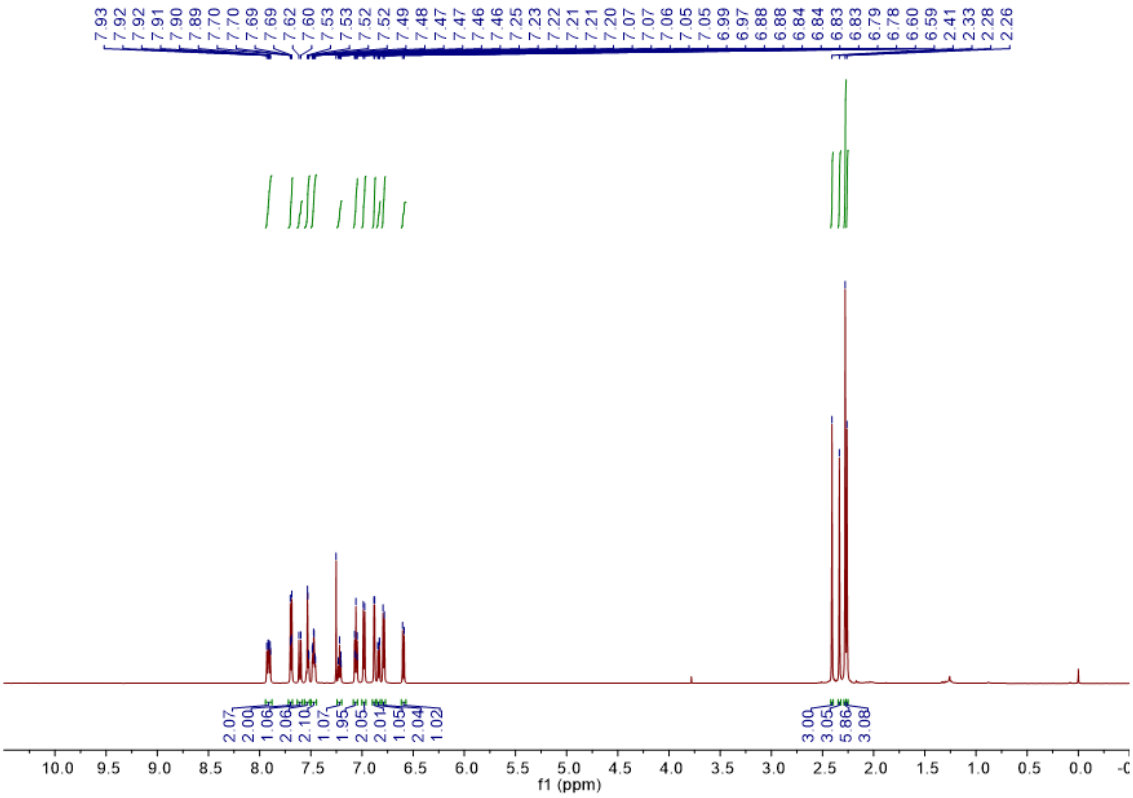
## $^{1}$H NMR of 48 ($CDCl_3$)



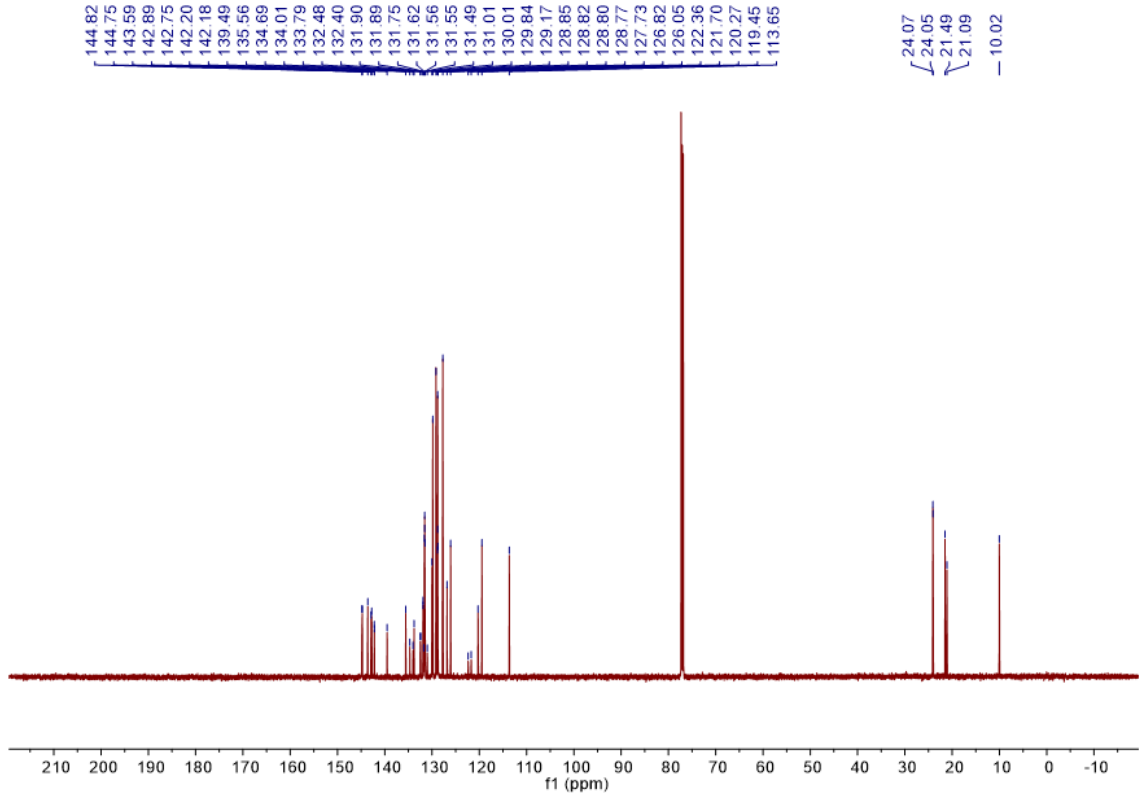

## $^{13}$C NMR of 48 ($CDCl_3$)



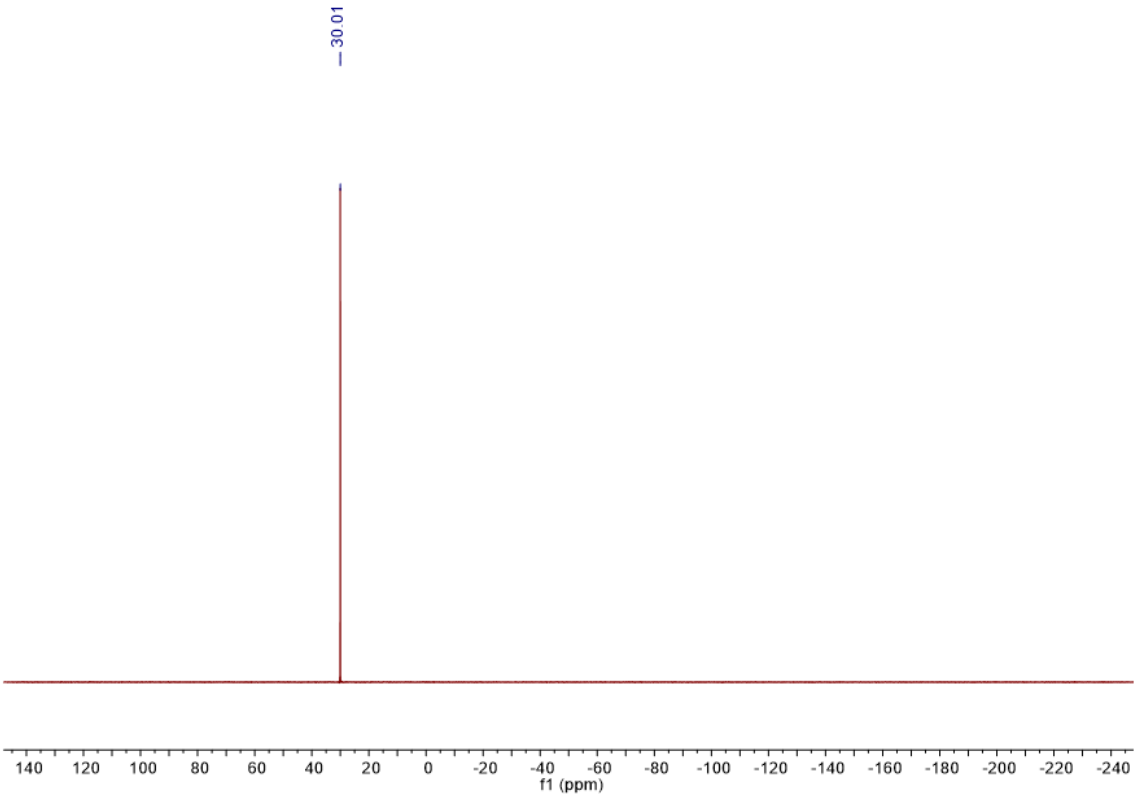
## $^{31}$P NMR of 48 ($CDCl_3$)



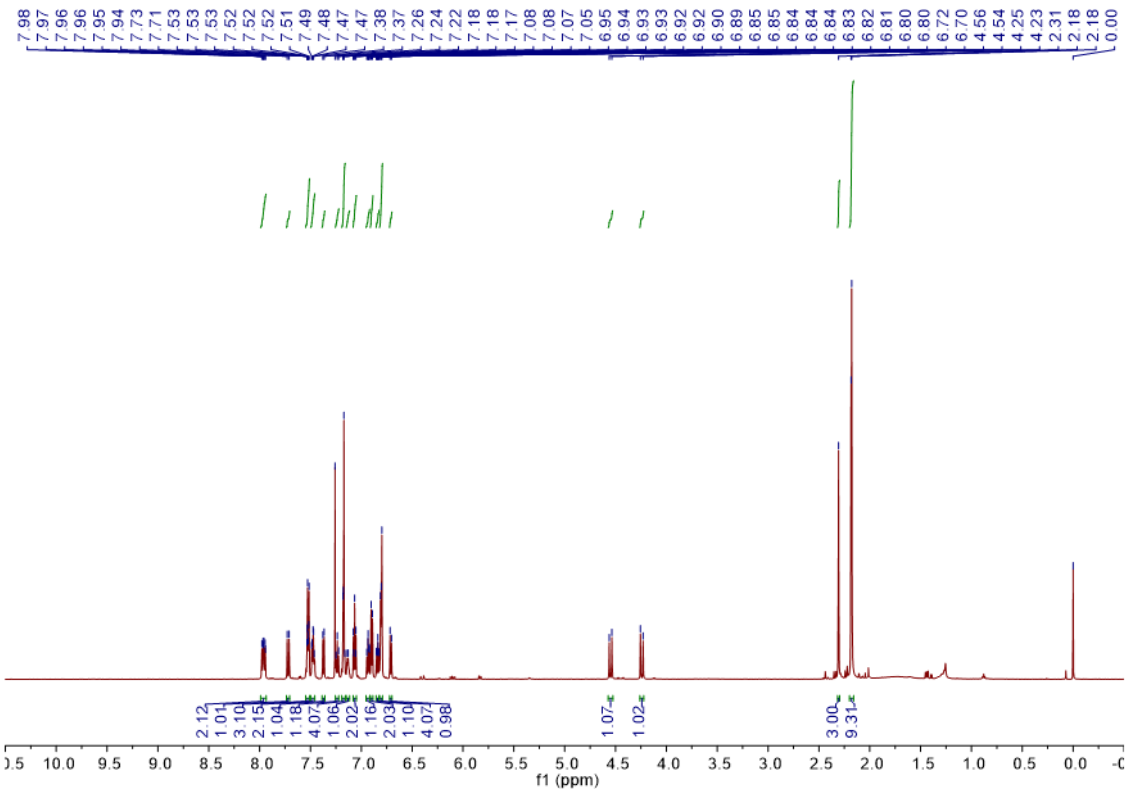

## $^{1}$H NMR of 49 ($CDCl_3$)



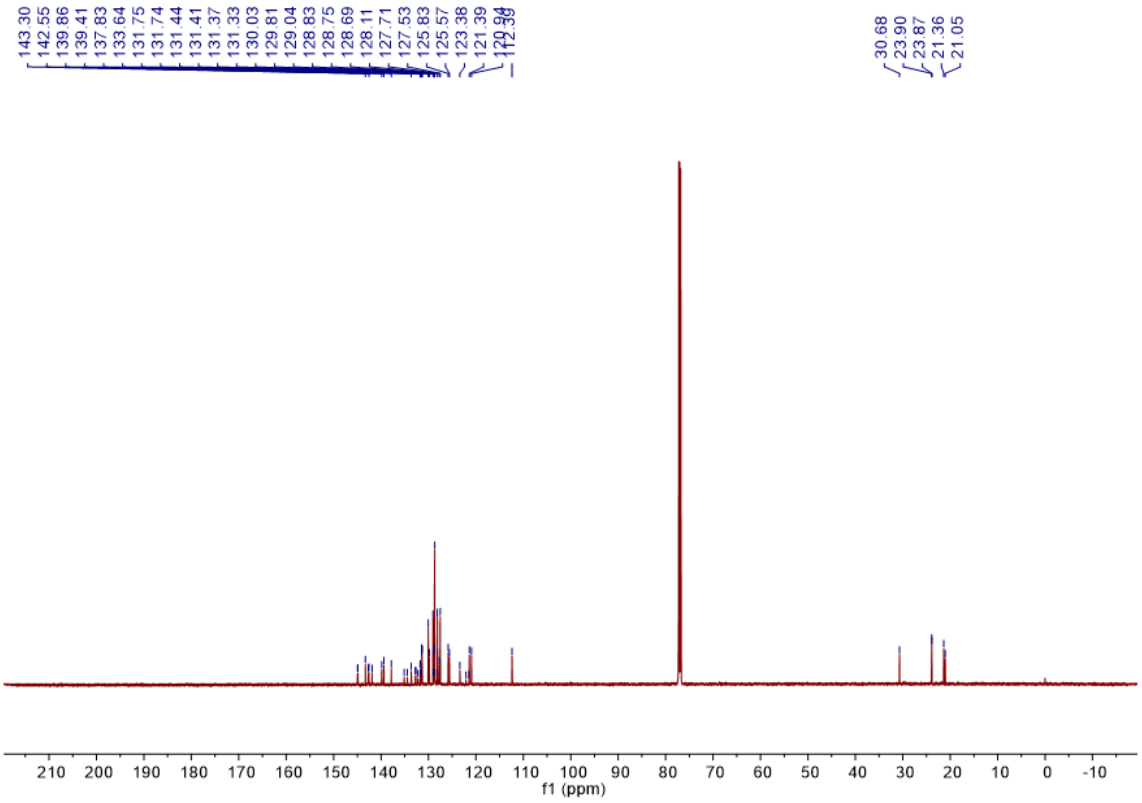
## $^{13}C$ NMR of 49 ($CDCl_3$)



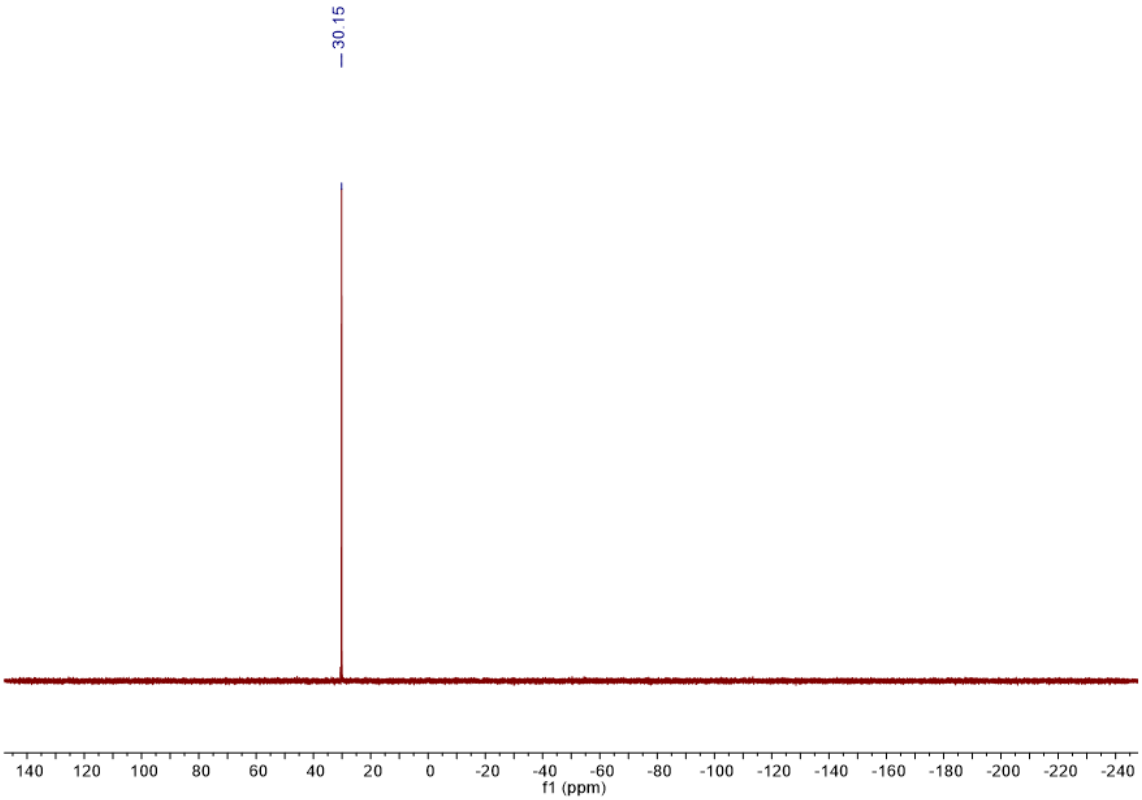

## $^{31}P$ NMR of 49 ($CDCl_3$)



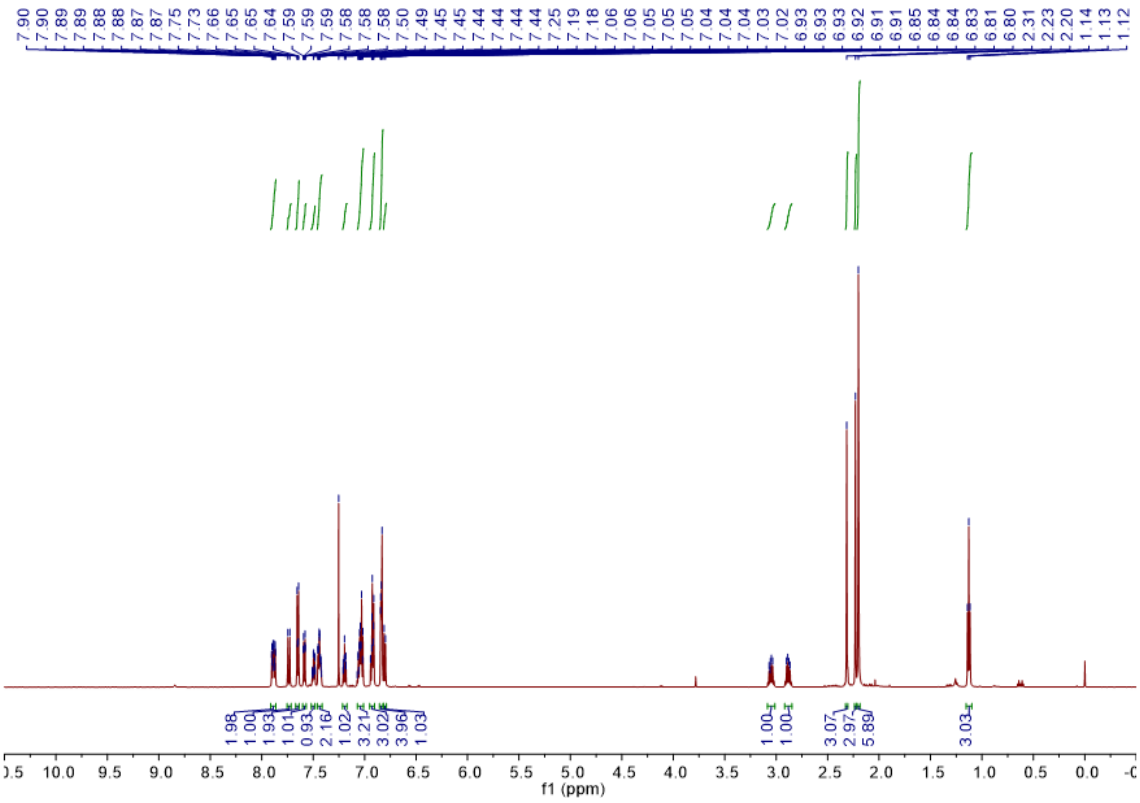
## $^{1}$H NMR of 50 ($CDCl_3$)



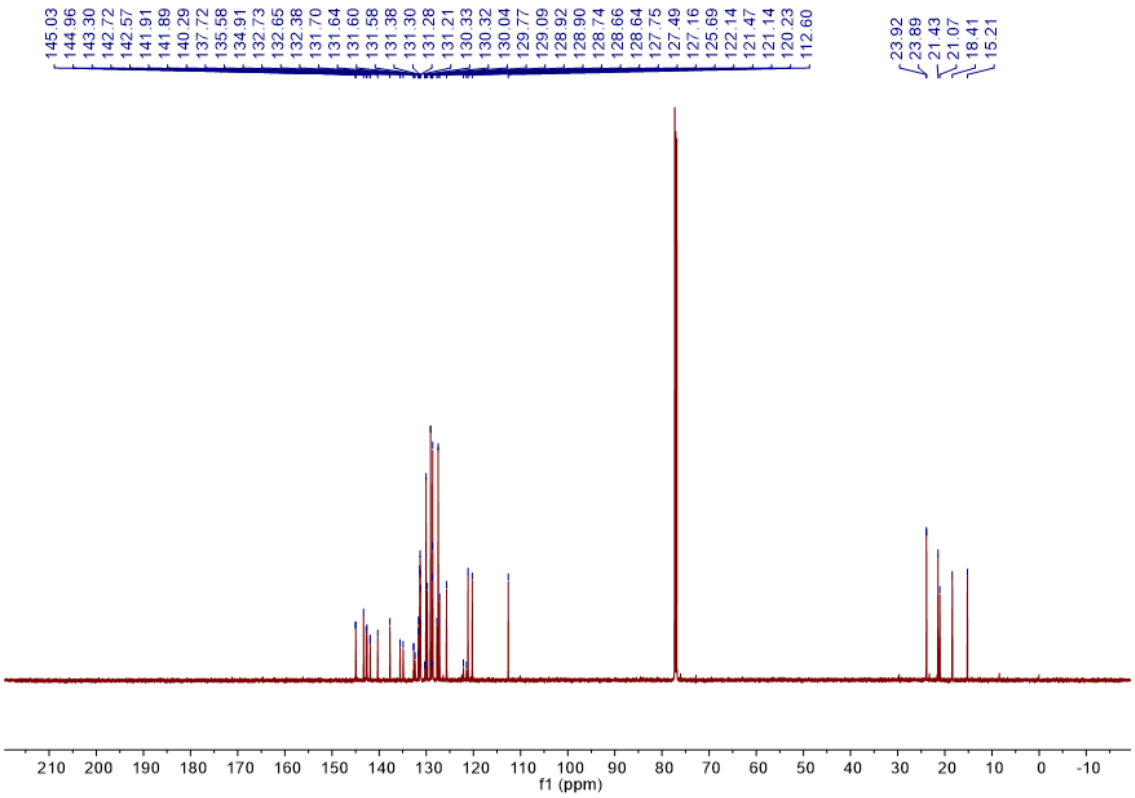

## $^{13}$C NMR of 50 ($CDCl_3$)



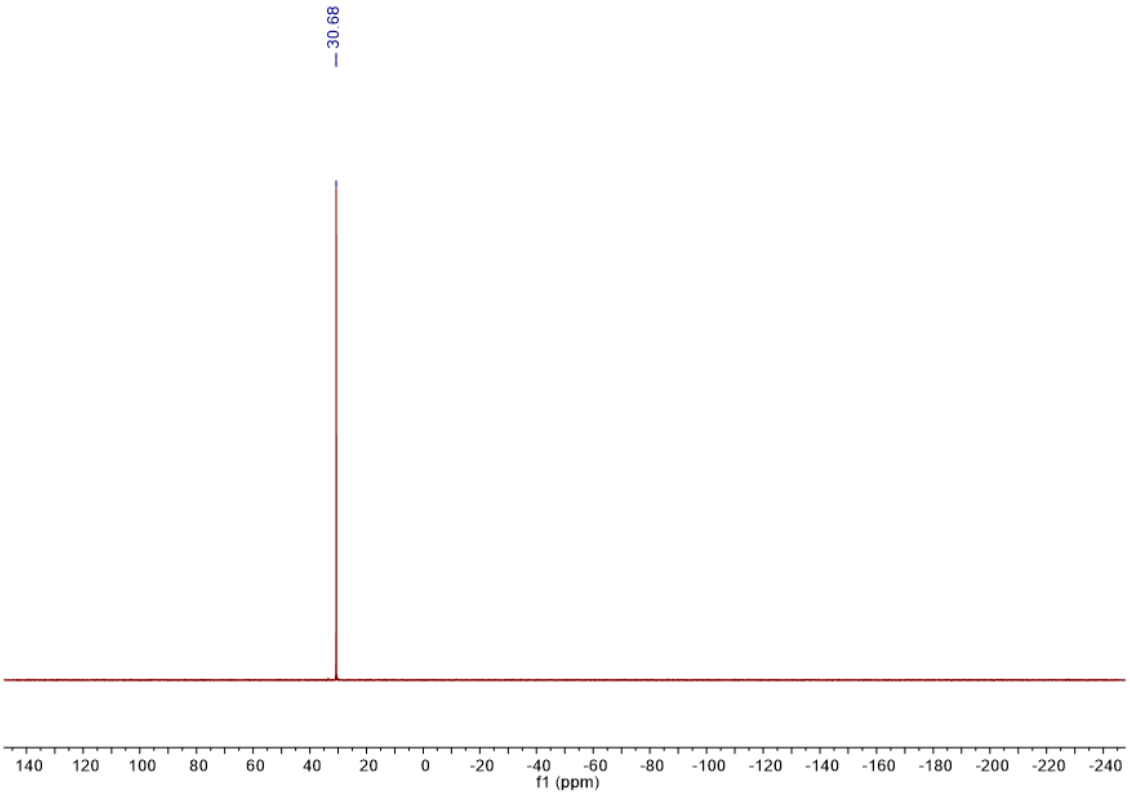
## $^{31}$P NMR of 50 ($CDCl_3$)



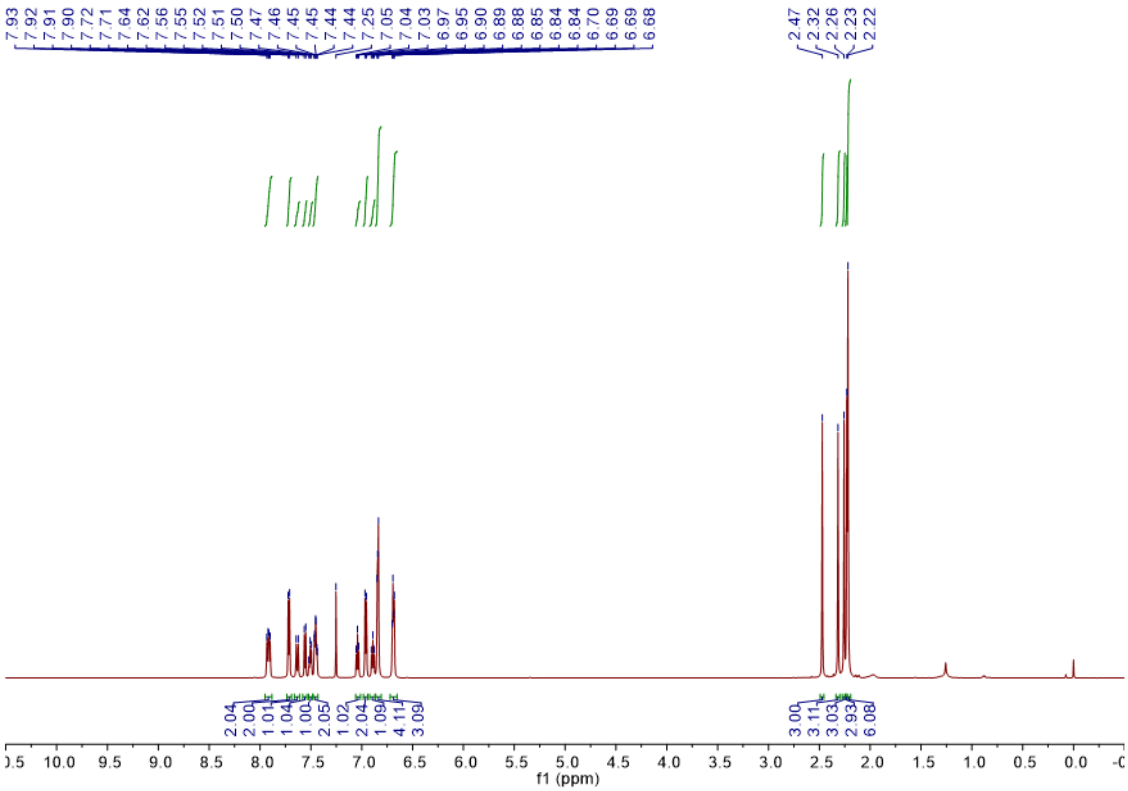

## $^{1}$H NMR of 51 ($CDCl_3$)



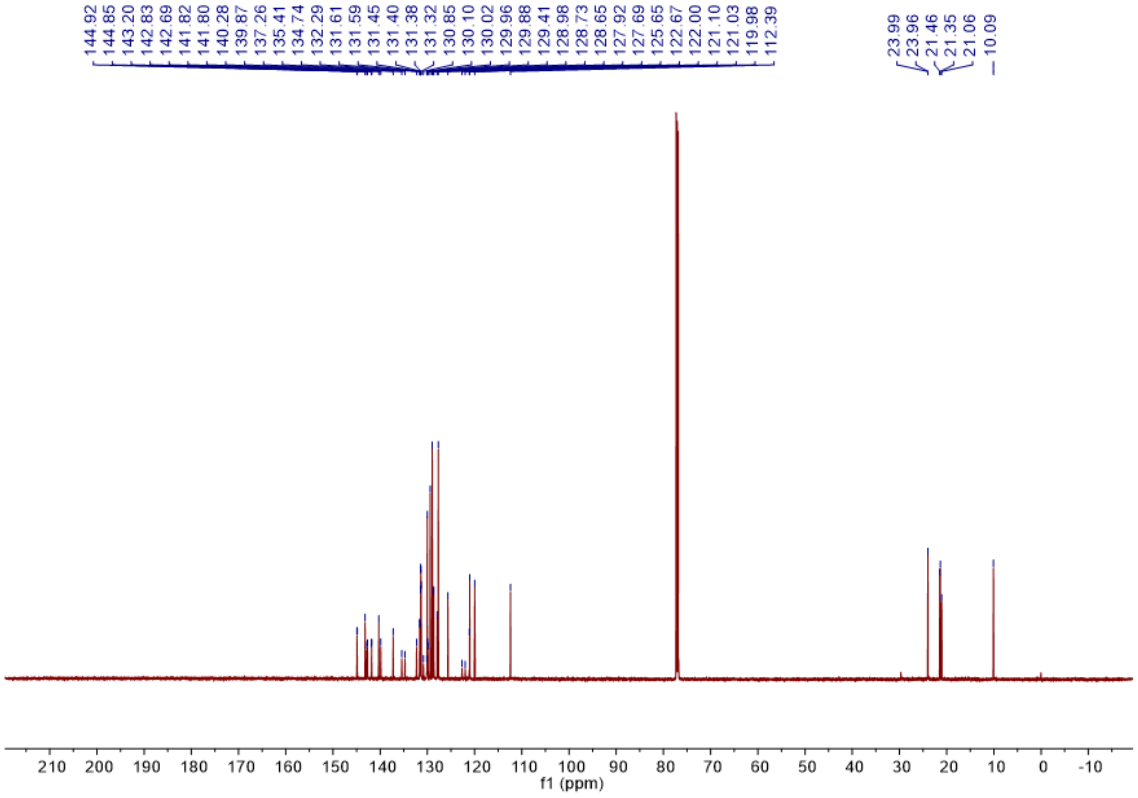
## $^{13}C$ NMR of 51 ($CDCl_3$)



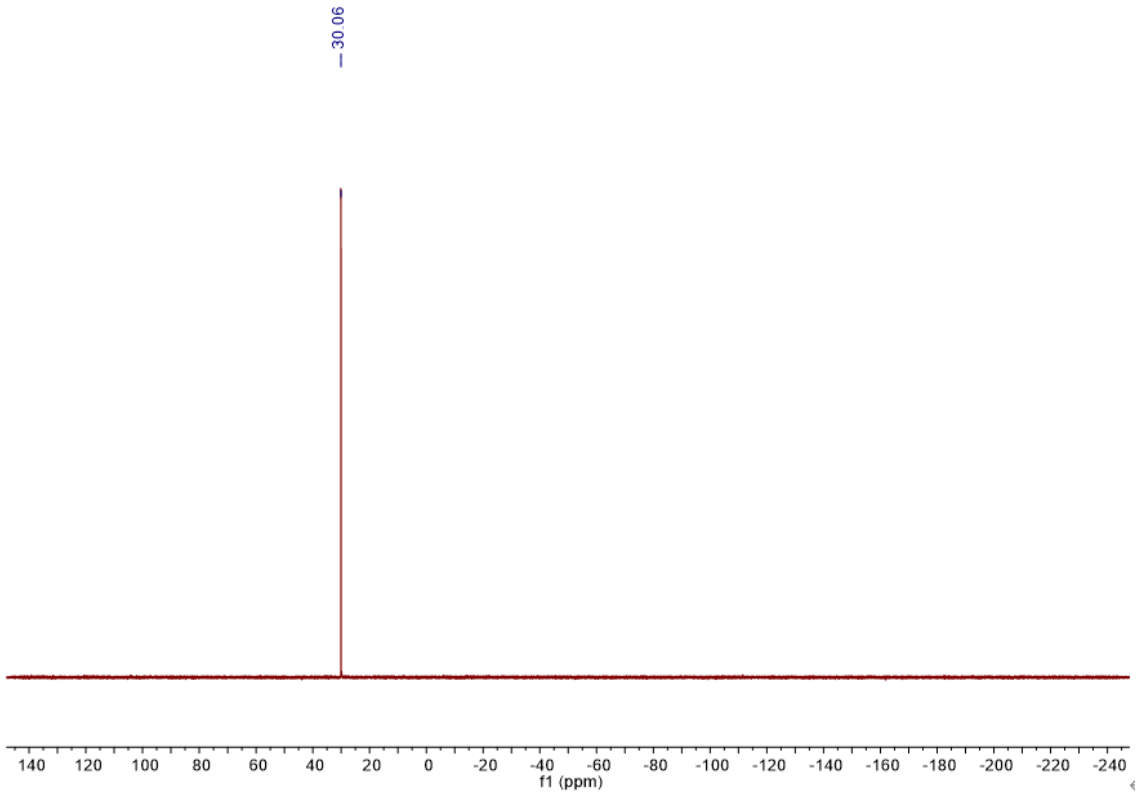

## $^{31}P$ NMR of 51 ($CDCl_3$)



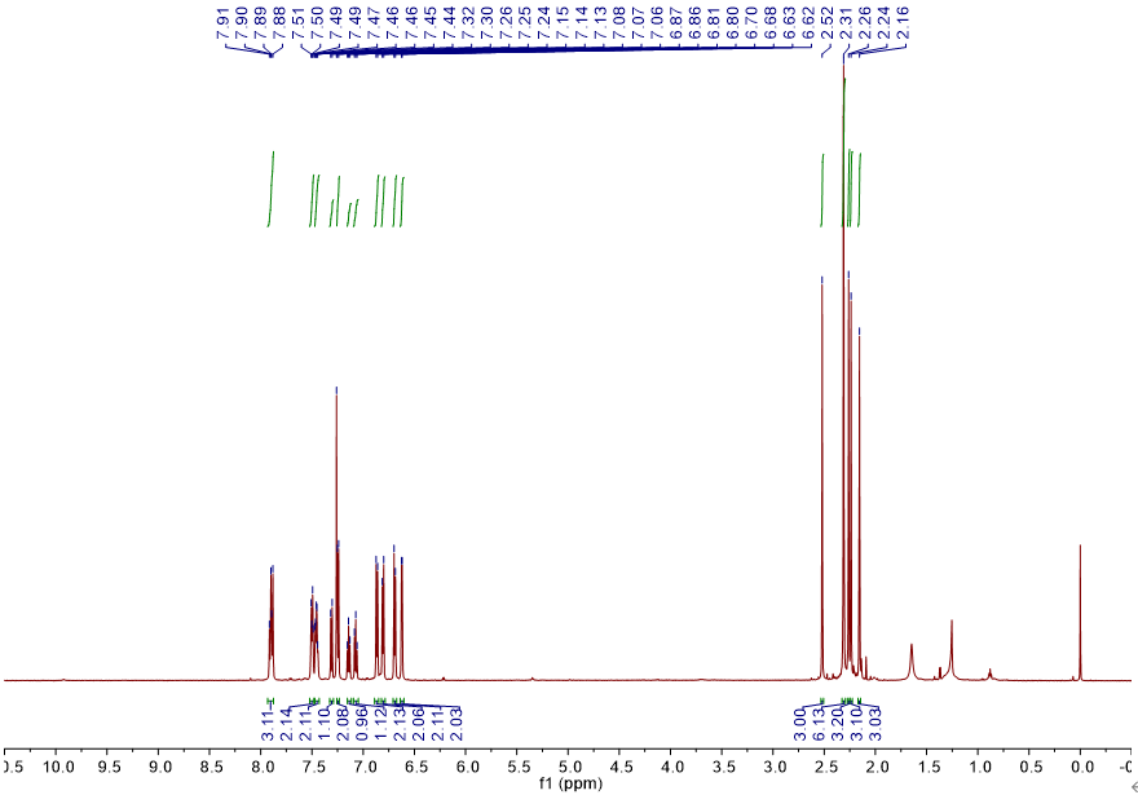
## $^{1}$H NMR of 52 ($CDCl_3$)



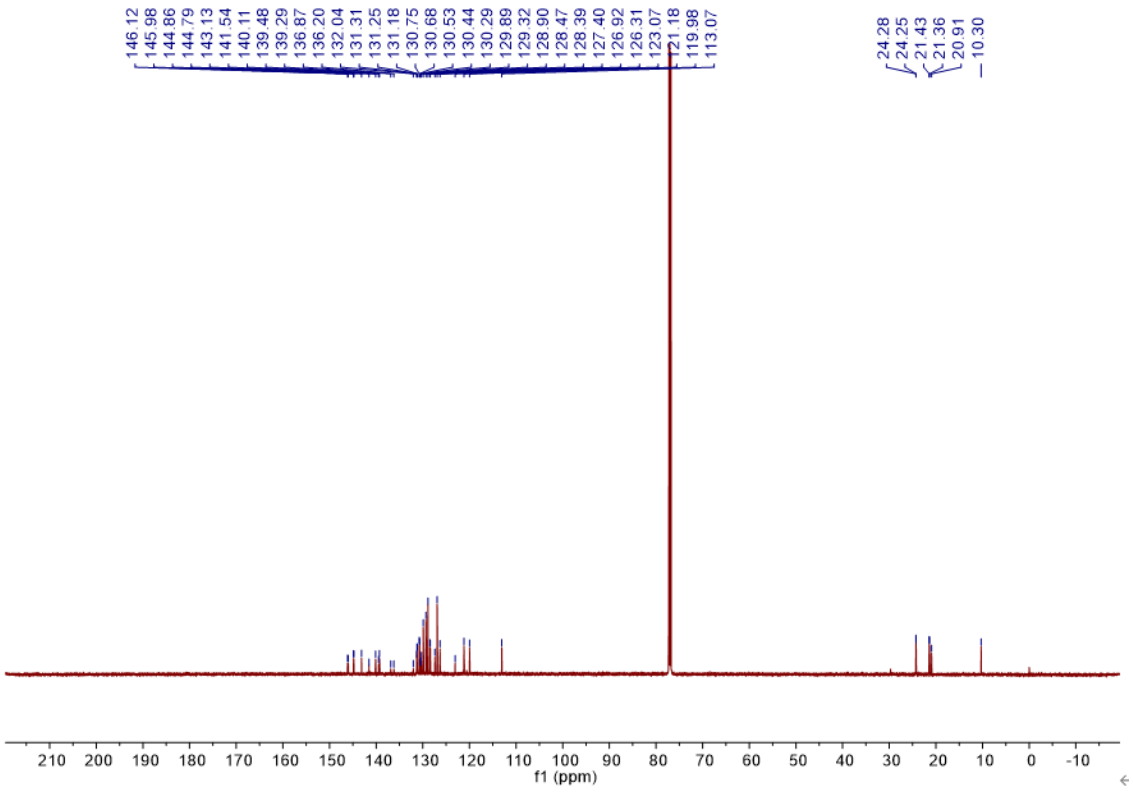

## $^{13}$C NMR of 52 ($CDCl_3$)



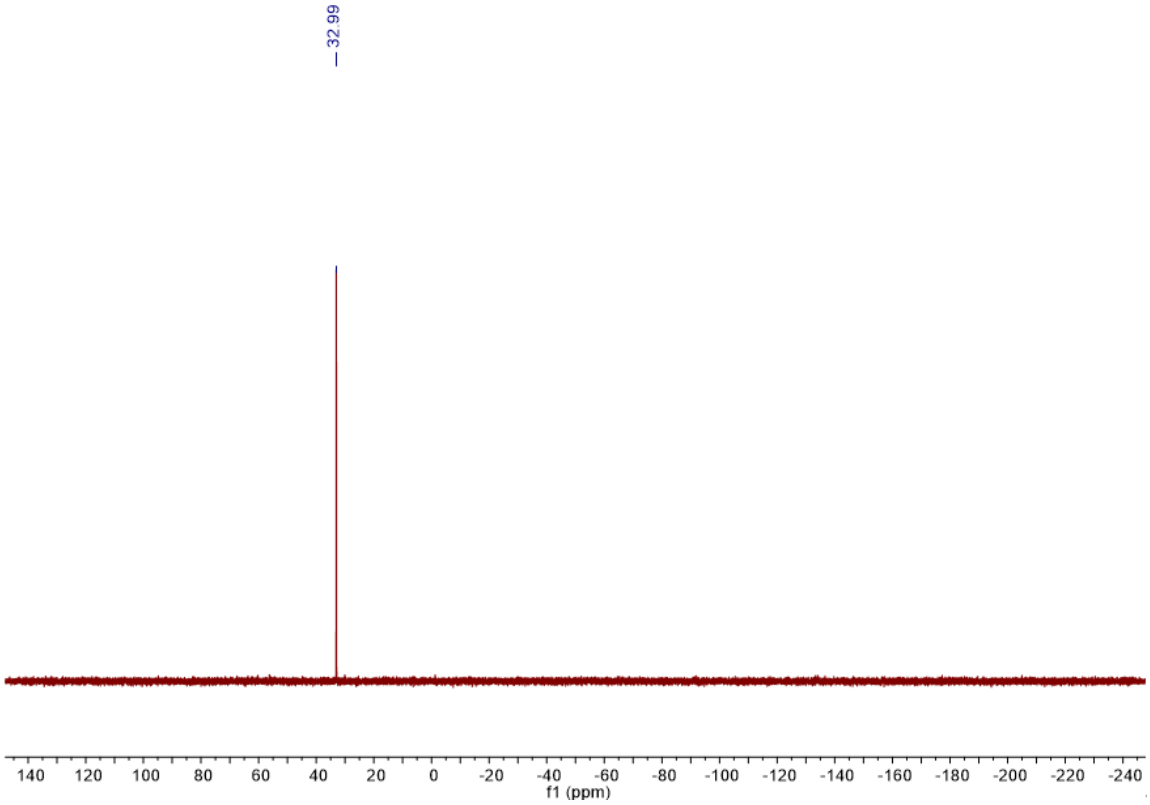
## $^{31}P$ NMR of 52 ($CDCl_3$)



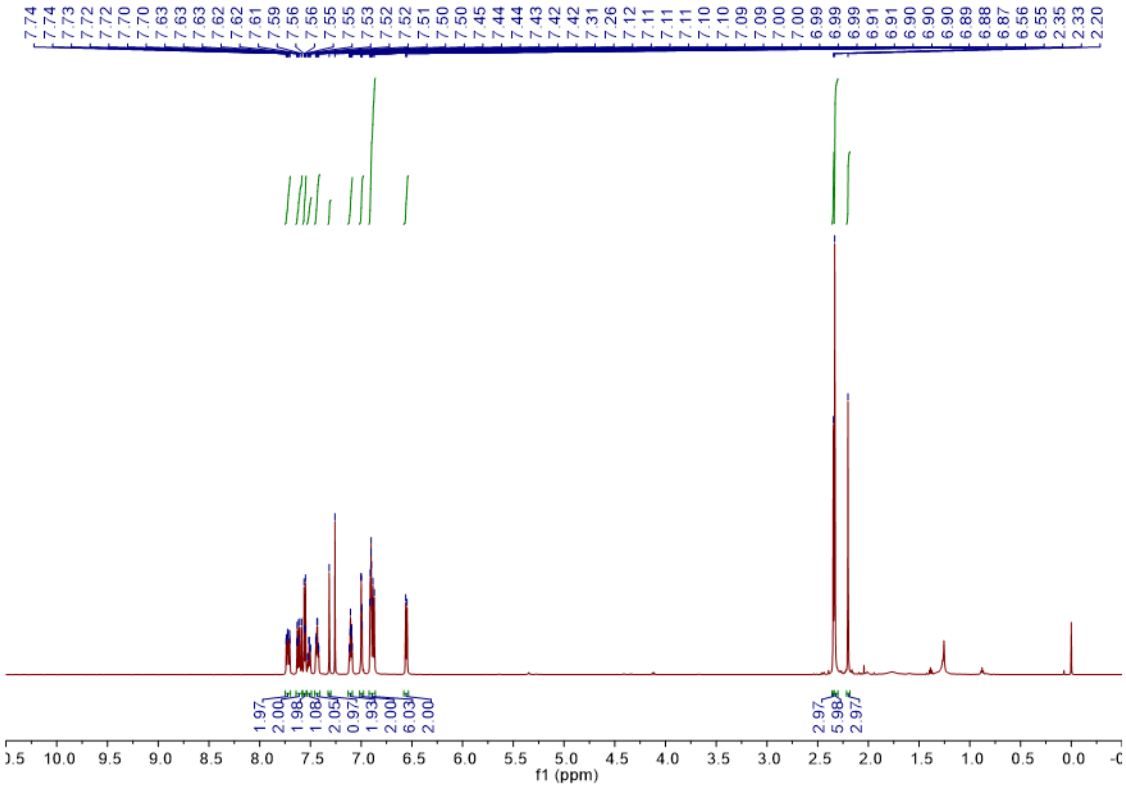

## $^{1}H$ NMR of 52 (Another diastereomer, $CDCl_3$)



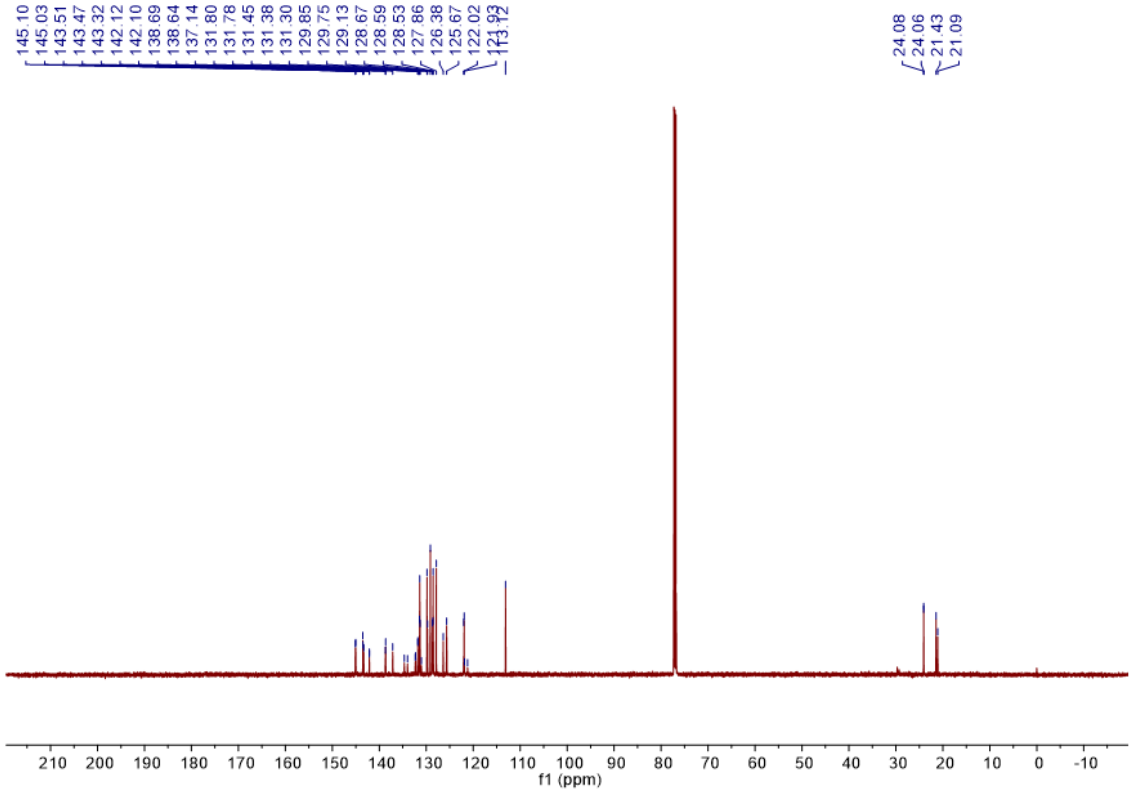
## $^{13}C$ NMR of 52 (Another diastereomer, $CDCl_3$)



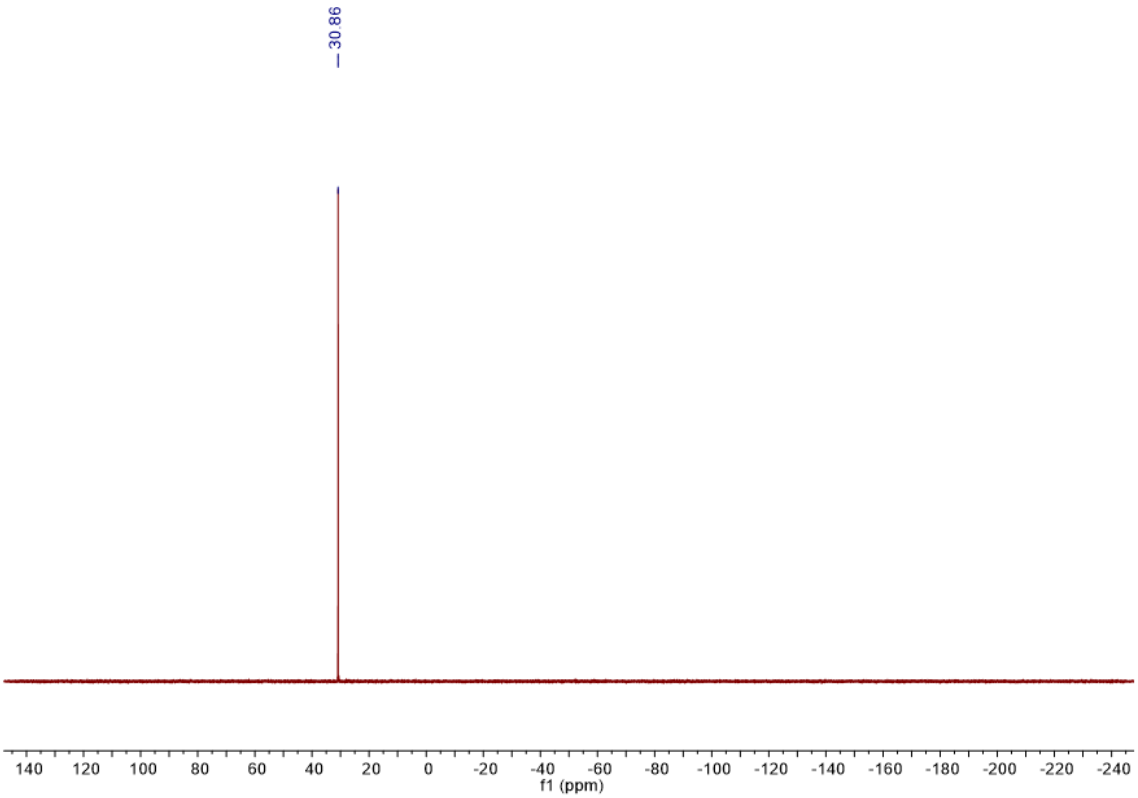

## $^{31}P$ NMR of 52 (Another diastereomer, $CDCl_3$)



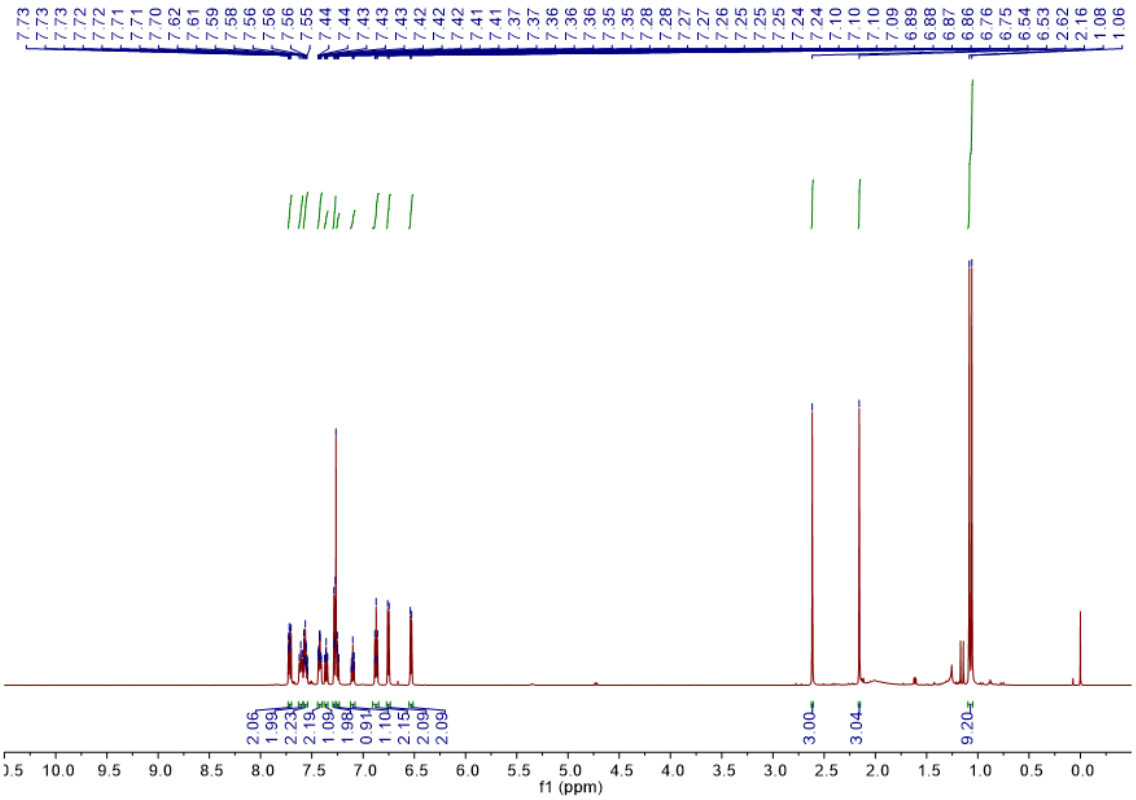
## $^{1}$H NMR of 53 ($CDCl_3$)



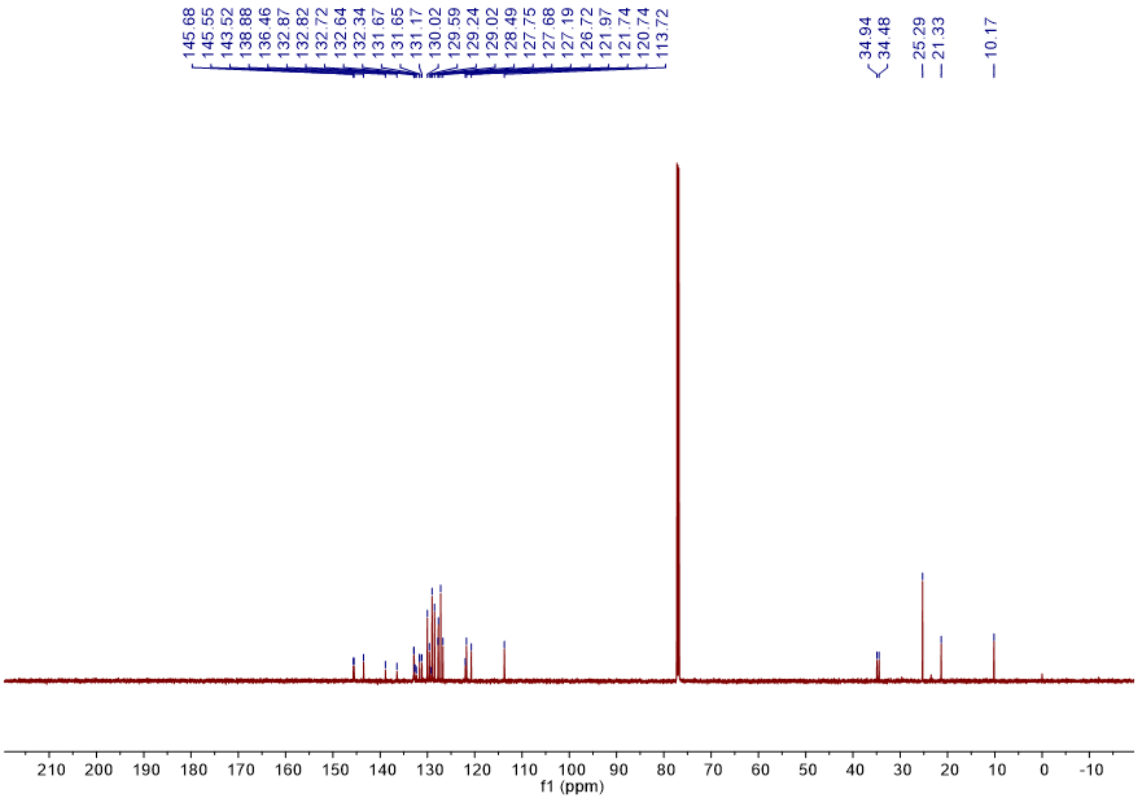

## $^{13}$C NMR of 53 ($CDCl_3$)



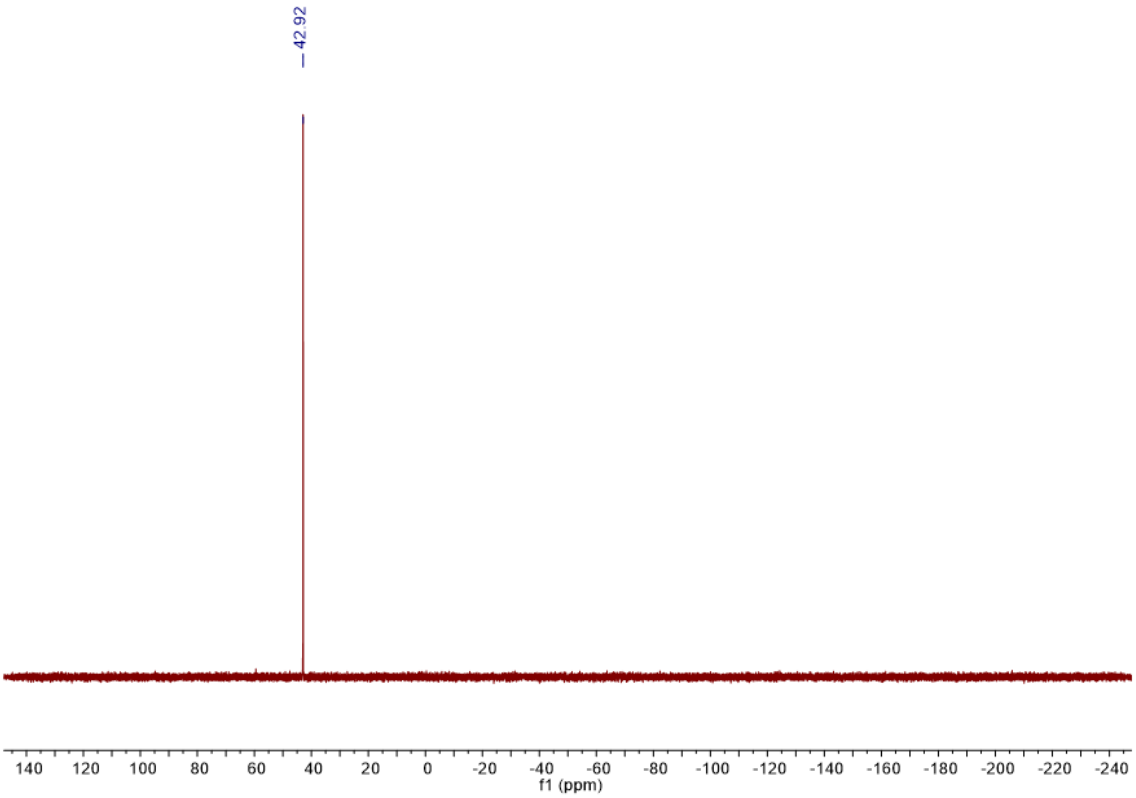
## $^{31}P$ NMR of 53 ($CDCl_3$)



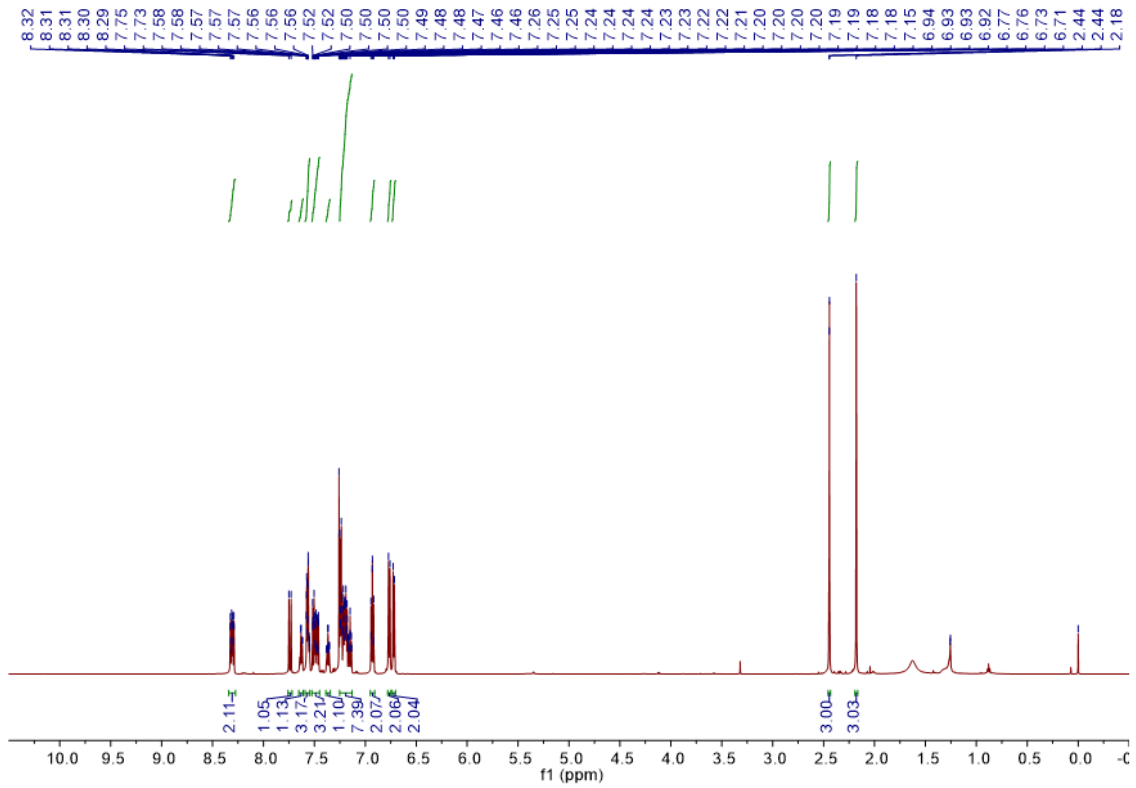

## $^{1}H$ NMR of 54 ($CDCl_3$)



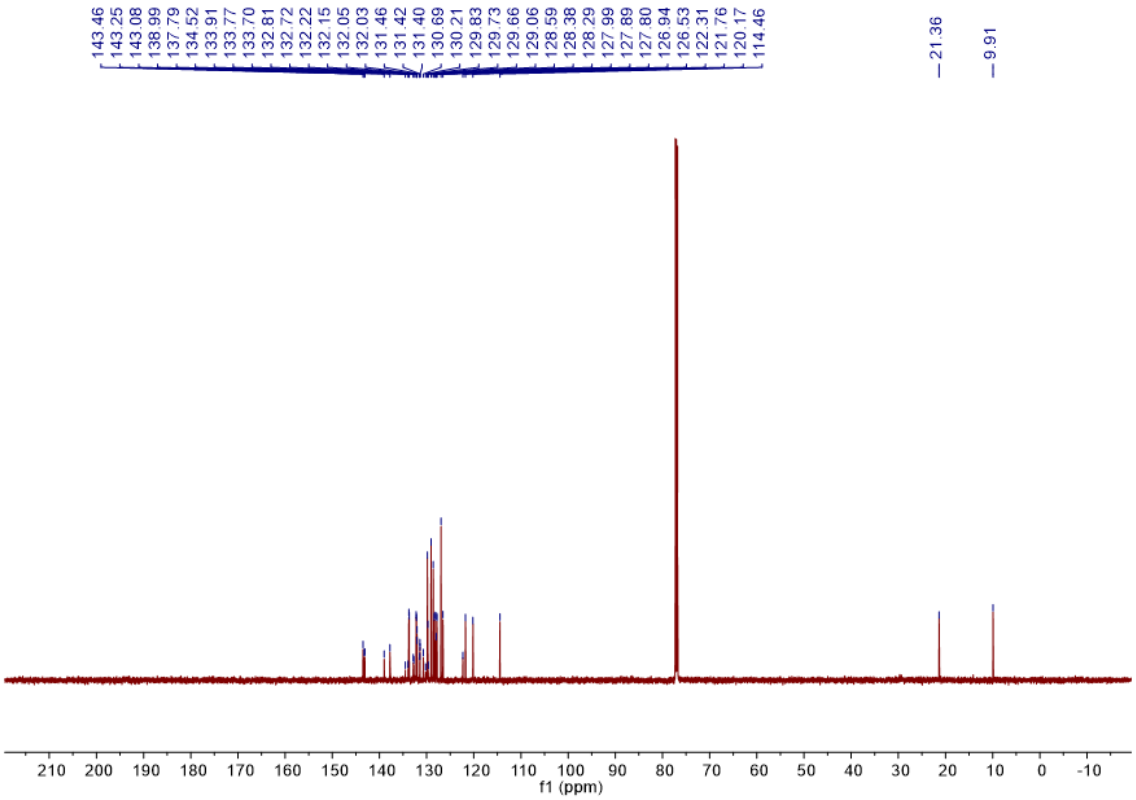
## $^{13}C$ NMR of 54 ($CDCl_3$)



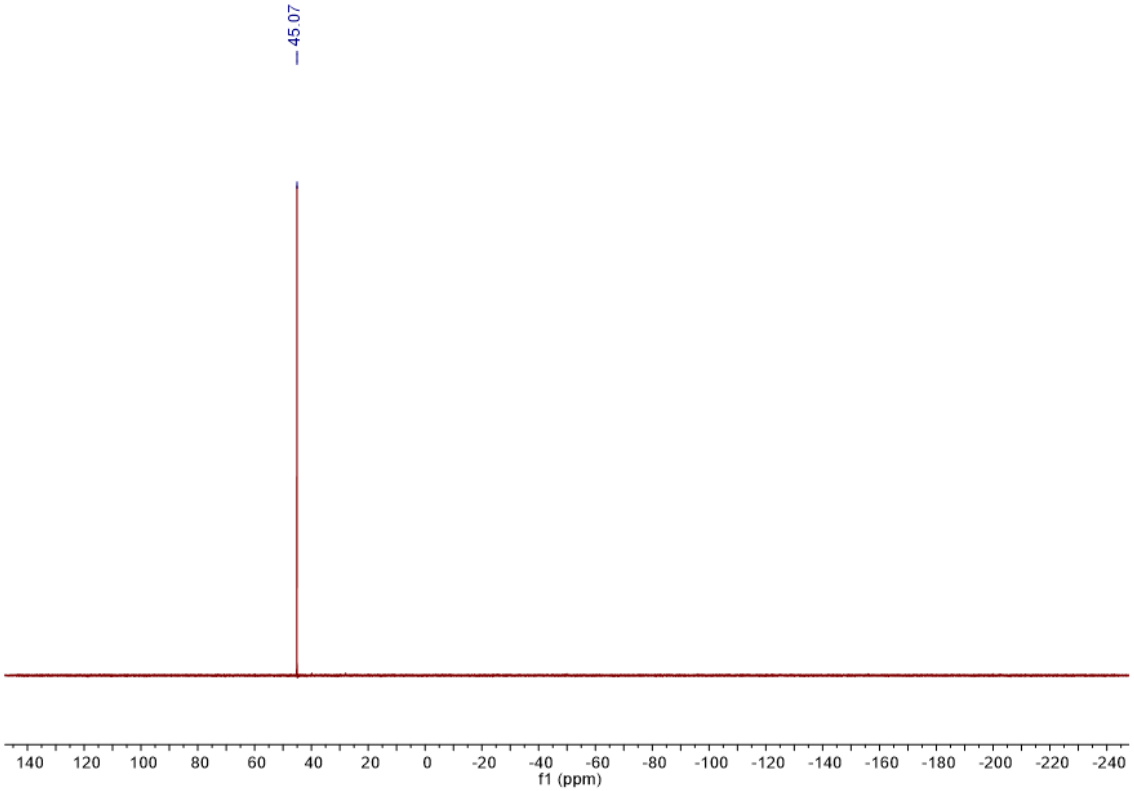

## $^{31}P$ NMR of 54 ($CDCl_3$)



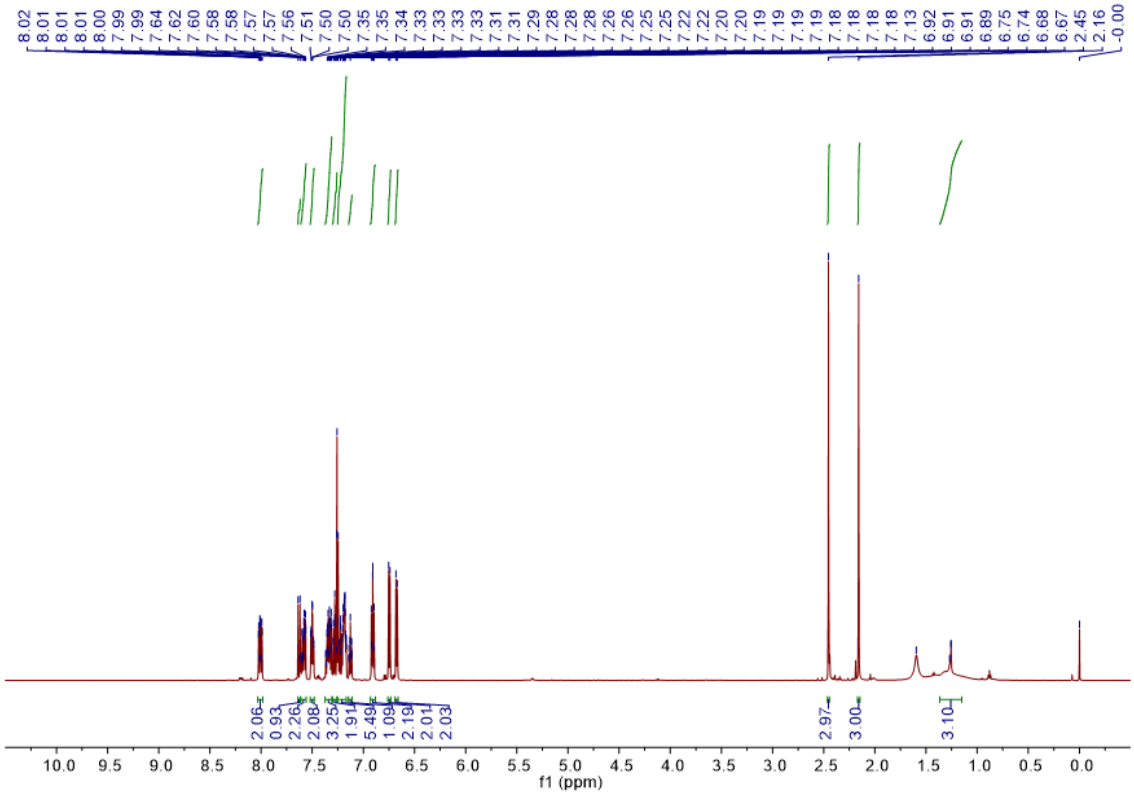
## $^{1}$H NMR of 55 ($CDCl_3$)



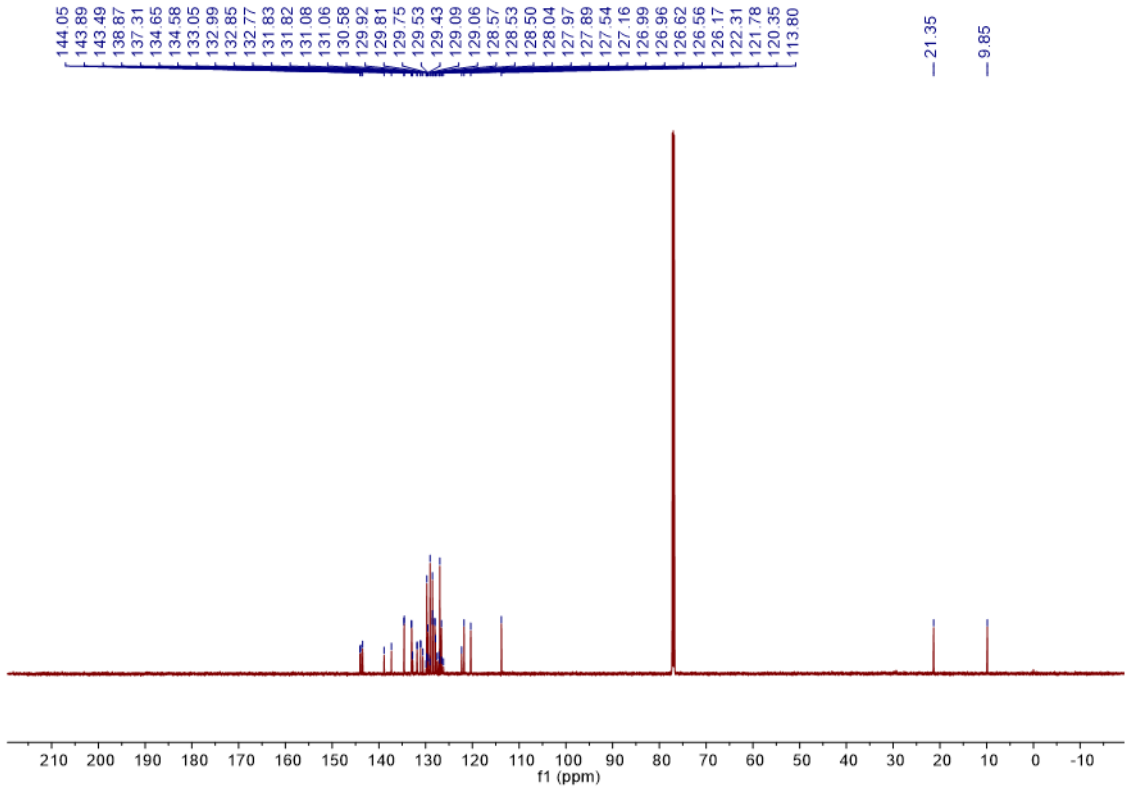

## $^{13}$C NMR of 55 ($CDCl_3$)



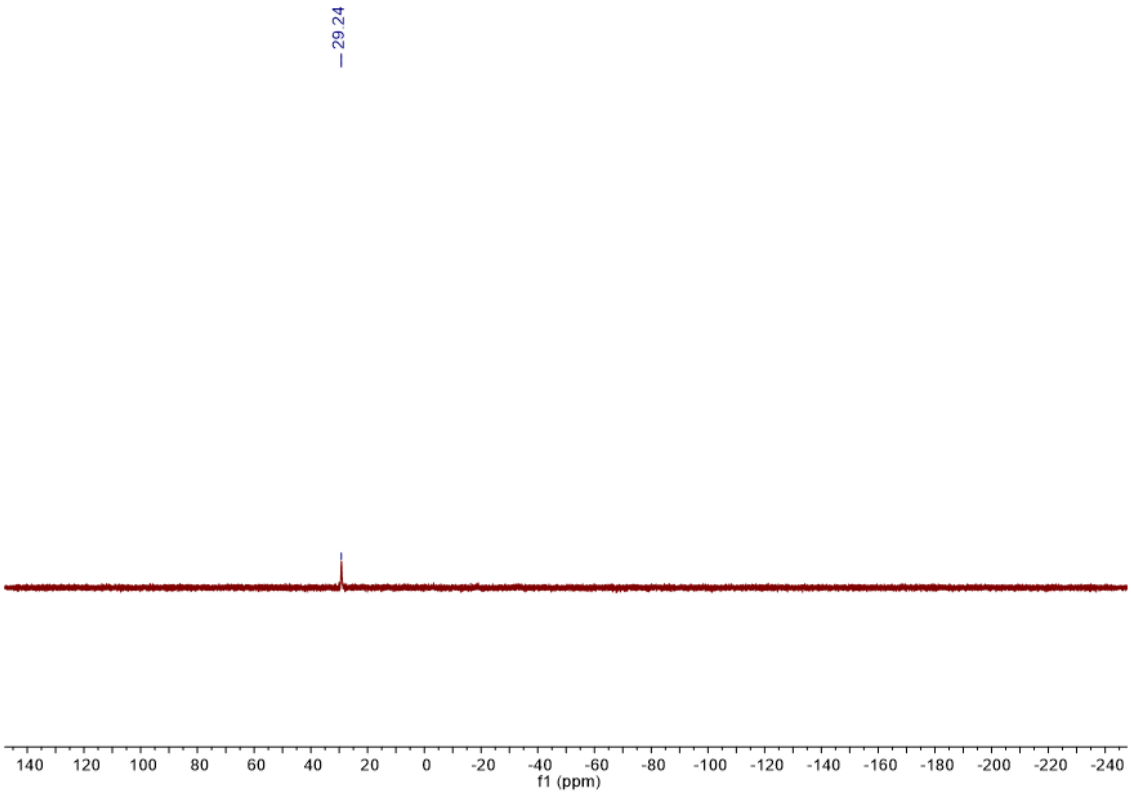
## $^{31}P$ NMR of 55 ($CDCl_3$)



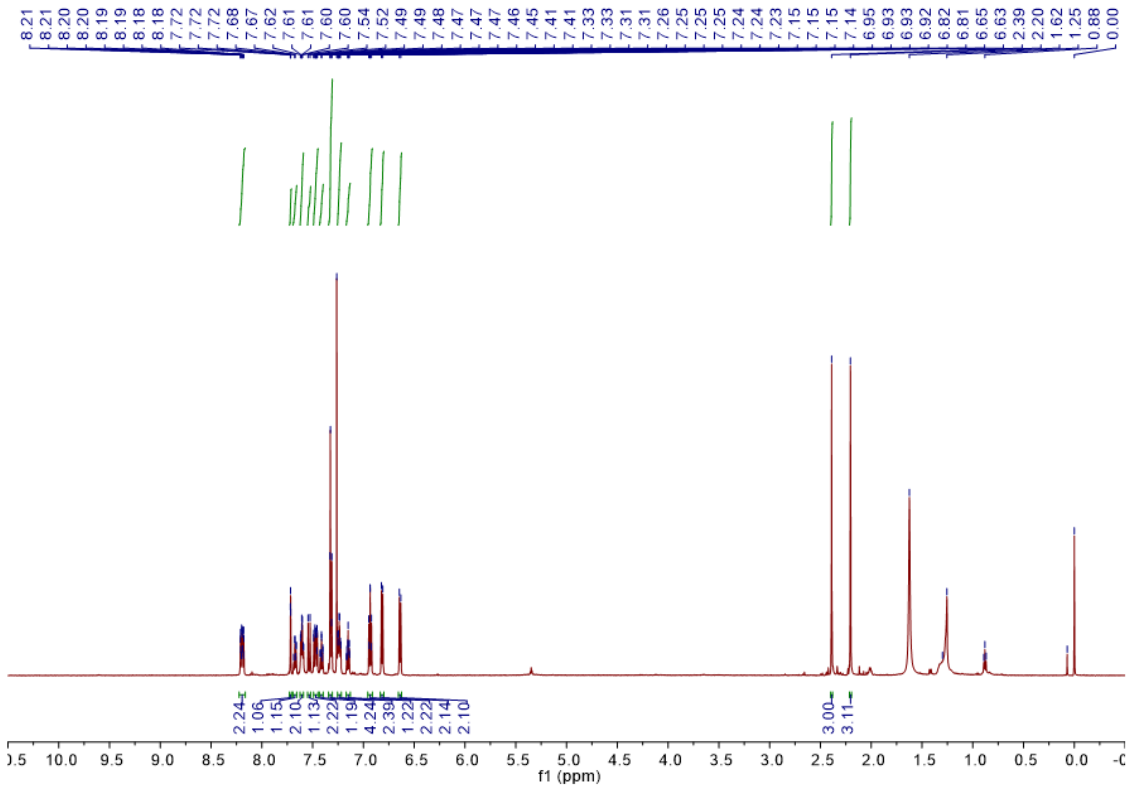
## $^{1}H$ NMR of 56 ($CDCl_3$)



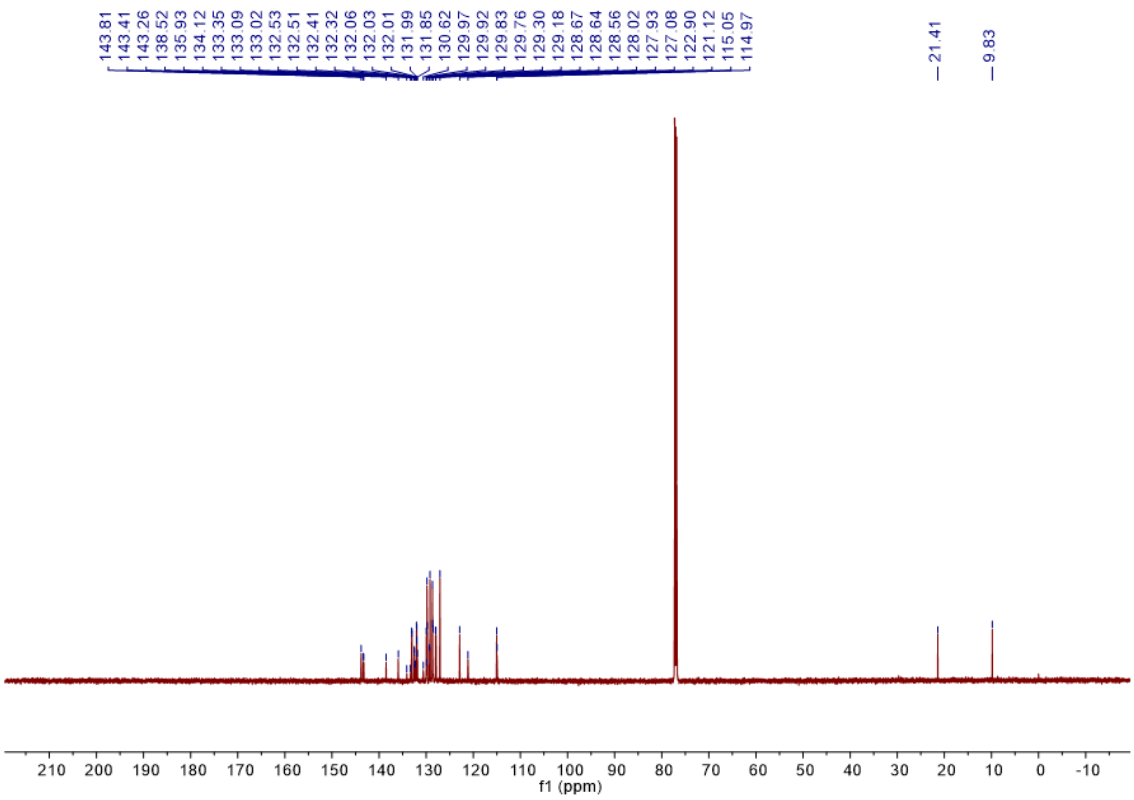
## $^{13}C$ NMR of 56 ($CDCl_3$)



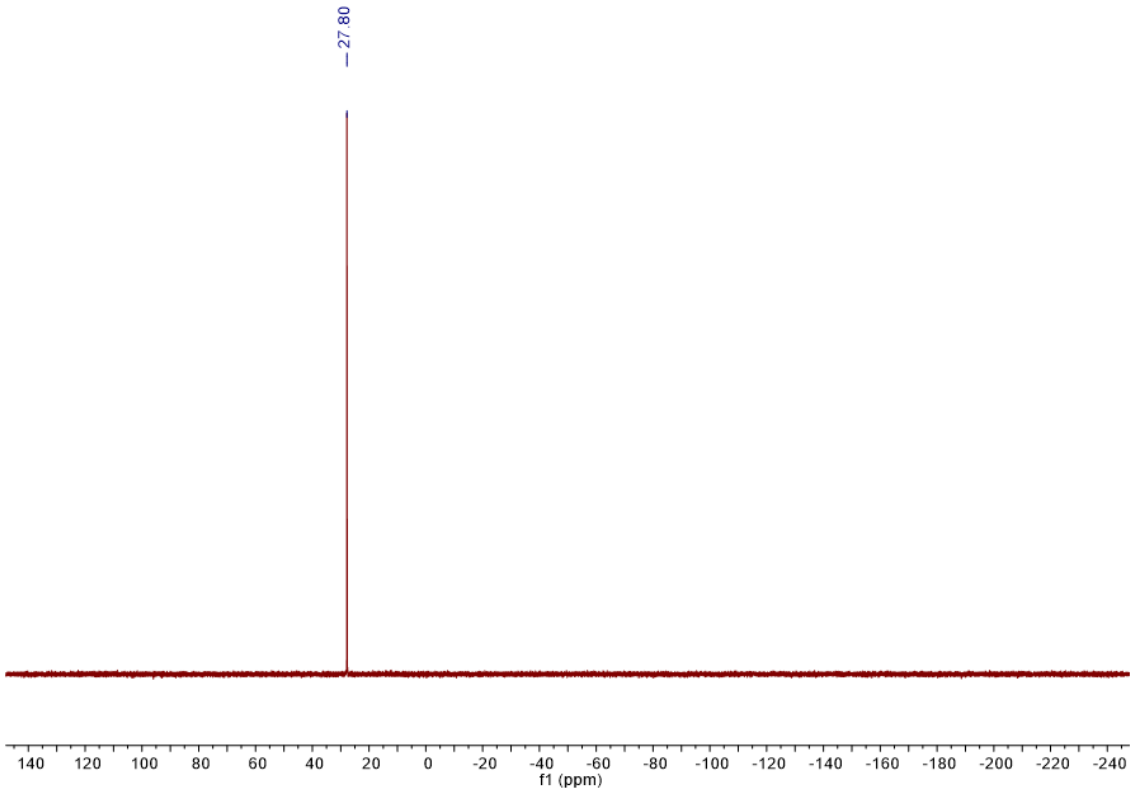

## $^{31}P$ NMR of 56 ($CDCl_3$)



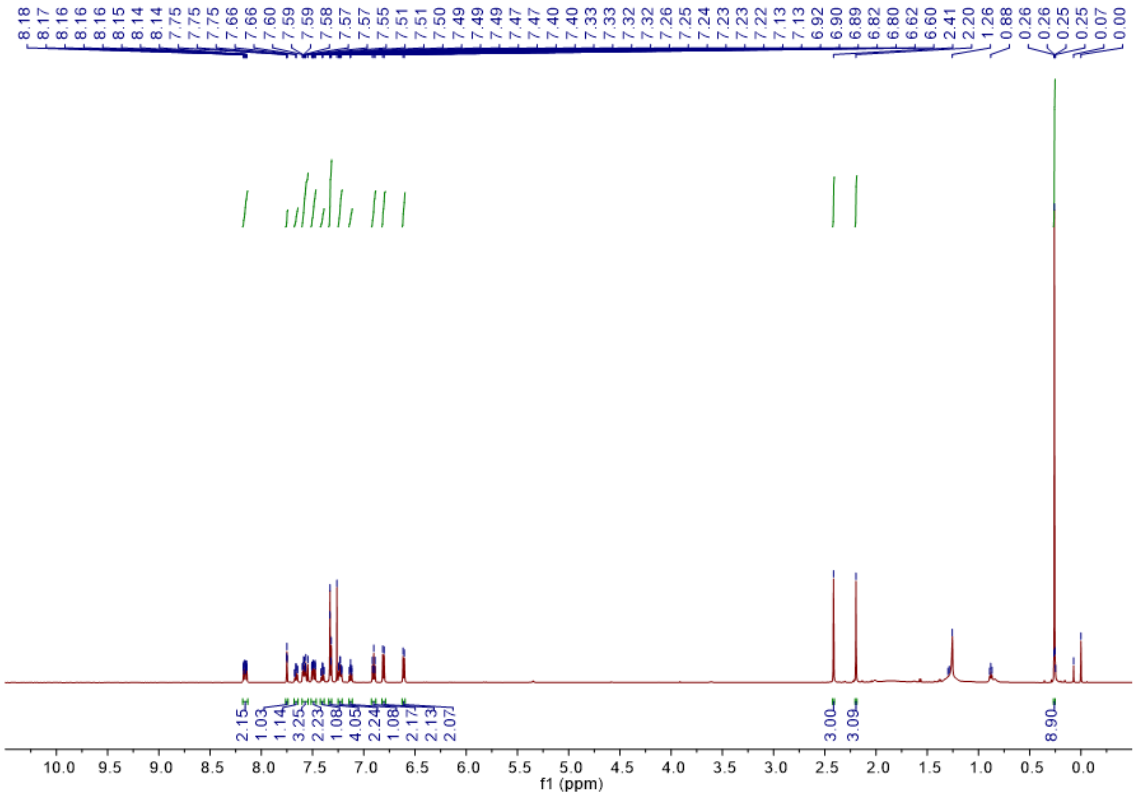
## $^{1}$H NMR of 57 ($CDCl_3$)



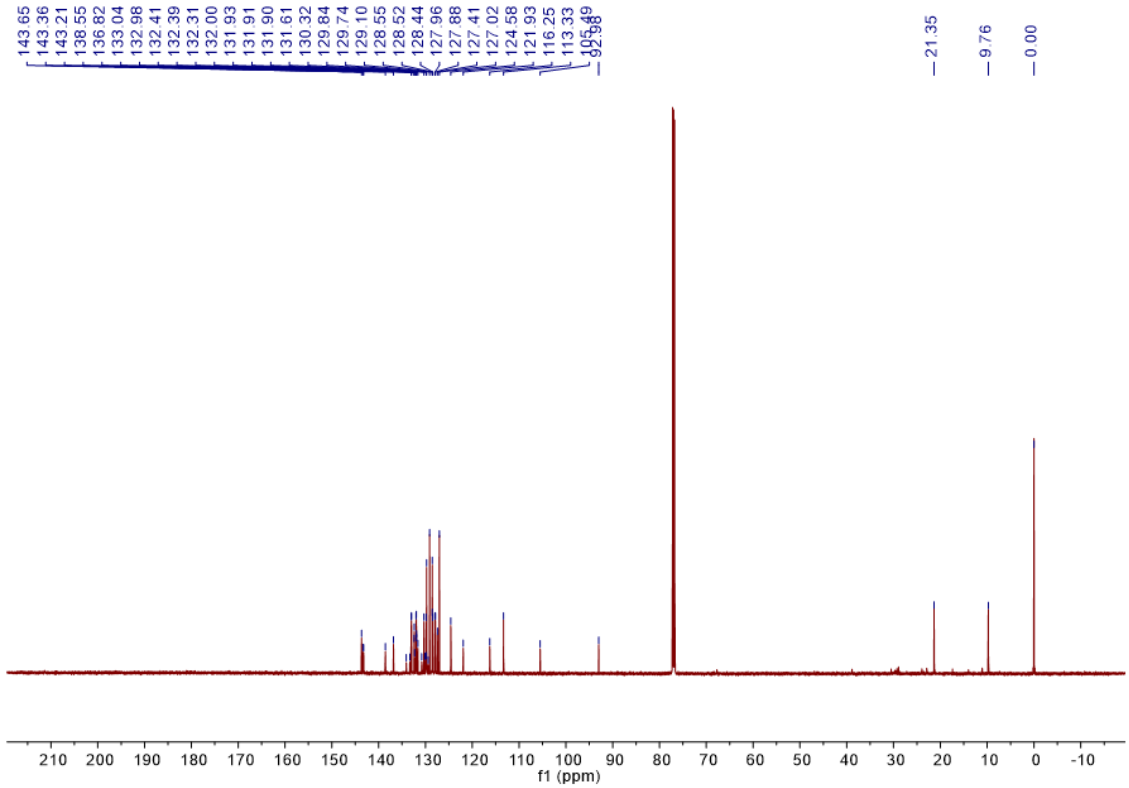

## $^{13}$C NMR of 57 ($CDCl_3$)



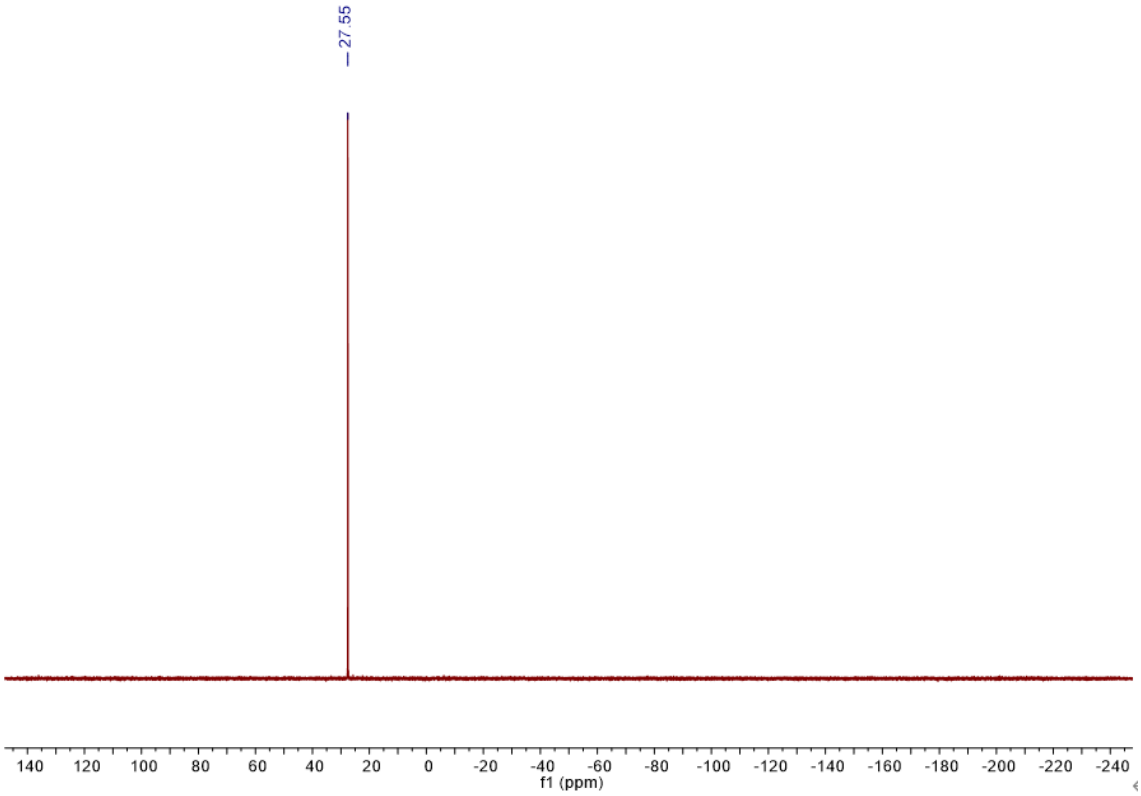
## $^{31}P$ NMR of 57 ($CDCl_3$)



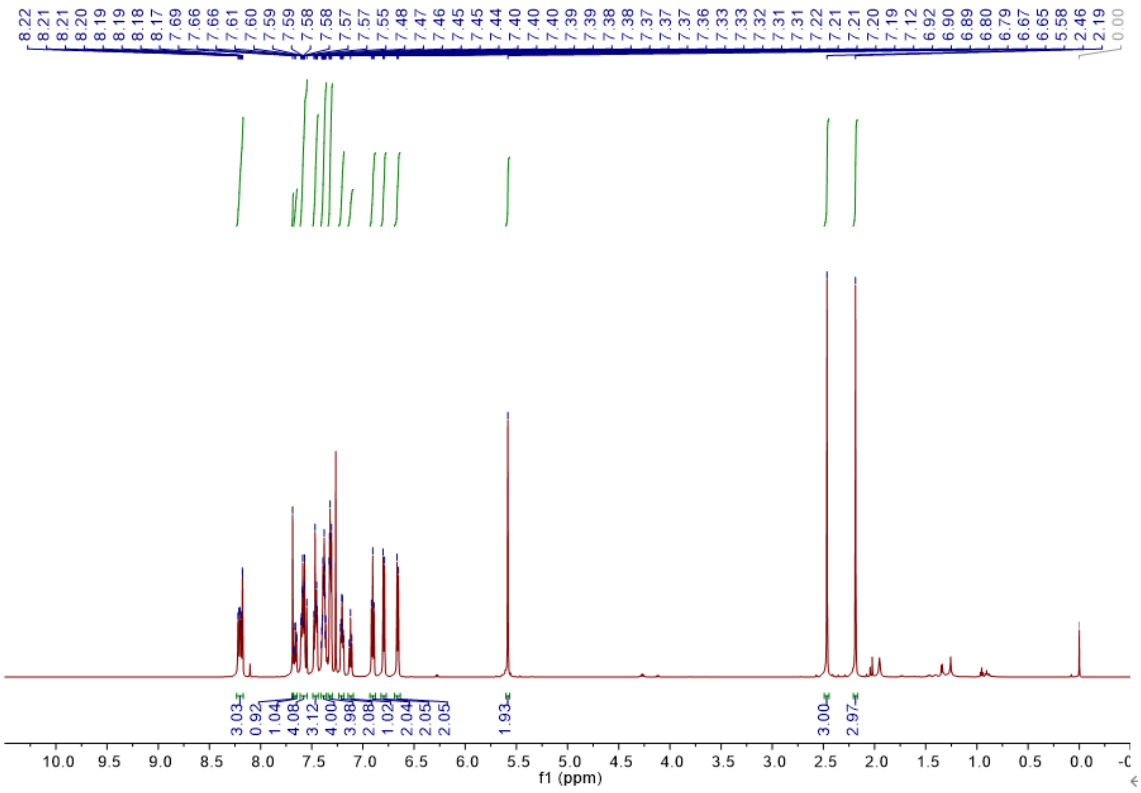
## $^{1}H$ NMR of 58 ($CDCl_3$)



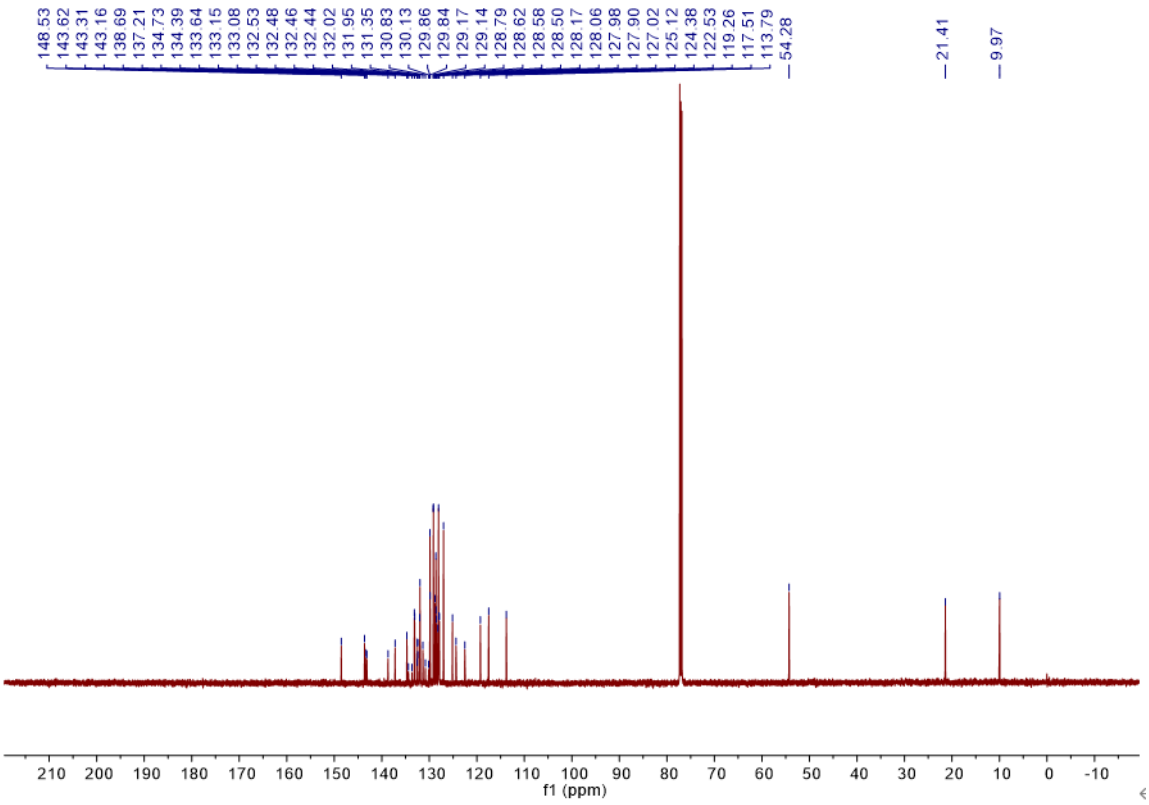
## $^{13}C$ NMR of 58 ($CDCl_3$)



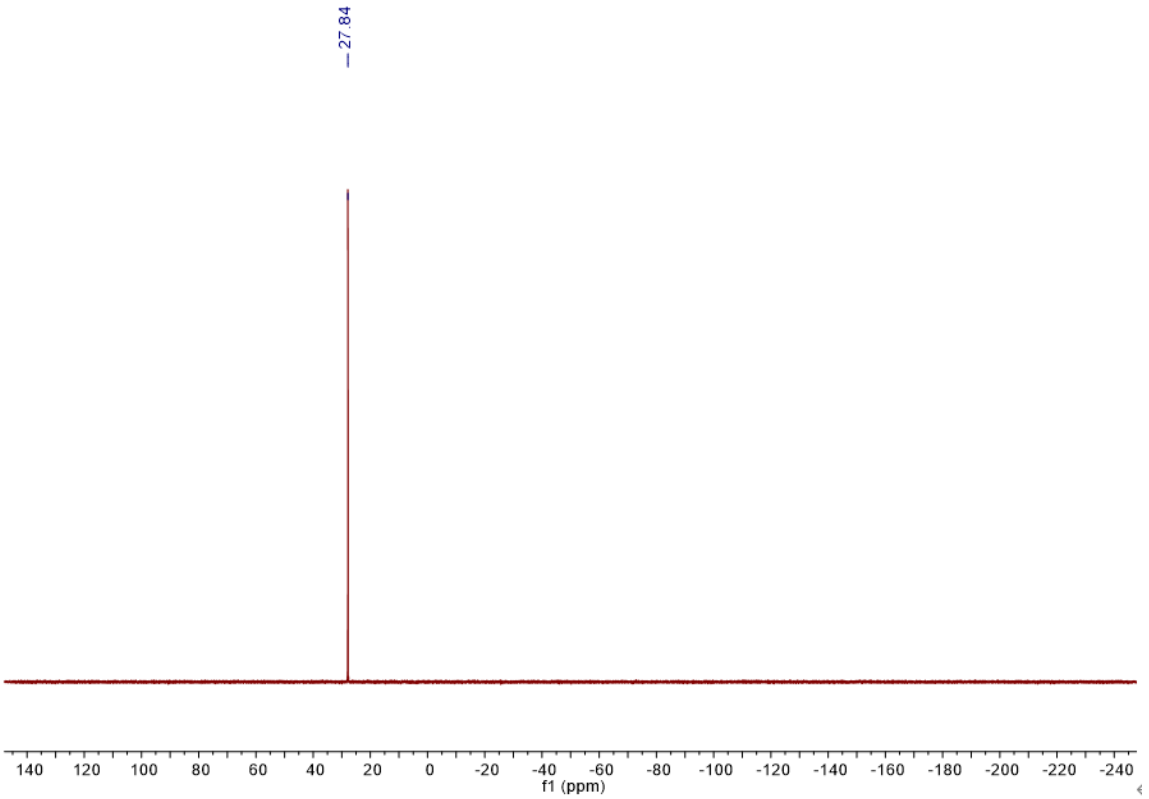

## $^{31}P$ NMR of 58 ($CDCl_3$)



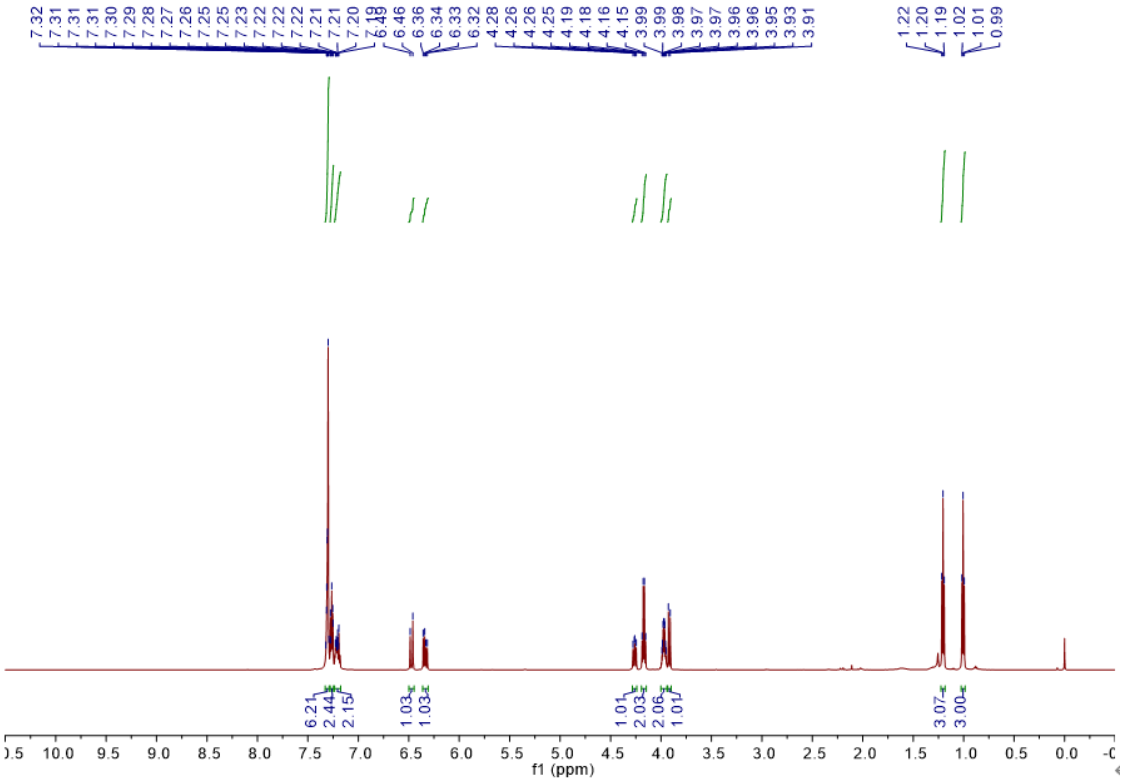
## $^{1}$H NMR of 59' ($CDCl_3$)




## $^{13}$C NMR of 59' ($CDCl_3$)



## $^{31}$P NMR of 59' ($CDCl_3$)




## $^{1}$H NMR of 60 ($CDCl_3$)