# Supporting Information

## A Selective and Stable Tetraphosphite for Rh-catalyzed Linear Hydroaminomethylation of Aliphatic and Aromatic Olefins

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# 1. General information

Unless otherwise mentioned, all the experiments were carried out using standard Schlenk techniques or under inert atmosphere in a glovebox. Anhydrous solvents and amines were purchased from commercial sources (Sigma-Aldrich or TCI) and used without further purification except for toluene, which was dried over $CaH_2$, distilled and stored under inert atmosphere. PE refers to petroleum ether.

**Reagents:** Commercially available reagents and solvents were purchased at the highest commercial quality from Sigma-Aldrich or TCI and were used as received, without further purification, unless otherwise stated.

**Analytical methods:** NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz for $^{1}H$ NMR, 101 MHz for $^{13}C$ NMR and 162 MHz for $^{31}P$ NMR or a Bruker DPX 500 spectrometer at 500 MHz for $^{1}H$ NMR, 126 MHz for $^{13}C$ NMR and 202 MHz for $^{31}P$ NMR in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in ppm and coupling constants were given in Hz. Chemical shifts were reported relative to TMS (0.00 ppm) or $CDCl_3$ (7.26 ppm) for $^{1}H$ NMR and relative to $CDCl_3$ (77.0 ppm) for $^{13}C$ NMR. The following abbreviations were used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad signal .

High-resolution mass spectra (HRMS) were recorded on a Thermo Fisher Q Exactive focus using APCI-TOF (electrospray ionization-time of flight). Samples were introduced to the mass spectrometer ion source by direct injection using a syringe pump and were externally calibrated using sodium formate. The instrument was operating in the positive ion mode.

Reactions were monitored by TLC carried out on 0.25 mm silica gel or neutra-alumina glass plates. Flash column chromatography was carried out using forced flow of the indicated solvent on silica gel (300-400 mesh).

GC analysis was conducted on an Agilent 7890B gas chromatograph using HP-5 column (30 m × 0.32 mm × 0.25 μm) using 2-methoxyethyl ether as internal standard. Ar (99.99%), $N_2$ (99.99%), CO (99.9%) and $H_2$ (99.999%) were purchased from Air Products. All isolated compounds were estimated to be >98% pure as determined by GC and/or NMR.

GS-MS spectroscopy was carried out on a Agilent 7890B-5799A GC/MSD system, with a HP-5ms column (30 m × 0.25 mm × 0.25 μm), injector $T$ = 250 ºC, helium flowrate 15 ml/min.

HPLC analysis was carried out on an Agilent HPLC 1260 Infinity II with CHIRALPAK® IB N-3 column, 285 nm, 30 ºC, n-hexane: EtOH: Ethanolamine = 95: 5: 0.1; flow rate 1.0 mL/min.

**Qualitative analysis for hydroaminomethylation experiments**

Qualitative analysis of the reaction mixtures was carried out on an Agilent 7890B-5799A GC/MSD system coupled with EI source and EM detector. For all olefins, a HP-5ms column (30 m × 0.25 mm × 0.25 μm) was used. Helium was used as carrier gas with a flow of 15 mL/min and a split ratio of 20/1. Table S1 shows the temperature profile for the GC/MSD.

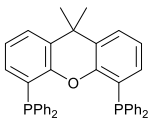
**Table S1.** Oven parameters for GC analysis

| | **Rate [ºC/min]** | **Temperature [ºC]** | **Hold time [min]** |
|---|---|---|---|
| start | - | 35 | 5 |
| ramp 1 | 5 | 150 | 2 |
| ramp 2 | 10 | 250 | 5 |
| ramp 3 | 50 | 320 | 2 |

**Quantitative analysis for hydroaminomethylation experiments**

Quantitative analysis of the reaction mixtures was carried out on an Agilent 7890B gas chromatograph coupled with a Flame Ionization Detector (FID). For all olefins, a HP-5 column (30 m × 0.32 mm × 0.25 μm) was used. Nitrogen was used as carrier gas with a flow of 20 mL/min and a split ratio of 20/1. The temperature profile for the GC is the same as GC/MSD.

**Catalysis**: Ligands (**L4, L5, L6, L7, L2** and **(*R*)-DTBM-C$_3$-TunePhos**) used in this protocol were synthesized according to the procedures reported by our group,[1-5,8] **L3** was synthesized according to a literature method,[6] **L1** was purchased from Sigma-Aldrich (Shanghai) (Figure S1). Rhodium ($Rh(acac)(CO)_2$, $Rh(COD)BF_4$, $Rh(nbd)_2BF_4$, $[Rh(nbd)Cl]_2$, $[Rh(OAc)_2]_2$) and ruthenium ($Ru(OAc)_2$) metal precursors were purchased from J&K Scientific.



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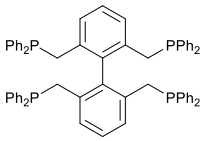
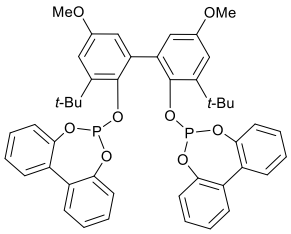
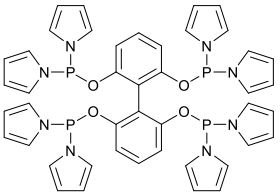


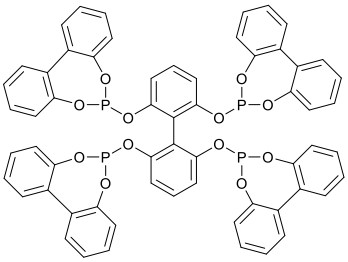
L2



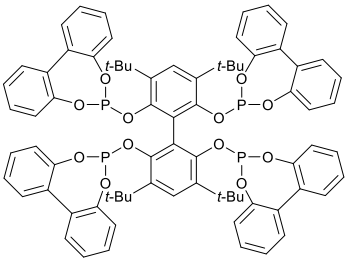
L3



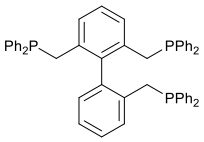
L4



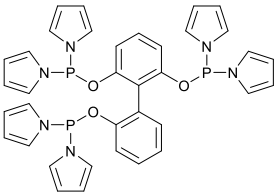
L5



L6



L7



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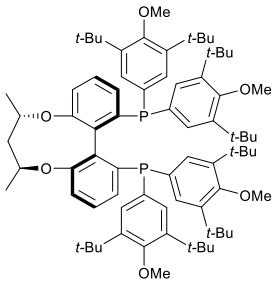
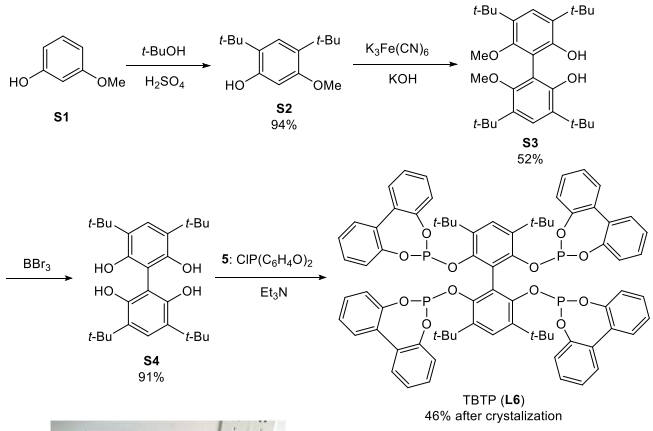
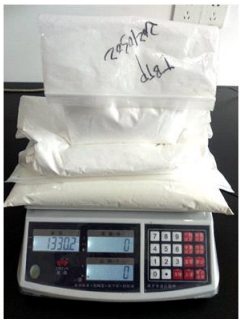


(*R*)-DTBM-$C_3$-TunePhos

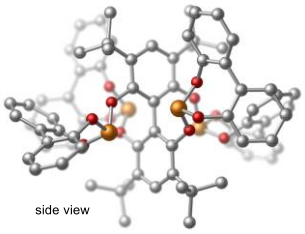
**Figure S1** Structures of tested ligands

## 2. Synthesis of TBTP ligand and substrates



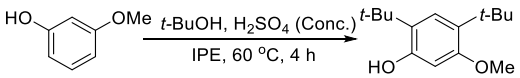
TBTP synthesized in kilgram scale




single crystal structure (CCDC No. 1993523)

2.1 Synthesis of TBTP (**L6**):

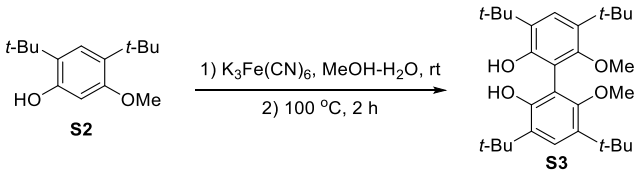
2.1.1 Synthesis of compound **S2**[7]




**S1** **S2**

To a 500 mL flask was added 3-methoxyphenol **S1** (6.2 g, 50 mmol) and 50 mL dry IPE. *t*-BuOH (8.16 g, 110 mmol) was then added dropwise followed by the addition of concentrated $H_2SO_4$ (2.5 mmol). The reaction mixture was allowed to stir at rt for 10 h till completion (TLC). The reaction was diluted by water at 0 °C. The organic layer was extracted with 100 mL EtOAc (x2). The combined organic phase was concentrated under reduced pressure to provide crude product **S2** as light-yellow solid (94% yield, 11.1 g). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 6.27 (s, 1H), 4.69 (s, 1H), 3.78 (s, 3H), 1.40 (s, 9H), 1.35 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ 157.2, 152.7, 129.8, 126.6, 125.4, 101.5, 55.3, 34.6, 34.2, 30.2, 30.2.

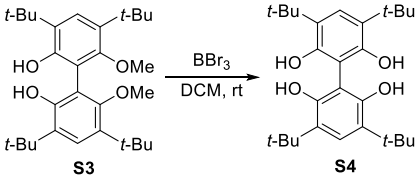
2.1.2 Synthesis of compound **S3**:




**S2** **S3**

To a solution of MeOH (100 mL) in a 500 mL flask of **S2** (6.0 g, 25.4 mmol) was added an aqueous solution of $K_3Fe(CN)_6$ (8.36 g, 25.4 mmol) and KOH (4.58 g, 90.4 mmol), the reaction mixture was allowed to stir at rt for 4 h. The reaction mixture reacted at 100 °C for 2h, and the crude product was crystallized from petroleum ether to afford pure **S3** as white solid (3.1 g, 52%). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 2H), 5.76 (s, 2H), 3.31 (s, 6H), 1.40 (d, *J* = 9.8 Hz, 36H), $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 155.4, 151.4, 134.1, 131.9, 126, 115.0, 59.7, 35.1, 35.0, 31.1, 29.9.

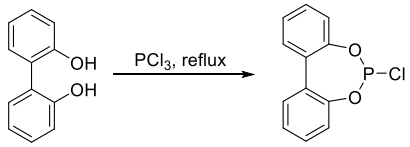
2.1.3 Synthesis of compound **S4**:



**S3** **S4**

To a 100 mL flask containing a DCM (50 mL) solution of crude product **S3** (3.0 g, 6.4 mmol) was added $BBr_3$ (3.51 g, 14.0 mmol). The reaction mixture was allowed to stir at -40 °C for 2 h. The crude product was purified by column chromatography (PE/EA = 50/1) to afford pure **S4** as white solid (2.6 g, 91%). $^1$H NMR (600 MHz, $CDCl_3$): δ = 7.35 (s, 2H), 4.89 (s, 4H), 1.40 (s, 36H), $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 151.2, 128.0, 127.9, 102.4, 34.8, 29.9.

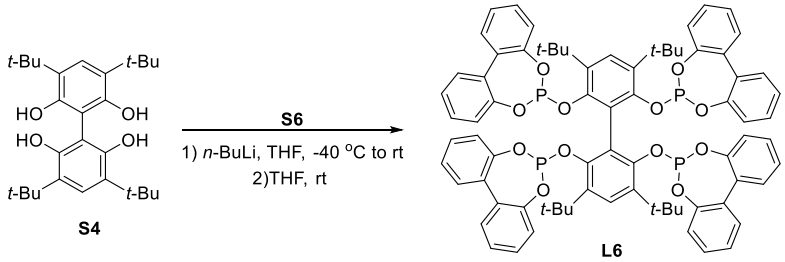
2.1.4 Synthesis of compound **S6**[6]:



**S5** **S6**

A solution of 2,2'-biphenol **S5** (28.1 g, 0.15 mol) in 49 mL phosphorus trichloride was heated at reflux for 2 h. The excess $PCl_3$ was removed by distillation. The residue was purified by vacuum distillation (140-143 °C at 0.5mm Hg) to give 1,1'-biphenyl-2,2'-diyl phosphorochloridite **S6** (30.70 g, 81% yield) (as a clear viscous oil which solidified to give a white solid upon standing at RT in an inert atmosphere for an extended period of time).

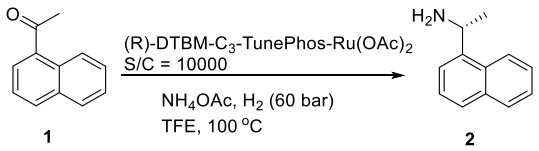
2.1.5 Synthesis of ligand **L6**:



**S4** **L6**

*n*-BuLi (2.82 g, 44 mmol) was added to a solution of **S4** (4.4 g, 10 mmol) in THF (50 ml) at -40 °C. The reaction mixture warmed up to rt for 2 h, and the reaction mixture was added to a solution of **S6** (15.0 g, 60 mmol) in THF (50 ml) dropwise followed by stirring at rt for 10 h till completion (detected by TLC). The reaction mixture was filtered in an inert atmosphere. The filtrate was evaporated under reduced pressure to produce crude solid **L6**. The solid was recrystallized from acetonitrile to give white powder (6.0 g, 46 % yield). $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 7.43-7.35 (m, 12H), 7.32 (d, *J* = 8.1Hz, 2H), 7.22 (tdd, *J* = 6.7, 4.9, 1.6Hz, 15H), 6.88 (dt, *J* = 7.2, 1.5Hz, 5H), 1.84–0.95 (m, 36H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 152.3, 149.6, 134.9, 131.5, 129.5, 128.7, 124.9, 123.4, 35.4, 30.3. $^{31}$P NMR (243 MHz, $CDCl_3$): δ = 144.35; APCI-TOF/HRMS: Calculated for $C_{76}H_{71}O_{12}P_4$ $[M+H]^+$: 1299.3896; Found: 1299.3891.

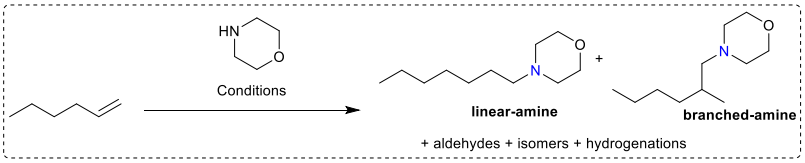
2.2 Asymmetric synthesis of (*R*)-1-(naphthalen-1-yl)ethan-1-amine[8]

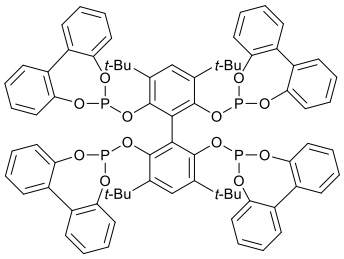



In a glovebox, required amount of the catalyst, 2-acetonaphthone (0.2 mmol), ammonium salt and solvent were successively added to a 5 mL vial equipped with a magnetic stirring bar. The mixture was then transferred to a stain-less autoclave and purged by three cycles of pressurization/venting with $H_2$. The required $H_2$ pressure was then installed and the autoclave was placed in an oil bath preheated to the indicated temperature. The autoclave was cooled down in an ice bath after the indicated reaction time and the pressure was slowly released. Hydrochloric acid (1 mL, 1M) was added to the reaction mixture and the aqueous phase was washed with diethyl ether for three times and basified with sodium hydroxide (0.5 mL, 5 M), followed by extraction with ethyl ether (1 mL x 3). The combined organic phase was dried over sodium sulfate, filtered and evaporated under reduced pressure. The resulting amine product was pure enough and directly subjected to NMR analysis (87%, 0.74 g). The enantiomeric excess was determined by HPLC 1260 II on CHIRALPAK® IB N-3 column, 285 nm, 30 °C, *n*-hexane : EtOH : Ethanolamine = 95: 5: 0.1; flow rate 1.0 mL/min; $t_R$ (minor) = 11.5 min, $t_R$ (major) = 11.9 min. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ = 8.14 (d, *J* = 8.4 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.1 Hz, 1H), 7.58 – 7.43 (m, 3H), 4.97 (q, *J* = 6.6 Hz, 1H), 1.77 (s, 2H), 1.56 (d, *J* = 6.6 Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-*d*) δ = 143.4, 134.0, 130.9, 129.1, 127.4, 126.1, 125.8, 125.6, 123.0, 121.5, 46.6, 24.9.

# 3. Optimization of reaction conditions

## 3.1 **Table S2** Solvent screening for HAM of 1-hexene with TBTP ligand



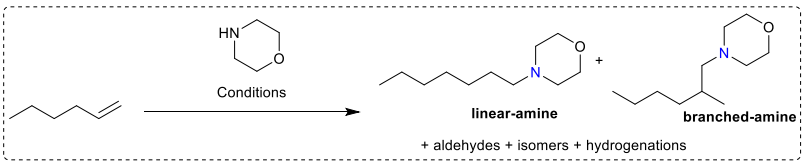



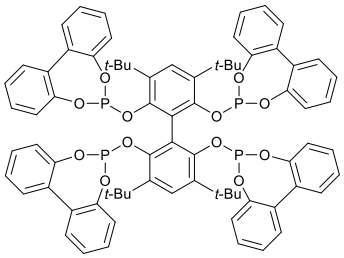

L6: Tetraphosphite-t-Bu (TBTP)

| Entry | Solvent | Conversion [%] | amine select. [%][b] | linear amine yield [%][c] | linear select. [%][d] |
|---|---|---|---|---|---|
| 1 | *i*-PrOH | 99 | 96 | 95 | 97 |
| 2 | Toluene | 100 | 95 | 95 | >99 |
| 3 | PhMe/MeOH=1:1 | 80 | 98 | 78 | 97 |
| 4 | MeOH | 58 | 99 | 57 | 98 |
| 5 | THF | 100 | 96 | 96 | 99 |
| 6 | EtOAc | 99 | 97 | 96 | 99 |
| 7 | EtOH | 99 | 97 | 96 | 79 |
| 8 | Butanol | 95 | 97 | 92 | 99 |
| 9 | PhMe/THF | 99 | 97 | 96 | 99 |
| 10 | Dioxane | 98 | 98 | 96 | 99 |
| 11 | 2-butanol | 98 | 97 | 95 | 99 |

Reaction conditions: olefin (1 mmol), amine (1 mmol), $Rh(acac)(CO)_2$ (1 µmol), TBTP (4 µmol), toluene (3 mL). *P*($CO/H_2$= 10:30 bar), time= 2 h, T= 100 ºC. Amine selectivity and yield were determined by GC analysis. 2-methoxyethyl ether (0.1 mL) was used as internal standard, no hydrogenation products were detected. [b] Amine selectivity: percentage of linear and branched amines from the reaction products including isomerized alkenes, aldehydes and hydrogenation productions, determined by GC; [c] Isolated yield of linear-amine; [d] Percentage of linear amine in all amines.

**3.2 Table S3** Optimization for the HAM of 1-hexene with morpholine.[a]



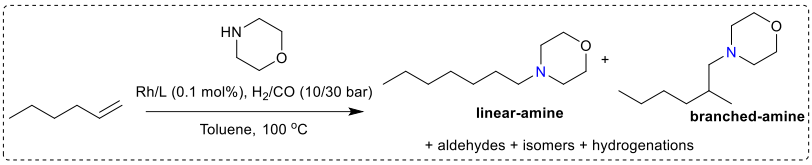



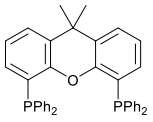

L6: Tetraphosphite-t-Bu (TBTP)

| Entry | $P_{CO/H2}$ [bar] | temp. [°C] | *t* [h] | L/Rh | conv. [%] | amine select. [%][b] | linear amine yield [%][c] | linear select. [%][d] |
|---|---|---|---|---|---|---|---|---|
| 1 | 20:10 | 100 | 6 | 4 | 99.9 | 85.2 | 33.0 | 93.7 |
| 2 | 10:10 | 100 | 6 | 4 | 99.7 | 93.7 | 47.0 | 96.7 |
| 3 | 10:20 | 100 | 6 | 4 | 99.6 | 95.8 | 85.5 | 99.4 |
| 4 | 10:30 | 100 | 6 | 4 | 99.7 | 97.0 | 92.6 | 99.2 |
| 5 | 5:20 | 100 | 6 | 4 | 99.7 | 96.2 | 63.2 | 97.6 |
| 6 | 5:25 | 100 | 6 | 4 | 99.2 | 94.8 | 91.8 | 95.8 |
| 7 | 5:30 | 100 | 6 | 4 | 99.3 | 93.3 | 84.0 | 96.8 |
| 8[e] | 10:30 | 100 | 2 | 4 | 99.6 | 97.3 | 91.1 | 99.9 |
| 9 | 10:30 | 100 | 2 | 3 | 99.6 | 96.7 | 93.0 | 99.2 |
| 10 | 10:30 | 100 | 2 | 2 | 99.8 | 96.9 | 92.3 | 99.1 |
| 11 | 10:30 | 100 | 0.5 | 4 | 97.6 | 65.4 | 53.4 | 99.9 |
| 12 | 10:30 | 100 | 1 | 4 | 99.0 | 97.5 | 89.8 | 99.9 |
| 13 | 10:30 | 100 | 4 | 4 | 99.0 | 96.0 | 91.7 | 99.3 |
| 14 | 10:30 | 100 | 8 | 4 | 99.8 | 90.3 | 82.3 | 98.9 |
| 15 | 10:30 | 80 | 2 | 4 | 85.5 | 94.7 | 75.1 | 99.9 |
| 16 | 10:30 | 90 | 2 | 4 | 99.5 | 97.4 | 91.1 | 99.9 |
| 17 | 10:30 | 110 | 2 | 4 | 99.8 | 97.2 | 92.8 | 98.4 |
| 18 | 10:30 | 120 | 2 | 4 | 99.8 | 97.7 | 96.9 | 98.2 |

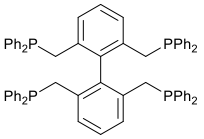
[a] Reaction conditions: 1-hexene (2 mmol), amine (2 mmol), $Rh(acac)(CO)_2$ (1 μmol), TBTP (4 μmol), toluene (3 mL). Amine selectivity and yield were determined by GC analysis. 2-methoxyethyl ether (0.1 mL) was used as internal standard; [b] Amine selectivity: percentage of linear and branched amines from the reaction products including isomerized alkenes, aldehydes and hydrogenation productions, determined by GC; [c] Isolated yield of linear-amine; [d] Percentage of linear amine in all amines; [e] entries 11-18: S/C=1000.

**3.3 Table S4** Evaluation of various ligands for the HAM of 1-hexene with morpholine.[a]

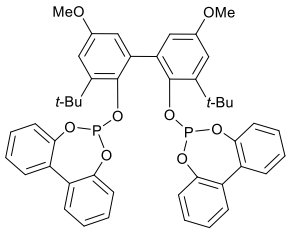


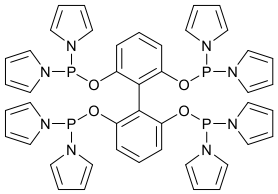

L1



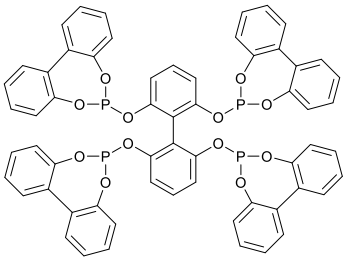

L2



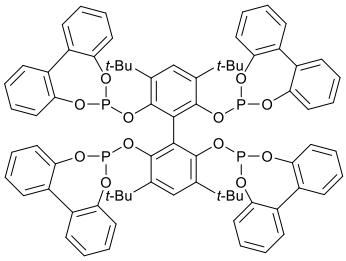

L3



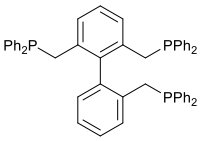

L4



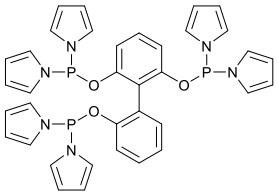

L5




L6




L7




L8

| Entry | ligand | conv. [%] | amine select. [%][b] | linear amine yield [%][c] | linear select. [%][d] |
|---|---|---|---|---|---|
| 1 | L1 | 99.0 | 90.5 | 86.3 | 99.9 |
| 2 | L8 | 97.5 | 89.3 | 75.6 | 99.9 |
| 3 | L4 | 83.7 | 99.1 | 12.6 | 99.9 |
| 4 | L5 | 20.7 | 75.4 | 12.4 | 61.2 |
| 5 | L6 | 99.0 | 97.5 | 89.8 | 99.9 |
| 6 | L1 | 49.3 | 87.7 | 34.3 | 99.9 |
| 7 | L7 | 30.9 | 91.6 | 25.7 | 99.9 |
| 8 | L2 | 46.4 | 94.9 | 35.4 | 99.9 |

[a] Reaction conditions: $CO/H_2$ = 10 : 30 bar, 1-hexene (1 mmol), morpholine (1 mmol), $Rh(acac)(CO)_2$ (1μmol), ligand (0.4 μmol),toluene (3 mL), *T* = 100 °C, t = 1 h. [b] Amine selectivity: percentage of linear and branched amines from the reaction products including isomerized alkenes, aldehydes and hydrogenation productions, determined by GC; [c] Isolated yield of linear-amine; [d] Percentage of linear amine in all amines.

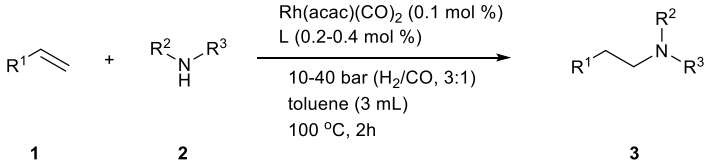
**3.4 Table S5** Time courses of 1-hexene HAM with TBTP ligand at S/C = 10000

| **Entry** | **Time [h]** | **Conversion [%]** | **Amine Selectivity [%]** | **Linear Selectivity [%]** |
|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 0 |
| 2 | 0.5 | 60.3 | 92.7 | 99.9 |
| 3 | 1 | 88.4 | 93.2 | 99.9 |
| 4 | 2 | 96.8 | 99.9 | 99.9 |
| 5 | 4 | 99.8 | 97.3 | 99.7 |
| 6 | 6 | 99.9 | 96.8 | 99.7 |

Reaction conditions: olefin (10 mmol), amine (10 mmol), $Rh(acac)(CO)_2$ (1 µmol), TBTP (4 µmol), toluene (3 mL), *P*($CO/H_2$= 10:30 bar), T= 100 °C. Amine selectivity and yield were determined by GC analysis. 2-methoxyethyl ether (0.1 mL) was used as internal standard, no hydrogenation products were detected.

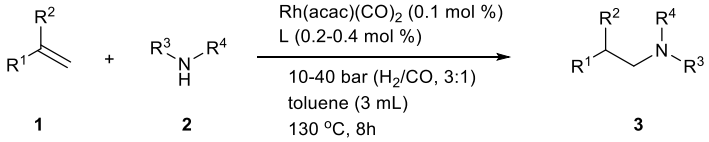
## 4. General procedures for Rh-catalyzed HAM with amines

**General procedure A** : rhodium-catalyzed HAM of monosubstituted terminal olefins with amines.



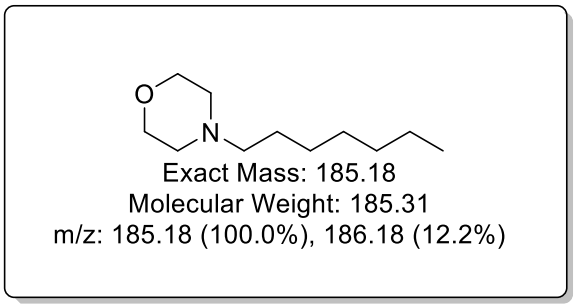

A 5 mL glass vial with a magnetic stirring bar was charged with $Rh(acac)(CO)_2$ (0.001 mmol) with tetraphosphite ligand **L6** (0.004 mmol) in 0.1 mL toluene. The mixture was stirred for 15 min. Olefins (1 mmol) and morpholine (1 mmol) was then added, followed by the addition of 2-methoxyethyl ether (1mmol) as internal standard. Additional toluene was added to bring the total reaction volume to 3 mL. The reaction mixture was transferred to an autoclave. The autoclave was purged with hydrogen three times and subsequently charged with $H_2$ (30 bar) and CO (10 bar). The autoclave was then immersed in a preheated oil bath (100 ℃) and left stirring at 1000 rpm. After desired time, the autoclave was cooled in an ice-water bath, and the pressure was carefully released in a well-ventilated hood. The reaction mixture was immediately analyzed by GC to determine conversion and regioselectivity prior to the further purification on column chromatography.

**General procedure B** : rhodium-catalyzed HAM of disubstituted terminal olefins with amines.

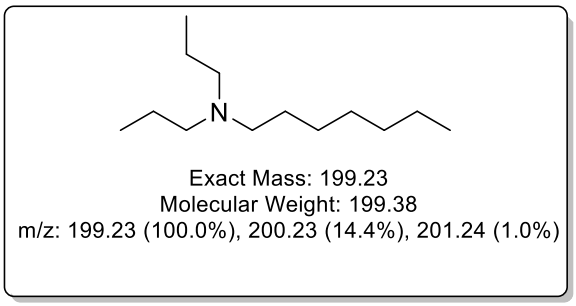



A 5mL glass vial with a magnetic stirring bar was charged with $Rh(acac)(CO)_2$ (0.001 mmol) with tetraphosphite ligand **L6** (0.004 mmol) in 0.1 mL toluene. The mixture was stirred for 15 min. Olefins (1 mmol) and morpholine (1 mmol) was then added, followed by the addition of 2-methoxyethyl ether (1 mmol) as internal standard. Aditional toluene was added to bring the total reaction volume to 3 mL. The reaction mixture was transferred to an autoclave. The autoclave was purged with hydrogen three times and subsequently charged with $H_2$ (30 bar) and CO (10 bar). The autoclave was then immersed in a preheated oil bath (130 ℃) and left stirring at 1000 rpm. After desired time, the autoclave was cooled in an ice-water bath, and the pressure was carefully released in a well-ventilated hood. The reaction mixture was immediately analyzed by GC to determine conversion and regioselectivity prior to the further purification on column chromatography.

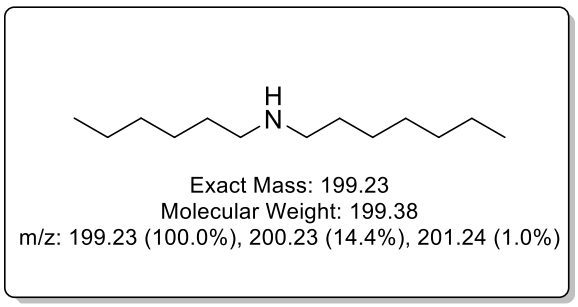
## 5. Characterization data for the synthesized amines



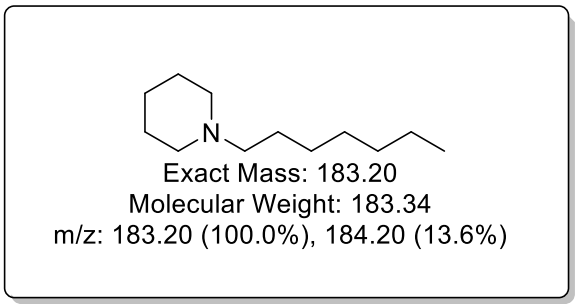

**4-heptylmorpholine (5-1[9]),** clear viscous oil, purified on chromatography by gradient elution (PE/Ethyl acetate = 1:1, Ethyl acetate, then 1% MeOH in Ethyl acetate with 0.1% $Et_3N$). The $^1H$ NMR and $^{13}C$ NMR data obtained corresponded to the literature.[9] ESI-MS, Calcd for$[M+H]^+$: 186.18, found: 186.24.



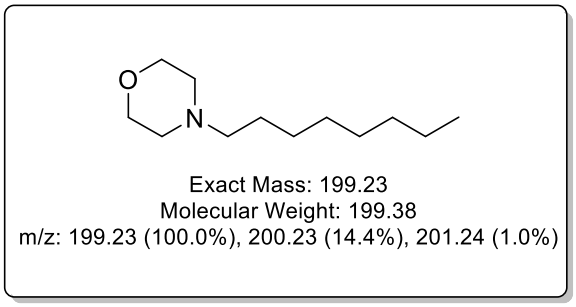

***N,N*-dipropylheptan-1-amine (5-2),** off-white solid, purified on chromatography by gradient elution (PE/Ethyl acetate = 1:1, Ethyl acetate, then 1% MeOH in Ethyl acetate with 0.1% $Et_3N$). $^1H$ NMR ($CDCl_3$, 400 MHz): δ = 2.69 (ddt, *J* = 12.2, 9.3, 4.7 Hz, 6H), 1.63 – 1.55 (m, 3H), 1.11 – 0.94 (m, 11H), 0.74 (t, *J* = 7.3 Hz, 6H), 0.64 – 0.59 (m, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) δ: = 54.1, 52.5, 31.7, 28.8, 27.0, 23.2, 22.6, 17.0, 14.1, 11.4. ESI-MS, Calcd for $[M+H]^+$: 200.38, found: 200.34.



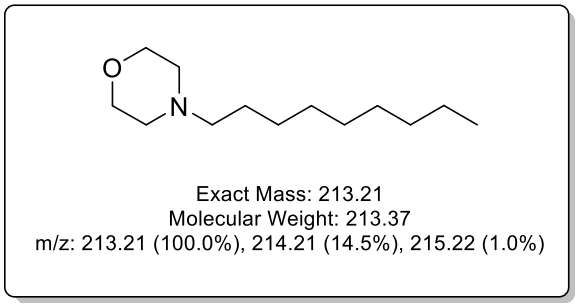

**N-hexylheptan-1-amine (5-3),** clear viscous oil, purified on chromatography by gradient elution (PE/Ethyl acetate = 1:1, Ethyl acetate, then 1% MeOH in Ethyl acetate with 0.1% $Et_3N$). $^1H$ NMR ($CDCl_3$, 400 MHz) δ: 2.82 – 2.57 (m, 4H), 1.33 – 1.20 (m, 19H), 0.88 – 0.85 (m, 6H).; $^{13}C$ NMR ($CDCl_3$, 100 MHz) δ: 49.2, 31.8, 31.7, 29.1, 28.4, 28.3, 27.3, 27.0, 22.7, 22.7, 14.1, 14.1. ESI-MS, Calcd for $[M+H]^+$: 200.38, found: 200.23.



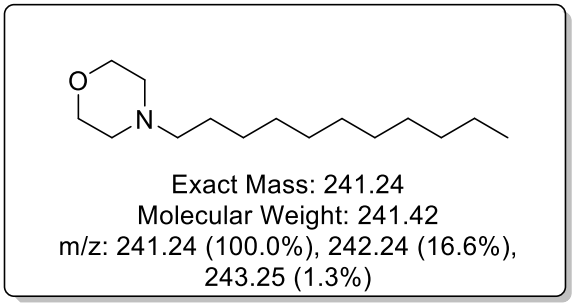

**1-heptylpiperidine (5-4[10]),** clear viscous oil , purified on chromatography by gradient elution (PE/Ethyl acetate = 1:1, Ethyl acetate, then 1% MeOH in Ethyl acetate with 0.1% $Et_3N$). The $^1H$ NMR and $^{13}C$ NMR data obtained corresponded to the literature.[10] ESI-MS, Calcd for $[M+H]^+$: 184.20, found: 185.26.



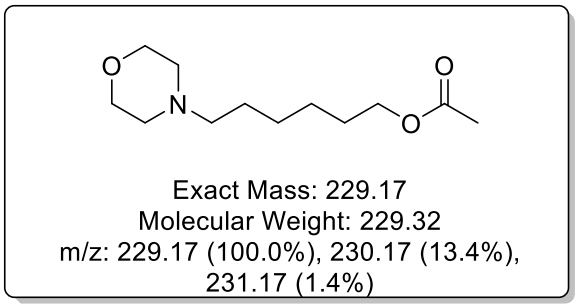

**4-octylmorpholine (5-5[11]),** clear viscous oil, purified on chromatography by gradient elution (PE/Ethyl acetate = 1:1, Ethyl acetate, then 1% MeOH in Ethyl acetate with 0.1% $Et_3N$). The $^1H$ NMR and $^{13}C$ NMR data obtained corresponded to the literature.[11] ESI-MS, Calcd for$[M+H]^+$: 200.38, found: 200.24.



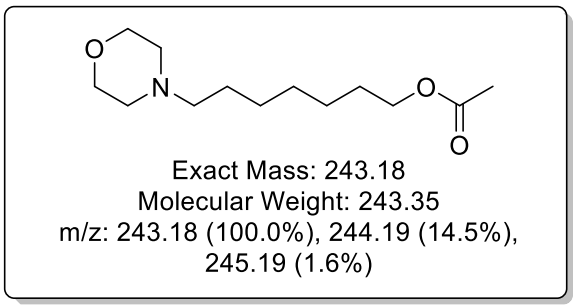

**4-nonylmorpholine (5-6[12]),** clear viscous oil, purified on chromatography by gradient elution (PE/Ethyl acetate = 1:1, Ethyl acetate, then 1% MeOH in Ethyl acetate with 0.1% $Et_3N$). The $^1H$ NMR and $^{13}C$ NMR data obtained corresponded to the literature.[12] ESI-MS, Calcd for$[M+H]^+$: 214.37, found: 214.25.



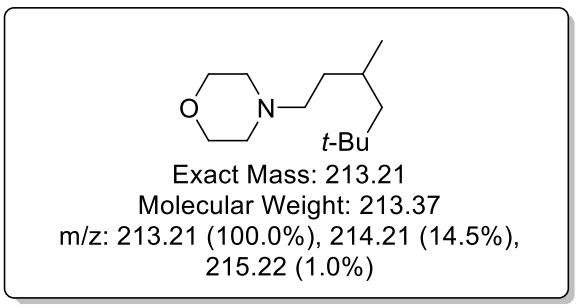
**4-undecylmorpholine (5-7[13]),** clear viscous oil, purified on chromatography by gradient elution (PE/Ethyl acetate = 1:1, Ethyl acetate, then 1% MeOH in Ethyl acetate with 0.1% $Et_3N$). The $^1H$ NMR and $^{13}C$ NMR data obtained corresponded to the literature [13]. ESI-MS, Calcd for$[M+H]^+$: 242.42, found: 242.35.



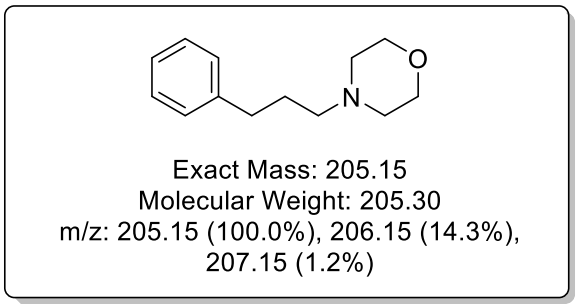

**4-(6-(prop-1-en-2-yloxy)hexyl)morpholine (5-8),** light yellow oil, purified on chromatography by gradient elution (PE/Ethyl acetate= 1:1, Ethyl acetate, then 1% MeOH in Ethyl acetate with 0.1% $Et_3N$). $^1H$ NMR ($CDCl_3$, 400 MHz) δ: 4.03 (t, *J* = 6.7 Hz, 2H), 3.80 – 3.73 (m, 4H), 2.54 – 2.45 (m, 4H), 2.42 – 2.33 (m, 2H), 2.02 (s, 3H), 1.67 – 1.48 (m, 4H), 1.41 – 1.28 (m, 4H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) δ: = 171.4, 66.6, 64.6, 59.0, 53.6, 28.6, 27.1, 26.1, 25.9, 21.1. ESI-MS, Calcd for$[M+H]^+$: 230.32, found: 230.20.



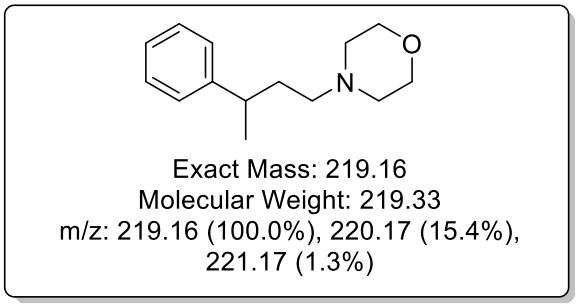

**7-morpholinoheptyl acetate (5-9),** light yellow oil, purified on chromatography by gradient elution (PE/Ethyl acetate = 1:1, Ethyl acetate, then 1% MeOH in Ethyl acetate with 0.1% $Et_3N$). $^1H$ NMR ($CDCl_3$, 400 MHz) δ: 4.04 (t, *J* = 6.7 Hz, 2H), 3.76 (t, *J* = 4.4 Hz, 4H), 2.52 (t, *J* = 4.6 Hz, 4H), 2.43 (t, *J* = 7.4 Hz, 2H), 2.04 (s, 3H), 1.66 – 1.55 (m, 4H), 1.42 – 1.27 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) δ: 172.3, 66.8, 64.6, 53.8, 40.5, 28.9, 28.6, 25.9, 23.69, 21.1. ESI-MS, Calcd for$[M+H]^+$: 244.35, found: 244.23.



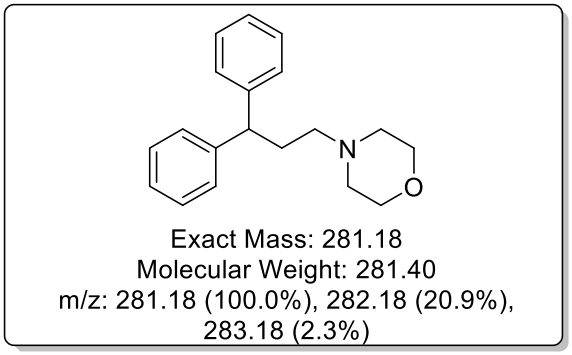
**4-(3,5,5-trimethylhexyl)morpholine (5-10),** light yellow oil, purified on chromatography by gradient elution (PE/Ethyl acetate = 1:1, Ethyl acetate, then 1% MeOH in Ethyl acetate with 0.1% $Et_3N$). $^1H$ NMR ($CDCl_3$, 400 MHz) δ: 3.80 – 3.68 (m, 4H), 2.50 (t, *J* = 4.7 Hz, 4H), 2.43 – 2.33 (m, 2H), 1.57 – 1.44 (m, 2H), 1.37 (tdd, *J* = 9.7, 6.9, 3.9 Hz, 1H), 1.25 – 1.15 (m, 2H), 1.05 (dd, *J* = 14.0, 6.1 Hz, 1H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (s, 9H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) δ: 66.7, 57.3, 53.7, 51.4, 35.6, 31.2, 30.1, 27.8, 22.9. ESI-MS, Calcd for$[M+H]^+$: 214.37, found: 214.25.



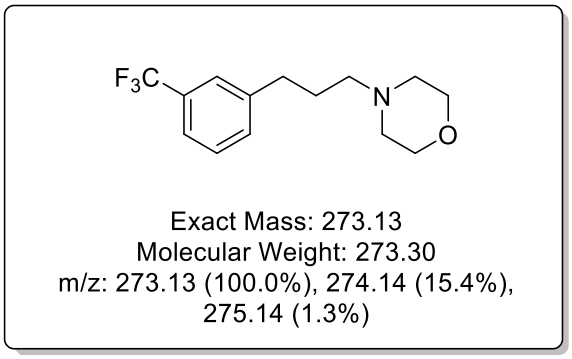

**4-(3-phenylpropyl)morpholine (5-11[14]),** light yellow oil, purified on chromatography by gradient elution (PE/ Ethyl acetate= 1:1, Ethyl acetate, then 1% MeOH in Ethyl acetate with 0.1% $Et_3N$). The $^1H$ NMR and $^{13}C$ NMR data obtained corresponded to the literature.[14] ESI-MS, Calcd for$[M+H]^+$: 206.30, found: 206.15.



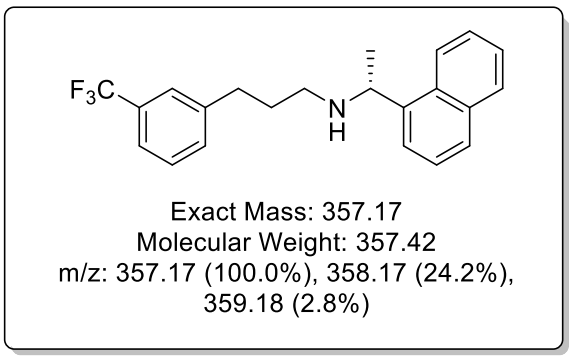

**4-(3-phenylbutyl)morpholine (5-12[15]),** light yellow oil, purified on chromatography by gradient elution (PE/Ethyl acetate = 1:1, Ethyl acetate, then 1% MeOH in Ethyl acetate with 0.1% $Et_3N$). The $^1H$ NMR and $^{13}C$ NMR data obtained corresponded to the literature.[15] ESI-MS, Calcd for$[M+H]^+$: 220.36, found: 220.20.



**4-(3,3-diphenylpropyl)morpholine (5-13[16]),** light yellow oil, purified on chromatography by gradient elution (PE/Ethyl acetate = 1:1, Ethyl acetate, then 1% MeOH in Ethyl acetate with 0.1% $Et_3N$). The $^1H$ NMR and $^{13}C$ NMR data obtained corresponded to the literature.[16] ESI-MS, Calcd for$[M+H]^+$: 282.40, found: 282.18.




**4-(3-(3-(trifluoromethyl)phenyl)propyl)morpholine (5-14),** light yellow oil, purified on chromatography by gradient elution (PE/Ethyl acetate = 1:1, Ethyl acetate, then 1% MeOH in Ethyl acetate with 0.1% $Et_3N$). $^1H$ NMR ($CDCl_3$, 400 MHz) δ: 7.19 (dd, *J* = 4.7, 2.0 Hz, 2H), 7.14 – 7.10 (m, 2H), 3.56 (s, 4H), 2.47 (t, *J* = 7.7 Hz, 2H), 2.37 (s, 2H), 2.28 (s, 2H), 1.70 (s, 4H); $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 132.0, 129.0, 125.3, 123.1, 66.1, 57.9, 53.3, 32.1, 29.9. ESI-MS, Calcd for$[M+H]^+$: 274.14, found: 274.18.




**(*R*)-*N*-(1-(naphthalen-1-yl)ethyl)-3-(3-(trifluoromethyl)phenyl)propan-1-amine (Cinacalcet),** light yellow oil, purified on chromatography by gradient elution (2.55 g, 71.1% yield, >99% ee)**.** The enantiomeric excess was determined by HPLC 1260 on CHIRALPAK® IA column, 280 nm, 35 °C, *n*-hexane : EtOH : trifluoroacetic = 96: 4: 0.1; flow rate 1.0 mL/min; $t_R$ (minor) = 8.0 min, $t_R$ (major) = 9.9 min. $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.13 (m, 1H), 7.92 – 7.84 (m, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.55 – 7.45 (m, 3H), 7.40 (d, *J* = 9.3 Hz, 2H), 7.31 (q, *J* = 7.6 Hz, 2H), 4.85 – 4.60 (m, 1H), 2.76 – 2.55 (m, 4H), 1.88 (dd, *J* = 10.0, 5.0 Hz, 2H), 1.55 (d, *J* = 6.6 Hz, 3H).$^{13}C$ NMR (151 MHz, $CDCl_3$) δ 143.0, 134.1, 131.9, 131.4 130.8, 130.6, 129.2, 128.8, 127.6, 126.1, 125.9, 125.6,

125.2, 125.2, 123.1, 122.8, 122.8, 53.7, 47.2, 33.5, 29.9, 23.4. ESI-MS, Calcd for$[M+H]^+$: 358.17, found: 358.17.

## 6. Correction factors for olefins and decane (internal standard)

$$\frac{n_s}{n_p} = \frac{M_p}{M_s}\frac{f_s}{f_p}\frac{A_s}{A_p}$$

$$\frac{n_s}{n_p} = K\frac{A_s}{A_p}$$

$n_s$– molar amount of decane

$n_p$– molar amount of olefin

$M_s$ –molecular weight of decane

$M_p$ – molecular weight of olefin

$A_s$ – peak area of decane

$A_p$ – peak area of olefin

$K$ – correction factor

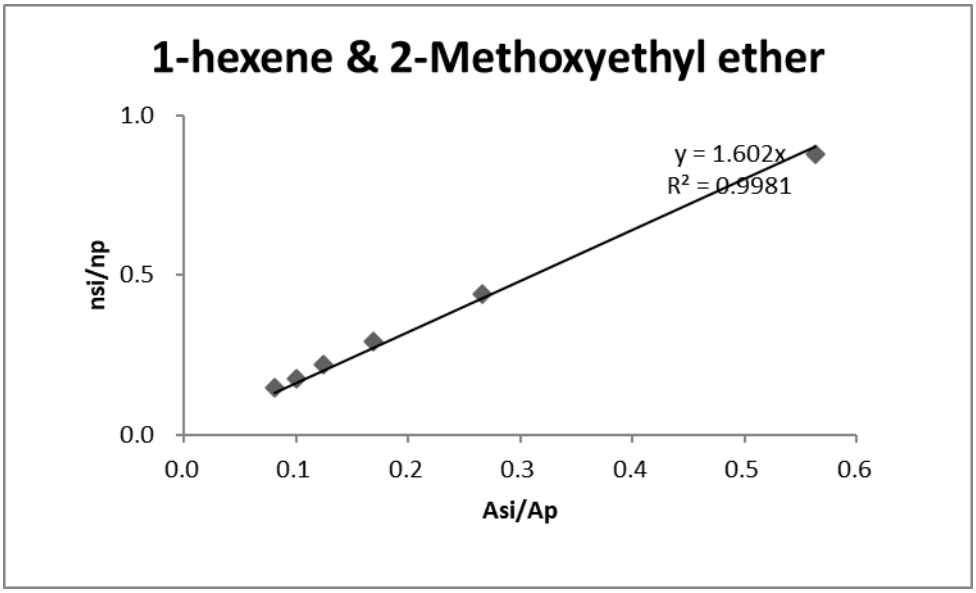



Figure S2. Correction factor ($K$) for 1-hexene & 2-Methoxyethyl ether

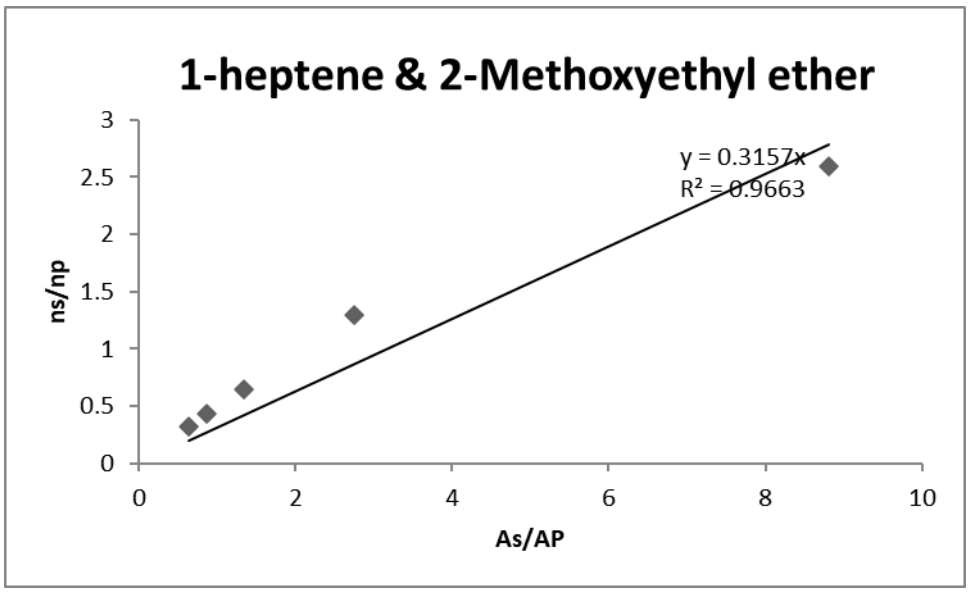



Figure S3. Correction factor (K) for 1-heptene & 2-Methoxyethyl ether

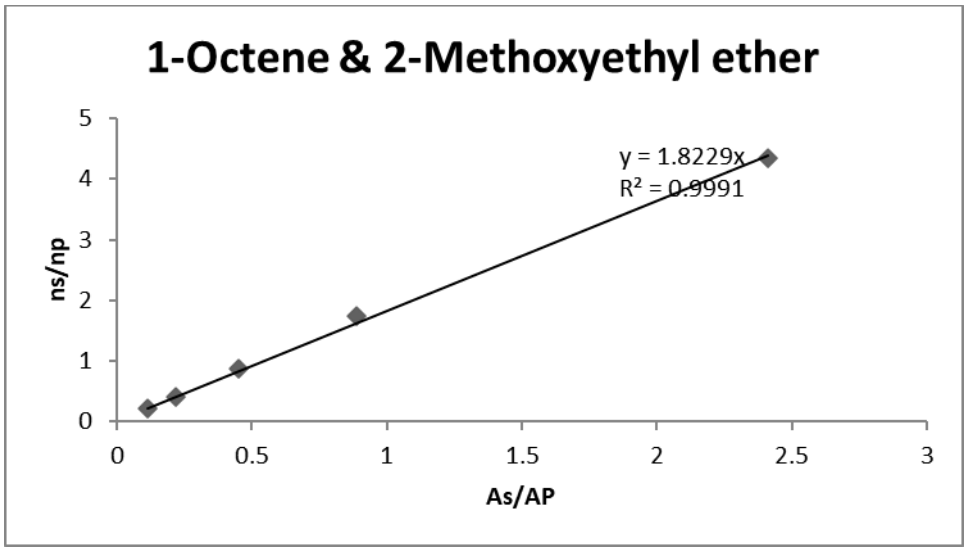



Figure S4. Correction factor (K) for 1-octene & 2-Methoxyethyl ether

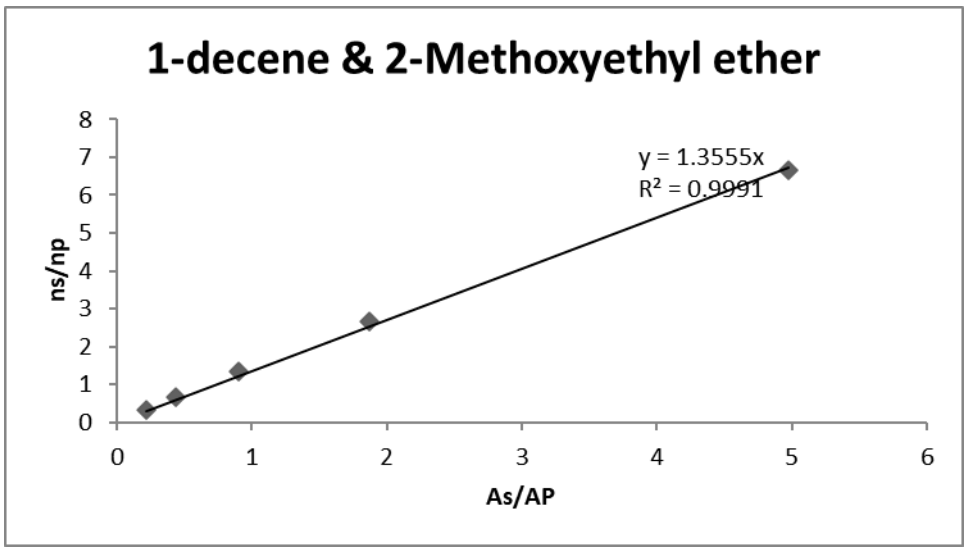



Figure S5. Correction factor (K) for 1-decene & 2-Methoxyethyl ether

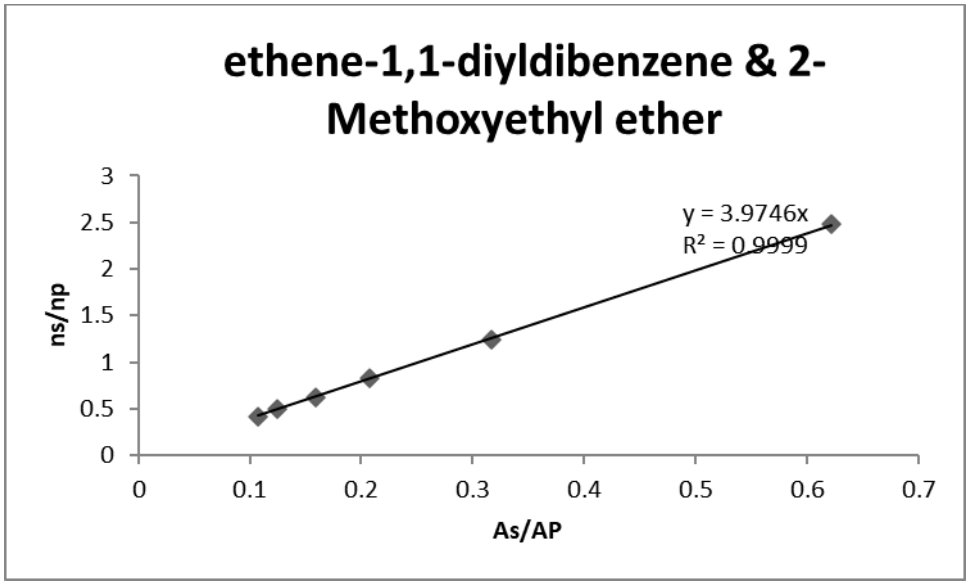



Figure S6. Correction factor (K) for ethene-1,1-diyldibenzene & 2-Methoxyethyl ether

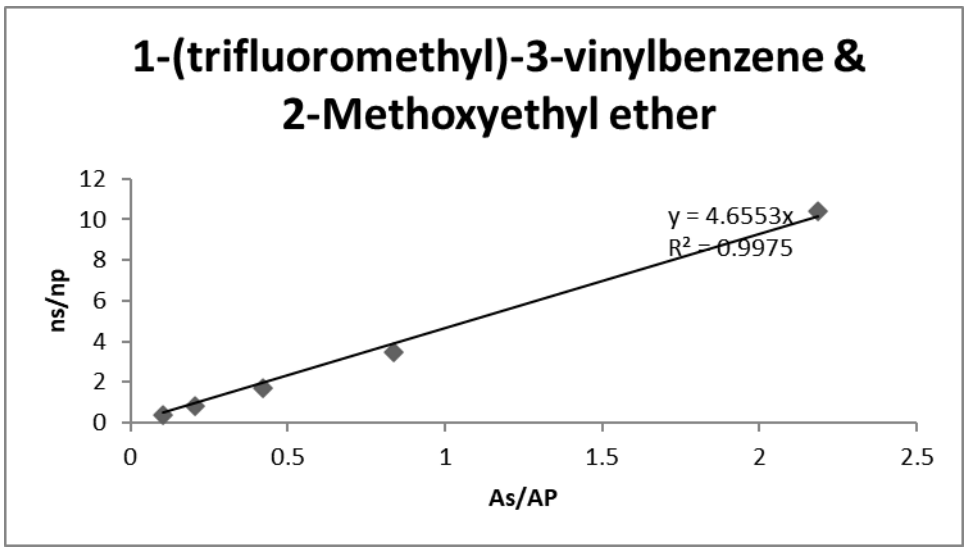
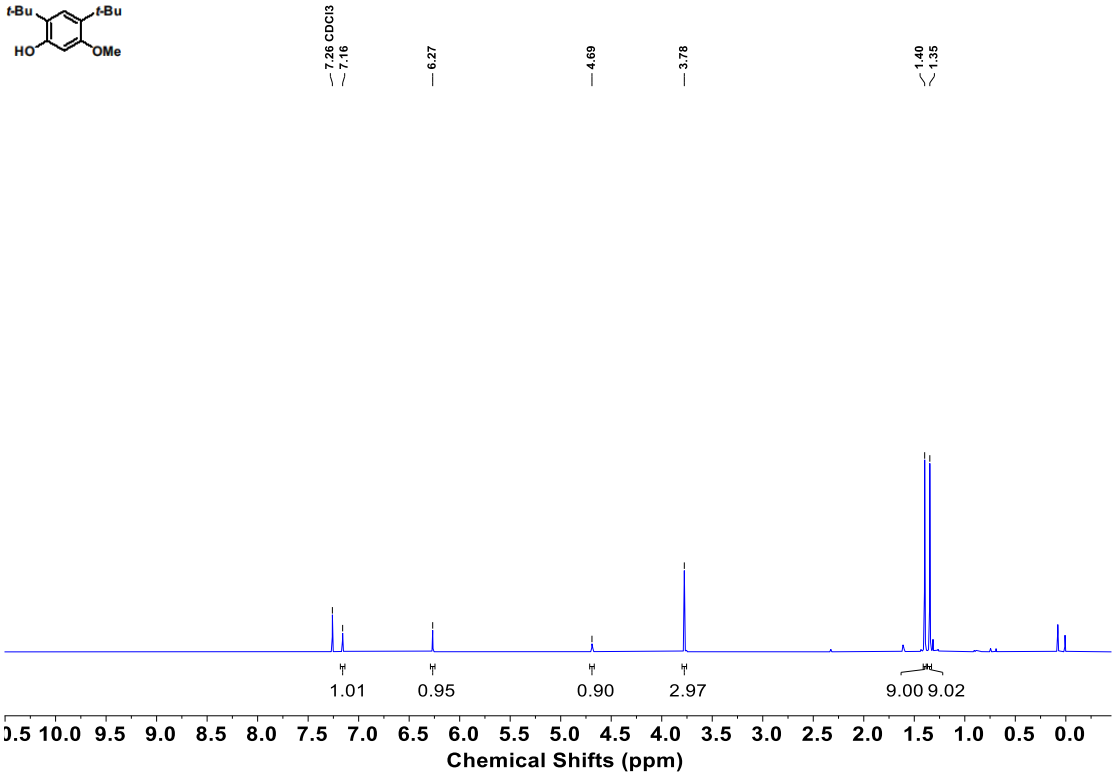
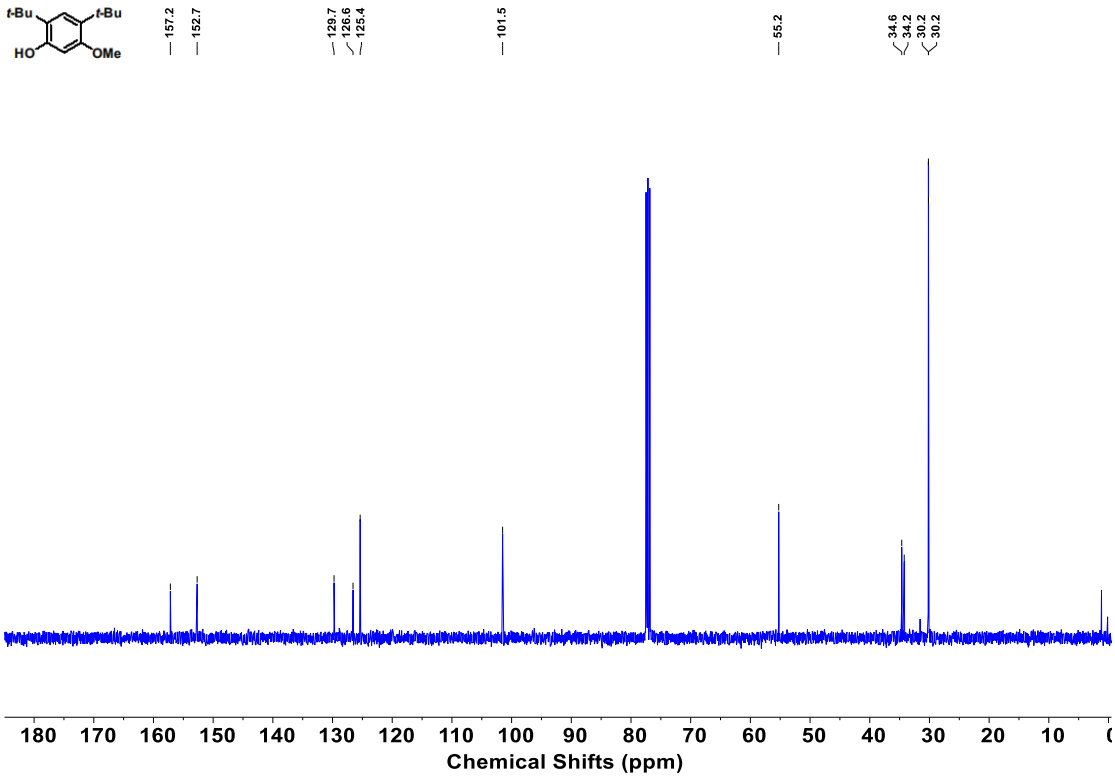



Figure S7. Correction factor (K) for 1-(trifluoromethyl-3-vinybenzene & 2-Methoxyethyl ether

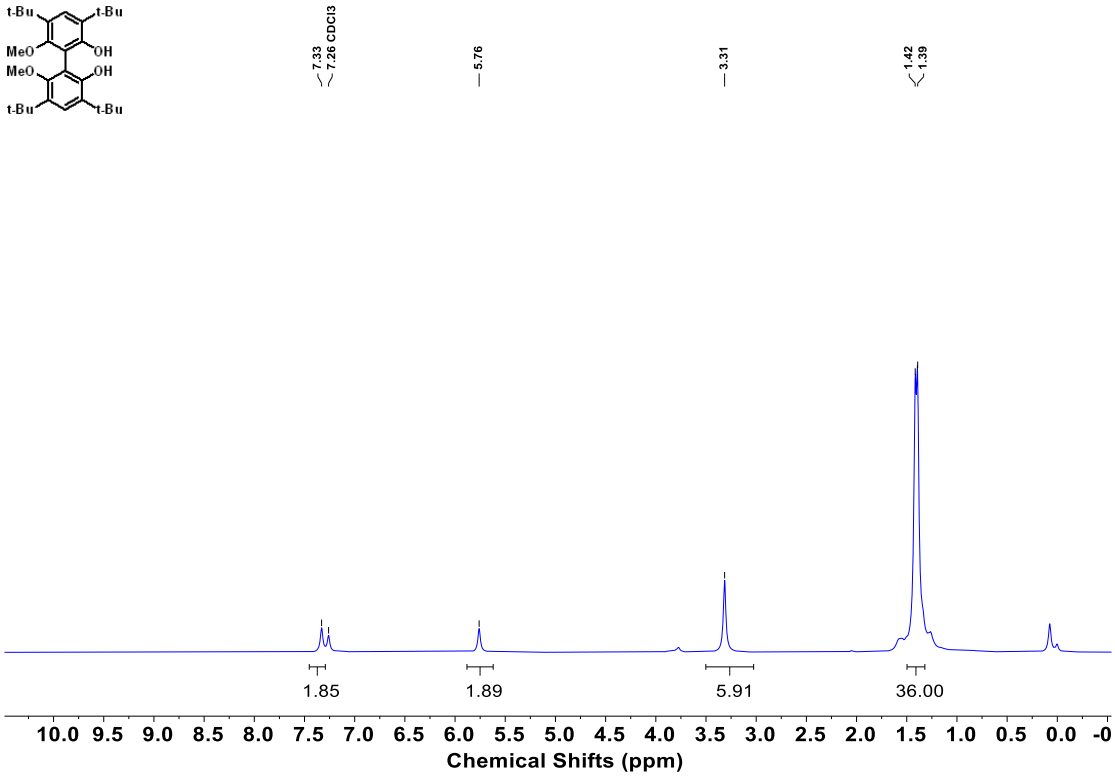
## 7. NMR Spectra of synthesized ligands and amines



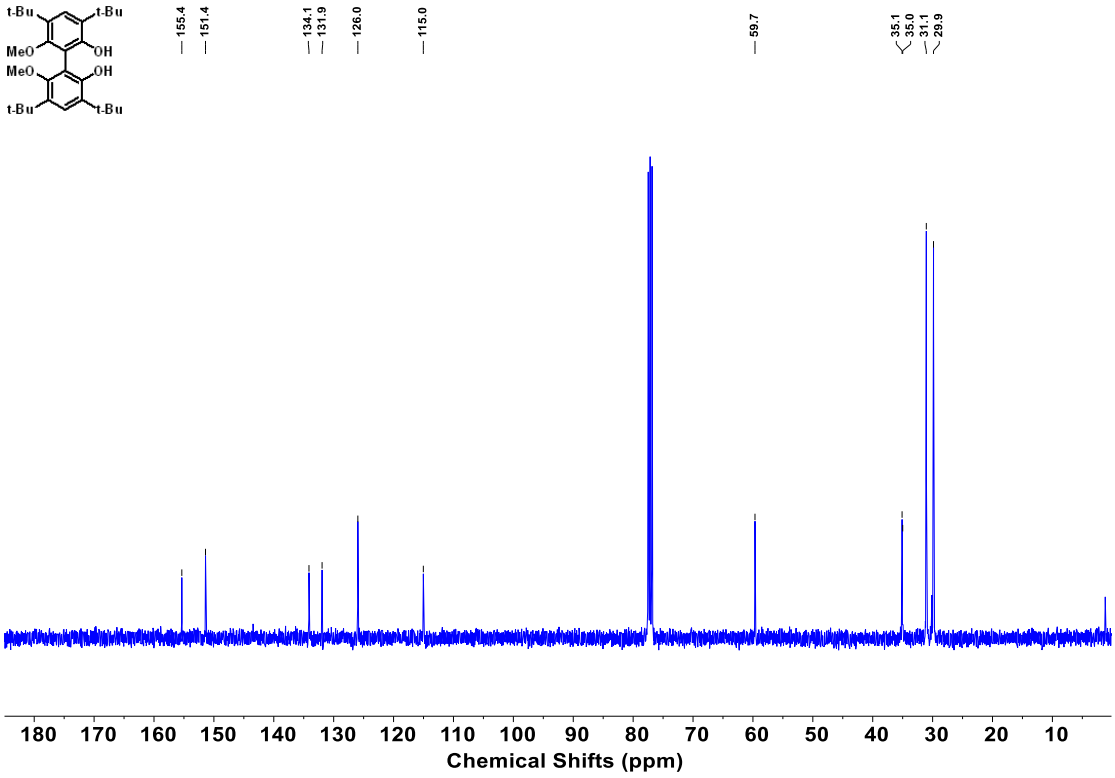

$^{1}$H NMR (400 MHz, $CDCl_3$) of **S2**



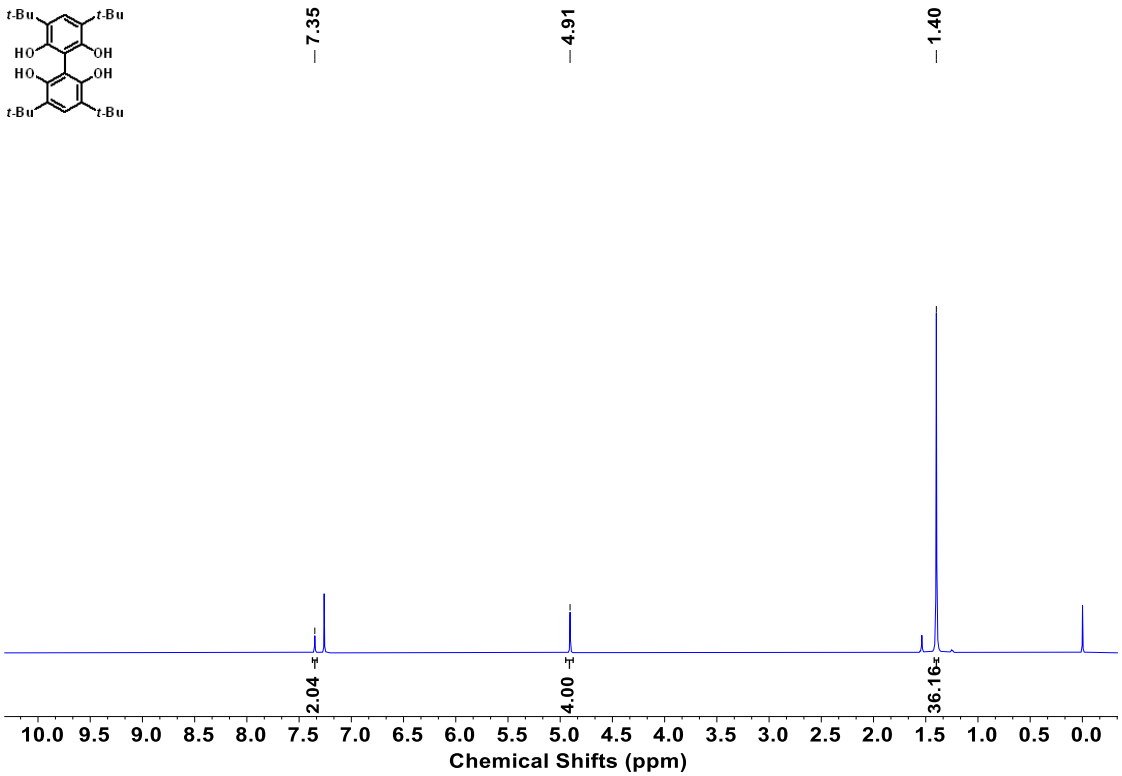

$^{13}$C NMR (101 MHz, $CDCl_3$) of **S2**



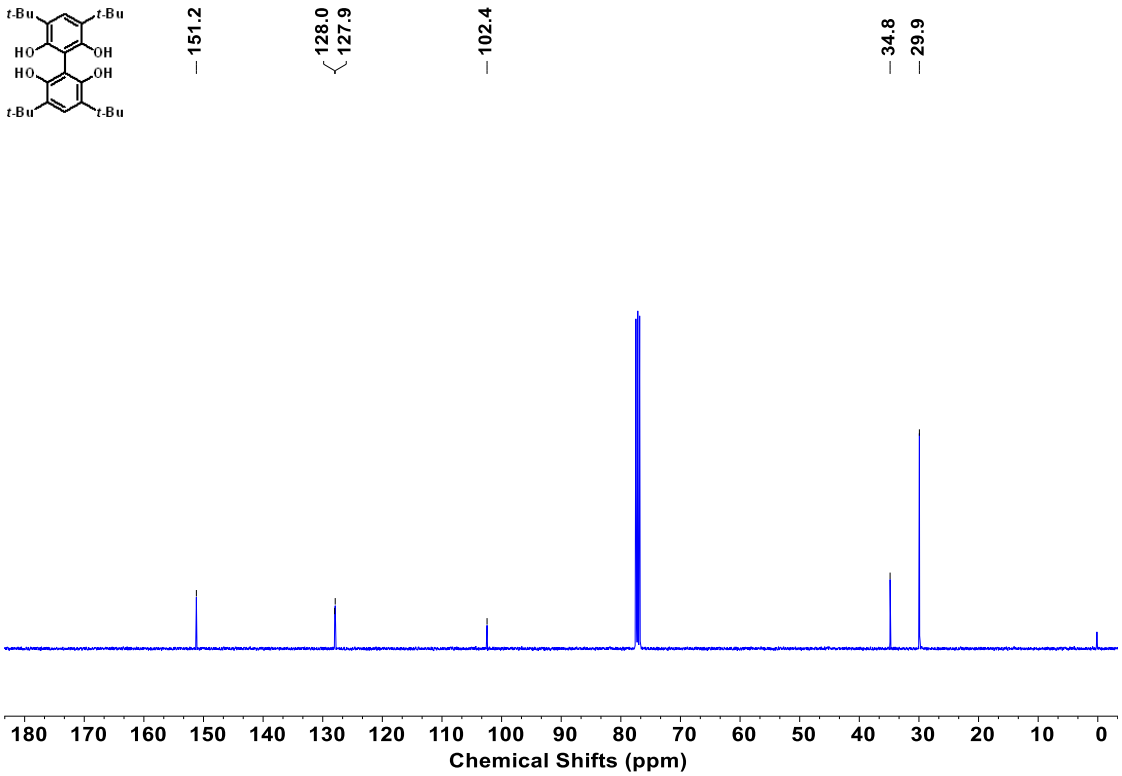

$^{1}$H NMR (400 MHz, $CDCl_3$) of **S3**



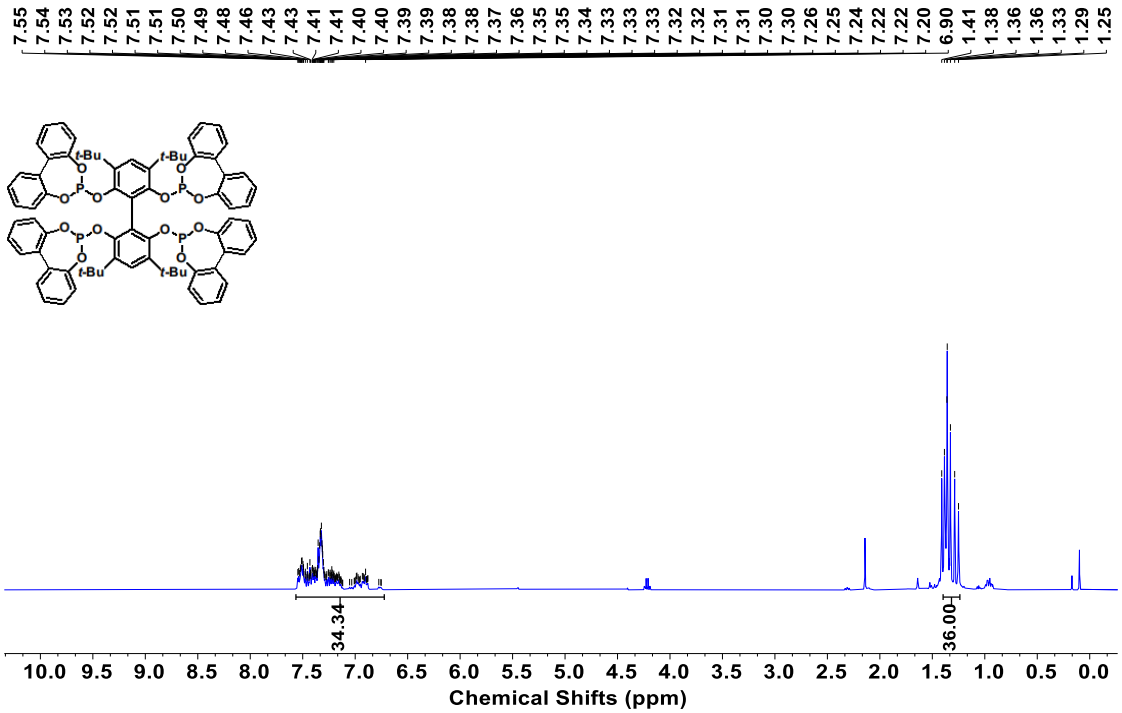

$^{13}$C NMR (101 MHz, $CDCl_3$) of **S3**



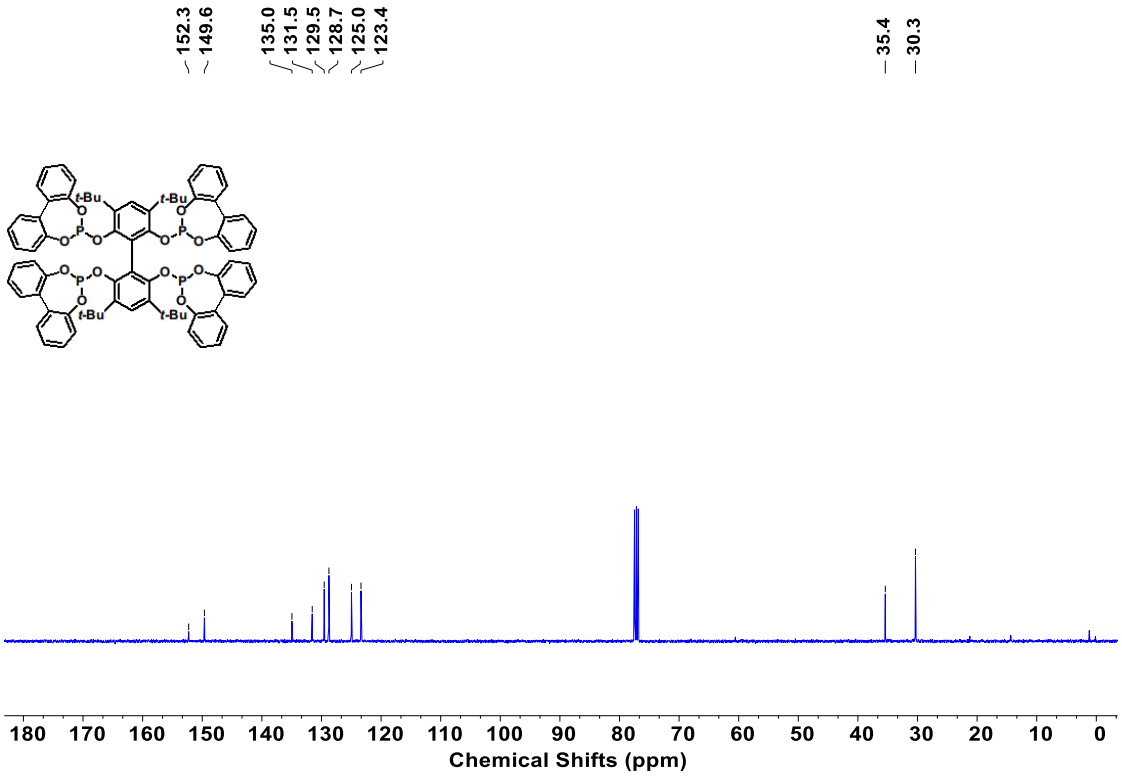

$^{1}$H NMR (400 MHz, $CDCl_3$) of **S4**



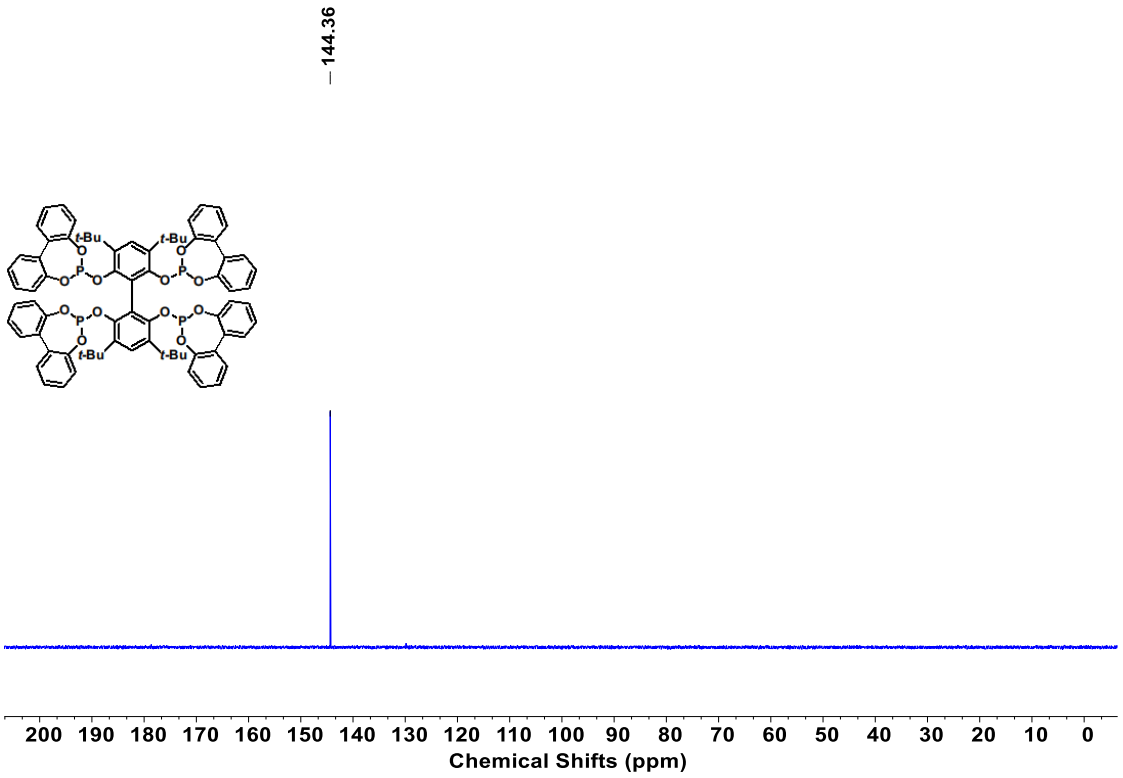

$^{13}$C NMR (101 MHz, $CDCl_3$) of **S4**



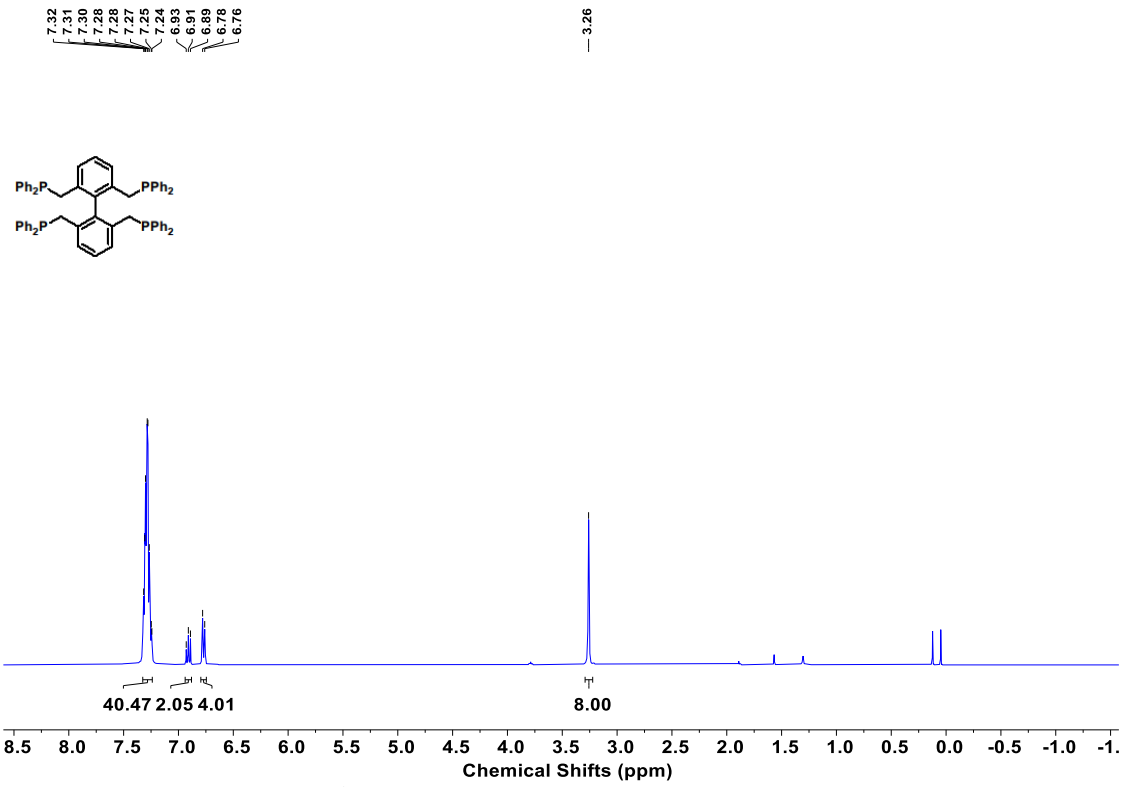

$^{1}$H NMR (400 MHz, $CDCl_3$) of **L6**



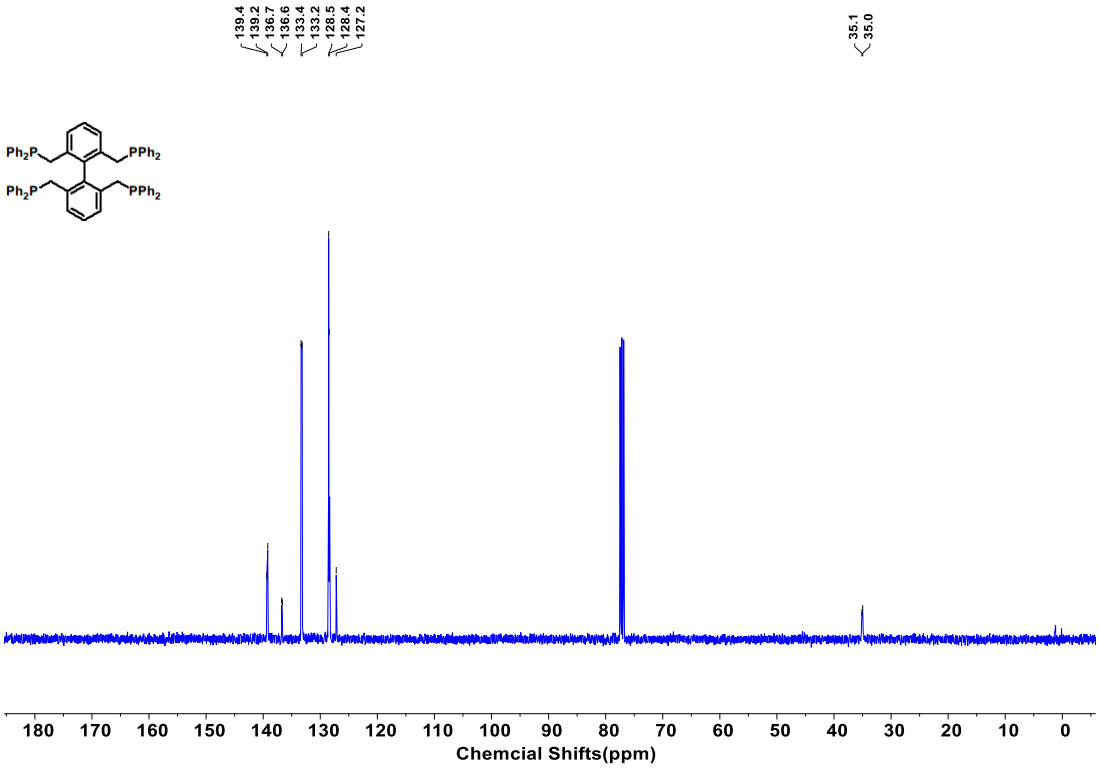

$^{13}$C NMR (101 MHz, $CDCl_3$) of **L6**



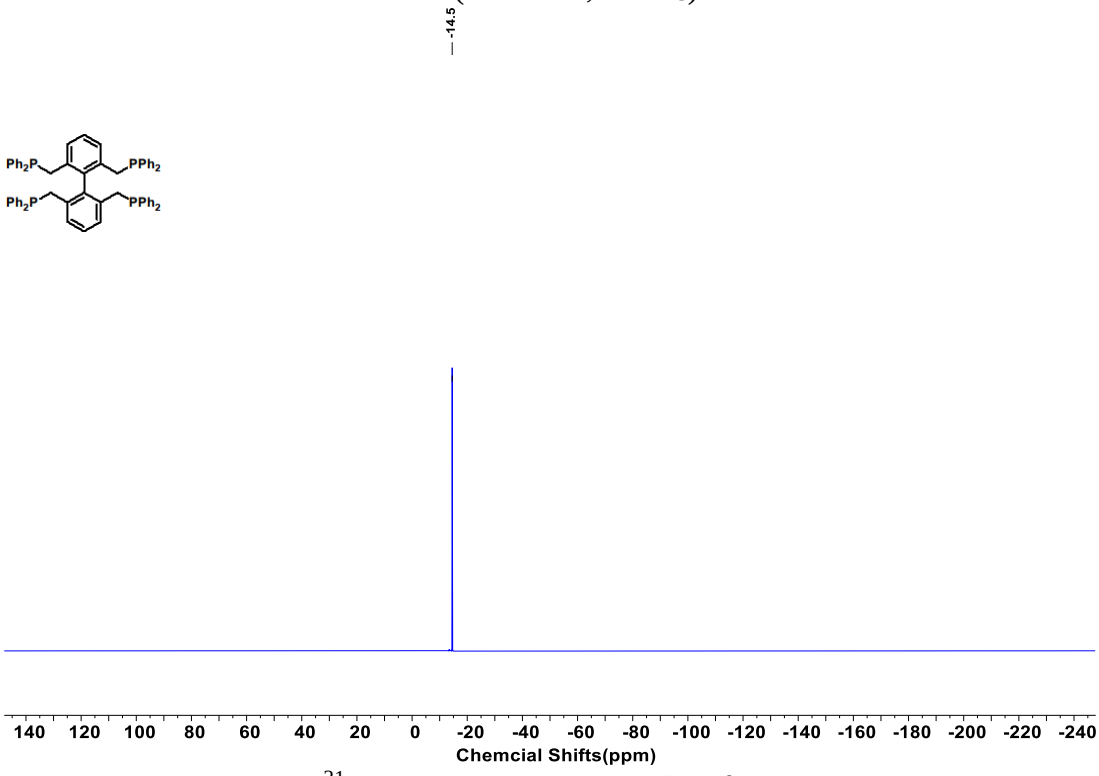

$^{31}$P NMR (243 MHz, $CDCl_3$) of **L6**



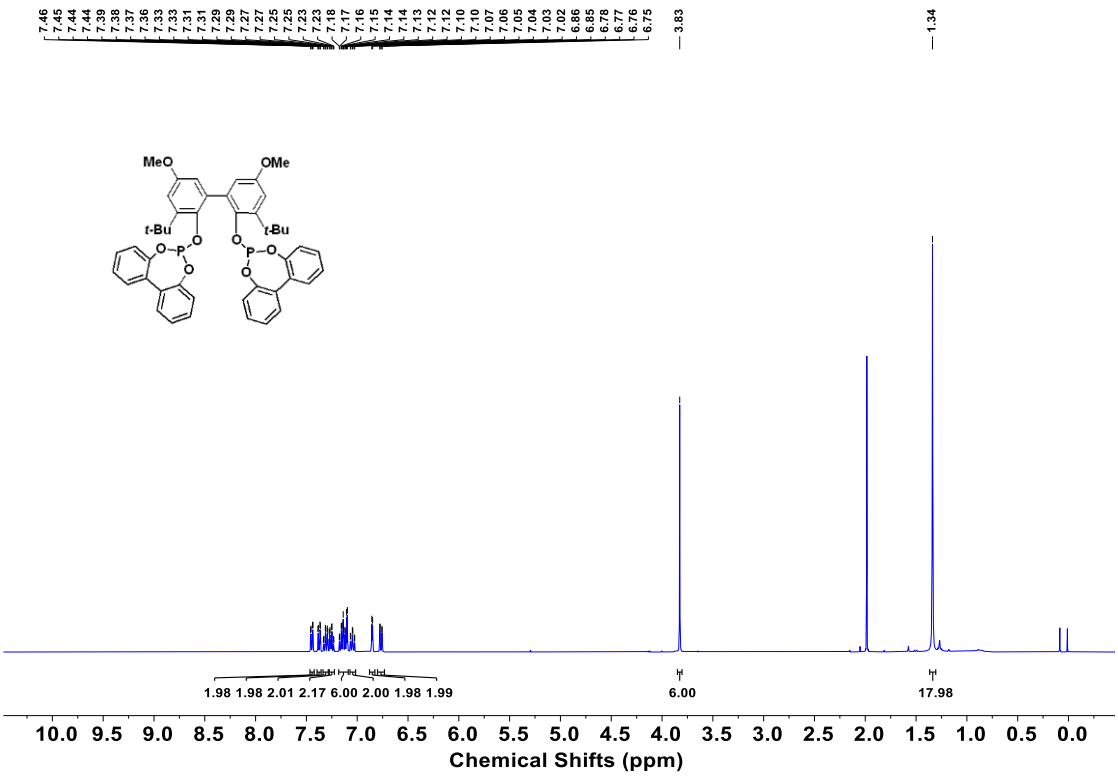

$^{1}$H NMR (400 MHz, $CDCl_3$) of **L2**



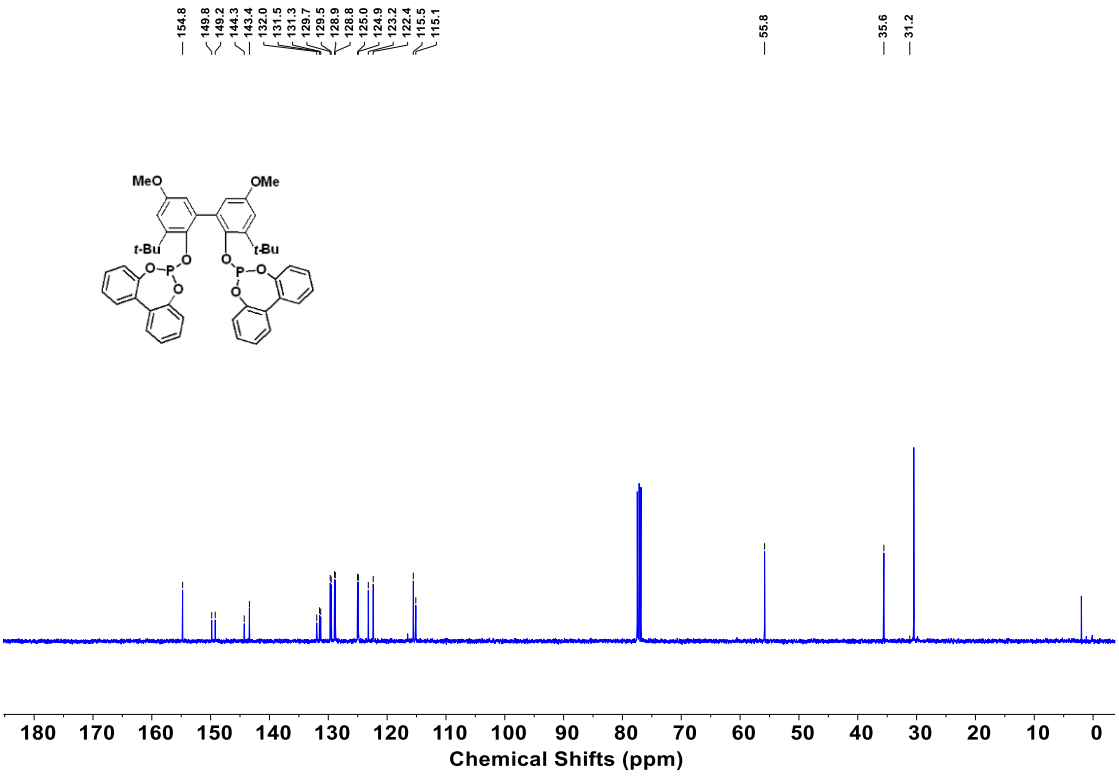

$^{13}$C NMR (101 MHz, $CDCl_3$) of **L2**



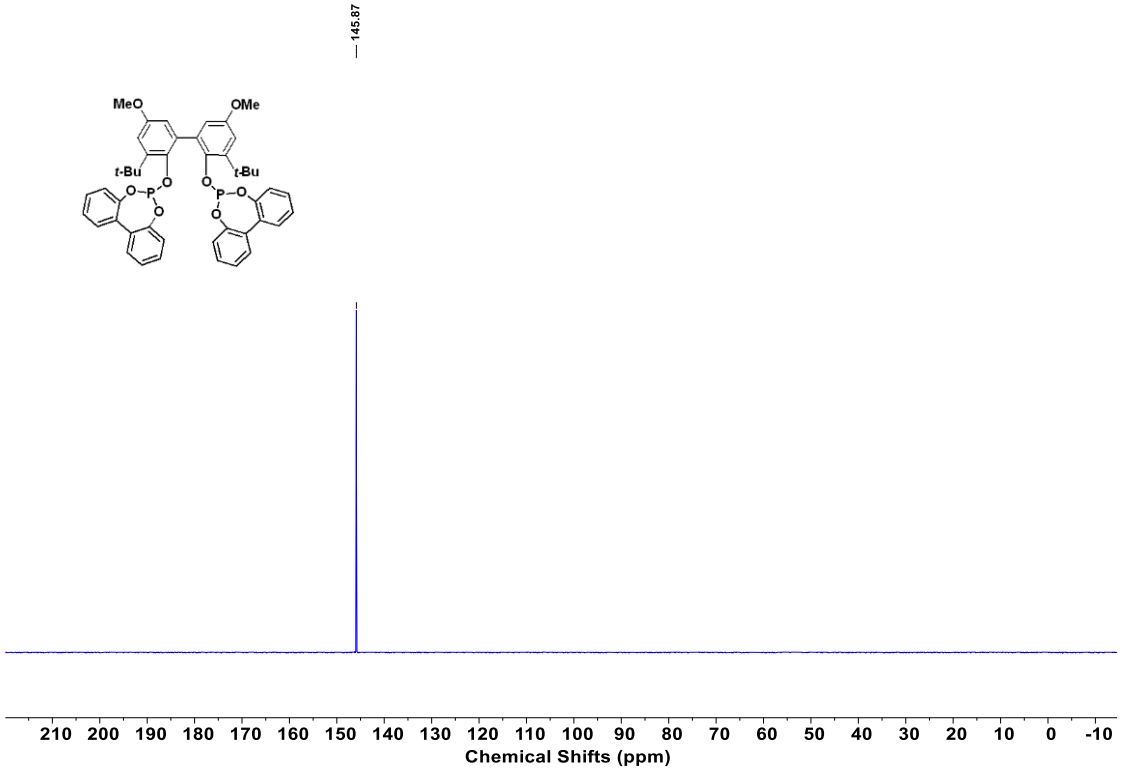

$^{31}$P NMR (243 MHz, $CDCl_3$) of **L2**



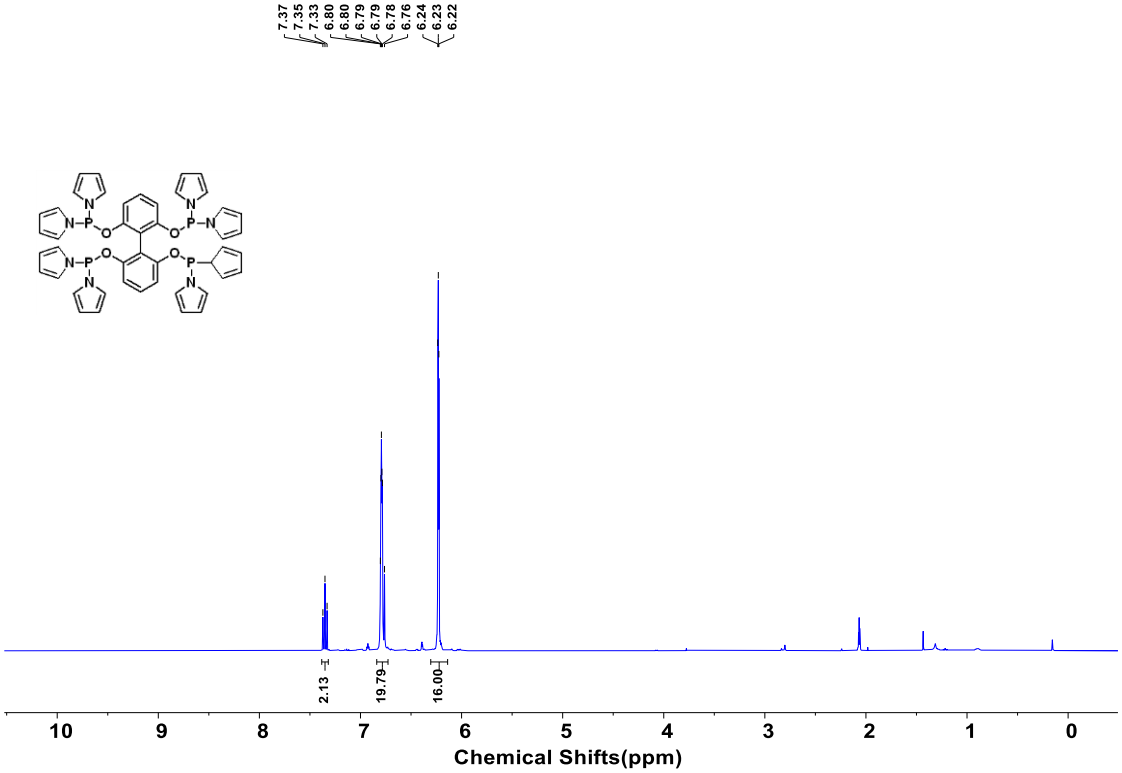

$^{1}$H NMR (400 MHz, $CDCl_3$) of **L3**



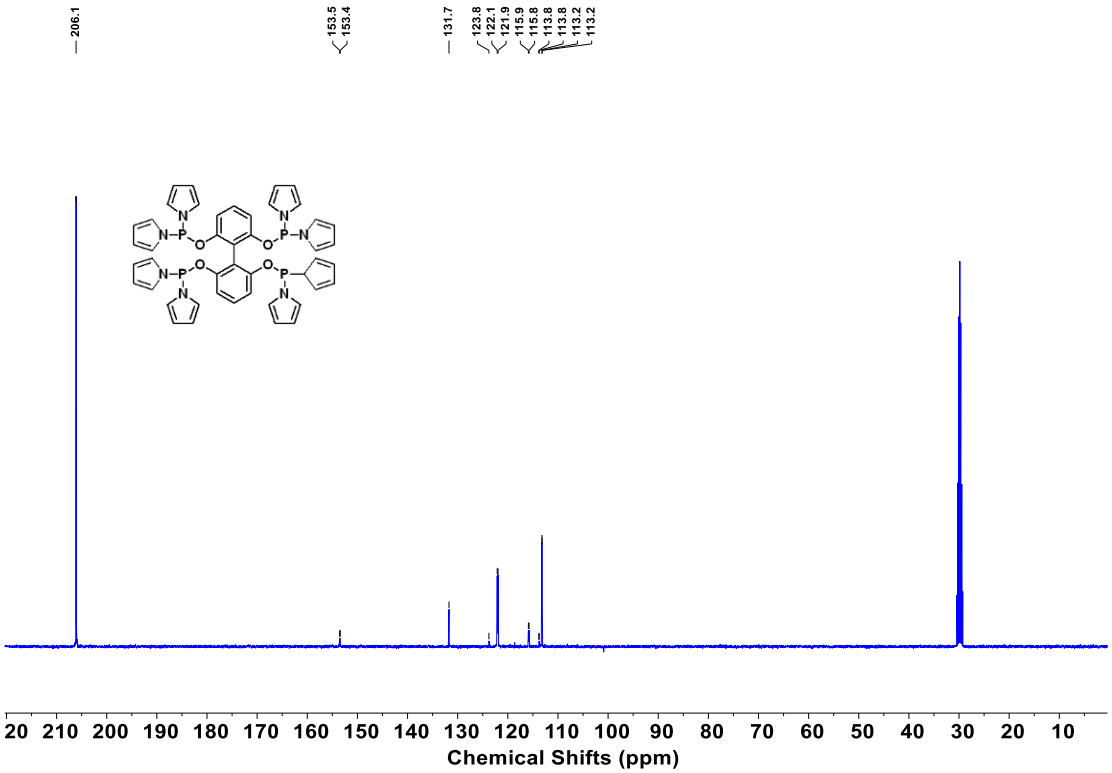

$^{13}$C NMR (101 MHz, $CDCl_3$) of **L3**



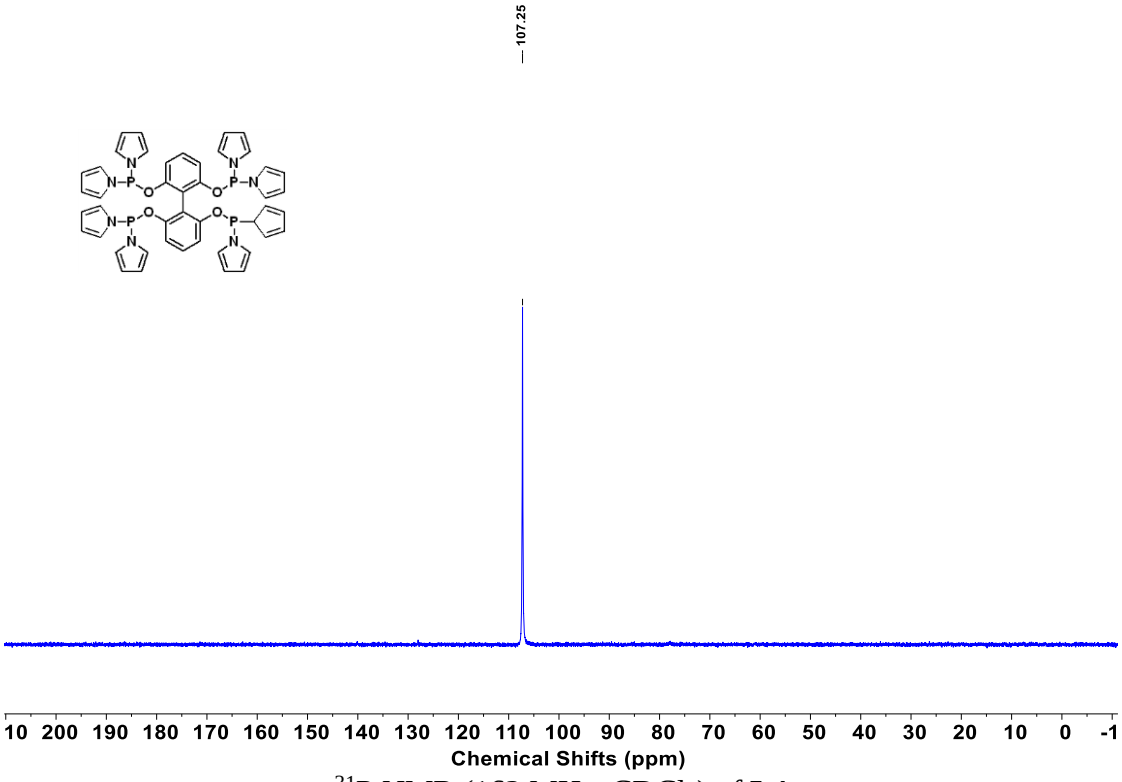

$^{31}$P NMR (243 MHz, $CDCl_3$) of **L3**



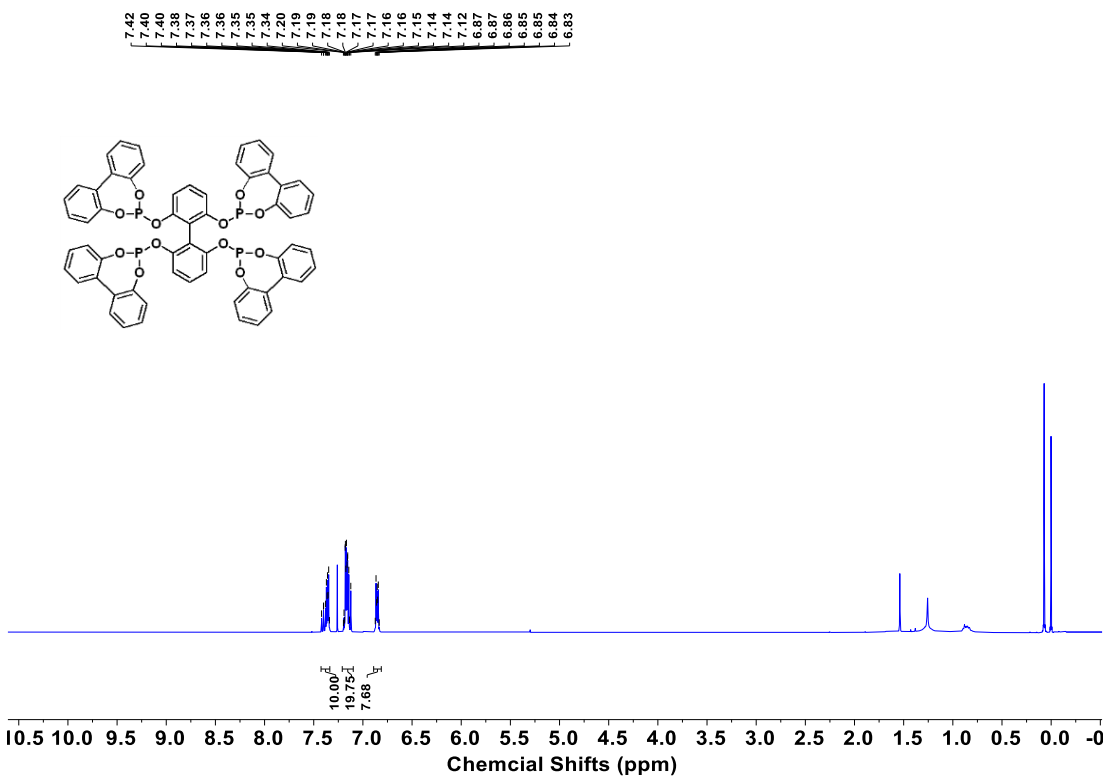

$^{1}$H NMR (400 MHz, $CDCl_3$) of **L4**



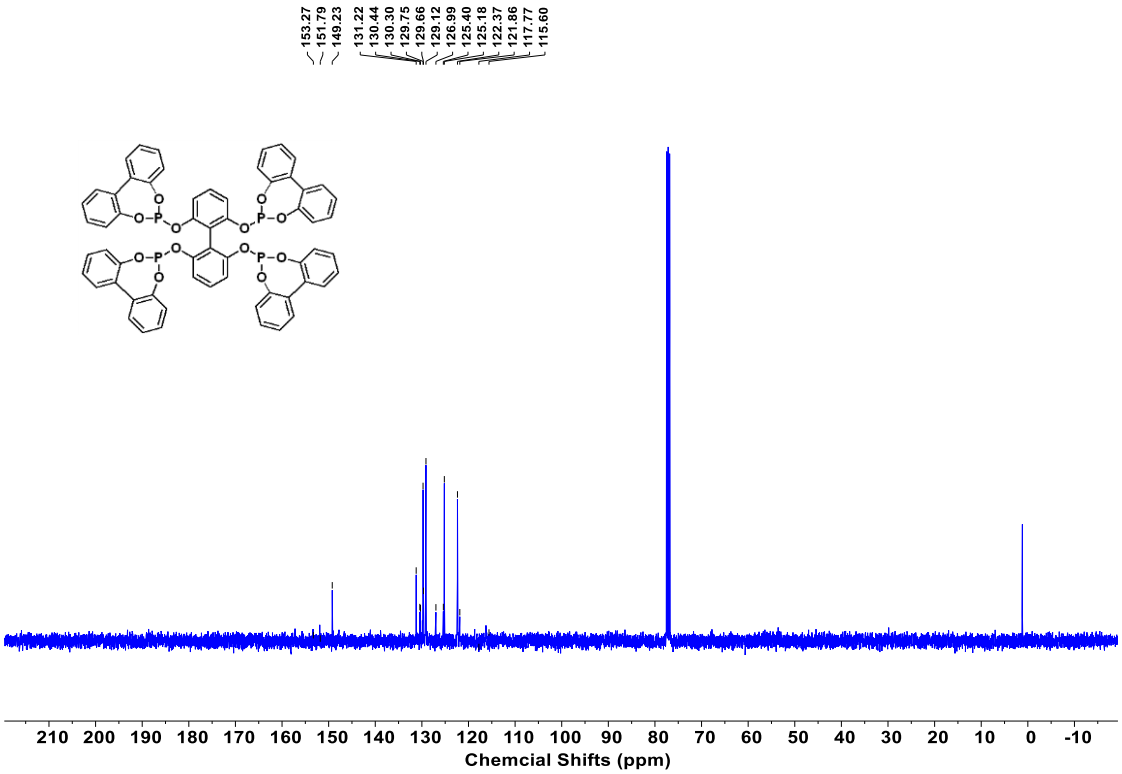

$^{13}$C NMR (101 MHz, Acetone-$d_6$) of **L4**



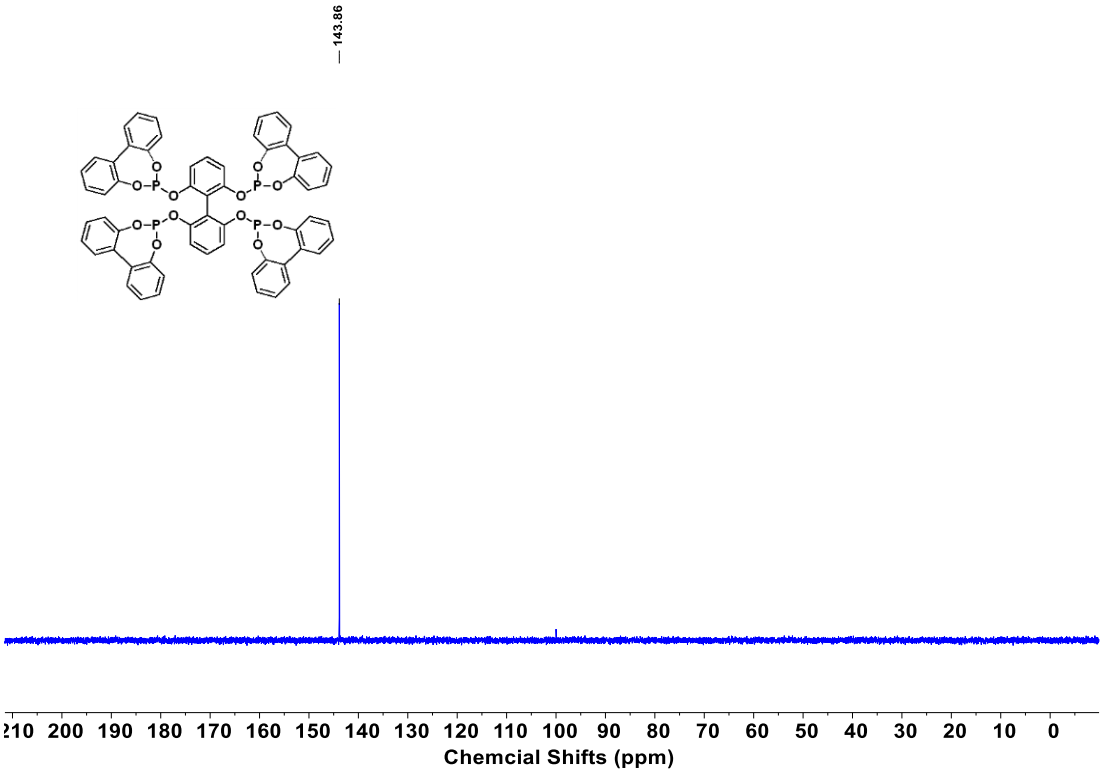

$^{31}$P NMR (162 MHz, $CDCl_3$) of **L4**



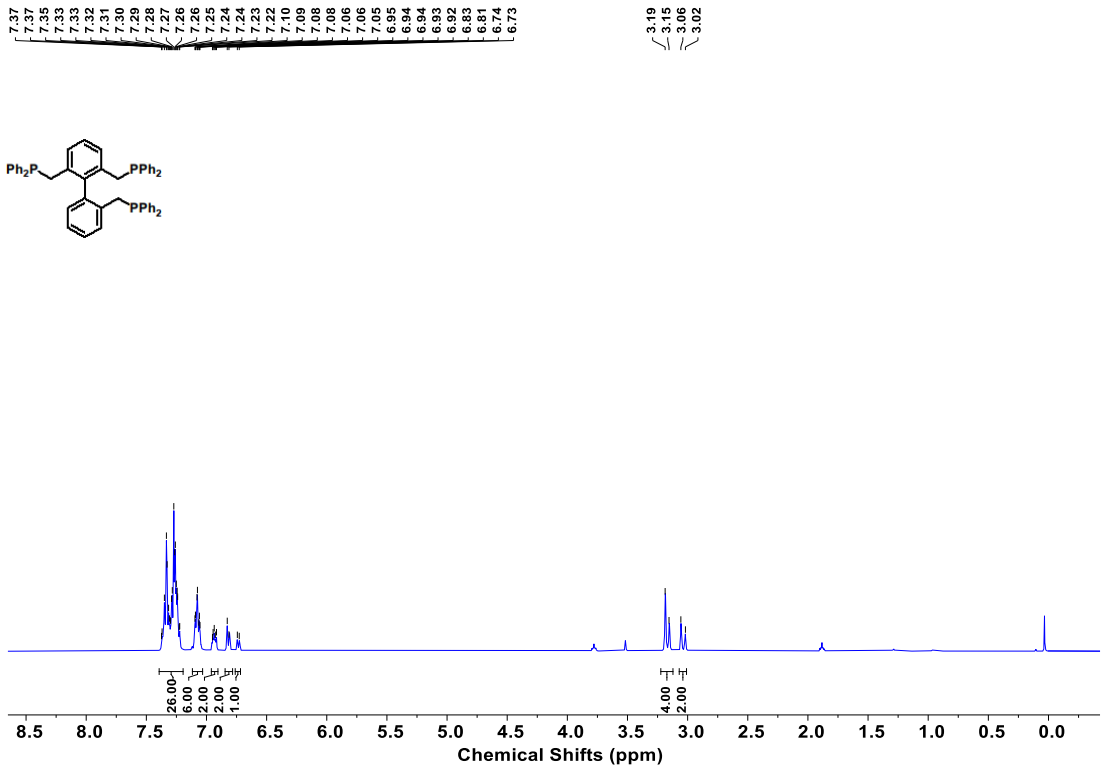

$^{1}$H NMR (400 MHz, $CDCl_3$) of **L5**



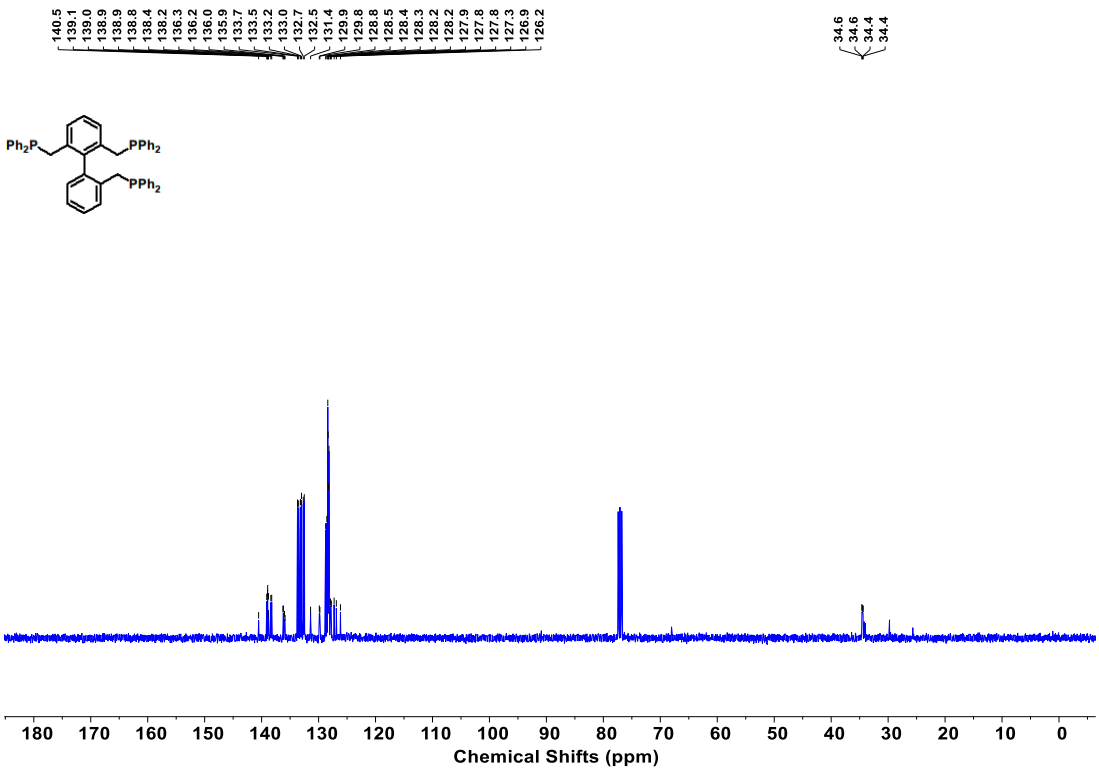

$^{13}$C NMR (101 MHz, Acetone-$d_6$) of **L5**



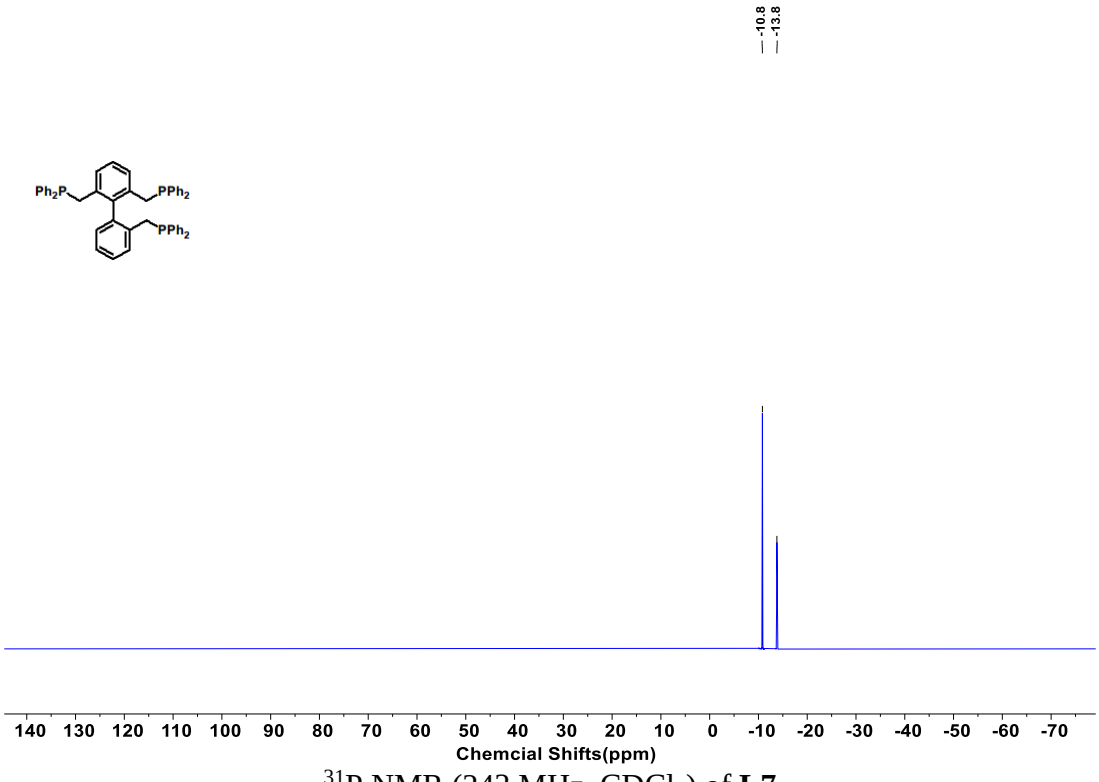

$^{31}$P NMR (162 MHz, $CDCl_3$) of **L5**



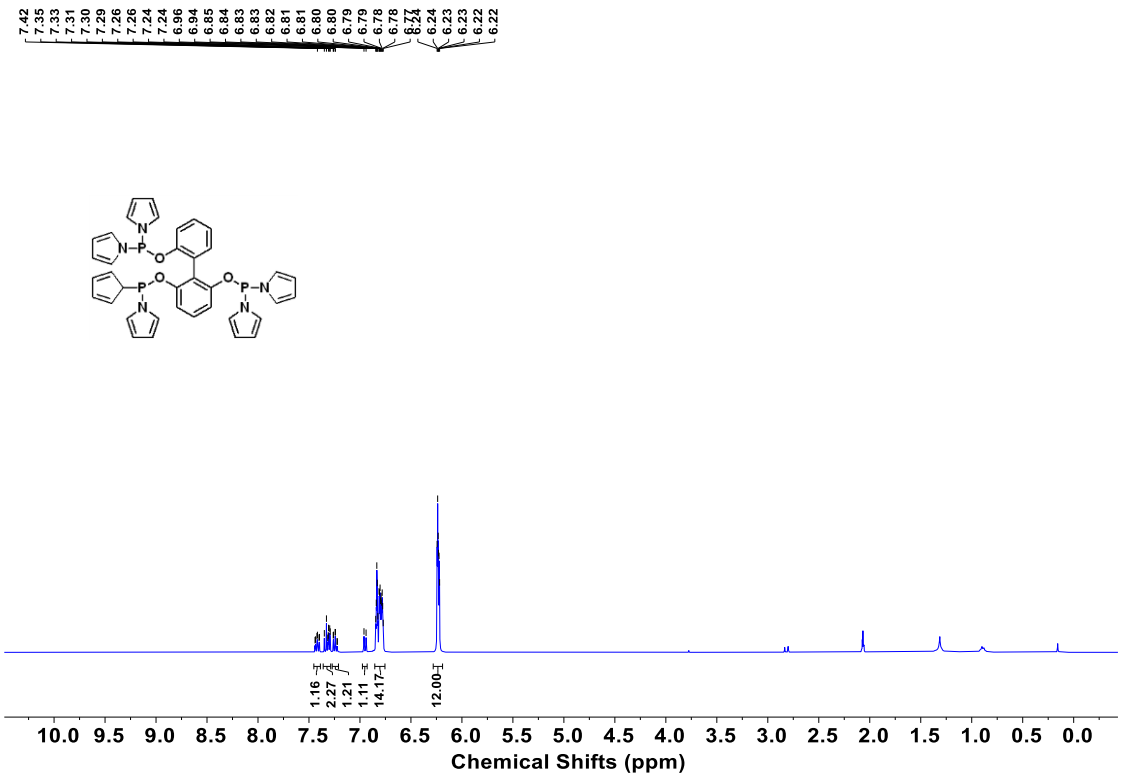

$^{1}$H NMR (400 MHz, $CDCl_3$) of **L7**



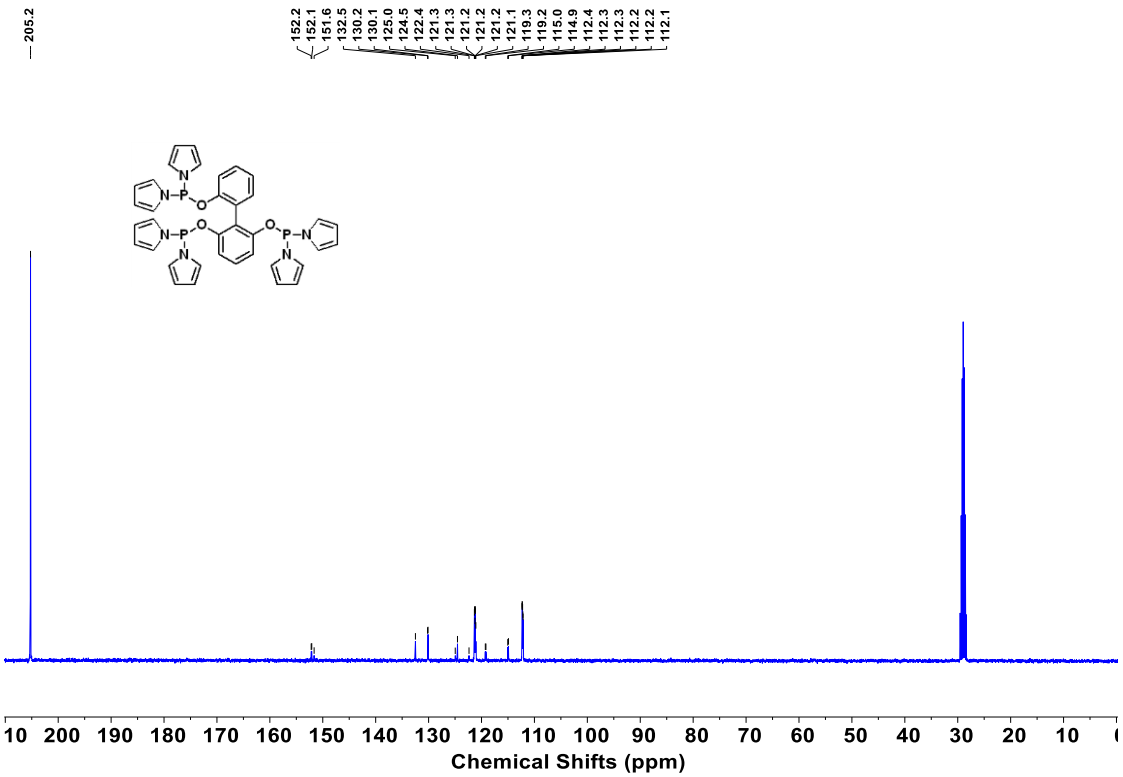

$^{13}C$ NMR (101 MHz, $CDCl_3$) of **L7**



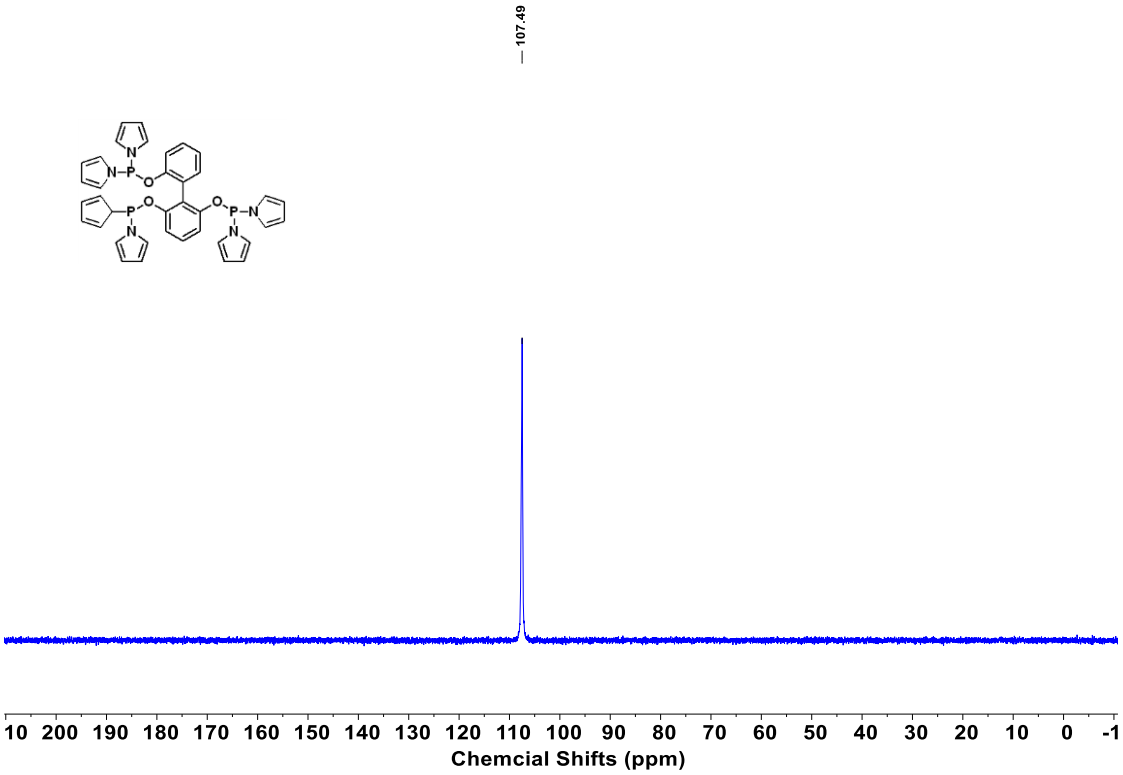

$^{31}P$ NMR (243 MHz, $CDCl_3$) of **L7**



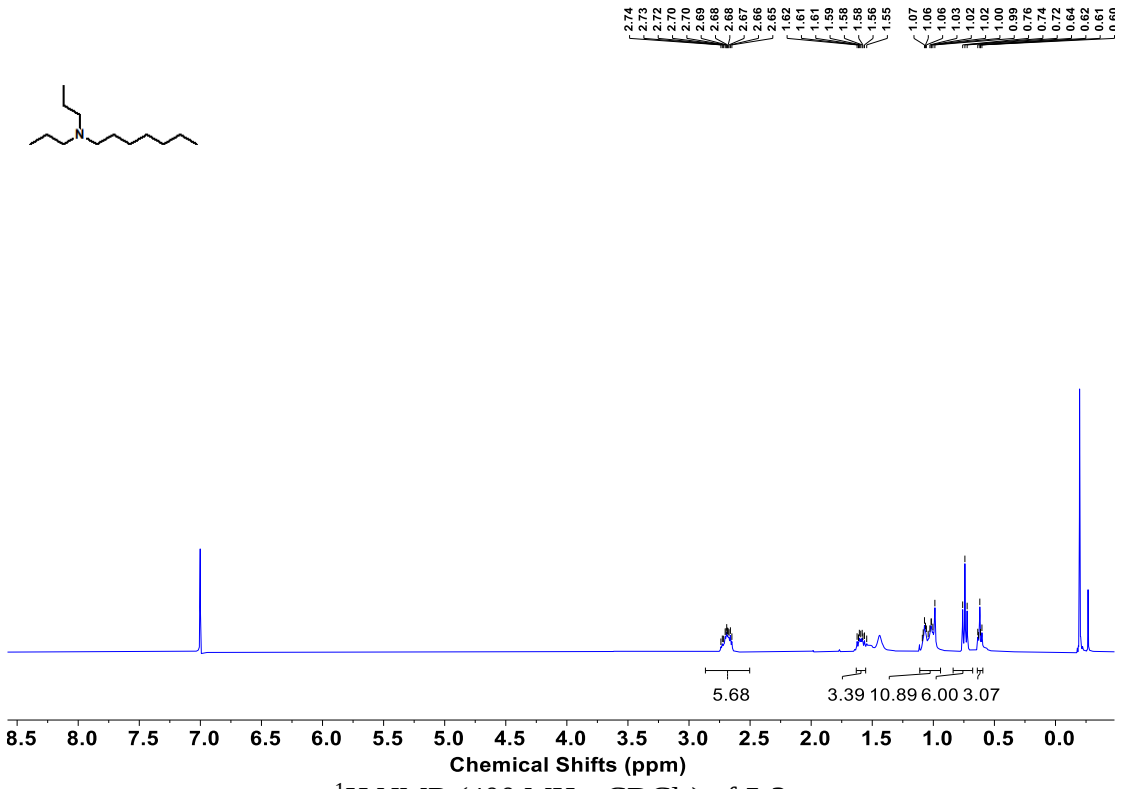

$^{1}$H NMR (400 MHz, $CDCl_3$) of **L8**



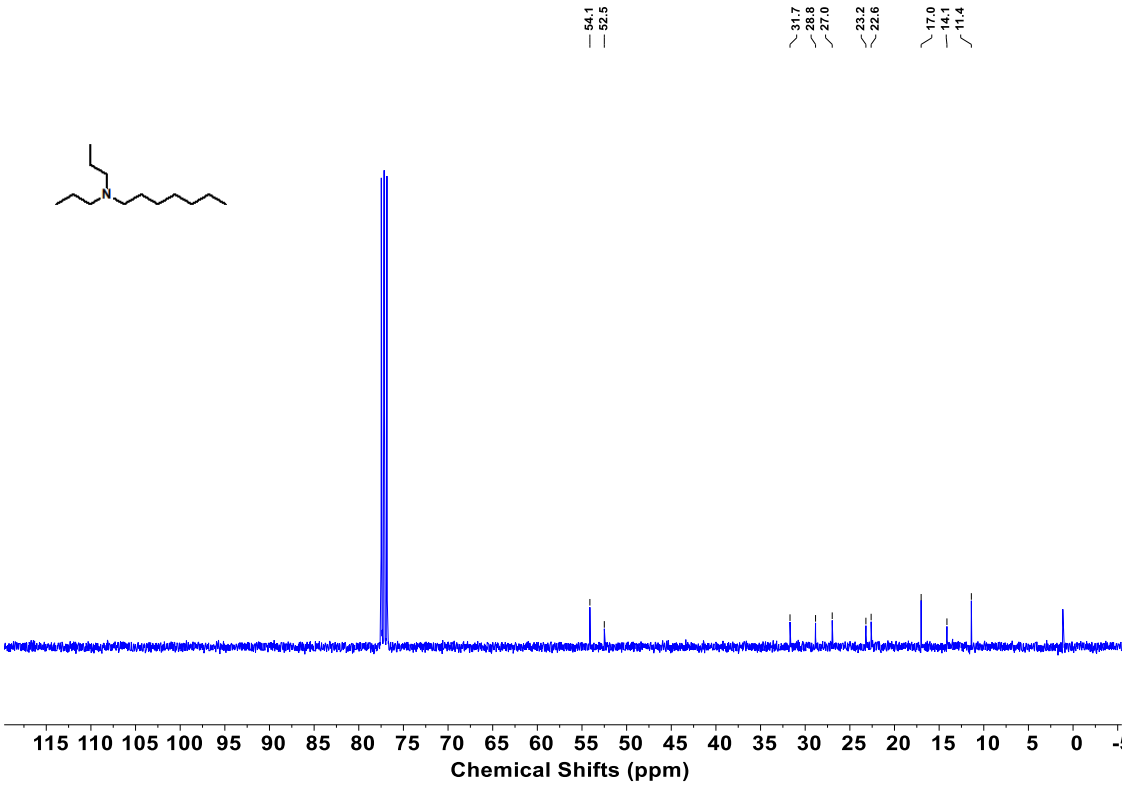

$^{13}$C NMR (101 MHz, $CDCl_3$) of **L8**



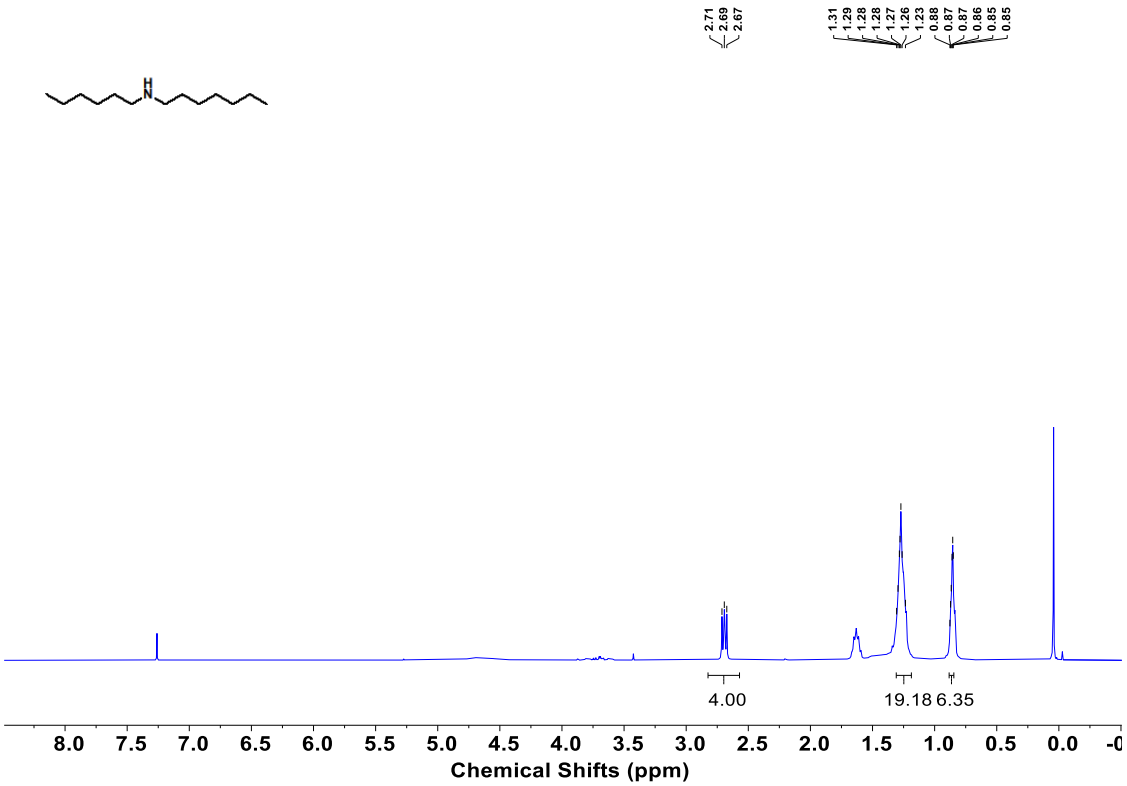

$^{31}$P NMR (162 MHz, $CDCl_3$) of **L8**



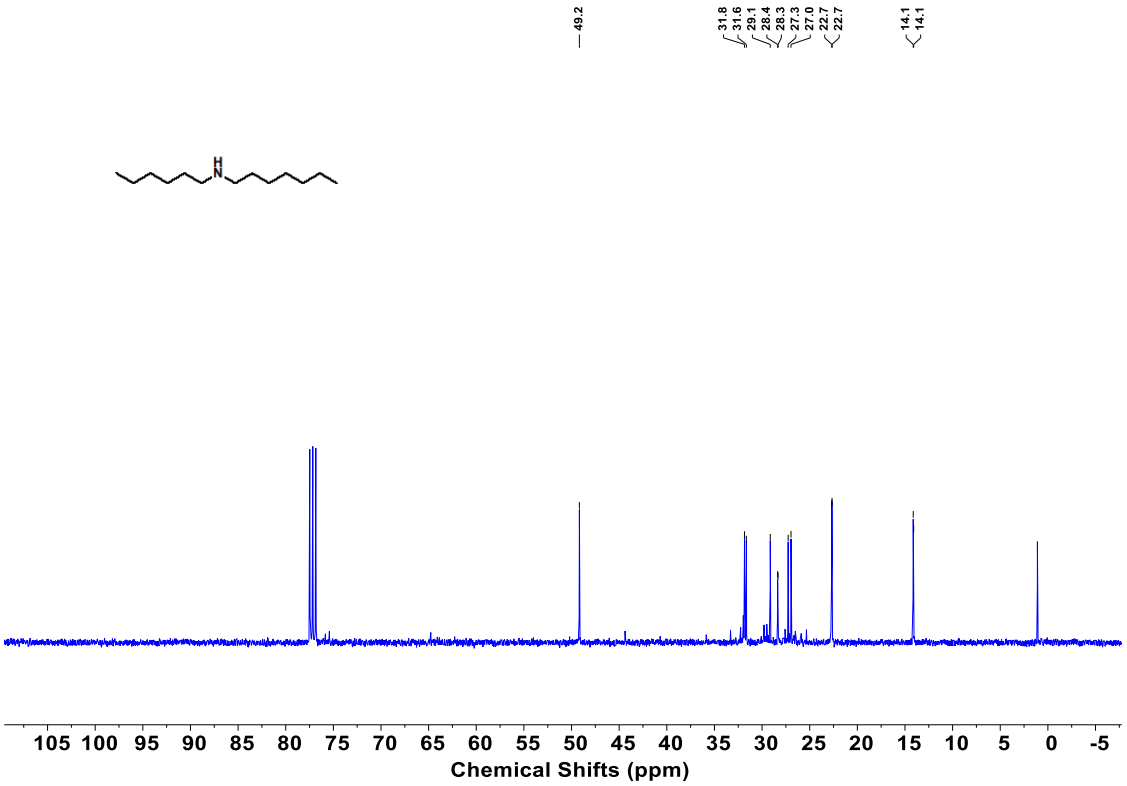

$^{1}$H NMR (400 MHz, $CDCl_3$) of **5-2**



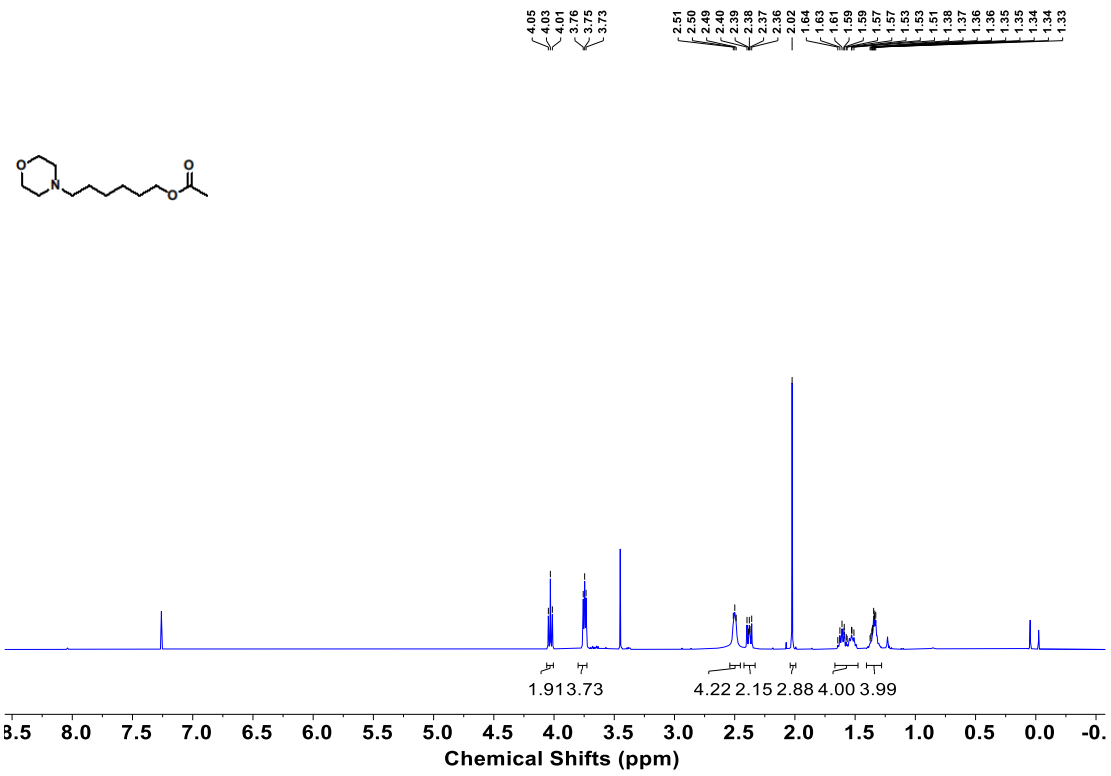

$^{13}$C NMR (101 MHz, $CDCl_3$) of **5-2**



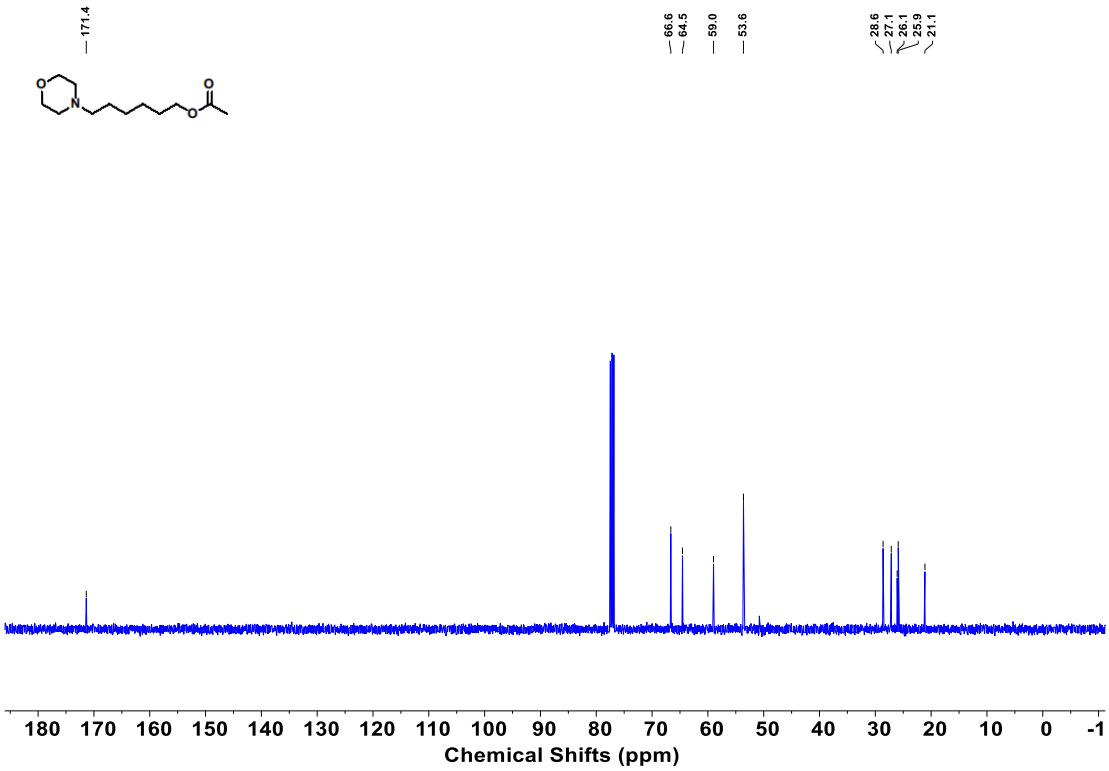

$^{1}$H NMR (400 MHz, $CDCl_3$) of **5-3**



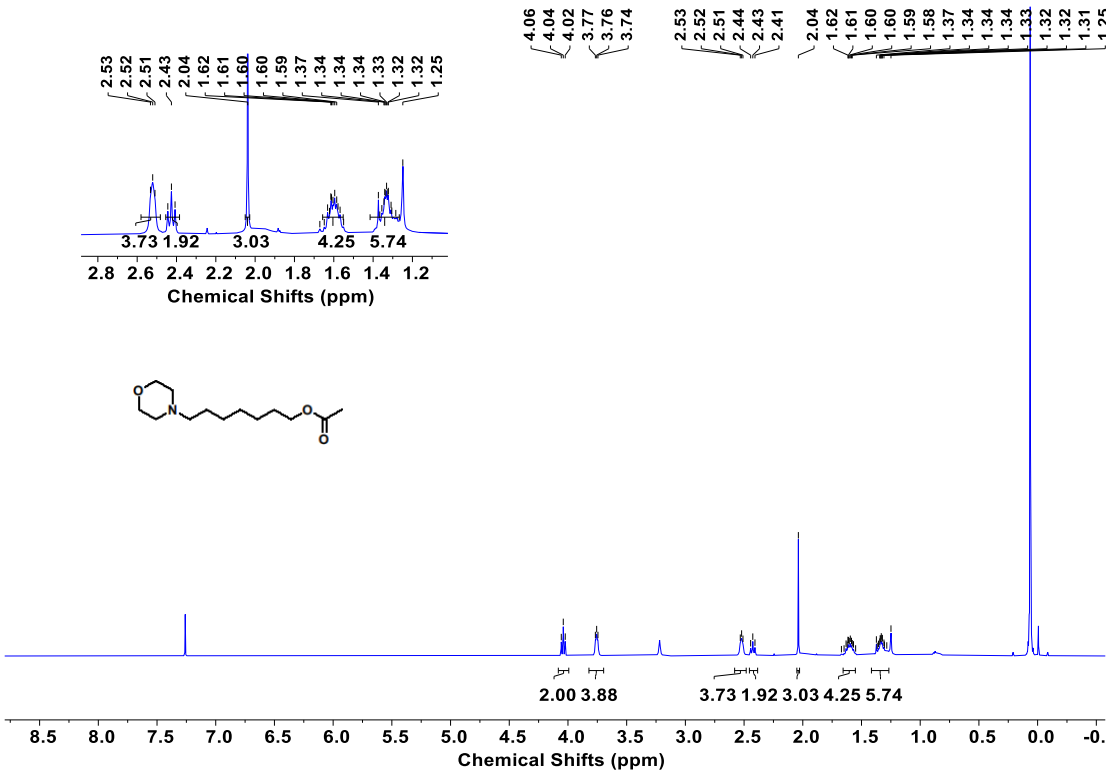

$^{13}$C NMR (101 MHz, $CDCl_3$) of **5-3**



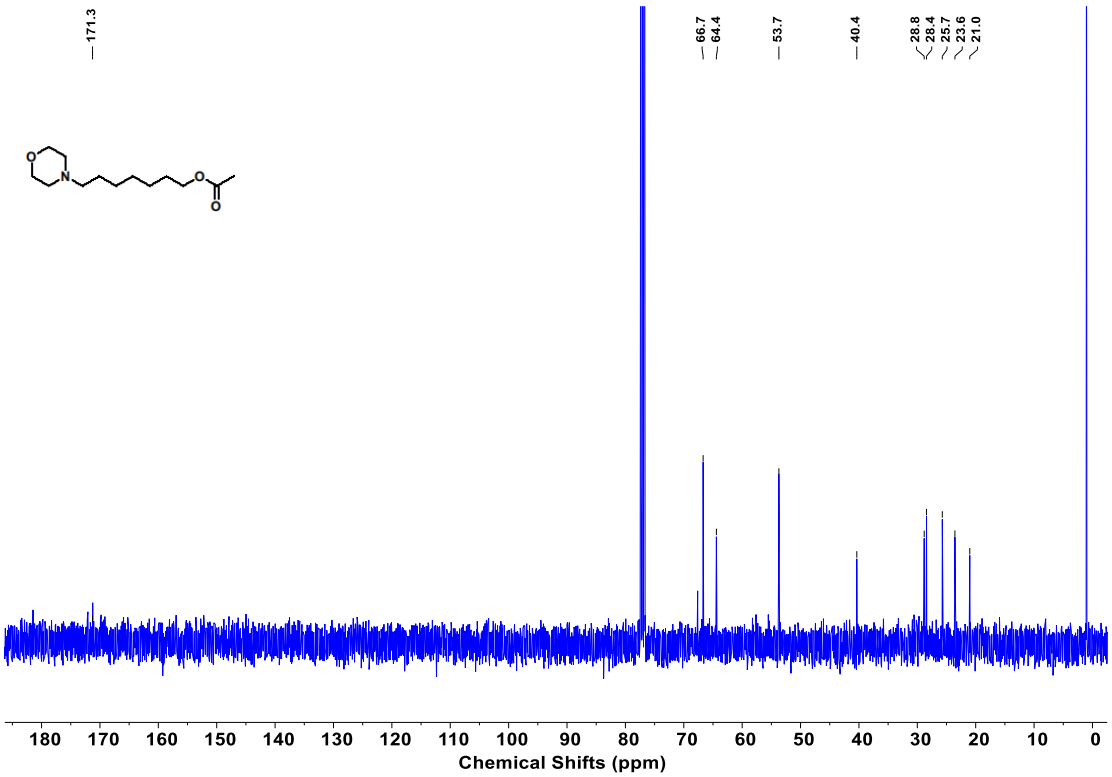

$^{1}$H NMR (400 MHz, $CDCl_3$) of **5-8**



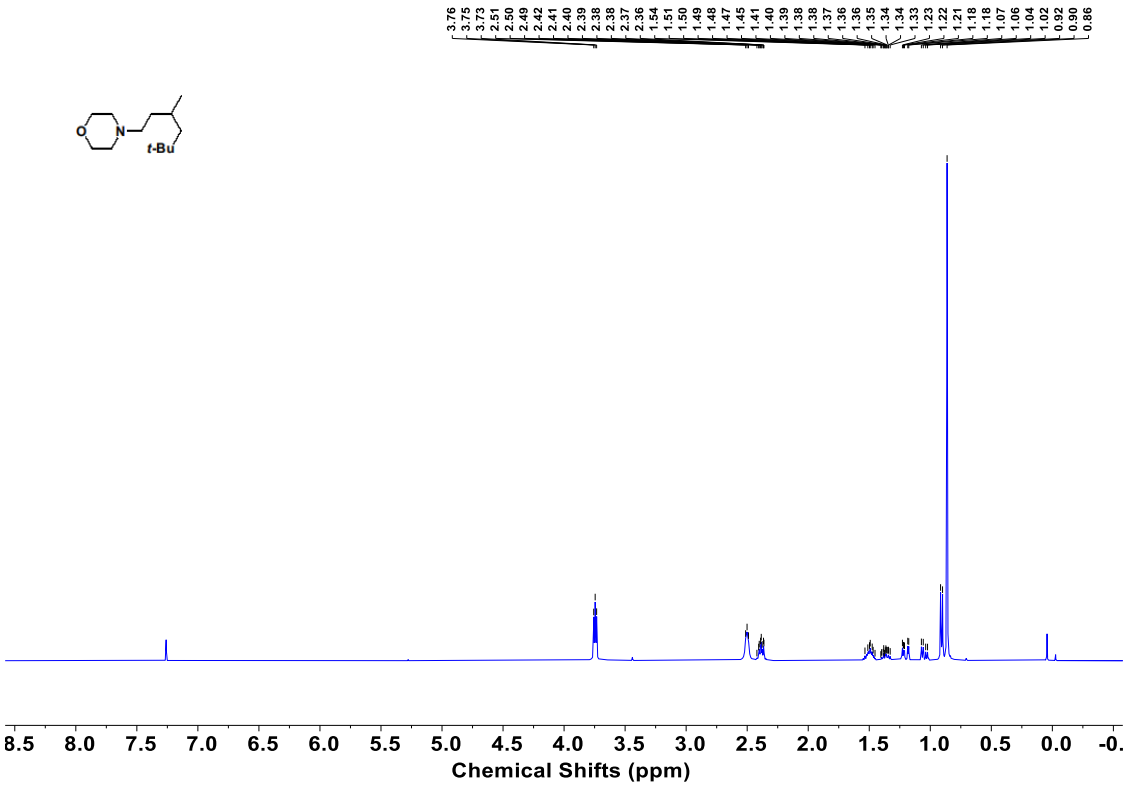

$^{13}$C NMR (101 MHz, $CDCl_3$) of **5-8**



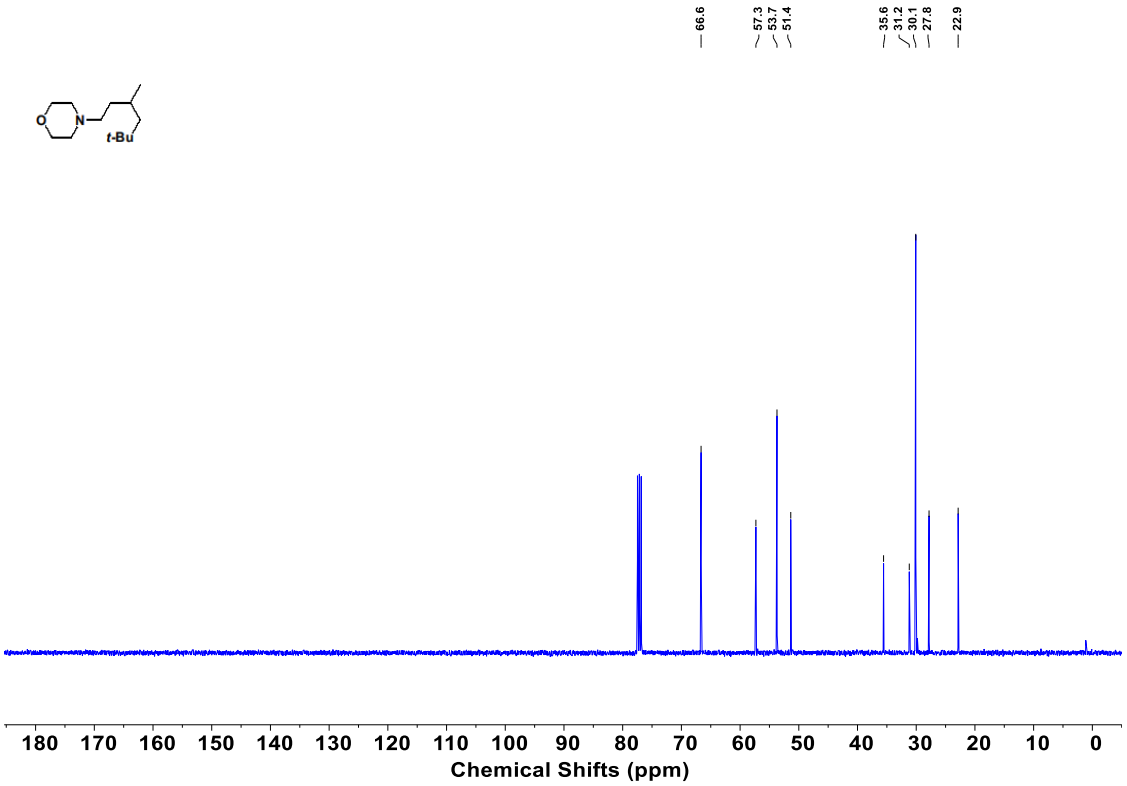

$^{1}$H NMR (400 MHz, $CDCl_3$) of **5-9**



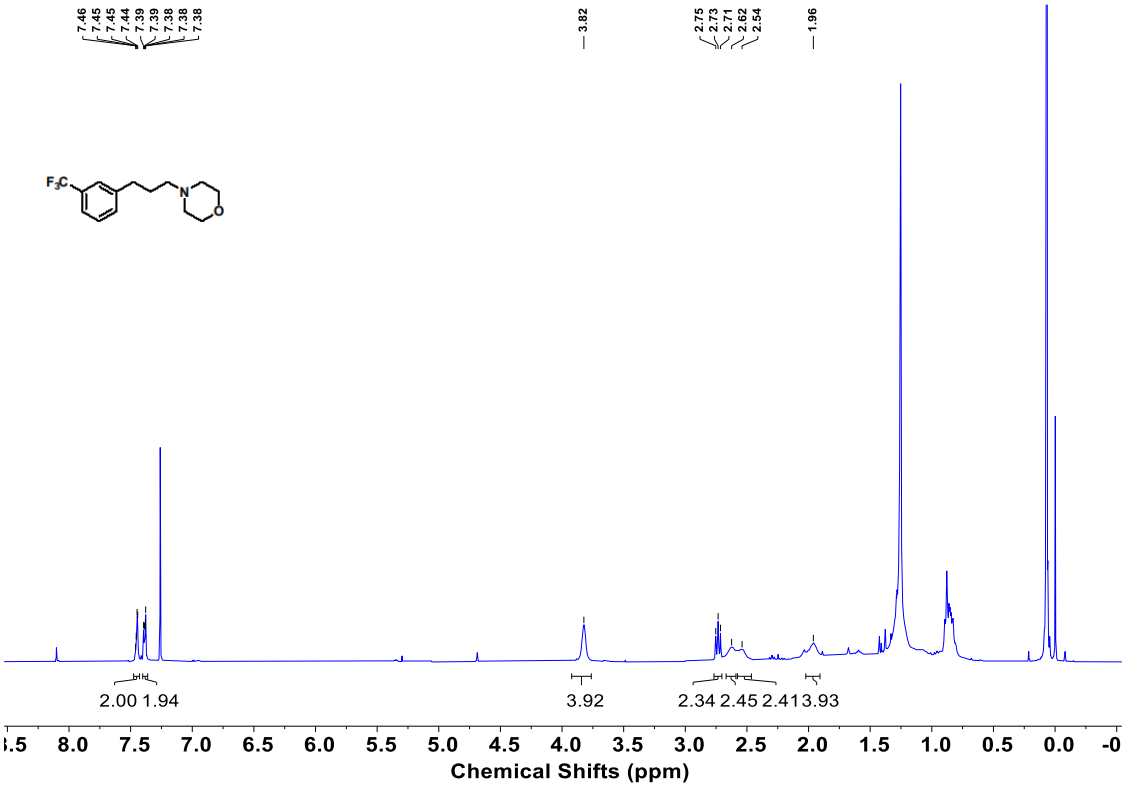

$^{13}$C NMR (101 MHz, $CDCl_3$) of **5-9**



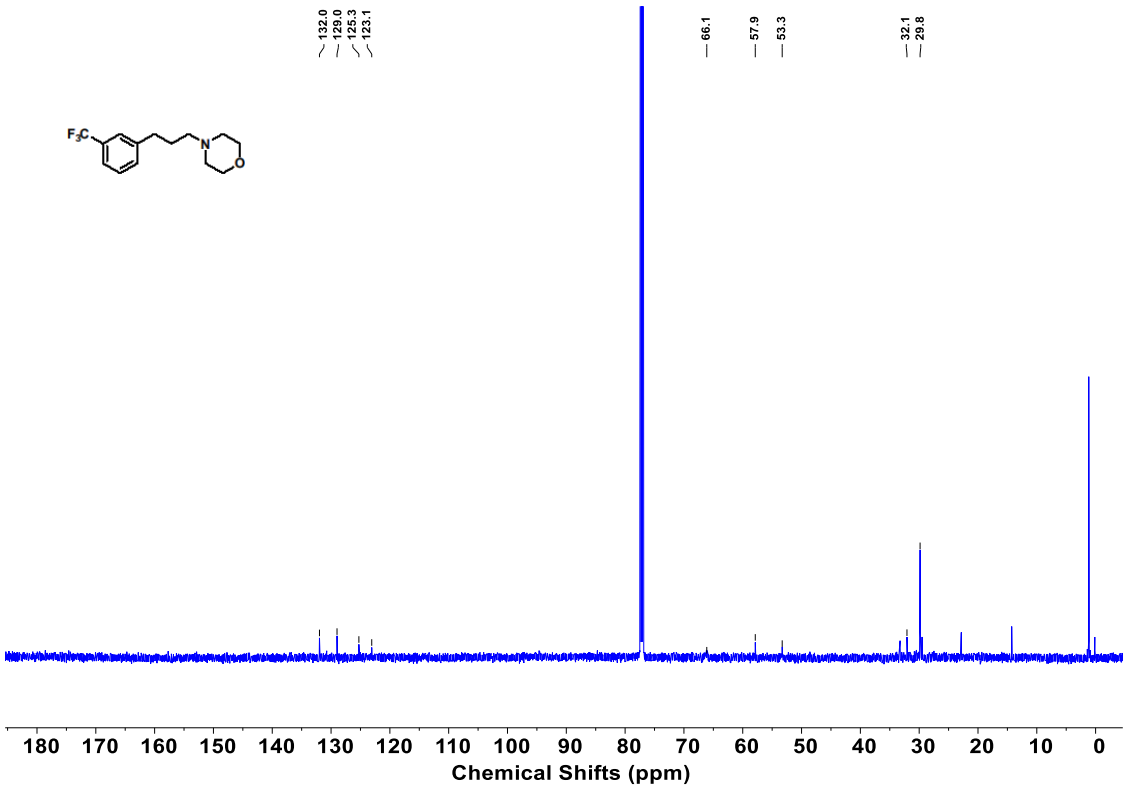

$^{1}$H NMR (400 MHz, $CDCl_3$) of **5-10**



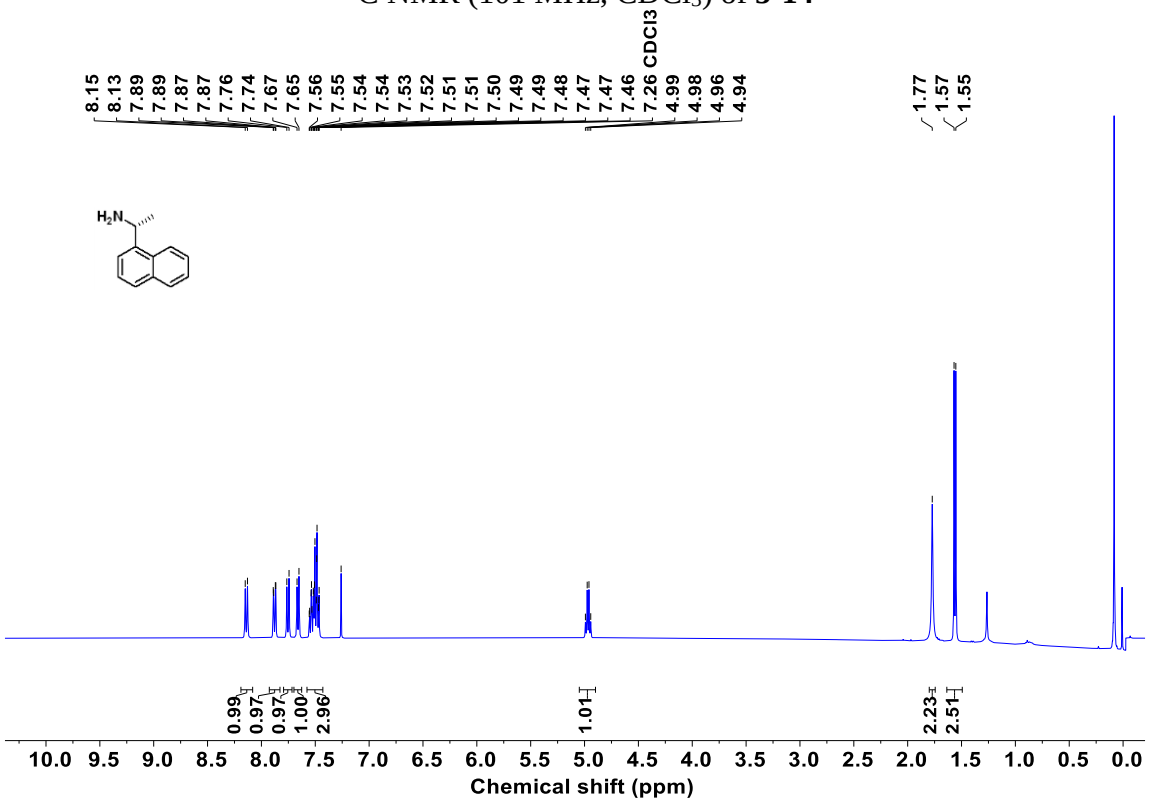

$^{13}C$ NMR (101 MHz, $CDCl_3$) of **5-10**



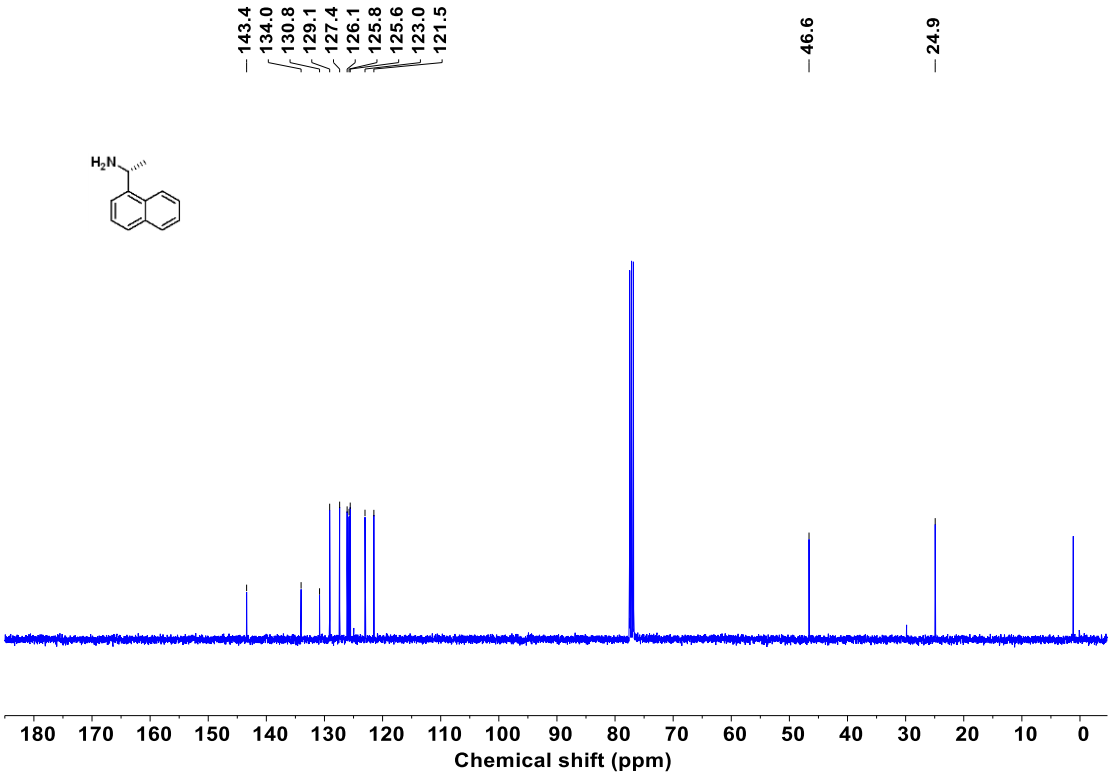

$^{1}H$ NMR (400 MHz, $CDCl_3$) of **5-14**



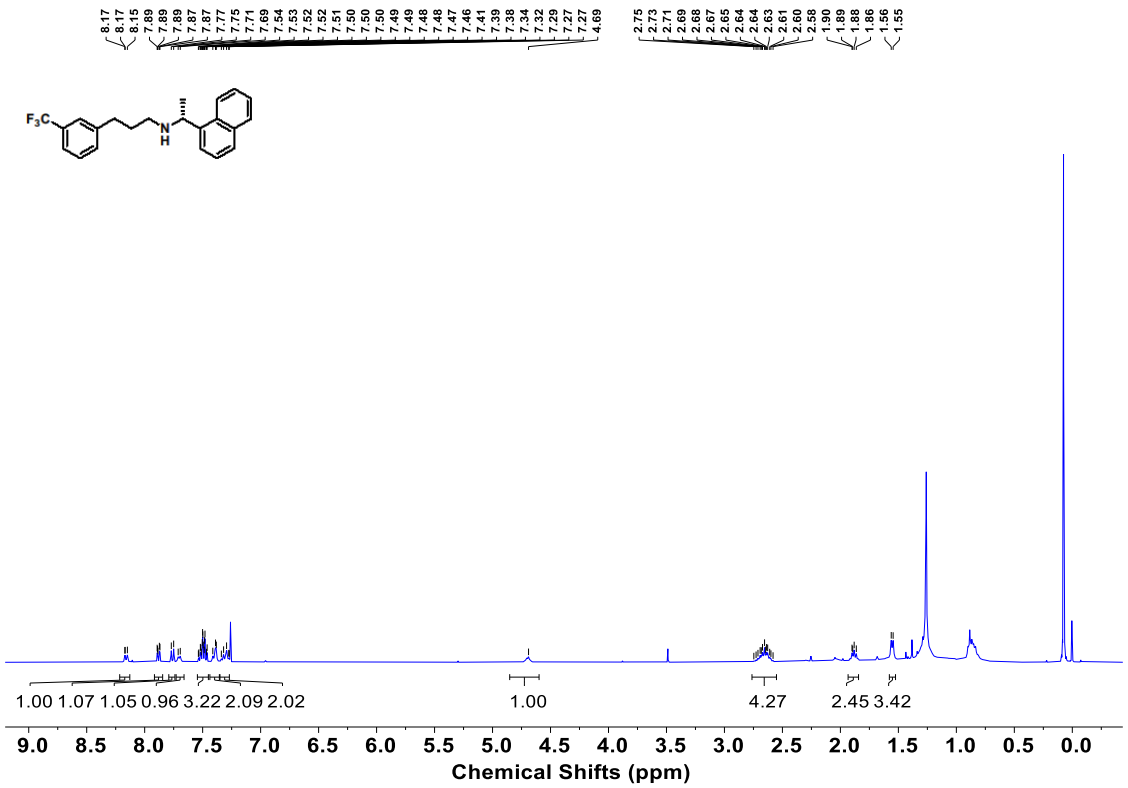

$^{13}C$ NMR (101 MHz, $CDCl_3$) of **5-14**



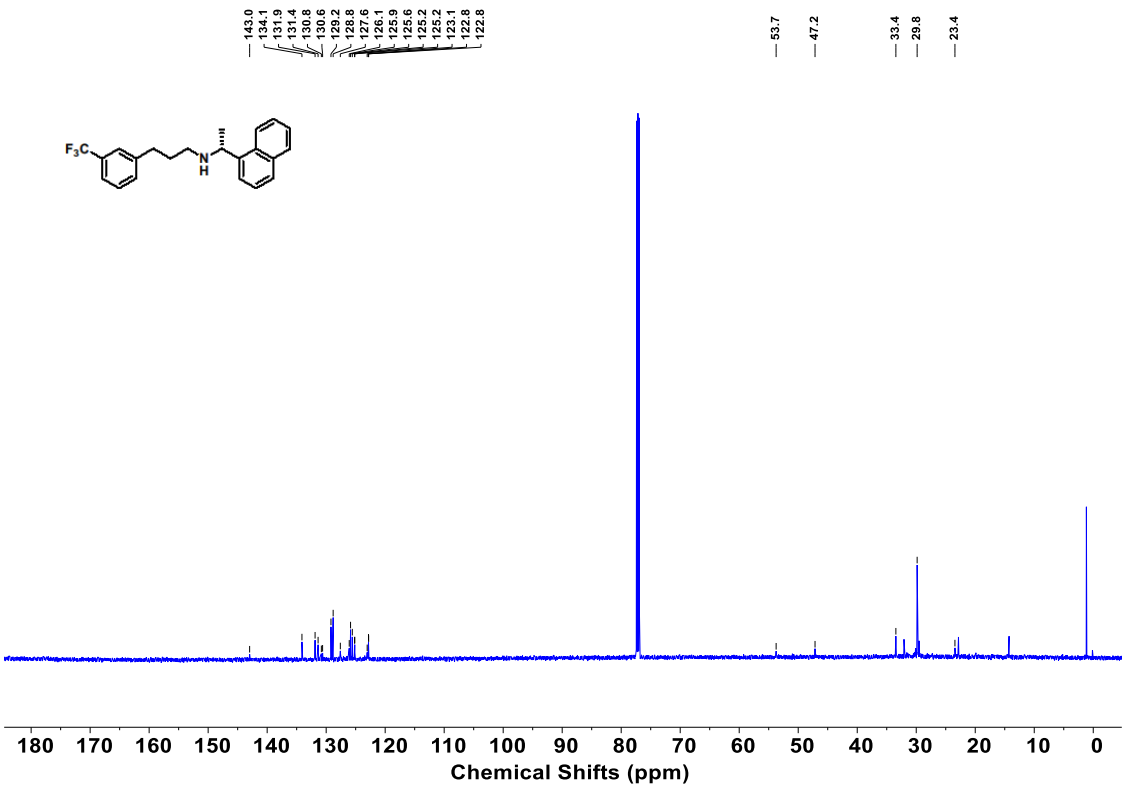

$^{1}H$ NMR (400 MHz, $CDCl_3$) of **2 ((*R*)-1-(naphthalen-1-yl)ethan-1-amine)**




$^{13}$C NMR (101 MHz, $CDCl_3$) of **2 ((*R*)-1-(naphthalen-1-yl)ethan-1-amine)**




$^{1}$H NMR (400 MHz, $CDCl_3$) of (*R*)-N-(1-(naphthalen-1-yl)ethyl)-3-(3-(trifluoromethyl)phenyl)propan-1-amine (Cinacalcet)

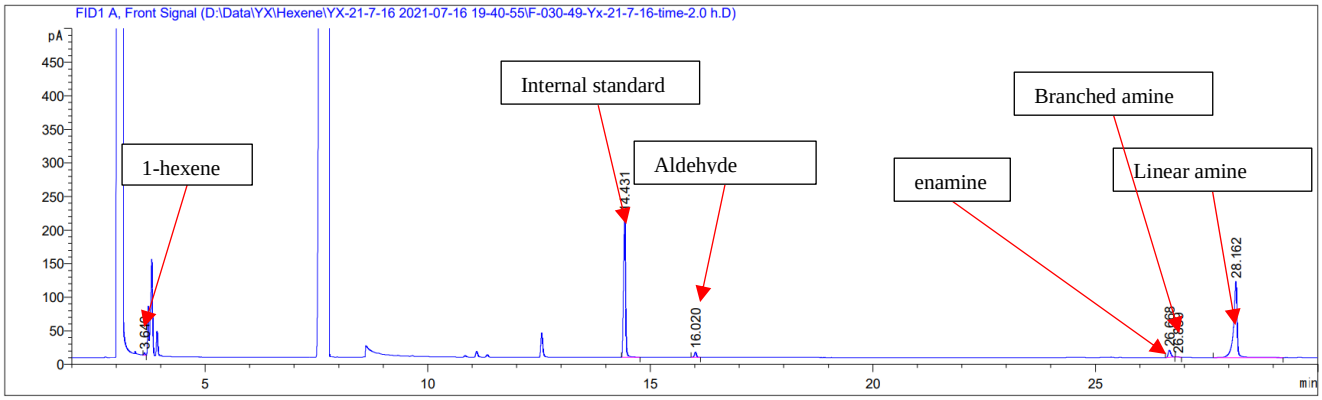



$^{13}$C NMR (101 MHz, $CDCl_3$) of (*R*)-N-(1-(naphthalen-1-yl)ethyl)-3-(3-(trifluoromethyl)phenyl)propan-1-amine (Cinacalcet)

# 8. Representative GC traces

## GC traces of the probable products in the optimization of hydroaminomethylation

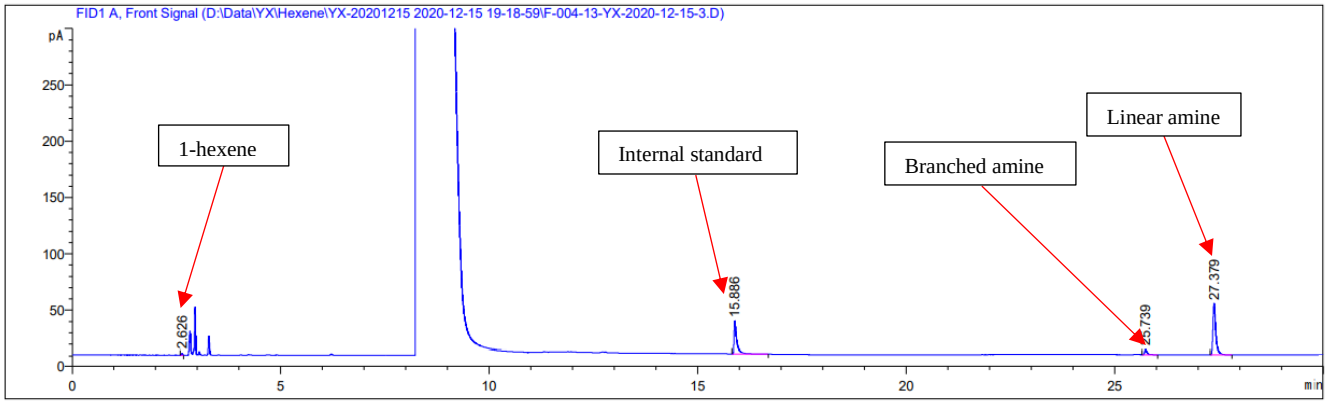
### 1-hexene with morpholine




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 3.640 | MM R | 0.0311 | 6.66555 | 3.56942 | 0.47966 |
| 2 | 14.431 | BB | 0.0503 | 679.52588 | 211.17171 | 48.89960 |
| 3 | 16.020 | BB | 0.0493 | 24.24740 | 7.74468 | 1.74488 |
| 4 | 26.668 | MM R | 0.0665 | 42.27722 | 10.59543 | 3.04233 |
| 5 | 26.859 | MM R | 0.0665 | 1.75040 | 4.38596e-1 | 0.12596 |
| 6 | 28.162 | BB | 0.0815 | 635.16852 | 113.19576 | 45.70758 |
| Totals : | | | | 1389.63497 | 346.71558 | |

*** End of Report ***

**1-hexene with n-hexylamine**




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 2.626 | BB | 0.0245 | 1.96342 | 1.26308 | 0.54868 |
| 2 | 15.886 | BB | 0.0631 | 127.45654 | 28.65000 | 35.61760 |
| 3 | 25.739 | BB | 0.0675 | 17.94028 | 3.93898 | 5.01339 |
| 4 | 27.379 | BB | 0.0707 | 210.48685 | 44.89297 | 58.82033 |
| Totals : | | | | 357.84709 | 78.74503 | |

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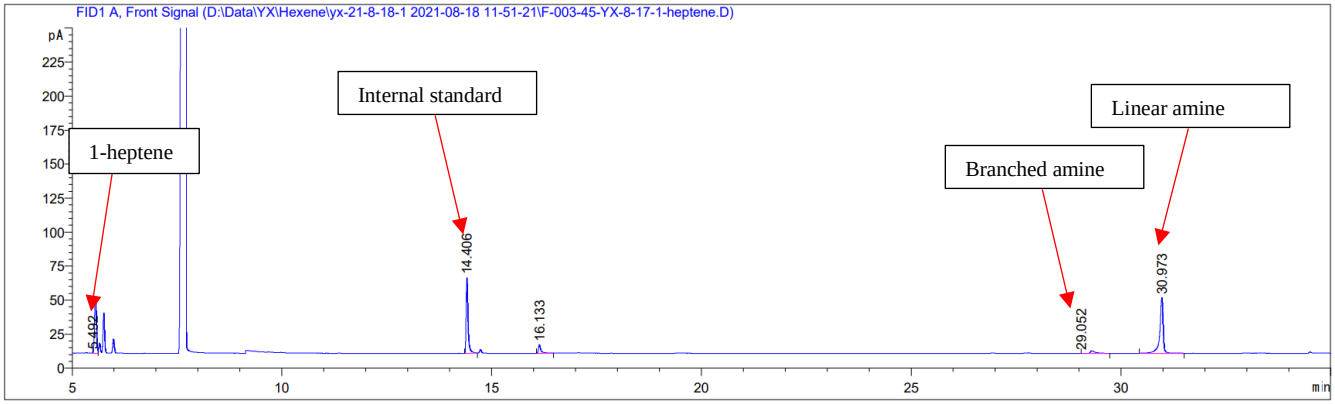
*** End of Report ***

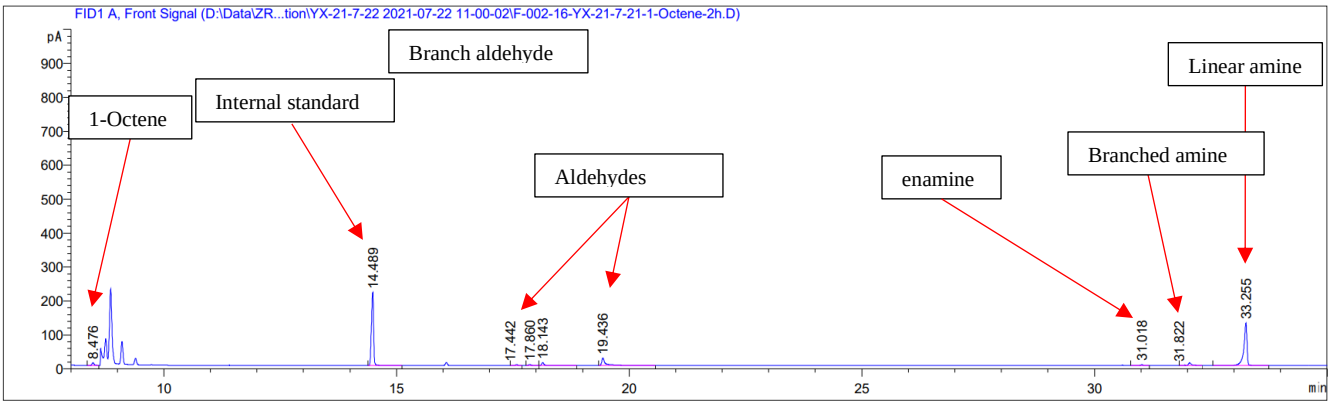
## 1-heptene with morpholine




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.492 | MM R | 0.0578 | 143.48712 | 3.26031e-1 | 24.36488 |
| 2 | 14.406 | BB | 0.0482 | 175.98598 | 55.46539 | 29.88335 |
| 3 | 16.133 | BB | 0.0622 | 25.50084 | 6.11781 | 4.33018 |
| 4 | 29.052 | MM R | 0.1372 | 15.23434 | 3.02422e-2 | 2.58687 |
| 5 | 30.973 | BB | 0.0824 | 228.70143 | 40.70325 | 38.83472 |
| Totals : | | | | 588.90972 | 102.64272 | |

*** End of Report ***

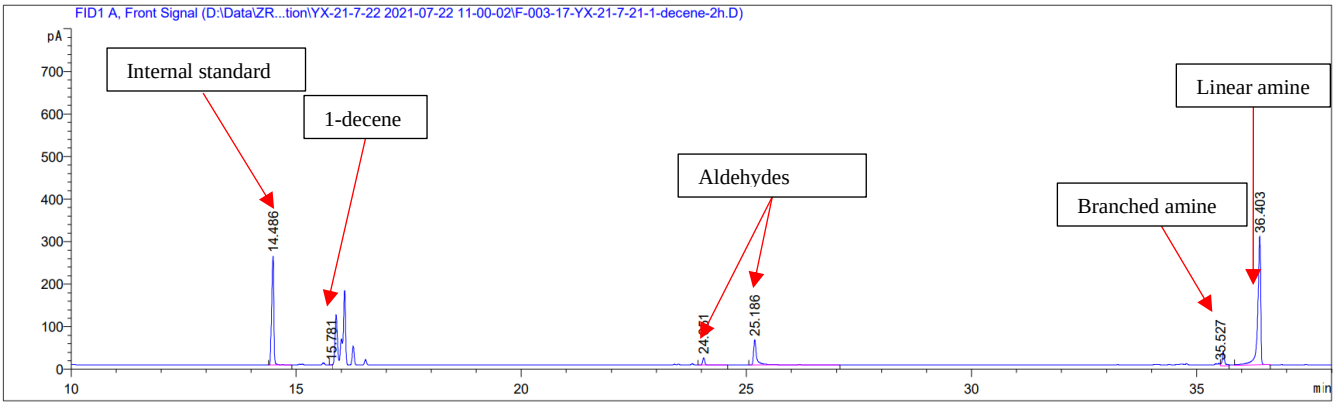
## 1-octene with morpholine




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.476 | BB | 0.0482 | 26.13537 | 8.19186 | 1.66597 |
| 2 | 14.489 | BB | 0.0500 | 702.04449 | 215.74413 | 44.75092 |
| 3 | 17.442 | MM R | 0.0553 | 8.55441 | 3.15797e-2 | 0.54529 |
| 4 | 17.860 | VV | 0.0574 | 11.11761 | 2.79810 | 0.70868 |
| 5 | 18.143 | VB | 0.0570 | 32.20775 | 8.53433 | 2.05304 |
| 6 | 19.436 | BB | 0.0861 | 138.22537 | 22.38093 | 8.81100 |
| 7 | 31.018 | BB | 0.0630 | 10.66749 | 2.53752 | 0.67999 |
| 8 | 31.822 | MM R | 0.0938 | 47.20641 | 1.04015e-1 | 3.00911 |
| 9 | 33.255 | BB | 0.0683 | 592.62335 | 125.02903 | 37.77601 |
| Totals : | | | | 1568.78225 | 385.35150 | |

*** End of Report ***

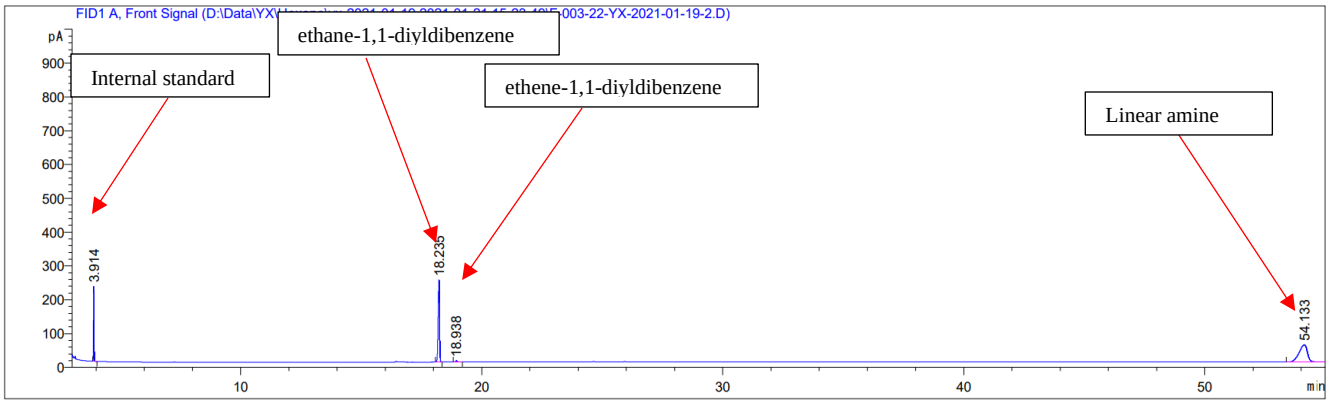
## 1-decene with morpholine




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.486 | BV R | 0.0531 | 859.93604 | 255.73369 | 31.46633 |
| 2 | 15.781 | BB | 0.0343 | 5.93265e-1 | 2.85275e-1 | 0.02171 |
| 3 | 24.051 | BV R | 0.0516 | 56.48885 | 16.79249 | 2.06701 |
| 4 | 25.186 | BV R | 0.0724 | 307.66660 | 59.16333 | 11.25798 |
| 5 | 35.527 | MM R | 0.0614 | 117.33967 | 3.27060 | 4.29363 |
| 6 | 36.403 | MM R | 0.0769 | 1390.85242 | 301.32950 | 50.89334 |
| Totals : | | | | 2732.87683 | 636.57489 | |

*** End of Report ***

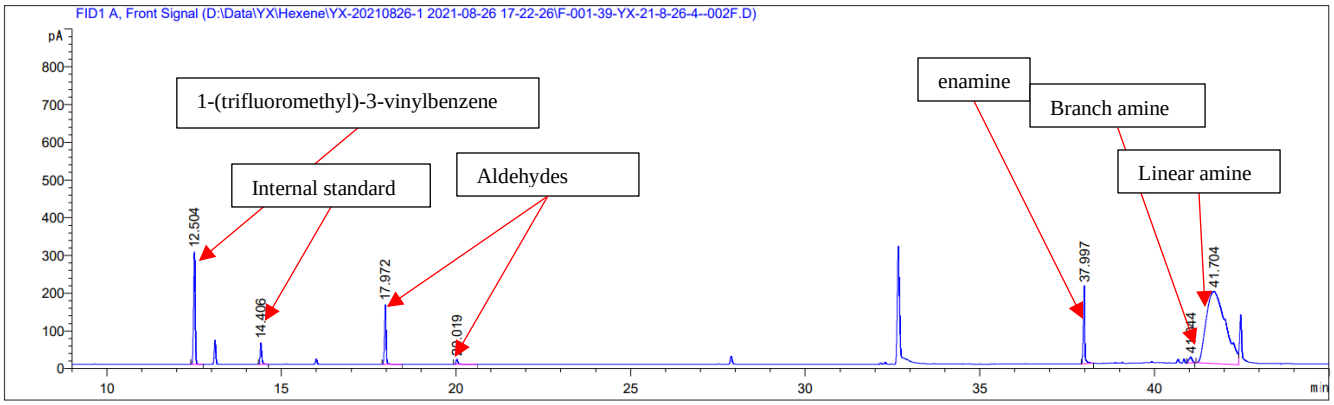
**ethene-1,1-diyldibenzene with morpholine**




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 3.914 | BB | 0.0269 | 374.38919 | 222.26883 | 14.54447 |
| 2 | 18.235 | BB | 0.0616 | 963.27106 | 242.26289 | 37.42166 |
| 3 | 18.938 | BB | 0.0670 | 16.00274 | 3.54846 | 0.62168 |
| 4 | 54.133 | BB | 0.2828 | 1220.43750 | 51.06858 | 47.41219 |
| Totals : | | | | 2574.10049 | 519.14877 | |

*** End of Report ***

## 1-(trifluoromethyl)-3-vinylbenzene with Naphthylethylamine



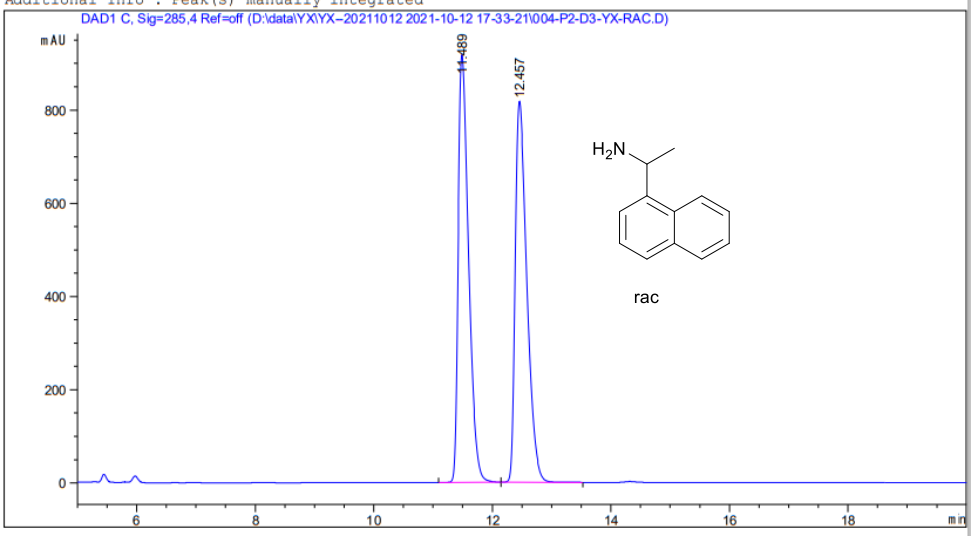

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.504 | BB | 0.0520 | 983.58759 | 298.80151 | 10.08389 |
| 2 | 14.406 | BB | 0.0478 | 180.18155 | 57.46218 | 1.84725 |
| 3 | 17.972 | BB | 0.0497 | 499.98431 | 158.26346 | 5.12592 |
| 4 | 20.019 | BB | 0.0605 | 56.01868 | 13.47058 | 0.57431 |
| 5 | 37.997 | BB | 0.0435 | 596.71277 | 205.53816 | 6.11759 |
| 6 | 41.044 | BB | 0.0840 | 101.18405 | 16.39051 | 1.03735 |
| 7 | 41.704 | MM R | 0.6382 | 7336.37549 | 191.59303 | 75.21368 |
| Totals : | | | | 9754.04444 | 941.51943 | |

*** End of Report ***

# 9. HPLC spectra

## (*rac*)-1-(naphthalen-1-yl)ethan-1-amine:

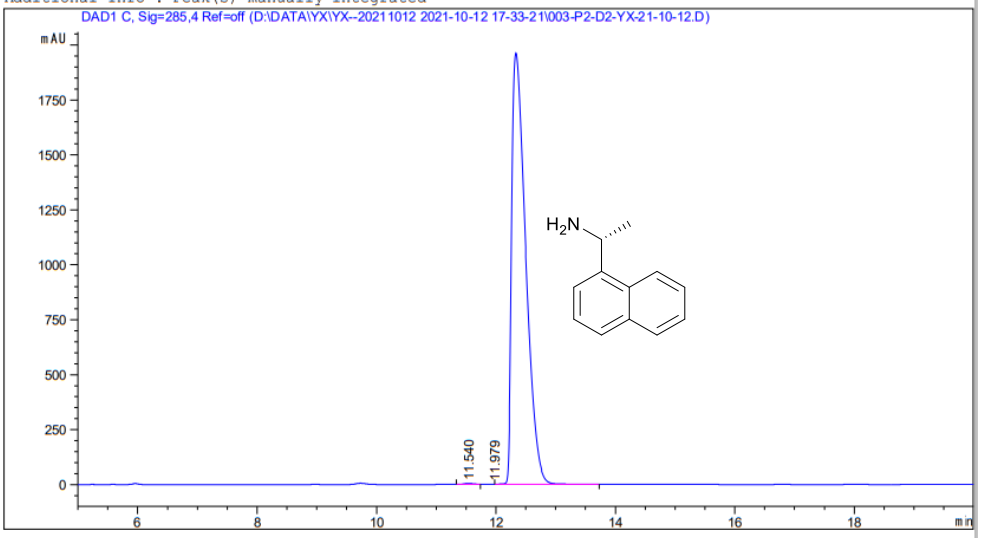
```
======================================================================
Acq. Operator   : SYSTEM                       Seq. Line :   4
Sample Operator : SYSTEM
Acq. Instrument : LC-1260                       Location :   P2-D-03
Injection Date  : 10/12/2021 7:11:51 PM             Inj :   1
                                               Inj Volume : 5.000 µl
Acq. Method     : D:\data\YX\YX--20211012 2021-10-12 17-33-21\R&D-nya-IBN-3-0.1%AE-5-95-
                  alcohol-20210317.M
Last changed    : 3/17/2021 3:47:01 PM by SYSTEM
Analysis Method : D:\data\YX\YX--20211012 2021-10-12 17-33-21\R&D-nya-IBN-3-0.1%AE-5-95-
                  alcohol-20210317.M (Sequence Method)
Last changed    : 10/13/2021 9:36:24 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=285,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.489 BB    0.1856 1.11364e4   917.56555  49.9876
   2  12.457 BV    0.2111 1.11419e4   817.09113  50.0124

Totals :                  2.22783e4  1734.65668
```

**(*R*)-1-(naphthalen-1-yl)ethan-1-amine:**

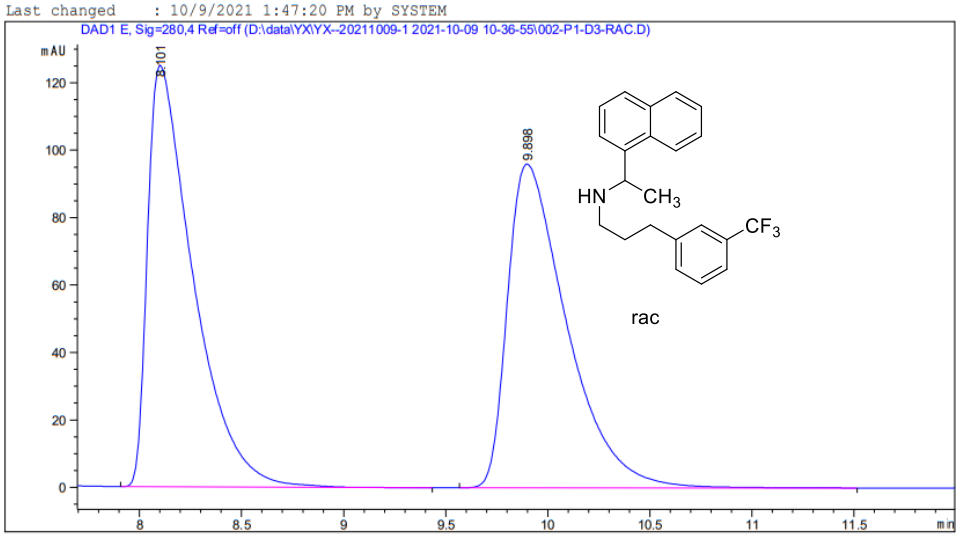
```
======================================================================
Acq. Operator    : SYSTEM                          Seq. Line :   3
Sample Operator  : SYSTEM
Acq. Instrument  : LC-1260                          Location :   P2-D-02
Injection Date   : 10/12/2021 6:41:00 PM                Inj :   1
                                                  Inj Volume : 5.000 µl
Acq. Method      : D:\data\YX\YX--20211012 2021-10-12 17-33-21\R&D-nya-IBN-3-0.1%AE-5-95-
                   alcohol-20210317.M
Last changed     : 3/17/2021 3:47:01 PM by SYSTEM
Analysis Method  : D:\data\YX\YX--20211012 2021-10-12 17-33-21\R&D-nya-IBN-3-0.1%AE-5-95-
                   alcohol-20210317.M (Sequence Method)
Last changed     : 10/13/2021 9:36:24 AM by SYSTEM
                   (modified after loading)
Additional Info  : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=285,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.540 BB    0.1551   43.46658    4.40544   0.1361
   2  11.979 MM R  0.2711 3.18957e4  4.44938e-3  99.8639

Totals :                  3.19392e4     4.40988
```

**(*rac*)-N-(1-(naphthalen-1-yl)ethyl)-3-(3-(trifluoromethyl)phenyl)propan-1-amine (Cinacalcet):**

```
Sample Name: RAC

    ================================================================
    Acq. Operator   : SYSTEM                       Seq. Line :   2
    Sample Operator : SYSTEM
    Acq. Instrument : LC-1260                       Location :   P1-D-03
    Injection Date  : 10/9/2021 11:13:45 AM             Inj :   2
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\data\YX\YX--20211009-1 2021-10-09 10-36-55\R&D-YX-IA-alcohol-0.1 TFA-
                      20211009-96-4.M
    Last changed    : 10/9/2021 10:23:59 AM by SYSTEM
    Analysis Method : D:\data\YX\YX--20211009-1 2021-10-09 10-36-55\R&D-YX-IA-alcohol-0.1 TFA-
                      20211009-96-4.M (Sequence Method)
    Last changed    : 10/9/2021 1:47:20 PM by SYSTEM
```

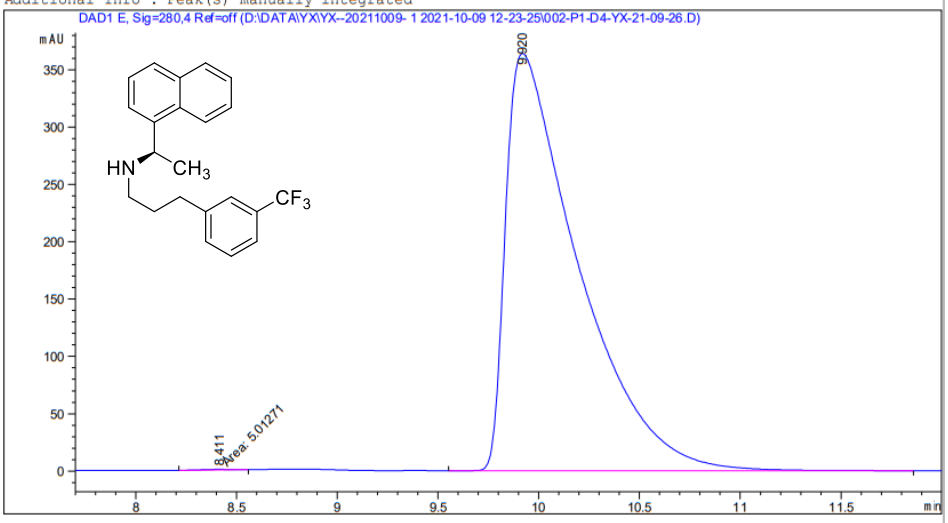



```
    ================================================================
                            Area Percent Report
    ================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 E, Sig=280,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   8.101 BB    0.2293 1943.05212  125.00645  49.9643
       2   9.898 BB    0.3044 1945.82800   96.03473  50.0357

    Totals :                   3888.88013  221.04118
```

**(*R*)-N-(1-(naphthalen-1-yl)ethyl)-3-(3-(trifluoromethyl)phenyl)propan-1-amine (Cinacalcet):**

Data File D:\DATA\YX\YX--20211009- 1 2021-10-09 12-23-25\002-P1-D4-YX-21-09-26.D
Sample Name: YX-21-09-26

```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   2
Sample Operator : SYSTEM
Acq. Instrument : LC-1260                       Location :   P1-D-04
Injection Date  : 10/9/2021 1:00:13 PM              Inj :   1
                                               Inj Volume : 5.000 µl
Acq. Method     : D:\data\YX\YX--20211009- 1 2021-10-09 12-23-25\R&D-YX-IA-alcohol-0.1 TFA-
                  20211009-96-4.M
Last changed    : 10/9/2021 10:23:59 AM by SYSTEM
Analysis Method : D:\data\YX\YX--20211009- 1 2021-10-09 12-23-25\R&D-YX-IA-alcohol-0.1 TFA-
                  20211009-96-4.M (Sequence Method)
Last changed    : 10/9/2021 1:48:06 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

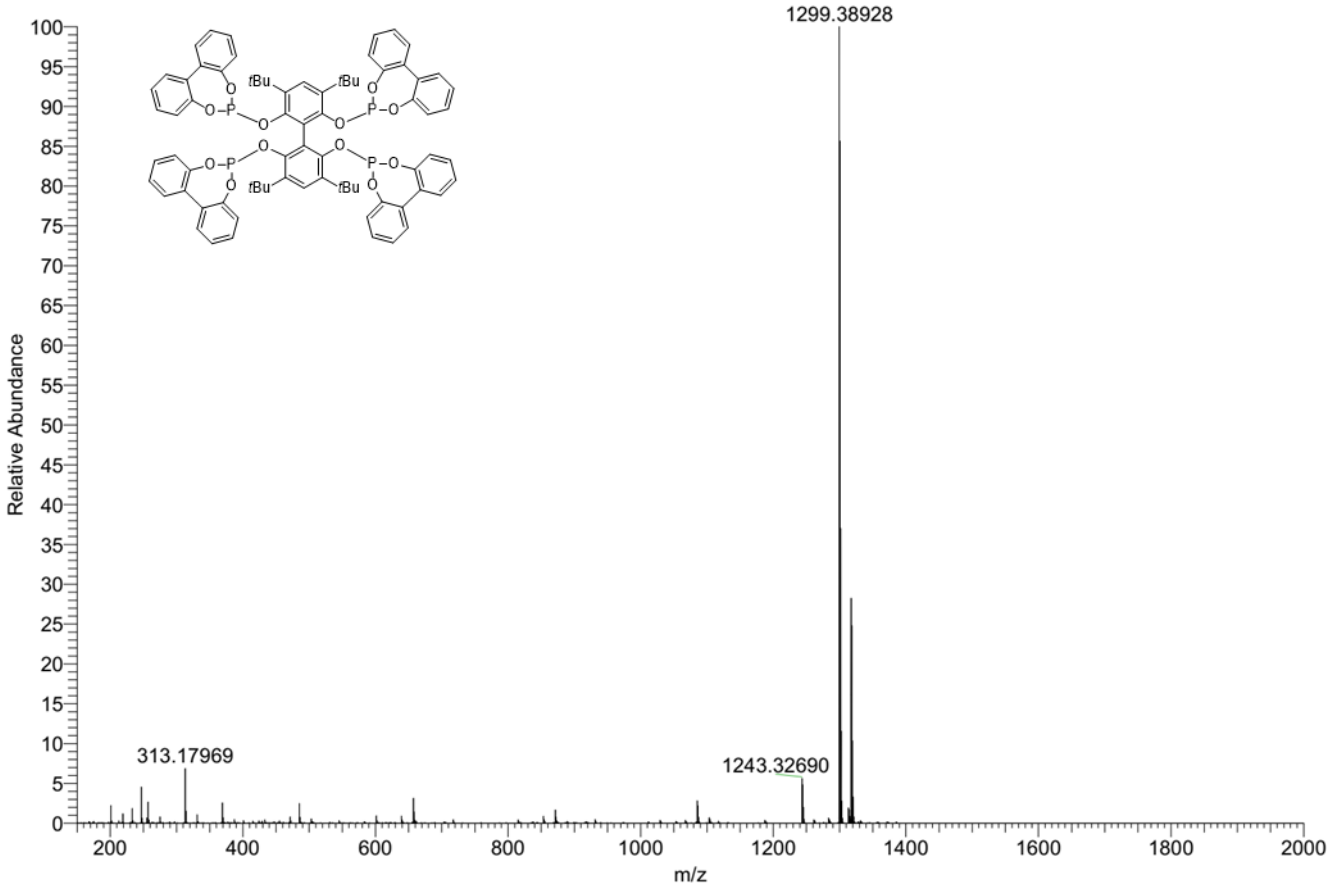


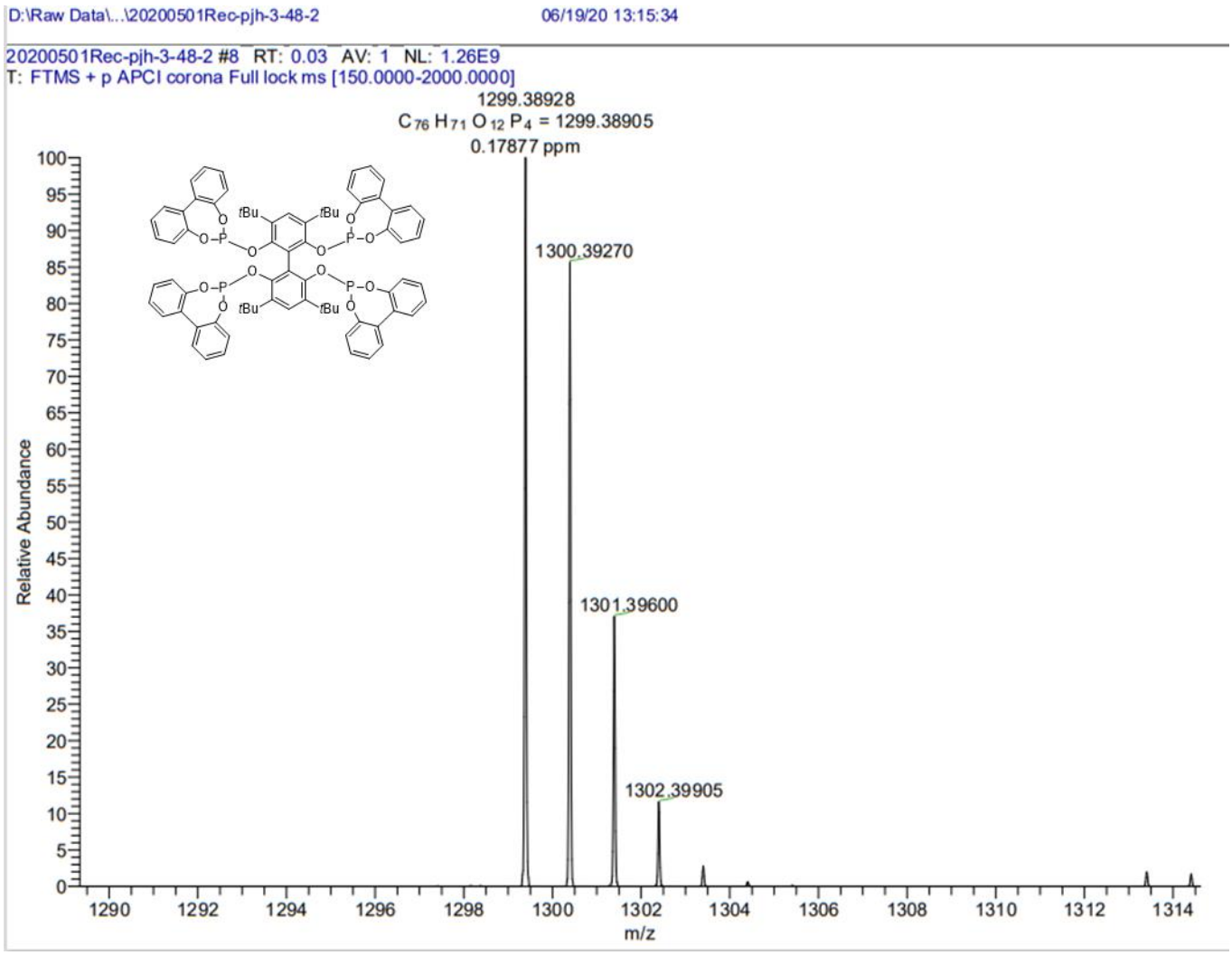

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 E, Sig=280,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.411 MM    0.1551    5.01271 5.38579e-1   0.0550
   2   9.920 BB    0.3620 9113.21582  364.11194  99.9450

Totals :                  9118.22853  364.65052
```

# 10. HRMS spectra for TBTP ligand

D:\Raw Data\...\20200501Rec-pjh-3-48-2 06/19/20 13:15:34

20200501Rec-pjh-3-48-2 #8 RT: 0.03 AV: 1 NL: 1.26E9
T: FTMS + p APCI corona Full lock ms [150.0000-2000.0000]




D:\Raw Data\...\20200501Rec-pjh-3-48-2
06/19/20 13:15:34
20200501Rec-pjh-3-48-2 #8 RT: 0.03 AV: 1 NL: 1.26E9
T: FTMS + p APCI corona Full lock ms [150.0000-2000.0000]
1299.38928
C76 H71 O12 P4 = 1299.38905
0.17877 ppm
1300.39270
1301.39600
1302.39905
tBu
Relative Abundance
m/z

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