

Supporting information

Phosphination of Aryl/Alkyl Bromides via Mn-Mediated Reductive C-P Coupling

Likun Dong¹, Bing Zhong¹, Yu-Shan Zhang¹, Jin-Dong Yang^{1,*}, and Jin-Pei Cheng^{1,2}

¹ Center of Basic Molecular Science (CBMS), Department of Chemistry, Tsinghua University, Beijing 100084, China.

² Haihe Laboratory of Sustainable Chemical Transformations, Tianjin 300192, China.

*Corresponding author. Email: jdyang@mail.tsinghua.edu.cn.

Table of contents

1. General information	3
2. Reaction optimization	3
3. General procedures	5
4. Transformation of 3a & 4g	9
5. Gram-scale experiment of 1a & 2s	11
6. Mechanism studies	11
6. Data of products	14
7. NMR spectra	37
8. References	119

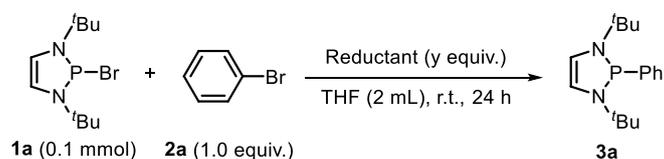
1. General information

Experimental: Air and moisture-sensitive reactions were carried out in oven-dried Schlenk tubes or sealed tubes with Teflon caps under an argon atmosphere or in an inert gas (Argon gas) glove box. Reactions were stirred using Teflon-coated magnetic stir bars. Organic solutions were concentrated using a rotary evaporator with a diaphragm vacuum pump. Analytical TLC was performed on silica gel GF254 plates. The TLC plates were visualized under the ultraviolet light ($\lambda = 254$ nm). Purification of products was accomplished by recrystallization with poor solvents or flash column chromatography on silica gel (Innochem SilicaFlash P60, 230-400 mesh). Solvents were purified by MBRAUN SPS 800 solvent purification or purchased as anhydrous solvents from J&K Chemical (99.9 %, extra dry, water < 10 ppm, J&K seal). Other reagents were purchased at the highest commercial quality and used without further purification, unless otherwise noted. Reaction temperature refers to the temperature of an aluminum heating block, which was controlled by an electronic temperature modulator from Heidolph.

Analytics: NMR spectra were recorded on a Bruker AVANCE III HD 400 (^1H at 400 MHz, ^{13}C at 101 MHz, ^{19}F at 376 MHz, ^{31}P at 162 MHz) or 600 nuclear magnetic resonance spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts are given in ppm with respect to the solvent peak of CDCl_3 (δ_{H} 7.26 ppm, δ_{C} 77.16 ppm), and $\text{DMSO}-d_6$ (δ_{H} 2.50 ppm, δ_{C} 39.52 ppm). Multiplicities are described as s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, sept = septet, dd = doublet of doublets, td = triplet of doublets, m = multiplet. Coupling constants are reported in Hertz (Hz). ^{19}F NMR chemical shifts are given in ppm with respect to CFCl_3 (δ 0 ppm) as an external standard. ^{31}P NMR chemical shifts are given in ppm with respect to $\text{P}(\text{OPh})_3$ (δ 128 ppm) as an external standard. High-resolution mass spectra (HRMS) data was obtained by using Thermo Scientific™ Q-Exactive Orbitrap™ Mass Spectrometer.

2. Reaction optimization

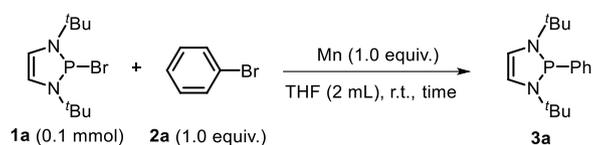
Table S1. Optimization of reductants^a



Entry	Reductant	Equivalent [y]	Yields of 3a [%] ^b
1	Li ^c	3.0	83
2	Cu ^{c,d}	3.0	0
3	Mn ^c	3.0	88
4	Mn	3.0	91
5	Mn	2.0	90
6	Mn	1.5	92

^a Reaction conditions: **1a** (0.1 mmol, 1.0 eq.), aryl bromide **2a** (1.0 eq.), reductant (y eq.) in THF (2 mL) in a sealed tube at r.t. for 24 h. ^b ³¹P-NMR yields with triphenyl phosphite as the internal standard. ^c 1 mL THF was added. ^d Cu powder was activated before used.

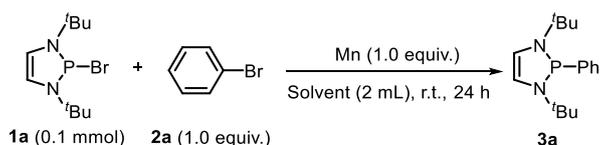
Table S2. Optimization of the reaction time^a



Entry	Reaction time/h	Yields of 3a [%] ^b
1	24	92
2	4	61
3	8	70
4	20	89
5	72	79
6	36	90
7	30	90

^a Reaction conditions: **1a** (0.1 mmol, 1.0 eq.), aryl bromide **2a** (1.0 eq.), reductant Mn (1.0 eq.) in THF (2 mL) in a sealed tube at r.t. for some time. ^b ³¹P-NMR yields with triphenyl phosphite as the internal standard.

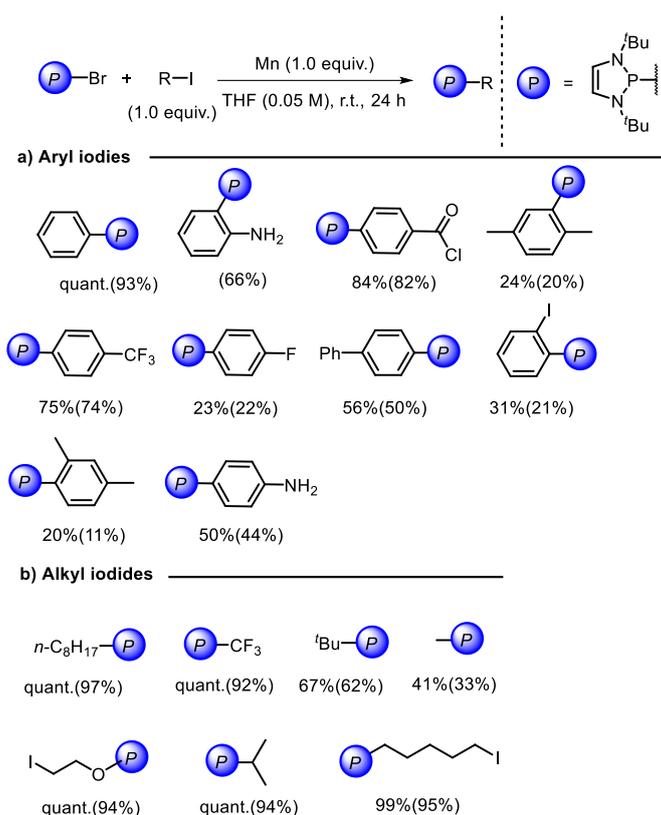
Table S3. Optimization of solvents^a



Entry	Solvent	Yields of 3a [%] ^b
-------	---------	--------------------------------------

1	THF	92
2	1,2-DCE	61
3	Et ₂ O	70
4	<i>n</i> -Hexane	68
5	EtOAc	47

^a Reaction conditions: **1a** (0.1 mmol, 1.0 eq.), aryl bromide **2a** (1.0 eq.), Mn (1.0 eq.) in solvent (2 mL) in a sealed tube at r.t. for 24 h. ^b ³¹P-NMR yields with triphenyl phosphite as the internal standard.



Scheme S1. R-I (aryl iodides & alkyl iodides) substrate scope. ^a **1a** (0.1 mmol, 1.0 eq.), aryl/alkyl iodide (1.0 eq.), Mn (1.0 eq.) in THF (0.05 M) in a sealed tube at r.t. for 24 h. ^b ³¹P-NMR yields were determined with triphenyl phosphite as the internal standard. ^b Isolated yields shown in parentheses.

3. General procedures

General procedure (GP1) for synthesis of *N*-heterocyclic phospholenes (**1a-1c**):

Substates **1a-1c** was prepared according to former literatures.¹ In a 250 mL round-bottom flask, 1° amine (2.0 equiv., 100 mmol) was dissolved in anhydrous DCM (50 mL) and the mixture was cooled to -15 °C using an NaCl/ice bath. Glyoxal (5.7 mL, 8.8 M, 40 w.t.% in H₂O, 50 mmol) was added

dropwise, after which the cooling was removed. Then the reaction was left to stir for 3 h. Phases were separated and the aqueous phase was extracted with DCM (3×10 mL), and the combined organic phases were dried over anhydrous Na_2SO_4 , filtered and the crude product was collected by removing the solvent DCM in vacuo carefully (Note: this product could be sublimated under reduced pressure). This crude product was then weighted and transferred in a 200 mL Schlenk flask and dissolved in anhydrous DCM (80 mL). Cyclohexene (3.0 equiv.) was added and the mixture was cooled to -15 °C using an NaCl/ice bath. Then PBr_3 (1.0 equiv.) was added dropwise within 5 min, after which the cooling was removed. Then the reaction was left to stir for 24 h. The reaction was monitored by ^{31}P -NMR before completed. The solvent was then removed in vacuo. The Schlenk flask was taken into a glovebox, and 100 mL anhydrous diethyl ether was added. The mixture was then stirred for 10 minutes, and any solid stuck to the side was scraped off with a spatula. The mixture was filtered, and the solid was washed with 3×100 mL of ether. The collected solid was then dried under vacuum on the frit, to yield compound **1a** (off-white solid, 13.3 g, 95% yield), **1b** (ivory solid, 22.4 g, 92% yield), **1c** (dark green solid, 18.9 g, 88% yield). Spectroscopic data was identical to that reported previously.¹

Synthesis of 4,5-bis(2,5-dimethyl-3-thienyl)-2,3-dihydro-1,3-phenyl-2-bromo-1H-1,3,2-diazaphosphole (1d):

Substates **1d** was prepared according to former literatures.²

Step 1: Synthesis of 1,2-Bis(2,5-dimethylthiophen-3-yl)ethane-1,2-dione.^{2a}

A three-necked flask equipped with a thermometer was charged with AlCl_3 (6.0 g, 44.9 mmol) and purged with Ar. DCM (50 mL) was added, and the suspension formed upon stirring was cooled to -15 °C using an NaCl/ice bath. Pyridine (1.8 mL, 22.3 mmol) dissolved in DCM (10 mL) and 2,5-dimethylthiophene (5.0 g, 44.6 mmol) dissolved in DCM (25 mL) were added followed by the dropwise addition of oxalyl chloride (2.3 mL, 26.8 mmol) dissolved in DCM (25 mL) in ~ 90 min at -15 °C. After the addition was complete, the reaction was allowed to warm to 5 °C in 60 min. The mixture was poured on ice cold water (200 mL), and the organic phase was separated. The aqueous layer was extracted with CHCl_3 (3×200 mL) and the combined organic layer was washed with water and saturated Na_2CO_3 solution and dried over Na_2SO_4 . The solvent was evaporated under reduced pressure, and the dark residue was further purified by column chromatography (SiO_2 , *n*-

hexane/EtOAc 9:1) to obtain the product as a red oil (2.6 g, 43%). Spectroscopic data was identical to that reported previously.^{2a}

Step 2: (*1E,2E*)-1,2-bis(2,5-dimethylthiophen-3-yl)-*N*¹,*N*²-diphenylethane-1,2-diimine.^{2b}

A 10 mL DCM solution of aniline (10.87 mL, 119.80 mmol) was cooled to 0 °C in an ice bath. To the reaction mixture TiCl₄ (1.61 mL, 14.80 mmol) was added *via* syringe and the reaction stirred for 20 min. at 0 °C. A 10 mL DCM solution of 1,2-bis(2,5-dimethyl-3-thienyl)ethandione (4.15 g, 14.80 mmol) was then added *via* cannula and the dark red solution stirred at r.t. for 12 h. Upon completion, 5 mL of water was added to the reaction mixture and a white solid precipitated immediately, which was removed by filtration. The orange filtrate was then subsequently washed with water and dried with Na₂SO₄ and concentrated. The resulting residue was crystallized from EtOH to give the product. Yield: 76 % (4.82 g, 11.2 mol). Spectroscopic data was identical to that reported previously.^{2b}

Step 3: Synthesis of 4,5-bis(2,5-dimethyl-3-thienyl)-2,3-dihydro-1,3-phenyl-2-bromo-1*H*-1,3,2-diazaphosphole.^{2b}

Phosphorus tribromide (0.22 mL, 2.33 mmol) was added to a 10 mL DCM solution of (*1E,2E*)-1,2-bis(2,5-dimethylthiophen-3-yl)-*N*¹,*N*²-diphenylethane-1,2-diimine (1 g, 2.33 mmol) and cyclohexene (1.41 mL, 13.9 mmol) and stirred for 12 h at r.t. The orange solution was concentrated yielding a yellow solid, which was washed with pentane (3 × 5 mL) yielding the desired product as a light yellow powder. Yield: 92 % (1.13 g, 2.1 mmol). Spectroscopic data was identical to that reported previously.^{2b}

Synthesis of 2,3-dihydro-1,3-di-isopropyl-2-chloro-1*H*-naphtho[1,8-*de*][1,3,2]diazaphosphinine (1e):

Substates **1e** was prepared according to former literatures.³ Spectroscopic data was identical to that reported previously.³

Synthesis of 2-chloro-1,3-dimethyl-benzodiazaphosphole (1f):

Substates **1f** was prepared according to former literatures.⁴ Spectroscopic data was identical to that reported previously.⁴

Synthesis of 2-chloro-1,3-diisopropyl-benzodiazaphosphole (1g):

Substates **1g** was prepared according to former literatures.⁵

Step 1: Synthesis of *N*¹,*N*²-diisopropylbenzene-1,2-diamine. A round-bottomed flask equipped with

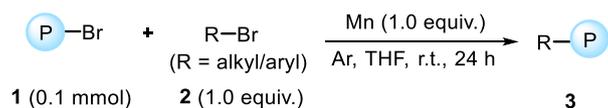
a magnetic stirrer bar was charged with *o*-phenylenediamine (2.0 g, 18.5 mmol, 1 equiv.), potassium carbonate (5.1 g, 37.0 mmol, 2 equiv.), and excess 2-iodopropane (20.4 g, 120.0 mmol, 6.5 equiv.). The solution was heated to reflux for 2 h, after which time the solution was cooled to ambient temperature. Hexane (30 mL) was subsequently added and the mixture was washed with water (50 mL). The product was extracted from the aqueous phase using hexane (3 × 20 mL), the organic phases being combined after each extraction. The solution was dried using anhydrous magnesium sulfate, and the solvent was removed under reduced pressure to afford a viscous dark brown oil. Subsequently the oil was filtered through Celite and the solvent was again removed under reduced pressure to give a red-brown oil. Yield: 2.9 g, 15.1 mmol, 80%. Spectroscopic data was identical to that reported previously.⁵

Step 2: Synthesis of 2-chloro-1,3-diisopropyl-benzodiazphosphole. A three-necked flask was fitted with a magnetic stirrer bar and charged with *N*¹,*N*²-diisopropylbenzene-1,2-diamine *N*¹,*N*²-diisopropylbenzene-1,2-diamine (1.50 g, 7.8 mmol, 1 equiv.) in toluene (10 mL) and phosphorus trichloride (0.82 mL, 9.4 mmol, 1.2 equiv.). The solution was cooled to 0 °C, and triethylamine (2.61 mL, 18.7 mmol, 2.4 equiv.) was added dropwise with stirring. The reaction mixture was warmed to ambient temperature and stirred for 24 h. Using a filter cannula, the solution was transferred to a Schlenk tube and the solvent was removed in vacuo. The precipitate was washed with pentane (3 × 5 mL) to yield the product as a white-pink solid. Yield: 1.68 g, 6.54 mmol, 84%. Spectroscopic data was identical to that reported previously.⁵

Synthesis of 2-phenyl-1,3-di-*tert*-butyl-benzodiazphosphole (**1h**):

Substates **1h** was prepared according to former literatures.⁶

General procedure (GP2) for Mn-Mediated Reductive Coupling of Aryl/Alkyl Bromides with Bromodiazaphospholes

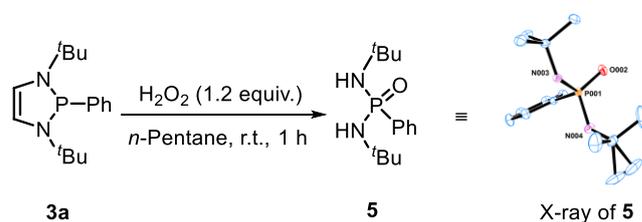


1 (27.80 mg, 0.10 mmol, 1.0 equiv.) and Mn (5.50 mg, 0.1 mmol, 1.0 equiv.) were added to an oven-dried sealed tube (volume: 10 mL) with a stir bar at the Argon atmosphere glove box. 2 mL THF was added in the tube and reactants were stirred. Then aryl/alkyl bromide **2** (0.1 mmol, 1.0 equiv.)

was added. Finally, a sealed tube of this solution was stirred for 24 hours at r.t. After the reaction was completed, the tube was moved into the glove box again. In the glove box, the sealed tube was opened and the solvent THF was removed under vacuum, the resulting mixture was washed with *n*-Pentane (3 mL × 3) and filtered. The combined filtrates were collected and the solvent *n*-Pentane was removed in vacuo to afford the reductive cross coupling P-C product **3**. Crystallization might be taken for a purer product.

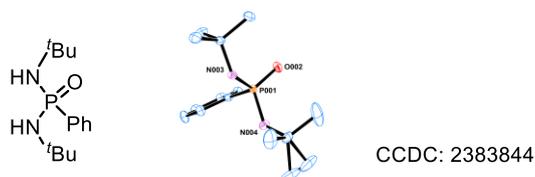
Note: This reaction can also be done in a Schlenk line with a slight influence on yields.

4. Transformation of **3a** & **4g**



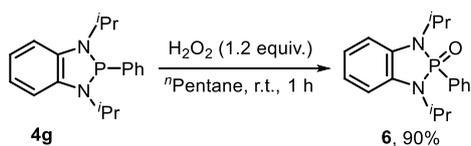
The flask was added 2 mL THF to redissolve **3a**. Then H₂O₂ (0.12 mmol, 1.2 equiv.) was added. Finally, this solution was stirred for 1 hour at r.t. The resulting mixture was concentrated in vacuo and purified by flash column chromatography (silica gel) to afford the product phosphamide **5** (72% yield).

Table S4. X-ray crystallographic data for **5**



Empirical formula	C ₁₄ H ₂₅ N ₂ OP
Formula weight	268.33
Temperature/K	172.99(10)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	8.23900(10)

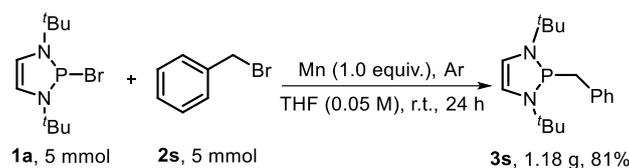
b/Å	10.4970(2)
c/Å	18.2476(3)
α /°	90
β /°	97.989(2)
γ /°	90
Volume/Å ³	1562.82(4)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.140
μ/mm^{-1}	1.486
F(000)	584.0
Crystal size/mm ³	0.15 × 0.12 × 0.10
Radiation	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	9.744 to 153.288
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 9, -22 ≤ l ≤ 23
Reflections collected	10560
Independent reflections	3142 [R_{int} = 0.0290, R_{sigma} = 0.0303]
Data/restraints/parameters	3142/6/180
Goodness-of-fit on F ²	1.062
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0458, wR_2 = 0.1220
Final R indexes [all data]	R_1 = 0.0507, wR_2 = 0.1256
Largest diff. peak/hole / e Å ⁻³	0.64/-0.58



After finishing GP2, the flask was added 2 mL THF to redissolve **4g**. Then H₂O₂ (0.12 mmol, 1.2 equiv.) was added. Finally, this solution was stirred for 1 hour at r.t. The resulting mixture was concentrated in vacuo and purified by flash column chromatography (silica gel) to afford the product

phosphamide **6** (90% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.34 (m, 2H), 7.26 (1 peak overlap with CDCl_3 , 1H), 7.20 (m, 2H), 6.62 (dd, $J = 7.5, 1.5$ Hz, 2H), 6.52 (dd, $J = 7.5, 1.5$ Hz, 2H), 2.83 (sept, $J = 6.8$ Hz, 2H), 1.13 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 134.9, 134.1, 133.1, 132.3, 128.8, 117.9, 111.0, 49.9, 22.1. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 23.2 (d). GC-MS: $m/z = 314, 272, 230$.

5. Gram-scale experiment of **1a** & **2s**

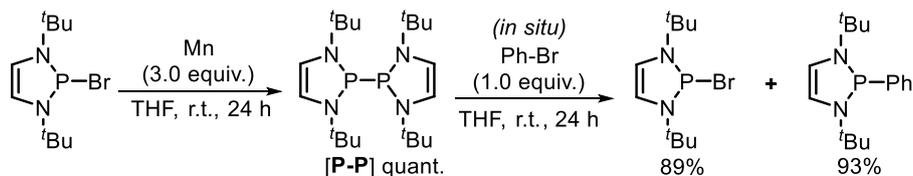


Scheme S2. Gram-scale experiment of **1a** & **2s**

1a (1.39 g, 5.0 mmol, 1.0 equiv.) and Mn (274.7 mg, 5.0 mmol, 1.0 equiv.) were added to an oven-dried Schlenk flask with a suitable stir bar. Then the flask was refilled three times with Argon gas. Then 100 mL THF was added followed by injecting benzyl bromide **2s** (593.9 μL , 5.0 mmol, 1.0 equiv.). This solution was stirred vigorously under Argon atmosphere. Using $^{31}\text{P NMR}$ to monitor this reaction until **1a** was totally consumed (48 h). The resulting mixture solvent THF was removed in vacuo and extracted with n -Pentane (50 mL \times 3). The filtrate was collected together and n -Pentane was removed in vacuo to afford the P-C reductive coupling product **3s** (liquid, 1.18 g, 81% yield).

6. Mechanism studies

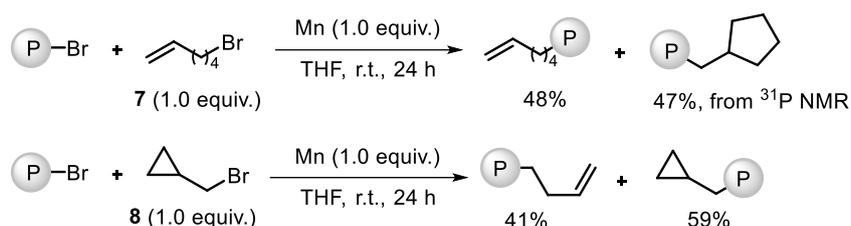
Intermediate synthesis:⁷



The intermediate synthesis experiment was conducted according to **GP2**: [P-Br] reagent **1a** (27.80 mg, 0.10 mmol, 1.0 equiv.) and Mn (16.48 mg, 0.3 mmol, 3.0 equiv.) were added to an oven-dried

sealed tube (volume: 10 mL) with a stir bar at the Argon atmosphere glove box. 2 mL THF was added in the tube and the reactants were stirred. After 24 h this reaction finished, the yield was determined by ^{31}P NMR integrals. ^{31}P NMR (162 MHz, CDCl_3) δ 80.08 ([P-P]). Then the crude solution was added bromobenzene **2a** (10.5 μL , 0.1 mmol, 1.0 equiv.) as an internal standard. The yield was determined by ^{31}P NMR integrals. ^{31}P NMR (162 MHz, CDCl_3) δ 186.53 ([P-Br], **1a**), 74.55 ([P-Ph], **3a**).

Radical-clock experiments:⁷



The first radical-clock experiment was conducted following **GP2** using 6-bromo-1-hexene (0.1 mmol, 1.0 equiv.) as a starting material. After finishing this reaction, the crude solution was added $\text{P}(\text{OPh})_3$ (0.05 mmol) as an internal standard. The yields were determined by ^{31}P NMR integrals. ^{31}P NMR (162 MHz, CDCl_3) δ 92.12 (linear product), 86.00 (cyclic product).

The second radical-clock experiment⁷ was conducted following **GP2** using (bromomethyl)cyclopropane (0.1 mmol, 1.0 equiv.) as a starting material. After finishing this reaction, the crude solution was added $\text{P}(\text{OPh})_3$ (0.05 mmol) as an internal standard. The yields were determined by ^{31}P NMR integrals. ^{31}P NMR (162 MHz, CDCl_3) δ 85.85 (linear product), 77.43 (cyclic product).

Radical-trap experiment:

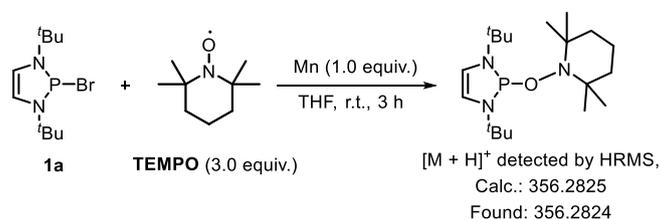


Figure S1. Radical-trap experiment for P-C coupling.

This radical-trap experiment was conducted according to **GP2**: [P-Br] reagent **1a** (27.80 mg, 0.10 mmol, 1.0 equiv.) and Mn (5.49 mg, 0.1 mmol, 1.0 equiv.) were added to an oven-dried sealed tube

(volume: 10 mL) with a stir bar at the Argon atmosphere glove box. 2 mL THF was added in the tube and the reactants were stirred. Then Mn (5.49 mg, 0.1 mmol, 1.0 equiv.) were added. After 3 h this crude solution was tested by HRMS. **HRMS** (ESI⁺) calculated for C₁₉H₃₉N₃OP⁺ [M+H]⁺ m/z 356.2825, found 356.2824.

Chemoselectivity test experiments:

The chemoselectivity test experiment was conducted following **GP2** using *p*-chlorobromobenzene (**2n'**, 0.1 mmol, 1.0 equiv.) and *p*-bromiodobenzene (**2o'**, 0.1 mmol, 1.0 equiv.) as starting materials, respectively. After finishing these reactions, crude solutions were added P(OPh)₃ (0.05 mmol) as the internal standard. The yields were determined by ³¹P NMR integrals. The products were determined by ³¹P NMR and HRMS.

In reaction (1), **3n'** (³¹P NMR (162 MHz, CDCl₃) δ 74.82. **HRMS** (ESI⁺): calculated for C₁₆H₂₅ClN₃P⁺ [M + H⁺] 311.1438; found: 311.1440.), **3o'** (³¹P NMR (162 MHz, CDCl₃) δ 74.89 not found. **HRMS** (ESI⁺): calculated for C₁₆H₂₅BrN₃P⁺ [M + H⁺] 355.0933, C₁₆H₂₄BrN₃NaP⁺ [M + Na⁺] 377.0753, C₁₆H₂₄BrKNP⁺ [M + K⁺] 393.0492; not found.), **3n'a** (³¹P NMR (162 MHz, CDCl₃) δ 87.73 not found. **HRMS** (ESI⁺): calculated for C₂₆H₄₅N₄P₂⁺ [M + H⁺] 475.3114, C₂₆H₄₄N₄NaP₂⁺ [M + Na⁺] 497.2933, C₂₆H₄₄KN₄P₂⁺ [M + K⁺] 513.2673; not found.).

In reaction (2), **3o'** (³¹P NMR (162 MHz, CDCl₃) δ 74.89. **HRMS** (ESI⁺): calculated for C₁₆H₂₅BrN₃P⁺ [M + H⁺] 292.1937; found: 292.1944.), **3o'a** (³¹P NMR (162 MHz, CDCl₃) δ 72.83. **HRMS** (ESI⁺): calculated for C₁₆H₂₅IN₂P⁺ [M + H⁺] 403.0794; found: 403.0788.), **3n'a** (³¹P NMR (162 MHz, CDCl₃) δ 87.73. **HRMS** (ESI⁺): calculated for C₂₆H₄₅N₄P₂⁺ [M + H⁺] 475.3114; found: 475.3109.) We concluded that the reaction activity is Ar-I > Br >> Cl (no reaction).

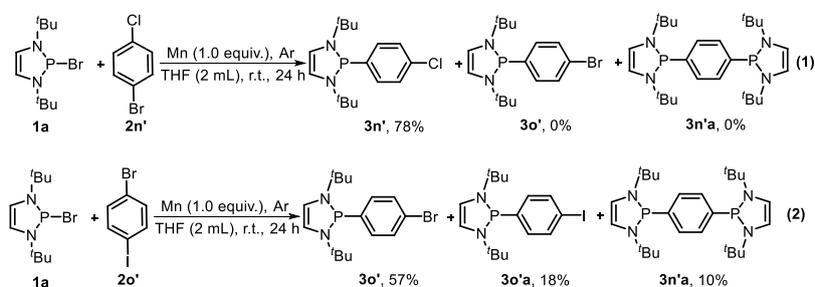
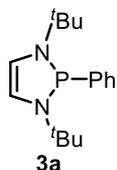


Figure S2. Chemoselectivity test experiments for P-C coupling.

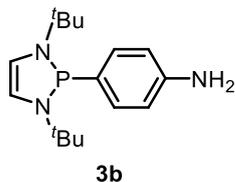
6. Data of products

2,3-dihydro-1,3-di-*tert*-butyl-2-phenyl-1*H*-1,3,2-diazaphosphole (3a)



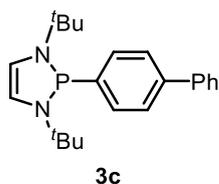
According to **GP 2**, "Pentane-wash gave the desired product **3a** as a yellow liquid (24.6 mg, 92% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.44 (m, 1H), 7.42 (m, 2H), 7.15 (m, 2H), 4.85 (d, $^3J_{\text{HP}} = 4.5$ Hz, 2H), 1.23 (s, 18H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.3 (d, $^1J_{\text{CP}} = 20.0$ Hz), 129.4 (d, $^2J_{\text{CP}} = 19.8$ Hz), 127.7, 127.1, 118.3 (d, $^2J_{\text{CP}} = 5.8$ Hz), 54.3 (d, $^2J_{\text{CP}} = 16.8$ Hz), 30.2 (d, $^3J_{\text{CP}} = 8.8$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 77.64. Spectroscopic data was identical to that reported previously.⁷ **HRMS (ESI⁺)**: calculated for $\text{C}_{16}\text{H}_{26}\text{N}_2\text{P}^+$ [$\text{M} + \text{H}^+$] 277.1828; found: 277.1819.

2,3-dihydro-1,3-di-*tert*-butyl-2-(4'-amimophenyl)-1*H*-1,3,2-diazaphosphole (3b)



According to **GP 2**, "Pentane-wash gave the desired product **3b** as yellow liquid (22.1 mg, 92% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.00 (m, 2H), 6.82 (m, 2H), 5.50 (br, 2H), 4.84 (d, $^3J_{\text{HP}} = 4.5$ Hz, 2H), 1.22 (s, 18H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.71 (d, $^1J_{\text{CP}} = 20.0$ Hz), 129.50 (d, $^2J_{\text{CP}} = 19.8$ Hz), 128.00, 127.10, 118.35 (d, $^2J_{\text{CP}} = 5.8$ Hz), 54.56 (d, $^2J_{\text{CP}} = 16.8$ Hz), 30.16 (d, $^3J_{\text{CP}} = 10.1$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 63.11. **HRMS (ESI⁺)**: calculated for $\text{C}_{16}\text{H}_{27}\text{N}_3\text{P}^+$ [$\text{M} + \text{H}^+$] 292.1937; found: 292.1944.

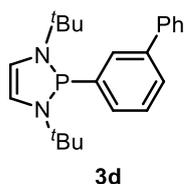
2,3-dihydro-1,3-di-*tert*-butyl-2-(4'-phenylphenyl)-1*H*-1,3,2-diazaphosphole (3c)



According to **GP 2**, "Pentane-wash gave the desired product **3c** as yellow liquid (24.6 mg, 62%

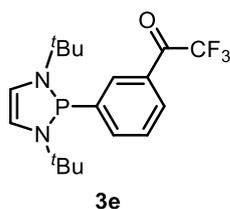
yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.79 (m, 2H), 7.72 (m, 2H), 7.49 (m, 2H), 7.40 (m, 1H), 7.34 (m, 2H), 4.84 (d, ³J_{HP} = 4.5 Hz, 2H), 1.22 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 142.30 (d, ¹J_{CP} = 20.0 Hz), 140.75, 140.33, 131.46 (d, ²J_{CP} = 19.8 Hz), 129.77, 127.79, 127.41, 127.13, 118.35 (d, ²J_{CP} = 5.8 Hz), 54.64, 30.15 (d, ³J_{CP} = 8.8 Hz). **³¹P NMR** (162 MHz, CDCl₃) δ 75.10. **HRMS (ESI⁺)**: calculated for C₂₂H₃₀N₂P⁺ [M + H⁺] 353.2141; found: 353.2136.

2,3-dihydro-1,3-di-*tert*-butyl-2-(3'-phenylphenyl)-1*H*-1,3,2-diazaphosphole (3d)



According to **GP 2**, "Pentane-wash gave the desired product **3d** as yellow liquid (26.3 mg, 25% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.75 (m, 2H), 7.67 (m, 1H), 7.57 (m, 1H), 7.50 (m, 1H), 7.49 (m, 2H), 7.40 (m, 1H), 7.24 (m, 1H), 4.84 (d, ³J_{HP} = 4.5 Hz, 2H), 1.22 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 142.45 (d, ¹J_{CP} = 20.2 Hz), 140.71, 136.32, 130.46 (d, ²J_{CP} = 19.8 Hz), 129.49, 129.14, 127.75, 127.43, 127.40 (d, ²J_{CP} = 19.6 Hz), 127.10, 118.35 (d, ²J_{CP} = 5.7 Hz), 54.64, 30.15 (d, ³J_{CP} = 8.3 Hz). **³¹P NMR** (162 MHz, CDCl₃) δ 75.07. **HRMS (ESI⁺)**: calculated for C₂₂H₃₀N₂P⁺ [M + H⁺] 353.2141; found: 353.2145.

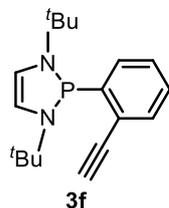
2,3-dihydro-1,3-di-*tert*-butyl-2-(3'-(2,2,2-trifluoroacetyl)phenyl)-1*H*-1,3,2-diazaphosphole (3e)



According to **GP 2**, "Pentane-wash gave the desired product **3e** as yellow liquid (19.1 mg, 92% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.95 (m, 1H), 7.90 (m, 1H), 7.47 (m, 1H), 7.34 (m, 1H), 4.84 (d, ³J_{HP} = 4.6 Hz, 2H), 1.22 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 180.01, 143.44 (d, ¹J_{CP} = 20.2 Hz), 137.76 (d, ²J_{CP} = 19.8 Hz), 131.46 (d, ²J_{CP} = 20.2 Hz), 130.09, 129.45, 118.35 (d, ²J_{CP} = 5.7 Hz), 117.41, 54.64, 30.15 (d, ³J_{CP} = 8.3 Hz). **¹⁹F NMR** (376 MHz, CDCl₃) δ -72.48. **³¹P NMR** (162 MHz, CDCl₃) δ 77.45. **HRMS (APCI)**: calculated for C₁₈H₂₅F₃N₂OP⁺ [M + H⁺] 373.1651; found:

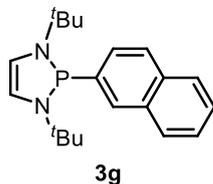
373.1652.

2,3-dihydro-1,3-di-*tert*-butyl-2-(2'-ethynylphenyl)-1*H*-1,3,2-diazaphosphole (3f)



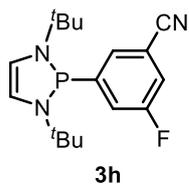
According to **GP 2**, ⁿPentane-wash gave the desired product **3f** as yellow liquid (34.8 mg, 89% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.55 (m, 1H), 7.43 (m, 1H), 7.40 (m, 1H), 7.14 (m, 1H), 4.85 (d, ³J_{HP} = 4.7 Hz, 2H), 4.00 (s, 1H), 1.22 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 137.76 (d, ¹J_{CP} = 20.2 Hz), 132.09, 131.46 (d, ²J_{CP} = 19.8 Hz), 128.49, 128.00, 118.34 (d, ²J_{CP} = 5.7 Hz), 87.29, 81.20, 54.64, 30.16 (d, ³J_{CP} = 8.3 Hz). **³¹P NMR** (162 MHz, CDCl₃) δ 77.49. **HRMS (ESI⁺)**: calculated for C₁₈H₂₆N₂P⁺ [M + H⁺] 301.1828; found: 301.1821.

2,3-dihydro-1,3-di-*tert*-butyl-2-(2-naphthyl)-1*H*-1,3,2-diazaphosphole (3g)



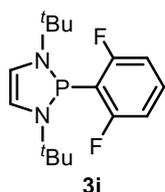
According to **GP 2**, ⁿPentane-wash gave the desired product **3g** as a yellow liquid (18.9 mg, 62% yield). **¹H NMR** (400 MHz, CDCl₃) δ 8.17 (d, ³J_{HH} = 8.4 Hz, 1H), 7.89 (dd, ³J_{HH} = 8.4 Hz, 1H), 7.72 (m, 2H), 7.63 (m, 1H), 7.16 (m, 2H), 5.75 (d, ³J_{HH} = 4.2 Hz, 2H), 1.20 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 144.0 (d, ¹J_{CP} = 21.5 Hz), 134.1, 133.0 (d, ³J_{CP} = 6.9 Hz), 129.5 (d, ¹J_{CP} = 22.1 Hz), 127.9, 127.6, 126.6 (d, ¹J_{CP} = 18.5 Hz), 126.3 (d, ¹J_{CP} = 11.5 Hz), 118.3 (d, ²J_{CP} = 5.5 Hz), 54.9 (d, ²J_{CP} = 17.5 Hz), 30.5 (d, ³J_{CP} = 8.5 Hz). **³¹P NMR** (162 MHz, CDCl₃) δ 75.28. Spectroscopic data was identical to that reported previously.⁷ **HRMS (ESI⁺)**: calculated for C₂₀H₂₇N₂P⁺ [M + H⁺] 326.1906; found: 326.1897.

2,3-dihydro-1,3-di-*tert*-butyl-2-(3-fluoro-5-cyano-phenyl)-1*H*-1,3,2-diazaphosphole (3h)



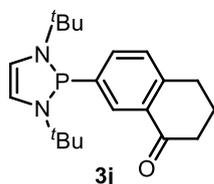
According to **GP 2**, ⁿPentane-wash gave the desired product **3h** as yellow liquid (15.5 mg, 91% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.40 (m, 1H), 7.32 (m, 1H), 7.25 (s, 1H), 4.84 (d, ³J_{HP} = 4.5 Hz, 2H), 1.22 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 163.19, 147.00 (d, ¹J_{CP} = 20.0 Hz), 129.51 (d, ²J_{CP} = 19.8 Hz), 127.18, 126.34 (d, ²J_{CP} = 5.8 Hz), 119.12, 54.64, 30.16 (d). ¹⁹F NMR (376 MHz, CDCl₃) δ -63.21. ³¹P NMR (162 MHz, CDCl₃) δ 75.23. **HRMS (APCI):** calculated for C₁₇H₂₄FN₃P⁺ [M + H⁺] 320.1686; found: 326.1680.

2,3-dihydro-1,3-di-tert-butyl-2-(2,6-difluorophenyl)-1H-1,3,2-diazaphosphole (3i)



According to **GP 2**, ⁿPentane-wash gave the desired product **3i** as yellow liquid (15.5 mg, 98% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.40 (m, 1H), 6.95 (m, 2H), 4.84 (d, ³J_{HP} = 4.6 Hz, 2H), 1.23 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 166.15, 140.06, 129.55, 109.12, 54.63, 30.15 (d). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.94 (dd, J = 8.4, 2.8 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 77.83. **HRMS (APCI):** calculated for C₁₆H₂₄F₂N₂P⁺ [M + H⁺] 313.1640; found: 313.1639.

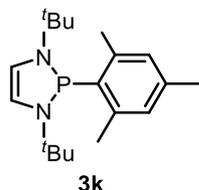
2,3-dihydro-1,3-di-tert-butyl-2-(tetralin-1-one-7-yl)-1H-1,3,2-diazaphosphole (3j)



According to **GP 2**, ⁿPentane-wash gave the desired product **3j** as yellow liquid (15.5 mg, 72% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, ³J_{HH} = 8.4 Hz, 1H), 7.39 (d, ³J_{HH} = 8.4 Hz, 1H), 7.22 (m, 1H), 5.75 (d, ³J_{HH} = 4.2 Hz, 2H), 2.78 (m, 2H), 2.73 (m, 2H), 2.13 (m, 2H), 1.20 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 200.00, 142.37, 140.00 (d, ¹J_{CP} = 21.5 Hz), 137.06 (d, ³J_{CP} = 6.9 Hz), 135.12

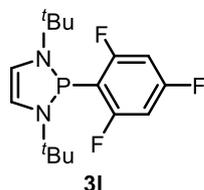
(d, $^2J_{CP} = 20.5$ Hz), 133.60, 128.69 (d, $^2J_{CP} = 20.0$ Hz), 128.31 (d, $^3J_{CP} = 6.9$ Hz), 118.35 (d, $^2J_{CP} = 5.5$ Hz), 54.63, 39.06, 30.15 (d, $^3J_{CP} = 8.5$ Hz), 29.60, 22.55. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 93.05. **HRMS (ESI⁺)**: calculated for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{OP}^+$ [$\text{M} + \text{H}^+$] 345.2090; found: 345.2095.

2,3-dihydro-1,3-di-*tert*-butyl-2-(2,4,6-trimethyl-phenyl)-1*H*-1,3,2-diazaphosphole (3k)



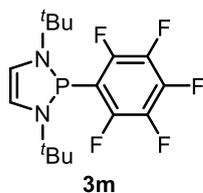
According to **GP 2**, ⁿPentane-wash gave the desired product **3k** as yellow liquid (15.5 mg, 71% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.00 (m, 2H), 4.84 (d, $^3J_{HP} = 4.5$ Hz, 2H), 2.33 (s, 6H), 2.18 (s, 3H), 1.22 (s, 18H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.35 (d, $^1J_{CP} = 20.0$ Hz), 139.47 (d, $^2J_{CP} = 20.8$ Hz), 138.71, 127.18, 118.35 (d, $^2J_{CP} = 5.8$ Hz), 54.62, 30.16, 22.18, 21.13. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) 75.42. **HRMS (ESI⁺)**: calculated for $\text{C}_{19}\text{H}_{32}\text{N}_2\text{P}^+$ [$\text{M} + \text{H}^+$] 319.2298; found: 345.2095.

2,3-dihydro-1,3-di-*tert*-butyl-2-(2,4,6-trifluoro-phenyl)-1*H*-1,3,2-diazaphosphole (3l)



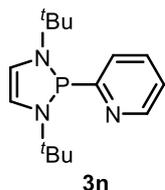
According to **GP 2**, ⁿPentane-wash gave the desired product **3l** as yellow liquid (15.5 mg, 67% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.55 (m, 2H), 4.85 (d, $^3J_{HP} = 4.5$ Hz, 2H), 1.23 (s, 18H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 170.00 (d, $^2J_{CP} = 19.8$ Hz), 168.15, 118.34 (d, $^2J_{CP} = 5.8$ Hz), 102.36 (d, $^1J_{CP} = 20.0$ Hz), 100.43, 54.63, 30.15 (d). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -102.73 (2F), -108.75 (1F). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) 75.09. **HRMS (APCI)**: calculated for $\text{C}_{16}\text{H}_{23}\text{F}_3\text{N}_2\text{P}^+$ [$\text{M} + \text{H}^+$] 321.1546; found: 321.1550.

2,3-dihydro-1,3-di-*tert*-butyl-2-(pentafluoro-phenyl)-1*H*-1,3,2-diazaphosphole (3m)



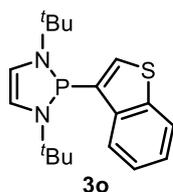
According to **GP 2**, "Pentane-wash gave the desired product **3m** as a yellow liquid (15.5 mg, 94% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.6 (d, $^3J_{\text{HP}} = 3.7$ Hz, 2H), 1.15 (s, 18H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.4, 141.0, 136.9, 117.9 (d, $^2J_{\text{CP}} = 8.8$ Hz), 54.9 (d, $^2J_{\text{CP}} = 18.2$ Hz), 29.6 (d, $^3J_{\text{CP}} = 10.3$ Hz). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -133.63 (t, $^3J_{\text{FF}} = 5.05$ Hz, 2F), -154.58 (quintet, $^3J_{\text{FF}} = 4.54$ Hz, 1F), -160.54 (q, $^3J_{\text{FF}} = 5.05$ Hz, 2F). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) 77.74. Spectroscopic data was identical to that reported previously.⁷ **HRMS (APCI)**: calculated for $\text{C}_{16}\text{H}_{21}\text{F}_5\text{N}_2\text{P}^+$ [$\text{M} + \text{H}^+$] 367.1357; found: 367.1362.

2,3-dihydro-1,3-di-*tert*-butyl-2-(2-pyridyl)-1H-1,3,2-diazaphosphole (**3n**)



According to **GP 2**, "Pentane-wash gave the desired product **3n** as a yellow liquid (15.5 mg, 77% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.66 (dt, $^3J_{\text{HH}} = 4.7, 1.0$ Hz, 1H), 7.69 (dt, $^3J_{\text{HH}} = 7.0, 1.0$ Hz, 1H), 7.14 (tt, $^3J_{\text{HH}} = 7.7, 1.7$ Hz, 1H), 6.53 (dd, $^3J_{\text{HH}} = 7.7, 4.6$ Hz, 1H), 5.70 (d, $^3J_{\text{HP}} = 4.0$ Hz, 2H), 1.35 (s, 18H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 170.4 (d, $^1J_{\text{CP}} = 4.8$ Hz), 150.0 (d, $^3J_{\text{CP}} = 12.8$ Hz), 133.9, 122.9 (d, $^2J_{\text{CP}} = 11.8$ Hz), 122.6, 118.8 (d, $^2J_{\text{CP}} = 5.8$ Hz), 54.9 (d, $^2J_{\text{CP}} = 18.2$ Hz), 30.6 (d, $^3J_{\text{CP}} = 8.3$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) 66.18. Spectroscopic data was identical to that reported previously.⁷ **HRMS (ESI⁺)**: calculated for $\text{C}_{15}\text{H}_{25}\text{N}_3\text{P}^+$ [$\text{M} + \text{H}^+$] 278.1781; found: 278.1787.

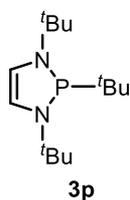
2,3-dihydro-1,3-di-*tert*-butyl-2-(3-benzothieryl)-1H-1,3,2-diazaphosphole (**3o**)



According to **GP 2**, "Pentane-wash gave the desired product **3n** as yellow liquid (15.5 mg, 45%

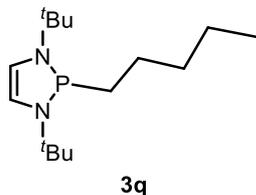
yield). **¹H NMR** (400 MHz, CDCl₃) δ 8.46 (d, ³J_{HH} = 8.7 Hz, 1H), 7.69 (d, ³J_{HP} = 3.0 Hz, 2H), 7.54 (d, ³J_{HH} = 8.7 Hz, 1H), 7.23 (1H), 7.00 (1H), 5.77 (d, ³J_{HP} = 4.0 Hz, 2H), 1.30 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 142.4 (d, ¹J_{CP} = 2.0 Hz), 141.0 (d, ²J_{CP} = 39.0 Hz), 139.9 (d, ³J_{CP} = 22.0 Hz), 130.9 (d, ¹J_{CP} = 12.0 Hz), 124.6 (d, ¹J_{CP} = 25.0 Hz), 123.8 (d, ¹J_{CP} = 6.8 Hz), 123.4, 121.3, 117.9 (d, ¹J_{CP} = 5.8 Hz), 54.9 (d, ²J_{CP} = 18.2 Hz), 30.6 (d, ³J_{CP} = 8.3 Hz). **³¹P NMR** (162 MHz, CDCl₃) 75.12. Spectroscopic data was identical to that reported previously.⁷ **HRMS (ESI⁺)**: calculated for C₁₈H₂₅N₂PS⁺ [M + H⁺] 332.1470; found: 332.1475.

2,3-dihydro-1,3-di-*tert*-butyl-2-(*tert*-butyl)-1*H*-1,3,2-diazaphosphole (**3p**)



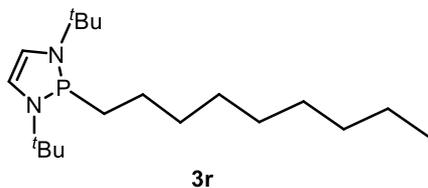
According to **GP 2**, *n*-Pentane-wash gave the desired product **3p** as yellow liquid (24.9 mg, 97% yield). **¹H NMR** (400 MHz, CDCl₃) δ 5.73 (d, ³J_{HP} = 4.7 Hz, 2H), 1.26 (s, 9H), 1.15 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 117.82 (d, ²J_{CP} = 5.8 Hz), 53.48 (d, ²J_{CP} = 16.8 Hz), 37.98, 35.66 (d, ³J_{CP} = 17.3 Hz), 24.61 (d, ²J_{CP} = 14.3 Hz). **³¹P NMR** (162 MHz, CDCl₃) 98.51. **HRMS (ESI⁺)**: calculated for C₁₄H₃₀N₂P⁺ [M + H⁺] 257.2141; found: 257.2142.

2,3-dihydro-1,3-di-*tert*-butyl-2-(*n*-pentyl)-1*H*-1,3,2-diazaphosphole (**3q**)



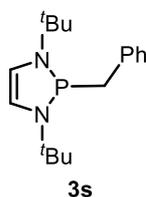
According to **GP 2**, *n*-Pentane-wash gave the desired product **3q** as yellow liquid (24.5 mg, 91% yield). Further dissolved in DCM and remove in vacuo to get rid of *n*-Pentane peaks in ¹H NMR & ¹³C NMR. **¹H NMR** (400 MHz, CDCl₃) δ 5.74 (d, ³J_{HP} = 4.8 Hz, 2H), 1.77 (m, 2H), 1.28-1.25 (m, 6H), 1.15 (s, 18H), 0.89 (m, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 117.82 (d, ²J_{CP} = 6.0 Hz), 54.64, 37.95 (d, ³J_{CP} = 11.0 Hz), 35.66 (d, ¹J_{CP} = 21.0 Hz), 25.04, 24.63, 22.05, 14.11. **³¹P NMR** (162 MHz, CDCl₃) 92.62. **HRMS (ESI⁺)**: calculated for C₁₅H₃₂N₂P⁺ [M + H⁺] 271.2298; found: 271.2302.

2,3-dihydro-1,3-di-*tert*-butyl-2-(*n*-nonyl)-1*H*-1,3,2-diazaphosphole (3r)



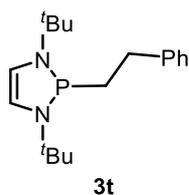
According to **GP 2**, ⁿPentane-wash gave the desired product **3r** as liquid (31.5 mg, 96% yield). Further dissolved in DCM and remove in vacuo to get rid of ⁿPentane peaks in ¹H NMR & ¹³C NMR. ¹H NMR (400 MHz, CDCl₃) δ 5.74 (d, ³J_{HP} = 4.8 Hz, 2H), 1.47 (m, 2H), 1.33-1.30 (m, 4H), 1.29-1.28 (m, 6H), 1.26-1.22 (m, 4H), 1.15 (s, 18H), 0.90 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 117.82 (d, ²J_{CP} = 6.0 Hz), 54.64, 37.89 (d, ³J_{CP} = 11.0 Hz), 33.68 (d, ¹J_{CP} = 19.0 Hz), 33.05, 30.01, 29.13, 25.04, 24.63, 22.05, 20.29, 14.55. ³¹P NMR (162 MHz, CDCl₃) 86.91. **HRMS (ESI⁺)**: calculated for C₁₉H₄₀N₂P⁺ [M + H⁺] 327.2924; found: 327.2922.

2,3-dihydro-1,3-di-*tert*-butyl-2-(benzyl)-1*H*-1,3,2-diazaphosphole (3s)



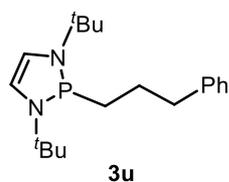
According to **GP 2**, ⁿPentane-wash gave the desired product **3s** as yellow liquid (26.2 mg, 90% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.22 (t, 1H), 7.20 (d, 2H), 7.16 (d, 2H), 5.74 (d, ³J_{HP} = 4.8 Hz, 2H), 4.04 (m, 2H), 1.14 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 130.09, 128.84 (d, ²J_{CP} = 6.2 Hz), 127.91, 125.75, 116.85 (d, ²J_{CP} = 6.2 Hz), 54.64, 37.92 (d, ³J_{CP} = 11.0 Hz), 36.66 (d, ¹J_{CP} = 21.0 Hz). ³¹P NMR (162 MHz, CDCl₃) 87.04. **HRMS (ESI⁺)**: calculated for C₁₇H₂₈N₂P⁺ [M + H⁺] 291.1985; found: 291.1982.

2,3-dihydro-1,3-di-*tert*-butyl-2-(2-phenyl-1-ethyl)-1*H*-1,3,2-diazaphosphole (3t)



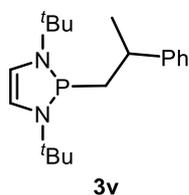
According to **GP 2**, "Pentane-wash gave the desired product **3t** as liquid (29.5 mg, 98% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.15 (d, 2H), 7.09 (d, 2H), 7.04 (t, 1H), 5.73 (d, $^3J_{\text{HP}} = 4.7$ Hz, 2H), 2.60 (t, $^3J_{\text{HH}} = 7.7$ Hz, 2H), 1.77 (m, 2H), 1.35 (m, 2H), 1.15 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.45, 128.63, 126.95, 125.42, 117.84 (d, $^2J_{\text{CP}} = 5.8$ Hz), 54.64, 33.60 (d, $^1J_{\text{CP}} = 17.3$ Hz), 24.67 (d, $^2J_{\text{CP}} = 14.3$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 86.17. HRMS (ESI⁺): calculated for $\text{C}_{18}\text{H}_{30}\text{N}_2\text{P}^+$ [M + H⁺] 305.2141; found: 305.2136.

2,3-dihydro-1,3-di-tert-butyl-2-(3-phenyl-1-propyl)-1H-1,3,2-diazaphosphole (**3u**)



According to **GP 2**, "Pentane-wash gave the desired product **3t** as liquid (31.0 mg, 98% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.16 (d, 2H), 7.09 (d, 2H), 7.04 (t, 1H), 5.73 (d, $^3J_{\text{HP}} = 4.7$ Hz, 2H), 3.05 (m, 2H), 1.77 (m, 2H), 1.16 (s, 18H). ^{31}P NMR (162 MHz, CDCl_3) 86.39. Spectroscopic data was identical to that reported previously.⁷ HRMS (ESI⁺): calculated for $\text{C}_{19}\text{H}_{32}\text{N}_2\text{P}^+$ [M + H⁺] 319.2298; found: 319.2305.

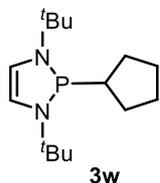
Racemic 2,3-dihydro-1,3-di-tert-butyl-2-(3-phenyl-2-propyl)-1H-1,3,2-diazaphosphole (**3v**)



According to **GP 2**, "Pentane-wash gave the desired product **3v** as liquid (23.5 mg, 74% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, 2H), 7.09 (d, 2H), 7.04 (t, 1H), 5.73 (d, $^3J_{\text{HP}} = 4.7$ Hz, 2H), 2.60 (m, 2H), 1.35 (m, 1H), 1.27 (d, 3H), 1.15 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.05, 142.44, 128.66, 126.91, 118.03 (d, $^2J_{\text{CP}} = 5.8$ Hz), 54.64, 40.67 (d, $^1J_{\text{CP}} = 17.4$ Hz), 24.67 (d, $^2J_{\text{CP}} = 14.6$

Hz), 20.60. ^{31}P NMR (162 MHz, CDCl_3) 91.44. **HRMS (ESI⁺):** calculated for $\text{C}_{19}\text{H}_{32}\text{N}_2\text{P}^+$ [$\text{M} + \text{H}^+$] 319.2298; found: 319.2302.

2,3-dihydro-1,3-di-*tert*-butyl-2-(cyclopentyl)-1*H*-1,3,2-diazaphosphole (3w)



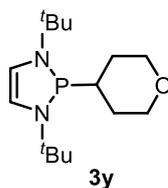
According to **GP 2**, *n*-Pentane-wash gave the desired product **3w** as liquid (25.5 mg, 95% yield). ^1H NMR (400 MHz, CDCl_3) δ 5.70 (d, $^3J_{\text{HP}} = 5.0$ Hz, 2H), 1.88 (m, 1H), 1.77 (m, 2H), 1.63 (m, 2H), 1.60 (m, 2H), 1.43 (m, 2H), 1.15 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 116.82 (d, $^2J_{\text{CP}} = 6.0$ Hz), 54.64, 35.67 (d, $^1J_{\text{CP}} = 21.0$ Hz), 30.06 (d, $^3J_{\text{CP}} = 8.5$ Hz), 27.95 (d, $^2J_{\text{CP}} = 15.0$ Hz), 20.95 (d, $^3J_{\text{CP}} = 11.0$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 90.40. **HRMS (ESI⁺):** calculated for $\text{C}_{15}\text{H}_{30}\text{N}_2\text{P}^+$ [$\text{M} + \text{H}^+$] 269.2141; found: 269.2137.

2,3-dihydro-1,3-di-*tert*-butyl-2-(1-adamantyl)-1*H*-1,3,2-diazaphosphole (3x)



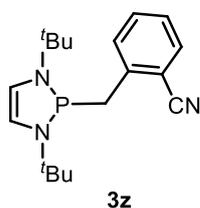
According to **GP 2**, *n*-Pentane-wash gave the desired product **3x** (29.5 mg, 88% yield). ^1H NMR (400 MHz, CDCl_3) δ 5.76 (d, $^3J_{\text{HP}} = 4.7$ Hz, 2H), 1.99 (m, 3H), 1.74 (m, 12H), 1.23 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 120.4 (d, $^2J_{\text{CP}} = 4.8$ Hz), 54.0 (d, $^2J_{\text{CP}} = 14.8$ Hz), 38.9 (d, $^1J_{\text{CP}} = 16.8$ Hz), 37.9, 35.6 (d, $^2J_{\text{CP}} = 13.8$ Hz), 30.8 (d, $^3J_{\text{CP}} = 7.8$ Hz), 28.9 (d, $^3J_{\text{CP}} = 9.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 94.72. Spectroscopic data was identical to that reported previously.⁷ **HRMS (ESI⁺):** calculated for $\text{C}_{20}\text{H}_{36}\text{N}_2\text{P}^+$ [$\text{M} + \text{H}^+$] 335.2611; found: 335.2609.

2,3-dihydro-1,3-di-*tert*-butyl-2-(4-tetrahydropyranyl)-1*H*-1,3,2-diazaphosphole (3y)



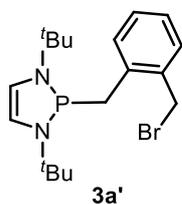
According to **GP 2**, ⁿPentane-wash gave the desired product **3y** as liquid (26.5 mg, 94% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.70 (d, ³J_{HP} = 5.0 Hz, 2H), 3.68 (m, 2H), 3.57 (m, 2H), 2.08 (m, 1H), 1.77 (m, 2H), 1.63 (m, 2H), 1.14 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 116.82 (d, ²J_{CP} = 6.2 Hz), 68.98 (d, ³J_{CP} = 11.0 Hz), 54.64, 34.63 (d, ¹J_{CP} = 21.0 Hz), 30.06 (d, ³J_{CP} = 8.5 Hz), 24.95 (d, ²J_{CP} = 15.2 Hz). ³¹P NMR (162 MHz, CDCl₃) 88.07. HRMS (ESI⁺): calculated for C₁₅H₃₀N₂OP⁺ [M + H⁺] 285.2090; found: 285.2085.

2,3-dihydro-1,3-di-*tert*-butyl-2-(2-cyanobenzyl)-1*H*-1,3,2-diazaphosphole (**3z**)



According to **GP 2**, ⁿPentane-wash gave the desired product **3z** as yellow liquid (28.9 mg, 92% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.55 (m, 1H), 7.53-7.50 (m, 2H), 7.36 (m, 1H), 5.74 (d, ³J_{HP} = 4.8 Hz, 2H), 4.24 (m, 2H), 1.14 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 132.99, 132.05, 129.84 (d, ²J_{CP} = 6.2 Hz), 127.91, 126.75, 116.85 (d, ²J_{CP} = 6.2 Hz), 115.81, 113.33, 54.64, 37.92 (d, ³J_{CP} = 11.0 Hz), 36.65 (d, ¹J_{CP} = 21.0 Hz). ³¹P NMR (162 MHz, CDCl₃) 87.37. HRMS (ESI⁺): calculated for C₁₈H₂₇N₃P⁺ [M + H⁺] 316.1937; found: 316.1935.

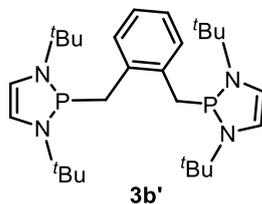
2,3-dihydro-1,3-di-*tert*-butyl-2-(2-bromomethylbenzyl)-1*H*-1,3,2-diazaphosphole (**3a'**)



According to **GP 2**, ⁿPentane-wash gave the desired product **3a'** as liquid (29.3 mg, 77% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.23 (m, 3H), 7.15 (m, 1H), 5.74 (d, ³J_{HP} = 4.8 Hz, 2H), 4.56 (m, 2H), 4.24 (m, 2H), 1.14 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 138.95, 137.05, 130.84 (d, ²J_{CP} = 6.0 Hz), 129.91, 128.75, 125.82, 116.85 (d, ²J_{CP} = 6.2 Hz), 54.64, 37.92 (d, ³J_{CP} = 11.0 Hz), 36.65 (d, ¹J_{CP} = 21.0 Hz), 31.13. ³¹P NMR (162 MHz, CDCl₃) 85.18. HRMS (ESI⁺): calculated for

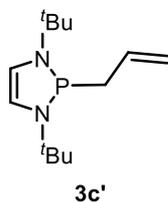
C₁₉H₂₉BrN₂P⁺ [M + H⁺] 383.1246; found: 316.1935.

1,2-bis((1,3-di-*tert*-butyl-1,3-dihydro-2H-1,3,2-diazaphosphol-2-yl)methyl)benzene (3b')



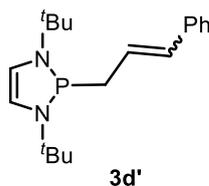
According to **GP 2**, "Pentane-wash gave the desired product **3b'** as yellow liquid (40.2 mg, 80% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.17 (m, 2H), 7.10 (m, 2H), 5.74 (d, ³J_{HP} = 5.0 Hz, 4H), 4.56 (m, 4H), 1.14 (s, 36H). ¹³C NMR (101 MHz, CDCl₃) δ 138.89 (d, ²J_{CP} = 6.0 Hz), 129.95, 125.87, 116.85 (d, ²J_{CP} = 6.2 Hz), 54.64, 37.92 (d, ³J_{CP} = 11.0 Hz), 36.66 (d, ¹J_{CP} = 21.2 Hz). ³¹P NMR (162 MHz, CDCl₃) 85.29. **HRMS (ESI⁺)**: calculated for C₂₈H₄₉N₄P₂⁺ [M + H⁺] 503.3427; found: 316.1935.

2,3-dihydro-1,3-di-*tert*-butyl-2-allyl-1H-1,3,2-diazaphosphole (3c')



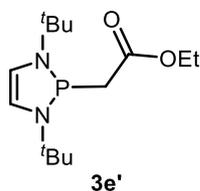
According to **GP 2**, "Pentane-wash gave the desired product **3c'** as liquid (21.0 mg, 87% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.77 (m, 1H), 5.74 (m, 2H), 5.07 (dd, *J* = 17.0, 4.8 Hz, 1H), 5.02 (dd, *J* = 10.0, 4.8 Hz, 1H), 4.54 (m, 2H), 1.14 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 132.04 (d, ²J_{CP} = 6.2 Hz), 116.85 (d, ²J_{CP} = 6.2 Hz), 115.70, 54.64, 37.92 (d, ³J_{CP} = 11.0 Hz), 36.65 (d, ¹J_{CP} = 21.2 Hz). ³¹P NMR (162 MHz, CDCl₃) 85.88. **HRMS (ESI⁺)**: calculated for C₁₃H₂₆N₂P⁺ [M + H⁺] 241.1828; found: 241.1833.

2,3-dihydro-1,3-di-*tert*-butyl-2-cinnamyl-1H-1,3,2-diazaphosphole (3d')



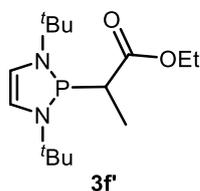
According to **GP 2**, "Pantane-wash gave the desired product **3d'** as yellow liquid (29.1 mg, 92% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.36 (d, 2H), 7.19 (d, 2H), 7.04 (t, 1H), 6.33 (dd, *J* = 15.7, 3.4 Hz, 1H), 6.20 (m, 1H), 5.77 (d, ³*J*_{HP} = 3.9 Hz, 2H), 2.35 (dd, *J* = 7.7, 4.4 Hz, 2H), 1.17 (s, 18H). **³¹P NMR** (162 MHz, CDCl₃) 84.92. Spectroscopic data was identical to that reported previously.⁷ **HRMS (APCI)**: calculated for C₁₉H₃₀N₂P⁺ [M + H⁺] 317.2141; found: 317.2135.

2,3-dihydro-1,3-di-*tert*-butyl-2-(ethyl 2-acetyl)-1*H*-1,3,2-diazaphosphole (**3e'**)



According to **GP 2**, "Pantane-wash gave the desired product **3e'** as liquid (25.7 mg, 90% yield). **¹H NMR** (400 MHz, CDCl₃) δ 5.70 (d, ³*J*_{HP} = 5.0 Hz, 2H), 4.18 (q, 2H), 3.38 (m, 2H), 1.23 (t, 3H), 1.15 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 168.95, 116.85 (d, ²*J*_{CP} = 6.0 Hz), 61.37, 54.64, 34.66 (d, ¹*J*_{CP} = 21.0 Hz), 30.05 (d, ³*J*_{CP} = 8.5 Hz), 14.43. **³¹P NMR** (162 MHz, CDCl₃) 93.81. **HRMS (ESI⁺)**: calculated for C₁₄H₂₈N₂O₂P⁺ [M + H⁺] 287.1883; found: 287.1879.

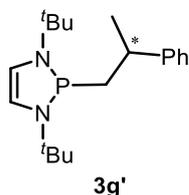
2,3-dihydro-1,3-di-*tert*-butyl-2-(ethyl 2-propionyl)-1*H*-1,3,2-diazaphosphole (**3f'**)



According to **GP 2**, "Pantane-wash gave the desired product **3f'** as liquid (26.7 mg, 89% yield). **¹H NMR** (400 MHz, CDCl₃) δ 5.70 (d, ³*J*_{HP} = 5.0 Hz, 2H), 4.25 (m, 1H), 4.20 (q, 2H), 1.25 (d, 3H), 1.23 (t, 3H), 1.15 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 170.9, 116.85 (d, ²*J*_{CP} = 6.0 Hz), 61.30, 54.64, 34.65 (d, ¹*J*_{CP} = 21.0 Hz), 30.05 (d, ³*J*_{CP} = 8.5 Hz), 14.49, 10.90. **³¹P NMR** (162 MHz, CDCl₃) 93.88. **HRMS (ESI⁺)**: calculated for C₁₅H₃₀N₂O₂P⁺ [M + H⁺] 301.2039; found: 301.2041.

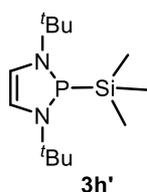
Non-racemic 2,3-dihydro-1,3-di-*tert*-butyl-2-(3-phenyl-2-propyl)-1*H*-1,3,2-diazaphosphole

(3g')



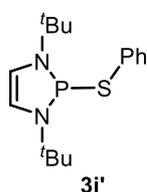
According to **GP 2**, (*R*)-2-bromo-1-phenylpropane was used as the starting material.⁸ ¹⁸Pentane-wash gave the desired mixed product **3g'**. Enantiomeric excess ratio (44%(*R*) : 30%(*S*)) was determined by HPLC analysis, using AD-H column, 0.5% *i*-PrOH in hexanes, 0.25 mL/min, 230 nm.

2,3-dihydro-1,3-di-*tert*-butyl-2-trimethylsilyl-1*H*-1,3,2-diazaphosphole (3h')



According to **GP 2**, ¹⁸Pentane-wash gave the desired product **3h'** as liquid (11.5 mg, 42% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.73 (d, ³J_{HP} = 4.7 Hz, 2H), 1.15 (s, 18H), 0.08 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 117.82 (d, ²J_{CP} = 5.8 Hz), 53.48 (d, ²J_{CP} = 16.8 Hz), 35.64 (d, ³J_{CP} = 17.3 Hz), -1.05 (d, ²J_{CP} = 5.0 Hz). ³¹P NMR (162 MHz, CDCl₃) 86.34. ²⁹Si NMR (79 MHz, CDCl₃) 16.38. **HRMS (ESI⁺)**: calculated for C₁₃H₃₀N₂PSi⁺ [M + H⁺] 273.1910; found: 273.1906.

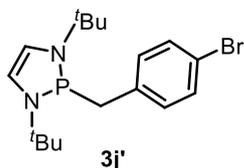
2,3-dihydro-1,3-di-*tert*-butyl-2-phenylthio-1*H*-1,3,2-diazaphosphole (3i')



According to **GP 2**, ¹⁸Pentane-wash gave the desired product **3i'** (29.7 mg, 96% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.36 (t, 1H), 7.27 (d, 2H), 7.23 (d, 2H), 5.76 (d, ³J_{HP} = 4.8 Hz, 2H), 1.14 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 133.8 (d, ²J_{CP} = 6.4 Hz), 137.9, 129.7, 125.7, 53.7 (d, ²J_{CP} = 17.0 Hz), 37.9 (d, ³J_{CP} = 11.0 Hz). ³¹P NMR (162 MHz, CDCl₃) 148.17. Spectroscopic data was

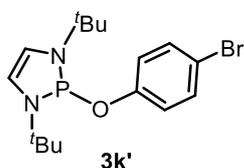
identical to that reported previously.⁷ **HRMS (ESI⁺)**: calculated for C₁₆H₂₆N₂PS⁺ [M + H⁺] 309.1549; found: 309.1556.

2,3-dihydro-1,3-di-*tert*-butyl-2-(4-bromobenzyl)-1*H*-1,3,2-diazaphosphole (3j')



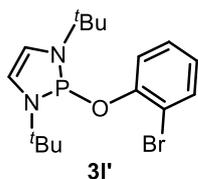
According to **GP 2**, "Pentane-wash gave the desired product **3j'** as yellow liquid (34.9 mg, 95% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.72 (d, 2H), 7.06 (m, 2H), 5.74 (d, ³J_{HP} = 4.8 Hz, 2H), 4.06 (m, 2H), 1.14 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 132.05, 131.22, 128.84 (d, ²J_{CP} = 6.2 Hz), 120.91, 54.64, 37.92 (d, ³J_{CP} = 11.0 Hz), 36.65 (d, ¹J_{CP} = 21.0 Hz). **³¹P NMR** (162 MHz, CDCl₃) 86.91. **HRMS (ESI⁺)**: calculated for C₁₇H₂₇BrN₂P⁺ [M + H⁺] 369.1090; found: 369.1088.

2,3-dihydro-1,3-di-*tert*-butyl-2-(4-bromophenoxy)-1*H*-1,3,2-diazaphosphole (3k')



According to **GP 2**, "Pentane-wash gave the desired product **3k'** as solid (35.2 mg, 95% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.42 (m, 2H), 7.10 (m, 2H), 4.85 (d, ³J_{HP} = 4.5 Hz, 2H), 1.14 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 145.34 (d, ²J_{CP} = 10.8 Hz), 133.25, 118.42 (d, ²J_{CP} = 18.8 Hz), 118.03, 115.77, 54.64, 30.26 (d, ³J_{CP} = 8.8 Hz). **³¹P NMR** (162 MHz, CDCl₃) 106.99. **HRMS (ESI⁺)**: calculated for C₁₆H₂₅BrN₂OP⁺ [M + H⁺] 371.0882; found: 371.0875.

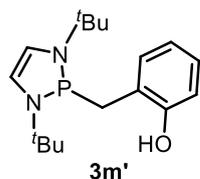
2,3-dihydro-1,3-di-*tert*-butyl-2-(2-bromophenoxy)-1*H*-1,3,2-diazaphosphole (3l')



According to **GP 2**, "Pentane-wash gave the desired product **3l'** as solid (34.4 mg, 93% yield). **¹H**

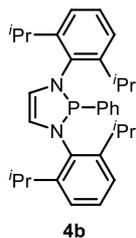
NMR (400 MHz, CDCl₃) δ 7.46 (d, 1H), 7.16 (m, 1H), 6.76 (m, 1H), 6.66 (d, 1H), 4.85 (d, ³J_{HP} = 4.5 Hz, 2H), 1.24 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 145.31 (d, ²J_{CP} = 10.8 Hz), 136.25, 129.23, 123.27, 118.35 (d, ²J_{CP} = 18.8 Hz), 118.11, 115.70, 54.64, 30.15 (d, ³J_{CP} = 8.8 Hz). **³¹P NMR** (162 MHz, CDCl₃) 107.30. **HRMS (ESI⁺)**: calculated for C₁₆H₂₅BrN₂OP⁺ [M + H⁺] 371.0882; found: 371.0877.

2,3-dihydro-1,3-di-*tert*-butyl-2-(3-hydroxybenzyl)-1*H*-1,3,2-diazaphosphole (3m')



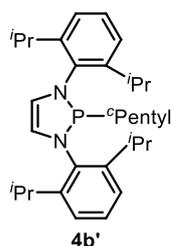
According to **GP 2**, ⁿPentane-wash gave the desired product **3m'** as liquid (21.1 mg, 69% yield). **¹H NMR** (400 MHz, CDCl₃) δ 8.68 (br, 1H), 7.05 (m, 1H), 6.99 (m, 1H), 6.81 (m, 1H), 6.75 (m, 1H), 5.74 (d, ³J_{HP} = 4.8 Hz, 2H), 4.11 (m, 2H), 1.14 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 146.15, 132.96, 130.07, 129.84 (d, ²J_{CP} = 6.2 Hz), 127.95, 126.16, 116.85 (d, ²J_{CP} = 6.2 Hz), 54.64, 37.92 (d, ³J_{CP} = 11.0 Hz), 36.65 (d, ¹J_{CP} = 22.0 Hz). **³¹P NMR** (162 MHz, CDCl₃) 86.60. **HRMS (ESI⁺)**: calculated for C₁₇H₂₈N₂OP⁺ [M + H⁺] 307.1934; found: 307.1929.

2,3-dihydro-1,3-(2,6-di-isopropylphenyl)-2-phenyl-1*H*-1,3,2-diazaphosphole (4b)



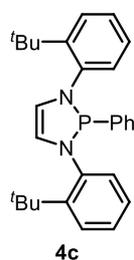
According to **GP 2**, ⁿPentane-wash gave the desired product **4b** as liquid (34.4 mg, 71% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.45-7.40 (m, 2H), 7.38-7.36 (m, 3H), 7.32-7.28 (m, 4H), 7.14 (d, 2H), 6.60 (d, *J* = 8.0 Hz, 2H), 3.37 (septet, *J* = 8.0 Hz, 4H), 1.38 (d, *J* = 8.0 Hz, 12H), 1.24 (d, *J* = 8.0 Hz, 12H). **¹³C NMR** (101 MHz, CDCl₃) δ 147.19 (d, ³J_{CP} = 4.0 Hz), 147.01 (d, ¹J_{CP} = 19.9 Hz), 132.88 (d, ²J_{CP} = 8.1 Hz), 129.47, 129.09 (d, ²J_{CP} = 19.7 Hz), 127.88, 127.62, 124.69, 123.52 (d, ²J_{CP} = 8.1 Hz), 28.89, 25.45, 24.54. **³¹P NMR** (162 MHz, CDCl₃) 93.47. **HRMS (ESI⁺)**: calculated for C₃₂H₄₂N₂P⁺ [M + H⁺] 485.3080; found: 485.3079.

2,3-dihydro-1,3-(2,6-di-isopropylphenyl)-2-cyclopentyl-1*H*-1,3,2-diazaphosphole (4b')



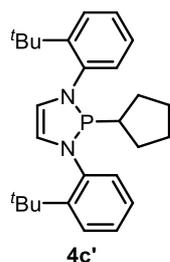
According to **GP 2**, ⁿPentane-wash gave the desired product **4b'** as liquid (31.8 mg, 78% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.45-7.40 (m, 2H), 7.32-7.28 (m, 4H), 6.60 (d, *J* = 8.0 Hz, 2H), 3.37 (septet, *J* = 8.0 Hz, 4H), 1.88 (m, 1H), 1.77 (m, 2H), 1.63 (m, 2H), 1.60 (m, 2H), 1.43 (m, 2H), 1.38 (d, *J* = 8.0 Hz, 12H), 1.24 (d, *J* = 8.0 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 147.19 (d, ³*J*_{CP} = 4.0 Hz), 132.88 (d, ²*J*_{CP} = 8.1 Hz), 129.47, 124.69, 123.52 (d, ²*J*_{CP} = 8.1 Hz), 35.65 (d, ¹*J*_{CP} = 21.0 Hz), 28.89, 27.98 (d, ²*J*_{CP} = 15.0 Hz), 25.45, 24.54, 20.99 (d, ³*J*_{CP} = 11.0 Hz). ³¹P NMR (162 MHz, CDCl₃) 119.74. **HRMS (ESI⁺)**: calculated for C₃₁H₄₆N₂P⁺ [M + H⁺] 477.3393; found: 477.3389.

2,3-dihydro-1,3-(2-*tert*-butyl-phenyl)-2-phenyl-1*H*-1,3,2-diazaphosphole (4c)



According to **GP 2**, ⁿPentane-wash gave the desired product **4c** as liquid (30.0 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.01-7.96 (m, 2H), 7.71 (m, 2H), 7.58-7.51 (m, 2H), 7.44-7.34 (m, 4H), 7.24 (m, 2H), 7.12 (m, 1H), 6.70 (m, 2H), 1.43 (m, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 147.31 (d, ³*J*_{CP} = 6.0 Hz), 147.03 (d, ¹*J*_{CP} = 19.9 Hz), 132.06 (d, ²*J*_{CP} = 7.1 Hz), 129.35, 129.05, 127.89, 127.67, 127.40, 127.13, 125.92 (d, ²*J*_{CP} = 7.1 Hz), 35.92, 32.35 (d, ²*J*_{CP} = 4.0 Hz). ³¹P NMR (162 MHz, CDCl₃) 74.55. **HRMS (ESI⁺)**: calculated for C₂₈H₃₄N₂P⁺ [M + H⁺] 429.2454; found: 429.2448.

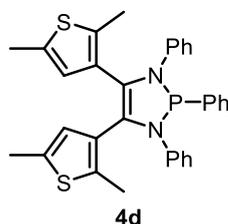
2,3-dihydro-1,3-(2-*tert*-butyl-phenyl)-2-cyclopentyl-1*H*-1,3,2-diazaphosphole (4c')



According to **GP 2**, "Pentane-wash gave the desired product **4c'** as liquid (36.9 mg, 88% yield). **¹H NMR** (400 MHz, CDCl₃) δ 8.01-7.96 (m, 2H), 7.58-7.51 (m, 2H), 7.44-7.34 (m, 4H), 6.70 (m, 2H), 1.88 (m, 1H), 1.77 (m, 2H), 1.63 (m, 2H), 1.60 (m, 2H), 1.45-1.41 (m, 20H). **¹³C NMR** (101 MHz, CDCl₃) δ 147.31 (d, ³J_{CP} = 6.0 Hz), 132.06 (d, ²J_{CP} = 7.1 Hz), 129.35, 127.67, 127.13, 125.92 (d, ²J_{CP} = 7.1 Hz), 35.92, 35.64 (d, ¹J_{CP} = 21.0 Hz), 32.35 (d, ²J_{CP} = 4.0 Hz), 27.91 (d, ²J_{CP} = 15.0 Hz), 20.90 (d, ³J_{CP} = 11.0 Hz). **³¹P NMR** (162 MHz, CDCl₃) 84.84. **HRMS (ESI⁺)**: calculated for C₂₇H₃₈N₂P⁺ [M + H⁺] 421.2767; found: 429.2448.

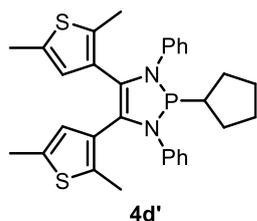
4,5-bis(2,5-dimethyl-3-thienyl)-2,3-dihydro-1,3-phenyl-2-phenyl-1*H*-1,3,2-diazaphosphole

(4d)



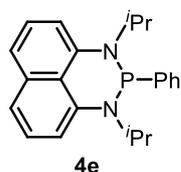
According to **GP 2**, "Pentane-wash gave the desired product **4d** as liquid (27.3 mg, 51% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.71 (m, 2H), 7.34-7.27 (m, 10H), 7.24 (m, 2H), 7.12 (m, 1H), 6.11 (s, 2H), 2.18 (s, 3H), 2.16 (s, 3H), 1.95 (s, 6H); **¹³C NMR** (101 MHz, CDCl₃) δ 147.09 (d, ¹J_{CP} = 19.9 Hz), 138.39, 137.47, 137.01, 137.94 (d, ²J_{CP} = 12.1 Hz), 136.00, 129.42 (d, ³J_{CP} = 8.1 Hz), 129.05, 129.03 (d, ²J_{CP} = 19.7 Hz), 127.88, 127.56 (d, ²J_{CP} = 12.1 Hz), 127.39, 126.36 (d, ³J_{CP} = 9.1 Hz), 126.10 (d, ³J_{CP} = 7.1 Hz), 125.54 (d, ³J_{CP} = 8.0 Hz), 124.92, 15.29, 15.13, 14.11, 14.05. **³¹P NMR** (162 MHz, CDCl₃) 73.79. **HRMS (ESI⁺)**: calculated for C₃₂H₃₀N₂PS₂⁺ [M + H⁺] 537.1583; found: 537.1577.

4,5-bis(2,5-dimethyl-3-thienyl)-2,3-dihydro-1,3-phenyl-2-cyclopentyl-1*H*-1,3,2-diazaphosphole (**4d'**)



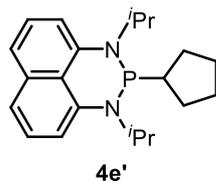
According to **GP 2**, "Pentane-wash gave the desired product **4d'** as liquid (37.5 mg, 71% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.34-7.27 (m, 10H), 6.11 (s, 2H), 2.18 (s, 3H), 2.16 (s, 3H), 1.95 (s, 6H), 1.88 (m, 1H), 1.77 (m, 2H), 1.63 (m, 2H), 1.60 (m, 2H), 1.43 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 138.39, 137.47, 137.01, 137.94 (d, ²J_{CP} = 12.1 Hz), 136.00, 129.42 (d, ³J_{CP} = 8.1 Hz), 129.05, 127.56 (d, ²J_{CP} = 12.1 Hz), 126.36 (d, ³J_{CP} = 9.1 Hz), 126.10 (d, ³J_{CP} = 7.1 Hz), 125.54 (d, ³J_{CP} = 8.0 Hz), 124.92, 35.60 (d, ¹J_{CP} = 21.0 Hz), 27.91 (d, ²J_{CP} = 15.0 Hz), 20.92 (d, ³J_{CP} = 11.0 Hz), 15.29, 15.13, 14.11, 14.05. **³¹P NMR** (162 MHz, CDCl₃) 83.32. **HRMS (ESI⁺)**: calculated for C₃₁H₃₄N₂PS₂⁺ [M + H⁺] 529.1896; found: 529.1902.

2,3-dihydro-1,3-di-isopropyl-2-phenyl-1*H*-naphtho[1,8-*de*][1,3,2]diazaphosphinine (**4e**)



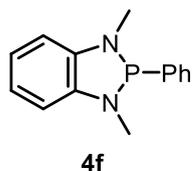
According to **GP 2**, "Pentane-wash gave the desired product **4e** as liquid (20.2 mg, 58% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.71 (m, 2H), 7.37 (dd, *J* = 4.0, 4.0 Hz, 4H), 7.24 (m, 2H), 7.12 (m, 1H), 6.85 (quintet, *J* = 4.0 Hz, 2H), 4.33 (m, 2H), 1.60 (m, 12H). **¹³C NMR** (101 MHz, CDCl₃) δ 147.08 (d, ¹J_{CP} = 20.0 Hz), 138.02 (d, *J*_{CP} = 5.0 Hz), 135.83, 129.00 (d, ²J_{CP} = 19.7 Hz), 127.85, 127.32, 126.46, 120.94, 119.24, 108.23 (d, *J*_{CP} = 2.0 Hz), 50.43 (d, *J*_{CP} = 28.3 Hz), 23.37 (d, *J*_{CP} = 20.2 Hz), 20.88 (d, *J*_{CP} = 15.2 Hz). **³¹P NMR** (162 MHz, CDCl₃) 73.23. **HRMS (ESI⁺)**: calculated for C₂₂H₂₆N₂P⁺ [M + H⁺] 349.1828; found: 349.1822.

2,3-dihydro-1,3-di-isopropyl-2-cyclopentyl-1*H*-naphtho[1,8-*de*][1,3,2]diazaphosphinine (**4e'**)



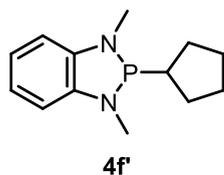
According to **GP 2**, "Pentane-wash gave the desired product **4e'** as liquid (24.1 mg, 71% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.37 (dd, *J* = 4.0, 4.0 Hz, 4H), 6.85 (quintet, *J* = 4.0 Hz, 2H), 4.33 (m, 2H), 1.88 (m, 1H), 1.77 (m, 2H), 1.63 (m, 4H), 1.60 (m, 14H), 1.43 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 138.02 (d, *J*_{CP} = 5.0 Hz), 135.83, 126.46, 120.94, 119.24, 108.23 (d, *J*_{CP} = 2.0 Hz), 50.43 (d, *J*_{CP} = 28.3 Hz), 35.60 (d, ¹*J*_{CP} = 21.0 Hz), 27.91 (d, ²*J*_{CP} = 14.0 Hz), 23.37 (d, *J*_{CP} = 20.2 Hz), 20.92 (d, ³*J*_{CP} = 11.0 Hz), 20.88 (d, *J*_{CP} = 15.2 Hz). **³¹P NMR** (162 MHz, CDCl₃) 87.37. **HRMS (ESI⁺)**: calculated for C₂₁H₃₀N₂P⁺ [M + H⁺] 341.2141; found: 341.2135.

2-phenyl-1,3-dimethyl-benzodiazaphosphole (**4f**)



According to **GP 2**, "Pentane-wash gave the desired product **4f** as liquid (14.8 mg, 61% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.71 (m, 2H), 7.24 (m, 2H), 7.12 (m, 1H), 7.03 (dd, *J* = 4.0, 4.0 Hz, 2H), 6.92 (dd, *J* = 4.0, 4.0 Hz, 2H), 3.30 (d, ³*J*_{PH} = 12.0 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 147.02 (d, ¹*J*_{CP} = 20.0 Hz), 137.26 (d, ²*J*_{CP} = 11.1 Hz), 129.02 (d, ²*J*_{CP} = 19.7 Hz), 127.70, 127.33, 121.26 (d, ²*J*_{CP} = 13.1 Hz), 110.08 (d, ³*J*_{CP} = 1.0 Hz), 29.43 (q, ²*J*_{CP} = 20.2 Hz). **³¹P NMR** (162 MHz, CDCl₃) 82.62. **HRMS (ESI⁺)**: calculated for C₁₄H₁₆N₂P⁺ [M + H⁺] 243.1046; found: 243.1050.

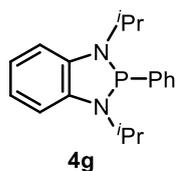
2-phenyl-1,3-dimethyl-benzodiazaphosphole (**4f'**)



According to **GP 2**, "Pentane-wash gave the desired product **4f'** as liquid (16.3 mg, 70% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.03 (dd, *J* = 4.0, 4.0 Hz, 2H), 6.92 (dd, *J* = 4.0, 4.0 Hz, 2H), 3.30 (d,

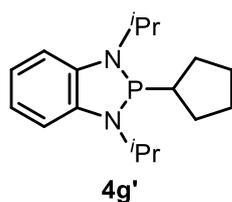
$^3J_{\text{PH}} = 12.0$ Hz, 6H), 1.88 (m, 1H), 1.77 (m, 2H), 1.63 (m, 2H), 1.60 (m, 2H), 1.43 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.26 (d, $^2J_{\text{CP}} = 11.1$ Hz), 121.26 (d, $^2J_{\text{CP}} = 13.1$ Hz), 110.08 (d, $^3J_{\text{CP}} = 1.0$ Hz), 35.60 (d, $^1J_{\text{CP}} = 21.0$ Hz), 29.43 (q, $^2J_{\text{CP}} = 20.2$ Hz), 27.91 (d, $^2J_{\text{CP}} = 15.0$ Hz), 20.92 (d, $^3J_{\text{CP}} = 11.0$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 116.95. HRMS (ESI⁺): calculated for $\text{C}_{13}\text{H}_{20}\text{N}_2\text{P}^+$ [M + H⁺] 235.1359; found: 235.1361.

2-phenyl-1,3-diisopropyl-benzodiazphosphole (4g)



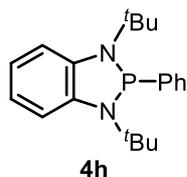
According to **GP 2**, "Pentane-wash gave the desired product **4g** as liquid (7.5 mg, 25% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (m, 2H), 7.24-7.12 (m, 1H), 7.10 (s, 4H), 4.34 (septet, $J = 8.0$ Hz, 2H), 1.71 (d, $J = 4.0$ Hz, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.06 (d, $^1J_{\text{CP}} = 20.1$ Hz), 136.77 (d, $J_{\text{CP}} = 10.1$ Hz), 129.03 (d, $^2J_{\text{CP}} = 19.7$ Hz), 127.31, 127.01, 121.19, 111.47, 47.98 (d, $J_{\text{CP}} = 13.1$ Hz), 22.08. ^{31}P NMR (162 MHz, CDCl_3) 85.63. HRMS (ESI⁺): calculated for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{P}^+$ [M + H⁺] 299.1672; found: 299.1668.

2-cyclopentyl-1,3-diisopropyl-benzodiazphosphole (4g')



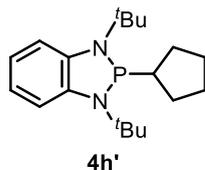
According to **GP 2**, "Pentane-wash gave the desired product **4g'** as yellow liquid (14.3 mg, 49% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.10 (s, 4H), 4.34 (septet, $J = 8.0$ Hz, 2H), 1.88 (m, 1H), 1.77 (m, 2H), 1.71 (d, $J = 4.0$ Hz, 12H), 1.63-1.60 (m, 4H), 1.43 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.77 (d, $J_{\text{CP}} = 10.1$ Hz), 121.19, 111.47, 47.98 (d, $J_{\text{CP}} = 13.1$ Hz), 35.66 (d, $^1J_{\text{CP}} = 21.0$ Hz), 27.92 (d, $^2J_{\text{CP}} = 15.0$ Hz), 22.08, 20.90 (d, $^3J_{\text{CP}} = 11.0$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 93.47. HRMS (ESI⁺): calculated for $\text{C}_{17}\text{H}_{28}\text{N}_2\text{P}^+$ [M + H⁺] 291.1985; found: 291.1980.

2-phenyl-1,3-di-*tert*-butyl-benzodiazphosphole (4h)



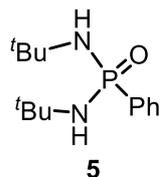
According to **GP 2**, "Pentane-wash gave the desired product **4h** as liquid (5.5 mg, 17% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (dd, 2H), 7.43 (dd, $J = 4.0$ Hz, 2H), 7.24 (m, 2H), 7.12 (m, 1H), 7.07 (dd, $J = 4.0$ Hz, 2H), 1.84 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.06 (d, $^1J_{\text{CP}} = 19.9$ Hz), 136.92 (d, $^3J_{\text{CP}} = 5.0$ Hz), 129.02 (d, $^2J_{\text{CP}} = 19.7$ Hz), 127.94, 127.55, 120.44, 115.15, 56.74 (d, $^3J_{\text{CP}} = 11.1$ Hz), 29.37 (d, $^2J_{\text{CP}} = 14.1$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 83.08. HRMS (ESI $^+$): calculated for $\text{C}_{20}\text{H}_{28}\text{N}_2\text{P}^+$ [M + H $^+$] 327.1985; found: 327.1979.

2-cyclopentyl-1,3-di-*tert*-butyl-benzodiazphosphole (4h')



According to **GP 2**, "Pentane-wash gave the desired product **4h'** as liquid (18.5 mg, 58% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.43 (t, $J = 4.0$ Hz, 2H), 7.07 (t, $J = 4.0$ Hz, 2H), 1.88 (m, 1H), 1.84 (s, 18H), 1.77 (m, 2H), 1.63 (m, 2H), 1.60 (m, 2H), 1.43 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.92 (d, $J_{\text{CP}} = 5.0$ Hz), 120.44, 115.15, 56.74 (d, $J_{\text{CP}} = 11.1$ Hz), 35.68 (d, $^1J_{\text{CP}} = 21.0$ Hz), 29.37 (d, $J_{\text{CP}} = 14.1$ Hz), 27.95 (d, $^2J_{\text{CP}} = 15.0$ Hz), 20.97 (d, $^3J_{\text{CP}} = 11.0$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 105.26. HRMS (ESI $^+$): calculated for $\text{C}_{19}\text{H}_{32}\text{N}_2\text{P}^+$ [M + H $^+$] 319.2298; found: 319.2302.

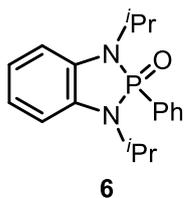
N,N'-di-*tert*-butyl-*P*-phenylphosphonic diamide (5)



According to **GP 2** and subsequent H_2O_2 oxidation, FC (PE:EA = 1:1) gave the desired product **5** as a white solid (15.5 mg, 72% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.83 (m, 2H), 7.39 (m, 3H),

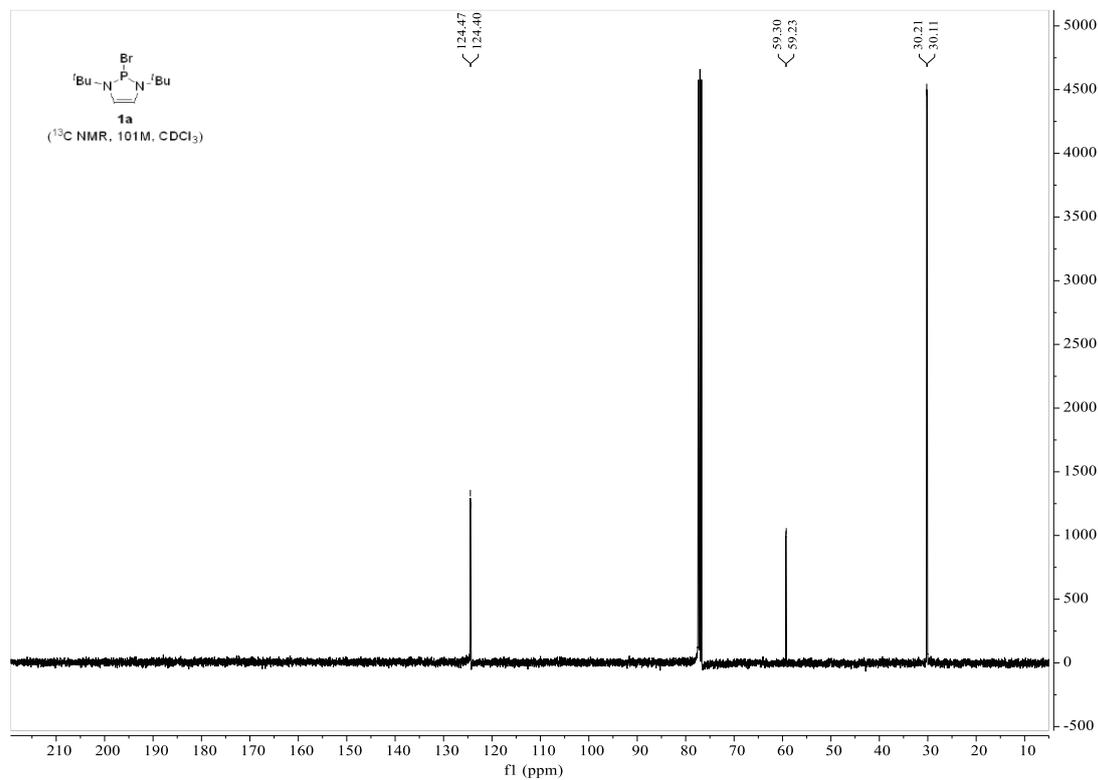
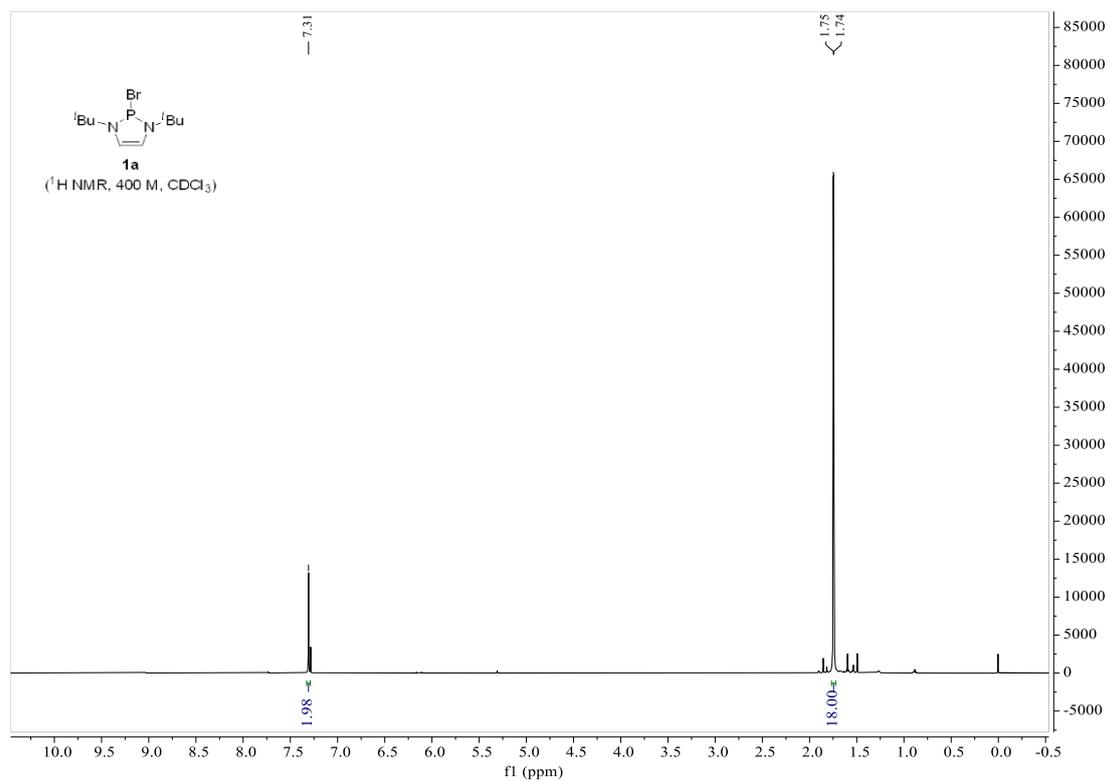
2.42 (d, $^2J_{\text{PH}} = 9.1$ Hz, 2H), 1.23 (m, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.9 (d, $^1J_{\text{PC}} = 156.7$ Hz), 131.2 (d, $^2J_{\text{PC}} = 9.7$ Hz), 130.4, 127.9 (d, $^3J_{\text{PC}} = 13.7$ Hz), 51.9 (s), 32.2 (d, $^3J_{\text{PC}} = 4.3$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 14.11. Spectroscopic data was identical to that reported previously.⁹
HRMS (ESI⁺): calculated for $\text{C}_{14}\text{H}_{26}\text{N}_2\text{OP}^+$ [$\text{M} + \text{H}^+$] 269.1777; found: 269.1781.

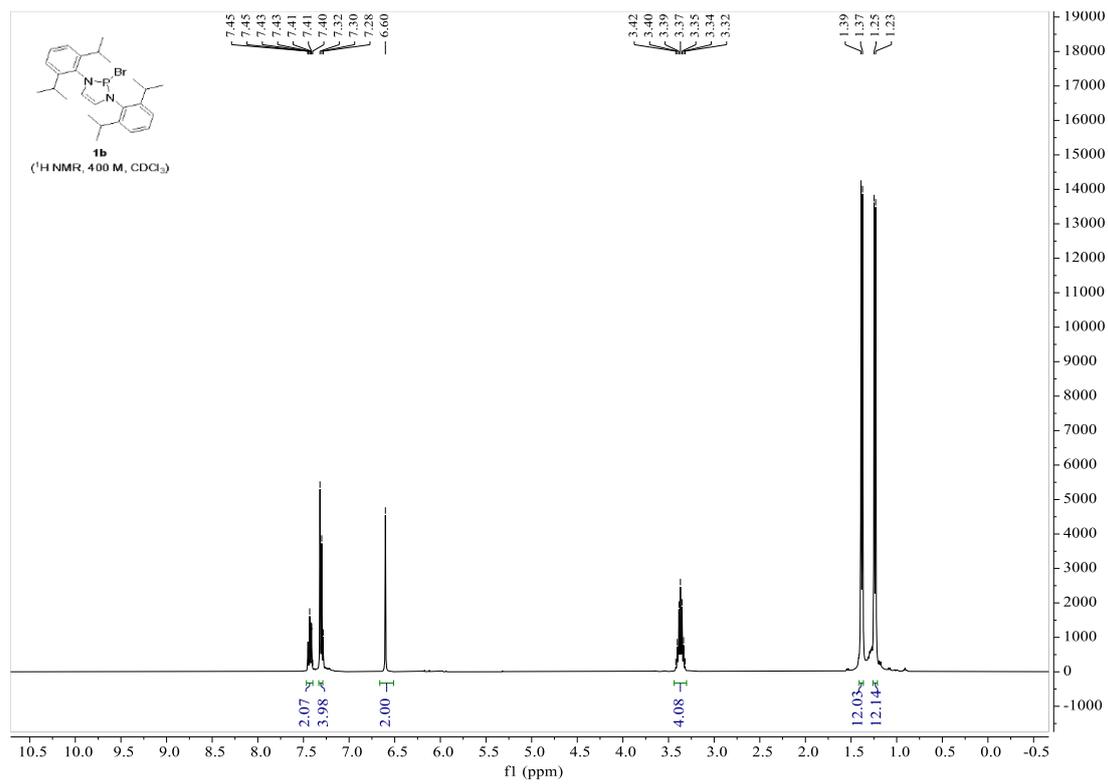
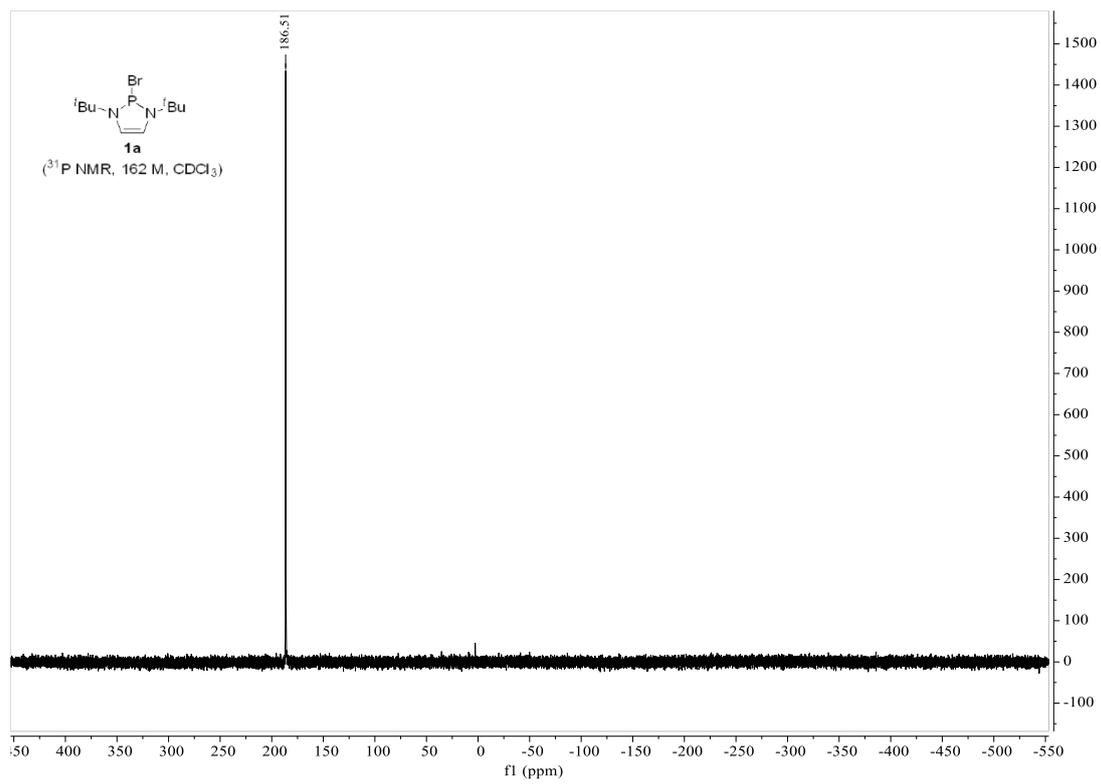
1,3-diisopropyl-2-phenyl-1,3-dihydrobenzo[d][1,3,2]diazaphosphole 2-oxide (6)

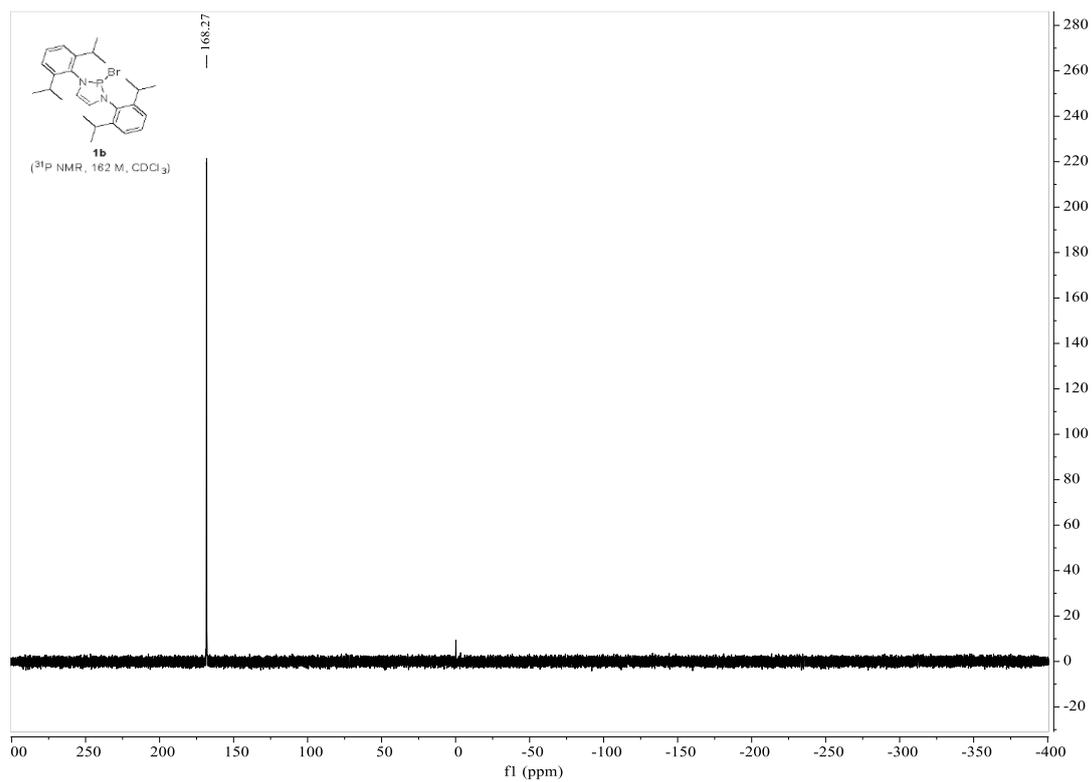
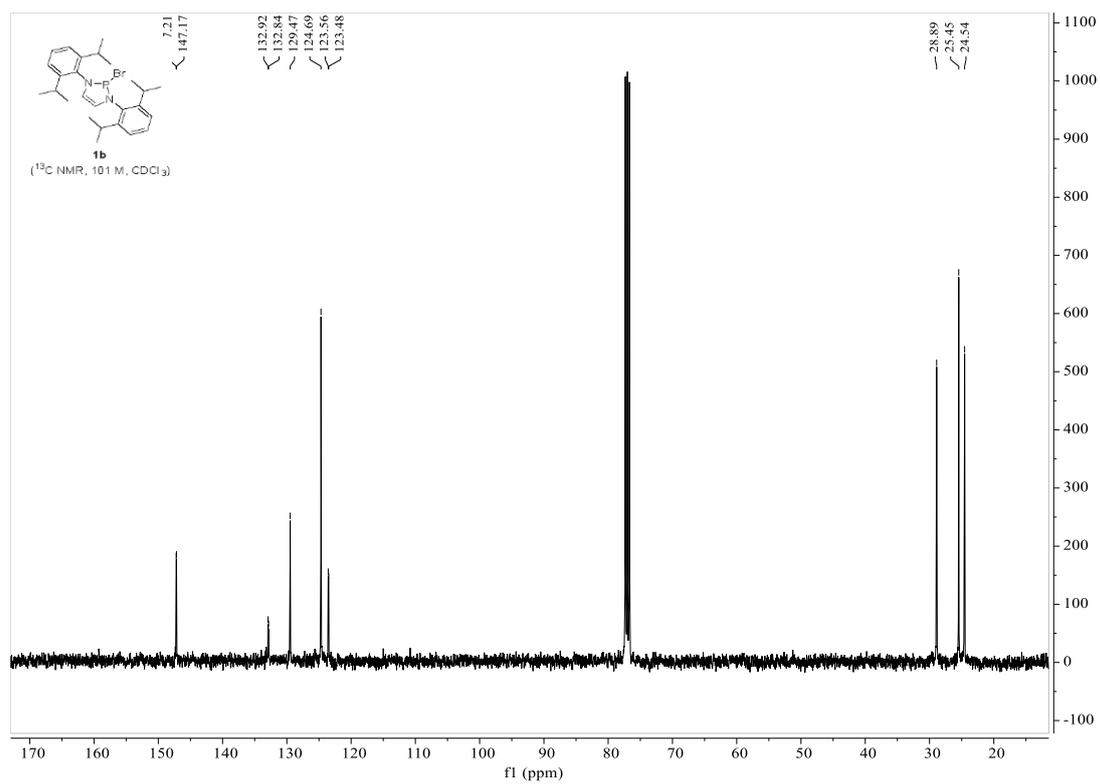


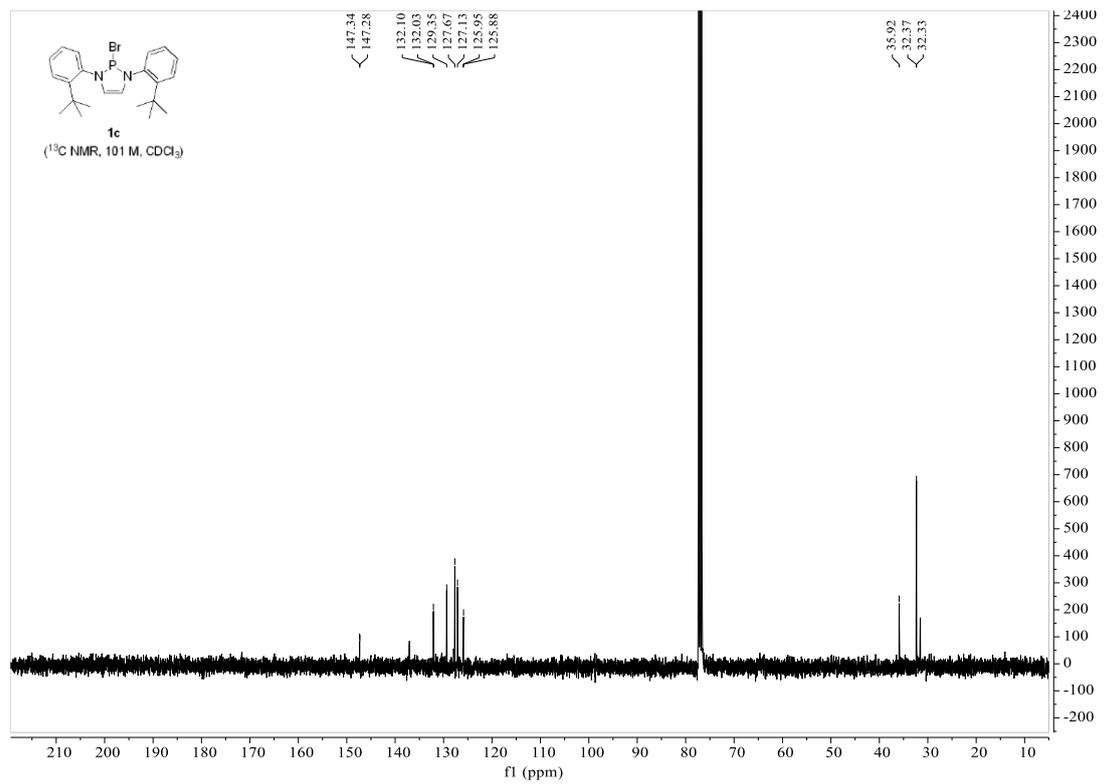
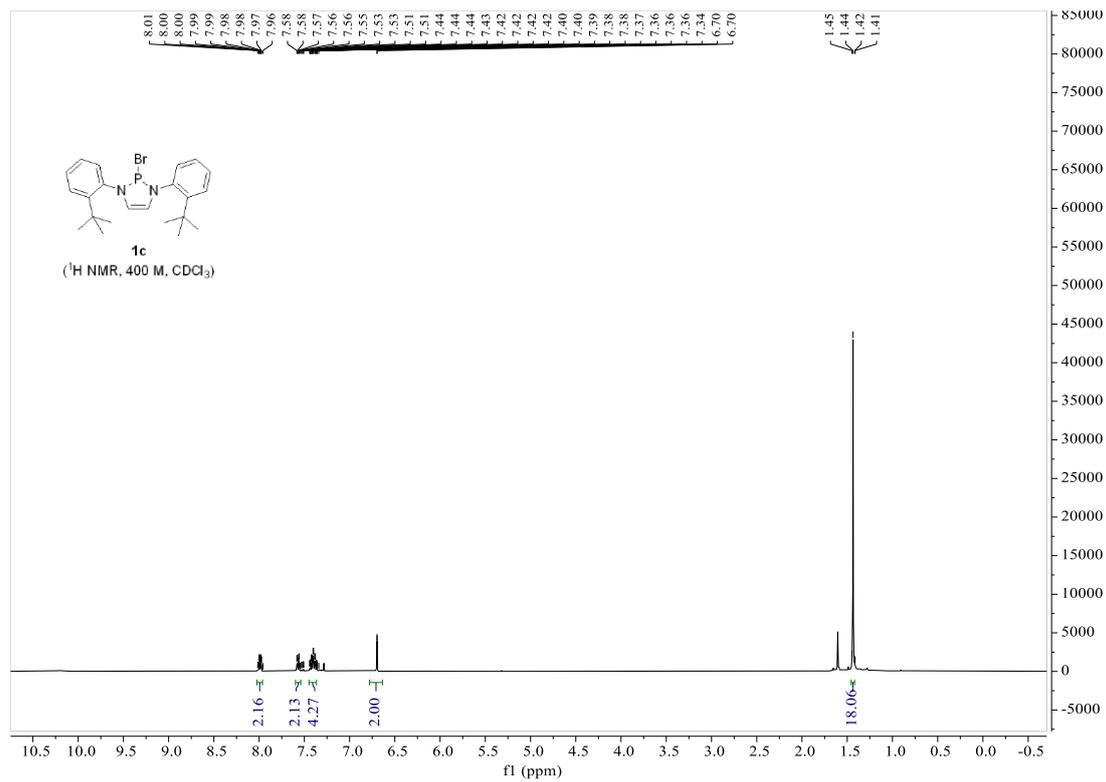
According to **GP 2** and subsequent H_2O_2 oxidation, FC ($\text{DCM}:\text{MeOH} = 10:1$) gave the desired product **6** as yellow liquid (15.5 mg, 90% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.34 (m, 2H), 7.26 (1 peak overlap with CDCl_3 , 1H), 7.20 (m, 2H), 6.62 (dd, $J = 7.5, 1.5$ Hz, 2H), 6.52 (dd, $J = 7.5, 1.5$ Hz, 2H), 2.83 (sept, $J = 6.8$ Hz, 2H), 1.13 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 134.9, 134.1, 133.1, 132.3, 128.8, 117.9, 111.0, 49.9, 22.1. ^{31}P NMR (162 MHz, CDCl_3) δ 23.2 (d).
HRMS (ESI⁺): calculated for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{OP}^+$ [$\text{M} + \text{H}^+$] 315.1621; found: 315.1619.

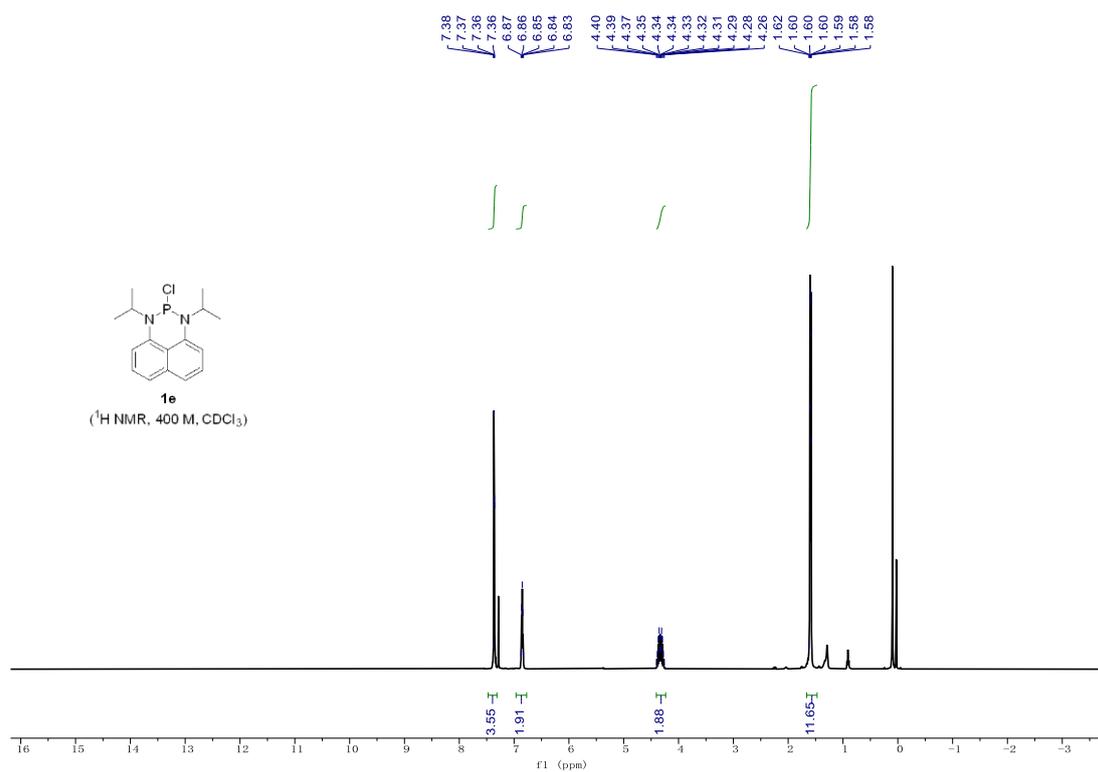
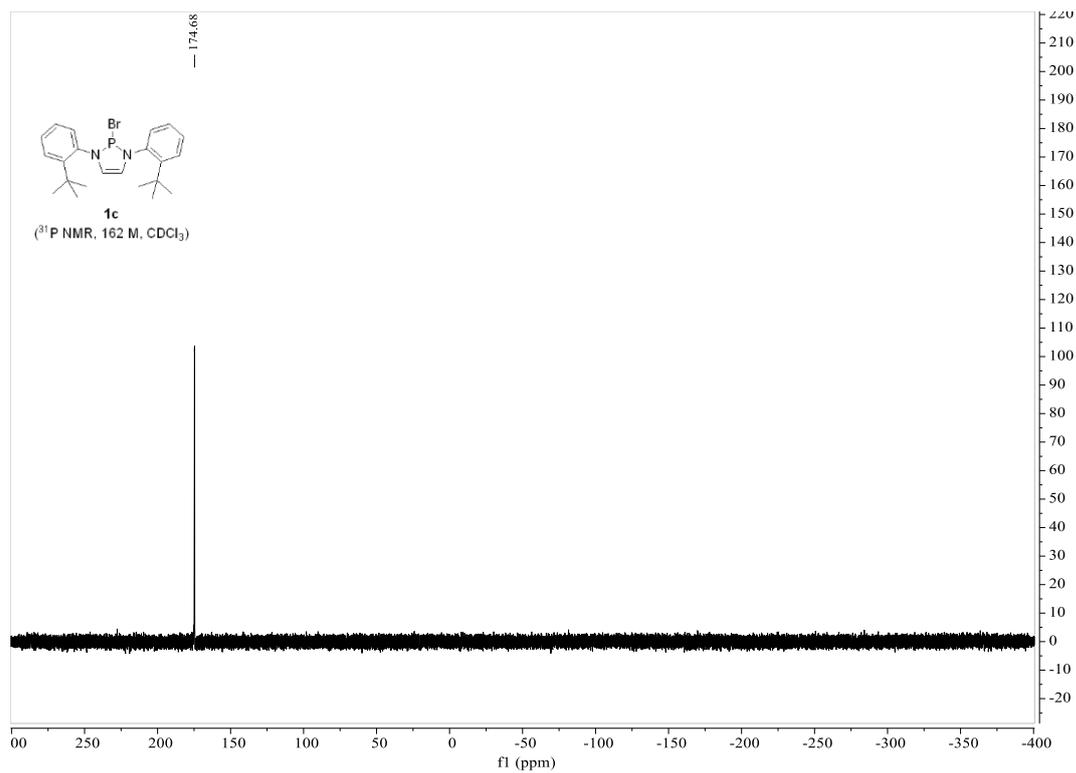
7. NMR spectra

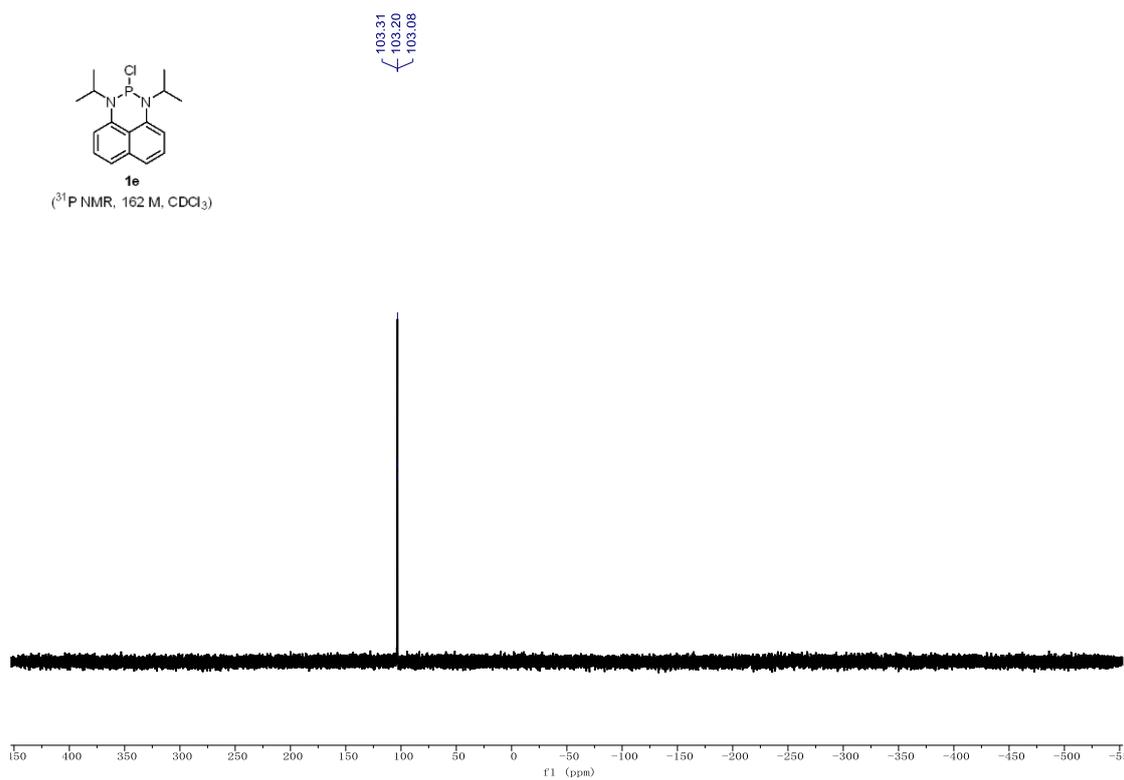
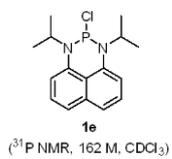
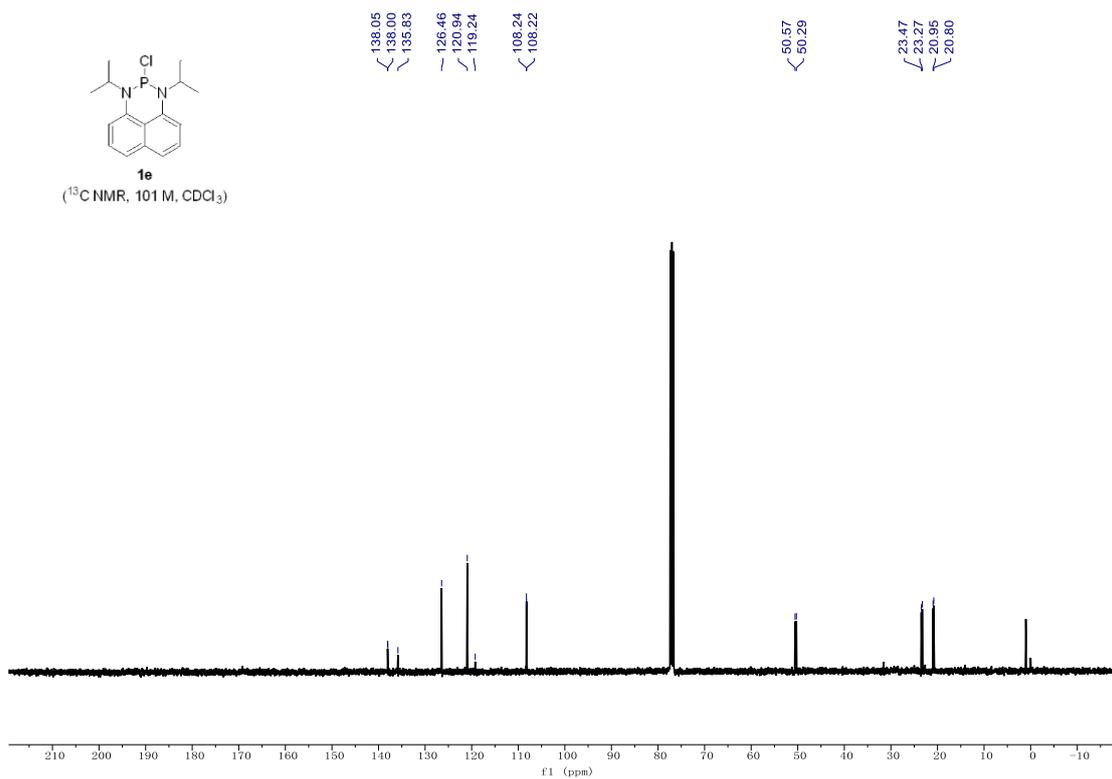
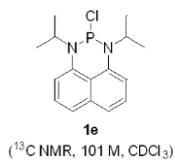


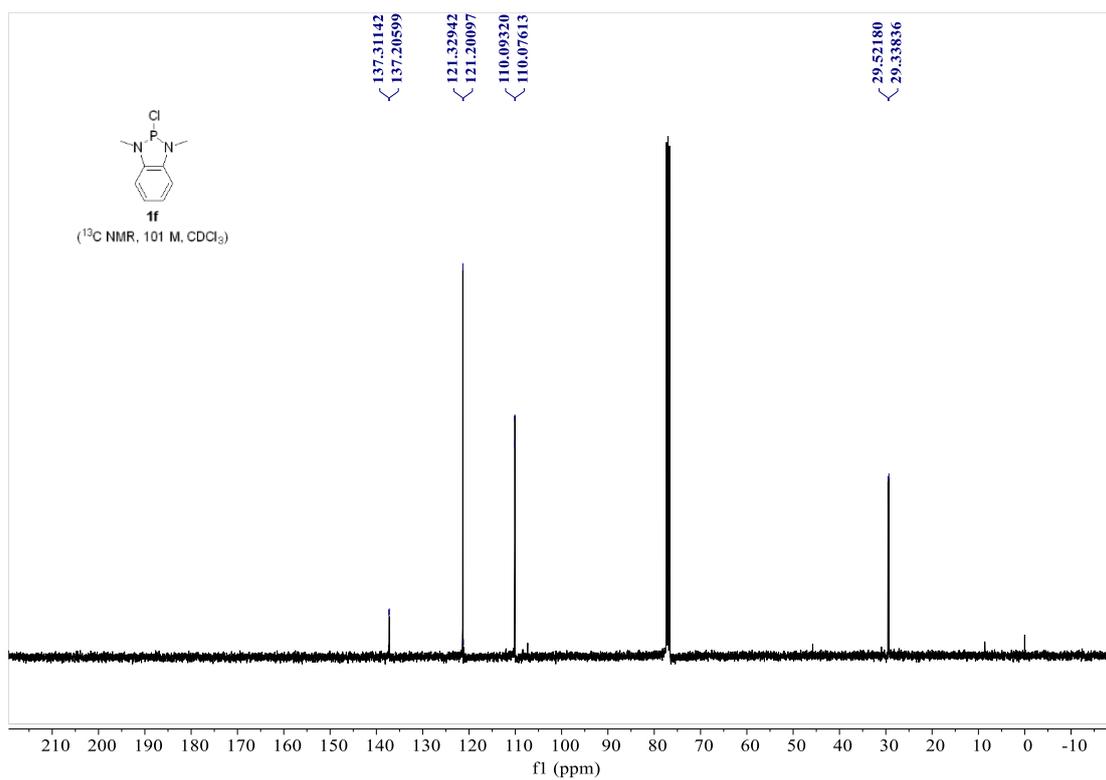
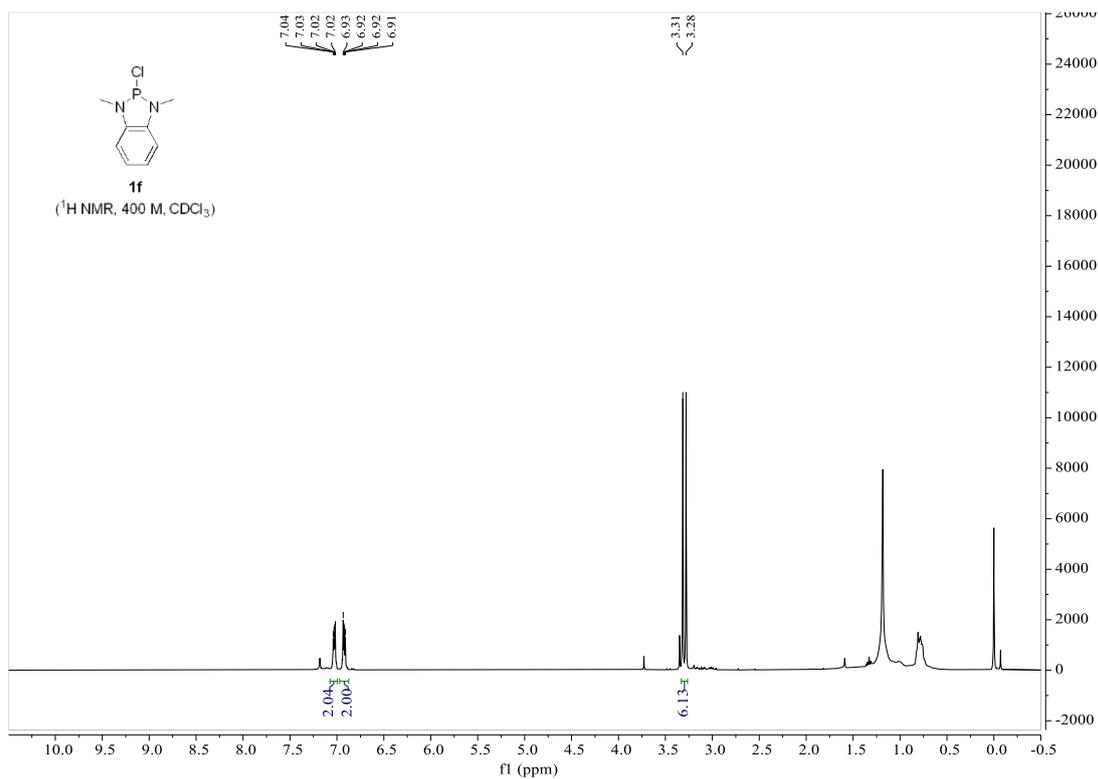


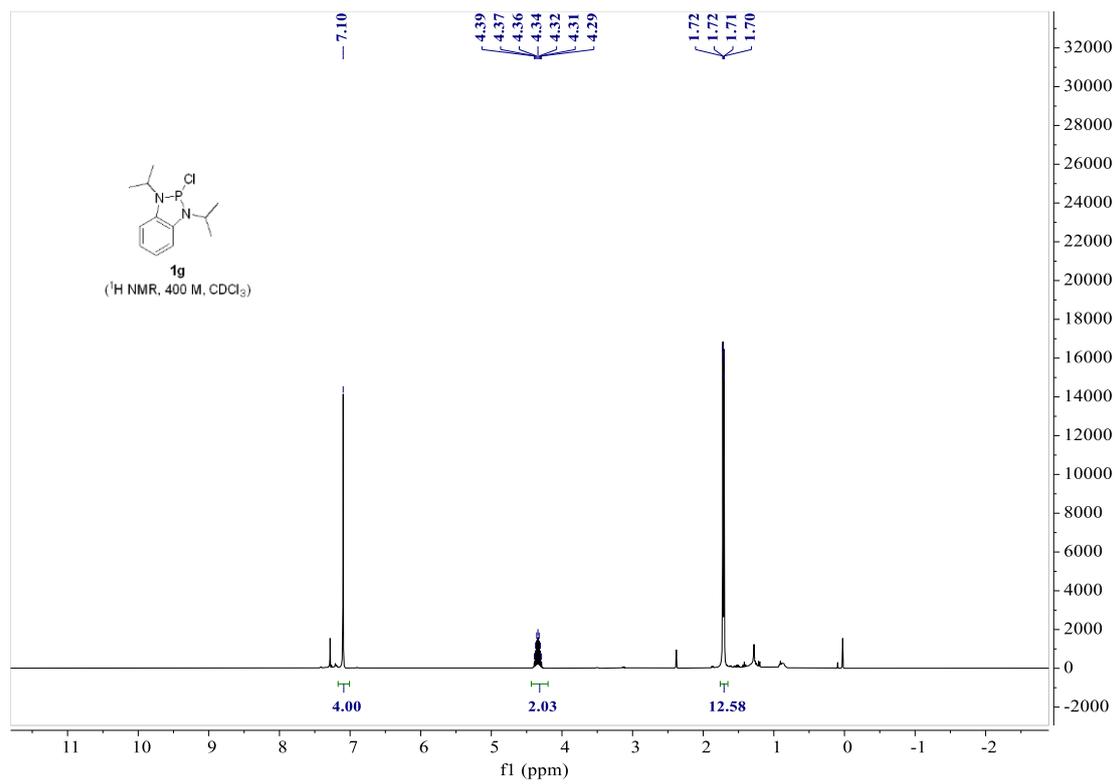
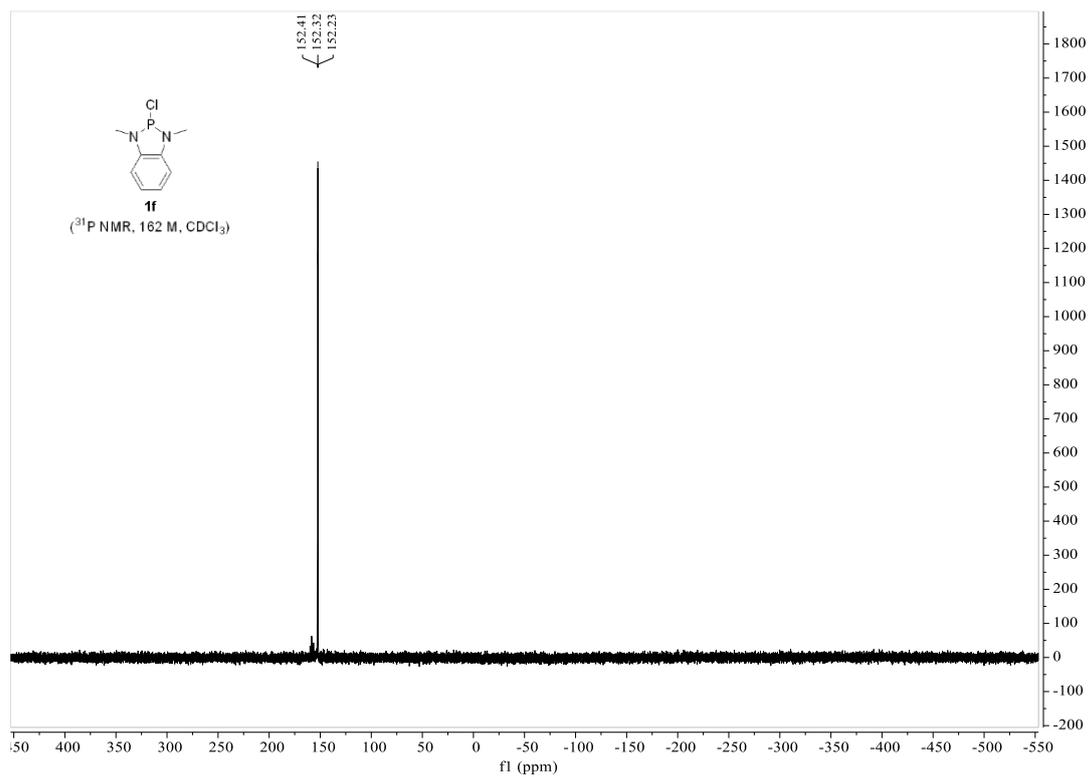


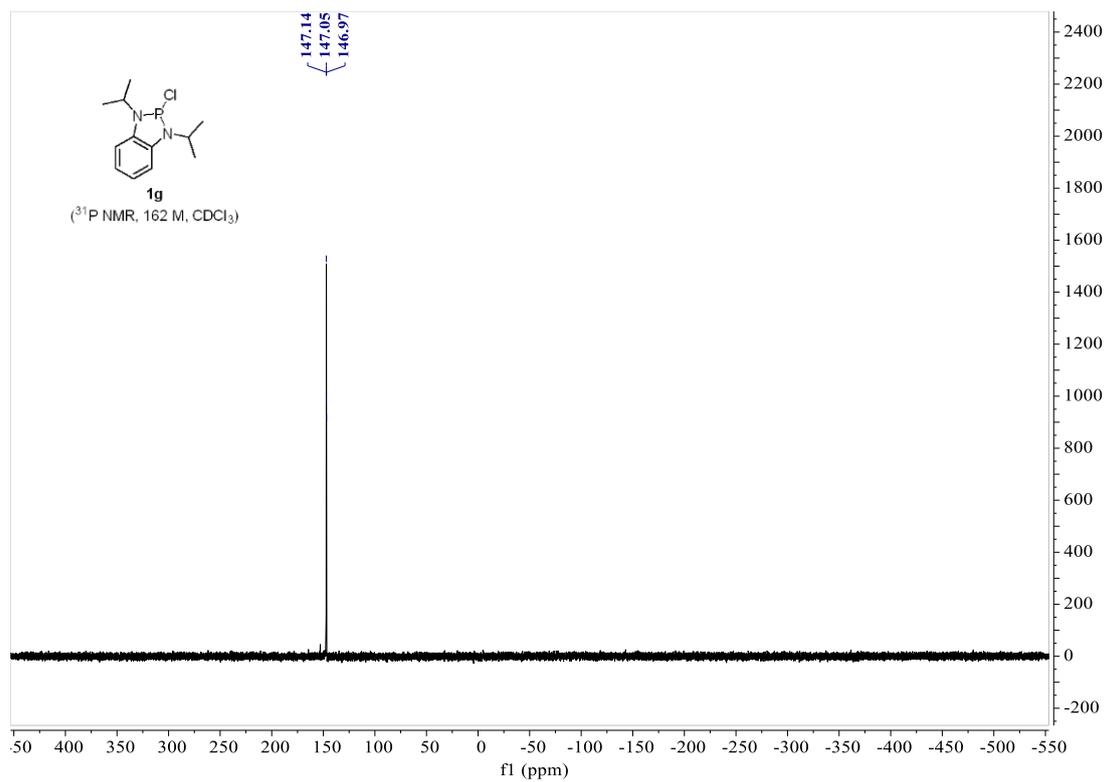
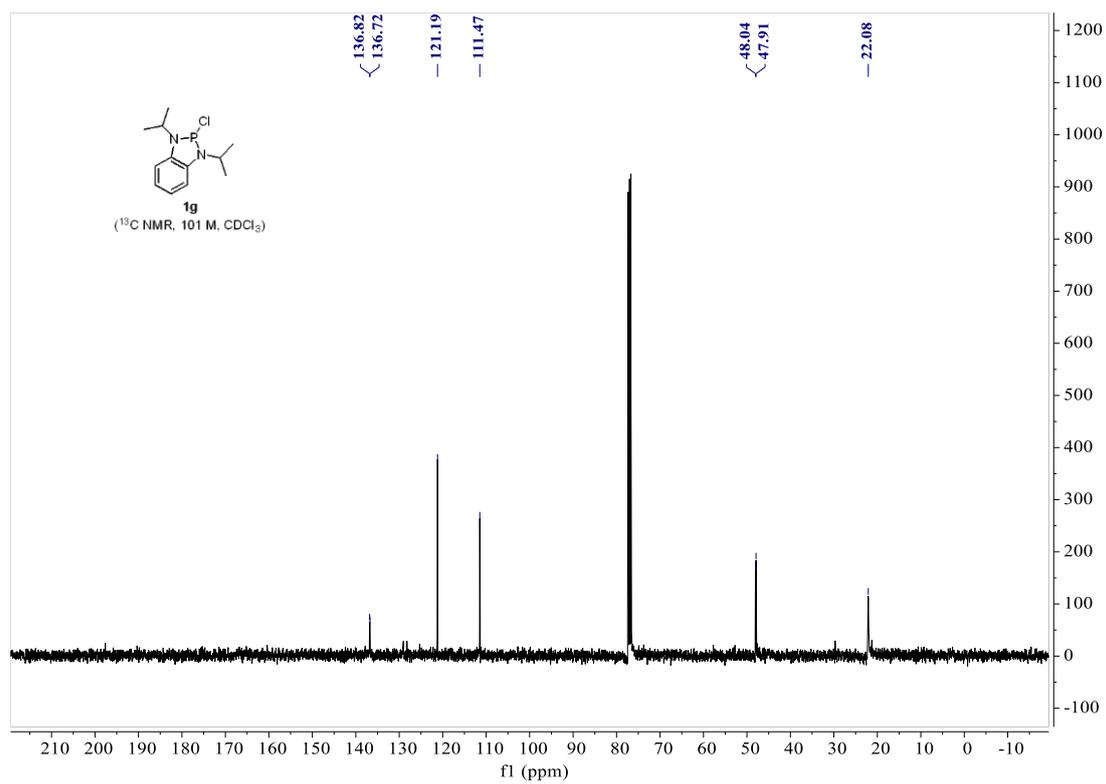


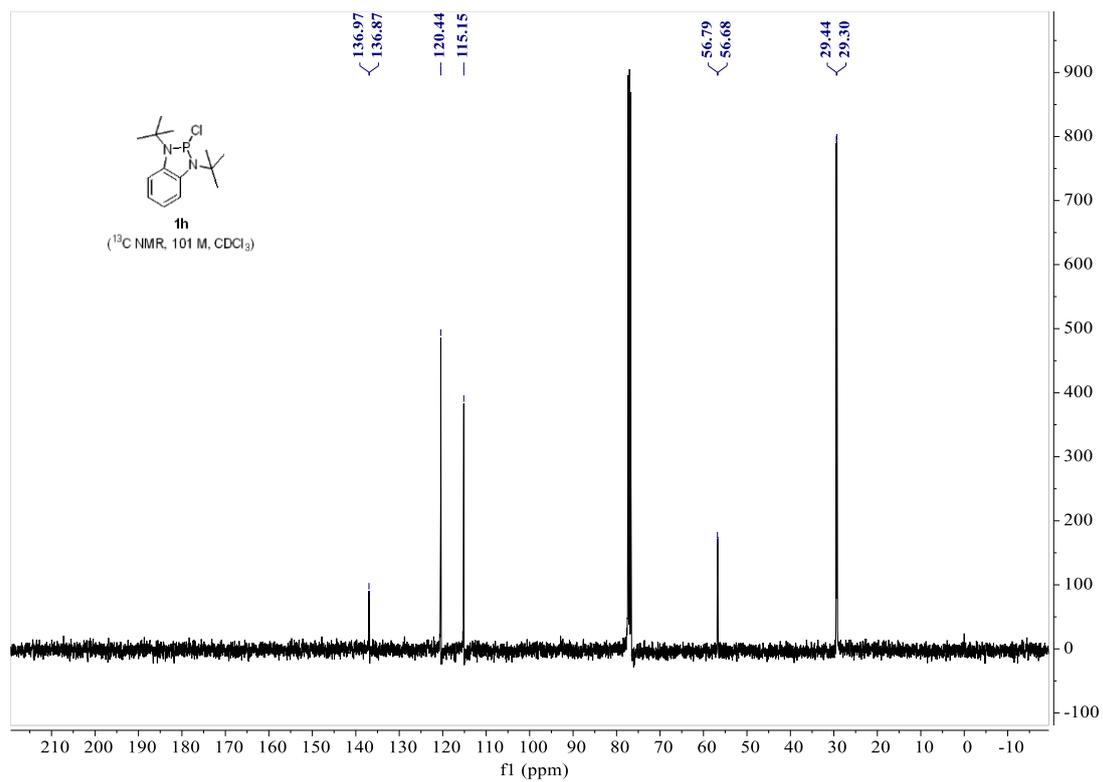
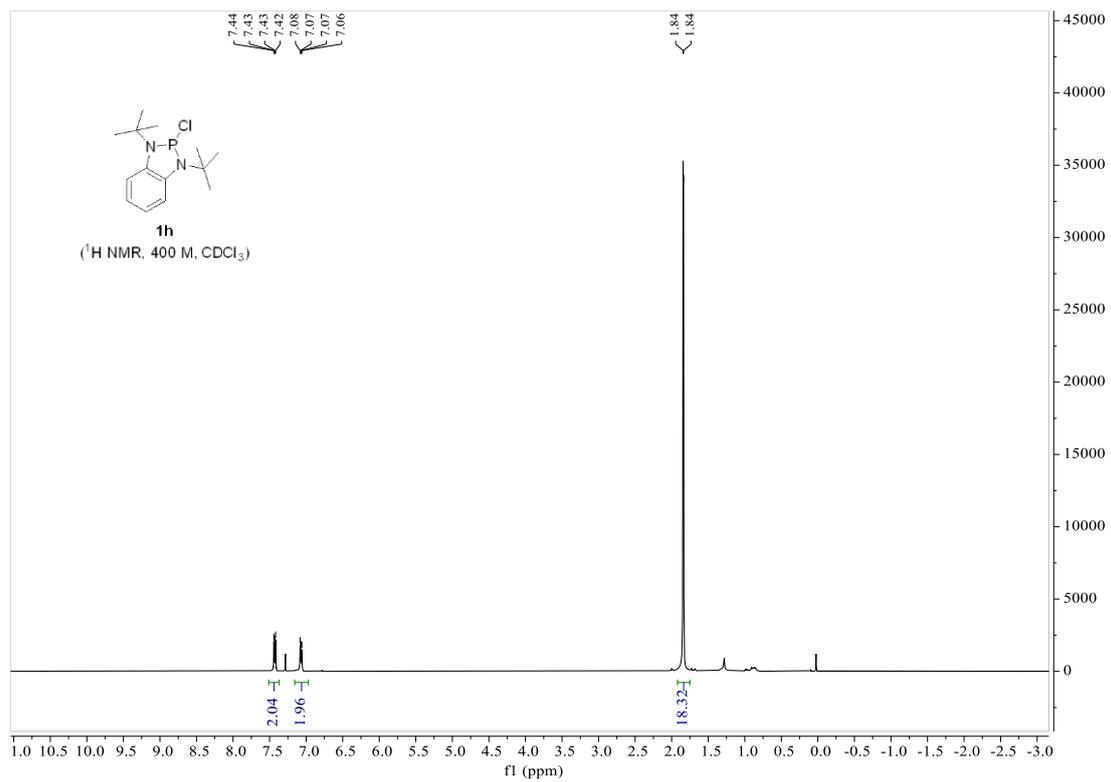


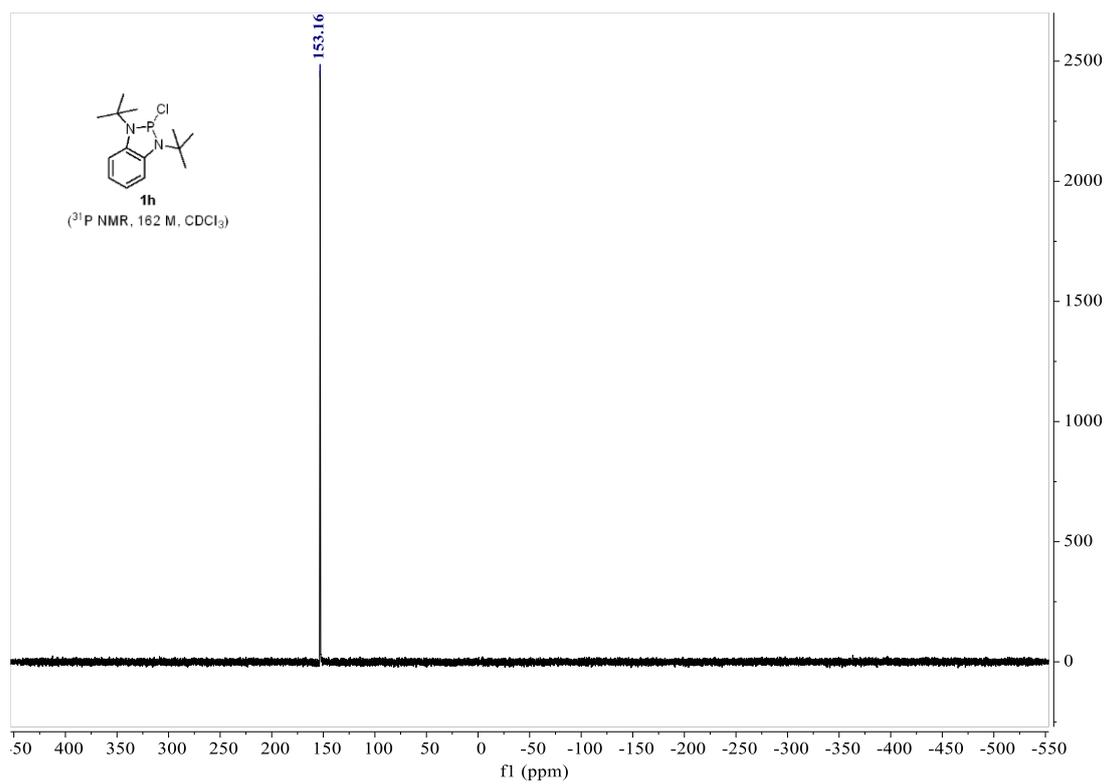


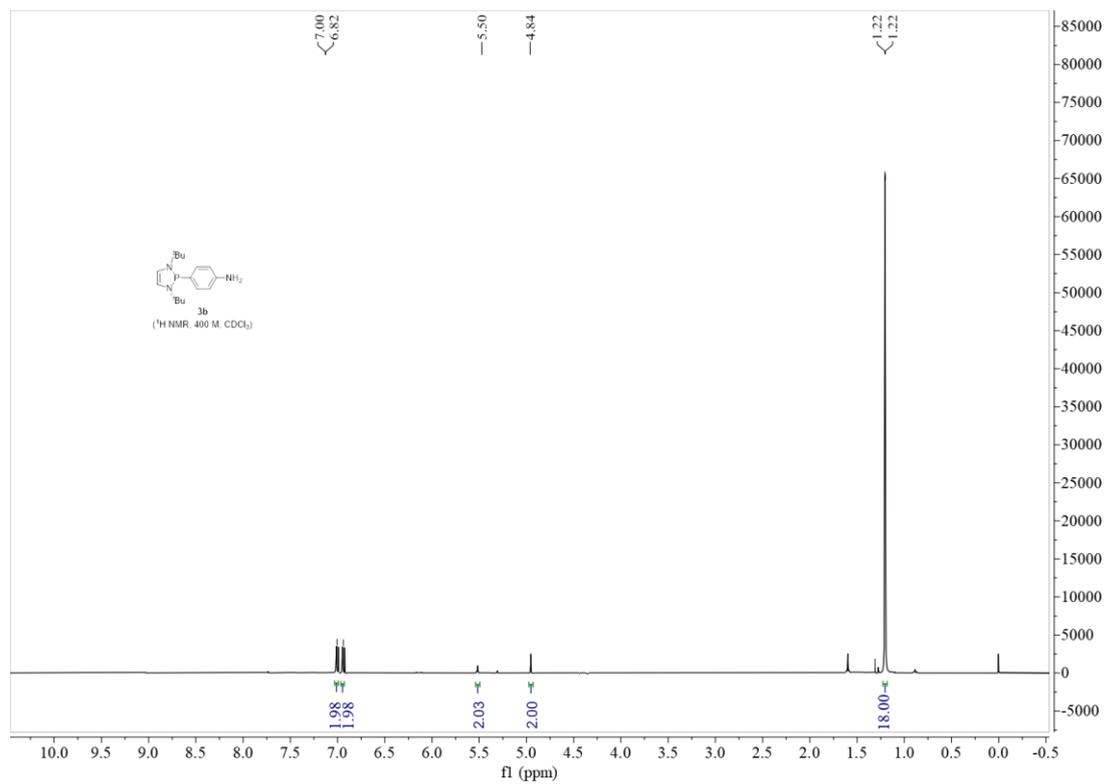
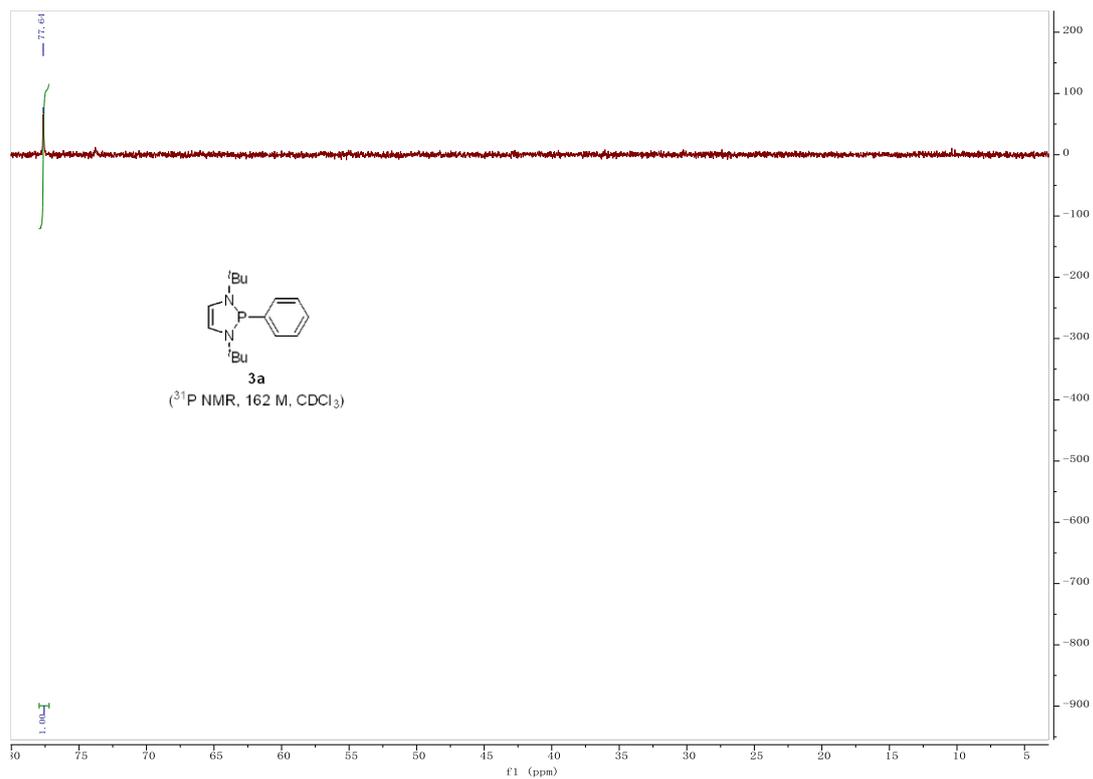


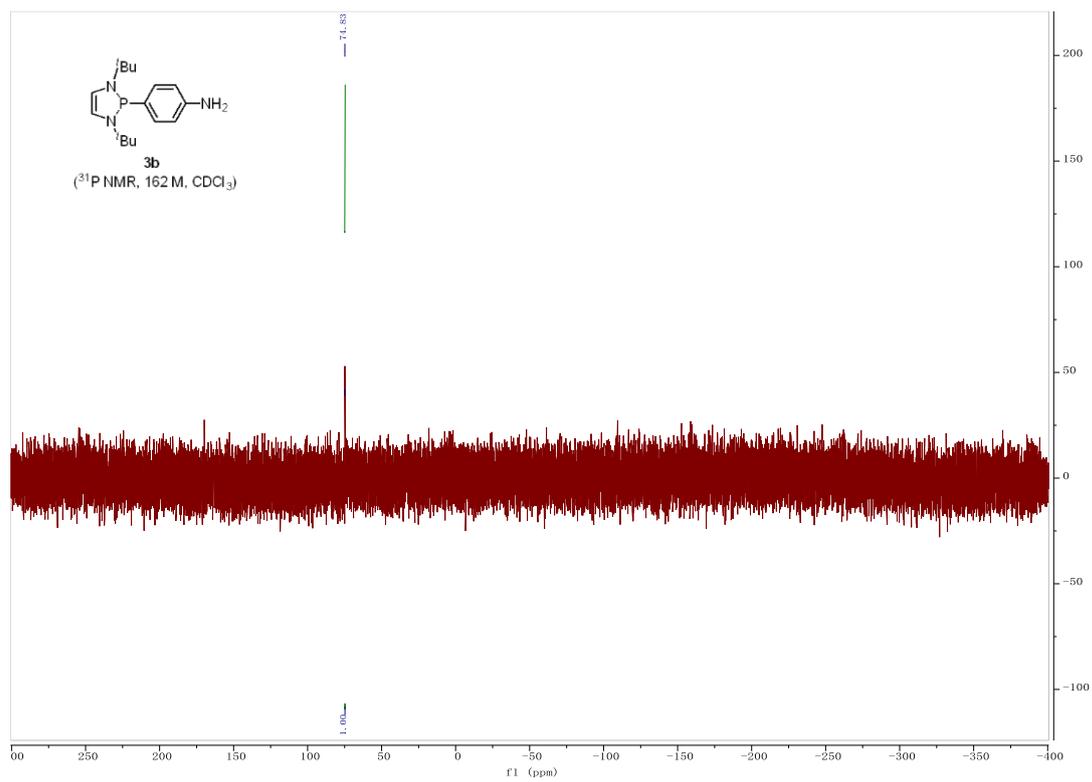
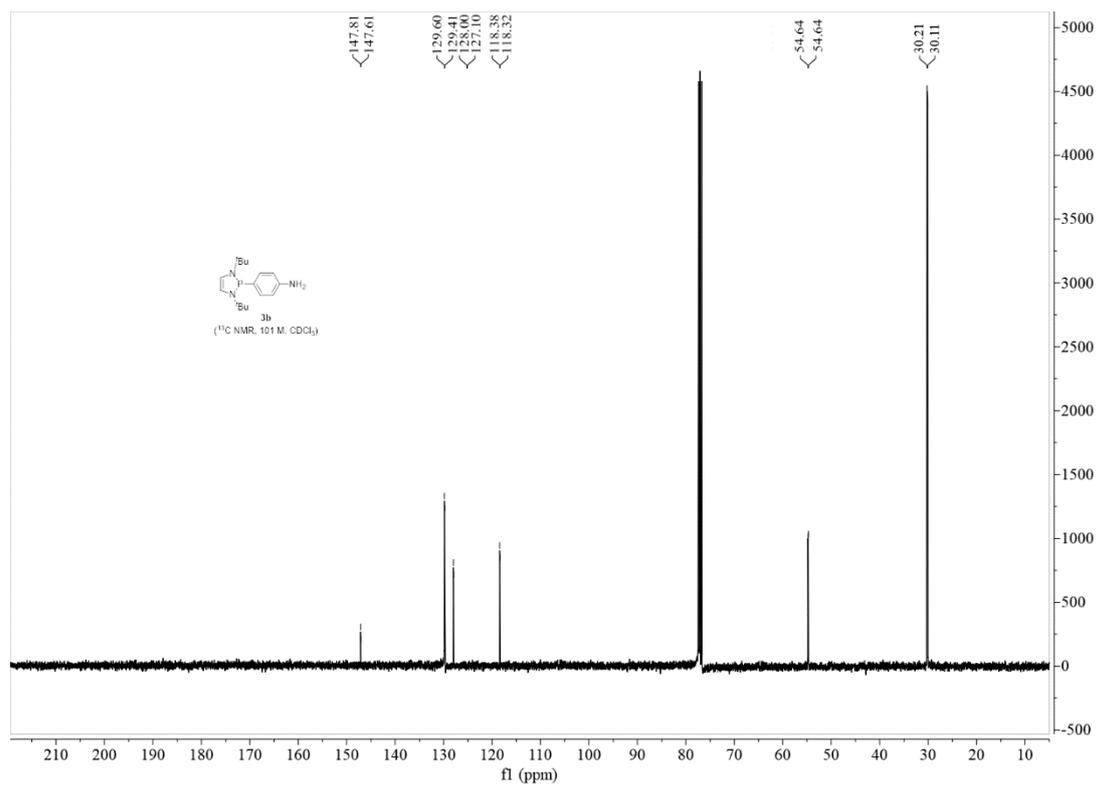


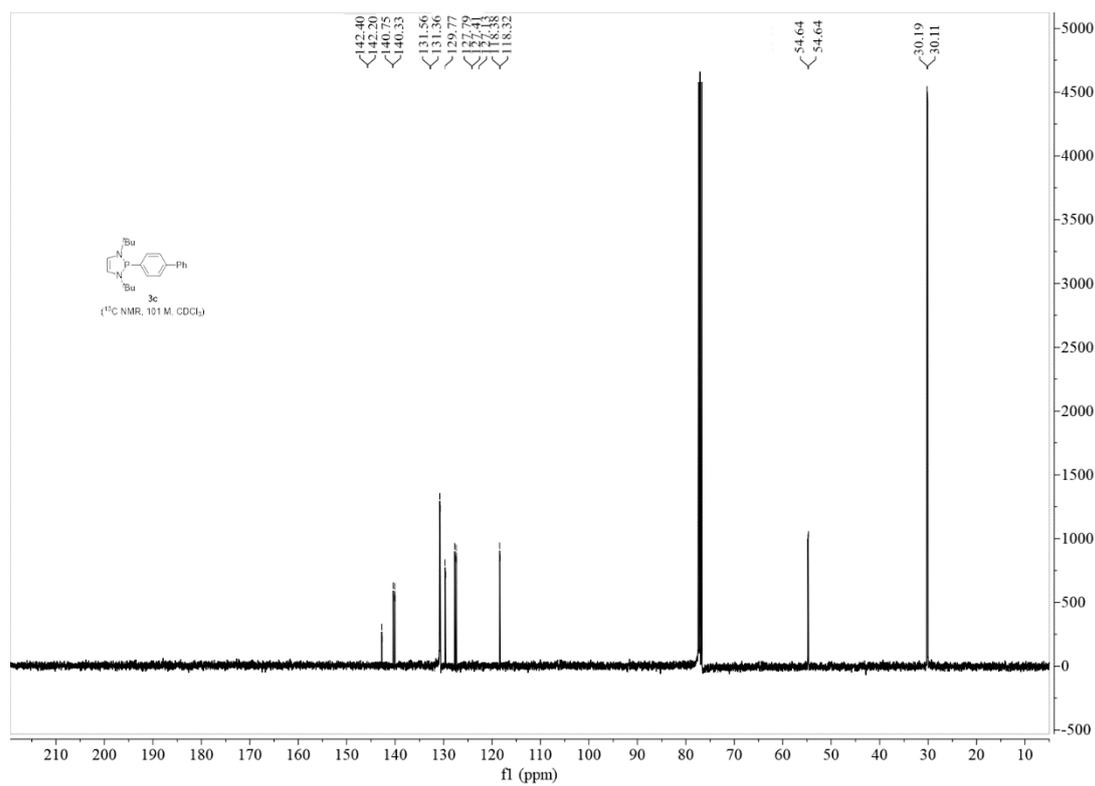
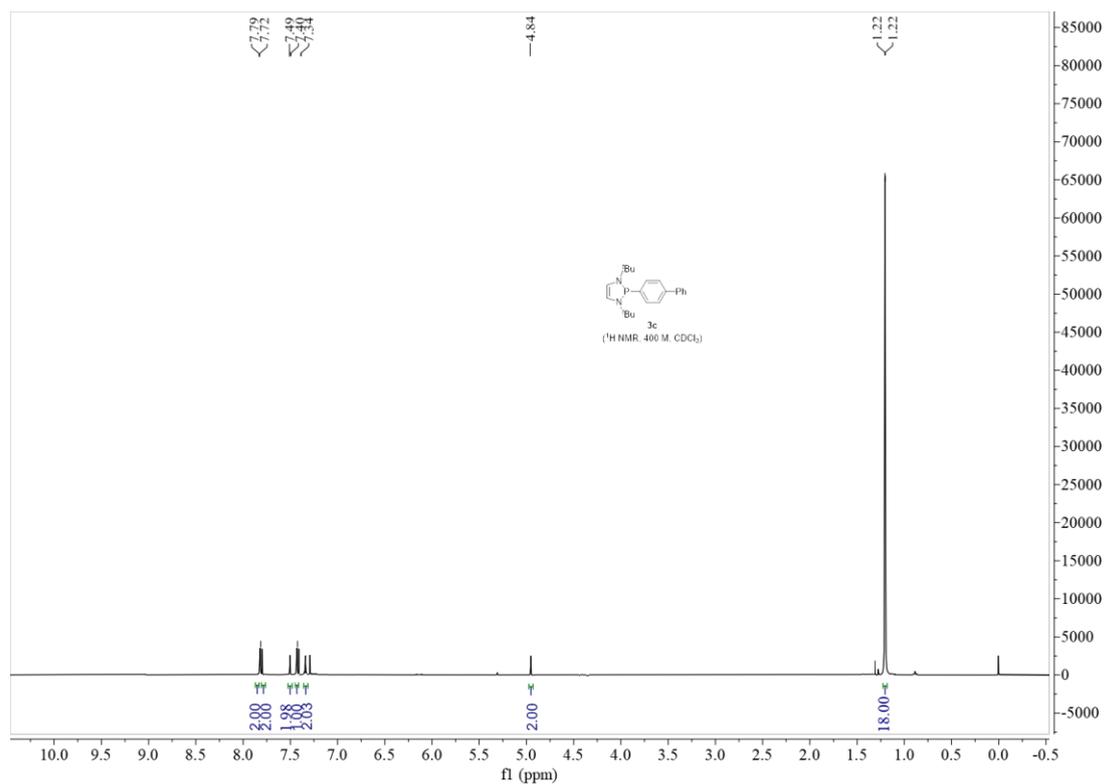


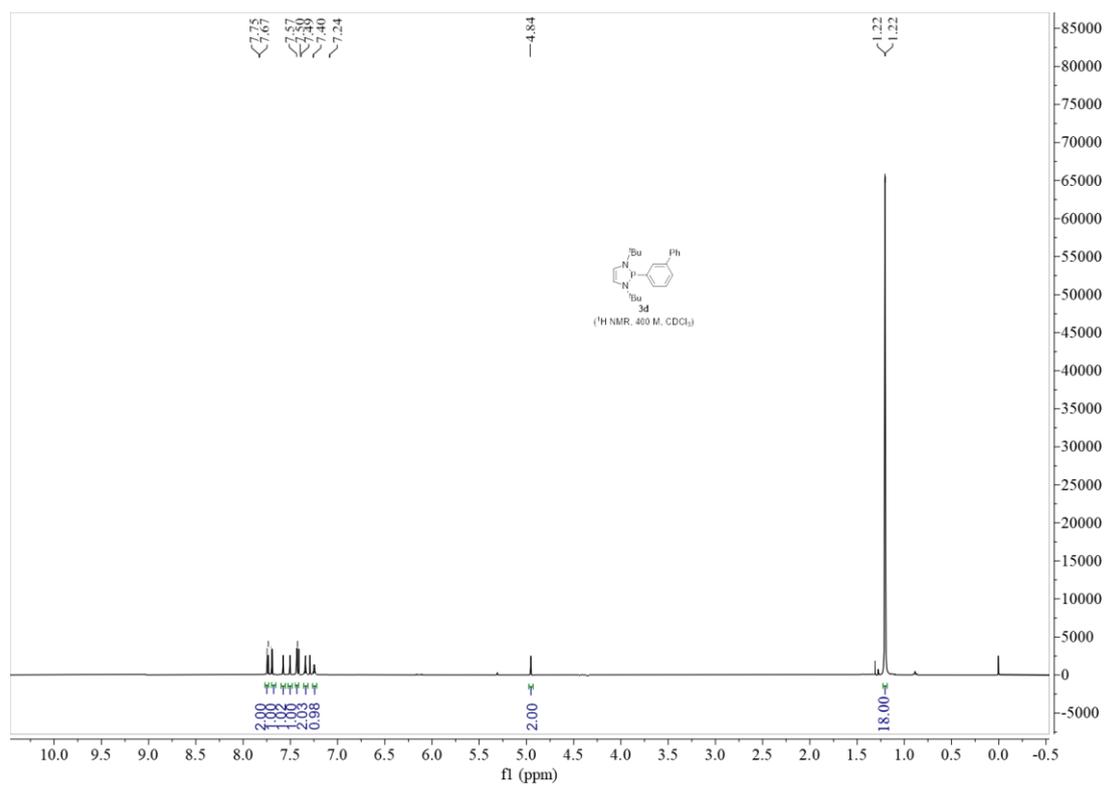
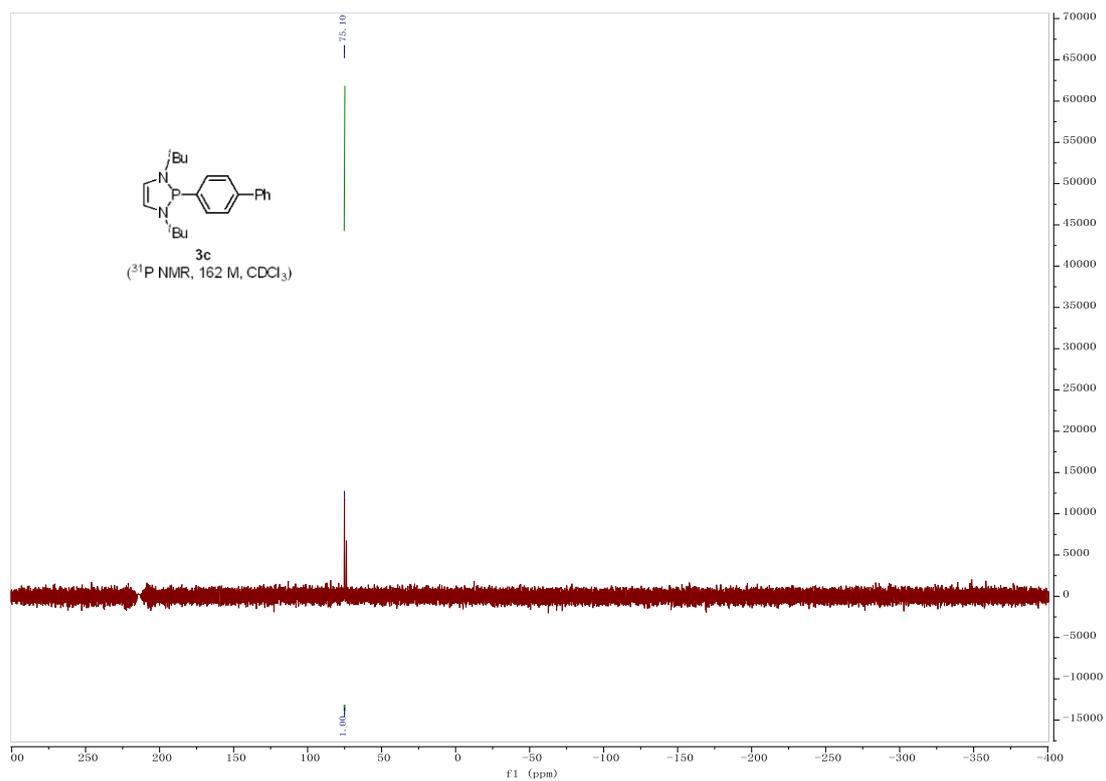


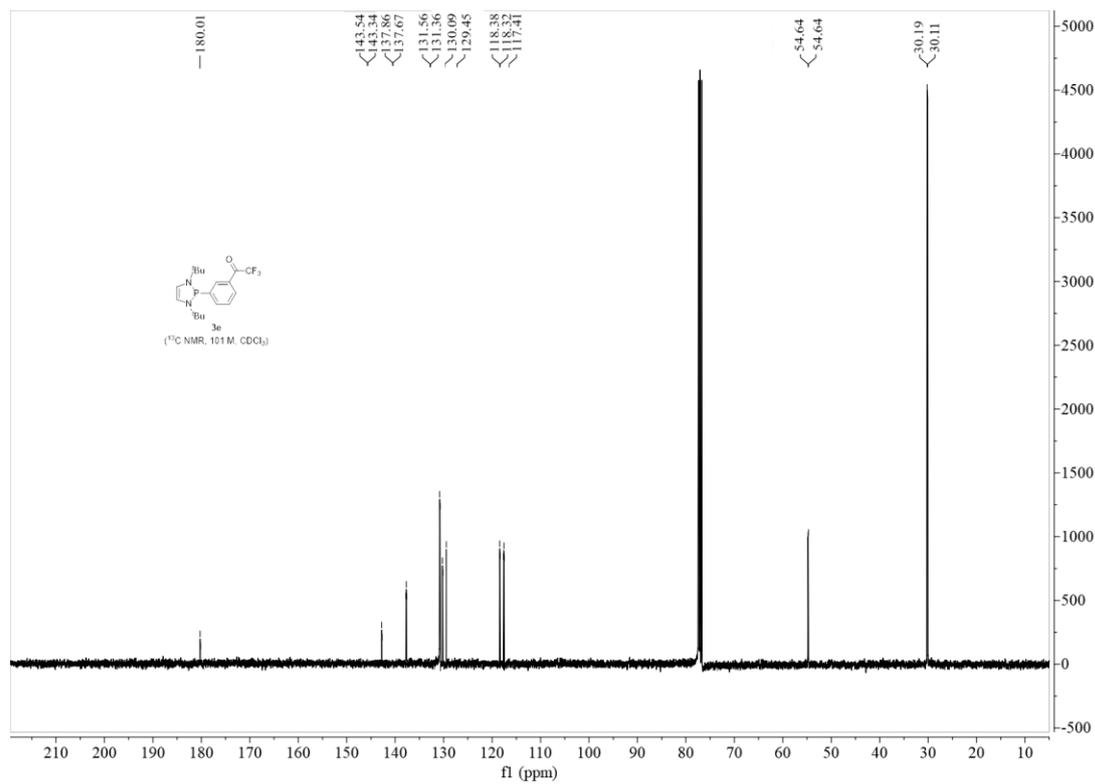
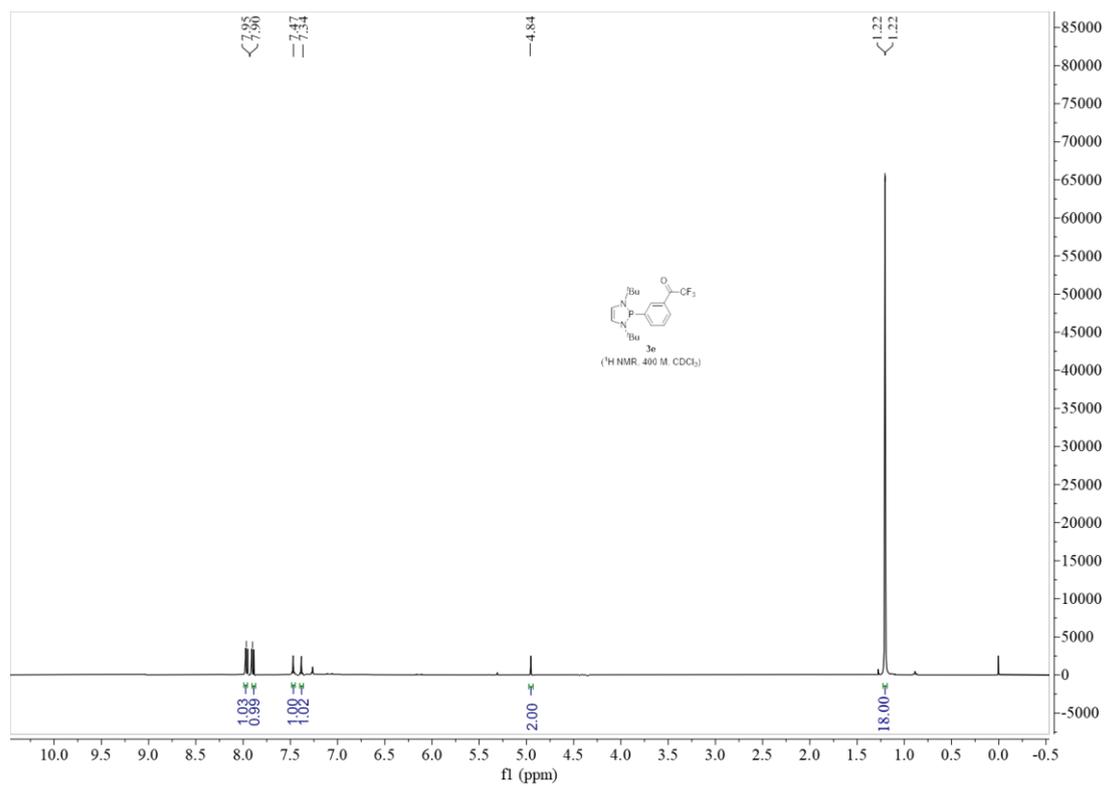


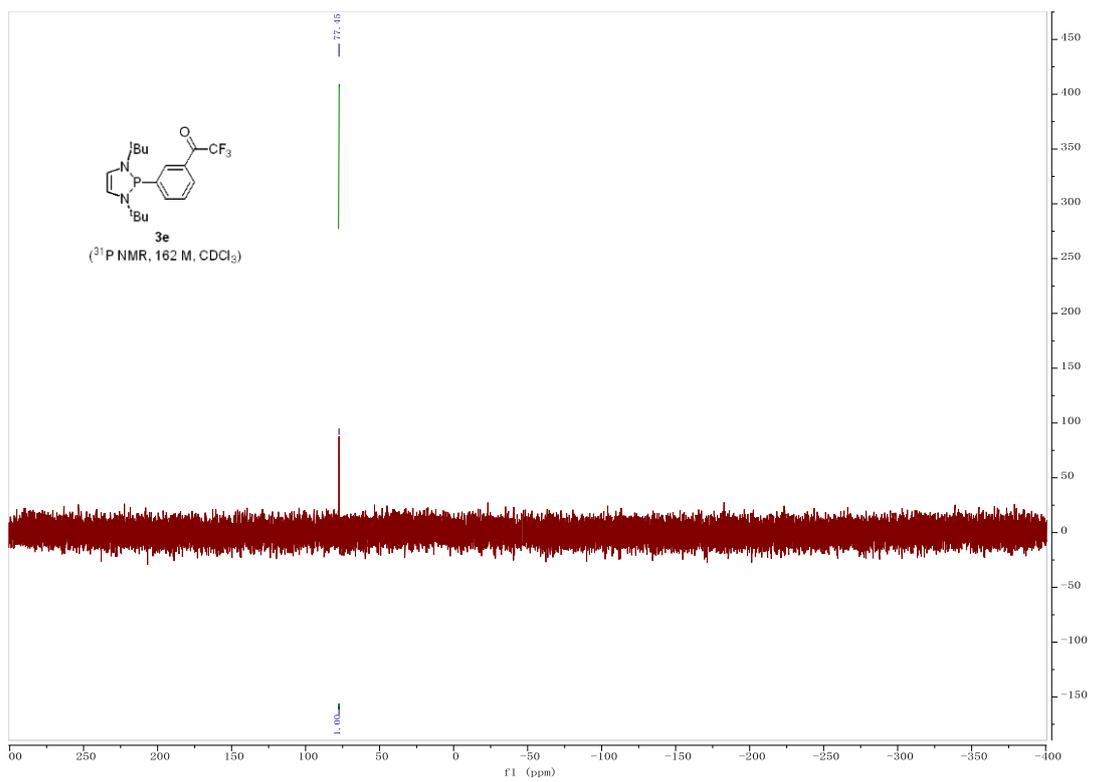
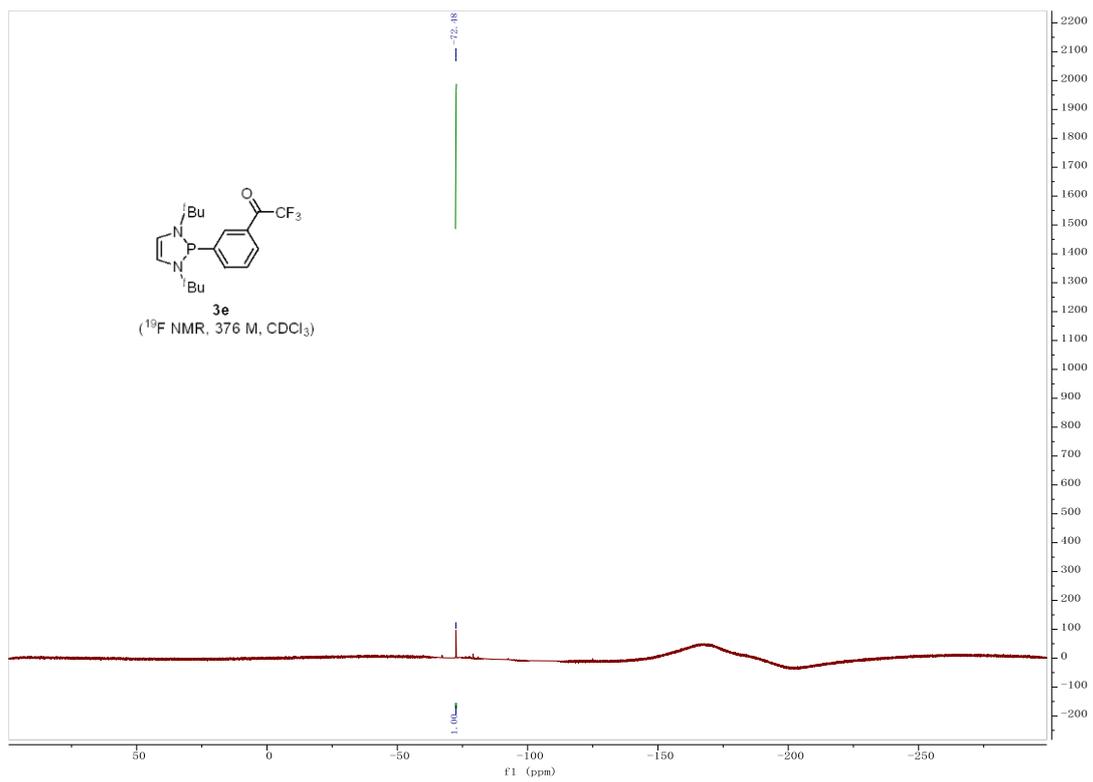


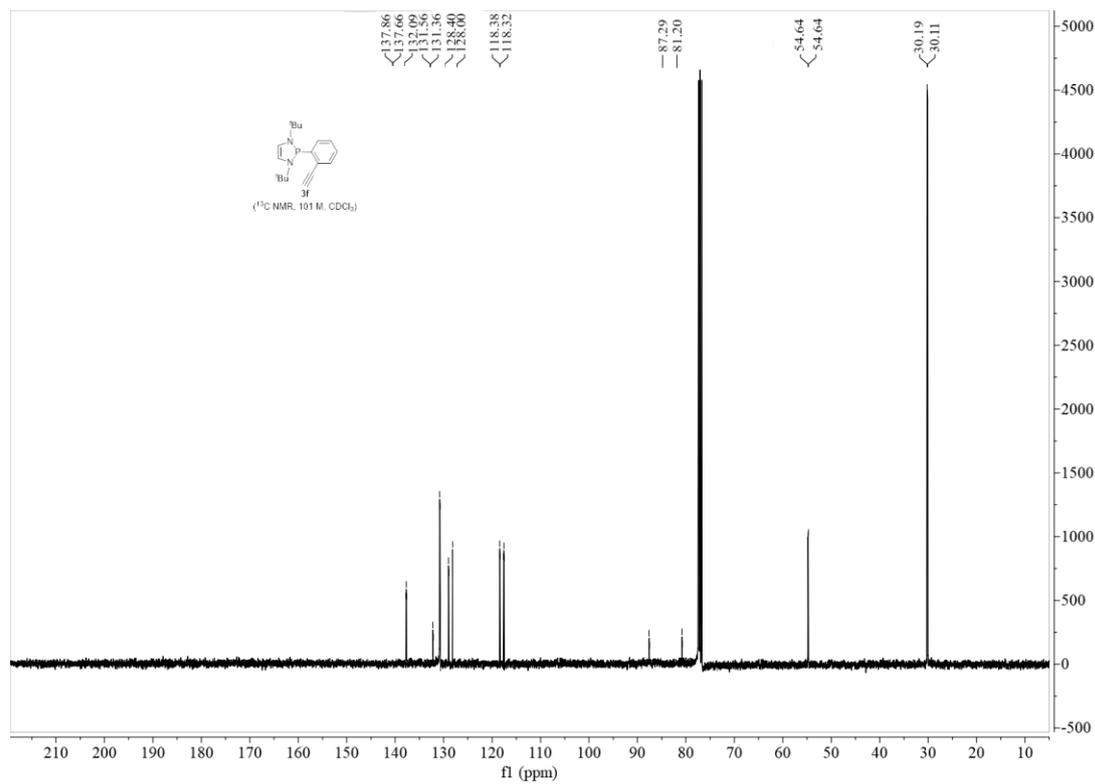
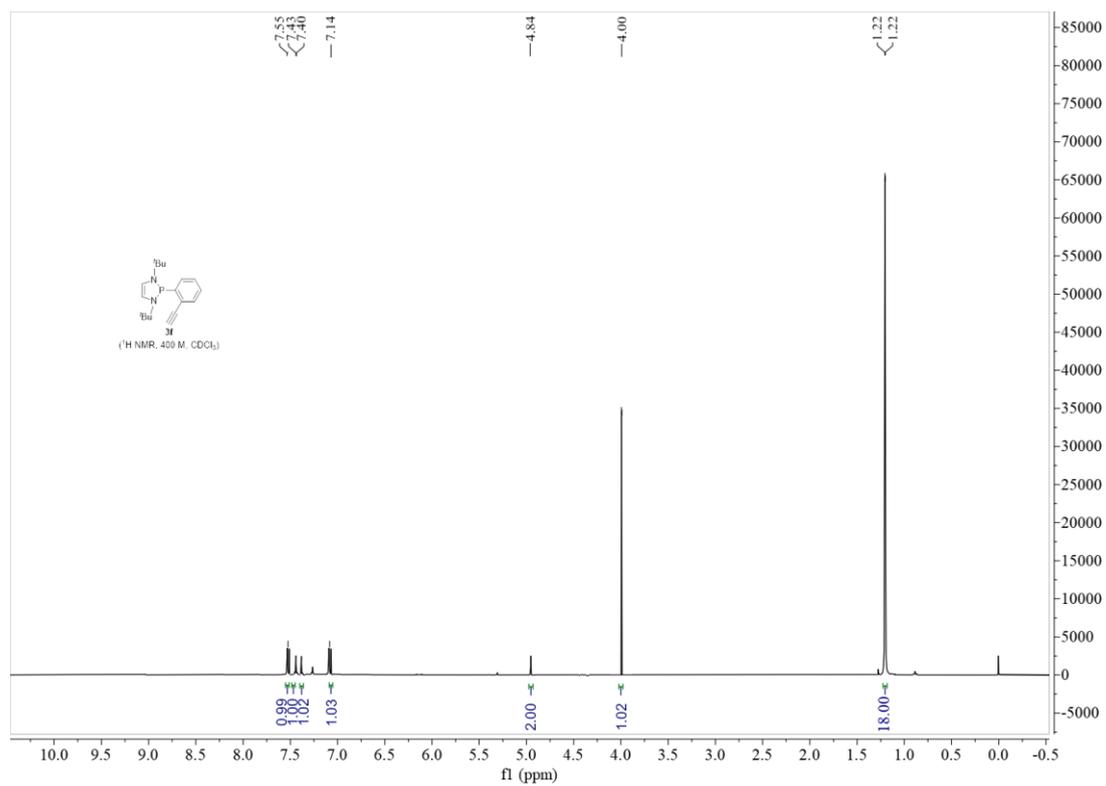


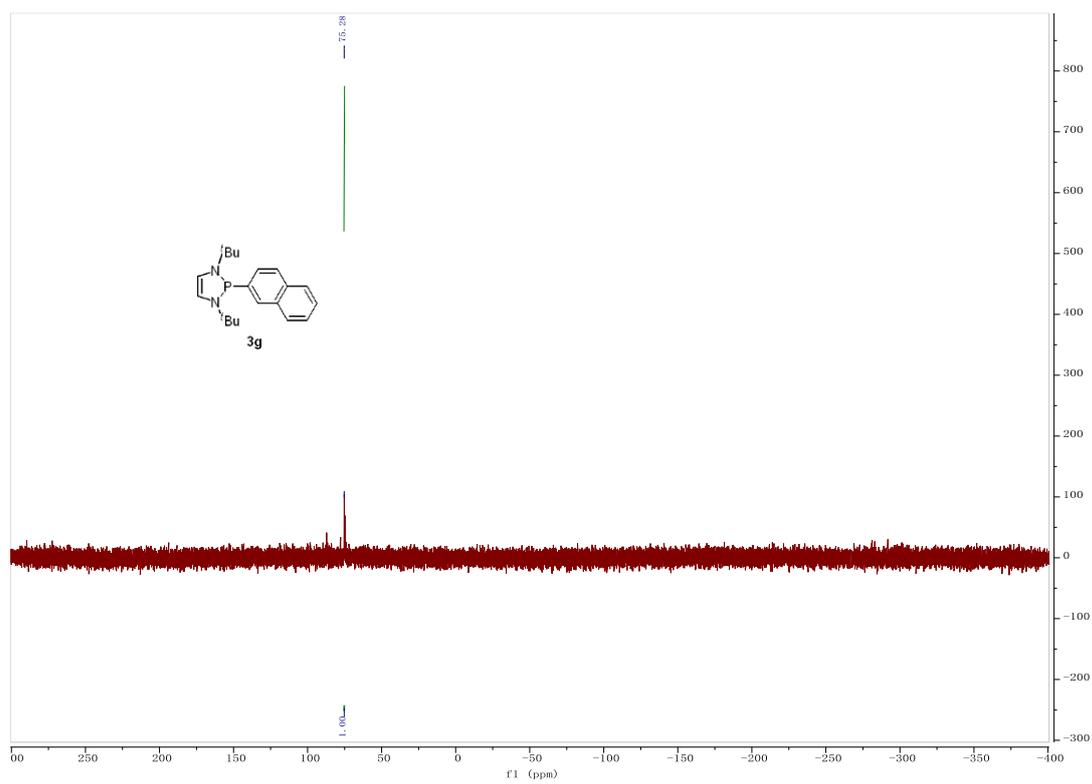
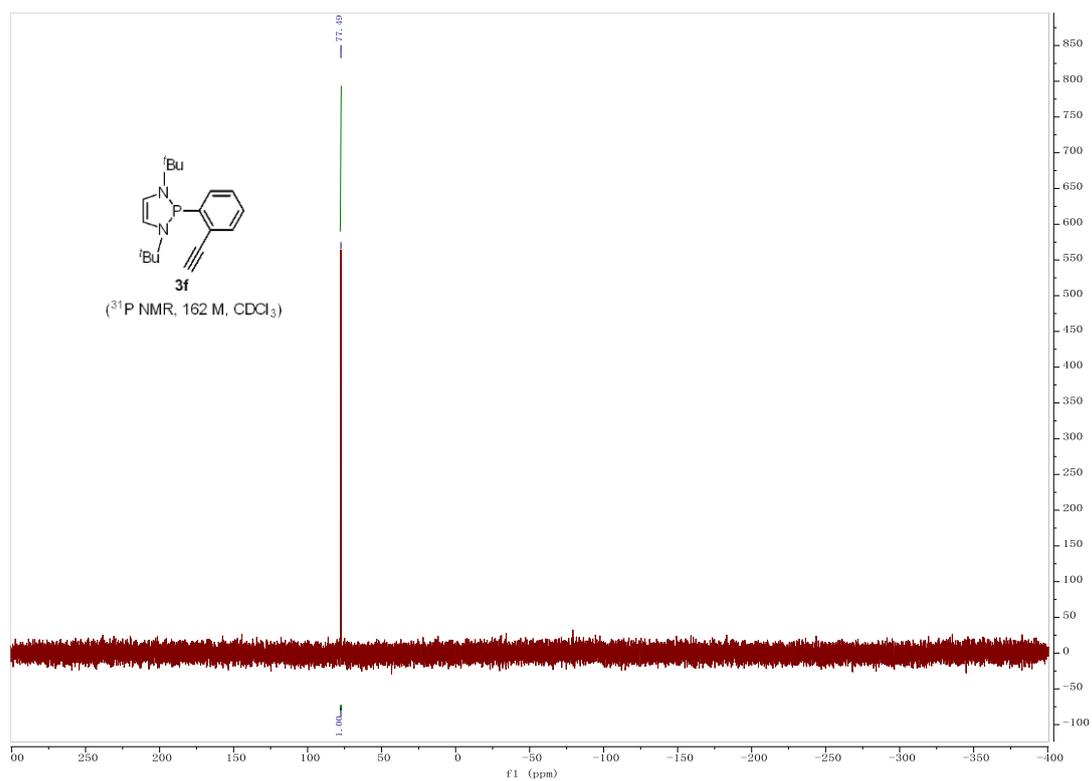


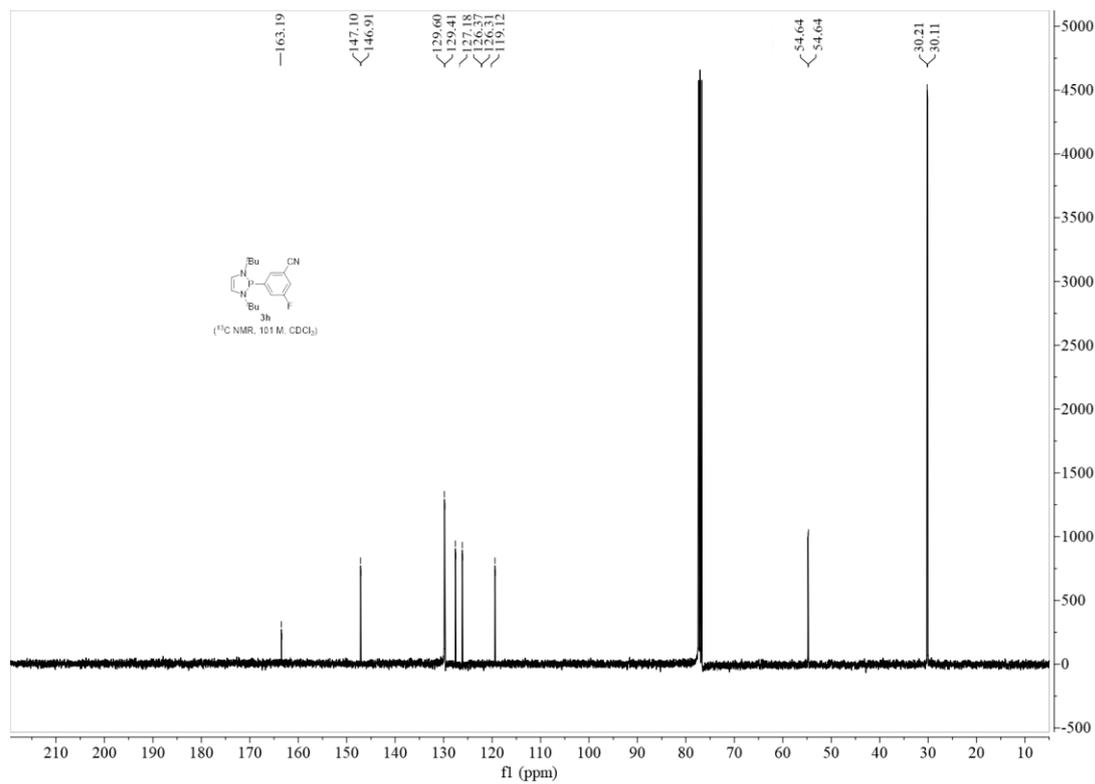
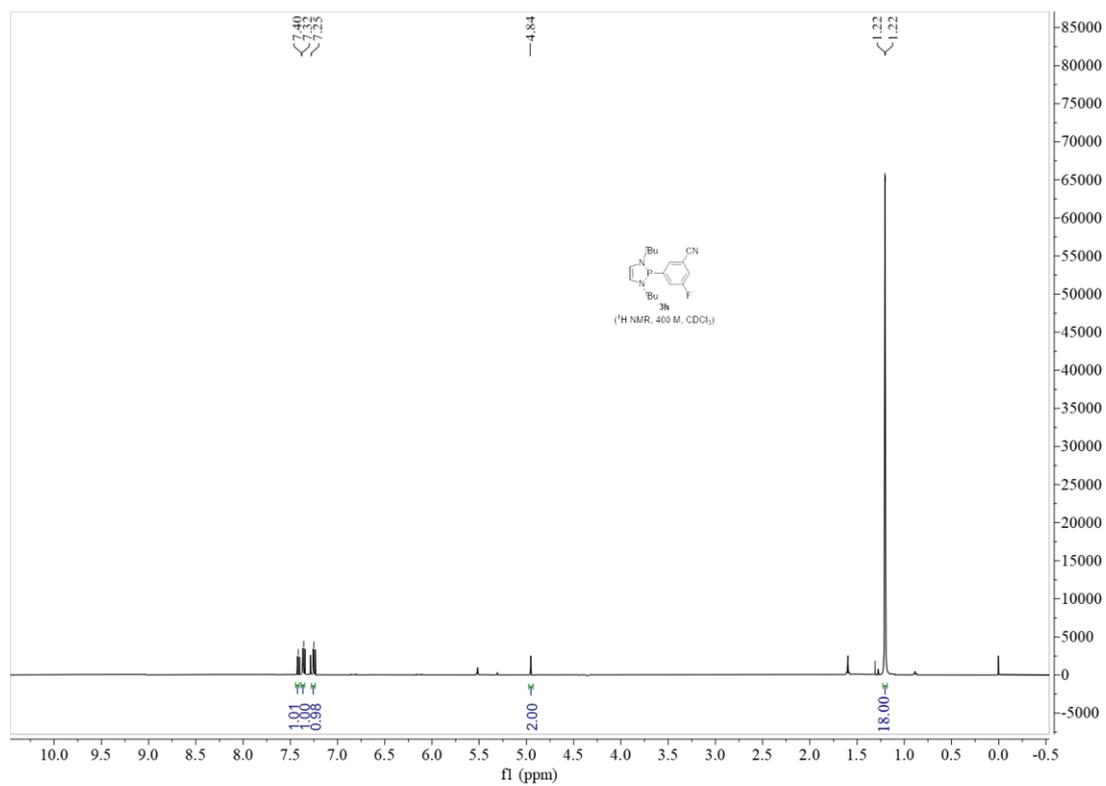


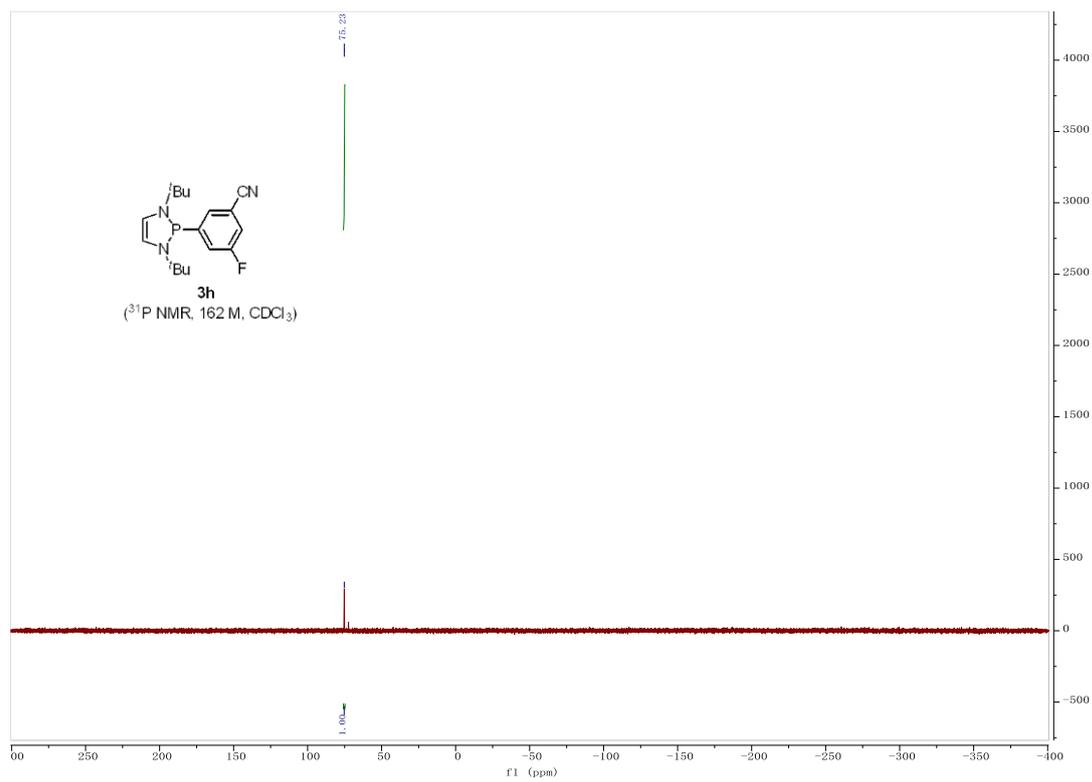
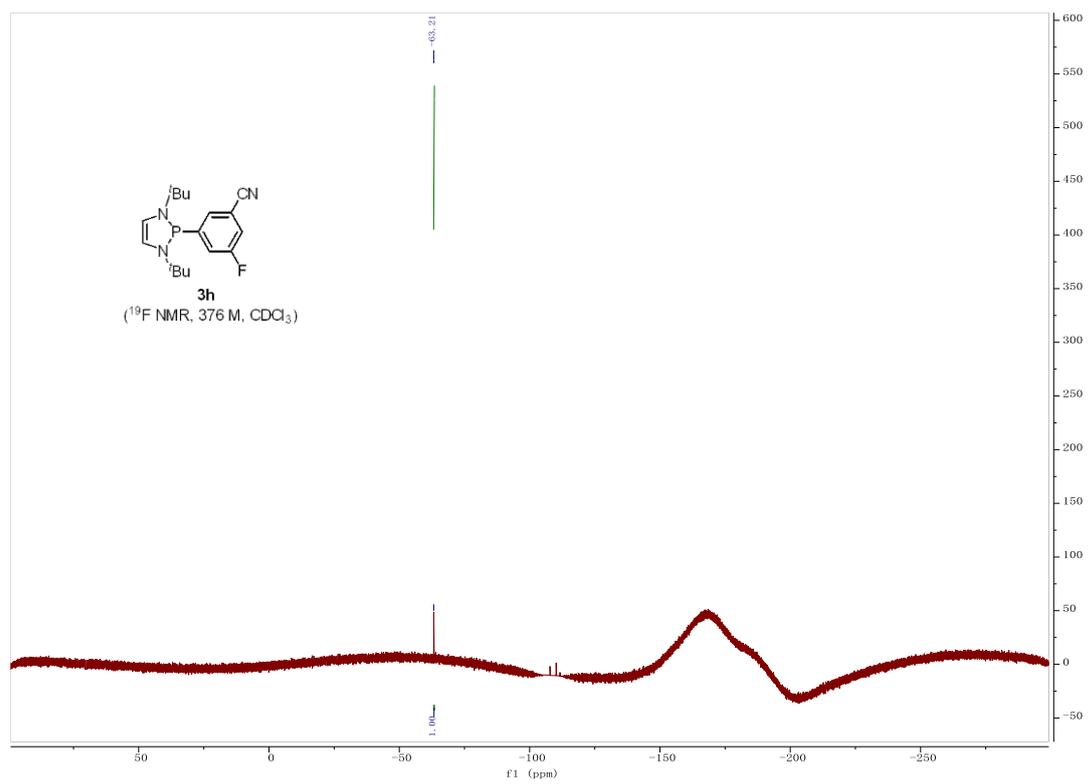


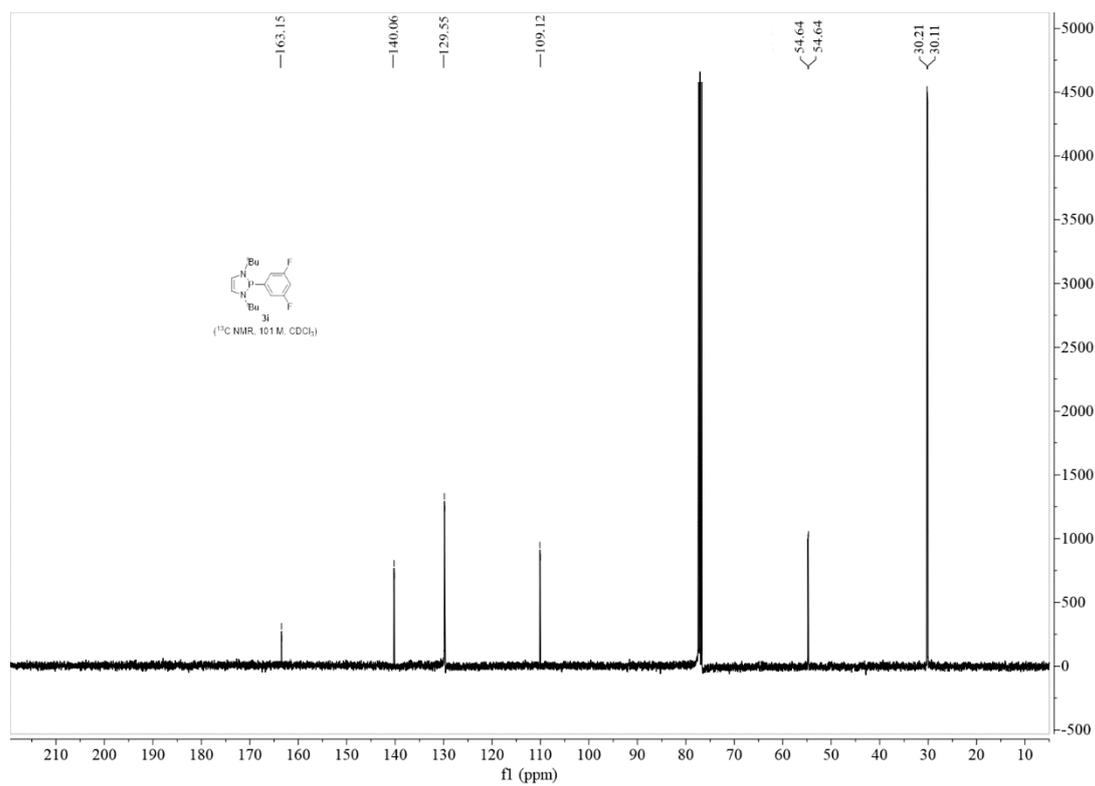
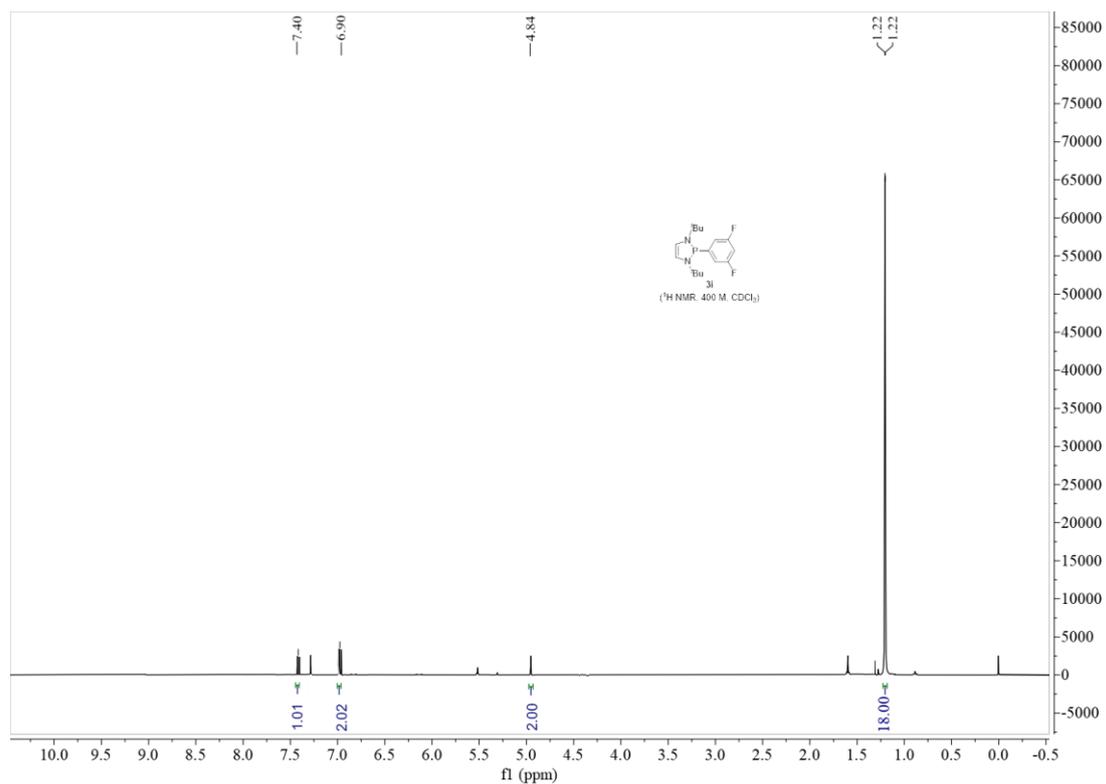


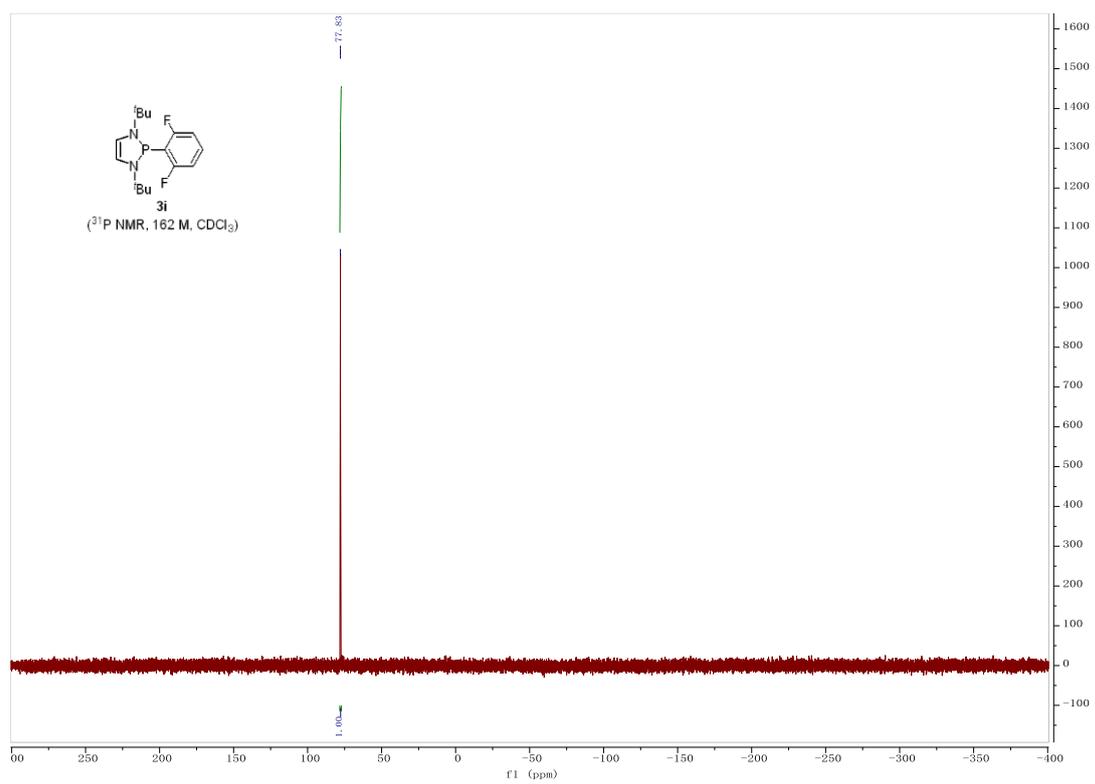
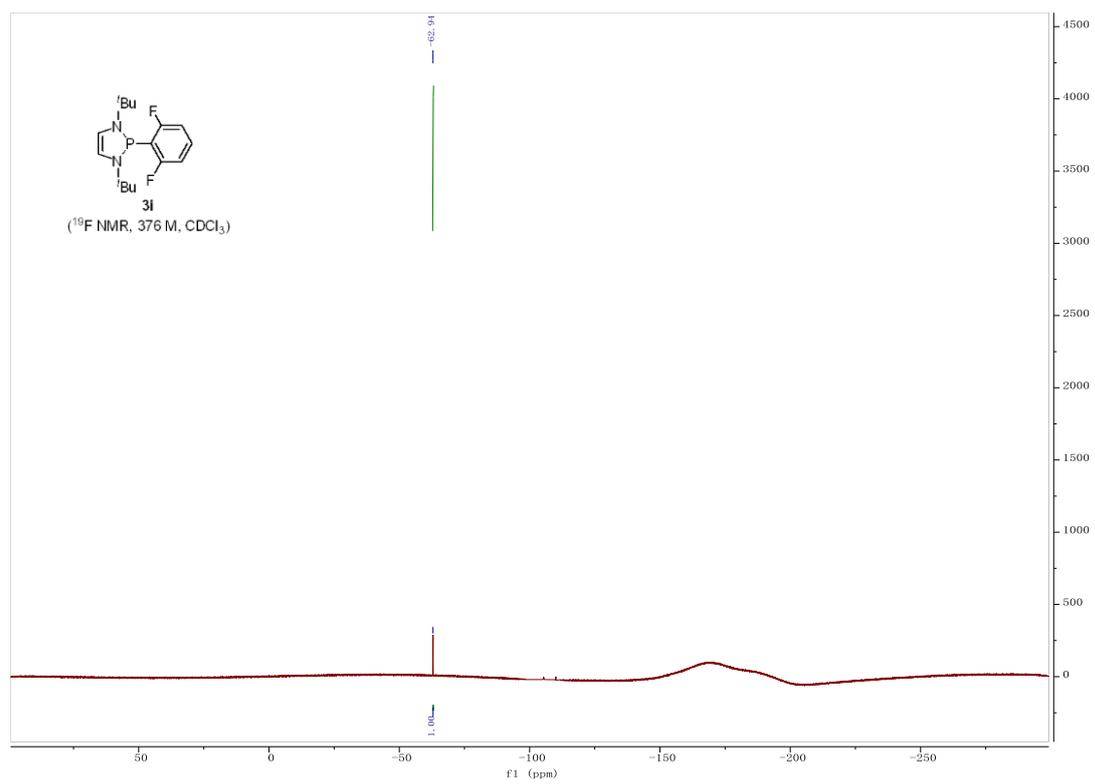


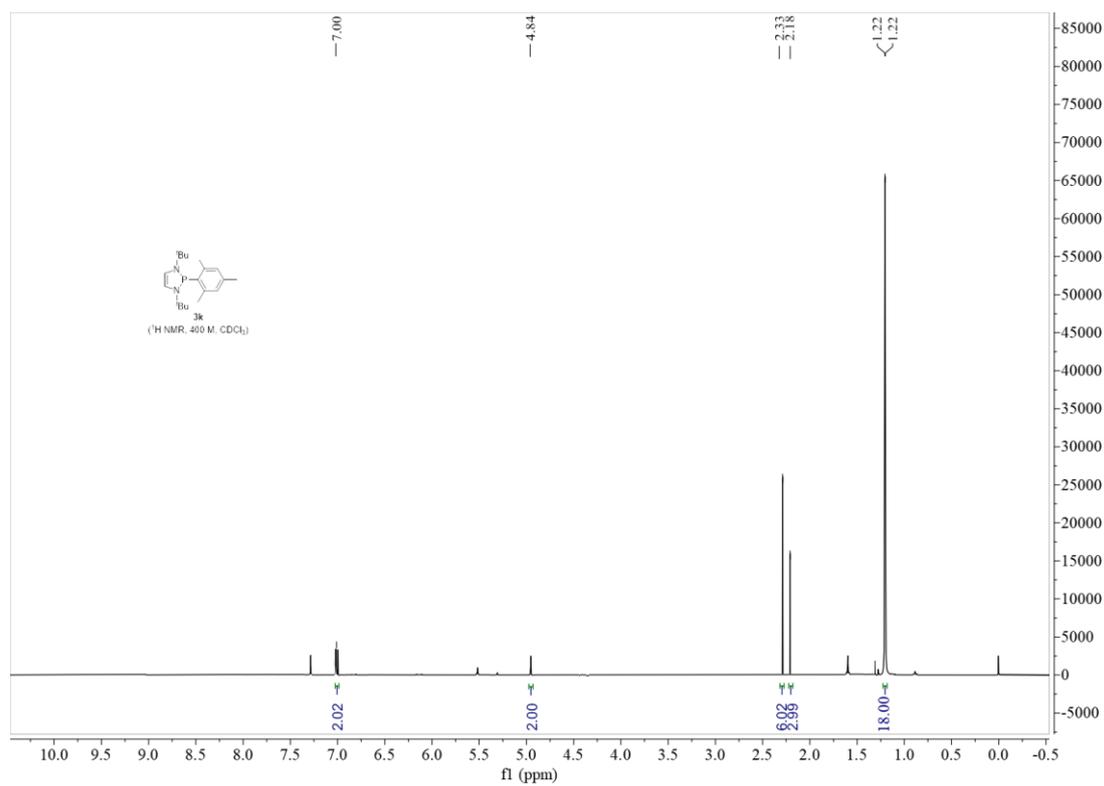
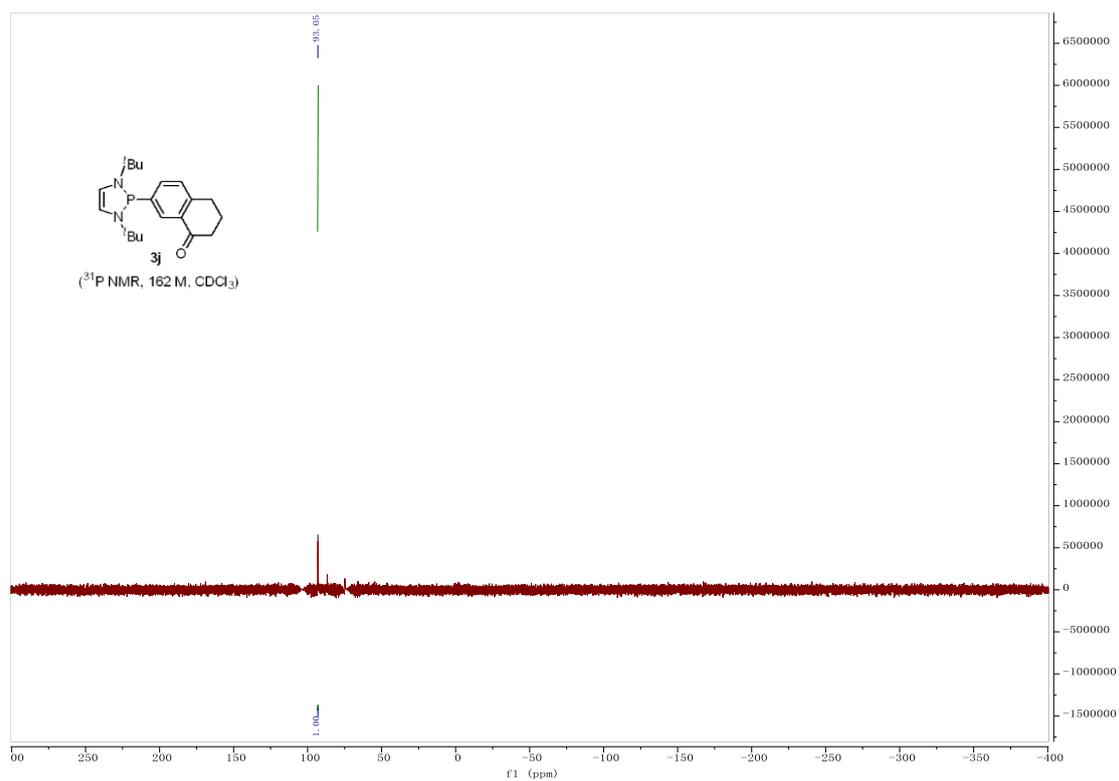


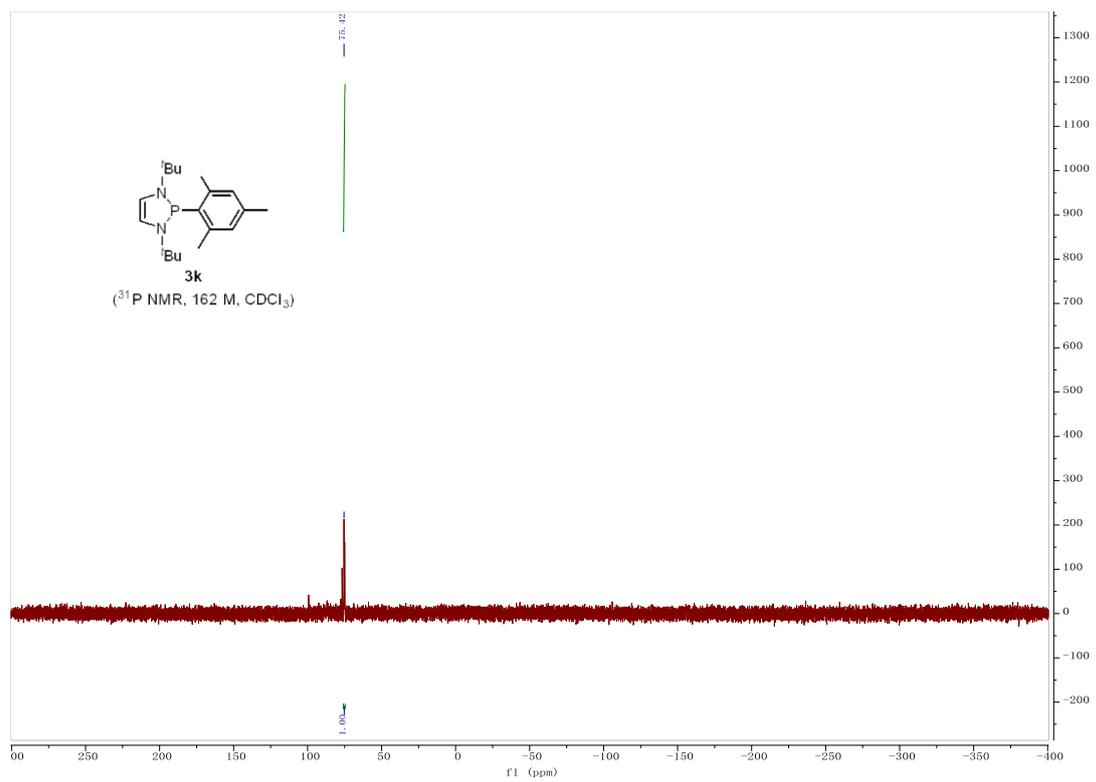
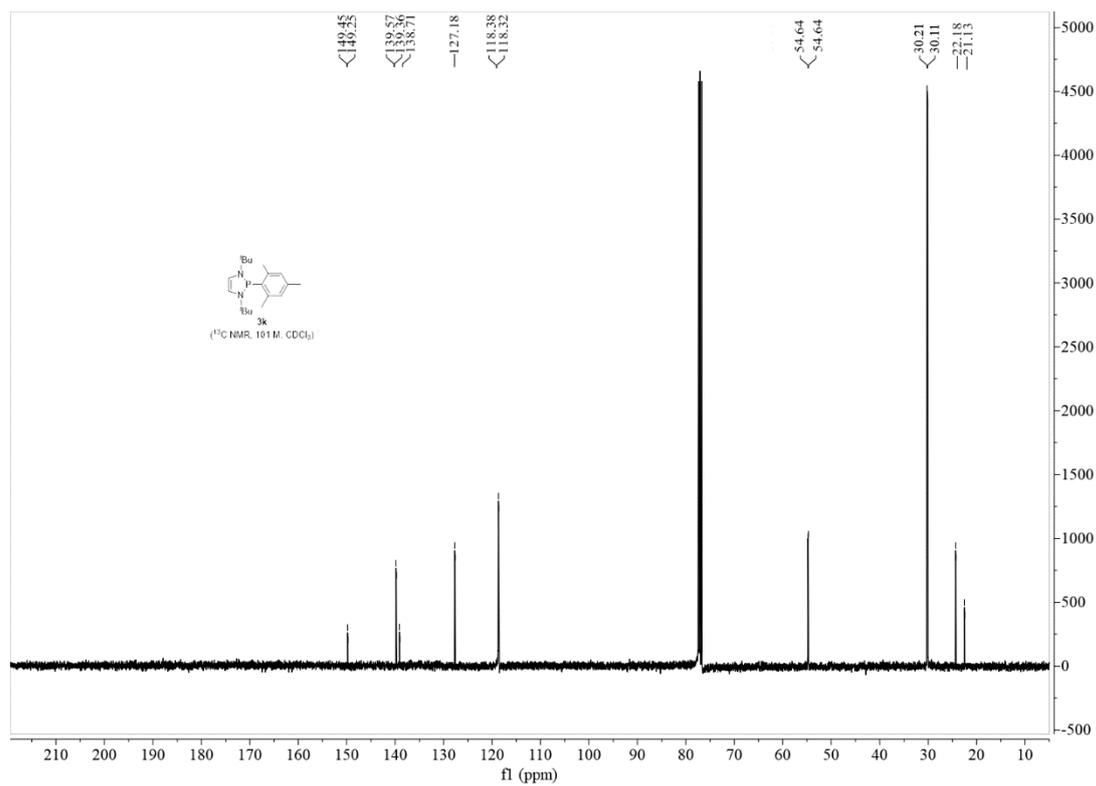


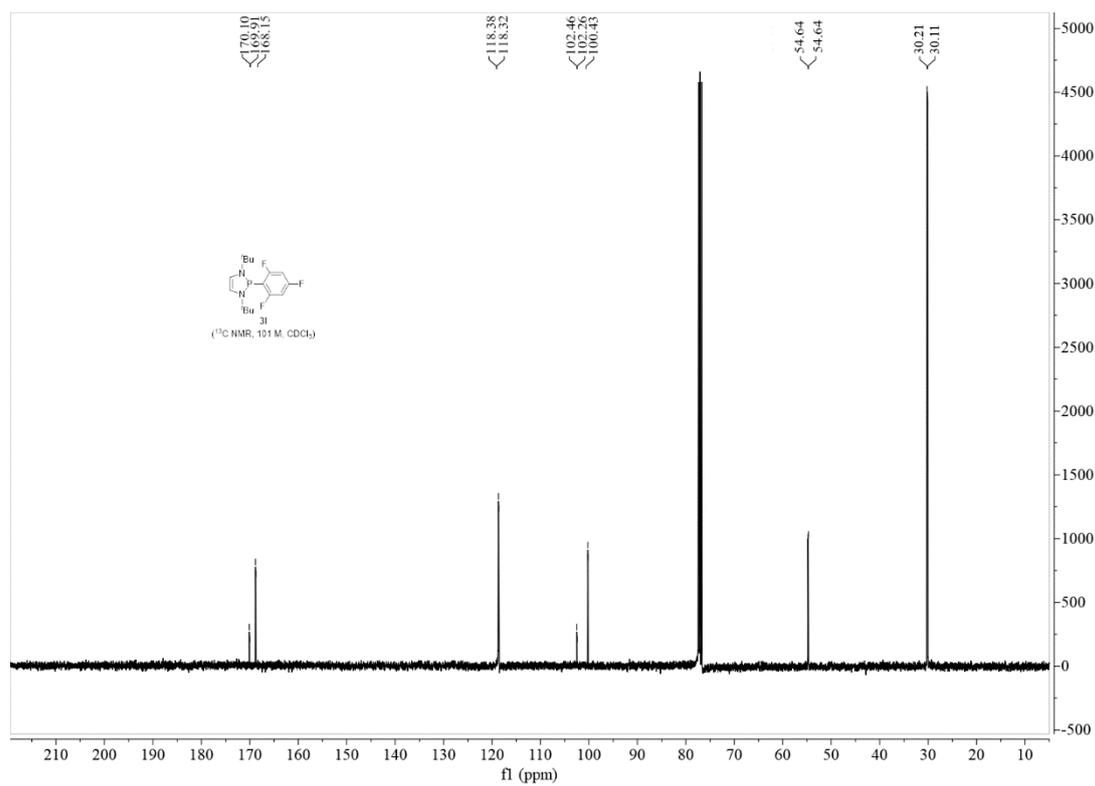
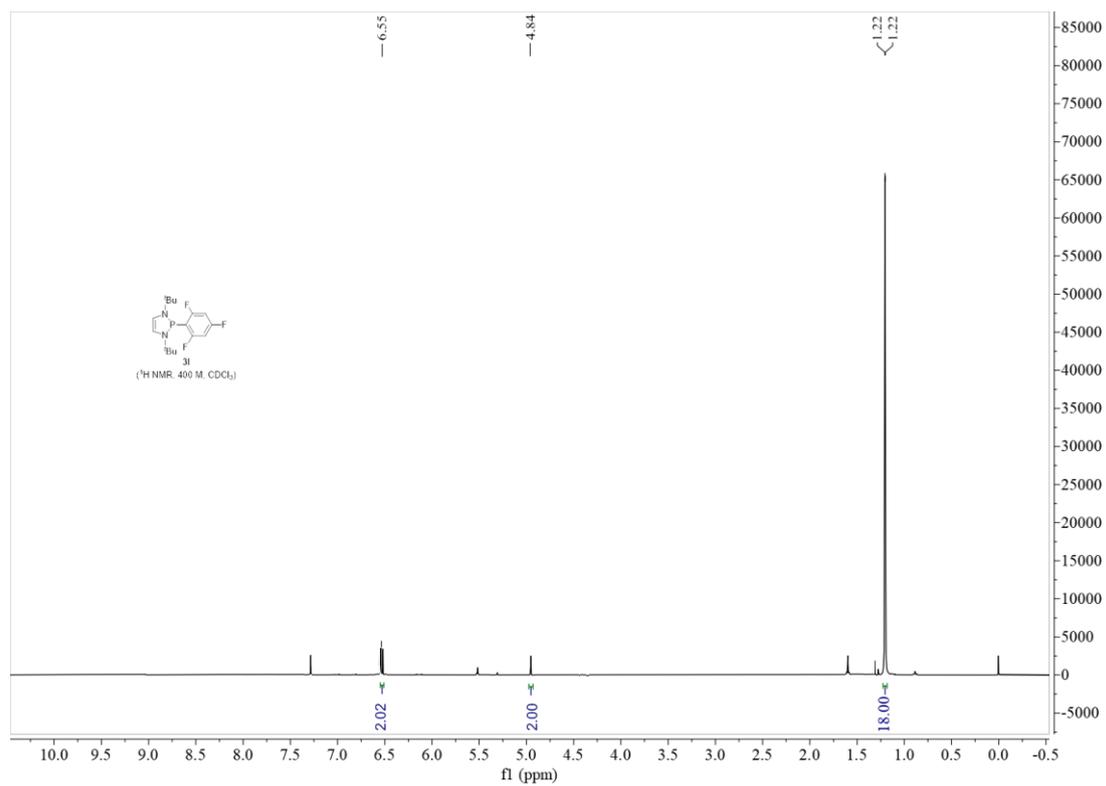


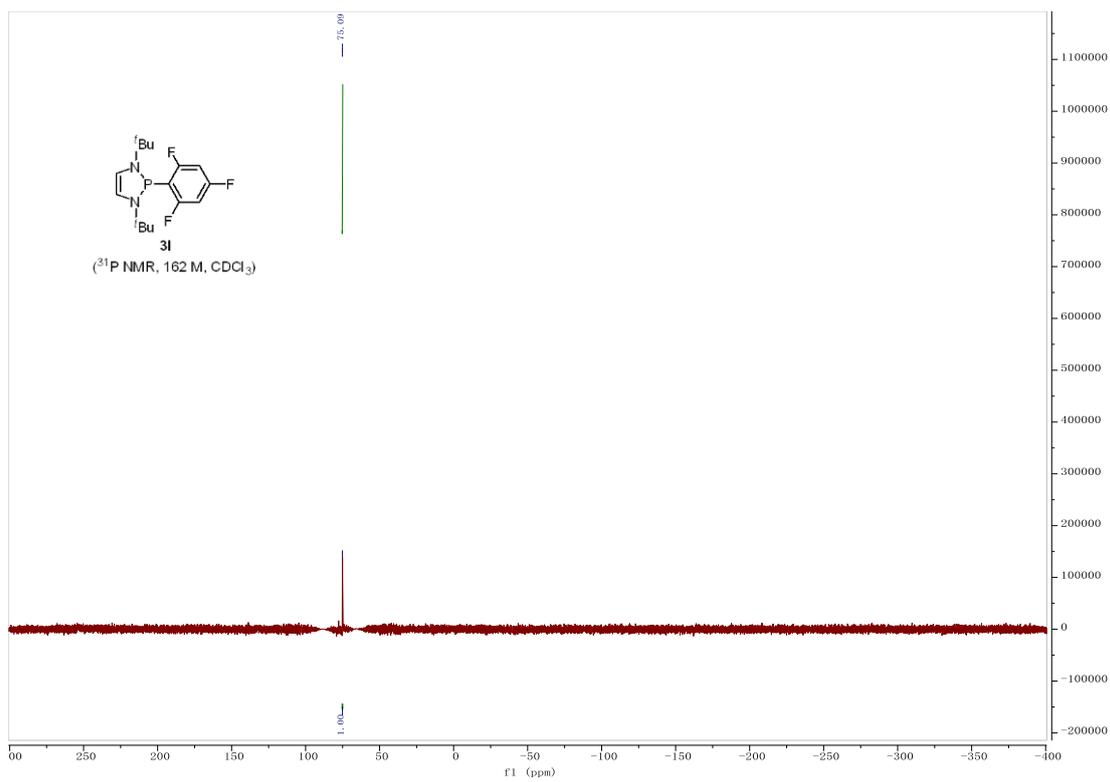
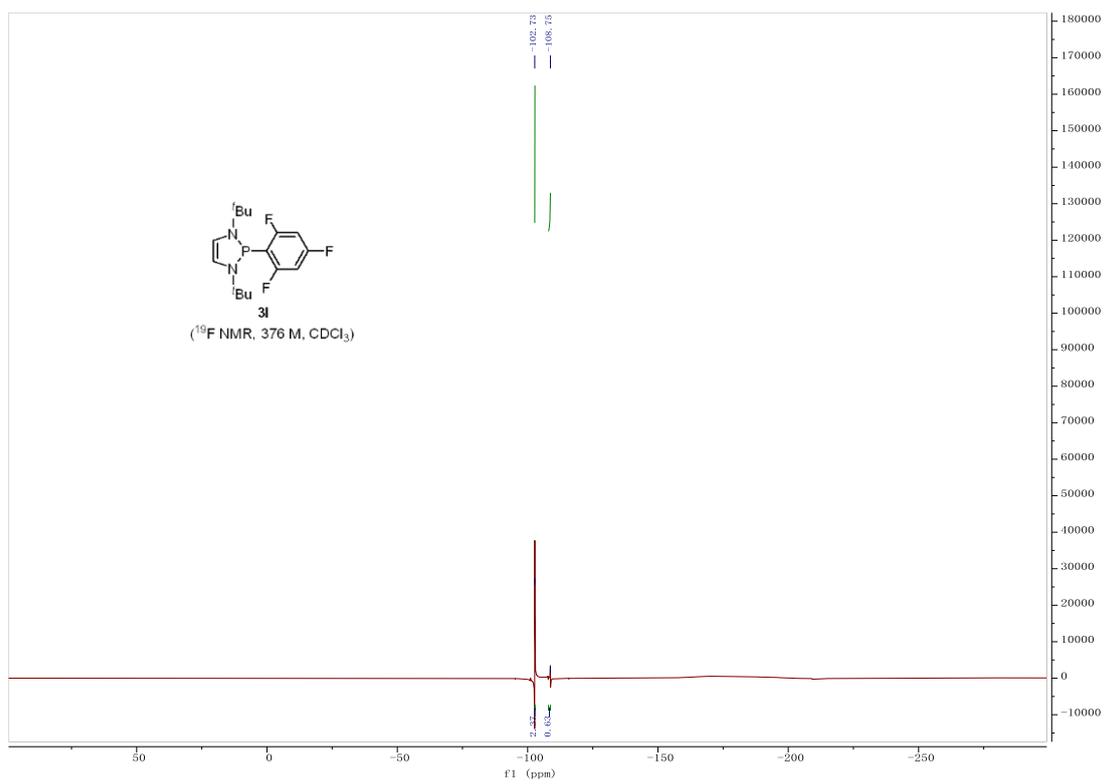


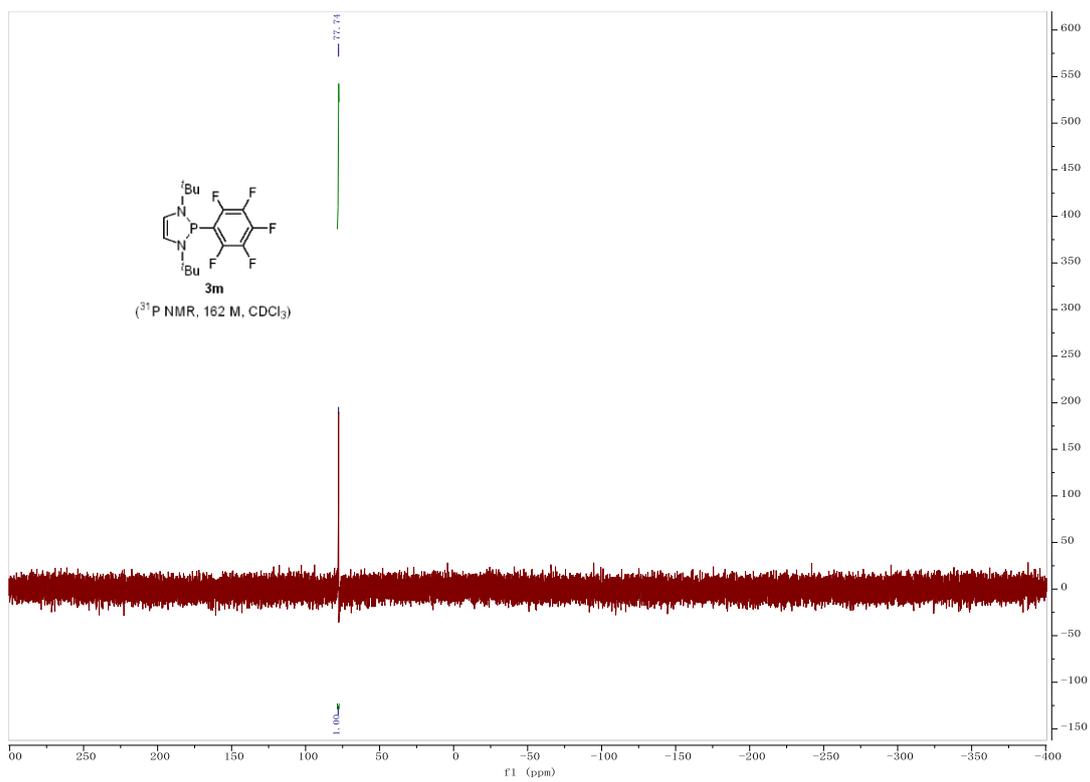
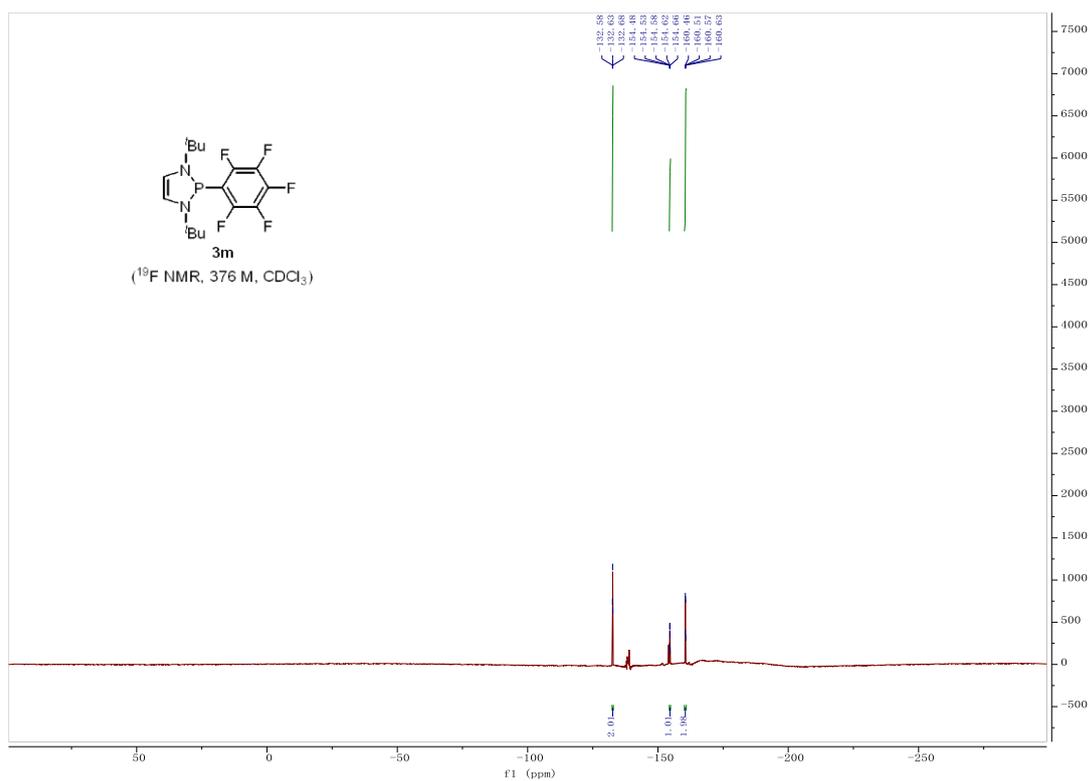


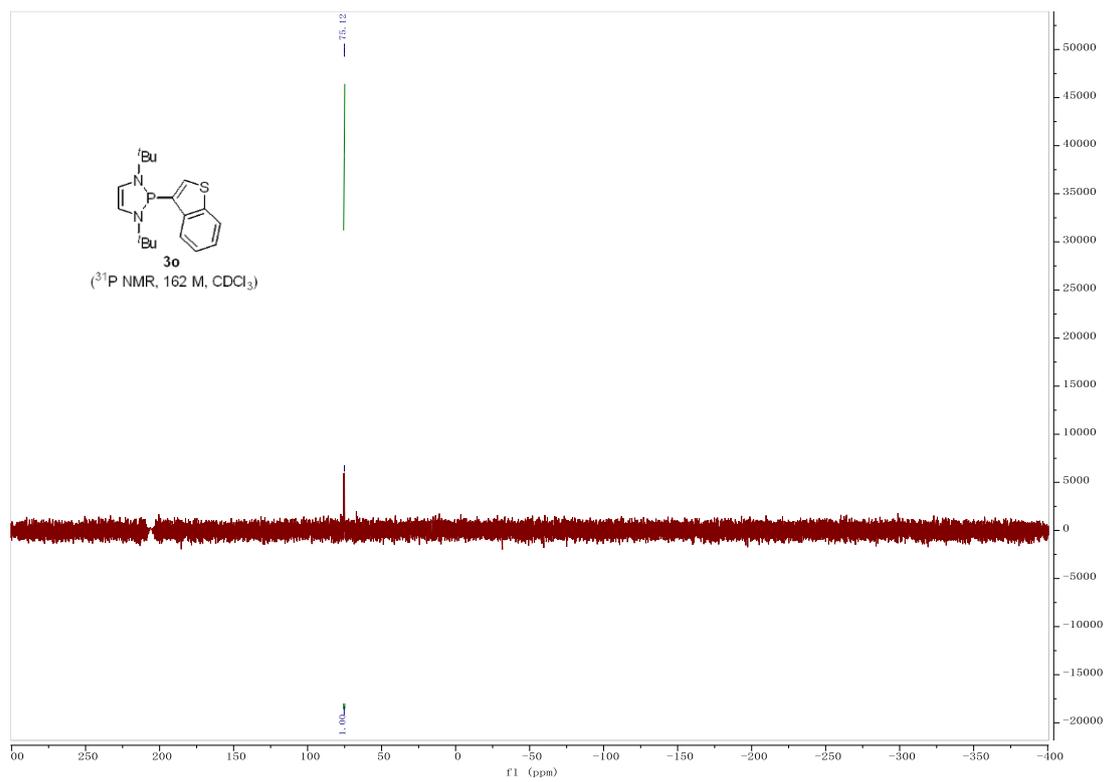
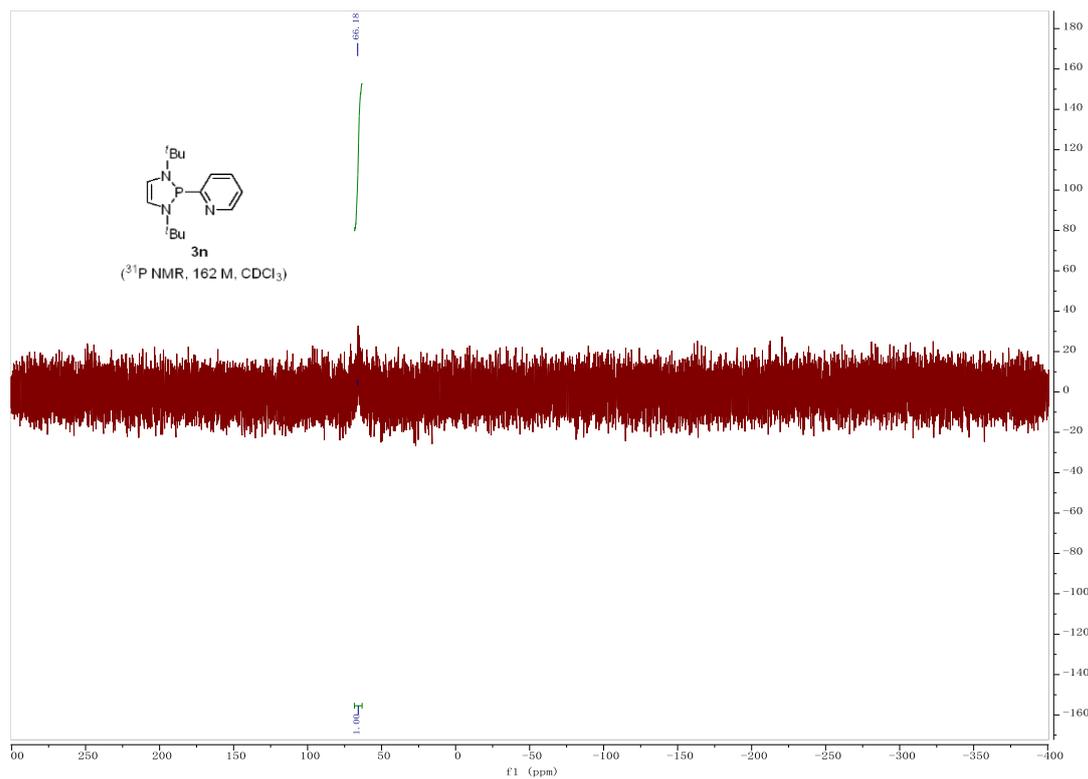


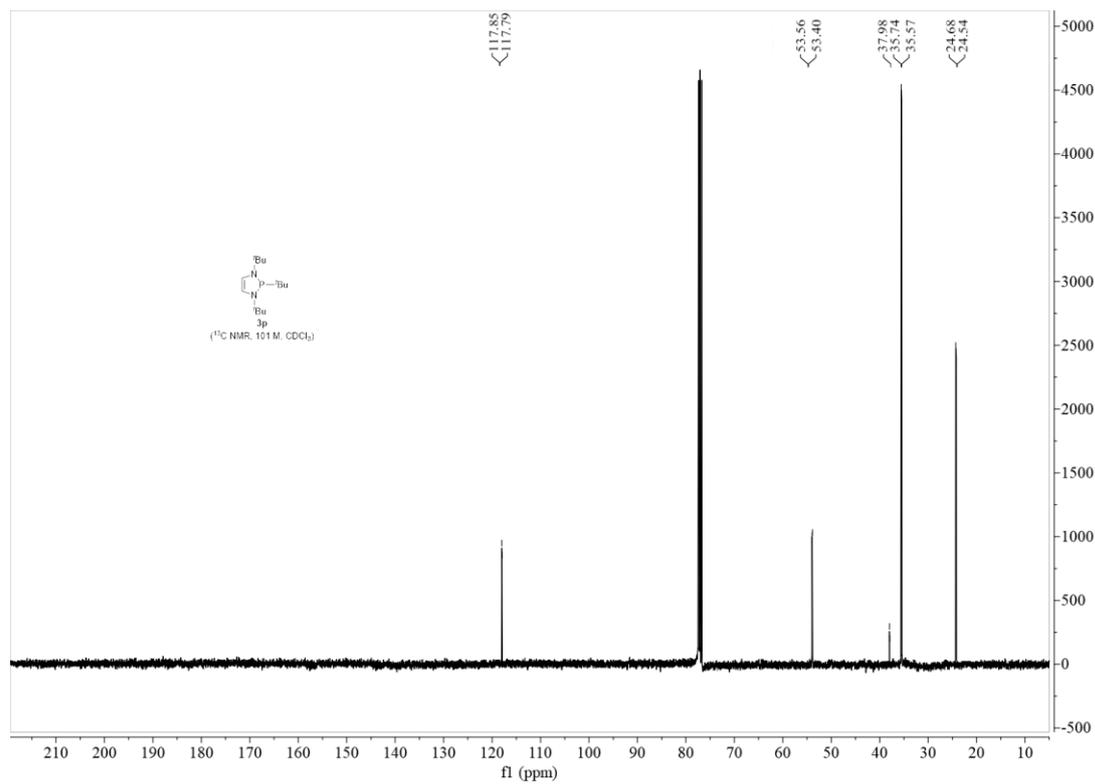
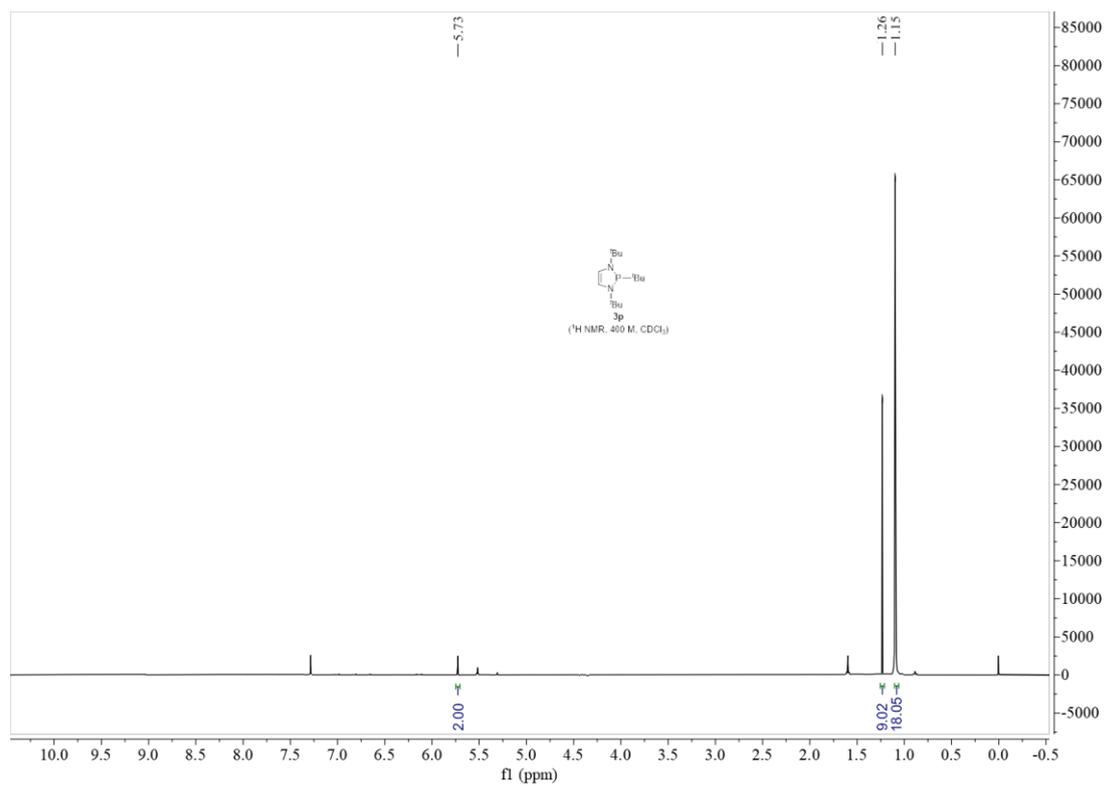


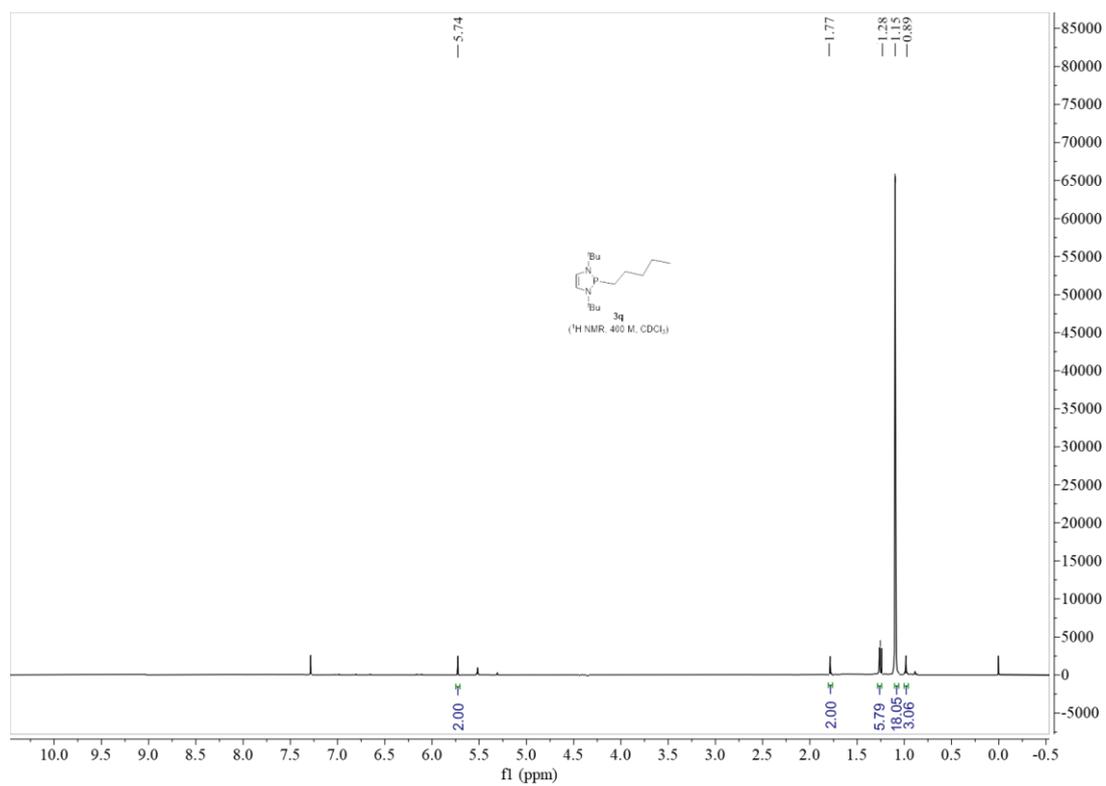
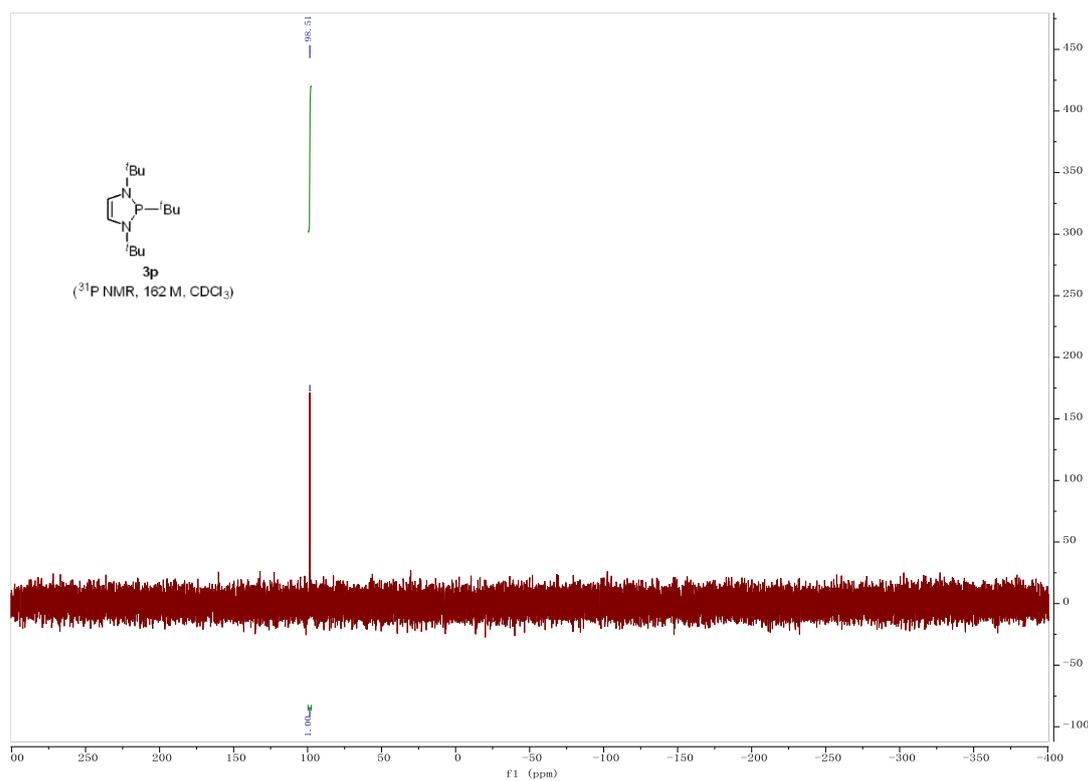


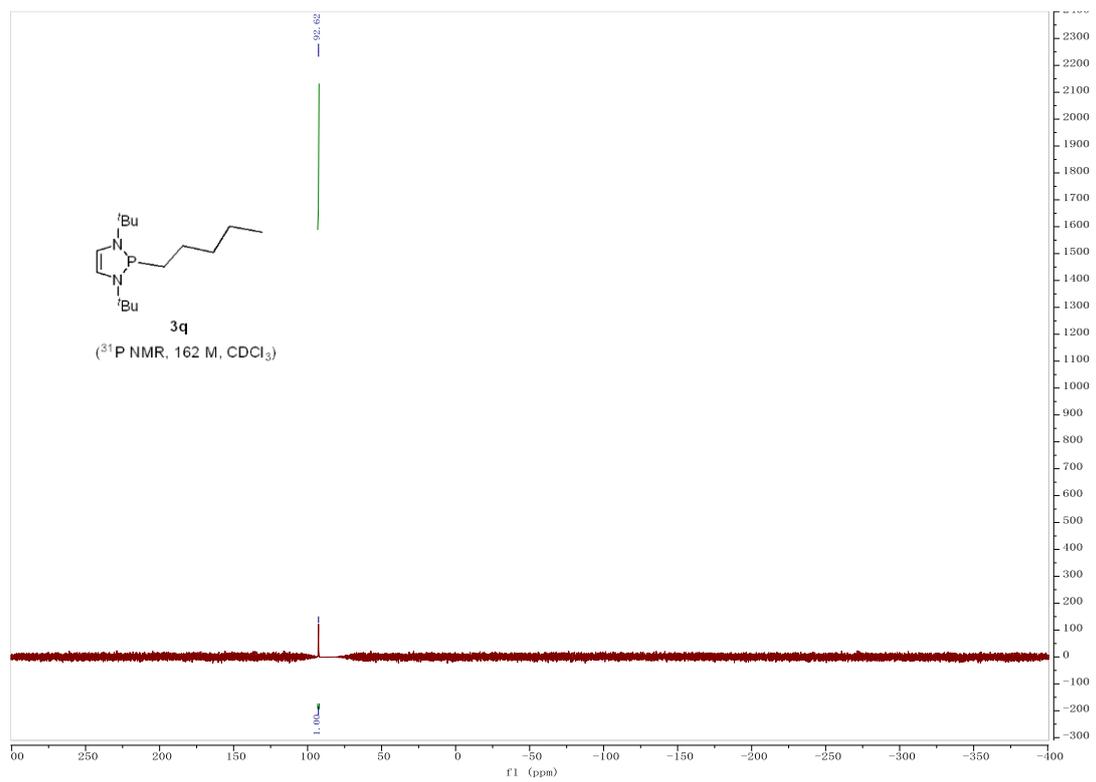
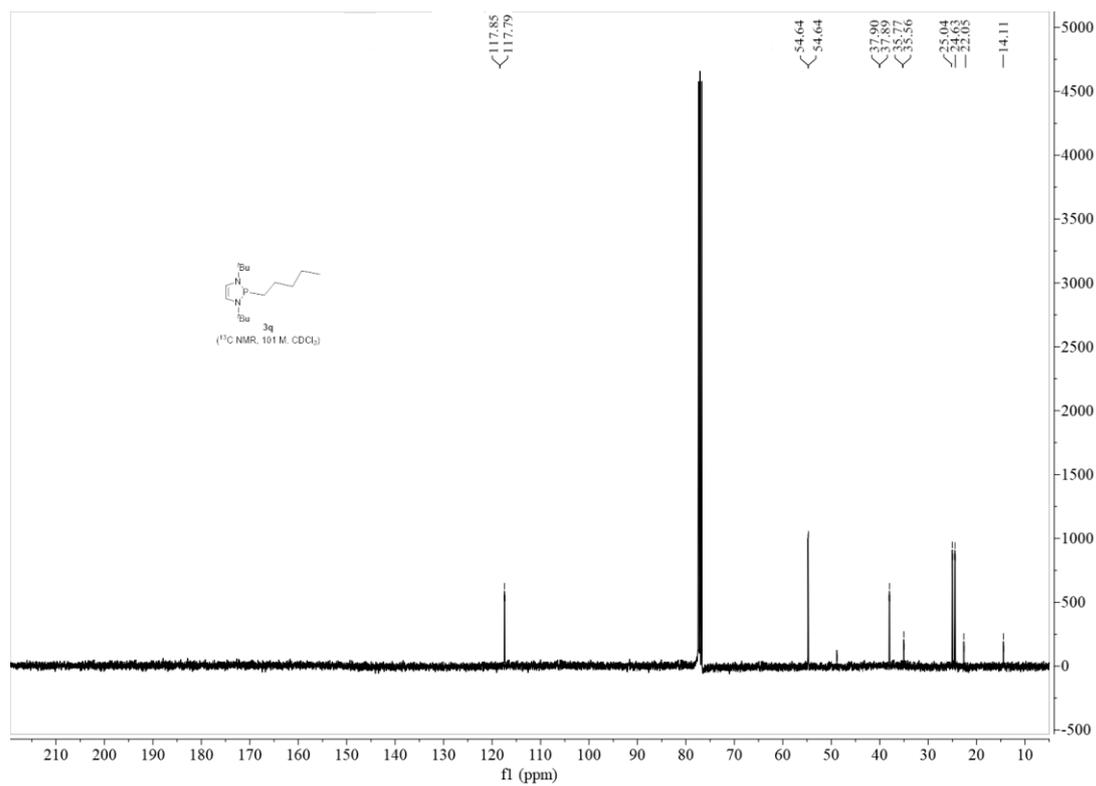


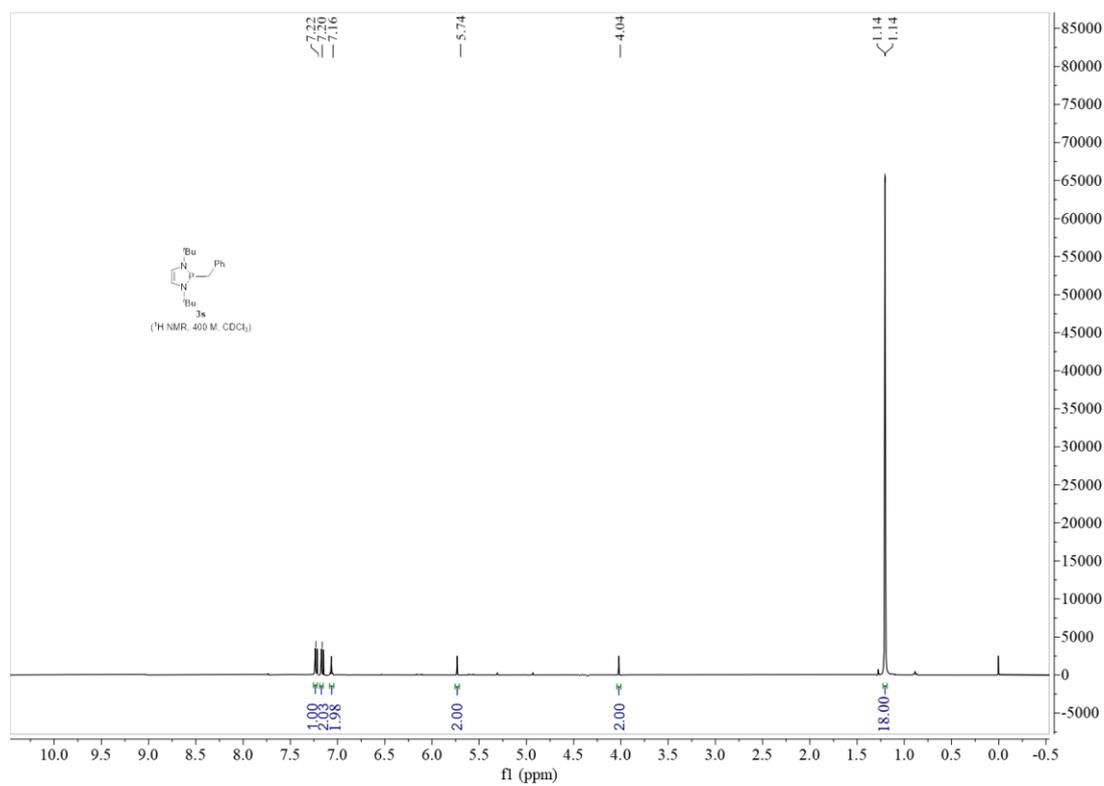
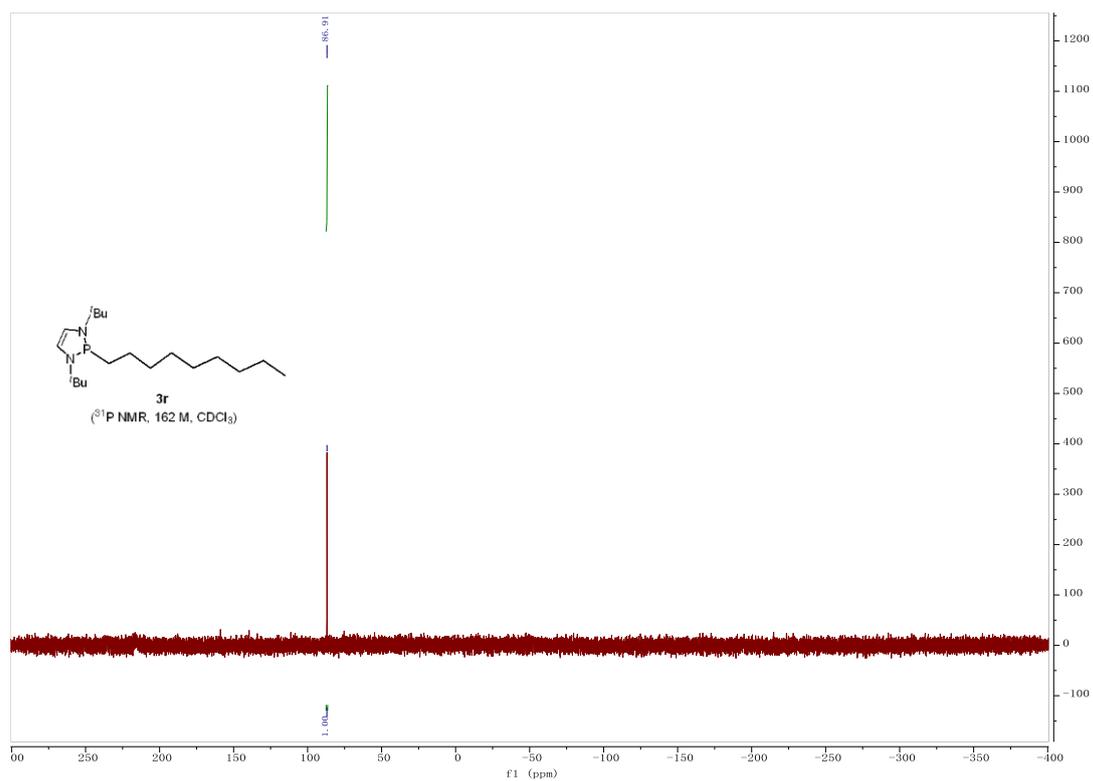


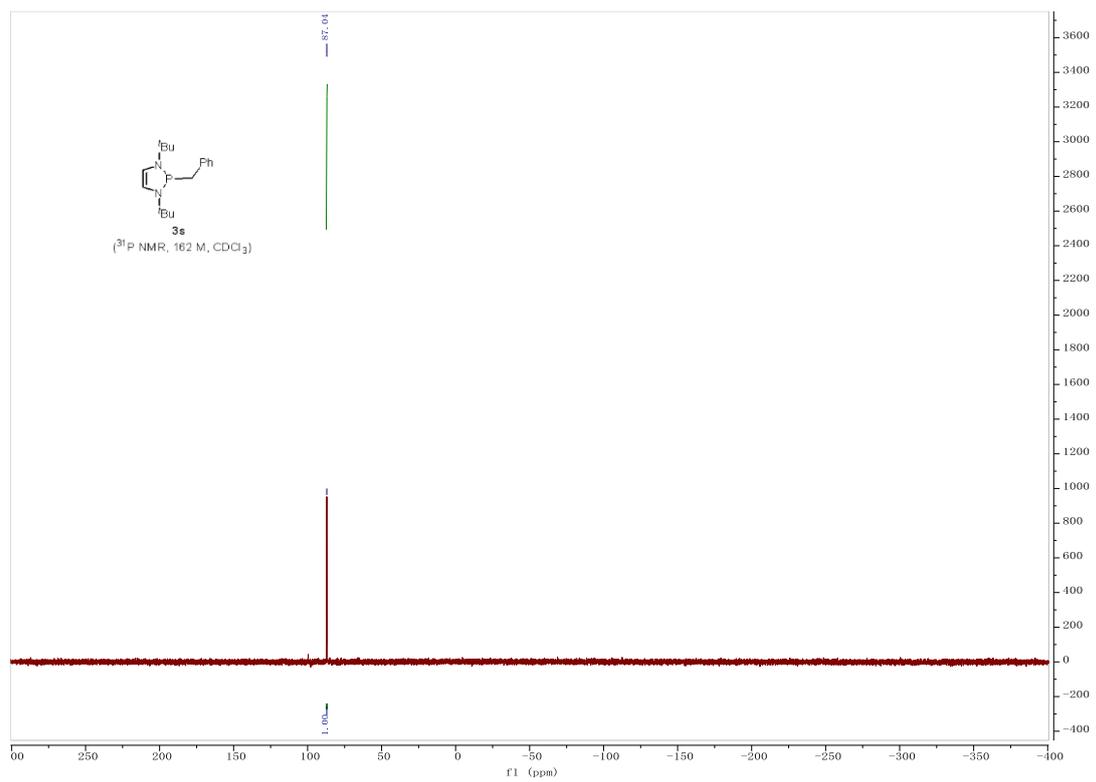
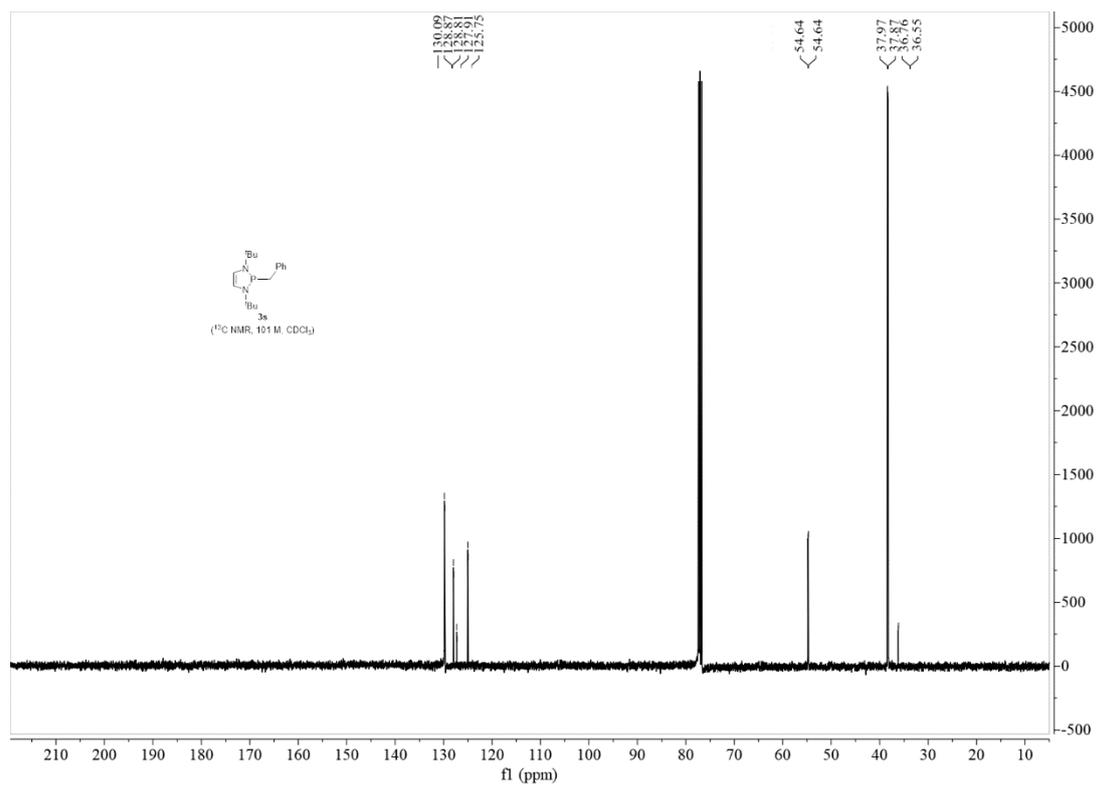


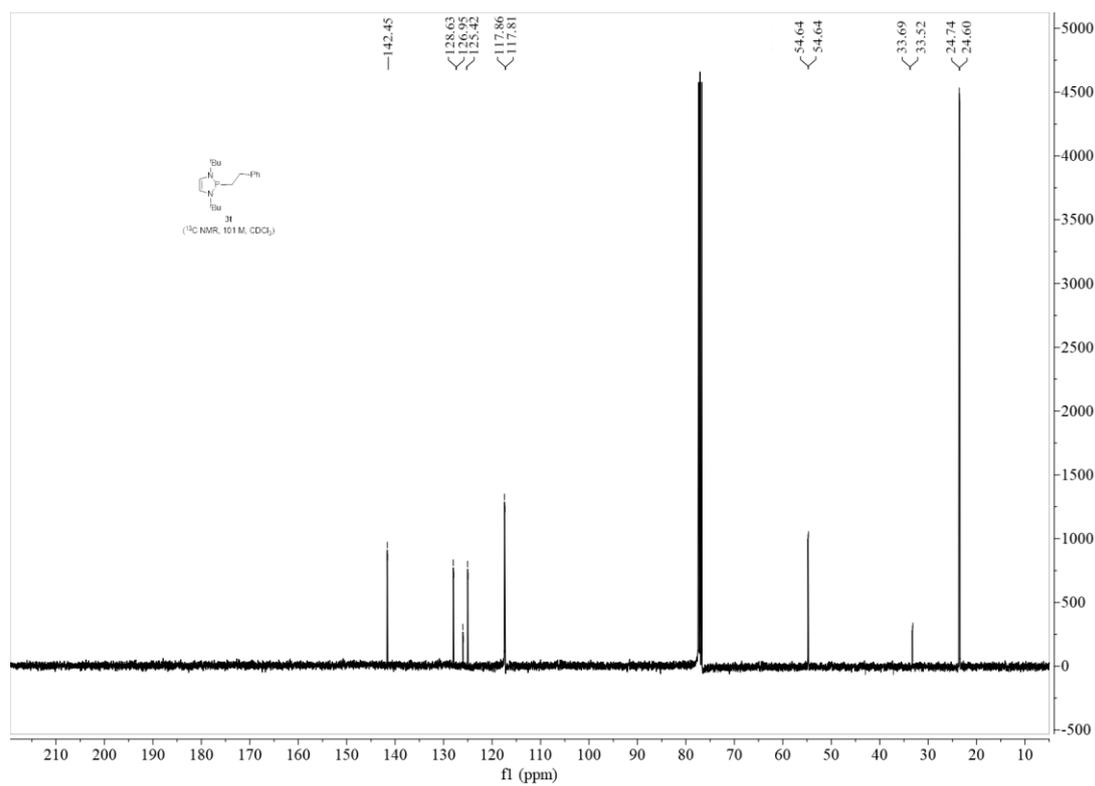
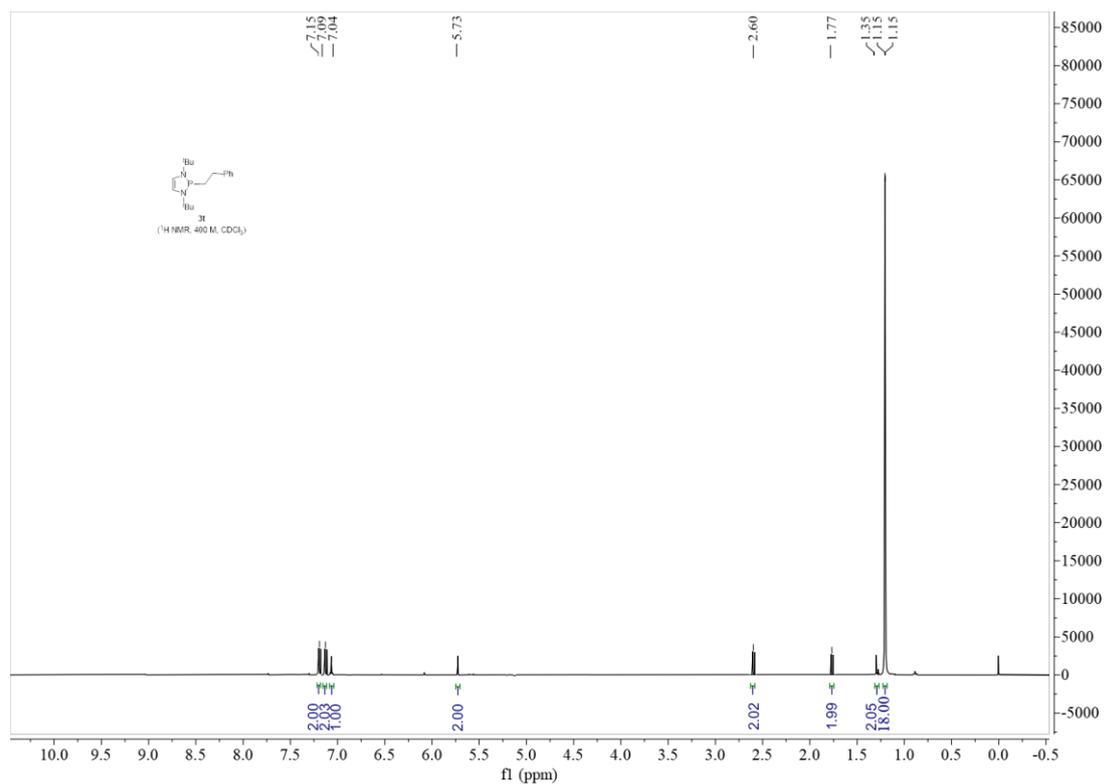


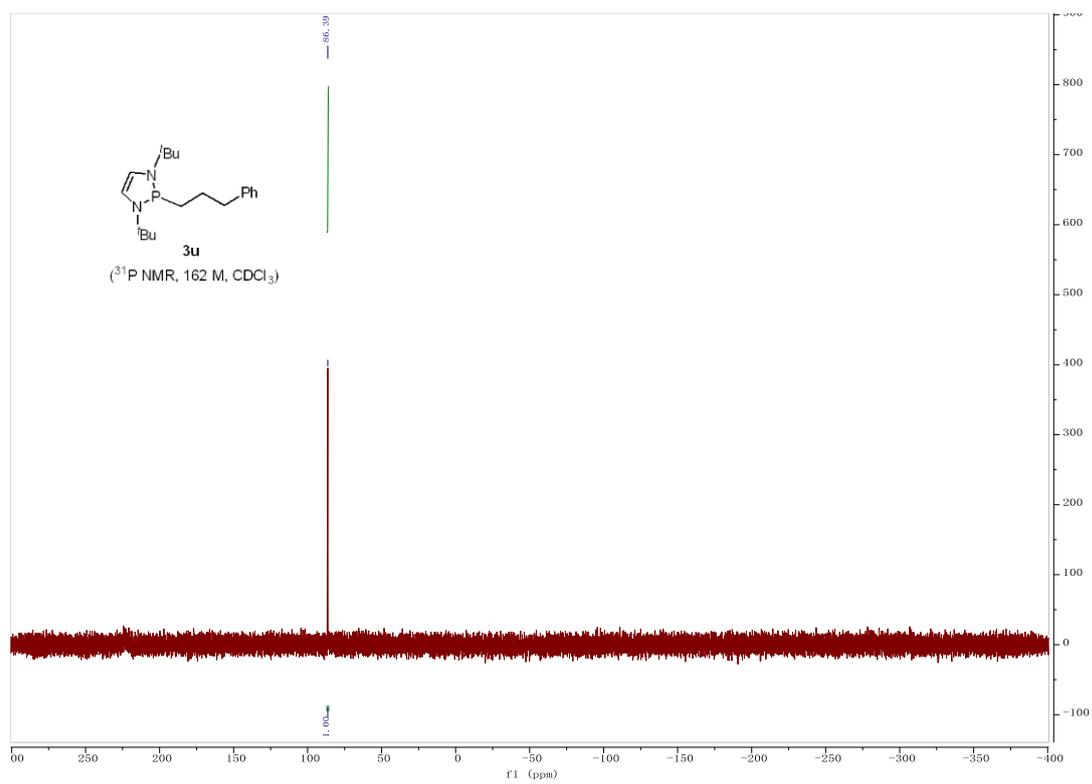
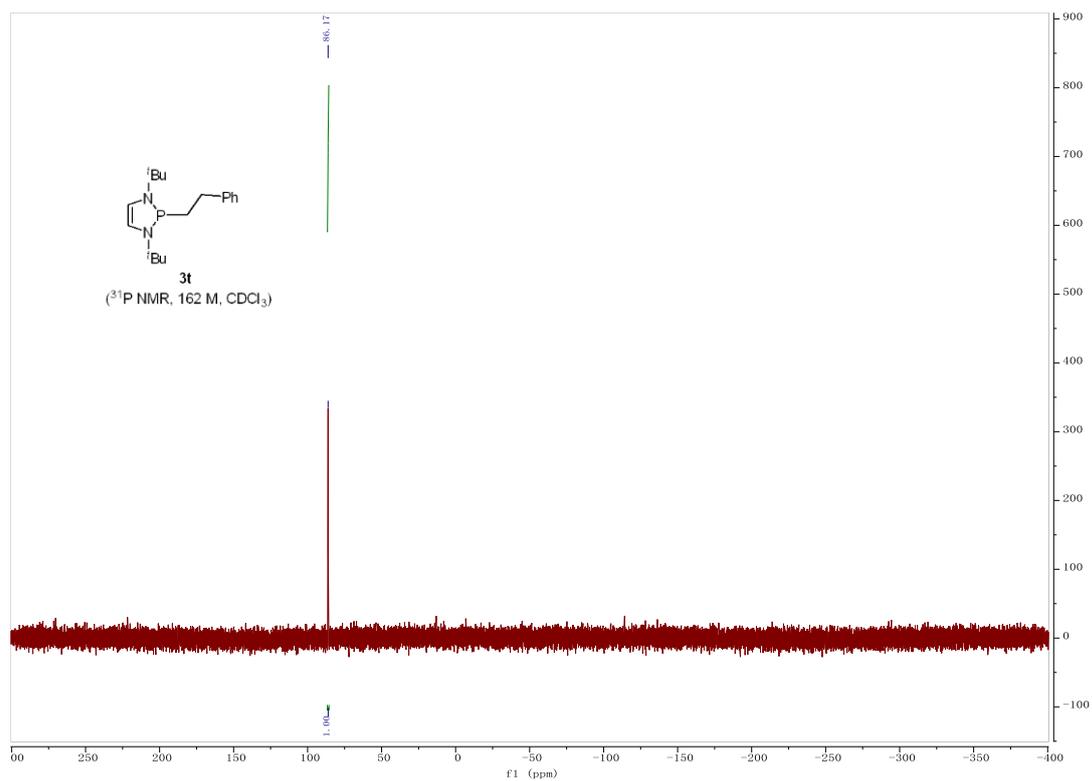


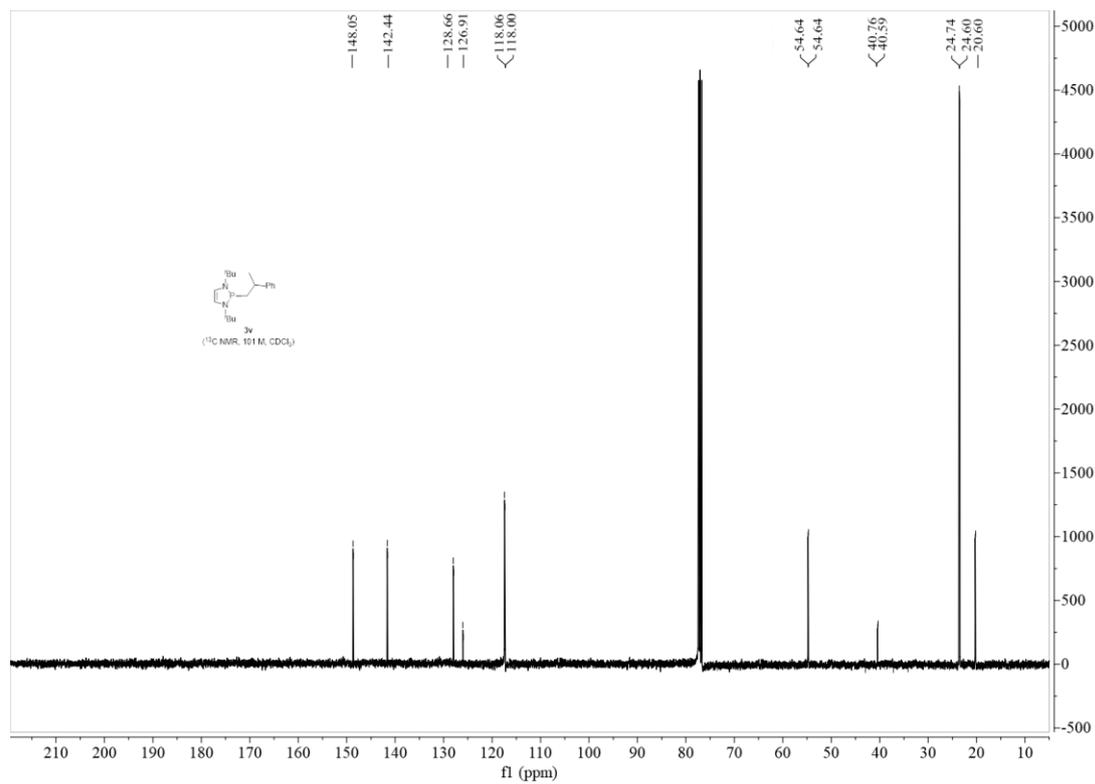
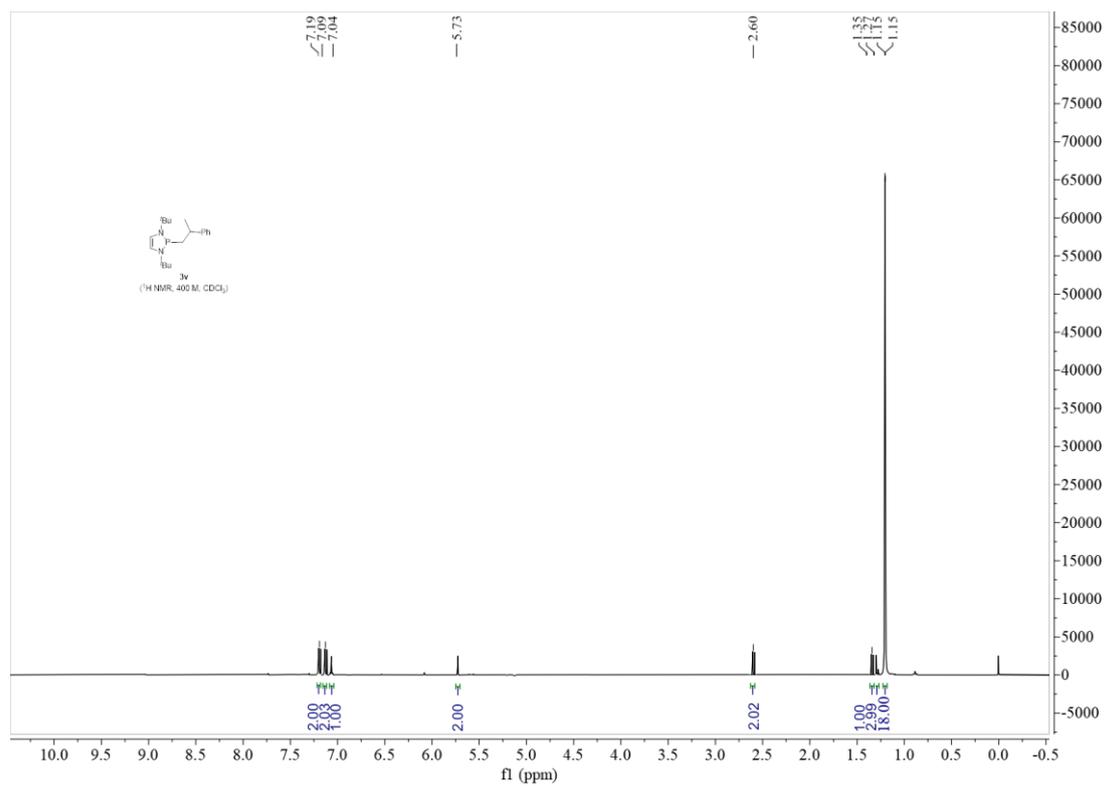


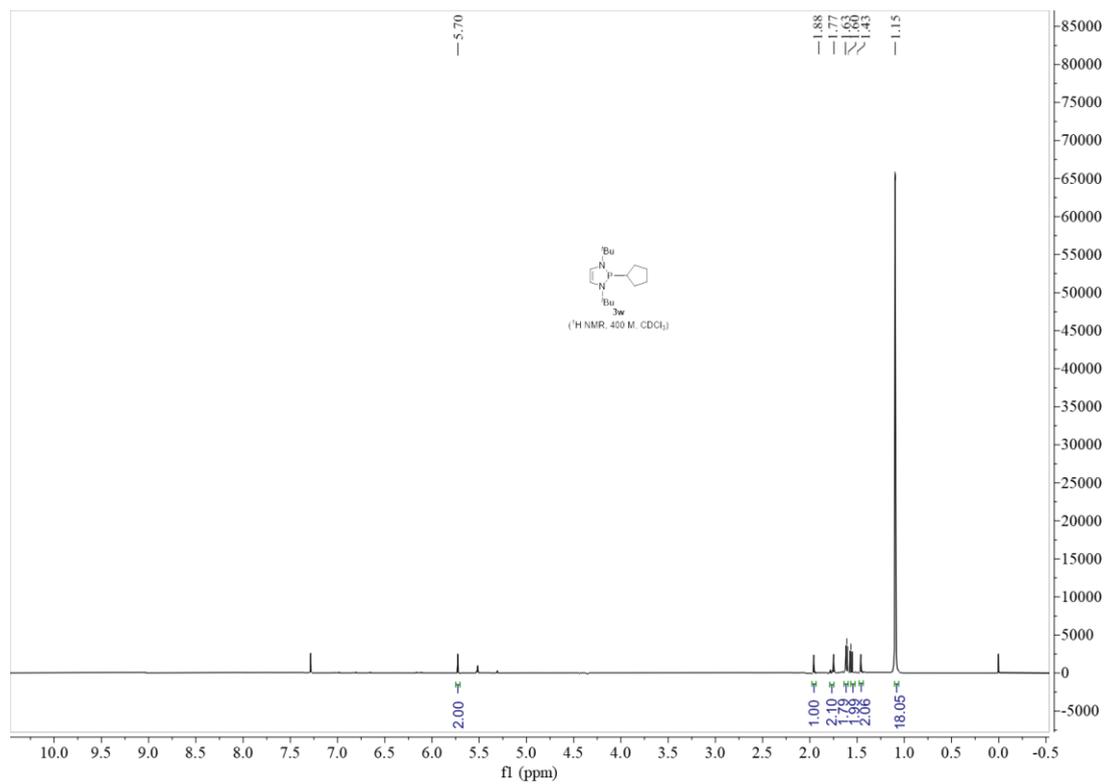
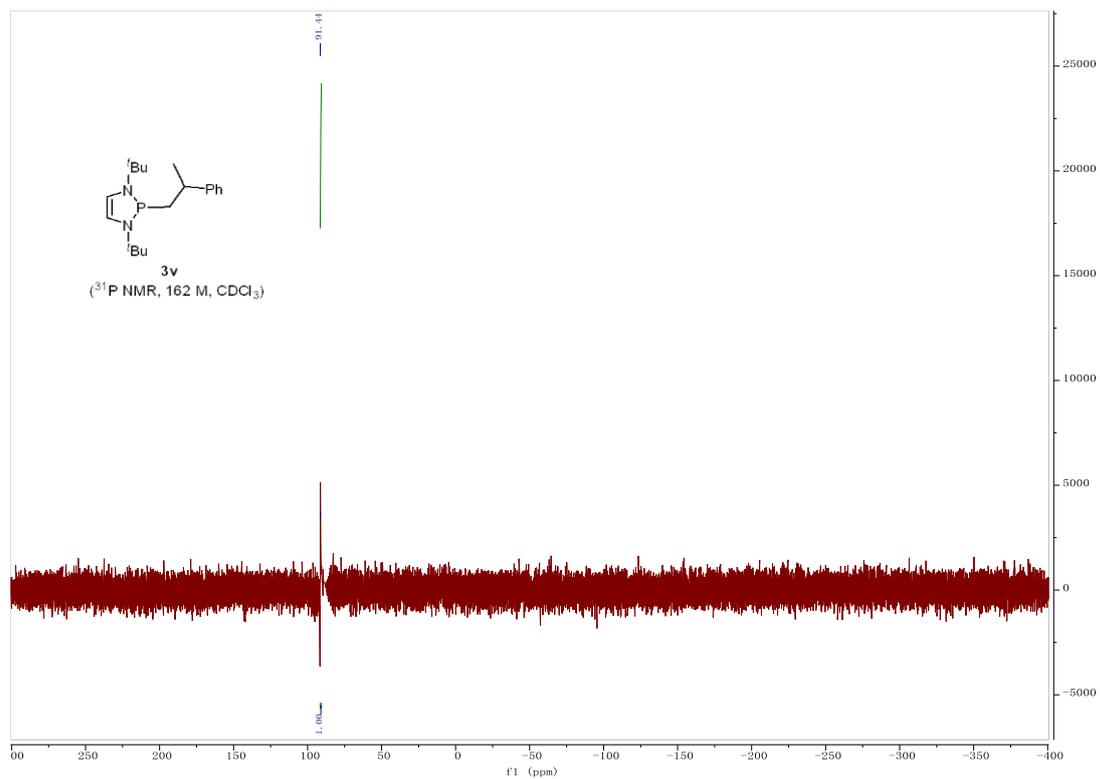


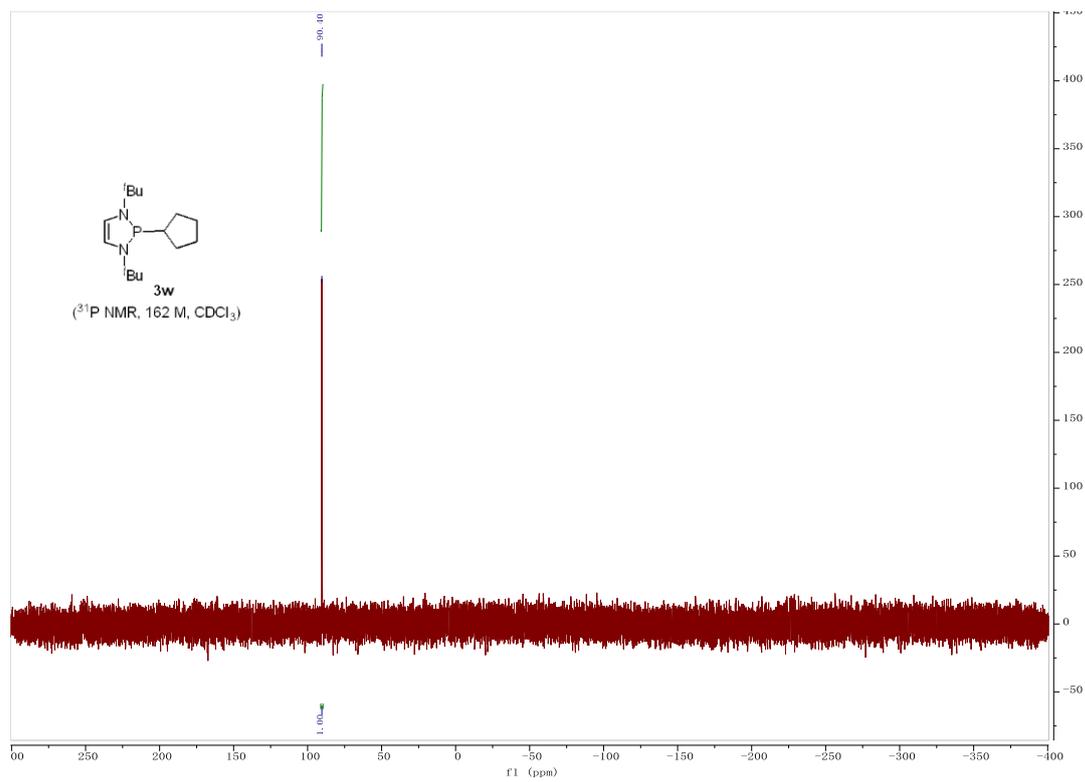
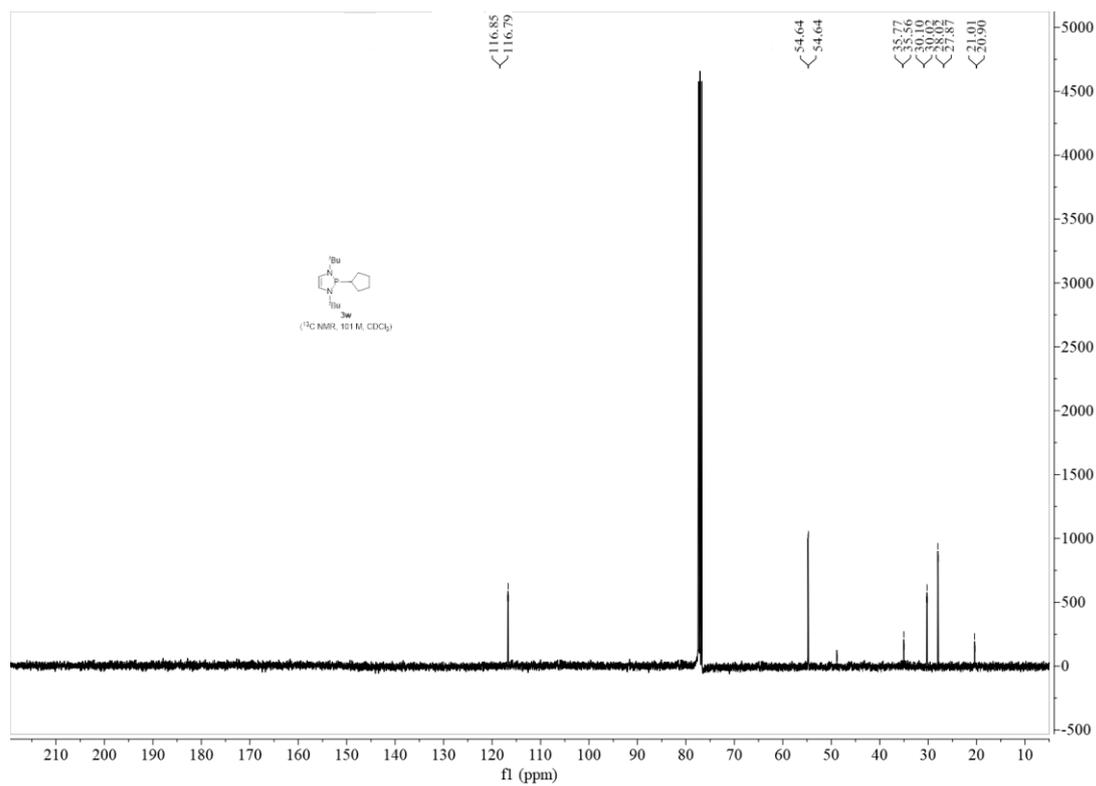


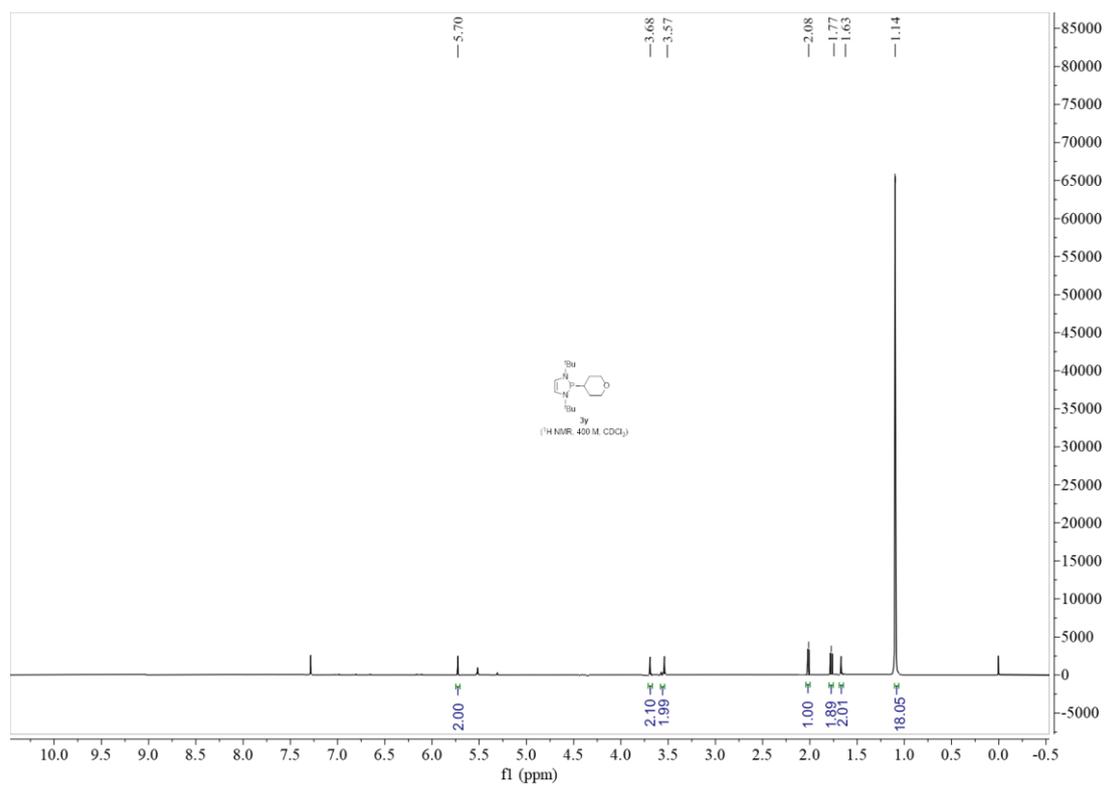
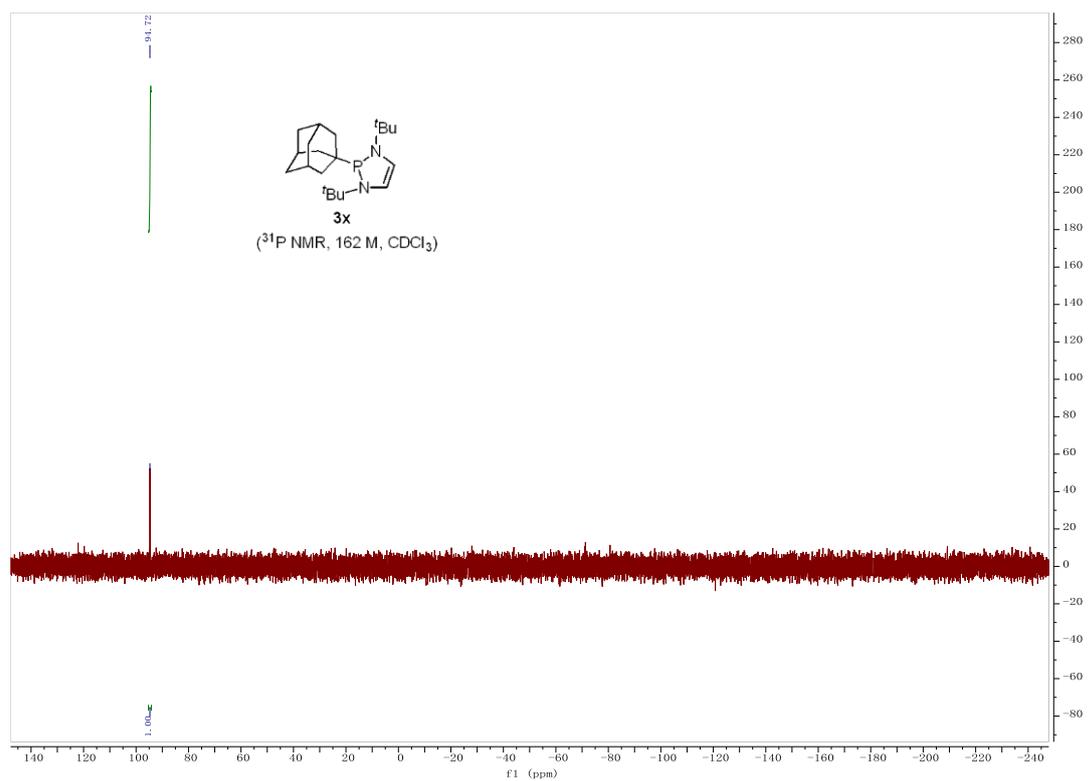


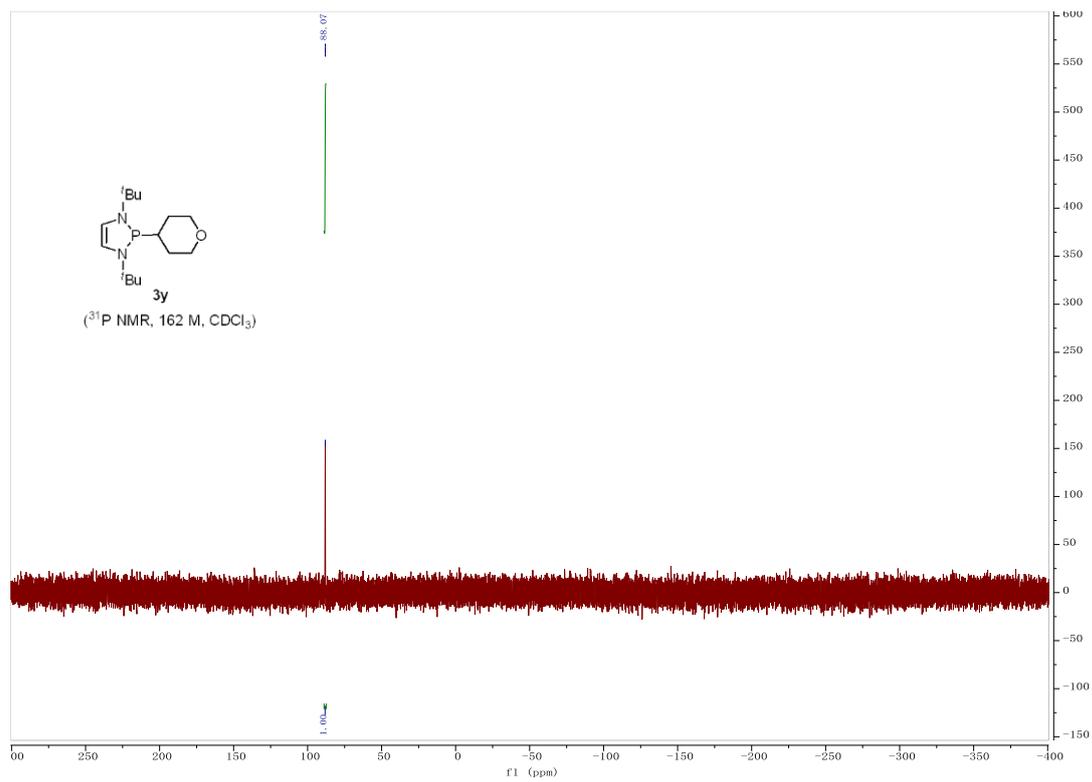
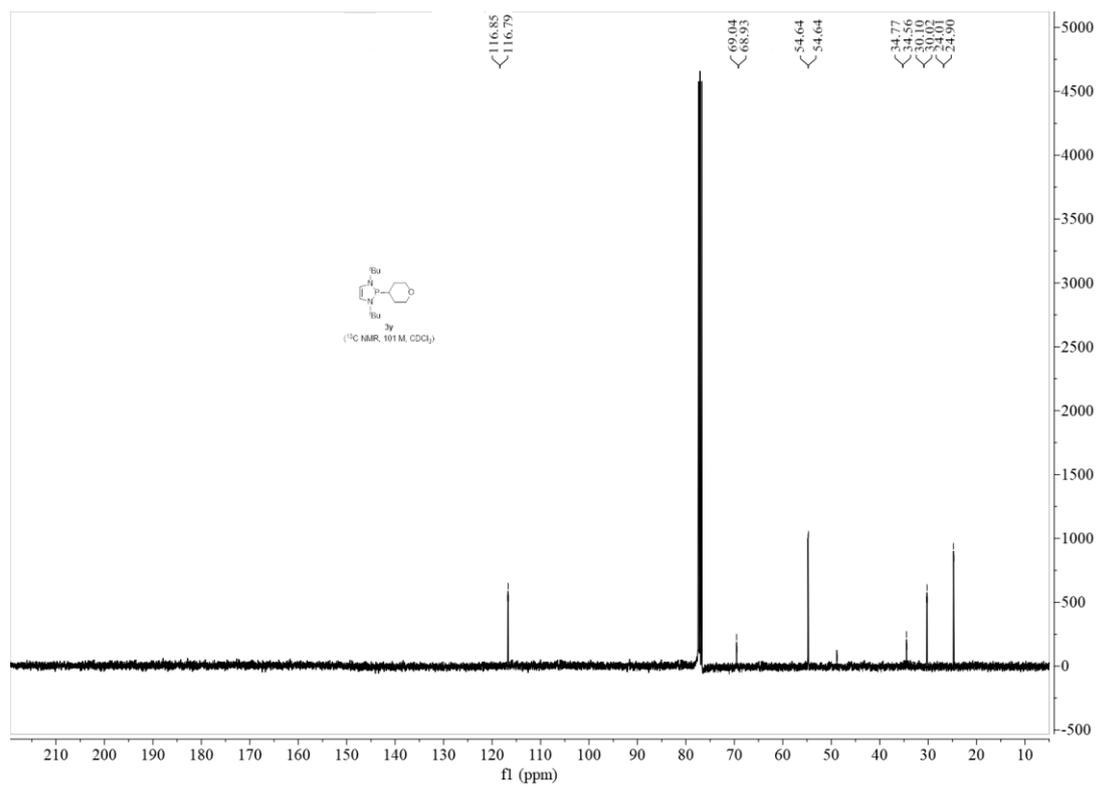


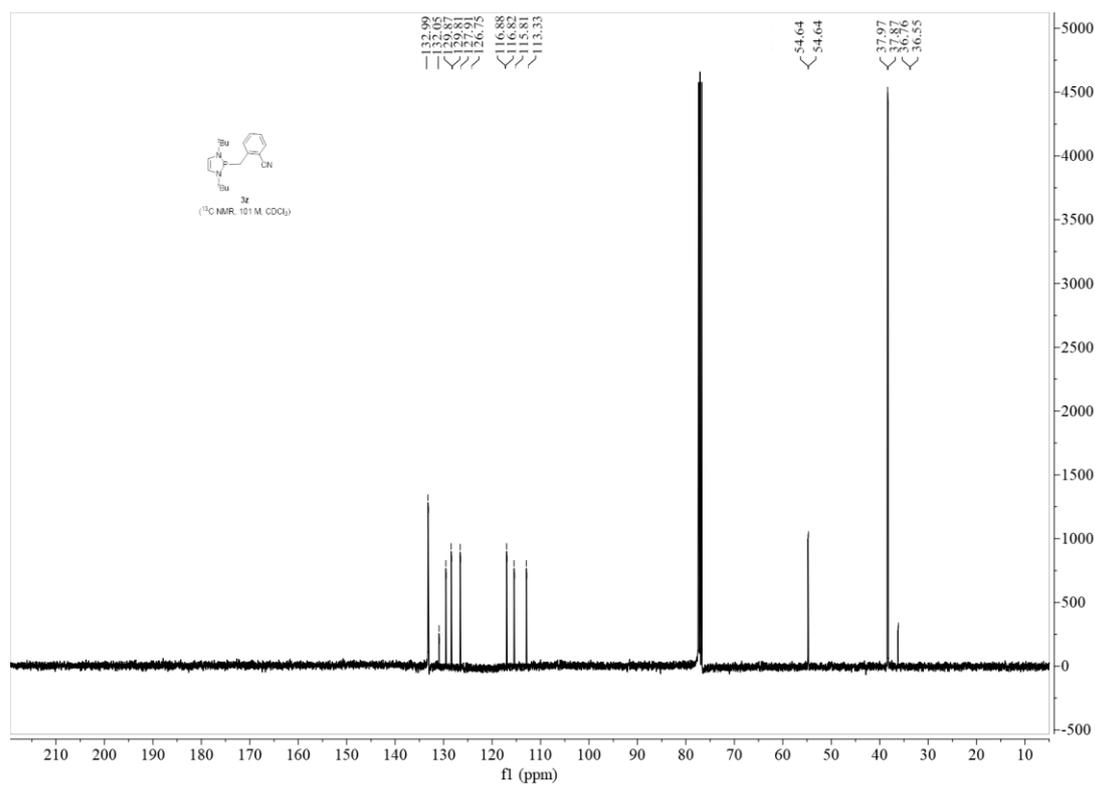
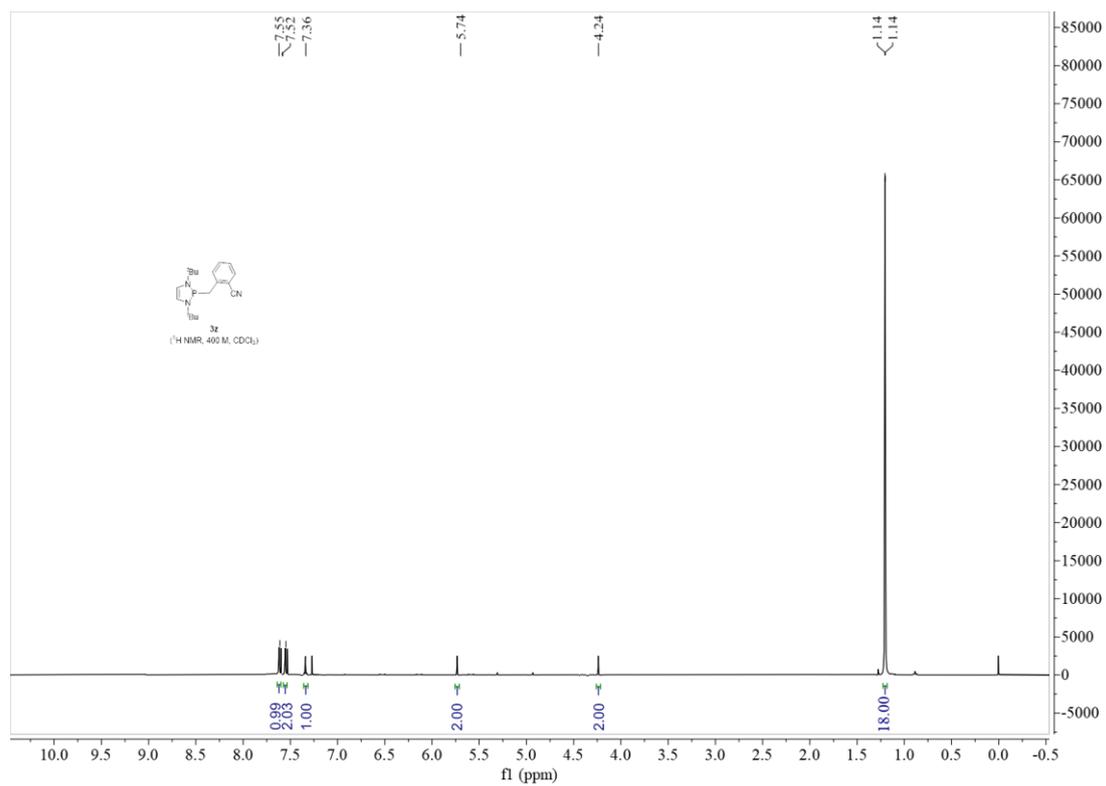


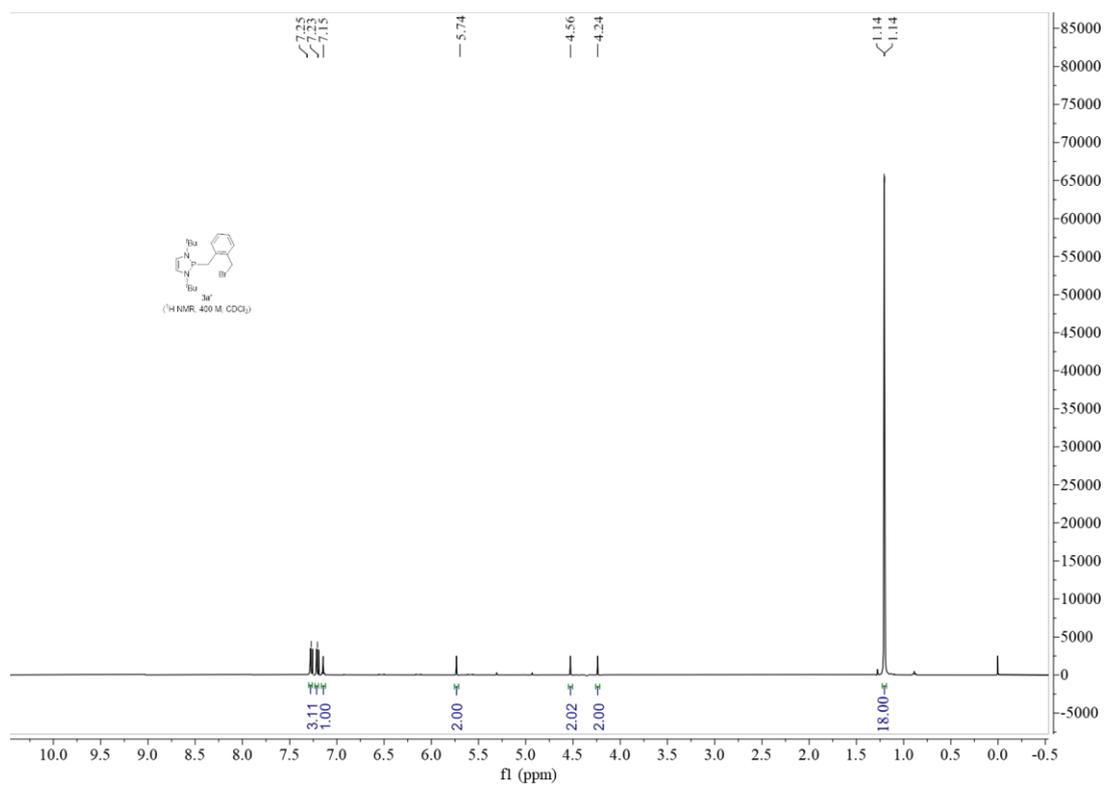
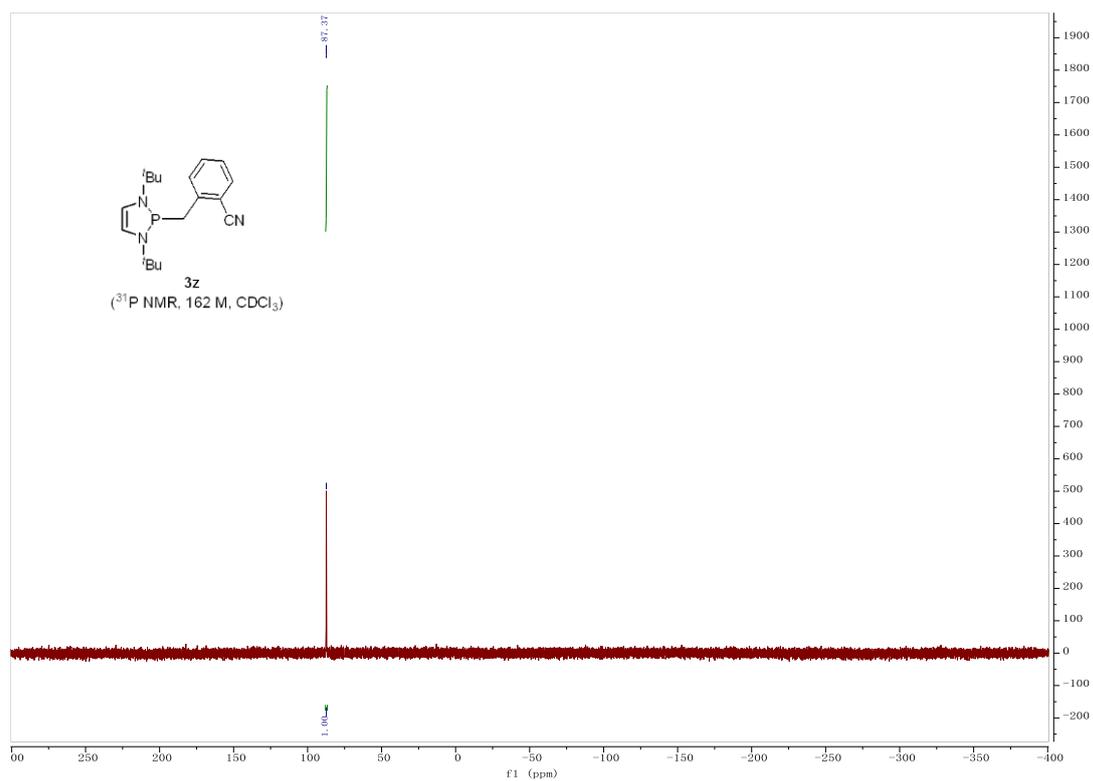


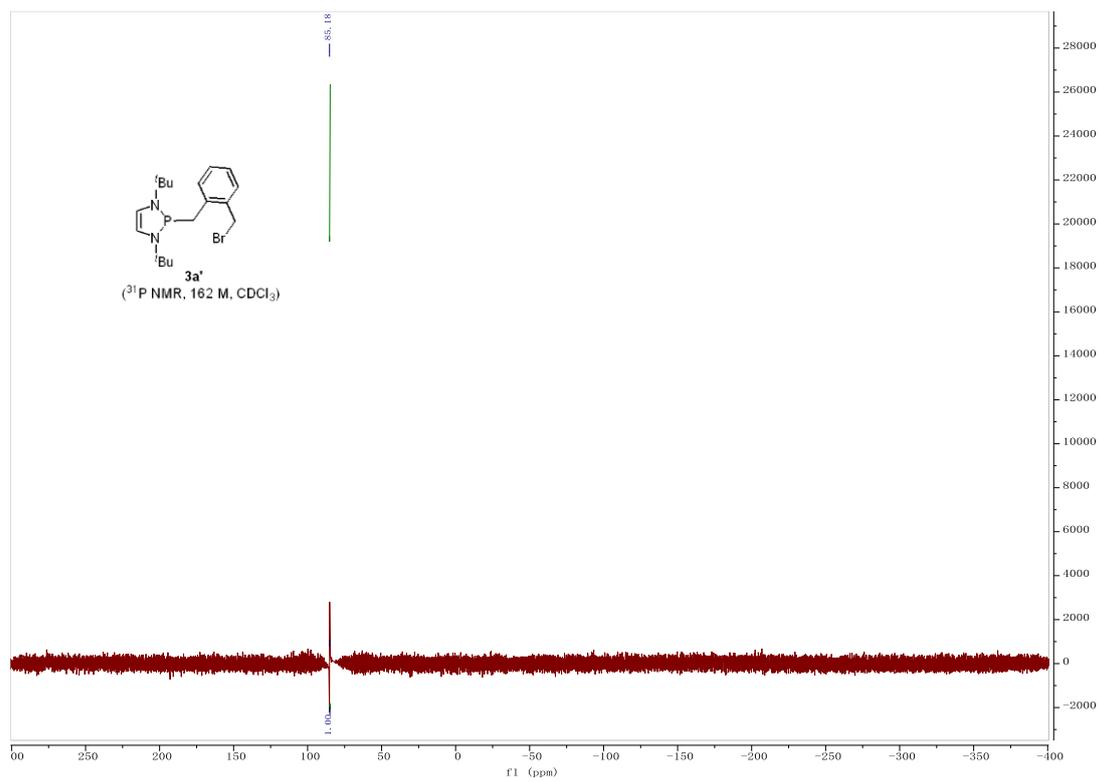
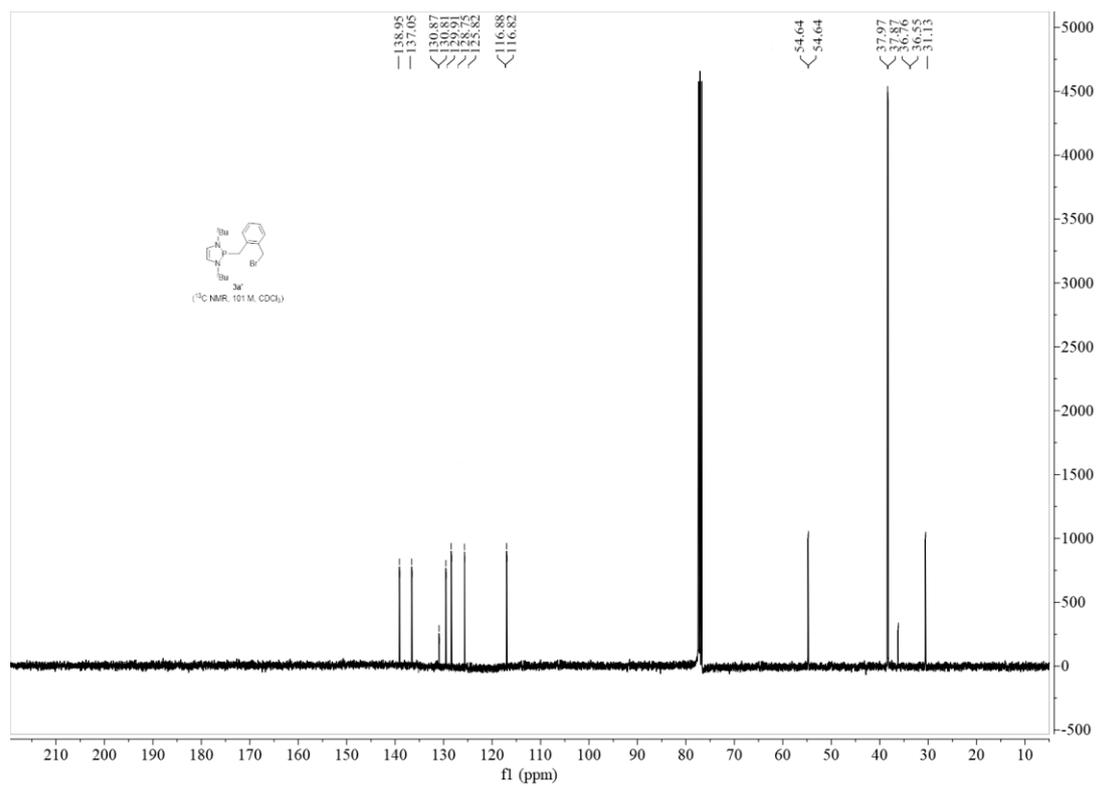


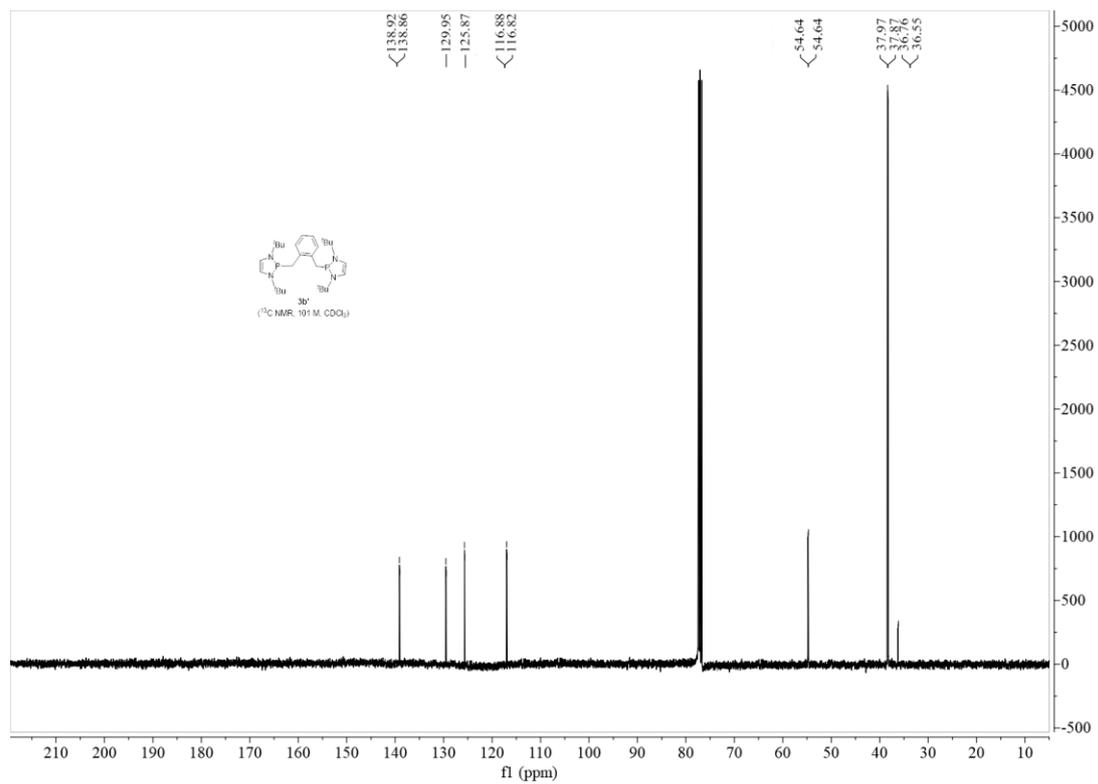
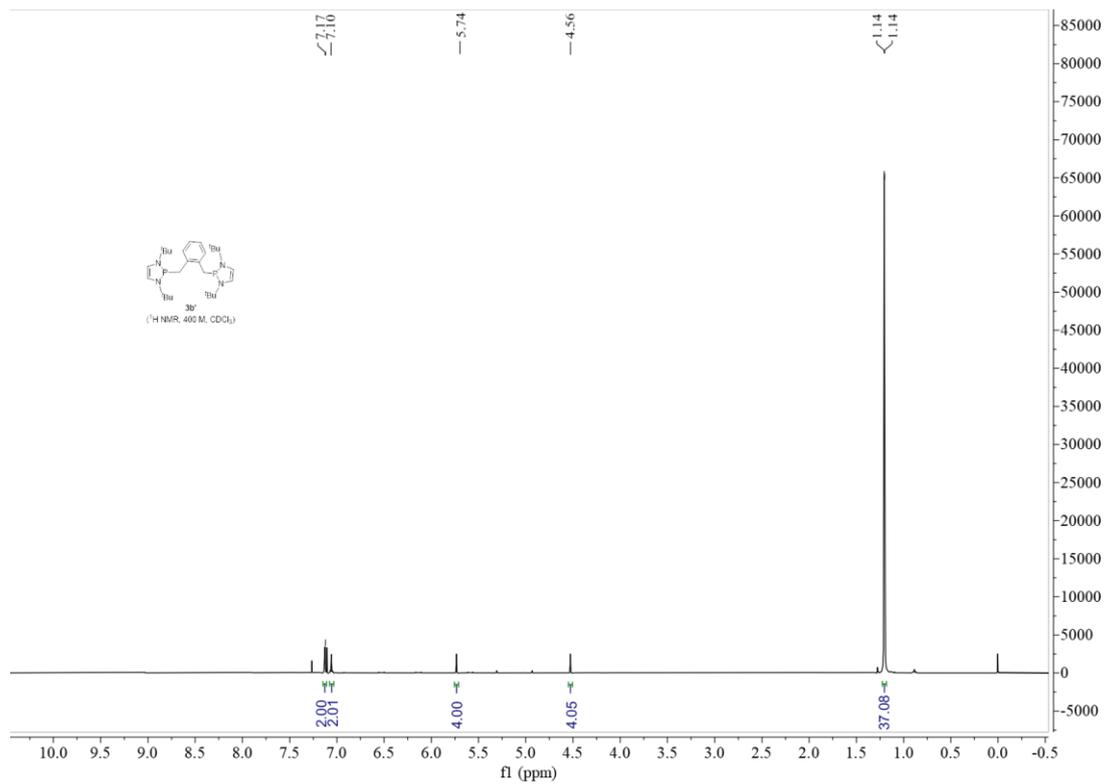


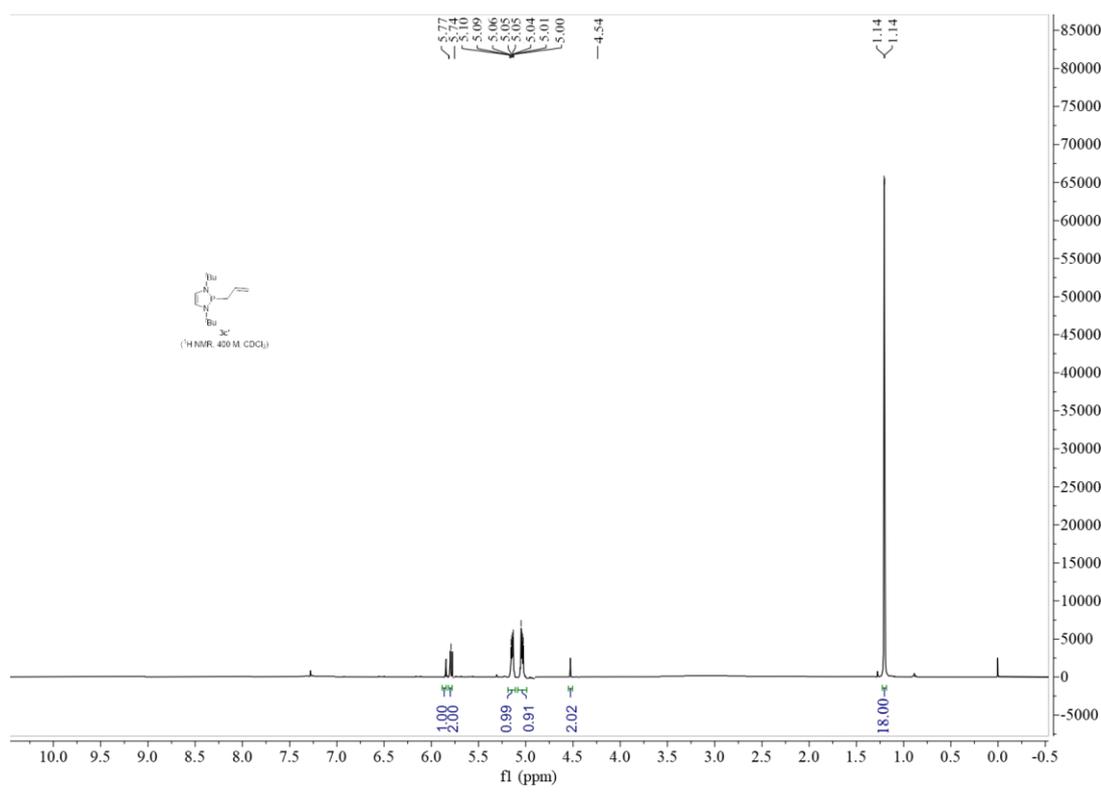
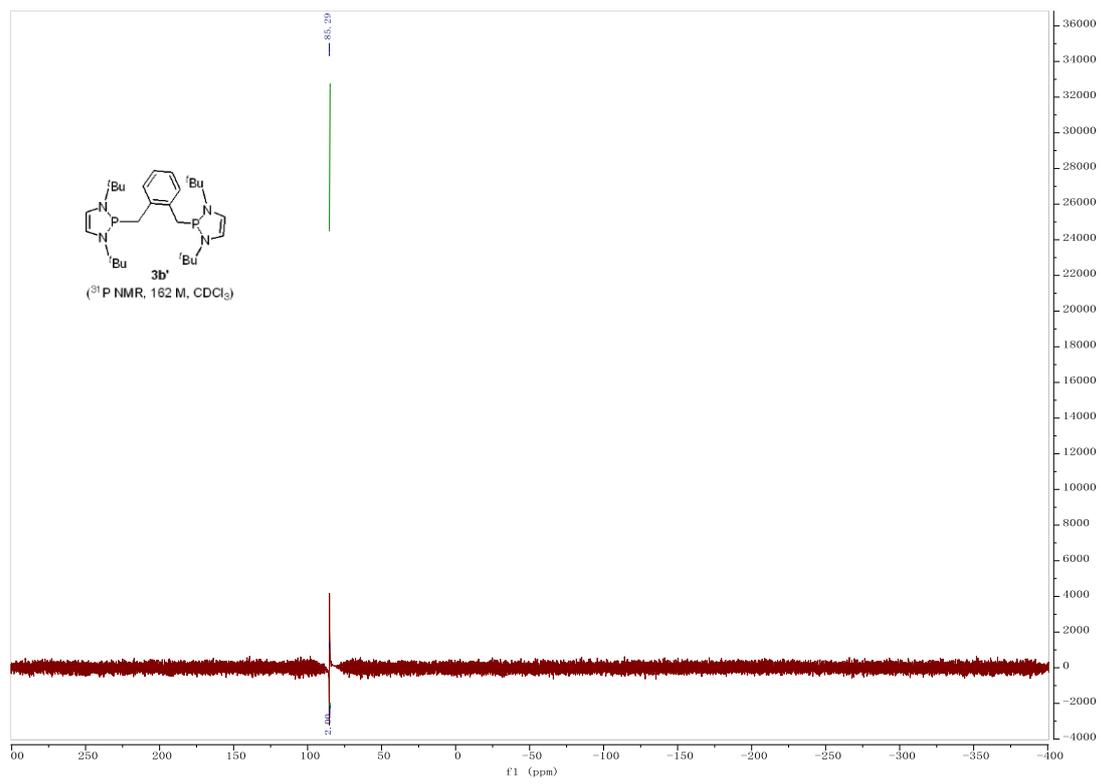


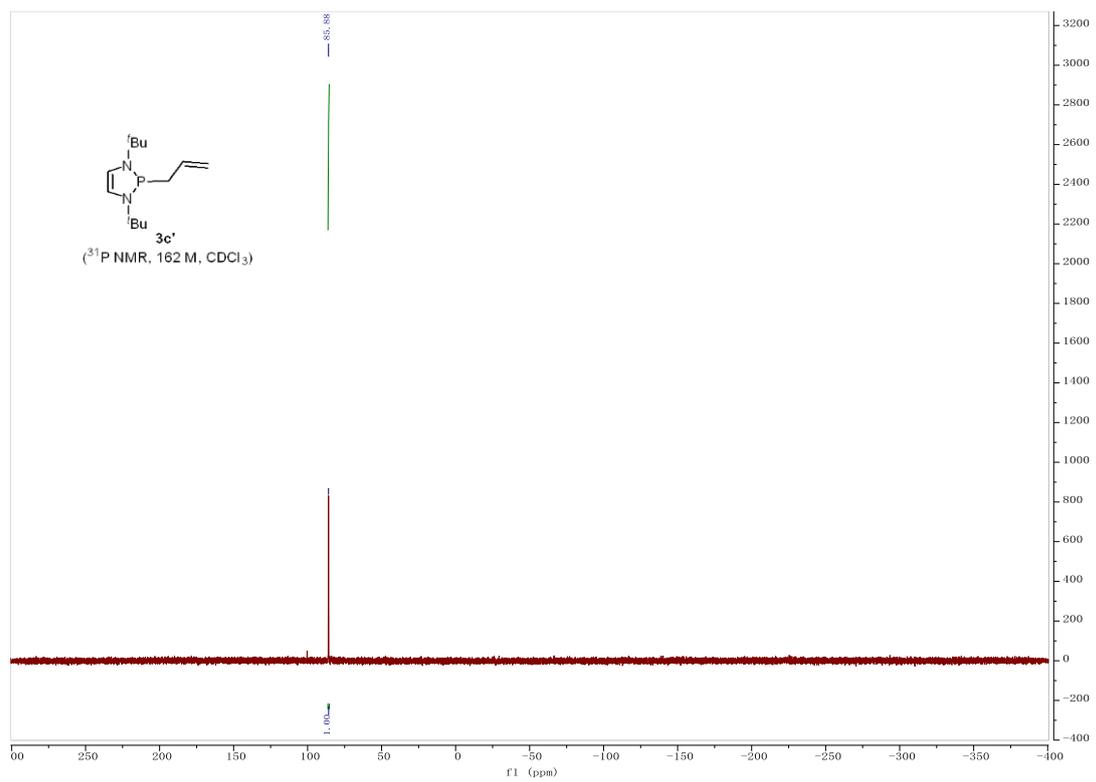
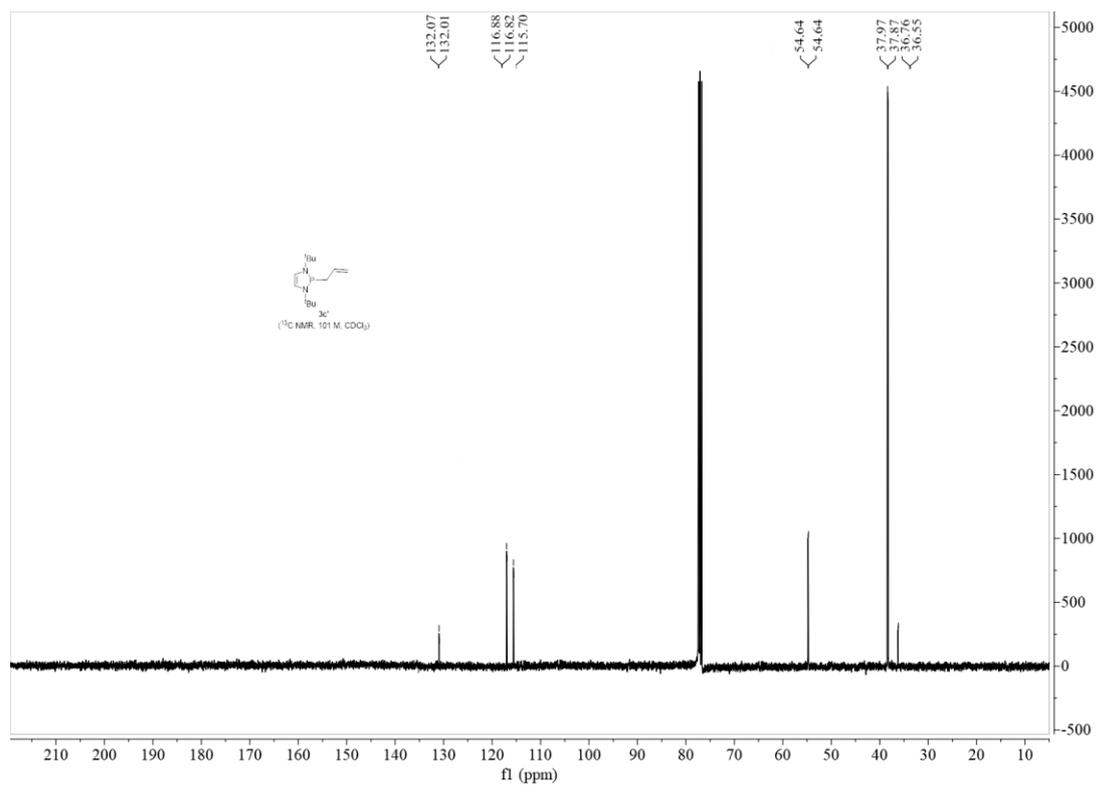


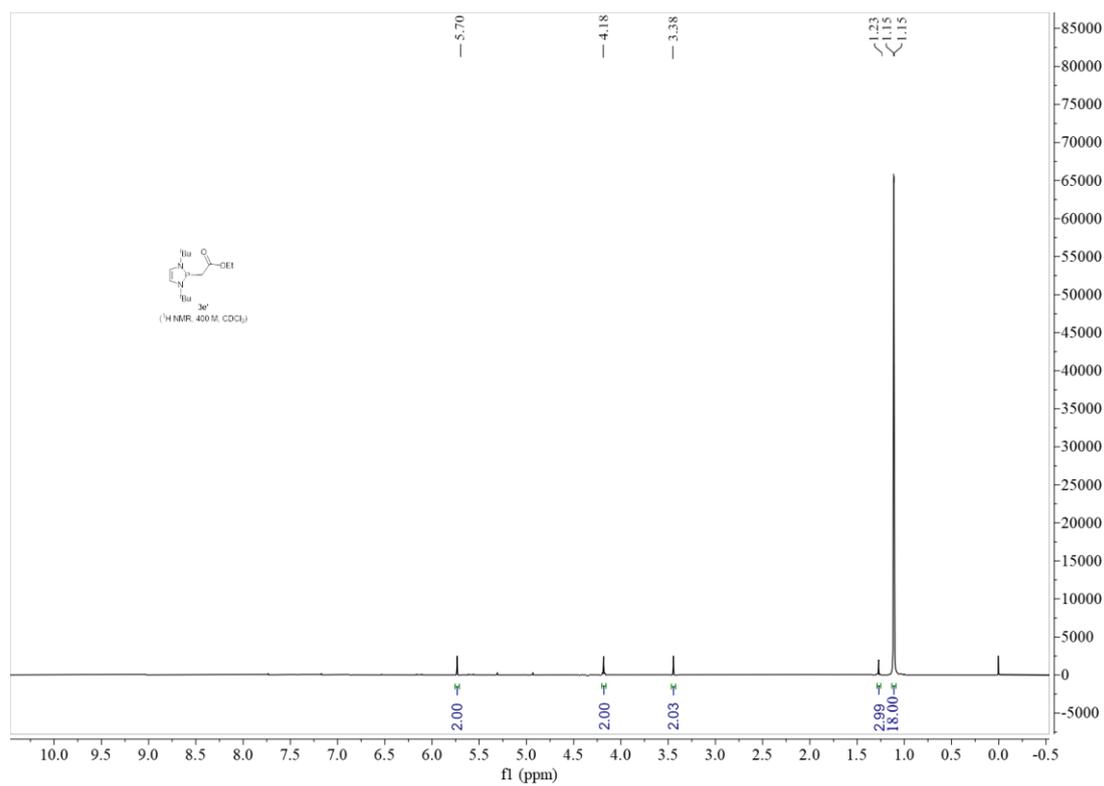
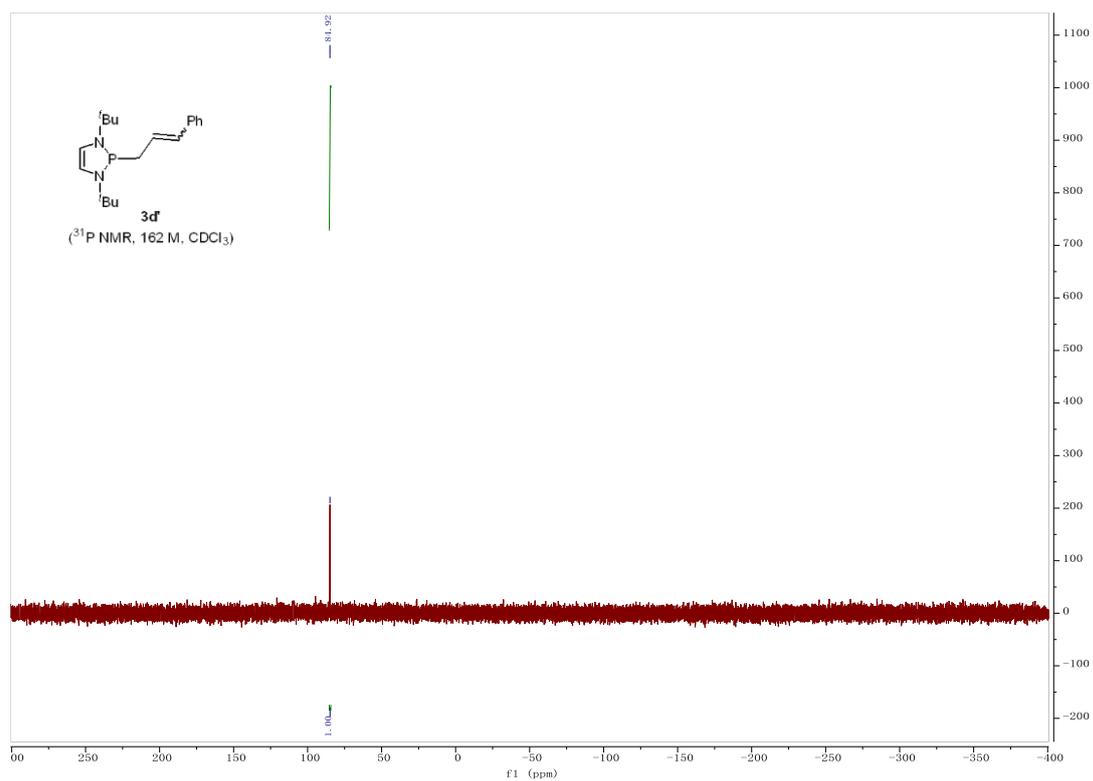


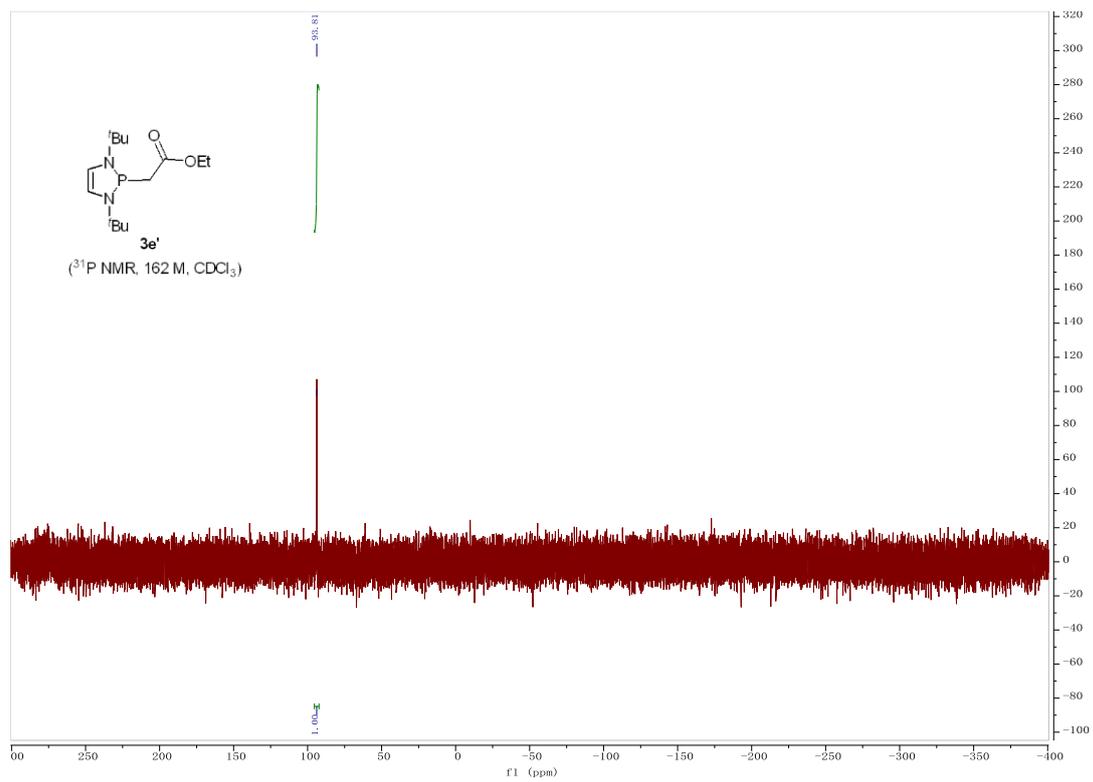
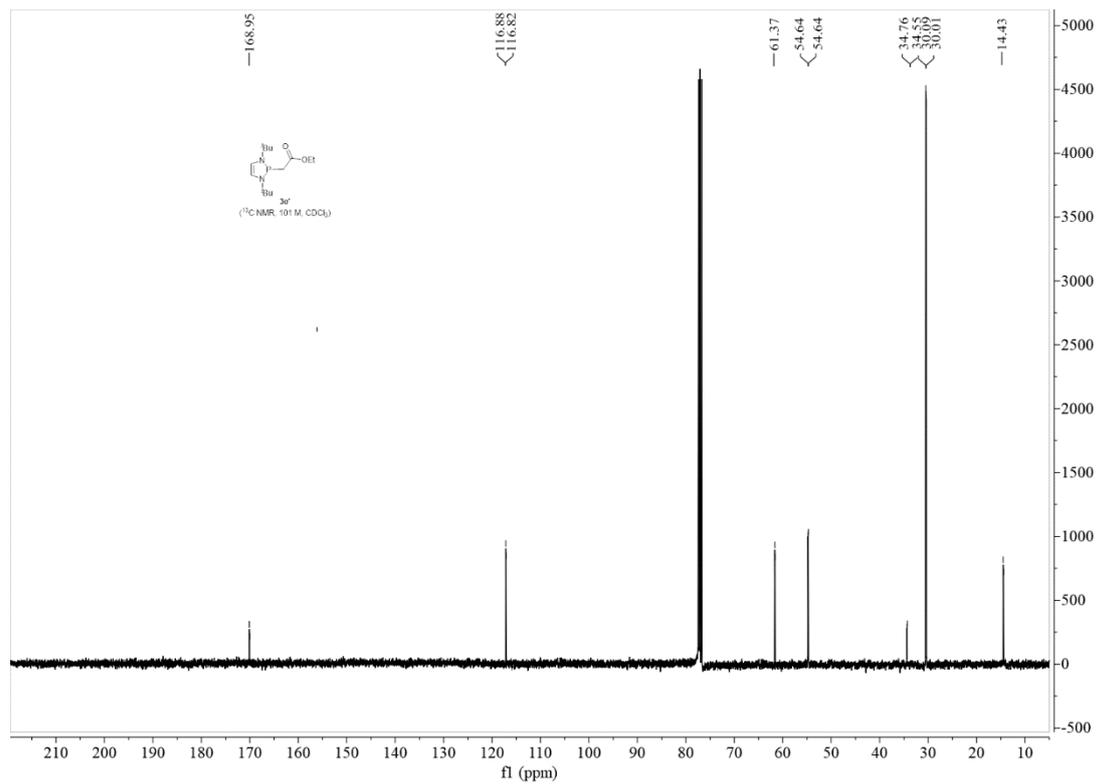


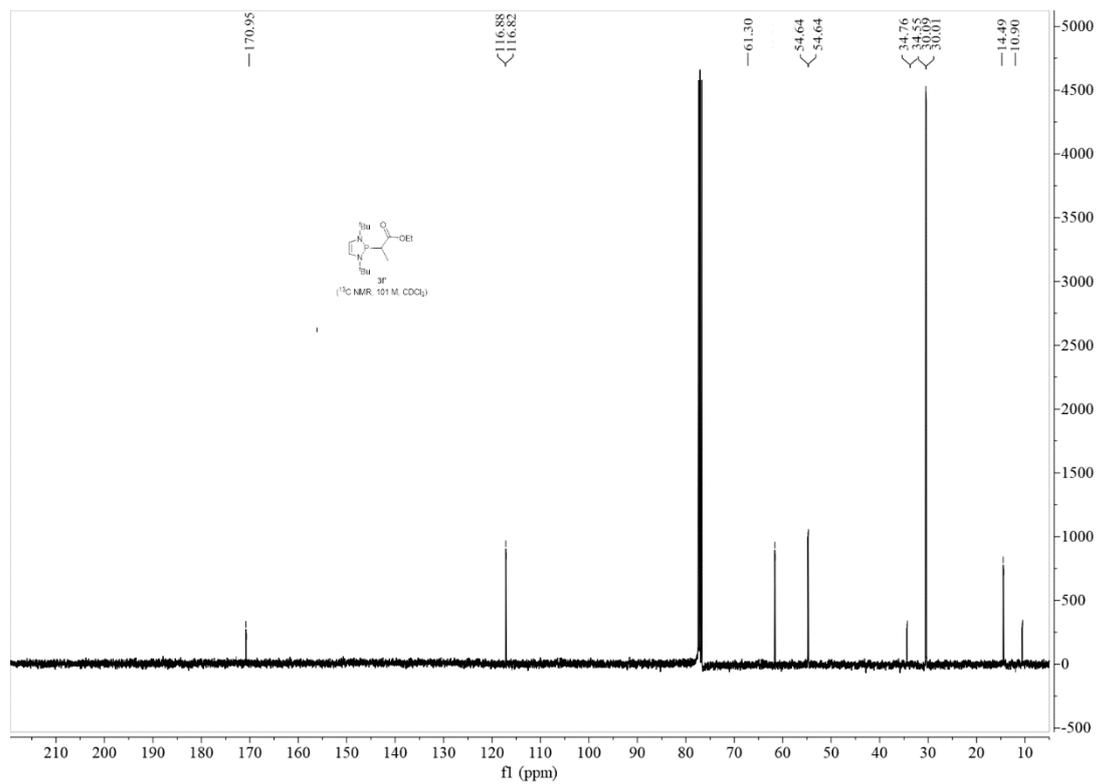
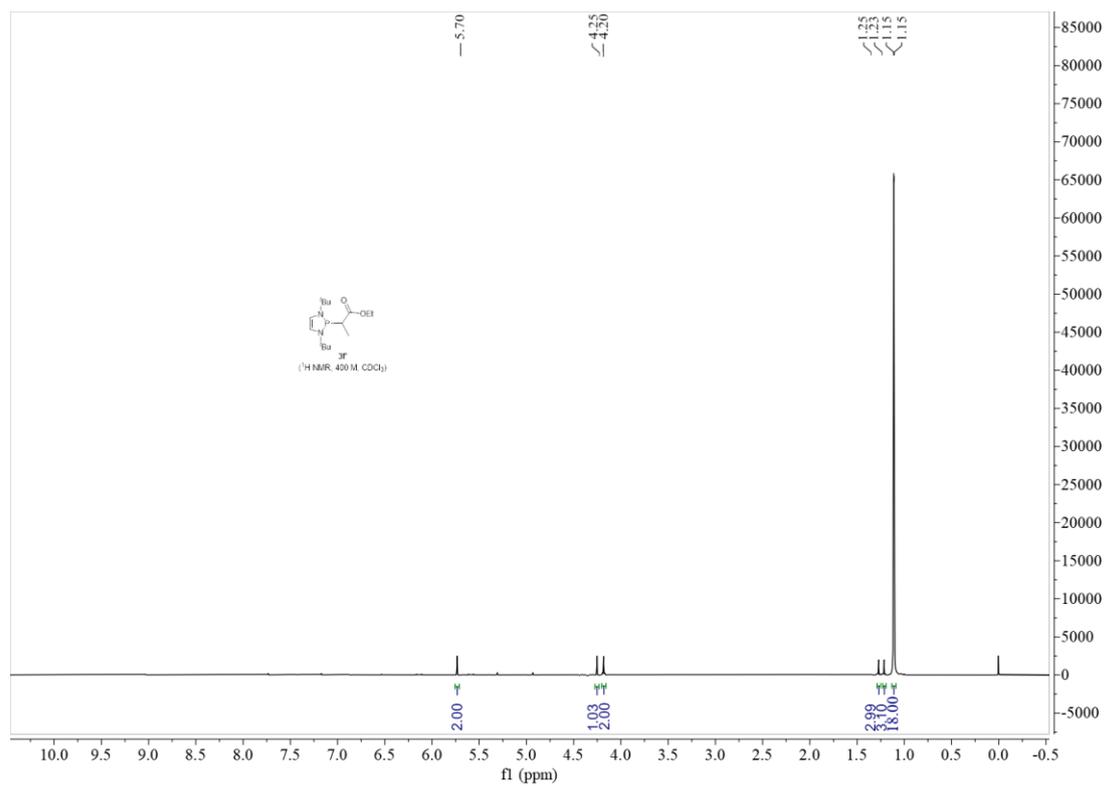


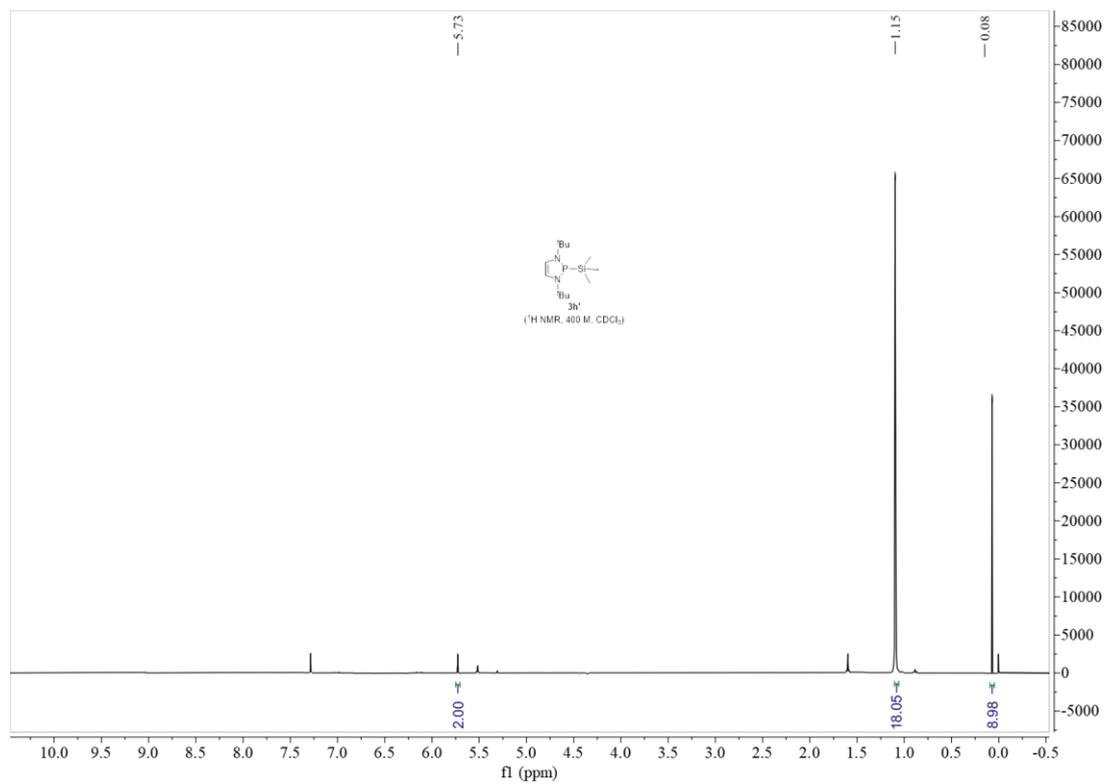
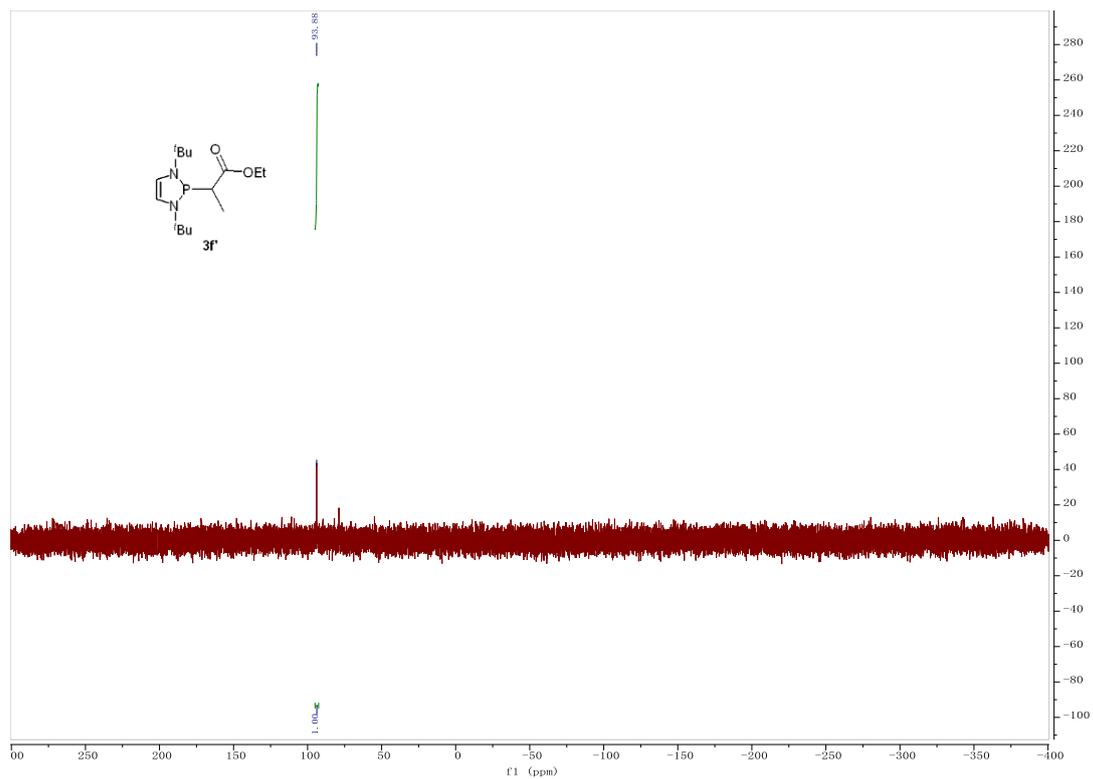


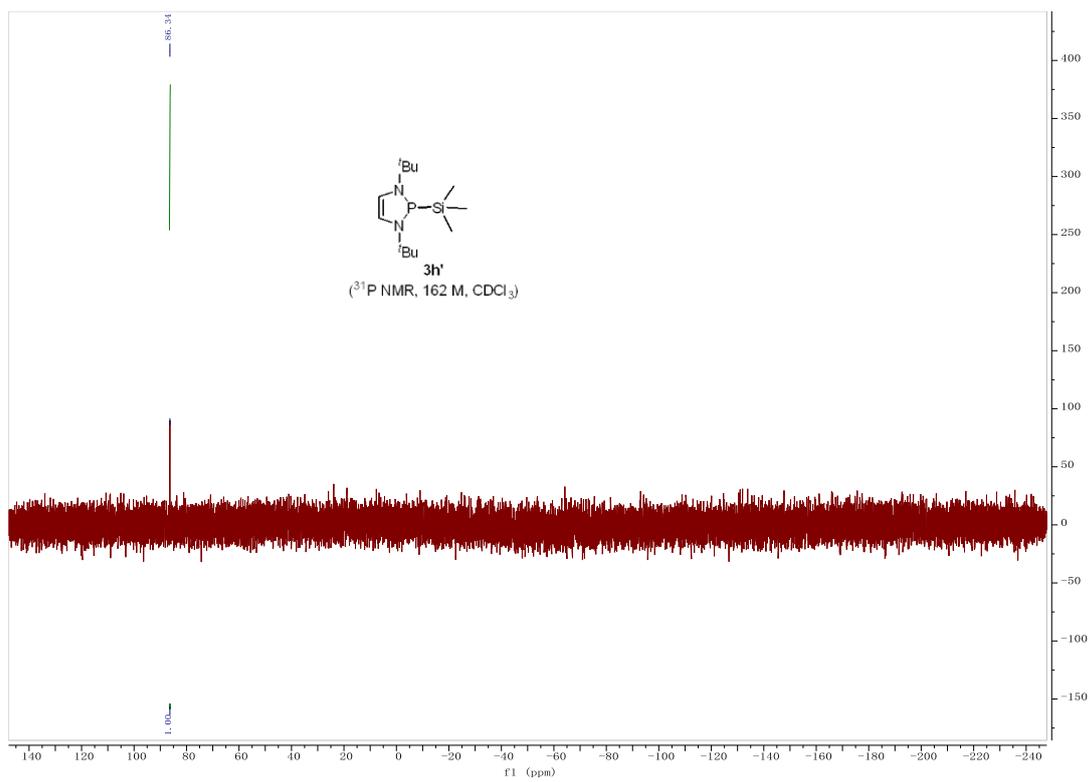
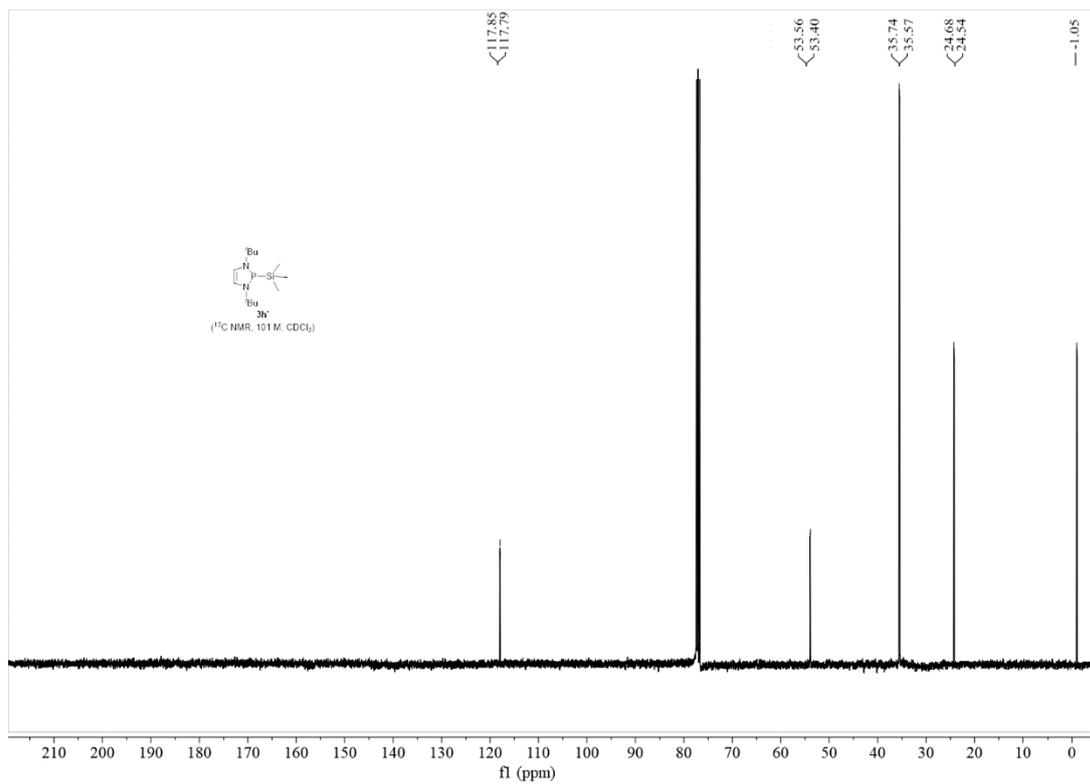


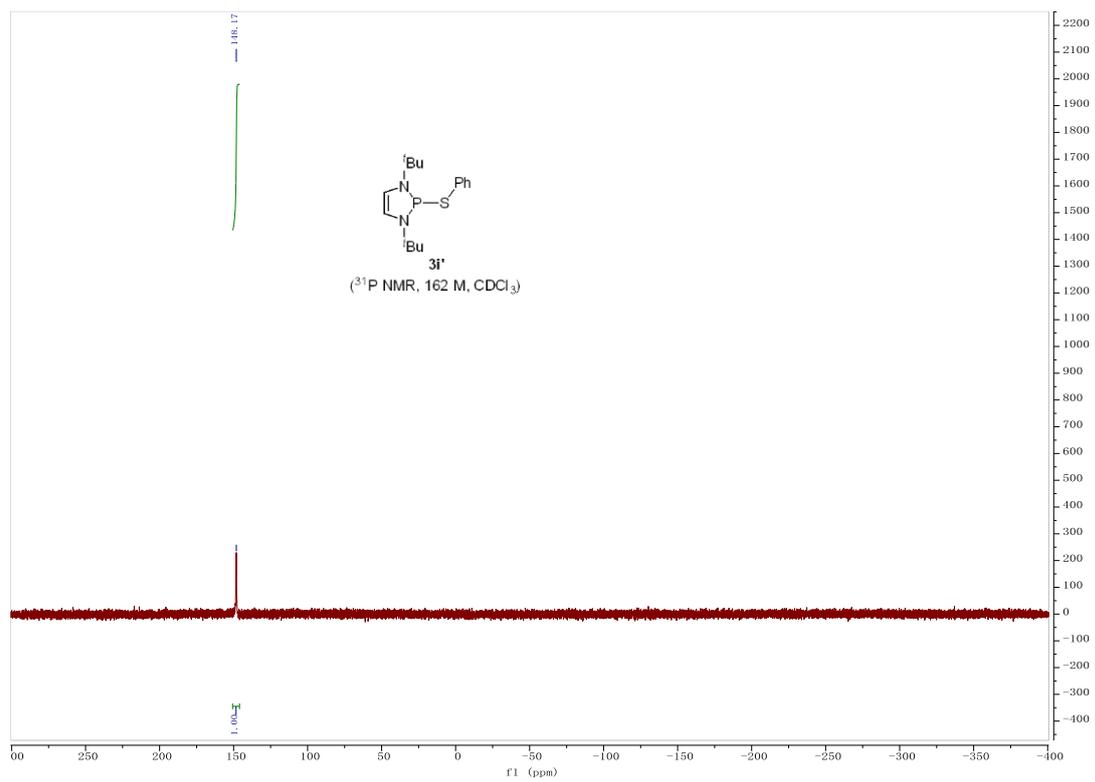
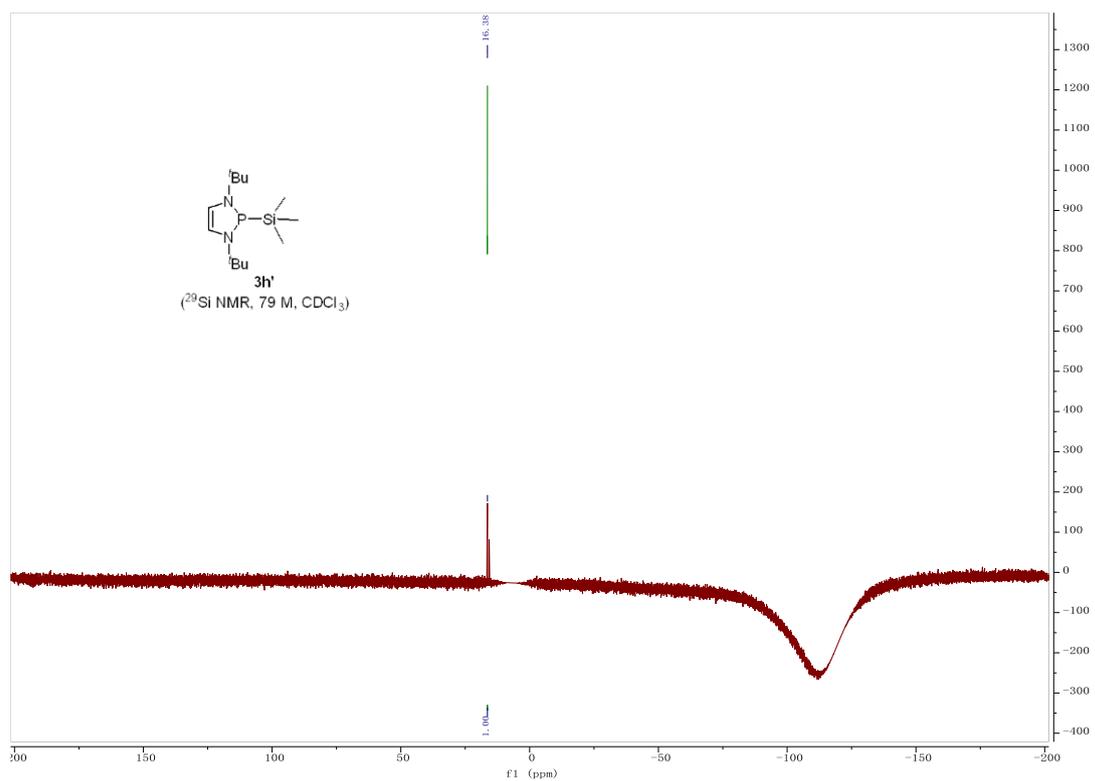


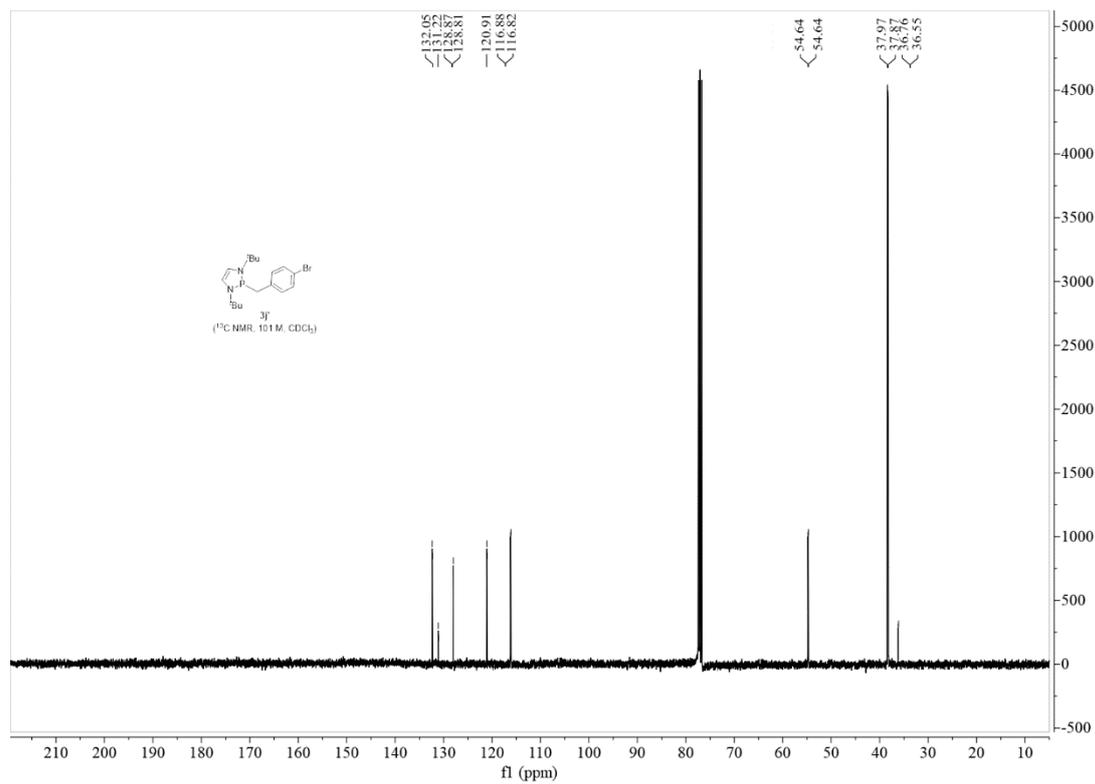
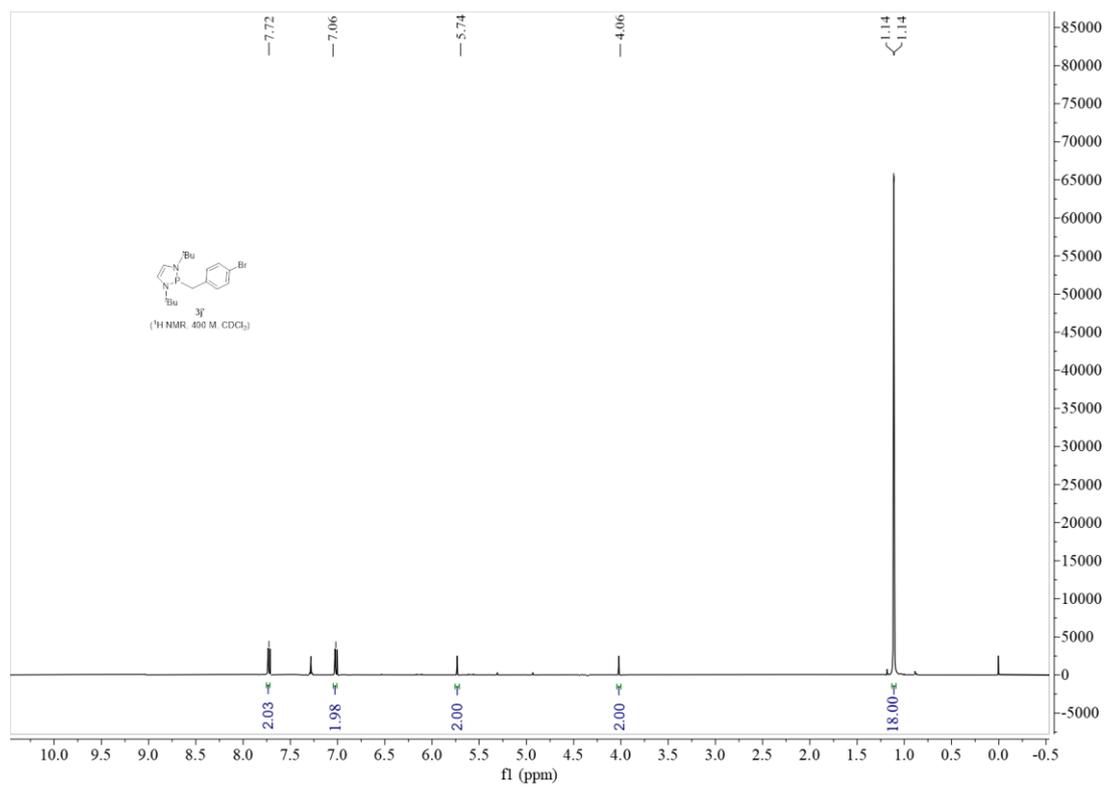


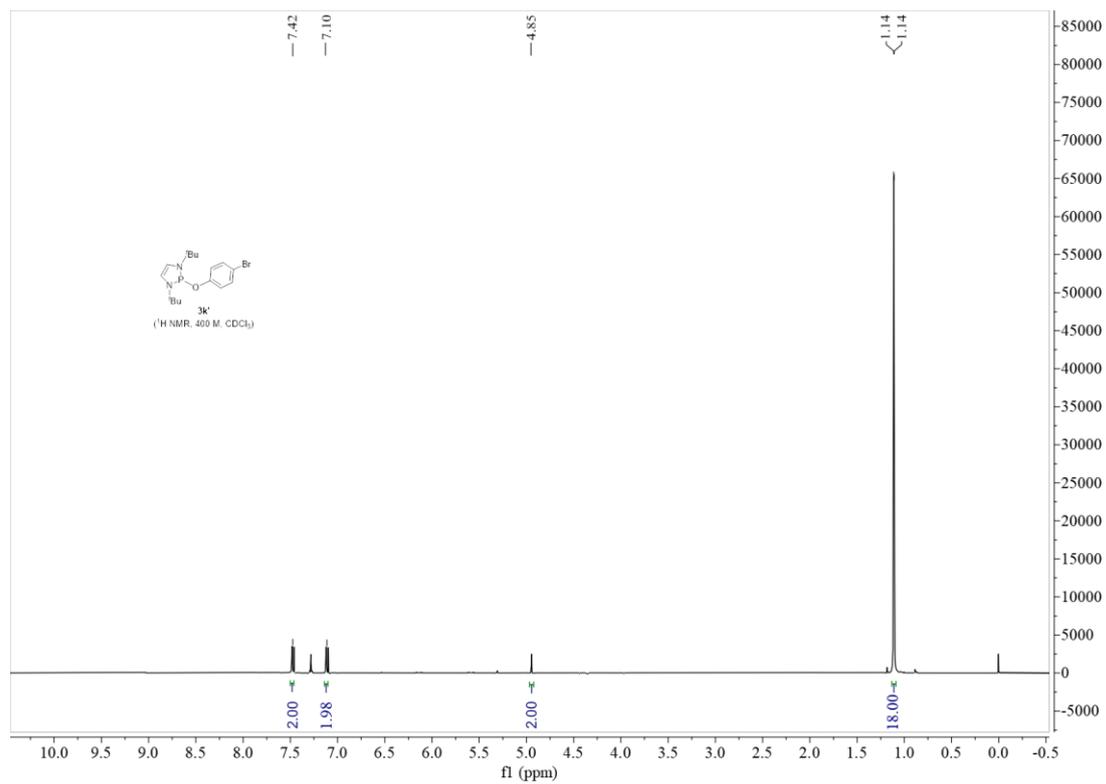
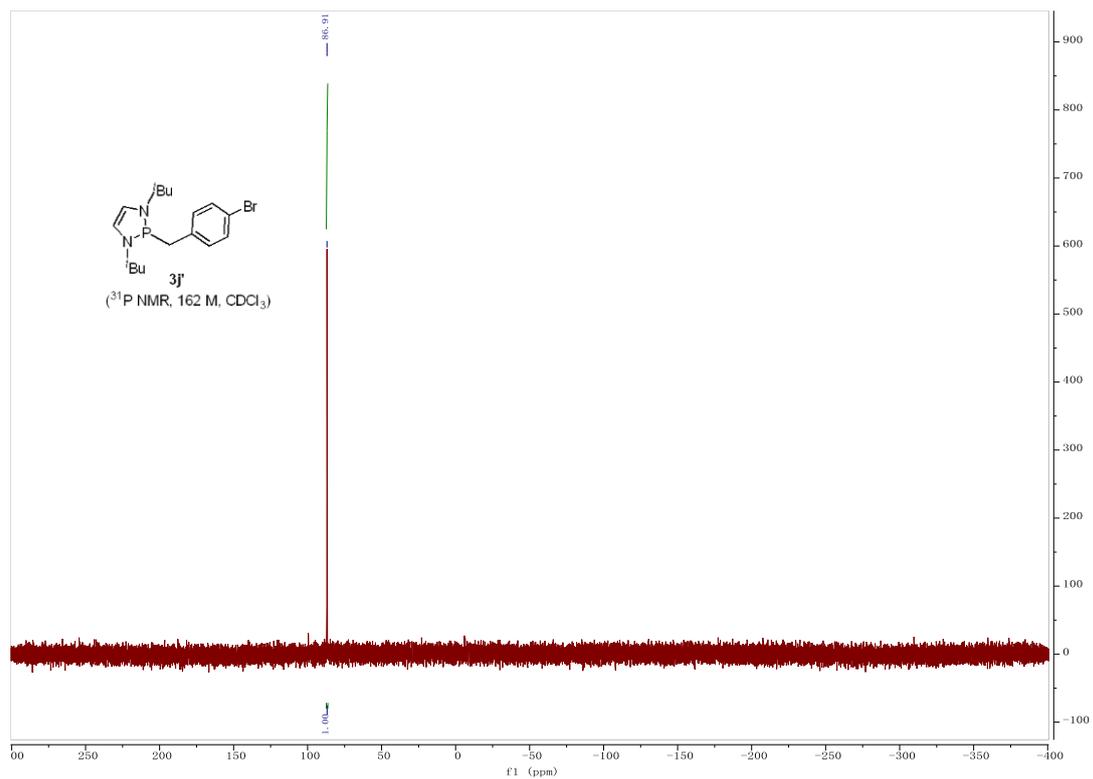


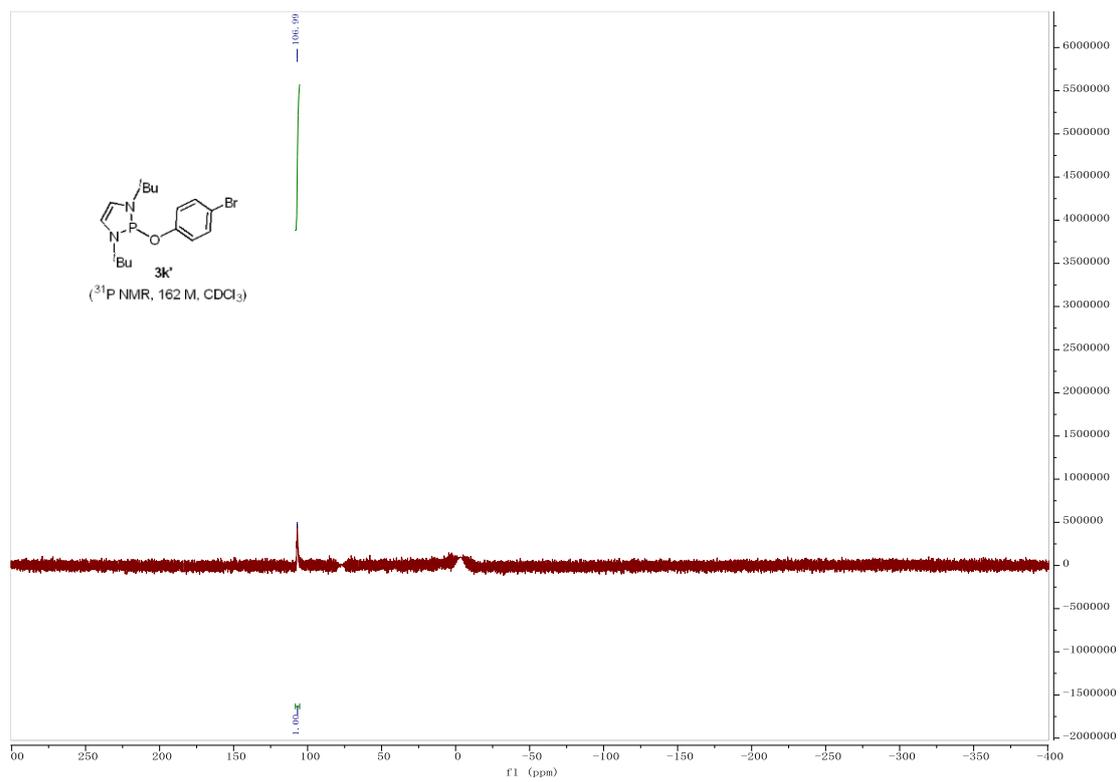
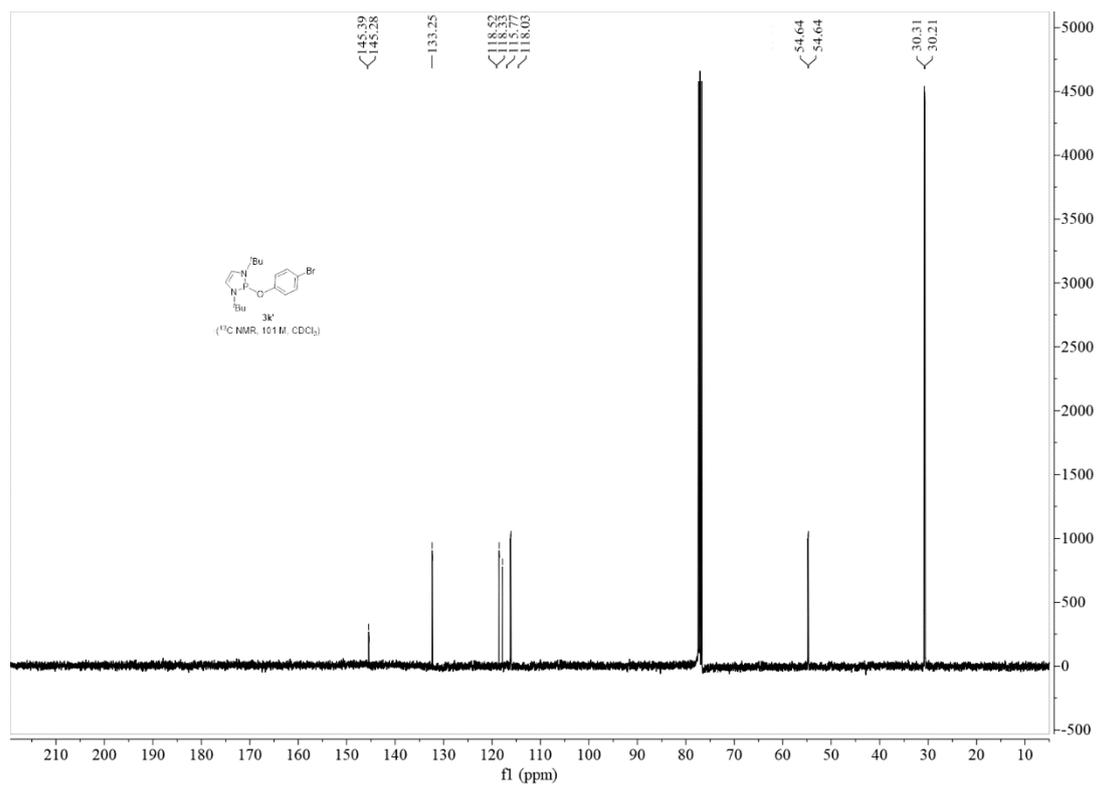


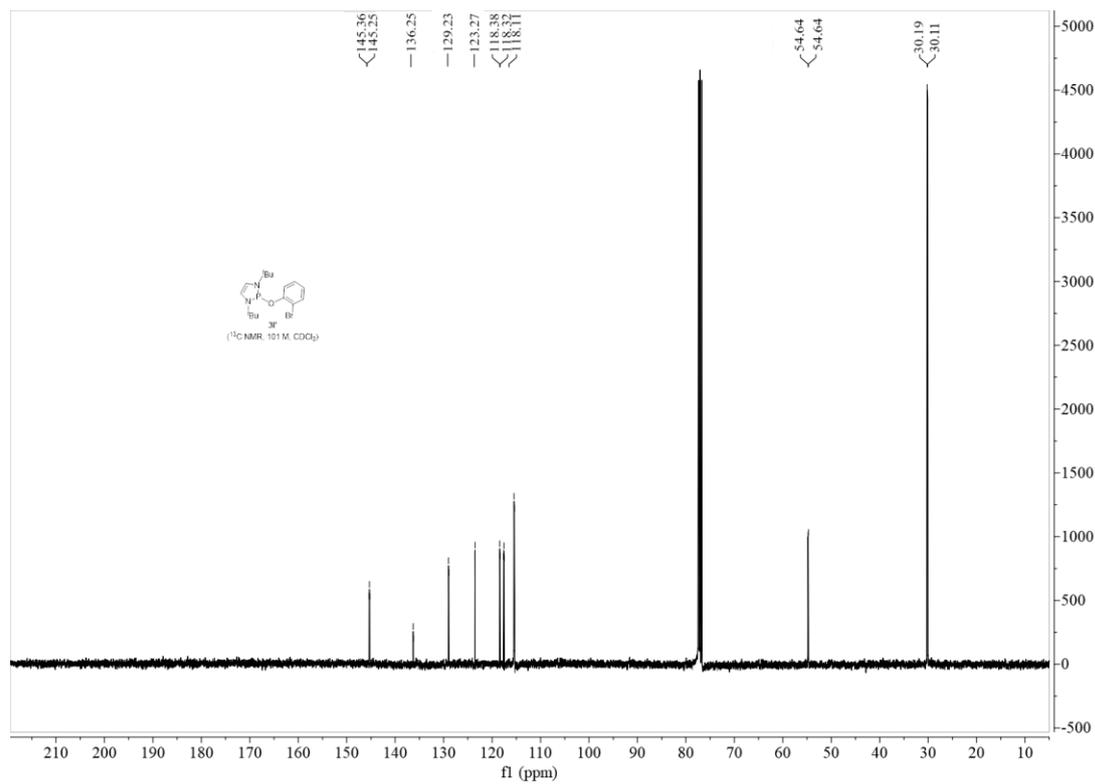
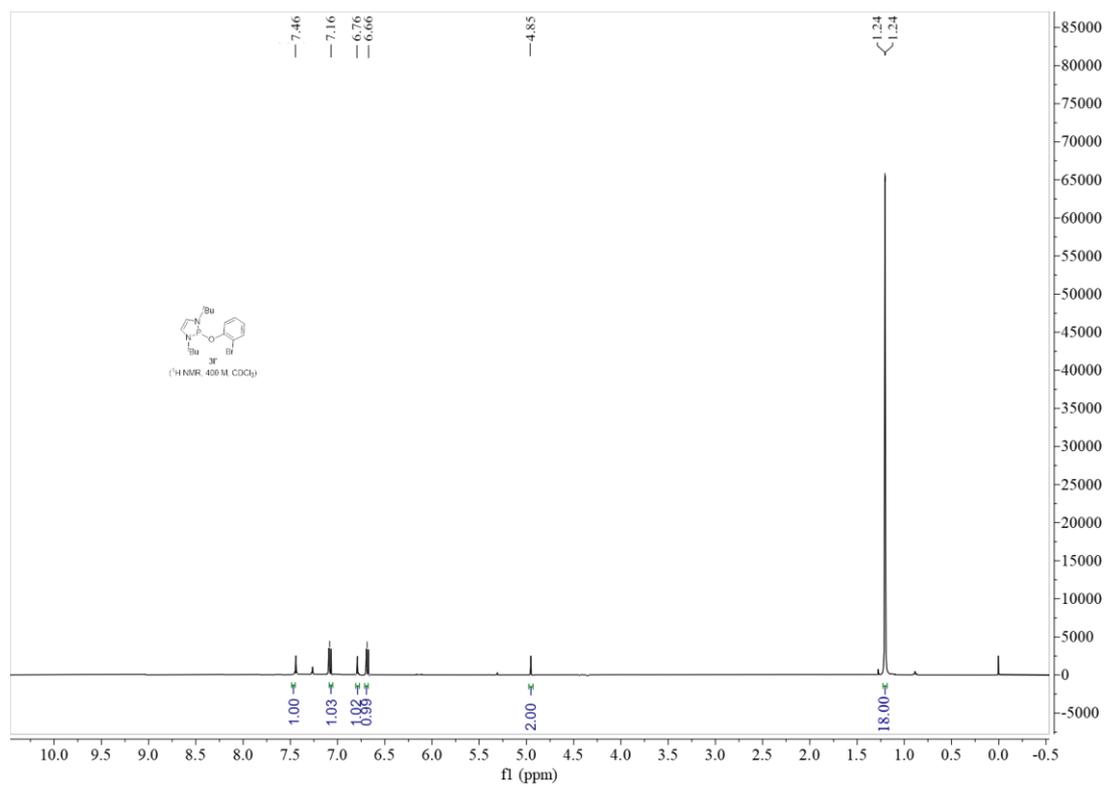


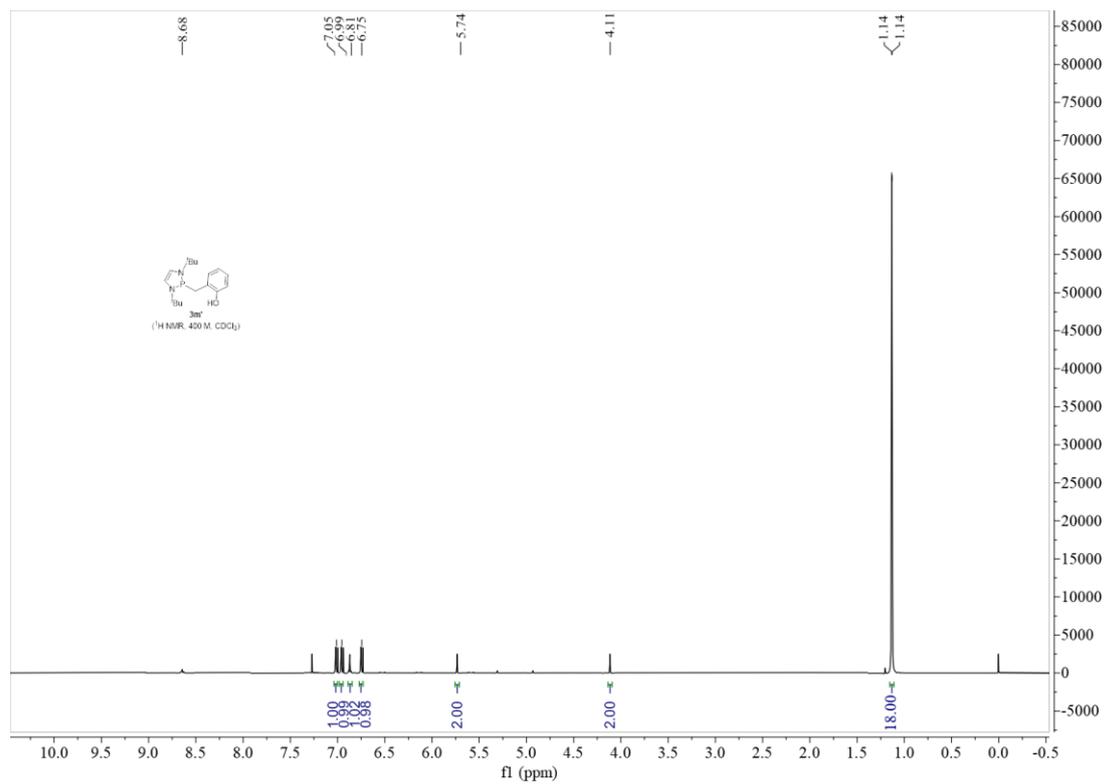
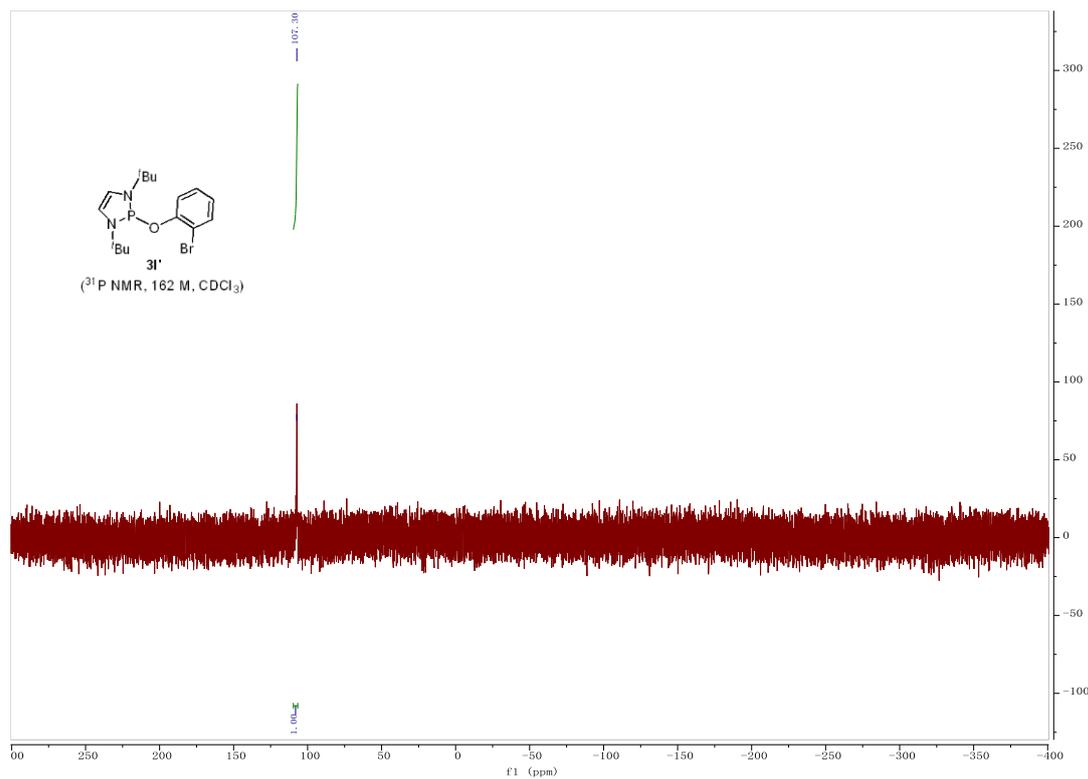


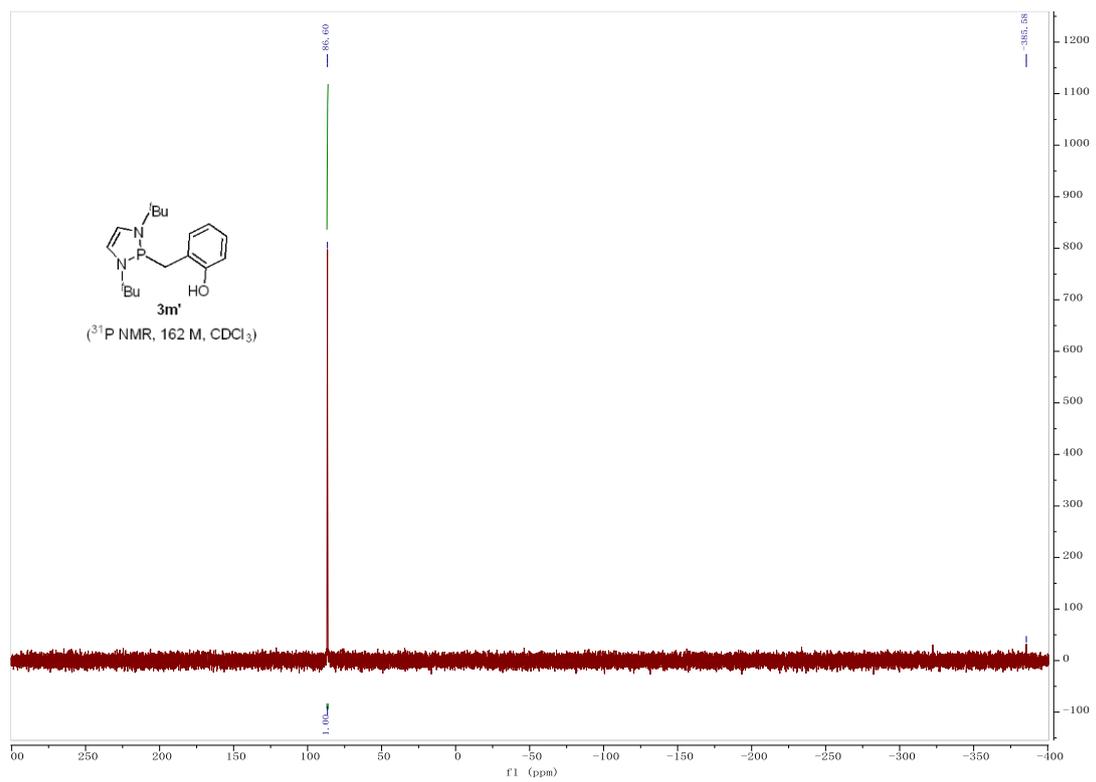
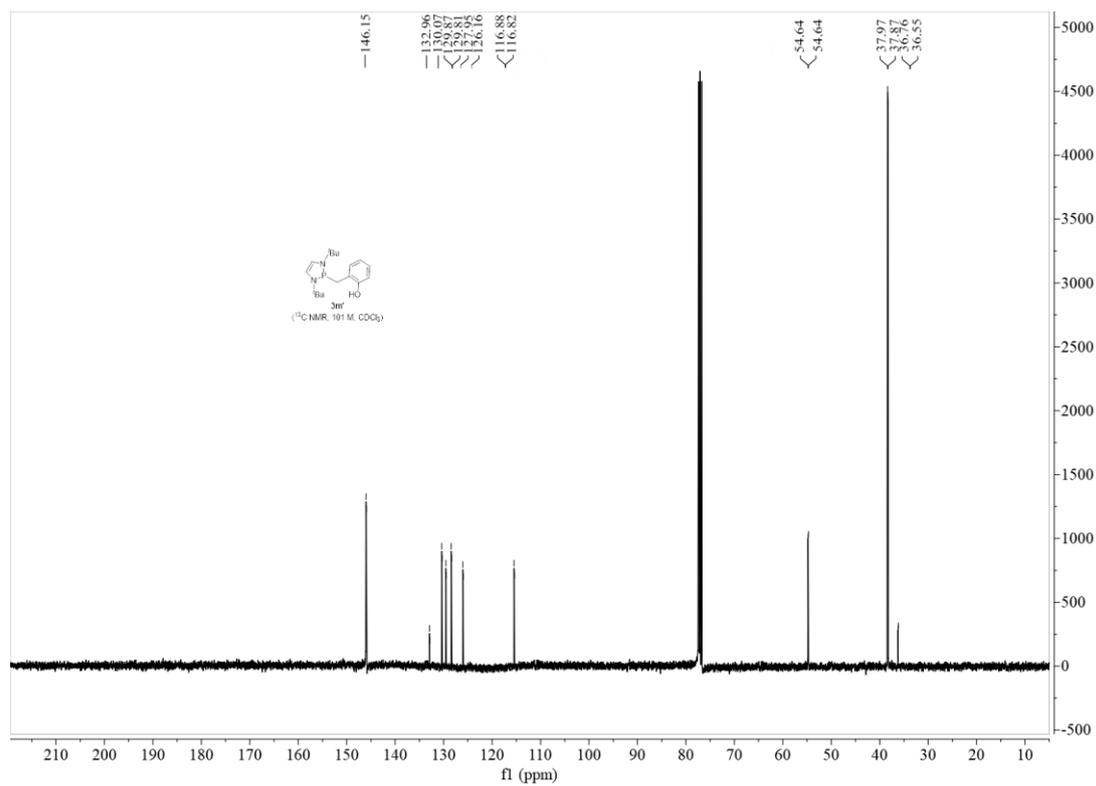


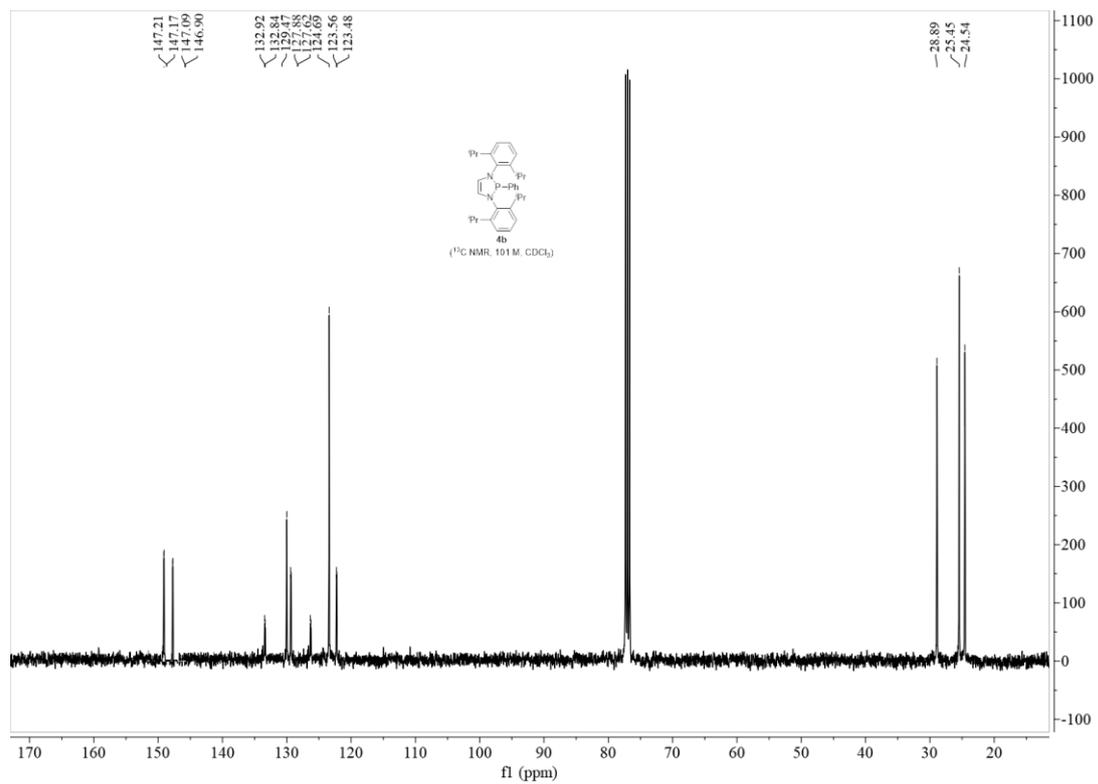
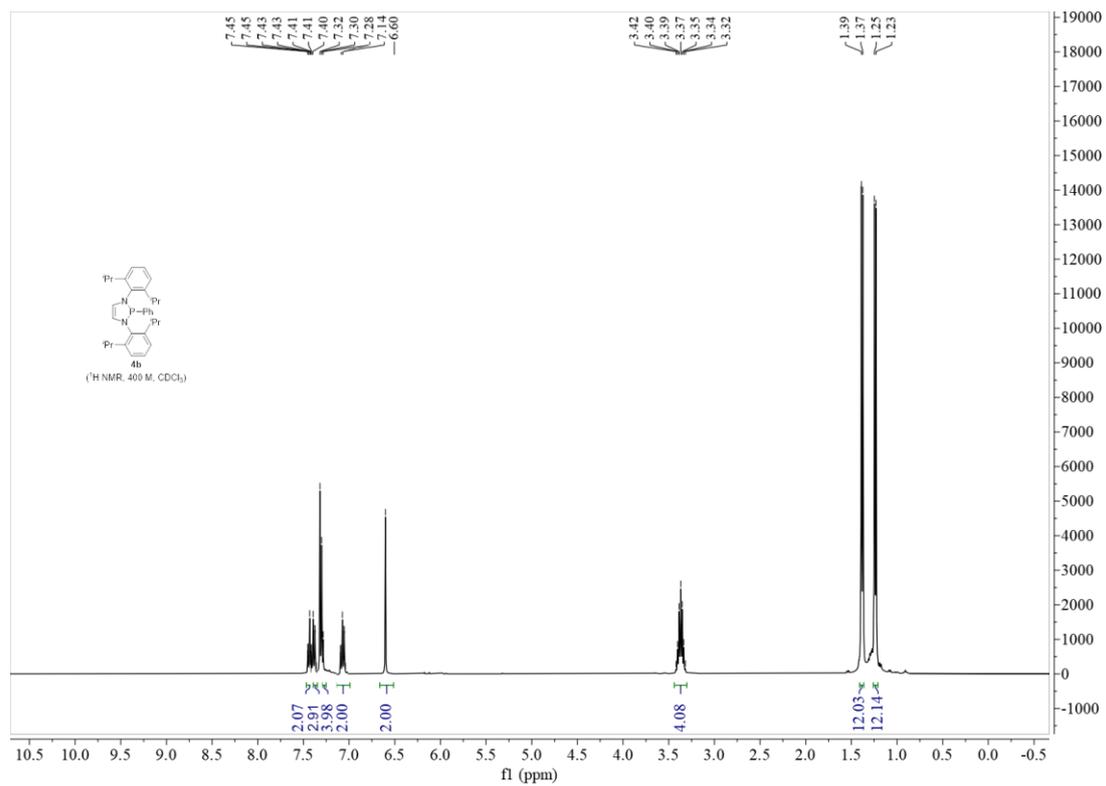


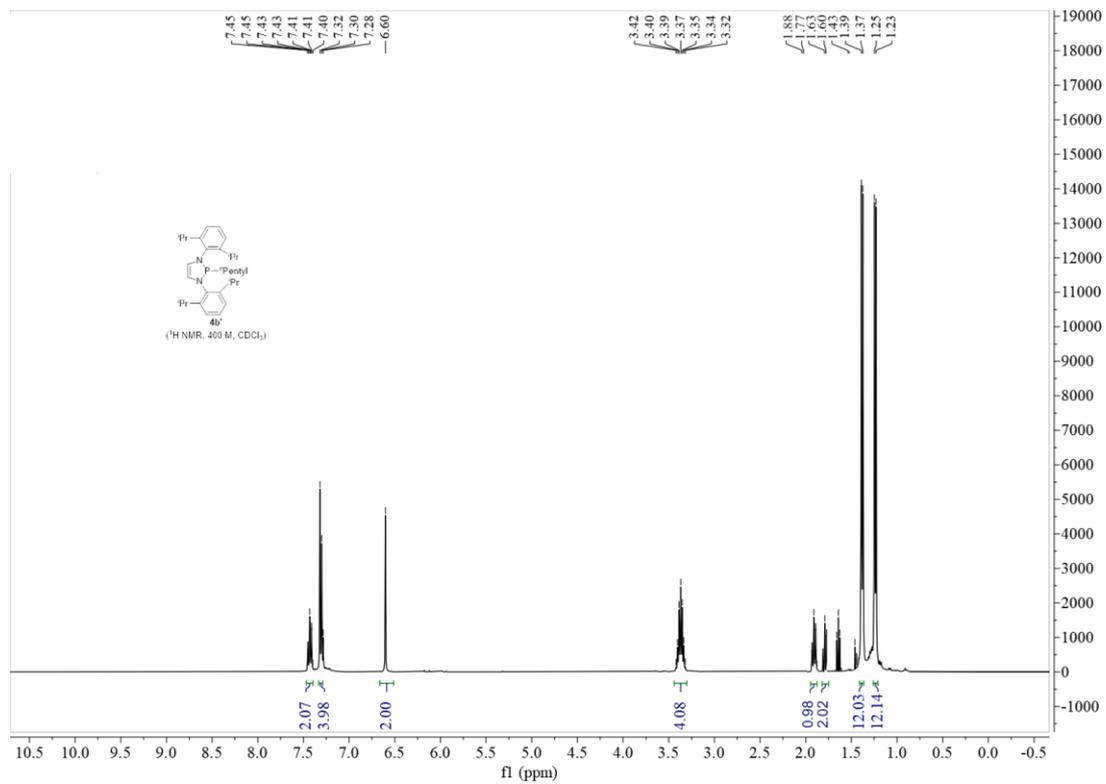
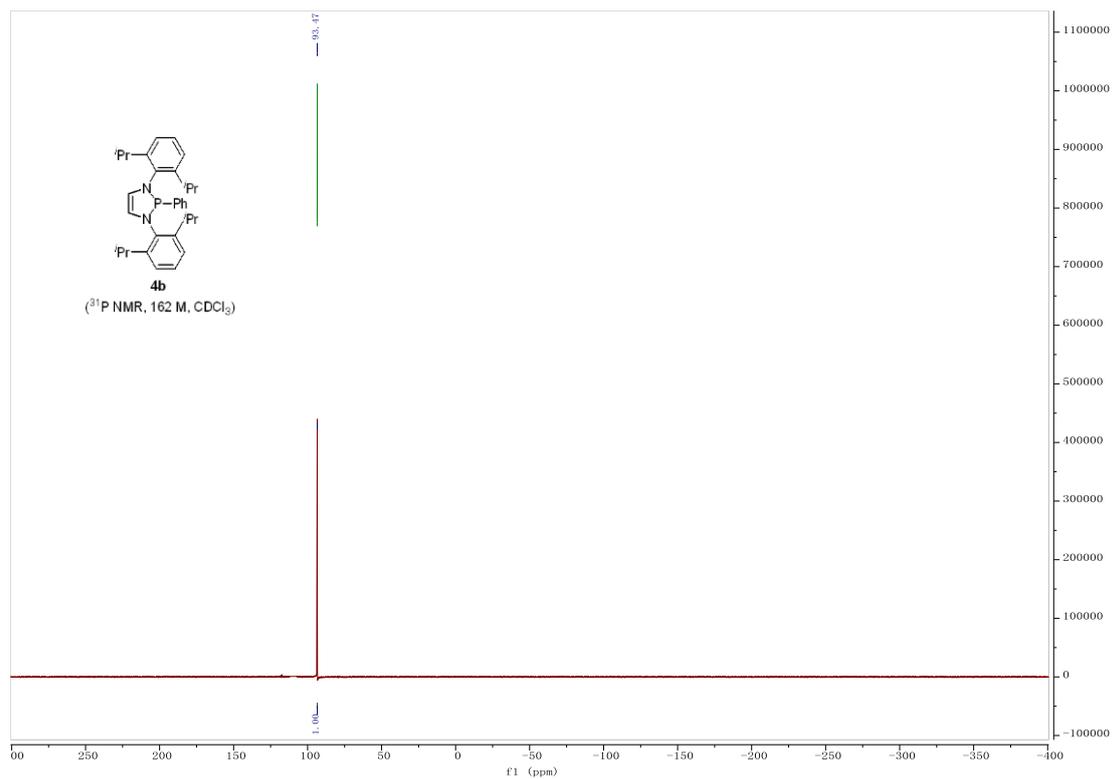


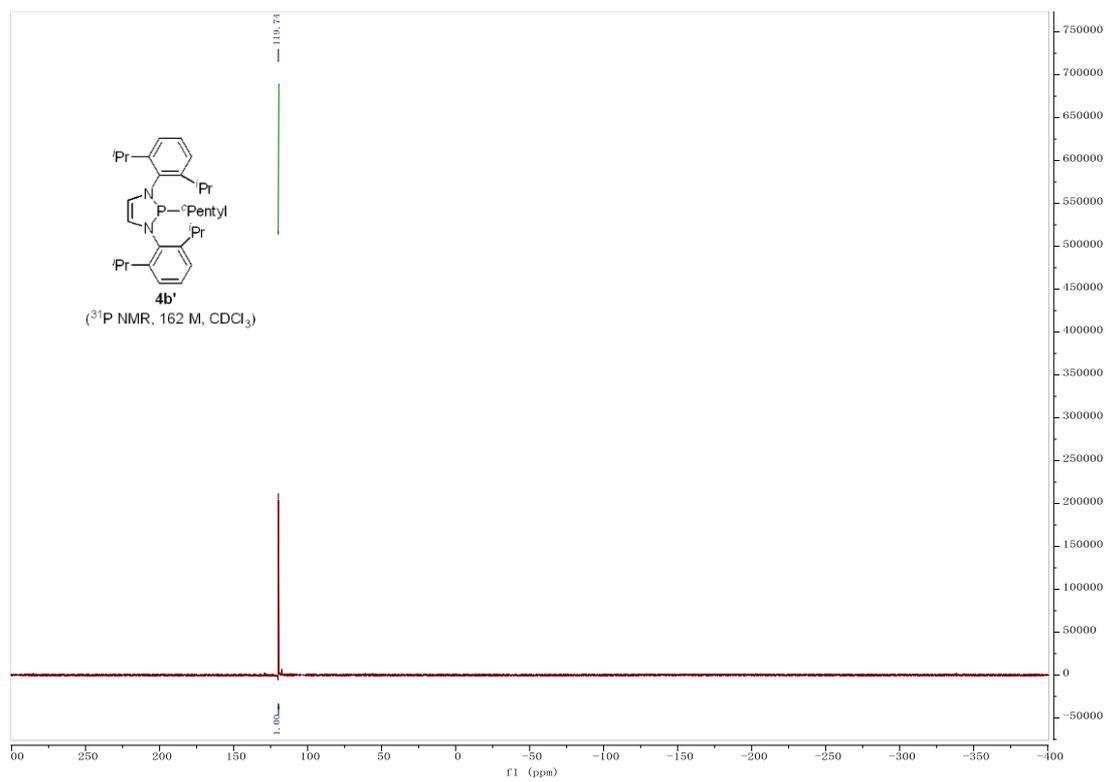
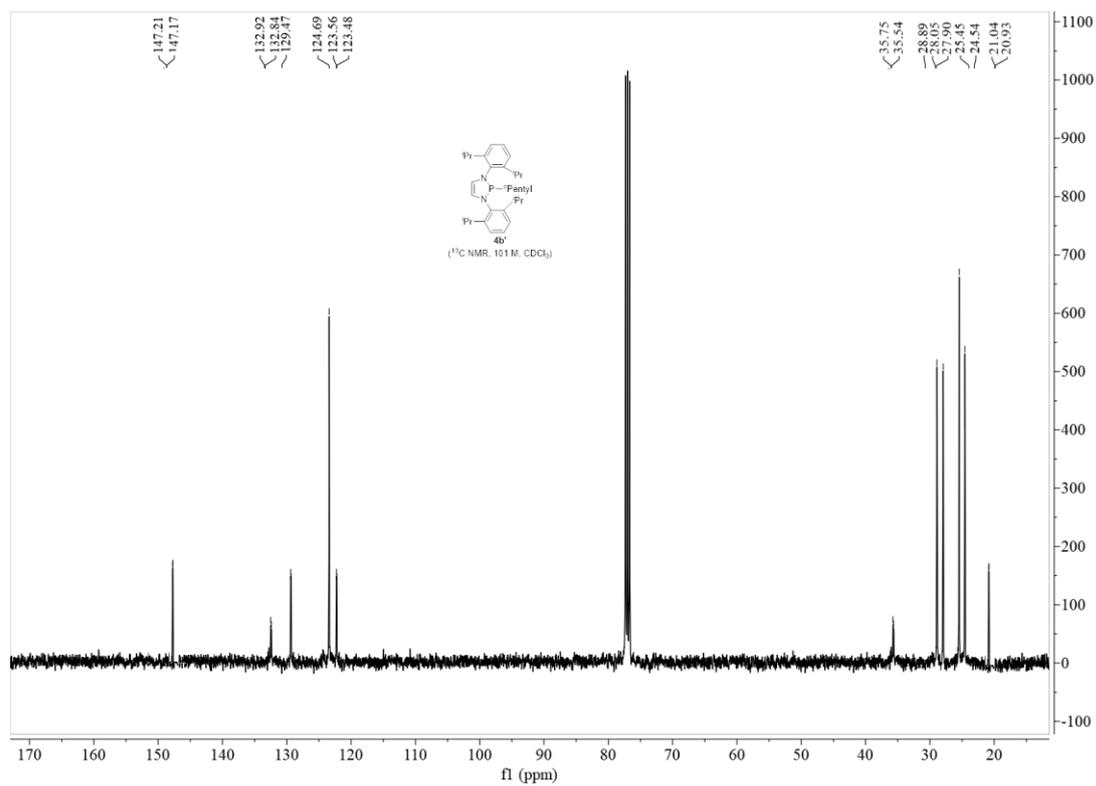


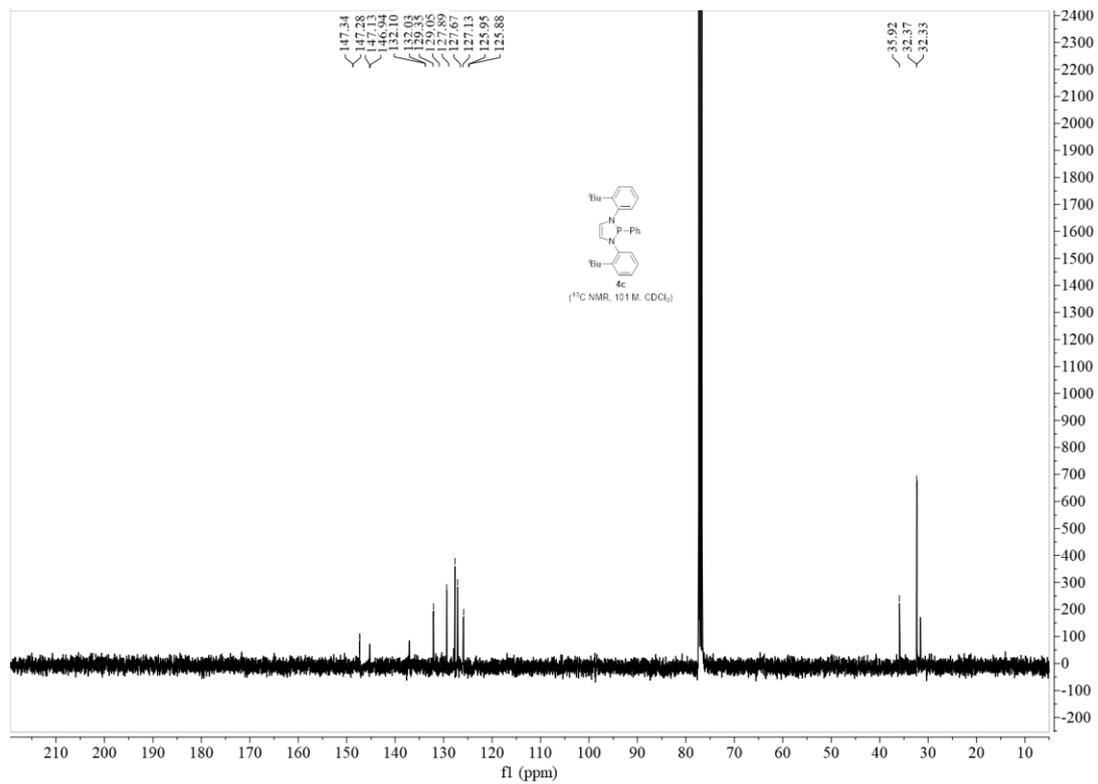
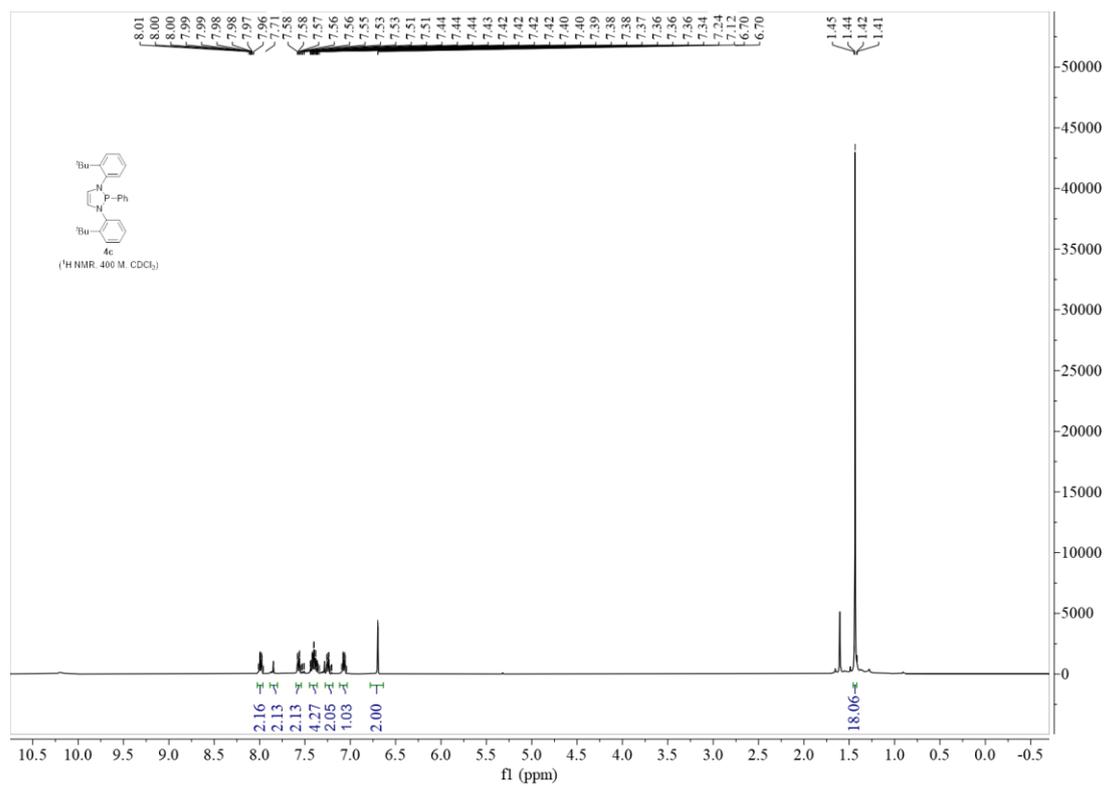


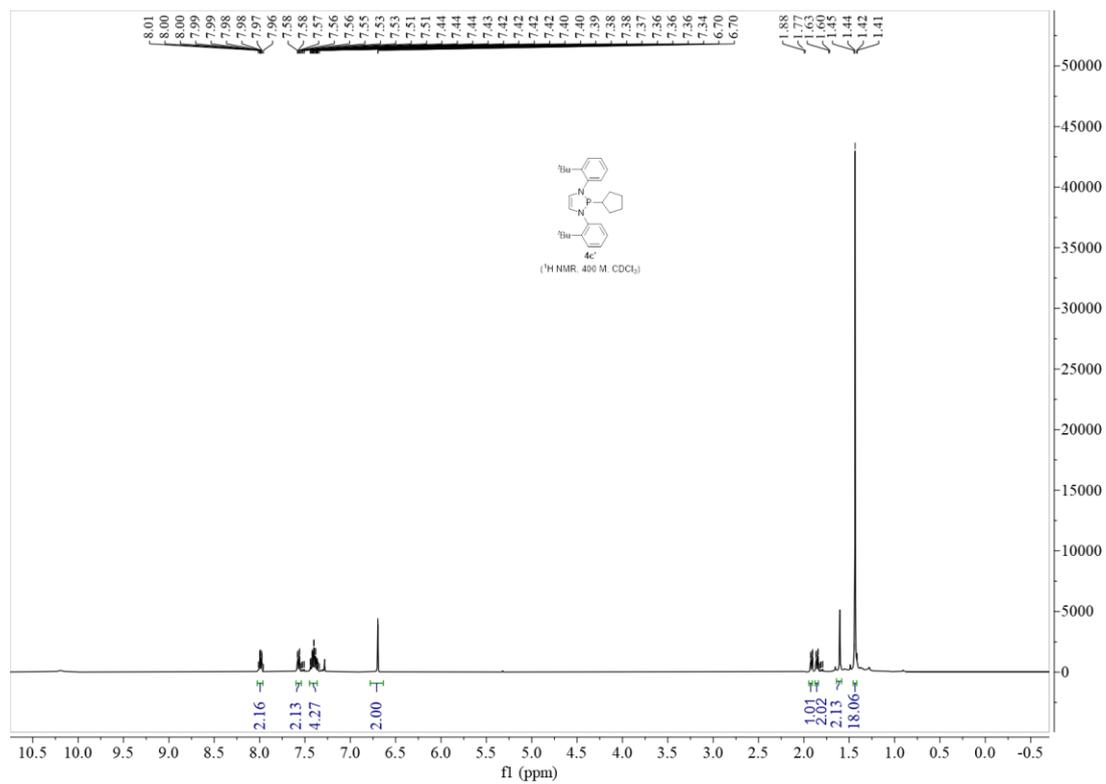
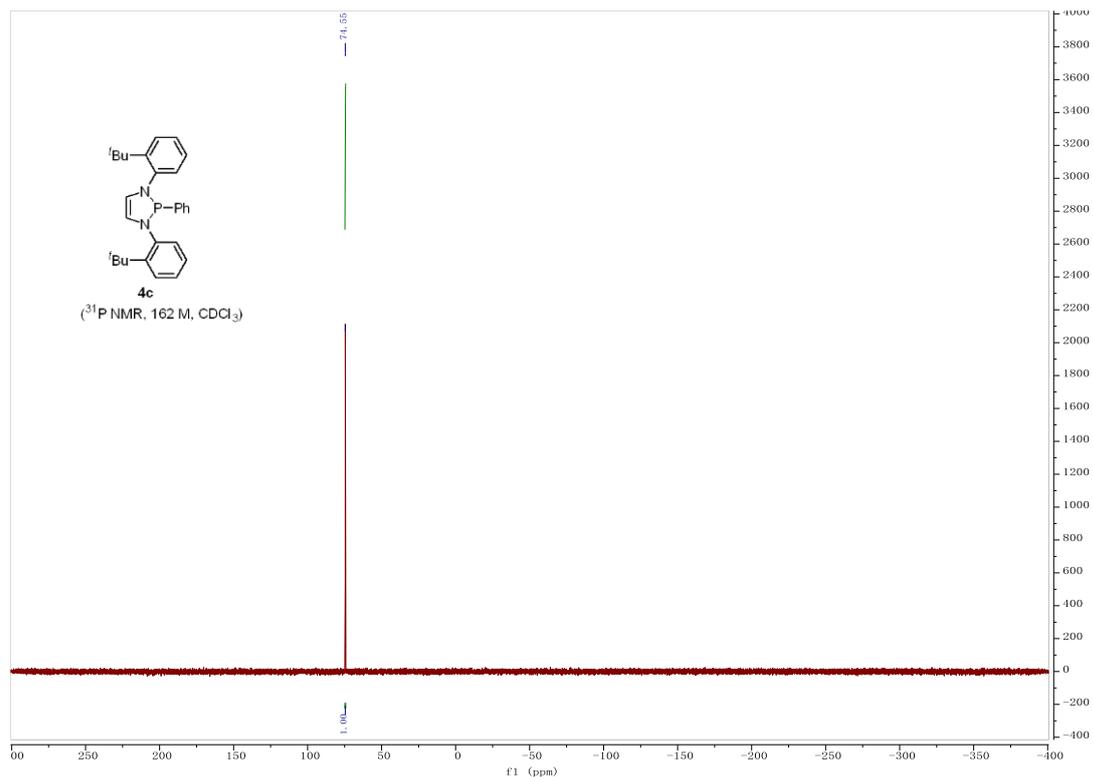


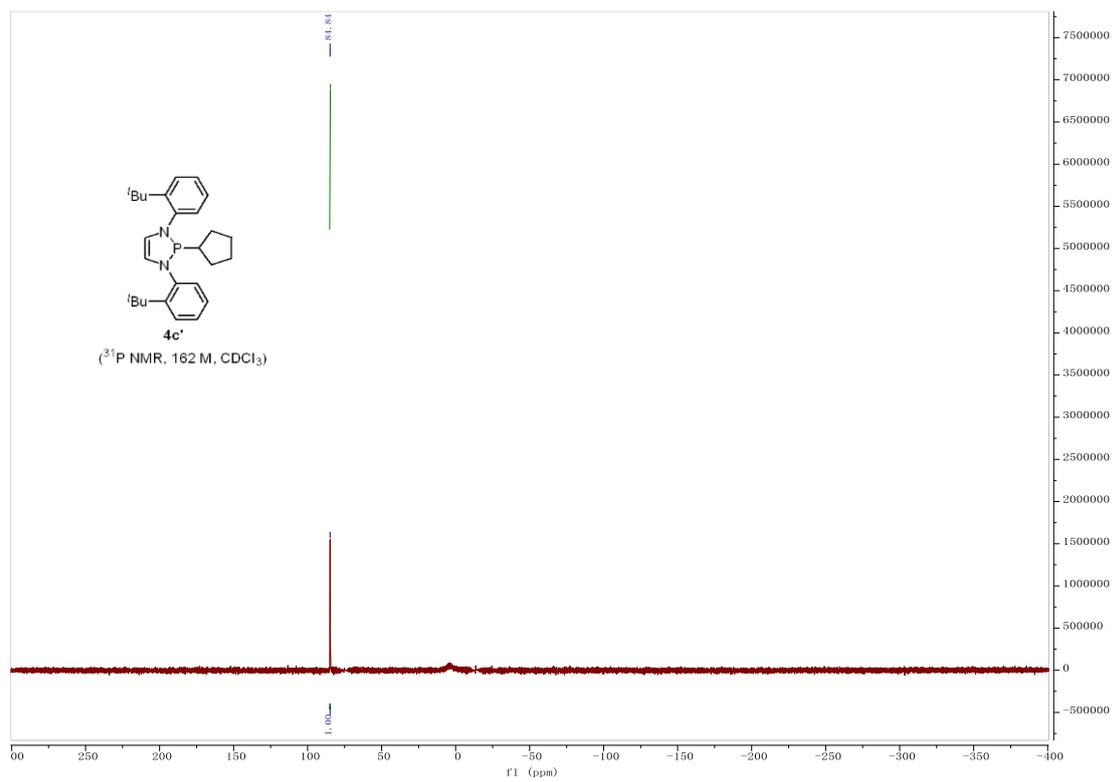
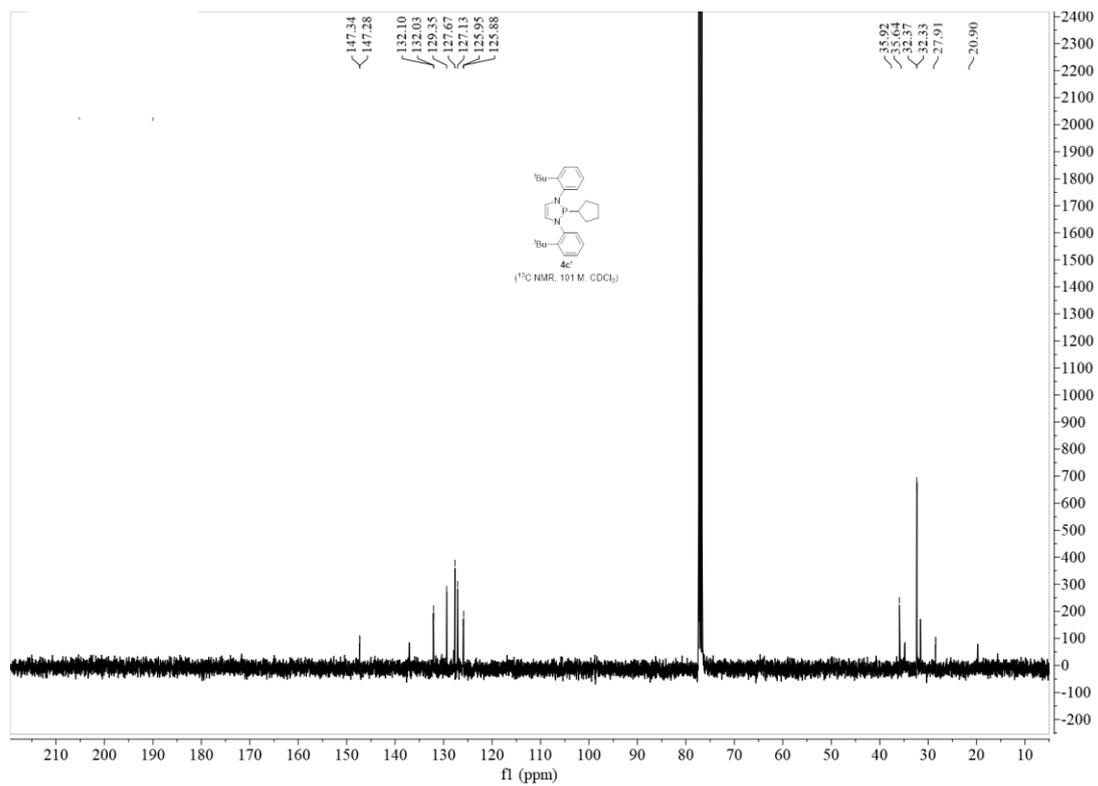


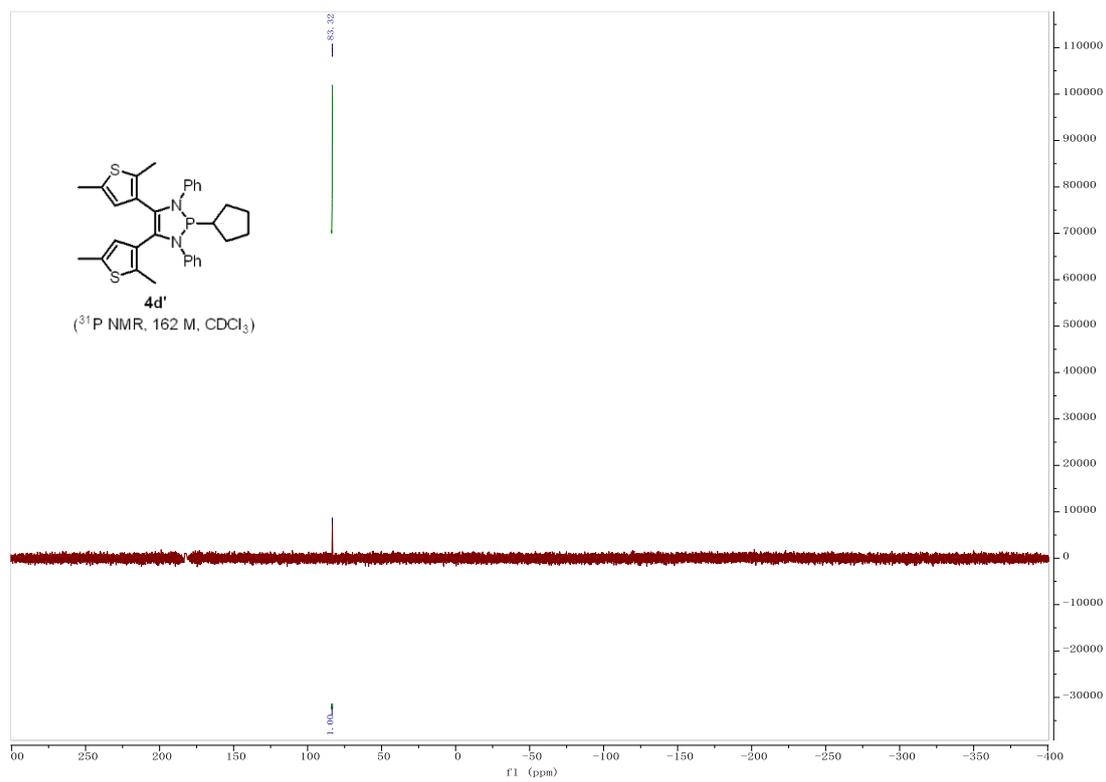
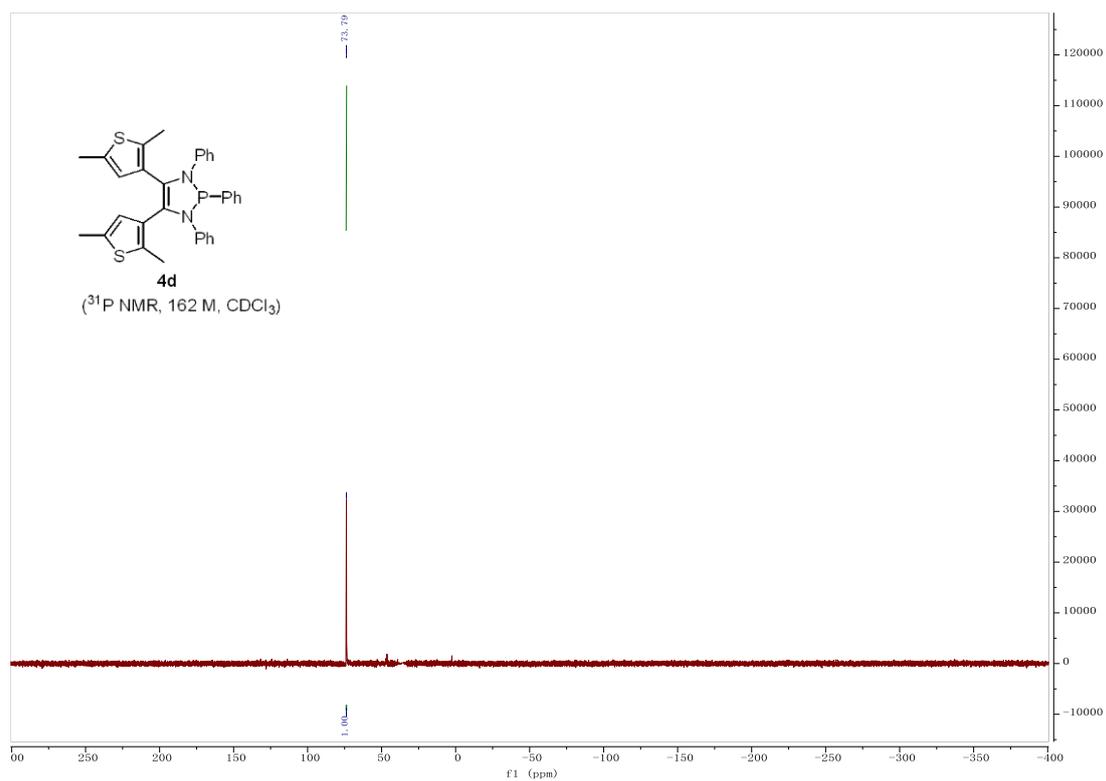


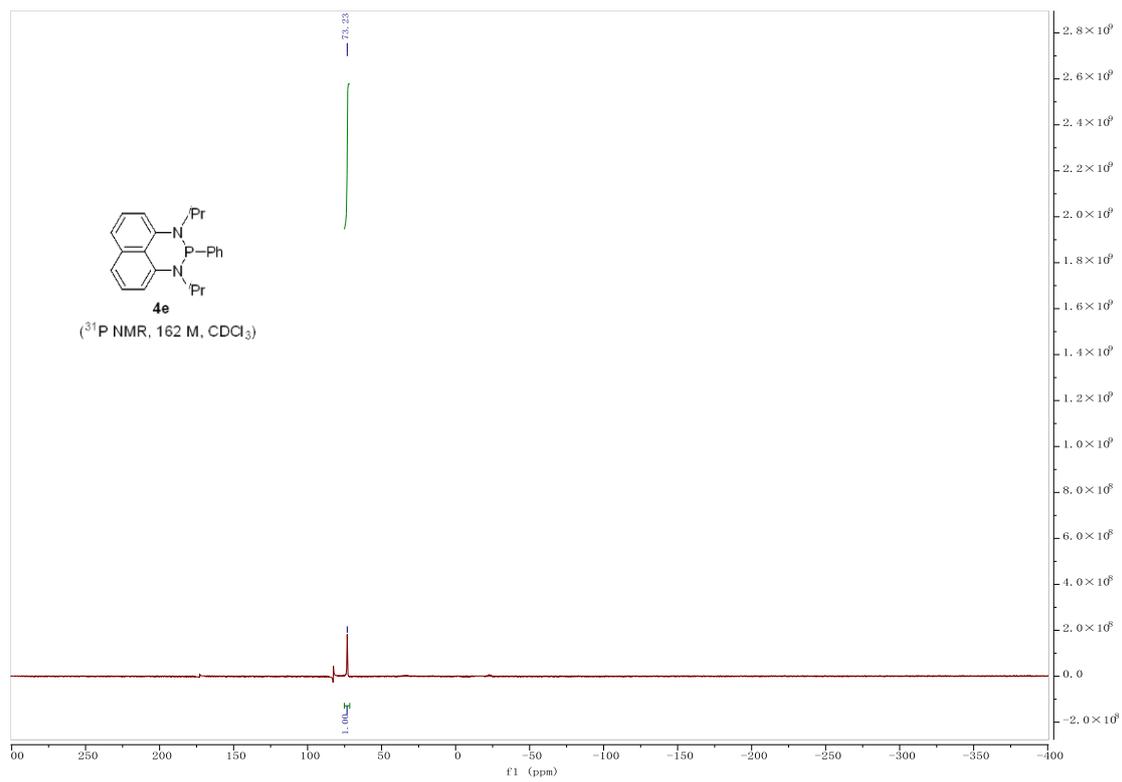


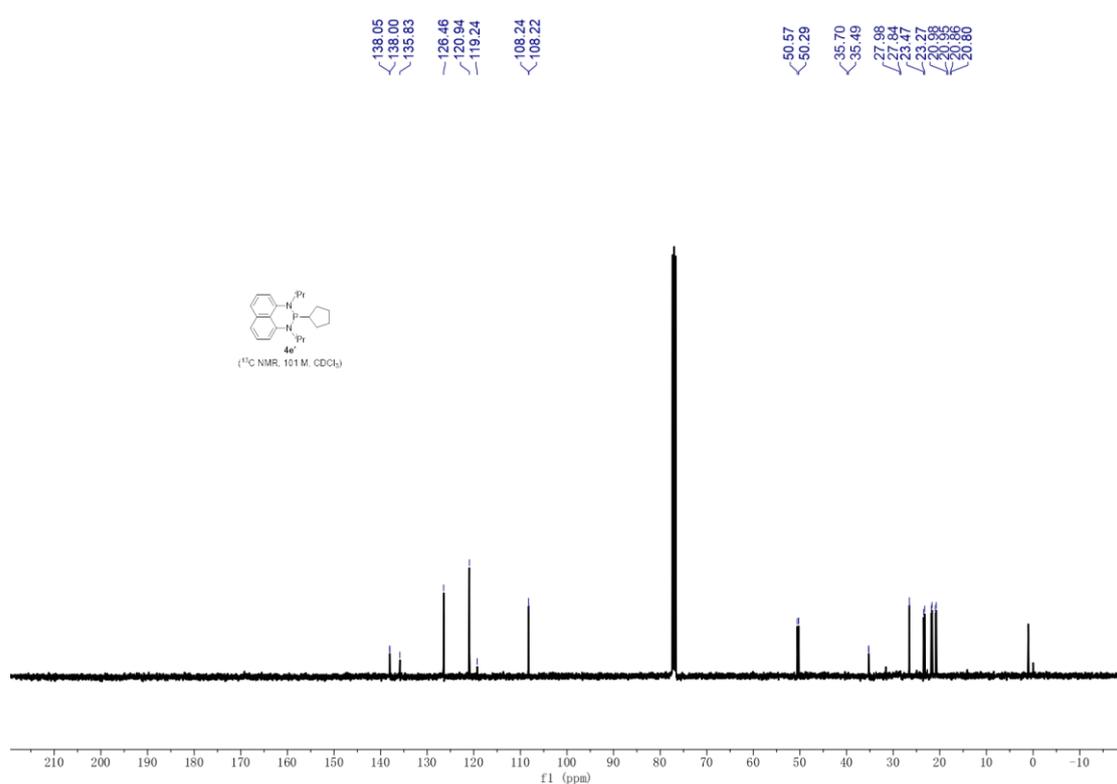
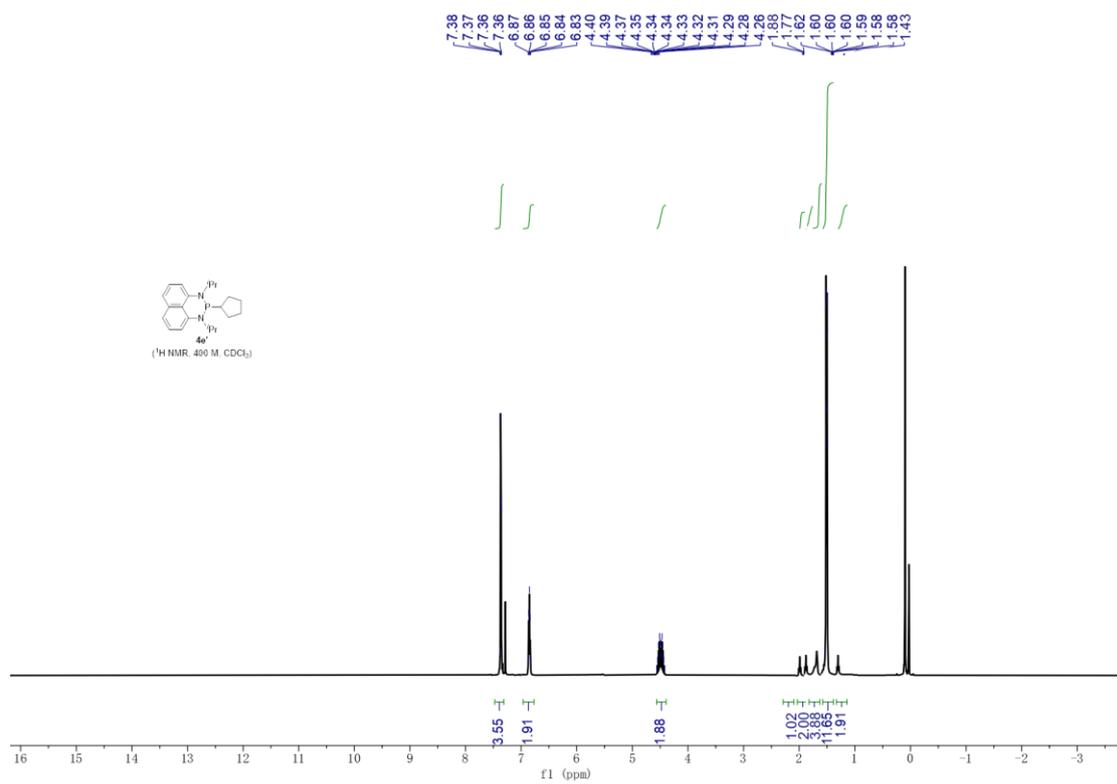


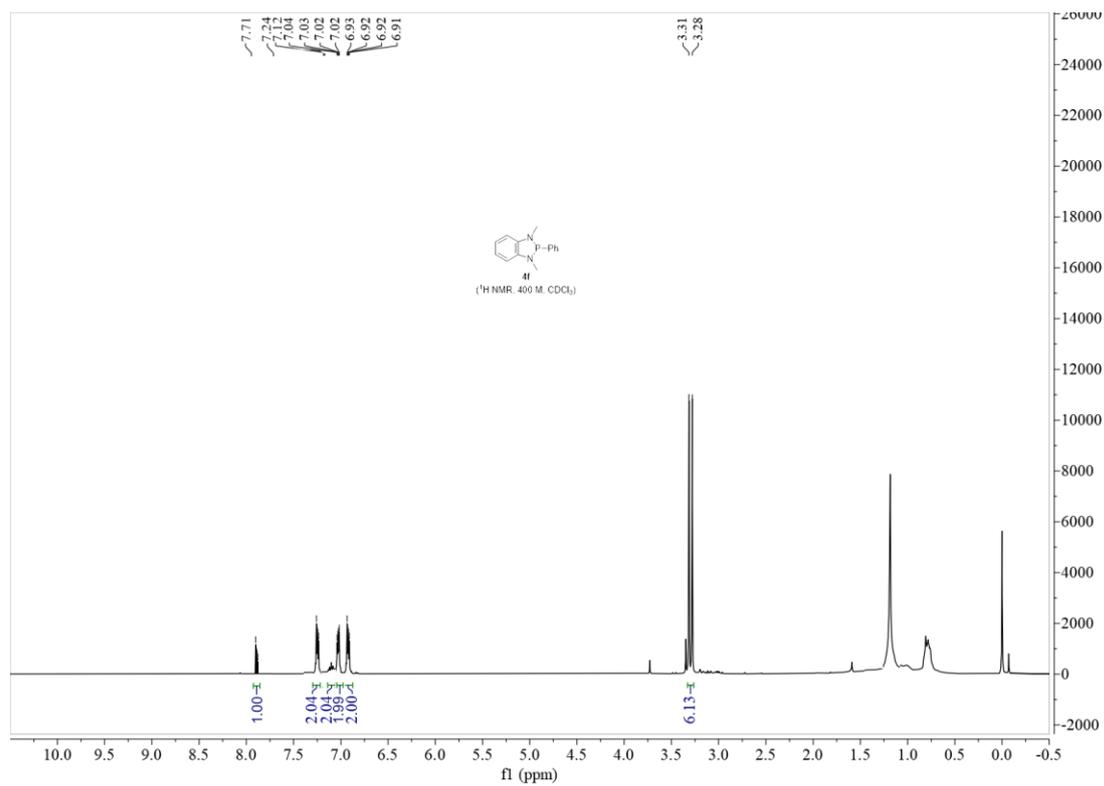
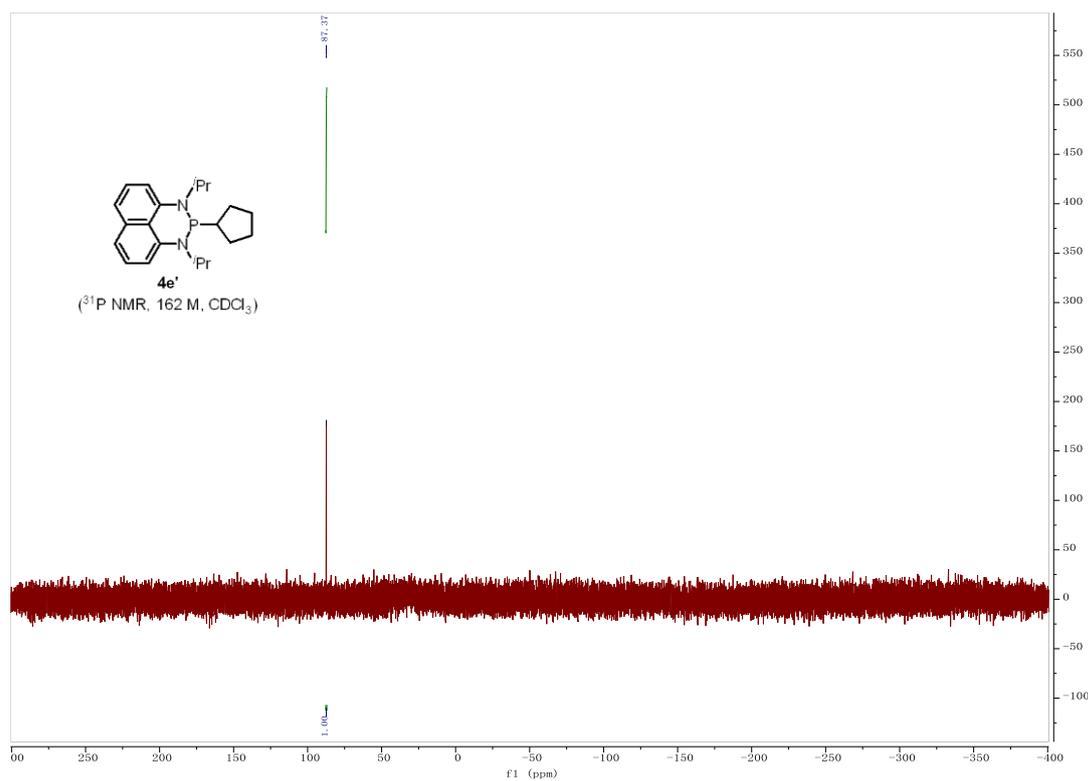


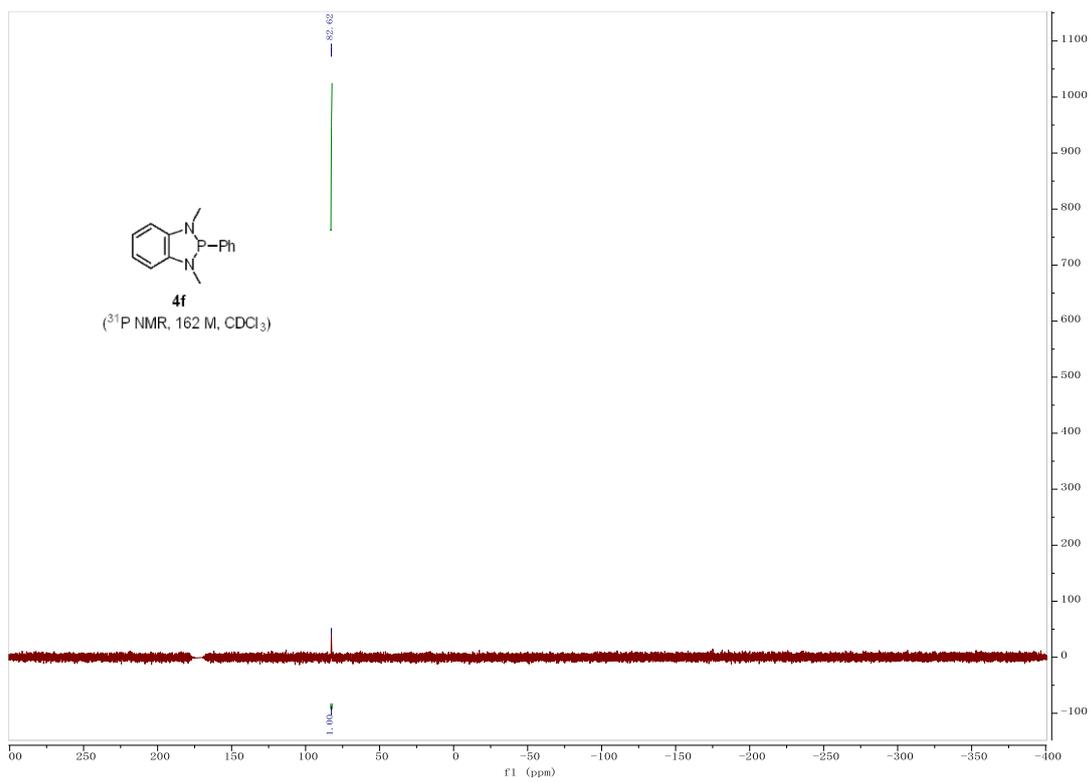
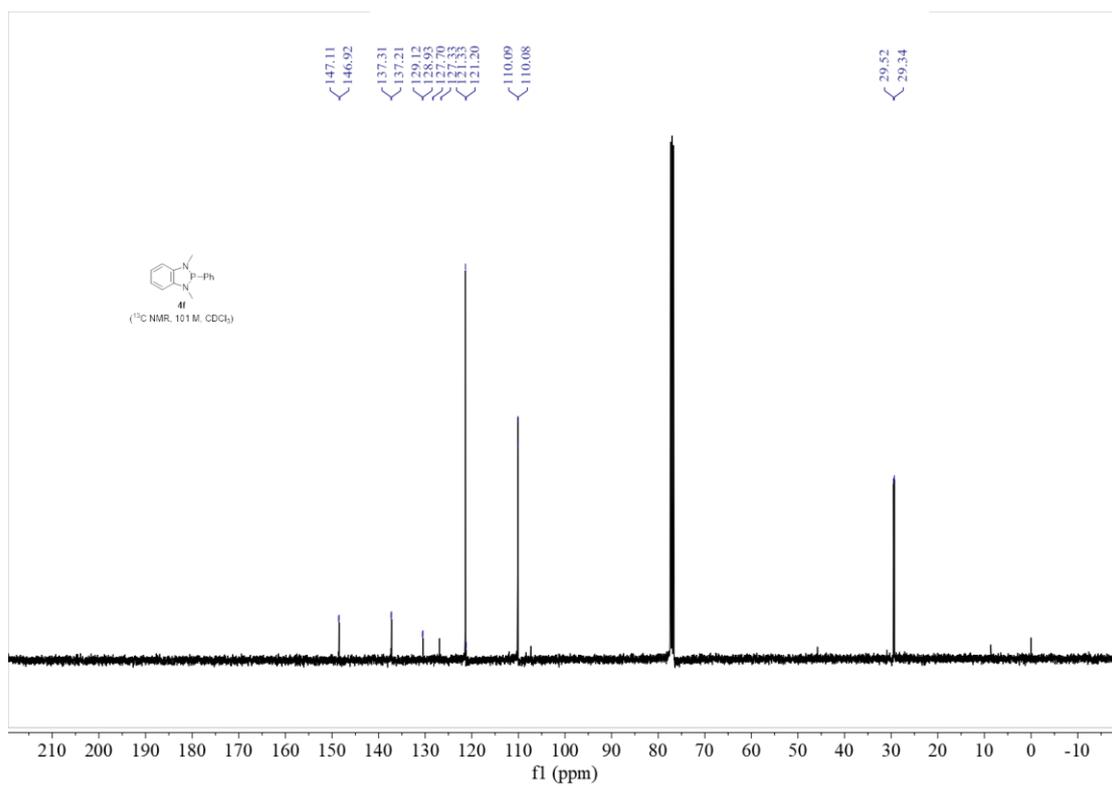


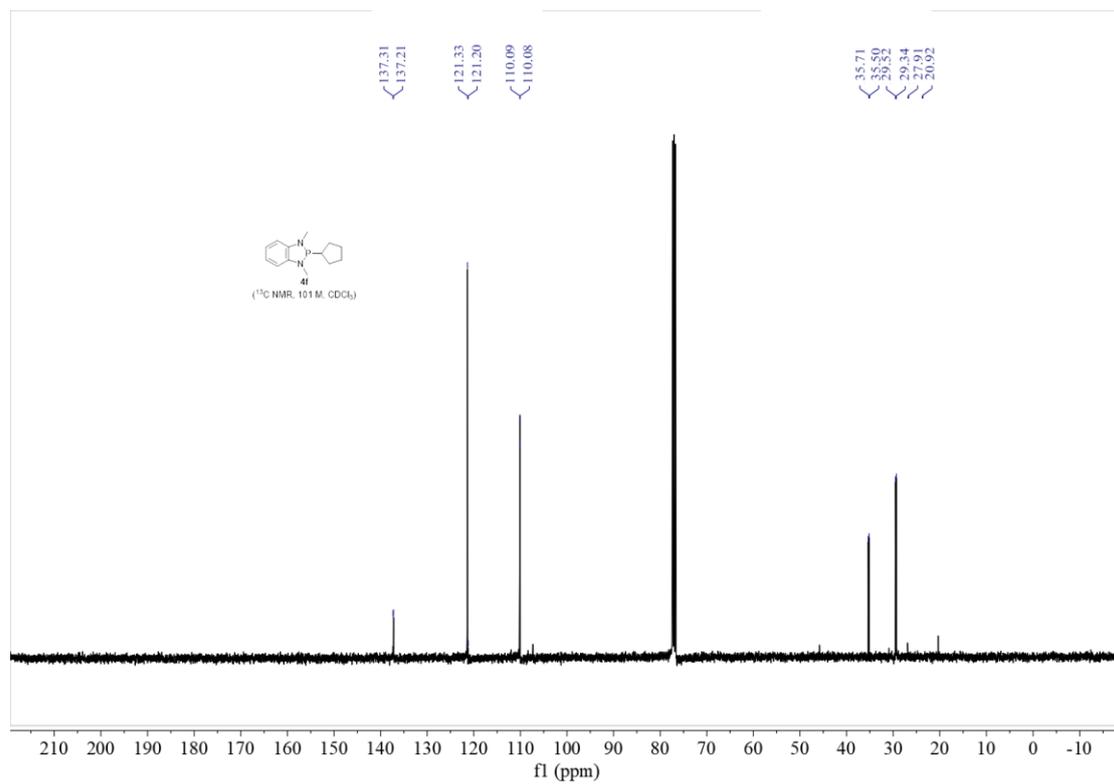
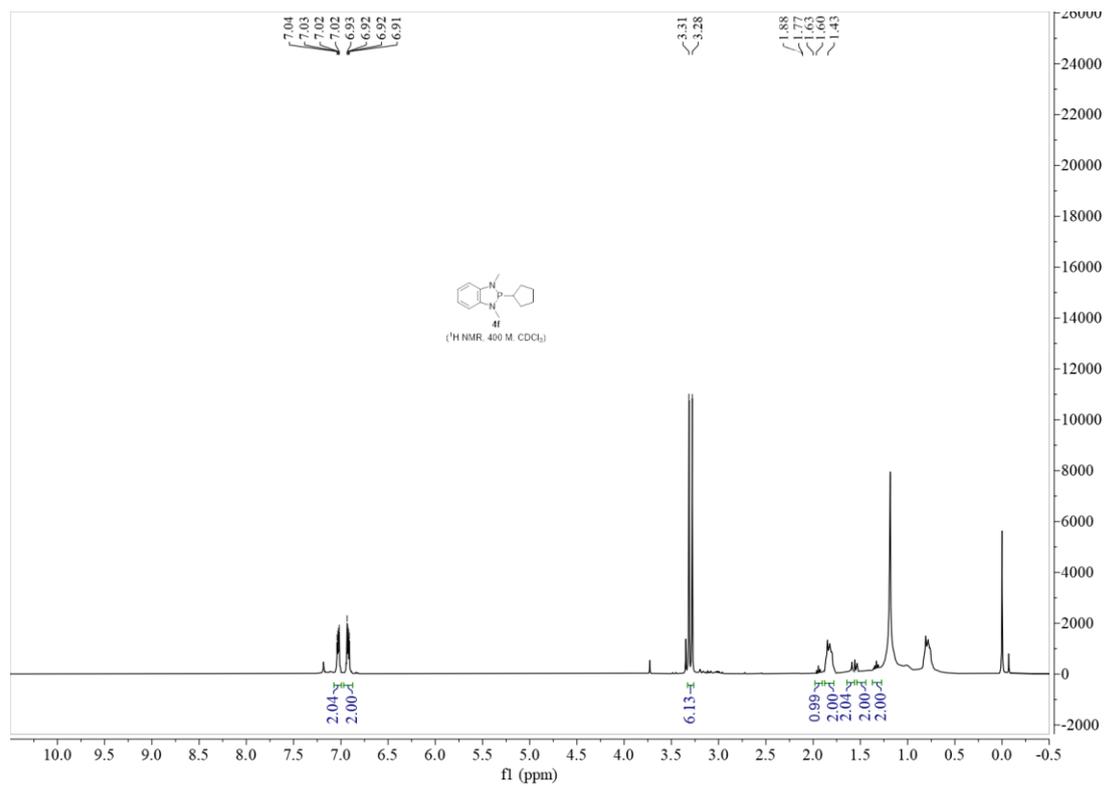


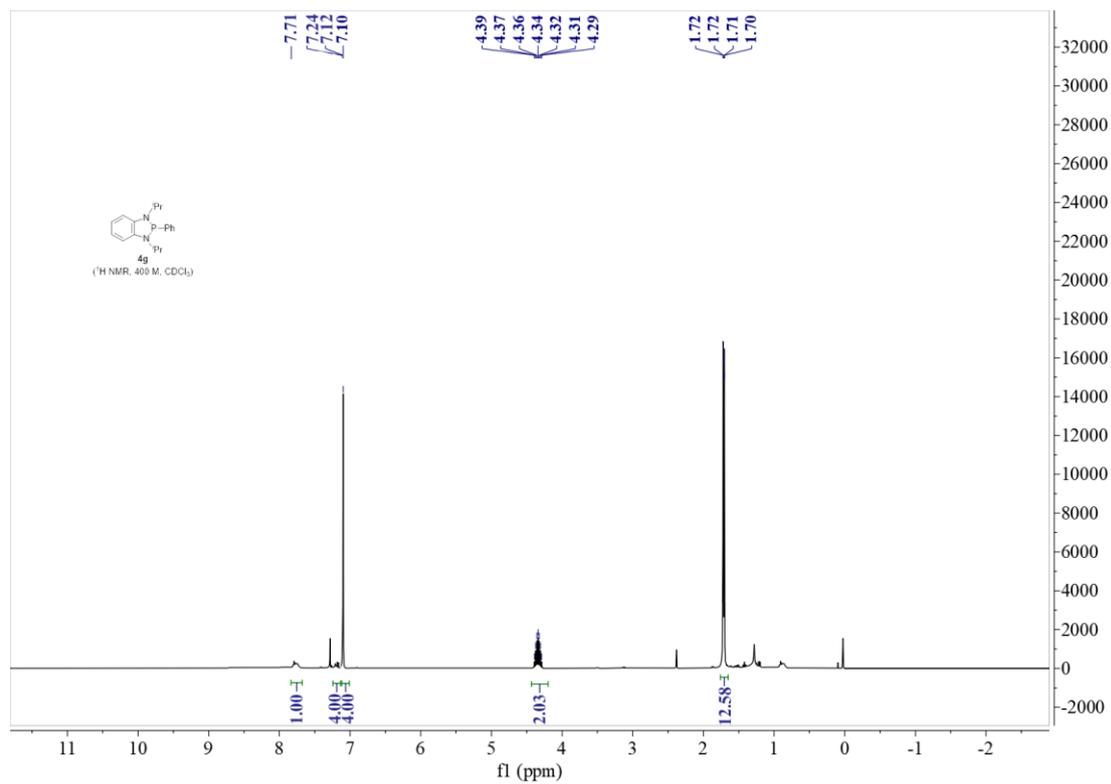
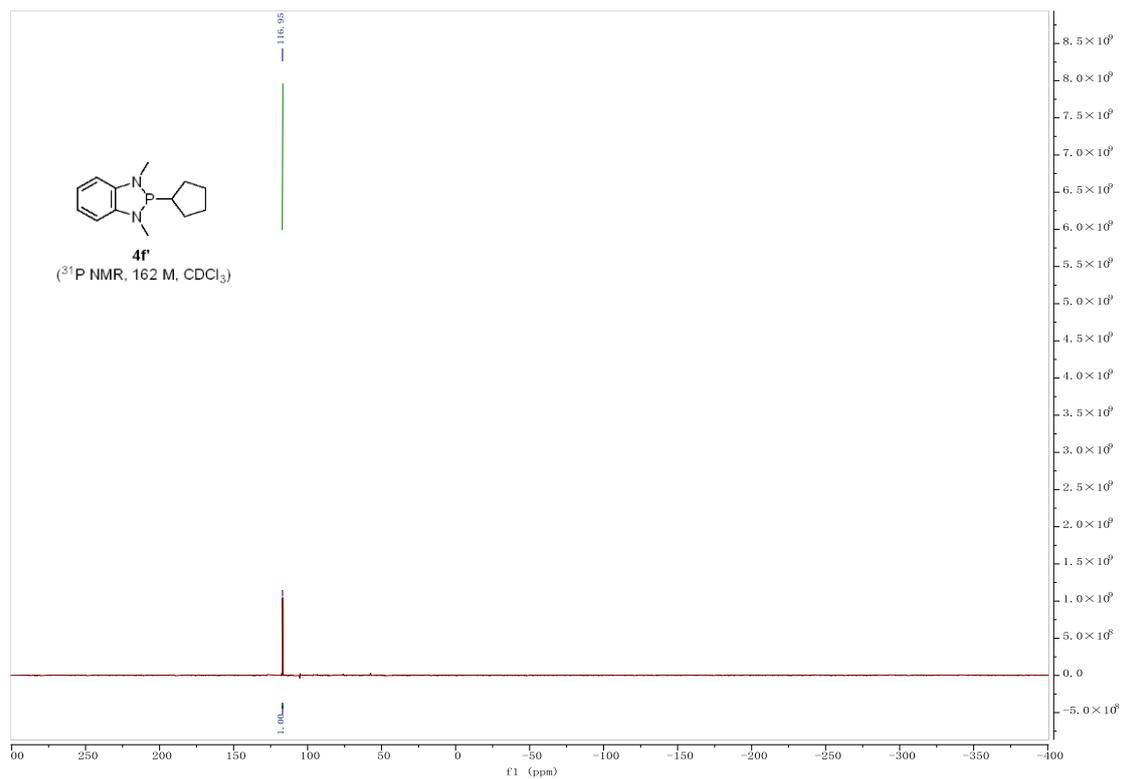


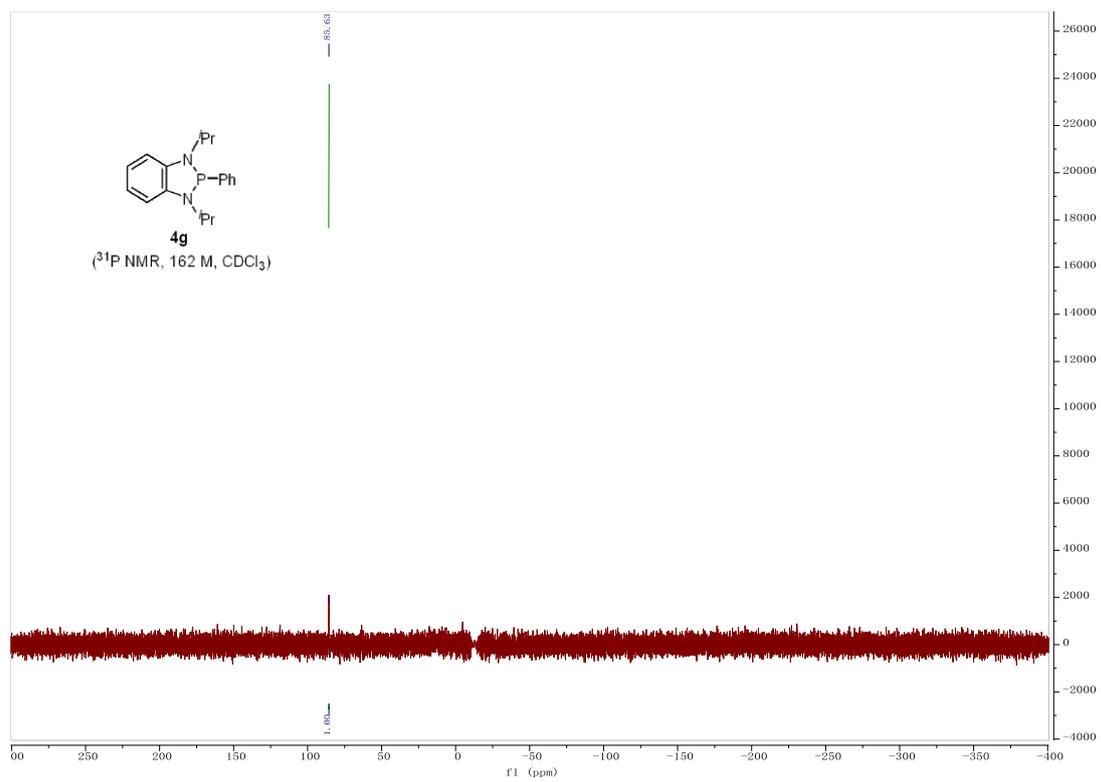
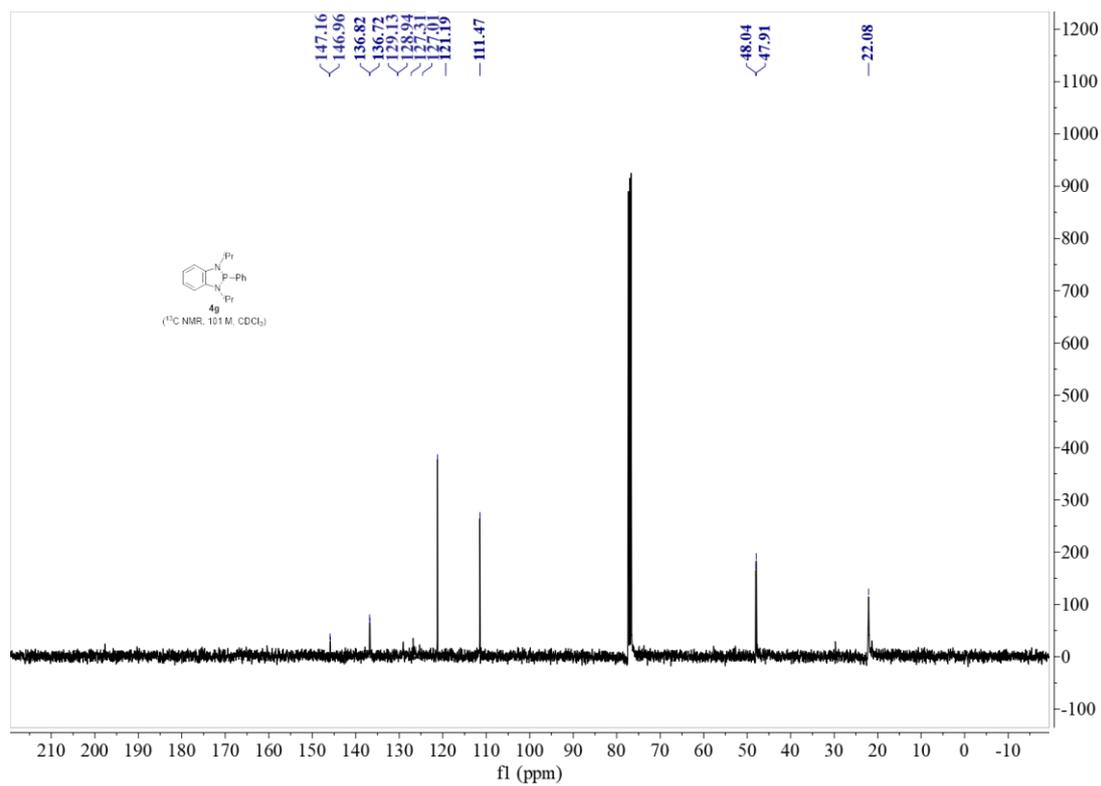


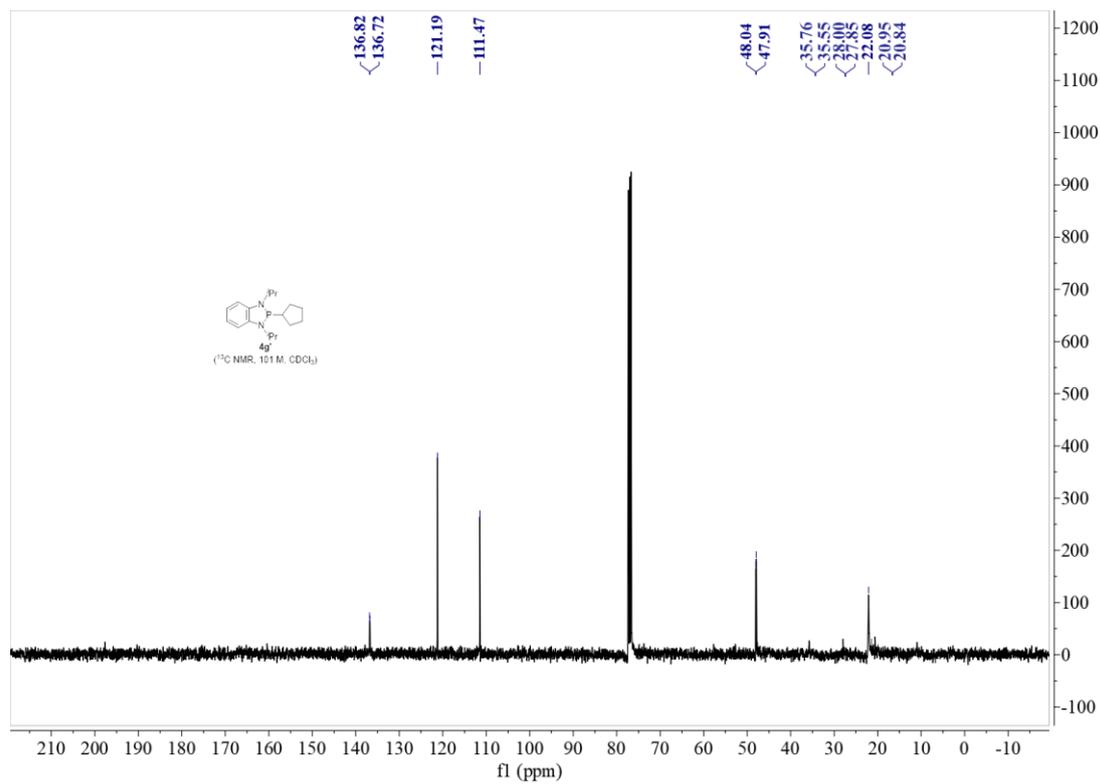
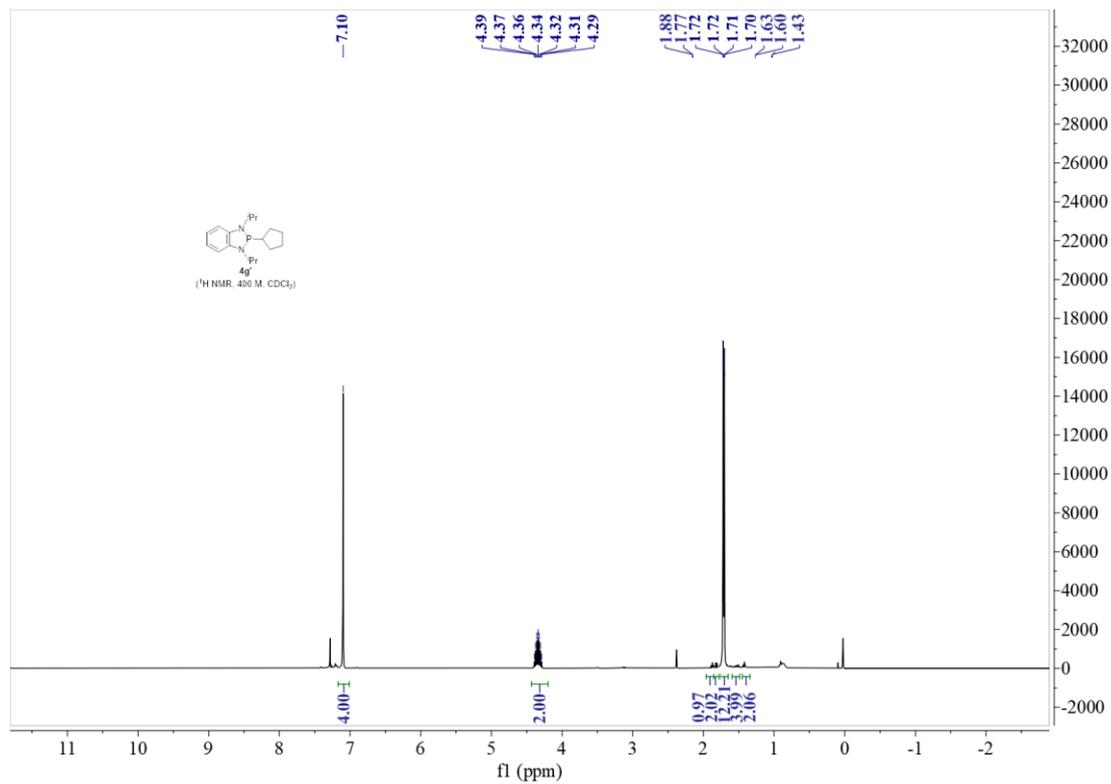


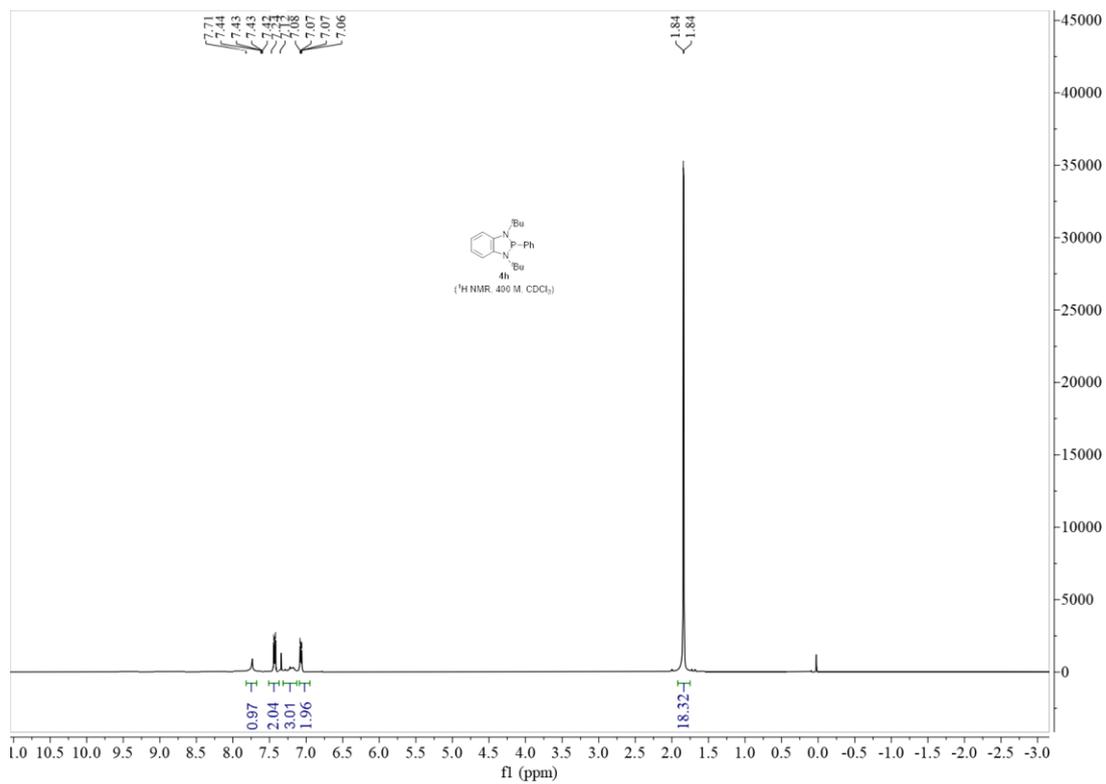
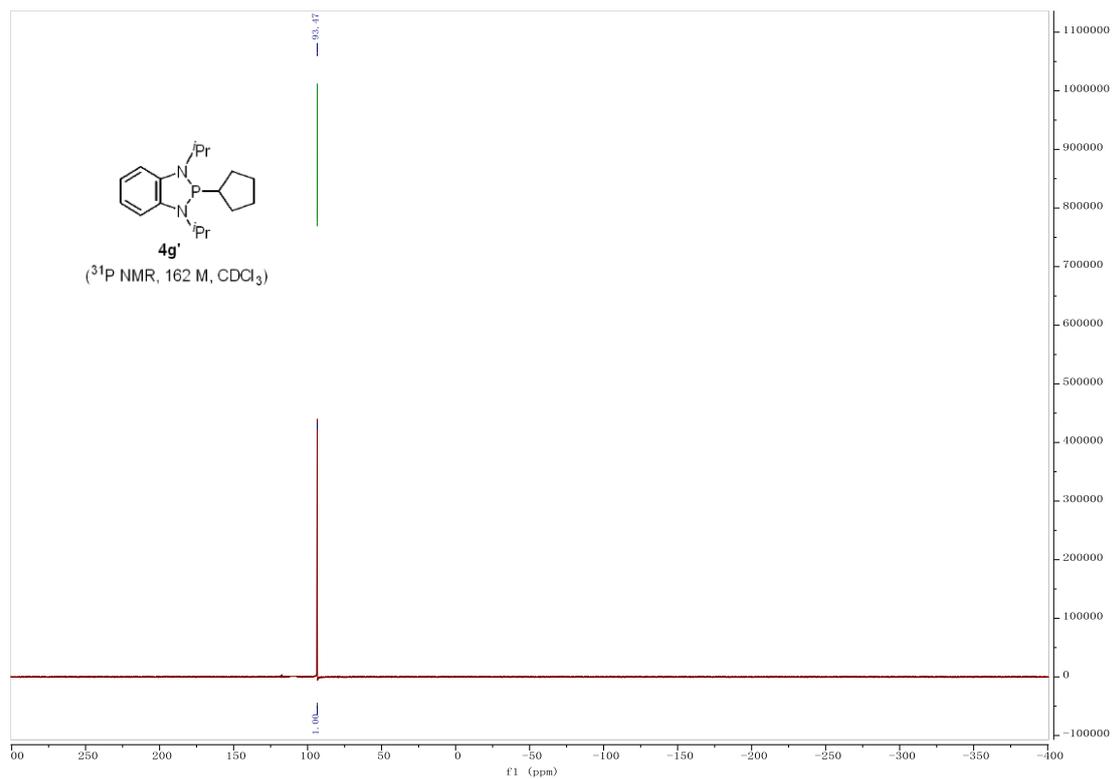


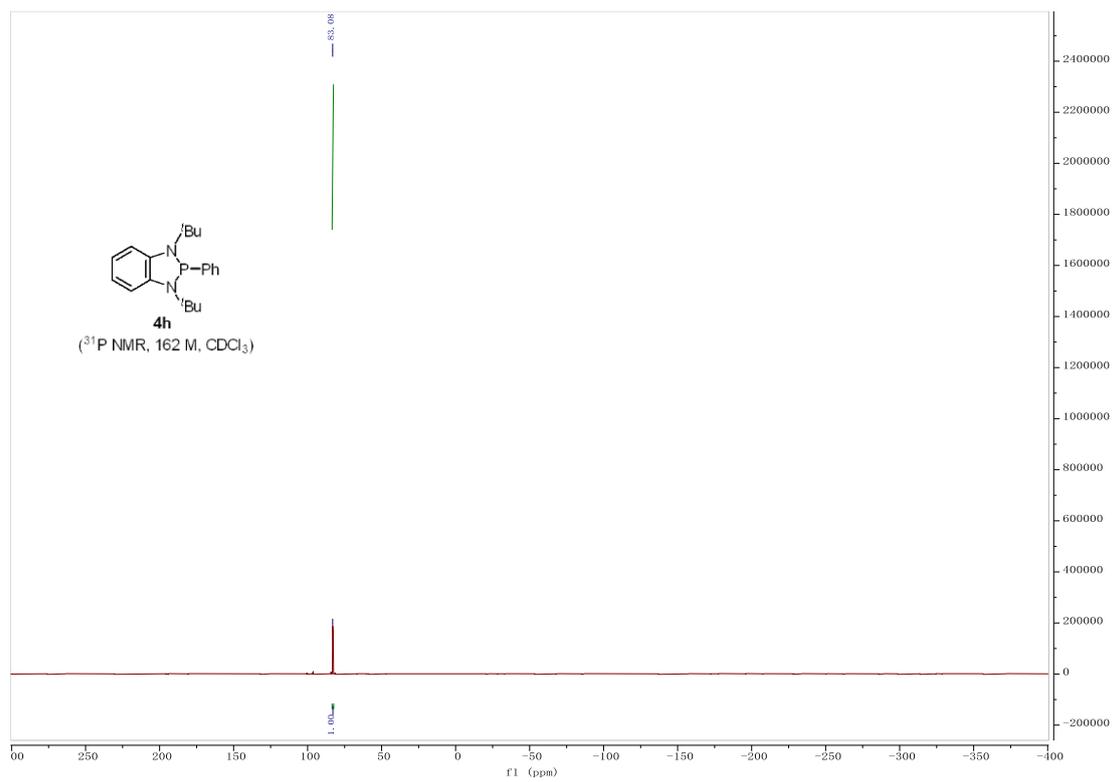
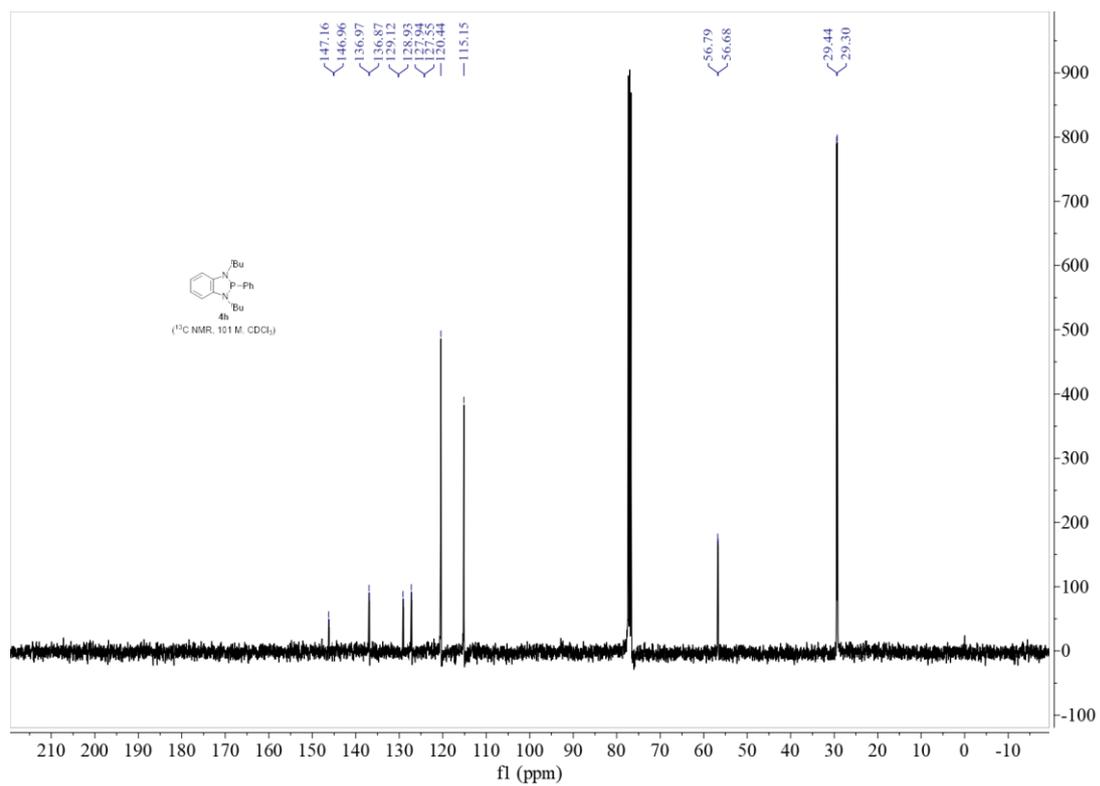


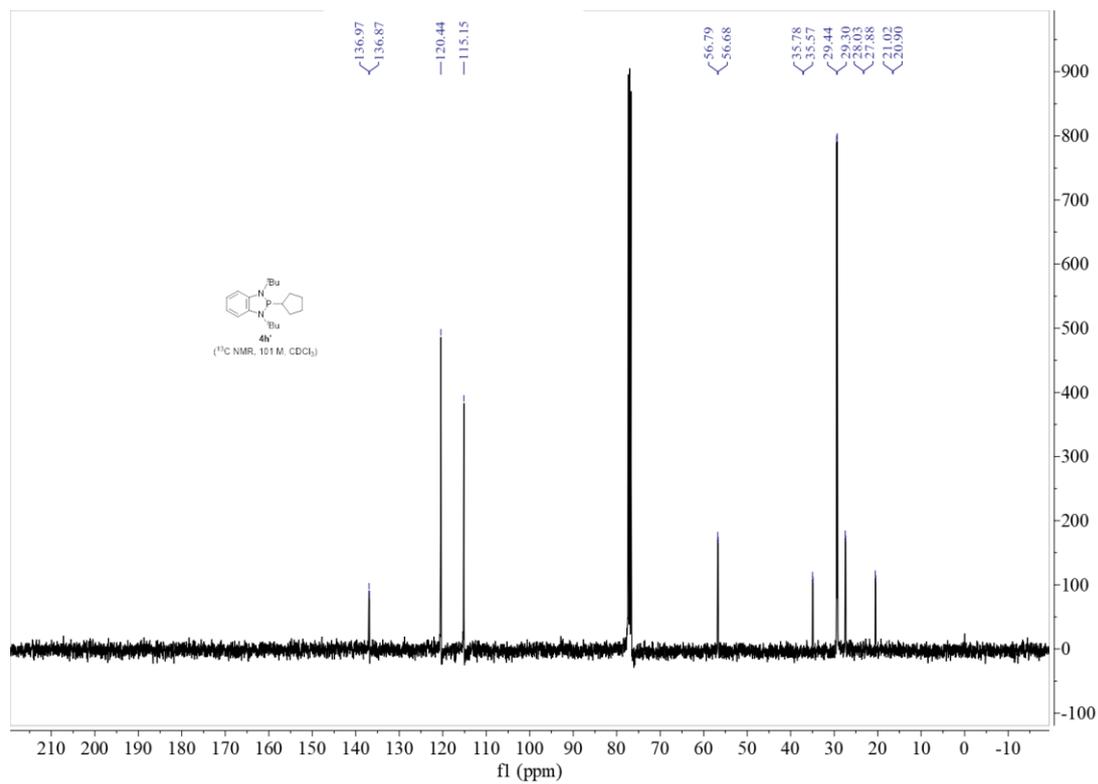
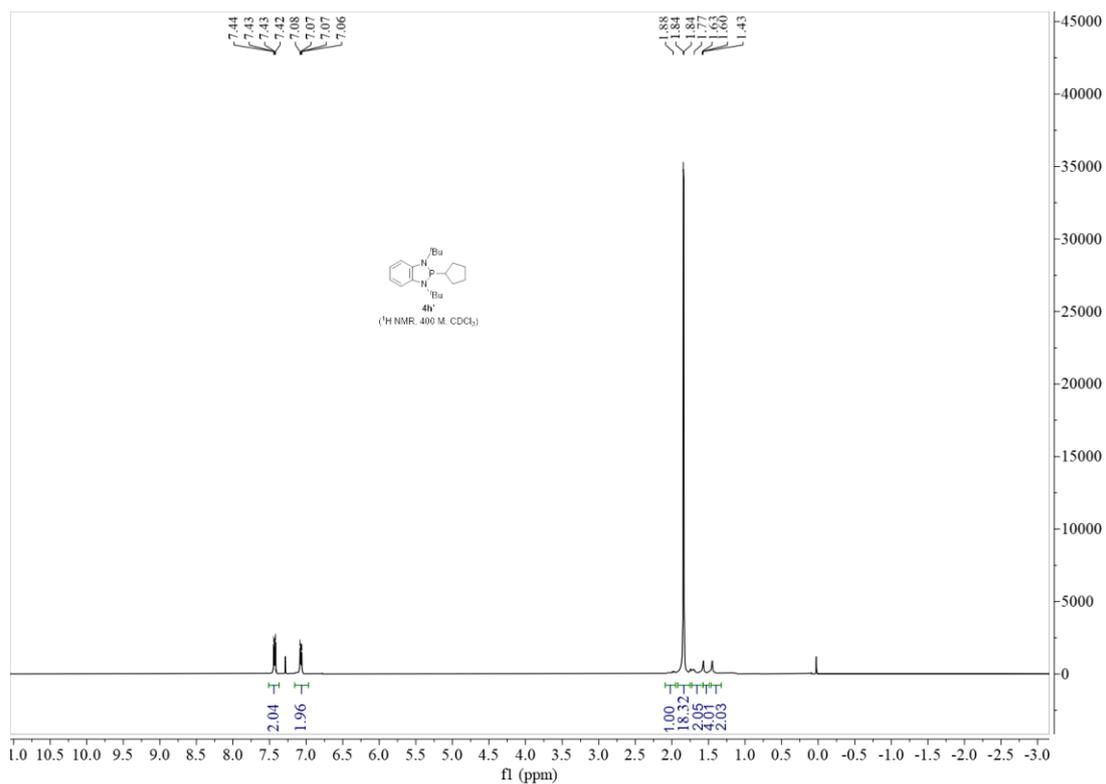


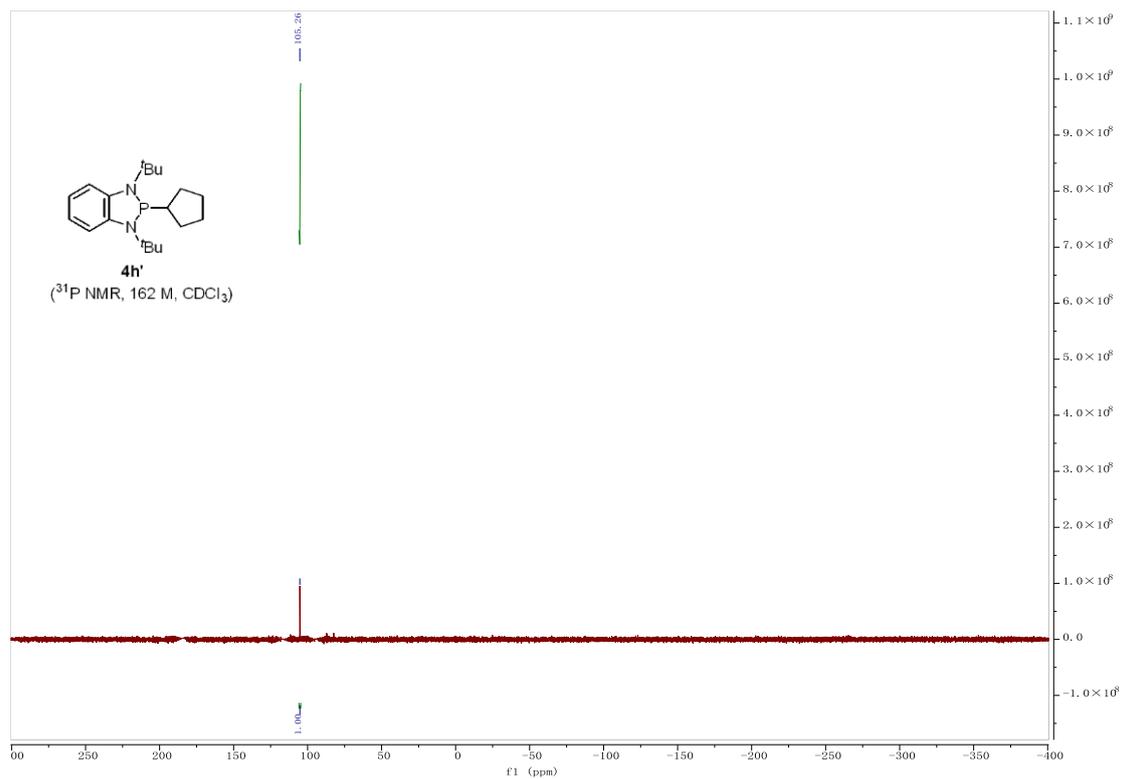












8. References

- 1 J. Klett, Ł. Woźniak and N. Cramer, *Angew. Chem. Int. Ed.*, 2022, **61**, e202202306.
- 2 (a) P. P. Kalapos, P. J. Mayer, T. Gazdag, A. Demeter, B. Oruganti, B. Durbeej and G. London, *J. Org. Chem.*, 2022, **87**, 9532–9542; (b) J. T. Price and P. J. Ragogna, *Chem. Eur. J.*, 2013, **19**, 8473–8477.
- 3 J. Zhang, J.-D. Yang and J.-P. Cheng, *Chem. Sci.*, 2020, **11**, 3672–3679.
- 4 (a) B. Bostai, Z. Novák, A. C. Bényei and A. Kotschy, *Org. Lett.*, 2007, **9**, 3437–3439; (b) W. B. Jennings, D. Randall, S. D. Worley and J. H. Hargis, *J. Chem. Soc., Perkin Trans. 2*, 1981, **10**, 1411–1416.
- 5 D. M. C. Ould, A. C. Rigby, L. C. Wilkins, S. J. Adams, J. A. Platts, S. J. A. Pope, E. Richards and R. L. Melen, *Organometallics*, 2018, **37**, 712–719.
- 6 (a) D. M. Khramov, A. J. Boydston and C. W. Bielawski, *Org. Lett.*, 2006, **8**, 1831–1834; (b) B. Rao, C. C. Chong and R. Kinjo, *J. Am. Chem. Soc.*, 2018, **140**, 652–656.
- 7 B. S. N. Huchenski, K. N. Robertson and A. W. H. Speed, *Eur. J. Org. Chem.*, 2020, **32**, 5140–5144.
- 8 W. Zhang and S. Lin, *J. Am. Chem. Soc.*, 2020, **142**, 20661–20670.
- 9 R. Murugavel and R. Pothiraja, *New J. Chem.*, 2003, **27**, 968–974.