

Accessing Diverse Phosphorylated 2-Aryl Pyridines: A Strategic Protocol from Pd-PEPPSI to Palladium Acetate Catalysis

Mandapalli Sreeshitha and Peddiahgari Vasu Govardhana Reddy*

Department of Chemistry, Yogi Vemana University, Kadapa-516005, Andhra Pradesh, India

Corresponding author email: pvgr@yogivemanauniversity.ac.in

Supporting information

Table of Contents

S. No.	Contents	P. No.
1.	Experimental section	S2
2.	Characteristic data	S2-S11
3.	¹ H, ¹³ C and ³¹ P NMR copies	S12-S34
4.	References	S35

1. Experimental section

1.1 Synthesis of Pd-PEPPSI Complexes

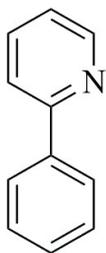
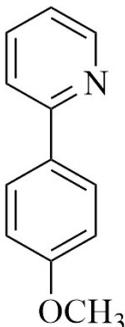
1.1.1 Preparation of Benzimidazolium salts

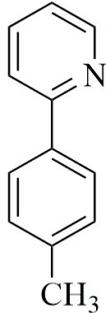
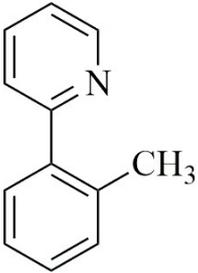
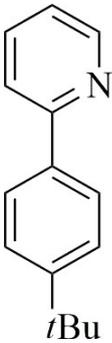
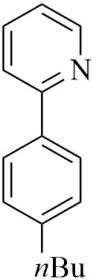
Benzimidazolium salts of corresponding Pd-PEPPSI Complexes were synthesized by following the our previous literature reports.¹

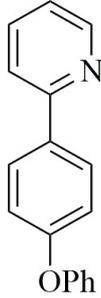
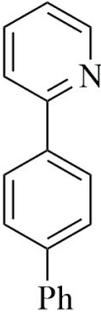
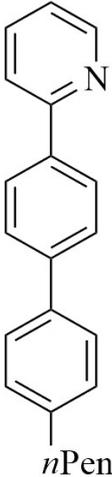
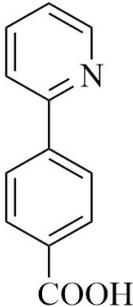
1.1.2 General Procedure for the synthesis of Pd-PEPPSI Complexes (C1-C6)

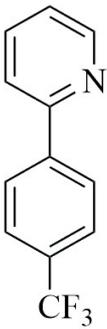
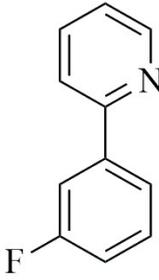
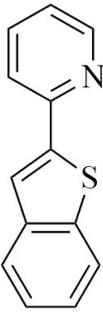
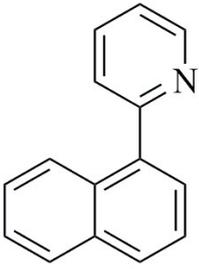
Pd-PEPPSI complexes were prepared under air by heating corresponding benzimidazolium salt (1 mmol, 1 equiv.), K₂CO₃ (5 mmol, 5 equiv.), and PdCl₂ (1.1 mmol, 1.1 equiv.) in 3-chloropyridine (3 mL) at 80 °C for 10–12 h. After cooling, the mixture was filtered through Celite, extracted with ethyl acetate and water, dried over Na₂SO₄, and concentrated. Purification by column chromatography (20% ethyl acetate in hexane) afforded complexes C1-C6 as pale yellow solids.¹

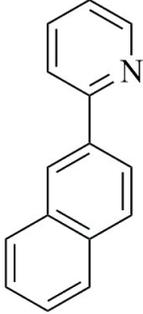
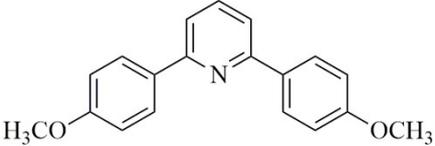
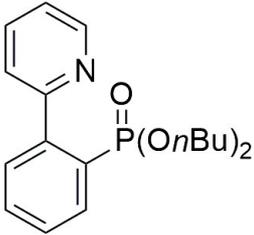
2. Characteristic data

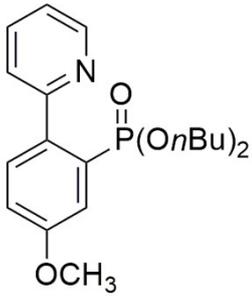
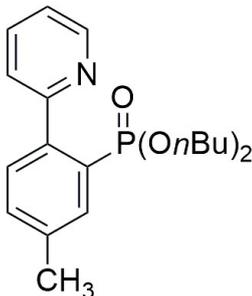
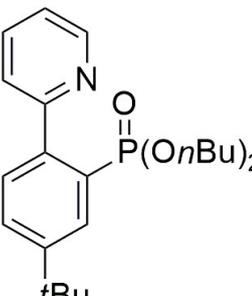
<p>2-Phenylpyridine (3a)²⁻⁵</p> 	<p>Colorless oil; 33 mg, yield 69%; R_f = 0.85 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.66–8.64 (m, 1H, Ar-H), 8.00–7.98 (m, 2H, Ar-H), 7.64–7.58 (m, 2H, Ar-H), 7.46–7.32 (m, 3H, Ar-H), 7.24–7.12 (m, 1H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 157.21 (Ar-C), 149.34 (Ar-C), 139.21 (Ar-C), 136.23 (Ar-C), 128.67 (Ar-C), 128.23 (Ar-C), 126.51 (Ar-C), 121.72 (Ar-C), 120.32 (Ar-C); HRMS (ESI⁺) m/z calcd for C₁₁H₉N [M+H]⁺ 156.0735, found: 156.0732. The spectral data of this compound are in complete agreement with those reported in the literature.³</p>
<p>2-(4-Methoxyphenyl)pyridine (3b)^{2,4,5}</p> 	<p>Colorless solid; m.p. 55-58 °C; 53 mg, yield 92%; R_f = 0.85 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.56 (d, J = 4.6 Hz, 1H, Ar-H), 7.96 (d, J = 8.6 Hz, 2H, Ar-H), 7.72–7.70 (m, 2H, Ar-H), 7.19–7.16 (m, 1H, Ar-H), 7.12 (d, J = 7.6 Hz, 2H, Ar-H), 3.85 (s, 3H, Ar-OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.21 (Ar-C), 156.21 (Ar-C), 148.32 (Ar-C), 136.52 (Ar-C), 132.75 (Ar-C), 129.21 (Ar-C), 122.23 (Ar-C), 119.43 (Ar-C), 113.08 (Ar-C), 52.87 (Ar-OCH₃); HRMS (ESI⁺) m/z calcd for C₁₂H₁₁NO [M+H]⁺ 186.0841, found: 186.0843. The spectral data of this compound are in complete agreement with those reported in the literature.^{2,4,5}</p>

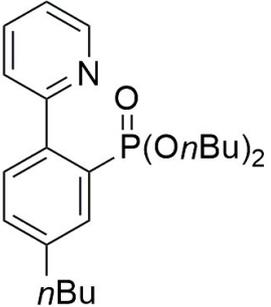
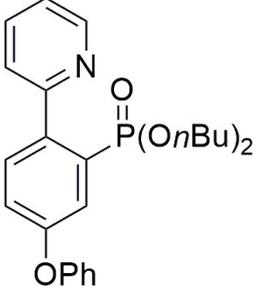
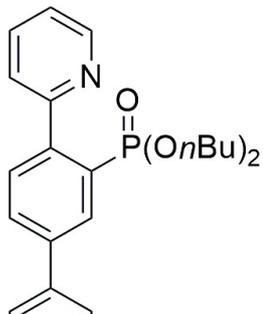
<p>2-(<i>p</i>-Tolyl)pyridine (3c)²⁻⁵</p> 	<p>Colorless oil; 47 mg, yield 89%; $R_f = 0.85$ (EtOAc); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.63 (d, $J = 4.6$ Hz, 1H, Ar-H), 7.88 (d, $J = 8.1$ Hz, 2H, Ar-H), 7.65–7.63 (m, 2H, Ar-H), 7.14 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.12–7.10 (m, 1H, Ar-H), 2.36 (s, 3H, Ar-CH_3); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 156.21 (Ar-C), 148.51 (Ar-C), 136.81 (Ar-C), 135.62 (Ar-C), 134.51 (Ar-C), 128.41 (Ar-C), 124.71 (Ar-C), 120.72 (Ar-C), 121.16 (Ar-C), 21.26 (Ar-CH_3); HRMS (ESI⁺) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{N}$ [$\text{M}+\text{H}$]⁺ 170.0891, found: 170.0893. The spectral data of this compound are in complete agreement with those reported in the literature.³</p>
<p>2-(<i>o</i>-Tolyl)pyridine (3d)^{3,4,6}</p> 	<p>Colorless oil; 46 mg, yield 87%; $R_f = 0.85$ (EtOAc); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.66–8.64 (m, 1H, Ar-H), 7.74 (dt, 1H, $J = 7.6$ & 1.8 Hz, Ar-H), 7.36 (td, 1H, $J = 7.8$ & 1.2 Hz, Ar-H), 7.40 (m, 1H, Ar-H), 7.26 (m, 3H, Ar-H), 7.21–7.24 (m, 1H, Ar-H), 2.36 (s, 3H, Ar-CH_3); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 156.21 (Ar-C), 148.31 (Ar-C), 138.62 (Ar-C), 135.23 (Ar-C), 135.21 (Ar-C), 128.23 (Ar-C), 125.52 (Ar-C), 121.52 (Ar-C), 121.01 (Ar-C), 21.61 (Ar-CH_3); HRMS (ESI⁺) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{N}$ [$\text{M}+\text{H}$]⁺ 170.0891, found: 170.0893. The spectral data of this compound are in complete agreement with those reported in the literature.^{3,4}</p>
<p>2-(4-(<i>tert</i>-Butyl)phenyl)pyridine (3e)⁷</p> 	<p>Colorless oil; 60 mg, yield 91%; $R_f = 0.85$ (EtOAc); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.65 (d, $J = 4.6$ Hz, 1H, Ar-H), 8.10 (d, $J = 7.6$ Hz, 2H, Ar-H), 7.56 (d, $J = 3.5$ Hz, 2H, Ar-H), 7.45 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.21 (dd, $J = 8.3$ & 5.1 Hz, 1H, Ar-H), 1.42 (s, 9H, -$\text{C}(\text{CH}_3)_3$); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 156.21 (Ar-C), 152.51 (Ar-C), 149.01 (Ar-C), 136.30 (Ar-C), 136.08 (Ar-C), 126.25 (Ar-C), 125.12 (Ar-C), 121.85 (Ar-C), 121.21 (Ar-C), 33.34 (-$\text{C}(\text{CH}_3)_3$), 32.36 (-$\text{C}(\text{CH}_3)_3$); HRMS (ESI⁺) m/z calcd for $\text{C}_{15}\text{H}_{17}\text{N}$ [$\text{M}+\text{H}$]⁺ 212.1361, found: 212.1364. The spectral data of this compound are in complete agreement with those reported in the literature.⁷</p>
<p>2-(4-Butylphenyl)pyridine (3f)</p> 	<p>Colorless oil; 60 mg, yield 90%; $R_f = 0.85$ (EtOAc); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.67–8.66 (m, 1H, Ar-H), 7.90–7.88 (m, 2H, Ar-H), 7.74–7.68 (m, 2H, Ar-H), 7.290 (d, $J = 6.4$ Hz, 2H, Ar-H), 7.21–7.18 (m, 1H, Ar-H), 2.67 (t, $J = 6.0$ Hz, 2H, Ar-CH_2-), 1.66–1.60 (m, 2H, -CH_2-), 1.39–1.35 (m, 2H, -CH_2-CH_3), 0.95 (t, $J = 5.6$ Hz, 3H, -CH_2-CH_3); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 157.57 (Ar-C), 149.50 (Ar-C), 144.06 (Ar-C), 136.83 (Ar-C), 129.35 (Ar-C), 128.89 (Ar-C), 126.86 (Ar-C), 121.85 (Ar-C), 120.47 (Ar-C), 115.18 (Ar-C), 35.43 (Ar-CH_2-), 33.55 (-CH_2-), 22.38 (-CH_2-CH_3), 13.99 (-CH_2-CH_3); HRMS (ESI⁺) m/z calcd for $\text{C}_{15}\text{H}_{17}\text{N}$</p>

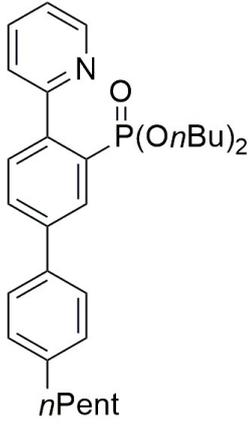
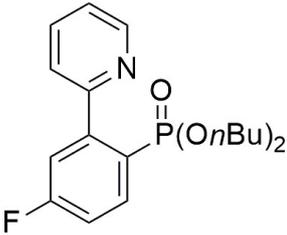
<p>2-(4-Phenoxyphenyl)pyridine (3g)</p> 	<p>[M+H]⁺ 212.1361, found: 212.1364.</p> <p>Colorless solid; m. p. 46-48 °C; 72 mg, yield 92%; R_f = 0.85 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.60-8.58 (m, 1H, Ar-H), 7.91-7.87 (m, 2H, Ar-H), 7.68-7.59 (m, 2H, Ar-H), 7.30-7.25 (m, 2H, Ar-H), 7.14-7.11 (m, 1H, Ar-H), 7.07-6.97 (m, 5H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.33 (Ar-C), 156.87 (Ar-C), 149.58 (Ar-C), 136.86 (Ar-C), 134.35 (Ar-C), 129.85 (Ar-C), 128.47 (Ar-C), 123.60 (Ar-C), 121.83 (Ar-C), 120.21 (Ar-C), 119.23 (Ar-C), 118.84 (Ar-C); HRMS (ESI⁺) m/z calcd for C₁₇H₁₃NO [M+H]⁺ 248.0997, found: 248.0995.</p>
<p>2-([1,1'-Biphenyl]-4-yl)pyridine (3h)⁷</p> 	<p>Colorless solid; m.p. 48-50 °C; 62 mg, yield 85%; R_f = 0.85 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.73 (d, <i>J</i> = 4.7 Hz, 1H, Ar-H), 8.21 (d, <i>J</i> = 8.4 Hz, 2H, Ar-H), 7.86 – 7.80 (m, 2H, Ar-H), 7.76 (d, <i>J</i> = 8.3 Hz, 2H, Ar-H), 7.75 – 7.66 (m, 2H, Ar-H), 7.45 (t, <i>J</i> = 7.6 Hz, 2H, Ar-H), 7.39 (t, <i>J</i> = 7.3 Hz, 1H, Ar-H), 7.31-7.25 (m, 1H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 156.21 (Ar-C), 148.34 (Ar-C), 141.76 (Ar-C), 140.87 (Ar-C), 139.38 (Ar-C), 135.96 (Ar-C), 126.14 (Ar-C), 127.58 (Ar-C), 127.44 (Ar-C), 127.35 (Ar-C), 127.10 (Ar-C), 122.65 (Ar-C), 120.87 (Ar-C); HRMS (ESI⁺) m/z calcd for C₁₇H₁₃N [M+H]⁺ 232.1048, found: 232.1045. The spectral data of this compound are in complete agreement with those reported in the literature.⁷</p>
<p>2-(4'-pentyl-[1,1'-biphenyl]-4-yl)pyridine (3i)</p> 	<p>Colorless solid; m.p. 85-87 °C; 83 mg, yield 88%; R_f = 0.85 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.71 (d, <i>J</i> = 3.6 Hz, 1H, Ar-H), 8.07 (d, <i>J</i> = 6.8 Hz, 2H, Ar-H), 7.78 – 7.73 (m, 2H, Ar-H), 7.71 (d, <i>J</i> = 6.4 Hz, 2H, Ar-H), 7.58 (d, <i>J</i> = 6.4 Hz, 2H, Ar-H), 7.28 (d, <i>J</i> = 6.4 Hz, 2H, Ar-H), 7.24-7.21 (m, 1H, Ar-H), 2.67 (t, <i>J</i> = 6.4 Hz, 2H, Ar-CH₂-), 1.69 (quin, = 6.0 Hz, 2H, Ar-CH₂-CH₂-CH₂-), 1.38-1.34 (m, 4H, -CH₂-CH₂-), 0.92 (t, <i>J</i> = 5.6 Hz, 3H, -CH₂-CH₃) ; ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 157.15 (Ar-C), 149.74 (Ar-C), 142.48 (Ar-C), 141.70 (Ar-C), 137.98 (Ar-C), 137.89 (Ar-C), 136.76 (Ar-C), 128.93 (Ar-C), 127.27 (Ar-C), 126.94 (Ar-C), 122.06 (Ar-C), 120.43 (Ar-C), 35.64 (Ar-CH₂-), 31.59 (Ar-CH₂-CH₂-CH₂-), 31.22 (Ar-CH₂-CH₂-CH₂-), 22.60 (-CH₂-CH₃), 14.08 (-CH₂-CH₃) ; HRMS (ESI⁺) m/z calcd for C₂₂H₂₃N [M+H]⁺ 302.1830, found: 302.1834.</p>
<p>4-(Pyridin-2-yl)benzoic acid (3j)</p> 	<p>Colorless solid; m.p. 191-193 °C; 42 mg, yield 67 %; R_f = 0.85 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.85-7.79 (m, 1H, Ar-H), 7.70-7.66 (m, 1H, Ar-H), 7.44 – 7.32 (m, 3H, Ar-H), 7.24-7.21 (m, 2H, Ar-H), 6.79 (d, <i>J</i> = 3.2 Hz, 1H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 142.96 (Ar-C), 135.00 (Ar-C), 134.03 (d, <i>J</i> = 7.3</p>

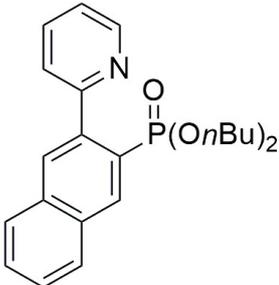
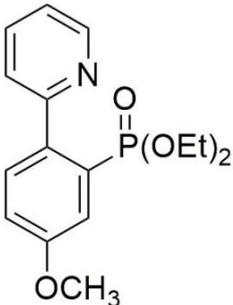
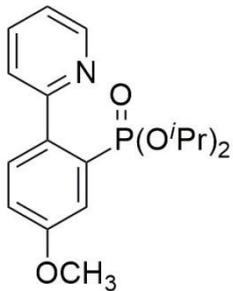
	<p>Hz, Ar-C), 133.44 (d, $J = 14.6$ Hz, Ar-C), 132.57 (d, $J = 10.2$ Hz, Ar-C), 132.09 (d, $J = 9.1$ Hz, Ar-C), 131.16 (d, $J = 22.0$ Hz, Ar-C), 129.56 (Ar-C), 128.50 (Ar-C), 127.42 (Ar-C), 125.88 (Ar-C); HRMS (ESI⁺) m/z calcd for C₁₂H₉NO₂ [M+H]⁺ 200.0633, found: 200.0637.</p>
<p>2-(4-(Trifluoromethyl)phenyl)pyridine (3k)⁷</p> 	<p>Colorless solid; m.p. 76-78 °C; 45 mg, yield 65%; $R_f = 0.85$ (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.72 (d, $J = 4.6$ Hz, 1H, Ar-H), 8.12 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.84-7.65 (m, 4H, Ar-H), 7.35 (t, $J = 6.5$ Hz, 1H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 156.32 (Ar-C), 149.65 (Ar-C), 142.65 (Ar-C), 135.23 (Ar-C), 131.54 (Ar-C), 126.43 (Ar-C), 125.21 (Ar-C), 124.23 (q, $J = 272.0$ Hz, Ar-CF₃), 122.84 (Ar-C), 121.21 (Ar-C); HRMS (ESI⁺) m/z calcd for C₁₂H₈F₃N [M+H]⁺ 224.0609, found: 224.0612. The spectral data of this compound are in complete agreement with those reported in the literature.⁷</p>
<p>2-(3-Fluorophenyl)pyridine (3m)^{10,11}</p> 	<p>Colorless oil; 43 mg, yield 80%; $R_f = 0.85$ (EtOAc); ¹H NMR (400 MHz, DMSO-<i>d</i>₆): δ (ppm) 7.16-8.08 (m, 7H, Ar-H), 8.66-8.79 (m, 1H, Ar-H); ¹³C NMR (100 MHz, DMSO-<i>d</i>₆): δ (ppm) 156.21 (Ar-C), 148.67 (Ar-C), 137.23 (Ar-C), 136.43 (Ar-C), 129.54 (Ar-C), 128.64 (Ar-C), 128.23 (Ar-C), 128.35 (Ar-C), 126.40 (Ar-C), 122.51 (Ar-C), 120.10 (Ar-C); HRMS (ESI⁺) m/z calcd for C₁₁H₈FN [M+H]⁺ 174.0641, found: 174.0645. The spectral data of this compound are in complete agreement with those reported in the literature.¹⁰</p>
<p>2-(Benzo[<i>b</i>]thiophen-2-yl)pyridine (3o)^{8,9}</p> 	<p>Colorless solid; m.p. 124-126 °C; 43 mg, yield 80%; $R_f = 0.85$ (EtOAc); ¹H NMR (400 MHz, DMSO-<i>d</i>₆): δ (ppm) 8.62 (d, $J = 4.3$ Hz, 1H, Ar-H), 8.15 (s, 1H, Ar-H), 8.16 (d, $J = 8.2$ Hz, 1H, Ar-H), 7.99 (dt, $J = 7.9$ & 2.4 Hz, 1H, Ar-H), 7.89-7.86 (m, 2H, Ar-H), 7.36-7.32 (m, 3H, Ar-H); ¹³C NMR (100 MHz, DMSO-<i>d</i>₆): δ (ppm) 151.62 (Ar-C), 148.53 (Ar-C), 144.64 (Ar-C), 141.32 (Ar-C), 138.93 (Ar-C), 137.34 (Ar-C), 125.21 (Ar-C), 124.42 (Ar-C), 124.23 (Ar-C), 123.65 (Ar-C), 122.62 (Ar-C), 121.45 (Ar-C), and 119.74 (Ar-C); HRMS (ESI⁺) m/z calcd for C₁₃H₉NS [M+H]⁺ 212.0456, found: 212.0460. The spectral data of this compound are in complete agreement with those reported in the literature.⁹</p>
<p>2-(Naphthalen-1-yl)pyridine (3p)³</p> 	<p>Yellow oil; 53 mg, yield 83%; $R_f = 0.85$ (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.78 (dd, $J = 4.8$ & 1.7 Hz, 1H, Ar-H), 8.15 (dd, $J = 7.2$ & 2.6 Hz, 1H, Ar-H), 7.86 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.81 (dt, $J = 7.7$ & 1.7 Hz, 1H, Ar-H), 7.57-7.53 (m, 5H, Ar-H), 7.33-7.31 (m, 1H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.79 (Ar-C), 149.31 (Ar-C), 139.46 (Ar-C), 135.15 (Ar-C), 133.81 (Ar-C), 130.22 (Ar-C), 128.31 (Ar-C),</p>

	128.08 (Ar-C), 127.12 (Ar-C), 126.82 (Ar-C), 126.01 (Ar-C), 125.71 (Ar-C), 125.21 (Ar-C), 124.26 (Ar-C), 122.01 (Ar-C); HRMS (ESI ⁺) m/z calcd for C ₁₅ H ₁₁ N [M+H] ⁺ 206.0891, found: 206.0895. The spectral data of this compound are in complete agreement with those reported in the literature. ³
2-(naphthalen-2-yl)pyridine (3q)³ 	Yellow solid; m.p. 77-78 °C; 54 mg, yield 85%; R _f = 0.85 (EtOAc); ¹H NMR (400 MHz, CDCl ₃): 8.76 (d, <i>J</i> = 4.2 Hz, 1H, Ar-H), 8.50 (s, 1H, Ar-H), 8.15 (dd, <i>J</i> = 8.6 & 1.5 Hz, 1H, Ar-H), 7.92 (m, 4H, Ar-H), 7.84 (td, <i>J</i> = 7.5 & 1.8 Hz, 1H, Ar-H), 7.54 (m, 2H, Ar-H), 7.24 (dd, <i>J</i> = 7.5 & 4.2 Hz, 1H, Ar-H); ¹³C NMR (100 MHz, CDCl ₃): δ (ppm) 156.21 (Ar-C), 148.52 (Ar-C), 136.98 (Ar-C), 133.21 (Ar-C), 133.31 (Ar-C), 128.91 (Ar-C), 128.51 (Ar-C), 127.81 (Ar-C), 126.51 (Ar-C), 126.31 (Ar-C), 123.21 (Ar-C), 122.11 (Ar-C), 120.12 (Ar-C). HRMS (ESI ⁺) m/z calcd for C ₁₅ H ₁₁ N [M+H] ⁺ 206.0891, found: 206.0895. The spectral data of this compound are in complete agreement with those reported in the literature. ³
2,6-bis(4-methoxyphenyl)pyridine (6) 	Colorless solid; m.p. 143-145 °C; 82 mg, yield 90%; R _f = 0.85 (EtOAc); ¹H NMR (400 MHz, CDCl ₃): δ (ppm) 8.11 (d, <i>J</i> = 7.2 Hz, 4H, Ar-H), 7.75 (t, <i>J</i> = 6.4 Hz, 1H, Ar-H), 7.57 (d, <i>J</i> = 6.0 Hz, 2H, Ar-H), 7.25 (s, 1H, Ar-H), 7.02 (d, <i>J</i> = 7.2 Hz, 3H, Ar-H), 3.87 (s, 6H, Ar-OCH ₃); ¹³C NMR (100 MHz, CDCl ₃): δ (ppm) 160.51 (Ar-C), 156.34 (Ar-C), 137.31 (Ar-C), 132.32 (Ar-C), 128.24 (Ar-C), 117.19 (Ar-C), 114.03 (Ar-C), 55.39 (Ar-OCH ₃); HRMS (ESI ⁺) m/z calcd for C ₁₉ H ₁₇ NO ₂ [M+H] ⁺ 292.1259, found: 292.1256.
Dibutyl (2-(pyridin-2-yl)phenyl)phosphonate (5a)¹² 	Colorless oil; 13 mg, yield 10%; R _f = 0.85 (EtOAc); ¹H NMR (400 MHz, CDCl ₃): δ (ppm) 8.64 (d, <i>J</i> = 4.8 Hz, 1H, Ar-H), 7.98 (dd, <i>J</i> = 14.4 Hz, 1H, Ar-H), 7.71-7.64 (m, 2H, Ar-H), 7.64-7.61 (m, 1H, Ar-H), 7.58-7.55 (m, 1H, Ar-H), 7.49-7.46 (m, 1H, Ar-H), 7.26-7.23 (m, 1H, Ar-H), 3.96-3.87 (m, 2H, -OCH ₂ -), 3.88-3.79 (m, 2H, -O-CH ₂ -), 1.52-1.44 (m, 4H, -O-CH ₂ -CH ₂ -CH ₂ -), 1.32-1.23 (m, 4H, -CH ₂ -CH ₃), 0.83 (t, <i>J</i> = 7.6 Hz, 6H, -CH ₂ -CH ₃); ¹³C NMR (100 MHz, CDCl ₃): δ (ppm) 158.6 (d, <i>J</i> = 4.0 Hz, Ar-C), 148.80 (Ar-C), 143.5 (Ar-C), 135.43 (Ar-C), 132.63 (d, <i>J</i> = 9.6 Hz, Ar-C), 128.41 (d, <i>J</i> = 2.9 Hz, Ar-C), 130.6 (Ar-C), 127.89 (Ar-C), 125.02 (Ar-C), 118.73 (d, <i>J</i> = 8.2 Hz, Ar-C), 118.03 (d, <i>J</i> = 2.6 Hz, Ar-C), 65.60 (d, <i>J</i> = 4.8 Hz, O-CH ₂ -), 32.30 (d, <i>J</i> = 5.4 Hz, O-CH ₂ -CH ₂ -), 18.62 (-CH ₂ -CH ₃), 13.30 (-CH ₂ -CH ₃); ³¹P NMR (162 MHz, CDCl ₃): δ (ppm) 24.02; HRMS (ESI ⁺) m/z calcd for C ₁₉ H ₂₆ NO ₃ P [M+H] ⁺ 348.1650, found: 348.1654. The spectral data of this compound are in complete agreement with those reported in the literature. ¹²
Dibutyl (5-methoxy-2-(pyridin-2-yl)phenyl)phosphonate (5b)	Colorless oil; 96 mg, yield 79%; R _f = 0.15 (EtOAc); ¹H NMR

	<p>NMR (400 MHz, CDCl₃): δ (ppm) 8.65 (d, <i>J</i> = 4.8 Hz, 1H, Ar-H), 7.72-7.64 (m, 2H, Ar-H), 7.58 (dd, <i>J</i> = 2.4 & 13.2 Hz, 1H, Ar-H), 7.49-7.46 (m, 1H, Ar-H), 7.26-7.23 (m, 1H, Ar-H), 7.14 (dd, <i>J</i> = 2.4 & 6.0 Hz, 1H, Ar-H), 3.95-3.89 (m, 2H, -OCH₂-), 3.89 (s, 3H, Ar-OCH₃), 3.88-3.81 (m, 2H, -O-CH₂-), 1.51-1.43 (m, 4H, -O-CH₂-CH₂-CH₂-), 1.31-1.22 (m, 4H, -CH₂-CH₃), 0.88 (t, <i>J</i> = 7.6 Hz, 6H, -CH₂-CH₃); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.05 (d, <i>J</i> = 14.1 Hz, Ar-C), 158.68 (d, <i>J</i> = 3.4 Hz, Ar-C), 148.80 (Ar-C), 137.15 (d, <i>J</i> = 7.3 Hz, Ar-C), 135.43 (Ar-C), 132.63 (d, <i>J</i> = 12.7 Hz, Ar-C), 128.41 (Ar-C), 126.94 (Ar-C), 124.89 (Ar-C), 122.02 (Ar-C), 118.73 (d, <i>J</i> = 8.2 Hz, Ar-C), 118.03 (d, <i>J</i> = 2.4 Hz, Ar-C), 65.80 (d, <i>J</i> = 4.8 Hz, O-CH₂-), 55.58 (Ar-OCH₃), 32.30 (d, <i>J</i> = 5.4 Hz, O-CH₂-CH₂-), 18.68 (-CH₂-CH₃), 13.60 (-CH₂-CH₃); ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 23.48; HRMS (ESI⁺) <i>m/z</i> calcd for C₂₀H₂₈NO₄P [M+H]⁺ 378.1756, found: 378.1760.</p>
<p>Dibutyl (5-methyl-2-(pyridin-2-yl)phenyl)phosphonate (5c)</p> 	<p>Colorless oil; 102 mg, yield 80%; R_f = 0.15 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.66-8.64 (m, 1H, Ar-H), 7.87 (d, <i>J</i> = 12.0 Hz, 1H, Ar-H), 7.72-7.68 (m, 1H, Ar-H), 7.65-7.63 (m, 1H, Ar-H), 7.43-7.42 (m, 2H, Ar-H), 7.28-7.25 (m, 1H, Ar-H), 3.94-3.80 (m, 4H, -O-CH₂-), 2.44 (s, 3H, Ar-CH₃), 1.49-1.43 (m, 4H, -O-CH₂-CH₂-), 1.30-1.22 (m, 4H, -CH₂-CH₃), 0.87 (t, <i>J</i> = 5.6 Hz, 6H, -CH₂-CH₃); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.99 (d, <i>J</i> = 4.3 Hz, Ar-C), 148.82 (Ar-C), 141.89 (d, <i>J</i> = 9.4 Hz, Ar-C), 137.92 (d, <i>J</i> = 14.3 Hz, Ar-C), 135.44 (Ar-C), 134.49 (d, <i>J</i> = 9.2 Hz, Ar-C), 132.90 (Ar-C), 131.10 (d, <i>J</i> = 14.4 Hz, Ar-C), 127.07 (Ar-C), 127.84 (Ar-C), 122.17 (Ar-C), 65.71 (d, <i>J</i> = 6.0 Hz, -O-CH₂-), 32.33 (d, <i>J</i> = 6.6 Hz, -O-CH₂-CH₂-), 21.15 (Ar-CH₃), 18.70 (-CH₂-CH₃), 13.62 (-CH₂-CH₃); ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 24.22; HRMS (ESI⁺) <i>m/z</i> calcd for C₂₀H₂₈NO₃P [M+H]⁺ 362.1807, found: 362.1804.</p>
<p>dibutyl (5-(tert-butyl)-2-(pyridin-2-yl)phenyl)phosphonate (5d)</p> 	<p>Colorless oil; 96 mg, yield 84%; R_f = 0.15 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.64-8.62 (m, 1H, Ar-H), 8.04 (dd, <i>J</i> = 2.4 & 13.2 Hz, 1H, Ar-H), 7.71-7.60 (m, 3H, Ar-H), 7.47-7.43 (m, 1H, Ar-H), 7.27-7.25 (m, 1H, Ar-H), 3.92-3.79 (m, 4H, -O-CH₂-), 1.48-1.38 (m, 4H, -O-CH₂-CH₂-), 1.35 (s, 9H, -C(CH₃)₃), 1.30-1.20 (m, 4H, -CH₂-CH₃), 0.86 (t, <i>J</i> = 7.2 Hz, 6H, -CH₂-CH₃); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.13 (d, <i>J</i> = 4.6 Hz, Ar-C), 151.05 (d, <i>J</i> = 13.3 Hz, Ar-C), 148.89 (Ar-C), 141.97 (d, <i>J</i> = 9.9 Hz, Ar-C), 135.50 (Ar-C), 131.00 (Ar-C), 129.43 (d, <i>J</i> = 3.3 Hz, Ar-C), 126.96 (Ar-C), 125.11 (Ar-C), 124.82 (Ar-C), 122.20 (Ar-C), 65.75 (d, <i>J</i> = 6.5 Hz, O-CH₂-), 34.87 (-C(CH₃)₃), 32.39 (d, <i>J</i> = 6.8 Hz, -O-CH₂-CH₂-), 31.25 (C(CH₃)₃), 18.77 (-CH₂-CH₃), 13.67 (-CH₂-CH₃); ³¹P NMR (162 MHz, CDCl₃): δ (ppm)</p>

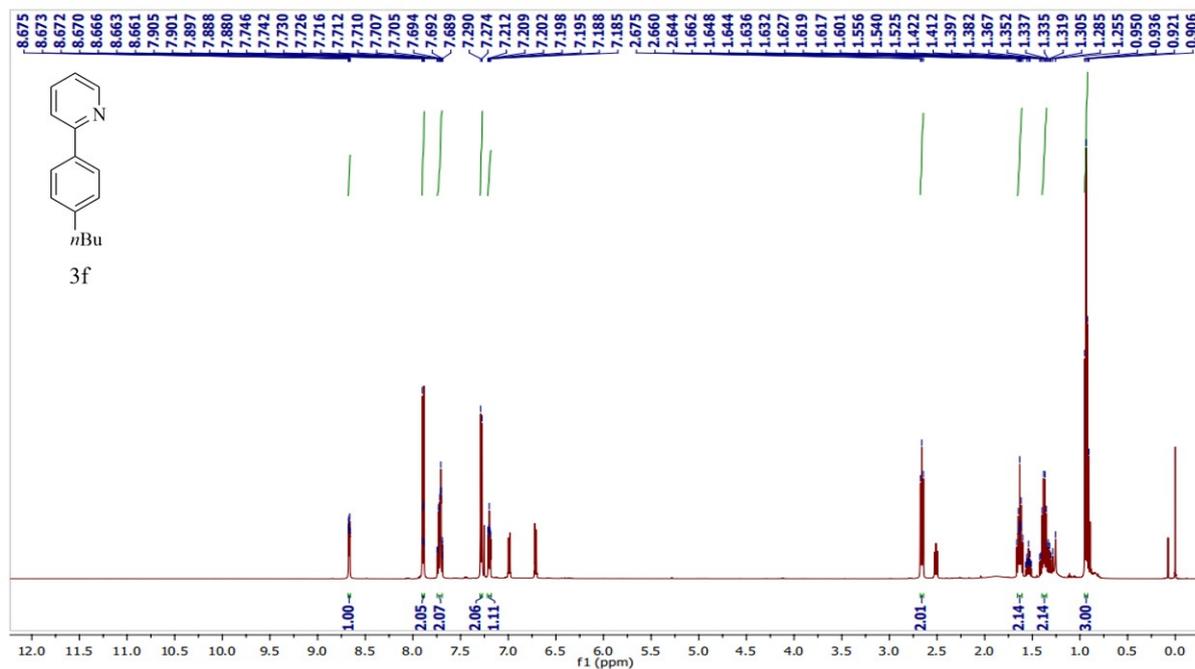
	24.37; HRMS (ESI ⁺) m/z calcd for C ₂₃ H ₃₄ NO ₃ P [M+H] ⁺ 404.2276, found: 404.2274.
<p>Dibutyl (5-butyl-2-(pyridin-2-yl)phenyl)phosphonate (5e)</p> 	<p>Colorless oil; 93 mg, yield 82%; R_f = 0.15 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.66-8.64 (m, 1H, Ar-H), 7.86 (d, J = 14.4 Hz, 1H, Ar-H), 7.72-7.64 (m, 2H, Ar-H), 7.46-7.41 (m, 2H, Ar-H), 7.28-7.25 (m, 1H, Ar-H), 3.94-3.80 (m, 4H, -O-CH₂-), 2.71 (t, J = 7.6 Hz, 2H, Ar-CH₂-), 1.68- 1.60 (m, 2H, Ar-CH₂-CH₂-), 1.50-1.42 (m, 4H, O-CH₂-CH₂-), 1.40-1.33 (m, 2H, Ar-CH₂-CH₂-CH₂-CH₃), 1.30-1.21 (m, 4H, -O-CH₂-CH₂-CH₂-CH₃), 0.95 (t, J = 7.2 Hz, 3H, Ar-CH₂-CH₂-CH₂-CH₃), 0.87 (t, J = 7.6 Hz, 6H, -CH₂-CH₃); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.04 (Ar-C), 148.79 (Ar-C), 142.89 (d, J = 13.8 Hz, Ar-C), 142.05 (d, J = 9.3 Hz, Ar-C), 135.47 (Ar-C), 133.90 (d, J = 9.3 Hz, Ar-C), 132.32 (Ar-C), 131.10 (d, J = 14.3 Hz, Ar-C), 127.06 (Ar-C), 124.81 (Ar-C), 122.17 (Ar-C), 116.16 (Ar-C), 65.72 (d, J = 6.0 Hz, O-CH₂-), 35.26 (Ar-CH₂-), 33.41 (Ar-CH₂-CH₂-), 32.34 (d, J = 6.6 Hz, -O-CH₂-CH₂-), 22.29 (Ar-CH₂-CH₂-CH₂-), 18.71 (-O-CH₂-CH₂-CH₂-CH₃), 13.93 (Ar-CH₂-CH₂-CH₂-CH₃), 13.62 (O-CH₂-CH₂-CH₂-CH₃); ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 24.22; HRMS (ESI⁺) m/z calcd for C₂₃H₃₄NO₃P [M+H]⁺ 404.2276, found: 404.2350.</p>
<p>Dibutyl (5-phenoxy-2-(pyridin-2-yl)phenyl)phosphonate (5f)</p> 	<p>Colorless oil; 67 mg, yield 63%; R_f = 0.15 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.67-8.65 (m, 1H, Ar-H), 7.73-7.71 (m, 2H, Ar-H), 7.64 (dd, J = 2.8 & 12.8 Hz, 1H, Ar-H), 7.53-7.49 (m, 1H, Ar-H), 7.39-7.35 (m, 2H, Ar-H), 7.29-7.27 (m, 1H, Ar-H), 7.23-7.20 (m, 1H, Ar-H), 7.17-7.13 (m, 1H, Ar-H), 7.07-7.05 (m, 2H, Ar-H), 3.92-3.79 (m, 4H, -O-CH₂-), 1.47-1.40 (m, 4H, O-CH₂-CH₂-), 1.28-1.18 (m, 4H, -CH₂-CH₃), 0.86 (t, J = 7.6 Hz, 6H, -CH₂-CH₃); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.36 (d, J = 4.1 Hz, Ar-C), 157.20 (d, J = 18.2 Hz, Ar-C), 156.40 (Ar-C), 148.87 (Ar-C), 139.37 (d, J = 9.6 Hz, Ar-C), 135.62 (Ar-C), 132.92 (d, J = 15.8 Hz, Ar-C), 129.95 (Ar-C), 127.55 (Ar-C), 124.85 (Ar-C), 123.99 (Ar-C), 123.33 (d, J = 9.9 Hz, Ar-C), 122.27 (Ar-C), 121.94 (d, J = 2.4 Hz, Ar-C), 119.38 (Ar-C), 65.93 (d, J = 6.2 Hz, -O-CH₂-), 32.26 (d, J = 6.6 Hz, -O-CH₂-CH₂-), 18.65 (-CH₂-CH₃), 13.58 (-CH₂-CH₃); ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 22.68; HRMS (ESI⁺) m/z calcd for C₂₅H₃₀NO₄P [M+H]⁺ 440.1912, found: 440.1999.</p>
<p>Dibutyl (4-(pyridin-2-yl)-[1,1'-biphenyl]-3-yl)phosphonate (5g)</p> 	<p>Colorless oil; 56 mg, yield 51%; R_f = 0.15 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.69-8.67 (m, 1H, Ar-H), 8.27 (dd, J = 2.0 & 12.8 Hz, 1H, Ar-H), 7.84-7.81 (m, 1H, Ar-H), 7.74-7.72 (m, 2H, Ar-H), 7.66-7.59 (m, 3H, Ar-H), 7.48-7.44 (m, 2H, Ar-H), 7.40-7.36 (m, 1H, Ar-H), 7.31-7.27 (m, 1H, Ar-H), 3.97-3.83 (m, 4H, -O-</p>

	<p>CH₂-), 1.51-1.43 (m, 4H, -O-CH₂-CH₂-), 1.32-1.28 (m, 4H, -CH₂-CH₃), 0.86 (t, <i>J</i> = 7.2 Hz, 6H, -CH₂-CH₃); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 149.00 (Ar-C), 135.65 (Ar-C), 132.66 (d, <i>J</i> = 10.2 Hz, Ar-C), 131.79 (d, <i>J</i> = 14.2 Hz, Ar-C), 130.75 (d, <i>J</i> = 3.3 Hz, Ar-C), 129.01 (Ar-C), 127.99 (Ar-C), 127.30 (Ar-C), 124.91 (Ar-C), 124.06 (Ar-C), 123.52 (Ar-C), 122.46 (Ar-C), 115.98 (Ar-C), 114.13 (Ar-C), 65.95 (d, <i>J</i> = 6.5 Hz, O-CH₂-), 32.41 (d, <i>J</i> = 6.8 Hz, -O-CH₂-CH₂-), 18.77 (-CH₂-CH₃), 13.66 (-CH₂-CH₃); ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 23.56; HRMS (ESI⁺) <i>m/z</i> calcd for C₂₅H₃₀NO₃P [M+H]⁺ 424.1963, found: 424.1967.</p>
<p>Dibutyl (4'-pentyl-4-(pyridin-2-yl)-[1,1'-biphenyl]-3-yl)phosphonate (5h)</p> 	<p>Colorless oil; 52 mg, yield 53%; R_f = 0.15 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.69 (d, <i>J</i> = 4.8 Hz, 1H, Ar-H), 8.27 (dd, <i>J</i> = 2.0 & 13.2 Hz, 1H, Ar-H), 7.84-7.81 (m, 1H, Ar-H), 7.75-7.73 (m, 2H, Ar-H), 7.62-7.56 (m, 3H, Ar-H), 7.32-7.27 (m, 3H, Ar-H), 3.98-3.84 (m, 4H, -O-CH₂-), 2.68 (t, <i>J</i> = 7.6 Hz, 2H, Ar-CH₂-), 1.70-1.62 (m, 2H, Ar-CH₂-CH₂-), 1.52-1.44 (m, 4H, -O-CH₂-CH₂-), 1.43-1.40 (m, 2H, Ar-CH₂-CH₂-CH₂-), 1.38-1.34 (m, 2H, Ar-CH₂-CH₂-CH₂-CH₂-CH₃), 1.33-1.28 (m, 4H, O-CH₂-CH₂-CH₂-), 0.93-0.89 (m, 3H, Ar-CH₂-CH₂-CH₂-CH₂-CH₃), 0.88 (t, <i>J</i> = 7.2 Hz, 6H, O-CH₂-CH₂-CH₂-CH₂-CH₃); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.63 (Ar-C), 148.82 (Ar-C), 142.92 (Ar-C), 140.88 (d, <i>J</i> = 13.3 Hz, Ar-C), 136.91 (Ar-C), 135.65 (Ar-C), 132.35 (d, <i>J</i> = 9.7 Hz, Ar-C), 131.67 (d, <i>J</i> = 14.5 Hz, Ar-C), 130.48 (Ar-C), 129.01 (Ar-C), 127.03 (Ar-C), 124.89 (Ar-C), 122.38 (Ar-C), 120.85 (d, <i>J</i> = 4.5 Hz, Ar-C), 116.15 (Ar-C), 65.89 (d, <i>J</i> = 6.0 Hz, O-CH₂-), 35.60 (Ar-CH₂-), 32.33 (d, <i>J</i> = 6.8 Hz, -O-CH₂-CH₂-), 31.93 (Ar-CH₂-CH₂-), 31.16 (Ar-CH₂-CH₂-CH₂-), 22.69 (d, <i>J</i> = 13.4 Hz, Ar-CH₂-CH₂-CH₂-CH₂-CH₃), 18.70 (-O-CH₂-CH₂-CH₂-CH₂-CH₃), 14.12 (d, <i>J</i> = 7.9 Hz, Ar-CH₂-CH₂-CH₂-CH₂-CH₃), 13.60 (-O-CH₂-CH₂-CH₂-CH₃); ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 23.64; HRMS (ESI⁺) <i>m/z</i> calcd for C₃₀H₄₀NO₃P [M+H]⁺ 494.2746, found: 494.2801.</p>
<p>Dibutyl (4-fluoro-2-(pyridin-2-yl)phenyl)phosphonate (5i)</p> 	<p>Colorless oil; 99 mg, yield 78%; R_f = 0.15 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.68-8.66 (m, 1H, Ar-H), 8.07-8.00 (m, 1H, Ar-H), 7.76-7.72 (m, 1H, Ar-H), 7.69-7.67 (m, 1H, Ar-H), 7.33-7.30 (m, 1H, Ar-H), 7.28-7.24 (m, 1H, Ar-H), 7.21-7.16 (m, 1H, Ar-H), 3.94-3.80 (m, 4H, -O-CH₂-), 1.50-1.44 (m, 4H, -O-CH₂-CH₂-), 1.29-1.21 (m, 4H, -CH₂-CH₃), 0.88 (t, <i>J</i> = 7.6 Hz, 6H, -CH₂-CH₃); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 157.56 (Ar-C), 148.97 (Ar-C), 147.66 (Ar-C), 136.67 (t, <i>J</i> = 9.5 Hz, Ar-C), 135.73 (Ar-C), 124.62 (Ar-C), 123.72 (d, <i>J</i> = 2.5 Hz, Ar-C), 122.80 (Ar-C), 118.58 (Ar-C), 116.12 (Ar-C), 115.21 (Ar-C), 65.88 (d, <i>J</i> = 6.1 Hz, O-</p>

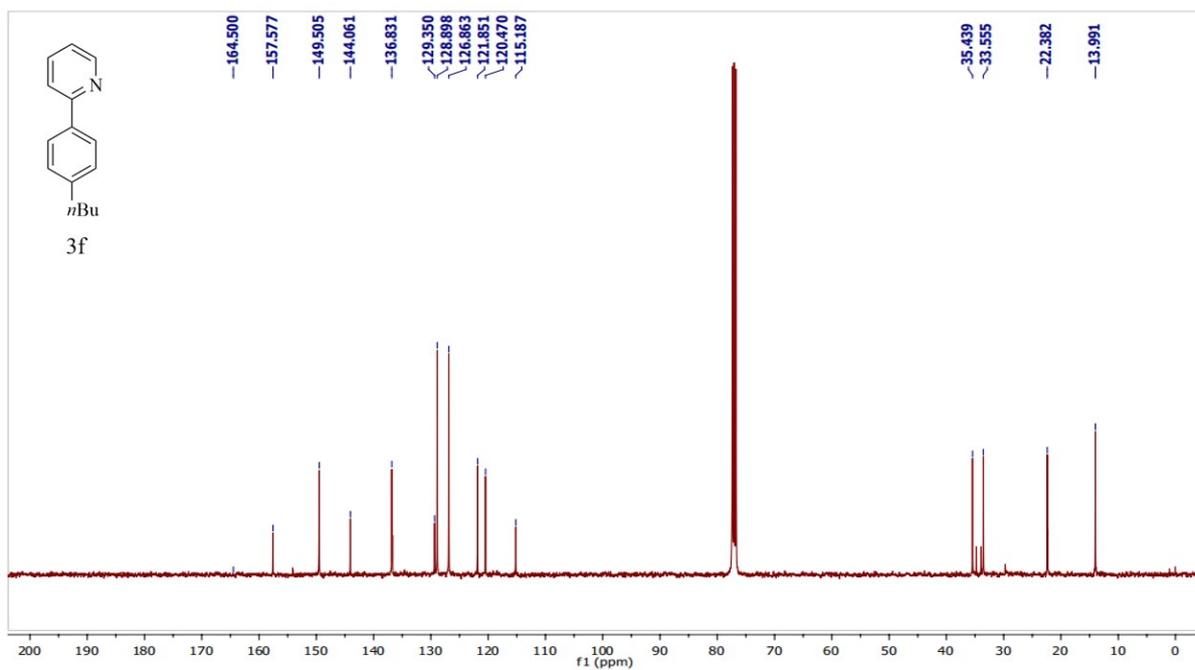
	<p>CH₂-), 32.30 (d, <i>J</i> = 6.6 Hz, -O-CH₂-CH₂-), 18.67 (-CH₂-CH₃), 13.58 (-CH₂-CH₃); ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 22.64; HRMS (ESI⁺) <i>m/z</i> calcd for C₁₉H₂₅FNO₃P [M+H]⁺ 366.1556, found: 366.1550.</p>
<p>Dibutyl (3-(pyridin-2-yl)naphthalen-2-yl)phosphonate (5j)</p> 	<p>Colorless oil; 83 mg, yield 72%; R_f = 0.15 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.71-8.69 (m, 1H, Ar-H), 8.66 (d, <i>J</i> = 16.4 Hz, 1H, Ar-H), 7.99-7.97 (m, 2H, Ar-H), 7.90 (d, <i>J</i> = 7.6 Hz, 1H, Ar-H), 7.78-7.72 (m, 2H, Ar-H), 7.64-7.56 (m, 2H, Ar-H), 7.34-7.30 (m, 1H, Ar-H), 4.00-3.85 (m, 4H, -O-CH₂-), 1.54-1.47 (m, 4H, -O-CH₂-CH₂-), 1.33-1.27 (m, 4H, -CH₂-CH₃), 0.88 (t, <i>J</i> = 7.6 Hz, 6H, -CH₂-CH₃); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 148.74 (Ar-C), 136.54 (d, <i>J</i> = 9.1 Hz, Ar-C), 135.57 (Ar-C), 134.58 (Ar-C), 131.79 (d, <i>J</i> = 15.7 Hz, Ar-C), 130.59 (d, <i>J</i> = 12.9 Hz, Ar-C), 128.74 (Ar-C), 128.02 (Ar-C), 127.20 (Ar-C), 124.97 (Ar-C), 122.31 (Ar-C), 65.87 (d, <i>J</i> = 5.7 Hz, -O-CH₂-), 32.35 (d, <i>J</i> = 6.7 Hz, -O-CH₂-CH₂-), 18.71 (-CH₂-CH₃), 13.54 (-CH₂-CH₃); ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 23.96; HRMS (ESI⁺) <i>m/z</i> calcd for C₂₃H₂₈NO₃P [M+H]⁺ 398.1807, found: 398.1811.</p>
<p>Diethyl (5-methoxy-2-(pyridin-2-yl)phenyl)phosphonate (5bb)</p> 	<p>Colorless oil; 60 mg, yield 58%; R_f = 0.15 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.66-8.64 (m, 1H, Ar-H), 7.73 (dt, <i>J</i> = 1.6 & 6.0 Hz, 1H, Ar-H), 7.65-7.63 (m, 1H, Ar-H), 7.58 (dd, <i>J</i> = 2.8 & 12.8 Hz, 1H, Ar-H), 7.49-7.45 (m, 1H, Ar-H), 7.28-7.26 (m, 1H, Ar-H), 7.15-7.12 (m, 1H, Ar-H), 4.03-3.90 (m, 4H, -O-CH₂-), 3.89 (s, 3H, Ar-OCH₃), 1.17 (t, <i>J</i> = 6.8 Hz, 6H, -CH₂-CH₃); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.17 (Ar-C), 148.83 (Ar-C), 137.25 (d, <i>J</i> = 9.3 Hz, Ar-C), 135.57 (Ar-C), 132.65 (d, <i>J</i> = 16.1 Hz, Ar-C), 128.62 (Ar-C), 126.78 (Ar-C), 124.96 (Ar-C), 122.17 (Ar-C), 118.85 (d, <i>J</i> = 11.0 Hz, Ar-C), 118.11 (d, <i>J</i> = 3.6 Hz, Ar-C), 62.14 (d, <i>J</i> = 6.3 Hz, -O-CH₂-CH₃), 55.66 (Ar-OCH₃), 16.16 (d, <i>J</i> = 7.0 Hz, -O-CH₂-CH₃); ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 18.30; HRMS (ESI⁺) <i>m/z</i> calcd for C₁₆H₂₀NO₄P [M+H]⁺ 322.1130, found: 322.1134.</p>
<p>Diisopropyl (5-methoxy-2-(pyridin-2-yl)phenyl)phosphonate (5bc)¹³</p> 	<p>Colorless oil; 70 mg, yield 62%; R_f = 0.15 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.66-8.64 (m, 1H, Ar-H), 7.71-7.69 (m, 2H, Ar-H), 7.62 (dd, <i>J</i> = 3.6 Hz & 18.0 Hz, 1H, Ar-H), 7.50-7.45 (m, 1H, Ar-H), 7.28-7.23 (m, 1H, Ar-H), 7.14-7.10 (m, 1H, Ar-H), 4.67-4.56 (m, 2H, -O-CH(CH₃)₂), 3.89 (s, 3H, Ar-OCH₃), 1.22 (d, <i>J</i> = 8.4 Hz, 6H, -O-CH(CH₃)₂), 1.16 (d, <i>J</i> = 8.4 Hz, 6H, -O-CH(CH₃)₂); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.11 (Ar-C), 148.42 (Ar-C), 135.59 (Ar-C), 132.80 (d, <i>J</i> = 21.2 Hz, Ar-C), 125.41 (Ar-C), 122.04, 118.75 (d, <i>J</i> = 14.1 Hz, Ar-C), 117.75 (d, <i>J</i> = 3.6 Hz, Ar-C), 71.10 (d, <i>J</i> = 8.1 Hz, -O-C-(CH₃)₂), 55.59 (Ar-OCH₃), 29.71 (-O-CH-(CH₃)₃), 22.97 (dd, <i>J</i> = 5.1 & 16.6 Hz, -O-CH-</p>

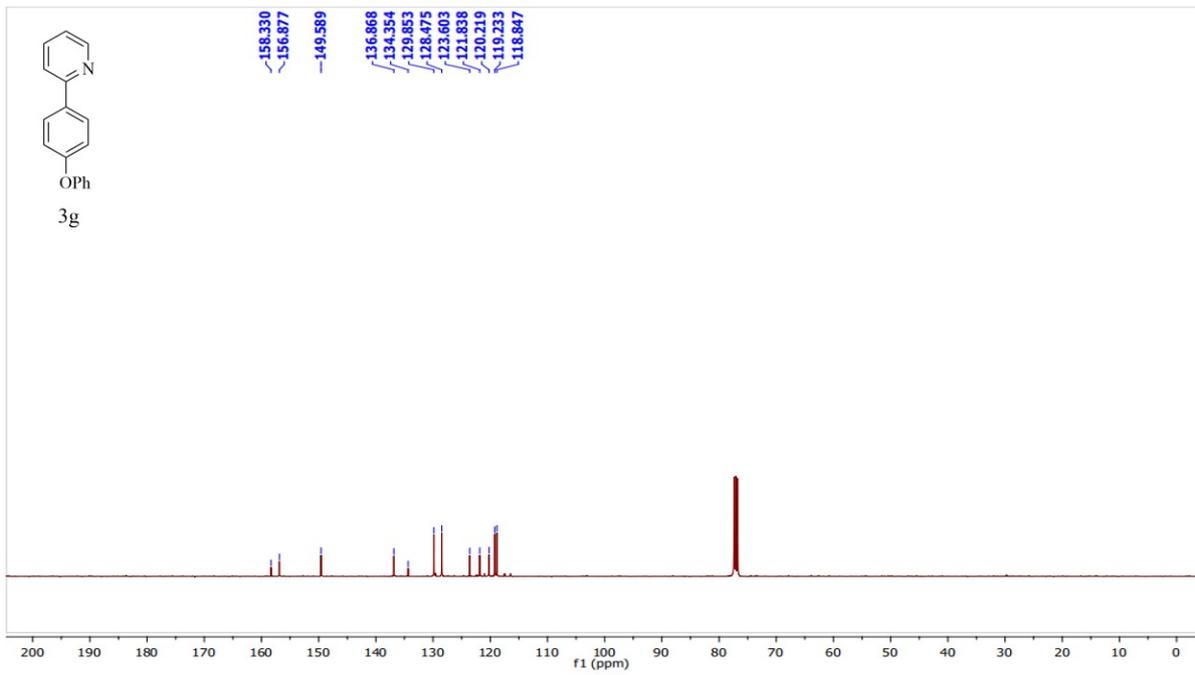
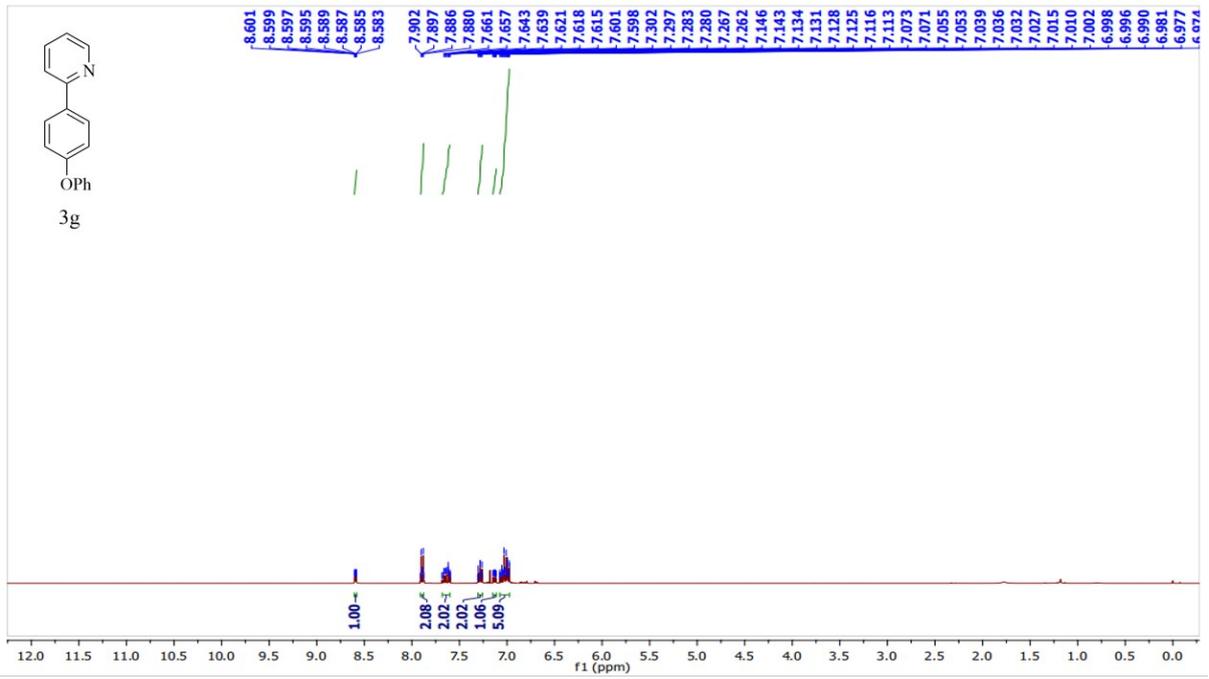
(CH₃)₃); **³¹P NMR** (162 MHz, CDCl₃): δ (ppm) 16.27; **HRMS** (ESI⁺) m/z calcd for C₁₈H₂₄NO₄P [M+H]⁺ 349.1443, found: 349.1447. The spectral data of this compound are in complete agreement with those reported in the literature.¹³

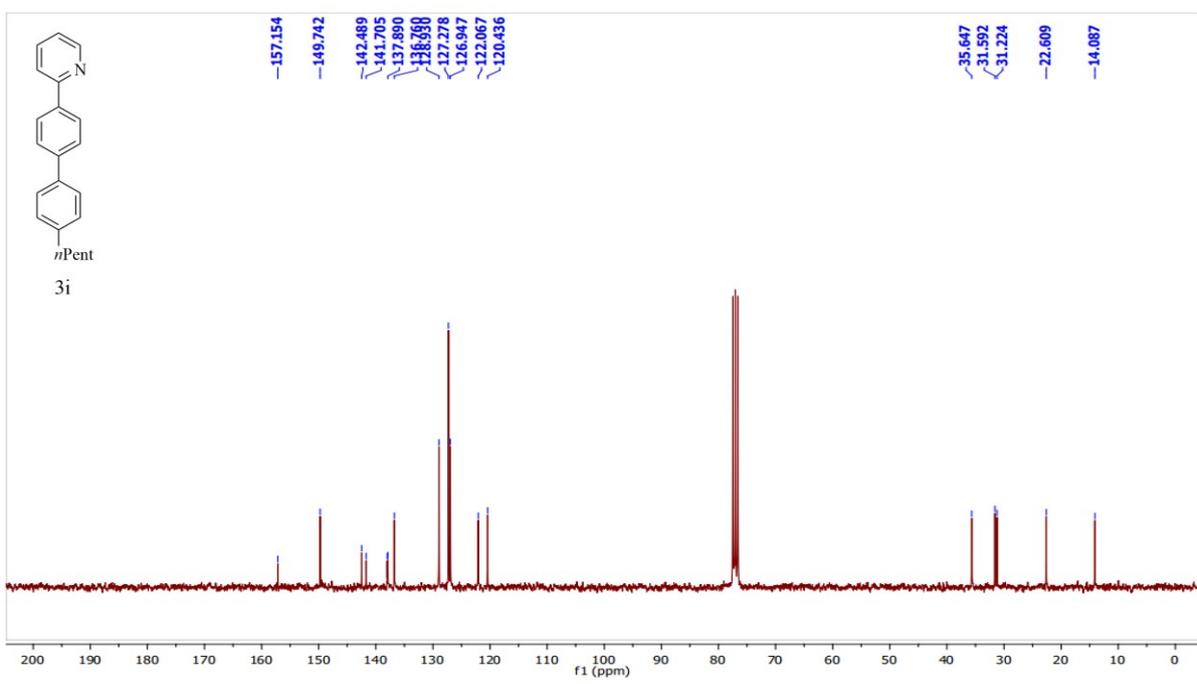
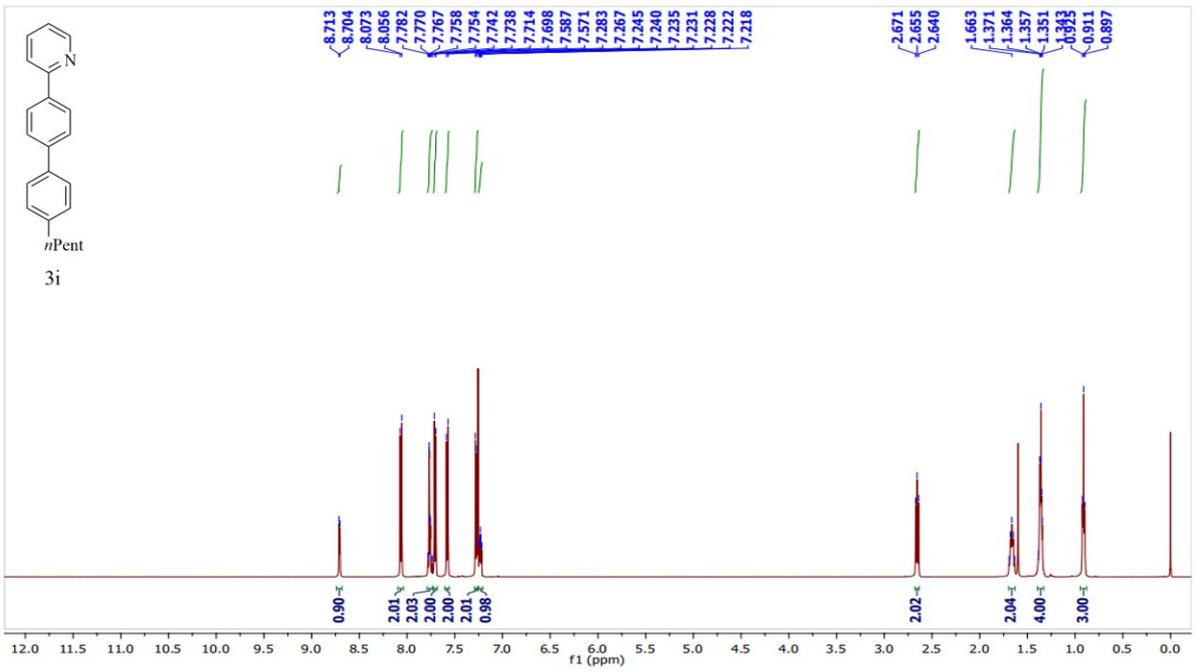
3. ^1H , ^{13}C and ^{31}P NMR copies

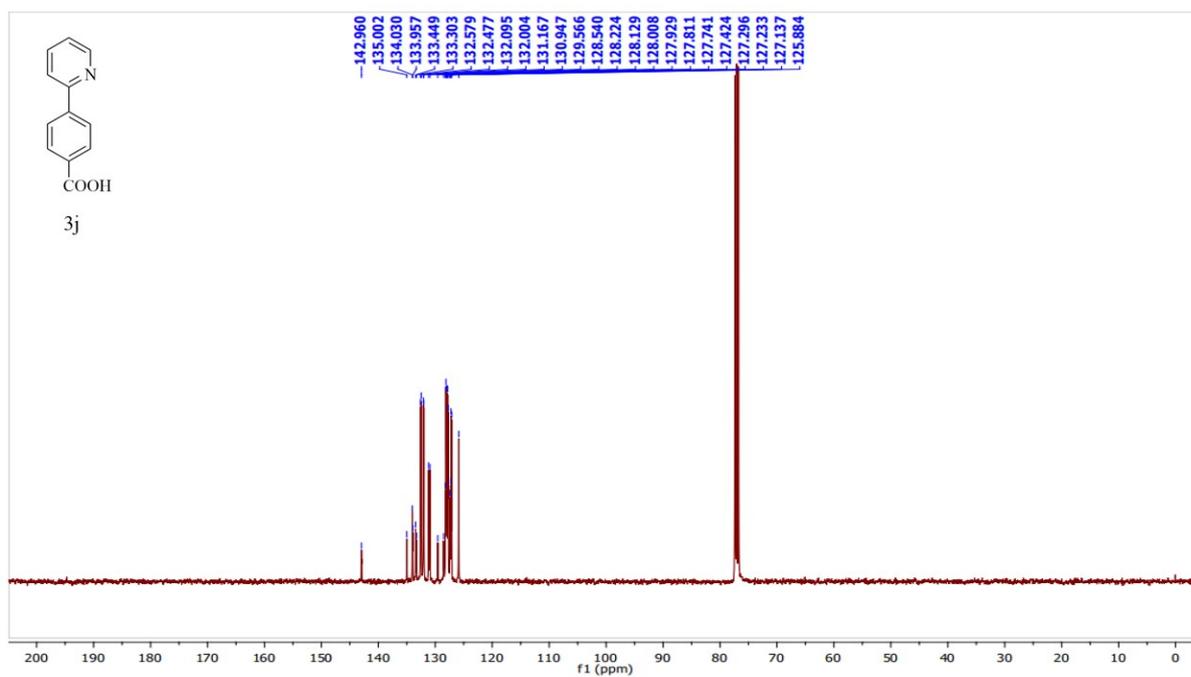
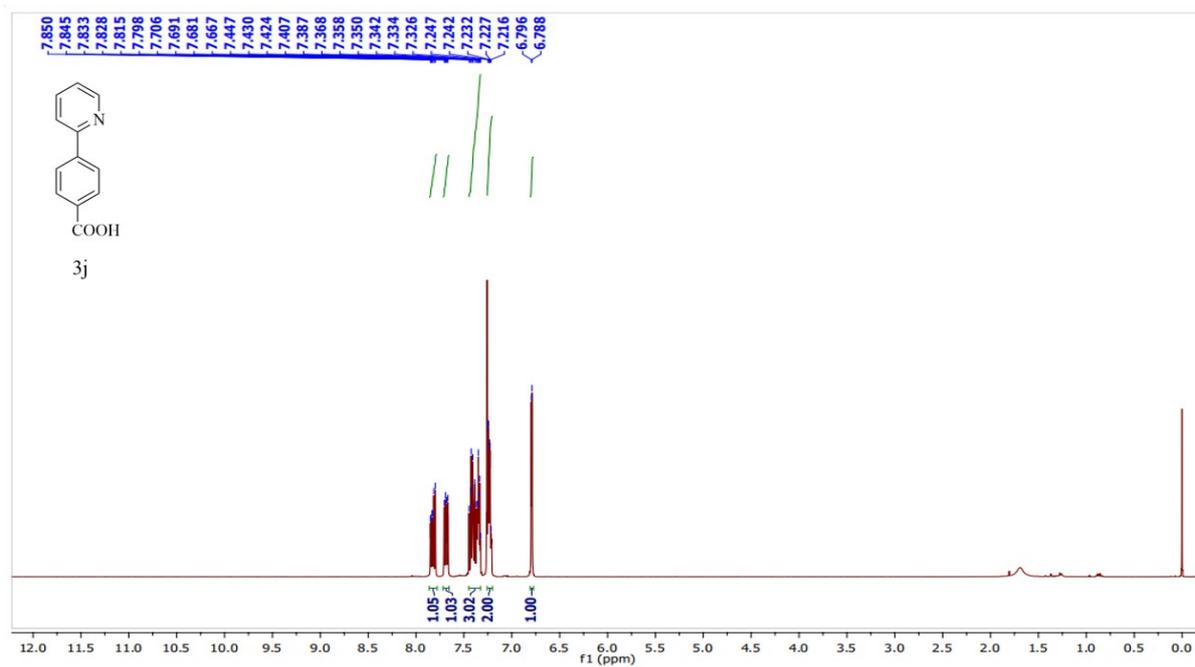


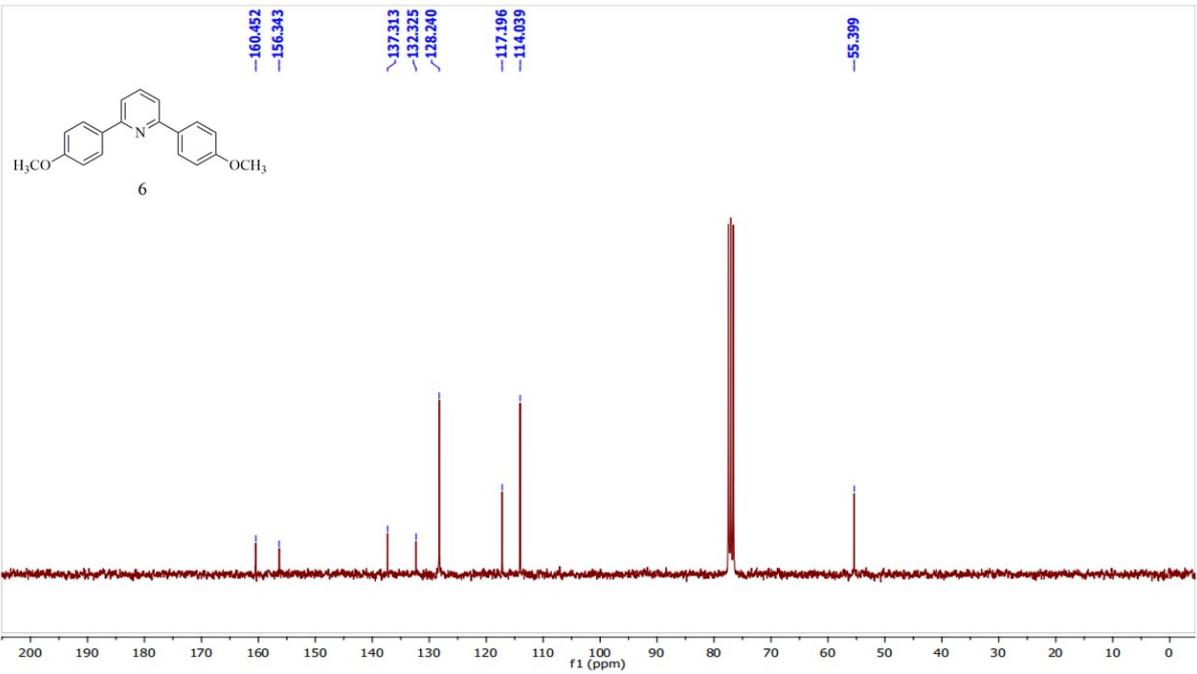
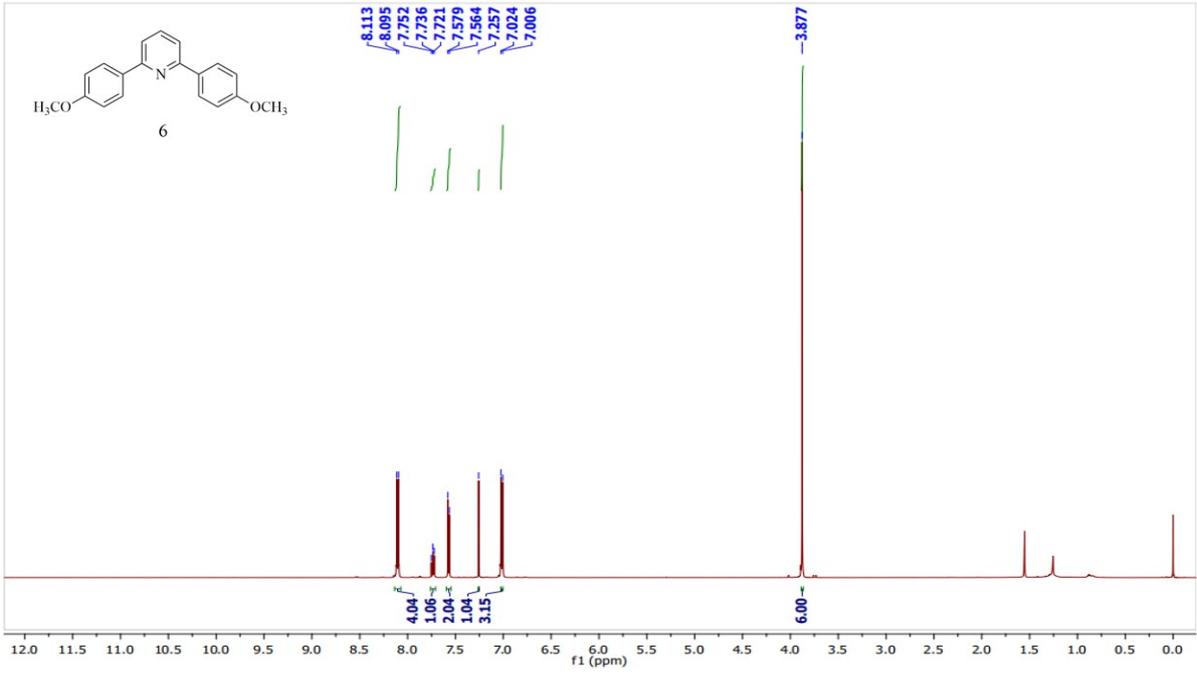
2.

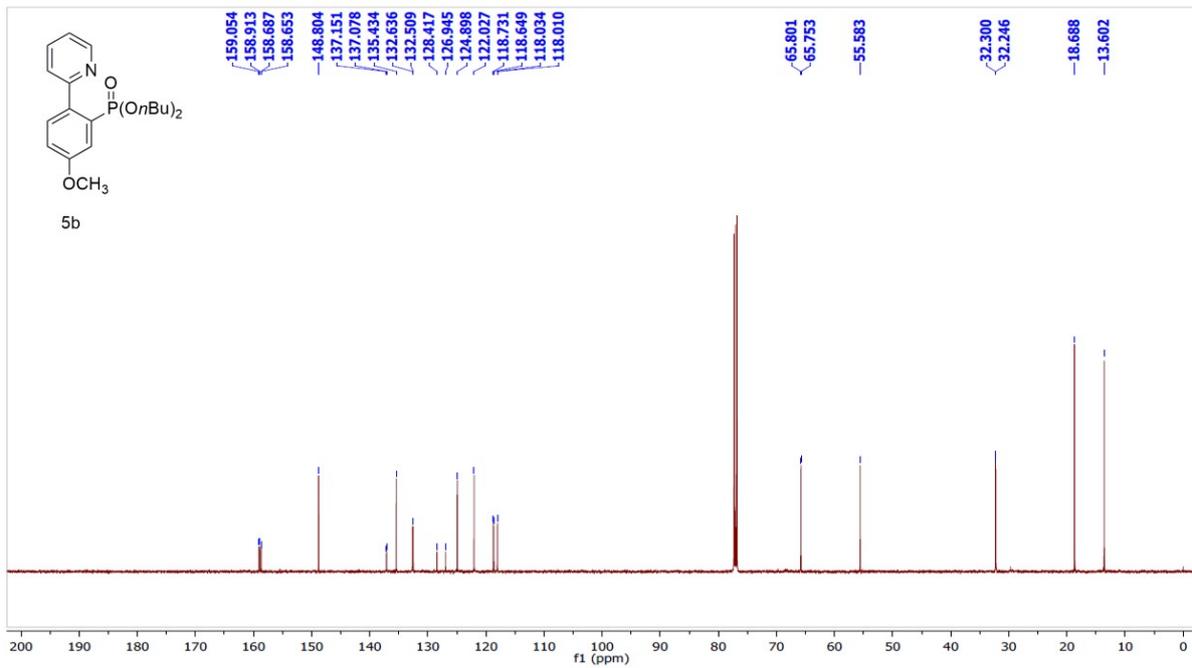
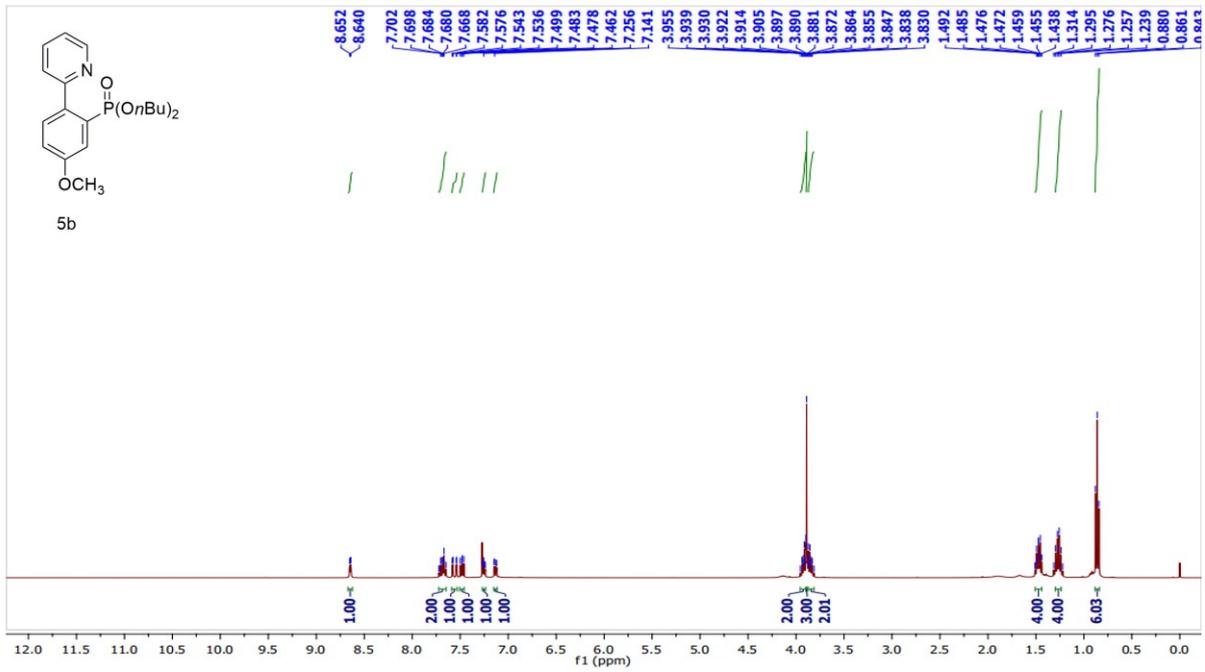


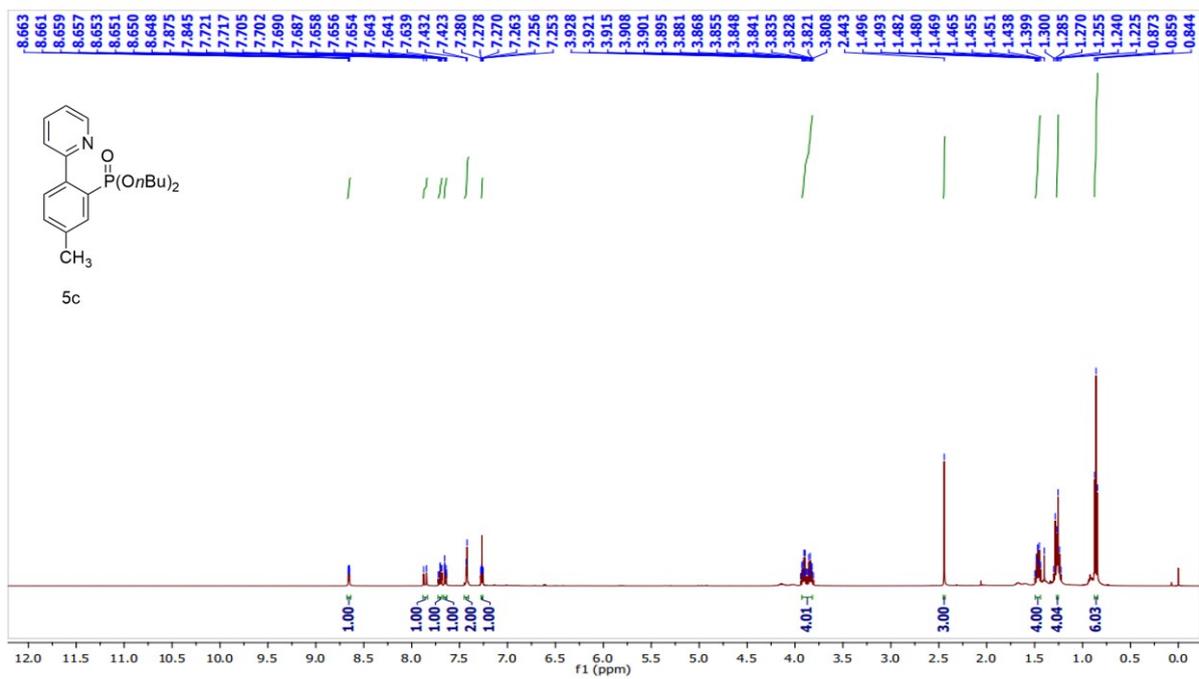
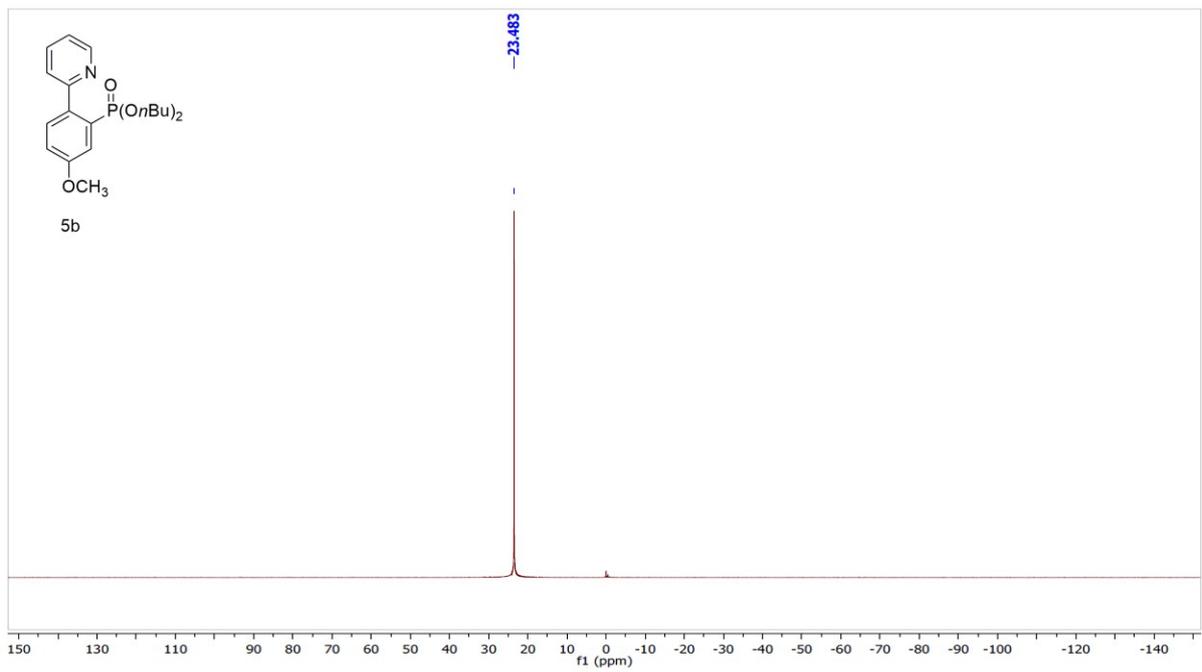


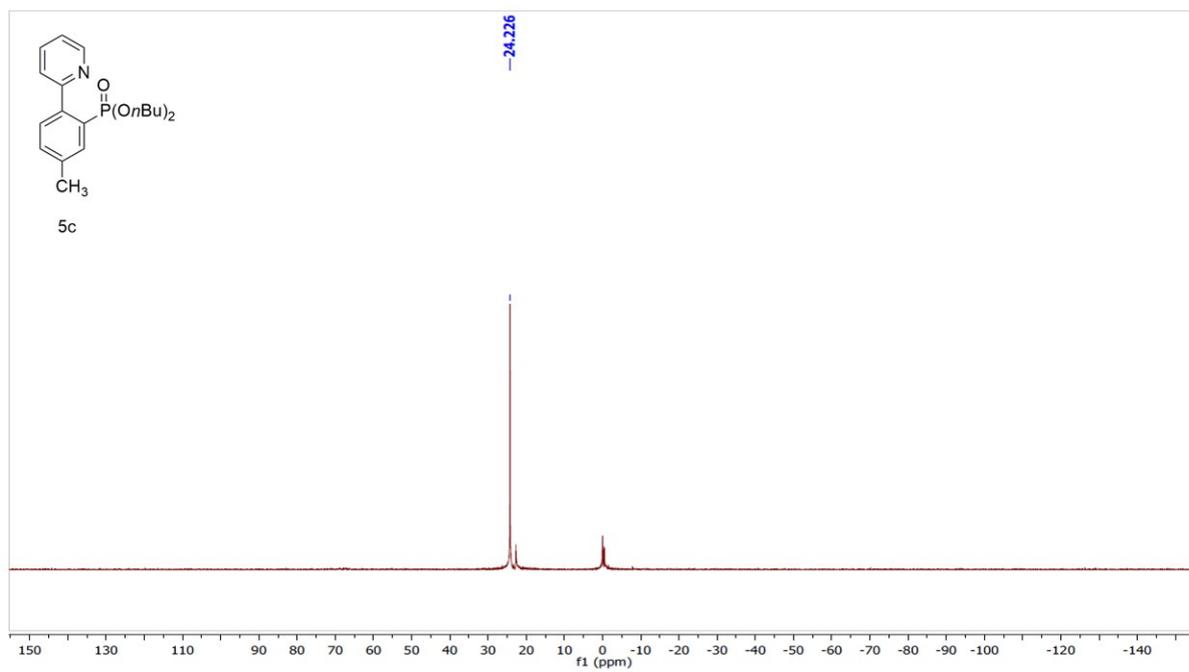
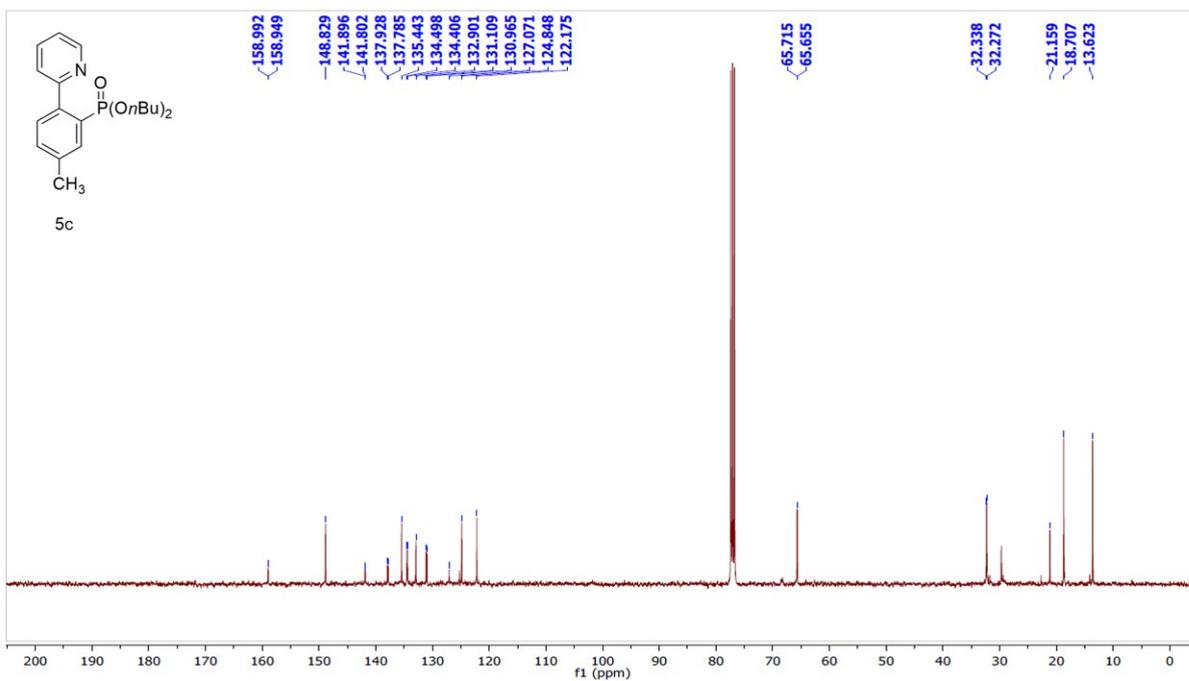


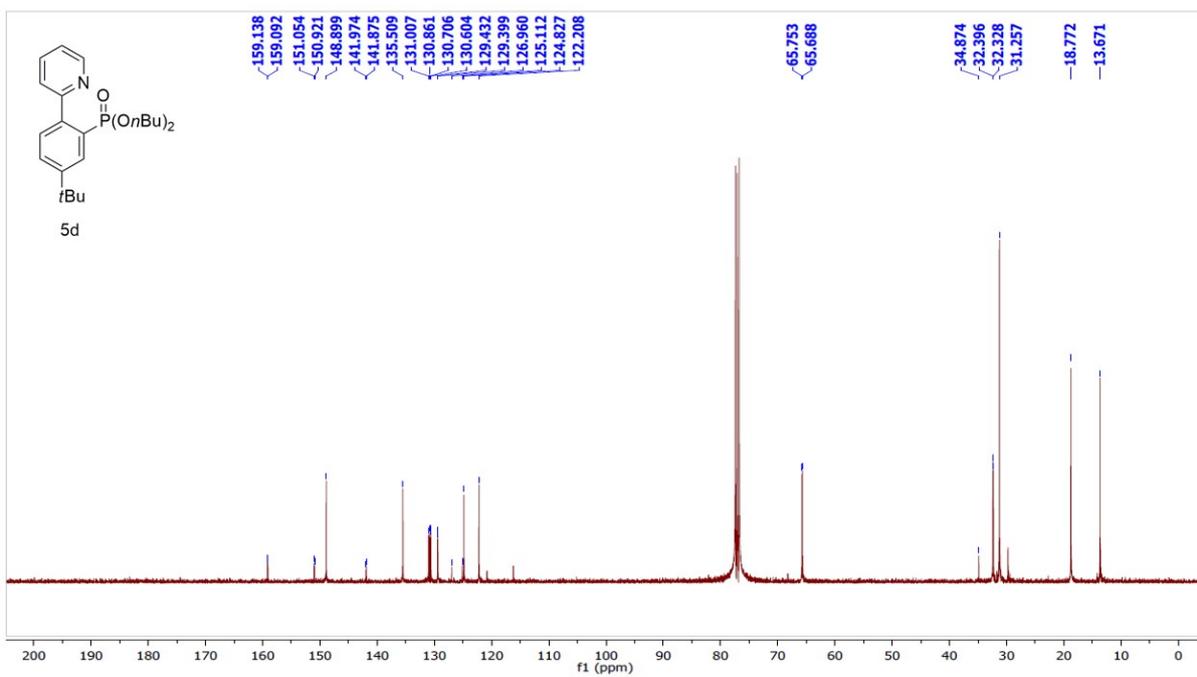
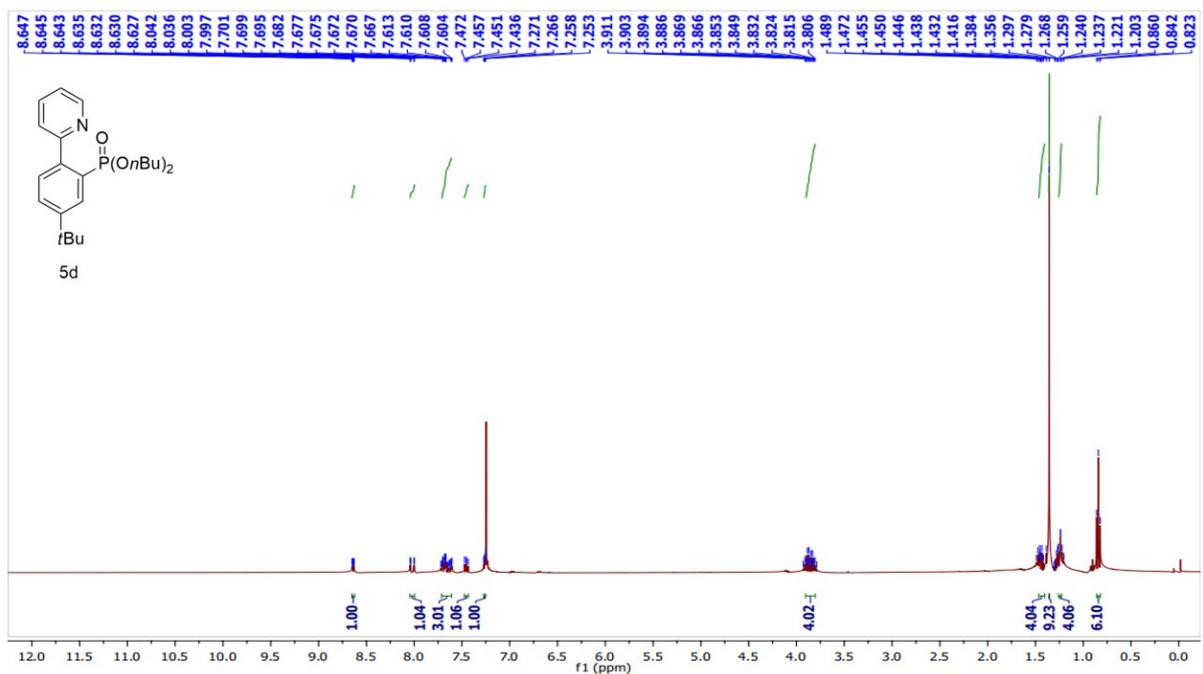


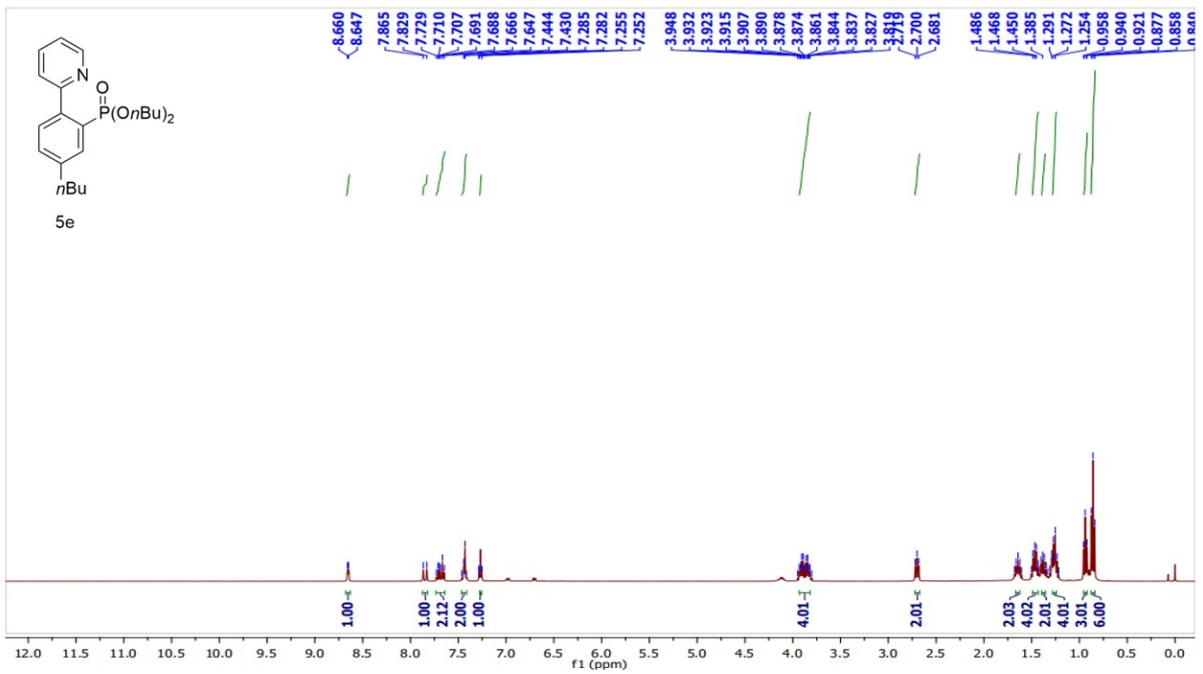
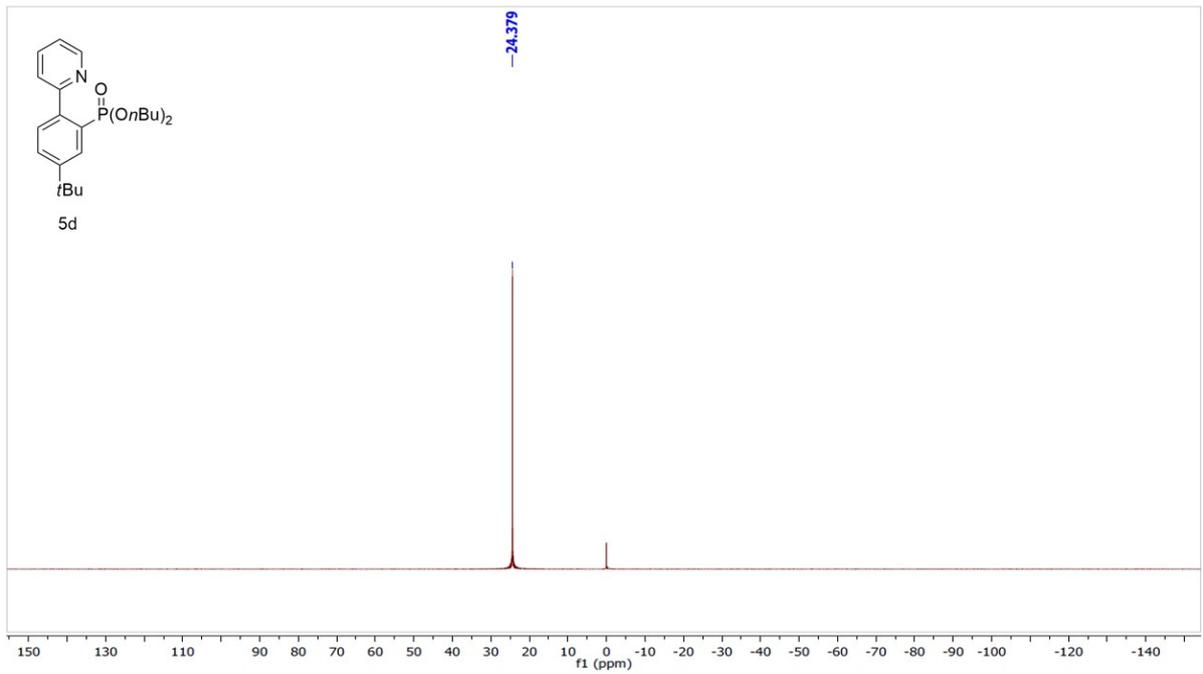


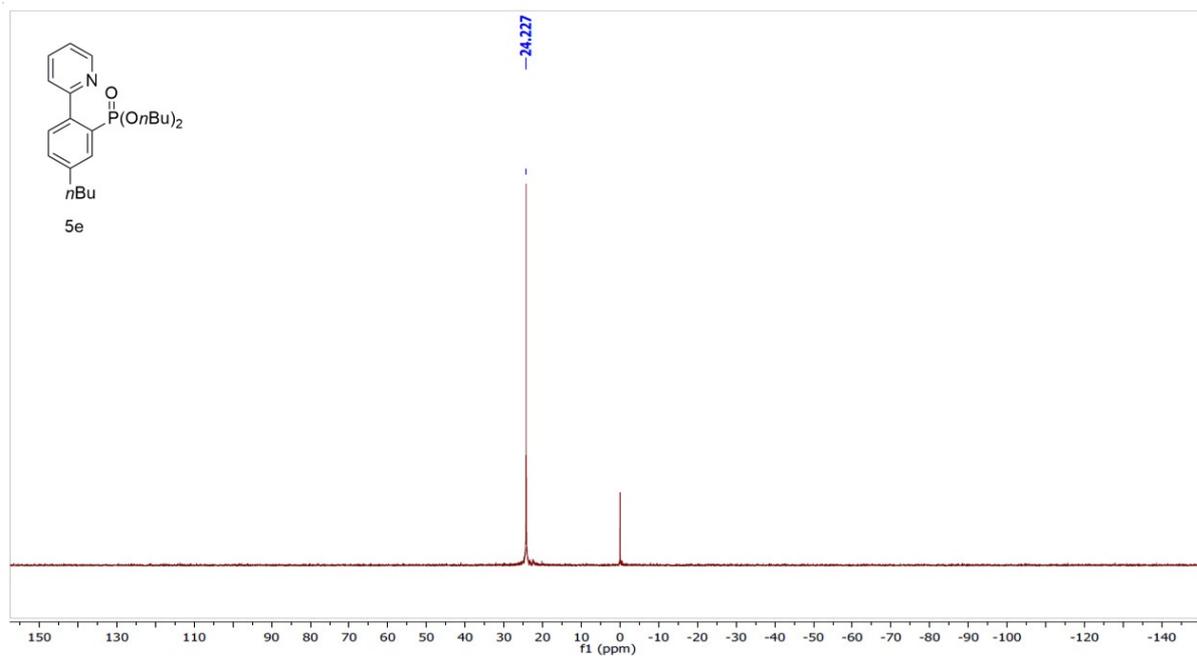
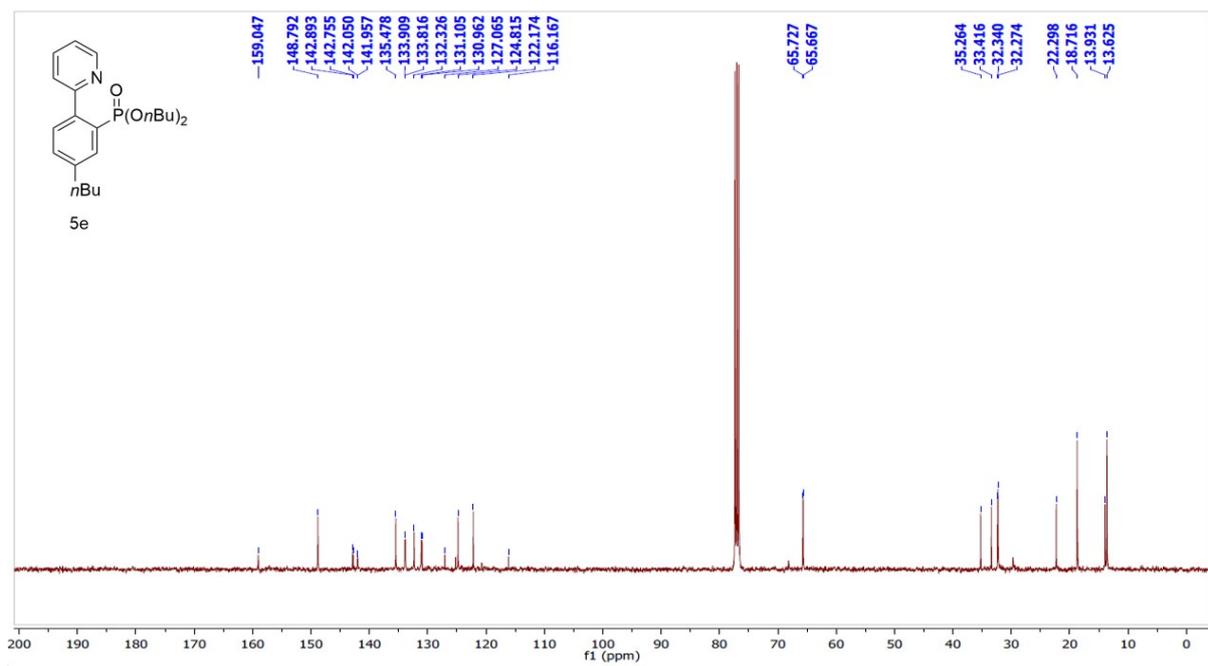




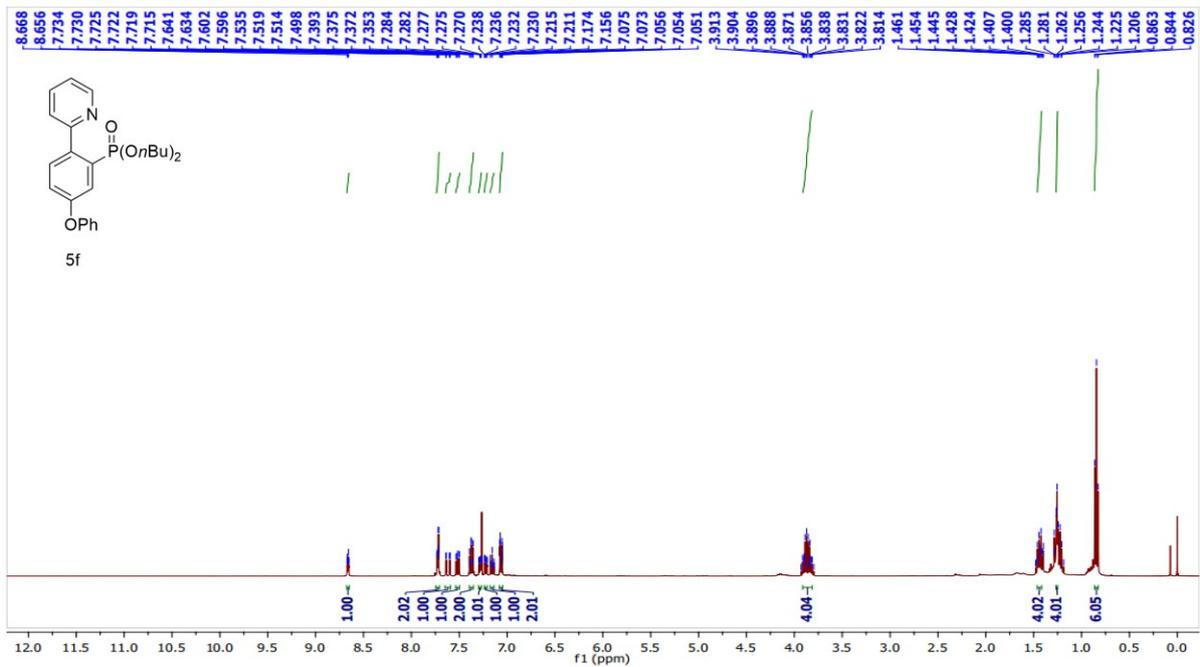
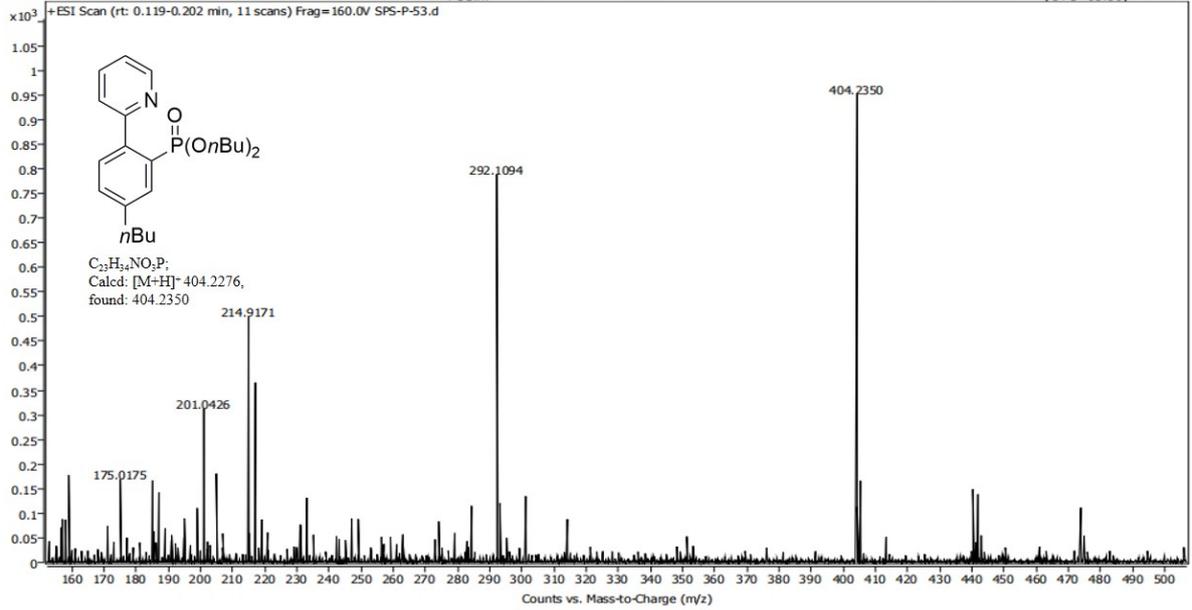


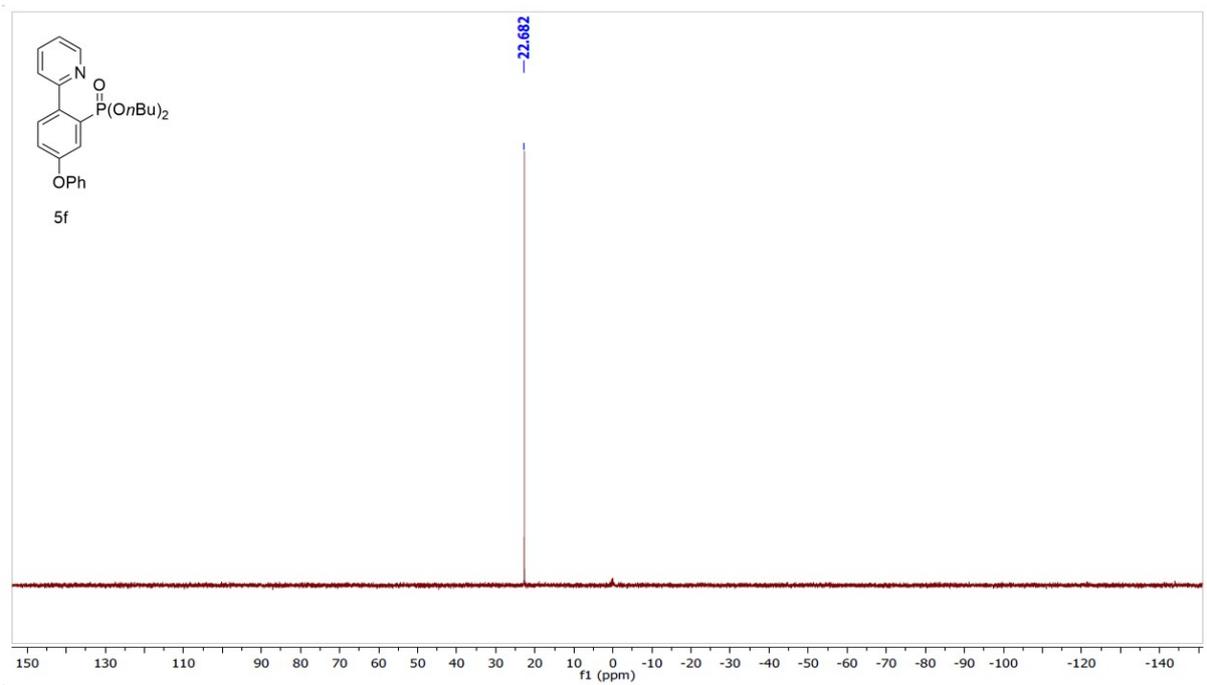
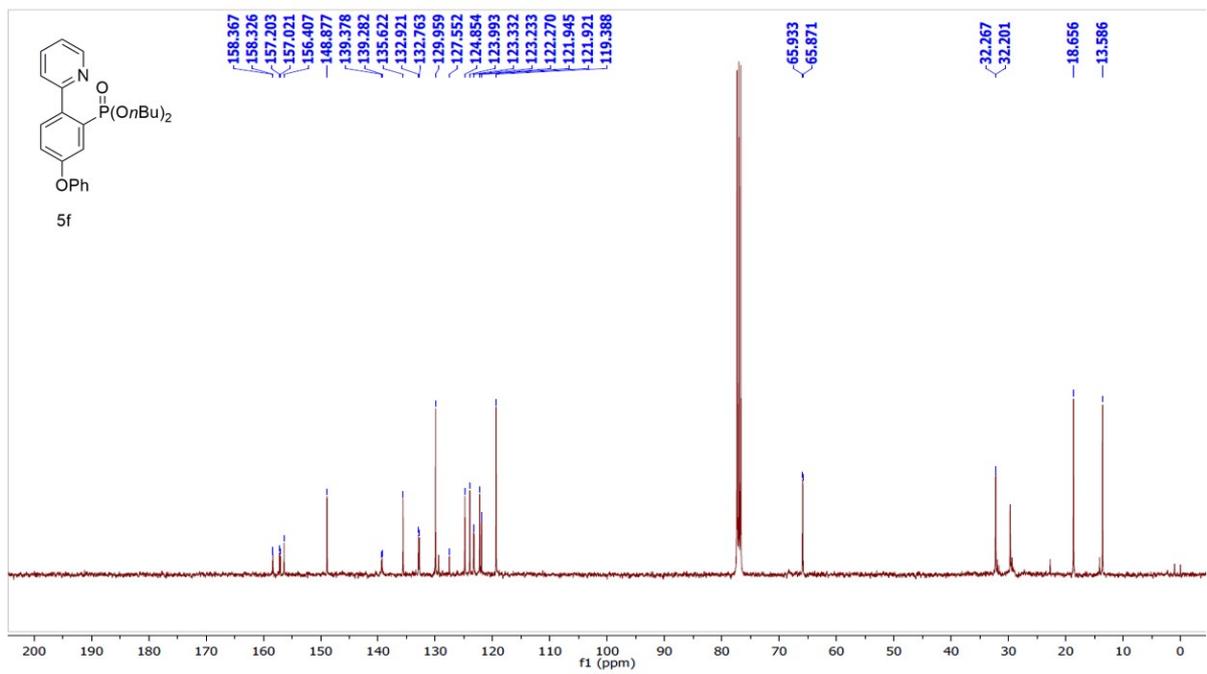




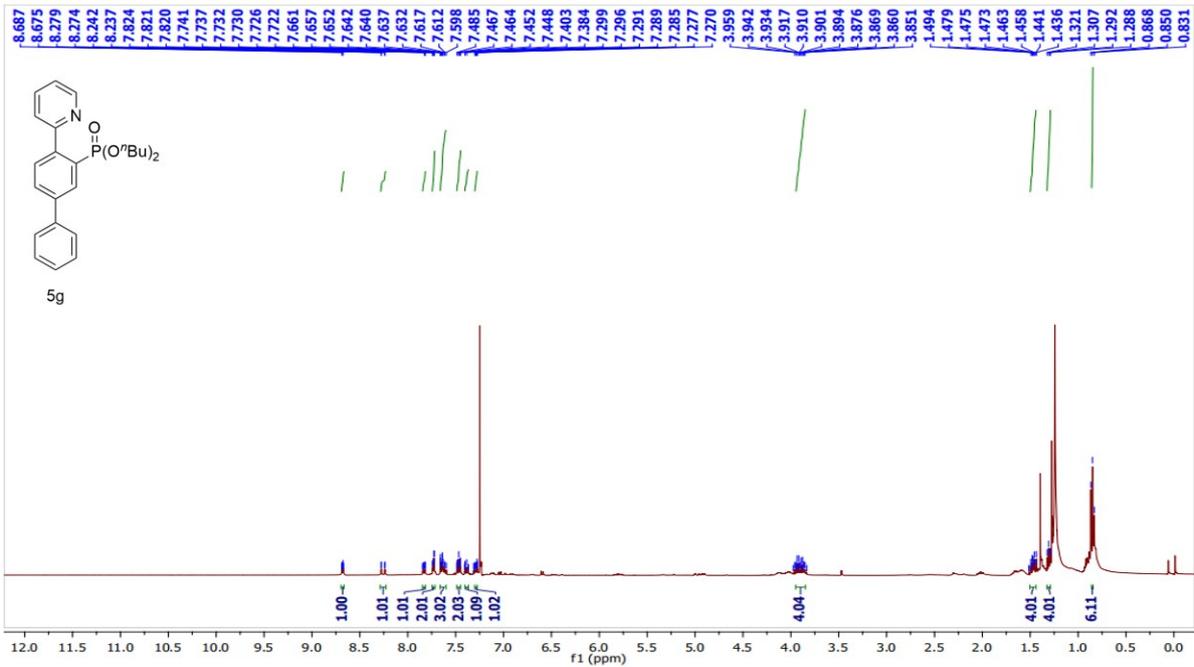
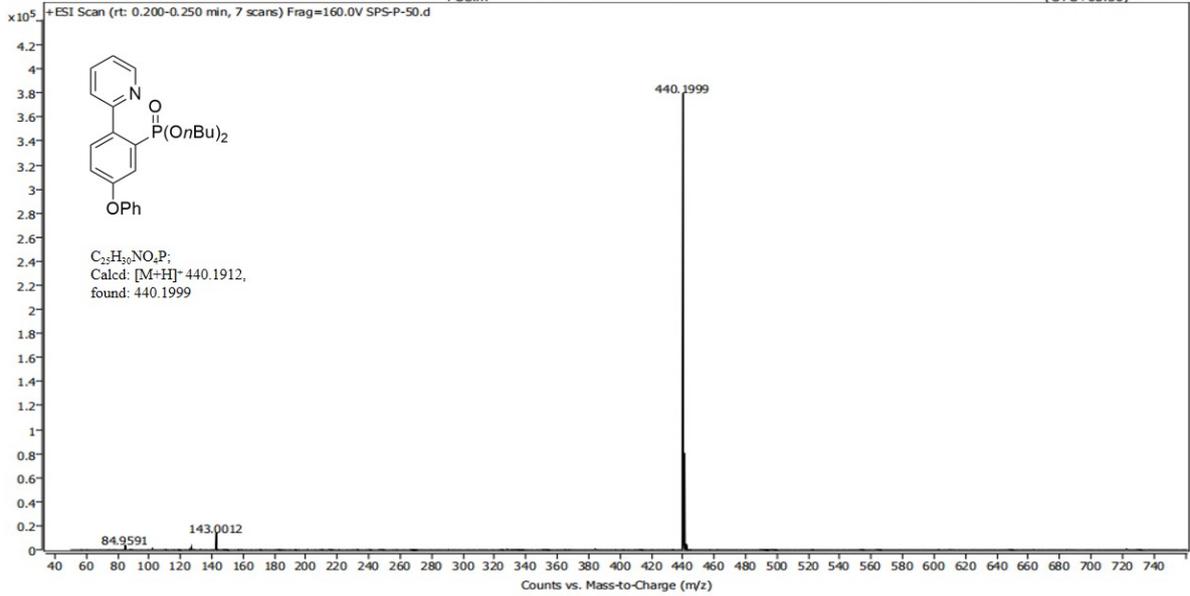


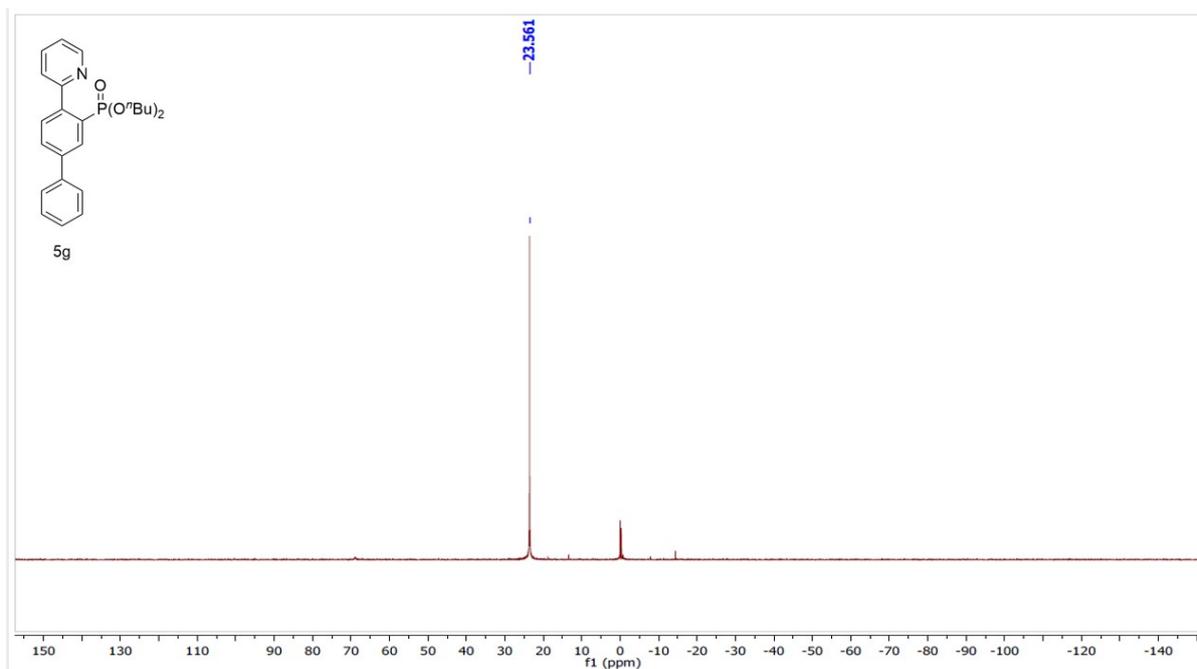
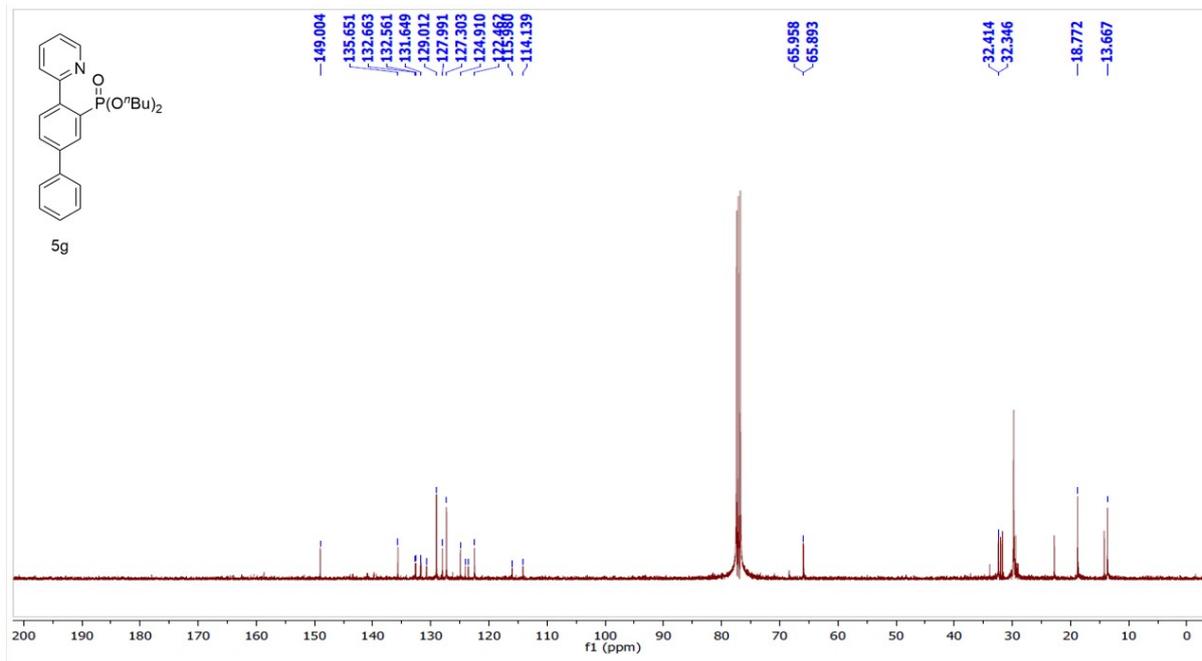
Name Inj. Vol. (ul) 0.4 Rack Pos. Plate Pos. Instrument SPS-P-53.d HRMS-17-11-2025 LCMC Success Operator
 Data File Method (Acq) POS.m Acq. Time (Local) 08-01-2026 11:39:41
 (UTC+05:30)

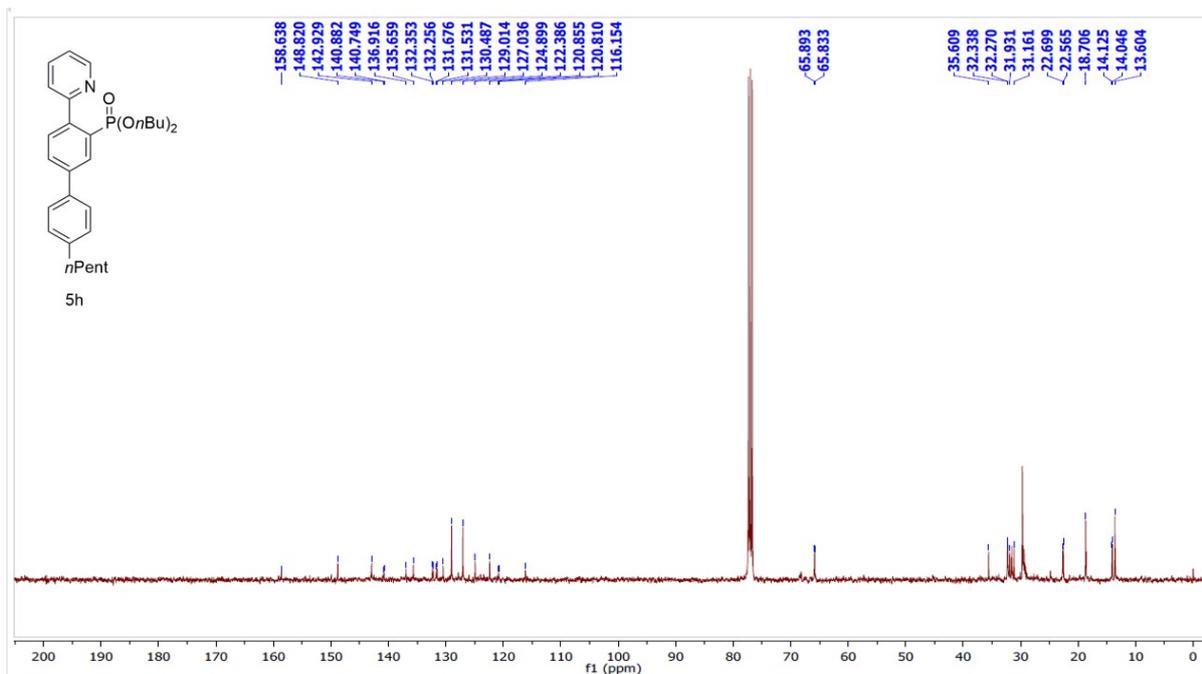
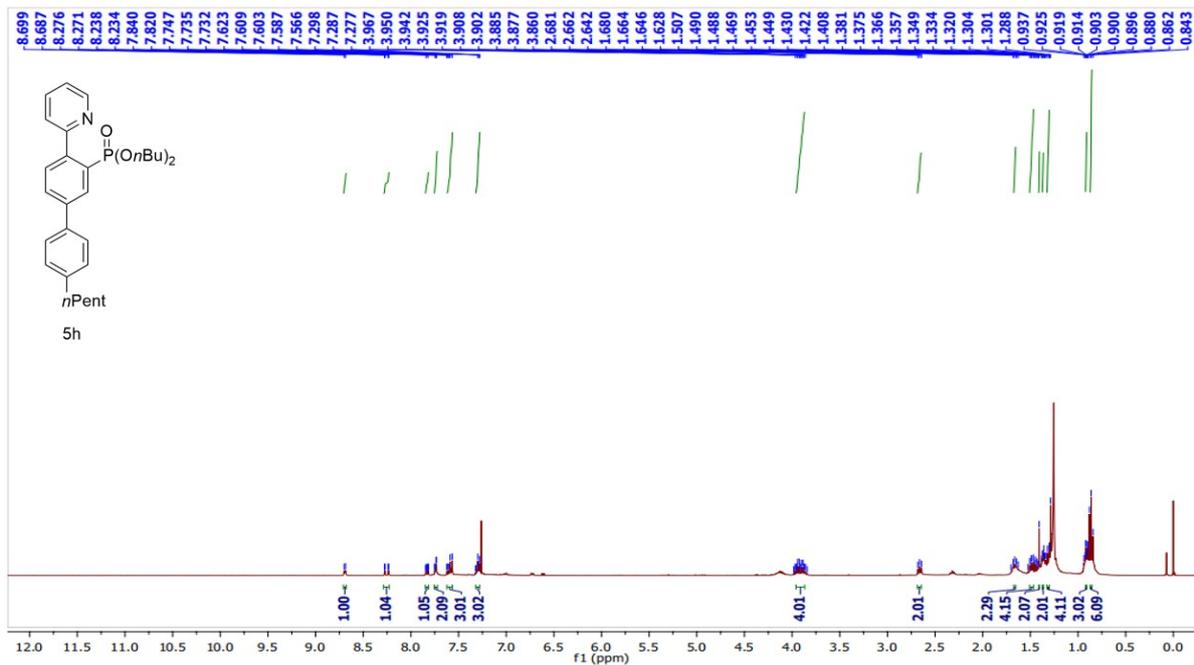


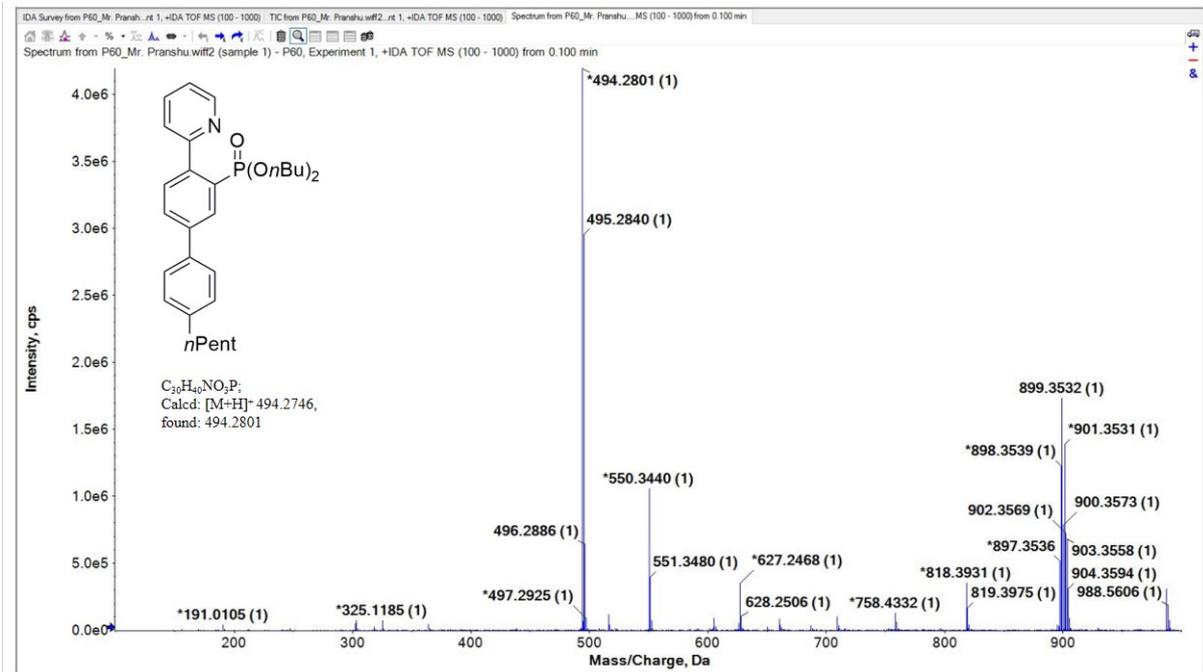
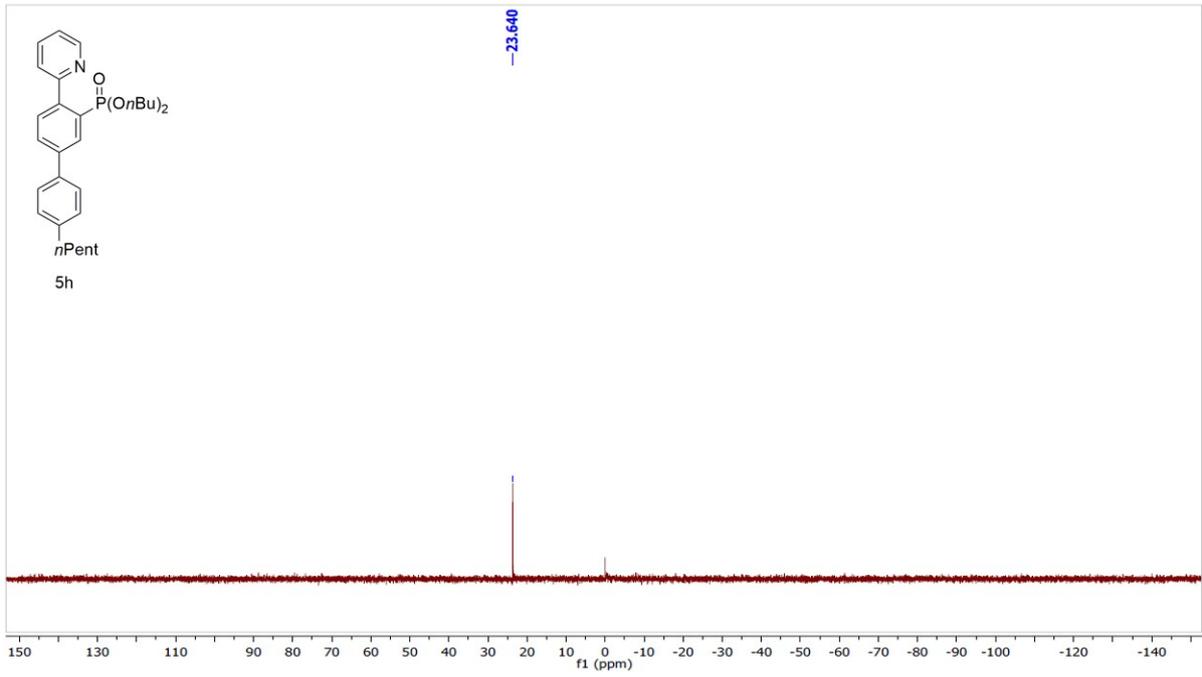


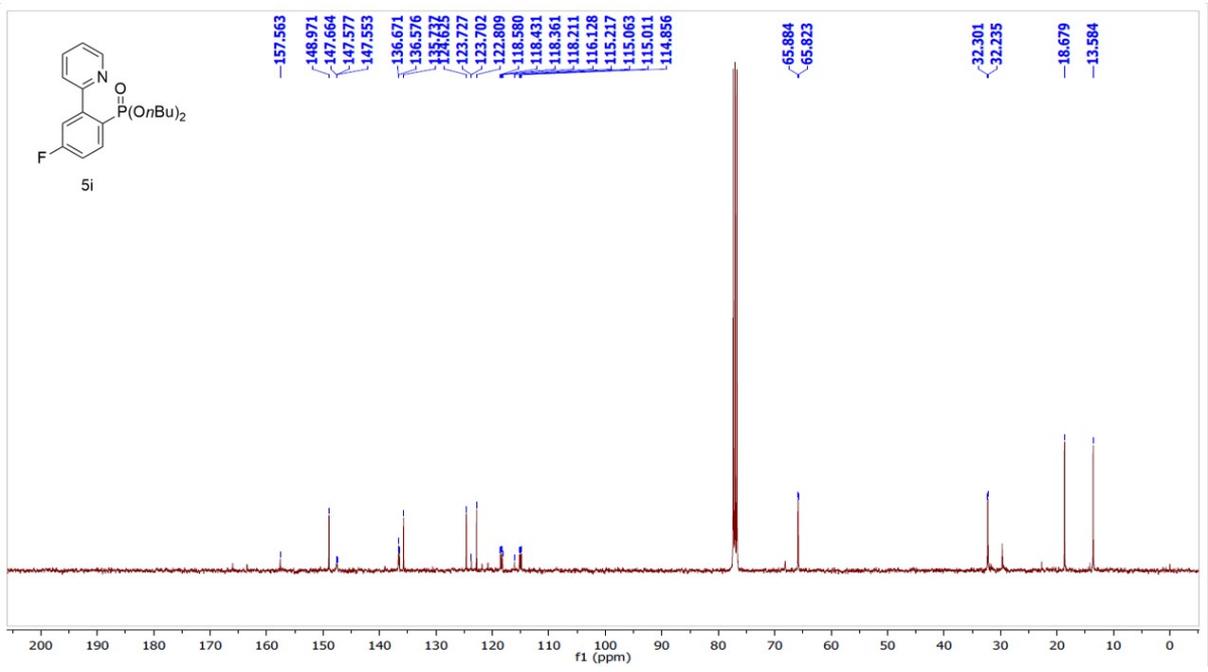
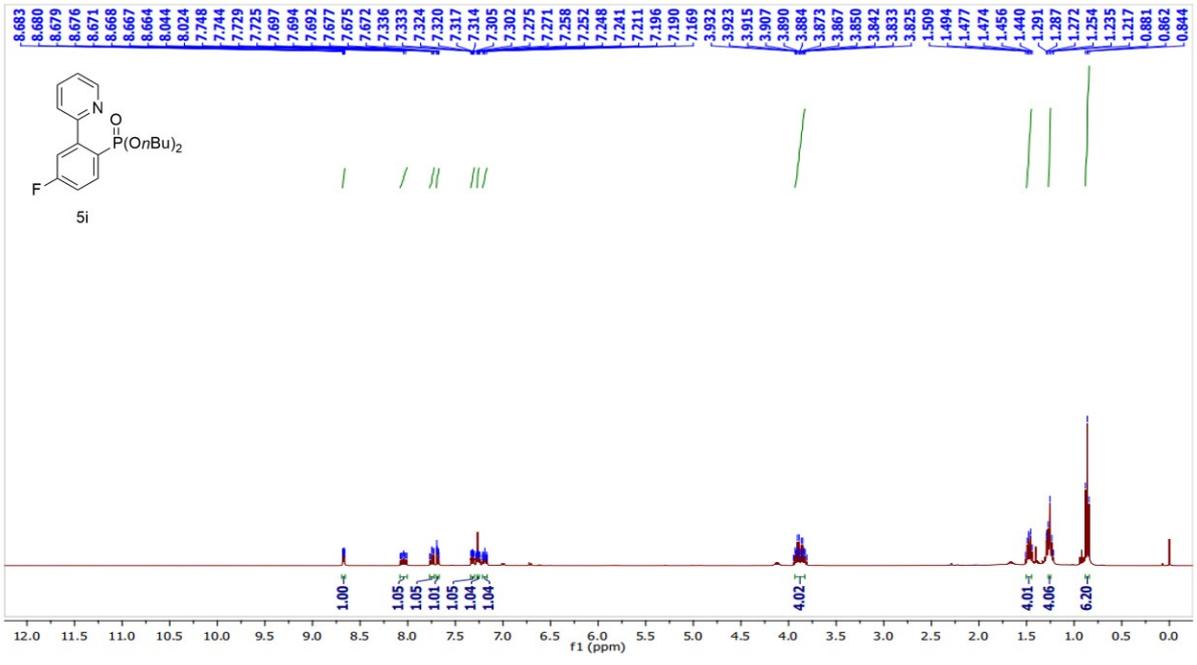
Name	Rack Pos.	Instrument	LCMS	Operator
Inj. Vol. (ul)	Plate Pos.	IRM Status	Success	
Data File	Method (Acq)	Comment		Acq. Time (Local)
0.4	SPS-P-50.d	HRMS-17-11-2025		08-01-2026 11:35:57
		POS.m		(UTC+05:30)

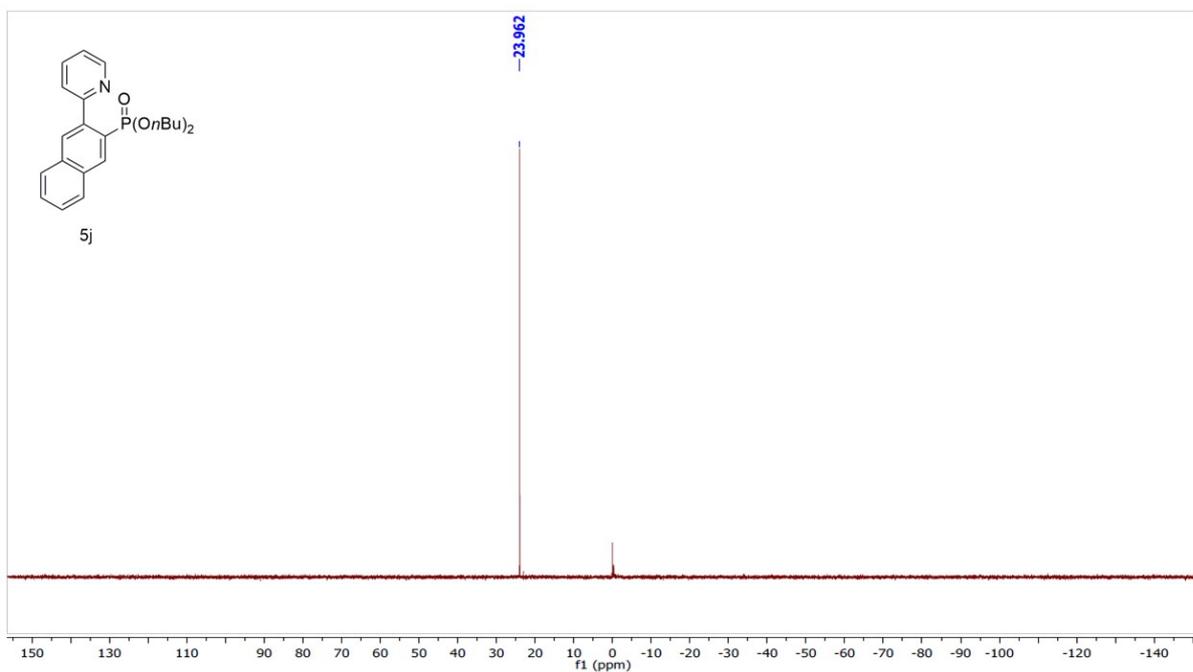
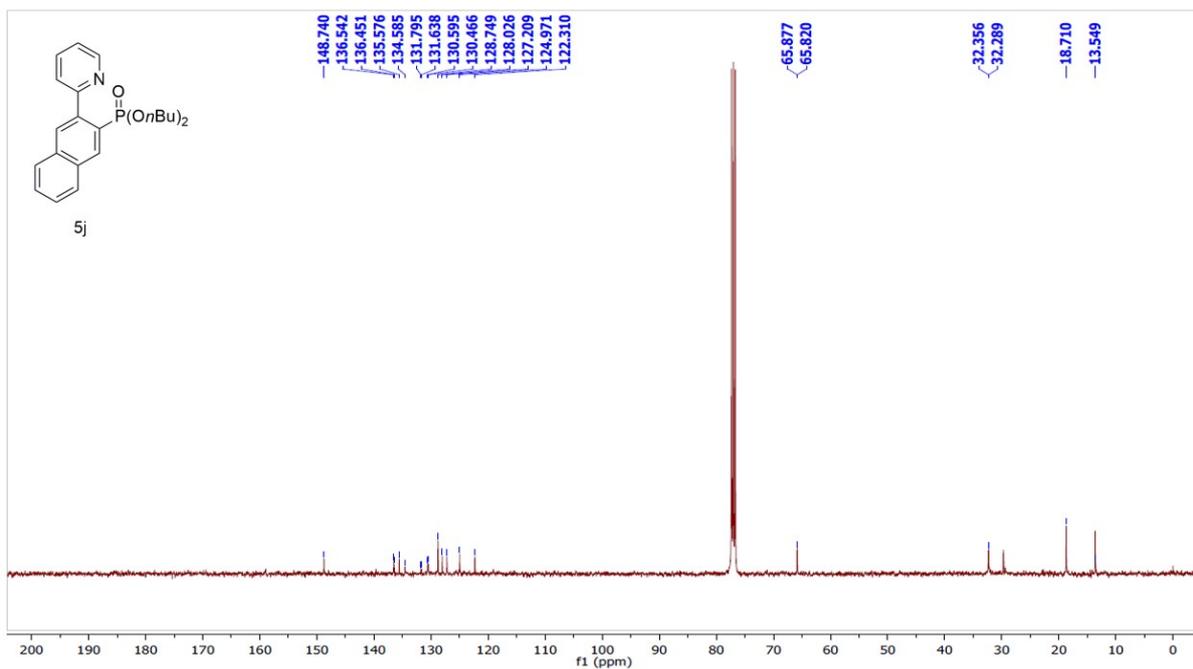


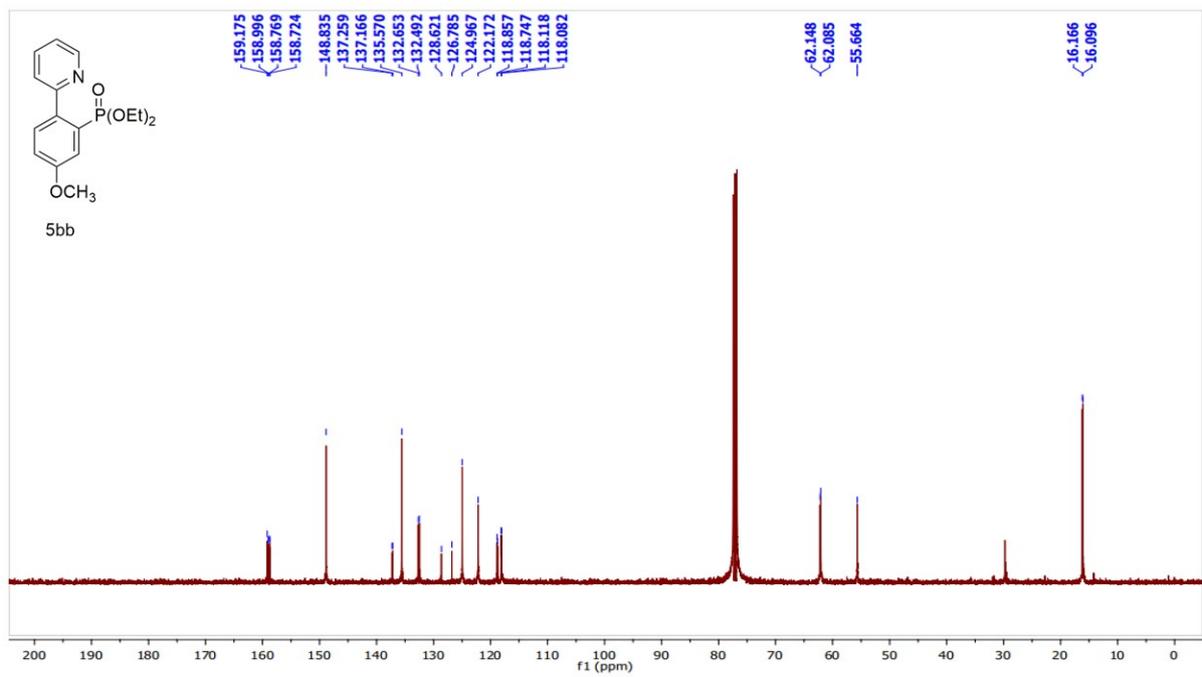
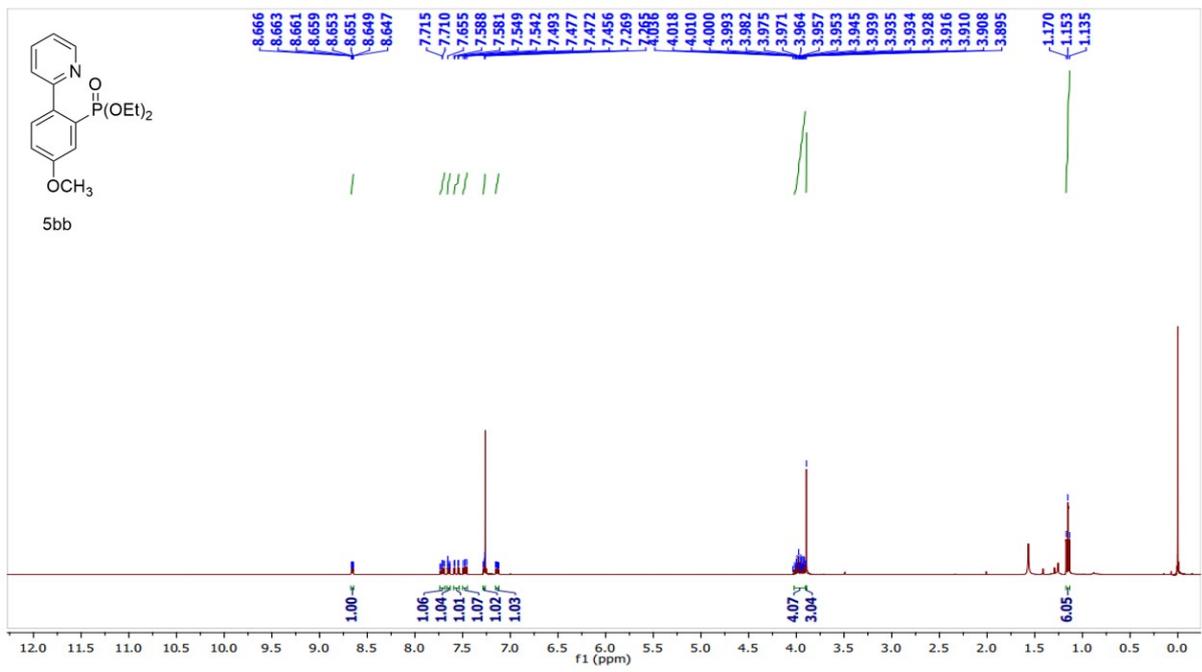


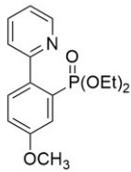




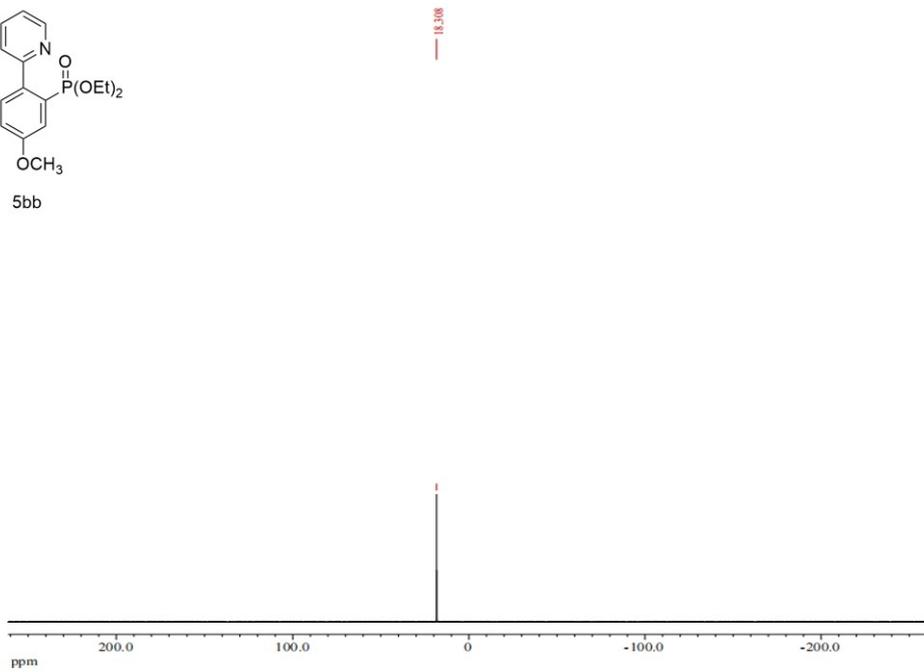








5bb



```

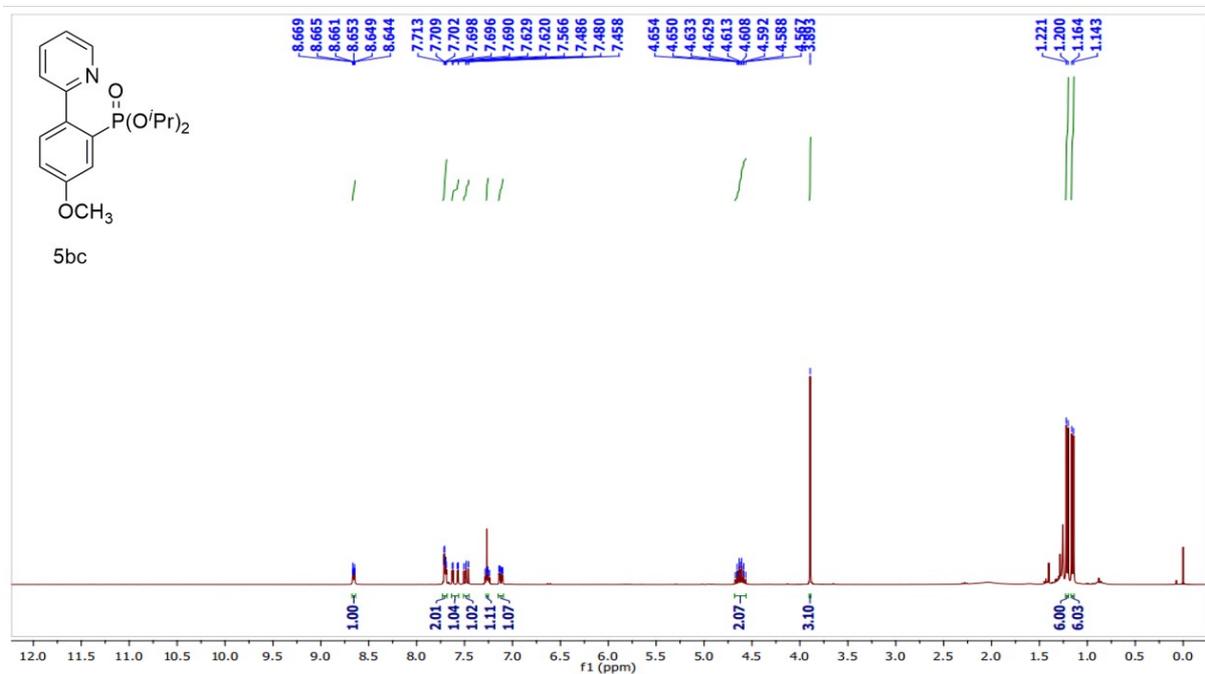
---- PROCESSING PARAMETERS ----
sepf( 4.33488[Hz], 0.0[s] )
trapzoid( 0[Hz], 0[Hz], 80[Hz], 100[Hz] )
sarofill( 2, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
auto_reference( 5[Hz], TRUE )
phase( -4.01367, 0, 47.39308[Hz] )
phase( -2.42144, 0, 47.3106[Hz] )
Derived from: P44_31P-1-1.jdf

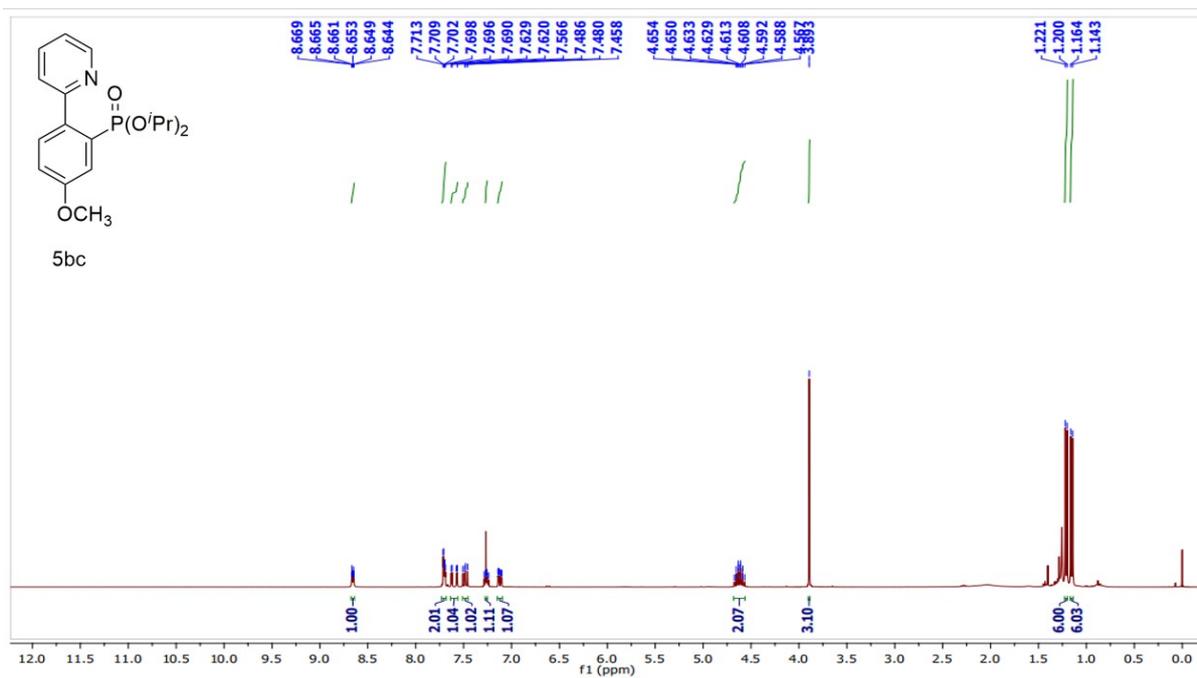
```

```

Creation_Time = 20-JAN-2025 22:04:16
Instrument = NMR-400MHz (3XQJ)
Spectrometer = NMR-700106411
Instrument Id = ABN1/QC/NMR-01
Author = 1037
Reviewed by = BRM
Solvent = CHLOROFORM-D
Acquisition Parameters
Experiment = single_pulse_dec.jsp
X_Offset = 0[ppm]
X_Bump = 142.0454535[kHz]
Relaxation_Delay = 2[s]
Scans = 512

```





4. References

- [1] a) M. V. K. Reddy, G. Anusha, P. V. G. Reddy, *New J. Chem.*, 2020, **44**, 11694-11703, DOI: <https://doi.org/10.1039/D0NJ01294G>. b) A. Gokanapalli, V. K. R. Motakatla, V. G. R. Peddiahgari, *Appl. Organomet. Chem.*, 2020, **34**, e5869, DOI: <https://doi.org/10.1002/aoc.5869>. c) A. Gokanapalli, V. K. R. Motakatla, V. G. R. Peddiahgari, *Appl. Organomet. Chem.*, 2021, **35**, e6296, DOI: <https://doi.org/10.1002/aoc.6296>. d) M. Sreeshitha, G. Hong, M. Indira, S. Farheen Banu, P. V. G. Reddy, *Appl. Organomet. Chem.*, 2024, **38**, e7719, DOI: <https://doi.org/10.1002/aoc.7719>.
- [2] Y. Kitamura, S. Sako, T. Udzu, A. Tsutsui, T. Maegawa, Y. Monguchi, H. Sajiki, *Chem. Commun.*, 2007, 5069-5071, DOI: <https://doi.org/10.1039/B712207A>.
- [3] A. Núñez, A. Sánchez, C. Burgos, J. A. Builla, *Tetrahedron*, 2004, **60**, 6217-6224, DOI: <https://doi.org/10.1016/j.tet.2004.05.038>.
- [4] C. Liu, W. Yang, *Chem. Commun.*, 2009, 6267-6269, DOI: <https://doi.org/10.1039/B912364D>.
- [5] C. Liu, Q. Ni, F. Bao, J. Qiu, *Green Chem.*, 2011, **13**, 1260-1266, DOI: <https://doi.org/10.1039/C0GC00176G>.
- [6] X. Chen, C. E. Goodhue, J. Q. Yu, *J. Am. Chem. Soc.*, 2006, **128**, 12634–12635, DOI: <https://doi.org/10.1021/ja0646747>.
- [7] X. Wang, X. Ji, C. Shao, Y. Zhang, Y. Zhang, *Org. Biomol. Chem.*, 2017, **15**, 5616-5624, DOI: <https://doi.org/10.1039/C7OB01232B>.
- [8] G. N. Li, Y. P. Zeng, K. X. Li, H. H. Chen, H. Xie, F. L. Zhang, G. Y. Chen, Z. G. Niu, 2016, 26, 323-331. DOI: <https://doi.org/10.1007/s10895-015-1718-7>.
- [9] S. Gu, D. Li, D. Long, X. Yu, S. Ma, W. Li, J. Liu, P. Tao, W. Y. Wong, *Inorg. Chem.*, 2025, **64**, 22513–22521, DOI: <https://doi.org/10.1021/acs.inorgchem.5c04352>.
- [10] O. P. Shkurko, S. G. Baram, V. P. Manaev, *Heterocycl. Compd.*, 1983, 19, 60-65. DOI: <https://doi.org/10.1007/BF00512817>.
- [11] F. Mongin, A. S. Rebstock, F. Trécourt, G. Quéguiner, F. Marsais, *J. Org. Chem.*, 2004, **69**, 6766-6671, DOI: <https://doi.org/10.1021/jo049454v>.
- [12] C. Li, T. Yano, N. Ishida, M. Murakami, *Angew. Chem.*, 2013, **125**, 9983-9986, DOI: <https://doi.org/10.1002/ange.201305202>.
- [13] C. G. Feng, M. Ye, K. J. Xiao, S. Li, J. Q. Yu, *J. Am. Chem. Soc.*, 2013, **135**, 9322–9325, DOI: <https://doi.org/10.1021/ja404526x>.