Electronic Supplementary Material (ESI) for Green Chemistry.

Visible Light Induced Hydrophosphinylation of Unactivated Alkenes Catalyzed by Salicylaldehyde

Zeqin Yuan, Simin Wang, Miaomiao Li, Tian Chen, Jiaye Fan, Fuying Xiong, Qianggen Li, Ping Hu, Bi-Qin Wang, Peng Cao and Yang Li*

College of Chemistry and Materials Science, Sichuan Normal University

Chengdu 610068, China

e-mail: yangli@sicnu.edu.cn

Supporting Information

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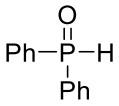
1. General methods

NMR spectra were acquired on a Bruker Ascend 600 spectrometer or a Varian 400 spectrometer, running at 600 MHz for ^{1}H, 150 MHz for ^{13}C, 162 or 243 MHz for ^{31}P and 376 or 564 MHz for ^{19}F. Chemical shifts (δ) are reported in ppm relative to internal standard signals (tetramethylsilane TMS, 0.00 ppm for ^{1}H NMR; chloroform $CDCl_3$, 77.16 ppm for ^{13}C NMR; phosphoric acid H_3PO_4, 0.00 ppm for ^{31}P NMR). The following abbreviations are used to indicate the multiplicity in NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; bs, broad signal. ^{13}C NMR spectra were acquired in a broad band decoupled mode. For characterization of isomeric mixtures, *denotes minor isomer, $^{+}$denotes overlap of signals from both isomers. Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded on a Bruke P-SIMS-Gly FT-ICR mass spectrometer. Analytical thin layer chromatography (TLC) was performed using silica gel (SiO_2, 8±2 um ≥ 80%) visualized by ultraviolet irradiation or $KMnO_4$ dip. For flash chromatography (FC) silica gel (SiO_2, 200-300 mesh) was used. For high performance thin layer chromatography (HPTLC) silica gel (SiO_2, 10-40 um) was used. Unless otherwise noted, commercially available reagents were used without further purification.

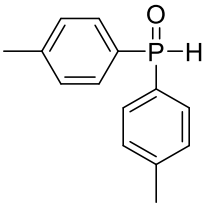
2. Synthesis of substrates

Numbering of starting materials

Secondary phosphine oxide (**1**):



1a



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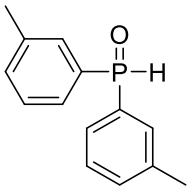

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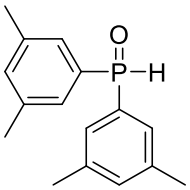

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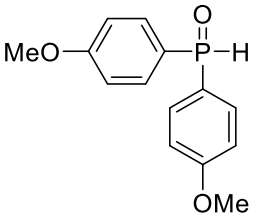
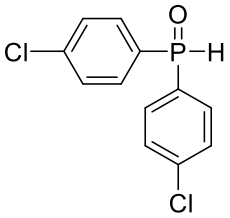
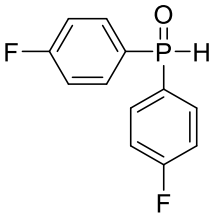


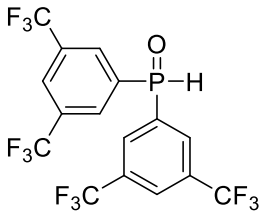
1e



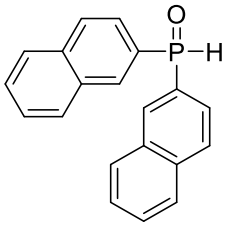
1f



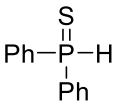
1g



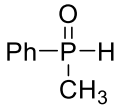
1h



1i



1j



1k

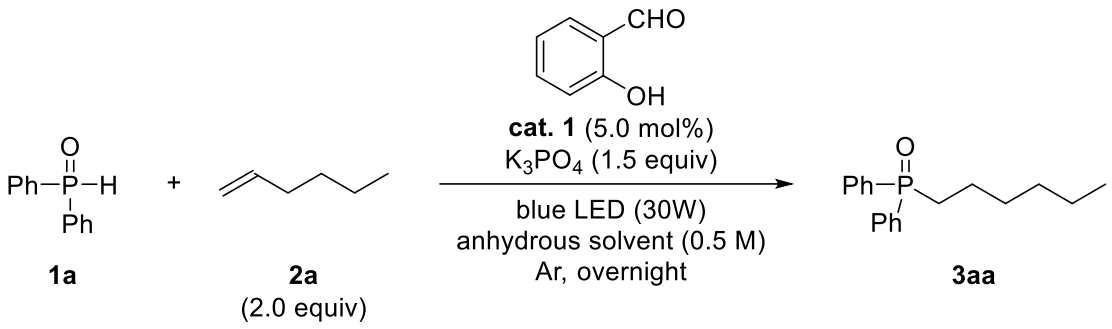
Secondary phosphine oxide **1a**, **1d** and **1i** are commercially available. Secondary phosphine oxide **1b**-**c** and **1e**-**h** were prepared according to the procedure reported.[1] Secondary phosphine oxide **1j** was prepared according to known procedure.[2] Secondary phosphine oxide **1k** was prepared according to known procedure.[3] All spectroscopic data are identical to those reported.

[1] W. Huang, J. Byun, I. Rörich, C. Ramanan, P. W. M. Blom, H. Lu, D. Wang, L. C. Silva, R. Li, L. Wang, K. Landfester, K. A. I. Zhang, *Angew. Chem., Int. Ed.*, 2018, **57**, 8316.

[2] G. Peters, *J. Am. Chem. Soc.* 1960, **82**, 4751.

[3] (*a*) Y. Bai, N. Liu, S. Wang, S. Wang, S. Ning, L. Shi, L. Cui, Z. Zhang, J. Xiang, *Org. Lett.*, 2019, **21**, 6835; (*b*) Q. Xu, C.-Q. Zhao, L.-B. Han, *J. Am. Chem. Soc.*, 2008, **130**, 12648.

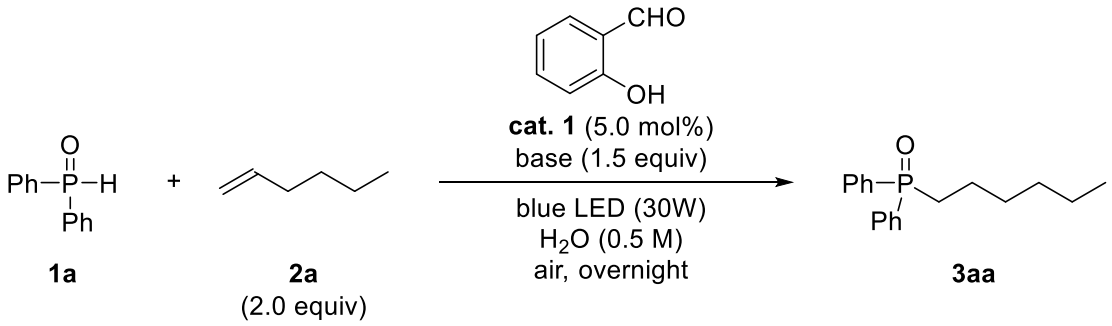
3. Screening results



1a **2a** (2.0 equiv) **3aa**

Entry	Anhydrous solvent	NMR yield
1	DMF	42%
2	DMSO	40%
3	MeOH	No **3aa** was obtained, 94% NMR yield of $Ph_2P(O)OMe$
4	MeCN	32%

All reactions were performed using **1a** (0.1 mmol), **2a** (0.2 mmol), 5.0 mol% **cat.1**, 1.5 equivalent K_3PO_4 and 0.2 mL anhydrous solvent under 30W blue LED irradiation in argon atmosphere. Yields were determined by crude ^1H NMR using 1,2-dichloroethane ($ClCH_2CH_2Cl$) as internal standard.

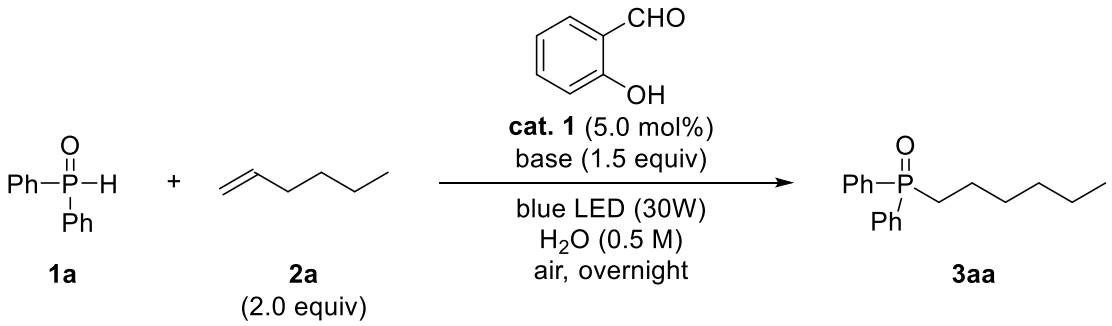


1a **2a** (2.0 equiv) **3aa**

Entry	base	NMR yield
1	K_3PO_4	71%
2	KH_2PO_4	17%
3	KHF_2	48%
4	KF	48%
5	KCl	59%

6	KBr	>59%
7	KI	18%
8	KOH	60%
9	KOMe	56%
10	KO^{t}Bu	67%
11	K_2CO_3	79%

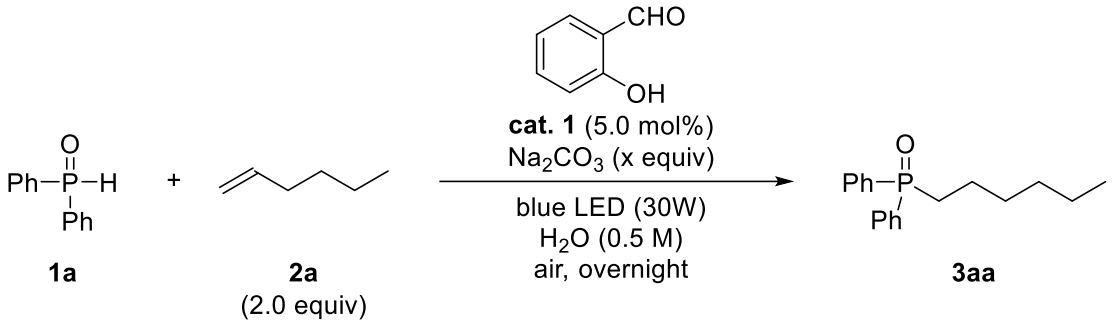
All reactions were performed using **1a** (0.1 mmol), **2a** (0.2 mmol), 5.0 mol% **cat.1**, 1.5 equivalent base and 0.2 mL distilled H_2O under 30W blue LED irradiation in air atmosphere. Yields were determined by crude ^1H NMR using 1,2-dichloroethane ($ClCH_2CH_2Cl$) as internal standard.



1a **2a** (2.0 equiv) **3aa**

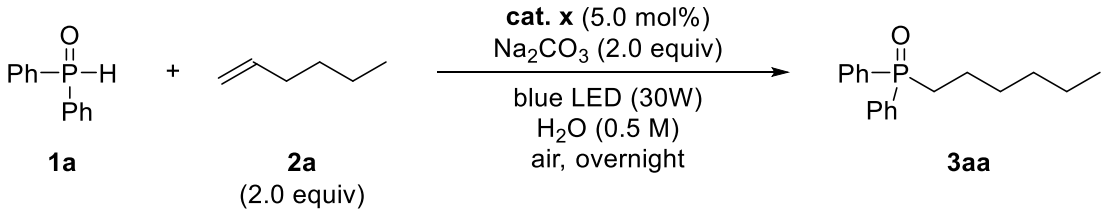
Entry	base	NMR yield
1	Li_2CO_3	64%
2	Na_2CO_3	79%
3	Cs_2CO_3	56%
4	Ag_2CO_3	17%
5	$NaHCO_3$	59%

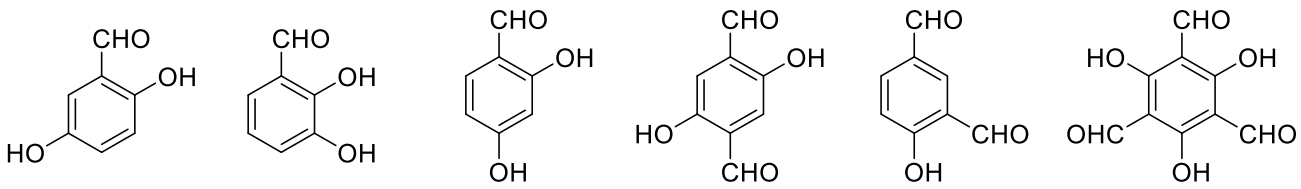
All reactions were performed using **1a** (0.1 mmol), **2a** (0.2 mmol), 5.0 mol% **cat.1**, 1.5 equivalent base and 0.2 mL distilled H_2O under 30W blue LED irradiation in air atmosphere. Yields were determined by crude ^1H NMR using 1,2-dichloroethane ($ClCH_2CH_2Cl$) as internal standard.

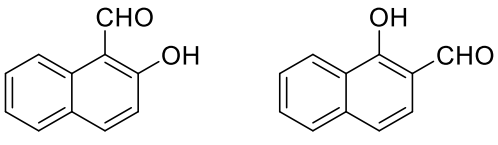


Entry	Na_2CO_3	NMR yield
1	0.5 equiv	26%
2	1.0 equiv	73%
3	2.0 equiv	83%
4	3.0 equiv	78%

All reactions were performed using **1a** (0.1 mmol), **2a** (0.2 mmol), 5.0 mol% **cat.1**, Na_2CO_3 and 0.2 mL distilled H_2O under 30W blue LED irradiation in air atmosphere. Yields were determined by crude ^1H NMR using 1,2-dichloroethane ($ClCH_2CH_2Cl$) as internal standard.

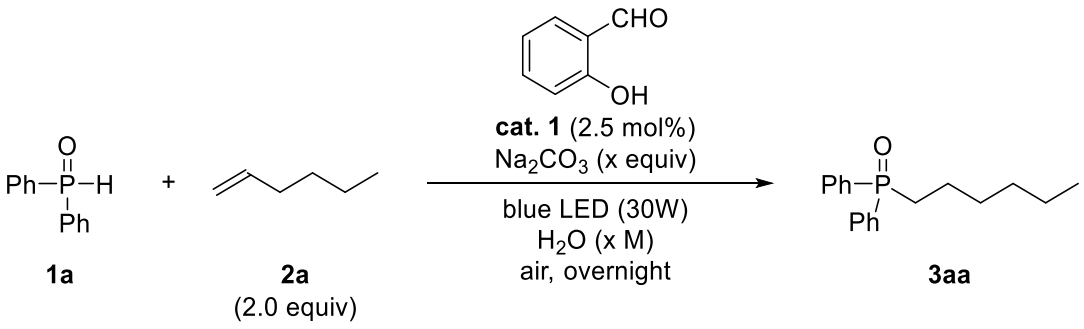






Entry	catalyst	NMR yield
1	**Cat. a**	31%
2	**Cat. b**	<5%
3	**Cat. c**	56%
4	**Cat. d**	23%
5	**Cat. e**	68%
6	**Cat. f**	44%
7	**Cat. g**	80%
8	**Cat. h**	50%

All reactions were performed using **1a** (0.1 mmol), **2a** (0.2 mmol), 5.0 mol% catalyst, 2.0 equivalent Na_2CO_3 and 0.2 mL distilled H_2O under 30W blue LED irradiation in air atmosphere. Yields were determined by crude ^1H NMR using 1,2-dichloroethane ($ClCH_2CH_2Cl$) as internal standard.

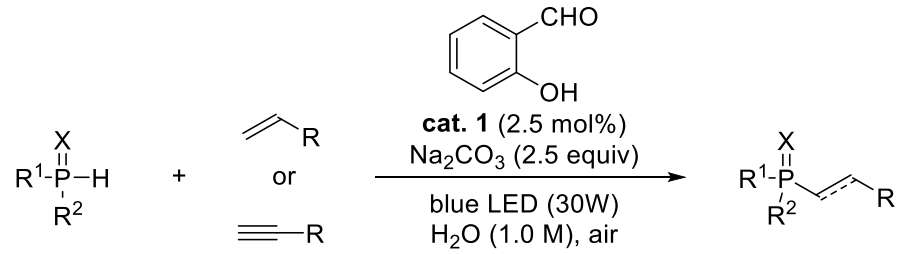


1a **2a** (2.0 equiv) **3aa**

Entry	Na_2CO_3	H_2O	NMR yield
1	2.0 equiv	0.5M	89%
2	2.5 equiv	0.5M	90%
3	2.5 equiv	1.0M	95%
4	2.5 equiv	0.33M	86%
5	2.5 equiv	0.25M	88%

All reactions were performed using **1a** (0.1 mmol), **2a** (0.2 mmol), 2.5 mol% **cat.1**, Na_2CO_3 and distilled H_2O under 30W blue LED irradiation in air atmosphere. Yields were determined by crude ^1H NMR using 1,2-dichloroethane ($ClCH_2CH_2Cl$) as internal standard.

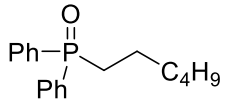
4. General procedure for the salicylaldehyde catalyzed hydrophosphinylation and spectroscopic data of novel compounds



1 **2** or **4** **3** or **5**

In a screw cap glass vial equipped with a magnetic stirring bar, secondary phosphine oxide **1** (0.2 mmol), Na_2CO_3 (0.5 mmol), distilled water (0.2 mL), alkene **2** or alkyne **4** (0.4 mmol) and catalyst **1** (0.005 mmol) was added. The two phase solution was stirred under the irradiation of 30W blue LED for noted time. After full conversion of **1**, the reaction was extracted with ethyl acetate, dried over Na_2SO_4, and purified by FC or HPTLC.

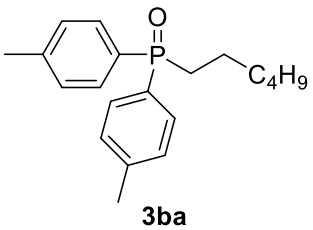
Hexyldiphenylphosphine oxide (**3aa**):



3aa

Following the procedure (3h), **3aa** was obtained after FC on silica gel (Petro ether/EtOAc 1:1-1:4) in 90% yield (51.2 mg) as colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.77 – 7.71 (m, 4H), 7.52 – 7.43 (m, 6H), 2.30 – 2.23 (m, 2H), 1.67 – 1.58 (m, 2H), 1.43 – 1.35 (m, 2H), 1.28 – 1.22 (m, 4H), 0.84 (t, J = 6.6 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 133.15 (d, J = 97.7 Hz, 2C), 131.64 (d, J = 2.7 Hz, 2C), 130.77 (d, J = 9.2 Hz, 4C), 128.62 (d, J = 11.5 Hz, 4C), 31.26, 30.65 (d, J = 14.6 Hz), 29.74 (d, J = 72.1 Hz), 22.40, 21.39 (d, J = 3.9 Hz), 14.00. **^{31}P NMR (243 MHz, $CDCl_3$)** δ 33.18 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}OP^+$ 287.1565; found: 287.1562.

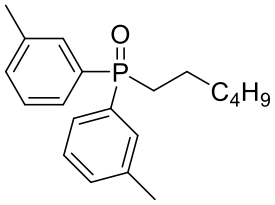
Hexyldi-*p*-tolylphosphine oxide (**3ba**):



3ba

Following the procedure (3h), **3ba** was obtained after FC on silica gel (Petro ether/EtOAc 1:1-1:4-EtOAc) in 94% yield (58.5 mg) as colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.64 – 7.58 (m, 4H), 7.28 – 7.23 (m, 4H), 2.37 (s, 6H), 2.25 – 2.18 (m, 2H), 1.64 – 1.56 (m, 2H), 1.41 – 1.34 (m, 2H), 1.28 – 1.22 (m, 4H), 0.84 (t, J = 6.9 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 141.95 (d, J = 3.1 Hz, 2C), 130.78 (d, J = 9.6 Hz, 4C), 130.06 (d, J = 100.3 Hz, 2C), 129.32 (d, J = 11.9 Hz, 4C), 31.28, 30.68 (d, J = 14.3 Hz), 29.91 (d, J = 72.8 Hz), 22.41, 21.54 (2C), 21.45 (d, J = 4.1 Hz), 14.00. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 33.69 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{28}OP^+$ 315.1878; found: 315.1880.

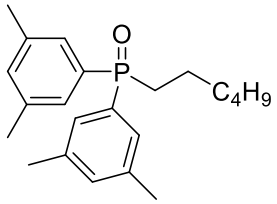
Hexyldi-*m*-tolylphosphine oxide (**3ca**):



3ca

Following the procedure (overnight), **3ca** was obtained after FC on silica gel (Petro ether/EtOAc 1:2) in 77% yield (48.1 mg) as colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.60 (d, J = 11.8 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.37 – 7.28 (m, 4H), 2.38 (s, 6H), 2.28 – 2.20 (m, 2H), 1.66 – 1.57 (m, 2H), 1.45 – 1.34 (m, 2H), 1.30 – 1.21 (m, 4H), 0.84 (t, J = 6.2 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 138.53 (d, J = 11.0 Hz), 133.16 (d, J = 97.1 Hz), 132.42 (d, J = 2.9 Hz), 131.40 (d, J = 8.7 Hz), 128.48 (d, J = 12.0 Hz), 127.68 (d, J = 9.0 Hz), 31.29, 30.70 (d, J = 14.9 Hz), 29.78 (d, J = 71.9 Hz), 22.45, 21.47 (2C), 21.42 (d, J = 4.2 Hz), 14.03. **^{31}P NMR (243 MHz, $CDCl_3$)** δ 33.37 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{28}OP^+$ 315.1878; found: 315.1880.

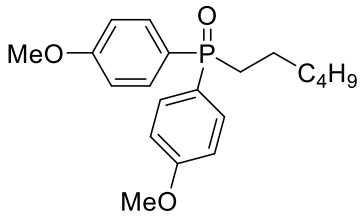
Bis(3,5-dimethylphenyl)(hexyl)phosphine oxide (**3da**):



3da

Following the procedure (3h), **3da** was obtained after FC on silica gel (Petro ether/EtOAc 1:1-1:4-EtOAc) in 77% yield (52.3 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.34 (d, J = 11.6 Hz, 4H), 7.11 (s, 2H), 2.34 (s, 12H), 2.27 – 2.16 (m, 2H), 1.66 – 1.52 (m, 2H), 1.44 – 1.36 (m, 2H), 1.30 – 1.22 (m, 4H), 0.85 (t, J = 7.0 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 138.23 (d, J = 12.0 Hz, 4C), 133.52 – 132.76 (m, 4C), 128.30 (d, J = 8.8 Hz, 4C), 31.26, 30.68 (d, J = 15.0 Hz), 29.69 (d, J = 71.8 Hz), 22.42, 21.44 – 21.26 (m, 5C), 14.01. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 33.55 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{32}OP^+$ 343.2191; found: 343.2164.

Hexylbis(4-methoxyphenyl)phosphine oxide (**3ea**):

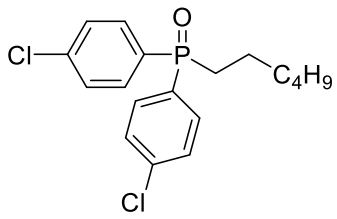


3ea

Following the procedure (overnight), **3ea** was obtained after FC on silica gel (Petro ether/EtOAc 1:2) in 86% yield (59.3 mg) as colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.69 – 7.54 (m, 4H), 6.97 (d, J = 8.1 Hz, 4H), 3.83 (s, 6H), 2.27 – 2.11 (m, 2H), 1.62 – 1.53 (m, 2H), 1.41 – 1.33 (m, 2H), 1.28 – 1.21 (m, 4H), 0.84 (t, J = 6.7 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 162.25 (d, J = 2.7 Hz, 2C), 132.70 (d, J = 10.6 Hz, 4C), 124.82 (d, J = 104.1 Hz, 2C), 114.23 (d, J = 12.4 Hz, 4C), 55.43 (2C), 31.42, 30.82 (d, J = 14.7 Hz), 30.35 (d, J = 72.9 Hz), 22.54, 21.65 (d, J = 3.8 Hz), 14.12.

^{31}P NMR (162 MHz, $CDCl_3$) δ 33.40 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{28}O_3P^+$ 347.1776; found: 347.1768.

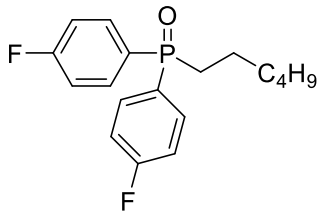
Bis(4-chlorophenyl)(hexyl)phosphine oxide (**3fa**):



3fa

Following the procedure (overnight), **3fa** was obtained after FC on silica gel (Petro ether/EtOAc 1:1-1:4-EtOAc) in 71% yield (50.0 mg) as colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.60 – 7.55 (m, 4H), 7.40 – 7.36 (m, 4H), 2.19 – 2.11 (m, 2H), 1.56 – 1.45 (m, 2H), 1.38 – 1.27 (m, 2H), 1.23 – 1.13 (m, 4H), 0.77 (t, J = 6.8 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 138.57 (d, J = 3.2 Hz, 2C), 132.19 (d, J = 10.0 Hz, 4C), 131.38 (d, J = 99.0 Hz, 2C), 129.21 (d, J = 12.0 Hz, 4C), 31.30, 30.65 (d, J = 15.0 Hz), 29.71 (d, J = 72.8 Hz), 22.45, 21.37 (d, J = 4.1 Hz), 14.05. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 32.25 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}Cl_2OP^+$ 355.0785, 357.0756, 359.0726; found: 359.0705, 357.0730, 355.0772.

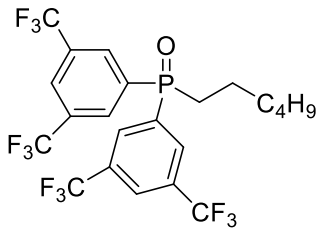
Bis(4-fluorophenyl)(hexyl)phosphine oxide (**3ga**):



3ga

Following the procedure (overnight), **3ga** was obtained after FC on silica gel (Petro ether/EtOAc 1:1-1:4-EtOAc) in 80% yield (51.1 mg) as colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.64 (dd, J = 14.0, 8.9 Hz, 4H), 7.09 (t, J = 8.3 Hz, 4H), 2.16 (m, 2H), 1.56 – 1.46 (m, 2H), 1.40 – 1.27 (m, 2H), 1.21 – 1.13 (m, 4H), 0.77 (t, J = 6.5 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 165.02 (d, J = 253.1 Hz, 2C), 133.27 (t, J = 9.5 Hz, 4C), 129.06 (d, J = 100.8 Hz, 2C), 116.19 (dd, J = 21.6, 11.9 Hz, 4C), 31.30, 30.65 (d, J = 14.2 Hz), 30.07 (d, J = 73.1 Hz), 22.45, 21.42 (d, J = 2.5 Hz), 14.03. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 32.24 (s). **^{19}F NMR (564 MHz, $CDCl_3$)** δ -106.82 – -107.08 (m). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}F_2OP^+$ 323.1376; found: 323.1368.

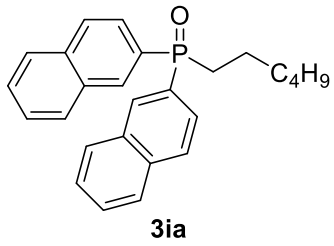
Bis(3,5-bis(trifluoromethyl)phenyl)(hexyl)phosphine oxide (**3ha**):



3ha

Following the procedure (overnight), **3ha** was obtained after HPTLC (Petro ether/EtOAc 1:1) in 59% yield (65.7 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.23 (d, J = 11.0 Hz, 4H), 8.08 (s, 2H), 2.44 (d, J = 5.4 Hz, 2H), 1.70 – 1.60 (m, 2H), 1.50 – 1.42 (m, 2H), 1.32 – 1.24 (m, 4H), 0.86 (t, J = 6.9 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 135.63 (d, J = 95.2 Hz, 2C), 132.94 (qd, J = 34.0, 11.4 Hz, 4C), 130.81 (d, J = 6.4 Hz, 4C), 126.39 (d, J = 3.0 Hz, 2C), 122.79 (q, J = 273.3 Hz, 2C), 31.18, 30.44 (d, J = 14.6 Hz), 29.31 (d, J = 73.1 Hz), 22.39, 21.16 (d, J = 4.2 Hz), 13.94.**^{31}P NMR (162 MHz, $CDCl_3$)** δ 29.26 (s). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.10 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}F_{12}OP^+$ 559.1060; found: 559.1050.

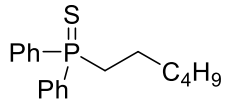
Hexyldi(naphthalen-2-yl)phosphine oxide (**3ia**):



3ia

Following the procedure (overnight), **3ia** was obtained after FC on silica gel (Petro ether/EtOAc 1:1-1:4-EtOAc) in 85% yield (65.5 mg) as colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.43 (d, J = 13.1 Hz, 2H), 7.91 (dd, J = 14.3, 5.4 Hz, 4H), 7.85 (d, J = 8.0 Hz, 2H), 7.71 (t, J = 8.9 Hz, 2H), 7.61 – 7.51 (m, 4H), 2.44 (dt, J = 27.0, 13.5 Hz, 2H), 1.73 – 1.64 (m, 2H), 1.49 – 1.38 (m, 2H), 1.31 – 1.20 (m, 4H), 0.83 (t, J = 6.9 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 134.69 (d, J = 1.8 Hz, 2C), 132.85 (d, J = 8.3 Hz, 2C), 132.70 (d, J = 12.7 Hz, 2C), 130.37 (d, J = 98.0 Hz, 2C), 128.96 (2C), 128.60 (d, J = 11.3 Hz, 2C), 128.17 (2C), 127.91 (2C), 127.04 (2C), 125.79 (d, J = 10.6 Hz, C), 31.36, 30.80 (d, J = 14.9 Hz), 29.70 (d, J = 72.2 Hz), 22.49, 21.58 (d, J = 3.5 Hz), 14.07. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 33.58 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{28}OP^+$ 387.1878; found: 387.1851.

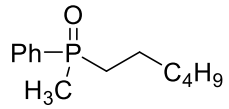
Hexyldiphenylphosphine sulfide (**3ja**):



3ja

Following the procedure (overnight), **3ja** was obtained after FC on silica gel (Petro ether/EtOAc 1:2) in 50% yield (30 mg) as colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.85 – 7.78 (m, 4H), 7.51 – 7.41 (m, 6H), 2.48 – 2.38 (m, 2H), 1.67 – 1.55 (m, 2H), 1.42 – 1.34 (m, 2H), 1.29 – 1.22 (m, 4H), 0.84 (t, J = 6.7 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 133.12 (d, J = 79.6 Hz, 2C), 131.48 (d, J = 2.8 Hz, 2C), 131.18 (d, J = 10.1 Hz, 4C), 128.71 (d, J = 12.0 Hz, 4C), 32.69 (d, J = 56.5 Hz), 31.39, 30.42 (d, J = 16.4 Hz), 22.55, 22.22 (d, J = 2.9 Hz), 14.10.**^{31}P NMR (162 MHz, $CDCl_3$)** δ 43.35 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}PS^+$ 303.1336; found: 303.1316.

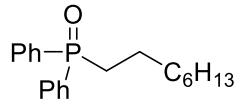
Hexyl(methyl)(phenyl)phosphine oxide (**3ka**):



3ka

Following the procedure (overnight), **3ka** was obtained after HPTLC (EtOAc) in 67% yield (49.8 mg) as colorless liquid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.74 – 7.69 (m, 2H), 7.55 – 7.47 (m, 3H), 1.99 – 1.84 (m, 2H), 1.70 (d, J = 12.7 Hz, 3H), 1.66 – 1.55 (m, 1H), 1.53 – 1.42 (m, 1H), 1.40 – 1.31 (m, 2H), 1.30 – 1.21 (m, 4H), 0.85 (t, J = 6.9 Hz, 3H).**^{13}C NMR (150 MHz, $CDCl_3$)** δ 133.79 (d, J = 95.6 Hz), 131.65 (d, J = 2.2 Hz), 130.08 (d, J = 8.9 Hz, 2C), 128.72 (d, J = 11.1 Hz, 2C), 31.84 (d, J = 70.5 Hz), 31.33, 30.64 (d, J = 14.9 Hz), 22.46, 21.65 (d, J = 4.0 Hz), 16.08 (d, J = 69.6 Hz), 14.07. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 38.37 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{22}OP^+$ 225.1408; found: 225.1413.

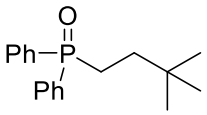
Octyldiphenylphosphine oxide (**3ab**):



3ab

Following the procedure (overnight), **3ab** was obtained after HPTLC (Petro ether/EtOAc 1:1) in 83% yield (52.3 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 – 7.58 (m, 4H), 7.46 – 7.32 (m, 6H), 2.20 – 2.14 (m, 2H), 1.58 – 1.49 (m, 2H), 1.34 – 1.26 (m, 2H), 1.20 – 1.10 (m, 8H), 0.77 (t, J = 7.1 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 133.21 (d, J = 97.9 Hz, 2C), 131.67 (d, J = 2.2 Hz, 2C), 130.80 (d, J = 8.9 Hz, 4C), 128.65 (d, J = 11.8 Hz, 4C), 31.78, 31.00 (d, J = 14.4 Hz), 29.76 (d, J = 72.0 Hz), 29.06, 29.04, 22.63, 21.43 (d, J = 3.5 Hz), 14.11. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 33.28 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{28}OP^+$ 315.1878; found: 315.1880.

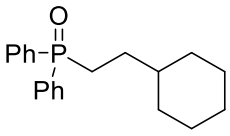
(3,3-Dimethylbutyl)diphenylphosphine oxide (**3ac**):



3ac

Following the procedure (overnight), **3ac** was obtained after HPTLC (Petro ether/EtOAc 1:2) in 77% yield (44.1 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.68 – 7.64 (m, 4H), 7.46 – 7.36 (m, 6H), 2.17 – 2.10 (m, 2H), 1.46 – 1.39 (m, 2H), 0.81 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 133.14 (d, J = 97.9 Hz, 2C), 131.73 (d, J = 2.8 Hz, 2C), 130.84 (d, J = 8.9 Hz, 4C), 128.72 (d, J = 11.8 Hz, 4C), 34.81 (d, J = 3.7 Hz), 30.60 (d, J = 14.0 Hz), 28.89, 25.11 (d, J = 72.6 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 34.23 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}OP^+$ 287.1565; found: 287.1562.

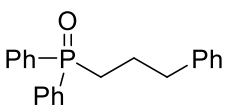
(2-Cyclohexylethyl)diphenylphosphine oxide (**3ad**):



3ad

Following the procedure (overnight), **3ad** was obtained after HPTLC (Petro ether/EtOAc 1:1) in 80% yield (50.2 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 – 7.70 (m, 4H), 7.53 – 7.42 (m, 6H), 2.30 – 2.21 (m, 2H), 1.74 – 1.64 (m, 4H), 1.64 – 1.59 (m, 1H), 1.55 – 1.47 (m, 2H), 1.31 – 1.05 (m, 4H), 0.91 – 0.83 (m, 2H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 133.21 (d, J = 98.0 Hz, 2C), 131.66 (d, J = 2.4 Hz, 2C), 130.80 (d, J = 9.7 Hz, 4C), 128.65 (d, J = 11.9 Hz, 4C), 38.68 (d, J = 14.1 Hz), 32.79 (2C), 28.53 (d, J = 4.2 Hz), 27.22 (d, J = 72.2 Hz), 26.50, 26.20 (2C). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 33.78 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{26}OP^+$ 313.1721; found: 313.1720.

Diphenyl(3-phenylpropyl)phosphine oxide (**3ae**):

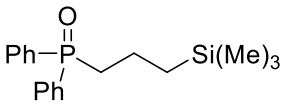


3ae

Following the procedure (overnight), **3ae** was obtained after HPTLC (Petro ether/EtOAc 1:2) in 70% yield (45.1 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.62 – 7.56 (m, 4H), 7.44 – 7.33 (m, 6H), 7.20 – 7.16 (m, 2H), 7.13 – 7.08 (m, 1H), 7.05 – 7.00 (m, 2H), 2.64 (t, J = 7.4 Hz, 2H), 2.21 – 2.13 (m, 2H), 1.92 – 1.84 (m, 2H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 140.92, 133.03 (d, J = 98.1 Hz, 2C), 131.78 (d, J = 2.5 Hz, 2C), 130.85 (d, J = 9.4 Hz, 4C), 128.77 (2C), 128.65 (d, J = 11.8 Hz, 4C), 128.52 (2C), 126.21, 36.74 (d, J = 15.1 Hz), 29.02 (d, J =

72.0 Hz), 23.10 (d, J = 3.5 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 33.15 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}OP^+$ 321.1408; found: 321.1395.

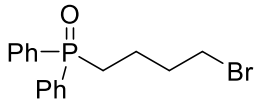
Diphenyl(3-(trimethylsilyl)propyl)phosphine oxide (**3af**):



3af

Following the procedure (overnight), **3af** was obtained after HPTLC (Petro ether/EtOAc 1:2) in 77% yield (48.7 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.74 – 7.69 (m, 4H), 7.52 – 7.43 (m, 6H), 2.33 – 2.25 (m, 2H), 1.68 – 1.58 (m, 2H), 0.65 – 0.58 (m, 2H), -0.08 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 133.36 (d, J = 97.2 Hz, 2C), 131.72 (d, J = 2.3 Hz, 2C), 130.85 (d, J = 9.6 Hz, 4C), 128.72 (d, J = 11.1 Hz, 4C), 33.77 (d, J = 69.8 Hz), 18.94 (d, J = 12.9 Hz), 16.49 (d, J = 4.2 Hz), -1.64 (3C).**^{31}P NMR (162 MHz, $CDCl_3$)** δ 32.65 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{26}OPSi^+$ 317.1491; found: 317.1487.

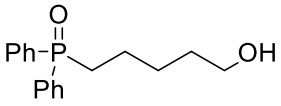
(4-Bromobutyl)diphenylphosphine oxide (**3ag**):



3ag

Following the procedure (12h, 2.0 equivalent extra alkene was added and reacted for additional 12h), **3ag** was obtained after HPTLC (Petro ether/EtOAc 1:2) in 50% yield (33.8 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 – 7.63 (m, 4H), 7.56 – 7.37 (m, 6H), 3.30 (t, J = 6.7 Hz, 2H), 2.25 – 2.17 (m, 2H), 1.96 – 1.83 (m, 2H), 1.77 – 1.67 (m, 2H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 132.89 (d, J = 98.4 Hz, 2C), 131.95 (d, J = 2.2 Hz, 2C), 130.88 (d, J = 9.5 Hz, 4C), 128.85 (d, J = 11.4 Hz, 4C), 33.61 (d, J = 14.1 Hz), 32.72 (s), 28.92 (d, J = 71.9 Hz), 20.48 (d, J = 3.6 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 32.74 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}BrOP^+$ 337.0357, 339.0336; found: 337.0328, 339.0338.

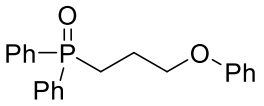
(5-Hydroxypentyl)diphenylphosphine oxide (**3ah**):



3ah

Following the procedure (overnight), **3ah** was obtained after HPTLC (MeOH/DCM 1:10) in 69% yield (39.5 mg) as colorless liquid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.68 – 7.61 (m, 4H), 7.46 – 7.36 (m, 6H), 3.51 (t, J = 6.2 Hz, 2H), 2.24 – 2.16 (m, 2H), 1.61 – 1.53 (m, 2H), 1.51 – 1.37 (m, 4H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 133.00 (d, J = 98.1 Hz, 2C), 131.85 (d, J = 2.7 Hz, 2C), 130.84 (d, J = 9.5 Hz, 4C), 128.78 (d, J = 11.8 Hz, 4C), 62.27 (s), 32.18 (s), 29.63 (d, J = 71.9 Hz), 27.12 (d, J = 13.9 Hz), 21.30 (d, J = 4.1 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 33.71 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{22}O_2P^+$ 289.1357; found: 289.1355.

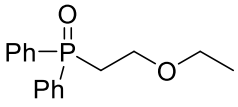
(3-Phenoxypropyl)diphenylphosphine oxide (**3ai**):



3ai

Following the procedure (overnight), **3ai** was obtained after HPTLC (Petro ether/EtOAc 1:2) in 74% yield (49.8 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 – 7.64 (m, 4H), 7.47 – 7.34 (m, 6H), 7.23 – 7.09 (m, 2H), 6.88 – 6.82 (m, 1H), 6.81 – 6.73 (m, 2H), 3.92 (t, J = 5.9 Hz, 2H), 2.45 – 2.36 (m, 2H), 2.09 – 1.98 (m, 2H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 158.69, 132.91 (d, J = 98.9 Hz, 2C), 131.88 (d, J = 2.7 Hz, 2C), 130.86 (d, J = 9.0 Hz, 4C), 129.54 (2C), 128.79 (d, J = 11.9 Hz, 4C), 120.91, 114.54 (2C), 67.51 (d, J = 14.2 Hz), 26.50 (d, J = 72.9 Hz), 21.89 (d, J = 3.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 33.17 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}O_2P^+$ 337.1357; found: 337.1342.

(2-Ethoxyethyl)diphenylphosphine oxide (**3aj**):

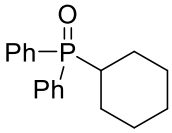


3aj

Following the procedure (overnight), **3aj** was obtained after HPTLC (Petro ether/EtOAc 1:2) in 45% yield (23.4 mg) as colorless liquid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.70 – 7.65 (m, 4H), 7.46 – 7.37 (m, 6H), 3.67 (dd, J = 16.4, 7.8 Hz, 2H), 3.32 (q, J = 7.0 Hz, 2H), 2.60 – 2.55 (m, 2H), 1.00 (t, J = 7.0 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ

133.05 (d, J = 99.7 Hz, 2C), 131.89 (d, J = 2.7 Hz, 2C), 130.82 (d, J = 9.7 Hz, 4C), 128.72 (d, J = 11.5 Hz, 4C), 66.37, 63.89, 30.99 (d, J = 70.8 Hz), 15.07. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 30.46 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}O_2P^+$ 275.1201; found: 275.1207.

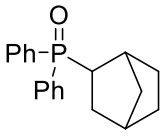
Cyclohexyldiphenylphosphine oxide (**3ak**):



3ak

Following the procedure (overnight), **3ak** was obtained after HPTLC (Petro ether/EtOAc 1:1) in 85% yield (48.0 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.73 – 7.68 (m, 4H), 7.45 – 7.36 (m, 6H), 2.21 – 2.12 (m, 1H), 1.77 – 1.70 (m, 2H), 1.69 – 1.59 (m, 3H), 1.52 – 1.40 (m, 2H), 1.24 – 1.14 (m, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** 132.18 (d, J = 94.7 Hz, 2C), 131.56 (d, J = 2.2 Hz, 2C), 131.20 (d, J = 8.6 Hz, 4C), 128.66 (d, J = 11.0 Hz, 4C), 37.31 (d, J = 73.1 Hz), 26.49 (d, J = 13.2 Hz, 2C), 25.89, 24.90 (d, J = 2.9 Hz, 2C). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 35.11 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}OP^+$ 285.1408; found: 285.1387.

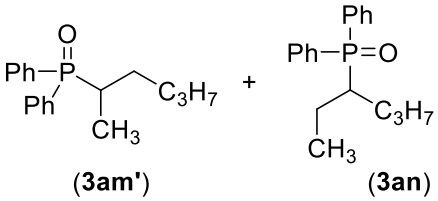
Bicyclo[2.2.1]heptan-2-yldiphenylphosphine oxide (**3al**):



3al

Following the procedure (overnight), **3al** was obtained after FC on silica gel (Petro ether/EtOAc 4:1-1:1-EtOAc) in 90% yield (53.3 mg) and 1:1 dr as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.83 – 7.71$^+$ (m, 4H, 4H*), 7.51 – 7.40$^+$ (m, 6H, 6H*), 2.51 – 2.47$^+$ (m, 1H, 1H*), 2.36$^+$ (d, J = 4.1 Hz, 1H, 1H*), 2.29$^+$ (td, J = 7.8, 7.1, 1.8 Hz, 1H, 1H*), 1.98 – 1.88$^+$ (m, 1H, 1H*), 1.85$^+$ (dt, J = 9.8, 2.0 Hz, 1H, 1H*), 1.58$^+$ (ddt, J = 11.1, 7.6, 3.4 Hz, 2H, 2H*), 1.42$^+$ (dddd, J = 12.2, 9.6, 7.6, 2.5 Hz, 1H, 1H*), 1.35 – 1.22$^+$ (m, 2H, 2H*), 1.17$^+$ (dt, J = 10.0, 1.7 Hz, 1H, 1H*). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 133.60$^+$ (dd, J = 95.6, 46.0 Hz, 2C, 2C*), 131.41$^+$ (dd, J = 9.7, 2.2 Hz, 2C, 2C*), 131.12 – 130.82$^+$ (m, 4C, 4C*), 128.57$^+$ (dd, J = 15.6, 11.3 Hz, 4C, 4C*), 40.00$^+$ (d, J = 73.0 Hz, 1C, 1C*), 38.20$^+$ (1C, 1C*), 37.35$^+$ (1C, 1C*), 36.48$^+$ (d, J = 2.4 Hz, 1C, 1C*), 32.17$^+$ (d, J = 14.7 Hz, 1C, 1C*), 31.50$^+$ (d, J = 4.3 Hz, 1C, 1C*), 28.73$^+$ (1C, 1C*). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 34.43$^+$ (s, 1P, 1P*). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{22}OP^+$ 297.1408; found: 297.1386.

Hexan-2-yldiphenylphosphine oxide + hexan-3-yldiphenylphosphine oxide (**3am**):

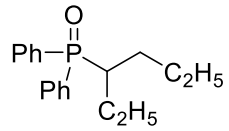


(**3am'**) (**3an**)

3am (mixture of **3am'** and **3an**)

Following the procedure (overnight), **3am** was obtained after FC on silica gel (Petro ether/EtOAc 1:1) as white solid. For substrate (*E*)-2-hexene, the yield is 75% (42.7 mg), **3am'**:**3an** = 1.1:1; for substrate (*Z*)-2-hexene, the yield is 62% (35.5 mg), **3am'**:**3an** = 1.5:1. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.83 – 7.76$^+$ (m, 4H, 4H*), 7.52 – 7.43$^+$ (m, 6H, 6H*), 2.39 – 2.31 (m, 1H), 2.22 – 2.16* (m, 1H*), 1.81 – 1.70* (m, 1H*), 1.70 – 1.52$^+$ (m, 1H, 3H*), 1.52 – 1.41 (m, 2H, 1H*), 1.31 – 1.12 (m, 6H, 1H*), 0.94* (t, J = 7.4 Hz, 3H*), 0.85 – 0.78$^+$ (m, 3H, 3H*). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 133.27* (d, J = 93.5 Hz, 2C*), 132.58 (dd, J = 94.3, 14.9 Hz, 2C), 131.53 (dd, J = 7.6, 2.7 Hz, 2C), 131.44* (t, J = 2.4 Hz, 2C*), 131.14 (dd, J = 8.6, 1.9 Hz, 4C), 131.03* (dd, J = 8.5, 4.5 Hz, 4C*), 128.72 – 128.55$^+$ (m, 4C, 4C*), 38.46* (d, J = 70.9 Hz), 32.04 (d, J = 72.3 Hz), 29.74 (d, J = 12.6 Hz), 29.17* (d, J = 1.9 Hz), 28.54 (d, J = 2.0 Hz), 22.49, 21.31*, 20.70* (d, J = 1.9 Hz), 14.25*, 13.98, 12.68* (d, J = 9.5 Hz), 12.14 (d, J = 2.7 Hz). **^{31}P NMR (243 MHz, $CDCl_3$)** δ 37.48* (s, 1P*), 36.87 (s, 1P). For substrate (*E*)-2-hexene: **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}OP^+$ 287.1559; found: 287.1559. For substrate (*Z*)-2-hexene: **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}OP^+$ 287.1559; found: 287.1559.

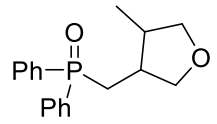
Hexan-3-yldiphenylphosphine oxide (**3an**):



3an

Following the procedure (overnight), **3an** was obtained after FC on silica gel (Petro ether/EtOAc 1:1) as white solid. For substrate (*E*)-3-hexene, the yield is 50% (28.5 mg); for substrate (*Z*)-3-hexene, the yield is 72% (41.1 mg). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.83 – 7.77 (m, 4H), 7.51 – 7.43 (m, 6H), 2.23 – 2.16 (m, 1H), 1.81 – 1.70 (m, 1H), 1.70 – 1.52 (m, 3H), 1.52 – 1.42 (m, 1H), 1.29 – 1.20 (m, 1H), 0.94 (t, J = 7.5 Hz, 3H), 0.81 (t, J = 7.3 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 133.20 (d, J = 93.7 Hz, 2C), 131.45 (t, J = 2.2 Hz, 2C), 131.01 (dd, J = 8.6, 4.4 Hz, 4C), 128.62 (d, J = 11.0 Hz, 4C), 38.43 (d, J = 70.9 Hz), 29.15 (d, J = 1.7 Hz), 21.27 (d, J = 9.8 Hz), 20.68 (d, J = 1.9 Hz), 14.24, 12.67 (d, J = 9.3 Hz). **^{31}P NMR (243 MHz, $CDCl_3$)** δ 37.22 (s). For substrate (*E*)-3-hexene: **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}OP^+$ 287.1559; found: 287.1558. For substrate (*Z*)-3-hexene: **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}OP^+$ 287.1559; found: 287.1561.

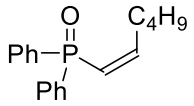
((4-Methyltetrahydrofuran-3-yl)methyl)diphenylphosphine oxide (**3ao**):



3ao

Following the procedure (4.0 equivalent of corresponding alkene was used; overnight), **3am** was obtained after HPTLC (DCM/MeOH 10:1) in 40% yield (24.1 mg) and 4.7:1 dr as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 – 7.65$^+$ (m, 4H, 4H*), 7.48 – 7.37$^+$ (m, 6H, 6H*), 3.90 – 3.80* (m, 2H*), 3.76 (ddd, J = 25.2, 8.5, 6.7 Hz, 2H), 3.40 – 3.35 (m, 2H), 3.33 – 3.29* (m, 1H*), 3.17* (t, J = 8.2 Hz, 1H*), 2.51$^+$ (ddtt, J = 15.0, 11.3, 7.7, 4.0 Hz, 1H, 1H*), 2.35 (ddd, J = 15.8, 11.8, 4.4 Hz, 1H), 2.26 (hd, J = 6.9, 4.1 Hz, 1H), 2.14$^+$ (dtd, J = 15.1, 10.5, 5.1 Hz, 1H, 1H*), 2.01 – 1.95* (m, 1H*), 1.91* (p, J = 7.3 Hz, 1H*), 0.92* (d, J = 6.6 Hz, 3H*), 0.89 (d, J = 7.1 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 133.62 – 132.59$^+$ (m, 2C, 2C*), 132.05 – 131.90$^+$ (m, 2C, 2C*), 130.94 – 130.71$^+$ (m, 4C, 4C*), 128.94 – 128.73$^+$ (m, 4C, 4C*), 74.64, 74.24*, 73.80* (d, J = 4.1 Hz), 71.90 (d, J = 4.7 Hz), 41.62* (d, J = 12.5 Hz), 41.03* (d, J = 3.3 Hz), 36.74 (d, J = 9.9 Hz), 36.37 (d, J = 3.3 Hz), 32.78* (d, J = 71.0 Hz), 28.14 (d, J = 72.8 Hz), 15.82*, 13.56. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 31.83 (s), 31.01* (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}O_2P^+$ 301.0357; found: 301.1367.

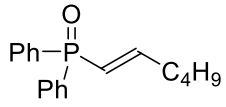
(*Z*)-hex-1-en-1-yldiphenylphosphine oxide (**5aa**):



5aa

Following the procedure (overnight), **5aa** was obtained after HPTLC (Petro ether/EtOAc 1:1) in 47% yield (26.6 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.70 – 7.63 (m, 4H), 7.44 – 7.33 (m, 6H), 6.61 (ddt, J = 40.5, 12.9, 7.7 Hz, 1H), 6.03 (dd, J = 25.6, 12.9 Hz, 1H), 2.49 – 2.41 (m, 2H), 1.29 – 1.20 (m, 2H), 1.20 – 1.10 (m, 2H), 0.72 (t, J = 7.3 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 155.23, 134.66 (d, J = 103.7 Hz, 2C), 131.58 (d, J = 2.2 Hz, 2C), 131.01 (d, J = 9.8 Hz, 4C), 128.61 (d, J = 11.9 Hz, 4C), 121.37 (d, J = 100.8 Hz), 31.04 (d, J = 1.4 Hz), 30.77 (d, J = 7.8 Hz), 22.33, 13.90. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 21.60 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}OP^+$ 285.1408; found: 285.1387.

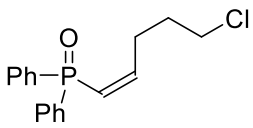
(*E*)-hex-1-en-1-yldiphenylphosphine oxide (**5aa'**):



5aa'

Following the procedure (overnight), **5aa'** was obtained after HPTLC (Petro ether/EtOAc 1:1) in 16% yield (9.2 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.65 – 7.59 (m, 4H), 7.47 – 7.42 (m, 2H), 7.41 – 7.36 (m, 4H), 6.66 (ddt, J = 19.5, 17.1, 6.5 Hz, 1H), 6.16 (dd, J = 24.6, 17.0 Hz, 1H), 2.26 – 2.20 (m, 2H), 1.42 – 1.36 (m, 2H), 1.31 – 1.24 (m, 2H), 0.83 (t, J = 7.3 Hz, 2H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 153.13, 133.33 (d, J = 104.7 Hz, 2C), 131.81 (d, J = 2.8 Hz, 2C), 131.44 (d, J = 9.8 Hz, 4C), 128.64 (d, J = 12.0 Hz, 4C), 121.64 (d, J = 103.2 Hz), 34.38 (d, J = 17.2 Hz), 30.15, 22.39, 13.97. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 24.13 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}OP^+$ 285.1408; found: 285.1387.

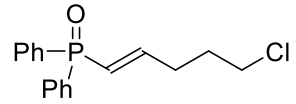
(*Z*)-(5-chloropent-1-en-1-yl)diphenylphosphine oxide (**5ab**):



5ab

Following the procedure (48h), **5ab** was obtained after HPTLC (Petro ether/EtOAc 1:2) in 44% yield (27.1 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 – 7.70 (m, 4H), 7.54 – 7.49 (m, 2H), 7.48 – 7.43 (m, 4H), 6.68 (ddt, J = 39.7, 12.8, 7.7 Hz, 1H), 6.18 (ddd, J = 25.4, 12.8, 1.6 Hz, 1H), 3.45 (t, J = 6.9 Hz, 2H), 2.76 – 2.70 (m, 2H), 1.87 (p, J = 7.1 Hz, 2H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 152.76, 134.32 (d, J = 104.3 Hz, 2C), 131.79 (d, J = 2.8 Hz, 2C), 130.98 (d, J = 9.9 Hz, 4C), 128.73 (d, J = 12.0 Hz, 4C), 122.89 (d, J = 99.6 Hz), 44.23, 32.04, 28.40 (d, J = 7.8 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 21.81 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}ClOP^+$ 305.0862, 307.0833; found: 305.0865, 307.0836.

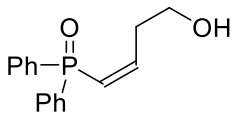
(*E*)-(5-chloropent-1-en-1-yl)diphenylphosphine oxide (**5ab'**):



5ab'

Following the procedure (48h), **5ab'** was obtained after HPTLC (Petro ether/EtOAc 1:2) in 19% yield (11.3 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 – 7.66 (m, 4H), 7.56 – 7.51 (m, 2H), 7.49 – 7.44 (m, 4H), 6.73 (ddt, J = 19.2, 17.2, 6.6 Hz, 1H), 6.32 (dd, J = 24.4, 17.0 Hz, 1H), 3.55 (t, J = 6.4 Hz, 2H), 2.51 – 2.46 (m, 2H), 1.97 (p, J = 6.7 Hz, 2H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 150.57, 133.07 (d, J = 104.9 Hz, 2C), 131.96 (d, J = 2.7 Hz, 2C), 131.38 (d, J = 9.9 Hz, 4C), 128.72 (d, J = 12.2 Hz, 4C), 123.39 (d, J = 102.3 Hz), 44.17, 31.64 (d, J = 16.8 Hz), 30.72. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 23.62 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}ClOP^+$ 305.0862, 307.0833; found: 305.0865, 307.0836.

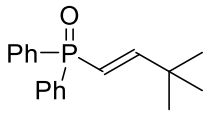
(*Z*)-(4-hydroxybut-1-en-1-yl)diphenylphosphine oxide (**5ac**):



5ac

Following the procedure (48h), **5ac** was obtained after HPTLC (DCM/MeOH 20:1) in 66% yield and 5:1 dr (36.1 mg, mixture of *Z*- and *E*-configuration) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 – 7.70 (m, 4H), 7.56 – 7.50 (m, 2H), 7.49 – 7.44 (m, 4H), 6.85 (ddt, J = 39.9, 12.7, 8.5 Hz, 1H), 6.31 (dd, J = 26.9, 12.8 Hz, 1H), 4.19 (bs, 1H), 3.76 (t, J = 5.8 Hz, 2H), 2.84 – 2.78 (m, 2H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 151.39 (s), 133.64 (d, J = 105.1 Hz, 2C), 132.02 (d, J = 2.2 Hz, 2C), 131.13 (d, J = 9.9 Hz, 4C), 128.83 (d, J = 12.1 Hz, 4C), 124.54 (d, J = 99.0 Hz), 60.35 (d, J = 1.9 Hz), 33.91 (d, J = 8.3 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 24.65 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}O_2P^+$ 273.1044; found: 273.1054.

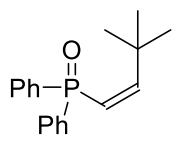
(*E*)-(3,3-dimethylbut-1-en-1-yl)diphenylphosphine oxide (**5ad**):



5ad

Following the procedure (48h), **5ad** was obtained after HPTLC (Petro ether/EtOAc 1:2) in 47% yield (26.7 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.63 – 7.58 (m, 4H), 7.47 – 7.41 (m, 2H), 7.41 – 7.35 (m, 4H), 6.70 (dd, J = 20.4, 17.3 Hz, 1H), 6.04 (dd, J = 24.4, 17.3 Hz, 1H), 1.03 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 162.45, 133.44 (d, J = 104.6 Hz, 2C), 131.75 (d, J = 2.8 Hz, 2C), 131.39 (d, J = 9.8 Hz, 4C), 128.60 (d, J = 12.0 Hz, 4C), 116.50 (d, J = 103.5 Hz), 35.37 (d, J = 15.2 Hz), 28.73 (3C). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 24.75 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}OP^+$ 285.1408; found: 285.1387.

(*Z*)-(3,3-dimethylbut-1-en-1-yl)diphenylphosphine oxide (**5ad'**):



5ad'

Following the procedure (48h), **5ad'** was obtained after HPTLC (Petro ether/EtOAc 1:2) in 24% yield (13.5 mg) as white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.71 – 7.63 (m, 4H), 7.43 – 7.33 (m, 6H), 6.61 (dd, J = 43.5, 14.6 Hz, 1H), 5.89 (dd, J = 22.3, 14.6 Hz, 1H), 1.13 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.70, 135.81 (d, J = 105.2 Hz, 2C), 131.41 (d, J = 2.2 Hz, 2C), 130.97 (d, J = 9.4 Hz, 4C), 128.59 (d, J = 12.0 Hz, 4C), 119.37 (d, J = 98.8 Hz), 35.60 (d, J = 5.5 Hz), 30.38 (3C). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 20.18 (s). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for

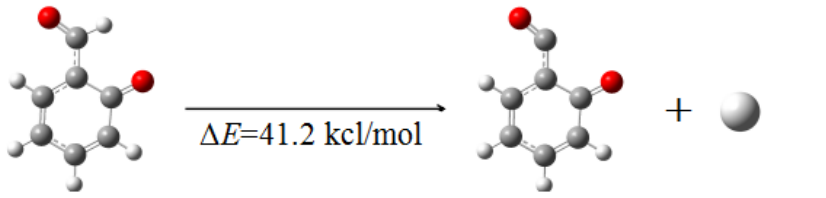
$C_{18}H_{22}OP^+$ 285.1408; found: 285.1387.

5. Computational studies

All calculations were performed with the Gaussian 09 package.[4] All species were fully optimized without symmetry constraints with M062X[5] method in combination with 6−311+G(d,p) basis sets in solvent water (ε = 78.355) by using PCM model.[6] Harmonic vibration frequency calculations were carried out for all the stationary points to confirm each structure being either a minimum (no imaginary frequency) or a transition structure (one imaginary frequency). The reported relative energies are electronic energies in water (ΔE, kcal/mol) at the M062X/6−311+G(d,p) level of theory without ZPVE corrections.

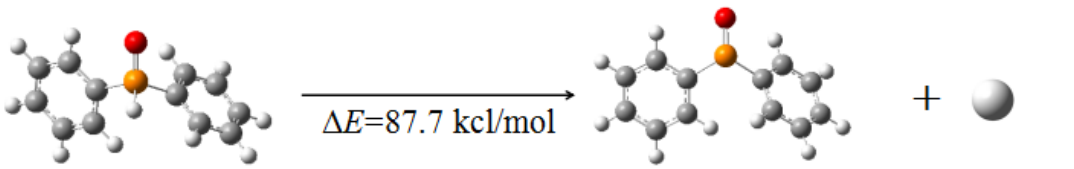
S1. Relative electronic energies in water at the M062X/6−311+G(d,p) level of theory.

Species	E(a.u.)	ΔE(kcl/mol)
cat.1	-420.284183	0.0
cat.1*	-420.197010	54.7
1a	-880.402182	0.0
1a*	-880.266790	85.0
1a'	-880.400352	0.0
1a'*	-880.295853	65.6
1a	-880.402182	0.0
1a'	-880.400352	1.1



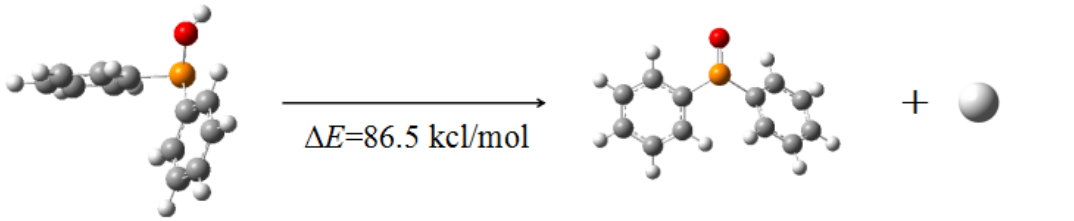
The acyl-H bond dissociating energy of **cat.1*** was about 41.2 kcal/mol.

[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson et al. , *Gaussian 09*, Revision A0; Gaussian, Inc., Wallingford CT, 2009.
[5] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.
[6] J. Tomasi, M. Persico, *Chem. Rev.*, 1994, **94**, 2027.



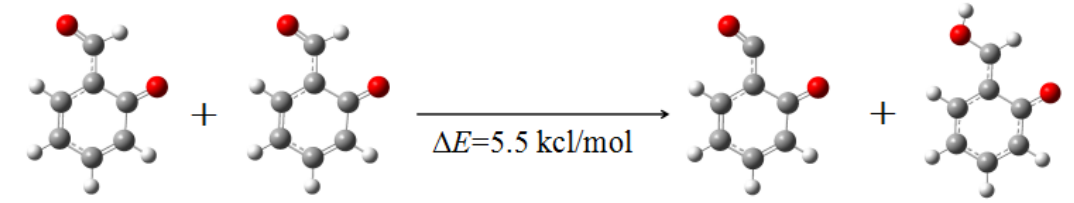
1a -880.4021819 | **I** -879.7642907 | **H·** -0.4981577

The P-H bond dissociating energy of **1a** was about 87.7 kcal/mol.



1a' -880.4003523 | **I** -879.7642907 | **H·** -0.4981577

The O-H bond dissociating energy of **1a'** was about 86.5 kcal/mol.



cat.1 -420.2841832 | **cat.1*** -420.19700973 | **cat.1'** -419.6332429 | **cat.1''** -420.8392369

The **cat.1*** interacts with a ground state molecule of **cat.1** furnishing two radicals: the benzoyl radical **cat.1'** and the hydroxybenzyl radical **cat.1''**. This radical-pair mechanism has been reported in 1970.[7]

S2. Calculated Cartesian coordinates of the stationary points

Cat.1

6	0	1.758623	0.756578	0.000027
6	0	0.349318	1.082372	-0.000541
6	0	-0.536435	-0.061800	-0.000218
6	0	-0.031872	-1.378260	-0.000124
6	0	1.319059	-1.638034	-0.000070

[7] (*a*) M. Cocivera, A. M. Trozzolo, *J. Am. Chem. Soc.*, 1970, **6**, 1772-1774; (*b*) G. L. Closs, D. R. Paulson, *J. Am. Chem. Soc.*, 1970, **24**, 7229-7231.

6	0	2.211103	-0.538643	0.000103
1	0	2.457460	1.587045	0.000293
1	0	-0.751616	-2.191448	-0.000064
1	0	1.696377	-2.652859	0.000018
1	0	3.281086	-0.725383	0.000331
6	0	-1.966592	0.156694	-0.000038
1	0	-2.273297	1.215263	0.000023
8	0	-2.826662	-0.720353	0.000288
8	0	-0.051992	2.282095	0.000283

Cat.1*

6	0	1.786807	0.750676	0.000038
6	0	0.393035	1.053916	0.000022
6	0	-0.585726	-0.065722	-0.000081
6	0	-0.067474	-1.373467	-0.000049
6	0	1.319476	-1.603913	0.000036
6	0	2.257291	-0.566354	0.000061
1	0	2.467227	1.595560	0.000031
1	0	-0.755445	-2.209331	-0.000090
1	0	1.673024	-2.630661	0.000049
1	0	3.317815	-0.780396	0.000091
6	0	-1.985066	0.206912	-0.000171
1	0	-2.278567	1.263404	0.000130
8	0	-2.872494	-0.701579	0.000172
8	0	-0.019269	2.245221	-0.000092

Cat.1'

6	0	1.740617	0.730954	-0.000005
6	0	0.337352	1.091154	-0.000161
6	0	-0.567202	-0.037511	-0.000053
6	0	-0.092906	-1.371796	-0.000018
6	0	1.250805	-1.655567	-0.000020
6	0	2.164713	-0.571865	0.000011
1	0	2.456420	1.546544	0.000072

1	0	-0.826501	-2.172590	0.000017
1	0	1.608622	-2.677419	0.000006
1	0	3.230575	-0.780391	0.000061
6	0	-1.989121	0.195443	0.000006
8	0	-2.909388	-0.570535	0.000073
8	0	-0.032445	2.295409	0.000088

Cat.1''

6	0	-1.837431	0.703583	0.000048
6	0	-0.467769	1.083949	-0.000024
6	0	0.502216	-0.019779	0.000130
6	0	0.041823	-1.365169	0.000067
6	0	-1.311269	-1.668914	-0.000042
6	0	-2.250685	-0.627149	-0.000030
1	0	-2.570642	1.505034	0.000130
1	0	0.778912	-2.161339	0.000142
1	0	-1.639501	-2.702363	-0.000054
1	0	-3.311566	-0.857306	-0.000006
6	0	1.855807	0.300453	0.000193
1	0	2.212613	1.320105	-0.000138
8	0	2.790066	-0.703351	-0.000358
8	0	-0.082120	2.300007	-0.000095
1	0	3.670468	-0.319225	0.001505

1a

15	0	0.017417	1.386404	-0.423544
1	0	-0.092062	1.622820	-1.808069
8	0	0.148720	2.630212	0.409767
6	0	-1.441337	0.367948	-0.095558
6	0	-2.405195	0.162300	-1.082520
6	0	-1.595630	-0.212437	1.167372
6	0	-3.521093	-0.625165	-0.808635
1	0	-2.287908	0.610022	-2.063878
6	0	-2.711516	-0.993199	1.437889

1	0	-0.841594	-0.059387	1.933389
6	0	-3.672749	-1.200256	0.448611
1	0	-4.268628	-0.787001	-1.575832
1	0	-2.832326	-1.444268	2.415488
1	0	-4.540908	-1.812750	0.661778
6	0	1.433153	0.270932	-0.236993
6	0	1.435226	-0.988004	-0.842068
6	0	2.521960	0.686196	0.527508
6	0	2.531179	-1.827099	-0.684744
1	0	0.581887	-1.314430	-1.429069
6	0	3.615815	-0.161023	0.688043
1	0	2.503850	1.664586	0.994563
6	0	3.619791	-1.413136	0.082120
1	0	2.536145	-2.803859	-1.153110
1	0	4.461994	0.156119	1.285785
1	0	4.470899	-2.071963	0.207829

1a*

15	0	0.769894	1.517434	-0.499166
1	0	0.856325	1.713109	-1.891474
8	0	1.016462	2.732071	0.350045
6	0	-0.849732	0.751918	-0.268747
6	0	-1.463595	0.052695	-1.310400
6	0	-1.425587	0.769821	1.003460
6	0	-2.647932	-0.637062	-1.073882
1	0	-1.020610	0.043306	-2.301056
6	0	-2.609516	0.078304	1.234411
1	0	-0.945003	1.319201	1.805981
6	0	-3.215777	-0.628709	0.198170
1	0	-3.128423	-1.178076	-1.880311
1	0	-3.058429	0.089713	2.220359
1	0	-4.137954	-1.167799	0.380726
6	0	1.968163	0.178813	-0.192021
6	0	1.983698	-0.905283	-1.197775

6	0	2.032036	-0.238292	1.227056
6	0	1.322084	-2.038888	-0.854482
1	0	2.422237	-0.757317	-2.177879
6	0	1.364050	-1.379396	1.537983
1	0	2.507113	0.386067	1.973945
6	0	0.880509	-2.236000	0.497030
1	0	1.189193	-2.839490	-1.574011
1	0	1.261027	-1.695096	2.570495
1	0	0.344004	-3.139212	0.755531

1a'

15	0	-0.001442	1.446058	-0.669429
8	0	0.147351	2.421285	0.681688
1	0	0.025910	3.347588	0.451132
6	0	-1.403264	0.370007	-0.165128
6	0	-2.460738	0.192594	-1.057357
6	0	-1.440150	-0.266394	1.080316
6	0	-3.543182	-0.618222	-0.715606
1	0	-2.439617	0.687917	-2.022865
6	0	-2.524286	-1.062293	1.427377
1	0	-0.616096	-0.137969	1.775295
6	0	-3.575587	-1.241366	0.526348
1	0	-4.357912	-0.756716	-1.416405
1	0	-2.550566	-1.550278	2.394854
1	0	-4.417950	-1.867514	0.796857
6	0	1.382213	0.296314	-0.300065
6	0	1.389672	-0.969897	-0.894762
6	0	2.466799	0.689338	0.484747
6	0	2.460817	-1.833212	-0.698466
1	0	0.548535	-1.287917	-1.504253
6	0	3.539095	-0.179406	0.682619
1	0	2.465428	1.669229	0.947389
6	0	3.539241	-1.438792	0.092526
1	0	2.453697	-2.814726	-1.157990

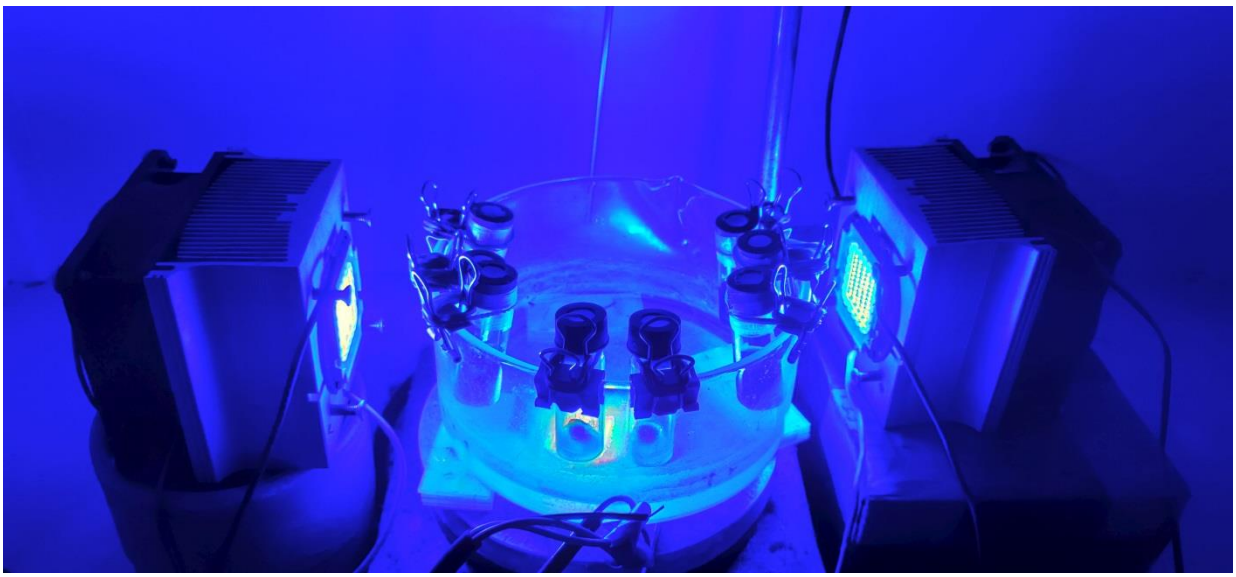
1	0	4.374449	0.130212	1.300245
1	0	4.373151	-2.113010	0.248369

I

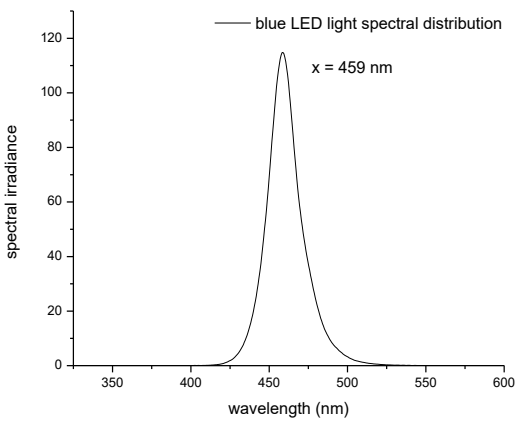
15	0	0.047453	1.221119	-0.594791
8	0	0.103831	2.600482	0.016304
6	0	-1.472695	0.316191	-0.220146
6	0	-1.863389	-0.771435	-1.007264
6	0	-2.280567	0.748493	0.834825
6	0	-3.042185	-1.447079	-0.714170
1	0	-1.255324	-1.085230	-1.849660
6	0	-3.460993	0.070227	1.118538
1	0	-1.980480	1.605926	1.426463
6	0	-3.838824	-1.027407	0.348664
1	0	-3.342988	-2.293360	-1.319733
1	0	-4.085785	0.398019	1.940683
1	0	-4.759467	-1.552730	0.573054
6	0	1.478532	0.193886	-0.166287
6	0	1.395568	-1.192599	-0.008306
6	0	2.712151	0.841111	-0.034488
6	0	2.541537	-1.921884	0.290984
1	0	0.444282	-1.703336	-0.098072
6	0	3.851521	0.104966	0.266137
1	0	2.772959	1.916692	-0.157793
6	0	3.767458	-1.276350	0.427338
1	0	2.474080	-2.994955	0.423958
1	0	4.804543	0.608393	0.375819
1	0	4.657049	-1.848774	0.661757

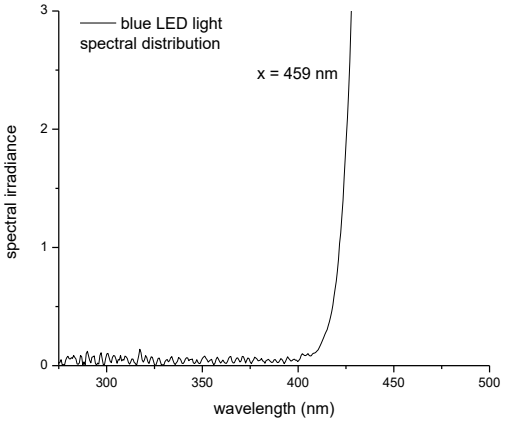
6. Photo of the reaction set up and spectral distribution of the blue LED light

A photo of the blue LEDs (3 × 10W) and reaction set up is shown below.



The spectral irradiance for the blue LED was measured at National Institute of Measurement and Testing Technology (No. 10, Yushuang Road, Chengdu, 610021, China), and the spectral distribution is shown blow.



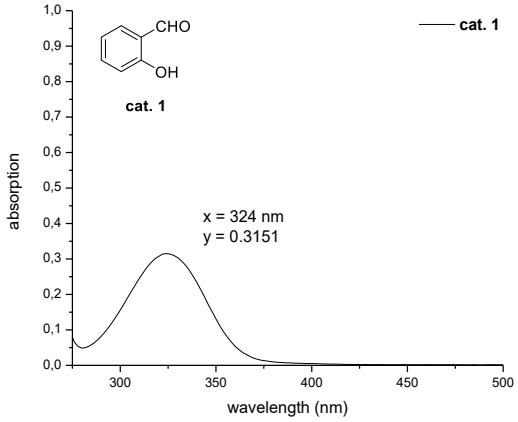


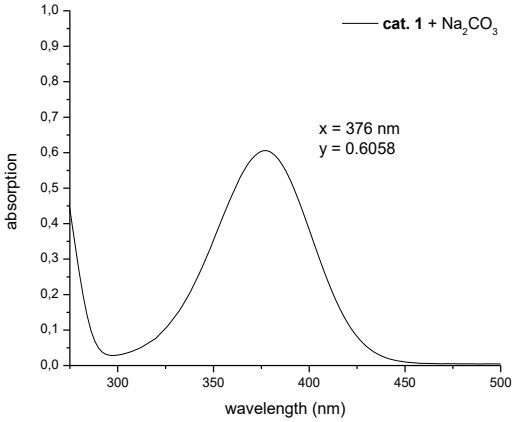
7. UV-visible light absorption spectra of aldehyde catalysts and 1a

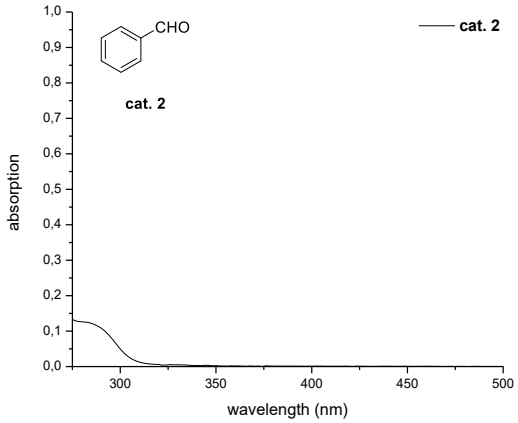
UV-visible light absorption spectra were measured by PerkinElmer Lambda 950 UV/VIS/NIR Spectrometer.

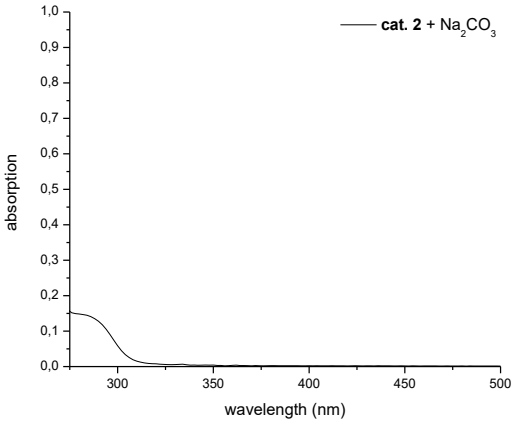
Sample (left): catalyst (10^{-4} mol/L) in distilled water.

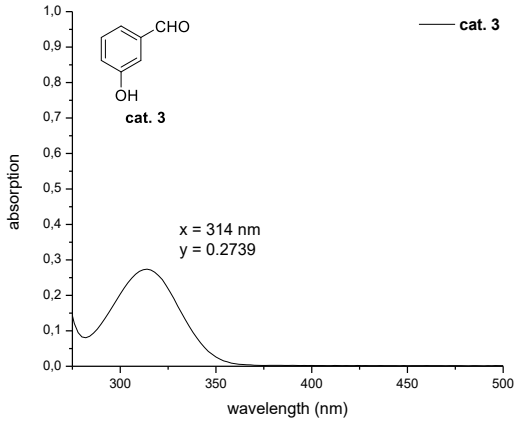
Sample (right): catalyst (10^{-4} mol/L) and Na_2CO_3 (10^{-2} mol/L) in distilled water.

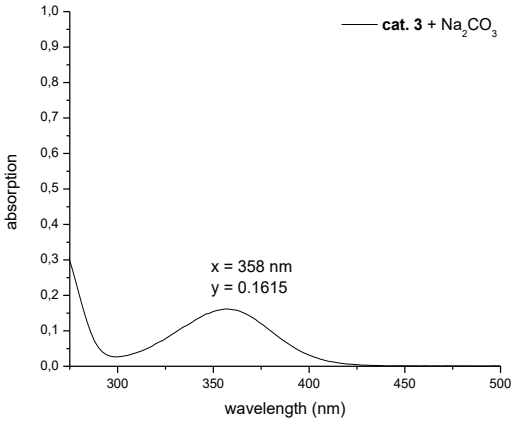


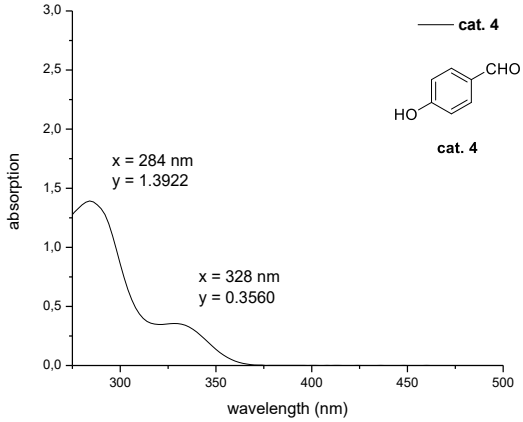


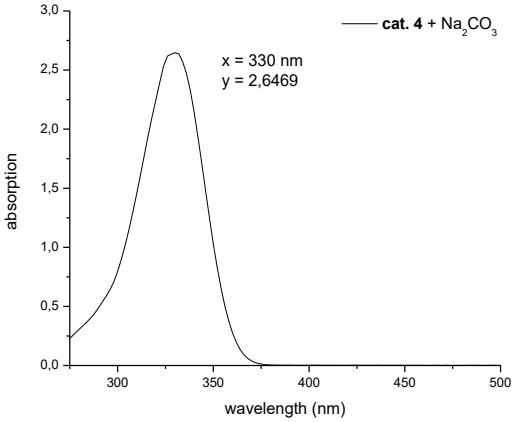


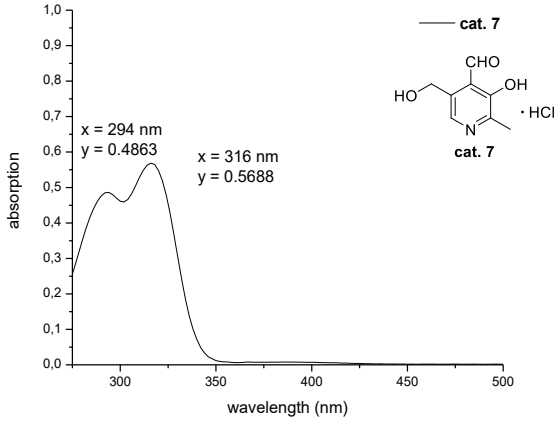


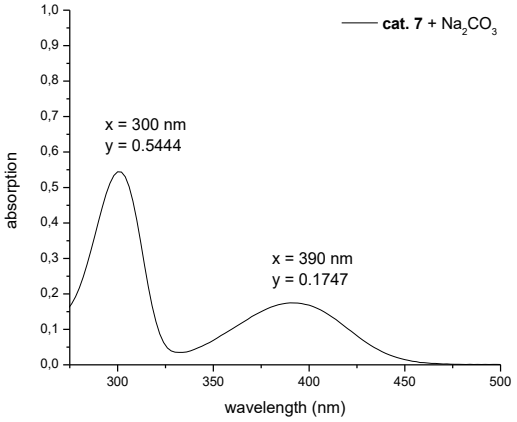

cat. 3
CHO
OH
cat. 3
x = 314 nm
y = 0.2739
absorption
wavelength (nm)

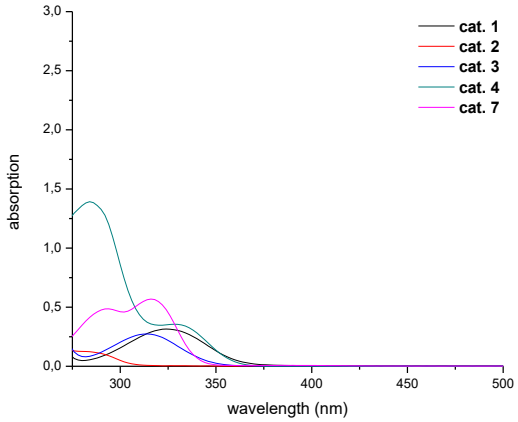

cat. 3 + Na2CO3
x = 358 nm
y = 0.1615
absorption
wavelength (nm)

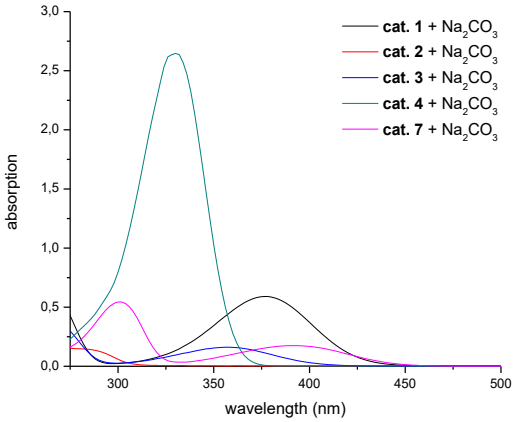

cat. 4
CHO
HO
cat. 4
x = 284 nm
y = 1.3922
x = 328 nm
y = 0.3560
absorption
wavelength (nm)


cat. 4 + Na2CO3
x = 330 nm
y = 2,6469
absorption
wavelength (nm)


cat. 7
CHO
OH
HO
· HCl
N
cat. 7
x = 294 nm
y = 0.4863
x = 316 nm
y = 0.5688
absorption
wavelength (nm)

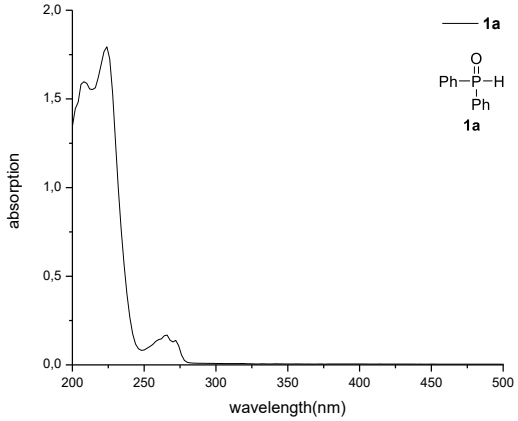

cat. 7 + Na2CO3
x = 300 nm
y = 0.5444
x = 390 nm
y = 0.1747
absorption
wavelength (nm)

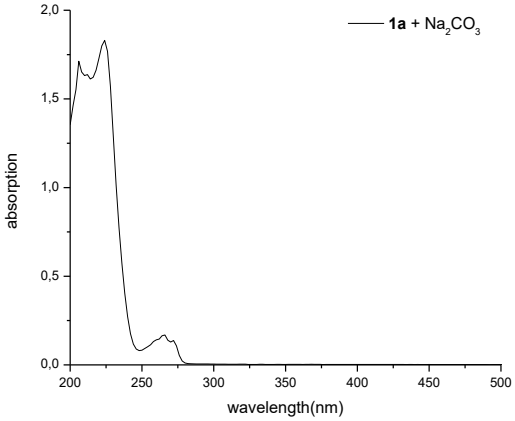




Sample (left): **1a** (10^{-4} mol/L) in distilled water.

Sample (right): **1a** (10^{-4} mol/L) and Na_2CO_3 (2.5×10^{-4} mol/L) in distilled water.

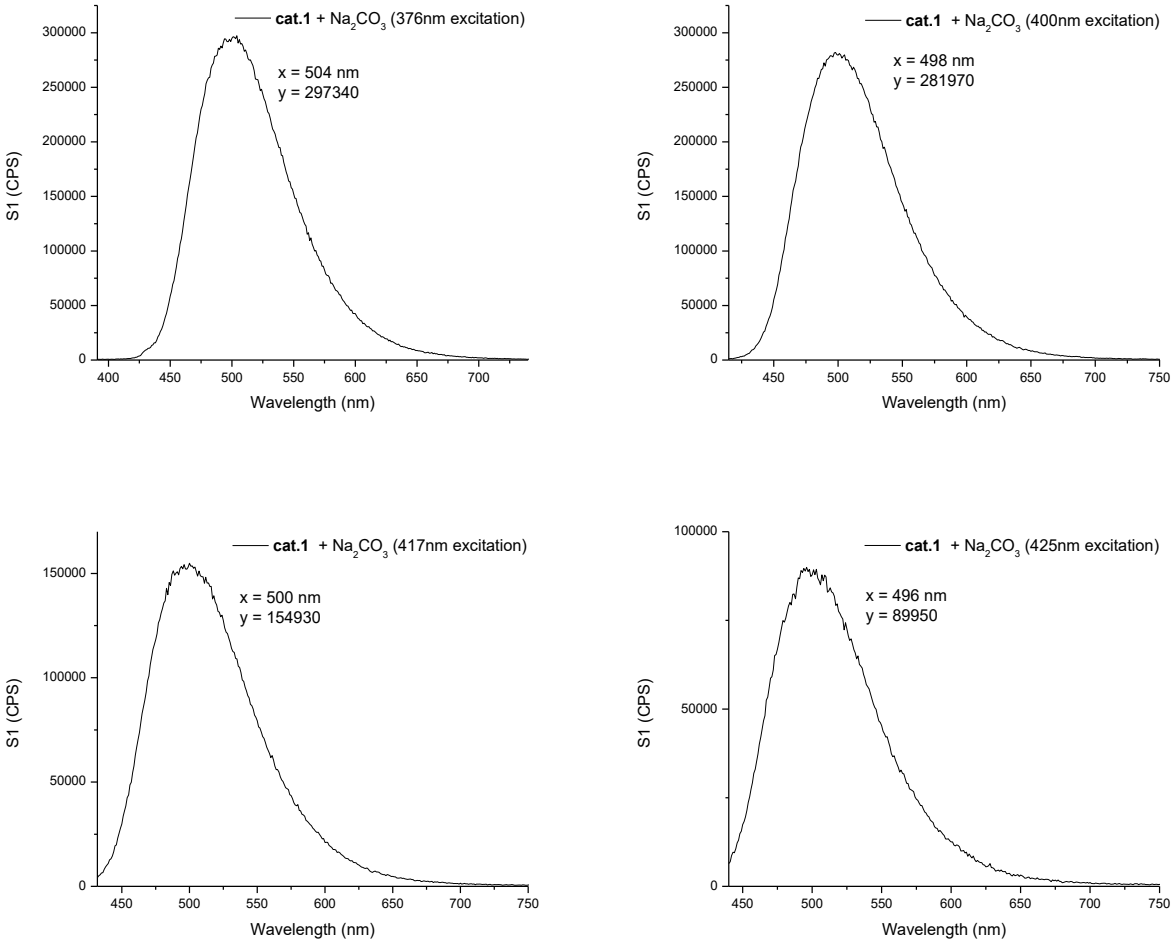




8. Fluorescence emission spectra and fluorescence quantum yield of salicylaldehyde

Fluorescence emission spectra of salicylaldehyde were measured by Horiba FluoroMax-4 Spectrofluorometer under excitation at 376nm, 400nm, 417 nm and 425 nm (slit 2nm).

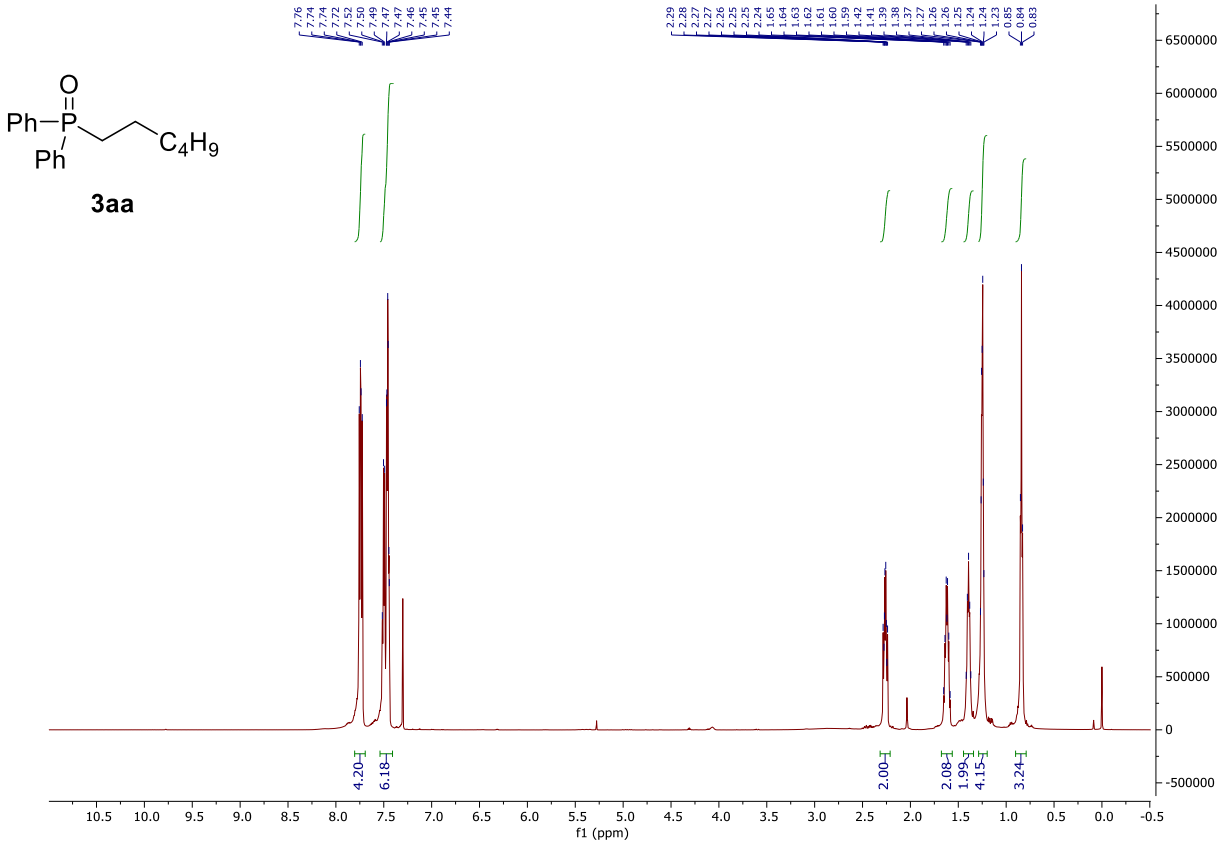
Sample: salicylaldehyde **cat. 1** (10^{-4} mol/L) and Na_2CO_3 (10^{-2} mol/L) in distilled water.

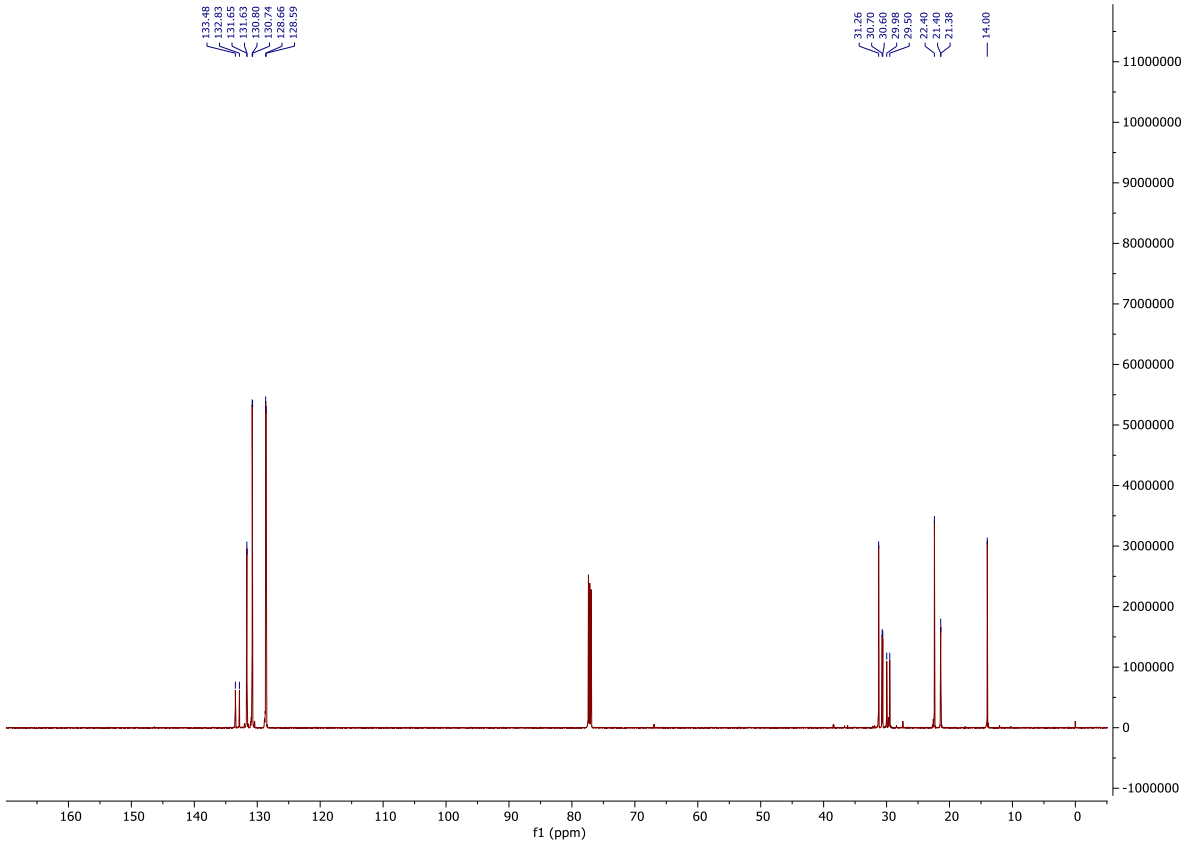


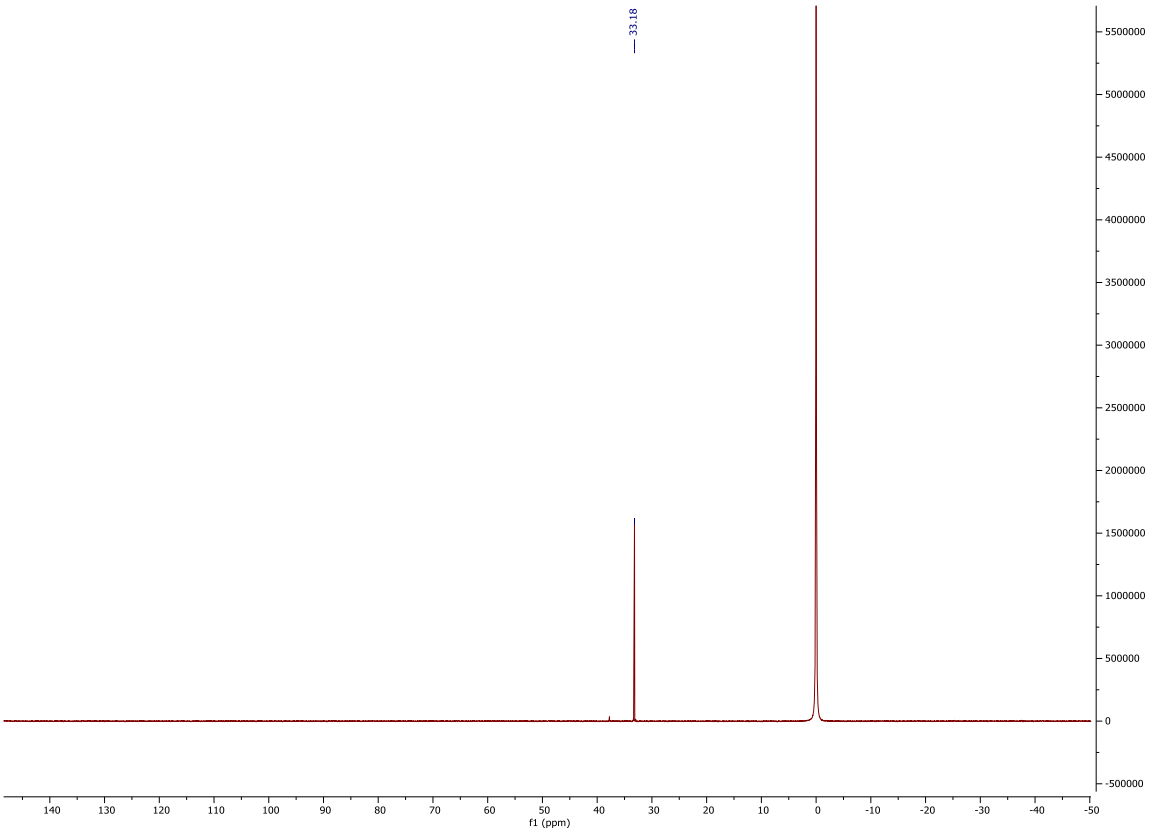
The absolute fluorescence quantum yield of salicylaldehyde was measured by Horiba Quanta-φ Spectrometer at 417nm: 2.10 (abs error ± 0.136, relative error ± 0.06488).

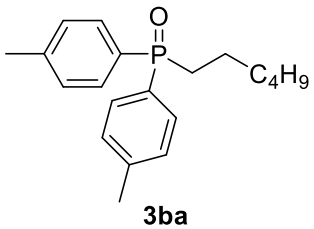
Sample: salicylaldehyde **cat. 1** (10^{-4} mol/L) and Na_2CO_3 (10^{-2} mol/L) in distilled water.

9. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of novel compounds



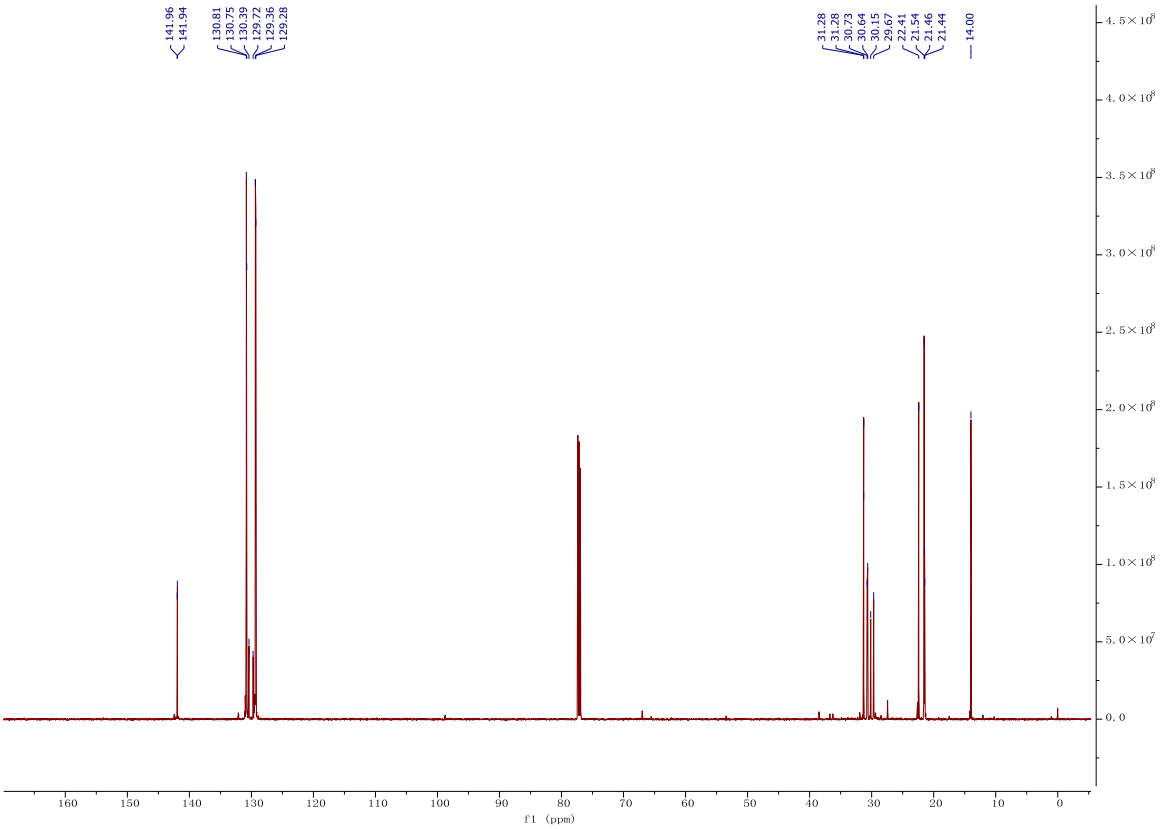


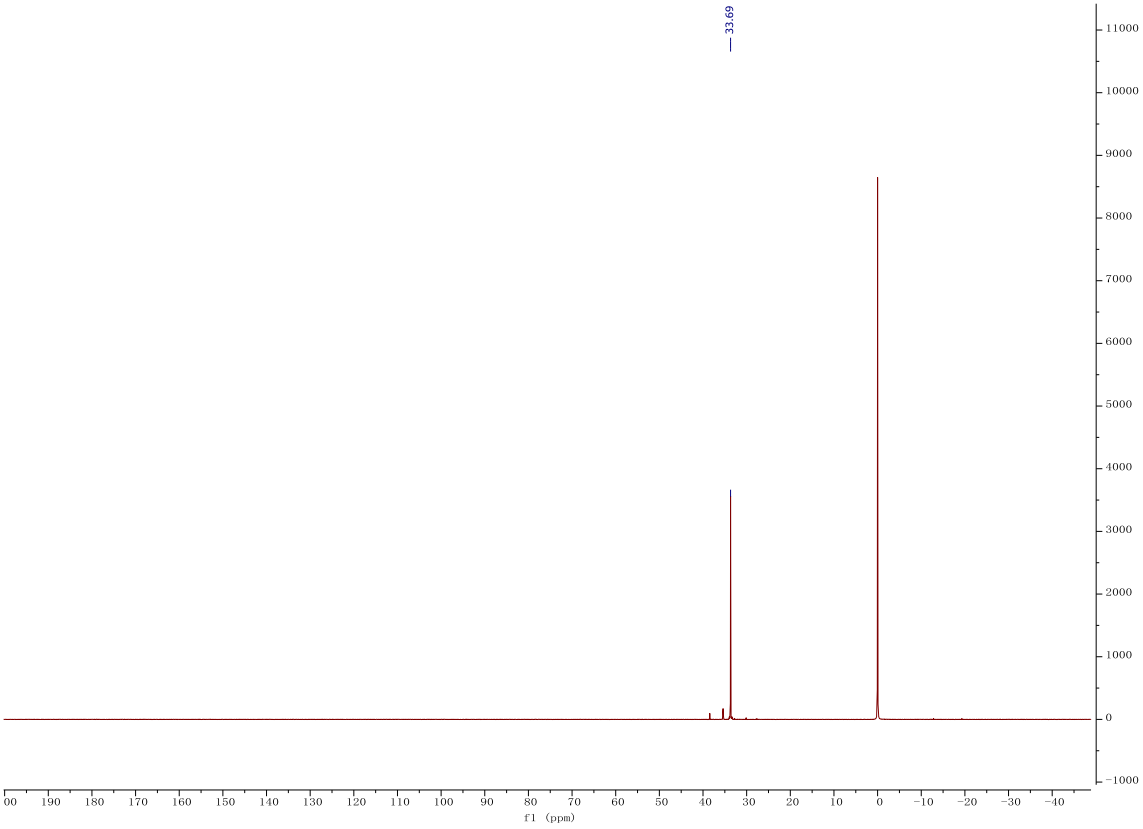

33.18
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
f1 (ppm)

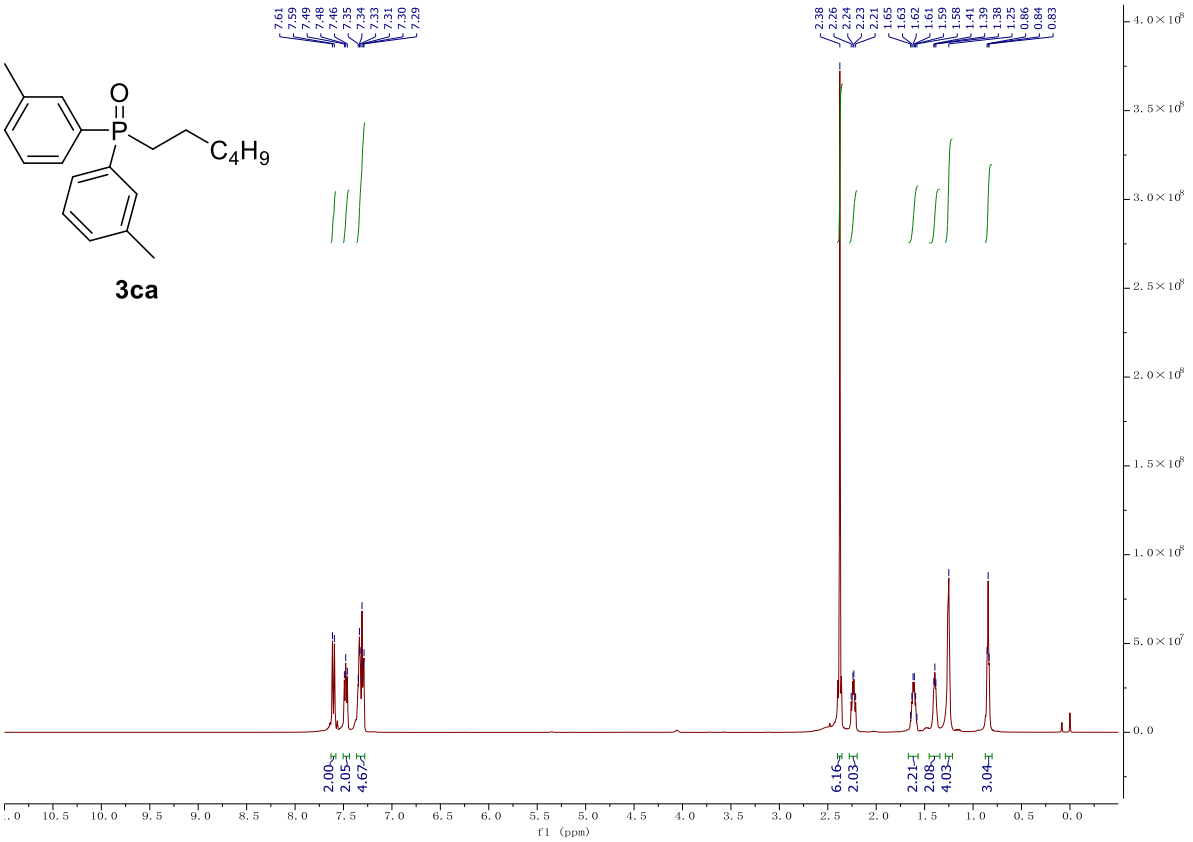

O
P
C_4H_9

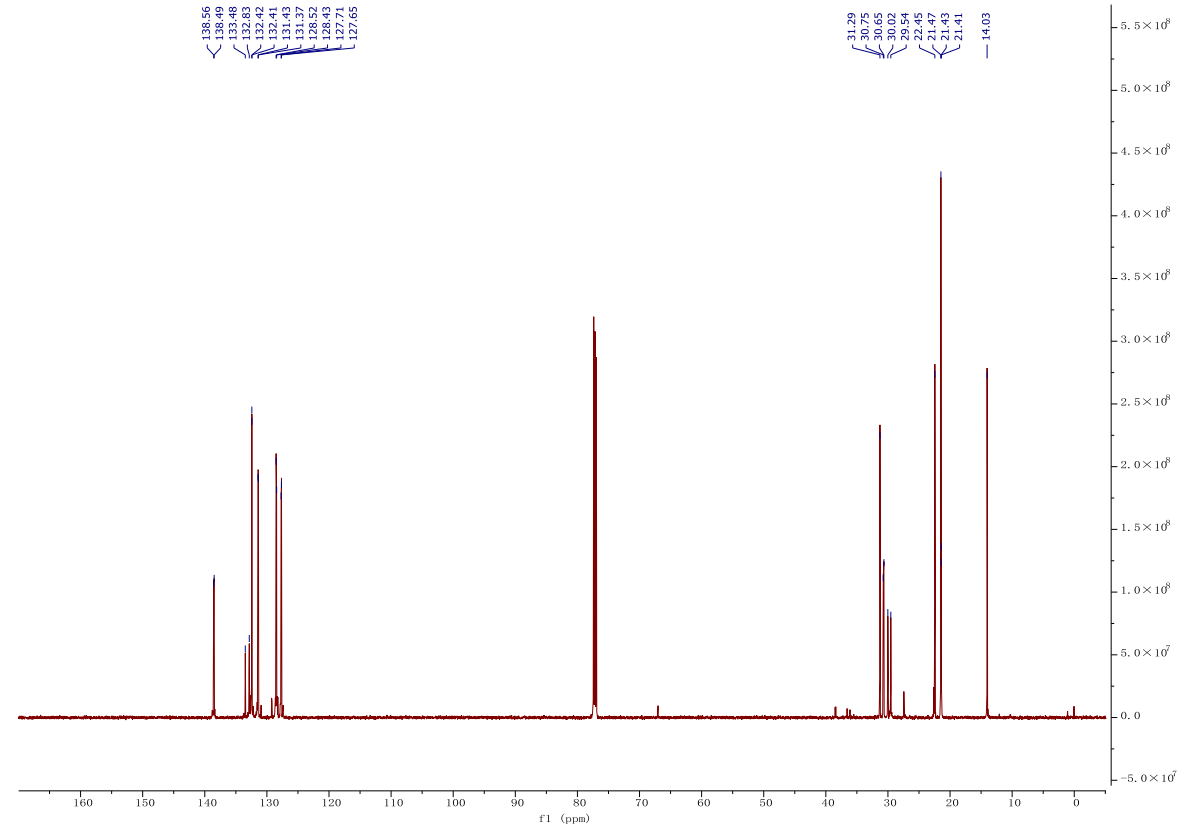
3ba

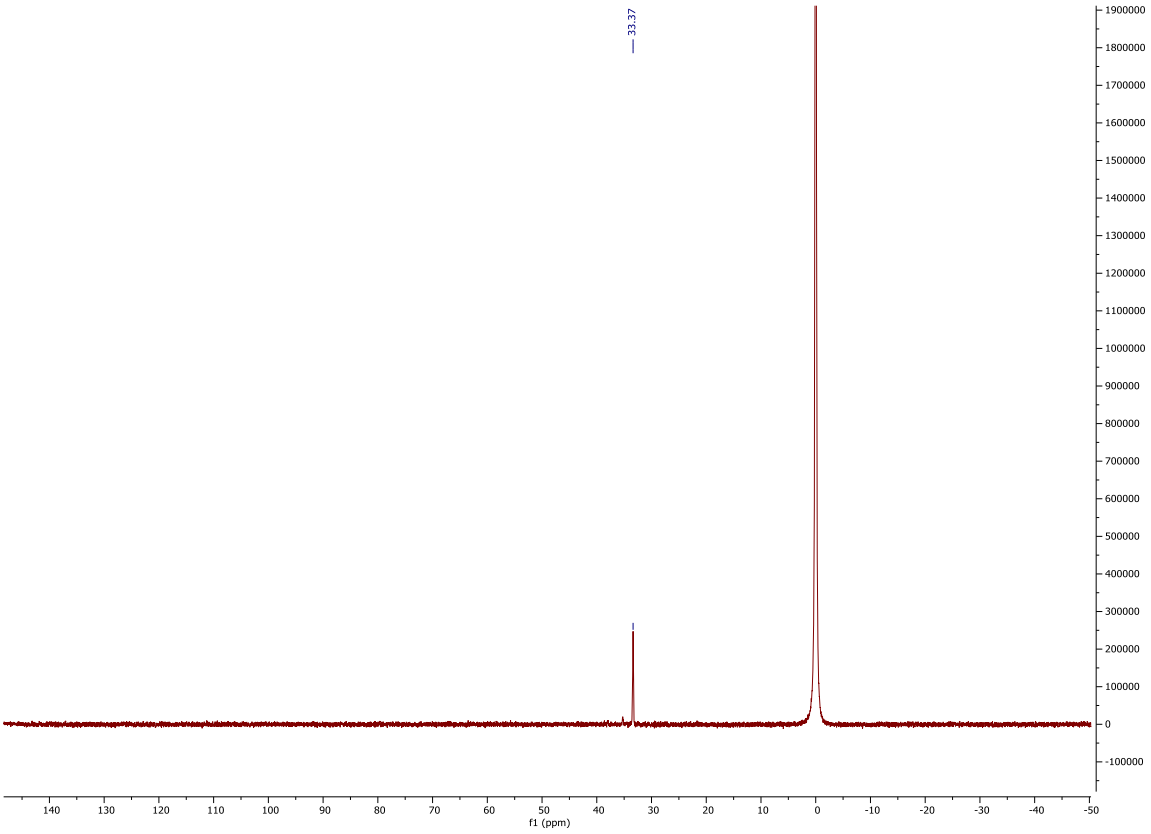
7.63
7.61
7.61
7.59
7.30
7.27
7.26
7.25
7.25
2.37
2.24
2.23
2.22
2.21
2.19
1.63
1.62
1.61
1.60
1.59
1.58
1.57
1.41
1.39
1.38
1.37
1.36
1.28
1.28
1.26
1.25
1.25
1.24
1.24
1.23
0.85
0.84
0.83
4.02
4.00
6.07
2.04
2.05
1.97
4.03
3.00
f1 (ppm)

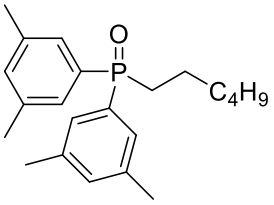

141.96
141.94
130.81
130.75
130.39
129.72
129.36
129.28
31.28
31.28
30.73
30.64
30.15
29.67
22.41
21.54
21.46
21.44
14.00
f1 (ppm)


33.69
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


O
P
C4H9
3ca
7.61
7.59
7.49
7.48
7.46
7.35
7.34
7.33
7.31
7.30
7.29
2.38
2.26
2.24
2.23
2.21
1.65
1.63
1.62
1.61
1.59
1.58
1.41
1.39
1.38
1.25
0.86
0.84
0.83
2.00
2.05
4.67
6.16
2.03
2.21
2.08
4.03
3.04
f1 (ppm)

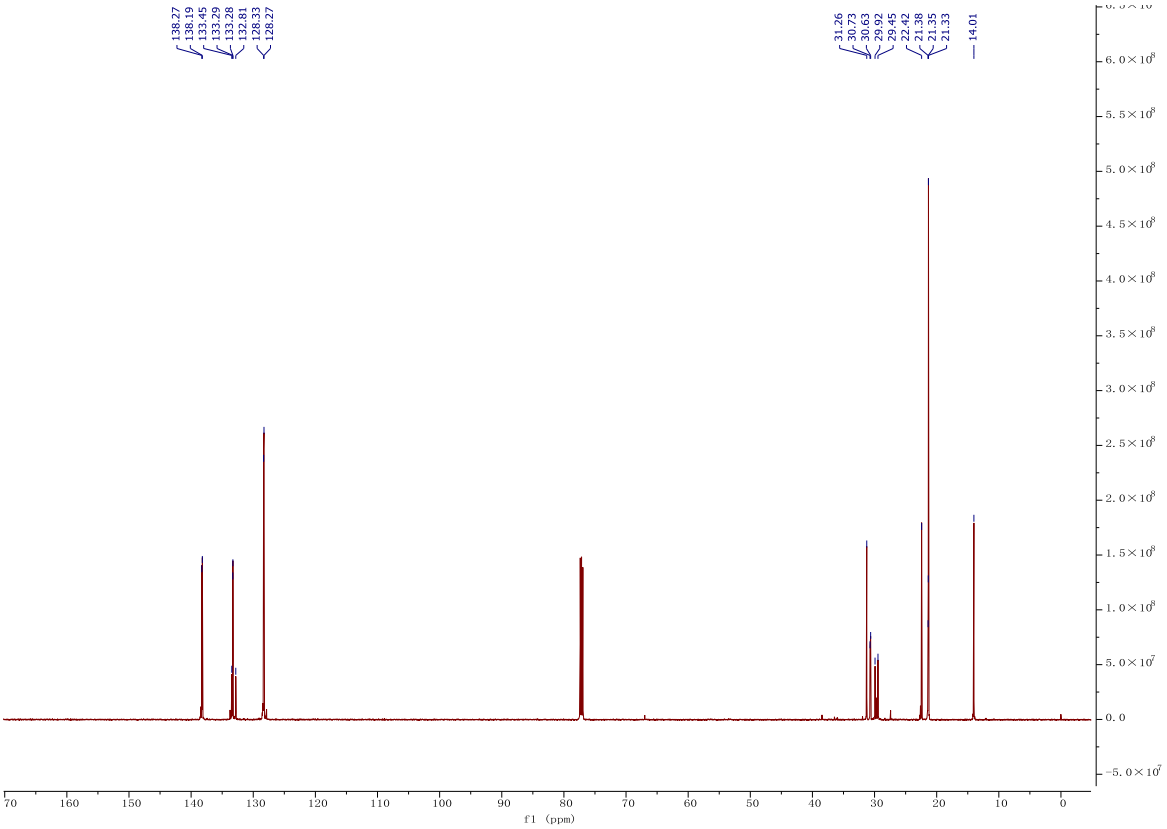

138.56
138.49
133.48
132.83
132.42
132.41
131.43
131.37
128.52
128.43
127.71
127.65
31.29
30.75
30.65
30.02
29.54
22.45
21.47
21.43
21.41
14.03
f1 (ppm)

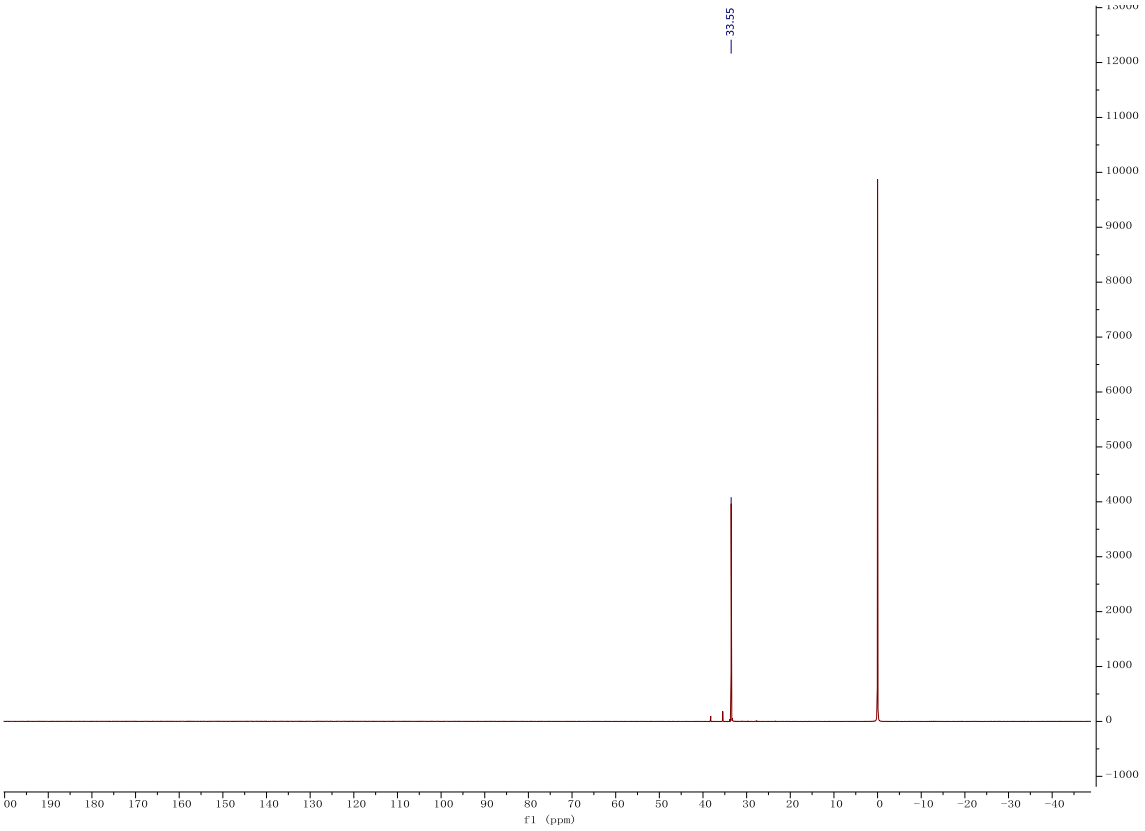

33.37
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
f1 (ppm)

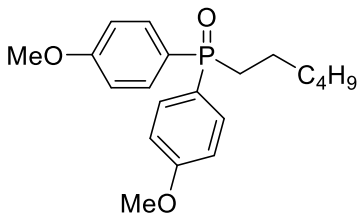

O
P
C4H9

3da

7.35
7.33
7.11
2.35
2.33
2.24
2.23
2.22
2.21
2.19
1.64
1.63
1.62
1.61
1.61
1.60
1.59
1.57
1.42
1.41
1.40
1.39
1.37
1.30
1.28
1.27
1.26
1.26
1.25
1.24
1.23
0.86
0.86
0.85
0.84
3.95
2.15
12.04
2.05
2.00
1.99
4.06
3.03
f1 (ppm)

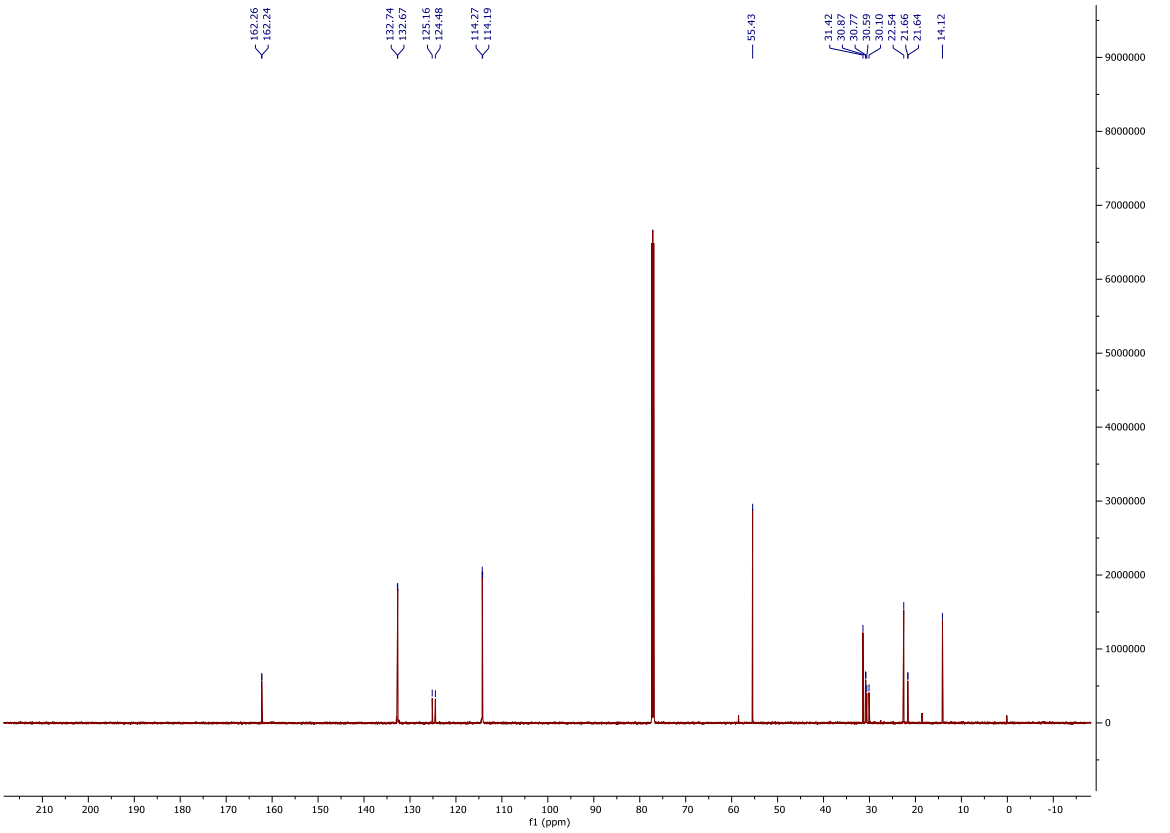

138.27
138.19
133.45
133.29
133.28
132.81
128.33
128.27
31.26
30.73
30.63
29.92
29.45
22.42
21.38
21.35
21.33
14.01
f1 (ppm)

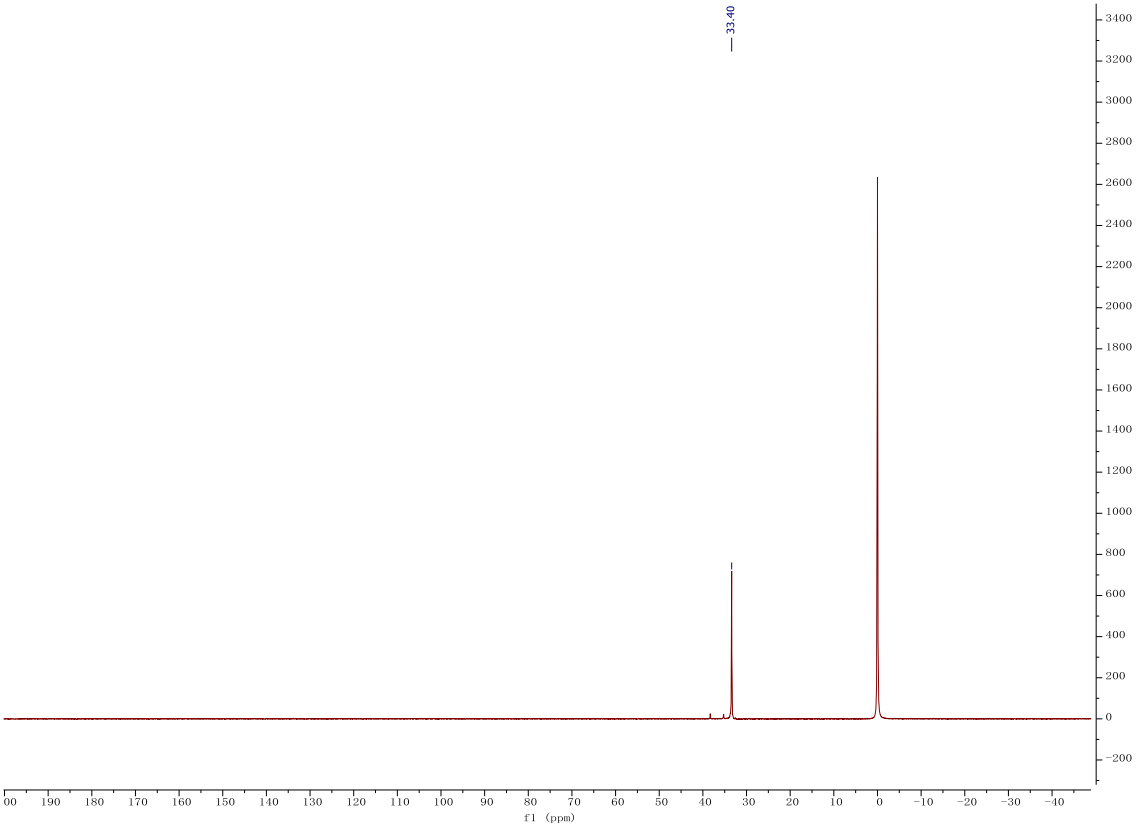

33.55
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

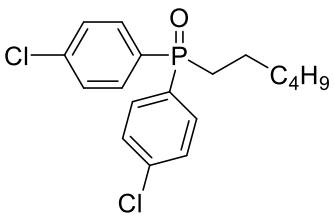

MeO
O
P
C_4H_9
MeO

3ea

7.65
7.63
7.61
6.97
6.96
3.83
1.62
1.60
1.59
1.58
1.56
1.55
1.40
1.39
1.38
1.37
1.26
1.25
1.24
1.24
0.86
0.84
0.83
4.06
4.08
6.27
2.00
2.12
2.12
4.11
3.12
f1 (ppm)

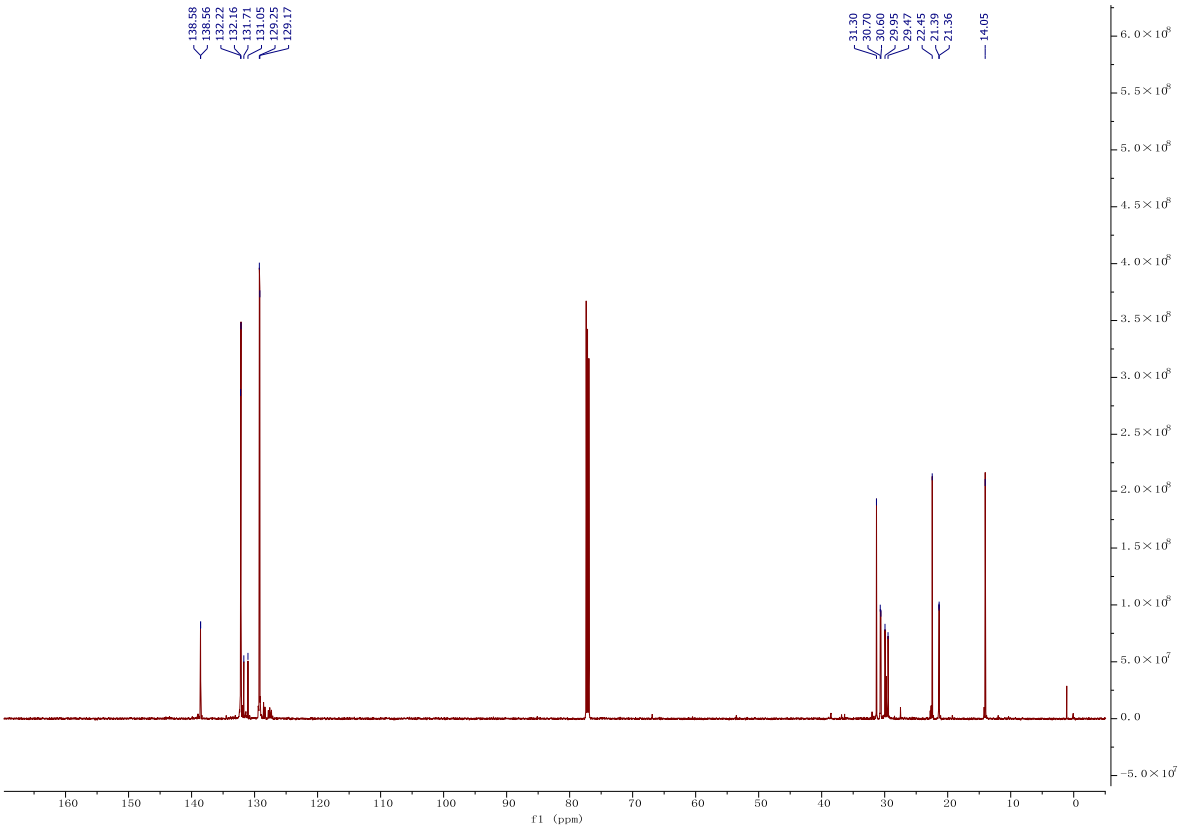

162.26
162.24
132.74
132.67
125.16
124.48
114.27
114.19
55.43
31.42
30.87
30.77
30.59
30.10
22.54
21.66
21.64
14.12
f1 (ppm)

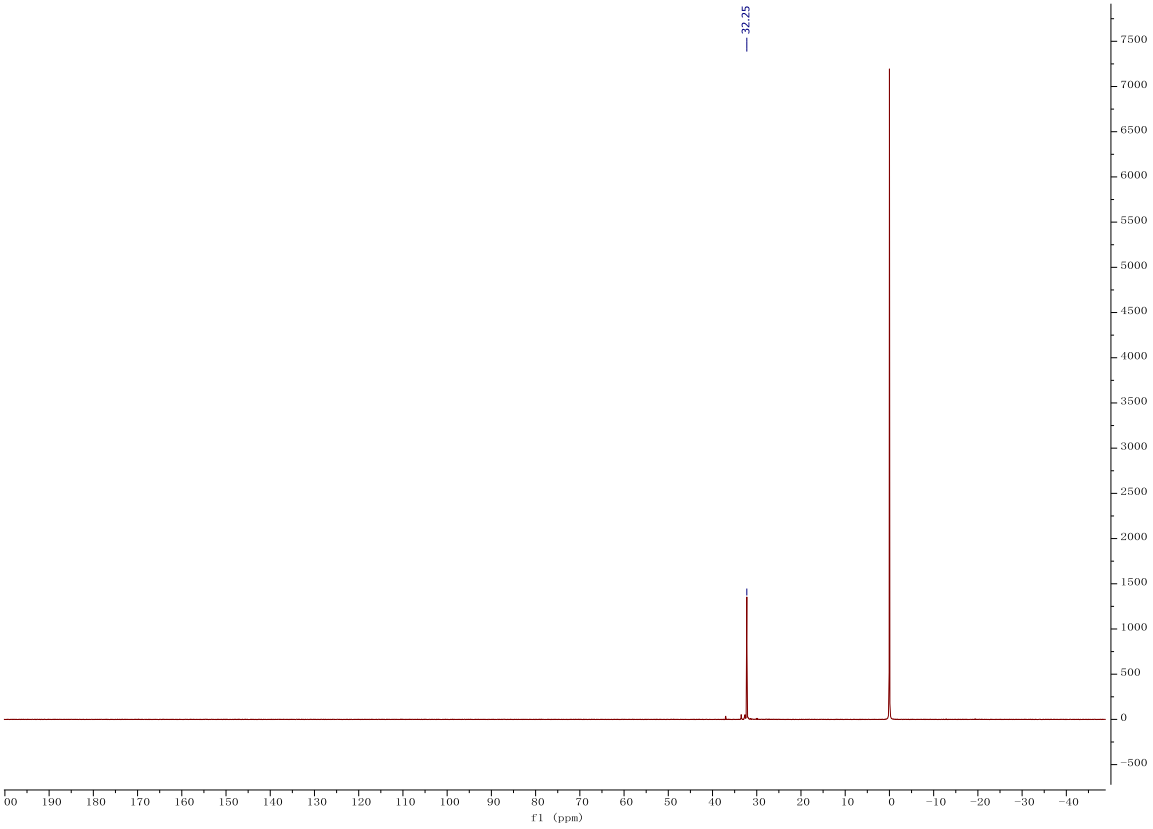

33.40
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

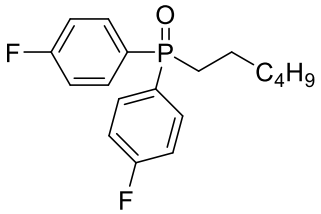

Cl
O
P
C_4H_9
Cl

3fa

7.59
7.58
7.57
7.56
7.39
7.39
7.38
7.37
2.17
2.16
2.15
2.13
1.55
1.54
1.52
1.52
1.51
1.50
1.48
1.34
1.33
1.32
1.31
1.29
1.18
1.17
1.17
0.79
0.77
0.76
4.00
3.92
2.04
2.01
2.12
4.25
3.10
f1 (ppm)

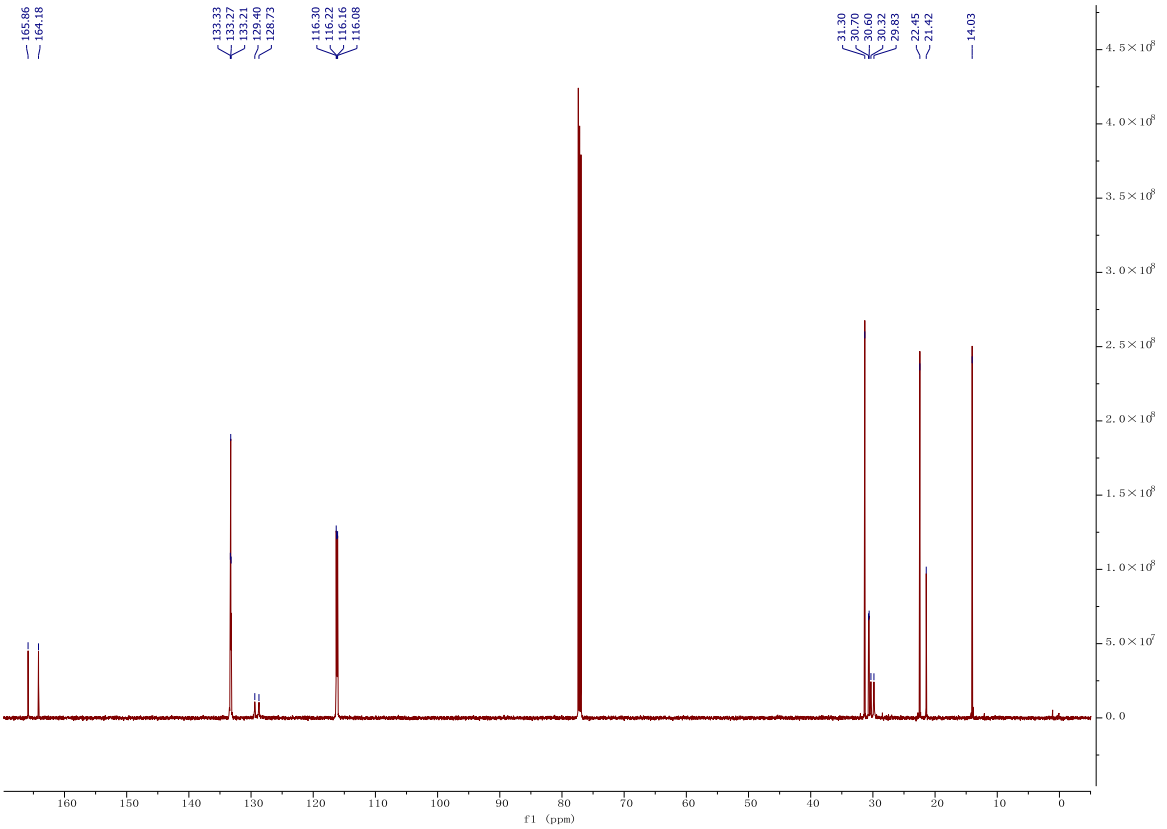

138.58
138.56
132.22
132.16
131.71
131.05
129.25
129.17
31.30
30.70
30.60
29.95
29.47
22.45
21.39
21.36
14.05
f1 (ppm)

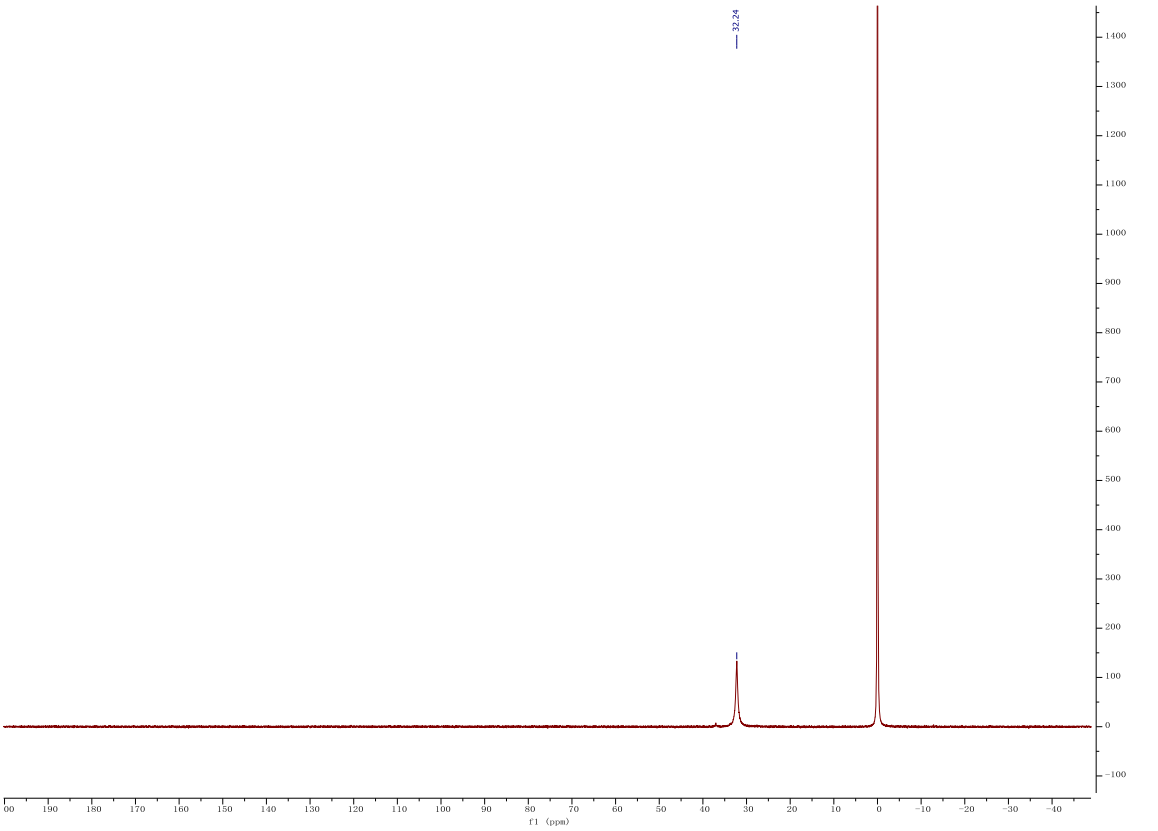

32.25
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)

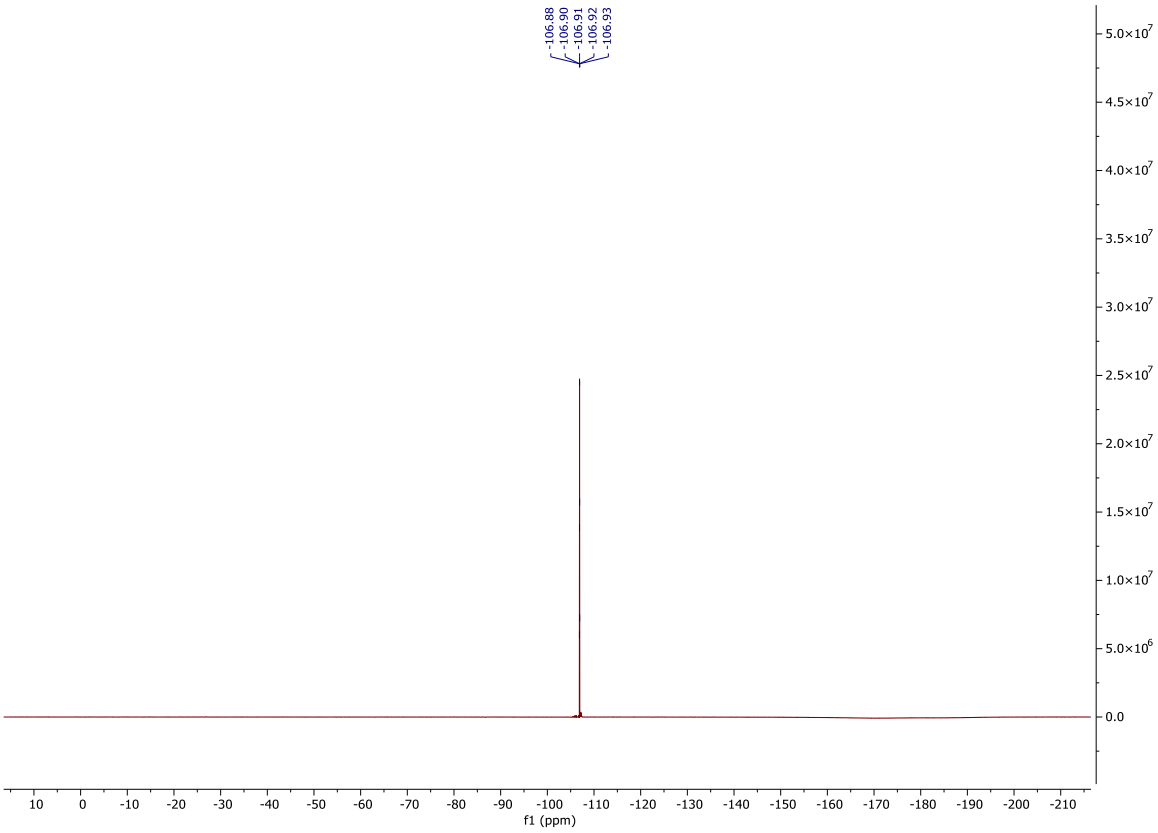

O
F
P
C_4H_9
F

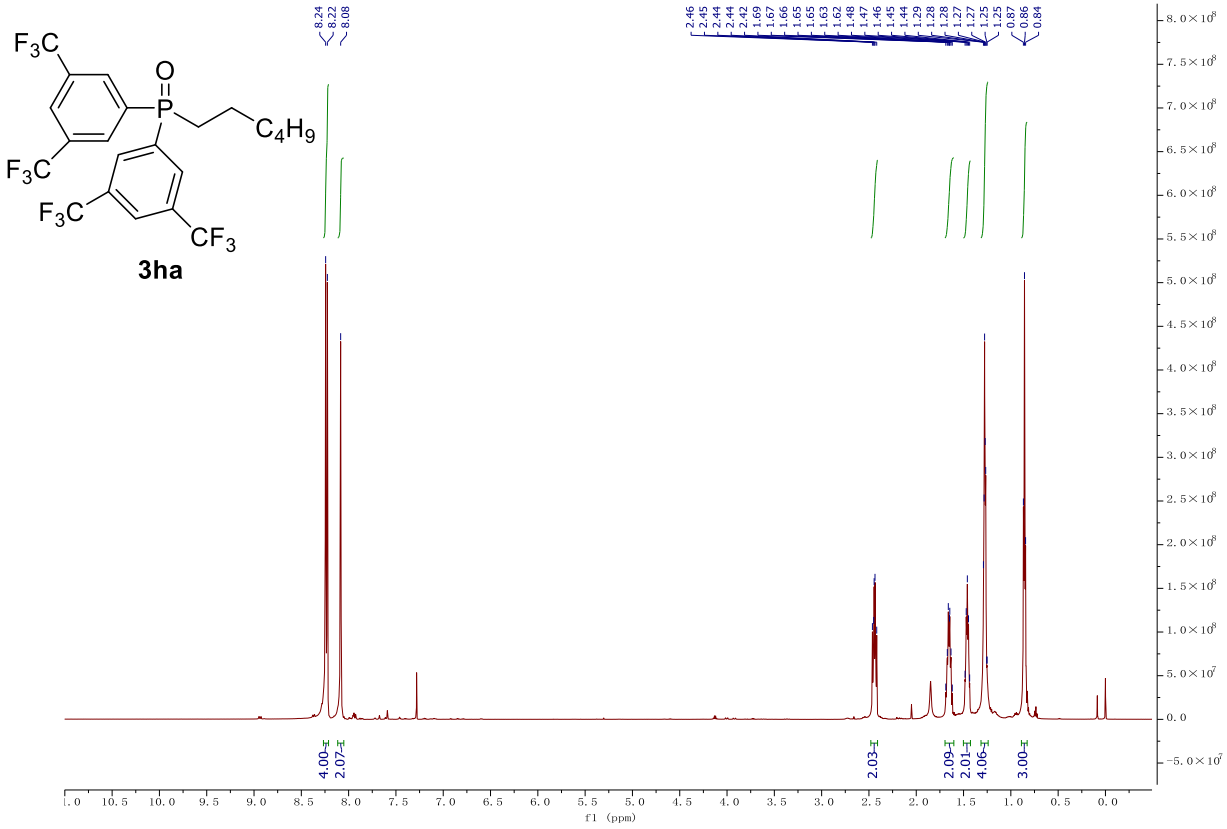
3ga

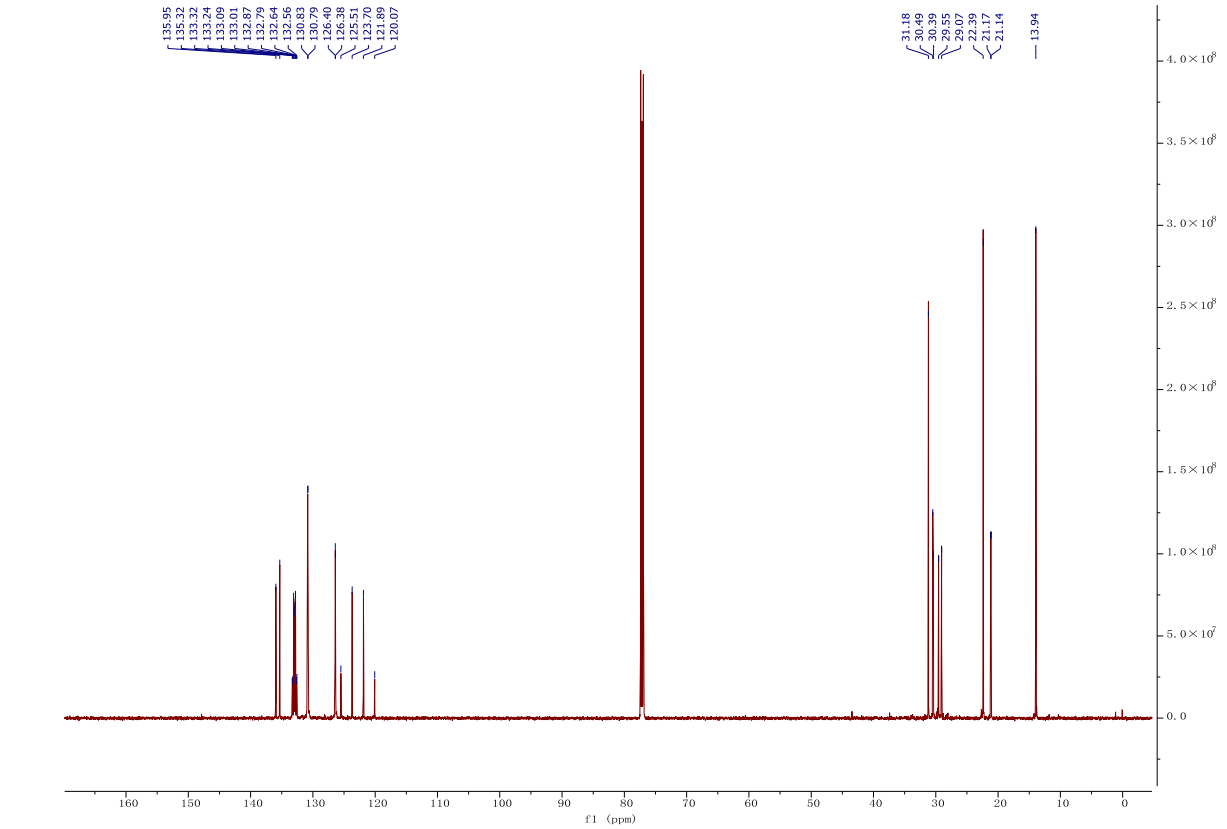
7.66
7.65
7.64
7.63
7.11
7.09
7.08
2.17
2.16
1.52
1.51
1.33
1.32
1.31
1.18
1.17
0.78
0.77
0.76
3.98
4.03
1.83
2.00
1.94
4.08
3.01
f1 (ppm)

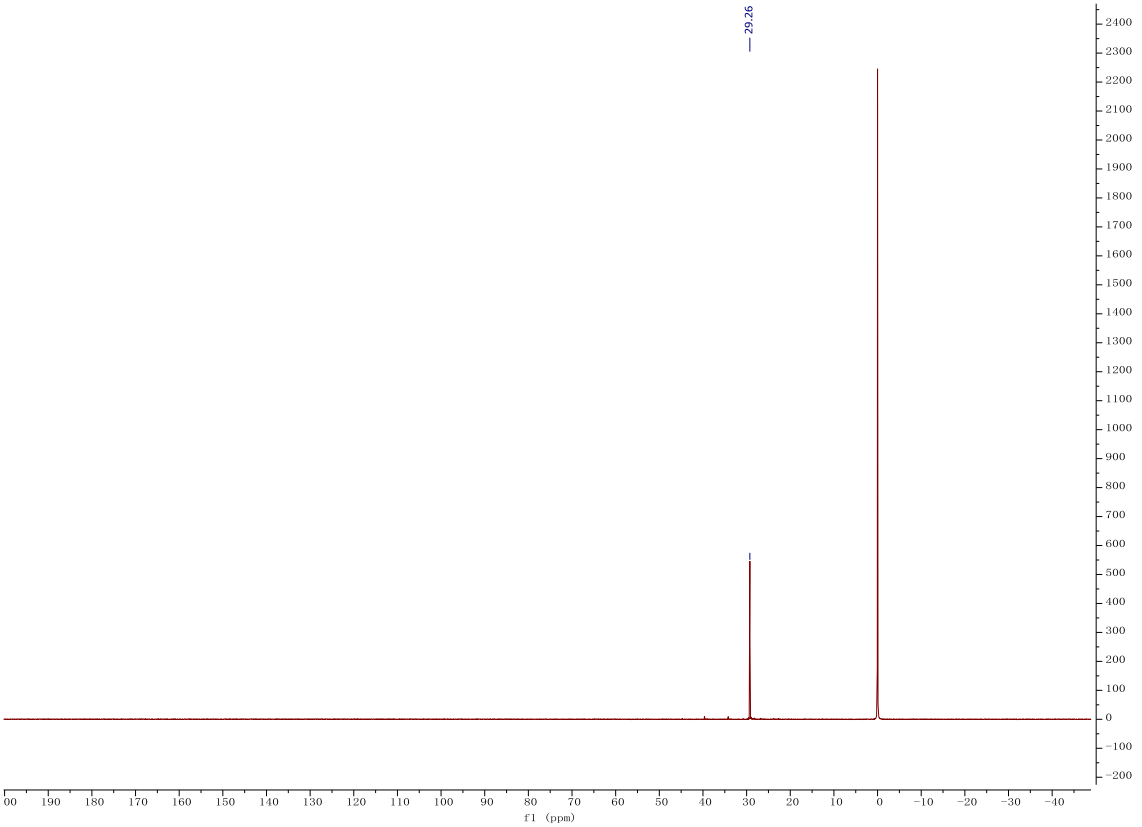

165.86
164.18
133.33
133.27
133.21
129.40
128.73
116.30
116.22
116.16
116.08
31.30
30.70
30.60
30.32
29.83
22.45
21.42
14.03
f1 (ppm)

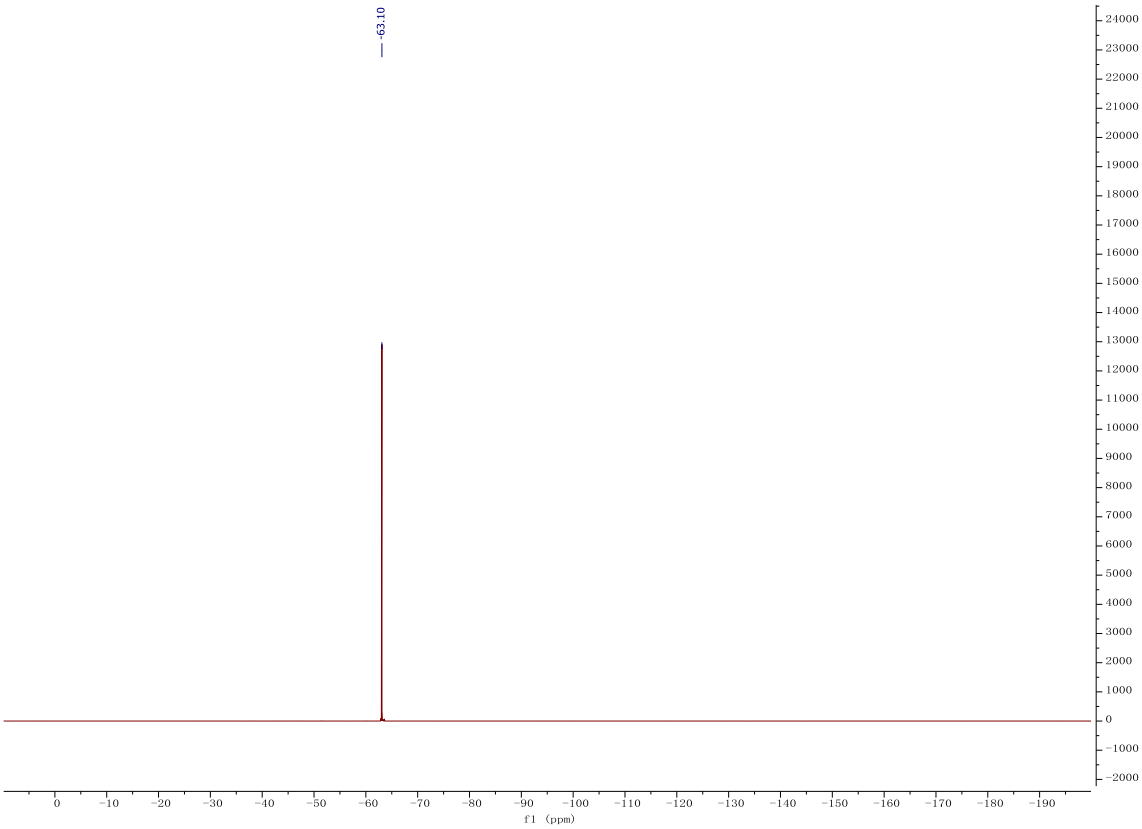

32.24
f1 (ppm)

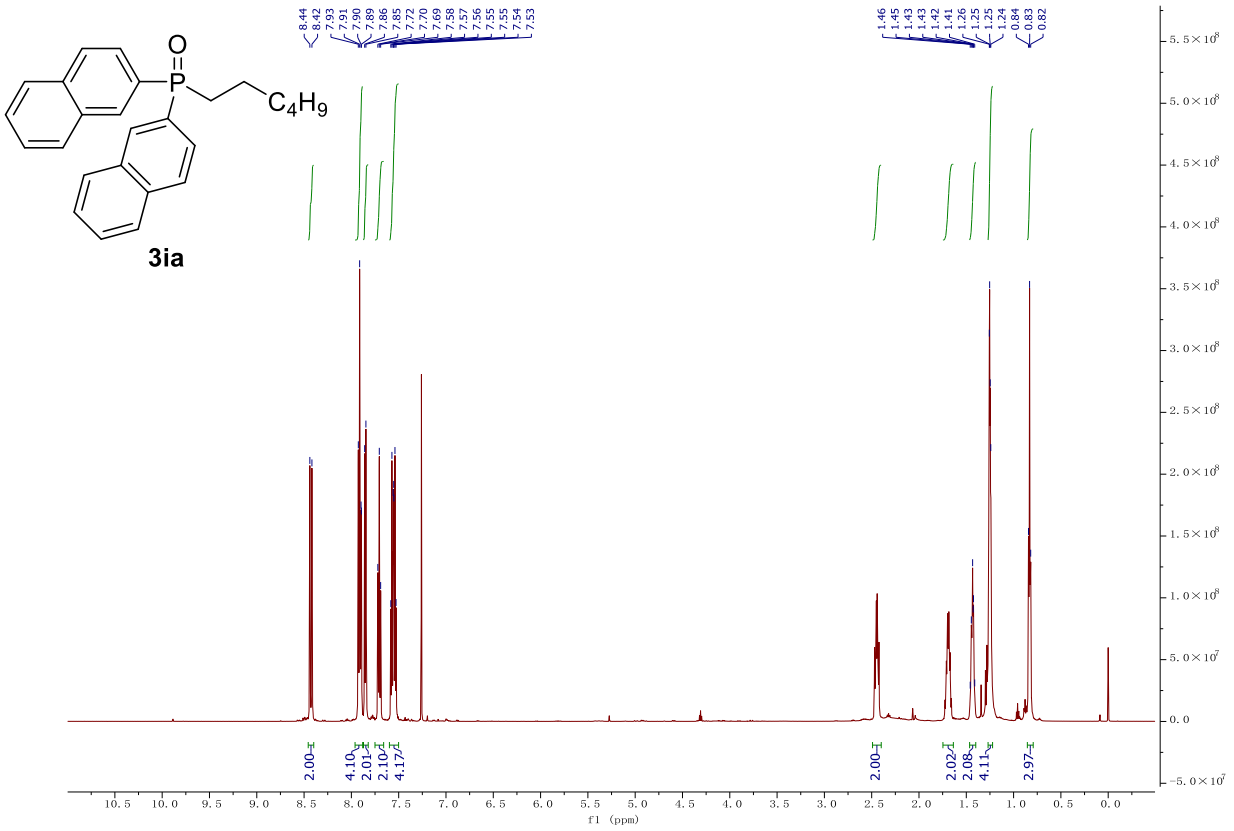

-106.88
-106.90
-106.91
-106.92
-106.93
f1 (ppm)

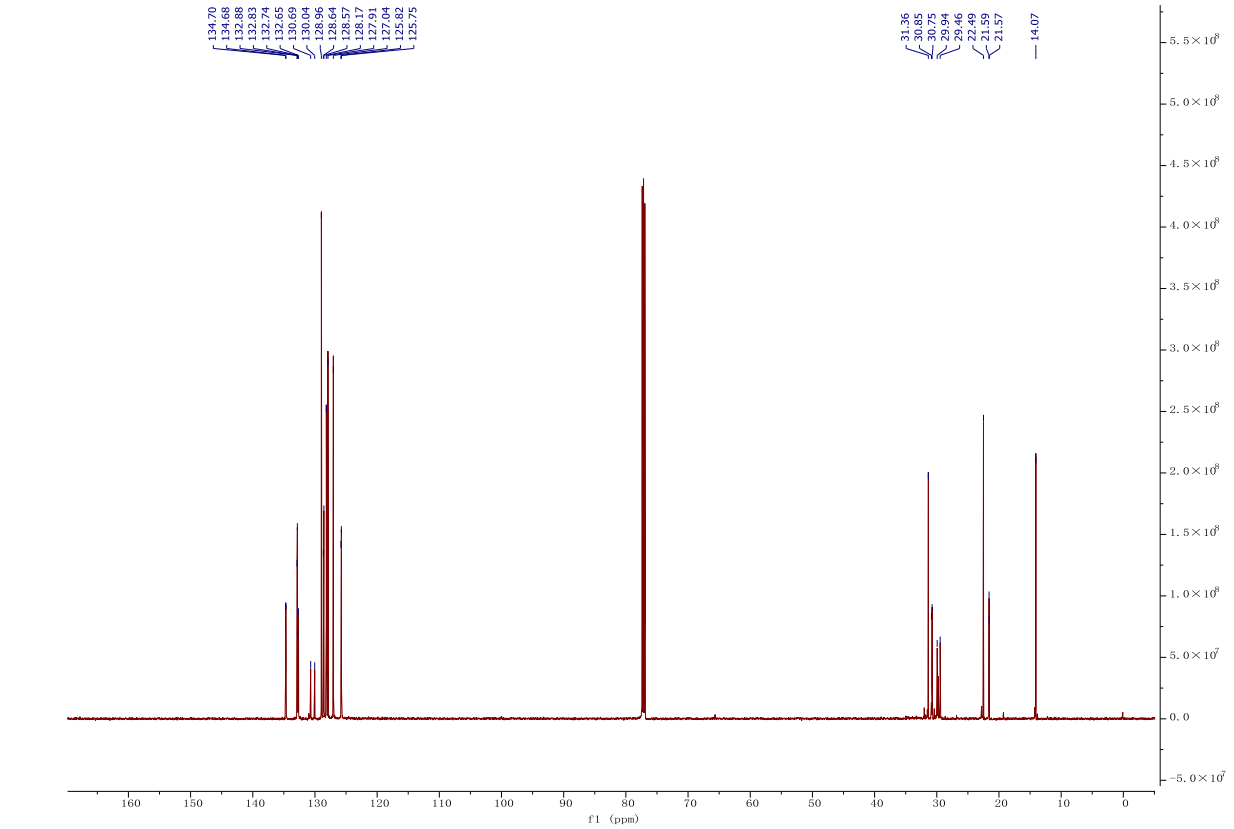

F3C
O
P
C4H9
F3C
F3C
CF3
3ha
8.24
8.22
8.08
2.46
2.45
2.44
2.44
2.42
1.69
1.67
1.66
1.65
1.65
1.63
1.62
1.48
1.47
1.46
1.45
1.44
1.29
1.28
1.28
1.27
1.27
1.25
1.25
0.87
0.86
0.84
4.00
2.07
2.03
2.09
2.01
4.06
3.00
f1 (ppm)

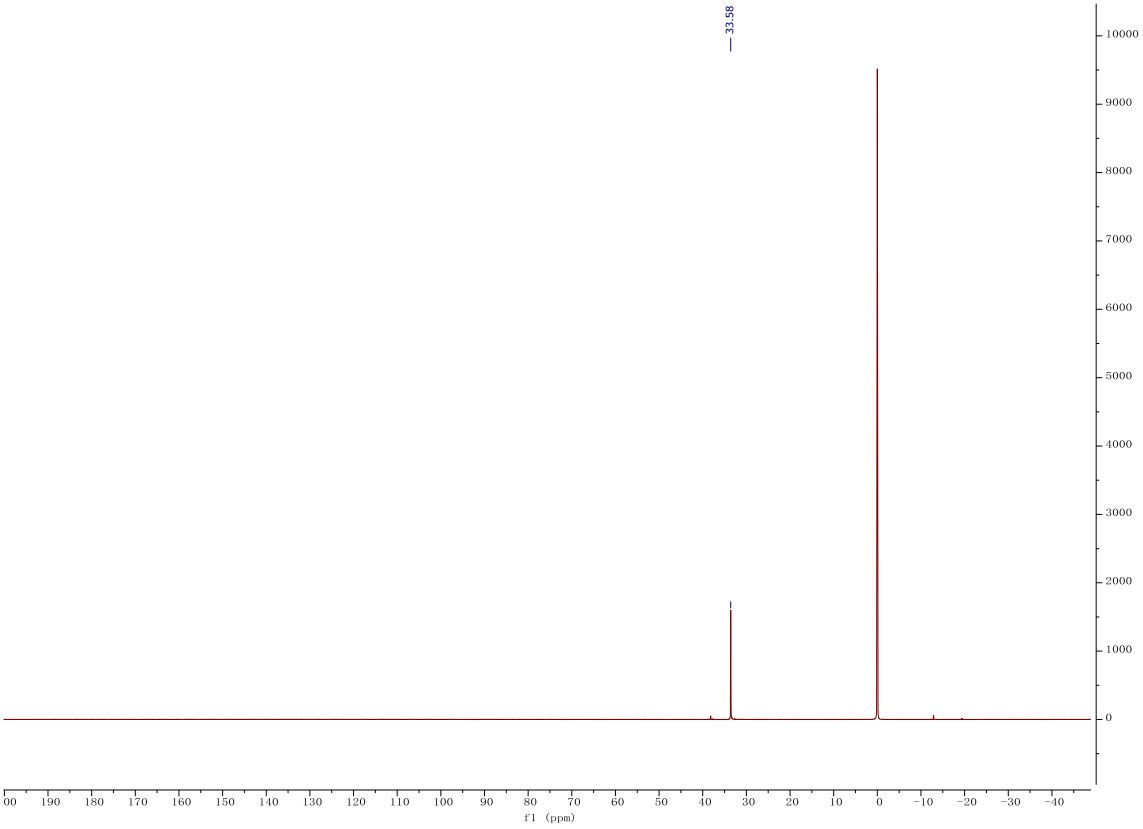

135.95
135.32
133.32
133.24
133.09
133.01
132.87
132.79
132.64
132.55
130.83
130.79
126.40
126.38
125.51
123.70
121.89
120.07
31.18
30.49
30.39
29.55
29.07
29.03
21.17
21.14
13.94
f1 (ppm)

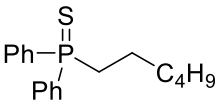

29.26
f1 (ppm)


-63.10
f1 (ppm)


O
P
C4H9
3ia
8.44
8.42
7.93
7.91
7.90
7.89
7.86
7.85
7.72
7.70
7.69
7.58
7.57
7.56
7.55
7.55
7.54
7.53
1.46
1.45
1.43
1.43
1.42
1.41
1.26
1.25
1.25
1.24
0.84
0.83
0.82
2.00
4.10
2.01
2.10
4.17
2.00
2.02
2.08
4.11
2.97
f1 (ppm)

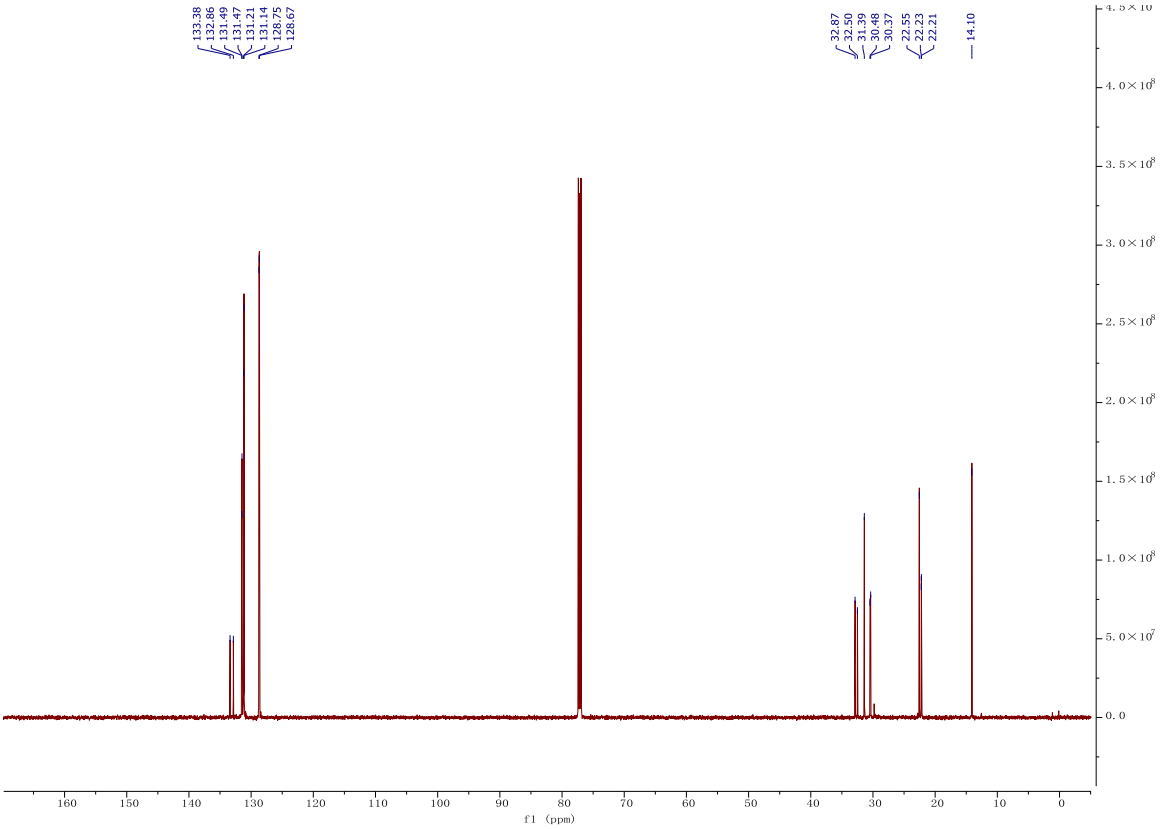

134.70
134.68
132.88
132.83
132.74
132.65
130.69
130.04
128.96
128.64
128.57
128.17
127.91
127.04
125.82
125.75
31.36
30.85
30.75
29.94
29.46
22.49
21.59
21.57
14.07
f1 (ppm)

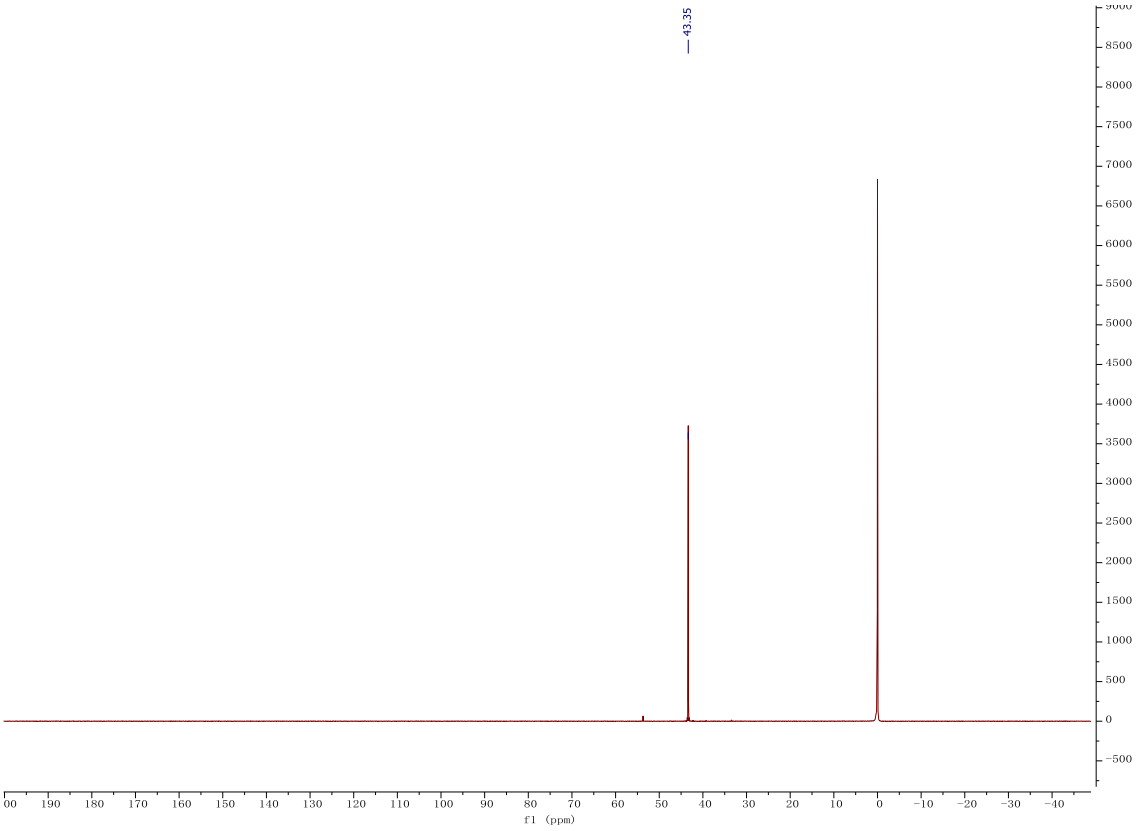

33.58
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)

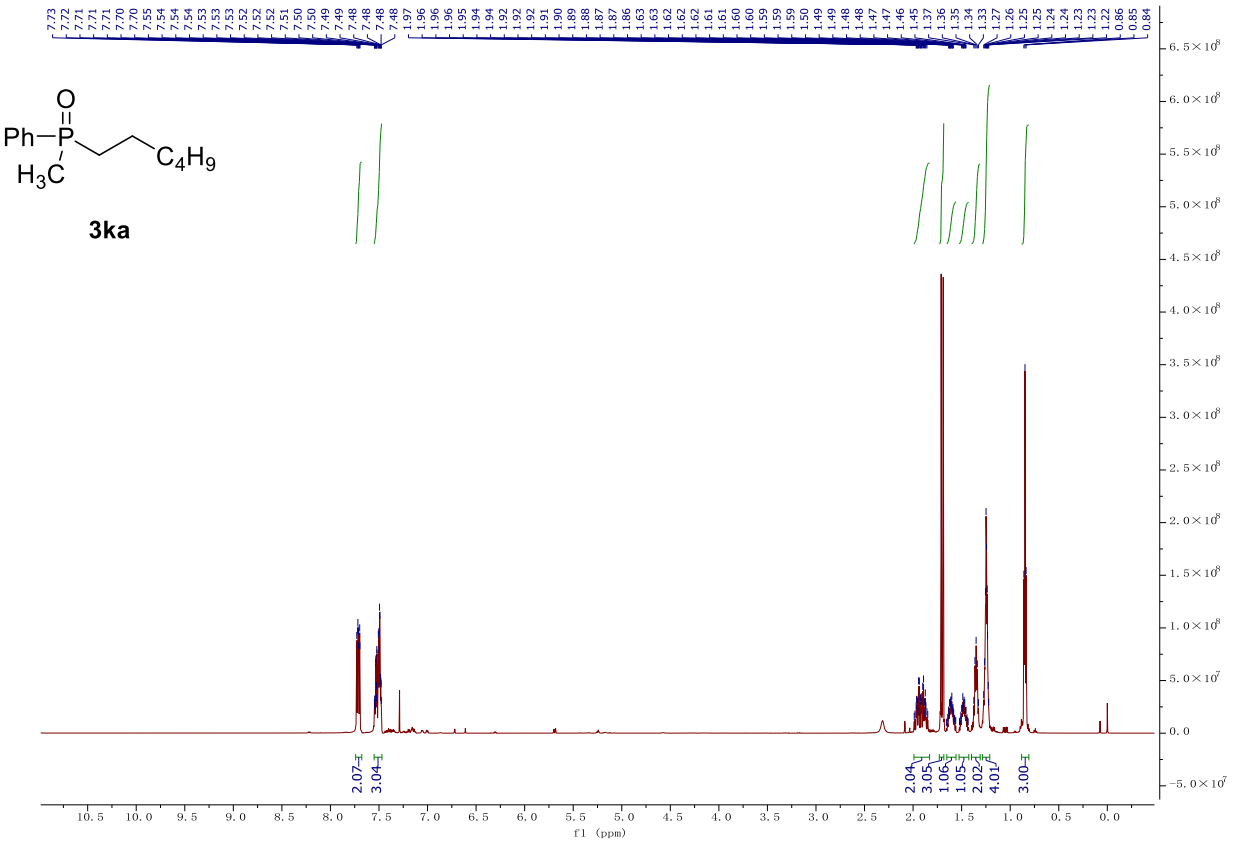

S
Ph
P
Ph
C4H9

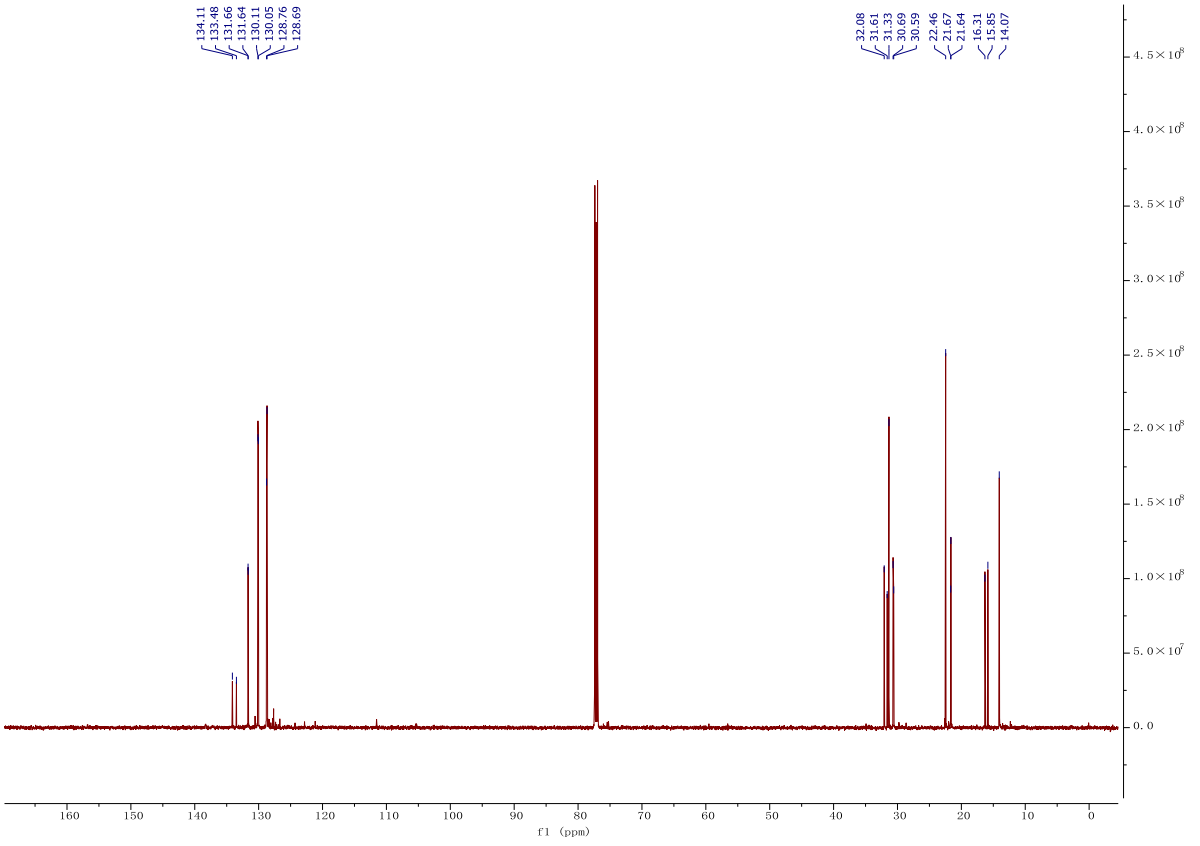
3ja

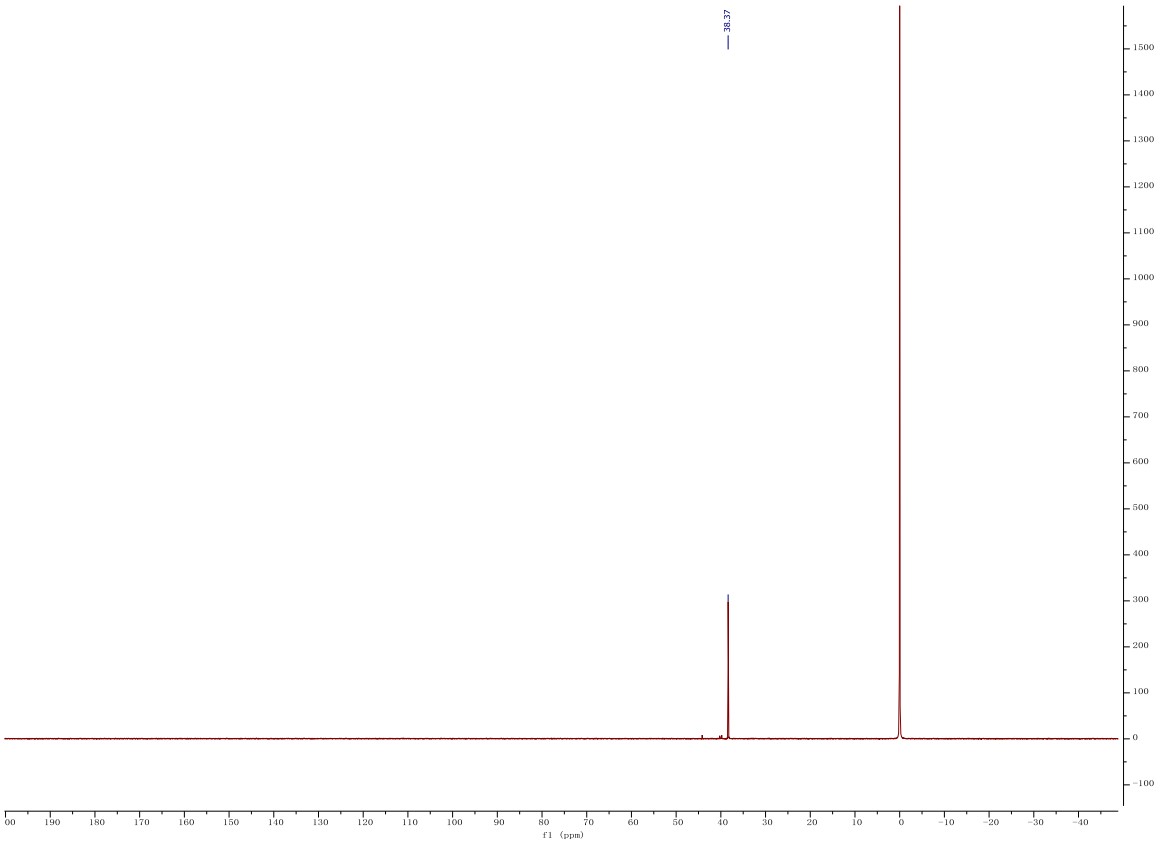
7.84
7.83
7.82
7.81
7.50
7.49
7.49
7.48
7.46
7.46
7.45
7.44
7.44
2.46
2.45
2.44
2.43
2.43
2.41
1.65
1.64
1.62
1.61
1.60
1.58
1.41
1.40
1.38
1.37
1.25
1.25
0.85
0.84
0.83
4.00
6.03
1.96
2.13
2.10
4.07
3.02
f1 (ppm)

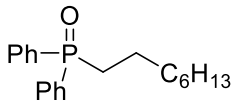

133.38
132.86
131.49
131.47
131.21
131.14
128.75
128.67
32.87
32.50
31.39
30.48
30.37
22.55
22.23
22.21
14.10
f1 (ppm)


43.35
f1 (ppm)


Ph
P
O
H3C
C4H9
3ka
f1 (ppm)

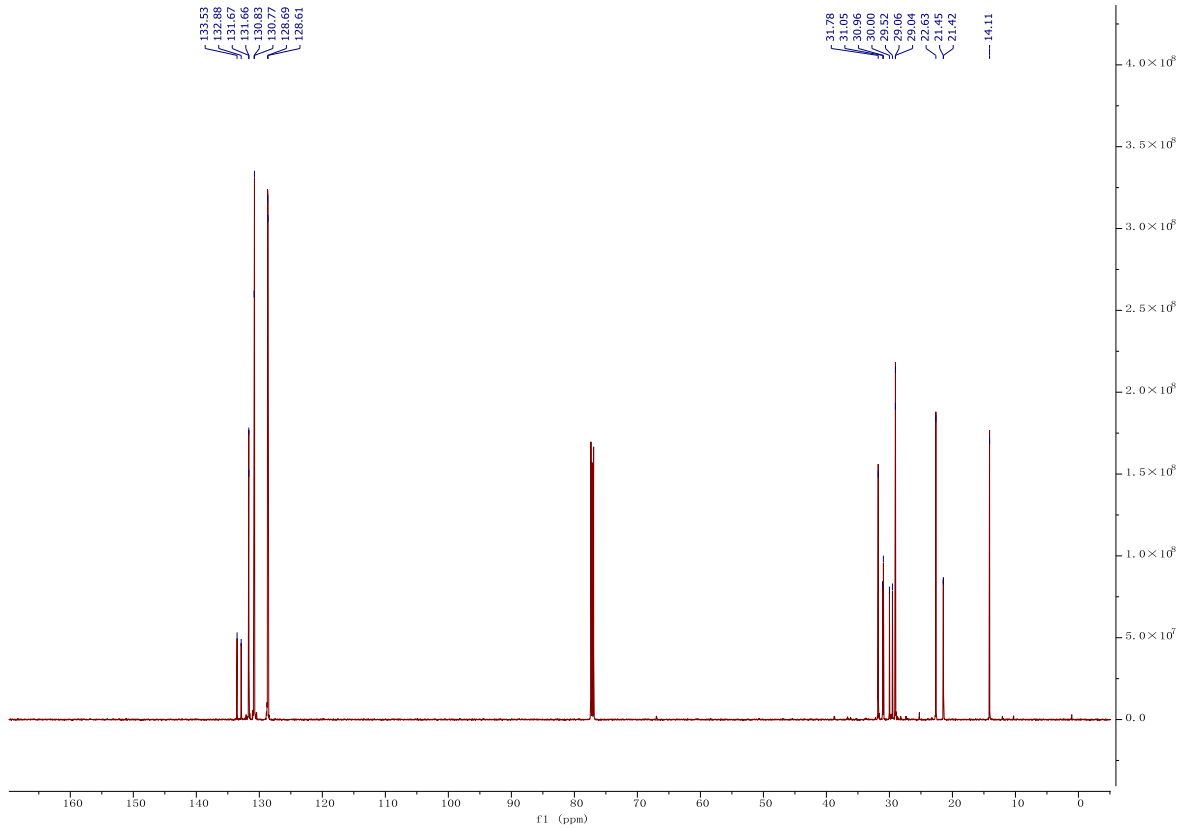

f1 (ppm)

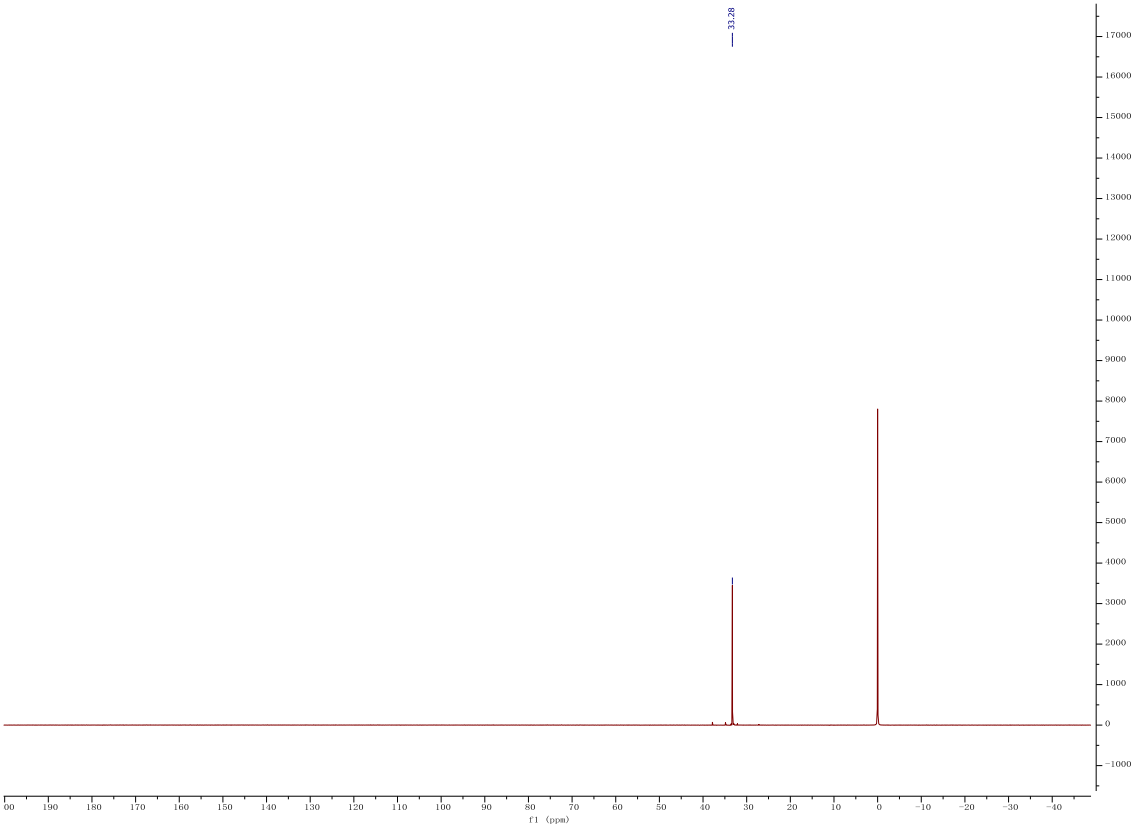

38.37
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

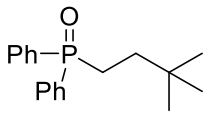

O
Ph—P
Ph
C6H13

3ab

7.67 7.66 7.66 7.65 7.64 7.64 7.44 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.39 7.39 7.38 7.37 7.37 7.36 7.36
2.20 2.19 2.18 2.18 2.17 2.16 2.15 1.57 1.56 1.55 1.54 1.54 1.53 1.52 1.50 1.33 1.32 1.31 1.29 1.28 1.20 1.19 1.18 1.16 1.15 1.14 1.14 1.13 1.12 1.12 1.10 0.78 0.77 0.76
4.00 6.08 2.03 2.05 2.07 8.02 3.00
f1 (ppm)

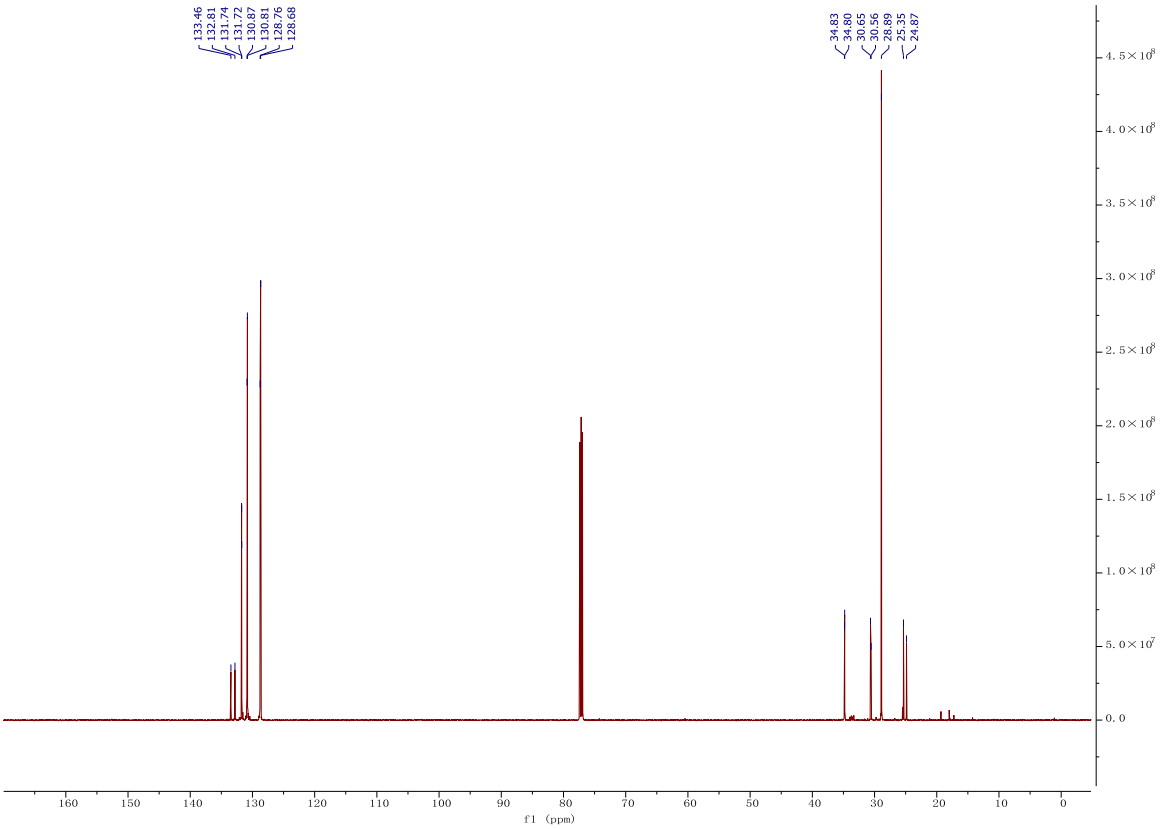

133.53 132.88 131.67 131.66 130.83 130.77 128.69 128.61
31.78 31.05 30.96 30.00 29.52 29.06 29.04 22.63 21.45 21.42 14.11
f1 (ppm)

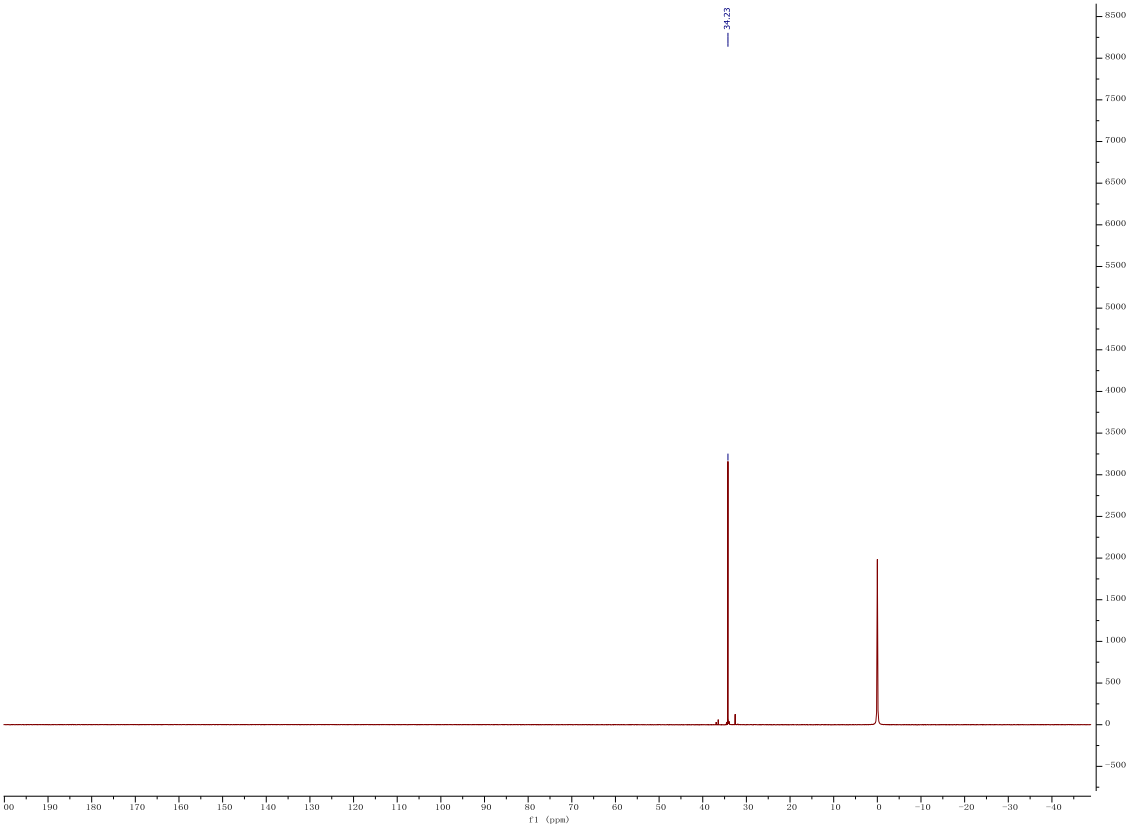

33.28
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

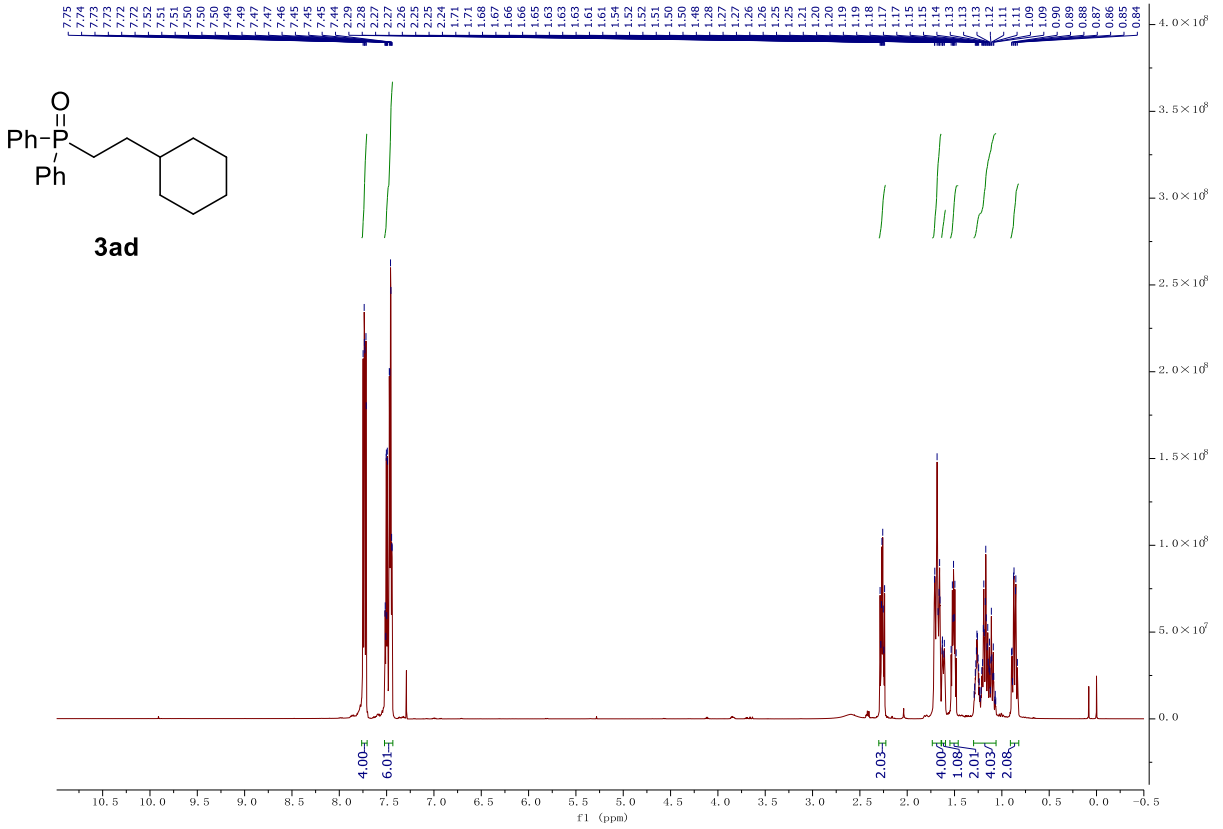

O
Ph
P
Ph

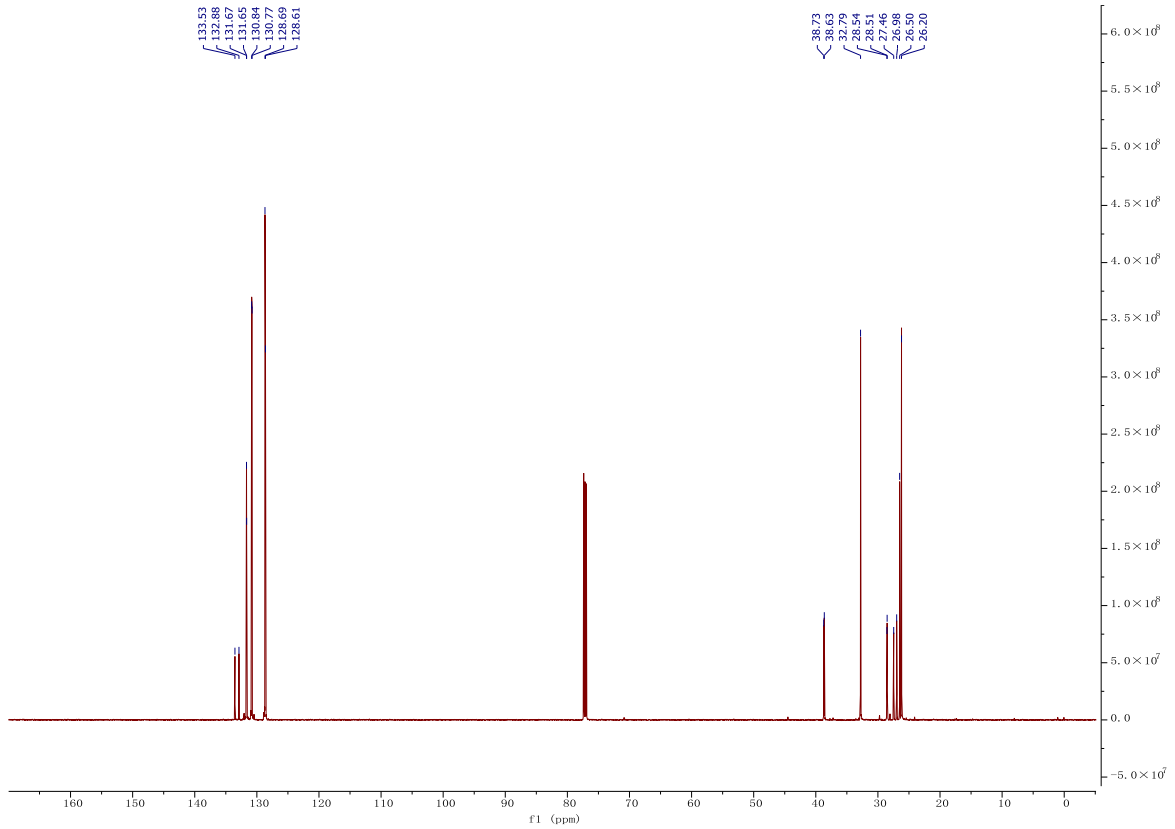
3ac

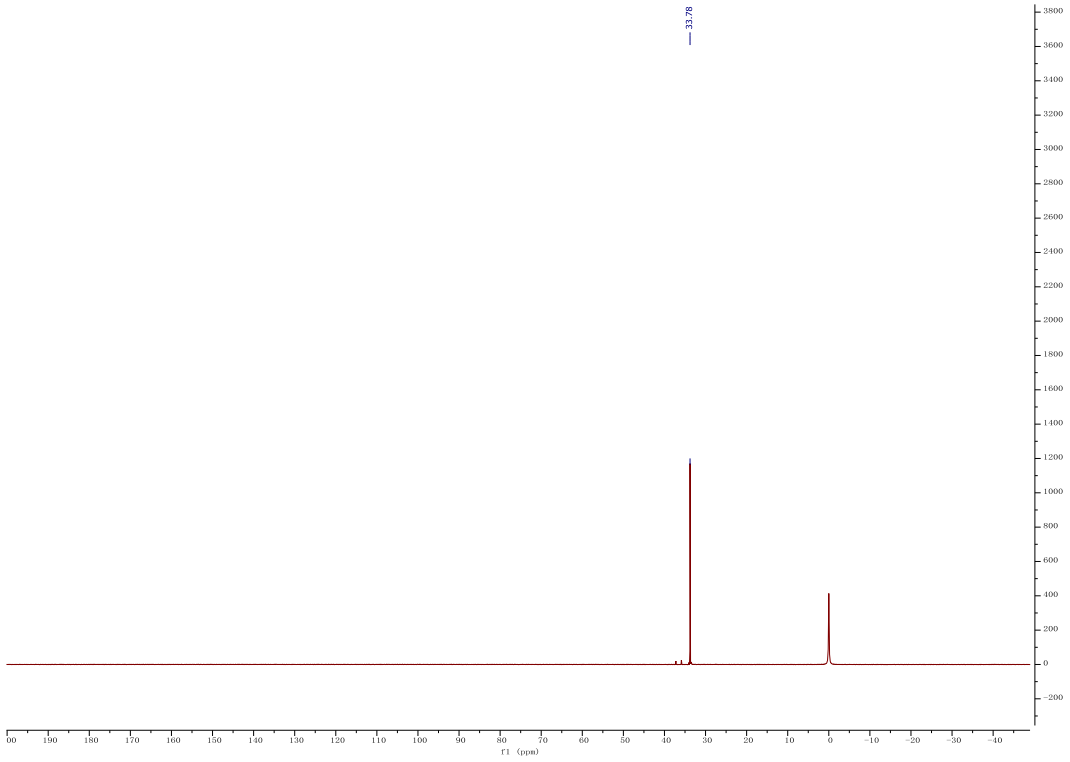
7.68
7.67
7.66
7.66
7.65
7.64
7.45
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.41
7.40
7.39
7.39
7.39
7.38
7.38
7.38
7.37
2.16
2.16
2.15
2.15
2.14
2.13
2.13
2.12
2.11
1.44
1.44
1.43
1.43
1.42
1.42
1.41
1.40
0.81
4.10
6.05
2.00
2.09
9.00
f1 (ppm)

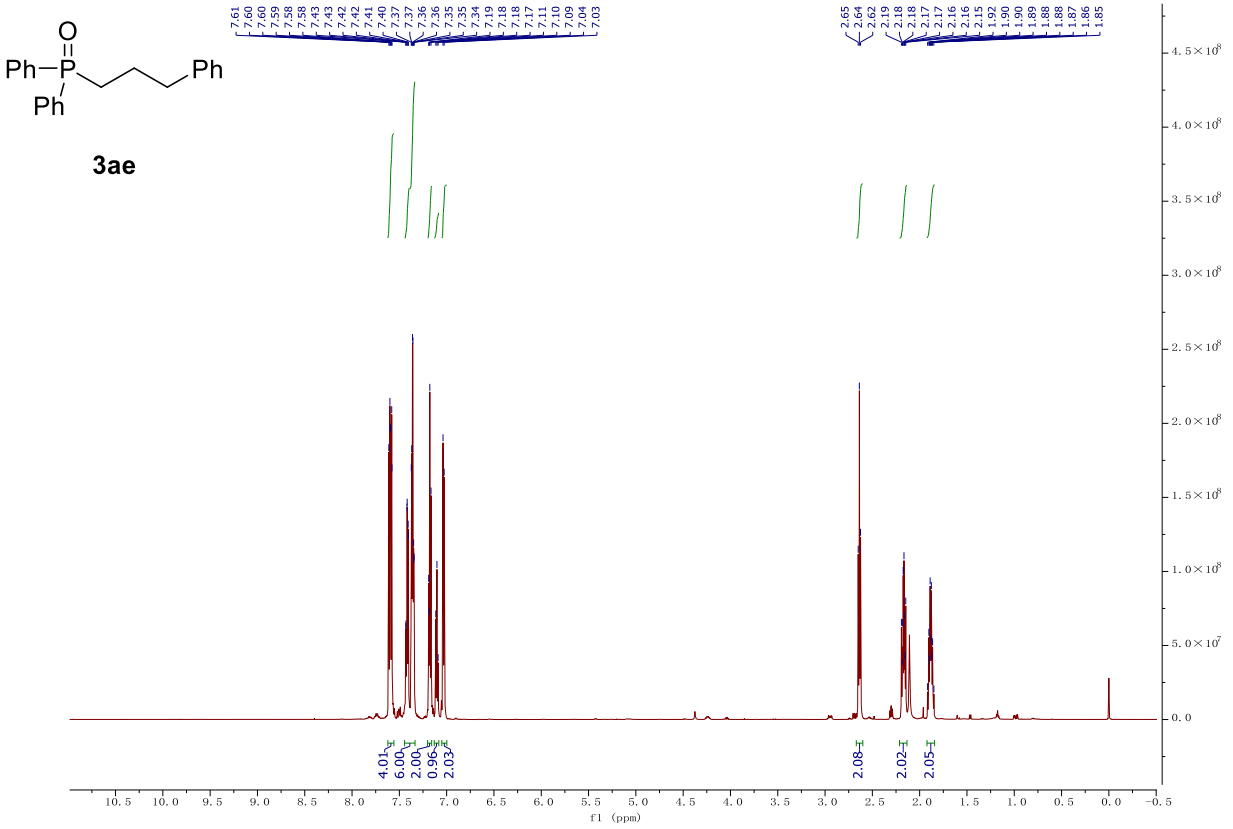

133.46
132.81
131.74
131.72
130.87
130.81
128.76
128.68
34.83
34.80
30.65
30.56
28.89
25.35
24.87
f1 (ppm)

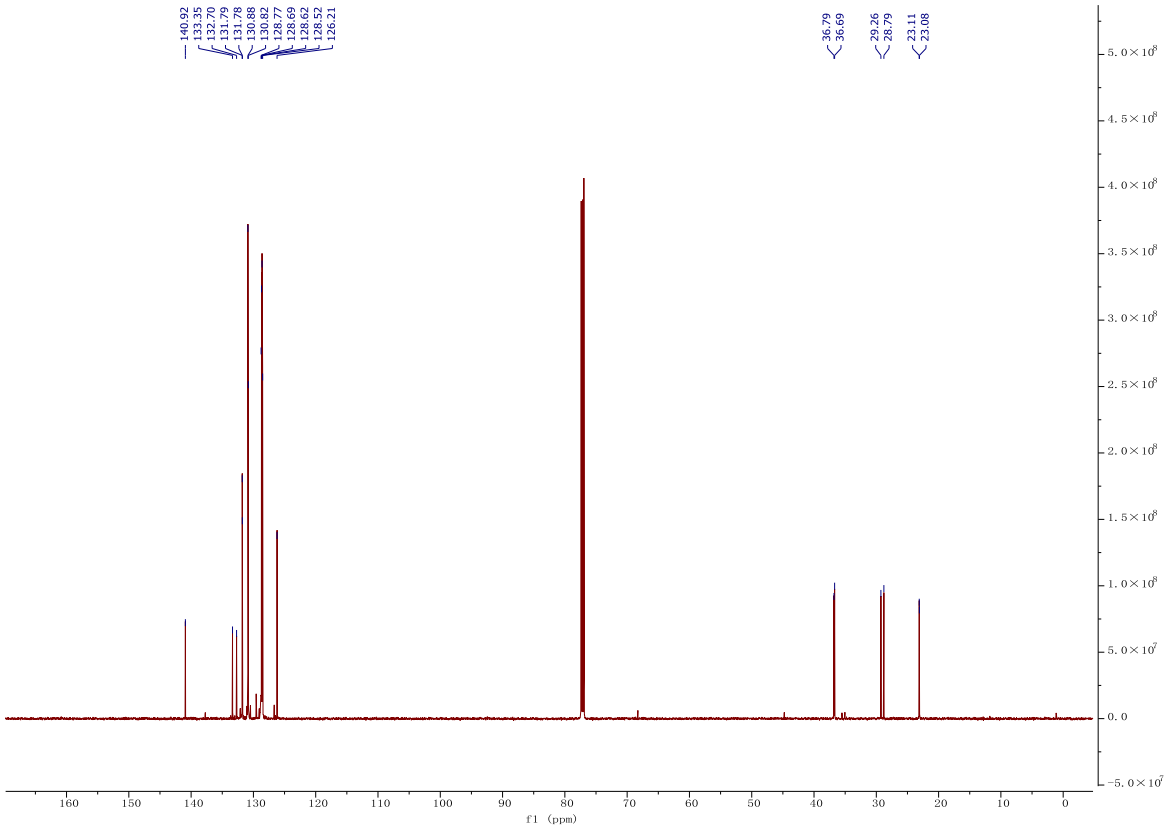

34.23
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

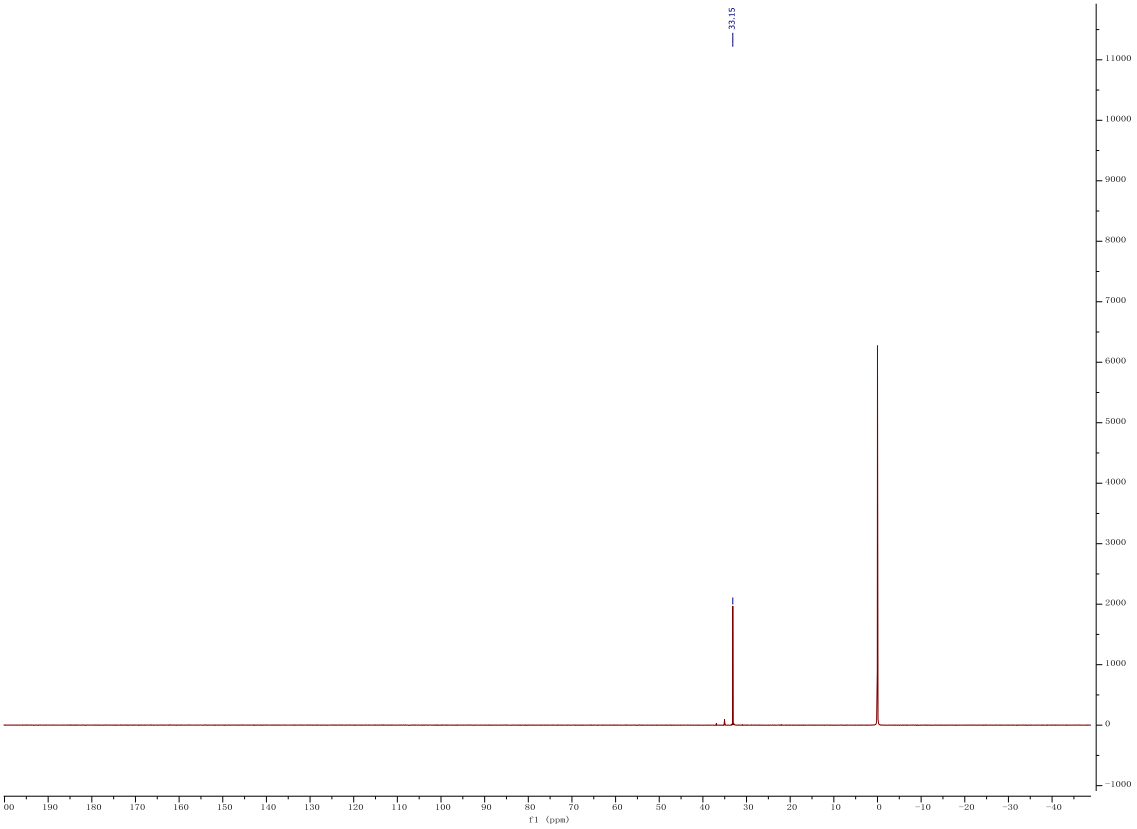

Ph–P
O
Ph
3ad
f1 (ppm)

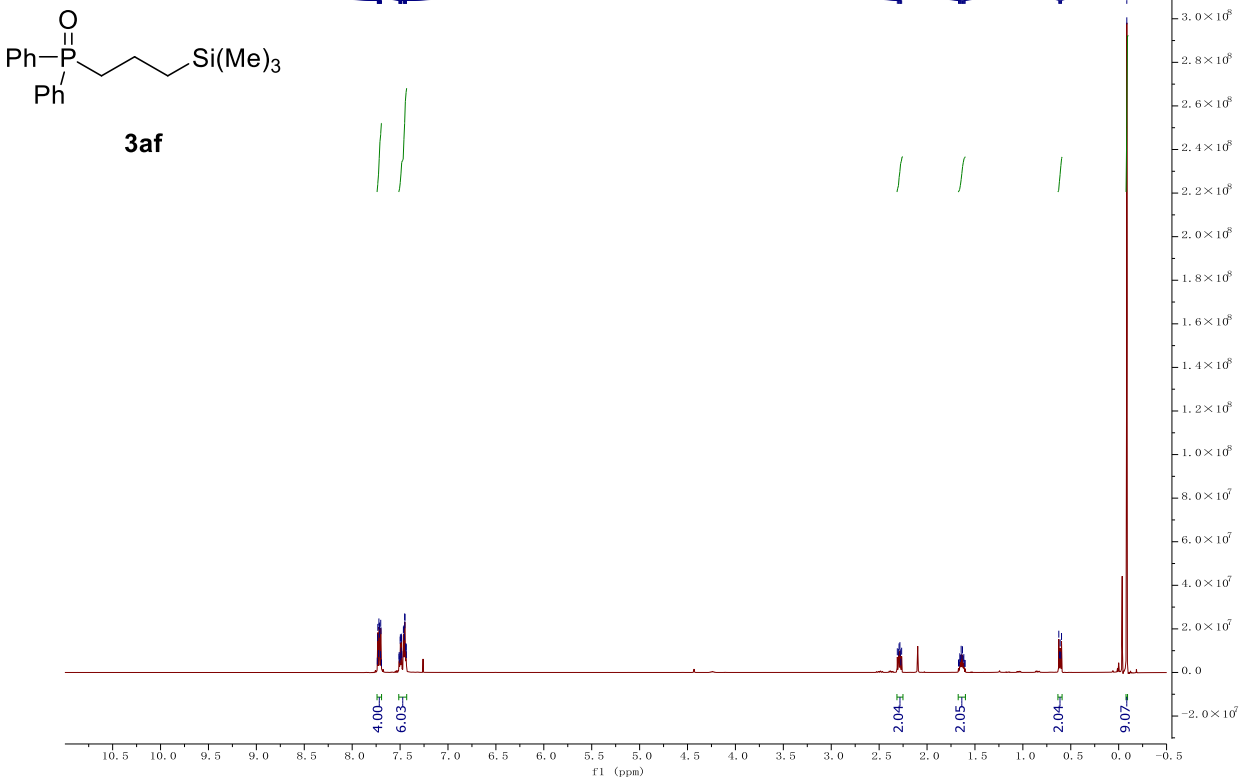

f1 (ppm)

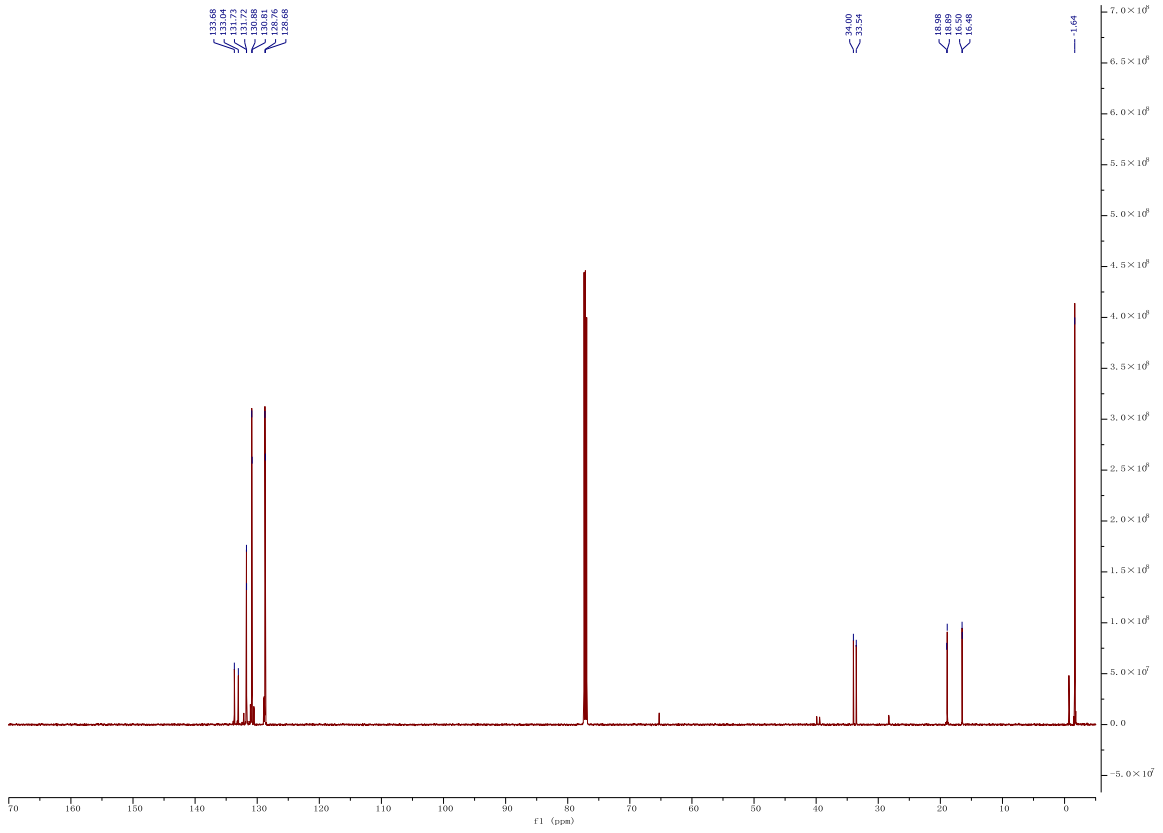

33.78
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)

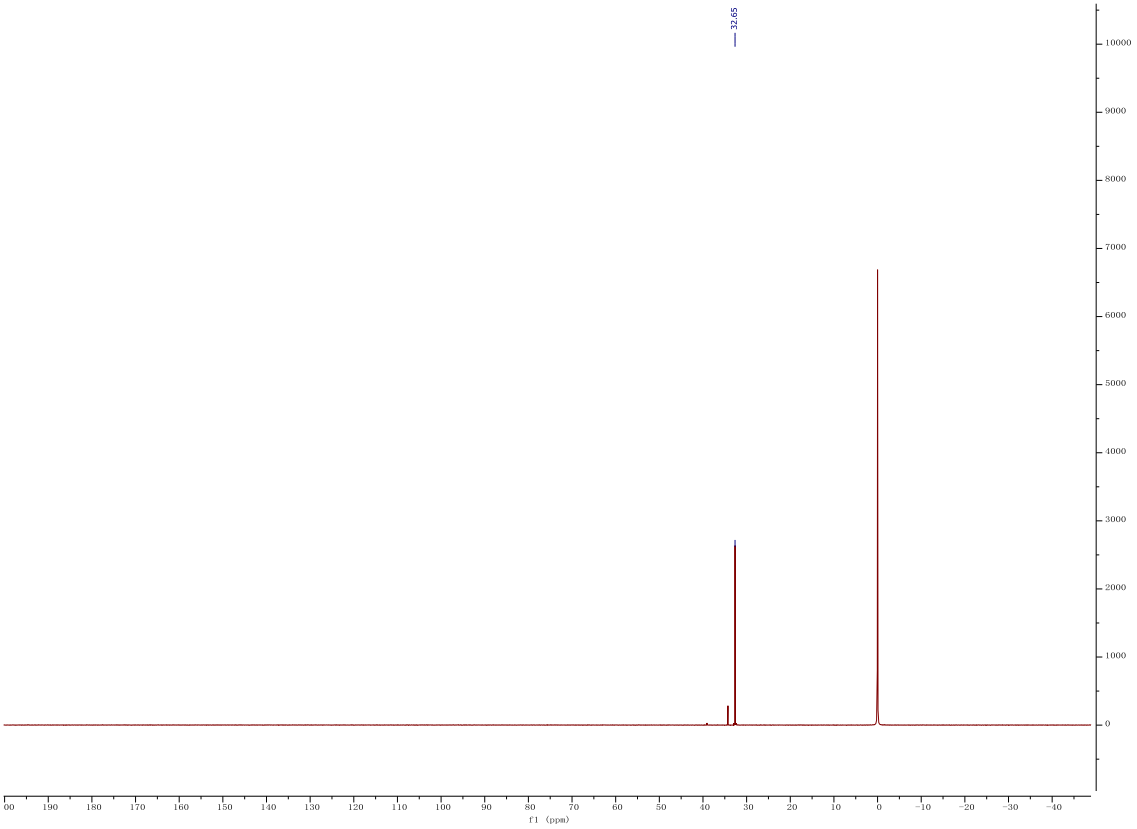

Ph
P
O
Ph
Ph
3ae
f1 (ppm)

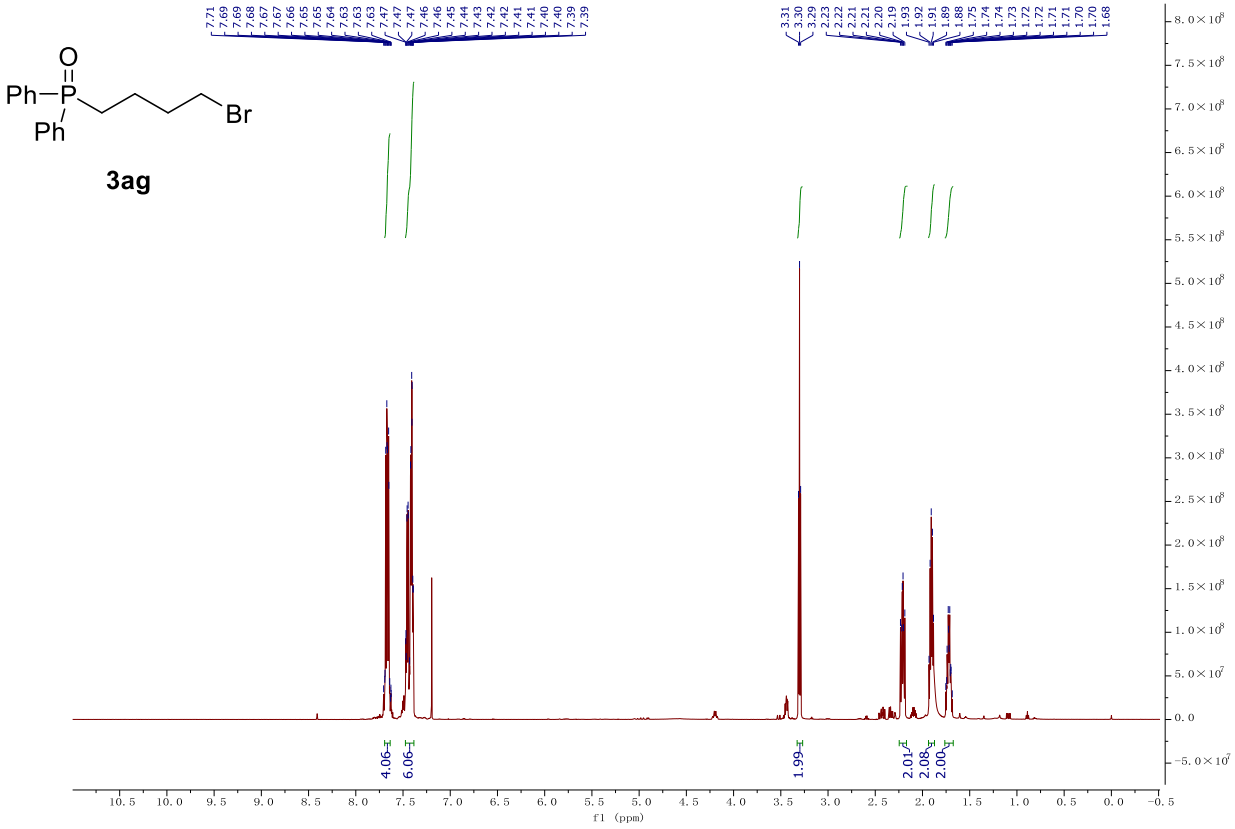

f1 (ppm)

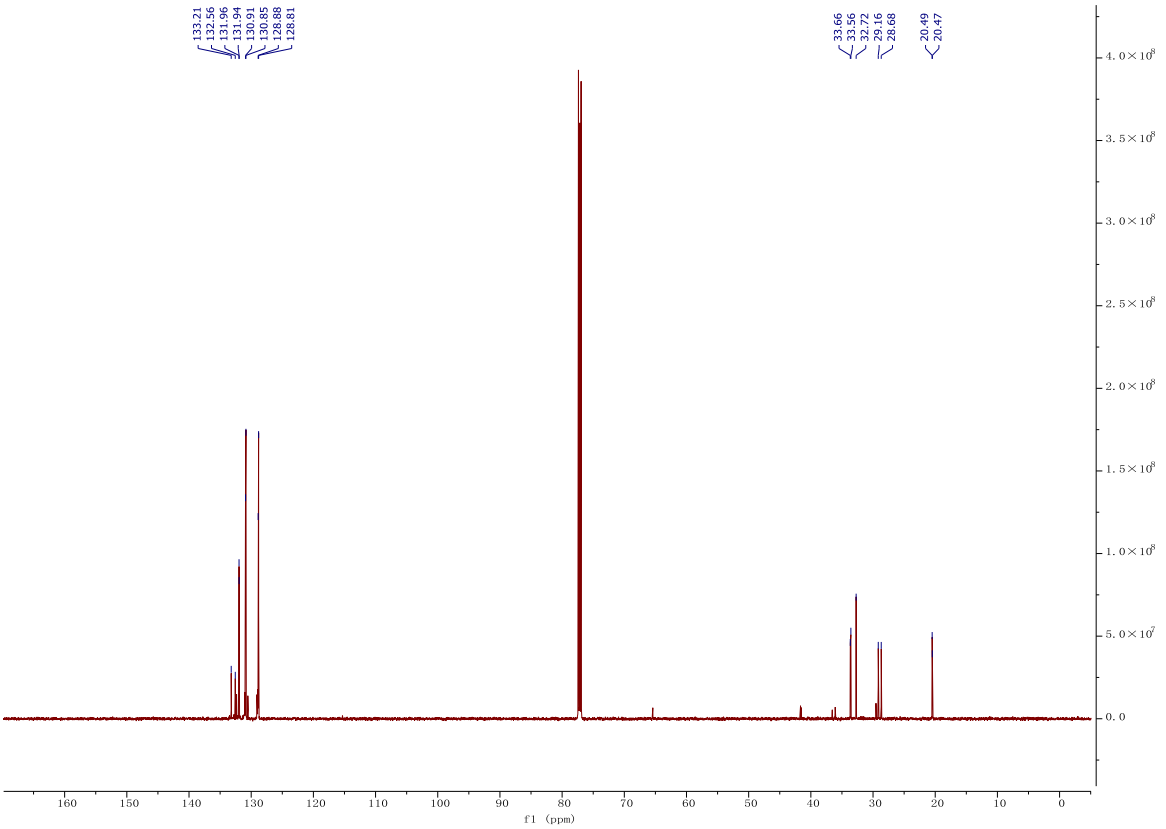

33.15
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

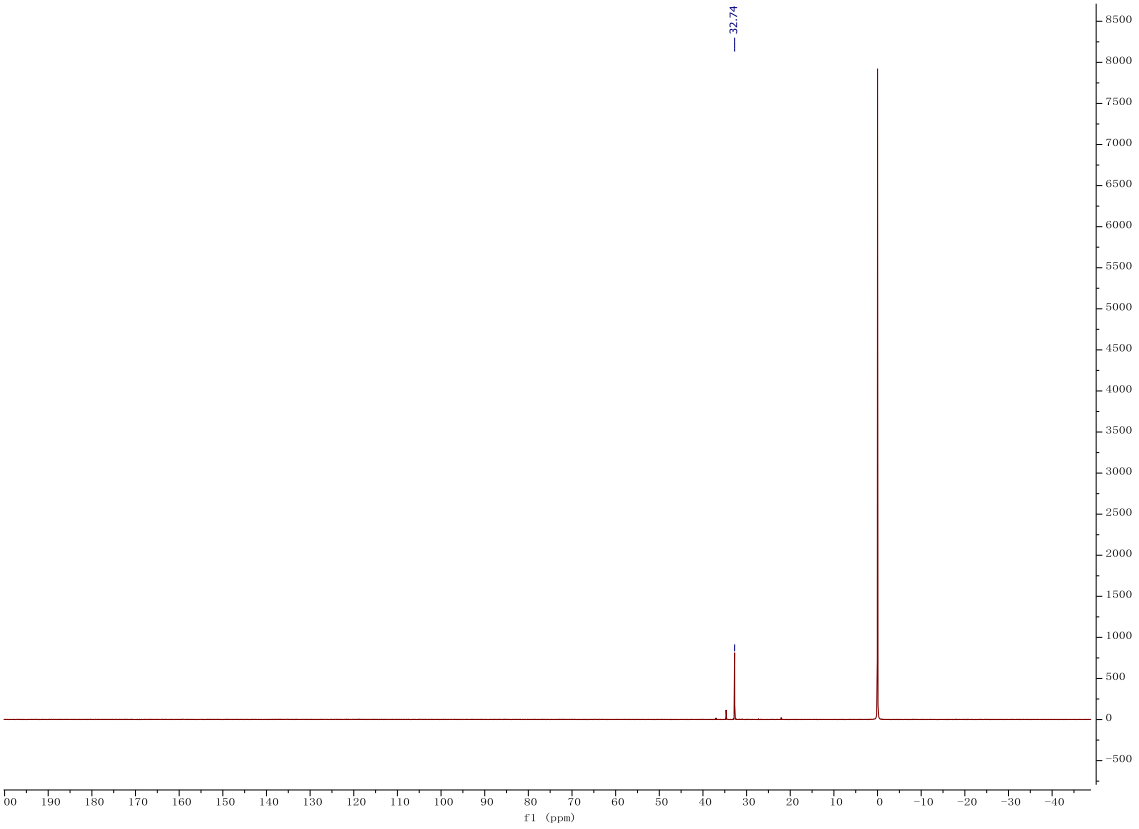

Ph
P
O
Ph
Si(Me)3
3af
f1 (ppm)

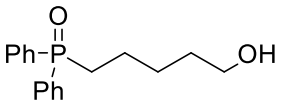

f1 (ppm)


32.65
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
f1 (ppm)


O
Ph
P
Ph
Br
3ag
7.71 7.69 7.68 7.67 7.67 7.66 7.65 7.65 7.64 7.63 7.63 7.47 7.47 7.47 7.46 7.46 7.45 7.44 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.39
3.31 3.30 3.29 2.23 2.22 2.21 2.21 2.20 2.19 1.93 1.92 1.91 1.89 1.88 1.75 1.74 1.74 1.73 1.72 1.72 1.71 1.71 1.70 1.70 1.68
4.06
6.06
1.99
2.01
2.08
2.00
f1 (ppm)

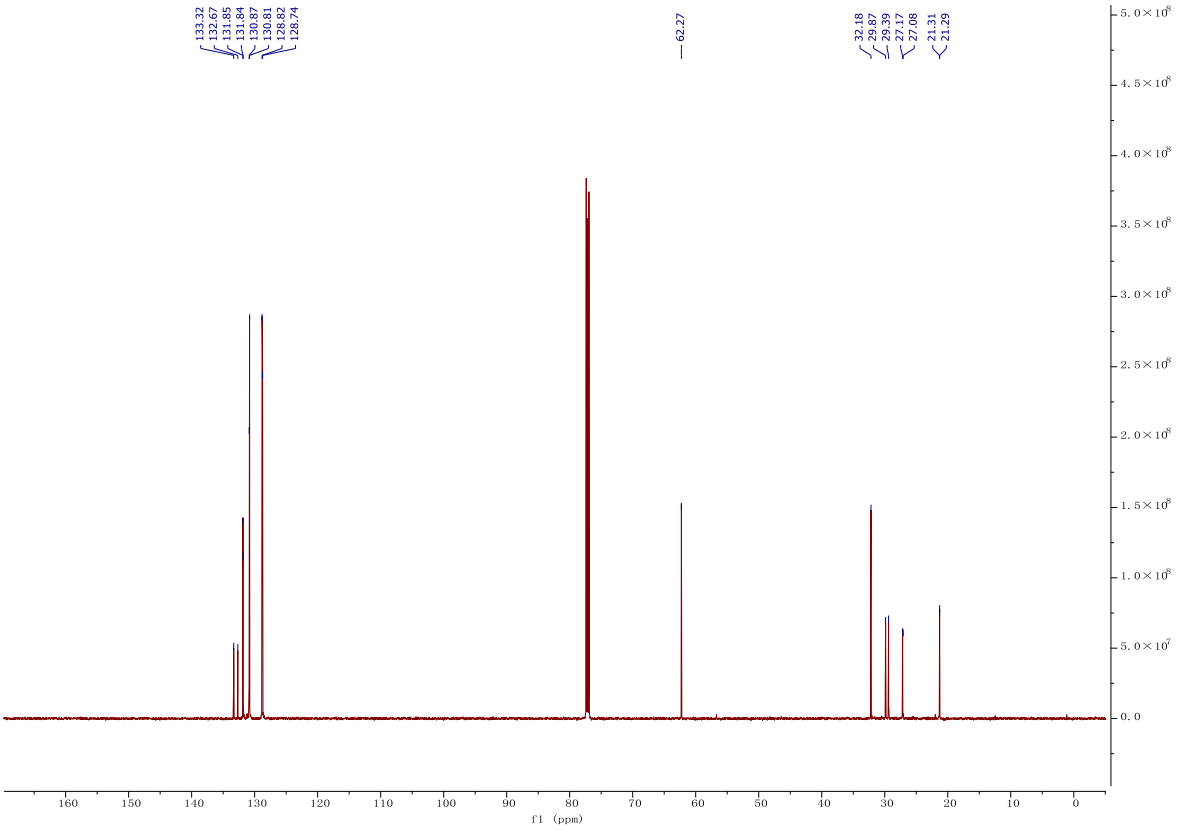

133.21 132.56 131.96 131.94 130.91 130.85 128.88 128.81
33.66 33.56 32.72 29.16 28.68 20.49 20.47
f1 (ppm)

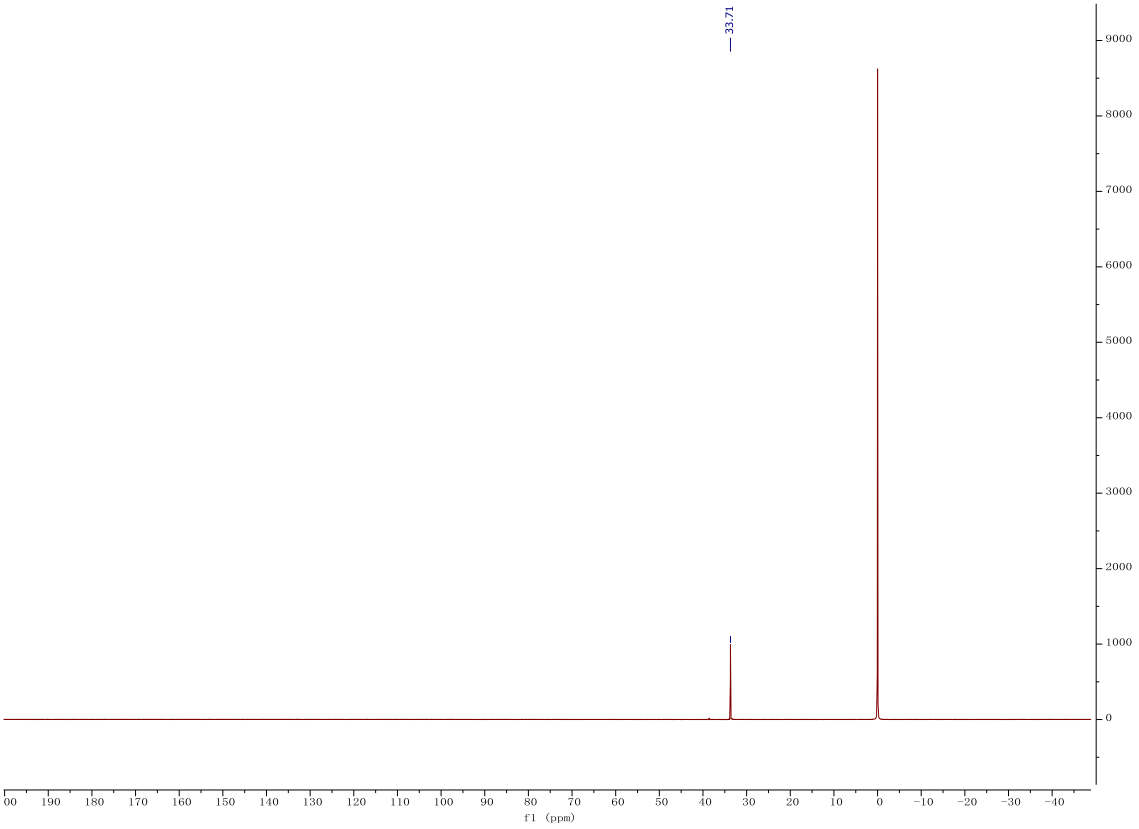

32.74
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

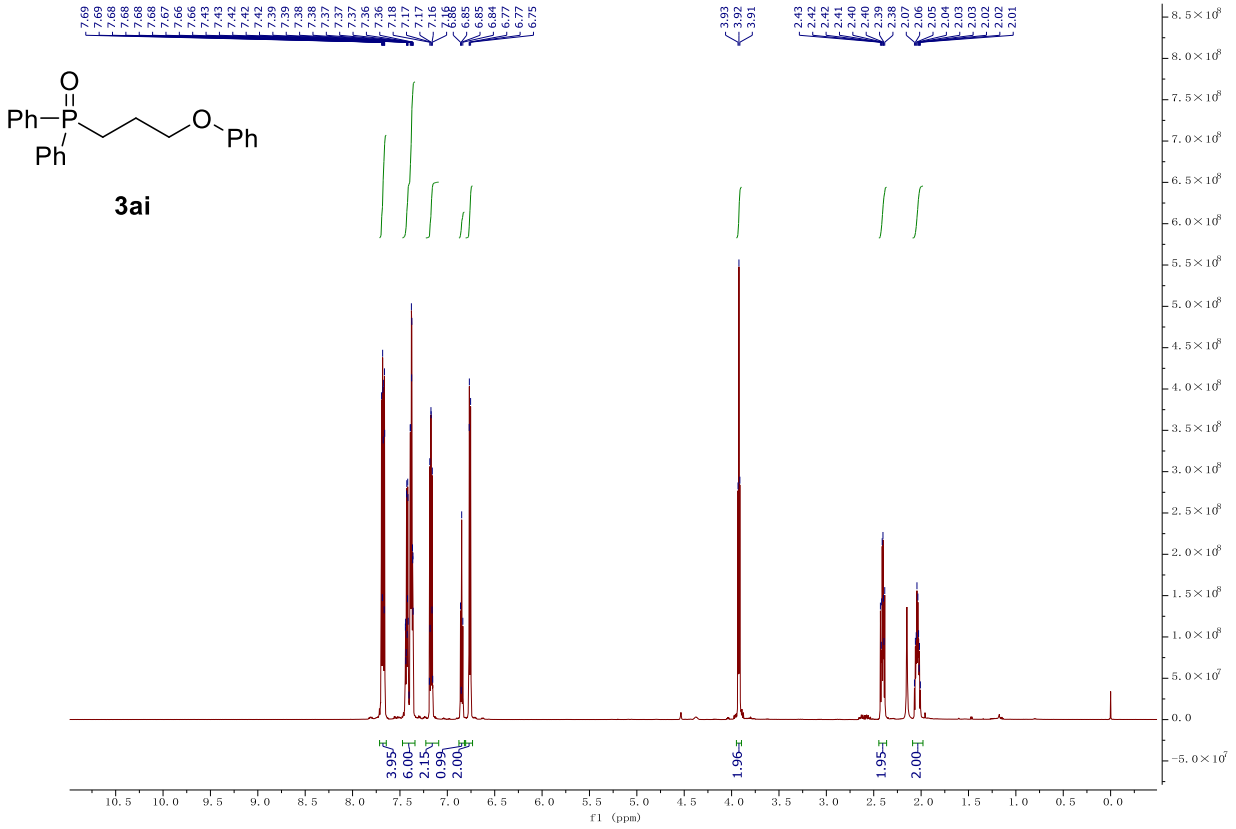


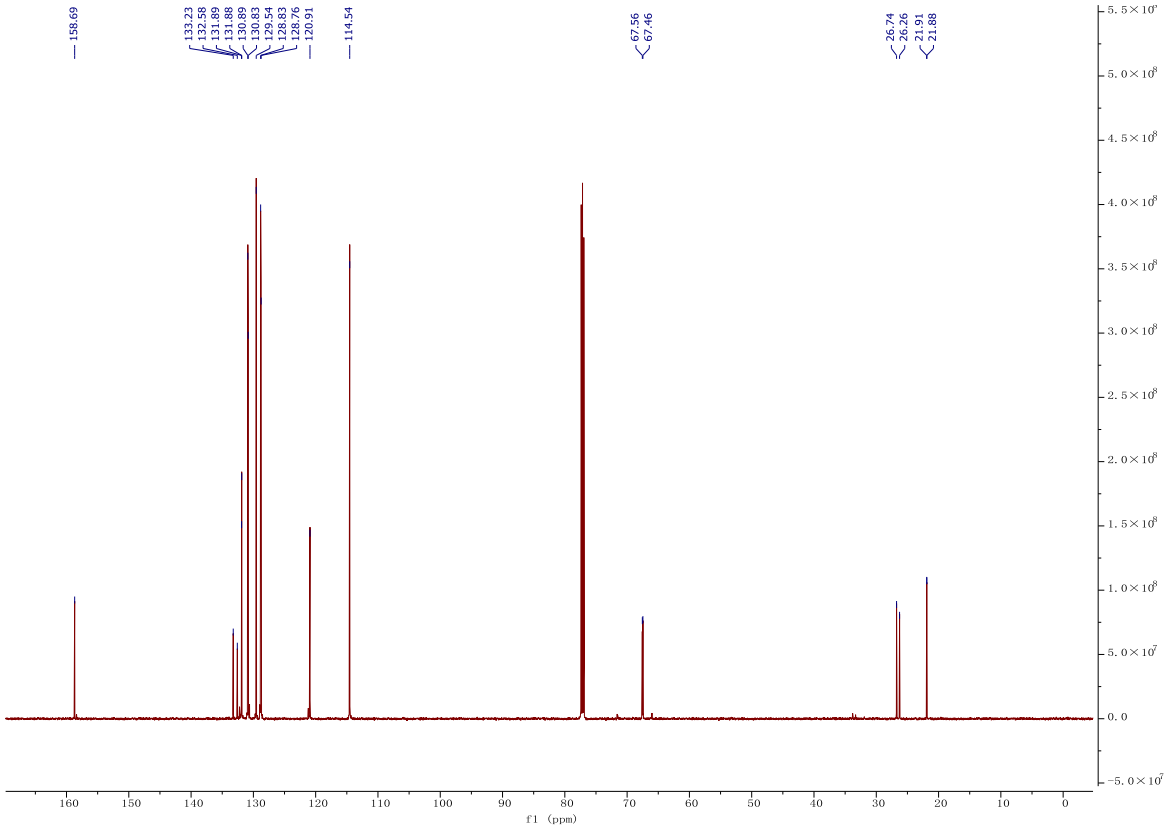
3ah

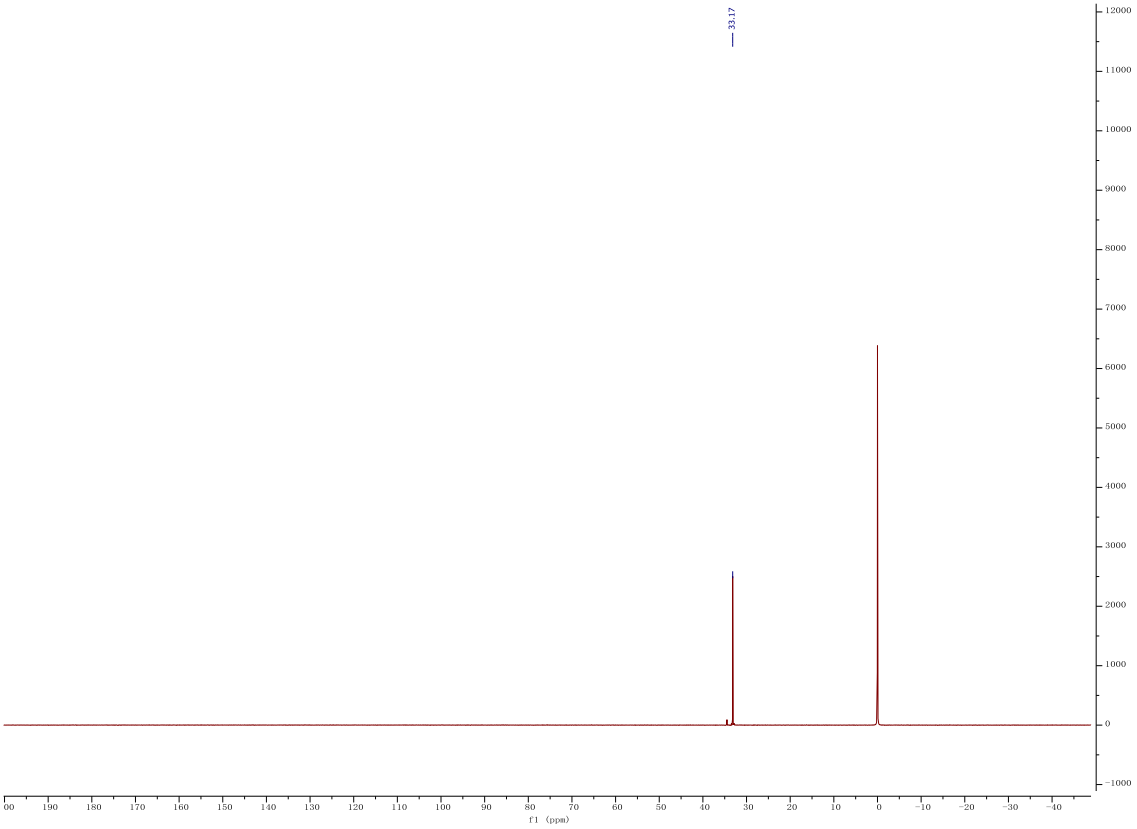
7.66 7.65 7.65 7.64 7.63 7.45 7.45 7.44 7.43 7.40 7.40 7.39 7.39 7.38 7.37
3.52 3.51 3.50
2.22 2.21 2.20 2.19 2.19 2.17
1.59 1.58 1.56 1.55 1.54 1.49 1.49 1.48 1.47 1.46 1.45 1.44 1.43 1.41 1.41 1.40
4.00 6.16 2.09 2.04 2.02 4.07
f1 (ppm)


133.32 132.67 131.85 131.84 130.87 130.81 128.82 128.74
62.27
32.18 29.87 29.39 27.17 27.08 21.31 21.29
f1 (ppm)


33.71
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


3ai
f1 (ppm)


f1 (ppm)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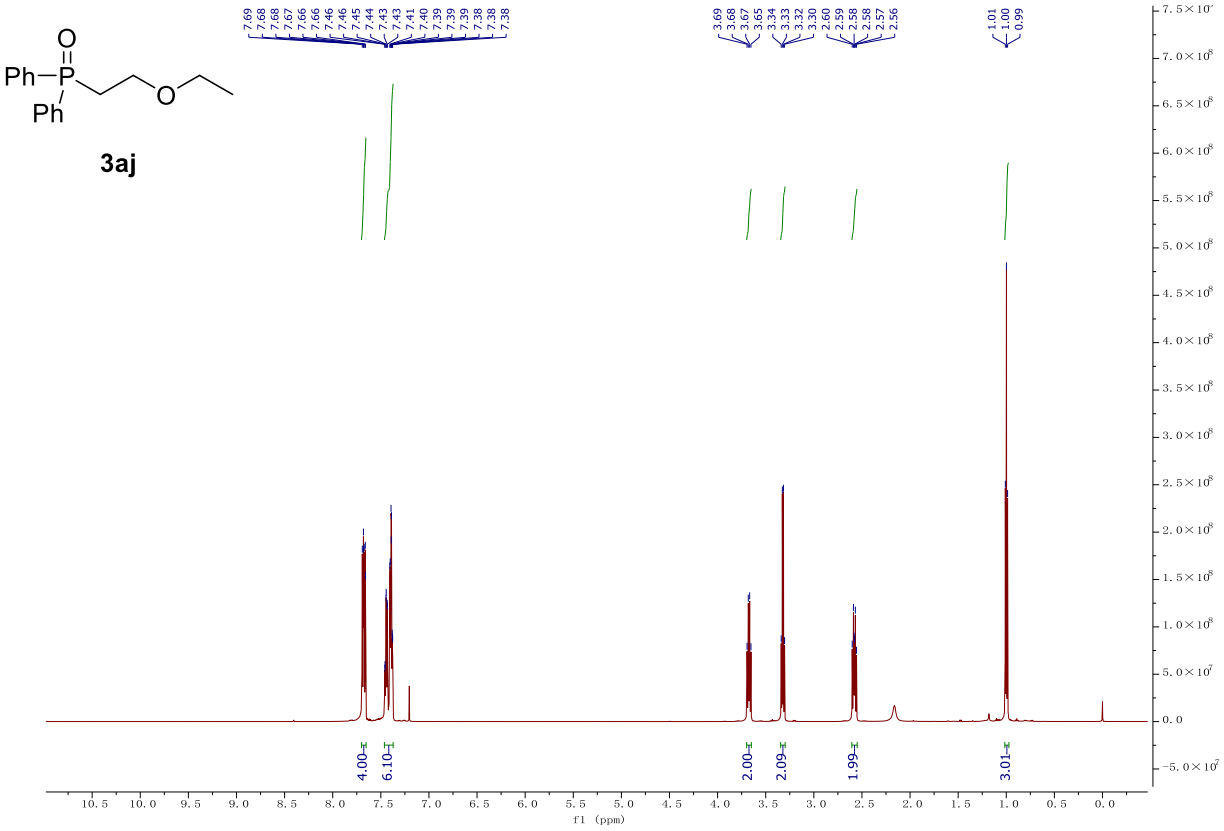
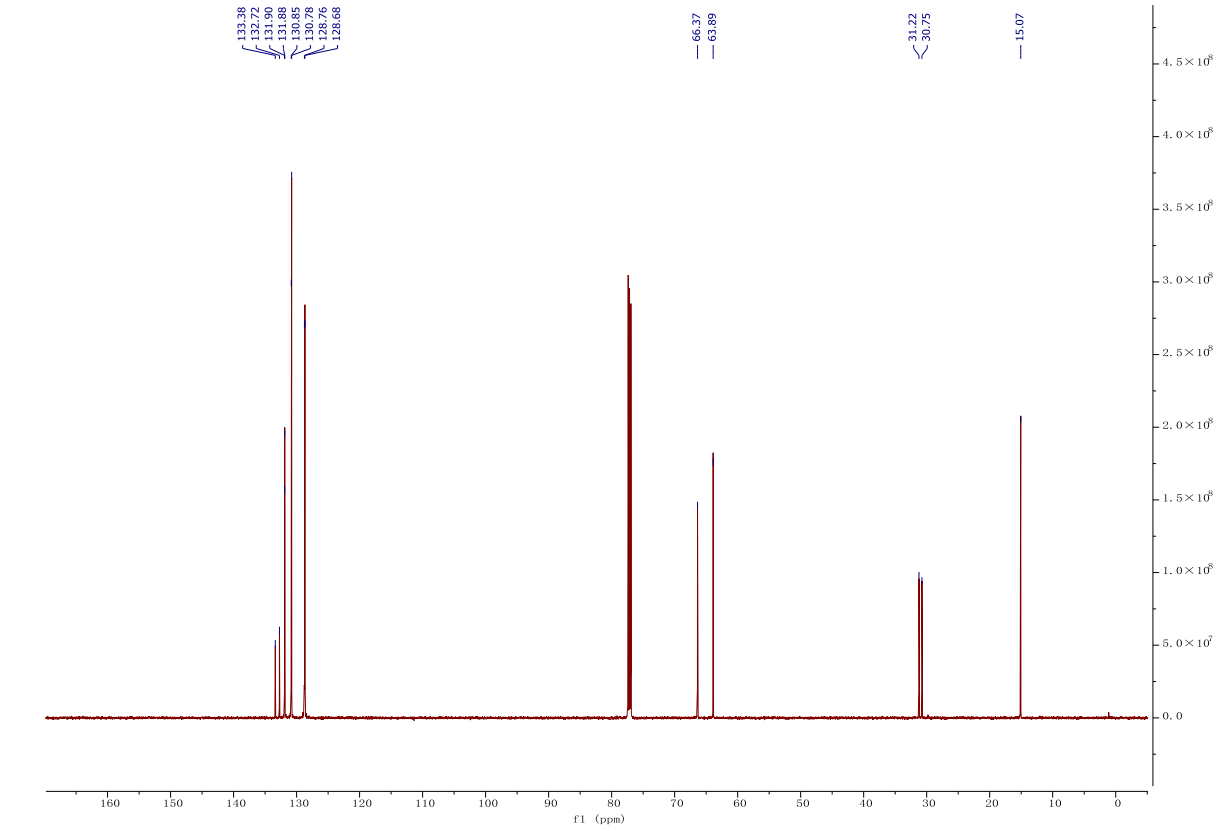
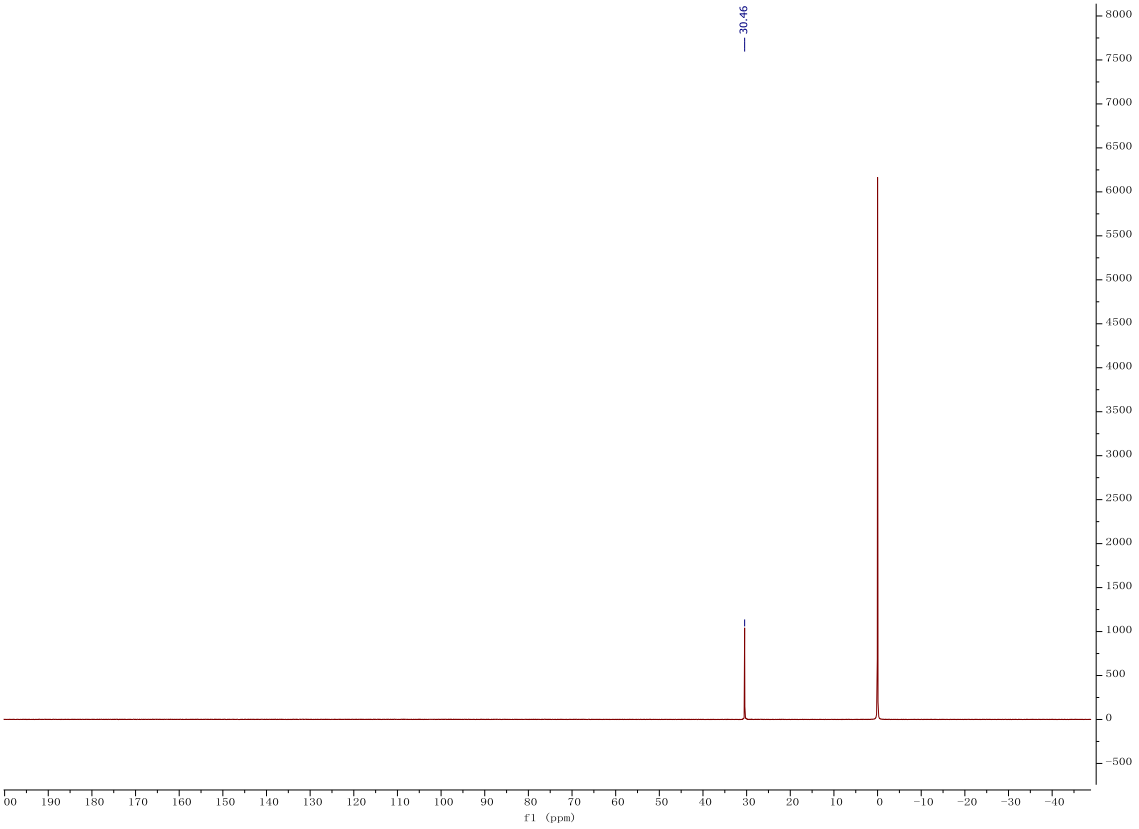
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


3aj
7.69
7.68
7.68
7.67
7.66
7.66
7.46
7.45
7.44
7.43
7.43
7.41
7.40
7.39
7.39
7.38
7.38
7.38
3.69
3.68
3.67
3.65
3.34
3.33
3.32
3.30
2.60
2.59
2.58
2.58
2.57
2.56
1.01
1.00
0.99
4.00
6.10
2.00
2.09
1.99
3.01
f1 (ppm)


133.38
132.72
131.90
131.88
130.85
130.78
128.76
128.68
66.37
63.89
31.22
30.75
15.07
f1 (ppm)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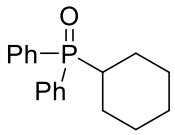
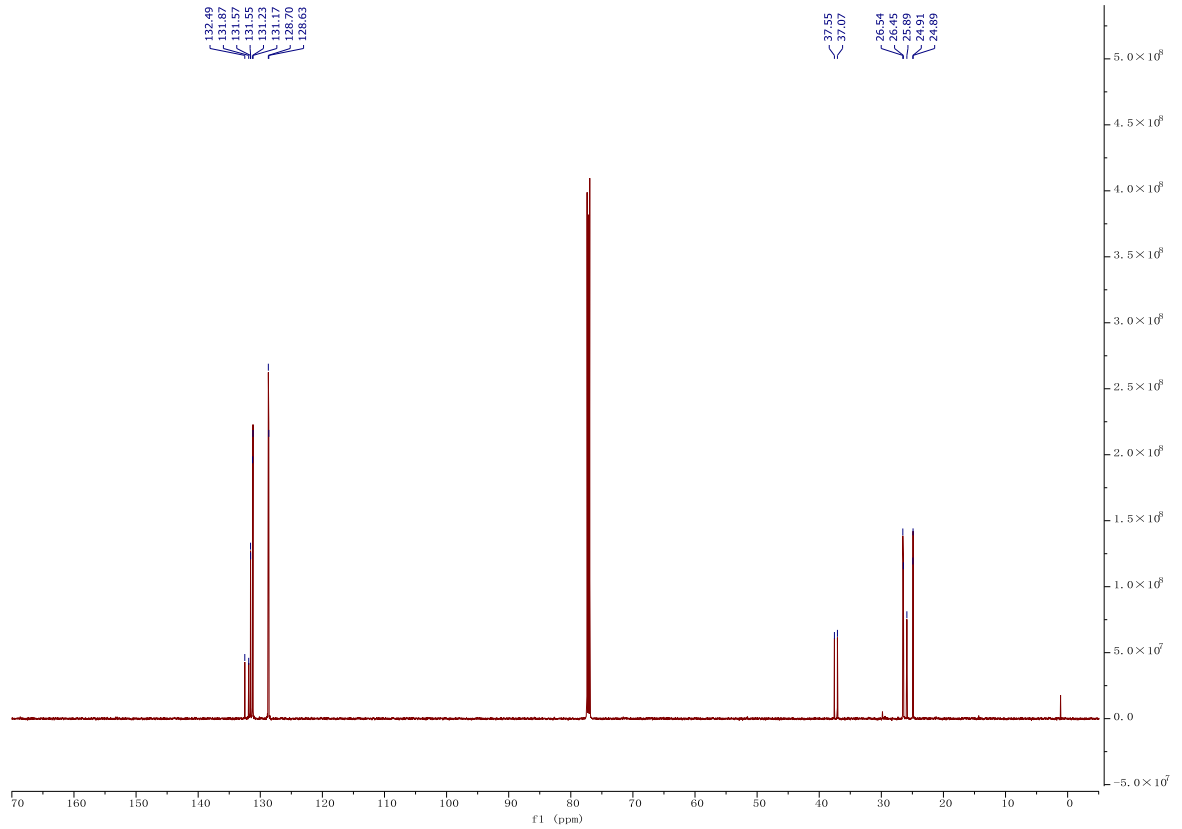
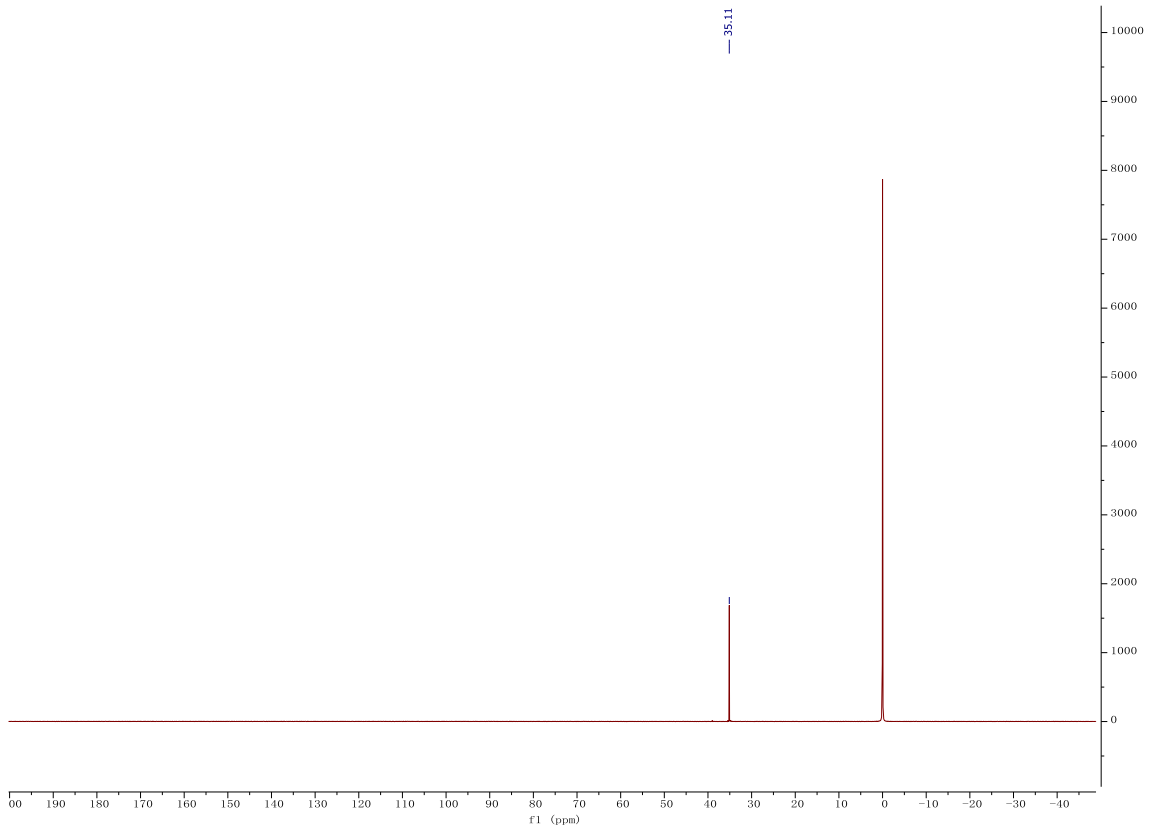
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

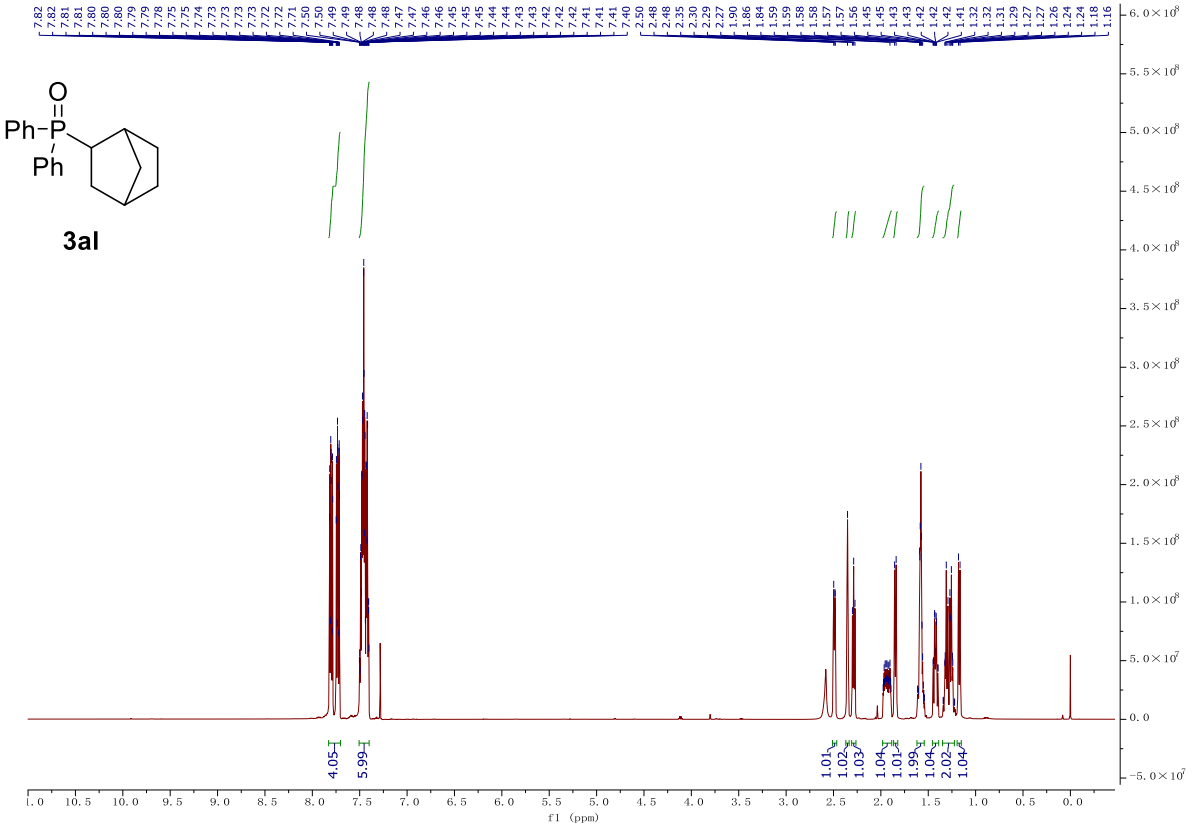

O
Ph
P
Ph

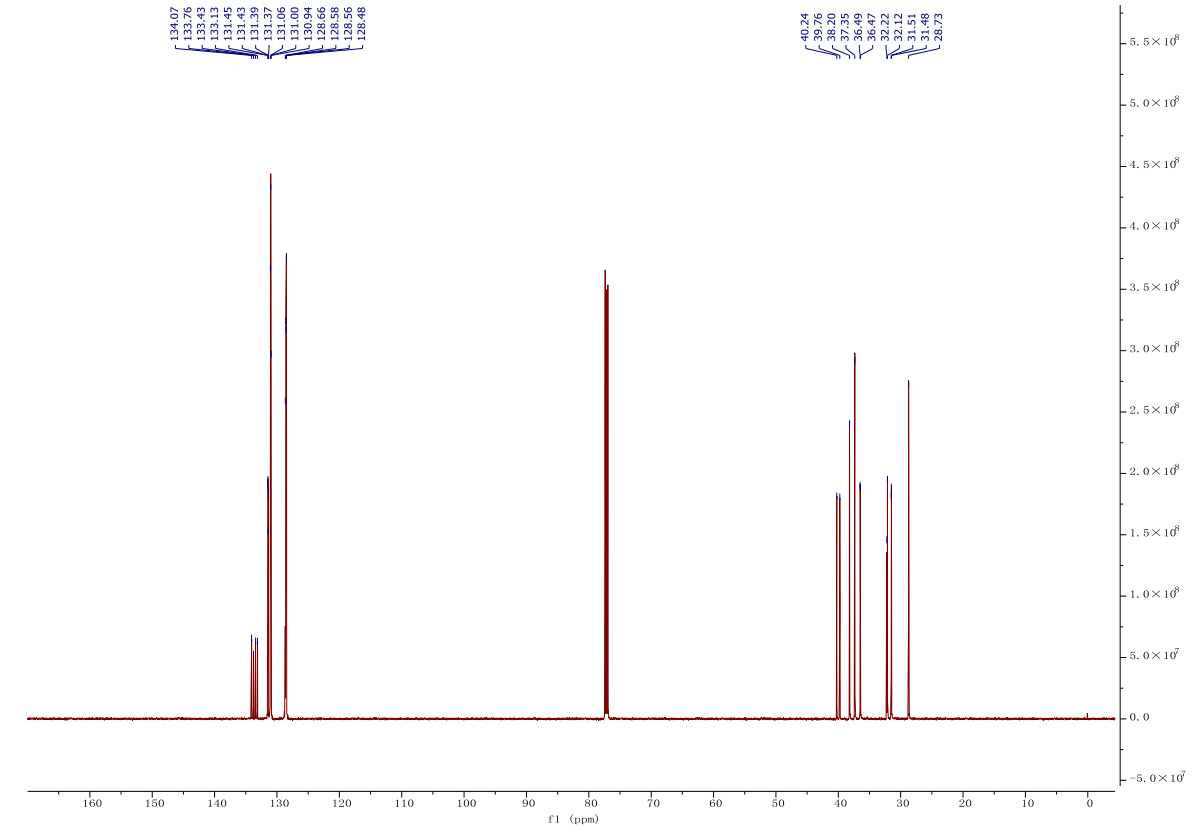
3ak

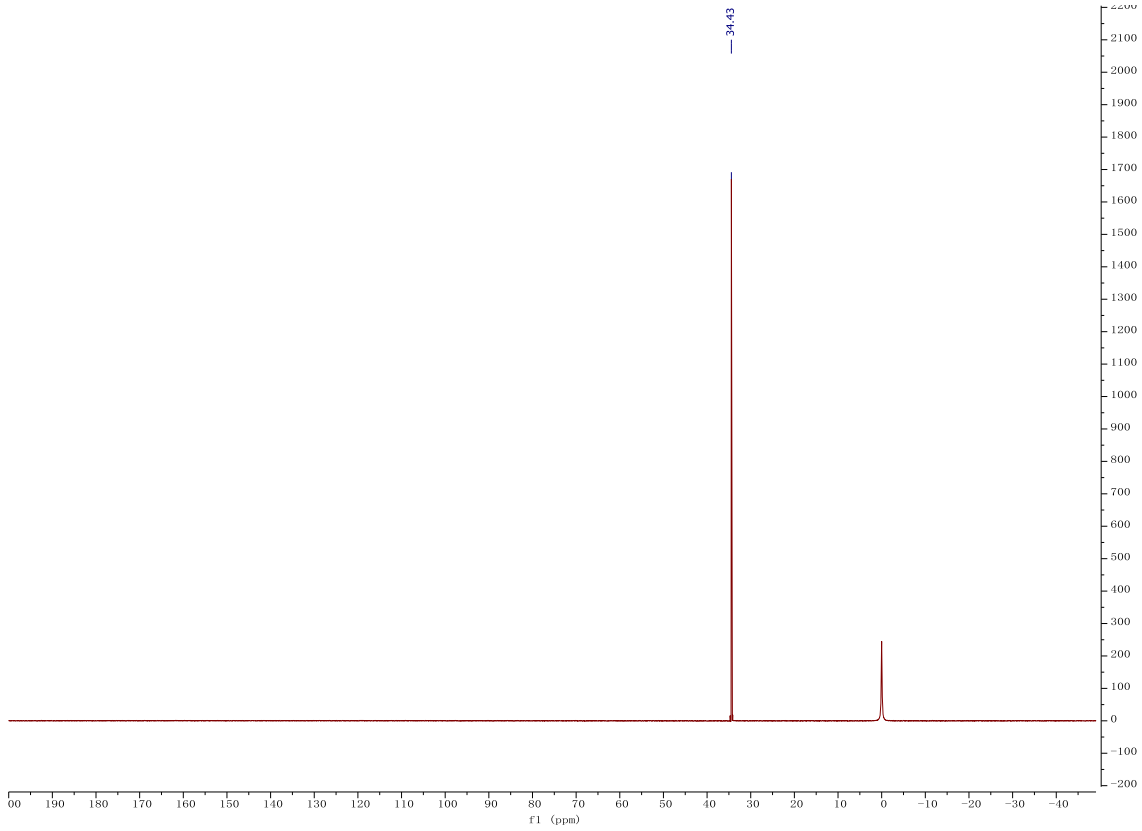
7.72 7.72 7.71 7.71 7.70 7.70 7.69 7.69 7.44 7.43 7.43 7.42 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.37
2.19 2.19 2.18 2.18 2.17 2.17 2.16 2.16 2.15 2.15 2.14 2.14 2.13
1.75 1.74 1.73 1.73 1.66 1.64 1.49 1.48 1.47 1.45 1.45 1.23 1.21 1.21 1.18 1.17 1.15
4.00
6.02
1.09
2.02
3.02
2.02
3.06
f1 (ppm)

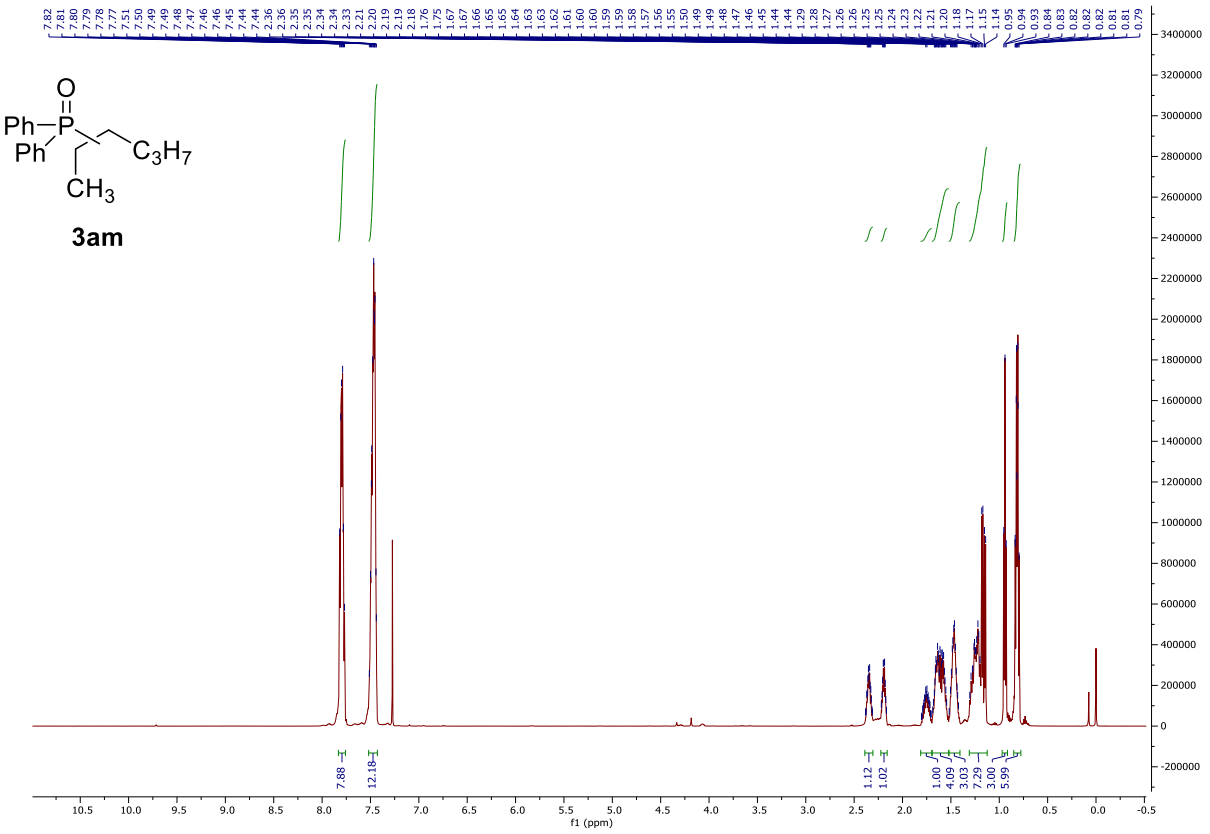

132.49 131.87 131.57 131.55 131.23 131.17 128.70 128.63
37.55 37.07
26.54 26.45 25.89 24.91 24.89
f1 (ppm)

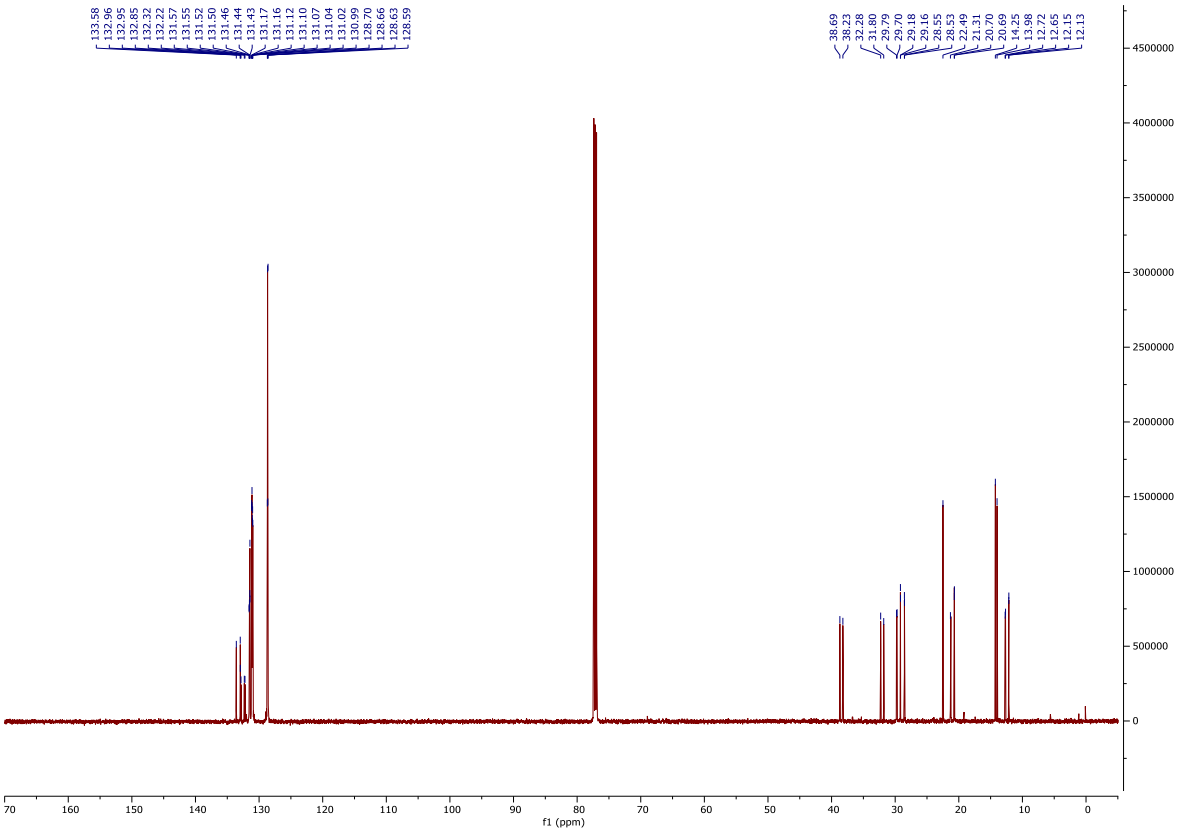

35.11
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)

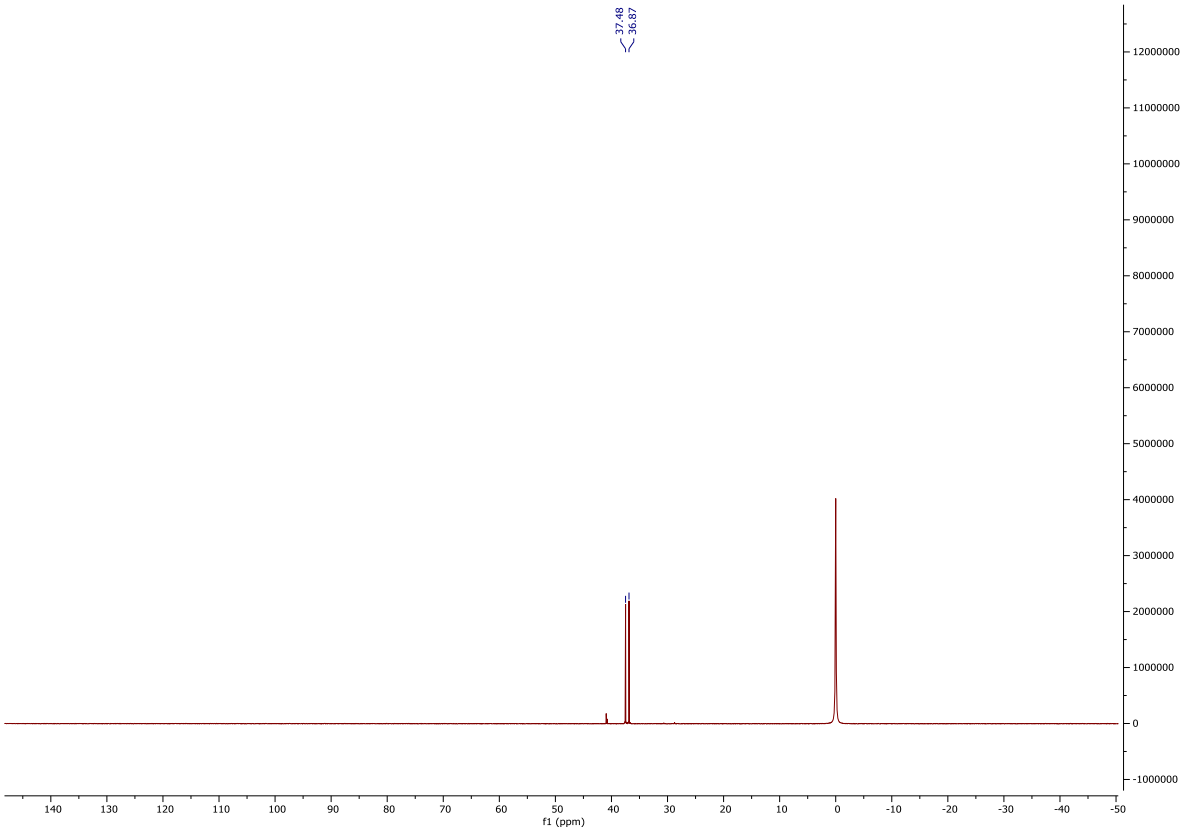

3al
f1 (ppm)


f1 (ppm)


34.43
f1 (ppm)


Ph
P
O
Ph
C_3H_7
CH_3
3am
f1 (ppm)


f1 (ppm)


37.48
36.87
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7000000
6000000
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4000000
3000000
2000000
1000000
0
-1000000
140
130
120
110
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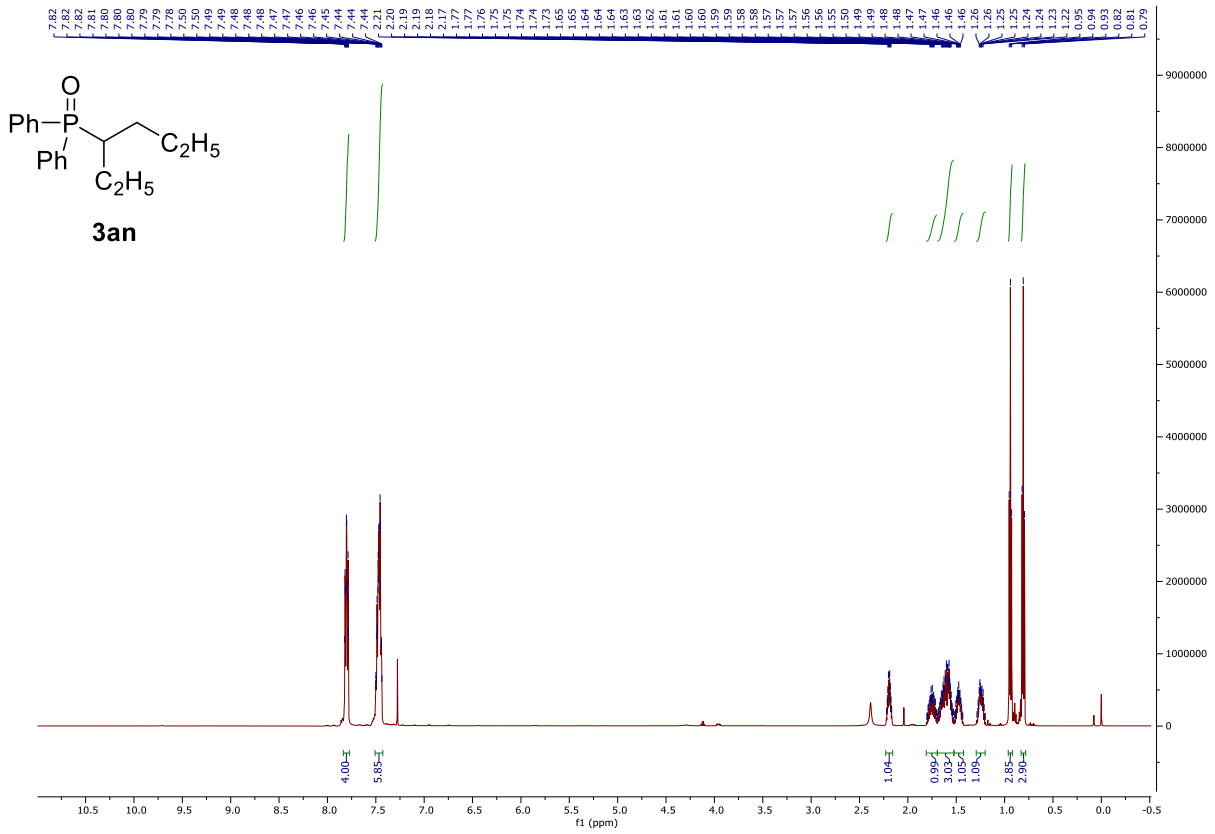
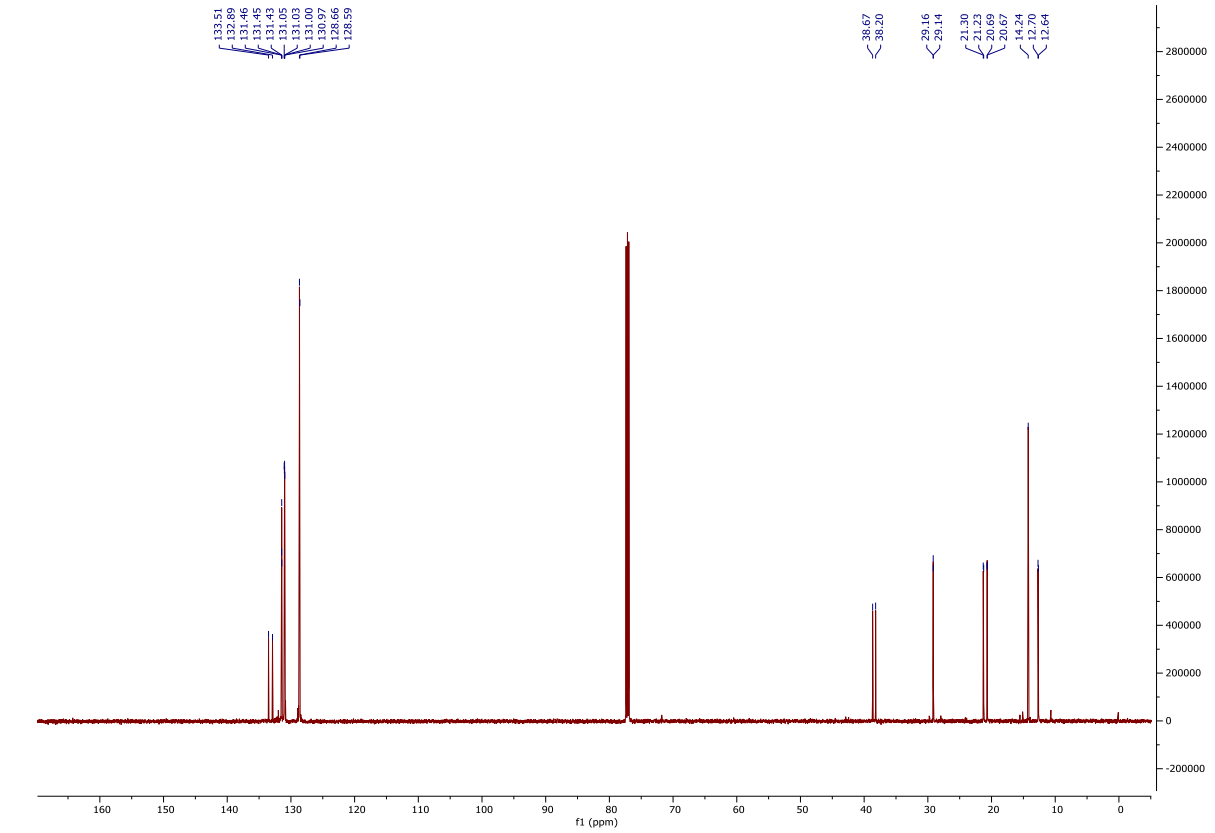
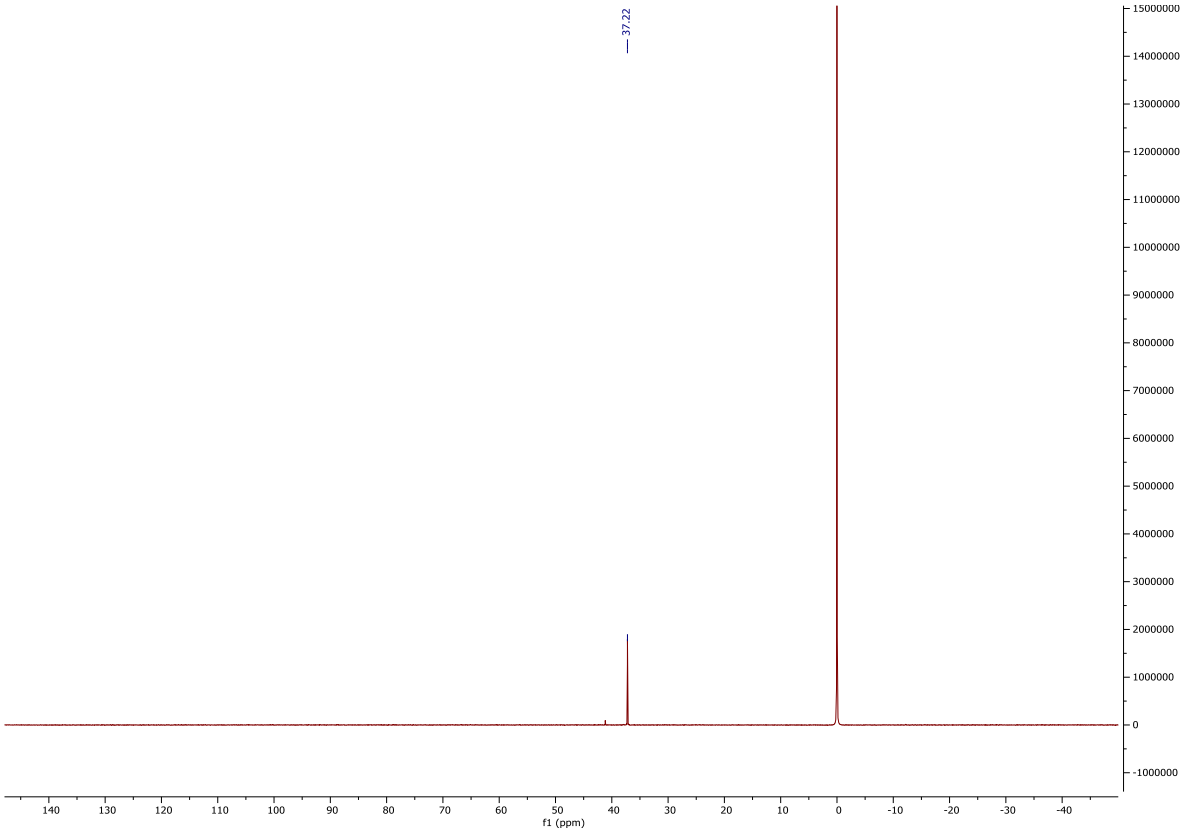
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
f1 (ppm)


3an
f1 (ppm)


f1 (ppm)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7000000
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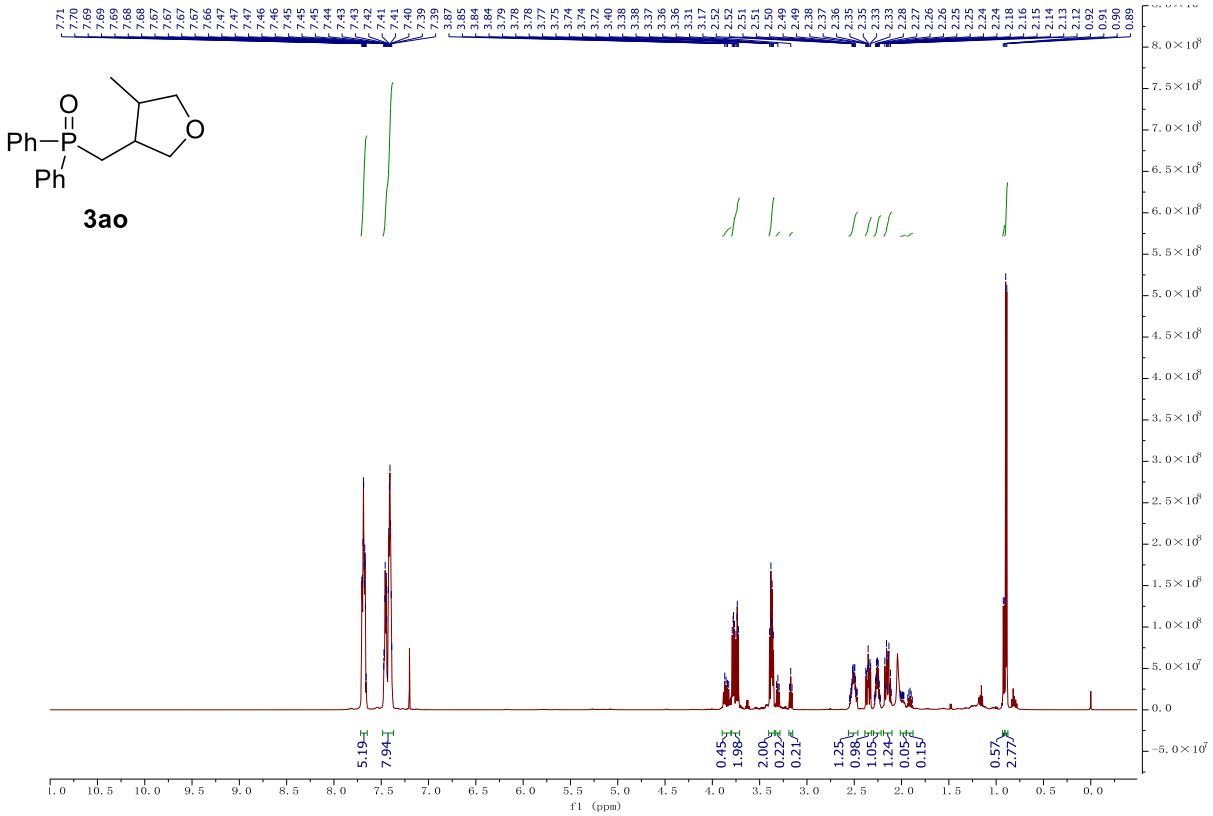
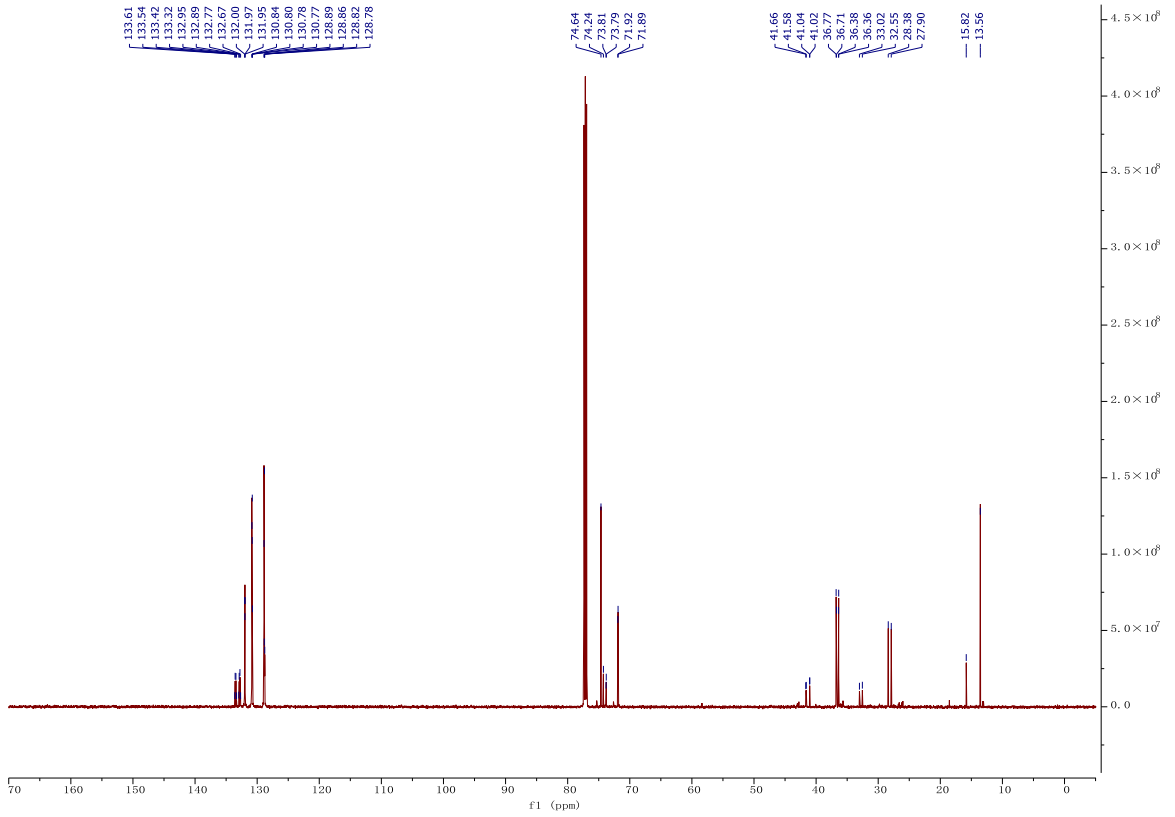
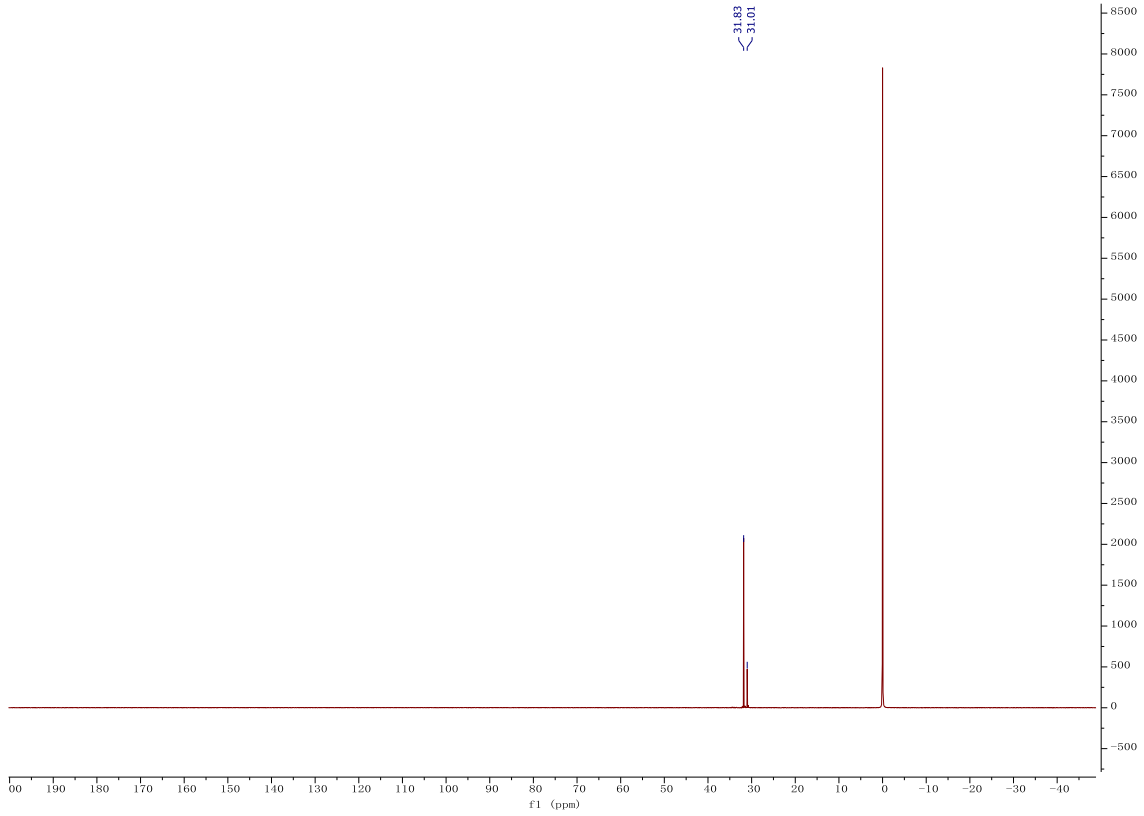
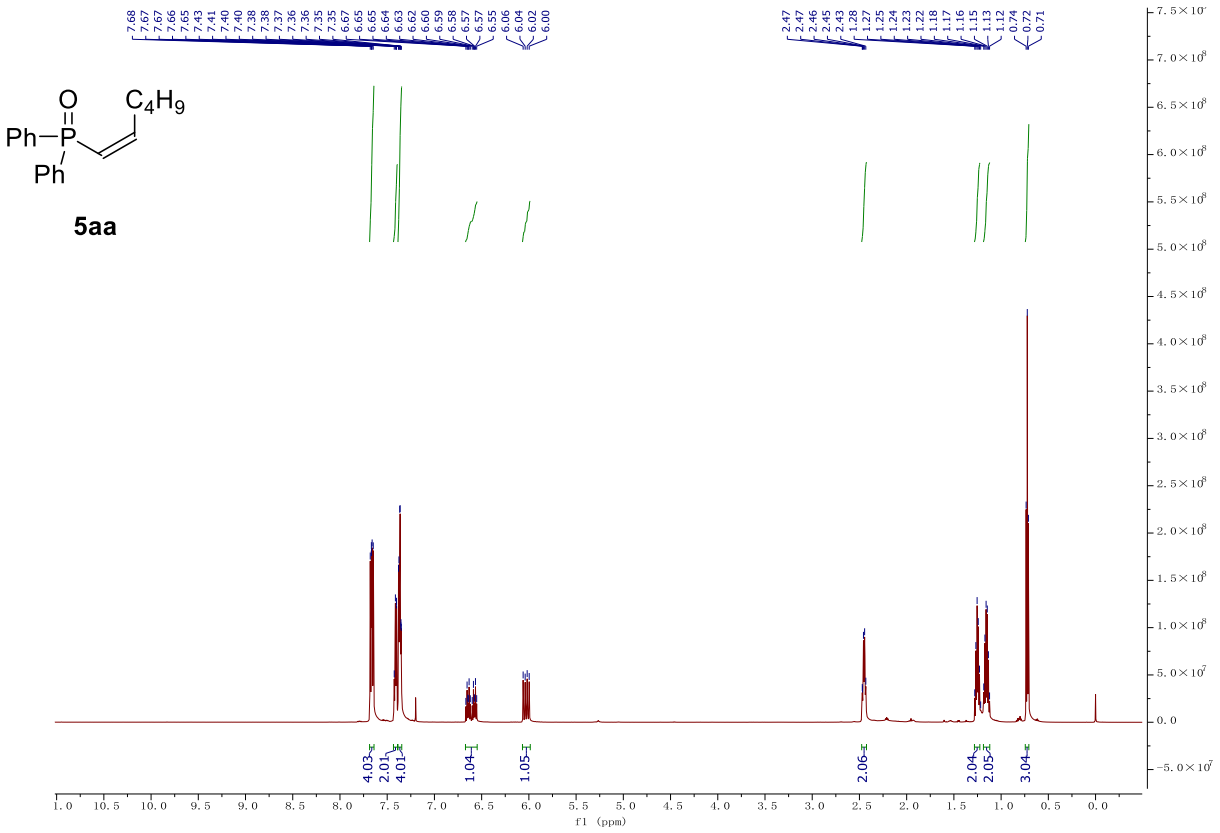
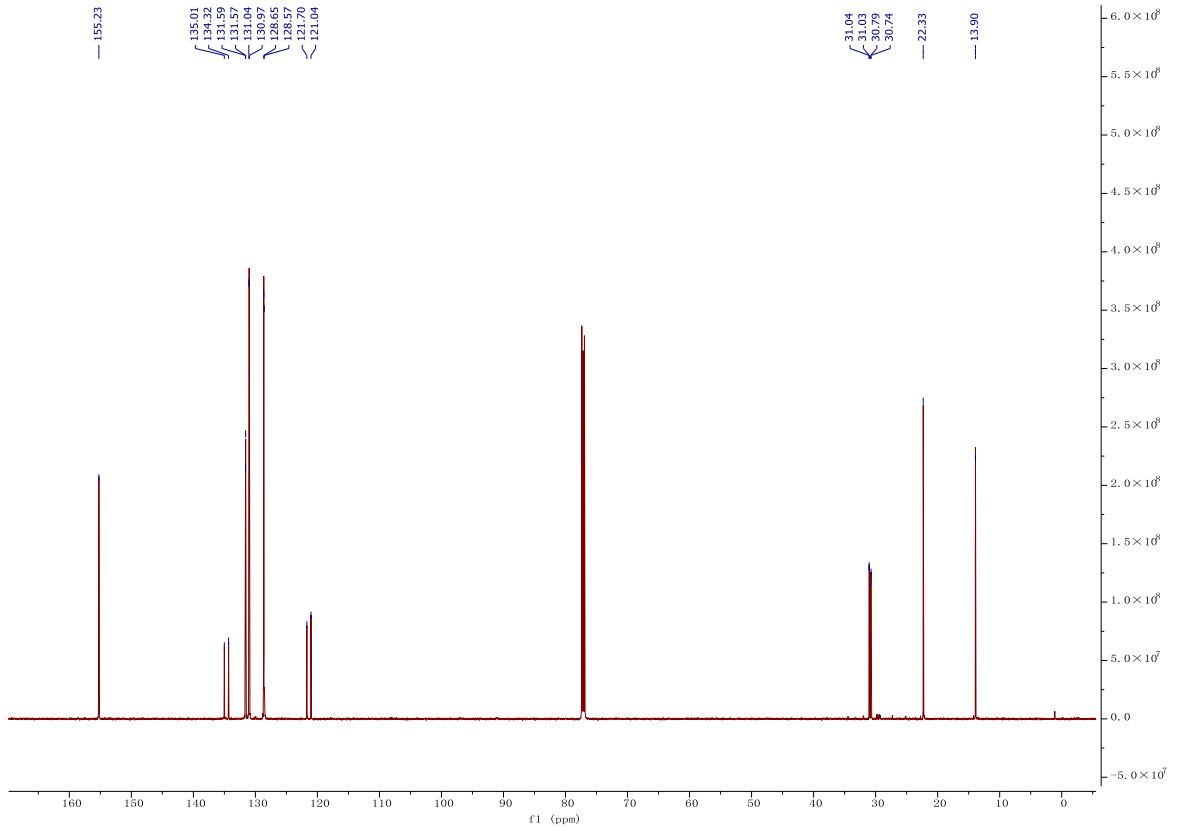
5000000
4000000
3000000
2000000
1000000
0
-1000000
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

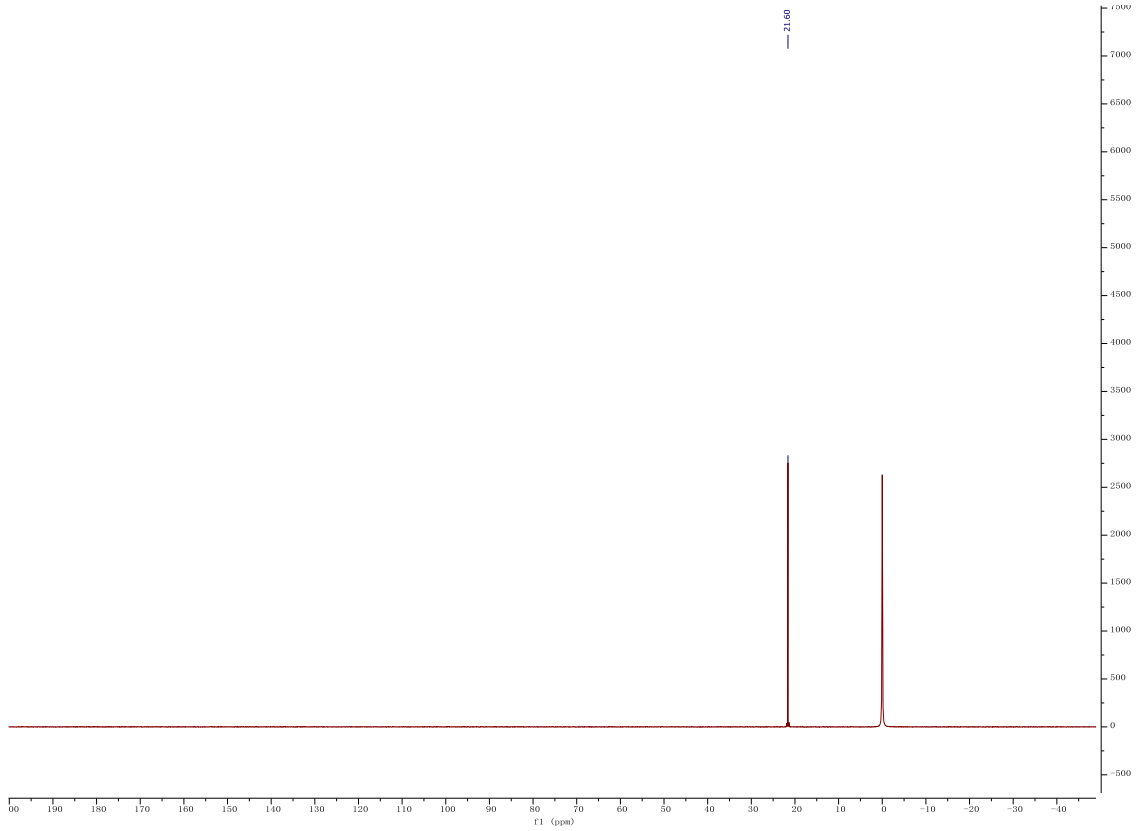

Ph
P
O
O
Ph
3ao
f1 (ppm)


f1 (ppm)


31.83
31.01
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)


O
C4H9
Ph—P
Ph
5aa
f1 (ppm)


f1 (ppm)


21.60
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6500
6000
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5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
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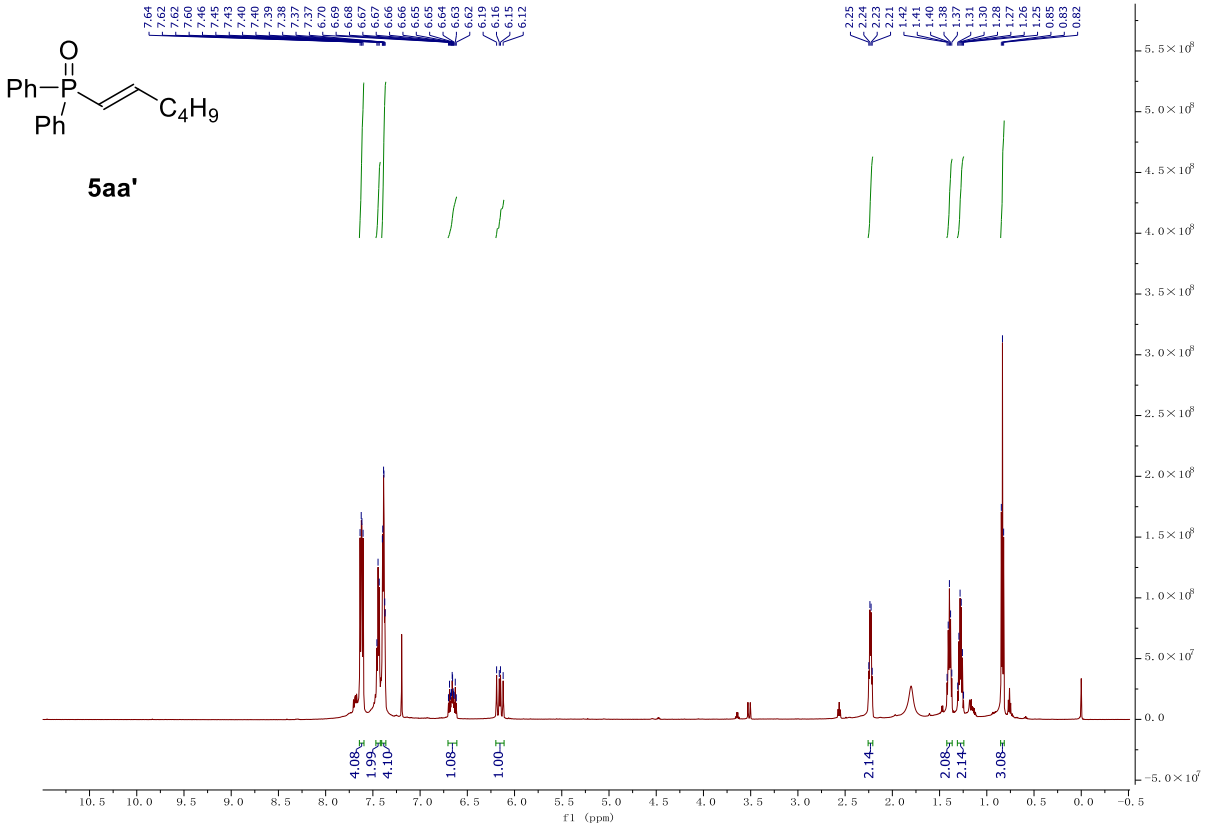
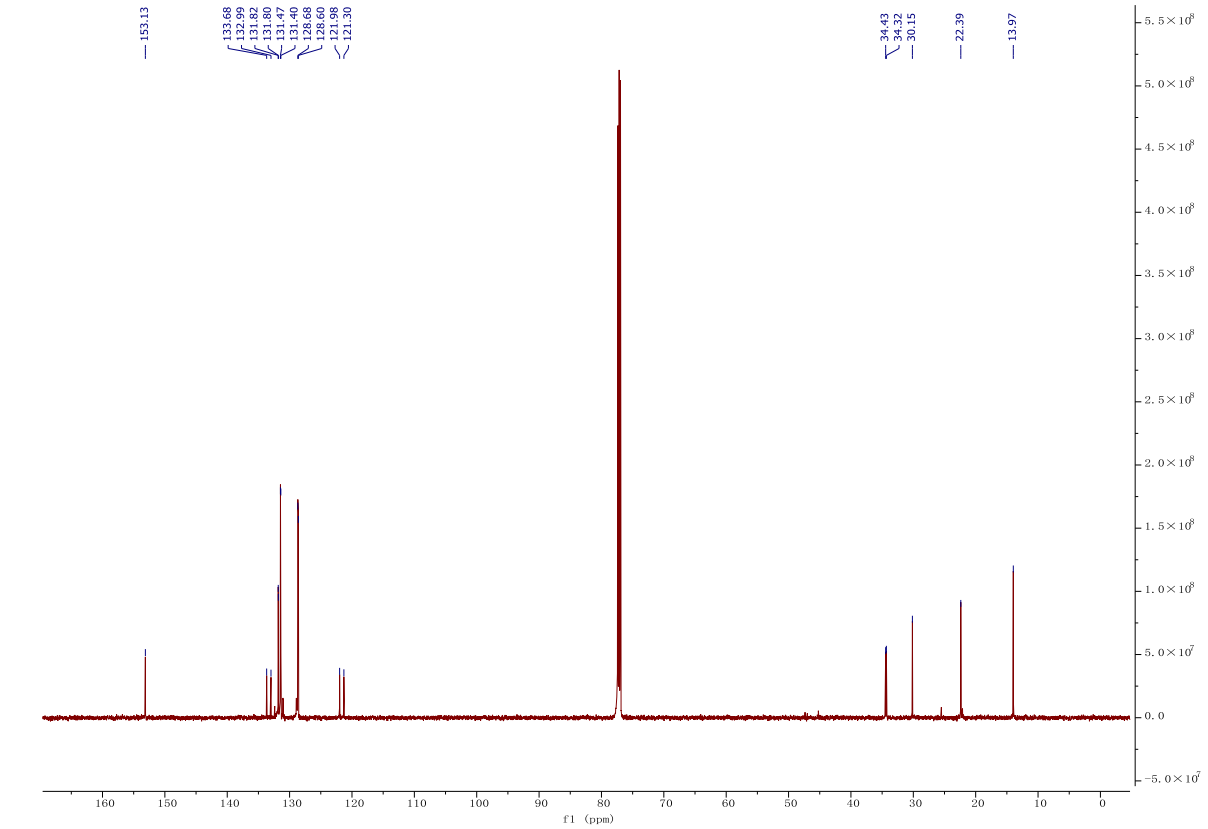
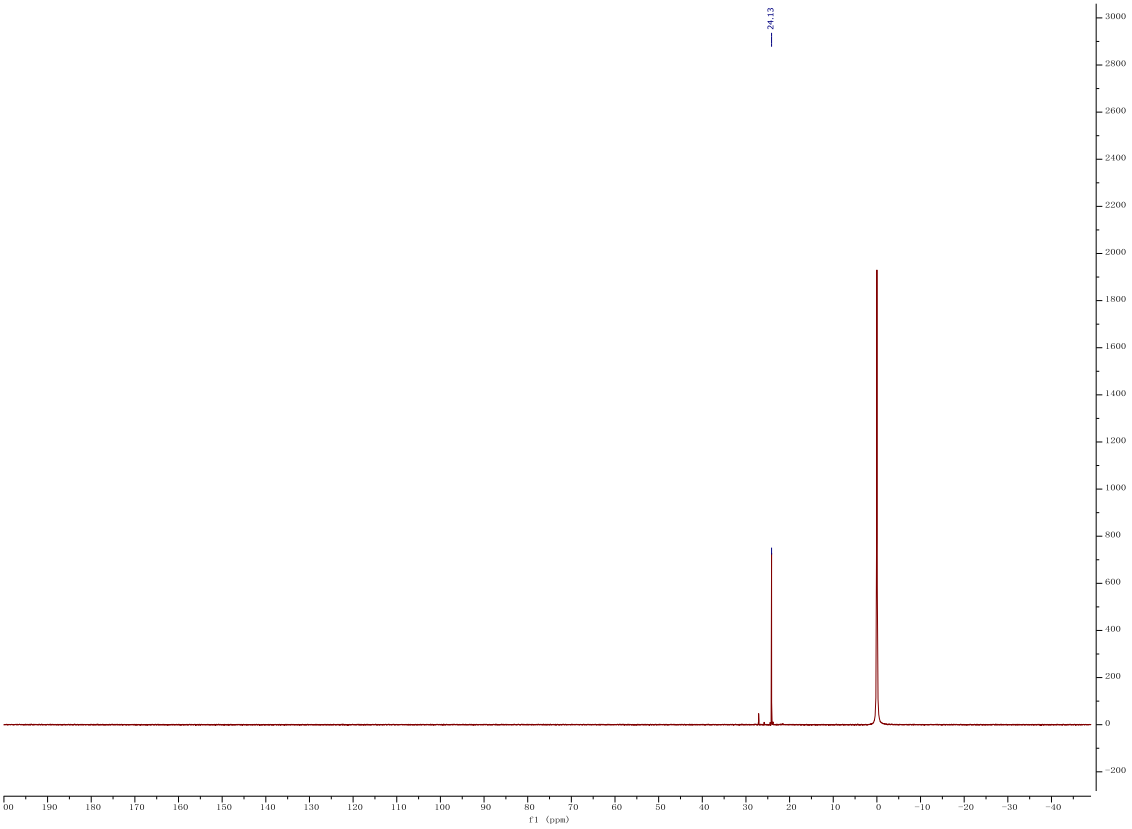
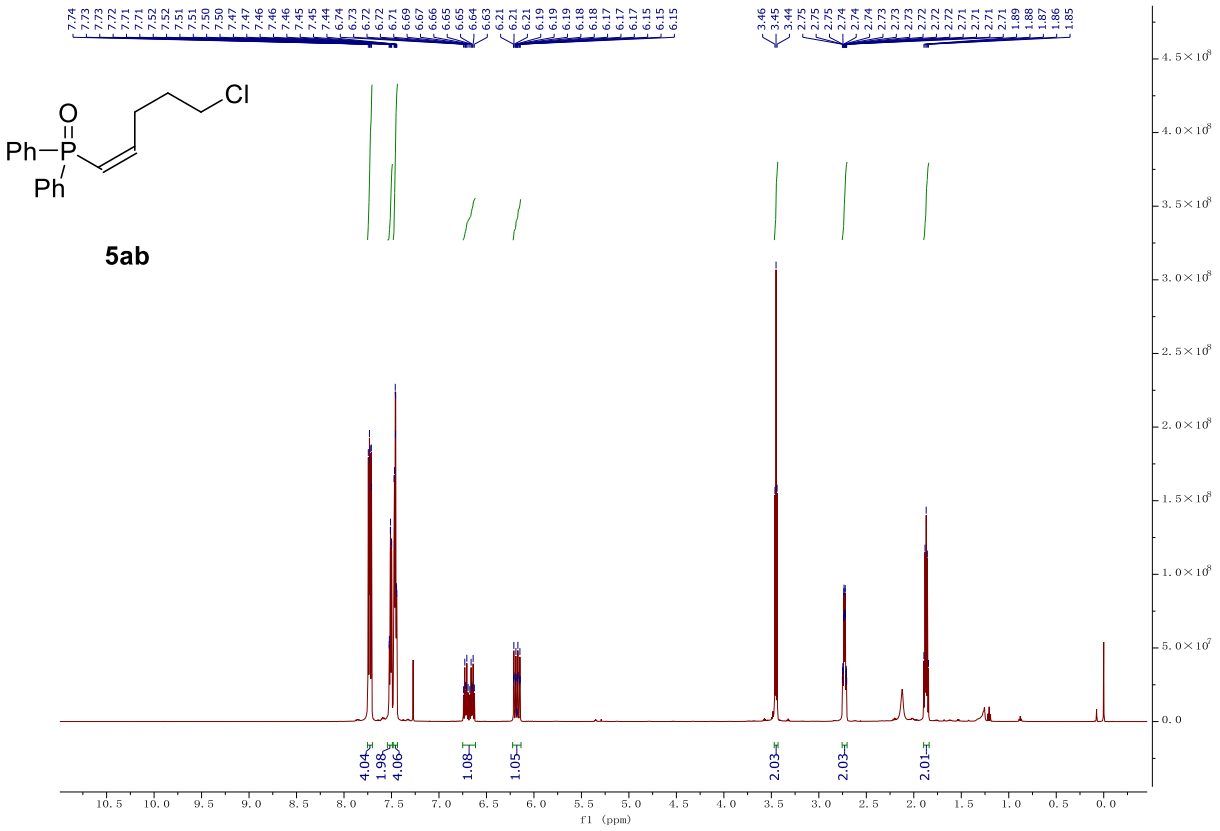
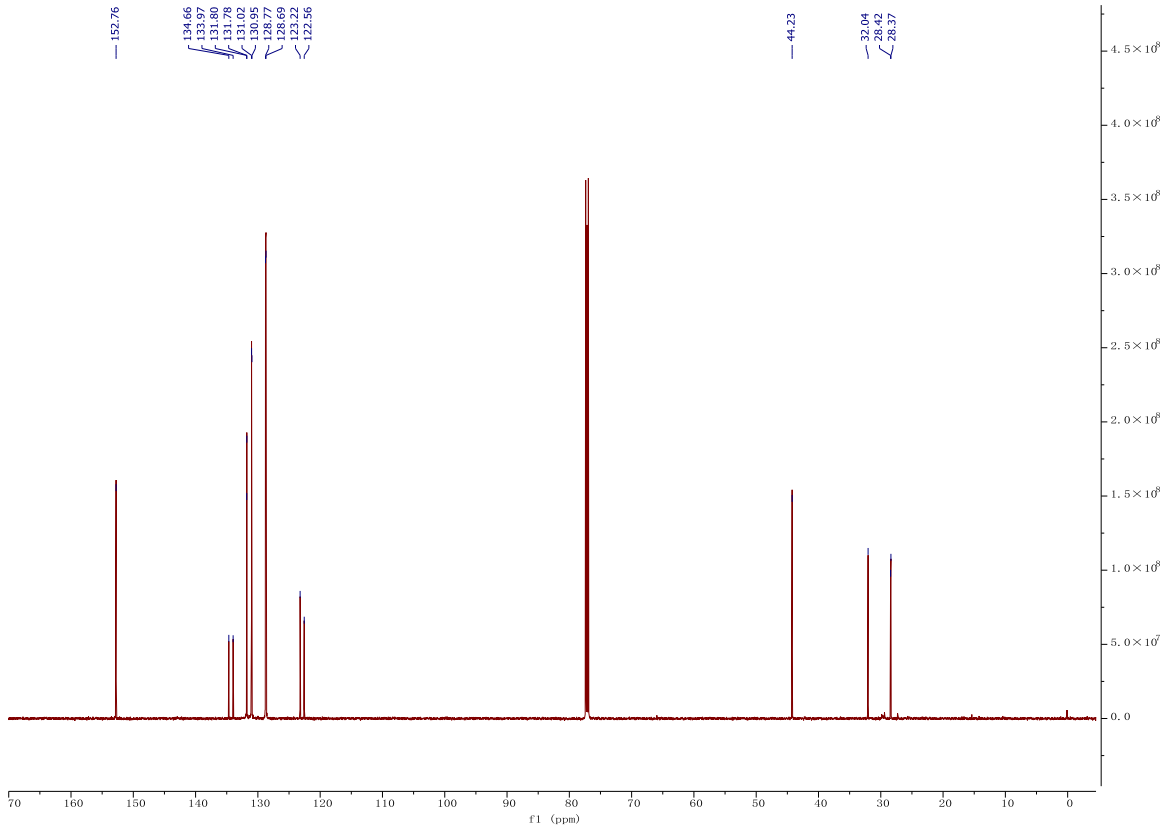
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

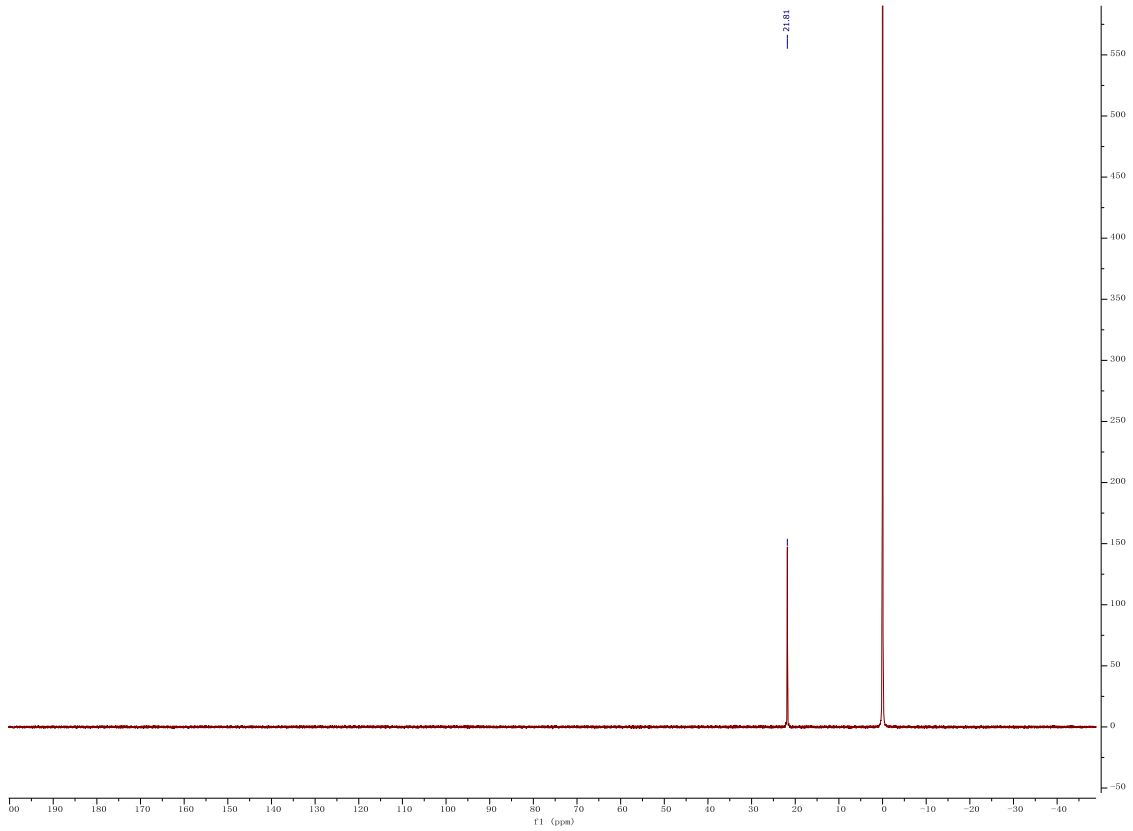

Ph
P
O
Ph
C4H9
5aa'
f1 (ppm)

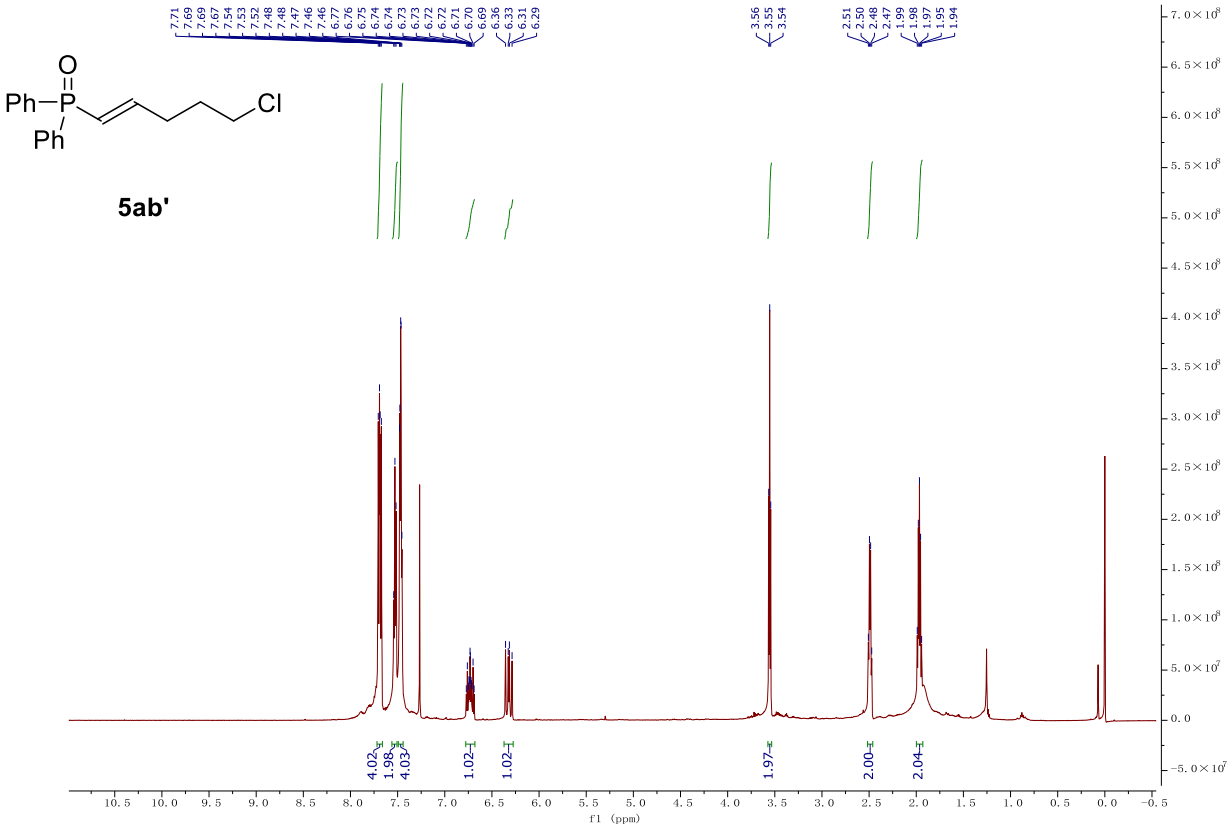

f1 (ppm)

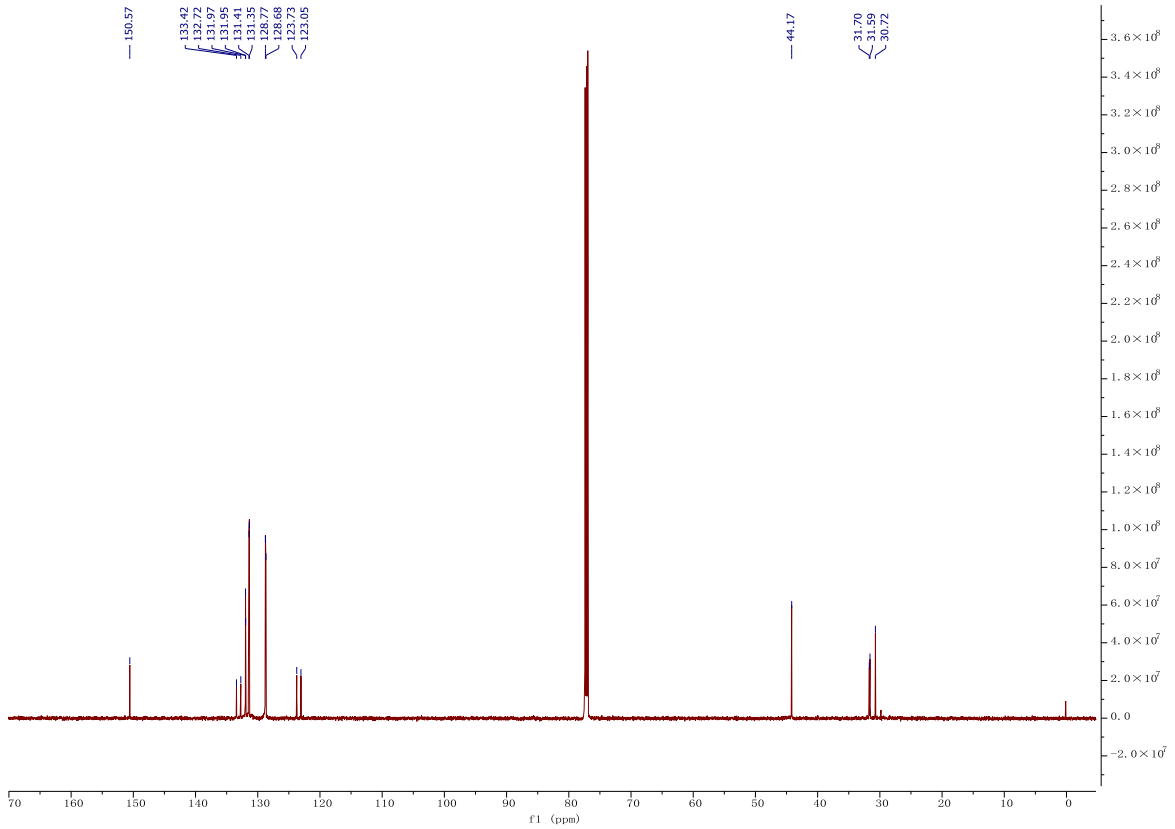

24.13
f1 (ppm)

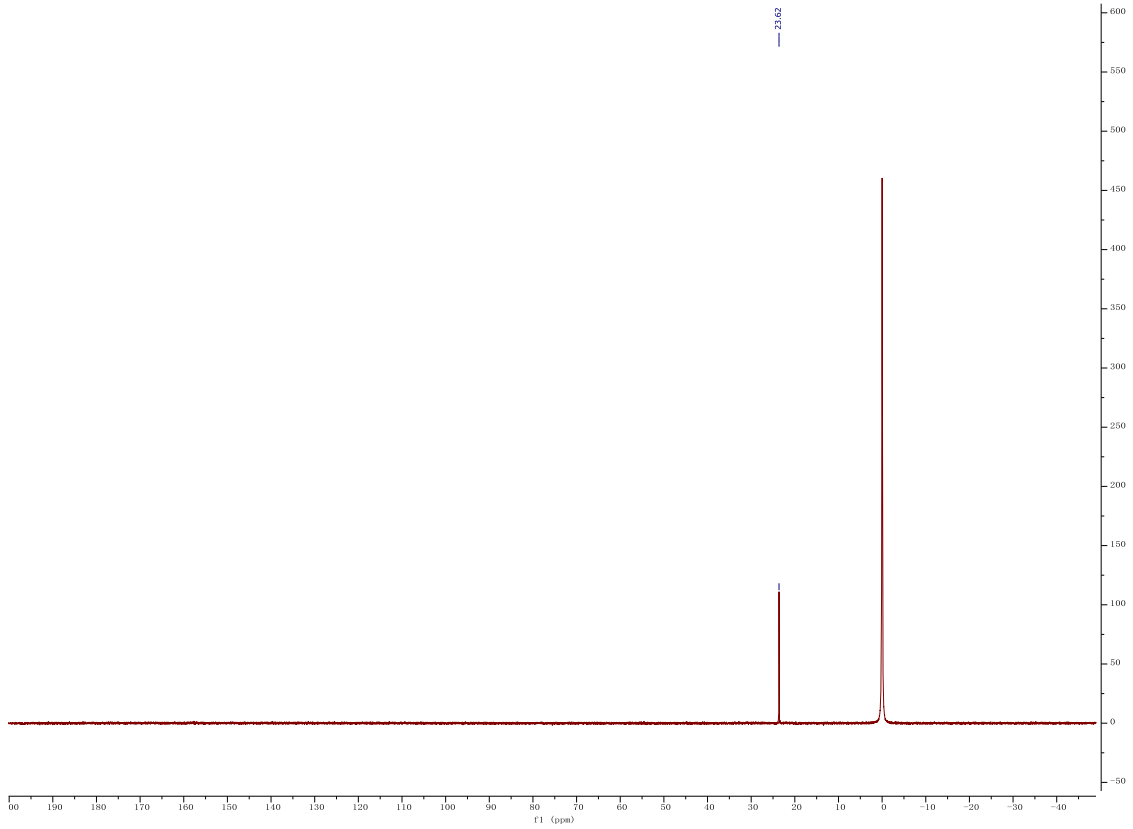

Cl
O
Ph
P
Ph
5ab
f1 (ppm)

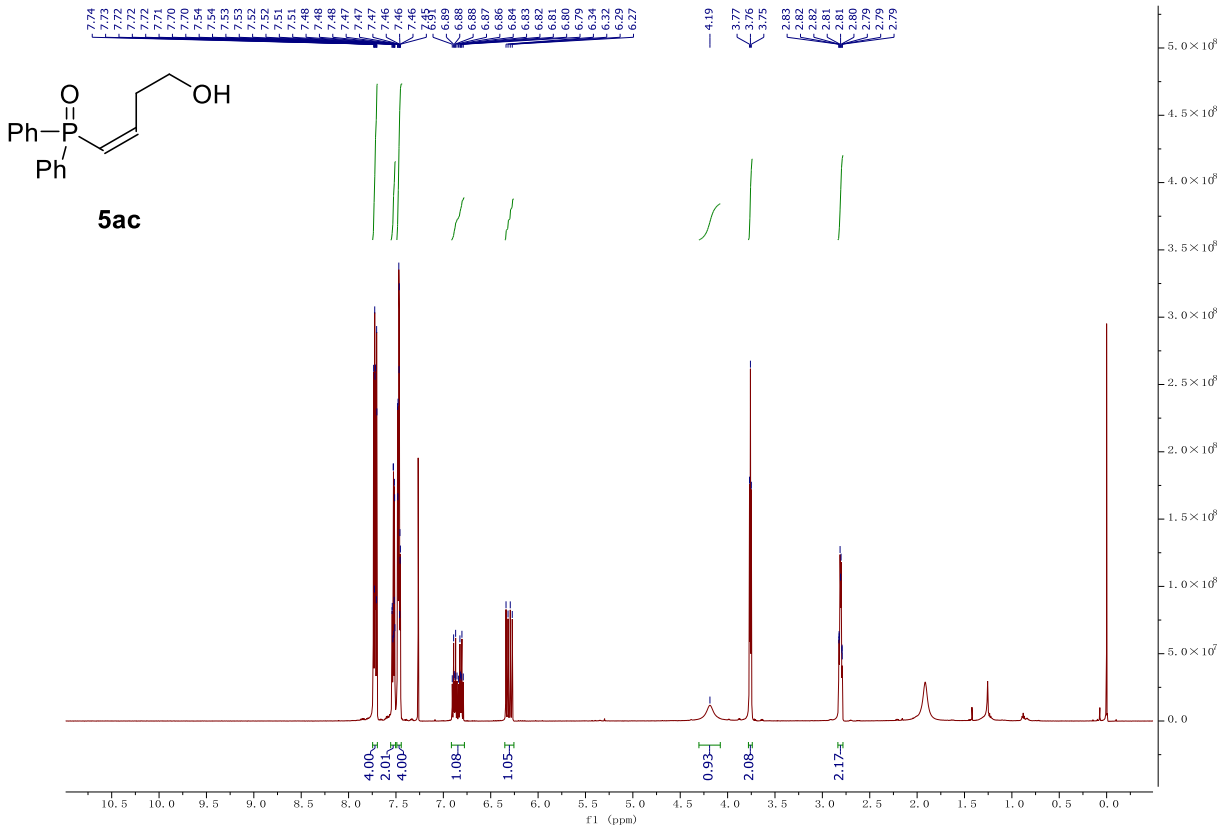

152.76
134.66
133.97
131.80
131.78
131.02
130.95
128.77
128.69
123.22
122.56
44.23
32.04
28.42
28.37
f1 (ppm)

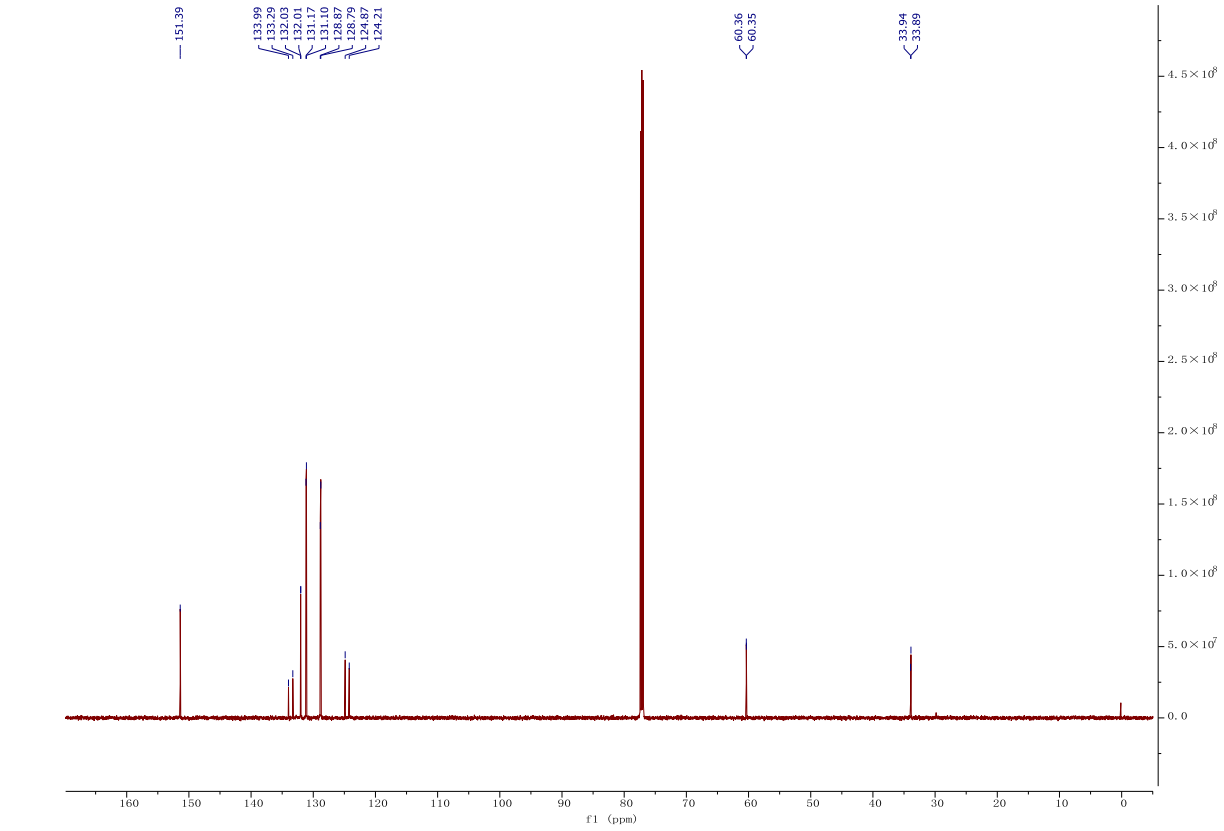

21.81
550
500
450
400
350
300
250
200
150
100
50
0
-50
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

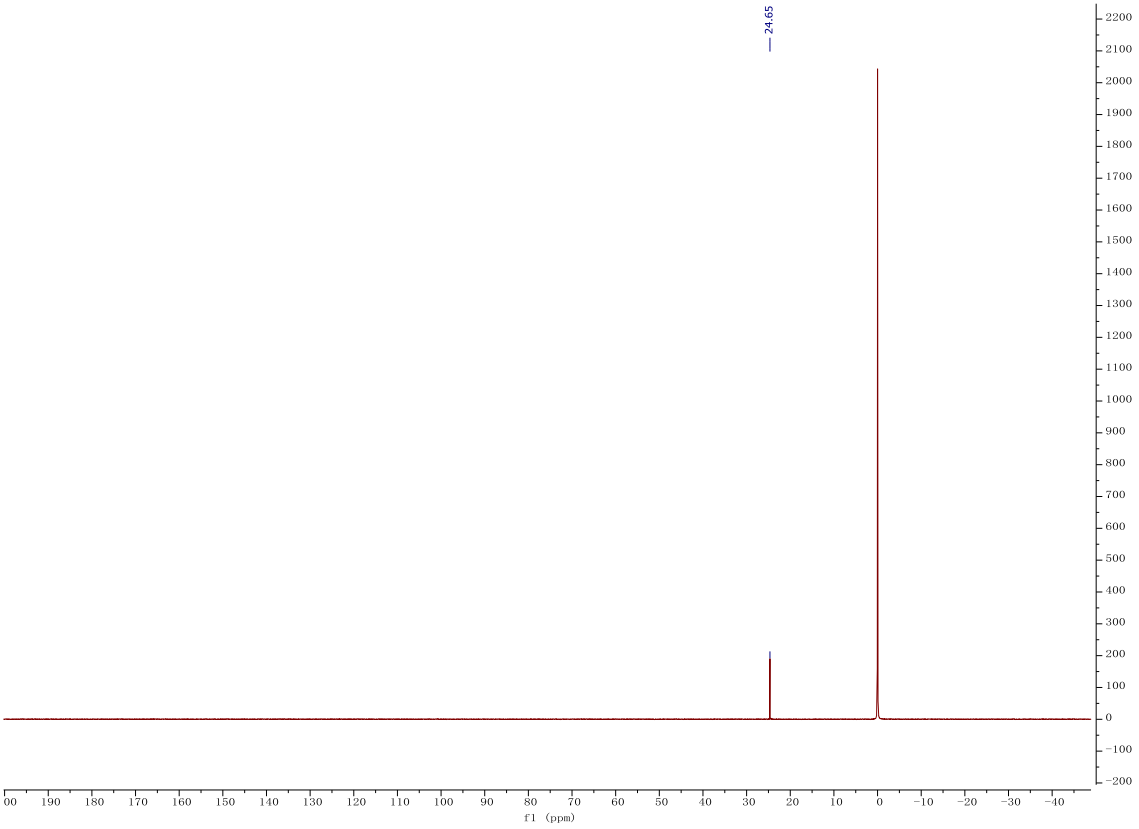

5ab'
7.71 7.69 7.69 7.67 7.54 7.53 7.52 7.48 7.48 7.47 7.46 7.46 6.77 6.76 6.75 6.74 6.74 6.73 6.73 6.72 6.72 6.71 6.70 6.69 6.36 6.33 6.31 6.29
3.56 3.55 3.54
2.51 2.50 2.48 2.47 1.99 1.98 1.97 1.95 1.94
4.02 1.98 4.03 1.02 1.02 1.97 2.00 2.04
f1 (ppm)

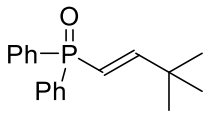

150.57
133.42 132.72 131.97 131.95 131.41 131.35 128.77 128.68 123.73 123.05
44.17
31.70 31.59 30.72
f1 (ppm)


23.62
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


7.74 7.73 7.72 7.72 7.72 7.71 7.70 7.70 7.54 7.54 7.53 7.53 7.52 7.52 7.51 7.51 7.48 7.48 7.48 7.47 7.47 7.47 7.46 7.46 7.46 7.45 6.91 6.89 6.88 6.88 6.87 6.86 6.84 6.83 6.82 6.81 6.80 6.79 6.34 6.32 6.29 6.27
4.19
3.77 3.76 3.75
2.83 2.82 2.82 2.81 2.81 2.80 2.79 2.79 2.79
O
Ph—P
Ph
OH
5ac
4.00 2.01 4.00 1.08 1.05 0.93 2.08 2.17
f1 (ppm)

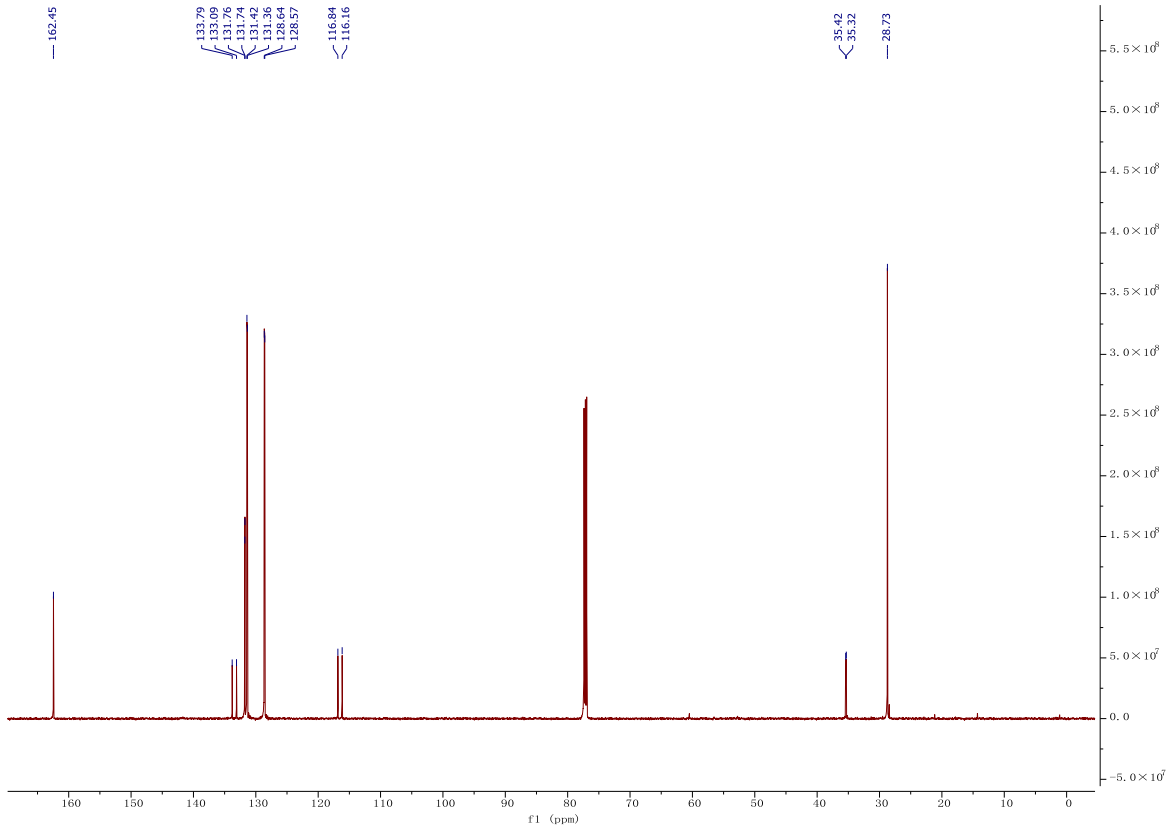

151.39
133.99 133.29 132.03 132.01 131.17 131.10 128.87 128.79 124.87 124.21
60.36 60.35
33.94 33.89
f1 (ppm)

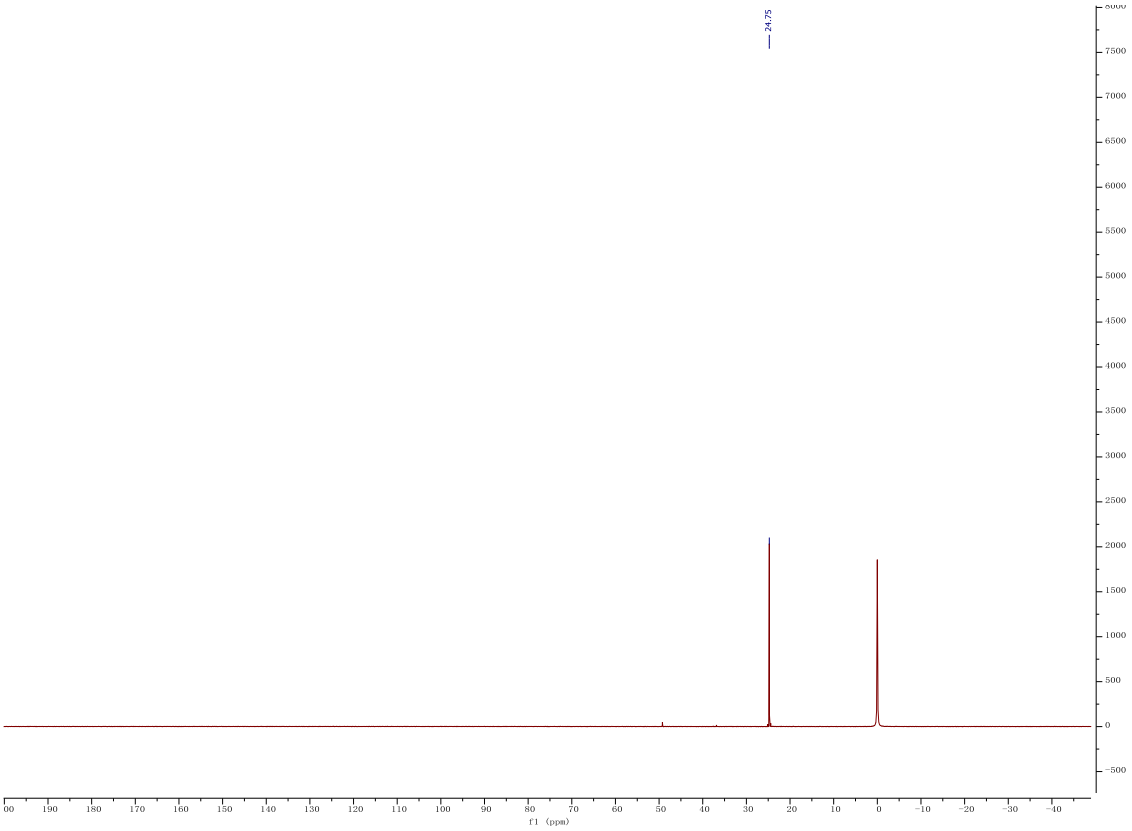

24.65
f1 (ppm)

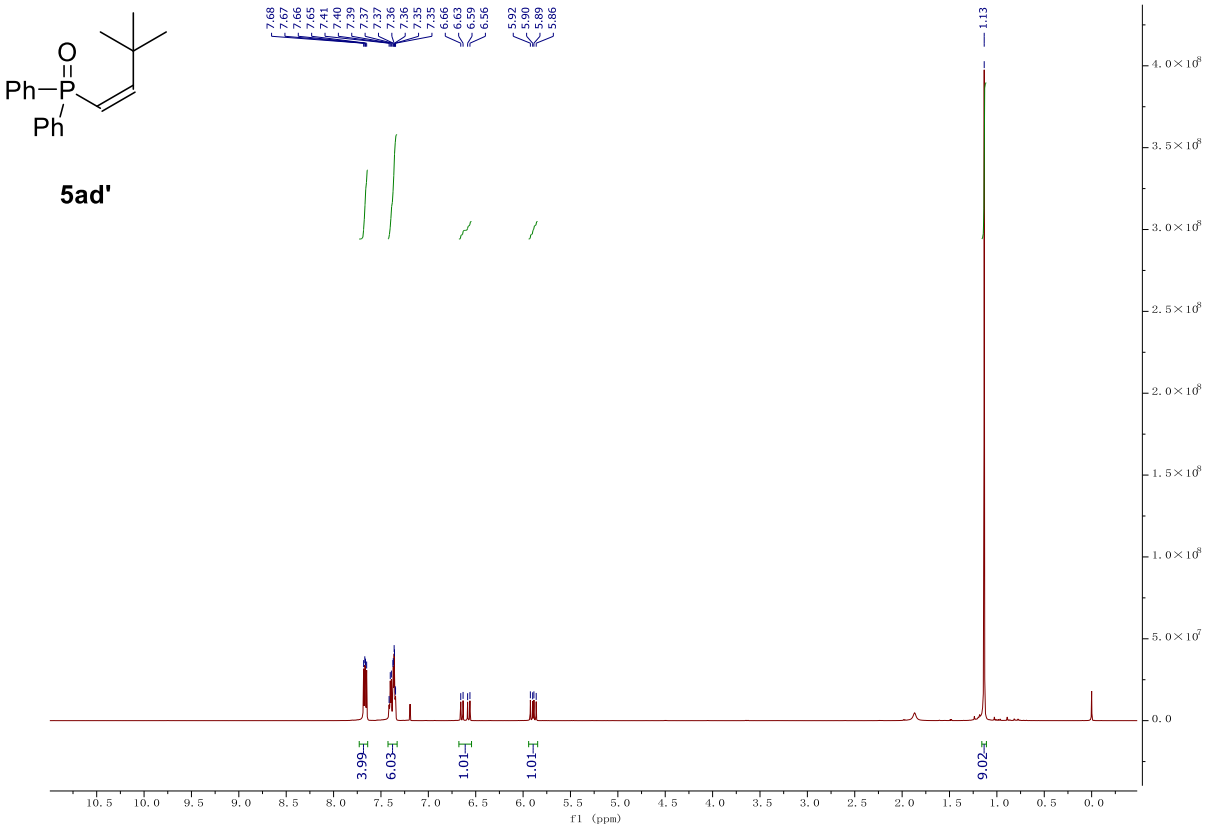

O
Ph
P
Ph

5ad

7.62
7.61
7.60
7.59
7.45
7.44
7.43
7.39
7.39
7.38
7.38
7.37
7.37
6.73
6.70
6.69
6.66
6.07
6.04
6.03
6.00
1.03
4.00
2.02
4.05
1.00
1.00
9.03
f1 (ppm)


162.45
133.79
133.09
131.76
131.74
131.42
131.36
128.64
128.57
116.84
116.16
35.42
35.32
28.73
f1 (ppm)


24.75
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)


5ad'
7.68
7.67
7.66
7.65
7.41
7.40
7.39
7.37
7.37
7.36
7.36
7.35
7.35
6.66
6.63
6.59
6.56
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5.89
5.86
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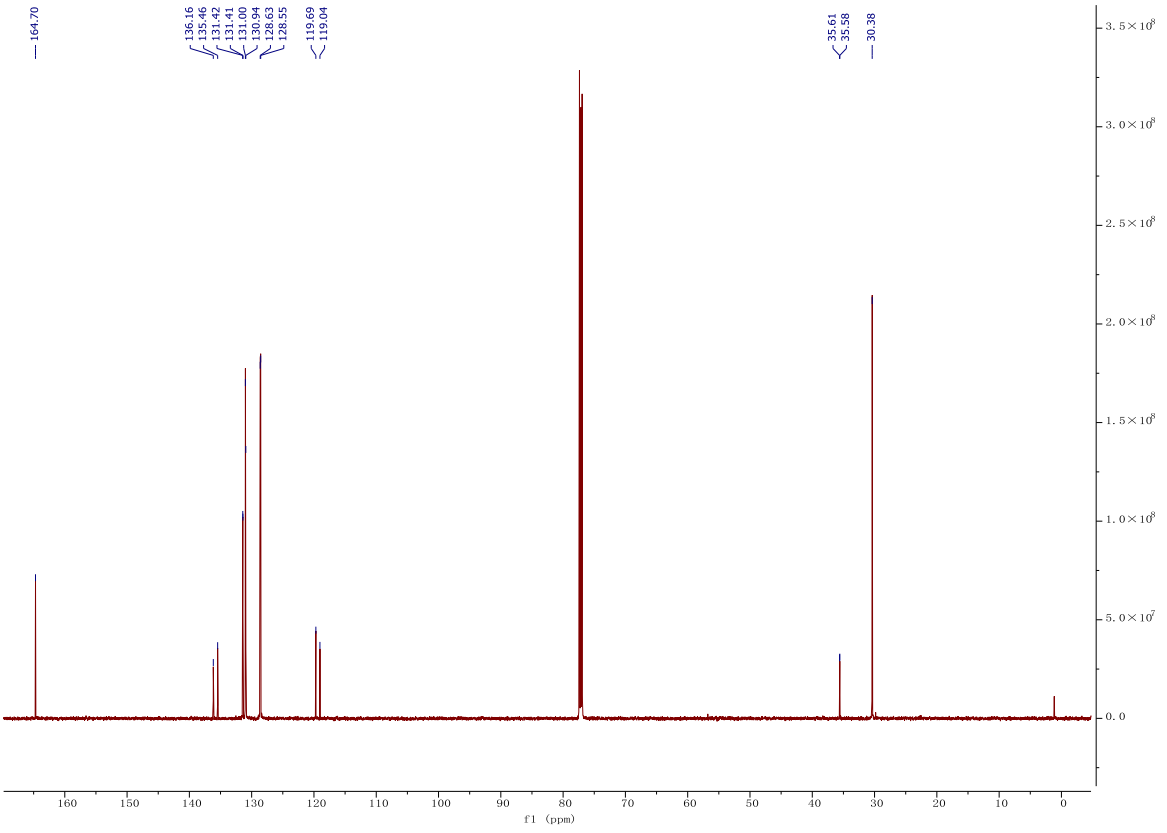
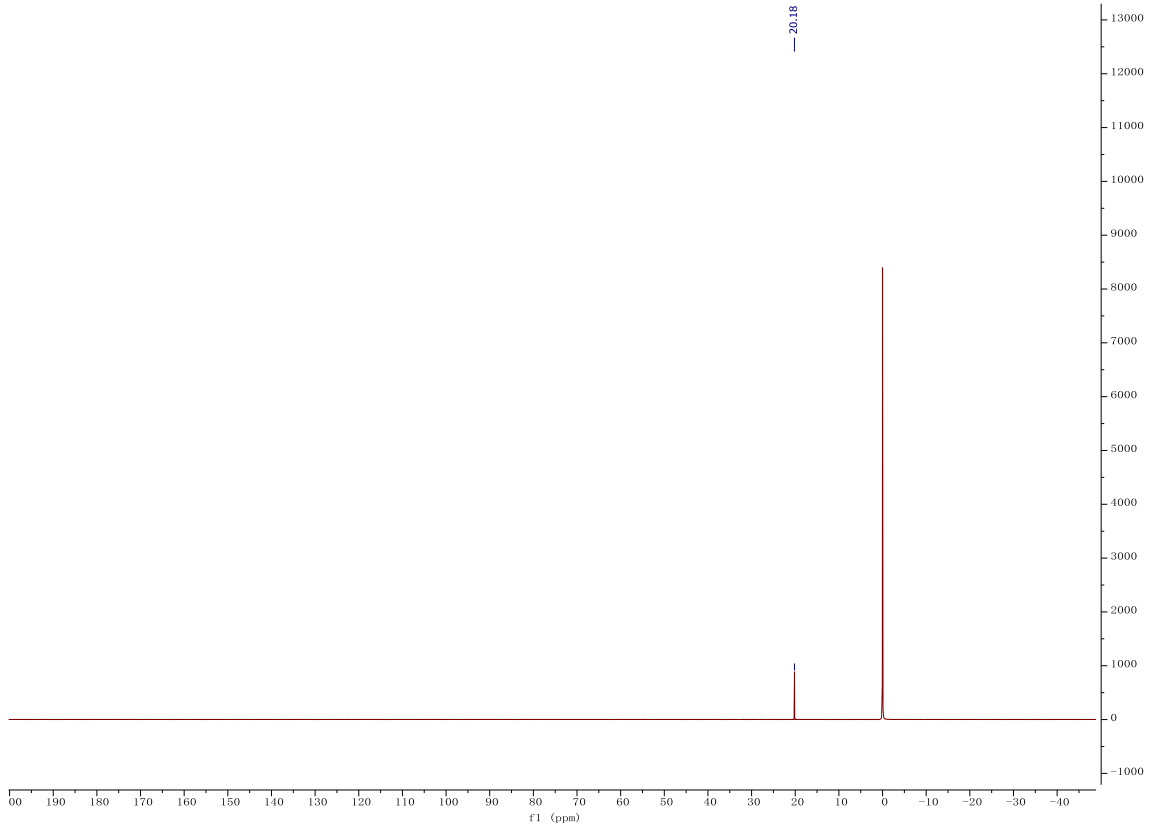
3.99
6.03
1.01
1.01
9.02
f1 (ppm)


164.70
136.16
135.46
131.42
131.41
131.00
130.94
128.63
128.55
119.69
119.04
35.61
35.58
30.38
f1 (ppm)


20.18
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)