Electronic Supplementary Information

Silver(I)-catalyzed highly *para*-selective phosphonation of 2-aryloxazolines

Peng-Cheng Cui[a] and Guan-Wu Wang*[abc]

[a] Hefei National Research Center for Physical Sciences at the Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China. E-mail: gwang@ustc.edu.cn

[b] Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, and School of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241002, P. R. China.

[c] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, Gansu 730000, P. R. China.

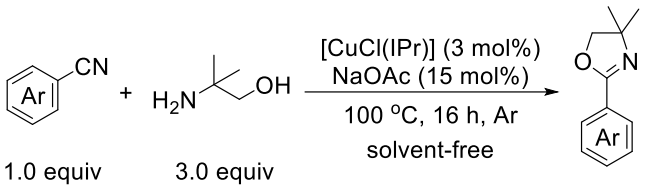
Table of Contents

1. General information

All the reactions were performed in sealed Schlenk tubes. NMR spectra were recorded on a Bruker spectrometer (400 MHz or 500 MHz for ^{1}H NMR; 101 MHz or 126 MHz for ^{13}C NMR; 376 MHz or 471 MHz for ^{19}F NMR and 162 MHz or 202 MHz for ^{31}P NMR). ^{1}H NMR chemical shifts were determined relative to the internal TMS at δ 0.00 ppm. ^{13}C NMR chemical shifts were determined relative to that of $CDCl_3$ at δ 77.16 ppm. The ^{1}H NMR and ^{13}C NMR data were recorded as follows: chemical shift (δ, ppm) and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). High-resolution mass spectral analysis (HRMS) was performed on a Waters XEVO G2 Q-TOF. **1a**–**i**[1] and **2c**–**q**[2] were synthesized according to the reported literature. Other chemicals were purchased from *J&K*, *Adamas-beta* and *Aladdin* and were used directly. Solvents were purchased from *Sinopharm Chemical Reagent Co., Ltd.* and used directly.

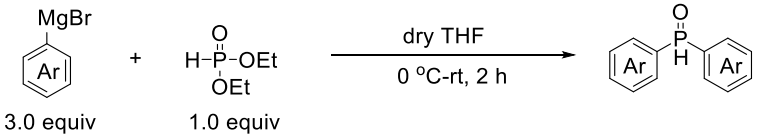
2. Synthesis of 2-aryloxazolines 1 and phosphine oxides 2

General procedure for the synthesis of 2-aryloxazolines 1

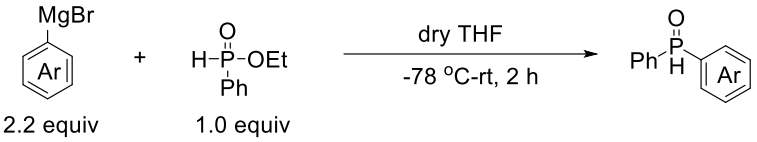


According to the reported literature,[1] a mixture of a nitrile (5.0 mmol), 2-amino-2-methyl-1-propanol (15.0 mmol), [CuCl(IPr)] (0.15 mmol) and NaOAc (0.75 mmol) was added to a 25 mL Schlenk flask. The tube was evacuated and backfilled with argon three times. The resulting mixture was stirred at 100 °C for 16 h. Then the organic phase was collected and concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as the eluent to give the corresponding 2-aryloxazoline **1**.

General procedure for the synthesis of phosphine oxides 2



According to the reported literature,[2] to a 100 mL round bottom flask, the corresponding Grignard reagent (30.0 mmol, 1.0 mol/L in THF) was added and cooled to 0 °C. Subsequently, diethyl phosphite (10.0 mmol) was dissolved in dry THF (5.0 mL) and added dropwise to the solution. After the addition, the reaction mixture was gradually warmed up to room temperature and stirred for 2 h. Then, the mixture was cooled to 0 °C, and NH_4Cl (10 mL) was added to quench the reaction. The crude mixture was then extracted with dichloromethane and dried over Na_2SO_4, and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) as the eluent to give the corresponding phosphine oxide **2c**–**i**. Phosphine oxides **2p** and **2q** could be similarly prepared by using the corresponding Grignard reagent.

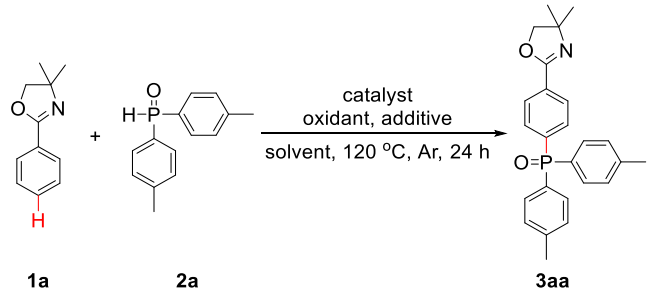


According to the reported literature,[2] to a 100 mL round bottom flask, the corresponding Grignard reagent (22.0 mmol, 1.0 mol/L in THF) was added and cooled to -78 °C. Subsequently, ethyl phenylphosphinate (10.0 mmol) was dissolved in dry THF (5.0 mL) and added dropwise to the solution. After the addition, the reaction mixture was gradually warmed up to room temperature and stirred for 2 h. Then, the mixture was cooled to 0 °C, and NH_4Cl (10 mL) was added to quench the reaction. The crude mixture was then extracted with dichloromethane and dried over Na_2SO_4, and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) as the eluent to give the corresponding phosphine oxide **2j**–**n**.

3. Optimization of the reaction conditions

In our initial investigation, we chose 4,4-dimethyl-2-phenyl-4,5-dihydrooxazole (**1a**) and di-*p*-tolylphosphine oxide (**2a**) as model substrates to screen the reaction conditions (Table S1). Initially, when Ag_2CO_3, AgOAc, Ag_2O and $AgNO_3$ were used as catalysts, (4-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)di-*p*-tolylphosphine oxide (**3aa**) could be obtained in 16–34% yields (entries 1–4). Gratifyingly, if $AgNTf_2$ was employed as a catalyst, **3aa** was isolated in 73% yield (entry 5). However, the yield of **3aa** was slightly decreased to 65% when $AgSbF_6$ was utilized as the catalyst (entry 6). In the presence of other Lewis acids, such as $FeCl_3$, $CuCl_2$ and $AlCl_3$, **3aa** was obtained in yields of 0–21% (entries 7–9). Subsequently, no better results were obtained with $Na_2S_2O_8$, $(NH_4)_2S_2O_8$ and Oxone as oxidants (entries 10–12). When we replaced pivalic acid (PivOH) with $P^tBu_3 \cdot HBF_4$, PPh_3 and $MesCO_2H$ as additives, the yields of **3aa** were decreased to 6–64% (entries 13–15). The solvent had an important effect on the reaction; when DMSO, DMF or 1,4-dioxane was used in place of MeCN, **3aa** could not be obtained (entries 16–18). In addition, a reaction temperature of 120 °C was found to be optimal. Either lowering the temperature to 110 °C or raising the temperature to 130 °C resulted in a lower efficiency (entries 19 and 20). Finally, the yield of **3aa** was reduced to 17% when the reaction mixture was exposed to air (entry 21), indicating that O_2 in air had a detrimental effect. Control experiments showed that $K_2S_2O_8$ played a crucial role in this system, and **3aa** was not obtained in its absence; both $AgNTf_2$ and PivOH also had important effects on the yield of **3aa** (entries 22–25). Regardless of whether the amounts of **2a** and $K_2S_2O_8$ were reduced or increased, the yield of **3aa** dropped to 12–15% (entries 26 and 27).

Table S1 Optimization of the reaction conditions[a]



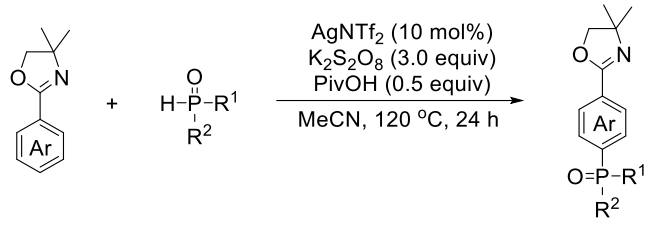
1a **2a** **3aa**

Entry	Catalyst	Oxidant	Additive	Solvent	Yield (%)[b]
1	Ag_2CO_3	$K_2S_2O_8$	PivOH	MeCN	25
2	AgOAc	$K_2S_2O_8$	PivOH	MeCN	34
3	Ag_2O	$K_2S_2O_8$	PivOH	MeCN	16
4	$AgNO_3$	$K_2S_2O_8$	PivOH	MeCN	22
5	***$AgNTf_2$***	***$K_2S_2O_8$***	***PivOH***	***MeCN***	***73***
6	$AgSbF_6$	$K_2S_2O_8$	PivOH	MeCN	65
7	$FeCl_3$	$K_2S_2O_8$	PivOH	MeCN	0
8	$CuCl_2$	$K_2S_2O_8$	PivOH	MeCN	0
9	$AlCl_3$	$K_2S_2O_8$	PivOH	MeCN	21
10	$AgNTf_2$	$Na_2S_2O_8$	PivOH	MeCN	37
11	$AgNTf_2$	$(NH_4)_2S_2O_8$	PivOH	MeCN	31
12	$AgNTf_2$	Oxone	PivOH	MeCN	0
13	$AgNTf_2$	$K_2S_2O_8$	$P^tBu_3 \cdot HBF_4$	MeCN	64
14	$AgNTf_2$	$K_2S_2O_8$	PPh_3	MeCN	6
15	$AgNTf_2$	$K_2S_2O_8$	$MesCO_2H$	MeCN	14
16	$AgNTf_2$	$K_2S_2O_8$	PivOH	DMSO	0
17	$AgNTf_2$	$K_2S_2O_8$	PivOH	DMF	0
18	$AgNTf_2$	$K_2S_2O_8$	PivOH	1,4-Dioxane	0
19[c]	$AgNTf_2$	$K_2S_2O_8$	PivOH	MeCN	37
20[d]	$AgNTf_2$	$K_2S_2O_8$	PivOH	MeCN	23
21[e]	$AgNTf_2$	$K_2S_2O_8$	PivOH	MeCN	17
22	$AgNTf_2$	—	PivOH	MeCN	0
23	—	$K_2S_2O_8$	—	MeCN	13
24	—	$K_2S_2O_8$	PivOH	MeCN	19
25	$AgNTf_2$	$K_2S_2O_8$	—	MeCN	26
26[f]	$AgNTf_2$	$K_2S_2O_8$	PivOH	MeCN	12
27[g]	$AgNTf_2$	$K_2S_2O_8$	PivOH	MeCN	15

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), catalyst (10 mol%), oxidant (0.6 mmol), additive (0.1 mmol), solvent (1.0 mL) at 120 °C for 24 h under an argon atmosphere. [b]Isolated yields based on **1a**. [c]110 °C. [d]130 °C. [e]under an air atmosphere. [f]**2a** (0.4 mmol), $K_2S_2O_8$ (0.4 mmol). [g]**2a** (0.8 mmol), $K_2S_2O_8$ (0.8 mmol).

4. Synthesis and characterization of compounds 3

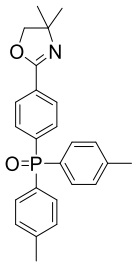
General procedure for the silver(I)-catalyzed highly *para*-selective phosphonation of 2-aryloxazolines.



1 **2** **3**

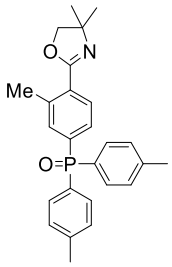
To a 25 mL Schlenk tube with a magnetic stir bar were added **1** (0.2 mmol), phosphine oxide **2** (0.6 mmol, 3.0 equiv), $AgNTf_2$ (0.02 mmol, 10 mol%), $K_2S_2O_8$ (0.6 mmol, 3.0 equiv) and PivOH (0.1 mmol, 0.5 equiv). The mixture was then evacuated and backfilled with argon three times. Subsequently, MeCN (1.0 mL) was added via syringe. After stirring at 120 ℃ for 24 h, the reaction mixture was cooled to room temperature. Then, the reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL). The solution was extracted with dichloromethane (3 × 20 mL). The organic phase was collected, dried with anhydrous Na_2SO_4 and concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) as the eluent to give compound **3**.

(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)di-*p*-tolylphosphine oxide (3aa)



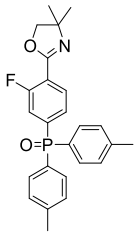
By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2a** (138.2 mg, 0.6 mmol), $AgNTf_2$ (8.0 mg, 0.02 mmol), $K_2S_2O_8$ (162.5 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3aa** (58.5 mg, 73% yield). Colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.7 Hz, 2H), 7.71 (dd, J = 11.2, 7.7 Hz, 2H), 7.53 (dd, J = 11.7, 7.5 Hz, 4H), 7.26 (d, J = 7.5 Hz, 4H), 4.12 (s, 2H), 2.40 (s, 6H), 1.38 (s, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 142.7 (2C, d, $J_{C\text{-}P}$ = 2.8 Hz), 136.1 (1C, d, $J_{C\text{-}P}$ = 102.3 Hz), 132.15 (4C, d, $J_{C\text{-}P}$ = 10.3 Hz), 132.09 (2C, d, $J_{C\text{-}P}$ = 10.0 Hz), 131.2 (1C, d, $J_{C\text{-}P}$ = 2.8 Hz), 129.4 (4C, d, $J_{C\text{-}P}$ = 12.6 Hz), 129.0 (2C, d, $J_{C\text{-}P}$ = 106.7 Hz), 128.1 (2C, d, $J_{C\text{-}P}$ = 12.1 Hz), 79.4 (1C), 67.9 (1C), 28.4 (2C), 21.7 (2C);
^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9;
HRMS (ESI) *m/z*: Calcd for $C_{25}H_{27}NO_2P$ $[M+H]^+$ 404.1774; found 404.1776.

(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-3-methylphenyl)di-*p*-tolylphosphine oxide (3ba)



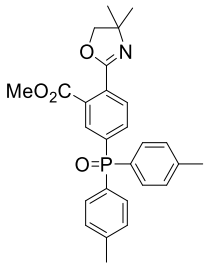
By following the general procedure, the reaction of **1b** (37.1 mg, 0.2 mmol) with **2a** (138.3 mg, 0.6 mmol), $AgNTf_2$ (7.7 mg, 0.02 mmol), $K_2S_2O_8$ (163.8 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ba** (49.9 mg, 61% yield). Colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 8.1, 2.6 Hz, 1H), 7.62 (d, J = 12.2 Hz, 1H), 7.52 (dd, J = 11.8, 7.4 Hz, 4H), 7.42 (dd, J = 10.7, 8.1 Hz, 1H), 7.25 (d, J = 7.4 Hz, 4H), 4.08 (s, 2H), 2.56 (s, 3H), 2.40 (s, 6H), 1.39 (s, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (1C), 142.6 (2C, d, $J_{C\text{-}P}$ = 2.7 Hz), 138.9 (1C, d, $J_{C\text{-}P}$ = 11.8 Hz), 135.0 (1C, d, $J_{C\text{-}P}$ = 102.6 Hz), 134.6 (1C, d, $J_{C\text{-}P}$ = 9.5 Hz), 132.1 (4C, d, $J_{C\text{-}P}$ = 10.3 Hz), 131.0 (1C, d, $J_{C\text{-}P}$ = 2.9 Hz), 129.63 (1C, d, $J_{C\text{-}P}$ = 12.5 Hz), 129.3 (4C, d, $J_{C\text{-}P}$ = 12.6 Hz), 129.14 (1C, d, $J_{C\text{-}P}$ = 10.1 Hz), 129.135 (2C, d, $J_{C\text{-}P}$ = 107.1 Hz), 78.9 (1C), 68.2 (1C), 28.5 (2C), 21.7 (2C), 21.5 (1C);
^{31}P NMR (162 MHz, $CDCl_3$) δ 29.0;
HRMS (ESI) *m/z*: Calcd for $C_{26}H_{29}NO_2P$ $[M+H]^+$ 418.1930; found 418.1934.

(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-3-fluorophenyl)di-*p*-tolylphosphine oxide (3ca)



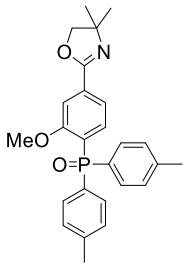
By following the general procedure, the reaction of **1c** (38.4 mg, 0.2 mmol) with **2a** (138.1 mg, 0.6 mmol), $AgNTf_2$ (7.9 mg, 0.02 mmol), $K_2S_2O_8$ (162.3 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ca** (38.5 mg, 46% yield). Colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (ddd, J = 10.4, 7.4, 3.2 Hz, 1H), 7.57−7.47 (m, 5H), 7.42 (t, J = 11.3, Hz, 1H), 7.28 (dd, J = 7.6, 2.1 Hz, 4H), 4.11 (s, 2H), 2.41 (s, 6H), 1.40 (s, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6 (1C, dd, $J_{C\text{-}F}$ = 261.7 Hz, $J_{C\text{-}P}$ = 16.5 Hz), 158.3 (1C, d, $J_{C\text{-}F}$ = 5.0 Hz), 143.0 (2C, d, $J_{C\text{-}P}$ = 2.8 Hz), 138.9 (1C, dd, $J_{C\text{-}P}$ = 100.4 Hz, $J_{C\text{-}F}$ = 6.2 Hz), 132.1 (4C, d, $J_{C\text{-}P}$ = 10.4 Hz), 131.5 (1C, d, $J_{C\text{-}P}$ = 13.2 Hz), 129.5 (4C, d, $J_{C\text{-}P}$ = 12.7 Hz), 128.4 (2C, d, $J_{C\text{-}P}$ = 108.0 Hz), 127.4 (1C, dd, $J_{C\text{-}P}$ = 8.9 Hz, $J_{C\text{-}F}$ = 4.0 Hz), 120.3 (1C, dd, $J_{C\text{-}F}$ = 23.3 Hz, $J_{C\text{-}P}$ = 10.8 Hz), 119.6 (1C, dd, $J_{C\text{-}F}$ = 10.9 Hz, $J_{C\text{-}P}$ = 2.6 Hz), 79.1 (1C), 68.2 (1C), 28.4 (2C), 21.7 (2C);
^{19}F NMR (377 MHz, $CDCl_3$) δ –108.1 (1F, d, J = 4.3 Hz);
^{31}P NMR (162 MHz, $CDCl_3$) δ 27.7 (1P, d, J = 4.1 Hz);
HRMS (ESI) *m/z*: Calcd for $C_{25}H_{26}FNO_2P$ $[M+H]^+$ 422.1680; found 422.1682.

Methyl 5-(di-*p*-tolylphosphoryl)-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)benzoate (3da)



By following the general procedure, the reaction of **1d** (47.2 mg, 0.2 mmol) with **2a** (138.2 mg, 0.6 mmol), $AgNTf_2$ (7.8 mg, 0.02 mmol), $K_2S_2O_8$ (162.6 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3da** (39.2 mg, 42% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 11.6 Hz, 1H), 7.85−7.78 (m, 2H), 7.50 (dd, J = 12.0, 7.8 Hz, 4H), 7.27 (d, J = 7.8 Hz, 4H), 4.12 (s, 2H), 3.84 (s, 3H), 2.41 (s, 6H), 1.39 (s, 6H);
^{13}C NMR (126 MHz, $CDCl_3$) δ167.4 (1C), 161.4 (1C), 143.0 (2C, d, $J_{C\text{-}P}$ = 2.6 Hz), 136.2 (1C, d, $J_{C\text{-}P}$ = 101.5 Hz), 134.5 (1C, d, $J_{C\text{-}P}$ = 9.5 Hz), 132.4 (1C, d, $J_{C\text{-}P}$ = 10.9 Hz), 132.3 (1C, d, $J_{C\text{-}P}$ = 11.9 Hz), 132.2 (4C, d, $J_{C\text{-}P}$ = 10.3 Hz), 131.6 (1C, d, $J_{C\text{-}P}$ = 2.5 Hz), 129.8 (1C, d, $J_{C\text{-}P}$ = 11.8 Hz), 129.6 (4C, d, $J_{C\text{-}P}$ = 12.8 Hz), 128.4 (2C, d, $J_{C\text{-}P}$ = 108.2 Hz), 80.1 (1C), 68.4 (1C), 52.7 (1C), 28.2 (2C), 21.8 (2C);
^{31}P NMR (202 MHz, $CDCl_3$) δ 28.2;
HRMS (ESI) *m/z*: Calcd for $C_{27}H_{29}NO_4P$ $[M+H]^+$ 462.1829; found 462.1825.

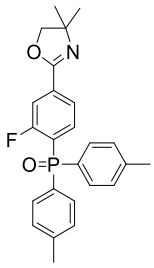
(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-2-methoxyphenyl)di-*p*-tolylphosphine oxide (3ea)



By following the general procedure, the reaction of **1e** (41.2 mg, 0.2 mmol) with **2a** (138.0 mg, 0.6 mmol), $AgNTf_2$ (7.8 mg, 0.02 mmol), $K_2S_2O_8$ (162.5 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ea** (67.9 mg, 78% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, J = 13.1, 7.9 Hz, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.53−7.46 (m, 5H), 7.19 (dd, J = 8.1, 2.3 Hz, 4H), 4.12 (s, 2H), 3.60 (s, 3H), 2.38 (s, 6H), 1.38 (s, 6H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 (1C), 160.8 (1C, d, $J_{C\text{-}P}$ = 3.1 Hz), 142.2 (2C, d, $J_{C\text{-}P}$ = 2.6 Hz), 134.9 (1C, d, $J_{C\text{-}P}$ = 7.3 Hz), 133.7 (1C), 131.8 (4C, d, $J_{C\text{-}P}$ = 10.9 Hz), 129.2 (2C, d, $J_{C\text{-}P}$ = 111.0 Hz), 129.1 (4C, d, $J_{C\text{-}P}$ = 13.0 Hz), 123.6 (1C, d, $J_{C\text{-}P}$ = 102.0 Hz), 120.7 (1C, d, $J_{C\text{-}P}$ = 11.8 Hz), 111.1 (1C, d, $J_{C\text{-}P}$ = 6.4 Hz), 79.4 (1C), 67.9 (1C), 55.8 (1C), 28.4 (2C), 21.7 (2C);
^{31}P NMR (202 MHz, $CDCl_3$) δ 28.1;

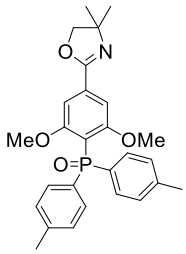
HRMS (ESI) *m/z*: Calcd for $C_{26}H_{29}NO_3P$ $[M+H]^+$ 434.1880; found 434.1869.

(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-2-fluorophenyl)di-*p*-tolylphosphine oxide (3fa)



By following the general procedure, the reaction of **1f** (38.8 mg, 0.2 mmol) with **2a** (138.1 mg, 0.6 mmol), $AgNTf_2$ (7.8 mg, 0.02 mmol), $K_2S_2O_8$ (162.6 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3fa** (35.2 mg, 41% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (ddd, J = 12.4, 7.8, 6.6 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.50 (ddd, J = 10.1, 4.6, 1.2 Hz, 1H), 7.60 (dd, J = 12.6, 8.0 Hz, 4H), 7.27 (dd, J = 8.0, 2.6 Hz, 4H), 4.12 (s, 2H), 2.40 (s, 6H), 1.38 (s, 6H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6 (1C, dd, $J_{C\text{-}F}$ = 250.9 Hz, $J_{C\text{-}P}$ = 1.9 Hz), 160.5 (1C, d, $J_{C\text{-}F}$ = 2.6 Hz), 142.9 (2C, d, $J_{C\text{-}P}$ = 2.7 Hz), 135.0 (1C, dd, $J_{C\text{-}F}$ = 4.8 Hz, $J_{C\text{-}P}$ = 4.8 Hz), 134.5 (1C, dd, $J_{C\text{-}P}$ = 8.7 Hz, $J_{C\text{-}F}$ = 2.0 Hz), 131.8 (4C, dd, $J_{C\text{-}P}$ = 11.0 Hz, $J_{C\text{-}F}$ = 1.3 Hz), 129.4 (4C, d, $J_{C\text{-}P}$ = 13.3 Hz), 128.8 (2C, d, $J_{C\text{-}P}$ = 111.0 Hz), 124.2 (1C, dd, $J_{C\text{-}P}$ = 10.4 Hz, $J_{C\text{-}F}$ = 3.0 Hz), 123.7 (1C, dd, $J_{C\text{-}P}$ = 96.3 Hz, $J_{C\text{-}F}$ = 17.6 Hz), 115.9 (1C, dd, $J_{C\text{-}F}$ = 25.5 Hz, $J_{C\text{-}P}$ = 5.6 Hz), 79.6 (1C), 68.1 (1C), 28.4 (2C), 21.8 (2C);
^{19}F NMR (471 MHz, $CDCl_3$) δ –99.5;
^{31}P NMR (202 MHz, $CDCl_3$) δ 24.1;
HRMS (ESI) *m/z*: Calcd for $C_{25}H_{26}FNO_2P$ $[M+H]^+$ 422.1680; found 422.1680.

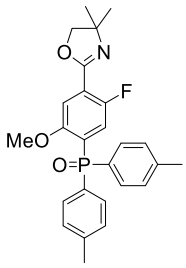
(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-2,6-dimethoxyphenyl)di-*p*-tolylphosphine oxide (3ga)



By following the general procedure, the reaction of **1g** (47.0 mg, 0.2 mmol) with **2a** (138.1 mg, 0.6 mmol), $AgNTf_2$ (7.7 mg, 0.02 mmol), $K_2S_2O_8$ (162.6 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ga** (48.9 mg, 53% yield). Colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 12.4, 8.0 Hz, 4H), 7.18 (dd, J = 8.0, 2.5 Hz, 4H), 7.08 (d, J = 4.1 Hz, 2H), 4.12 (s, 2H), 3.42 (s, 6H), 2.36 (s, 6H), 1.39 (s, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (2C), 161.4 (1C), 140.8 (2C, d, $J_{C\text{-}P}$ = 2.9 Hz), 133.9 (1C), 133.1 (2C, d, $J_{C\text{-}P}$ = 112.3 Hz), 130.7 (4C, d, $J_{C\text{-}P}$ = 10.4 Hz), 128.7 (4C, d, $J_{C\text{-}P}$ = 13.1 Hz), 111.7 (1C, d, $J_{C\text{-}P}$ = 101.4 Hz), 104.5 (2C, d, $J_{C\text{-}P}$ = 6.0 Hz), 79.3 (1C),

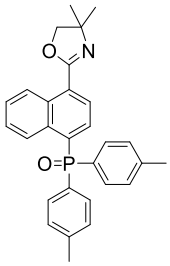
68.0 (1C), 55.9 (2C), 28.4 (2C), 21.6 (2C, d, $J_{C\text{-}P}$ = 1.1 Hz);
^{31}P NMR (162 MHz, $CDCl_3$) δ 22.9;
HRMS (ESI) *m/z*: Calcd for $C_{27}H_{31}NO_4P$ $[M+H]^+$ 464.1985; found 464.1984.

(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-5-fluoro-2-methoxyphenyl)di-*p*-tolylphosphine oxide (3ha)



By following the general procedure, the reaction of **1h** (44.6 mg, 0.2 mmol) with **2a** (138.2 mg, 0.6 mmol), $AgNTf_2$ (7.7 mg, 0.02 mmol), $K_2S_2O_8$ (162.5 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ha** (56.8 mg, 63% yield). Colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.48 (m, 5H), 7.36 (dd, J = 5.4, 5.4 Hz, 1H), 7.22 (dd, J = 7.9, 2.8 Hz, 4H), 4.12 (s, 2H), 3.58 (s, 3H), 2.39 (s, 6H), 1.40 (s, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7 (1C, d, $J_{C\text{-}F}$ = 5.2 Hz), 156.3 (1C, dd, $J_{C\text{-}P}$ = 2.5 Hz, $J_{C\text{-}F}$ = 2.4 Hz), 155.2 (1C, dd, $J_{C\text{-}F}$ = 253.7 Hz, $J_{C\text{-}P}$ = 15.4 Hz), 142.5 (2C, d, $J_{C\text{-}P}$ = 2.8 Hz), 131.9 (4C, d, $J_{C\text{-}P}$ = 10.8 Hz), 129.1 (4C, d, $J_{C\text{-}P}$ = 13.1 Hz), 128.7 (2C, d, $J_{C\text{-}P}$ = 111.6 Hz), 126.0 (1C, dd, $J_{C\text{-}P}$ = 99.2 Hz, $J_{C\text{-}F}$ = 5.6 Hz), 122.9 (1C, dd, $J_{C\text{-}F}$ = 25.7 Hz, $J_{C\text{-}P}$ = 7.7 Hz), 120.7 (1C, dd, $J_{C\text{-}P}$ = 12.6 Hz, $J_{C\text{-}F}$ = 2.3 Hz), 113.4 (1C, d, $J_{C\text{-}F}$ = 7.2 Hz), 79.3 (1C), 68.0 (1C), 56.2 (1C), 28.4 (2C), 21.7 (2C, d, $J_{C\text{-}P}$ = 1.2 Hz);
^{19}F NMR (377 MHz, $CDCl_3$) δ –118.9 (1F, d, J = 2.9 Hz);
^{31}P NMR (162 MHz, $CDCl_3$) δ 26.3 (1P, d, J = 2.4 Hz);
HRMS (ESI) *m/z*: Calcd for $C_{26}H_{28}FNO_3P$ $[M+H]^+$ 452.1785; found 452.1790.

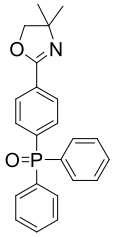
(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)naphthalen-1-yl)di-*p*-tolylphosphine oxide (3ia)



By following the general procedure, the reaction of **1i** (45.6 mg, 0.2 mmol) with **2a** (138.2 mg, 0.6 mmol), $AgNTf_2$ (8.0 mg, 0.02 mmol), $K_2S_2O_8$ (162.5 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ia** (44.9 mg, 49% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.03 (d, J = 8.6 Hz, 1H), 8.70 (d, J = 8.6 Hz, 1H), 7.88 (dd, J = 7.4, 2.1 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.52 (dd, J = 11.9, 7.4 Hz, 4H), 7.46 (t, J = 7.6 Hz, 1H), 7.31 (dd, J = 15.5, 7.5 Hz, 1H), 7.25 (d, J = 7.4 Hz, 4H), 4.16 (s, 2H), 2.39 (s, 6H), 1.48 (s, 6H);

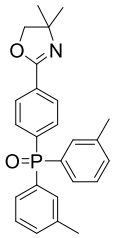
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 (1C), 142.5 (2C, d, $J_{C\text{-}P}$ = 2.7 Hz), 134.2 (1C, d, $J_{C\text{-}P}$ = 8.3 Hz), 132.8 (1C, d, $J_{C\text{-}P}$ = 99.9 Hz), 132.4 (1C, d, $J_{C\text{-}P}$ = 11.4 Hz), 132.1 (4C, d, $J_{C\text{-}P}$ = 10.2 Hz), 131.5 (1C, d, $J_{C\text{-}P}$ = 8.5 Hz), 129.8 (1C), 129.7 (1C, d, $J_{C\text{-}P}$ = 2.7 Hz), 129.45 (4C, d, $J_{C\text{-}P}$ = 12.7 Hz), 129.40 (2C, d, $J_{C\text{-}P}$ = 107.4 Hz), 129.0 (1C), 128.1 (1C, d, $J_{C\text{-}P}$ = 5.8 Hz), 127.7 (1C), 127.6 (1C), 126.9 (1C), 126.6 (1C, d, $J_{C\text{-}P}$ = 14.3 Hz), 78.6 (1C), 68.8 (1C), 28.6 (2C), 21.7 (2C);
^{31}P NMR (202 MHz, $CDCl_3$) δ 32.6;
HRMS (ESI) *m/z*: Calcd for $C_{29}H_{29}NO_2P$ $[M+H]^+$ 454.1930; found 454.1929.

(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)diphenylphosphine oxide (3ab)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2b** (121.7 mg, 0.6 mmol), $AgNTf_2$ (7.8 mg, 0.02 mmol), $K_2S_2O_8$ (162.6 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ab** (50.2 mg, 67% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.4, 2.5 Hz, 2H), 7.71 (dd, J = 11.6, 8.4 Hz, 2H), 7.64 (dd, J = 12.1, 7.7 Hz, 4H), 7.55 (td, J = 7.5, 1.1 Hz, 2H), 7.55 (td, J = 7.6, 2.8 Hz, 4H), 4.12 (s, 2H), 1.38 (s, 6H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3 (1C), 135.5 (1C, d, $J_{C\text{-}P}$ = 102.6 Hz), 132.3 (2C, d, $J_{C\text{-}P}$ = 2.6 Hz), 132.16 (6C, d, $J_{C\text{-}P}$ = 10.0 Hz), 132.14 (2C, d, $J_{C\text{-}P}$ = 104.7 Hz), 131.5 (1C, d, $J_{C\text{-}P}$ = 2.7 Hz), 128.7 (4C, d, $J_{C\text{-}P}$ = 12.5 Hz), 128.3 (2C, d, $J_{C\text{-}P}$ = 12.4 Hz), 79.4 (1C), 68.0 (1C), 28.5 (2C);
^{31}P NMR (202 MHz, $CDCl_3$) δ 28.8;
HRMS (ESI) *m/z*: Calcd for $C_{23}H_{23}NO_2P$ $[M+H]^+$ 376.1461; found 376.1464.

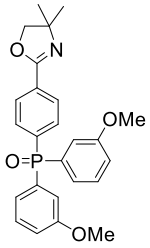
(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)di-*m*-tolylphosphine oxide (3ac)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2c** (137.8 mg, 0.6 mmol), $AgNTf_2$ (8.0 mg, 0.02 mmol), $K_2S_2O_8$ (162.8 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ac** (44.7 mg, 56% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.5, 2.5 Hz, 2H), 7.72 (dd, J = 11.6, 8.5 Hz, 2H), 7.54 (d, J = 12.5 Hz, 2H), 7.38−7.33 (m, 6H), 4.13 (s, 2H), 2.36 (s, 6H), 1.39 (s, 6H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 (1C), 138.7 (2C, d, $J_{C\text{-}P}$ = 12.1 Hz), 135.9 (1C, d, $J_{C\text{-}P}$ = 101.5 Hz), 133.1 (2C, d, $J_{C\text{-}P}$ = 2.7 Hz), 132.6 (2C, d, $J_{C\text{-}P}$ = 9.7 Hz), 132.2 (2C,

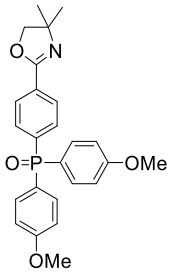
d, $J_{C\text{-}P}$ = 10.1 Hz), 132.1 (2C, d, $J_{C\text{-}P}$ = 104.1 Hz), 131.3 (1C, d, $J_{C\text{-}P}$ = 2.7 Hz), 129.3 (2C, d, $J_{C\text{-}P}$ = 10.2 Hz), 128.5 (2C, d, $J_{C\text{-}P}$ = 12.9 Hz), 128.2 (2C, d, $J_{C\text{-}P}$ = 12.1 Hz), 79.4 (1C), 68.0 (1C), 28.5 (2C), 21.6 (2C);
^{31}P NMR (202 MHz, $CDCl_3$) δ 29.0;
HRMS (ESI) *m/z*: Calcd for $C_{25}H_{27}NO_2P$ $[M+H]^+$ 404.1774; found 404.1772.

(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)bis(3-methoxyphenyl)phosphine oxide (3ad)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2d** (157.6 mg, 0.6 mmol), $AgNTf_2$ (7.7 mg, 0.02 mmol), $K_2S_2O_8$ (162.2 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ad** (54.6 mg, 63% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.5, 2.6 Hz, 2H), 7.71 (dd, J = 11.7, 8.5 Hz, 2H), 7.36 (ddd, J = 11.8, 7.9, 3.9 Hz, 2H), 7.26 (ddd, J = 13.5, 2.5, 1.3 Hz, 2H), 7.12 (dd, J = 11.9, 7.5 Hz, 2H), 7.08 (dd, J = 8.3, 2.6 Hz, 2H), 4.13 (s, 2H), 3.79 (s, 6H), 1.39 (s, 6H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 (1C), 159.7 (2C, d, $J_{C\text{-}P}$ = 14.8 Hz), 135.4 (1C, d, $J_{C\text{-}P}$ = 102.9 Hz), 133.3 (2C, d, $J_{C\text{-}P}$ = 104.1 Hz), 132.1 (2C, d, $J_{C\text{-}P}$ = 10.1 Hz), 131.5 (1C, d, $J_{C\text{-}P}$ = 2.7 Hz), 129.9 (2C, d, $J_{C\text{-}P}$ = 14.6 Hz), 128.3 (2C, d, $J_{C\text{-}P}$ = 12.1 Hz), 124.4 (2C, d, $J_{C\text{-}P}$ = 10.2 Hz), 118.5 (2C, d, $J_{C\text{-}P}$ = 2.5 Hz), 116.8 (2C, d, $J_{C\text{-}P}$ = 10.9 Hz), 79.4 (1C), 68.0 (1C), 55.6 (2C), 28.5 (2C);
^{31}P NMR (202 MHz, $CDCl_3$) δ 29.3;
HRMS (ESI) *m/z*: Calcd for $C_{25}H_{27}NO_4P$ $[M+H]^+$ 436.1672; found 436.1667.

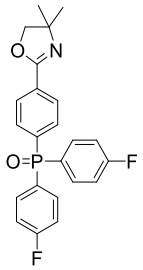
(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)bis(4-methoxyphenyl)phosphine oxide (3ae)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2e** (157.8 mg, 0.6 mmol), $AgNTf_2$ (8.0 mg, 0.02 mmol), $K_2S_2O_8$ (162.6 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ae** (58.9 mg, 68% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, J = 8.2, 2.0 Hz, 2H), 7.69 (dd, J = 11.6, 8.2 Hz, 2H), 7.54 (dd, J = 11.5, 8.7 Hz, 4H), 6.94 (dd, J = 8.7, 1.7 Hz, 4H), 4.12 (s, 2H), 3.84 (s, 6H), 1.38 (s, 6H);

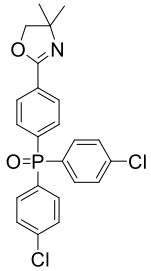
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6 (2C, d, $J_{C\text{-}P}$ = 2.6 Hz), 161.4 (1C), 136.5 (1C, d, $J_{C\text{-}P}$ = 103.1 Hz), 134.0 (4C, d, $J_{C\text{-}P}$ = 11.6 Hz), 132.0 (2C, d, $J_{C\text{-}P}$ = 10.0 Hz), 131.2 (1C), 128.2 (2C, d, $J_{C\text{-}P}$ = 12.1 Hz), 123.6 (2C, d, $J_{C\text{-}P}$ = 111.6 Hz), 114.2 (4C, d, $J_{C\text{-}P}$ = 13.1 Hz), 79.4 (1C), 68.0 (1C), 55.5 (2C), 28.5 (2C);
^{31}P NMR (202 MHz, $CDCl_3$) δ 28.6;
HRMS (ESI) *m/z*: Calcd for $C_{25}H_{26}NO_4PNa$ $[M+Na]^+$ 458.1492; found 458.1501.

(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)bis(4-fluorophenyl)phosphine oxide (3af)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2f** (117 mg, 0.6 mmol), $AgNTf_2$ (7.8 mg, 0.02 mmol), $K_2S_2O_8$ (95.9 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3af** (50.8 mg, 62% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.3, 2.5 Hz, 2H), 7.73−7.61 (m, 6H), 7.18 (td, J = 8.7, 2.0 Hz, 4H), 4.14 (s, 2H), 1.39 (s, 6H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3 (2C, dd, $J_{C\text{-}F}$ = 254.3 Hz, $J_{C\text{-}P}$ = 3.2 Hz), 161.2 (1C), 135.0 (1C, d, $J_{C\text{-}P}$ = 105.5 Hz), 134.6 (4C, dd, $J_{C\text{-}P}$ = 11.4 Hz, $J_{C\text{-}F}$ = 9.0 Hz), 132.0 (2C, d, $J_{C\text{-}P}$ = 10.1 Hz), 131.8 (1C, d, $J_{C\text{-}P}$ = 2.7 Hz), 128.4 (2C, d, $J_{C\text{-}P}$ = 12.5 Hz), 128.0 (2C, dd, $J_{C\text{-}P}$ = 108.1 Hz, $J_{C\text{-}F}$ = 3.1 Hz), 116.3 (4C, dd, $J_{C\text{-}F}$ = 21.5 Hz, $J_{C\text{-}P}$ = 13.4 Hz), 79.5 (1C), 68.0 (1C), 28.5 (2C);
^{19}F NMR (471 MHz, $CDCl_3$) δ –105.8;
^{31}P NMR (202 MHz, $CDCl_3$) δ 27.2;
HRMS (ESI) *m/z*: Calcd for $C_{23}H_{21}F_2NO_2P$ $[M+H]^+$ 412.1272; found 412.1287.

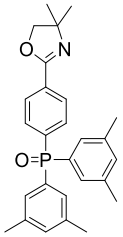
Bis(4-chlorophenyl)(4-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)phosphine oxide (3ag)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2g** (162.5 mg, 0.6 mmol), $AgNTf_2$ (7.9 mg, 0.02 mmol), $K_2S_2O_8$ (162.6 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ag** (41.5 mg, 47% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ8.05 (dd, J = 8.5, 2.7 Hz, 2H), 7.68 (dd, J = 11.9, 8.5 Hz, 2H), 7.57 (dd, J = 11.6, 8.6 Hz, 4H), 7.46 (dd, J = 8.6, 2.3 Hz, 4H), 4.14 (s, 2H), 1.39

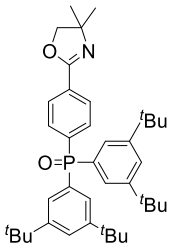
(s, 6H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.2 (1C), 139.2 (2C, d, $J_{C\text{-}P}$ = 3.0 Hz), 134.6 (1C, d, $J_{C\text{-}P}$ = 104.4 Hz), 133.5 (4C, d, $J_{C\text{-}P}$ = 10.9 Hz), 132.04 (2C, d, $J_{C\text{-}P}$ = 10.3 Hz), 131.96 (1C, d, $J_{C\text{-}P}$ = 2.6 Hz), 130.3 (2C, d, $J_{C\text{-}P}$ = 106.4 Hz), 129.3 (4C, d, $J_{C\text{-}P}$ = 12.9 Hz), 128.5 (2C, d, $J_{C\text{-}P}$ = 12.3 Hz), 79.5 (1C), 68.1 (1C), 28.5 (2C);
^{31}P NMR (202 MHz, $CDCl_3$) δ 27.4;
HRMS (ESI) *m/z*: Calcd for $C_{23}H_{21}{}^{35}Cl_2NO_2P$ $[M+H]^+$ 444.0681; found 444.0693.

(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)bis(3,5-dimethylphenyl)phosphine oxide (3ah)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2h** (155.1 mg, 0.6 mmol), $AgNTf_2$ (7.8 mg, 0.02 mmol), $K_2S_2O_8$ (162.4 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ah** (52.3 mg, 61% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, J = 8.4, 2.5 Hz, 2H), 7.72 (dd, J = 11.6, 8.4 Hz, 2H), 7.25 (d, J = 12.4 Hz, 4H), 7.17 (s, 2H), 4.13 (s, 2H), 2.31 (s, 12H), 1.39 (s, 6H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5 (1C), 138.4 (2C, d, $J_{C\text{-}P}$ = 12.8 Hz), 136.1 (1C, d, $J_{C\text{-}P}$ = 101.4 Hz), 134.0 (2C, d, $J_{C\text{-}P}$ = 2.7 Hz), 132.2 (4C, d, $J_{C\text{-}P}$ = 10.0 Hz), 132.0 (2C, d, $J_{C\text{-}P}$ = 103.7 Hz), 131.2 (1C, d, $J_{C\text{-}P}$ = 2.7 Hz), 129.7 (4C, d, $J_{C\text{-}P}$ = 10.0 Hz), 128.1 (2C, d, $J_{C\text{-}P}$ = 12.2 Hz), 79.4 (1C), 68.0 (1C), 28.5 (2C), 21.4 (4C);
^{31}P NMR (202 MHz, $CDCl_3$) δ 29.3;
HRMS (ESI) *m/z*: Calcd for $C_{27}H_{31}NO_2P$ $[M+H]^+$ 432.2087; found 432.2090.

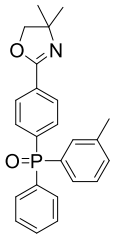
Bis(3,5-di-*tert*-butylphenyl)(4-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)phosphine oxide (3ai)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2i** (259.6 mg, 0.6 mmol), $AgNTf_2$ (7.8 mg, 0.02 mmol), $K_2S_2O_8$ (162.6 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ai** (69.2 mg, 58% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ8.01 (dd, J = 8.3, 2.3 Hz, 2H), 7.74 (dd, J = 11.3, 8.3 Hz, 2H), 7.59 (d, J = 1.0 Hz, 2H), 7.49 (dd, J = 12.9, 1.8 Hz, 4H), 4.13 (s, 2H), 1.39 (s, 6H), 1.27 (s, 36H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6 (1C), 151.1 (4C, d, $J_{C\text{-}P}$ = 11.9 Hz), 137.0 (1C, d, $J_{C\text{-}P}$ = 100.5 Hz), 132.2 (2C, d, $J_{C\text{-}P}$ = 9.8 Hz), 131.3 (2C, d, $J_{C\text{-}P}$ = 104.0 Hz), 131.0 (1C,

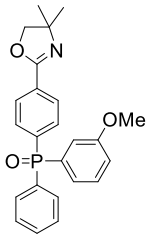
d, $J_{C\text{-}P}$ = 2.6 Hz), 128.0 (2C, d, $J_{C\text{-}P}$ = 11.9 Hz), 126.4 (4C, d, $J_{C\text{-}P}$ = 10.5 Hz), 126.2 (2C, d, $J_{C\text{-}P}$ = 2.5 Hz), 79.4 (1C), 67.9 (1C), 35.1 (4C), 31.4 (12C), 28.5 (2C);
^{31}P NMR (202 MHz, $CDCl_3$) δ 30.8;
HRMS (ESI) *m/z*: Calcd for $C_{39}H_{55}NO_2P$ $[M+H]^+$ 600.3965; found 600.3967.

(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)(phenyl)(*m*-tolyl)phosphine oxide (3aj)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2j** (129.9 mg, 0.6 mmol), $AgNTf_2$ (7.9 mg, 0.02 mmol), $K_2S_2O_8$ (162.5 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3aj** (50.4 mg, 65% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.4, 2.5 Hz, 2H), 7.71 (dd, J = 11.6, 8.4 Hz, 2H), 7.65 (dd, J = 12.1, 7.7 Hz, 2H), 7.57−7.51 (m, 2H), 7.46 (td, J = 7.7, 2.7 Hz, 2H), 7.38−7.31 (m, 3H), 4.13 (s, 2H), 2.36 (s, 3H), 1.38 (s, 6H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 (1C), 138.7 (1C, d, $J_{C\text{-}P}$ = 12.0 Hz), 135.7 (1C, d, $J_{C\text{-}P}$ = 102.2 Hz), 133.1 (1C, d, $J_{C\text{-}P}$ = 2.6 Hz), 132.5 (1C, d, $J_{C\text{-}P}$ = 9.5 Hz), 132.24 (1C, d, $J_{C\text{-}P}$ = 3.4 Hz),, 132.22 (1C, d, $J_{C\text{-}P}$ = 104.7 Hz), 132.16 (4C, d, $J_{C\text{-}P}$ = 10.3 Hz), 131.4 (1C, d, $J_{C\text{-}P}$ = 2.9 Hz), 131.0 (1C, d, $J_{C\text{-}P}$ = 98.8 Hz), 129.3 (1C, d, $J_{C\text{-}P}$ = 10.3 Hz), 128.7 (2C, d, $J_{C\text{-}P}$ = 12.2 Hz), 128.5 (1C, d, $J_{C\text{-}P}$ = 13.0 Hz), 128.2 (2C, d, $J_{C\text{-}P}$ = 12.1 Hz), 79.4 (1C), 68.0 (1C), 28.5 (2C), 21.5 (1C);
^{31}P NMR (202 MHz, $CDCl_3$) δ 29.0;
HRMS (ESI) *m/z*: Calcd for $C_{24}H_{25}NO_2P$ $[M+H]^+$ 390.1617; found 390.1626.

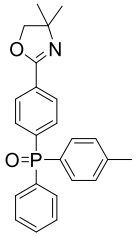
(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)(3-methoxyphenyl)(phenyl)phosphine oxide (3ak)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2k** (139.1 mg, 0.6 mmol), $AgNTf_2$ (7.9 mg, 0.02 mmol), $K_2S_2O_8$ (162.6 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ak** (55.6 mg, 69% yield). Colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.5, 2.6 Hz, 2H), 7.71 (dd, J = 11.7, 8.5 Hz, 2H), 7.64 (dd, J = 12.1, 7.7 Hz, 2H), 7.56 (td, J = 7.4, 1.5 Hz, 1H), 7.46 (td, J = 7.4, 3.0 Hz, 2H), 7.37 (ddd, J = 11.8, 7.9, 3.9 Hz, 1H), 7.28−7.23 (m, 1H), 7.15−7.05 (m, 2H), 4.13 (s, 2H), 3.79 (s, 3H), 1.39 (s, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (1C), 159.7 (1C, d, $J_{C\text{-}P}$ = 15.0 Hz), 135.4 (1C, d,

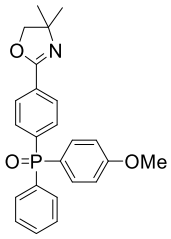
$J_{C\text{-}P}$ = 102.7 Hz), 133.3 (1C, d, $J_{C\text{-}P}$ = 104.0 Hz), 132.3 (1C, d, $J_{C\text{-}P}$ = 2.8 Hz), 132.1 (4C, d, $J_{C\text{-}P}$ = 10.1 Hz), 132.0 (1C, d, $J_{C\text{-}P}$ = 104.8 Hz), 131.5 (1C, d, $J_{C\text{-}P}$ = 2.9 Hz), 129.9 (1C, d, $J_{C\text{-}P}$ = 14.5 Hz), 128.7 (2C, d, $J_{C\text{-}P}$ = 12.3 Hz), 128.3 (2C, d, $J_{C\text{-}P}$ = 12.3 Hz), 124.4 (1C, d, $J_{C\text{-}P}$ = 10.2 Hz), 118.5 (1C, d, $J_{C\text{-}P}$ = 2.6 Hz), 116.8 (1C, d, $J_{C\text{-}P}$ = 10.9 Hz), 79.4 (1C), 68.0 (1C), 55.6 (1C), 28.5 (2C);
^{31}P NMR (162 MHz, $CDCl_3$) δ 29.1;
HRMS (ESI) *m/z*: Calcd for $C_{24}H_{25}NO_3P$ $[M+H]^+$ 406.1567; found 406.1583.

(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)(phenyl)(*p*-tolyl)phosphine oxide (3al)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2l** (129.9 mg, 0.6 mmol), $AgNTf_2$ (7.8 mg, 0.02 mmol), $K_2S_2O_8$ (162.6 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3al** (49.6 mg, 64% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, J = 8.5, 2.6 Hz, 2H), 7.71 (dd, J = 11.6, 8.5 Hz, 2H), 7.64 (dd, J = 12.1, 7.6 Hz, 2H), 7.57−7.49 (m, 3H), 7.45 (td, J = 7.5, 2.9 Hz, 2H), 7.27 (dd, J = 8.3, 2.2 Hz, 2H), 4.12 (s, 2H), 2.41 (s, 3H), 1.38 (s, 6H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 (1C), 142.9 (1C, d, $J_{C\text{-}P}$ = 2.7 Hz), 135.8 (1C, d, $J_{C\text{-}P}$ = 102.3 Hz), 132.4 (1C, d, $J_{C\text{-}P}$ = 104.7 Hz), 132.20 (2C, d, $J_{C\text{-}P}$ = 10.1 Hz), 132.18 (1C), 132.14 (4C, d, $J_{C\text{-}P}$ = 10.0 Hz), 131.4 (1C, d, $J_{C\text{-}P}$ = 2.7 Hz), 129.5 (2C, d, $J_{C\text{-}P}$ = 12.8 Hz), 128.70 (1C, d, $J_{C\text{-}P}$ = 106.8 Hz), 128.67 (2C, d, $J_{C\text{-}P}$ = 12.1 Hz), 128.2 (2C, d, $J_{C\text{-}P}$ = 12.1 Hz), 79.4 (1C), 68.0 (1C), 28.5 (2C), 21.8 (1C);
^{31}P NMR (202 MHz, $CDCl_3$) δ 28.9;
HRMS (ESI) *m/z*: Calcd for $C_{24}H_{25}NO_2P$ $[M+H]^+$ 390.1617; found 390.1636.

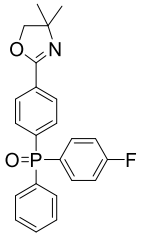
(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)(4-methoxyphenyl)(phenyl)phosphine oxide (3am)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2m** (139.2 mg, 0.6 mmol), $AgNTf_2$ (7.8 mg, 0.02 mmol), $K_2S_2O_8$ (162.4 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3am** (57.2 mg, 71% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, J = 8.5, 2.6 Hz, 2H), 7.70 (dd, J = 11.6, 8.5 Hz, 2H), 7.64 (dd, J = 12.1, 7.7 Hz, 2H), 7.59−7.52 (m, 3H), 7.45 (td, J = 7.5, 2.9 Hz, 2H), 6.96 (dd, J = 8.9, 2.3 Hz, 2H), 4.13 (s, 2H), 3.85 (s, 3H), 1.38 (s, 6H);

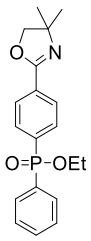
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8 (1C, d, $J_{C\text{-}P}$ = 2.7 Hz), 161.4 (1C), 136.0 (1C, d, $J_{C\text{-}P}$ = 102.9 Hz), 134.1 (2C, d, $J_{C\text{-}P}$ = 11.6 Hz), 132.6 (1C, d, $J_{C\text{-}P}$ = 103.9 Hz), 132.2 (1C), 132.1 (4C, d, $J_{C\text{-}P}$ = 9.9 Hz), 131.4 (1C, d, $J_{C\text{-}P}$ = 2.7 Hz), 128.7 (2C, d, $J_{C\text{-}P}$ = 12.3 Hz), 128.2 (2C, d, $J_{C\text{-}P}$ = 12.1 Hz), 123.1 (1C, d, $J_{C\text{-}P}$ = 111.2 Hz), 114.3 (2C, d, $J_{C\text{-}P}$ = 13.5 Hz), 79.4 (1C), 68.0 (1C), 55.5 (1C), 28.5 (2C);
^{31}P NMR (202 MHz, $CDCl_3$) δ 28.7;
HRMS (ESI) *m/z*: Calcd for $C_{24}H_{24}NO_3PNa$ $[M+Na]^+$ 428.1386; found 428.1397.

(4-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)(4-fluorophenyl)(phenyl)phosphine oxide (3an)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2n** (129.7 mg, 0.6 mmol), $AgNTf_2$ (7.7 mg, 0.02 mmol), $K_2S_2O_8$ (162.7 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3an** (46.2 mg, 59% yield). Colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.5, 2.6 Hz, 2H), 7.70 (dd, J = 11.7, 8.5 Hz, 2H), 7.68−7.61 (m, 4H), 7.57 (td, J = 7.5, 1.5 Hz, 1H), 7.48 (td, J = 7.6, 3.0 Hz, 2H), 7.16 (ddd, J = 10.8, 8.8, 2.1 Hz, 2H), 4.13 (s, 2H), 1.39 (s, 6H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3 (1C, dd, $J_{C\text{-}F}$ = 254.0 Hz, $J_{C\text{-}P}$ = 3.2 Hz), 161.3 (1C), 135.2 (1C, d, $J_{C\text{-}P}$ = 103.6 Hz), 134.7 (2C, dd, $J_{C\text{-}P}$ = 11.4 Hz, $J_{C\text{-}F}$ = 8.9 Hz), 132.5 (1C, d, $J_{C\text{-}P}$ = 2.6 Hz), 132.1 (4C, d, $J_{C\text{-}P}$ = 10.1 Hz), 131.9 (1C, d, $J_{C\text{-}P}$ = 105.6 Hz), 131.7 (1C, d, $J_{C\text{-}P}$ = 2.8 Hz), 128.8 (2C, d, $J_{C\text{-}P}$ = 12.4 Hz), 128.4 (2C, d, $J_{C\text{-}P}$ = 12.2 Hz), 128.1 (1C, dd, $J_{C\text{-}P}$ = 107.4 Hz, $J_{C\text{-}F}$ = 3.3 Hz), 116.2 (2C, dd, $J_{C\text{-}F}$ = 21.4 Hz, $J_{C\text{-}P}$ = 13.4 Hz), 79.5 (1C), 68.0 (1C), 28.5 (2C);
^{19}F NMR (471 MHz, $CDCl_3$) δ –106.1;
^{31}P NMR (202 MHz, $CDCl_3$) δ 28.2;
HRMS (ESI) *m/z*: Calcd for $C_{23}H_{22}FNO_2P$ $[M+H]^+$ 394.1367; found 394.1377.

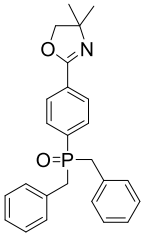
Ethyl (4-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)(phenyl)phosphinate (3ao)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2o** (90 μL, 0.6 mmol), $AgNTf_2$ (7.9 mg, 0.02 mmol), $K_2S_2O_8$ (162.5 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ao** (25.3 mg, 37% yield). White solid;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, J = 8.5, 3.2 Hz, 2H), 7.85 (dd, J = 11.9, 8.5 Hz, 2H), 7.80 (dd, J = 12.0, 8.0 Hz, 2H), 7.55−7.50 (m, 1H), 7.45 (td, J = 7.4, 3.5 Hz, 2H),

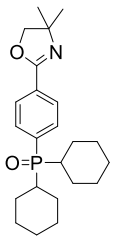
4.14−4.09 (m, 4H), 1.39−1.35 (m, 9H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 (1C), 134.6 (1C, d, $J_{C\text{-}P}$ = 135.4 Hz), 132.4 (1C, d, $J_{C\text{-}P}$ = 2.6 Hz), 131.8 (2C, d, $J_{C\text{-}P}$ = 3.4 Hz), 131.7 (2C, d, $J_{C\text{-}P}$ = 3.2 Hz), 131.6 (1C, d, $J_{C\text{-}P}$ = 2.8 Hz), 131.3 (1C, d, $J_{C\text{-}P}$ = 138.1 Hz), 128.7 (2C, d, $J_{C\text{-}P}$ = 13.0 Hz), 128.3 (2C, d, $J_{C\text{-}P}$ = 13.0 Hz), 79.4 (1C), 68.0 (1C), 61.5 (1C, d, $J_{C\text{-}P}$ = 5.7 Hz), 28.5 (2C), 16.6 (1C, d, $J_{C\text{-}P}$ = 6.5 Hz);
^{31}P NMR (202 MHz, $CDCl_3$) δ 30.5;
HRMS (ESI) *m/z*: Calcd for $C_{19}H_{23}NO_3P$ $[M+H]^+$ 344.1410; found 344.1418.

Dibenzyl(4-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)phosphine oxide (3ap)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2p** (137.5 mg, 0.6 mmol), $AgNTf_2$ (7.9 mg, 0.02 mmol), $K_2S_2O_8$ (162.5 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3ap** (57.7 mg, 72% yield). White solid;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, J = 8.4, 2.6 Hz, 2H), 7.53 (dd, J = 10.6, 8.4 Hz, 2H), 7.25−7.18 (m, 6H), 7.13−7.08 (m, 4H), 4.12 (s, 2H), 3.37 (dd, J = 13.9, 2.4 Hz, 4H), 1.39 (s, 6H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 (1C), 133.9 (1C, d, $J_{C\text{-}P}$ = 92.9 Hz), 131.26 (2C, d, $J_{C\text{-}P}$ = 8.5 Hz), 131.25 (1C, d, $J_{C\text{-}P}$ = 3.4 Hz), 131.1 (2C, d, $J_{C\text{-}P}$ = 7.5 Hz), 130.0 (4C, d, $J_{C\text{-}P}$ = 5.3 Hz), 128.8 (4C, d, $J_{C\text{-}P}$ = 2.6 Hz), 128.0 (2C, d, $J_{C\text{-}P}$ = 11.3 Hz), 127.1 (2C, d, $J_{C\text{-}P}$ = 2.8 Hz), 79.4 (1C), 68.0 (1C), 37.5 (2C, d, $J_{C\text{-}P}$ = 63.6 Hz), 28.5 (2C);
^{31}P NMR (202 MHz, $CDCl_3$) δ 35.2;
HRMS (ESI) *m/z*: Calcd for $C_{25}H_{27}NO_2P$ $[M+H]^+$ 404.1774; found 404.1789.

Dicyclohexyl(4-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)phosphine oxide (3aq)



By following the general procedure, the reaction of **1a** (34.0 μL, 0.2 mmol) with **2q** (128.9 mg, 0.6 mmol), $AgNTf_2$ (8.0 mg, 0.02 mmol), $K_2S_2O_8$ (163.6 mg, 0.6 mmol) and PivOH (11.0 μL, 0.1 mmol) afforded **3aq** (33.9 mg, 44% yield). White solid;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, J = 8.5, 2.2 Hz, 2H), 7.71 (dd, J = 9.3, 8.5 Hz, 2H), 4.14 (s, 2H), 2.07−2.03 (m, 4H), 1.86−1.72 (m, 4H), 1.71−1.58 (m, 4H), 1.40 (s, 6H), 1.28−1.10 (m, 10H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6 (1C), 133.4 (1C, d, $J_{C\text{-}P}$ = 83.0 Hz), 131.6 (2C, d,

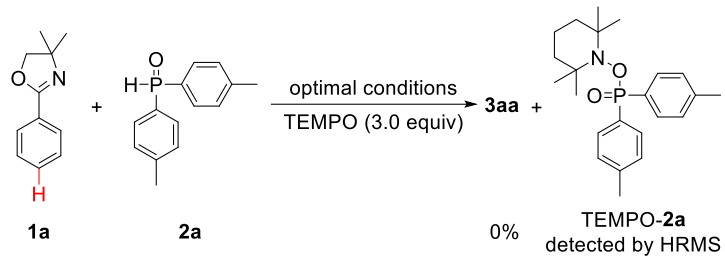
$J_{C\text{-}P}$ = 8.0 Hz), 130.9 (1C, d, $J_{C\text{-}P}$ = 2.6 Hz), 128.0 (2C, d, $J_{C\text{-}P}$ = 10.5 Hz), 79.4 (1C), 67.9 (1C), 35.3 (2C, d, $J_{C\text{-}P}$ = 67.2 Hz), 28.5 (2C), 26.5 (2C, d, $J_{C\text{-}P}$ = 12.5 Hz), 26.4 (2C, d, $J_{C\text{-}P}$ = 11.8 Hz), 25.9 (2C), 25.6 (2C, d, $J_{C\text{-}P}$ = 2.4 Hz), 24.7 (2C, d, $J_{C\text{-}P}$ = 3.0 Hz);

^{31}P NMR (202 MHz, $CDCl_3$) δ 45.2;

HRMS (ESI) *m/z*: Calcd for $C_{23}H_{35}NO_2P$ $[M+H]^+$ 388.2400; found 388.2415.

5. Preliminary mechanistic studies

5.1 Trapping experiments with TEMPO



To a 25 mL Schlenk tube with a magnetic stir bar were added **1a** (34.0 μL, 0.2 mmol), **2a** (138.0 mg, 0.6 mmol), $AgNTf_2$ (7.9 mg, 0.02 mmol), $K_2S_2O_8$ (162.4 mg, 0.6 mmol), PivOH (11 μL, 0.1 mmol) and 2,2,6,6-tetramethylpiperidinooxy (TEMPO, 94.0 mg, 0.6 mmol). The mixture was then evacuated and backfilled with argon three times. Subsequently, MeCN (1.0 mL) was added via syringe. After stirring at 120 °C for 24 h, the mixture was analyzed by thin layer chromatography (TLC), and it was found that no desired product **3aa** could be identified. However, the TEMPO-**2a** adduct could be detected by high-resolution mass spectrometry (HRMS). HRMS (ESI) *m/z*: Calcd for $C_{23}H_{32}NO_2PNa$ $[M+Na]^+$ 408.2063; found 408.2048 (Figure S1).

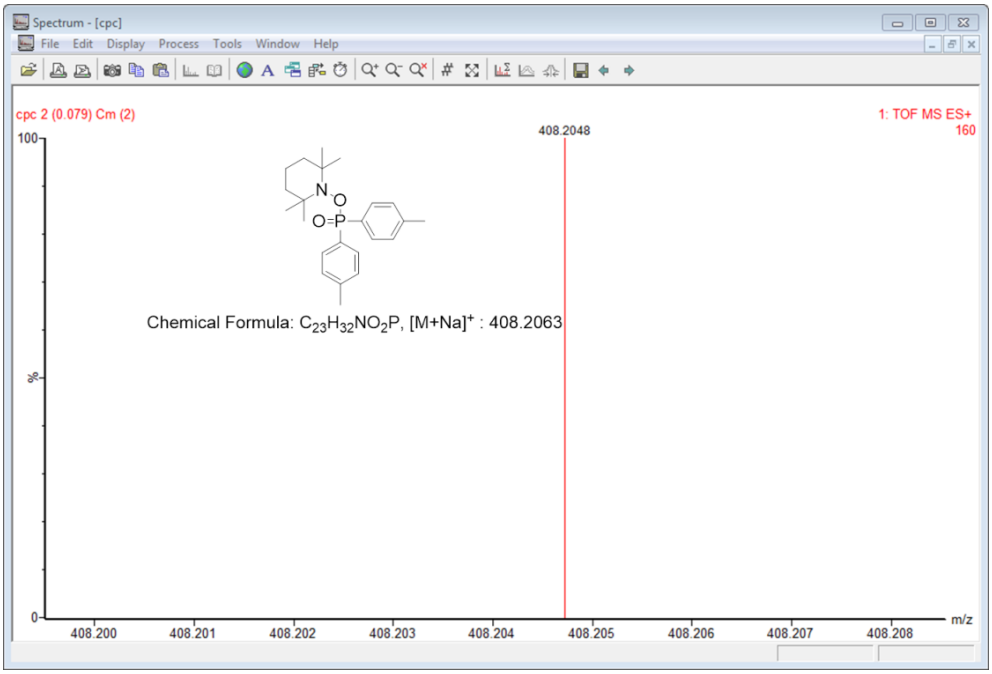
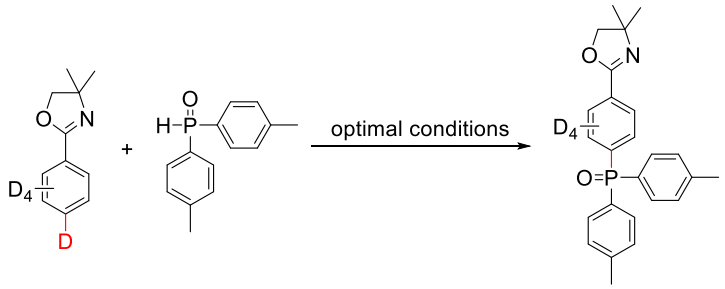


Figure S1 HRMS of the TEMPO-**2a** adduct

5.2 H/D exchange experiment



1a-D$_5$ **2a** **3aa-D$_4$**, 61%

A mixture of **1a-D$_5$** (36.1 mg, 0.2 mmol), **2a** (138.2 mg, 0.6 mmol), $AgNTf_2$ (7.7 mg, 0.02 mmol), $K_2S_2O_8$ (162.6 mg, 0.6 mmol) and PivOH (11 μL, 0.1 mmol) was added to a 25 mL Schlenk flask. The tube was evacuated and backfilled with argon three times. Subsequently, MeCN (1.0 mL) was added via syringe. The resulting mixture was stirred at 120 ºC for 24 h. Then, the reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL). The solution was extracted with dichloromethane (3 × 20 mL). The organic phase was collected, dried with anhydrous Na_2SO_4 and concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) as the eluent to give product **3aa-D$_4$** (49.7 mg, 61% yield). According to the ^{1}H NMR analysis, no H/D exchange occurred (**Figure S2**).

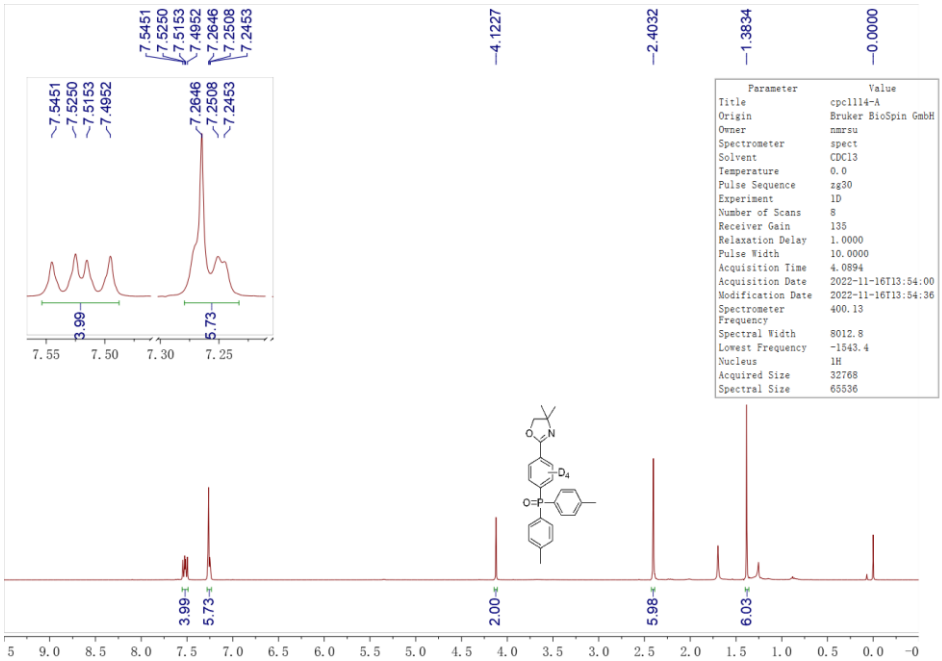
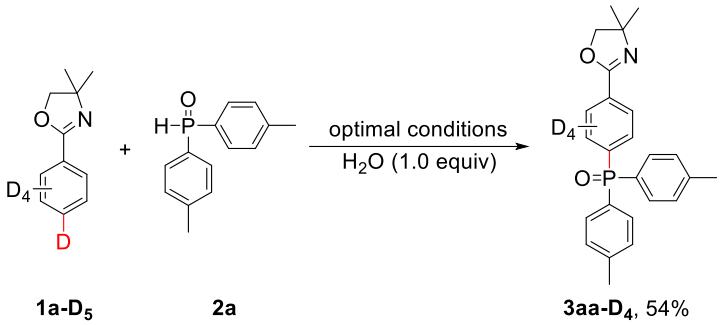


Figure S2 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3aa-D$_4$**



A mixture of **1a-D$_5$** (36.2 mg, 0.2 mmol), **2a** (138.2 mg, 0.6 mmol), $AgNTf_2$ (7.7 mg, 0.02 mmol), $K_2S_2O_8$ (162.2 mg, 0.6 mmol), PivOH (11 μL, 0.1 mmol) and H_2O (3.6 μL, 0.2 mmol) was added to a 25 mL Schlenk flask. The tube was evacuated and backfilled with argon three times. Subsequently, MeCN (1.0 mL) was added via syringe. The resulting mixture was stirred at 120 °C for 24 h. Then, the reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL). The solution was extracted with dichloromethane (3 × 20 mL). The organic phase was collected, dried with anhydrous Na_2SO_4 and concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) as the eluent to give product **3aa-D$_4$** (44.1 mg, 54% yield). According to the ^{1}H NMR analysis, no H/D exchange occurred (**Figure S3**).

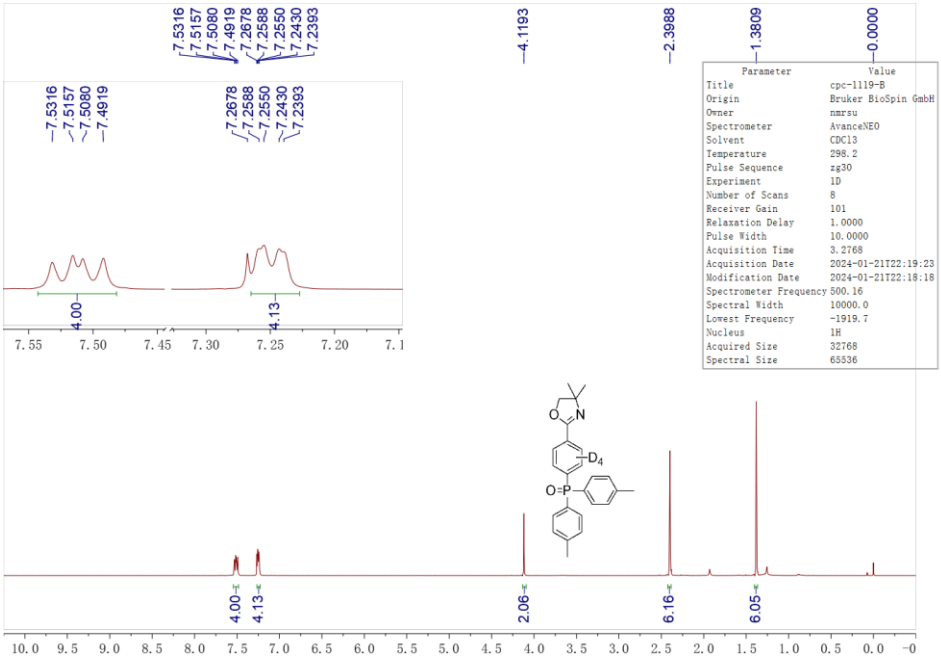
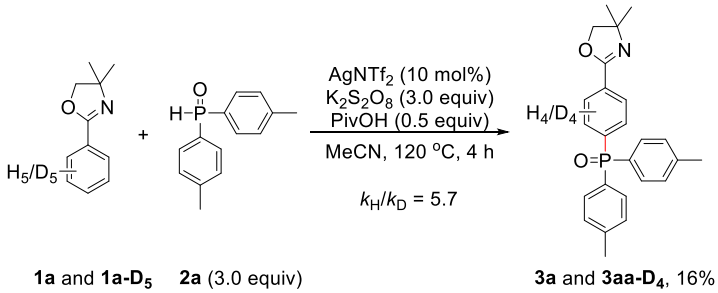


Figure S3 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3aa-D$_4$**

5.3 Intermolecular kinetic isotope effect study



A mixture of **1a** (17.0 μL, 0.1 mmol), **1a-D5** (18.0 mg, 0.1 mmol), **2a** (138.2 mg, 0.6 mmol), $AgNTf_2$ (7.7 mg, 0.02 mmol), $K_2S_2O_8$ (162.5 mg, 0.6 mmol) and PivOH (11 μL, 0.1 mmol) was added to a 25 mL Schlenk flask. The tube was evacuated and backfilled with argon three times. Subsequently, MeCN (1.0 mL) was added via syringe. The resulting mixture was stirred at 120 °C for 4 h. Then, the reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL). The solution was extracted with dichloromethane (3 × 20 mL). The organic phase was collected, dried with anhydrous Na_2SO_4 and concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) as the eluent to give products **3aa** and **3aa-D4** (12.9 mg, 16% yield). Based on the integrations related to different proton resonances (**Figure S4**), the kinetic isotope effect (KIE) was determined to be k_H/k_D = 5.7.

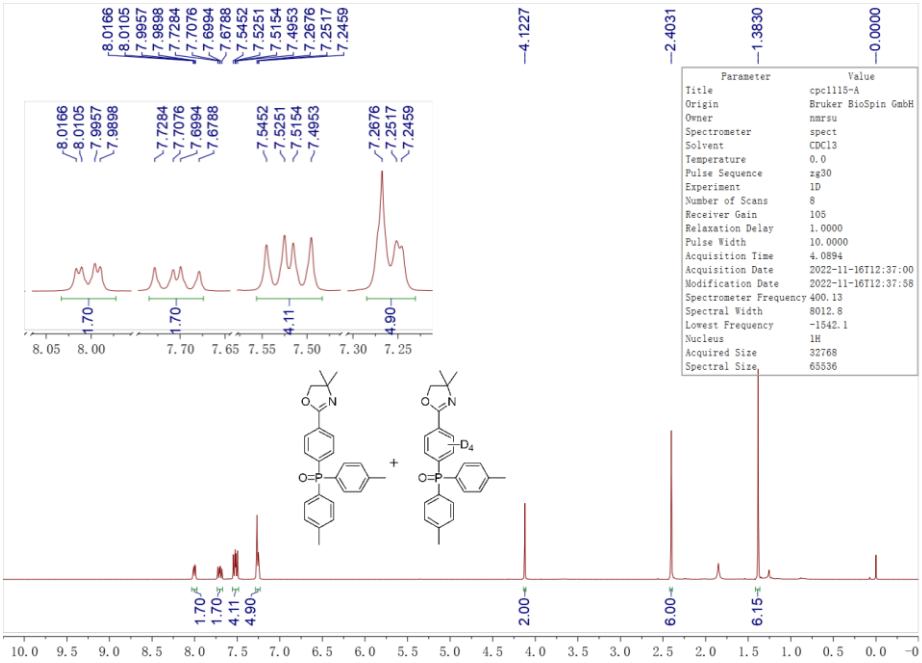
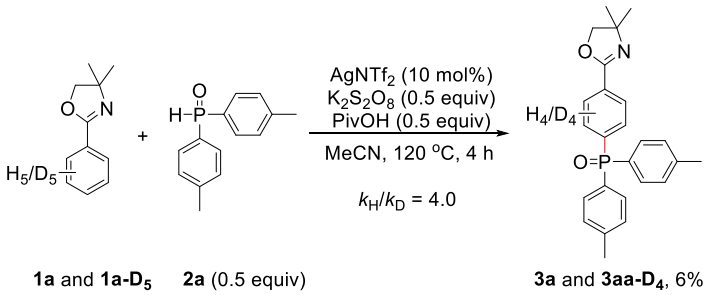


Figure S4 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compounds **3aa** and **3aa-D4**



A mixture of **1a** (17.0 μL, 0.1 mmol), **1a-D5** (18.1 mg, 0.1 mmol), **2a** (23.1 mg, 0.1 mmol), $AgNTf_2$ (7.8 mg, 0.02 mmol), $K_2S_2O_8$ (27.5 mg, 0.1 mmol) and PivOH (11 μL, 0.1 mmol) was added to a 25 mL Schlenk flask. The tube was evacuated and backfilled with argon three times. Subsequently, MeCN (1.0 mL) was added via syringe. The resulting mixture was stirred at 120 °C for 4 h. Then, the reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL). The solution was extracted with dichloromethane (3 × 20 mL). The organic phase was collected, dried with anhydrous Na_2SO_4 and concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) as the eluent to give products **3aa** and **3aa-D4** (4.7 mg, 6% yield). Based on the integrations related to different proton resonances (**Figure S5**), the kinetic isotope effect (KIE) was determined to be k_H/k_D = 4.0.

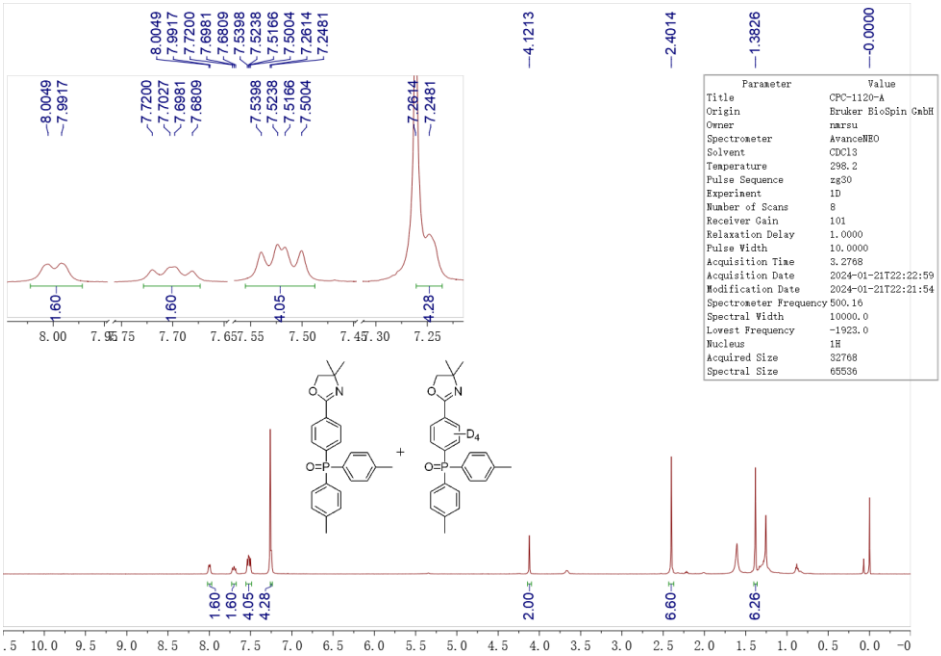


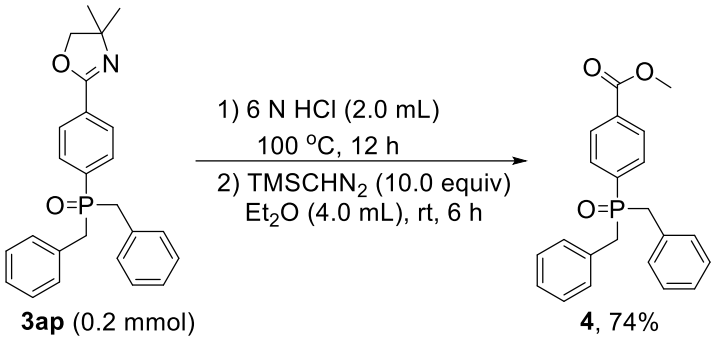
Figure S5 ^1H NMR (500 MHz, $CDCl_3$) spectra of compounds **3aa** and **3aa-D4**

6. Typical reaction at the 5.0-mmol scale

To a 100 mL Schlenk tube with a magnetic stir bar were added **1a** (850 μL, 5.0 mmol), **2b** (3.03 g, 15.0 mmol), $AgNTf_2$ (194.1 mg, 0.5 mmol), $K_2S_2O_8$ (4.05 g, 15.0 mmol) and PivOH (275 μL, 2.5 mmol). The mixture was then evacuated and backfilled with argon three times. Subsequently, MeCN (25 mL) was added via syringe. The resulting mixture

was stirred at 120 ºC for 36 h. Then, the reaction was quenched with saturated aqueous $NaHCO_3$ (25 mL). The solution was extracted with dichloromethane (3 × 40 mL). The organic phase was collected, dried with anhydrous Na_2SO_4 and concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) as the eluent to give product **3ab** (953.6 mg, 51% yield).

7. Synthesis and characterization of product 4



To a 25 mL tube with a magnetic stir bar were added **3ap** (80.5 mg, 0.2 mmol) and 6 N HCl (2.0 mL). After stirring at 100 ℃ for 12 h, the reaction mixture was cooled to room temperature. Then, the solution was concentrated under vacuum. Then, (trimethylsilyl)diazomethane ($TMSCHN_2$, 295.5 μL, 2.0 mmol) was added, followed by Et_2O (4.0 mL). The resulting mixture was stirred at room temperature for another 6 h. Then, the reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL). The solution was extracted with dichloromethane (3 × 20 mL). The organic phase was collected, dried with anhydrous Na_2SO_4 and concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) as the eluent to give product **4** (53.7 mg, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.4, 2.5 Hz, 2H), 7.58 (dd, J = 10.4, 8.4 Hz, 2H), 7.25−7.18 (m, 6H), 7.13−7.09 (m, 4H), 3.93 (s, 3H), 3.38 (dd, J = 13.9, 3.6 Hz, 4H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4 (1C), 136.1 (1C, d, $J_{C\text{-}P}$ = 91.4 Hz), 133.1 (1C, d, $J_{C\text{-}P}$ = 2.8 Hz), 131.4 (2C, d, $J_{C\text{-}P}$ = 8.6 Hz), 131.0 (2C, d, $J_{C\text{-}P}$ = 7.5 Hz), 130.0 (4C, d, $J_{C\text{-}P}$ = 5.4 Hz), 129.3 (2C, d, $J_{C\text{-}P}$ = 11.6 Hz), 128.8 (4C, d, $J_{C\text{-}P}$ = 2.5 Hz), 127.2 (2C, d, $J_{C\text{-}P}$ = 2.8 Hz), 52.6 (1C), 37.4 (2C, d, $J_{C\text{-}P}$ = 63.6 Hz);

^{31}P NMR (202 MHz, $CDCl_3$) δ 34.9;

HRMS (ESI) *m/z*: Calcd for $C_{22}H_{22}O_3P$ $[M+H]^+$ 365.1301; found 365.1299.

8. References

1) M. Trose, F. Lazreg, M. Lesieur and C. S. J. Cazin, *J. Org. Chem.* 2015, **80**, 9910–9914.

2) E. Jablonkai and G. Keglevich, *Tetrahedron Lett.* 2015, **56**, 1638–1640.

9. NMR spectra of compounds 3 and 4

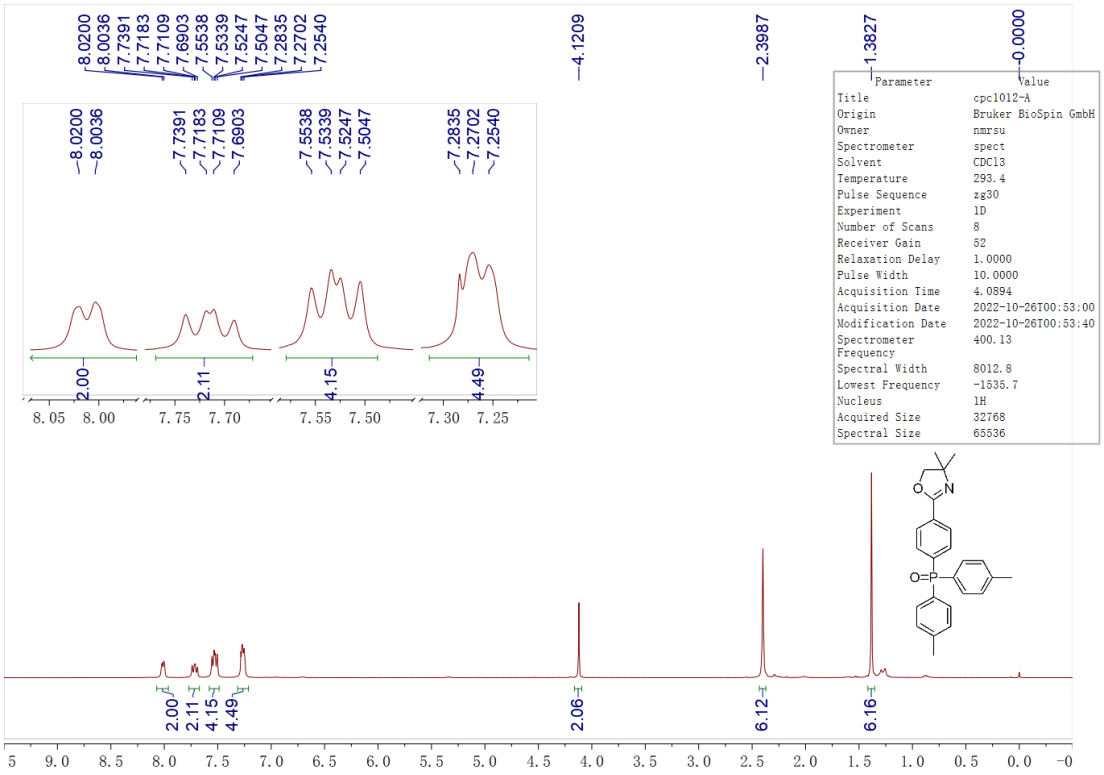


Figure S6 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3aa**

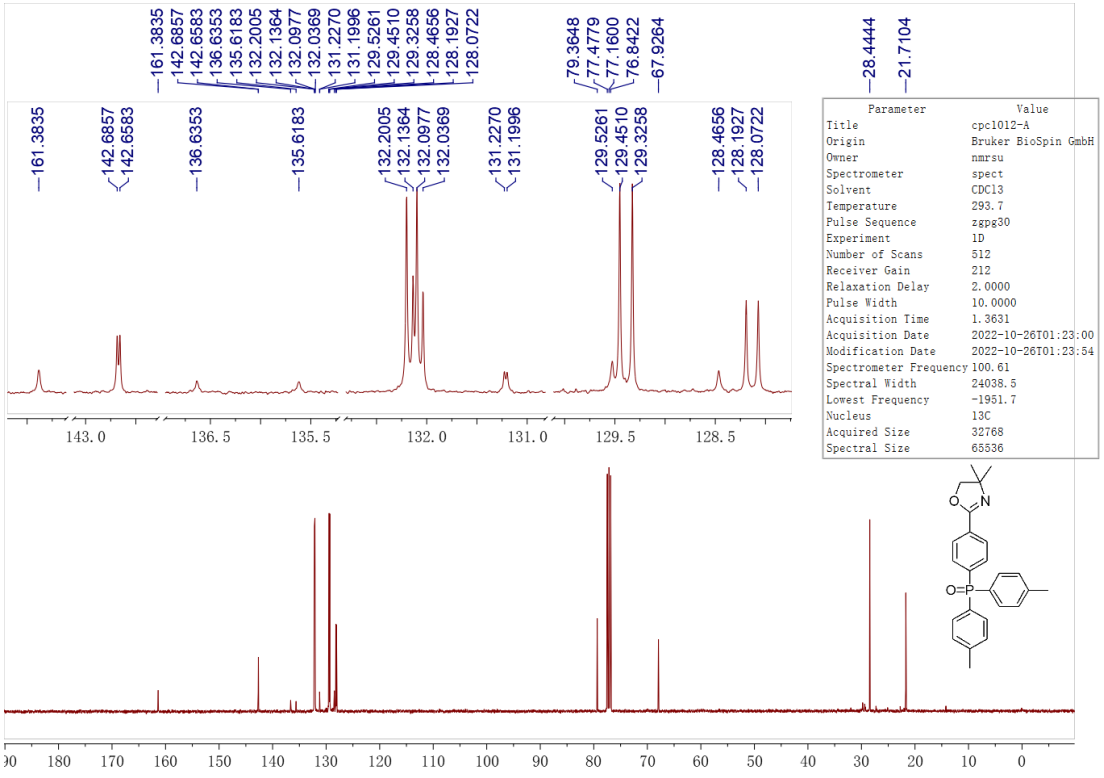


Figure S7 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3aa**

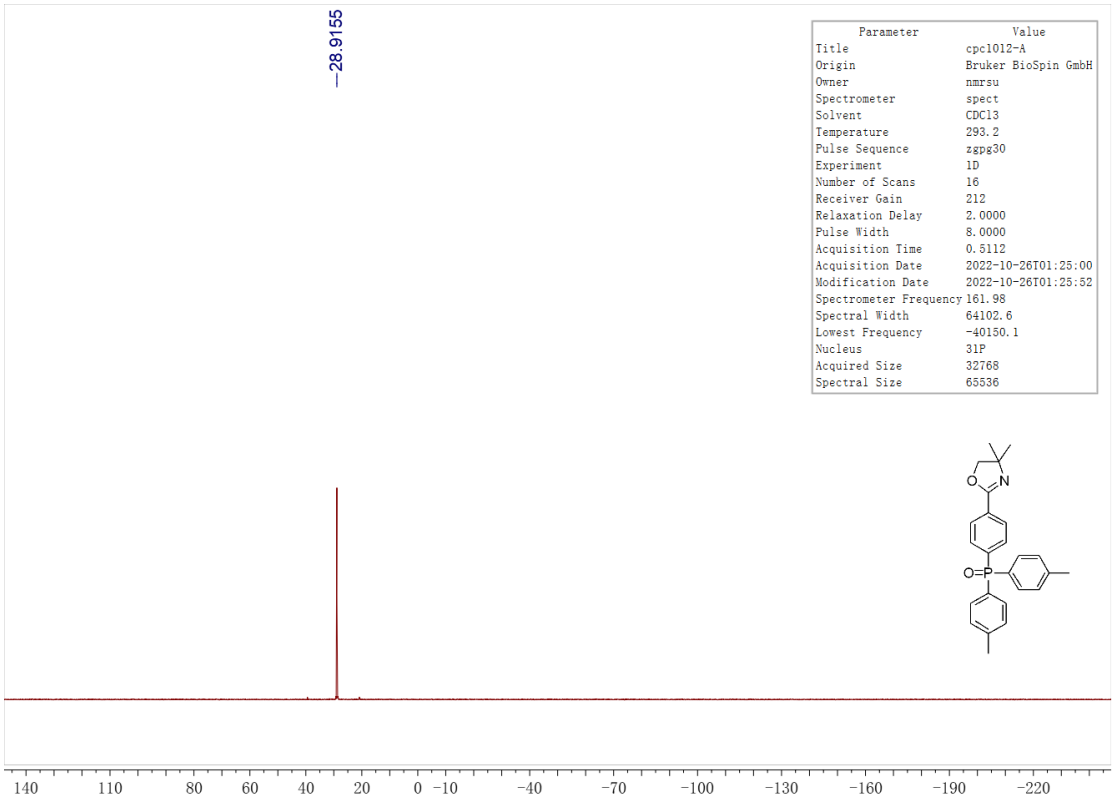


Figure S8 ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3aa**

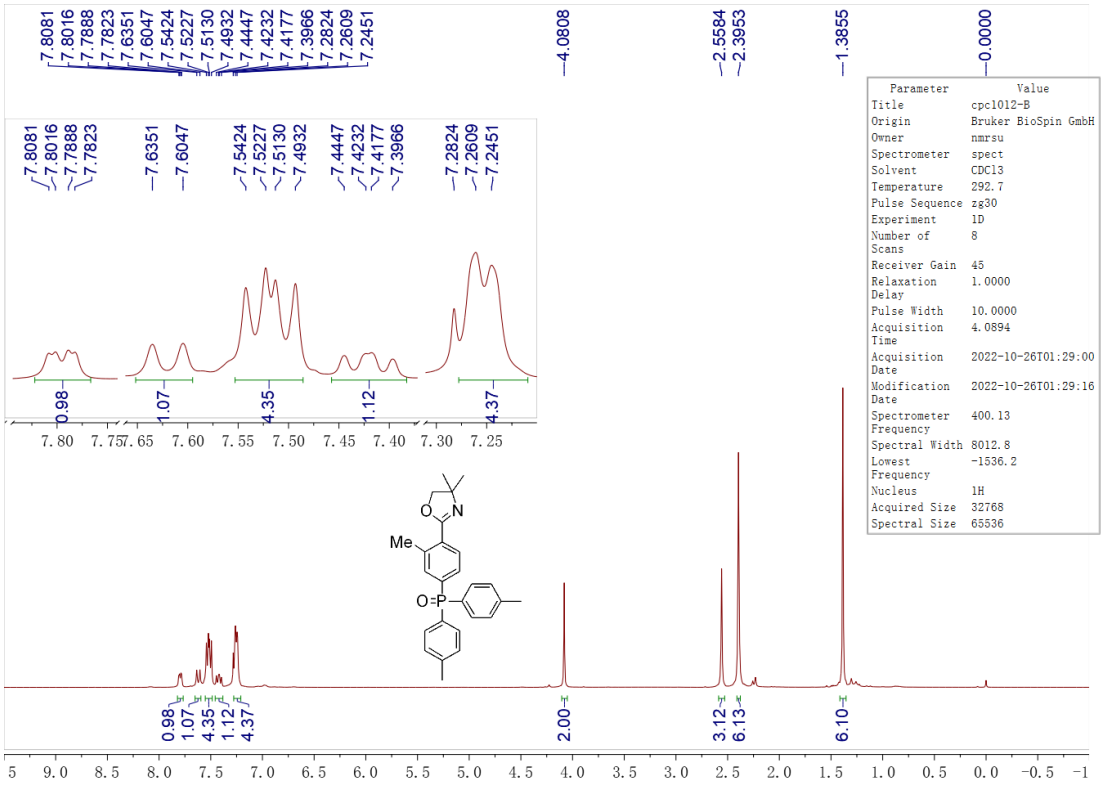


Figure S9 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ba**

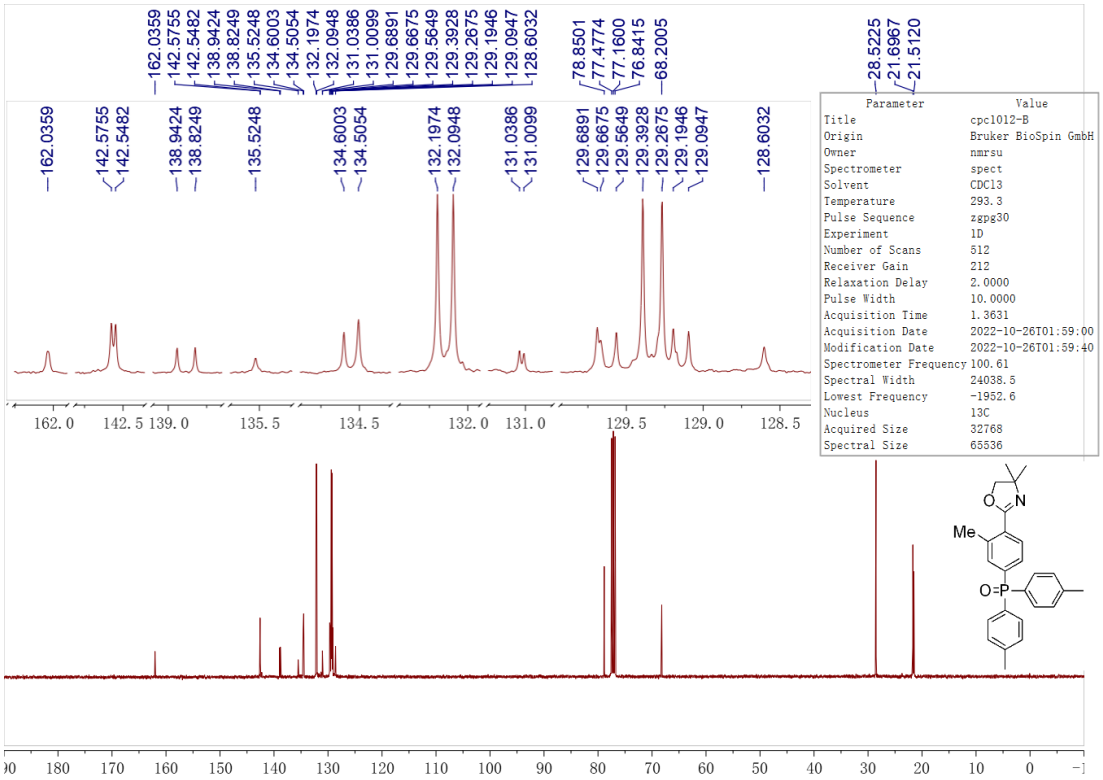


Figure S10 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3ba**

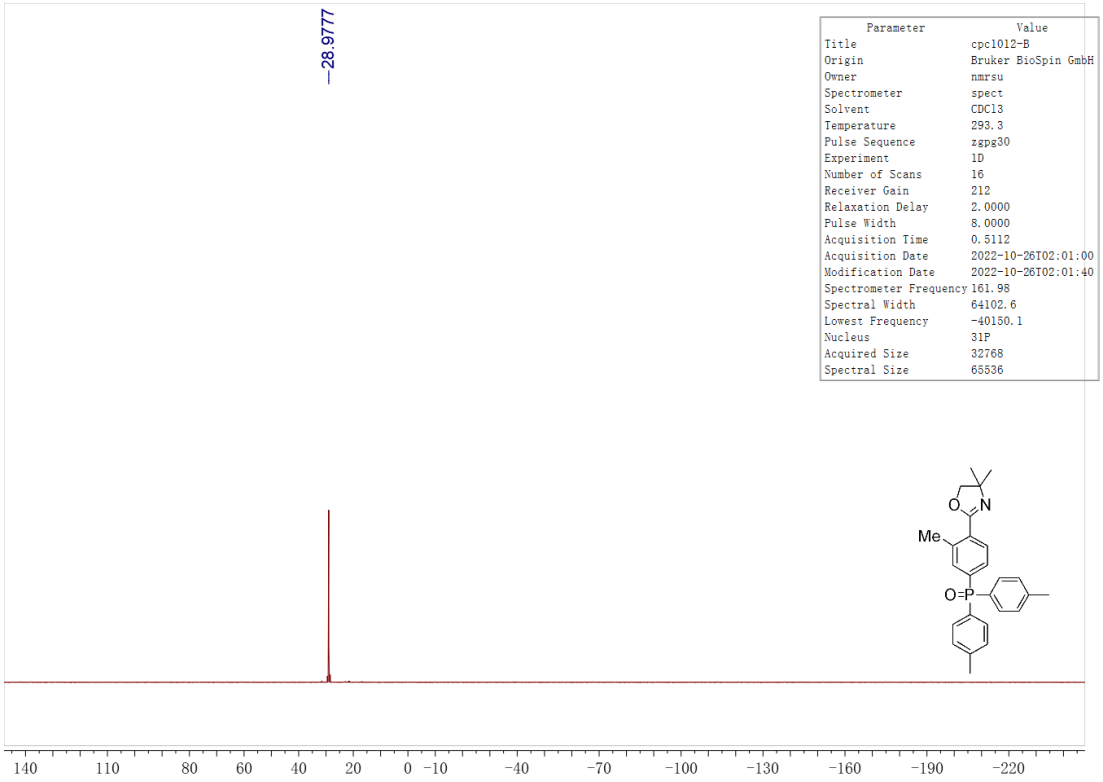


Figure S11 ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3ba**

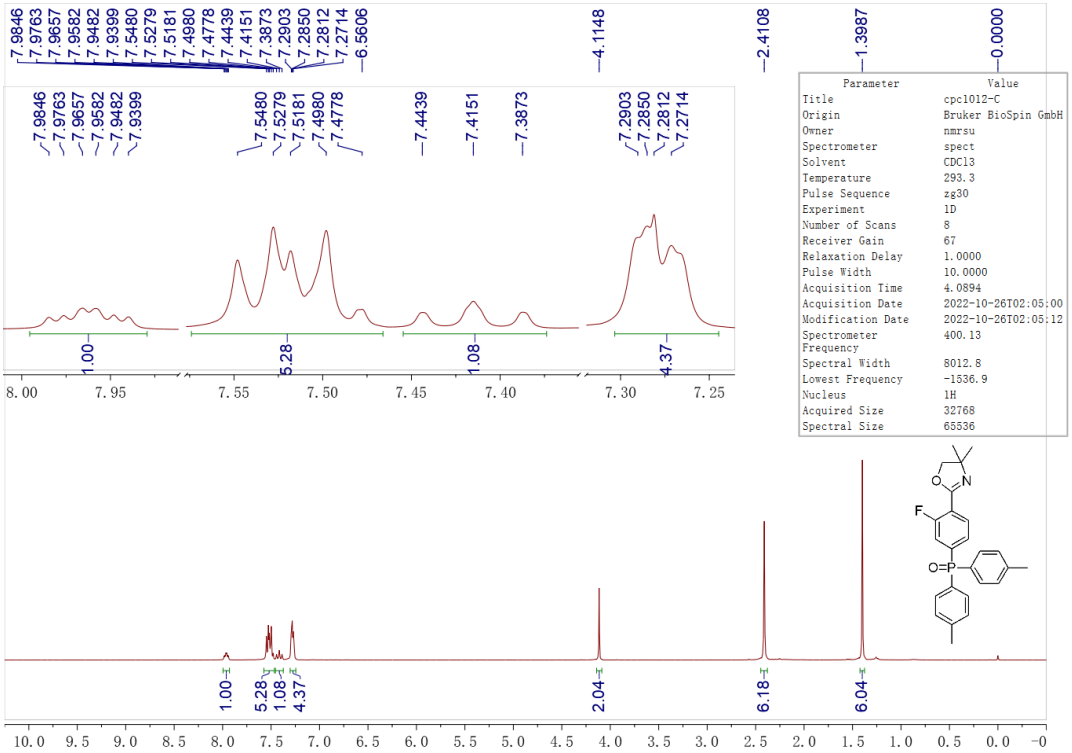


Figure S12 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ca**

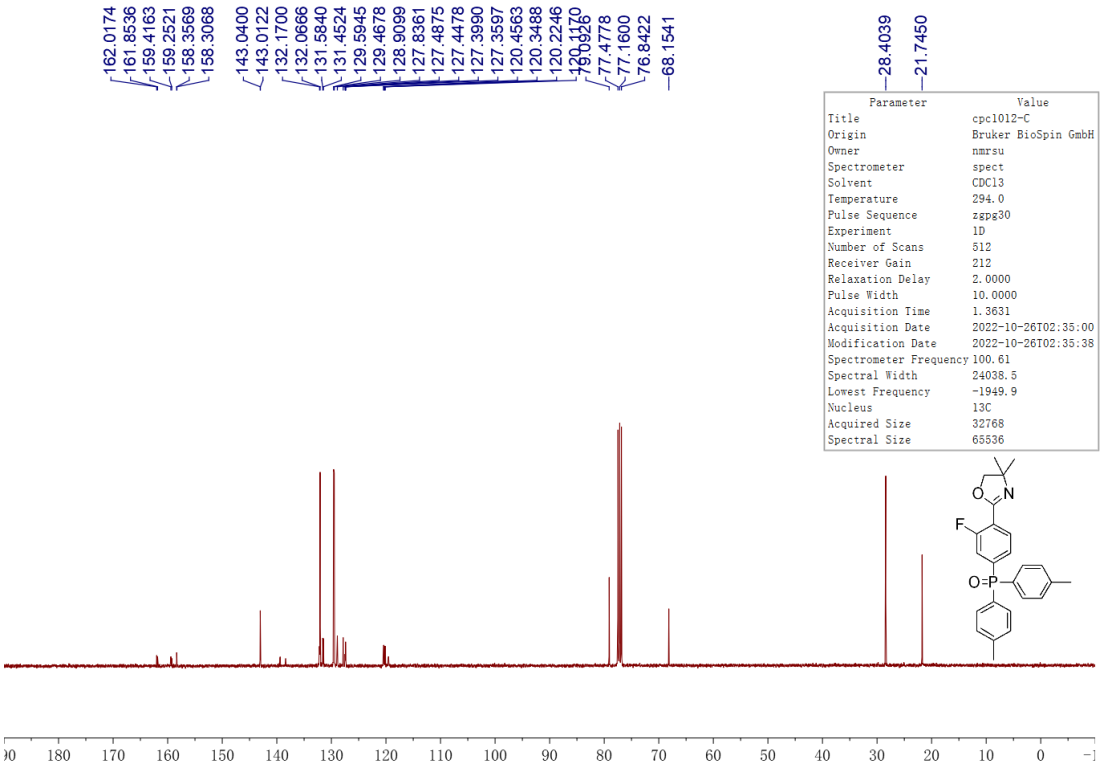


Figure S13 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3ca**

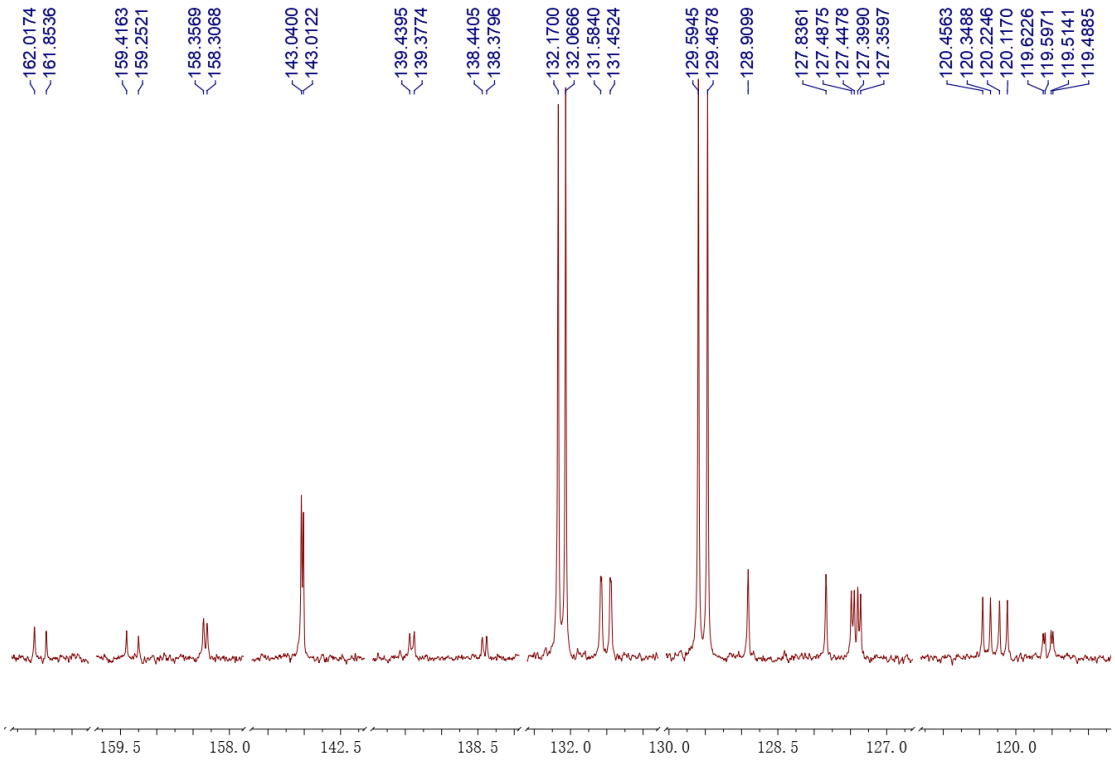


Figure S14 Expanded ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3ca**

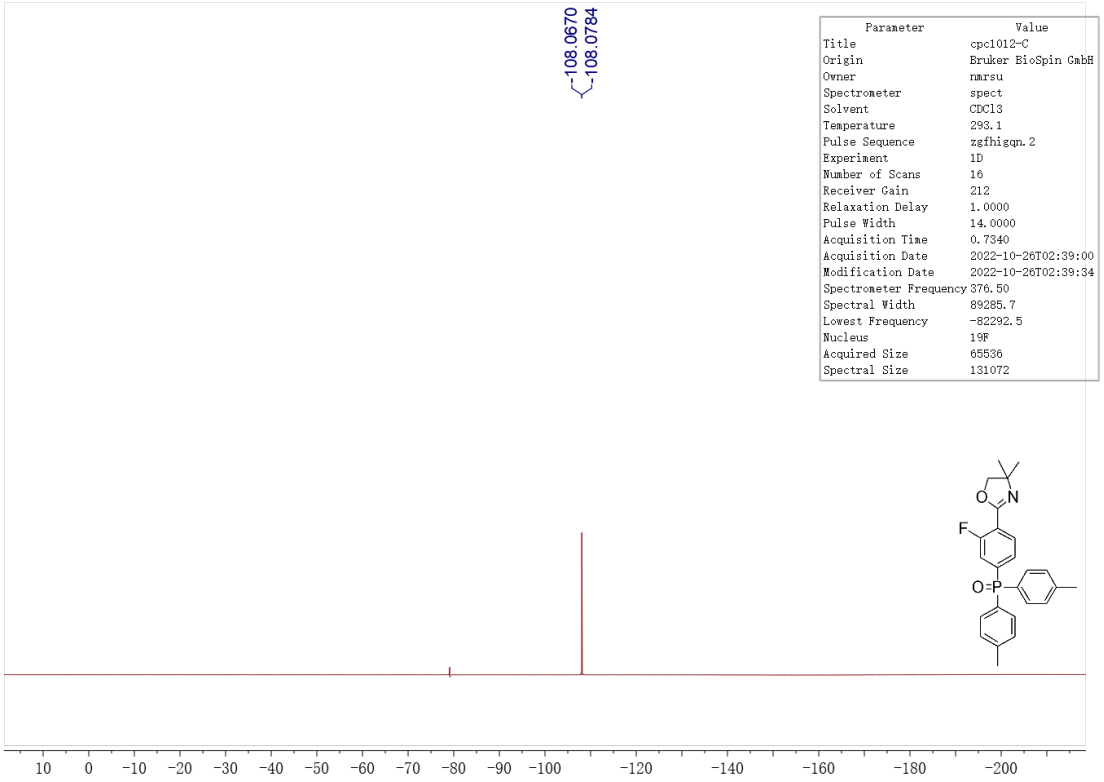


Figure S15 ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of compound **3ca**

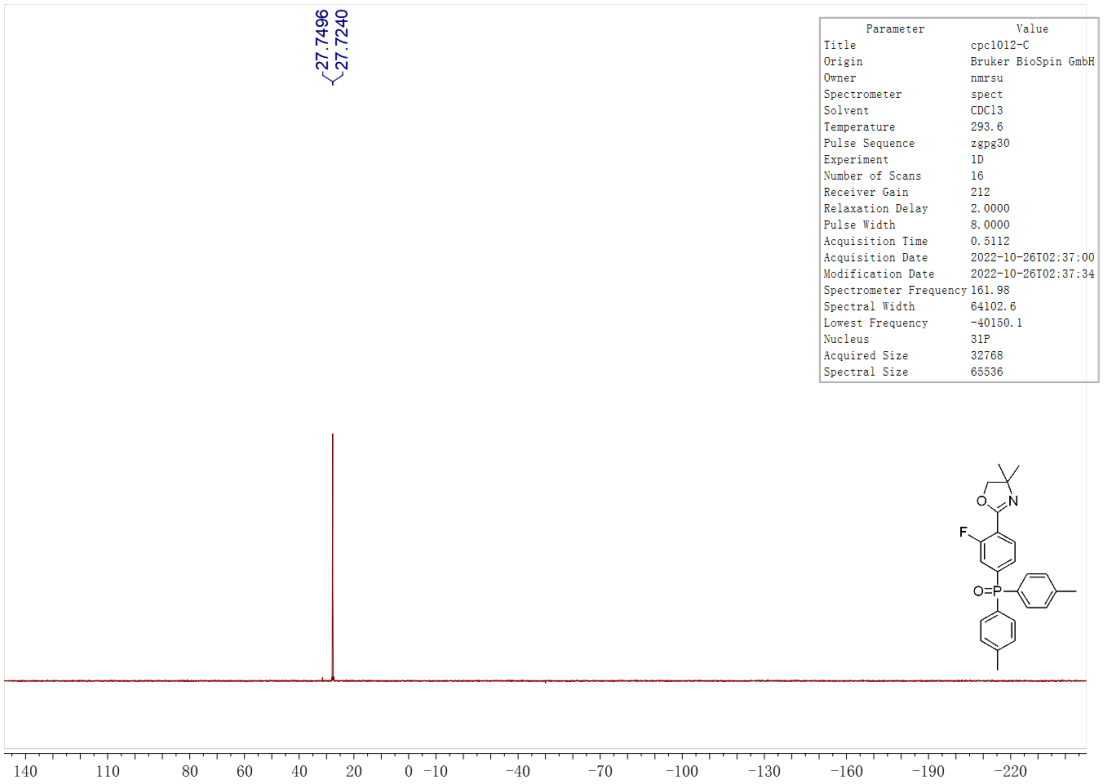


Figure S16 ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3ca**

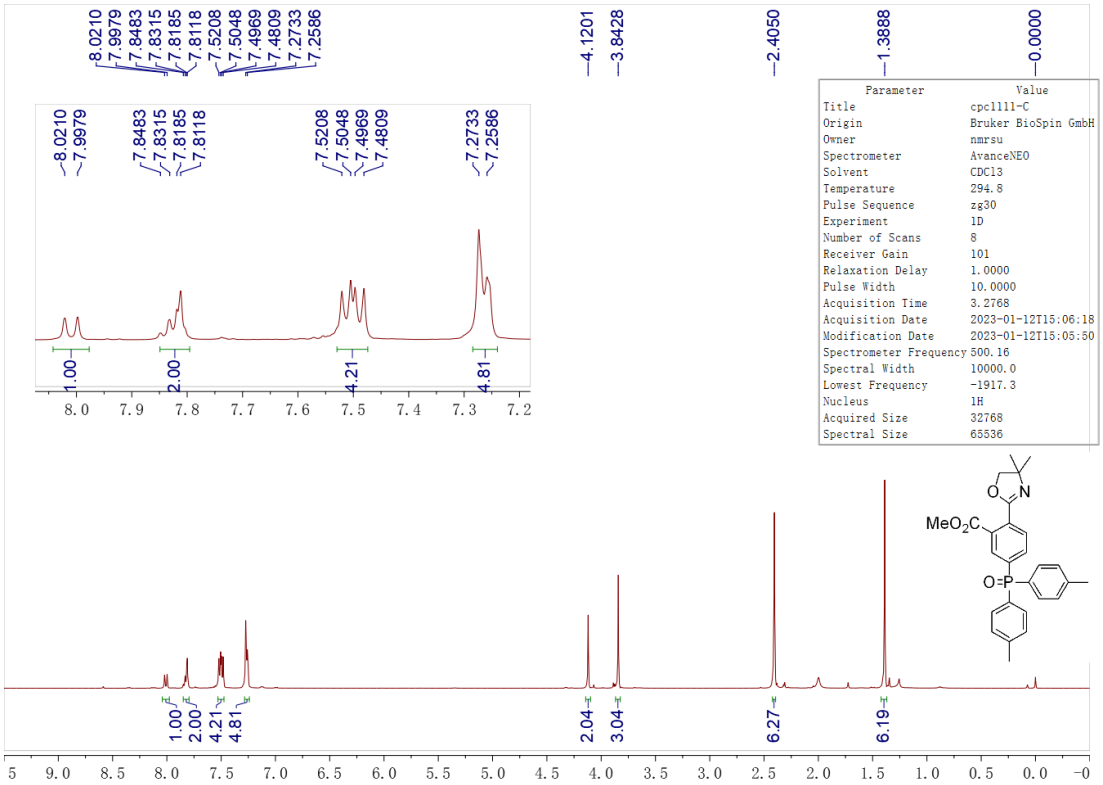


Figure S17 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3da**

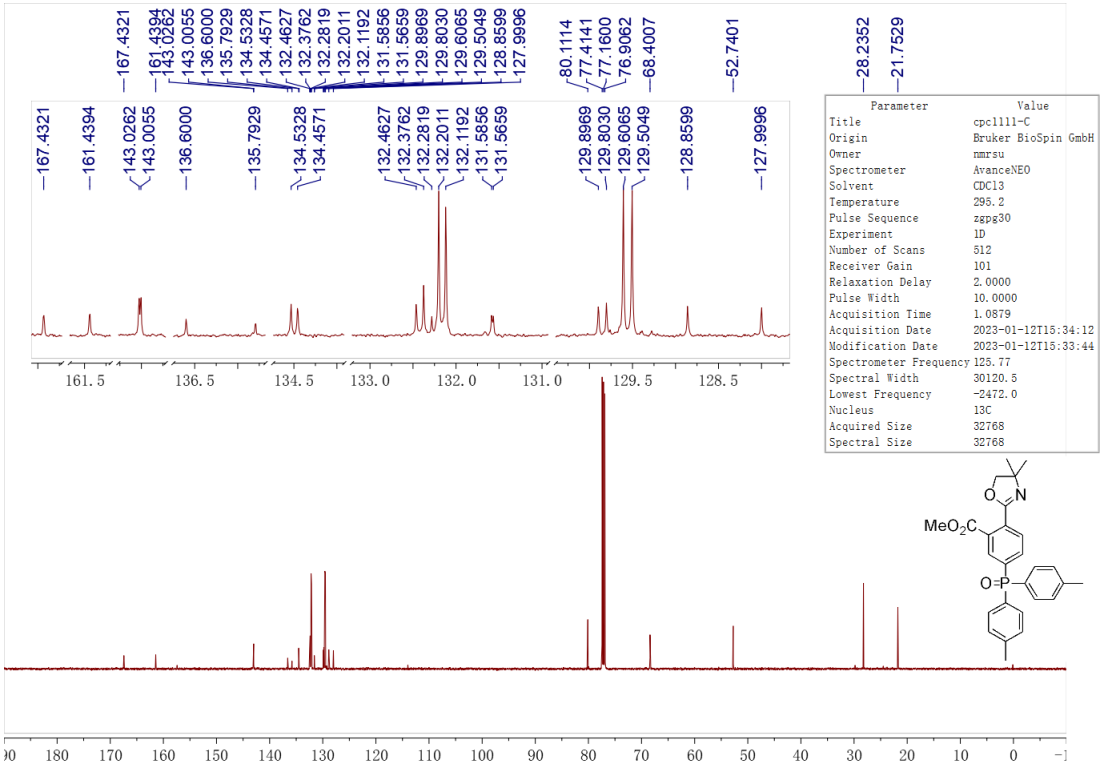


Figure S18 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3da**

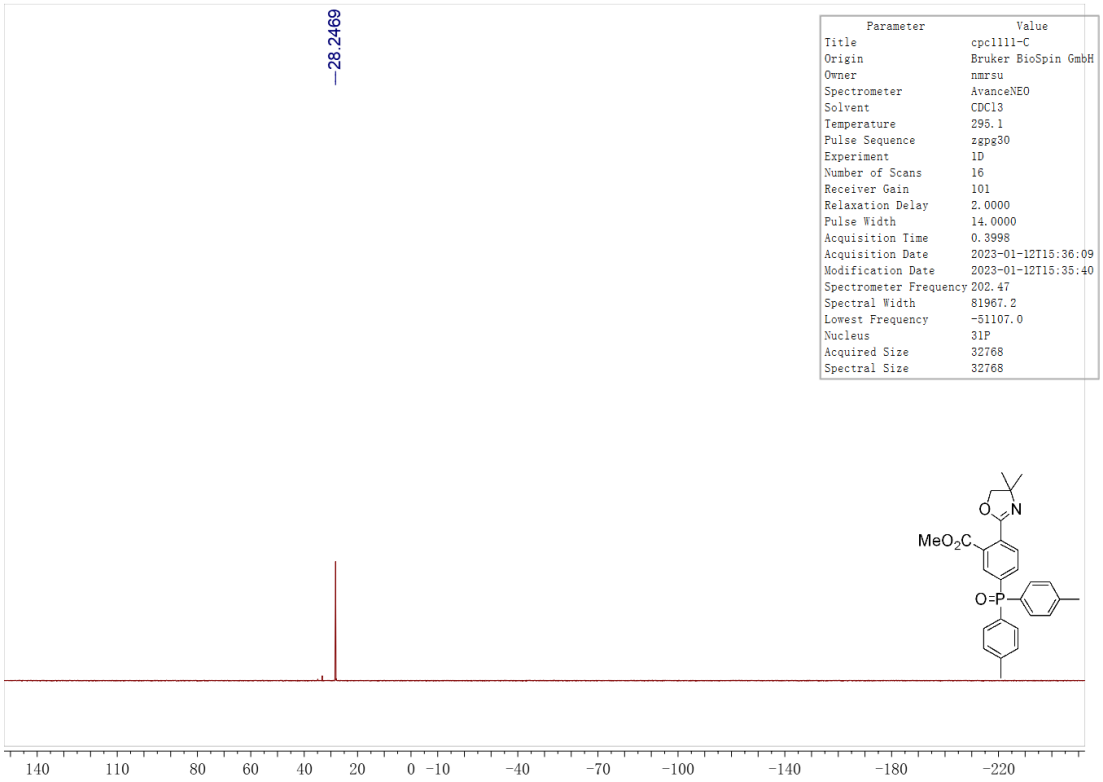


Figure S19 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3da**

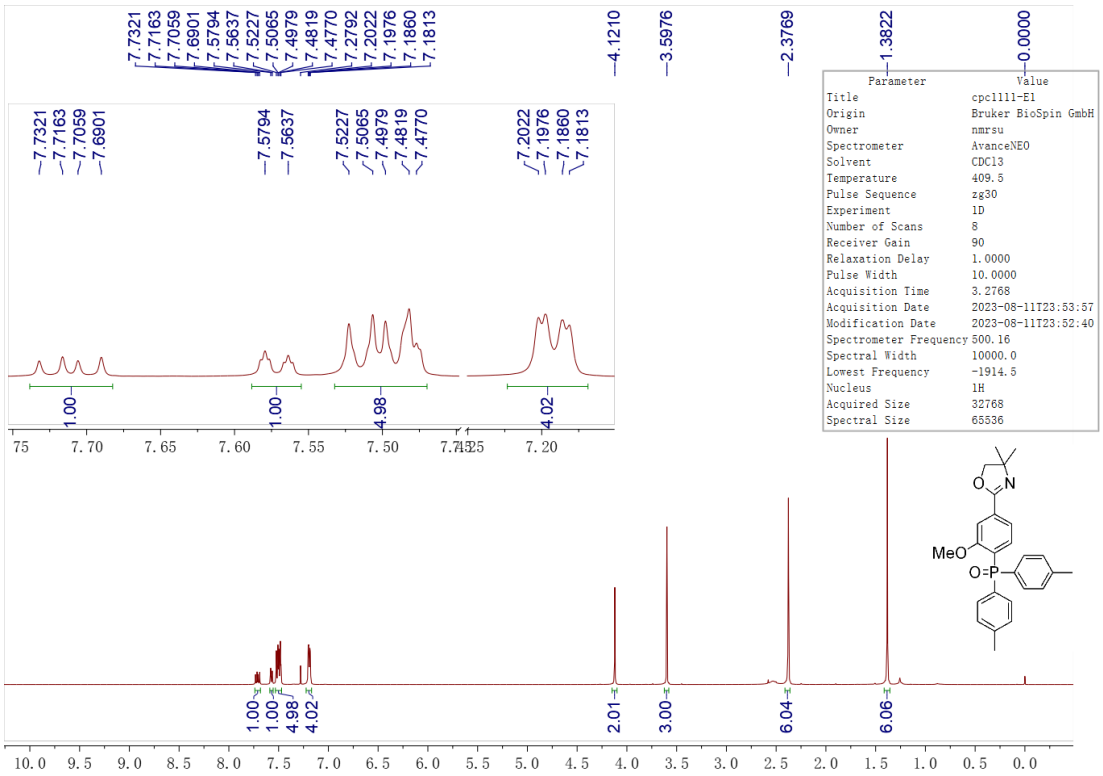


Figure S20 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3ea**

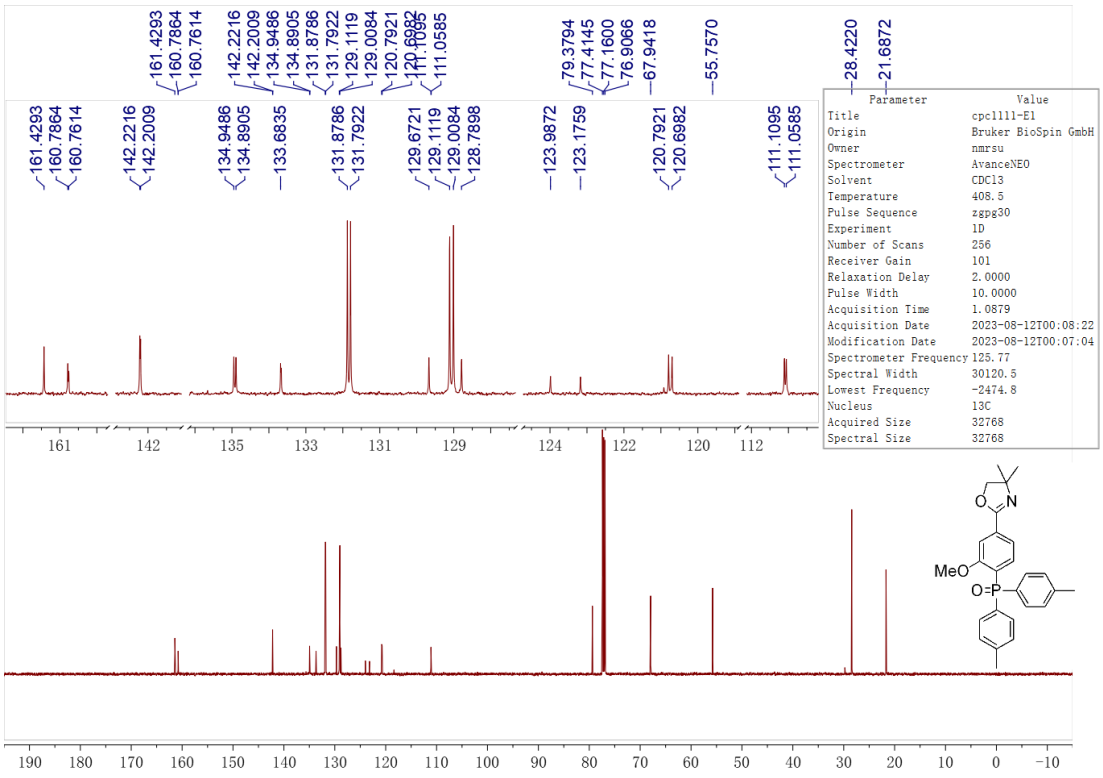


Figure S21 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3ea**

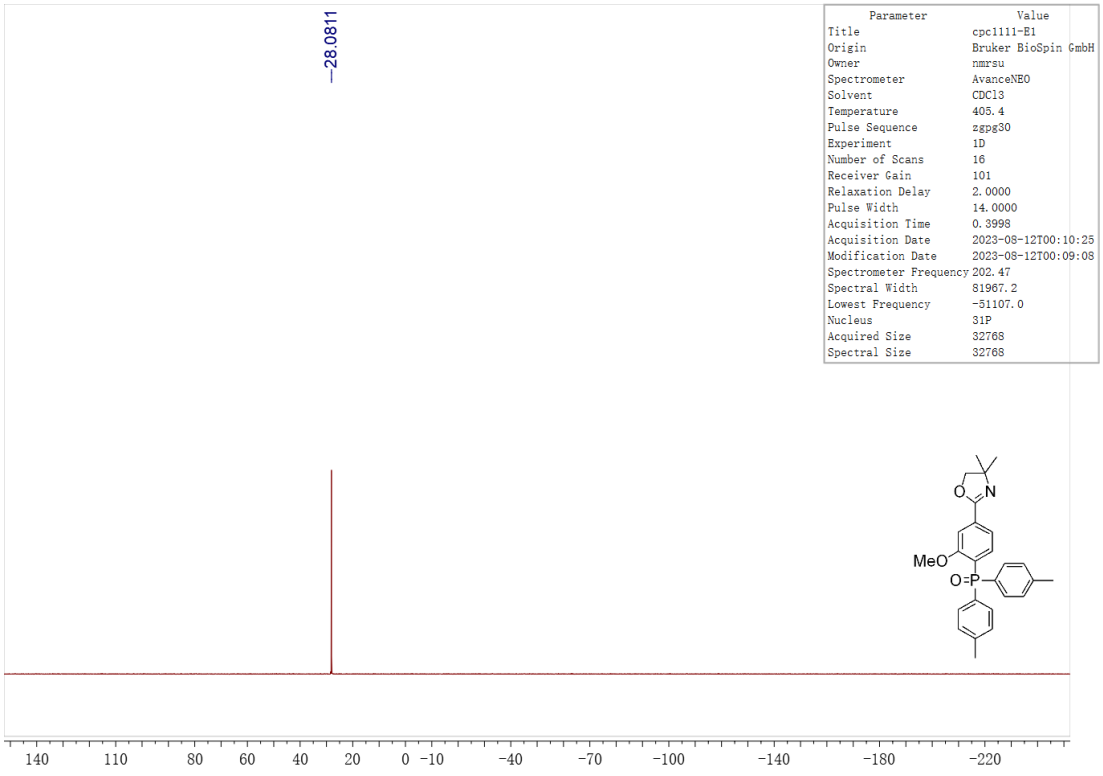


Figure S22 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3ea**

Figure S23 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3fa**

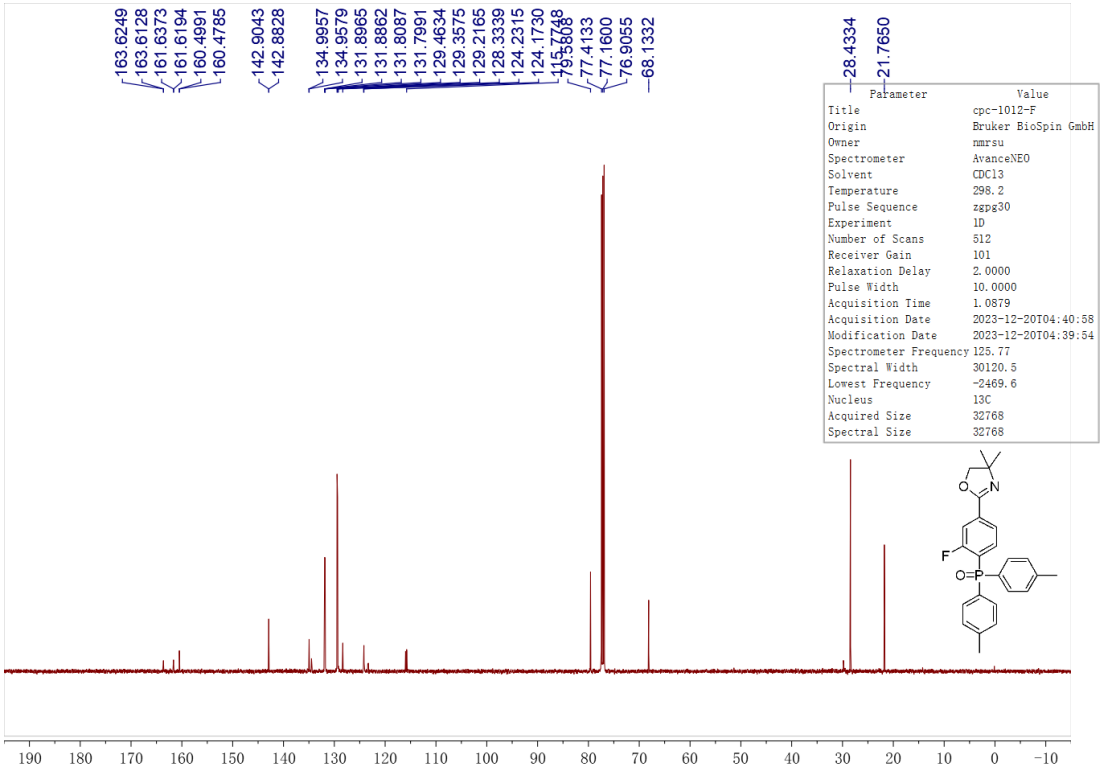


Figure S24 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3fa**

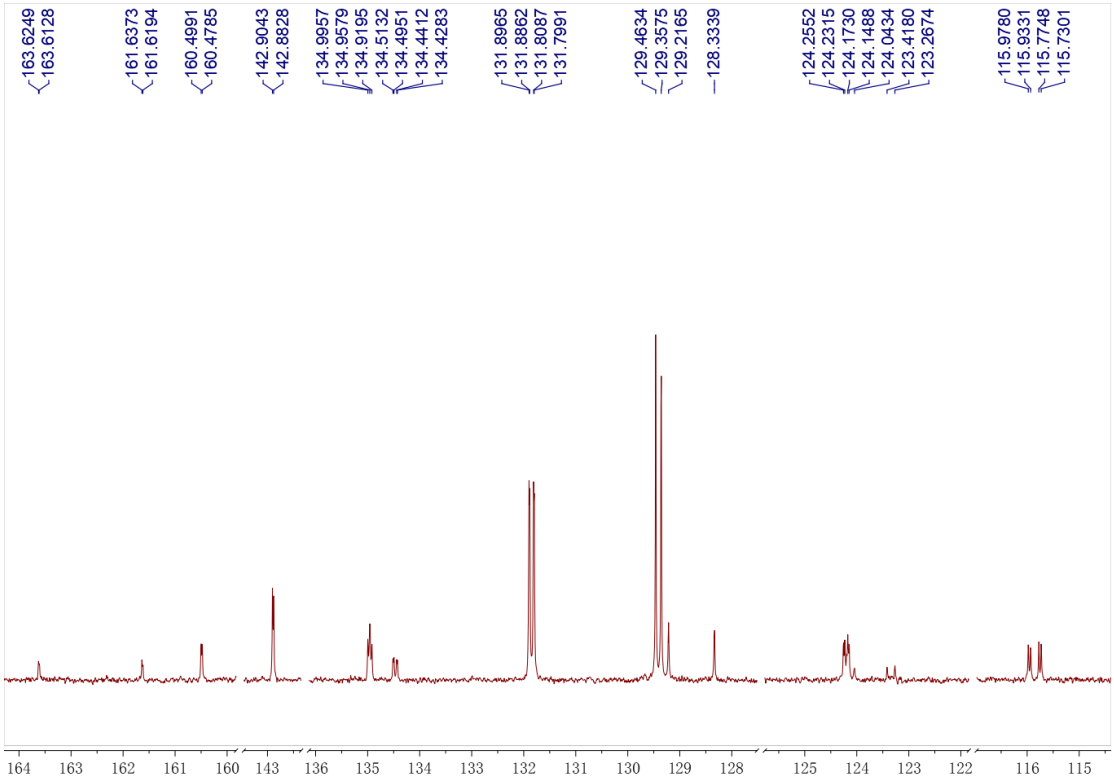


Figure S25 Expanded ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3fa**

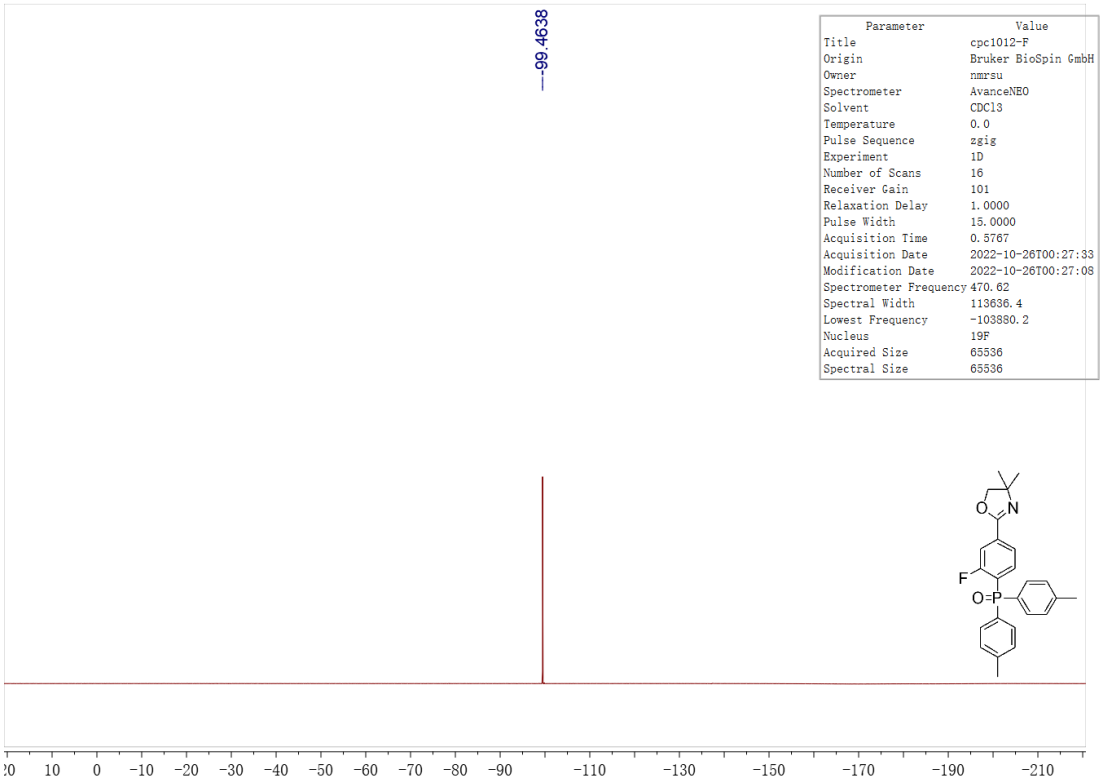


Figure S26 ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound **3fa**

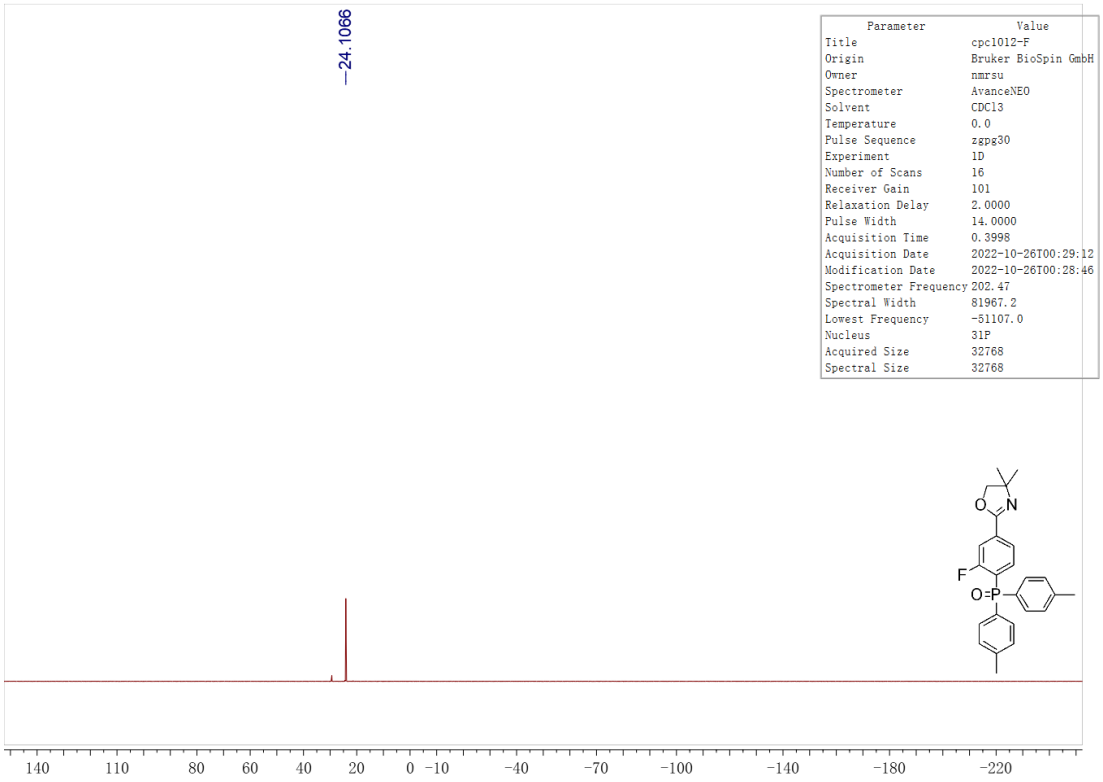


Figure S27 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3fa**

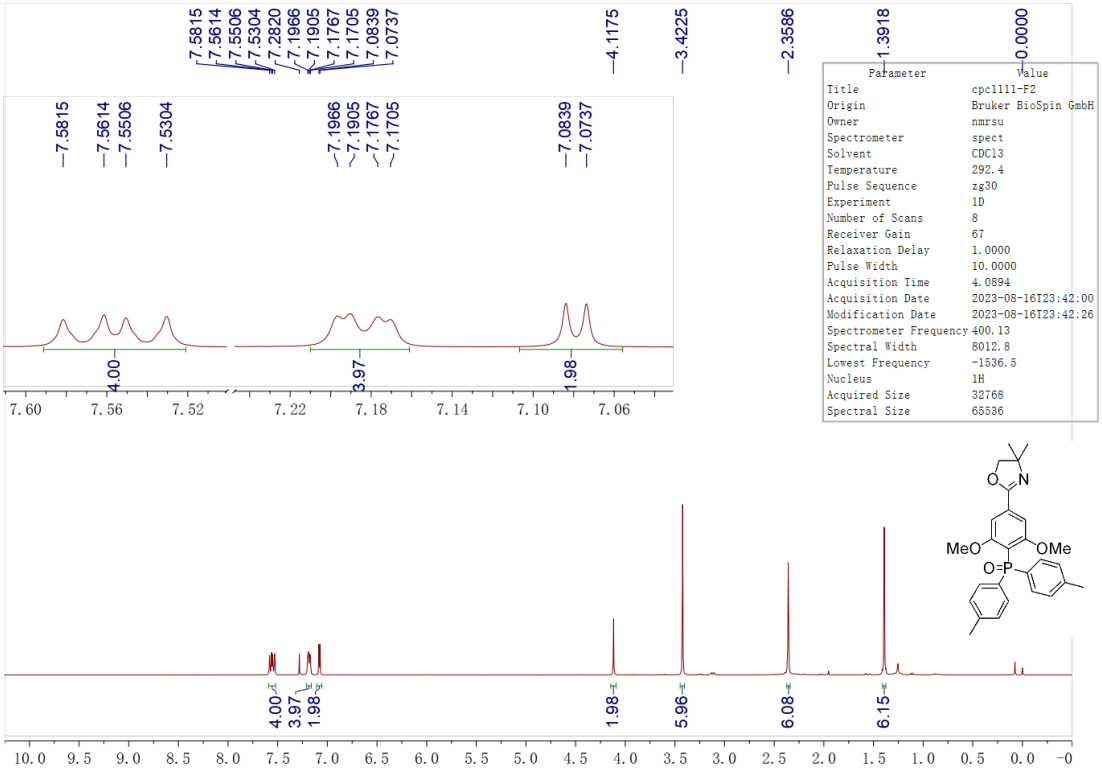


Figure S28 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ga**

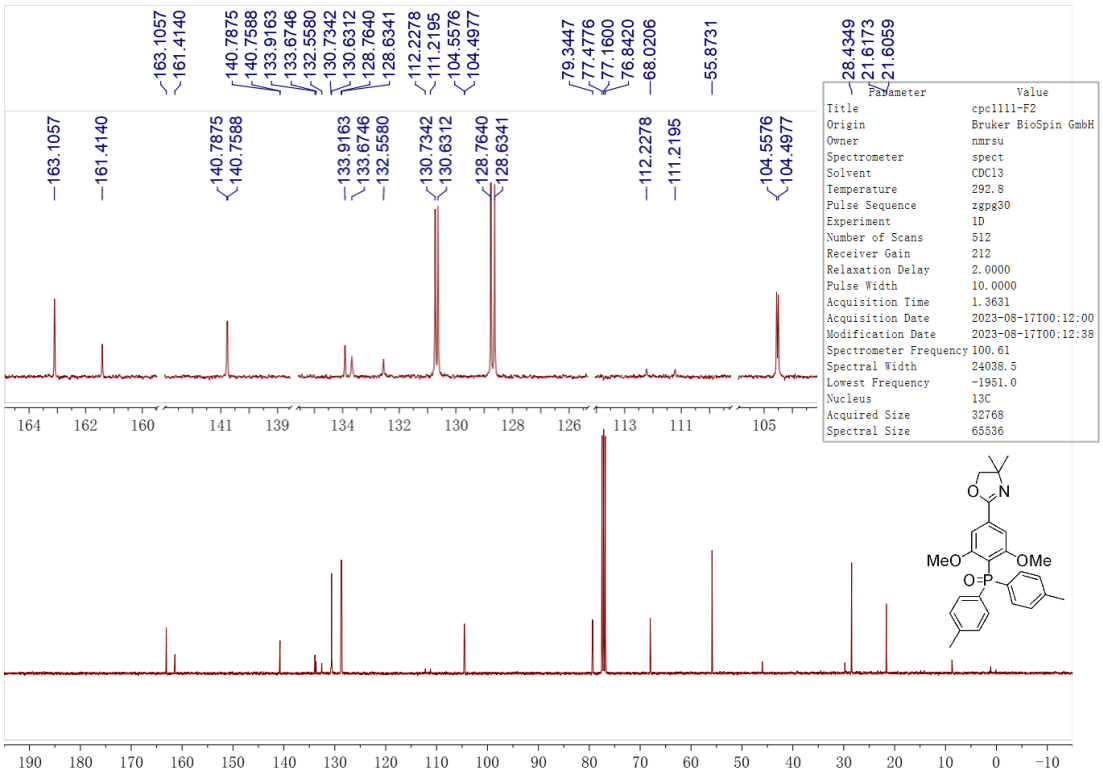


Figure S29 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3ga**

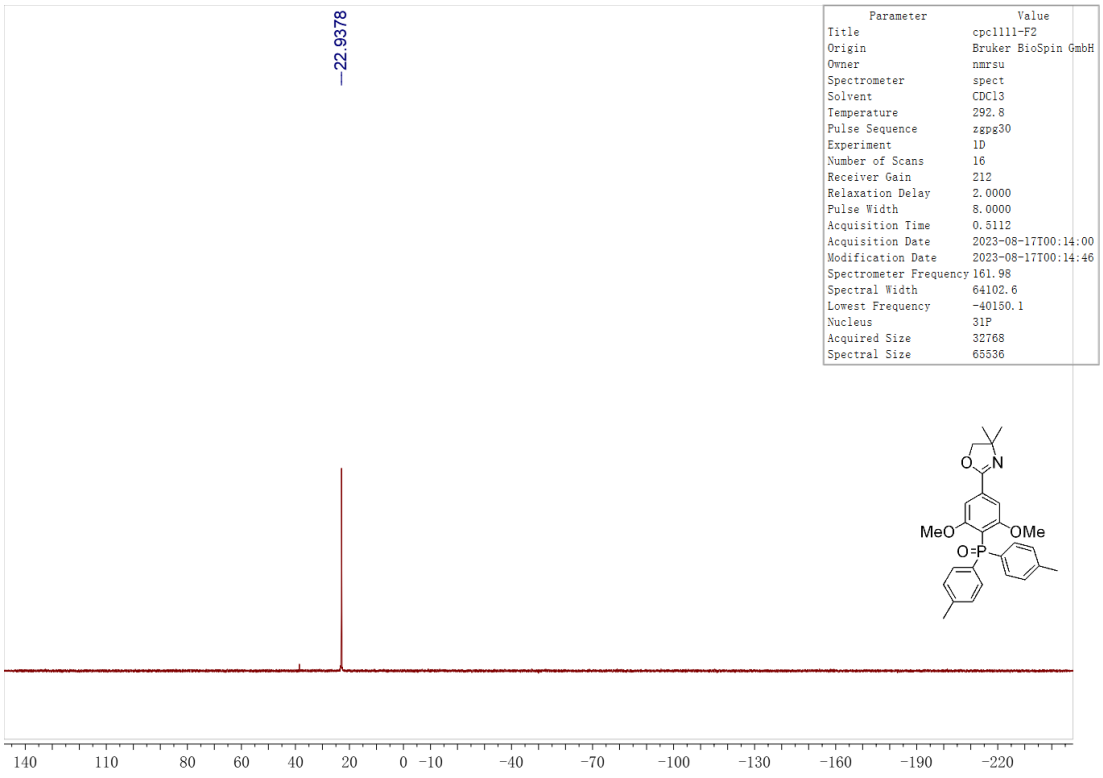


Figure S30 ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3ga**

Figure S31 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ha**

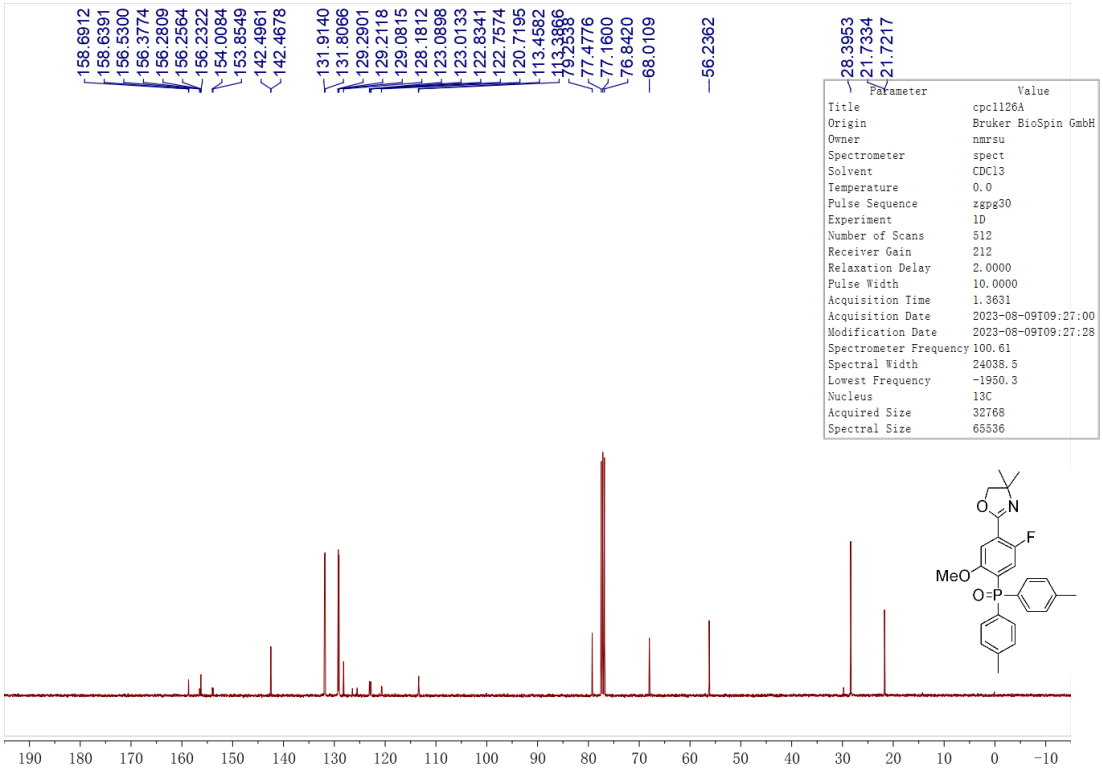


Figure S32 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3ha**

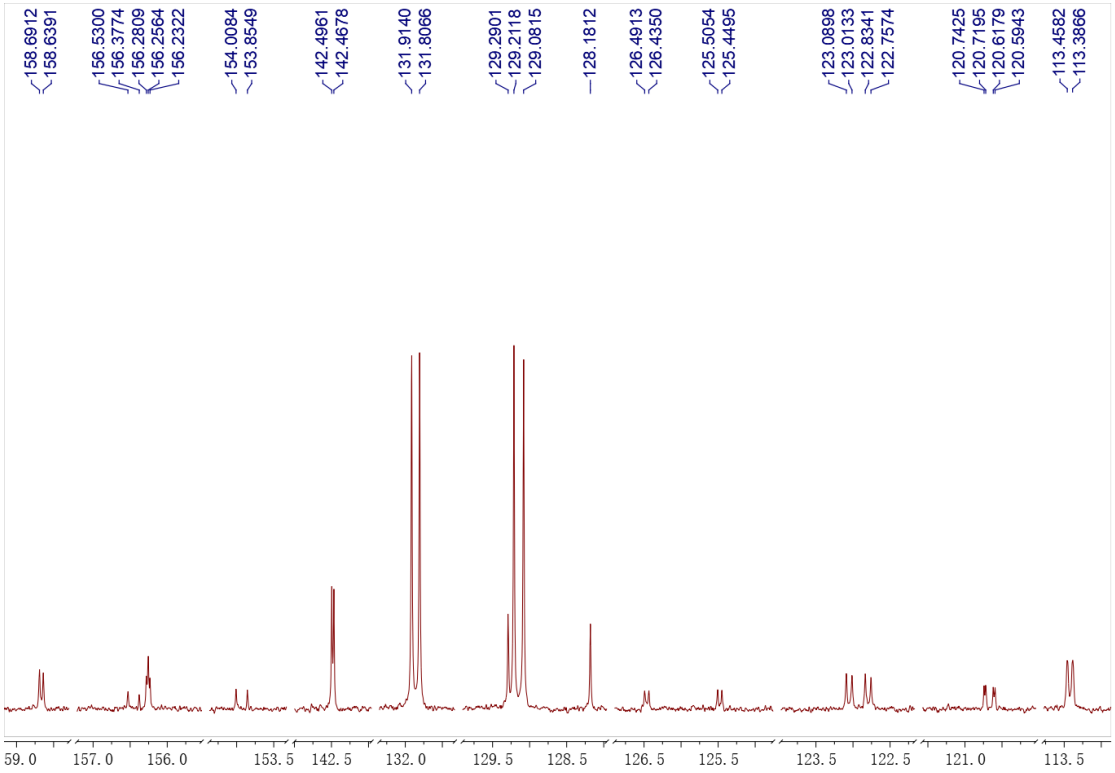


Figure S33 Expanded ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3ha**

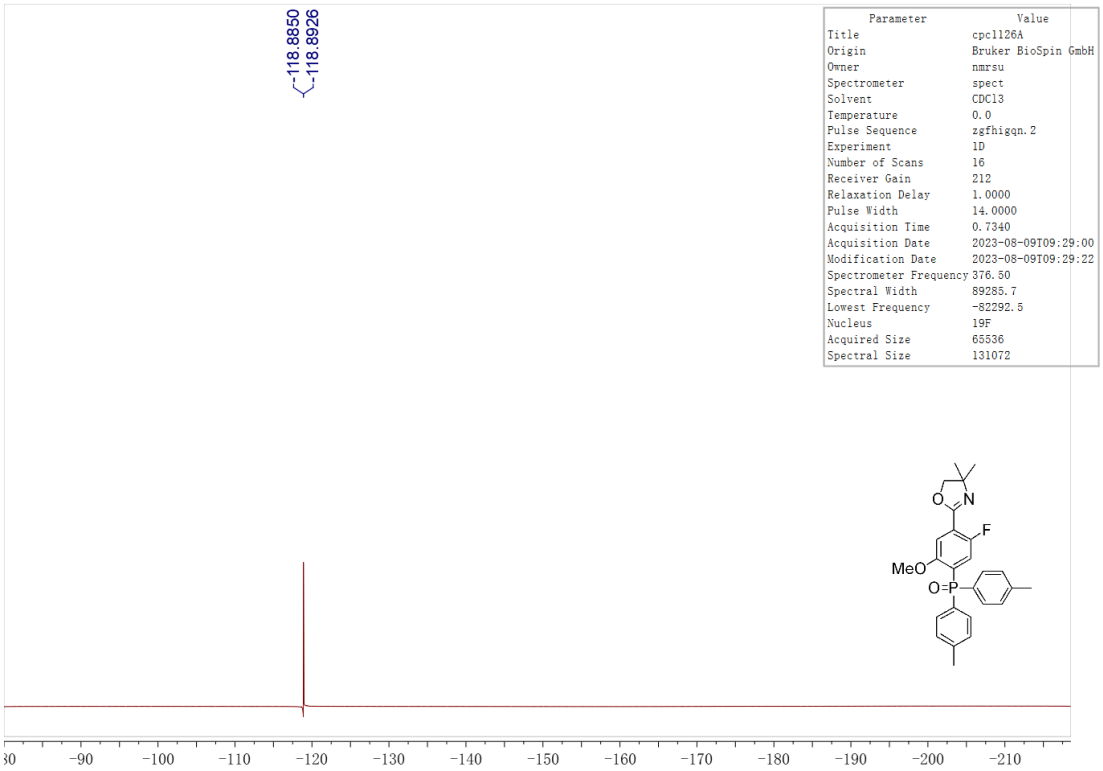


Figure S34 ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of compound **3ha**

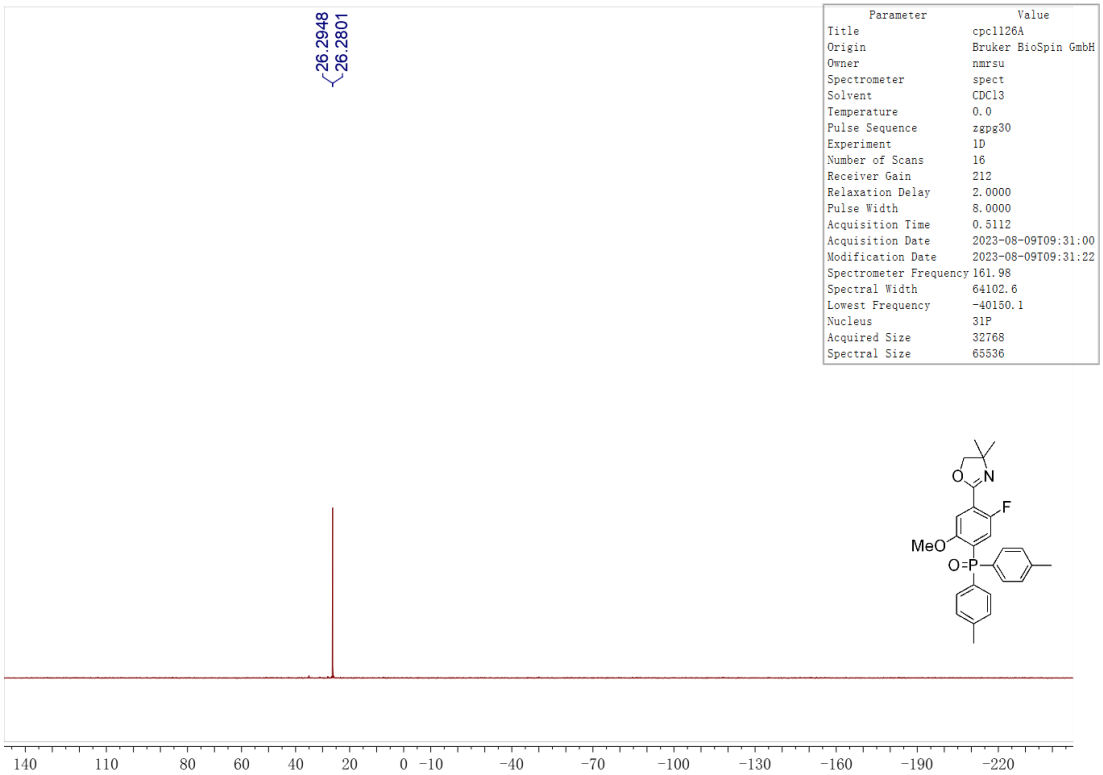


Figure S35 ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3ha**

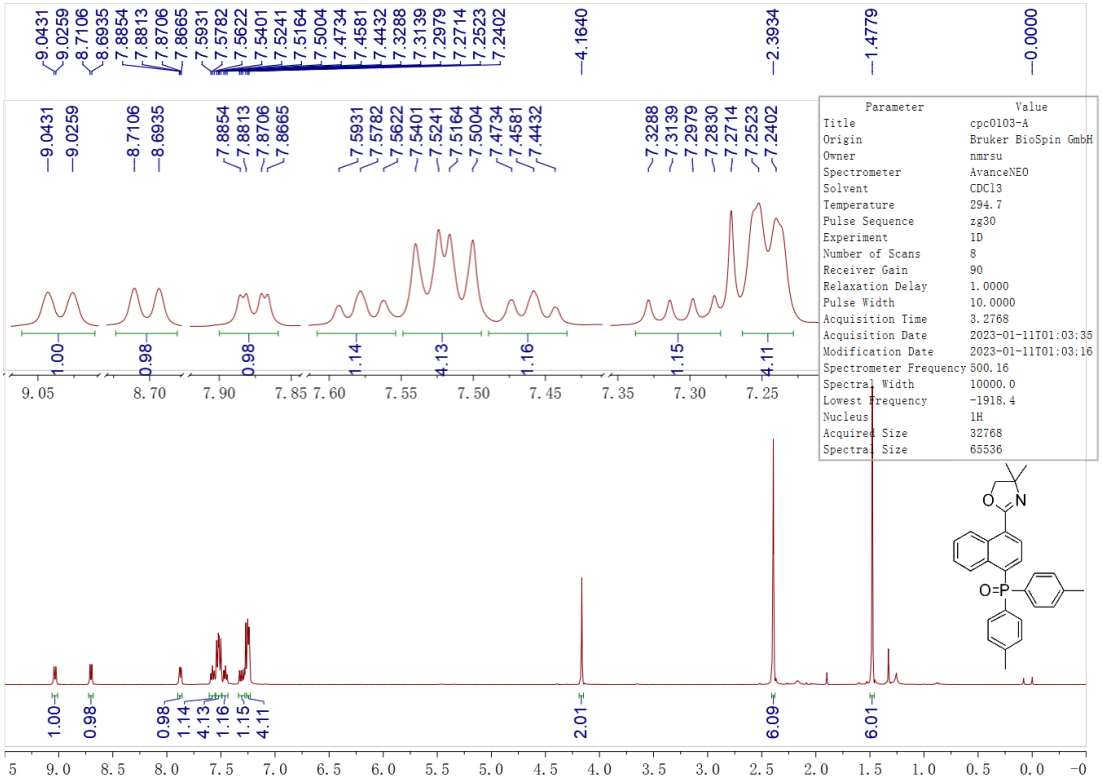


Figure S36 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3ia**

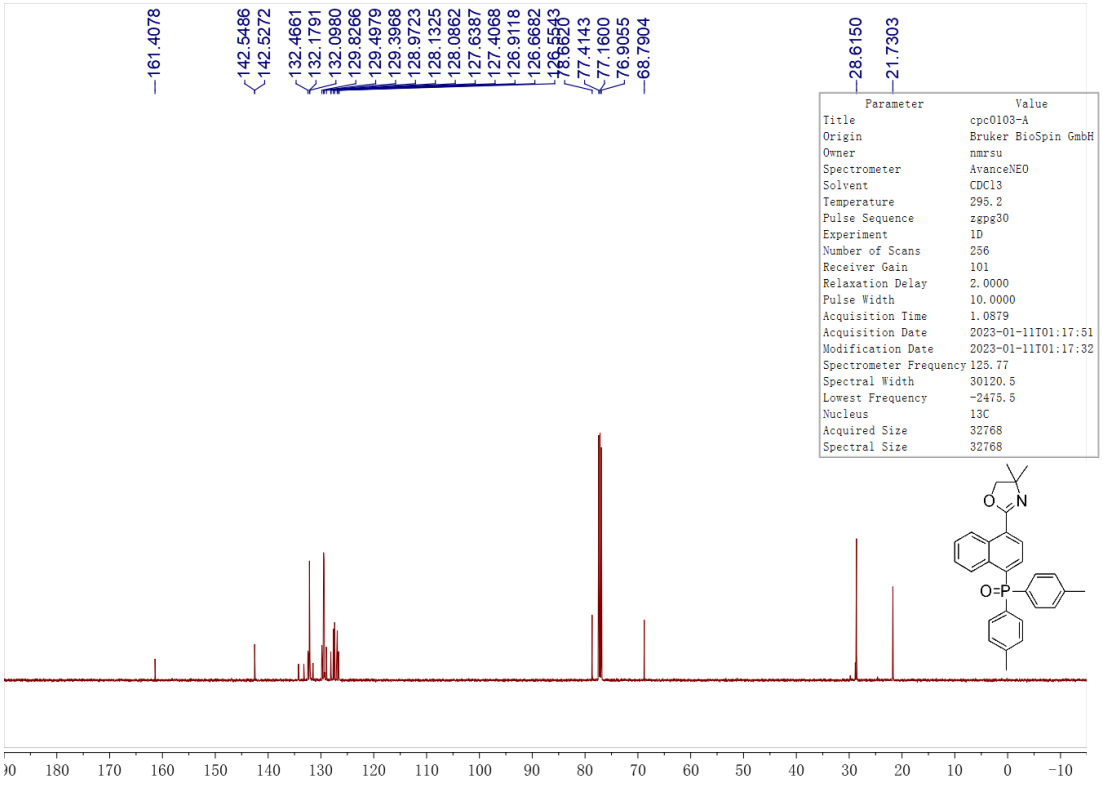


Figure S37 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3ia**

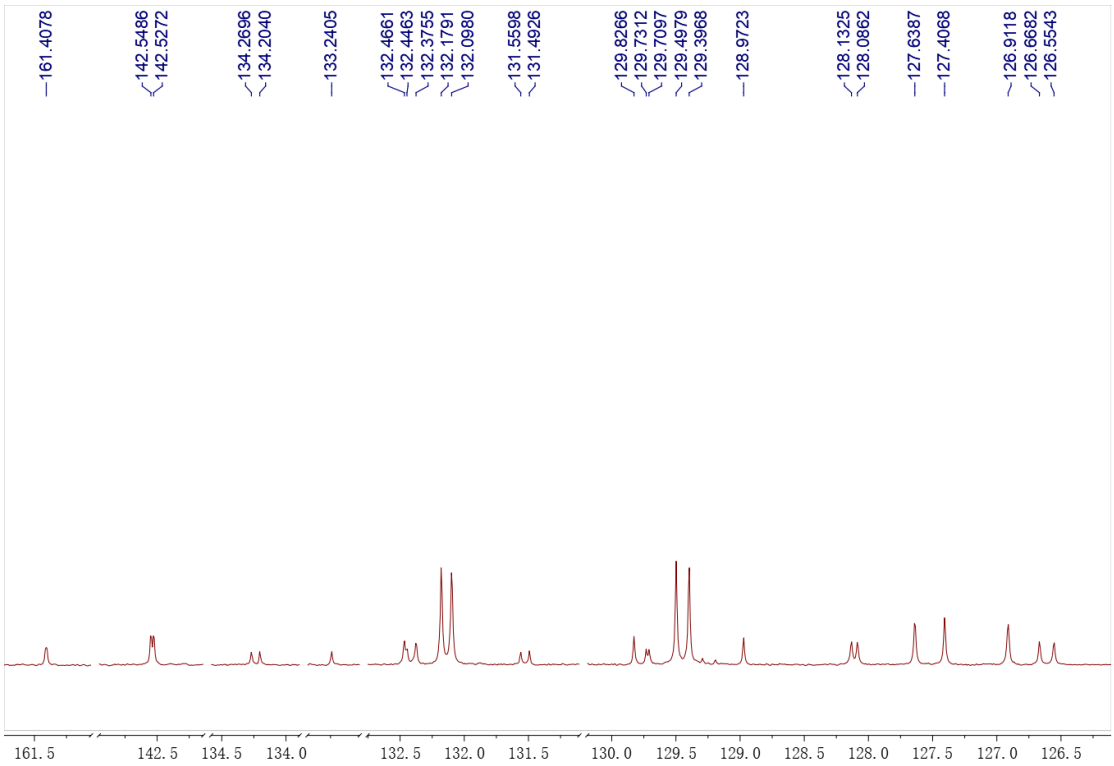


Figure S38 Expanded ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3ia**

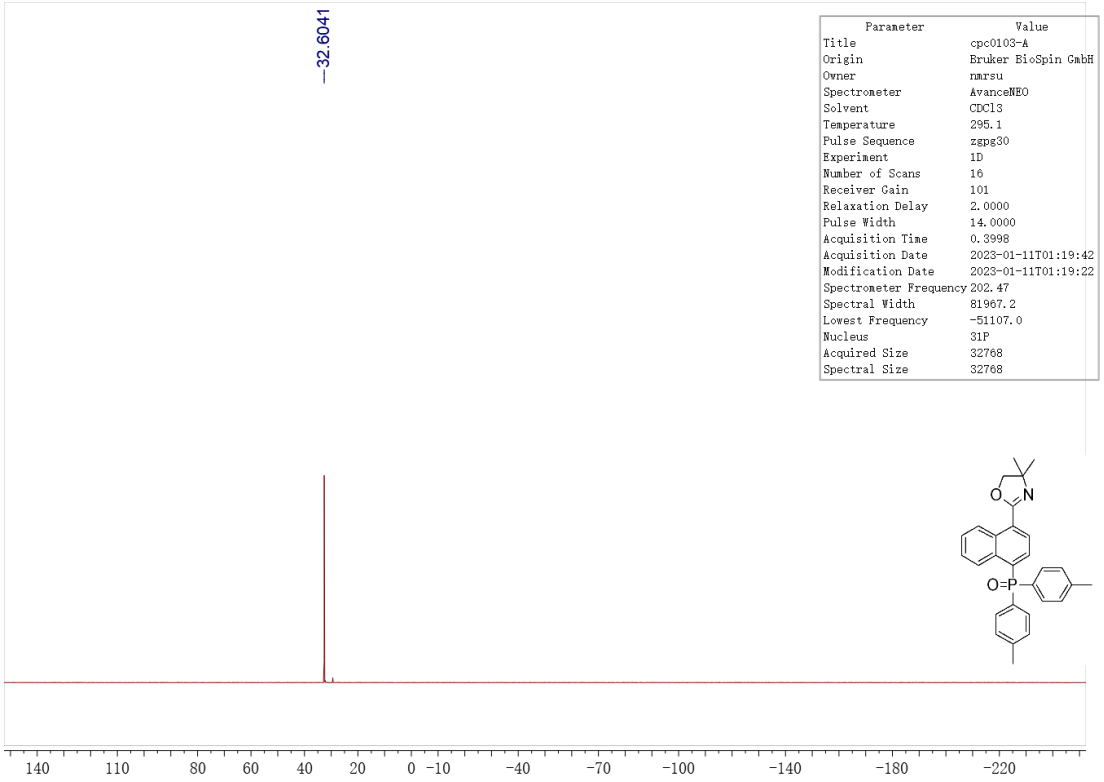


Figure S39 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3ia**

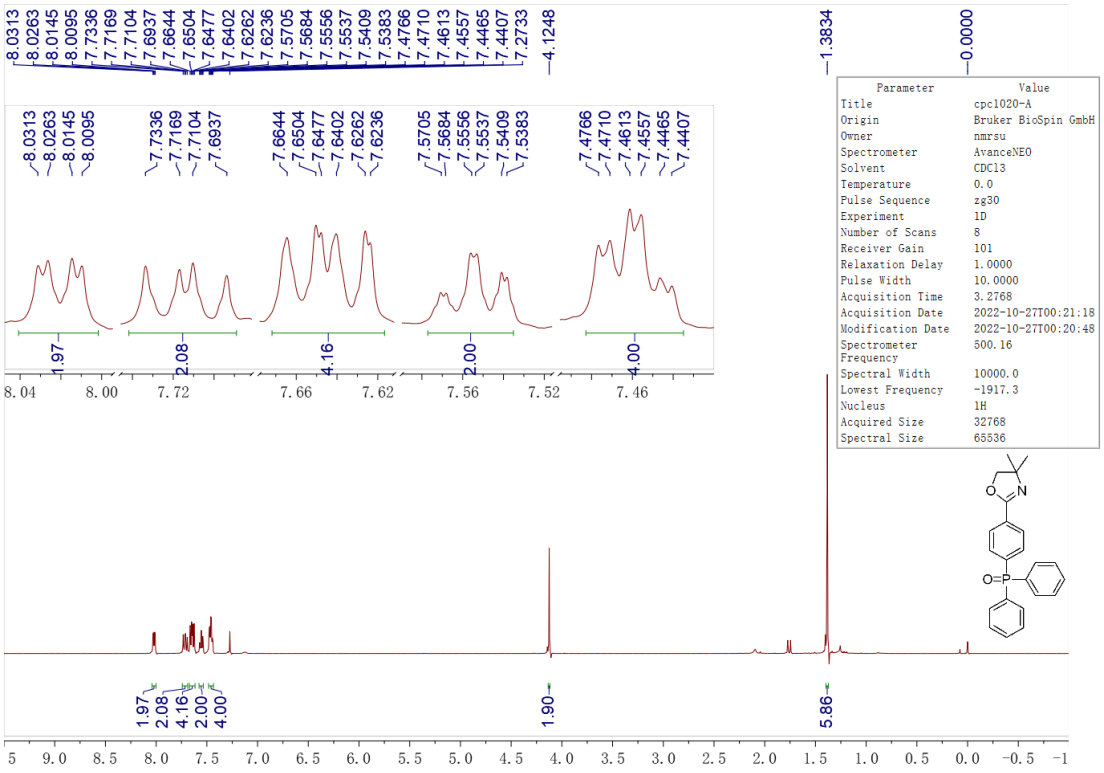


Figure S40 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3ab**

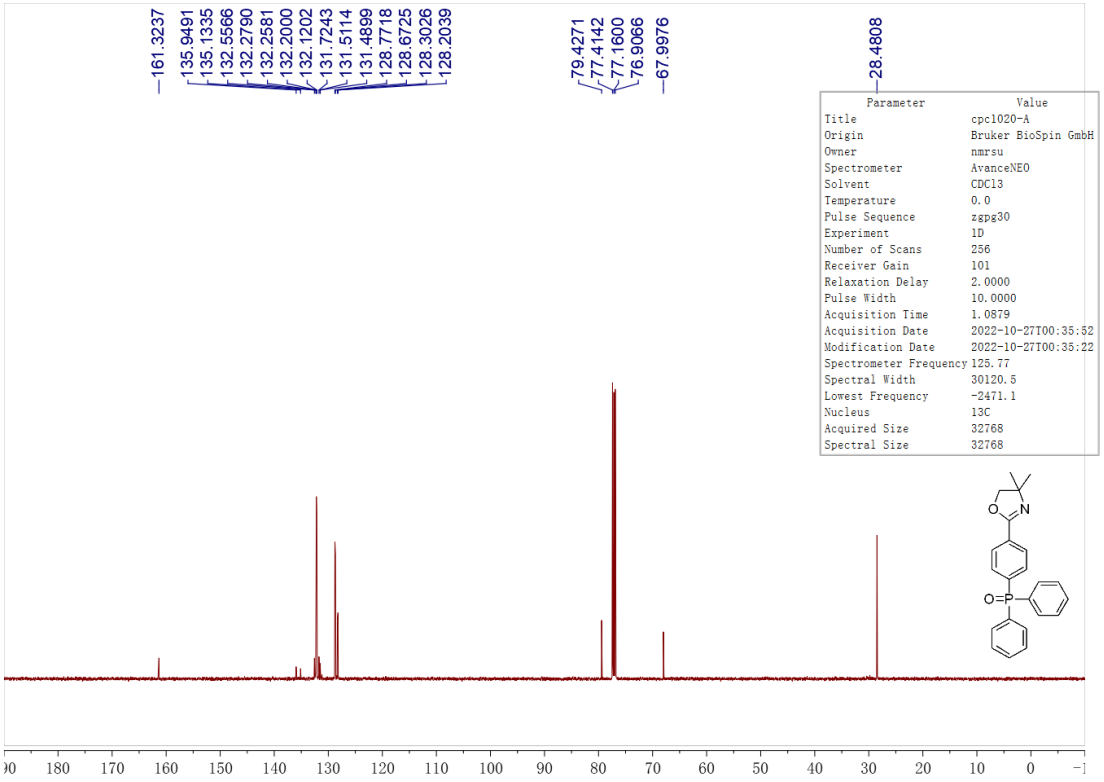


Figure S41 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3ab**

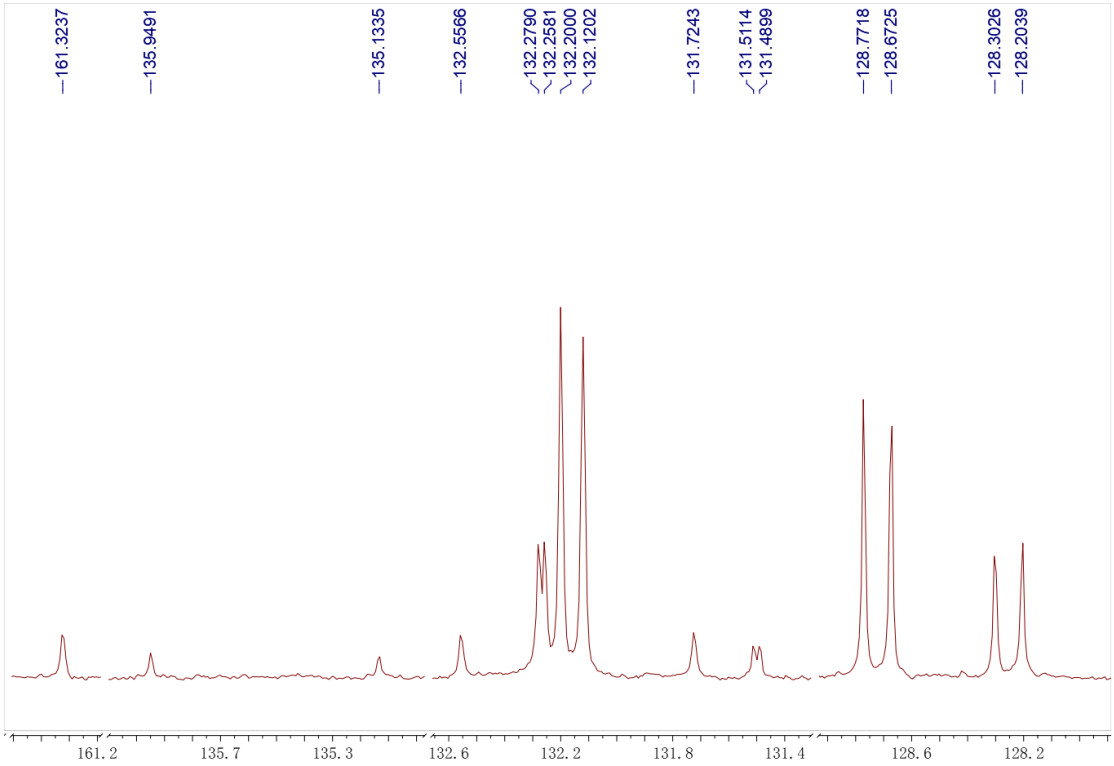


Figure S42 Expanded ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3ab**

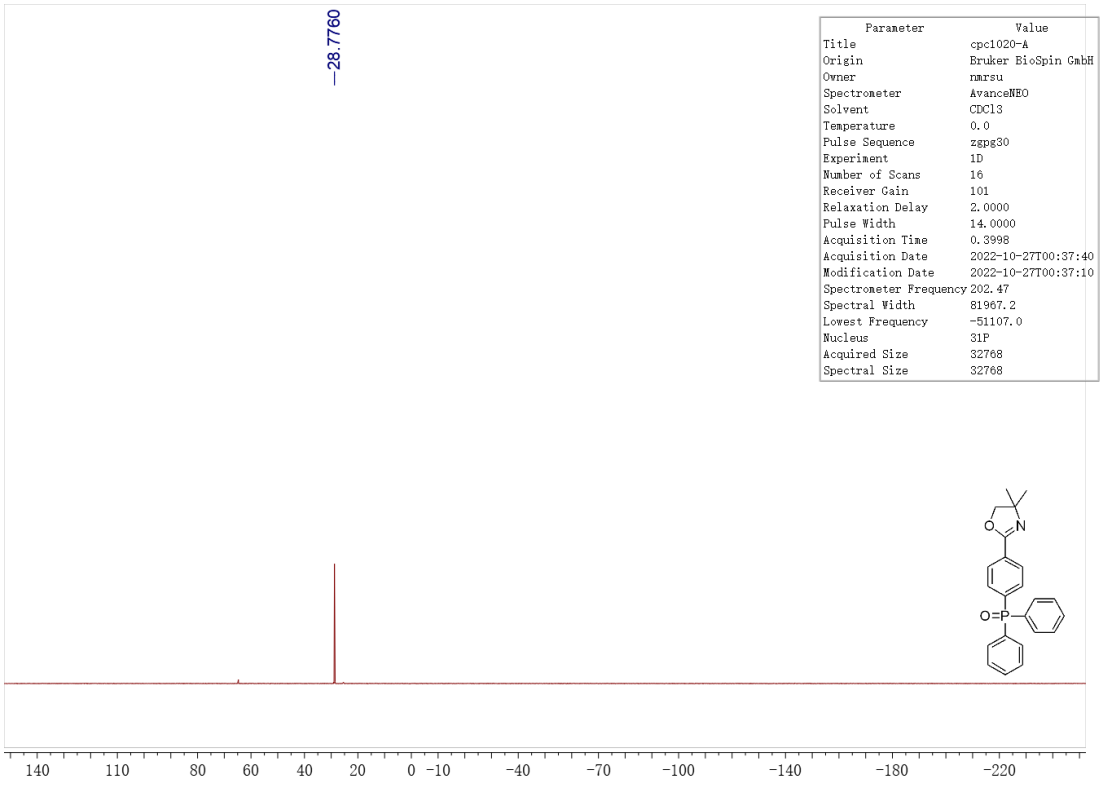


Figure S43 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3ab**

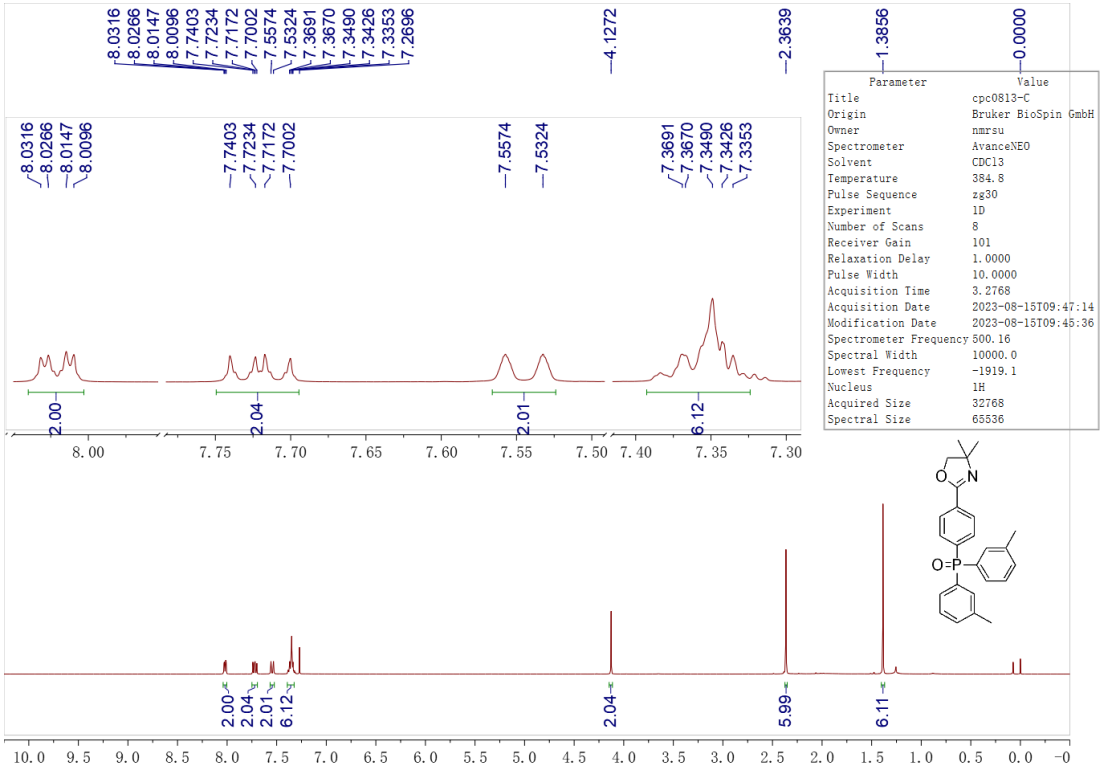


Figure S44 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3ac**

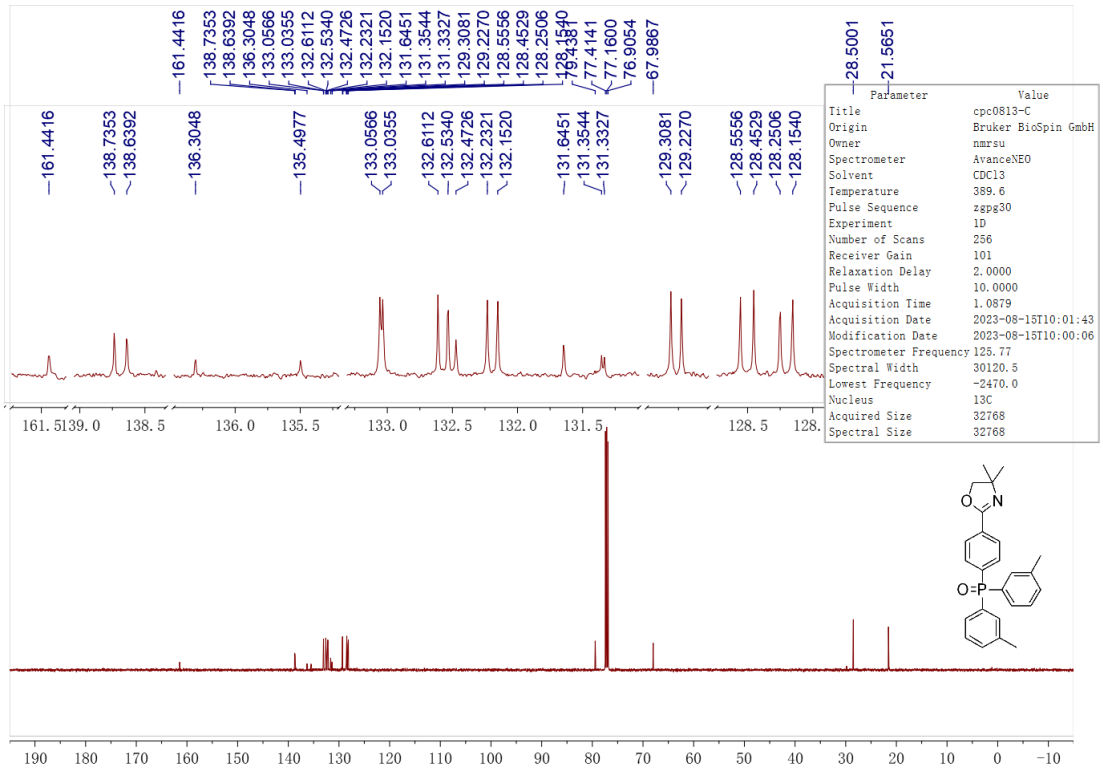


Figure S45 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3ac**

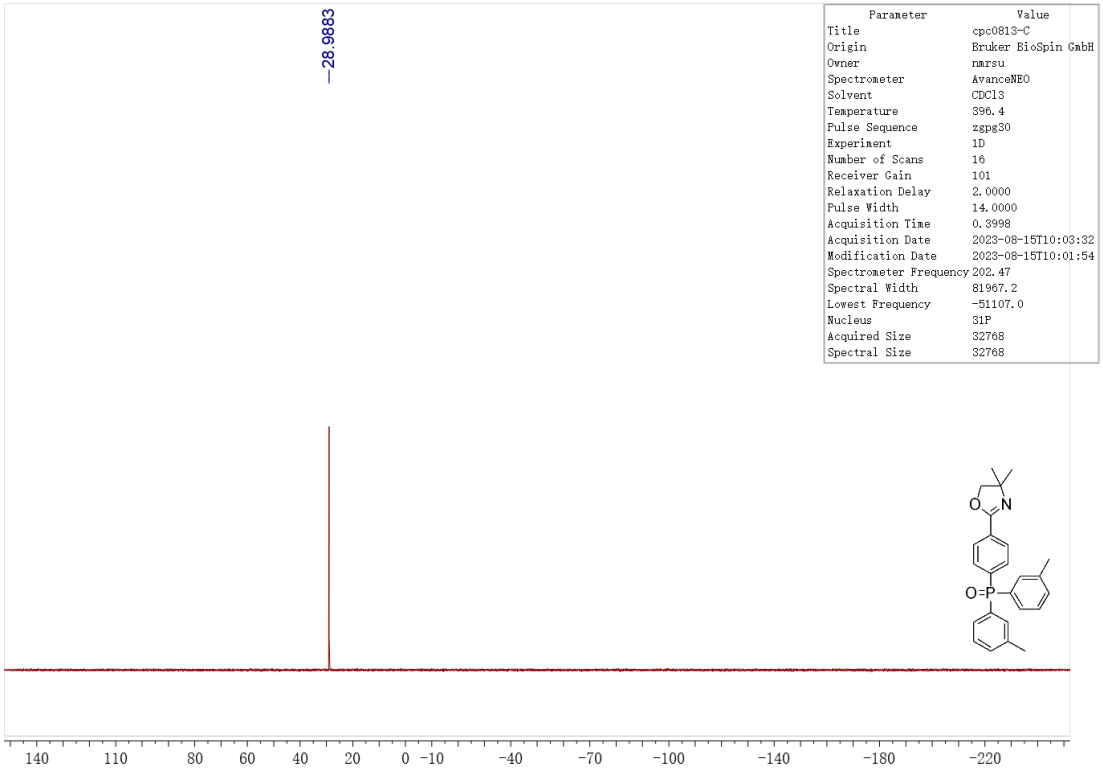


Figure S46 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3ac**

Figure S47 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3ad**

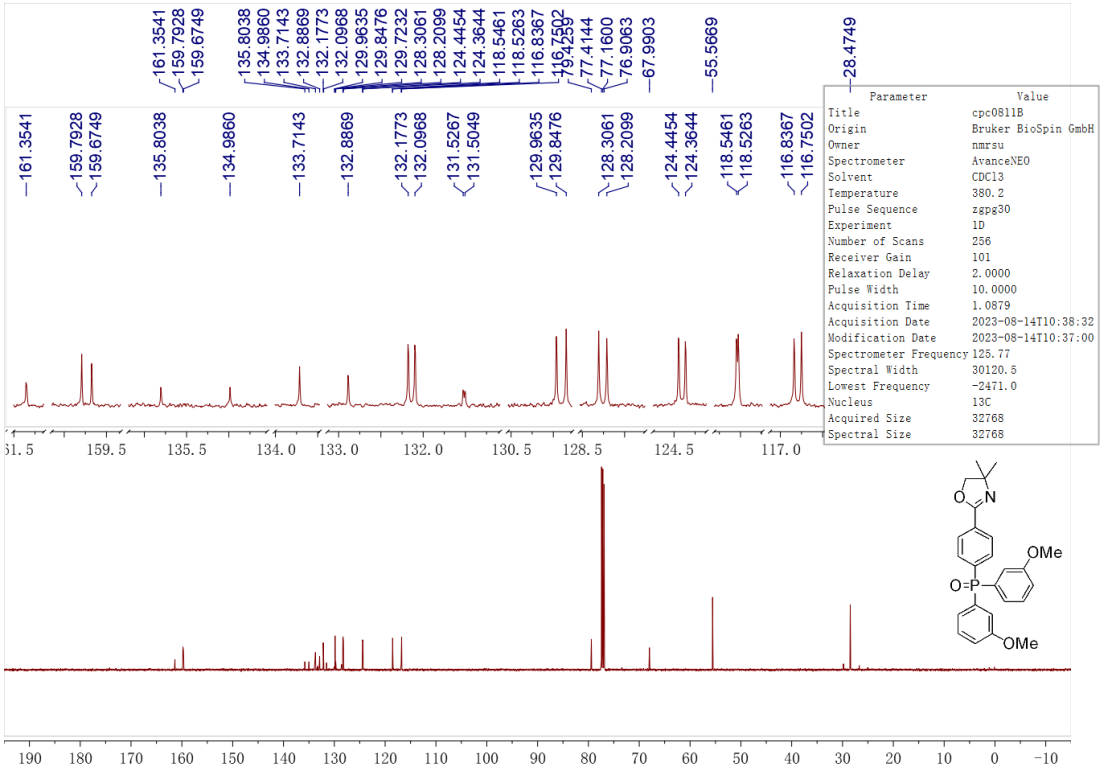


Figure S48 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3ad**

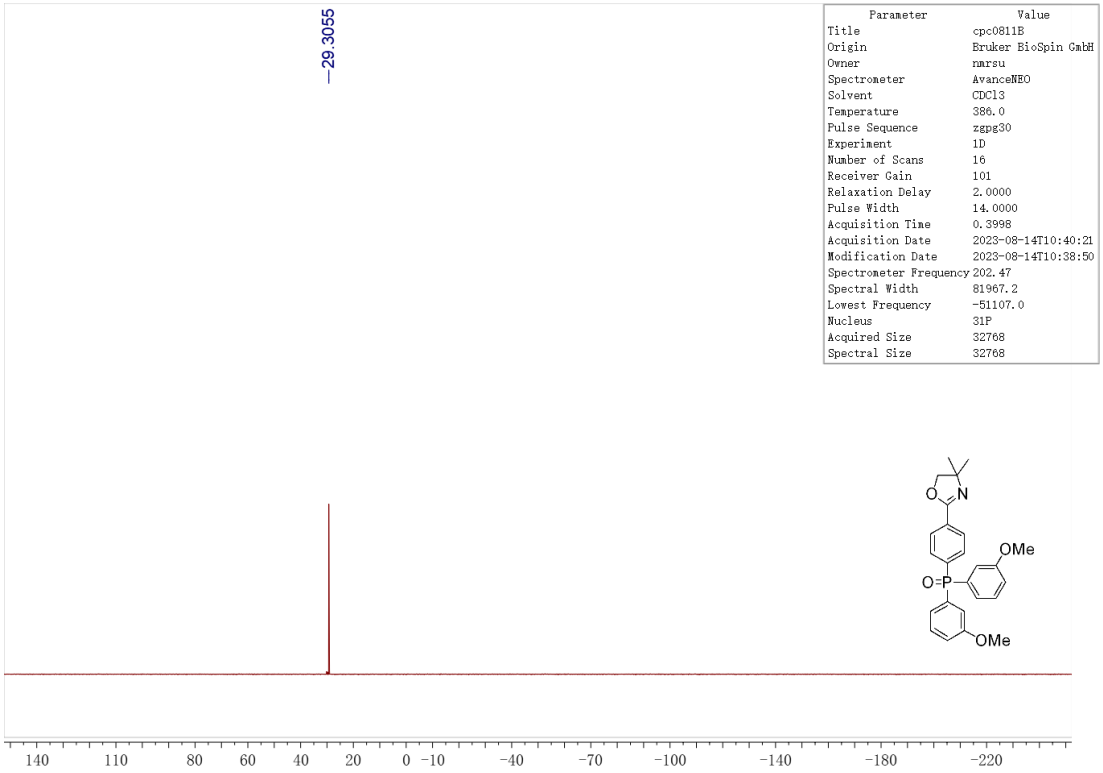


Figure S49 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3ad**

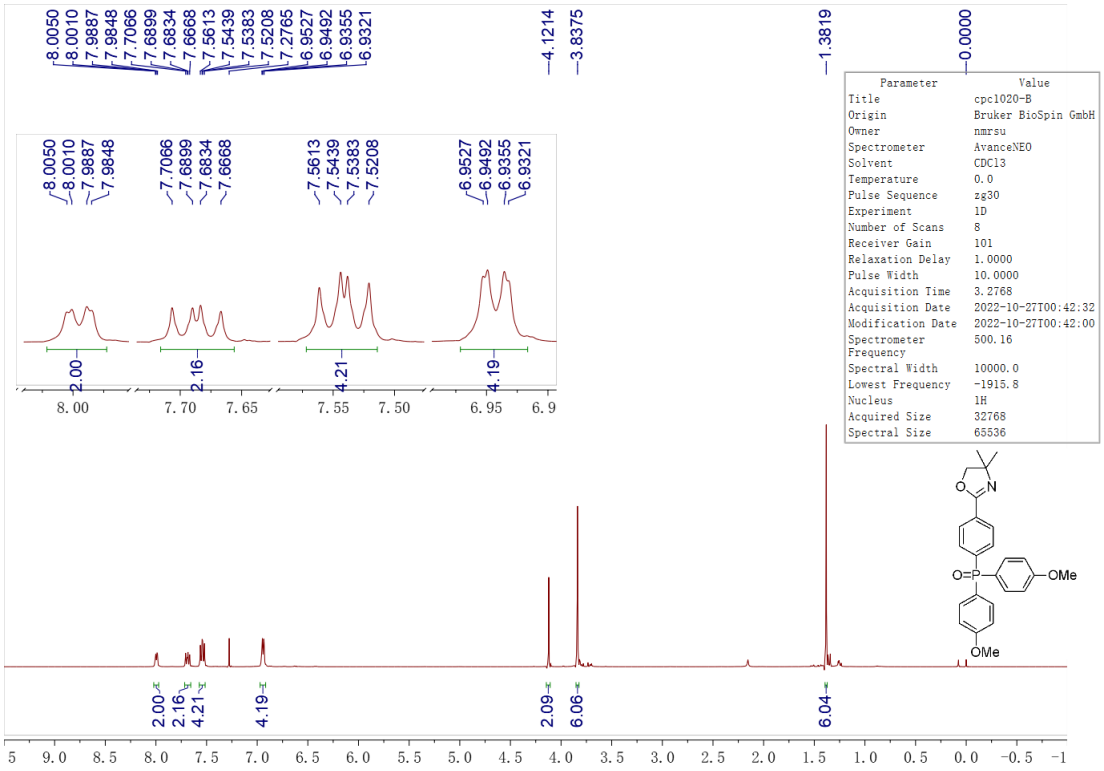


Figure S50 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3ae**

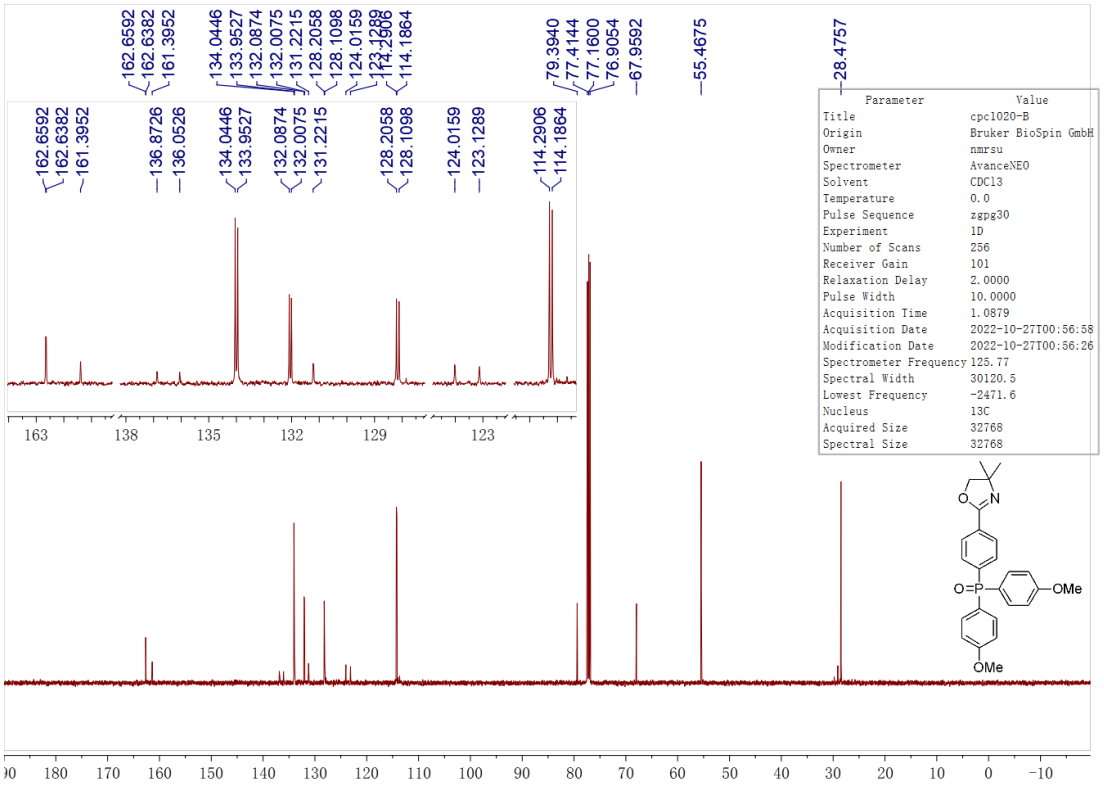


Figure S51 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3ae**

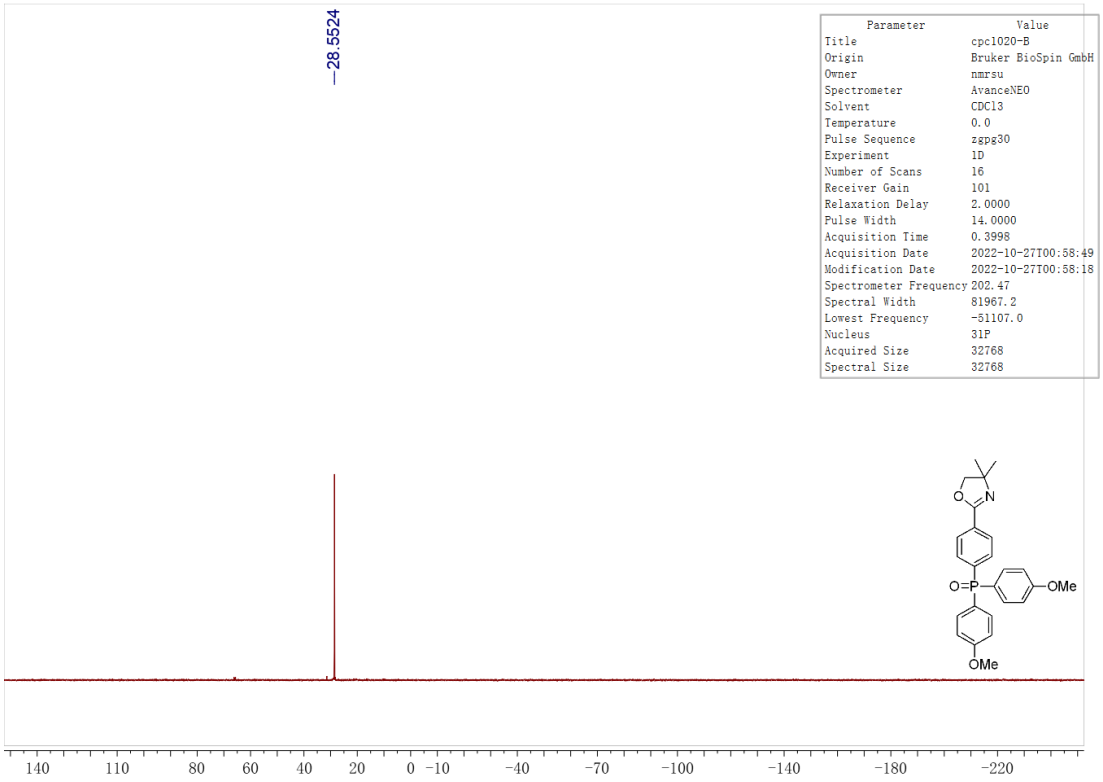


Figure S52 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3ae**

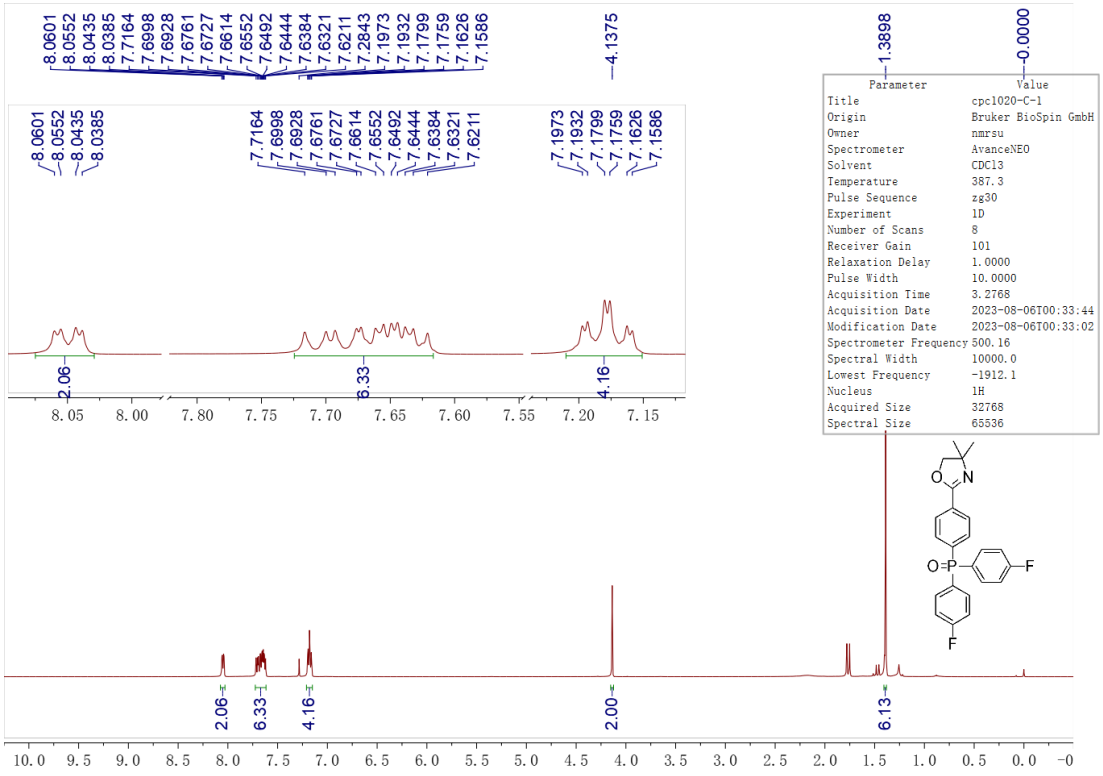
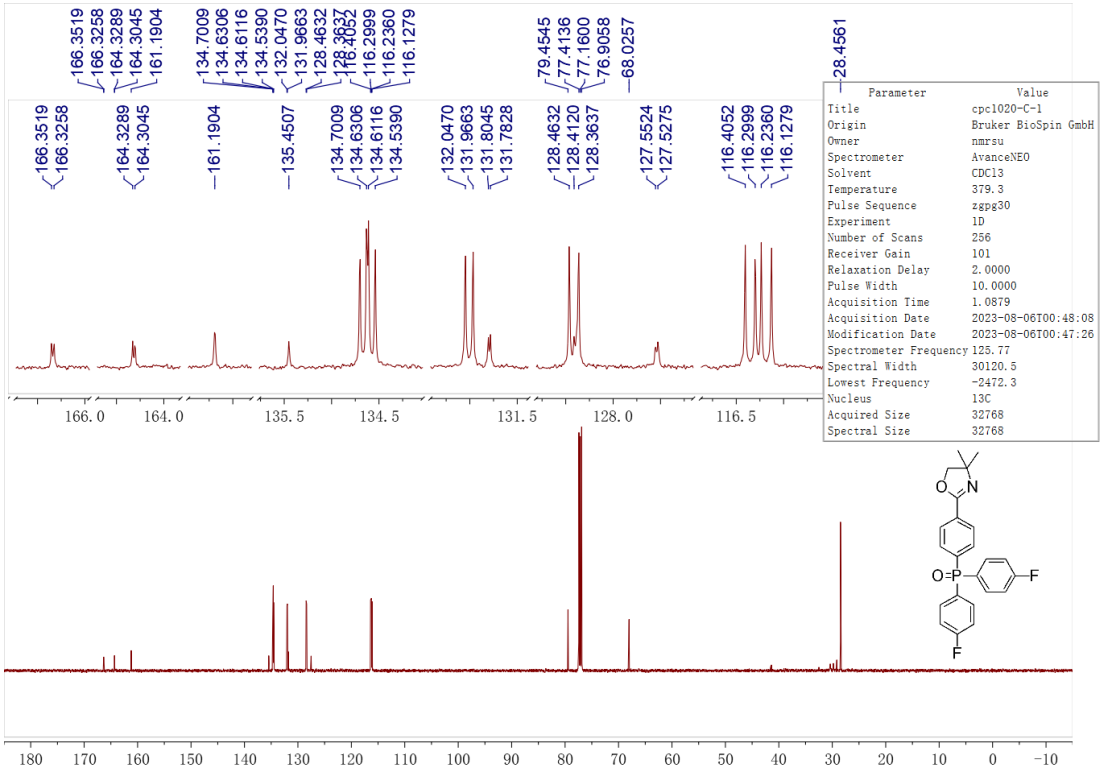
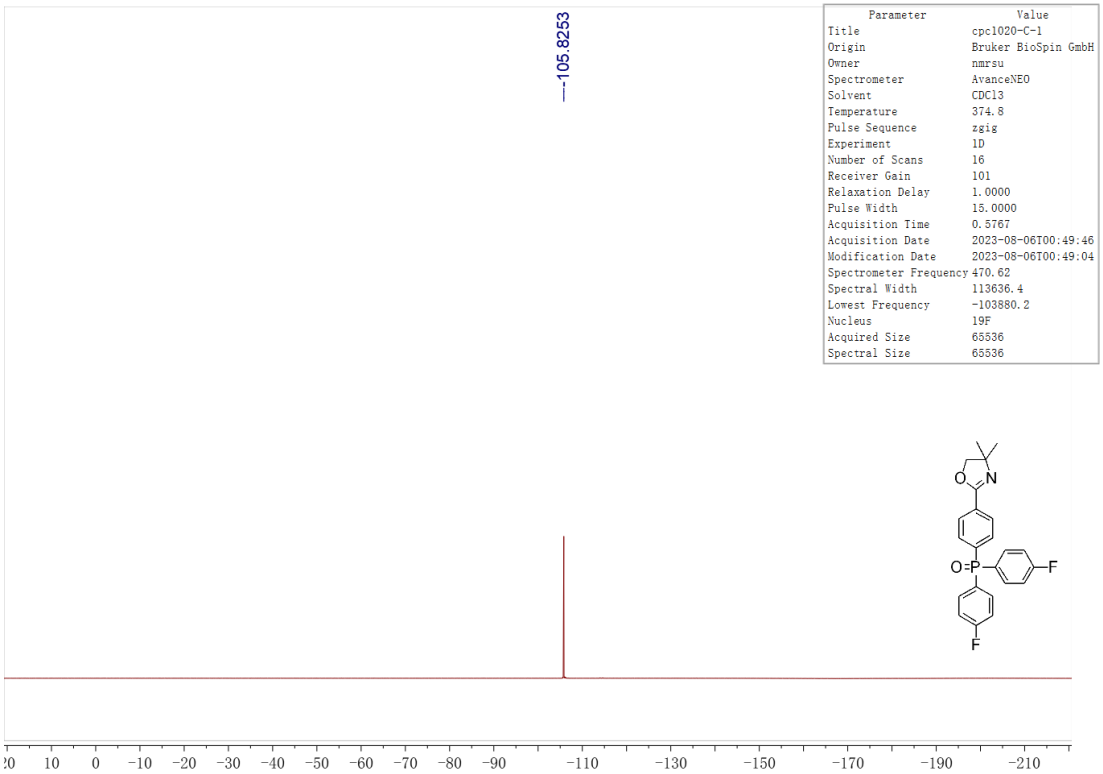


Figure S53 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3af**



Parameter	Value
Title	cpc1020-C-1
Origin	Bruker BioSpin GmbH
Owner	nmrsu
Spectrometer	AvanceNEO
Solvent	CDCl3
Temperature	379.3
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	101
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.0879
Acquisition Date	2023-08-06T00:48:08
Modification Date	2023-08-06T00:47:26
Spectrometer Frequency	125.77
Spectral Width	30120.5
Lowest Frequency	-2472.3
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

Figure S54 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3af**



Parameter	Value
Title	cpc1020-C-1
Origin	Bruker BioSpin GmbH
Owner	nmrsu
Spectrometer	AvanceNEO
Solvent	CDCl3
Temperature	374.8
Pulse Sequence	zgig
Experiment	1D
Number of Scans	16
Receiver Gain	101
Relaxation Delay	1.0000
Pulse Width	15.0000
Acquisition Time	0.5767
Acquisition Date	2023-08-06T00:49:46
Modification Date	2023-08-06T00:49:04
Spectrometer Frequency	470.62
Spectral Width	113636.4
Lowest Frequency	-103880.2
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

Figure S55 ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound **3af**

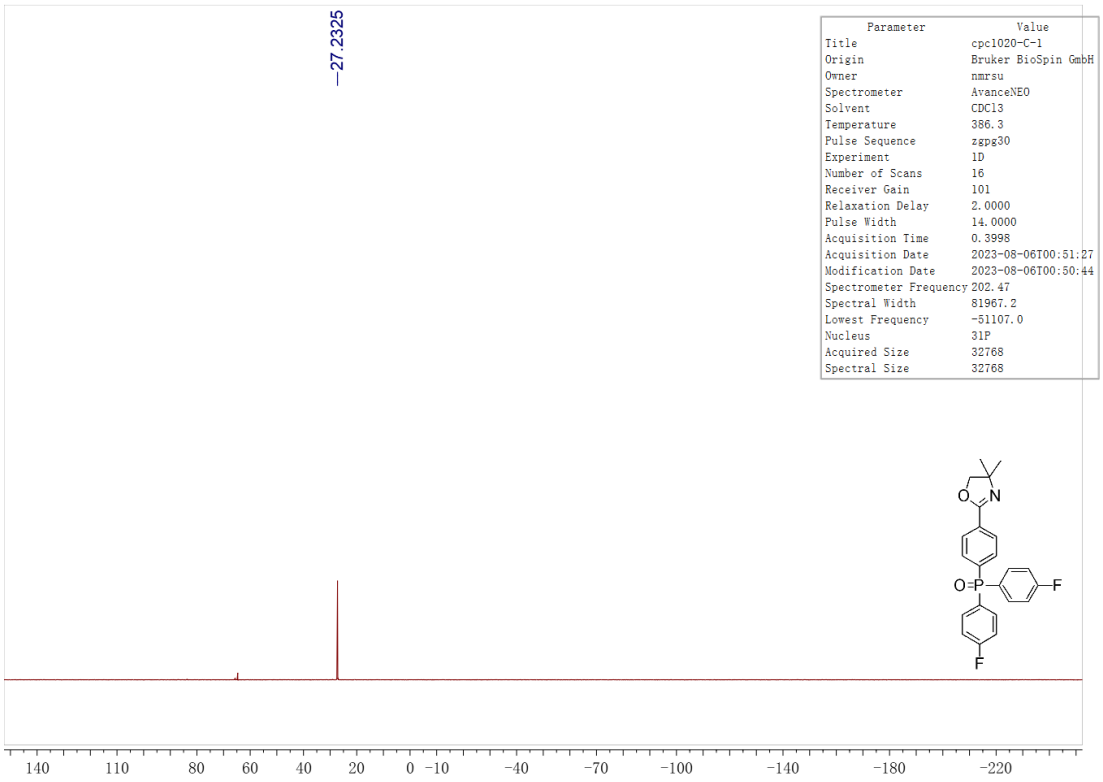


Figure S56 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3af**

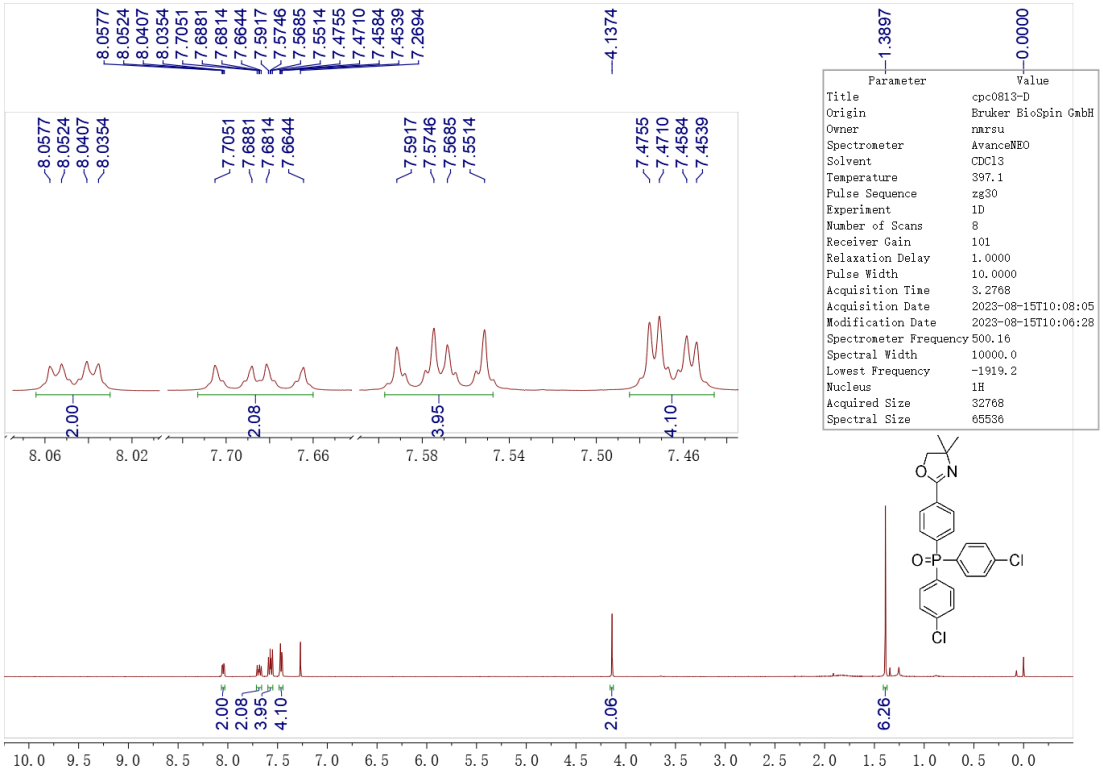


Figure S57 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3ag**

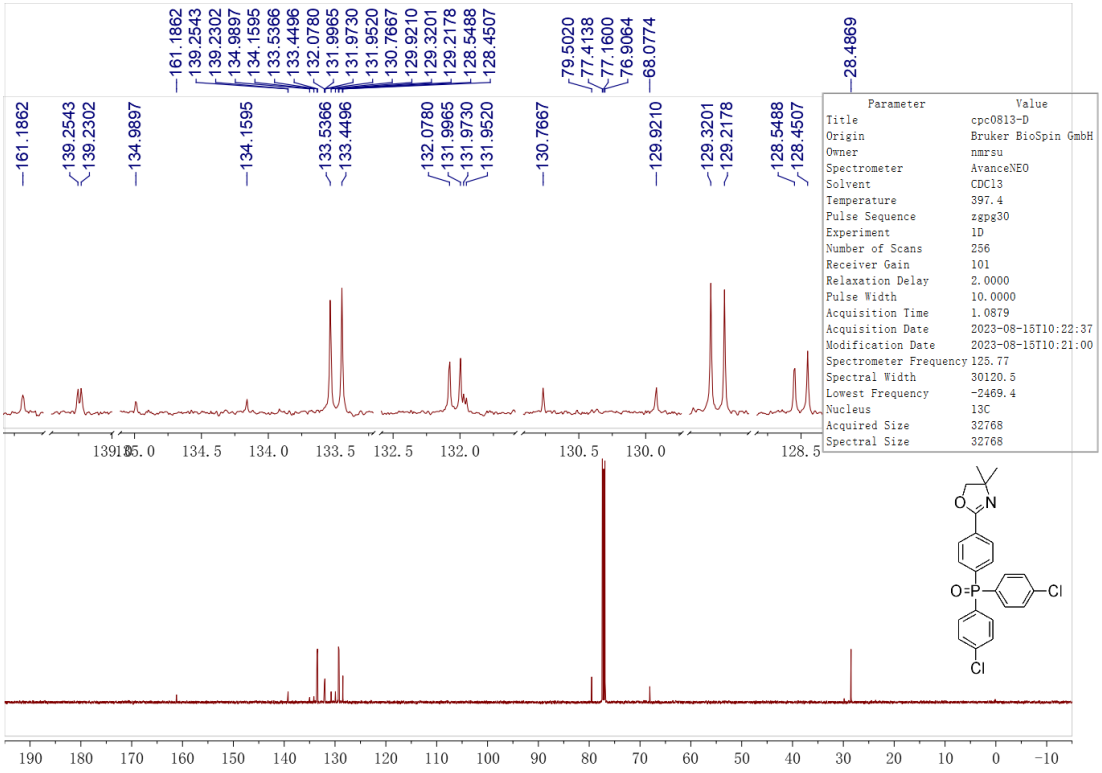


Figure S58 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3ag**

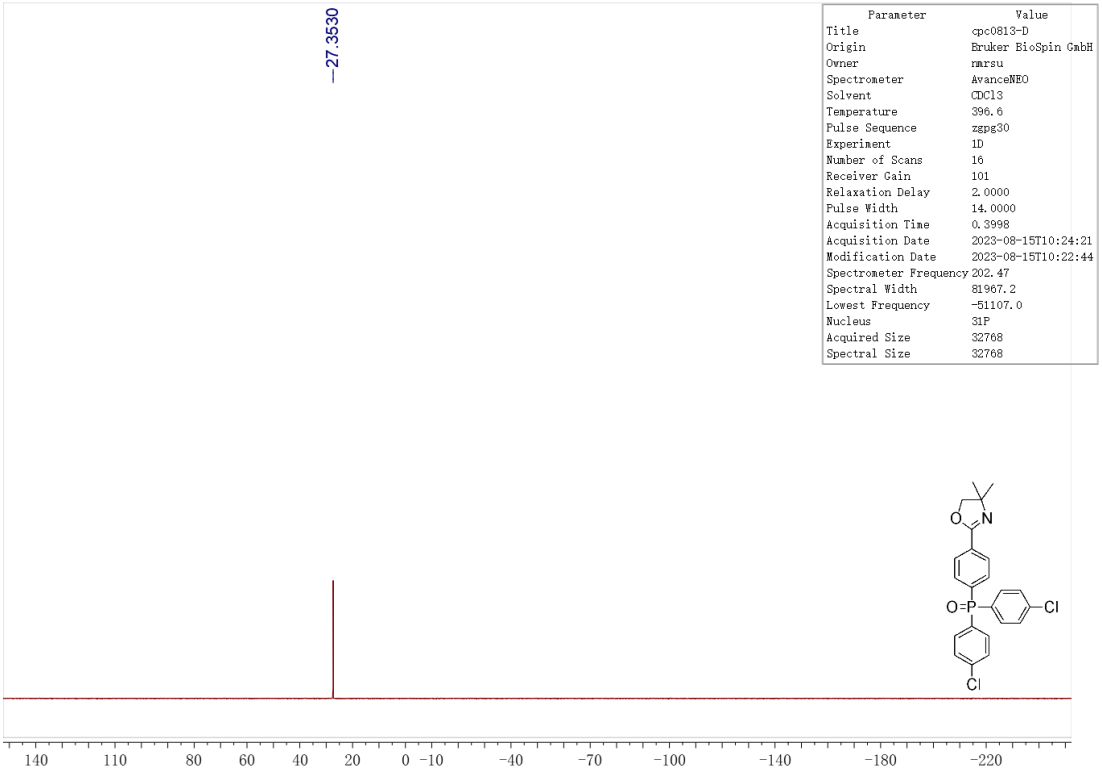


Figure S59 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3ag**

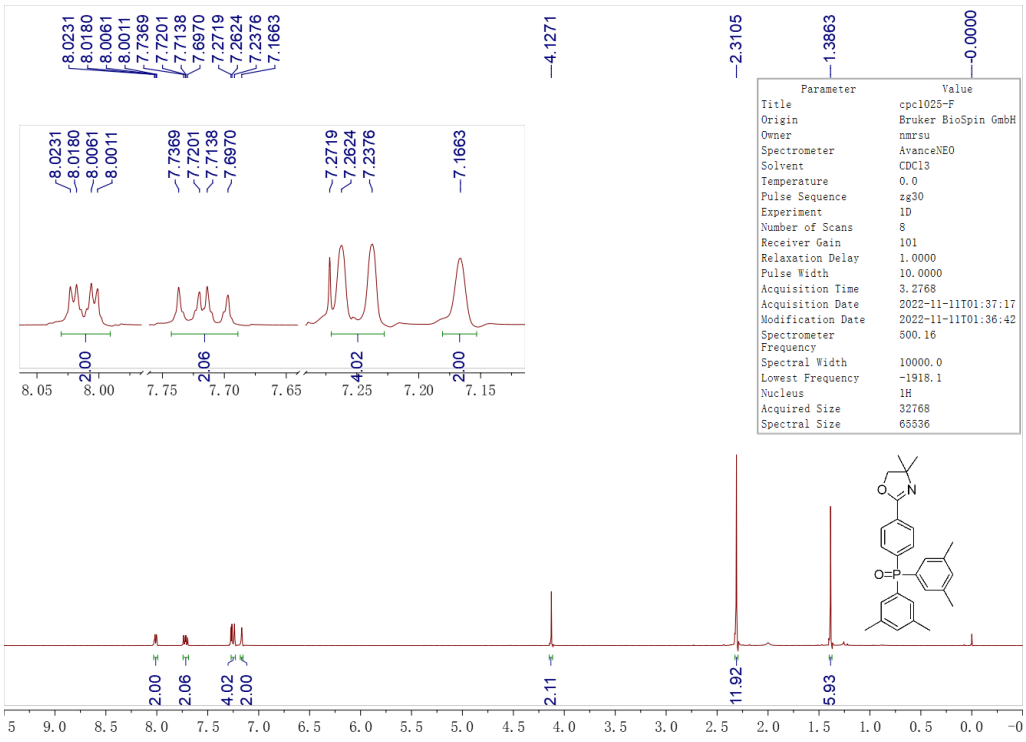


Figure S60 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3ah**

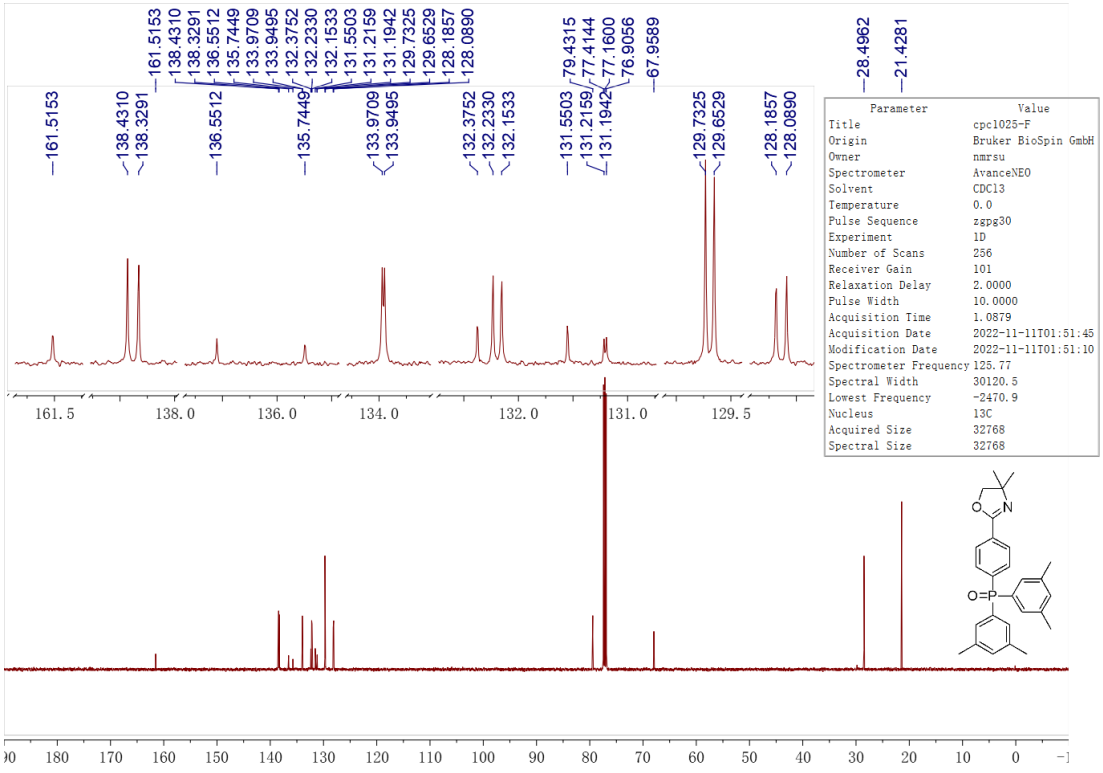


Figure S61 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3ah**

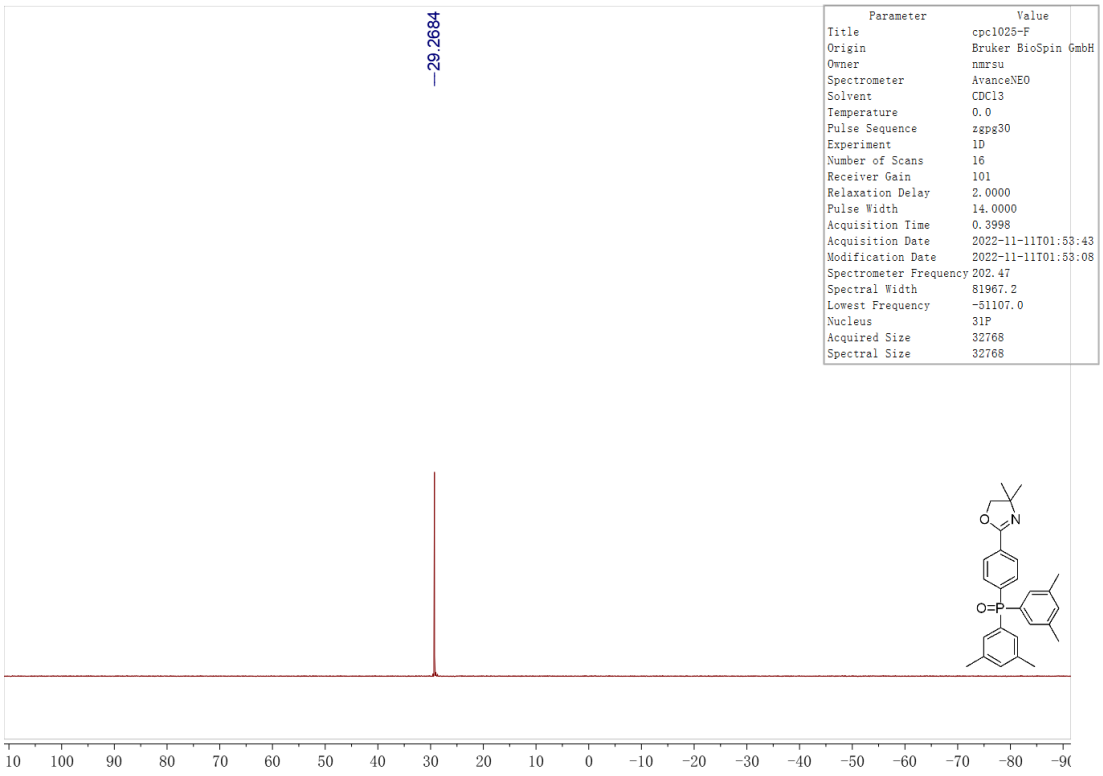


Figure S62 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3ah**

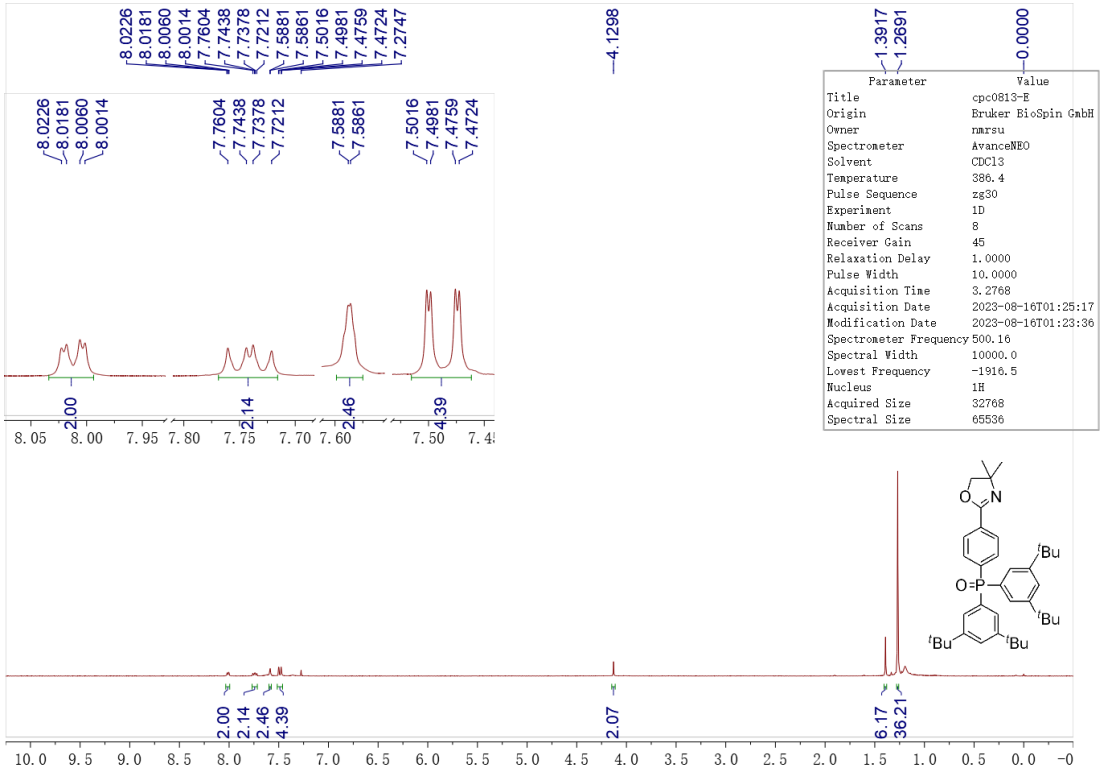


Figure S63 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3ai**

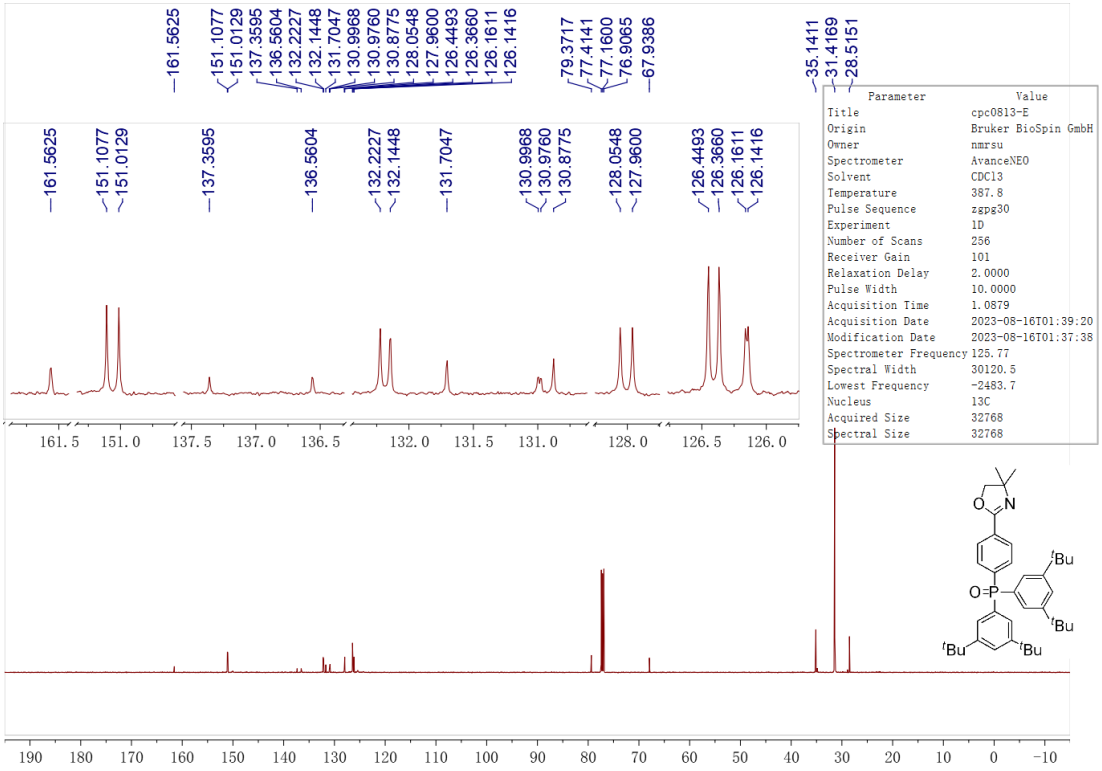


Figure S64 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3ai**

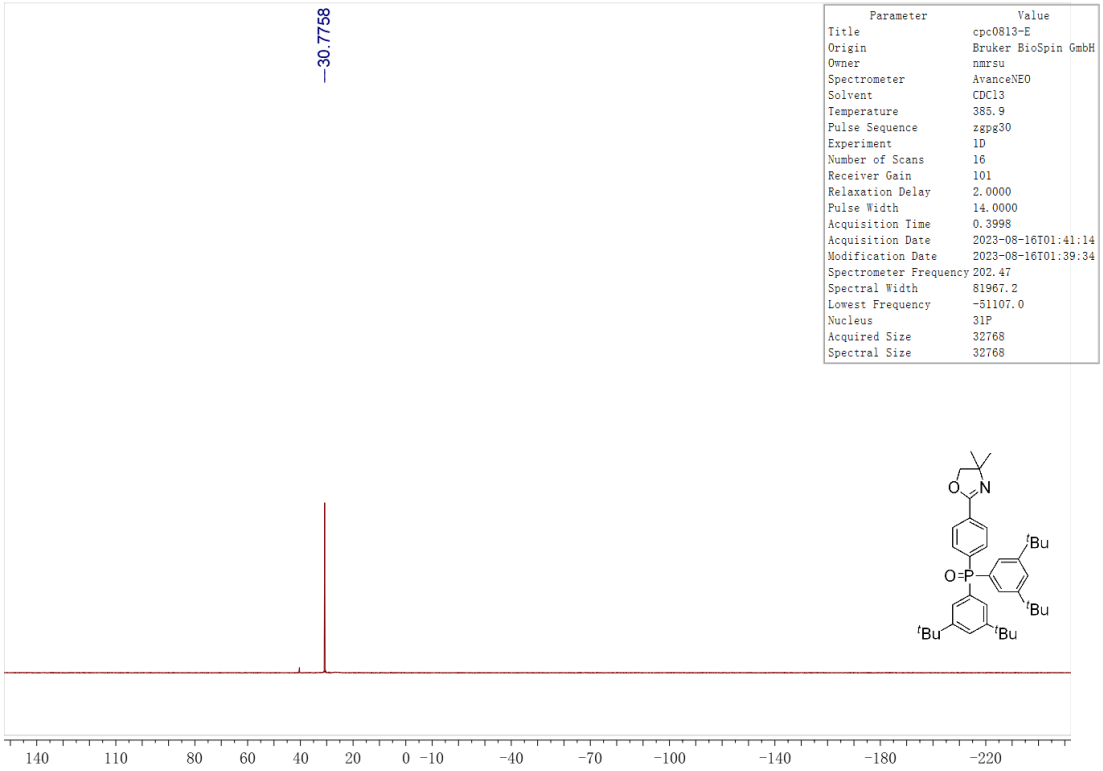


Figure S65 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3ai**

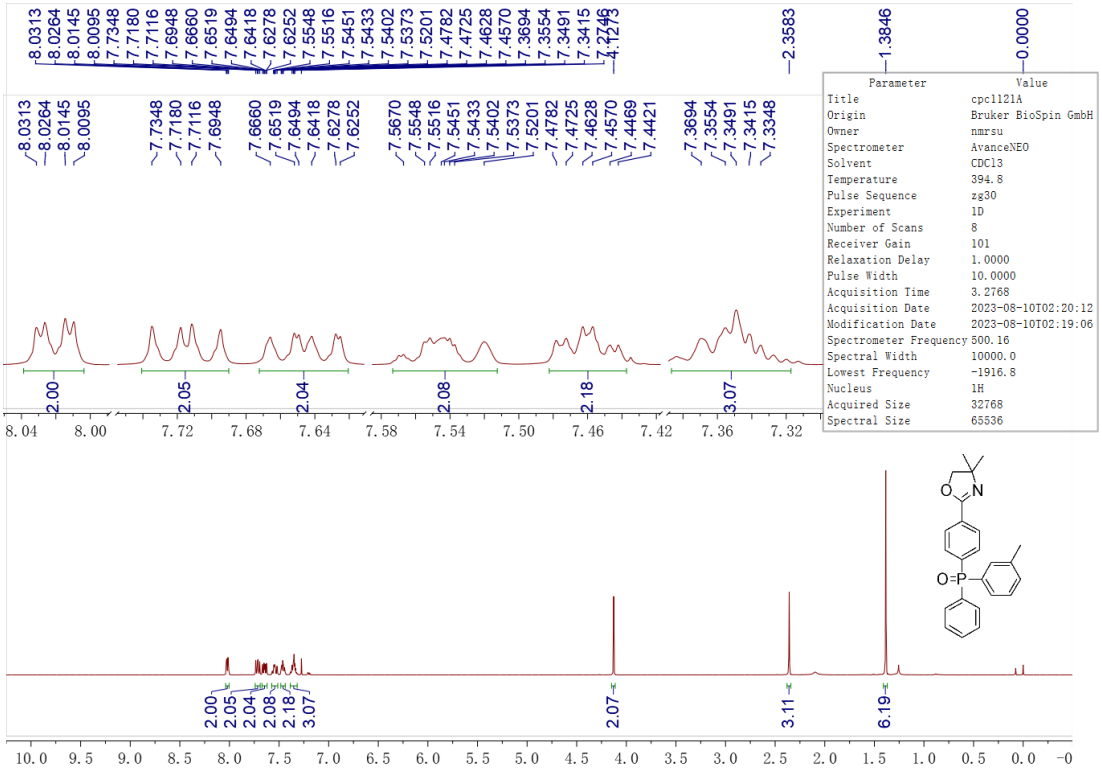


Figure S66 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3aj**

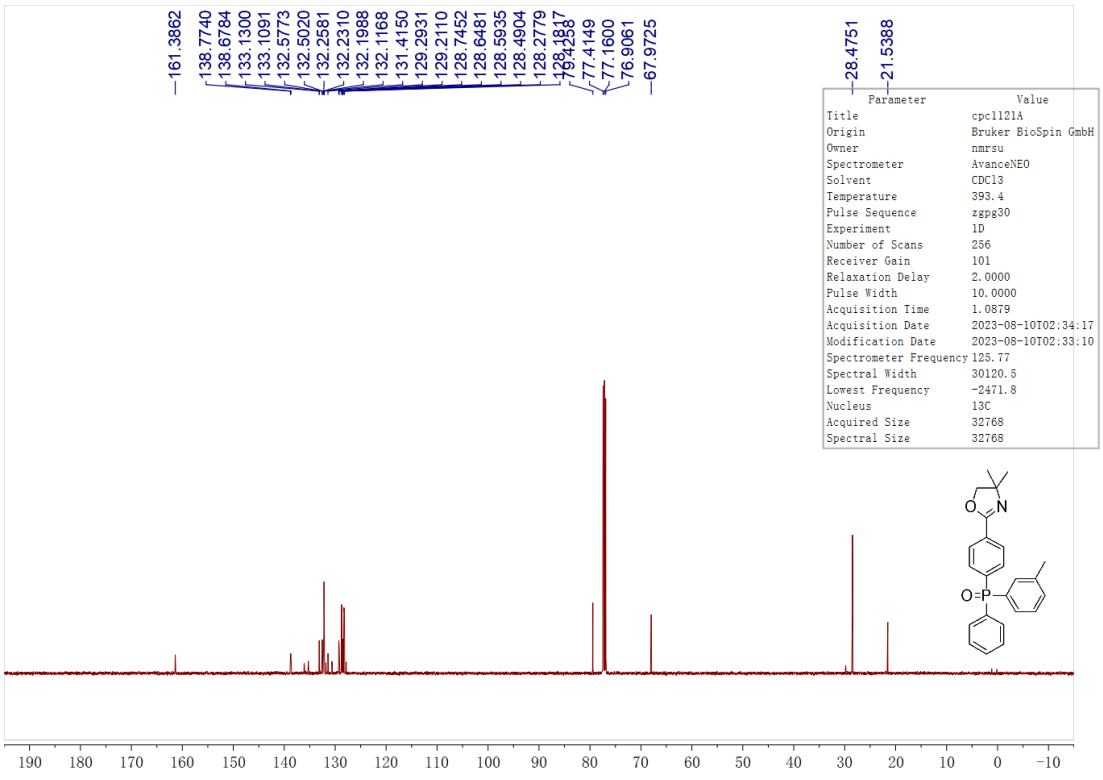


Figure S67 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3aj**

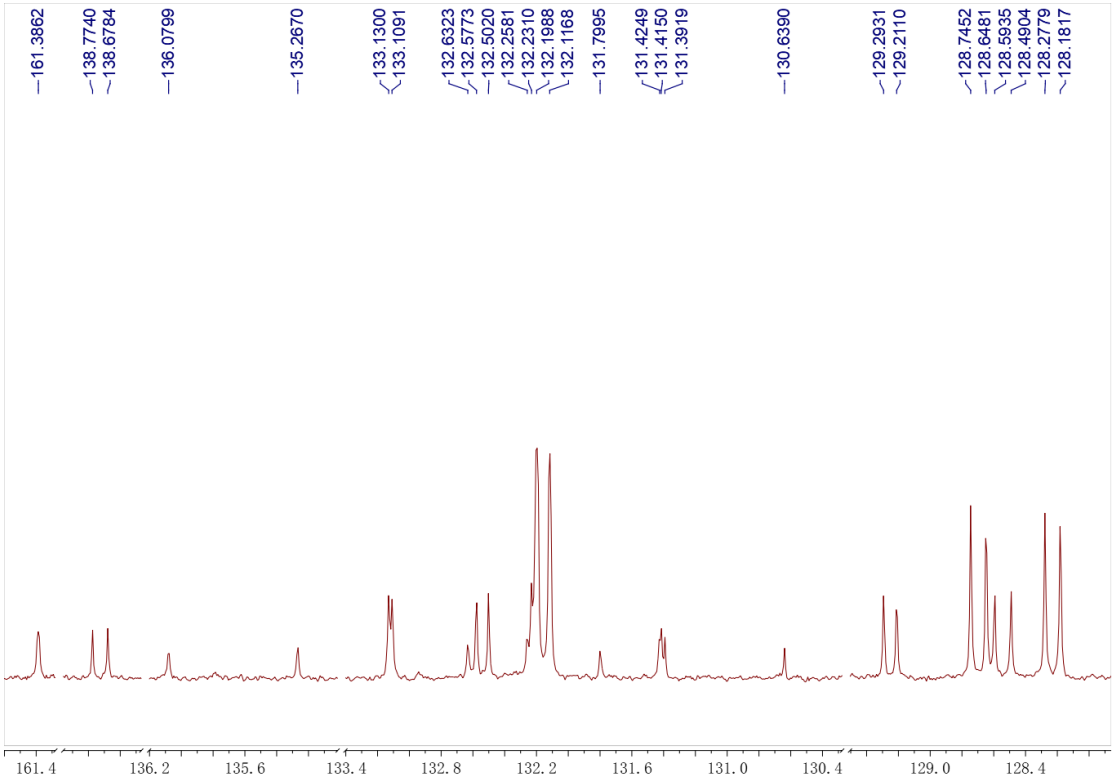


Figure S68 Expanded ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3aj**

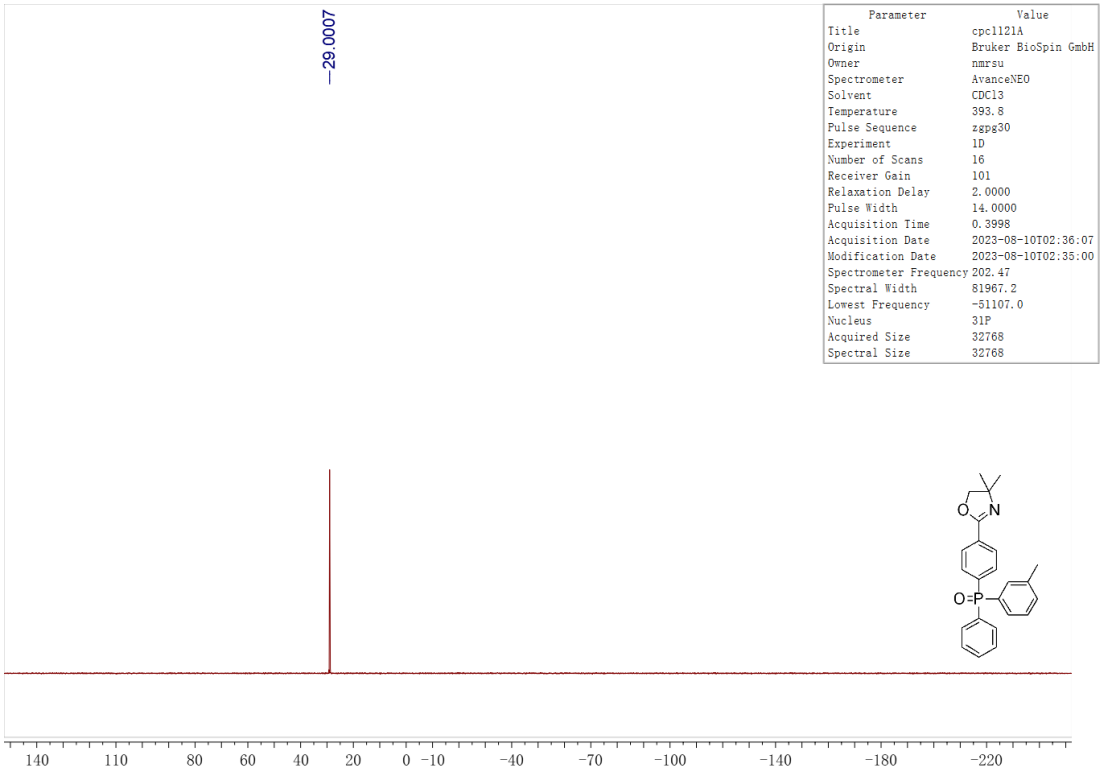


Figure S69 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3aj**

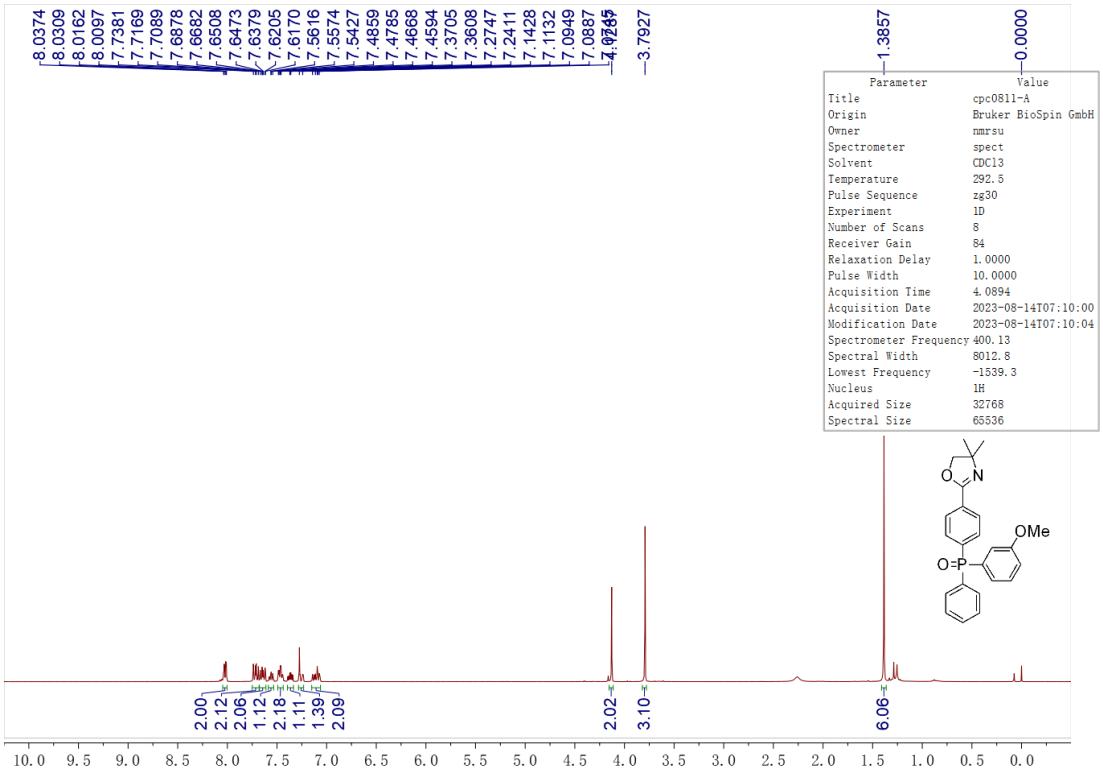


Figure S70 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ak**

Figure S71 Expanded ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ak**

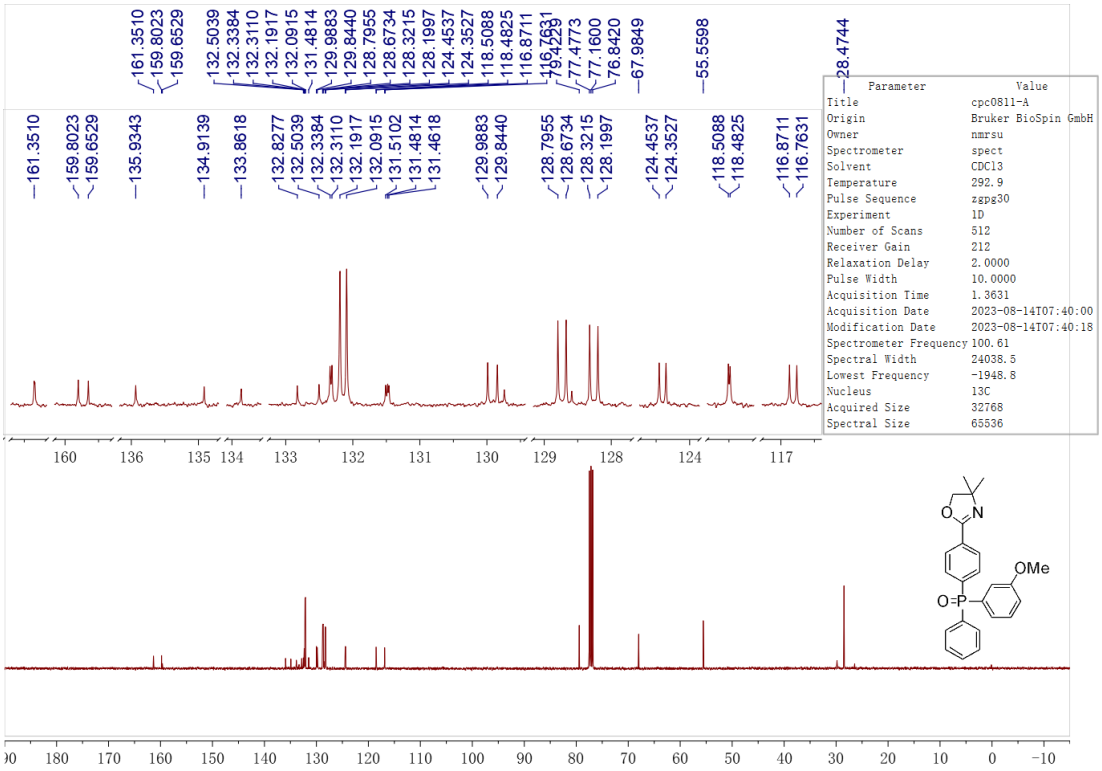


Figure S72 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3ak**

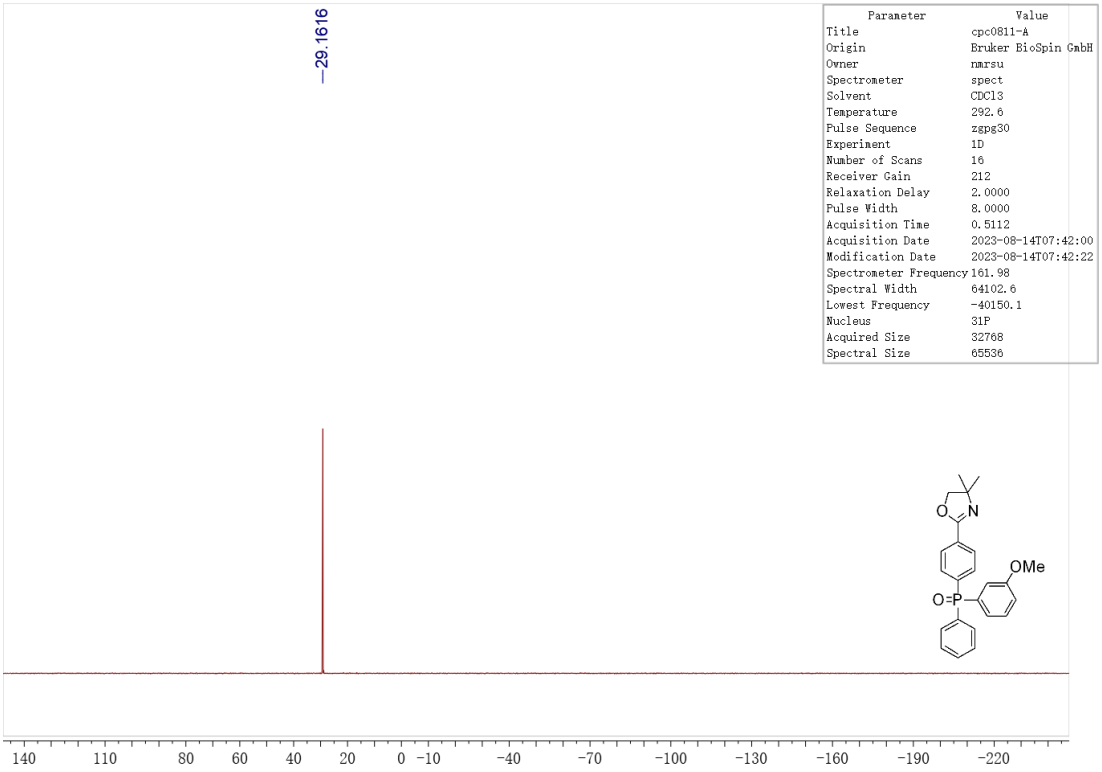


Figure S73 ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3ak**

Figure S74 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3al**

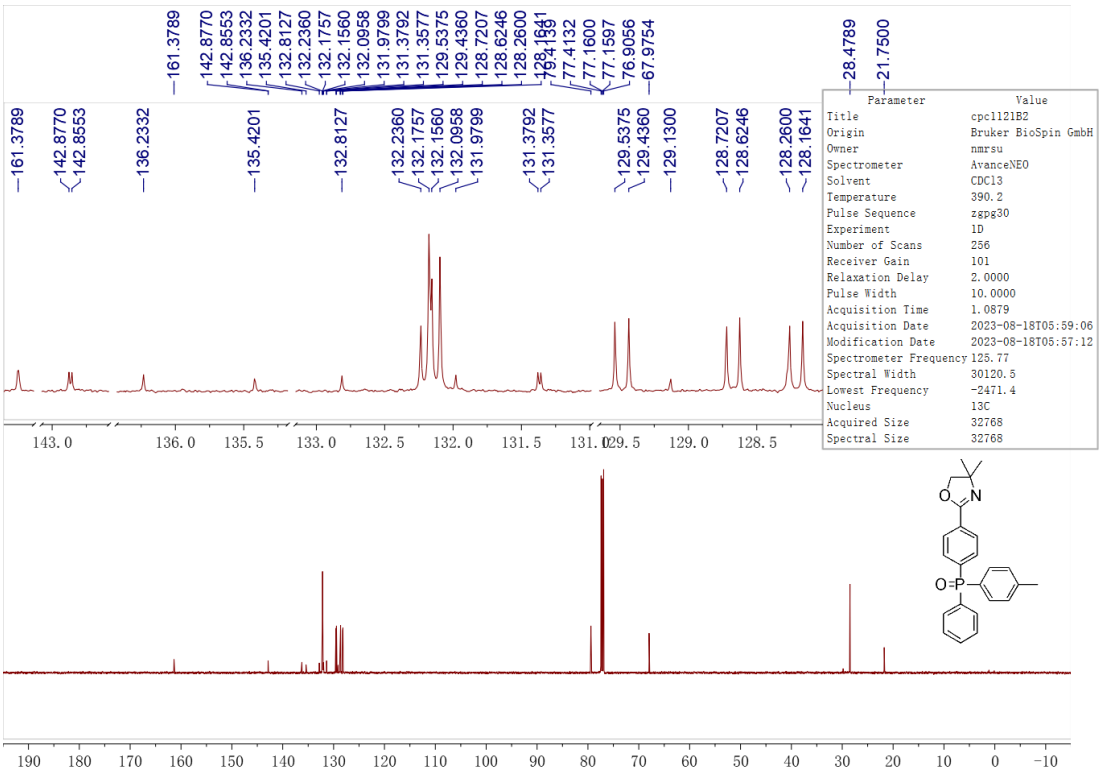


Figure S75 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3al**

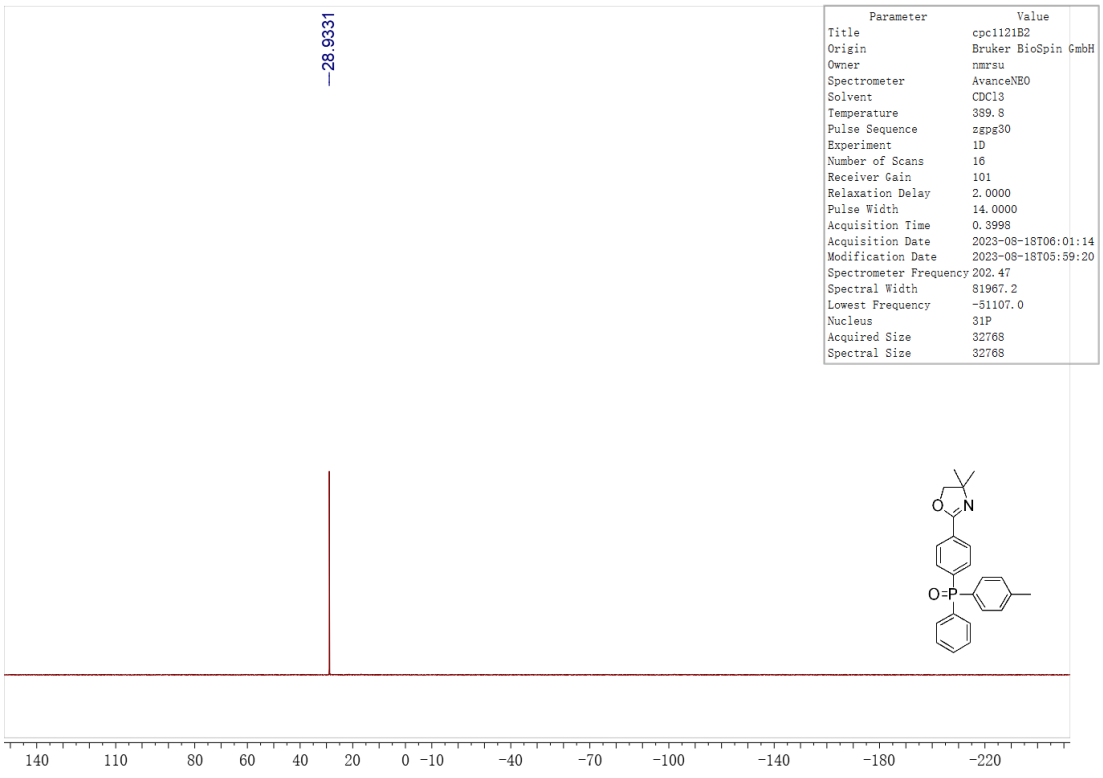


Figure S76 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3al**

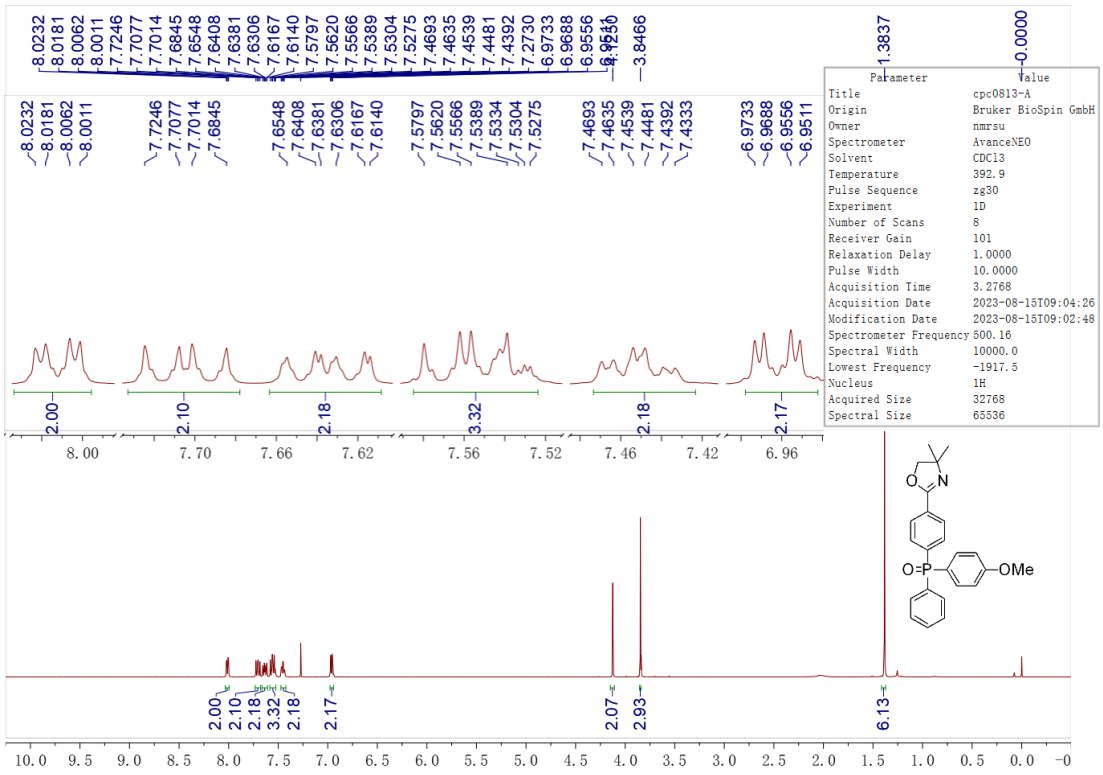


Figure S77 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3am**

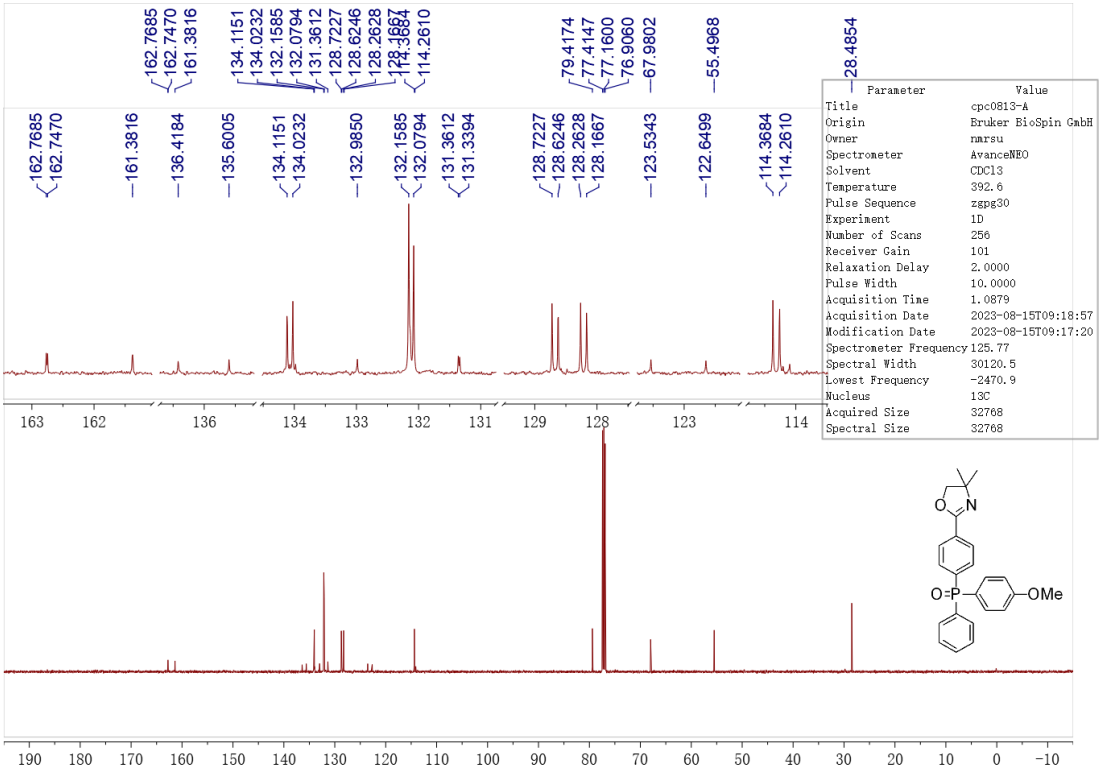


Figure S78 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3am**

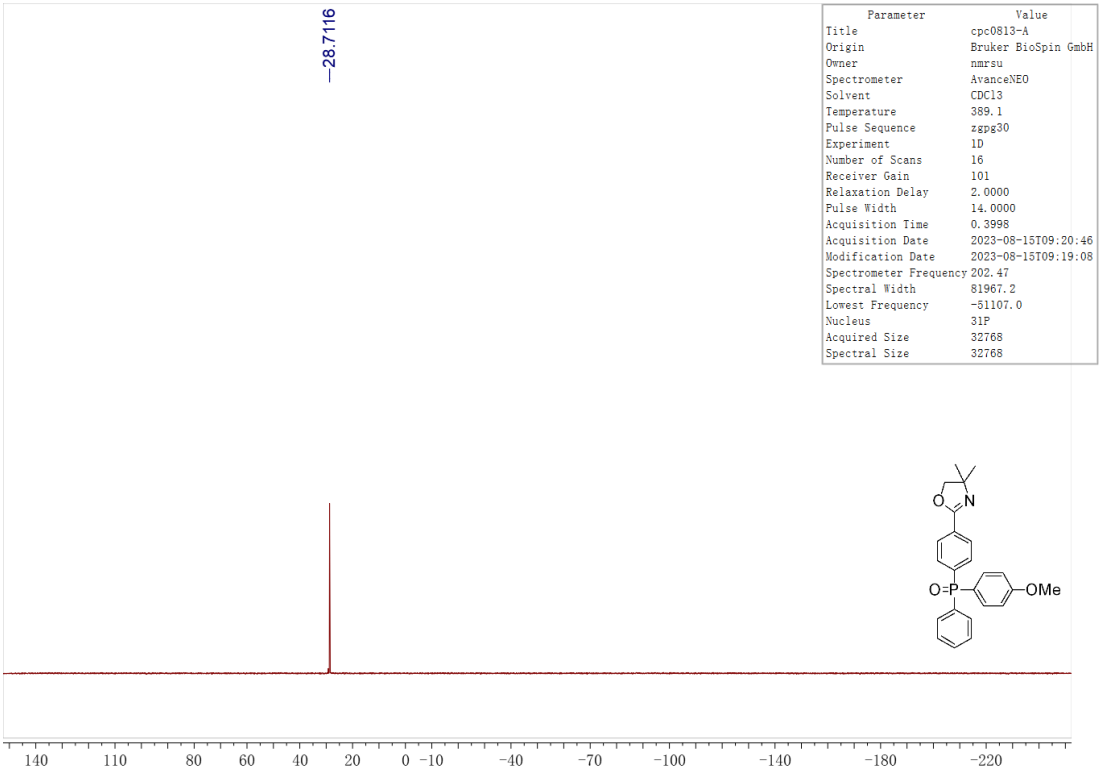


Figure S79 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3am**

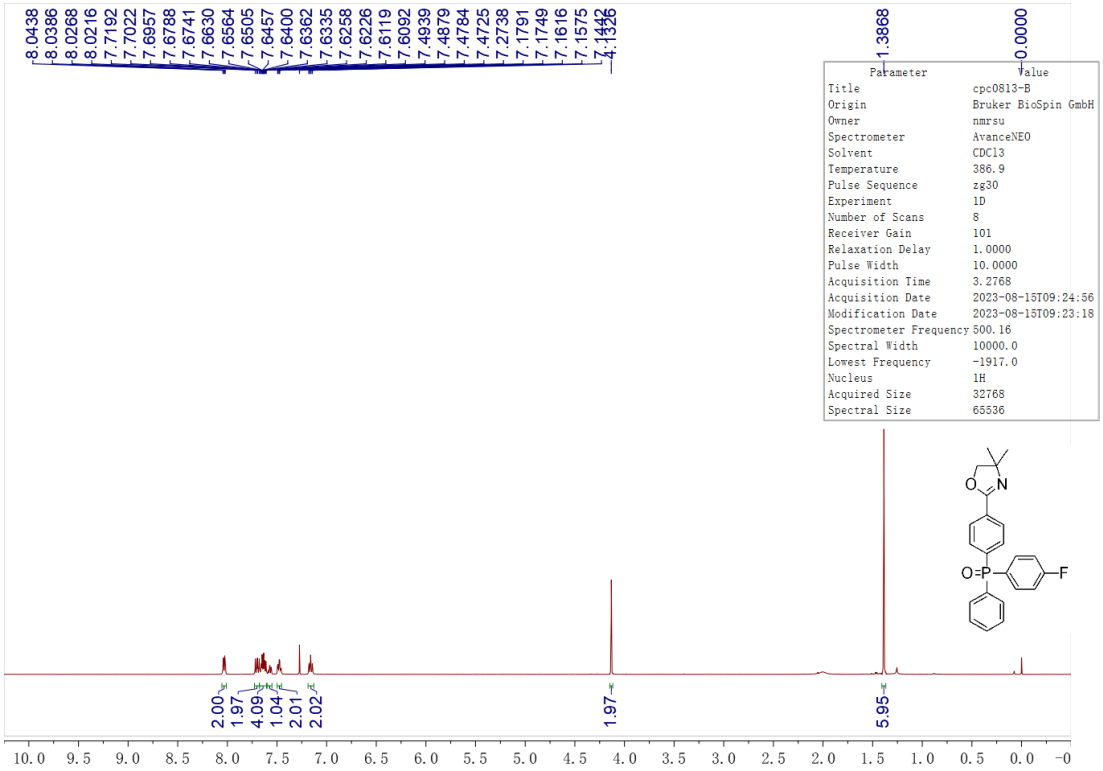


Figure S80 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3an**

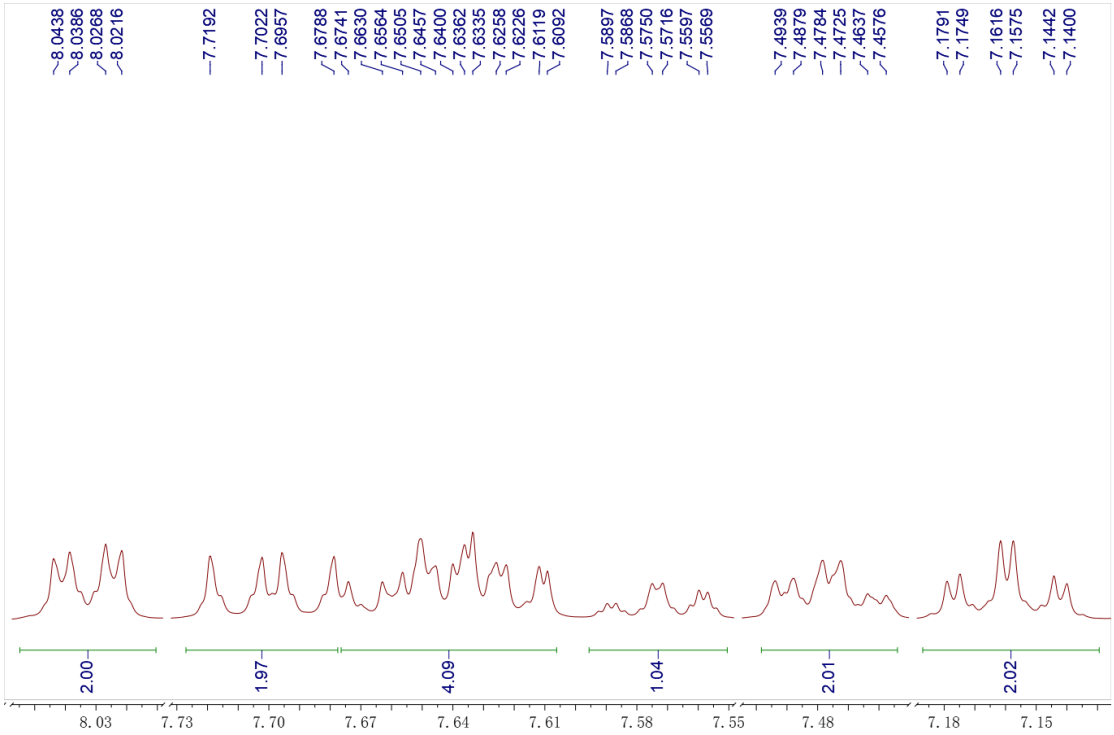


Figure S81 Expanded ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3an**

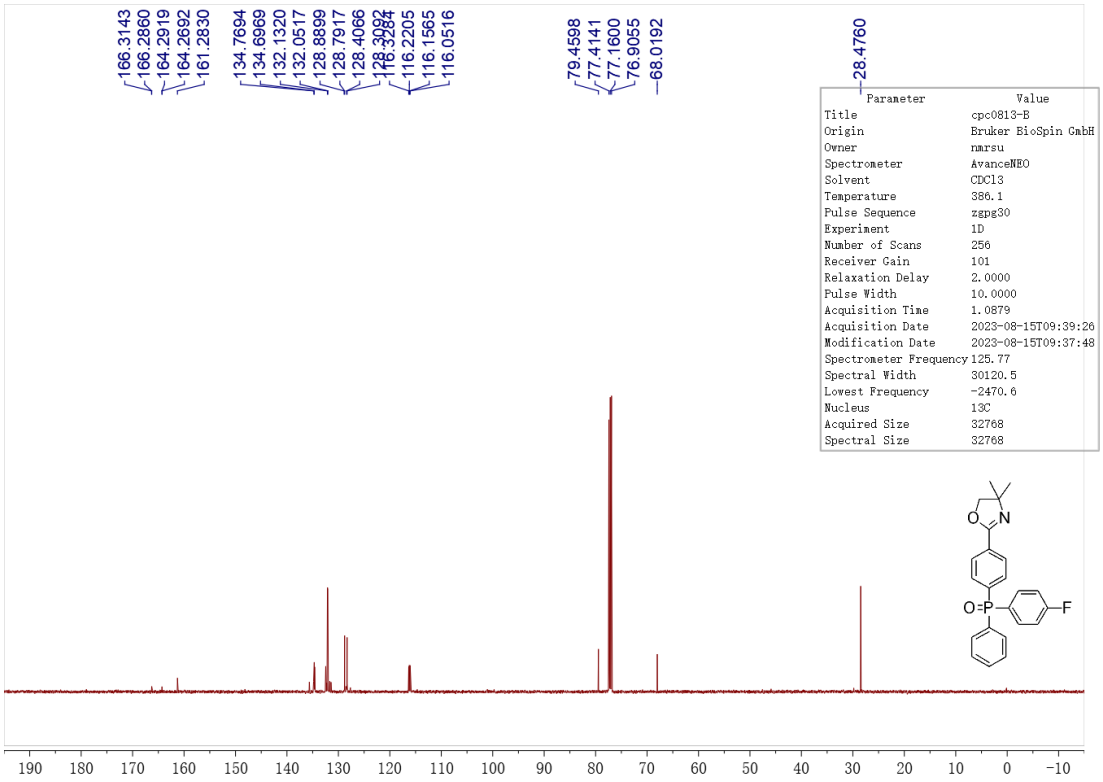


Figure S82 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3an**

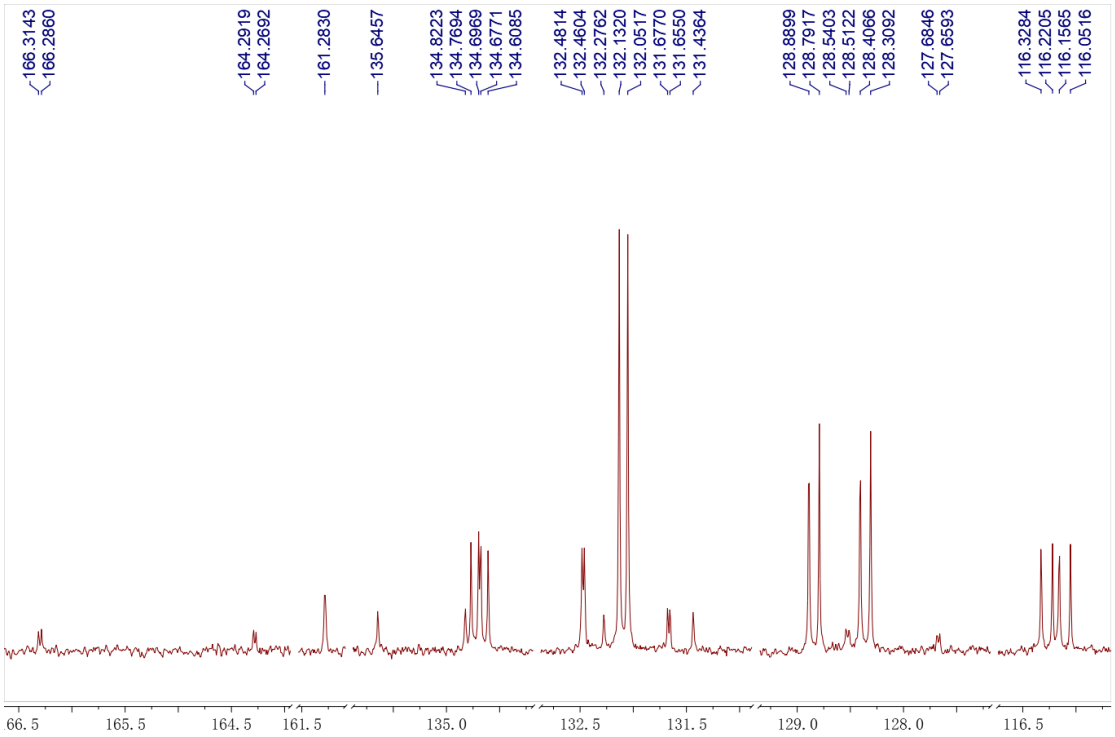


Figure S83 Expanded ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3an**

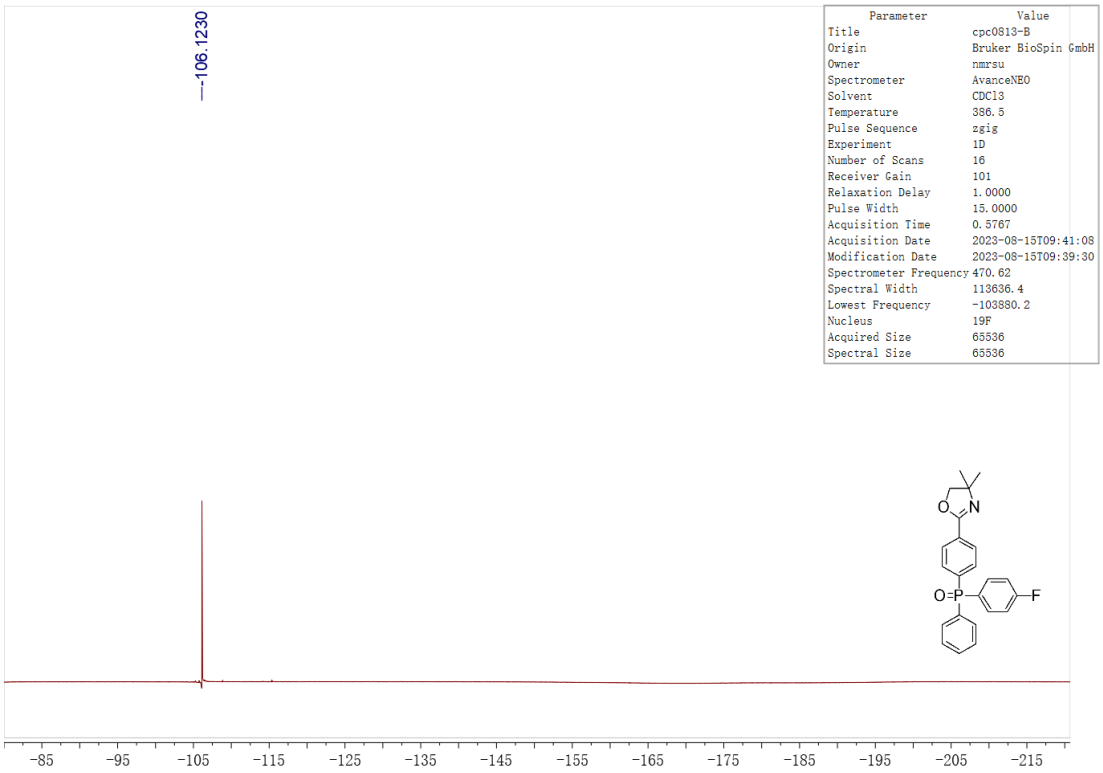


Figure S84 ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound **3an**

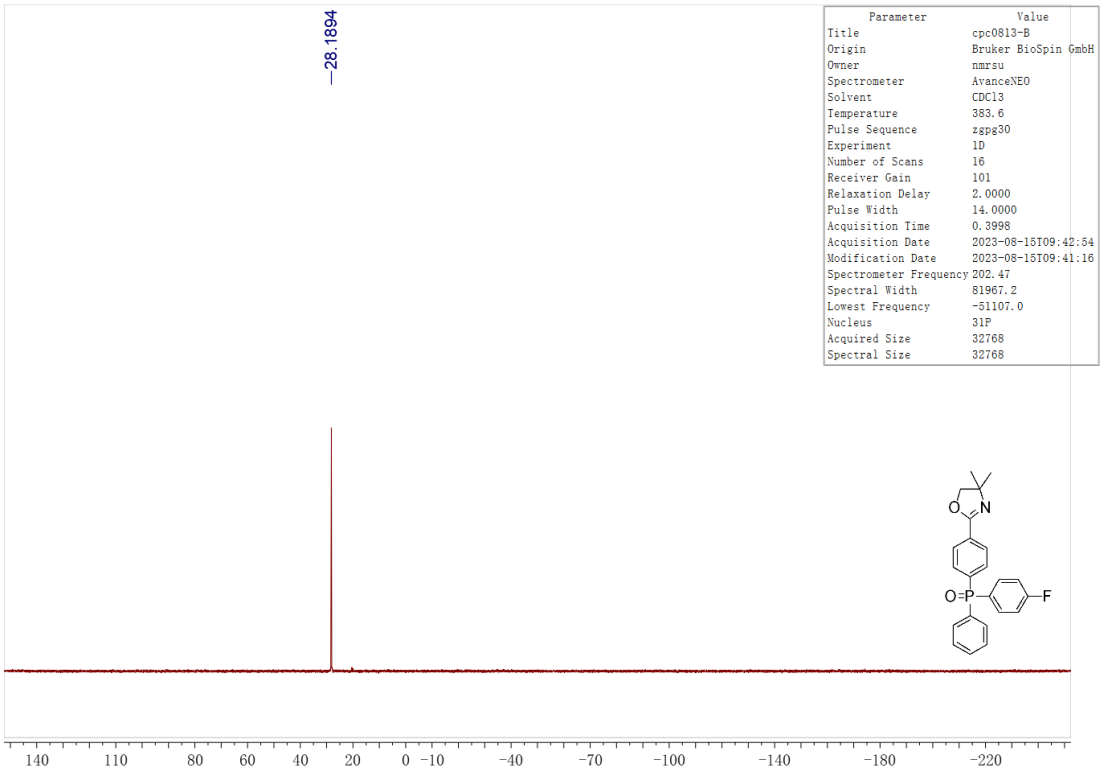


Figure S85 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3an**

Figure S86 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3ao**

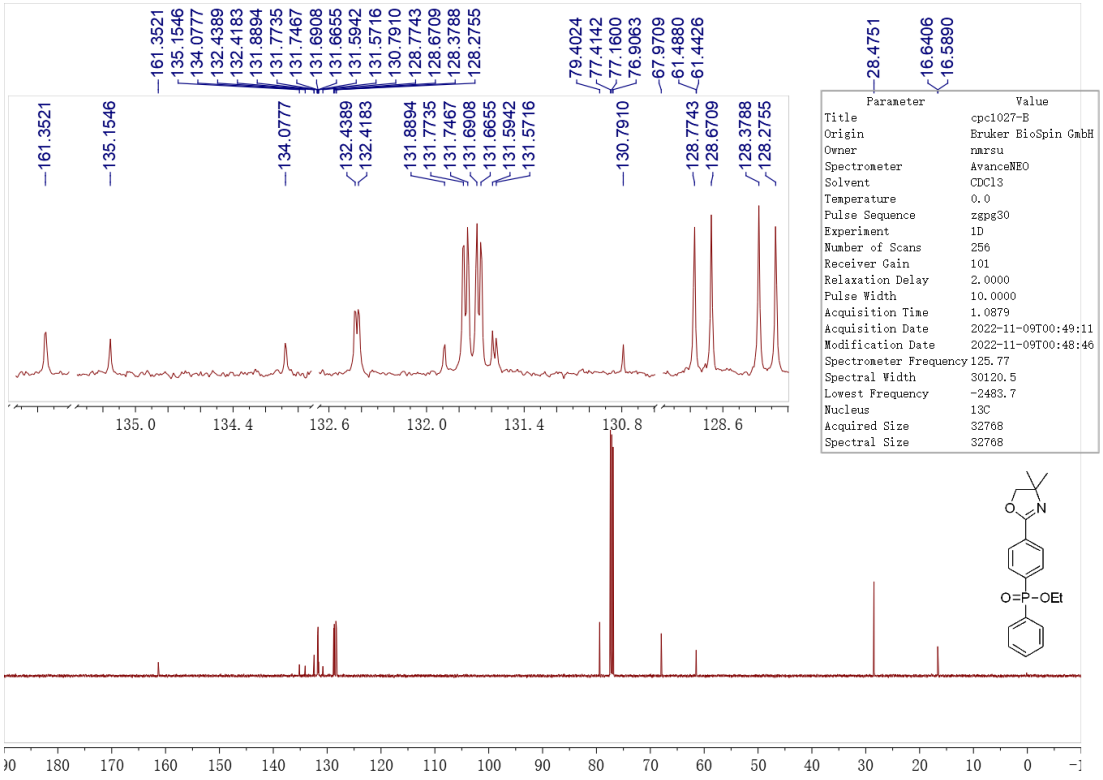


Figure S87 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3ao**

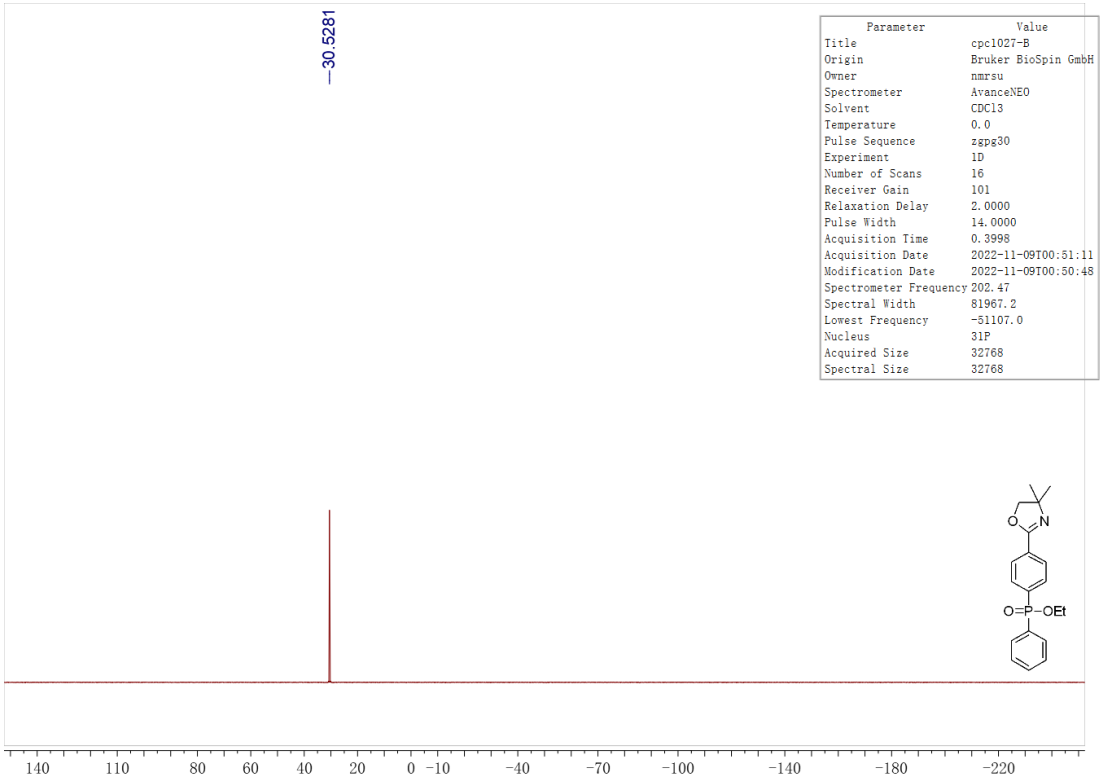


Figure S88 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3ao**

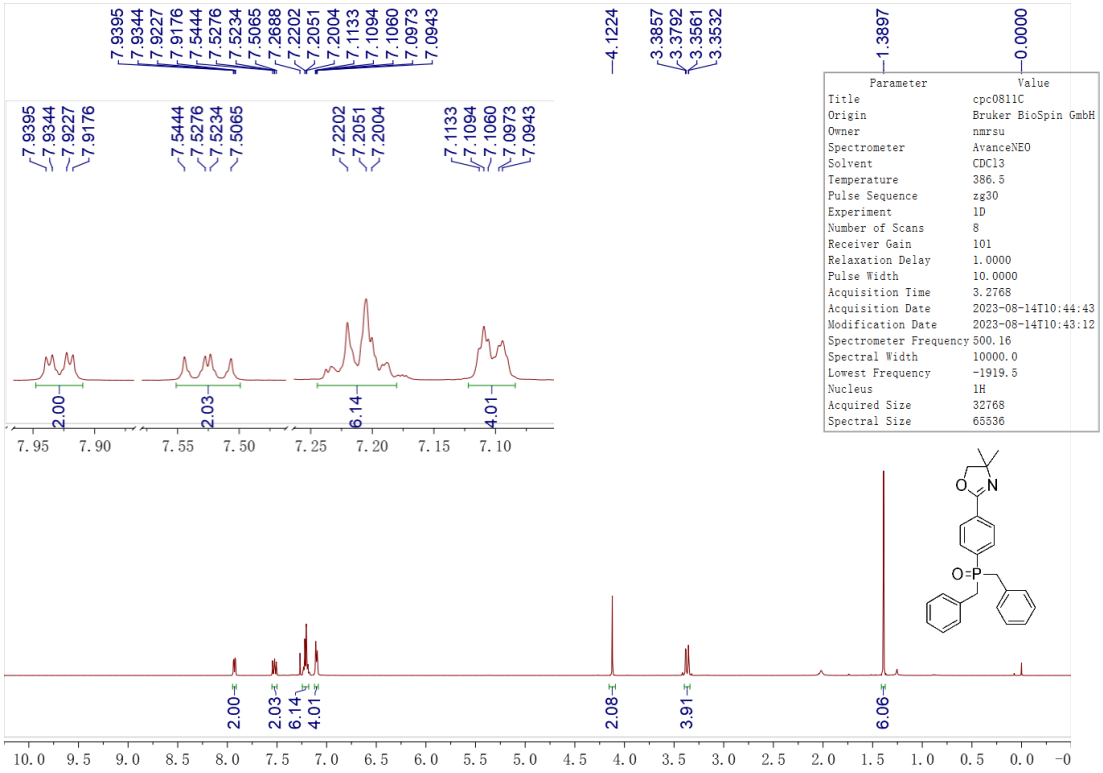


Figure S89 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3ap**

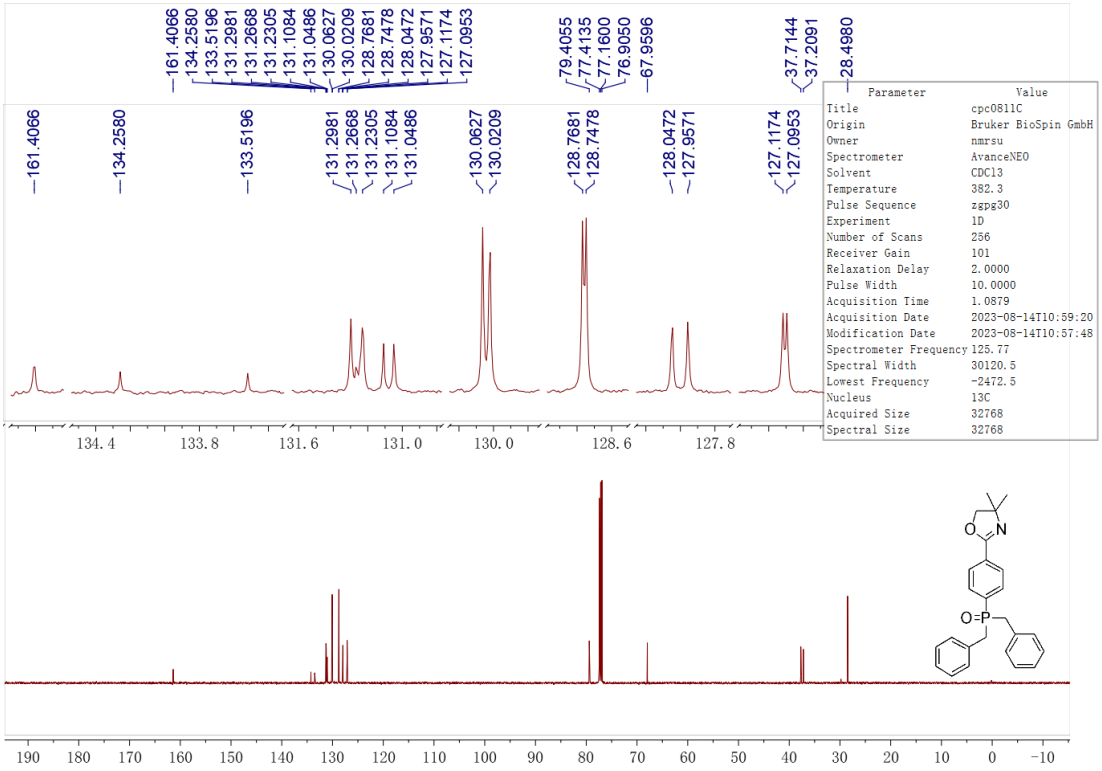


Figure S90 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3ap**

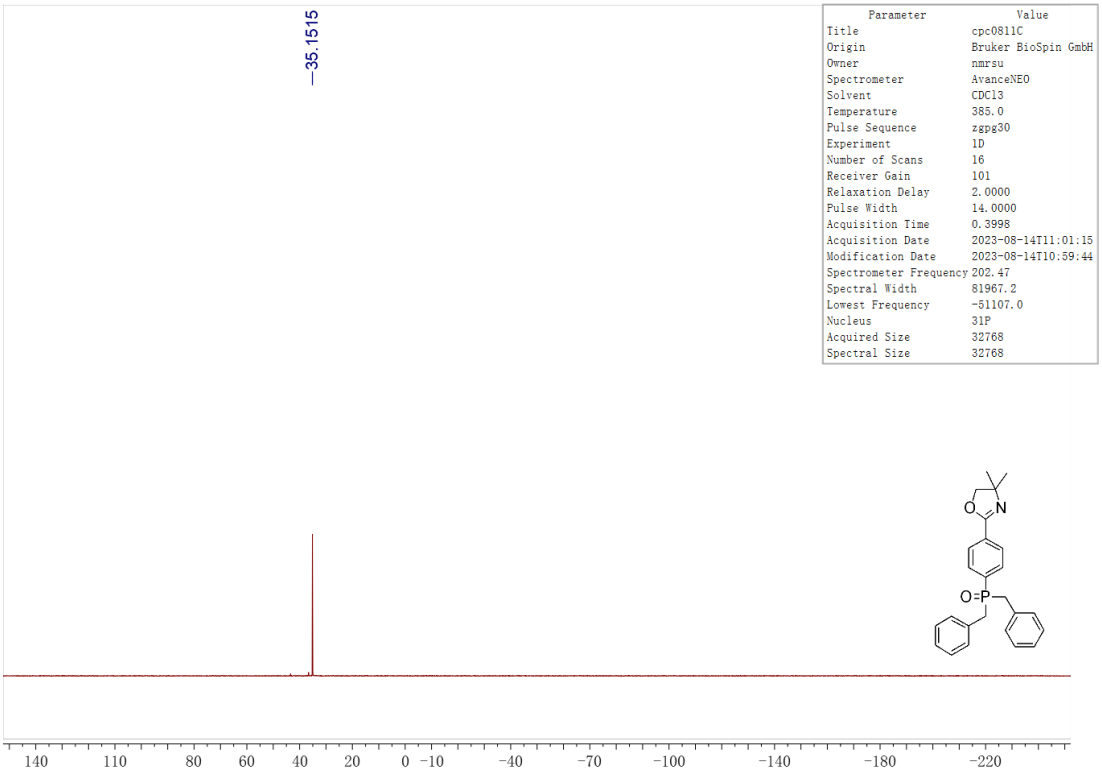


Figure S91 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3ap**

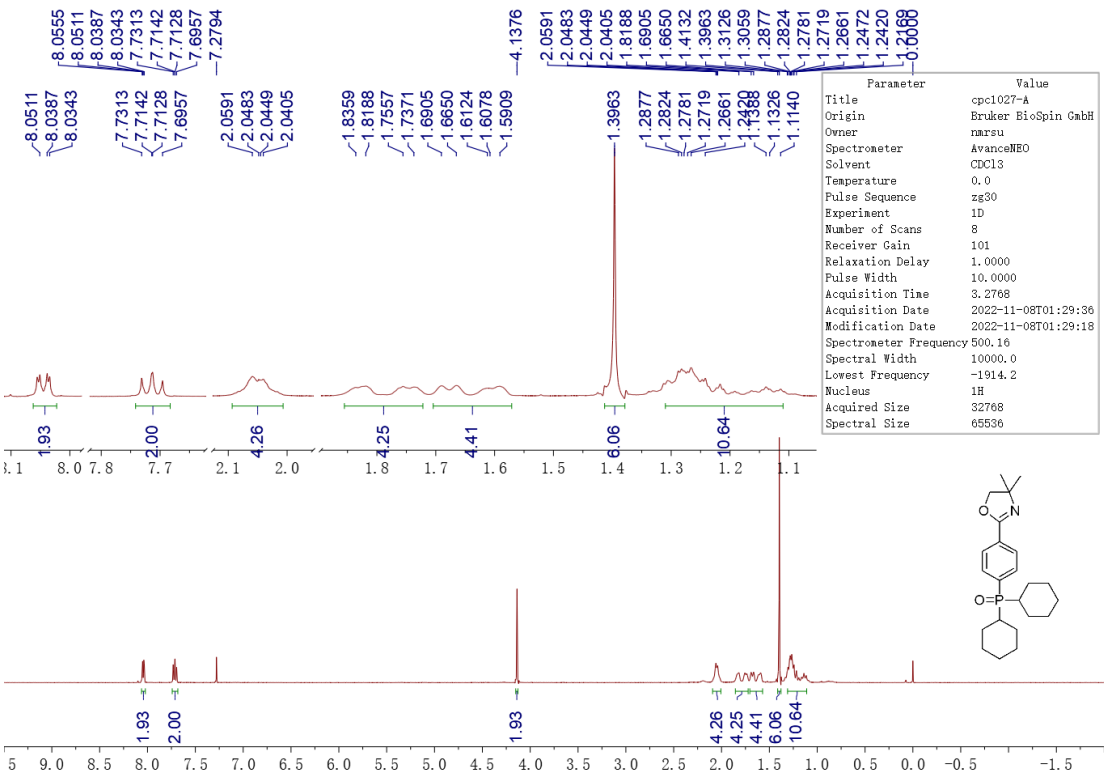


Figure S92 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3aq**

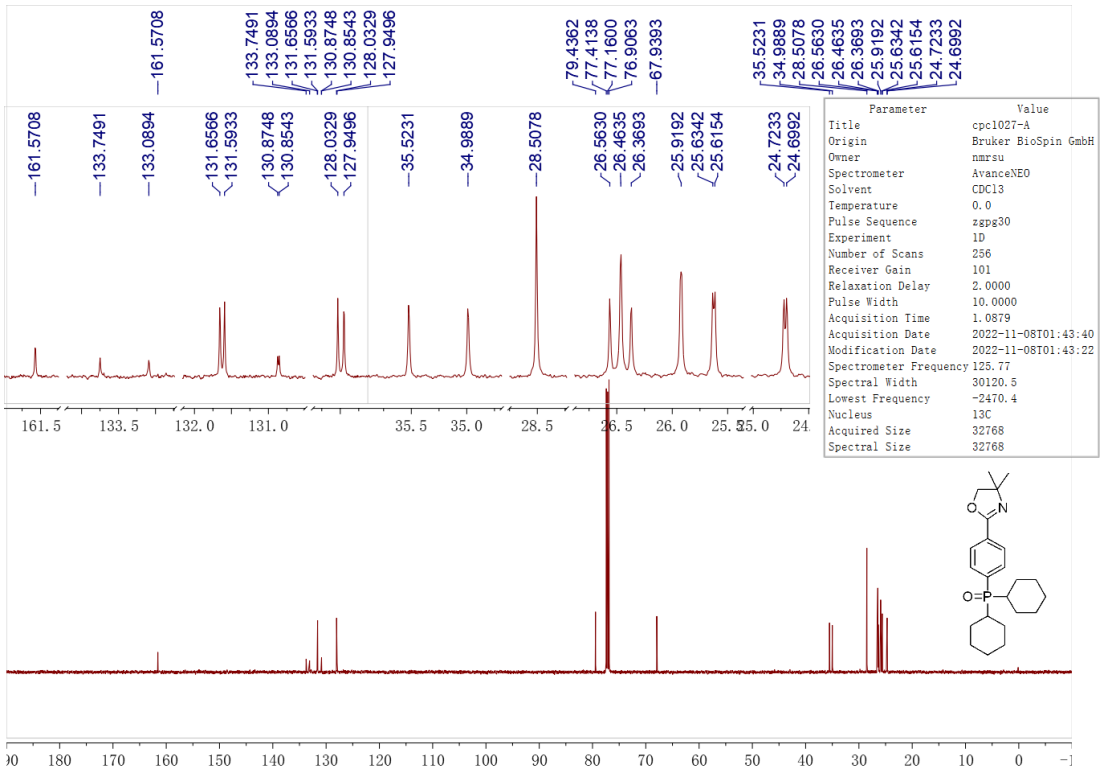


Figure S93 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3aq**

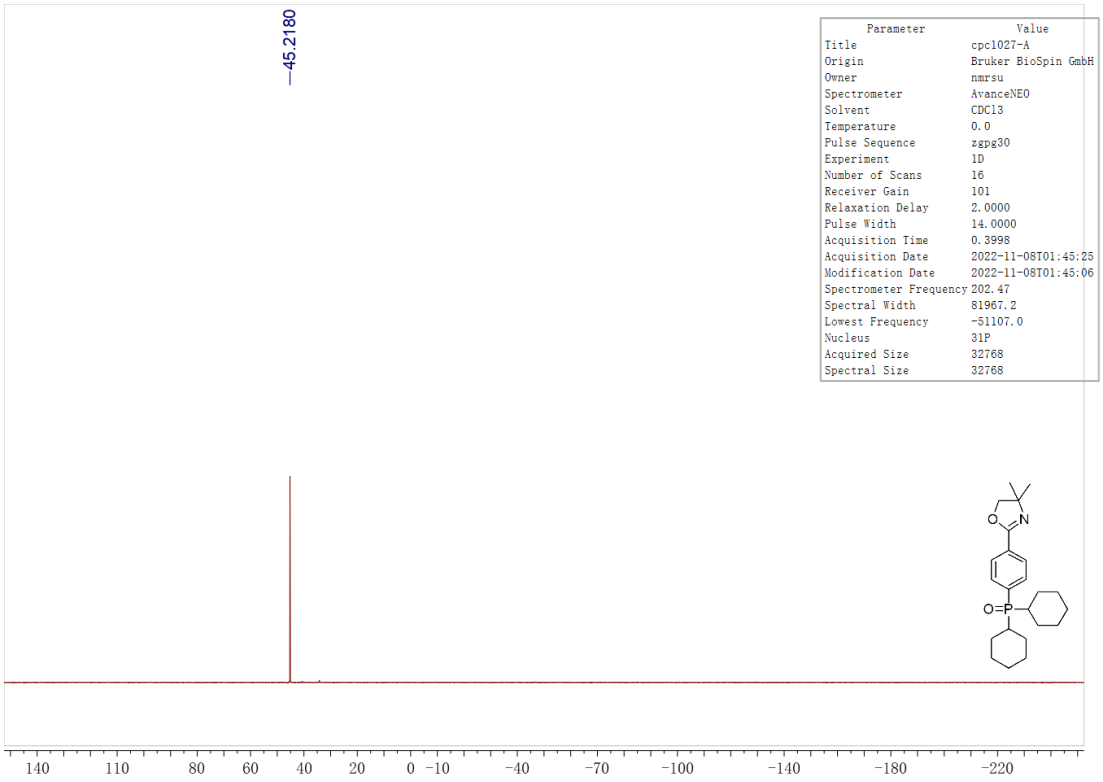


Figure S94 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3aq**

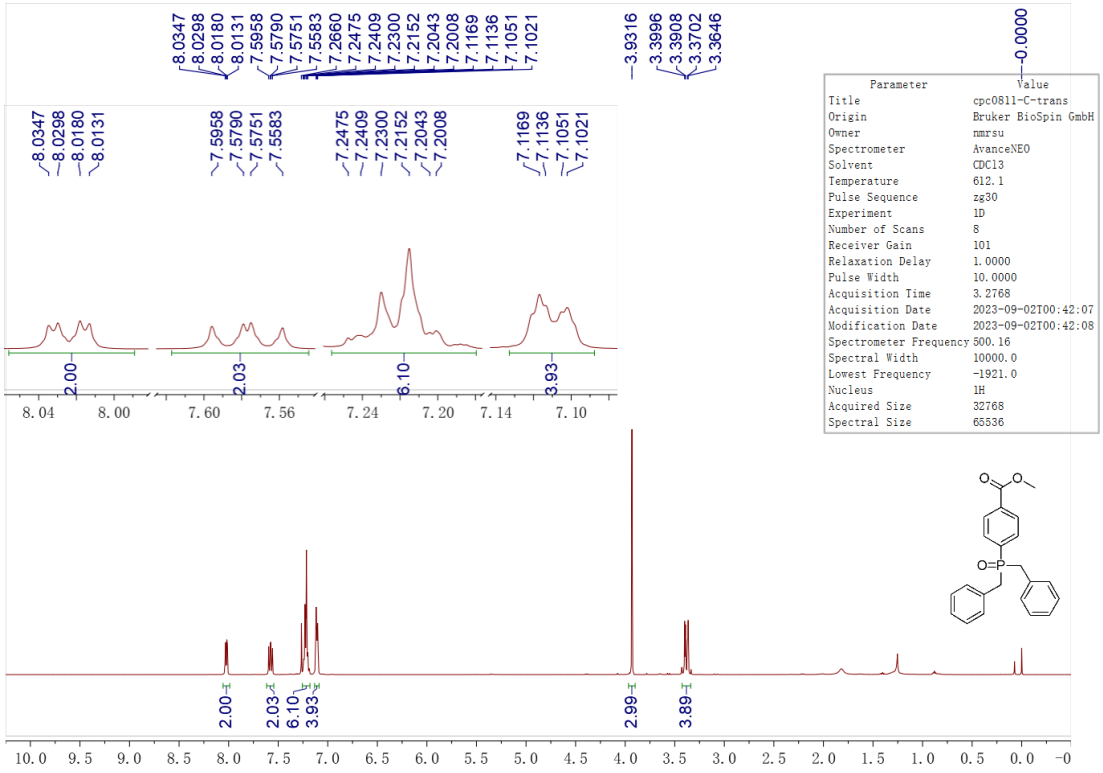


Figure S95 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4**

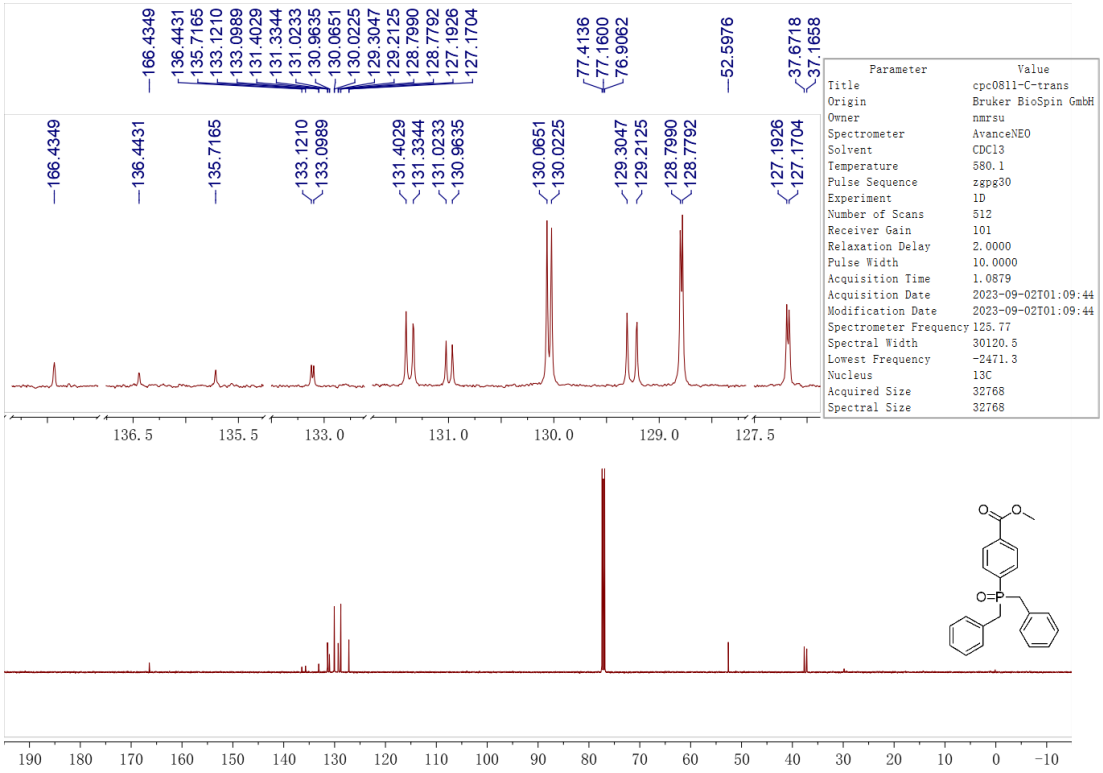


Figure S96 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **4**

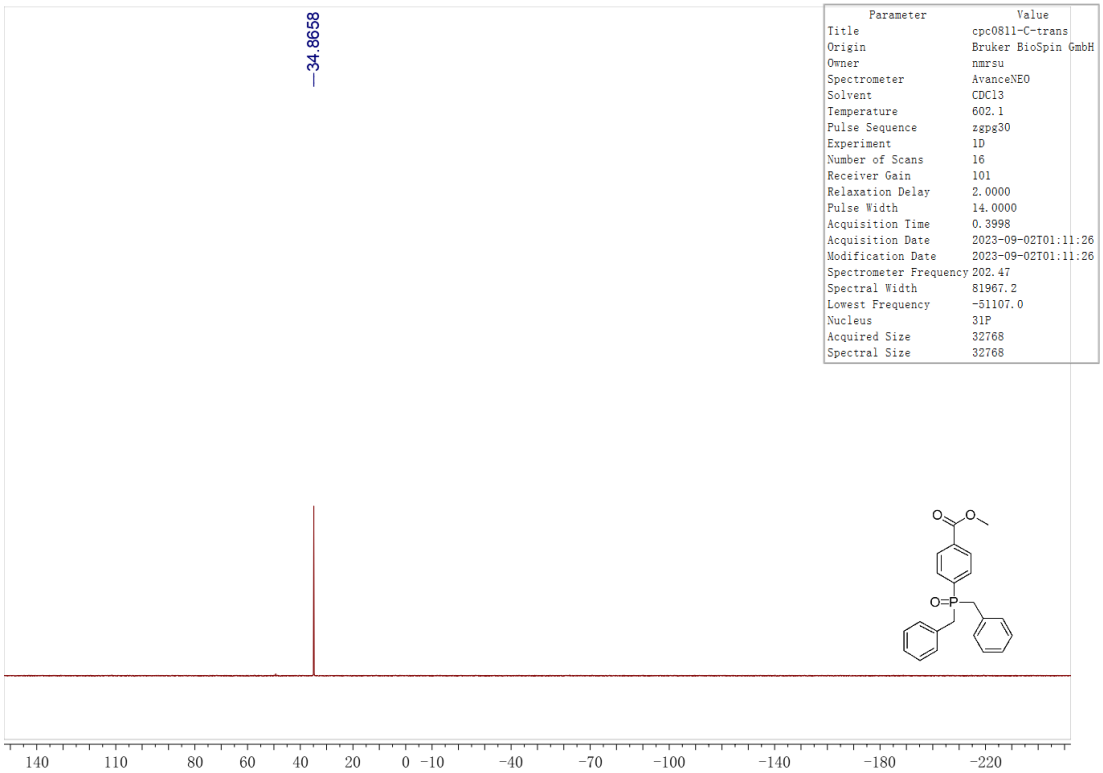


Figure S97 ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **4**