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Supporting Information for

Site-selective C-H difunctionalization of N-alkyl activated azaarenes

via the synergistic catalysis of graphene oxide and visible light

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1. General Methods

Unless otherwise specified, commercial reagents and solvents were used without further purification. Commercially available chemicals were purchased from Shanghai Haohong Scientific Co., Ltd. (Leyan) and used without any further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker spectrometers at 400 and 100 MHz, respectively. LC-electrospray ionization mass spectra were were recorded with Waters Xevo G2-XSTof LC-MS apparatus. Elemental analysis were carried out on a Perkin-Elmer 240B instrument. HRFABMS spectra were recorded on a FTMS apparatus. Silica gel (300-400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with an ethyl acetate/petroleum ether (PE) (60-90 °C) mixture.

The graphene oxide sample was recorded with Zeiss Sigma 300. Fourier transform infrared spectroscopy of graphene oxide recorded on a Jasco ATR MIRacle spectrophotometer. Samples were scanned in the 400-4000 cm⁻¹ region with KBr pellet. X-ray photoelectron spectroscopy recorded with Thermo Fisher Scientific K-Alpha using Al K_{α} radiation ($\hbar \omega = 1253.6 \text{ eV}$). The Xray power was 125 W. The spectra were recorded in the constant analyzer energy (CAE) mode with analyzer pass energies of 50 eV for the high resolution spectra. Charging effects were corrected by energy calibration on Al level relative to 284.80 eV. Steady state emission of 4e was recorded using Edinburgh, FLS 980 Fluorescence spectrometer. Time-resolved photoluminescence decay measurements were carried out using a time-correlated single-photon counting (TCSPC) spectrometer (Edinburgh, FLS 980). Compounds **3h** and **4b** were collected by a diffractometer Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation (1.54178 Å) by using a w scan mode.

2. Experimental Procedures

2.1 General procedures for synthesis of C4-phosphonated products



Halogenated pyridinium/quinolinium salts (1) (0.20 mmol), phosphine oxides (2) (0.24 mmol), DABCO (0.6 mmol), GO (50 wt%), were added to a 10-mL quartz tube in CH₃CN (2 mL), and then the mixture was irradiated with blue LED strip (20 W) (approximately 1.5 cm away from the light source) at room temperature under air atmosphere. After complete conversion of the substrate (monitored by TLC), the reaction mixture was diluted with 20 mL of DCM, and the solution was filtered by flash chromatography (petroleum ether/ethyl acetate 1:1). The filtrate was evaporated by rotary evaporator, and the residue was purified by silica gel column chromatography to give the desired products **3**.

2.2 General procedures for synthesis of C2-phosphonated quinolones



Halogenated quinolinium salts (1) (0.20 mmol), phosphine oxides (2) (0.24 mmol), NaOH (0.2 mmol), GO (50 wt%), were added to a 10-mL quartz tube in CH₃OH (2 mL), and then the mixture was irradiated with blue LED strip (20 W) (approximately 1.5 cm away from the light source) at room temperature under air atmosphere. After complete conversion of the substrate (monitored by TLC), the reaction mixture was diluted with 20 mL of DCM, and the solution was filtered by flash chromatography (petroleum ether/ethyl acetate 1:2). The filtrate was evaporated by rotary evaporator, and the residue was purified by silica gel column chromatography to give the 2-phosphonated quinolones **4**.

	+ Ph	O Pr P P Ph H	notocatalyst Base Light Solvent	O _∑ Ph Ph Ph O∑ P∕ O	
	1a	2a		3a	
Entry	Photocatalyst	Base	Light	Solvent	Yield(%)
1	GO	DABCO	Blue	CH ₃ OH	28
2	GO	DABCO	Blue	DMSO	NR
3	GO	DABCO	Blue	DMF	28
4	GO	DABCO	Blue	DCE	36
5	GO	DABCO	Blue	DCM	52
6	GO	DABCO	Blue	THF	30
7	GO	DABCO	Blue	1,4-Dioxane	43
8	GO	DABCO	Blue	Acetone	55
9	GO	DABCO	Blue	CH ₃ CN	80
10	Graphene	DABCO	Blue	CH ₃ CN	15
11	Graphite	DABCO	Blue	CH ₃ CN	12
12	Eosin Y (5 mol%)	DABCO	Blue	CH ₃ CN	18
13	Rhodamine B (5 mol%)	DABCO	Blue	CH ₃ CN	25
14	GO	Et ₃ N	Blue	CH ₃ CN	trace
15	GO	NaOH	Blue	CH ₃ CN	37
17	GO	Cs_2CO_3	Blue	CH ₃ CN	42
18	GO	^t BuOK	Blue	CH ₃ CN	44
19	GO	KHCO ₃	Blue	CH ₃ CN	NR
20	GO	DABCO	Green	CH ₃ CN	46
21	GO	DABCO	White	CH ₃ CN	62
22 ^c	GO	DABCO	Blue	CH ₃ CN	NR
23^d	GO	DABCO	Blue	CH ₃ CN	82
24 ^e	GO	DABCO	Blue	CH ₃ CN	59
25	_	DABCO	Blue	CH ₃ CN	12
26	GO	_	Blue	CH ₃ CN	NR
27	GO	DABCO	_	CH ₃ CN	10

2.3 Table S1. Optimization study of C4-phosphonated products^a

^{*a*}Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.24 mmol, 1.2 equiv), DABCO (0.6 mmol), GO (50 wt%), 20w blue LEDs, for 12 h at rt under open air. ^{*b*}Isolated yield. ^{*c*}Ar. ^{*d*}O₂. ^{*e*}GO (25 wt%).

	+ Ph	O Photo P E H Ph L Sc	ocatalyst Base ∟ight olvent	O Ph Ph	
Entry	Photocostalyst	Dasa	Light	4a Solvent	Viald(%)
Linu y	Thotocatalyst	Dase	Light	Solvent	b
1	GO	NaOH	Blue	Acetone	23
2	GO	NaOH	Blue	DMSO	NR
3	GO	NaOH	Blue	DMF	17
4	GO	NaOH	Blue	DCM	32
5	GO	NaOH	Blue	THF	27
6	GO	NaOH	Blue	1,4-Dioxane	22
7	GO	NaOH	Blue	СН ₃ ОН	42
8	GO	NaOH	Blue	CH ₃ CN	35
9	Graphene	NaOH	Blue	CH ₃ OH	< 5
10	Graphite	NaOH	Blue	CH ₃ OH	< 5
11	Eosin Y (5 mol%)	NaOH	Blue	CH ₃ OH	11
12	Rhodamine B (5 mol%)	NaOH	Blue	CH ₃ OH	12
13	GO	Et ₃ N	Blue	CH ₃ OH	trace
14	GO	DABCO	Blue	CH ₃ OH	35
15	GO	Cs_2CO_3	Blue	CH ₃ OH	32
16	GO	^t BuOK	Blue	CH ₃ OH	32
17	GO	KHCO ₃	Blue	CH ₃ OH	NR
18	GO	NaOH	Green	CH ₃ OH	25
19	GO	NaOH	White	CH ₃ OH	33
20 ^c	GO	NaOH	Blue	CH ₃ OH	NR
21^d	GO	NaOH	Blue	CH ₃ OH	43
22 ^e	GO	NaOH	Blue	CH ₃ OH	28
23 ^f	GO	NaOH	Blue	CH ₃ OH	30
24	_	NaOH	Blue	CH ₃ OH	< 5
25	GO	-	Blue	CH ₃ OH	NR
26	GO	NaOH	_	CH ₃ OH	< 5

2.4. Table S2. Optimization study of C2-phosphonated quinolones^a

^{*a*}Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.24 mmol, 1.2 equiv), NaOH (0.2 mmol), GO (50 wt%), 20w blue LEDs, for 12 h at rt under open air. ^{*b*}Isolated yield. ^{*c*}Ar. ^{*d*}O₂. ^{*e*}GO (25 wt%).

3. Characterization of Graphene Oxide (GO)

3.1 The scanning electron microscope of GO (pre-reaction and post-reaction)

GO was prepared by graphite oxidation using the Hummers and Offeman method and subsequent exfoliation.¹ Considering the π - π interactions and oxygen-containing functional groups could facilitate the mass transfer and then increase catalytic performance, scanning electron microscope (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), Fourier Transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) were used to analyze and characterize this inorganic-organic hybrid material. The SEM image of the sample, a black flaky and blocky structure, was clearly observed that the GO has 10 µm in Figure S1. The surface of GO showed a classic folded morphology,² and its specific surface area was large, providing an ideal catalytic surface for the introduction of active centers (Figure S1 A). After the reaction completed, the fold surface of GO (post-reaction) was decreased and damaged (Figure S1 B).



Figure S1. SEM image of GO (pre-reaction, A) and GO (post-reaction, B).

Compared with GO (pre-reaction, C), GO (post-reaction, D) showed more amount of obvious peeling state.



Figure S2. TEM image of GO (pre-reaction, C) and GO (post-reaction, D). Similarly, GO (post-reaction, F) emerged obvious division with a single layer sheet. These analysis showed that GO participated in the C–H functionalization reaction.



Figure S3. AFM image of GO (pre-reaction, E) and GO (post-reaction, F).

3.2 Fourier transform infrared (FT-IR) spectroscopy of GO (pre-reaction and post-reaction)

For the GO, the FT-IR spectroscopy analysis was further carried out. As shown in Figure S4, the wide peak at 3600-2800 cm⁻¹ could be ascribed to the vibration deformation and vibration stretching of hydroxyl (O-H) and the vibration deformation peak of water. The peaks of 1739 cm⁻¹ and 1627 cm⁻¹ were vibration stretching absorption of carbonyl group (C=O) and carbon-carbon double bond (C=C), respectively, and the wide peak at 1226-491 cm⁻¹ was the vibration stretching of epoxy group (C-O) and vibration stretching of alkoxy group (C-O) at the surface of GO.³ The peak at 1367 cm⁻¹ was the vibration stretching of O=C-O group. The above FT-IR data indicated that GO surface was rich in hydroxyl, carbonyl, epoxide, ether and other oxygen-containing functional groups. After the C–H functionalization reaction, a new peak at 1629 cm⁻¹ emerged in the spectrum of GO (post-reaction), which could be attributed to the characteristic bands of amide (δ NH).⁴ Compared with GO (pre-reaction), the range of recovered heterogeneous GO (Post-

reaction) became wide at the peaks of hydroxyl (O-H) and epoxy group (C-O), indicating that the cooperative action of the oxygen-containing moieties, Brønsted acidity and π -surface of the GO was crucial in the reaction course of the regioselective protocol.



Figure S4. The FT-IR spectrum of GO (pre-reaction and post-reaction).

3.3 The X-ray photoelectron spectroscopy (XPS) of GO (pre-reaction and post-reaction)

The samples were analyzed by XPS in order to study the surface chemical state and chemical composition of GO (pre-reaction and post-reaction). Compared with the surface oxygen functionalities on pre-reacted GO sheets, the post-reaction of GO varied according to the proportion of oxidized groups, which were associated with the aromatic C=C/C=O, C-C/C-H, and C-OH groups. XPS analysis (Figure S5) confirmed that the populations of C-O and C=O groups became significantly reduced after the phosphinoyl radical-based processes. For GO (post-reaction), the presence of C, O, P and I was confirmed by survey full-scale XPS spectrum (Figure S6), indicating that *N*-alkyl activated azaarenes and phosphine oxides were successfully doped in GO sheets. Furthermore, the percentage of C was increased to 75.4% from 65.4%, while the O content was decreased to 19.4% from 33.4%. The removal of oxygen functionalities is attributed to the effective removal of oxidative fragments and to a dehydration reaction driven by the base conditions.⁵ As shown in the FT–IR and XPS spectra, although some groups were reduced after the reaction, oxygen functionalities still remained in the GO (post-reaction), and it wasn't totally transformed into graphene.



Figure S5. The XPS C1s and O1s spectra GO (pre-reaction and post-reaction).



Binding Energy (eV)

Figure S6. The full-scale XPS spectrum of GO (pre-reaction and post-reaction).

3.4 Stern-Volmer fluorescence experiments of GO

We investigated the excitation spectra of the GO in CH₃CN and CH₃OH, respectively. The tested liquid was extracted supernate from a solution of GO in solvent. The fluorescence excitation spectrum was obtained with the detection wavelength of 480 nm (Figure S7). The solution was excited two sharp peaks around 393 nm and 405 nm (excitation maximum of GO), respectively, and the fluorescence quenching experiments revealed that C4- and C2-selective difunctionalizations of pyridiniums/quinoliniums were effectively excited in blue spectral regions.



Figure S7. The fluorescence excitation spectrum of GO with the detection wavelength of 480 nm.

4. Control Experiments

4.1 ¹⁸O-Labeling experiments

The ¹⁸O-labeling experiments were performed with ¹⁸O₂ (innochem, ¹⁸O atom 97%), and high resolution positive ion electrospray mass spectra (HRMS-ESI) for the final products were shown in Figures S8. The results showed that origin of oxygen element in the desired products **3** and **4** was mainly from the oxygen of air.





Figure S8. ¹⁸O-Labeling ¹⁸O₂ experiments and the HRMS-ESI positive ion mass spectrum for the final products. ¹⁸O-labeling products **3a'** and **4a'** were observed. Reaction conditions: ¹⁸O₂ atmosphere and irradiation with 20 W blue LEDs, standard conditions in a 25-mL Schlenk tube.

4.2 Control experiments from the C-H functionalization reactions of site-selective azaarenes

Some control experiments were performed to further investigate the mechanism of the photoredox aerobic oxidation reaction (Figure S9). At first, the yield of **3a** or **4a** was not observed under argon conditions. 2,2,6,6-Tetramethylpiperidinooxy (TEMPO) or 2,6-di-tert-butyl-4-methylphenol (BHT) was added to the reaction system, and the yield of **3a** or **4a** obviously decreased, which suggested the reactions could undergo a radical process. We used quinolinone or quinolone instead of *N*-methylquinolinium salt (**1a**), and the reaction was completely inhibited. Therefore, phosphonyl radicals was firstly added to the quinoliniums before oxidation.



Figure S9. Control experiments under different conditions.

4.3 Intermediates by ESI-HRMS





Figure S10. 0.4 mmol TEMPO in standard conditions at a 10 mL quartz test tube.



Figure S11. Detection of intermediate G.

5. Study on Anti-tumor Activity

5.1 In vitro cytotoxicity assays

The MGC-803, T-24, Hela, HepG2, A549 cell lines were all obtained from the Institute of Biochemistry and Cell Biology, China Academy of Sciences. Cells were cultured in DMEM, which supplemented with 10% fetal bovine serum in a humidified atmosphere of 5% CO₂/95% air at 37 °C. All compounds and 5-FU were dissolved in the Phosphate Buffered Saline (PBS) with 1% DMSO to give various concentrations to 96-well plates and control wells contained supplemented media with 1% DMSO. Continue incubating for 48 h at 37 °C and in 5% CO₂ atmosphere. MTT (5 mg·mL⁻¹) was added into the wells, and the plates were incubated at 37 °C for 4 h. The MTT assay was stopped by adding dimethyl sulfoxide (100 μ L per well) and mixed for 10 min vigorously before measuring absorbance at 490 nm in a multi well plate reader. The cytotoxicity was estimated based on the percentage cell survival in a dose dependent manner relative to the negative control. The final IC₅₀ (a drug concentration killing 50% cells) values were calculated by the Bliss method. All target compounds were tested against T-24, MGC-803, HepG2, Hela and A549 cancer cell lines, respectively.

Compd.	T24	Hela	A549	HepG2	MGC-803	HL-7702
3a	37.65±1.08	42.81±0.68	35.45±0.56	29.21±0.27	45.79±1.45	>50
3b	>50	38.73±0.88	>50	26.57±0.41	41.21±1.03	>50
3c	18.65±1.01	12.92±1.04	19.47±0.96	16.81±1.43	22.75±1.11	>50
3d	28.28±0.76	27.41±1.06	28.01±1.22	25.77±1.38	26.78±0.95	>50
3e	34.29±0.99	37.25±0.46	31.09±0.51	30.84±0.68	33.19±1.15	>50
3f	36.86±0.70	28.08±1.07	38.50±0.37	34.01±1.54	33.14±1.82	>50
3g	>50	>50	>50	>50	>50	>50
3h	>50	>50	>50	>50	>50	>50
3i	>50	>50	>50	>50	>50	>50
3g	>50	>50	>50	>50	>50	>50
3k	27.79±0.07	28.77±0.89	27.69±0.93	22.83±1.24	19.66±1.92	>50
3l–3ah	>50	>50	>50	>50	>50	>50
4a–4k	>50	>50	>50	>50	>50	>50
5-FU	40.45±1.89	43.69±1.63	39.29±1.27	42.03±0.52	48.23±0.98	49.81±1.09

Table S3. The IC₅₀ (μ M)^{*a,b*} values of inhibition against different tumor cell lines.

^{*a*}Data are expressed as means \pm SD of three independent experiments. ^{*b*}Compounds with IC₅₀ (μ M) values > 50 μ M are considered inactive.

5.2 Apoptosis by flow cytometry

Apoptosis was discriminated with the Annexin V-FITC/propidium iodide (BD, Pharmingen) test.

The Hela cells were seeded in 6-well plates (2×106 cells/well) and cultured for 24 h, then treated with compound **3c** for 24 h. The cells were collected and washed twice with cold PBS and then resuspended in 1×Binding Buffer (0.1 M Hepes/NaOH (pH = 7.4), 1.4 M NaCl, 25 mM CaCl₂) at a concentration of 1×106 cells/ml. Transfered 100 μ L of the solution (1×105 cells) to 1.5 mL culture tube, then added 5 μ L of Annexin V- FITC and 5 μ L propidium iodide (PI) to each tube. After incubation for 30 minutes in the dark, the specimens were quantified by flow cytometry on a FACS Canto II (BD Biosciences, USA).

5.3 Hoechst 33342 staining

Hela cells were seeded into 6-well tissue culture plates and incubated for 24 h before the treatment. Cells were treated with compound **3c** for 24 h before incubation with Hoechst 33342. Removed the culture medium containing compounds and fixed the cells in 4% paraformaldehyde for 10 min. The cells were stained with 0.5 mL of Hoechst 33342 for 15 min and then washed twice with PBS. The stained nuclei were observed under a BioTek Cytation microscope fluorescence microscope.



Figure S10. Morphological analysis of the nucleus treated with compound **3c** for 24 h by Cytation (BioTek, 20^{\times}) microscopy.

5.4 Mitochondrial dysfunction

JC-1 red/green fluorescence intensity changes as analyzed by flow cytometry. Hela cells were treated with compound **3c** for 24 h, respectively. Intracellular green fluorescence and red fluorescence were measured. The representative JC-1 green signals recorded by flow cytometry are exhibited in Figure S11. The flow cytometry was used to confirm whether complex **3c**-induced apoptosis occurred by damaging mitochondria, and we found that the mitochondria was markedly increased from 4.14% (control group) to 42.2% (21 μ M) in Hela cells.



Figure S11. Changes of MMP in Hela cells treated with complex **3c** with a JC-1 staining kit were analyzed using flow cytometry.

6. The Fluorescence Spectrum of 4e

Ultraviolet–visible absorption experiments were performed using an Agilent Cary Eclipse UVvisible spectrophotometer. In each experiment, the varying samples were combined in CH₃CN with screw-top 1.0 cm quartz cuvettes. First, UV–vis absorption experiments showed that **4e** possessed obvious absorption in the visible-light region (Figure S12). We sequentially investigated the emission and excitation spectra of the photocatalyst **4e**. A solution of **4e** (1.0 mM) in CH₃CN was chosen as the model. The fluorescence excitation spectrum was obtained with the detection wavelength of 650 nm (Figure S13), and the fluorescence emission spectrum was excited at 495 nm (excitation maximum of **4e**) (Figure S14). The fluorescence quenching experiments revealed that *N*-benzyl-2-mercaptopyridinium **5a** effectively quenched the excited state of **4e**. The quantum yield was measured on a FLS980 fluorescence spectrometer. The quantum yield of **4e** was also investigated by using the integrating sphere (BaSO₄ as reference). The results showed that the luminous efficiency of **4e** was 48.21% (Figure S15).



Figure S12. The UV–Vis absorption spectra of 4e (10⁻⁵ M).



Figure S13. The fluorescence excitation spectrum of 4e with the detection wavelength of 650 nm.



Figure S14. The fluorescence emission spectrum of 4e excited at 448 nm.



Figure S15. The quantum yield of 4e.

7. The X-ray Crystal Structures of 3h and 4c



Complex	3h
Empirical formula	C ₂₈ H ₂₂ NO ₂ P
Formula weight	435.43
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.6642(18)
b/Å	9.2490(10)
c/Å	18.762(2)
α/°	90
β/°	94.668(10)
γ/°	90
Volume/Å ³	2709.1(5)
Z	4
$\rho_{calc}g/cm^3$	1.068
µ/mm ⁻¹	0.123
F(000)	912.0
Crystal size/mm ³	$0.13 \times 0.12 \times 0.11$
Radiation	Mo Ka ($\lambda = 0.71073$)
2Θ range for data collection/°	4.356 to 49.996
Index ranges	$-18 \le h \le 18, -9 \le k \le 10, -16 \le l \le 22$
Reflections collected	12345
Independent reflections	4758 [$R_{int} = 0.0527$, $R_{sigma} = 0.0717$]
Data/restraints/parameters	4758/28/289
Goodness-of-fit on F ²	1.073
Final R indexes [I>=2 σ (I)]	$R_1 = 0.0784, wR_2 = 0.2080$
Final R indexes [all data]	$R_1 = 0.1250, wR_2 = 0.2425$
Largest diff. peak/hole / e Å ⁻³	0.38/-0.38

Table S4. Crystal data and structure refinement for 3h.



Table S5. Crystal data and structure refinement for 4c.

Complex	4c
Empirical formula	$C_{70}H_{62}Cl_2N_3O_6P_3$
Formula weight	1205.03
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.6477(5)
b/Å	15.5381(8)
c/Å	20.6214(9)
α/°	101.740(4)
β/°	97.775(4)
γ/°	91.950(4)
Volume/Å ³	2992.8(2)
Z	2
$ ho_{calc}g/cm^3$	1.337
µ/mm ⁻¹	2.192
F(000)	1260.0
Crystal size/mm ³	$0.14 \times 0.13 \times 0.12$
Radiation	Cu Ka ($\lambda = 1.54184$)
2Θ range for data collection/°	4.424 to 160.066
Index ranges	$-11 \le h \le 11, -19 \le k \le 18, -25 \le l \le 24$
Reflections collected	21889
Independent reflections	11794 [$R_{int} = 0.0689, R_{sigma} = 0.0924$]
Data/restraints/parameters	11794/59/782
Goodness-of-fit on F ²	1.029
Final R indexes [I>=2 σ (I)]	$R_1 = 0.0825, wR_2 = 0.2108$
Final R indexes [all data]	$R_1 = 0.1135, wR_2 = 0.2425$
Largest diff. peak/hole / e Å ⁻³	0.82/-0.75

8. ¹H, ¹³C, ³¹P, ¹⁹F NMR, MP and MS Data of All products

4-(Diphenylphosphoryl)-1-methylquinolin-2(1*H*)-one (3a)

Yellow solid (57.5 mg, 80%). Mp: 227.4 – 228.5 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.36 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.61 (m, 4H), 7.55 – 7.41 (m, 7H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.47 (d, *J* = 17.3 Hz, 1H), 3.67 (s, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.3 (d, *J*_{CP} = 17.3 Hz), 142.0 (d, *J*_{CP} = 90.3 Hz), 140.2 (d, *J*_{CP} = 9.1 Hz), 132.6 (d, *J*_{CP} = 2.8 Hz), 131.8 (d, *J*_{CP} = 10.0 Hz), 131.2, 130.4 (d, *J*_{CP} = 105.9 Hz), 129.5/ (d, *J*_{CP} = 9.7 Hz), 129.2 (d, *J*_{CP} = 4.5 Hz), 128.9 (d, *J*_{CP} = 12.5 Hz), 122.6, 119.3 (d, *J*_{CP} = 7.8 Hz), 114.6, 29.8. ³¹P NMR (162 MHz, Chloroform-d) δ 31.2. HRESIMS calcd for C₂₂H₁₉NO₂P [M + H]⁺: 360.1148; found 360.1169.

4-(Diphenylphosphoryl)-1,3-dimethylquinolin-2(1*H*)-one (**3b**)



White solid (54.5 mg, 73%). Mp: 204.6 – 206.1 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 8.22 (d, J = 8.3 Hz, 1H), 7.76 – 7.68 (m, 4H), 7.63 – 7.57 (m, 2H), 7.55 – 7.46 (m, 4H), 7.23 (s, 1H), 6.96 (d, J = 8.3 Hz, 1H), 6.37 (d, J = 17.3 Hz, 1H), 3.68 (s, 3H), 2.45 (s, 3H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 160.7 (d, $J_{CP} = 17.4$ Hz), 142.6, 142.2 (d, $J_{CP} = 90.5$ Hz), 141.1 (d, $J_{CP} = 9.2$ Hz), 133.0 (d, $J_{CP} = 2.8$ Hz), 132.3 (d, $J_{CP} = 9.9$ Hz), 131.4 (d, $J_{CP} = 105.3$ Hz), 129.4 (d, $J_{CP} = 12.4$ Hz), 129.2 (d, $J_{CP} = 4.5$ Hz), 128.9 (d, $J_{CP} = 9.6$ Hz), 124.1, 117.5 (d, $J_{CP} = 7.9$ Hz), 115.5 (d, $J_{CP} = 1.5$ Hz), 30.0, 22.3. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 29.9. HRESIMS calcd for C₂₃H₂₁NO₂P [M + H]⁺: 374.1304; found 374.1329.

4-(Diphenylphosphoryl)-1,6-dimethylquinolin-2(1*H*)-one (**3c**)



Brown solid (58.2 mg, 78%). Mp: 203.5 – 204.5 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 8.16 (s, 1H), 7.75 – 7.68 (m, 4H), 7.64 – 7.58 (m, 2H), 7.56 – 7.47 (m, 4H), 7.41 – 7.35 (m, 1H), 7.31 (d, *J* = 8.7 Hz, 1H), 6.42 (d, *J* = 17.4 Hz, 1H), 3.66 (s, 3H), 2.26 (s, 3H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 161.0 (d, *J*_{CP} = 17.3 Hz), 142.6 (d, *J*_{CP} = 90.3 Hz), 139.6 (d, *J*_{CP} = 9.2 Hz), 133.6 (d, *J*_{CP} = 2.8 Hz), 133.4, 133.0, 132.9 (d, *J*_{CP} = 9.9 Hz), 132.0 (d, *J*_{CP} = 105.4 Hz), 130.6 (d, *J*_{CP} = 9.6 Hz), 129.9 (d, *J*_{CP} = 12.4 Hz), 129.7 (d, *J*_{CP} = 4.4 Hz), 120.3 (d, *J*_{CP} = 7.8 Hz), 115.7 (d, *J*_{CP} = 1.5 Hz), 30.6, 21.6. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 29.9. HRESIMS calcd for C₂₃H₂₁NO₂P [M + H]⁺: 374.1304; found 374.1289.

4-(Diphenylphosphoryl)-1,7-dimethylquinolin-2(1*H*)-one (3d)



Yellow solid (59.0 mg, 79%). Mp: 164.9 – 166.1 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.14 (s, 1H), 7.68 – 7.61 (m, 4H), 7.54 – 7.48 (m, 2H), 7.47 – 7.39 (m 4H), 7.31 – 7.26 (m, 1H), 7.22 (d, *J* = 8.7 Hz, 1H), 6.43 (d, *J* = 17.5 Hz, 1H), 3.63 (s, 3H), 2.19 (s, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.1 (d, *J*_{CP} = 17.4 Hz), 141.5 (d, *J*_{CP} = 90.5 Hz), 138.1 (d, *J*_{CP} = 9.2 Hz), 132.5 (d, *J*_{CP} = 2.8 Hz), 132.4, 132.2, 131.8 (d, *J*_{CP} = 9.9 Hz), 130.4 (d, *J*_{CP} = 105.9 Hz), 129.4 (d, *J*_{CP} = 9.9 Hz), 128.9, 128.8, 119.2 (d, *J*_{CP} = 7.7 Hz), 114.5 (d, *J*_{CP} = 1.3 Hz), 29.7, 20.7. ³¹P NMR (162 MHz, Chloroform-d) δ 31.3. HRESIMS calcd for C₂₃H₂₁NO₂P [M + H]⁺: 374.1304; found 374.1299.

4-(Diphenylphosphoryl)-6-methoxy-1-methylquinolin-2(1*H*)-one (3e)



Yellow solid (55.3 mg, 71%). Mp: 242.8 – 244.3 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.86 (d, *J* = 2.7 Hz, 1H), 7.77 – 7.68 (m, 4H), 7.63 – 7.55 (m, 2H), 7.54 – 7.45 (m, 4H), 7.35 – 7.28 (m, 1H), 7.15 (dd, *J* = 9.3, 2.8 Hz, 1H), 6.53 (d, *J* = 17.3 Hz, 1H), 3.71 (s, 3H), 3.61 (s, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.1 (d, *J*_{CP} = 17.3 Hz), 154.7, 141.5 (d, *J*_{CP} = 90.7 Hz), 134.9 (d, *J*_{CP} = 9.1 Hz), 132.8 (d, *J*_{CP} = 2.8 Hz), 131.9 (d, *J*_{CP} = 9.9 Hz), 130.5 (d, *J*_{CP} = 94.6 Hz), 129.9, 129.1 (d, *J*_{CP} = 12.5 Hz), 120.7, 120.1 (d, *J*_{CP} = 7.5 Hz), 115.9 (d, *J*_{CP} = 1.4 Hz), 110.6 (d, *J*_{CP} = 4.7 Hz), 55.6, 30.1. ³¹P NMR (162 MHz, Chloroform-d) δ 30.8. HRESIMS calcd for C₂₃H₂₁NO₃P [M + H]⁺: 390.1254; found 390.1253.

6-Bromo-4-(diphenylphosphoryl)-1-methylquinolin-2(1H)-one (3f)



Yellow solid (71.9 mg, 82%). Mp: 185.2 – 186.7 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 8.54 (s, 1H), 7.94 – 7.56 (m, 8H), 7.55 – 7.47 (m, 3H), 7.28 (d, *J* = 8.8 Hz, 1H), 6.63 – 6.35 (m, 1H), 3.64 (s, 3H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 160.2 (d, *J*_{CP} = 14.8 Hz), 141.2 (d, *J*_{CP} = 93.3 Hz), 140.1 (d, *J*_{CP} = 5.4 Hz), 134.4 (d, *J*_{CP} = 8.5 Hz), 133.4 (d, *J*_{CP} = 12.4 Hz), 132.4 (d, *J*_{CP} = 9.3 Hz), 131.6, 131.1 (d, *J*_{CP} = 9.0 Hz), 130.9 (d, *J*_{CP} = 106.2 Hz), 129.5 (d, *J*_{CP} = 10.1 Hz), 121.3 (d, *J*_{CP} = 3.9 Hz), 117.0, 115.8 (d, *J*_{CP} = 7.4 Hz), 30.2. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 29.9. HRESIMS calcd for C₂₂H₁₈BrNO₂P [M + H]⁺: 438.0253, 440.0233; found 438.0247, 440.0260.

Methyl 4-(diphenylphosphoryl)-1-methyl-2-oxo-1,2-dihydroquinoline-6-carboxylate (3g)



White solid (69.3 mg, 83%). Mp: 211.3 – 213.2 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 9.01 (s, 1H), 8.15 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.78 – 7.71 (m, 4H), 7.65 – 7.60 (m, 2H), 7.57 – 7.51 (m, 4H), 7.44 (d, *J* = 8.9 Hz, 1H), 6.51 (d, *J* = 17.1 Hz, 1H), 3.83 (s, 3H), 3.70 (s, 3H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 166.4, 160.6 (d, *J*_{CP} = 17.0 Hz), 143.9 (d, *J*_{CP} = 8.9 Hz), 142.9 (d, *J*_{CP} = 89.4 Hz), 133.3 (d, *J*_{CP} = 2.8 Hz), 132.4 (d, *J*_{CP} = 9.9 Hz), 132.1, 131.3 (d, *J*_{CP} = 4.4 Hz), 131.0 (d, *J*_{CP} = 105.8 Hz), 130.7 (d, *J*_{CP} = 9.2 Hz), 129.5 (d, *J*_{CP} = 12.4 Hz), 124.6, 119.3 (d, *J*_{CP} = 7.8 Hz), 115.4 (d, *J*_{CP} = 1.4 Hz), 52.7, 30.4. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 29.2. HRESIMS calcd for C₂₄H₂₁NO₄P [M + H]⁺: 418.1203; found 418.1206.

1-Benzyl-4-(diphenylphosphoryl)quinolin-2(1*H*)-one (3h)



Gray solid (67.1 mg, 77%). Mp: 223.4 – 225.1 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.38 (d, J = 8.0 Hz, 1H), 7.81 – 7.67 (m, 4H), 7.66 – 7.56 (m, 2H), 7.55 – 7.46 (m, 4H), 7.43 – 7.35 (m, 1H), 7.32 – 7.25 (m, 4H), 7.21 – 7.15 (m, 2H), 7.12 – 7.05 (m, 1H), 6.60 (dd, J = 17.3, 3.2 Hz, 1H), 5.56 (s, 2H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.7 (d, $J_{CP} = 17.6$ Hz), 142.8 (d, $J_{CP} = 90.0$ Hz), 139.8 (d, $J_{CP} = 9.1$ Hz), 135.7, 132.8 (d, $J_{CP} = 2.6$ Hz), 132.0 (d, $J_{CP} = 10.0$ Hz), 131.3, 130.5 (d, $J_{CP} = 106.1$ Hz), 129.6 (d, $J_{CP} = 9.7$ Hz), 129.5 (d, $J_{CP} = 4.4$ Hz), 129.1 (d, $J_{CP} = 12.5$ Hz), 129.0, 127.6, 126.6, 122.9, 119.7 (d, $J_{CP} = 7.7$ Hz), 115.7, 46.4. ³¹P NMR (162 MHz, Chloroform-d) δ 31.3. HRESIMS calcd for C₂₈H₂₃NO₂P [M + H]⁺: 436.1461; found 436.1460.

4-(Diphenylphosphoryl)-1-(2-methylbenzyl)quinolin-2(1*H*)-one (**3i**)



Yellow solid (63.8 mg, 71%). Mp: 262.7 – 264.5 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.41 (d, *J* = 8.0 Hz, 1H), 7.87 – 7.69 (m, 4H), 7.68 – 7.59 (m, 2H), 7.58 – 7.43 (m, 4H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.20 – 6.92 (m, 4H), 6.76 – 6.41 (m, 2H), 5.48 (s, 2H), 2.48 (s, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.6 (d, *J*_{CP} = 17.5 Hz), 142.8 (d, *J*_{CP} = 89.9 Hz), 139.8 (d, *J*_{CP} = 9.1 Hz), 134.9, 132.9 (d, *J*_{CP} = 2.8 Hz), 132.0 (d, *J*_{CP} = 10.0 Hz), 131.4, 131.0, 130.6, 130.5 (d, *J*_{CP} = 106.0 Hz), 129.6 (d, *J*_{CP} = 9.8 Hz), 129.5 (d, *J*_{CP} = 4.6 Hz), 129.1 (d, *J*_{CP} = 12.5 Hz), 127.3, 126.5, 124.6, 122.9, 119.6 (d, *J*_{CP} = 7.7 Hz), 115.8 (d, *J*_{CP} = 1.3 Hz), 44.6, 19.3. ³¹P NMR (162 MHz, Chloroform-d) δ 31.4. HRESIMS calcd for C₂₉H₂₅NO₂P [M + H]⁺: 450.1617;

found 450.1619.

4-(Diphenylphosphoryl)-1-(3-methoxybenzyl)quinolin-2(1*H*)-one (3j)

Yellow solid (60.5 mg, 65%). Mp: 172.2 – 173.8 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 8.35 (d, *J* = 8.0 Hz, 1H), 7.91 – 7.68 (m 4H), 7.67 – 7.45 (m, 6H), 7.44 – 7.38 (m, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.93 – 6.64 (m, 3H), 6.53 (d, *J* = 17.3 Hz, 1H), 5.49 (s, 2H), 3.74 (s, 3H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 160.8 (d, *J*_{CP} = 17.4 Hz), 160.7, 143.2 (d, *J*_{CP} = 89.8 Hz), 140.4 (d, *J*_{CP} = 9.1 Hz), 138.2, 133.2 (d, *J*_{CP} = 2.7 Hz), 132.4 (d, *J*_{CP} = 9.9 Hz), 132.2, 131.5, 131.2 (d, *J*_{CP} = 105.7 Hz), 130.4, 130.1 (d, *J*_{CP} = 9.6 Hz), 129.7 (d, *J*_{CP} = 4.5 Hz), 129.5 (d, *J*_{CP} = 12.4 Hz), 122.9, 120.0 (d, *J*_{CP} = 7.8 Hz), 119.1, 116.1 (d, *J*_{CP} = 1.1 Hz), 113.0 (d, *J*_{CP} = 6.1 Hz), 55.7, 46.7. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 30.1. HRESIMS calcd for C₂₉H₂₅NO₃P [M + H]⁺: 466.1567; found 466.1585.

4-(Diphenylphosphoryl)-1-(3-(trifluoromethyl)benzyl)quinolin-2(1H)-one (3k)



Yellow solid (75.5 mg, 75%). Mp: 98.1 – 100.0 °C. 1H NMR (400 MHz, Methylene Chloride-d2) δ 8.39 (d, J = 8.1 Hz, 1H), 7.84 – 7.72 (m, 4H), 7.70 – 7.48 (m, 8H), 7.46 – 7.32 (m, 3H), 7.23 (d, J = 8.6 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.56 (d, J = 17.2 Hz, 1H), 5.59 (s, 2H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 160.8 (d, $J_{CP} = 17.4$ Hz), 143.5 (d, $J_{CP} = 89.4$ Hz), 140.9, 140.1 (d, $J_{CP} = 9.1$ Hz), 133.2 (d, $J_{CP} = 2.8$ Hz), 132.4, 132.3, 131.7, 131.1 (d, $J_{CP} = 105.7$ Hz), 130.0 (q, J = 32.4), 129.9 (d, $J_{CP} = 7.8$ Hz), 129.8, 129.6, 129.4, 127.5, 126.3 (q, J = 3.7), 124.7 (q, J = 271.9), 123.1, 120.0 (d, $J_{CP} = 7.8$ Hz), 115.8 (d, $J_{CP} = 1.3$ Hz), 46.3. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 30.0. ¹⁹F NMR (376 MHz, Methylene Chloride-d2) δ -62.8. HRESIMS calcd for C₂₉H₂₂F₃NO₂P [M + H]⁺: 504.1335; found 504.1352.

4-(Diphenylphosphoryl)-1-(3-nitrobenzyl)quinolin-2(1H)-one (3l)



Pink solid (71.1 mg, 74%). Mp: 221.4 – 223.2 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ

8.39 (d, J = 8.1 Hz, 1H), 8.25 – 7.95 (m, 2H), 7.79 – 7.71 (m, 4H), 7.66 – 7.59 (m, 2H), 7.57 – 7.48 (m, 6H), 7.45 – 7.40 (m, 1H), 7.23 (d, J = 8.6 Hz, 1H), 7.10 (t, J = 7.7 Hz, 1H), 6.54 (d, J = 17.2 Hz, 1H), 5.61 (s, 2H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 160.8 (d, $J_{CP} = 17.4$ Hz), 149.2, 143.8 (d, $J_{CP} = 89.2$ Hz), 140.0 (d, $J_{CP} = 9.0$ Hz), 138.9, 133.4, 133.3 (d, $J_{CP} = 2.8$ Hz), 132.4 (d, $J_{CP} = 9.9$ Hz), 131.8, 131.1 (d, $J_{CP} = 105.7$ Hz), 130.5, 130.0 (d, $J_{CP} = 4.5$ Hz), 129.9 (d, $J_{CP} = 9.6$ Hz), 129.5 (d, $J_{CP} = 12.4$ Hz), 123.3, 123.1, 122.3, 120.2 (d, $J_{CP} = 7.8$ Hz), 115.6 (d, $J_{CP} = 1.4$ Hz), 46.1. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 29.9. HRESIMS calcd for C₂₈H₂₂N₂O₄P [M + H]⁺: 481.1312; found 481.1306.

1-(4-Chlorobenzyl)-4-(diphenylphosphoryl)quinolin-2(1H)-one (3m)



Yellow solid (65.8 mg, 70%). Mp: 196.4 – 197.8 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.42 (d, J = 7.7 Hz, 1H), 8.18 – 7.72 (m, 4H), 7.72 – 7.47 (m, 6H), 7.47 – 7.39 (m, 1H), 7.37 – 7.25 (m, 3H), 7.24 – 7.01 (m, 3H), 6.62 (d, J = 17.2 Hz, 1H), 5.55 (s, 2H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.5 (d, $J_{CP} = 17.4$ Hz), 142.9 (d, $J_{CP} = 89.8$ Hz), 139.5 (d, $J_{CP} = 9.0$ Hz), 134.2, 133.4, 132.8 (d, $J_{CP} = 2.7$ Hz), 131.9 (d, $J_{CP} = 10.0$ Hz), 131.3, 130.3 (d, $J_{CP} = 106.2$ Hz), 129.6 (d, $J_{CP} = 17.0$ Hz), 129.5 (d, $J_{CP} = 10.1$ Hz), 129.1 (d, $J_{CP} = 4.8$ Hz), 129.0, 128.0, 123.0, 119.5 (d, $J_{CP} = 7.8$ Hz), 115.4 (d, $J_{CP} = 1.2$ Hz), 45.7. ³¹P NMR (162 MHz, Chloroform-d) δ 31.3. HRESIMS calcd for C₂₈H₂₂ClNO₂P [M + H]⁺: 470.1071, 472.1042; found 470.1090, 472.1067.

4-((4-(Diphenylphosphoryl)-2-oxoquinolin-1(2*H*)-yl)methyl)benzonitrile (**3n**)



White solid (66.3 mg, 72%). Mp: 168.4 – 169.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.38 (d, J = 8.1 Hz, 1H), 7.79 – 7.67 (m, 4H), 7.65 – 7.56 (m, 4H), 7.55 – 7.47 (m, 4H), 7.40 (t, J = 7.9 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.12 (dd, J = 14.4, 7.9 Hz, 2H), 6.57 (d, J = 17.2 Hz, 1H), 5.58 (s, 2H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.5 (d, $J_{CP} = 17.4$ Hz), 143.3 (d, $J_{CP} = 89.4$ Hz), 141.2, 139.3 (d, $J_{CP} = 9.0$ Hz), 132.9 (d, $J_{CP} = 2.7$ Hz), 132.8, 131.8 (d, $J_{CP} = 10.7$ Hz), 131.5, 130.1 (d, $J_{CP} = 106.3$ Hz), 129.8 (d, $J_{CP} = 4.5$ Hz), 129.3 (d, $J_{CP} = 9.9$ Hz), 129.1 (d, $J_{CP} = 12.5$ Hz), 127.3, 123.2, 119.6 (d, $J_{CP} = 7.7$ Hz), 118.5, 115.1 (d, $J_{CP} = 1.0$ Hz), 111.6, 46.0. ³¹P NMR (162 MHz, Chloroform-d) δ 31.3. HRESIMS calcd for C₂₉H₂₂N₂O₂P [M + H]⁺: 461.1413; found 461.1411.

Ethyl 4-((4-(diphenylphosphoryl)-2-oxoquinolin-1(2H)-yl)methyl)benzoate (30)



Yellow solid (74.1 mg, 73%). Mp: 222.1 – 223.7 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.40 (d, *J* = 5.2 Hz, 1H), 8.05 – 7.94 (m, 2H), 7.87 – 7.70 (m, 4H), 7.69 – 7.44 (m, 6H), 7.43 – 7.34 (m, 1H), 7.29 – 7.06 (m, 4H), 6.76 – 6.46 (m, 1H), 5.60 (s, 2H), 4.57 – 4.17 (m, 2H), 1.40 – 1.31 (m, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 166.3, 160.7 (d, *J*_{CP} = 16.5 Hz), 143.1 (d, *J*_{CP} = 94.7 Hz), 140.8, 139.6 (d, *J*_{CP} = 6.5 Hz), 132.9, 132.0 (d, *J*_{CP} = 9.5 Hz), 130.9, 131.0 (d, *J*_{CP} = 97.6 Hz), 130.3, 129.9 (d, *J*_{CP} = 12.4 Hz), 129.7, 129.5 (d, *J*_{CP} = 9.0 Hz), 129.2 (d, *J*_{CP} = 12.0 Hz), 126.5, 123.1, 119.7 (d, *J*_{CP} = 5.3 Hz), 115.5 (d, *J*_{CP} = 2.7 Hz), 61.1, 46.3, 14.4. ³¹P NMR (162 MHz, Chloroform-d) δ 31.3. HRESIMS calcd for C₃₁H₂₇NO₄P [M + H]⁺: 508.1672; found 508.1660.

4-(Diphenylphosphoryl)-1-phenethylquinolin-2(1*H*)-one (**3p**)



Brown solid (64.7 mg, 72%). Mp: 166.4 – 167.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.43 (d, J = 8.0 Hz, 1H), 7.75 – 7.67 (m, 4H), 7.59 – 7.41 (m, 8H), 7.35 – 7.21 (m, 5H), 7.12 (t, J = 7.3 Hz, 1H), 6.51 (d, J = 17.4 Hz, 1H), 4.50 (t, J = 7.9 Hz, 2H), 3.02 (t, J = 8.0 Hz, 2H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.0 (d, $J_{CP} = 17.4$ Hz), 142.2 (d, $J_{CP} = 90.2$ Hz), 139.3 (d, $J_{CP} = 9.1$ Hz), 137.9, 132.7 (d, $J_{CP} = 2.6$ Hz), 131.9 (d, $J_{CP} = 10.0$ Hz), 131.2, 130.5 (d, $J_{CP} = 106.0$ Hz), 129.7 (d, $J_{CP} = 12.9$ Hz), 129.6, 129.0 (d, $J_{CP} = 12.5$ Hz), 128.8, 128.7, 126.8, 122.6, 119.6 (d, $J_{CP} = 7.8$ Hz), 114.5, 44.0, 33.5. ³¹P NMR (162 MHz, Chloroform-d) δ 31.3. HRESIMS calcd for C₂₉H₂₅NO₂P [M + H]⁺: 450.1617; found 450.1614.

1-(Cyclohexylmethyl)-4-(diphenylphosphoryl)quinolin-2(1*H*)-one (**3q**)



White solid (57.4 mg, 65%). Mp: 151.4 – 152.7 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.34 (d, J = 8.1 Hz, 1H), 7.74 – 7.62 (m, 4H), 7.57 – 7.41 (m, 7H), 7.34 (d, J = 8.7 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.46 (d, J = 17.4 Hz, 1H), 4.17 (s, 2H), 1.90 – 1.54 (m, 6H), 1.21 – 1.06 (m, 5H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.6 (d, $J_{CP} = 17.3$ Hz), 141.7 (d, $J_{CP} = 90.5$ Hz), 139.8 (d, $J_{CP} = 17.3$ Hz), 141.7 (d, $J_{CP} = 90.5$ Hz), 139.8 (d, $J_{CP} = 17.3$ Hz), 141.7 (d, $J_{CP} = 12.5$ Hz), 139.8 (d, $J_{CP} = 12.5$ Hz), 141.7 (d, $J_{CP} = 12.5$ Hz), 139.8 (d, $J_{CP} = 12.5$ Hz), 141.7 (d, J_{CP} = 12.5 Hz), 141.7 (d,

= 9.1 Hz), 132.6 (d, J_{CP} = 2.7 Hz), 131.8 (d, J_{CP} = 10.0 Hz), 130.9, 130.4 (d, J_{CP} = 105.9 Hz), 129.6 (d, J_{CP} = 9.7 Hz), 129.4 (d, J_{CP} = 4.6 Hz), 128.9 (d, J_{CP} = 12.5 Hz), 122.4, 119.5 (d, J_{CP} = 7.7 Hz), 115.1 (d, J_{CP} = 1.1 Hz), 48.0, 36.5, 30.7, 26.2, 25.8. ³¹P NMR (162 MHz, Chloroform-d) δ 31.3. HRESIMS calcd for C₂₈H₂₉NO₂P [M + H]⁺: 442.1930; found 442.1935.

1-Butyl-4-(diphenylphosphoryl)quinolin-2(1*H*)-one (**3r**)



Brown solid (49.8 mg, 62%). Mp: 185.1 – 186.1 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.36 (d, J = 8.0 Hz, 1H), 7.75 – 7.63 (m, 4H), 7.58 – 7.42 (m, 7H), 7.36 (d, J = 8.5 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 6.47 (d, J = 17.4 Hz, 1H), 4.26 (t, J = 7.5 Hz, 2H), 1.75 – 1.64 (m, 2H), 1.50 – 1.39 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.1 (d, $J_{CP} = 17.3$ Hz), 141.8 (d, $J_{CP} = 90.5$ Hz), 139.4 (d, $J_{CP} = 9.1$ Hz), 132.6 (d, $J_{CP} = 2.7$ Hz), 131.9 (d, $J_{CP} = 10$ Hz), 131.1, 130.4 (d, $J_{CP} = 105.9$ Hz), 129.7 (d, $J_{CP} = 9.7$ Hz), 129.4 (d, $J_{CP} = 4.6$ Hz), 128.9 (d, $J_{CP} = 12.5$ Hz), 122.4, 119.5 (d, $J_{CP} = 7.8$ Hz), 114.7 (d, $J_{CP} = 1.1$ Hz), 42.5, 29.4, 20.2, 13.8. ³¹P NMR (162 MHz, Chloroform-d) δ 31.3. HRESIMS calcd for C₂₅H₂₅NO₂P [M + H]⁺: 402.1617; found 402.1615.

1-Allyl-4-(diphenylphosphoryl)quinolin-2(1*H*)-one (3s)



Orange solid (46.2 mg, 60%). Mp: 112.0 – 113.5 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.35 (d, J = 13.2 Hz, 1H), 7.84 – 7.63 (m, 4H), 7.62 – 7.37 (m, 7H), 7.36 – 7.27 (m, 1H), 7.15 – 7.00 (m, 1H), 6.62 – 6.37 (m, 1H), 6.03 – 5.80 (m, 1H), 5.27 – 5.15 (m, 1H), 5.07 (t, J = 18.8 Hz, 1H), 4.91 (d, J = 15.6 Hz, 2H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.1 (d, $J_{CP} = 17.1$ Hz), 142.5 (d, $J_{CP} = 88.6$ Hz), 139.7 (d, $J_{CP} = 8.7$ Hz), 132.8, 132.0 (d, $J_{CP} = 9.8$ Hz), 131.2, 131.0, 130.4 (d, $J_{CP} = 105.9$ Hz), 129.6 (d, $J_{CP} = 9.9$ Hz), 129.4, 129.1 (d, $J_{CP} = 12.1$ Hz), 122.8, 119.5 (d, $J_{CP} = 5.2$ Hz), 117.5, 115.4 (d, $J_{CP} = 2.7$ Hz), 45.0. ³¹P NMR (162 MHz, Chloroform-d) δ 31.3. HRESIMS calcd for C₂₄H₂₁NO₂P [M + H]⁺: 386.1304; found 386.1320.

4-(Diphenylphosphoryl)-1-(2,2,2-trifluoroethyl)quinolin-2(1H)-one (3t)



White solid (56.5 mg, 64%). Mp: 215.4 – 216.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.43 (d, J = 8.1 Hz, 1H), 7.87 – 7.64 (m, 4H), 7.64 – 7.54 (m, 3H), 7.54 – 7.38 (m, 4H), 7.35 (d, J = 8.6 Hz,

1H), 7.16 (t, J = 7.7 Hz, 1H), 6.48 (d, J = 17.3 Hz, 1H), 4.53 (t, J = 7.8 Hz, 2H), 2.78 – 2.40 (m, 2H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.0 (d, $J_{CP} = 17.5$ Hz), 143.0 (d, $J_{CP} = 89.6$ Hz), 138.9 (d, $J_{CP} = 9.1$ Hz), 132.9 (d, $J_{CP} = 2.7$ Hz), 131.9 (d, $J_{CP} = 10.0$ Hz), 131.7, 130.3 (d, $J_{CP} = 106.2$ Hz), 130.1 (d, $J_{CP} = 4.5$ Hz), 129.3 (d, $J_{CP} = 9.7$ Hz), 129.1 (d, $J_{CP} = 12.7$ Hz), 125.8 (q, $J_{CF} = 276.8$ Hz), 123.2, 119.7 (d, $J_{CP} = 7.8$ Hz), 113.7, 36.1 (q, $J_{CF} = 3.8$ Hz), 31.5 (q, $J_{CF} = 29.0$ Hz). ³¹P NMR (162 MHz, Chloroform-d) δ 31.1. ¹⁹F NMR (376 MHz, Chloroform-d) δ -65.4. HRESIMS calcd for C₂₄H₂₀F₃NO₂P [M + H]⁺: 442.1178; found 442.1173.

4-(Diphenylphosphoryl)-1-(2-oxo-2-phenylethyl)quinolin-2(1*H*)-one (3u)



Yellow solid (62.1 mg, 67%). Mp: 63.8 – 65.1 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 8.38 (d, *J* = 8.1 Hz, 1H), 8.09 (d, *J* = 7.6 Hz, 2H), 7.79 – 7.67 (m, 5H), 7.67 – 7.61 (m, 2H), 7.61 – 7.47 (m, 6H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.49 (d, *J* = 17.3 Hz, 1H), 5.80 (s, 2H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 192.5, 160.5 (d, *J*_{CP} = 17.5 Hz), 143.4 (d, *J*_{CP} = 89.8 Hz), 140.4 (d, *J*_{CP} = 9.1 Hz), 135.3, 134.7, 133.2 (d, *J*_{CP} = 2.7 Hz), 132.4 (d, *J*_{CP} = 10.0 Hz), 131.2 (d, *J*_{CP} = 105.6 Hz), 129.8 (d, *J*_{CP} = 4.6 Hz), 129.7 (d, *J*_{CP} = 9.7 Hz), 129.6, 129.5, 129.4, 128.6, 123.0, 119.9 (d, *J*_{CP} = 7.9 Hz), 115.2 (d, *J*_{CP} = 1.2 Hz), 49.7. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 30.2. HRESIMS calcd for C₂₉H₂₃NO₃P [M + H]⁺: 464.1410; found 464.1452.

4-(Diphenylphosphoryl)-1-((tetrahydrofuran-2-yl)methyl)quinolin-2(1H)-one (3v)



Brown solid (59.3 mg, 69%). Mp: 164.4 – 165.8 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.35 (d, J = 8.1 Hz, 1H), 7.78 – 7.67 (m, 3H), 7.63 (d, J = 8.6 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.53 – 7.37 (m, 5H), 7.26 (s, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.49 (d, J = 17.4 Hz, 1H), 4.82 – 4.43 (m, 1H), 4.42 – 4.15 (m, 2H), 3.90 (q, J = 7.1 Hz, 1H), 3.73 (q, J = 7.2 Hz, 1H), 2.14 – 1.70 (m, 4H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.8 (d, $J_{CP} = 17.5$ Hz), 142.4 (d, $J_{CP} = 90.3$ Hz), 140.2 (d, $J_{CP} = 9.0$ Hz), 132.7 (d, $J_{CP} = 2.6$ Hz), 132.1 (d, $J_{CP} = 4.3$ Hz), 131.9 (d, $J_{CP} = 4.3$ Hz), 130.5 (d, $J_{CP} = 105.8$ Hz), 129.6 (d, $J_{CP} = 9.8$ Hz), 129.3 (d, $J_{CP} = 4.6$ Hz), 129.0 (d, $J_{CP} = 12.5$ Hz), 122.7, 119.5 (d, $J_{CP} = 7.7$ Hz), 115.7 (d, $J_{CP} = 1.2$ Hz), 77.1, 68.3, 46.7, 29.7, 25.6. ³¹P NMR (162 MHz, Chloroform-d) δ 31.2. HRESIMS calcd for C₂₆H₂₅NO₃P [M + H]⁺: 430.1567; found 430.1571.

4-(Di-*p*-tolylphosphoryl)-1-methylquinolin-2(1*H*)-one (**3**w)



Yellow solid (61.2 mg, 79%). Mp: 183.1 – 184.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.33 (d, *J* = 8.1 Hz, 1H), 7.50 (dd, *J* = 12.1, 8.0 Hz, 4H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.22 – 7.14 (m, 4H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 17.2 Hz, 1H), 3.60 (s, 3H), 2.28 (s, 6H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.2 (d, *J*_{CP} = 17.2 Hz), 143.0 (d, *J*_{CP} = 2.8 Hz), 142.3 (d, *J*_{CP} = 90.1 Hz), 139.9 (d, *J*_{CP} = 9.0 Hz), 131.6 (d, *J*_{CP} = 10.3 Hz), 130.9, 129.4 (d, *J*_{CP} = 12.9 Hz), 129.1 (d, *J*_{CP} = 14.0 Hz), 129.1, 127.1 (d, *J*_{CP} = 108.5 Hz), 122.3, 119.1 (d, *J*_{CP} = 7.7 Hz), 114.4 (d, *J*_{CP} = 0.9 Hz), 29.5, 21.4. ³¹P NMR (162 MHz, Chloroform-d) δ 31.3. HRESIMS calcd for C₂₄H₂₃NO₂P [M + H]⁺: 388.1461; found 388.1483.

4-(Bis(3,5-dimethylphenyl)phosphoryl)-1-methylquinolin-2(1*H*)-one (**3**x)



Yellow solid (66.5 mg, 80%). Mp: 110.2 – 112.0 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 8.34 (d, *J* = 7.9 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.36 – 7.25 (m, 4H), 7.23 (s, 2H), 7.16 – 7.10 (m, 1H), 6.41 (dd, *J* = 17.2, 3.0 Hz, 1H), 3.69 (s, 3H), 2.33 (s, 12H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 160.8 (d, *J*_{CP} = 17.1 Hz), 142.9 (d, *J*_{CP} = 89.3 Hz), 141.0 (d, *J*_{CP} = 8.9 Hz), 139.3 (d, *J*_{CP} = 13.0 Hz), 134.8 (d, *J*_{CP} = 2.8 Hz), 131.4, 131.0 (d, *J*_{CP} = 104.7 Hz), 130.0 (d, *J*_{CP} = 9.6 Hz), 129.8 (d, *J*_{CP} = 9.9 Hz), 129.6 (d, *J*_{CP} = 4.4 Hz), 122.7, 119.9 (d, *J*_{CP} = 7.8 Hz), 115.2 (d, *J*_{CP} = 1.0 Hz), 30.2, 21.6. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 31.8. HRESIMS calcd for C₂₆H₂₇NO₂P [M + H]⁺: 416.1774; found 416.1777.

4-(Di(naphthalen-2-yl)phosphoryl)-1-methylquinolin-2(1*H*)-one (3y)



White solid (71.7 mg, 78%). Mp: 201.7 – 202.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.49 (d, J = 7.9 Hz, 1H), 8.38 (d, J = 14.2 Hz, 2H), 7.98 – 7.88 (m, 2H), 7.87 – 7.76 (m, 4H), 7.72 (t, J = 9.1 Hz, 2H), 7.60 – 7.41 (m, 5H), 7.31 (d, J = 8.3 Hz, 1H), 7.05 (t, J = 7.4 Hz, 1H), 6.61 (d, J = 17.4 Hz, 1H), 3.66 (s, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 160.3 (d, $J_{CP} = 17.4$ Hz), 142.1 (d, $J_{CP} = 90.6$ Hz), 140.1 (d, $J_{CP} = 9.1$ Hz), 134.9 (d, $J_{CP} = 2.3$ Hz), 133.9 (d, $J_{CP} = 9.6$ Hz), 132.4 (d, $J_{CP} = 13.7$ Hz), 131.1, 129.6 (d, $J_{CP} = 9.7$ Hz), 129.1 (d, $J_{CP} = 4.3$ Hz), 128.9, 128.8, 128.6, 127.8, 127.5 (d, $J_{CP} = 106.4$ Hz), 127.1, 126.2 (d, $J_{CP} = 10.7$ Hz), 122.6, 119.2 (d, $J_{CP} = 7.8$ Hz), 114.6, 29.7. ³¹P NMR (162 MHz, Chloroform-d) δ 31.4. HRESIMS calcd for C₃₀H₂₃NO₂P [M + H]⁺: 460.1461; found 460.1492.

1-(2,6-Dichlorobenzyl)-4-(diphenylphosphoryl)pyridin-2(1*H*)-one (**3**z)



White solid (49.1 mg, 54%). Mp: 66.3 – 68.2 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.71 – 7.63 (m, 4H), 7.61 – 7.55 (m, 2H), 7.53 – 7.45 (m, 4H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 1H), 6.96 (dd, *J* = 7.0, 3.8 Hz, 1H), 6.65 (d, *J* = 14.9 Hz, 1H), 6.49 – 6.37 (m, 1H), 5.42 (s, 2H). ¹³C NMR (100 MHz, Chloroform-d) δ 161.2 (d, *J*_{CP} = 16.4 Hz), 145.5 (d, *J*_{CP} = 92.8 Hz), 137.4, 135.7 (d, *J*_{CP} = 12.8 Hz), 132.8 (d, *J*_{CP} = 2.8 Hz), 132.1 (d, *J*_{CP} = 10.1 Hz), 131.1, 130.6, 130.1 (d, *J*_{CP} = 105.7 Hz), 129.0 (d, *J*_{CP} = 1.3 Hz), 128.9, 125.7 (d, *J*_{CP} = 9.0 Hz), 106.3 (d, *J*_{CP} = 8.9 Hz), 46.7. ³¹P NMR (162 MHz, Chloroform-d) δ 28.0. HRESIMS calcd for C₂₄H₁₉Cl₂NO₂P [M + H]⁺: 454.0525, 456.0495; found 454.0508, 456.0488.

1-Benzyl-4-(diphenylphosphoryl)-6-methylpyridin-2(1*H*)-one (**3aa**)



Brown solid (43.8 mg, 53%). Mp: 89.5 – 90.8 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.70 – 7.63 (m, 4H), 7.60 – 7.54 (m, 2H), 7.50 – 7.45 (m, 4H), 7.36 (dd, J = 6.9, 3.9 Hz, 1H), 6.93 (s, 1H), 6.89 (s, 2H), 6.64 (dd, J = 15.0, 1.3 Hz, 1H), 6.51 – 6.44 (m, 1H), 5.04 (s, 2H), 2.27 (s, 6H). ¹³C NMR (100 MHz, Chloroform-d) δ 161.2 (d, $J_{CP} = 16.4$ Hz), 145.5 (d, $J_{CP} = 92.7$ Hz), 138.7, 138.0 (d, $J_{CP} = 12.8$ Hz), 135.3, 132.7 (d, $J_{CP} = 2.7$ Hz), 131.9 (d, $J_{CP} = 10.1$ Hz), 130.0, 129.9 (d, $J_{CP} = 105.6$ Hz), 128.8 (d, $J_{CP} = 12.4$ Hz), 126.2, 126.0 (d, $J_{CP} = 8.9$ Hz), 106.2 (d, $J_{CP} = 8.9$ Hz), 52.1, 21.2. ³¹P NMR (162 MHz, Chloroform-d) δ 27.9. HRESIMS calcd for C₂₆H₂₅NO₂P [M + H]⁺: 414.1617; found 414.1612.

1-(4-Bromobenzyl)-4-(diphenylphosphoryl)pyridin-2(1H)-one (3ab)



Brown solid (52.0 mg, 56%). Mp: 67.4 – 68.5 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.72 – 7.62 (m, 4H), 7.61 – 7.55 (m, 2H), 7.52 – 7.42 (m, 6H), 7.37 (dd, J = 6.9, 3.9 Hz, 1H), 7.17 (d, J = 8.3 Hz, 2H), 6.64 (d, J = 14.9 Hz, 1H), 6.56 – 6.43 (m, 1H), 5.05 (s, 2H). ¹³C NMR (100 MHz,

Chloroform-d) δ 161.1 (d, J_{CP} = 16.4 Hz), 146.1 (d, J_{CP} = 92.3 Hz), 137.9 (d, J_{CP} = 12.7 Hz), 134.6, 132.8 (d, J_{CP} = 2.7 Hz), 132.2, 132.0 (d, J_{CP} = 10.1 Hz), 130.1, 129.9 (d, J_{CP} = 105.8 Hz), 128.9 (d, J_{CP} = 12.4 Hz), 126.3 (d, J_{CP} = 8.9 Hz), 122.6, 106.5 (d, J_{CP} = 8.9 Hz), 52.0. ³¹P NMR (162 MHz, Chloroform-d) δ 27.7. HRESIMS calcd for C₂₄H₂₀BrNO₂P [M + H]⁺: 464.0410, 466.0389; found 464.0395, 466.0374.

4-((4-(Diphenylphosphoryl)-2-oxopyridin-1(2H)-yl)methyl)benzonitrile (3ac)



Brown solid (41.0 mg, 50%). Mp: 70.4 – 72.2 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.71 – 7.57 (m, 8H), 7.53 – 7.46 (m, 4H), 7.43 – 7.34 (m, 3H), 6.65 (d, *J* = 14.9 Hz, 1H), 6.60 – 6.50 (m, 1H), 5.15 (s, 2H). ¹³C NMR (100 MHz, Chloroform-d) δ 161.1 (d, *J*_{CP} = 16.4 Hz), 146.6 (d, *J*_{CP} = 91.9 Hz), 140.8, 138.0 (d, *J*_{CP} = 12.6 Hz), 132.9 (d, *J*_{CP} = 2.7 Hz), 132.8, 132.1 (d, *J*_{CP} = 10.1 Hz), 129.8 (d, *J*_{CP} = 106.0 Hz), 129.0 (d, *J*_{CP} = 12.5 Hz), 128.7, 126.5 (d, *J*_{CP} = 8.9 Hz), 118.4, 112.4, 106.8 (d, *J*_{CP} = 8.9 Hz), 52.4. ³¹P NMR (162 MHz, Chloroform-d) δ 28.1. HRESIMS calcd for C₂₅H₂₀N₂O₂P [M + H]⁺: 411.1257; found 411.1283.

4-(Diphenylphosphoryl)-1-(4-methylbenzyl)pyridin-2(1H)-one (3ad)



Yellow solid (33.5 mg, 42%). Mp: 157.0 – 158.1 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.70 – 7.57 (m, 4H), 7.53 – 7.45 (m, 2H), 7.44 – 7.34 (m, 4H), 7.25 – 7.12 (m, 3H), 7.11 – 6.95 (m, 2H), 6.50 (d, *J* = 14.9 Hz, 1H), 6.36 (d, *J* = 8.7 Hz, 1H), 5.24 (s, 2H), 2.19 (s, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 161.3 (d, *J*_{CP} = 16.5 Hz), 145.7 (d, *J*_{CP} = 92.7 Hz), 138.8, 138.0 (d, *J*_{CP} = 12.8 Hz), 135.4, 132.8 (d, *J*_{CP} = 2.8 Hz), 132.1 (d, *J*_{CP} = 10.1 Hz), 130.1, 130.0 (d, *J*_{CP} = 105.7 Hz), 129.0 (d, *J*_{CP} = 12.4 Hz), 126.3, 126.1 (d, *J*_{CP} = 9.0 Hz), 106.3 (d, *J*_{CP} = 9.0 Hz), 52.2, 21.4. ³¹P NMR (162 MHz, Chloroform-d) δ 28.2. HRESIMS calcd for C₂₅H₂₃NO₂P [M + H]⁺: 400.1461; found 400.1473.

1-Benzyl-4-(di-p-tolylphosphoryl)pyridin-2(1H)-one (3ae)



Brown solid (44.6 mg, 54%). Mp: 183.8 – 185.6 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.60 – 7.47 (m, 4H), 7.40 – 7.20 (m, 10H), 6.62 (d, *J* = 14.9 Hz, 1H), 6.53 – 6.42 (m, 1H), 5.11 (s, 2H), 2.39 (s, 6H). ¹³C NMR (100 MHz, Chloroform-d) δ 161.3 (d, *J*_{CP} = 16.3 Hz), 146.4 (d, *J*_{CP} = 92.5 Hz), 143.3 (d, *J*_{CP} = 2.8 Hz), 137.8 (d, *J*_{CP} = 12.7 Hz), 135.6, 132.0 (d, *J*_{CP} = 10.4 Hz), 129.6 (d, *J*_{CP} = 12.8 Hz), 129.0, 128.4, 128.2, 126.9 (d, *J*_{CP} = 108.1 Hz), 126.0 (d, *J*_{CP} = 8.9 Hz), 106.4 (d, *J*_{CP} = 8.8 Hz), 52.3, 21.7. ³¹P NMR (162 MHz, Chloroform-d) δ 28.0. HRESIMS calcd for C₂₆H₂₅NO₂P [M + H]⁺: 414.1617; found 414.1612.

1-Benzyl-4-(bis(4-methoxyphenyl)phosphoryl)pyridin-2(1H)-one (3af)



Brown solid (38.3 mg, 43%). Mp: 87.5 – 88.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.63 – 7.53 (m, 3H), 7.38 – 7.23 (m, 7H), 6.98 (d, J = 8.2 Hz, 4H), 6.62 (d, J = 14.8 Hz, 1H), 6.49 (t, J = 7.6 Hz, 1H), 5.12 (s, 2H), 3.85 (s, 6H). ¹³C NMR (100 MHz, Chloroform-d) δ 163.1 (d, J_{CP} = 2.8 Hz), 161.4 (d, J_{CP} = 16.2 Hz), 137.8 (d, J_{CP} = 12.6 Hz), 135.7, 134.1, 133.9, 129.1, 128.5, 126.0 (d, J_{CP} = 8.9 Hz), 121.5 (d, J_{CP} = 112.6 Hz), 114.6, 114.5, 106.5 (d, J_{CP} = 8.7 Hz), 55.6, 52.3. ³¹P NMR (162 MHz, Chloroform-d) δ 27.6. HRESIMS calcd for C₂₆H₂₅NO₄P [M + H]⁺: 446.1516; found 446.1522.

1-Benzyl-4-(bis(3,5-dimethylphenyl)phosphoryl)pyridin-2(1*H*)-one (**3ag**)



Brown solid (39.7 mg, 45%). Mp: 58.2 – 60.0 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.43 – 7.33 (m, 3H), 7.33 – 7.27 (m, 5H), 7.27 – 7.24 (m, 2H), 7.22 – 7.17 (m, 2H), 6.64 (d, *J* = 14.8 Hz, 1H), 6.57 – 6.47 (m, 1H), 5.15 (s, 2H), 2.33 (s, 12H). ¹³C NMR (100 MHz, Chloroform-d) δ 161.4 (d, *J*_{CP} = 16.4 Hz), 146.4 (d, *J*_{CP} = 91.6 Hz), 138.6 (d, *J*_{CP} = 13.1 Hz), 137.8 (d, *J*_{CP} = 12.6 Hz), 135.6, 134.5 (d, *J*_{CP} = 2.8 Hz), 129.8 (d, *J*_{CP} = 104.8 Hz), 129.6, 129.5, 129.1, 128.4, 126.1 (d, *J*_{CP} = 9.1 Hz), 106.6 (d, *J*_{CP} = 8.7 Hz), 52.4, 21.4. ³¹P NMR (162 MHz, Chloroform-d) δ 28.6. HRESIMS calcd for C₂₈H₂₉NO₂P [M + H]⁺: 442.1930; found 442.1952.

1-benzyl-4-(di(naphthalen-2-yl)phosphoryl)pyridin-2(1H)-one (3ah)



White solid (53.4 mg, 55%). Mp: 190.7 – 192.3 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.34 (d, J = 14.2 Hz, 2H), 7.94 (dd, J = 8.5, 2.9 Hz, 2H), 7.88 (d, J = 8.4 Hz, 4H), 7.73 – 7.66 (m, 2H), 7.65 – 7.47 (m, 5H), 7.39 (dd, J = 6.9, 3.9 Hz, 1H), 7.34 – 7.28 (m, 4H), 6.78 (d, J = 15.0 Hz, 1H), 6.66 – 6.48 (m, 1H), 5.13 (s, 2H). ¹³C NMR (100 MHz, Chloroform-d) δ 161.2 (d, $J_{CP} = 16.4$ Hz), 145.9 (d, $J_{CP} = 92.8$ Hz), 138.1 (d, $J_{CP} = 12.8$ Hz), 135.5, 135.0 (d, $J_{CP} = 2.4$ Hz), 134.3 (d, $J_{CP} = 9.6$ Hz), 132.5 (d, $J_{CP} = 13.6$ Hz), 129.0, 128.9, 128.8, 128.7, 128.4, 128.0, 127.3, 127.1 (d, $J_{CP} = 106.1$ Hz), 126.6, 126.4 (d, $J_{CP} = 10.8$ Hz), 126.2 (d, $J_{CP} = 8.9$ Hz), 106.3 (d, $J_{CP} = 9.0$ Hz), 52.3. ³¹P NMR (162 MHz, Chloroform-d) δ 27.9. HRESIMS calcd for C₃₂H₂₅NO₂P [M + H]⁺: 486.1617; found 486.1637.

2-(Diphenylphosphoryl)-1-methylquinolin-4(1H)-one (4a)



Yellow solid (30.2 mg, 42%). Mp: 182.9 – 184.7 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 8.47 – 8.23 (m, 1H), 7.93 – 7.69 (m, 6H), 7.68 – 7.61 (m, 2H), 7.59 – 7.52 (m, 4H), 7.49 – 7.31 (m, 1H), 5.99 (d, *J* = 14.1 Hz, 1H), 3.96 (s, 3H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 177.3 (d, *J*_{CP} = 12.5 Hz), 147.4 (d, *J*_{CP} = 98.7 Hz), 143.8 (d, *J*_{CP} = 8.0 Hz), 133.6, 133.5 (d, *J*_{CP} = 2.9 Hz), 132.5 (d, *J*_{CP} = 10.1 Hz), 130.7 (d, *J*_{CP} = 108.3 Hz), 129.7 (d, *J*_{CP} = 12.7 Hz), 127.6, 126.8, 124.7, 119.8 (d, *J*_{CP} = 12.5 Hz), 116.6 (d, *J*_{CP} = 1.5 Hz), 38.4. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 31.3. HRESIMS calcd for C₂₂H₁₉NO₂P [M + H]⁺: 360.1148; found 360.1162.

2-(Diphenylphosphoryl)-1,3-dimethylquinolin-4(1*H*)-one (4b)



White solid (29.9 mg, 40%). Mp: 147.7 – 148.9 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 8.19 (d, J = 7.8 Hz, 1H), 7.91 – 7.62 (m, 6H), 7.61 – 7.41 (m, 4H), 7.40 – 7.31 (m, 1H), 7.26 (d, J = 7.7 Hz, 1H), 5.99 (d, J = 14.0 Hz, 1H), 3.96 (s, 3H), 2.52 (s, 3H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 176.9 (d, $J_{CP} = 13.4$ Hz), 147.2 (d, $J_{CP} = 99.1$ Hz), 144.9, 143.9 (d, $J_{CP} = 10.3$ Hz), 133.5 (d, $J_{CP} = 2.6$ Hz), 132.4 (d, $J_{CP} = 10.0$ Hz), 130.7 (d, $J_{CP} = 108.4$ Hz), 129.6 (d, $J_{CP} = 12.7$ Hz), 126.7, 126.5, 125.4, 119.6 (d, $J_{CP} = 12.8$ Hz), 116.3 (d, $J_{CP} = 1.6$ Hz), 38.4 (d, $J_{CP} = 4.7$ Hz), 22.6. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 33.3. HRESIMS calcd for C₂₃H₂₁NO₂P [M + H]⁺: 374.1304; found 374.1299.

2-(Dhenylphosphoryl)-1,6-dimethylquinolin-4(1*H*)-one (4c)



Yellow solid (31.4 mg, 42%). Mp: 226.8 – 228.2 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 10.06 (s, 1H), 9.70 – 9.57 (m, 6H), 9.56 – 9.45 (m, 5H), 9.40 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 14.0 Hz, 1H), 5.90 (s, 3H), 4.41 (s, 3H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 176.6 (d, *J*_{CP} = 12.5 Hz), 146.3 (d, *J*_{CP} = 99.1 Hz), 141.3 (d, *J*_{CP} = 7.5 Hz), 134.5, 134.4, 133.0 (d, *J*_{CP} = 2.9 Hz), 131.8 (d, *J*_{CP} = 10.0 Hz), 130.2 (d, *J*_{CP} = 108.3 Hz), 129.1 (d, *J*_{CP} = 12.7 Hz), 126.9, 125.6, 118.8 (d, *J*_{CP} = 12.7 Hz), 115.9 (d, *J*_{CP} = 1.8 Hz), 37.8 (d, *J*_{CP} = 4.6 Hz), 20.5. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 33.3. HRESIMS calcd for C₂₃H₂₁NO₂P [M + H]⁺: 374.1304; found 374.1299.

2-(Diphenylphosphoryl)-1,7-dimethylquinolin-4(1*H*)-one (4d)



White solid (32.1 mg, 43%). Mp: 203.1 – 204.8 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 8.10 (d, J = 8.2 Hz, 1H), 7.68 – 7.60 (m, 4H), 7.59 – 7.53 (m, 2H), 7.51 – 7.41 (m, 4H), 7.24 (s, 1H), 7.16 (d, J = 8.2 Hz, 1H), 5.87 (d, J = 14.1 Hz, 1H), 3.86 (s, 3H), 2.42 (s, 3H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 177.0 (d, $J_{CP} = 12.6$ Hz), 147.0 (d, $J_{CP} = 99.1$ Hz), 144.7, 143.8 (d, $J_{CP} = 7.4$ Hz), 133.5 (d, $J_{CP} = 2.8$ Hz), 132.4 (d, $J_{CP} = 10.1$ Hz), 130.7 (d, $J_{CP} = 108.3$ Hz), 129.6 (d, $J_{CP} = 12.7$ Hz), 126.6, 126.4, 125.5, 119.7 (d, $J_{CP} = 12.6$ Hz), 116.3 (d, $J_{CP} = 1.7$ Hz), 38.3 (d, $J_{CP} = 4.7$ Hz), 22.6. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 31.3. HRESIMS calcd for C₂₃H₂₁NO₂P [M + H]⁺: 374.1304; found 374.1338.

2-(Diphenylphosphoryl)-6-methoxy-1-methylquinolin-4(1*H*)-one (4e)



White solid (31.9 mg, 41%). Mp: 144.7 – 145.9 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 7.94 – 7.68 (m, 6H), 7.68 – 7.61 (m, 2H), 7.60 – 7.48 (m, 4H), 7.33 (d, *J* = 9.4 Hz, 1H), 6.16 – 5.83 (m, 1H), 3.97 (s, 3H), 3.89 (s, 3H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 176.6 (d, *J*_{CP} = 12.4 Hz), 157.3, 146.2 (d, *J*_{CP} = 99.4 Hz), 138.4 (d, *J*_{CP} = 7.4 Hz), 133.5 (d, *J*_{CP} = 2.6 Hz), 132.4 (d, *J*_{CP} = 10.1 Hz), 130.7 (d, *J*_{CP} = 108.4 Hz), 129.7, 129.6, 128.8, 124.2, 118.4 (d, *J*_{CP} = 59 Hz), 105.7, 56.3, 38.5 (d, *J*_{CP} = 4.6 Hz). ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 31.3. HRESIMS calcd for C₂₃H₂₁NO₃P [M + H]⁺: 390.1254; found 390.1253.

6-Bromo-2-(diphenylphosphoryl)-1-methylquinolin-4(1H)-one (4f)



Yellow solid (39.4 mg, 45%). Mp: 140.1 – 141.8 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 8.62 – 8.38 (m, 1H), 7.95 – 7.76 (m, 3H), 7.76 – 7.63 (m, 5H), 7.62 – 7.51 (m, 3H), 7.43 (d, J = 9.2 Hz, 1H), 6.00 (d, J = 13.9 Hz, 1H), 3.94 (s, 3H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 176.0 (d, $J_{CP} =$ 12.4 Hz), 147.8 (d, $J_{CP} =$ 96.2 Hz), 147.3, 142.5 (d, $J_{CP} =$ 7.5 Hz), 136.4, 133.7 (d, $J_{CP} =$ 2.8 Hz), 132.4 (d, $J_{CP} =$ 10.0 Hz), 130.3 (d, $J_{CP} =$ 108.8 Hz), 129.7 (d, $J_{CP} =$ 12.7 Hz), 129.3, 128.8, 120.0 (d, $J_{CP} =$ 12.7 Hz), 118.7 (d, $J_{CP} =$ 12.1 Hz), 38.5 (d, $J_{CP} =$ 4.5 Hz). ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 31.4. HRESIMS calcd for C₂₂H₁₈BrNO₂P [M + H]⁺: 438.0253, 440.0233; found 438.0247, 440.0260.

1-Benzyl-6-chloro-2-(diphenylphosphoryl)quinolin-4(1H)-one (4g)



Yellow solid (45.1 mg, 48%). Mp: 57.8 – 59.6 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 8.28 (s, 1H), 7.83 – 7.67 (m, 4H), 7.63 – 7.56 (m, 2H), 7.55 – 7.38 (m, 5H), 7.30 (d, J = 9.2 Hz, 1H), 7.22 – 7.04 (m, 3H), 6.95 – 6.76 (m, 2H), 6.16 (d, J = 13.8 Hz, 1H), 5.95 (s, 2H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 176.2 (d, $J_{CP} = 13.8$ Hz), 148.3 (d, $J_{CP} = 95.9$ Hz), 141.5 (d, $J_{CP} = 7.2$ Hz), 136.1, 133.6 (d, $J_{CP} = 2.4$ Hz), 133.5, 132.6 (d, $J_{CP} = 10.0$ Hz), 130.9, 129.9 (d, $J_{CP} =$ 108.8 Hz), 129.6 (d, $J_{CP} = 12.7$ Hz), 129.0, 128.8, 127.8, 126.2, 126.0, 120.1, 119.9, 53.8 (d, $J_{CP} =$ 4.0 Hz). ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 31.2. HRESIMS calcd for $C_{28}H_{22}$ CINO₂P [M + H]⁺: 470.1071, 472.1042; found 470.1072, 472.1068.

2-(Diphenylphosphoryl)-1-(2-methylbenzyl)quinolin-4(1H)-one (4h)



Yellow solid (38.6 mg, 43%). Mp: 263.4 – 265.3 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 8.40 – 8.30 (m, 1H), 7.78 – 7.66 (m, 4H), 7.61 – 7.49 (m, 4H), 7.48 – 7.39 (m, 3H), 7.38 – 7.32 (m, 1H), 7.25 – 7.16 (m, 1H), 7.11 – 6.92 (m, 2H), 6.82 – 6.67 (m, 1H), 6.18 (dd, *J* = 17.0, 10.9 Hz, 2H), 5.92 (s, 2H), 2.26 (s, 3H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 177.3 (d, *J*_{CP} = 12.1 Hz), 147.9 (d, *J*_{CP} = 96.4 Hz), 143.3 (d, *J*_{CP} = 6.9 Hz), 134.6, 134.0, 133.5 (d, *J*_{CP} = 8.3 Hz), 133.4, 132.5, 132.4, 130.4, 129.4, 129.3, 127.6, 127.3, 126.2 (d, *J*_{CP} = 116.5 Hz), 126.1, 124.8, 120.1 (d, *J*_{CP} = 12.5 Hz), 117.8, 51.4 (d, *J*_{CP} = 3.4 Hz), 19.3. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 31.0. HRESIMS calcd for C₂₉H₂₅NO₂P [M + H]⁺: 450.1617; found 450.1618.

2-(Diphenylphosphoryl)-1-(3-methoxybenzyl)quinolin-4(1H)-one (4i)



Yellow solid (37.2 mg, 40%). Mp: 153.8 – 155.3 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.39 (dd, J = 8.2, 1.5 Hz, 1H), 7.71 – 7.68 (m, 4H), 7.58 – 7.55 (m, 2H), 7.53 – 7.48 (m, 4H), 7.45 – 7.40 (m, 3H), 7.35 – 7.32 (m, 2H), 6.96 (t, J = 7.9 Hz, 1H), 6.59 (dd, J = 8.2, 2.2 Hz, 1H), 6.33 (d, J = 7.7 Hz, 1H), 6.28 (s, 2H), 3.64 (s, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 177.5 (d, $J_{CP} = 12.5$ Hz), 159.6, 147.3 (d, $J_{CP} = 96.7$ Hz), 142.8 (d, $J_{CP} = 7.3$ Hz), 137.3, 133.3, 133.1 (d, $J_{CP} = 2.8$ Hz), 132.7 (d, $J_{CP} = 2.8$ Hz), 132.2 (d, $J_{CP} = 10.1$ Hz), 131.5 (d, $J_{CP} = 101.6$ Hz), 130.8 (d, $J_{CP} = 11.5$ Hz), 129.1 (d, $J_{CP} = 12.8$ Hz), 129.0 (d, $J_{CP} = 12.9$ Hz), 126.8, 124.6, 119.8 (d, $J_{CP} = 12.8$ Hz), 118.1, 117.5 (d, $J_{CP} = 1.4$ Hz), 112.0 (d, $J_{CP} = 54.6$ Hz), 55.2, 52.9 (d, $J_{CP} = 4.2$ Hz). ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 31.3. HRESIMS calcd for C₂₉H₂₅NO₃P [M + H]⁺: 466.1567; found 466.1566.

1-(2,6-Dichlorobenzyl)-2-(diphenylphosphoryl)quinolin-4(1H)-one (4j)



Yellow solid (38.3 mg, 38%). Mp: 210.1 – 211.5 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 8.17 (dd, J = 8.0, 1.3 Hz, 1H), 7.73 – 7.63 (m, 4H), 7.58 – 7.51 (m, 2H), 7.49 – 7.41 (M, 4H), 7.40 – 7.34 (m, 1H), 7.21 (t, J = 7.3 Hz, 1H), 7.14 (d, J = 7.8 Hz, 2H), 7.08 – 6.99 (m, 2H), 6.12 (s, 2H), 6.06 (d, J = 14.1 Hz, 1H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 177.6 (d, J_{CP} = 12.4 Hz), 148.4 (d, J_{CP} = 97.4 Hz), 142.9 (d, J_{CP} = 7.1 Hz), 134.8, 133.6 (d, J_{CP} = 2.8 Hz), 133.1, 132.6 (d, J_{CP} = 10.0 Hz), 130.8, 130.5 (d, J_{CP} = 108.3 Hz), 130.2, 129.8, 129.6 (d, J_{CP} = 12.7 Hz), 127.7, 126.9, 124.7, 120.8 (d, J_{CP} = 12.6 Hz), 116.9 (d, J_{CP} = 1.4 Hz), 51.1 (d, J_{CP} = 4.3 Hz). ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 31.1. HRESIMS calcd for C₂₈H₂₁Cl₂NO₂P [M + H]⁺: 504.0681, 506.0652; found 504.0690, 506.0637.

2-(Bis(3,5-dimethylphenyl)phosphoryl)-1-methylquinolin-4(1*H*)-one (4k)



Orange solid (35.7 mg, 43%). Mp: 82.1 – 83.8 °C. ¹H NMR (400 MHz, Methylene Chloride-d2) δ 8.31 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.35 – 7.25 (m, 6H), 5.99 (d, *J* = 13.9 Hz, 1H), 3.96 (s, 3H), 2.34 (s, 12H). ¹³C NMR (100 MHz, Methylene Chloride-d2) δ 177.4 (d, *J*_{CP} = 12.4 Hz), 147.9 (d, *J*_{CP} = 97.1 Hz), 143.7 (d, *J*_{CP} = 7.3 Hz), 139.6 (d, *J*_{CP} = 13.4 Hz), 135.2 (d, *J*_{CP} = 3.0 Hz), 133.5, 130.4 (d, *J*_{CP} = 107.2 Hz), 129.8 (d, *J*_{CP} = 10.0 Hz), 127.5, 126.8, 124.6, 119.6 (d, *J*_{CP} = 12.7 Hz), 116.6 (d, *J*_{CP} = 1.7 Hz), 38.4 (d, *J*_{CP} = 4.6 Hz), 21.6. ³¹P NMR (162 MHz, Methylene Chloride-d2) δ 32.1. HRESIMS calcd for C₂₆H₂₇NO₂P [M + H]⁺: 416.1774; found 416.1781.
9. References

- Jr. W. S. Hummers, R. E. Offeman. Preparation of graphitic oxide. J. Am. Chem. Soc., 1958, 80, 1339–1339.
- D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen, R. S. Ruoff. Preparation and characterization of graphene oxide paper. *Nature*, 2007, 448, 457–460.
- (a) T. Soejima, Y. Maru, S. Ito. Facile low-temperature synthesis and photocatalytic activity of graphene oxide/TiO₂ composite. *Bull. Chem. Soc. Jpn.*, **2013**, *86*, 1065–1070; (b) C.-M. Chen, J.-Q. Huang, Q. Zhang, W.-Z. Gong, Q.-H. Yang, M.-Z. Wang, Y.-G. Yang. Annealing a graphene oxide film to produce a free standing high conductive graphene film. *Carbon*, **2012**, *50*, 659–667; (c) C. W. Lo, D. Zhu, H. Jiang. An infrared-light responsive graphene-oxide incorporated poly (N-isopropylacrylamide) hydrogel nanocomposite. *Soft Matter*, **2011**, *7*, 5604–5609; (d) S, Lv. Y. Ma, C. Qiu, T. Sun, J. Liu, Q. Zhou. Effect of graphene oxide nanosheets of microstructure and mechanical properties of cement composites. *Constr. Build. Mater.*, **2013**, *49*, 121–127.
- V. B. Rana, S. K. Sahni, S. K. Sangal. Oxovanadium (IV) complexes of potential pentadentate ligands. J. Inorg. Nucl. Chem., 1979, 41, 1498–1500.
- K.-H. Liao, A. Mittal, S. Bose, C. Leighton, K. A. Mkhoyan, C. W. Macosko. Aqueous only route toward graphene from graphite oxide. *ACS Nano*, 2011, *5*, 1253–1258.

10. Copies of ¹H NMR, ¹³C NMR, ¹⁹F NMR and ³¹P NMR

and Spectra for All Compounds

¹H, ¹³C and ³¹P NMR Spectra for **3a** in CDCl₃



f1 (ppm)



120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 f1 (ppm)

¹H, ¹³C and ³¹P NMR Spectra for **3b** in CD₂Cl₂





¹H, ¹³C and ³¹P NMR Spectra for 3c in CD_2Cl_2













¹H, ¹³C and ³¹P NMR Spectra for **3e** in CDCl₃





130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 f1 (ppm)

 $^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for 3f in CD_2Cl_2





¹H, ¹³C and ³¹P NMR Spectra for **3g** in CD₂Cl₂







¹H, ¹³C and ³¹P NMR Spectra for **3i** in CDCl₃





















 $^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for **31** in CD_2Cl_2





130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 f1 (ppm)

 $^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for 3m in CDCl_3





¹H, ¹³C and ³¹P NMR Spectra for **3n** in CDCl₃









¹H, ¹³C and ³¹P NMR Spectra for **3p** in CDCl₃







-40 -60 f1 (ppm) 120 100 -120 -140 -180 -200 -220 80 60 40 20 -80 -100 -160 0 -20

 $^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for 3q in CDCl_3





¹H, ¹³C and ³¹P NMR Spectra for **3r** in CDCl₃



f1 (ppm)



¹H, ¹³C and ³¹P NMR Spectra for **3s** in CDCl₃





¹H, ¹³C, ³¹P and ¹⁹F NMR Spectra for **3t** in CDCl₃



110 100 f1 (ppm)





$^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for 3u in CD_2Cl_2



100 90 fl (ppm)



-170 -190 -210 -230 130 -130 110 90 -10 -50 f1 (ppm) -70 -110 -150 70 50 30 10 -30 -90

 $^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for 3v in CDCl_3





130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 f1 (ppm)

 $^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for 3w in CDCl_3




¹H, ¹³C and ³¹P NMR Spectra for 3x in CD_2Cl_2







 $^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for 3y in CDCl_3





f1 (ppm)



-40 -60 f1 (ppm) 40 0

 $^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for 3z in CDCl_3





¹H, ¹³C and ³¹P NMR Spectra for **3aa** in CDCl₃





¹H, ¹³C and ³¹P NMR Spectra for **3ab** in CDCl₃





¹H, ¹³C and ³¹P NMR Spectra for **3ac** in CDCl₃









¹H, ¹³C and ³¹P NMR Spectra for **3ae** in CDCl₃





-230 -170 -190 130 110 90 -50 fl (ppm) -110 -130 -150 -210 70 50 30 10 -10 30 -70 -90

 $^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for 3af in CDCl_3





¹H, ¹³C and ³¹P NMR Spectra for **3ag** in CDCl₃









¹H, ¹³C and ³¹P NMR Spectra for **4a** in CD₂Cl₂





 $^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for 4b in CD_2Cl_2





-50 f1 (ppm) Т 130 110 -10 -30 -70 -90 -110 -130 -150 -170 -190 -210 -230 90 70 50 30 10

 $^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for 4c in CD_2Cl_2





¹H, ¹³C and ³¹P NMR Spectra for **4d** in CD₂Cl₂





 $^1\text{H}\text{, }^{13}\text{C}$ and ^{31}P NMR Spectra for 4e in CD_2Cl_2





 1 H, 13 C and 31 P NMR Spectra for **4f** in CD₂Cl₂





 $^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for 4g in CD_2Cl_2





 $^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for 4h in CD_2Cl_2





¹H, ¹³C and ³¹P NMR Spectra for 4i in CDCl₃





130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 f1 (ppm)

 $^1\text{H},\,^{13}\text{C}$ and ^{31}P NMR Spectra for 4j in CD_2Cl_2





¹H, ¹³C and ³¹P NMR Spectra for **4k** in CD₂Cl₂



