Supporting Information for

Aggregation-Induced Polarization (AIP) of Derivatives of BINOL and BINAP

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1. General Information

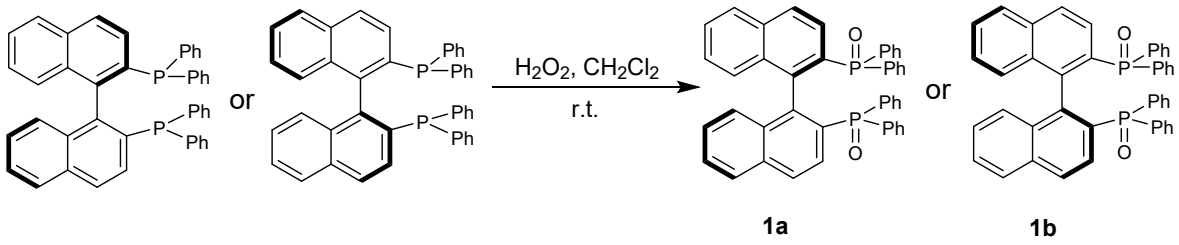
Unless otherwise stated, all reactions were magnetically stirred and conducted in oven-dried glassware in anhydrous solvents under Ar. Solvents and liquid reagents, as well as solutions of solid or liquid reagents were added directly or via syringes, or micropipette. Cooling baths were prepared in Dewar vessels filled with ice/water (0 °C). Heated oil baths were used for reactions requiring elevated temperatures. Solvents were removed under reduced pressure at 40-65 °C using a rotavapor. All given yields for small molecules are isolated yields of chromatographically and NMR spectroscopically materials.

All commercially available chemicals were used as received without further purification. Solvents as follows: MeOH, EtOH, toluene, EtOAc, DCM, dioxane, hexane, acetone and THF were used without further purification.

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on 400 MHz and 100MHz instruments with TMS as internal standard. For referencing of the ^{1}H NMR spectra, the residual solvent signal (δ = 7.26 for $CDCl_3$) were used. In the case of the ^{13}C NMR spectra, the signal of solvents (δ = 77.06 ± 0.03 for $CDCl_3$) were used. Chemical shifts(δ) were reported in ppm with respect to TMS. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (*J*, Hz), and integration. Fluorescence spectra were collected by Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer G9800A and Eclipse ADL program. Optical rotation was determined by the Rudolph polarimeter (Rudolph Research Analytical APIV/2W).

2. Synthetic Procedures

General procedure for the oxidation of BINAP

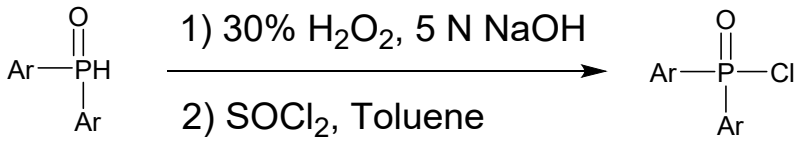


To an oven-dried 100 mL, round bottle flask with a magnetic stirrer, chiral BINAP (0.5 g, 0.8 mmol, 1eq.) was dissolved in 20 mL DCM at 0 °C. 30% H_2O_2 (4.4 mL 70 eq.) was added dropwise, and the resulting solution was stirred vigorously at room temperature overnight. NH_4Cl quenched the reaction, and the organic layer was washed with brine and dried with $MgSO_4$. Evaporated the solvent to obtain the product without further purification.

(R) & (S)-[1,1'-binaphthalene]-2,2'-diylbis(diphenylphosphine oxide) (1a &1b)

White solid (0.49 g, yield: 94%) ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.01 (d, *J* = 8.9 Hz, 2H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.43 (m, 4H), 7.33 – 7.27 (m, 2H), 7.22 (s, 2H), 1.88 (s, 6H). ^{31}P NMR (162 MHz, CHLOROFORM-*D*) δ 28.83. $[\alpha]_D^{25}$ = +273.7 (**1a**, *c* = 0.4, THF). $[\alpha]_D^{25}$ = -258.5 (**1b**, *c* = 0.4, THF).

General Procedure for the Preparation of diphenylphosphinic chloride

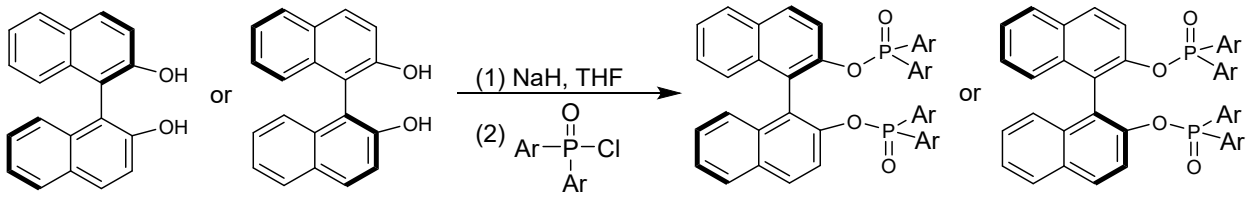


Ar = benzene, 3,5-dimethyl benzene, 4-methyl benzene, 4-methoxy benzene

To an oven-dried 50 mL round bottle flask with a magnetic stirrer, 30% H_2O_2 (4 mL) was added dropwise to a suspension of phosphine oxide (1.7 mmol) in aqueous 5N NaOH (4 mL) at 95 °C, and the resulting mixture was stirred for 1 hour at 100 °C. After the reaction was completed, the reaction mixture was cooled to 0 °C, and concentrated HCl was added dropwise to precipitate the white solid. The precipitate was collected by filtration and washed with excess amounts of diethyl ether. The resulting white solid was dried under a vacuum to get phosphonic acid without further purification.

To an oven-dried 50 mL, round bottle flask with a magnetic stirrer, $SOCl_2$ (2 mL) was added to a suspension of phosphonic acid in 6 mL anhydrous toluene. The resulting solution was heated to 80 °C for 3 hours. After the reaction was complete, the solvent was removed by reduced pressure. The excess amount of thionyl chloride was removed by redissolving the residue with toluene (5 mL) two times, and the obtained diphenylphosphinic chloride was directly run to the protection step.

General procedure for the protections of BINOL (2a-5b)

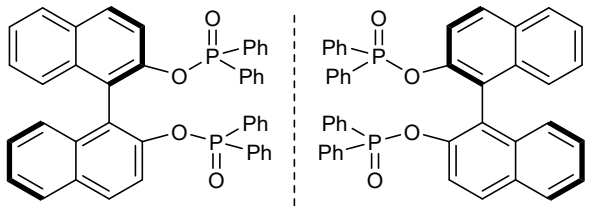


2a, Ar = benzene
3a, Ar = 3,5-dimethyl benzene
4a, Ar = 4-methyl benzene
5a, Ar = 4-methoxy benzene

2b, Ar = benzene
3b, Ar = 3,5-dimethyl benzene
4b, Ar = 4-methyl benzene
5b, Ar = 4-methoxy benzene

To an oven-dried 50 mL, two-neck Schlenk flask with a magnetic stirrer, chiral BINOL (1.8 mmol, 1 eq.) was dissolved in anhydrous THF under a nitrogen atmosphere at 0 °C, Sodium hydride (60% w/ oil suspension, 4.0 mmol) was added portion, and the resulting solution was stirred at 0 °C for 15 minutes. Diphenylphosphinic chloride or acetyl chloride (4.0 mmol) was added dropwise, and the reaction was kept stirring for another 15 minutes and then stirred at room temperature overnight. The reaction was quenched by NH_4Cl at 0 °C, and the solvent was removed by vacuum. The residue was dissolved with ethyl acetate and washed with water and brine. The organic phase was concentrated under reduced pressure, and the product can be obtained by GAP wash (Hexane/ ethyl acetate) or flash column chromatography.

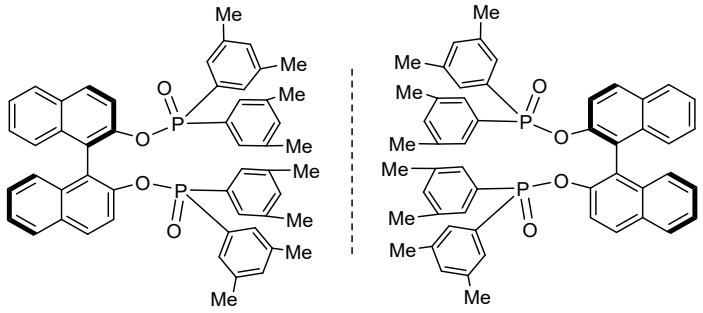
(R) & (S)-[1,1'-binaphthalene]-2,2'-diyl bis(diphenylphosphinate) (2a&2b)



2a **2b**

White solid (1.11 g, yield: 90%) ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.05 (dd, *J* = 9.1, 1.0 Hz, 2H), 7.94 (d, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.29 (m, 6H), 7.26 – 7.19 (m, 5H), 7.19 – 7.04 (m, 10H), 7.04 – 6.96 (m, 5H). ^{31}P NMR (162 MHz, CHLOROFORM-*D*) δ 30.36. $[\alpha]_D^{25}$ = +25.0 (**2a**, *c* = 0.4, THF). $[\alpha]_D^{25}$ = -22.5 (**2b**, *c* = 0.4, THF).

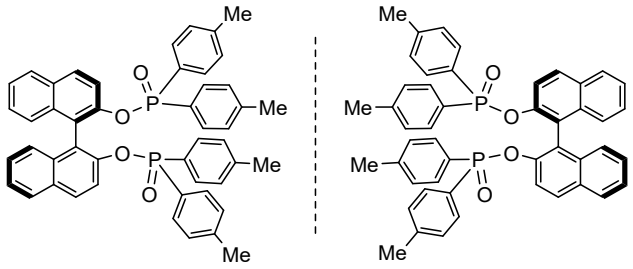
(R) & (S)-[1,1'-binaphthalene]-2,2'-diyl bis(bis(3,5-dimethylphenyl)phosphinate) (3a&3b)



3a **3b**

White solid (0.93 g, yield: 65 %) ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.10 (d, *J* = 9.0 Hz, 2H), 7.92 (d, *J* = 9.0 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.34 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 2H), 7.12 (ddd, *J* = 8.3, 6.7, 1.3 Hz, 2H), 7.05 – 6.94 (m, 6H), 6.89 (s, 2H), 6.83 – 6.71 (m, 6H), 2.05 (s, 12H), 1.99 (s, 12H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 147.74 (d, *J* = 7.6 Hz), 138.11 (d, *J* = 14.4 Hz), 137.72 (d, *J* = 14.3 Hz), 133.89, 133.86, 133.72, 131.53, 131.29, 130.50, 130.13, 129.99, 129.96, 129.13 (d, *J* = 3.4 Hz), 129.03 (d, *J* = 3.2 Hz), 127.38 (d, *J* = 112.8 Hz), 125.48 (d, *J* = 112.5 Hz), 121.56 (d, *J* = 7.4 Hz), 120.25 (d, *J* = 3.8 Hz), 21.11 (d, *J* = 9.2 Hz).^{31}P NMR (162 MHz, CHLOROFORM-*D*) δ 31.49. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{52}H_{49}O_4P_2$ 799.3100; Found 799.3150. $[\alpha]_D^{25}$ = -2.2 (**3a**, *c* = 0.4, THF). $[\alpha]_D^{25}$ = +1.7 (**3b**, *c* = 0.4, THF).

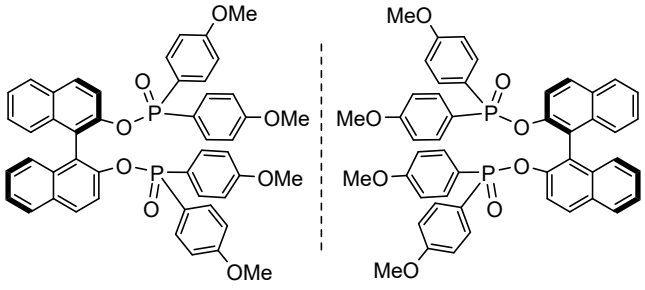
(R) & (S)-[1,1'-binaphthalene]-2,2'-diyl bis(di-p-tolylphosphinate) (4a&4b)



4a **4b**

White solid (0.96 g, yield: 72 %) ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.06 (d, *J* = 9.0 Hz, 2H), 7.94 (d, *J* = 9.0 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.37 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 2H), 7.25 – 7.18 (m, 4H), 7.13 (ddd, *J* = 8.2, 6.7, 1.2 Hz, 2H), 7.01 – 6.93 (m, 6H), 6.87 (dd, *J* = 8.1, 3.5 Hz, 4H), 6.76 (dd, *J* = 8.0, 3.4 Hz, 4H), 2.17 (d, *J* = 7.3 Hz, 12H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 147.65 (d, *J* = 7.7 Hz), 142.51 (d, *J* = 2.9 Hz), 142.36 (d, *J* = 3.0 Hz), 133.67, 131.63 (d, *J* = 3.5 Hz), 131.52 (d, *J* = 3.1 Hz), 130.61, 129.87, 129.12 (d, *J* = 14.1 Hz), 128.83 (d, *J* = 14.1 Hz), 128.47, 128.23, 127.36 (d, *J* = 118.8 Hz), 127.03, 126.86, 125.67 (d, *J* = 133.7 Hz), 121.66 (d, *J* = 7.2 Hz), 120.37 (d, *J* = 3.8 Hz), 21.55 (d, *J* = 6.2 Hz). ^{31}P NMR (162 MHz, CHLOROFORM-*D*) δ 31.36. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{48}H_{41}O_4P_2$ 743.2474; Found 743.2524. $[\alpha]_D^{25}$ = +31.2 (**4a**, *c* = 0.4, THF). $[\alpha]_D^{25}$ = -27.2 (**4b**, *c* = 0.4, THF).

(R) & (S)-[1,1'-binaphthalene]-2,2'-diyl bis(bis(4-methoxyphenyl)phosphinate) (5a,5b)

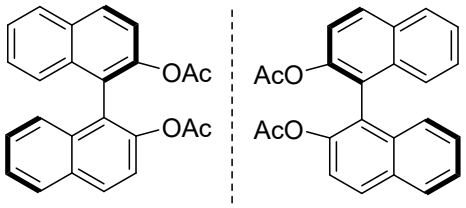


5a **5b**

White solid (1.09 g, yield: 75 %) ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.08 (d, *J* = 9.0 Hz, 2H), 7.94 (d, *J* = 9.1 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.35 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 2H), 7.30 – 7.23 (m, 4H), 7.12 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 2H), 7.03 – 6.93 (m, 6H), 6.59 (dd, *J* = 8.8, 2.9 Hz, 4H), 6.43 (dd, *J* = 9.4, 2.8 Hz, 4H), 3.67 (d, *J* = 4.3 Hz, 12H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 162.48 (d, *J* = 3.1 Hz), 162.28 (d, *J* = 3.0 Hz), 147.63 (d, *J* = 7.7 Hz), 133.67, 133.51, 133.44, 133.33, 130.60, 129.87, 127.94, 126.57 (d, *J* = 43.8 Hz), 125.04, 123.11

(d, *J* = 135.4 Hz), 122.13 (d, *J* = 123.2 Hz), 120.45, 113.93 (d, *J* = 14.6 Hz), 113.61 (d, *J* = 15.0 Hz), 113.48 (d, *J* = 14.4 Hz), 55.25 (d, *J* = 2.9 Hz), 55.17 (d, *J* = 2.9 Hz). ^{31}P NMR (162 MHz, CHLOROFORM-*D*) δ 31.50. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{48}H_{41}O_8P_2$ 807.2271; Found 807.2338. $[\alpha]_D^{25}$ = +44.0 (**5a**, *c* = 0.4, THF). $[\alpha]_D^{25}$ = -33.0 (**5b**, *c* = 0.4, THF).

(R) & (S)-[1,1'-binaphthalene]-2,2'-diyl diacetate (7a,7b)



7a **7b**

White solid (0.64 g, yield: 96 %) ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.01 (d, *J* = 8.9 Hz, 2H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.43 (m, 4H), 7.33 – 7.27 (m, 2H), 7.22 (s, 2H), 1.88 (s, 6H). $[\alpha]_D^{25}$ = -20.2 (**7a**, *c* = 0.4, THF). $[\alpha]_D^{25}$ = +19.0 (**7b**, *c* = 0.4, THF).

3. NMR Spectra

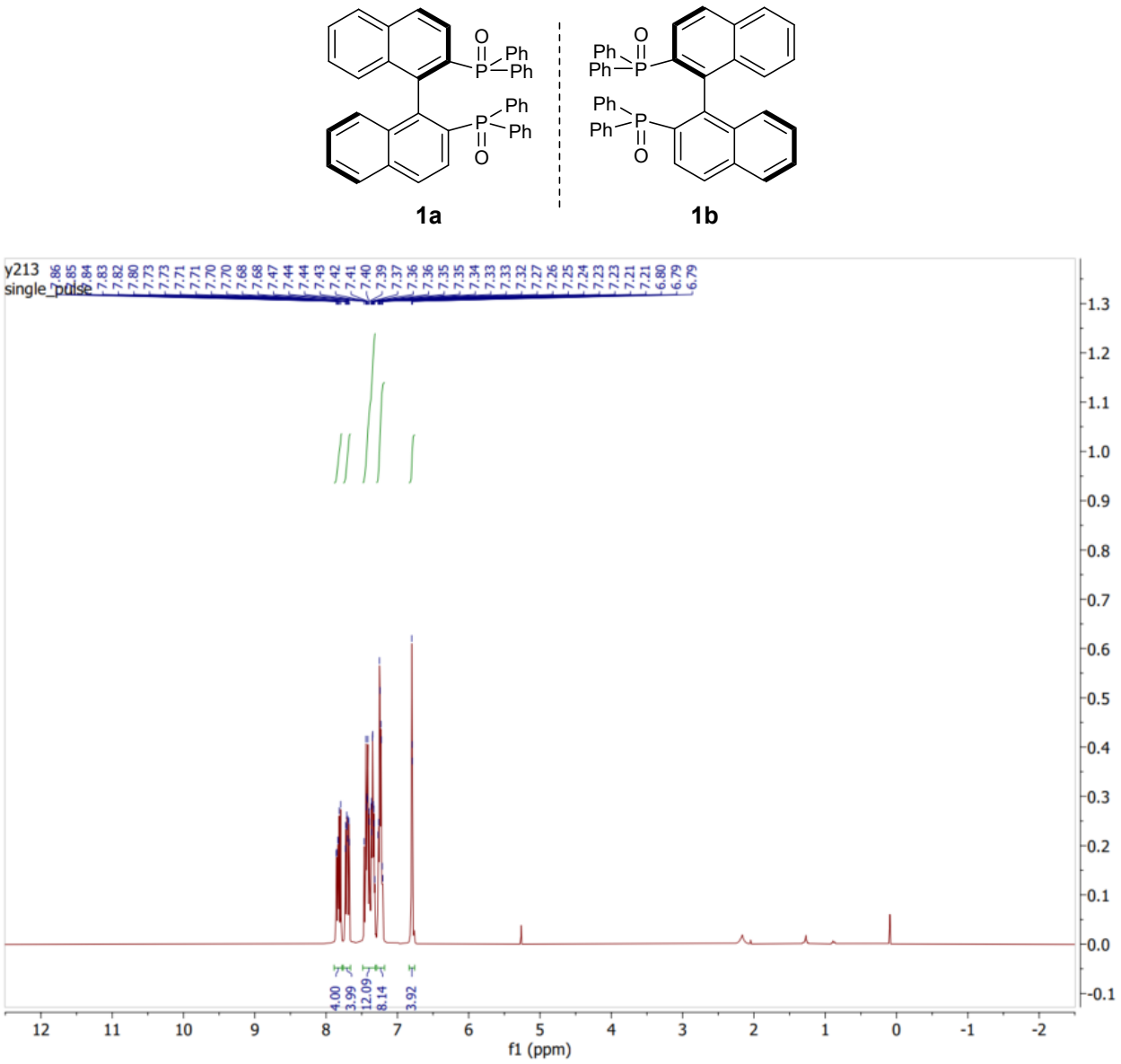


Figure S1. ^{1}H NMR Spectrum of 1a and 1b ($CDCl_3$, 400 MHz)

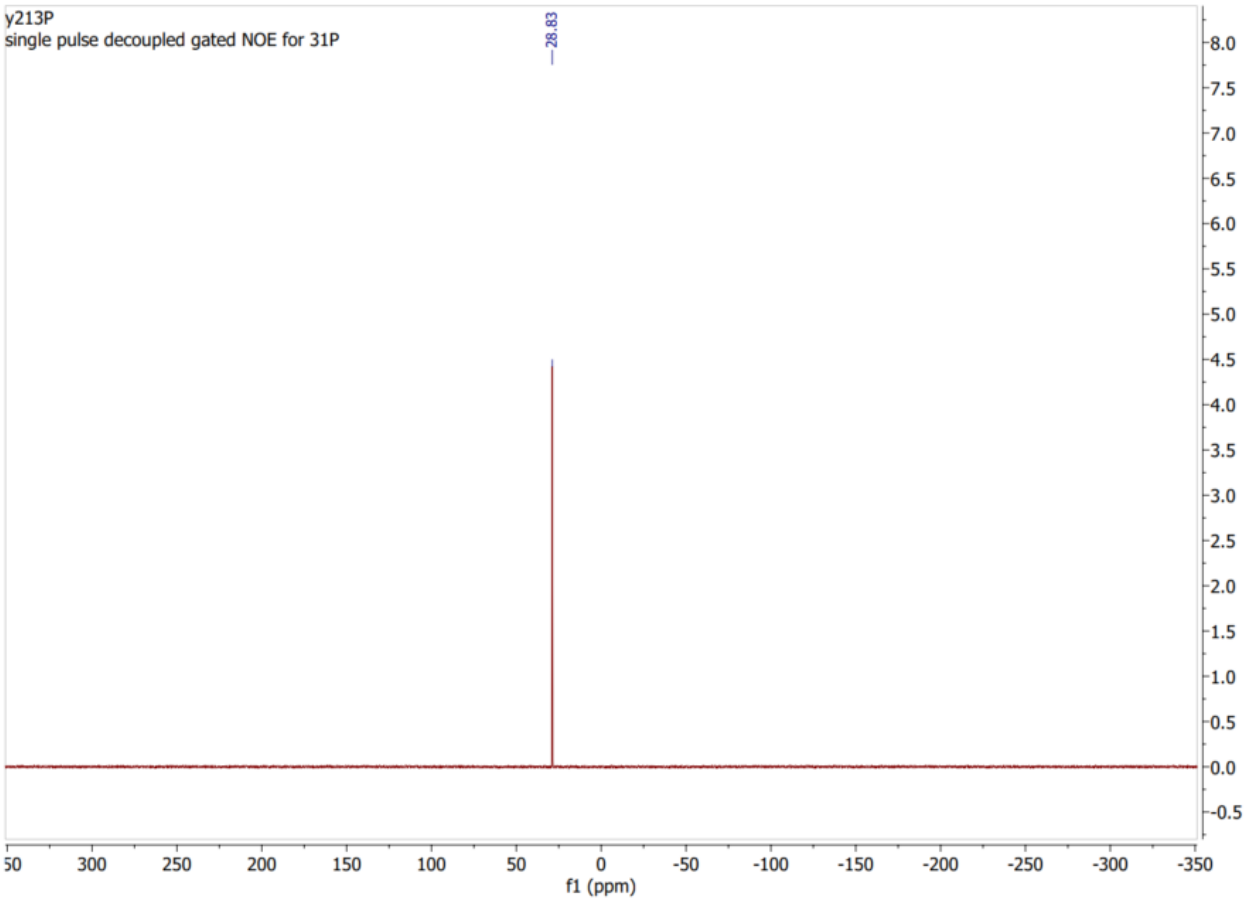
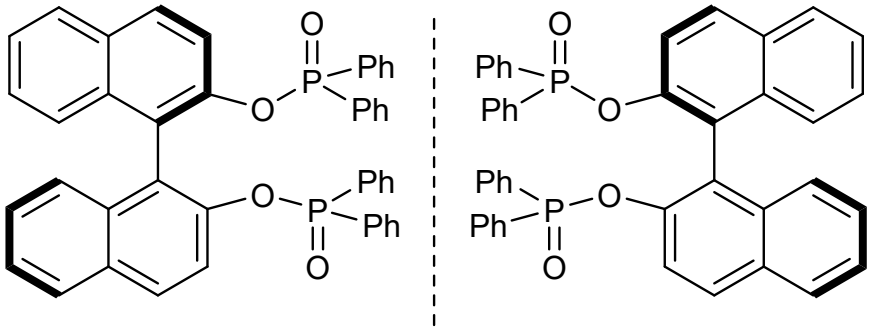


Figure S2. ^{31}P NMR Spectrum of 1a and 1b ($CDCl_3$, 162 MHz)



2a **2b**

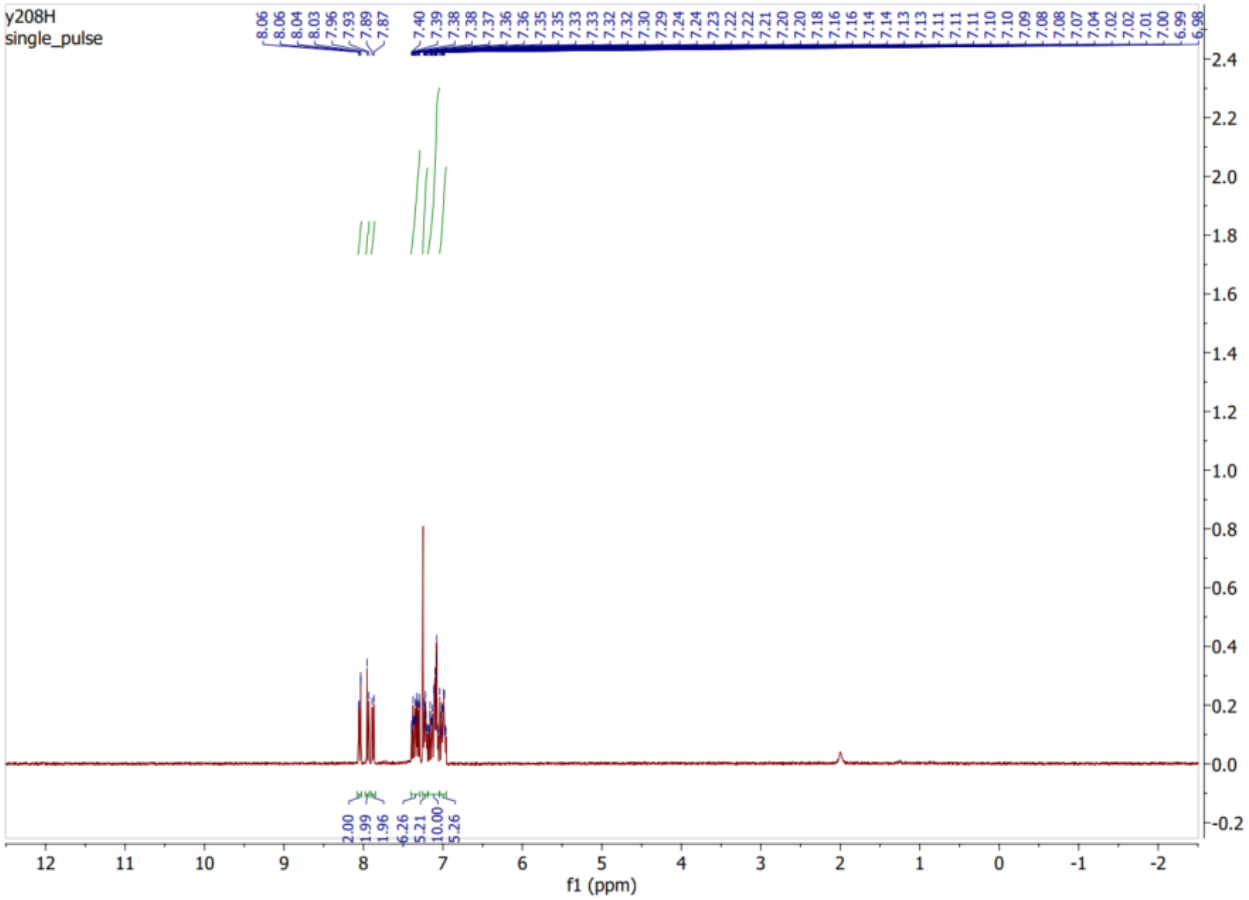


Figure S3. ^{1}H NMR Spectrum of 2a and 2b ($CDCl_3$, 400 MHz)

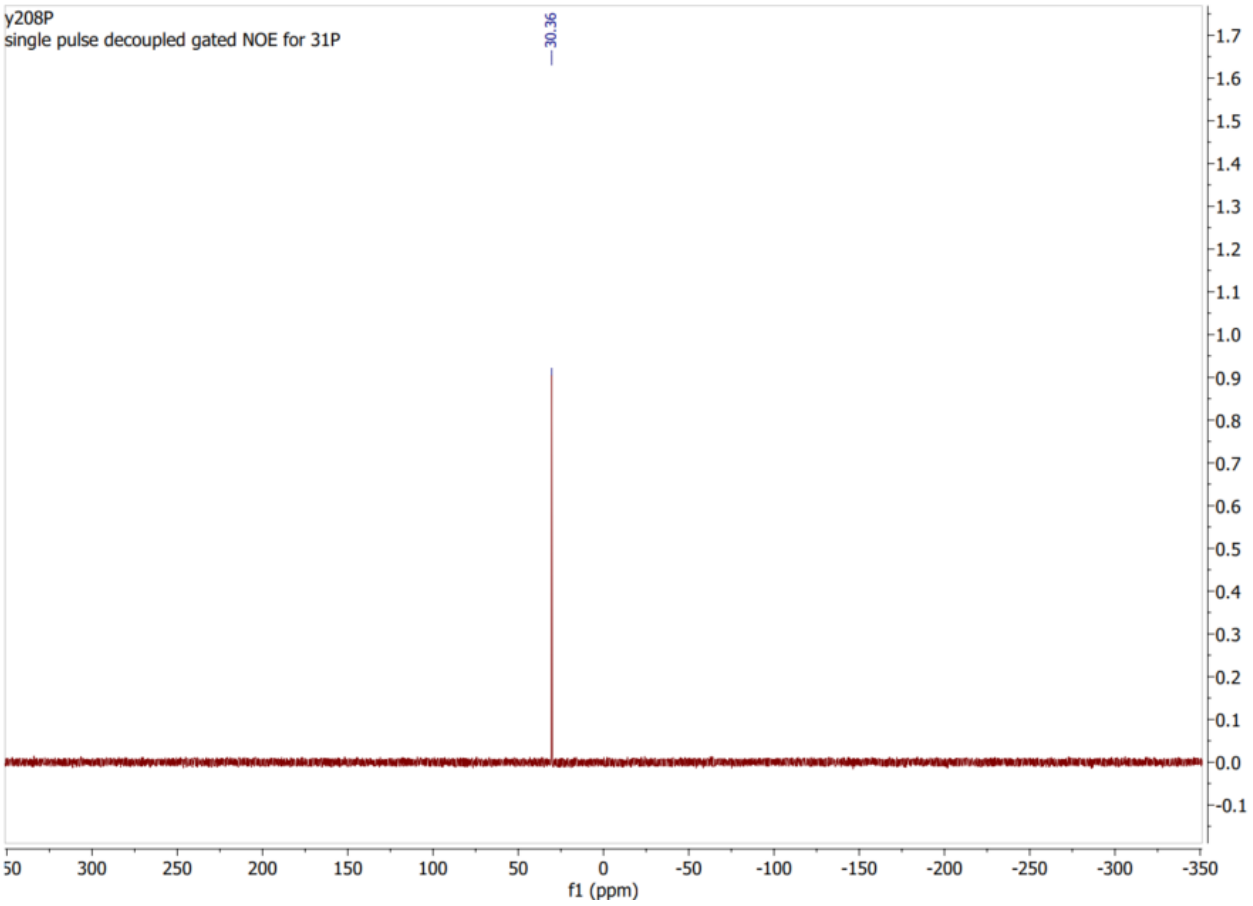
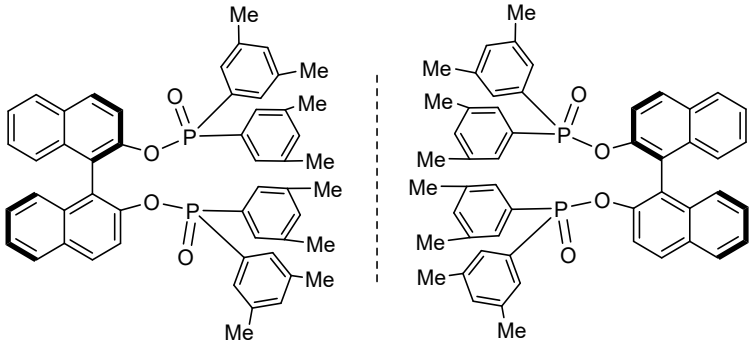


Figure S4. ^{31}P NMR Spectrum of 2a and 2b ($CDCl_3$, 162 MHz)



3a **3b**

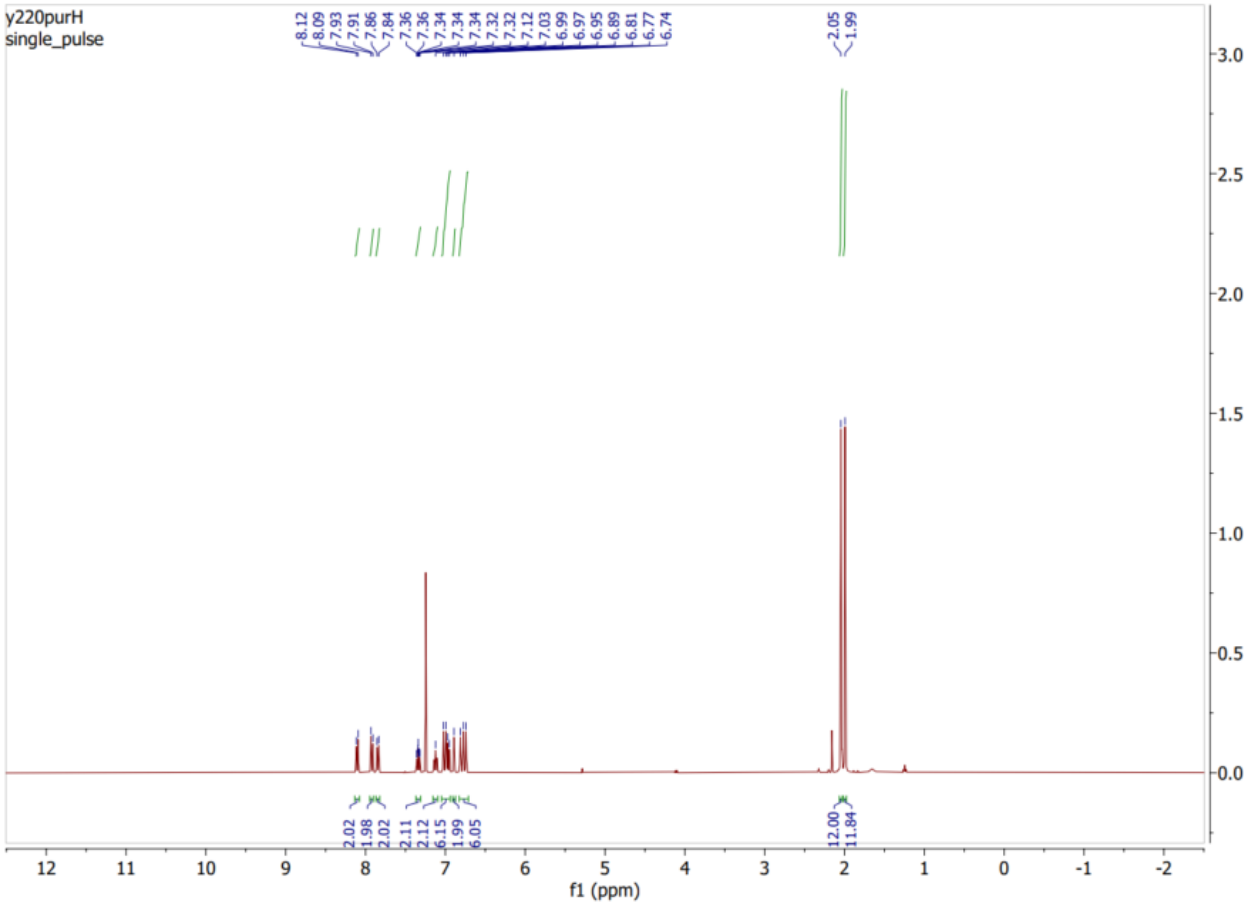


Figure S5. ^{1}H NMR Spectrum of 3a and 3b ($CDCl_3$, 400 MHz)

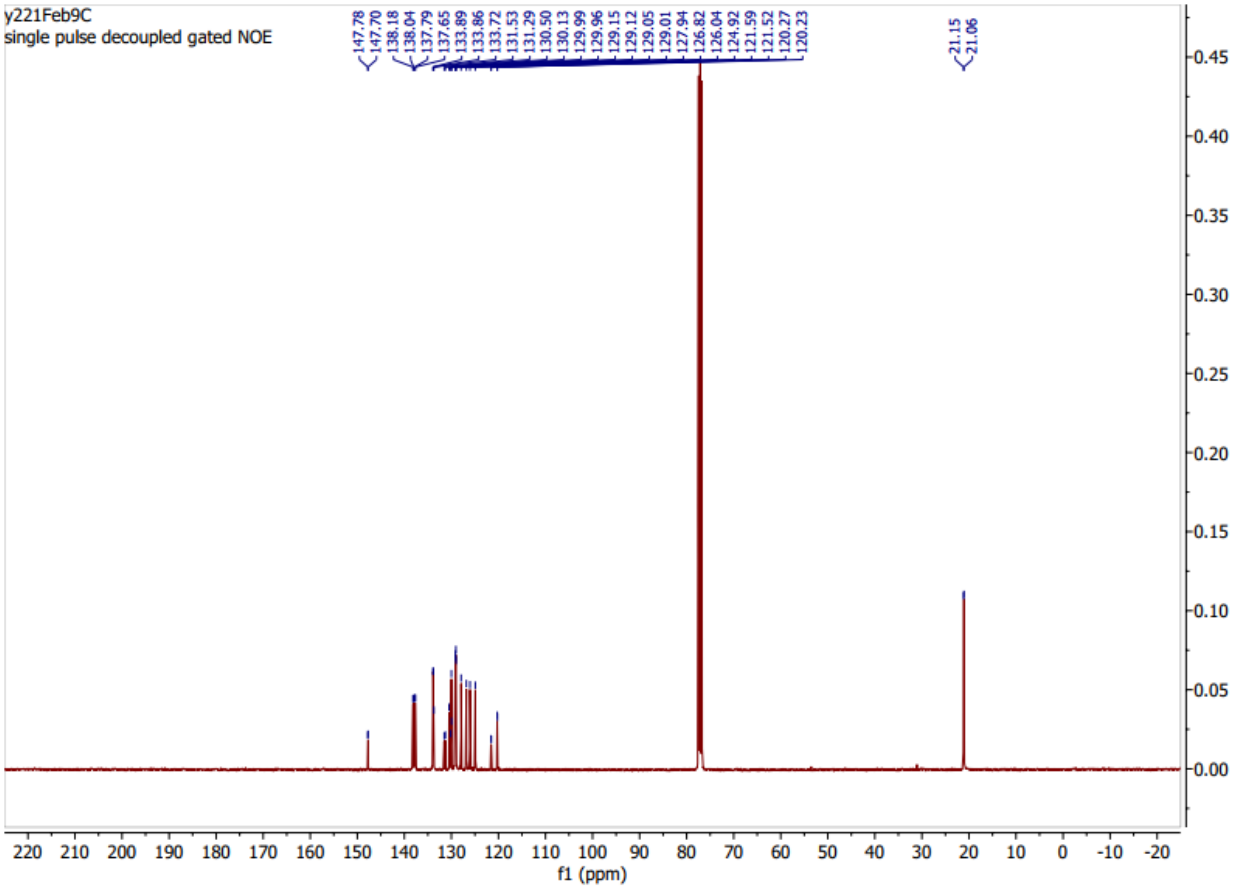


Figure S6. ^{13}C NMR Spectrum of 3a and 3b ($CDCl_3$, 101 MHz)

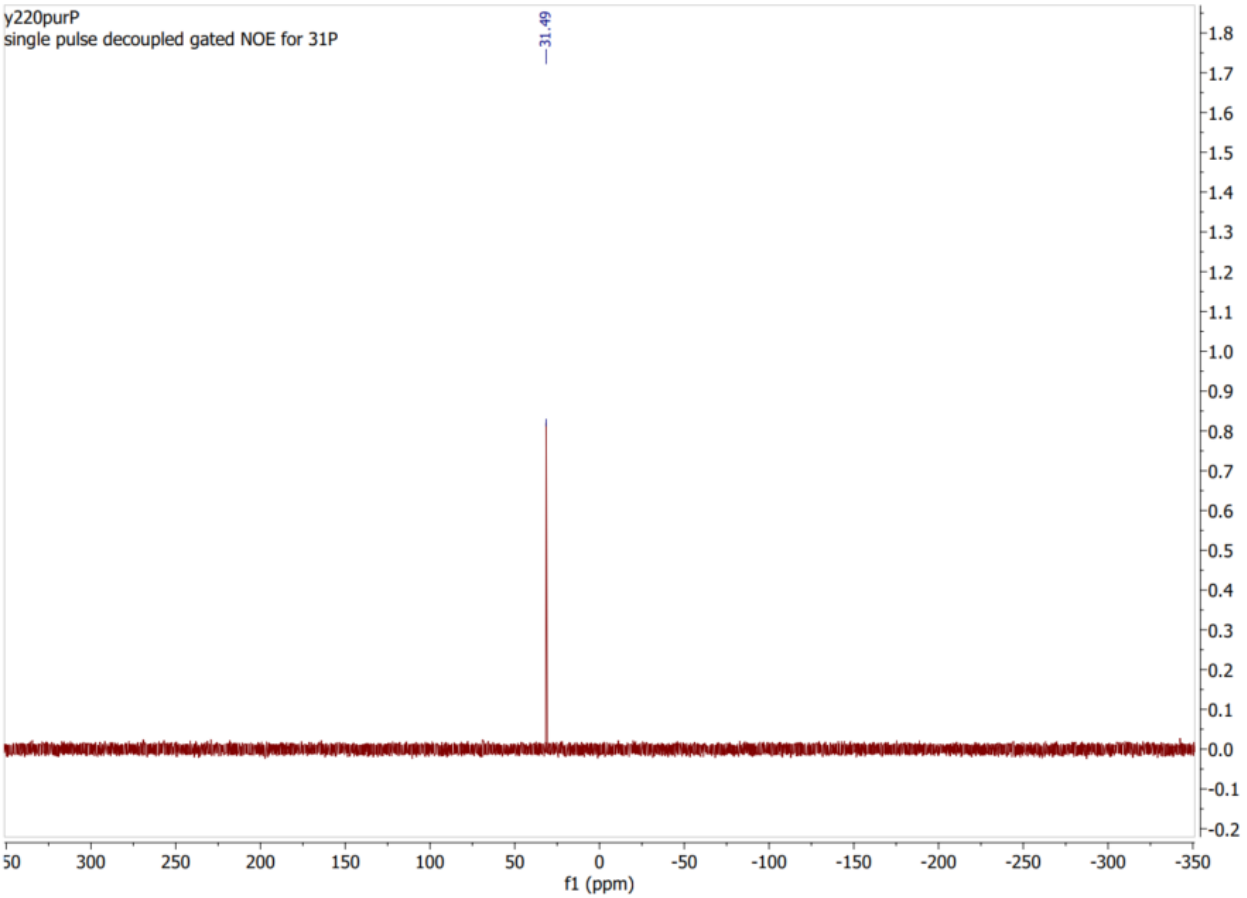
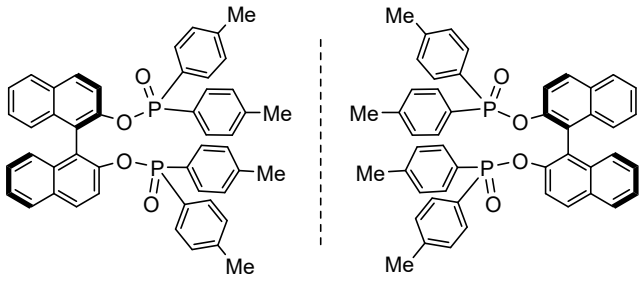


Figure S7. ^{31}P NMR Spectrum of 3a and 3b ($CDCl_3$, 162 MHz)



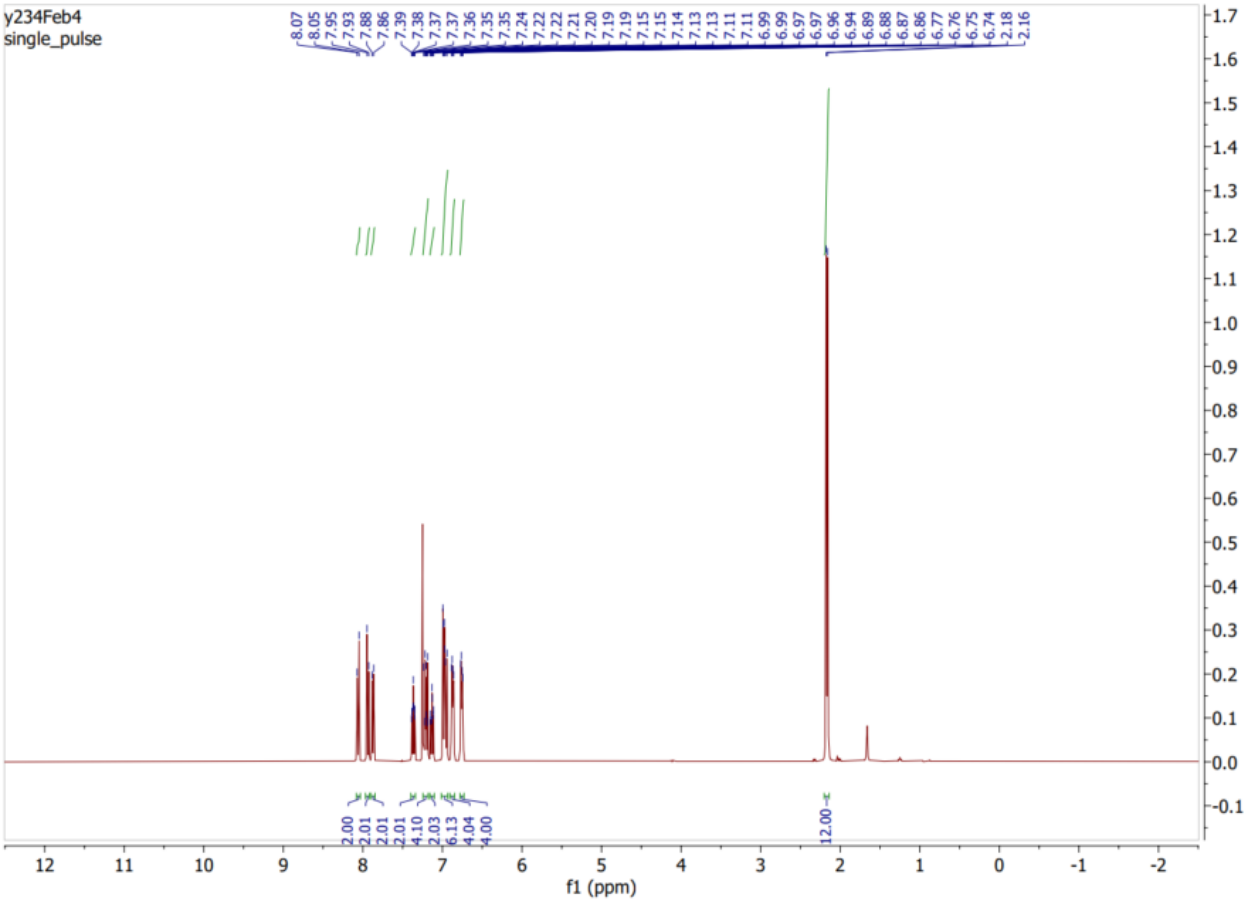


Figure S8. ^{1}H NMR Spectrum of 4a and 4b ($CDCl_3$, 400 MHz)

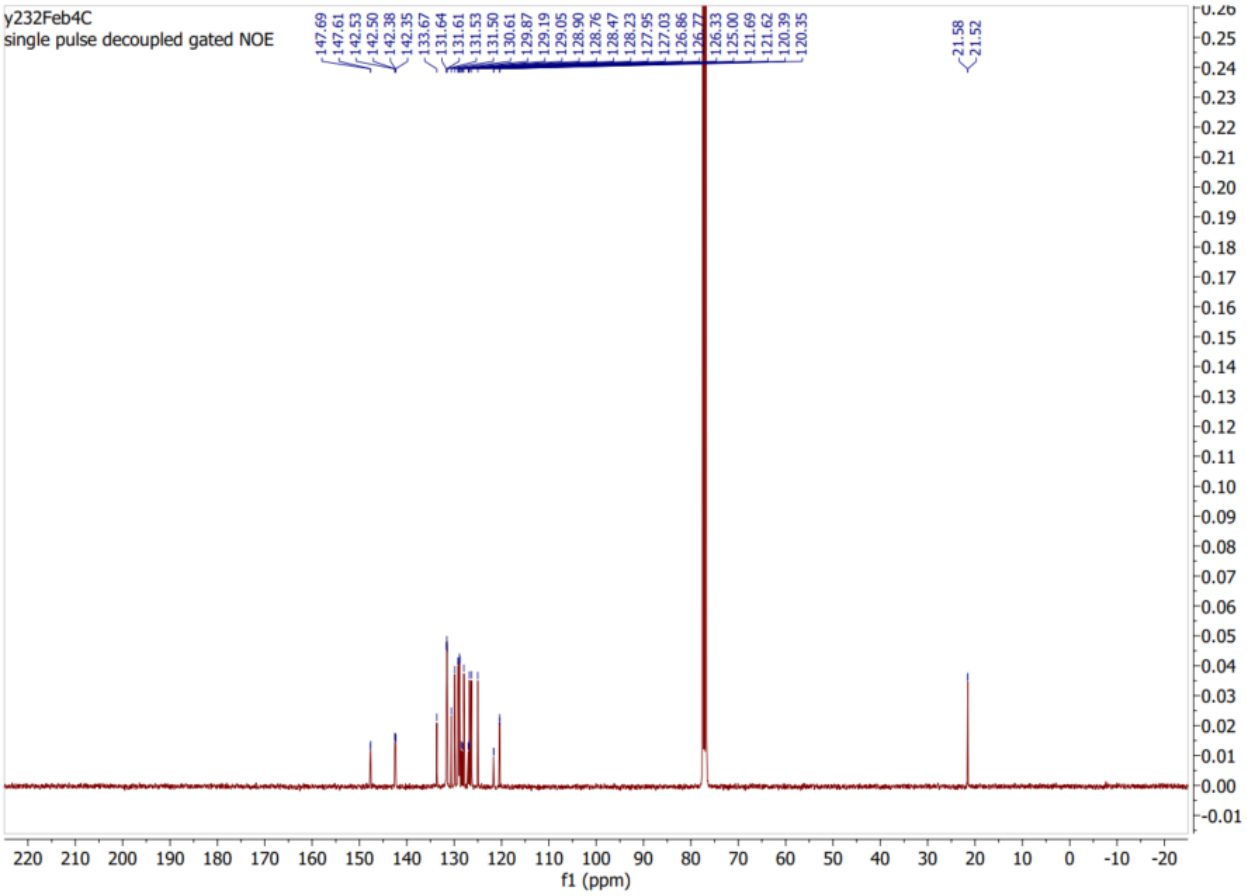


Figure S9. ^{13}C NMR Spectrum of 4a and 4b ($CDCl_3$, 101 MHz)

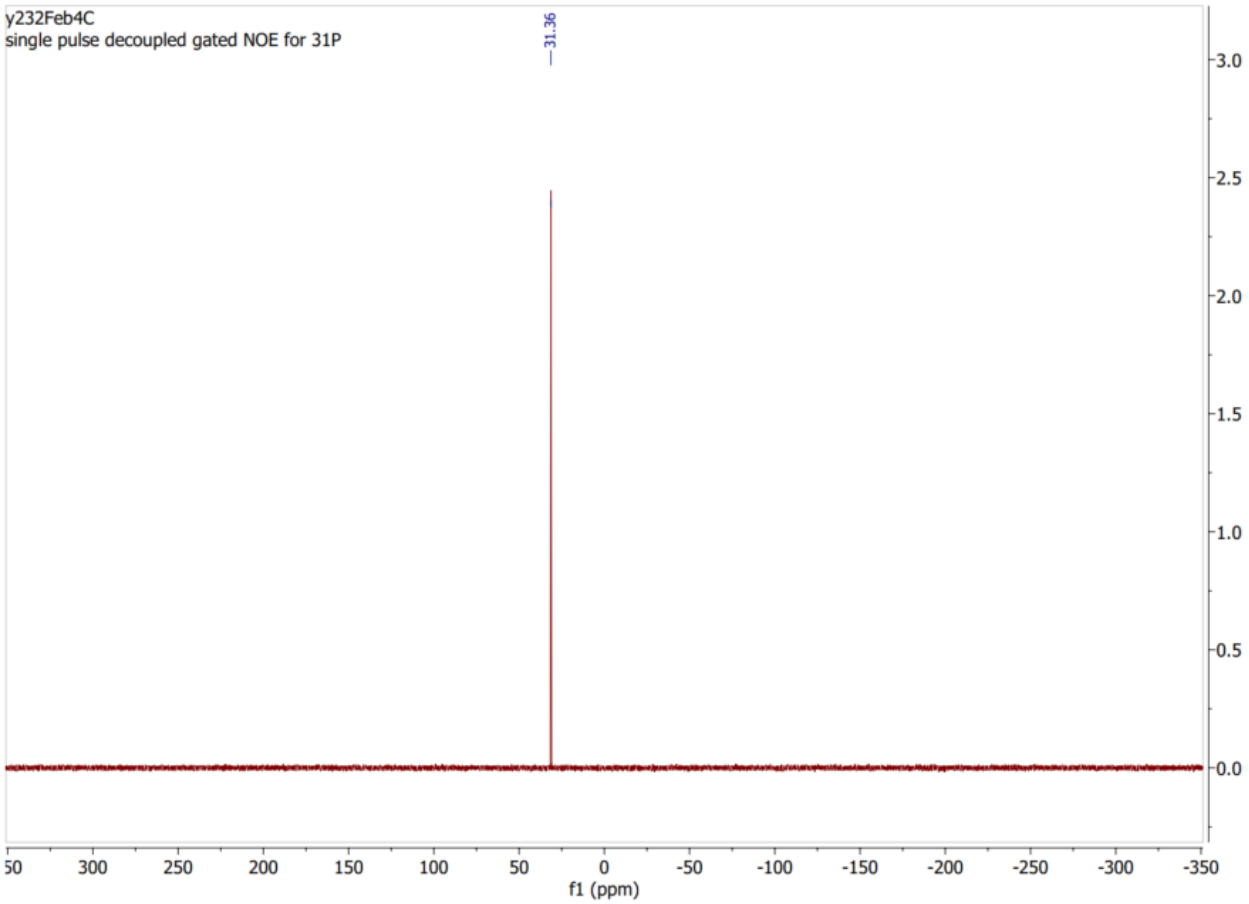
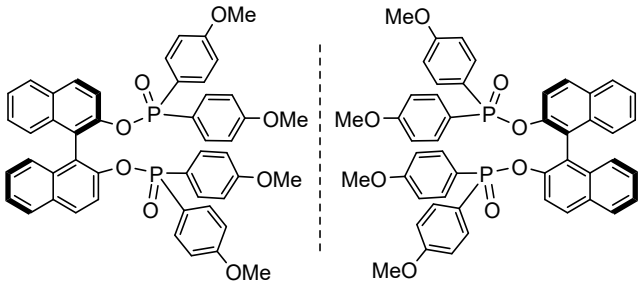


Figure S10. ^{31}P NMR Spectrum of 4a and 4b ($CDCl_3$, 162 MHz)



5a **5b**

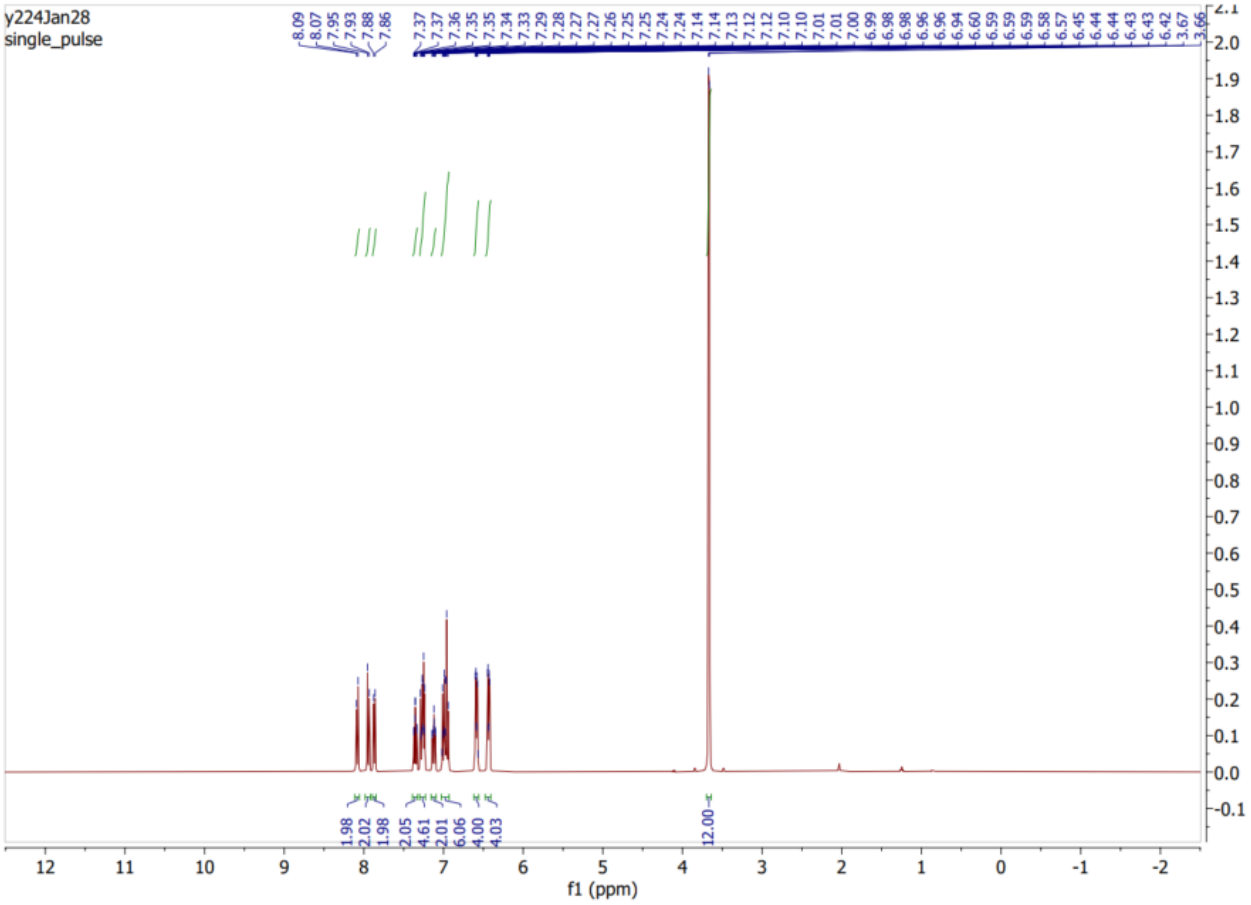


Figure S11. ^{1}H NMR Spectrum of 5a and 5b ($CDCl_3$, 400 MHz)

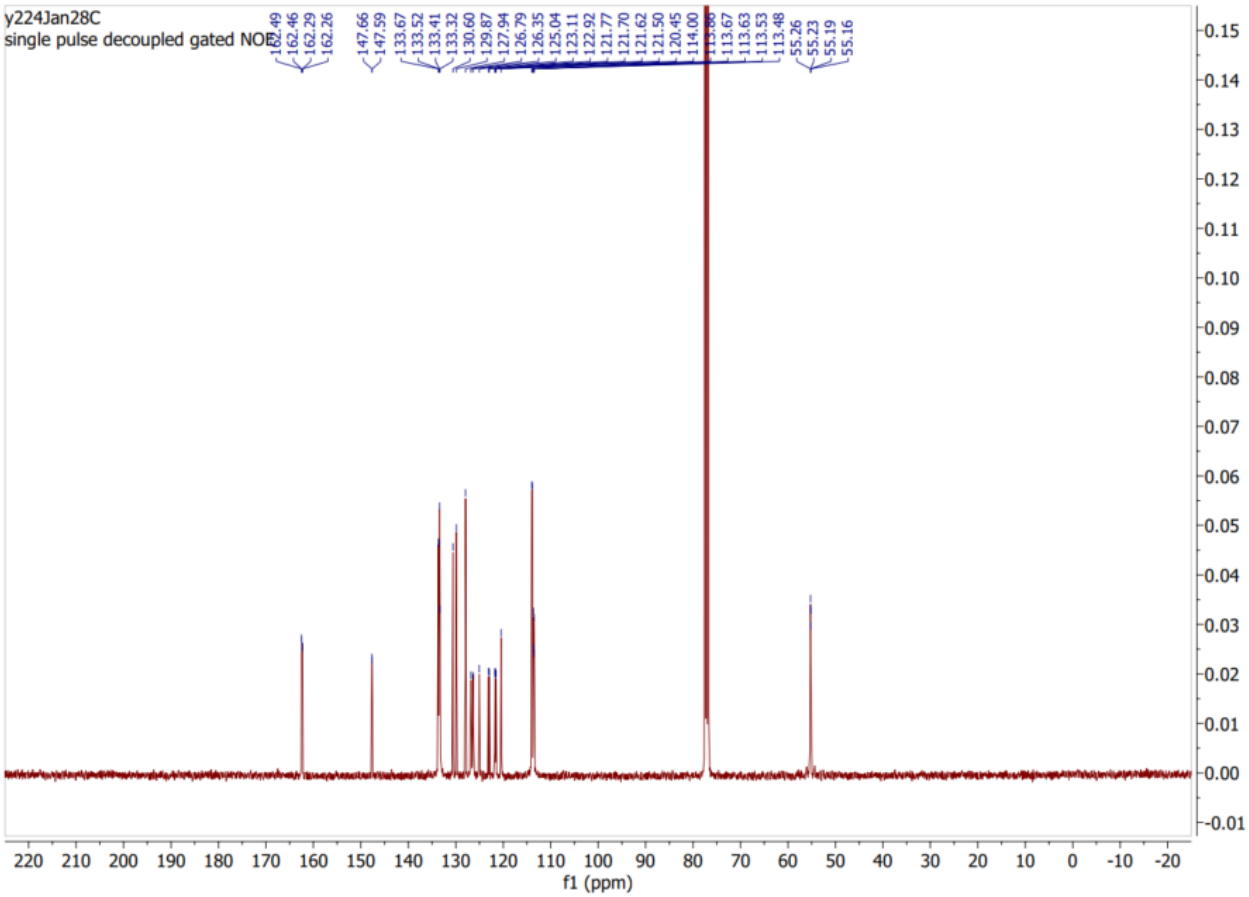


Figure S12. ^{13}C NMR Spectrum of 5a and 5b ($CDCl_3$, 101 MHz)

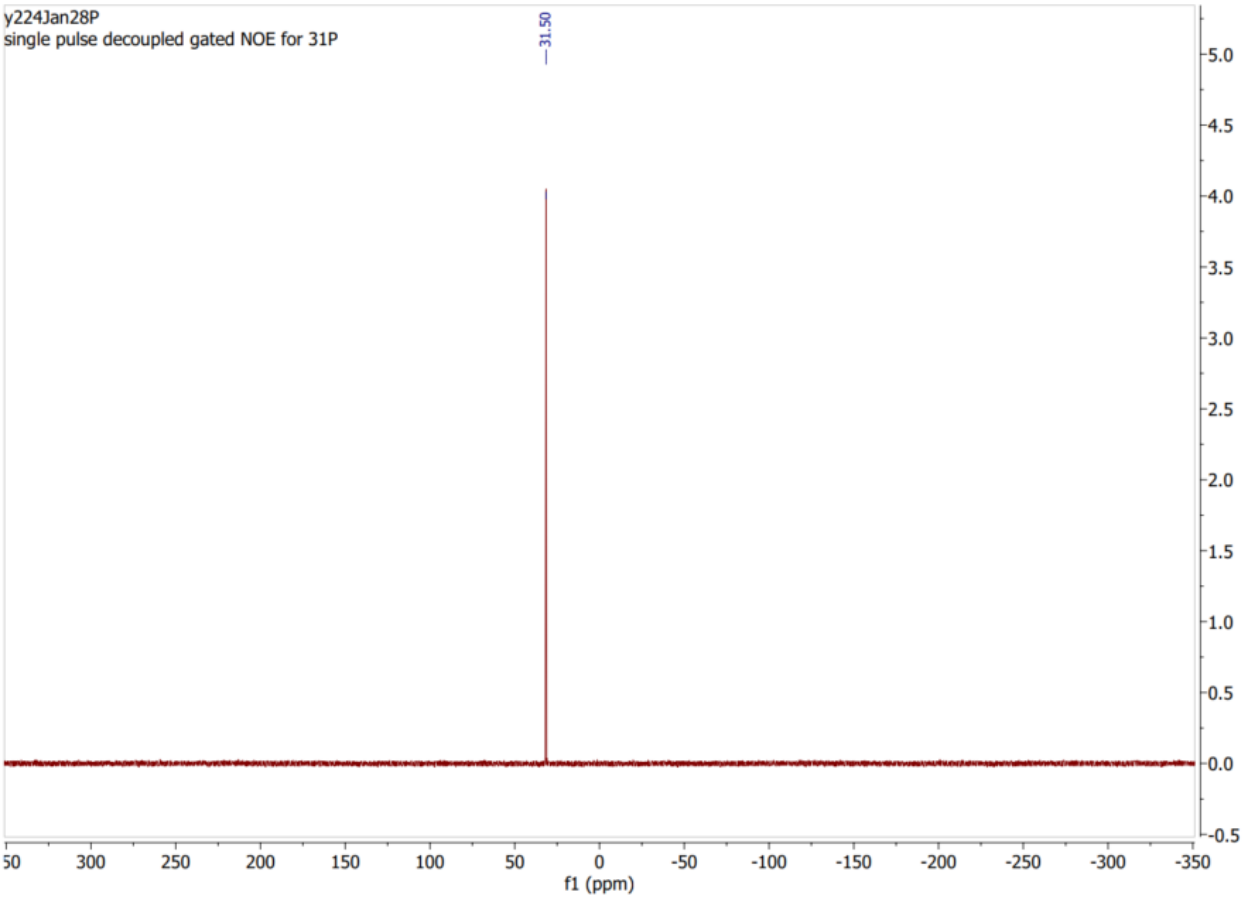


Figure S13. ^{31}P NMR Spectrum of 5a and 5b ($CDCl_3$, 162 MHz)

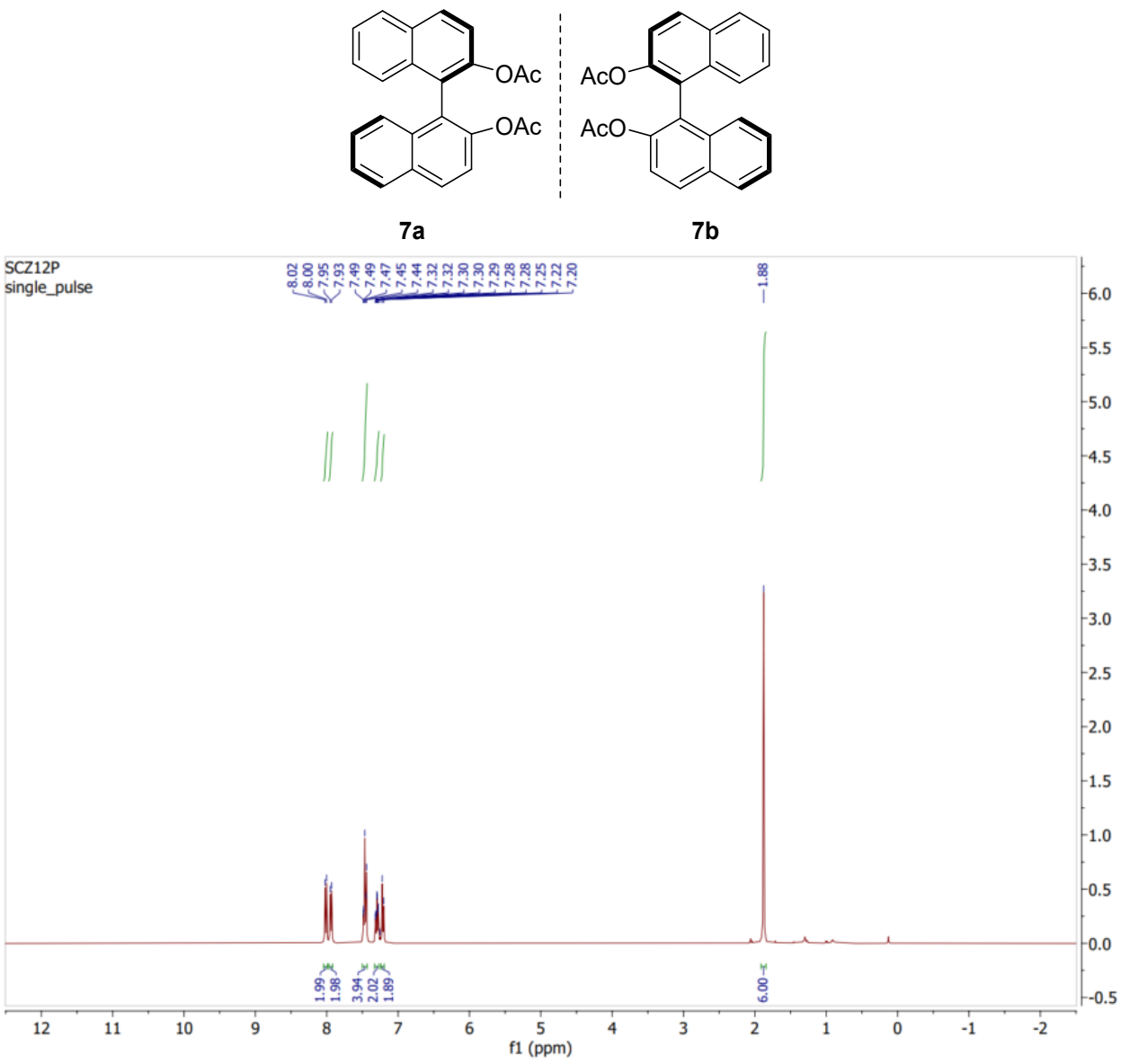
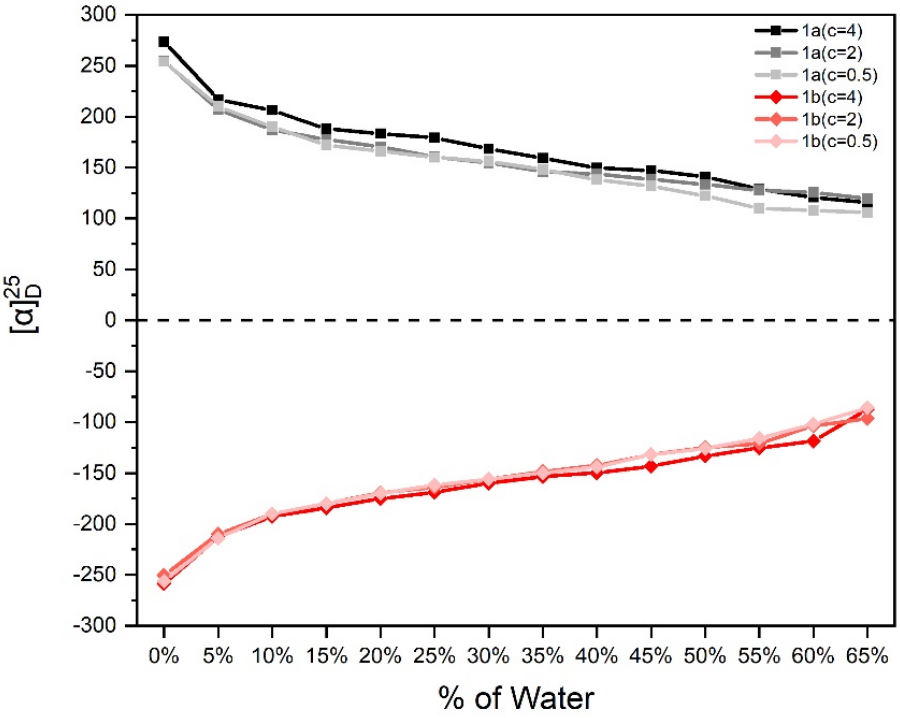


Figure S14. ^{1}H NMR Spectrum of 7a and 7b ($CDCl_3$, 400 MHz)



4. Concentration experiments on AIP phenomenon

Figure S15. Effects of concentrations on AIP phenomenon (*c* = mg/mL)

5. PL Spectra of 2a-5a

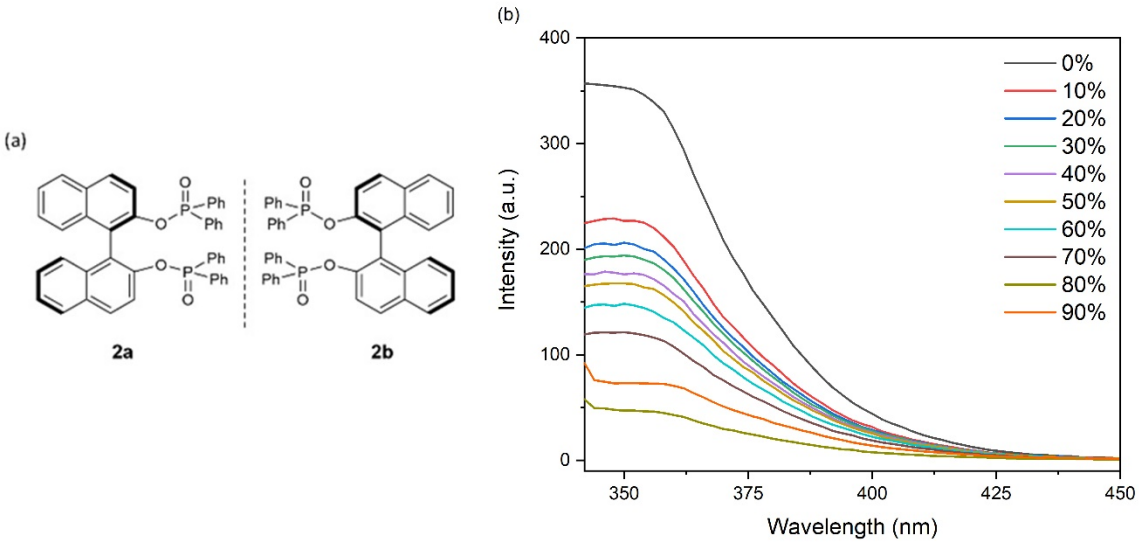


Figure S16. (a) Structure of 2a and 2b. (b) PL spectra of 2a in THF/water mixtures with different water fractions (f_w); c = 0.1 mM; λ_{ex} = 334 nm.

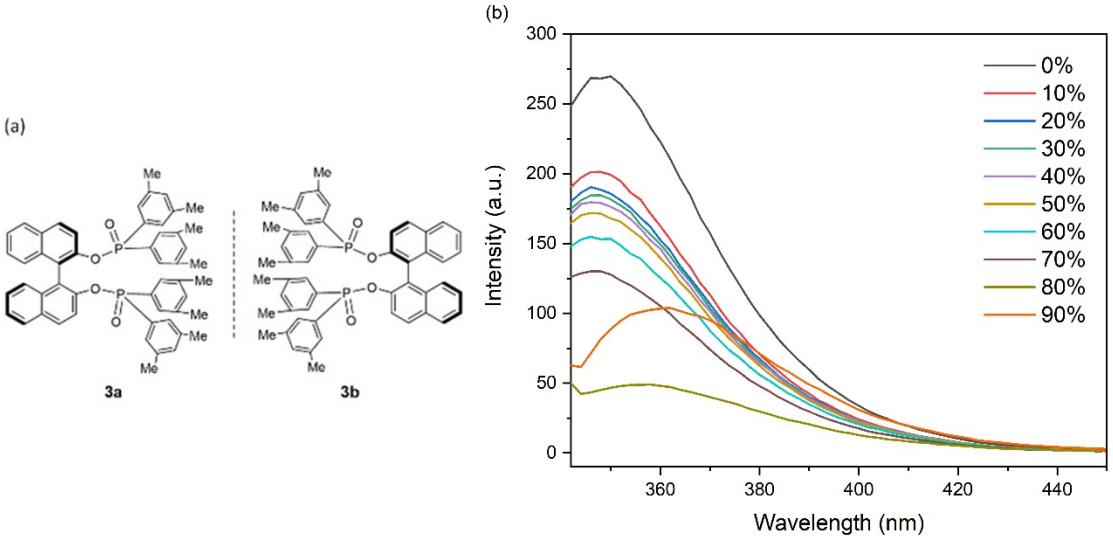


Figure S17. (a) Structure of 3a and 3b. (b) PL spectra of 3a in THF/water mixtures with different water fractions (f_w); c = 0.1 mM; λ_{ex} = 334 nm.

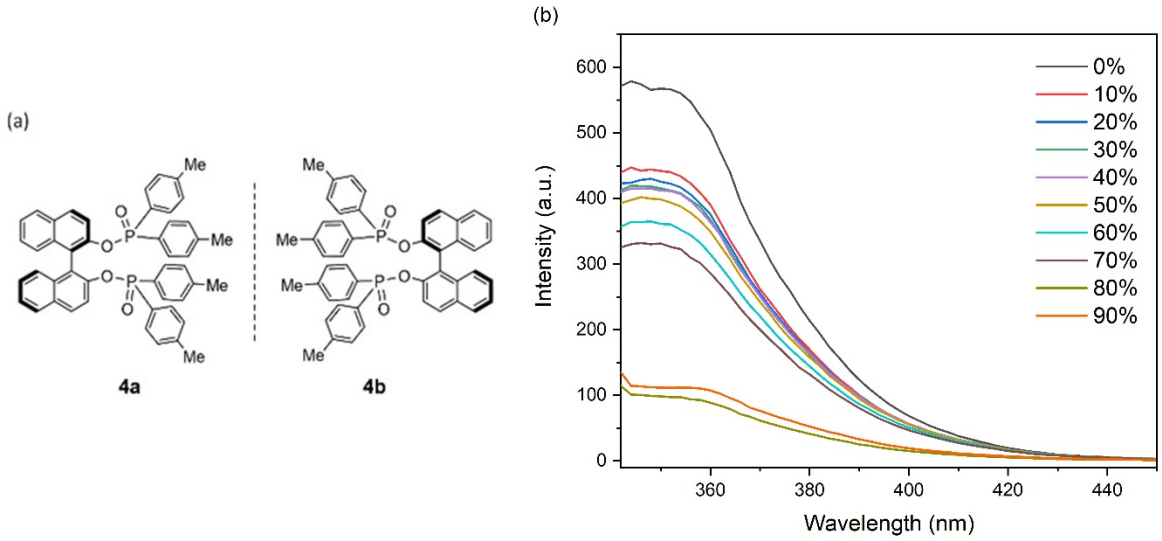


Figure S18. (a) Structure of 4a and 4b. (b) PL spectra of 4a in THF/water mixtures with different water fractions (f_w); c = 0.1 mM; λ_{ex} = 336 nm.

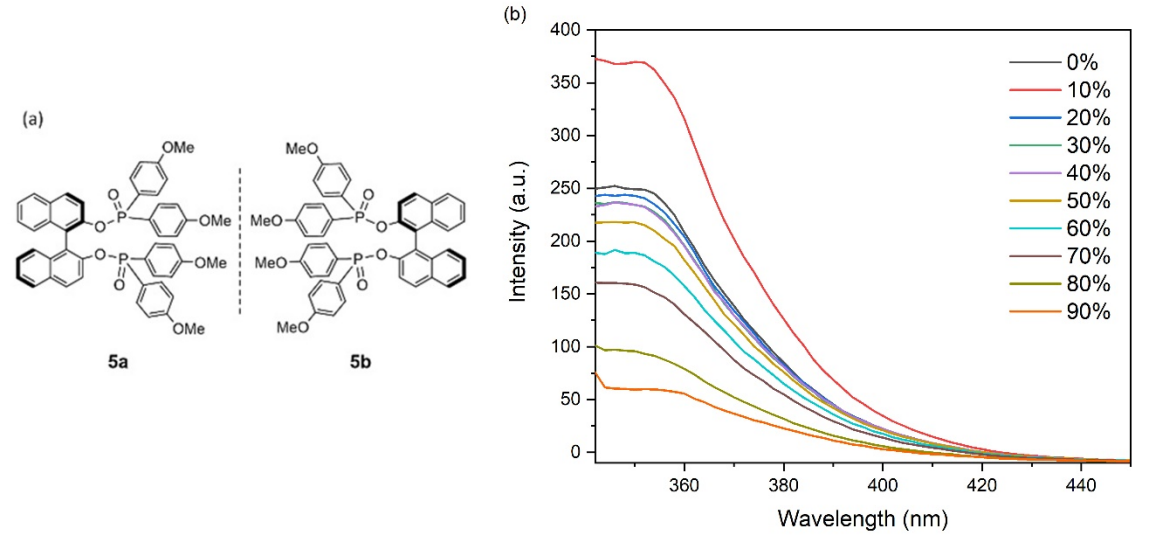


Figure S19. (a) Structure of 5a and 5b. (b) PL spectra of 5a in THF/water mixtures with different water fractions (f_w); c = 0.1 mM; λ_{ex} = 334 nm.