Enantioselective synthesis of P-chiral tertiary phosphine oxides with an ethynyl group via Cu(I)-catalyzed azide−alkyne cycloaddition

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Supporting Information
(Part I)

1. General information

Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. Infrared (IR) spectra were obtained using a Nicolet Nexus 670 FT-IR spectrometer with KBr pellets in the range 4000-400 cmm^{-1}. Chiral HPLC analysis was performed on a Shimadzu LC-20AD instrument using Daicel Chiracel columns at 30 °C and a mixture of HPLC-grade hexanes and isopropanol as eluent. Optical rotation was measured using a JASCO P-1030 Polarimeter equipped with a sodium vapor lamp at 589 nm. ^{1}H, ^{13}C and ^{19}F NMR spectra were obtained using a Bruker DPX-400 and Bruker DPX-300 spectrometer. The ^{31}P NMR spectra were recorded at 162 MHz with 85% H_3PO_4 as external standard. Chemical shifts are reported in ppm from $CDCl_3$ or $(CD_3)_2SO$ with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

Unless mentioned, all reactions were performed under an atmosphere of N_2. Anhydrous halogenated solvents and CH_3CN were prepared by first distillation over P_2O_5 and then from CaH_2. CuBr (99.998%) and CuCl (99.998%) were purchased from Alfa-Aesar and used as received. Other cuprous salts were purchased from Aldrich. Arylphosphonic or alkylphosphonic dichlorides were prepared using the literature procedure.[1]

List of abbreviation:

Entry	Chemical name	Abbreviation
1	Petroleum ether	PE
2	Ethyl acetate	EtOAc
3	Tetrahydrofuran	THF
4	Diethylaminosulfur trifluoride	DAST
5	Dichloromethane	CH_2Cl_2
6	1,2-Dichloroethane	DCE

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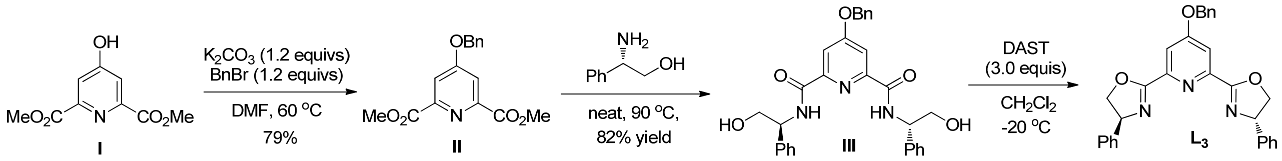
[1] (*a*) L.-N. Qin, X.-F. Ren, Y.-P. Lu, Y.-X. Li and J.-R. Zhou, *Angew. Chem.; Int. Ed.*, 2012, **51**, 5915; (*b*) N. D. Contrella, J. R. Sampson and R. F. Jordan, *Organometallics,* 2014, **33**, 3546; (*c*) R. C. Grabiak, J. A. Miles and G. M. Schwenzer, *Phosphorus sulfur*, 1980, **9**, 197.

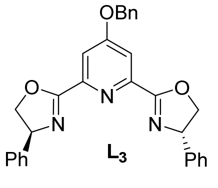
2. General procedure for the synthesis of PYBOX ligands L_{2-8}

Starting from commercially available dimethyl 4-hydroxypyridine-2,6-dicarboxylate **I**, it is easy to prepare all the ligands $\mathbf{L_{2-8}}$ using the following modified procedures.[2,3] All the aromatic bromides involved are synthesized from the corresponding aromatic aldehyde through a reduction using $NaBH_4$ and a bromination using PBr_3.[4]

2.1 The synthesis of ligand L_3 and L_{6-8}



Ligand $\mathbf{L_3}$ was prepared from **I** in three steps. The corresponding *O*-benzyl ether **II** was synthesized according to literature method.[3] The synthesis of **III** was achieved by using a modified method. To a 50 mL sealed tube was added **II** (301 mg, 1.0 mmol) and (*S*)-2-amino-2-phenylethanol (411 mg, 3.0 mmol), and then the mixture was heated 90 °C until the disappearance of **II** by TLC analysis. The residue was directly subjected to column chromatography using CH_2Cl_2/EtOAc (4/1, v/v) as the eluent, affording **III** in 82% yield. The synthesis of $\mathbf{L_3}$ from **III** was as follow. To a flame-fried 25 mL Schlenk tube was added **III** (256 mg, 0.5 mmol), followed by the addition of 5.0 mL of CH_2Cl_2. The resulting solution was cooled to -20 °C and was charged with DAST (198 uL, 1.5 mmol) by dropwise addition over 5 min. The reaction was allowed to proceed at -20 °C for 24 h, and then was quenched with aqueous NH_4OH, diluted with H_2O. The aqueous layer was extracted with CH_2Cl_2, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography using CH_2Cl_2/EtOAc (20/1, v/v) as the elution to afford $\mathbf{L_3}$ in 63% yield.



White solid. Mp 160-162 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 2H), 7.41-7.28 (m, 15 H), 5.45 (dd, J = 8.0 Hz, 1.6 Hz, 2H), 5.21 (AB, J = 12.0 Hz, 2H), 4.92 (dd, J = 8.0 Hz, 1.6 Hz, 2H), 4.41 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.75, 163.55, 148.29, 141.68, 135.02, 128.80, 128.71, 128.47, 127.78, 127.49, 126.81, 113.03, 75.54, 70.50, 70.24; IR (KBr): 3024, 2904, 1641, 1471, 697 cm^{-1}; MS (EI): 475 (M^+, 9.7), 91 (100), 104 (17); HRMS (EI): Exact mass calcd for $C_{30}H_{25}N_3O_3$: 475.1896, Found: 475.1890.

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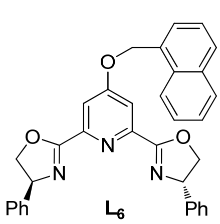
[2] N. Madhavan, W. Sommer and M. Weck, *J. Mol. Catal. A*: *Chem*., 2011, **334**, 1.

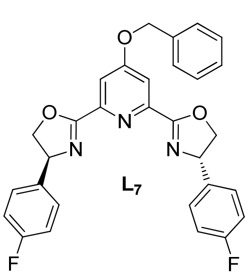
[3] A. T. Parsons and J. S. Johnson, *J. Am. Chem. Soc*., 2009, **131**, 3122.

[4] J. R. Shah, P. D. Mosier, B. L. Roth, G. E. Kellogg and R. B. Westkaemper, *Bioorg. Med. Chem*., 2009, **17**, 6496.



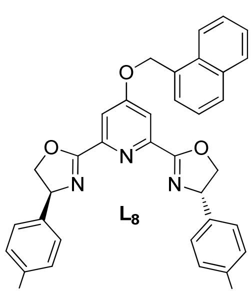
L$_6$

Ligand **L$_6$** is prepared by the same procedure. Column chromatography afforded **L$_6$** in 68% yield as white solid. Mp 212-214 ºC; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.04 (s, 2H), 7.99-7.97 (m, 1 H), 7.90-7.87 (m, 2H), 7.60-7.45 (m, 4H), 7.39-7.29 (m, 10H), 5.62 (s, 2H), 5.46 (t, J = 13.2 Hz, 2H), 4.93 (t, J = 13.6 Hz, 2H), 4.43 (t, J = 11.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 165.69, 163.49, 148.30, 141.60, 133.65, 131.28, 130.37, 129.56, 128.74, 128.68, 127.72, 126.92, 126.76, 126.67, 126.04, 125.14, 123.38, 112.98, 70.19, 69.16; IR (KBr): 2962, 1589, 1387, 1009, 698 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{34}H_{28}N_3O_3$ [M+H]$^+$: 526.2125, Found: 526.2127.



L$_7$

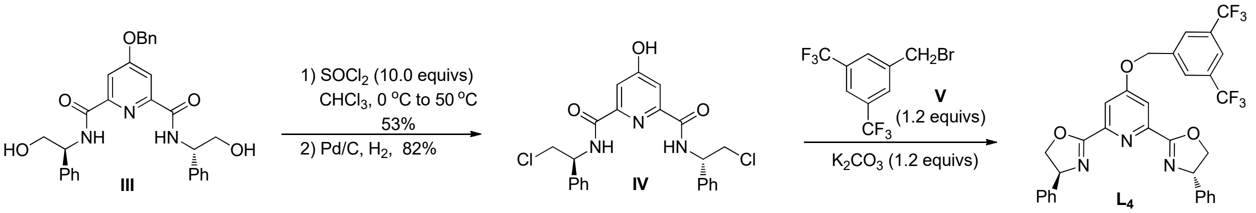
Ligand **L$_7$** is prepared by the same procedure. Column chromatography afforded **L$_7$** in 70% yield as white solid. Mp 208-210 ºC; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.94 (s, 2H), 7.41-7.38 (m, 5H), 7.31-7.27 (m, 4H), 7.08-7.03 (m, 4H), 5.46-5.42 (dd, J = 10.2, 8.6 Hz, 2H), 5.24-5.18 (m, 2H), 4.91 (dd, J = 10.3, 8.7 Hz, 2H), 4.37 (t, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 165.82, 163.64, 162.37 (d, J = 246.0 Hz), 148.20, 137.50 (d, J = 3.0 Hz), 134.96, 128.79, 128.58, 128.52 (d, J = 9.0 Hz) , 127.56, 115.72 (d, J = 22.0 Hz), 113.12, 75.57, 70.58, 69.58; ^{19}F NMR (282 MHz, CDCl$_3$): δ -114.58; IR (KBr): 3442, 2988, 1634, 1562, 1427, 1375, 1157, 1087, 963, 879 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{30}H_{23}N_3O_3F_2$: 511.1707, Found: 511.1700.



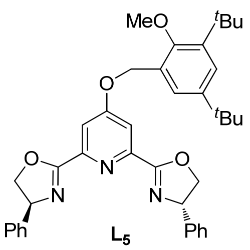
L$_8$

Ligand **L$_8$** is prepared by the same procedure. Column chromatography afforded **L$_8$** in 63% yield as white solid. Mp 222-224 ºC; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.02 (s, 2H), 7.98-7.96 (m, 1H), 7.92-7.88 (m, 2H), 7.60-7.45 (m, 4H), 7.31-7.26 (m, 4H), 7.05 (t, J = 8.6 Hz, 4H), 5.63 (s, 2H), 5.44 (t, J = 9.4 Hz, 2H), 4.91 (dd, J = 10.1, 9.0 Hz, 2H), 4.37 (t, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 165.85, 163.66, 162.38 (d, J = 246.0 Hz), 148.28, 137.48 (d, J = 3.0 Hz), 133.76 , 131.39, 130.37, 129.76, 128.83, 128.53 (d, J = 9.0 Hz), 127.10, 126.82, 126.20, 125.26, 123.47, 115.73 (d, J = 22.0 Hz), 113.13, 75.58, 69.61, 69.34; ^{19}F NMR (376 MHz, CDCl$_3$): δ -114.56; IR (KBr): 3423, 2895, 1733, 1636, 1508, 1473, 1369, 1089, 922, 793 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{34}H_{25}N_3O_3F_2$: 561.1864, Found: 561.1862.

2.2 The synthesis of ligand L$_{4-5}$

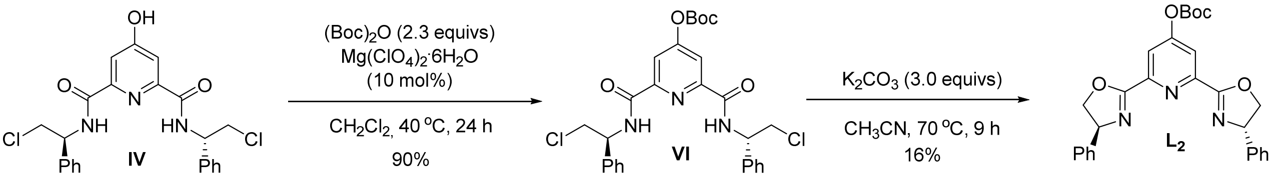


The compound **IV** was synthesized from **III** by using a reported literature method.[2] The procedure for synthesis of ligand **L$_4$** from **IV** as follows: To a 25 mL Schlenk tube was added precursor **IV** (229 mg, 0.5 mmol) and bromide **V** (187.2 mg, 0.6 mmol), followed by the successive addition of 5.0 mL anhydrous CH$_3$CN and K$_2$CO$_3$ (82.8 mg, 0.6 mmol). After the mixture was stirred at 70 °C for 1 h, K$_2$CO$_3$ (138 mg, 1.0 mmol) was then added. The resulting mixture was stirred at 70 °C for 24 h, and the solvent was removed under reduced pressure. The residue was directly subjected to column chromatography using CH$_2$Cl$_2$/EtOAc (20/1, v/v) as the eluent, affording **L$_4$** in 46% yield as white solid. Mp 70-72 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.99 (s, 2H), 7.88 (s, 3H), 7.38-7.28 (m, 10 H), 5.45 (dd, J = 8.8 Hz, 1.6 Hz, 2H), 5.30 (AB, J = 12.8 Hz, 2H), 4.93 (dd, J = 8.8 Hz, 1.6 Hz, 2H), 4.43 (t, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 164.93, 163.33, 148.59, 141.51, 137.69, 132.15 (q, J = 33.0 Hz), 128.80, 127.81, 127.13 (q, J = 3.0 Hz), 126.77, 123.02 (q, J = 271.0 Hz), 122.37-122.29 (m), 112.73, 75.38, 70.23, 68.64; ^{19}F NMR (376 MHz, CDCl$_3$): δ -62.92; IR (KBr): 2894, 1590, 1362, 1280, 1134, 720 cm^{-1}; MS (EI): 611 (M$^+$, 8), 135 (100), 44 (41); HRMS (EI): Exact mass calcd for C$_{32}$H$_{23}$N$_3$O$_3$F$_6$: 611.1644, Found: 611.1648.



Ligand **L$_5$** were prepared by using the same procedure. Column chromatography afforded **L$_5$** in 58% yield as white solid. Mp 188-190 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.97 (s, 2H), 7.39-7.28 (m, 12H), 5.45 (t, J = 8.8 Hz, 2H), 5.25 (AB, J = 10.4 Hz, 1H), 5.21 (AB, J = 10.4 Hz, 1H), 4.92 (t, J = 8.4 Hz, 2H), 4.42 (t, J = 8.80 Hz, 2H), 3.78 (s, 3H), 1.40 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 165.78, 163.50, 156.03, 148.23, 146.03, 142.04, 141.62, 128.73, 127.70, 127.58, 126.77, 125.61, 125.03, 112.97, 75.44, 70.21, 66.60, 63.06, 35.27, 34.45, 31.37, 30.95; IR (KBr): 2958, 2898, 1593, 1476, 1367, 1014, 698 cm^{-1}; HRMS (EI): Exact mass calcd for C$_{39}$H$_{43}$N$_3$O$_4$: 617.3254, Found: 617.3260.

2.3 The synthesis of ligand L_2



The intermediate **VI** was prepared according to a literature report.[5] To a 25 mL Schlenk tube was added $Mg(ClO_4)_2 \cdot 6H_2O$ (32.9 mg, 0.10 mmol), which was dried under vacuum at 130°C for 2 h before use. After cooling to room temperature, **IV** (458 mg, 1.0 mmol) was added in one portion, followed by addition of 5.0 mL of anhydrous CH_3CN. Then Boc_2O (500 mg, 2.3 mmol) was added, and the mixture was stirred at 40 °C until TLC analysis revealed the disappearance of **IV**. The crude mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was separated, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, affording the crude intermediate **VI** in 90% yield, which was used directly for the next step.

To a 25 mL Schlenk tube was added precursor **VI** (256.5 mg, 0.5 mmol) and K_2CO_3 (207 mg, 1.5 mmol), followed by addition of 5.0 mL anhydrous CH_3CN. The mixture was stirred at 70 °C for 9 hours, and then the solvent was removed under reduced pressure. The residue was directly subjected to column chromatography using CH_2Cl_2/EtOAc (50/1, v/v) as the elution, and afforded the ligand $\mathbf{L_2}$ in 16% yield. White solid, Mp 154-156 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 2H), 7.39-7.30 (m, 10 H), 5.46 (t, J = 8.80 Hz, 2H), 4.93 (t, J = 12.0 Hz, 2H), 4.21 (t, J = 11.6 Hz, 2H), 1.55 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.97, 158.81, 149.75, 148.61, 141.50, 128.83, 127.82, 126.82, 119.03, 85.23, 75.64, 70.31, 27.57; IR (neat): 2922, 2850, 1607, 1464, 1245, 1053, 836, 760, 689 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{28}H_{28}N_3O_5$ $[M+H]^+$: 486.2023, Found: 486.2026.

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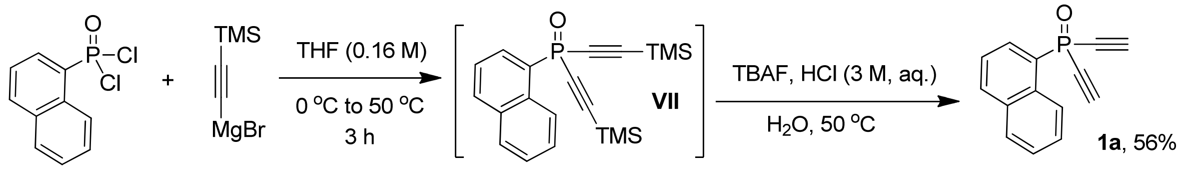
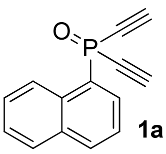
[5] G. Bartoli, M. Bosco, M. Locatelli, E. Marcantono, P. Melchiorre and L. Sambri, *Org. Lett.*, 2005, **7**, 427.

3. General procedure for the synthesis of diethynylphosphine oxides 1, racemic monoethynylphosphine oxides 4 and phosphole oxide-diynes 6

3.1 The synthesis of diethynylphosphine oxides 1



Diethynylphosphine oxide **1a** was prepared from the corresponding phosphonic dichlorides[6] by using the following general procedure: To a solution of 1-naphthyl phosphonic dichloride (2.3 g, 9.5 mmol) in anhydrous THF (20 mL) was slowly added 2-(trimethylsilyl)ethynylmagnesium bromide (40 mL, 20 mmol) at 0°C. The mixture was warmed slowly to room temperature and stirred at 50 ºC for 3 h. Then 3.0 mL of TBAF (1 M in THF), 5.0 mL of HCl (3 M, aq) and 20 mL of water were added at 0 ºC. The resulting mixture was stirred at 50 ºC till the consumption of intermediate **VII** by TLC analysis. The solvent was removed under vacuum and the residue was dissolved in 100 mL of CH_2Cl_2 and 100 mL of HCl (3 M, aq). The aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL). The organic phase was combined, dried over anhydrous Na_2SO_4 and concentrated to give the crude residue, which was purified by flash chromatography using PE/EtOAc (2:1, v/v) as the eluent to provide **1a** in 56% yield as a white solid. Other diethynylphosphine oxides **1** were prepared by using the above same procedure.


1a

Characterization of compound **1a** (white solid): 56% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.70 (d, *J* = 8.3 Hz, 1H), 8.35 (dd, *J* = 20.1, 7.1 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.69-7.56 (m, 3H), 3.35 (d, *J* = 11.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.68 (d, *J* = 3.0 Hz), 133.67 (d, *J* = 11.0 Hz), 132.60 (d, *J* = 13.0 Hz), 131.91 (d, *J* = 12.0 Hz), 129.23 (d, *J* = 2.0 Hz), 127.86, 126.92, 126.14 (d, *J* = 140.0 Hz), 125.65 (d, *J* = 8.0 Hz), 124.66 (d, *J* = 17.0 Hz), 93.46 (d, *J* = 36.0 Hz), 78.54 (d, *J* = 193.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ -21.23; IR (neat): 3406, 3147, 2054, 1680, 1505, 1335, 1214, 1179, 1026, 986, 832, 798, 770 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{14}H_9OP$: 224.0391, Found: 224.0393.

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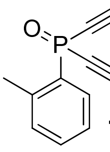
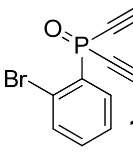
[6] Phosphonic dichlorides were prepared by literature methods: (*a*) R. C. Grabiak, J. A. Miles and G. M. Schwenzer, *Phosphorus sulfur*, 1980, **9**, 197; (*b*) F. Slowinski, C. Aubert and M. Malacria, *J. Org. Chem.*, 2003, **68**, 378.



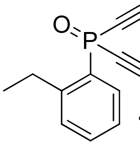
1b

Characterization of compound **1b** (white solid): 61% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.06 (dd, *J* = 17.6, 7.2 Hz, 1H), 7.55-7.50 (m, 1H), 7.40-7.28 (m, 2H), 3.34 (d, *J* = 10.9 Hz, 2H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 141.77 (d, *J* = 12.0 Hz), 133.38 (d, *J* = 3.0 Hz), 131.90 (d, *J* = 1.0 Hz), 131.76, 128.44 (d, *J* = 140.0 Hz), 125.96 (d, *J* = 15.0 Hz), 93.05 (dd, *J* = 35.0, 1.0 Hz), 78.31 (d, *J* = 191.0 Hz), 20.89 (dd, *J* = 6.0, 2.0 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ -20.77; IR (neat): 3675, 3209, 2901, 2050, 1452, 1406, 1393, 1250, 1190, 1077, 892, 781, 757 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{11}H_9OP$: 188.0391, Found: 188.0394.



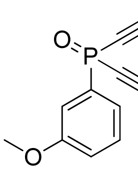
1c

Characterization of compound **1c** (white solid): 52% yield. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.19-8.11 (m, 1H), 7.75-7.68 (m, 1H), 7.53-7.47 (m, 2H), 3.30 (d, *J* = 11.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 134.68 (d, *J* = 1.0 Hz), 134.59, 134.58 (d, *J* = 6.0 Hz), 129.94 (d, *J* = 148.0 Hz), 127.52 (d, *J* = 14.0 Hz), 124.98 (d, *J* = 6.0 Hz), 93.14 (d, *J* = 37.0 Hz), 77.44 (d, *J* = 203.0 Hz); ^{31}P NMR (122 MHz, CDCl$_3$) δ -23.72; IR (neat): 3173, 2053, 1578, 1450, 1255, 1115, 1025, 754 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{10}H_6{}^{79}BrOP$: 251.9340, Found: 251.9341



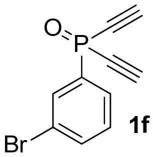
1d

Characterization of compound **1d** (white solid): 47% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.07 (dd, *J* = 18.4, 6.9 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.44-7.34 (m, 2H), 3.34 (d, *J* = 10.9 Hz, 2H), 3.18 (q, *J* = 7.4 Hz, 2H), 1.36 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 148.19 (d, *J* = 12.0 Hz), 133.53 (d, *J* = 3.0 Hz), 131.84 (d, *J* = 15.0 Hz), 129.94 (d, *J* = 13.0 Hz), 128.22 (d, *J* = 141.0 Hz), 125.88 (d, *J* = 16.0 Hz), 92.94 (d, *J* = 35.0 Hz), 78.81 (d, *J* = 191.0 Hz), 26.76 (d, *J* = 6.0 Hz), 15.24; ^{31}P NMR (162 MHz, CDCl$_3$): δ -20.13; IR (neat): 3656, 3149, 2965, 2048, 1476, 1452, 1437, 1205, 1190, 1087, 1053, 776, 751 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{12}H_{11}OP$: 202.0548, Found: 202.0551.



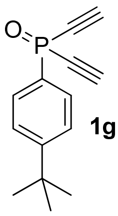
1e

Characterization of compound **1e** (white solid): 51% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.56-7.41 (m, 3H), 7.15-7.12 (m, 1H), 3.86 (s, 3H), 3.31 (d, *J* = 11.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 159.85 (d, *J* = 19.0 Hz), 132.10 (d, *J* = 141.0 Hz), 130.37 (d, *J* = 18.0 Hz), 122.64 (d, *J* = 13.0 Hz), 119.83 (d, *J* = 4.0 Hz), 114.96 (d, *J* = 15.0 Hz), 92.94 (d, *J* = 36.0 Hz), 78.48 (d, *J* = 193.0 Hz), 55.66; ^{31}P NMR (122 MHz, CDCl$_3$): δ -20.84; IR (neat): 3237, 3161, 2063, 2044, 1594, 1575, 1483, 1420, 1316, 1289, 1246, 1197, 1039, 887, 779 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{11}H_9O_2P$: 204.0340, Found: 204.0341.



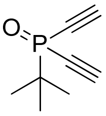
1f

Characterization of compound **1f** (white solid): 33% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.07 (dt, *J* = 16.1, 1.5 Hz, 1H), 7.89 (dd, *J* = 15.5, 7.6 Hz, 1H), 7.77-7.75 (m, 1H), 7.43 (td, *J* = 7.8, 4.3 Hz, 1H), 3.32 (d, *J* = 11.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 136.43 (d, *J* = 3.0 Hz), 133.35 (d, *J* = 140.0 Hz), 133.11 (d, *J* = 14.0 Hz), 130.61 (d, *J* = 16.0 Hz), 128.92 (d, *J* = 12.0 Hz), 123.29 (d, *J* = 19.0 Hz), 93.52 (d, *J* = 37.0 Hz), 77.91 (d, *J* = 196.0 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ -23.12; IR (neat): 3452, 3161, 3141, 2049, 1558, 1464, 1398, 1194, 1127, 1066, 994, 900, 775, 719, 679 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{10}H_6{}^{79}BrOP$: 251.9340, Found: 251.9344.



1g

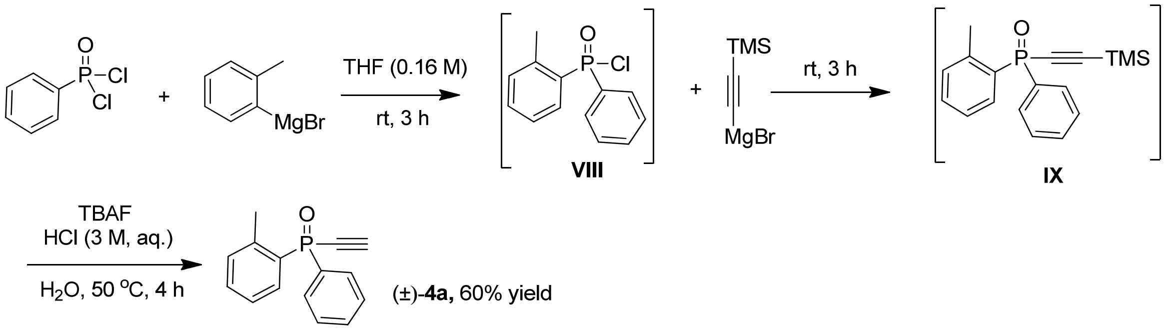
Characterization of compound **1g** (yellow solid): 50% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.92-7.84 (m, 2H), 7.59-7.54 (m, 2H), 3.27 (d, *J* = 10.9 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 157.21 (d, *J* = 4.0 Hz), 130.30 (d, *J* = 13.0 Hz), 127.57 (d, *J* = 144.0 Hz), 126.00 (d, *J* = 16.0 Hz), 92.52 (d, *J* = 35.0 Hz), 78.69 (d, *J* = 192.0 Hz), 35.20, 31.05; ^{31}P NMR (162 MHz, CDCl$_3$): δ -20.54; IR (Neat): 3666, 3190, 2964, 2053, 1679, 1597, 1461, 1392, 1269, 1207, 1190, 1130, 1093, 834, 737 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{14}H_{15}OP$: 230.0861, Found: 230.0865.



1h

Characterization of compound **1h** (white solid): 60% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.21 (d, *J* = 10.1 Hz, 2H), 1.30 (d, *J* = 19.6 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 92.17 (d, *J* = 28.0 Hz), 76.35 (d, *J* = 96.0 Hz), 33.90 (d, *J* = 96.0 Hz), 22.80 (d, *J* = 2.0 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ 6.64; IR (neat): 3364, 3153, 2934, 1474, 1367, 1218, 1168, 1012, 942, 812 cm^{-1}; HRMS (EI): Exact mass calcd for $C_8H_{11}OP$: 154.0548, Found: 154.0546.

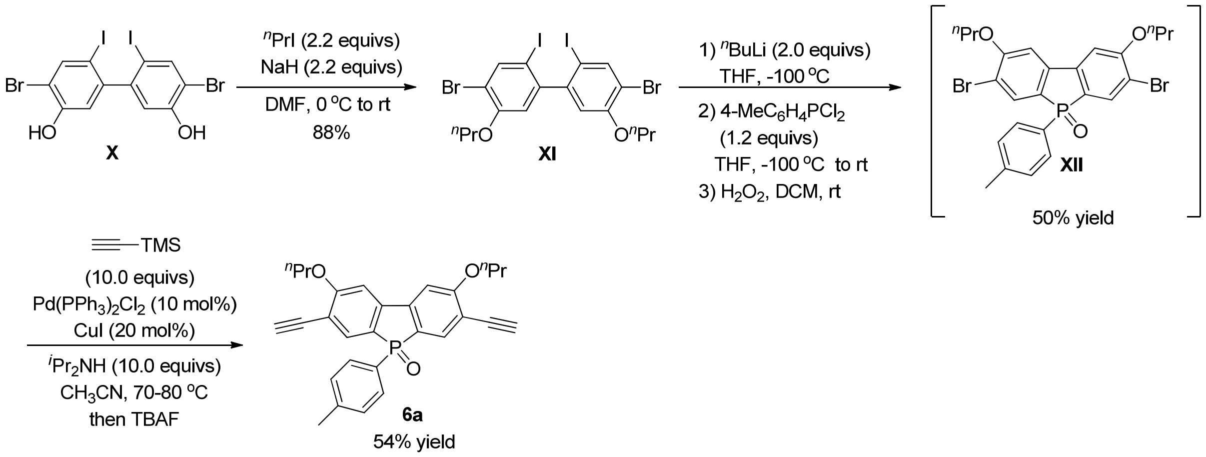
3.2 The synthesis of racemic monoethynyl phosphine oxides 4



Procedure for synthesis of racemic monoethynyl phosphine oxides **4a**: To a solution of phenylphosphonic dichloride (1.95 g, 10 mmol) in anhydrous THF (20 mL) was slowly added *o*-tolylmagnesium bromide (10 mL, 1.0 M) at 25 °C. After the resulting mixture was vigorously stirred at the same temperature for 3 h, 2-(trimethylsilyl)ethynylmagnesium bromide (20 mL, 0.5 M) was slowly added. The reaction was kept stirring for another 3 h, and then 3.0 mL of TBAF (1 M in THF), 5.0 mL of HCl (3 M, aq) and 20.0 mL of water were added at 0 °C. The resulting mixture was stirred at 50 °C till the consumption of intermediate **IX** by TLC analysis. The solvent was removed under vacuum and the residue was dissolved in 100 mL of CH_2Cl_2 and 100 mL of HCl (3 M, aq). The aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL). The organic phase was combined, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash chromatography using PE:EtOAc (2:1, v/v) as the eluent to give monoethynyl phosphine oxides **4a** as a white solid in 60% yield. All the other racemic monoethynyl phosphine oxides **4** were prepared in about 50% total yield of three steps by such a one-pot procedure. And all other racemic monoethynyl phosphine oxides **4** are also prepared from the corresponding phosphonic dichlorides by using the above procedure.

For the full characterization of all monoethynyl phosphine oxides **4**, please see section 6, including ^{1}H, ^{13}C and ^{31}P NMR data, together with IR and HRMS data.

3.3 The synthesis of phosphole oxide-diynes 6



Phosphole based prochiral phosphole oxide-diynes **6** were prepared from the easily available compound **X**[7] by the following procedure, as illustrated by the synthesis of phosphole oxide-diynes **6a**. To an oven-dried three-necked bottle was added **X** (1.2 g, 2 mmol) and then dissolved in 15 mL of anhydrous DMF. NaH (105.6 mg, 4.4 mmol) was added carefully to the mixture at 0 °C with evolution of hydrogen. After the mixture was stirred for 15 min, ^{n}PrI (748 mg, 430 uL, 4.4 mmol) was added in one portion with vigorously stirring till full conversion of **X** by TLC analysis. The reaction mixture was then poured into saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic layor was washed with water and brine, dried, filtered and concentrated to afford the crude product **XI** in 88% yield, which was pure enough to be used in the next step. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 2H), 6.70 (s, 2H), 4.02-3.91 (m, 4H), 1.90-1.82 (m, 4H), 1.06 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.50, 148.00, 141.90, 114.18, 112.76, 87.20, 70.81, 22.33, 10.49.

The benzophosphole was synthesized in moderate yield using a modified procedure. To the mixture of **XI** (4.1g, 6.0 mmol) and dry THF (50 mL) was added a 2.4 M *n*-butyllithium/hexane solution (5.0 mL, 12.0 mmol) at -100°C. The resulting mixture was allowed to stir at this temperature for 0.5 h, and then 4-methylphenyl phosphonic dichloride (1.4 g, 7.2 mmol) was added dropwise into the mixture. The mixture was warmed naturally to room temperature with stirring for 2-3 h. Then the reaction mixture was hydrolyzed with water and extracted with CH_2Cl_2. H_2O_2 was then added to the mixture and stirred vigorously for 0.5 h. Water was added and the organic layer was combined, dried over anhydrous Na_2SO_4, filtered and evaporated to remove the solvent. The resulting crude product was chromatographed on a silica gel with CH_2Cl_2/ethyl acetate as eluent. Recrystallizing from ethyl

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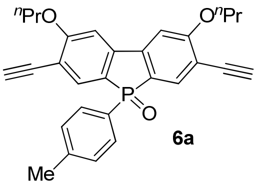
[7] R. M. Chalke and V. R. Patil, *J. Macromol. Sci. Part A Pure Appl. Chem.,* 2017, **54**, 556.

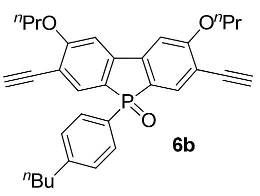
acetate afforded the pure compound **XII** in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 9.2 Hz, 2H), 7.53-7.47 (m, 2H), 7.22-7.16 (m, 4H), 4.21-4.11 (m, 4H), 2.37 (s, 3H), 1.99-1.90 (m, 4H), 1.14 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.60 (d, J = 2.0 Hz), 143.12 (d, J = 3.0 Hz), 142.14 (d, J = 21.0 Hz), 134.14 (d, J = 11.0 Hz), 131.06 (d, J = 12.0 Hz), 129.62 (d, J = 13.0 Hz), 126.48 (d, J = 109.0 Hz), 125.64 (d, J = 111.0 Hz), 113.84 (d, J = 15.0 Hz), 104.99 (d, J = 12.0 Hz), 70.97, 22.44, 21.61, 10.64; ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.19.

To a 50 mL sealed tube was added $Pd(PPh_3)_2Cl_2$ (120 mg, 0.17 mmol), CuI (66 mg, 0.34 mmol) and benzophosphole **XII** (955 mg, 1.7 mmol), followed by the addition of 10 mL anhydrous CH_3CN and ^{i}Pr$_2$NH (2.4 mL, 17 mmol). The mixture was then cooled using liquid nitrogen and vacuumized for 10 minutes to exclude oxygen, back-filled with N_2. After warming back to room temperature, trimethylsilylacetylene (2.4 mL, 17 mmol) was added and the resulting mixture was vigorously stirred in a pre-heated oil bath (90 ºC) till full conversion of **XII**. The solvent was removed under reduced pressure and then subjected directly to column chromatography to give the Sonogashira coupling product, which was then dissolved in anhydrous THF (20 mL), followed by the addition of TBAF (1 M in THF). After full conversion, water was added, and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was dried over Na_2SO_4 and concentrated to afford the crude product, which was then subjected to column chromatography to afford the phosphole oxide-diynes **6a** in 54% yield.



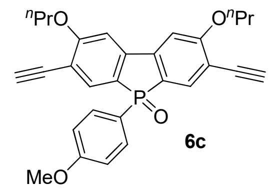
6a

Characterization of compound **6a** (brown solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 12.8 Hz, 2H), 7.51-7.46 (m, 2H), 7.20-7.18 (m, 4H), 4.21-4.10 (m, 4H), 3.32 (s, 2H), 2.34 (s, 3H), 1.96-1.88 (m, 4H), 1.11 (t, J = 9.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.34 (d, J = 2.0 Hz), 143.22 (d, J = 22.0 Hz), 142.84 (d, J = 3.0 Hz), 135.27 (d, J = 11.0 Hz), 131.06 (d, J = 12.0 Hz), 129.51 (d, J = 13.0 Hz), 127.09 (d, J = 108.0 Hz), 125.44 (d, J = 111.0 Hz), 113.50 (d, J = 14.0 Hz), 104.30 (d, J = 11.0 Hz), 83.25, 79.00, 70.68, 22.47, 21.59, 10.54; ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.87; IR (KBr): 3180, 2950, 1590, 1249, 1159, 1044, 591 cm^{-1}; MS (EI): 454 (M$^+$, 56), 44 (100), 263 (16), 91 (14); HRMS (EI): Exact mass calcd for $C_{29}H_{27}O_3P$: 454.1698, Found: 454.1696.



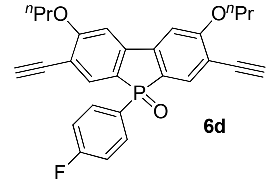
6b

Characterization of compound **6b** (brown solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J*= 9.6 Hz, 2H), 7.53-7.48 (m, 2H), 7.20-7.18 (m, 4H), 4.21-4.11 (m, 4H), 3.33 (s, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.98-1.89 (m, 4H), 1.60-1.52 (m, 2H), 1.36-1.24 (m, 2H), 1.12 (t, *J* = 7.2 Hz, 6H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.29 (d, *J* = 2.0 Hz), 147.74 (d, *J* = 3.0 Hz), 143.22 (d, *J* = 21.0 Hz), 135.29 (d, *J* = 11.0 Hz), 131.02 (d, *J* = 11.0 Hz), 128.88 (d, *J* = 13.0 Hz), 127.16 (d, *J* = 108.0 Hz), 125.40 (d, *J* = 111.0 Hz), 113.36 (d, *J* = 14.0 Hz), 104.20 (d, *J* = 11.0 Hz), 83.22, 78.94, 70.58, 35.65, 32.23, 22.42, 22.27, 13.86, 10.53; ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.81; IR (KBr): 3817, 325, 2962, 1596, 1460, 1064, 678, 524 cm^{-1}; MS (EI): 496 (M$^+$, 1), 172 (100), 108 (91), 244 (71), 216 (46), 440 (6), 356 (5); HRMS (EI): Exact mass calcd for $C_{32}H_{33}O_3P$: 496.2167, Found: 496.2164.



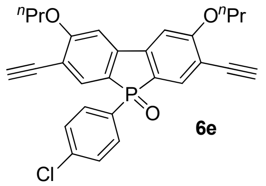
6c

Characterization of Compound **6c** (brown solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 9.6 Hz, 2H), 7.56-7.51 (m, 2H), 7.18 (d, *J* = 2.0 Hz, 2H), 6.91-6.88 (m, 2H), 4.20-4.14 (m, 4H), 3.81 (s, 3H), 3.33 (s, 2H), 1.98-1.89 (m, 4H), 1.12 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.32 (d, *J* = 2.0 Hz), 162.87 (d, *J* = 3.0 Hz), 143.15 (d, *J* = 21.0 Hz), 135.25 (d, *J* = 11.0 Hz), 132.94 (d, *J* = 12.0 Hz), 125.60 (d, *J* = 111.0 Hz), 121.16 (d, *J* = 107.0 Hz), 114.41 (d, *J* = 14.0 Hz), 113.50 (d, *J* = 11.0 Hz), 104.26 (d, *J* = 11.0 Hz), 83.23, 78.97, 70.65, 55.34, 22.45, 10.52; ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.61; IR (KBr): 3186, 2986, 1595, 1388, 1249, 1159, 1044, 661cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{29}H_{28}O_4P$ [M+H]$^+$: 471.1720, Found: 471.1721.



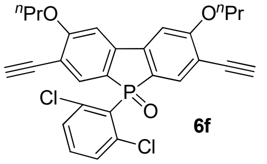
6d

Characterization of compound **6d** (brown solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.70 (m, 2H), 7.64-7.58 (m, 2H), 7.19-7.18 (m, 2H), 7.10-7.05 (m, 2H), 4.22-4.12 (m, 4H), 3.33 (s, 2H), 1.98-1.89 (m, 4H), 1.12 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.60 (d, *J* = 4.0 Hz), 164.54 (d, *J* = 1.0 Hz), 164.08 (d, *J* = 4.0 Hz), 143.18 (d, *J* = 22.0 Hz), 135.22 (d, *J* = 11.0 Hz), 133.62 (d, *J* = 9.0 Hz), 133.50 (d, *J* = 9.0 Hz), 126.51 (d, *J* = 106.0 Hz), 124.87 (d, *J* = 112.0 Hz), 116.26 (d, *J* = 14.0 Hz), 116.04 (d, *J* = 14.0 Hz), 113.72 (d, *J* = 13.0 Hz), 104.42 (d, *J* = 11.0 Hz), 83.41, 78.82, 70.71, 22.44, 10.49; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.64; ^{19}F (376 MHz, $CDCl_3$): δ -106.25; IR (KBr): 3290, 2985, 1595, 1273, 1160, 1040, 710, 528 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{28}H_{24}O_3FP$: 458.1447, Found: 458.1450.



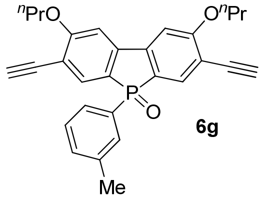
6e

Characterization of compound **6e** (brown solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 9.6 Hz, 2H), 7.55-7.50 (m, 2H), 7.37-7.34 (m, 2H), 7.18 (d, J = 1.6 Hz, 2H), 4.22-4.11 (m, 4H), 3.34 (s, 2H), 1.96-1.83 (m, 4H), 1.12 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.55 (d, J = 3.0 Hz), 143.20 (d, J = 22.0 Hz), 138.80 (d, J = 4.0 Hz), 135.22 (d, J = 12.0 Hz), 132.45 (d, J = 12.0 Hz), 129.22 (d, J = 107.0 Hz), 129.10 (d, J = 13.0 Hz), 124.59 (d, J = 112.0 Hz), 113.66 (d, J = 14.0 Hz), 104.38 (d, J = 12.0 Hz), 83.47, 78.75, 70.67, 22.42, 10.51; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.52; IR (KBr): 3289, 2967, 1595, 1273, 1087, 708, 528 cm^{-1}; MS (EI): 474, 476 (M^+, 100, 34), 263 (30), 279 (22), 308 (9), 390 (16); HRMS (EI): Exact mass calcd for $C_{28}H_{24}O_3P^{35}Cl$: 474.1152, Found: 474.1151.



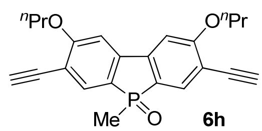
6f

Characterization of compound **6f** (brown solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 10.4 Hz, 2H), 7.34-7.28 (m, 3H), 7.15 (d, J = 2.0 Hz, 2H), 4.22-4.11 (m, 4H), 3.34 (s, 2H), 1.96-1.91 (m, 4H), 1.13 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.58 (d, J = 2.0 Hz), 143.38 (d, J = 24.0 Hz), 139.53 (d, J = 4.0 Hz), 135.25 (d, J = 11.0 Hz), 132.58, 130.66 (d, J = 6.0 Hz),127.62 (d, J = 101.0 Hz), 124.96 (d, J = 119.0 Hz), 113.27 (d, J = 14.0 Hz), 104.57 (d, J = 12.0 Hz), 83.20, 79.03, 70.61, 22.45, 10.54; ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.45; IR (KBr): 3292, 2965, 1595, 1419, 1194, 1050, 778, 526 cm^{-1}; MS (EI): 508 510, 512 (M^+, 100, 57, 12), 279 (82), 389 (28), 424 (8), 466 (7); HRMS (EI): Exact mass calcd for $C_{28}H_{23}O_3P^{35}Cl_2$: 508.0762, Found: 508.0756.



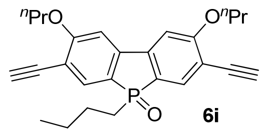
6g

Characterization of compound **6g** (brown solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 9.2 Hz, 2H), 7.48-7.45 (m, 1H), 7.35-7.28 (m, 2H), 7.25-7.24 (m, 1H), 7.19 (d, J = 2.0 Hz, 2H), 4.22-4.12 (m, 4H), 3.33 (s, 2H), 2.32 (s, 3H), 1.96-1.91 (m, 4H), 1.12 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.37 (d, J = 2.0 Hz), 143.27 (d, J = 22.0 Hz), 138.67 (d, J = 13.0 Hz), 135.39 (d, J = 12.0 Hz), 133.07 (d, J = 3.0 Hz), 131.44 (d, J = 10.0 Hz), 130.30 (d, J = 106.0 Hz),128.62 (d, J = 14.0 Hz), 128.00 (d, J = 12.0 Hz), 125.28 (d, J = 111.0 Hz), 113.48 (d, J = 14.0 Hz), 104.32 (d, J = 13.0 Hz), 83.25, 78.95, 70.63, 22.44, 21.31, 10.51; ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.73; IR (KBr): 3290, 2966, 1695, 1272, 1062, 691 cm^{-1}; MS (EI): 454 (M^+, 100), 143 (18), 263 (17), 279 (13), 322 (10), 370 (8); HRMS (EI): Exact mass calcd for $C_{29}H_{27}O_3P$: 454.1698, Found: 454.1693.



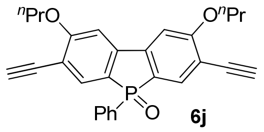
6h

Characterization of compound **6h** (brown solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 9.6 Hz, 2H), 7.13 (d, *J* = 2.0 Hz, 2H), 4.19-4.10 (m, 4H), 3.38 (s, 2H), 1.97-1.88 (m, 4H), 1.80 (d, *J* = 13.6 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.25 (d, *J* = 2.0 Hz), 142.20 (d, *J* = 21.0 Hz), 134.48 (d, *J* = 11.0 Hz), 125.54 (d, *J* = 8.0 Hz), 113.30 (d, *J* = 13.0 Hz), 104.30 (d, *J* = 11.0 Hz), 83.32, 78.93, 70.63, 22.41, 16.42 (d, *J* = 74.0 Hz), 10.49; ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.92; IR (KBr): 3296, 2980, 1695, 1270, 1044, 698 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{23}H_{23}O_3NaP$ $[M+Na]^+$: 401.1283, Found: 401.1272.



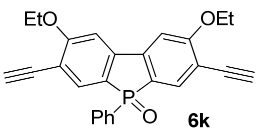
6i

Characterization of compound **6i** (brown solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 9.2 Hz, 2H), 7.12 (s, 2H), 4.18-4.08 (m, 4H), 3.38 (s, 2H), 2.07-1.99 (m, 2H), 1.96-1.87 (m, 4H), 1.43-1.29 (m, 4H), 1.11 (t, *J* = 7.2 Hz, 6H), 0.82 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.18 (d, *J* = 2.0 Hz), 142.68 (d, *J* = 21.0 Hz), 134.70 (d, *J* = 11.0 Hz), 124.16 (d, *J* = 104.0 Hz), 113.14 (d, *J* = 13.0 Hz), 104.32 (d, *J* = 10.0 Hz), 83.25, 79.00, 70.57, 29.98 (d, *J* = 71.0 Hz), 24.19 (d, *J* = 4.0 Hz), 23.89 (d, *J* = 16.0 Hz), 22.40, 13.42, 10.48; ^{31}P NMR (162 MHz, $CDCl_3$): δ 40.89; IR (neat): 3297, 3188, 2926, 2876, 1591, 1457, 1184, 1050, 763 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{26}H_{29}O_3P$: 420.1854, Found: 420.1856.

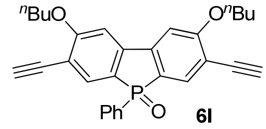


6j

Characterization of compound **6j** (brown solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 9.6 Hz, 2H), 7.63-7.58 (m, 2H), 7.51-7.47 (m, 1H), 7.40-7.36 (m, 2H), 7.18 (d, *J* = 2.4 Hz, 2H), 4.22-4.17 (m, 4H), 3.33 (s, 2H), 1.98-1.89 (m, 4H), 1.12 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.38 (d, *J* = 2.0 Hz), 143.23 (d, *J* = 22.0 Hz), 135.20 (d, *J* = 11.0 Hz), 132.15 (d, *J* = 2.0 Hz), 131.07 (d, *J* = 10.0 Hz), 130.48 (d, *J* = 84.0 Hz), 128.69 (d, *J* = 12.0 Hz), 124.98 (d, *J* = 111.0 Hz), 113.48 (d, *J* = 13.0 Hz), 104.35 (d, *J* = 11.0 Hz), 83.28, 78.88, 70.61, 22.39, 10.49; ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.54; IR (KBr): 3228, 2966, 2875, 1590, 1246, 1064, 842, 730, 690 cm^{-1}; MS (EI): 440 (M^+, 100), 263 (19), 279 (15), 356 (12), 398 (6); HRMS (EI): Exact mass calcd for $C_{28}H_{25}O_3P$: 440.1541, Found: 440.1543.

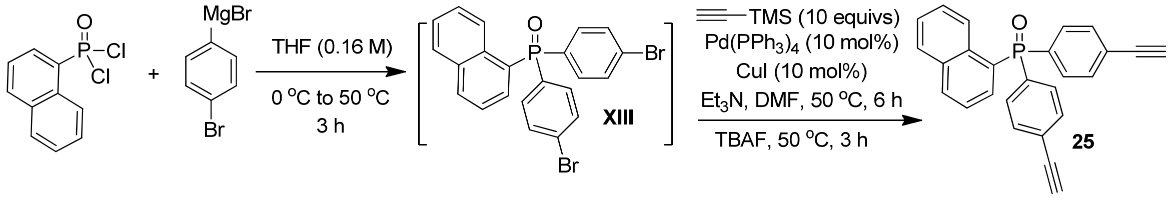

6k

Characterization of compound **6k** (brown solid). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.75 (d, J = 9.6 Hz, 2H), 7.64-7.58 (m, 2H), 7.52-7.48 (m, 1H), 7.41-7.37 (m, 2H), 7.19 (d, J = 2.4 Hz, 2H), 4.33-4.25 (m, 4H), 3.35 (s, 2H), 1.55 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 164.24 (d, J = 2.0 Hz), 143.27 (d, J = 22.0 Hz), 135.39 (d, J = 12.0 Hz), 132.22 (d, J = 3.0 Hz), 131.01 (d, J = 11.0 Hz), 130.02, 128.74 (d, J = 12.0 Hz), 125.17 (d, J = 111.0 Hz), 113.48 (d, J = 14.0 Hz), 104.31 (d, J = 12.0 Hz), 83.38, 78.97 , 64.91, 14.56; ^{31}P NMR (162 MHz, CDCl$_3$): δ 30.56; IR (KBr): 3669, 3213, 2931, 1593, 1255, 1048, 822, 731, 692 cm^{-1}; MS (EI): 412 (M$^+$, 100), 263 (14), 279 (12), 319 (8); HRMS (EI): Exact mass calcd for $C_{26}H_{21}O_3P$: 412.1228, Found: 412.1226.


6l

Characterization of compound **6l** (brown solid). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.73 (d, J = 9.6 Hz, 2H), 7.63-7.58 (m, 2H), 7.51-7.47 (m, 1H), 7.40-7.36 (m, 2H), 7.19 (d, J = 2.0 Hz, 2H), 4.26-4.16 (m, 4H), 3.33 (s, 2H), 1.93-1.86 (m, 4H), 1.63-1.54 (m, 4H), 1.02 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 164.44 (d, J = 2.0 Hz), 143.28 (d, J = 22.0 Hz), 135.34 (d, J = 11.0 Hz), 132.18 (d, J = 3.0 Hz), 131.02 (d, J = 85.0 Hz), 130.64 (d, J = 105.0 Hz), 128.72 (d, J = 13.0 Hz), 125.18 (d, J = 111.0 Hz), 113.52 (d, J = 13.0 Hz), 104.29 (d, J = 11.0 Hz), 83.30, 78.93, 68.92, 31.02, 19.17, 13.83; ^{31}P NMR (162 MHz, CDCl$_3$): δ 30.44; IR (KBr): 3290, 2955, 2872, 1591, 1246, 1042, 900, 731, 691 cm^{-1}; MS (EI): 468 (M$^+$, 100), 263 (21), 356 (20), 412 (9); HRMS (EI): Exact mass calcd for $C_{30}H_{29}O_3P$: 468.1854, Found: 468.1857.

3.4 The synthesis of diethynylphosphine oxides 25



Diethynylphosphine oxide **25** was synthesized by two steps: to a solution of 1-naphthyl phosphonic dichloride (2.3 g, 9.5 mmol) in anhydrous THF (20 mL) was slowly added (4-bromophenyl)magnesium bromide (20 mmol) at 0°C. The mixture was warmed slowly to room temperature and stirred at 50 ºC for 3 h. The solvent was removed under vacuum and the residue was dissolved in 100 mL of CH_2Cl_2 and 100 mL of HCl (3 M, aq). The aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL). The organic phase was combined, dried over anhydrous Na_2SO_4 and concentrated to give the crude residue, which was purified by a short flash chromatography using PE/EtOAc (2:1, v/v) as the eluent to provide crude **XIII** in 68% yield as a white solid.

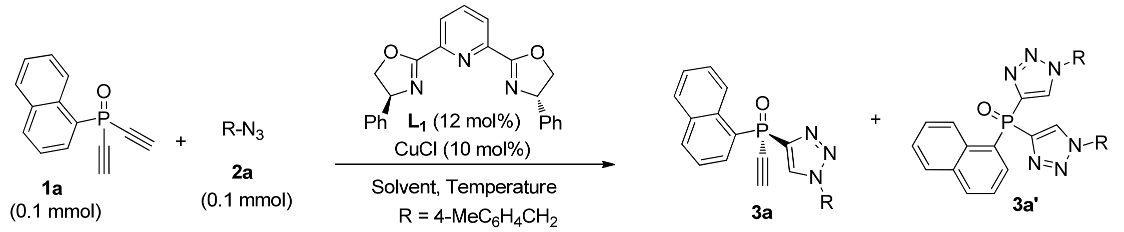
To a 50 mL sealed tube was added Pd(PPh_3)$_4$ (231 mg, 0.2 mmol), CuI (38 mg, 0.2 mmol) and crude **XIII** (972 mg, 2 mmol), followed by the addition of 5 mL anhydrous DMF and Et_3N (2.02 g, 20 mmol). The mixture was then cooled using liquid nitrogen and vacuumized for 10 minutes to exclude oxygen, back-filled with N_2. After warming back to room temperature, trimethylsilylacetylene (1.96 g, 20 mmol) was added and the resulting mixture was vigorously stirred in a pre-heated oil bath (50 °C) till full conversion of **XIII**. The solvent was removed under reduced pressure and then subjected directly to a short column chromatography to give the Sonogashira coupling product, which was then dissolved in anhydrous THF (20 mL), followed by the addition of TBAF (20 mL, 1 M in THF). After full conversion, water was added, and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was dried over Na_2SO_4 and concentrated to afford the crude product, which was then subjected to column chromatography to afford the **25** in 54% yield. Characterization of compound **25** (white solid, Mp: 198-200 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.66-7.56 (m, 8H), 7.54-7.50 (m, 1H), 7.48-7.43 (m, 1H), 7.42-7.37 (m, 1H), 7.31-7.25 (m, 1H), 3.21 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.94 (d, *J* = 9.0 Hz), 133.73 (d, *J* = 12.0 Hz), 133.68 (d, *J* = 3.0 Hz), 133.57 (d, *J* = 8.0 Hz), 132.99 (d, *J* = 104.0 Hz), 132.24 (d, *J* = 12.0 Hz), 131.94 (d, *J* = 10.0 Hz), 128.93, 128.04 (d, *J* = 103.0 Hz), 127.59, 127.35 (d, *J* = 6.0 Hz), 126.71, 126.07 (d, *J* = 3.0 Hz), 124.19 (d, *J* = 15.0 Hz), 82.60 (d, *J* = 1.0 Hz), 80 .06; ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 31.27; IR (KBr): 3275, 2974, 2893, 1597, 1489, 1386, 1265, 1190, 1147, 1095, 985, 804, 775 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{26}H_{17}OP$: 376.1017, Found: 376.1014.

4. Condition optimization

4.1 Desymmetrizing CuAAC reaction of diethynylphosphine oxide 1a

We first examined the solvent effects of the reaction of **1a** and **2a** by running the reaction at 25 ºC, in the presence of chiral complex **L$_1$**/CuCl, as shown in Table S1. Of several typical solvents we screened (entries 1-6), MeCN turned out to be the best, affording the desired monotriazole **3a** in 60% yield and 78% ee, with the **3a**/**3a'** ratio as 4.5:1 (entry 6). Then we evaluated the effect of temperature by running the reaction in CH_3CN (entries 6-9), and found that lowering reaction temperature could further improve the enantioselectivity and **3a**/**3a'** ratio (entries 7-8). The reaction running at -20 ºC could finish within 96 h, affording **3a** in 83% ee, with the ratio of **3a**/**3a'** improved to 6.8:1 (entry 8). Further lowering the temperature to -30 ºC failed to afford better result (entry 9).

Table S1. Condition optimization of the reaction of 1a and 2a

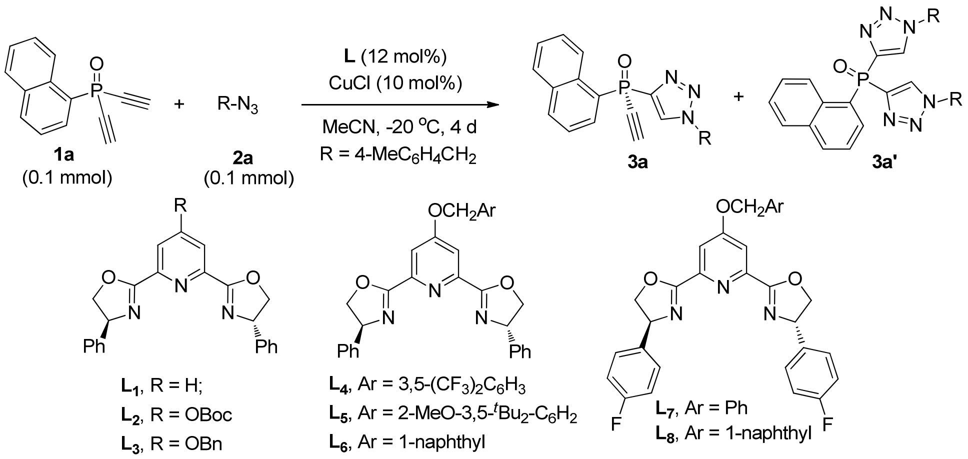


entry	solvent	temp. (ºC)	time (h)	**3a**:**3a'**[a]	NMR yield of **3a** (%)[a]	ee of **3a** (%)[b]
1	THF	25	20	2.0:1	42	49
2	Toluene	25	14	2.1:1	42	6
3	Acetone	25	14	3.6:1	54	74
4	EtOAc	25	20	2.3:1	47	49
5	CH_2Cl_2	25	14	2.6:1	51	67
6	MeCN	25	14	4.5:1	60	78
7	MeCN	0	48	4.8:1	62	80
8	MeCN	-20	96	6.8:1	63	83
9	MeCN	-30	120	6.5:1	62	81

[a] Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard. [b] Determined by chiral HPLC analysis.

In the following, we evaluated the performance of our newly developed PYBOX ligands **L$_2$**-**L$_8$** with different size of C4 shielding groups, and the results were summarized in Table S2. Interestingly, PYBOX **L$_6$** bearing a C4 1-naphthyl group afforded the promising result, showing a suitable shielding group could indeed improve the enantioselectivity and inhibiting achiral triazole formation. It could achieve a high **3a**/**3a'** ratio (13.9:1) and 93% ee for **3a**, obviously better than unmodified ligand $\mathbf{L_1}$ (entry 6 vs 1). The variation of the substituent at the chiral center of the ligand also influenced the result, as exemplified by the good result obtained by using ligand $\mathbf{L_{7\text{-}8}}$ (entries 7 and 8).

Table S2. Evaluation of the influence of the C4 shielding group of PYBOX/CuCl

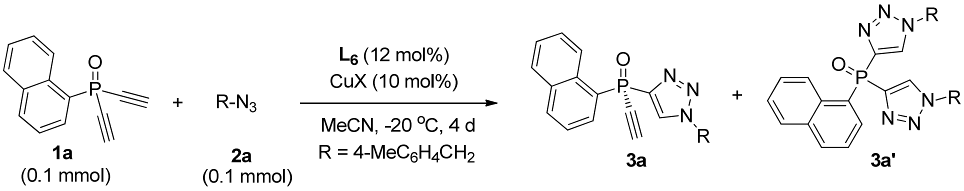


entry	ligand	**3a**:**3a'**[a]	NMR yield of **3a** (%)[a]	ee of **3a** (%)[b]
1	$\mathbf{L_1}$	6.8:1	63	83
2	$\mathbf{L_2}$	5.1:1	51	84
3	$\mathbf{L_3}$	10.4:1	71	90
4	$\mathbf{L_4}$	6.4:1	60	84
5	$\mathbf{L_5}$	12.0:1	79	91
6	$\mathbf{L_6}$	13.9:1	80	93
7	$\mathbf{L_7}$	11.4:1	77	91
8	$\mathbf{L_8}$	9.3:1	74	89

[a] Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard. [b] Determined by chiral HPLC analysis.

Finally, we evaluated different copper salts by running the reaction in MeCN (entries 1-5), and the results were summarized in Table S3. We found that the use of CuBr could slightly improve the enantioselectivity of **3a** to 95%, with unchanged 13.9:1 **3a**/**3a'** ratio (entry 2 vs 1). Lower **3a**/**3a'** ratio and enantioselectivity of **3a** were obtained when using CuI or CuCN (entries 3, 4). Further varying CuCl to $CuPF_6\cdot(MeCN)_4$ decreased the ee to 91%, with the **3a**/**3a'** ratio of 9.2:1 (entry 5).

Table S3. Evaluation of the different copper salts



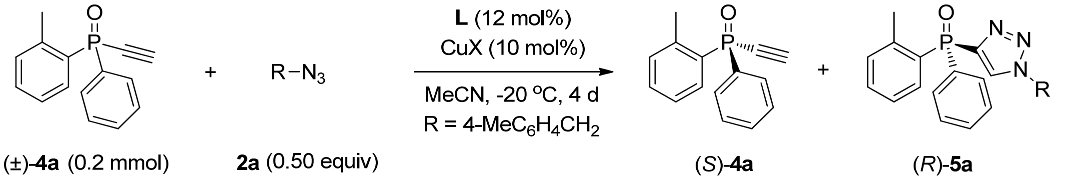
entry	CuX	**3a**:**3a'**[a]	NMR yield of **3a** (%)[a]	ee of **3a** (%)[b]
1	CuCl	13.9:1	80	93
2	CuBr	13.9:1	80[c]	95
3	CuI	4.4:1	51	66
4	CuCN	2.2:1	36	32
5	$CuPF_6 \cdot (MeCN)_4$	9.2:1	66	91

[a] Determined by ^1H NMR using 1,3,5-trimethoxybenzene as the internal standard. [b] Determined by chiral HPLC analysis. [c] Isolated yield.

4.2 Kinetic resolution of ethynylphosphine oxide 4a via CuAAC reaction

Typical results for the kinetic resolution of **4a** via CuAAC were shown in Table S4. Our ligand $\mathbf{L_6}$ proved to be better than $\mathbf{L_1}$ once again, as it allowed the recovery of (*S*)-**4a** in higher ee value (80% vs 70%, entry 3 vs 1). Ligand $\mathbf{L_7}$ was found to be the best in the kinetic resolution of **4a**, with (*S*)-**4a** being recovered in 91% ee (entry 4). On the other hand, $\mathbf{L_8}$ was more suitable for the CuAAC reaction of **4a**, giving (*R*)-**5a** in 86% ee (entry 5). The screening of different copper salts and solvents afforded no better result (entry 6-10). The use of 15 mol% $\mathbf{L_7}$/CuBr enabled the recovery of (*S*)-**4a** in 93% ee (entry 11). By increasing the usage of **2a** from 0.5 equiv to 0.52 equiv, (*S*)-**4a** was recovered in 96% ee with 42% recovery (entry 12). The use of 15 mol% $\mathbf{L_8}$/CuBr also improve the ee value of the CuAAC reaction of **4a**, affording (*R*)-**5a** in 89% ee (entry 13). By decreasing the amount of **2a** to 0.48 equiv, (*R*)-**5a** could be obtained in 90% ee with 47% yield (entry 14).

Table S4. **The condition optimization for the kinetic resolution of 4a**



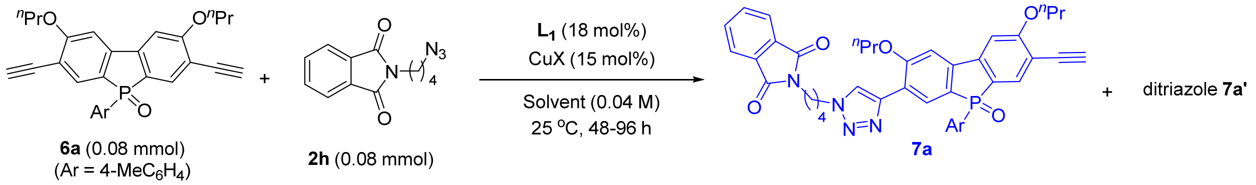
entry	solvent	CuX	ligand	Recovery of **4a** (%)[a]	ee of **4a** (%)[b]	yield of **5a** (%)[a]	ee of **5a** (%)[b]
1	MeCN	CuBr	$\mathbf{L_1}$	48	70	41	85
2	MeCN	CuBr	$\mathbf{L_3}$	47	73	43	86
3	MeCN	CuBr	$\mathbf{L_6}$	44	80	44	85
4	MeCN	CuBr	$\mathbf{L_7}$	45	91	47	81
5	MeCN	CuBr	$\mathbf{L_8}$	44	84	47	86
6	MeCN	CuCl	$\mathbf{L_7}$	45	83	45	73
7	MeCN	$\mathrm{CuPF_6\cdot(MeCN)_4}$	$\mathbf{L_7}$	55	66	37	82
8	$\mathrm{CH_2Cl_2}$	CuBr	$\mathbf{L_7}$	44	59	47	48
9	Acetone	CuBr	$\mathbf{L_7}$	42	85	48	68
10[c]	MeCN	CuBr	$\mathbf{L_7}$	47	93	45	81
11[c,d]	**MeCN**	**CuBr**	$\mathbf{L_7}$	**42**	**96**	**>49**	**77**
12[c]	MeCN	CuBr	$\mathbf{L_8}$	44	84	47	89
13[c,e]	**MeCN**	**CuBr**	$\mathbf{L_8}$	**>49**	**80**	**47**	**90**

[a] Isolated yield. [b] Determined by chiral HPLC analysis. [c] 15 mol% catalytic loading. [d] 0.52 equiv of **2a**. [e] 0.48 equiv of **2a**.

4.3 Remote desymmetric enantioselective CuAAC of phosphole oxide-diyne 6a

As shown in Table S5, the reaction of **6a** and azide **2h** catalyzed by **L$_1$**/CuCl was first run at 25 °C in 2,5-hexanedione, but product **7a** was obtained in only 73% ee, with **7a**/**7a'** ratio as 3.7:1 (entry 1). After screening some typical solvents, it was found that diyne **6a** had a good solubility in halogenated solvent, but dissolved poorly in other solvents. Fortunately, the reaction run in CH_2Cl_2 afforded chiral monotriazole **7a** in 88% ee, although the **7a**/**7a'** ratio decreased to 1.9:1 (entry 3). Then modified PYBOX ligands **L$_3$**-**L$_6$** were examined by using CH_2Cl_2 as the solvent (entries 5-8), and **L$_5$** proved to be the best (entry 7). By using **L$_5$** was the optimized ligand, we further evaluated different copper salts, and the use of CuBr could afford **7a**/**7a'** ratio up to 6.6:1 and 98% ee for **7a** (entry 11). Varying the ratio of diyne **6a** and azide **2h** from 1:1 to 1.2:1 enhanced the **7a**/**7a'** ratio to 12:1 (entry 12). Lowering the catalyst loading to 10 mol% resulted in slightly diminished yield and **7a**/**7a'** ratio (Entry 18).

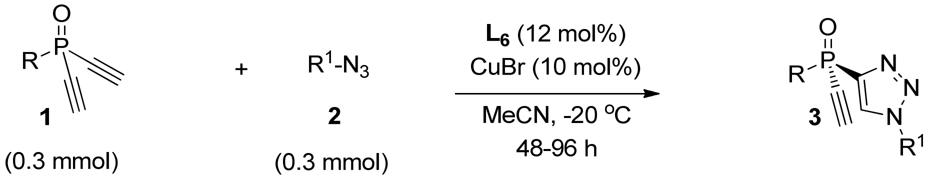
Table S5. Condition optimization for remote desymmetric enantioselective CuAAC of 6a



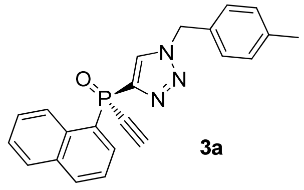
entry	ligand	CuX	solvent	**4a**:**4a'**[a]	NMR yield of **4a** (%)[a]	ee of **4a** (%)[b]
1	**L$_1$**	CuCl	2,5-hexanedione	3.7:1	50	73
2	**L$_1$**	CuCl	Toluene	1.4:1	19	49
3	**L$_1$**	CuCl	CH_2Cl_2	1.9:1	45	88
4	**L$_1$**	CuCl	CH_2ClCH_2Cl	1.5:1	40	89
5	**L$_3$**	CuCl	CH_2Cl_2	3.6:1	57	92
6	**L$_4$**	CuCl	CH_2Cl_2	4.4:1	61	97
7	**L$_5$**	CuCl	CH_2Cl_2	4.6:1	62	96
8	**L$_6$**	CuCl	CH_2Cl_2	3.5:1	57	93
9	**L$_5$**	CuI	CH_2Cl_2	3.9:1	60	87
10	**L$_5$**	$CuPF_6$	CH_2Cl_2	5.4:1	64	99
11	**L$_5$**	CuBr	CH_2Cl_2	6.6:1	66	98
12[c]	**L$_5$**	CuBr	CH_2Cl_2	12.0:1	81[d]	96
13[e]	**L$_5$**	CuBr	CH_2Cl_2	10.5:1	75[d]	97

[a] Determined by ^{1}H NMR (800 MHz) analysis, NMR yield using anisole as the internal standard; [b] Determined by chiral HPLC analysis. [c] **6a**/**2h** = 1.2/1; 0.15 mmol of **2h** used (reaction time 2 d). [d] Isolated yield. [e] 10 mol% CuBr and 12 mol% **L$_5$** used.

5. Desymmetric CuAAC reaction of diethynylphosphine oxides 1

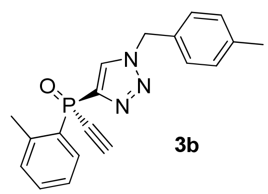


To a 25 mL Schlenk tube was added **L$_6$** (18.9 mg, 0.036 mmol) and CuBr (4.3 mg, 0.030 mmol), followed by the addition of 6.0 mL of anhydrous MeCN. The solution was stirred at 25 °C for 2 h, and then diethynylphosphine oxides **1** (0.30 mmol) was added. After the mixture was cooled to -20 °C for 0.5 h, azide **2** (0.30 mmol) was added. The resulting mixture was stirred at -20 °C for 48 h to 96 h till full conversion of **2** by TLC analysis. After the solvent was removed under reduced pressure, the residue was directly subjected to a short column chromatography to remove the copper salt, using an eluent of CH_2Cl_2/EtOAc (2:1, v/v). A portion of the combined homogenous solution was used to determine the ratio of **3**/**3**' by ^{1}H NMR (400 MHz) analysis. And then the sample for NMR analysis and the remaining mixture were combined for column chromatography purification using CH_2Cl_2/EtOAc (2:1, v/v) as the eluent, to afford the desired monotriazole **3**.



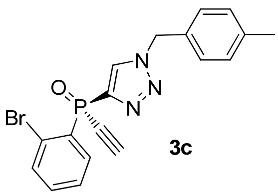
3a

Product **3a** was obtained in 80% yield as white solid, Mp: 188-190 °C. IR (neat): 3101, 2923, 2349, 2048, 1653, 1547, 1437, 1361, 1216, 1047, 986, 801 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 11.39 min, t_r (minor) = 7.82 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{25}$= - 25.5 (c = 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67-8.65 (m, 1H), 8.30 (dd, *J* = 18.7, 7.1 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 8.01 (s, 1H), 7.90-7.89 (m, 1H), 7.58-7.51 (m, 3H), 7.18-7.14 (m, 4H), 5.56-5.45 (m, 2H), 3.39 (d, *J* = 10.3 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.82 (d, *J* = 161.0 Hz), 139.19, 134.30 (d, *J* = 3.0 Hz), 133.70 (d, *J* = 11.0 Hz), 133.17 (d, *J* = 11.0 Hz), 132.41 (d, *J* = 11.0 Hz), 130.45, 130.17 (d, *J* = 30.0 Hz), 129.96, 129.07 (d, *J* = 2.0 Hz), 128.44, 127.56, 126.64, 126.52 (d, *J* = 127.0 Hz), 126.07 (d, *J* = 7.0 Hz), 124.68 (d, *J* = 16.0 Hz), 94.54 (d, *J* = 31.0 Hz), 78.73 (d, *J* = 173.0 Hz), 54.24, 21.16; ^{31}P NMR (122 MHz, $CDCl_3$): δ -4.07; HRMS (EI): Exact mass calcd for $C_{22}H_{18}N_3OP$: 371.1188, Found: 371.1192.



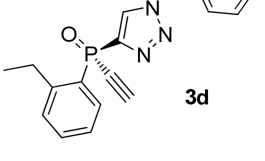
3b

Product **3b** was obtained in 81% yield as white solid, Mp: 120-122 ºC. IR (neat): 3121, 2988, 2049, 1591, 1514, 1452, 1360, 1259, 1048, 862, 807 cm^{-1}; HPLC analysis (Chiralcel AD-H, 20% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 15.94 min, t_r (minor) = 14.45 min) gave the isomeric composition of the product: 94% ee. $[\alpha]_D^{25}$ = - 13.0 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.99 (dd, *J* = 15.6 Hz, 8.0 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.31 (td, *J* = 7.6, 2.5 Hz, 1H), 7.26-7.23 (m, 1H), 7.21-7.16 (m, 4H), 5.58-5.50 (m, 2H), 3.34 (d, *J* = 10.2 Hz, 1H), 2.56 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.10 (d, *J* = 11.0 Hz), 141.77 (d, *J* = 160.0 Hz), 139.19, 133.07 (d, *J* = 2.0 Hz), 132.56 (d, *J* = 13.0 Hz), 131.76 (d, *J* = 12.0 Hz), 130.41 (d, *J* = 21.0 Hz), 130.02, 129.98, 128.52 (d, *J* = 128.0 Hz), 128.45, 125.84 (d, *J* = 14.0 Hz), 94.13 (d, *J* = 31.0 Hz), 78.62 (d, *J* = 171.0 Hz), 54.24, 21.17, 21.16; ^{31}P NMR (122 MHz, $CDCl_3$): δ -3.34; HRMS (EI): Exact mass calcd for $C_{19}H_{18}N_3OP$: 335.1188, Found: 335.1192.



3c

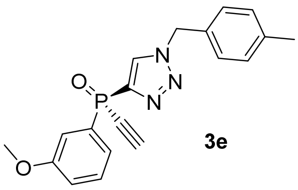
Product **3c** was obtained in 77% yield as white solid, Mp: 152-154 ºC. IR (neat): 3367, 3127, 2050, 2054, 1574, 1493, 1420, 1202, 1048, 805, 757 cm^{-1}; HPLC analysis (Chiralcel OD-H, 30% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 17.00 min, t_r (minor) = 21.56 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{25}$ = - 8.0 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.19 (m, 1H), 8.02 (s, 1H), 7.64-7.61 (m, 1H), 7.52-7.42 (m, 2H), 7.20-7.16 (m, 4H), 5.56 (s, 2H), 3.37 (d, *J* = 10.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.76 (d, *J* = 168.0 Hz), 139.12, 135.44 (d, *J* = 10.0 Hz), 134.56 (d, *J* = 9.0 Hz), 134.46 (d, *J* = 2.0 Hz), 130.82 (d, *J* = 30.0 Hz), 130.63, 130.23 (d, *J* = 134.0 Hz), 129.95, 128.30, 127.48 (d, *J* = 13.0 Hz), 125.30 (d, *J* = 6.0 Hz), 94.85 (d, *J* = 32.0 Hz), 77.32 (d, *J* =181.0 Hz), 54.20, 21.20; ^{31}P NMR (162 MHz, $CDCl_3$): δ -5.75; HRMS (EI): Exact mass calcd for $C_{18}H_{15}N_3{}^{79}BrOP$: 399.0136, Found: 399.0134.



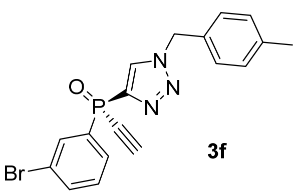
3d

Product **3d** was obtained in 72% yield as white solid, Mp: 98-100 ºC. IR (neat): 3120, 2989, 2050, 1868, 1716, 1559, 1494, 1258, 1075, 929, 718 cm^{-1}; HPLC analysis (Chiralcel OD-H, 20% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 17.07 min, t_r (minor) = 23.75 min) gave the isomeric composition of the product: 92% ee. $[\alpha]_D^{25}$ = - 16.3 (c = 1.03, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04-7.96 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.37-7.29 (m, 2H), 7.25-7.18 (m, 4H), 5.56 (s, 2H), 3.37 (d, *J* = 10.2 Hz, 1H), 3.01 (q, *J* = 7.4 Hz, 2H), 2.38 (s, 3H), 1.15 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

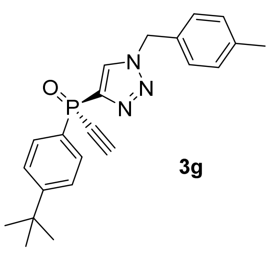
148.48 (d, J = 11.0 Hz), 142.20 (d, J = 159.0 Hz), 139.22, 133.20 (d, J = 3.0 Hz), 132.57 (d, J = 13.0 Hz), 130.34 (d, J = 34.0 Hz), 129.98, 129.88, 129.86, 128.47, 128.22 (d, J = 128.0 Hz), 125.79 (d, J = 15.0 Hz), 94.01 (d, J = 31.0 Hz), 79.07 (d, J = 171.0 Hz), 54.26, 26.95 (d, J = 6.0 Hz), 21.16, 15.31; ^{31}P NMR (122 MHz, CDCl$_3$): δ -2.90; HRMS (EI): Exact mass calcd for $C_{20}H_{20}N_3OP$: 349.1344, Found: 349.1339.


3e

Product **3e** was obtained in 65% yield as white solid, Mp: 122-124 °C. IR (neat): 3138, 2922, 2349, 2053, 1600, 1573, 1483, 1294, 1153, 925, 784 cm^{-1}; HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 7.53 min, t$_r$ (minor) = 6.59 min) gave the isomeric composition of the product: 92% ee. $[\alpha]_D^{25}$ = - 22.8 (c = 1.00, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.97 (s, 1H), 7.58-7.48 (m, 2H), 7.40 (td, J = 7.9, 4.7 Hz, 1H), 7.22-7.14 (m, 4H), 7.10-7.07 (m, 1H), 5.56-5.46 (m, 2H), 3.83 (s, 3H), 3.32 (d, J = 10.3 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 159.66 (d, J = 18.0 Hz), 141.45 (d, J = 161.0 Hz), 139.21, 132.10 (d, J = 128.0 Hz), 130.28 (d, J = 27.0 Hz), 130.00, 129.97, 129.72, 128.55, 123.14 (d, J = 12.0 Hz), 119.43 (d, J = 3.0 Hz), 115.30 (d, J = 13.0 Hz), 93.92 (d, J = 32.0 Hz), 78.67 (d, J = 173.0 Hz), 55.49 (d, J = 2.0 Hz), 54.22, 21.15; ^{31}P NMR (122 MHz, CDCl$_3$): δ -5.35; HRMS (EI): Exact mass calcd for $C_{19}H_{18}N_3O_2P$: 351.1137, Found: 351.1138.

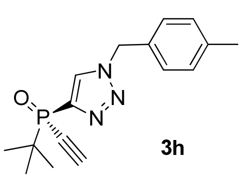

3f

Product **3f** was obtained in 60% yield, Mp: 150-152 °C. IR (neat): 3123, 2972, 2901, 1559, 1395, 1257, 1067, 784 cm^{-1}; HPLC analysis (Chiralcel AD-H, 20% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 17.00 min, t$_r$ (minor) = 14.14 min) gave the isomeric composition of the product: 83% ee. $[\alpha]_D^{25}$ = - 27.9 (c = 1.00, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.11 (d, J = 14.7 Hz, 1H), 8.00-7.91 (m, 2H), 7.70 (d, J = 7.5 Hz, 1H), 7.38 (td, J = 7.8, 4.1 Hz, 1H), 7.24-7.14 (m, 4H), 5.57-5.49 (m, 2H), 3.34 (d, J = 10.5 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 140.76 (d, J = 163.0 Hz), 139.30, 136.00 (d, J = 3.0 Hz), 133.56 (d, J = 13.0 Hz), 133.40 (d, J = 127.0 Hz), 130.46 (d, J = 15.0 Hz), 130.28 (d, J = 10.0 Hz), 130.02, 129.99, 129.48 (d, J = 11.0 Hz), 128.62, 123.14 (d, J = 18.0 Hz), 94.71 (d, J = 32.0 Hz), 78.24 (d, J = 175.0 Hz), 54.31, 21.21; ^{31}P NMR (162 MHz, CDCl$_3$): δ -7.21; HRMS (EI): Exact mass calcd for $C_{18}H_{15}{}^{79}BrN_3OP$: 399.0136, Found: 399.0138.



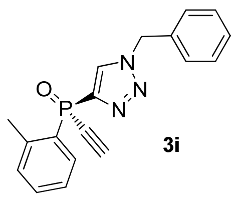
3g

Product **3g** was obtained in 80% yield as white solid, Mp: 220-222 °C. IR (neat): 3152, 2973, 2924, 2055, 1658, 1513, 1465, 1393, 1131, 1066, 757 cm^{-1}; HPLC analysis (Chiralcel AD-H, 20% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 12.27 min, t_r (minor) = 11.62 min) gave the isomeric composition of the product: 90% ee. $[\alpha]_D^{25}$ = - 45.0 (c = 1.00, CHCl$_3$); ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.99 (s, 1H), 7.97-7.90 (m, 2H), 7.54 (dd, *J* = 8.0, 2.3 Hz, 2H), 7.24-7.17 (m, 4H), 5.59-5.48 (m, 2H), 3.31 (d, *J* = 10.2 Hz, 1H), 2.38 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 156.62 (d, *J* = 3.8 Hz), 141.68 (d, *J* = 161.3 Hz), 139.18, 130.81 (d, *J* = 12.5 Hz), 130.10 (d, *J* = 87.5 Hz), 129.97, 129.75, 128.59, 127.46 (d, *J* = 132.5 Hz), 125.86 (d, *J* = 13.8 Hz), 93.76 (d, *J* = 31.2 Hz), 78.88 (d, *J* = 171.2 Hz), 54.21, 35.13, 31.06, 21.19; ^{31}P NMR (122 MHz, CDCl$_3$): δ -5.05; HRMS (EI): Exact mass calcd for $C_{22}H_{24}N_3OP$: 377.1657, Found: 377.1660.



3h

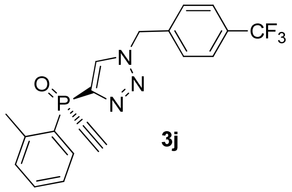
Product **3h** was obtained in 51% yield as white solid, Mp: 114-116 °C. IR (neat): 3160, 2962, 2050, 1516, 1496, 1473, 1365, 1219, 1169, 1106, 1051, 882, 815, 759 cm^{-1}; HPLC analysis (Chiralcel AD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 13.26 min, t_r (minor) = 11.70 min) gave the isomeric composition of the product: 75% ee. $[\alpha]_D^{25}$ = - 11.5 (c = 1.00, CHCl$_3$); ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.97 (s, 1H), 7.17 (s, 4H), 5.57-5.46 (m, 2H), 3.17 (d, *J* = 9.5 Hz, 1H), 2.33 (s, 3H), 1.26 (d, *J* = 18.1 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 139.26 (d, *J* = 143.0 Hz), 139.16, 131.11 (d, *J* = 24.0 Hz), 130.51, 129.97, 128.44, 93.12 (d, *J* = 25.0 Hz), 77.88 (d, *J* =150.0 Hz), 54.17, 33.73 (d, *J* = 87.0 Hz), 23.25, 21.16; ^{31}P NMR (162 MHz, CDCl$_3$): δ 19.36; HRMS (EI): Exact mass calcd for $C_{16}H_{20}N_3OP$: 301.1344, Found: 301.1346.



3i

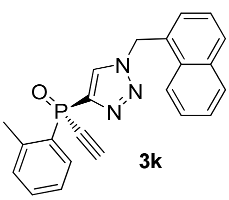
Product **3i** was obtained in 85% yield as white solid, Mp: 227-229 °C. IR (neat): 3146, 2051, 2049, 1591, 1495, 1454, 1360, 1275, 1076, 865, 757 cm^{-1}; HPLC analysis (Chiralcel AD-H, 20% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 17.64 min, t_r (minor) = 15.83 min) gave the isomeric composition of the product: 96% ee. $[\alpha]_D^{25}$ = - 6.70 (c = 1.00, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.03 (s, 1H), 7.99 (dd, *J* = 17.0, 7.8 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.40-7.38 (m, 3H), 7.33-7.24 (m, 4H), 5.63-5.55 (m, 2H), 3.34 (d, *J* = 10.2 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 141.44 (d, *J* = 161.2 Hz), 139.24, 132.96 (d, *J* = 3.8 Hz), 130.90 (d, *J* = 11.3 Hz), 130.20 (d, *J* = 43.8 Hz), 129.99, 129.50 (d, *J* = 77.5 Hz), 129.34, 128.77 (d, *J* = 15.0 Hz), 128.59, 128.42, 125.88 (d, *J* = 15.0 Hz), 94.02 (d, *J* = 31.2

Hz), 78.65 (d, J = 172.5 Hz), 54.24, 21.19; ^{31}P NMR (122 MHz, CDCl$_3$): δ -3.42; HRMS (EI): Exact mass calcd for $C_{18}H_{16}N_3OP$: 321.1031, Found: 321.1034.



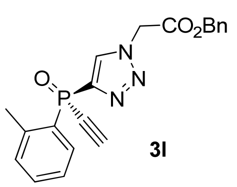
3j

Product **3j** was obtained in 83% yield as white solid, Mp: 190-192 ºC. IR (neat): 3119, 2349, 2049, 1620, 1494, 1453, 1324, 1197, 1066, 857, 774 cm^{-1}; HPLC analysis (Chiralcel AD-H, 20% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 16.74 min, t$_r$ (minor) = 14.85 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{25}$ = - 6.1 (c = 1.00, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.13 (s, 1H), 7.99 (dd, J = 16.9, 7.7 Hz, 1H), 7.65 (d, J = 8.1 Hz, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.41 (d, J = 8.1 Hz, 2H), 7.32 (td, J = 7.5, 2.5 Hz, 1H), 7.28-7.25 (m, 1H), 5.70-5.62 (m, 2H), 3.37 (d, J = 10.2 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 142.36 (d, J = 158.0 Hz), 142.09 (d, J = 11.0 Hz), 137.63, 133.20 (d, J = 3.0 Hz), 132.54 (d, J = 13.0 Hz), 131.83 (d, J = 13.0 Hz), 131.40 (q, J = 33.0 Hz), 130.50 (d, J = 28.0 Hz), 128.56, 128.31 (d, J = 128.0 Hz), 126.27 (q, J = 4.0 Hz), 125.90 (d, J = 15.0 Hz), 123.68 (q, J = 271.0 Hz), 94.28 (d, J = 30.0 Hz), 78.51 (d, J = 172.0 Hz), 53.67, 21.15 (d, J = 5.0 Hz); ^{31}P NMR (122 MHz, CDCl$_3$): δ -3.60; ^{19}F NMR (282 MHz, CDCl$_3$): δ -62.84; HRMS (EI): Exact mass calcd for $C_{19}H_{15}F_3N_3OP$: 389.0905, Found: 389.0907.



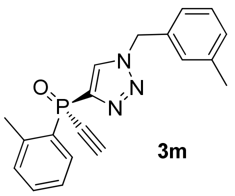
3k

Product **3k** was obtained in 84% yield as white solid, Mp: 122-124 ºC. IR (neat): 3133, 2921, 2349, 2045, 1593, 1491, 1454, 1284, 1097, 842, 787 cm^{-1}; HPLC analysis (Chiralcel AD-H, 20% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 25.44 min, t$_r$ (minor) = 21.39 min) gave the isomeric composition of the product: 91% ee. $[\alpha]_D^{25}$ = - 16.1 (c = 1.00, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.97-7.87 (m, 5H), 7.54-7.42 (m, 5H), 7.30-7.26 (m, 1H), 7.23-7.20 (m, 1H), 6.07-6.00 (m, 2H), 3.31 (d, J = 10.2 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 142.08 (d, J = 11.0 Hz), 141.72 (d, J = 159.0 Hz), 134.07, 133.06 (d, J = 3.0 Hz), 132.55 (d, J = 13.0 Hz), 131.74 (d, J = 13.0 Hz), 131.07, 130.56, 130.27 (d, J = 29.0 Hz), 129.13, 128.79, 128.44, 127.87, 127.49, 126.54, 125.81 (d, J = 15.0 Hz), 125.38, 122.59, 94.11 (d, J = 31.0 Hz), 78.56 (d, J = 171.0 Hz), 52.52, 21.07 (d, J = 6.0 Hz); ^{31}P NMR (122 MHz, CDCl$_3$): δ -3.26; HRMS (EI): Exact mass calcd for $C_{22}H_{18}N_3OP$: 371.1188, Found: 371.1190.



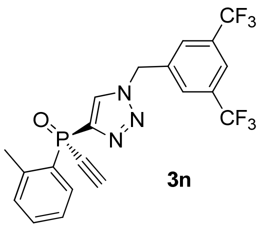
3l

Product **3l** was obtained in 77% yield as sticky oil. IR (Neat): 3130, 2955, 2053, 1750, 1593, 1498, 1453, 1384, 1192, 959, 791 cm^{-1}; HPLC analysis (Chiralcel AD-H, 20% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 26.18 min, t_r (minor) = 20.32 min) gave the isomeric composition of the product: 90% ee. $[\alpha]_D^{25}$ = - 1.58 (c = 1.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 8.01 (dd, *J* = 17.0, 6.9 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.39-7.31 (m, 6H), 7.28-7.24 (m, 1H), 5.34-5.28 (m, 2H), 5.23 (s, 2H), 3.37 (d, *J* = 10.2 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.80, 142.06 (d, *J* = 11.0 Hz), 141.81 (d, *J* =160.0 Hz), 134.47, 133.20 (d, *J* = 3.0 Hz), 132.57 (d, *J* = 13.0 Hz), 132.34 (d, *J* = 29.0 Hz), 131.83 (d, *J* = 13.0 Hz), 128.80, 128.73, 128.49, 128.33 (d, *J* = 128.0 Hz), 125.92 (d, *J* = 15.0 Hz), 94.86 (dd, *J* = 31.0, 2.0 Hz), 78.28 (d, *J* = 171.0, Hz), 68.10, 50.87, 21.04 (dd, *J* = 6.0, 2.0 Hz); ^{31}P NMR (122 MHz, $CDCl_3$): δ -3.65; HRMS (EI): Exact mass calcd for $C_{20}H_{18}N_3O_3P$: 379.1086, Found: 379.1082.



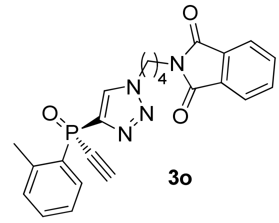
3m

Product **3m** was obtained in 80% yield as white solid, Mp: 161-163 °C. IR (neat): 3107, 2923, 2356, 2047, 1703, 1657, 1493, 1357, 1192, 1046, 747 cm^{-1}; HPLC analysis (Chiralcel AD-H, 20% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 14.91 min, t_r (minor) = 13.54 min) gave the isomeric composition of the product: 93% ee. $[\alpha]_D^{25}$ = - 15.5 (c = 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.99 (dd, *J* = 17.0, 7.8 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.34-7.31 (m, 1H), 7.29-7.24 (m, 2H), 7.20-7.18 (m, 1H), 7.10-7.08 (m, 2H), 5.58-5.50 (m, 2H), 3.36 (d, *J* = 10.2 Hz, 1H), 2.57 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.10 (d, *J* = 11.0 Hz), 141.8 5 (d, *J* = 160.0 Hz), 139.24, 133.42, 133.07 (d, *J* = 3.0 Hz), 132.57 (d, *J* = 13.0 Hz), 131.76 (d, *J* = 13.0 Hz), 130.23 (d, *J* = 29.0 Hz), 129.94, 129.21, 129.12, 128.54 (d, *J* = 128.0 Hz), 125.84 (d, *J* = 15.0 Hz), 125.49, 94.05 (d, *J* = 31.0 Hz), 78.65 (d, *J* = 172.0 Hz), 54.46, 21.31, 21.15 (d, *J* = 4.0 Hz); ^{31}P NMR (122 MHz, $CDCl_3$): δ -3.43; HRMS (EI): Exact mass calcd for $C_{19}H_{18}N_3O_3P$: 335.1188, Found: 335.1191.



3n

Product **3n** was obtained in 72% yield as white solid, Mp: 114-116 °C. IR (neat): 3217, 2925, 2349, 2054, 1627, 1503, 1456, 1381, 1349, 1278, 1124, 1001, 910, 887 cm^{-1}; HPLC analysis (Chiralcel AD-H, 5% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 36.81 min, t_r (minor) = 34.37 min) gave the isomeric composition of the product: 91% ee. $[\alpha]_D^{25}$ = - 4.6 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 8.00 (dd, *J* = 17.4, 7.3 Hz, 1H), 7.90 (s, 1H), 7.78 (s, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.33 (td, *J* = 7.6, 2.5 Hz, 1H), 7.29-7.26 (m, 1H), 5.76 (s, 2H), 3.39 (d, *J* = 10.3 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 142.32 (d, *J* = 159.0 Hz), 141.98 (d, *J* = 11.0 Hz), 136.77, 133.31 (d, *J* = 3.0 Hz), 132.58 (q, *J* = 34.0 Hz), 132.48 (d, *J* = 14.0 Hz), 131.87 (d, *J* = 12.0 Hz), 131.15 (d, *J* = 28.0 Hz), 128.49 (d, *J* = 2.0 Hz), 128.15 (d, *J* = 128.0 Hz), 125.94 (d, *J* = 14.0 Hz), 123.00 – 122.86 (m), 122.84 (q, *J* = 271.0 Hz), 94.74 (d, *J* = 31.0 Hz), 78.19 (d, *J* = 181.0 Hz), 52.92, 20.93; ^{31}P NMR (122 MHz, CDCl$_3$): δ -3.49; ^{19}F NMR (282 MHz, CDCl$_3$): δ -62.95; HRMS (EI): Exact mass calcd for C$_{20}$H$_{14}$F$_6$N$_3$OP: 457.0779, Found: 457.0783.

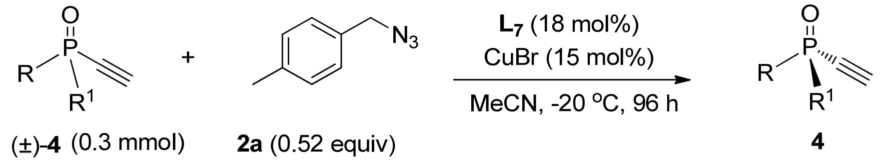


3o

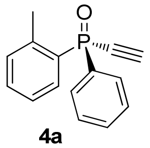
Product **3o** was obtained in 73% yield as sticky oil. IR (neat): 3126, 2925, 2052, 2049, 1768, 1702, 1496, 1362, 1284, 1081, 754 cm^{-1}; HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 15.17 min, t$_r$ (minor) = 14.34 min) gave the isomeric composition of the product: 90% ee. [α]$_D^{25}$ = - 3.50 (c = 1.00, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.16 (s, 1H), 7.98 (dd, *J* = 16.5, 7.3 Hz, 1H), 7.84-7.82 (m, 2H), 7.74-7.71 (m, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.34-7.29 (m, 1H), 7.27-7.24 (m, 1H), 4.50 (t, *J* = 7.3 Hz, 2H), 3.74 (t, *J* = 6.8 Hz, 2H), 3.37 (d, *J* = 10.2 Hz, 1H), 2.58 (s, 3H), 2.02-1.94 (m, 2H), 1.78-1.71 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.36, 142.13 (d, *J* = 11.0 Hz), 141.61 (d, *J* = 159.0 Hz), 134.11, 133.07 (d, *J* = 3.0 Hz), 132.57 (d, *J* = 13.0 Hz), 131.96, 131.77 (d, *J* = 13.0 Hz), 130.32 (d, *J* = 29.0 Hz), 128.52 (d, *J* = 128.0 Hz), 125.85 (d, *J* = 15.0 Hz), 123.37, 94.07 (d, *J* = 31.0 Hz), 78.65 (d, *J* = 171.0 Hz), 49.83, 36.69, 27.41, 25.52, 21.16 (d, *J* = 6.0 Hz); ^{31}P NMR (122 MHz, CDCl$_3$): δ -3.28; HRMS (EI): Exact mass calcd for C$_{23}$H$_{21}$N$_4$O$_3$P: 432.1351, Found: 432.1354.

6. Kinetic resolution of racemic monoethynylphosphine oxides 4 and their catalytic enantioselective CuAAC reaction.

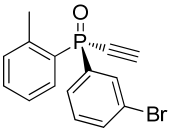
6.1 Kinetic resolution of racemic monoethynylphosphine oxides 4



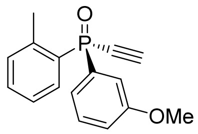
To a 25 mL Schlenk tube was added **L**$_7$ (27.6 mg, 0.054 mmol) and CuBr (6.4 mg, 0.045 mmol), followed by the addition of 4.0 mL of anhydrous MeCN. The mixture was stirred at 25 °C for 2 h, and racemic monoethynylphosphine oxides **4** (0.30 mmol) was added. After the reaction was cooled down to -20 °C for 0.5 h, azide **2a** (0.156 mmol, 0.52 equiv) was added. The resulting mixture was stirred at -20 °C for 96 h till full conversion of **2a** by TLC analysis. After the solvent was removed under reduced pressure, the residue was subjected to column chromatography for purification using PE/EtOAc/CH_2Cl_2 (4:2:1, v/v/v) as the eluent, to afford the desired chiral monoethynylphosphine oxides **4**.


4a

The reaction afforded **4a** in 42% recovery as white solid, Mp: 120-122 °C. IR (neat): 3142, 2048, 1595, 1438, 1289, 1187, 1078, 1031, 805, 790, 722 cm^{-1}; HPLC analysis (Chiralcel AD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 10.80 min, t$_r$ (minor) = 11.78 min) gave the isomeric composition of the product: 96% ee. $[\alpha]_D^{25}$ = + 3.4 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 15.9, 7.6 Hz, 1H), 7.82-7.76 (m, 2H), 7.56 (td, *J* = 7.2, 1.4 Hz, 1H), 7.51-7.45(m, 3H), 7.32 (t, *J* = 6.5 Hz, 1H), 7.26-7.22 (m, 1H), 3.34 (d, *J* = 9.6 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.97 (d, *J* = 10.0 Hz), 132.85 (d, *J* = 7.0 Hz), 132.77 (d, *J* = 2.0 Hz), 132.39 (d, *J* = 3.0 Hz), 132.37 (d, *J* = 119.0 Hz), 131.75 (d, *J* = 12.0 Hz), 130.95 (d, *J* = 12.0 Hz), 129.40 (d, *J* = 120.0 Hz), 128.74 (d, *J* = 13.0 Hz), 125.70 (d, *J* = 14.0 Hz), 94.18 (d, *J* = 27.0 Hz), 79.01 (d, *J* = 158.0 Hz), 21.16 (d, *J* = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 9.40; HRMS (EI): Exact mass calcd for $C_{15}H_{13}OP$: 240.0704, Found: 240.0706.

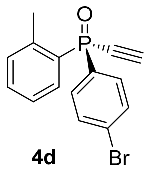

4b

The reaction afforded **4b** in 47% recovery as white solid, Mp: 150-152 °C. IR (neat): 3421, 3102, 2047, 1556, 1453, 1394, 1280, 1194, 1171, 1143, 1124, 1064, 993, 785 cm^{-1}; HPLC analysis (Chiralcel AD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 10.25 min, t$_r$ (minor) = 12.66 min) gave the isomeric composition of the product: 91% ee. $[\alpha]_D^{25}$ = - 2.2 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.89 (m, 2H), 7.71-7.66 (m, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.37-7.33 (m, 2H), 7.26-7.23 (m, 1H), 3.41 (d, J = 9.8 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.01 (d, J = 11.0 Hz), 135.46 (d, J = 3.0 Hz),135.18 (d, J = 117.0 Hz), 133.62 (d, J = 13.0 Hz), 133.12 (d, J = 3.0 Hz), 132.82 (d, J = 12.0 Hz), 131.91 (d, J = 12.0 Hz), 130.41 (d, J = 14.0 Hz), 129.44 (d, J = 11.0 Hz), 128.67 (d, J = 121.0 Hz), 125.86 (d, J = 14.0 Hz), 123.22 (d, J = 17.0 Hz), 94.85 (d, J = 28.0 Hz), 78.50 (d, J = 161.0 Hz), 21.19 (d, J = 4.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 7.82; HRMS (EI): Exact mass calcd for $C_{15}H_{12}{}^{79}BrOP$: 317.9809, Found: 317.9813.



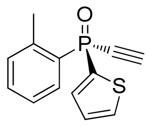
4c

The reaction afforded **4c** in 43% recovery as white solid, Mp: 122-124 °C. IR (neat): 3118, 2045, 1576, 1482, 1286, 1181, 1040, 859, 779, 695 cm^{-1}; HPLC analysis (Chiralcel AD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 12.41 min, t_r (minor) = 14.01 min) gave the isomeric composition of the product: 85% ee. $[\alpha]_D^{25}$ = - 3.5 (c = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (dd, J = 16.1, 7.6 Hz, 1H), 7.50-7.29 (m, 5H), 7.26-7.22 (m, 1H), 7.10-7.07 (m, 1H), 3.83 (s, 3H), 3.34 (d, J = 9.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.66 (d, J = 16.0 Hz), 142.05 (d, J = 10.0 Hz), 133.66 (d, J = 119.0 Hz), 132.84 (d, J = 4.0 Hz), 132.76 (d, J = 6.0 Hz), 131.74 (d, J = 12.0 Hz), 130.02 (d, J = 16.0 Hz), 129.36 (d, J = 120.0 Hz), 125.68 (d, J = 14.0 Hz), 123.14 (d, J = 12.0 Hz), 118.57 (d, J = 3.0 Hz), 115.72 (d, J = 13.0 Hz), 94.15 (d, J = 27.0 Hz), 78.99 (d, J = 159.0 Hz), 55.50, 21.18 (d, J = 4.0 Hz); ^{31}P NMR (122 MHz, $CDCl_3$): δ 9.57; HRMS (EI): Exact mass calcd for $C_{16}H_{15}O_2P$: 270.0810, Found: 270.0811.



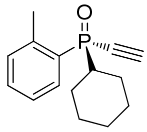
4d

The reaction afforded **4d** in 42% recovery as white solid, Mp: 138-140 °C. IR (neat): 3166, 2047, 1574, 1474, 1386, 1191, 1107, 1011, 828, 1278, 756 cm^{-1}; HPLC analysis (Chiralcel AD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 12.04 min, t_r (minor) = 15.37 min) gave the isomeric composition of the product: 94% ee. $[\alpha]_D^{25}$ = -27.4 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, J = 16.1, 7.6 Hz, 1H), 7.68-7.63 (m, 4H), 7.49 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 6.5 Hz, 1H), 7.28-7.24 (m, 1H), 3.41 (d, J = 9.8 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.97 (d, J = 10.0 Hz), 133.04 (d, J = 2.0 Hz), 132.77 (d, J = 13.0 Hz), 132.48 (d, J = 12.0 Hz), 132.07 (d, J = 14.0 Hz), 131.87 (d, J = 12.0 Hz), 131.57 (d, J = 120.0 Hz), 128.90 (d, J = 121.0 Hz), 127.63 (d, J = 4.0 Hz), 125.81 (d, J = 14.0 Hz), 94.63 (d, J = 27.0 Hz), 78.65 (d, J = 161.0 Hz), 21.15 (d, J = 4.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.61; HRMS (EI): Exact mass calcd for $C_{15}H_{12}{}^{79}BrOP$: 317.9809, Found: 317.9811.



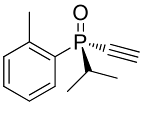
4e

The reaction afforded **4e** in 48% recovery as white solid, Mp: 110-112 °C. IR (neat): 3099, 2047, 1592, 1451, 1334, 1274, 1180, 1092, 1016, 854, 756 cm^{-1}; HPLC analysis (Chiralcel AD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 12.35 min, t$_r$ (minor) = 11.74 min) gave the isomeric composition of the product: 99% ee. $[\alpha]_D^{25}$ = -3.6 (c = 1.00, CHCl$_3$); ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.96 (dd, *J* = 16.9, 7.1 Hz, 1H), 7.77-7.74 (m, 1H), 7.60 (dd, *J* = 8.5, 3.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.36-7.33 (m, 1H), 7.29-7.25 (m, 1H), 7.21-7.17 (m, 1H), 3.38 (d, *J* = 10.0 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 142.11 (d, *J* = 10.0 Hz), 136.31 (d, *J* = 12.0 Hz), 134.27 (d, *J* = 6.0 Hz), 133.74 (d, *J* = 133.0 Hz), 133.04 (d, *J* = 3.0 Hz), 132.51 (d, *J* = 13.0 Hz), 131.82 (d, *J* = 12.0 Hz), 129.68 (d, *J* = 126.0 Hz), 128.42 (d, *J* = 16.0 Hz), 125.79 (d, *J* = 14.0 Hz), 94.04 (d, *J* = 30.0 Hz), 79.14 (d, *J* = 169.0 Hz), 21.16 (d, *J* = 5.0 Hz); ^{31}P NMR (122 MHz, CDCl$_3$): δ -0.49; HRMS (EI): Exact mass calcd for $C_{13}H_{11}OPS$: 246.0268, Found: 246.0266.



4f

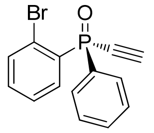
The reaction afforded **4f** in 44% recovery as white solid, Mp: 100-102 °C. IR (neat): 3119, 2849, 2042, 1593, 1448, 1347, 1208, 1115, 1001, 888, 804, 755 cm^{-1}; HPLC analysis (Chiralcel AD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 7.80 min, t$_r$ (minor) = 6.35 min) gave the isomeric composition of the product: 94% ee. $[\alpha]_D^{25}$ = + 28.0 (c = 1.00, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.89 (dd, *J* = 14.7, 7.6 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.30-7.23 (m, 2H), 3.20 (d, *J* = 9.0 Hz, 1H), 2.66 (s, 3H), 2.04-1.82 (m, 5H), 1.70 (s, 1H), 1.46-1.41 (m, 2H), 1.31-1.18 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 141.69 (d, *J* = 10.0 Hz), 132.87 (d, *J* = 11.0 Hz), 132.16 (d, *J* = 3.0 Hz), 131.81 (d, *J* = 11.0 Hz), 127.65 (d, *J* = 109.0 Hz), 125.57 (d, *J* = 12.0 Hz), 92.95 (d, *J* = 23.0 Hz), 78.23 (d, *J* = 141.0 Hz), 40.53 (d, *J* = 83.0 Hz), 26.26 (d, *J* = 4.0 Hz), 26.11 (d, *J* = 4.0 Hz), 25.70 (d, *J* = 2.0 Hz), 25.47 (d, *J* = 2.0 Hz), 24.60 (d, *J* = 2.0 Hz), 21.44 (d, *J* = 3.0 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ 25.91; HRMS (EI): Exact mass calcd for $C_{15}H_{19}OP$: 246.1174, Found: 246.1170.



4g

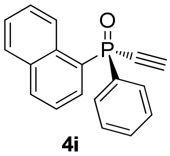
The reaction afforded **4g** in 43% recovery as white solid, Mp: 98-100 °C. IR (neat): 3099, 2969, 2044, 1721, 1679, 1536, 1451, 1384, 1262, 1178, 879, 802, 767 cm^{-1}; HPLC analysis (Chiralcel AD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 7.68 min, t$_r$ (minor) = 6.60 min) gave the isomeric composition of the product: 90% ee. $[\alpha]_D^{25}$ = + 26.2 (c = 1.00, CHCl$_3$); ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.95-7.88 (m, 1H), 7.46-7.40 (m, 1H), 7.32-7.24 (m, 2H), 3.21 (d, *J* = 9.0 Hz, 1H), 2.67 (s, 3H), 2.33-2.25 (m, 1H), 1.27-1.13 (m, 6H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 141.62 (d, J = 10.0 Hz), 132.84 (d, J = 10.0 Hz), 132.25 (d, J = 3.0 Hz), 131.85 (d, J = 12.0 Hz), 127.75 (d, J = 110.0 Hz), 125.59 (d, J = 13.0 Hz), 93.10 (d, J = 22.0 Hz), 77.92 (d, J = 108.0 Hz), 30.48 (d, J = 82.0 Hz), 21.37 (d, J = 4.0 Hz), 15.87 (d, J = 2.0 Hz), 14.83 (d, J = 3.0 Hz); ^{31}P NMR (122 MHz, $CDCl_3$): δ 29.33; HRMS (EI): Exact mass calcd for $C_{12}H_{15}OP$: 206.0861, Found: 206.0865.



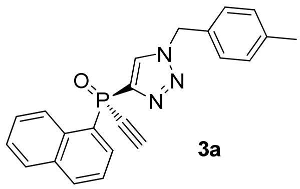
4h

The reaction afforded **4h** in 44% recovery as white solid, Mp: 134-136 °C. IR (neat): 3328, 3173, 2049, 1573, 1437, 1254, 1159, 1109, 1024, 802, 762, 718, 674 cm^{-1}; HPLC analysis (Chiralcel AD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 15.41 min, t_r (minor) = 13.45 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{25}$ = + 24.7 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (ddd, J = 14.3, 7.6, 1.8 Hz, 1H), 7.83-7.78 (m, 2H), 7.61-7.43 (m, 6H), 3.38 (d, J = 10.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.57 (d, J = 9.0 Hz), 134.56 (d, J = 8.0 Hz), 134.11 (d, J = 2.0 Hz), 132.54 (d, J = 3.0 Hz),131.62 (d, J = 126.0 Hz), 131.19 (d, J = 124.0 Hz), 131.15 (d, J = 12.0 Hz), 128.64 (d, J = 14.0 Hz), 127.31 (d, J = 12.0 Hz), 125.47 (d, J = 7.0 Hz), 94.64 (d, J = 29.0 Hz), 77.77 (d, J = 168.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 7.56; HRMS (EI): Exact mass calcd for $C_{14}H_{10}{}^{79}BrOP$: 303.9653, Found: 303.9651.



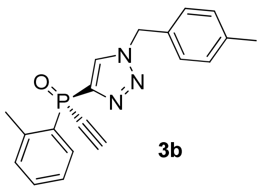
4i

The reaction afforded **4i** in 45% recovery as white solid, Mp: 152-154 °C. IR (neat): 3187, 2049, 1589, 1507, 1437, 1206, 1151, 1026, 982, 830, 780, 722, 688 cm^{-1}; HPLC analysis (Chiralcel OD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 15.57 min, t_r (minor) = 14.38 min) gave the isomeric composition of the product: 97% ee. $[\alpha]_D^{25}$ = + 17.1 (c = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (d, J = 7.5 Hz, 1H), 8.20 (dd, J = 17.6, 6.9 Hz, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.89-7.82 (m, 3H), 7.55-7.48 (m, 6H), 3.40 (d, J = 9.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.00 (d, J = 3.0 Hz), 133.74 (d, J = 10.0 Hz), 133.30 (d, J = 11.0 Hz), 132.58, 132.52 (d, J = 121.0 Hz), 132.51 (d, J = 3.0 Hz), 131.02 (d, J = 11.0 Hz), 129.02 (d, J = 1.0 Hz), 128.79 (d, J = 14.0 Hz), 127.50, 127.28 (d, J = 119.0 Hz), 126.61, 126.34 (d, J = 6.0 Hz), 124.55 (d, J = 15.0 Hz), 94.66 (d, J = 28.0 Hz), 79.22 (d, J = 160.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 9.34; HRMS (EI): Exact mass calcd for $C_{18}H_{13}OP$: 276.0704, Found: 276.0707.



3a

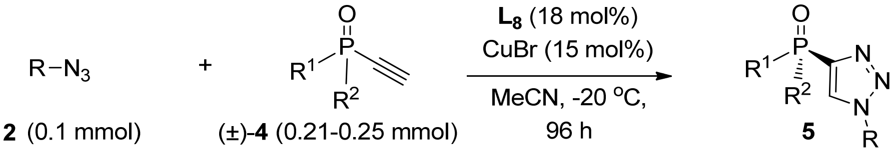
To a 25 mL Schlenk tube was added **L**$_7$ (27.6 mg, 0.054 mmol) and CuBr (6.4 mg, 0.045 mmol), followed by the addition of 7.5 mL of anhydrous MeCN. The mixture was stirred at 25 °C for 2 h, and the racemic **3a** (0.30 mmol) was added. After the reaction was cooled down to -10 °C for 0.5 h, azide **2a** (0.165 mmol, 0.55 equiv) was added. The resulting mixture was stirred at -10 °C for 96 h till full conversion of **2a** by TLC analysis. After the solvent was removed under reduced pressure, the residue was directly subjected to column chromatography for purification using PE/EtOAc/CH_2Cl_2 (4:2:1, v/v/v) as the eluent, to afford the desired chiral **3a** in 42% recovery yield, 93% ee.



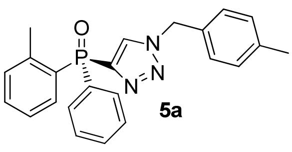
3b

To a 25 mL Schlenk tube was added **L**$_7$ (27.6 mg, 0.054 mmol) and CuBr (6.4 mg, 0.045 mmol), followed by the addition of 7.5 mL of anhydrous MeCN. The mixture was stirred at 25 °C for 2 h, and the racemic **3b** (0.30 mmol) was added. After the reaction was cooled down to -10 °C for 0.5 h, azide **2a** (0.165 mmol, 0.55 equiv) was added. The resulting mixture was stirred at -10 °C for 96 h till full conversion of **2a** by TLC analysis. After the solvent was removed under reduced pressure, the residue was directly subjected to column chromatography for purification using PE/EtOAc/CH_2Cl_2 (4:2:1, v/v/v) as the eluent, to afford the desired chiral **3b** in 44% recovery yield, 92% ee.

6.2 Enantioselective CuAAC reaction of racemic monoethynylphosphine oxides 4

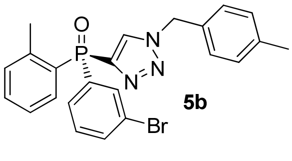


To a 25 mL Schlenk tube was added $\mathbf{L_8}$ (10.2 mg, 0.018 mmol) and CuBr (2.2 mg, 0.015 mmol), followed by the addition of 4.0 mL of anhydrous CH_3CN. The solution was stirred at 25 °C for 2 h, and then monoethynylphosphine oxides **4** (0.21-0.25 mmol, as indicated below) was added. After the reaction mixture was cooled down to -20 °C for 0.5 h, azide **2** (0.1 mmol) was added. The resulting mixture was stirred at -20 °C for 96 h till full conversion of **2** by TLC analysis. After the solvent was removed under reduced pressure, the residue was directly subjected to column chromatography for purification using CH_2Cl_2/EtOAc (2:1, v/v) as the eluent, to afford the desired products **5**.



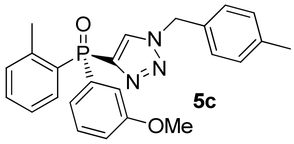
5a

The reaction used 0.21 mmol of racemic **4a**, affording **5a** in 94% yield as sticky oil, IR (neat): 3406, 1592, 2349, 1492, 1437, 1181, 1136, 1046, 998, 804, 747 cm^{-1}; HPLC analysis (Chiralcel AD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 25.63 min, t_r (minor) = 34.87 min) gave the isomeric composition of the product: 90% ee. $[\alpha]_D^{25}$ = + 53.7 (c = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.84 (dd, *J* = 12.8, 6.9 Hz, 2H), 7.53-7.38 (m, 5H), 7.23-7.16 (m, 6H), 5.53 (s, 2H), 2.39 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.57 (d, *J* = 9.0 Hz), 142.28 (d, *J* = 135.0 Hz), 139.00, 132.97 (d, *J* = 12.0 Hz), 132.48 (d, *J* = 109.0 Hz) 132.39 (d, *J* = 3.0 Hz), 131.99 (d, *J* = 3.0 Hz), 131.77 (d, *J* = 11.0 Hz), 131.47 (d, *J* = 10.0 Hz), 130.94, 130.92 (d, *J* = 52.0 Hz), 130.40 (d, *J* = 109.0 Hz), 129.90, 128.55, 128.52 (d, *J* = 13.0 Hz), 125.42 (d, *J* = 13.0 Hz), 54.11, 21.36 (d, *J* = 4.0 Hz), 21.18; ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.90; HRMS (EI): Exact mass calcd for $C_{23}H_{22}N_3OP$: 287.1501, Found: 387.1503.

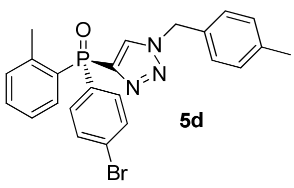


5b

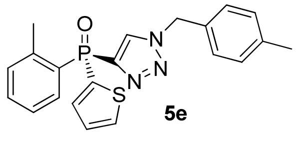
The reaction used 0.25 mmol of racemic **4b**, affording **5b** in 82% yield as sticky oil, IR (neat): 3424, 3053, 2049, 1593, 1557, 1492, 1395, 1285, 1184, 1046, 995, 804, 788 cm^{-1}; HPLC analysis (Chiralcel AD-H, 30% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 13.32 min, t_r (minor) = 17.06 min) gave the isomeric composition of the product: 90% ee. $[\alpha]_D^{25}$ = + 17.6 (c = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (s, 1H), 8.03-7.97 (m, 1H), 7.74 (dd, *J* = 12.4, 7.6 Hz, 1H), 7.65-7.61 (m, 1H), 7.52-7.40 (m, 2H), 7.31 (td, *J* = 7.8, 3.5 Hz, 1H), 7.25-7.16 (m, 6H), 5.54 (s, 2H), 2.40 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.62 (d, *J* = 9.0 Hz), 141.58 (d, *J* = 137.0 Hz), 139.17, 135.20 (d, *J* = 106.0 Hz), 135.05 (d, *J* = 2.0 Hz), 134.06 (d, *J* = 11.0 Hz), 132.95 (d, *J* = 13.0 Hz), 132.68 (d, *J* = 3.0 Hz), 131.88 (d, *J* = 12.0 Hz), 131.41 (d, *J* = 24.0 Hz), 130.35 (d, *J* = 26.0 Hz), 130.09, 129.98, 129.62 (d, *J* = 110.0 Hz), 128.64, 125.55 (d, *J* = 13.0 Hz), 123.03 (d, *J* = 15.0 Hz), 54.26, 21.39 (d, *J* = 5.0 Hz), 21.20; ^{31}P NMR (122 MHz, $CDCl_3$): δ 18.76; HRMS (EI): Exact mass calcd for $C_{23}H_{21}N_3{}^{79}BrOP$: 465.0606, Found: 465.0608.


5c

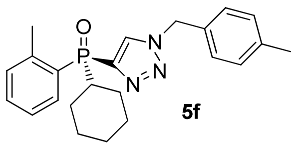
The reaction used 0.25 mmol of racemic **4c**, affording **5c** in 68% yield as sticky oil, IR (neat): 3423, 3055, 2838, 2315, 1702, 1649, 1543, 1358, 1287, 1135, 1035, 857, 757 cm^{-1}; HPLC analysis (Chiralcel AD-H, 30% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 13.31 min, t_r (minor) = 17.56 min) gave the isomeric composition of the product: 80% ee. $[\alpha]_D^{25}$ = + 19.6 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.47 (dd, *J* = 14.9, 7.7 Hz, 1H), 7.42-7.30 (m, 4H), 7.21-7.13 (m, 6H), 7.02 (dd, *J* = 6.2, 2.5 Hz, 1H), 5.50 (s, 2H), 3.76 (s, 3H), 2.40 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.51 (d, *J* = 15.0 Hz), 142.66 (d, *J* = 9.0 Hz), 142.34 (d, *J* = 135.0 Hz), 139.11, 133.78 (d, *J* = 107.0 Hz), 132.99 (d, *J* = 12.0 Hz), 132.40 (d, *J* = 3.0 Hz), 131.75 (d, *J* = 12.0 Hz), 130.96 (d, *J* = 23.0 Hz), 130.57, 130.30 (d, *J* = 109.0 Hz), 129.95, 129.78 (d, *J* = 15.0 Hz), 128.57, 125.42 (d, *J* = 13.0 Hz), 123.81 (d, *J* = 11.0 Hz), 118.40 (d, *J* = 2.0 Hz), 115.94 (d, *J* = 11.0 Hz), 55.41, 54.17, 21.37 (d, *J* = 5.0 Hz), 21.19; ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.04; HRMS (EI): Exact mass calcd for $C_{24}H_{24}N_3O_2P$: 417.1606, Found: 417.1609.


5d

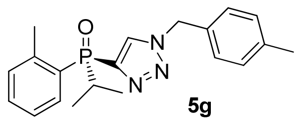
The reaction used 0.23 mmol of racemic **4d**, affording **5d** in 90% yield as sticky oil, IR (neat): 3065, 1702, 1650, 1574, 1474, 1383, 1183, 1103, 1067, 1009, 804, 734 cm^{-1}; HPLC analysis (Chiralcel AD-H, 30% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 13.92 min, t_r (minor) = 12.65 min) gave the isomeric composition of the product: 90% ee. $[\alpha]_D^{25}$ = + 52.2 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.70 (dd, *J* = 12.2, 8.4 Hz, 2H), 7.60-7.55 (m, 2H), 7.46 (dd, *J* = 15.0, 7.7 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.22-7.14 (m, 6H), 5.51 (s, 2H), 2.38 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.56 (d, *J* = 10.0 Hz), 141.86 (d, *J* = 137.0 Hz), 139.18, 133.06 (d, *J* = 11.0 Hz), 132.89 (d, *J* = 13.0 Hz), 132.62 (d, *J* = 3.0 Hz), 131.88 (d, *J* = 12.0 Hz), 131.82 (d, *J* = 13.0 Hz), 131.62 (d, *J* = 109.0 Hz), 131.06 (d, *J* = 23.0 Hz), 130.47, 129.98, 129.94 (d, *J* = 109.0 Hz), 128.60, 127.23 (d, *J* = 3.0 Hz), 125.53 (d, *J* = 13.0 Hz), 54.24, 21.34 (d, *J* = 4.0 Hz), 21.21; ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.36; HRMS (EI): Exact mass calcd for $C_{23}H_{21}N_3{}^{79}BrOP$: 465.0606, Found: 465.0609.


5e

The reaction used 0.21 mmol of racemic **4e**, affording **5e** in 92% yield as sticky oil, IR (neat): 3459, 2924, 2049, 1593, 1493, 1334, 1261, 1184, 1094, 1014, 804, 757, 714 cm^{-1}; HPLC analysis (Chiralcel AD-H, 30% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 11.05 min, t_r (minor) = 16.79 min) gave the isomeric composition of the product: 92% ee. $[\alpha]_D^{25}$ = - 26.3 (c = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.75-7.71 (m, 1H), 7.62-7.55 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.26-7.16 (m, 7H), 5.54 (s, 2H), 2.48 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.69 (d, *J* = 9.0 Hz), 142.58 (d, *J* = 143.0 Hz), 139.19, 136.52 (d, *J* = 11.0 Hz), 134.03 (d, *J* = 5.0 Hz), 133.68 (d, *J* = 119.0 Hz), 132.82 (d, *J* = 13.0 Hz), 132.61 (d, *J* = 3.0 Hz), 131.80 (d, *J* = 11.0 Hz), 130.72 (d, *J* = 25.0 Hz), 130.50 (d, *J* = 114.0 Hz), 130.49, 129.99, 128.58, 128.30 (d, *J* = 15.0 Hz), 125.54 (d, *J* = 14.0 Hz), 54.24, 21.41 (d, *J* = 4.0 Hz), 21.20; ^{31}P NMR (122 MHz, $CDCl_3$): δ 13.47; HRMS (EI): Exact mass calcd for $C_{21}H_{20}N_3OPS$: 393.1065, Found: 393.1070.

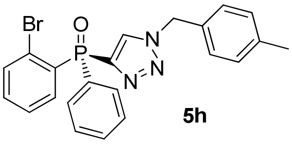

5f

The reaction used 0.21 mmol of racemic **4f**, affording **5f** in 90% yield as sticky oil, IR (neat): 2930, 2855, 1516, 1492, 1448, 1285, 1176, 1102, 1047, 887, 820 cm^{-1}; HPLC analysis (Chiralcel AD-H, 30% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 5.89 min, t_r (minor) = 10.38 min) gave the isomeric composition of the product: 93% ee. $[\alpha]_D^{25}$ = - 29.6 (c = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.91-7.84 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.24-7.13 (m, 6H), 5.53-5.44 (m, 2H), 2.65 (s, 3H), 2.52-2.41 (m, 1H), 2.33 (s, 3H), 1.85-1.57 (m, 6H), 1.44-1.17 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.30 (d, *J* = 121.0 Hz), 142.18 (d, *J* = 9.0 Hz), 139.06, 132.63 (d, *J* = 10.0 Hz), 131.64 (d, *J* =15.0 Hz), 131.59, 130.97 (d, *J* = 21.0 Hz), 130.50, 129.92, 129.04 (d, *J* = 98.0 Hz), 128.62, 125.56 (d, *J* = 12.0 Hz), 54.13, 38.84 (d, *J* = 75.0 Hz), 26.26 (d, *J* = 30.0 Hz), 26.25 (d, *J* = 2.0 Hz), 25.77 (d, *J* = 1.0 Hz), 24.91 (d, *J* = 4.0 Hz), 24.14 (d, *J* = 2.0 Hz), 21.52 (d, *J* = 1.0 Hz), 21.17; ^{31}P NMR (122 MHz, $CDCl_3$): δ 31.79; HRMS (EI): Exact mass calcd for $C_{23}H_{28}N_3OP$: 393.1970, Found: 393.1971.



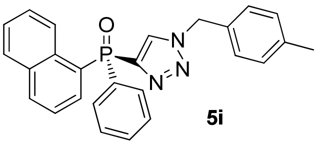
5g

The reaction used 0.21 mmol of racemic **4g**, affording **5g** in 84% yield as sticky oil, IR (neat): 3086, 2960, 2361, 1593, 1496, 1383, 1290, 1182, 1050, 1022, 924, 894 cm^{-1}; HPLC analysis (Chiralcel AD-H, 30% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 5.27 min, t_r (minor) = 7.81 min) gave the isomeric composition of the product: 90% ee. $[\alpha]_D^{25}$ = - 18.1 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.86 (dd, *J* = 13.1, 7.6 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.20-7.10 (m, 6H), 5.50-5.42 (m, 2H), 2.73-2.66 (m, 1H), 2.60 (s, 3H), 2.28 (s, 3H), 1.19 (dd, *J* = 17.2, 7.1 Hz, 3H), 1.08 (dd, *J* = 17.6, 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.32 (d, *J* = 121.0 Hz), 142.07 (d, *J* = 9.0 Hz), 139.07, 132.60 (d, *J* = 11.0 Hz), 131.78, 131.66, 130.92 (d, *J* = 21.0 Hz), 130.52, 129.93, 129.22 (d, *J* = 97.0 Hz), 128.57, 125.57 (d, *J* = 12.0 Hz), 54.13, 28.94 (d, *J* = 75.0 Hz), 21.46 (d, *J* = 2.0 Hz), 21.18, 15.44 (d, *J* = 3.0 Hz), 14.58 (d, *J* = 2.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.22; HRMS (EI): Exact mass calcd for $C_{20}H_{24}N_3OP$: 353.1657, Found: 353.1656.



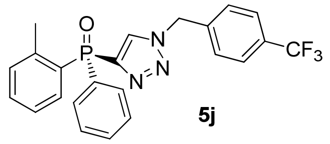
5h

The reaction used 0.21 mmol of racemic **4h**, affording **5h** in 84% yield as sticky oil, IR (neat): 3218, 2935, 2350, 2054, 1707, 1505, 1456, 1399, 1300, 1278, 1125, 1001, 887, 747 cm^{-1}; HPLC analysis (Chiralcel OD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 25.80 min, t_r (minor) = 22.90 min) gave the isomeric composition of the product: 90% ee. $[\alpha]_D^{25}$ = + 28.4 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.94-7.89 (m, 2H), 7.58-7.41 (m, 5H), 7.32-7.30 (m, 2H), 7.17-7.12 (m, 4H), 5.55-5.47 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.44 (d, *J* = 141.0 Hz), 139.05, 135.42 (d, *J* = 11.0 Hz), 134.75 (d, *J* = 8.0 Hz), 133.71 (d, *J* = 2.0 Hz), 132.69 (d, *J* = 112.0 Hz), 132.22 (d, *J* = 3.0 Hz), 131.85 (d, *J* = 10.0 Hz), 131.51 (d, *J* = 24.0 Hz), 131.13 (d, *J* = 114.0 Hz), 130.65, 129.92, 128.50 (d, *J* = 13.0 Hz), 128.47, 126.99 (d, *J* = 11.0 Hz), 126.44 (d, *J* = 5.0 Hz), 54.15, 21.20; ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.87; HRMS (EI): Exact mass calcd for $C_{22}H_{19}N_3{}^{79}BrOP$: 451.0449, Found: 451.0444.



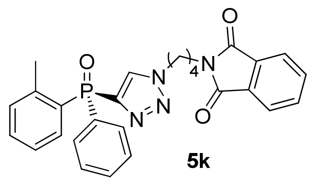
5i

The reaction used 0.23 mmol of racemic **4i**, affording **5i** in 86% yield as sticky oil, IR (neat): 3416, 2925, 3054, 1619, 1590, 1492, 1335, 1215, 1109, 1025, 983, 801, 774, 693 cm^{-1}; HPLC analysis (Chiralcel AD-H, 30% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 34.77 min, t_r (minor) = 18.17 min) gave the isomeric composition of the product: 90% ee. $[\alpha]_D^{25}$ = + 10.0 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, *J* = 8.2 Hz, 1H), 8.14 (s, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.91-7.83 (m, 4H), 7.48-7.39 (m, 6H), 7.18-7.13 (m, 4H), 5.53-5.46 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.42 (d, *J* = 136.0 Hz), 139.10, 133.78 (d, *J* = 10.0 Hz), 133.56, 133.52 (d, *J* = 15.0 Hz), 133.14 (d, *J* = 4.0 Hz), 132.64 (d, *J* = 115.0 Hz), 132.14 (d, *J* = 3.0 Hz), 131.60 (d, *J* = 11.0 Hz), 131.15 (d, *J* = 23.0 Hz), 130.57, 129.95, 128.90 (d, *J* = 1.0 Hz), 128.58 (d, *J* = 13.0 Hz), 128.57, 128.18 (d, *J* = 108.0 Hz), 127.31, 126.82 (d, *J* = 6.0 Hz), 126.43, 124.46 (d, *J* = 14.0 Hz), 54.18, 21.20; ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.04; HRMS (EI): Exact mass calcd for $C_{26}H_{22}N_3OP$: 423.1501, Found: 423.1505.



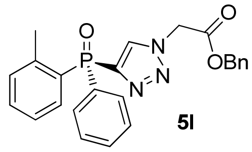
5j

The reaction used 0.21 mmol of racemic **4a**, affording **5j** in 90% yield as sticky oil, IR (neat): 3220, 2935, 2350, 2055, 1630, 1593, 1466, 1382, 1344, 1278, 1125, 1001, 960, 887 cm^{-1}; HPLC analysis (Chiralcel AD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 34.31 min, t_r (minor) = 47.03 min) gave the isomeric composition of the product: 90% ee. $[\alpha]_D^{25}$ = + 65.9 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.85-7.80 (m, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.52-7.38 (m, 7H), 7.22-7.17 (m, 2H), 5.64 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.87 (d, *J* = 134.0 Hz), 141.55 (d, *J* = 10.0 Hz), 136.74 (d, *J* = 1.0 Hz), 131.83, 131.47 (d, *J* = 3.0 Hz), 131.41 (d, *J* = 110.0 Hz), 131.06 (d, *J* = 3.0 Hz), 130.75, 130.42 (d, *J* = 24.0 Hz), 130.41 (d, *J* = 10.0 Hz), 130.19 (q, *J* = 34.0 Hz), 129.18 (d, *J* = 109.0 Hz), 127.62, 127.48, 125.17 (q, *J* = 4.0 Hz), 124.44 (d, *J* = 13.0 Hz), 122.68 (q, *J* = 271.0 Hz), 52.53, 20.30 (d, *J* = 5.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.87; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.76; HRMS (EI): Exact mass calcd for $C_{23}H_{19}F_3N_3OP$: 441.1218, Found: 441.1212.



5k

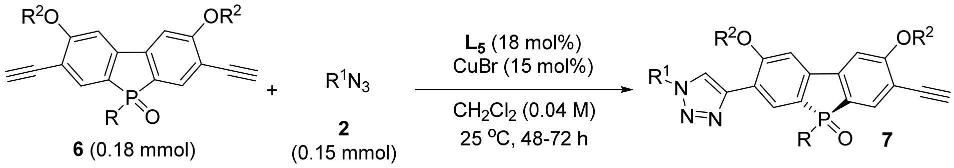
The reaction used 0.21 mmol of racemic **4a**, affording **5k** in 82% yield as sticky oil, IR (neat): 3450, 3056, 2953, 1768, 1704, 1593, 1494, 1362, 1285, 1109, 997, 862, 751 cm^{-1}; HPLC analysis (Chiralcel AD-H, 30% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 32.21 min, t_r (minor) = 44.91 min) gave the isomeric composition of the product: 90% ee. $[\alpha]_D^{25}$ = + 10.9 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.85-7.79 (m, 4H), 7.70-7.69 (m, 2H), 7.50-7.39 (m, 5H), 7.22-7.16 (m, 2H), 4.48 (t, *J* = 7.2 Hz, 2H), 3.72 (t, *J* = 6.8 Hz, 2H), 2.39 (s, 3H), 2.01-1.92 (m, 2H), 1.75-1.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.34, 142.60 (d, *J* = 10.0 Hz), 142.22 (d, *J* = 135.0 Hz), 134.10, 133.0 (d, *J* = 12.0 Hz), 132.45 (d, *J* = 110.0 Hz), 132.39 (d, *J* = 3.0 Hz), 131.98 (d, *J* = 3.0 Hz), 131.90, 131.77 (d, *J* = 11.0 Hz), 131.49 (d, *J* = 10.0 Hz), 131.10 (d, *J* = 23.0 Hz), 130.35 (d, *J* = 109.0 Hz), 128.53 (d, *J* = 13.0 Hz), 125.43 (d, *J* = 13.0 Hz), 123.33, 49.76, 36.71, 27.40, 25.54, 21.36 (d, *J* = 5.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.00; HRMS (EI): Exact mass calcd for $C_{27}H_{25}N_4O_3P$: 484.1664, Found: 484.1660.



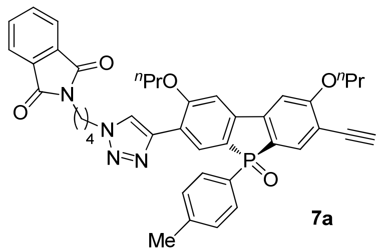
5l

The reaction used 0.21 mmol of racemic **4a**, affording **5l** in 92% yield as sticky oil, IR (neat): 3322, 3056, 2951, 2353, 1769, 1683, 1559, 1520, 1456, 1203, 1117, 1054, 980, 735 cm^{-1}; HPLC analysis (Chiralcel AD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 46.27 min, t_r (minor) = 58.91 min) gave the isomeric composition of the product: 90% ee. $[\alpha]_D^{25}$ = + 32.8 (c = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.87-7.80 (m, 2H), 7.56-7.39 (m, 5H), 7.36-7.28 (m, 5H), 7.25-7.16 (m, 2H), 5.34-5.20 (m, 2H), 5.20 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.73, 142.68 (d, *J* = 9.0 Hz), 142.65 (d, *J* = 134.0 Hz), 134.38, 133.04 (d, *J* = 13.0 Hz), 132.90 (d, *J* = 24.0 Hz), 132.49 (d, *J* = 3.0 Hz), 132.09 (d, *J* = 2.0 Hz), 131.82 (d, *J* = 11.0 Hz), 131.54 (d, *J* = 10.0 Hz), 131.22 (d, *J* = 91.0 Hz), 129.10 (d, *J* = 113.0 Hz), 128.86, 128.77, 128.65, 128.54, 125.50 (d, *J* = 14.0 Hz), 68.15, 50.83, 21.34 (d, *J* = 3.0 Hz); ^{31}P NMR (122 MHz, $CDCl_3$): δ 20.08; HRMS (EI): Exact mass calcd for $C_{24}H_{22}N_3O_3P$: 431.1399, Found: 431.1392.

7. Remote desymmetric CuAAC reaction of phosphole oxide-diynes 6

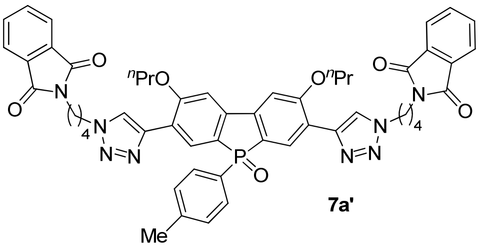


Under an atmosphere of N_2, to a 25 mL oven-dried Schlenk tube were added **L₅** (16.6 mg, 0.027mmol) and CuBr (3.2 mg, 0.0225 mmol), followed by the addition of 4.0 mL anhydrous CH_2Cl_2. After the solution was stirred at 25 °C for 1 h, phosphole oxide-diynes **6** (0.18 mmol) and azide **2** (0.15 mmol) was added. The mixture was stirred at 25 °C for 48 h till full conversion of **2** by TLC analysis. The mixture was directly subjected to column chromatography using CH_2Cl_2/ethyl acetate (from 4:1 to 2:1) as the eluent, giving the monotrizaole product **7**. The following use of EtOAc as the eluent allowed the isolation of ditriazole **7'**. The ratio of **7/7'** was determined by the isolated yield of **7/7'**.



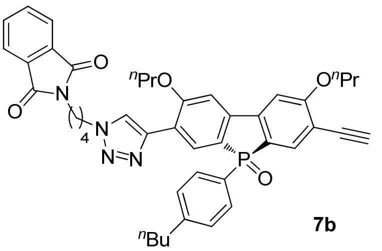
7a

Compound **7a** was obtained in 81% yield as brown solid, Mp: 238-240 °C. IR (KBr): 3290, 2926, 1705, 1544, 1244, 1044, 719 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 12.44 min, t_r (minor) = 26.39 min) gave the isomeric composition of the product: 96% ee. $[\alpha]_D^{20}$ = -16.3 (c = 0.53, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, J = 10.0 Hz, 1H), 7.94 (s, 1H), 7.83-7.81 (m, 2H), 7.71-7.69 (m, 3H), 7.54-7.48 (m, 2H), 7.21-7.13 (m, 4H), 4.48-4.30 (m, 3H), 4.18-4.07 (m, 3H), 3.73 (t, J = 6.8 Hz, 2H), 3.31 (s, 1H), 2.33 (s, 3H), 2.04-1.89 (m, 6H), 1.79-1.70 (m, 2H), 1.14-1.10 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.15 (d, J = 2.0 Hz), 164.12, 158.56 (d, J = 2.0 Hz), 143.62 (d, J = 21.0 Hz), 142.35 (d, J = 3.0 Hz), 141.94, 141.68 (d, J = 22.0 Hz), 134.59 (d, J = 11.0 Hz), 133.89, 131.81, 130.95 (d, J = 12.0 Hz), 129.27 (d, J = 13.0 Hz), 128.29, 127.61 (d, J = 108.0 Hz), 125.56 (dd, J = 53.0 Hz, 8.0 Hz), 124.45 (dd, J = 52.0 Hz, 8.0 Hz), 123.69, 123.15 (d, J = 9.0 Hz), 120.86 (d, J = 12.0 Hz), 112.54 (d, J = 13.0 Hz), 104.50 (d, J = 11.0 Hz), 104.02 (d, J = 11.0 Hz), 82.63, 79.24, 70.40, 70.34, 49.22, 36.76, 27.43, 25.44, 22.46, 22.32, 21.40, 10.77, 10.45; ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.16; HRMS (ESI): Exact mass calcd for $C_{41}H_{39}N_4O_5NaP$ $[M+Na]^+$: 721.2556, Found: 721.2530.



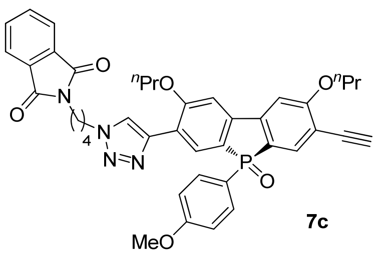
7a'

Compound **7a'** was obtained in 7% yield as brown solid, Mp: 242-244 °C. IR (KBr): 2938, 2877, 1710, 1602, 1487, 1287, 1039, 720 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.47 (d, J = 10.0 Hz, 2H), 7.80-7.76 (m, 6H), 7.70-7.66 (m, 4H), 7.50-7.45 (m, 2H), 7.14-7.08 (m, 4H), 4.46-4.33 (m, 4H), 4.28-4.21 (m, 2H), 4.06-4.00 (m, 2H), 3.74-3.67 (m, 4H), 2.28 (s, 3H), 1.93-1.86 (m, 8H), 1.73-1.68 (m, 4H), 1.07 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.25, 158.84 (d, J = 2.0 Hz), 142.41, 142.40 (d, J = 22.0 Hz), 142.05 (d, J = 2.0 Hz), 133.96, 131.91, 131.08 (d, J = 12.0 Hz), 129.23 (d, J = 13.0 Hz), 128.16 (d, J = 107.0 Hz), 128.10 (d, J = 12.0 Hz), 125.20 (d, J = 112.0 Hz), 123.20, 122.98, 120.20 (d, J = 12.0 Hz), 104.42 (d, J = 13.0 Hz), 70.36, 49.21, 36.80, 27.55, 25.51, 22.51, 21.45, 10.90; ^{31}P NMR (162 MHz, CDCl$_3$): δ 31.70; HRMS (ESI): Exact mass calcd for $C_{53}H_{51}N_8O_7NaP$ [M+Na]$^+$: 965.3516, Found: 965.3563.



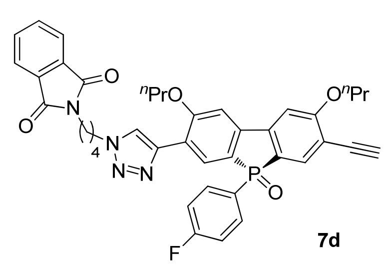
7b

Compound **7b** was obtained in 77% yield as brown solid, Mp: 238-240 °C. IR (KBr): 3287, 2960, 1710, 1465, 1242, 1049, 719, 521 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 11.45 min, t_r (minor) = 25.51 min) gave ee value of the product: 97% ee. $[\alpha]_D^{20}$ = - 18.3 (c = 0.62, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.57 (d, J = 10.0 Hz, 1H), 7.92 (s, 1H), 7.82-7.79 (m, 2H), 7.71-7.68 (m, 3H), 7.54-7.49 (m, 2H), 7.19-7.11 (m, 4H), 4.47-4.31 (m, 3H), 4.17-4.05 (m, 3H), 3.73 (t, J = 6.8 Hz, 2H), 3.31 (s, 1H), 2.58 (t, J = 7.6 Hz, 2H), 2.03-1.88 (m, 6H), 1.76-1.69 (m, 2H), 1.58-1.50 (m, 2H), 1.33-1.28 (m, 2H), 1.14-1.10 (m, 6H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.19, 164.14, 158.88, 147.29 (d, J = 2.0 Hz), 143.63 (d, J = 22.0 Hz), 142.02, 141.73 (d, J = 22.0 Hz), 134.70 (d, J = 11.0 Hz), 133.91, 131.85, 130.98 (d, J = 11.0 Hz), 128.70 (d, J = 13.0 Hz), 128.34 (d, J = 11.0 Hz), 127.23, 125.69 (d, J = 50.0 Hz), 124.58 (d, J = 49.0 Hz), 123.19, 123.13, 120.86 (d, J = 12.0 Hz), 112.58 (d, J = 13.0 Hz), 104.48 (d, J = 11.0 Hz), 104.05 (d, J = 11.0 Hz), 82.65, 79.26, 70.42, 70.37, 49.24, 36.78, 35.53, 33.11, 27.46, 25.46, 22.49, 22.37, 22.12, 13.74, 10.81, 10.50; ^{31}P NMR (162 MHz, CDCl$_3$): δ 31.19; HRMS (ESI): Exact mass calcd for $C_{44}H_{45}N_4O_5NaP$ [M+Na]$^+$: 763.3025, Found: 763.3047.



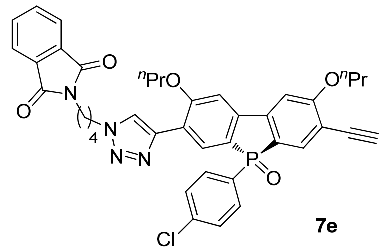
7c

Compound **7c** was obtained in 75% yield as brown solid, Mp: 198-200 °C. IR (KBr): 3293, 2963, 1710, 1466, 1295, 1044, 720, 590 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 13.65 min, t$_r$ (minor) = 32.61 min) gave ee value of the product: 98% ee. $[\alpha]_D^{20}$ = - 12.4 (c = 1.10, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.46 (d, J = 10.0 Hz, 1H), 7.83 (s, 1H), 7.77-7.75 (m, 2H), 7.66-7.61 (m, 3H), 7.52-7.47 (m, 2H), 7.11 (d, J = 1.6 Hz, 1H), 7.03 (d, J = 1.6 Hz, 1H), 6.83-6.80 (m, 2H), 4.42-4.24 (m, 3H), 4.10-3.96 (m, 3H), 3.74 (s, 3H), 3.68 (t, J = 6.8 Hz, 2H), 3.29 (s, 1H), 1.96-1.84 (m, 6H), 1.69-1.66 (m, 2H), 1.09-1.05 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.15, 164.11 (d, J = 2.0 Hz), 162.54 (d, J = 3.0 Hz), 158.84 (d, J = 1.0 Hz), 143.52 (d, J = 21.0 Hz), 141.96, 141.61 (d, J = 22.0 Hz), 134.55 (d, J = 11.0 Hz), 133.89, 132.76 (d, J = 12.0 Hz), 131.79, 128.17 (d, J = 12.0 Hz), 125.69 (d, J =50.0 Hz), 124.58 (d, J = 49.0 Hz), 123.16, 123.09, 121.76 (d, J = 111.0 Hz), 120.84 (d, J = 13.0 Hz), 114.19 (d, J = 14.0 Hz), 112.56 (d, J = 14.0 Hz), 104.46 (d, J = 11.0 Hz), 104.05 (d, J = 11.0 Hz), 82.66, 79.22, 70.40, 70.34, 55.18, 49.21, 36.75, 27.43, 25.43, 22.45, 22.33, 10.76, 10.46; ^{31}P NMR (162 MHz, CDCl$_3$): δ 31.04; HRMS (ESI): Exact mass calcd for $C_{41}H_{39}N_4O_6NaP$ [M+Na]$^+$: 737.2505, Found: 737.2511.



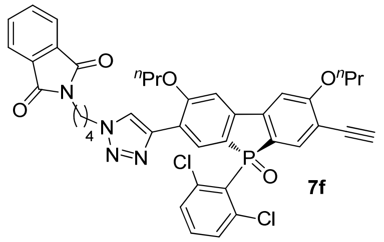
7d

Compound **7d** was obtained in 68% yield as yellow solid, Mp: 236-238 °C. IR (KBr): 3295, 2964, 1703, 1589, 1395, 1243, 1186, 1044, 840, 717 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 10.94 min, t$_r$ (minor) = 13.09 min) gave the isomeric composition of the product: 99% ee. $[\alpha]_D^{26}$ = - 19.6 (c = 1.0, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.59 (d, J = 10.0 Hz, 1H), 7.95 (s, 1H), 7.83-7.80 (m, 2H), 7.73-7.69 (m, 3H), 7.66-7.59 (m, 2H), 7.22 (d, J = 2.4 Hz, 1H), 7.15 (d, J = 2.0 Hz, 1H), 7.04 (s, 1H), 7.05 (td, J = 8.0 Hz, 2.4 Hz, 2H), 4.49-4.31 (m, 3H), 4.20-4.09 (m, 3H), 3.73 (t, J = 6.8 Hz, 2H), 3.32 (s, 1H), 2.05-1.89 (m, 6H), 1.77-1.71 (m, 2H), 1.13 (td, J = 8.0 Hz, 1.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.32, 166.52, 164.46, 159.17, 143.69 (d, J = 22.0 Hz), 142.05, 141.84 (d, J = 22.0 Hz), 134.95 (d, J = 11.0 Hz), 134.04, 133.64, 133.62 (d, J = 22.0 Hz), 131.98, 128.72 (d, J = 11.0 Hz), 127.00 (d, J = 112.0 Hz), 126.83, 125.48 (d, J = 59.0 Hz), 124.36 (d, J = 58.0 Hz), 123.27, 116.14 (d, J = 13.0 Hz), 115.93 (d, J = 14.0 Hz), 113.04 (d, J = 13.0 Hz), 104.54 (d, J = 11.0 Hz), 104.16 (d, J = 11.0 Hz), 83.02, 79.11, 70.59, 49.43, 36.90, 27.59, 25.59, 22.62, 22.49, 10.88, 10.58; ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 29.98; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -106.77; HRMS (ESI): Exact mass calcd for $C_{40}H_{36}FN_4O_5P$ $[M+Na]^+$: 725.2300, Found: 725.2324.



7e

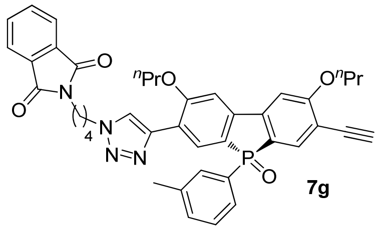
Compound **7e** was obtained in 81% yield as brown solid, Mp: 226-228 °C. IR (KBr): 3290, 2963, 1710, 1592, 1437, 1243, 1045, 719 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 12.77 min, t_r (minor) = 30.28 min) gave the isomeric composition of the product: 93% ee. $[\alpha]_D^{20}$ = - 22.4 (c = 0.55, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.45 (d, *J* = 10.0 Hz, 1H), 7.83 (s, 1H), 7.78-7.76 (m, 2H), 7.67-7.60 (m, 3H), 7.52-7.47 (m, 2H), 7.30-7.27 (m, 2H), 7.13 (s, 1H), 7.04 (s, 1H), 4.43-4.35 (m, 2H), 4.31-4.24 (m, 1H), 4.12-3.89 (m, 3H), 3.69 (t, *J* = 6.8 Hz, 2H), 3.31 (s, 1H), 1.98-1.85 (m, 6H), 1.70-1.66 (m, 2H), 1.09 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 168.19, 164.37 (d, *J* = 2.0 Hz), 159.07 (d, *J* = 2.0 Hz), 143.58 (d, *J* = 23.0 Hz), 141.83, 141.68 (d, *J* = 23.0 Hz), 138.37 (d, *J* = 3.0 Hz), 134.60 (d, *J* = 11.0 Hz), 133.92, 132.39 (d, *J* = 12.0 Hz), 131.83, 129.78 (d, *J* = 106.0 Hz), 128.87 (d, *J* = 14.0 Hz), 128.20 (d, *J* =12.0 Hz), 124.80 (d, *J* = 55.0 Hz), 123.66 (d, *J* = 53.0 Hz), 123.21, 123.13, 121.10 (d, *J* = 13.0 Hz), 112.84 (d, *J* = 13.0 Hz), 104.64 (d, *J* = 11.0 Hz), 104.16 (d, *J* = 11.0 Hz), 82.94, 79.01, 70.50, 70.42, 49.26, 36.77, 27.46, 25.46, 22.47, 22.35, 10.80, 10.50; ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 29.94; HRMS (ESI): Exact mass calcd for $C_{40}H_{37}{}^{35}ClN_4O_5P$ $[M+H]^+$: 719.2185, Found: 719.2183.



7f

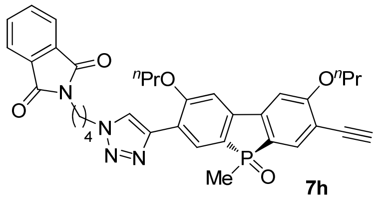
Compound **7f** was obtained in 68% yield as brown solid, Mp: 206-208 °C. IR (KBr): 3290, 2964, 1702, 1416, 1050, 710, 524 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 15.75 min, t_r (minor) = 20.25 min) gave the isomeric composition of the product: 92% ee. $[\alpha]_D^{20}$ = - 1.2 (c = 0.53, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.60 (d, *J* = 10.8 Hz, 1H), 7.82-7.76 (m, 4H), 7.70-7.69 (m, 2H), 7.31-7.26 (m, 3H), 7.14 (d, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 1.6 Hz, 1H), 4.55-4.42 (m, 2H), 4.30-4.23 (m, 1H), 4.18-4.13 (m, 1H), 4.07-3.98 (m, 2H), 3.78-3.69 (m, 2H), 3.34 (s, 1H), 2.01-1.87 (m, 6H), 1.74-1.67 (m, 2H), 1.16-1.10 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 168.16, 164.32 (d, *J* = 2.0 Hz), 159.02 (d, *J* = 2.0 Hz), 143.79 (d, *J* = 24.0 Hz), 142.11 (d, *J* = 24.0 Hz), 142.07, 139.59 (d, *J* = 3.0 Hz), 134.08 (d, *J* = 11.0 Hz), 133.89, 132.32, 131.80, 130.52 (d, *J* = 7.0 Hz), 127.72 (d, *J* = 12.0 Hz), 127.44 (d, *J* = 99.0 Hz), 126.94, 124.86 (d, *J* =35.0 Hz), 123.68 (d, *J* = 35.0 Hz), 123.11, 120.32

(d, *J* = 13.0 Hz), 112.28 (d, *J* = 14.0 Hz), 105.10 (d, *J* = 13.0 Hz), 104.43 (d, *J* = 12.0 Hz), 82.59, 79.33, 70.41, 70.25, 49.14, 36.71, 27.46, 25.42, 22.45, 22.38, 10.88, 10.61; ^{31}P NMR (162 MHz, CDCl$_3$): δ 29.25; HRMS (ESI): Exact mass calcd for $C_{40}H_{36}{}^{35}Cl_2N_4O_5P$ [M+H]$^+$: 753.1795, Found: 753.1792



7g

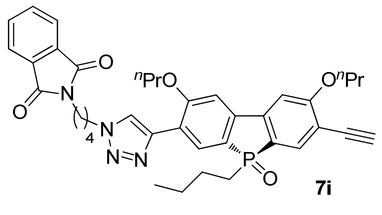
Compound **7g** was obtained in 68% yield as brown solid, Mp: 176-178 °C. IR (KBr): 3297, 2964, 1710, 1487, 1243, 1045, 720 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 8.66 min, t$_r$ (minor) = 16.96 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{20}$ = - 10.9 (c = 0.68, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.47 (d, *J* = 10.4 Hz, 1H), 7.85 (s, 1H), 7.78-7.76 (m, 2H), 7.69-7.63 (m, 3H), 7.46-7.43 (m, 1H), 7.31-7.27 (m, 1H), 7.21-7.18 (m, 2H), 7.14 (s, 1H), 7.06 (s, 1H), 4.43-4.25 (m, 3H), 4.12-3.98 (m, 3H), 3.69 (t, *J* = 6.8Hz, 2H), 3.30 (s, 1H), 2.27 (s, 3H), 2.00-1.82 (m, 6H), 1.72-1.65 (m, 2H), 1.11-1.07 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.18, 164.19 (d, *J* = 2.0 Hz), 158.91 (d, *J* = 2.0 Hz), 143.70 (d, *J* = 24.0 Hz), 141.99, 141.77 (d, *J* = 22.0 Hz), 138.38 (d, *J* = 12.0 Hz), 134.66 (d, *J* = 11.0 Hz), 133.91, 132.72, 131.83, 131.40 (d, *J* = 11.0 Hz), 130.76 (d, *J* = 105.0 Hz), 128.42 (d, *J* = 13.0 Hz), 128.26, 127.94 (d, *J* = 11.0 Hz), 125.50 (d, *J* = 52.0 Hz), 124.38 (d, *J* = 51.0 Hz), 123.19, 123.12, 120.86 (d, *J* = 13.0 Hz), 112.60 (d, *J* = 13.0 Hz), 104.52 (d, *J* = 11.0 Hz), 104.06 (d, *J* = 10.0 Hz), 82.70, 79.22, 70.43, 70.37, 49.24, 36.77, 27.45, 25.45, 22.48, 22.36, 21.21, 10.80, 10.49; ^{31}P NMR (162 MHz, CDCl$_3$): δ 31.17; HRMS (ESI): Exact mass calcd for $C_{41}H_{40}N_4O_5P$ [M+H]$^+$: 699.2731, Found: 699.2729.



7h

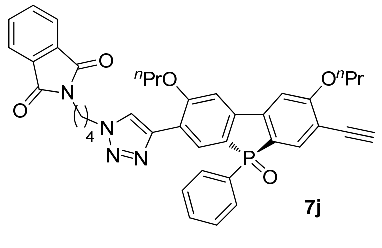
Compound **7h** was obtained in 77% yield as brown solid, Mp: 168-170 °C. IR (KBr): 3274, 2964, 2872, 1706, 1487, 1245, 1048, 765 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 8.77 min, t$_r$ (minor) = 20.38 min) gave the isomeric composition of the product: 94% ee. $[\alpha]_D^{20}$ = - 4.5 (c = 1.00, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.62 (d, *J* = 10.0 Hz, 1H), 7.87 (s, 1H), 7.79-7.77 (m, 3H), 7.68-7.66 (m, 2H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.94 (d, *J* = 1.6 Hz, 1H), 4.44-4.38 (m, 1H), 4.36-4.25 (m, 2H), 4.04-3.93 (m, 3H), 3.70 (t, *J* = 6.8 Hz, 2H), 3.35 (s, 1H), 1.96-1.82 (m, 6H), 1.76 (d, *J* = 13.6 Hz, 3H), 1.73-1.69 (m, 2H), 1.07 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.20, 164.02 (d, *J* = 2.0 Hz), 158.73 (d, *J* = 3.0 Hz), 142.56 (d, *J* = 22.0 Hz), 141.96, 140.68 (d, *J* = 22.0 Hz), 133.94, 133.83, 131.79, 127.49 (d, *J* = 12.0 Hz), 125.24

(d, *J* = 50.0 Hz), 124.16 (d, *J* =49.0 Hz), 123.21, 123.13, 120.68 (d, *J* = 12.0 Hz), 112.36 (d, *J* = 13.0 Hz), 104.36 (d, *J* = 11.0 Hz), 103.98 (d, *J* = 11.0 Hz), 82.80, 79.17, 70.36, 70.34, 49.30, 36.77, 27.45, 25.48, 22.38 (d, *J* = 13.0 Hz), 16.78, 16.05, 10.74, 10.44; ^{31}P NMR (162 MHz, CDCl$_3$): δ 36.38; HRMS (ESI): Exact mass calcd for $C_{35}H_{36}N_4O_5P$ [M+H]$^+$: 623.2418, Found: 623.2418.



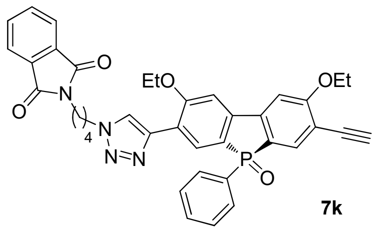
7i

Compound **7i** was obtained in 81% yield as brown solid, Mp: 113-115 ºC. IR (neat): 2964, 2876, 1769, 1394, 1241, 1040, 719 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 8.07 min, t$_r$ (minor) = 18.36 min) gave the isomeric composition of the product: 94% ee. $[\alpha]_D^{28}$ = - 38.6 (c = 1.00, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.67 (d, *J* = 13.2 Hz, 1H), 7.94 (s, 1H), 7.84-7.79 (m, 3H), 7.72-7.69 (m, 2H), 7.09 (d, *J* = 2.0 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 4.49-4.34 (m, 2H), 4.32-4.27 (m, 1H), 4.12-4.01 (m, 3H), 3.74 (t, *J* = 8.0 Hz, 2H), 3.37 (s, 1H), 2.11-2.02 (m, 2H), 2.00-1.86 (m, 6H), 1.78-1.71 (m, 2H), 1.39-1.26 (m, 4H), 1.11 (t, *J* = 8.0 Hz, 6H), 0.79 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.31, 164.09, 158.79 (d, *J* = 2.0 Hz), 143.21 (d, *J* = 20.0 Hz), 142.14, 141.38 (d, *J* = 21.0 Hz), 134.45 (d, *J* = 10.0 Hz), 131.90, 128.14 (d, *J* = 11.0 Hz), 124.64 (d, *J* = 56.0 Hz), 123.59 (d, *J* = 54.0 Hz), 123.24, 112.82 (d, *J* = 12.0 Hz), 112.42 (d, *J* = 13.0 Hz), 104.31 (d, *J* = 10.0 Hz), 104.00 (d, *J* = 10.0 Hz), 82.84, 79.28, 70.43, 49.40, 36.86, 29.96 (d, *J* = 71.0 Hz), 27.56, 25.57, 24.18, 24.15, 23.90 (d, *J* = 16.0 Hz), 22.49 (d, *J* = 14.0 Hz), 13.42, 10.84, 10.53; ^{31}P NMR (162 MHz, CDCl$_3$): δ 41.41; HRMS (ESI): Exact mass calcd for $C_{38}H_{41}N_4NaO_5P$ [M+Na]$^+$: 687.2707, Found: 687.2703.



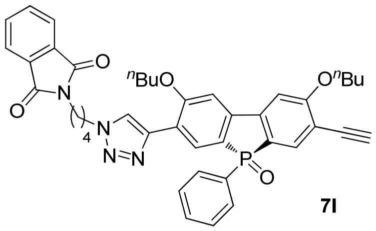
7j

Compound **7j** was obtained in 80% yield as brown solid, Mp: 234-236 ºC. IR (KBr): 3292, 2926, 1705, 1500, 1390, 1244, 1090, 719 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 12.44 min, t$_r$ (minor) = 26.40 min) gave the isomeric composition of the product: 96% ee. $[\alpha]_D^{20}$ = - 16.7 (c = 0.71, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.55 (d, *J* = 10.0 Hz, 1H), 7.90 (s, 1H), 7.81-7.79 (m, 2H), 7.70-7.67 (m, 3H), 7.63-7.58 (m, 2H), 7.44-7.43 (m, 1H), 7.36-7.33 (m, 2H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 4.46-4.30 (m, 3H), 4.16-4.04 (m, 3H), 3.72 (t, *J* = 6.8 Hz, 2H), 3.31 (s, 1H), 2.00-1.88 (m, 6H), 1.73-1.69 (m, 2H), 1.13-1.09 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.23, 164.25, 158.78, 143.69 (d, J = 22.0 Hz), 141.98, 141.81 (d, J = 22.0 Hz), 134.76 (d, J = 11.0 Hz), 133.95, 131.84, 131.04 (d, J = 105.0 Hz), 130.98 (d, J = 11.0 Hz), 128.61, 128.48, 128.35, 125.40 (d, J = 51.0 Hz), 124.28 (d, J = 50.0 Hz), 123.21, 123.17, 120.94 (d, J = 13.0 Hz), 112.66 (d, J = 13.0 Hz), 104.50 (d, J = 11.0 Hz), 104.04 (d, J = 11.0 Hz), 82.79, 79.17, 70.46, 70.40, 49.28, 36.78, 27.48, 25.47, 22.51, 22.38, 10.83, 10.53; ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.93; HRMS (ESI): Exact mass calcd for $C_{40}H_{38}N_4O_5P$ $[M+H]^+$: 685.2574, Found: 685.2574.



7k

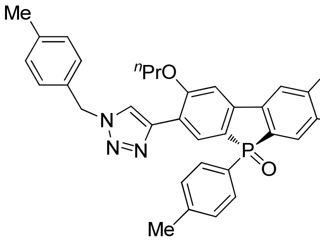
Compound **7k** was obtained in 79% yield as brown solid, Mp: 176-178 °C. IR (KBr): 3284, 2926, 1703, 1487, 1244, 1050, 719 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 13.75 min, t_r (minor) = 32.22 min) gave the isomeric composition of the product: 93% ee. $[\alpha]_D^{20}$ = - 21.2 (c = 0.55, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, J = 10.0 Hz, 1H), 7.79-7.75 (m, 3H), 7.65-7.53 (m, 5H), 7.40-7.38 (m, 1H), 7.32-7.29 (m, 2H), 7.09 (s, 1H), 7.01 (s, 1H), 4.48-4.34 (m, 2H), 4.27-4.06 (m, 4H), 3.72-3.65 (m, 2H), 3.32 (s, 1H), 1.89-1.86 (m, 2H), 1.69-1.66 (m, 2H), 1.54 (t, J = 6.8 Hz, 3H), 1.46 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.18, 164.00, 158.78, 143.62 (d, J = 22.0 Hz), 141.86, 141.67 (d, J = 22.0 Hz), 134.56 (d, J = 11.0 Hz), 133.89, 131.83, 131.78, 131.02 (d, J = 105.0 Hz), 130.90 (d, J = 11.0 Hz), 128.50 (d, J = 22.0 Hz), 127.99 (d, J = 12.0 Hz), 125.10 (d, J = 40.0 Hz), 123.99 (d, J = 38.0 Hz), 123.25, 123.11, 120.70 (d, J = 12.0 Hz), 112.42 (d, J = 13.0 Hz), 104.56 (d, J = 10.0 Hz), 104.00 (d, J = 11.0 Hz), 82.77, 79.28, 64.61, 64.53, 49.17, 36.73, 27.44, 25.41, 14.66, 14.46; ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.99; HRMS (ESI): Exact mass calcd for $C_{38}H_{34}N_4O_5P$ $[M+H]^+$: 657.2261, Found: 657.2260.



7l

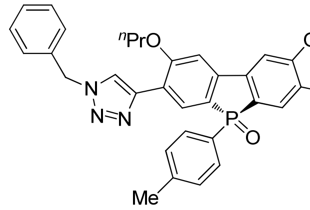
Compound **7l** was obtained in 71% yield as brown solid, Mp: 184-186 °C. IR (KBr): 3290, 2966, 2119, 1709, 1591, 1415, 1187, 721 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 10.16 min, t_r (minor) = 16.12 min) gave the isomeric composition of the product: 96% ee. $[\alpha]_D^{20}$ = - 14.0 (c = 0.58, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 10.0 Hz, 1H), 7.92 (s, 1H), 7.82-7.80 (m, 2H), 7.70-7.68 (m, 3H), 7.64-7.59 (m, 2H), 7.46-7.43 (m, 1H), 7.36-7.33 (m, 2H), 7.21 (d, J = 2.0 Hz, 1H), 7.13 (s, 1H), 4.47-4.32 (m, 3H), 4.22-4.10 (m, 3H), 3.72 (t, J = 6.8 Hz, 2H), 3.31 (s, 1H), 1.97-1.85

(m, 6H), 1.75-1.67 (m, 2H), 1.62-1.53 (m, 4H), 1.05-0.99 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.24, 164.29, 159.01, 143.72 (d, J = 22.0 Hz), 142.01, 141.76, 134.84 (d, J = 11.0 Hz), 133.96, 131.86, 131.02 (d, J = 105.0 Hz) ,131.01 (d, J = 11.0 Hz), 128.56, 125.48 (d, J = 56.0 Hz), 124.36 (d, J = 55.0 Hz), 123.24, 123.18, 121.02 (d, J = 13.0 Hz), 112.72 (d, J = 13.0 Hz), 104.52 (d, J = 11.0 Hz), 104.06 (d, J = 11.0 Hz), 82.80, 79.21, 68.74, 68.58, 49.32, 36.82, 31.13, 31.02, 27.49, 25.48, 19.36, 19.15, 13.86, 13.85; ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.89; HRMS (ESI): Exact mass calcd for $C_{42}H_{42}N_4O_5P$ $[M+H]^+$: 713.2887, Found: 713.2887.



7m

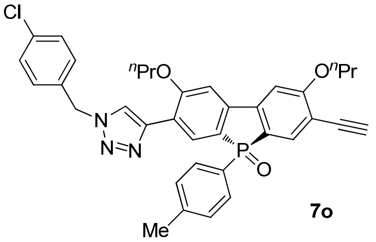
Compound **7m** was obtained in 75% yield as brown solid, Mp: 270-272 ºC. IR (KBr): 3293, 2964, 1592, 1462, 1242, 1046, 663 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 6.85 min, t_r (minor) = 13.35 min) gave the isomeric composition of the product: 93% ee. $[\alpha]_D^{20}$ = + 5.50 (c = 0.7, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, J = 10.6 Hz, 1H), 7.76 (s, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.51-7.46 (m, 2H), 7.18-7.14 (m, 6H), 7.11 (s, 1H), 7.03 (s, 1H), 5.46 (AB, J = 14.4 Hz, 1H), 5.30 (AB, J = 10.4 Hz, 1H), 4.36-4.31 (m, 1H), 4.12-4.06 (m, 1H), 4.03-3.97 (m, 2H), 3.29 (s, 1H), 2.32 (s, 6H), 1.91-1.80 (m, 4H), 1.10 (t, J = 7.6 Hz, 3H), 0.96 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.15 (d, J = 1.0 Hz), 158.90 (d, J = 2.0 Hz), 143.59 (d, J = 22.0 Hz), 142.36 (d, J = 3.0 Hz), 142.18, 141.73 (d, J = 22.0 Hz), 138.43, 134.62 (d, J = 10.0 Hz), 131.56, 130.98 (d, J = 11.0 Hz), 129.60, 129.30 (d, J = 13.0 Hz), 128.25, 128.12, 127.16, 125.63 (d, J = 48.0 Hz), 124.52 (d, J = 47.0 Hz), 123.28, 120.88 (d, J = 12.0 Hz), 112.62 (d, J = 13.0 Hz), 104.48 (d, J = 11.0 Hz), 104.04 (d, J = 11.0 Hz), 82.65, 79.25, 70.37, 53.62, 22.41, 22.38, 21.44, 21.01, 10.77, 10.50; ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.07; HRMS (ESI): Exact mass calcd for $C_{37}H_{37}N_3O_3P$ $[M+H]^+$: 602.2567, Found: 602.2567.



7n

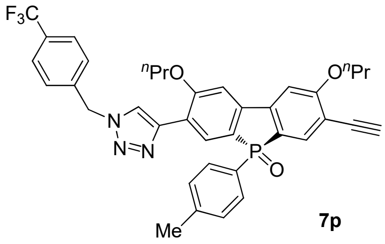
Compound **7n** was obtained in 70% yield as brown solid, Mp: 264-266 ºC. IR (KBr): 3800, 2964, 1592, 1461, 1242, 1047, 693, 523 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 6.88 min, t_r (minor) = 14.41 min) gave the isomeric composition of the product: 93% ee. $[\alpha]_D^{20}$ = + 0.8 (c = 0.94, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, J = 10.0 Hz, 1H), 7.79 (s, 1H), 7.64 (d, J = 9.2 Hz, 1H), 7.50-7.44 (m, 2H), 7.36-7.30 (m, 3H), 7.29-7.24 (m, 2H), 7.14-7.11 (m, 3H), 7.03 (s, 1H), 5.50 (AB, J

= 14.4 Hz, 1H), 5.35 (AB, *J* = 14.4 Hz, 1H), 4.34-4.29 (m, 1H), 4.08-4.05 (m, 1H), 4.02-3.97 (m, 2H), 3.28 (s, 1H), 2.30 (s, 3H), 1.89-1.78 (m, 4H), 1.08 (t, *J* = 7.6 Hz, 3H), 0.95 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 164.17, 158.93, 143.58 (d, *J* = 22.0 Hz), 142.39, 142.27, 141.78 (d, *J* = 12.0 Hz), 134.66, 134.59, 130.98 (d, *J* = 11.0 Hz), 129.30 (d, *J* = 13.0 Hz), 128.95, 128.54, 128.20 (d, *J* = 11.0 Hz), 128.05, 127.13, 125.60 (d, *J* = 50.0 Hz), 124.49 (d, *J* = 48.0 Hz), 123.38, 120.82 (d, *J* = 12.0 Hz), 112.64 (d, *J* = 13.0 Hz), 104.52 (d, *J* = 10.0 Hz), 104.07 (d, *J* = 10.0 Hz), 82.67, 79.25, 70.40, 70.38, 53.83, 22.40, 22.36, 21.43, 10.76, 10.47; ^{31}P NMR (162 MHz, CDCl$_3$): δ 31.14; HRMS (ESI): Exact mass calcd for $C_{36}H_{35}N_3O_3P$ [M+H]$^+$: 588.2411, Found: 588.2414.



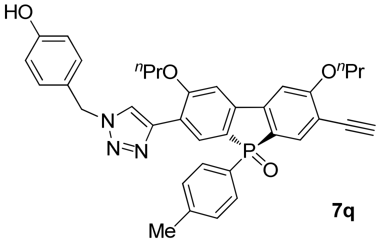
7o

Compound **7o** was obtained in 77% yield as brown solid, Mp: 258-260 ºC. IR (KBr): 3287, 2966, 1592, 1463, 1241, 1047, 660, 528 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 7.49 min, t$_r$ (minor) = 14.39 min) gave the isomeric composition of the product: 96% ee. $[\alpha]_D^{20}$ = - 2.30 (c = 0.60, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.48 (d, *J* = 10.0 Hz, 1H), 7.80 (s, 1H), 7.66 (d, *J* = 10.6 Hz, 1H), 7.50-7.44 (m, 2H), 7.32-7.30 (m, 2H), 7.20-7.18 (m, 2H), 7.15-7.11 (m, 3H), 7.03 (d, *J* = 2.0 Hz, 1H), 5.47 (AB, *J* = 14.8 Hz, 1H), 5.36 (AB, *J* = 14.8 Hz, 1H), 4.36-4.31 (m, 1H), 4.09-3.97 (m, 3H), 3.29 (s, 1H), 2.32 (s, 3H), 1.91-1.82 (m, 4H), 1.09 (t, *J* = 7.6 Hz, 3H), 0.98 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 164.23 (d, *J* = 2.0 Hz), 158.97 (d, *J* = 2.0 Hz), 143.60 (d, *J* = 22.0 Hz), 142.48 (d, *J* = 3.0 Hz), 141.89 (d, *J* = 22.0 Hz), 134.78 (d, *J* = 11.0 Hz), 134.65, 133.22, 131.04 (d, *J* = 11.0 Hz), 129.42, 129.30, 129.19, 128.36 (d, *J* = 12.0 Hz), 127.61 (d, *J* = 108.0 Hz), 125.82 (d, *J* = 51.0 Hz), 124.70 (d, *J* = 50.0 Hz), 123.34, 120.76 (d, *J* = 12.0 Hz), 112.76 (d, *J* = 13.0 Hz), 104.50 (d, *J* = 11.0 Hz), 104.08 (d, *J* = 11.0 Hz), 82.75, 79.23, 70.46, 53.12, 22.50, 22.41, 21.49, 10.77, 10.50; ^{31}P NMR (162 MHz, CDCl$_3$): δ 31.15; HRMS (ESI): Exact mass calcd for $C_{36}H_{34}{}^{35}ClN_3O_3P$ [M+H]$^+$: 622.2021, Found: 622.2021.



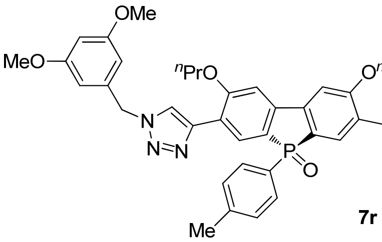
7p

Compound **7p** was obtained in 70% yield as brown solid, Mp: 258-260 °C. IR (KBr): 3300, 2966, 2932, 1602, 1463, 1242, 1067, 661 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 6.18 min, t_r (minor) = 10.01 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{20}$ = - 4.10 (c = 0.58, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.49-8.47 (m, 1H), 7.85 (s, 1H), 7.67 (d, J = 9.6 Hz, 1H), 7.61-7.59 (m, 2H), 7.50-7.45 (m, 2H), 7.37-7.35 (m, 2H), 7.15-7.12 (m, 3H), 7.04 (s, 1H), 5.58 (AB, J = 15.2 Hz, 1H), 5.48 (AB, J = 15.2 Hz, 1H), 4.36-4.30 (m, 1H), 4.06-4.00 (m, 3H), 3.30 (s, 1H), 2.32 (s, 3H), 1.91-1.79 (m, 4H), 1.08 (t, J = 7.6 Hz, 3H), 0.95 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 164.23 (d, J = 1.0 Hz), 158.98 (d, J = 2.0 Hz), 143.58 (d, J = 22.0 Hz), 142.54, 141.95 (d, J = 22.0 Hz), 138.68, 134.78 (d, J = 11.0 Hz), 131.02 (d, J = 12.0 Hz), 129.52 (q, J = 227.0 Hz), 129.38 (d, J = 12.0 Hz), 128.25, 128.01, 126.93, 125.96 (q, J = 3.0 Hz), 125.27 (d, J = 38.0 Hz), 124.61 (d, J = 50.0 Hz), 123.52, 120.60 (d, J = 12.0 Hz), 112.74 (d, J = 13.0 Hz), 104.50 (d, J = 11.0 Hz), 104.06 (d, J = 11.0 Hz), 82.82, 79.18, 70.46, 53.20, 22.44, 22.38, 21.50, 10.70, 10.50; ^{31}P NMR (162 MHz, CDCl$_3$): δ 31.16; ^{19}F NMR (376 MHz, CDCl$_3$): δ -62.79; HRMS (ESI): Exact mass calcd for $C_{37}H_{34}F_3N_3O_3P$ [M+H]$^+$: 656.2284, Found: 656.2284.



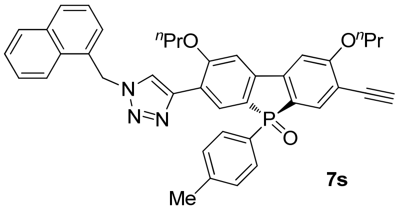
7q

Compound **7q** was obtained in 71% yield, Mp: 224-226 °C. IR (KBr): 3290, 2963, 1593, 1460, 1241, 1046 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 5.46 min, t_r (minor) = 8.02 min) gave the isomeric composition of the product: 97% ee. $[\alpha]_D^{20}$ = + 10.60 (c = 0.50, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$+DMSO-d$_6$): δ 9.48 (s, 1H), 8.34-8.31 (m, 1H), 8.17 (s, 1H), 7.86-7.82 (m, 2H), 7.62-7.59 (m, 1H), 7.46-7.41 (m, 2H), 7.25-7.19 (m, 4H), 6.77-6.75 (m, 2H), 5.52 (s, 2H), 4.29-4.21 (m, 5H), 2.30 (s, 3H), 1.90-1.81 (m, 4H), 1.06 (t, J = 7.2 Hz, 3H), 0.99 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$+DMSO-d$_6$): δ 163.93, 158.80, 157.43, 142.48 (d, J = 21.0 Hz), 142.16, 141.68 (d, J = 22.0 Hz), 141.01, 133.75 (d, J = 12.0 Hz), 130.44 (d, J = 11.0 Hz), 129.58, 129.36 (d, J = 13.0 Hz), 128.08 (d, J = 106.0 Hz), 126.84 (d, J = 11.0 Hz), 125.58, 125.52 (d, J = 63.0 Hz), 124.40 (d, J = 59.0 Hz), 123.47, 120.64 (d, J = 12.0 Hz), 115.83, 112.20 (d, J = 13.0 Hz), 106.44, 105.92 (d, J = 11.0 Hz), 85.63, 79.11, 70.55, 70.23, 52.65, 21.94, 21.90, 21.00, 10.64, 10.36; ^{31}P NMR (162 MHz, CDCl$_3$+DMSO-d$_6$): δ 29.43; HRMS (ESI): Exact mass calcd for $C_{36}H_{35}N_3O_4P$ [M+H]$^+$: 604.2360, Found: 604.2360.



7r

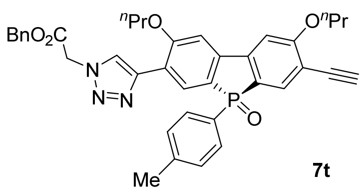
Compound **7r** was obtained in 76% yield as brown solid, Mp: 236-238 °C. IR (KBr): 3290, 2964, 2935, 1593, 1430, 1298, 1064, 809, 661, 522 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 9.44 min, t_r (minor) = 15.47 min) gave the isomeric composition of the product: 94% ee. $[\alpha]_D^{20}$ = +8.40 (c = 0.53, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, br, 1H), 7.85 (s, 1H), 7.69 (s, 1H), 7.52 (s, br, 2H), 7.17-7.15 (m, 3H), 7.09 (s, 1H), 6.40 (s, 3H), 5.45 (AB, *J* = 14.8 Hz, 1H), 5.32 (AB, *J* = 14.8 Hz, 1H), 4.33-4.28 (m, 1H), 4.15-4.03 (m, 3H), 3.74 (s, 6H), 3.29 (s, 1H), 2.33 (s, 3H), 1.92-1.83 (m, 4H), 1.10 (t, *J* = 7.6 Hz, 3H), 0.99 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.22, 161.26, 158.98, 143.63 (d, *J* = 22.0 Hz), 142.40 (d, *J* = 12.0 Hz), 141.88 (d, *J* = 22.0 Hz), 136.73, 134.79 (d, *J* = 10.0 Hz), 131.07 (d, *J* = 10.0 Hz), 129.36 (d, *J* = 13.0 Hz), 128.42 (d, *J* = 11.0 Hz), 127.69 (d, *J* = 109.0 Hz), 125.76 (d, *J* = 54.0 Hz), 124.64 (d, *J* = 53.0 Hz), 123.36, 120.94 (d, *J* = 12.0 Hz), 112.76 (d, *J* = 13.0 Hz), 106.07, 104.49 (d, *J* = 10.0 Hz), 104.09 (d, *J* = 10.0 Hz), 100.47, 82.74, 79.24, 70.45, 55.34, 53.98, 22.49, 22.42, 21.48, 10.73, 10.52; ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.20; HRMS (ESI): Exact mass calcd for $C_{38}H_{39}N_3O_5P$ $[M+H]^+$: 648.2622, Found: 648.2621.



7s

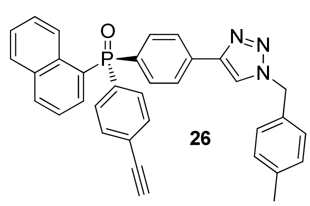
Compound **7s** was obtained in 74% yield as brown solid, Mp: 248-250 °C. IR (KBr): 3290, 2962, 2926, 1592, 1460, 1285, 1045, 1209, 665, 522 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 9.26 min, t_r (minor) = 13.77 min) gave the isomeric composition of the product: 92% ee. $[\alpha]_D^{20}$ = - 8.0 (c = 0.53, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 10.0 Hz, 1H), 7.97-7.94 (m, 1H), 7.89-7.85 (m, 2H), 7.70 (s, 1H), 7.66 (d, *J* = 9.6 Hz, 1H), 7.50-7.44 (m, 6H), 7.15-7.12 (m, 2H), 7.05-7.02 (m, 2H), 6.04 (AB, *J* = 14.8 Hz, 1H), 5.81 (AB, *J* = 14.8 Hz, 1H), 4.19-4.14 (m, 1H), 4.10-3.98 (m, 2H), 3.90-3.85 (m, 1H), 3.27 (s, 1H), 2.32 (s, 3H), 1.92-1.83 (m, 2H), 1.57-1.50 (m, 2H), 1.08 (t, *J* = 7.6 Hz, 3H), 0.72 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.19, 158.92 (d, *J* = 2.0 Hz), 143.61 (d, *J* = 22.0 Hz), 142.44 (d, *J* = 3.0 Hz), 142.19, 141.79 (d, *J* = 22.0 Hz), 134.86 (d, *J* = 11.0 Hz), 133.90, 131.15, 131.04 (d, *J* = 11.0 Hz), 129.90 (d, *J* = 7.0 Hz), 129.36 (d, *J* = 13.0 Hz), 128.80, 128.40 (d, *J* = 11.0 Hz), 128.16, 127.93, 127.09, 126.27, 125.89 (d, *J* = 54.0 Hz), 125.31, 124.78 (d, *J* = 52.0 Hz), 123.38, 122.85, 120.98 (d, *J* = 13.0 Hz), 112.76 (d, *J* = 13.0 Hz), 104.30 (d, *J*

= 11.0 Hz), 104.00 (d, J = 11.0 Hz), 82.72, 79.21, 70.45, 70.31, 51.96, 22.42, 22.27, 21.49, 10.59, 10.50; ^{31}P NMR (162 MHz, CDCl$_3$): δ 31.13; HRMS (ESI): Exact mass calcd for $C_{40}H_{37}N_3O_3P$ $[M+H]^+$: 638.2567, Found: 638.2566.



7t

Compound **7t** was obtained in 65% yield as brown solid, Mp: 196-198 °C. IR (KBr): 3287, 2963, 2932, 1781, 1592, 1461, 1244, 1046 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 8.66 min, t_r (minor) = 19.69 min) gave the isomeric composition of the product: 93% ee. $[\alpha]_D^{20}$ = - 4.20 (c = 1.00, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.59 (d, J = 10.0 Hz, 1H), 8.08 (s, 1H), 7.66 (d, J = 9.2 Hz, 1H), 7.52-7.47 (m, 2H), 7.36-7.31 (m, 5H), 7.17-7.12 (m, 4H), 5.26-5.20 (m, 2H), 5.17 (s, 2H), 4.29-4.20 (m, 2H), 4.10-4.07 (m, 2H), 3.30 (s, 1H), 2.33 (s, 3H), 1.94-1.83 (m, 4H), 1.13 (t, J = 7.6 Hz, 3H), 1.08 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 166.41, 164.15, 158.99, 143.54 (d, J = 12.0 Hz), 142.47, 142.03 (d, J = 22.0 Hz), 134.58 (d, J = 11.0 Hz), 134.42, 131.02 (d, J = 11.0 Hz), 129.34 (d, J = 13.0 Hz), 128.75, 128.66, 128.50, 128.24 (d, J = 10.0 Hz), 126.48 (d, J = 113.0 Hz), 124.77, 124.63 (d, J = 110.0 Hz), 120.52 (d, J = 12.0 Hz), 112.64 (d, J = 13.0 Hz), 104.44 (d, J = 11.0 Hz), 104.23 (d, J = 11.0 Hz), 82.74, 79.28, 70.46, 70.34, 67.87, 50.63, 22.43, 22.34, 21.50, 10.81, 10.61; ^{31}P NMR (162 MHz, CDCl$_3$): δ 31.12; HRMS (ESI): Exact mass calcd for $C_{38}H_{37}N_3O_5P$ $[M+H]^+$: 646.2465, Found: 646.2465.

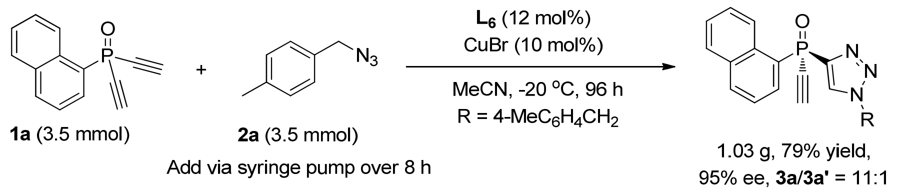


26

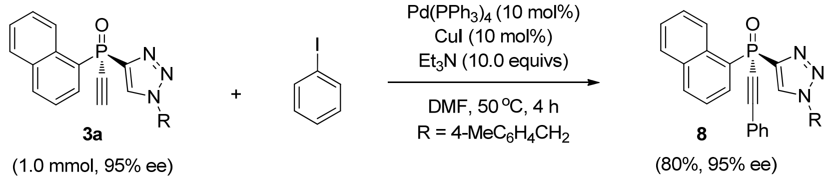
Compound **26** was obtained in 55% yield, Mp: 238-240 °C. IR (KBr): 3286, 2974, 1506, 1433, 1265, 1188, 1095, 987cm^{-1}. HPLC analysis (Chiralcel OD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 16.17 min, t_r (minor) = 19.24 min) gave the isomeric composition of the product: 10% ee. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.53 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.90-7.87 (m, 3H), 7.72 (s, 1H), 7.69-7.62 (m, 4H), 7.57-7.55 (m, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.45-7.36 (m, 2H), 7.33-7.26 (m, 1H), 7.21-7.17 (m, 4H), 5.53 (s, 2H), 3.20 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 146.91, 138.85, 134.33 (d, J =3.0 Hz), 133.93 (d, J = 9.0 Hz), 133.83, 133.64 (d, J = 25.0 Hz), 133.57 (d, J = 2.0 Hz), 133.22 (d, J = 84.0 Hz), 132.58 (d, J = 10.0 Hz), 132.20 (d, J = 12.0 Hz), 131.95 (d, J = 10.0 Hz), 131.74 (d, J =104.0 Hz), 131.43, 129.86, 128.90, 128.38 (d, J = 103.0 Hz), 128.15, 127.50, 127.40 (d, J = 6.0 Hz), 126.65, 125.93 (d, J = 3.0 Hz), 125.79 (d, J = 12.0 Hz), 124.22 (d, J = 14.0 Hz), 120.46, 82.66, 79.97, 54.13, 21.17; ^{31}P NMR (162 MHz, CDCl$_3$): δ 31.51; HRMS (EI): Exact mass calcd for $C_{34}H_{26}N_3OP$: 523.1814, Found: 523.1823.

8. Diversifying reactions of optically active P-chiral ethynylphosphine oxides.

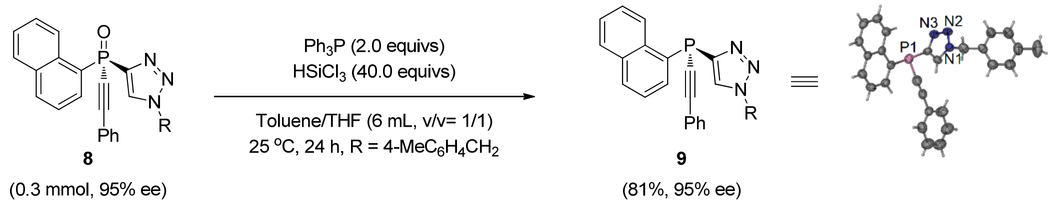
8.1 The synthesis of compounds 8-9, and 11-14



Gram-scale synthesis of 3a: To a 100 mL Schlenk bottle was added **L$_6$** (221 mg, 0.42 mmol) and CuBr (50 mg, 0.35 mmol), followed by the addition of 50 mL anhydrous CH_3CN. The solution was stirred at 25 °C for 2 h, and then diethynylphosphine oxides **1a** (784 mg, 3.5 mmol) was added. After the mixture was cooled to -20 °C for 0.5 h, azide **2a** (515 mg, 3.5 mmol) was diluted in 10 mL anhydrous MeCN and added dropwise by syringe pump for 8 h. The resulting mixture was stirred at -20 °C for 96 h till full conversion of **2a** by TLC analysis. A portion of the combined homogenous solution was used to determine the **3a**/**3a'** ratio by ^{1}H NMR analysis. After removing the solvent under reduced pressure, the sample for NMR analysis and the rest mixture was used for column chromatography purification using CH_2Cl_2/EtOAc (2:1, v/v) as the eluent, giving 1.03 g of monotriazole **3a** in 79% yield and 95% ee.

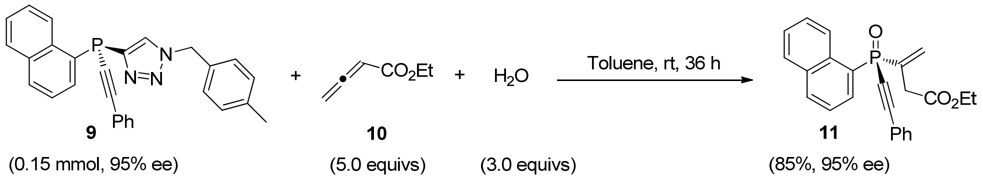


To an oven-dried Schlenk tube was successively added **3a** (371 mg, 1.0 mmol), $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol), CuI (19.0 mg, 0.1 mmol), Et_3N (1.01 g, 10.0 mmol) and anhydrous DMF (6.0 mL), followed by the addition of iodobenzene (306 mg, 1.5 mmol). The resulting mixture was stirred at 50 °C for 4 h. After full consumption of **3a** by TLC analysis, EtOAc (40 mL) was added and the organic layer was washed with H_2O and brine (3 × 30 mL) and then dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography on silica gel using CH_2Cl_2/EtOAc (2:1, v/v) as the eluent, affording product **8** as white solid in 80% yield, Mp: 185-187 °C. IR (neat): 2987, 2171, 1589, 1488, 1335, 1147, 1024, 984, 801, 756 cm^{-1}; HPLC analysis (Chiralcel AD-H, 20% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 44.20 min, t_r (minor) = 26.10 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{25}$ = + 3.5 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 7.6 Hz, 1H), 8.42-8.36 (m, 1H), 8.07-8.05 (m, 2H), 7.96-7.89 (m, 1H), 7.60-7.51 (m, 5H), 7.46-7.40 (m, 1H), 7.35-7.31 (m, 2H), 7.20-7.13 (m, 4H), 5.50 (q, *J* = 14.6 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.59 (d, *J* = 161.0 Hz), 139.13, 134.03 (d, *J* = 3.0 Hz), 133.75 (d, *J* = 11.0 Hz), 133.10 (d, *J* = 11.0 Hz), 132.67 (d, *J* = 2.0 Hz), 132.53 (d, *J* = 11.0 Hz), 132.10 (d, *J* = 10.0 Hz), 130.75, 130.55, 130.04 (d, *J* = 29.0 Hz), 129.94, 129.02 (d, *J* = 2.0 Hz), 128.47 (d, *J* = 3.0 Hz), 127.46 (d, *J* = 127.0 Hz), 127.40, 126.53, 126.28 (d, *J* = 7.0 Hz), 124.73 (d, *J* = 16.0 Hz), 119.87 (d, *J* = 5.0 Hz), 106.03 (d, *J* = 34.0 Hz), 82.93 (d, *J* = 184.0 Hz), 54.20, 21.16; ^{31}P NMR (162 MHz, $CDCl_3$): δ -4.08; HRMS (EI): Exact mass calcd for $C_{28}H_{22}N_3OP$: 447.1501, Found: 447.1507.

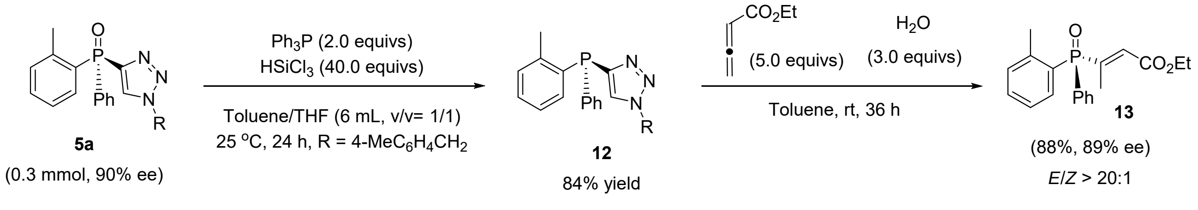


To an oven-dried 25 mL Schlenk tube was added **8** (134.1 mg, 0.3 mmol), Ph_3P (157.2 mg, 0.6 mmol), toluene/THF 6.0 mL (1/1, v/v). After the solution was stirred for 5 min, $HSiCl_3$ (1.2 mL, 40 equivs) was added, and the resulting mixture was stirred at 25 ºC for 24 h. After full consumption of **8** by TLC analysis, the mixture was diluted with 20 mL cold Et_2O and transferred to a 250 mL flask. After the mixture was stirred at 0 ºC for 10 min, ice (10 g) was added in one-portion, followed by the dropwise addition of 10 mL NaOH solution (20%, aq). The mixture was transferred to a separating funnel. The organic layer was separated, and the aqueous phase was extracted with cold Et_2O (3 × 20 mL). The combined organic phase was washed successively with cold saturated brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by a short pad of silica gel which was cooled at 0 ºC using cold PE/EtOAc (10:1, v/v, cooled at -20 ºC for 30 min) as the eluent to afford the P-chiral phosphine **9** in 81% yield (104.7 mg) as white solid. Mp: 50-53 ºC; IR (neat): 3107, 2948, 2162, 1591, 1503, 1486, 1357, 1205, 1046, 969, 841,755 cm^{-1}; HPLC analysis (Chiralcel AD-H, 20% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 10.29 min, t_r (minor) = 11.84 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{25}$ = + 18.88 (c = 0.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.56-8.52 (m, 1H), 8.14 (td, *J* = 7.2, 1.1 Hz, 1H), 7.89-7.84 (m, 2H), 7.55-7.48 (m, 6H), 7.34-7.32 (m, 3H), 7.15-7.07 (m, 4H), 5.48-5.37 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.29 (d, *J* = 4.0 Hz), 138.64, 134.27 (d, *J* = 23.0 Hz), 133.65 (d, *J* = 5.0 Hz), 131.88 (d, *J* = 2.0 Hz), 131.74, 131.54 (d, *J* = 30.0 Hz), 130.88 (d, *J* = 6.0 Hz), 129.73, 129.72 (d, *J* = 135.0 Hz), 128.76 (d, *J* = 1.0 Hz), 128.33, 128.19, 128.04, 127.77 (d, *J* = 163.0 Hz), 126.48 (d, *J* = 2.0

Hz), 126.10 (d, *J* = 1.0 Hz), 125.81 (d, *J* = 22.0 Hz), 125.66, 122.61 (d, *J* = 1.0 Hz), 108.22 (d, *J* = 7.0 Hz), 83.93, 53.84, 21.14; ^{31}P NMR (122 MHz, $CDCl_3$): δ -65.59; HRMS (EI): Exact mass calcd for $C_{28}H_{22}N_3P$: 431.1551, Found: 431.1545.



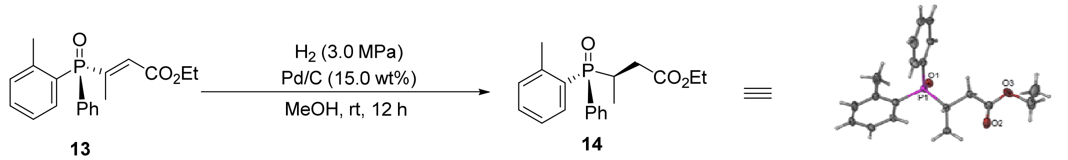
To an oven-dried 25 mL Schlenk tube was added **9** (64.7 mg, 0.15 mmol), **10** (84.0 mg, 0.75 mmol), H_2O (8.1 mg, 0.45 mmol), toluene (1.5 mL). The solution was stirred for 36 h at room temperature. After full consumption of **9** by TLC analysis, EtOAc (10 mL) was added and the organic layer was washed with 10 mL brine and then dried over anhydrous Na_2SO_4. After concentration, the residue was purified by silica gel column chromatography using PE/EtOAc/CH_2Cl_2 (2:1:1, v/v/v) as the eluent, affording product **11** as sticky oil in 85% yield; IR (neat): 3457, 2979, 2173, 1731, 1506, 1488, 1443, 1367, 1329, 1187, 1027, 985, 846, 802, 774, 758 cm^{-1}; HPLC analysis (Chiralcel OD-H, 20% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 9.12 min, t_r (minor) = 10.19 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{25}$ = -21.8 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 8.3 Hz, 1H), 8.38 (dd, *J* = 17.8, 7.0 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.61-7.54 (m, 5H), 7.47-7.44 (m, 1H), 7.40-7.36 (m, 2H), 6.49 (d, *J* = 21.8 Hz, 1H), 6.24 (d, *J* = 42.7 Hz, 1H), 3.87-3.73 (m, 2H), 3.29 (d, *J* = 13.3 Hz, 2H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.56 (d, *J* = 7.0 Hz), 136.73 (d, *J* = 110.0 Hz), 133.95 (d, *J* = 3.0 Hz), 133.69 (d, *J* = 11.0 Hz), 133.61 (d, *J* = 10.0 Hz), 132.84 (d, *J* = 11.0 Hz), 132.74 (d, *J* = 8.0 Hz), 132.55 (d, *J* = 2.0 Hz), 130.81, 128.98 (d, *J* = 1.0 Hz), 128.61, 127.48, 126.65, 126.32 (d, *J* = 6.0 Hz), 125.94 (d, *J* = 119.0 Hz), 124.66 (d, *J* = 15.0 Hz), 119.86 (d, *J* = 4.0 Hz), 105.95 (d, *J* = 29.0 Hz), 81.84 (d, *J* = 170.0 Hz), 60.94, 36.63 (d, *J* = 15.0 Hz), 13.85; ^{31}P NMR (162 MHz, $CDCl_3$): δ 10.0; HRMS (EI): Exact mass calcd for $C_{24}H_{21}O_3P$: 388.1228, Found: 388.1232.



To an oven-dried 25 mL of Schlenk tube was added **5a** (116.1 mg, 0.3 mmol), Ph_3P (157.2 mg, 0.6 mmol), toluene/THF 6.0 mL (1/1, v/v). After the solution was stirred for 5 min, $HSiCl_3$ (1.2 mL, 40 equivs) was added, and the resulting mixture was stirred at 25 °C for 24 h. After full consumption of **5a** by TLC analysis, the mixture was diluted with 20 mL of cold Et_2O and transferred to a 250 mL flask. After the mixture was stirred at 0 °C for 10 min, ice (10 g) was added in one-portion, followed by the dropwise addition of 10 mL NaOH solution (20%, aq). The mixture was transferred to a separating funnel. The organic layer was separated, and the aqueous phase was extracted with cold Et_2O (3 × 20 mL). The combined organic phase was washed successively with cold saturated brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by a short pad of silica gel which was cooled at 0 °C using cold PE/EtOAc (10:1, v/v, , cooled at -20 °C for 30 mins) as the eluent, to afford the P-stereogenic phosphine **12** in 84% yield (93.5 mg) as white solid. Mp: 62-63 °C; IR (neat): 2925, 2853, 2362, 1687, 1453, 1312, 1206, 1093, 1044, 909, 805, 742 cm^{-1}; we failed to resolute the racemic compound of **12** by HPLC. $[\alpha]_D^{25}$ = + 23.0 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (m, 2H), 7.33-7.27 (m, 3H), 7.24-7.20 (m, 2H), 7.17-7.14 (m, 3H), 7.11-7.07 (m, 3H), 7.04-7.01 (m, 1H), 5.46 (s, 2H), 2.36 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.32 (d, *J* = 4.0 Hz), 141.97 (d, *J* = 26.0 Hz), 138.61, 135.50 (d, *J* = 7.0 Hz), 134.83 (d, *J* = 8.0 Hz), 133.62 (d, *J* = 20.0 Hz), 132.78, 131.66, 130.17 (d, *J* = 5.0 Hz), 129.76, 129.44 (d, *J* = 2.0 Hz), 129.22 (d, *J* = 2.0 Hz), 128.95 (d, *J* = 7.0 Hz), 128.57 (d, *J* = 8.0 Hz), 127.89, 126.09, 53.77, 21.30 (d, *J* = 3.0 Hz), 21.13; ^{31}P NMR (162 MHz, $CDCl_3$): δ -39.75; HRMS (EI): Exact mass calcd for $C_{23}H_{22}N_3P$: 371.1551, Found: 371.1549.

To an oven-dried 25 mL Schlenk tube was added **12** (55.7 mg, 0.15 mmol), **10** (84.0 mg, 0.75 mmol), H_2O (8.1 mg, 0.45 mmol), toluene (1.5 mL). The solution was stirred for 36 h at room temperature. After full consumption of **12** by TLC analysis, EtOAc (10 mL) was added. The organic layer was washed with brine (10 mL) and then dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography on silica gel using PE/EtOAc/CH_2Cl_2 (2:1:1, v/v) as the eluent, affording the desired product **13** as sticky oil in 88% yield; *E*/Z >20:1; IR (neat): 3098, 2922, 2043, 1731, 1560, 1452, 1402, 1193, 1125, 803, 764 cm^{-1}; HPLC analysis (Chiralcel AD-H, 20% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 9.12 min, t_r (minor) = 10.18 min) gave the isomeric composition of the product: 89% ee. $[\alpha]_D^{25}$ = -17.9 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.70-7.65 (m, 2H), 7.59-7.56 (m, 1H), 7.53-7.43 (m, 3H), 7.32-7.29 (m, 1H), 7.23-7.17 (m, 2H), 6.38 (dd, *J* = 20.7, 1.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.52 (s, 3H), 2.33 (dd, *J* = 13.4, 1.4 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.07 (d, *J* = 25.0 Hz), 149.37 (d, *J* = 87.0 Hz), 143.49 (d, *J* = 8.0 Hz), 132.92 (d, *J* = 13.0 Hz), 132.41 (d, *J* = 3.0 Hz), 132.22 (d, *J* = 3.0

Hz), 132.18 (d, *J* = 9.0 Hz), 131.88 (d, *J* = 10.0 Hz), 130.48 (d, *J* = 11.0 Hz), 130.38 (d, *J* = 102.0 Hz), 128.76 (d, *J* = 12.0 Hz), 128.35 (d, *J* = 102.0), 125.47 (d, *J* = 13.0 Hz), 60.67, 21.59 (d, *J* = 4.0 Hz), 15.72 (d, *J* = 8.0 Hz), 14.15; ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.52; HRMS (EI): Exact mass calcd for $C_{19}H_{21}O_3P$: 328.1228, Found: 328.1233.



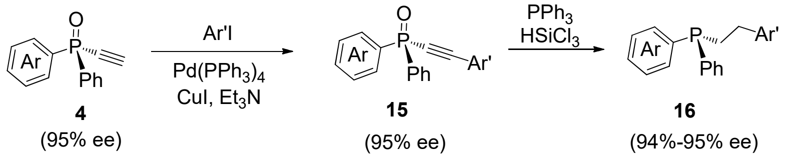
13
(0.6 mmol, 89% ee)

14
(91%, 89% ee, 1.6:1 dr)

X-ray structure of the major diastereomer of **14**
(>99% ee, >20:1 dr)

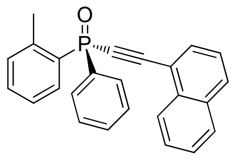
To an oven-dried hydrogen autoclave, **13** (200 mg, 0.6 mmol), Pd/C (30 mg, 15.0 wt%), MeOH (6.0 mL) were successively added. Under 3.0 MPa pressure of hydrogen gas, the solution was stirred for 12 h at room temperature. After full consumption of **13** by TLC analysis, the residue was purified by column chromatography on silica gel using PE/EtOAc (1:2, v/v) as the eluent, affording the desired product **14** in 91% yield as white solid. ^{1}H NMR analysis revealed the dr value was 1.6:1. HPLC analysis (Chiralcel AS-H, 5% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; major diastereomer: t_r (major) = 16.55 min, t_r (minor) = 24.91 min; minor diasteroer: t_r (major) = 18.44 min, t_r (minor) = 30.15 min) gave the isomeric composition of major diasteromer: 89% ee, gave the isomeric composition of minor diasteromer: 89% ee. Recrystallization from PE/CH_2Cl_2 by two times afforded the single crystal of the major diastereomer **14** to >20:1 dr and above 99% ee. HPLC analysis (Chiralcel AS-H, 5% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 14.94 min, t_r (minor) = 23.89 min) gave the isomeric composition of the major diastereomer **14**: >99% ee. $[\alpha]_D^{20}$ = -11.9 (c = 0.36, $CHCl_3$); IR (neat): 3691, 2976, 1724, 1591, 1436, 1371, 1284, 1170, 1051, 997, 721 cm^{-1}; ^{1}H NMR for mixture diastereomer (500 MHz, $CDCl_3$): δ 7.74-7.70 (m, 1.2H), 7.68-7.63 (m, 1.9H), 7.50-7.39 (m, 4.0H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.22-7.15 (m, 1.1H), 4.16-4.01 (m, 2.1H), 3.13-3.05 (m, 1H), 2.91-2.86 (m, 0.23H), 2.56-2.48 (m, 1H), 2.44 (s, 2.6H), 2.43-2.34 (m, 1.2H), 1.34 (dd, *J* = 15.7, 7.0 Hz, 2.49H), 1.27 (t, *J* = 7.1 Hz, 0.8H), 1.21 (t, *J* = 7.1 Hz, 2.2H), 1.14 (dd, *J* = 15.7, 7.0 Hz, 0.54H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.63 (d, *J* = 17.5 Hz), 142.88 (d, *J* = 6.25 Hz), 131.95 (d, *J* = 11.25 Hz), 131.90 (d, *J* = 93.75 Hz), 131.45, 131.14 (d, *J* = 2.5 Hz), 130.89 (d, *J* = 10.0 Hz), 130.76 (d, *J* = 8.75 Hz), 128.95 (d, *J* = 95.0 Hz), 128.16 (d, *J* = 11.25 Hz), 125.03 (d, *J* = 11.25 Hz), 60.42, 34.47, 28.14 (d, *J* = 73.75 Hz), 21.04 (d, *J* = 3.75 Hz), 13.72 , 12.94 (d, *J* = 3.75 Hz); ^{31}P NMR (202 MHz, $CDCl_3$): δ 38.24; HRMS (ESI): Exact mass calcd for $C_{19}H_{23}NaO_3P[M+Na]^+$: 353.1277, Found: 353.1283.

8.2 The synthesis of P-chiral tertiary phosphines 16 and their application



General procedure for the synthesis of 15: To an oven-dried 25 mL Schlenk tube was successively added **4** (0.3 mmol), $Pd(PPh_3)_4$ (34.68 mg, 0.03 mmol), CuI (5.7 mg, 0.03 mmol), Et_3N (303 mg, 3.0 mmol) and anhydrous DMF (3.0 mL), followed by the addition of Ar'I (0.45 mmol). The resulting mixture was stirred at 50 °C for 4 h. After the full consumption of **4** by TLC analysis, EtOAc (20 mL) was added and the organic layer was washed with H_2O and brine (3 × 20 mL) and then dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography on silica gel using PE/EtOAc (2:1, v/v) as the eluent, affording the desired products **15** as white solid.

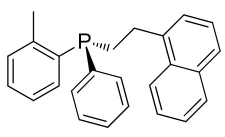
General procedure for the synthesis of 16: To an oven-dried 10 mL of sealing tube was added **15** (0.2 mmol), Ph_3P (104.8 mg, 0.4 mmol), Toluene/THF 6.0 mL (1/1, v/v). After the solution was stirred for 5 min, $HSiCl_3$ (0.8 mL, 40 equivs) was added, and the resulting mixture was stirred at 70 °C for 1.0-2.5 h. After full consumption of **15** by TLC analysis, the mixture was diluted with 20 mL of cold Et_2O and transferred to a 250 mL flask. After the mixture was stirred at 0 °C for 10 min, ice (10 g) was added in one-portion, followed by the dropwise addition of 10 mL NaOH solution (20%, aq). The mixture was transferred to a separating funnel. The organic layer was separated, and the aqueous phase was extracted with cold Et_2O (3 × 20 mL). The combined organic phase was washed successively with cold saturated brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by a short pad of silica gel which was cooled at 0 °C using cold PE/EtOAc (10:1, v/v, cooled at -20 °C for 30 min) as the eluent, to afford the desired P-stereogenic phosphines **16**.



15a

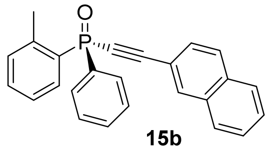
The reaction afforded **15a** in 86% yield as white solid, Mp: 180-182 °C. IR (neat): 3057, 2976, 2166, 1587, 1436, 1336, 1274, 1192, 1051, 883, 771 cm^{-1}; HPLC analysis (Chiralcel AD-H, 5% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 75.29 min, t_r (minor) = 78.57 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{20}$ = - 9.3 (c = 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 7.9 Hz, 1H), 8.10 (dd, J = 15.8, 7.6 Hz, 1H), 7.95-7.85 (m, 4H), 7.60-7.43 (m, 7H), 7.36 (t, J = 6.7 Hz, 1H), 7.29-7.26 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.91 (d, J = 10.0 Hz), 133.33, 133.20 (d, J =

117.5 Hz), 132.97 (d, *J* = 3.75 Hz), 132.89, 132.74 (d, *J* = 2.5 Hz), 132.54 (d, *J* = 1.25 Hz), 132.34 (d, *J* = 2.5 Hz), 131.85 (d, *J* = 12.5 Hz), 131.38, 131.06 (d, *J* = 11.25 Hz), 130.23 (d, *J* = 120.0 Hz), 128.84 (d, *J* = 13.75 Hz), 128.63, 127.77, 126.99, 125.81 (d, *J* = 13.75 Hz), 125.63, 125.11, 117.51 (d, *J* = 3.75 Hz), 104.14 (d, *J* = 30.0 Hz), 87.72 (d, *J* = 168.75 Hz), 21.40 (d, *J* = 5.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$): δ 9.43; HRMS (ESI): Exact mass calcd for $C_{25}H_{19}NaOP$[M+Na]$^+$: 389.1066, Found: 389.1052.



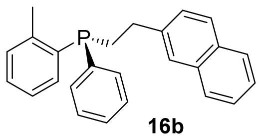
16a

The reaction afforded **16a** in 56% yield as sticky oil, IR (neat): 2976, 1629, 1587, 1433, 1340, 1269, 1095, 1051, 979, 893, 779 cm^{-1}; HPLC analysis (Chiralcel OD-H, 1% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 8.12 min, t_r (minor) = 7.52 min) gave the isomeric composition of the product: 94% ee. $[\alpha]_D^{20}$ = + 8.4 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.72-7.68 (m, 2H), 7.45-7.31 (m, 10H), 7.28-7.18 (m, 3H), 3.26-3.08 (m, 2H), 2.49-2.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.71 (d, *J* = 24.0 Hz), 138.97 (d, *J* = 14.0 Hz), 138.48 (d, *J* = 13.0 Hz), 136.38 (d, *J* = 13.0 Hz), 133.95, 133.00 (d, *J* = 19.0 Hz), 131.53, 130.75, 130.33 (d, *J* = 5.0 Hz), 128.82, 128.72, 128.66, 128.55, 128.48, 126.86, 126.03, 125.90, 125.65 (d, *J* = 7.0 Hz), 125.52, 123.59, 29.37 (d, *J* = 20.0 Hz), 29.17 (d, *J* = 13.0 Hz), 21.43 (d, *J* = 19.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ -25.88; HRMS (ESI): Exact mass calcd for $C_{25}H_{24}P$[M+H]$^+$: 355.1610, Found: 355.1608.



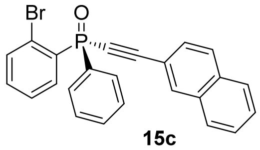
15b

The reaction afforded **15b** in 86% yield as white solid, Mp: 188-190 °C. IR (neat): 2976, 1436, 1336, 1274, 1111, 1051, 902, 827, 805, 804, 744 cm^{-1}; HPLC analysis (Chiralcel OD-H, 20% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 10.50 min, t_r (minor) = 11.57 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{20}$ = + 8.8 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 8.07 (dd, *J* = 15.6, 7.5 Hz, 1H), 7.89 (dd, *J* = 14.0, 7.1 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 3H), 7.59-7.47 (m, 7H), 7.36 (t, *J* = 6.7 Hz, 1H), 7.28-7.27 (m, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.92 (d, *J* = 10.0 Hz), 133.79, 133.57 (d, *J* = 2.0 Hz), 133.31(d, *J* = 120.0 Hz), 132.93 (d, *J* = 12.0 Hz), 132.61, 132.57 (d, *J* = 3.0 Hz), 132.19 (d, *J* = 2.0 Hz), 131.76 (d, *J* = 12.0 Hz), 131.06 (d, *J* = 11.0 Hz), 130.37 (d, *J* = 120.0 Hz), 128.74 (d, *J* = 14.0 Hz), 128.44, 128.14, 127.97, 127.93, 127.85 (d, *J* = 2.0 Hz), 127.10, 125.73 (d, *J* = 14.0 Hz), 117.28 (d, *J* = 4.0 Hz), 105.82 (d, *J* = 30.0 Hz), 83.33 (d, *J* = 168.0 Hz), 21.32 (dd, *J* = 5.1, 3.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 9.04; HRMS (ESI): Exact mass calcd for $C_{25}H_{19}NaOP$[M+Na]$^+$: 389.1066, Found: 389.1055.



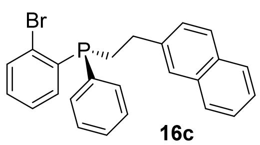
16b

The reaction gave **16b** in 62% yield as an oil, IR (neat): 2976, 1506, 1433, 1269, 1186, 1114, 1095, 1051, 960, 854, 779 cm^{-1}; HPLC analysis (Chiralcel OD-H, 1% ^{i}PrOH/hexane, 1.0 mL/min, 205 nm; t$_r$ (major) = 8.05 min, t$_r$ (minor) = 7.35 min) gave the isomeric composition of the product: 94% ee. $[\alpha]_D^{20}$ = + 13.4 (c = 1.00, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.77-7.72 (m, 3H), 7.58 (s, 1H), 7.43-7.37 (m, 5H), 7.30-7.28 (m, 4H), 7.25-7.21 (m, 2H), 7.19-7.16 (m, 1H), 2.98-2.81 (m, 2H), 2.47-2.33 (m, 5H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 142.79 (d, *J* = 23.75 Hz), 140.27 (d, *J* = 13.75 Hz), 138.52 (d, *J* = 13.75 Hz), 136.38 (d, *J* = 13.75 Hz), 133.73, 132.96 (d, *J* = 18.75 Hz), 132.17, 130.73, 130.41 (d, *J* = 5.0 Hz), 128.77, 128.63 (d, *J* = 5.0 Hz), 128.56, 128.12, 127.73, 127.55, 127.12, 126.17, 126.15, 126.07, 125.33, 32.50 (d, *J* = 18.75 Hz), 29.61 (d, *J* = 13.75 Hz), 21.49 (d, *J* = 21.25 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ -26.11; HRMS (ESI): Exact mass calcd for C$_{25}$H$_{24}$P[M+H]$^+$: 355.1610, Found: 355.1611.



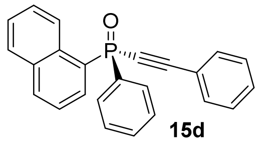
15c

The reaction afforded **15c** in 85% yield as white solid, Mp: 199-200 ºC. IR (neat): 2976, 1433, 1338, 1274, 1134, 1051, 856, 815, 732, 692, 628 cm^{-1}; HPLC analysis (Chiralcel OD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 18.55 min, t$_r$ (minor) = 15.23 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{20}$ = + 79.3 (c = 1.00, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.32 (ddd, *J* = 14.0, 7.7, 1.7 Hz, 1H), 8.18 (s, 1H), 7.95-7.89 (m, 2H), 7.83 (d, *J* = 8.6 Hz, 3H), 7.67-7.43 (m, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 135.57 (d, *J* = 9.0 Hz), 134.58 (d, *J* = 9.0 Hz), 133.93 (d, *J* = 2.0 Hz), 133.85, 133.74 (d, *J* = 2.0 Hz), 132.53, 132.39 (d, *J* = 127.0 Hz), 132.38 (d, *J* = 3.0 Hz), 132.08 (d, *J* = 124.0 Hz), 131.27 (d, *J* = 12.0 Hz), 128.65 (d, *J* = 14.0 Hz), 128.47, 128.17, 128.04, 127.94, 127.83 (d, *J* = 2.0 Hz), 127.36 (d, *J* = 12.0 Hz), 127.12, 125.58 (d, *J* = 7.0 Hz), 117.15 (d, *J* = 4.0 Hz), 106.16 (d, *J* = 31.0 Hz), 82.01 (d, *J* = 178.0 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ 7.27; HRMS (ESI): Exact mass calcd for C$_{24}$H$_{16}$BrNaOP[M+Na]$^+$: 453.0014, Found: 453.0021.

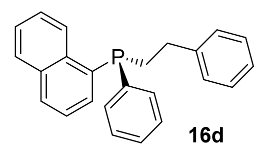


16c

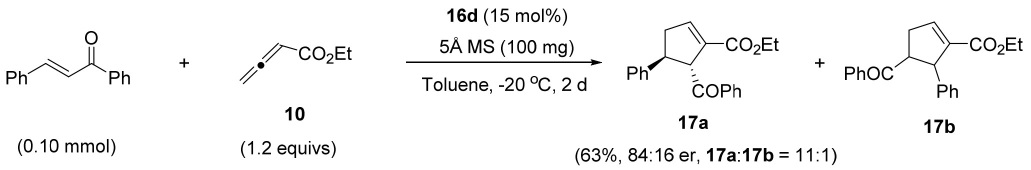
The reaction afforded **16c** in 55% yield as sticky oil, IR (neat): 2976, 1734, 1446, 1433, 1342, 1274, 1176, 1095, 1051, 979, 854 cm^{-1}; HPLC analysis (Chiralcel OD-H, 1% ^{i}PrOH/hexane, 1.0 mL/min, 205 nm; t$_r$ (major) = 13.05 min, t$_r$ (minor) = 10.74 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{25}$ = + 9.6 (c = 1.00, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.81-7.76 (m, 3H), 7.62 (s, 1H), 7.60-7.57 (m, 1H), 7.54-7.50 (m, 2H), 7.47-7.42 (m, 2H), 7.39-7.38 (m, 3H), 7.34-7.26 (m, 3H), 7.21-7.17 (m, 1H), 3.05-2.84 (m, 2H), 2.56-2.37 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 139.97 (d, *J* = 13.75 Hz), 139.55 (d, *J* = 13.75 Hz), 136.86 (d, *J* = 13.75 Hz), 133.66, 133.39, 133.24, 133.21 (d, *J* = 2.5 Hz), 132.59, 132.13, 130.36 (d, *J* = 30.0 Hz), 130.10, 129.12, 128.74, 128.69, 128.11, 127.67, 127.50, 127.01, 126.08 (d, *J* = 11.25 Hz), 125.32, 32.38 (d, *J* = 20.0 Hz), 29.38 (d, *J* = 13.75 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ -15.65; HRMS (ESI): Exact mass calcd for $C_{24}H_{21}BrP[M+H]^+$: 419.0559, Found: 419.0556.


15d

The reaction afforded **15d** in 85% yield as white solid, Mp: 175-177 °C. IR (neat): 3056, 2172, 1732, 1590, 1488, 1437, 1334, 1192, 985, 801, 755 cm^{-1}; HPLC analysis (Chiralcel OD-H, 10% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 26.37 min, t$_r$ (minor) = 21.98 min) gave the isomeric composition of the product: 96% ee. $[\alpha]_D^{25}$ = + 13.5 (c = 1.00, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.57-8.55 (m, 1H), 8.28 (dd, *J* = 17.5, 7.1 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.94-7.86 (m, 3H), 7.58-7.37 (m, 9H), 7.32 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 133.80 (d, *J* = 10.0 Hz), 133.77 (d, *J* = 3.0 Hz), 133.46 (d, *J* = 121.0 Hz), 133.26 (d, *J* = 11.0 Hz), 132.65 (d, *J* = 10.0 Hz), 132.51 (d, *J* = 2.0 Hz), 132.26 (d, *J* = 3.0 Hz), 131.05 (d, *J* = 11.0 Hz), 130.67, 129.01 (d, *J* = 2.0 Hz), 128.76 (d, *J* = 14.0 Hz), 128.57, 128.17 (d, *J* = 120.0 Hz), 127.36, 126.52, 126.49 (d, *J* = 6.0 Hz), 124.62 (d, *J* = 15.0 Hz), 120.08 (d, *J* = 4.0 Hz), 105.91 (d, *J* = 30.0 Hz), 83.45 (d, *J* = 170.0 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ 8.98; HRMS (EI): Exact mass calcd for $C_{24}H_{17}OP$: 352.1017, Found: 352.1015.


16d

The reaction afforded **16d** in 68% yield as sticky oil, IR (neat): 3052, 2917, 1948, 1810, 1699, 1312, 1206, 1093, 1044, 909, 805, 742 cm^{-1}; HPLC analysis (Chiralcel OD-H, 1% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 8.91 min, t$_r$ (minor) = 8.04 min) gave the isomeric composition of the product: 94% ee. $[\alpha]_D^{25}$ = + 36.7 (c = 1.0, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.53 (dd, *J* = 9.2, 4.6 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.58-7.55 (m, 1H), 7.49-7.41 (m, 5H), 7.32 -7.23 (m, 5H), 7.18 – 7.16 (m, 3H), 2.86-2.68 (m, 2H), 2.55-2.39 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 142.66 (d, *J* = 14.0 Hz), 138.29 (d, *J* = 13.0 Hz), 135.74 (d, *J* = 21.0 Hz), 135.25 (d, *J* = 16.0 Hz), 133.63 (d, *J* = 4.0 Hz), 132.79 (d, *J* = 19.0 Hz), 129.86 (d, *J* = 1.0 Hz), 129.46, 128.72 (d, *J* = 2.0 Hz), 128.62, 128.55 (d, *J* = 7.0 Hz), 128.47, 128.18, 126.16 (d, *J* = 2.0 Hz), 126.06, 126.04 (d, *J* = 27.0 Hz), 125.96 (d, *J* = 1.0 Hz), 125.51 (d, *J* = 2.0 Hz), 32.39 (d, *J* = 19.0 Hz), 29.81 (d, *J* = 13.0 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ -27.59; HRMS (EI): Exact mass calcd for $C_{24}H_{21}P$: 340.1381, Found: 340.1376.



To an oven-dried 25 mL of Schlenk tube was added **16d** (5.1 mg, 0.015 mmol), chalcone (20.8 mg, 0.10 mmol), 5Å MS (100 mg), toluene 1.0 mL. After the solution was stirred for 5 min under -20 °C, **10** (13.5 mg, 0.12 mmol) was added, and the resulting mixture was stirred at -20 °C for 48 h. Then the product was directly purified by flash chromatography using PE/EtOAc (3:1, v/v) as the eluent to afford the mixture of **17a** and **17b** as white solid in 63% yield. HPLC analysis (Chiralcel OD-H, 10% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 16.48 min, t_r (minor) = 10.65 min) gave the ee value of product **17a**: 68% ee (84:16 er). The NMR data was in accord with literature.[8] ^{1}H NMR analysis revealed that the ratio of **17a** and **17b** was 11:1. ^{1}H NMR (400 MHz, $CDCl_3$) for **17a**: δ 7.78-7.76 (m, 2H), 7.52-7.48 (m, 1H), 7.37-7.19 (m, 7H), 7.11-7.10 (m, 1H), 4.88-4.86 (m, 1H), 4.16-4.08 (m, 2H), 3.57 (dt, J = 9.9, 5.1 Hz, 1H), 3.19 (ddt, J = 18.9, 9.0, 2.5 Hz, 1H), 2.75-2.68 (m, 1H), 1.15 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **17a**: δ 200.79, 164.03, 145.09, 144.97, 136.55, 135.70, 133.07, 128.93, 128.79, 128.45, 127.02, 126.84, 60.54, 60.29, 48.94, 42.15, 14.04; HRMS (EI): Exact mass calcd for $C_{21}H_{20}O_3$: 320.1412, Found: 320.1413.

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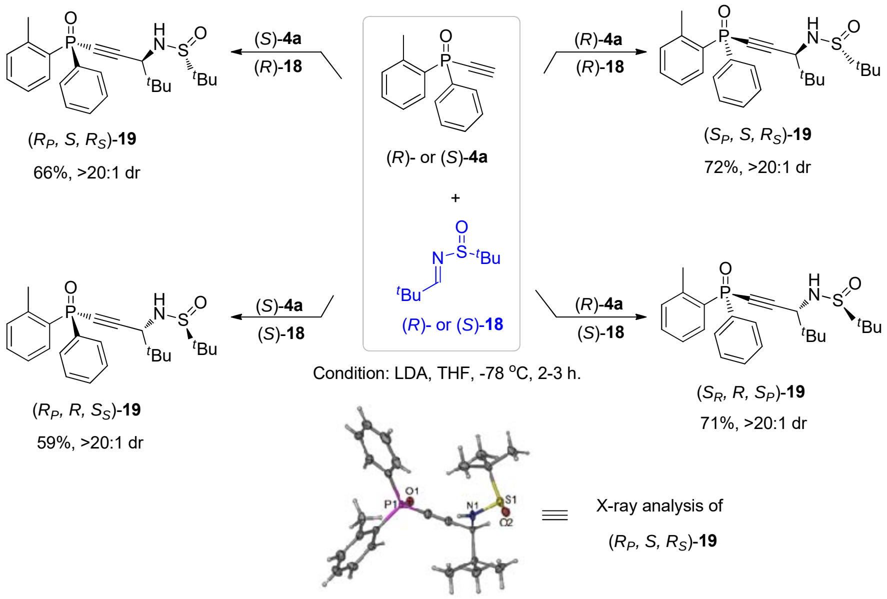
[8] J. E. Wilson and G. C. Fu, *Angew. Chem.; Int. Ed.,* 2006, **45**, 1426.

8.3 Diastereodivergent synthesis of P-chiral tertiary phosphine oxides sulfinamide 19



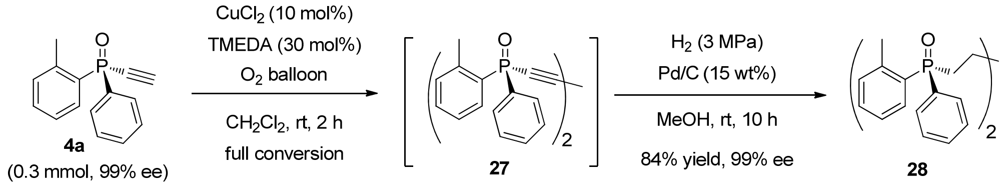
In an oven-dried 25 mL Schlenk tube, to a solution (*S*)**-4a** (72 mg, 0.30 mmol) in anhydrous THF (5 mL) was slowly added LDA (0.30 mmol, 1.5 M in THF/heptane/ethylbenzene) at -78 °C. The resulting mixture was stirred at -78 °C for 15 minutes, then (*R*)**-18** (62.4 mg, 0.33 mmol) diluted with 3 mL THF was slowly added and the resulting mixture was stirred at -78 °C for another 2-3 h. After full consumption of (*S*)**-4a** by TLC analysis, saturated NH_4Cl (aq. 10 mL) and EtOAc (10 mL) were added. The organic layer was washed with H_2O and brine (3×15 mL) and then dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography on silica gel using PE/EtOAc/CH_2Cl_2 (4:2:1, v/v/v) as the eluent to afford the desired product (R_P, *S*, R_S)**-19** as white solid in 66% yield, Mp: 132-134 °C. IR (neat): 3574, 2976, 2191, 1591, 1440, 1361, 1340, 1276, 1176, 1112, 1095, 1049, 937, 881, 723, 696 cm^{-1}; >20:1 dr; $[\alpha]_D^{20}$ = - 34.3 (c = 1.07, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (dd, *J* = 15.9, 7.5 Hz, 1H), 7.79-7.75 (m, 2H), 7.56-7.53 (m, 1H), 7.49-7.43 (m, 3H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.24-7.21 (m, 1H), 4.03 (dd, *J* = 5.5, 2.9 Hz, 1H), 3.35 (d, *J* = 5.4 Hz, 1H), 2.43 (s, 3H), 1.16 (s, 9H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.89 (d, *J* = 11.25 Hz), 133.01 (d, *J* = 120.0 Hz), 132.71 (d, *J* = 12.5 Hz), 132.57 (d, *J* = 2.5 Hz), 132.19 (d, *J* = 3.75 Hz), 131.68 (d, *J* = 11.25 Hz), 130.91 (d, *J* = 11.25 Hz), 130.09 (d, *J* = 118.75 Hz), 128.65 (d, *J* = 13.75 Hz), 125.57 (d, *J* = 13.75 Hz), 104.96 (d, *J* = 27.25 Hz), 80.99 (d, *J* = 162.5 Hz), 58.62 (d, *J* = 2.5 Hz), 56.45, 36.15, 26.19, 22.36, 21.18 (d, *J* = 5.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$): δ 8.89; HRMS (ESI): Exact mass calcd for $C_{24}H_{32}NNaO_2PS$ $[M+Na]^+$: 452.1784, Found: 452.1803.

In an oven-dried 25 mL Schlenk tube, to a solution (*S*)-**4a** (72 mg, 0.30 mmol) in anhydrous THF (5 mL) was slowly added LDA (0.30 mmol, 1.5 M in THF/heptane/ethylbenzene) at -78 °C. The resulting mixture was stirred at -78 °C for 15 minutes, then (*S*)-**18** (62.4 mg, 0.33 mmol) diluted with 3 mL THF was slowly added and the resulting mixture was stirred at -78 °C for another 2-3 h. After full consumption of (*S*)-**4a** by TLC analysis, saturated NH_4Cl (aq. 10 mL) and EtOAc (10 mL) were added. The organic layer was washed with H_2O and brine (3×15 mL) and then dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography on silica gel using PE/EtOAc/CH_2Cl_2 (4:2:1, v/v/v) as the eluent to afford the desired product (R_P, *R*, S_S)-**19** as white solid in 59% yield, Mp: 125-127 ºC. IR (neat): 3433, 2976, 2189, 1506, 1433, 1338, 1274, 1178, 1136, 1095, 979, 881, 723 cm^{-1}; >20:1 dr; $[\alpha]_D^{20}$ = + 21.9 (c = 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 15.8, 7.6 Hz, 1H), 7.77 (dd, *J* = 13.9, 7.1 Hz, 2H), 7.55-7.52 (m, 1H), 7.48-7.42 (m, 3H), 7.30-7.26 (m, 1H), 7.23-7.20 (m, 1H), 4.03 (dd, *J* = 5.5, 2.9 Hz, 1H), 3.36 (d, *J* = 5.3 Hz, 1H), 2.43 (s, 3H), 1.15 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.91 (d, *J* = 10.0 Hz), 133.06 (d, *J* = 120.0 Hz), 132.63 (d, *J* = 16.0 Hz), 132.58 (d, *J* = 1.0 Hz), 132.14 (d, *J* = 3.0 Hz), 131.69 (d, *J* = 12.0 Hz), 130.95 (d, *J* = 11.0 Hz), 130.13 (d, *J* = 120.0 Hz), 128.59 (d, *J* = 14.0 Hz), 125.58 (d, *J* = 13.0 Hz), 104.99 (d, *J* = 27.0 Hz), 81.05 (d, *J* = 163.0 Hz), 58.62, 56.43, 36.14, 26.18, 22.34, 21.16; ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.84; HRMS (ESI): Exact mass calcd for $C_{24}H_{32}NNaO_2PS$ $[M+Na]^+$: 452.1784, Found: 452.1803.

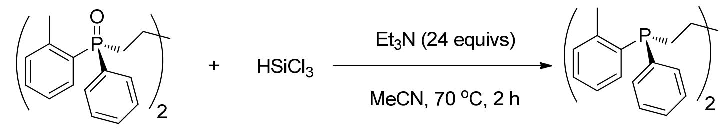
In an oven-dried 25 mL of Schlenk tube, to a solution (*R*)-**4a** (72 mg, 0.30 mmol) in anhydrous THF (5 mL) was slowly added LDA (0.30 mmol, 1.5 M in THF/heptane/ethylbenzene) at -78 °C. The resulting mixture was stirred at -78 °C for 15 minutes, then (*R*)-**18** (62.4 mg, 0.33 mmol) diluted with 3 mL THF was slowly added and the resulting mixture was stirred at -78 °C for another 2-3 h. After full consumption of (*R*)-**4a** by TLC analysis, saturated NH_4Cl (aq. 10 mL) and EtOAc (10 mL) were added, and the organic layer was washed with H_2O and brine (3×15 mL) and then dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography on silica gel using PE/EtOAc/CH_2Cl_2 (4:2:1, v/v/v) as the eluent to afford the desired product (S_P, *S*, R_S)-**19** as white solid in 72% yield, Mp: 125-127 ºC. IR (neat): 3445, 2976, 2175, 1587, 1502, 1456, 1330, 1274, 1138, 1095, 933, 881, 792 cm^{-1}; >20:1 dr; $[\alpha]_D^{20}$ = -21.9 (c = 0.94, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 15.9, 7.6 Hz, 1H), 7.81-7.77 (m, 2H), 7.52-7.49 (m, 1H), 7.46-7.39 (m, 3H), 7.29 (t, *J* = 6.6 Hz, 1H), 7.20-7.17 (m, 1H), 3.84 (dd, *J* = 9.2, 3.0 Hz, 1H), 3.47 (d, *J* = 9.2 Hz, 1H), 2.43 (s, 3H), 1.21 (s, 9H), 0.99 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.89 (d, *J* = 10.0 Hz), 133.03 (d, *J* = 12.5 Hz), 132.98 (d, *J* = 120.0 Hz), 132.47 (d, *J* = 2.5 Hz), 132.08 (d, *J* = 2.5 Hz), 131.56 (d, *J* = 11.25 Hz), 131.02 (d, *J* = 11.25 Hz), 130.06 (d, *J* = 120.0 Hz), 128.61 (d, *J* = 13.75 Hz), 125.71 (d, *J* = 13.75 Hz), 105.64 (d, *J* = 27.5 Hz), 80.57 (d, *J* = 163.75 Hz), 58.56 (d, *J* = 2.5 Hz), 57.00, 36.70, 26.12, 22.75, 21.17 (d, *J* = 5.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$): δ 8.84; HRMS (ESI): Exact mass calcd for $C_{24}H_{32}NNaO_2PS$ [M+Na]$^+$: 452.1784, Found: 452.1782.

In an oven-dried 25 mL of Schlenk tube, to a solution (*R*)**-4a** (72 mg, 0.30 mmol) in anhydrous THF (5 mL) was slowly added LDA (0.30 mmol, 1.5 M in THF/heptane/ethylbenzene) at -78 °C. The resulting mixture was stirred at -78 °C for 15 minutes, then (*S*)**-18** (62.4 mg, 0.33 mmol) diluted with 3 mL THF was slowly added and the resulting mixture was stirred at -78 °C for another 2-3 h. After full consumption of (*R*)**-4a** by TLC analysis, saturated NH_4Cl (aq. 10 mL) and EtOAc (10 mL) were added, and the organic layer was washed with H_2O and brine (3×15 mL) and then dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography on silica gel using PE/EtOAc/CH_2Cl_2 (4:2:1, v/v/v) as the eluent to afford the desired product (S_P*, R,* S_S)**-19** as white solid in 71% yield, Mp: 130-132 ºC. IR (neat): 3402, 2976, 2189, 1732, 1438, 1340, 1278, 1180, 1083, 1053, 937, 883, 723 cm^{-1}; >20:1 dr; $[\alpha]_D^{20}$ = + 34.3 (c = 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (dd, *J* = 15.9, 7.5 Hz, 1H), 7.87-7.81 (m, 2H), 7.52-7.40 (m, 4H), 7.30-7.26 (m, 1H), 7.22-7.19 (m, 1H), 3.84 (dd, *J* = 9.2, 3.0 Hz, 1H), 3.44 (d, *J* = 9.2 Hz, 1H), 2.44 (s, 3H), 1.22 (s, 9H), 1.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.83 (d, *J* = 11.0 Hz), 133.00 (d, *J* = 119.0 Hz), 132.85 (d, *J* = 13.0 Hz),132.43 (d, *J* = 3.0 Hz), 132.08 (d, *J* = 2.0 Hz), 131.56 (d, *J* = 12.0 Hz), 131.17 (d, *J* = 11.0 Hz), 130.21 (d, *J* = 120.0 Hz), 128.62 (d, *J* = 14.0 Hz), 125.68 (d, *J* = 13.0 Hz), 105.56 (d, *J* = 27.0 Hz), 80.64 (d, *J* = 163.0 Hz), 58.57, 57.01, 36.68, 26.12, 22.73, 21.14; ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.89; HRMS (ESI): Exact mass calcd for $C_{24}H_{32}NNaO_2PS$ [M+Na]$^+$: 452.1784, Found: 452.1769.

8.4 The synthesis of digold Au(I) complex 21

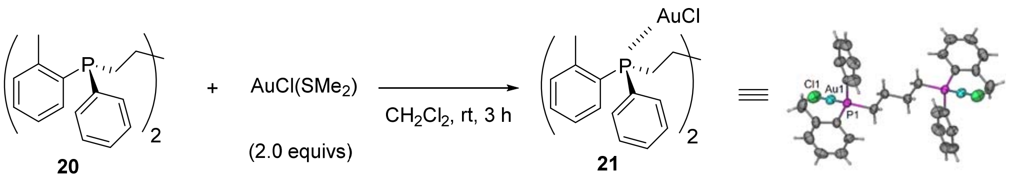


Under an atmosphere of O_2 balloon, to an oven-dried 25 mL Schlenk tube was successively added **4a** (72 mg, 0.3 mmol), $CuCl_2$ (4.0 mg, 0.03 mmol), TMEDA (10.4 mg, 0.09 mmol), followed by the addition of CH_2Cl_2 (2 mL). The resulting mixture was stirred at room temperature for 2 h. After full consumption of **4a** by TLC analysis, the crude product was passed through a short column chromatography on silica gel using EtOAc/CH_2Cl_2 (1:1, v/v) as the eluent affording the desired product **27** as white solid in 99% yield. The product **27**was directly used for the next step. To a high pressure hydrogen reactor was successively added **27** (72 mg, 0.3 mmol), Pd/C (11.0 mg, 15 wt%), followed by the addition of MeOH (4 mL). Under the hydrogen pressure of 3 MPa, the resulting mixture was stirred at room temperature for 10 h. After full consumption of **27** by TLC analysis, the crude product was passed through a column chromatography on silica gel using EtOAc/CH_2Cl_2 (1:1, v/v) as the eluent affording the desired product **28** as white solid in 84% yield, Mp: 180-182 °C. IR (neat): 3504, 2976, 1435, 1340, 1276, 1176, 1134, 1111, 1051, 858, 844, 744, 725 cm^{-1}; HPLC analysis (Chiralcel AD-H, 30% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 9.85 min, t_r (minor) = 22.59 min) gave the isomeric composition of the product: 99% ee. $[\alpha]_D^{20}$ = - 16.3 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.53 (m, 6H), 7.52-7.47 (m, 2H), 7.44-7.39 (m, 6H), 7.29-7.26 (m, 2H), 7.21-7.19 (m, 2H), 2.39-2.29 (m, 8H), 2.28-2.18 (m, 2H), 1.80-1.78 (m, 2H), 1.67-1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.38 (d, J = 8.0 Hz, 2C), 133.50 (dd, J = 96.0, 3.0 Hz, 2C), 132.08 (2C), 131.98 (2C), 131.52 (2C), 131.40 (d, J = 1.0 Hz, 2C), 130.68 (d, J = 9.0 Hz, 2C), 131.58 (dd, J = 97.0 Hz, 3.0 Hz, 2C), 128.61 (d, J = 12.0 Hz, 2C), 125.54 (d, J = 11.0 Hz, 2C), 29.34 (d, J = 71.0 Hz), 23.06 (dd, J = 15.0 Hz , 3.0 Hz, 2C), 21.36 (2C); ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.69; HRMS (ESI): Exact mass calcd for $C_{30}H_{32}NaO_2P_2$ $[M+Na]^+$: 509.1770, Found: 509.1772.



28 (0.185 mmol, 99% ee) (40.0 equivs) **20** 80% yield, 99% ee

To an oven-dried 25 mL of Schlenk tube was added **28** (90.0 mg, 0.185 mmol), Et_3N (448 mg, 4.4 mmol), MeCN (4.0 mL). After the solution was stirred for 5 min, $HSiCl_3$ (0.74 mL, 40 equivs) was added, and the resulting mixture was stirred at 70 ºC for 2 h. After full consumption of **28** by TLC analysis, the mixture was diluted with 20 mL of cold Et_2O and transferred to a 250 mL flask. After the mixture was stirred at 0 ºC for 10 min, ice (10 g) was added in one-portion, followed by the dropwise addition of 10 mL NaOH solution (20%, aq). The mixture was transferred to a separating funnel. The organic layer was separated, and the aqueous phase was extracted with cold Et_2O (3 × 20 mL). The combined organic phase was washed successively with cold saturated brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by a short pad of silica gel which was cooled at 0 ºC using PE/EtOAc (10:1, v/v) as the eluent (the eluent was cooled at -20 ºC for 30 min) to afford the P, P-stereogenic phosphine **20** in 80% yield (67 mg) as white solid. Mp: 53-55 ºC. IR (neat): 3442, 2976, 2920, 1587, 1431, 1413, 1340, 1273, 1095, 937, 893, 815, 729 cm^{-1}; HPLC analysis (Chiralcel OD-H, 1% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 7.16 min, t_r (minor) = 9.93 min) gave the isomeric composition of the product: >99% ee. $[\alpha]_D^{20}$ = + 14.8 (c = 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.16 (m, 18H), 2.35 (s, 6H), 2.02-1.91 (m, 4H), 1.64-1.57 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.63 (d, *J* = 24.0 Hz, 2C), 138.74 (d, *J* = 13.0 Hz, 2C), 136.61 (d, *J* = 14.0 Hz, 2C), 132.81 (d, *J* = 18.0 Hz, 2C), 130.64 (2C), 130.23 (d, *J* = 4.0 Hz, 2C), 128.55 (2C), 128.42 (2C), 128.37 (2C), 125.97 (2C), 27.71 (dd, *J* = 21.25, 3.0 Hz, 2C), 27.26 (d, *J* = 11.0 Hz, 2C), 21.37 (d, *J* = 21.0 Hz, 2C); ^{31}P NMR (162 MHz, $CDCl_3$): δ -26.82; HRMS (ESI): Exact mass calcd for $C_{30}H_{33}P_2$ $[M+H]^+$: 455.2052, Found: 455.2064.



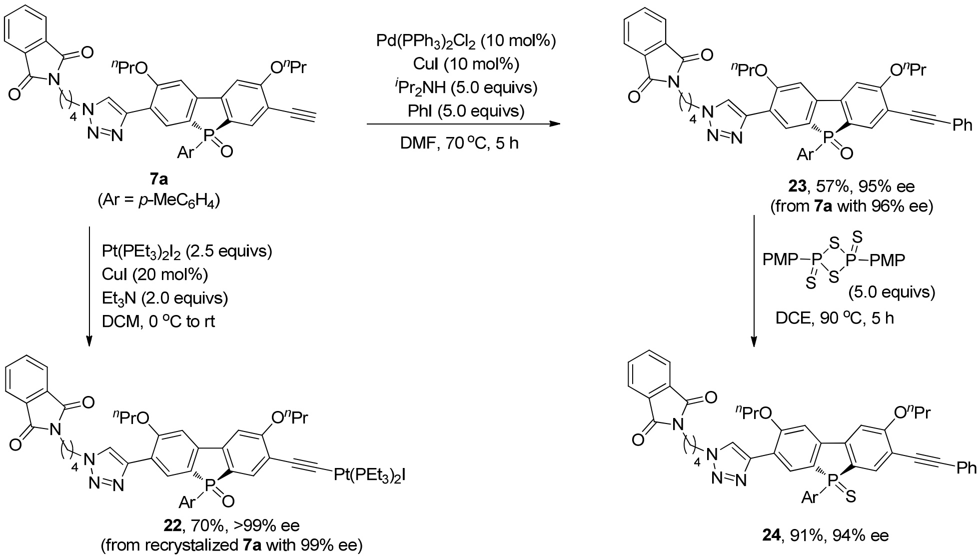
20
(0.10 mmol, 99% ee)

21
95% yield, 99% ee

To an oven-dried 25 mL of Schlenk tube was added **20** (45.4 mg, 0.10 mmol), AuCl(SMe_2) (58.8 mg, 0.2 mmol), CH_2Cl_2 (2.0 mL), and the resulting mixture was stirred at room temperature for 3 h. After full consumption of **20** by TLC analysis, The residue was purified through a short pad of silica gel by using PE/CH_2Cl_2 (1:2, v/v) as the eluent to afford the P, P-bimetallic Au(I) complex **21** in 95% yield (99 mg) as white solid. Mp: 112-114 ºC. IR (neat): 2974, 2923, 1734, 1436, 1340, 1278, 1178, 1147, 1095, 1051, 979, 883, 804 cm^{-1}; $[\alpha]_D^{20}$ = + 61.7 (c = 0.68, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.57-7.36 (m, 16H), 7.23-7.22 (m, 2H), 2.59-2.47 (m, 2H), 2.37-2.20 (m, 8H), 2.02-1.94 (m, 2H), 1.68-1.59 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.93 (d, *J* = 11.25 Hz, 2C), 133.41 (d, *J* = 13.75 Hz, 2C), 132.36 (d, *J* = 8.75 Hz, 2C), 132.19 (2C), 132.06 (2C), 130.84 (d, *J* = 8.75 Hz, 2C), 129.43 (d, *J* = 12.5 Hz, 2C), 129.03 (d, *J* = 61.25 Hz, 2C), 126.62 (d, *J* = 58.75 Hz, 2C), 126.55 (d, *J* = 10.0 Hz, 2C), 27.69 (d, *J* = 38.75 Hz, 2C), 27.17 (dd, *J* = 18.75, 3.75 Hz, 2C), 22.38 (d, *J* = 11.25 Hz, 2C); ^{31}P NMR (202 MHz, $CDCl_3$): δ 21.09; MALDI: Exact mass calcd for $C_{30}H_{32}NaAu_2Cl_2P_2$ $[M+Na]^+$: 941.06, Found: 941.39.

8.5 The synthesis of compounds 22-24 and their photophysical properties

8.5.1 The synthesis of compounds 22-24



7a
(Ar = *p*-MeC$_6$H$_4$)

23, 57%, 95% ee
(from **7a** with 96% ee)

22, 70%, >99% ee
(from recrystalized **7a** with 99% ee)

24, 91%, 94% ee

Under an atmosphere of N$_2$, to the Schlenk tube was added **7a** (139.6 mg, 0.2 mmol, >99% ee), Pt(PEt$_3$)$_2$I$_2$ (226.0 mg, 0.4 mmol), CuI (7.6 mg, 0.04 mmol), Et$_3$N (40.4 mg,0.4 mmol) and CH$_2$Cl$_2$ (5.0 mL). The resulting solution was stirred at 25 °C for 0.5 hour. After concentration, the residue was purified by silica gel column chromatography using CH$_2$Cl$_2$/acetone (from 4:1 to 2:1) as the eluent, affording the desired product **22** in 70% yield as yellow solid. Mp: 135-137 °C. IR (KBr): 3552, 3476, 3414, 2963, 2108, 1712, 1396, 1238, 1035, 808, 721, 523 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t$_r$ (major) = 7.25 min) gave the isomeric composition of the product: >99% ee. $[\alpha]_D^{20}$ = + 72.6 (c = 1.37, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.60 (d, J = 10.4 Hz, 1H), 7.98 (s, 1H), 7.82-7.80 (m, 2H), 7.70-7.68 (m, 2H), 7.57-7.52 (m, 3H), 7.21 (s, 1H), 7.16-7.12 (m, 3H), 4.45-4.40 (m, 2H), 4.27-4.16 (m, 2H), 4.11 (t, J = 6.4 Hz, 2H), 3.72 (t, J = 6.8 Hz, 2H), 2.32 (s, 3H), 2.21-2.17 (m, 12H), 2.03-1.84 (m, 6H), 1.76-1.68 (m, 2H); 1.14-1.06 (m, 24H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.15, 163.05, 158.94, 142.70 (d, J = 23.0 Hz), 142.20, 142.13, 139.97 (d, J = 22.0 Hz), 133.92, 133.47, 131.72, 130.99 (d, J = 12.0 Hz), 129.16 (d, J = 13.0 Hz), 128.78 (d, J = 11.0 Hz), 128.44, 127.37, 125.69 (d, J = 84.0 Hz), 124.59 (d, J = 84.0 Hz), 123.08, 122.85, 120.14 (d, J = 12.0 Hz), 119.23 (d, J = 14.0 Hz), 103.58 (d, J = 12.0 Hz), 97.38, 95.31, 70.34, 70.17, 49.29, 36.73, 29.51, 27.43, 25.41, 22.48, 22.47, 21.43, 16.37 (t, J = 17.0 Hz), 10.75, 10.56, 8.13; ^{31}P NMR (162 MHz, CDCl$_3$): δ 32.03 (s, 1P), 8.76 (t, J = 1542.2 Hz, 2P); HRMS (ESI): Exact mass calcd for C$_{53}$H$_{68}$N$_4$O$_5$NaIP$_3$Pt [M+Na]$^+$: 1278.2993, Found: 1278.2970.

Under an atmosphere of N_2, to the Schlenk tube was added **7a** (279.2 mg, 0.4 mmol, 96% ee), $Pd(PPh_3)_2Cl_2$ (28.0 mg, 0.04 mmol), CuI (7.6 mg, 0.04 mmol), $^i Pr_2NH$ (258 mg, 2.0 mmol) and DMF (8.0 mL). After the addition of iodobenzene (408 mg, 2.0 mmol), the solution was stirred at 70 °C for 5 h. After the completion of the reaction, EtOAc (20 mL) was added. The resulting mixture was washed with brine (5×10 mL), and the combined organic layer was dried over Na_2SO_4, and concentrated under vacuo to give the residue, which was purified by column chromatography using CH_2Cl_2/acetone (from 4:1 to 2:1) as the eluent, affording the product **23** in 57% yield as yellow solid. Mp: 244-246 °C. IR (KBr): 2925, 2872, 1711, 1590, 1397, 1239, 1046, 719, 526 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 9.42 min, t_r (minor) = 15.57 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{20}$ = + 64.0 (c = 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, J = 10.0 Hz, 1H), 7.86 (s, 1H), 7.82-7.80 (m, 2H), 7.71-7.68 (m, 3H), 7.54-7.49 (m, 2H), 7.46-7.44 (m, 2H), 7.28-7.26 (m, 3H), 7.19-7.14 (m, 3H), 7.10 (d, J = 2.0 Hz, 1H), 4.42-4.37 (m, 2H), 4.32-4.27 (m, 1H), 4.18-4.03 (m, 3H), 3.72 (t, J = 7.2 Hz, 2H), 2.32 (s, 3H), 2.03-1.97 (m, 2H), 1.95-1.86 (m, 4H), 1.74-1.67 (m, 2H); 1.15-1.11 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.27, 163.64 (d, J = 2.0 Hz), 158.96 (d, J = 3.0 Hz), 143.18 (d, J = 22.0 Hz), 142.40 (d, J = 3.0 Hz), 142.18, 141.96, 133.97, 133.78 (d, J = 11.0 Hz), 131.94, 131.48, 131.12 (d, J = 11.0 Hz), 129.36 (d, J = 13.0 Hz), 128.51, 128.38 (d, J = 14.0 Hz), 128.16 (d, J = 13.0 Hz), 127.28, 125.84 (d, J = 45.0 Hz), 124.72 (d, J = 44.0 Hz), 123.48, 123.22, 123.15, 120.80 (d, J = 12.0 Hz), 114.06 (d, J = 14.0 Hz), 104.48 (d, J = 11.0 Hz), 104.08 (d, J = 11.0 Hz), 95.28, 85.41, 70.47, 70.35, 49.30, 36.86, 27.54, 25.53, 22.60, 22.55, 21.51, 10.90, 10.62; ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.39; HRMS (ESI): Exact mass calcd for $C_{47}H_{43}N_4O_4NaP$ $[M+Na]^+$: 797.2659, Found: 797.2696.

A suspension of the above coupling product **23** (38.7 mg, 0.05 mmol) and Lawesson's reagent (100 mg, 0.25 mmol) in dry 1,2- dichloroethane (1 mL) was heated at 70 °C for 5 h. After the solvent being evaporated, the residue was purified by column chromatography on silica gel using CH_2Cl_2/acetone = 4:1 to 2:1) to give **24** (35.8 mg, 91% yield) as yellow solid. Mp: 258-260 °C. IR (KBr): 2962, 2934, 2872, 1713, 1437, 1238, 1048, 719, 678 cm^{-1}. HPLC analysis (Chiralcel AD-H, 40% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 6.48 min, t_r (minor) = 9.47 min) gave the isomeric composition of the product: 94% ee. $[\alpha]_D^{20}$ = + 30.7 (c = 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, J = 10.8 Hz, 1H), 7.81-7.79 (m, 2H), 7.70-7.68 (m, 2H), 7.62-7.54 (m, 4H), 7.36-7.34 (m, 2H), 7.23-7.19 (m, 4H), 7.18-7.09 (m, 3H), 4.56-4.52 (m, 1H), 4.50-4.41 (m, 1H), 4.34-4.29 (m, 1H), 4.22-4.15 (m, 1H), 4.07-3.98 (m, 2H), 3.74-3.66 (m, 2H), 2.29 (s, 3H), 1.98-1.94

(m, 4H), 1.86-1.83 (m, 2H), 1.68-1.66 (m, 2H); 1.19 (t, *J* = 7.6 Hz, 3H), 1.11 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.26, 163.08 (d, *J* = 3.0 Hz), 158.45 (d, *J* = 2.0 Hz), 142.72 (d, *J* = 19.0 Hz), 142.39, 142.12, (d, *J* = 13.0 Hz), 141.82 (d, *J* = 19.0 Hz), 133.97, 132.89 (d, *J* = 12.0 Hz), 131.89, 131.41, 131.00 (d, *J* = 12.0 Hz), 129.18 (d, *J* = 13.0 Hz), 128.54, 128.08, 127.82, 127.40 (d, *J* = 57.0 Hz), 127.38 (d, *J* = 13.0 Hz), 126.45 (d, *J* = 58.0 Hz), 123.59, 123.22, 123.00, 120.70 (d, *J* = 13.0 Hz), 114.28 (d, *J* = 14.0 Hz), 104.81 (d, *J* = 10.0 Hz), 104.15 (d, *J* = 10.0 Hz), 95.16, 85.66, 70.74, 70.31, 49.18, 36.76, 27.65, 25.44, 22.58, 22.45, 21.37, 10.82, 10.74; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.57; HRMS (ESI): Exact mass calcd for $C_{47}H_{43}N_4O_4NaSP$ $[M+Na]^+$: 813.2640, Found: 813.2671.

8.5.2 Photophysical properties

UV-vis spectra was recorded in a quartz cell (light path 10 mm) on a Cary 50Bio UV-visible spectrophotometer (Figure S3). Steady-state fluorescence spectra was recorded in a conventional quartz cell (light path 10 mm) on a Cary Eclipse fluorescence spectrophotometer (Figure S4). Fluorescence quantum yield were obtained relative to quinine sulfate on a Cary Eclipse fluorescence spectrophotometer. All the samples were diluted with CH_2Cl_2 to obtain an absorbance below 0.05 at the excitation wavelength. Five different concentration for each sample and quinine sulfate were measured to get the relationship between integrated fluorescence intensity and absorbance. The gradients were used to calculate the relative quantum yield of the measured sample relative to quinine sulfate according to the following equation:

$$\phi_X = \phi_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right)\left(\frac{\eta^2{}_X}{\eta^2{}_{ST}}\right)$$

Where the subscripts ST and X denote the standard (here is quinine sulfate) and test sample, respectively, *Φ*, *Grad* and *η* represent fluorescence quantum yield, gradient from the plot of integrated fluorescence intensity *vs* absorbance and refractive index of the solvent, respectively. Due to the solvent for the standard (quinine sulfate) and test samples are H_2O and CH_2Cl_2, η_{ST} and η_X should be 1.34 and 1.42, respectively.

Considering the lack of literature report for the study of the optical properties of chiral phosphole oxides, we initially checked the optical properties of compounds **6a**, **7a**, **23** and **24**, with absorption and emission data shown in Table S6. As compared with **6a**, the UV/Vis absorption and emission band maxima of compound **7a** is slightly red-shifted, but that of product **23** with extended π-system is obviously red-shift. Additionally, the quantum yield (QY) of **7a** was significantly higher than that of

6a (0.40 *vs* 0.14) and the chiral *P*-sulfide **24** showed a relatively lower QY than that of **23**. These results showed that the properties of chiral phosphole **7** could be readily tuned for optoelectronic application.

Table S6. Optical properties of compound 6a, 7a, 23 and 24 in CH_2Cl_2 at 25 °C

Compounds	UV/Vis absorption λ_{abs} [nm]^a	Fluorescence λ_{max} (nm)	$\Phi_F{}^b$
6a	267, 276, 350, 365	400	0.14
7a	270, 280, 352, 367	405	0.40
23	280, 290, 365, 382	421	0.33
24	282, 298, 367, 385	420	0.09

^{a}At 2.0×10^{-5} M. ^{b} Excited at λ =350 nm, measured relative to quinine sulfate

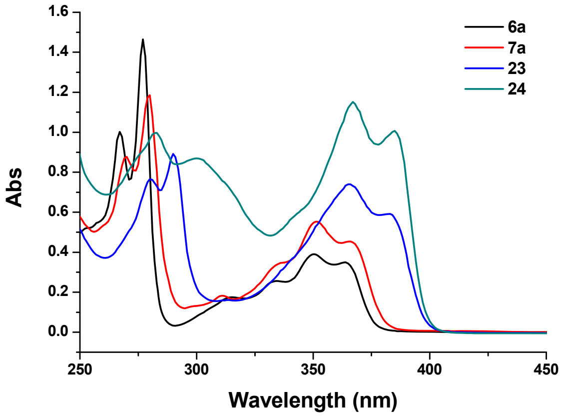


Figure S1. UV-vis spectra of **6a, 7a, 23** and **24** at 2.0×10^{-5} M in CH_2Cl_2 at 25 °C.

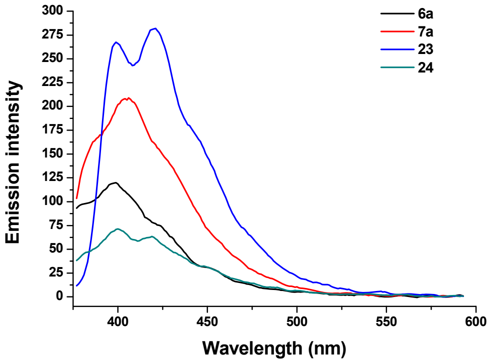


Figure S2. Fluorescence spectra of **6a, 7a, 23 and 24** at 1.0×10^{-6} M in CH_2Cl_2 at 25 °C, excited at 350 nm.

We also examined the CD spectra of **7a**, and found (*R*)-**7a** showed an obvious positive first (λ=270 nm) and negative second (λ=235 nm) Cotton effect peak. (*S*)-**7a** showed mirror image with (*R*)-**7a** in the 230-300 nm region. In the region of 300-400 nm, (*R*)/(*S*)-**7a** also showed symmetry CD spectrum, however, no Cotton effect peak were observed. The highest optical anisotropy factor was observed at 235 nm ($g_{abs}=3\times10^{-4}$) for both (*R*)-**7a** and (*S*)-**7a**, this value was in the region of most chiral organic molecule (from 10^{-5} to 10^{-2}). Based on these data, we tried to measure the circularly polarized luminescence (CPL) of (*R*)/(*S*)-**7a** with CPL-200. Unfortunately, due to the low chiral optical activity of these compound and measurement limit (g_{lum}~10^{-4}), we failed to collect high quality CPL spectrum.

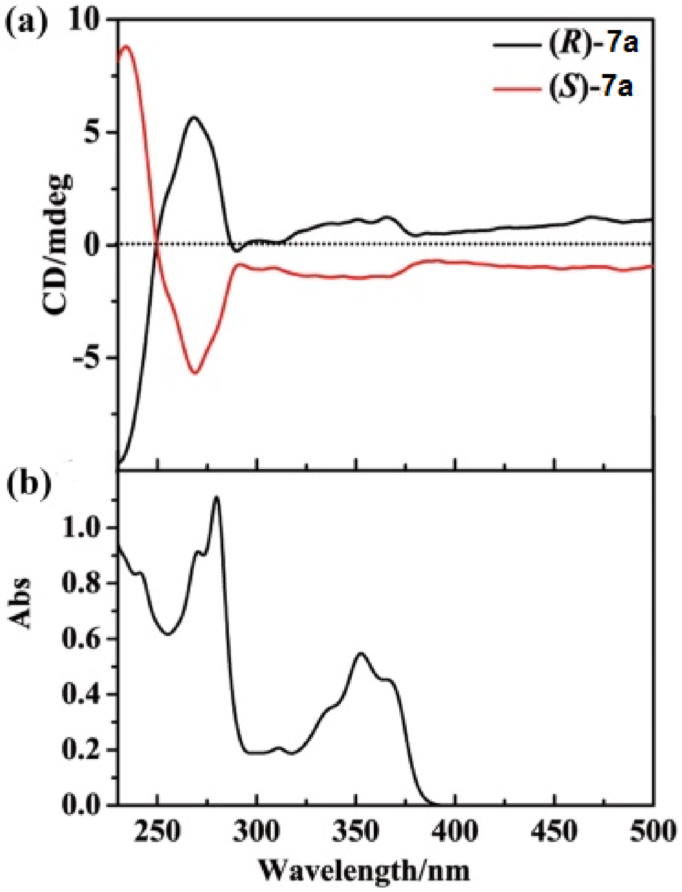


Figure S3. (a) CD spectra of (*R*)-**7a** (black line) and (*S*)-**7a** (red line) at 2×10^{-5} M (10 mm path length) in CH_2Cl_2 at 25 °C. (b) UV-vis spectra of (*R*)-**7a** in CH_2Cl_2 at 25 °C.

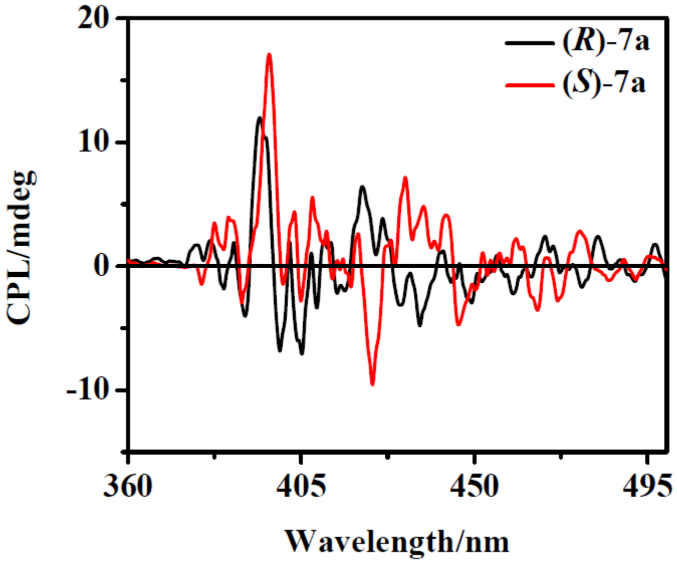
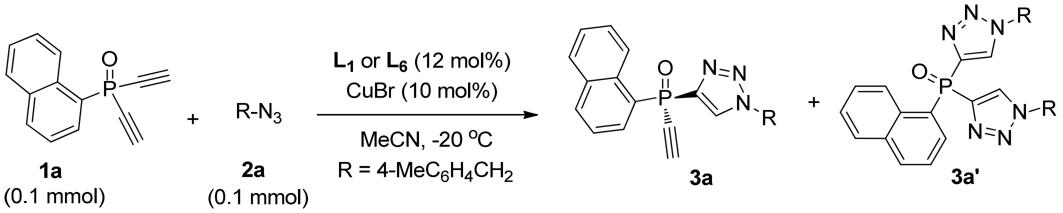


Figure S4. Baseline corrected CPL spectra of (*R*)-**7a** (black line; at 5×10^{-4} M; 96% ee) and (*S*)-**7a** (red line; at 5×10^{-4} M; 96% ee) excited at 320 nm in CH_2Cl_2 at 25 °C

9. Experimental evidence for synergic desymmetrization and kinetic resolution, and a possible model to explain the stereoselectivity of the progress

The procedure for the determination of the time-dependence enantioselectivity of the CuAAC reaction of **1a** and **2a** is as follows. Under an atmosphere of N_2, to a 25 mL Schlenk tube was added **L$_1$** or **L$_6$** (0.012 mmol) and CuBr (1.43 mg, 0.01 mmol), followed by the addition of 2.0 mL anhydrous CH_3CN. After stirring at 25 °C for 2 h, diethynylphosphine oxides **1a** (22.4 mg, 0.10 mmol) was added and the reaction mixture was then cooled to -20 °C and stirred for 0.5 h. Then azide **2a** (14.7 mg, 0.10 mmol) was added in one portion. The resulting homogenous solution was kept stirring at -20 °C. Aliquots (0.2 mL of the reaction mixture) were taken at the indicated reaction time and quickly passed through a 5 cm of silica gel using eluent CH_2Cl_2/EtOAc (2:1, v/v) that was pre-stored at -20 °C before use. Then the residue was used for ^{1}H NMR analysis to determine the conversion and the ratio of **3a/3a'**, and for the HPLC analysis of the ee value of **3a**. The results were shown in Table S7.

Table S7. The time-dependence enantioselectivity of the reaction of **1a** and **2a**

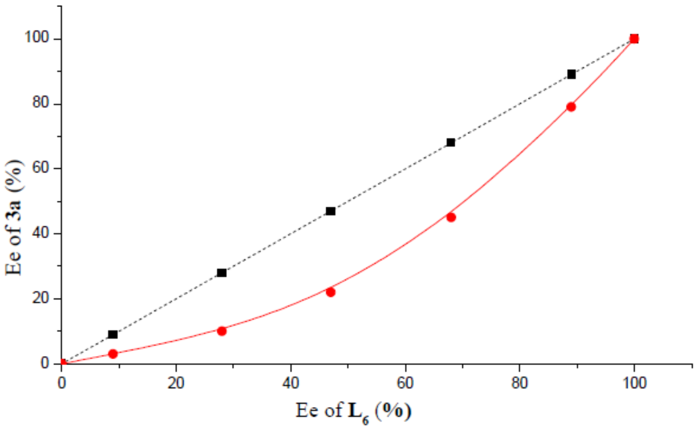


entry	time (h)	by **L$_1$** conv. (%)	by **L$_1$** **3a/3a'**[a]	by **L$_1$** ee of **3a** (%)[b]	by **L$_6$** conv. (%)	by **L$_6$** **3a/3a'**[a]	by **L$_6$** ee of **3a** (%)[b]
1	4	54	>20:1	82	50	>20:1	90
2	8	60	>20:1	84	58	>20:1	91
3	12	66	>20:1	86	65	>20:1	92
4	16	76	19:1	88	79	>20:1	93
5	24	84	17:1	89	87	19:1	94
6	48	90	11:1	91	95	14.8:1	95
7	96	>99	6.0:1	93	>99	14:1	95

[a] Determined by ^{1}H NMR (400 MHz) analysis using 1,3,5-trimethoxybenzene as the internal standard. [b] Determined by chiral HPLC analysis.

The time-dependence enantioselectivity of the reaction of **1a** and **2a** by using ligand **L$_1$** or **L$_6$** is shown above. Whereas similar conversion was found with a time of 4 h, with only trace amount of **3a'** formed in both cases, the reaction using **L$_6$** afforded **3a** with a clearly higher ee than by using **L$_1$** (90 vs. 82%). This clearly showed that with a bulk shielding group, **L$_6$** could achieve higher enantioselectivity in the desymmetrization. In addition, **L$_6$** was also more enantioselective than **L$_1$** in the kinetic resolution of racemic monotriazole **3a** using 0.5 equiv of **2a** (70% vs 48% ee for recovered (*R*)-**3a**, respectively).

Strong negative NLE was observed in the reaction of **1a** and **2a** mediated by **L$_6$**/CuBr. This is also a proof to support the possible involvement of dinuclear copper intermediates as the catalytically active species in CuAAC. Such asymmetric depletion might be rationalized by the hypothesis that the homochiral dimeric species is less reactive than the corresponding heterodimer. Studies of the exact nature of the catalytic species are currently underway.



A possible model to explain the stereoselectivity of the progress

The observed strong negative NLE effect was in accordance to the generally believed mechanism of CuAAC that involves an active dinuclear copper intermediate.[8] In light of this, together with the X-ray structure of PyBOX/Cu(I) complex reported by Gamasa and coworkers,[9] we proposed two possible homochiral dinuclear Cu(I) activation model **A** and **B** to account for the observed stereochemistry, and to rationalize the role of the C4 shielding group. As shown below, the C4 shielding group of newly developed PYBOX-type ligand might be of benefit to form a deeper pocket

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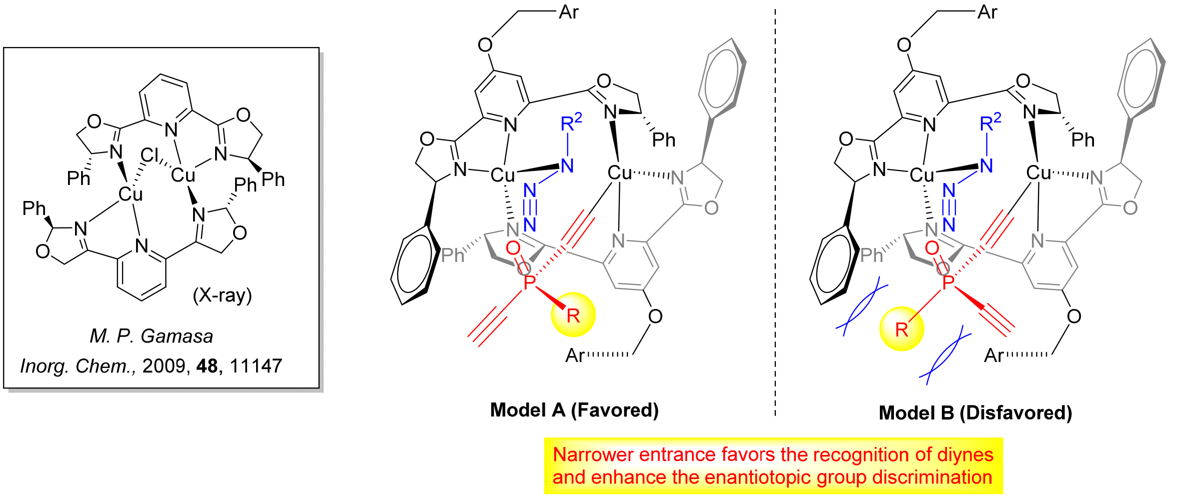
[8] (*a*) B. T. Worrell, J. A. Malik, V. V. Fokin, *Science* 2013, **340**, 457; (*b*) M. S. Ziegler, K. V. Lakshmi, T. D. Tilley, *J. Am. Chem. Soc.* 2017, **139**, 5378.

[9] (*a*) J. Díez, M. P. Gamasa, M. Panera, *Inorg. Chem.,* 2006, **45**, 10043; (*b*) M. Panera, J. Díez, I. Merino, E. Rubio, M. P. Gamasa, *Inorg. Chem.,* 2009, **48**, 11147.

with a narrower entrance, thus prevent monotriazoles from entering the pocket, leading to a better recognition of diynes over monotriazoles and affording better M/D ratio. In addition, the enhanced chiral pocket is also helpful to improve the enantioselection. Due to the steric hindrance of R group over ethynyl group, model **A** is favored, leading to chiral product with *R*-configuration.



M. P. Gamasa
Inorg. Chem., 2009, **48**, 11147

Model A (Favored)

Model B (Disfavored)

Narrower entrance favors the recognition of diynes and enhance the enantiotopic group discrimination

Figure S5. A possible model to explain the stereoselectivity of the catalytic progress

10. X-ray crystallographic data of 3b, 4a, 7o, 9, 14, 19 and 21

Data intensity of **3b**[9] was collected using a 'Bruker APEX-II CCD' diffractometer at 296(2) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **3b**: $C_{19}H_{17}N_3OP$, T = 296(2) K, Orthorhombic, P2(1)2(1)2(1), a = 9.0625(7) Å, b = 10.9721(8) Å, c = 18.2236(13) Å, α = 90 deg, β = 90 deg, γ = 90 deg, V = 1812.1(2) Å^3. Z = 4, d_{calc} = 1.225 Mg/m^3. 21121 reflections measured, 3182 unique [Rint = 0.0392], R1 = 0.0485, wR2 = 0.1274 ($I > 2\sigma(I)$, final), R1 = 0.0596, wR2 = 0.1359 (all data), GOF = 1.045, and 217 parameters.

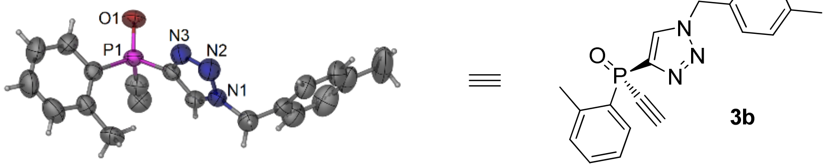


Table S8. Crystal data and structure refinement for **3b.**

Identification code	**3b**	
Empirical formula	$C_{19}H_{17}N_3OP$	
Formula weight	334.33	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.0625(7) Å	α = 90 deg.
	b = 10.9721(8) Å	β = 90 deg.
	c = 18.2236(13) Å	γ= 90 deg.
Volume	1812.1(2) Å^3	
Z, Calculated density	4, 1.225 Mg/m^3	
Absorption coefficient	0.161 mm^{-1}	
F(000)	700	
Crystal size	0.44 x 0.41 x 0.31 mm	
Theta range for data collection	2.17 to 25.01 deg.	

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[9] Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC number: 1508003).

Limiting indices	-10<=h<=10, -13<=k<=12, -21<=l<=21
Reflections collected / unique	21121 / 3182 [R(int) = 0.0392]
Completeness to theta = 25.01	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9517 and 0.9324
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3182 / 1 / 217
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0485, wR2 = 0.1274
R indices (all data)	R1 = 0.0596, wR2 = 0.1359
Absolute structure parameter	0.02(14)
Largest diff. peak and hole	0.559 and -0.148 e. Å^{-3}

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 3b. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
P(1)	7217(1)	1640(1)	8211(1)	55(1)
O(1)	6395(3)	2752(2)	8019(1)	82(1)
N(1)	11082(3)	1197(2)	7299(1)	62(1)
N(2)	11188(4)	2335(3)	7557(2)	76(1)
N(3)	9928(3)	2580(2)	7880(2)	66(1)
C(1)	8178(3)	554(3)	9539(2)	65(1)
C(2)	8197(5)	564(4)	10305(2)	92(1)
C(3)	7421(5)	1398(4)	10696(2)	100(1)
C(4)	6618(6)	2276(4)	10354(2)	102(1)
C(5)	6588(4)	2305(3)	9601(2)	81(1)
C(6)	7378(3)	1452(3)	9185(2)	57(1)
C(7)	9043(5)	-402(4)	9132(2)	86(1)
C(8)	6438(4)	309(3)	7866(2)	67(1)

C(9)	5842(4)	-546(4)	7610(2)	82(1)
C(10)	9029(3)	1609(3)	7816(1)	52(1)
C(11)	9756(4)	732(3)	7438(2)	60(1)
C(12)	12339(4)	651(4)	6906(2)	81(1)
C(13)	12341(4)	958(3)	6101(2)	65(1)
C(14)	11522(5)	298(4)	5613(2)	92(1)
C(15)	11529(6)	608(5)	4876(3)	110(1)
C(16)	12321(5)	1561(5)	4608(2)	94(1)
C(17)	13142(5)	2191(4)	5098(3)	94(1)
C(18)	13158(4)	1898(4)	5837(2)	78(1)
C(19)	12323(7)	1889(8)	3804(3)	164(3)

Table S10. Bond lengths [Å] and angles [deg] for **3b.**

P(1)-O(1)	1.472(2)
P(1)-C(8)	1.739(4)
P(1)-C(10)	1.793(3)
P(1)-C(6)	1.793(3)
N(1)-C(11)	1.330(4)
N(1)-N(2)	1.336(4)
N(1)-C(12)	1.473(4)
N(2)-N(3)	1.313(4)
N(3)-C(10)	1.347(4)
C(1)-C(6)	1.383(4)
C(1)-C(2)	1.396(5)
C(1)-C(7)	1.505(5)
C(2)-C(3)	1.356(6)
C(2)-H(2A)	0.9300
C(3)-C(4)	1.358(6)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.374(6)

C(4)-H(4A)	0.9300
C(5)-C(6)	1.401(4)
C(5)-H(5A)	0.9300
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-C(9)	1.179(5)
C(9)-H(9A)	1.1258
C(10)-C(11)	1.355(4)
C(11)-H(11A)	0.9300
C(12)-C(13)	1.504(4)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-C(18)	1.358(5)
C(13)-C(14)	1.366(5)
C(14)-C(15)	1.385(6)
C(14)-H(14A)	0.9300
C(15)-C(16)	1.359(7)
C(15)-H(15A)	0.9300
C(16)-C(17)	1.353(7)
C(16)-C(19)	1.507(6)
C(17)-C(18)	1.384(6)
C(17)-H(17A)	0.9300
C(18)-H(18A)	0.9300
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
O(1)-P(1)-C(8)	113.90(15)
O(1)-P(1)-C(10)	112.56(15)
C(8)-P(1)-C(10)	102.20(15)
O(1)-P(1)-C(6)	111.79(14)

C(8)-P(1)-C(6)	107.12(15)
C(10)-P(1)-C(6)	108.68(13)
C(11)-N(1)-N(2)	110.9(3)
C(11)-N(1)-C(12)	129.4(3)
N(2)-N(1)-C(12)	119.7(3)
N(3)-N(2)-N(1)	106.7(3)
N(2)-N(3)-C(10)	109.0(2)
C(6)-C(1)-C(2)	117.8(3)
C(6)-C(1)-C(7)	122.7(3)
C(2)-C(1)-C(7)	119.5(3)
C(3)-C(2)-C(1)	121.6(4)
C(3)-C(2)-H(2A)	119.2
C(1)-C(2)-H(2A)	119.2
C(2)-C(3)-C(4)	121.1(4)
C(2)-C(3)-H(3A)	119.5
C(4)-C(3)-H(3A)	119.5
C(3)-C(4)-C(5)	119.0(4)
C(3)-C(4)-H(4A)	120.5
C(5)-C(4)-H(4A)	120.5
C(4)-C(5)-C(6)	121.0(4)
C(4)-C(5)-H(5A)	119.5
C(6)-C(5)-H(5A)	119.5
C(1)-C(6)-C(5)	119.4(3)
C(1)-C(6)-P(1)	125.9(2)
C(5)-C(6)-P(1)	114.7(2)
C(1)-C(7)-H(7A)	109.5
C(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5

C(9)-C(8)-P(1)	175.7(3)
C(8)-C(9)-H(9A)	174.5
N(3)-C(10)-C(11)	108.1(3)
N(3)-C(10)-P(1)	120.3(2)
C(11)-C(10)-P(1)	131.5(2)
N(1)-C(11)-C(10)	105.3(3)
N(1)-C(11)-H(11A)	127.3
C(10)-C(11)-H(11A)	127.3
N(1)-C(12)-C(13)	112.6(3)
N(1)-C(12)-H(12A)	109.1
C(13)-C(12)-H(12A)	109.1
N(1)-C(12)-H(12B)	109.1
C(13)-C(12)-H(12B)	109.1
H(12A)-C(12)-H(12B)	107.8
C(18)-C(13)-C(14)	117.9(3)
C(18)-C(13)-C(12)	121.1(3)
C(14)-C(13)-C(12)	121.1(3)
C(13)-C(14)-C(15)	119.9(4)
C(13)-C(14)-H(14A)	120.0
C(15)-C(14)-H(14A)	120.0
C(16)-C(15)-C(14)	122.7(4)
C(16)-C(15)-H(15A)	118.6
C(14)-C(15)-H(15A)	118.6
C(17)-C(16)-C(15)	116.4(4)
C(17)-C(16)-C(19)	121.3(5)
C(15)-C(16)-C(19)	122.3(5)
C(16)-C(17)-C(18)	122.0(4)
C(16)-C(17)-H(17A)	119.0
C(18)-C(17)-H(17A)	119.0
C(13)-C(18)-C(17)	121.1(4)
C(13)-C(18)-H(18A)	119.5

C(17)-C(18)-H(18A)	119.5
C(16)-C(19)-H(19A)	109.5
C(16)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3b.** The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
P(1)	60(1)	49(1)	57(1)	1(1)	-5(1)	9(1)
O(1)	90(2)	70(2)	84(2)	16(1)	-3(1)	27(1)
N(1)	73(2)	58(2)	54(1)	6(1)	6(1)	12(1)
N(2)	84(2)	67(2)	79(2)	-5(2)	8(2)	-12(2)
N(3)	77(2)	56(2)	64(1)	-8(1)	4(1)	-7(1)
C(1)	64(2)	69(2)	61(2)	10(2)	-1(2)	-3(2)
C(2)	93(3)	107(3)	77(2)	27(2)	-4(2)	-2(2)
C(3)	116(3)	123(4)	61(2)	5(2)	13(2)	1(3)
C(4)	122(4)	113(3)	70(2)	-10(2)	29(2)	11(3)
C(5)	90(2)	77(2)	77(2)	-3(2)	14(2)	12(2)
C(6)	56(2)	56(2)	58(2)	0(1)	4(1)	-5(1)
C(7)	92(3)	73(2)	93(3)	24(2)	0(2)	21(2)
C(8)	59(2)	71(2)	72(2)	-2(2)	-17(2)	-3(2)
C(9)	77(2)	83(2)	86(2)	-11(2)	-6(2)	-3(2)
C(10)	69(2)	45(1)	44(1)	3(1)	-3(1)	1(2)
C(11)	73(2)	44(2)	64(2)	0(1)	6(2)	0(2)
C(12)	82(2)	87(2)	74(2)	15(2)	13(2)	24(2)

C(13)	64(2)	61(2)	69(2)	-2(2)	13(2)	12(2)
C(14)	85(2)	94(3)	96(3)	-7(2)	7(2)	-11(2)
C(15)	88(3)	149(4)	92(3)	-35(3)	-13(2)	-6(3)
C(16)	77(2)	144(3)	62(2)	-2(2)	13(2)	40(2)
C(17)	94(3)	101(3)	87(3)	11(2)	35(2)	2(2)
C(18)	77(2)	81(2)	77(2)	-11(2)	10(2)	-6(2)
C(19)	132(4)	286(8)	73(3)	29(4)	19(3)	78(5)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **3b**.

	x	y	z	U(eq)
H(2A)	8755	-15	10553	111
H(3A)	7439	1368	11205	120
H(4A)	6096	2848	10627	122
H(5A)	6035	2901	9364	98
H(7A)	8923	-284	8613	129
H(7B)	8688	-1196	9265	129
H(7C)	10068	-334	9257	129
H(9A)	5234	-1304	7324	99
H(11A)	9404	-32	7304	72
H(12A)	12304	-227	6963	97
H(12B)	13251	938	7124	97
H(14A)	10961	-359	5775	110
H(15A)	10969	146	4552	132
H(17A)	13713	2841	4935	113
H(18A)	13737	2352	6158	94
H(19A)	12942	2587	3727	246
H(19B)	11335	2075	3651	246

H(19C)	12692	1214	3524	246

Table S13. Torsion angles [deg] for **3b.**

C(11)-N(1)-N(2)-N(3)	1.7(3)
C(12)-N(1)-N(2)-N(3)	-179.8(3)
N(1)-N(2)-N(3)-C(10)	-0.9(3)
C(6)-C(1)-C(2)-C(3)	2.1(6)
C(7)-C(1)-C(2)-C(3)	-179.2(4)
C(1)-C(2)-C(3)-C(4)	-1.5(7)
C(2)-C(3)-C(4)-C(5)	0.6(7)
C(3)-C(4)-C(5)-C(6)	-0.4(7)
C(2)-C(1)-C(6)-C(5)	-1.9(5)
C(7)-C(1)-C(6)-C(5)	179.4(3)
C(2)-C(1)-C(6)-P(1)	178.9(3)
C(7)-C(1)-C(6)-P(1)	0.2(5)
C(4)-C(5)-C(6)-C(1)	1.1(5)
C(4)-C(5)-C(6)-P(1)	-179.6(3)
O(1)-P(1)-C(6)-C(1)	-174.7(3)
C(8)-P(1)-C(6)-C(1)	59.8(3)
C(10)-P(1)-C(6)-C(1)	-49.9(3)
O(1)-P(1)-C(6)-C(5)	6.0(3)
C(8)-P(1)-C(6)-C(5)	-119.4(3)
C(10)-P(1)-C(6)-C(5)	130.9(3)
O(1)-P(1)-C(8)-C(9)	3(5)
C(10)-P(1)-C(8)-C(9)	-119(5)
C(6)-P(1)-C(8)-C(9)	127(5)
N(2)-N(3)-C(10)-C(11)	-0.2(3)
N(2)-N(3)-C(10)-P(1)	179.3(2)
O(1)-P(1)-C(10)-N(3)	49.0(3)

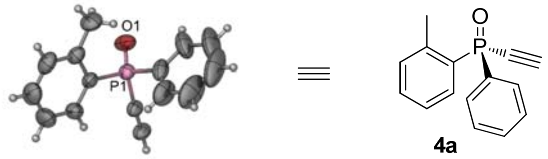
C(8)-P(1)-C(10)-N(3)	171.6(2)
C(6)-P(1)-C(10)-N(3)	-75.4(2)
O(1)-P(1)-C(10)-C(11)	-131.7(3)
C(8)-P(1)-C(10)-C(11)	-9.1(3)
C(6)-P(1)-C(10)-C(11)	103.9(3)
N(2)-N(1)-C(11)-C(10)	-1.8(3)
C(12)-N(1)-C(11)-C(10)	179.9(3)
N(3)-C(10)-C(11)-N(1)	1.2(3)
P(1)-C(10)-C(11)-N(1)	-178.2(2)
C(11)-N(1)-C(12)-C(13)	92.3(4)
N(2)-N(1)-C(12)-C(13)	-85.9(4)
N(1)-C(12)-C(13)-C(18)	96.3(4)
N(1)-C(12)-C(13)-C(14)	-83.8(4)
C(18)-C(13)-C(14)-C(15)	-0.9(6)
C(12)-C(13)-C(14)-C(15)	179.2(4)
C(13)-C(14)-C(15)-C(16)	-0.3(7)
C(14)-C(15)-C(16)-C(17)	1.3(7)
C(14)-C(15)-C(16)-C(19)	179.9(5)
C(15)-C(16)-C(17)-C(18)	-1.1(6)
C(19)-C(16)-C(17)-C(18)	-179.7(4)
C(14)-C(13)-C(18)-C(17)	1.1(5)
C(12)-C(13)-C(18)-C(17)	-179.0(4)
C(16)-C(17)-C(18)-C(13)	-0.1(6)

Symmetry transformations used to generate equivalent atoms:

Table S14. Hydrogen bonds for **3b** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

Data intensity of **4a**[10] was collected using a 'Bruker APEX-II CCD' diffractometer at 296(2) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **4a**: $C_{15}H_{13}OP$, T = 296(2) K, Orthorhombic, P2(1)2(1)2(1), a = 7.6851(3) Å, b = 12.5057(5) Å, c = 13.9472(5) Å, α = 90 deg, β = 90 deg, γ = 90 deg, V = 1340.43(9) Å^3. Z = 4, d_{calc} = 1.190 Mg/m^3. 15650 reflections measured, 2362 unique [Rint = 0.0259], R1 = 0.0317, wR2 = 0.0897 ($I > 2\sigma(I)$, final), R1 = 0.0338, wR2 = 0.0925 (all data), GOF = 1.003, and 154 parameters.



4a

Table S15. Crystal data and structure refinement for **4a.**

Identification code	**4a**	
Empirical formula	$C_{15}H_{13}OP$	
Formula weight	240.22	
Temperature	296(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.6851(3) Å	α = 90 deg.
	b = 12.5057(5) Å	β = 90 deg.
	c = 13.9472(5) Å	γ = 90 deg.
Volume	1340.43(9) Å^3	
Z, Calculated density	4, 1.190 Mg/m^3	
Absorption coefficient	0.186 mm^{-1}	
F(000)	504	
Crystal size	0.50 x 0.47 x 0.26 mm	
Theta range for data collection	2.92 to 25.00 deg.	
Limiting indices	-9<=h<=9, -14<=k<=14, -16<=l<=15	

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[10] Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC number: 1548228).

Reflections collected / unique	15650 / 2362 [R(int) = 0.0259]
Completeness to theta = 25.00	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9532 and 0.9128
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2362 / 0 / 154
Goodness-of-fit on F^2	1.003
Final R indices [I>2σ(I)]	R1 = 0.0317, wR2 = 0.0897
R indices (all data)	R1 = 0.0338, wR2 = 0.0925
Absolute structure parameter	-0.08(10)
Largest diff. peak and hole	0.223 and -0.114 e. Å^{-3}

Table S16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **4a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
P(1)	1652(1)	9403(1)	4064(1)	45(1)
O(1)	3235(2)	8976(1)	3601(1)	66(1)
C(1)	-13(2)	9846(1)	3254(1)	46(1)
C(2)	365(3)	10621(2)	2559(1)	54(1)
C(3)	-965(3)	10913(2)	1944(2)	72(1)
C(4)	-2606(3)	10483(3)	2011(2)	86(1)
C(5)	-2981(3)	9731(2)	2696(2)	88(1)
C(6)	-1689(3)	9417(2)	3312(2)	65(1)
C(7)	2086(3)	10475(2)	4885(1)	66(1)
C(8)	771(5)	11033(2)	5302(2)	101(1)
C(9)	1154(9)	11815(3)	5977(3)	151(2)
C(10)	2826(10)	12008(3)	6216(3)	167(3)
C(11)	4155(8)	11467(4)	5795(3)	156(2)
C(12)	3815(5)	10678(3)	5127(2)	105(1)
C(13)	2136(3)	11102(2)	2452(2)	79(1)

C(14)	645(3)	8435(1)	4795(1)	50(1)
C(15)	92(3)	7769(2)	5303(1)	59(1)

Table S17. Bond lengths [Å] and angles [deg] for **4a.**

P(1)-O(1)	1.4780(15)
P(1)-C(14)	1.7613(18)
P(1)-C(7)	1.794(2)
P(1)-C(1)	1.7950(18)
C(1)-C(6)	1.397(3)
C(1)-C(2)	1.401(2)
C(2)-C(3)	1.384(3)
C(2)-C(13)	1.496(3)
C(3)-C(4)	1.374(4)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.372(4)
C(4)-H(4A)	0.9300
C(5)-C(6)	1.371(3)
C(5)-H(5A)	0.9300
C(6)-H(6A)	0.9300
C(7)-C(8)	1.359(4)
C(7)-C(12)	1.394(4)
C(8)-C(9)	1.389(5)
C(8)-H(8A)	0.9300
C(9)-C(10)	1.350(8)
C(9)-H(9A)	0.9300
C(10)-C(11)	1.359(8)
C(10)-H(10A)	0.9300
C(11)-C(12)	1.382(5)
C(11)-H(11A)	0.9300

C(12)-H(12A)	0.9300
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(15)	1.173(3)
C(15)-H(15A)	0.9600
O(1)-P(1)-C(14)	111.47(8)
O(1)-P(1)-C(7)	113.35(11)
C(14)-P(1)-C(7)	103.09(9)
O(1)-P(1)-C(1)	115.03(8)
C(14)-P(1)-C(1)	105.25(9)
C(7)-P(1)-C(1)	107.68(9)
C(6)-C(1)-C(2)	119.79(17)
C(6)-C(1)-P(1)	120.13(14)
C(2)-C(1)-P(1)	120.08(15)
C(3)-C(2)-C(1)	117.28(19)
C(3)-C(2)-C(13)	120.28(18)
C(1)-C(2)-C(13)	122.42(17)
C(4)-C(3)-C(2)	122.2(2)
C(4)-C(3)-H(3A)	118.9
C(2)-C(3)-H(3A)	118.9
C(5)-C(4)-C(3)	120.6(2)
C(5)-C(4)-H(4A)	119.7
C(3)-C(4)-H(4A)	119.7
C(4)-C(5)-C(6)	118.7(2)
C(4)-C(5)-H(5A)	120.6
C(6)-C(5)-H(5A)	120.6
C(5)-C(6)-C(1)	121.4(2)
C(5)-C(6)-H(6A)	119.3
C(1)-C(6)-H(6A)	119.3
C(8)-C(7)-C(12)	120.8(3)

C(8)-C(7)-P(1)	121.2(2)
C(12)-C(7)-P(1)	117.9(2)
C(7)-C(8)-C(9)	119.6(4)
C(7)-C(8)-H(8A)	120.2
C(9)-C(8)-H(8A)	120.2
C(10)-C(9)-C(8)	119.7(5)
C(10)-C(9)-H(9A)	120.1
C(8)-C(9)-H(9A)	120.1
C(9)-C(10)-C(11)	121.3(4)
C(9)-C(10)-H(10A)	119.4
C(11)-C(10)-H(10A)	119.4
C(10)-C(11)-C(12)	120.4(5)
C(10)-C(11)-H(11A)	119.8
C(12)-C(11)-H(11A)	119.8
C(7)-C(12)-C(11)	118.2(4)
C(7)-C(12)-H(12A)	120.9
C(11)-C(12)-H(12A)	120.9
C(2)-C(13)-H(13A)	109.5
C(2)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(2)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-P(1)	175.16(19)
C(14)-C(15)-H(15A)	176.4

Symmetry transformations used to generate equivalent atoms:

Table S18. Anisotropic displacement parameters (Å ^{2} x 10^{3}) for **4a.** The anisotropic displacement factor exponent takes the form: -2 π^{2} [h^{2} a^{*2} U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
P(1)	49(1)	42(1)	45(1)	10(1)	1(1)	0(1)
O(1)	54(1)	74(1)	71(1)	27(1)	11(1)	16(1)
C(1)	49(1)	49(1)	41(1)	3(1)	3(1)	7(1)
C(2)	66(1)	49(1)	46(1)	7(1)	5(1)	12(1)
C(3)	95(2)	71(1)	51(1)	14(1)	-2(1)	19(1)
C(4)	73(2)	109(2)	76(2)	16(2)	-18(1)	22(2)
C(5)	55(1)	121(2)	88(2)	16(2)	-9(1)	0(1)
C(6)	54(1)	80(1)	60(1)	13(1)	-1(1)	-6(1)
C(7)	100(2)	47(1)	50(1)	12(1)	-14(1)	-19(1)
C(8)	149(3)	72(2)	81(2)	-24(1)	7(2)	-8(2)
C(9)	267(6)	89(2)	96(2)	-34(2)	9(3)	-11(3)
C(10)	330(10)	88(2)	82(2)	-4(2)	-50(4)	-58(4)
C(11)	211(6)	121(3)	136(4)	22(3)	-95(4)	-84(3)
C(12)	121(2)	91(2)	103(2)	17(2)	-51(2)	-40(2)
C(13)	90(2)	74(1)	74(1)	32(1)	7(1)	-10(1)
C(14)	61(1)	43(1)	46(1)	2(1)	2(1)	-4(1)
C(15)	75(1)	50(1)	52(1)	9(1)	5(1)	-11(1)

Table S19. Hydrogen coordinates (x 10^{4}) and isotropic displacement parameters (A^{2} x 10^{3}) for **4a**.

	x	y	z	U(eq)
H(3A)	-741	11417	1469	87
H(4A)	-3470	10705	1589	104
H(5A)	-4091	9439	2741	106

H(6A)	-1932	8908	3779	78
H(8A)	-379	10892	5137	121
H(9A)	262	12204	6263	181
H(10A)	3074	12522	6679	200
H(11A)	5299	11629	5956	187
H(12A)	4716	10292	4847	126
H(13A)	2126	11609	1935	119
H(13B)	2965	10548	2315	119
H(13C)	2455	11457	3036	119
H(15A)	-363	7195	5685	89

Table S20. Torsion angles [deg] for **4a**.

O(1)-P(1)-C(1)-C(6)	123.55(17)
C(14)-P(1)-C(1)-C(6)	0.46(18)
C(7)-P(1)-C(1)-C(6)	-109.01(17)
O(1)-P(1)-C(1)-C(2)	-56.29(17)
C(14)-P(1)-C(1)-C(2)	-179.39(14)
C(7)-P(1)-C(1)-C(2)	71.15(17)
C(6)-C(1)-C(2)-C(3)	-1.1(3)
P(1)-C(1)-C(2)-C(3)	178.78(15)
C(6)-C(1)-C(2)-C(13)	-179.3(2)
P(1)-C(1)-C(2)-C(13)	0.6(3)
C(1)-C(2)-C(3)-C(4)	1.1(3)
C(13)-C(2)-C(3)-C(4)	179.4(3)
C(2)-C(3)-C(4)-C(5)	-0.6(4)
C(3)-C(4)-C(5)-C(6)	0.1(4)
C(4)-C(5)-C(6)-C(1)	-0.1(4)
C(2)-C(1)-C(6)-C(5)	0.6(3)
P(1)-C(1)-C(6)-C(5)	-179.25(19)

O(1)-P(1)-C(7)-C(8)	173.36(19)
C(14)-P(1)-C(7)-C(8)	-66.0(2)
C(1)-P(1)-C(7)-C(8)	45.0(2)
O(1)-P(1)-C(7)-C(12)	-10.4(2)
C(14)-P(1)-C(7)-C(12)	110.22(19)
C(1)-P(1)-C(7)-C(12)	-138.83(19)
C(12)-C(7)-C(8)-C(9)	0.1(4)
P(1)-C(7)-C(8)-C(9)	176.2(2)
C(7)-C(8)-C(9)-C(10)	-0.4(6)
C(8)-C(9)-C(10)-C(11)	1.4(7)
C(9)-C(10)-C(11)-C(12)	-2.0(7)
C(8)-C(7)-C(12)-C(11)	-0.7(4)
P(1)-C(7)-C(12)-C(11)	-176.9(2)
C(10)-C(11)-C(12)-C(7)	1.6(6)
O(1)-P(1)-C(14)-C(15)	41(2)
C(7)-P(1)-C(14)-C(15)	-81(2)
C(1)-P(1)-C(14)-C(15)	167(2)

Symmetry transformations used to generate equivalent atoms:

Table S21. Hydrogen bonds for **4a** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

Data intensity of **7o**[11] was collected using a 'Bruker APEX-II CCD' diffractometer at 293(2) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **7o**: $C_{36}H_{33}$ Cl N_3 O_3 P, T = 293(2) K, monoclinic, space group P 21, a = 14.421(2) Å, b = 7.7894(13) Å, c = 16.028(3) Å, α = 90 deg, β = 114.539(4) deg, γ = 90 deg, V = 1637.8(5) Å^3. Z = 2, d_{calc} = 1.261 Mg/m^3. 9105 reflections measured, 5518 unique [Rint = 0.0570], R1 = 0.0879, wR2 = 0.1703 ($I > 2\sigma(I)$, final), R1 = 0.1285, wR2 = 0.1920 (all data), GOF = 1.095, and 410 parameters.

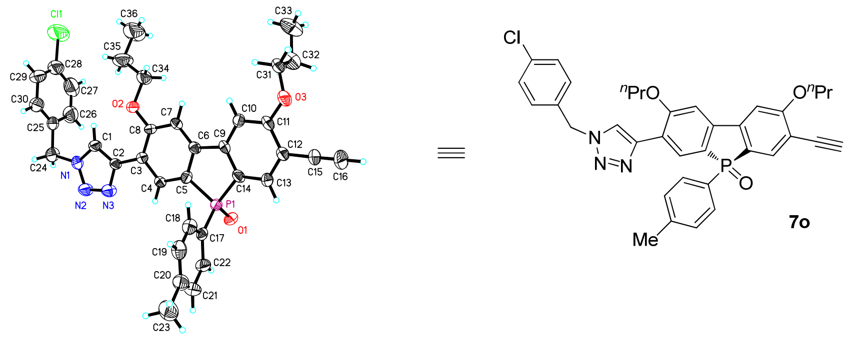

Table S22. Crystal data and structure refinement for **7o**.

Identification code	**7o**	
Empirical formula	$C_{36}H_{33}ClN_3O_3P$	
Formula weight	622.07	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 14.421(2) Å	α = 90°.
	b = 7.7894(13) Å	β = 114.539(4)°.
	c = 16.028(3) Å	γ = 90°.
Volume	1637.8(5) Å^3	
Z	2	

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[11] Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC number: 1450187).

Density (calculated)	1.261 Mg/m^3
Absorption coefficient	0.205 mm^{-1}
F(000)	652
Crystal size	0.19 x 0.10 x 0.04 mm^3
Theta range for data collection	1.552 to 24.998°.
Index ranges	-17<=h<=16, -9<=k<=9, -12<=l<=19
Reflections collected	9105
Independent reflections	5518 [R(int) = 0.0570]
Completeness to theta = 25.242°	97.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6328
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5518 / 9 / 410
Goodness-of-fit on F^2	1.095
Final R indices [I>2sigma(I)]	R1 = 0.0879, wR2 = 0.1703
R indices (all data)	R1 = 0.1285, wR2 = 0.1920
Absolute structure parameter	0.00(11)
Extinction coefficient	n/a
Largest diff. peak and hole	0.278 and -0.206 e.Å^{-3}

Table S23. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **7o**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	10274(2)	9256(11)	11786(3)	237(4)
P(1)	2844(1)	9359(3)	4532(1)	46(1)
N(1)	5299(5)	8551(11)	9600(4)	66(2)
N(2)	4316(5)	8861(13)	9171(5)	82(3)
N(3)	4093(5)	8904(12)	8298(4)	76(3)
O(1)	2408(4)	11083(8)	4456(4)	61(2)

O(2)	6655(4)	8180(9)	7814(4)	66(2)
O(3)	5550(4)	7889(9)	2689(4)	71(2)
C(1)	5700(6)	8357(15)	8976(5)	72(3)
C(2)	4927(5)	8625(11)	8159(5)	46(2)
C(3)	4902(5)	8606(12)	7224(5)	50(2)
C(4)	3970(5)	8855(9)	6474(5)	42(2)
C(5)	3923(5)	8851(11)	5590(5)	50(2)
C(6)	4794(6)	8566(11)	5440(5)	48(2)
C(7)	5714(6)	8329(11)	6176(5)	47(2)
C(8)	5768(5)	8359(11)	7061(5)	47(2)
C(9)	4583(6)	8571(10)	4448(5)	45(2)
C(10)	5275(6)	8243(11)	4076(5)	52(2)
C(11)	4962(6)	8254(11)	3135(5)	54(2)
C(12)	3925(6)	8607(12)	2552(5)	56(2)
C(13)	3247(6)	8881(12)	2925(5)	54(2)
C(14)	3570(6)	8900(11)	3872(5)	54(2)
C(15)	3595(6)	8610(14)	1565(6)	67(3)
C(16)	3344(8)	8682(18)	785(7)	103(4)
C(17)	1882(6)	7712(11)	4270(5)	46(2)
C(18)	2082(7)	6027(13)	4192(6)	64(2)
C(19)	1357(9)	4807(13)	3966(7)	76(3)
C(20)	384(9)	5242(17)	3820(7)	81(3)
C(21)	161(8)	6901(19)	3924(8)	90(4)
C(22)	902(6)	8119(14)	4132(6)	67(3)
C(23)	-436(9)	3885(18)	3572(9)	125(5)
C(24)	5801(7)	8450(18)	10614(5)	87(4)
C(25)	6948(7)	8667(19)	10962(6)	72(3)
C(26)	7339(11)	10250(20)	11001(9)	109(4)
C(27)	8364(14)	10430(20)	11275(10)	128(5)
C(28)	8998(10)	9040(30)	11491(9)	126(6)
C(29)	8581(9)	7490(20)	11449(9)	112(5)

C(30)	7561(9)	7332(17)	11188(7)	86(3)
C(31)	6639(6)	8046(11)	3163(6)	57(2)
C(32)	6952(8)	9837(13)	3289(8)	87(3)
C(33)	8071(8)	10056(19)	3607(9)	121(5)
C(34)	7598(6)	8498(17)	7754(6)	87(3)
C(35)	8410(7)	8540(20)	8701(8)	127(5)
C(36)	9400(12)	9200(40)	8758(15)	184(11)
C(36')	8440(40)	10270(50)	9140(40)	183(12)

Table S24. Bond lengths [Å] and angles [°] for **7o**.

Cl(1)-C(28)	1.707(14)
P(1)-O(1)	1.467(6)
P(1)-C(17)	1.806(9)
P(1)-C(5)	1.806(8)
P(1)-C(14)	1.806(7)
N(1)-N(2)	1.316(9)
N(1)-C(1)	1.355(9)
N(1)-C(24)	1.481(10)
N(2)-N(3)	1.300(9)
N(3)-C(2)	1.328(8)
O(2)-C(8)	1.353(8)
O(2)-C(34)	1.424(10)
O(3)-C(11)	1.347(8)
O(3)-C(31)	1.438(9)
C(1)-C(2)	1.337(10)
C(1)-H(1)	0.9300
C(2)-C(3)	1.486(10)
C(3)-C(8)	1.390(9)
C(3)-C(4)	1.395(10)
C(4)-C(5)	1.390(10)

C(4)-H(4)	0.9300
C(5)-C(6)	1.392(9)
C(6)-C(7)	1.373(10)
C(6)-C(9)	1.489(10)
C(7)-C(8)	1.389(10)
C(7)-H(7)	0.9300
C(9)-C(10)	1.384(9)
C(9)-C(14)	1.390(10)
C(10)-C(11)	1.383(10)
C(10)-H(10)	0.9300
C(11)-C(12)	1.422(11)
C(12)-C(13)	1.358(10)
C(12)-C(15)	1.451(11)
C(13)-C(14)	1.391(10)
C(13)-H(13)	0.9300
C(15)-C(16)	1.150(12)
C(16)-H(16)	0.9300
C(17)-C(18)	1.360(12)
C(17)-C(22)	1.374(11)
C(18)-C(19)	1.347(12)
C(18)-H(18)	0.9300
C(19)-C(20)	1.366(13)
C(19)-H(19)	0.9300
C(20)-C(21)	1.359(15)
C(20)-C(23)	1.511(15)
C(21)-C(22)	1.362(14)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600

C(24)-C(25)	1.520(12)
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(25)-C(30)	1.315(14)
C(25)-C(26)	1.347(16)
C(26)-C(27)	1.364(17)
C(26)-H(26)	0.9300
C(27)-C(28)	1.36(2)
C(27)-H(27)	0.9300
C(28)-C(29)	1.34(2)
C(29)-C(30)	1.358(15)
C(29)-H(29)	0.9300
C(30)-H(30)	0.9300
C(31)-C(32)	1.454(13)
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(32)-C(33)	1.486(13)
C(32)-H(32A)	0.9700
C(32)-H(32B)	0.9700
C(33)-H(33A)	0.9600
C(33)-H(33B)	0.9600
C(33)-H(33C)	0.9600
C(34)-C(35)	1.483(13)
C(34)-H(34A)	0.9700
C(34)-H(34B)	0.9700
C(35)-C(36)	1.485(16)
C(35)-C(36')	1.51(3)
C(35)-H(35A)	0.9598
C(35)-H(35B)	0.9602
C(35)-H(35C)	0.9601
C(35)-H(35D)	0.9602

C(36)-H(36A)	0.9600
C(36)-H(36B)	0.9600
C(36)-H(36C)	0.9600
C(36')-H(36D)	0.9600
C(36')-H(36E)	0.9600
C(36')-H(36F)	0.9600
O(1)-P(1)-C(17)	111.7(4)
O(1)-P(1)-C(5)	116.8(4)
C(17)-P(1)-C(5)	110.0(4)
O(1)-P(1)-C(14)	117.8(4)
C(17)-P(1)-C(14)	107.4(4)
C(5)-P(1)-C(14)	91.4(3)
N(2)-N(1)-C(1)	109.4(6)
N(2)-N(1)-C(24)	120.9(6)
C(1)-N(1)-C(24)	129.8(7)
N(3)-N(2)-N(1)	107.4(6)
N(2)-N(3)-C(2)	109.8(6)
C(8)-O(2)-C(34)	119.8(6)
C(11)-O(3)-C(31)	119.5(6)
C(2)-C(1)-N(1)	105.5(7)
C(2)-C(1)-H(1)	127.2
N(1)-C(1)-H(1)	127.2
N(3)-C(2)-C(1)	107.9(6)
N(3)-C(2)-C(3)	121.8(7)
C(1)-C(2)-C(3)	130.4(7)
C(8)-C(3)-C(4)	118.5(6)
C(8)-C(3)-C(2)	122.9(7)
C(4)-C(3)-C(2)	118.6(6)
C(5)-C(4)-C(3)	120.0(6)
C(5)-C(4)-H(4)	120.0
C(3)-C(4)-H(4)	120.0

C(4)-C(5)-C(6)	120.7(7)
C(4)-C(5)-P(1)	128.0(5)
C(6)-C(5)-P(1)	111.1(5)
C(7)-C(6)-C(5)	119.5(6)
C(7)-C(6)-C(9)	127.9(6)
C(5)-C(6)-C(9)	112.6(7)
C(6)-C(7)-C(8)	120.0(6)
C(6)-C(7)-H(7)	120.0
C(8)-C(7)-H(7)	120.0
O(2)-C(8)-C(7)	122.7(6)
O(2)-C(8)-C(3)	115.9(6)
C(7)-C(8)-C(3)	121.4(7)
C(10)-C(9)-C(14)	119.7(7)
C(10)-C(9)-C(6)	126.6(7)
C(14)-C(9)-C(6)	113.7(6)
C(9)-C(10)-C(11)	120.1(7)
C(9)-C(10)-H(10)	119.9
C(11)-C(10)-H(10)	119.9
O(3)-C(11)-C(10)	125.8(7)
O(3)-C(11)-C(12)	114.5(7)
C(10)-C(11)-C(12)	119.7(7)
C(13)-C(12)-C(11)	119.6(7)
C(13)-C(12)-C(15)	120.7(7)
C(11)-C(12)-C(15)	119.7(7)
C(12)-C(13)-C(14)	120.4(7)
C(12)-C(13)-H(13)	119.8
C(14)-C(13)-H(13)	119.8
C(13)-C(14)-C(9)	120.4(6)
C(13)-C(14)-P(1)	128.9(6)
C(9)-C(14)-P(1)	110.6(5)
C(16)-C(15)-C(12)	177.2(13)

C(15)-C(16)-H(16)	180.0
C(18)-C(17)-C(22)	116.8(9)
C(18)-C(17)-P(1)	122.3(7)
C(22)-C(17)-P(1)	120.9(7)
C(19)-C(18)-C(17)	122.3(9)
C(19)-C(18)-H(18)	118.9
C(17)-C(18)-H(18)	118.9
C(18)-C(19)-C(20)	119.9(10)
C(18)-C(19)-H(19)	120.0
C(20)-C(19)-H(19)	120.0
C(21)-C(20)-C(19)	119.6(10)
C(21)-C(20)-C(23)	119.9(12)
C(19)-C(20)-C(23)	120.5(12)
C(20)-C(21)-C(22)	119.4(10)
C(20)-C(21)-H(21)	120.3
C(22)-C(21)-H(21)	120.3
C(21)-C(22)-C(17)	121.9(10)
C(21)-C(22)-H(22)	119.0
C(17)-C(22)-H(22)	119.0
C(20)-C(23)-H(23A)	109.5
C(20)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(20)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
N(1)-C(24)-C(25)	111.0(7)
N(1)-C(24)-H(24A)	109.4
C(25)-C(24)-H(24A)	109.4
N(1)-C(24)-H(24B)	109.4
C(25)-C(24)-H(24B)	109.4
H(24A)-C(24)-H(24B)	108.0

C(30)-C(25)-C(26)	119.4(11)
C(30)-C(25)-C(24)	121.2(13)
C(26)-C(25)-C(24)	119.3(12)
C(25)-C(26)-C(27)	118.9(15)
C(25)-C(26)-H(26)	120.5
C(27)-C(26)-H(26)	120.5
C(28)-C(27)-C(26)	121.7(17)
C(28)-C(27)-H(27)	119.1
C(26)-C(27)-H(27)	119.1
C(29)-C(28)-C(27)	117.6(14)
C(29)-C(28)-Cl(1)	120.7(16)
C(27)-C(28)-Cl(1)	121.7(19)
C(28)-C(29)-C(30)	120.1(14)
C(28)-C(29)-H(29)	120.0
C(30)-C(29)-H(29)	120.0
C(25)-C(30)-C(29)	122.2(13)
C(25)-C(30)-H(30)	118.9
C(29)-C(30)-H(30)	118.9
O(3)-C(31)-C(32)	111.3(8)
O(3)-C(31)-H(31A)	109.4
C(32)-C(31)-H(31A)	109.4
O(3)-C(31)-H(31B)	109.4
C(32)-C(31)-H(31B)	109.4
H(31A)-C(31)-H(31B)	108.0
C(31)-C(32)-C(33)	112.8(10)
C(31)-C(32)-H(32A)	109.0
C(33)-C(32)-H(32A)	109.0
C(31)-C(32)-H(32B)	109.0
C(33)-C(32)-H(32B)	109.0
H(32A)-C(32)-H(32B)	107.8
C(32)-C(33)-H(33A)	109.5

C(32)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
C(32)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
O(2)-C(34)-C(35)	107.8(8)
O(2)-C(34)-H(34A)	110.2
C(35)-C(34)-H(34A)	110.2
O(2)-C(34)-H(34B)	110.2
C(35)-C(34)-H(34B)	110.2
H(34A)-C(34)-H(34B)	108.5
C(34)-C(35)-C(36)	113.7(12)
C(34)-C(35)-C(36')	111(3)
C(34)-C(35)-H(35A)	107.9
C(36)-C(35)-H(35A)	108.5
C(34)-C(35)-H(35B)	108.8
C(36)-C(35)-H(35B)	108.8
H(35A)-C(35)-H(35B)	109.0
C(34)-C(35)-H(35C)	110.0
C(36')-C(35)-H(35C)	107.9
C(34)-C(35)-H(35D)	108.4
C(36')-C(35)-H(35D)	110.2
H(35C)-C(35)-H(35D)	109.6
C(35)-C(36)-H(36A)	109.5
C(35)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(35)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(35)-C(36')-H(36D)	109.5
C(35)-C(36')-H(36E)	109.5

H(36D)-C(36')-H(36E)	109.5
C(35)-C(36')-H(36F)	109.5
H(36D)-C(36')-H(36F)	109.5
H(36E)-C(36')-H(36F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S25. Anisotropic displacement parameters (Å^{2}x 10^3) for **7o**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	72(2)	422(10)	184(4)	82(6)	20(2)	-44(4)
P(1)	46(1)	52(1)	43(1)	1(1)	21(1)	8(1)
N(1)	70(5)	94(6)	42(4)	7(4)	33(4)	8(5)
N(2)	58(4)	142(9)	50(4)	0(5)	27(4)	7(5)
N(3)	57(4)	134(9)	42(4)	-10(5)	26(3)	8(5)
O(1)	51(3)	61(4)	64(4)	5(3)	17(3)	14(3)
O(2)	47(3)	104(5)	48(3)	12(3)	21(3)	12(3)
O(3)	77(4)	97(5)	52(3)	-2(3)	40(3)	-1(4)
C(1)	46(4)	123(9)	48(5)	15(6)	19(4)	10(6)
C(2)	44(4)	55(5)	45(4)	-2(4)	23(4)	2(4)
C(3)	43(4)	58(6)	46(4)	4(4)	17(4)	0(4)
C(4)	47(4)	34(5)	53(4)	0(4)	29(4)	4(3)
C(5)	56(4)	52(6)	41(4)	4(4)	21(4)	14(4)
C(6)	53(4)	48(5)	53(5)	-2(4)	31(4)	4(4)
C(7)	49(4)	54(5)	46(4)	-3(4)	28(4)	-3(4)
C(8)	31(4)	55(6)	52(5)	2(4)	15(4)	2(4)
C(9)	58(5)	39(5)	50(4)	2(4)	33(4)	-4(4)
C(10)	55(4)	54(6)	46(5)	6(4)	21(4)	6(4)
C(11)	69(5)	49(6)	60(5)	1(5)	44(5)	-2(5)
C(12)	58(5)	66(6)	52(5)	3(5)	30(4)	-2(5)
C(13)	56(4)	68(7)	41(4)	3(4)	21(4)	3(4)
C(14)	56(5)	67(7)	49(5)	-2(4)	33(4)	-3(4)

C(15)	71(5)	89(8)	45(5)	8(5)	27(4)	2(5)
C(16)	109(8)	152(13)	57(6)	13(8)	44(6)	18(9)
C(17)	48(5)	57(6)	31(4)	0(4)	14(4)	7(4)
C(18)	75(6)	58(7)	62(6)	-1(5)	30(5)	10(6)
C(19)	106(8)	51(8)	74(7)	1(5)	40(7)	0(6)
C(20)	71(7)	85(9)	78(7)	3(7)	21(6)	-23(7)
C(21)	56(6)	119(12)	99(9)	14(8)	37(6)	-1(7)
C(22)	51(5)	78(8)	71(6)	5(5)	24(5)	11(5)
C(23)	119(9)	117(13)	125(11)	11(9)	37(9)	-48(9)
C(24)	80(6)	144(11)	40(5)	6(6)	27(5)	16(7)
C(25)	66(6)	114(10)	36(5)	13(6)	22(4)	7(7)
C(26)	110(11)	98(11)	113(11)	13(9)	41(9)	-9(9)
C(27)	138(14)	138(15)	105(11)	6(10)	47(12)	-41(12)
C(28)	71(8)	210(20)	92(9)	35(12)	25(7)	-2(12)
C(29)	60(8)	163(16)	105(10)	26(10)	27(7)	20(8)
C(30)	75(7)	111(11)	70(7)	7(7)	27(6)	0(7)
C(31)	71(6)	51(6)	64(6)	3(5)	43(5)	4(5)
C(32)	111(9)	60(9)	113(9)	-13(6)	69(8)	0(6)
C(33)	108(9)	145(13)	138(11)	-55(9)	79(9)	-52(9)
C(34)	65(6)	120(10)	73(6)	4(7)	25(5)	-17(7)
C(35)	54(6)	205(17)	109(10)	-10(11)	21(7)	-13(9)
C(36)	87(12)	290(30)	153(18)	10(20)	31(12)	-68(18)
C(36')	88(15)	290(30)	150(20)	10(20)	31(15)	-70(20)

Table S26. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **7o**.

	x	y	z	U(eq)
H(1)	6371	8093	9092	87
H(4)	3381	9025	6566	50

H(7)	6301	8148	6082	56
H(10)	5953	8014	4459	62
H(13)	2562	9056	2545	65
H(16)	3142	8741	153	124
H(18)	2743	5707	4297	77
H(19)	1518	3669	3910	91
H(21)	-491	7203	3855	108
H(22)	739	9259	4181	81
H(23A)	-263	2936	3281	187
H(23B)	-1076	4363	3158	187
H(23C)	-490	3493	4117	187
H(24A)	5653	7347	10812	105
H(24B)	5530	9340	10874	105
H(26)	6916	11210	10843	130
H(27)	8638	11521	11316	153
H(29)	8992	6513	11598	134
H(30)	7286	6245	11169	104
H(31A)	6958	7468	2814	69
H(31B)	6868	7491	3757	69
H(32A)	6742	10353	3734	105
H(32B)	6606	10442	2713	105
H(33A)	8405	9802	4250	181
H(33B)	8217	11218	3502	181
H(33C)	8314	9288	3273	181
H(34A)	7570	9587	7451	104
H(34B)	7735	7598	7402	104
H(35A)	8510	7388	8936	152
H(35B)	8188	9245	9074	152
H(35C)	9063	8348	8690	152
H(35D)	8276	7648	9050	152
H(36A)	9597	8575	8341	276

H(36B)	9911	9065	9372	276
H(36C)	9332	10398	8597	276
H(36D)	8985	10943	9115	275
H(36E)	8556	10105	9772	275
H(36F)	7805	10850	8822	275

Table S27. Torsion angles [°] for **7o**.

C(1)-N(1)-N(2)-N(3)	-1.3(12)
C(24)-N(1)-N(2)-N(3)	179.0(9)
N(1)-N(2)-N(3)-C(2)	-0.1(12)
N(2)-N(1)-C(1)-C(2)	2.2(12)
C(24)-N(1)-C(1)-C(2)	-178.2(10)
N(2)-N(3)-C(2)-C(1)	1.5(12)
N(2)-N(3)-C(2)-C(3)	-179.8(9)
N(1)-C(1)-C(2)-N(3)	-2.2(12)
N(1)-C(1)-C(2)-C(3)	179.3(9)
N(3)-C(2)-C(3)-C(8)	178.4(9)
C(1)-C(2)-C(3)-C(8)	-3.2(16)
N(3)-C(2)-C(3)-C(4)	-1.2(13)
C(1)-C(2)-C(3)-C(4)	177.1(10)
C(8)-C(3)-C(4)-C(5)	0.1(12)
C(2)-C(3)-C(4)-C(5)	179.7(8)
C(3)-C(4)-C(5)-C(6)	1.2(12)
C(3)-C(4)-C(5)-P(1)	-173.1(6)
O(1)-P(1)-C(5)-C(4)	59.4(9)
C(17)-P(1)-C(5)-C(4)	-69.2(8)
C(14)-P(1)-C(5)-C(4)	-178.3(8)
O(1)-P(1)-C(5)-C(6)	-115.3(6)
C(17)-P(1)-C(5)-C(6)	116.1(6)
C(14)-P(1)-C(5)-C(6)	6.9(7)

C(4)-C(5)-C(6)-C(7)	-1.6(12)
P(1)-C(5)-C(6)-C(7)	173.6(7)
C(4)-C(5)-C(6)-C(9)	178.7(8)
P(1)-C(5)-C(6)-C(9)	-6.1(9)
C(5)-C(6)-C(7)-C(8)	0.6(12)
C(9)-C(6)-C(7)-C(8)	-179.7(8)
C(34)-O(2)-C(8)-C(7)	20.1(13)
C(34)-O(2)-C(8)-C(3)	-158.9(9)
C(6)-C(7)-C(8)-O(2)	-178.1(8)
C(6)-C(7)-C(8)-C(3)	0.8(13)
C(4)-C(3)-C(8)-O(2)	177.9(7)
C(2)-C(3)-C(8)-O(2)	-1.8(12)
C(4)-C(3)-C(8)-C(7)	-1.1(13)
C(2)-C(3)-C(8)-C(7)	179.3(8)
C(7)-C(6)-C(9)-C(10)	3.7(14)
C(5)-C(6)-C(9)-C(10)	-176.6(8)
C(7)-C(6)-C(9)-C(14)	-178.1(8)
C(5)-C(6)-C(9)-C(14)	1.6(10)
C(14)-C(9)-C(10)-C(11)	0.4(12)
C(6)-C(9)-C(10)-C(11)	178.5(8)
C(31)-O(3)-C(11)-C(10)	-22.3(13)
C(31)-O(3)-C(11)-C(12)	160.3(8)
C(9)-C(10)-C(11)-O(3)	-177.2(8)
C(9)-C(10)-C(11)-C(12)	0.1(13)
O(3)-C(11)-C(12)-C(13)	175.7(8)
C(10)-C(11)-C(12)-C(13)	-1.9(14)
O(3)-C(11)-C(12)-C(15)	-2.1(12)
C(10)-C(11)-C(12)-C(15)	-179.6(8)
C(11)-C(12)-C(13)-C(14)	3.1(14)
C(15)-C(12)-C(13)-C(14)	-179.1(9)
C(12)-C(13)-C(14)-C(9)	-2.6(13)

C(12)-C(13)-C(14)-P(1)	175.9(7)
C(10)-C(9)-C(14)-C(13)	0.8(12)
C(6)-C(9)-C(14)-C(13)	-177.5(8)
C(10)-C(9)-C(14)-P(1)	-178.0(7)
C(6)-C(9)-C(14)-P(1)	3.7(9)
O(1)-P(1)-C(14)-C(13)	-63.1(9)
C(17)-P(1)-C(14)-C(13)	63.9(9)
C(5)-P(1)-C(14)-C(13)	175.4(9)
O(1)-P(1)-C(14)-C(9)	115.5(6)
C(17)-P(1)-C(14)-C(9)	-117.4(6)
C(5)-P(1)-C(14)-C(9)	-6.0(7)
O(1)-P(1)-C(17)-C(18)	172.3(6)
C(5)-P(1)-C(17)-C(18)	-56.4(7)
C(14)-P(1)-C(17)-C(18)	41.7(8)
O(1)-P(1)-C(17)-C(22)	-7.1(7)
C(5)-P(1)-C(17)-C(22)	124.3(7)
C(14)-P(1)-C(17)-C(22)	-137.6(7)
C(22)-C(17)-C(18)-C(19)	1.7(13)
P(1)-C(17)-C(18)-C(19)	-177.7(7)
C(17)-C(18)-C(19)-C(20)	-0.9(15)
C(18)-C(19)-C(20)-C(21)	-1.6(16)
C(18)-C(19)-C(20)-C(23)	-179.7(10)
C(19)-C(20)-C(21)-C(22)	3.1(17)
C(23)-C(20)-C(21)-C(22)	-178.8(10)
C(20)-C(21)-C(22)-C(17)	-2.3(16)
C(18)-C(17)-C(22)-C(21)	-0.1(13)
P(1)-C(17)-C(22)-C(21)	179.3(8)
N(2)-N(1)-C(24)-C(25)	-161.4(11)
C(1)-N(1)-C(24)-C(25)	19.0(17)
N(1)-C(24)-C(25)-C(30)	-99.0(12)
N(1)-C(24)-C(25)-C(26)	78.0(13)

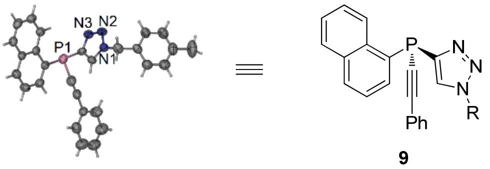
C(30)-C(25)-C(26)-C(27)	0.0(17)
C(24)-C(25)-C(26)-C(27)	-177.1(10)
C(25)-C(26)-C(27)-C(28)	1(2)
C(26)-C(27)-C(28)-C(29)	-2(2)
C(26)-C(27)-C(28)-Cl(1)	177.1(11)
C(27)-C(28)-C(29)-C(30)	1(2)
Cl(1)-C(28)-C(29)-C(30)	-178.1(10)
C(26)-C(25)-C(30)-C(29)	-1.0(17)
C(24)-C(25)-C(30)-C(29)	176.0(10)
C(28)-C(29)-C(30)-C(25)	1(2)
C(11)-O(3)-C(31)-C(32)	-73.7(10)
O(3)-C(31)-C(32)-C(33)	-168.7(8)
C(8)-O(2)-C(34)-C(35)	169.2(10)
O(2)-C(34)-C(35)-C(36)	-168.3(17)
O(2)-C(34)-C(35)-C(36')	-81(2)

Symmetry transformations used to generate equivalent atoms:

Table S28. Hydrogen bonds for **7o** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1)...O(2)	0.93	2.25	2.741(9)	112.3
C(1)-H(1)...O(2)	0.93	2.25	2.741(9)	112.3
C(1)-H(1)...O(2)	0.93	2.25	2.741(9)	112.3
C(1)-H(1)...O(2)	0.93	2.25	2.741(9)	112.3
C(1)-H(1)...O(2)	0.93	2.25	2.741(9)	112.3

Data intensity of **9**[12] was collected using a 'Bruker APEX-II CCD' diffractometer at 296(2) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **9**: $C_{28}H_{22}N_3P$, T = 296(2) K, Hexagonal, R3, a = 34.841(3) Å, b = 34.841(3) Å, c = 5.5660(6) Å, α = 90 deg, β = 90 deg, γ = 120 deg, V = 5851.2(9) Å^3. Z = 9, d_{calc} = 1.102 Mg/m^3. 22882 reflections measured, 4512 unique [Rint = 0.0533], R1 = 0.0489, wR2 = 0.1154 ($I > 2\sigma(I)$, final), R1 = 0.0668, wR2 = 0.1267 (all data), GOF = 1.054, and 289 parameters.



9

Table S29. Crystal data and structure refinement for **9.**

Identification code	**9**	
Empirical formula	$C_{28}H_{22}N_3P$	
Formula weight	431.46	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Hexagonal, R3	
Unit cell dimensions	a = 34.841(3) Å	α = 90 deg.
	b = 34.841(3) Å	β = 90 deg.
	c = 5.5660(6) Å	γ = 120 deg.
Volume	5851.2(9) Å^3	
Z, Calculated density	9, 1.102 Mg/m^3	
Absorption coefficient	0.124 mm^{-1}	
F(000)	2034	
Crystal size	0.46 x 0.19 x 0.17 mm	
Theta range for data collection	2.34 to 25.01 deg.	
Limiting indices	-41<=h<=36, -41<=k<=41, -6<=l<=6	

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[12] Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC number: 1552231).

Reflections collected / unique	22882 / 4512 [R(int) = 0.0533]
Completeness to theta = 25.01	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9793 and 0.9453
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4512 / 13 / 289
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0489, wR2 = 0.1154
R indices (all data)	R1 = 0.0668, wR2 = 0.1267
Absolute structure parameter	0.00(11)
Largest diff. peak and hole	0 .196 and -0.186 e. Å^{-3}

Table S30. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **9**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
P(1)	8611(1)	7156(1)	9401(2)	58(1)
N(1)	8149(1)	5925(1)	11637(5)	54(1)
N(2)	8190(1)	5892(1)	9262(5)	69(1)
N(3)	8343(1)	6294(1)	8359(5)	66(1)
C(1)	9116(1)	7438(1)	11226(6)	50(1)
C(2)	9154(1)	7703(1)	13126(6)	61(1)
C(3)	9554(1)	7936(1)	14420(7)	70(1)
C(4)	9907(1)	7894(1)	13843(7)	62(1)
C(5)	9886(1)	7624(1)	11908(6)	49(1)
C(6)	9491(1)	7395(1)	10539(5)	48(1)
C(7)	9489(1)	7142(1)	8549(6)	55(1)
C(8)	9854(1)	7112(1)	7990(6)	62(1)
C(9)	10240(1)	7329(1)	9390(7)	66(1)
C(10)	10255(1)	7576(1)	11295(6)	57(1)

C(11)	8247(1)	7258(1)	11119(7)	69(1)
C(12)	7976(1)	7336(1)	11890(7)	67(1)
C(13)	7672(1)	7436(1)	13064(6)	57(1)
C(14)	7261(1)	7292(2)	12117(9)	94(1)
C(15)	6975(2)	7405(2)	13298(10)	111(1)
C(16)	7107(2)	7654(2)	15299(10)	109(1)
C(17)	7500(2)	7781(2)	16233(10)	111(1)
C(18)	7784(1)	7674(1)	15158(8)	83(1)
C(19)	8400(1)	6575(1)	10129(5)	50(1)
C(20)	8275(1)	6339(1)	12251(6)	54(1)
C(21)	7983(1)	5524(1)	13124(6)	65(1)
C(22)	7499(1)	5201(1)	12734(6)	59(1)
C(23)	7362(1)	4934(1)	10741(8)	83(1)
C(24)	6919(2)	4644(2)	10362(8)	93(1)
C(25)	6607(1)	4612(1)	11921(9)	82(1)
C(26)	6748(2)	4877(2)	13887(9)	90(1)
C(27)	7183(1)	5170(1)	14270(8)	74(1)
C(28)	6114(2)	4292(2)	11413(13)	132(2)

Table S31. Bond lengths [Å] and angles [deg] for **9.**

P(1)-C(11)	1.761(4)
P(1)-C(19)	1.820(3)
P(1)-C(1)	1.836(3)
N(1)-C(20)	1.325(4)
N(1)-N(2)	1.342(4)
N(1)-C(21)	1.473(4)
N(2)-N(3)	1.323(4)
N(3)-C(19)	1.334(4)
C(1)-C(2)	1.367(4)

C(1)-C(6)	1.436(4)
C(2)-C(3)	1.411(5)
C(2)-H(2A)	0.9300
C(3)-C(4)	1.347(5)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.408(5)
C(4)-H(4A)	0.9300
C(5)-C(10)	1.418(4)
C(5)-C(6)	1.420(4)
C(6)-C(7)	1.415(4)
C(7)-C(8)	1.361(4)
C(7)-H(7A)	0.9300
C(8)-C(9)	1.405(5)
C(8)-H(8A)	0.9300
C(9)-C(10)	1.351(5)
C(9)-H(9A)	0.9300
C(10)-H(10A)	0.9300
C(11)-C(12)	1.185(4)
C(12)-C(13)	1.427(5)
C(13)-C(14)	1.365(5)
C(13)-C(18)	1.371(5)
C(14)-C(15)	1.404(6)
C(14)-H(14A)	0.9300
C(15)-C(16)	1.344(7)
C(15)-H(15A)	0.9300
C(16)-C(17)	1.319(7)
C(16)-H(16A)	0.9300
C(17)-C(18)	1.354(6)
C(17)-H(17A)	0.9300
C(18)-H(18A)	0.9300
C(19)-C(20)	1.380(4)

C(20)-H(20A)	0.9300
C(21)-C(22)	1.503(5)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-C(27)	1.356(5)
C(22)-C(23)	1.371(5)
C(23)-C(24)	1.374(5)
C(23)-H(23A)	0.9300
C(24)-C(25)	1.351(6)
C(24)-H(24A)	0.9300
C(25)-C(26)	1.356(6)
C(25)-C(28)	1.537(6)
C(26)-C(27)	1.354(6)
C(26)-H(26A)	0.9300
C(27)-H(27A)	0.9300
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
C(11)-P(1)-C(19)	99.99(15)
C(11)-P(1)-C(1)	100.72(16)
C(19)-P(1)-C(1)	102.60(14)
C(20)-N(1)-N(2)	111.0(3)
C(20)-N(1)-C(21)	130.4(3)
N(2)-N(1)-C(21)	118.6(3)
N(3)-N(2)-N(1)	106.6(2)
N(2)-N(3)-C(19)	109.3(3)
C(2)-C(1)-C(6)	119.5(3)
C(2)-C(1)-P(1)	122.1(2)
C(6)-C(1)-P(1)	118.3(2)
C(1)-C(2)-C(3)	121.1(3)
C(1)-C(2)-H(2A)	119.5

C(3)-C(2)-H(2A)	119.5
C(4)-C(3)-C(2)	120.6(3)
C(4)-C(3)-H(3A)	119.7
C(2)-C(3)-H(3A)	119.7
C(3)-C(4)-C(5)	120.7(3)
C(3)-C(4)-H(4A)	119.7
C(5)-C(4)-H(4A)	119.7
C(4)-C(5)-C(10)	121.1(3)
C(4)-C(5)-C(6)	119.8(3)
C(10)-C(5)-C(6)	119.1(3)
C(7)-C(6)-C(5)	118.1(3)
C(7)-C(6)-C(1)	123.6(3)
C(5)-C(6)-C(1)	118.4(3)
C(8)-C(7)-C(6)	120.9(3)
C(8)-C(7)-H(7A)	119.5
C(6)-C(7)-H(7A)	119.5
C(7)-C(8)-C(9)	120.9(3)
C(7)-C(8)-H(8A)	119.6
C(9)-C(8)-H(8A)	119.6
C(10)-C(9)-C(8)	119.9(3)
C(10)-C(9)-H(9A)	120.1
C(8)-C(9)-H(9A)	120.1
C(9)-C(10)-C(5)	121.1(3)
C(9)-C(10)-H(10A)	119.5
C(5)-C(10)-H(10A)	119.5
C(12)-C(11)-P(1)	168.3(4)
C(11)-C(12)-C(13)	173.8(4)
C(14)-C(13)-C(18)	118.6(4)
C(14)-C(13)-C(12)	120.3(3)
C(18)-C(13)-C(12)	121.1(3)
C(13)-C(14)-C(15)	118.5(4)

C(13)-C(14)-H(14A)	120.7
C(15)-C(14)-H(14A)	120.7
C(16)-C(15)-C(14)	120.5(5)
C(16)-C(15)-H(15A)	119.7
C(14)-C(15)-H(15A)	119.7
C(17)-C(16)-C(15)	120.3(5)
C(17)-C(16)-H(16A)	119.8
C(15)-C(16)-H(16A)	119.8
C(16)-C(17)-C(18)	120.8(5)
C(16)-C(17)-H(17A)	119.6
C(18)-C(17)-H(17A)	119.6
C(17)-C(18)-C(13)	121.1(4)
C(17)-C(18)-H(18A)	119.4
C(13)-C(18)-H(18A)	119.4
N(3)-C(19)-C(20)	107.9(3)
N(3)-C(19)-P(1)	118.9(2)
C(20)-C(19)-P(1)	133.2(2)
N(1)-C(20)-C(19)	105.2(3)
N(1)-C(20)-H(20A)	127.4
C(19)-C(20)-H(20A)	127.4
N(1)-C(21)-C(22)	112.9(3)
N(1)-C(21)-H(21A)	109.0
C(22)-C(21)-H(21A)	109.0
N(1)-C(21)-H(21B)	109.0
C(22)-C(21)-H(21B)	109.0
H(21A)-C(21)-H(21B)	107.8
C(27)-C(22)-C(23)	117.5(3)
C(27)-C(22)-C(21)	122.1(3)
C(23)-C(22)-C(21)	120.3(3)
C(22)-C(23)-C(24)	120.4(4)
C(22)-C(23)-H(23A)	119.8

C(24)-C(23)-H(23A)	119.8
C(25)-C(24)-C(23)	121.6(4)
C(25)-C(24)-H(24A)	119.2
C(23)-C(24)-H(24A)	119.2
C(24)-C(25)-C(26)	117.4(4)
C(24)-C(25)-C(28)	120.2(5)
C(26)-C(25)-C(28)	122.4(5)
C(27)-C(26)-C(25)	121.9(4)
C(27)-C(26)-H(26A)	119.1
C(25)-C(26)-H(26A)	119.1
C(26)-C(27)-C(22)	121.3(4)
C(26)-C(27)-H(27A)	119.4
C(22)-C(27)-H(27A)	119.4
C(25)-C(28)-H(28A)	109.5
C(25)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(25)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S32. Anisotropic displacement parameters (Å ^{2} x 10^3) for **9.** The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^*b^*U12]$

	U11	U22	U33	U23	U13	U12
P(1)	52(1)	65(1)	62(1)	5(1)	2(1)	33(1)
N(1)	51(2)	60(2)	49(2)	-7(1)	-4(1)	27(1)
N(2)	76(2)	73(2)	50(2)	-13(2)	6(1)	31(2)
N(3)	72(2)	66(2)	52(2)	-7(2)	9(1)	28(2)
C(1)	47(2)	50(2)	55(2)	7(1)	6(1)	25(2)

C(2)	50(2)	64(2)	72(2)	0(2)	9(2)	32(2)
C(3)	66(2)	73(2)	75(2)	-20(2)	-3(2)	38(2)
C(4)	59(2)	58(2)	69(2)	-10(2)	-6(2)	28(2)
C(5)	46(2)	42(2)	57(2)	6(1)	4(1)	21(1)
C(6)	50(2)	42(2)	49(2)	13(1)	8(1)	22(1)
C(7)	56(2)	55(2)	56(2)	3(2)	2(2)	30(2)
C(8)	66(2)	68(2)	62(2)	4(2)	12(2)	41(2)
C(9)	52(2)	69(2)	84(3)	14(2)	13(2)	36(2)
C(10)	46(2)	54(2)	74(2)	3(2)	1(2)	27(2)
C(11)	52(2)	68(2)	91(3)	-5(2)	-4(2)	34(2)
C(12)	49(2)	57(2)	91(3)	-6(2)	1(2)	24(2)
C(13)	45(2)	55(2)	74(2)	0(2)	6(2)	28(2)
C(14)	67(3)	130(4)	100(3)	-32(3)	-13(2)	61(3)
C(15)	90(2)	126(3)	128(3)	-11(2)	14(2)	62(2)
C(16)	92(2)	122(2)	127(3)	-14(2)	19(2)	63(2)
C(17)	94(2)	121(2)	125(3)	-16(2)	20(2)	60(2)
C(18)	68(2)	78(3)	92(3)	-9(2)	-6(2)	29(2)
C(19)	47(2)	64(2)	45(2)	-7(2)	2(1)	32(2)
C(20)	59(2)	54(2)	48(2)	-11(2)	-5(2)	27(2)
C(21)	74(2)	67(2)	53(2)	0(2)	-11(2)	35(2)
C(22)	67(2)	53(2)	56(2)	-4(2)	-12(2)	30(2)
C(23)	67(2)	81(3)	76(3)	-16(2)	-2(2)	17(2)
C(24)	81(3)	88(3)	83(3)	-24(2)	-12(2)	23(2)
C(25)	65(2)	66(2)	108(3)	8(2)	-7(2)	28(2)
C(26)	80(3)	85(3)	110(4)	-16(3)	9(3)	45(2)
C(27)	77(3)	71(2)	77(3)	-8(2)	0(2)	39(2)
C(28)	65(3)	107(4)	187(6)	11(4)	-19(3)	15(3)

Table S33. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **9**.

	x	y	z	U(eq)
H(2A)	8911	7731	13573	73
H(3A)	9574	8120	15684	84
H(4A)	10167	8045	14732	75
H(7A)	9235	6994	7609	65
H(8A)	9847	6947	6664	75
H(9A)	10485	7302	9006	79
H(10A)	10511	7717	12220	69
H(14A)	7172	7123	10721	113
H(15A)	6692	7307	12691	133
H(16A)	6920	7738	16029	131
H(17A)	7584	7945	17646	133
H(18A)	8059	7765	15854	99
H(20A)	8278	6447	13784	65
H(21A)	8032	5609	14804	78
H(21B)	8152	5379	12756	78
H(23A)	7570	4949	9638	100
H(24A)	6832	4465	9000	111
H(26A)	6541	4857	15005	108
H(27A)	7266	5353	15613	89
H(28A)	6084	4137	9934	199
H(28B)	5961	4456	11286	199
H(28C)	5988	4081	12702	199

Table S34. Torsion angles [deg] for **9.**

C(20)-N(1)-N(2)-N(3)	-0.5(3)
C(21)-N(1)-N(2)-N(3)	-179.9(3)
N(1)-N(2)-N(3)-C(19)	0.4(3)

C(11)-P(1)-C(1)-C(2)	-9.3(3)
C(19)-P(1)-C(1)-C(2)	-112.2(3)
C(11)-P(1)-C(1)-C(6)	174.0(2)
C(19)-P(1)-C(1)-C(6)	71.1(2)
C(6)-C(1)-C(2)-C(3)	0.2(5)
P(1)-C(1)-C(2)-C(3)	-176.5(3)
C(1)-C(2)-C(3)-C(4)	-1.5(5)
C(2)-C(3)-C(4)-C(5)	1.2(6)
C(3)-C(4)-C(5)-C(10)	-179.6(3)
C(3)-C(4)-C(5)-C(6)	0.4(5)
C(4)-C(5)-C(6)-C(7)	177.4(3)
C(10)-C(5)-C(6)-C(7)	-2.6(4)
C(4)-C(5)-C(6)-C(1)	-1.7(4)
C(10)-C(5)-C(6)-C(1)	178.3(3)
C(2)-C(1)-C(6)-C(7)	-177.7(3)
P(1)-C(1)-C(6)-C(7)	-0.9(4)
C(2)-C(1)-C(6)-C(5)	1.4(4)
P(1)-C(1)-C(6)-C(5)	178.2(2)
C(5)-C(6)-C(7)-C(8)	1.2(4)
C(1)-C(6)-C(7)-C(8)	-179.8(3)
C(6)-C(7)-C(8)-C(9)	0.7(5)
C(7)-C(8)-C(9)-C(10)	-1.1(5)
C(8)-C(9)-C(10)-C(5)	-0.3(5)
C(4)-C(5)-C(10)-C(9)	-177.8(3)
C(6)-C(5)-C(10)-C(9)	2.2(5)
C(19)-P(1)-C(11)-C(12)	-113.1(16)
C(1)-P(1)-C(11)-C(12)	141.9(16)
P(1)-C(11)-C(12)-C(13)	-167(2)
C(11)-C(12)-C(13)-C(14)	-157(3)
C(11)-C(12)-C(13)-C(18)	23(4)
C(18)-C(13)-C(14)-C(15)	1.6(7)

C(12)-C(13)-C(14)-C(15)	-178.6(4)
C(13)-C(14)-C(15)-C(16)	0.8(8)
C(14)-C(15)-C(16)-C(17)	-2.7(9)
C(15)-C(16)-C(17)-C(18)	2.0(8)
C(16)-C(17)-C(18)-C(13)	0.5(7)
C(14)-C(13)-C(18)-C(17)	-2.3(6)
C(12)-C(13)-C(18)-C(17)	177.9(4)
N(2)-N(3)-C(19)-C(20)	-0.2(4)
N(2)-N(3)-C(19)-P(1)	179.8(2)
C(11)-P(1)-C(19)-N(3)	135.0(3)
C(1)-P(1)-C(19)-N(3)	-121.5(3)
C(11)-P(1)-C(19)-C(20)	-44.9(3)
C(1)-P(1)-C(19)-C(20)	58.5(3)
N(2)-N(1)-C(20)-C(19)	0.3(3)
C(21)-N(1)-C(20)-C(19)	179.6(3)
N(3)-C(19)-C(20)-N(1)	-0.1(3)
P(1)-C(19)-C(20)-N(1)	179.9(2)
C(20)-N(1)-C(21)-C(22)	109.8(4)
N(2)-N(1)-C(21)-C(22)	-71.0(4)
N(1)-C(21)-C(22)-C(27)	-100.2(4)
N(1)-C(21)-C(22)-C(23)	77.7(4)
C(27)-C(22)-C(23)-C(24)	-0.9(6)
C(21)-C(22)-C(23)-C(24)	-178.9(4)
C(22)-C(23)-C(24)-C(25)	0.0(7)
C(23)-C(24)-C(25)-C(26)	-0.2(7)
C(23)-C(24)-C(25)-C(28)	178.6(4)
C(24)-C(25)-C(26)-C(27)	1.3(7)
C(28)-C(25)-C(26)-C(27)	-177.5(4)
C(25)-C(26)-C(27)-C(22)	-2.2(6)
C(23)-C(22)-C(27)-C(26)	1.9(5)
C(21)-C(22)-C(27)-C(26)	179.9(4)

Symmetry transformations used to generate equivalent atoms:

Table S35. Hydrogen bonds for 9 [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

Data intensity of **14**[13] was collected using a 'Bruker APEX-II CCD' diffractometer at 100(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **14**: $C_{19}H_{23}O_3P$, T = 100(10) K, monoclinic, $P2_1$, a = 8.3114(2) Å, b = 10.1411(2) Å, c = 10.8128(2) Å, α = 90 deg, β = 107.963(2) deg, γ = 90 deg, V = 866.95(3) $Å^3$. Z = 2, d_{calc} = 1.265 Mg/cm^3. 21852 reflections measured, 3414 [R_{int} = 0.0546, R_{sigma} = 0.0263], R1 = 0.0356, wR2 = 0.0875 ($I > 2\sigma(I)$, final), R1 = 0.0357, wR2 = 0.0876 (all data), GOF = 1.070, and 230 parameters.

14

Table S36. Crystal data and structure refinement for **14**.

Identification code	**14**
Empirical formula	$C_{19}H_{23}O_3P$
Formula weight	330.34
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.3114(2)
b/Å	10.1411(2)
c/Å	10.8128(2)
α/°	90
β/°	107.963(2)
γ/°	90
Volume/$Å^3$	866.95(3)
Z	2

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[13] Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC number: 1920853).

ρ_{calc}g/cm^3	1.265
μ/mm^{-1}	1.503
F(000)	352.0
Crystal size/mm^3	0.32 × 0.28 × 0.22
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.596 to 149.048
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected	21852
Independent reflections	3414 [R_{int} = 0.0546, R_{sigma} = 0.0263]
Data/restraints/parameters	3414/4/230
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0356, wR_2 = 0.0875
Final R indexes [all data]	R_1 = 0.0357, wR_2 = 0.0876
Largest diff. peak/hole / e Å^{-3}	0.25/-0.33
Flack parameter	0.041(11)

Table S37. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **14**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
P1	2628.1(7)	232.5(7)	3802.0(5)	16.86(15)
O1	3861(2)	1031.0(19)	3380.4(18)	23.5(4)
O2	3633(3)	418(2)	8230.5(18)	33.7(5)
O3	3561(4)	2601(3)	8058(2)	54.8(8)
C1	555(3)	993(3)	3351(2)	20.9(5)
C2	408(4)	2285(3)	2880(3)	26.3(6)
C3	-1168(4)	2895(4)	2507(3)	35.2(7)
C4	-2572(4)	2228(4)	2594(3)	37.7(8)
C5	-2429(4)	950(4)	3072(4)	41.4(8)
C6	-856(3)	331(4)	3456(3)	32.0(6)
C7	2191(3)	-1406(3)	3095(2)	20.8(5)

C8	1768(3)	-2432(3)	3793(3)	23.5(5)
C9	1301(4)	-3666(3)	3236(3)	28.9(6)
C10	1288(4)	-3887(3)	1976(3)	36.9(7)
C11	1723(5)	-2878(4)	1278(3)	42.8(8)
C12	2165(4)	-1623(3)	1800(3)	30.8(6)
C13	2518(7)	-542(4)	966(3)	54.4(11)
C14	3299(3)	45(3)	5568(2)	20.5(5)
C15	4991(3)	-695(3)	6000(3)	25.7(6)
C16	3445(4)	1431(3)	6167(3)	23.9(6)
C17	3570(4)	1396(3)	7594(3)	25.3(6)
C182	3361(9)	2555(6)	9398(5)	21.1(12)
C192	2876(8)	3934(6)	9696(5)	23.4(12)
C191	2540(11)	3117(13)	9718(8)	56(2)
C181	4188(11)	2838(9)	9483(8)	41.6(19)

Table S38. Anisotropic Displacement Parameters (Å^{2}×10^{3}) for **14**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P1	17.5(3)	16.1(3)	19.7(3)	-0.2(3)	9.8(2)	0.1(2)
O1	23.3(9)	24.5(11)	27.8(9)	0.7(8)	15.3(7)	-2.1(8)
O2	48.9(12)	30.0(13)	23.0(9)	1.8(9)	12.0(8)	-8.6(10)
O3	114(2)	32.8(14)	19.7(11)	1.6(9)	24.1(13)	27.3(15)
C1	21.0(12)	22.8(15)	21.2(11)	-3.3(10)	9.9(10)	1.7(10)
C2	31.0(14)	27.0(16)	23.2(13)	1.2(11)	11.9(11)	7.6(12)
C3	45.8(17)	37.8(19)	21.9(13)	1.1(12)	10.2(12)	18.7(14)
C4	30.2(15)	49(2)	28.7(15)	-13.2(14)	1.6(12)	19.1(14)
C5	21.1(14)	47(2)	58(2)	-23.5(17)	16.2(13)	-2.5(13)
C6	24.1(12)	26.9(16)	49.2(16)	-5.6(15)	17.5(11)	0.8(13)
C7	18.3(12)	20.8(14)	22.5(12)	-2.4(10)	5.1(10)	1.4(10)
C8	25.4(12)	19.0(14)	27.7(13)	-1.0(10)	10.6(10)	0.4(10)

C9	29.6(14)	18.5(15)	36.3(15)	0.9(12)	6.8(12)	0.8(11)
C10	49.1(18)	21.2(16)	32.7(15)	-6.2(12)	1.3(13)	0.5(14)
C11	72(2)	29.6(18)	21.9(15)	-5.6(12)	6.5(15)	-2.6(17)
C12	42.9(17)	26.2(16)	20.1(12)	0.2(11)	5.1(11)	1.0(13)
C13	107(3)	37(2)	17.7(14)	-1.1(14)	16.4(18)	-14(2)
C14	21.6(11)	19.7(15)	22.2(11)	-0.3(10)	9.7(9)	0.2(10)
C15	23.8(13)	25.9(15)	26.6(13)	1.8(10)	6.5(11)	2.7(11)
C16	32.2(14)	20.3(15)	20.4(12)	0.1(10)	10.0(10)	-0.9(11)
C17	29.8(13)	26.7(16)	21.1(12)	1.1(11)	10.1(10)	1.3(11)
C182	33(3)	26(3)	7(2)	-2(2)	10(2)	3(3)
C192	34(3)	21(3)	19(3)	-8(2)	12(2)	-4(2)
C191	66(6)	71(7)	32(4)	-7(4)	19(4)	4(5)
C181	56(5)	42(5)	32(4)	-11(3)	21(4)	-9(4)

Table S39. Bond Lengths for **14.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O1	1.4836(19)	C5	C6	1.393(4)
P1	C1	1.812(3)	C7	C8	1.393(4)
P1	C7	1.818(3)	C7	C12	1.410(4)
P1	C14	1.826(2)	C8	C9	1.391(4)
O2	C17	1.199(4)	C9	C10	1.377(4)
O3	C17	1.322(4)	C10	C11	1.384(5)
O3	C182	1.509(6)	C11	C12	1.395(5)
O3	C181	1.487(8)	C12	C13	1.505(5)
C1	C2	1.397(4)	C14	C15	1.534(4)
C1	C6	1.386(4)	C14	C16	1.537(4)
C2	C3	1.391(4)	C16	C17	1.515(4)
C3	C4	1.377(5)	C182	C192	1.518(8)
C4	C5	1.387(6)	C191	C181	1.495(8)

Table S40. Bond Angles for **14.**

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	P1	C1	111.99(12)	C12	C7	P1	120.0(2)
O1	P1	C7	115.90(12)	C9	C8	C7	121.4(3)
O1	P1	C14	111.16(11)	C10	C9	C8	119.4(3)
C1	P1	C7	103.06(12)	C9	C10	C11	119.7(3)
C1	P1	C14	106.49(11)	C10	C11	C12	122.3(3)
C7	P1	C14	107.55(13)	C7	C12	C13	122.3(3)
C17	O3	C182	110.5(3)	C11	C12	C7	117.8(3)
C17	O3	C181	120.1(4)	C11	C12	C13	119.8(3)
C2	C1	P1	117.8(2)	C15	C14	P1	108.96(17)
C6	C1	P1	122.0(2)	C15	C14	C16	111.9(2)
C6	C1	C2	120.2(3)	C16	C14	P1	107.71(18)
C3	C2	C1	119.4(3)	C17	C16	C14	112.3(2)
C4	C3	C2	120.3(3)	O2	C17	O3	123.5(2)
C3	C4	C5	120.5(3)	O2	C17	C16	125.6(3)
C4	C5	C6	119.8(3)	O3	C17	C16	110.9(2)
C1	C6	C5	119.8(3)	O3	C182	C192	106.9(4)
C8	C7	P1	120.4(2)	O3	C181	C191	99.2(6)
C8	C7	C12	119.5(3)				

Table S41. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **14.**

Atom	x	y	z	U(eq)
H2	1355.5	2733.39	2817.1	32
H3	-1273.87	3756.06	2196.28	42
H4	-3624.14	2638.15	2330.58	45
H5	-3379.89	507.79	3136.77	50
H6	-753.26	-524.77	3781.1	38

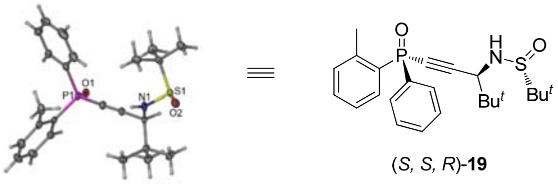
H8	1799.09	-2289.36	4649.97	28
H9	1000.43	-4335.55	3710	35
H10	988.75	-4710.22	1596.5	44
H11	1719.96	-3042.63	431.57	51
H13A	1708.3	154.57	880.62	82
H13B	2431.99	-887.67	121.32	82
H13C	3636.96	-203.28	1362.86	82
H14	2446.58	-462.01	5820.56	25
H15A	4807.34	-1605.56	5753.02	39
H15B	5473.05	-632.42	6926.74	39
H15C	5752.18	-310.79	5589.57	39
H16A	4439.95	1864.54	6069.92	29
H16B	2463.64	1946.68	5697.6	29
H18A	4413.81	2287.09	10033.85	25
H18B	2487.2	1929.2	9418.45	25
H19A	1752.06	4131.85	9149.3	35
H19B	3655.02	4560.7	9536.01	35
H19C	2914.13	3982.96	10591.2	35
H19D	2048.9	3901.47	9257.53	83
H19E	2726.96	3241.76	10632.1	83
H19F	1784.47	2387.67	9415.98	83
H18C	4949.31	3587.22	9702.36	50
H18D	4741.1	2066.24	9956.15	50

Table S42. Atomic Occupancy for **14.**

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
C182	0.5	H18A	0.5	H18B	0.5
C192	0.5	H19A	0.5	H19B	0.5
H19C	0.5	C191	0.5	H19D	0.5

H19E	0.5	H19F	0.5	C181	0.5
H18C	0.5	H18D	0.5		

Data intensity of **19**[14] was collected using a 'Bruker APEX-II CCD' diffractometer at 100(11) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **19**: $C_{24}H_{32}NO_2PS$, T = 100(11) K, monoclinic, $P2_1$, a = 6.07450(10), b = 19.8094(2) Å, c = 9.96830(10) Å, α = 90 deg, 98.0600(10) deg, γ = 90 deg, 1187.66(3) Å^3. Z = 2, d_{calc} = 1.201 Mg/cm^3. 26423 reflections measured, 4775 [R_{int} = 0.0552, R_{sigma} = 0.0344], R1 = 0.0311, wR2 = 0.0745 ($I > 2\sigma(I)$, final), R1 = 0.0328, wR2 = 0.0753 (all data), GOF = 1.044, and 272 parameters.



(*S*, *S*, *R*)-**19**

Table S43. Crystal data and structure refinement for **19**.

Identification code	**19**
Empirical formula	$C_{24}H_{32}NO_2PS$
Formula weight	429.53
Temperature/K	100.00(11)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.07450(10)
b/Å	19.8094(2)
c/Å	9.96830(10)
α/°	90
β/°	98.0600(10)
γ/°	90
Volume/Å^3	1187.66(3)
Z	2
ρ_{calc}g/cm^3	1.201

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[14] Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC number: 1920855).

μ/mm^{-1}	1.989
F(000)	460.0
Crystal size/mm^3	0.32 × 0.26 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.96 to 148.808
Index ranges	$-7 \le h \le 7$, $-24 \le k \le 24$, $-12 \le l \le 12$
Reflections collected	26423
Independent reflections	4775 [R_{int} = 0.0552, R_{sigma} = 0.0344]
Data/restraints/parameters	4775/1/272
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0311, wR_2 = 0.0745
Final R indexes [all data]	R_1 = 0.0328, wR_2 = 0.0753
Largest diff. peak/hole / e Å^{-3}	0.25/-0.20
Flack parameter	0.011(8)

Table S44. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **19**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
S1	10798.6(11)	6474.6(3)	8754.0(6)	23.50(15)
P1	2851.8(11)	4483.5(3)	6259.7(6)	19.05(14)
O1	598(3)	4727.4(9)	6439.4(17)	23.2(4)
O2	13100(3)	6632.1(10)	8511.9(19)	29.8(4)
N1	9552(4)	6017.0(11)	7504(2)	25.4(5)
C1	2835(4)	4139.3(12)	4579(3)	21.8(5)
C2	914(5)	4273.5(13)	3674(3)	26.3(6)
C3	667(5)	4028.6(16)	2362(3)	34.0(7)
C4	2352(6)	3657.0(16)	1936(3)	38.2(7)
C5	4275(5)	3521.4(15)	2818(3)	34.1(7)
C6	4574(5)	3755.0(13)	4151(3)	25.9(6)
C7	6650(5)	3583.2(15)	5064(3)	31.2(6)

C8	3825(5)	3851.7(13)	7497(3)	25.4(6)
C9	2308(6)	3334.0(13)	7681(3)	30.4(6)
C10	2928(7)	2830.5(15)	8617(3)	41.1(8)
C11	5011(7)	2837.8(17)	9368(3)	45.7(9)
C12	6507(7)	3346.7(19)	9206(3)	47.8(9)
C13	5910(6)	3861.0(16)	8255(3)	36.1(7)
C14	4831(5)	5126.7(13)	6447(3)	24.7(6)
C15	5962(4)	5627.6(13)	6594(3)	22.1(5)
C16	7435(4)	6222.2(12)	6748(2)	19.8(5)
C17	7598(4)	6563.7(13)	5360(3)	24.1(5)
C18	8505(5)	6074.2(14)	4392(3)	32.2(7)
C19	5272(5)	6800.3(14)	4762(3)	30.1(6)
C20	9143(5)	7175.5(14)	5612(3)	30.4(6)
C21	11117(5)	5849.6(14)	10150(2)	24.9(6)
C22	12439(5)	5241.7(14)	9774(3)	30.1(6)
C23	8782(5)	5664.8(16)	10408(3)	33.2(6)
C24	12388(5)	6219.6(17)	11370(3)	35.7(7)

Table S45. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **19**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	25.8(3)	20.5(3)	23.4(3)	-6.2(2)	0.4(2)	-3.6(3)
P1	20.7(3)	12.7(3)	23.3(3)	-1.7(2)	1.3(2)	-0.5(2)
O1	22.5(10)	19.6(8)	27.2(9)	-3.9(7)	2.4(7)	-0.5(7)
O2	29.0(11)	32.2(11)	27.8(9)	-5.6(8)	3.0(8)	-10.1(8)
N1	28.4(13)	17.1(10)	28.3(11)	-7.6(9)	-4.8(10)	4.6(9)
C1	26.3(14)	13.8(11)	25.7(12)	-0.1(9)	4.4(10)	-1.8(10)
C2	31.9(15)	21.0(12)	25.7(13)	0.5(9)	3.3(11)	2.1(11)
C3	39.9(18)	35.3(15)	25.2(13)	0.8(11)	-1.4(12)	0.9(13)

C4	51(2)	38.5(16)	25.7(14)	-7.5(12)	8.0(13)	-0.7(15)
C5	40.1(18)	29.3(14)	36.0(15)	-5.6(12)	16.0(13)	-1.9(13)
C6	27.9(15)	17.6(11)	33.6(14)	-2.5(10)	9.5(11)	-3.6(10)
C7	27.4(15)	26.2(13)	40.8(15)	-8.6(12)	7.7(12)	0.5(12)
C8	33.2(15)	18.4(12)	24.2(13)	-4.5(9)	2.3(11)	5.6(11)
C9	44.6(18)	19.5(13)	27.4(13)	-2.0(10)	6.3(13)	3.7(12)
C10	70(2)	21.9(13)	32.7(15)	3.3(12)	12.0(15)	8.2(15)
C11	80(3)	32.4(16)	24.8(14)	1.8(12)	8.4(16)	26.4(18)
C12	55(2)	52(2)	31.7(16)	-10.8(15)	-10.5(15)	24.2(18)
C13	39.2(18)	33.4(16)	33.1(15)	-6.5(12)	-4.3(13)	11.1(14)
C14	28.1(15)	19.1(12)	27.0(13)	-2.7(10)	4.4(11)	0.2(11)
C15	23.5(14)	19.1(12)	23.4(12)	-2.7(9)	2.5(10)	-0.2(10)
C16	21.7(13)	13.8(10)	23.3(12)	-4.0(9)	1.1(10)	-2.2(10)
C17	27.2(14)	18.6(12)	26.5(12)	0.7(10)	4.1(10)	-0.4(11)
C18	42.7(18)	28.2(14)	27.2(13)	0.2(11)	10.0(13)	3.4(13)
C19	30.7(16)	24.6(13)	32.7(14)	3.3(11)	-4.1(12)	2.6(12)
C20	28.9(16)	20.9(13)	41.5(16)	6.0(11)	5.5(12)	-3.3(11)
C21	25.0(14)	29.2(14)	20.7(12)	-4.4(10)	3.4(10)	-0.6(11)
C22	31.7(16)	33.4(15)	25.1(13)	2.3(11)	3.2(12)	3.9(12)
C23	28.2(16)	36.1(15)	36.6(15)	-1.6(12)	9.5(12)	-2.1(13)
C24	36.5(17)	44.2(17)	25.2(13)	-7.7(12)	0.7(12)	-3.6(14)

Table S46. Bond Lengths for **19**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O2	1.485(2)	C8	C9	1.408(4)
S1	N1	1.638(2)	C8	C13	1.381(4)
S1	C21	1.852(3)	C9	C10	1.381(4)
P1	O1	1.4861(19)	C10	C11	1.377(6)
P1	C1	1.808(3)	C11	C12	1.382(6)

P1	C8	1.798(3)	C12	C13	1.404(5)
P1	C14	1.744(3)	C14	C15	1.204(4)
N1	C16	1.454(3)	C15	C16	1.474(3)
C1	C2	1.396(4)	C16	C17	1.556(3)
C1	C6	1.416(4)	C17	C18	1.525(4)
C2	C3	1.384(4)	C17	C19	1.528(4)
C3	C4	1.375(4)	C17	C20	1.532(4)
C4	C5	1.386(5)	C21	C22	1.523(4)
C5	C6	1.394(4)	C21	C23	1.521(4)
C6	C7	1.487(4)	C21	C24	1.533(4)

Table S47. Bond Angles for **19**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O2	S1	N1	109.76(12)	C10	C9	C8	119.5(3)
O2	S1	C21	105.14(12)	C11	C10	C9	120.2(3)
N1	S1	C21	100.94(12)	C10	C11	C12	120.9(3)
O1	P1	C1	110.40(12)	C11	C12	C13	119.8(3)
O1	P1	C8	111.32(12)	C8	C13	C12	119.3(3)
O1	P1	C14	112.50(12)	C15	C14	P1	171.2(3)
C8	P1	C1	109.39(11)	C14	C15	C16	177.2(3)
C14	P1	C1	106.79(12)	N1	C16	C15	108.1(2)
C14	P1	C8	106.24(13)	N1	C16	C17	114.9(2)
C16	N1	S1	121.36(18)	C15	C16	C17	111.6(2)
C2	C1	P1	115.0(2)	C18	C17	C16	111.1(2)
C2	C1	C6	120.0(2)	C18	C17	C19	110.2(2)
C6	C1	P1	125.1(2)	C18	C17	C20	109.8(2)
C3	C2	C1	120.9(3)	C19	C17	C16	108.0(2)
C4	C3	C2	119.5(3)	C19	C17	C20	109.5(2)
C3	C4	C5	120.4(3)	C20	C17	C16	108.2(2)

C4	C5	C6	121.7(3)	C22	C21	S1	110.28(18)
C1	C6	C7	122.9(2)	C22	C21	C24	110.4(2)
C5	C6	C1	117.5(3)	C23	C21	S1	106.65(19)
C5	C6	C7	119.5(3)	C23	C21	C22	112.8(2)
C9	C8	P1	116.0(2)	C23	C21	C24	111.0(2)
C13	C8	P1	123.6(2)	C24	C21	S1	105.3(2)
C13	C8	C9	120.4(3)				

Table S48. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **19.**

Atom	x	y	z	U(eq)
H1	10090(50)	5700(18)	7260(30)	31
H2	-215.38	4530.98	3957.86	32
H3	-628.61	4114.63	1771.58	41
H4	2200.35	3495.77	1051.92	46
H5	5394.82	3268.05	2513.39	41
H7A	7256.37	3984.2	5513.33	47
H7B	7710.61	3394.05	4540.83	47
H7C	6321.49	3260.3	5726.03	47
H9	898.51	3331.03	7177.1	36
H10	1937.01	2485.76	8739.91	49
H11	5416.34	2495.64	9992.55	55
H12	7903.72	3348.57	9725.01	57
H13	6909.45	4204.43	8136.65	43
H16	6768.64	6551.24	7305.73	24
H18A	9955.95	5923.45	4783.1	48
H18B	8603.95	6298.06	3547.93	48
H18C	7527.42	5693.03	4234.23	48
H19A	4303.85	6416.93	4602.24	45

H19B	5343.23	7031.13	3922.79	45
H19C	4706.16	7101.64	5386.87	45
H20A	8565.24	7481.47	6223.5	46
H20B	9235.39	7400.81	4769.44	46
H20C	10598.11	7027.68	6002.75	46
H22A	11544.07	4981.67	9089.86	45
H22B	12851.35	4966.69	10561.79	45
H22C	13754.81	5393.7	9432.32	45
H23A	7957.39	6069.29	10521.33	50
H23B	8867.36	5395.4	11214.21	50
H23C	8048.24	5413.12	9651.66	50
H24A	13846.93	6335.71	11178.35	54
H24B	12513.69	5931.59	12151.27	54
H24C	11601.27	6623.36	11543.82	54

Data intensity of **21**[15]was collected using a 'Bruker APEX-II CCD' diffractometer at 293(2) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **21**: $C_{24}H_{32}NO_2PS$, T = 293(2) K, triclinic, P-1, a = 8.6866(3) Å, b = 10.7017(4) Å, c = 11.1556(3) Å, α = 72.428(3) deg, β = 86.595(3) deg, γ = 70.591(3) deg, V = 931.50(6) Å^3. Z = 2, d_{calc} = 1.942 Mg/cm^3. 17430 reflections measured, 3313 [R_{int} = 0.1194, R_{sigma} = 0.0633], R1 = 0.0570, wR2 = 0.1508 ($I > 2\sigma(I)$, final), R1 = 0.0604, wR2 = 0.1531 (all data), GOF = 1.081, and 191 parameters.

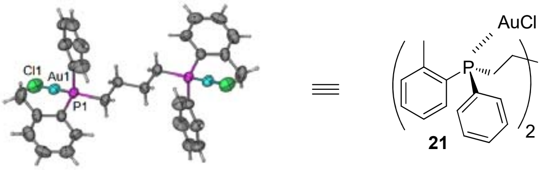

Table S49. Crystal data and structure refinement for **21**.

Identification code	**21**
Empirical formula	$C_{30}H_{32}Au_2Cl_2P_2$
Formula weight	918.59
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.6866(3)
b/Å	10.7017(4)
c/Å	11.1556(3)
α/°	72.428(3)
β/°	86.595(3)
γ/°	70.591(3)
Volume/Å^3	931.50(6)
Z	2
ρ_{calc}g/cm^3	1.942

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[15] Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC number: 1826888).

μ/mm^{-1}	19.528
F(000)	518.0
Crystal size/mm^3	0.31 × 0.17 × 0.07
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.322 to 134.096
Index ranges	$-10 \leq h \leq 9$, $-12 \leq k \leq 12$, $-13 \leq l \leq 13$
Reflections collected	17430
Independent reflections	3313 [R_{int} = 0.1194, R_{sigma} = 0.0633]
Data/restraints/parameters	3313/0/191
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0570, wR_2 = 0.1508
Final R indexes [all data]	R_1 = 0.0604, wR_2 = 0.1531
Largest diff. peak/hole / e Å^{-3}	2.27/-2.08

Table S50. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **21**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Au1	7402.2(4)	3666.6(3)	7697.4(2)	50.9(2)
P1	6801(3)	5789(2)	7897.4(18)	43.9(5)
Cl1	8014(4)	1480(3)	7542(3)	80.4(7)
Cl2	3076(7)	3435(5)	7605(4)	129.2(13)
Cl3	2709(9)	1026(5)	9548(6)	169(2)
C1	7491(10)	6982(8)	6616(6)	47.1(17)
C7	4630(10)	6675(7)	7952(7)	48.2(16)
C8	3548(11)	6857(8)	6983(8)	57(2)
C6	8510(13)	6483(10)	5734(8)	68(2)
C13	7761(10)	5736(8)	9314(7)	49.4(17)
C14	9590(9)	5006(8)	9402(6)	49.6(17)
C12	3996(11)	7184(9)	8959(8)	58(2)
C11	2358(13)	7871(9)	9002(9)	68(2)
C2	6999(15)	8373(9)	6513(10)	79(3)
C10	1309(12)	8020(9)	8072(10)	71(3)

C9	1906(13)	7529(10)	7086(10)	73(3)
C15	4144(15)	6401(13)	5854(10)	87(3)
C5	9009(16)	7379(12)	4739(9)	81(3)
C4	8502(15)	8765(12)	4640(9)	78(3)
C3	7502(15)	9284(10)	5521(11)	83(3)
C16	3670(30)	1580(20)	8105(19)	160(9)

Table S51. Anisotropic Displacement Parameters (Å^2×10^3) for **21**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au1	60.6(3)	42.3(2)	44.1(2)	-8.70(15)	2.26(17)	-13.49(17)
P1	49.3(12)	42.1(9)	36.5(9)	-8.2(7)	-2.9(8)	-12.4(8)
Cl1	108(2)	48.8(12)	81.9(15)	-24.3(11)	15.4(14)	-20.4(12)
Cl2	146(3)	119(3)	114(3)	-39(2)	20(2)	-30(2)
Cl3	211(6)	109(3)	203(6)	-50(3)	27(5)	-75(4)
C1	49(5)	47(4)	39(3)	-7(3)	2(3)	-13(3)
C7	53(5)	45(4)	43(4)	-7(3)	-7(3)	-16(3)
C8	62(5)	48(4)	55(4)	-8(3)	-19(4)	-15(3)
C6	84(7)	55(5)	59(5)	-13(4)	10(4)	-22(4)
C13	52(5)	51(4)	40(3)	-11(3)	-7(3)	-11(3)
C14	49(5)	53(4)	42(4)	-5(3)	-7(3)	-17(3)
C12	60(5)	60(5)	49(4)	-15(3)	7(4)	-14(4)
C11	71(6)	50(4)	64(5)	-5(4)	11(5)	-9(4)
C2	102(8)	39(4)	79(6)	0(4)	7(5)	-17(4)
C10	49(5)	50(4)	92(7)	-1(4)	10(5)	-10(4)
C9	63(6)	62(5)	83(6)	-3(5)	-24(5)	-17(4)
C15	86(8)	99(8)	68(6)	-29(5)	-25(5)	-11(6)
C5	103(9)	90(7)	55(5)	-14(5)	19(5)	-49(6)
C4	89(8)	77(6)	57(5)	11(4)	-1(5)	-42(6)
C3	87(8)	47(5)	101(8)	7(5)	-1(6)	-30(5)
C16	200(20)	119(13)	124(13)	-58(11)	-17(13)	20(13)

Table S52. Bond Lengths for **21.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	P1	2.233(2)	C8	C9	1.383(14)
Au1	Cl1	2.279(3)	C8	C15	1.489(14)
P1	C1	1.827(8)	C6	C5	1.384(13)
P1	C7	1.814(8)	C13	C14	1.514(11)
P1	C13	1.808(7)	C14	C14^{1}	1.544(14)
Cl2	C16	1.79(2)	C12	C11	1.373(13)
Cl3	C16	1.80(2)	C11	C10	1.360(15)
C1	C6	1.393(12)	C2	C3	1.393(14)
C1	C2	1.375(12)	C10	C9	1.362(15)
C7	C8	1.402(10)	C5	C4	1.370(17)
C7	C12	1.399(11)	C4	C3	1.392(17)

Table S53. Bond Angles for **21.**

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
P1	Au1	Cl1	178.69(7)	C9	C8	C7	117.5(8)
C1	P1	Au1	114.0(3)	C9	C8	C15	121.0(8)
C7	P1	Au1	113.9(3)	C5	C6	C1	120.5(9)
C7	P1	C1	104.7(3)	C14	C13	P1	112.7(5)
C13	P1	Au1	111.4(3)	C13	C14	C14^{1}	112.5(8)
C13	P1	C1	105.2(4)	C11	C12	C7	121.6(9)
C13	P1	C7	106.9(4)	C10	C11	C12	119.6(9)
C6	C1	P1	119.8(6)	C1	C2	C3	120.2(10)
C2	C1	P1	120.4(7)	C11	C10	C9	119.5(9)
C2	C1	C6	119.8(8)	C10	C9	C8	123.2(9)
C8	C7	P1	120.4(6)	C4	C5	C6	119.2(10)
C12	C7	P1	121.2(6)	C5	C4	C3	121.3(8)
C12	C7	C8	118.5(8)	C4	C3	C2	119.0(9)
C7	C8	C15	121.4(8)	Cl2	C16	Cl3	109.3(9)

Table S54. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **21.**

Atom	x	y	z	U(eq)
H6	8858.54	5539.43	5812.78	81
H13A	7543.51	6678.61	9336.29	59
H13B	7279.97	5262.12	10040.14	59
H14A	10069.24	5466.67	8666.66	60
H14B	9808.29	4056.62	9400.81	60
H12	4700.62	7053.48	9615.25	70
H11	1968.8	8233.73	9663.29	82
H2	6328.1	8705.95	7107.31	95
H10	192.54	8452.2	8108.91	85
H9	1174.37	7652.06	6450.85	88
H15A	4318.37	7158.87	5202.94	130
H15B	3344.55	6109.13	5558.1	130
H15C	5152.46	5639.99	6073.22	130
H5	9680.56	7045.21	4145.55	97
H4	8832.74	9369.78	3971.15	94
H3	7173.8	10225.15	5448.29	100
H16A	4843.58	1182.71	8233.99	192
H16B	3333.37	1272.07	7462.72	192