Electronic Supplementary Material (ESI) for RSC Advances.

Syntheses of New Chiral Chimeric Photo-Organocatalysts

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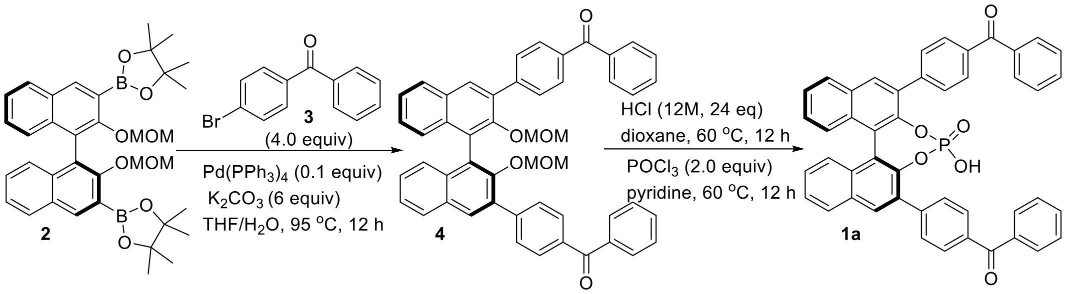
1. General introduction

All reactions requiring anhydrous conditions or inert atmosphere were carried out under argon atmosphere in dried glassware. Immersion coolers IMC-40 and TC100E fitted with a probe and a flexible cooling tube were used to perform slow reactions at low temperature. Solvents were distilled by standard methods using the appropriate drying agent and stored over molecular sieve under argon. All other reagents were obtained from commercial suppliers unless otherwise noted. Flash column chromatography was carried out using 40-63 µm particle sized silica gel with air pressure. Analytical thin layer chromatography (TLC) plates (silica gel 60 F254) were visualized either with a UV lamp (254 nm), or by submersion in potassium permanganate, ninhydrine or iodine. Melting points were recorded using a melting point apparatus (Büchi B-540) and are uncorrected. Specific rotations for chiral compounds were recorded on a Perkin Elmer 141 using sodium D ray (589 nm). Infrared spectra were recorded on a Perkin Elmer Spectrum BX FT-IR spectrometer and the characteristic IR absorption frequencies are reported in cm^{-1}. Proton NMR (^{1}H) spectra were recorded on a Bruker Avance 500 MHz or 300 MHz and carbon NMR (^{13}C) spectra were recorded at 75 MHz or126 MHz. NMR experiments were carried out in $CDCl_3$, DMSO-d_6 and acetone-d_6. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent as an internal reference (^{1}H: 7.26, ^{13}C: 77.16 ppm for $CHCl_3$, ^{1}H: 2.50, ^{13}C: 39.52 ppm for DMSO-*d*6 and ^{1}H: 2.05, ^{13}C: 29.84, 206.26 ppm for Acetone-d_6). The following abbreviations are used for the multiplicities: s: singlet; d: doublet; t: triplet; q: quadruplet; quint: quintuplet; m: multiplet or overlap of non-equivalent resonances; br s: broad singlet; app: apparent; rot: rotamer. Coupling constants (*J*) are reported in Hertz (Hz). Mass spectra were obtained from a MALDI-TOF type instrument for the high resolution mass spectra.

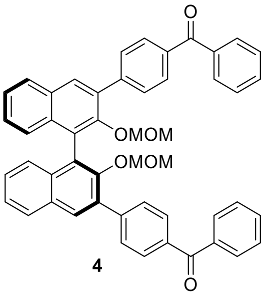
2. General procedure for the synthesis photocatalysts

2.1. Preparation of catalyst 1**a**



91% yield

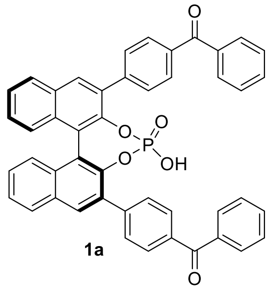
87% yield over 2 steps



Chemical Formula: $C_{50}H_{38}O_6$
Molecular Weight: 734,85

(*S*)-((2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-diyl)bis(4,1-phenylene))bis(phenylmethanone) 4

A 100 mL round bottom flask was charged with a magnetic stirring bar,(*S*)-2,2'-(2,2'-bis(methoxymetho-xy)-[1,1'-binaphthalene]-3,3'-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **2**[4] (1 equiv, 2.0 mmol, 1.3 g), 4-bromo-benzophenone **3** (4 equiv, 8 mmol, 2.1 g), K_2CO_3 (6 equiv, 12 mmol, 1.7 g) and $Pd(PPh_3)_4$ (0.1 equiv, 0.2 mmol, 0.23 g) and purged with argon. THF (50 mL) and H_2O (6 mL) were degassed by bubbling argon for 15 min in an ultrasonic bath and added sequentially to the flask at room temperature. The reaction mixture was refluxed at 75 °C. Upon completion (12 h, monitored by TLC), water (20 mL) was added at room temperature and the mixture was extracted with CH_2Cl_2 (3×50 mL).The combined organic phases were washed with brine, dried over $MgSO_4$ filtered and concentrated under vacuum. Purification by flash column chromatography on silica gel (petroleum/EtOAc = 10:1) afforded **4** as a yellow solid in 91% yield (1.33 g, 1.8 mmol). $[\alpha]_D^{25}$ -54 (*c* 1.0, CH_2Cl_2); IR (neat) ν (cm^{-1}) 1629, 1598, 1575, 1499, 1447, 1427, 1338, 1323, 1261, 1209, 1180, 1148, 1094, 1021, 943, 893, 854, 748, 698; mp 226 °C. ^1H {^{13}C} NMR (300 MHz, $CDCl_3$) δ 8.03 (s, 2H), 7.90 (dt, *J* = 15.2, 6.7 Hz, 14H), 7.62 (t, *J* = 7.2 Hz, 2H), 7.56 – 7.42 (m, 6H), 7.38 – 7.28 (m, 4H), 4.43 (dd, *J* = 12.7, 5.8 Hz, 4H), 2.40 (s, 6H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$) δ 196.5, 151.4, 143.5, 137.9, 136.5, 134.6, 134.0, 132.6, 131.0, 131.0, 130.4, 130.3, 130.3, 130.2, 129.7, 128.5, 128.2, 127.0, 126.7, 126.6, 125.7, 99.0, 56.2. HRMS (ESI/Q-TOF) *m/z* [M + $NH_4]^+$ $C_{50}H_{42}NO_6$ calcd 752.3012, found 752.3002.



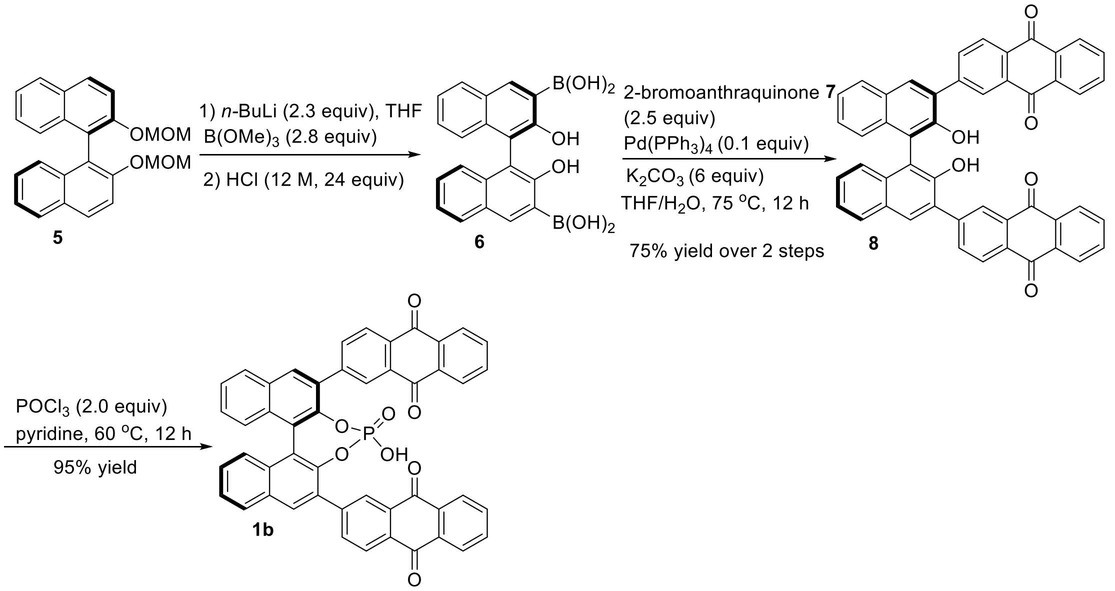
Chemical Formula: $C_{46}H_{29}O_6P$
Molecular Weight: 708,71

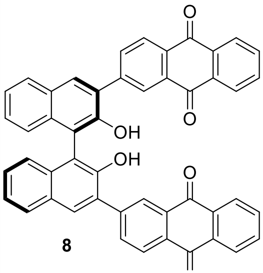
(((11bS)-4-hydroxy-4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-2,6-diyl)bis(4,1-phenylene))bis(phenylmethanone) 1a

4 (1 equiv, 0.2 mmol, 0.15 g) was dissolved in dioxane (4 mL). An aqueous solution of HCl (12 M, 24 equiv, 4.8 mmol, 0.4 mL) was added and the resulting reaction solution was stirred at 60 °C. Upon completion (12 h, monitored by TLC), water (5 mL) was added at room temperature and the mixture was extracted with CH_2Cl_2 (3x10 mL), dried over $MgSO_4$, filtered, concentrated on a rotary evaporator and dried under high vacuum for 2 h. The residue was dissolved in pyridine (5 mL). Freshly distilled $POCl_3$ (2.0 equiv, 0.4 mmol, 40 μL) was added and the the resulting reaction solution was stirred at 60

°C. Upon completion (12 h, monitored by TLC), water (3 mL) was added at room temperature and the mixture was reflux for 3 h. An aqueous solution of HCl (6 M, 12 mL) was added and the mixture was further heated at reflux with vigorous stirring for 1 h. The reaction mixture was then extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with aq. HCl (2 M, 50 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH= 20:1-10:1). The obtained compound was dissolved in CH_2Cl_2 (15 mL) and vigorously washed with aq HCl (2 M, 3 × 10 mL), filtered and concentrated to afford **1a** as a white solid in 87% yield over two steps (123 mg, 0.17 mmol). $[\alpha]_D^{25}$ +337 (*c* 1.0, CH_2Cl_2); IR (neat) ν (cm^{-1}) 1652, 1604, 1578, 1556, 1497, 1447, 1421, 1399, 1362, 1316, 1263, 1276, 1196, 1180, 1152, 1141, 1019, 997, 958, 939, 926, 886, 849, 793, 776, 750, 729, 666, 653; mp 188 °C. ^1H {^{13}C} NMR (300 MHz, $CDCl_3$) δ 8.12 – 7.92 (m, 4H), 7.72 (d, *J* = 8.3 Hz, 4H), 7.68 – 7.60 (m, 8H), 7.54 (ddd, *J* = 12.0, 7.0, 4.4 Hz, 2H), 7.36 (t, *J* = 5.9 Hz, 5H), 7.15 (dd, *J* = 8.4, 6.1 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 4H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$) δ 196.6, 144.3, 144.1, 140.9, 137.5, 136.9, 133.2, 133.1, 132.3, 132.2, 131.7, 130.1, 130.0, 129.9, 128.8, 128.1, 127.2, 126.5, 122.7. ^{31}P NMR (202 MHz, $CDCl_3$) δ 3.75. HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ $C_{46}H_{30}O_6P$ calcd 709.1780, found 709.1802.

2.2. Preparation of catalyst 1**b**





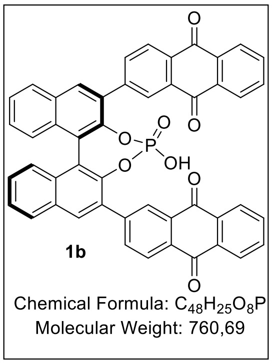
8

Chemical Formula: $C_{48}H_{26}O_6$
Molecular Weight: 698,73

(R)- 2,2'-(2,2'-dihydroxy-[1,1'-binaphthalene]-3,3'-diyl)bis(anthracene-9,10-dione) 8

To a stirred solution of (S)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene **5** (1 equiv, 3.0 mmol, 1.12 g) in THF (30 mL) was added *n*-BuLi (2.5 M in hexanes, 2.3 equiv, 6.9 mmol, 2.8 mL) at 0 °C. After 30 min, freshly distilled $B(OMe)_3$ (2.8 equiv, 8.4 mmol, 0.92 mL) was added, and the reaction mixture was stirred for 1 h at 0 °C. Aq. NH_4Cl (20 mL) was carefully added at 0 °C and the resulting mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated got the residue **6**. The residue was dissolved in dioxane (30 mL). An aqueous solution of

HCl (12 M, 24 equiv, 72 mmol, 6 mL) was added and the resulting reaction solution was stirred at 60 ºC. Upon completion (monitored by TLC), remove dioxane on a rotary evaporator and the reaction mixture was extracted with EtOAc (3 × 30 mL), dried over $MgSO_4$, filtered, concentrated on a rotary evaporator and dried under high vacuum for 2 h. The residue was dissolved in a minimum amount of CH_2Cl_2 and 50 mL of PE was added. The resulting white solid was filtered and dried under high vacuum for 2 h in a 100 mL round-bottom flask then a magnetic stir bar, 2-bromoanthraquinone **7** (2.5 equiv, 7.5 mmol, 2.1 g), K_2CO_3 (6 equiv, 18 mmol, 2.5 g), and $Pd(PPh_3)_4$ (0.1 equiv, 0.3 mmol, 0.35 g) were added. The flask was purged with argon. A mixture of THF/H_2O (9:1, 84 mL, freshly degassed by bubbling argon for 15 min) was added. The reaction mixture was heated at 75 °C for 12 h. After being cooled to room temperature, water (10 mL) was added and the reaction mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE/EtOAc as eluent (gradient from 15:1 to 5:1) to afford **8** as a yellow solid in 75% yield (1.6 g, 2.3 mmol). $[\alpha]_D^{25}$ -125 (*c* 1.0, CH_2Cl_2); IR (neat) ν (cm^{-1}) 1670, 1620, 1591, 1503, 1457, 1379, 1361, 1327, 1311, 1288, 1263, 1202, 1168, 1146, 1092, 1010, 957, 934, 896, 862, 796, 705, 677; mp 252 ºC. ^1H {^{13}C} NMR (500 MHz, Acetone-d_6) δ 8.72 (d, *J* = 1.8 Hz, 2H), 8.43 – 8.27 (m, 10H), 8.22 (s, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.99 – 7.89 (m, 4H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.35 (ddd, *J* = 8.2, 6.5, 1.3 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H). ^{13}C {^1H} NMR (126 MHz, Acetone-d_6) δ 183.6, 183.3, 152.7, 146.0, 136.3, 135.5, 135.2, 135.1, 134.6, 134.6, 134.2, 133.0, 132.2, 130.9, 130.2, 129.6, 129.0, 128.2, 127.8, 127.7, 127.7, 125.2, 124.7, 114.8. HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ $C_{48}H_{27}O_6$ calcd 699.1808, found 699.1794.



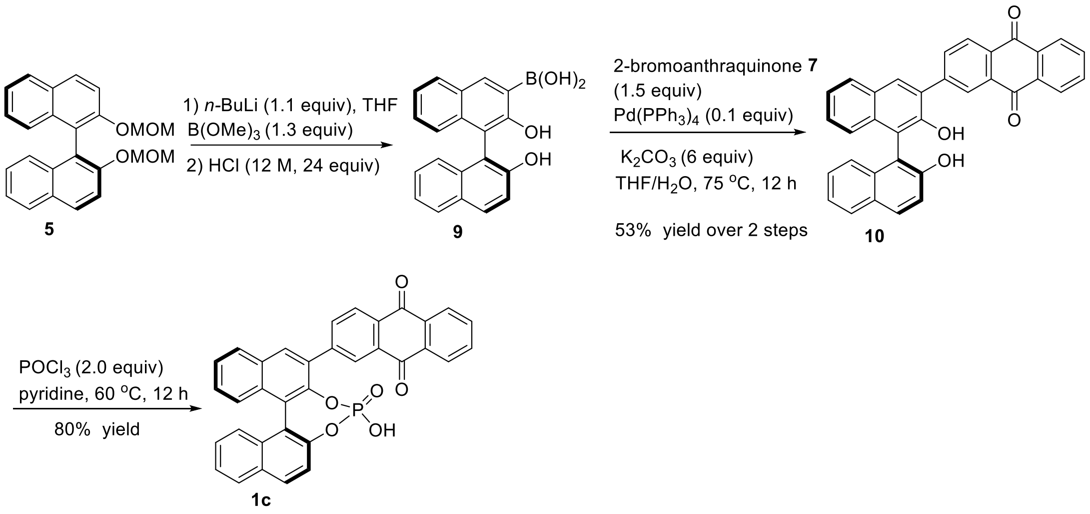
1b

Chemical Formula: $C_{48}H_{25}O_8P$
Molecular Weight: 760,69

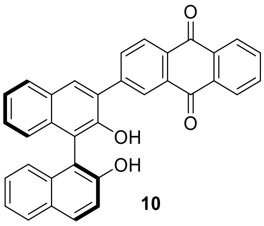
2,2'-((11bR)-4-hydroxy-4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-2,6-diyl)bis(anthracene-9,10-dione) 1b

8 (1 equiv, 0.29 mmol, 0.2 g) was dissolved in pyridine (8 mL). Freshly distilled $POCl_3$ (2.0 equiv, 0.58 mmol, 50 μL) was added and the resulting reaction solution was stirred at 60 ˚C. Upon completion (monitored by TLC), water (3 mL) was added at room temperature and the mixture was reflux for 3 h. An aqueous solution of HCl (6 M, 12 mL) was added and the mixture was further heated at reflux with vigorous stirring for 1 h. The reaction mixture was then extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated. The residue was dissolved in a minimum amount of CH_2Cl_2, and 50 mL of PE was added. Filtration and vacuum drying afford **1b** as a yellow solid in 95% yield (210 mg, 0.28 mmol). $[\alpha]_D^{25}$ -30 (*c* 1.0, CH_2Cl_2); IR (neat) ν (cm^{-1}) 1673, 1592, 1497, 1447, 1404, 1362, 1326, 1311, 1247, 1190, 1152, 1102, 1019, 949, 934, 913, 884, 849, 813, 752, 732, 711, 687, 677; mp 328 ˚C. ^1H {^{13}C} NMR (300 MHz, DMSO-d_6) δ 8.71 – 8.53 (m, 4H), 8.40 – 8.17 (m, 10H), 8.05 – 7.93 (m, 4H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.48 – 7.37 (m, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 4.43 (s, 1H). ^{13}C {^1H} NMR (126 MHz, DMSO-d_6) δ 182.5, 182.3, 146.1, 146.1, 143.7, 136.0, 134.6, 134.5, 133.1, 132.9, 132.3, 132.1, 131.8, 131.1, 130.4, 128.9, 127.9, 127.2, 126.8, 126.7, 126.6, 126.0, 125.5, 122.7. ^{31}P NMR (202 MHz, DMSO-d_6) δ 2.61. HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ $C_{48}H_{26}O_8P$ calcd 761.1365, found 761.1367.

2.3. Preparation of catalyst 1**c**



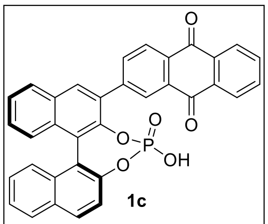
(S)-2-(2,2'-dihydroxy-[1,1'-binaphthalen]-3-yl)anthracene-9,10-dione10



10

Chemical Formula: $C_{34}H_{20}O_4$
Molecular Weight: 492.53

To a stirred solution of (S)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene **5** (1 equiv, 3.0 mmol, 1.12 g) in THF (30 mL) was added *n*-BuLi (2.5 M in hexanes, 1.1 equiv, 3.3 mmol, 1.3 mL) at 0 °C. After the mixture was stirred 30 min at 0 °C, freshly distilled $B(OMe)_3$ (1.3 equiv, 4 mmol, 0.43 mL) was added, and the reaction mixture was stirred 1 h at 0 °C, quenched by NH_4Cl aqueous extracted by CH_2Cl_2 (3 × 20 mL) got the residue. Then the residue was dissolved in dioxane (30 mL), HCl (6M, 5 mL) was added, and the reaction mixture was stirred at 60 °C. Upon completion (monitored by TLC), remove dioxane on a rotary evaporator and the reaction mixture was extracted with EtOAc (3 × 30 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was dissolved in mini amount of CH_2Cl_2 again and then add this solution to 50 mL PE got white solid **9**. After 2 h vacuum this solid was placed in a 100 mL round-bottom flask a magnetic stir bar, 2-bromoanthraquinone **7** (1.5 equiv, 4.5 mmol, 1.3 g), K_2CO_3 (6 equiv, 18 mmol, 2.5 g), and $Pd(PPh_3)_4$ (0.1 equiv, 0.3 mmol, 0.35 g) were added. The flask was purged with argon. A mixture of THF/H_2O (9:1, 84 mL, freshly degassed by bubbling argon for 15 min) was added. The reaction mixture was heat at 75 °C for 12 h. After being cooled to room temperature, the reaction mixture was extracted by CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE/EtOAc as eluent (gradient from 15:1 to 5:1) to afford **10** in 53% yield (784 mg, 1.6 mmol). $[\alpha]_D^{25}$ -156 (c 1.0, CH_2Cl_2); IR (neat) ν (cm^{-1})1670, 1620, 1590, 1503, 1466, 1449, 1381, 1361, 1326, 1287, 1263, 1237, 1212, 1203, 1176, 1146, 1127, 1104, 1067, 1013, 967, 954, 932, 895, 854, 816, 796, 734, 710, 684, 671, 665; mp 173 °C. ^1H {^{13}C} NMR (500 MHz, Acetone-*d*$_6$) δ 8.74 – 8.65 (m, 1H), 8.38 – 8.24 (m, 4H), 8.16 (s, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.92 (dt, *J* = 12.6, 8.6 Hz, 4H), 7.42 – 7.23 (m, 5H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H). ^{13}C {^1H} NMR (126 MHz, Acetone-*d*$_6$) δ 183.6, 183.2, 155.4, 151.8, 146.7, 136.3, 135.6, 135.4, 135.1, 135.1, 134.6, 134.2, 132.9, 131.5, 131.3, 130.5, 130.1, 130.0, 129.5, 129.4, 129.0, 129.0, 127.8, 127.7, 127.7, 127.6, 127.5, 125.4, 125.2, 124.4, 123.9, 119.8, 116.3, 113.5. HRMS (ESI/Q-TOF) *m/z* [M + H]$^+$ $C_{34}H_{21}O_4$ calcd 493.1440, found 493.1461.

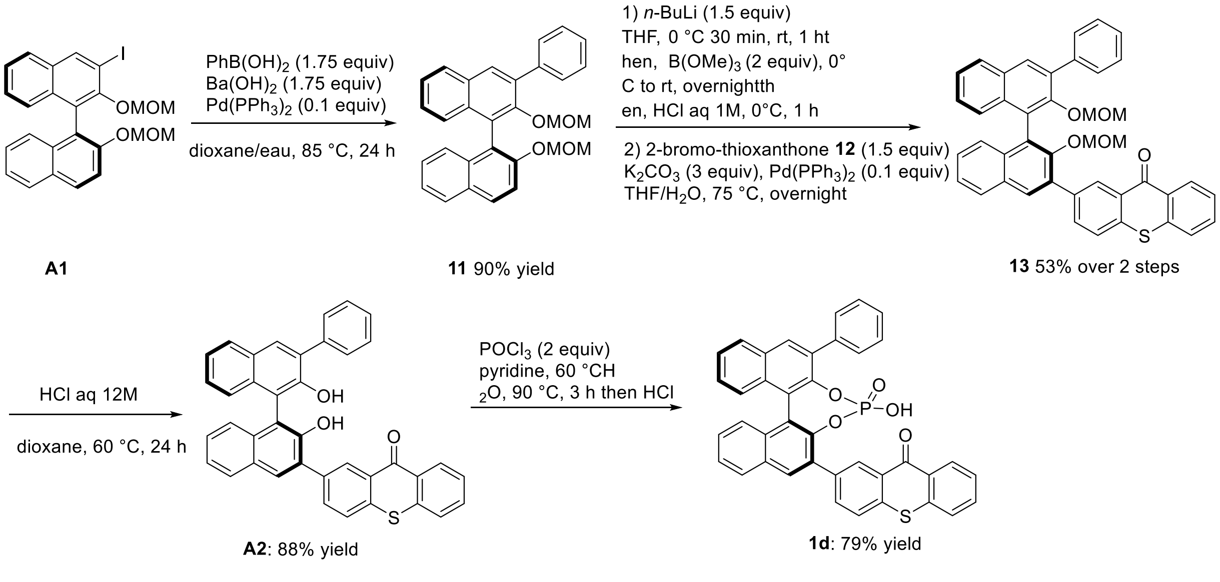


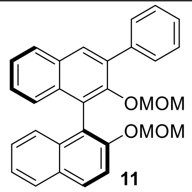
Chemical Formula: $C_{34}H_{19}O_6P$
Molecular Weight: 554.49

2-((11cS)-4-hydroxy-4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-2-yl)anthracene-9,10-dione 1c

To a 25 mL dry high presure flask add 2-(2,2'-dihydroxy-[1,1'-binaphthalen]-3-yl)anthracene-9,10-dio-ne **10** (1 equiv, 0.2 mmol, 0.1 g), pyridine (5 mL), $POCl_3$ (2.0 equiv, 0.4 mmol, 0.04 mL). The mixture stirred 12 h at 60 ºC. The mixture was cooled to the room temperature, water (3 mL) was added and refleux 3 h. Add 6N HCl (10 mL) at 0 ºC and stir 30 min at room temperature, extraction by CH_2Cl_2 (3 × 50 mL) the organic phases were dried over Na_2SO_4 and concentrated under vacum, the residue was dissolved in mini amount of CH_2Cl_2 again and then add this solution to 50 mL PE then after filtration got **1c** as yellow solid in 80% yield (89 mg, 0.16 mmol). $[\alpha]_D^{25}$ -139 (c 1.0, CH_2Cl_2); IR (neat) ν (cm^{-1}) 1674, 1593, 1510, 1499, 1478, 1461, 1438, 1421, 1402, 1361, 1325, 1307, 1284, 1264, 1247, 1216, 1194, 1175, 1151, 1093, 1073, 1013, 977, 949, 932, 894, 862, 852, 817, 795, 703; mp 278 ºC. ^1H {^{13}C} NMR (500 MHz, DMSO-d_6) δ 8.59 – 8.55 (m, 1H), 8.50 (dd, *J* = 8.2, 1.9 Hz, 1H), 8.37 (s, 1H), 8.33 (d, *J* = 8.1 Hz, 1H), 8.27 (p, *J* = 5.3 Hz, 2H), 8.18 (dd, *J* = 19.8, 8.5 Hz, 2H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.97 (p, *J* = 5.9 Hz, 2H), 7.64 – 7.48 (m, 3H), 7.39 (dt, *J* = 13.9, 7.6 Hz, 2H), 7.25 (dd, *J* = 19.9, 8.7 Hz, 2H). ^{13}C {^1H} NMR (126 MHz, DMSO-d_6) δ 182.5, 182.3, 148.2, 148.1, 145.3, 145.2, 143.4, 135.9, 134.6, 134.6, 133.1, 132.9, 132.1, 131.9, 131.9, 131.2, 130.9, 130.6, 129.0, 128.6, 127.9, 127.3, 126.8, 126.8, 126.7, 126.1, 126.0, 125.8, 125.3, 122.5, 121.5, 121.2. ^{31}P NMR (202 MHz, DMSO-d_6) δ 2.34. HRMS (ESI/Q-TOF) *m/z* [M + H]$^+$ $C_{34}H_{20}O_6P$ calcd 555.0998, found 555.0991.

2.4. Preparation of catalyst 1**d**



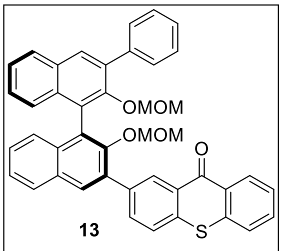


11

Chemical Formula: $C_{30}H_{26}O_4$
Molecular Weight: 450,53

(S)-2,2'-bis(methoxymethoxy)-3-phenyl-1,1'-binaphthalene 11.

In a 100 mL round-bottom flask equipped with a stir bar were placed **A1** (1 equiv, 2.73 mmol, 1.36 g), $PhB(OH)_2$ (1.75 equiv, 4.77 mmol, 589 mg), $Ba(OH)_2.8H_2O$ (1.75 equiv, 4.77 mmol, 1.506 g), and $Pd(PPh_3)_4$ (0.1 equiv, 0.27 mmol, 0.315 g) under argon. A mixture of dioxane/H_2O (3:1, 21 mL, freshly degassed by bubbling argon for 15 min) was added and the flask was equipped with a reflux condenser. The resulting mixture was stirred at 85 °C for 24 h under an argon atmosphere. Water (20 mL) was added at room temperature and the aqueous layer was extracted with CH_2Cl_2 (3 x 40 mL). The combined organic phases were washed with aq HCl 1M (2 x 50 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE/EtOAc as eluent (gradient from 10:0 to 9:1) to afford **11** as a white solid in 90% yield (2.47 mmol, 1.111 g): $[\alpha]_D^{20}$ -88.53 (*c* 0.340, $CHCl_3$); IR (neat) *ν* (cm^{-1}) 1698, 1612, 1310, 1293, 1185; mp 149-151 °C; ^1H {^{13}C} NMR (500 MHz, CDCl3) δ 8.01 – 7.95 (m, 2H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.48 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.43 (ddd, *J* = 8.1, 5.5, 2.3 Hz, 1H), 7.39 (ddd, *J* = 8.2, 6.0, 2.1 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.30 – 7.23 (m, 2H), 5.21 (d, *J* = 6.9 Hz, 1H), 5.11 (d, *J* = 6.9 Hz, 1H), 4.39 (d, *J* = 5.8 Hz, 1H), 4.34 (d, *J* = 5.8 Hz, 1H), 3.26 (s, 3H), 2.33 (s, 3H); ^{13}C {^1H } NMR (126 MHz, CDCl3) δ 153.1, 151.2, 139.3, 135.8, 134.3, 133.5, 131.1, 130.4, 129.9, 129.8, 129.8, 128.4, 128.1, 127.9, 127.3, 126.7, 126.4, 126.3, 126.1, 126.0, 125.3, 124.3, 121.4, 117.0, 98.8, 95.3, 56.1; HRMS (ESI/Q-TOF) m/z $[M + Na]^+$ calcd for $C_{30}H_{26}O_4Na$ 473.1729, found 473.1732.



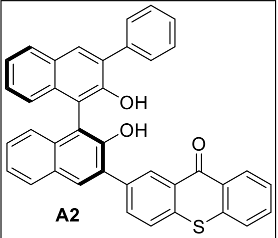
13

Chemical Formula: $C_{43}H_{32}O_5S$
Molecular Weight: 660,78

(*S*)-2-(2,2'-bis(methoxymethoxy)-3'-phenyl-[1,1'-binaphthalen]-3-yl)-9H-thioxanthen-9-one 13

To a stirred suspension of **11** (1 equiv, 1.69 mmol, 762 mg) in distilled THF (28 mL) was added dropwise *n*-BuLi (2.3 M in hexanes, 1.5 equiv, 2.54 mmol, 1.1 mL) at 0 °C. The resulting mixture was stirred at 0°C for 30 min and at room temperature for 1 h. Then freshly distilled $B(OMe)_3$ (2 equiv, 3.38 mmol, 0.380 mL) was slowly added at 0 °C. The resulting mixture was stirred at 0 °C for 10 min and then at room temperature overnight. Aq HCl (1M, 10 mL) was added at 0 °C and the resulting mixture was further stirred at 0 °C for 1 h. The aqueous phase was extracted with EtOAc (3 × 30 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure and dried under high vacuum. Then a magnetic stir bar, 2-bromoanthraquinone **12** (1.5 equiv, 2.5 mmol, 723 mg), K_2CO_3 (3 equiv, 5 mmol, 692 mg), and $Pd(PPh_3)_4$ (0.1 equiv, 0.17 mmol, 193 mg) were added to the residue. The flask was backfilled with argon. Then a degassed mixture of THF/H_2O (9:1, 11 mL) was added and the flask was equipped with a reflux condenser. The resulting mixture was stirred at 75 °C overnight under an argon atmosphere. Water (10 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using

PE/EtOAc as eluent (gradient from 10:0 to 7:3) to afford **13** as a yellow solid in 53% yield over 2 steps (0.895 mmol, 591 mg) : $[\alpha]_D^{20}$ +94.44 (*c* 0.293, $CHCl_3$); IR (neat) *v* (cm^{-1}) 1670, 1590, 1323, 1281, 1237, 1147, 1005; mp 146-148 °C; ^1H {^{13}C} NMR (500 MHz, $CDCl_3$) δ 8.95 (d, *J* = 2.1 Hz, 1H), 8.62 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.10 (dd, *J* = 8.4, 2.1 Hz, 1H), 8.04 (s, 1H), 7.91 (s, 1H), 7.86 (dd, *J* = 16.1, 8.2 Hz, 2H), 7.75 – 7.68 (m, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.48 – 7.34 (m, 5H), 7.34 – 7.28 (m, 1H), 7.28 – 7.20 (m, 4H), 4.38 (dd, *J* = 12.5, 5.8 Hz, 2H), 4.33 (d, *J* = 5.7 Hz, 2H), 2.37 (s, 3H), 2.29 (s, 3H); ^{13}C {^1H } NMR (126 MHz, $CDCl_3$) δ 180.1, 151.6, 151.2, 139.1, 137.7, 137.3, 136.4, 135.6, 134.3, 134.1, 134.0, 133.7, 132.5, 131.1, 131.0, 130.6, 130.3, 130.1, 129.7, 129.5, 129.4, 128.5, 128.2, 128.1, 127.5, 126.9, 126.8, 126.6, 126.5, 126.5, 126.4, 126.2, 126.0, 125.7, 125.6, 125.4, 99.0, 98.8, 98.7, 56.2, 56.0, 29.8; HRMS (ESI/Q-TOF) m/z $[M + Na]^+$ calcd for $C_{43}H_{32}O_5SNa$ 683.1868, found 683.1849.

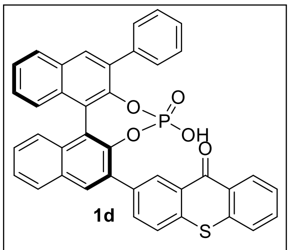


A2

Chemical Formula: $C_{39}H_{24}O_3S$
Molecular Weight: 572,68

(S)-2-(2,2'-dihydroxy-3'-phenyl-[1,1'-binaphthalen]-3-yl)-9H-thioxanthen-9-one A2.

To a stirred solution of **13** (1 equiv, 0.486 mmol, 321 mg) in dioxane (9.5 mL) was added aq HCl (12M, 24 equiv, 11.7 mmol, 1 mL). The resulting suspension was stirred at 60 °C overnight. Water (10 mL) was added at room temperature and the aqueous phase was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic phases were washed with aq $NaHCO_3$ (40mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE/EtOAc as eluent (gradient from 9:1 to 7:3) to afford **A2** as a yellow solid in 88% yield (0.428 mmol, 245 mg) : $[\alpha]_D^{20}$ -12.43 (*c* 0.233, $CHCl_3$); IR (neat) *v* (cm^{-1}) 2919, 2850, 1628, 1588, 1427, 1234, 1122; mp 180-182 °C; ^1H{^{13}C} NMR (300 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.65 (d, *J* = 8.6 Hz, 1H), 8.15 (s, 1H), 8.09 (dd, *J* = 8.4, 2.1 Hz, 1H), 8.03 (s, 1H), 8.00 – 7.88 (m, 2H), 7.76 – 7.59 (m, 5H), 7.49 (d, *J* = 7.8 Hz, 3H), 7.38 (d, *J* = 22.0 Hz, 5H), 7.22 – 7.26 (m, 2H), 5.44 (s, 1H), 5.40 (s, 1H); ^{13}C {^1H } NMR 179.8, 150.5, 150.4, 137.5, 137.3, 136.4, 136.4, 133.8, 133.4, 133.3, 132.3, 131.7, 131.5, 130.8, 130.2, 129.7, 129.6, 129.5, 129.3, 129.2, 129.1, 128.7, 128.6, 128.5, 127.8, 127.6, 127.5, 126.4, 126.1, 125.9, 124.5, 124.4, 124.4, 112.9, 112.3; HRMS (ESI/Q-TOF) m/z $[M + H]^+$ calcd for $C_{39}H_{25}O_3S$ 573.1524, found 573.1522.



1d

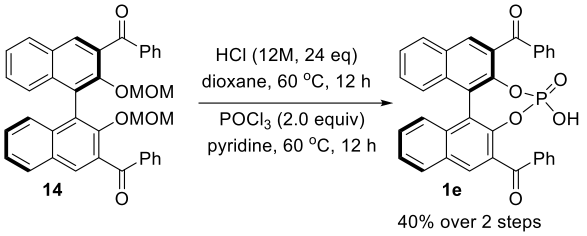
Chemical Formula: $C_{39}H_{23}O_5PS$
Molecular Weight: 634,64

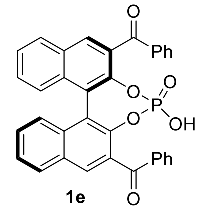
2-((11bS)-4-hydroxy-4-oxido-6-phenyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-2-yl)-9H-thioxanthen-9-one 1d

To a stirred solution of **A2** (1 equiv, 0.422 mmol, 242 mg) in pyridine (10 mL) was added freshly distilled $POCl_3$ (2 equiv, 0.844 mmol, 0.07 mL) was added and the resulting mixture was stirred at 60 °C. Upon completion (12 h, monitored by TLC), water (10 mL) was added at room temperature and the mixture was reflux for 3 h. An aqueous solution of HCl (6 M, 20 mL) was added and the mixture was further heated at reflux with vigorous stirring for 1 h. The reaction mixture was then extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using CH_2Cl_2 /MeOH as eluent (gradient from

98:2 to 95:5) to afford **1d** as a yellow solid in 79% (0.333 mmol, 211 mg). $[\alpha]_D^{25}$ 244 (*c* 1.0, CH_2Cl_2); IR (neat) ν (cm^{-1}) 1635, 1591, 1498, 1478, 1461, 1439, 1414, 1391, 1362, 1319, 1284, 1264, 1244, 1208, 1184, 1151, 1127, 1071, 1012, 979, 959, 948; mp 266-268 °C; ^1H {^{13}C} NMR (300 MHz, DMSO-d_6) δ 8.78 (s, 1H), 8.51 (d, *J* = 7.6 Hz, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.34 (s, 1H), 8.24 – 8.07 (m, 3H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 3H), 7.80 (t, *J* = 7.0 Hz, 1H), 7.48 (dddd, *J* = 43.8, 19.8, 14.9, 7.1 Hz, 8H), 7.20 (t, *J* = 9.0 Hz, 2H), 4.45 (br s, 1H); ^{13}C {^1H} NMR (75 MHz, DMSO-d_6) δ 178.8, 145.8, 145.6, 145.5, 137.3, 136.5, 135.9, 135.8, 134.6, 133.8, 133.0, 132.4, 131.8, 131.5, 131.0, 130.7, 130.6, 129.9, 129.9, 129.1, 128.8, 128.6, 128.3, 128.0, 127.4, 126.9, 126.9, 126.6, 126.3, 126.0, 125.6, 125.5, 122.6, 122.2. ^{31}P NMR (122 MHz, DMSO-d_6) δ 1.46. HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ calcd for $C_{39}H_{24}O_5PS$ 635.1082, found 635.1079.

2.5. Preparation of catalyst 1**e**





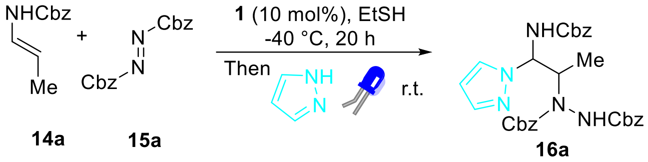
1e

Chemical Formula: $C_{34}H_{21}O_6P$
Molecular Weight: 556.51

((11bR)-4-hydroxy-4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-2,6-diyl)bis(phenylmethanone) 1e

(***R***)-(2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-diyl)-bis(phenyl-methanone) **14**[1] (1 equiv, 2 mmol, 1.2 g) was dissolved in dioxane (40 mL). An aqueous solution of HCl (12 M, 24 equiv, 48 mmol, 4 mL), The mixture was heated under 60 °C. Upon completion (12 h, monitored by TLC), water (5 mL) was added at room temperature and the mixture was extracted with CH_2Cl_2 (3x10 mL), dried over $MgSO_4$, filtered, concentrated on a rotary evaporator and dried under high vacuum for 2 h. The residue was dissolved in pyridine (12 mL). Freshly distilled $POCl_3$ (2.0 equiv, 4 mmol, 0.36 mL) was added and the the resulting reaction solution was stirred at 60 °C. Upon completion (12 h, monitored by TLC), water (20 mL) was added at room temperature and the mixture was reflux for 3 h. An aqueous solution of HCl (6 M, 6 mL) was added and the mixture was further heated at reflux with vigorous stirring for 1 h. The reaction mixture was then extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with aq. HCl (2 M, 50 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (DCM/MeOH= 20:1-10:1). The obtained compound was dissolved in CH_2Cl_2 (30 mL) and vigorously washed with aq HCl (2 M, 3 × 20 mL), filtered and concentrated to afford **1e** as a yellow solid in 40% yield over two steps (445 mg, 0.8 mmol). $[\alpha]_D^{25}$ -256 (*c* 1.0, CH_2Cl_2); IR (neat) ν (cm^{-1}) 1660, 1631, 1595, 1578, 1499, 1449, 1432, 1360, 1318, 1279, 1261, 1216, 1178, 1149, 1091, 1037, 1021, 968, 942, 903, 847, 823, 801, 774, 734, 678; mp 190 $^{)}$C. ^1H {^{13}C} NMR (300 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.19 – 7.75 (m, 8H), 7.47 (d, *J* = 35.3 Hz, 12H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$) δ 194.5, 144.6, 144.5, 136.8, 133.8, 133.3, 132.6, 131.0, 130.7, 130.2, 129.8, 129.4, 128.4, 128.3, 127.0, 126.7, 122.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 3.11. HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ $C_{34}H_{22}O_6P$ calcd 557.1154, found 557.1130.

3. General procedure for the enantioselective synthesis of azoles substituted vicinal diamines



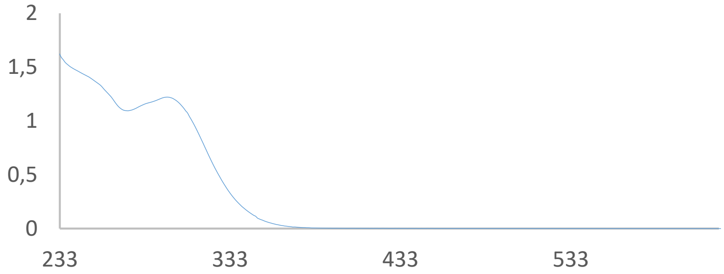
Under argon, the E-enecarbamate **14a** (0.1 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (0.4 mL) in a flame-dried flask containing activated powdered 3Å molecular sieves (20 mg). The solution was stirred at room temperature for 10 min before being cooled to −40 °C and stirred for additional 10 min. Dibenzyl azodicarboxylate **15a** (44.7 mg, 0.15 mmol, 1.5 equiv) dissolved in CH_2Cl_2 (0.3 mL) was added and the reaction mixture was stirred for 10 min. Then EtSH (7 µL, 0.1 mmol, 1 equiv) and finally the chiral photocatalyst **1** (0.01 mmol, 0.1 equiv) were added as a solution in CH_2Cl_2 (0.3 mL) and the reaction mixture was stirred for 16 h at −40 °C. Then, the 1H-pyrazole was added (0.3 mmol, 3 equiv) and the reaction was stirred at room temperature under an O_2 atmosphere and blue light irradiation for 16 h. Completion of the reaction was checked by TLC. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (PE/EtOAc 8:3).

4. UV-Vis Absorption and Fluorescence for compounds 1a to 1e

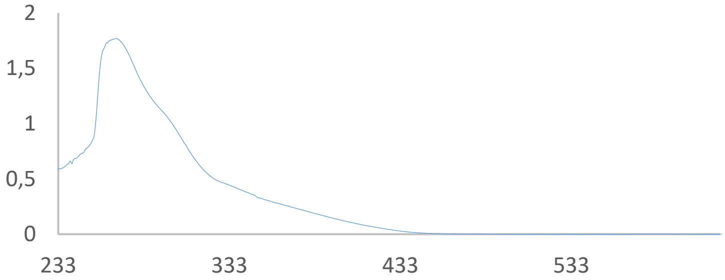
Spectroscopic measurements: UV-visible absorption spectra were recorded on a Cary 100 spectrophotometer spectrophotometer in 1 cm optical length quartz cuvettes. Corrected emission spectra were obtained on a Jobin-Yvon Horiba Spex FluoroMax-3 spectrofluorometer. Dichloromethane, Dimethylformamide (Aldrich, spectrometric grade or SDS, spectrometric grade) were employed as solvents for absorption and fluorescence measurements. The fluorescence quantum yields were determined by using quinine sulfate in H_2SO_4 0.5N as a standard (Φ_F=0.544). The estimated experimental error is less than 10%. For the emission measurements, a right-angle configuration was used and the absorbance at the excitation wavelength are kept below 0.1 in order to avoid reabsorption artefacts.

Figure S1 Uv-vis absorption spectra of Pcat **1a 1c 1d** and **1e** in CH_2Cl_2 and **1b** in DMSO

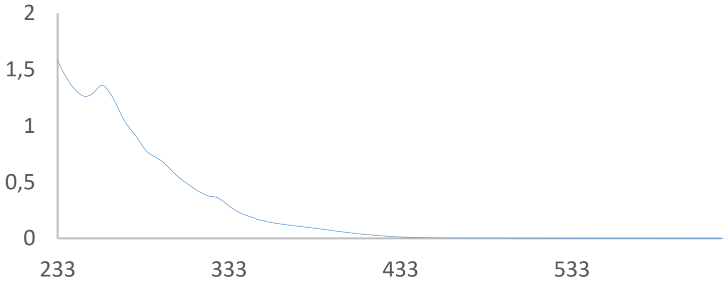
Uv-vis absorption spectra of **1a**



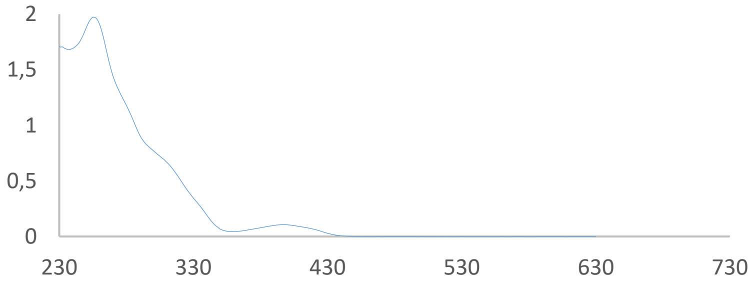
Uv-vis absorption spectra of **1b**



Uv-vis absorption spectra of **1c**



Uv-vis absorption spectra of **1d**



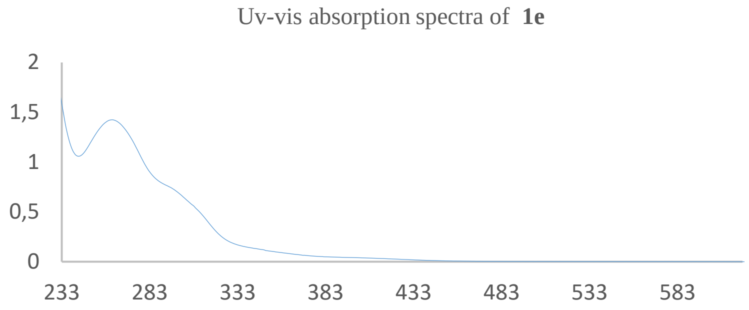
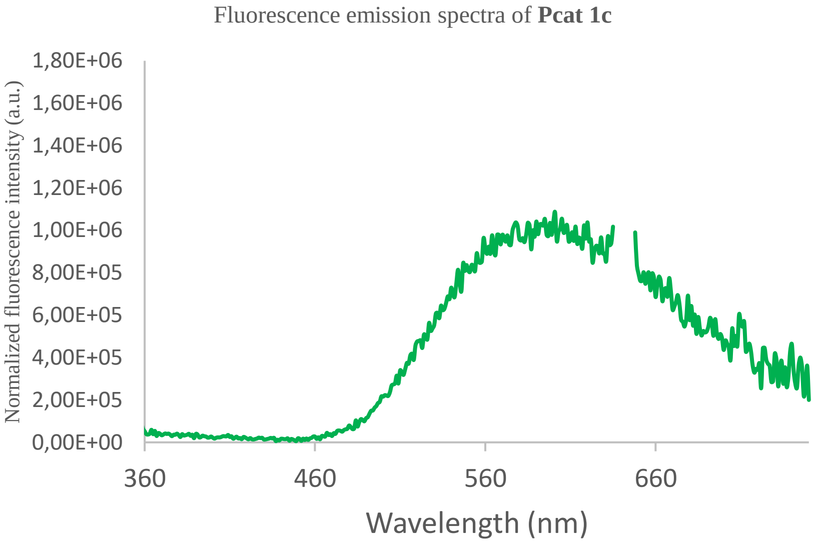
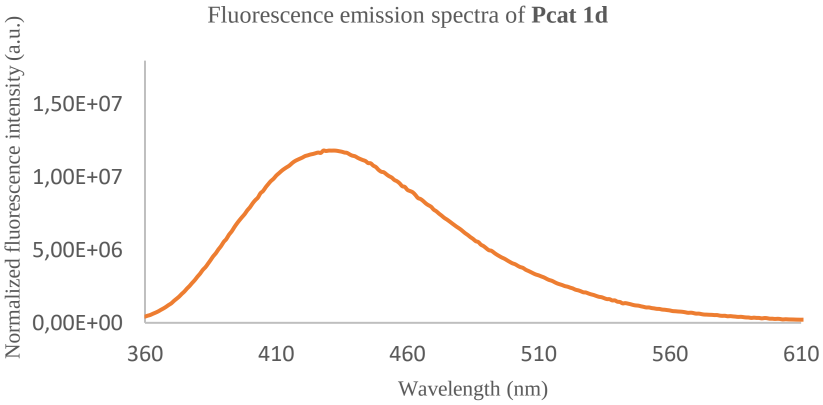


Figure S2 Fluorescence emission spectra of **Pcat 1c** and **1d** in CH_2Cl_2

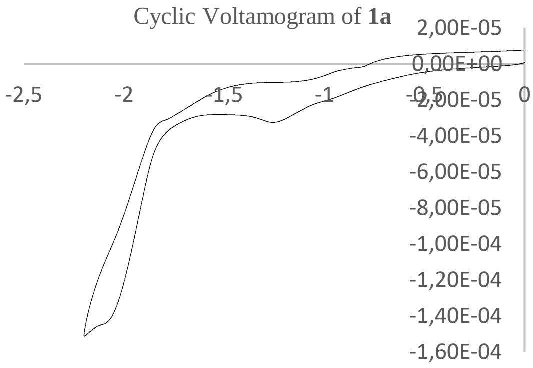


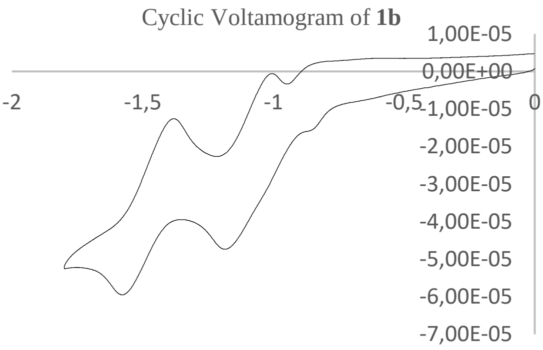


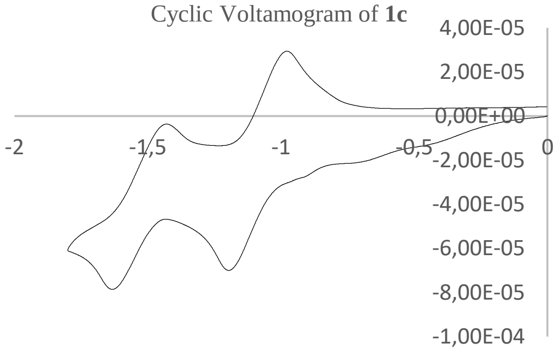
5. Electrochemical data for compounds 1a to 1e

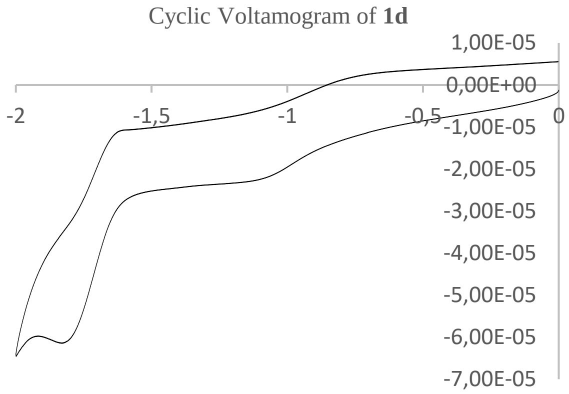
Cyclic voltammetry of photocatalysts (V vs. Ag+/AgCl), in dichloromethane (with 0.1 M Bu_4NPF_6 as electrolyte) on glassy carbon electrode Concentrations are about 2×10^{-3} mmol /mL. Scan rate: 100 mV s-1 Reductions were measured by scanning potentials in the negative direction and oxidations in the positive direction

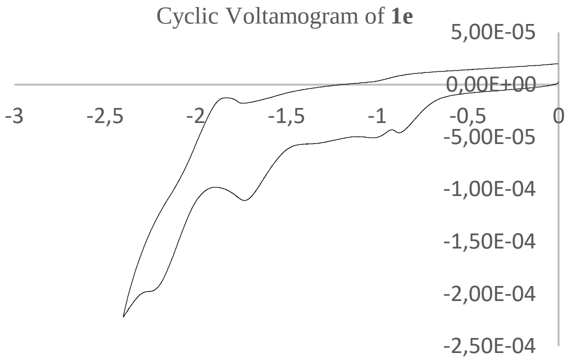
Figure S3 Fluorescence emission spectra of **Photocatalysts 1a to 1e** in CH_2Cl_2











6. Reference

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2. Minabe, M., Mochizuki, H., Yoshida, M., Toda, T., *Bull, Chem, Soc, Jpn*, **1989**, *62*, 68-72.

3. Shin, N. Y.; Ryss, J. M.; Zhang, X.; Miller, S.J.; Knowles, R. R. *Science*, **2019**, *366*, 364–369.

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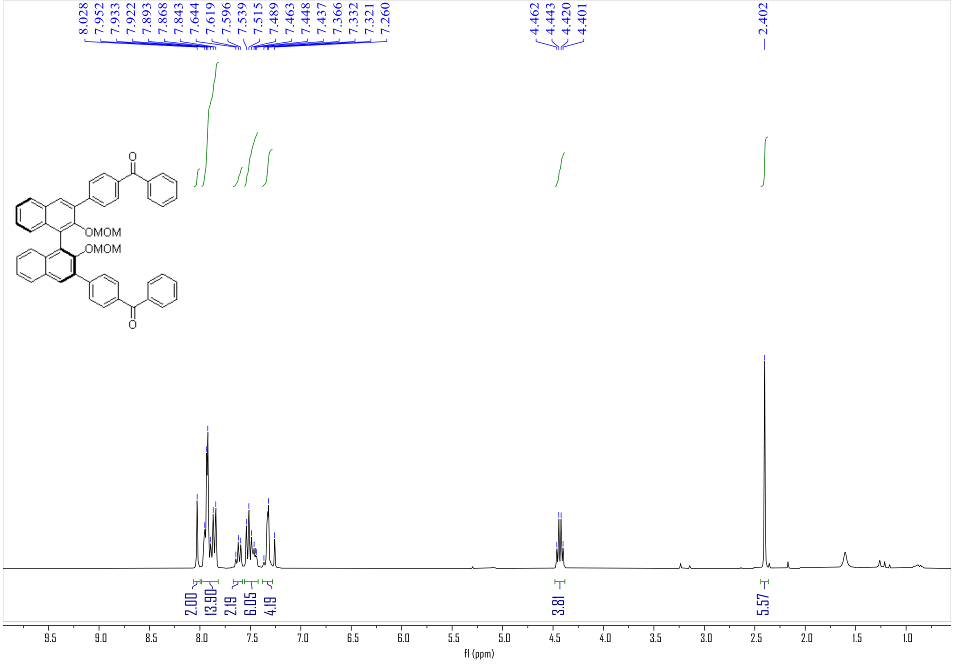
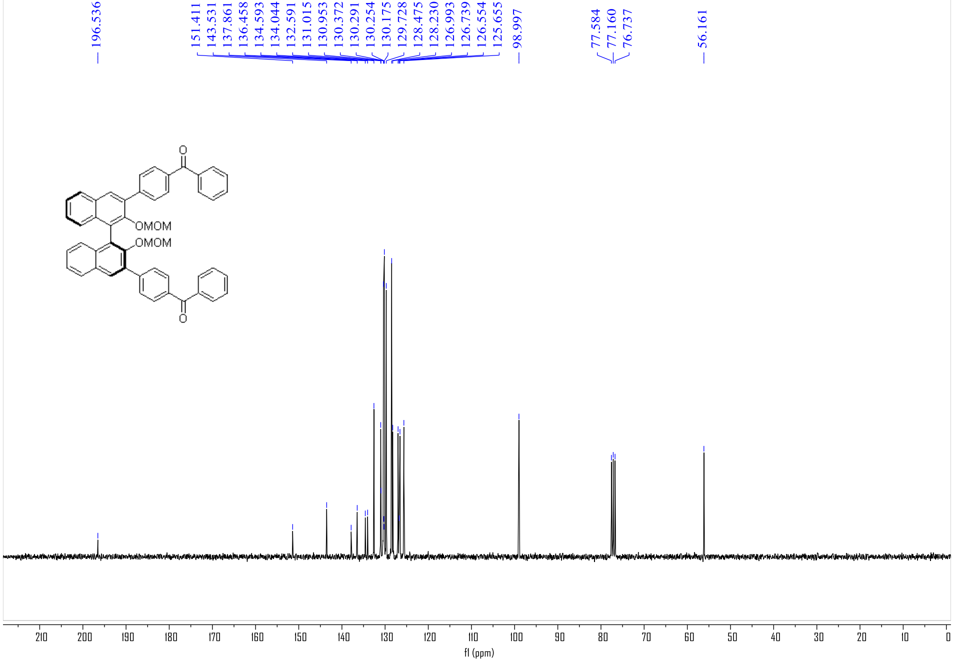
7. Copies of the spectra of compounds 4-1e

(*S*)-((2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-diyl)bis(4,1-phenylene))bis(phenylmethanone) 4

^{1}H NMR (300 MHz, CDCl$_3$)

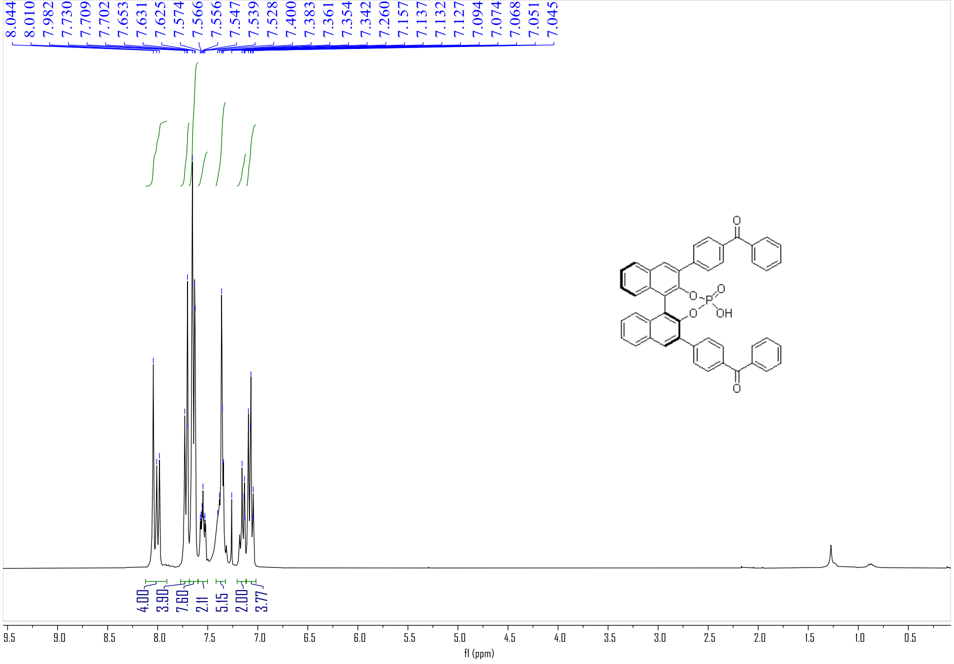


^{13}C {NMR (75 MHz, CDCl$_3$)

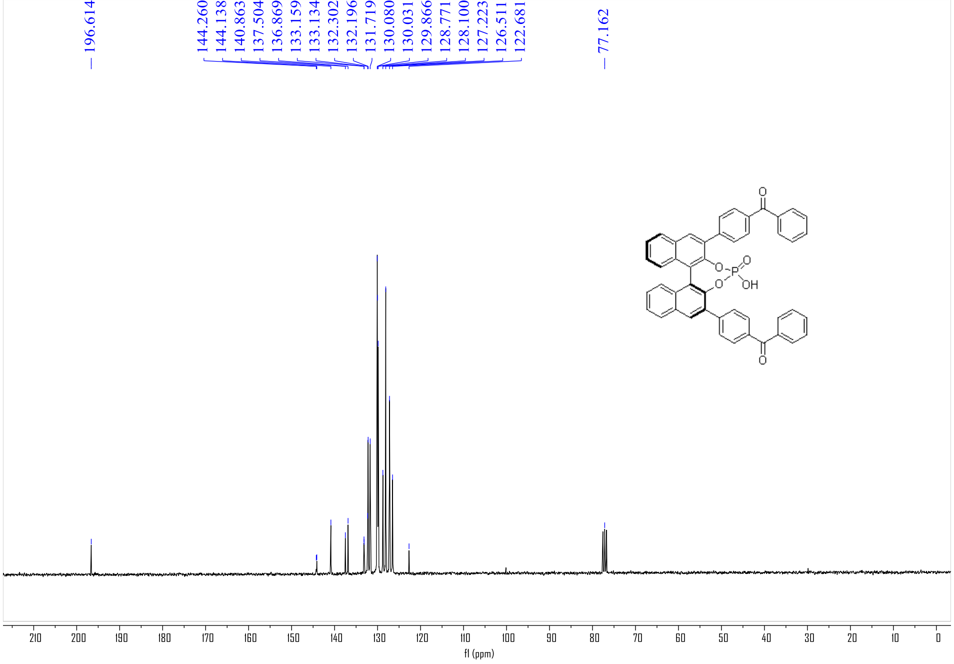


(((11bS)-4-hydroxy-4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-2,6-diyl)bis(4,1-phenylene))bis(phenylmethanone) 1a

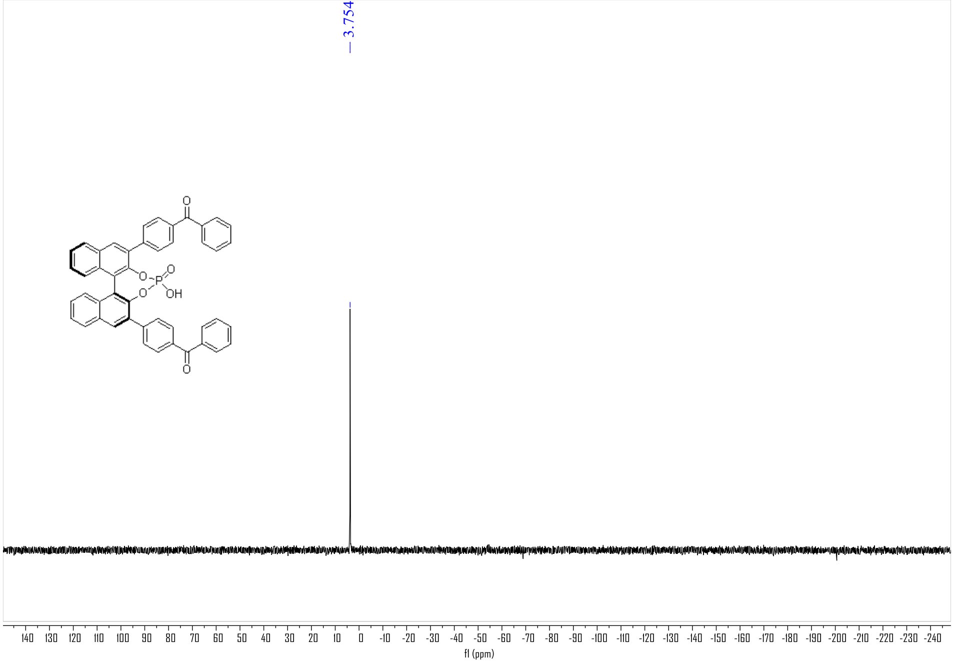
^{1}H NMR (300 MHz, CDCl$_3$)



^{13}C NMR (75 MHz, CDCl$_3$)

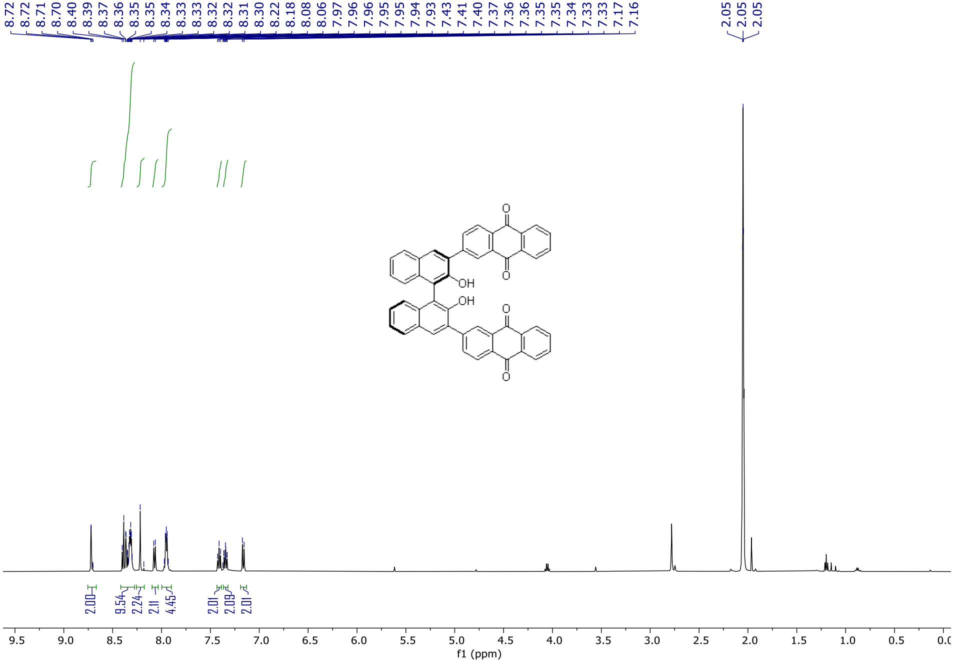


^{31}P NMR (202 MHz, $CDCl_3$)

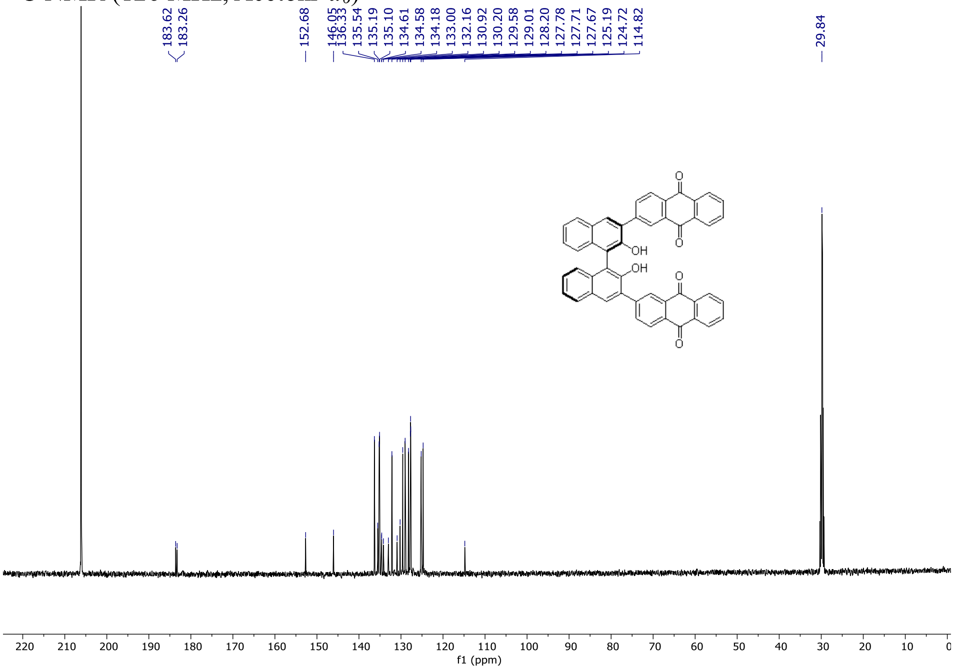


(R)-2,2'-(2,2'-dihydroxy-[1,1'-binaphthalene]-3,3'-diyl)bis(anthracene-9,10-dione 8

^{1}H NMR (500 MHz, Acetone-d_6)

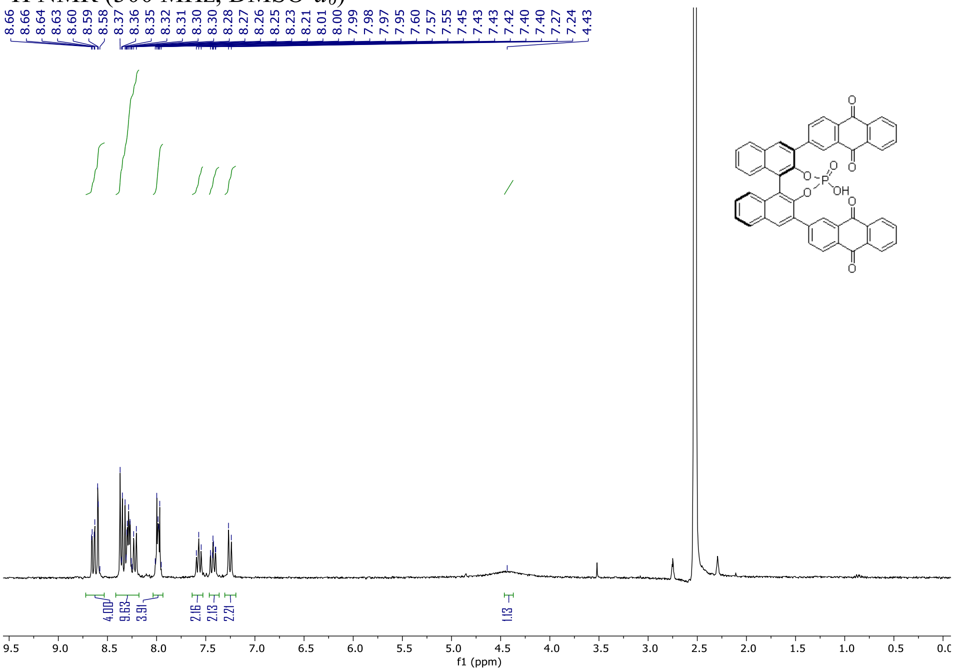


^{13}C NMR (126 MHz, Acetonr-*d₆*)

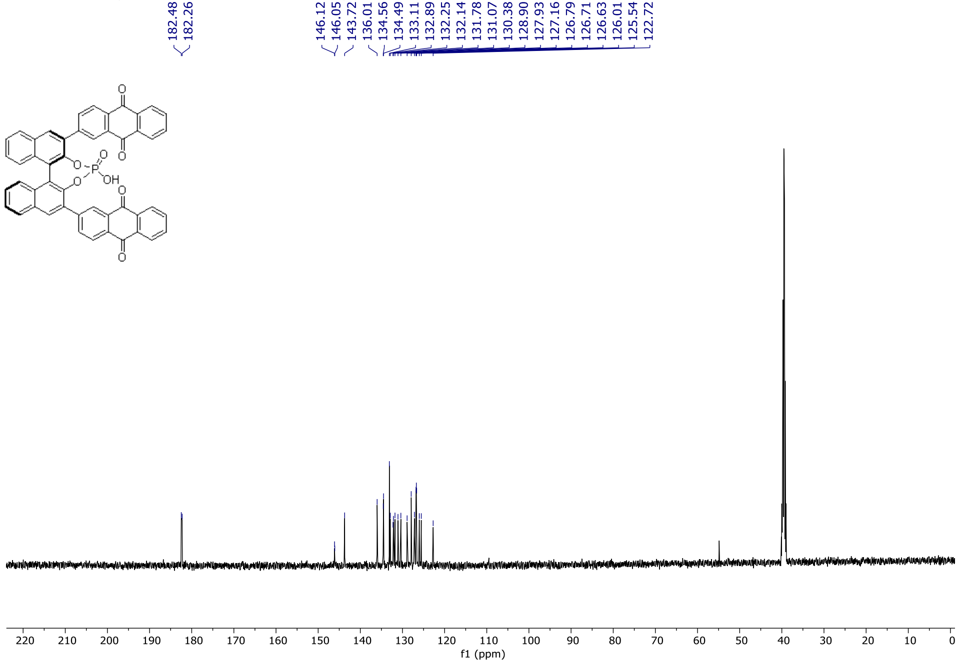


2,2'-((11bR)-4-hydroxy-4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-2,6-diyl)bis(anthracene-9,10-dione 1b

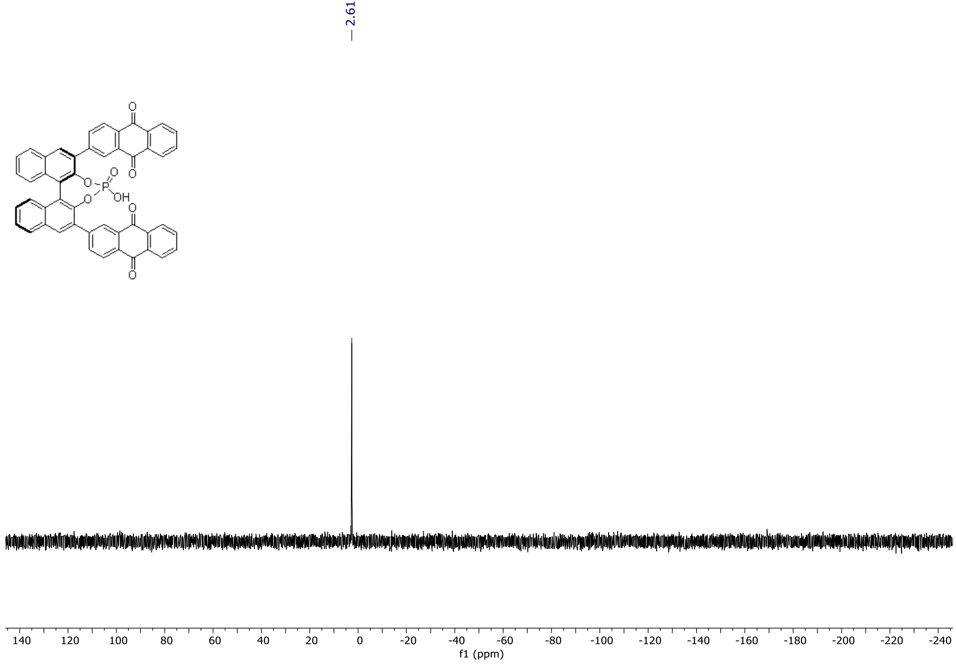
^{1}H NMR (300 MHz, DMSO-*d₆*)



^{13}C NMR (126 MHz, DMSO-d_6)

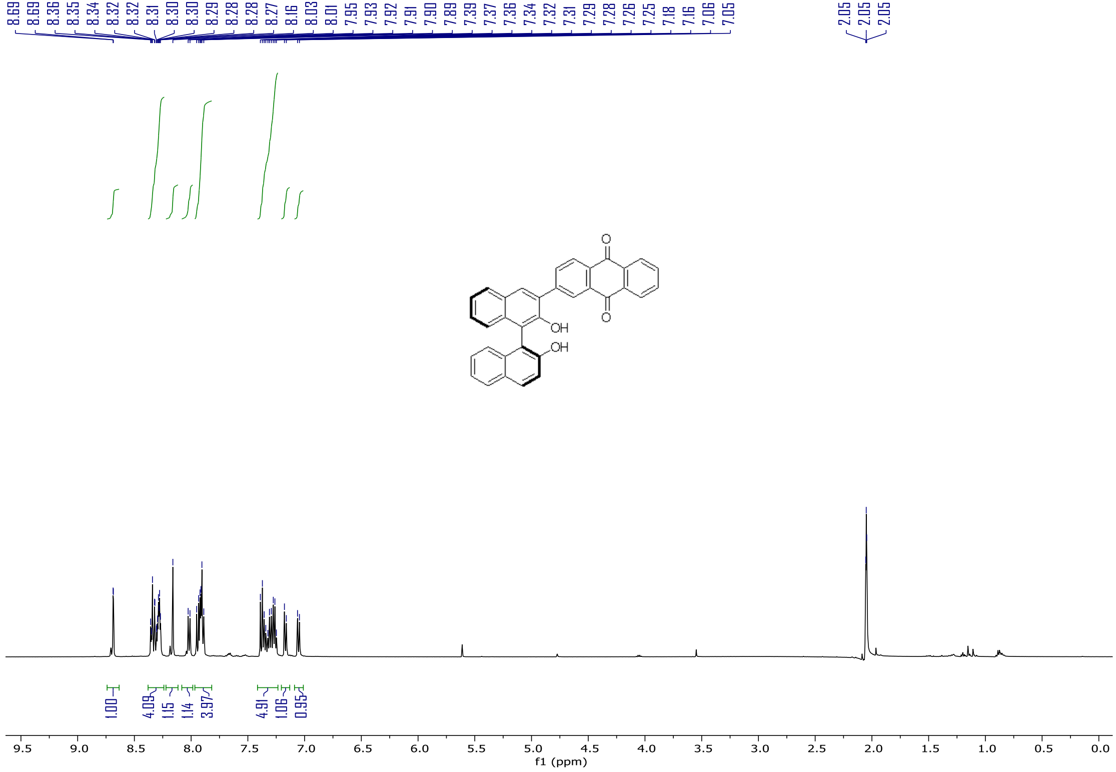


^{31}P NMR (202 MHz, DMSO-d_6)

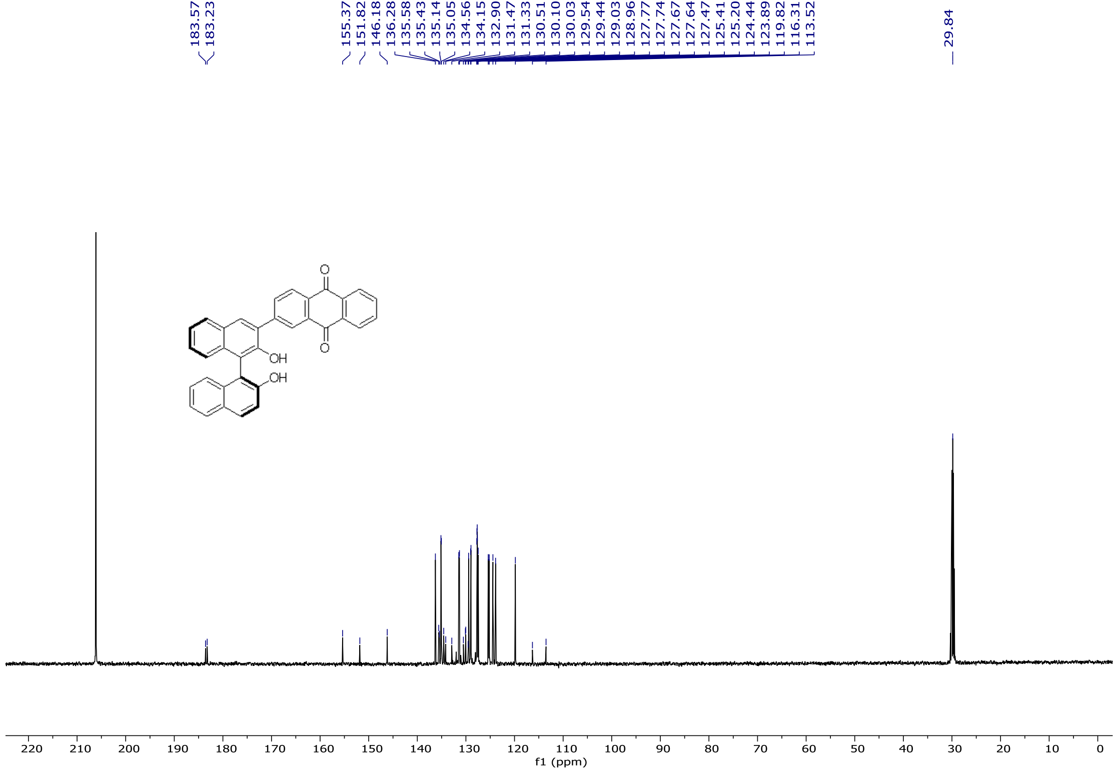


(S)-2-(2,2'-dihydroxy-[1,1'-binaphthalen]-3-yl)anthracene-9,10-dione 10

^{1}H NMR (500 MHz, Acetone-d_6)

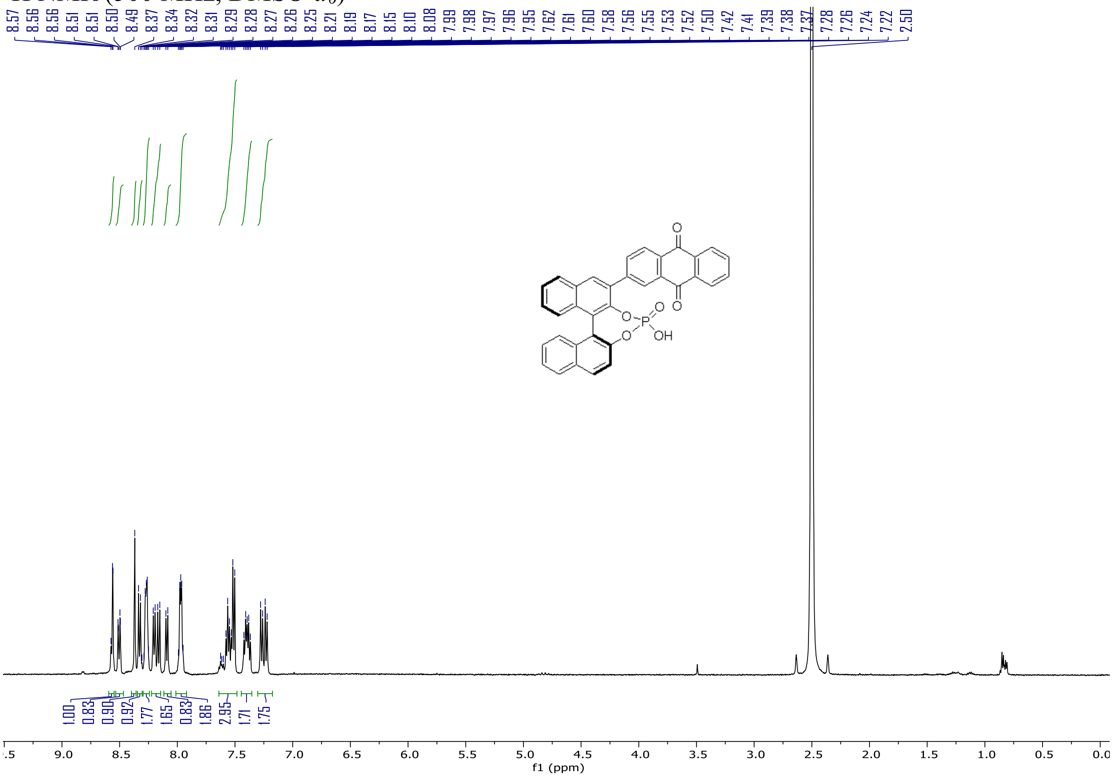


^{13}C NMR (126 MHz, Acetone-d_6)

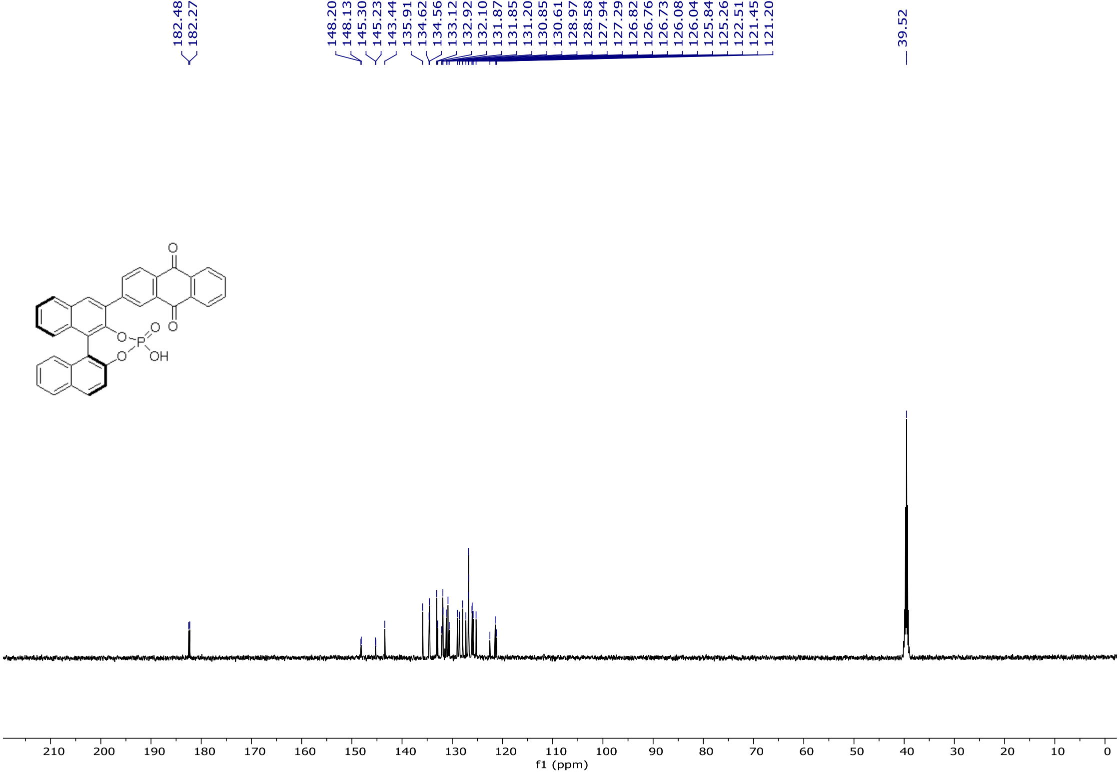


2-((11cS)-4-hydroxy-4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-2-yl)anthracene-9,10-dione 1c

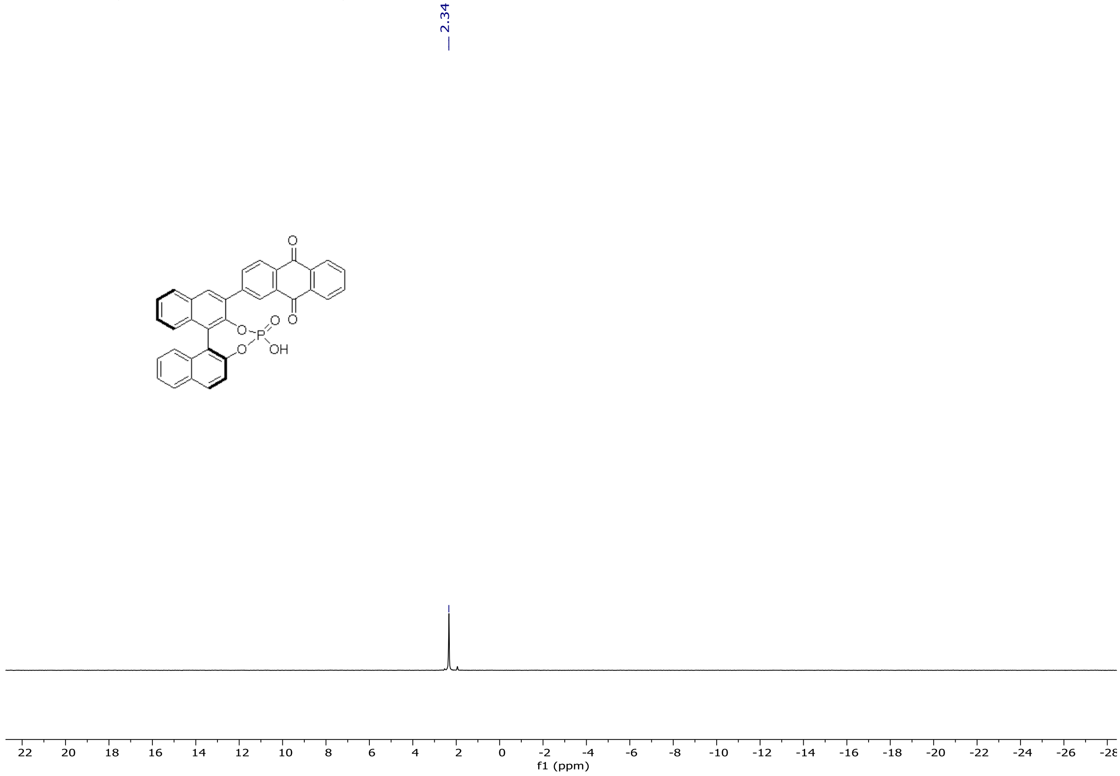
^{1}H NMR (500 MHz, DMSO-d_6)



^{13}C NMR (126 MHz, DMSO-d_6)

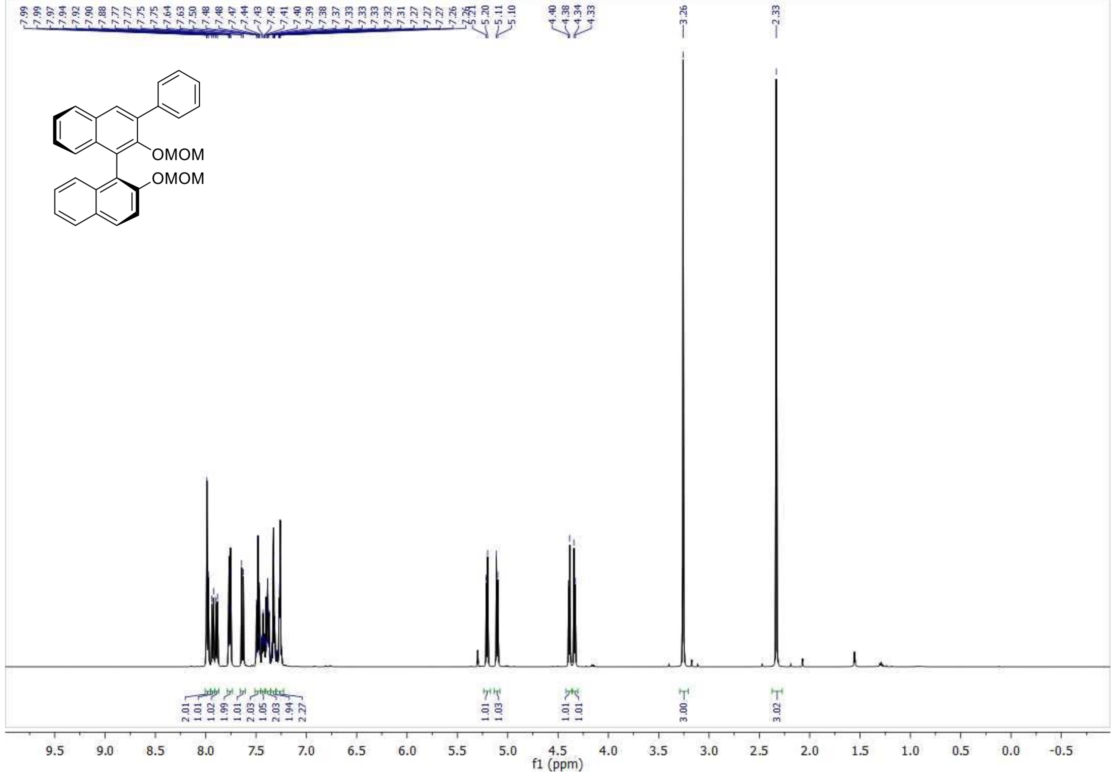


^{31}P NMR (202 MHz, DMSO-d_6)

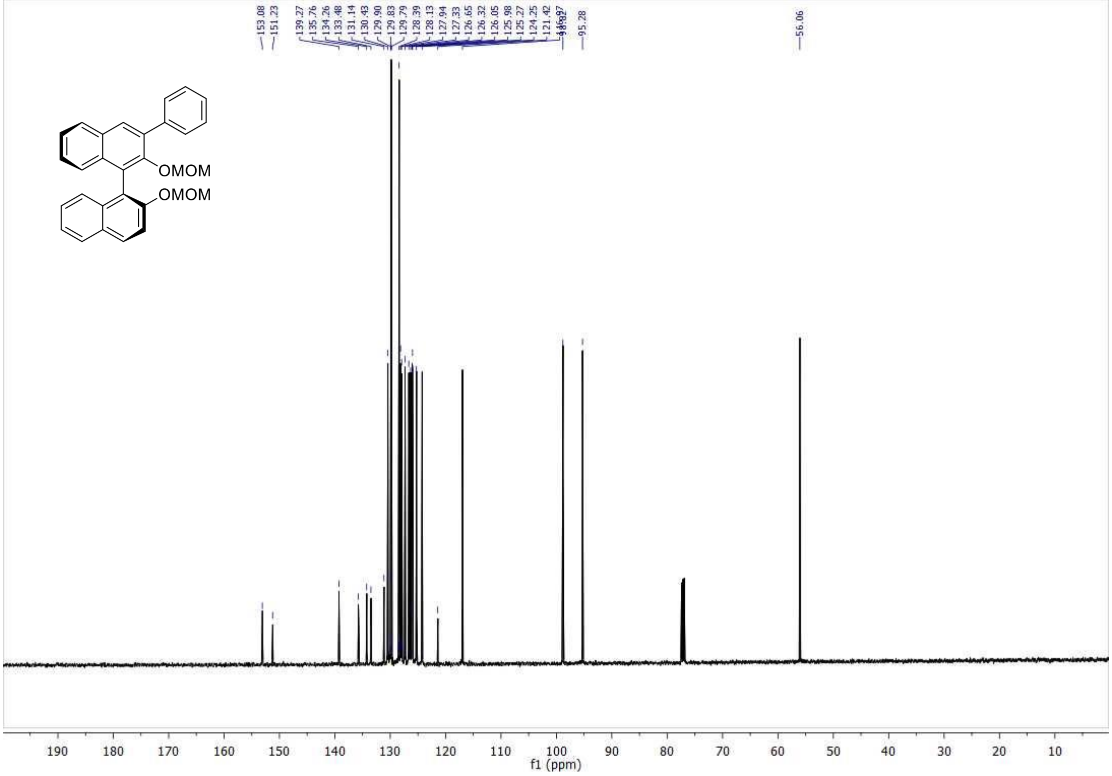


(S)-2,2'-bis(methoxymethoxy)-3-phenyl-1,1'-binaphthalene 11

^{1}H NMR (500 MHz, $CDCl_3$)

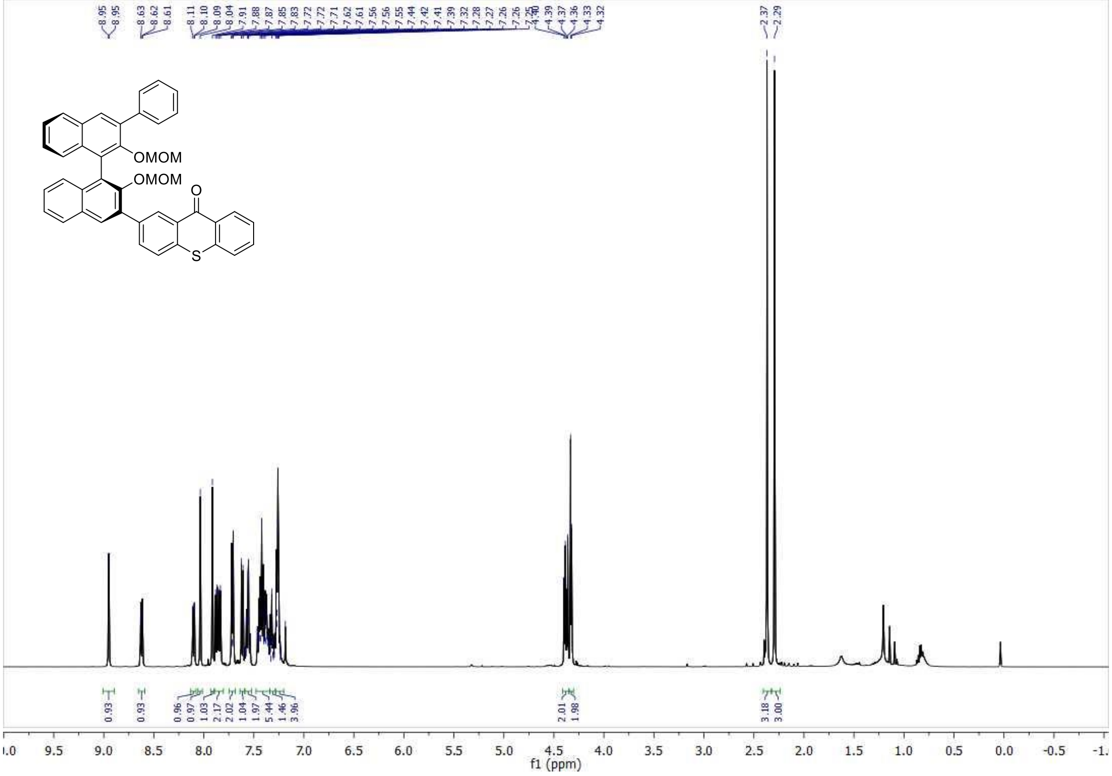


^{13}C NMR (500 MHz, CDCl$_3$)

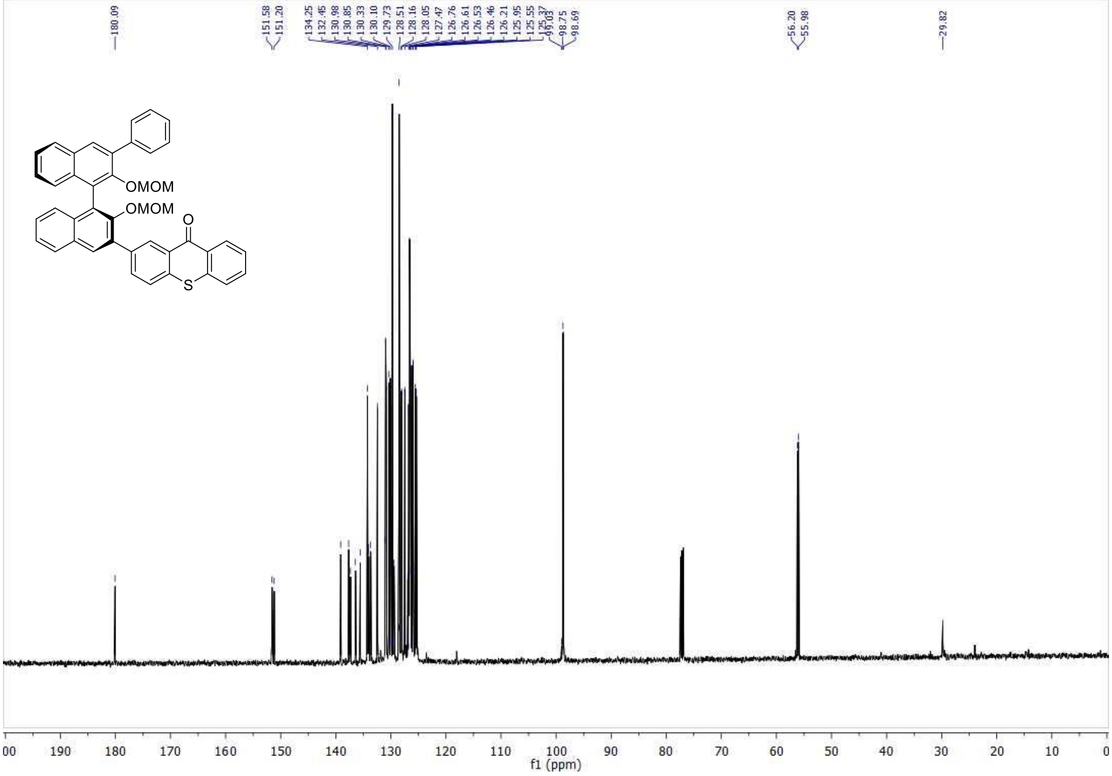


(*S*)-2-(2,2'-bis(methoxymethoxy)-3'-phenyl-[1,1'-binaphthalen]-3-yl)-9H-thioxanthen-9-one 13.

^{1}H NMR (500 MHz, CDCl$_3$)

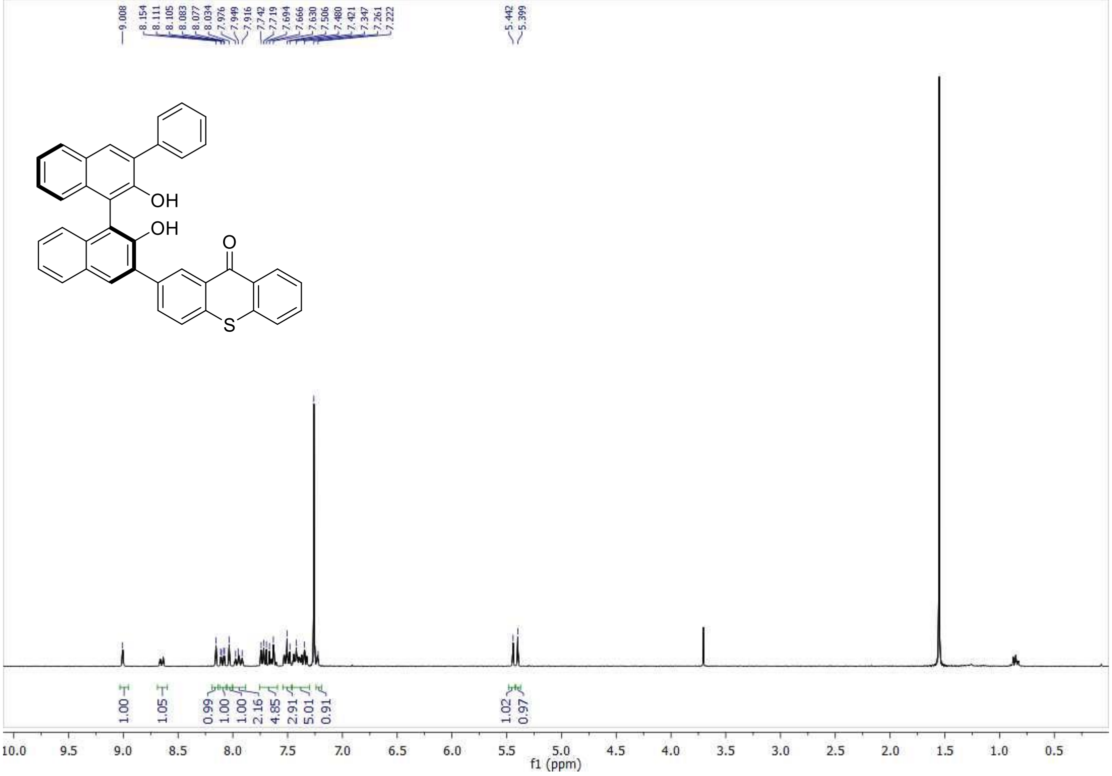


^{13}C NMR (500 MHz, CDCl$_3$)

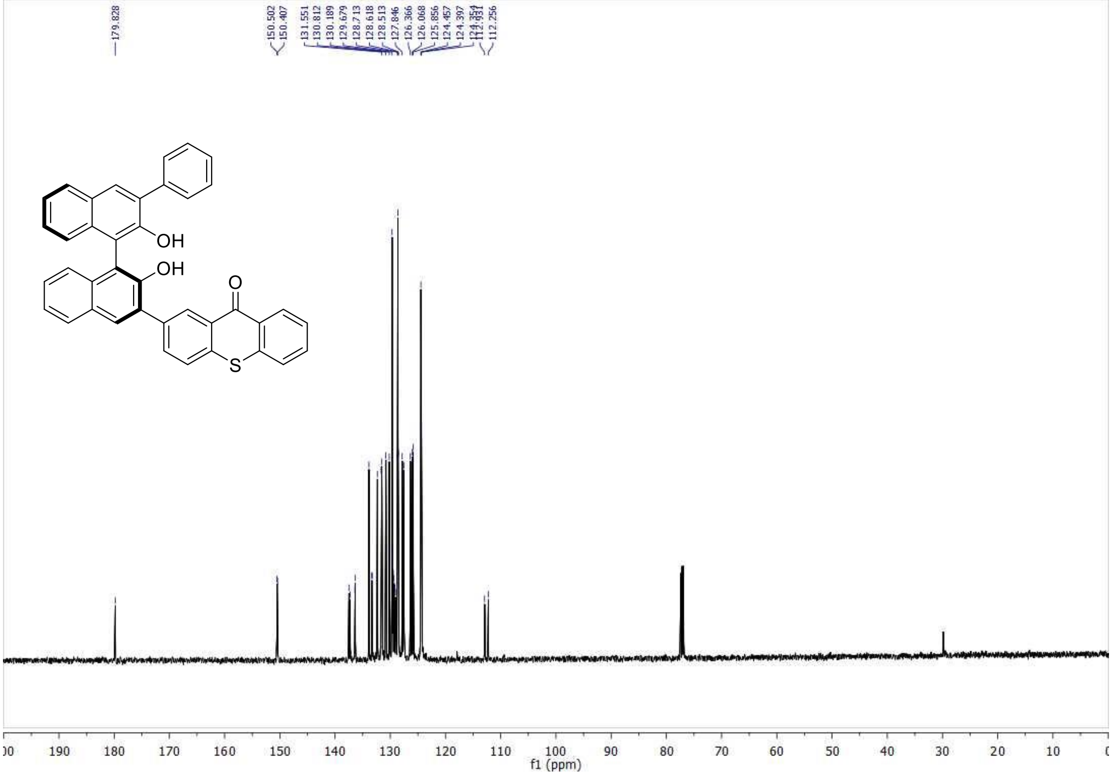


(S)-2-(2,2'-dihydroxy-3'-phenyl-[1,1'-binaphthalen]-3-yl)-9H-thioxanthen-9-one A2

^{1}H NMR (300 MHz, CDCl$_3$)

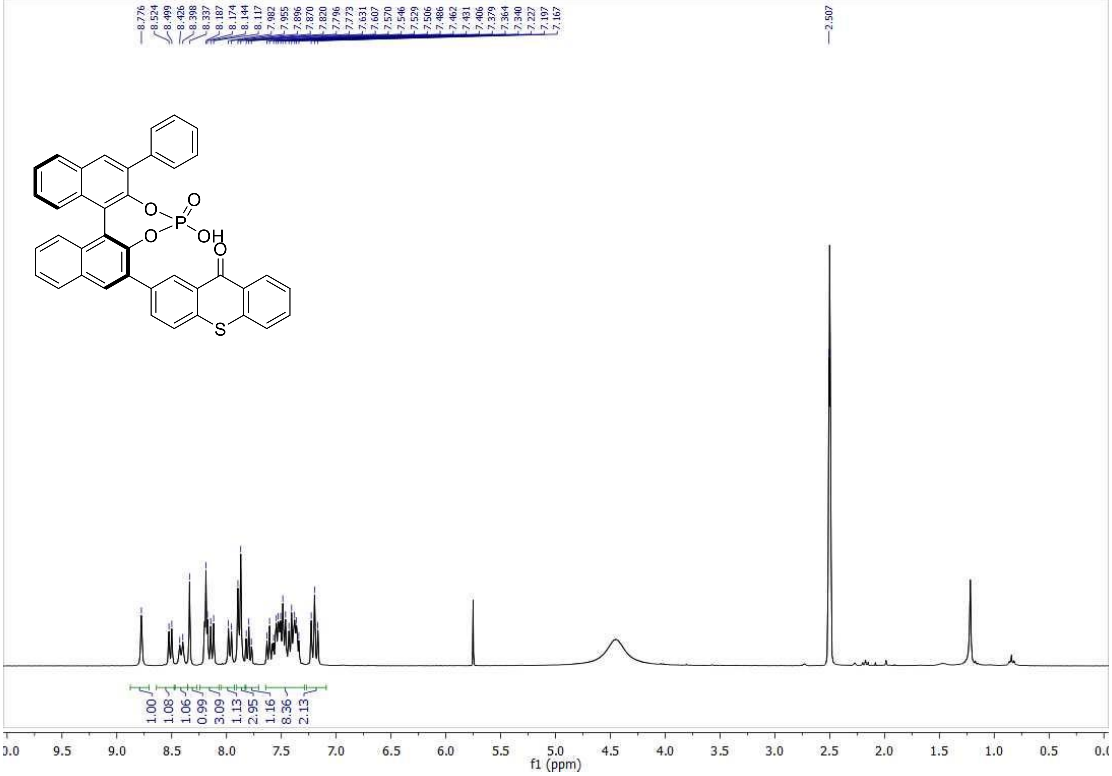


^{13}C NMR (500 MHz, CDCl$_3$)

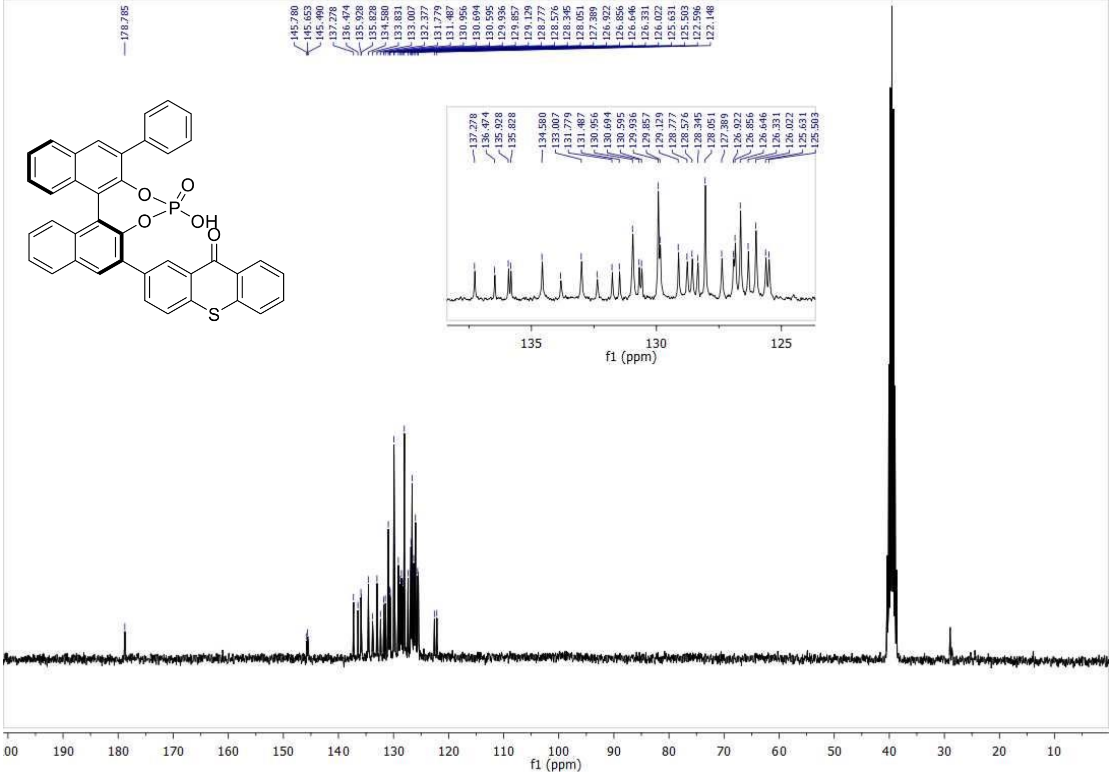


2-((11bS)-4-hydroxy-4-oxido-6-phenyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-2-yl)-9H-thioxanthen-9-one 1d

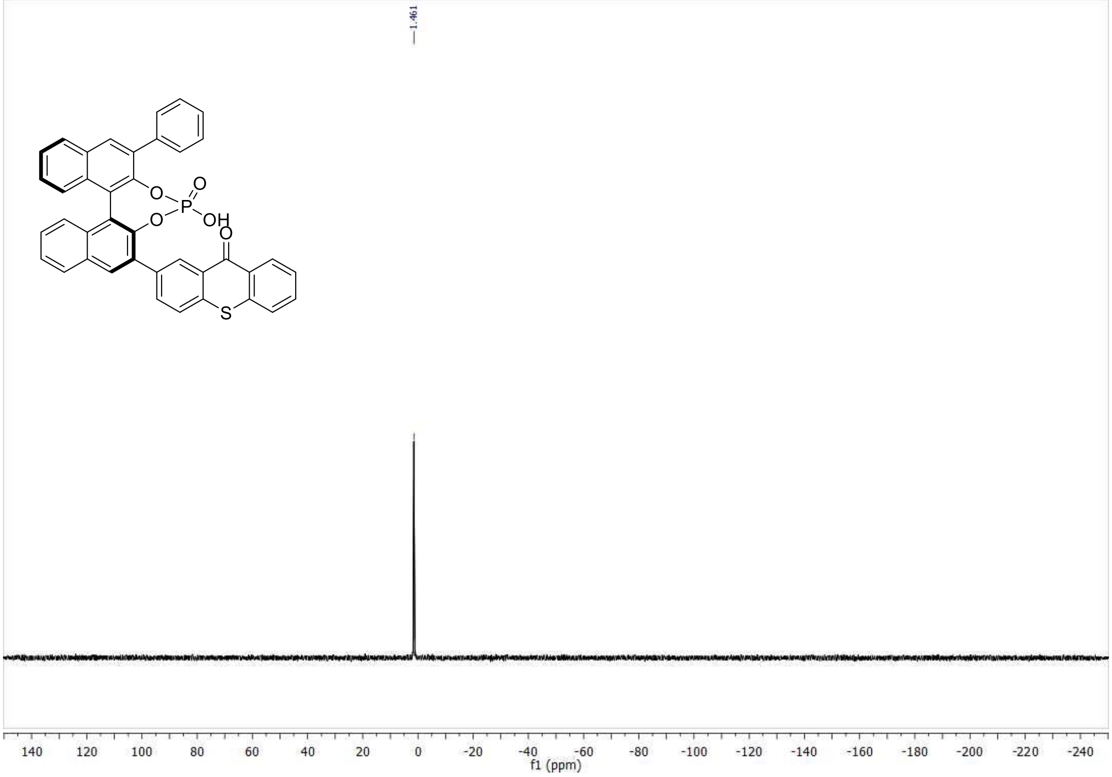
^{1}H NMR (300 MHz, DMSO-d_6)



^{13}C NMR (300 MHz, DMSO-d_6)

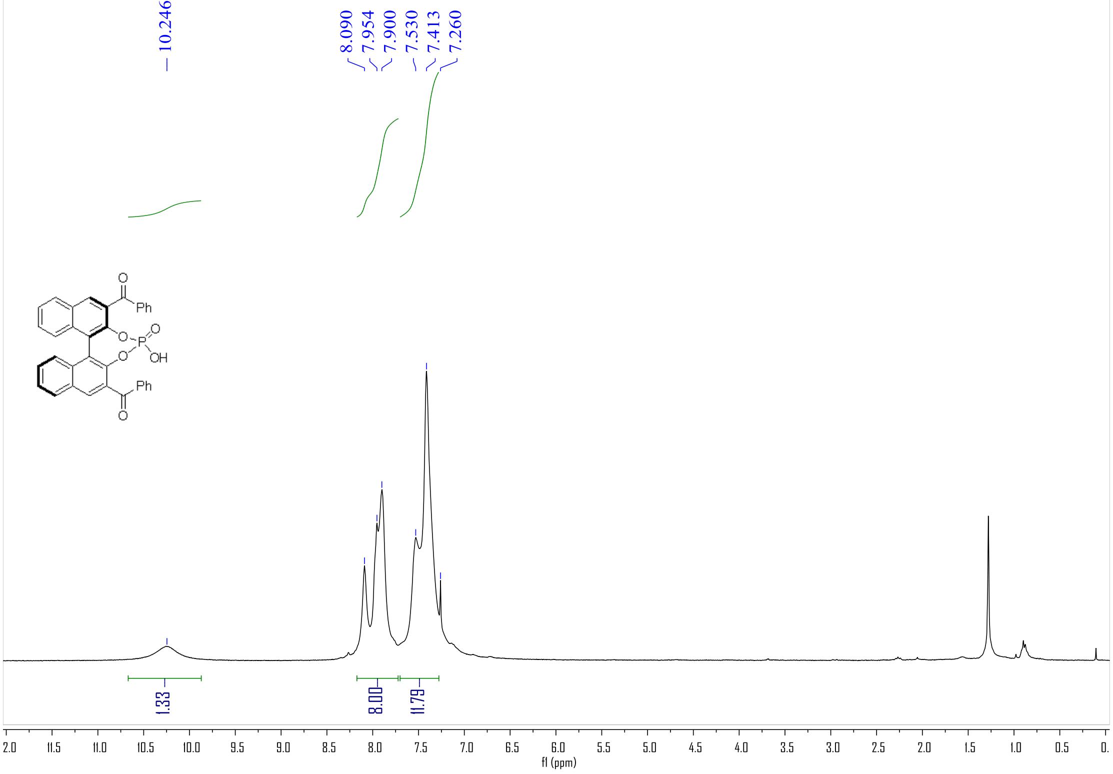


^{31}P NMR (202 MHz, DMSO-d_6)

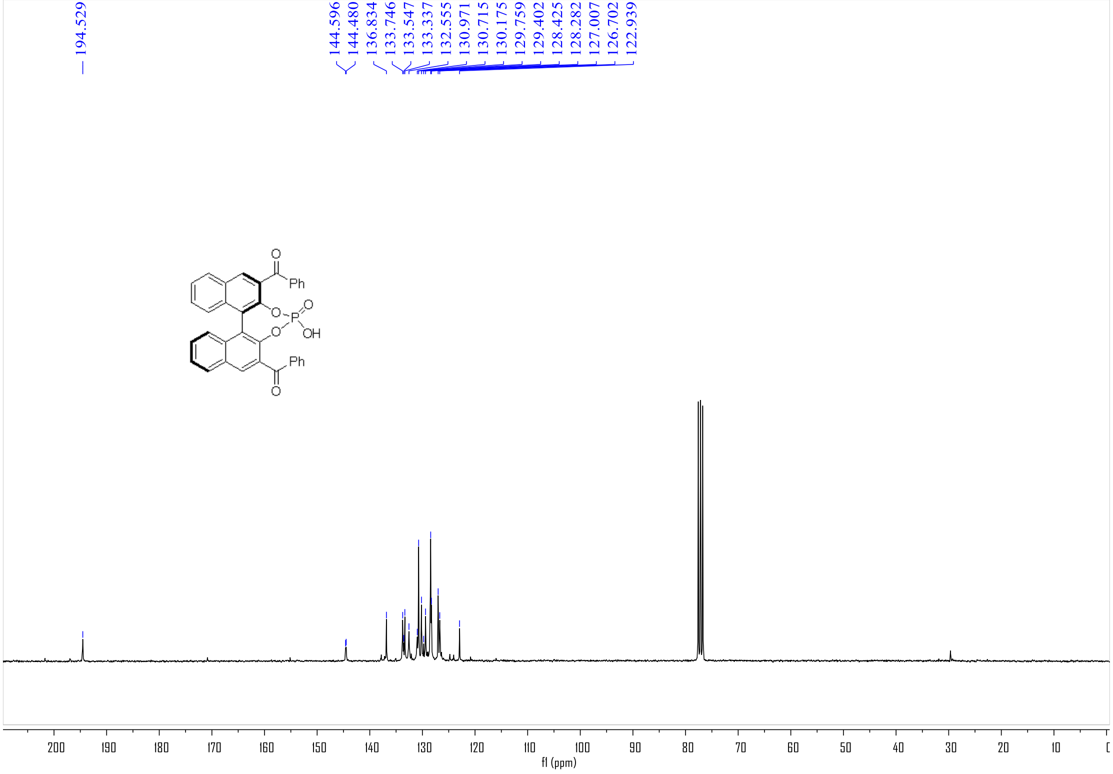


((11b*R*)-4-hydroxy-4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-2,6-diyl)bis(phenylmethanone 1e

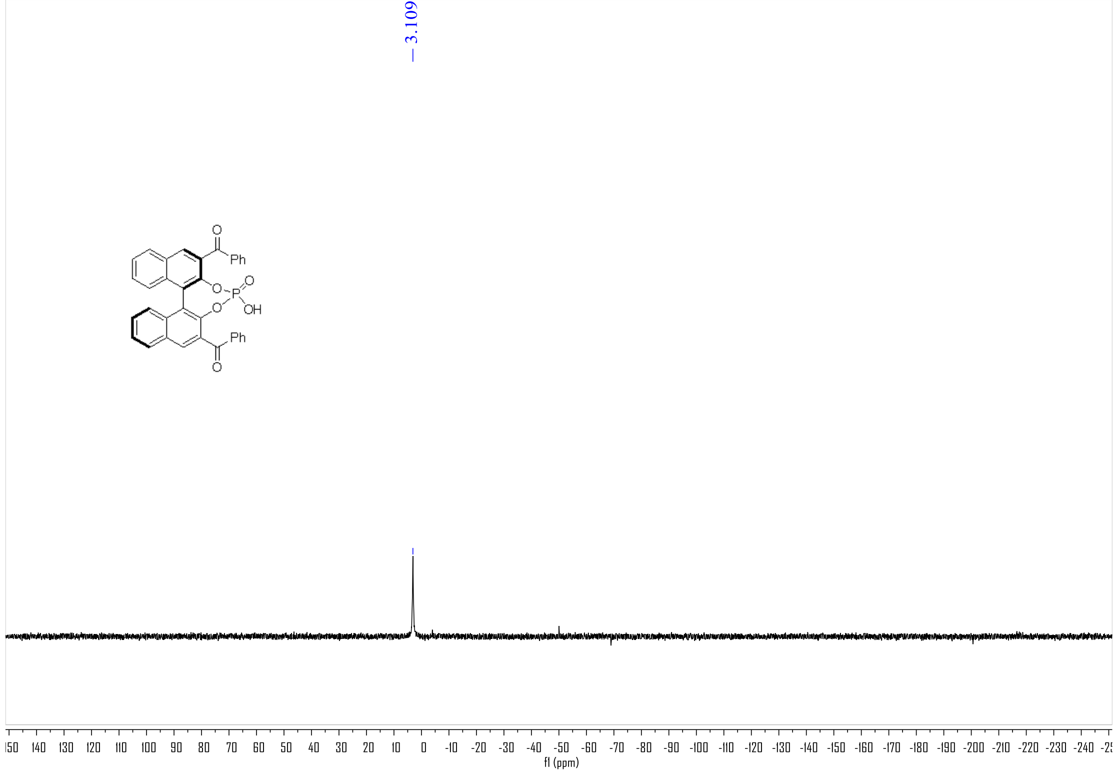
^{1}H NMR (300 MHz, CDCl$_3$)



^{13}C NMR (75 MHz, CDCl$_3$)

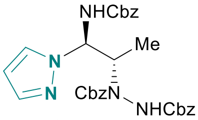


^{31}P NMR (202 MHz, CDCl3)



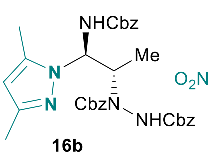
8. General comments regarding the synthesis and analysis of compound 16a to 16e

1-(hetero)aryl-1,2-diamines **16a to 16e** were synthesized following a reported procedure: J. Lyu, A. Claraz, M. R. Vitale, C. Allain and G. Masson, *J. Org. Chem.*, 2020, **85**, 12843 and were previously fully described.
Of note, severe rotamers were observed for each compound leading to NMR spectra that are poorly resolved. Partial coalescence can be observed at higher temperature even if the phenomena persist at 70°C (see**:** A. Dumoulin, G. Bernadat and G. Masson *J. Org. Chem.* 2017, **82**, 1775). Nevertheless, diastereomeric ratio can be determined even at room temperature by integrating various peaks as noted below:



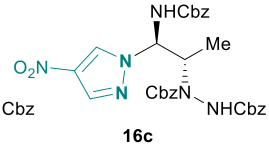
16a

^{1}H
6.24 vs 6.21ppm



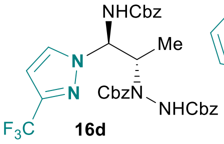
16b

^{1}H
5.76 vs 5.69 ppm



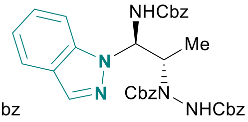
16c

^{1}H
1.31 vs1.03-0.9 ppm



16d

19F
-61.8 vs -62.0 ppm

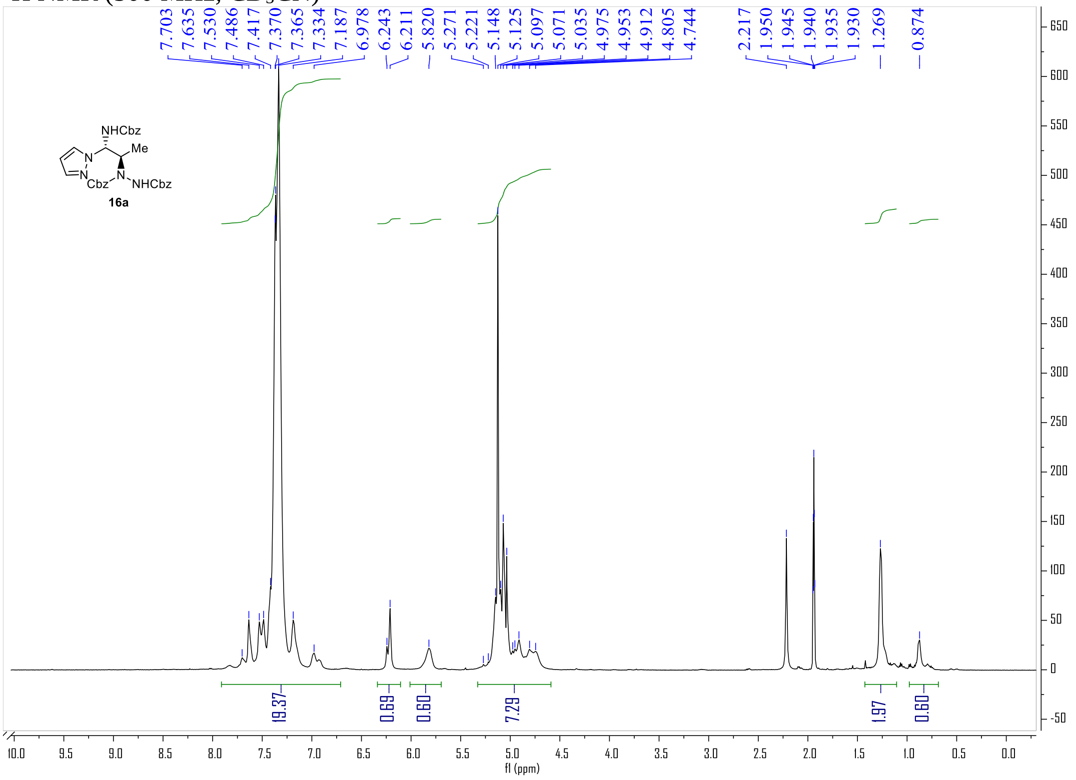


16e

^{1}H
8.02 vs 7.99 ppm

Reported clean spectra for compound 16a:

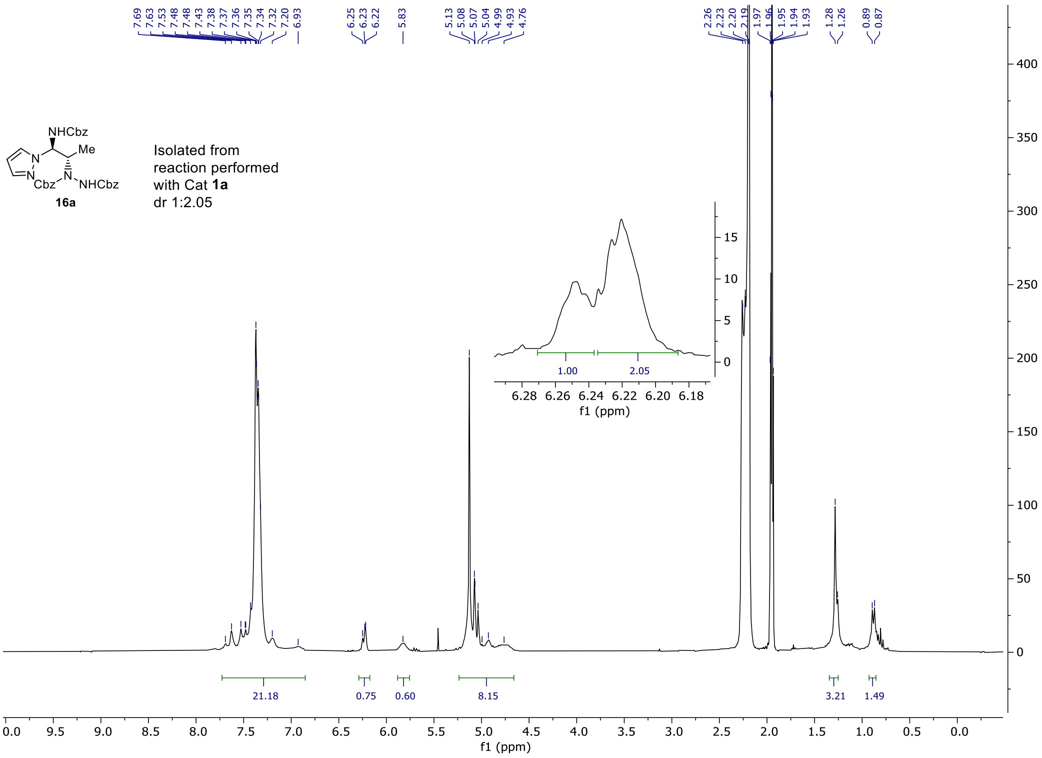
Dibenzyl 1-((1*S*,2*R*)-1-(((benzyloxy)carbonyl)amino)-1-(1H-pyrazol-1-yl)propan-2-yl)hydrazine-1,2-dicarboxylate (6a)
^{1}H NMR (500 MHz, CD_3CN)



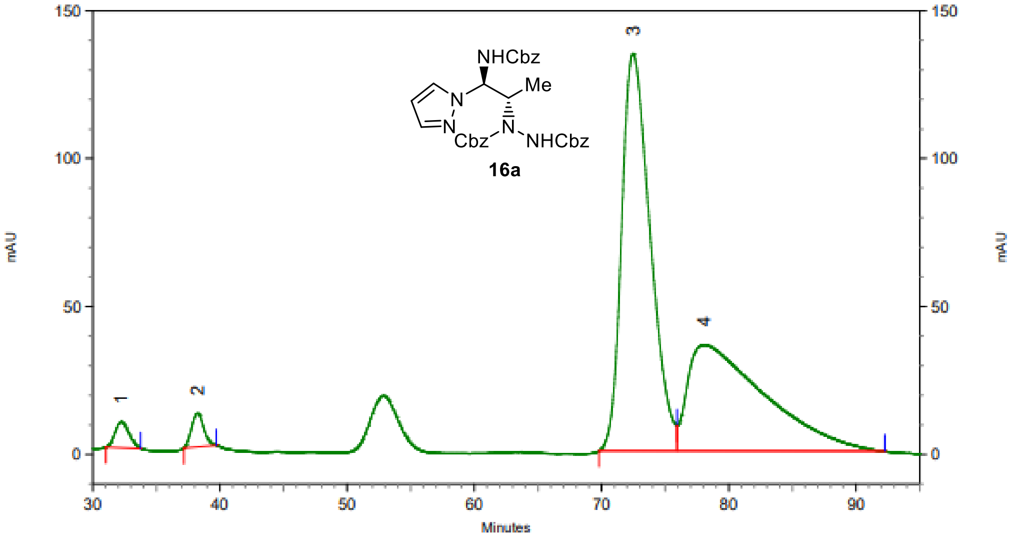
9. NMR and HPLC traces of compound 16a with Catalysts 1a-e

Dibenzyl 1-((1*R*,2*S*)-1-(((benzyloxy)carbonyl)amino)-1-(1H-pyrazol-1-yl)propan-2-yl)hydrazine-1,2-dicarboxylate (16a)

^{1}H NMR (500 MHz, CD_3CN)



IA- HEP/iPrOH 85/15 214nm



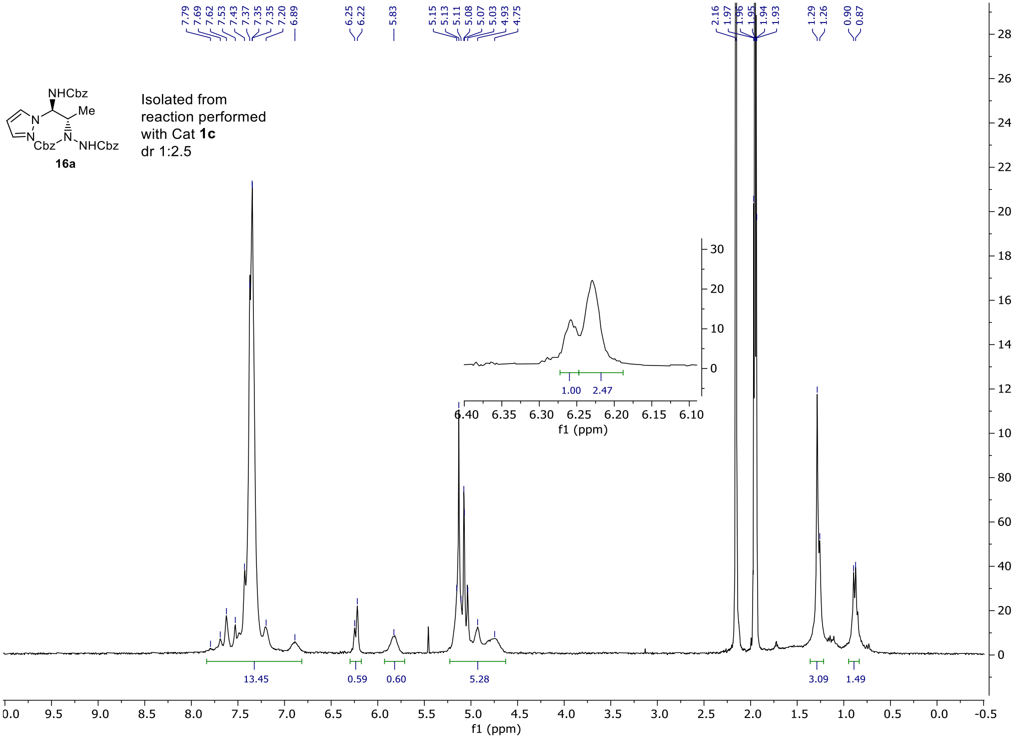
DAD-CH3 214 nm

Results

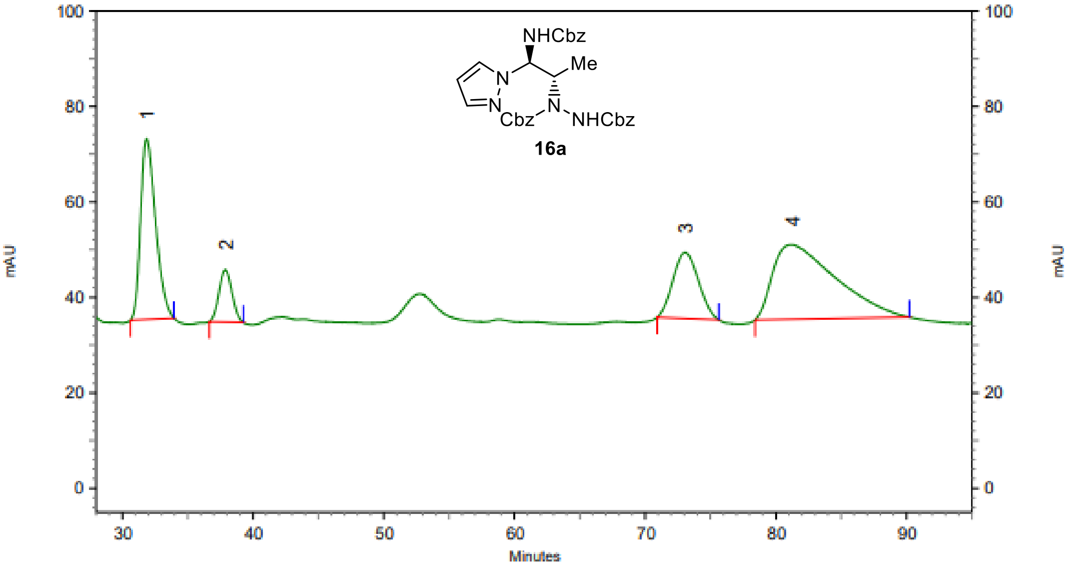
Pk #	Retention Time	Area	Area %
1	32,24	2633737	1,76
2	38,25	2987698	2,00
3	72,47	83811849	56,13
4	78,09	59887236	40,11

Dibenzyl 1-((1*R*,2*S*)-1-(((benzyloxy)carbonyl)amino)-1-(1H-pyrazol-1-yl)propan-2-yl)hydrazine-1,2-dicarboxylate (16a)

^{1}H NMR (500 MHz, CD_3CN)



IA- HEP/iPrOH 85/15 214nm

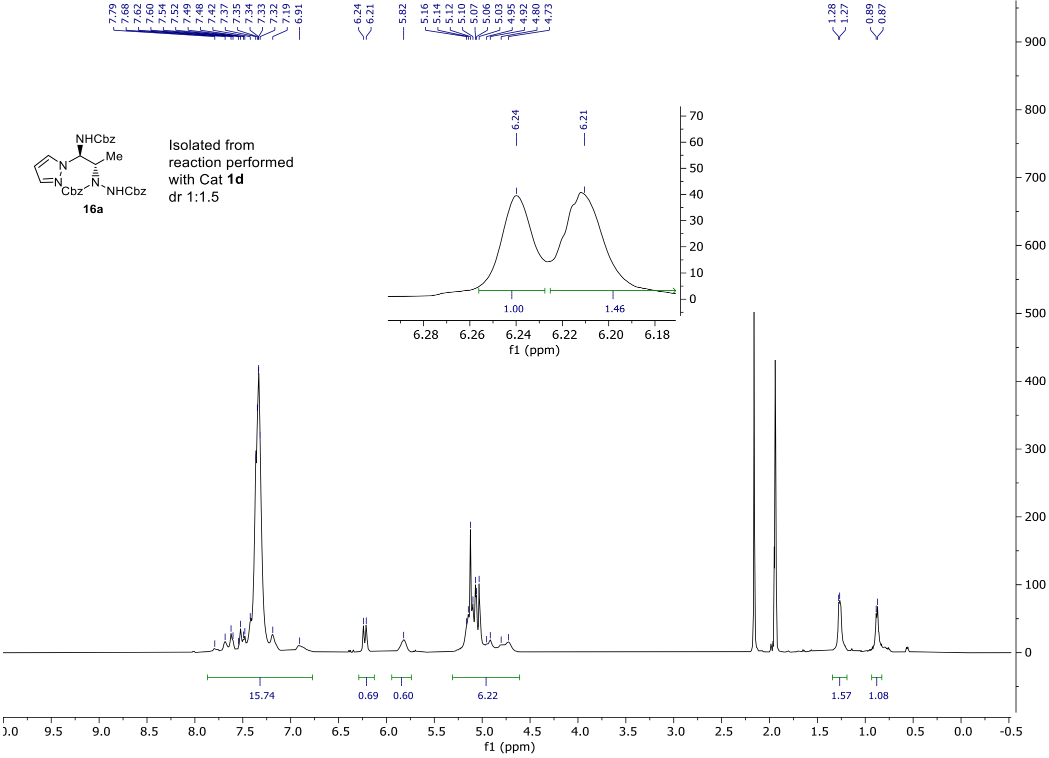


Results

Pk #	Retention Time	Area	Area %
1	31,86	12129227	27,91
2	37,88	3016192	6,94
3	73,06	7501841	17,26
4	81,20	20811406	47,89

Dibenzyl 1-((1*R*,2*S*)-1-(((benzyloxy)carbonyl)amino)-1-(1H-pyrazol-1-yl)propan-2-yl)hydrazine-1,2-dicarboxylate (16a)

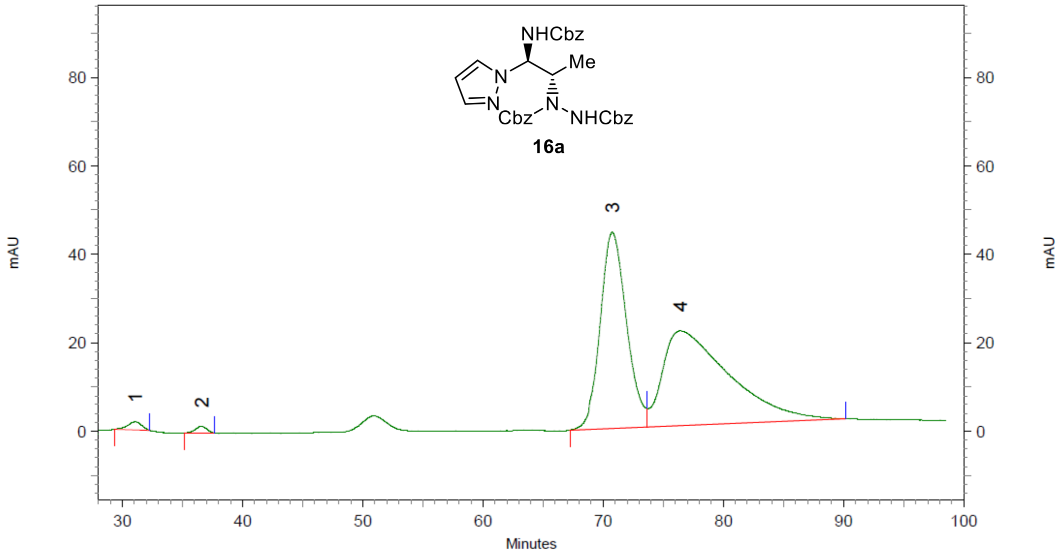
^{1}H NMR (500 MHz, CD_3CN)



16a

Isolated from reaction performed with Cat **1d** dr 1:1.5

IA- HEP/iPrOH 85/15 214nm



16a

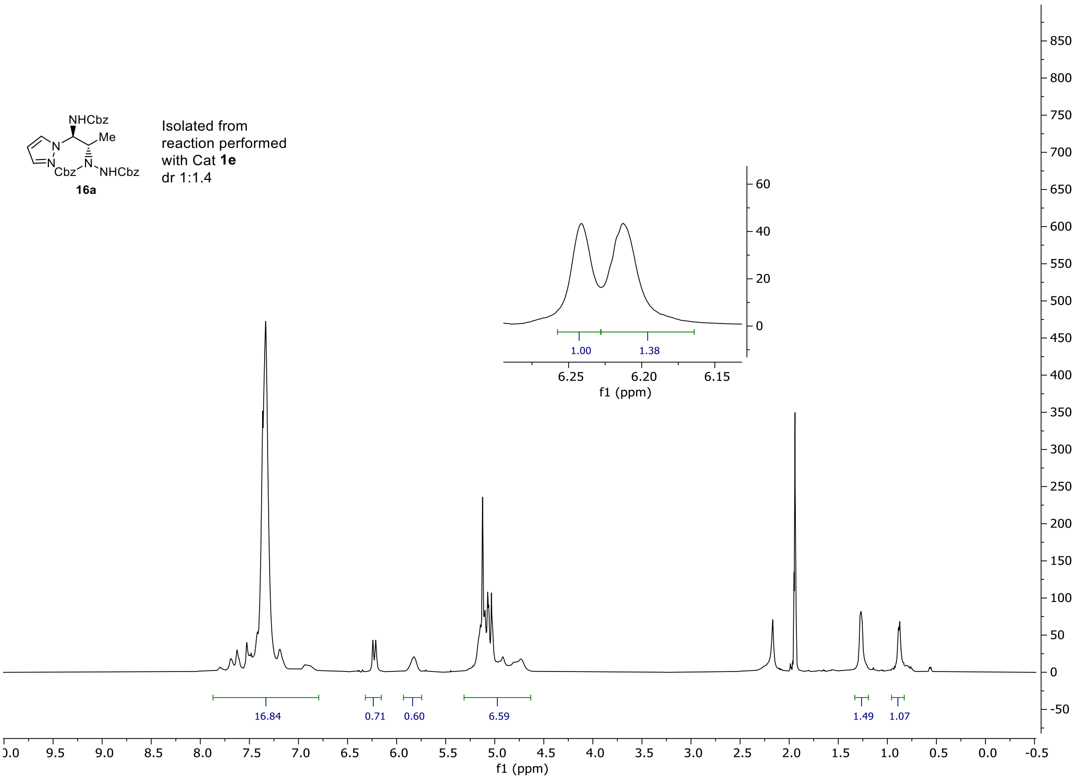
DAD-CH3 214 nm

Results

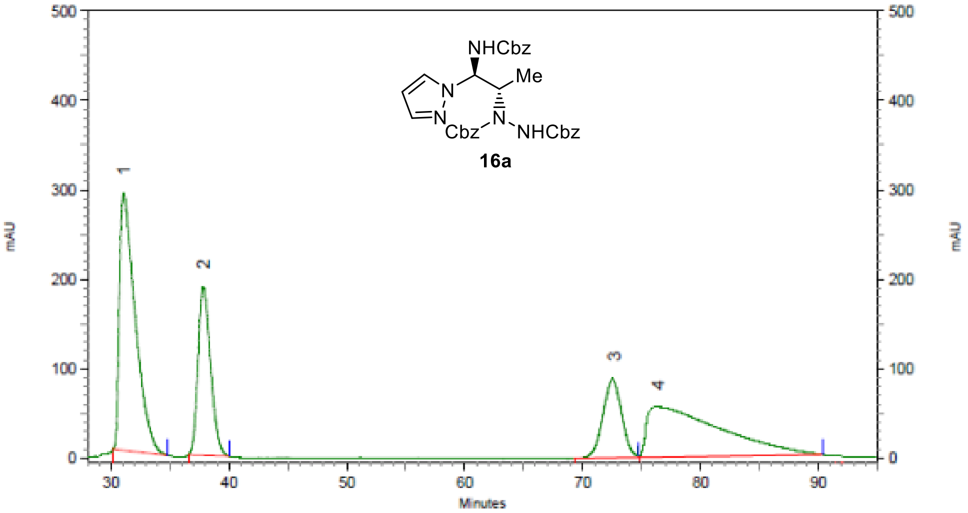
Pk #	Retention Time	Area	Area %
1	31,07	608367	1,00
2	36,59	395185	0,65
3	70,75	26991663	44,22
4	76,41	33049040	54,14

Dibenzyl 1-((1*S*,2*R*)-1-(((benzyloxy)carbonyl)amino)-1-(1H-pyrazol-1-yl)propan-2-yl)hydrazine-1,2-dicarboxylate (16a)

^{1}H NMR (500 MHz, CD_3CN)



IA- HEP/iPrOH 85/15 214nm



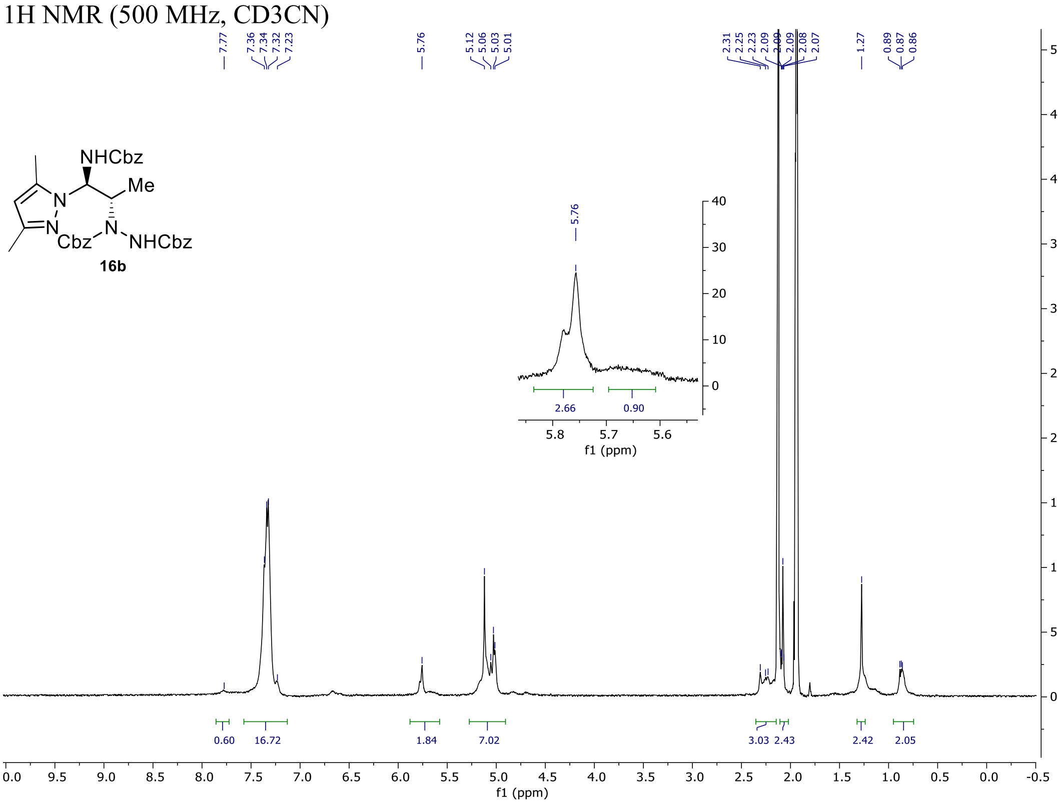
Results

Pk #	Retention Time	Area	Area %
1	31,07	106996530	33,85
2	37,83	55685691	17,62
3	72,68	52207808	16,52
4	76,40	101203547	32,01

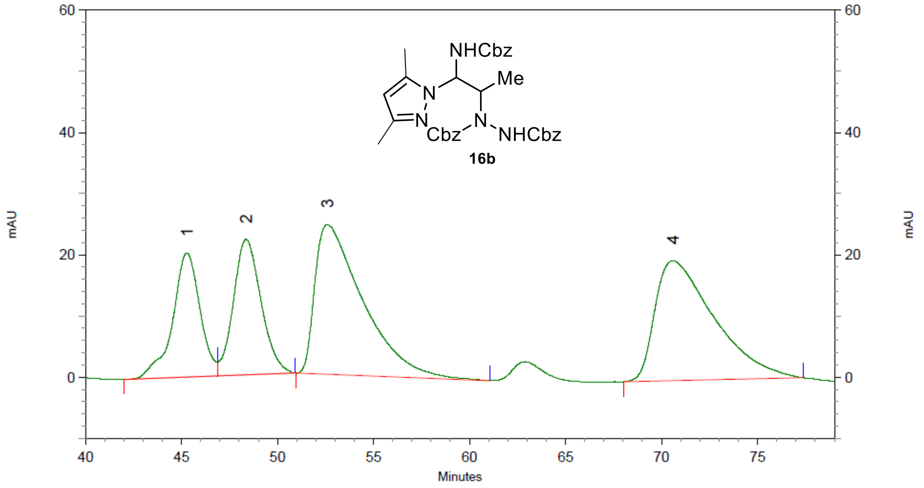
10. NMR and HPLC traces of compound 16b-e

Dibenzyl 1-((1R,2S)-1-(((benzyloxy)carbonyl)amino)-1-(3,5-dimethyl-1H-pyrazol-1-yl)propan-2-yl)hydrazine1,2-dicarboxylate (1 6b)

1H NMR (500 MHz, CD3CN)



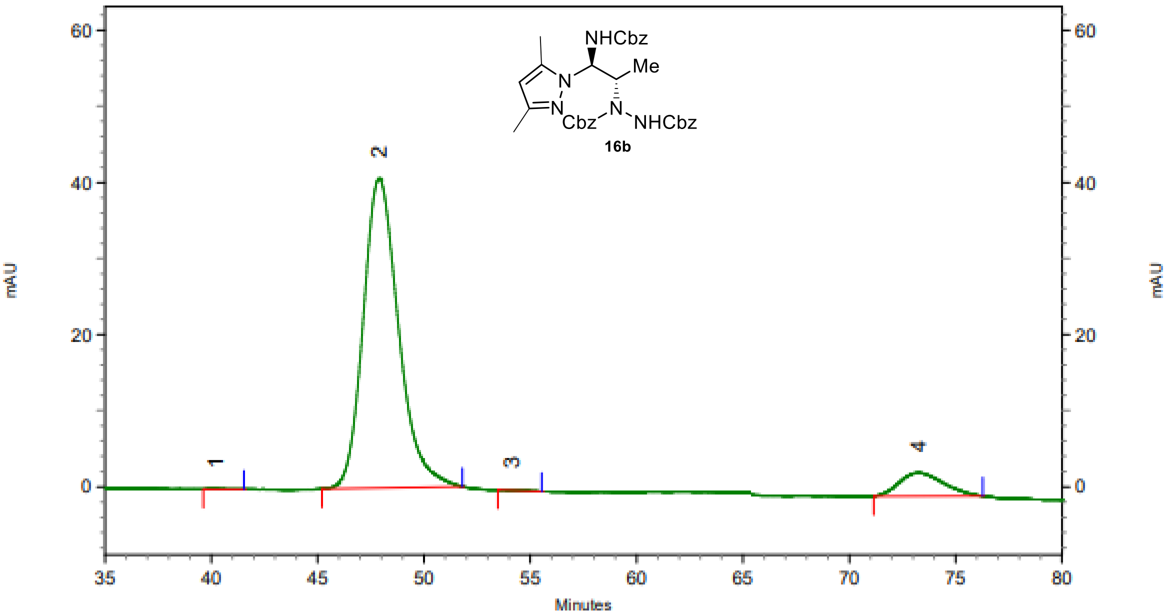
IA Hept/*i*PrOH 95:5 214nm



DAD-CH3 214 nm
Results

Pk #	Retention Time	Area	Area %
1	45,28	8050108	15,89
2	48,36	8875168	17,51
3	52,59	17000092	33,55
4	70,58	16747134	33,05

IA- HEP/iPrOH 95/5 214nm

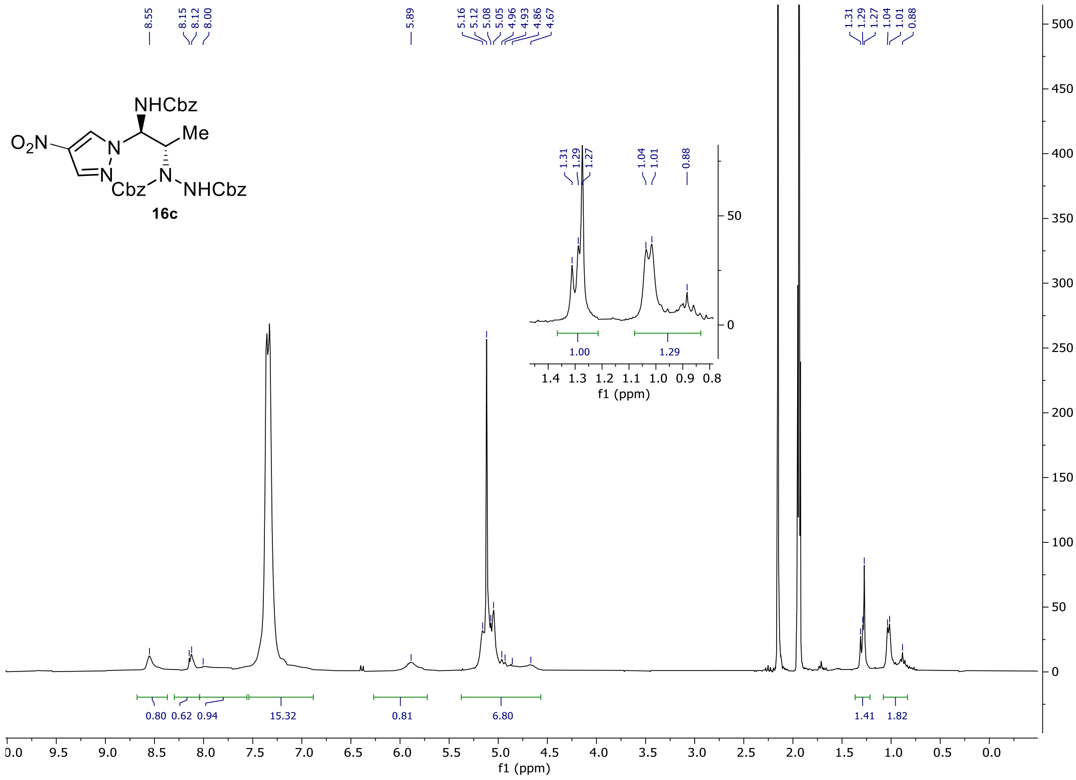


DAD-CH3 214 nm
Results

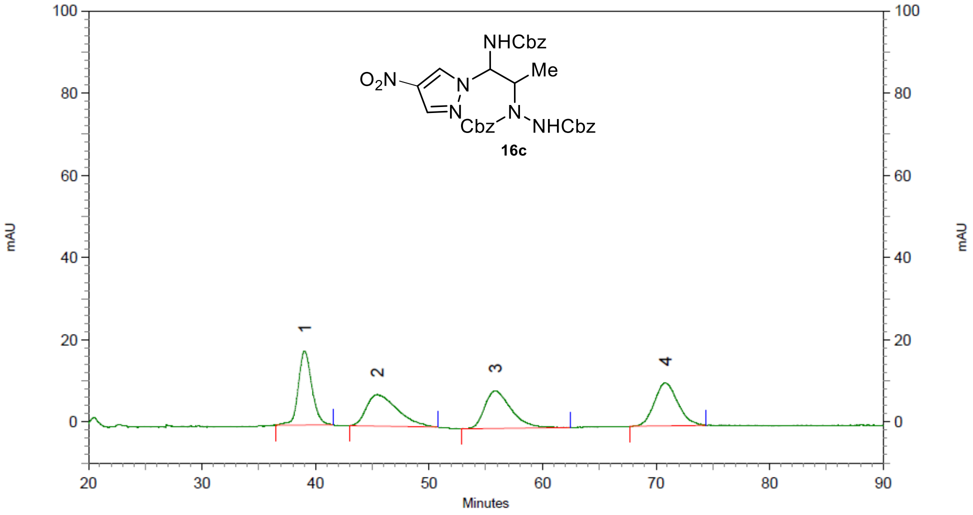
Pk #	Retention Time	Area	Area %
1	40,21	8114	0,04
2	47,89	18769673	91,34
3	54,15	3373	0,02
4	73,26	1768821	8,61

Dibenzyl 1-((1R,2S)-1-(((benzyloxy)carbonyl)amino)-1-(4-nitro-1H-pyrazol-1-yl)propan-2-yl)hydrazine-1,2-dicarboxylate (16c)

1H NMR (500 MHz, CD3CN)



IA Hept/i-PrOH 85:15 1 214nm

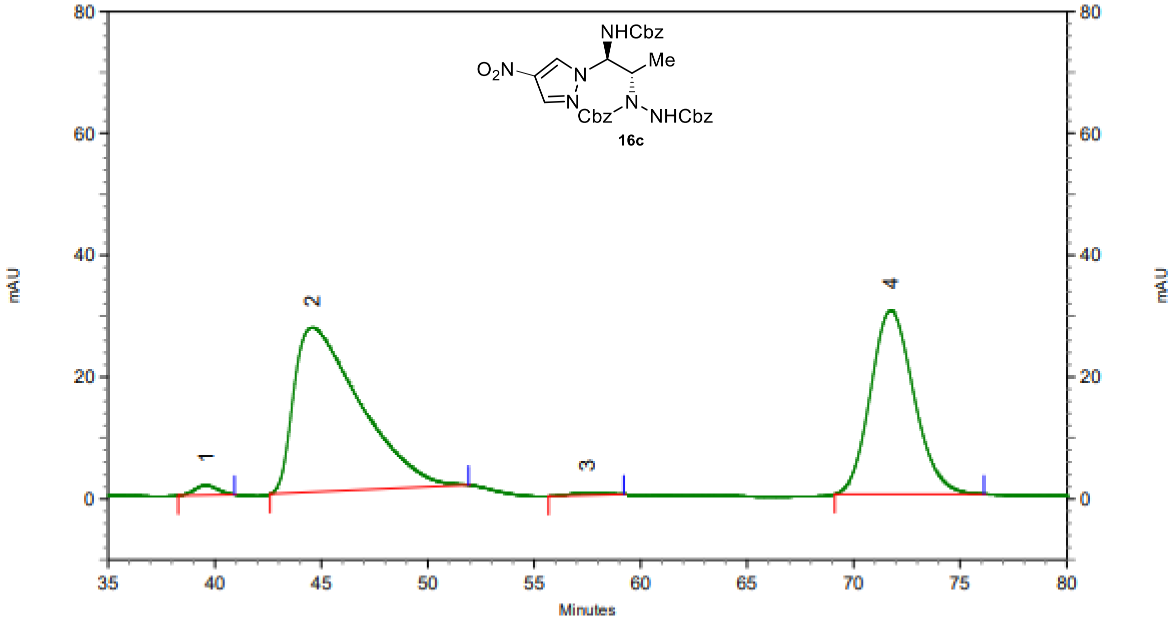


DAD-CH3 214 nm

Results

Pk #	Retention Time	Area	Area %
1	39,04	5961554	25,11
2	45,43	5863537	24,69
3	55,81	5930829	24,98
4	70,82	5990232	25,23

IA- HEP/iPrOH 85/15 214nm



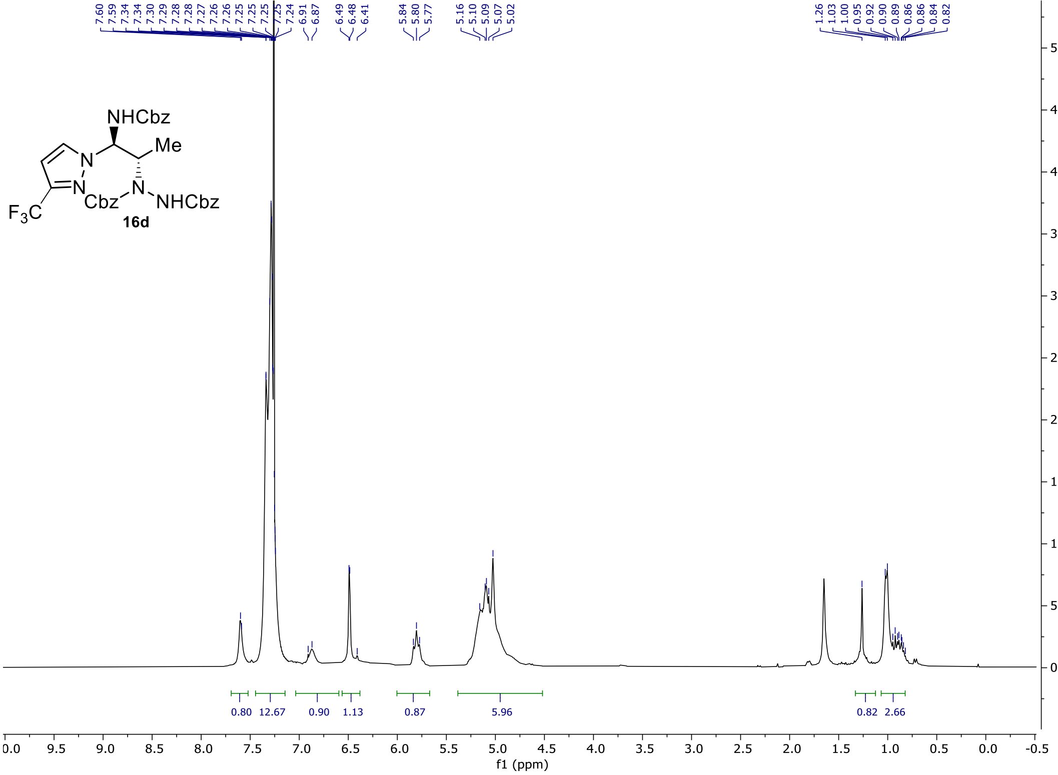
DAD-CH3 214 nm

Results

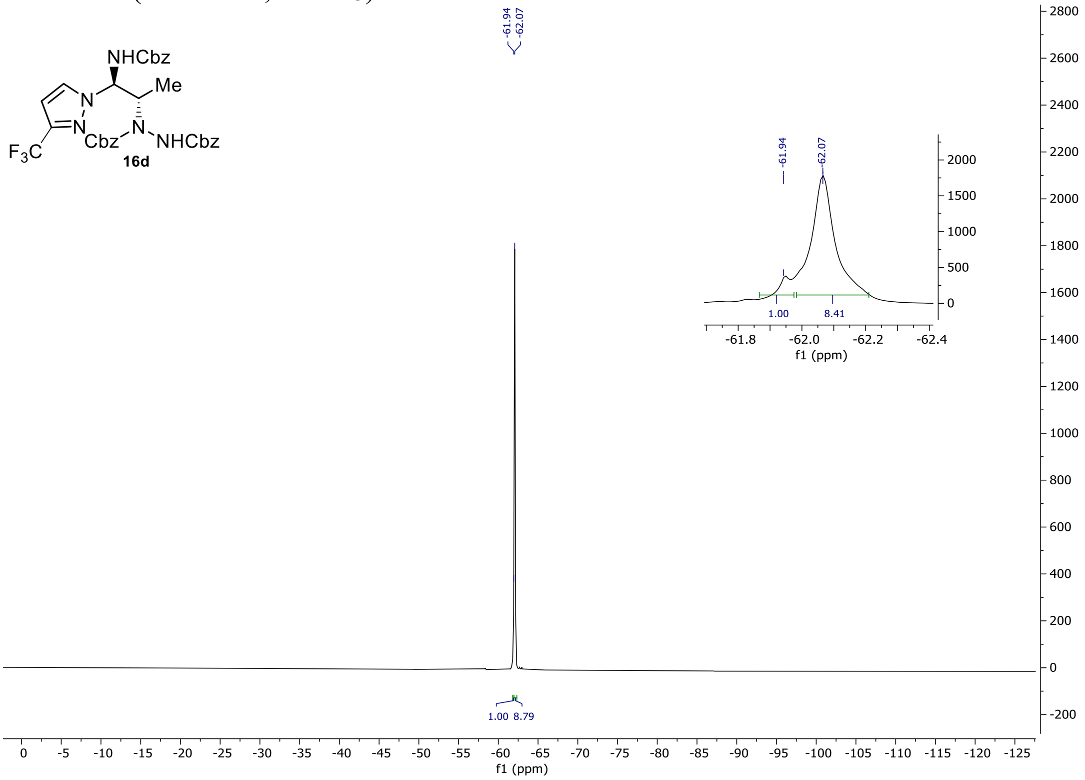
Pk #	Retention Time	Area	Area %
1	39,58	486762	1,19
2	44,57	23238125	56,72
3	57,51	164652	0,40
4	71,75	17077950	41,69

Dibenzyl 1-((1R,2S)-1-(((benzyloxy)carbonyl)amino)-1-(3-(trifluoromethyl)-1H-pyrazol-1-yl)propan-2- yl)hydrazine-1,2-dicarboxylate (16d)

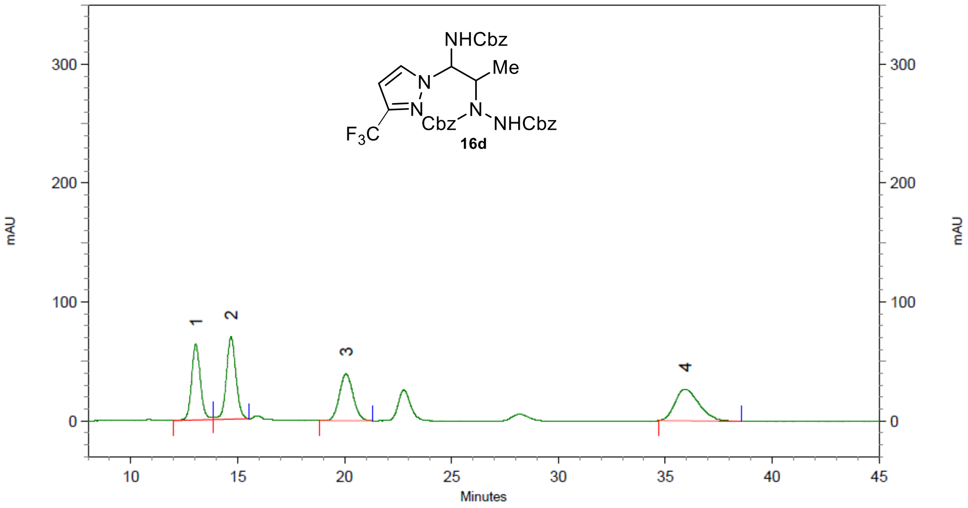
1H NMR (500 MHz, CDCl3)



^{19}F NMR (282 MHz, $CDCl_3$)



IA Hept/i-PrOH 85:15 214nm

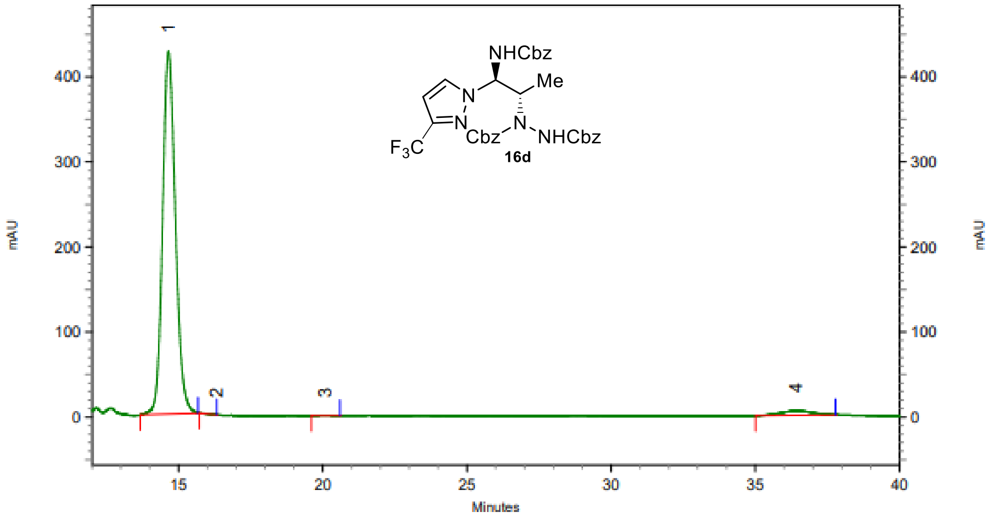


DAD-CH3 214 nm

Results

Pk #	Retention Time	Area	Area %
1	13,04	7308931	23,35
2	14,69	8596770	27,46
3	20,07	7037036	22,48
4	35,93	8363246	26,71

IA-HEP/iPrOH 85/15 214nm



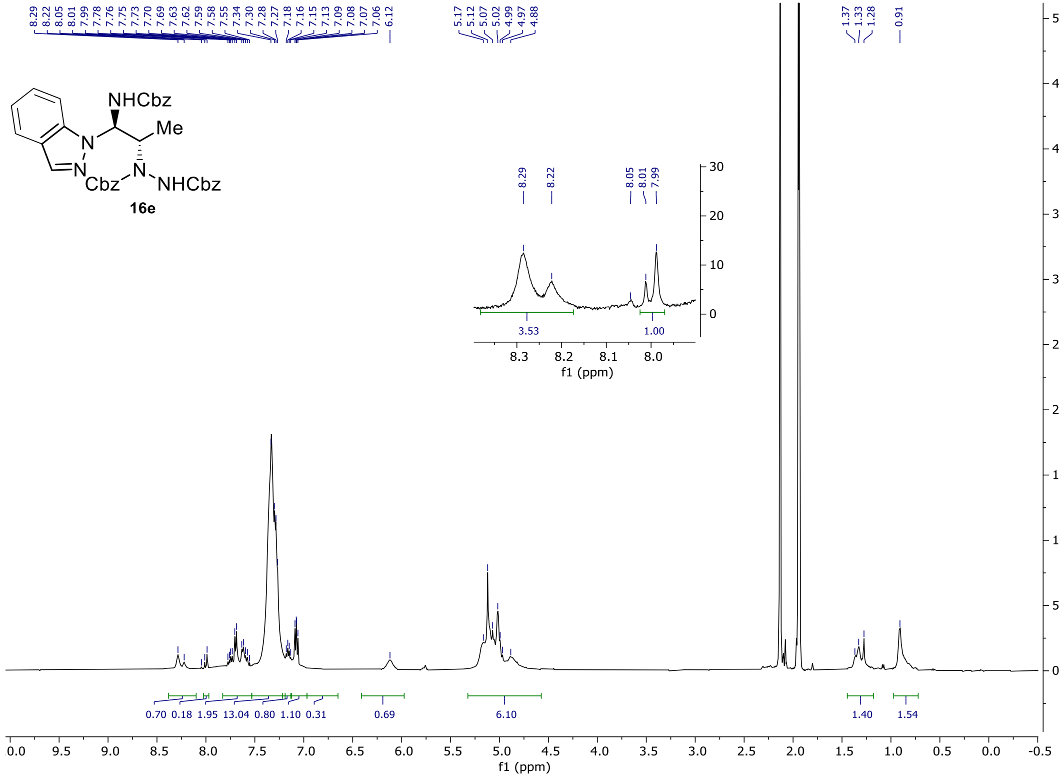
DAD-CH3 214 nm

Results

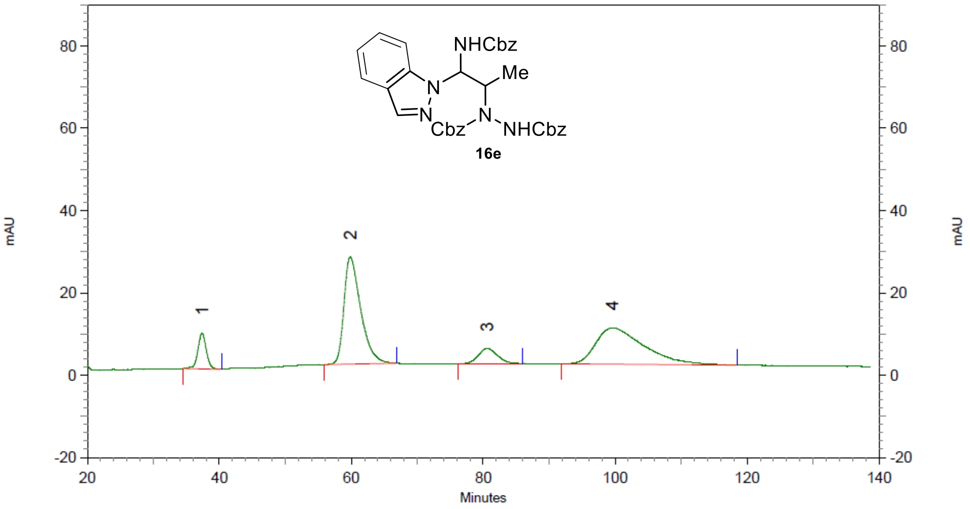
Pk #	Retention Time	Area	Area %
1	14,65	52626434	97,00
2	16,31	11535	0,02
3	20,09	43722	0,08
4	36,41	1574556	2,90

Dibenzyl 1-((1R,2S)-1-(((benzyloxy)carbonyl)amino)-1-(1H-indazol-1-yl)propan-2-yl)hydrazine-1,2-dicarboxylate (16e)

1H NMR (500 MHz, CD3CN)



IA Hep/*i*PrOH 85:15 214nm

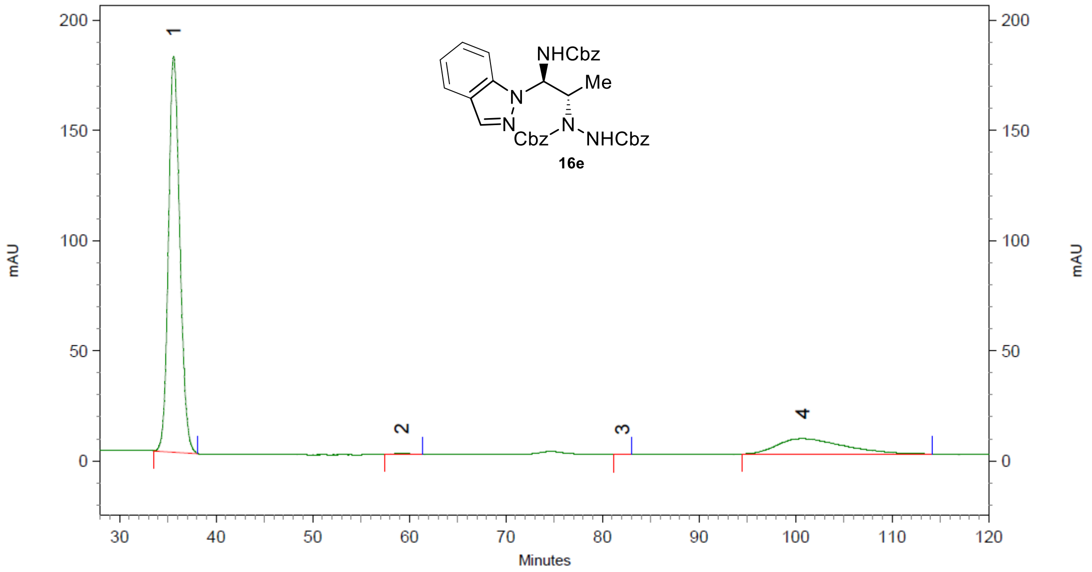


DAD-CH3 214 nm

Results

Pk #	Retention Time	Area	Area %
1	37,37	3150089	7,38
2	59,85	18385775	43,06
3	80,59	3007375	7,04
4	99,55	18158532	42,52

IA- HEP/iPrOH 85/15 214nm



DAD-CH3 214 nm

Results

Pk #	Retention Time	Area	Area %
1	35,60	58749570	81,06
2	59,19	174798	0,24
3	82,03	6916	0,01
4	100,68	13543110	18,69