

Supporting information for:

Modular Chiral Gold(I) Phosphite Complexes

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General Methods

Unless specified, all reactions were carried out at room temperature, under Ar, using magnetic stirring and in solvents dried using a Solvent Purification System (SPS). Analytical thin layer chromatography was carried out using TLC-aluminium sheets with 0.2 mm of silica gel (Merck GF234). Chromatography purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 μm). Commercial grade reagents and solvents were used without further purification. PCl_3 was distilled prior to use.¹

NMR spectra were recorded at 23 °C on a Bruker Avance 400 Ultrashield and Bruker Avance 500 Ultrashield apparatus. NMR chemical shifts (δ) are expressed in ppm. ^1H NMR chemical shifts are referenced to TMS (in the case of CDCl_3) or to the solvent residual signal (in the case of other NMR solvents).² ^{13}C NMR chemical shifts are referenced to the solvent signal. $^{31}\text{P}\{^1\text{H}\}$ -NMR chemical shifts are referenced to an external standard (85% aqueous H_3PO_4). Mass spectra were recorded on a Waters LCT Premier (ESI) and Waters GCT (EI, CI) spectrometers. Chiral HPLC analyses were performed on a Waters system using a Chiralpak IA column (4.6x250 mm, 5 μm) and Chiralpak IB column (4.6x250 mm, 5 μm).

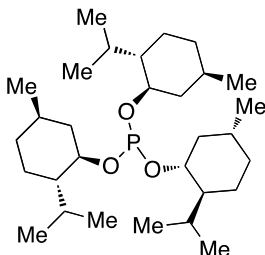
The following ligands were commercially available: (*R*)-**L1**, (*R*)-**L2**, (*R*)-**L3**, (*R*)-BINOL, (*R*)-MOP (**L4**), (*R*)-Monophos (**L5**), (*R,R,R*)-(+)-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*:3,4-*a'*]dinaphthalen-4-yl)bis(1-phenylethyl)amine (**L6**), (*S*)-ShiP (**L8**), (*R*)-3,3'-bis(2,4,6-triisopropylphenyl)-1,1'-bi-2-naphthol. The Au(I) complexes **L1**(AuCl)₂,³ **L2**(AuCl)₂,³ **L3**(AuCl),⁴ **L4**(AuCl),³ **L5**(AuCl),⁵ **L6**(AuCl),⁵ and **L8**(AuCl),⁶ were prepared according to the reported procedures.

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- 1 Amarego, W. L. F.; Chai, C. L. L., *Purification of Laboratory Chemicals* **2003**, 5th edition. Butterworth-Heinemann.
 - 2 Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512–7515.
 - 3 Muñoz, M. P.; Adrio, J.; Carretero, J. C.; Echavarren, A. M. *Organometallics* **2005**, *24*, 1293–1300.
 - 4 Johansson, M. J.; Gorin, D. J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 18002–18003
 - 5 (a) Alonso, I.; Trillo, B.; López, F.; Montserrat, S.; Ujaque, G.; Castedo, L.; Lledós, A.; Mascareñas, J. L. *J. Am. Chem. Soc.* **2009**, *131*, 13020–13030. (b) González, A. Z.; Toste, F. D. *Org. Lett.* **2009**, *12*, 200–203.
 - 6 González, A. Z.; Benitez, D.; Tkatchouk, E.; Goddard III, W. A.; Toste, F. D. *J. Am. Chem. Soc.* **2011**, *133*, 5500–5507.

1,6-Enynes **1a-e** were prepared according to the reported methods.⁷

Synthesis of Chiral Ligands

(-)-Menthol-derived phosphite L8

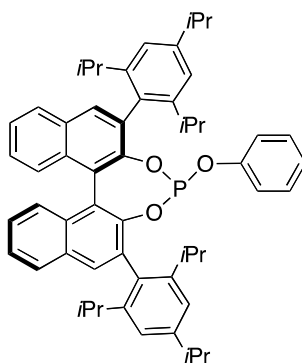


To a solution of PCl_3 (0.87 mL, 0.01 mol) in toluene (15 mL), a solution of (-)-menthol (4.7 g, 0.03 mol) and NEt_3 (5 mL, 0.036 mol) in toluene (25 mL) was added dropwise at $-20\text{ }^\circ\text{C}$. The reaction mixture was stirred for 2 hours at room temperature. The reaction mixture was filtered off and the solvent was evaporated. Purification by column chromatography on silica gel (toluene, Ar) provided the desired phosphite ligand **L8** (3.05 g, 68%). ^1H NMR (400 MHz, CDCl_3) δ 3.84 (ddd, $J = 19.5, 10.5, 4.4$ Hz, 3H), 2.21 (tdd, $J = 10.4, 7.5, 2.9$ Hz, 3H), 2.09 (dt, $J = 9.0, 4.3$ Hz, 3H), 1.68-1.59 (m, 6H), 1.45-1.32 (m, 3H), 1.30-1.22 (m, 3H), 1.11 (dd, $J = 23.3, 12.2$ Hz, 3H), 0.98 (ddd, $J = 17.0, 14.2, 4.3$ Hz, 3H), 0.89 (dd, $J = 6.8, 1.4$ Hz, 18H), 0.87-0.80 (m, 3H), 0.76 (d, $J = 6.9$ Hz, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 77.36, 77.16, 63.53, 49.12, 49.10, 45.91, 43.03, 42.05, 34.97, 34.70, 34.41, 34.25, 31.92, 31.79, 25.74, 25.67, 25.47, 25.19, 24.40, 23.31, 22.05, 22.03, 22.01, 21.59, 21.31, 21.16, 21.15, 21.04, 21.02, 16.26. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 150.1.

BINOL Phosphite L11⁸

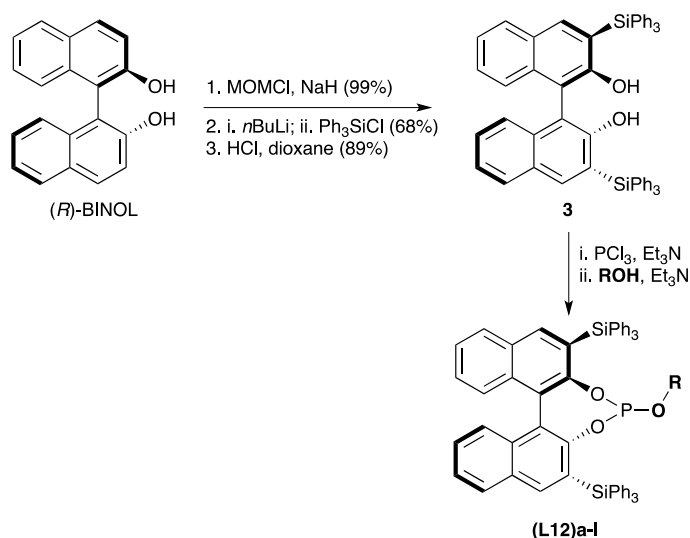
7 (a) Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178–6179; (b) Nieto-Oberhuber, C.; Pérez-Galán, P.; Herrero-Gómez, E.; Lauterbach, T.; Rodríguez, C.; López, S.; Bour, C.; Rosellón, A.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2008**, *130*, 269–279.

8 Kawasaki, M.; Li, P.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2008**, *47*, 3795–3597.



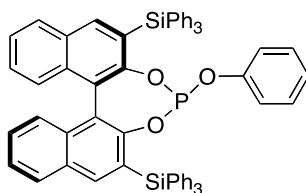
To a solution of (*R*)-3,3'-bis(2,4,6-triisopropylphenyl)-1,1'-bi-2-naphthol (150 mg, 0.21 mmol) and Et₃N (0.21 ml, 0.45 mmol) in toluene (10 mL) was added PCl₃ (40 mg, 0.32 mmol) dropwise at 0 °C. The resulting mixture was stirred vigorously for 1 h and then at 80 °C for 1h. The mixture was cooled to 0 °C, Et₃N (0,03 ml, 0,22 mmol) and phenol (22 mg, 0.23 mmol) were added. The resultant mixture was stirred at 0 °C for 1h, then at room temperature for 1 h. The reaction mixture was filtered off and the solvent was evaporated. Chromatographic purification (toluene, Ar) afforded **L11** as a fluffy yellow solid (104 mg, 70%). ¹H NMR (400 MHz, CD₂Cl₂) δ 7.95 (dd, *J* = 11.2, 8.4 Hz, 1H), 7.89 (s, 1H), 7.49 (ddd, *J* = 10.9, 8.2, 6.98 Hz, 1H), 7.41 (ddd, *J* = 7.9, 8.2, 6.98 Hz, 1H), 7.33-7.28 (m, 1H), 7.15-7.10 (m, 4H), 7.06-6.93 (m, 2H), 6.07 (d, *J* = 7.5 Hz, 1H), 3.01 (m, *J* = 7.0 Hz, 1H), 3.00 (m, *J* = 7.0 Hz, 1H), 2.91 (m, *J* = 6.6 Hz, 1H), 2.81 (m, *J* = 6.6 Hz, 1H), 2.73 (m, *J* = 6.6 Hz, 1H), 2.60 (m, *J* = 6.6 Hz, 1H), 1.20-0.94 (m, 36H). ³¹P{¹H}-NMR (162 MHz, CD₂Cl₂) δ 140.4.

BINOL Phosphites L12 – General methodology



In a typical procedure,^{9,10} a solution of PCl_3 (42.7 mg, 374 μmol , 3.0 eq.) in THF (0.5 mL) was added dropwise to a solution of (*R*)-3,3'-bis(triphenylsilyl)-[1,1'-binaphthalene]-2,2'-diol (**3**, 100 mg, 125 μmol , 1.0 eq.) in THF (0.5 mL) at $-40\text{ }^\circ\text{C}$. After stirring at $-40\text{ }^\circ\text{C}$ for 10 min, a solution of NEt_3 (63 mg, 623 μmol , 5.0 eq.) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for another 2 h before being filtered through a Celite pad (rinsing with THF). The filtrate was concentrated under reduced pressure and the residue was treated with toluene (1 mL), and evaporated. The obtained solid was redissolved in THF (2 mL) and treated with a solution of NEt_3 (63.0 mg, 623 μmol , 5.0 eq.) in THF (0.5 mL) at RT. A solution of the appropriate phenol or alcohol (249 μmol , 2.0 eq.) in THF (0.5 mL) was added dropwise and the resulting mixture was stirred for 2 h at room temperature. After evaporation of the volatiles under reduced pressure, the residue was purified by column chromatography on silica gel (toluene, Ar) to provide the desired phosphite ligand (**L12**)a-l.

(*R*)-BINOL Phosphite **L12a**¹¹



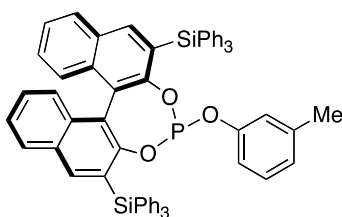
^1H NMR (400 MHz, CDCl_3) δ 8.07 (s, 1H), 7.93 (s, 1H), 7.83 (d, $J = 8.3$ Hz, 1H), 7.77 (d, $J = 8.3$ Hz, 1H), 7.59 (dt, $J = 6.6, 1.7$ Hz, 10 H), 7.54–7.52 (m, 5H), 7.34–7.31 (m, 6H), 7.25–7.21 (m, 10H), 6.82 (dd, $J = 7.5, 7.1$ Hz, 1H), 6.72 (t, $J = 7.8$ Hz, 2H), 5.78 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 157.46, 137.37, 136.91, 136.89, 136.75, 136.71, 136.66, 136.47, 136.43, 136.25, 134.70, 133.98, 133.02, 129.95, 129.84, 129.55, 129.48, 129.32, 129.18, 128.81, 128.23, 127.93, 127.84, 127.79, 127.75, 127.68, 127.60, 126.99, 125.77, 119.04, 115.69. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 150.5.

(*R*)-BINOL Phosphite **L12b**

9 Albrow, V. E.; Blake, A. J.; Fryatt, R.; Wilson, C.; Woodward, S. *Eur. J. Org. Chem.* **2006**, 2006, 2549–2557.

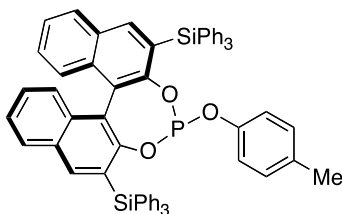
10 (a) Bedford, R. B.; Chang, Y.-N.; Haddow, M. F.; McMullin, C. L. *Dalton Trans.* **2011**, 40, 9034–9041. (b) Bedford, R. B.; Chang, Y.-N.; Haddow, M. F.; McMullin, C. L. *Dalton Trans.* **2011**, 40, 9042–9050.

11 Sakakura, A.; Sakuma, M.; Ishihara, K. *Org. Lett.* **2011**, 13, 3130–3133.



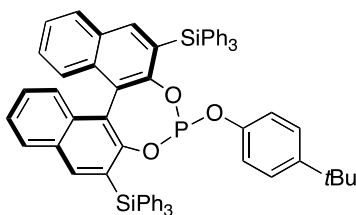
^1H NMR (400 MHz, CDCl_3) δ 8.06 (s, 1H), 7.90 (s, 1H), 7.81 (d, $J = 8.2$ Hz, 1H), 7.74 (d, $J = 8.1$ Hz, 1H), 7.68–7.65 (m, 1H), 7.58 (dd, $J = 8.0, 1.3$ Hz, 6H), 7.54 (dd, $J = 8.0, 1.3$ Hz, 6H), 7.43–7.38 (m, 2H), 7.37–7.28 (m, 10H), 7.24–7.19 (m, 11H), 6.62–6.56 (m, 2H), 5.59 (m, 2H), 1.90 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 156.61, 139.39, 136.77, 136.57, 136.56, 129.48, 129.31, 129.14, 129.09, 127.84, 127.78, 127.61, 127.57, 120.57, 116.23, 112.54. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 150.8.

(R)-BINOL Phosphite L12c



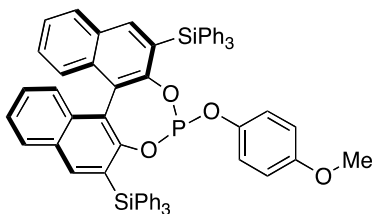
^1H NMR (400 MHz, CDCl_3) δ 8.06 (s, 1H), 7.90 (s, 1H), 7.80 (d, $J = 8.2$ Hz, 1H), 7.74 (d, $J = 8.2$ Hz, 1H), 7.57 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.53 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.42–7.37 (m, 2H), 7.36–7.29 (m, 8H), 7.26–7.19 (m, 14H), 6.49 (d, $J = 8.4$ Hz, 2H), 5.63 (d, $J = 8.3$ Hz, 2H), 2.15 (s, 3H). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 150.8.

(R)-BINOL Phosphite L12d



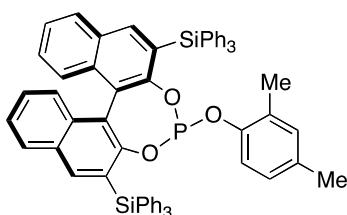
^1H NMR (400 MHz, CDCl_3) δ 8.04 (s, 1H), 7.91 (s, 1H), 7.80 (d, $J = 8.1$ Hz, 1H), 7.75 (d, $J = 8.1$ Hz, 1H), 7.57 (dd, $J = 8.0, 1.3$ Hz, 6H), 7.49 (dd, $J = 7.9, 1.2$ Hz, 6H), 7.42–7.29 (m, 12H), 7.24–7.19 (m, 12H), 6.68 (d, $J = 8.7$ Hz, 2H), 5.75 (d, $J = 8.6$ Hz, 2H), 1.21 (s, 9H). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 150.4.

(R)-BINOL Phosphite L12e



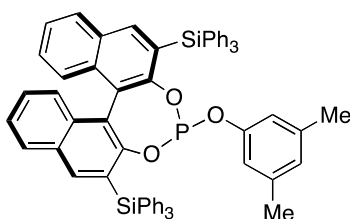
^1H NMR (400 MHz, CDCl_3) δ 8.05 (s, 1H), 7.90 (s, 1H), 7.80 (d, $J = 8.2$ Hz, 1H), 7.75 (d, $J = 8.2$ Hz, 1H), 7.63–7.68 (m, 1H), 7.58 (dd, $J = 8.0, 1.3$ Hz, 6H), 7.52 (dd, $J = 8.0, 1.3$ Hz, 6H), 7.45–7.10 (m, 23H), 6.21 (d, $J = 9.1$, 2H), 5.68 (d, $J = 8.7$, 2H), 3.67 (s, 3H). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 150.8.

(*R*)-BINOL Phosphite L12f



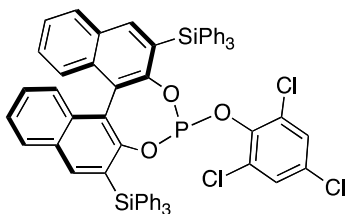
^1H NMR (400 MHz, CDCl_3) δ 7.99 (s, 1H), 7.92 (s, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.75 (d, $J = 8.7$ Hz, 1H), 7.56 (d, $J = 6.7$ Hz, 6H), 7.43 (d, $J = 6.9$ Hz, 6H), 7.39–7.34 (m, 2H), 7.30–7.26 (m, 6H), 7.24–7.12 (m, 16H), 6.58 (s, 1H), 6.31 (d, $J = 6.9$ Hz, 1H), 5.55 (d, $J = 8.1$ Hz, 1H), 2.15 (s, 3H), 1.27 (s, 3H). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 149.3.

(*R*)-BINOL Phosphite L12g



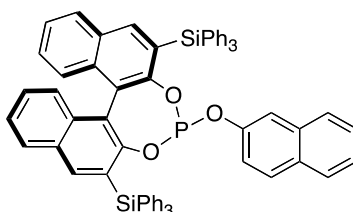
^1H NMR (400 MHz, CDCl_3) δ 8.06 (s, 1H), 7.88 (s, 1H), 7.81 (d, $J = 8.3$ Hz, 1H), 7.73 (d, $J = 8.3$ Hz, 1H), 7.58 (dd, $J = 7.9, 1.1$ Hz, 6H), 7.55 (dd, $J = 7.9, 1.0$ Hz, 6H), 7.42–7.37 (m, 2H), 7.35–7.27 (m, 10H), 7.25–7.19 (m, 12H), 6.44 (s, 1H), 5.42 (s, 2H), 1.85 (s, 6H). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 151.3.

(*R*)-BINOL Phosphite L12h



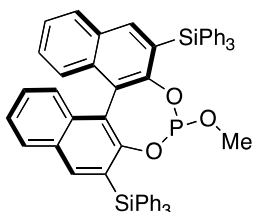
^1H NMR (400 MHz, CDCl_3) δ 7.93 (s, 1H), 7.91 (s, 1H), 7.78 (d, $J = 2.6$ Hz, 1H), 7.76 (d, $J = 2.5$ Hz, 1H), 7.60–7.58 (m, 6H), 7.48–7.45 (m, 6H), 7.38–7.41 (m, 2H), 7.11–7.32 (m, 22H), 6.83 (s, 2H). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 142.8.

(R)-BINOL Phosphite L12i



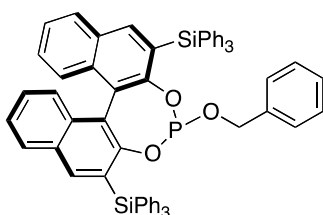
^1H NMR (400 MHz, CDCl_3) δ 8.09 (s, 1H), 7.91 (s, 1H), 7.82 (d, $J = 8.3$ Hz, 1H), 7.75 (d, $J = 8.1$ Hz, 1H), 7.71–7.63 (m, 2H), 7.60 (d, $J = 6.7$ Hz, 6H), 7.53 (d, $J = 6.9$ Hz, 6H), 7.42–7.13 (m, 26H), 7.03–7.00 (m, 1H), 6.19 (m, 1H), 5.94 (dd, $J = 8.9, 2.3$ Hz, 1H). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 150.1.

(R)-BINOL Phosphite L12j



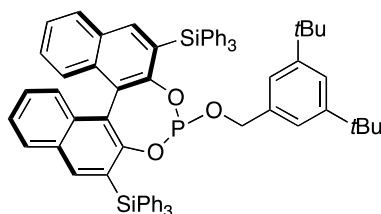
^1H NMR (400 MHz, CDCl_3) δ 8.05 (s, 1H), 7.96 (s, 1H), 7.80–7.75 (dd, $J = 7.7$ Hz, 2H), 7.66–7.63 (m, 1H), 7.62–7.58 (m, 10H), 7.43–7.27 (m, 20H), 7.24–7.14 (m, 5H), 2.37–2.34 (d, $J = 10.5$ Hz, 3H). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 148.7.

(R)-BINOL Phosphite L12k



^1H NMR (400 MHz, CDCl_3) δ 8.06 (s, 1H), 7.93 (s, 1H), 7.79 (d, $J = 8.2$ Hz, 1H), 7.75 (d, $J = 8.2$ Hz, 1H), 7.65–7.63 (m, 1H), 7.57–7.55 (m, 12H), 7.42–7.32 (m, 10H), 7.31–7.27 (m, 10H), 7.23–7.17 (m, 3H), 7.05 (t, $J = 7.4$ Hz, 1H), 6.88 (t, $J = 7.6$ Hz, 2H), 6.50 (d, $J = 7.6$ Hz, 2H), 3.60 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 140.76, 136.80, 136.73, 136.55, 136.48, 136.44, 136.37, 136.26, 134.67, 134.49, 134.31, 133.84, 130.65, 130.12, 129.95, 129.55, 129.46, 129.43, 128.71, 128.68, 128.35, 128.29, 128.22, 127.98, 127.85, 127.79, 127.66, 127.60, 127.56, 127.26, 126.96, 126.90, 126.79, 126.70, 126.45, 124.71, 124.67. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 151.1.

(*R*)-BINOL Phosphite L121

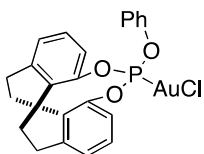


^1H NMR (400 MHz, CDCl_3) δ 8.04 (s, 1H), 7.97 (s, 1H), 7.79 (d, $J = 8.2$ Hz, 1H), 7.75 (d, $J = 8.1$ Hz, 1H), 7.65–7.63 (m, 1H), 7.58 (dd, $J = 8.0, 1.3$ Hz, 6H), 7.51 (dd, $J = 7.9, 1.2$ Hz, 6H), 7.44–7.27 (m, 14H), 7.24–7.20 (m, 10H), 6.53 (d, $J = 1.7$ Hz, 2H), 3.87 (dd, $J = 12.2, 6.6$ Hz, 1H), 3.60 (dd, $J = 12.1, 6.6$ Hz, 1H), 1.18 (s, 18H). ^{13}C NMR (126 MHz, CDCl_3) δ 150.93, 140.30, 136.75, 136.52, 136.50, 136.46, 136.28, 135.46, 134.70, 134.25, 134.02, 133.06, 129.96, 129.56, 129.54, 129.51, 129.11, 128.24, 127.94, 127.83, 127.81, 127.61, 127.59, 127.56, 127.13, 125.47, 123.86, 122.74, 122.34, 121.55, 121.33, 100.02, 100.00, 65.75, 34.85, 31.49, 31.42, 30.34. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 147.2.

Synthesis of Chiral Au(I) Complexes.

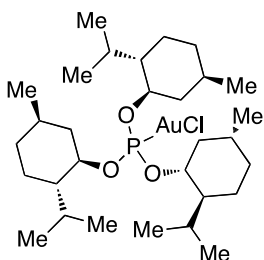
In a typical experiment, a solution of the desired ligand (46.3 μmol , 1.0 eq.) in CH_2Cl_2 (0.5 mL) was added dropwise to a suspension of $(\text{Me})_2\text{SAuCl}$ (46.3 μmol , 1.0 eq.) in CH_2Cl_2 (0.5 mL) at 0 °C. The resulting clear solution was allowed to warm to room temperature and stirred for another 30 min. The solvent was removed to give the corresponding chiral Au(I) chloride phosphite complex as a white solid (46.3 μmol , quantitative).

Gold complex L7(AuCl)⁶



^1H NMR (400 MHz, CDCl_3) δ 7.44 (t, $J = 7.8$ Hz, 2H), 7.36-7.28 (m, 3H), 7.25-7.22 (m, 4H), 7.19 (d, $J = 8.1$ Hz, 1H), 7.01 (d, $J = 7.7$ Hz, 2H), 3.24-3.01 (m, 2H), 2.95 (td, $J = 15.9, 7.8$ Hz, 2H), 2.35 (ddd, $J = 11.8, 6.5, 4.3$ Hz, 2H), 2.14-2.03 (m, 2H).

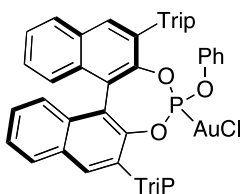
Gold complex L8(AuCl)



^1H NMR (400 MHz, CDCl_3) δ 4.31-4.23 (m, 3H), 2.22-2.16 (m, 3H), 2.13 (qt, $J = 7.0, 2.0$ Hz, 3H), 1.70 (brs, 3H), 1.67 (brs, 1H), 1.45-1.35 (m, 6H), 1.18 (td, $J = 12.3, 11.0$ Hz, 3H), 1.03 (qd, $J = 13.1, 3.2$ Hz, 3H), 0.93 (dd, $J = 6.8, 2.9$ Hz, 18H), 0.86 (d, $J = 7.0$ Hz, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 73.69, 73.57, 63.49, 49.08, 49.06, 45.19, 44.50, 44.48, 43.52, 43.39, 34.66, 34.37, 34.21, 31.88, 31.75, 25.70, 25.63, 25.43, 25.15, 24.36, 23.27, 23.02, 22.94, 22.88, 22.32, 22.22, 22.09, 22.01, 21.99, 21.97, 15.79. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 116.4.

The structure of this complex was determined by X-ray crystallography: **CCDC 933756**.

Gold complex L11 (AuCl)

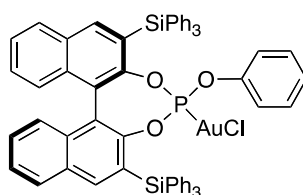


^1H NMR (400 MHz, CDCl_3) δ 8.0 (d, $J = 24.7$ Hz, 2H), 7.97 (dd, $J = 14.5, 8.2$ Hz, 2H), 7.59 (ddd, $J = 8.0, 6.2, 1.8$ Hz, 1H), 7.54 (ddd, $J = 8.1, 6.8, 1.3$ Hz, 1H), 7.41-7.36 (m, 3H), 7.33-7.26 (m, 2H), 7.21-7.13 (m, 5H), 7.08 (dd, $J = 10.6, 1.6$ Hz, 2H), 7.04-7.00 (m, 3H), 6.17 (dm, $J = 7.2, 1.4$ Hz, 2H), 2.99 (m, $J = 6.8$ Hz, 2H), 2.84 (m, $J = 6.8$ Hz, 2H), 2.61 (m, $J = 6.8$ Hz, 2H), 1.38 (d, $J = 6.9$ Hz, 6H), 1.32 (d, $J = 6.8$ Hz,

24H), 1.20 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 147.65, 147.55, 147.38, 147.07, 146.84, 132.61, 132.23, 131.87, 130.91, 129.84, 128.50, 128.33, 127.53, 127.23, 126.39, 126.25, 125.81, 125.66, 121.52, 121.22, 120.93, 120.54, 34.39, 34.37, 31.33, 31.00, 27.55, 26.08, 25.76, 25.33, 24.92, 24.32, 24.19, 24.17, 24.09, 23.84, 23.73, 23.43, 23.27. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CD_2Cl_2) δ 123.9.

The structure of this complex was determined by X-ray crystallography: **CCDC 933751**.

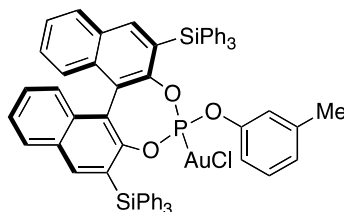
Gold complex L12(AuCl)a



^1H NMR (400 MHz, CDCl_3) δ 8.18 (s, 1H), 8.08 (s, 1H), 7.89 (d, $J = 8.3$ Hz, 1H), 7.83 (d, $J = 8.3$ Hz, 1H), 7.59-7.56 (m, 6H), 7.51-7.48 (m, 6H), 7.39-7.30 (m, 12H), 7.26-7.22 (m, 12H), 7.03 (t, $J = 7.7$ Hz, 1H), 6.90 (t, $J = 7.7$ Hz, 2H), 6.05 (d, $J = 8.2$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.47, 137.12, 137.03, 136.92, 136.86, 136.82, 136.78, 136.58, 136.55, 136.52, 136.40, 134.64, 134.49, 129.70, 129.67, 129.63, 129.56, 128.37, 128.16, 128.06, 128.00, 127.91, 127.88, 127.81, 127.75, 120.12, 115.58. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 123.7.

The structure of this complex was determined by X-ray crystallography: **CCDC 933752**.

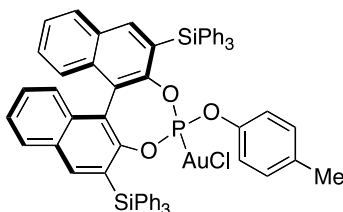
Gold complex L12(AuCl)b



^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 1H), 8.08 (s, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.68-7.65 (m, 1H), 7.56 (dd, $J = 8.0, 1.4$ Hz, 6H), 7.51 (dd, $J = 8.0, 1.2$ Hz, 6H), 7.48-7.27 (m, 16H), 7.25-7.21 (m, 7H), 6.82 (d, $J = 7.4$ Hz, 1H), 6.77 (t, $J = 7.8$ Hz, 1H), 5.87 (d, $J = 7.8$ Hz, 1H), 5.83 (s, 1H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.45, 139.57, 137.10, 136.90, 136.84, 136.80, 136.75, 136.58,

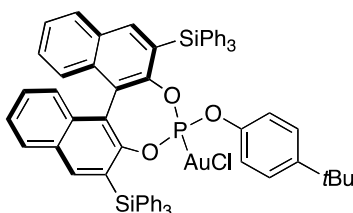
136.54, 136.51, 136.39, 135.29, 134.39, 133.48, 133.25, 130.05, 130.01, 129.91, 129.42, 129.29, 128.33, 128.16, 128.08, 128.05, 127.91, 127.88, 127.79, 120.91, 116.28, 112.57, 21.47. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 123.1.

Gold complex L12(AuCl)c



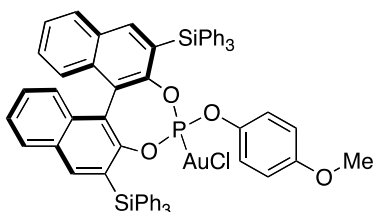
^1H NMR (400 MHz, CDCl_3) δ 8.17 (s, 1H), 8.07 (s, 1H), 7.87 (d, $J = 8.1$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.57 (dd, $J = 8.0, 1.4$ Hz, 6H), 7.50 (dd, $J = 8.0, 1.3$ Hz, 6H), 7.50-7.45 (m, 2H), 7.40-7.28 (m, 15H), 7.25-7.18 (m, 7H), 6.67 (d, $J = 8.6$ Hz, 2H), 5.89 (dd, $J = 8.5, 1.4$ Hz, 2H), 2.24 (s, 3H). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 123.8.

Gold complex L12(AuCl)d



^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 1H), 8.09 (s, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.59-7.54 (m, 6H), 7.53-7.44 (m, 8H), 7.40-7.26 (m, 15H), 7.24-7.19 (m, 7H), 6.88 (d, $J = 8.7$ Hz, 2H), 6.03 (d, $J = 8.5$ Hz, 2H), 1.27 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 136.81, 136.60, 133.58, 133.32, 130.09, 130.05, 128.38, 128.21, 127.97, 126.21, 120.60, 120.56, 34.49, 31.52, 29.86. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 123.8. HRMS-ESI m/z calculated for $\text{C}_{63}\text{H}_{47}\text{AuClO}_3\text{PSi}_2^+$ [$\text{M}^+ - \text{Cl}$]: 1177.2931. Found 1177.2927.

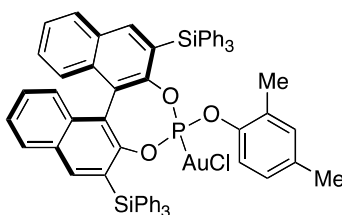
Gold complex L12(AuCl)e



^1H NMR (400 MHz, CDCl_3) δ 8.17 (s, 1H), 8.07 (s, 1H), 7.87 (d, $J = 7.9$ Hz, 1H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.68-7.65 (m, 1H), 7.59-7.57 (m, 6H), 7.51-7.49 (m, 6H), 7.39-7.15 (m, 23H), 6.37 (d, $J = 9.1$ Hz, 2H), 5.93 (dd, $J = 9.0, 1.4$ Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 156.95, 156.92, 151.21, 151.03, 149.83, 142.28, 142.11, 142.05, 141.96, 136.70, 136.61, 136.46, 136.38, 136.08, 134.65, 134.35, 134.08, 133.44, 133.16, 131.29, 130.93, 130.02, 129.98, 129.06, 128.98, 128.90, 128.30, 128.25, 128.11, 127.90, 127.81, 127.75, 126.92, 126.69, 126.25, 126.15, 125.95, 125.86, 125.32, 122.44, 122.40, 122.01, 121.97, 121.82, 121.75, 114.18, 55.61. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 124.2. HRMS-ESI m/z calculated for $\text{C}_{63}\text{H}_{47}\text{AuClO}_4\text{PSi}_2^+ [\text{M}^+ - \text{Cl}]$: 1151.2411. Found 1151.2402.

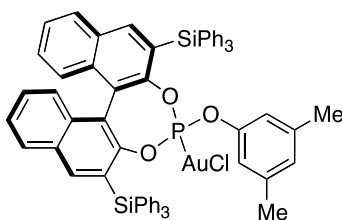
The structure of this complex was determined by X-ray crystallography: **CCDC 933757**.

Gold complex L12(AuCl)f



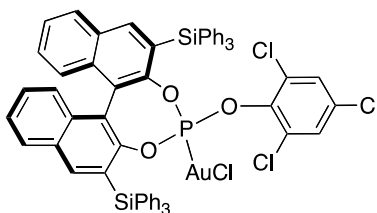
^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1H), 8.09 (s, 1H), 7.87 (d, $J = 8.2$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.59-7.42 (m, 14H), 7.40-7.20 (m, 16H), 7.19-7.13 (m, 6H), 6.70 (bs, 1H), 6.48 (dd, $J = 8.6, 1.9$ Hz, 1H), 6.00 (d, $J = 8.2$ Hz, 1H), 2.23 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.25, 151.15, 149.98, 145.48, 145.42, 142.27, 141.97, 136.70, 136.55, 134.85, 134.41, 134.10, 133.48, 133.25, 131.71, 131.38, 131.00, 130.00, 129.92, 129.24, 129.21, 129.10, 129.05, 128.28, 128.10, 128.01, 127.98, 127.03, 126.72, 126.59, 126.24, 126.21, 126.18, 126.04, 122.72, 122.69, 122.21, 122.19, 120.72, 120.68, 29.85, 20.80, 16.20. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 123.2. HRMS-ESI m/z calculated for $\text{C}_{64}\text{H}_{49}\text{AuClO}_3\text{PSi}_2^+ [\text{M}^+ - \text{Cl}]$: 1149.2618. Found 1149.2652.

Gold complex L12(AuCl)g



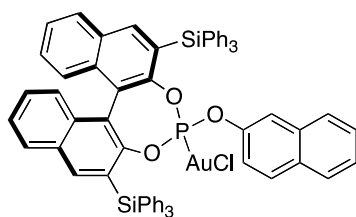
^1H NMR (400 MHz, CDCl_3) δ 8.14 (s, 1H), 8.07 (s, 1H), 7.87 (d, $J = 8.2$ Hz, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.58-7.45 (m, 14H), 7.40-7.19 (m, 22H), 6.63 (bs, 1H), 5.68 (bs, 2H), 1.94 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.41, 148.82, 148.77, 142.39, 142.04, 139.06, 136.82, 136.68, 134.43, 134.22, 133.53, 133.34, 131.40, 131.04, 130.06, 130.01, 129.06, 128.35, 128.20, 128.05, 128.01, 127.18, 126.97, 126.79, 126.39, 126.25, 126.07, 118.55, 118.51, 29.85, 21.02. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 122.6. HRMS-ESI m/z calculated for $\text{C}_{64}\text{H}_{49}\text{AuClO}_3\text{PSi}_2^+$ [$\text{M}^+ - \text{Cl}$]: 1149.2618 found 1149.2611.

Gold complex L12(AuCl)h



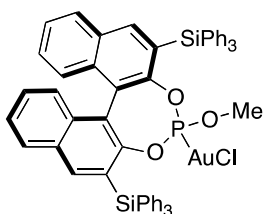
^1H NMR (400 MHz, CDCl_3) δ 8.18 (s, 1H), 8.03 (s, 1H), 7.88 (d, $J = 8.1$ Hz, 1H), 7.81 (d, $J = 8.3$ Hz, 1H), 7.64 (dd, $J = 7.9, 1.4$ Hz, 6H), 7.53-7.47 (m, 2H), 7.45 (dd, $J = 8.0, 1.2$ Hz, 6H), 7.39-7.14 (m, 22H), 6.89 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.48, 151.37, 149.41, 149.35, 147.06, 142.51, 142.07, 140.68, 140.59, 136.75, 136.33, 134.54, 134.35, 134.34, 133.29, 133.12, 131.48, 131.08, 131.02, 131.01, 129.94, 129.91, 129.16, 129.08, 128.99, 128.66, 128.53, 128.50, 128.36, 128.22, 128.16, 128.07, 128.04, 127.10, 126.70, 126.45, 126.15, 125.82, 125.79, 125.45, 122.69, 122.66, 122.55, 122.52, 121.75. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 124.1. HRMS-ESI m/z calculated for $\text{C}_{62}\text{H}_{42}\text{AuCl}_3\text{O}_3\text{PSi}_2^+$ [$\text{M}^+ - \text{Cl}$]: 1223.1136 found 1226.1160.

Gold complex L12(AuCl)i



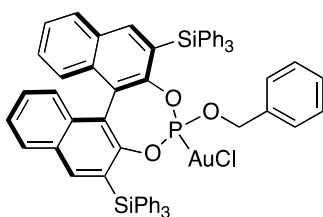
^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 1H), 8.08 (s, 1H), 7.89 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 8.1$ Hz, 1H), 7.74 (d, $J = 8.4$ Hz, 1H), 7.56-7.53 (m, 6H), 7.48-7.45 (m, 6H), 7.44-7.27 (m, 16H), 7.25-7.23 (m, 4H), 7.15-7.11 (m, 7H), 6.43 (t, $J = 1.9$ Hz, 1H), 6.22 (ddd, $J = 8.9, 2.4, 0.8$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.36, 151.25, 149.30, 149.24, 146.95, 142.39, 141.96, 140.57, 140.48, 136.64, 136.22, 134.43, 134.24, 134.22, 133.17, 133.01, 131.37, 130.97, 130.91, 130.89, 129.82, 129.79, 129.05, 128.97, 128.88, 128.55, 128.41, 128.39, 128.24, 128.10, 128.04, 127.96, 127.93, 126.98, 126.58, 126.34, 126.04, 125.71, 125.68, 125.34, 122.57, 122.55, 122.43, 122.40, 121.63. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 122.8. HRMS-ESI m/z calculated for $\text{C}_{66}\text{H}_{47}\text{AuClO}_3\text{PSi}_2^+$ [$\text{M}^+ - \text{Cl}$]: 1170.7673 found 1170.7670.

Gold complex L12(AuCl)j



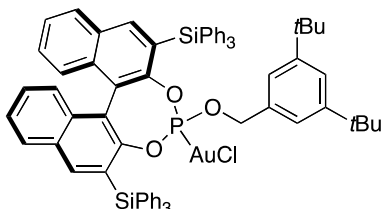
^1H NMR (400 MHz, CDCl_3) δ 8.14 (s, 1H), 8.13 (s, 1H), 7.84 (s, 1H), 7.82 (s, 1H), 7.64-7.59 (m, 12H), 7.49-7.33 (m, 24H), 2.53 (d, $J = 15.6$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 150.95, 150.78, 149.56, 149.48, 142.22, 141.86, 137.05, 136.68, 136.33, 134.28, 134.07, 133.95, 133.86, 133.42, 131.22, 130.83, 130.12, 129.90, 129.56, 129.06, 128.92, 128.25, 128.16, 127.92, 127.85, 126.84, 126.75, 126.13, 126.08, 125.91, 125.80, 125.33, 122.94, 122.89, 121.85, 121.82, 67.15. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 130.5. HRMS-ESI m/z calculated for $\text{C}_{57}\text{H}_{43}\text{AuClO}_3\text{PSi}_2^+$ [$\text{M}^+ - \text{Cl}$]: 1059.2148 found 1059.2140.

Gold complex L12(AuCl)k



^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 5.8$ Hz, 2H), 7.86 (d, $J = 7.7$ Hz, 1H), 7.84 (d, $J = 7.7$ Hz, 1H), 7.66-7.63 (m, 1H), 7.60 (dd, $J = 8.0, 1.3$ Hz, 6H), 7.49 (dd, $J = 8.0, 1.3$ Hz, 8H), 7.41-7.32 (m, 10H), 7.29 (dd, $J = 7.6, 2.4$ Hz, 10H), 7.25-7.18 (m, 2H), 7.14 (t, $J = 7.5$ Hz, 2H), 6.68 (d, $J = 7.2$ Hz, 2H), 3.94 (dd, $J = 11.8, 9.0$ Hz, 1H), 3.70 (dd, $J = 11.9, 7.5$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 140.76, 136.80, 136.73, 136.55, 136.48, 136.44, 136.37, 136.26, 134.67, 134.49, 134.31, 133.84, 130.65, 130.12, 129.95, 129.55, 129.46, 129.43, 128.71, 128.68, 128.35, 128.29, 128.22, 127.98, 127.85, 127.79, 127.66, 127.60, 127.56, 127.26, 126.96, 126.90, 126.79, 126.70, 126.45, 124.71, 124.67, 99.99, 67.94, 67.26, 65.23, 65.12, 64.82, 45.86. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 126.8. HRMS-ESI m/z calculated for $\text{C}_{63}\text{H}_{47}\text{AuClO}_3\text{PSi}_2^+$ [$\text{M}^+ - \text{Cl}$]: 1134.7673 found 1134.7670.

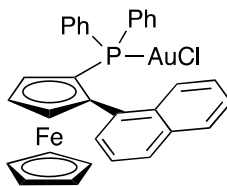
Gold complex L12(AuCl)



^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 6.2$ Hz, 2H), 7.84 (d, $J = 8.4$ Hz, 2H), 7.67-7.64 (m, 1H), 7.59 (dd, $J = 8.0, 1.3$ Hz, 6H), 7.48 (dd, $J = 8.0, 1.3$ Hz, 6H), 7.52-7.45 (m, 2H), 7.39-7.31 (m, 11H), 7.30-7.26 (m, 5H), 7.25-7.18 (m, 6H), 6.61 (d, $J = 1.8$ Hz, 2H), 3.93 (dd, $J = 11.3, 8.4$ Hz, 1H), 3.78 (dd, $J = 11.4, 6.9$ Hz, 1H), 1.20 (s, 18H). ^{13}C NMR (75 MHz, CDCl_3) δ 152.97, 151.22, 149.85, 149.75, 148.89, 148.81, 142.21, 141.98, 136.62, 136.54, 134.28, 134.07, 133.37, 133.16, 131.28, 130.95, 129.94, 129.87, 128.96, 128.87, 128.21, 128.02, 127.89, 126.93, 126.73, 126.28, 126.15, 126.11, 126.07, 125.94, 122.64, 122.44, 122.09, 122.04, 117.92, 34.64, 31.08, 29.73. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 125.6. HRMS-ESI m/z calculated for $\text{C}_{71}\text{H}_{63}\text{AuClO}_3\text{PSi}_2^+$ [$\text{M}^+ - \text{Cl}$]: 1224.6273 found 1224.6271.

Synthesis of Ferrocenyl Phosphine Au(I) Complexes

Chiral ferrocenyl phosphines **L9** and **L10** were prepared following a reported procedure.¹²



Preparation of gold complex **L9(AuCl)**

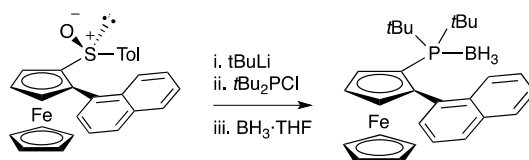
To a stirred solution of (tht)AuCl (24 mg, 0.10 mmol) in THF (2 mL) a solution of (*S*)-2-(1-naphtyl)-1-(diphenylphosphanyl)ferrocene¹³ in THF (2 mL) was dropwise added at 0 °C. The mixture was stirred for 55 min. The solvent was evaporated, then hexane was added (2 mL) and quickly evaporated. The procedure was repeated three times. The crude green-yellowish solid was purified by flash chromatography (7:3 hexanes/EtOAc) to give a bright-orange solid, which was crystallized from 25/1 diethyl ether/dichloromethane mixture to give **L9(AuCl)** in 92% yield. $[\alpha]_D = -41.4$. ¹H NMR (400 MHz, CDCl₃) δ 8.51 (d, $J = 6.9$ Hz, 1H), 7.84 – 7.76 (m, 3H), 7.71 (dd, $J = 10.3, 2.7$ Hz, 1H), 7.60 (dt, $J = 10.6, 5.3$ Hz, 1H), 7.57 – 7.47 (m, 3H), 7.25 (ddd, $J = 9.3, 7.6, 3.4$ Hz, 4H), 7.21 – 7.14 (m, 1H), 7.06 (ddd, $J = 5.8, 5.2, 2.1$ Hz, 3H), 4.77 (dd, $J = 3.7, 2.0$ Hz, 1H), 4.73 (td, $J = 2.5, 0.7$ Hz, 1H), 4.45 (s, 5H), 4.24 – 4.19 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 134.40 (d, $J = 14.4$ Hz), 133.34, 133.29 (d, $J = 14.5$ Hz), 132.38 (d, $J = 90.1$ Hz), 131.78, 131.67 (d, $J = 2.5$ Hz), 131.00 (d, $J = 2.6$ Hz), 130.66 (d, $J = 5.7$ Hz), 128.80 (d, $J = 6.6$ Hz), 128.68, 128.38, 128.19 (d, $J = 5.6$ Hz), 94.79 (d, $J = 16.0$ Hz), 77.25, 76.44, 72.49 (d, $J = 7.6$ Hz), 70.41 (d, $J = 7.8$ Hz). ³¹P NMR (162 MHz, CDCl₃) δ 24.43. HRMS (MALDI+, m/z) calcd. for C₃₂H₂₅AuClFeP (M⁺) 728.03919, found 728.0669.

The structure of this complex was determined by X-ray crystallography: **CCDC 933753**.

(*S*)-2-(1-Naphtyl)-1-[di-*tert*-butylphosphanyl(borane)]ferrocene (**L10·BH₃**).

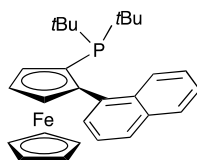
12 Jensen, J. F.; Sjøtofte, I.; Sørensen, H. O.; Johannsen M. *J. Org. Chem.* **2003**, *68*, 1258–1265.

13 Pedersen, H. L.; Johannsen, M. *J. Org. Chem.* **2002**, *67*, 7982–7994.



To a stirred solution of (S_P, S_S)-sulfoxide (1000 mg, 2.22 mmol) in THF (44 mL, 0.05 M) at $-78\text{ }^\circ\text{C}$ was added dropwise $t\text{-BuLi}$ (1.7 M solution in pentane, 2.1 mL, 3.55 mmol). The reaction was stirred for additional 15 min and $t\text{-Bu}_2\text{PCl}$ (1.054 mL, 5.55 mmol) was added dropwise to the dark red solution of the lithiated ferrocene. After being stirred for 30 min at $-78\text{ }^\circ\text{C}$, the reaction was heated quickly to $70\text{ }^\circ\text{C}$ and stirred for 48 h. The deep-red solution was then cooled to $-78\text{ }^\circ\text{C}$ and $\text{BH}_3\cdot\text{THF}$ (1M in THF, 11.100 mL, 11.1 mmol) was added slowly to the reaction via syringe. The reaction was heated quickly to $23\text{ }^\circ\text{C}$ and stirred at that temperature for 1 h followed by quenching with 2M NaOH and extraction with diethyl ether. The organic layer was washed with saturated brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The resulting residue was flash chromatographed through a short column of silica gel (99:1 hexane/diethyl ether) to give 285 mg (yield 28%) of **L10·BH₃** as an orange oil: $[\alpha]_D = -26.8$. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.38 (d, $J = 7.0\text{ Hz}$, 1H), 7.84 (d, $J = 8.1\text{ Hz}$, 2H), 7.70 (d, $J = 8.5\text{ Hz}$, 1H), 7.54 (t, $J = 7.7\text{ Hz}$, 1H), 7.39 (t, $J = 7.3\text{ Hz}$, 1H), 7.33 – 7.26 (m, 1H), 7.32 – 7.26 (m, 1H), 4.83 – 4.71 (m, 3H), 4.42 (s, 5H), 1.51 (d, $J = 7.9\text{ Hz}$, 3H), 1.30 (d, $J = 13.2\text{ Hz}$, 9H), 0.94 (d, $J = 12.8\text{ Hz}$, 9H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 134.93, 133.61, 133.07, 132.82, 128.36, 128.21, 126.24, 125.11, 124.91, 124.41, 94.18, 75.47, 75.18, 71.78, 71.17, 70.24, δ 34.39 (d, $J = 7.0\text{ Hz}$), 34.17 (d, $J = 7.2\text{ Hz}$), 29.36 (d, $J = 1.4\text{ Hz}$), 28.82. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 48.04 (dd, $J = 102.5, 49.4\text{ Hz}$). HRMS (ESI+, m/z) calcd. for $\text{C}_{28}\text{H}_{36}\text{BNaFeP}$ ($\text{M}+\text{Na}$) 493.1895, found 493.1897.

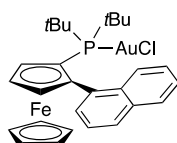
(*S*)-2-(1-Naphthyl)-1-(di-*tert*-butylphosphanyl)ferrocene (L10).



To a solution of **L10·BH₃** (185 mg, 0.39 mmol) in anhydrous toluene (19.5 mL, 0.02 M) was added DABCO (218 mg, 1.59 mmol), and the mixture was heated to $60\text{ }^\circ\text{C}$ for 7.5 h. After being concentrated under reduced pressure, the crude residue was purified by flash chromatography (9:1 pentane/AcOEt) to give **L10** 130 mg (73%

yield %) as a red-orange oil. ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 7.2$ Hz, 1H), 8.04 (d, $J = 8.4$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.77 (d, $J = 8.2$ Hz, 1H), 7.58 (dd, $J = 8.1, 7.3$ Hz, 1H), 7.38 (dddd, $J = 21.7, 8.2, 6.7, 1.3$ Hz, 2H), 4.90 (td, $J = 2.3, 1.3$ Hz, 1H), 4.70 (td, $J = 2.5, 0.8$ Hz, 1H), 4.53 (dd, $J = 2.6, 1.3$ Hz, 1H), 4.21 (d, $J = 4.0$ Hz, 5H), 1.61 (dd, $J = 11.6, 4.0$ Hz, 9H), 0.70 (t, $J = 7.5$ Hz, 9H). ^{31}P NMR (162 MHz) δ 17.7; HRMS (ESI+, m/z) calcd. for $\text{C}_{28}\text{H}_{33}\text{FeP}$ (M+1) 457.1748, found 457.1769.

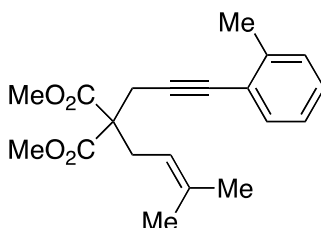
Gold complex L10(AuCl)



Gold complex **L10(AuCl)** was synthesized according to the procedure described for **L9(AuCl)**. $[\alpha]_{\text{D}} = +60.6$. ^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, $J = 6.9$ Hz, 1H), 7.94 (dd, $J = 30.9, 8.2$ Hz, 2H), 7.72 (d, $J = 8.4$ Hz, 1H), 7.69 – 7.64 (m, 1H), 7.42 (t, $J = 7.0$ Hz, 1H), 7.34 (dd, $J = 11.2, 4.1$ Hz, 1H), 5.00 (s, 1H), 4.88 (t, $J = 2.3$ Hz, 1H), 4.59 (s, 1H), 4.36 (s, 5H), 1.80 (d, $J = 15.6$ Hz, 9H), 0.95 (d, $J = 15.4$ Hz, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 133.81, 133.26, 132.98, 132.29, 128.90, 128.65, 126.04, 125.58, 125.52, 125.41, 94.96 (d, $J = 13.6$ Hz), 74.68 (d, $J = 6.5$ Hz), 72.94 (d, $J = 47.1$ Hz), 72.57 (d, $J = 8.4$ Hz), 71.97, 70.84 (d, $J = 5.8$ Hz), 37.28 (d, $J = 8.2$ Hz), 36.90 (d, $J = 8.2$ Hz), 30.99 (d, $J = 6.1$ Hz), 30.06 (d, $J = 6.1$ Hz). ^{31}P NMR (202 MHz, CDCl_3) δ 59.92 (s); HRMS (ESI+, m/z) calcd for $\text{C}_{28}\text{H}_{23}\text{FePNa}$ (M+Na) 711.0921, found 711.0921.

The structure of this complex was determined by X-ray crystallography: **CCDC 933754**.

2-(3-Methyl-but-2-enyl)-2-(3-*o*-tolyl-prop-2-ynyl)-malonic acid dimethyl ester (1e).

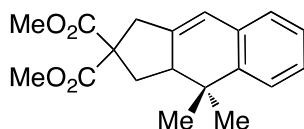


Enyne **1e** prepared in 72 % yield by Sonogashira coupling using 2-methyl-iodobenzene according to the reported procedure.⁷ ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, J = 7.5 Hz, 1H), 7.20-7.06 (m, 3H), 4.97 (t, J = 7.7 Hz, 1H), 3.75 (s, 6H), 3.05 (s, 2H), 2.85 (d, J = 7.7 Hz, 2H), 2.37 (s, 3H), 1.72 (s, 3H), 1.66 (s, 3H). ¹³C-NMR (101 MHz, CDCl₃) δ 171.3 (CO), 140.7 (C), 137.5 (C), 132.7 (CH), 130.0 (CH), 128.6 (CH), 126.1 (CH), 123.7 (C), 117.8 (CH), 89.2 (C), 82.8 (C), 58.2 (C), 53.3 (CH₃), 31.6 (CH₂), 26.8 (CH₂), 24.3 (CH₃), 21.4 (CH₃), 18.7 (CH₃).

Enantioselective Gold-Catalyzed [4+2] Cycloaddition

In a typical experiment, chiral gold(I) complex **L12(AuCl)d** (5mol%) and AgNTf₂ (5 mol%) were weighed in a glove box. CH₂Cl₂ (0.008 M) was added and the resulting solution was stirred for 10 min at 0 °C and further 10 min at room temperature. The obtained catalyst solution was cooled to the indicated temperature followed by dropwise addition of a solution of the desired enyne **I-13** (1.0 equiv) in CH₂Cl₂ (0.2 M) over 10 min. After complete addition, stirring was continued at the indicated temperature until the starting material was consumed. After quenching with a solution of NEt₃ in hexane (0.1 M, 1 mL), the solids were removed by filtration over silica. Evaporation of the solvent and chromatographic purification on silica (hexanes/EtOAc) provided the title compound. Enantiomeric excess was determined by chiral HPLC.

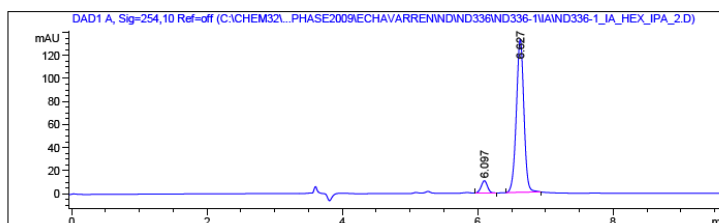
Dimethyl 4,4-Dimethyl-3a,4-dihydro-1H-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (2a)



2a was synthesized from **1a** according to the general procedure after stirring at -20 °C for 18 h (126 mg, 98% yield). Analytical data are in agreement with those reported.⁷

$[\alpha]_D^{25} = -25.0 \pm 2.0$ ($c = 0.1065$, CHCl_3). Enantiomeric excess: 88% *ee* (Chiralpak IA 250x4.6mm, 5 μm , HEX / IPA 98:2, 1 mL/min).

Sample Info : Chiralpak IA250x4.6mm, 5 μm
HEX / IPA 98:2
1 mL/min
2mg/mL (DCM)



=====
Area Percent Report
=====

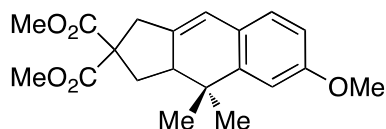
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.097	BB	0.0996	69.22163	10.68395	6.2756
2	6.627	BB	0.1186	1033.80090	133.07730	93.7244
Totals :				1103.02253	143.76125	

When the cyclization of **1a** was carried out in with $\text{L}(\text{AuCl})_2$ ($\text{L} = (R)\text{-4-MeO-3,5-}(t\text{Bu})_2\text{MeOBIPHEP} = \text{DTBM-MeO-BIPHEP}$) (3 mol%) and AgOTf (6 mol%) in Et_2O , in addition to **2a** (74 *ee*, estimated by chiral HPLC), known **4**¹⁴ was also obtained (72:28 ratio). We could not find conditions that would allow the full resolution of **4** and the enantiomers of **2a** by chiral HPLC. Presumably, in the presence of solvent such as Et_2O , more basic than CH_2Cl_2 , elimination to form **4** competes with the cycloaddition to form **2a**.

Dimethyl 6-Methoxy-4,4-dimethyl-3a,4-dihydro-1H-cyclopenta[*b*]naphthalene-2,2(3H)-dicarboxylate (2b)

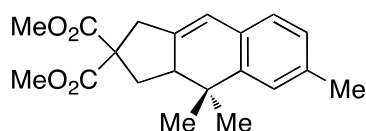


2b was synthesized from **1b** according to the general procedure after stirring at $-20\text{ }^\circ\text{C}$ for 30 h (120 mg, 85.5% yield). Analytical data are in agreement with those reported.⁷

14 Porcel, S.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2007**, *46*, 2672–2676.

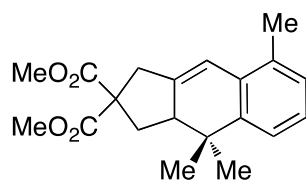
Enantiomeric excess: 86% *ee* (Chiralpak IC 250x4.6mm, 5 μ m, Hex / THF 98:2, 1 mL/min).

Dimethyl-4,4,6-trimethyl-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (2c)



2c was synthesized from **1c** according to the general procedure after stirring at -20 °C for 15 h (134 mg, 98% yield). Analytical data are in agreement with those reported.⁷ Enantiomeric excess: 87% *ee* (Chiralpak IC 250x4.6mm, 5 μ m, Hex / IPA 99:1, 1 mL/min).

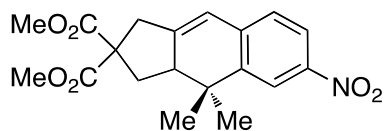
Dimethyl-4,4,8-trimethyl-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (2d)



2d was synthesized from **1e** according to the general procedure after stirring at -20 °C for 30 h (93 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.15 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.57-6.54 (m, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.32 (d, *J* = 19.2 Hz, 1H), 3.01 (dt, *J* = 17.9, 3 Hz, 1H), 2.70-2.55 (m, 2H), 2.32 (s, 3H), 2.14 (t, *J* = 12 Hz, 1H), 1.40 (s, 3H), 0.91 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.3, 172.1, 144.3, 143.1, 133.2, 132.3, 128.3, 126.6, 121.4, 116.2, 59.1, 53.0, 47.9, 39.8, 37.0, 35.0, 26.1, 21.8, 19.8; HRAPCI-MS *m/z* = 351.1 [M+Na]⁺, calc. for C₂₀H₂₄O₄ = 328.17.

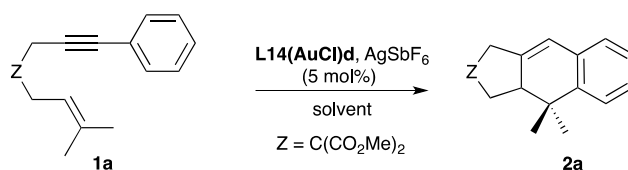
Enantiomeric excess: 79% *ee* (Chiralpak IC 250x4.6mm, 5 μ m, Hex / IPA 99:1, 1 mL/min)

Dimethyl 4,4-Dimethyl-6-nitro-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (2e)



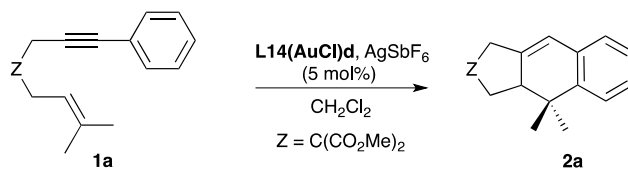
2d was synthesized from **1d** according to the general procedure after stirring at 0 °C for 15 h (118 mg, 80% yield). Analytical data are in agreement with those reported.⁷ Enantiomeric excess: 73% *ee* (Chiralpak IB 250x4.6mm, 5µm, HEX / IPA 96:4, 1 mL/min).

Influence of solvent on the cyclization of 1a to 2a.



Entry	Solvent	<i>t</i>	<i>ee</i> (%)
1	CH ₂ Cl ₂	2 h	82
2	CDCl ₃	1 h	79
3	DCE	20 h	63
4	Et ₂ O	20 h	82
5	toluene	2 days	n.r.
6	MeNO ₂	16 h	66
7	dioxane	1 day	n.r.
8	acetone- <i>d</i> ₆	1 day	82

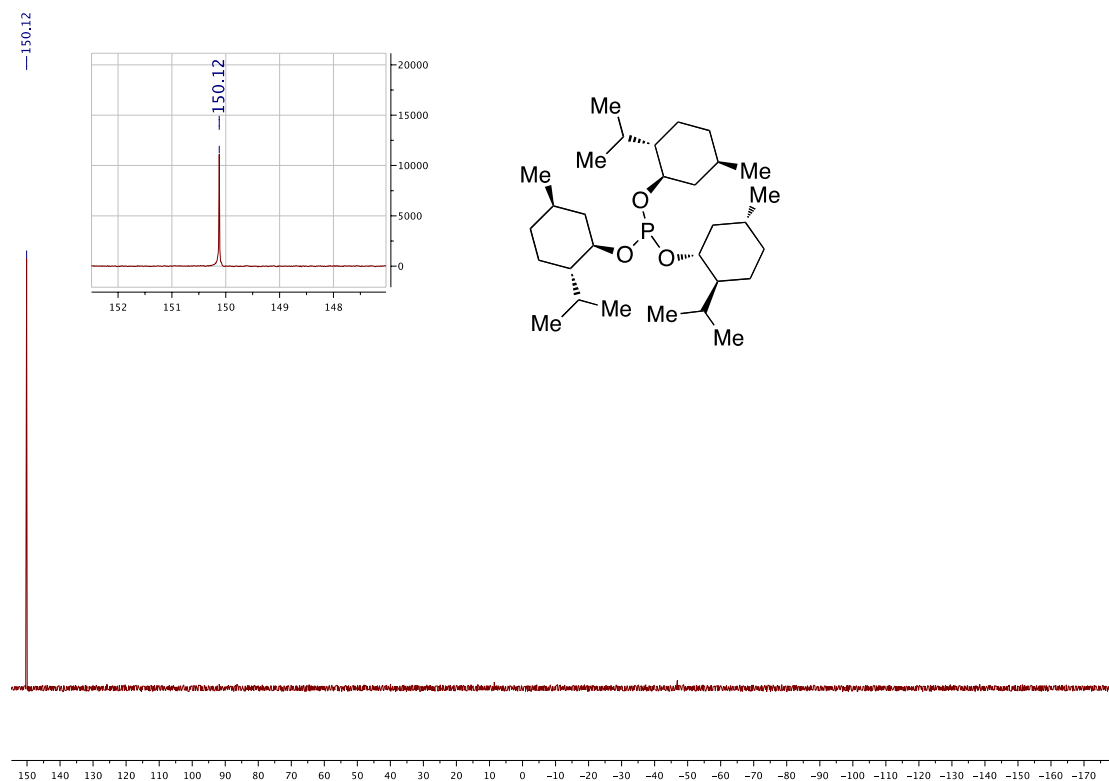
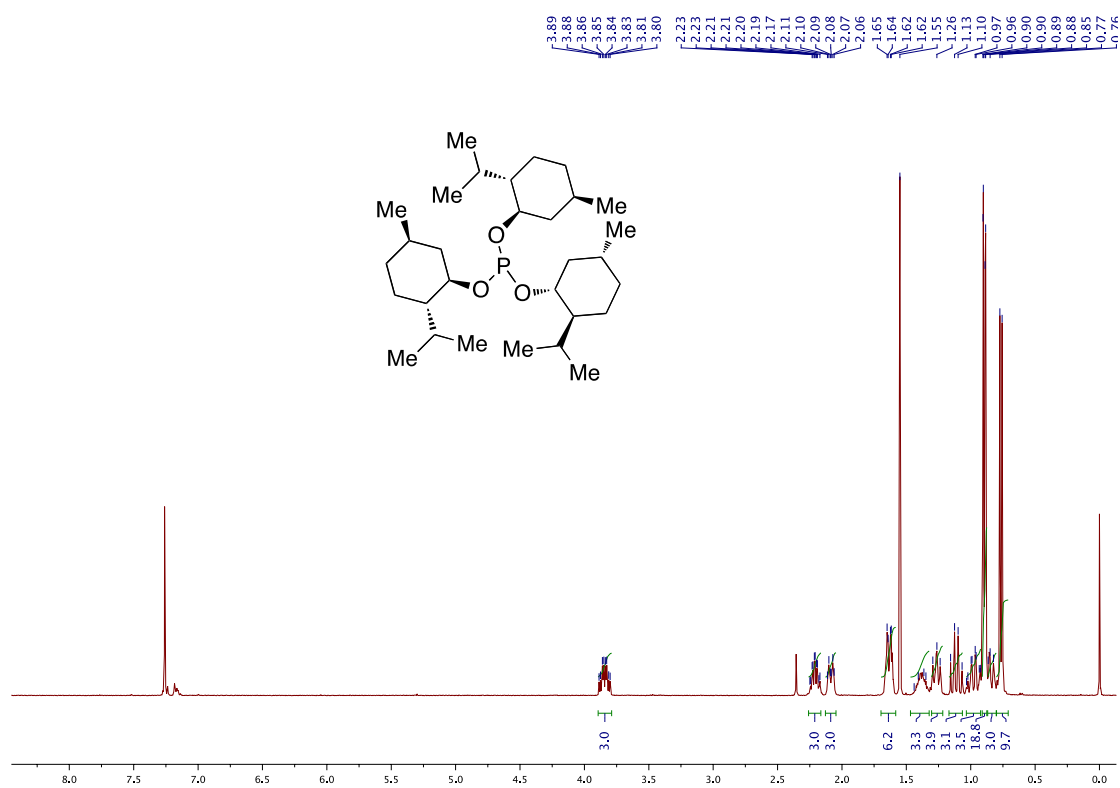
Influence of anion on the cyclization of 1a to 2a

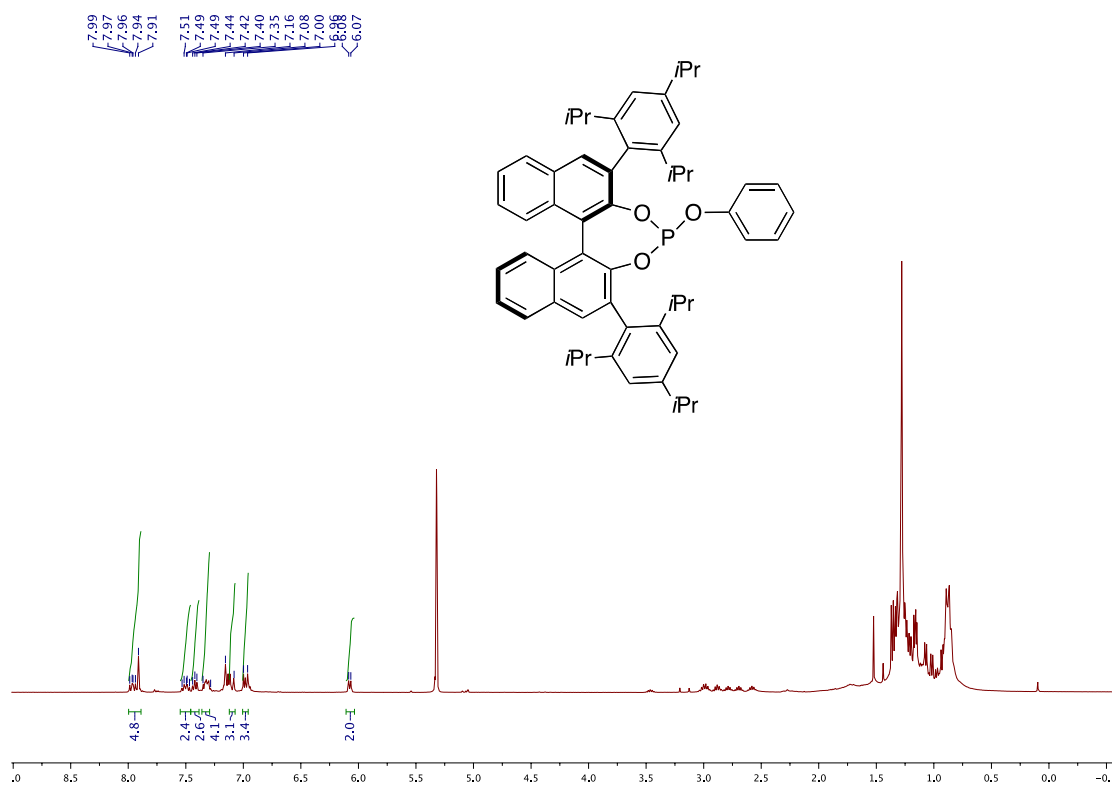
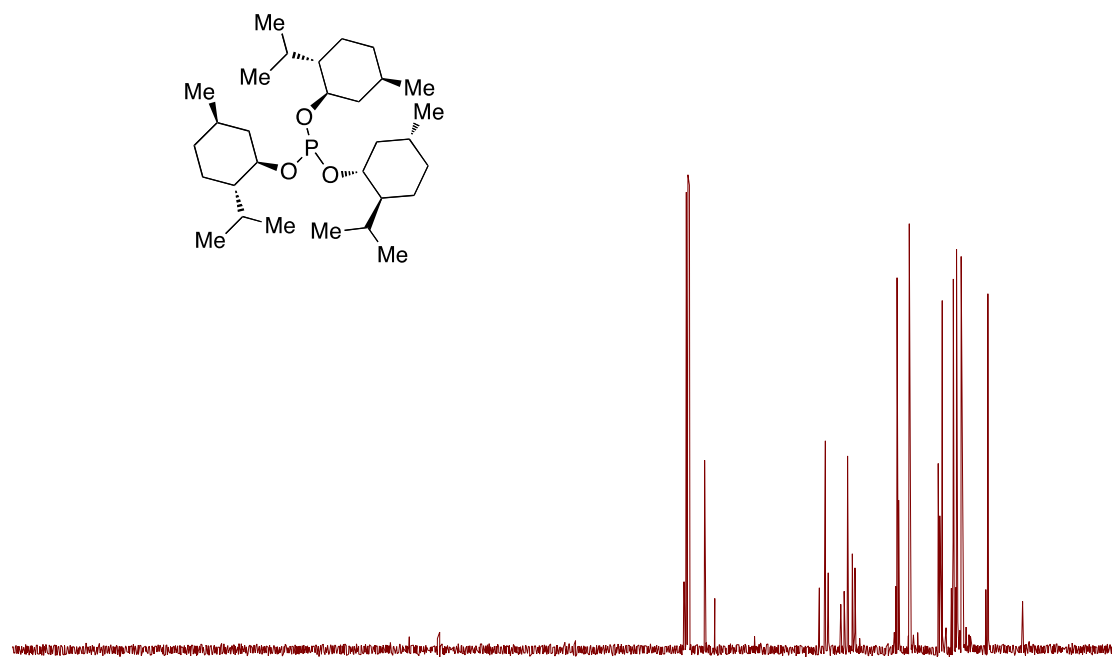


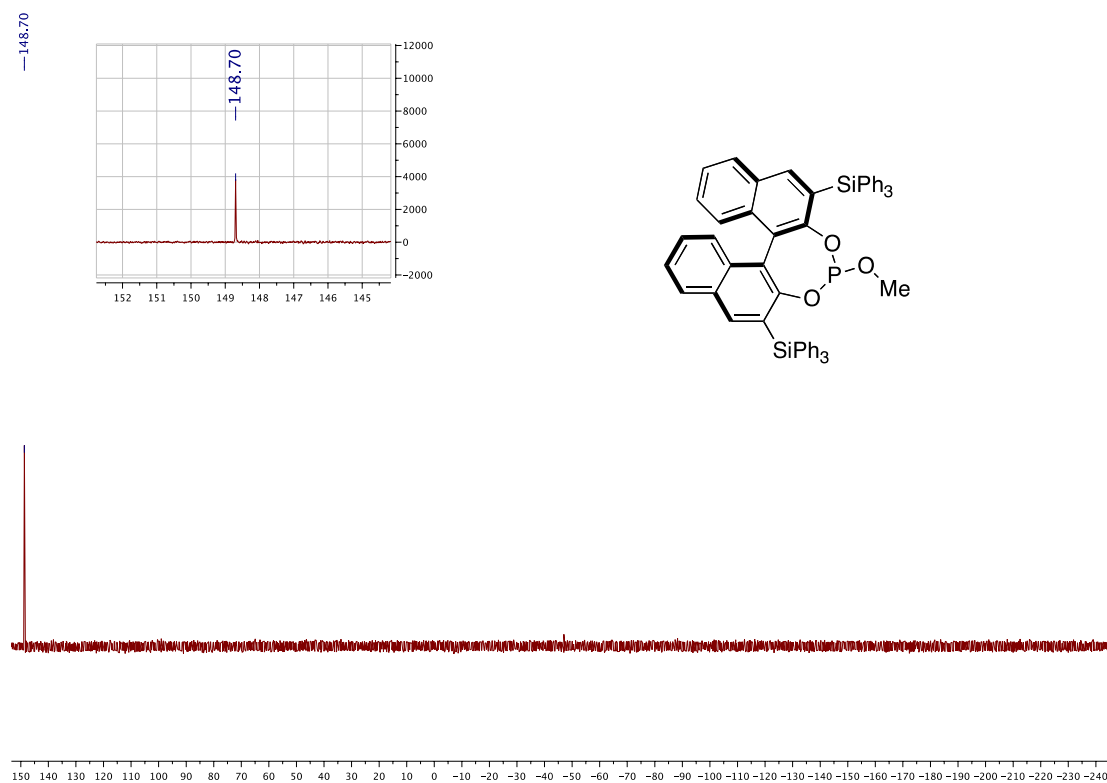
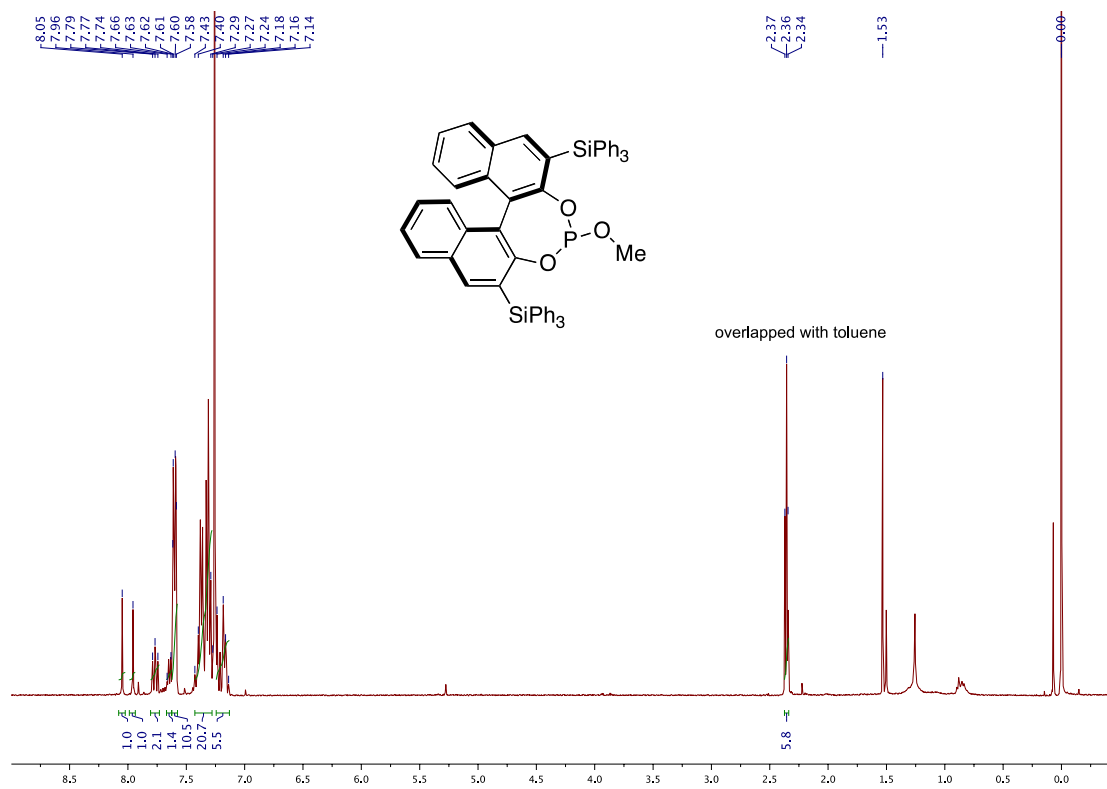
Entry	AgX	<i>t</i>	<i>ee</i> (%)
1	AgSbF ₆	2 h	82
2	AgOTf	2 h	80
3	AgOBz	1 day	n.r.
4	AgPF ₆	1 day	72
5	AgNTf ₂	2 h	82
6	NaBAR _F	1 day	81

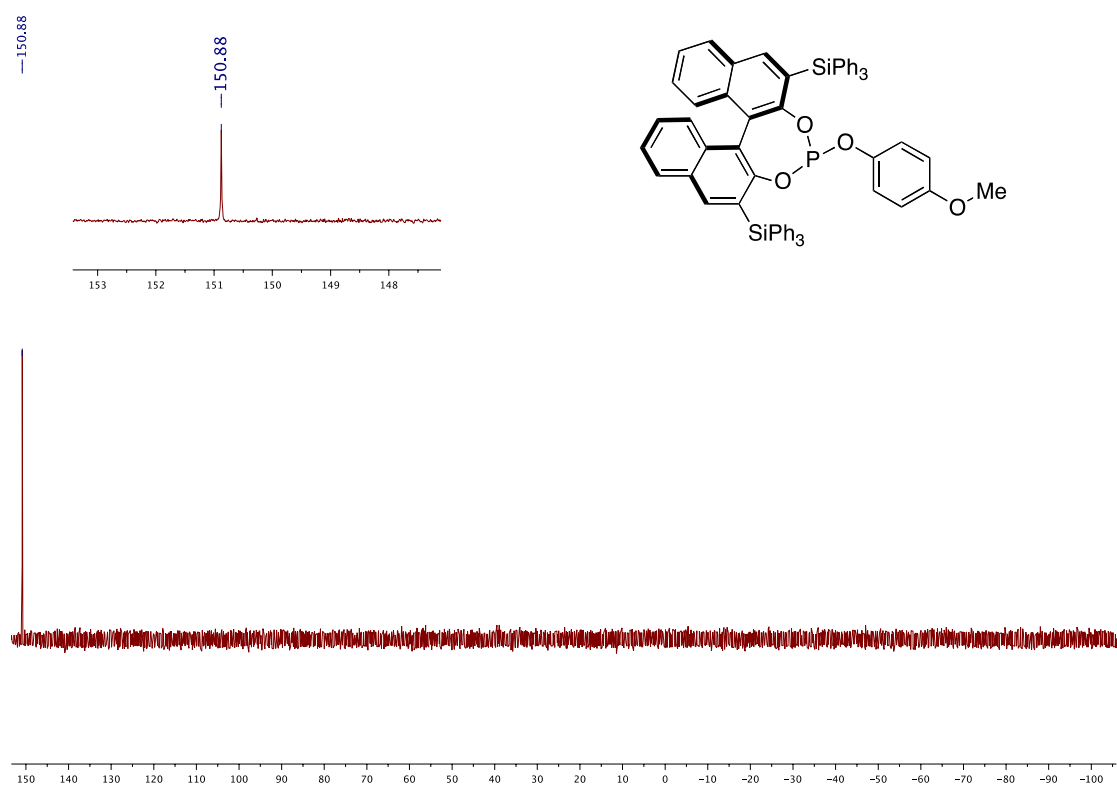
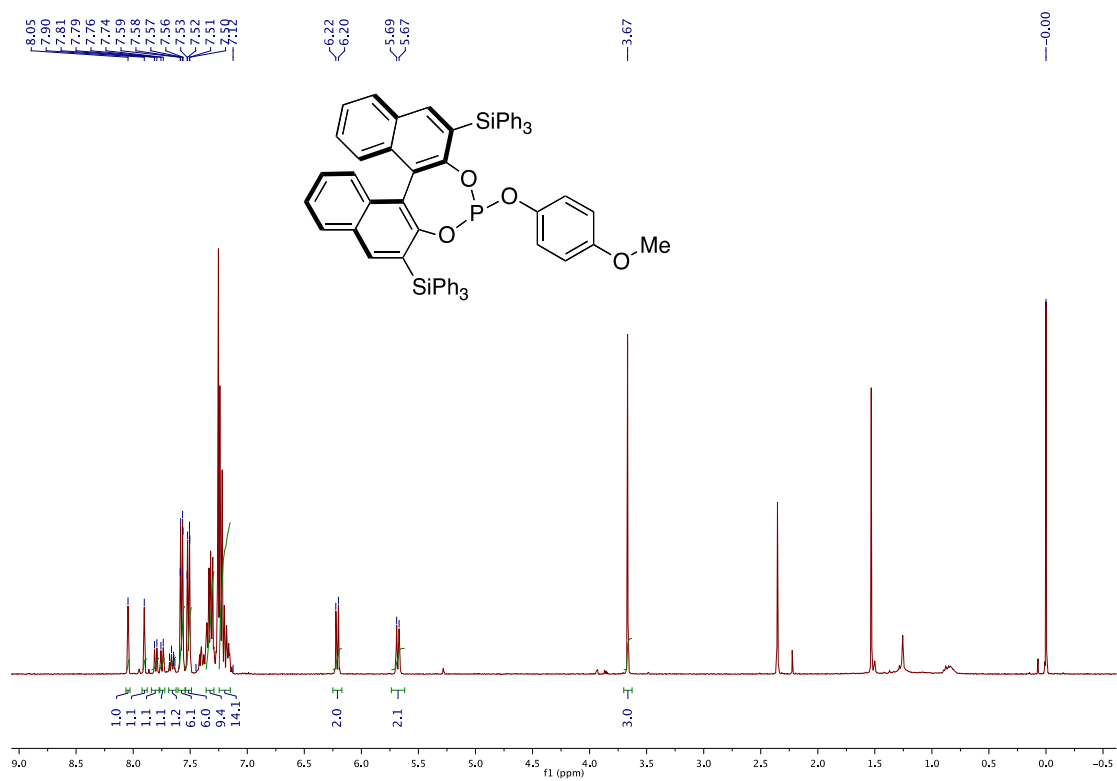
All Reactions were performed at 0 °C and slowly warmed to room temperature until complete conversion. Enantiomeric excesses were measured by chiral HPLC.

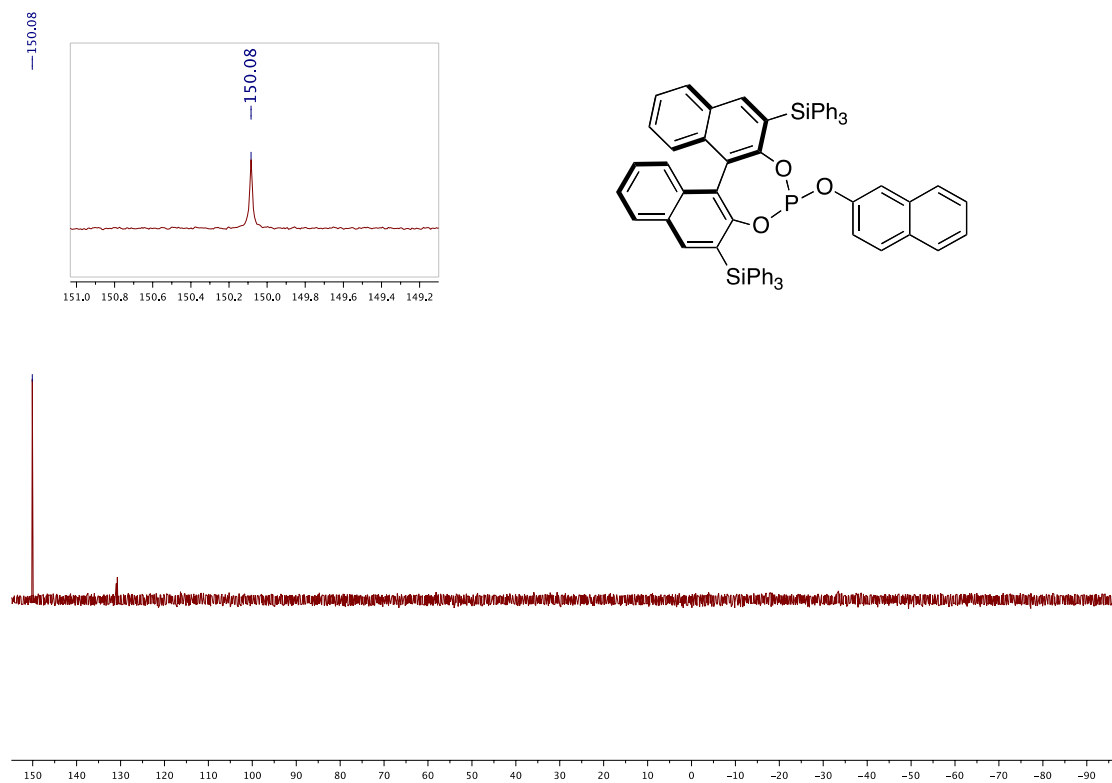
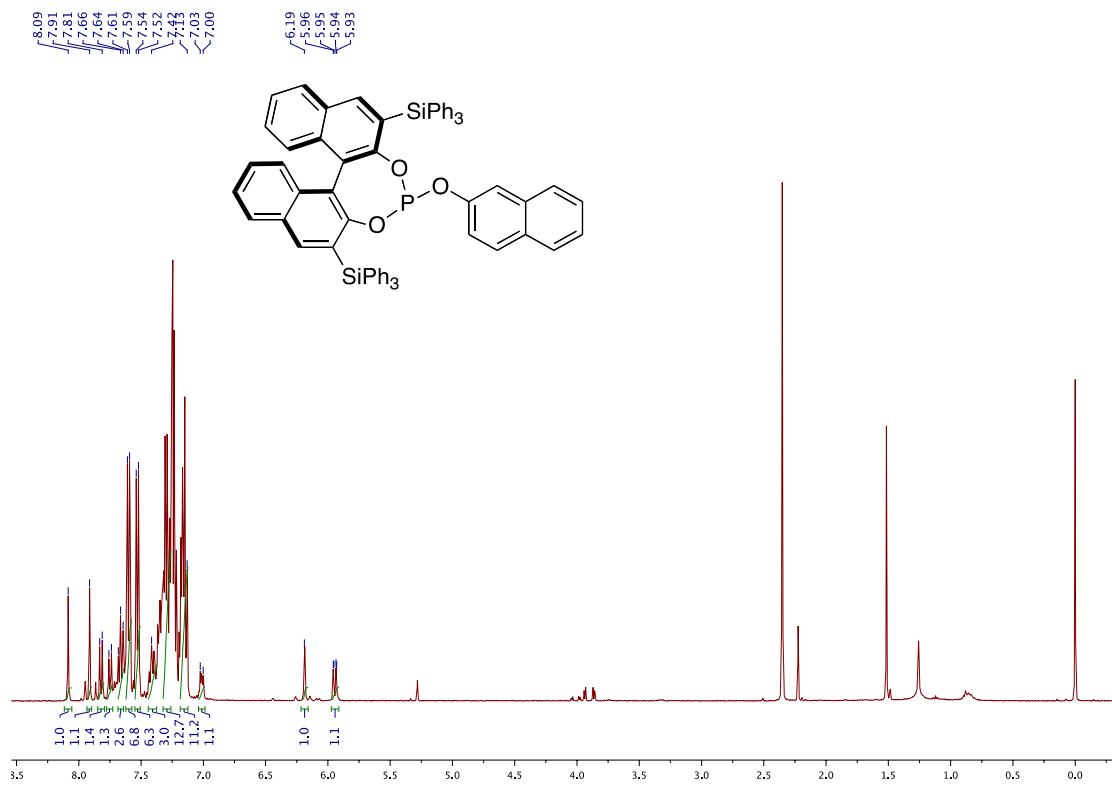
NMR Data

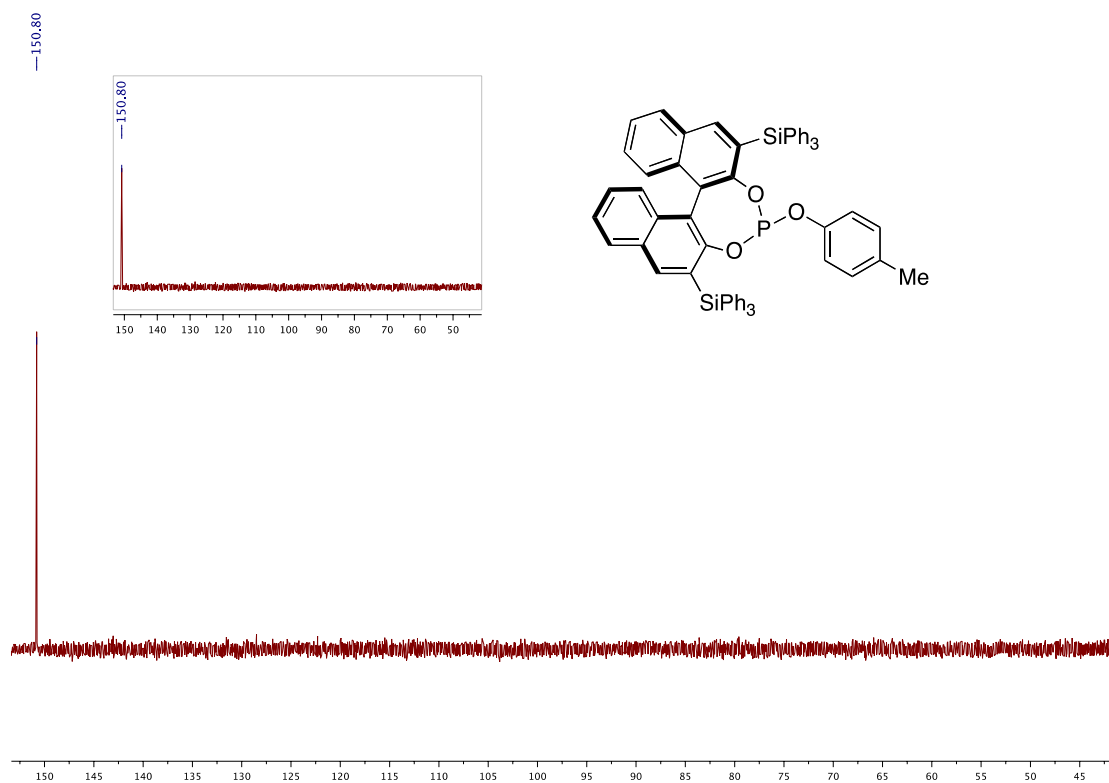
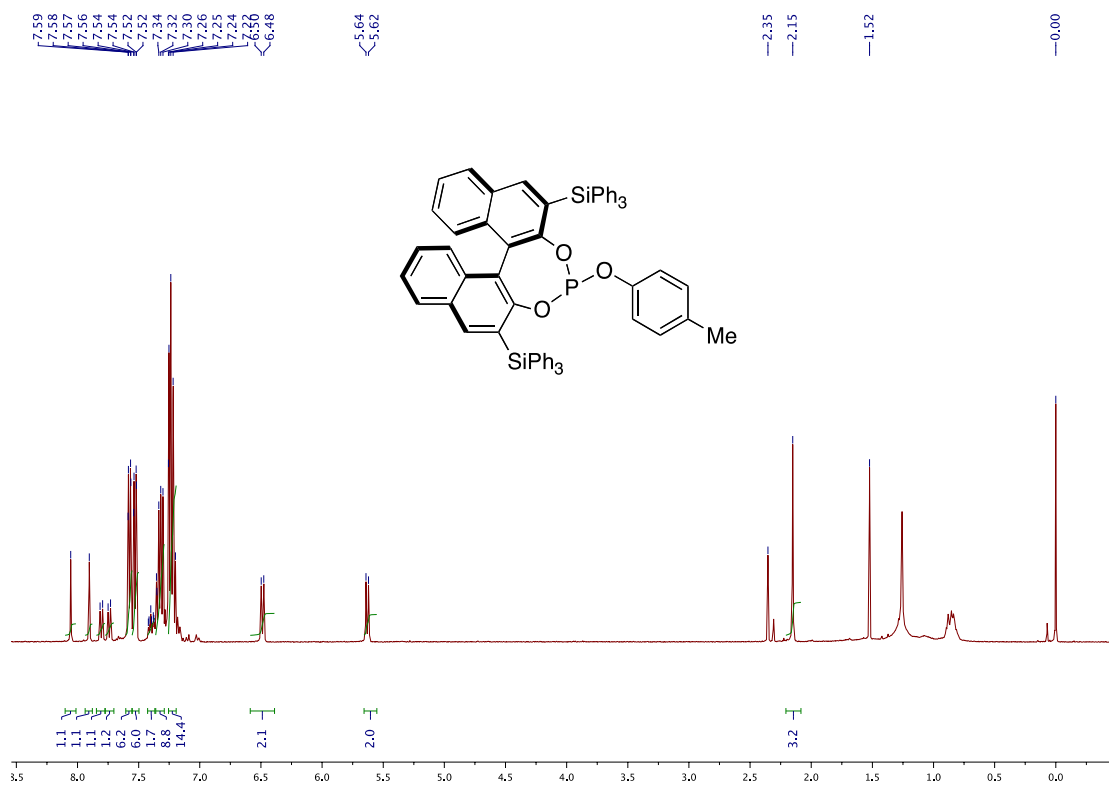


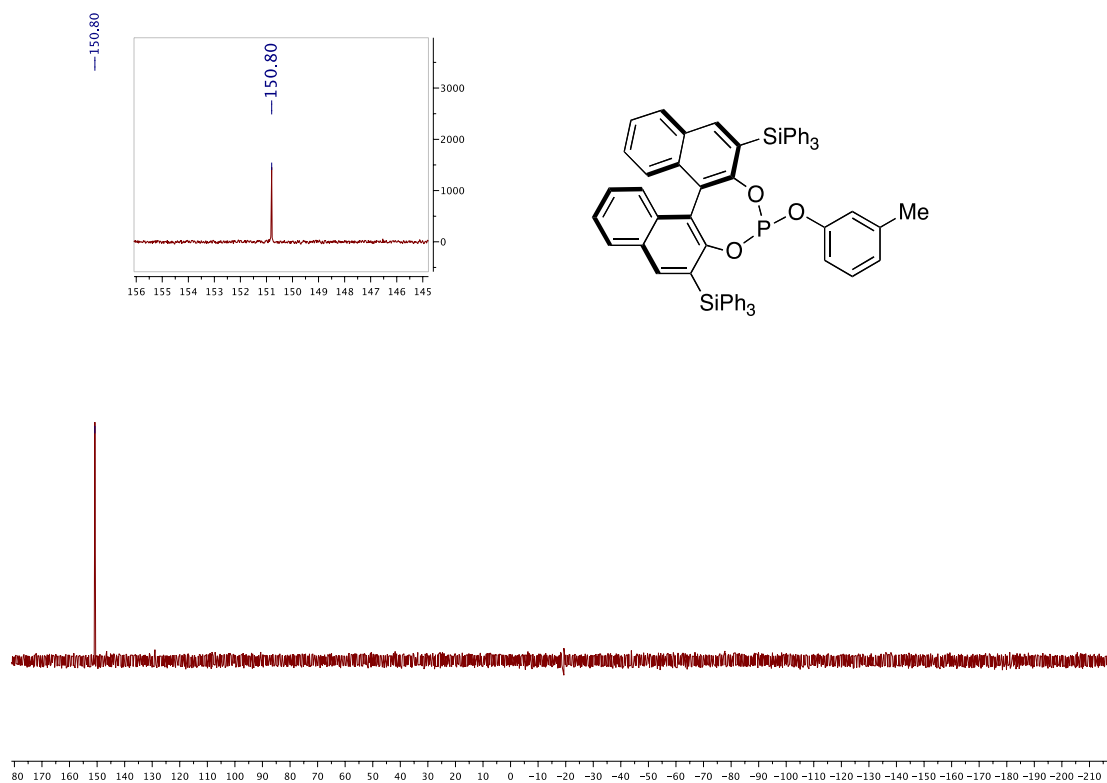
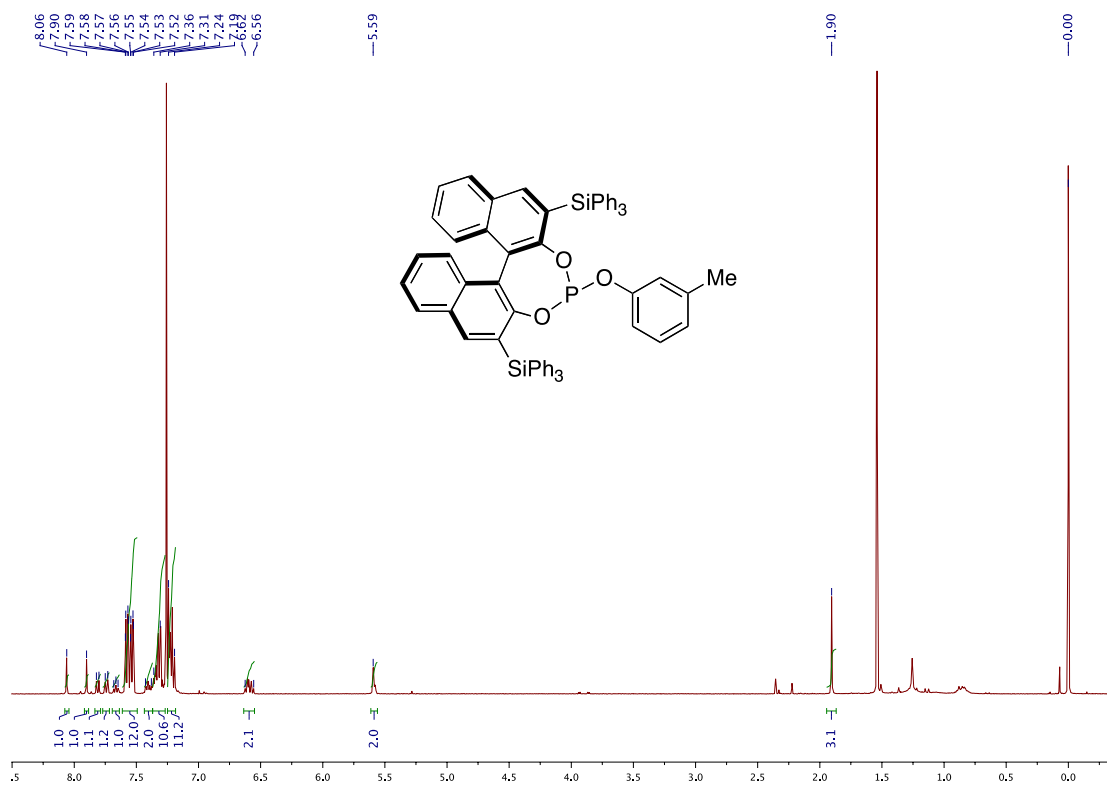


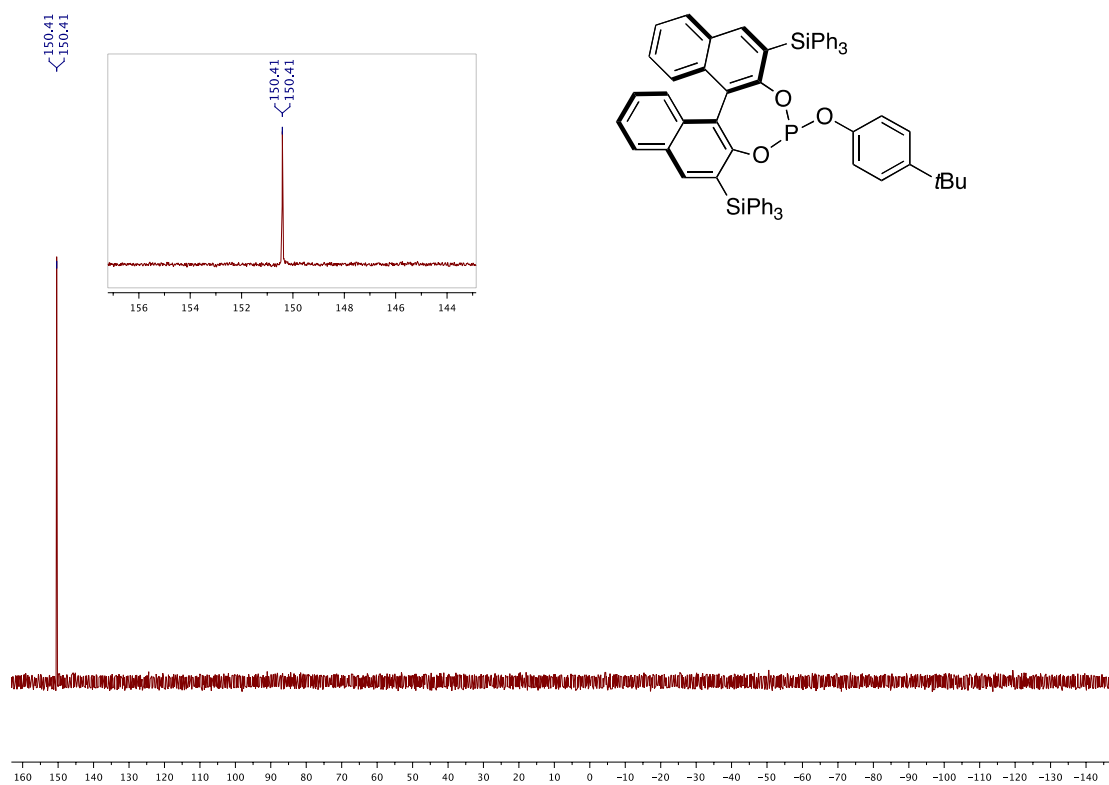




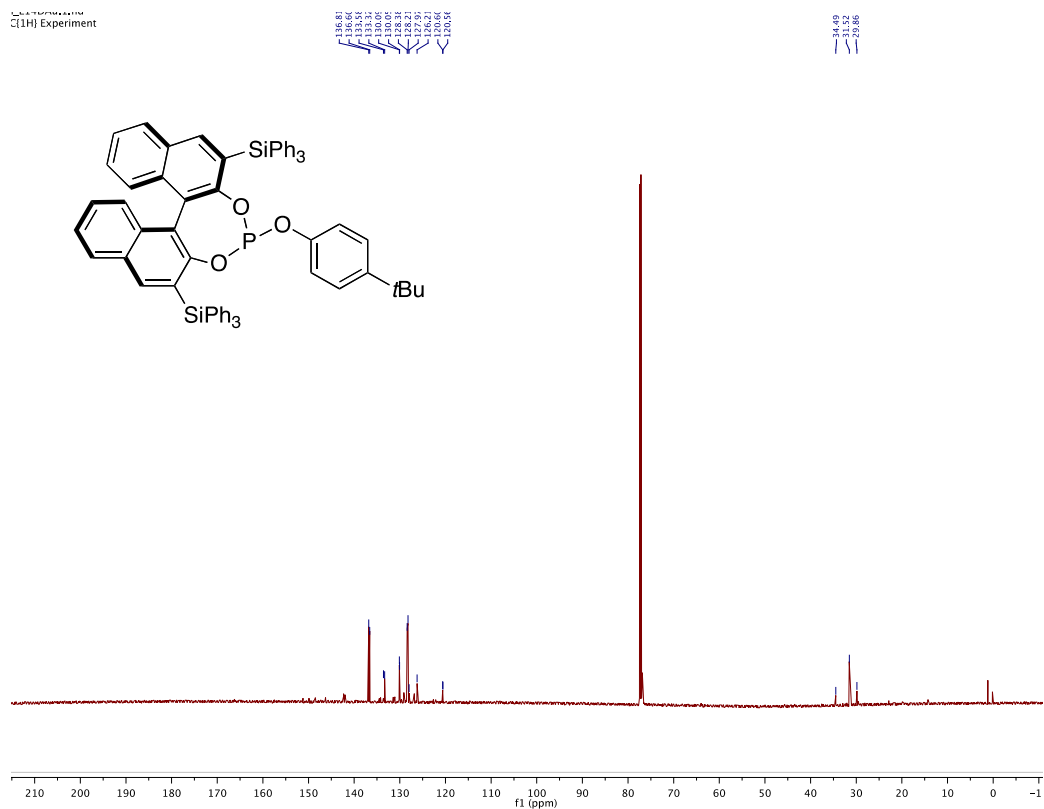


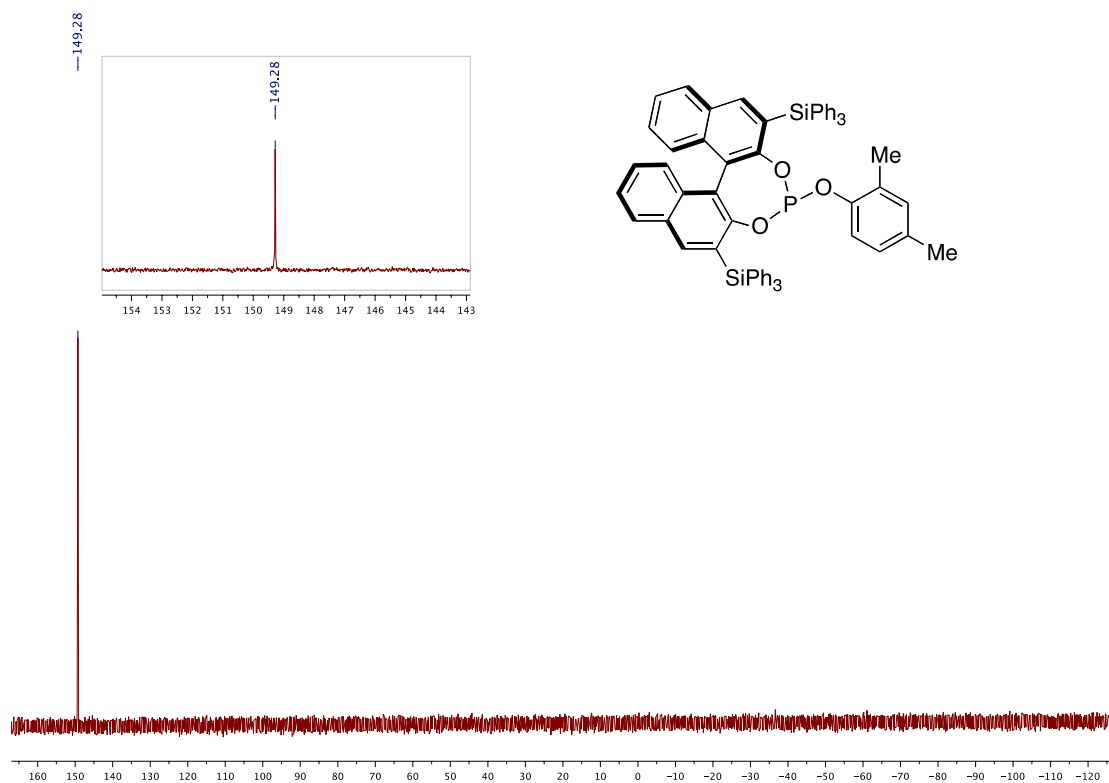
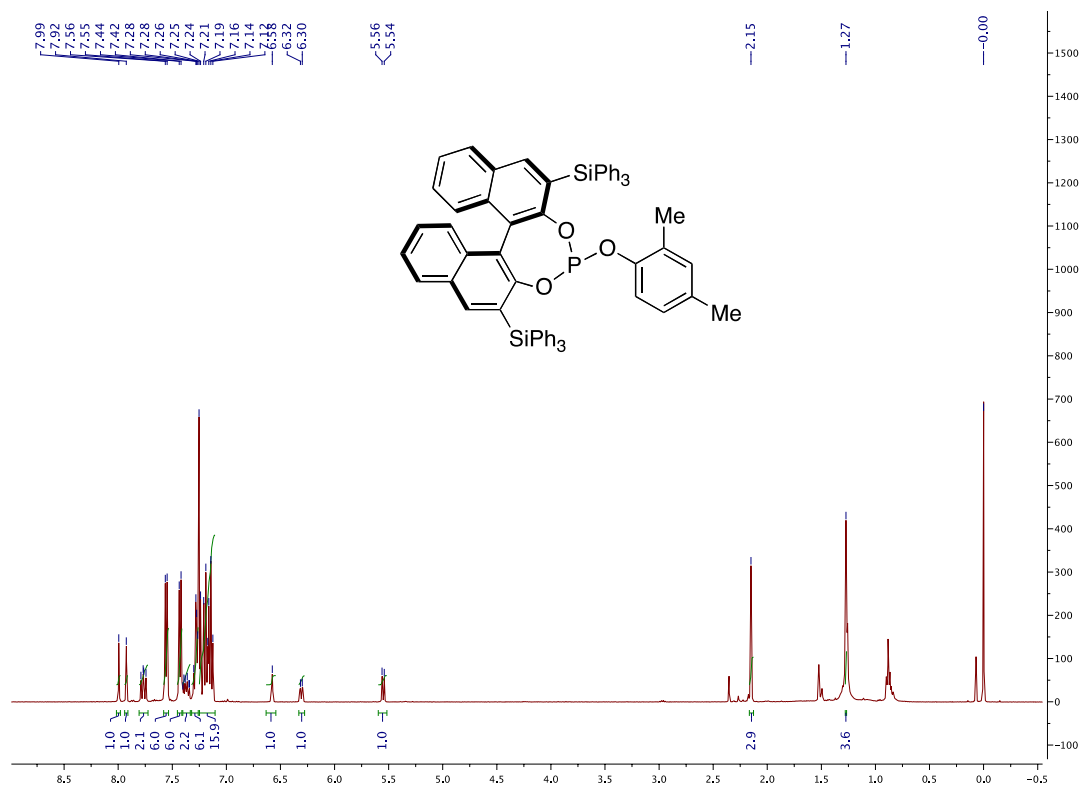


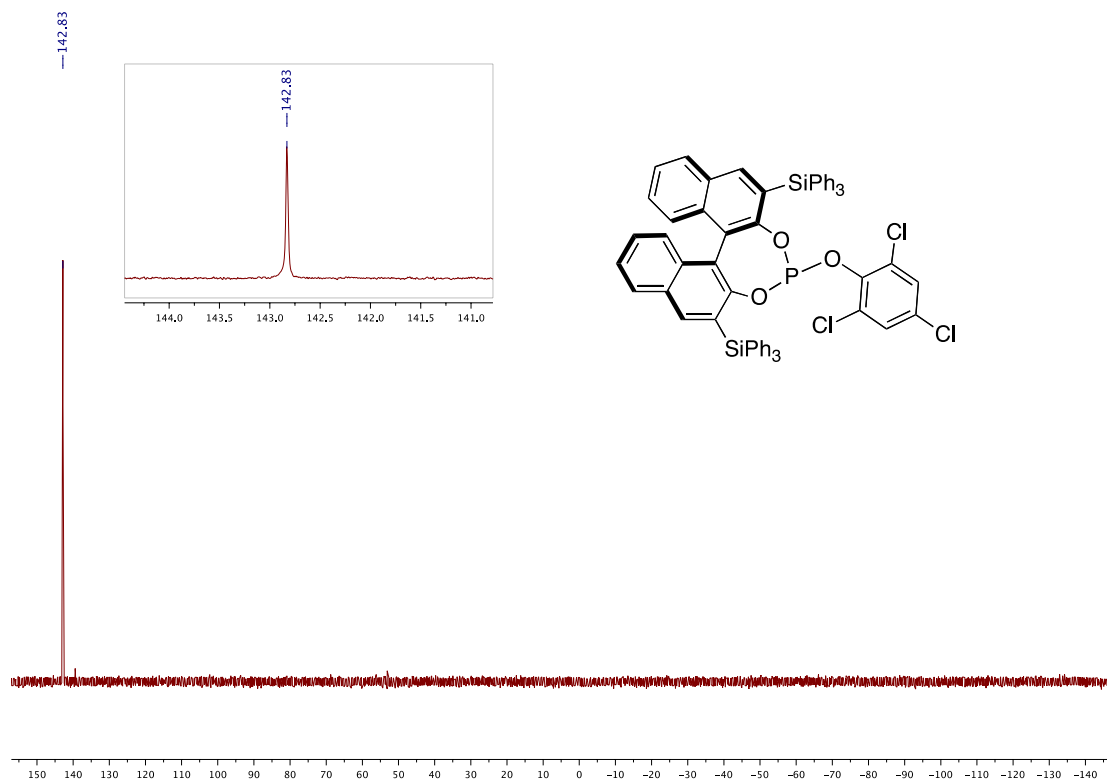
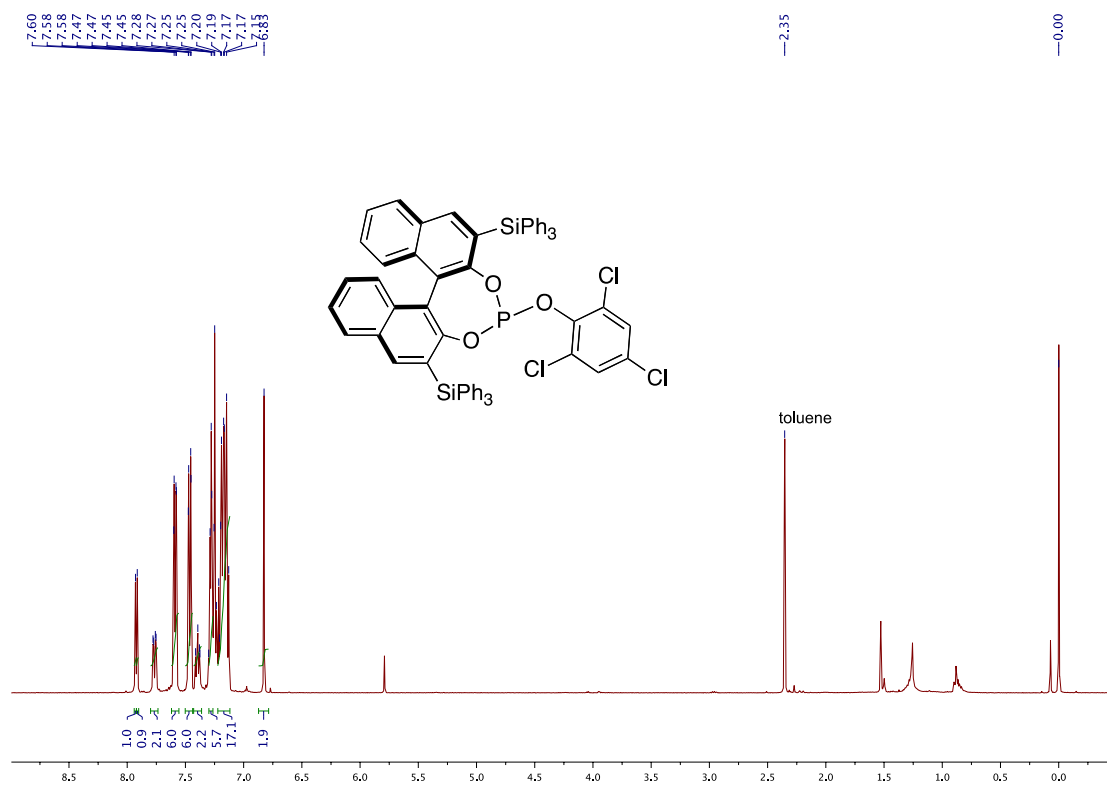


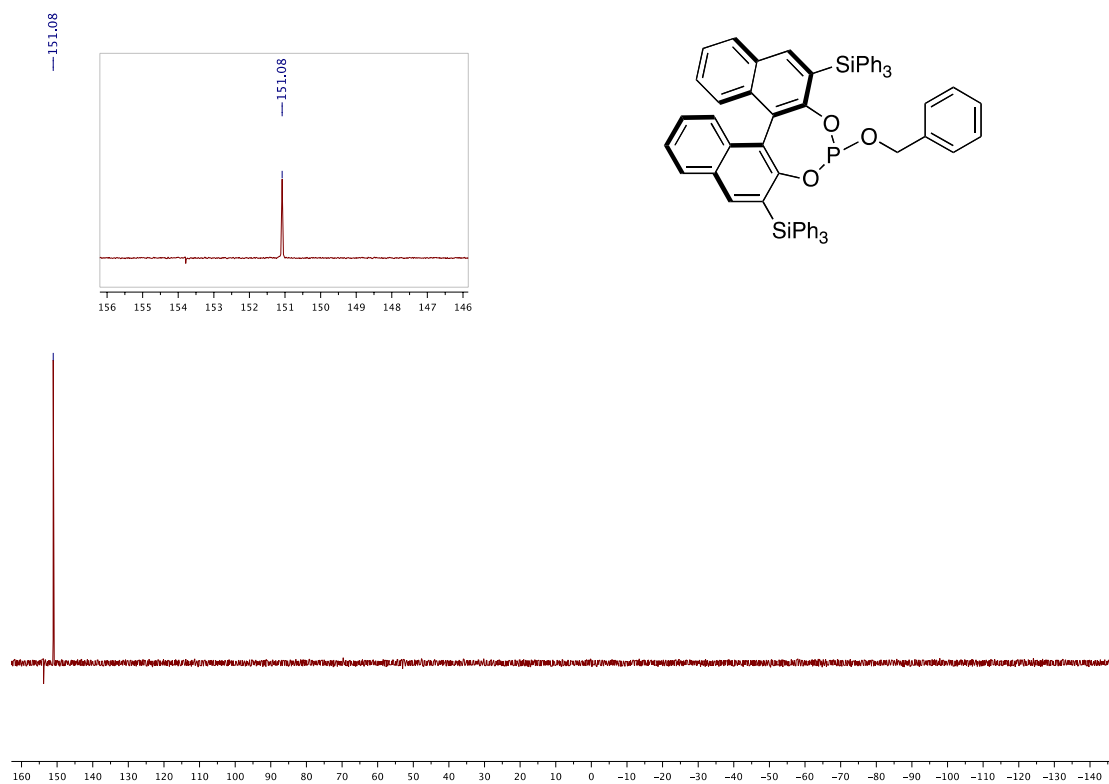
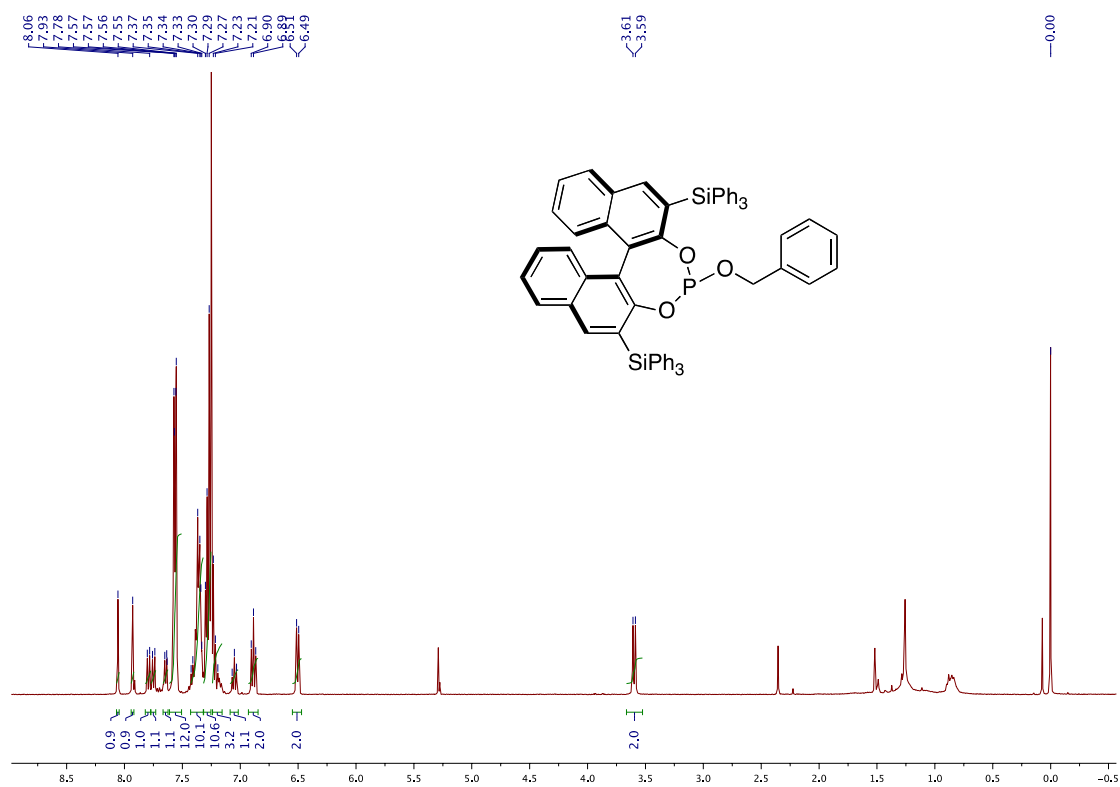


13C NMR
[1H] Experiment









L1499_13-110
archGroup Echavarren
_13C[1H]512s CDCl3 /opt/topspin iescofet 4

140.77
136.81
136.74
136.74
134.32
134.02
133.85
133.85
130.13
129.56
129.44
129.44
128.72
128.56
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126.97
126.46
126.46
124.72
124.68

