# Thioether-phosphite: new ligands for the highly enantioselective Ir-catalyzed hydrogenation of minimally functionalized olefins

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## Supporting Information

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**1. General Considerations**. All reactions were carried out using standard Schlenk techniques under an atmosphere of argon. Solvents were purified and dried by standard procedures. Phosphorochloridites are easily prepared in one step from the corresponding biaryls.[1] Phosphite-thioether ligand **L1-L3a** and thioether-hydroxyl **8** were prepared as previously described.[2] $^{1}H$, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are relative to that of $SiMe_4$ ($^{1}H$ and $^{13}C$) as internal standard or $H_3PO_4$ ($^{31}P$) as external standard. $^{1}H$ and $^{13}C$ assignments were done based on $^{1}H$-$^{1}H$ gCOSY and $^{1}H$-$^{13}C$ gHSQC experiments.

**2. Typical procedure for the preparation of ligands L1-L8a-d**. The corresponding phosphorochloridite (1.1 mmol) produced *in situ* was dissolved in toluene (5 mL) and pyridine (0.3 mL, 3.9 mmol) was added. The corresponding thioether-hydroxyl compound (1 mmol) was azeotropically dried with toluene (3 x 2 mL) and then dissolved in toluene (5 mL) to which pyridine (0.3 mL, 3.9 mmol) was added. The alcohol solution was transferred slowly to the solution of phosphorochloridite. The reaction mixture was stirred at 80 ºC for 90 min, and the pyridine salts were removed by filtration. Evaporation of the solvent gave a white foam, which was purified by flash chromatography in alumina (toluene/$NEt_3$= 100/1) to produce the corresponding ligand as a white solid.

**L1c**: Yield: 435 mg, 73 %. $^{31}P$ NMR (400 MHz, $C_6D_6$) δ: 148.6 (s). $^{1}H$ NMR (400 MHz, $C_6D_6$) δ: 0.97 (s, 3H, $CH_3$), 1.18 (s, 3H, $CH_3$), 3.27 (m, 2H, H-5' and H-5), 4.49 (m, 1H, H-4), 4.68 (d, 1H, H-2, $^{2}J_{2\text{-}1}$= 4.0 Hz), 4.97 (dd, 1H, H-3, $J_{3\text{-}P}$= 5.6 Hz, $^{3}J_{3\text{-}4}$= 2.0 Hz), 5.82 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 4.0 Hz), 6.8-7.6 (m, 17H, CH=). $^{13}C$ NMR (400 MHz, $C_6D_6$) δ: 26.0 ($CH_3$), 26.5 ($CH_3$), 30.9 (C-5), 78.0 (d, C-3, $J_{C\text{-}P}$= 16 Hz), 78.7 (C-4), 84.5 (C-2), 105.0 (C-1), 111.7 ($CMe_2$), 121.4 (CH=), 121.7 (CH=), 123.0 (C), 124.4 (C), 124.9 (d, CH=, $J_{C\text{-}P}$= 7.1 Hz), 126.0 (CH=), 126.3 (CH=), 127.1 (CH=), 128.3 (CH=), 128.4 (CH=), 19.3 (CH=), 130.0 (CH=), 130.5 (CH=), 131.2 (C), 131.7 (C),

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[1] Buisman, G. J. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1993**, *4*, 1625.

[2] a) Pàmies, O.; Diéguez, M. Net, G.; Ruiz, A.; Claver, C. *Organometallics* **2000**, *19*, 1488. b) Diéguez, M.; Pàmies, O.; Claver, C. *Tetrahedron: Asymmetry* **2005**, *16*, 3877.

132.8 (C), 132.9 (C), 135.6 (C), 147.3 (C), 148.2 (d, C, $J_{C\text{-}P}$= 5.3 Hz). Anal. calcd (%) for $C_{34}H_{29}O_6PS$: C 68.45, H 4.90, S 5.37; found: C 68.54, H 4.86, S 5.24.

**L1d**: Yield: 393 mg, 66%. $^{31}$P NMR (400 MHz, $C_6D_6$) δ: 145.7 (s). $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 0.89 (s, 3H, $CH_3$), 1.16 (s, 3H, $CH_3$), 3.03 (dd, 1H, H-5', $^{2}J_{5'\text{-}5}$= 13.2 Hz, $^{3}J_{5'\text{-}4}$= 5.6 Hz), 3.90 (dd, 1H, H-5, $^{2}J_{5\text{-}5'}$= 13.2 Hz, $^{3}J_{5\text{-}4}$= 4.6 Hz), 4.39 (d, 1H, H-2, $^{2}J_{2\text{-}1}$= 3.6 Hz), 4.41 (m, 1H, H-4), 4.89 (dd, 1H, H-3, $J_{3\text{-}P}$= 9.2 Hz, $^{3}J_{3\text{-}4}$= 2.8 Hz), 5.68 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 3.6 Hz), 6.8-7.6 (m, 17H, CH=). $^{13}$C NMR (400 MHz, $C_6D_6$) δ: 24.4 ($CH_3$), 27.0 ($CH_3$), 32.4 (C-5), 76.6 (d, C-3, $J_{C\text{-}P}$= 10.5 Hz), 79.4 (d, C-4, $J_{C\text{-}P}$= 5.3 Hz), 85.1 (C-2), 105.6 (C-1), 112.1 ($CMe_2$), 122.2 (CH=), 122.3 (CH=), 123.5 (C), 125.1 (C), 125.6 (CH=), 125.7 (CH=), 126.7 (CH=), 127.0 (d, CH=, $J_{C\text{-}P}$= 3.5 Hz), 127.7 (d, CH=, $J_{C\text{-}P}$= 14.7 Hz), 129.0 (d, CH=, $J_{C\text{-}P}$= 4.0 Hz), 129.6 (CH=), 130.3 (CH=), 130.9 (C), 131.3 (C), 131.8 (C), 132.4 (C), 133.4 (C), 133.7 (C), 135.1 (C), 147.9 (d, C, $J_{C\text{-}P}$= 4.0 Hz) , 148.9 (d, C, $J_{C\text{-}P}$= 6.0 Hz). Anal. calcd (%) for $C_{34}H_{29}O_6PS$: C 68.45, H 4.90, S 5.37; found: C 68.51, H 4.92, S 5.44.

**L4a**: Yield: 520 mg, 69 %. $^{31}$P NMR (400 MHz, $C_6D_6$) δ: 142.7 (bs). $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 1.15 (s, 3H, $CH_3$), 1.25 (s, 9H, $CH_3$, $^{t}$Bu), 1.31 (s, 9H, $CH_3$, $^{t}$Bu), 1.43 (s, 3H, $CH_3$), 1.52 (s, 9H, $CH_3$, $^{t}$Bu), 1.60 (s, 9H, $CH_3$, $^{t}$Bu), 2.59 (s, 6H, $CH_3$-Ar), 2.72 (dd, 1H, H-5', $^{2}J_{5'\text{-}5}$= 14 Hz, $^{3}J_{5'\text{-}4}$= 7.2 Hz), 3.13 (dd, 1H, H-5, $^{2}J_{5\text{-}5'}$= 14 Hz, $^{3}J_{5\text{-}4}$= 3.2 Hz), 3.98 (m, 1H, H-2), 4.03 (m, 1H, H-4), 4.19 (m, 1H, H-3), 5.43 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 3.6 Hz), 6.8-7.6 (m, 7H, CH=). $^{13}$C NMR (400 MHz, $C_6D_6$) δ: 22.1 ($CH_3$-Ar), 26.4 ($CH_3$), 27.0 ($CH_3$), 31.0 ($CH_3$, $^{t}$Bu) 31.2 ($CH_3$, $^{t}$Bu), 34.3 (C, $^{t}$Bu), 35.2 (C, $^{t}$Bu), 35.4 (C-5), 75.4 (C-3), 76.5 (C-4), 78.3 (C-2), 104.0 (C-1), 112.8 ($CMe_2$), 124.0 (d, CH=, $J_{C\text{-}P}$= 12 Hz), 126.7 (CH=), 126.8 (CH=), 128.1 (CH=), 128.2 (CH=), 129.2 (CH=), 133.6 (C), 137.8 (C), 140.4 (C), 141.3 (C), 143.2 (C), 146.8 (C). Anal. calcd (%) for $C_{44}H_{61}O_6PS$: C 70.56, H 8.21, S 4.28; found: C 70.62, H 8.25, S 4.21.

**L5a**: Yield: 532 mg, 73 %. $^{31}$P NMR (400 MHz, $C_6D_6$) δ: 143.1 (s). $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 1.12 (s, 3H, $CH_3$), 1.25 (s, 9H, $CH_3$, $^{t}$Bu), 1.27 (s, 9H, $CH_3$, $^{t}$Bu), 1.44 (s, 3H, $CH_3$), 1.57 (s, 9H, $CH_3$, $^{t}$Bu), 1.59 (s, 9H, $CH_3$, $^{t}$Bu), 2.90 (dd, 1H, H-5', $^{2}J_{5'\text{-}5}$= 13.6 Hz, $^{3}J_{5'\text{-}4}$= 5.2 Hz), 3.23 (dd, 1H, H-5, $^{2}J_{5\text{-}5'}$= 13.6 Hz, $^{3}J_{5\text{-}4}$= 3.2 Hz), 3.96 (m, 1H, H-2), 4.41 (m, 1H, H-3), 4.48 (m, 1H, H-4), 5.41 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 3.2 Hz), 6.8-7.6 (m, 9H, CH=). $^{13}$C NMR (400 MHz, $C_6D_6$) δ: 26.4 ($CH_3$), 26.6 ($CH_3$), 31.0 ($CH_3$, $^{t}$Bu), 31.1 ($CH_3$, $^{t}$Bu), 31.2 ($CH_3$, $^{t}$Bu), 34.3 (C, $^{t}$Bu), 35.2 (C, $^{t}$Bu), 35.3 (C-5), 76.2 (C-3), 77.5 (d, C-4, $J_{C\text{-}P}$= 3.1 Hz), 78.3 (C-2), 103.8 (C-1), 112.6 ($CMe_2$), 123.9 (d, CH=, $J_{C\text{-}P}$=

25.9 Hz), 125.6 (CH=), 126.7 (CH=), 126.9 (CH=), 128.6 (CH=), 128.9 (CH=), 129.4 (CH=), 133.1 (C), 133.4 (C), 137.0 (C), 140.4 (C), 140.6 (C), 146.1 (C), 146.2 (C), 146.7 (C). Anal. calcd (%) for $C_{42}H_{57}O_6PS$: C 69.97, H 7.97, S 4.45; found: C 69.95, H 8.01, S 4.41.

**L5b**: Yield: 397 mg, 62 %. $^{31}$P NMR (400 MHz, $C_6D_6$) δ: 141.7 (s). $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 0.37 (s, 9H, $CH_3$-Si), 0.42 (s, 9H, $CH_3$-Si) 1.09 (s, 3H, $CH_3$), 1.45 (s, 3H, $CH_3$), 2.84 (dd, 1H, H-5', $^{2}J_{5'-5}$= 14.0 Hz, $^{3}J_{5'-4}$= 6.4 Hz), 3.20 (dd, 1H, H-5, $^{2}J_{5-5'}$= 14.0 Hz, $^{3}J_{5-4}$= 3.2 Hz), 3.91 (m, 1H, H-2), 4.29 (m, 1H, H-3), 4.46 (m, 1H, H-4), 5.32 (d, 1H, H-1, $^{3}J_{1-2}$= 4.0 Hz), 6.8-7.6 (m, 11H, CH=). $^{13}$C NMR (400 MHz, $C_6D_6$) δ: 0 ($CH_3$-Si), 0.1 ($CH_3$-Si), 26.6 ($CH_3$), 26.7 ($CH_3$), 35.9 (C-5), 76.3 (C-3), 77.8 (C-4), 78.5 (C-2), 104.0 (C-1), 112.7 ($CMe_2$), 125.1 (CH=), 125.3 (CH=), 125.8 (C), 126.0 (CH=), 126.9 (C), 128.2 (CH=), 128.8 (CH=), 129.8 (CH=), 130.9 (C), 132.5 (CH=), 132.7 (CH=), 133.1 (C), 135.2 (CH=), 135.7 (CH=), 145.9 (C), 146.6 (C). Anal. calcd (%) for $C_{32}H_{41}O_6PS$: C 59.97, H 6.45, S 5.00; found: C 60.02, H 6.49, S 4.98.

**L5c**: Yield: 322 mg, 54 %. $^{31}$P NMR (400 MHz, $C_6D_6$) δ: 141.8 (s). $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 1.10 (s, 3H, $CH_3$), 1.42 (s, 3H, $CH_3$), 2.89 (dd, 1H, H-5', $^{2}J_{5'-5}$= 14.0 Hz, $^{3}J_{5'-4}$= 4.4 Hz), 3.20 (dd, 1H, H-5, $^{2}J_{5-5'}$= 14.0 Hz, $^{3}J_{5-4}$= 3.2 Hz), 4.04 (m, 1H, H-2), 4.38 (m, 2H, H-3 and H-4), 5.24 (d, 1H, H-1, $^{3}J_{1-2}$= 3.2 Hz), 6.8-7.6 (m, 17H, CH=). $^{13}$C NMR (400 MHz, $C_6D_6$) δ: 26.4 ($CH_3$), 26.5 ($CH_3$), 34.5 (C-5), 76.3 (C-3), 77.8 (C-4), 78.5 (C-2), 104.0 (C-1), 112.8 ($CMe_2$), 121.6 (CH=), 121.9 (CH=), 123.1 (C), 124.9 (d, CH=, $J_{C-P}$= 7.8 Hz), 125.6 (CH=), 126.3 (d, CH=, $J_{C-P}$= 3.1 Hz), 127.0 (d, CH=, $J_{C-P}$= 8.9 Hz), 127.8 (CH=), 128.2 (CH=), 128.6 (CH=), 129.0 (CH=), 129.7 (CH=), 130.5 (CH=), 131.2 (C), 131.7 (C), 132.9 (C), 133.0 (C), 137.0 (C), 147.4 (d, C, $J_{C-P}$= 2.3 Hz), 148.0 (d, C, $J_{C-P}$= 4.6 Hz). Anal. calcd (%) for $C_{34}H_{29}O_6PS$: C 68.45, H 4.90, S 5.37; found: C 68.52, H 4.89, S 5.34.

**L5d**: Yield: 364 mg, 61 %. $^{31}$P NMR (400 MHz, $C_6D_6$) δ: 140.9 (s). $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 1.11 (s, 3H, $CH_3$), 1.46 (s, 3H, $CH_3$), 3.00 (dd, 1H, H-5', $^{2}J_{5'-5}$= 14.0 Hz, $^{3}J_{5'-4}$= 6.6 Hz), 3.31 (dd, 1H, H-5, $^{2}J_{5-5'}$= 14.0 Hz, $^{3}J_{5-4}$= 3.6 Hz), 4.12 (m, 1H, H-2), 4.19 (m, 1H, H-3), 4.47 (m, 1H, H-4), 5.17 (d, 1H, H-1, $^{3}J_{1-2}$= 3.2 Hz), 6.8-7.6 (m, 17H, CH=). $^{13}$C NMR (400 MHz, $C_6D_6$) δ: 27.1 ($CH_3$), 35.7 (C-5), 77.4 (d, C-3, $J_{C-P}$= 4.6 Hz), 77.8 (d, C-4, $J_{C-P}$= 3.9 Hz), 79.2 (C-2), 104.6 (C-1), 113.2 ($CMe_2$), 122.4 (CH=), 122.8 (CH=), 123.4 (C), 125.2 (C), 125.6 (d, CH=, $J_{C-P}$= 12.2 Hz), 126.5 (CH=), 127.2 (CH=), 127.0 (d, CH=, $J_{C-P}$= 17.0 Hz), 129.0 (CH=), 129.5 (CH=), 129.9 (CH=), 130.6 (CH=), 131.3 (CH=), 131.9 (C), 132.4 (C), 133.4 (C), 133.7 (d, C, $J_{C-P}$= 1.5 Hz),

137.6 (C), 148.2, 149.4 (d, C, $J_{C\text{-}P}$= 4.5 Hz). Anal. calcd (%) for $C_{34}H_{29}O_6PS$: C 68.45, H 4.90, S 5.37; found: C 68.48, H 4.82, S 5.35.

**L6a**: Yield: 452 mg, 60 %. $^{31}$P NMR (400 MHz, $C_6D_6$) δ: 142.7 (bs). $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 1.11(s, 3H, $CH_3$), 1.24 (s, 9H, $CH_3$, $^t$Bu), 1.26 (s, 9H, $CH_3$, $^t$Bu), 1.41 (s, 3H, $CH_3$), 1.52 (s, 9H, $CH_3$, $^t$Bu), 1.56 (s, 9H, $CH_3$, $^t$Bu), 2.58 (s, 6H, $CH_3$-Ar), 2.62 (dd, 1H, H-5', $^2J_{5'\text{-}5}$= 14 Hz, $^3J_{5'\text{-}4}$= 8.8 Hz), 3.06 (dd, 1H, H-5, $^2J_{5\text{-}5'}$= 14 Hz, $^3J_{5\text{-}4}$= 2.4 Hz), 3.93 (m, 1H, H-2), 4.16 (m, 1H, H-4), 4.28 (m, 1H, H-3), 5.40 (d, 1H, H-1, $^3J_{1\text{-}2}$= 3.2 Hz), 6.8-7.6 (m, 7H, CH=). $^{13}$C NMR (400 MHz, $C_6D_6$) δ: 21.9 ($CH_3$-Ar), 26.4 ($CH_3$), 31.0 ($CH_3$, $^t$Bu), 31.2 ($CH_3$, $^t$Bu), 34.3 (C, $^t$Bu), 35.2 (C, $^t$Bu), 35.3 (C-5), 76.6 (C-4), 77.5 (C-3), 78.2 (C-2), 103.6 (C-1), 112.5 ($CMe_2$), 123.9 (d, CH=, $J_{C\text{-}P}$= 15.3 Hz), 126.6 (CH=), 126.9 (CH=), 128.1 (CH=), 128.2 (CH=), 128.9 (CH=), 133.5 (C), 137.5 (C), 140.4 (C), 140.7 (C), 143.3 (C), 146.6 (C), 146.7 (C). Anal. calcd (%) for $C_{44}H_{61}O_6PS$: C 70.56, H 8.21, S 4.28; found: C 70.53, H 8.23, S 4.30.

**L7a**: Yield: 536 mg, 72 %. $^{31}$P NMR (400 MHz, $C_6D_6$) δ: 136.4 (s). $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 0.95 (s, 3H, $CH_3$), 1.26 (s, 9H, $CH_3$, $^t$Bu), 1.28 (s, 9H, $CH_3$, $^t$Bu), 1.38 (s, 3H, $CH_3$), 1.59 (s, 9H, $CH_3$, $^t$Bu), 1.60 (s, 9H, $CH_3$, $^t$Bu), 3.68 (d, 1H, H-3, $^3J_{3\text{-}4}$= 3.6 Hz), 4.38 (m, 2H, H-5' and H-5), 4.47 (d, 1H, H-2, $^3J_{1\text{-}2}$= 3.6 Hz), 4.82 (m, 1H, H-4), 5.78 (d, 1H, H-1, $^3J_{1\text{-}2}$= 3.6 Hz), 6.8-7.6 (m, 9H, CH=). $^{13}$C NMR (400 MHz, $C_6D_6$) δ: 26.7 ($CH_3$), 27.2 ($CH_3$), 31.5 ($CH_3$, $^t$Bu), 31.6 ($CH_3$, $^t$Bu), 31.9 ($CH_3$, $^t$Bu), 32.0 ($CH_3$, $^t$Bu), 35.0 (C, $^t$Bu), 36.0 (C, $^t$Bu), 53.8 (C-3), 64.4 (C-5), 78.9 (C-4), 86.2 (C-2), 105.8 (C-1), 112.3 ($CMe_2$), 124.1 (d, CH=, $J_{C\text{-}P}$= 13.0 Hz), 125.3 (CH=), 126.3 (CH=), 126.7 (d, CH=, $J_{C\text{-}P}$= 20 Hz), 128.1 (CH=), 128.9 (CH=), 129.0 (CH=), 129.6 (CH=), 133.1 (C), 133.3 (C), 134.3 (C), 137.5 (C), 140.1 (C), 140.3 (C), 146.5 (C), 146.6 (C). Anal. calcd (%) for $C_{42}H_{57}O_6PS$: C 69.97, H 7.97, S 4.45; found: C 69.99, H 8.01, S 4.47.

**L8a**: Yield: 415 mg, 57 %. $^{31}$P NMR (400 MHz, $C_6D_6$) δ: 142.5 (bs). $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 1.09 (s, 3H, $CH_3$), 1.23 (s, 9H, $CH_3$, $^t$Bu), 1.27 (s, 9H, $CH_3$, $^t$Bu), 1.39 (s, 3H, $CH_3$), 1.50 (s, 9H, $CH_3$, $^t$Bu), 1.52 (s, 9H, $CH_3$, $^t$Bu), 3.39 (dd, 1H, H-3, $^3J_{3\text{-}2}$= 4 Hz, $^3J_{3\text{-}4}$= 10 Hz), 3.87 (m, 1H, H-5'), 4.03 (m, 1H, H-4), 4.19 (m, 1H, H-2), 4.31 (m, 1H, H-5), 5.71 (d, 1H, H-1, $^3J_{1\text{-}2}$= 3.6 Hz), 6.8-7.6 (m, 9H, CH=). $^{13}$C NMR (400 MHz, $C_6D_6$) δ: 26.2 ($CH_3$), 26.6 ($CH_3$), 30.7 ($CH_3$, $^t$Bu), 30.9 ($CH_3$, $^t$Bu), 31.2 ($CH_3$, $^t$Bu), 31.1 ($CH_3$, $^t$Bu), 34.3 (C, $^t$Bu), 35.3 (C, $^t$Bu), 49.6 (C-3), 61.9 (d, C-5, $J_{C\text{-}P}$= 8 Hz), 80.7 (C-4), 81.1 (C-2), 104.4 (C-1), 111.7 ($CMe_2$), 123.9 (d, CH=, $J_{C\text{-}P}$= 7.6 Hz), 125.3 (CH=), 126.4 (CH=), 126.6 (d, CH=, $J_{C\text{-}P}$= 13 Hz), 128.1 (CH=), 128.8 (CH=), 128.9 (CH=), 130.8 (CH=),

133.2 (C), 133.5 (C), 135.1 (C), 140.3 (C), 146.2 (C), 146.5 (C). Anal. calcd (%) for $C_{42}H_{57}O_6PS$: C 69.97, H 7.97, S 4.45; found: C 70.01, H 8.02, S 4.43.

### 3. Typical procedure for the preparation of [Ir(cod)(L)]$BAr_F$ (L= L1-L8a-d)

The corresponding ligand (0.037 mmol) was dissolved in $CH_2Cl_2$ (2 mL) and [Ir(μ-Cl)(cod)]$_2$ (12.5 mg, 0.0185 mmol) was added. The reaction was refluxed at 50 °C for 1 hour. After 5 min at room temperature, $NaBAr_F$ (38.6 mg, 0.041 mmol) and water (2 mL) were added and the reaction mixture was stirred vigorously for 30 min at room temperature. The phases were separated and the aqueous phase was extracted twice with $CH_2Cl_2$. The combined organic phases were dried with $MgSO_4$, filtered through a plug of celite and the solvent was evaporated to give the product as red-orange solids.

[Ir(cod)(**L1a**)]BArF. Yield 64 mg (91 %). $^{31}$P NMR ($CDCl_3$, 298 K), δ: 112.9 (b). Anal. calc (%) for $C_{82}H_{81}BF_{24}IrO_6PS$: C 52.26, H 4.33, S 1.70; found: C 52.32, H 4.41, N 1.65. Major isomer (60%): $^{31}$P NMR ($CDCl_3$, 213 K), δ: 117.3 (s). $^1$H NMR ($CDCl_3$, 213 K), δ: 1.19 (s, 3H, $CH_3$), 1.33 (s, 18H, $CH_3$, $^t$Bu), 1.37 (s, 3H, $CH_3$), 1.64 (s, 18H, $CH_3$, $^t$Bu), 1.8-2.4 (b, 8H, $CH_2$, cod), 3.48 (m, 2H, H-5' and H-2), 3.87 (m, 2H, CH=, cod and H-5), 4.10 (m, 1H, CH=, cod), 4.34 (m, 1H, CH=, cod), 4.54 (m, 1H, H-4), 4.71 (m, 1H, H-3), 5.01 (m, 1H, CH=, cod), 5.58 (b, 1H, H-1), 7.0-8.0 (m, 21H, CH= aromatics). $^{13}$C NMR ($CDCl_3$, 213 K), δ: 25.5 ($CH_3$), 26.2 ($CH_3$), 30.2 (b, $CH_2$, cod), 30.7 (b, $CH_2$, cod), 31.2-31.8 ($CH_3$, $^t$Bu), 33.9 (b, $CH_2$, cod), 34.7-35.5 (C, tBu), 46.5 (C-5), 71.1 (b, CH=, cod), 75.5 (C-3), 78.0 (b, CH=, cod), 78.7 (b, C-4), 83.3 (C-2), 104.3 (b, CH=, cod), 104.6 (C-1), 105.9 (d, CH=, cod, $J_{C\text{-}P}$= 15 Hz), 112.6 ($CMe_2$), 117.5-162.3 (aromatic carbons). Minor isomer (40%): $^{31}$P NMR ($CDCl_3$, 213 K), δ: 109.9 (s). $^1$H NMR ($CDCl_3$, 213 K), δ: 1.14 (s, 3H, $CH_3$), 1.33 (s, 3H, $CH_3$), 1.41 (s, 9H, $CH_3$, $^t$Bu), 1.47 (s, 9H, $CH_3$, $^t$Bu), 1.69 (s, 18H, $CH_3$, $^t$Bu), 1.8-2.4 (b, 8H, $CH_2$, cod), 3.97 (m, 1H, H-5'), 4.10 (m, 1H, H-5), 4.18 (m, 1H, CH=, cod), 4.45 (m, 2H, H-4 and H-2), 4.54 (m, 1H, CH=, cod), 4.71 (m, 1H, H-3), 4.92 (m, 1H, CH=, cod), 5.01 (m, 1H, CH=, cod), 5.92 (b, 1H, H-1), 7.0-8.0 (m, 21H, CH= aromatics). $^{13}$C NMR ($CDCl_3$, 213 K), δ: 26.2 ($CH_3$), 26.6 (b, $CH_2$, cod), 27.2 (b, $CH_2$, cod), 28.7 (b, $CH_2$, cod), 29.8 (b, $CH_2$, cod), 31.2-31.8 ($CH_3$, $^t$Bu), 34.7-35.5 (C, tBu), 41.4 (C-5), 69.1 (b, CH=, cod), 74.3 (C-3), 76.8 (b, C-4), 82.0 (b, CH=, cod), 84.7 (C-2), 104.3 (b, CH=, cod), 104.6 (C-1), 106.4 (b, CH=, cod), 113.2 ($CMe_2$), 117.5-162.3 (aromatic carbons).

[Ir(cod)(**L1c**)]BArF. Yield 65 mg (96 %). Anal. calc (%) for $C_{74}H_{53}BF_{24}IrO_6PS$: C 50.49, H 3.03, S 1.82; found: C 50.53, H 3.11, N 1.77. Major isomer (65%): $^{31}$P NMR ($CDCl_3$), δ: 119.6 (s). $^{1}$H NMR ($CDCl_3$), δ: 1.27 (s, 3H, $CH_3$), 1.40 (s, 3H, $CH_3$), 1.8-2.4 (b, 8H, $CH_2$, cod), 2.98 (m, 1H, CH=, cod), 3.66 (dd, 1H, H-5', $^{2}J_{5'-5}$= 13.6 Hz, $^{3}J_{5'-4}$= 10.2 Hz), 3.93 (m, 1H, H-5), 4.38 (m, 1H, CH=, cod), 4.48 (m, 1H, H-4), 4.62 (d, 1H, H-2, $^{3}J_{2-1}$ = 4.0 Hz), 4.88 (m, 1H, CH= cod), 5.24 (m, 1H, CH=, cod), 5.48 (m, 1H, H-3), 5.77 (d, 1H, H-1, $^{3}J_{1-2}$ = 4.0 Hz), 7.0-8.1 (m, 29H, CH= aromatics). $^{13}$C NMR ($CDCl_3$), δ: 26.1 ($CH_3$), 26.5 ($CH_3$), 27.4 (b, $CH_2$, cod), 29.3 (b, $CH_2$, cod), 31.3 (b, $CH_2$, cod), 33.5 (b, $CH_2$, cod), 40.8 (C-5), 74.3 (b, CH=, cod), 75.9 (C-4), 77.8 (b, CH=, cod), 79.0 (C-3), 83.7 (C-2), 100.9 (b, CH=, cod), 105.1 (C-1), 107.2 (b, CH=, cod), 113.2 ($CMe_2$), 117.4-162.4 (aromatic carbons). Minor isomer (35%): $^{31}$P NMR ($CDCl_3$), δ: 114.6 (s). $^{1}$H NMR ($CDCl_3$), δ: 1.31 (s, 3H, $CH_3$), 1.39 (s, 3H, $CH_3$), 1.8-2.4 (b, 8H, $CH_2$, cod), 2.81 (m, 1H, CH=, cod), 3.33 (m, 1H, H-5'), 3.49 (m, 1H, H-5), 4.04 (m, 1H, H-4), 4.18 (d, 1H, H-2, $^{3}J_{2-1}$ = 3.6 Hz), 4.88 (m, 3H, CH= cod), 5.44 (m, 1H, H-3), 5.57 (d, 1H, H-1, $^{3}J_{1-2}$ = 3.6 Hz), 7.0-8.1 (m, 29H, CH= aromatics). $^{13}$C NMR ($CDCl_3$), δ: 26.3 ($CH_3$), 26.7 ($CH_3$), 28.1 (b, $CH_2$, cod), 29.6 (b, $CH_2$, cod), 31.0 (b, $CH_2$, cod), 31.8 (b, $CH_2$, cod), 40.8 (C-5), 75.3 (b, CH=, cod), 75.9 (C-4), 78.3 (b, CH=, cod), 79.2 (C-3), 83.8 (C-2), 100.9 (b, CH=, cod), 105.1 (C-1), 108.1 (b, CH=, cod), 112.9 ($CMe_2$), 117.4-162.4 (aromatic carbons).

[Ir(cod)(**L1d**)]BArF. Yield 62 mg (93 %). Anal. calc (%) for $C_{74}H_{53}BF_{24}IrO_6PS$: C 50.49, H 3.03, S 1.82; found: C 50.55, H 3.12, N 1.75. Major isomer (90%): $^{31}$P NMR ($CDCl_3$), δ: 115.0 (s). $^{1}$H NMR ($CDCl_3$), δ: 1.15 (s, 3H, $CH_3$), 1.35 (s, 3H, $CH_3$), 1.8-2.4 (b, 8H, $CH_2$, cod), 3.64 (m, 1H, CH=, cod), 4.18 (dd, 1H, H-5', $^{2}J_{5'-5}$= 12.4 Hz, $^{3}J_{5'-4}$= 9.2 Hz), 4.30 (m, 2H, CH=, cod and H-5), 4.39 (d, 1H, H-2, $^{3}J_{2-1}$ = 3.6 Hz), 4.52 (m, 2H, CH= cod and H-4), 4.89 (m, 2H, CH=, cod), 5.14 (m, 1H, H-3), 5.82 (d, 1H, H-1, $^{3}J_{1-2}$ = 3.6 Hz), 7.0-8.1 (m, 29H, CH= aromatics). $^{13}$C NMR ($CDCl_3$), δ: 26.0 ($CH_3$), 26.5 ($CH_3$), 29.7 (b, $CH_2$, cod), 30.3 (b, $CH_2$, cod), 30.9 (b, $CH_2$, cod), 44.0 (C-5), 74.9 (b, CH=, cod), 77.3 (C-4), 82.2 (C-3), 83.3 (b, CH=, cod), 83.5 (C-2), 100.9 (b, CH=, cod), 104.8 (C-1), 113.2 ($CMe_2$), 117.4 (b, CH=, BArF), 119-132 (aromatic carbons), 134.7 (b, CH=, BArF), 138-150 (aromatic carbons), 161.8 (q, C-B, BArF, $^{1}J_{C-B}$ = 49 Hz). Minor isomer (10%): $^{31}$P NMR ($CDCl_3$), δ: 107.6 (s). $^{1}$H NMR ($CDCl_3$), δ: 1.22 (s, 3H, $CH_3$), 1.33 (s, 3H, $CH_3$), 1.8-2.4 (b, 8H, $CH_2$, cod), 4.01 (m, 1H, CH=, cod), 4.33 (m, 2H, CH=, cod and H-5'), 4.52 (m, 2H, H-5 and H-4),

4.77 (m, 2H, CH= cod and H-2), 4.89 (m, 1H, CH=, cod), 5.21 (m, 1H, H-3), 5.75 (d, 1H, H-1, $^{3}J_{1\text{-}2}$ = 3.2 Hz), 7.0-8.1 (m, 29H, CH= aromatics).

[Ir(cod)(**L2a**)]BArF. Yield 62 mg (92 %). $^{31}$P NMR ($CDCl_3$, 298 K), δ: 115.1 (b). Anal. calc (%) for $C_{77}H_{79}BF_{24}IrO_6PS$: C 50.75, H 4.37, S 1.76; found: C 50.81, H 4.40, N 1.74. Major isomer (95%): $^{31}$P NMR ($CDCl_3$, 213 K), δ: 120.4 (s). $^{1}$H NMR ($CDCl_3$, 213 K), δ: 1.22 (s, 3H, $CH_3$), 1.28 (s, 9H, $CH_3$, $^{t}$Bu), 1.32 (s, 9H, $CH_3$, $^{t}$Bu), 1.41 (s, 9H, $CH_3$, $^{t}$Bu), 1.46 (s, 3H, $CH_3$), 1.65 (s, 9H, $CH_3$, $^{t}$Bu), 2.15 (b, 4H, $CH_2$, cod), 2.28 (b, 2H, $CH_2$, cod), 2.37 (b, 2H, $CH_2$, cod), 3.30 (m, 1H, H-5'), 3.89 (m, 1H, H-5), 4.02 (d, 1H, H-2, $^{3}J_{2\text{-}1}$= 3.6 Hz), 4.41 (m, 1H, CH=, cod), 4.55 (m, 2H, CH=, cod and H-4), 5.14 (m, 1H, CH=, cod), 5.36 (m, 2H, CH=, cod and H-3), 5.71 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 3.6 Hz), 7.0-7.8 (m, 16H, CH= aromatics). $^{13}$C NMR ($CDCl_3$, 213 K), δ: □25.7 ($CH_3$), 26.4 ($CH_3$), 28.0 (b, $CH_2$, cod), 29.9 (b, $CH_2$, cod), 30.7 ($CH_3$, $^{t}$Bu), 30.9 ($CH_3$, $^{t}$Bu), 31.3 ($CH_3$, $^{t}$Bu), 31.5 (b, $CH_2$, cod), 32.9 (b, $CH_2$, cod), 34.7 (C, tBu), 34.8 (C, tBu), 35.4 (C, tBu), 53.4 (C-5), 74.0 (C-4), 75.0 (b, CH=, cod), 75.8 (C-3), 79.9 (b, CH=, cod), 83.7 (C-2), 100.5 (d, CH=, cod, $J_{C\text{-}P}$= 15.5 Hz), 104.4 (d, CH=, cod, $J_{C\text{-}P}$= 13.2 Hz), 104.9 (C-1), 113.0 ($CMe_2$), 117.4 (b, CH=, BArF), 120-131 (aromatic carbons), 134.7 (b, CH=, BArF), 138-149 (aromatic carbons), 161.7 (q, C-B, BArF, $^{1}J_{C\text{-}B}$ = 49 Hz). Minor isomer (5%): $^{31}$P NMR ($CDCl_3$, 213 K), δ: 109.0 (s).

[Ir(cod)(**L3a**)]BArF. Yield 62 mg (91 %). $^{31}$P NMR ($CDCl_3$, 298 K), δ: 112.5 (b). Anal. calc (%) for $C_{79}H_{83}BF_{24}IrO_6PS$: C 51.27, H 4.52, S 1.73; found: C 51.33, H 4.55, N 1.70. Major isomer (70%): $^{31}$P NMR ($CDCl_3$, 213 K), δ: 114.9 (s). $^{1}$H NMR ($CDCl_3$, 213 K), δ: 1.31-1.36 (b, 30H, $CH_3$ and $CH_3$ $^{t}$Bu), 1.39 (s, 3H, $CH_3$), 1.46 (b, 6H, $CH_3$, $^{i}$Pr), 1.55 (s, 9H, $CH_3$, $^{t}$Bu), 1.9-2.4 (b, 2H, $CH_2$, cod), 3.26 (m, 2H, H-5' and CH $^{i}$Pr), 3.46 (d, 1H, H-2, $^{3}J_{2\text{-}1}$= 3.2 Hz), 3.75 (m, 1H, H-5), 4.35 (m, 1H, CH=, cod), 4.41 (m, 1H, H-4), 4.55 (m, 2H, CH=, cod), 4.84 (m, 1H, H-3), 5.35 (m, 1H, CH=, cod), 5.46 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 3.2 Hz), 7.1-7.8 (m, 16H, CH= aromatics). $^{13}$C NMR ($CDCl_3$, 213 K), δ: □22.0 ($CH_3$, $^{i}$Pr), 23.6 ($CH_3$, $^{i}$Pr), 25.3 ($CH_3$), 26.0 ($CH_3$), 27-35 ($CH_3$ $^{t}$Bu, C $^{t}$Bu, $CH_2$ cod and C-5), 43.6 (b, CH $^{i}$Pr), 70.2 (b, CH=, cod), 75.3 (b, CH=, cod), 77.2 (C-4), 77.9 (C-3), 82.3 (b, C-2), 104.1 (b, CH=, cod), 104.9 (C-1), 112.7 ($CMe_2$), 117.5 (b, CH=, BArF), 120-130 (aromatic carbons), 134.6 (b, CH=, BArF), 138-149 (aromatic carbons), 161.7 (q, C-B, BArF, $^{1}J_{C\text{-}B}$ = 49 Hz). Minor isomer (30%): $^{31}$P NMR ($CDCl_3$, 213 K), δ: 109.2 (s). $^{1}$H NMR ($CDCl_3$, 213 K), δ: 1.15 (s, 3H, $CH_3$), 1.31-1.36 (b, 27H, $CH_3$ $^{t}$Bu), 1.37 (s, 3H, $CH_3$), 1.46 (b, 6H, $CH_3$, $^{i}$Pr), 1.55 (s, 9H, $CH_3$, $^{t}$Bu), 1.9-2.4 (b, 2H, $CH_2$, cod), 3.26 (m, 1H, CH $^{i}$Pr), 3.44 (d, 1H, H-2, $^{3}J_{2\text{-}1}$= 3.2 Hz), 3.75 (m, 1H,

H-5'), 3.84 (m, 1H, H-3), 3.96 (m, 1H, H-5), 4.25 (m, 1H, CH=, cod), 4.41 (m, 1H, H-4), 4.55 (m, 1H, CH=, cod), 4.92 (m, 1H, CH=, cod), 5.62 (m, 1H, CH=, cod), 5.85 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 3.2 Hz), 7.1-7.8 (m, 16H, CH= aromatics). $^{13}$C NMR ($CDCl_3$, 213 K); δ: 21.7 ($CH_3$, $^{i}$Pr), 22.9 ($CH_3$, $^{i}$Pr), 25.8 ($CH_3$), 26.5 ($CH_3$), 27-35 ($CH_3$ $^{t}$Bu, C $^{t}$Bu, $CH_2$ cod and C-5), 43.6 (b, CH $^{i}$Pr), 69.8 (b, CH=, cod), 73.5 (C-4), 77.5 (b, CH=, cod), 78.2 (C-3), 82.3 (b, C-2), 103.2 (b, CH=, cod), 104.3 (b, CH=, cod), 104.9 (C-1), 113.2 ($CMe_2$), 117.5 (b, CH=, BArF), 120-130 (aromatic carbons), 134.6 (b, CH=, BArF), 138-149 (aromatic carbons), 161.7 (q, C-B, BArF, $^{1}J_{C\text{-}B}$ = 49 Hz).

[Ir(cod)(**L4a**)]BArF. Yield 59 mg (90 %). $^{31}$P NMR ($CDCl_3$, 298 K), δ: 111.9 (s). Anal. calc (%) for $C_{84}H_{85}BF_{24}IrO_6PS$: C 52.75, H 4.48, S 1.68; found: C 52.77, H 4.52, N 1.65. Major isomer (65%): $^{31}$P NMR ($CDCl_3$, 213 K), δ: 105.8 (s). $^{1}$H NMR ($CDCl_3$, 213 K), δ: 1.19 (s, 3H, $CH_3$), 1.39 (s, 18H, $CH_3$, $^{t}$Bu), 1.43 (s, 3H, $CH_3$), 1.57 (s, 9H, $CH_3$, $^{t}$Bu), 1.67 (s, 9H, $CH_3$, $^{t}$Bu), 1.8-2.4 (b, 8H, $CH_2$, cod), 2.83 (b, 6H, $CH_3$-Ar), 2.91 (b, 3H, $CH_3$-Ar), 3.65 (m, 1H, H-5'), 3.91 (m, 1H, H-5), 4.02 (d, 1H, H-2, $^{3}J_{2\text{-}1}$= 3.6 Hz), 4.03 (m, 2H, CH=, cod and H-3), 4.39 (m, 2H, H-4 and CH=, cod), 4.54 (m, 1H, CH=, cod), 4.71 (b, 1H, CH= cod), 5.42 (d, 1H, H-1, $^{3}J_{1\text{-}2}$ = 3.6 Hz), 7.2-7.8 (m, 19H, CH= aromatics). $^{13}$C NMR ($CDCl_3$), δ: 22.9 ($CH_3$-Ar), 23.5 ($CH_3$-Ar), 25.3 ($CH_3$), 26.9 ($CH_3$), 27.9 (b, $CH_2$, cod), 31-32.5 ($CH_3$, $^{t}$Bu), 33.1 ($CH_2$, cod), 33.4 ($CH_2$, cod), 34.5-35.5 (C, tBu), 46.3 (C-5), 70.4 (CH=, cod), 72.1 (CH=, cod), 72.5 (C-4), 75.3 (C-3), 79.4 (C-2), 102.3 (d, CH= cod, $J_{C\text{-}P}$= 16.0 Hz), 103.8 (b, CH= cod), 104.3 (C-1), 112.8 ($CMe_2$), 117.4 (b, CH=, BArF), 120-132 (aromatic carbons), 134.7 (b, CH=, BArF), 138-149 (aromatic carbons), 161.7 (q, C-B, BArF, $^{1}J_{C\text{-}B}$ = 49 Hz). Minor isomer (35%): $^{31}$P NMR ($CDCl_3$, 213 K), δ: 117.2 (s). $^{1}$H NMR ($CDCl_3$, 213 K), δ: 1.24 (s, 3H, $CH_3$), 1.39 (s, 18H, $CH_3$, $^{t}$Bu), 1.43 (s, 3H, $CH_3$), 1.54 (s, 9H, $CH_3$, $^{t}$Bu), 1.67 (s, 9H, $CH_3$, $^{t}$Bu), 1.8-2.4 (b, 8H, $CH_2$, cod), 2.83 (b, 6H, $CH_3$-Ar), 2.91 (b, 3H, $CH_3$-Ar), 3.85 (m, 1H, H-5'), 3.91 (m, 1H, H-5), 4.05 (m, 1H, CH=, cod), 4.13 (d, 1H, H-2, $^{3}J_{2\text{-}1}$= 3.6 Hz), 4.49 (m, 2H, H-4 and CH=, cod), 4.76 (m, 1H, CH=, cod), 4.84 (b, 2H, CH= cod and H-3), 5.67 (d, 1H, H-1, $^{3}J_{1\text{-}2}$ = 3.6 Hz), 7.2-7.8 (m, 19H, CH= aromatics). $^{13}$C NMR ($CDCl_3$), δ: 23.2 ($CH_3$-Ar), 23.7 ($CH_3$-Ar), 25.7 ($CH_3$), 26.7 ($CH_3$), 28.3 (b, $CH_2$, cod), 28.9 (b, $CH_2$, cod), 31-32.5 ($CH_3$, $^{t}$Bu), 33.3 ($CH_2$, cod), 33.7 ($CH_2$, cod), 34.5-35.5 (C, tBu), 46.3 (C-5), 69.8 (CH=, cod), 70.3 (CH=, cod), 71.2 (C-4), 75.5 (C-3), 79.6 (C-2), 102.5 (b, CH= cod), 103.9 (b, CH= cod), 104.3 (C-1), 113.3 ($CMe_2$), 117.4 (b, CH=, BArF), 120-132 (aromatic carbons), 134.7 (b, CH=, BArF), 138-149 (aromatic carbons), 161.7 (q, C-B, BArF, $^{1}J_{C\text{-}B}$ = 49 Hz).

[Ir(cod)(**L5a**)]BArF. Yield 64 mg (91 %). $^{31}$P NMR ($CDCl_3$), δ: 109.5 (s). $^{1}$H NMR ($CDCl_3$), δ: 1.19 (s, 3H, $CH_3$), 1.36 (s, 9H, $CH_3$, $^{t}$Bu), 1.38 (s, 9H, $CH_3$, $^{t}$Bu), 1.41 (s, 3H, $CH_3$), 1.57 (s, 9H, $CH_3$, $^{t}$Bu), 1.65 (s, 9H, $CH_3$, $^{t}$Bu), 1.90-2.18 (b, 8H, $CH_2$, cod), 3.64 (dd, 1H, H-5', $^{2}J_{5'-5}$= 13.2 Hz, $^{3}J_{5'-4}$= 8.8 Hz), 3.96 (m, 1H, CH=, cod), 4.19 (m, 1H, H-2), 4.22 (m, 1H, H-5), 4.31 (m, 1H, H-4), 4.54 (b, 2H, CH= cod and H-3), 4.61 (m, 1H, CH=, cod), 4.92 (b, 1H, CH=, cod), 5.66 (d, 1H, H-1, $^{3}J_{1-2}$ = 4.4 Hz), 7.1-7.8 (m, 21H, CH= aromatics). $^{13}$C NMR ($CDCl_3$), δ: □26.2 ($CH_3$), 26.4 ($CH_3$), 28.4 (b, $CH_2$, cod), 28.6 (b, $CH_2$, cod), 31.5 ($CH_3$, $^{t}$Bu), 31.7 ($CH_3$, $^{t}$Bu), 32.1 ($CH_3$, $^{t}$Bu), 32.5 (b, $CH_2$, cod), 33.3 (b, $CH_2$, cod), 34.9 (C, tBu), 35.0 (C, tBu), 35.7 (C, tBu), 45.1 (C-5), 71.4 (b, CH=, cod), 72.6 (C-3), 76.2 (b, CH=, cod), 78.3 (d, C-4, $J_{C-P}$= 5.2 Hz), 78.8 (C-2), 103.7 (b, CH=, cod), 104.5 (C-1), 105.2 (b, CH=, cod), 114.3 ($CMe_2$), 117.6 (b, CH=, BArF), 120.6-133 (aromatic carbons), 135.0 (b, CH=, BArF), 139-150 (aromatic carbons), 161.9 (q, C-B, BArF, $^{1}J_{C-B}$ = 49 Hz). Anal. calc (%) for $C_{82}H_{81}BF_{24}IrO_6PS$: C 52.26, H 4.33, S 1.70; found: C 52.21, H 4.28, N 1.68.

[Ir(cod)(**L5b**)]BArF. Yield 60 mg (89 %). $^{31}$P NMR ($CDCl_3$), δ: 109.0 (s). $^{1}$H NMR ($CDCl_3$), δ: 0.51 (m, 9H, $CH_3$-Si), 0.61 (m, 9H, $CH_3$-Si), 1.19 (s, 3H, $CH_3$), 1.36 (s, 3H, $CH_3$), 2.0-2.3 (b, 8H, $CH_2$, cod), 3.56 (dd, 1H, H-5', $^{2}J_{5'-5}$= 14.4 Hz, $^{3}J_{5'-4}$= 10.8 Hz), 3.82 (m, 1H, CH=, cod), 4.28 (m, 3H, H-2, H-4, H-5), 4.50 (m, 1H, H-3), 4.66 (m, 2H, CH=, cod), 5.08 (b, 1H, CH=, cod), 5.66 (d, 1H, H-1, $^{3}J_{1-2}$ = 3.6 Hz), 7.3-7.9 (m, 23H, CH= aromatics). $^{13}$C NMR ($CDCl_3$), δ: 0.50 ($CH_3$-Si), 1.60 ($CH_3$-Si), 26.5 ($CH_3$), 26.6 ($CH_3$), 28.2 ($CH_2$, cod), 29.9 ($CH_2$, cod), 30.2 ($CH_2$, cod), 34.6 ($CH_2$, cod), 45.2 (C-5), 71.8 (CH=, cod), 72.8 (C-4), 78.2 (CH=, cod), 79.0 (C-2), 79.2 (C-3), 104.4 (CH=, cod), 104.8 (C-1), 106.5 (d, CH=, cod, $J_{C-P}$= 12 Hz), 114.7 ($CMe_2$), 117.9 (b, CH=, BArF), 123-134 (aromatic carbons), 135.3 (b, CH=, BArF), 137-155 (aromatic carbons), 162.3 (q, C-B, BArF, $^{1}J_{C-B}$ = 49 Hz). Anal. calc (%) for $C_{72}H_{65}BF_{24}IrO_6PSSi_2$: C 47.52, H 3.63, S 1.78; found: C 47.54, H 3.65, N 1.77.

[Ir(cod)(**L5c**)]BArF. Yield 62 mg (95 %). $^{31}$P NMR ($CDCl_3$), δ: 111.1 (s). $^{1}$H NMR ($CDCl_3$), δ: 1.30 (s, 3H, $CH_3$), 1.52 (s, 3H, $CH_3$), 1.8-2.4 (b, 8H, $CH_2$, cod), 3.09 (m, 1H, CH=, cod), 3.80 (dd, 1H, H-5', $^{2}J_{5'-5}$= 13.6 Hz, $^{3}J_{5'-4}$= 10.0 Hz), 4.15 (m, 1H, H-5), 4.36 (m, 2H, CH=, cod and H-4), 4.46 (m, 1H, H-2), 4.68 (m, 1H, CH= cod), 4.86 (m, 1H, H-3), 4.97 (m, 1H, CH=, cod), 5.59 (d, 1H, H-1, $^{3}J_{1-2}$ = 3.2 Hz), 7.2-8.1 (m, 29H, CH= aromatics). $^{13}$C NMR ($CDCl_3$), δ: 26.1 ($CH_3$), 26.3 ($CH_3$), 26.9 (b, $CH_2$, cod), 31.9 ($CH_2$, cod), 33.0 ($CH_2$, cod), 44.4 (C-5), 78.4 (C-4), 75.7 (b, CH=, cod), 78.4 (C-2), 80.6 (C-3), 103.4 (b, CH=, cod and C-1), 107.1 (b, CH=, cod), 114.3 ($CMe_2$), 123.2 (b,

CH=, BArF), 125-133 (aromatic carbons), 134.8 (b, CH=, BArF), 137-148 (aromatic carbons), 161.7 (q, C-B, BArF, $^{1}J_{C\text{-}B}$ = 49 Hz). Anal. calc (%) for $C_{74}H_{53}BF_{24}IrO_6PS$: C 50.49, H 3.03, S 1.82; found: C 50.58, H 3.13, N 1.78.

[Ir(cod)(**L5d**)]BArF. Yield 62 mg (95 %). $^{31}$P NMR ($CDCl_3$), δ: 117.4 (s). $^{1}$H NMR ($CDCl_3$), δ: 1.24 (s, 3H, $CH_3$), 1.34 (s, 3H, $CH_3$), 1.8-2.4 (b, 8H, $CH_2$, cod), 3.03 (m, 1H, CH=, cod), 4.03 (dd, 1H, H-5', $^{2}J_{5'\text{-}5}$= 12.0 Hz, $^{3}J_{5'\text{-}4}$= 9.2 Hz), 4.18 (dd, 1H, H-5, $^{2}J_{5\text{-}5'}$= 12.0 Hz, $^{3}J_{5\text{-}4}$= 3.6 Hz), 4.45 (m, 1H, CH=, cod), 4.56 (m, 1H, H-4), 4.62 (m, 1H, CH= cod), 4.88 (m, 1H, H-2), 5.03 (m, 1H, H-3), 5.16 (m, 1H, CH=, cod), 5.92 (d, 1H, H-1, $^{3}J_{1\text{-}2}$ = 3.6 Hz), 7.2-8.2 (m, 29H, CH= aromatics). $^{13}$C NMR ($CDCl_3$), δ: 26.1 ($CH_3$), 28.5 ($CH_2$, cod), 29.2 ($CH_2$, cod), 30.4 ($CH_2$, cod), 30.9 ($CH_2$, cod), 43.8 (C-5), 75.2 (C-4), 76.4 (CH=, cod), 77.2 (CH=, cod), 78.5 (C-3), 78.9 (C-2), 103.9 (C-1), 105.8 (CH=, cod), 107.3 (CH=, cod), 114.7 ($CMe_2$), 117.4 (b, CH=, BArF), 120-132 (aromatic carbons), 134.7 (b, CH=, BArF), 138-148 (aromatic carbons), 161.9 (q, C-B, BArF, $^{1}J_{C\text{-}B}$ = 49 Hz). Anal. calc (%) for $C_{74}H_{53}BF_{24}IrO_6PS$: C 50.49, H 3.03, S 1.82; found: C 50.57, H 3.18, N 1.75.

[Ir(cod)(**L6a**)]BArF. Yield 66 mg (93 %). $^{31}$P NMR ($CDCl_3$), δ: 107.6 (s). $^{1}$H NMR ($CDCl_3$), δ: 1.18 (s, 3H, $CH_3$), 1.37 (s, 9H, $CH_3$, $^{t}$Bu), 1.38 (s, 9H, $CH_3$, $^{t}$Bu), 1.46 (s, 3H, $CH_3$), 1.54 (s, 9H, $CH_3$, $^{t}$Bu), 1.71 (s, 9H, $CH_3$, $^{t}$Bu), 1.8-2.4 (b, 8H, $CH_2$, cod), 2.76 (s, 3H, $CH_3$-Ar), 2.90 (s, 3H, $CH_3$-Ar), 3.74 (dd, 1H, H-5', $^{2}J_{5'\text{-}5}$= 13.2 Hz, $^{3}J_{5'\text{-}4}$= 9.2 Hz), 3.92 (m, 2H, H-5, H-2), 4.05 (m, 1H, CH=, cod), 4.40 (m, 3H, H-4, H-3 and CH=, cod), 4.71 (b, 2H, CH= cod), 5.62 (d, 1H, H-1, $^{3}J_{1\text{-}2}$ = 3.2 Hz), 7.2-7.8 (m, 19H, CH= aromatics). $^{13}$C NMR ($CDCl_3$), δ: 22.7 ($CH_3$-Ar), 24.3 ($CH_3$-Ar), □25.9 ($CH_3$), 27.9 ($CH_2$, cod), 28.9 ($CH_2$, cod), 30.8 ($CH_3$, $^{t}$Bu), 31.0 ($CH_3$, $^{t}$Bu), 31.1 ($CH_3$, $^{t}$Bu), 31.9 ($CH_2$, cod), 33.5 ($CH_2$, cod), 34.6 (C, tBu), 35.3 (C, tBu), 35.5 (C, tBu), 45.9 (C-5), 68.5 (CH=, cod), 73.2 (CH=, cod), 73.6 (C-4), 78.1 (d, C-2, $J_{C\text{-}P}$= 4.5 Hz), 79.0 (d, C-3, $J_{C\text{-}P}$= 7.2 Hz), 102.5 (d, CH= cod, $J_{C\text{-}P}$= 16.0 Hz), 104.7 (C-1), 105.8 (d, CH= cod, $J_{C\text{-}P}$= 15.9 Hz), 114.0 ($CMe_2$), 117.4 (b, CH=, BArF), 120-132 (aromatic carbons), 134.7 (b, CH=, BArF), 138-149 (aromatic carbons), 161.7 (q, C-B, BArF, $^{1}J_{C\text{-}B}$ = 49 Hz). Anal. calc (%) for $C_{84}H_{85}BF_{24}IrO_6PS$: C 52.75, H 4.48, S 1.68; found: C 52.81, H 4.54, N 1.63.

[Ir(cod)(**L7a**)]BArF. Yield 60 mg (90 %). $^{31}$P NMR ($CDCl_3$), δ: 120.7 (s). $^{1}$H NMR ($CDCl_3$), δ: 1.11 (s, 3H, $CH_3$), 1.35 (s, 18H, $CH_3$, $^{t}$Bu), 1.40 (s, 3H, $CH_3$), 1.45 (s, 9H, $CH_3$, $^{t}$Bu), 1.74 (s, 9H, $CH_3$, $^{t}$Bu), 1.9-2.3 (b, 8H, $CH_2$, cod), 3.93 (m, 1H, CH=, cod), 4.20 (d, 1H, H-2, $^{3}J_{2\text{-}1}$= 3.2 Hz), 4.34 (m, 1H, H-3), 4.38 (m, 2H, H-5' and H-5), 4.67 (m, 1H, CH=, cod), 4.47 (m, 1H, CH=, cod), 4.82

(m, 1H, H-4), 4.92 (b, 1H, CH=, cod), 5.51 (d, 1H, H-1, $^{3}J_{1\text{-}2}$ = 3.2 Hz), 7.1-7.8 (m, 21H, CH= aromatics). $^{13}$C NMR ($CDCl_3$), δ: □26.1 ($CH_3$), 26.5 ($CH_3$), 27.5 (b, $CH_2$, cod), 29.2 (b, $CH_2$, cod), 31.2 ($CH_3$, $^{t}$Bu), 31.4 ($CH_3$, $^{t}$Bu), 31.5 ($CH_3$, $^{t}$Bu), 32.2 (b, $CH_2$, cod), 33.7 (b, $CH_2$, cod), 34.9 (C, tBu), 35.0 (C, tBu), 35.5 (C, tBu), 35.8 (C, tBu), 59.1 (C-3), 63.8 (C-5), 69.5 (b, CH=, cod), 75.8 (b, CH=, cod), 75.9 (C-4), 83.9 (C-2), 104.5 (d, CH=, cod, $J_{C\text{-}P}$= 22.2 Hz), 104.9 (C-1), 105.4 (d, CH=, cod, $J_{C\text{-}P}$= 13 Hz), 113.4 ($CMe_2$), 117.6 (b, CH=, BArF), 130.6-133.8 (aromatic carbons), 134.9 (b, CH=, BArF), 138-149 (aromatic carbons), 161.9 (q, C-B, BArF, $^{1}J_{C\text{-}B}$ = 49 Hz). Anal. calc (%) for $C_{82}H_{81}BF_{24}IrO_6PS$: C 52.26, H 4.33, S 1.70; found: C 52.31, H 4.39, N 1.67.

[Ir(cod)(**L8a**)]BArF. Yield 68 mg (94 %). $^{31}$P NMR ($CDCl_3$), δ: 120.7 (s). $^{1}$H NMR ($CDCl_3$), δ: 1.05 (s, 3H, $CH_3$), 1.13 (s, 3H, $CH_3$), 1.37 (s, 18H, $CH_3$, $^{t}$Bu), 1.51 (s, 9H, $CH_3$, $^{t}$Bu), 1.73 (s, 9H, $CH_3$, $^{t}$Bu), 1.9-2.4 (b, 8H, $CH_2$, cod), 3.77 (m, 1H, H-3), 4.02 (m, 1H, CH=, cod), 4.41 (m, 1H, H-4), 4.50 (m, 1H, H-5'), 4.58 (m, 1H, H-2), 4.69 (m, 2H, CH=, cod), 4.91 (m, 1H, H-5), 4.97 (b, 1H, CH=, cod), 5.74 (d, 1H, H-1, $^{3}J_{1\text{-}2}$ = 3.6 Hz), 7.1-7.8 (m, 21H, CH= aromatics). $^{13}$C NMR ($CDCl_3$), δ: □25.2 ($CH_3$), 25.6 ($CH_3$), 28.0 (b, $CH_2$, cod), 28.3 (b, $CH_2$, cod), 31.0 ($CH_3$, $^{t}$Bu), 32.0 ($CH_3$, $^{t}$Bu), 32.5 (b, $CH_2$, cod), 32.8 (b, $CH_2$, cod), 34.6 (C, tBu), 34.7 (C, tBu), 35.3 (C, tBu), 35.5 (C, tBu), 57.2 (C-3), 55.8 (C-5), 70.0 (b, CH=, cod), 74.9 (b, CH=, cod), 75.3 (C-4), 81.2 (C-2), 103.8 (C-1), 104.7 (d, CH=, cod, $J_{C\text{-}P}$= 14.5 Hz), 105.0 (d, CH=, cod, $J_{C\text{-}P}$= 16 Hz), 113.8 ($CMe_2$), 117.4 (b, CH=, BArF), 120.5-132.7 (aromatic carbons), 134.7 (b, CH=, BArF), 135-149 (aromatic carbons), 161.9 (q, C-B, BArF, $^{1}J_{C\text{-}B}$ = 49 Hz). Anal. calc (%) for $C_{82}H_{81}BF_{24}IrO_6PS$: C 52.26, H 4.33, S 1.70; found: C 52.33, H 4.38, N 1.72.

## 4. Typical procedure for the hydrogenation of olefins

The alkene (1 mmol) and Ir complex (2 mol%) were dissolved in $CH_2Cl_2$ (2 mL) in a high-pressure autoclave. The autoclave was purged 4 times with hydrogen. Then, it was pressurized at the desired pressure. After the desired reaction time, the autoclave was depressurised and the solvent evaporated off. The residue was dissolved in $Et_2O$ (1.5 ml) and filtered through a short plug

of celite. The conversions were determined by $^1$H NMR or GC and enantiomeric excess was determined by chiral GC or chiral HPLC as previously described.[3]

**5. Synthesis of ligand precursors**

*1,2-O-Isopropylidene-5-O-trifluoromethanesulfonyl-α-D-ribofuranose*

Diol **2** (1 g, 5.2 mmol) was azeotropically dried with toluene (3 x 2 mL) and then dissolved in $CH_2Cl_2$ (24.5 mL) to which pyridine (0.57 mL, 7.6 mmol) was added. The alcohol solution was cooled to -15ºC and $Tf_2O$ (0.9 mL, 5.3 mmol) was added slowly over 2 min aprox. The reaction mixture was stirred at -15 ºC for 2 h. Evaporation of the solvent gave a yellow foam, which was purified by flash chromatography (AcOEt/hexane= 1/2) to produce the corresponding triflate as a white solid. Yield: 1.1 g, 65 %. $^1$H NMR (400 MHz, $CDCl_3$) δ: 1.38 (s, 3H, $CH_3$), 1.57 (s, 3H, $CH_3$), 3.97 (m, 2H, H-3 and H-4), 4.60 (m, 2H, H-5' and H2), 4.82 (dd, 1H, H-5, $^2J_{5\text{-}5'}$= 11.2 Hz, $^3J_{5\text{-}4}$= 1.8 Hz), 5.84 (d, 1H, H-1, $^3J_{1\text{-}2}$= 3.2 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 26.7 ($CH_3$), 71.2 (C-3), 73.8 (C-5), 78.0 (C-4), 78.1 (C-2), 104.2 (C-1), 113.4 ($CMe_2$).

*1,2-O-Isopropylidene-5-phenylsulfanyl-α-D-ribofuranose* ***9***

To a suspension of NaH (0.5 g, 20.8 mmol) in THF (7 mL) a solution of PhSH (0.5 mL, 4.8 mmol) in THF (5 mL) was added. After 2 min, the suspension was cooled to -78 °C and a solution of 1,2-*O*-isopropylidene-5-*O*-trifluoromethanesulfonyl-α-D-ribofuranose (0.85 g, 2.6 mmol) in THF (8.5 mmol) was added. After 90 min, water (25 mL) was added and the THF was evaporated. The crude product was extracted in $CH_2Cl_2$ (3 x 25 mL), dried with $MgSO_4$ and dried in the rotavapor. The crude was purified by flash chromatography (AcOEt/hexane= 1/3) to produce **9** as a white solid. Yield: 0.5 g, 67 %. $^1$H NMR (400 MHz, $CDCl_3$) δ: 1.36 (s, 3H, $CH_3$), 1.53 (s, 3H, $CH_3$), 3.15 (dd, 1H, H-5', $^2J_{5'\text{-}5}$= 14.0 Hz, $^3J_{5'\text{-}4}$= 6 Hz), 3.37 (dd, 1H, H-5, $^2J_{5\text{-}5'}$= 14.0 Hz, $^3J_{5\text{-}4}$= 4.0 Hz), 3.88 (m, 1H, H-3), 3.97 (m, 1H, H-4), 4.88 (dd, 1H, H-2, $^3J_{2\text{-}1}$= 4.0 Hz, $^3J_{2\text{-}3}$= 5.2 Hz), 5.82 (d, 1H, H-1, $^3J_{1\text{-}2}$= 4.0 Hz), 7.14 (m, 1H, CH=), 7.23 (m, 2H, CH=), 7.43 (m, 2H, CH=). $^{13}$C

[3] a) Källström, K.; Hedberg, C. Brandt, P.; Bayer, P.; Andersson, P. G. *J. Am. Chem. Soc.* **2004**, *126*, 14308. b) Mazuela, J.; Verendel, J.J.; Coll, M.; Schäffner, B.; Börner, A.; Andersson, P.G.; Pàmies, O.; Diéguez, M. *J. Am. Chem. Soc.* **2009**, *131*, 12344.

NMR (100 MHz, $CDCl_3$) δ: 26.6 ($CH_3$), 26.7 ($CH_3$), 35.7 (C-5), 74.7 (C-3), 78.7 (C-2), 78.9 (C-4), 104.0 (C-1), 112.9 ($CMe_2$) 128.7 (CH=), 128.9 (CH=), 135.8 (C).

*1,2-O-Isopropylidene-5-(2,6-dimethyl-phenyl)sulfanyl -α-D-ribofuranose* ***10***

Treatment of 2,6-dimethylbenzenethiol (0.64 mL, 4.8 mmol) with 1,2-*O*-isopropylidene-5-*O*-trifluoromethanesulfonyl-α-D-ribofuranose (0.85 g, 2.6 mmol) as described for **9** produces **10** as a white solid. Yield: 565 mg, 70 %. $^1$H NMR (400 MHz, $CDCl_3$) δ: 1.35 (s, 3H, $CH_3$), 1.49 (s, 3H, $CH_3$), 2.30 (b, 1H, OH), 2.57 (s, 6H, $CH_3$-Ar), 2.76 (dd, 1H, H-5', $^2J_{5'-5}$= 13.4 Hz, $^3J_{5'-4}$= 7.0 Hz), 3.11 (dd, 1H, H-5, $^2J_{5-5'}$= 13.4 Hz, $^3J_{5-4}$= 2.8 Hz), 3.80 (m, 2H, H-3 and H-4), 4.56 (m, 1H, H-2), 5.82 (d, 1H, H-1, $^3J_{1-2}$= 3.6 Hz), 7.!2 (m, 3H, CH=). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 22.2 ($CH_3$-Ar), 26.5 ($CH_3$), 26.8 ($CH_3$), 36.6 (C-5), 74.8 (C-3), 78.7 (C-2), 78.9 (C-4), 103.9 (C-1), 112.8 ($CMe_2$), 128.3 (CH=), 128.6 (CH=), 130.0 (C), 143.5 (C).

*1,2-O-Isopropylidene-5-O-benzoyl-3-O-trifluoromethanesulfonyl-α-D-ribofuranose*

Treatment of alcohol **3** (1.53 g, 5.2 mmol) with $Tf_2O$ (0.9 mL, 5.3 mmol) as previously described for **2** afforded the desired crude product. After 2 hours, water (10 mL) was added and the reaction mixture was extracted with dichloromethane (3 x 50 mL), dried with $MgSO_4$ and all the volatiles were removed in the rotavapor. To the crude product petroleum ether (25 mL) was added and the insoluble impurities were removed by filtration. Evaporation of the solvent provided 1,2-*O*-isopropylidene-5-*O*-benzoyl-3-*O*-trifluoromethanesulfonyl-α-D-ribofuranose as a white solid. Yield: 1.75 g, 79 %. $^1$H NMR (400 MHz, $CDCl_3$) δ: 1.39 (s, 3H, $CH_3$), 1.62 (s, 3H, $CH_3$), 4.44 (dd, 1H, H-5', $^2J_{5'-5}$= 12.4 Hz, $^3J_{5'-4}$= 4.0 Hz), 4.53 (m, 1H), 4.77 (dd, 1H, H-5, $^2J_{5-5'}$= 12.4 Hz, $^3J_{5-4}$= 2.8 Hz), 4.82 (m, 1H), 4.94 (m, 1H), 5.88 (d, 1H, H-1, $^3J_{1-2}$= 3.2 Hz), 7.48 (m, 2H, CH=), 7.60 (m, 1H, CH=), 8.02 (m, 2H, CH=).

*1,2-O-Isopropylidene-5-O-benzoyl-3-phenylsulfanyl-α-D-xylofuranose* ***11***

Treatment of benzenethiol (0.50 mL, 4.8 mmol) with 1,2-*O*-isopropylidene-5-*O*-benzoyl-3-*O*-trifluoromethanesulfonyl-α-D-ribofuranose (1.1 g, 2.6 mmol) as described for **9** produces **11** as a white solid together with small amount of **12** (8% yield). Yield: 472 mg, 47 %. $^1$H NMR (400 MHz, $CDCl_3$) δ: 1.31 (s, 3H, $CH_3$), 1.53 (s, 3H, $CH_3$), 3.85 (d, 1H, H-3, $^3J_{3-4}$= 4.0 Hz), 4.59 (dd, 1H, H-5',

$^{2}J_{5'-5}$= 11.6 Hz, $^{3}J_{5'-4}$= 3.2 Hz), 4.73 (m, 2H, H-5, H-2), 4.81 (m, 1H, H-4), 5.79 (d, 1H, H-1, $^{3}J_{1-2}$= 3.2 Hz), 7.2-8.1 (m, 10 H, CH=).

*1,2-O-Isopropylidene-3-phenylsulfanyl-α-D-xylofuranose* ***12***

To a solution of **11** (386.5 mg, 1 mmol) in methanol (4 mL) ammonia 30% (4 mL) was added. The reaction was stirred overnight at room temperature. Then, the volatiles were removed and the crude was purified by flash chromatography (AcOEt/hexane= 1/3) to produce **12** as a white solid. Yield: 133 mg, 47%. $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 1.29 (s, 3H, $CH_3$), 1.53 (s, 3H, $CH_3$), 2.01 (b, 1H, OH), 3.82 (d, 1H, H-3, $^{3}J_{3-4}$= 4.0 Hz), 3.88 (dd, 1H, H-5', $^{2}J_{5'-5}$= 12.0 Hz, $^{3}J_{5'-4}$= 4.8 Hz), 3.98 (dd, 1H, H-5, $^{2}J_{5-5'}$= 12.0 Hz, $^{3}J_{5-4}$= 6.8 Hz), 4.64 (m, 2H, H-4 and H-2), 5.96 (d, 1H, H-1, $^{3}J_{1-2}$= 3.6 Hz), 7.28 (m, 1H, CH=), 7.35 (m, 2H, CH=), 7.43 (m, 2 H, CH=). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 26.6 ($CH_3$), 26.8 ($CH_3$), 53.2 (C-3), 62.4 (C-5), 79.5 (C-2), 85.8 (C-4), 105.1 (C-1), 112.2 ($CMe_2$), 127.3 (CH=), 129.6 (CH=), 130.5 (CH=), 133.8 (C).

*1,2-O-Isopropylidene-5-O-benzoyl-3-O-trifluoromethanesulfonyl-α-D-xylofuranose*

Treatment of alcohol **4** (1.53 g, 5.2 mmol) with $Tf_2O$ (0.9 mL, 5.3 mmol) as previously described for 1,2-*O*-isopropylidene-5-*O*-benzoyl-3-*O*-trifluoromethanesulfonyl-α-D-ribofuranose afforded the desired product as a white solid. Yield: 1.53 g, 69 %. $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 1.36 (s, 3H, $CH_3$), 1.54 (s, 3H, $CH_3$), 4.48 (m, 1H), 4.68 (m, 2H), 4.80 (d, 1H, H-2, $^{3}J_{2-1}$= 3.6 Hz), 5.34 (d, 1H, $^{3}J$= 2 Hz), 6.07 (d, 1H, H-1, $^{3}J_{1-2}$= 3.6 Hz), 7.4 – 8.2 (m, 5H, CH=).

*1,2-O-Isopropylidene-5-O-benzoyl-3-phenylsulfanyl-α-D-ribofuranose* ***13***

Treatment of benzenethiol (0.50 mL, 4.8 mmol) with 1,2-*O*-isopropylidene-5-*O*-benzoyl-3-*O*-trifluoromethanesulfonyl-α-D-xylofuranose (1.1 g, 2.6 mmol) as described for **11** were stirred overnight at room temperature. After the same workup as **11**, compound **13** was obtained as a white solid together with small amount of **14** (6% yield). Yield: 100 mg, 10 %. $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 1.38 (s, 3H, $CH_3$), 1.59(s, 3H, $CH_3$), 3.41 (dd, 1H, H-3, $^{3}J_{3-4}$= 6.4 Hz, $^{3}J_{3-2}$= 3.2 Hz), 4.26 (dd, 1H, H-5', $^{2}J_{5'-5}$= 12.0 Hz, $^{3}J_{5'-4}$= 3.6 Hz), 4.35 (m, 1H, H-4), 4.81 (dd, 1H, H-5, $^{2}J_{5-5'}$= 12.0 Hz, $^{3}J_{5-4}$= 2.0 Hz), 4.87 (m, 1H, H-2), 5.85 (d, 1H, H-1, $^{3}J_{1-2}$= 4.0 Hz), 7.2-8.1 (m, 10 H, CH=).

*1,2-O-Isopropylidene-3-phenylsulfanyl-α-D-ribofuranose* ***14***

Treatment of **13** (193 mg, 0.5 mmol), as previously described for **11,** afforded the desired product as a white solid. Yield: 89 mg, 63 %. $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 1.36 (s, 3H, $CH_3$), 1.55 (s, 3H, $CH_3$), 1.88 (b, 1H, OH), 3.52 (dd, 1H, H-3, $^{3}J_{3\text{-}4}$= 10.2 Hz, $^{3}J_{3\text{-}4}$= 4.6 Hz), 3.62 (dd, 1H, H-5', $^{2}J_{5'\text{-}5}$= 12.6 Hz, $^{3}J_{5'\text{-}4}$= 2.6 Hz), 3.93 (dd, 1H, H-5, $^{2}J_{5\text{-}5'}$= 12.6 Hz, $^{3}J_{5\text{-}4}$= 2.4 Hz), 4.09 (m, 1H, H-4), 4.79 (m, 1H, H-2), 5.80 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 3.6 Hz), 7.28 (m, 3H, CH=), 7.48 (m, 2H, CH=). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 26.5 ($CH_3$), 26.8 ($CH_3$), 49.6 (C-3), 60.0 (C-5), 81.8 (C-2), 82.1 (C-4), 104.4 (C-1), 112.6 ($CMe_2$), 127.3 (CH=), 129.3 (CH=), 131.1 (CH=), 134.8 (C).