Supporting Information

Iron(II)/$(NH)_2P_2$ Macrocycles: Modular, Highly Enantioselective Transfer Hydrogenation Catalysts

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General. Reactions with air- or moisture-sensitive materials were carried out under an argon atmosphere using Schlenk techniques or in a glove box under argon. All solvents were distilled from an appropriate drying agent under argon prior to use and used within one day (Et_2O and THF from Na/benzophenone; PhMe from Na; EtOH from Na/ethyl phthalate; CH_2Cl_2, MeCN, MeOH and ^{i}PrOH from CaH_2; hexane from Na/benzophenone/tetraglyme). ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on the following instruments: Bruker Avance DPX 300 (^{1}H, 300.1; ^{13}C{^{1}H}, 75.5; ^{31}P{^{1}H}, 121.5), 400 (^{1}H, 400.1; ^{13}C{^{1}H}, 100.6; ^{31}P{^{1}H}, 162.0) and 500 (^{1}H, 500.2; ^{13}C{^{1}H}, 125.8; ^{31}P{^{1}H}, 202.5). ^{1}H and ^{13}C positive chemical shifts in ppm are downfield from tetramethylsilane. ^{31}P{^{1}H} NMR spectra are referenced to external 85% H_3PO_4. For complexes **8b** and **3a**-**c**, ^{13}C{^{31}P,^{1}H} spectra were measured with ^{31}P (and ^{1}H) decoupling to improve the S/N ratio. Mass spectra were measured by the MS service of the Laboratory of Organic Chemistry (ETH Zürich). Elemental analyses were carried out by the Laboratory of Microelemental Analysis (ETH Zürich). Ketones **10a**-**y** were purified by distillation from CaH_2 under reduced pressure or by recrystallization from hexane prior to use. Phosphinic amide **10z** was crystallized from CH_2Cl_2/hexane prior to use.

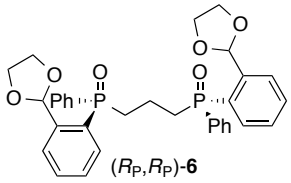
Titanium(IV) *iso*-propoxide (98%) was obtained from ABCR. 1,3-Diiodopropane (98%) was obtained from Fluka. 1,8-Diazabicycloundec-7-ene (DBU) was obtained from Fluorochem. *n*-Butyllithium (1.6 M in hexanes), iron(II) tetrafluoroborate hexahydrate (97%), lithium aluminum hydride powder (95%), sodium *tert*-butoxide (97%), and 1,1,3,3-tetramethyldisiloxane (TMDS, 97%) were obtained from Sigma-Aldrich. (1*S*,2*S*)-Cyclohexane-1,2-diamine (>98%) was obtained from TCI.

Thin layer chromatography was performed on Merck silica gel 60 F254 glass plates and visualized with UV fluorescence at 254 nm or stained in potassium permanganate solutions. Column chromatographic purifications were performed as flash column chromatography with

0.3 – 0.8 bar overpressure using Silicycle silica gel (SiliaFlash® P60, 230 – 400 mesh) as stationary phase.

(*R*)-(2-(1,3-Dioxolan-2-yl)phenyl)(phenyl)phosphine oxide ((R_P)-**5**),[S1] 3-ethyl-3-isocyanopentane,[S2] *N*-isocyano-*N*-isopropylpropan-2-amine,[S2] and 1-isocyanoadamantane[S3] were prepared following literature procedures.

Synthesis of Macrocycles



(R_P,R_P)-**6**

Synthesis of (1*R*,1'*R*)-Propane-1,3-diylbis((2-(1,3-dioxolan-2-yl)phenyl)(phenyl)phosphine oxide), (R_P,R_P)-6. A flame-dried 100 mL two-neck round-bottom flask was charged with (*R*)-(2-(1,3-dioxolan-2-yl)phenyl)(phenyl)phosphine oxide ((R_P)-**5**, 2.25 g, 8.21 mmol, 2.15 equiv)[S1] and THF (22 mL), and then cooled to –78 °C. After 10 min, *n*-butyllithium (5.1 mL, 1.6 M in hexanes, 8.2 mmol, 2.2 equiv) was added dropwise over 5 min, and the solution was stirred for 30 min at –78 °C (*Note*: A color change from light orange to dark red indicates full deprotonation of the secondary phosphine oxide). 1,3-Diiodopropane (0.44 mL, 3.8 mmol) was added dropwise, and the solution was warmed to room temperature overnight (*Note*: The product partially precipitates from the solution). Silica gel (10 g) was added, and the solvent was removed at the rotary evaporator (20 mbar, 40 °C). Flash column chromatography on silica gel (gradient CH_2Cl_2 : MeOH = 100 : 0 to 94 : 6) afforded the product as a white solid. Yield: 2.01 g (89%, d.r. ≥ 95 : 5). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.76 (*dd*, $^3J_{H,H'}$ = 7.9 Hz, $^4J_{H,H'}$ = 3.8 Hz, 2H, Ar-*H*), 7.67 – 7.43 (*m*, 10H, Ar-*H*), 7.42 – 7.33 (*m*, 6H, Ar-*H*), 6.38 (*s*, 2H, C*H*(OCH_2)$_2$), 4.04 – 3.78 (*m*, 8H, CH(OC*H*H)$_2$), 2.68 – 2.56 (*m*, 4H, PC*H*H), 2.01 (*tdd*, $^3J_{P,H}$ = 20.5 Hz, $^3J_{H,H'}$ = 7.6, 7.3 Hz, 2H, PCH_2CH_2). **^{31}P{^{1}H} NMR** (122 MHz, $CDCl_3$): 35.4 (*s*). **^{31}P NMR** (122 MHz, $CDCl_3$): 35.4 (br *s*). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): 141.9 (*d*, $^2J_{P,C}$ = 7.0 Hz, arom.), 133.3 (*d*, $^1J_{P,C}$ = 101.8 Hz, arom.), 132.1 (arom.), 131.9 (*d*, $^2J_{P,C}$ = 13.8 Hz, arom.), 131.8 (arom.), 131.5 (*d*, $^1J_{P,C}$ = 79.3 Hz, arom.), 130.9 (*d*, $^3J_{P,C}$ = 9.6 Hz, arom.), 128.9 (*d*, $^3J_{P,C}$ = 11.7 Hz, arom.), 128.7 (*d*, $^2J_{P,C}$ = 11.9 Hz, arom.), 127.6 (*d*, $^3J_{P,C}$ = 9.5 Hz, arom.), 101.1

(*d*, $^{3}J_{P,C}$ = 4.3 Hz, *C*H(OCH$_2$)$_2$), 65.34 (CH(O*C*H$_2$)$_2$), 65.33 (CH(O*C*H$_2$)$_2$), 30.9 (br *d*, $^{1}J_{P,C}$ = 74.7 Hz, P*C*H$_2$), 15.3 (*t*, $^{2}J_{P,C}$ = 3.3 Hz, PCH$_2$*C*H$_2$). **Melting Point**: 69 °C. **IR** (liquid film, cm^{-1}): 3058 (C-H), 2953 (C-H), 2889 (C-H), 2227 (P=O), 1641, 1591, 1572, 1484, 1473, 1437, 1396, 1348, 1312, 1244, 1177, 1132, 1111, 1093, 1061, 1026. **EA**: Calcd. for $C_{33}H_{34}O_6P_2$: C, 67.34; H, 5.82; found: C, 67.20; H, 5.94. **HRMS** (ESI): Calcd. for $C_{33}H_{35}O_6P_2$ *m*/*z* = 589.1903, found *m*/*z* = 589.1899 $[M+H]^+$. **HPLC**: No separation obtained with standard columns. $[\alpha]_D^{20}$: –0.30 (c = 1.0, CH_2Cl_2).

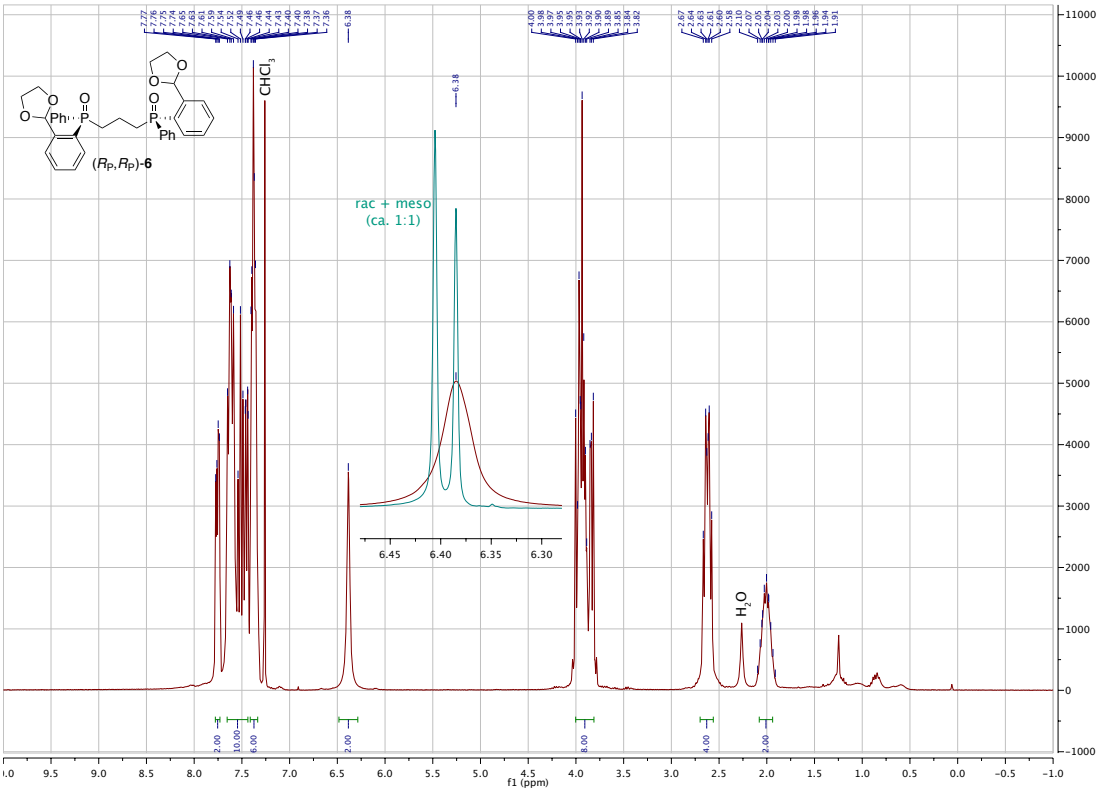


Figure S1: ^{1}H NMR spectrum of (R_P,R_P)-**6** (300 MHz, $CDCl_3$).

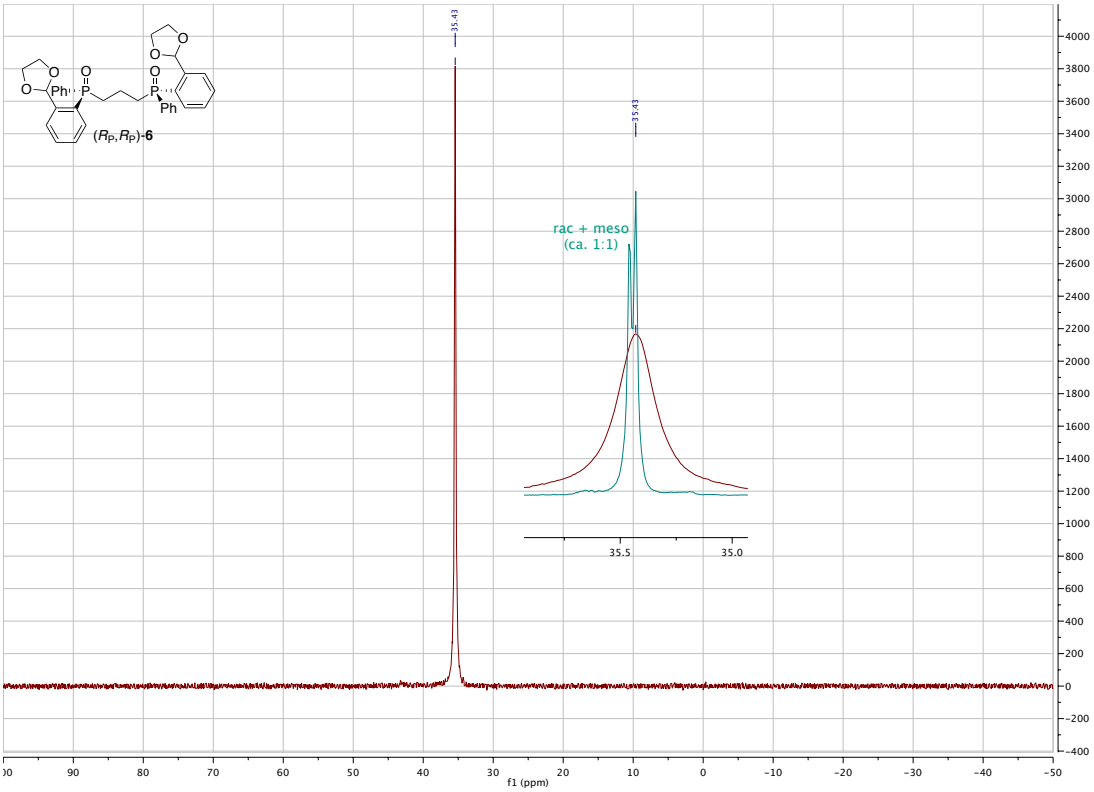


Figure S2: $^{31}P\{^{1}H\}$ NMR spectrum of (R_P,R_P)-**6** (122 MHz, $CDCl_3$).

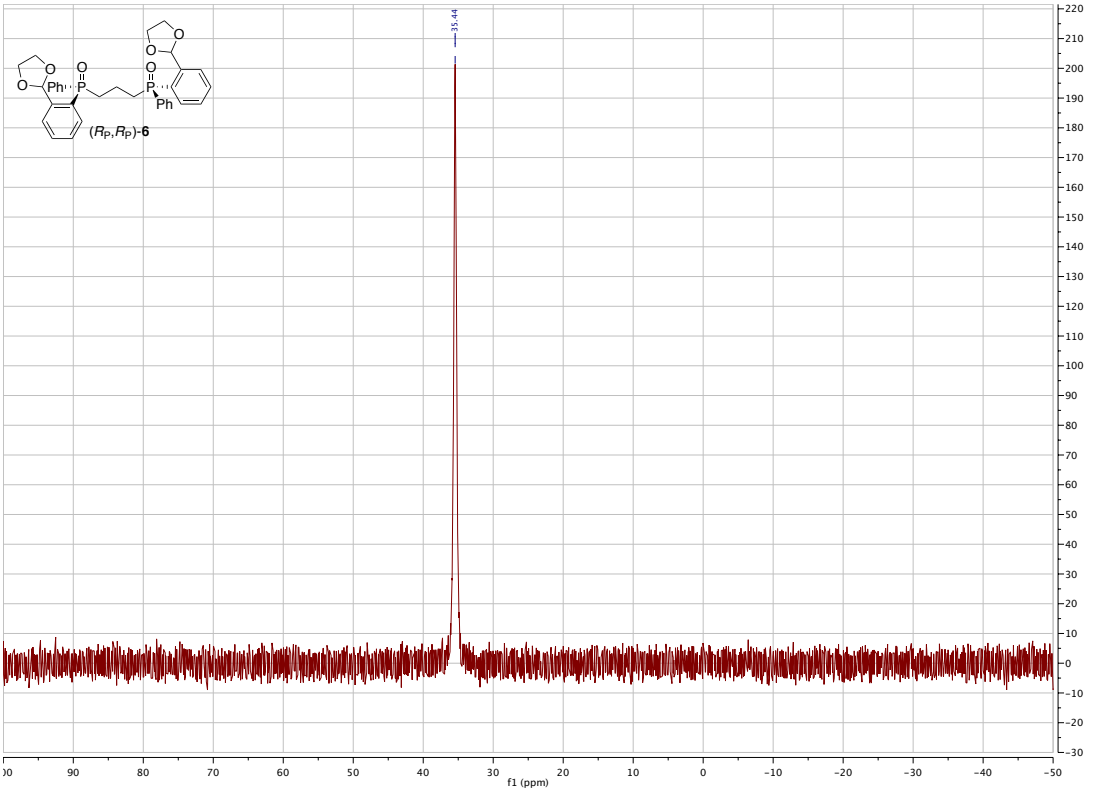


Figure S3: ^{31}P NMR spectrum of (R_P,R_P)-**6** (122 MHz, $CDCl_3$).

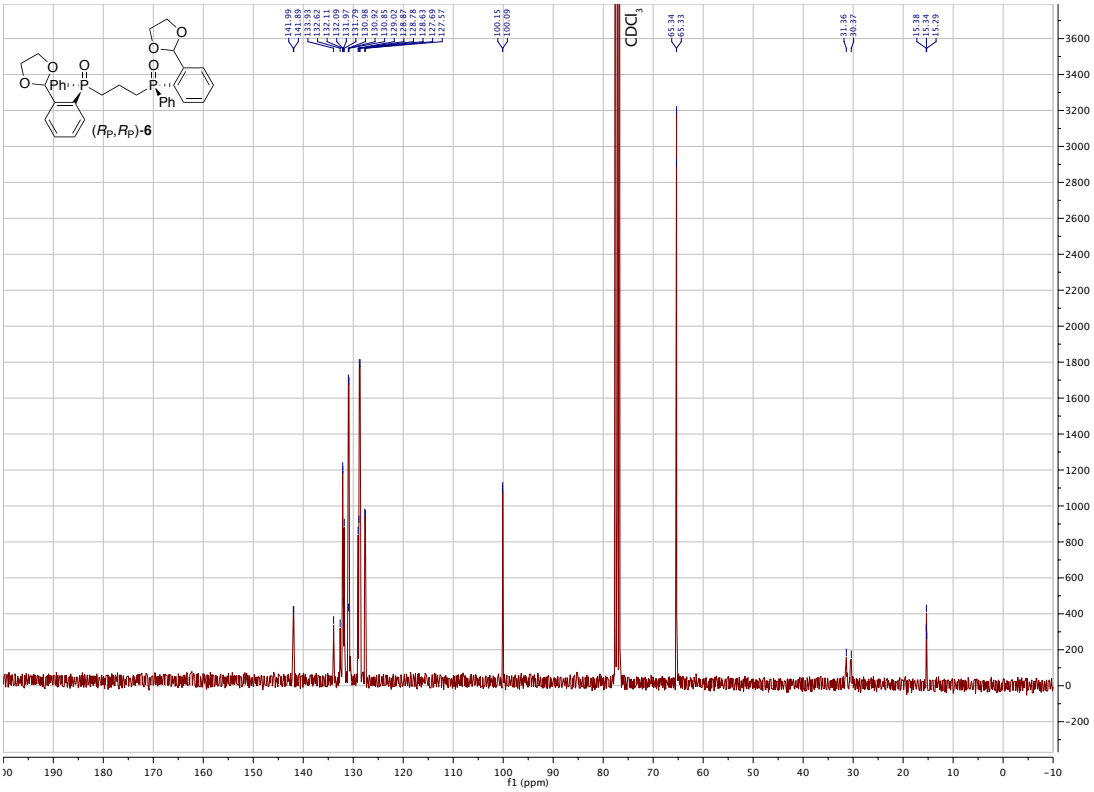
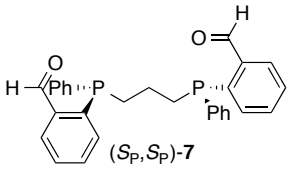


Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum of (R_P,R_P)-**6** (75 MHz, $CDCl_3$).



Synthesis of 2,2'-((1*S*,1'*S*)-Propane-1,3-diylbis(phenylphosphanediyl))dibenzaldehyde, (S_P,S_P)-7. A flame-dried 50 mL two-neck round-bottom flask was charged with powdered (R_P,R_P)-**6** (2.50 g, 4.25 mmol), Na_2SO_4 (0.603 g, 4.25 mmol, 1 equiv) and PhMe (21 mL), and then heated to 60 °C (*Note*: (R_P,R_P)-**6** is only poorly soluble in PhMe and a suspension is obtained). After 15 min, titanium(IV) *iso*-propoxide (2.8 mL, 9.1 mmol, 2.2 equiv) was added dropwise over 5 min. After 15 min, 1,1,3,3-tetramethyldisiloxane (TMDS, 5.6 mL, 32 mmol, 7.5 equiv) was added dropwise over 5 min, and the solution was stirred for 5 h at 60 °C to give a deep blue solution (*Notes*: (R_P,R_P)-**6** fully dissolves during the course of the reaction; the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution shows complete reduction to the diphosphine).

After cooling to room temperature, the solution was transferred to a stirred, saturated aqueous Na_2CO_3 solution (150 mL; degassed by bubbling nitrogen through for 1 h) using a Teflon® cannula. The resulting suspension was filtered through a pad of Celite® (10 g) and washed with PhMe (2 × 50 mL). The aqueous phase was separated and extracted twice with PhMe (2 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered into a 500 mL two-neck round-bottom flask, and the solvent was removed at the rotary evaporator (20 mbar, 40 °C). The residue was dissolved in THF (90 mL) and aqueous 5% HCl solution (45 mL; water degassed by bubbling nitrogen through for 1 h) was added. After stirring vigorously at room temperature for 6 h, saturated aqueous $NaHCO_3$ solution (100 mL; degassed by bubbling nitrogen through for 1 h) was added thereto (*Notes*: Gas evolution; the pH of the solution was neutral (if the solution is still acidic, solid $NaHCO_3$ has to be added until a neutral solution is obtained)), and the organic solvent was removed at the rotary evaporator (120 mbar, 40 °C). The aqueous phase was extracted three times with CH_2Cl_2 (3 × 75 mL; degassed by bubbling nitrogen through for 1 h). The combined organic phases were dried over $MgSO_4$, filtered, and the solvent was removed at the rotary evaporator (20 mbar, 40 °C). Flash column chromatography on silica gel (EtOAc : hexane = 1 : 3; solvent degassed by bubbling nitrogen through for 1 h) (*Note*: The product appears as a yellow band) affords the product as a yellow oil. Yield: 1.76 g (88%, d.r. = 9.4 : 1). **^{1}H NMR** (300 MHz, CD_2Cl_2): 10.57 (*d*, $^4J_{P,H}$ = 5.7 Hz, 2H, O=C*H*), 7.92 – 7.86 (*m*, 2H, Ar-*H*), 7.56 – 7.44 (*m*, 4H, Ar-*H*), 7.43 – 7.28 (*m*, 12H, Ar-*H*), 2.36 – 2.14 (*m*, 4H, PC*H*H), 1.70 – 1.52 (*m*, 2H, PCH_2CH_2). **^{31}P{^{1}H} NMR** (122 MHz, CD_2Cl_2): –27.4 (*s,* (*l*)-**7**), –27.5 (*s, meso*-**7**), d.r. = 9.4:1. **^{13}C{^{1}H} NMR** (75 MHz, CD_2Cl_2): 192.4 (*d*, $^3J_{P,C}$ = 21.6 Hz, *C*HO), 143.0 (*d*, $^2J_{P,C}$ = 28.1 Hz, arom.), 139.0 (*d*, $^1J_{P,C}$ = 88.0 Hz, arom.), 138.8 (*d*, $^1J_{P,C}$ = 86.2 Hz, arom.), 134.1 (arom.), 133.7 (arom.), 133.4 (arom.), 132.5 (arom.), 130.8 (*d*, $^3J_{P,C}$ = 4.3 Hz, arom.), 129.4 (*d*,

$^2J_{P,C}$ = 9.2 Hz, arom.), 129.2 (*d*, $^2J_{P,C}$ = 7.2 Hz, arom.), 29.6 (*m*, P*C*H$_2$), 23.1 (*t*, $^2J_{P,C}$ = 18.4 Hz, PCH$_2$*C*H$_2$). **IR** (liquid film, cm^{-1}): 3053 (C-H), 3014 (C-H), 3001 (C-H), 2958 (C-H), 2928 (C-H), 2853 (C-H), 2824 (C-H), 2738, 1690 (C=O), 1584, 1561, 1481, 1461, 1433, 1385, 1292, 1196, 1164, 1116, 1093, 1069, 1026. **HRMS** (ESI): Calcd. for $C_{29}H_{27}O_2P_2$ *m*/*z* = 469.1481, found *m*/*z* = 469.1481 $[M+H]^+$. **HPLC**: no separation obtained with standard columns. **[α]$_D^{20}$**: +44.0 (c = 0.5, $CHCl_3$).

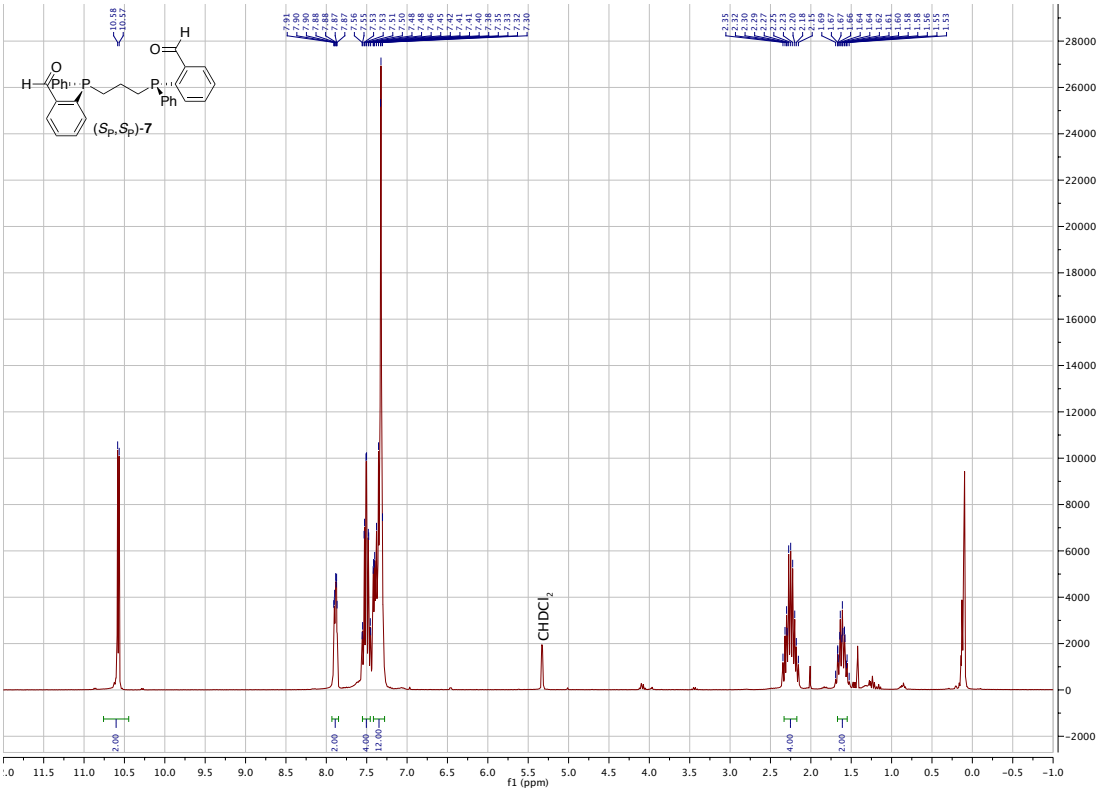


Figure S5: ^{1}H NMR spectrum of (S_P,S_P)-**7** (300 MHz, CD_2Cl_2).

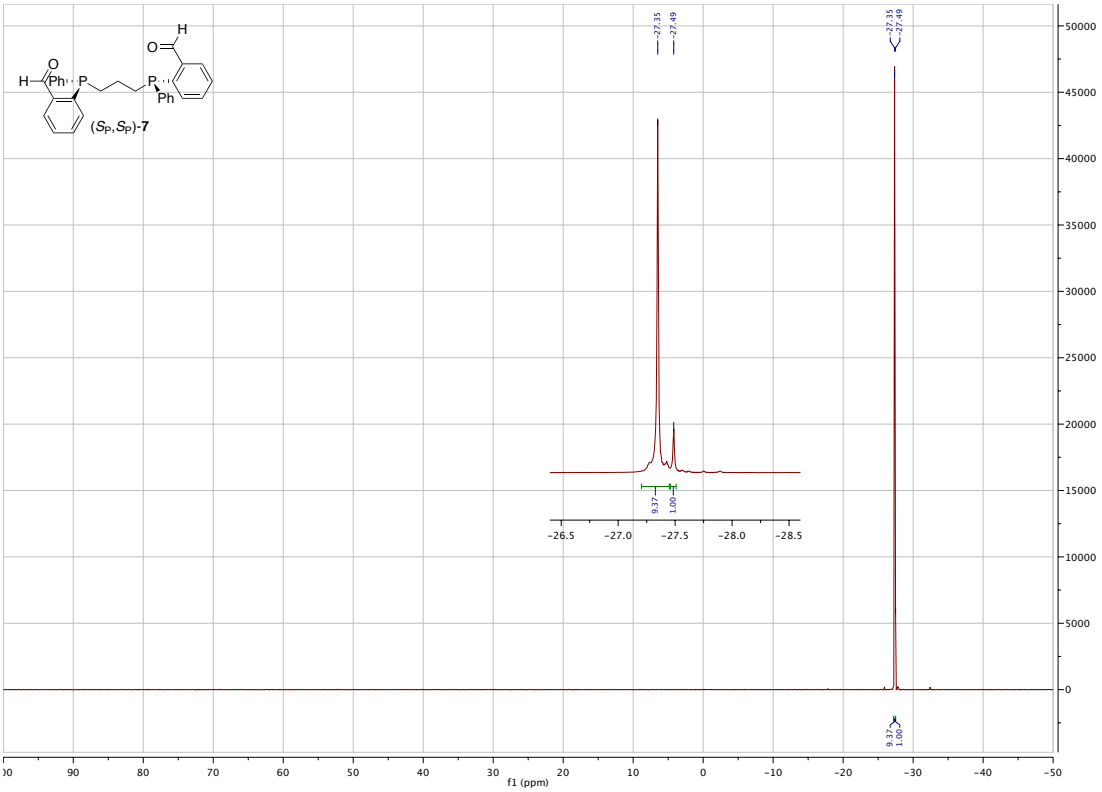


Figure S6: $^{31}P\{^{1}H\}$ NMR spectrum of (S_P,S_P)-**7** (122 MHz, CD_2Cl_2).

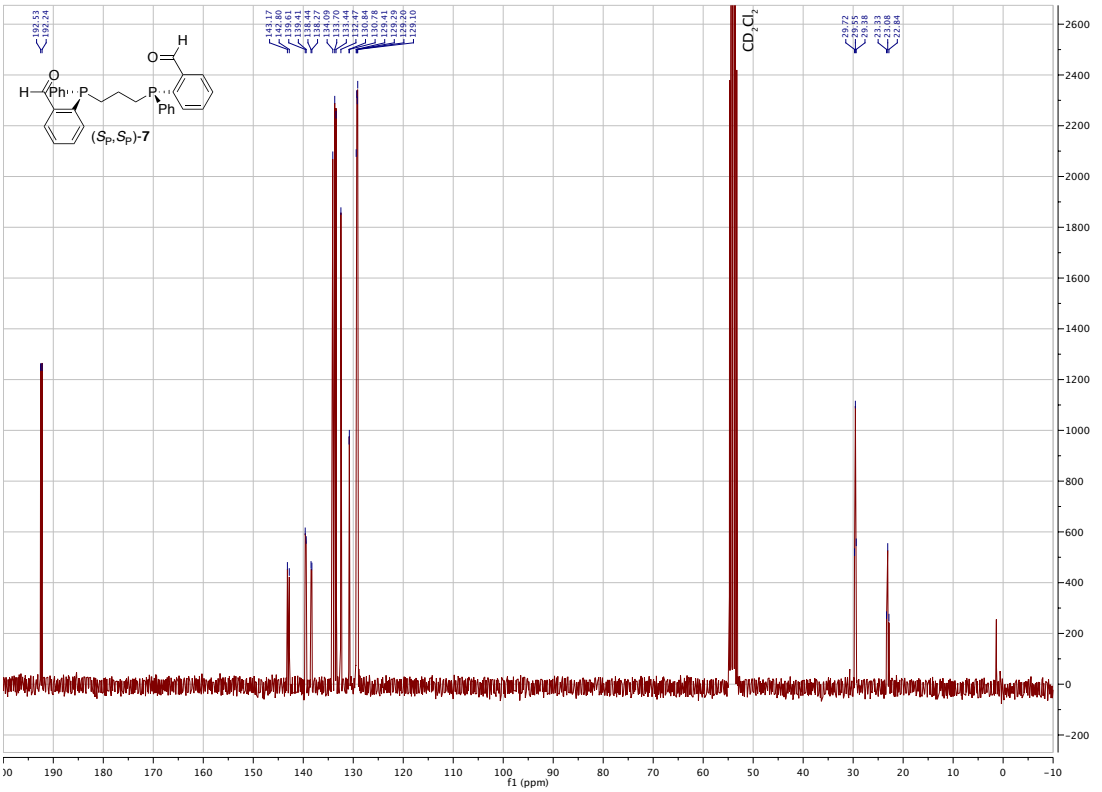
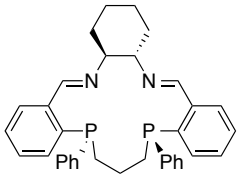


Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum of (S_P,S_P)-**7** (75 MHz, CD_2Cl_2).



Synthesis of (4a*S*,5*E*,11*S*,15*S*,20*E*,21a*S*)-11,15-Diphenyl-2,3,4,4a,11,12,13,14,15,21a-decahydro-1*H*-tribenzo[*b*,*f*,*m*][1,4]diaza[8,12]diphosphacyclopentadecine. A flame-dried 500 mL two-neck round-bottom flask was charged with (S_P,S_P)-**7** (1.72 g, 3.67 mmol), EtOH (350 mL), (1*S*,2*S*)-cyclohexane-1,2-diamine (0.419 g, 3.67 mmol, 1.0 equiv), and the solids were washed down with EtOH (20 mL) and stirred at room temperature overnight. The solvent was removed using an external cooling trap to afford the crude product as an off-white solid, which was used without further purification (86% pure by $^{31}P\{^1H\}$ NMR) (*Note*: The macrocycle does not precipitate upon concentration). Yield: 1.99 g (99%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.17 (*d*, $^4J_{P,H}$ = 3.9 Hz, 2H, N=C*H*), 7.85 – 7.79 (*m*, 2H, Ar-*H*), 7.38 – 7.21 (*m*, 14H, Ar-*H*), 7.06 – 7.00 (*m*, 2H, Ar-*H*), 3.74 – 3.64 (*m*, 2H, N-C*H*), 1.96 – 1.65 (*m*, 10H, PC*H*H (4H) + C*H*H (6H)), 1.59 – 1.44 (*m*, 2H, C*H*H), 1.21 – 1.03 (*m*, 2H, PCH_2CH_2). **^{31}P{^{1}H} NMR** (122 MHz, $CDCl_3$): –32.0 (*s*). **^{13}C{^{1}H} NMR** (75 MHz, CD_2Cl_2): 160.2 (*d*, $^3J_{P,C}$ = 23.3 Hz, N=*C*H), 144.3 (*d*, $^2J_{P,C}$ = 23.3 Hz, arom.), 139.7 (*d*, $^1J_{P,C}$ = 124.0 Hz, arom.), 139.5 (*d*, $^1J_{P,C}$ = 113.5 Hz, arom.), 133.2 (*d*, $^2J_{P,C}$ = 3.4 Hz, arom.), 132.5 (arom.), 132.3 (arom.), 130.5 (arom.), 129.6 (arom.), 128.9 (*d*, $^2J_{P,C}$ = 5.4 Hz, arom.), 128.6 (*m*, arom.), 74.0 (N-*C*H), 34.1 (CH_2), 31.5 (*m*, P*C*H_2), 24.9 (CH_2), 22.1 (*t*, $^2J_{P,C}$ = 17.6 Hz, PCH_2CH_2). **HRMS** (ESI): Calcd. for $C_{35}H_{37}N_2P_2$ *m*/*z* = 547.2426, found *m*/*z* = 547.2425 $[M+H]^+$.

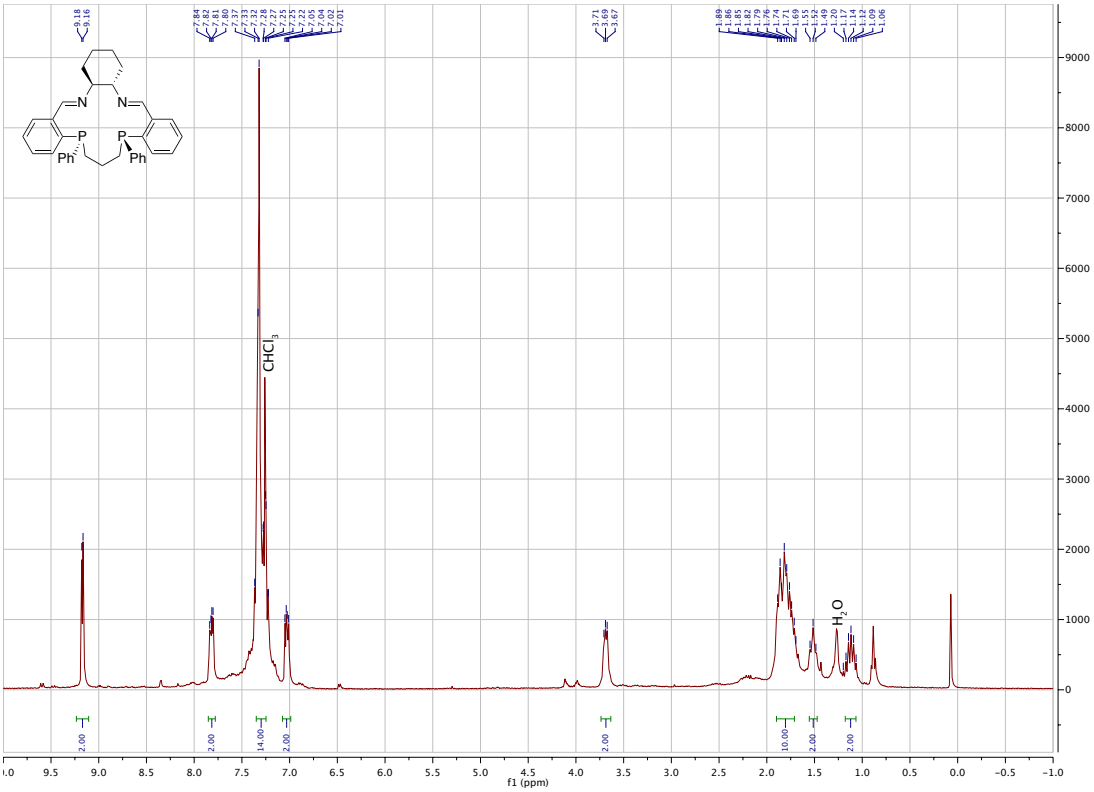


Figure S8: ^{1}H NMR spectrum of the N_2P_2 macrocycle (300 MHz, $CDCl_3$).

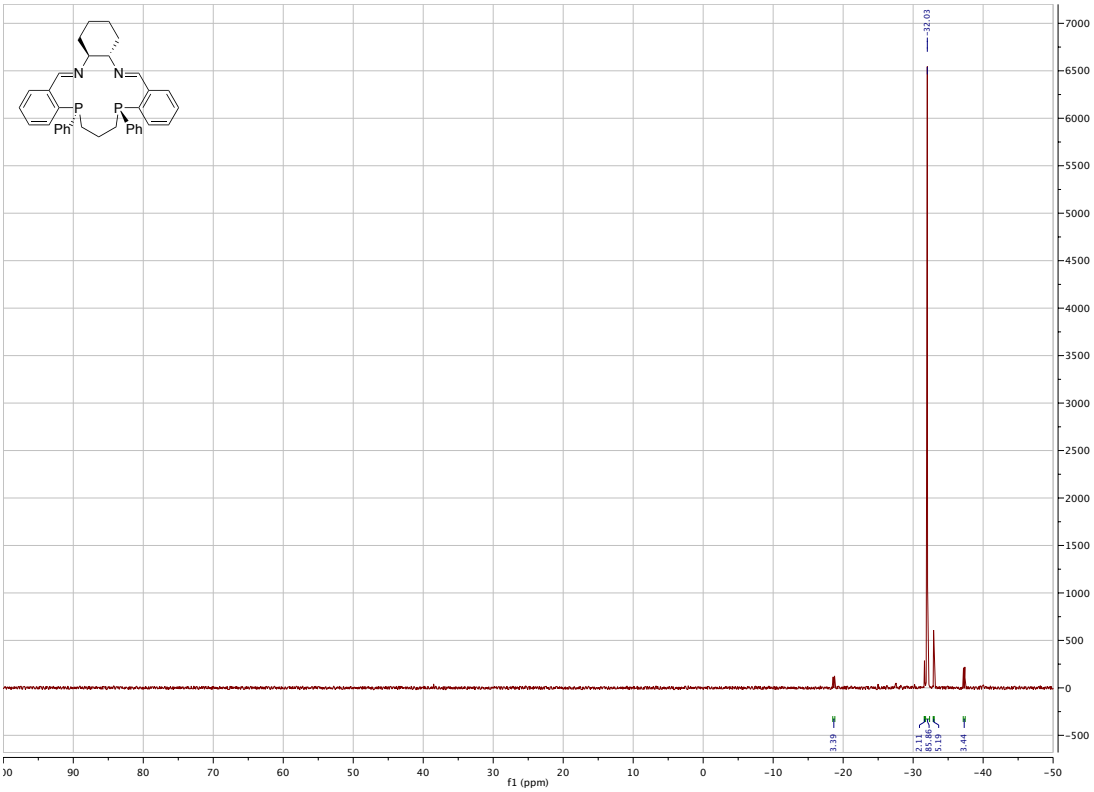


Figure S9: $^{31}P\{^{1}H\}$ NMR spectrum of the N_2P_2 macrocycle (122 MHz, $CDCl_3$).

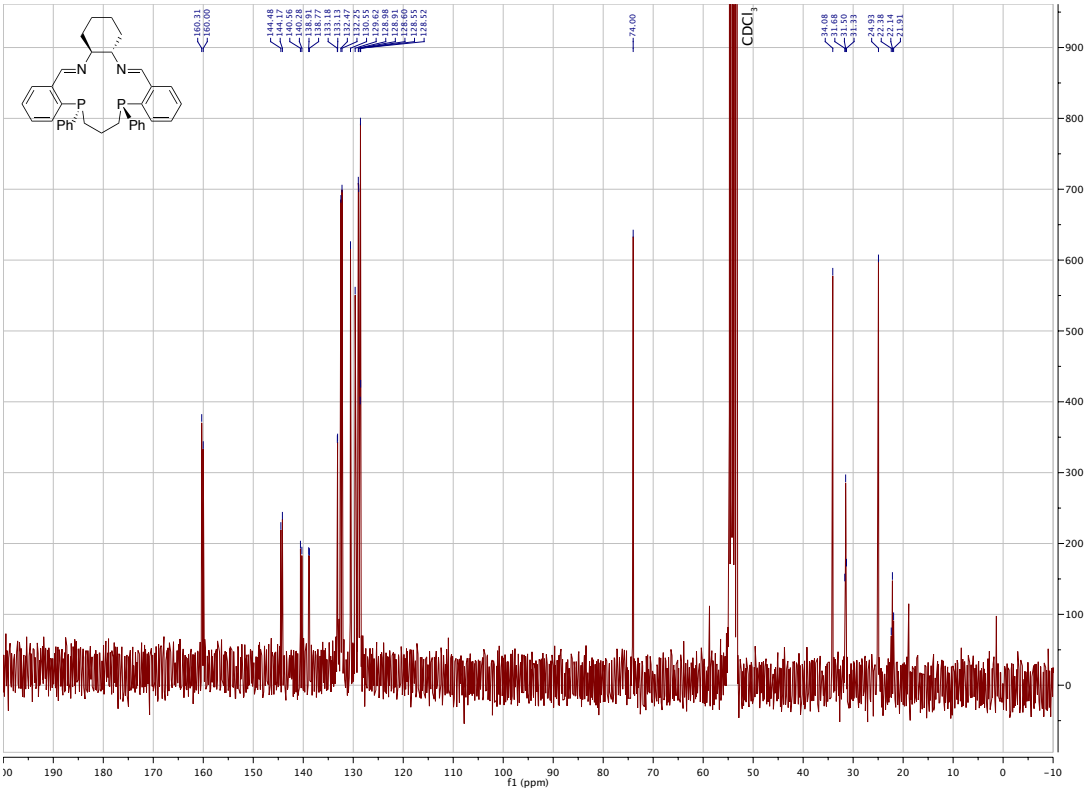
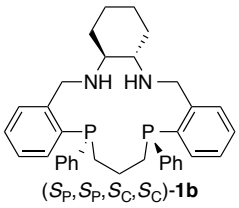


Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum of the N_2P_2 macrocycle (75 MHz, CD_2Cl_2).



(S_P,S_P,S_C,S_C)-**1b**

Synthesis of (4a*S*,11*S*,15*S*,21a*S*)-11,15-Diphenyl-2,3,4,4a,5,6,11,12,13,14,15,20,21,21a-tetradecahydro-1*H*-tribenzo[*b*,*f*,*m*][1,4]diaza[8,12]diphosphacyclopentadecine, (S_P,S_P,S_C,S_C)-1b. A flame-dried 250 mL Schlenk flask was charged with lithium aluminum hydride (1.39 g, 36.7 mmol, 10 equiv) and THF (25 mL), and the solution was cooled to 0 °C. After 10 min, the N_2P_2 macrocycle (1.99 g, 3.64 mmol, as obtained above) in a 500 mL two-neck round-bottom flask was dissolved in THF (25 mL) and added to the lithium aluminum suspension using a Teflon® cannula. The solution was warmed to room temperature overnight. The flask was cooled to 0 °C, and, after 10 min, EtOAc (7.5 mL; degassed by bubbling nitrogen through for

1 h) was carefully added (*Note*: Exothermic reaction). After stirring the solution at 0 °C for 45 min, a 2 : 1 weight mixture of Na_2SO_4/Celite® (15 g) was added. After 15 min, water (7.5 mL; degassed by bubbling nitrogen through for 1 h) was added and the suspension was vigorously stirred at room temperature. After 3 h, the suspension was rapidly filtered in air through a 2 : 1 weight mixture of Na_2SO_4/Celite® (30 g) on a glass frit into a 500 mL two-neck round-bottom flask and thoroughly washed with THF (250 mL). The solvent was removed using an external cooling trap. The crude product was dissolved in $CHCl_3$ (4 mL; degassed by bubbling nitrogen through for 1 h), and then filtered with EtOAc : NEt_3 (400 mL, 19 : 1; degassed by bubbling nitrogen through for 1 h) through silica gel (50 g) in a column under nitrogen. The solvent was rapidly removed at the rotary evaporator (20 mbar, 40 °C) to afford the product as an off-white solid, which was used without further purification (83% pure by $^{31}P\{^1H\}$ NMR). Yield: 1.90 g (95%). **^{1}H NMR** (300 MHz, CD_2Cl_2): 7.41 – 7.14 (*m*, 18H, Ar-*H*), 4.42 – 4.35 (*m*, 2H, NC*H*H), 3.84 – 3.76 (*m*, 2H, NC*H*H), 2.52 – 2.43 (*m*, 2H, PC*H*H), 2.39 – 2.25 (*m*, 4H, PC*H*H (2H) + N*H* (2H)), 2.16 – 2.03 (*m*, 2H, NC*H*), 1.92 – 1.73 (*m*, 4H, C*H*H), 1.67 – 1.52 (*m*, 2H, C*H*H), 1.43 – 1.32 (*m*, 2H, C*H*H), 1.21 – 1.04 (*m*, 2H, PCH_2CH_2). **^{31}P{^{1}H} NMR** (122 MHz, CD_2Cl_2): –32.5 (*s*). **^{13}C{^{1}H} NMR** (75 MHz, CD_2Cl_2): 147.6 (*d*, $^2J_{P,C}$ = 30.1 Hz, arom.), 140.9 (*m*, arom.), 138.8 (*m*, arom.), 133.6 (*m*, arom.), 132.0 (*m*, 2C, arom.), 130.8 (*m*, arom.), 129.6 (arom.), 128.6 (*m*, arom.), 127.9 (*d*, $J_{P,C}$ = 3.5 Hz, arom.), 62.8 (N*C*H), 50.6 (*m*, N*C*H_2), 32.3 (*C*H_2), 30.9 (*m*, P*C*H_2), 25.7 (*C*H_2), 23.4 (*t*, $^2J_{P,C}$ = 19.2 Hz, PCH_2CH_2). **HRMS** (ESI): Calcd. for $C_{35}H_{41}N_2P_2$ *m*/*z* = 551.2739, found *m*/*z* = 551.2736 $[M+H]^+$.

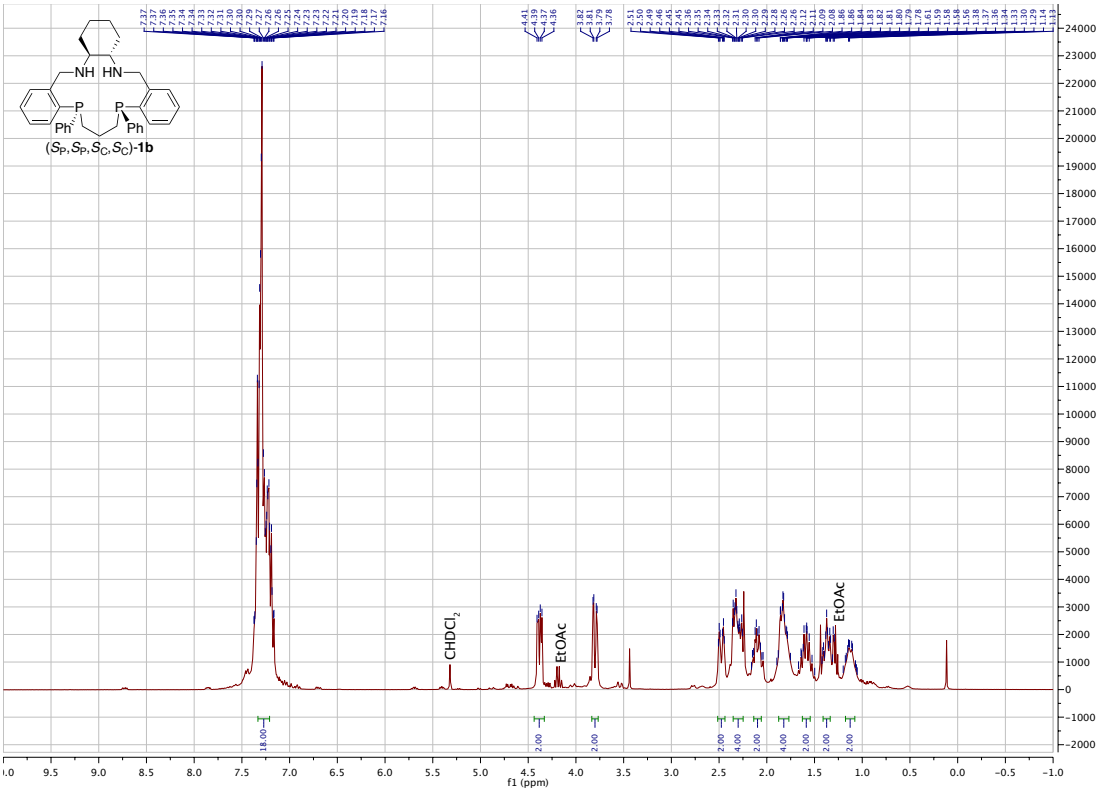


Figure S11: ^{1}H NMR spectrum of (S_P,S_P,S_C,S_C)-**1b** (300 MHz, CD_2Cl_2).

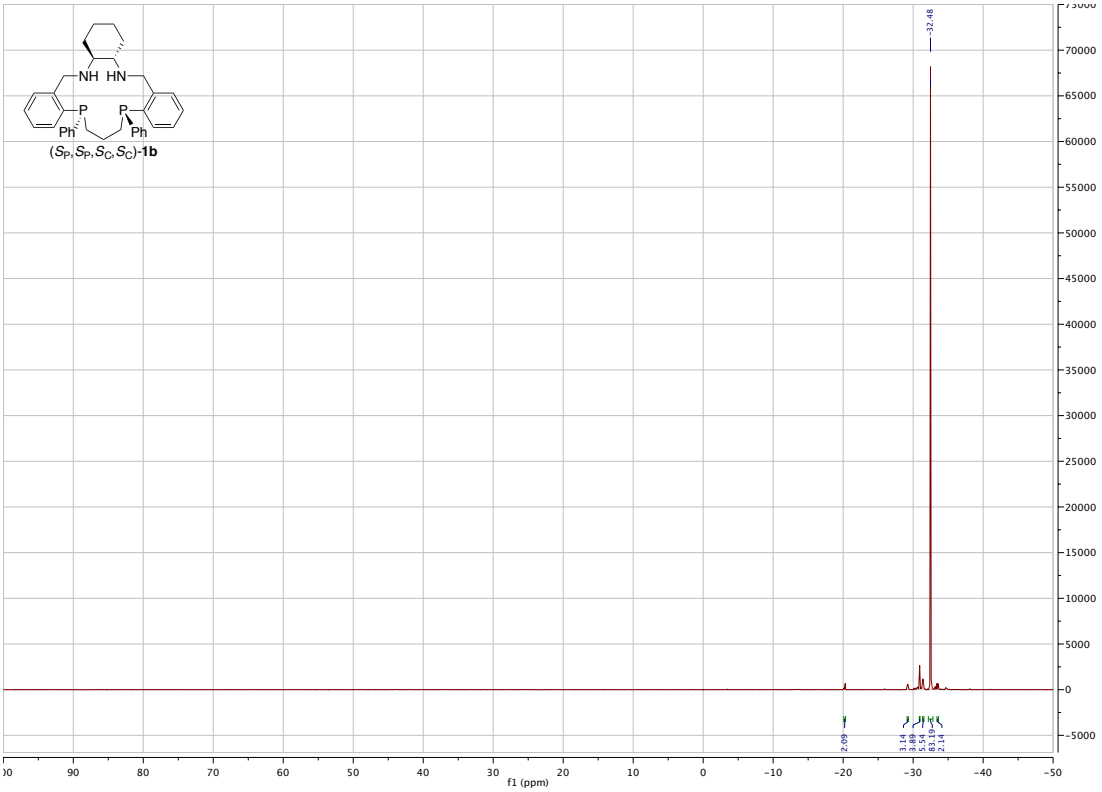


Figure S12: ^{31}P{^{1}H} NMR spectrum of (S_P,S_P,S_C,S_C)-**1b** (122 MHz, CD_2Cl_2).

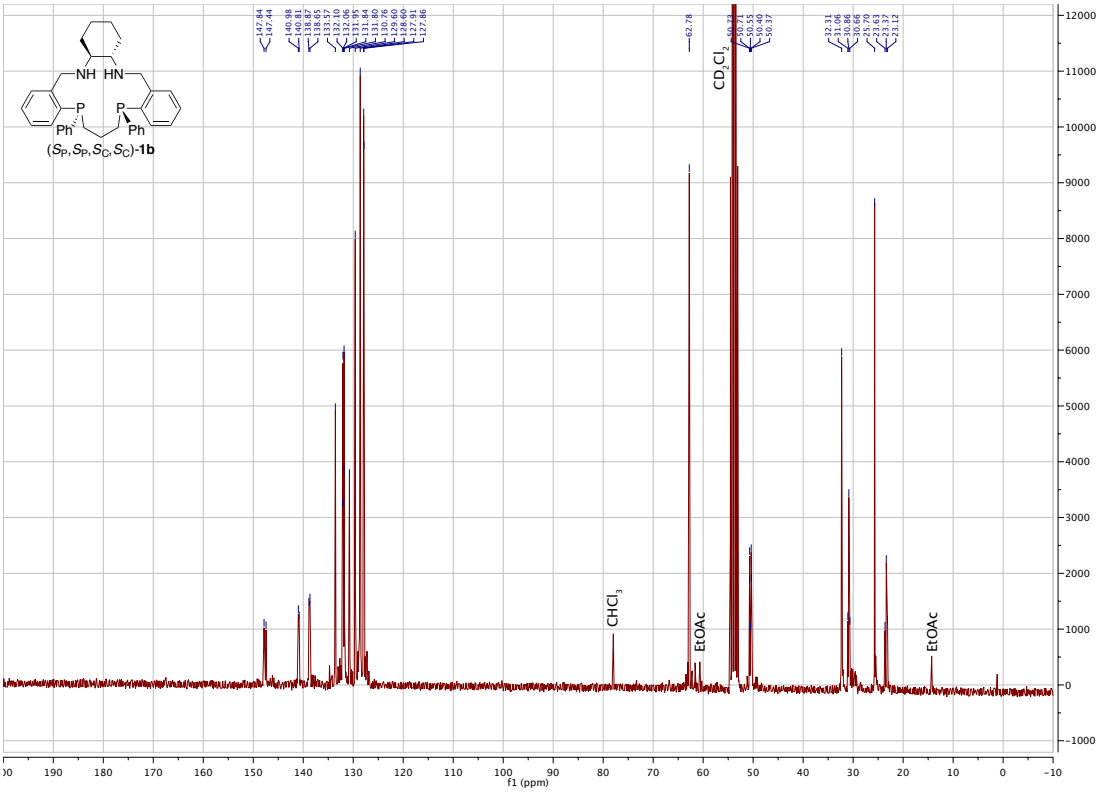
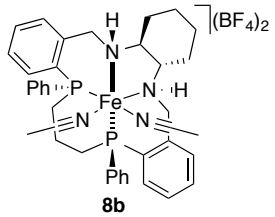


Figure S13: $^{13}C\{^{1}H\}$ NMR spectrum of (S_P,S_P,S_C,S_C)-**1b** (75 MHz, CD_2Cl_2).

Synthesis of Iron(II) Complexes



8b

Synthesis of [Fe(MeCN)$_2$((S_P,S_P,S_C,S_C)-1b)](BF$_4$)$_2$, 8b. A 250 mL two-neck round-bottom flask connected to a reflux condenser was charged with (S_P,S_P,S_C,S_C)-**1b** (1.84 g, 3.35 mmol, 1.1 equiv), CH_2Cl_2 (40 mL; degassed by 10 vacuum/argon cycles) and MeCN (25 mL; degassed by 10 vacuum/argon cycles). A separate 100 mL Schlenk flask was charged with iron(II) tetrafluoroborate hexahydrate (1.02 g, 3.04 mmol) and MeCN (45 mL; degassed by 10 vacuum/argon cycles), and the resulting solution was transferred to the round-bottom flask using a Teflon® cannula to give a red solution. The Schlenk flask was washed twice with MeCN (2 × 5 mL; degassed by 10 vacuum/argon cycles), and the solution was heated in an oil bath at 55 °C. After 0.5 h, 1,8-diazabicycloundec-7-ene (DBU, 23 μL, 0.15 mmol, 5 mol%) was added, and the reaction solution was stirred for 0.75 h at 55 °C. This process was repeated until the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution started to show the isomerization process to the preferred *cis-β* isomer (*Note*: 5-10 additions of DBU are necessary). After stirring for another 1.5 h, the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution showed full conversion to the desired isomer. Then, the solution was cooled to room temperature and filtered with MeCN (3 × 10 mL; degassed by 10 vacuum/argon cycles) through Celite® (5 g) in a Young filter into a flame-dried 250 mL Schlenk flask, and the solvent was removed using an external cooling trap. The product was dissolved in MeCN (15 mL; degassed by 10 vacuum/argon cycles) and filtered into a 150 mL Schlenk flask using a Teflon® cannula attached to a paper filter. The solution was cooled to –20 °C and carefully layered with MeCN (5 mL; degassed by 10 vacuum/argon cycles)

and Et_2O (130 mL). After 7 days, the supernatant was removed to afford the product as red crystals. The product exists as a single Λ-*cis*-*β* isomer. Yield: 1.46 g (56%). **^{1}H NMR** (300 MHz, CD_2Cl_2): 7.94 – 7.80 (*m*, 2H, Ar-*H*), 7.71 (*t*, $^3J_{H,H'}$ = 7.4 Hz, 1H, Ar-*H*), 7.67 – 7.44 (*m*, 7H, Ar-*H*), 7.31 – 7.14 (*m*, 4H, Ar-*H*), 6.94 (br *s*, 2H, Ar-*H*), 6.28 (*t*, $^3J_{H,H'}$ = 7.4 Hz, 2H, Ar-*H*), 5.57 (*d*, $^3J_{H,H'}$ = 9.0 Hz, 1H, N*H*), 4.74 (*d*, $^2J_{H,H'}$ = 17.5 Hz, 1H, NC*H*H), 4.60 (*d*, $^2J_{H,H'}$ = 17.5 Hz, 1H, NC*H*H), 3.56 – 3.40 (*m*, 2H, NC*H*H), 3.20 – 2.79 (*m*, 4H, C*H*H), 2.58 – 2.33 (*m*, 5H, CH_3 (3H) + C*H*H (2H)), 2.28 – 2.08 (*m*, 2H, C*H*H), 2.05 – 1.93 (*m*, 2H, NC*H*), 1.88 (*s*, 3H, CH_3), 1.78 – 1.67 (*m*, 1H, C*H*H), 1.59 – 1.36 (*m*, 2H, C*H*H), 1.20 – 1.03 (*m*, 1H, C*H*H), 0.85 – 0.67 (*m*, 1H, C*H*H), 0.38 – 0.20 (*m*, 1H, N*H*), –0.32 – –0.49 (*m*, 1H, C*H*H). **^{31}P{^{1}H} NMR** (122 MHz, CD_2Cl_2): 56.2 (*d*, $^2J_{P,P'}$ = 60.6 Hz), 49.1 (*d*, $^2J_{P,P'}$ = 60.6 Hz). **^{13}C{^{31}P,^{1}H} NMR** (126 MHz, CD_2Cl_2): 142.1 (arom.), 140.8 (arom.), 136.6 (arom.), 135.0 (arom.), 133.9 (arom.), 133.6 (arom.), 133.2 (arom.), 133.1 (arom.), 132.8 (3C, arom.), 132.1 (arom.), 131.6 (arom.), 131.3 (arom.), 130.8 (arom.), 130.7 (arom.), 130.1 (2C, arom.), 129.8 (arom.), 129.4 (arom.), 125.7 (CH_3CN), 123.4 (CH_3CN), 65.1 (N*C*H), 63.4 (N*C*H), 53.4 (N*C*H_2), 47.8 (N*C*H_2), 31.0 (*C*H_2), 29.7 (*C*H_2), 27.0 (*C*H_2), 24.8 (*C*H_2), 24.6 (*C*H_2), 21.4 (*C*H_2), 20.8 (*C*H_2), 5.5 (*C*H_3CN), 3.7 (*C*H_3CN). **IR** (liquid film, cm^{-1}): 3250 (N-H), 3229 (N-H), 3060 (C-H), 2938 (C-H), 2859 (C-H), 1631, 1481, 1462, 1450, 1433, 1416, 1402, 1320, 1283, 1160, 1055. **IR** (KBr, cm^{-1}): 2317 (CH_3CN), 2284 (CH_3CN), 2267 (CH_3CN). **HRMS** (MALDI): Calcd. for $C_{35}H_{40}FFeN_2P_2$ *m*/*z* 625.1995, found *m*/*z* 625.1993 [FeF((*S*$_P$,*S*$_P$,*S*$_C$,*S*$_C$)-**1b**)]$^+$. **EA**: Calcd. for $C_{39}H_{46}B_2F_8FeN_4P_2$: C, 54.33; H, 5.38; N, 6.50; found: C, 54.26; H, 5.55; N, 6.47.

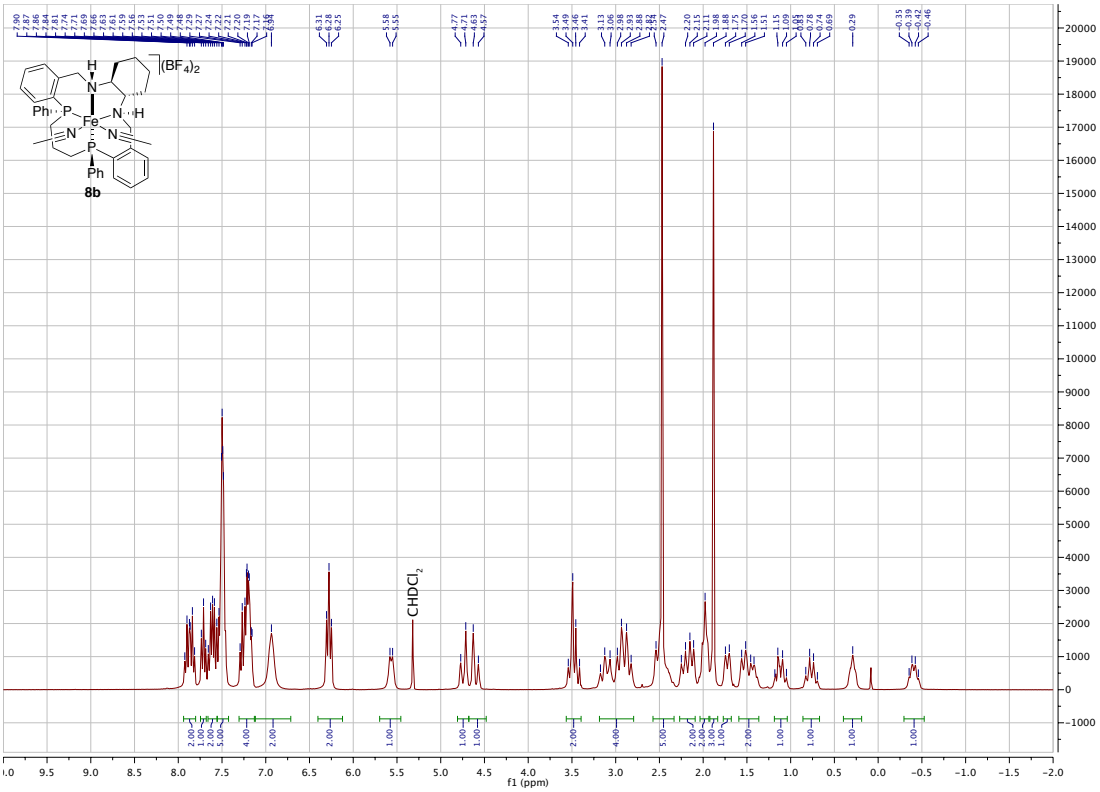


Figure S14: ^{1}H NMR spectrum of **8b** (300 MHz, CD_2Cl_2).

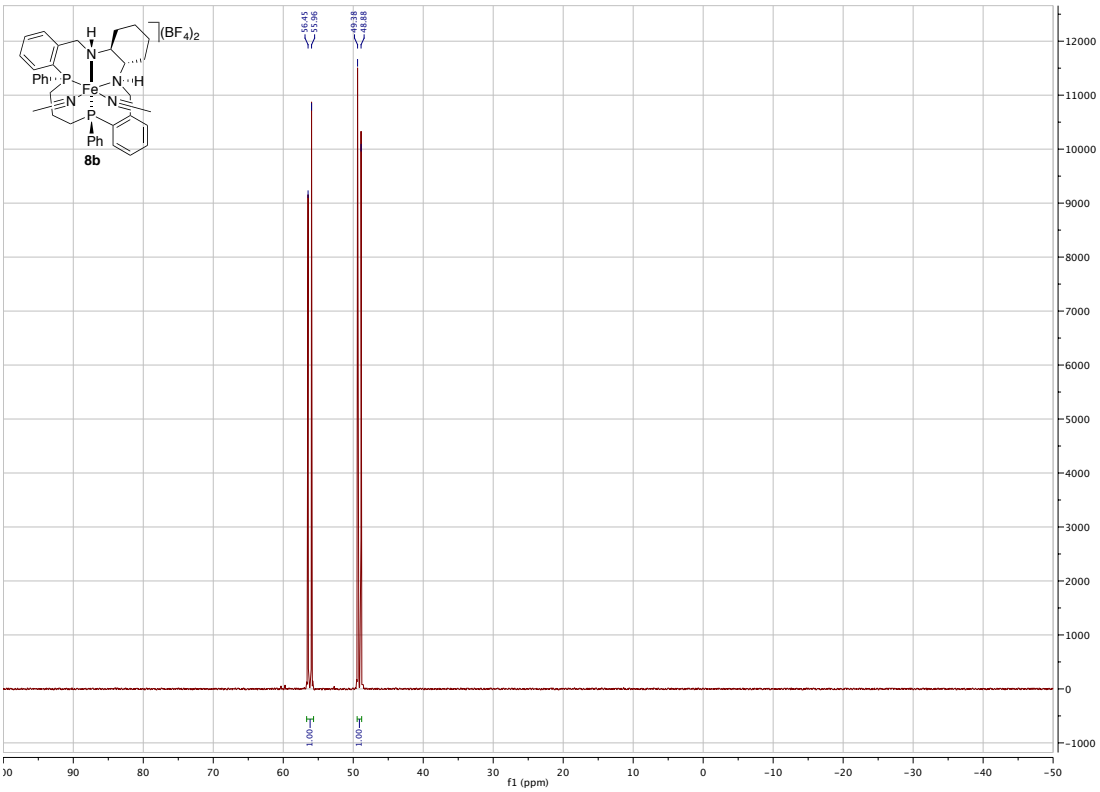


Figure S15: $^{31}P\{^{1}H\}$ NMR spectrum of **8b** (122 MHz, CD_2Cl_2).

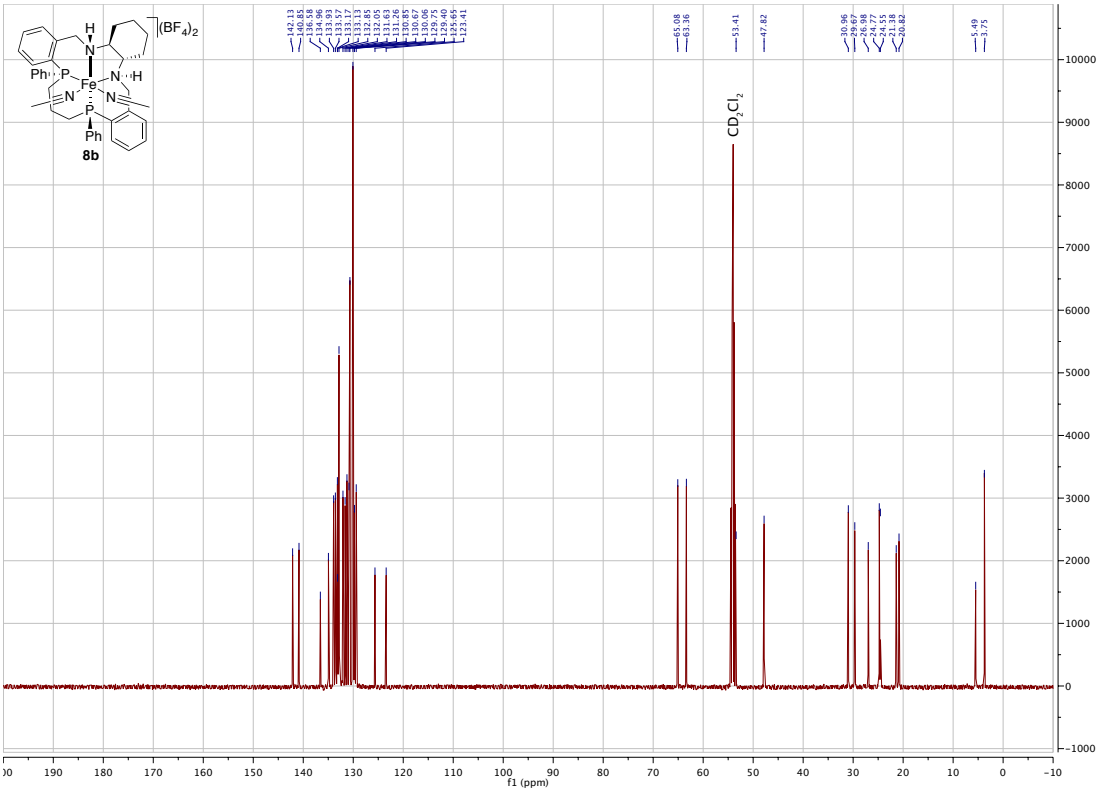


Figure S16: $^{13}C\{^{31}P,^{1}H\}$ NMR spectrum of **8b** (126 MHz, CD_2Cl_2).

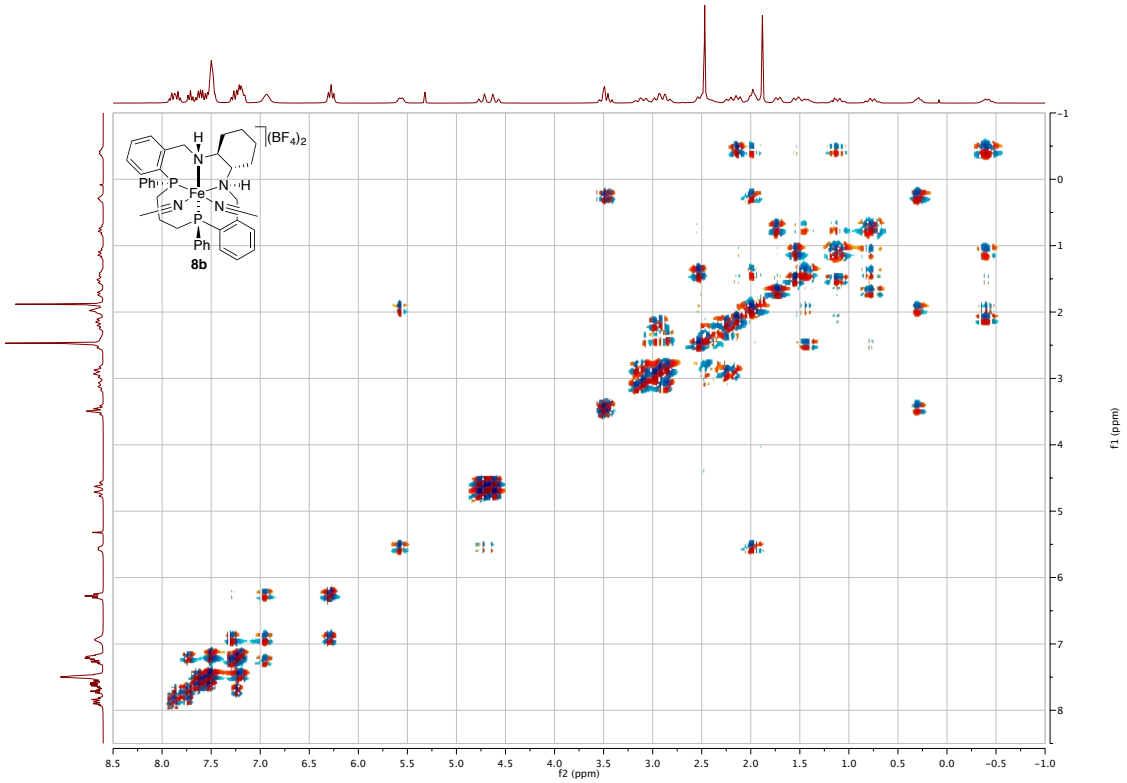


Figure S17: ^{1}H-^{1}H COSY spectrum of **8b**.

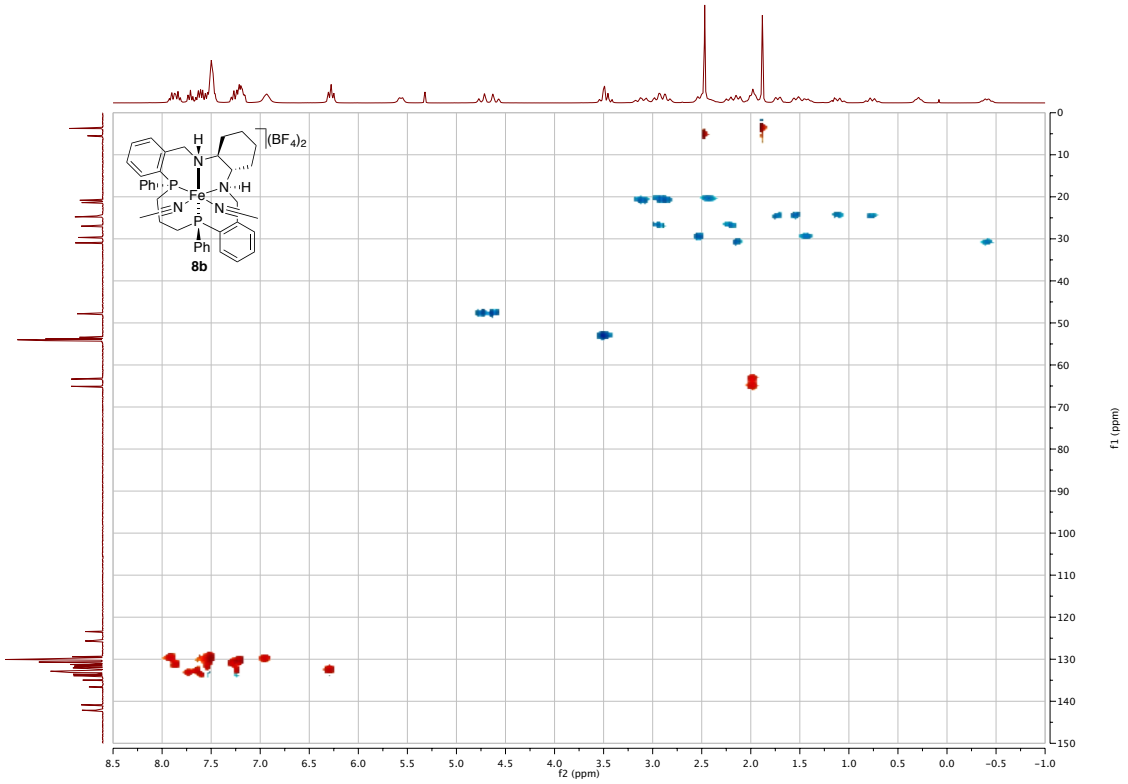


Figure S18: Phase-sensitive ^{1}H-^{13}C HSQC spectrum of **8b**.

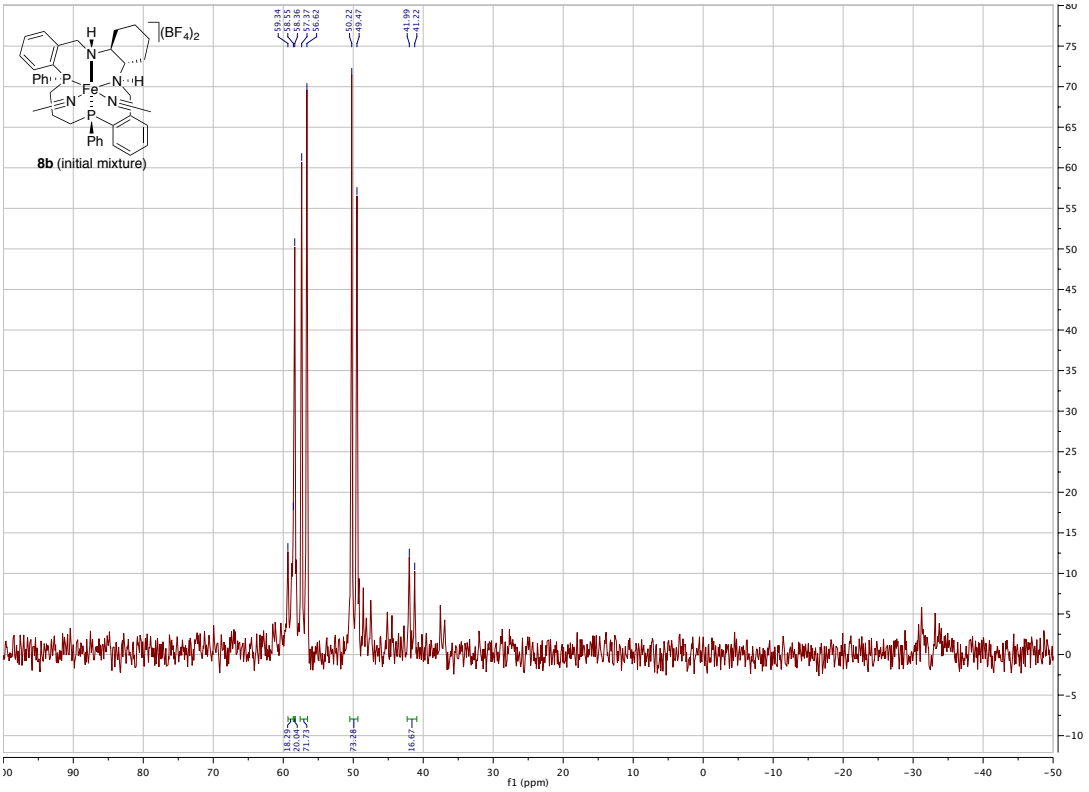


Figure S19: $^{31}P\{^{1}H\}$ NMR spectrum of the initial complexation mixture (122 MHz).

X-Ray Structure of $[Fe_2(MeCN)_2((S_P,S_P,S_C,S_C)\text{-}1b)](BF_4)_2$, 8b. Red crystals were obtained by layering a MeCN solution of **8b** with Et_2O. Crystal data for $C_{39}H_{46}B_2F_8FeN_4P_2$: block (0.48 × 0.038 × 0.018 mm), monoclinic, $P2_1$, cell dimensions (102 K) a = 10.9646(6), b = 16.3287(9), c = 11.9006(7) Å, β = 110.493(2)°, and V = 1 995.8(2) Å^3 with Z = 2, D_C = 1.435 Mg/m^3, μ = 0.530 mm^{-1} (Mo K_α, graphite monochromated), λ = 0.71073 Å, F(000) = 892. The data were collected at 100 K on a Bruker AXS SMART APEX platform in the θ range 2.343–30.584°. The structure was solved with SHELXTL using direct methods. Of the 47 933 measured reflections with index ranges $-15 \le h \le 14$, $-23 \le k \le 23$, $-16 \le l \le 17$, 12 196 independent reflections (R_{int} = 0.0600) were used in the refinement (full-matrix least squares on F^2) with anisotropic displacement parameters for all non-H atoms. Hydrogen atoms were introduced at calculated positions (except those on N1 and N2) and refined with the riding model and individual isotropic thermal parameters. The asymmetric unit contains the complex dication and two BF_4^- anions (one of which is heavily disordered and was split in two units roughly rotated by 60° about a direction close to the B2–F8/F9 vector). Final residuals were $R1$ = 0.0527 (for 12 196 reflections with $I > 2\sigma(I)$) and w$R2$ = 0.1271 (all data), GOF = 1.022, absolute structure parameter 0.007(6) from 4 106 selected quotients (Parson's method) of –0.003(18) by hole-in-one fit to all intensities. Max. and min. difference peaks were +1.67 and –0.74 eÅ^{-3}, the largest and mean Δ/σ = 0.000 and 0.000.

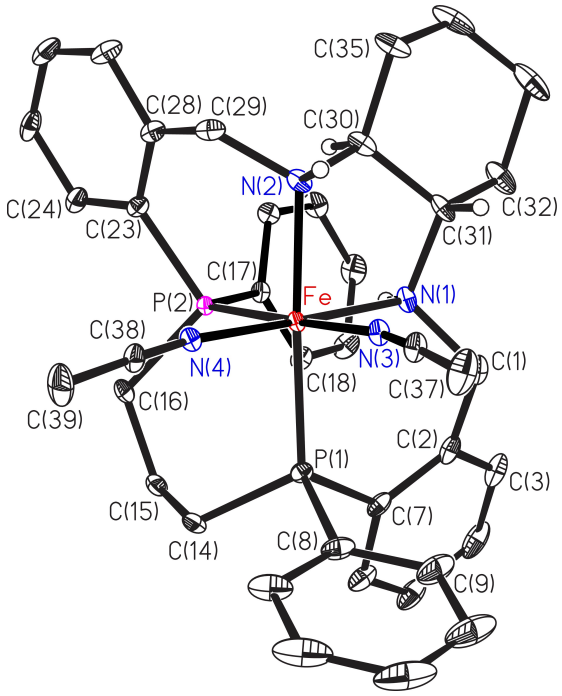
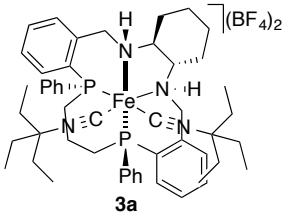


Figure S20: X-ray structure of the dication of [Fe(MeCN)$_2$((S_P,S_P,S_C,S_C)-**1b**)](BF$_4$)$_2$ (**8b**).

Table S1: Selected distances (Å) and angles (°) of [Fe(MeCN)$_2$((S_P,S_P,S_C,S_C)-**1b**)](BF$_4$)$_2$ (**8b**).

Fe–P(1)	2.2187(12)	Fe–P(2)	2.2193(11)
Fe–N(1)	2.035(3)	Fe–N(2)	2.048(4)
Fe–N(3)	1.979(3)	Fe–N(4)	1.932(3)
N(3)–C(36)	1.140(6)	N(4)–C(38)	1.141(5)

P(1)–Fe–P(2)	92.92(4)	N(1)–Fe–N(2)	84.35(15)
P(1)–Fe–N(1)	94.32(11)	P(2)–Fe–N(2)	90.75(11)
P(1)–Fe–N(2)	176.16(11)	P(2)–Fe–N(1)	93.25(11)
P(1)–Fe–N(3)	89.39(11)	P(2)–Fe–N(3)	175.81(11)
P(1)–Fe–N(4)	87.87(11)	P(2)–Fe–N(4)	91.17(11)
N(1)–Fe–N(3)	90.06(14)	N(2)–Fe–N(3)	87.01(15)
N(1)–Fe–N(4)	174.95(15)	N(2)–Fe–N(4)	93.17(15)
N(3)–Fe–N(4)	85.42(14)		



3a

Synthesis of [Fe(CNCEt$_3$)$_2$((S_P,S_P,S_C,S_C)-1b)](BF$_4$)$_2$, 3a. A 20 mL Young flask was charged with **8b** (250 mg, 0.290 mmol), CH_2Cl_2 (4.0 mL; degassed by 10 vacuum/argon cycles), and 3-ethyl-3-isocyanopentane (182 mg, 1.45 mmol, 5.0 equiv),[S2] and the solution was stirred for 24 h at 50 °C (*Note*: 3-Ethyl-3-isocyanopentane was weighted and added using a syringe). The solution was cooled to room temperature and filtered into a 50 mL Schlenk flask using a Teflon® cannula attached to a paper filter. The Young flask was rinsed twice with CH_2Cl_2 (2 × 3.0 mL; degassed by 10 vacuum/argon cycles), and the solvent was removed using an external cooling trap. The crude product was dissolved in CH_2Cl_2 (5.0 mL; degassed by 10 vacuum/argon cycles) and carefully layered with hexane (45 mL). After 2 days, an orange oil had separated. The supernatant was removed using a syringe. This purification process was repeated once to afford the title product as a yellow solid after drying under high vacuum. The product exists as a single Λ-*cis*-*β* isomer. Yield: 285 mg (95%). **^{1}H NMR** (300 MHz, CD_2Cl_2): 7.97 – 7.76 (*m*, 3H, Ar-*H*), 7.71 – 7.62 (*m*, 2H, Ar-*H*), 7.58 – 7.49 (*m*, 3H, Ar-*H*), 7.48 – 7.34 (*m*, 4H, Ar-*H*), 7.28 – 6.88 (*m*, 4H, Ar-*H*), 6.30 (br *s*, 2H, Ar-*H*), 5.20 (*d*, $^3J_{H,H'}$ = 12.0 Hz, 1H, N*H*), 4.69 (*d*, $^2J_{H,H'}$ = 18.1 Hz, 1H, NC*H*H), 4.53 (*d*, $^2J_{H,H'}$ = 18.1 Hz, 1H, NC*H*H), 4.11 (*d*, $^2J_{H,H'}$ = 13.0 Hz, 1H, NC*H*H), 3.96 (*dd*, $^2J_{H,H'}$ = 13.0 Hz, $^3J_{H,H'}$ = 10.4 Hz, 1H, NC*H*H), 3.22 – 3.07 (*m*, 1H, C*H*H), 3.03 – 2.70 (*m*, 2H, C*H*H), 2.46 – 2.18 (*m*, 5H, N*H* (1H) + C*H*H (4H)), 2.11 (*dddd*, $^3J_{H,H'}$ = 11.1, 11.1, 11.1, 3.4 Hz, 1H, NC*H*), 1.89 – 1.54 (*m*, 11H, NC*H* (1H) + C*H*H (4H) + C*H*HCH$_3$ (6H)), 1.53 – 1.40 (*m*, 3H, C*H*HCH$_3$), 1.39 – 1.22 (*m*, 3H, C*H*HCH$_3$), 1.13 – 0.93 (*m*, 1H, C*H*H (1H)), 0.81 (*t*, $^3J_{H,H'}$ = 7.4 Hz, 9H, CH$_2$C*H*$_3$), 0.73 (*t*, $^3J_{H,H'}$ = 7.4 Hz, 9H, CH$_2$C*H*$_3$), 0.72 – 0.56 (*m*, 1H, C*H*H), –0.40 (*dddd*, $^3J_{H,H'}$ = 12.7, 12.7, 12.6,

3.6 Hz, 1H, C*H*H). **^{31}P{^{1}H} NMR** (122 MHz, CD_2Cl_2): 45.9 (*d*, $^{2}J_{P,P'}$ = 58.3 Hz), 33.8 (*d*, $^{2}J_{P,P'}$ = 58.3 Hz). **^{13}C{^{31}P,^{1}H} NMR** (126 MHz, CD_2Cl_2): 159.2 (*m*, *C*NCEt$_3$), 154.7 (*m*, *C*NCEt$_3$), 141.7 (arom.), 141.0 (arom.), 137.6 (arom.), 134.4 (arom.), 134.0 (arom.), 133.9 (arom.), 133.4 (arom.), 133.1 (br *s*, arom.), 132.4 (arom.), 132.3 (arom.), 132.1 (arom.), 131.7 (arom.), 131.5 (arom.), 130.8 (2C, arom.), 130.7 (br *s*, arom.), 130.3 (arom.), 130.0 (arom.), 124.0 (arom.), 122.5 (arom.), 72.6 (CN*C*Et$_3$), 71.9 (CN*C*Et$_3$), 66.9 (N*C*H), 63.4 (N*C*H), 56.0 (N*C*H$_2$), 50.5 (N*C*H$_2$), 31.2 (*C*H$_2$), 30.7 (*C*H$_2$CH$_3$), 29.5 (*C*H$_2$), 29.4 (*C*H$_2$CH$_3$), 27.9 (*C*H$_2$), 26.5 (*C*H$_2$), 24.7 (*C*H$_2$), 24.6 (*C*H$_2$), 20.7 (*C*H$_2$), 8.8 (CH$_2$*C*H$_3$), 8.3 (CH$_2$*C*H$_3$). **IR** (liquid film, cm^{-1}): 3246 (N-H), 3224 (N-H), 3061 (C-H), 2974 (C-H), 2943 (C-H), 2882 (C-H), 2864 (C-H), 2155 (isonitrile), 2110 (isonitrile), 1629, 1592, 1480, 1454, 1435, 1416, 1399, 1387, 1338, 1319, 1306, 1281, 1272, 1243, 1205, 1162, 1149, 1054. **HRMS** (MALDI): Calcd. for $C_{51}H_{70}BF_4FeN_4P_2$ *m*/*z* 943.4458, found *m*/*z* 943.4445 [M–BF_4]$^+$. **EA**: Calcd. for $C_{51}H_{70}B_2F_8FeN_4P_2$: C, 59.44; H, 6.85; N, 5.44; found: C, 59.47; H, 7.25; N, 5.16.

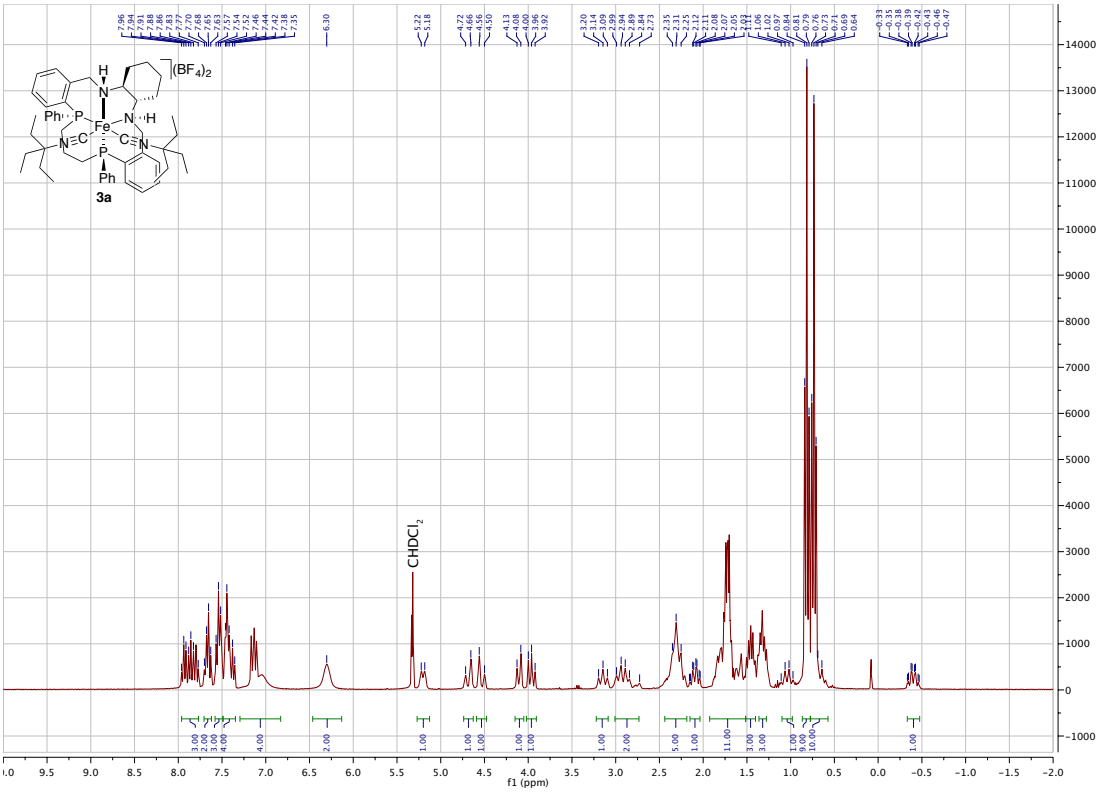


Figure S21: ^{1}H NMR spectrum of **3a** (300 MHz, CD_2Cl_2).

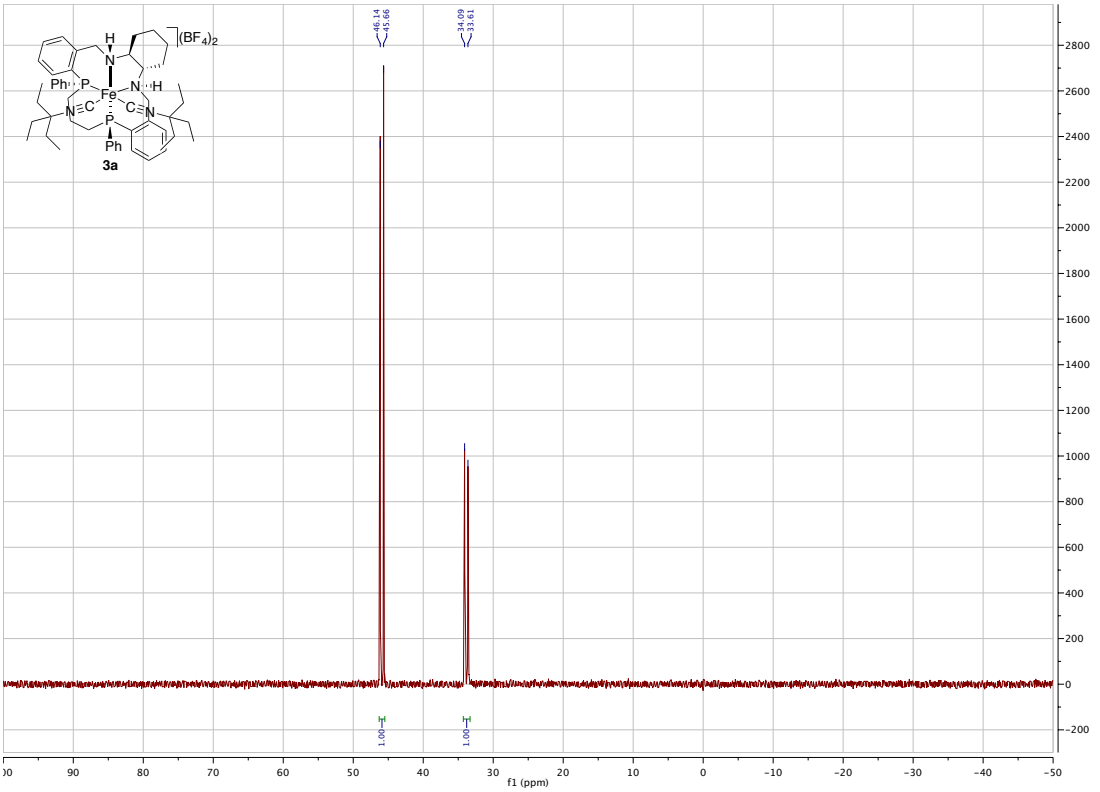


Figure S22: $^{31}P\{^{1}H\}$ NMR spectrum of **3a** (122 MHz, CD_2Cl_2).

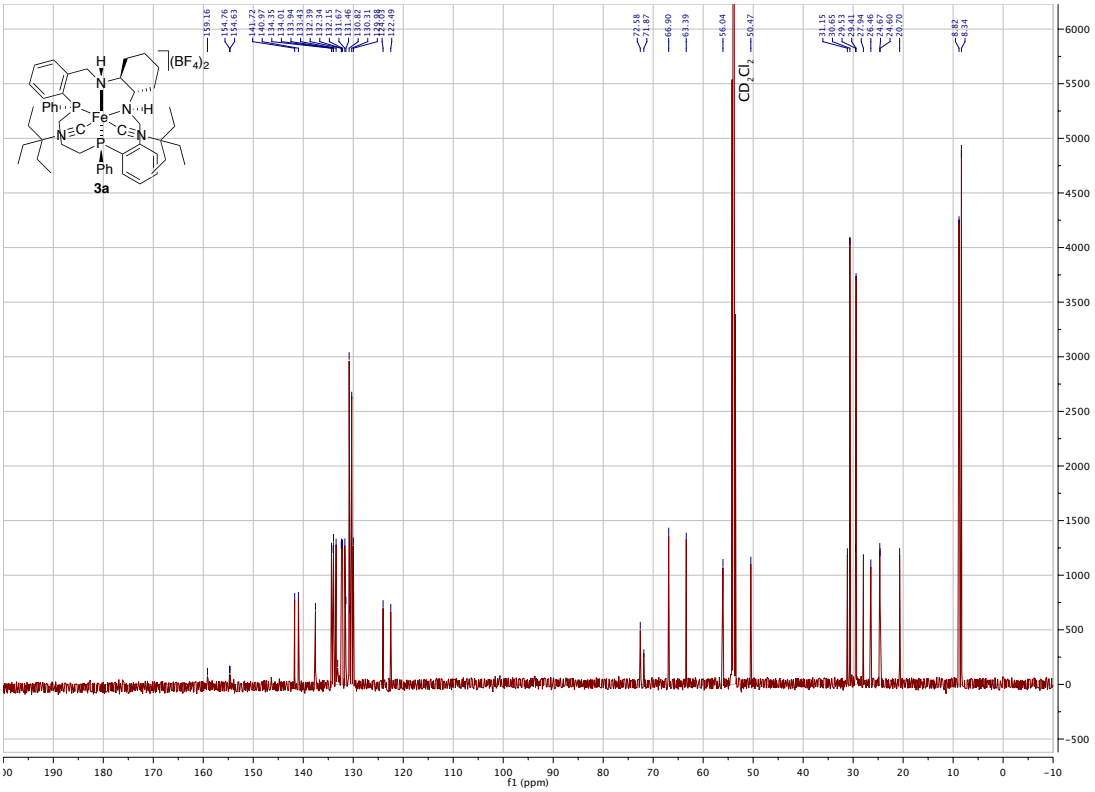


Figure S23: $^{13}C\{^{31}P,^{1}H\}$ NMR spectrum of **3a** (126 MHz, CD_2Cl_2).

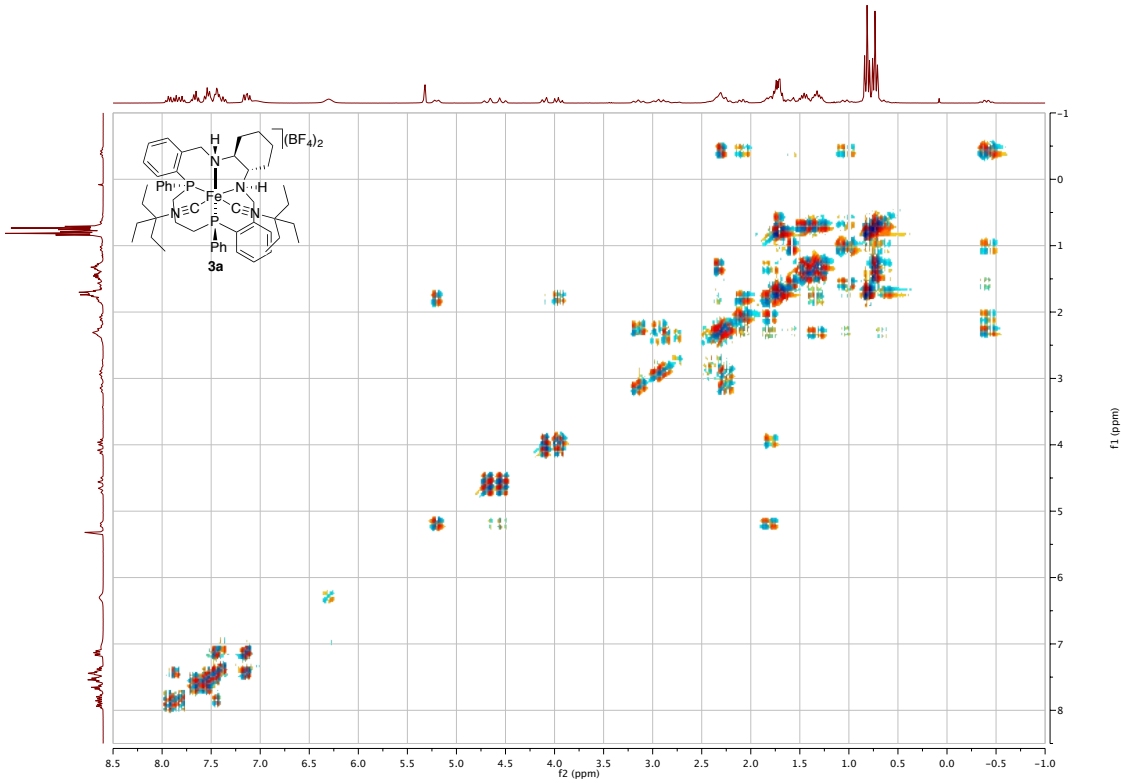


Figure S24: ^{1}H-^{1}H COSY spectrum of **3a**.

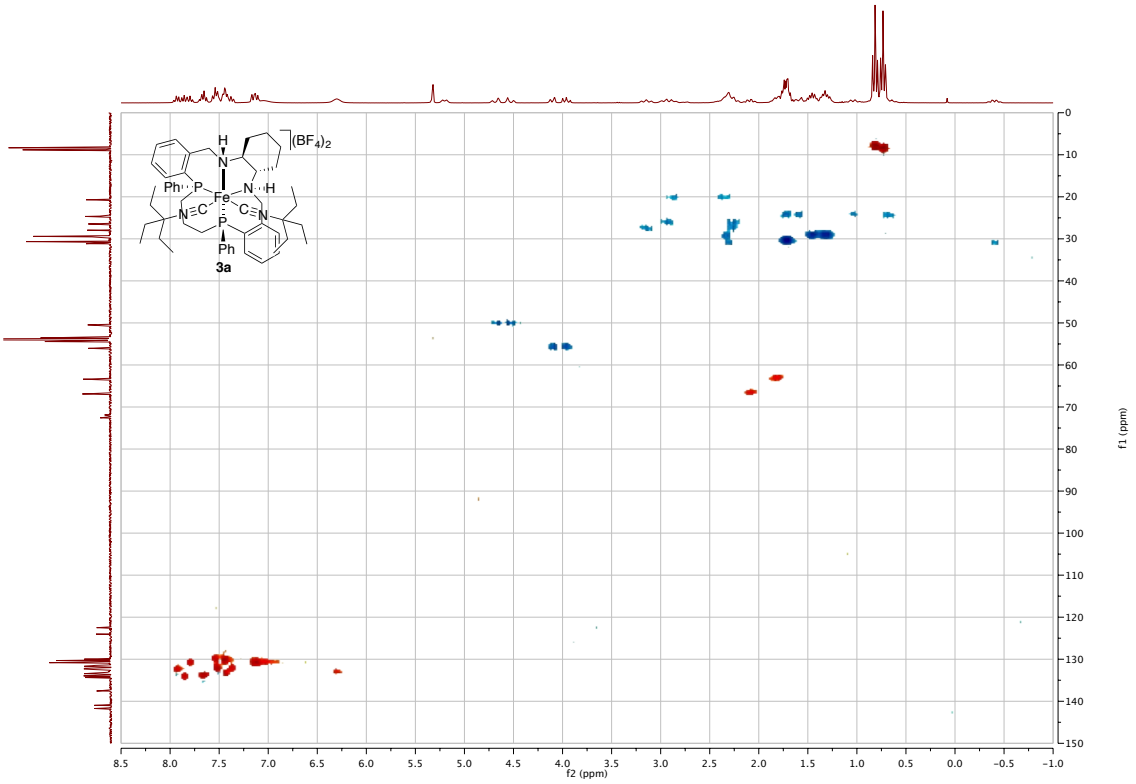
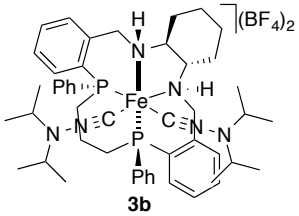


Figure S25: Phase-sensitive ^{1}H-^{13}C HSQC spectrum of **3a**.



Synthesis of [Fe(CNN^{i}Pr$_2$)$_2$((S_P,S_P,S_C,S_C)-1b)](BF$_4$)$_2$, 3b. A 20 mL Young flask was charged with **8b** (250 mg, 0.290 mmol), CH_2Cl_2 (4.0 mL; degassed by 10 vacuum/argon cycles), and *N*-isocyano-*N*-isopropylpropan-2-amine (183 mg, 1.45 mmol, 5.0 equiv),[S2] and the solution was stirred for 24 h at 50 °C (*Notes*: *N*-Isocyano-*N*-isopropylpropan-2-amine was purified by flash column chromatography (Et_2O : pentane = 1 : 19) directly before use; it was weighted and added using a syringe). The solution was cooled to room temperature and filtered into a 50 mL Schlenk flask using a Teflon® cannula attached to a paper filter. The Young flask was rinsed twice with CH_2Cl_2 (2 × 3.0 mL; degassed by 10 vacuum/argon

cycles), and the solvent was removed using an external cooling trap. The crude product was dissolved in CH_2Cl_2 (5.0 mL; degassed by 10 vacuum/argon cycles) and carefully layered with hexane (45 mL). After 2 days, a brown oil had separated. The supernatant was removed using a syringe. This purification process was repeated once to afford the title product as an orange solid after drying under high vacuum. The product exists as a single Λ-*cis*-*β* isomer. Yield: 288 mg (96%). **^{1}H NMR** (300 MHz, CD_2Cl_2): 7.94 – 7.74 (*m*, 3H, Ar-*H*), 7.72 – 7.62 (*m*, 2H, Ar-*H*), 7.58 – 7.36 (*m*, 7H, Ar-*H*), 7.16 – 6.99 (*m*, 4H, Ar-*H*), 6.30 (br *s*, 2H, Ar-*H*), 5.13 (*d*, $^3J_{H,H'}$ = 12.2 Hz, 1H, N*H*), 4.65 (*d*, $^2J_{H,H'}$ = 18.5 Hz, 1H, NC*H*H), 4.53 (*d*, $^2J_{H,H'}$ = 18.5 Hz, 1H, NC*H*H), 4.16 (*d*, $^2J_{H,H'}$ = 12.4 Hz, 1H, NC*H*H), 4.05 (*dd*, $^2J_{H,H'}$ = 12.4 Hz, $^3J_{H,H'}$ = 10.6 Hz, 1H, NC*H*H), 3.42 – 3.28 (*m*, 2H, C*H*(CH_3)$_2$), 3.24 – 3.09 (*m*, 3H, C*H*(CH_3)$_2$ (2H) + C*H*H (1H)), 3.06 – 2.74 (*m*, 2H, C*H*H), 2.42 – 2.21 (*m*, 5H, N*H* (1H) + C*H*H (4H)), 2.11 (*dddd*, $^3J_{H,H'}$ = 11.1, 11.1, 11.0, 3.5 Hz, 1H, NC*H*), 1.93 – 1.66 (*m*, 3H, NC*H* (1H) + C*H*H (2H)), 1.63 – 1.53 (*m*, 1H, C*H*H), 1.43 – 1.26 (*m*, 2H, C*H*H), 1.16 (*d*, $^3J_{H,H'}$ = 6.6 Hz, 6H, CH(C*H*$_3$)(CH_3)), 1.07 (*d*, $^3J_{H,H'}$ = 6.5 Hz, 6H, CH(C*H*$_3$)(CH_3)), 1.00 (*d*, $^3J_{H,H'}$ = 6.5 Hz, 6H, CH(C*H*$_3$)(CH_3)), 0.92 (*d*, $^3J_{H,H'}$ = 6.5 Hz, 6H, CH(C*H*$_3$)(CH_3)), 0.73 – 0.56 (*m*, 1H, C*H*H), –0.44 (*dddd*, $^3J_{H,H'}$ = 12.6, 12.4, 12.4, 3.7 Hz, 1H, C*H*H). **^{31}P{^{1}H} NMR** (122 MHz, CD_2Cl_2): 47.6 (*d*, $^2J_{P,P'}$ = 58.4 Hz), 36.4 (*d*, $^2J_{P,P'}$ = 58.4 Hz). **^{13}C{^{31}P,^{1}H} NMR** (126 MHz, CD_2Cl_2): 141.9 (arom.), 141.1 (arom.), 140.2 (*m*, *C*NN^{i}Pr$_2$), 137.8 (arom.), 134.6 (*m*, *C*NN^{i}Pr$_2$), 134.1 (arom.), 133.8 (arom.), 133.7 (arom.), 133.4 (arom.), 133.0 (br *s*, arom.), 132.4 (arom.), 132.3 (arom.), 132.1 (2C, arom.), 131.4 (arom.), 130.8 (br *s*, 2C, arom.), 130.6 (arom.), 130.4 (arom.), 129.8 (arom.), 124.7 (arom.), 122.8 (arom.), 67.3 (N*C*H), 63.3 (N*C*H), 56.9 (N*C*H$_2$), 55.3 (*C*H(CH_3)$_2$), 53.9 (*C*H(CH_3)$_2$), 50.3 (N*C*H$_2$), 31.2 (*C*H$_2$), 29.4 (*C*H$_2$), 28.8 (*C*H$_2$), 26.0 (*C*H$_2$), 24.66 (*C*H$_2$), 24.63 (*C*H$_2$), 21.2 (CH(*C*H$_3$)(CH_3)), 21.1 (CH(*C*H$_3$)(CH_3)), 20.6 (*C*H$_2$), 20.2 (CH(*C*H$_3$)(CH_3)), 19.9 (CH(*C*H$_3$)(CH_3)). **IR** (liquid film, cm^{-1}): 3226 (N-H), 3062 (C-H), 2978 (C-H), 2937 (C-H), 2866 (C-H), 2136 (isonitrile), 2102

(isonitrile), 1592, 1464, 1449, 1434, 1418, 1390, 1371, 1352, 1320, 1280, 1272, 1242, 1162, 1122, 1047, 1033. **HRMS** (MALDI): Calcd. for $C_{49}H_{68}BF_4FeN_6P_2$ *m*/*z* 945.4363, found *m*/*z* 945.4348 $[M–BF_4]^+$. **EA**: Calcd. for $C_{49}H_{68}B_2F_8FeN_6P_2$: C, 57.00; H, 6.64; N, 8.14; found: C, 56.87; H, 6.99; N, 7.84.

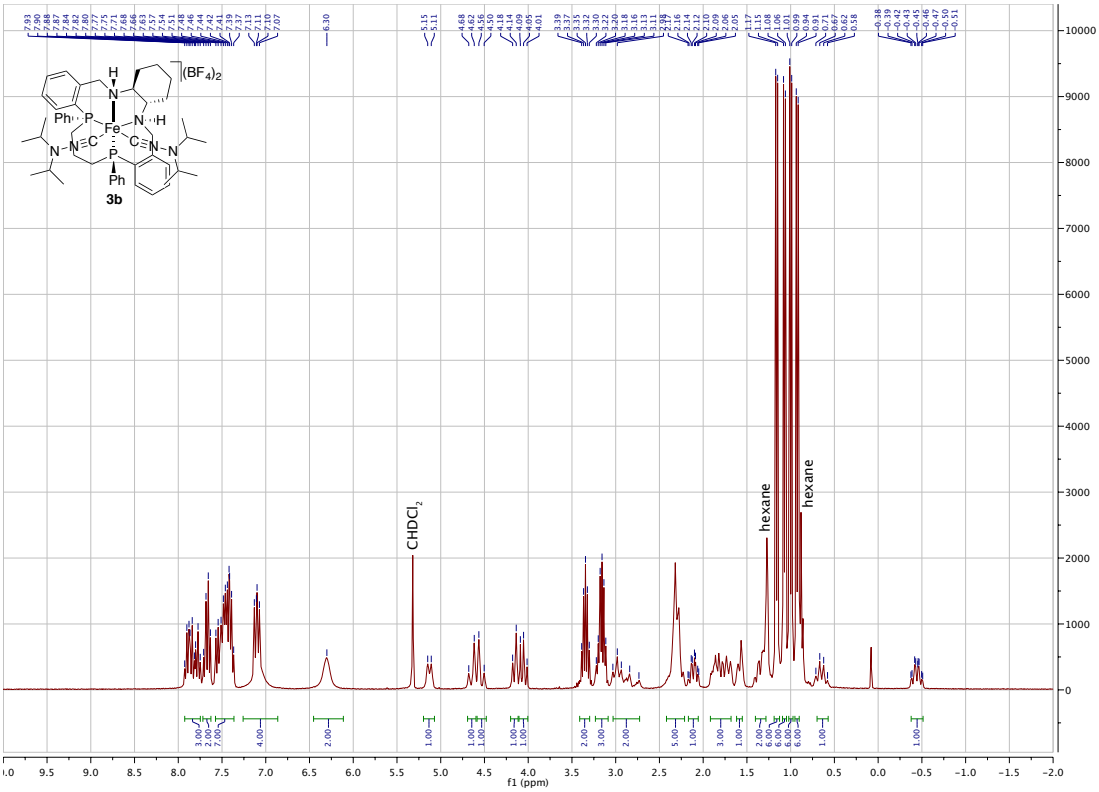


Figure S26: ^{1}H NMR spectrum of **3b** (300 MHz, CD_2Cl_2).

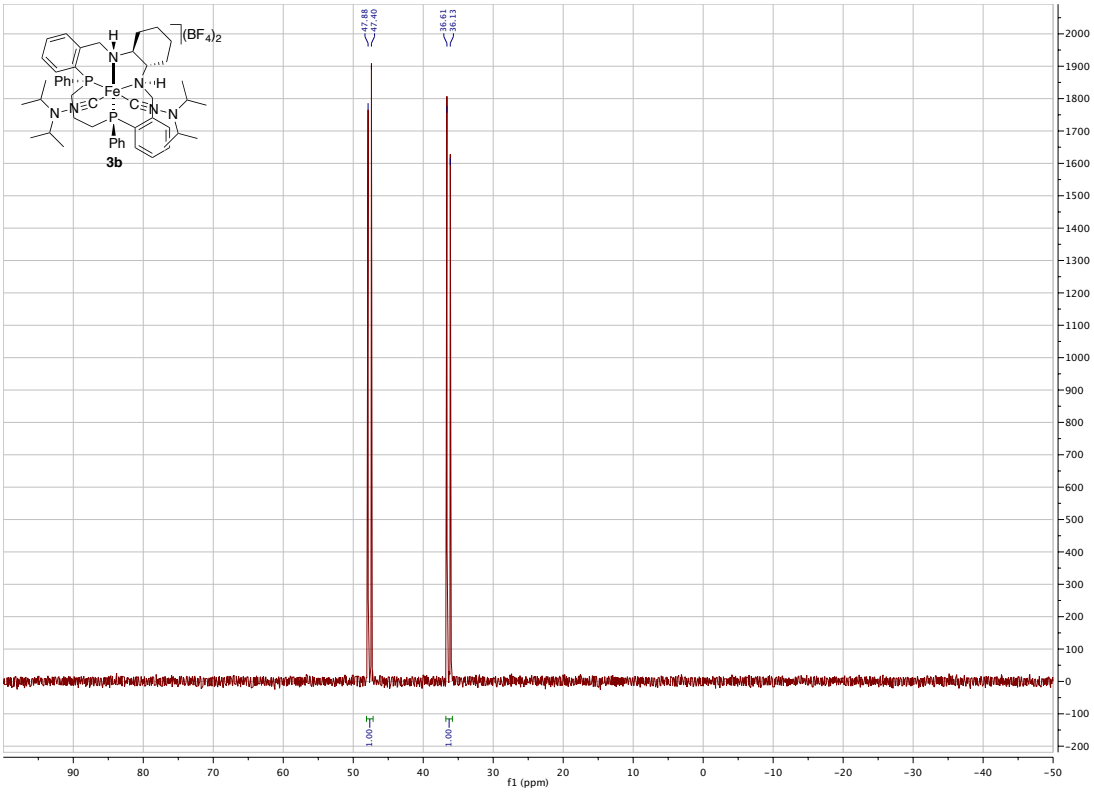


Figure S27: $^{31}P\{^{1}H\}$ NMR spectrum of **3b** (122 MHz, CD_2Cl_2).

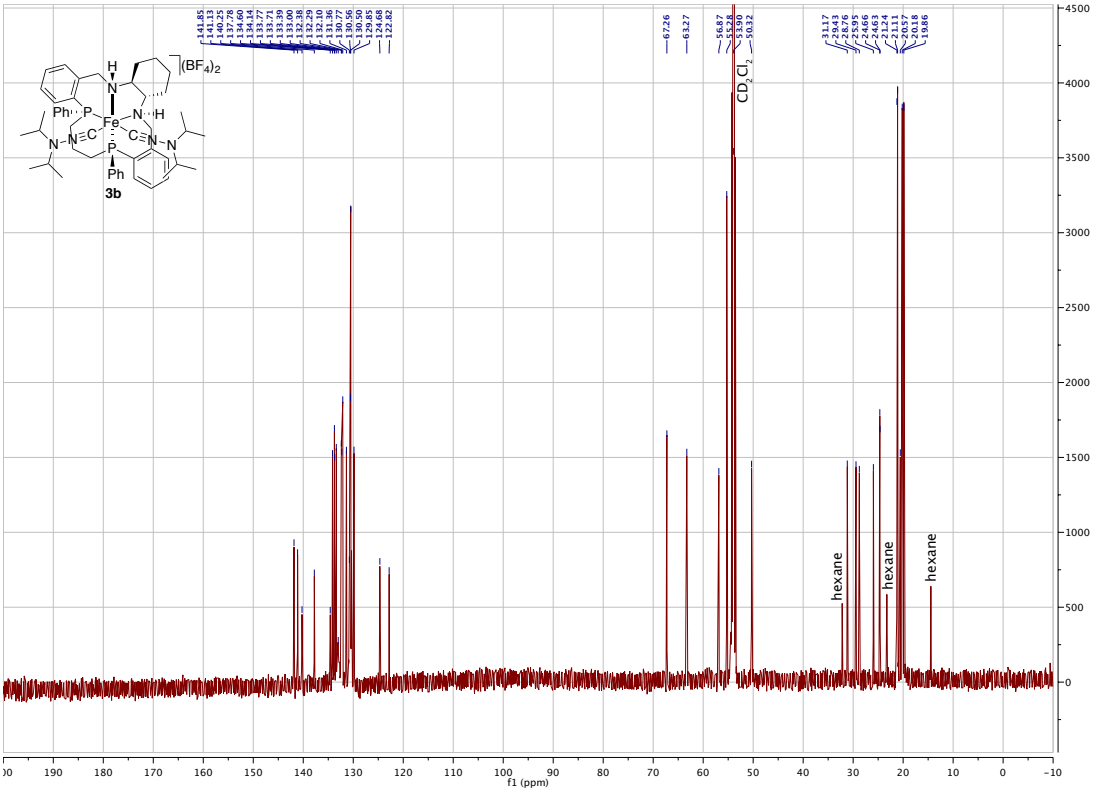


Figure S28: $^{13}C\{^{31}P,^{1}H\}$ NMR spectrum of **3b** (126 MHz, CD_2Cl_2).

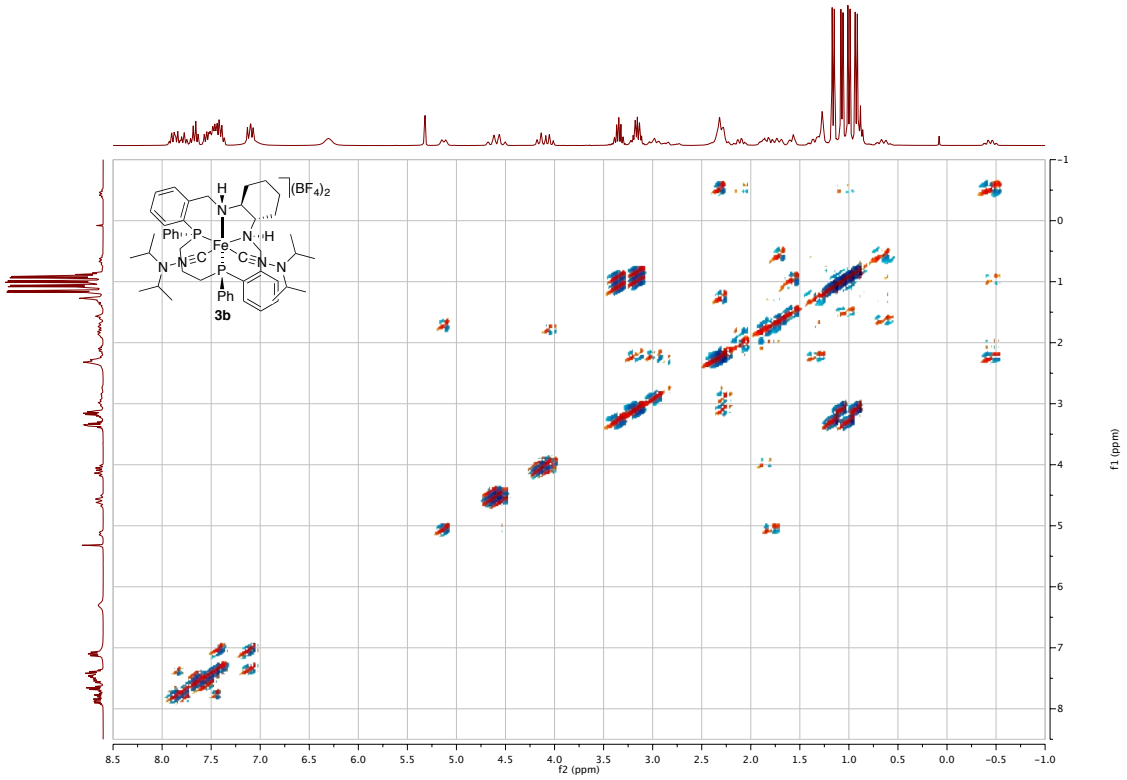


Figure S29: ^{1}H-^{1}H COSY spectrum of **3b**.

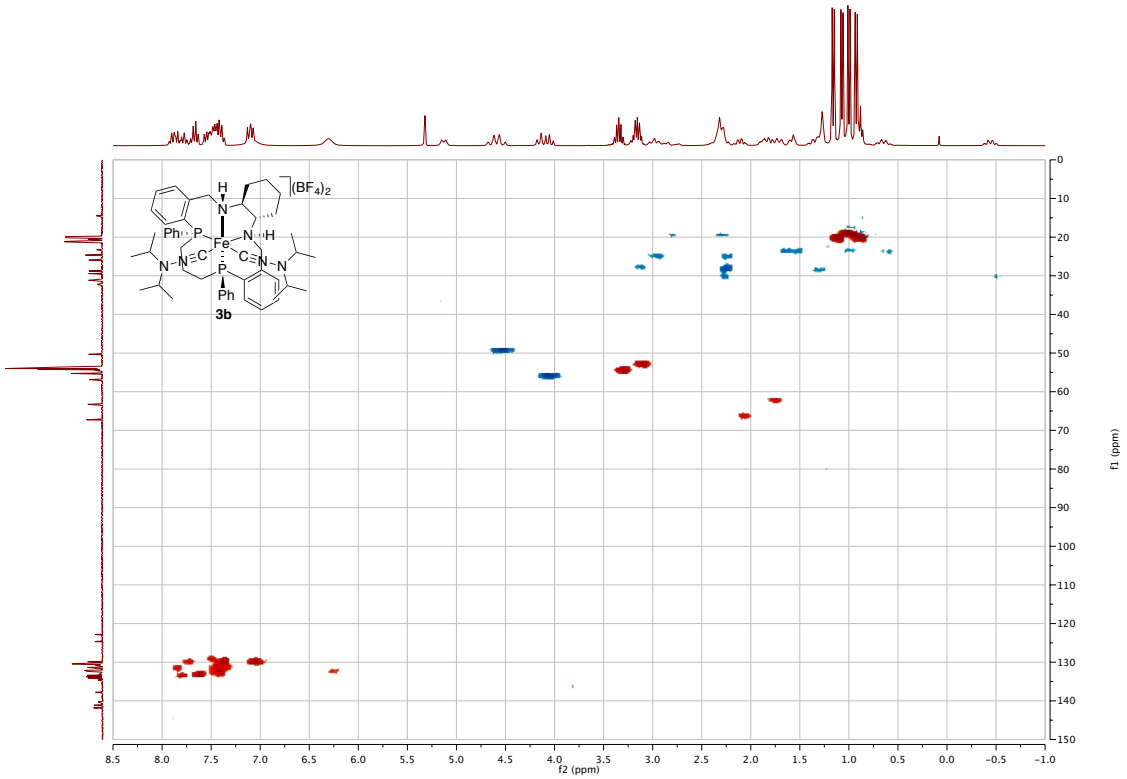
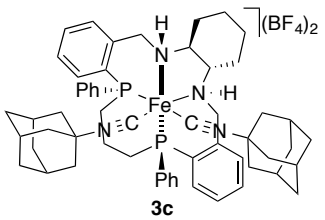


Figure S30: Phase-sensitive ^{1}H-^{13}C HSQC spectrum of **3b**.



3c

Synthesis of [Fe(CNAd)$_2$((S_P,S_P,S_C,S_C)-1b)](BF$_4$)$_2$, 3c. A Young NMR tube was charged with **8b** (17.0 mg, 19.7 μmol), 1-isocyanoadamantane (16.0 mg, 98.6 μmol, 5.0 equiv),[S3] and CH_2Cl_2 (0.5 mL; degassed by 10 vacuum/argon cycles), and the NMR tube was placed for 24 h in an oil bath at 50 °C. The solution was cooled to room temperature and filtered into a 20 mL Schlenk flask using a Teflon® cannula attached to a paper filter. The Young NMR tube was rinsed twice with CH_2Cl_2 (2 × 1 mL; degassed by 10 vacuum/argon cycles), and the solvent was removed using an external cooling trap. The crude product was dissolved in CH_2Cl_2 (2.5 mL; degassed by 10 vacuum/argon cycles) and carefully layered with hexane (17.5 mL). After 2 days, the supernatant was removed to afford the product as yellow crystals. The product exists as a single Λ-*cis*-*β* isomer. Yield: 14.5 mg (67%). **^{1}H NMR** (300 MHz, CD_2Cl_2): 7.96 – 7.75 (*m*, 3H, Ar-*H*), 7.71 – 7.62 (*m*, 2H, Ar-*H*), 7.59 – 7.33 (*m*, 7H, Ar-*H*), 7.21 – 7.10 (*m*, 2H, Ar-*H*), 7.05 (br *s*, 2H, Ar-*H*), 6.30 (*t*, $^3J_{H,H'}$ = 8.1 Hz, 2H, Ar-*H*), 5.19 (*d*, $^3J_{H,H'}$ = 11.5 Hz, 1H, N*H*), 4.68 (*d*, $^2J_{H,H'}$ = 19.0 Hz, 1H, NC*H*H), 4.57 (*d*, $^2J_{H,H'}$ = 19.0 Hz, 1H, NC*H*H), 4.10 (*d*, $^2J_{H,H'}$ = 12.4 Hz, 1H, NC*H*H), 3.85 (*dd*, $^2J_{H,H'}$ = 12.4 Hz, $^3J_{H,H'}$ = 11.2 Hz, 1H, NC*H*H), 3.14 (*dd*, $^3J_{H,H'}$ = 14.9, 14.9 Hz, 1H, C*H*H), 3.01 – 2.69 (*m*, 2H, C*H*H), 2.42 – 2.18 (*m*, 5H, C*H*H), 2.12 (br *s*, 3H, C*H* (Ad)), 2.06 – 1.91 (*m*, 10H, NC*H* (1H) + C*H* (Ad, 3H) + C*H*H (Ad, 6H)), 1.82 – 1.64 (*m*, 12H, NC*H* (1H) + N*H* (1H) + C*H*H (1H) + C*H*H (Ad, 9H)), 1.63 – 1.48 (*m*, 10H, C*H*H (1H) + C*H*H (Ad, 9H)), 1.38 – 1.21 (*m*, 1H, C*H*H), 1.17 – 0.99 (*m*, 1H, C*H*H), 0.77 – 0.59 (*m*, 1H, C*H*H), –0.37 (*dddd*, $^3J_{H,H'}$ = 12.6, 12.6, 12.5, 3.6 Hz, 1H, C*H*H). **^{31}P{^{1}H} NMR** (122 MHz, CD_2Cl_2): 47.3 (*d*, $^2J_{P,P'}$ = 57.9 Hz), 33.8 (*d*, $^2J_{P,P'}$ = 57.9 Hz). **^{13}C{^{31}P,^{1}H} NMR** (126 MHz, CD_2Cl_2): 161.2 (*m*, *C*NAd), 153.2 (*m*, *C*NAd), 142.0 (arom.),

141.9 (arom.), 140.9 (arom.), 137.1 (arom.), 134.2 (arom.), 134.0 (arom.), 133.7 (arom.), 133.52 (arom.), 133.47 (arom.), 132.9 (arom.), 132.3 (arom.), 132.1 (arom.), 132.0 (arom.), 131.6 (arom.), 130.84 (arom.), 130.80 (arom.), 130.73 (arom.), 130.66 (arom.), 130.34 (arom.), 130.29 (arom.), 129.7 (arom.), 124.0 (arom.), 123.8 (arom.), 122.3 (arom.), 66.9 (N*C*H), 63.4 (N*C*H), 61.1 (CN-*C*), 60.3 (CN-*C*), 56.1 (N*C*H_2), 50.1 (N*C*H_2), 43.7 (*C*H_2 (Ad)), 42.2 (*C*H_2 (Ad)), 35.7 (*C*H_2 (Ad)), 35.6 (*C*H_2 (Ad)), 31.2 (*C*H_2), 29.7 (*C*H_2), 29.6 (*C*H (Ad)), 29.5 (*C*H (Ad)), 28.1 (*C*H_2), 26.2 (*C*H_2), 24.6 (*C*H_2), 24.5 (*C*H_2), 20.7 (*C*H_2). **IR** (liquid film, cm^{-1}): 3243 (N-H), 3226 (N-H), 3061 (C-H), 2913 (C-H), 2856 (C-H), 2169 (isonitrile), 2121 (isonitrile), 1629, 1480, 1457, 1435, 1417, 1400, 1358, 1346, 1306, 1281, 1190, 1162, 1071, 1056. **HRMS** (MALDI): Calcd. for $C_{57}H_{70}BF_4FeN_4P_2$ *m/z* 1015.4459, found *m/z* 1015.4443 $[M–BF_4]^+$. **EA**: Calcd. for $C_{57}H_{70}B_2F_8FeN_4P_2$: C, 62.09; H, 6.40; N, 5.08; found: C, 61.54; H, 6.45; N, 5.10. A possible explanation for the unsatisfactory carbon analysis is a combustion problem due to the tetrafluoroborate anion.[S4]

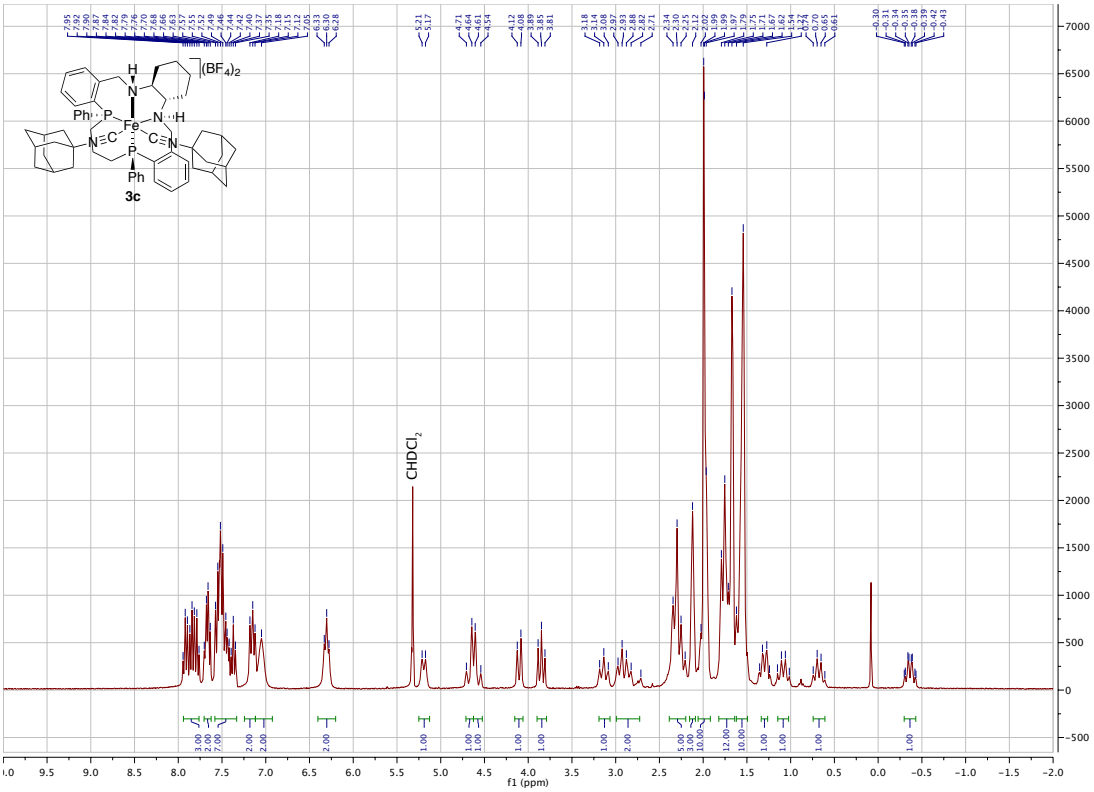


Figure S31: ^{1}H NMR spectrum of **3c** (300 MHz, CD_2Cl_2).

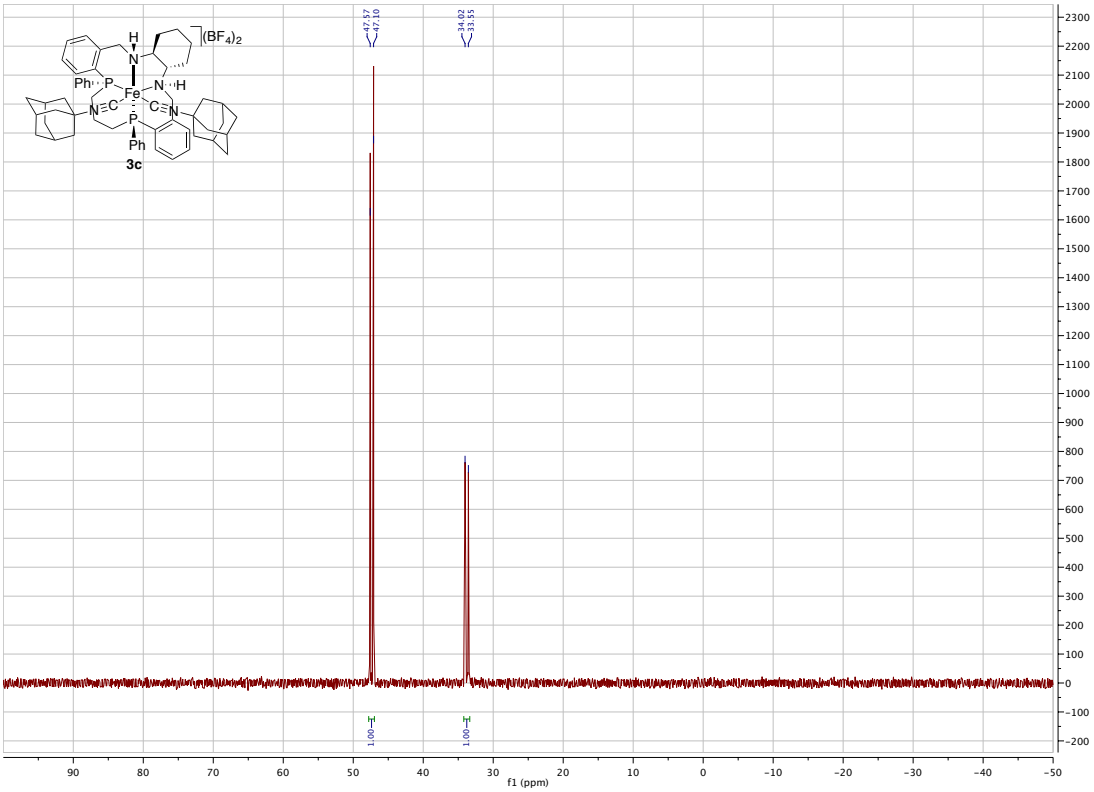


Figure S32: $^{31}P\{^{1}H\}$ NMR spectrum of **3c** (122 MHz, CD_2Cl_2).

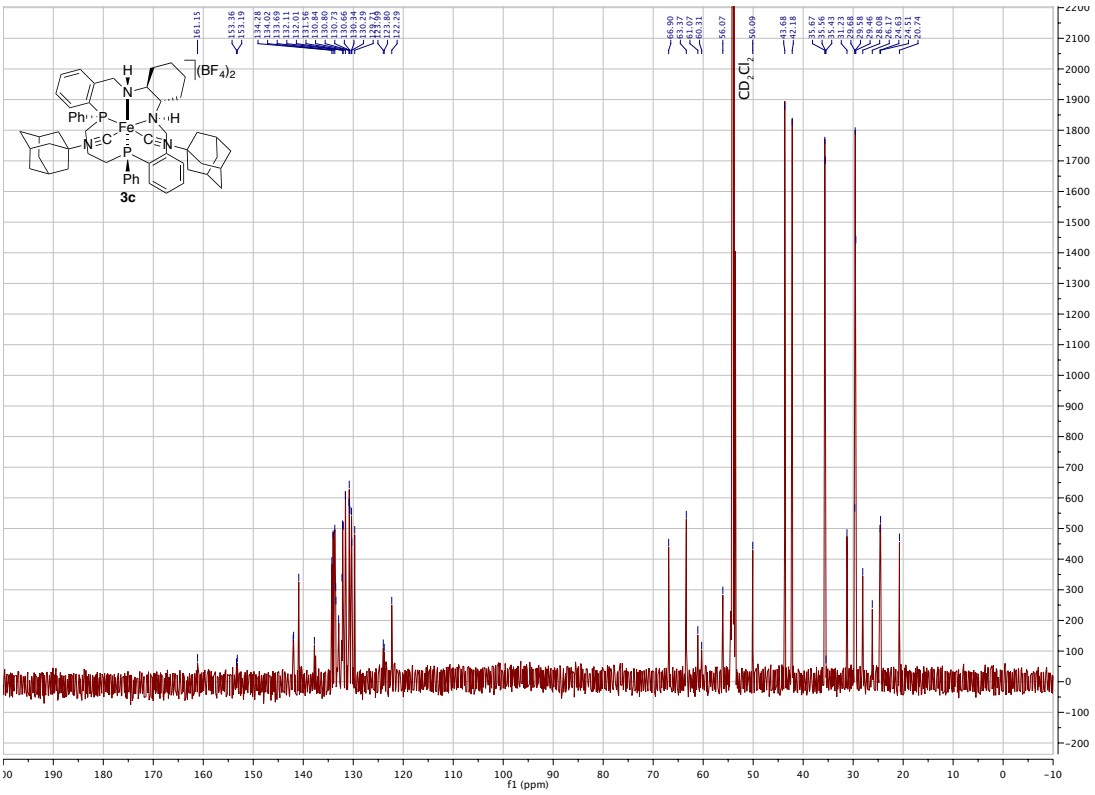


Figure S33: $^{13}C\{^{31}P,^{1}H\}$ NMR spectrum of **3c** (126 MHz, CD_2Cl_2).

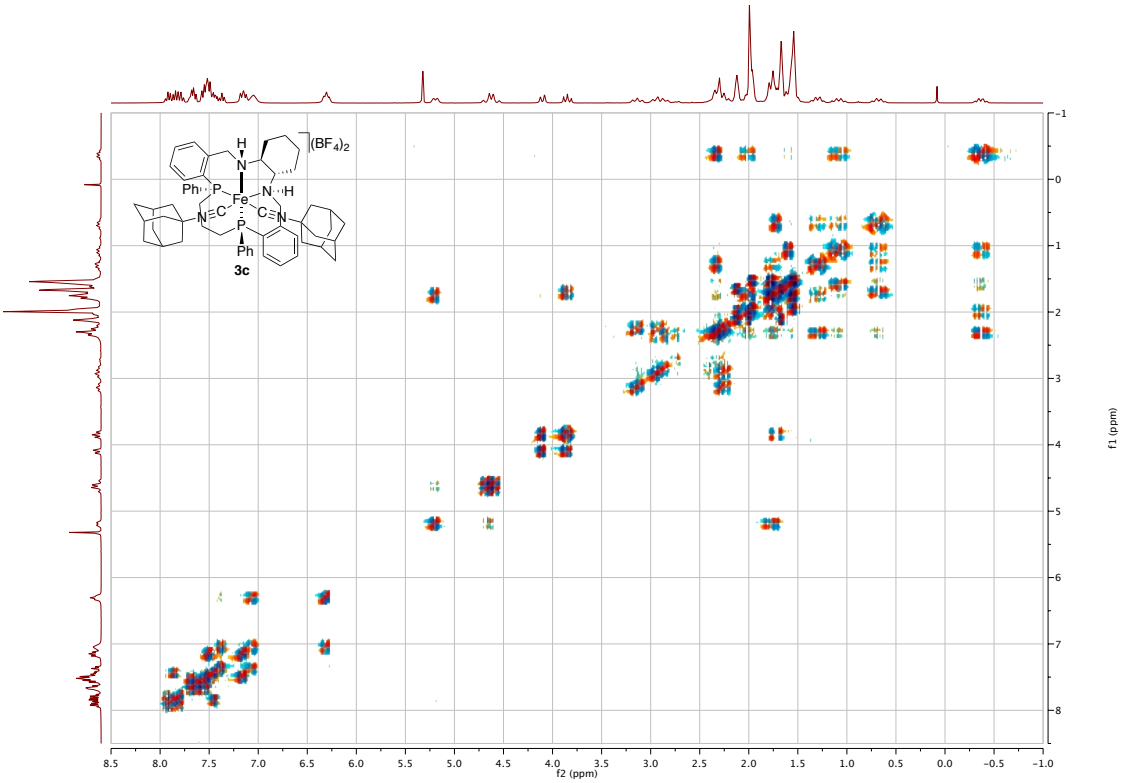


Figure S34: ^{1}H-^{1}H COSY spectrum of **3c**.

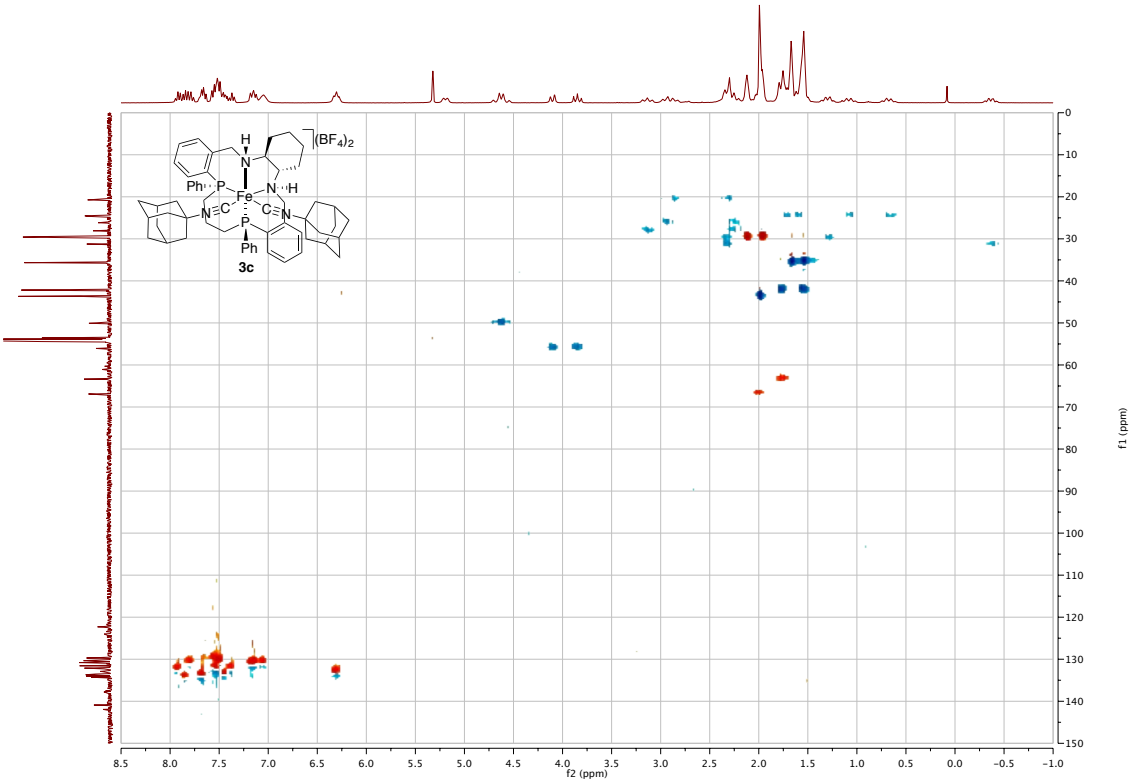


Figure S35: Phase-sensitive ^{1}H-^{13}C HSQC spectrum of **3c**.

X-Ray Structure of [Fe(CNAd)$_2$((S_P,S_P,S_C,S_C)-1b)](BF$_4$)$_2$, 3c. Yellow crystals were obtained by layering a CH_2Cl_2 solution of **3c** with hexane. Crystal data for $C_{57}H_{70}B_2Cl_4F_8FeN_4P_2$: block (0.14 × 0.12 × 0.10 mm), triclinic, *P*1, cell dimensions (103 K) a = 10.4939(10), b = 10.7859(10), c = 13.5065(13) Å, α = 101.154(3), β = 92.256(3), γ = 102.353(3) °, and V = 1 459.9(2) Å^3 with Z = 1, D_C = 1.447 Mg/m^3, μ = 0.565 mm^{-1} (Mo K$_a$, graphite monochromated), λ = 0.71073 Å, F(000) = 662. The data were collected at 103 K on a Bruker AXS SMART APEX platform in the θ range 2.241–37.159 °. The structure was solved with SHELXTL using direct methods. Of the 68 309 measured reflections with index ranges $-17 \le h \le 17$, $-18 \le k \le 18$, $-22 \le l \le 22$, 28 919 independent reflections (R_{int} = 0.0471) were used in the refinement (full-matrix least squares on F^2) with anisotropic displacement parameters for all non-H atoms. Hydrogen

atoms were introduced at calculated positions (except those on N1 and N2) and refined with the riding model and individual isotropic thermal parameters. The asymmetric unit contains the complex dication, two BF_4^- anions, and two adjacent CH_2Cl_2 molecules. For each CH_2Cl_2 molecule, one Cl atom is disordered over two positions (0.54:0.46 occupancy). Final residuals were R_1 = 0.0528 (for 24 414 reflections with $I > 2s(I)$) and wR_2 = 0.1304 (all data), GOF = 1.018, absolute structure parameter 0.030(4) from 10 272 selected quotients (Parsons' method) of 0.021(10) by hole-in-one fit to all intensities. Max. and min. difference peaks were +0.45 and –1.52 eÅ^{-3}, the largest and mean $\Delta/\sigma = -0.001$ and 0.000.

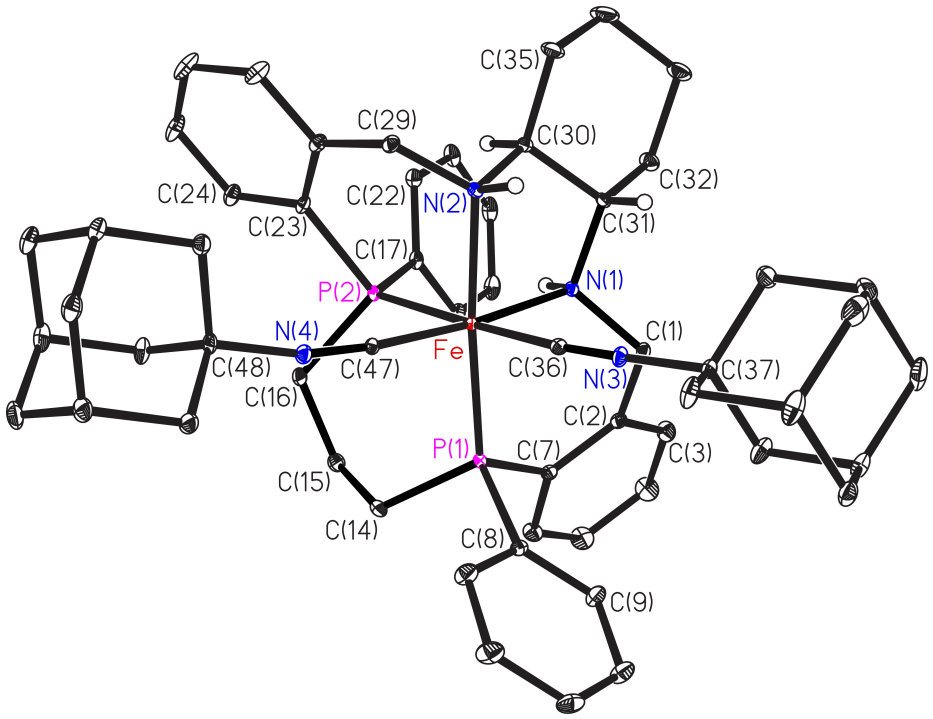


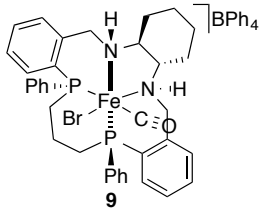
Figure S36: X-ray structure of the dication of [Fe(CNAd)$_2$((S_P,S_P,S_C,S_C)-**1b**)](BF$_4$)$_2$ (**3c**).

Table S2: Selected distances (Å) and angles (°) of [Fe(CNAd)$_2$((S_P,S_P,S_C,S_C)-**1b**)](BF$_4$)$_2$ (**3c**).

Fe–P(1)	2.2174(7)	Fe–P(2)	2.2525(6)
Fe–N(1)	2.063(2)	Fe–N(2)	2.072(2)
Fe–C(36)	1.898(2)	Fe–C(47)	1.853(2)
C(36)–N(3)	1.155(3)	C(47)–N(4)	1.161(3)
P(1)–Fe–P(2)	92.42(2)	N(1)–Fe–N(2)	82.82(8)
P(1)–Fe–N(1)	92.14(6)	P(2)–Fe–N(2)	89.44(6)
P(1)–Fe–N(2)	174.71(6)	P(2)–Fe–N(1)	92.94(6)
P(1)–Fe–C(36)	90.13(7)	P(2)–Fe–C(36)	177.32(7)
P(1)–Fe–C(47)	92.56(7)	P(2)–Fe–C(47)	84.34(7)
N(1)–Fe–C(36)	87.75(9)	N(2)–Fe–C(36)	88.11(9)
N(1)–Fe–C(47)	174.67(9)	N(2)–Fe–C(47)	92.55(9)
C(36)–Fe–C(47)	94.76(10)		

Table S3: Angles and torsion angles (°) involving the six-membered P(1)–Fe–P(2) chelate ring in [Fe(MeCN)$_2$((S_P,S_P,S_C,S_C)-**1b**)](BF$_4$)$_2$ (**8b**) and [Fe(CNAd)$_2$((S_P,S_P,S_C,S_C)-**1b**)](BF$_4$)$_2$ (**3c**).

	8b	**3c**
Fe(1)–P(1)–C(14)	114.72(15)	115.33(8)
P(1)–C(14)–C(15)	115.8(3)	115.57(17)
C(14)–C(15)–C(16)	114.4(4)	114.1(2)
C(15)–C(16)–P(2)	117.2(3)	117.09(16)
C(16)–P(2)–Fe(1)	116.65(14)	116.91(8)
P(2)–Fe–P(1)	92.92(4)	92.42(2)
Fe(1)–P(1)–C(14)–C(15)	59.4(4)	60.8(2)
P(1)–C(14)–C(15)–C(16)	–68.2(4)	–69.5(3)
C(14)–C(15)–C(16)–P(2)	63.6(4)	63.5(3)
C(15)–C(16)–P(2)–Fe(1)	–51.1(4)	–49.6(2)
C(16)–P(2)–Fe(1)–P(1)	35.7	34.4
P(2)–Fe(1)–P(1)–C(14)	–38.9	–38.7



9

Synthesis of [FeBr(CO)((S_P,S_P,S_C,S_C)-1b)]BPh_4, 9. A 50 mL Young flask was charged with **8b** (65.0 mg, 75.4 μmol), KBr (17.9 mg, 151 μmol, 2.0 equiv), and acetone (3.0 mL; degassed by 10 vacuum/argon cycles). After stirring at room temperature for 10 min, the solution was cooled to –78 °C. After 5 min, the argon atmosphere was removed under vacuum and the Young flask was placed under a CO atmosphere (2.25 bar) (*Notes*: Carbon monoxide is colorless, odorless, and highly toxic and should therefore be handled in a well ventilated fume hood; the reaction was performed behind a safety shield). The cooling bath was removed and the solution was stirred overnight at room temperature to give a dark green solution. The solvent was removed using an external cooling trap. In a separate 20 mL Schlenk flask, $NaBPh_4$ (25.8 mg, 75.4 μmol, 1.0 equiv) was dissolved in MeOH (1.0 mL; degassed by 10 vacuum/argon cycles). The crude bromocarbonyl complex was dissolved in MeOH (2.5 mL; degassed by 10 vacuum/argon cycles), and filtered to the $NaBPh_4$ solution using a Teflon® cannula attached to a paper filter (*Note*: The product precipitates only partially from the solution). After 30 min, the solvent was removed using an external cooling trap. The residue was dissolved in CH_2Cl_2 (3.0 mL; degassed by 10 vacuum/argon cycles), and filtered into a 10 mL Schlenk using a Teflon® cannula attached to a paper filter. The solvent was removed using an external cooling trap, and Et_2O (5.0 mL) was added to the residue. After stirring at room temperature for 30 min, the stirring bar was removed and the supernatant was decanted to afford the product as a green powder. The product exists as a single Λ-*cis*-*β* isomer. Yield: 45.6 mg (59%). **^{1}H NMR** (300 MHz, CD_2Cl_2): 7.87 – 7.23 (*m*, 23H, Ar-*H*), 7.14 – 6.84 (*m*, 13H, Ar-*H*), 6.42 (*t*, $^3J_{H,H'}$ = 8.1 Hz, 2H, Ar-*H*), 5.95 (*d*, $^3J_{H,H'}$ = 11.9 Hz, 1H, N*H*), 4.83 (*d*, $^2J_{H,H'}$ = 16.4 Hz, 1H, NC*H*H),

4.18 (*d*, $^{2}J_{H,H'}$ = 16.4 Hz, 1H, NC*H*H), 3.59 (*d*, $^{2}J_{H,H'}$ = 13.0 Hz, 1H, NC*H*H), 3.47 – 3.37 (*m*, 1H, NC*H*H), 3.30 – 3.05 (*m*, 3H, C*H*H), 3.01 – 2.48 (*m*, 3H, C*H*H), 2.28 (*d*, $^{3}J_{H,H'}$ = 12.7 Hz, 1H, C*H*H), 2.01 – 1.86 (*m*, 2H, NC*H* + C*H*H), 1.77 (*ddd*, $^{3}J_{H,H'}$ = 10.9, 10.2, 10.2 Hz, 1H, NC*H*), 1.67 – 1.50 (*m*, 2H, C*H*H), 1.48 – 1.36 (*m*, 1H, C*H*H), 1.06 – 0.88 (*m*, 1H, C*H*H), 0.68 – 0.48 (*m*, 1H, C*H*H), –0.17 – –0.30 (*m*, 1H, N*H*), –0.70 – –0.86 (*m*, 1H, C*H*H). **^{31}P{^{1}H} NMR** (122 MHz, CD_2Cl_2): 39.0 (*d*, $^{2}J_{P,P'}$ = 69.6 Hz), 21.3 (*d*, $^{2}J_{P,P'}$ = 69.6 Hz). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2): 216.0 (*dd*, $^{2}J_{P,C}$ = 52.7, 25.4 Hz, *C*O), 164.6 (*m*, arom. (BPh_4)), 141.1 (*d*, $^{2}J_{P,C}$ = 14.8 Hz, arom.), 140.9 (*d*, $^{2}J_{P,C}$ = 14.3 Hz, arom.), 136.9 (*dd*, $^{1}J_{P,C}$ = 46.2 Hz, $^{3}J_{P,C}$ = 3.9 Hz, arom.), 136.5 (*m*, arom. (BPh_4)), 134.8 (arom.), 134.2 (arom.), 133.9 (arom.), 133.5 (*d*, $J_{P,C}$ = 2.0 Hz, arom.), 133.0 (br *s*, arom.), 132.79 (*d*, $J_{P,C}$ = 2.2 Hz, arom.), 132.77 (*d*, $J_{P,C}$ = 1.9 Hz, arom.), 132.1 (*d*, $J_{P,C}$ = 5.1 Hz, arom.), 131.6 (*d*, $J_{P,C}$ = 9.6 Hz, arom.), 131.2 (*d*, $J_{P,C}$ = 10.8 Hz, arom.), 131.0 (*d*, $J_{P,C}$ = 8.3 Hz, arom.), 130.4 (arom.), 129.6 (*dd*, $^{1}J_{P,C}$ = 86.3 Hz, $^{3}J_{P,C}$ = 10.4 Hz, arom.), 129.38 (*d*, $J_{P,C}$ = 9.6 Hz, arom.), 129.35 (*d*, $J_{P,C}$ = 9.6 Hz, arom.), 126.1 (*m*, arom. (BPh_4)), 125.6 (*d*, $J_{P,C}$ = 33.7 Hz, arom.), 123.6 (*d*, $J_{P,C}$ = 40.1 Hz, arom.), 122.3 (arom. (BPh_4)), 66.8 (*d*, $^{3}J_{P,C}$ = 2.1 Hz, NCH), 62.7 (NCH), 58.6 (*m*, N*C*H_2), 46.9 (*d*, $^{3}J_{P,C}$ = 4.4 Hz, N*C*H_2), 30.8 (*C*H_2), 29.9 (*C*H_2), 24.6 (*C*H_2), 24.4 (*C*H_2), 23.8 (*dd*, $^{1}J_{P,C}$ = 29.5 Hz, $^{3}J_{P,C}$ = 3.6 Hz, P*C*H_2), 22.1 (*dd*, $^{1}J_{P,C}$ = 28.8 Hz, $^{3}J_{P,C}$ = 2.6 Hz, P*C*H_2), 20.8 (*d*, $^{2}J_{P,C}$ = 1.7 Hz, PCH_2*C*H_2). **IR** (liquid film, cm^{-1}): 3212 (N-H), 3053 (C-H), 2998 (C-H), 2982 (C-H), 2939 (C-H), 2858 (C-H), 1981 (CO), 1625, 1579, 1478, 1446, 1432, 1412, 1394, 1352, 1316, 1264, 1184, 1158, 1135, 1093, 1064, 1044, 1031, 1015. **HRMS** (MALDI): Calcd. for $C_{36}H_{40}BrFeN_2OP_2$ *m*/*z* 713.1145, found *m*/*z* 713.1137 $[M–BPh_4]^+$. **EA**: Calcd. for $C_{60}H_{60}BBrFeN_2OP_2$: C, 69.72; H, 5.85; N, 2.71; found: C, 65.64; H, 5.84; N, 2.83. A possible explanation for the unsatisfactory carbon analysis is a combustion problem due to the tetraphenylborate anion.[S4]

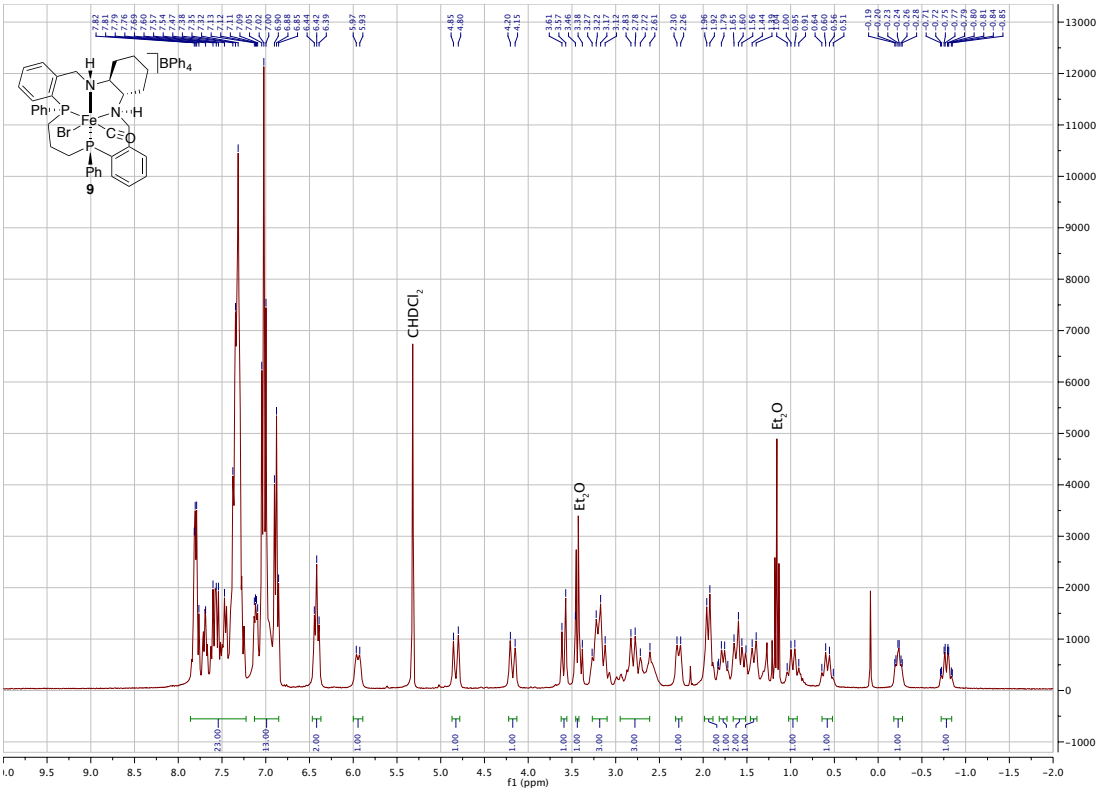


Figure S37: ^{1}H NMR spectrum of **9** (300 MHz, CD_2Cl_2).

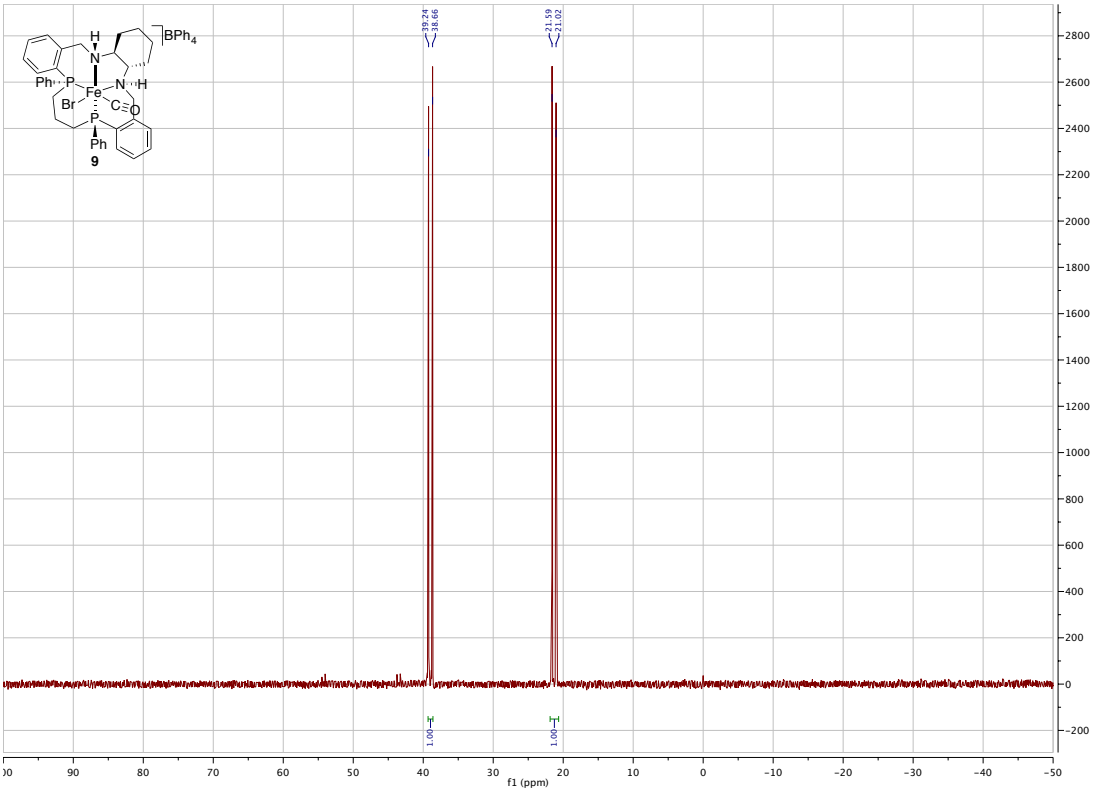


Figure S38: $^{31}P\{^{1}H\}$ NMR spectrum of **9** (122 MHz, CD_2Cl_2).

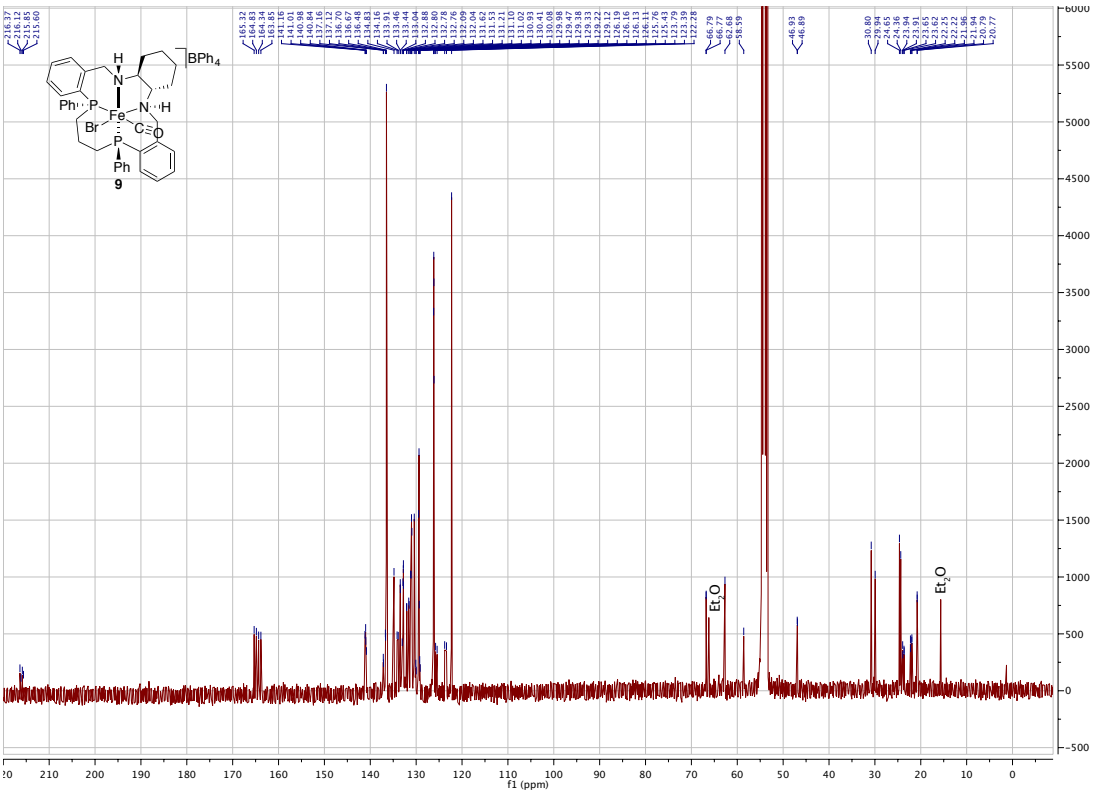


Figure S39: $^{13}C\{^{1}H\}$ NMR spectrum of **9** (100 MHz, CD_2Cl_2).

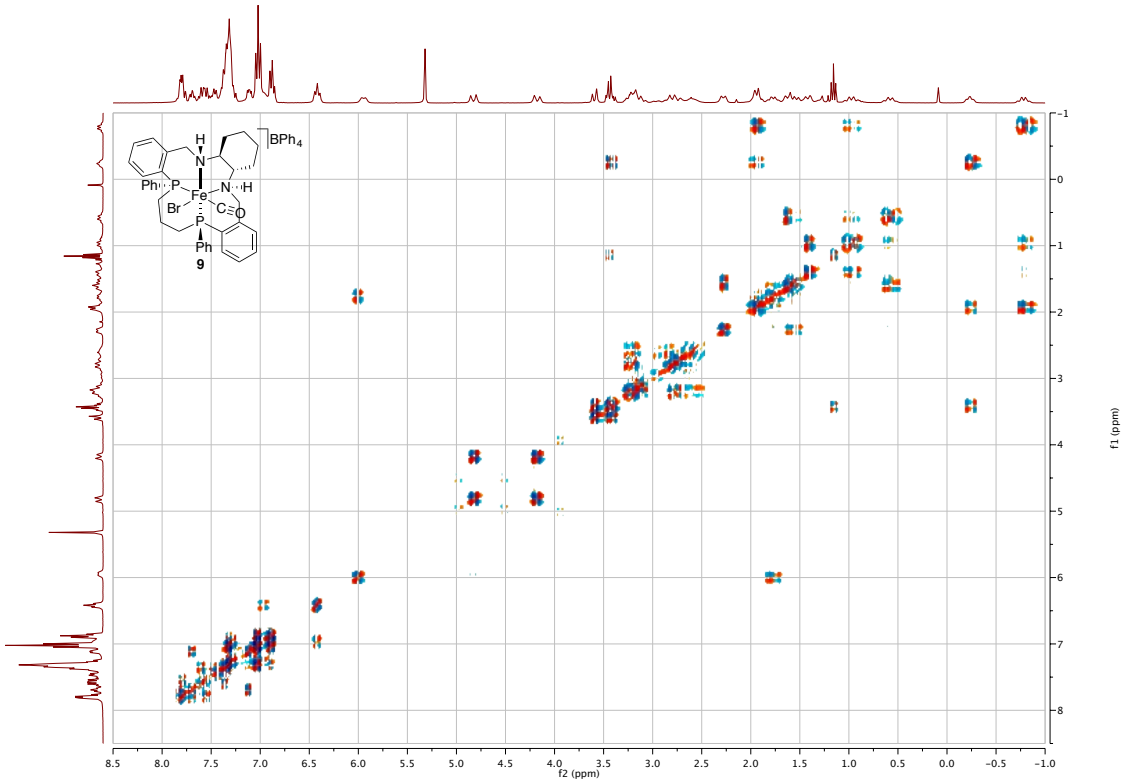


Figure S40: ^{1}H-^{1}H COSY spectrum of **9**.

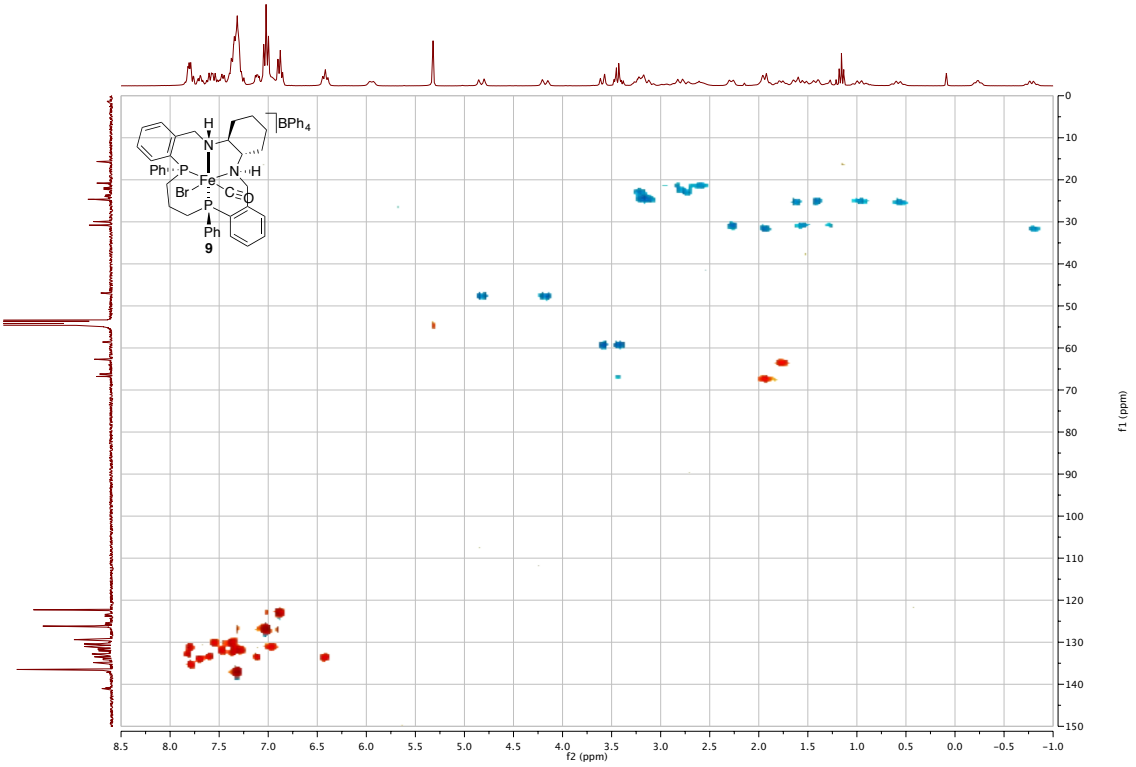


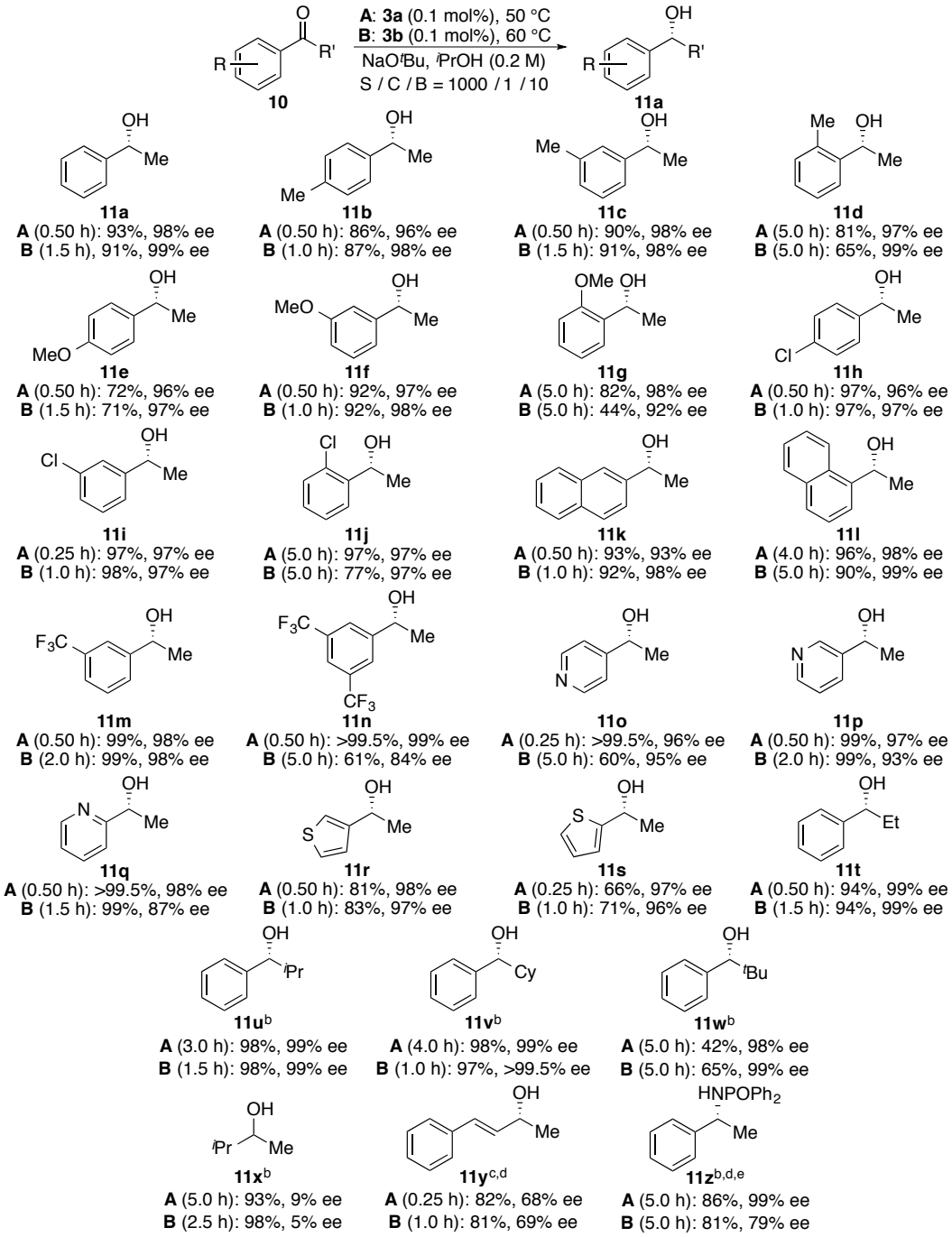
Figure S41: Phase-sensitive ^{1}H-^{13}C HSQC spectrum of **9**.

Asymmetric Transfer Hydrogenation

General Procedure (A) for the Asymmetric Transfer Hydrogenation of Ketones 10 to Alcohols 11 with Catalyst 3a. In a glove box, a glass vial was charged with **3a** (2.6 mg, 2.5 μmol, 0.1 mol%) and NaO^{t}Bu (2.4 mg, 25 μmol, 1 mol%). The solids were transferred to a 20 mL Young flask using a paper funnel, the flask was connected to the vacuum/argon line and the solids were dried for 5 min under high vacuum. 2-Propanol (2.5 mL) was added, and the flask was immersed in a preheated oil bath at 50 °C. After 5 min, 2-propanol (10 mL) was added. After additional 10 min, ketone **10** (2.50 mmol) was added, and the solution was stirred at 50 °C. After 0.25 h, 0.50 h, 1.0 h, 1.5 h, 2.0 h, 2.5 h, 3.0 h, 4.0 h, and 5.0 h, an aliquot (0.15 mL) was filtered with EtOAc (4 × 0.5 mL) through a short pad of silica gel in a Pasteur pipette (ca. 0.5 cm) and analyzed by GC or HPLC.

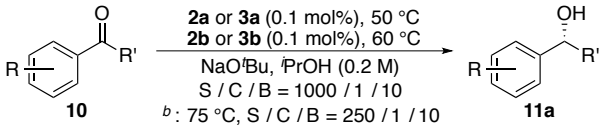
General Procedure (B) for the Asymmetric Transfer Hydrogenation of Ketones 10 to Alcohols 11 with Catalyst 3b. In a glove box, a glass vial was charged with **3b** (2.6 mg, 2.5 μmol, 0.1 mol%) and NaO^{t}Bu (2.4 mg, 25 μmol, 1 mol%). The solids were transferred to a 20 mL Young flask using a paper funnel, the flask was connected to the vacuum/argon line and the solids were dried for 5 min under high vacuum. 2-Propanol (2.5 mL) was added, and the flask was immersed in a preheated oil bath at 50 °C. After 5 min, 2-propanol (10 mL) was added. After additional 10 min, ketone **10** (2.50 mmol) was added, and the solution was stirred at 50 °C. After 0.25 h, 0.50 h, 1.0 h, 1.5 h, 2.0 h, 2.5 h, 3.0 h, 4.0 h, and 5.0 h, an aliquot (0.15 mL) was filtered with EtOAc (4 × 0.5 mL) through a short pad of silica gel in a Pasteur pipette (ca. 0.5 cm) and analyzed by GC or HPLC.

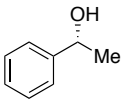
Chart S1: Substrate Scope for the Asymmetric Transfer Hydrogenation of C=X Bonds.



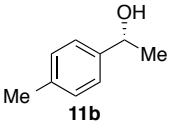
(a) Reactions were performed with 2.5 mmol of the substrate in 2-propanol (0.2 M). Yields and ee values were determined by GC (*β*-DEX). (b) The reaction was performed with 0.625 mmol of the substrate at 75 °C with S/C/B = 250/1/10. (c) Complete chemoselectivity for the allylic alcohol was observed (saturated alcohol or ketone < 1 %). (d) The ee values were determined by HPLC. (e) Isolated yield.

Chart S2: Comparison of Catalysts **2**[S2] and **3** (best catalyst in color, for conditions see Chart S1).

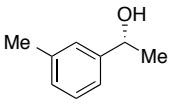




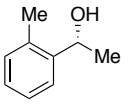
11a
2a (2.0 h): 90%, 96% ee
2b (1.5 h): 93%, 98% ee
3a (0.5 h): 93%, 98% ee
3b (1.5 h), 91%, 99% ee



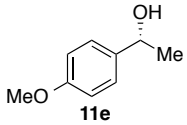
11b
2a (1.0 h): 84%, 93% ee
2b (2.5 h): 85%, 97% ee
3a (0.5 h): 86%, 96% ee
3b (1.0 h): 87%, 98% ee



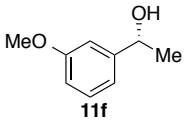
11c
2a (1.0 h): 90%, 96% ee
2b (2.5 h): 92%, 98% ee
3a (0.5 h): 90%, 98% ee
3b (1.5 h): 91%, 98% ee



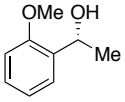
11d
2a (5.0 h): 83%, 95% ee
2b (5.0 h): 84%, 99% ee
3a (5.0 h): 81%, 97% ee
3b (5.0 h): 65%, 99% ee



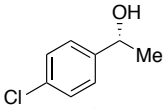
11e
2a (1.0 h): 64%, 91% ee
2b (1.5 h): 68%, 96% ee
3a (0.5 h): 72%, 96% ee
3b (1.5 h): 71%, 97% ee



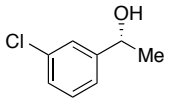
11f
2a (0.5 h): 91%, 97% ee
2b (1.5 h): 94%, 98% ee
3a (0.5 h): 92%, 97% ee
3b (1.0 h): 92%, 98% ee



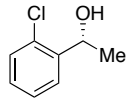
11g
2a (2.5 h): 97%, 99% ee
2b (5.0 h): 82%, 97% ee
3a (5.0 h): 82%, 98% ee
3b (5.0 h): 44%, 92% ee



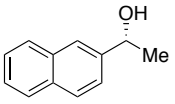
11h
2a (1.0 h): 95%, 92% ee
2b (1.5 h): 97%, 94% ee
3a (0.5 h): 97%, 96% ee
3b (1.0 h): 97%, 97% ee



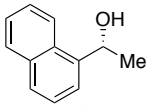
11i
2a (1.0 h): 98%, 95% ee
2b (1.5 h): 98%, 96% ee
3a (0.25 h): 97%, 97% ee
3b (1.0 h): 98%, 97% ee



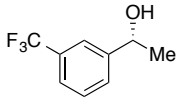
11j
2a (3.0 h): 98%, 97% ee
2b (3.0 h): 99%, 97% ee
3a (5.0 h): 97%, 97% ee
3b (5.0 h): 77%, 97% ee



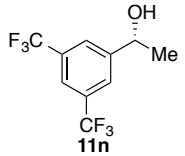
11k
2a (1.5 h): 91%, 91% ee
2b (1.0 h): 93%, 98% ee
3a (0.5 h): 93%, 93% ee
3b (1.0 h): 92%, 98% ee



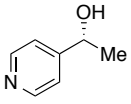
11l
2a (4.0 h): 93%, 96% ee
2b (4.0 h): 98%, 99% ee
3a (4.0 h): 96%, 98% ee
3b (5.0 h): 90%, 99% ee



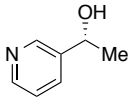
11m
2a (1.0 h): 99%, 96% ee
2b (5.0 h): 99%, 96% ee
3a (0.5 h): 99%, 98% ee
3b (2.0 h): 99%, 98% ee



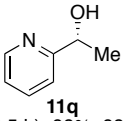
11n
2a (1.5 h): >99.5%, 98% ee
2b (5.0 h): 40%, 91% ee
3a (0.5 h): >99.5%, 99% ee
3b (5.0 h): 61%, 84% ee



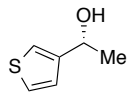
11o
2a (1.0 h): >99.5%, 90% ee
2b (5.0 h): 63%, 92% ee
3a (0.25 h): >99.5%, 96% ee
3b (5.0 h): 60%, 95% ee



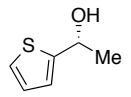
11p
2a (1.0 h): 99%, 93% ee
2b (1.5 h): 99%, 92% ee
3a (0.5 h): 99%, 97% ee
3b (2.0 h): 99%, 93% ee



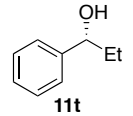
11q
2a (0.5 h): 98%, 98% ee
2b (2.0 h): 97%, 87% ee
3a (0.5 h): >99.5%, 98% ee
3b (1.5 h): 99%, 87% ee



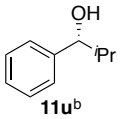
11r
2a (2.5 h): 76%, 97% ee
2b (3.0 h): 83%, 95% ee
3a (0.5 h): 81%, 98% ee
3b (1.0 h): 83%, 97% ee



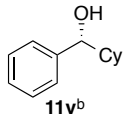
11s
2a (2.0 h): 66%, 95% ee
2b (2.0 h): 72%, 92% ee
3a (0.25 h): 66%, 97% ee
3b (1.0 h): 71%, 96% ee



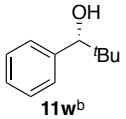
11t
2a (1.5 h): 94%, 97% ee
2b (2.5 h): 95%, 98% ee
3a (0.5 h): 94%, 99% ee
3b (1.5 h): 94%, 99% ee



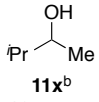
11u[b]
2a (5.0 h): 90%, 93% ee
2b (1.5 h): 98%, 97% ee
3a (3.0 h): 98%, 99% ee
3b (1.5 h): 98%, 99% ee



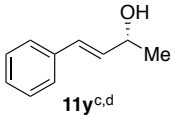
11v[b]
2a (5.0 h): 79%, 86% ee
2b (1.0 h): 98%, 98% ee
3a (4.0 h): 98%, 99% ee
3b (1.0 h): 97%, >99.5% ee



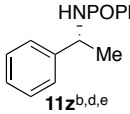
11w[b]
2a (5.0 h): 62%, 97% ee
2b (4.0 h): 99%, 97% ee
3a (5.0 h): 42%, 98% ee
3b (5.0 h): 65%, 99% ee



11x[b]
2a (5.0 h): 95%, 17% ee
2b (2.5 h): 99%, 24% ee
3a (5.0 h): 93%, 9% ee
3b (2.5 h): 98%, 5% ee

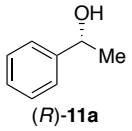


11y[c,d]
2a (0.5 h): 81%, 65% ee
2b (0.5 h): 76%, 70% ee
3a (0.25 h): 82%, 68% ee
3b (1.0 h): 81%, 69% ee



11z[b,d,e]
2a (5.0 h): 78%, 98% ee
2b (5.0 h): 75%, 68% ee
3a (5.0 h): 86%, 99% ee
3b (5.0 h): 81%, 79% ee

Characterization of Catalysis Products



(*R*)-**11a**

Synthesis of (*R*)-1-Phenylethan-1-ol, (*R*)-11a. The synthesis of racemic **11a** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 93.5% yield and with 97.8% ee following general procedure **A** using catalyst **3a** (reaction time: 0.50 h). **GC**: *β*-DEX column, 100 °C isotherm, retention times t_R(SM) = 13.5 min, t_R(major) = 22.2 min, t_R(minor) = 24.0 min. This compound was obtained in 91.3% yield and with 98.7% ee following general procedure **B** using catalyst **3b** (reaction time: 1.5 h). **GC**: *β*-DEX column, 100 °C isotherm, retention times t_R(SM) = 13.5 min, t_R(major) = 22.2 min, t_R(minor) = 23.9 min. Analytical data are in agreement with literature data.[S1,2,5] The absolute configuration was determined to be (*R*) by comparison with literature data.[S1]

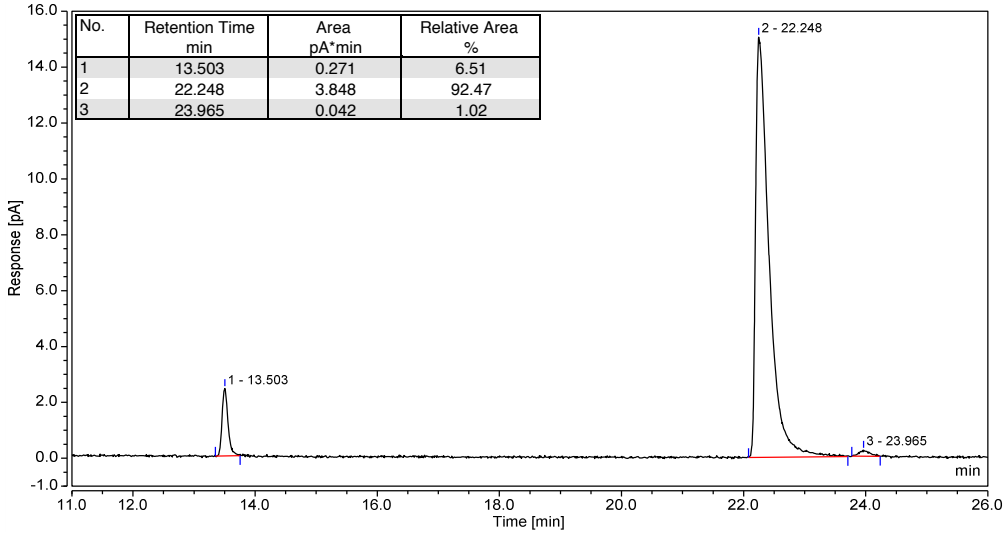


Figure S42: GC trace of enantioenriched (*R*)-**11a** (obtained by general procedure **A** using **3a**).

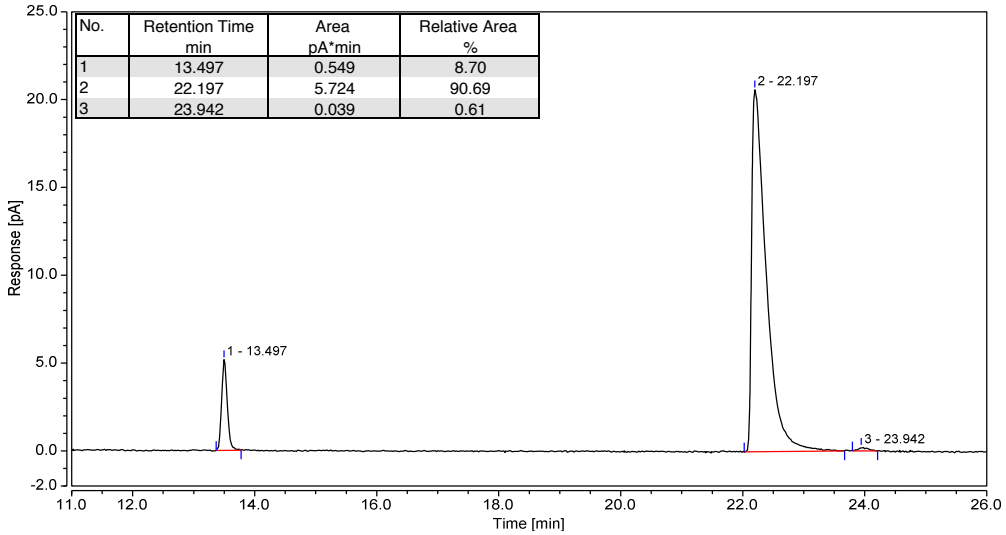
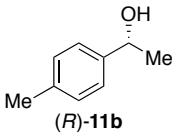


Figure S43: GC trace of enantioenriched (*R*)-**11a** (obtained by general procedure **B** using **3b**).



(*R*)-**11b**

Synthesis of (*R*)-1-(*p*-Tolyl)ethan-1-ol, (*R*)-11b. The synthesis of racemic **11b** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 86.0% yield and with 96.3% ee following general procedure **A** using catalyst **3a** (reaction time: 0.50 h). **GC**: *β*-DEX column, 110 °C isotherm, retention times t_R(SM) = 16.9 min, t_R(major) = 21.5 min, t_R(minor) = 23.2 min. This compound was obtained in 86.9% yield and with 98.2% ee following general procedure **B** using catalyst **3b** (reaction time: 1.0 h). **GC**: *β*-DEX column, 110 °C isotherm, retention times t_R(SM) = 16.9 min, t_R(major) = 21.5 min, t_R(minor) = 23.2 min. Analytical data are in agreement with literature data.[S2,5] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

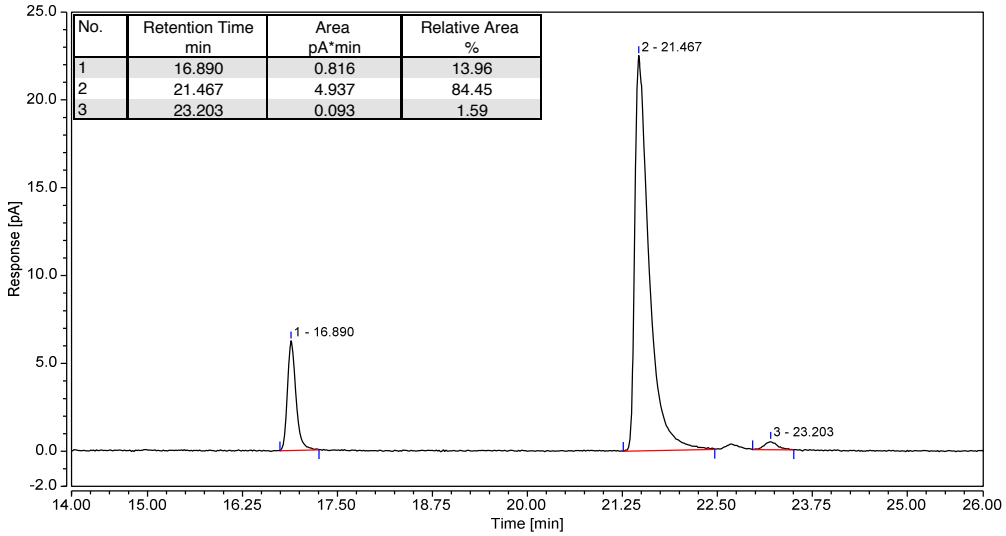


Figure S44: GC trace of enantioenriched (*R*)-**11b** (obtained by general procedure **A** using **3a**).

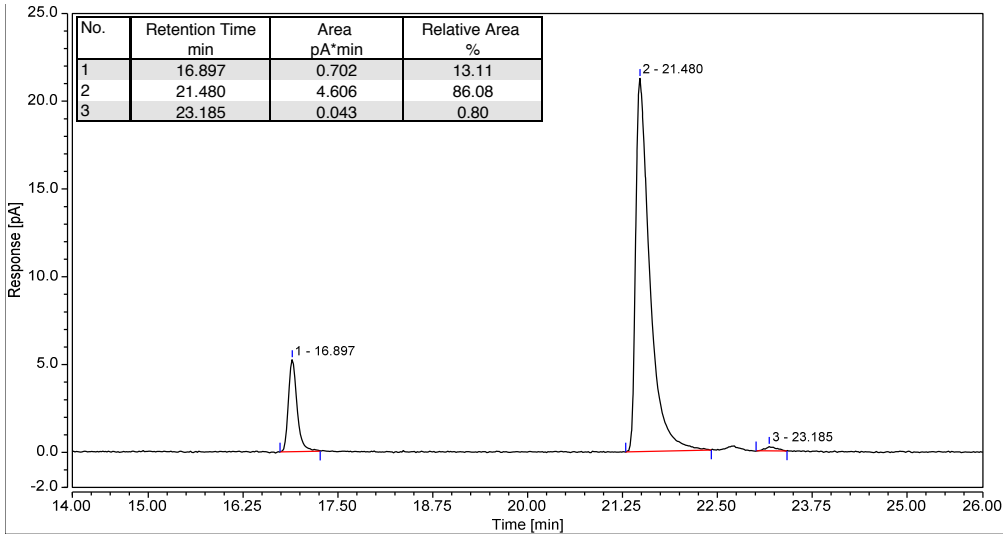
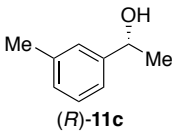


Figure S45: GC trace of enantioenriched (*R*)-**11b** (obtained by general procedure **B** using **3b**).



(*R*)-**11c**

Synthesis of (*R*)-1-(*m*-Tolyl)ethan-1-ol, (*R*)-11c. The synthesis of racemic **11c** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 89.8% yield and with 97.7% ee following general procedure **A** using catalyst **3a** (reaction time:

0.50 h). **GC**: *β*-DEX column, 110 °C isotherm, retention times t_R(SM) = 14.6 min, t_R(major) = 21.8 min, t_R(minor) = 23.3 min. This compound was obtained in 90.8% yield and with 98.0% ee following general procedure **B** using catalyst **3b** (reaction time: 1.5 h). **GC**: *β*-DEX column, 110 °C isotherm, retention times t_R(SM) = 14.6 min, t_R(major) = 22.0 min, t_R(minor) = 23.4 min. Analytical data are in agreement with literature data.[S2,5] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

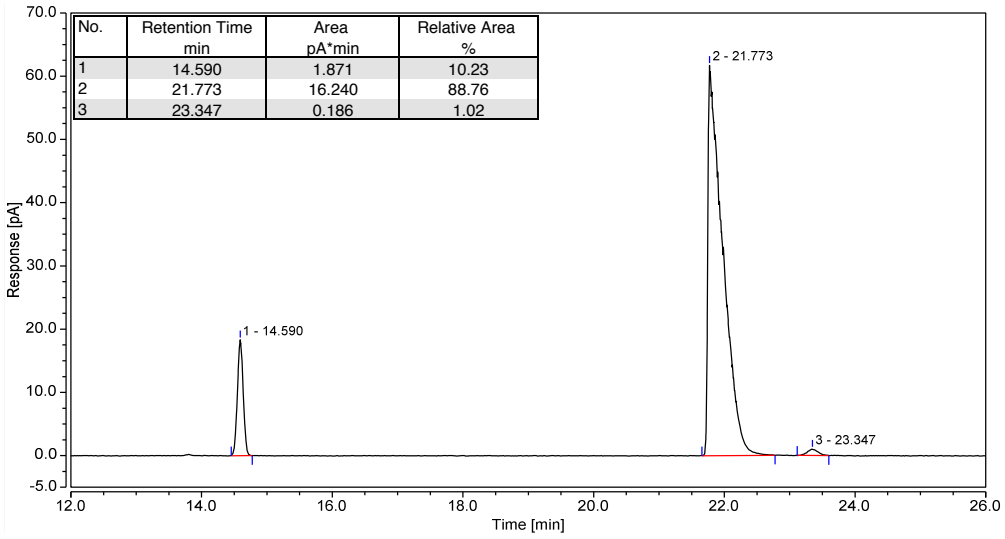


Figure S46: GC trace of enantioenriched (*R*)-**11c** (obtained by general procedure **A** using **3a**).

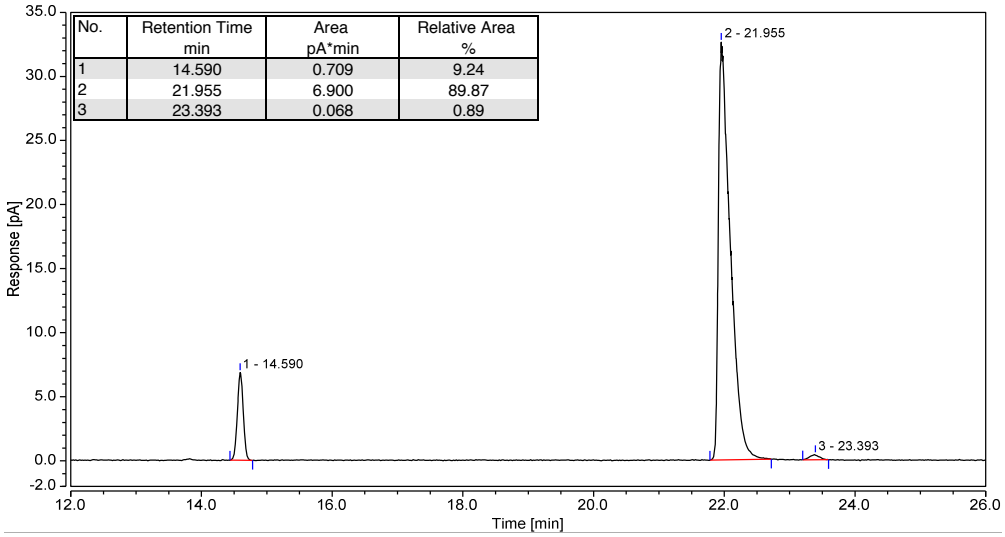
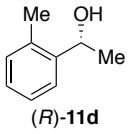


Figure S47: GC trace of enantioenriched (*R*)-**11c** (obtained by general procedure **B** using **3b**).



(*R*)-**11d**

Synthesis of (*R*)-1-(*o*-Tolyl)ethan-1-ol, (*R*)-11d. The synthesis of racemic **11d** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 81.1% yield and with 97.4% ee following general procedure **A** using catalyst **3a** (reaction time: 5.0 h). **GC**: *β*-DEX column, 130 °C isotherm, retention times t_R(SM) = 6.2 min, t_R(major) = 10.9 min, t_R(minor) = 12.0 min. This compound was obtained in 64.7% yield and with 99.3% ee following general procedure **B** using catalyst **3b** (reaction time: 5.0 h). **GC**: *β*-DEX column, 130 °C isotherm, retention times t_R(SM) = 6.2 min, t_R(major) = 11.0 min, t_R(minor) = 12.0 min. Analytical data are in agreement with literature data.[S2,5] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

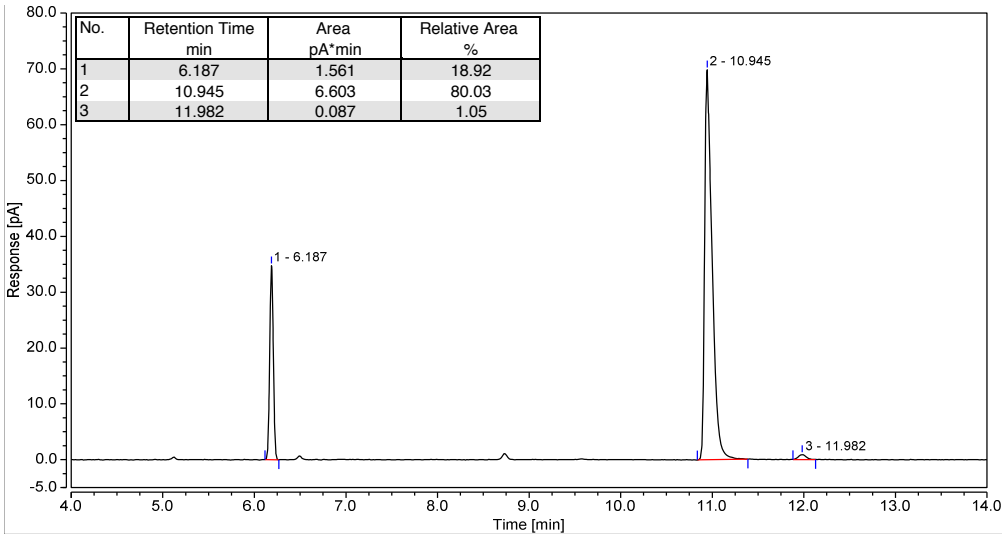


Figure S48: GC trace of enantioenriched (*R*)-**11d** (obtained by general procedure **A** using **3a**).

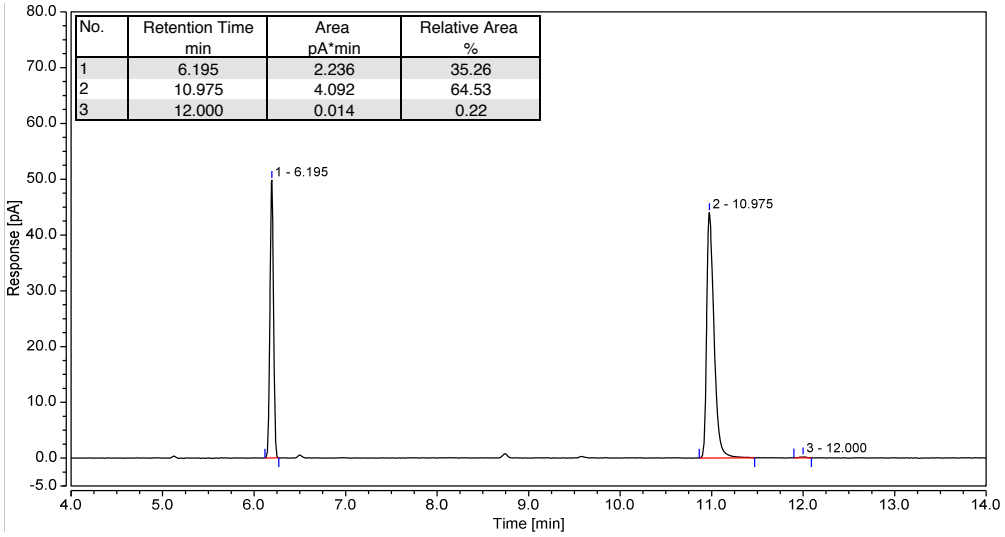
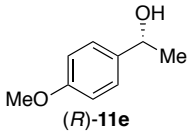


Figure S49: GC trace of enantioenriched (*R*)-**11d** (obtained by general procedure **B** using **3b**).



(*R*)-**11e**

Synthesis of (*R*)-1-(4-Methoxyphenyl)ethan-1-ol, (*R*)-11e. The synthesis of racemic **11e** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 71.6% yield and with 95.6% ee following general procedure **A** using catalyst **3a**

(reaction time: 0.50 h). **GC**: *β*-DEX column, 115 °C isotherm, retention times t_R(SM) = 44.4 min, t_R(major) = 49.7 min, t_R(minor) = 52.2 min. This compound was obtained in 70.8% yield and with 96.8% ee following general procedure **B** using catalyst **3b** (reaction time: 1.5 h). **GC**: *β*-DEX column, 115 °C isotherm, retention times t_R(SM) = 44.3 min, t_R(major) = 49.7 min, t_R(minor) = 52.1 min. Analytical data are in agreement with literature data.[S2,5] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

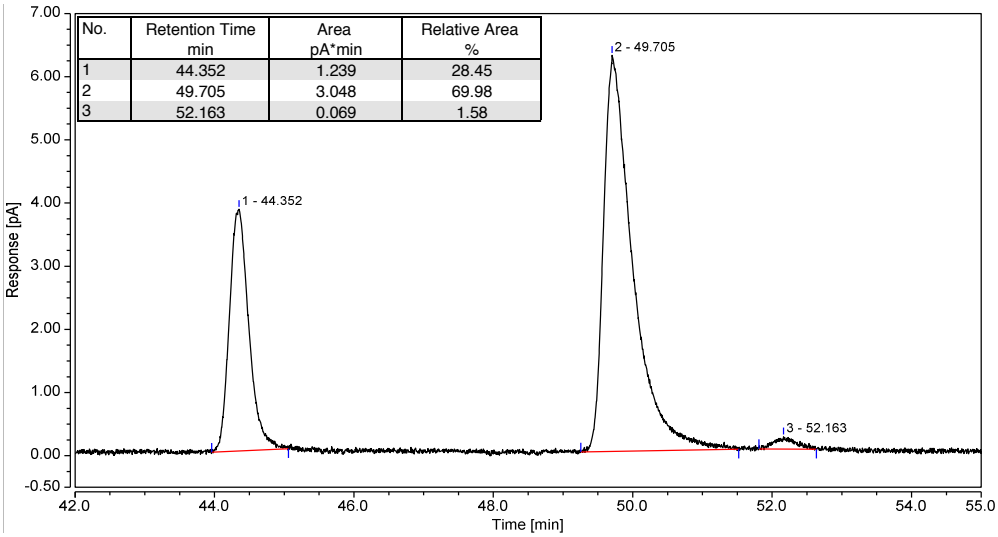


Figure S50: GC trace of enantioenriched (*R*)-**11e** (obtained by general procedure **A** using **3a**).

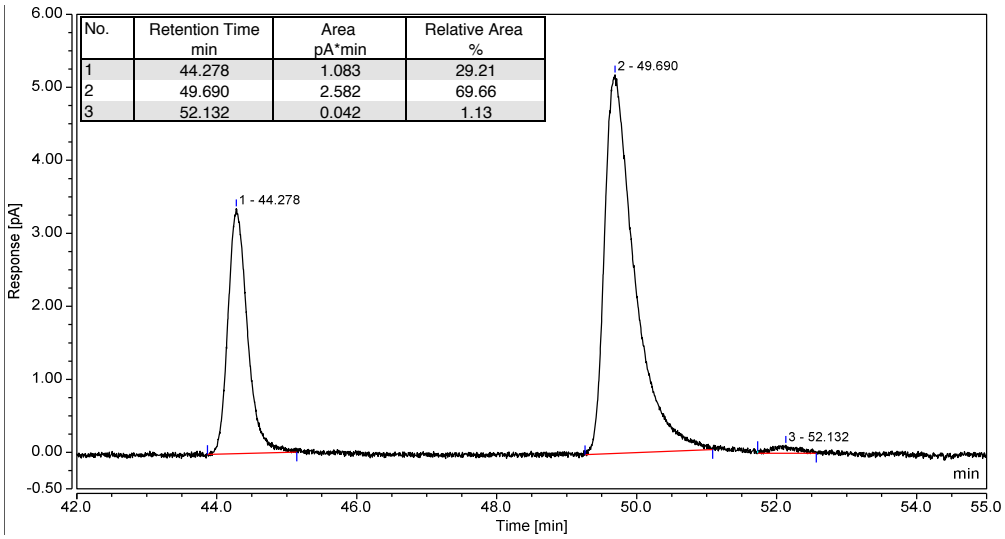
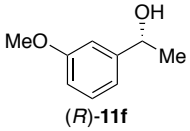


Figure S51: GC trace of enantioenriched (*R*)-**11e** (obtained by general procedure **B** using **3b**).



(*R*)-**11f**

Synthesis of (*R*)-1-(3-Methoxyphenyl)ethan-1-ol, (*R*)-11f. The synthesis of racemic **11f** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 91.9% yield and with 97.2% ee following general procedure **A** using catalyst **3a** (reaction time: 0.50 h). **GC**: *β*-DEX column, 120 °C isotherm, retention times t_R(SM) = 22.9 min, t_R(major) = 37.1 min, t_R(minor) = 39.2 min. This compound was obtained in 92.4% yield and with 98.2% ee following general procedure **B** using catalyst **3b** (reaction time: 1.0 h). **GC**: *β*-DEX column, 120 °C isotherm, retention times t_R(SM) = 22.9 min, t_R(major) = 37.3 min, t_R(minor) = 39.2 min. Analytical data are in agreement with literature data.[S2,5] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

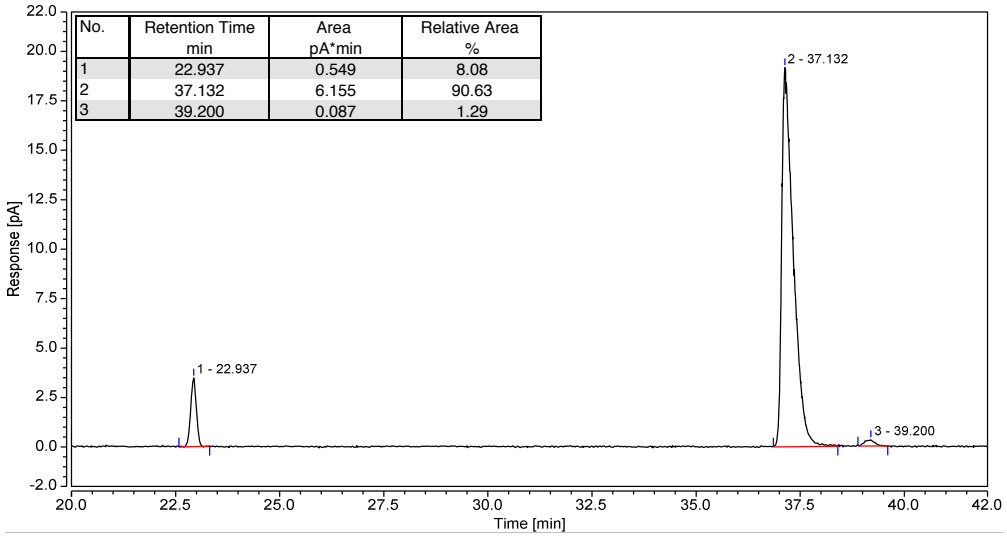


Figure S52: GC trace of enantioenriched (*R*)-**11f** (obtained by general procedure **A** using **3a**).

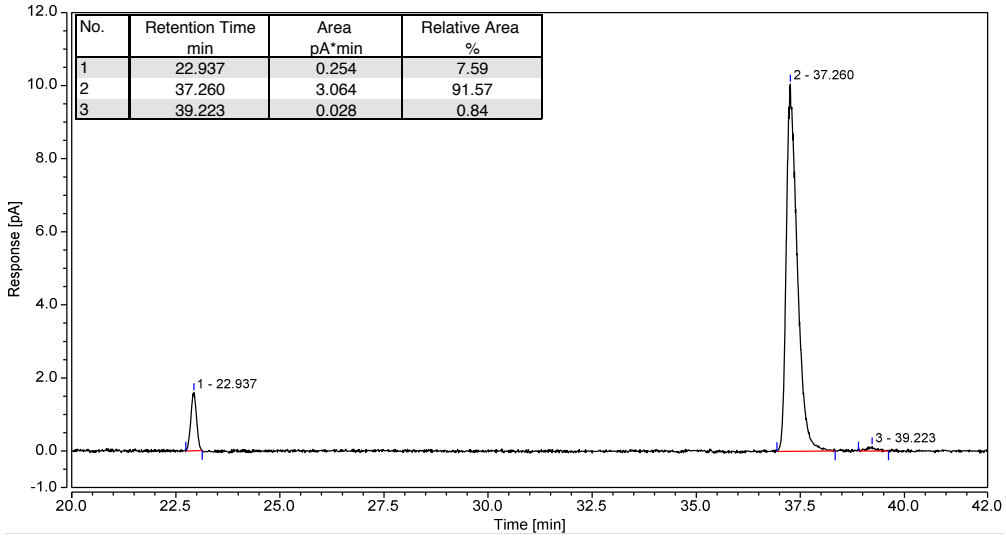
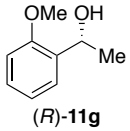


Figure S53: GC trace of enantioenriched (*R*)-**11f** (obtained by general procedure **B** using **3b**).



(*R*)-**11g**

Synthesis of (*R*)-1-(2-Methoxyphenyl)ethan-1-ol, (*R*)-11g. The synthesis of racemic **11g** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 81.8% yield and with 97.7% ee following general procedure **A** using catalyst **3a**

(reaction time: 5.0 h). **GC**: *β*-DEX column, 130 °C isotherm, retention times t_R(SM) = 14.0 min, t_R(minor) = 17.9 min, t_R(major) = 18.6 min. This compound was obtained in 44.4% yield and with 91.9% ee following general procedure **B** using catalyst **3b** (reaction time: 5.0 h). **GC**: *β*-DEX column, 130 °C isotherm, retention times t_R(SM) = 14.0 min, t_R(minor) = 17.9 min, t_R(major) = 18.6 min. Analytical data are in agreement with literature data.[S1,2,5] The absolute configuration was determined to be (*R*) by comparison with literature data.[S1]

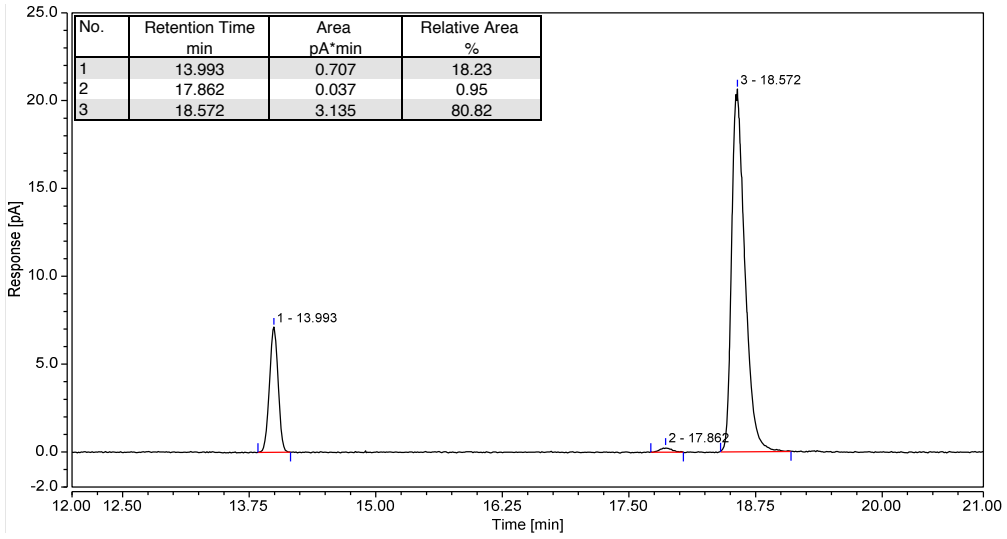


Figure S54: GC trace of enantioenriched (*R*)-**11g** (obtained by general procedure **A** using **3a**).

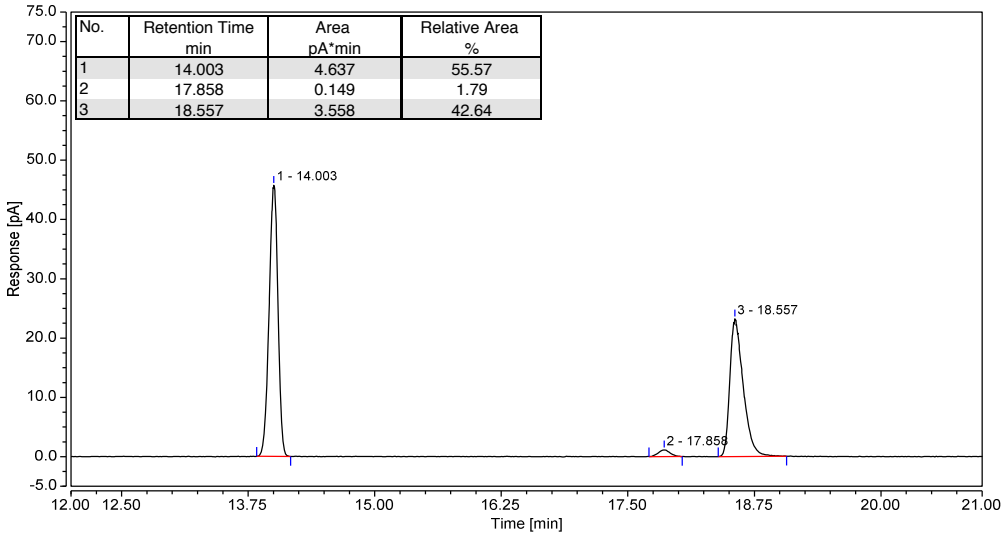
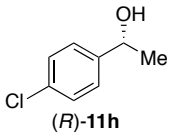


Figure S55: GC trace of enantioenriched (*R*)-**11g** (obtained by general procedure **B** using **3b**).



(*R*)-**11h**

Synthesis of (*R*)-1-(4-Chlorophenyl)ethan-1-ol, (*R*)-11h. The synthesis of racemic **11h** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 96.6% yield and with 96.1% ee following general procedure **A** using catalyst **3a** (reaction time: 0.50 h). **GC**: *β*-DEX column, 125 °C isotherm, retention times t_R(SM) = 14.0 min, t_R(major) = 24.5 min, t_R(minor) = 26.5 min. This compound was obtained in 96.9% yield and with 97.1% ee following general procedure **B** using catalyst **3b** (reaction time: 1.0 h). **GC**: *β*-DEX column, 125 °C isotherm, retention times t_R(SM) = 14.0 min, t_R(major) = 24.5 min, t_R(minor) = 26.5 min. Analytical data are in agreement with literature data.[S2,5] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

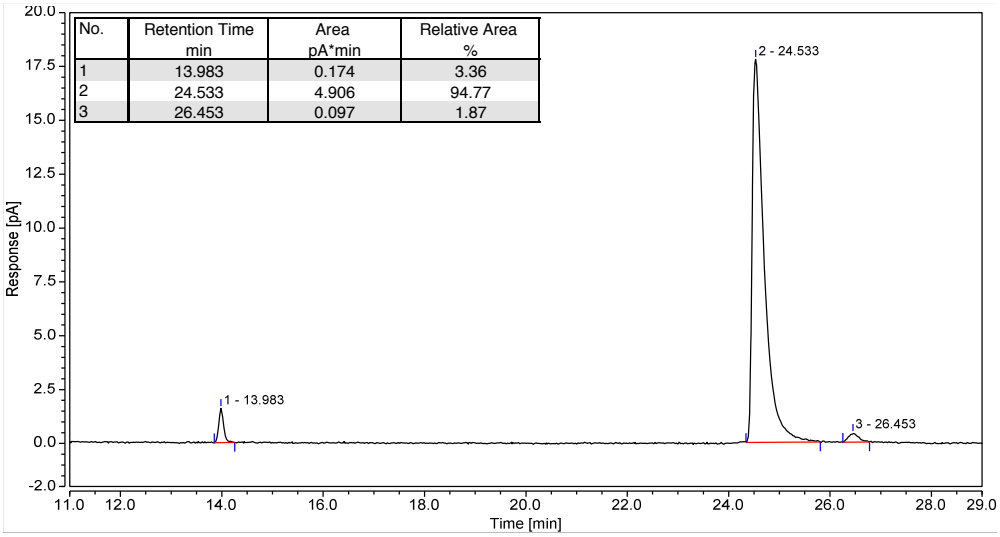


Figure S56: GC trace of enantioenriched (*R*)-**11h** (obtained by general procedure **A** using **3a**).

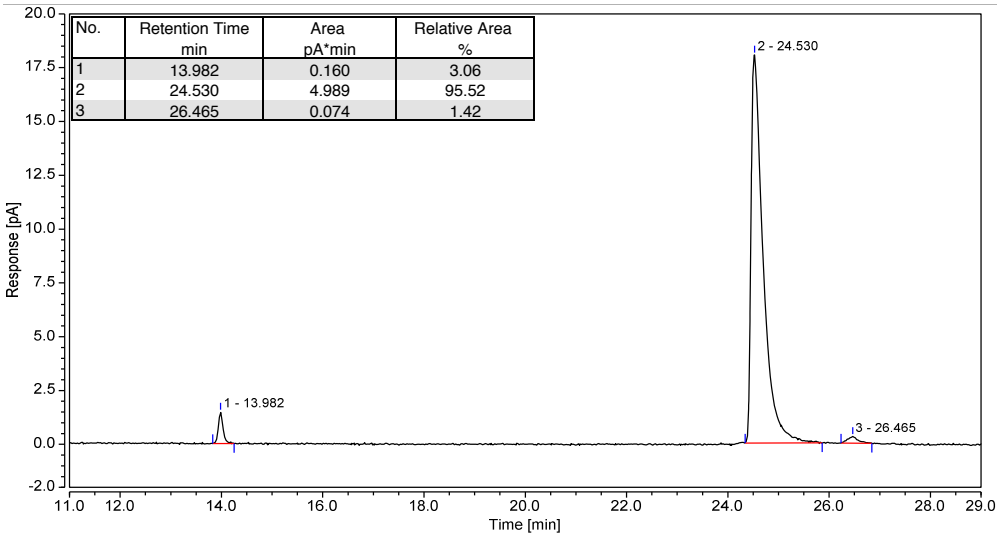
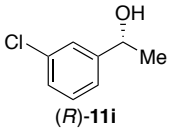


Figure S57: GC trace of enantioenriched (*R*)-**11h** (obtained by general procedure **B** using **3b**).



(*R*)-**11i**

Synthesis of (*R*)-1-(3-Chlorophenyl)ethan-1-ol, (*R*)-11i. The synthesis of racemic **11i** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 97.4% yield and with 97.1% ee following general procedure **A** using catalyst **3a**

(reaction time: 0.25 h). **GC**: *β*-DEX column, 130 °C isotherm, retention times t_R(SM) = 10.2 min, t_R(major) = 18.6 min, t_R(minor) = 19.5 min. This compound was obtained in 98.3% yield and with 96.8% ee following general procedure **B** using catalyst **3b** (reaction time: 1.0 h). **GC**: *β*-DEX column, 130 °C isotherm, retention times t_R(SM) = 10.2 min, t_R(major) = 18.5 min, t_R(minor) = 19.5 min. Analytical data are in agreement with literature data.[S2,5] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

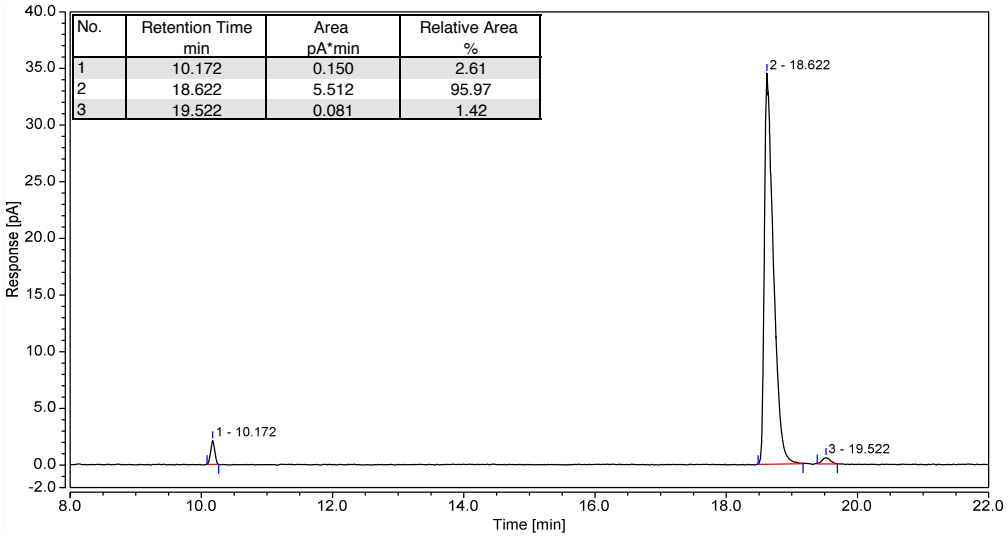


Figure S58: GC trace of enantioenriched (*R*)-**11i** (obtained by general procedure **A** using **3a**).

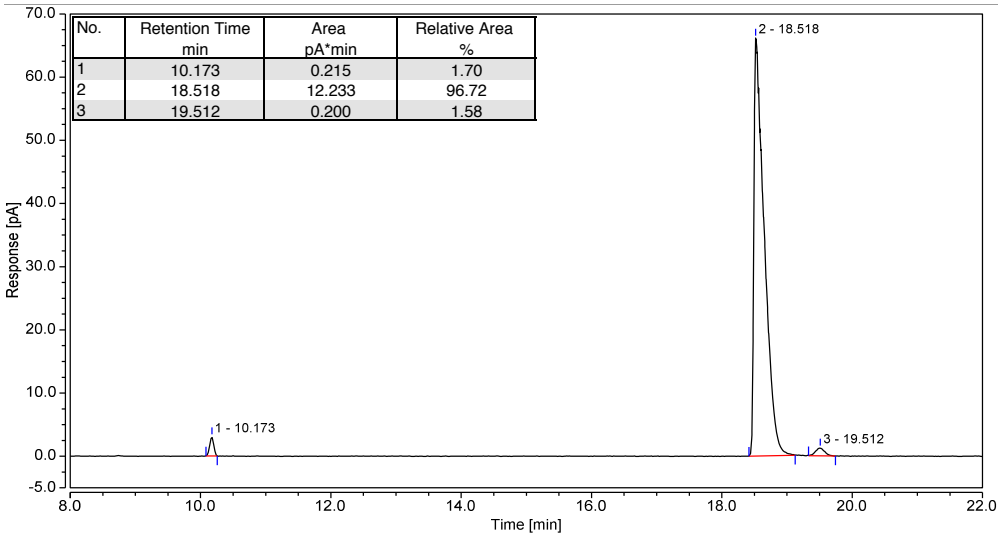
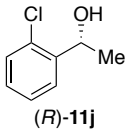


Figure S59: GC trace of enantioenriched (*R*)-**11i** (obtained by general procedure **B** using **3b**).



(*R*)-**11j**

Synthesis of (*R*)-1-(2-Chlorophenyl)ethan-1-ol, (*R*)-11j. The synthesis of racemic **11j** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 97.2% yield and with 96.7% ee following general procedure **A** using catalyst **3a** (reaction time: 5.0 h). **GC**: *β*-DEX column, 130 °C isotherm, retention times t_R(SM) = 8.7 min, t_R(major) = 16.1 min, t_R(minor) = 18.9 min. This compound was obtained in 76.7% yield and with 97.3% ee following general procedure **B** using catalyst **3b** (reaction time: 5.0 h). **GC**: *β*-DEX column, 130 °C isotherm, retention times t_R(SM) = 8.7 min, t_R(major) = 16.2 min, t_R(minor) = 18.9 min. Analytical data are in agreement with literature data.[S1,2,5] The absolute configuration was determined to be (*R*) by comparison with literature data.[S1]

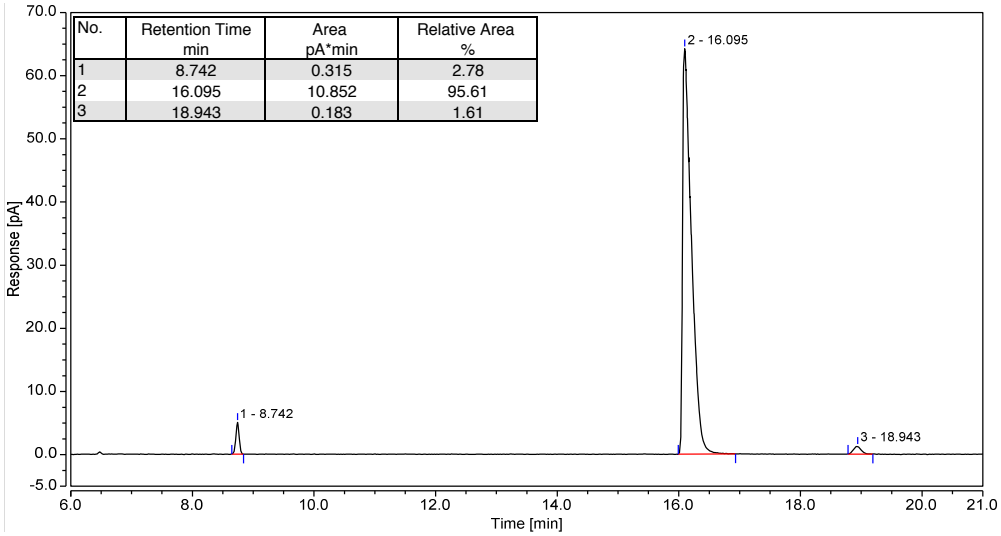


Figure S60: GC trace of enantioenriched (*R*)-**11j** (obtained by general procedure **A** using **3a**).

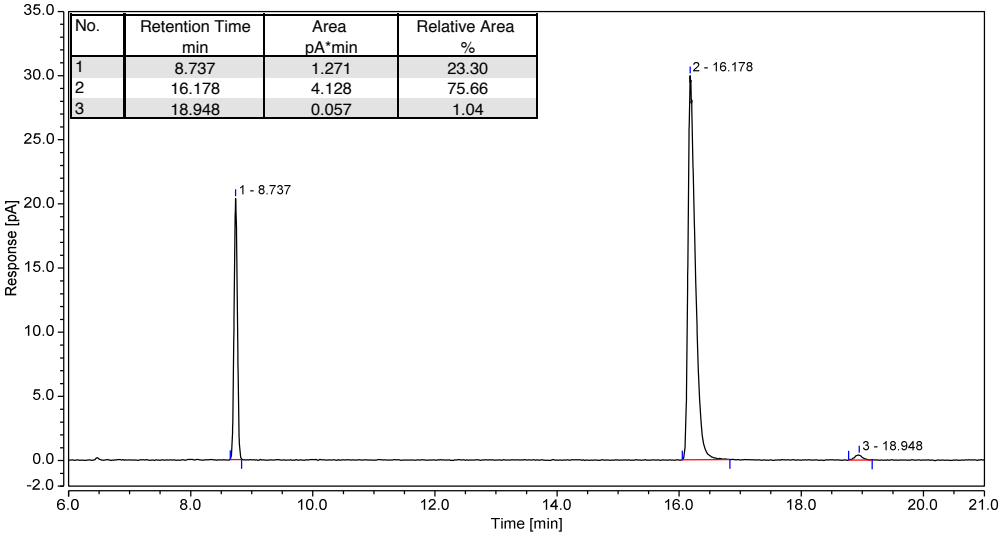
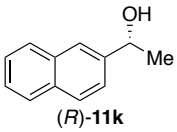


Figure S61: GC trace of enantioenriched (*R*)-**11j** (obtained by general procedure **B** using **3b**).



(*R*)-**11k**

Synthesis of (*R*)-1-(Naphthalen-2-yl)ethan-1-ol, (*R*)-11k. The synthesis of racemic **11k** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 92.8% yield and with 93.4% ee following general procedure **A** using catalyst **3a**

(reaction time: 0.50 h). **GC**: *β*-DEX column, 140 °C isotherm, retention times t_R(SM) = 52.5 min, t_R(major) = 71.3 min, t_R(minor) = 74.1 min. This compound was obtained in 91.8% yield and with 98.1% ee following general procedure **B** using catalyst **3b** (reaction time: 1.0 h). **GC**: *β*-DEX column, 140 °C isotherm, retention times t_R(SM) = 52.5 min, t_R(major) = 71.5 min, t_R(minor) = 74.1 min. Analytical data are in agreement with literature data.[S2,5] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

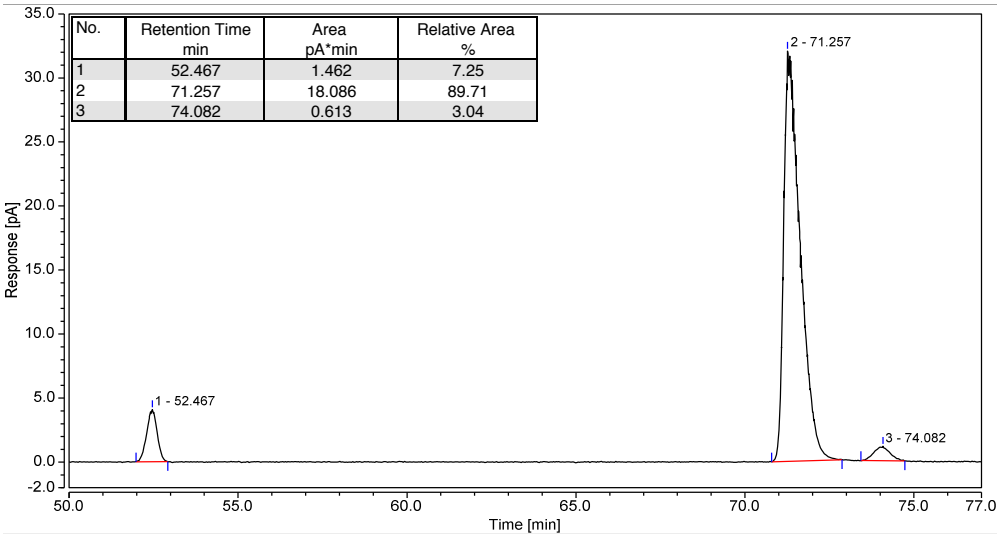


Figure S62: GC trace of enantioenriched (*R*)-**11k** (obtained by general procedure **A** using **3a**).

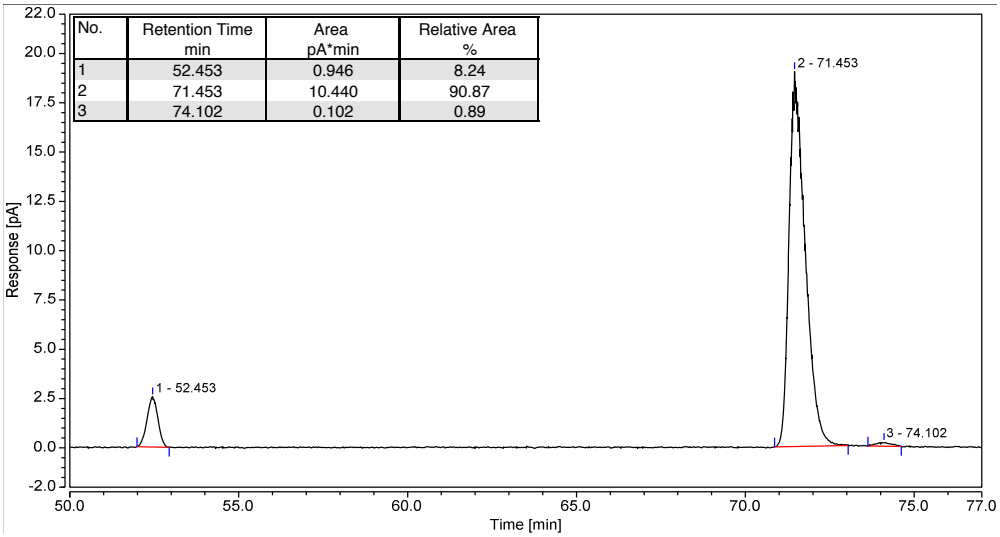
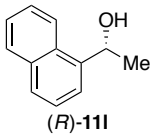


Figure S63: GC trace of enantioenriched (*R*)-**11k** (obtained by general procedure **B** using **3b**).



(*R*)-**11l**

Synthesis of (*R*)-1-(Naphthalen-1-yl)ethan-1-ol, (*R*)-11l. The synthesis of racemic **11l** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 96.3% yield and with 97.7% ee following general procedure **A** using catalyst **3a** (reaction time: 4.0 h). **GC**: *β*-DEX column, 165 °C isotherm, retention times t_R(SM) = 16.5 min, t_R(minor) = 24.0 min, t_R(major) = 24.6 min. This compound was obtained in 89.7% yield and with 99.4% ee following general procedure **B** using catalyst **3b** (reaction time: 5.0 h). **GC**: *β*-DEX column, 165 °C isotherm, retention times t_R(SM) = 16.5 min, t_R(minor) = 24.1 min, t_R(major) = 24.6 min. Analytical data are in agreement with literature data.[S1,2,5] The absolute configuration was determined to be (*R*) by comparison with literature data.[S1]

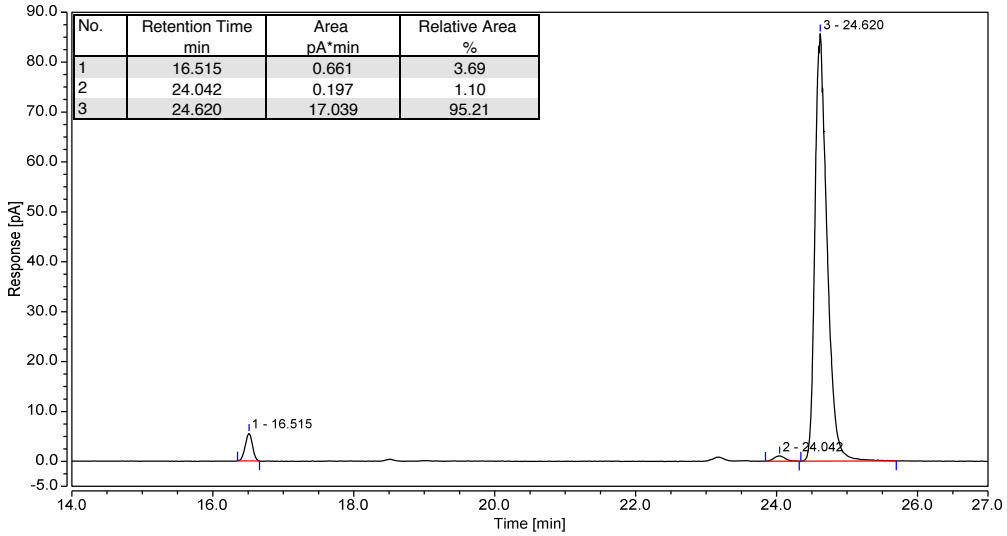


Figure S64: GC trace of enantioenriched (*R*)-**11l** (obtained by general procedure **A** using **3a**).

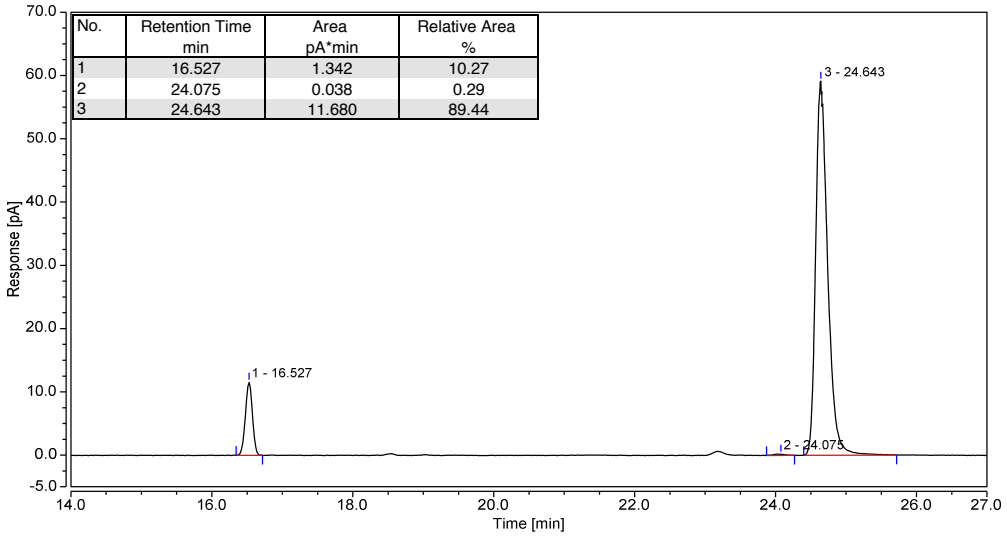
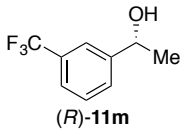


Figure S65: GC trace of enantioenriched (*R*)-**11l** (obtained by general procedure **B** using **3b**).



(*R*)-**11m**

Synthesis of (*R*)-1-(3-(Trifluoromethyl)phenyl)ethan-1-ol, (*R*)-11m. The synthesis of racemic **11m** and its spectroscopic data has previously been reported.[S2] This compound was obtained in 99.1% yield and with 98.4% ee following general procedure **A** using

catalyst **3a** (reaction time: 0.50 h). **GC**: *β*-DEX column, 90 °C isotherm, retention times t_R(SM) = 13.5 min, t_R(major) = 42.4 min, t_R(minor) = 46.9 min. This compound was obtained in 98.9% yield and with 97.8% ee following general procedure **B** using catalyst **3b** (reaction time: 2.0 h). **GC**: *β*-DEX column, 90 °C isotherm, retention times t_R(SM) = 13.5 min, t_R(major) = 41.9 min, t_R(minor) = 47.0 min. Analytical data are in agreement with literature data.[S1,2] The absolute configuration was determined to be (*R*) by comparison with literature data.[S1]

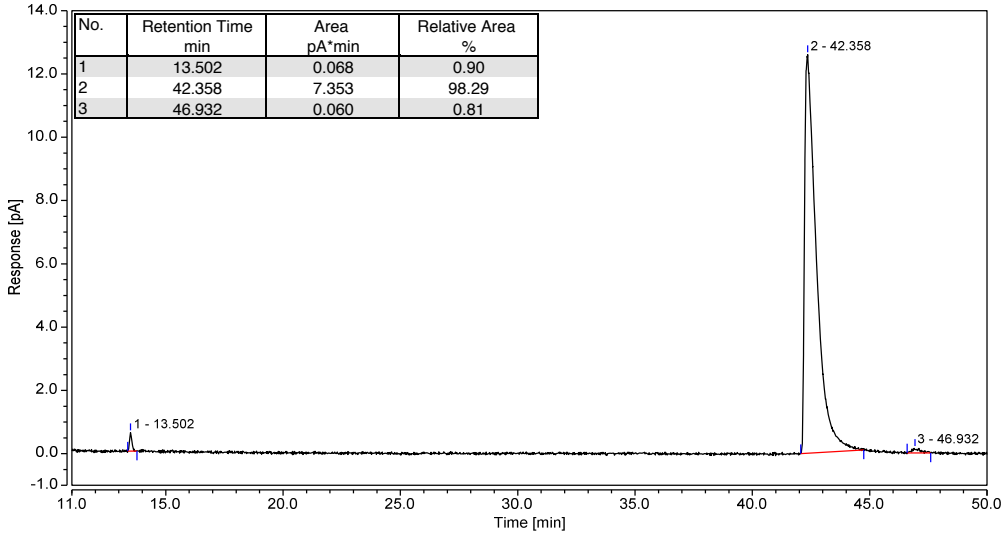


Figure S66: GC trace of enantioenriched (*R*)-**11m** (obtained by general procedure **A** using **3a**).

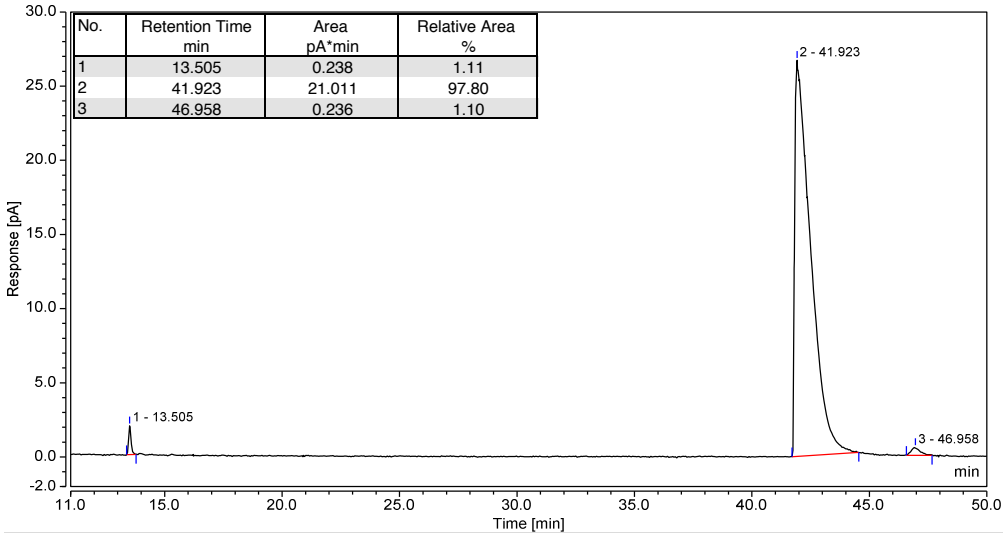
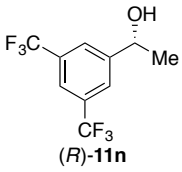


Figure S67: GC trace of enantioenriched (*R*)-**11m** (obtained by general procedure **B** using **3b**).



(*R*)-**11n**

Synthesis of (*R*)-1-(3,5-Bis(trifluoromethyl)phenyl)ethan-1-ol, (*R*)-11n. The synthesis of racemic **11n** and its spectroscopic data has previously been reported.[S2] This compound was obtained in 99.8% yield and with 98.6% ee following general procedure **A** using catalyst **3a** (reaction time: 0.50 h). **GC**: *β*-DEX column, 100 °C isotherm, retention times t_R(SM) = 4.0 min, t_R(minor) = 13.2 min, t_R(major) = 14.7 min. This compound was obtained in 61.3% yield and with 83.6% ee following general procedure **B** using catalyst **3b** (reaction time: 5.0 h). **GC**: *β*-DEX column, 100 °C isotherm, retention times t_R(SM) = 4.0 min, t_R(minor) = 13.2 min, t_R(minor) = 14.7 min. Analytical data are in agreement with literature data.[S1,2] The absolute configuration was determined to be (*R*) by comparison with literature data.[S1]

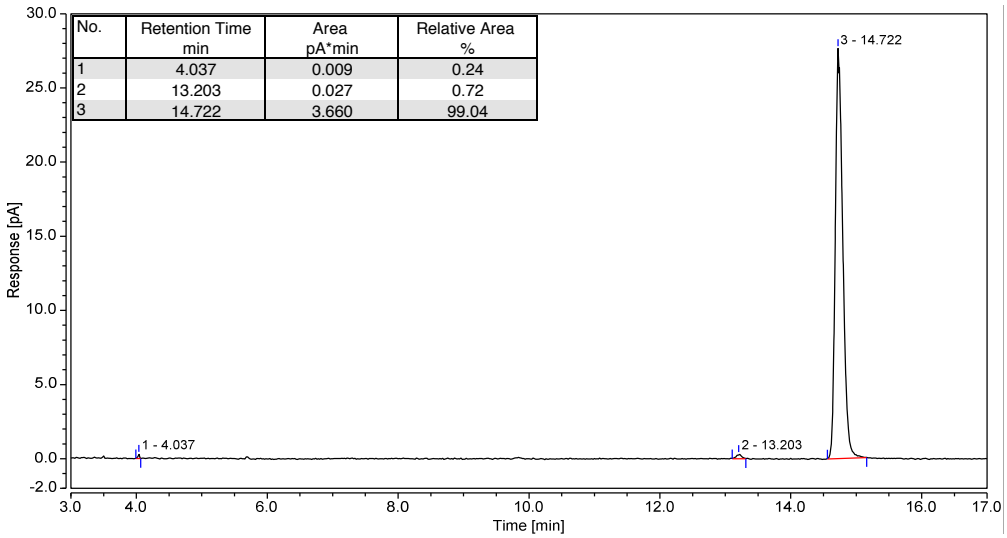


Figure S68: GC trace of enantioenriched (*R*)-**11n** (obtained by general procedure **A** using **3a**).

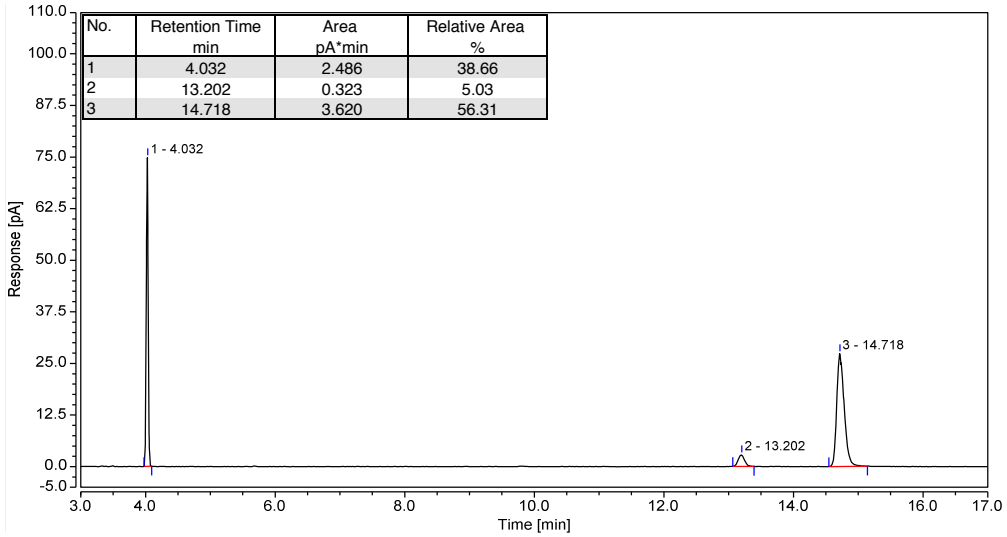
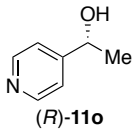


Figure S69: GC trace of enantioenriched (*R*)-**11n** (obtained by general procedure **B** using **3b**).



(*R*)-**11o**

Synthesis of (*R*)-1-(Pyridin-4-yl)ethan-1-ol, (*R*)-11o. The synthesis of racemic **11o** and its spectroscopic data has previously been reported.[S2] This compound was obtained in >99.9% yield and with 95.9% ee following general procedure **A** using catalyst **3a** (reaction time:

0.25 h). **GC**: *β*-DEX column, 120 °C isotherm, retention times t_R(SM) = 9.1 min, t_R(major) = 24.9 min, t_R(minor) = 26.2 min. This compound was obtained in 60.0% yield and with 94.7% ee following general procedure **B** using catalyst **3b** (reaction time: 5.0 h). **GC**: *β*-DEX column, 120 °C isotherm, retention times t_R(SM) = 9.1 min, t_R(major) = 24.9 min, t_R(minor) = 26.3 min. Analytical data are in agreement with literature data.[S2] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

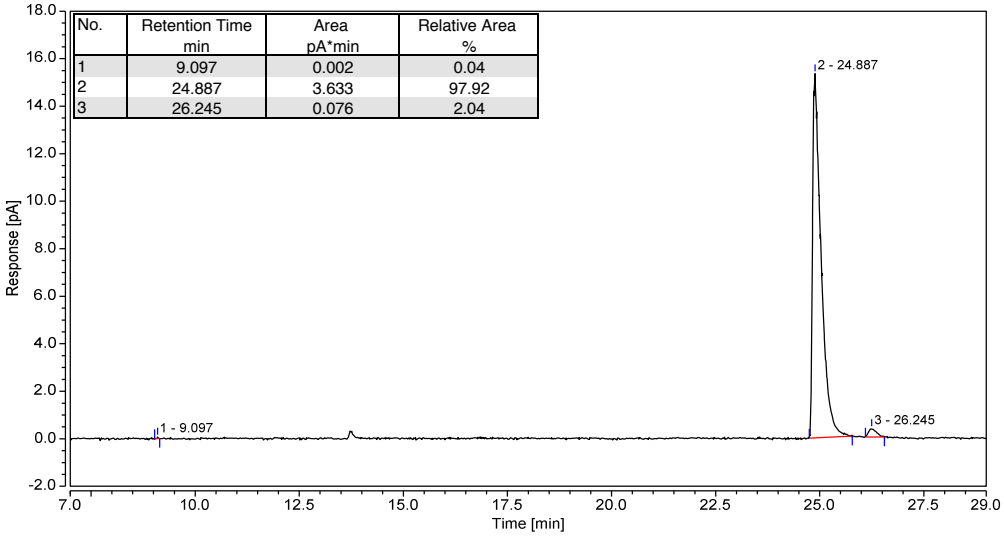


Figure S70: GC trace of enantioenriched (*R*)-**11o** (obtained by general procedure **A** using **3a**).

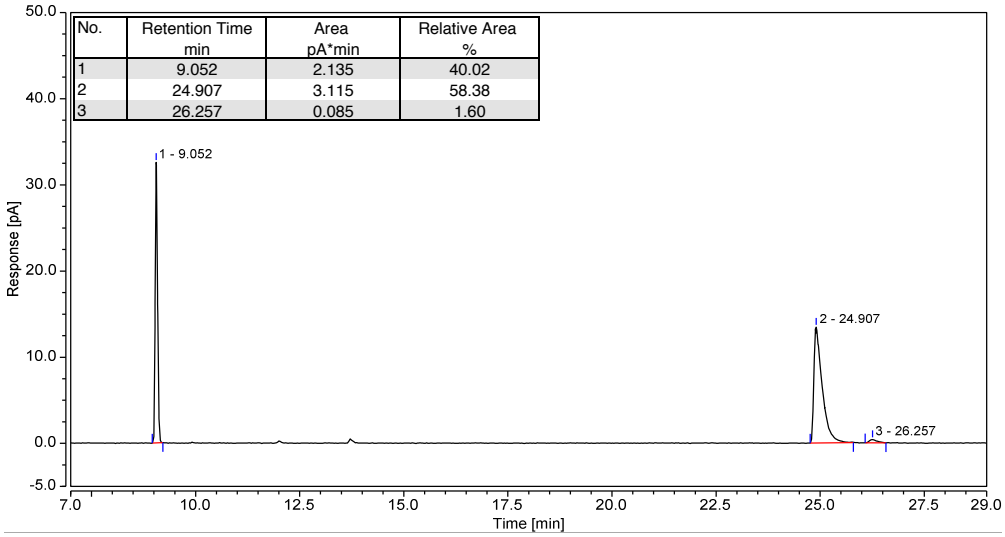
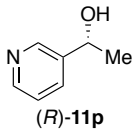


Figure S71: GC trace of enantioenriched (*R*)-**11o** (obtained by general procedure **B** using **3b**).



(*R*)-**11p**

Synthesis of (*R*)-1-(Pyridin-3-yl)ethan-1-ol, (*R*)-11p. The synthesis of racemic **11p** and its spectroscopic data has previously been reported.[S2] This compound was obtained in 99.4% yield and with 96.6% ee following general procedure **A** using catalyst **3a** (reaction time: 0.50 h). **GC**: *β*-DEX column, 120 °C isotherm, retention times t_R(SM) = 9.9 min, t_R(major) = 22.5 min, t_R(minor) = 23.8 min. This compound was obtained in 99.4% yield and with 92.8% ee following general procedure **B** using catalyst **3b** (reaction time: 2.0 h). **GC**: *β*-DEX column, 120 °C isotherm, retention times t_R(SM) = 9.9 min, t_R(major) = 22.4 min, t_R(minor) = 23.8 min. Analytical data are in agreement with literature data.[S2] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

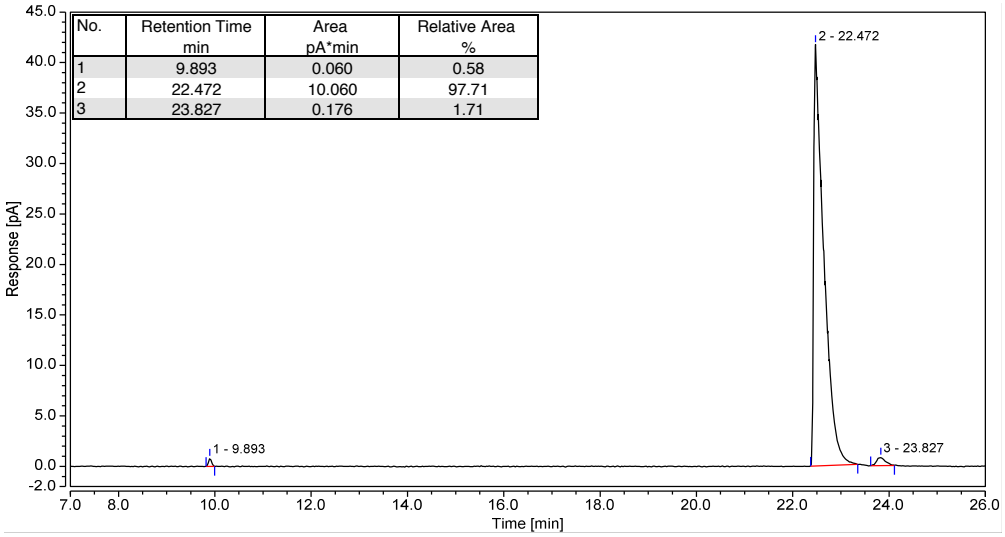


Figure S72: GC trace of enantioenriched (*R*)-**11p** (obtained by general procedure **A** using **3a**).

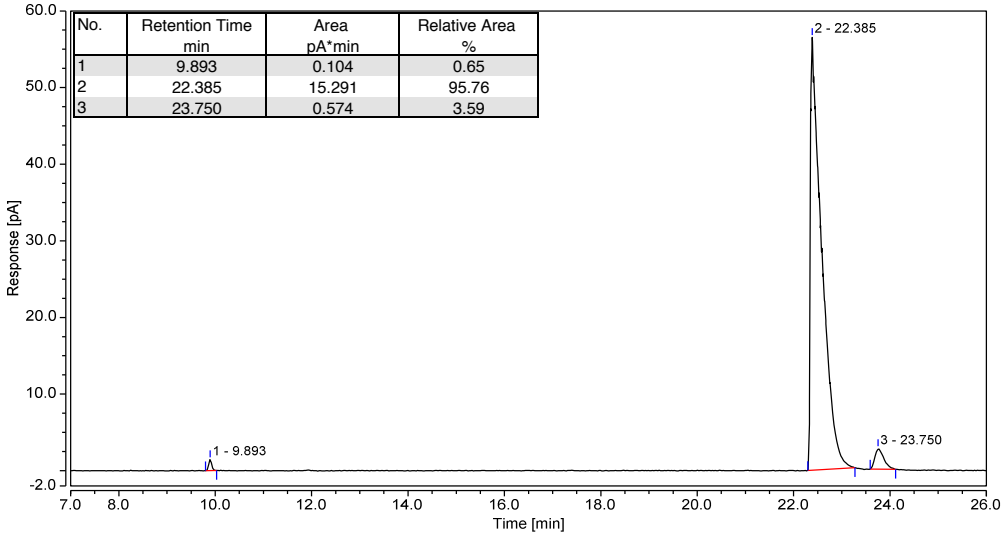
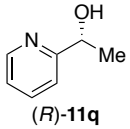


Figure S73: GC trace of enantioenriched (*R*)-**11p** (obtained by general procedure **B** using **3b**).



(*R*)-**11q**

Synthesis of (*R*)-1-(Pyridin-2-yl)ethan-1-ol, (*R*)-11q. The synthesis of racemic **11q** and its spectroscopic data has previously been reported.[S1,2] This compound was obtained in 99.6% yield (determined by GC) and with 98.1% ee (determined by HPLC) following general

procedure **A** using catalyst **3a** (reaction time: 0.50 h). **GC**: *β*-DEX column, 100 °C isotherm, retention times t_R(SM) = 10.5 min, t_R(major) = 18.6 min, t_R(minor) = 19.2 min. The peaks are not baseline separated. **HPLC**: OD-H (hexane : 2-propanol = 99 : 1, flow rate 0.8 mL/min, λ = 254 nm), retention times t_R(major) = 23.8 min, t_R(minor) = 27.2 min. This compound was obtained in 99.4% yield (determined by GC) and with 87.0% ee (determined by HPLC) following general procedure **B** using catalyst **3b** (reaction time: 1.5 h). **GC**: *β*-DEX column, 100 °C isotherm, retention times t_R(SM) = 10.5 min, t_R(major) = 18.6 min, t_R(minor) = 19.2 min. The peaks are not baseline separated. **HPLC**: OD-H (hexane : 2-propanol = 99 : 1, flow rate 0.8 mL/min, λ = 254 nm), retention times t_R(major) = 23.9 min, t_R(minor) = 27.2 min. Analytical data are in agreement with literature data.[S1,2] The absolute configuration was determined to be (*R*) by comparison with literature data.[S1]

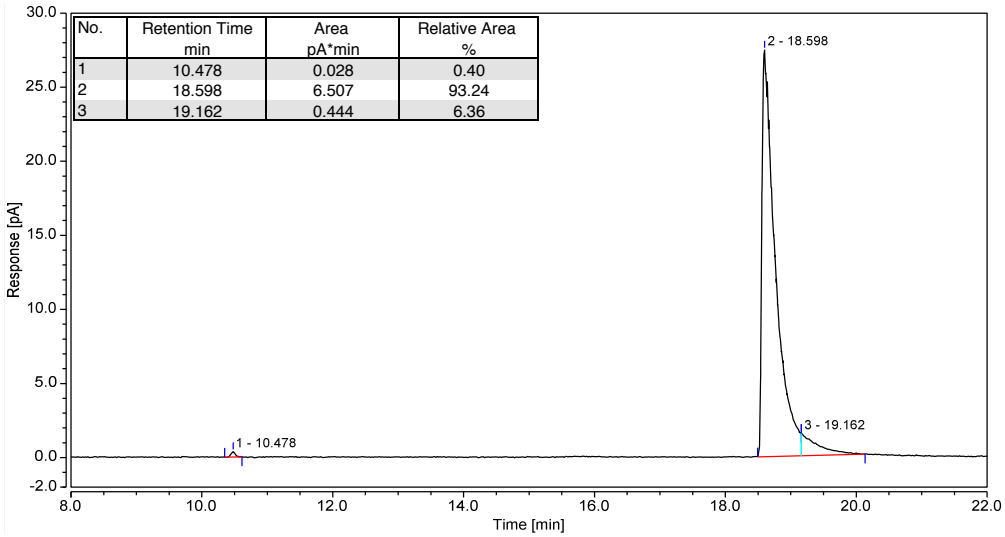


Figure S74: GC trace of enantioenriched (*R*)-**11q** (obtained by general procedure **A** using **3a**).

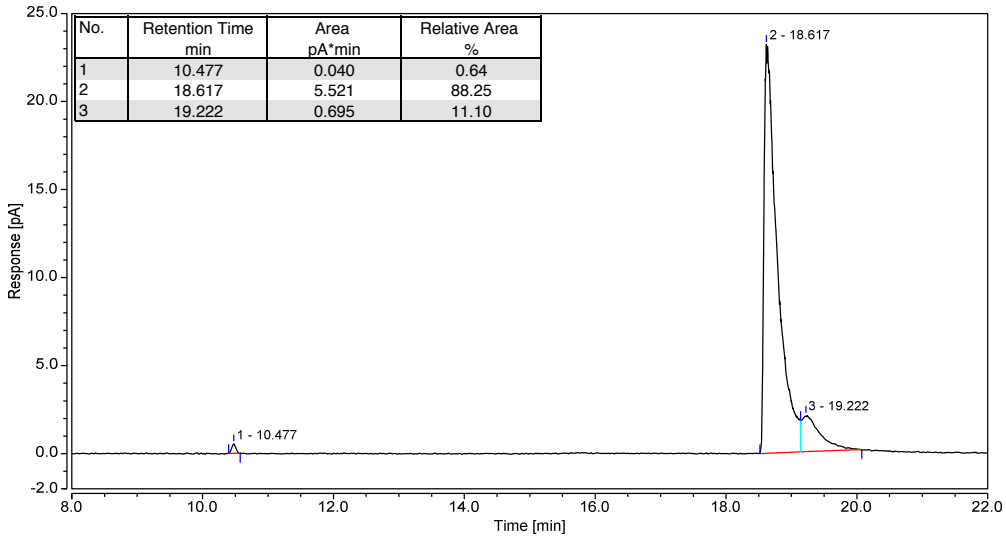


Figure S75: GC trace of enantioenriched (*R*)-**11q** (obtained by general procedure **B** using **3b**).

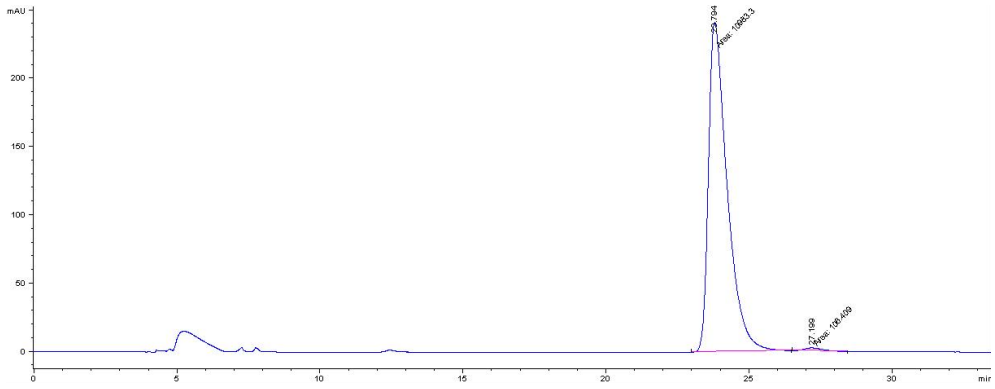


Figure S76: HPLC trace of enantioenriched (*R*)-**11q** (obtained by general procedure **A** using **3a**).

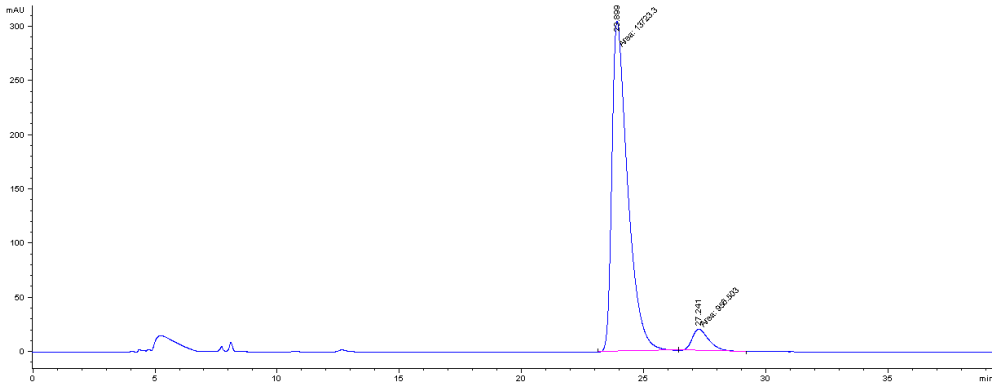
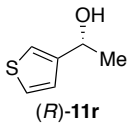


Figure S77: HPLC trace of enantioenriched (*R*)-**11q** (obtained by general procedure **B** using **3b**).



(*R*)-**11r**

Synthesis of (*R*)-1-(Thiophen-3-yl)ethan-1-ol, (*R*)-11r. The synthesis of racemic **11r** and its spectroscopic data has previously been reported.[S2] This compound was obtained in 81.1% yield and with 97.7% ee following general procedure **A** using catalyst **3a** (reaction time: 0.50 h). **GC**: *β*-DEX column, 100 °C isotherm, retention times t_R(SM) = 17.7 min, t_R(major) = 26.7 min, t_R(minor) = 28.6 min. This compound was obtained in 82.9% yield and with 96.9% ee following general procedure **B** using catalyst **3b** (reaction time: 1.0 h). **GC**: *β*-DEX column, 100 °C isotherm, retention times t_R(SM) = 17.7 min, t_R(major) = 26.7 min, t_R(minor) = 28.6 min. Analytical data are in agreement with literature data.[S2] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

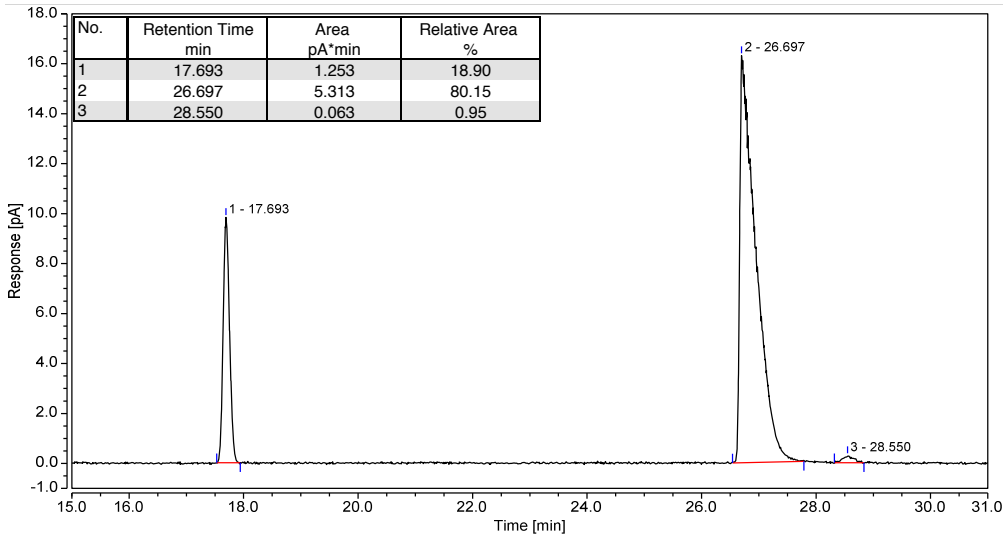


Figure S78: GC trace of enantioenriched (*R*)-**11r** (obtained by general procedure **A** using **3a**).

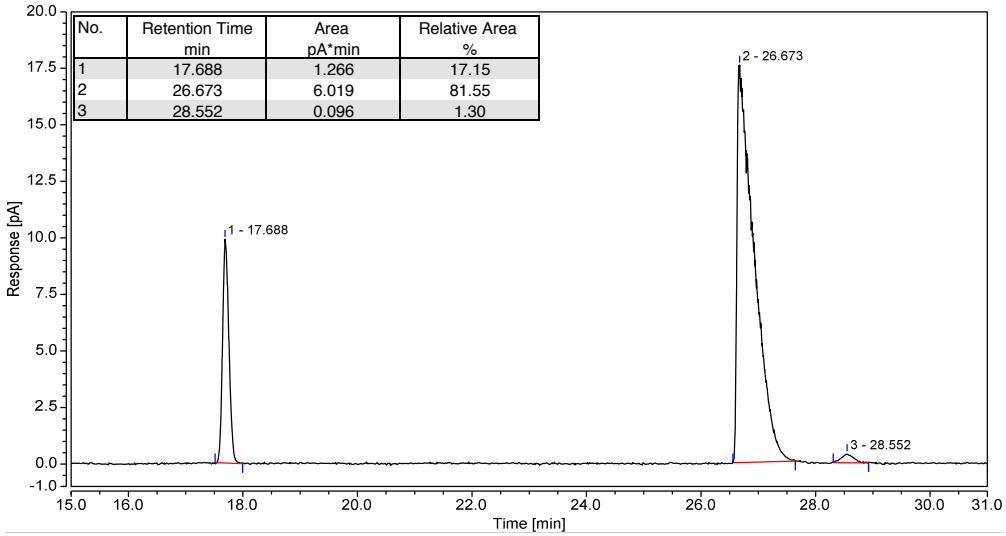
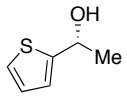


Figure S79: GC trace of enantioenriched (*R*)-**11r** (obtained by general procedure **B** using **3b**).



(*R*)-**11s**

Synthesis of (*R*)-1-(Thiophen-2-yl)ethan-1-ol, (*R*)-11s. The synthesis of racemic **11s** and its spectroscopic data has previously been reported.[S2] This compound was obtained in 65.5% yield and with 97.1% ee following general procedure **A** using catalyst **3a** (reaction time: 0.25 h). **GC**: *β*-DEX column, 110 °C isotherm, retention times t_R(SM) = 11.7 min, t_R(major) = 14.9 min, t_R(minor) = 15.9 min. This compound was obtained in 70.9% yield and with 95.8% ee following general procedure **B** using catalyst **3b** (reaction time: 1.0 h). **GC**: *β*-DEX column, 110 °C isotherm, retention times t_R(SM) = 11.7 min, t_R(major) = 15.0 min, t_R(minor) = 15.9 min. Analytical data are in agreement with literature data.[S2] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

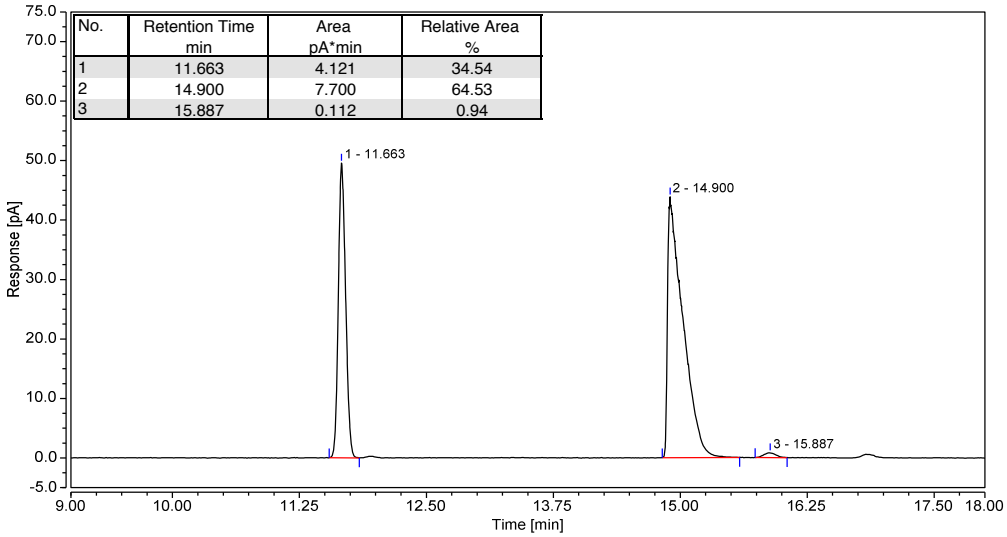


Figure S80: GC trace of enantioenriched (*R*)-**11s** (obtained by general procedure **A** using **3a**).

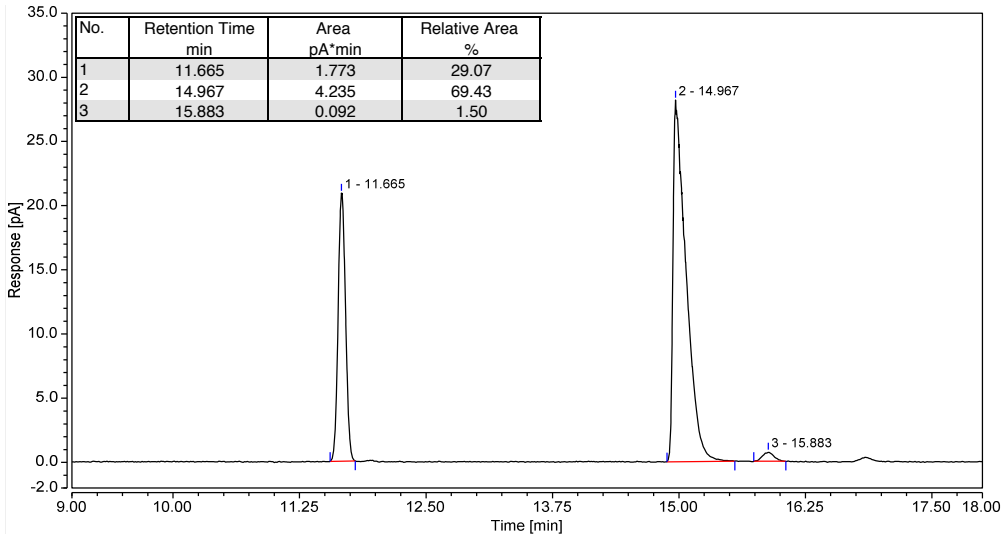
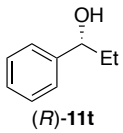


Figure S81: GC trace of enantioenriched (*R*)-**11s** (obtained by general procedure **B** using **3b**).



(*R*)-**11t**

Synthesis of (*R*)-1-Phenylpropan-1-ol, (*R*)-11t. The synthesis of racemic **11t** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 93.7% yield and with 98.9% ee following general procedure **A** using catalyst **3a** (reaction time: 0.50 h).

GC: *β*-DEX column, 110 °C isotherm, retention times t_R(SM) = 21.9 min, t_R(major) = 37.0 min, t_R(minor) = 39.4 min. This compound was obtained in 94.4% yield and with 98.9% ee following general procedure **B** using catalyst **3b** (reaction time: 1.5 h). **GC**: *β*-DEX column, 110 °C isotherm, retention times t_R(SM) = 21.9 min, t_R(major) = 37.1 min, t_R(minor) = 39.4 min. Analytical data are in agreement with literature data.[S2,5] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

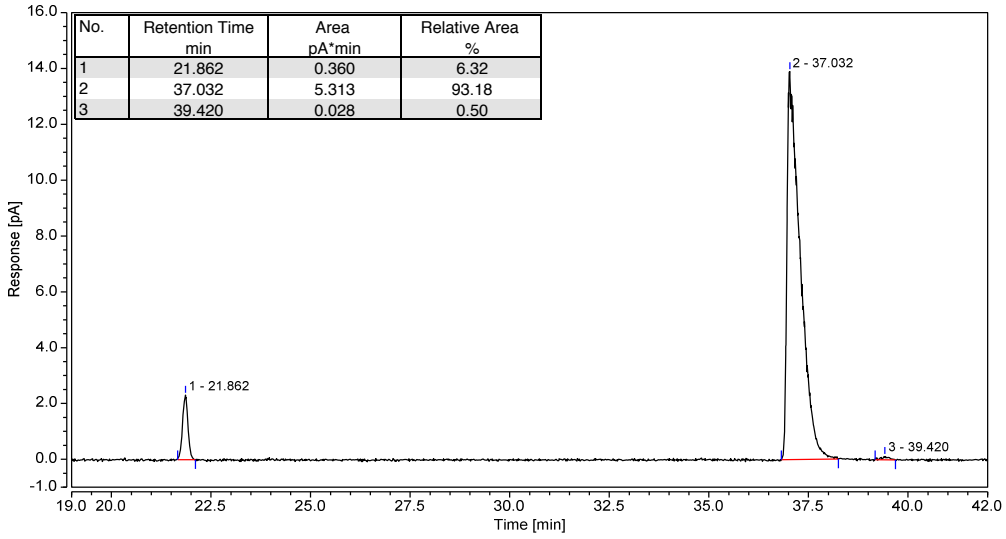


Figure S82: GC trace of enantioenriched (*R*)-**11t** (obtained by general procedure **A** using **3a**).

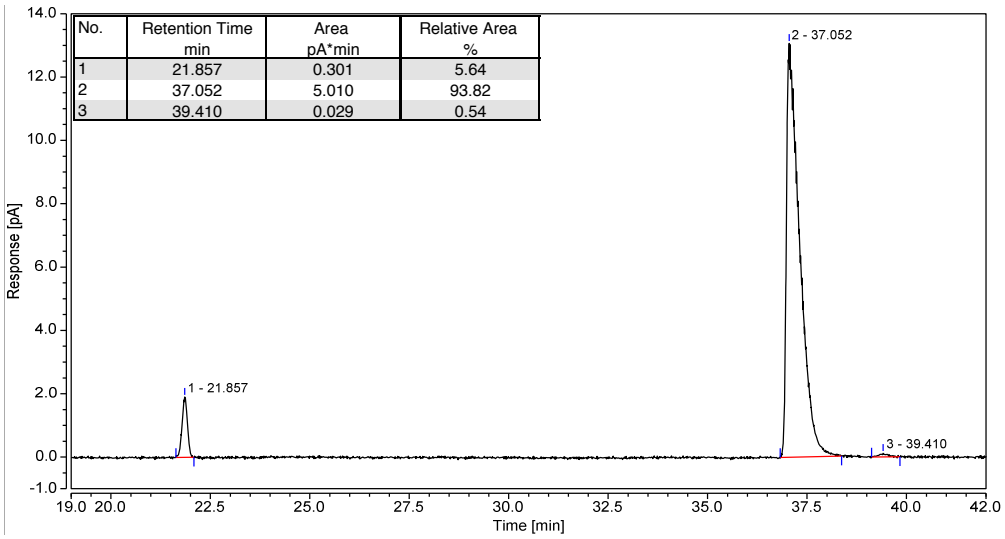
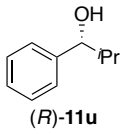


Figure S83: GC trace of enantioenriched (*R*)-**11t** (obtained by general procedure **B** using **3b**).



(*R*)-**11u**

Synthesis of (*R*)-2-Methyl-1-phenylpropan-1-ol, (*R*)-11u. The synthesis of racemic **11u** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 97.8% yield and with 99.2% ee following general procedure **A** (0.625 mmol scale; S/C/B = 250/1/10; T = 75 °C) using catalyst **3a** (reaction time: 3.0 h). **GC**: *β*-DEX column, 105 °C isotherm, retention times t_R(SM) = 19.3 min, t_R(major) = 39.3 min, t_R(minor) = 41.3 min. This compound was obtained in 97.7% yield and with 99.1% ee following general procedure **B** (0.625 mmol scale; S/C/B = 250/1/10; T = 75 °C) using catalyst **3b** (reaction time: 1.5 h). **GC**: *β*-DEX column, 105 °C isotherm, retention times t_R(SM) = 19.3 min, t_R(major) = 39.3 min, t_R(minor) = 41.2 min. Analytical data are in agreement with literature data.[S2,5] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

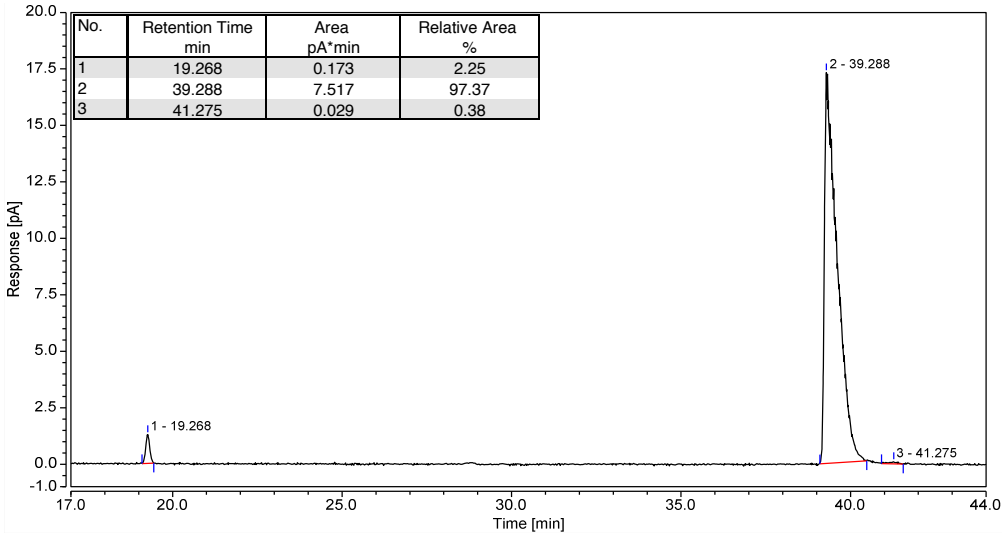


Figure S84: GC trace of enantioenriched (*R*)-**11u** (obtained by general procedure **A** using **3a**).

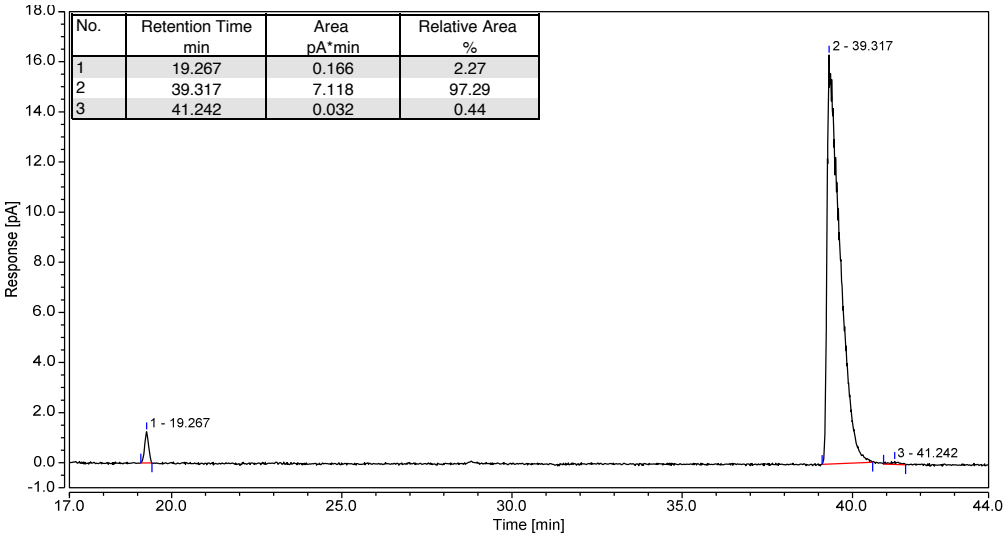
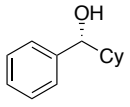


Figure S85: GC trace of enantioenriched (*R*)-**11u** (obtained by general procedure **B** using **3b**).



(*R*)-**11v**

Synthesis of (*R*)-Cyclohexyl(phenyl)methanol, (*R*)-11v. The synthesis of racemic **11v** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 97.9% yield and with 99.2% ee following general procedure **A** (0.625 mmol scale;

S/C B = 250/1/10; T = 75 °C) using catalyst **3a** (reaction time: 4.0 h). **GC**: *β*-DEX column, 130 °C isotherm, retention times t_R(SM) = 61.1 min, t_R(minor) = 95.0 min, t_R(major) = 96.0 min. This compound was obtained in 97.2% yield and with 99.6% ee following general procedure **B** (0.625 mmol scale; S/C/B = 250/1/10; T = 75 °C) using catalyst **3b** (reaction time: 1.0 h). **GC**: *β*-DEX column, 130 °C isotherm, retention times t_R(SM) = 61.0 min, t_R(minor) = 94.7 min, t_R(major) = 95.5 min. Analytical data are in agreement with literature data.[S2,5] The absolute configuration was determined to be (*R*) by comparison with literature data.[S1]

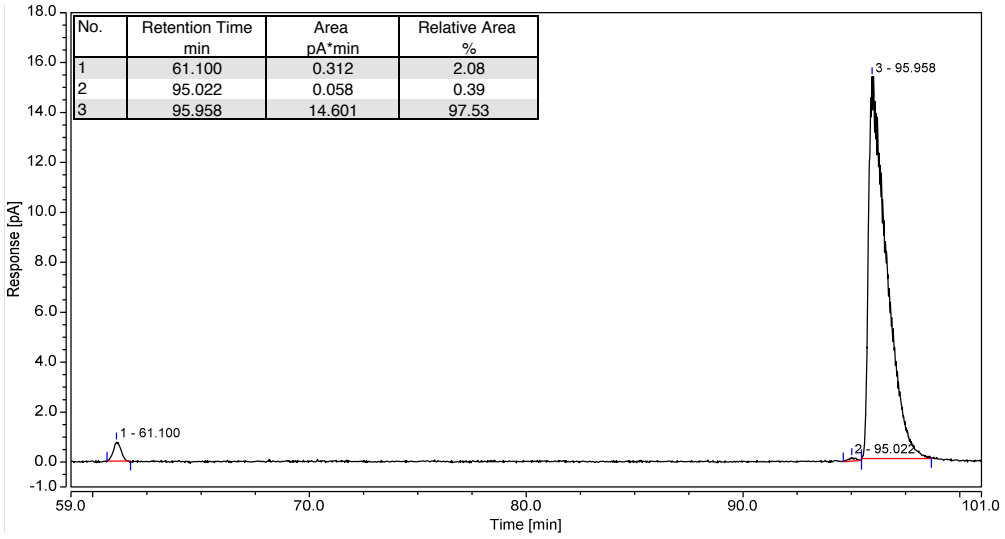


Figure S86: GC trace of enantioenriched (*R*)-**11v** (obtained by general procedure **A** using **3a**).

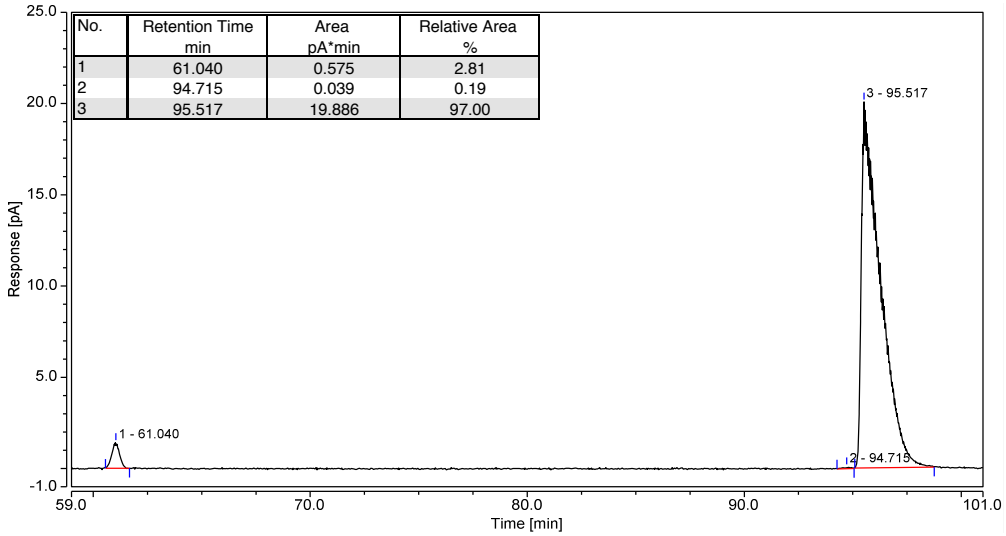
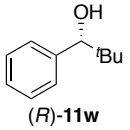


Figure S87: GC trace of enantioenriched (*R*)-**11v** (obtained by general procedure **B** using **3b**).



(*R*)-**11w**

Synthesis of (*R*)-2,2-Dimethyl-1-phenylpropan-1-ol, (*R*)-11w. The synthesis of racemic **11w** and its spectroscopic data has previously been reported.[S2,5] This compound was obtained in 41.7% yield and with 97.9% ee following general procedure **A** (0.625 mmol scale; S/C/B = 250/1/10; T = 75 °C) using catalyst **3a** (reaction time: 5.0 h). **GC**: *β*-DEX column, 110 °C isotherm, retention times t_R(SM) = 17.6 min, t_R(minor) = 43.1 min, t_R(major) = 43.7 min. This compound was obtained in 65.5% yield and with 98.7% ee following general procedure **B** (0.625 mmol scale; S/C/B = 250/1/10; T = 75 °C) using catalyst **3b** (reaction time: 5.0 h). **GC**: *β*-DEX column, 110 °C isotherm, retention times t_R(SM) = 17.6 min, t_R(minor) = 43.0 min, t_R(major) = 43.4 min. Analytical data are in agreement with literature data.[S2,5] The absolute configuration was determined to be (*R*) by comparison with literature data.[S1]

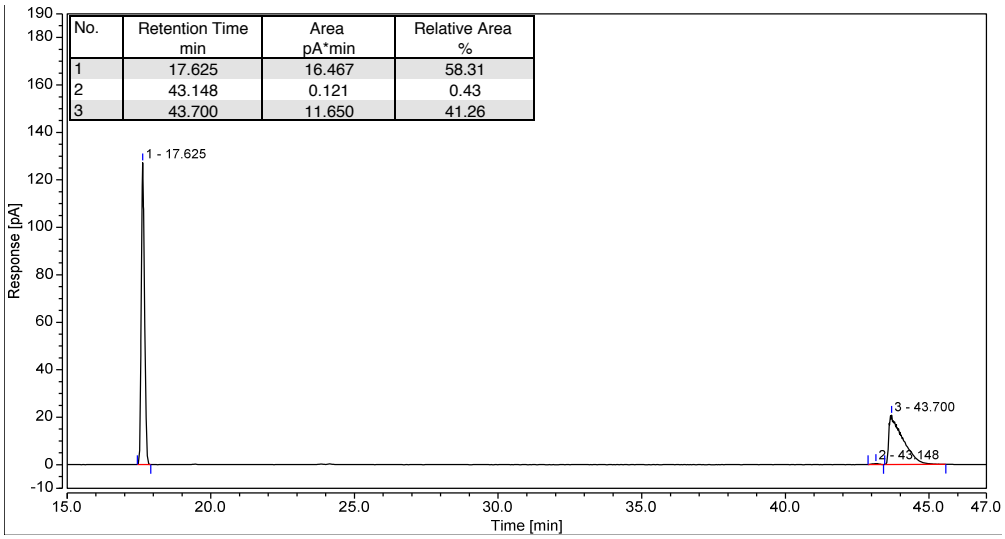


Figure S88: GC trace of enantioenriched (*R*)-**11w** (obtained by general procedure **A** using **3a**).

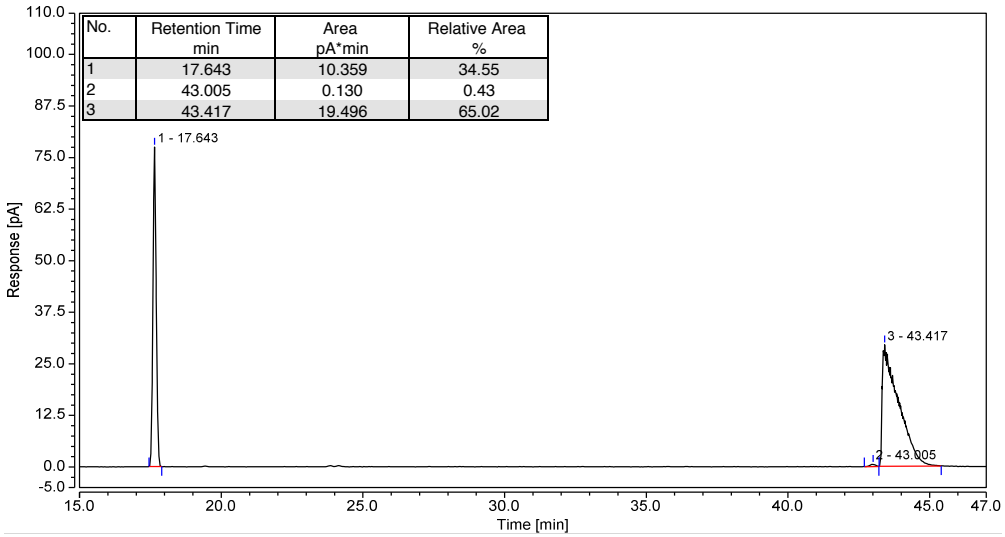


Figure S89: GC trace of enantioenriched (*R*)-**11w** (obtained by general procedure **B** using **3b**).

11x

Synthesis of 3-Methylbutan-2-ol, 11x. The spectroscopic data of **11x** have previously been reported.[S2] This compound was obtained in 93.0% yield and with 8.6% ee following general procedure **A** (0.625 mmol scale; S/C/B = 250/1/10; T = 75 °C) using catalyst

3a (reaction time: 5.0 h). **GC**: *β*-DEX column, 35 °C isotherm, retention times t_R(SM) = 7.7 min, t_R(minor) = 18.9 min, t_R(minor) = 19.9 min. This compound was obtained in 98.1% yield and with 4.7% ee following general procedure **B** (0.625 mmol scale; S/C/B = 250/1/10; T = 75 °C) using catalyst **3b** (reaction time: 2.5 h). **GC**: *β*-DEX column, 35 °C isotherm, retention times t_R(SM) = 7.8 min, t_R(major) = 19.0 min, t_R(minor) = 20.0 min. Analytical data are in agreement with literature data.[S2]

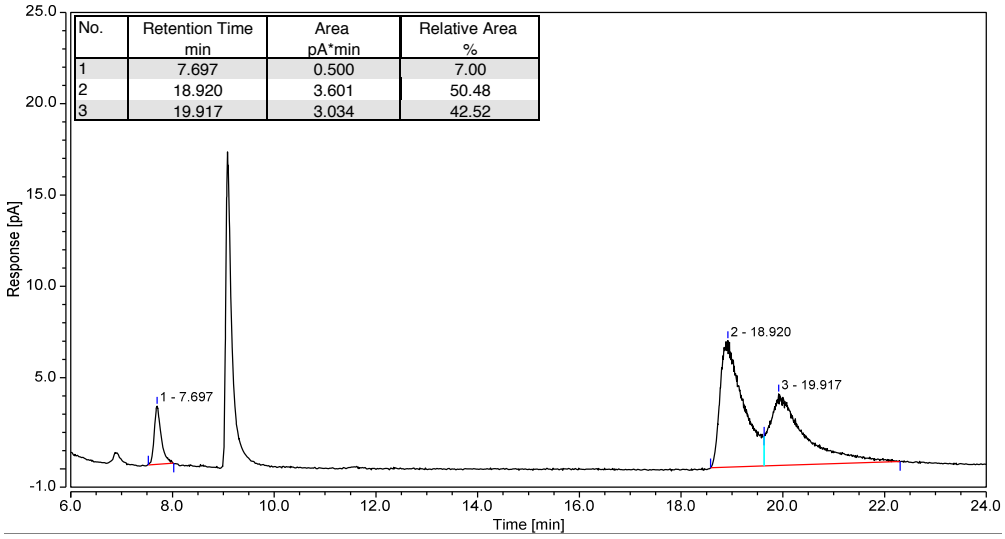


Figure S90: GC trace of **11x** (obtained by general procedure **A** using **3a**).

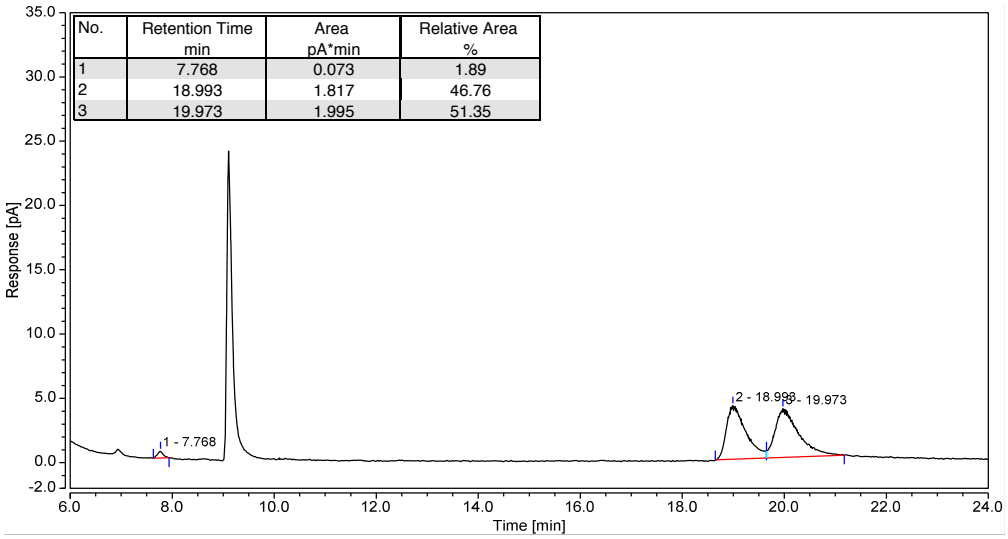
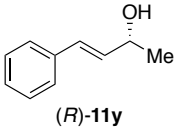


Figure S91: GC trace of **11x** (obtained by general procedure **B** using **3b**).



(*R*)-**11y**

Synthesis of (*R*,*E*)-4-Phenylbut-3-en-2-ol, (*R*)-11y. The synthesis of racemic **11y** and its spectroscopic data has previously been reported.[S2] This compound was obtained in 81.7% yield (determined by GC) and with 67.8% ee (determined by HPLC) following general procedure **A** using catalyst **3a** (reaction time: 0.25 h). **GC**: *β*-DEX column, 120 °C isotherm, retention times t_R(SM) = 33.8 min, t_R(major) = 36.0 min, t_R(minor) = 36.4 min. The peaks are not baseline separated. **HPLC**: Chiralpak IB-3 (hexane : 2-propanol = 98 : 2, flow rate 1.0 mL/min, λ = 210 nm), retention times t_R(major) = 14.0 min, t_R(minor) = 21.9 min. This compound was obtained in 81.3% yield (determined by GC) and with 69.0% ee (determined by HPLC) following general procedure **B** using catalyst **3b** (reaction time: 1.0 h). **GC**: *β*-DEX column, 120 °C isotherm, retention times t_R(SM) = 33.8 min, t_R(major) = 36.0 min, t_R(minor) = 36.4 min. The peaks are not baseline separated. **HPLC**: Chiralpak IB-3 (hexane : 2-propanol = 98 : 2, flow rate 1.0 mL/min, λ = 210 nm), retention times t_R(major) = 14.0 min, t_R(minor) = 21.7 min. Analytical

data are in agreement with literature data.[S2] The absolute configuration was assigned as (*R*) in analogy to (*R*)-**11a**.

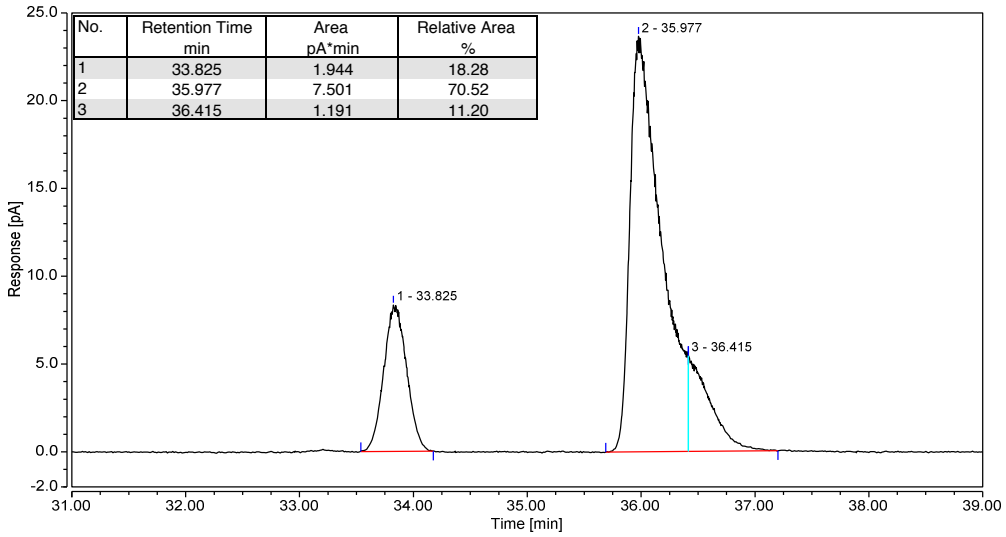


Figure S92: GC trace of enantioenriched (*R*)-**11y** (obtained by general procedure **A** using **3a**).

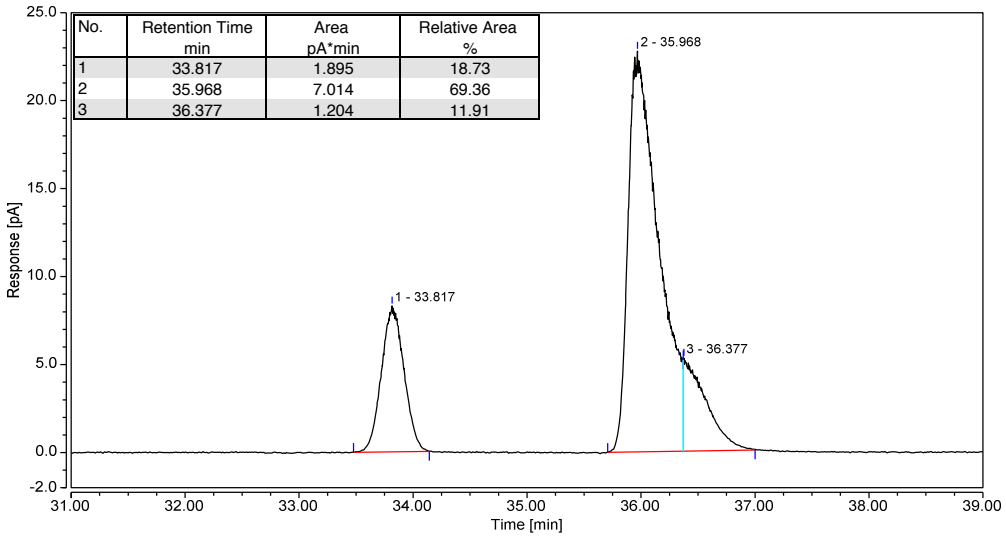


Figure S93: GC trace of enantioenriched (*R*)-**11y** (obtained by general procedure **B** using **3b**).

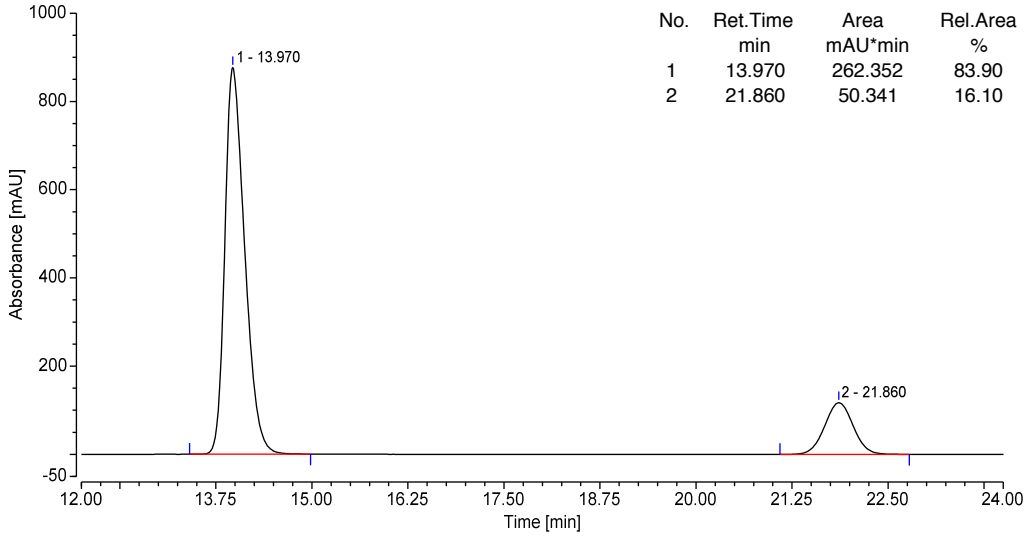


Figure S94: HPLC trace of enantioenriched (*R*)-**11y** (obtained by general procedure **A** using **3a**).

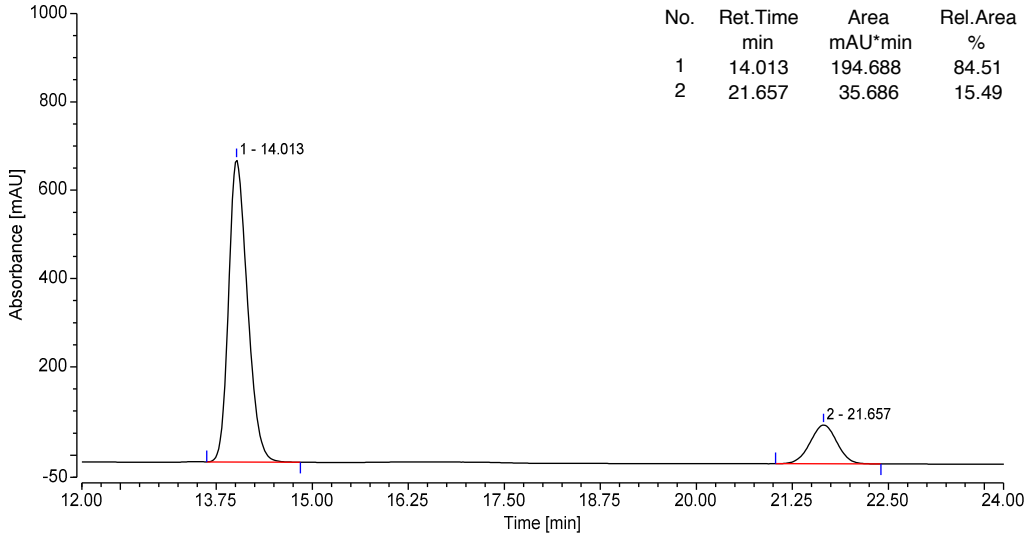
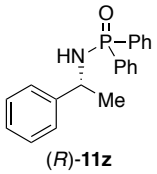


Figure S95: HPLC trace of enantioenriched (*R*)-**11y** (obtained by general procedure **B** using **3b**).



(*R*)-**11z**

Synthesis of (*R*)-*P,P*-Diphenyl-*N*-(1-phenylethyl)phosphinic amice, (*R*)-11z.

The synthesis of racemic **11z** and its spectroscopic data has previously been reported.[S1,2] This

compound was obtained in 86% yield and with 98.7% ee following general procedure **A** (0.625 mmol scale; S/C/B = 250/1/10; T = 75 °C) using catalyst **3a**. After 5.0 h, the solvent as removed at the rotary evaporator (20 mbar, 40 °C). Flash column chromatography on silica gel (acetone : CH_2Cl_2 = 1 : 4) afforded the product as a white solid. Yield: 174 mg (86%). **HPLC**: OD-H (hexane : 2-propanol = 90 : 10, flow rate 0.8 mL/min, λ = 211 nm), retention times t_R(major) = 10.5 min, t_R(minor) = 13.0 min. This compound was obtained in 81% yield and with 78.8% ee following general procedure **B** (0.625 mmol scale; S/C/B = 250/1/10; T = 75 °C) using catalyst **3b**. After 5.0 h, the solvent was removed at the rotary evaporator (20 mbar, 40 °C). Flash column chromatography on silica gel (acetone : CH_2Cl_2 = 1 : 4) afforded the product as a white solid. Yield: 163 mg (81%). **HPLC**: OD-H (hexane : 2-propanol = 90 : 10, flow rate 0.8 mL/min, λ = 211 nm), retention times t_R(major) = 10.9 min, t_R(minor) = 13.6 min. Analytical data are in agreement with literature data.[S1,2] The absolute configuration was determined to be (*R*) by comparison with literature data.[S1]

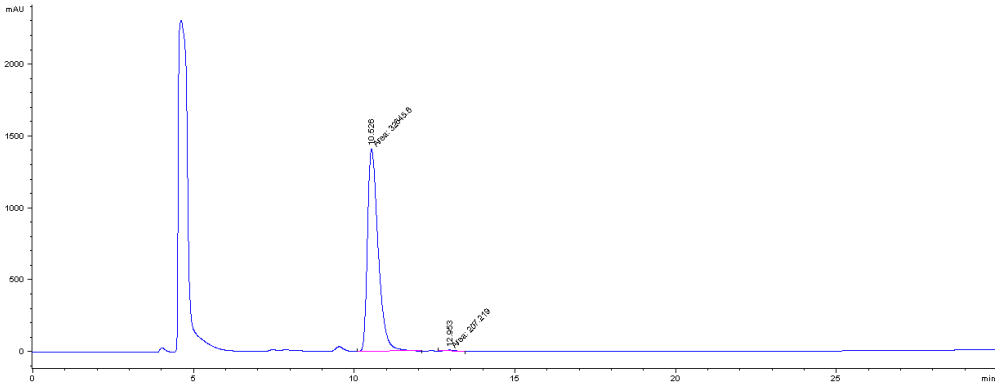


Figure S96: HPLC trace of enantioenriched (*R*)-**11z** (obtained by general procedure **A** using **3a**).

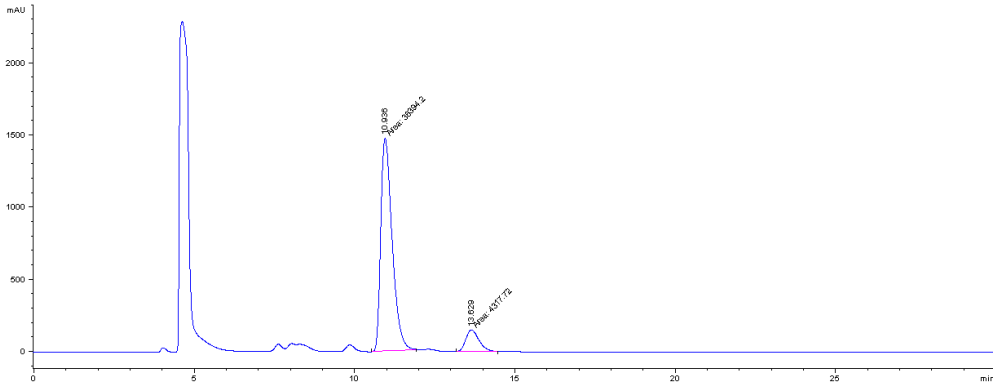


Figure S97: HPLC trace of enantioenriched (*R*)-**11z** (obtained by general procedure **B** using **3b**).

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(S2) Bigler, R.; Huber, R.; Mezzetti, A. *Angew. Chem. Int. Ed.* **2015**, *54*, 5171–5174.

(S3) Peng, J.; Zhao, J.; Hu, Z.; Liang, D.; Huang, J.; Zhu, Q. *Org. Lett.* **2012**, *14*, 4966–4969.

(S4) Marcó, A.; Compañó, R.; Rubio, R.; Casals, I. *Microchim. Acta* **2003**, *142*, 13–19.

(S5) Bigler, R.; Mezzetti, A. *Org. Lett.* **2014**, *16*, 6460–6463.