

図12.10-3 水素化・水素移動反応(表12.10-17～12.10-22)に用いられている触媒および配位子

(1) C_2 対称性ホスフィン

(2) C_2 対称性以外の構造をもつホスフィン

(3) リン-酸素結合をもつ光学活性配位子

(4) リン-窒素結合をもつ光学活性配位子

(5) 光学活性アミン配位子

(6) 光学活性ピリジン, フェナントロリン, オキサゾール, およびイミダゾリジン配位子

(7) 窒素上に官能基をもつ光学活性アミン配位子

(8) 光学活性アミノアルコールおよびアミノエーテル

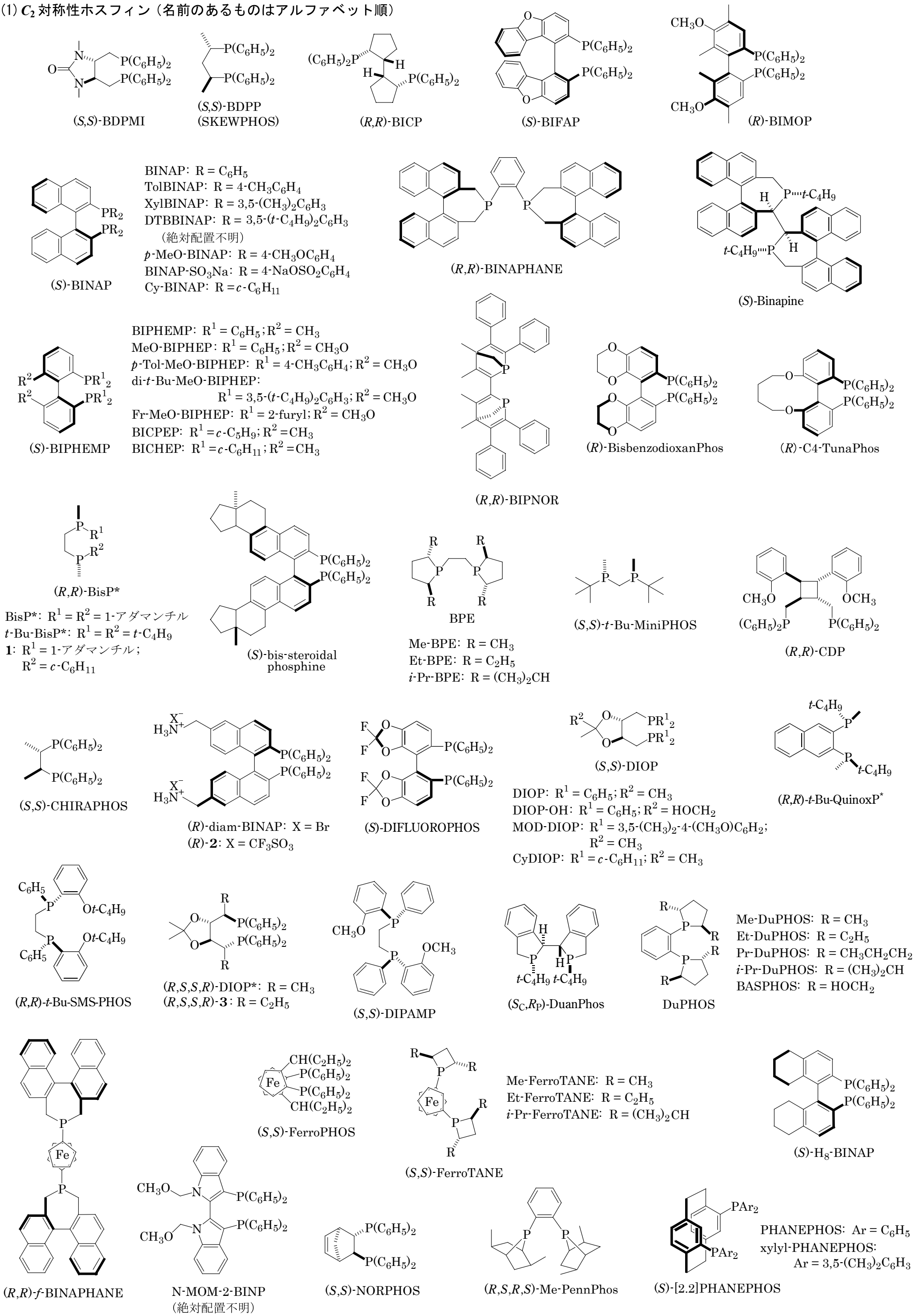
(9) 光学活性アミノおよびイミノホスフィン配位子

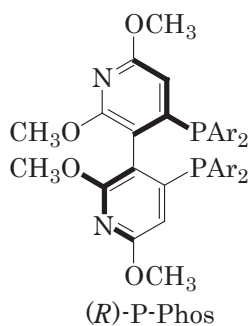
(10) 固定化された光学活性ジホスフィン配位子

(11) その他の配位子, 化合物

(12) その他: 表中にアルファベットあるいは略記で示した触媒

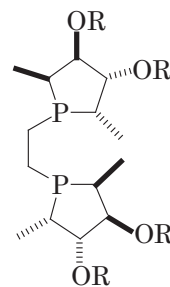
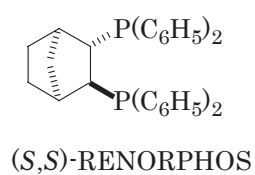
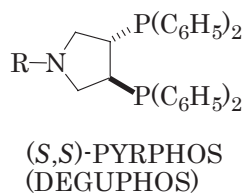
(1) C₂ 対称性ホスフィン（名前のあるものはアルファベット順）



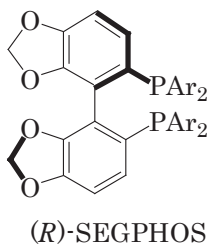
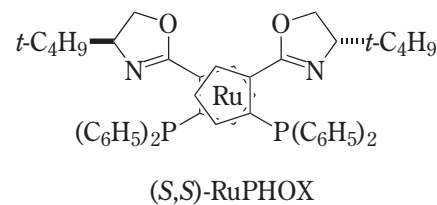


P-Phos: Ar = C₆H₅

Xyl-P-Phos: Ar = 3,5-(CH₃)₂C₆H₃



R = CH₂C₆H₅ または *t*-C₄H₉

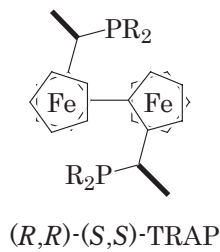
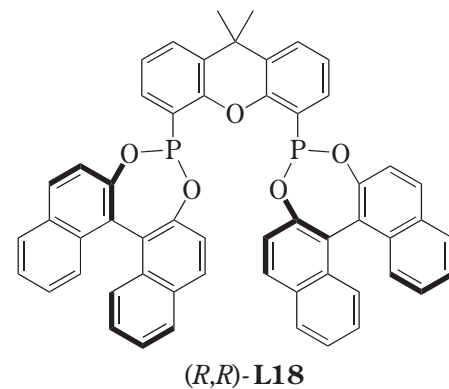
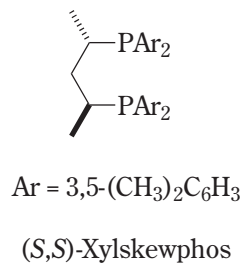
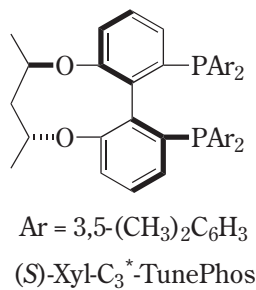
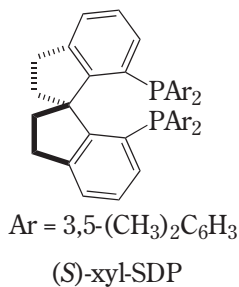
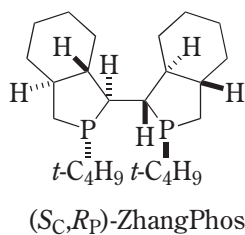
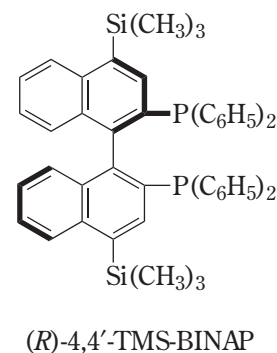
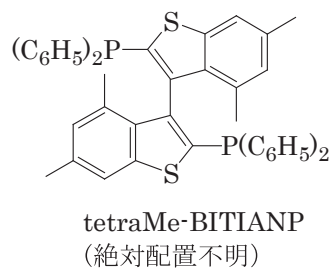
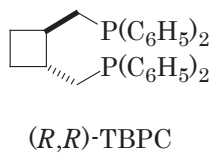
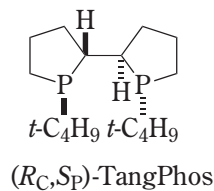


SEGPPOS: Ar = C₆H₅

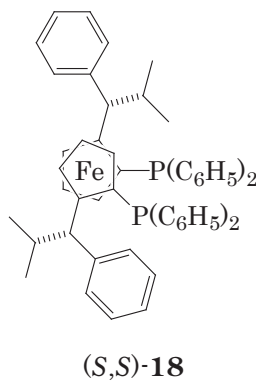
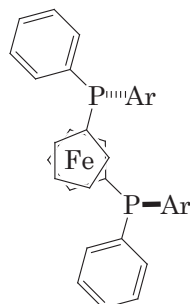
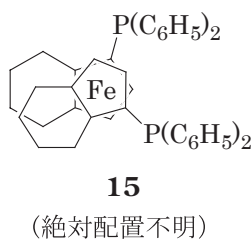
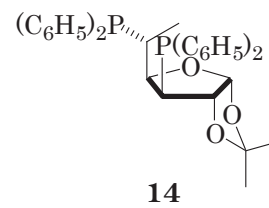
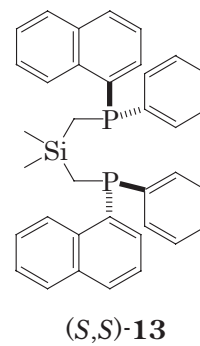
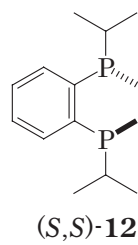
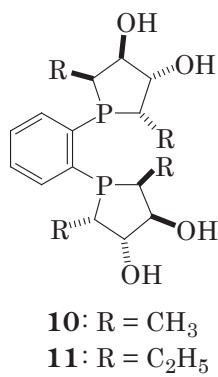
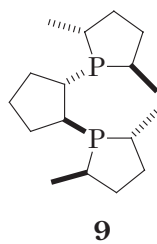
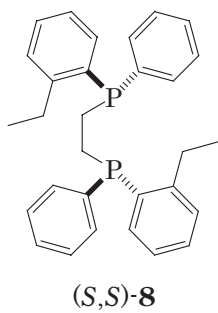
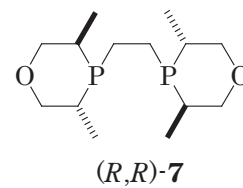
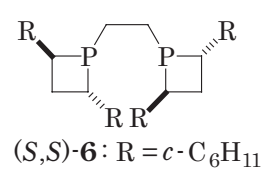
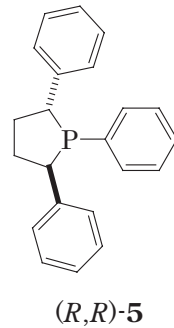
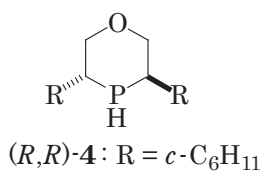
DTBM-SEGPPOS:

Ar = 4-CH₃O-3,5-(*t*-C₄H₉)₂C₆H₂

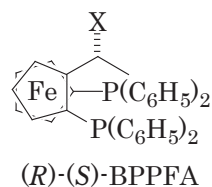
(絶対配置不明)



EtTRAP: R = C₂H₅
PrTRAP: R = CH₃(CH₂)₂
BuTRAP: R = CH₃(CH₂)₃
i-BuTRAP: R = (CH₃)₂CHCH₂
PhTRAP: R = C₆H₅



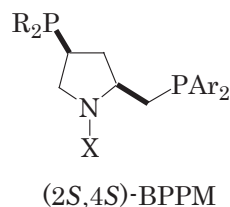
(2) C_2 対称性以外の構造をもつホスフィン（名前のあるものはアルファベット順）



BPPFA: $X = (CH_3)_2N$

19: $X = \text{N(CH}_2)_2\text{(CH}_3)_2\text{N}$

BPPFOH: $X = HO$



BPPM: $Ar = R = C_6H_5$; $X = (CH_3)_3COCO$

R'-CAPP: $Ar = R = C_6H_5$; $X = R'NHCO$

BCPM: $Ar = C_6H_5$; $R = c\text{-}C_6H_{11}$; $X = (CH_3)_3COCO$

MCCPM: $Ar = C_6H_5$; $R = c\text{-}C_6H_{11}$; $X = CH_3NHCO$

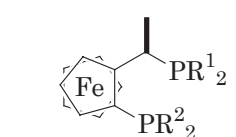
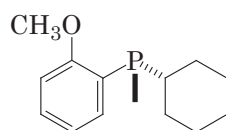
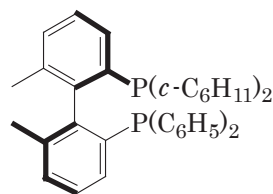
m-CH₃POPPM: $Ar = R = 3\text{-}CH_3C_6H_4$; $X = (C_6H_5)_2PO$

MCCXM: $Ar = 3,5\text{-(CH}_3)_2C_6H_3$; $R = c\text{-}C_6H_{11}$;

$X = CH_3NHCO$

MOD-BCPM: $Ar = 3,5\text{-(CH}_3)_2\text{-}4\text{-(CH}_3O)C_6H_2$;

$R = c\text{-}C_6H_{11}$; $X = (CH_3)_3COCO$



JOSIPHOS: $R^1 = c\text{-}C_6H_{11}$; $R^2 = C_6H_5$

XYLIPHOS: $R^1 = 3,5\text{-(CH}_3)_2C_6H_3$; $R^2 = C_6H_5$

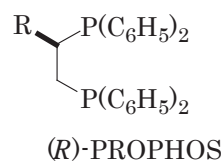
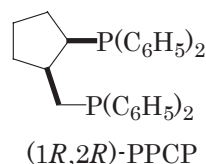
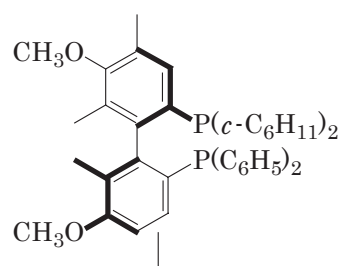
xyl₂PF-Pxyl₂: $R^1 = 3,5\text{-(CH}_3)_2C_6H_3$; $R^2 = 3,5\text{-(CH}_3)_2C_6H_3$

MOD-XYLIPHOS: $R^1 = 3,5\text{-(CH}_3)_2\text{-}4\text{-[(CH}_3)_2CH]_2NC_6H_2$;

$R^2 = C_6H_5$

20: $R^1 = c\text{-}C_6H_{11}$; $R^2 = 4\text{-CF}_3\text{-}C_6H_4$

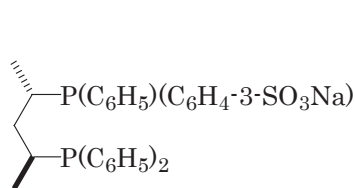
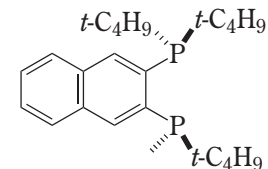
cy₂PF-Pcy₂: $R^1 = R^2 = c\text{-}C_6H_{11}$



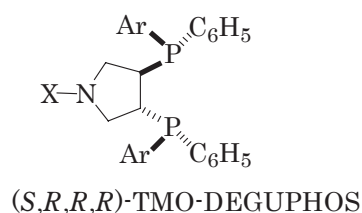
PROPHOS: $R = CH_3$

BENZPHOS: $R = C_6H_5CH_2$

CyCPHOS: $R = c\text{-}C_6H_{11}$

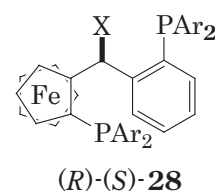
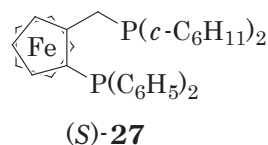
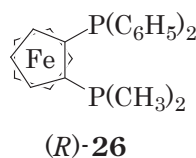
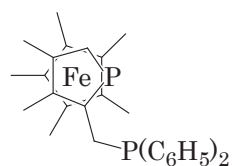
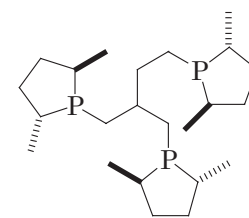
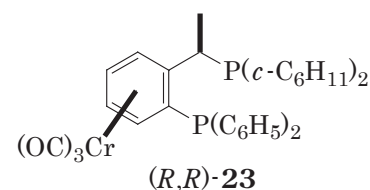
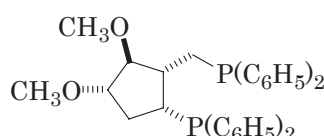
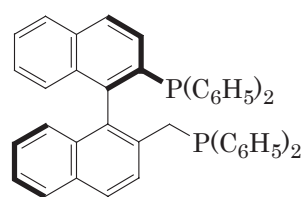
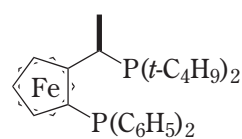
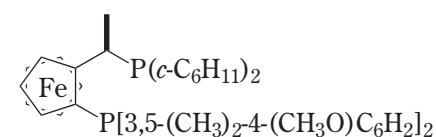
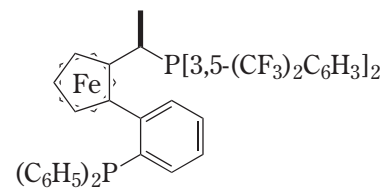


(ジアステレオ混合物)



$Ar = 2,4,6\text{-(CH}_3O)_3C_6H_2$;

$X = (CH_3)_3COCO$



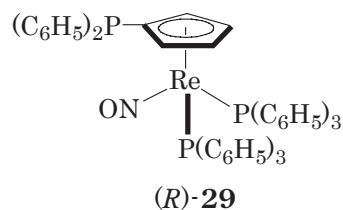
28a: $Ar = C_6H_5$; $X = CH_3$

28b: $Ar = C_6H_5$; $X = (CH_3)_2CH$

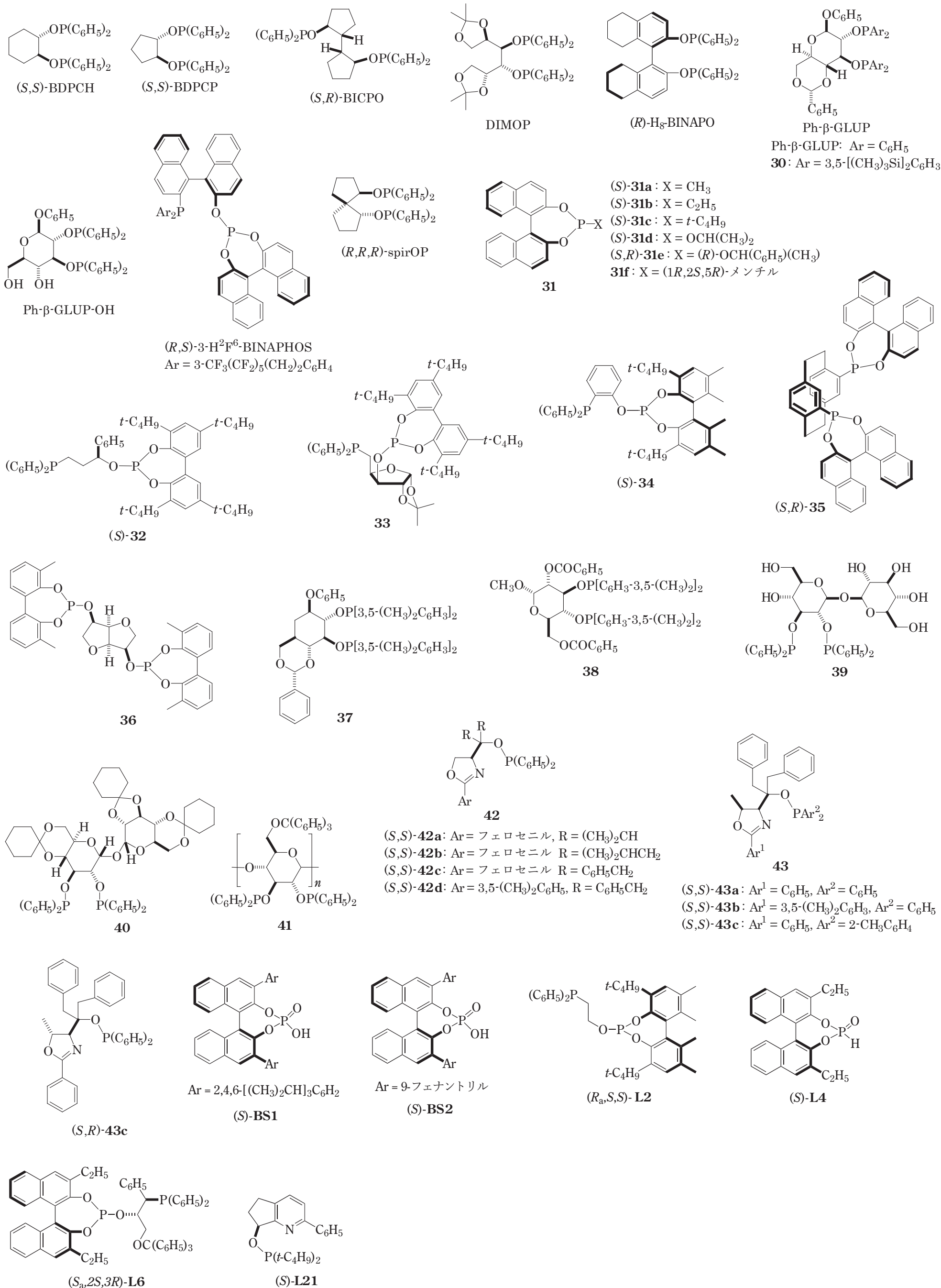
28c: $Ar = C_6H_5$; $X = (CH_3)_2N$

28d: $Ar = C_6H_5$; $X = [(CH_3)_2CHCH_2]_2N$

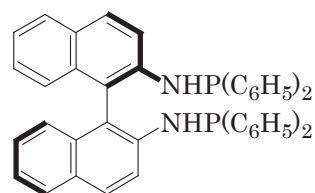
28e: $Ar = 3,5\text{-(CH}_3)_2C_6H_3$; $X = (CH_3)_2N$



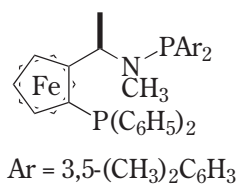
(3) リン-酸素結合をもつ光学活性配位子（名前のあるものはアルファベット順）



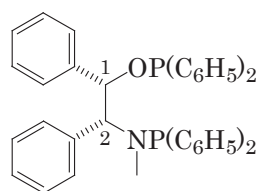
(4) リン-窒素結合をもつ光学活性配位子（名前のあるものはアルファベット順）



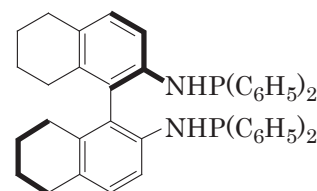
(*R*)-BDPAB



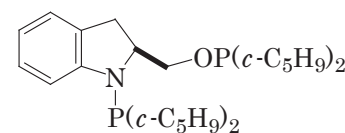
(*R,S*)-BoPhos



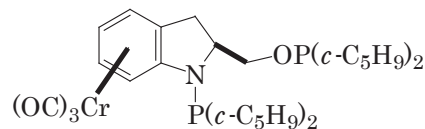
(1*S*,2*R*)-DPAMPP



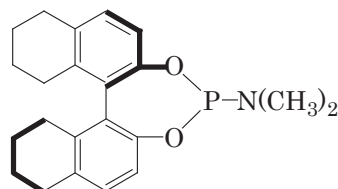
(*R*)-H₈-BDPAB



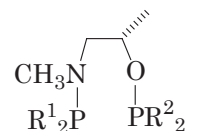
(*S*)-Cp,Cp-IndoNOP



(*S*,2*S*)-Cr(CO)₃-Cp,Cp-IndoNOP

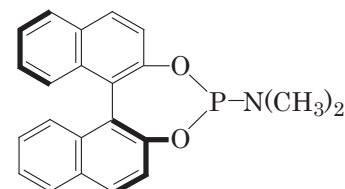


(*R*)-H₈-MonoPhos

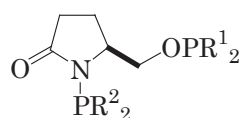


(*S*)-isoAlaNOP

Ph,Cp-isoAlaNOP: R¹ = C₆H₅; R² = *c*-C₅H₉
Cp,Cp-isoAlaNOP: R¹ = R² = *c*-C₅H₉

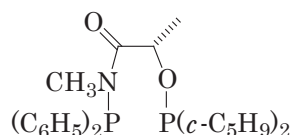


(*S*)-MonoPhos

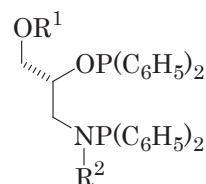


(*S*)-oxoProNOP

Ph,Ph-oxoProNOP: R¹ = R² = C₆H₅
Cp,Cp-oxoProNOP: R¹ = R² = *c*-C₅H₉
Cy,Cy-oxoProNOP: R¹ = R² = *c*-C₆H₁₁

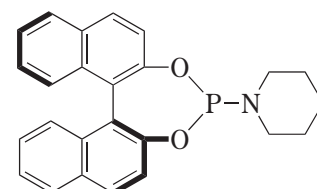


(*S*)-Ph,Cp-methylactamide

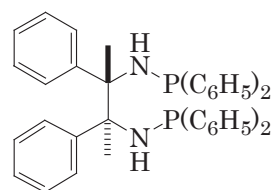


(*R*)-PINDOPHOS

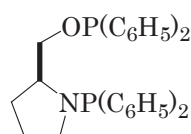
PINDOPHOS: R¹ = 7-インドリル; R² = (CH₃)₂CH
44: R¹ = 1-ナフチル; R² = *c*-C₅H₉



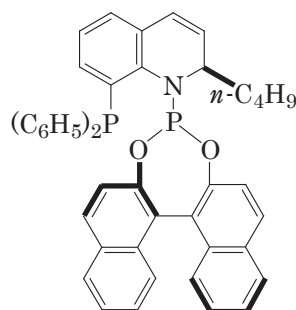
(*S*)-PipPhos



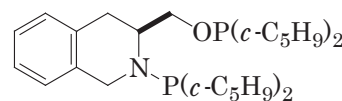
(*S,S*)-PNNP



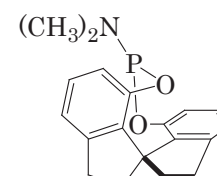
(*S*)-PROLOPHOS



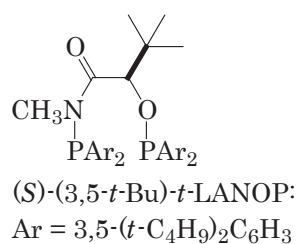
(*R,R*)-*n*-Bu-QUINAPHOS



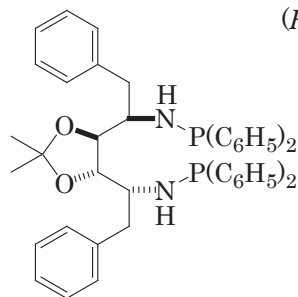
(*S*)-Cp,Cp-QuinoNOP



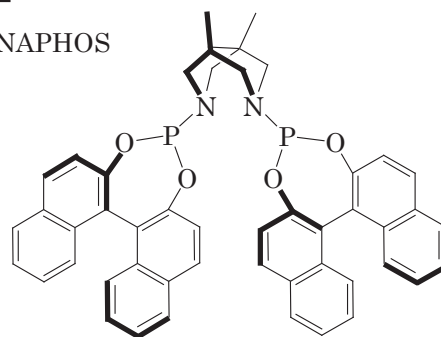
(*S*)-SIPHOS



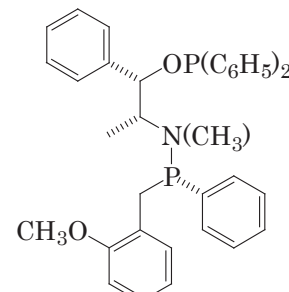
(*S*)-(3,5-*t*-Bu)-*t*-LANOP:
Ar = 3,5-(*t*-C₄H₉)₂C₆H₃



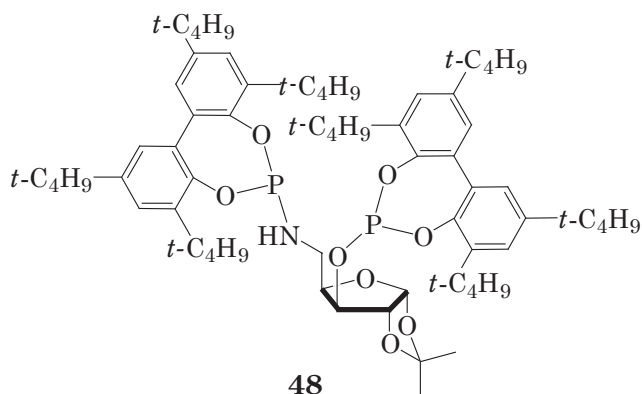
(*R,S,S,R*)-45



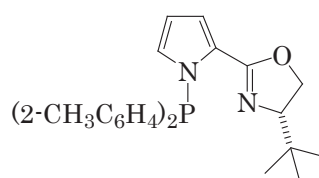
46



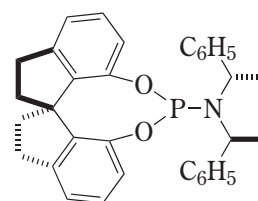
47



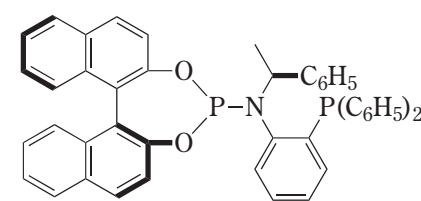
48



(*S*)-49

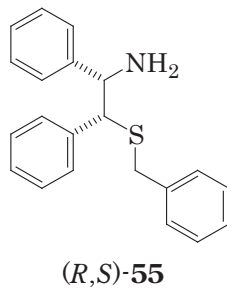
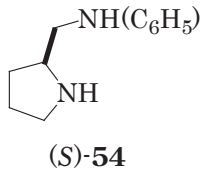
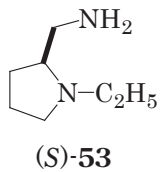
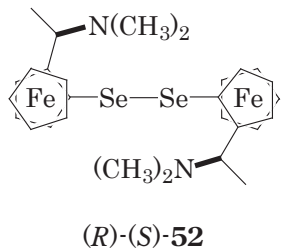
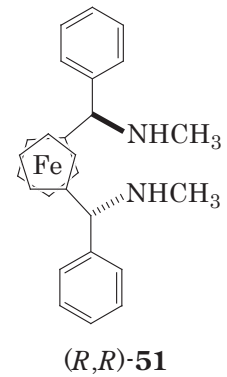
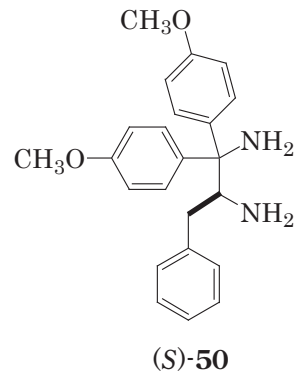
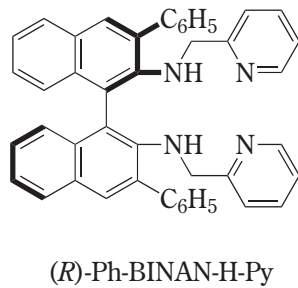
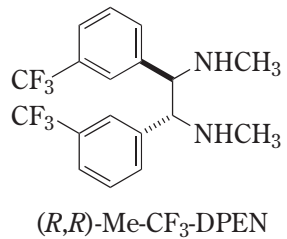
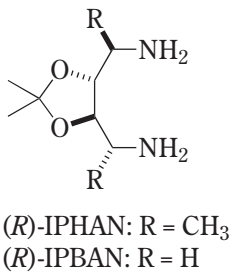
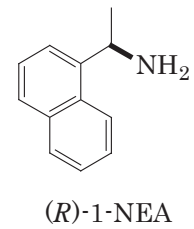
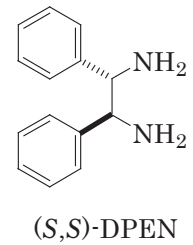
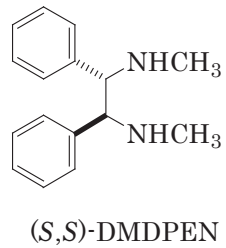
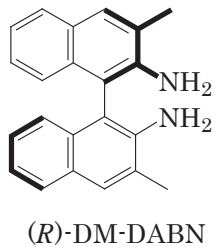
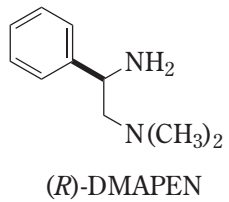
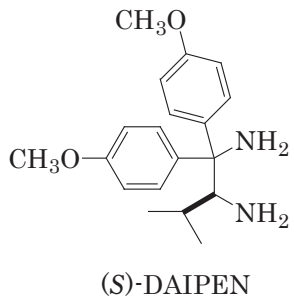


(*R,S,S*)-L1

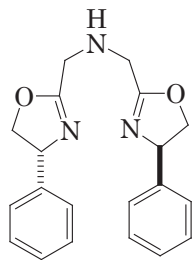


(*S,S,S*)-L7

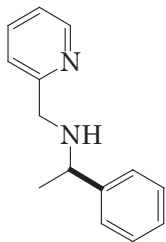
(5) 光学活性アミン配位子（名前のあるものはアルファベット順）



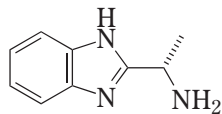
(6) 光学活性ピリジン，フェナントロリン，オキサゾール，およびイミダゾリジン配位子（名前のあるものはアルファベット順）



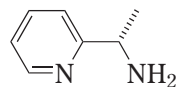
(R)-AMBOX



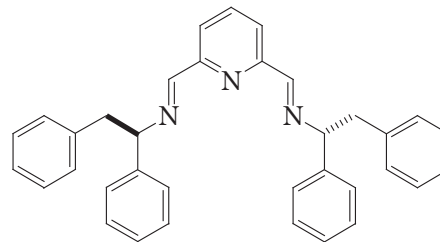
(R)-DHPPEI



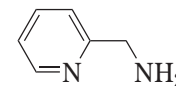
(S)-Me-bima



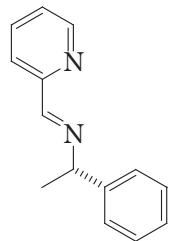
(R)-MePyme



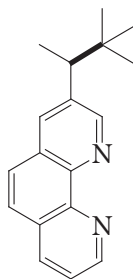
(R,R)-PDPBI



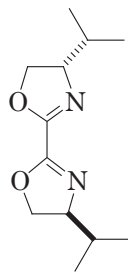
PICA
(アキラル)



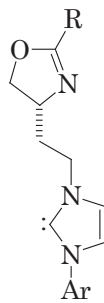
(S)-PPEI



(S)-56



(S,S)-57

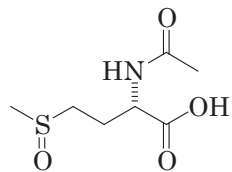


(R)-58

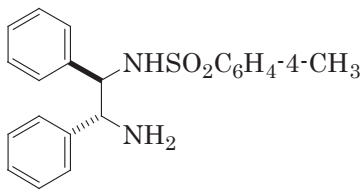
R = 1-アダマンチル

Ar = 2,6-(*i*-C₃H₇)₂C₆H₃

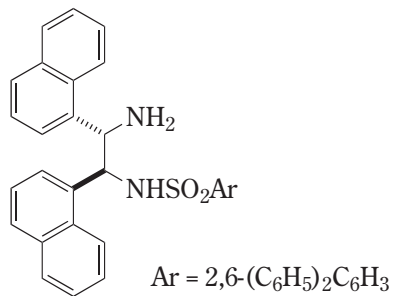
(7) 窒素上に官能基をもつ光学活性アミン配位子



(*S*)-AMSO

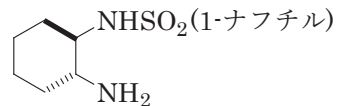


(*R,R*)-TsDPEN

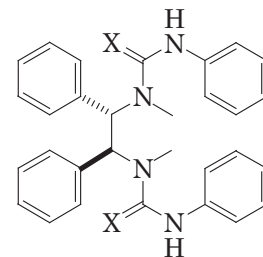


(*S,S*)-L18

Ar = 2,6-(C₆H₅)₂C₆H₃

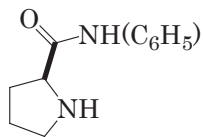


(*R,R*)-**59**



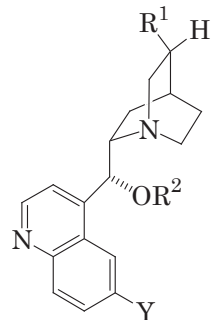
(*S,S*)-**60**: X = O

(*S,S*)-**61**: X = S



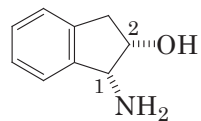
(*S*)-**62**

(8) 光学活性アミノアルコールおよびアミノエーテル

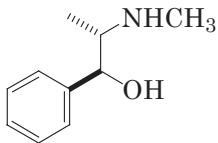


シンコニジン: $R^1 = \text{CH}_2 = \text{CH}$; $R^2 = \text{H}$; $Y = \text{H}$
 Hcd: $R^1 = \text{C}_2\text{H}_5$; $R^2 = \text{H}$; $Y = \text{H}$
 キニーネ: $R^1 = \text{CH}_2 = \text{CH}$; $R^2 = \text{H}$; $Y = \text{CH}_3\text{O}$
 CH_3OHcd : $R^1 = \text{C}_2\text{H}_5$; $R^2 = \text{CH}_3$; $Y = \text{H}$

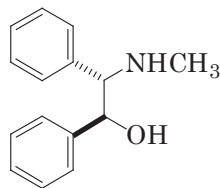
シンコナアルカロイド



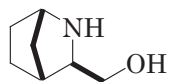
(1R,2S)-66



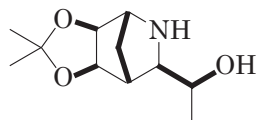
(S,S)-67



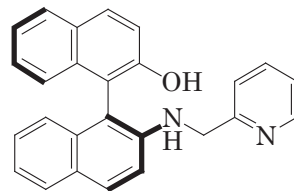
(S,S)-68



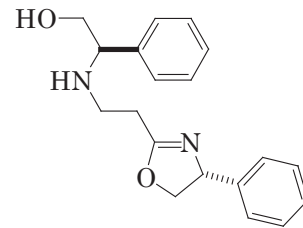
(S,R,R)-69



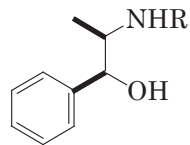
70



(S)-71

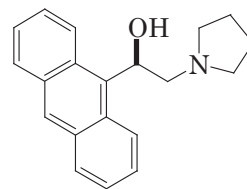


(R,R)-72



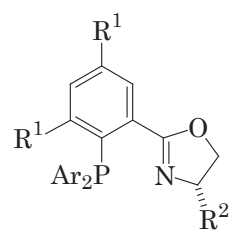
(R,S)-エフェドリン

ノルエフェドリン: $R = \text{H}$
 エフェドリン: $R = \text{CH}_3$
 63: $R = \text{CH}_2\text{-}i\text{-C}_6\text{H}_{11}$
 64: $R = \text{CH}_2\text{C}_6\text{H}_5$



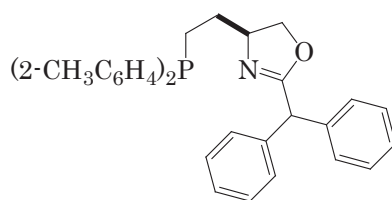
(R)-65

(9) 光学活性アミノおよびイミノホスフィン配位子

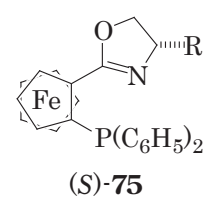


(S)-73

73a : $R^1 = H$; $R^2 = (CH_3)_2CH$; $Ar = C_6H_5$
73b : $R^1 = H$; $R^2 = (CH_3)_3C$; $Ar = C_6H_5$
73c : $R^1 = H$; $R^2 = (CH_3)_3C$; $Ar = 2-CH_3C_6H_4$
73d : $R^1 = H$; $R^2 = (CH_3)_3CCH_2$; $Ar = C_6H_5$
73e : $R^1 = CH_3$; $R^2 = (CH_3)_2CH$; $Ar = C_6H_5$



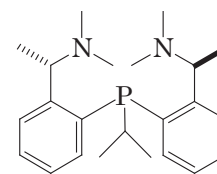
(S)-74



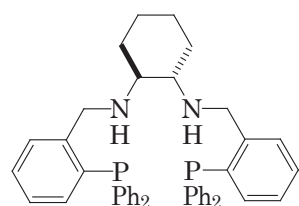
(S)-75

75a : $R = (CH_3)_2CH$

75b : $R = C_6H_5$

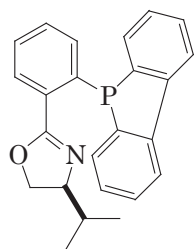


(S,S)-76

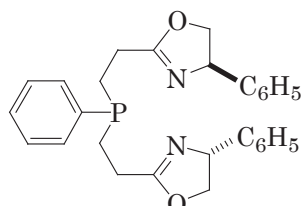


$Ph = C_6H_5$

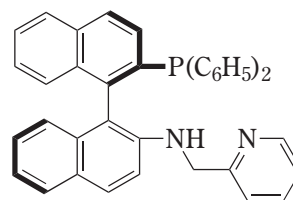
(S,S)-77



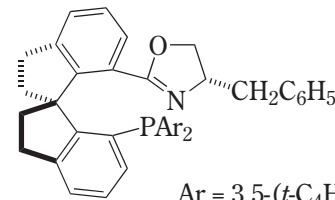
(S)-78



(R,R)-79

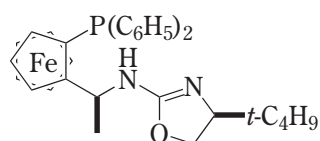


(R)-BINAN-Py-PPh₂

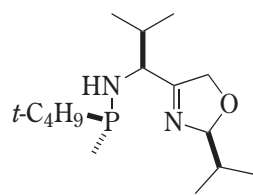


$Ar = 3,5-(t-C_4H_9)_2C_6H_3$

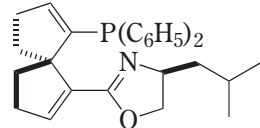
(S_a,S)-L3



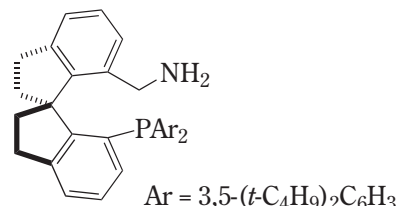
(S_C,S_C,R_{FC})-f-amphox



(S_P,S,R)-MaxPHOX

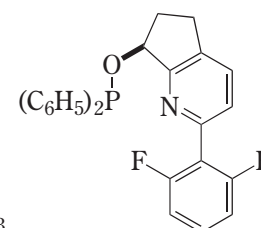


(S,S)-SpinPHOX

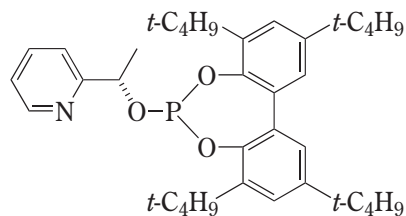


$Ar = 3,5-(t-C_4H_9)_2C_6H_3$

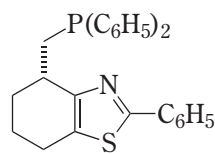
(S_a)-L5



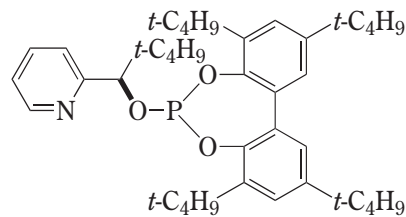
(S)-L8



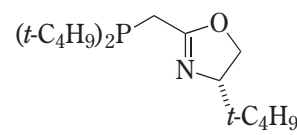
(S)-L9



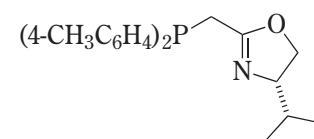
(S)-L10



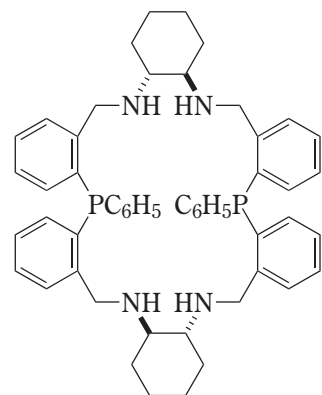
(R)-L11



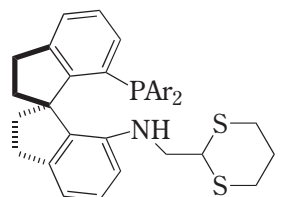
(S)-L12



(S)-L13

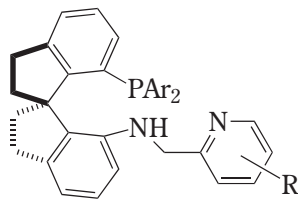


(R,R,R,R)-L14



$Ar = 3,5-(t-C_4H_9)_2C_6H_3$

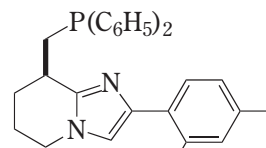
(R)-L15



$Ar = 3,5-(t-C_4H_9)_2C_6H_3$

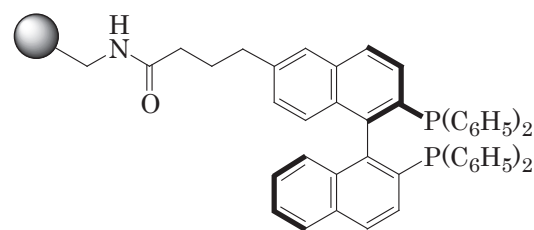
(R)-L16a: $R = 3-CH_3$

(R)-L16b: $R = 4-(t-C_4H_9)$



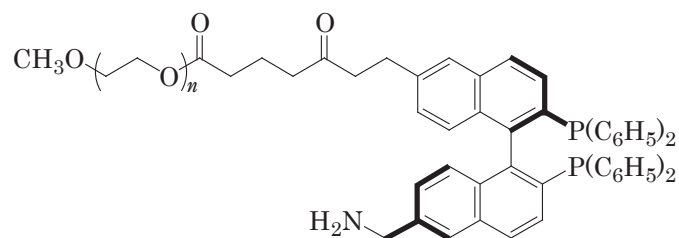
(R)-L19

(10) 固定化された光学活性ジホスフィン配位子

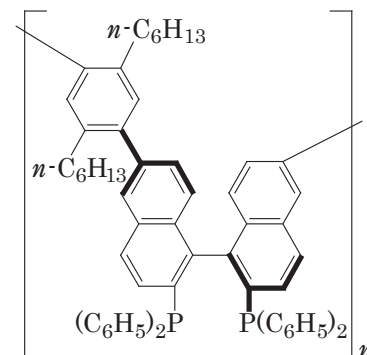


● = ポリスチレン

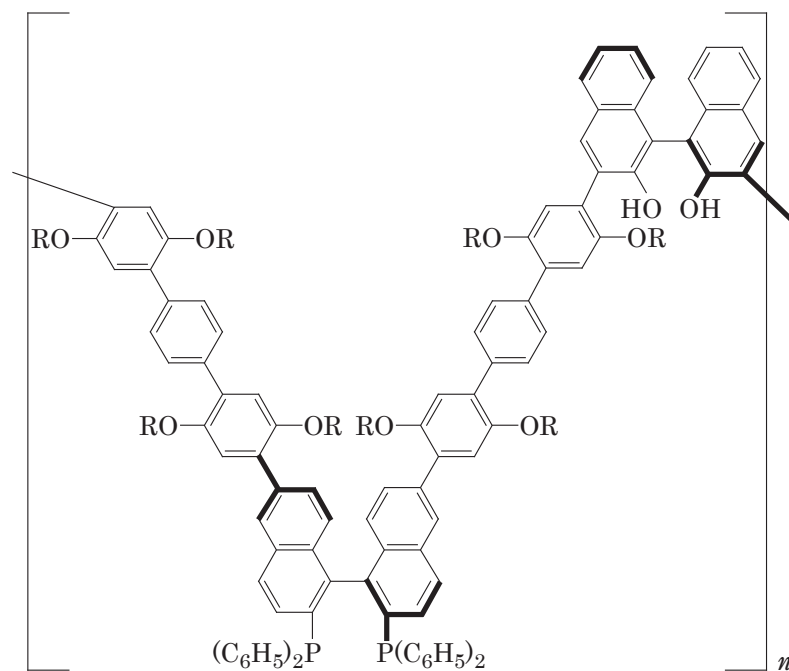
(*R*)-APBBINAP



PEG-(*R*)-Am-BINAP

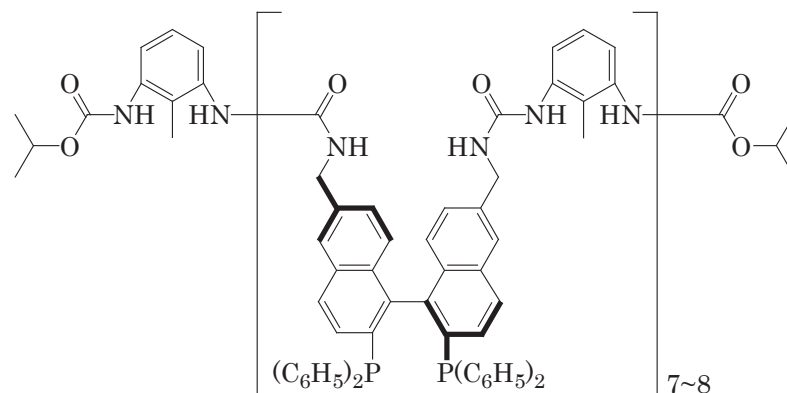


(*R*)-poly(BINAP)

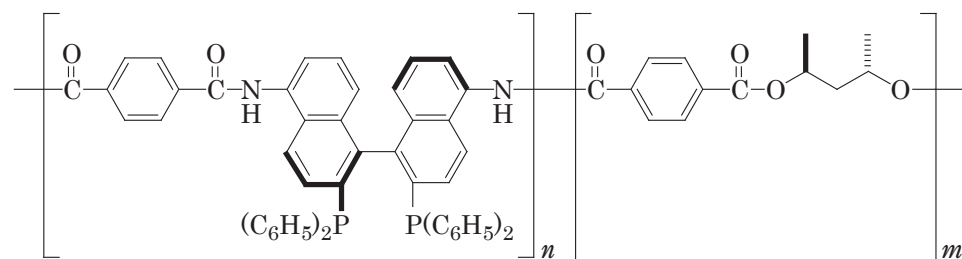


R = *n*-C₆H₁₃

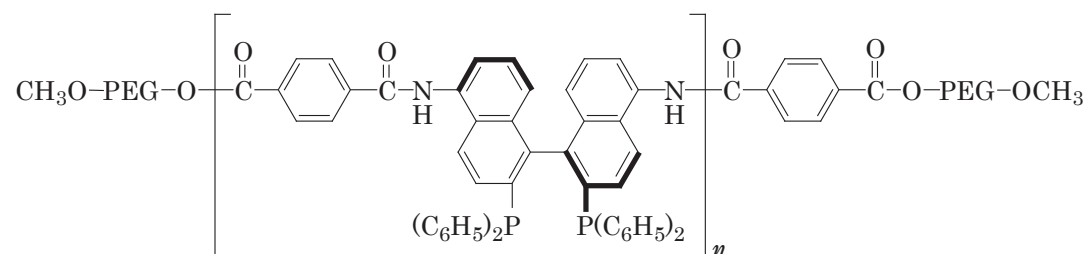
(*R,R*)-poly(BINOL-BINAP)



(*R*)-poly-NAP

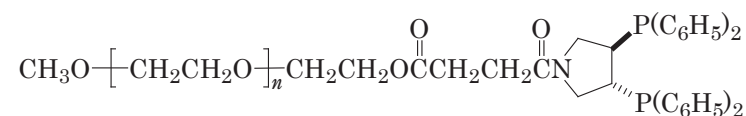


(*S*)-80



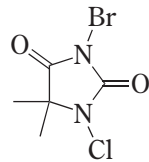
CH₃O-PEG-OH: ポリエチレングリコールモノメチルエーテル

(*R*)-81

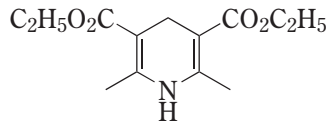


(*R,R*)-82

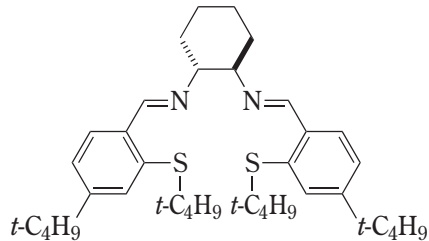
(11) その他の配位子，化合物



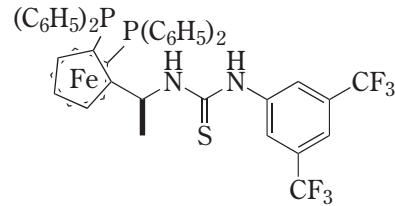
BCDMH



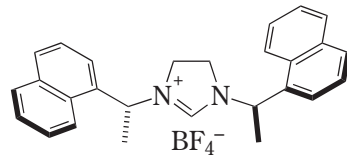
Hantzsch エステル



R,R-L17



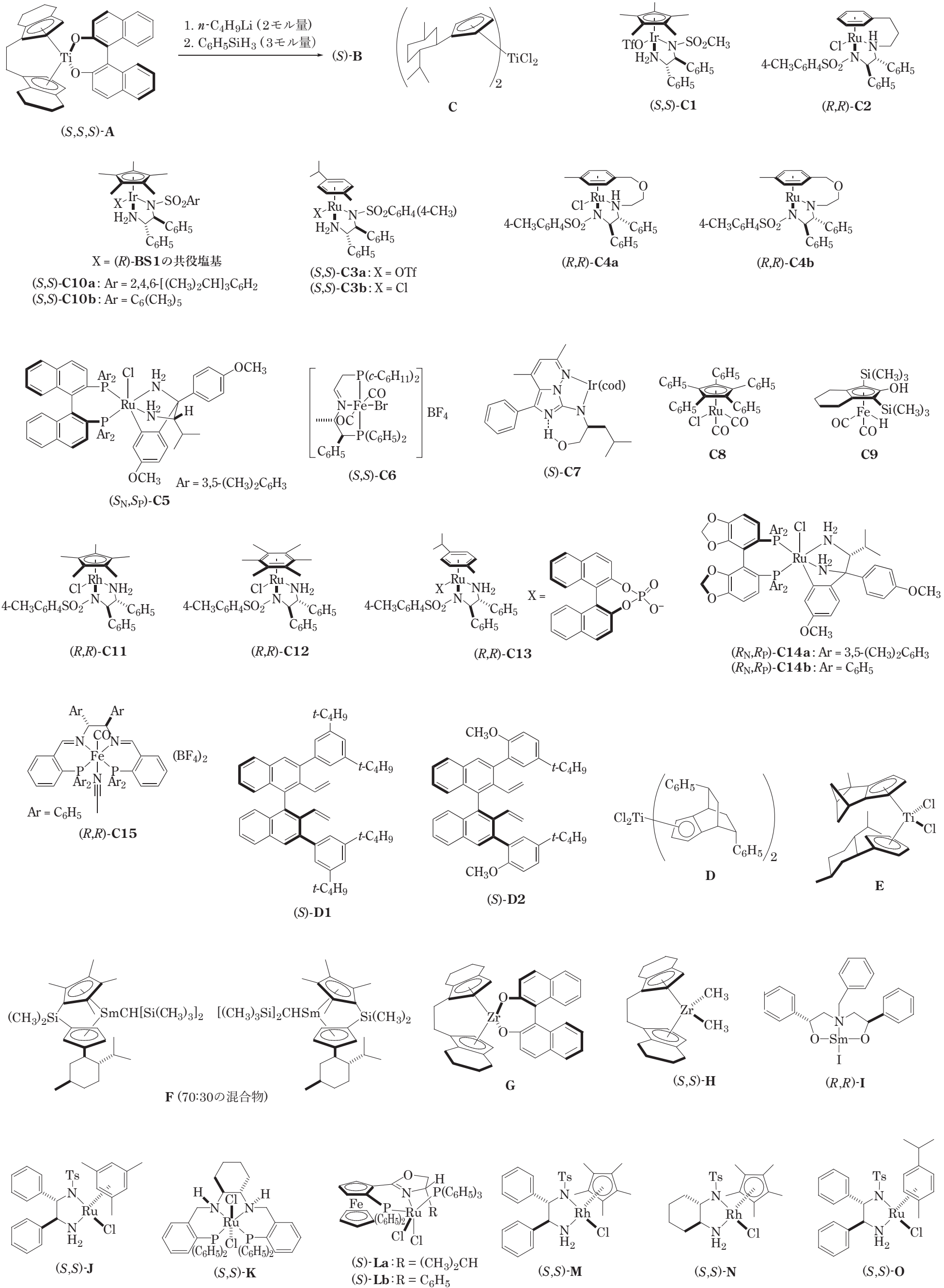
(*R,S*)-L20

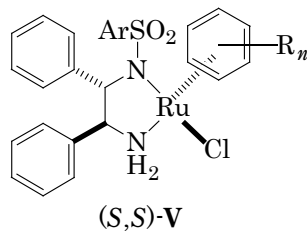
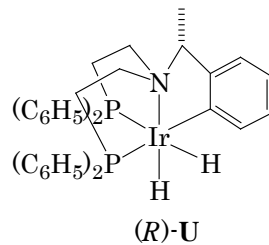
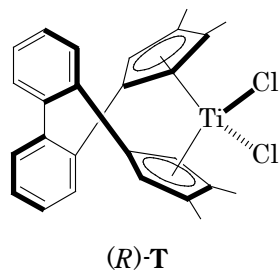
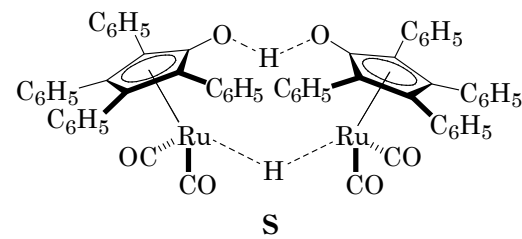
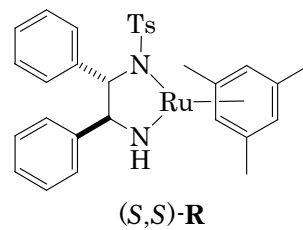
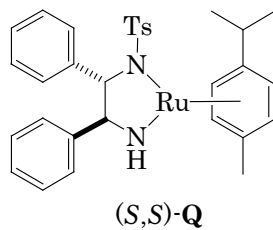
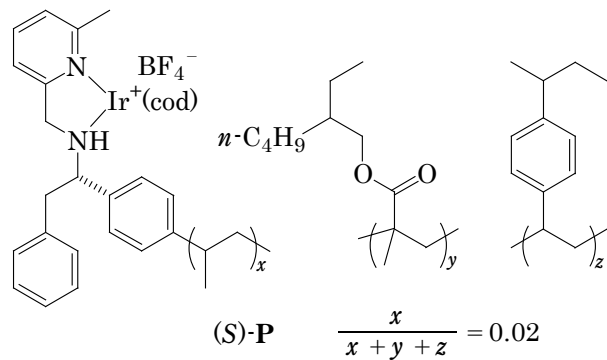


(*R,R*)-L22

著作権者の許諾なく，本図を複製，転載，配布することを禁じます。

(12) その他：表中にアルファベットあるいは略記で示した触媒





- a: η^6 -アレン = *p*-シメン; Ar = 2,4,6-(CH₃)₃C₆H₂
b: η^6 -アレン = ベンゼン; Ar = 2,4,6-(CH₃)₃C₆H₂
c: η^6 -アレン = ベンゼン; Ar = 1-ナフチル
d: η^6 -アレン = ベンゼン; Ar = 4-CH₃C₆H₄

