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Supporting Information

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Iridium–Catalyzed Asymmetric Hydrogenation of Unfunctionalized, Tetrasubstituted Olefins

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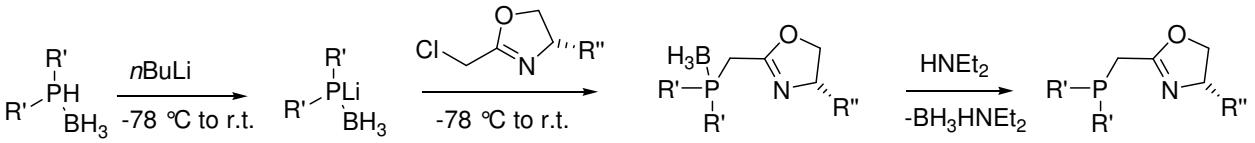
General: For general information regarding instrumentation refer to our previous publications.[1] All chemicals were purchased from Acros Organics, Aldrich, Fluka, Lancaster Synthesis, Merck Molecula and Strem Chemicals.

Substrate synthesis: Olefins were synthesized according to previously published procedures: Olefin **5** and **7** via Wittig-Olefination [2], Olefins **8** – **16** via Grignard-Addition and subsequent dehydration [2], Olefin **17** according to ref. [3].

Ligand and complex synthesis:

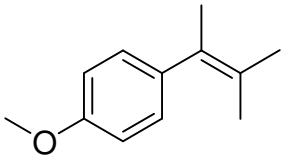


Scheme 1. Ligand synthesis

Ligand synthesis according Scheme 1.[4]
In a Schlenk tube under argon the secondary phosphine-borane adduct (1 eq) in THF was cooled to -78 °C. *n*BuLi (1.05 eq) was slowly added and the mixture was stirred for 15 minutes at -78 °C and for 2 hours at room temperature. After cooling to -78 °C chloro-methyl-4,5-dihydro-oxazoline (0.8-1.3 eq) in THF was added via cannula, and the cannula was rinsed with THF. The mixture was stirred at room temperature until TLC indicated the consumption of starting material. Then the mixture was poured in saturated $NaHCO_3$ solution and extracted with diethyl ether (3×10 to 20 mL). The combined organic layers were dried over $MgSO_4$ and the crude product was purified by flash column chromatography on silicagel eluting with diethyl ether and pentane. For deprotection the borane-protected phosphanyl-methyl-4,5-dihydro-oxazol was dissolved in diethylamine (1-2 mL) and stirred for 1 to 7 days. The conversion was controlled by ^{1}H–NMR. After completion of the reaction all volatiles were removed under high vacuum at 60 °C.
For alternative routes see refs. [6, 7].
Ir-complexes were obtained according to standard-procedures.[5]

General Asymmetric Hydrogenation Procedure: A high pressure steel autoclave (Premex Reactor AG; Lengnau, Switzerland; Model HPM-005) with a dry glass insert and a magnetic stir bar were taken into a glove box. The glass insert was loaded with the appropriate catalyst (0.002 mmol) and 0.5 ml of a 0.2 M degassed substrate solution freshly prepared from the corresponding substrate and dichloromethane (stirred over basic alumina and filtered). The hydrogenation vessel was sealed and taken out of the glove box. The autoclave was attached to a high pressure hydrogen line and purged with H_2. The autoclave was sealed under the appropriate H_2 pressure (see Tables) and the mixture was stirred for 3 - 8 hours at the appropriate pressure at room temperature. After release of H_2 the solution was concentrated in a stream of nitrogen, diluted

with 5 ml of hexane, passed through a Chromafil O-20/15 organic stable syringe filter (0.2 µm pore size), and the filtrate analyzed directly for conversion (GC) and *ee* (CG or HPLC).

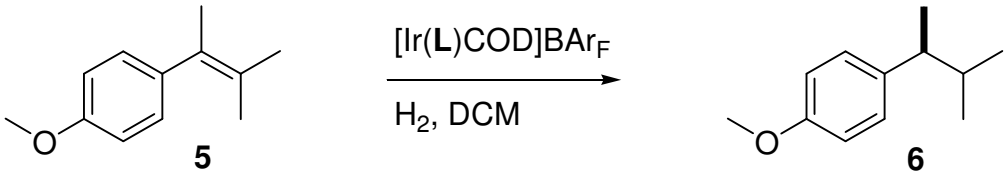


5

1-methoxy-4-(3-methylbut-2-en-2-yl)benzene

Elemental Analysis for $C_{12}H_{16}O$ (176.25) calc.: C, 81.77; H, 9.15; found: C, 82.04, H, 9.25; **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 1.59 (q, 3H, J_{HH} = 1.5 Hz, CH_3), 1.79 (q, 3H, J_{HH} = 0.9 Hz, CH_3), 1.94 (qq, 3H, J_{HH} = 1.5 Hz, J_{HH} = 0.9 Hz, CH_3), 3.80 (s, 3H, -OCH_3), 6.85 (m_c, 2H, H_{Ar}) 7.05 (m_c, 2H, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 20.6 (*C*H_3,), 20.9 (*C*H_3), 22. 1 (*C*H_3), 55.2 (O*C*H_3), 113.3 (H*C*$_{Ar}$), 126.9 (*C*=C), 129.3 (H*C*$_{Ar}$), 129.4 (*C*$_{Ar}$), 137.7 (C=*C*), 157.5 (O*C*$_{Ar}$); **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 100 °C, 0 min, 1 K/min, 120 °C, 0 min, 10 K/min, 180 °C, 2 min): t_R = 18.4 min; **MS** (EI): m/z (%) = 176 (M^+, 100), 161 (82), 145 (18), 133 (12), 115 (18), 91 (26), 77 (13), 65 (9), 51 (8), 41 (9); **IR** (υ[cm^{-1}]) = 2991w, 2910m, 2856w, 2833w, 1609m, 1574w, 1510s, 1464w, 1443w, 1371w, 1298w, 1283w, 1244s, 1175w, 1132w, 1105w, 1036w, 831w; **TLC** (SiO_2, hexanes:ethyl acetate 60:1) R_f = 0.38.

Hydrogenation Results

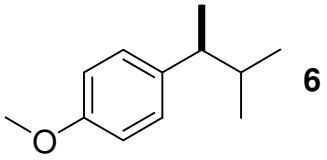


5 **6**

Ligand L	p (H_2) [bar]	Time [h]	mol% Cat.	Conv. [%]	ee [%]	opt. Rotation
***(S)*-1a**	50	4	2	>99	79	(–)
***(S)*-1b**	50	4	2	65	2	(+)
***(R,R)*-2a**	50	4	2	55	5	(–)
***(S,S)*-2b**	50	4	2	95	82	(–)
***(S)*-3a**	50	4	2	95	14	(–)
***(S)*-3b**	50	4	2	83	14	(+)
***(S)*-4a**	50	3	2	>99	88	(–)
***(S)*-4b**	50	3	2	>99	80	(–)
***(S)*-4c**	50	4	2	>99	92	(–)
***(S)*-4d**	50	4	2	>99	92	(–)
	50	4	1	>99	81	(–)
	50	4	0.5	92	73	(–)
	50	4	0.1	<1	n.d.	n.d.
	5	8	2	>99	96	(–)
	1	3	2	99	97	(–)
***(S)*-4e**	50	4	2	>99	71	(–)

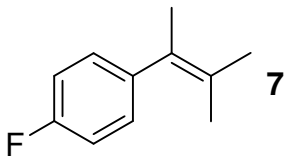
***(S)*-4f**	50	3	2	>99	74	(–)
***(S)*-4g**	50	3	2	>99	27	(–)
***(S)*-4h**	50	3	2	>99	85	(–)
***(S)*-4i**	50	3	2	>99	84	(–)
***(S)*-4j**	50	4	2	>99	62	(–)
***(S)*-4k**	50	4	2	>99	40	(–)
	10	4	2	>99	58	(–)
	5	4	2	>99	69	(–)
***(S)*-4l**	50	3	2	>99	30	(–)
***(S)*-4m**	50	3	2	60	62	(–)
***(R)*-4n**	50	4	2	>99	73	(+)
***(S)*-4o**	50	4	2	86	48	(–)
***(S)*-4p**	50	4	2	>99	42	(–)
***(S)*-4q**	50	4	2	>99	79	(–)

Analytical Data for the hydrogenation product of **5** obtained by reduction using [Ir(**4d**)COD]BAr_F at 5 bar.



1-methoxy-4-(3-methylbutan-2-yl)benzene

Elemental Analysis for $C_{12}H_{18}O$ (178.27) calc.: C, 80.85; H, 10.18; found: C, 80.59; H, 10.02; $[\alpha]_D^{20}$ = –28.4 (c = 1.50, $CHCl_3$ 96% ee); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 0.74 (d, 3H, J_{HH} = 6.7 Hz, CH_3), 0.91 (d, 3H, J_{HH} = 6.7 Hz, CH_3), 1.20 (d, 3H, J_{HH} = 7.1 Hz, CH_3), 1,71 [m, 1H, $(CH_3)_2CH$], 2.38 [m, 1H, CH_3CHC_{Ar}], 3.78 (s, 3H, OCH_3), 6.82 (m_c, 2H, H_{Ar}), 7.07 (m_c, 2H, H_{Ar}); **13C{1H}-NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 18.9 (CH_3), 20.2 (CH_3), 21.0 (CH_3), 34.5 (OCH_3), 45.9 ($C_{Ar}CHCH_3$), 55.2 (OCH_3), 113.3 (HC_{Ar}),128.4 (HC_{Ar}), 139.1(C_{Ar}), 157.6 (CH_3OC_{Ar}); **GC** (Restek Rtx-1701, 0.25 mm, 0.25 µm, 30m, 60 kPa He, 100 °C, 2 min, 7 K/min, 250°C, 15 min): t_R = 13.6 min; **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 100 °C, 0 min, 1 K/min, 120 °C, 0 min, 10 K/min, 180 °C, 2 min): $t_{R(+)}$ = 14.1 min, $t_{R(-)}$ = 14.4 min; **MS** (EI): m/z (%) = 178 (M^+, 12), 135 (100), 121 (4), 105 (11), 91 (10), 77 (6), 65 (4), 51 (2), 41 (4); **IR** (υ[cm^{-1}]) = 2958m, 2933w, 2906w, 2872w, 2834w, 1611m, 1583w, 1511s, 1464m, 1441w, 1373w, 1301w, 1286w, 1259s, 1245s, 1177m, 1088s,br, 1038s, 1015s, 866w, 795s, 638m,br; **TLC** (SiO_2, hexanes:ethyl acetate 50:1) R_f = 0.29.

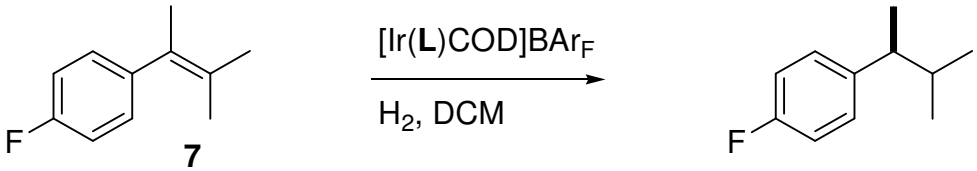


1-fluoro-4-(3-methylbut-2-en-2-yl)benzene

Elemental Analysis for $C_{11}H_{13}F$ (164.22) calc.: C, 80.45; H, 7.89; found: C, 80.52; H, 8.28; **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 1.57 (q, 3H, J_{HH} = 1.5 Hz, CH_3), 1.80 (q, 3H, J_{HH} = 0.9 Hz, CH_3), 1.93 (qq, 3H, J_{HH} = 1.5 Hz, J_{HH} = 0.9 Hz, CH_3), 6.98 (m_c, 2H, H_{Ar}), 7.07 (m_c, 2H, H_{Ar});

$^{13}C\{^1H\}$-NMR (100.6 MHz, $CDCl_3$, 300 K): δ = 20.5 (CH_3), 20.9 (CH_3), 22.0 (CH_3), 114.7 (d, $^2J_{CF}$ = 21.0 Hz, HC_{Ar}), 127.7 (C=C), 129.0 (C_{Ar}), 129.8 (d, $^3J_{CF}$ = 7.7 Hz, HC_{Ar}), 141.1 (C=C), 161.0 (d, $^1J_{CF}$ = 244 Hz, FC_{Ar}); **^{19}F-NMR** (376.5 MHz, $CDCl_3$, 300 K): δ = –118.7 ppm; **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 80 °C, 0 min, 1 K/min, 100 °C, 0 min, 10 K/min, 180 °C, 2 min): t_R = 14.3 min; **MS** (EI): m/z (%) = 164 (M^+, 71), 149 (100), 133 (19), 123 (9), 109 (54), 101 (11), 83 (8), 75 (10), 63 (6), 51 (10); **IR** (υ[cm^{-1}]) = 3042w, 2988w, 2914w, 1601w, 1508s, 1448w, 1373w, 1294w, 1221s, 1157w, 1132w, 1092w, 1016w, 835m, 798w; **TLC** (SiO_2, hexanes:ethyl acetate 60:1) R_f = 0.60.

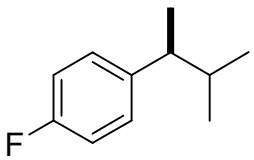
Hydrogenation Results



7

Ligand L	p (H_2) [bar]	Time [h]	mol% Cat.	Conv. [%]	ee [%]	opt. Rotation
***(S)*-4a**	50	4	2	84	48	(–)
***(S)*-4b**	50	4	2	51	65	(–)
***(S)*-4c**	50	4	2	98	69	(–)
***(S)*-4d**	50	4	2	99	79	(–)
***(S)*-4e**	50	4	2	99	75	(–)
	5	8	2	99	89	(–)
***(S)*-4f**	50	4	2	86	64	(–)
***(S)*-4g**	50	4	2	17	63	(–)
***(S)*-4h**	50	4	2	61	24	(–)

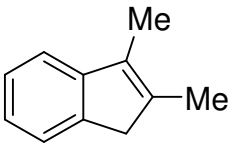
Analytical Data for the hydrogenation product of **7** obtained by reduction using [Ir(**4e**)COD]BAr_F at 5 bar.



1-fluoro-4-(3-methylbutan-2-yl)benzene

Elemental Analysis for $C_{11}H_{15}F$ (166.24) calc.: C, 79.48; H, 9.10; found: C, 79.56; H, 9.02; **$[\alpha]_D^{20}$** = –20.4 (c = 1.88, $CHCl_3$, 89% ee); **^1H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 0.73 (d, 3H, J_{HH} = 6.7 Hz, CH_3), 0.92 (d, 3H, J_{HH} = 6.7 Hz, CH_3), 1.21 (d, 3H, J_{HH} = 7.1 Hz, CH_3), 1.72 (m, 1H, CH), 2.40 (qd, 1H, J_{HH} = 7.2 Hz, J_{HH} = 14.5 Hz, $C_{Ar}CH$), 6.95 (m, 2H, H_{Ar}), 7.09 (m, 2H, H_{Ar}); **$^{13}C\{^1H\}$-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 18.9 (CH_3), 20.1 (CH_3), 21.0 (CH_3), 34.5 (CH), 46.1 ($C_{Ar}CH$), 114.7 (d, $^2J_{CF}$ = 20.8 Hz, HC_{Ar}), 128.9 (d, $^3J_{CF}$ = 7.6 Hz, HC_{Ar}), 142.6 (d, $^4J_{CF}$ = 3.1 Hz, C_{Ar}), 161.1 (d, $^1J_{CF}$ = 242.9 Hz, FC_{Ar}); **^{19}F-NMR** (376.5 MHz, $CDCl_3$, 300 K): δ = –119.3; **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 80 °C, 0 min, 1 K/min, 100 °C, 0 min, 10 K/min, 180 °C, 2 min): $t_{R(+)}$ = 9.5 min, $t_{R(–)}$ = 10.4 min; **MS** (EI): m/z (%) = 166 (M^+, 13), 123 (100), 109 (11), 103 (21), 77 (5); **IR** (υ[cm^{-1}])

= 2960m, 2872m, 1604m, 1508vs, 1460m, 1418w, 1386w, 1374m, 1366w, 1223s, 1096w, 1014m, 834s, 800w, 655m,br; **TLC** (SiO_2, hexanes) $R_f = 0.53$.

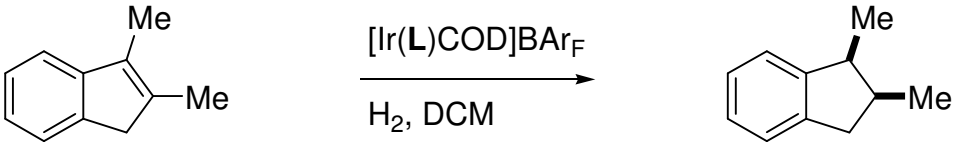


8

2,3-dimethyl-1H-indene

Elemental Analysis for $C_{11}H_{12}$ (144.21) calc.: C, 91.61; H, 8.39; found: C, 91.63; H, 8.44; **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 2.02 (m, 3H, CH_2CCH_3), 2.06 (qd, 3H, J_{HH} = 1.0 Hz, J_{HH} = 1.9Hz, $C_{Ar}CCH_3$), 3.25 (qdd, 2H, J_{HH} = 0.9 Hz, J_{HH} = 2.1 Hz, J_{HH} = 3.8 Hz, CH_2), 7.11 (dt, 1H, J_{HH} = 1.4 Hz, J_{HH} = 7.3 Hz, H_{Ar}), 7.20 (ddd, 1H, J_{HH} = 0.6 Hz, J_{HH} = 1.1 Hz, J_{HH} = 7.6 Hz, H_{Ar}), 7.26 (ttd, 1H, , J_{HH} = 0.6 Hz, J_{HH} = 1.1 Hz, J_{HH} = 7.3 Hz, H_{Ar}), 7.36 (tdd, 1H, J_{HH} = 0.8 Hz, J_{HH} = 1.6 Hz, J_{HH} = 7.3 Hz, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 10.1 ($C_{Ar}CCH_3$), 13.9 (CH_3CCH_2), 42.4 (CH_2), 117.9 (HC_{Ar}), 122.9 (HC_{Ar}), 123.5 (HC_{Ar}), 126.0 (HC_{Ar}), 132.4 (C=C), 138.0 (C=C), 142.3 ($C_{Ar}CH_2$), 147.5 ($C_{Ar}C$); **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 100 °C, 0 min, 4 K/min, 140 °C, 0 min, 10 K/min, 180 °C, 2 min): t_R = 8.6 min; **MS** (EI): m/z (%) = 144 (M^+, 52), 129 (100), 115 (16), 102 (5), 89 (4), 77 (7), 63 (10), 51 (9); **IR** (υ[cm^{-1}]) = 3022m, 3019m, 2958m, 2911s, 1637w, 1606w, 1465s, 1392m, 1228w, 1205w, 1094w, 1016w, 756s, 716s; **TLC** (SiO_2, hexanes) $R_f = 0.40$.

Hydrogenation Results

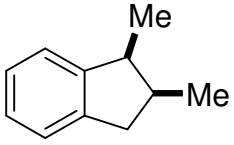


8

Ligand L	p (H_2) [bar]	Time [h]	mol% Cat.	Conv. [%]	ee [%]	opt. Rotation
***(S)*-1a**	50	4	2	>99	84	(+)
***(R,R)*-2a**	50	4	2	>99	83	(–)
***(S)*-3a**	50	4	2	>99	95	(+)
***(S)*-3b**	50	4	2	95	94	(+)
***(S)*-4a**	50	4	2	>99	79	(+)
***(S)*-4b**	50	4	2	>99	63	(+)
***(S)*-4c**	50	4	2	>99	30	(+)
***(S)*-4d**	50	4	2	>99	78	(+)
***(S)*-4e**	50	4	2	>99	78	(+)
***(S)*-4f**	50	4	2	>99	73	(+)
***(S)*-4g**	50	4	2	>99	58	(+)
***(S)*-4h**	50	4	2	>99	11	(+)
***(S)*-4i**	50	4	2	>99	73	(+)
***(S)*-4j**	50	4	2	>99	74	(+)

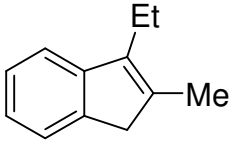
***(S)*-4k**	50	4	2	>99	86	(+)
	50	4	1	>99	86	(+)
	50	4	0.5	>99	83	(+)
	50	4	0.1	94	79	(+)
	5	8	2	>99	93	(+)
***(S)*-4l**	50	4	2	>99	84	(+)
***(S)*-4m**	50	4	2	>99	56	(+)
***(R)*-4n**	50	4	2	>99	80	(–)
***(S)*-4p**	50	4	2	>99	70	(+)
***(S)*-4q**	50	4	2	>99	66	(+)

Analytical Data for the hydrogenation product of **7** obtained by reduction using [Ir(**4k**)COD]BAr_F at 50 bar.



cis-1,2-dimethylindane

Elemental Analysis for $C_{11}H_{14}$ (146.23) calc.: C, 90.35; H, 9.65; found: C, 90.52; H, 9.78; $[\alpha]_D^{20}$ = +13.0 (c = 2.05, $CHCl_3$ 86% ee); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 0.96 (d, 3H, J_{HH} = 6.8, CH_3CHCH_2), 1.12 (d, 3H, J_{HH} = 7.1, CH_3CH), 2.51-2.61 (m, 2H), 2.96 (m_c, 1H), 3.14, (quintet, 1H, J_{HH} = 7.1, CH_3C*H*), 7.10-7.19 (m, 4H, H_{Ar}); **13C{1H}-NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 14.6 (CH_3), 15.1 (CH_2CH*C*H_3), 37.8 (*C*HCH_3),, 39.4 (*C*H_2), 42.4 (CH_2*C*HCH_3), 123.5 (HC_{Ar}), 124.4 (HC_{Ar}), 126.0 (HC_{Ar}), 126.1 (HC_{Ar}), 142.9 (C_{Ar}), 148.8 (C_{Ar}); **MS** (EI): m/z (%) = 146 (M^+, 30), 131 (100), 115 (20), 103 (4), 91 (25), 77 (7), 63 (7), 51 (8), 39 (10); **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 100 °C, 0 min, 4 K/min, 140 °C, 0 min, 10 K/min, 180 °C, 2 min): $t_{R(-)}$ = 5.5 min, $t_{R(+)}$ = 5.8 min; **IR** (υ[cm^{-1}]) = 3069w, 3042w, 3019w, 2958vs, 2928s, 2915s, 2870s, 2840s, 1476s, 1460s, 1448s, 1378m, 1327w, 1260w, 1145w, 1019w, 935w, 759s, 749vs, 730s, 726s, 676m; **TLC** (SiO_2, hexanes) R_f = 0.40.



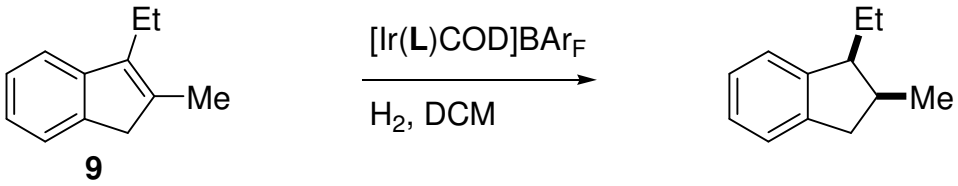
9

3-ethyl-2-methyl-1H-indene

Elemental Analysis for $C_{12}H_{14}$ (158.24) calc.: C, 91.08; H, 8.92; found: C, 91.05; H, 9.00; **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 1.14 (t, 3H, J_{HH} = 7.6 Hz, CH_3CH_2), 2.06 (s, 3H, CH_3), 2.50 (q, 2H, J_{HH} = 7.6 Hz, CH_3CH_2), 3.26 (s, 2H, CH_2), 7.11 (m_c, 1H, H_{Ar}), 7.25 (m_c, 2H, H_{Ar}), 7.36 (m_c, 1H, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 13.3 (*C*H_3), 13.7 (*C*H_3), 18.4 (*C*H_2CH_3), 42.5 (*C*H_2), 118.1 (HC_{Ar}), 123.2 (HC_{Ar}), 123.4 (HC_{Ar}), 125.9 (HC_{Ar}), 137.5 (C=*C*CH_3), 138.7 (C_2H_5*C*=C), 142.7 ($C_{Ar}CH_2$), 146.5 (C_{Ar}C); **GC** (chiral, γ-Cyclodextrin Trifluoracetyl, Chiradex G-TA, 0.25 mm, 30 m, 60 kPa H_2, 95 °C, 13 min, 10 K/min, 160 °C, 5 min): t_R = 16.5 min; **MS** (EI): m/z (%) = 158 (M^+, 64), 143 (100), 129 (53), 115 (16), 71 (5); **IR**

(υ[cm^{-1}]) = 3044s, 3016s, 2965s, 2928s, 2875s, 1629m, 1606m, 1461s, 1393s, 1222w, 1058m, 1020m, 935w, 763s, 721s; **TLC** (SiO_2, hexanes) R_f = 0.27.

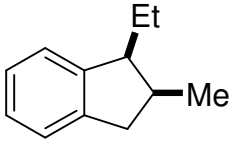
Hydrogenation Results



9

Ligand L	p (H_2) [bar]	Time [h]	mol% Cat.	Conv. [%]	ee [%]	opt. Rotation
***(S)*-1a**	50	4	2	>99	76	(+)
***(R,R)*-2a**	50	4	2	>99	86	(+)
***(S)*-3a**	50	4	2	>99	92	(+)
***(S)*-3b**	50	4	2	98	94	(+)
***(S)*-4a**	50	4	2	>99	79	(+)
***(S)*-4b**	50	4	2	>99	22	(+)
***(S)*-4c**	50	4	2	>99	68	(+)
***(S)*-4d**	50	4	2	>99	74	(+)
***(S)*-4e**	50	4	2	>99	79	(+)
***(S)*-4f**	50	4	2	>99	73	(+)
***(S)*-4g**	50	4	2	>99	1	(+)
***(S)*-4h**	50	4	2	>99	67	(+)
***(S)*-4i**	50	4	2	>99	69	(+)
***(S)*-4j**	50	4	2	>99	76	(+)
***(S)*-4k**	50	4	2	>99	84	(+)
	5	8	2	>99	93	(+)
***(S)*-4l**	50	4	2	>99	48	(+)
***(S)*-4m**	50	4	2	>99	81	(+)
***(R)*-4n**	50	4	2	>99	77	(–)
***(S)*-4p**	50	4	2	>99	75	(+)
***(S)*-4q**	50	4	2	>99	51	(+)

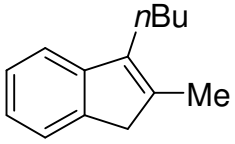
Analytical Data for the hydrogenation product of **9** obtained by reduction using [Ir(**3b**)COD]BAr_F at 50 bar. Residual **9** was oxidized with *m*CPBA [2] and the pure product was obtained after column chromatography (SiO_2, hexanes).



cis-1-ethyl-2-methylindane

Elemental Analysis for $C_{12}H_{16}$ (160.26) calc.: C, 89.94; H, 10.06; found: C, 89.98; H, 9.91; $[\alpha]_D^{20}$ = +1.7 (c = 1.85, $CHCl_3$, 94% ee); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 0.94 (d, 3H, $^3J_{HH}$ = 6.9 Hz, C*H*$_3$), 1.01 (t, 3H, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3), 1.49-1.68 (m, 2H), 2.51-2.66 (m, 2H),

2.87-2.96 (m, 2H), 7.10-7.20 (m, 4H, H_{Ar}); **13C{1H}-NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 12.3 (CH_2CH_3), 14.7 (CH_3), 21.2 (CH_2CH_3), 37.3 ($CHCH_3$), 39.7 (CH_2), 49.6 ($CHCH_2$), 124.2 (HC_{Ar}), 124.5 (HC_{Ar}), 125.7 (HC_{Ar}), 126.0 (HC_{Ar}), 143.4 (C_{Ar}), 147.1 (C_{Ar}); **GC** (Restek Rtx-1701, 0.25 mm, 0.25 µm, 30m, 60 kPa He, 100 °C, 2 min, 7 K/min, 250 °C, 15 min): t_R = 13, 56 min; **GC** (chiral, γ-Cyclodextrin Trifluoracetyl, Chiradex G-TA, 0.25 mm, 30 m, 60 kPa H_2, 95 °C, 13 min, 10 K/min, 180 °C, 2 min): $t_{R(-)}$ = 10.9 min, $t_{R(+)}$ = 11.3 min; **MS** (EI): m/z (%) = 160 (M^+, 16), 143 (1), 131 (100), 115 (14), 91 (17); **IR** (υ[cm^{-1}]) = 3070w, 3024w, 2955s, 2924s, 2839m, 1605w, 1458s, 1373m, 1335w, 1219w, 1142w, 1080w, 1018w, 933w, 748s, 663m; **TLC** (SiO_2, hexanes) R_f = 0.38.

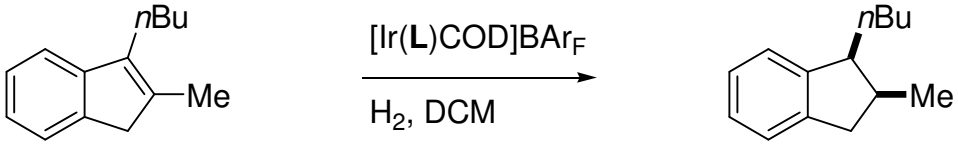


10

3-*butyl*-2-methyl-1H-indene

Elemental Analysis for $C_{14}H_{18}$ (186.29) calc.: C, 90.26; H, 9.74; found: C, 90.13; H, 9.82; **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 0.93 (t, 3H, J_{HH} = 7.3Hz, CH_3CH_2), 1.37 (m_c, 2H, $CH_2CH_2CH_3$), 1.53 (m_c, 2H, CCH_2CH_2), 2.06 (s, 3H, C=CCH_3), 2.51 (t, 2H, J_{HH} = 7.5 Hz, C=CCH_2), 3.26 (s, 2H, $C_{Ar}CH_2$), 7.10 (m_c, 1H, H_{Ar}), 7.24 (m_c, 2H, H_{Ar}), 7.36 (m_c, 1H, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 14.0 (CH_3), 14.0 (CH_3), 22.8 (*butyl*-CH_2), 25.0 (*butyl*-CH_2), 30.9 (*butyl*-CH_2), 42.5 (CH_2), 118.2 (HC_{Ar}), 123.1 (HC_{Ar}), 123.4 (HC_{Ar}), 125.9 (HC_{Ar}), 137.3 (C=CCH_3), 138.1 (C_4H_9C=C), 142.6 ($C_{Ar}CH_2$), 146.9 (C_{Ar}C); **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 130 °C, 10 min, 10 K/min, 180 °C, 2 min): t_R = 12.3 min; **MS** (EI): m/z (%) = 186 (M^+, 56), 143 (100), 129 (49), 128 (50), 115 (17), 77 (2); **IR** (υ[cm^{-1}]) = 3044m, 3016m, 2928s, 2860s, 2361m, 1628m, 1607m, 1461s, 1397m, 1210w, 1156w, 1108w, 1021w, 981w, 933w, 761s, 720s; **TLC** (SiO_2, hexanes:ethyl acetate, 10:1) R_f = 0.69.

Hydrogenation Results

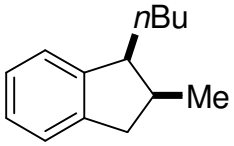


10

Ligand L	p (H_2) [bar]	Time [h]	mol% Cat.	Conv. [%]	ee [%]	opt. Rotation
***(S)*-1a**	50	4	2	>99	81	(–)
***(R,R)*-2a**	50	4	2	>99	88	(–)
***(S)*-3a**	50	4	2	>99	94	(–)
***(S)*-3b**	50	4	2	97	95	(–)
***(S)*-4a**	50	4	2	99	72	(–)
***(S)*-4b**	50	4	2	93	67	(–)
***(S)*-4c**	50	4	2	99	69	(–)
***(S)*-4d**	50	4	2	99	69	(–)

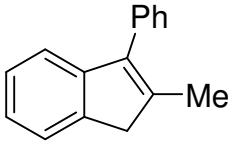
***(S)*-4f**	50	4	2	79	61	(–)
***(S)*-4i**	50	4	2	92	64	(–)
***(S)*-4j**	50	4	2	>99	77	(–)
***(S)*-4k**	50	4	2	>99	90	(–)
	5	8	2	>99	94	(–)
***(S)*-4l**	50	4	2	>99	85	(–)
***(S)*-4m**	50	4	2	22	47	(–)
***(S)*-4p**	50	4	2	>99	81	(–)

Analytical Data for the hydrogenation product of **10** obtained by reduction using [Ir(**4k**)COD]BAr_F at 50 bar.



cis-1-*butyl*-2-methylindane

Elemental Analysis for $C_{14}H_{20}$ (188.31) calc.: C, 89.29; H, 10.71; found: C, 89.45; H, 10.65; $[\alpha]_D^{20}$ = –6.4 (c = 1.39, $CHCl_3$ 90% ee); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 0.91-0.95 (m, 6H, 2×CH_3), 1.38 (m_c, 4H), 1.55 (m_c, 2H), 2.51-2.65 (m, 2H), 2.90-3.00 (m, 2H), 7.11-7.20 (m, 4H, H_{Ar}).**^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 14.1 (CH_3), 14.8 (CH_3), 23.1 (CH_2), 28.1 (CH_2), 30.0 (CH_2), 37.5 ($CHCH_3$), 39.7 (CH_2), 47.9 (CHC_{Ar}), 124.1 (HC_{Ar}), 124.5 (HC_{Ar}), 125.7 (HC_{Ar}), 126.0 (HC_{Ar}), 143.4 (C_{Ar}), 147.2 (C_{Ar}); **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 130 °C, 10 min, 10 K/min, 180 °C, 2 min): $t_{R(+)}$ = 8.5 min, $t_{R(-)}$ = 8.8 min; **MS** (EI): m/z (%) = 188 (M^+, 14), 131 (100), 115 (11), 91 (13); **IR** (υ[cm^{-1}]) = 3019w, 2955s, 2924s, 2871m, 2856m 1475m, 1457m, 1376m, 748m, 737m, 699w; **TLC** (SiO_2, hexanes) R_f = 0.41.

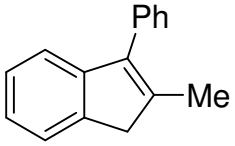


11

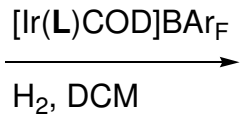
2-methyl-3-phenyl-1H-indene

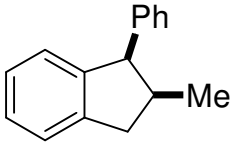
Elemental Analysis for $C_{16}H_{14}$ (206.28) calc.: C, 93.16; H, 6.84; found: C, 93.14; H, 6.88; **M.P.**: 55-56 °C; **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 2.14 (s, 3H, CH_3), 3.46 (s, 2H, CH_2), 7.14-7.17 (m_c, 1H, H_{Ar}), 7.23 (dd, 2H, J_{HH} = 3.6 Hz, H_{Ar}), 7.35 (m_c, 1H, H_{Ar}), 7.39-7.48 (m, 5H, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 14.8 (CH_3), 43.1 (CH_2), 119.2 (HC_{Ar}), 123.4 (HC_{Ar}), 123.9 (HC_{Ar}), 126.1 (HC_{Ar}), 127.0 (HC_{Ar}), 128.4 (HC_{Ar}), 129.1 (HC_{Ar}), 135.5 (*C*=C), 138.6 (C=C), 140.6 (C_{Ar}), 142.4 ($C_{Ar}CH_2$), 146.3 (C_{Ar}); **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 120 °C, 0 min, 4 K/min, 180 °C, 10 min): t_R = 18.3; **MS** (EI): m/z (%) = 206 (M^+, 100), 191 (61), 178 (6), 165 (15), 139 (3), 128 (16), 101 (7), 91 (13), 77 (5), 51 (7); **IR** (υ[cm^{-1}]) = 3076w, 3020w, 2970w, 2905w, 2851w, 2756w, 1616w, 1595w, 1491m, 1458s, 1435s, 1383m, 1352w, 1317w, 1292w, 1151w, 1072m, 1024m, 989w, 939w, 918w, 858w, 771s, 721s, 700s, 638s; **TLC** (SiO_2, hexanes) R_f = 0.29.

Hydrogenation Results



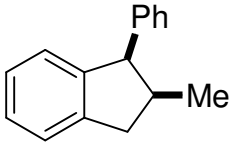
11





Ligand L	p (H_2) [bar]	Time [h]	mol% Cat.	Conv. [%]	ee [%]	opt. Rotation
***(S)*-1a**	50	4	2	99	90	(+)
***(S)*-1b**	50	4	2	11	75	(+)
***(R,R)*-2a**	50	4	2	14	66	(–)
***(S)*-3b**	50	4	2	9	96	(+)
***(S)*-4a**	50	4	2	85	92	(+)
***(S)*-4b**	50	4	2	13	81	(+)
***(S)*-4c**	50	4	2	54	80	(+)
***(S)*-4d**	50	4	2	75	90	(+)
***(S)*-4e**	50	4	2	99	91	(+)
***(S)*-4f**	50	4	2	57	87	(+)
***(S)*-4g**	50	4	2	3	78	(+)
***(S)*-4h**	50	4	2	32	82	(+)
***(S)*-4i**	50	8	2	97	85	(+)
***(S)*-4j**	50	4	2	93	87	(+)
***(S)*-4k**	50	4	2	99	95	(+)
	50	4	1	97	95	(+)
	50	4	0.5	95	95	(+)
	50	4	0.1	84	95	(+)
	10	4	2	91	96	(+)
	5	8	2	78	96	(+)
***(S)*-4l**	50	4	2	22	85	(+)
***(S)*-4m**	50	4	2	22	71	(+)
***(R)*-4n**	50	4	2	88	87	(–)
***(S)*-4p**	50	4	2	99	93	(+)
***(S)*-4q**	50	4	2	>99	92	(+)

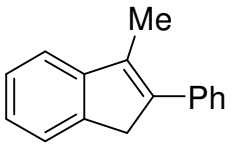
Analytical Data for the hydrogenation product of **11** obtained by reduction using [Ir(**4k**)COD]BAr$_F$ at 50 bar. Residual **11** was oxidized with *m*CPBA [2] and the pure product was obtained after column chromatography (SiO_2, hexanes:ethyl acetate 50:1).



cis-1-phenyl-2-methylindane

Elemental Analysis for $C_{16}H_{16}$ (208.30) calc.: C, 92.26; H, 7.74; found: C, 92.38; H, 7.94; $[\alpha]_D^{20}$ = +56.0 (c = 1.43, $CHCl_3$, 95% ee); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 0.70 (dd, 3H, J_{HH}

= 0.8 Hz, J_{HH} = 7.0 Hz, CH_3), 2.68 (dd, 1H, J_{HH} = 7.4 Hz, J_{HH} = 15.4 Hz, CH_{2a}), 2.83 (m, 1H CHCH$_3$), 3.05 (dd, 1H, J_{HH} = 7.4Hz, J_{HH} = 15.4Hz, CH_{2b}), 4.37 (d, 1H, J_{HH} = 7.9Hz, CHC$_6$H$_5$), 6.98 (m_c, 2H, H_{Ar}), 7.14-7.33 (m_c, 7H, H_{Ar}); **13C{1H}-NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 16.8 (*C*H$_3$), 39.5 (*C*HCH$_3$), 39.7 (*C*H$_2$), 55.3 (*C*HC$_6$H$_5$), 124.5 (H*C*$_{Ar}$), 125.4 (H*C*$_{Ar}$), 126.2 (H*C*$_{Ar}$), 126.4 (H*C*$_{Ar}$), 126.6 (H*C*$_{Ar}$), 128.0 (H*C*$_{Ar}$), 129.1 (H*C*$_{Ar}$), 141.6 (*C*$_{Ar}$), 144.0 (*C*$_{Ar}$), 146.2 (*C*$_{Ar}$); **GC** (Restek Rtx-1701, 0.25 mm, 0.25 µm, 30m, 60 kPa He, 100 °C, 2 min, 7 K/min, 250 °C, 15 min): t_R = 13.6 min; **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 120 °C, 0 min, 4 K/min, 180 °C, 10 min): $t_{R(-)}$ = 13.7 min, $t_{R(+)}$ = 13.9 min; **MS** (EI): m/z (%) = 208 (M^+, 78), 179 (100), 165 (17), 152 (8),130 (22), 115 (30), 91 (18), 77 (7), 63 (8), 51 (9); **IR** (υ[cm^{-1}]) = 3063w, 3022m, 2955m, 2925m, 2902m, 2869w, 2840w, 1600m, 1493m, 1479m, 1451s, 1376m, 1075m, 1031w, 795m, 750s, 737vs, 720m, 700vs; **TLC** (SiO_2, hexanes:ethyl acetate 50:1) R_f = 0.48.

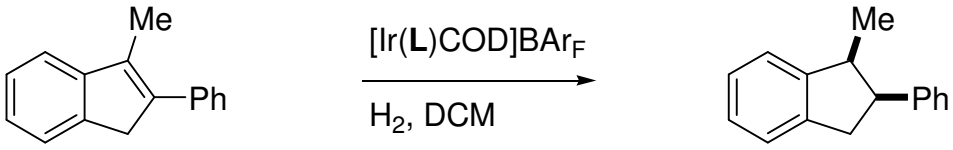


12

3-methyl-2-phenyl-1H-indene

Elemental Analysis for $C_{16}H_{14}$ (206.28) calc.: C, 93.16; H, 6.84; found: C, 93.04; H, 6.87; **M.P.**: 73-74 °C; **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 2.31 (t, 3H, J_{HH} = 2.1 Hz, CH_3), 3.74 (q, 2H, J_{HH} = 2.0 Hz, CH_2), 7.15 (m_c, 1H, H_{Ar}), 7.23 (m_c, 2H, H_{Ar}), 7.33-7-48 (m, 6H, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 11.9 (*C*H$_3$), 41.0 (*C*H$_2$), 119.1 (H*C*$_{Ar}$), 123.3 (H*C*$_{Ar}$), 124.7 (H*C*$_{Ar}$), 126.4 (H*C*$_{Ar}$), 126.6 (H*C*$_{Ar}$), 128.2 (H*C*$_{Ar}$), 128.4 (H*C*$_{Ar}$), 134.7 (*C*$_{quart}$), 137.6 (*C*$_{quart}$), 140.3 (*C*$_{quart}$), 142.4 (*C*$_{quart}$), 147.5 (*C*$_{quart}$); **GC** (Restek Rtx-1701, 0.25 mm, 0.25 µm, 30m, 60 kPa He, 100 °C, 2 min, 7 K/min, 250 °C, 7 min): t_R = 25.5 min; **HPLC** (Daicel Chiracel OJ, 0.46 cm × 25 cm, *n*-Heptane:*iso*-Propanol = 80:20, 0.5 mL/min, 20 °C): t_R = 14.2 min; **MS** (EI): m/z (%) = 206 (M^+, 100), 191 (62), 165 (13), 152 (4), 128 (15), 101 (6), 91 (12), 63 (5), 51 (7); **IR** (υ[cm^{-1}]) = 3070w, 3046w, 3019w, 2010w, 2902w, 2882w, 2858w, 2835w, 1596w, 1492m, 1457m 1438w, 1389m, 1373m, 1298w, 1244w, 1207m, 1187w, 1154w, 1133w, 1106w, 1061w, 1030w, 978w, 940w, 918w, 757vs, 717s, 707m, 697s, 650m; **TLC** (SiO_2, hexanes:ethyl acetate 50:1) R_f = 0.46.

Hydrogenation Results

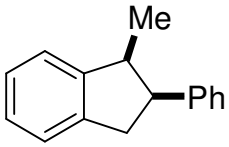


12

Ligand L	p (H_2) [bar]	Time [h]	mol% Cat.	Conv. [%]	ee [%]	opt. Rotation
***(S)*-4a**	50	4	2	11	24	(+)
***(S)*-4b**	50	4	2	2	13	(+)
***(S)*-4c**	50	4	2	11	67	(–)
***(S)*-4d**	50	4	2	15	6	(+)

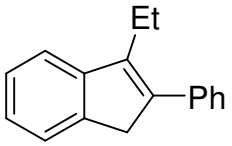
***(S)*-4e**	50	4	2	22	29	(+)
***(S)*-4f**	50	4	2	3	39	(–)
***(S)*-4i**	50	4	2	4	47	(–)
***(S)*-4j**	50	4	2	12	65	(–)
***(S)*-4k**	50	4	2	20	88	(+)
***(S)*-4m**	50	4	2	3	32	(+)
***(R)*-4n**	50	4	2	16	83	(–)
***(S)*-4p**	50	4	2	42	71	(+)

Analytical Data for the hydrogenation product of **12** obtained by reduction using [Ir(**4k**)COD]BAr_F at 50 bar. Residual **13** was oxidized with *m*CPBA [2] and the pure product was obtained after column chromatography (SiO_2, hexanes:ethyl acetate 50:1).



cis-1-methyl-2-phenylindane

Elemental Analysis for $C_{16}H_{16}$ (208.30) calc.: C, 92.26; H, 7.74; found: C, 92.16; H, 7.90; $[\alpha]_D^{20}$ = +163 (c = 1.0, $CHCl_3$ 88% ee); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 0.86 (d, 3H, J_{HH} = 7.3 Hz, CH_3), 3.26 (dq, 2H, J_{HH} = 7.8Hz, J_{HH} = 15.6Hz), 3.51 (quintett, 1H, J_{HH} = 7.3Hz), 3.77 (q, 1H, J_{HH} = 7.8Hz), 7.16-7.32 (m, 9H, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 16.1 (*C*H_3), 36.3 (*C*H_2), 43.7 (*C*H), 49.4 (*C*H), 123.7 (H*C*$_{Ar}$), 124.3 (H*C*$_{Ar}$), 126.1 (H*C*$_{Ar}$), 126.4 (H*C*$_{Ar}$), 126.5 (H*C*$_{Ar}$), 128.1 (H*C*$_{Ar}$), 128.2 (H*C*$_{Ar}$), 142.4 (*C*$_{quart}$), 142.6 (*C*$_{quart}$), 148.4 (*C*$_{quart}$); **GC** (Restek Rtx-1701, 0.25 mm, 0.25 µm, 30m, 60 kPa He, 100 °C, 2 min, 7 K/min, 250 °C, 7 min): t_R = 21.9 min; **HPLC** (Daicel Chiracel OJ, 0.46 cm × 25 cm, *n*-Heptane:*iso*-Propanol = 80:20, 0.5 mL/min, 20 °C): $t_{R(-)}$ = 10.7 min, $t_{R(+)}$ = 22.1 min; **MS** (EI): m/z (%) = 208 (M^+, 97), 193 (86), 178 (48), 165 (17), 151 (3), 130 (100), 115 (88), 91 (38), 77 (18), 65 (14), 63 (12), 51 (18); **IR** (υ[cm^{-1}]) = 3062m, 3041m, 3022m, 2958m, 2926m, 2868m, 2844m, 1603m, 1493s, 1476s, 1453s, 1371w, 1325w, 749vs, 700vs; **TLC** (SiO_2, hexanes:ethyl acetate 50:1) R_f = 0.46.



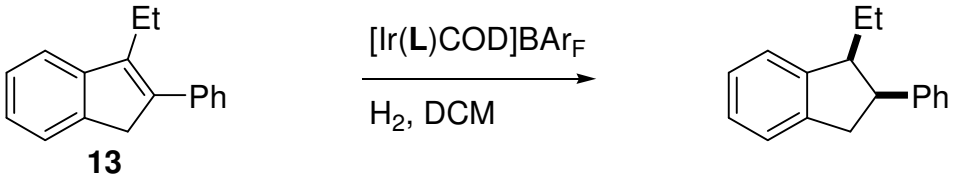
13

3-ethyl-2-phenyl-1H-indene

Elemental Analysis for $C_{17}H_{16}$ (220.31) calc.: C, 92.68; H, 7.32; found: C, 92.76; H, 7.44; **M.P.**: 41 – 42 °C; **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 1.32 (t, 3H, J_{HH} = 7.6 Hz, CH_2CH_3), 2.76 (tq, 2H, J_{HH} = 1.0 Hz, J_{HH} = 7.6 Hz, CH_2CH$_3$), 3.74 (s, 2H, CH_2), 7.21 (dt, 1H, J_{HH} = 1.2 Hz, J_{HH} = 7.4 Hz, H_{Ar}), 7.29 (m_c, 1H, H_{Ar}), 7.34 (m_c, 1H, H_{Ar}), 7.39-7.50 (m, 6H, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 13.7 (*C*H_3), 19.4 (*C*H_2), 41.3 (*C*H_2), 119.4 (H*C*$_{Ar}$), 123.5 (H*C*$_{Ar}$), 124.6 (H*C*$_{Ar}$), 126.3 (H*C*$_{Ar}$), 126.8 (H*C*$_{Ar}$), 128.1 (H*C*$_{Ar}$), 128.4 (H*C*$_{Ar}$), 137.6 (*C*$_{quart}$), 139.9 (*C*$_{quart}$), 140.8 (*C*$_{quart}$), 142.8 (*C*$_{quart}$), 146.4 (*C*$_{quart}$); **GC** (Restek Rtx-1701, 0.25 mm, 0.25 µm, 30m, 60 kPa He, 100 °C, 2 min, 7 K/min, 250 °C, 7 min): t_R = 25.6 min; **HPLC** (Daicel Chiracel OJ, 0.46 cm × 25 cm, *n*-Heptane:*iso*-Propanol = 80:20, 0.5 mL/min, 20 °C): t_R = 12.8 min; **MS** (EI): m/z (%) = 220 (M^+, 100.0), 205 (85), 191 (86), 178 (8), 165 (18), 142 (5), 128 (6),

115 (8), 101 (8), 77 (7), 51 (7); **IR** (υ[cm^{-1}]) = 3077w, 3064w, 3019w, 2965w, 2957w, 2930w, 2871w, 1597w, 1490m, 1458m, 1442m, 1383w, 1372w, 1238w, 1207w, 1151w, 1110w, 1068w, 1051w, 1034w, 1020w, 914w, 858w, 758s, 723s, 694s, 655w; **TLC** (SiO_2, hexanes:ethyl acetate 50:1) R_f = 0.46.

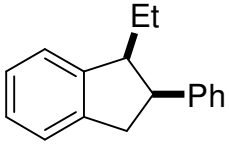
Hydrogenation Results



13

Ligand L	p (H_2) [bar]	Time [h]	mol% Cat.	Conv. [%]	ee [%]	opt. Rotation
***(S)*-4a**	50	4	2	12	70	(–)
***(S)*-4b**	50	4	2	2	55	(–)
***(S)*-4c**	50	4	2	7	19	(+)
***(S)*-4d**	50	4	2	11	37	(–)
***(S)*-4e**	50	4	2	19	72	(–)
***(S)*-4f**	50	4	2	2	48	(–)
***(S)*-4i**	50	4	2	4	24	(–)
***(S)*-4j**	50	4	2	6	30	(–)
***(S)*-4k**	50	4	2	23	93	(–)
***(S)*-4m**	50	4	2	3	31	(–)
***(R)*-4n**	50	4	2	19	82	(+)
***(S)*-4p**	50	4	2	30	84	(–)

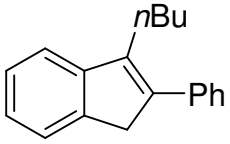
Analytical Data for the hydrogenation product of **13** obtained by reduction using [Ir(**4k**)COD]BAr_F at 50 bar. Residual **13** was oxidized with *m*CPBA [2] and the pure product was obtained after column chromatography (SiO_2, hexanes:ethyl acetate 50:1).



cis-1-ethyl-2-phenylindane

Elemental Analysis for $C_{17}H_{18}$ (222.32) calc.: C, 91.84; H, 8.16; found: C, 91.74; H, 8.20; $[\alpha]_D^{20}$ = -134 (c = 1.66, $CHCl_3$ 93% ee); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 0.82 (t, 3H, J_{HH} = 7.4 Hz, CH_3), 1.18 (dqd, 1H, J_{HH} = 6.2 Hz, J_{HH} = 7.3 Hz, J_{HH} = 14.4 Hz, CH_{2a}CH$_3$), 1.30 (m, 1H), 3.21 (m, 3H), 3.81 (dd, 1H, J_{HH} = 7.7 Hz, J_{HH} = 15.8 Hz), 7.17–7.30 (m, 9H, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 12.1 (CH_3), 22.5 (CH_2), 36.4 (CH_2), 49.7 (C$_{Ar}$CH), 51.0 (C$_{Ar}$CH), 124.5 (HC$_{Ar}$), 124.6 (HC$_{Ar}$), 125.9 (HC$_{Ar}$), 126.1 (HC$_{Ar}$), 126.4 (HC$_{Ar}$), 128.1 (HC$_{Ar}$), 128.2 (HC$_{Ar}$), 142.2 (C_{Ar}), 143.0 (C_{Ar}), 147.1 (C_{Ar}); **GC** (Restek Rtx-1701, 0.25 mm, 0.25 µm, 30m, 60 kPa He, 100 °C, 2 min, 7 K/min, 250 °C, 7 min): t_R = 25.6 min; **HPLC** (Daicel Chiracel OJ, 0.46 cm × 25 cm, *n*-Heptane:*iso*-Propanol = 80:20, 0.5 mL/min, 20 °C): $t_{R(+)}$ = 8.4 min, $t_{R(-)}$ = 19.8 min; **MS** (EI): m/z (%) = 222 (M^+, 47), 193 (100), 178 (22), 165 (9), 144 (5), 131 (13), 115

(63), 91 (26), 77 (8), 65 (7), 51 (7); **IR** (υ[cm^{-1}]) = 3064w, 3022m, 2957m, 2931m, 2872m, 1602w, 1493m, 1474m, 1453m, 1376w, 1329w, 1154w, 1069w, 1031w, 932w, 907w, 759s, 747vs, 728m, 697vs, 650w; **TLC** (SiO_2, hexanes:ethyl acetate 50:1) R_f = 0.37.

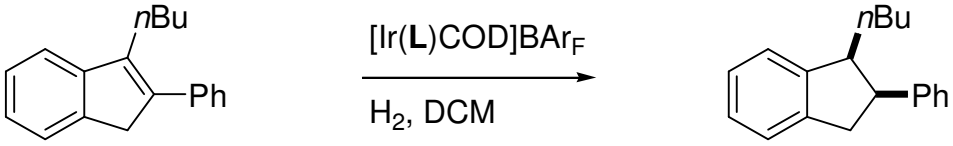


14

3-*butyl*-2-phenyl-1H-indene

Elemental Analysis for $C_{19}H_{20}$ (248.36) calc.: C, 91.88; H, 8.12; found: C, 91.93; H, 8.25; **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 0.94 (t, 3H, J_{HH} = 7.3Hz, CH_3), 1.44 (m, 2H, *butyl*-CH_2), 1.68 (m, 2H, *butyl*-CH_2), 2.72 (m, 2H, *butyl*-CH_2), 3.73 (s, 2H, CCH_2), 7.19-7.49 (m, 9H, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 13.9 (CH_3), 23.1 (CH_2), 26.0 (CH_2), 31.1 (CH_2), 41.4 (CH_2), 119.5 (HC_{Ar}), 123.5 (HC_{Ar}), 124.6 (HC_{Ar}), 126.3 (HC_{Ar}), 126.7 (HC_{Ar}), 128.1 (HC_{Ar}), 128.4 (HC_{Ar}), 137.7 (C_{quart}), 139.6 (C_{quart}), 140.3 (C_{quart}), 142.8 (C_{quart}), 146.7 (C_{quart}); **GC** (Restek Rtx-1701, 0.25 mm, 0.25 µm, 30m, 60 kPa He, 100 °C, 2 min, 7 K/min, 250 °C, 7 min): t_R = 28.2 min; **HPLC**, *Method B*: (Daicel Chiracel OJ, 0.46 cm × 25 cm, *n*-Heptane, 0.5 mL/min, 20 °C): $t_{R(+)}$ and **14** = 17.5 min; (Daicel Chiralpak AD-H, 0.46 cm × 25 cm, *n*-Heptane, 0.5 mL/min, 39 °C): t_R(**14**) = 9.6 min; **MS** (EI): m/z (%) = 248 (M^+, 62), 205 (100), 192 (39), 178 (7), 165 (10), 152 (4), 128 (7), 115 (6), 101 (5), 91 (10), 63 (2), 41 (6); **IR** (υ[cm^{-1}]) = 3054w, 3020w, 2955m, 2926m, 2858m, 1599m, 1492m, 1465s, 1459s, 1442m, 1393m, 1378w, 1245w, 1210w, 1036w, 1022w, 757vs, 718m, 696s; **TLC** (SiO_2, hexanes) R_f = 0.52.

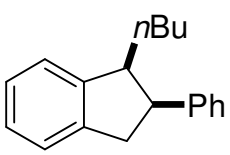
Hydrogenation Results



14

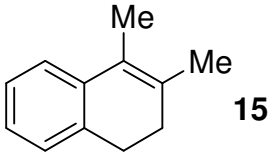
Ligand L	**p (H_2) [bar]**	**Time [h]**	**mol% Cat.**	**Conv. [%]**	**ee [%]**	**opt. Rotation**
***(S)*-1a**	50	4	2	30	75	(+)
***(R,R)*-2a**	50	4	2	4	8	(–)
***(S)*-4k**	50	4	2	14	90	(–)
***(S)*-4p**	50	4	2	21	81	(–)

Analytical Data for the hydrogenation product of **14** obtained by reduction using [Ir(**4k**)COD]BAr_F at 50 bar. Residual **14** was oxidized with *m*CPBA [2] and the pure product was obtained after column chromatography (SiO_2, hexanes).



cis-1-*butyl*-2-phenylindane

Elemental Analysis for $C_{19}H_{22}$ (250.38) calc.: C, 91.14; H, 8.86; found: C, 91.07; H, 8.98; $[\alpha]_D^{20}$ = -11.5 (c = 2.5, $CHCl_3$, 90% ee); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 0.76 (t, 3H, J_{HH} = 7.1Hz, CH_3), 1.15 (m_c, 4H, *butyl*-CH_2), 1.27 (m_c, 2H, *butyl*-CH_2), 3.15 (dd, 1H, J_{HH} = 7.5 Hz, J_{HH} = 15.3 Hz), 3.24–3.33 (m, 2H), 3.79 (q, 1H, J_{HH} = 7.7 Hz), 7.16–7.30 (m, 9H, H_{Ar});**^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 14.0 (*C*H_3), 22.7 (*C*H_2), 29.1 (*C*H_2), 29.7 (*C*H_2), 36.5 (*C*H_2), 49.1 (*C*H), 49.8 (*C*H), 124.5 (H*C*$_{Ar}$), 124.5 (H*C*$_{Ar}$), 125.9 (H*C*$_{Ar}$), 126.1 (H*C*$_{Ar}$), 126.4 (H*C*$_{Ar}$), 128.1 (H*C*$_{Ar}$), 128.2 (H*C*$_{Ar}$), 142.2 (*C*$_{Ar}$), 143.0 (*C*$_{Ar}$), 147.4 (*C*$_{Ar}$); **GC** (Restek Rtx-1701, 0.25 mm, 0.25 µm, 30m, 60 kPa He, 100 °C, 2 min, 7 K/min, 250 °C, 7 min): t_R = 25.4 min; **HPLC**, *Method A*: Residual **14** was oxidized with *m*CPBA [2] and the pure product was obtained after column chromatography (SiO_2, hexanes:ethyl acetate 50:1) for HPLC-analysis: (Daicel Chiracel OJ, 0.46 cm × 25 cm, *n*-Heptane, 0.3 mL/min, 39 °C): $t_{R(+)}$ = 14.6 min, $t_{R(-)}$ = 19.8 min; *Method B*: direct measurement including **14** (Daicel Chiracel OJ, 0.46 cm × 25 cm, *n*-Heptane, 0.5 mL/min, 20 °C): $t_{R(-)}$ = 11.1 min, $t_{R(+)}$ and **14** = 17.5 min; (Daicel Chiralpak AD-H, 0.46 cm × 25 cm, *n*-Heptane, 0.5 mL/min, 39 °C): $t_{R(+/-)}$ = 7.3 min, t_R(**14**) = 9.6 min; **MS** (EI): m/z (%) = 250 (M^+, 37), 193 (100), 178 (16), 117 (14), 115 (43), 91 (20); **IR** (υ[cm^{-1}]) = 3063w, 3021w, 2953w, 2925m, 2870w, 1602w, 1493m, 1475m, 1454m, 1077w, 1032w, 749s, 729w, 698vs; **TLC** (SiO_2, hexanes) R_f = 0.56.

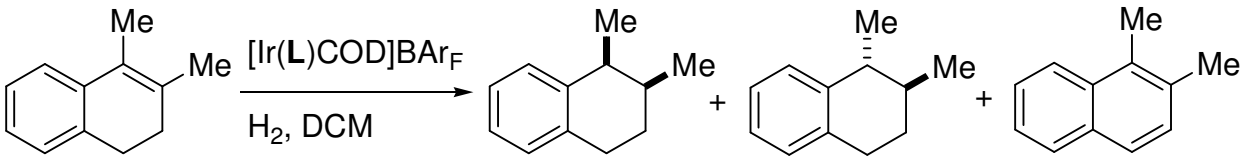


15

3,4-dimethyl-1,2-dihydronaphthalene

Elemental Analysis for $C_{12}H_{14}$ (158.24) calc.: C, 91.08; H, 8.92; found: C, 91.08; H, 8.88; **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 1.91 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.22 (t, 2H, J_{HH} = 7.9 Hz, CH_2CH_2), 2.72 (t, 2H, J_{HH} = 7.9 Hz, $C_{Ar}CH_2$) , 7.07-7.09 (m, 2H, H_{Ar}) , 7.16-7.24 (m, 2H, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 14.2 (*C*H_3), 20.4 (*C*H_3), 28.4 (*C*H_2), 30.6 (*C*H_2), 122.4 (H*C*$_{Ar}$), 125.0 (*C*$_{quart}$), 125.5 (H*C*$_{Ar}$), 126.2 (H*C*$_{Ar}$), 126.9 (H*C*$_{Ar}$), 132.3 (*C*$_{quart}$), 135.3 (*C*$_{quart}$), 137.2 (*C*$_{quart}$); **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 100 °C, 0 min, 4 K/min, 180 °C, 5 min): t_R = 11.6 min; **MS** (EI): m/z (%) = 158 (M^+, 55), 143 (100), 128 (55), 115 (26), 102 (3), 91 (4), 77 (7), 63 (9), 51 (9); **IR** (υ[cm^{-1}]) = 3569w, 3062m, 2989m, 2924s, 2881m, 2829m, 2362m, 1643w, 1487m, 1446m, 1380w, 1279w, 1227w, 1159w, 1073w, 1036m, 759s, 731m; **TLC** (SiO_2, hexanes: ethyl acetate, 10:1) R_f = 0.63.

Hydrogenation Results



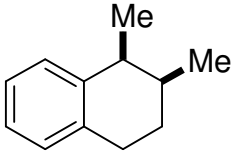
15 **19**

Ligand L	p(H_2) [bar]	Time [h]	mol% Cat.	Conv. [%]*	ee [%]	opt. Rotation	trans-Product [%]	19 [%]
***(R,R)*-2a**	50	4	2	46	77	(+)	0.5	4

***(S)*-3b**	50	4	2	99	70	(–)	13	34
***(S)*-4a**	50	4	2	>99	17	(–)	<0.2	2
***(S)*-4b**	50	4	2	97	8	(–)	<0.5	3
***(S)*-4c**	50	4	2	>99	36	(+)	<0.2	2
***(S)*-4d**	50	4	2	>99	1	(–)	<0.2	2
***(S)*-4e**	50	4	2	>99	16	(–)	<0.5	3
***(S)*-4f**	50	4	2	>99	9	(–)	1	4
***(S)*-4g**	50	4	2	91	9	(–)	1	4
***(S)*-4h**	50	4	2	>99	52	(+)	2	6
***(S)*-4i**	50	4	2	>99	12	(+)	2	4
***(S)*-4j**	50	4	2	93	12	(+)	<0.2	3
***(S)*-4k**	50	4	2	>99	65	(–)	<0.2	3
	50	4	1	>99	63	(–)	<0.2	3
	50	4	0.5	>99	60	(–)	<0.2	3
	50	4	0.1	>99	58	(–)	<0.2	3
	5	8	2	>99	73	(–)	<0.2	11
***(S)*-4l**	50	4	2	93	47	(–)	<0.2	3
***(S)*-4m**	50	4	2	94	39	(+)	<0.2	2
***(R)*-4n**	50	4	2	99	42	(+)	<0.2	3
***(S)*-4p**	50	4	2	>99	43	(–)	<0.2	3
***(S)*-4q**	50	4	2	>99	39	(–)	<0.2	3

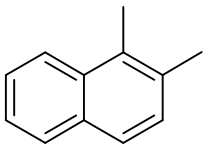
*Conversion includes *trans*-product and **19**.

Analytical Data for the hydrogenation product of **15** obtained by reduction using [Ir(**4k**)COD]BAr_F at 5 bar.



cis-1,2-dimethyl-1,2,3,4-tetrahydronaphthalene

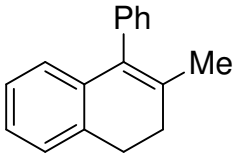
Elemental Analysis for $C_{12}H_{16}$ (160.26) calc.: C, 89.94; H, 10.06; found: C, 90.05; H, 9.90; $[\alpha]_D^{20}$ = –49.3 (c = 2.01, $CHCl_3$ 73% ee); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 0.99 (d, 3H, J_{HH} = 6.9Hz, CH_3), 1.11 (d, 3H, J_{HH} = 7.2Hz, CH_3), 1.64 (dq, 2H, J_{HH} = 2.0Hz, J_{HH} = 6.4Hz), 1.98 (m, 1H), 2.82 (m, 3H), 7.08–7.16 (m, 4H, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 17.4 (CH_3), 18.4 (CH_3), 25.8 (CH_2), 29.0 (CH_2), 32.1 (C*H*), 37.7 (C*H*), 125.4 (HC_{Ar}), 125.4 (HC_{Ar}), 128.9 (HC_{Ar}), 129.0 (HC_{Ar}), 135.9 (C_{Ar}), 143.3 (C_{Ar}); **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 100 °C, 0 min, 4 K/min, 180 °C, 5 min): $t_{R(+)}$ = 8.7 min, $t_{R(–)}$ = 9.3 min; **MS** (EI): m/z (%) = 160 (M^+, 46), 145 (100), 128 (17), 117 (64), 104 (10), 91 (27), 77 (12), 65 (9), 51 (11), 41 (9); **IR** (υ[cm^{-1}]) = 2957m, 2920m, 2871m, 1576m, 1488m, 1463m, 1446m, 1414w, 1377m, 1369m, 1340w, 1255w, 1123w, 1068w, 1052, 1038m, 953w, 909w, 787w, 753vs, 725vs; **TLC** (SiO_2, hexanes) R_f = 0.38.



19

1,2-dimethylnaphthalene

^{1}H-NMR (400.1 MHz, $CDCl_3$, 300K): δ = 2.47 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 7.28 (d, 1H, J_{HH} = 8.3 Hz, H_{Ar}), 7.39 (ddd, 1H, J_{HH} = 1.1 Hz, J_{HH} = 6.8 Hz, J_{HH} = 7.9 Hz, H_{Ar}), 7.47 (ddd, 1H, J_{HH} = 1.4 Hz, J_{HH} = 6.8 Hz, J_{HH} = 8.4 Hz, H_{Ar}), 7.60 (d, 1H, J_{HH} = 8.3 Hz, H_{Ar}), 7.77 (d, 1H, J_{HH} = 8.0 Hz, H_{Ar}), 8.01 (d, 1H, J_{HH} = 8.4Hz); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 14.5 (*C*H_3), 20.8 (*C*H_3), 123.7 (H*C*$_{Ar}$), 124.4 (H*C*$_{Ar}$), 125.6 (H*C*$_{Ar}$), 125.7 (H*C*$_{Ar}$), 128.4 (H*C*$_{Ar}$), 129.0 (H*C*$_{Ar}$), 131.1 (*C*$_{Ar}$), 132.2 (*C*$_{Ar}$), 132.7 (*C*$_{Ar}$), 133.1 (*C*$_{Ar}$); **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 100 °C, 0 min, 4 K/min, 180 °C, 5 min): t_R = 13.5 min; **MS** (EI): m/z (%) = 156 (M^+, 88), 141 (100), 128 (14), 115 (24), 102 (3), 89 (4), 77 (9), 63 (10), 51 (9); **TLC** (SiO_2, hexanes) R_f = 0.27.

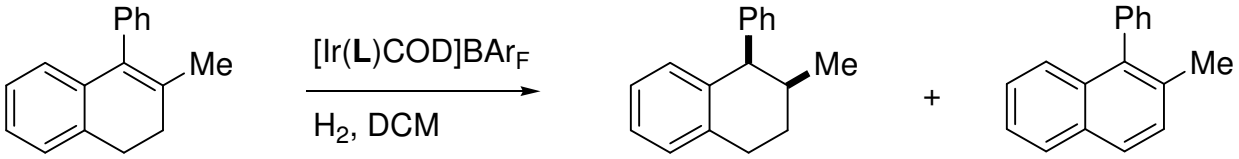


16

3-methyl-4-phenyl-1,2-dihydronaphthalene

Elemental Analysis for $C_{17}H_{16}$ (220.31) calc.: C, 92.68; H, 7.32; found: C, 9.44; H, 7.37; **M.P.**: 34-35 °C; **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 1.73 (s, 3H, CH_3), 2.39 (dt, 2H, J_{HH} = 0.7 Hz, J_{HH} = 8.0 Hz, CH_2) , 2.88 (*pst*, 2H, CH_2), 6.58 (dd, 1H, J_{HH} = 1.1 Hz, J_{HH} = 7.6 Hz, H_{Ar}), 7.00 (m, 1H, H_{Ar}), 7.06 (dt, 1H, J_{HH} = 1.4 Hz, J_{HH} = 7.3 Hz, H_{Ar}), 7.12-7.17 (m, 3H, H_{Ar}), 7.31 (m, 1H, H_{Ar}), 7.40 (m, 2H, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 21.4 (*C*H_3), 28.3 (*C*H_2), 30.2 (*C*H_2), 125.2 (H*C*$_{Ar}$), 125.7 (H*C*$_{Ar}$), 126.1 (H*C*$_{Ar}$), 126.5 (H*C*$_{Ar}$), 127.0 (H*C*$_{Ar}$), 128.3 (H*C*$_{Ar}$), 130.3 (H*C*$_{Ar}$), 133.5 (*C*$_{quart}$), 134.1 (*C*$_{quart}$), 134.8 (*C*$_{quart}$), 136.9 (*C*$_{quart}$), 139.9 (*C*$_{quart}$); **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 80 kPa H_2, 150 °C, 20 min, 10 K/min, 180 °C, 7 min): t_R = 21.6 min; **MS** (EI): m/z (%) = 220 (M^+, 100), 205 (86), 191 (36), 178 (14), 165 (9), 142 (8), 128 (11), 115 (9), 101 (11), 77 (5), 51 (5); **IR** (υ[cm^{-1}]) = 3059w, 3016w, 2984w, 2924m, 2895w, 2822m, 1598w, 1490m, 1481m, 1441m, 1421m, 1376w, 1330w, 1296w, 1277w, 1228w, 1195w, 1175w, 1102w, 1070m, 1042w, 1020m, 1006m, 936w, 921w, 886w, 864w, 822w, 782s, 765s, 751s, 729s, 701s, 661s; **TLC** (SiO_2, hexanes) R_f = 0.19.

Hydrogenation Results



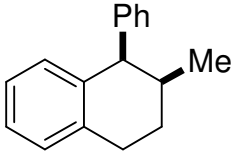
16 **20**

Ligand L	p(H_2) [bar]	Time [h]	mol% Cat.	Conv. [%]*	ee [%]	opt. Rotation	20 [%]

***(R,R)*-2a**	50	4	2	0	n.d.	n.d.	4
***(S)*-3b**	50	4	2	10	38	(–)	5
***(S)*-4a**	50	4	2	24	83	(–)	<1
***(S)*-4b**	50	4	2	3	58	(–)	<1
***(S)*-4c**	50	4	2	32	91	(–)	<1
***(S)*-4d**	50	4	2	36	87	(–)	1
***(S)*-4e**	50	4	2	51	80	(–)	<1
***(S)*-4f**	50	4	2	17	44	(–)	7
***(S)*-4g**	50	4	2	3	64	(–)	<1
***(S)*-4h**	50	4	2	28	84	(–)	4
***(S)*-4i**	50	4	2	50	56	(–)	10
***(S)*-4j**	50	4	2	38	59	(–)	7
***(S)*-4k**	50	4	2	23	88	(–)	<1
***(S)*-4l**	50	4	2	<1	n.d.	n.d.	<1
***(S)*-4m**	50	4	2	3	60	(–)	<1
***(R)*-4n**	50	4	2	17	78	(+)	<1
***(S)*-4p**	50	4	2	44	84	(–)	<1
***(S)*-4q**	50	4	2	45	83	(–)	<1

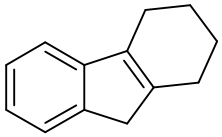
*Conversion includes **20**.

Analytical Data for the hydrogenation product of **16** obtained by reduction using [Ir(**4b**)COD]BAr_F at 50 bar. Residual **16** was oxidized with *m*CPBA [2] and the pure product was obtained after column chromatography (SiO_2, hexanes:ethyl acetate 50:1).



cis-2-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene

Elemental Analysis for $C_{17}H_{18}$ (222.32) calc.: C, 91.84; H, 8.16; found: C, 91.96; H, 8.30; $[\alpha]_D^{20}$ = –347 (c = 0.92, $CHCl_3$ 91% ee); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 0.79 (d, 3H, J_{HH} = 6.9 Hz, CH_3), 1.55-1.72 (m, 2H, CH_2), 2.17 (m_c, 1H, CHCH_3), 2.87-3.02 (m, 2H, CH_2), 4.09 (d, 1H, J_{HH} = 5.3 Hz, CH), 6.92 (d, 1H, J_{HH} = 7.6 Hz, H_{Ar}), 6.96-6.98 (m, 2H, H_{Ar}), 7.03 (t, 1H, J_{HH} = 7.3 Hz, H_{Ar}), 7.10-7.24 (m, 5H, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 19.5 (CH_3), 25.9 (CH_2), 29.0 (CH_2), 33.1 (CH_3CH), 50.3 (C_6H_5CH), 125.6 (HC_{Ar}), 125.8 (HC_{Ar}), 125.9 (HC_{Ar}), 127.4 (HC_{Ar}), 128.8 (HC_{Ar}), 130.5 (HC_{Ar}), 130.7 (HC_{Ar}), 136.8 (C_{Ar}), 139.8 (C_{Ar}), 143.3 (C_{Ar}); **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 80 kPa H_2, 150 °C, 20 min, 10 K/min, 180 °C, 7 min): $t_{R(+)}$ = 17.8 min, $t_{R(–)}$ = 18.6 min; t_R(**20**) = 21.5 min; **MS** (EI): m/z (%) = 222 (M^+, 68), 193 (11), 179 (100),165 (29), 144 (18), 129 (14), 115 (18), 91 (18), 77 (8), 51 (8); **IR** (υ[cm^{-1}]) = 3059w, 3022m, 2955m, 2925s, 2870s, 2837w, 1599w, 1492s, 1452s, 1448s, 1433w, 1376w, 767m, 751m, 737s, 703vs; **TLC** (SiO_2, hexanes:ethyl acetate 50:1) R_f = 0.51.

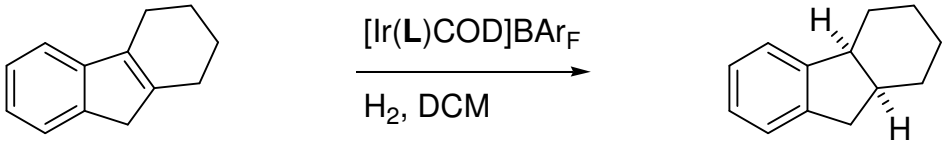


17

1,2,3,4,9-pentahydro-4H-fluorene

Elemental Analysis for $C_{13}H_{14}$ (170.25) calc.: C, 91.71; H, 8.29; found: C, 91.76; H, 8.43; **M.P.**: 42-43 °C; **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 1.79 (m, 4H, CH_2), 2.42 (m, 4H, CH_2), 3.23 (m, 2H, $C_{Ar}CH_2$), 7.11 (dt, 1H, J_{HH} = 1.3Hz, J_{HH} = 7.3Hz, H_{Ar}), 7.19 (ddd, 1H, J_{HH} = 0.7Hz, J_{HH} = 1.1Hz, J_{HH} = 7.4Hz, H_{Ar}), 7.24 (tdt, 1H, J_{HH} = 0.5Hz, J_{HH} = 1.0Hz, J_{HH} = 7.1Hz, H_{Ar}), 7.37 (m, 1H, H_{Ar}); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 22.2 (CH_2), 22.6 (CH_2), 23.2 (CH_2), 25.9 (CH_2), 40.7 ($C_{Ar}CH_2$), 117.4 (HC_{Ar}), 123.3 (HC_{Ar}), 123.6 (HC_{Ar}), 126.0 (HC_{Ar}), 135.8 ($C_{Ar}C$=C), 141.4 ($C_{Ar}C$=C), 142.7 (C_{Ar}), 146.2 (C_{Ar}); **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 100 °C, 0 min, 4 K/min, 140 °C, 0 min, 10 K/min, 180 °C, 4 min): t_R = 15.2; **MS** (EI): m/z (%) = 170 (M^+, 75), 155 (10), 141 (100), 128 (26), 115 (31), 102 (4), 89 (5), 76 (6), 63 (10), 51 (7), 41 (5); **IR** (υ[cm^{-1}]) = 3065w, 3040w, 2925m, 2854m, 2830m, 1630m, 1605w, 1466m, 1456m, 1437m, 1386m, 1277m, 1358w, 1334w, 1320w, 1277m, 1253w, 1235w, 1221w, 1189w, 1175w, 1148w, 1132w, 1110w, 1093w, 1061w, 1018m, 987w, 951w, 936w, 919w, 976w, 860w, 850w, 815w, 752s, 716s, 658m; **TLC** (SiO_2, hexanes) R_f = 0.28.

Hydrogenation Results

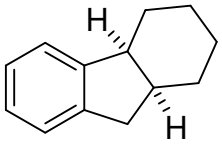


17 **18**

Ligand L	p(H_2) [bar]	Time [h]	mol% Cat.	Conv. [%]	ee [%]	opt. Rotation
***(S)*-1a**	50	4	2	>99	94	(+)
	50	4	1	>99	93	(+)
	50	4	0.5	>99	93	(+)
	50	4	0.1	>99	90	(+)
	5	8	2	>99	94	(+)
***(S)*-1b**	50	4	2	>99	27	(+)
***(S)*-4a**	50	4	2	97	47	(+)
***(S)*-4b**	50	4	2	41	54	(+)
***(S)*-4c**	50	4	2	86	23	(+)
***(S)*-4d**	50	4	2	>99	80	(+)
***(S)*-4e**	50	4	2	>99	86	(+)
***(S)*-4f**	50	4	2	72	7	(+)
***(S)*-4g**	50	4	2	36	30	(+)
***(S)*-4h**	50	4	2	81	0	(+)
***(S)*-4i**	50	4	2	92	5	(+)
***(S)*-4j**	50	4	2	98	5	(+)

***(S)*-4k**	50	4	2	>99	90	(+)
***(S)*-4m**	50	4	2	39	55	(+)
***(R)*-4n**	50	4	2	84	79	(–)
***(S)*-4p**	50	4	2	>99	93	(+)
	5	8	2	>99	96	(+)
***(S)*-4q**	50	4	2	>99	91	(+)

Analytical Data for the hydrogenation product of **17** obtained by reduction using [Ir(**4p**)COD]BAr_F at 50 bar.



cis-1,2,3,4,4a,9,9a-heptahydro-4aH-fluorene

Elemental Analysis for $C_{13}H_{16}$ (172.27) calc.: C, 90.64; H, 9.36; found: C, 90.63; H, 9.49; $[\alpha]_D^{20}$ = +27.6 (c = 1.08, $CHCl_3$, 93% ee); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ = 1.26 (m_c, 2H), 1.32 (m_c, 1H), 1.43 (m_c, 2H), 1.57 (m_c, 1H), 1.77 (m_c, 1H), 1.86 (m_c, 1H), 2.44 (m_c, 1H), 2.58 (dd, 1H, J_{HH} = 4.5 Hz, J_{HH},= 15.1 Hz), 2.85 (dd, 1H, J_{HH} = 6.7 Hz, J_{HH}, = 15.1 Hz), 3.09 (q, 1H, J_{HH} = 5.8 Hz), 7.12–7.16 (m, $3H_{Ar}$), 7.22 (m_c, $1H_{Ar}$); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ = 22.5 (CH_2), 23.8 (CH_2), 27.1 (CH_2), 27.9 (CH_2), 37.9 ($C_{Ar}CH_2$), 39.8 ($C_{Ar}CHCH$), 43.9 ($C_{Ar}CH$), 122.9 (HC_{Ar}), 125.2 (HC_{Ar}), 125.8 (HC_{Ar}), 125.9 (HC_{Ar}), 143.9 ($C_{Ar}CH_2$), 147.0 ($C_{Ar}CH$); **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 100 °C, 0 min, 4 K/min, 140 °C, 0 min, 10 K/min, 180 °C, 4 min): $t_{R(-)}$ = 11.4 min, $t_{R(+)}$ = 11.6 min; **MS** (EI): m/z (%) = 172 (M^+, 59), 157 (2), 143 (12), 129 (100), 115 (38), 104 (5), 91 (11), 77 (7), 63 (7), 51 (7), 41 (8); **IR** (υ[cm^{-1}]) = 3067w, 3042w, 3016w, 2920vs, 2850m, 2365w, 2360w, 1473m, 1458m, 1447m, 764w, 747w, 733m, 682w; **TLC** (SiO_2, hexanes) R_f = 0.38.

[1] Asymmetric Hydrogenation, see: a) A. Lightfoot, P. Schnider, A. Pfaltz, *Angew. Chem.* **1998**, *110*, 3047 – 3050; *Angew. Chem. Int. Ed.* **1998**, *37*, 2897 – 2899; b) A. Pfaltz, J. Blankenstein, R. Hilgraf, E. Hörmann, S. McIntyre, F. Menges, M. Schönleber, S. P. Smidt, B. Wüstenberg, N. Zimmermann, *Adv. Synth. Catal.* **2003**, *345*, 33 – 44; c) G. H. Bernardinelli, E. P. Kündig, P. Meier, A. Pfaltz, K. Radkowski, N. Zimmermann, M. Neuburger-Zehnder, *Helv. Chim. Acta* **2001**, *84*, 3233 – 3246.

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