# Supporting Information

## Asymmetric Synthesis of Axially Chiral Anilides by Enantiotopic Lithiation of Tricarbonyl(*N*-Methyl-*N*-Acyl 2,6-Dimethylanilide)chromium Complex

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**Preparation of tricarbonyl(*N*-methyl-*N*-pivaloyl 2,6-dimethylanilinechromium (1):** To a solution of tricarbonyl(*N*-methyl 2,6-dimethylaniline)chromium (1.0 g, 3.7 mmol) in dry THF (30 mL) was added *n*-BuLi (1.6 M in hexane, 3.5 mL, 5.52 mmol) at –78°C under argon and the resulting mixture was stirred for 1 h. Pivaloylchloride (7.4 mL, 0.9 g) was added to the reaction mixture at –78°C and the mixture was warmed to room temperature over 2 h. The reaction mixture was quenched with saturated aqueous $NH_4Cl$, and extracted with ether. The extract was washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by silica gel column chromatography (hexane/ethyl acetate; 3/1) to give 1.0 g (76%) of **1**. mp. 178°C; $^1$H-NMR ($CDCl_3$) $\delta$ 1.37 (s, 9H), 2.09 (s, 6H), 3.55 (s, 3H), 4.95 (d, 2H, $J = 6.3$ Hz), 5.54 (d, 1H, $J = 6.3$ Hz); IR ($CHCl_3$) 1970, 1880, 1630 cm$^{-1}$; Anal. Calcd. for $C_{17}H_{21}O_4NCr$: C, 57.46; H, 5.96; N, 3.94. Found. C, 57.72; H, 5.89; N, 3.97.

**Preparation of axially chiral anilides 2 by enantiotopic lithiation of *meso* chromium complex 1 with lithium amide 13 followed by electrophilic quenching:** Typical procedure is follows. To a solution of chiral amine **13** (130 mg, 0.45 mmol) in THF (2 mL) was added *n*-BuLi (1.6 M in hexane, 0.26 mL, 0.42 mmol) at 0°C under argon. The mixture was cooled to –78°C and stirred for 30 min. A solution of **1** (100 mg, 0.28 mmol) in THF (3 mL) was added to the above mixtute at –78°C and warmed to –30°C over 1 h. The reaction mixture was again cooled to –78°C and then, methyl iodide (80 mg, 0.56 mmol) was added to the reaction mixture, and the mixture was warmed to –30°C over 30 min. The reaction mixture was quenched with saturated aqueous $NH_4Cl$ and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate; 3/1) to give 90% yield of **2** (E = Me) as yellow crystals. mp. 108°C; $[\alpha]_D^{30}$ –29.4 (*c* 1.8 $CHCl_3$); $^1$H-NMR ($CDCl_3$) δ 1.16 (t, 3H, *J* = 7.6 Hz), 1.36 (s, 9H), 2.07 (s, 3H), 2.41 (dq, 1H, *J* = 15.0, 7.6 Hz), 2.44 (dq, 1H, *J* = 15.0, 7.6 Hz), 3.55 (s, 3H), 4.97 (d, 1H, *J* = 6.3 Hz), 4.98 (d, 1H, *J* = 6.3 Hz), 5.58 (t, 1H, *J* = 6.3 Hz); IR ($CHCl_3$) 1970, 1880, 1630 cm$^{-1}$; Anal. Calcd. for $C_{18}H_{23}O_4NCr$: C, 58.53; H, 6.28; N, 3.79. Found. C, 58.81; H, 6.37; N, 3.77. The enantiomeic excess was determined by chiral HPLC with Chiralpak AS eluted with hexane/2-propanol (20/1); flow rate, 1 mL/min; column temperature, 40°C; UV detector, 254 nm; retention time; 7.6 min and 8.8 min.

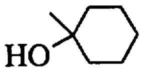
**2** (E = $CH_2Ph$): mp. 118°C; $[\alpha]_D^{30}$ –19.5 (*c* 2.1 $CHCl_3$); $^1$H-NMR ($CDCl_3$) δ 1.37 (s, 9H), 2.09 (s, 3H), 2.48-2.91 (m, 4H), 3.57 (s, 3H), 4.75 (d, 1H, *J* = 6.3 Hz), 4.96 (d, 1H, *J* = 6.3 Hz), 5.50 (t, 1H, *J* = 6.3 Hz), 7.15-7.31 (m, 5H); IR ($CHCl_3$) 1970, 1890, 1640 cm$^{-1}$; Anal. Calcd. for $C_{24}H_{27}O_4NCr$: C, 64.71; H, 6.11; N, 3.14. Found. C, 64.68; H, 6.14; N, 3.10. retention time of chiral HPLC; 8.0 min and 10.9 min.

**2** (E = $CH_2CH{=}CH_2$): mp. 90°C; $[\alpha]_D^{29}$ –25.9 (*c* 1.7 $CHCl_3$); $^1$H-NMR ($CDCl_3$) δ 1.36 (s, 9H), 2.07 (s, 3H), 2.16-2.54 (m, 4H), 3.56 (s, 3H), 4.96 (d, 2H, *J* = 6.3 Hz), 5.01-5.09 (m, 2H), 5.56 (t, 1H, *J* = 6.3 Hz), 5.74-5.89 (m, 1H); IR ($CHCl_3$) 1970, 1880, 1630 cm$^{-1}$; Anal. Calcd. for $C_{20}H_{25}O_4NCr$: C, 60.75; H, 6.37; N, 3.54. Found. C, 60.48; H, 6.09; N, 3.57. retention time of chiral HPLC; 6.7 min and 8.0 min.

**2** (E = $CH_2C{\equiv}CCH_3$): mp. 126°C; $[\alpha]_D^{23}$ –38.5 (*c* 2.0 $CHCl_3$); $^1$H-NMR ($CDCl_3$) δ 1.36 (s, 9H), 1.77 (t, 3H, *J* = 2.3 Hz), 2.06 (s, 3H), 2.24-2.63 (m, 4H), 3.56 (s, 3H), 4.97 (d, 1H, *J* = 6.3 Hz), 5.07 (d, 1H, *J* = 6.3 Hz), 5.57 (t, 1H, *J* = 6.3 Hz); IR ($CHCl_3$) 1960, 1880, 1630 cm$^{-1}$; Anal. Calcd. for $C_{21}H_{25}O_4NCr$: C, 62.20; H, 6.22; N, 3.44. Found. C, 62.50; H, 6.02; N, 3.40. retention time of chiral HPLC; 7.6 min and 10.2 min.

**2** (E = $CH_2C{\equiv}CPh$): mp. 108°C; $^1$H-NMR ($CDCl_3$) δ 1.39 (s, 9H), 2.08 (s, 3H), 2.52-2.71 (m, 4H), 3.59 (s, 3H), 4.99 (d, 1H, *J* = 6.3 Hz), 5.13 (d, 1H, *J* = 6.3 Hz), 5.89 (t, 1H, *J* = 6.3 Hz), 7.27-7.40 (m, 5H); IR ($CHCl_3$) 1980, 1880, 1640 cm$^{-1}$; Anal. Calcd. for $C_{26}H_{27}O_4NCr$: C, 66.52; H, 5.80; N, 2.98. Found. C, 66.40; H, 5.78; N, 2.92. $[\alpha]_D^{23}$ –51.1 (*c* 2.2 $CHCl_3$); retention time of chiral HPLC, 8.3 min and 14.6 min.

**2** (E = $C(OH)Ph_2$): mp. 178°C; $[\alpha]_D^{30}$ –75.7 (*c* 2.2 $CHCl_3$); $^1$H-NMR ($CDCl_3$) δ 1.23 (s, 9H), 2.07 (s, 3H), 3.21 (d, 1H, *J* = 13.8 Hz), 3.59 (s, 3H), 3.65 (d, 1H, *J* = 13.8 Hz), 4.09 (s, 1H), 4.28 (d, 1H, *J* = 6.3 Hz), 4.89 (d, 1H, *J* = 6.3 Hz), 5.28 (t, 1H, *J* = 6.3 Hz), 7.21-7.53 (m, 10H); IR ($CHCl_3$) 3300, 1970, 1890, 1620 cm$^{-1}$; Anal. Calcd. for $C_{30}H_{31}O_5NCr$: C, 67.03; H, 5.81; N, 2.61. Found. C, 67.28; H, 5.77; N, 2.88. retention time of chiral HPLC; 7.2 min and 13.4 min.

**2** (E = ): mp. 123°C; $[\alpha]_D^{30}$ –77.3 (*c* 1.5 $CHCl_3$); $^1$H-NMR ($CDCl_3$) δ 1.12-1.83 (m, 10H), 1.36 (s, 9H), 2.07 (s, 3H), 2.08 (s, 1H), 2.48 (d, 1H, *J* = 18.5 Hz), 2.53 (d, 1H, *J* = 18.5 Hz), 3.85 (s, 3H), 4.95 (d, 1H, *J* = 6.3 Hz), 5.10 (d, 1H, *J* = 6.3 Hz), 5.57 (t, 1H, *J* = 6.3 Hz); IR ($CHCl_3$) 3400, 1960, 1880, 1620 cm$^{-1}$; Anal. Calcd. for $C_{23}H_{31}O_5NCr$: C, 60.92; H, 6.89; N, 3.09. Found. C, 60.71; H, 6.64; N, 3.06. retention time of chiral HPLC; 11.9 min and 21.9 min.

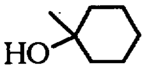
**2** (E = COPh): mp. 103°C; $[\alpha]_D^{22}$ –15.0 (*c* 0.8 $CHCl_3$); $^1$H-NMR ($CDCl_3$) δ 1.15 (s, 9H), 2.08 (s, 3H), 3.57 (s, 3H), 3.70 (d, 1H, *J* = 16.0 Hz), 4.21 (d, 1H, *J* = 16.0 Hz), 5.03 (d, 1H, *J* = 6.3 Hz), 5.16 (d, 1H, *J* = 6.3 Hz), 5.63 (t, 1H, *J* = 6.3 Hz), 7.45-7.62 (m, 3H), 7.92 (d, 2H, *J* = 7.7 Hz); IR ($CHCl_3$) 1980, 1890, 1680, 1640 cm$^{-1}$; Anal. Calcd. for $C_{24}H_{25}O_5NCr$: C, 62.74; H, 5.48; N, 3.05. Found. C, 63.47; H, 5.86; N, 2.82. retention time of chiral HPLC; 17.5 min and 20.3 min.

**Preparation of axially chiral anilides 14 by photo-oxidative metalation:** A solution of **2** (E = Me) (260 mg, 0.71 mmol) in ether (5 mL) was exposed to sunlight at 0°C for 1 h until a yellow color was disappeared. A precipitate was filtered and washed with ether. The ether layer was evaporated under reduced pressure to give 161 mg (98%) of **14** (E = Me) as colorless oil. Optical purity was determined by $^1$H-NMR spectrum in the presence of Eu(tfc)$_3$. mp. 33°C; $[\alpha]_D^{24}$ –4.9 (*c* 3.0 $CHCl_3$) $^1$H NMR ($CDCl_3$) for major *cis*-rotamer: δ 0.97 (s, 9H), 1.23 (t, 3H, *J* = 7.6 Hz), 2.24 (s, 3H), 2.58 (q, 2H, *J* = 7.6 Hz), 3.11 (s, 3H), 7.05-7.22 (m, 3H); for minor *trans*-rotamer: δ 1.20 (t, 3H, *J* = 7.6 Hz), 1.42 (s, 9H), 2.15 (s, 3H), 2.58 (q, 2H, *J* = 7.6 Hz), 3.34 (s, 3H), 7.05-7.22 (m, 3H); IR ($CHCl_3$) 1610, 1420 cm$^{-1}$.

**14** (E = $CH_2Ph$): Optical purity was determined by HPLC with chiralpak AS (hexane/2-propanol 20/1), flow rate 1 mL/min; column temperature 40°C; UV detector 254 nm; retention time 13.8 min for (*S*)-isomer, 15.1 min for (*R*)-isomer; mp. 43°C; $[\alpha]_D^{30}$ −11.9 (*c* 1.3 $CHCl_3$) $^1H$ NMR ($CDCl_3$) for major *cis*-rotamer: δ 0.96 (s, 9H), 2.23 (s, 3H), 2.86-2.93 (m, 4H), 3.00 (s, 3H), 7.10-7.30 (m, 8H); for minor *trans*-rotamer: δ 1.41 (s, 9H), 2.16 (s, 3H), 2.86-2.93 (m, 4H), 3.25 (s, 3H), 7.10-7.30 (m, 8H); IR ($CHCl_3$) 1620, 1460 $cm^{-1}$; Anal. Calcd. for $C_{21}H_{27}ON$: C, 81.51; H, 8.79; N, 4.53. Found. C, 81.80; H, 9.07; N, 4.42.

**14** (E = $CH_2CH{=}CH_2$): $[\alpha]_D^{21}$ −9.4 (*c* 2.6 $CHCl_3$); $^1H$ NMR ($CDCl_3$) for major *cis*-rotamer: δ 0.90 (s, 9H), 2.16 (s, 3H), 2.24-2.60 (m, 4H), 3.03 (s, 3H), 4.88-5.00 (m, 2H), 5.69-5.84 (m, 1H), 6.99-7.20 (m, 3H); minor *trans*-rotamer: δ 1.33 (s, 9H), 2.07 (s, 3H), 2.24-2.60 (m, 4H), 3.26 (s, 3H), 4.88-5.00 (m, 2H), 5.69-5.84 (m, 1H), 6.99-7.20 (m, 3H); IR ($CHCl_3$) 1610, 1440 $cm^{-1}$; MS (relative intensity) *m/z* 259 (M+, 64), 202 (47), 174 (26), 160 (22), 98 (100); HRMS calcd for $C_{17}H_{25}ON$: 259.1942, found 259.1939.

**14** (E = $C(OH)Ph_2$): mp. 183 °C; $[\alpha]_D^{22}$ +78.1 (*c* 3.7 $CHCl_3$); $^1H$ NMR ($CDCl_3$) for major *trans*-rotamer: δ 1.30 (s, 9H), 2.14 (s, 3H), 3.31 (s, 3H), 3.48 (d, 1H, *J* = 14.0 Hz), 3.74 (d, 1H, *J* = 14.0 Hz), 4.26 (s, 1H), 6.36-7.58 (m, 13H); minor *cis*-rotamer: δ 0.98 (s, 9H), 2.18 (s, 1H), 2.19 (s, 3H), 2.96 (s, 3H), 3.40 (d, 1H, *J* = 14.0 Hz), 3.68 (d, 1H, *J* = 14.0 Hz), 6.36-7.58 (m, 13H); IR ($CHCl_3$) 3320, 1610, 1460 $cm^{-1}$; Anal. Calcd. for $C_{27}H_{31}O_2N$: C, 80.76; H, 7.78; N, 3.49. Found. C, 80.98; H, 7.71; N, 3.39.

**14** (E =  ): mp 134 °C; $[\alpha]_D^{23}$ +9.0 (*c* 1.5 $CHCl_3$); $^1H$ NMR ($CDCl_3$) for major *trans*-rotamer: δ 1.24-1.65 (m, 10H), 1.42 (s, 9H), 2.14 (s, 3H), 2.66 (s, 1H), 2.67 (d, 1H, *J* = 14.0 Hz), 2.76 (d, *J* = 14.0 Hz), 3.34 (s, 3H), 7.12-7.43 (m, 3H); minor *cis*-rotamer: δ 0.94 (s, 9H), 1.24-1.65 (m, 10H), 2.24 (s, 3H), 2.32 (s, 1H), 2.67 (d, 1H, *J* = 14.0 Hz), 2.76 (d, *J* = 14.0 Hz), 3.16 (s, 3H), 7.12-7.43 (m, 3H); IR ($CHCl_3$) 3390, 1640, 1460 $cm^{-1}$; Anal. Calcd. for $C_{20}H_{31}ON$: C, 75.67; H, 9.84; N, 4.41. Found. C, 75.64; H, 9.73; N, 4.34.

**14** (E = $CH_2C{\equiv}CCH_3$): $[\alpha]_D^{22}$ −27.3 (*c* 1.5 $CHCl_3$); $^1H$ NMR ($CDCl_3$) for major *cis*-rotamer: δ 0.98 (s, 9H), 1.75 (t, 3H, *J* = 2.6 Hz), 2.24 (s, 3H), 2.34-2.47 (m, 2H), 2.66-2.82 (m, 2H), 3.13 (s, 3H), 7.09-7.23 (m, 3H); minor *trans*-rotamer: δ 1.42 (s, 9H), 1.76 (t, 3H, *J* = 2.6 Hz), 2.15 (s, 3H), 2.34-2.47 (m, 2H), 2.66-2.82 (m, 2H), 3.35 (s, 3H), 7.09-7.23 (m, 3H); IR ($CHCl_3$) 2320, 1610, 1420 cm$^{-1}$; MS (relative intensity) *m/z* 271 (M$^+$, 45), 256 (11), 214 (100), 98 (73); HRMS calcd for $C_{18}H_{25}ON$: 271.1916, found 271.1927.

**14** (E = $CH_2C{\equiv}CPh$): $[\alpha]_D^{22}$ –47.1 (*c* 1.3 $CHCl_3$); $^1H$ NMR ($CDCl_3$) for major *cis*-rotamer: δ 0.99 (s, 9H), 2.25 (s, 3H), 2.60-2.95 (m, 4H), 3.16 (s, 3H), 7.10-7.36 (m, 8H); minor *trans*-rotamer: δ 1.44 (s, 9H), 2.16 (s, 3H), 2.60-2.95 (m, 4H), 3.37 (s, 3H), 7.10-7.36 (m, 8H); IR ($CHCl_3$) 2320, 1610, 1420 cm$^{-1}$; MS (relative intensity) *m/z* 333 (M$^+$, 50), 318 (17), 276 (100), 215 (89); HRMS calcd for $C_{23}H_{27}ON$: 333.2100, found 333.2096.

**14** (E = COPh): $[\alpha]_D^{20}$ –40.9 (*c* 1.3 $CHCl_3$); $^1H$ NMR ($CDCl_3$) for major *cis*-rotamer: δ 1.02 (s, 9H), 2.27 (s, 3H), 3.03 (s, 3H), 4.20 (d, 1H *J* = 16.0 Hz), 4.38 (d, 1H *J* = 16.0 Hz), 7.05-8.02 (m, 8H); minor *trans*-rotamer: δ 1.31 (s, 9H), 2.19 (s, 3H), 3.25 (s, 3H), 4.12 (d, 1H *J* = 16.0 Hz), 4.21 (d, 1H *J* = 16.0 Hz), 7.05-8.02 (m, 8H); IR ($CHCl_3$) 1680, 1640, 1430 cm$^{-1}$; MS (relative intensity) *m/z* 323 (M$^+$, 89), 308 (13), 266 (40), 222 (100); HRMS calcd for $C_{21}H_{25}O_2N$: 323.1878, found 323.1882.