

## Supporting Materials:

### Asymmetric Synthesis of Axially Chiral Benzamides and Anilides by Enantiotopic Lithiation of Prochiral Arene Chromium Complexes

Hiroshige Koide,<sup>a</sup> Takeshi Hata<sup>a</sup> and Motokazu Uemura<sup>\*,a,b</sup>

<sup>a</sup>; *Department of Chemistry, Faculty of Integrated Arts and Sciences, Osaka Prefecture University, Sakai, Osaka 599-8531 Japan.*

<sup>b</sup>; *Research Institute for Advanced Science and Technology, Osaka Prefecture University, Sakai, Osaka 599-8570, Japan.*

#### Experimental Section

All manipulations involving organometallics were carried out under an atmosphere of nitrogen or argon with inert gas/vacuum double-manifold techniques. All melting points were determined on a Yanagimoto MPJ-2 micro melting point apparatus and uncorrected. <sup>1</sup>H-NMR spectra were measured on a JEOL EX-270. All NMR spectra were recorded in CDCl<sub>3</sub> solvent with tetramethylsilane as an internal reference. IR spectra were determined on a JASCO A-100 spectrometer. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl immediately before use. Methylene chloride was distilled over P<sub>2</sub>O<sub>5</sub> before use. Optical rotations were measured on a JASCO DIP-370 automatic polarimeter at 589 nm (sodium D line) using a 0.5 dm cell.

**Preparation of Tricarbonyl(*N,N*-diethyl 2,6-dimethylbenzamide)chromium (1).** To a solution of tricarbonyl(*N,N*-diethyl 2-methylbenzamide)chromium<sup>12</sup> (982 mg, 3.0 mmol), TMEDA (418 mg, 0.75 mmol) in dry THF (30 mL) was added *s*-BuLi (1.0 M in cyclohexane, 3.6 mL, 3.6 mmol) at -78 °C under argon and the resulting mixture was stirred for 1 h. Methyl iodide (1.28 g, 9.0 mmol) was added to the reaction mixture at -78 °C and the mixture was warmed to 0 °C over 2 h. The reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl, and extracted with ether. The extract was washed with brine, dried over MgSO<sub>4</sub> and evaporated in vacuo. The residue was purified by silica gel column

chromatography (hexane/ethyl acetate; 2/1) to give 768 mg (75%) of **1**. mp. 153 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 1.09 (t, 3H, *J* = 7.3 Hz), 1.22 (t, 3H, *J* = 7.3 Hz), 2.20 (s, 6H), 3.24 (q, 2H, *J* = 7.3 Hz), 3.53 (q, 2H, *J* = 7.3 Hz), 4.93 (d, 2H, *J* = 6.3 Hz), 5.36 (t, 1H, *J* = 6.3 Hz); IR (CHCl<sub>3</sub>) 1970, 1890, 1630 cm<sup>-1</sup>; Anal. Calcd. for C<sub>16</sub>H<sub>19</sub>NO<sub>4</sub>Cr: C, 56.31; H, 5.61; N, 4.10. Found. C, 56.53; H, 5.35; N, 3.85.

**Tricarbonyl(*N*-methyl-*N*-pivaloyl 2,6-dimethylaniline)chromium (14a).** 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 mmol, 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<sub>4</sub>Cl, and extracted with ether. The extract was washed with brine, dried over MgSO<sub>4</sub> 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 **14a**. mp. 178 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 1.37 (s, 9H), 2.09 (s, 6H), 3.55 (s, 3H), 4.95 (d, 2H, *J* = 6.3 Hz), 5.54 (t, 1H, *J* = 6.3 Hz); IR (CHCl<sub>3</sub>) 1970, 1880, 1630 cm<sup>-1</sup>; Anal. Calcd. for C<sub>17</sub>H<sub>21</sub>NO<sub>4</sub>Cr: C, 57.46; H, 5.96; N, 3.94. Found. C, 57.72; H, 5.89; N, 3.97.

**Tricarbonyl(*N*-ethyl-*N*-pivaloyl 2,6-dimethylaniline)chromium (14b).** mp. 141 °C (dec); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 1.38 (s, 9H), 1.51 (t, 3H, *J* = 7.0 Hz), 2.07 (s, 6H), 3.92 (q, 2H, *J* = 7.0 Hz), 4.99 (d, 2H, *J* = 6.2 Hz), 5.58 (t, 1H, *J* = 6.3 Hz); IR (CHCl<sub>3</sub>) 1970, 1880, 1630 cm<sup>-1</sup>; Anal. Calcd. for C<sub>18</sub>H<sub>23</sub>NO<sub>4</sub>Cr: C, 58.53; H, 6.28; N, 3.79. Found. C, 58.43; H, 5.99; N, 3.68.

**Tricarbonyl(*N*-methoxymethyl-*N*-pivaloyl 2,6-dimethylaniline)chromium (14c).** mp. 79 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 1.38 (s, 9H), 2.13 (s, 6H), 3.39 (s, 3H), 3.61-3.72 (m, 4H), 4.91 (d, 2H, *J* = 6.2 Hz), 5.17 (s, 2H), 5.59 (t, 1H, *J* = 6.2 Hz); IR (CHCl<sub>3</sub>) 1970, 1880, 1640 cm<sup>-1</sup>; Anal. Calcd. for C<sub>20</sub>H<sub>27</sub>NO<sub>6</sub>Cr: C, 55.94; H, 6.34; N, 3.26. Found. C, 56.20; H, 6.36; N, 3.19.

**Tricarbonyl(*N*-methyl-*N*-pivaloyl 2,6-diethylaniline)chromium (16).** mp. 130 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 1.17 (t, 6H, *J* = 7.3 Hz), 1.36 (s, 9H), 2.32-2.47 (m, 4H), 3.55 (s, 3H), 5.01 (d, 2H, *J* = 6.3 Hz), 5.63 (t, 1H, *J* = 6.3 Hz); IR (CHCl<sub>3</sub>) 1970, 1880, 1640 cm<sup>-1</sup>; Anal. Calcd. for C<sub>19</sub>H<sub>25</sub>NO<sub>4</sub>Cr: C, 59.52; H, 6.57; N, 3.65. Found. C, 59.80; H, 6.42; N, 3.75.

**Tricarbonyl(*N*-methyl-*N*-benzoyl 2,6-dimethylaniline)chromium (21a).** mp. 139 °C (dec); 1 : 1 ratio of *trans*- and *cis* rotamers in CDCl<sub>3</sub> solution; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) for *trans* rotamer: δ 2.27 (s, 6H), 3.36 (s, 3H), 4.85 (d, 2H, *J* = 6.3 Hz), 5.59 (t, 1H, *J* = 6.3 Hz), 7.18-7.52 (m, 5H); for *cis*

rotamer:  $\delta$  2.20 (s, 6H), 3.49 (s, 3H), 5.04 (d, 2H,  $J = 6.3$  Hz), 5.39 (t, 1H,  $J = 6.3$  Hz), 7.18-7.52 (m, 5H); IR (CHCl<sub>3</sub>) 1970, 1880, 1640 cm<sup>-1</sup>; Anal. Calcd. for C<sub>19</sub>H<sub>17</sub>NO<sub>4</sub>Cr: C, 60.80; H, 4.56; N, 3.73. Found. C, 61.05; H, 4.50; N, 3.64.

**Tricarbonyl(*N*-methyl-*N*-*o*-methylbenzoyl 2,6-dimethylaniline)chromium (21b).** mp. 140 °C (dec); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  2.30 (s, 6H), 2.36 (s, 3H), 3.21 (s, 3H), 5.04 (d, 2H,  $J = 6.3$  Hz), 5.59 (t, 1H,  $J = 6.3$  Hz), 7.15-7.37 (m, 4H); IR (CHCl<sub>3</sub>) 1970, 1880, 1640, 1410 cm<sup>-1</sup>; Anal. Calcd. for C<sub>20</sub>H<sub>19</sub>NO<sub>4</sub>Cr: C, 61.69; H, 4.92; N, 3.60. Found. C, 61.95; H, 4.65; N, 3.35.

### Asymmetric Lithiation of Prochiral Arene Chromium Complexes with Chiral Lithium Amide.

Typical procedure is as follows. To a solution of (*R,R*)-bis- $\alpha$ -phenylethylamine (**3**) (101 mg, 0.45 mmol) in dry THF (1.5 mL) was added *n*-BuLi (1.6 M in hexane, 0.23 mL, 0.36 mmol) at -78 °C under argon, and the mixture was stirred for 30 min. To the mixture was added a solution of *N,N*-diethyl 2,6-dimethylbenzamide chromium complex (**1**) (102 mg, 0.30 mmol) in THF (1.5 mL) at -78 °C and the mixture was warmed to -30 °C over 1 h. The reaction mixture was again cooled to -78 °C and then, a solution of MeI (90 mg, 0.60 mmol) in THF (0.5 mL) was added to the reaction mixture. The mixture was warmed to -30 °C and quenched with saturated aqueous NH<sub>4</sub>Cl, extracted with ether. The organic layer was washed with brine, dried over MgSO<sub>4</sub> and evaporated under reduced pressure. The residue was purified by silica gel column chromatography to give 90 mg (85%) of (+)-*N,N*-diethyl 2-ethyl-6-methylbenzamide chromium complex **2**. mp. 99 °C;  $[\alpha]_D^{26} +27.0$  (*c* 0.2, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.12 (t, 3H,  $J = 7.3$  Hz), 1.21 (t, 3H,  $J = 7.3$  Hz), 1.22 (t, 3H,  $J = 7.3$  Hz), 2.20 (s, 3H), 2.46-2.64 (m, 2H), 3.22-3.29 (m, 2H), 3.50-3.59 (m, 2H), 4.96 (d, 1H,  $J = 6.3$  Hz), 5.02 (d, 1H,  $J = 6.3$  Hz), 5.37 (t, 1H,  $J = 6.3$  Hz); IR (CHCl<sub>3</sub>) 1970, 1890, 1630 cm<sup>-1</sup>; Anal. Calcd. for C<sub>17</sub>H<sub>21</sub>NO<sub>4</sub>Cr: C, 57.46; H, 5.96; N, 3.94. Found. C, 57.30; H, 5.92; N, 3.93. The optical purity was determined as 86% ee by chiral HPLC with Chiralcell OJ-H eluted with hexane/2-propanol (1/1); flow rate, 0.5 mL/min; column temperature, 40 °C; UV detector, 254 nm; retention time; 13.5 min and 17.2 min.

**2 (E = CH<sub>2</sub>Ph).** mp. 144 °C;  $[\alpha]_D^{27} +24.0$  (*c* 0.2, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.14 (t, 3H,  $J = 7.3$  Hz), 1.20 (t, 3H,  $J = 7.3$  Hz), 2.21 (s, 3H), 2.75-2.93 (m, 4H), 3.18-3.35 (m, 2H), 3.54 (q, 2H,  $J = 7.3$  Hz), 4.98 (d, 2H,  $J = 6.3$  Hz), 5.34 (t, 1H,  $J = 6.3$  Hz), 7.16-7.32 (m, 5H); IR (CHCl<sub>3</sub>) 1970, 1890, 1630, 1435 cm<sup>-1</sup>; Anal. Calcd. for C<sub>23</sub>H<sub>25</sub>NO<sub>4</sub>Cr: C, 64.03; H, 5.84; N, 3.25. Found. C, 64.26; H, 5.66; N, 3.06. retention time; 13.4 min and 16.8 min.

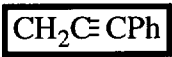
**2** (E = CH<sub>2</sub>CH=CH<sub>2</sub>). mp. 88 °C; [ $\alpha$ ]<sub>D</sub><sup>30</sup> +26.7 (c 0.6, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.14 (t, 3H, *J* = 7.3 Hz), 1.21 (t, 3H, *J* = 7.3 Hz), 2.20 (s, 3H), 2.29-2.37 (m, 2H), 2.57-2.62 (m, 2H), 3.18-3.33 (m, 2H), 3.41-3.69 (m, 2H), 4.97 (d, 1H, *J* = 6.3 Hz), 5.02 (d, 1H, *J* = 6.3 Hz), 5.03-5.13 (m, 2H), 5.36 (t, 1H, *J* = 6.3 Hz), 5.75-5.90 (m, 1H); IR (CHCl<sub>3</sub>) 1970, 1890, 1630, 1435 cm<sup>-1</sup>; Anal. Calcd. for C<sub>19</sub>H<sub>23</sub>NO<sub>4</sub>Cr: C, 59.83; H, 6.08; N, 3.67. Found. C, 60.12; H, 6.00; N, 3.77. retention time; 12.3 min and 18.1 min.

**15a** (E = Me). mp. 108 °C; [ $\alpha$ ]<sub>D</sub><sup>30</sup> -29.4 (c 1.8, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  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<sub>3</sub>) 1970, 1890, 1640 cm<sup>-1</sup>; Anal. Calcd. for C<sub>18</sub>H<sub>23</sub>NO<sub>4</sub>Cr: C, 58.53; H, 6.28; N, 3.79. Found. C, 58.81; H, 6.37; N, 3.77. The enantiomeric 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.

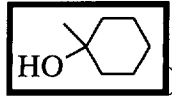
**15a** (E = CH<sub>2</sub>Ph). mp. 118 °C; [ $\alpha$ ]<sub>D</sub><sup>31</sup> -19.5 (c 2.1, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.37 (s, 9H), 2.09 (s, 3H), 2.48-2.91 (m, 4H), 3.57 (s, 3H), 4.75 (d, 1H, *J* = 6.3 Hz), 4.96 (d, 1H, *J* = 6.3 Hz), 5.50 (t, 1H, *J* = 6.3 Hz), 7.15-7.31 (m, 5H); IR (CHCl<sub>3</sub>) 1970, 1890, 1640 cm<sup>-1</sup>; Anal. Calcd. for C<sub>24</sub>H<sub>27</sub>NO<sub>4</sub>Cr: C, 64.71; H, 6.11; N, 3.14. Found. C, 64.68; H, 6.14; N, 3.10. retention time; 8.0 min and 10.9 min.

**15a** (E = CH<sub>2</sub>CH=CH<sub>2</sub>). mp. 90 °C; [ $\alpha$ ]<sub>D</sub><sup>29</sup> -25.9 (c 1.7, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.36 (s, 9H), 2.07 (s, 3H), 2.16-2.54 (m, 4H), 3.52 (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<sub>3</sub>) 1970, 1880, 1630 cm<sup>-1</sup>; Anal. Calcd. for C<sub>20</sub>H<sub>25</sub>NO<sub>4</sub>Cr: C, 60.75; H, 6.37; N, 3.54. Found. C, 60.48; H, 6.09; N, 3.57. retention time; 6.7 min and 8.0 min.

**15a** (E = CH<sub>2</sub>C≡CCH<sub>3</sub>). mp. 126 °C; [ $\alpha$ ]<sub>D</sub><sup>23</sup> -38.5 (c 2.0, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  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<sub>3</sub>) 2330, 1960, 1880, 1630 cm<sup>-1</sup>; Anal. Calcd. for C<sub>21</sub>H<sub>25</sub>NO<sub>4</sub>Cr: C, 62.20; H, 6.22; N, 3.44. Found. C, 62.50; H, 6.02; N, 3.40. retention time; 7.6 min and 10.2 min.

**15a** (E = ). mp. 108 °C;  $[\alpha]_D^{23} -51.1$  (c 2.2, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 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<sub>3</sub>) 2340, 1980, 1880, 1640 cm<sup>-1</sup>; Anal. Calcd. for C<sub>26</sub>H<sub>27</sub>NO<sub>4</sub>Cr: C, 66.52; H, 5.80; N, 2.98. Found. C, 66.40; H, 5.78; N, 2.92. retention time; 8.3 min and 14.6 min.

**15a** (E = C(OH)Ph<sub>2</sub>). mp. 178 °C;  $[\alpha]_D^{31} -75.7$  (c 2.2, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 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<sub>3</sub>) 3300, 1970, 1890, 1620 cm<sup>-1</sup>; Anal. Calcd. for C<sub>30</sub>H<sub>31</sub>NO<sub>5</sub>Cr: C, 67.03; H, 5.81; N, 2.61. Found. C, 67.28; H, 5.77; N, 2.88. retention time; 7.2 min and 13.4 min.

**15a** (E = ). mp. 123 °C;  $[\alpha]_D^{30} -77.3$  (c 1.5, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 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<sub>3</sub>) 3400, 1960, 1880, 1620 cm<sup>-1</sup>; Anal. Calcd. for C<sub>23</sub>H<sub>31</sub>NO<sub>5</sub>Cr: C, 60.92; H, 6.89; N, 3.09. Found. C, 60.71; H, 6.64; N, 3.06. retention time; 11.9 min and 21.9 min.

**15a** (E = C(Ph)<sub>2</sub>). mp. 103 °C;  $[\alpha]_D^{22} -15.0$  (c 0.8, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 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), 7.45-7.94 (m, 5H); IR (CHCl<sub>3</sub>) 1980, 1890, 1680, 1640 cm<sup>-1</sup>; Anal. Calcd. for C<sub>24</sub>H<sub>25</sub>NO<sub>5</sub>Cr: C, 62.74; H, 5.48; N, 3.05. Found. C, 62.50; H, 5.28; N, 3.12. retention time; 17.5 min and 20.3 min.

**15b** (E = Me). mp. 114 °C;  $[\alpha]_D^{25} -25.0$  (c 0.2, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 1.14 (t, 3H, *J* = 7.3 Hz), 1.37 (s, 9H), 1.50 (t, 3H, *J* = 7.3 Hz), 2.06 (s, 3H), 2.29-2.47 (m, 2H), 3.79-4.00 (m, 2H), 5.00 (d, 1H, *J* = 6.3 Hz), 5.02 (d, 1H, *J* = 6.3 Hz), 5.62 (t, 1H, *J* = 6.3 Hz); IR (CHCl<sub>3</sub>) 1970, 1880, 1640 cm<sup>-1</sup>; Anal. Calcd. for C<sub>19</sub>H<sub>25</sub>NO<sub>4</sub>Cr: C, 59.52; H, 6.57; N, 3.65. Found. C, 59.76; H, 6.29; N, 3.40. The enantiomeric excess was determined by chiral HPLC with Chiralpak AS eluted with hexane/2-propanol (40/1); flow rate, 0.5 mL/min; column temperature, 40 °C; UV detector, 254 nm; retention time; 15.7 min and 17.1 min.

**15b (E = CH<sub>2</sub>Ph).**  $[\alpha]_D^{21} -27.0$  (*c* 0.2, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.38 (s, 9H), 1.50 (t, 3H, *J* = 7.0 Hz), 2.06 (s, 3H), 2.46-2.91 (m, 4H), 3.93 (q, 2H, *J* = 7.0 Hz), 4.83 (d, 1H, *J* = 6.2 Hz), 5.01 (d, 1H, *J* = 6.2 Hz), 5.54 (t, 1H, *J* = 6.2 Hz), 7.14 (d, 2H, *J* = 6.9 Hz), 7.22 (d, 1H, *J* = 6.9 Hz), 7.29 (t, 2H, *J* = 6.9 Hz); IR (CHCl<sub>3</sub>) 1970, 1880, 1640 cm<sup>-1</sup>; MS (relative intensity) *m/z* 459 (M<sup>+</sup>, 15), 375 (100), 323 (14), 266 (32); HRMS calcd for C<sub>25</sub>H<sub>29</sub>NO<sub>4</sub>Cr: 459.1654, found 459.1647. retention time; 7.7 min and 10.5 min.

**15c (E = Me).**  $[\alpha]_D^{22} -18.2$  (*c* 1.7, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.12 (t, 3H, *J* = 7.7 Hz), 1.38 (s, 9H), 2.13 (s, 3H), 2.36-2.58 (m, 2H), 3.39 (s, 3H), 3.61-3.74 (m, 4H), 4.94 (d, 2H, *J* = 6.3 Hz), 5.09 (d, 1H, *J* = 9.9 Hz), 5.24 (d, 1H, *J* = 9.9 Hz), 5.63 (t, 1H, *J* = 6.3 Hz); IR (CHCl<sub>3</sub>) 1970, 1880, 1640 cm<sup>-1</sup>; MS (relative intensity) *m/z* 443 (M<sup>+</sup>, 14), 359 (100), 301 (31), 285 (36); HRMS calcd for C<sub>21</sub>H<sub>29</sub>NO<sub>6</sub>Cr: 443.1400, found 443.1405. retention time; 5.2 min and 5.8 min.

**15c (E = CH<sub>2</sub>Ph).**  $[\alpha]_D^{27} -13.7$  (*c* 2.3, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.39 (s, 9H), 2.14 (s, 3H), 2.46-2.56 (m, 1H), 2.62-2.72 (m, 1H), 2.78-2.87 (m, 1H), 2.94-3.03 (m, 1H), 3.36 (s, 3H), 3.59-3.71 (m, 4H), 4.72 (d, 1H, *J* = 6.2 Hz), 4.93 (d, 1H, *J* = 6.2 Hz), 5.15 (d, 1H, *J* = 9.5 Hz), 5.21 (d, 1H, *J* = 9.5 Hz), 5.48 (t, 1H, *J* = 6.2 Hz), 7.15 (d, 2H, *J* = 7.0 Hz), 7.21 (d, 1H, *J* = 7.0 Hz), 7.28 (t, 2H, *J* = 7.0 Hz); IR (CHCl<sub>3</sub>) 1970, 1880, 1640 cm<sup>-1</sup>; MS (relative intensity) *m/z* 519 (M<sup>+</sup>, 12), 435 (100), 360 (19), 276 (16); HRMS calcd for C<sub>27</sub>H<sub>33</sub>NO<sub>6</sub>Cr: 519.1713, found 519.1706.

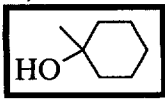
**17a.** mp. 154 °C;  $[\alpha]_D^{24} -9.9$  (*c* 2.2, EtOH); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.23 (t, 3H, *J* = 7.3Hz), 1.24 (d, 3H, *J* = 6.9Hz), 1.40 (s, 9H), 2.38-2.51 (m, 3H), 2.82-3.00 (m, 2H), 3.60 (s, 3H), 4.86 (d, 1H, *J* = 6.3Hz), 5.10 (d, 1H, *J* = 6.3Hz), 5.55 (t, 1H, *J* = 6.3Hz), 7.05-7.27 (m, 5H); IR (CHCl<sub>3</sub>) 1960, 1870, 1640 cm<sup>-1</sup>; Anal. Calcd. for C<sub>26</sub>H<sub>31</sub>NO<sub>4</sub>Cr: C, 65.95; H, 6.60; N, 2.96. Found. C, 66.15; H, 6.52; N, 3.01. Chiralpak AS eluted with hexane/2-propanol (20/1); flow rate, 1 mL/min; column temperature, 40 °C; UV detector, 254 nm; retention time; 5.2 min and 6.2 min.

**17b.** mp. 133 °C;  $[\alpha]_D^{22} -0.5$  (*c* 2.2, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.20 (t, 3H, *J* = 7.3Hz), 1.31 (d, 2H, *J* = 6.9Hz), 1.36 (s, 9H), 1.84-1.95 (m, 1H), 2.39 (q, 2H, *J* = 7.3Hz), 2.40-2.42 (m, 1H), 2.54-2.61 (m, 1H), 3.56 (s, 3H), 4.98-5.09 (m, 2H), 5.03 (d, 2H, *J* = 6.3Hz), 5.61 (t, 1H, *J* = 6.3Hz), 5.58-5.77 (m, 1H); IR (CHCl<sub>3</sub>) 1960, 1870, 1640, 1410 cm<sup>-1</sup>; Anal. Calcd. for C<sub>22</sub>H<sub>29</sub>NO<sub>4</sub>Cr: C, 62.40; H, 6.90; N, 3.31. Found. C, 62.56; H, 6.92; N, 3.38. retention time; 5.0 min and 5.6 min.

**22b (E = Me).** mp. 155 °C;  $[\alpha]_D^{24} -32.0$  (*c* 0.7, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.32 (t, 3H, *J* = 7.3 Hz), 2.30 (s, 3H), 2.40 (s, 3H), 2.51 (dq, 1H, *J* = 15.0, 7.3 Hz), 2.66 (dq, 1H, *J* = 15.0, 7.3 Hz), 3.21 (s, 3H), 5.06 (d, 2H *J* = 6.3 Hz), 5.64 (t, 1H, *J* = 6.3 Hz), 7.15-7.37 (m, 4H). IR (CHCl<sub>3</sub>) 1960, 1880, 1640 cm<sup>-1</sup>; Anal. Calcd. for C<sub>21</sub>H<sub>21</sub>NO<sub>4</sub>Cr: C, 62.53; H, 5.25; N, 3.47. Found. C, 62.80; H, 5.18; N, 3.26. retention time; 14.2 min and 17.2 min.

**22b (E = CH<sub>2</sub>Ph).** mp. 146 °C;  $[\alpha]_D^{26} -14.5$  (*c* 1.2, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.31 (s, 3H), 2.38 (s, 3H), 2.66-3.10 (m, 4H), 3.23 (s, 3H), 4.81 (d, 1H *J* = 6.3 Hz), 5.04 (d, 1H *J* = 6.3 Hz), 5.59 (t, 1H, *J* = 6.3 Hz), 7.17-7.36 (m, 9H). IR (CHCl<sub>3</sub>) 1960, 1880, 1640 cm<sup>-1</sup>; Anal. Calcd. for C<sub>27</sub>H<sub>25</sub>NO<sub>4</sub>Cr: C, 67.63; H, 5.26; N, 2.92. Found. C, 67.77; H, 4.99; N, 3.10. retention time; 13.4 min and 17.8 min.

**22b (E = CH<sub>2</sub>CH=CH<sub>2</sub>).** mp. 102 °C;  $[\alpha]_D^{24} -26.5$  (*c* 1.1, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.30 (s, 3H), 2.35-2.74 (m, 4H), 2.40 (s, 3H), 3.22 (s, 3H), 5.04-5.16 (m, 2H), 5.05 (d, 2H *J* = 6.3 Hz), 5.62 (t, 1H, *J* = 6.3 Hz), 5.82-5.97 (m, 1H), 7.18-7.37 (m, 4H). IR (CHCl<sub>3</sub>) 1960, 1880, 1640 cm<sup>-1</sup>; Anal. Calcd. for C<sub>23</sub>H<sub>23</sub>NO<sub>4</sub>Cr: C, 64.33; H, 5.40; N, 3.26. Found. C, 64.52; H, 5.23; N, 3.11. retention time; 11.6 min and 14.9 min.

**22b (E = .**) mp. 165 °C;  $[\alpha]_D^{24} -58.9$  (*c* 1.7, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.21-1.75 (m, 10H), 2.04 (s, 1H), 2.32 (s, 3H), 2.44 (s, 3H), 2.60 (d, 1H, *J* = 14.0 Hz), 2.71 (d, 1H, *J* = 14.0 Hz), 3.26 (s, 3H), 5.04 (d, 1H, *J* = 6.3 Hz), 5.23 (d, 1H *J* = 6.3 Hz), 5.62 (t, 1H, *J* = 6.3 Hz), 7.24-7.39 (m, 4H). IR (CHCl<sub>3</sub>) 3400, 1960, 1870, 1640 cm<sup>-1</sup>; Anal. Calcd. for C<sub>26</sub>H<sub>29</sub>NO<sub>5</sub>Cr: C, 64.06; H, 6.00; N, 2.87. Found. C, 64.30; H, 5.80; N, 2.77. retention time; 12.9 min and 29.2 min.

**Conversion of 23 to 25b:** To a suspension of LiAlH<sub>4</sub> (55.0 mg, 1.45 mmol) in THF (3 mL) was added a solution of **23** (216 mg, 0.48 mmol) in THF (7 mL) at room temperature and stirred for 3 h. The reaction mixture was quenched with aqueous 2M NaOH (0.06 mL). After filtration and washing with ether, the organic layer was dried over MgSO<sub>4</sub> and evaporated in a vacuo. The resulting yellow oil (101 mg) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). And then, (*E*)-cinnamoyl chloride (139 mg, 0.84 mmol) and pyridine (44.0 mg) were added to the above solution, and the reaction mixture was stirred at room temperature for 3h. Usual work up and purification with SiO<sub>2</sub> column chromatography gave 83.0 mg (60%) of **25b** was obtained. mp. 139 °C;  $[\alpha]_D^{26} -91.0$  (*c* 0.2 CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.17 (s,

3H), 2.64-2.92 (m, 4H), 3.49 (s, 3H), 4.84 (d, 1H,  $J = 6.2$  Hz), 5.02 (d, 1H  $J = 6.2$  Hz), 5.58 (t, 1H,  $J = 6.2$  Hz), 6.30 (d, 1H,  $J = 15.0$  Hz), 6.96-7.41 (m, 10H), 7.79 (d, 1H,  $J = 15.0$  Hz). IR (CHCl<sub>3</sub>) 1970, 1890, 1620, 1430 cm<sup>-1</sup>; Anal. Calcd. for C<sub>28</sub>H<sub>25</sub>NO<sub>4</sub>Cr: C, 68.42; H, 5.13; N, 2.85. Found. C, 68.20; H, 5.09; N, 2.75.

**27b**: 80% yield from **26**. mp. 142 °C;  $[\alpha]_D^{26} -32.8$  (c 0.1, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.14 (t, 3H,  $J = 7.3$  Hz), 2.11 (s, 3H), 2.17 (s, 3H), 2.46-2.70 (m, 2H), 3.54 (s, 3H), 4.85 (d, 1H,  $J = 6.2$  Hz), 4.96 (d, 1H  $J = 6.2$  Hz), 5.50 (t, 1H,  $J = 6.2$  Hz), 7.06 (d, 1H,  $J = 7.7$  Hz), 7.61 (d, 1H,  $J = 7.7$  Hz), 7.74 (t, 1H,  $J = 7.7$  Hz). IR (CHCl<sub>3</sub>) 1970, 1890, 1640, 1430 cm<sup>-1</sup>; Anal. Calcd. for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>Cr: C, 59.40; H, 4.98; N, 6.93. Found. C, 59.19; H, 4.92; N, 6.66.

### Preparation of Chromium-Free Axially Chiral Benamide and Anilides by Photo-

**Oxidative Demetalation.** Typical reaction is as follows. A solution of **15** (E = Me) (260 mg, 0.71 mmol) in ether (5 mL) was exposed to sunlight at 0 °C 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 **29** (E = Me) as colorless crystal. Optical purity was determined by <sup>1</sup>H-NMR spectrum in the presence of Eu(tfc)<sub>3</sub>. mp. 33 °C;  $[\alpha]_D^{24} -4.9$  (c 3.0 CHCl<sub>3</sub>) <sup>1</sup>H NMR (CDCl<sub>3</sub>) 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<sub>3</sub>) 1610, 1420 cm<sup>-1</sup>; Anal. Calcd. for C<sub>15</sub>H<sub>23</sub>NO: C, 77.21; H, 9.93; N, 6.00. Found. C, 77.31; H, 10.10; N, 5.79.

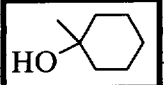
**29** (E = CH<sub>2</sub>Ph). mp. 43 °C;  $[\alpha]_D^{30} -11.9$  (c 1.3 CHCl<sub>3</sub>) <sup>1</sup>H NMR (CDCl<sub>3</sub>) for major *cis*-rotamer: δ 0.96 (s, 9H), 2.23 (s, 3H), 2.86-2.93 (m, 4H), 3.00 (s, 3H), 7.10-7.30 (m, 8H); for minor *trans*-rotamer: δ 1.41 (s, 9H), 2.16 (s, 3H), 2.86-2.93 (m, 4H), 3.25 (s, 3H), 7.10-7.30 (m, 8H); IR (CHCl<sub>3</sub>) 1620, 1460 cm<sup>-1</sup>; Anal. Calcd. for C<sub>21</sub>H<sub>27</sub>NO: C, 81.51; H, 8.79; N, 4.53. Found. C, 81.80; H, 9.07; N, 4.42.


**29** (E = CH<sub>2</sub>CH=CH<sub>2</sub>).  $[\alpha]_D^{21} -9.4$  (c 2.6 CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) 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); for 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<sub>3</sub>) 1610, 1440 cm<sup>-1</sup>; MS

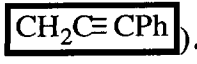


(relative intensity)  $m/z$  259 ( $M^+$ , 64), 202 (47), 174 (26), 160 (22), 98 (100); HRMS calcd for  $C_{17}H_{25}NO$ : 259.1942, found 259.1939.

**29** ( $E = C(OH)Ph_2$ ). mp. 183 °C;  $[\alpha]_D^{22} +78.1$  ( $c$  3.7,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ ) for major *trans*-rotamer:  $\delta$  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); for minor *cis*-rotamer:  $\delta$  0.98 (s, 9H), 2.19 (s, 3H), 2.96 (s, 3H), 3.40 (d, 1H,  $J = 14.0$  Hz), 3.64 (s, 1H), 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  $C_{27}H_{31}NO_2$ : C, 80.76; H, 7.76; N, 3.49. Found. C, 80.98; H, 7.71; N, 3.39.

**29** ( $E =$ ). mp 82 °C;  $[\alpha]_D^{23} +9.0$  ( $c$  1.5,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ ) for major *trans*-rotamer:  $\delta$  1.24-1.65 (m, 10H), 1.42 (s, 9H), 2.14 (s, 3H), 2.32 (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); for minor *cis*-rotamer:  $\delta$  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, 1H,  $J = 14.0$  Hz), 3.16 (s, 3H), 7.12-7.43 (m, 3H); IR ( $CHCl_3$ ) 3390, 1640, 1460  $cm^{-1}$ ; Anal. Calcd. for  $C_{20}H_{31}NO_2$ : C, 75.67; H, 9.84; N, 4.41. Found. C, 75.64; H, 9.73; N, 4.34.

**29** ( $E =$ ).  $[\alpha]_D^{22} -27.3$  ( $c$  1.2,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ ) for major *cis*-rotamer:  $\delta$  0.98 (s, 9H), 1.75 (t, 3H,  $J = 2.6$  Hz), 2.24 (s, 3H), 2.34-2.47 (m, 2H), 2.62-2.82 (m, 2H), 3.31 (s, 3H), 7.09-7.23 (m, 3H); for minor *trans*-rotamer:  $\delta$  1.42 (s, 9H), 1.76 (t, 3H,  $J = 2.6$  Hz), 2.15 (s, 3H), 2.34-2.47 (m, 2H), 2.62-2.82 (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  $C_{18}H_{25}NO$ : 271.1916, found 271.1927.

**29** ( $E =$ ).  $[\alpha]_D^{22} -47.1$  ( $c$  1.3,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ ) for major *cis*-rotamer:  $\delta$  0.99 (s, 9H), 2.25 (s, 3H), 2.60-2.95 (m, 4H), 3.16 (s, 3H), 7.10-7.36 (m, 8H); for minor *trans*-rotamer:  $\delta$  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  $C_{23}H_{27}NO$ : 333.2100, found 333.2096.

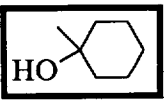
**29** ( $E = C(Ph)_2$ ).  $[\alpha]_D^{20} -40.9$  ( $c$  1.3,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ ) for major *cis*-rotamer:  $\delta$  1.02 (s, 9H), 2.27 (s, 3H), 3.03 (s, 3H), 4.20 (d, 1H  $J = 16.0$  Hz), 4.38 (d, 1H  $J = 16.0$  Hz), 7.05-8.02 (m, 8H); for minor *trans*-rotamer:  $\delta$  1.31 (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<sub>3</sub>) 1680, 1640, 1430 cm<sup>-1</sup>; MS (relative intensity)  $m/z$  323 (M<sup>+</sup>, 89), 308 (13), 266 (40), 222 (100); HRMS calcd for C<sub>21</sub>H<sub>25</sub>NO<sub>2</sub>: 323.1878, found 323.1882.

**30 (E = Me).**  $[\alpha]_D^{21} +2.3$  (c 2.1, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) for major *cis*-rotamer:  $\delta$  1.31 (t, 3H,  $J = 7.6$  Hz), 2.36 (s, 3H), 2.48 (s, 3H), 2.58-2.81 (m, 2H), 3.02 (s, 3H), 6.70-7.35 (m, 7H); for minor *trans*-rotamer:  $\delta$  1.18 (t, 3H,  $J = 7.6$  Hz), 2.25 (s, 3H), 2.49 (s, 3H), 2.58-2.81 (m, 2H), 3.33 (s, 3H), 6.70-7.35 (m, 7H); IR (CHCl<sub>3</sub>) 1630, 1420 cm<sup>-1</sup>; MS (relative intensity)  $m/z$  267 (M<sup>+</sup>, 100), 238 (28), 148 (33), 132 (41), 119 (89); HRMS calcd for C<sub>18</sub>H<sub>21</sub>NO: 267.1609, found 267.1616.

**30 (E = CH<sub>2</sub>Ph).**  $[\alpha]_D^{20} +10.8$  (c 2.2, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) for major *cis*-rotamer:  $\delta$  2.37 (s, 3H), 2.44 (s, 3H), 2.87-3.09 (m, 4H), 2.95 (s, 3H), 6.68-7.32 (m, 12H); for minor *trans*-rotamer:  $\delta$  2.26 (s, 3H), 2.43 (s, 3H), 2.87-3.09 (m, 4H), 3.21 (s, 3H), 6.70-7.35 (m, 12H); IR (CHCl<sub>3</sub>) 1640, 1430 cm<sup>-1</sup>; MS (relative intensity)  $m/z$  343 (M<sup>+</sup>, 100), 252 (17), 238 (18), 224 (32), 132 (33), 119 (80); HRMS calcd for C<sub>24</sub>H<sub>25</sub>NO: 343.1954, found 343.1945.

**30 (E = CH<sub>2</sub>CH=CH<sub>2</sub>).**  $[\alpha]_D^{23} +1.5$  (c 0.6, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) for major *cis*-rotamer:  $\delta$  2.32-2.70 (m, 2H), 2.36 (s, 3H), 2.49 (s, 3H), 2.70-2.81 (m, 2H), 3.02 (s, 3H), 4.99-5.14 (m, 2H), 5.88-5.98 (m, 1H), 6.71-7.32 (m, 7H); for minor *trans*-rotamer:  $\delta$  2.28 (s, 3H), 2.32-2.70 (m, 2H), 2.50 (s, 3H), 2.70-2.81 (m, 2H), 3.34 (s, 3H), 4.99-5.14 (m, 2H), 5.88-5.98 (m, 1H), 6.71-7.32 (m, 7H); IR (CHCl<sub>3</sub>) 1640, 1430 cm<sup>-1</sup>; MS (relative intensity)  $m/z$  293 (M<sup>+</sup>, 70), 238 (28), 174 (34), 119 (100); HRMS calcd for C<sub>20</sub>H<sub>23</sub>NO: 293.1790, found 293.1785.

**30 (E = .**  $[\alpha]_D^{21} +16.4$  (c 3.2, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) for major *cis*-rotamer:  $\delta$  1.23-1.74 (m, 10H), 2.13 (s, 1H), 2.37 (s, 3H), 2.35 (s, 3H), 2.75-2.88 (m, 2H), 3.04 (s, 3H), 6.60-7.44 (m, 7H); for minor *trans*-rotamer:  $\delta$  1.23-1.74 (m, 10H), 2.27 (s, 1H), 2.38 (s, 3H), 2.50 (s, 3H), 2.75-2.88 (m, 2H), 3.39 (s, 3H), 6.60-7.44 (m, 7H); IR (CHCl<sub>3</sub>) 3420, 1630, 1440 cm<sup>-1</sup>; MS (relative intensity)  $m/z$  351 (M<sup>+</sup>, 2), 333 (10), 253 (100), 238 (16), 119 (79); HRMS calcd for C<sub>23</sub>H<sub>29</sub>NO<sub>2</sub>: 351.2195, found 351.2198.

**28 (E = Me).**  $[\alpha]_D^{26} -13.0$  (c 0.1, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.02 (t, 3H,  $J = 7.3$  Hz), 1.23 (t, 3H,  $J = 7.3$  Hz), 2.25 (s, 3H), 2.50-2.61 (m, 2H), 3.10 (dq, 2H,  $J = 5.6, 7.3$  Hz), 3.61 (dq, 2H,  $J = 5.6, 7.3$  Hz), 7.02 (d, 1H,  $J = 7.3$  Hz), 7.08 (d, 1H,  $J = 7.3$  Hz), 7.19 (t, 1H,  $J = 7.3$  Hz); IR (CHCl<sub>3</sub>)

1620, 1440  $\text{cm}^{-1}$ ; MS (relative intensity)  $m/z$  219 ( $\text{M}^+$ , 34), 204 (10), 190 (14), 147 (100); HRMS calcd for  $\text{C}_{14}\text{H}_{21}\text{NO}$ : 219.1623, found 219.1619.

**28** (**E** = **CHCMe<sub>2</sub>**).  $[\alpha]_{\text{D}}^{23}$  -9.8 (*c* 0.5,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.04 (t, 3H,  $J = 7.3$  Hz), 1.21 (d, 3H,  $J = 6.9$  Hz), 1.25 (d, 3H,  $J = 6.9$  Hz), 1.28 (t, 3H,  $J = 7.3$  Hz), 2.25 (s, 3H), 2.83 (m, 1H), 3.12 (q, 1H,  $J = 7.3$  Hz), 3.13 (q, 1H,  $J = 7.3$  Hz), 3.49-3.75 (m, 2H), 7.02 (d, 1H,  $J = 7.3$  Hz), 7.15 (d, 1H,  $J = 7.3$  Hz), 7.22 (t, 1H,  $J = 7.3$  Hz); IR ( $\text{CHCl}_3$ ) 1620, 1440  $\text{cm}^{-1}$ ; MS (relative intensity)  $m/z$  233 ( $\text{M}^+$ , 15), 218 (12), 204 (20), 160 (100); HRMS calcd for  $\text{C}_{15}\text{H}_{23}\text{NO}$ : 233.1780, found 233.1754.