Supporting Information

Regio- and Chemoselective Direct Generation of Functionalized Aromatic Aluminum Compounds Using Aluminum Ate Base

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General Comments. Melting points were determined with a Yazawa micro melting point apparatus and uncorrected. ¹H-NMR spectra were recorded on a Varian Gemini 2000 using tetramethylsilane as an internal standard. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, quint = quintet, m = multiplet, and brs = broad singlet. Mass spectra were recorded on a JOEL JMS-O1SG-2 spectrometer.

Materials. Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used after appropriate purification (distillation or recrystallization). ⁴BuLi in n-pentane, ²BuLi in n-hexane and ²Bu₃Al in n-hexane were obtained from Kanto Chemical Co. Ltd. The concentrations of MeLi, ²BuLi and ⁴BuLi were determined by titration prior to use.¹

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Preparation of $i\text{Bu}_3\text{Al}(\text{TMP})\text{Li}$ THF Solution (2.2 mmol)

Under Ar atmosphere, $n\text{BuLi}$ (2.17 M $n\text{hexane}$ solution, 0.92 mL, 2.0 mmol) was added to mixture of dry THF (4 mL) and 2,2,6,6-tetramethylpiperidine (0.36 mL, 2.2 mmol) at -78°C and the mixture was stirred for 10 min at 0°C . Then, triisobutylaluminum (0.95 M, 2.2 mL, 2.1 mmol) was added to the mixture at -78°C and the mixture was stirred for 30 min at 0°C to give a pale yellow $i\text{Bu}_3\text{Al}(\text{TMP})\text{Li}$ THF solution (2.2 mmol)

A Representative Procedure for the Directed *ortho* Alumatation / Iodination Reaction of Aromatic Compounds

2-Iodoanisole (1a)

Anisole 111.1 mg (1.0 mmol) was added dropwise to prepared $i\text{Bu}_3\text{Al}(\text{TMP})\text{Li}$ THF solution (2.2 mmol) at -78°C . After the mixture was stirred for 3 h at rt, I_2 1.7 g (8.0 mmol) in dry THF was added to the mixture at -78°C and stirred up to 0°C for 1 h. The mixture was diluted with saturated aq. NaHS_2O_3 (10 mL) and saturated aq. NH_4Cl (40 mL) and extracted with CHCl_3 (30 mL x 3). The organic layer was dried over Mg_2SO_4 and solvent was removed under the reduced pressure. The residue was purified by SiO_2 column chromatography using ether-pentane (1:10) as an eluent to give 2-iodoanisole (238.6 mg, 99%). Colorless oil. 400MHz ^1H -NMR (CDCl_3/TMS) δ (ppm): 3.87 (s, 3H), 6.68-6.73 (m, 1H), 6.81-6.83 (m, 1H), 7.28-7.32 (m, 1H), 7.75-7.78 (m, 1H); MS m/z : 234 (M^+). HRMS Calcd for $\text{C}_7\text{H}_7\text{IO}$: 233.9542. Found: 233.9532.

2-Iodobenzonitrile (1b)

Recrystallized from ⁿhexane/Et₂O. Colorless needles, mp 54°C; *Anal.* Calcd for C₇H₄IN: C, 36.71; H, 1.76; I, 55.41; N, 6.12. Found: C, 36.77; H, 1.73; I, 55.70; N, 5.93.; 400MHz ¹H-NMR (CDCl₃/TMS) δ (ppm): 7.27-7.33 (m, 1H), 7.45-7.50 (m, 1H), 7.62-7.65 (m, 1H), 7.62-7.65 (m, 1H), 7.93-7.96 (m, 1H); *m/z* (EI) 229 (M⁺).

2-Iodo-*N,N*-diisopropylbenzamide (1c)

Recrystallized from ⁿhexane/Et₂O. Colorless plates, mp 190-191°C; *Anal.* Calcd for C₁₃H₁₈INO: C, 47.15; H, 5.48; I, 38.32; N, 4.23. Found: C, 46.64; H, 5.35; I, 38.14; N, 4.10.; 400MHz ¹H-NMR (CDCl₃/TMS) δ (ppm): 1.06-1.08 (m, 3H), 1.26-1.28 (m, 3H), 1.56-1.61 (m, 6H), 3.50-3.60 (m, 2H), 7.00-7.06 (m, 1H), 7.12-7.15 (m, 1H), 7.33-7.38 (m, 1H), 7.80-7.83 (m, 1H); *m/z* (EI) 331 (M⁺).

2,4-Diiodoanisole (1d)

Recrystallized from ⁿhexane. Colorless prisms, mp 65°C; 400MHz ¹H-NMR (CDCl₃/TMS) δ (ppm): 3.87 (s, 3H), 6.68-6.73 (m, 1H), 6.81-6.83 (m, 1H), 7.28-7.32 (m, 1H), 7.75-7.78 (m, 1H); MS *m/z*: 360 (M⁺). HRMS Calcd for C₇H₇IO: 359.8508. Found: 359.8506.

2,4-Diiodobenzonitrile (1e)

Recrystallized from n -hexane / Et_2O . Colorless needles, mp $111\text{--}112^\circ\text{C}$; *Anal.* Calcd for $\text{C}_7\text{H}_3\text{I}_2\text{N}$: C, 23.69; H, 0.85; N, 3.95. Found: C, 23.40; H, 1.01; N, 3.76; 400MHz $^1\text{H-NMR}$ (CDCl_3/TMS) δ (ppm): 7.28–7.31 (m, 1H), 7.79–7.82 (m, 1H), 8.31–8.32 (m, 1H); MS m/z : 355 (M^+). HRMS Calcd for $\text{C}_7\text{H}_3\text{I}_2\text{N}$: 354.8355. Found: 354.8365.

Iodo α, α, α -trifluorotoluene (1f)

2-iodo α, α, α -trifluorotolunene; 400MHz $^1\text{H-NMR}$ (CDCl_3/TMS) δ (ppm): 7.18–7.25 (m, 1H), 7.40–7.47 (m, 1H), 7.62–7.70 (m, 1H), 7.98–8.06 (m, 1H).²

3-iodo α, α, α -trifluorotolunene; 400MHz $^1\text{H-NMR}$ (CDCl_3/TMS) δ (ppm): 7.20–7.25 (m, 1H), 7.58–7.60 (m, 1H), 7.87–7.90 (m, 1H), 7.93–7.97 (m, 1H).³

4-iodo α, α, α -trifluorotoluene; 400MHz $^1\text{H-NMR}$ (CDCl_3/TMS) δ (ppm): 7.33–7.36 (m, 2H), 7.83–7.86 (m, 2H).

2-Iodo-1,3-dimethoxybenzene (1g)

Recrystallized from n -hexane/ CH_2Cl_2 . Colorless plates, mp 100°C ; *Anal.* Calcd for $\text{C}_8\text{H}_9\text{IO}_2$: C, 36.39; H, 3.44. Found: C, 36.40; H, 3.43.; 400MHz $^1\text{H-NMR}$ (CDCl_3/TMS) δ (ppm): 3.89 (s, 6H), 6.49–6.52 (m, 2H), 7.24–7.28 (m, 1H); MS m/z : 264 (M^+). HRMS Calcd for $\text{C}_8\text{H}_9\text{IO}_2$: 263.9647. Found: 263.9631.

3-Iodo-1,2-dimethoxybenzene (1h)

Colorless oil. 400MHz $^1\text{H-NMR}$ (CDCl_3/TMS) δ (ppm): 3.83 (s, 3H), 3.86 (s, 3H), 6.77-6.81 (m, 1H), 6.87-6.89 (m, 1H), 7.33-7.35 (m, 1H); MS m/z : 264 (M^+). HRMS Calcd for $\text{C}_8\text{H}_9\text{IO}_2$: 263.9647. Found: 263.9615.

1,3-Dichloro-2-iodobenzene (1i)

Colorless oil, 400MHz $^1\text{H-NMR}$ (CDCl_3/TMS) δ (ppm): 6.49-6.52 (m, 2H), 7.24-7.28 (m, 1H); MS m/z : 271 (M^+). HRMS Calcd for $\text{C}_6\text{H}_3\text{Cl}_2\text{I}$: 271.8657. Found: 271.8659.

1,2-Dichloro-3-iodobenzene (1j)

Colorless oil: 400MHz $^1\text{H-NMR}$ (CDCl_3/TMS) δ (ppm): 6.86-6.90 (m, 1H), 7.40-7.45 (m, 1H), 7.75-7.78 (m, 1H); MS m/z : 272 (M^+). HRMS Calcd for $\text{C}_6\text{H}_3\text{Cl}_2\text{I}$: 271.8657. Found: 271.8658.

2-Iodo-N-butoxycarbonylindole(1k)

Colorless oil. 400MHz ^1H -NMR (CDCl_3/TMS) δ (ppm): 1.72 (s, 9H), 6.99 (s, 1H) 7.17-7.28 (m, 2H), 7.44-7.47 (m, 1H), 8.07-8.90 (m, 1H); MS m/z : 343 (M^+). HRMS Calcd for $\text{C}_{13}\text{H}_{14}\text{INO}_2$: 343.0069. Found: 343.0054.

3-Iodo-4-methoxypyridine(1l)

Recrystallized from n -hexane. Colorless prisms, mp 66°C ; *Anal.* Calcd for $\text{C}_6\text{H}_6\text{INO}$: C, 30.66; H, 2.57; I, 54.00; N, 5.96, Found: C, 30.67; H, 2.54; I, 54.29; N, 5.93. ; 400MHz ^1H -NMR (CDCl_3/TMS) δ (ppm): 3.95 (s, 3H), 6.78-6.80 (m, 1H), 8.39-8.41 (m, 1H), 8.73-8.75 (m, 1H); MS m/z : 235 (M^+).

Electrophilic Trapping of the Functionalized Phenyl Intermediate (2c)

2-Allyl-*N,N*-diisopropylbenzamide

N,N-diisopropylbenzamide 207.3 mg (1.0 mmol) was added dropwise to prepared $t\text{-Bu}_3\text{Al}(\text{TMP})\text{Li}$ THF solution (2.2 mmol) at -78°C . After the mixture was stirred for 3 h at rt, $\text{Th}(\text{CN})\text{CuLi}$ 0.4 mL (0.25 M, 0.10 mmol) was added to the mixture at -78°C followed by the addition of allylbromide 0.68 mL (8.0 mmol). After stirring for 24 h at rt, the mixture was diluted with 2N HCl (10 mL) and saturated aq. NH_4Cl (30 mL) and extracted with CHCl_3 (30 mL $\times$ 3). The organic layer was washed with brine and dried over Na_2SO_4 . Solvent was removed under the reduced pressure. The residue was purified by SiO_2 column chromatography using AcOEt - n -hexane(1:6) as an eluent to give 2-allyl-*N,N*-diisopropylbenzamide (246.7 mg, 100%).

Recrystallized from n -hexane. Colorless needles, mp 49 - 50°C ; *Anal.* Calcd for $\text{C}_{16}\text{H}_{23}\text{NO}$: C, 78.32; H, 9.45; N, 5.71; O, 6.52. Found: C, 78.13; H, 9.49; N, 5.72; 400MHz ^1H -NMR (CDCl_3/TMS) δ (ppm): 1.10 (dd, 6H, $J = 2.8, 6.8$ Hz), 1.56 (d, 6H, $J = 6.8$ Hz), 3.41 (d, 2H, $J = 6.6$ Hz), 3.50 (septet,

1H, $J = 6.8$ Hz), 3.68 (septet, 1H, $J = 6.8$ Hz), 5.05-5.13 (m, 2H), 5.95 (1H, ddt, $J = 16.9, 10.1, 6.8$ Hz), 7.09-7.12 (m, 1H), 7.17-7.29 (m, 3H); MS m/z : 245 (M^+). HRMS Calcd for $C_{16}H_{23}ON$: 245.1780. Found: 245.1776.

N,N-Diisopropyl-2-phenylbenzamide

N,N-diisopropylbenzamide 205.3 mg (1.0 mmol) was added dropwise to prepared $t\text{-Bu}_3\text{Al}(\text{TMP})\text{Li}$ THF solution (2.2 mmol) at -78°C . After the mixture was stirred for 3 h at rt, iodobenzene 0.22 mL (2.0 mmol), tri-*t*-butylphosphine 0.45 mL (0.150 mmol) and $\text{Pd}_2(\text{dba})_3$ 22.9 mg (0.025 mmol) were added. After stirring for 24 h at rt, the mixture was diluted with saturated aq. NH_4Cl and extracted with CHCl_3 (30 mL $\times$ 3). The organic layer was washed with brine and dried over Na_2SO_4 . Solvent was removed under the reduced pressure. The residue was purified by SiO_2 column chromatography using AcOEt-hexane(1:4) as an eluent to give *N,N*-diisopropyl-2-phenylbenzamide (224.3 mg, 79%). Recrystallized from n -hexane. Colorless needles, mp $107\text{--}108^\circ\text{C}$; *Anal.* Calcd for $\text{C}_{19}\text{H}_{23}\text{NO}$: C, 81.1; H, 8.24; N, 4.98. Found: C, 81.18 H, 8.19; N, 4.95. ; 400MHz ^1H -NMR (CDCl_3/TMS) δ (ppm): 0.33 (d, $J = 6.6$ Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 3H), 1.28 (d, $J = 6.8$ Hz, 3H), 1.51 (d, $J = 6.8$ Hz, 3H), 3.22 (septet, $J = 6.8$ Hz, 1 H), 3.43 (septet, $J = 6.6$ Hz, 1H), 7.28-7.55 (m, 7H), 7.56-7.57 (m, 2H); MS m/z : 281(M^+). HRMS Calcd for $\text{C}_{20}\text{H}_{23}\text{O}_2\text{N}$: 281.1780. Found: 281.1777.

2-Benzoyl-*N,N*-diisopropylbenzamide

N,N-diisopropylbenzamide 205.3 mg (1.0 mmol) was added dropwise to prepared

$t\text{-Bu}_3\text{Al}(\text{TMP})\text{Li}$ THF solution (2.2 mmol) at -78°C . After the mixture was stirred for 3 h at rt, benzoyl chloride 280.5 mg (2.0 mmol), tri-*t*-butylphosphine 0.45 mL (0.150 mmol) and $\text{Pd}_2(\text{dba})_3$ 22.9 mg (0.025 mmol) were added. After stirring for 24 h at rt, the mixture was diluted with saturated aq. NH_4Cl and extracted with CHCl_3 (30 mL x 3). The organic layer was washed with brine and dried over Na_2SO_4 . Solvent was removed under the reduced pressure. The residue was purified by SiO_2 column chromatography using AcOEt-hexane (1:4) as an eluent to give 2-benzoyl-*N,N*-diisopropylbenzamide (246.0 mg, 81%). Recrystallized from n -hexane. Colorless needles, mp $124\text{--}125^\circ\text{C}$; *Anal.* Calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.61 H, 7.63; N, 4.43; 400MHz ^1H -NMR (CDCl_3/TMS) δ (ppm): 1.20 (d, $J = 6.5$ Hz, 6 H), 1.43 (d, $J = 6.7$ Hz, 6 H), 3.45 (septet, $J = 6.8$ Hz, 1 H), 3.84 (septet, $J = 6.5$ Hz, 1 H), 7.39-7.62 (m, 6H), 7.79-7.82 (m, 2H), 8.08-8.11 (m, 1H); MS m/z : 309 (M^+). HRMS Calcd for $\text{C}_{20}\text{H}_{23}\text{O}_2\text{N}$: 309.1729. Found: 309.1724.

2-Hydroxy-*N,N*-diisopropylbenzamide

N,N-diisopropylbenzamide 205.3 mg (1.0 mmol) was added dropwise to prepared $t\text{-Bu}_3\text{Al}(\text{TMP})\text{Li}$ THF solution (2.2 mmol) at -78°C . After the mixture was stirred for 3 h at rt, the mixture was diluted with 2N HCl (10 mL) and saturated aq. NH_4Cl (30 mL) and extracted with CHCl_3 (30 mL x 3). The organic layer was washed with brine and dried over Na_2SO_4 . Solvent was removed under the reduced pressure. The residue was purified by SiO_2 column chromatography using AcOEt-hexane(1:6) as an eluent to give 2-hydroxy-*N,N*-diisopropylbenzamide (124.0 mg, 56%). Recrystallized from n -hexane. Colorless needles, mp $162\text{--}163^\circ\text{C}$; *Anal.* Calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.43; H, 8.74; N, 6.30. ; 400MHz ^1H -NMR (CDCl_3/TMS) δ (ppm): 1.38(brs, 6H), 1.40(brs, 6H), 3.94(brs, 2H), 6.81-6.85(m, 1H), 7.00-7.02(m, 1H), 7.15-7.18(m, 1H), 7.26-7.30(m, 1H); MS m/z : 221 (M^+). HRMS Calcd. for $\text{C}_{13}\text{H}_{19}\text{O}_2\text{N}$: 221.1416. Found: 221.1418.

N,N-Diisopropyl- 3-bromo-2-iodobenzamide

According to representative procedure, *N,N*-diisopropyl-3-bromobenzamide 284.1 mg (1.0 mmol) was added to prepared $t\text{-Bu}_3\text{Al(TMP)Li}$ THF solution (1.1 mmol) solution at -78°C . The mixture was stirred for 2 h at -78°C . The residue was purified by SiO_2 column chromatography using AcOEt -hexane(1:7) as an eluent to give 3-bromo-2-iodo-*N,N*-diisopropylbenzamide (266.5 mg, 65%). Recrystallized from n -hexane, colorless plates, mp 207.0°C . *Anal.* Calcd for $\text{C}_{13}\text{H}_{17}\text{NO}$: C, 38.08; H, 4.18; N, 3.42. Found: C, 38.33; H, 4.15; N, 3.28.; 400MHz $^1\text{H-NMR}$ (CDCl_3/TMS) δ (ppm): 7.59 (1H, dd, $J = 7.8, 1.5$ Hz), 7.23 (1H, t, $J = 7.8$ Hz), 7.03 (1H, dd, $J = 7.8, 1.5$ Hz), 3.54 (2H, m), 1.59 (3H, d, $J = 6.6$ Hz), 1.56 (3H, d, $J = 6.6$ Hz), 1.29 (3H, d, $J = 6.6$ Hz), 1.07 (3H, d, $J = 6.6$ Hz). MS m/z : 411 (M^+). HRMS Calcd for $\text{C}_{13}\text{H}_{17}\text{OBrI}$: 410.9517. Found: 410.9482.

1-Diisopropylcarbamoyl- 9, 10-diphenyl -9, 10-epoxyanthracene

To a prepared $t\text{-Bu}_3\text{Al(TMP)Li}$ THF solution (2.2 mmol) were added 1,3-diphenylisobenzofuran (589.2 mg, 2.2 mmol) in THF solution and *N,N*-diisopropyl-3-bromobenzamide 284.1 mg (1.0 mmol) at -78°C . The mixture was stirred for 18 h at rt. Dropping sat. NH_4Cl quenched the reaction, and the mixture was extracted with CHCl_3 , dried over MgSO_4 , and evaporated under reduced pressure. Then it was purified by SiO_2 column chromatography (eluent; $\text{AcOEt} : n$ -hexane = 1:10) and 474.3 mg of 1-diisopropylcarbamoyl- 9, 10-diphenyl -9, 10-epoxyanthracene was obtained (100% yield).

Recrystallized from n -hexane/ethyl acetate, colorless prisms, mp $224.0\text{--}224.5^\circ\text{C}$. *Anal.* Calcd for $\text{C}_{33}\text{H}_{31}\text{NO}_2$: C, 83.49; H, 6.73; N, 2.96. Found: C, 83.69; H, 6.60; N, 2.96. ; 400MHz $^1\text{H-NMR}$

(CDCl₃/TMS) δ (ppm): 8.03 (2H, d, J = 7.0 Hz), 7.93 (2H, d, J = 7.6 Hz), 7.86 (1H, d, J = 7.6 Hz), 7.58 (2H, t, J = 7.0 Hz), 7.50-7.44 (3H, m), 7.40 (1H, d, J = 7.0 Hz), 7.32 (2H, t, J = 7.0 Hz), 7.11 (1H, t, J = 7.0 Hz), 7.01 (2H, t, J = 7.6 Hz), 6.79 (1H, d, J = 7.6 Hz), 3.84 (1H, m), 3.25 (1H, m), 1.36 (3H, d, J = 7.0 Hz), 1.13 (3H, d, J = 7.0 Hz), 0.92 (3H, d, J = 6.6 Hz), 0.76 (3H, d, J = 6.6 Hz). MS m/z : 473 (M^+). HRMS Calcd for C₃₃H₃₁NO₂: 473.2353. Found: 473.2371. IR (KBr, cm⁻¹) 3061 (C-H), 2967 (C-H), 1626 (C=O), 757 (C-H).

IR Spectroscopic Analyses. Samples were recorded using a ReactIR™ 1000 from ASI Applied Systems fitted with a one in an immersible DiComp™ ATR (Attenuated Total Reflectance) probe optimized for maximum sensitivity. The spectra were acquired in 128 scans per spectrum at a gain of one and a resolution of two using system ReactIR™ 2.1 software. A representative reaction was carried out as follows: The IR probe was inserted through a nylon adapter and O-ring seal into an oven-dried, cylindrical two necked flask fitted with magnetic stir bar. Following evacuation under full vacuum and flushing with Ar, the flask was charged with dry THF (4 mL) and 2,2,6,6-tetramethylpiperidine (0.36 mL, 2.2mmol) at rt. ⁿBuLi (2.17 M ⁿhexane solution, 0.92 mL, 2.0 mmol) was added to the mixture at -78°C and the mixture was stirred for 10 min at 0°C. Then, triisobutylaluminum (0.95 M, 2.2 mL, 2.1 mmol) was added to the mixture at -78°C and the mixture was stirred for 30 min at -25°C to give a ^tBu₃Al(TMP)Li THF/ hexane solution (2.2 mmol). Following the recording of a background spectrum, a 0.3M THF solution of *N,N*-diisopropylbenzamide (3 mL, 1.0 mmol) was added with stirring. IR spectra were recorded every 2 minutes over the course of the reaction. To account for mixing and temperature equilibration, spectra recorded in the first 2 min were discarded. Data manipulation and statistical analyses were carried out using the system 2.1 ReactIR™ software.

Figure S-1. FT-IR Spectroscopic Analysis of Directed *ortho* Alumatation Reaction of *N,N*-Diisopropylbenzamide

NMR Spectroscopic Analyses for Organometallic Species. ¹H, ¹³C, ⁷Li, ¹⁵N and ²⁷Al NMR spectra were obtained on a JEOL ECA-500 spectrometer, operating at 500.160, 125.765, 194.381, 50.681 and 130.326 MHz, respectively. Unless otherwise noted, samples were recorded as ca. 1.0 M THF solutions at -50°C. Chemical shifts δ are reported in ppm. The capillary tube contained THF-*d*₈ used as the ¹³C chemical shift reference and lock solvent. ¹H NMR spectra were referenced to a solvent signal (3.58 ppm). ¹³C NMR spectra were referenced to a THF-*d*₈ signal (67.4 ppm). ⁷Li NMR spectra were referenced to external 1.0 M LiBr in THF-*d*₈ at -50°C. ¹⁵N NMR spectra were referenced to external 0.15 M [¹⁵N]aniline in THF-*d*₈ at -50°C. ²⁷Al NMR spectra were recorded at 20°C and referenced to external 1.0 M Al(NO₃)₃ in THF-*d*₈ at 20°C. Complete ¹H and ¹³C NMR chemical shift assignments were made on the basis of decoupled 1D NMR, ¹H-¹³C HMQC, ¹H-¹³C HMBC and DEPT experiments.

	¹ H	¹³ C	⁷ Li	¹⁵ N	²⁷ Al
ⁱ Bu ₃ Al	-0.16 (d, 6H) 0.85 (m, 21H)	23.4 (α), 27.8 (β) 29.1 (γ)	-	-	174.4
LTMP	1.06 (s, 12H), 1.15 (4H) 1.56 (m, 2H)	20.9 (γ), 36.2 (Me) 43.3 (β), 53.1 (α)	0.61 (monomer) 1.26 (dimer)	79.9	-
ⁱ Bu ₃ Al(TMP)Li	0.98 (s, 12H), 1.20 (4H) 1.54 (m, 2H) -0.47 (6H), 0.77 (m, 21H)	19.3 (TMP ^γ), 32.3 (TMP ^{Me}) 39.0 (TMP ^β), 50.1 (TMP ^α) 24.4 (ⁱ Bu ^α), 30.2 (ⁱ Bu ^β) 29.4 (ⁱ Bu ^γ)	-0.75	77.0	153.4

Table S1. ¹H, ¹³C, ⁷Li, ¹⁵N, and ²⁷Al NMR Spectroscopic Data of LTMP, ⁱBu₃Al and ⁱBu₃Al(TMP)Li^a

^a Reported NMR data of ⁱBu₃Al (δ(ppm) α-H (0.30), β-H (1.94), γ-H (0.98) in benzene-*d*₆, ²⁷Al (276) in toluene-*d*₈⁵) and LTMP (δ(ppm) α-C (53.1), β-C (43.1), γ-C (20.9), Me (36.3), ⁷Li (0.7(monomer)) and (1.3(dimer))), ¹⁵N (79.7) in THF-*d*₈)^{6, 7, 8}.

Figure S-2. ^1H NMR Spectra of $t\text{Bu}_3\text{Al}$ in THF at -50°C

Figure S-3. ^{13}C NMR Spectra of $t\text{Bu}_3\text{Al}$ in THF at -50°C

Figure S-4. ^{27}Al NMR Spectra of $i\text{Bu}_3\text{Al}$ in THF at 20°C

Figure S-5. ^1H NMR Spectra of LTMP in THF at -50°C

Figure S-6. ^{13}C NMR Spectra of LTMP in THF at -50°C

Figure S-7. ^7Li NMR Spectra of LTMP in THF at -50°C

Figure S-8. ^1H - ^{15}N HMBC Spectra of LTMP in THF at -50°C

Figure S-9. ^1H NMR Spectra of $t\text{Bu}_3\text{Al}(\text{TMP})\text{Li}$ in THF at -50°C

Figure S-10. ^{13}C NMR Spectra of $t\text{Bu}_3\text{Al}(\text{TMP})\text{Li}$ in THF at -50°C

Figure S-11. ^7Li NMR Spectra of $t\text{Bu}_3\text{Al}(\text{TMP})\text{Li}$ in THF at -50°C

Figure S-12. ^1H - ^{15}N HMBC Spectra of $t\text{Bu}_3\text{Al}(\text{TMP})\text{Li}$ in THF at -50°C

Figure S-13. ^{27}Al NMR Spectra of $t\text{Bu}_3\text{Al}(\text{TMP})\text{Li}$ in THF at 20°C

Figure S-14. ¹³C NMR Spectra of Anisole in THF at -50°C

Figure S-15. ¹³C NMR Spectra of *ortho*-Lithiated Anisole in THF at -50°C

Figure S-16. ¹³C NMR Spectra of *ortho*-Lithiated Anisole + iBu₃Al in THF at -50°C

Figure S-17. ¹³C NMR Spectra of direct *ortho*-Aluminated Anisole in THF at -50°C

References for Supporting Information

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