Supporting Information

Homochiral and heterochiral associations observed in crystals of ArSO₂-(Aib)₅-OMe

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Scheme S1. Preparation of pentapeptides 1–3.



Synthetic pathway B



Reaction conditions: (a) EDC·HCl (1.2 equiv), HOBt·H₂O (1 equiv), *i*-Pr₂NEt (1 equiv), CH₂Cl₂, rt, 2-3 d; (b) LiOH·H₂O (3-6 equiv), THF, H₂O, rt or 50 °C, 2 h; (c) 4 M HCl/AcOEt, rt, 4 h; (d) Et₃N (8 equiv), DMAP (0.2 equiv), CH₂Cl₂, rt, 4-5 h.

Preparation of Boc-(Aib)₂**-OMe 6**: To the mixture of Boc-Aib-OH **4** (12.2 g, 60.1 mmol), α aminoisobutyric acid methyl ester hydrochloride **5** (9.29 g, 60.5 mmol), HOBt·H₂O (9.20 g, 60.1 mmol), and EDC·HCl (9.20 g, 60.0 mmol) in dichloromethane (200 mL) was added *N*,*N*-diisopropylethylamine (10.4 mL, 60.0 mmol). The resulting mixture was stirred at room temperature for 3 days under argon. The reaction mixture was poured into dichloromethane (200 mL), washed with 5%KHSO₄aq. (100 mLx2), 5%NaHCO₃ aq. (50 mLx3), and brine (50 mL), dried over Na₂SO₄, and concentrated in vacuo to give the desired product **6** (10.8 g, 35.8 mmol, 60%) as a white solid.

Boc-(Aib)₂**-OMe 6** ¹: ¹H NMR (400 MHz, CDCl₃) δ 1.45 (s, 9H), 1.47 (s, 6H), 1.54 (s, 6H), 3.73 (s, 3H), 4.92 (brs, 1H), 7.12 (brs, 1H).

Preparation of Boc-(Aib)₂**-OH 7**: To a solution of Boc-(Aib)₂-OMe **6** (9.5 g, 30.4 mmol) in THF (230 mL) was added to $\text{LiOH} \cdot \text{H}_2\text{O}$ (3.98 g, 104 mmol) in H_2O (140 mL), and the resulting mixture was stirred at rt for 2 h. After removal of THF in vacuo, the aqueous solution was extracted with Et₂O (230 mLx2) and acidified to pH 2 by addition of concentrated hydrochloric acid. The resulting precipitate was collected by filtration to give the desired product **7** (6.89 g, 23.9 mmol, 76%) as a white solid.

Boc-(Aib)₂**-OH 7** ²: ¹H NMR (400 MHz, CDCl₃) δ 1.45 (s, 9H), 1.48 (s, 6H), 1.56 (s, 6H), 5.02 (brs, 1H), 7.11 (brs, 1H).

Preparation of Boc-(Aib)₃**-OMe 8**: To the mixture of Boc-(Aib)₂-OH 7 (10.4 g, 35.9 mmol), H-Aib-OMe·HCl 5 (5.53 g, 36.0 mmol), HOBt·H₂O (8.34 g, 54.5 mmol), and EDC·HCl (10.4 g, 54.1 mmol) in dichloromethane (120 mL) was added *N*,*N*-diisopropylethylamine (9.4 mL, 54.0 mmol). The resulting mixture was stirred at room temperature for 3 days under argon. The reaction mixture was poured into dichloromethane (200 mL), washed with 5%KHSO₄aq. (100 mLx3), 5%NaHCO₃ aq. (100 mLx3), and brine (100 mL), dried over Na₂SO₄, and concentrated in vacuo to give the crude product (11.5 g, 29.7 mmol, 83%) as a white solid. The resulting product was recrystallized from *n*-hexane/EtOAc to give the desired product **8** (7.85 g).

Boc-(Aib)₃**-OMe 8** ³: mp 177-179 °C; IR (KBr) (cm⁻¹): 3380, 3303, 1726, 1693, 1683, 1660, 1531; ¹H NMR (400 MHz, CDCl₃) δ 1.45 (s, 6H), 1.46 (s, 9H), 1.47 (s, 6H), 1.51 (s, 6H), 3.70 (s, 3H), 4.89 (brs, 1H), 6.43 (brs, 1H), 7.46 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 24.8, 25.3, 25.4, 28.2, 52.2, 56.0, 56.6, 57.1, 77.2, 80.9, 155.1, 173.5, 175.2; MS (FAB): *m/z* 388 [M+H]⁺; Anal. Calcd for C₁₈H₃₃N₃O₆·1.2H₂O: C, 52.62; H, 8.10; N, 10.22. Found: C, 52.54; H, 8.03; N, 10.23.

Preparation of Boc-(Aib)₃**-OH 9**: To a solution of Boc-(Aib)₃-OMe **8** (7.8 g, 20.1 mmol) in THF (150 mL) was added to LiOH·H₂O (2.59 g, 67.8 mmol) in H₂O (90 mL), and the resulting mixture was stirred at rt for 2 h. After removal of THF in vacuo, the aqueous solution was extracted with Et₂O (150 mLx3) and acidified to pH 2 by addition of concentrated hydrochloric acid. The resulting precipitate was collected by filtration to give the desired product **9** (6.79 g, 18.2 mmol, 90%) as a white solid.

Boc-(Aib)₃**-OH 9**⁴: ¹H NMR (400 MHz, CDCl₃) δ 1.41-1.49 (m, 21H), 1.55-1.58 (m, 6H), 4.94 (brs, 1H), 6.56 (brs, 1H), 7.62 (brs, 1H).

Preparation of Boc-(Aib)₄**-OMe 10**: To the mixture of Boc-(Aib)₃-OH **9** (3.60 g, 9.65 mmol), H-Aib-OMe·HCl **5** (1.48 g, 9.7 mmol), HOBt·H₂O (2.34 g, 15.3 mmol), and EDC·HCl (2.87 g, 15.0 mmol) in dichloromethane (37 mL) was added *N*,*N*-diisopropylethylamine (2.6 mL, 14.9 mmol). The resulting mixture was stirred at room temperature for 3 days under argon. The reaction mixture was poured into dichloromethane (200 mL). After the resulting precipitation was removed by filtration, the filtrate was washed with 5%KHSO₄aq. (100 mLx3), 5%NaHCO₃ aq. (100 mLx3), and brine (100 mL), dried over Na₂SO₄, and concentrated in vacuo to give the crude product (4.34 g, 9.19 mmol, 95%). The resulting compound was recrystallized from *n*-hexane (10 mL)/EtOAc (6 mL) to give the pure compound **10** (2.89 g, 6.12 mmol, 63%) as a white solid.

Boc-(Aib)₄**-OMe 10:** mp ; 216-218 °C; IR (KBr) (cm⁻¹): 3364, 3333, 3298, 1728, 1678, 1656, 1526; ¹H NMR (400 MHz, CDCl₃) δ 1.44 (s, 6H), 1.45 (s, 6H), 1.47 (s, 9H), 1.49 (s, 6H), 1.52 (s, 6H), 3.70 (s, 3H), 4.95 (brs, 1H), 6.50 (brs, 1H), 7.34 (brs, 1H), 7.43 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 25.0, 25.2, 25.5, 28.3, 52.1, 55.8, 56.7, 56.9, 57.1, 77.3, 81.3, 155.3, 172.7, 174.1, 174.4, 175.5; MS (FAB): *m/z* 473 [M+H]⁺; Anal. Calcd for C₂₂H₄₀N₄O₇·0.2H₂O: C, 55.50; H, 8.47; N, 11.77. Found: C, 55.38; H, 8.53; N, 11.75.

Preparation of Boc-(Aib)₄**-OH 11**: To a solution of Boc-(Aib)₄**-OMe 10** (4.0 g, 8.48 mmol) in THF (60 mL) was added to LiOH·H₂O (2.1 g, 51 mmol) in H₂O (77 mL), and the resulting mixture was stirred at 50 °C for 2 h. After removal of THF in vacuo, the aqueous solution was extracted with Et₂O (50 mLx3) and acidified to pH 2 by addition of concentrated hydrochloric acid. The resulting precipitate was collected by filtration to give the desired product 11 (3.32 g, 7.25 mmol, 86%) as a white solid.

Boc-(Aib)₄**-OH 11** ⁴ mp ; 220-225 °C; IR (KBr) (cm⁻¹): 3356, 3333, 3278, 3062, 1737, 1686, 1671, 1630, 1531; ¹H NMR (400 MHz, DMSO-*d*₆) δ 1.26 (s, 6H), 1.28 (s, 6H), 1.31 (s, 6H), 1.33 (s, 6H), 1.43 (s, 9H), 7.34 (brs, 1H), 7.45 (brs, 1H), 7.53 (brs, 1H), 8.12 (brs, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 25.1, 25.2, 25.4, 25.7, 28.6, 56.1, 56.2, 56.3, 56.5, 79.5, 155.9, 173.8, 174.0, 175.6, 176.2; MS (FAB): *m/z* 459 [M+H]⁺; HRMS (FAB): Calcd. for C₂₁H₃₈N₄O₇Na: 481.2638, found: 481.2637.

Preparation of Boc-(Aib)₅**-OMe 12**: To the mixture of Boc-(Aib)₄-OH **11** (1.08 g, 2.35 mmol), H-Aib-OMe·HCl **5** (0.38 g, 2.50 mmol), HOBt·H₂O (0.60 g, 3.93 mmol), and EDC·HCl (0.70 g, 3.66 mmol) in dichloromethane (10 mL) was added *N*,*N*-diisopropylethylamine (0.614 mL, 3.53 mmol). The resulting mixture was stirred at room temperature for 5 days under argon. The reaction mixture was poured into dichloromethane (200 mL). The reaction mixture was poured into dichloromethane (200 mL). The reaction mixture was poured into dichloromethane (200 mL), washed with 5%KHSO₄aq. (50 mLx4), 5%NaHCO₃ aq. (50 mLx4), and brine (50 mLx2), dried over Na₂SO₄, and concentrated in vacuo to give the crude product (0.79 g, 1.41 mmol, 60%). The resulting product was recrystallized from *n*-hexane (8 mL)/EtOAc (2 mL) to give the desired compound **12** (0.67 g, 1.20 mmol, 51%) as a white solid.

Boc-(Aib)₅**-OMe 12**: mp ; 240-242 °C; IR (KBr) (cm⁻¹): 3330, 3304, 1726, 1679, 1656, 1523; ¹H NMR (400 MHz, CDCl₃) δ 1.44 (s, 6H), 1.44 (s, 6H), 1.46 (s, 6H), 1.47 (s, 9H), 1.51 (s, 6H), 1.53 (s, 6H), 3.69 (s, 3H), 5.02 (brs, 1H), 6.50 (brs, 1H), 7.25 (brs, 1H), 7.39 (brs, 1H), 7.73 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 25.0, 25.1, 25.3, 25.4, 28.3, 52.1, 55.8, 56.6, 56.7, 57.0, 77.3, 81.4, 155.5, 173.8, 174.2, 174.8, 175.7; MS (FAB): *m/z* 558 [M+H]⁺; Anal. Calcd for C₂₆H₄₇N₅O₈: C, 56.00; H, 8.50; N, 12.56. Found: C, 55.66; H, 8.51; N, 12.51.

Preparation of H-(Aib)₅**-OMe 13**: To a stirred suspension of Boc-(Aib)₅-OMe 12 (0.635 g, 1.14 mmol) in ethyl acetate (4 mL) was added 4M HCl/ethyl acetate (8 mL). The reaction mixture was stirred at room

temperature for 4 h under argon. The reaction mixture was neutralized by adding 4M NaOHaq., which was poured into ethyl acetate (100 mL). The organic layer was washed with brine, dried over Na₂SO₄ and concentrated in vacuo to give the crude product (0.2083 g, 0.4535 mmol, 40%). The resulting product was recrystallized from *n*-hexane/CHCl₃ to give the pure product **13** (0.154 g) as a white solid.

H-(Aib)₅**-OMe 13** ⁵: ¹H NMR (400 MHz, CDCl₃) δ 1.35-1.55 (m, 30H), 1.55-1.75 (m, 2H), 3.69 (s, 3H), 6.27 (brs, 1H), 7.32 (brs, 1H), 7.36 (brs, 1H), 8.17 (brs, 1H).

Preparation of ArSO₂-(Aib)₅-OMe (Ar = *p*-bromophenyl) **2**: A mixture of H-(Aib)₅-OMe **13** (68.8 mg, 0.15 mmol), *p*-bromobenzenesulfonyl chloride (39.4 mg, 0.154 mmol), triethylamine (200 μ L, 1.43 mmol), and 4-dimethylaminopyridine (3.8 mg, 0.03 mmol) in dichloromethane (1 mL) was stirred at room temperature for 5 h under argon. The reaction mixture was poured into dichloromethane (30 mL), washed with 2 M HClaq. (20 mL), water (20 mL), 5%NaHCO₃aq. (20 mL), and brine (20 mL), dried over Na₂SO₄, and concentrated in vacuo to give the crude product (53.6 mg, 0.0794 mmol, 53%). The resulting product was recrystallized from *n*-hexane (2 mL)/CHCl₃ (1 mL) to give the desired product **2** (25.3 mg, 0.0375 mmol) as a white solid.

Preparation of ArSO₂-(Aib)₅-OMe (Ar = *p*-methoxyphenyl) **3**: A mixture of H-(Aib)₅-OMe **13** (46.1 mg, 0.10 mmol), *p*-methoxybenzenesulfonyl chloride (26.9 mg, 0.130 mmol), triethylamine (120 μ L, 0.86 mmol), and 4-dimethylaminopyridine (2.5 mg, 0.02 mmol) in dichloromethane (1 mL) was stirred at room temperature for 5 h under argon. The reaction mixture was poured into dichloromethane (20 mL), washed with 2 M HClaq. (20 mL), water (20 mL), 5%NaHCO₃aq. (20 mL), and brine (20 mL), dried over Na₂SO₄, and concentrated in vacuo to give the crude product (36.4 mg, 0.058 mmol, 58%). The resulting product was recrystallized from *n*-hexane (2 mL)/CHCl₃ (1 mL) to give the desired product **3** (27.2 mg, 0.0434 mmol) as a white solid.

Preparation of Ts-Aib-OMe 14: A mixture of H-Aib-OMe **5** (3.38 g, 22.0 mmol), *p*-methoxybenzenesulfonyl chloride (3.81 g, 20.0 mmol), triethylamine (6.0 mL, 43.0 mmol), and 4-dimethylaminopyridine (562 mg, 4.5 mmol) in dichloromethane (200 mL) was stirred at room temperature for 21 h under argon. The reaction mixture was poured into dichloromethane (100 mL), washed with 2 M HClaq. (200 mL), water (200 mL), 5%NaHCO₃aq. (200 mL), and brine (200 mL), dried over Na₂SO₄, and concentrated in vacuo to give the desired product **14** (4.83 g, 17.8 mmol, 89%).

Ts-Aib-OMe 14 ⁶: ¹H NMR (400 MHz, CDCl₃) δ 1.35-1.55 (m, 30H), 1.55-1.75 (m, 2H), 3.69 (s, 3H), 6.27 (brs, 1H), 7.32 (brs, 1H), 7.36 (brs, 1H), 8.17 (brs, 1H).

Preparation of Ts-Aib-OH 15: To a solution of Ts-Aib-OMe **14** (4.82 g, 17.7 mmol) in THF (60 mL) was added to $\text{LiOH}\cdot\text{H}_2\text{O}$ (1.10 g, 26.2 mmol) in H_2O (30 mL), and the resulting mixture was stirred at

room temperature for 3 h. After removal of THF in vacuo, the aqueous solution was extracted with Et_2O (50 mLx4) and acidified to pH 2 by addition of concentrated hydrochloric acid. The resulting precipitate was collected by filtration to give the Ts-Aib-OH **15** (1.49 g, 5.82 mmol, 72%) as a white solid, which was used directly in further steps without any purification.

Ts-Aib-OH 15 ⁷: ¹H NMR (400 MHz, CDCl₃) δ 1.35-1.55 (m, 30H), 1.55-1.75 (m, 2H), 3.69 (s, 3H), 6.27 (brs, 1H), 7.32 (brs, 1H), 7.36 (brs, 1H), 8.17 (brs, 1H).

Preparation of Ts-(Aib)₂**-OMe 16**: To the mixture of Ts-Aib-OH **15** (2.95 g, 11.5 mmol), H-Aib-OMe·HCl **6** (1.76 g, 11.5 mmol), HOBt·H₂O (1.76 g, 11.5 mmol), and EDC·HCl (2.64 g, 13.8 mmol) in dichloromethane (77 mL) was added *N*,*N*-diisopropylethylamine (2.0 mL, 11.5 mmol). The resulting mixture was stirred at room temperature for 3 days under argon. The reaction mixture was poured into dichloromethane (150 mL), washed with 5%KHSO₄aq. (150 mLx3), 5%NaHCO₃ aq. (150 mLx3), and brine (150 mL), dried over Na₂SO₄, and concentrated in vacuo to give the crude product (2.60 g, 7.30 mmol, 63%) The resulting product was recrystallized from *n*-hexane/CHCl₃ to give the pure compound **16** (2.26 g) as a white solid.

Ts-(Aib)₂**-OMe 16** ⁸: ¹H NMR (400 MHz, CDCl₃) δ 1.35-1.55 (m, 30H), 1.55-1.75 (m, 2H), 3.69 (s, 3H), 6.27 (brs, 1H), 7.32 (brs, 1H), 7.36 (brs, 1H), 8.17 (brs, 1H).

Preparation of Ts-(Aib)₂-OH 17: To a solution of Ts-(Aib)₂-OMe 16 (1.03 g, 2.90 mmol) in THF (22 mL) was added to $\text{LiOH} \cdot \text{H}_2\text{O}$ (0.39 g, 9.2 mmol) in H_2O (11 mL), and the resulting mixture was stirred at 50 °C for 3 h. After removal of THF in vacuo, the aqueous solution was extracted with Et₂O (50 mLx2) and acidified to pH 2 by addition of concentrated hydrochloric acid. The resulting precipitate was collected by filtration to give the Ts-(Aib)₂-OH 17 (0.82 g, 2.41 mmol, 83%) as a white solid, which was used directly in further steps without any purification.

Ts-(Aib)₂**-OH 17** ⁸**:** ¹H NMR (400 MHz, CDCl₃) δ 1.35-1.55 (m, 30H), 1.55-1.75 (m, 2H), 3.69 (s, 3H), 6.27 (brs, 1H), 7.32 (brs, 1H), 7.36 (brs, 1H), 8.17 (brs, 1H).

Preparation of Ts-(Aib)₃**-OMe 18**: To the mixture of Ts-(Aib)₂-OH **17** (4.56 g, 13.3 mmol), H-Aib-OMe·HCl **6** (2.04 g, 13.3 mmol), HOBt·H₂O (2.04 g, 13.3 mmol), and EDC·HCl (3.06 g, 16.0 mmol) in dichloromethane (90 mL) was added *N*,*N*-diisopropylethylamine (2.33 mL, 13.3 mmol). The resulting mixture was stirred at room temperature for 3 days under argon. The reaction mixture was poured into dichloromethane (100 mL), washed with 5%KHSO₄aq. (300 mLx3), 5%NaHCO₃ aq. (300 mLx3), and brine (300 mL), dried over Na₂SO₄, and concentrated in vacuo to give the crude product (4.01 g, 9.08 mmol, 68%). The crude product was purified using column chromatography (silica gel, CHCl₃/MeOH) to give the desired product **18** (2.58 g, 56%) as a white solid.

Ts-(Aib)₃-OMe 18 8: 1H NMR (400 MHz, CDCl₃) & 1.35-1.55 (m, 30H), 1.55-1.75 (m, 2H), 3.69 (s, 3H),

6.27 (brs, 1H), 7.32 (brs, 1H), 7.36 (brs, 1H), 8.17 (brs, 1H).

Preparation of Ts-(Aib)₃-OH 19: To a solution of Ts-(Aib)₃-OMe 18 (0.48 g, 1.08 mmol) in THF (9.3 mL) was added to LiOH·H₂O (0.156 g, 3.74 mmol) in H₂O (4.6 mL), and the resulting mixture was stirred at 50 °C for 2 h. After removal of THF in vacuo, the aqueous solution was extracted with Et₂O (10 mLx2) and acidified to pH 2 by addition of concentrated hydrochloric acid. The resulting product was dissolved in AcOEt (15 mLx3), washed with brine (20 mL), dried over Na₂SO₄, and concentrated in vacuo to give the the Ts-(Aib)₃-OH 19 (0.33 g, 0.78 mmol, 72%) as a white solid, which was used directly in further steps without any purification.

Ts-(Aib)₃-OH 19⁸: ¹H NMR (400 MHz, CDCl₃) δ 1.35-1.55 (m, 30H), 1.55-1.75 (m, 2H), 3.69 (s, 3H), 6.27 (brs, 1H), 7.32 (brs, 1H), 7.36 (brs, 1H), 8.17 (brs, 1H).

Preparation of Ts-(Aib)₄**-OMe 20**: To the mixture of Ts-(Aib)₃-OH **19** (2.07 g, 4.86 mmol), H-Aib-OMe·HCl **5** (0.74 g, 4.86 mmol), HOBt·H₂O (0.74 g, 4.86 mmol), and EDC·HCl (1.12 g, 5.8 mmol) in dichloromethane (32 mL) was added *N*,*N*-diisopropylethylamine (0.85 mL, 4.86 mmol). The resulting mixture was stirred at room temperature for 3 days under argon. The reaction mixture was poured into dichloromethane (100 mL), washed with 5%KHSO₄aq. (110 mLx3), 5%NaHCO₃ aq. (110 mLx3), and brine (110 mL), dried over Na₂SO₄, and concentrated in vacuo to give the crude product (2.02 g, 3.84 mmol, 79%). The crude product was purified using column chromatography (silica gel, CHCl₃/MeOH) to give the desired product **20** (1.83 g, 71%) as a white solid.

Ts-(Aib)₄**-OMe 20**⁸: ¹H NMR (400 MHz, CDCl₃) δ 1.35-1.55 (m, 30H), 1.55-1.75 (m, 2H), 3.69 (s, 3H), 6.27 (brs, 1H), 7.32 (brs, 1H), 7.36 (brs, 1H), 8.17 (brs, 1H).

Preparation of Ts-(Aib)₄-OH 21: To a solution of Ts-(Aib)₄-OMe 20 (1.81 g, 3.43 mmol) in THF (26 mL) was added to LiOH·H₂O (0.448 g, 10.6 mmol) in H₂O (13 mL), and the resulting mixture was stirred at 50 °C for 3 h. After LiOH·H₂O (0.224 g, 5.3 mmol) and THF (13 mL) and H₂O (6.0 mL) were addedd, the resulting mixture was stirred at 50 °C for 1.5 h. After removal of THF in vacuo, the aqueous solution was extracted with Et₂O (150 mLx3) and acidified to pH 2 by addition of concentrated hydrochloric acid. The resulting product was dissolved in AcOEt (100 mL), washed with brine(150 mL), and concentrated in vacuo. The resulting precipitate was collected by filtration to give the Ts-(Aib)₄-OH 21 (1.83 g, 3.58 mmol, quant) as a white solid, which was used directly in further steps without any purification.

Ts-(Aib)₄**-OH 21**⁸: ¹H NMR (400 MHz, CDCl₃) δ 1.35-1.55 (m, 30H), 1.55-1.75 (m, 2H), 3.69 (s, 3H), 6.27 (brs, 1H), 7.32 (brs, 1H), 7.36 (brs, 1H), 8.17 (brs, 1H).

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Compound	1a	1b	1c	2	3
Empirical formula	$\begin{array}{c} C_{28}H_{45}N_5O_8\\ S{\cdot}0.5C_7H_8 \end{array}$	$C_{28}H_{45}N_5O_8S$	$\begin{array}{c} C_{28}H_{45}N_5O_8S{\cdot}0.5\\ CHCl_3{\cdot}0.5THF \end{array}$	C ₂₇ H ₄₂ BrN5 O ₈ S	$\begin{array}{c} C_{28}H_{45}N_5O_9\\ S{\cdot}0.5C_7H_8 \end{array}$
Formula weight	657.82	611.75	706.54	692.62	673.82
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic	triclinic
Space group	<i>P</i> -1	Pbca	$P2_{1}/c$	$P2_{1}/n$	<i>P</i> -1
<i>a</i> / Å	8.32010(10)	18.01208(8)	13.2585(7)	13.8934(4)	8.27710(10)
<i>b</i> / Å	11.5563(2)	16.32819(8)	12.4082(6)	15.6619(3)	11.4080(3)
<i>c</i> / Å	18.7213(3)	22.35160(10)	22.8754(10)	16.0905(4)	19.4068(4)
α / deg	95.4904(13)	90	90	90	89.945(2)
β / deg	96.5217(13)	90	94.548(4)	108.069(3)	79.6420(10)
γ/\deg	91.8701(14)	90	90	90	88.733(2)
V/	1778.47(5)	6573.71(5)	3751.5(3)	3328.58(15)	1802.18(6)
Ζ	2	8	4	4	2
Z'	1	1	1	1	1
Temperature / K	93	93	<mark>93</mark>	93	93
Goodness-of-fit ^{<i>a</i>} on F^2	1.068	1.024	1.074	1.053	1.108
$R_1 [I > 2\sigma(I)]^b$ on F	0.0483	0.0409	0.0661	<mark>0.0524</mark>	0.0446
wR_2^c (all data) on F^2	0.1308	0.1200	0.2188	<mark>0.1213</mark>	0.1350
Reflection collected (all data)	45045	52505	47682	51463	46978
Independent reflections $[I > 2\sigma(I)]$	6151	5540	3802	6168	5504
R _{int}	0.0427	0.0371	0.1275	0.0469	0.0584
Abs. corr.	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Radiation type	Cu-Ka	Cu-Ka	Cu-Ka	Μο-Κα	Cu-Ka
$T_{\rm max}$	0.622	0.612	0.481	0.509	0.639
T_{\min}	0.737	0.920	0.650	0.678	0.880
$2\theta_{\rm max}$	68.248	68.241	68.229	27.498	68.248
$D_{\rm calcd.}$ / gcm ⁻³	1.228	1.236	1.251	1.350	1.234
μ /mm ⁻¹	1.253	1.317	2.154	<mark>1.353</mark>	1.242
Restraints/parameters	<mark>0/431</mark>	<mark>9/395</mark>	<mark>0/473</mark>	<mark>0/394</mark>	<mark>0/457</mark>
Largest diff. peak/hole/eÅ ⁻³	0.28/-0.68	<mark>0.63/-0.46</mark>	0.45/-0.44	<mark>2.37/-2.05</mark>	0.24/-0.51
Index ranges	$ \begin{array}{l} -10 \le h \le 10 \\ -13 \le k \le 13 \\ -22 \le l \le 22 \end{array} $	$ \begin{array}{l} -21 \le h \le 21 \\ -19 \le k \le 19 \\ -26 \le 1 \le 26 \end{array} $	$ \begin{array}{l} -15 \le h \le 15 \\ -13 \le k \le 14 \\ -27 \le 1 \le 27 \end{array} $	$-18 \le h \le 17$ $-20 \le k \le 20$ $-20 \le l \le 16$	$-10 \le h \le 10$ $-14 \le k \le 14$ $-24 \le 1 \le 24$
CCDC code	2022589	2022590	2022591	2022592	2022593

Table S1. Crystallographic parameters

 $\frac{1}{a \text{GOF} = [\Sigma w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2} (N_o; \text{ number of observations, } N_v; \text{ number of variables}), \ bR_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, \ cwR_2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}.$

Boc-(Aib)₃-OMe 8



Boc-(Aib)₄-OMe 10



Boc-(Aib)5-OMe 12





ArSO₂-(Aib)₅-OMe (Ar = *p*-bromophenyl) 2



ArSO₂-(Aib)₅-OMe (Ar = *p*-methoxyphenyl) 3