Supporting Information for:

One-pot, Three-Component Synthesis of Novel Pyrroloacridinones via Intramolecular Ipso-Dearomatization / Intramolecular Aza-Michael Addition Sequence

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1. General Information.

All commercial reagents were used directly as obtained. Thin-layer chromatography was performed using commercially prepared Sorbfil UV-254 silica gel plates. Compounds on TLC were visualized under UV light (254 nm) and with a 0.5% p-chloranil solution in toluene. Column chromatography was performed using silica gel (0.06-0.20 mm, 70-230 mesh, Lancaster). Melting points (mp) were determined on a PTP apparatus and are uncorrected. Infra-red spectra (IR) were recorded on a Bruker IFS 66 FTIR spectrometer. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury Plus 300 spectrometer ($^1$H: 300.06 MHz, $^{13}$C: 75.46 MHz) and a Bruker AVANCE-500 spectrometer ($^1$H: 500.13 MHz, $^{13}$C: 125.76 MHz). The $^1$H chemical shifts were measured from internal SiMe$_4$, $^{13}$C — from the solvent signal (CDCl$_3$, δ$_C$ 77.0 ppm). All the signals in the $^1$H and $^{13}$C NMR spectra of the compounds 4g, 5h, 5h', 5i, 5i', 5j', and 7 were assigned on the basis of 2D $^1$H–$^1$H COSY and NOEY, $^1$H–$^{13}$C HSQC and HMBC experiments. The stereochemistry of 5a was determined by 2D $^1$H–$^1$H NOESY experiment. Mass spectra (MS) were obtained on an Agilent 6890N/5975B GC-MS system (column: HP-5ms, 30 m × 0.25 mm, 0.25 μm; helium as a carrier gas, electron impact ionization mode (200°C, 70 eV)). Elemental analyses were carried out on a Leco CHNS-932 analyzer. X-ray data were collected at 295(2) K with an XCALIBUR-3 diffractometer, CCD detector (ω-scanning technique, MoKα radiation, graphite monochromator). Structures were solved by direct method and refined with SHELX-97 program package. All non-hydrogen atoms were refined anisotropically. Crystallographic data and data collection parameters are summarized in Table 1.
2. Experimental procedures and Characterization Data

2,6-Di-tert-butyl-4-(1-hydroxy-2-methylpropyl)phenol (6). To a stirred suspension of sodium borohydride (1.75 g, 46 mmol) in 15 ml of ethanol was added a solution of 1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methylpropan-1-one\(^2\) (11.56 g, 42 mmol) in 15 ml of ethanol dropwise at such a rate that the temperature of the reaction mixture was maintained at 20-30 °C. The reaction mixture was stirred at room temperature for 4 hours. Then ethanol was removed on a rotary evaporator and 10 ml of a 10% NaOH solution was added. The aqueous phase was extracted with Et\(_2\)O (3×50 ml). The combined organic phases were washed with water, dried under Na\(_2\)SO\(_4\), and evaporated to dryness. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 20:1) to give pure compound 6 (8.01 g, 69%) as a colorless solid: \(R_f\) 0.44 (hexane/ethyl acetate, 10:1); mp: 92.5-94.5 °C; IR (film) \(\nu\): 3398, 2957, 2872, 1435, 1365 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)), \(\delta\), ppm, J/Hz: 0.76 (d, 3H, \(J = 6.7\), Me), 1.01 (d, 3H, \(J = 6.7\), Me), 1.44 (s, 18H, C\(_2\)(Me\(_3\)), C\(_6\)(Me\(_3\))), 1.87 (d, 1H, \(J = 2.9\), OH-C\(_1\)'), 1.91 (m, 1H, H-2'), 4.23 (dd, 1H, \(J = 7.5, 2.9\), H-1'), 5.15 (s, 1H, OH-C\(_1\)'), 7.09 (s, 2H, H-3 and H-5); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)), \(\delta\), ppm: 18.59 (Me), 19.09 (Me), 30.27 (2C(Me\(_3\))), 34.23 (2C(Me\(_3\))), 35.05 (C-2'), 80.53 (C-1'), 123.13 (C-3, C-5), 134.20 (C-4), 135.38 (C-2, C-6), 152.93 (C-1); MS (EI) m/z (%): 278 [M\(^+\)] (3), 260 [M-H\(_2\)O\(^+\)] (7), 245 (9), 235 [M-CH(Me)\(_2\)]\(^+\) (100); Anal. Calcd for C\(_{18}\)H\(_{30}\)O\(_2\): C 77.65, H 10.85; found: C 77.65, H 10.86.

(6a\(R^*\),14a\(S^*\))-13,13-Dimethyl-6a,7,13,14-tetrahydrobenzo[a]pyrrolo[2,3-m]acridin-5(6H)-one (5a). A mixture of 1-methoxynaphthalene \(1a\) (316 mg, 2.0 mmol), isobutyric aldehyde 2 (216 mg, 3.0 mmol), and 2-aminobenzonitrile \(3\) (236 mg, 2.0 mmol) was added dropwise to stirred concentrated sulfuric acid (92%, 1 ml, 17 mmol) at 5-7 °C. The reaction mixture was stirred at room temperature for 25 min and poured into a mixture of ice (25 g) and NH\(_3\) (aq) (7 mL). The product was extracted with CH\(_2\)Cl\(_2\) (3×15 ml), and the combined organic layers were washed with water, dried over anhydrous Na\(_2\)SO\(_4\), and filtered. After the solvent was removed, the crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1 to 2:1) to give pure 5a (516 mg, 82%). Data for 5a: Pale yellow solid; \(R_f\) 0.63 (hexane/ethyl acetate, 2:1); mp: 267-269 °C; IR (film) v: 3364, 3066, 3026, 2964, 2867, 1674, 1610 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)), \(\delta\), ppm, J/Hz: 1.42 (s, 3H, Me-C\(_{13}\)), 1.47 (s, 3H, Me-C\(_{13}\)), 2.05 (d, 1H, \(J = 13.1\), H-14\(^B\)), 2.10 (d, 1H, \(J = 13.1\), H-14\(^A\)), 2.79 (dd, 1H, \(J = 18.0, 3.0\), H-6\(^B\)), 3.02 (dd, 1H, \(J = 18.0, 3.0\), H-6\(^A\)),
3.96 (t, 1H, J = 3.0, H-6a), 4.32 (br s, 1H, NH), 6.41 (br d, 1H, J = 7.9, 7.1, 1.2, H-10), 7.06-7.10 (m, 2H, H-1 and H-9), 7.29 (td, 1H, J = 7.6, 1.0, H-3), 7.41 (td, 1H, J = 7.6, 1.4, H-2), 7.92 (dd, 1H, J = 7.9, 1.5, H-11), 8.03 (dd, 1H, J = 7.8, 1.4, H-4);

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\text{13C NMR (75 MHz, CDCl}_3\text{, }\delta, \text{ ppm: 29.29 (Me-C13), 32.46 (Me-C13), 40.53, 48.41 (C-6, C-14), 56.30 (C-14a), 58.45 (C-6a), 72.87 (C-13), 114.75 (C-8), 115.62 (C-11a), 118.32 (C-10), 126.85, 127.00, 127.31 and 127.90 (C-1, C-4, C-9, and C-11), 131.08 (C-4a), 131.81 and 134.17 (C-2, C-3), 143.59 and 147.00 (C-7a and C-14b), 166.59 (C-11b), 195.23 (C-5); MS (EI) m/z (%): 316 [M] + (78), 316 [M-Me] + (100); Anal. Calcd for C21H20N2O: C 79.72, H 6.37, N 8.85; found: C 79.42, H 6.43, N 8.64.}

(3aS*,7aR*)-2,2-Dimethyl-2,3,7a,8-tetrahydropyrrolo[3,2-l]acridin-6(7H)-one (5b). The title compound was prepared from anisole 1b (216 mg, 2.0 mmol), isobutyric aldehyde 2 (216 mg, 3.0 mmol), and 2-aminobenzonitrile 3 in a similar manner as described for the preparation of 5a. The crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate, 2:1) to give starting 2-aminobenzonitrile 3 (71 mg, 30%), and 5b (213 mg, 40%). Data for 5b: Yellow solid; Rf 0.30 (hexane/ethyl acetate, 1:1); mp: 230.5-232 °C; IR (film) ν: 3265, 3030, 2968, 2924, 1670, 1605 cm⁻¹. \[^1\text{H NMR (500 MHz, CDCl}_3\text{, }\delta, \text{ ppm, J/Hz: 1.40 (s, 3H, Me-C2), 1.48 (s, 3H, Me-C2), 2.04 (d, 1H, J = 12.9, H-3B), 2.19 (d, 1H, J = 12.9, H-3A), 2.56 (ddd, 1H, J = 17.1, 3.0, 0.9, H-7B), 2.75 (dd, 1H, J = 17.1, 2.7, H-7A), 3.85 (q, 1H, J = 2.6, H-7a), 4.39 (s, 1H, NH), 5.96 (dd, 1H, J = 10.0, 0.9, H-5), 6.57 (dd, 1H, J = 8.3, 1.0, H-9), 6.63 (dd, 1H, J = 10.0, 2.3, H-4), 6.72 (ddd, 1H, J = 7.9, 7.1, 1.0, H-11), 7.18 (dd, 1H, J = 8.3, 7.1, 1.5, H-10), 7.85 (dd, 1H, J = 7.9, 1.5, H-12); 13C NMR (75 MHz, CDCl}_3\text{, }\delta, \text{ ppm: 30.02 and 31.27 (2Me-C2), 40.85 (C-7), 49.24 (C-3), 53.71 (C-3a), 58.26 (C-7a), 72.13 (C-2), 114.69 (C-9), 114.97 (C-12a), 118.20 (C-11), 126.98 and 128.27 (C-12 and C-5), 132.51 (C-10), 146.40 (C-8a), 148.40 (C-4), 166.08 (C-12b), 195.80 (C-6); MS (EI) m/z (%): 266 [M] + (100); Anal. Calcd for C17H18N2O: C 76.66, H 6.81, N 10.52; found: C 76.83, H 6.58, N 10.48.}

(3aS*,7aR*)-2,2,5-Trimethyl-2,3,7a,8-tetrahydropyrrolo[3,2-l]acridin-6(7H)-one (5c). The title compound was prepared from 2-methylanisole 1c (244 mg, 2.0 mmol), isobutyraldehyde 2 (216 mg, 3.0 mmol), and 2-aminobenzonitrile 3 (236 mg, 2.0 mmol) in a similar manner as described for the preparation of 5a. The crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate, 2:1) to give pure 5c (406 mg, 73%).
**Data for 5c:** Yellow solid; $R_f$ 0.33 (hexane/ethyl acetate, 2:1); mp: 202-203.5 °C; IR (film) v: 3332, 2956, 1668, 1606 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$), $\delta$, ppm, $J$/Hz: 1.41 (s, 3H, Me-C$_2$), 1.47 (s, 3H, Me-C$_2$), 1.74 (d, 3H, $J = 1.5$, Me-C$_3$), 2.02 (d, 1H, $J = 12.8$, H-3$^B$), 2.17 (d, 1H, $J = 12.8$, H-3$^A$), 2.57 (dd, 1H, $J = 17.1$, 3.2, H-7$^B$), 2.76 (dd, 1H, $J = 17.1$, 2.7, H-7$^A$), 3.81 (q, 1H, $J = 2.7$, H-7a), 4.37 (s, 1H, NH), 6.38 (qd, 1H, $J = 1.7$, 1.5, H-4), 6.56 (dd, 1H, $J = 8.2$, 1.0, H-9), 6.71 (ddd, 1H, $J = 7.9$, 7.0, 1.0, H-11), 7.18 (ddd, 1H, $J = 8.2$, 7.1, 1.5, H-10), 7.85 (dd, 1H, $J = 7.9$, 1.5, H-12); $^{13}$C NMR (75 MHz, CDCl$_3$), $\delta$, ppm: 15.93 (Me-C$_5$), 30.00 and 31.28 (2Me-C$_2$), 40.84 (C-7), 49.25 (C-3), 53.96 (C-3a), 58.60 (C-7a), 71.91 (C-2), 114.66 (C-9), 114.94 (C-2a), 117.92 (C-11), 126.95 (C-12), 132.30 (C-10), 134.51 (C-5), 143.35 (C-4), 146.57 (C-8a), 166.59 (C-12b), 196.29 (C-6); MS (EI) m/z (%): 280 [M$^+$] (100); Anal. Calcd for C$_{18}$H$_{20}$N$_2$O: C 77.11, H 7.19, N 9.99; found: C 76.92, H 7.06, N 9.93.

($3a^S$,7a$^R$*)-4,5-Dimethoxy-2,2-dimethyl-2,3,7a,8-tetrahydropyrrolo[3,2-l]acridin-6(7H)-one (5d). A solution of 1,2,3-trimethoxybenzene 1d (336 mg, 2.0 mmol) and isobutyric aldehyde 2 (216 mg, 3.0 mmol) in CH$_2$Cl$_2$ (0.5 ml) was added dropwise to stirred solution of 2-aminobenzonitrile 3 (236 mg, 2.0 mmol) in concentrated sulfuric acid (92%, 1 ml, 17 mmol) at 5-7 °C. The reaction mixture was stirred at room temperature for 1.5 h and poured into a mixture of ice (25 g) and NH$_3$ (aq) (7 mL). The product was extracted with CH$_2$Cl$_2$ (3×15 ml), and the combined organic layers were washed with water, dried over anhydrous Na$_2$SO$_4$, and filtered. After the solvent was removed, the crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate, 3:1 to 1:1) to give starting 2-aminobenzonitrile 3 (89 mg, 38%) and 5d (290 mg, 44%). **Data for 5d:** Pale yellow solid; $R_f$ 0.25 (hexane/ethyl acetate, 1:1); mp: 197-199 °C; IR (film) v: 3348, 3245, 3004, 2962, 1665, 1632, 1612 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$), $\delta$, ppm, $J$/Hz: 1.41 (s, 3H, Me-C$_2$), 1.44 (s, 3H, Me-C$_2$), 2.02 (d, 1H, $J = 13.4$, H-3$^B$), 2.13 (d, 1H, $J = 13.4$, H-3$^A$), 2.53 (dd, 1H, $J = 17.2$, 3.0, H-7$^B$), 2.74 (dd, 1H, $J = 17.2$, 3.0, H-7$^A$), 3.59 (s, 3H, OMe), 3.74 (t, 1H, $J = 3.0$, H-7a), 3.93 (s, 3H, OMe), 4.40 (s, 1H, NH), 6.55 (dd, 1H, $J = 8.2$, 0.9, H-9), 6.69 (ddd, 1H, $J = 7.8$, 7.1, 0.9, H-11), 7.15 (ddd, 1H, $J = 8.2$, 7.1, 1.5, H-10), 7.75 (dd, 1H, $J = 7.8$, 1.5, H-12); $^{13}$C NMR (126 MHz, CDCl$_3$), $\delta$, ppm: 28.65 and 31.86 (2Me-C$_2$), 40.21 (C-7), 48.02 (C-3), 57.05 (OMe), 57.98 (C-7a), 60.89 (C-3a), 60.92 (OMe), 72.96 (C-2), 114.18 (C-9), 115.75 (C-12a), 117.77 (C-11), 126.79 (C-12), 131.85 (C-10), 135.72 (C-5), 145.96 (C-8a), 162.85 (C-4), 163.87 (C-12b), 192.41 (C-6); MS (EI) m/z (%): 326 [M$^+$] (98), 311 [M-Me$^-$] (59), 208 (16), 193 (40), 183 (17), 159 (100); Anal. Calcd for C$_{19}$H$_{22}$N$_2$O$_3$: C 69.92, H 6.79, N 8.58; found: C 70.03, H 6.68, N 8.51.
(3aS*,7aR*)-5-Methoxy-2,2,7a-trimethyl-2,3,7a,8-tetrahydropyrrolo[3,2-l]acridin-6(7H)-one (5e). The title compound was prepared from 1,2-dimethoxy-4-methylbenzene 1e (304 mg, 2.0 mmol), isobutyric aldehyde 2 (216 mg, 3.0 mmol) and 2-aminobenzonitrile 3 (236 mg, 2.0 mmol) in a similar manner as described for the preparation of 5a. The crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate, 2:1) to give starting 2-aminobenzonitrile 3 (77 mg, 33%) and 5e (340 mg, 55%).

**Data for 5e:** Pale yellow solid; R_t 0.18 (hexane/ethyl acetate, 2:1); mp: 245-247 °C; IR (film) ν: 3322, 2967, 1687, 1617 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)), δ, ppm, J/Hz: 1.23 (s, 3H, Me-C\(^{7a}\)), 1.45 (s, 3H, Me-C\(^{2}\)), 1.47 (s, 3H, Me-C\(^{2}\)), 1.97 (d, 1H, J = 13.4, H-3\(^B\)), 2.26 (d, 1H, J = 13.4, H-3\(^A\)), 2.62 (d, 1H, J = 16.9, H-7\(^B\)), 2.71 (d, 1H, J = 16.9, H-7\(^A\)), 3.50 (s, 3H, OMe), 4.14 (s, 1H, NH), 5.45 (s, 1H, H-4\(^A\)), 6.53 (d, 1H, J = 8.3, H-9), 6.71 (ddd, 1H, J = 7.9, 7.1, 0.9, H-11), 7.18 (ddd, 1H, J = 8.3, 7.1, 1.5, H-10), 7.91 (dd, 1H, J = 7.9, 1.5, H-12); \(^13\)C NMR (75 MHz, CDCl\(_3\)), δ, ppm: 23.15 (Me-C\(^{7a}\)), 30.59 and 31.54 (2Me-C\(^{2}\)), 45.81 (C-3), 48.35 (C-7), 54.91 (OMe), 57.81, 57.84 (C-3a, C-7a), 71.90 (C-2), 114.19 (C-12a), 115.14 (C-9), 117.04 and 117.67 (C-4, C-11), 126.96 (C-12), 132.24 (C-10), 145.16 (C-8a), 149.60 (C-5), 165.69 (C-12b), 192.18 (C-6); MS (EI) m/z (%): 310 [M] (+ 95), 295 [M-Me] (+ 100); Anal. Calcd for C\(_{19}\)H\(_{22}\)N\(_2\)O\(_2\): C 73.52, H 7.14, N 9.03; found: C 73.60, H 7.05, N 8.94.

1-(2-aminophenyl)-9-isopropyl-3,3,6-trimethyl-2-azaspiro[4.5]deca-1,6,9-trien-8-one (4f) and (3aS*,7aR*)-5-isopropyl-2,2,7a-trimethyl-2,3,7a,8-tetrahydropyrrolo[3,2-l]acridin-6(7H)-one (5f). The title compounds were prepared from 1-isopropyl-2-methoxy-4-methylbenzene 1f (328 mg, 2.0 mmol), isobutyric aldehyde 2 (216 mg, 3.0 mmol) and 2-aminobenzonitrile 3 (236 mg, 2.0 mmol) in a similar manner as described for the preparation of 5a. The crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1 to 1:1) to give 4f (59 mg, 9%) and 5f (340 mg, 53%).

**Data for 4f:** Colorless solid; R_t 0.75 (hexane/ethyl acetate, 2:1); mp: 136-138 °C; IR (film) ν: 3426, 3254, 2964, 2874, 1656, 1616 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)), δ, ppm, J/Hz: 1.04 (d, 3H, J = 6.9, Me-C\(^9\)), 1.09 (d, 3H, J = 6.9, Me-C\(^9\)), 1.47 (s, 3H, Me-C\(^3\)), 1.53 (s, 3H, Me-C\(^3\)), 1.83 (d, 3H, J = 1.3, Me-C\(^6\)), 1.98 (d, 1H, J = 13.8, H-4\(^B\)), 2.15 (d, 1H, J = 13.8, H-4\(^A\)), 3.07 (spd, 2H, J = 6.9, 1.1, H-9\(^a\)), 6.24 (q, 1H, J = 1.3, H-7), 6.40 (ddd, 1H, J = 8.1, 7.0, 1.2, H-5\(^a\)), 6.55 (br s, 2H, NH\(_2\)), 6.66 (dd, 1H, J = 8.3, 1.2, H-3\(^b\)), 6.77 (d, 1H, J = 1.1, H-10), 7.02 (dd, 1H, J = 8.1, 1.5, H-6\(^\prime\)), 7.08 (ddd, 1H, J = 8.3, 7.0, 1.5, H-4\(^\prime\)); \(^13\)C NMR
(75 MHz, CDCl₃), δ, ppm: 19.94 (Me-C⁶), 21.36 and 21.59 (2Me-C⁶), 25.84 (C-9'), 31.16 and 31.61 (2Me-C⁵), 49.47 (C-4), 65.29 (C-5), 72.06 (C-3), 114.11 (C-1'), 115.66 and 116.16 (C-3', C-5'), 127.69 and 128.65 (C-4', C-6'), 131.25 (C-7), 142.32 (C-9), 145.31 (C-10), 149.22 (C-2'), 160.28 (C-6), 167.36 (C-1), 185.41 (C-8); MS (EI) m/z (%): 322 [M]⁺ (14), 204 [M-H₂NC₆H₄CN]⁺ (79), 189 [M-H₂NC₆H₄CN-Me]⁺ (100); Anal. Calcd for C₂₁H₂₆N₂O: C 78.22, H 8.13, N 8.69; found: C 78.22, H 8.02, N 8.64.

Data for 5f: Pale yellow solid; Rₜ 0.38 (hexane/ethyl acetate, 2:1); mp: 166.5-167 °C; IR (film): 3359, 3316, 2963, 2876, 1669, 1618 cm⁻¹. ¹H NMR (500 MHz, CDCl₃), δ, ppm, J/Hz: 0.87 (d, 3H, J = 6.9, Me-C⁵'); 0.96 (d, 3H, J = 6.9, Me-C⁵'); 1.22 (s, 3H, Me-C⁷a), 1.43 (s, 3H, Me-C²), 1.46 (s, 3H, Me-C²), 1.88 (d, 1H, J = 13.4, H-3B), 2.22 (d, 1H, J = 13.4, H-3A), 2.52 (d, 1H, J = 16.7, H-7B), 2.60 (d, 1H, J = 16.7, H-7A), 2.80 (spd, 1H, J = 6.9, 1.1, H-5'), 3.86 (s, 1H, NH), 6.25 (d, 1H, J = 1.1, H-4), 6.49 (dd, 1H, J = 8.3, 0.9, H-9), 6.70 (ddd, 1H, J = 7.9, 7.1, 0.9, H-11), 7.16 (ddd, 1H, J = 8.3, 7.1, 1.5, H-10), 7.87 (dd, 1H, J = 7.9, 1.5, H-12); ¹³C NMR (75 MHz, CDCl₃), δ, ppm: 21.35 and 21.63 (2Me-C⁵), 23.30 and 26.00 (C5' and Me-C⁷a), 30.58 and 31.56 (2Me-C²), 45.40 (C-3), 45.51 (C-7), 57.68 and 58.51 (C-3a and C-7a), 71.88 (C-2), 114.12 (C-12a), 114.80 (C-9), 117.37 (C-11), 126.84 (C-12), 132.23 (C-10), 142.49, 142.83 and 145.19 (C-4, C-5, C-8a), 165.72 (C-12b), 196.92 (C-6); MS (EI) m/z (%): 322 [M]⁺ (74), 307 [M-Me]⁺ (100); Anal. Calcd for C₂₁H₂₆N₂O: C 78.20, H 8.12, N 8.66.

1-(2-Aminophenyl)-3,3,6,9-tetramethyl-2-azaspiro[4.5]deca-1,6,9-trien-8-one (4g) and (3aS*,7aR*)-2,2,5,7a-tetramethyl-2,3,7a,8-tetrahydropyrrolo[3,2-l]acridin-6(7H)-one (5g). The title compounds were prepared from 2-methoxy-1,4-dimethylbenzene 1f (272 mg, 2.0 mmol), isobutyric aldehyde 2 (216 mg, 3.0 mmol), and 2-aminobenzonitrile 3 (236 mg, 2.0 mmol) in a similar manner as described for the preparation of 5a. The crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate, 3:1 to 1:1) to give 4g (67 mg, 11%) and 5g (372 mg, 63%).

Data for 4g: Colorless solid; Rₜ 0.75 (hexane/ethyl acetate, 2:1); mp: 193-197 °C; IR (film): 3348, 3245, 3004, 2942, 2962, 1665, 1632, 1612 cm⁻¹; ¹H NMR (500 MHz, CDCl₃), δ, ppm, J/Hz: 1.46 (s, 3H, Me-C³), 1.53 (s, 3H, Me-C³), 1.84 (d, 3H, J = 1.3, Me-C⁶), 1.94 (d, 3H, J = 1.5, Me-C⁶), 2.03 (d, 1H, J = 13.9, H-4B), 2.14 (d, 1H, J = 13.9, H-4A), 2.62 (q, 1H, J = 1.3, H-7), 6.42 (ddd, 1H, J = 8.1, 7.0, 1.2, H-5'), 6.56 (br s, 2H, NH₂), 6.66 (dd, 1H, J = 8.2, 1.2, H-3'), 6.88 (q, 1H, J = 1.5, H-10), 7.04 (dd, 1H, J = 8.1, 1.4, H-6'), 7.09 (ddd,
1H, J = 8.2, 7.0, 1.4, H-4'); \textbf{13C NMR} (126 MHz, CDCl$_3$), δ, ppm: 15.70 (Me-C$_5$), 20.11 (Me-C$_5$), 31.23 and 31.64 (2Me-C$_3$), 49.29 (C-4), 65.60 (C-5), 72.18 (C-3), 114.16 (C-1'), 115.88 (C-5'), 116.21 (C-3'), 127.22 (C-7), 128.69 (C-6'), 131.33 (C-4'), 132.92 (C-9), 148.33 (C-10), 149.29 (C-2'), 161.31 (C-6), 167.17 (C-1), 186.47 (C-8); \textbf{MS} (EI) m/z (%): 294 [M$^+$] (10), 176 [M-H$_2$NC$_6$H$_4$CN]$^+$ (60), 161 [M-H$_2$NC$_6$H$_4$CN-Me]$^+$ (62), 118 [H$_2$NC$_6$H$_4$CN]$^+$ (100); \textbf{Anal. Calcd for} C$_{19}$H$_{22}$N$_2$O: C 77.52, H 7.53, N 9.52; found: C 77.70, H 7.42, N 9.50.

\textbf{Data for 5g:} Yellow solid; $R_f$ 0.38 (hexane/ethyl acetate, 2:1); mp: 228-229 °C; \textbf{IR} (film) ν: 3325, 2967, 1661, 1612 cm$^{-1}$; \textbf{1H NMR} (500 MHz, CDCl$_3$), δ, ppm, J/Hz: 1.23 (s, 3H, Me-C$_7$), 1.43 (s, 3H, Me-C$_2$), 1.46 (s, 3H, Me-C$_2$), 1.72 (d, 3H, J = 1.5, Me-C$_5$), 1.93 (d, 1H, J = 13.5, H-3B), 2.22 (d, 1H, J = 13.5, H-3A), 2.54 (d, 1H, J = 16.8, H-7B), 2.60 (d, 1H, J = 16.8, H-7A), 4.18 (s, 1H, NH), 6.36 (q, 1H, J = 1.5, H-4), 6.52 (dd, 1H, J = 8.3, 1.0, H-9), 6.70 (ddd, 1H, J = 7.9, 7.0, 1.0, H-11), 7.17 (ddd, 1H, J = 8.3, 7.0, 1.5, H-10), 7.88 (dd, 1H, J = 7.9, 1.5, H-12); \textbf{13C NMR} (126 MHz, CDCl$_3$), δ, ppm: 15.51 (Me-C$_5$), 23.38 (Me-C$_7$), 30.56 and 31.54 (2Me-C$_3$), 45.08 (C-3), 48.06 (C-7), 58.19 and 58.79 (C-3a and C-7a), 71.97 (C-2), 114.24 (C-12a), 114.97 (C-9), 117.50 (C-11), 126.88 and 132.25 (C10 and C12), 133.04 (C-5), 145.39 (C-8a), 145.52 (C-4), 165.44 (C-12b), 197.73 (C-6); \textbf{MS} (EI) m/z (%): 294 [M$^+$] (79), 279 [M-Me]$^+$ (100); \textbf{Anal. Calcd for} C$_{19}$H$_{22}$N$_2$O: C 77.52, H 7.53, N 9.52; found: C 77.26, H 7.52, N 9.48.

(3a$^s$,7S*,7aR$^*$)-2,2,5,7-Tetramethyl-2,3,7a,8-tetrahydropyrrolo[3,2-l]acridin-6(7H)-one (5h) and (3a$^s$,7R*,7aR$^*$)-2,2,5,7-tetramethyl-2,3,7a,8-tetrahydropyrrolo[3,2-l]acridin-6(7H)-one (5h'). 2,6-Dimethylphenol 1h (244 mg, 2.0 mmol), isobutyric aldehyde 2 (216 mg, 3.0 mmol), and 2-aminobenzonitrile 3 (236 mg, 2.0 mmol) were combined in CH$_2$Cl$_2$ (0.5 ml) and the mixture was added dropwise to stirred concentrated sulfuric acid (92%, 1 ml, 17 mmol) at 5-7 °C. The reaction mixture was stirred at room temperature for 25 min and poured into mixture of ice (25 g) and NH$_3$ (aq) (7 mL). The product was extracted with CH$_2$Cl$_2$ (3×15 ml), and the combined organic layers were washed with water, dried over anhydrous Na$_2$SO$_4$, and filtered. After the solvent was removed, the crude mixture was purified by column chromatography on silica gel (hexane/acetone, 7:1) to give a mixture of diastereomers 5h and 5h' (390 mg, 66%; 5h:5h' = 84:16). Pure 5h was obtained after recrystallization of the mixture of diastereomers from ethyl acetate.

\textbf{Data for 5h:} Pale yellow solid; $R_f$ 0.25 (hexane/acetone, 7:1); mp: 248-250°C; \textbf{IR} (film) ν: 3372, 2956, 2861, 1669, 1611 cm$^{-1}$; \textbf{1H NMR} (500 MHz, CDCl$_3$), δ, ppm, J/Hz: 1.29 (d, 3H, J = 7.2, Me-C$_7$), 1.41 (s, 3H,
1.48 (s, 3H, Me-C2), 1.73 (d, 3H, J = 1.5, Me-C5), 2.06 (d, 1H, J = 12.7, H-3B), 2.19 (d, 1H, J = 12.7, H-3A), 2.28 (qd, 1H, J = 2.2, 2.2, H-7), 3.65 (t, 1H, J = 2.3, H-7a), 4.12 (s, 1H, NH), 6.31 (dq, 1H, J = 2.5, 1.5, H-4), 6.55 (dd, 1H, J = 8.3, 1.0, H-9), 6.72 (ddd, 1H, J = 7.9, 7.0, 1.0, H-11), 7.18 (ddd, 1H, J = 8.3, 7.0, 1.5, H-10), 7.86 (ddd, 1H, J = 7.9, 1.5, H-12); 13C NMR (126 MHz, CDCl3), δ ppm: 11.43 (Me-C5), 16.01 (Me-C7), 30.00 and 31.37 (2Me-C2), 42.16 (C-7), 49.07 (C-3), 54.87 (C-3a), 64.20 (C-7a), 71.90 (C-2), 114.85 (C-9), 115.43 (C-12a), 118.01 (C-11), 126.90 (C-12), 132.21 (C-5), 142.09 (C-4), 146.32 (C-8a), 166.60 (C-12b), 198.80 (C-6); MS (EI) m/z (%): 294 [M]+ (100); Anal. Calcd for C19H22N2O: C 77.52, H 7.53, N 9.52; found: C 77.44, H 7.31, N 9.46.

The title compounds were prepared from 2,6-diisopropylphenol 1i (356 mg, 2.0 mmol), isobutyric aldehyde 2 (216 mg, 3.0 mmol), and 2-aminobenzonitrile 3 (236 mg, 2.0 mmol) in a similar manner as described for the preparation of 5h/5h’. The crude mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate, 5:1) to give 4i (155 mg, 22%), starting 2-aminobenzonitrile 3 (60 mg, 25%), and mixture of diastereomers 5i and 5i’ (305 mg, 44%; 5i:5i’=25:75). The mixture 5i+5i’ (305 mg) was separated by using silica gel column chromatography (hexane/isopropanol, 30:1) to give 5i (60 mg), 5i+5i’ (27 mg), and 5i’ (204 mg).

Data for 4i: Colorless solid; Rf 0.70 (hexane/ethyl acetate, 5:1); mp: 118-122 °C; IR (film) ν: 3439, 3252, 2964, 2873, 1623, 1611, 1550 cm−1; 1H NMR (500 MHz, CDCl3), δ ppm, J/Hz: 1.03 and 1.08 (both d, 3H, J = 6.9, Me-C7 and Me-C8), 1.49 (s, 6H, 2Me-C3), 2.07 (s, 2H, H-4), 3.10 (sp, 2H, J = 6.9, H-7, H-9), 6.37 (ddd, 1H, J = 8.2, 7.0, 1.2, H-5’), 6.55 (br s, 2H, NH2), 6.65 (dd, 1H, J = 8.2, 1.2, H-3’), 6.72 (s, 2H, H-6, H-10), 7.06 (ddd, 1H, J = 8.2, 7.0, 1.5, H-4’), 7.09 (ddd, 1H, J = 8.2, 1.5, H-6’); 13C NMR (75 MHz, CDCl3), δ ppm:
21.48 and 21.68 (2Me-C\textsuperscript{7}, 2Me-C\textsuperscript{9}), 26.31 (C-7', C-9'), 31.24 (2Me-C\textsuperscript{3}), 49.68 (C-4), 61.36 (C-5), 71.82 (C-3), 114.51 (C-1'), 115.30, 116.09 (C-3', C-5'), 129.49, 131.13 (C-4', C-6'), 143.56 (C-7, C-9), 144.32 (C-6, C-10), 149.19 (C-2'), 167.82 (C-1), 184.29 (C-8); MS (EI) m/z (%): 350 [M]\textsuperscript{+} (11), 232 [M-H\textsubscript{2}NC\textsubscript{6}H\textsubscript{4}CN]\textsuperscript{+} (100); Anal. Calcd for C\textsubscript{23}H\textsubscript{30}N\textsubscript{2}O: C 78.82, H 8.63, N 7.99; found: C 78.62, H 8.50, N 7.92.

**Data for 5i:** Pale yellow solid; R\textsubscript{f} 0.25 (hexane/isopropanol, 30:1); mp: 169-171°C; IR (film) ν: 3391, 3326, 2961, 2871, 1677, 1618 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}), δ, ppm, J/Hz: 0.89 (d, 3H, J = 6.9, Me-C\textsuperscript{5}), 0.95 (d, 3H, J = 6.9, Me-C\textsuperscript{5}), 1.01 (d, 3H, J = 6.5, Me-C\textsuperscript{7}), 1.42 (s, 3H, Me-C\textsuperscript{2}), 1.49 (s, 3H, Me-C\textsuperscript{2}), 2.00 (d, 1H, J = 12.8, H-3\textsuperscript{B}), 2.15 (d, 1H, J = 12.8, H-3\textsuperscript{A}), 2.34 (dd, 1H, J = 8.2, 1.7, H-7), 2.82 (spd, 1H, J = 6.9, 1.1, H-5'), 3.84 (dd, 1H, J = 2.1, 1.7, H-7a), 4.06 (s, 1H, NH), 6.13 (dd, 1H, J = 2.1, 1.1, H-4), 6.49 (dd, 1H, J = 8.4, 1.0, H-9), 6.69 (ddd, 1H, J = 7.8, 7.0, 1.0, H-11), 7.14 (ddd, 1H, J = 8.4, 7.0, 1.5, H-10), 7.85 (dd, 1H, J = 7.8, 1.5, H-12); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}), δ, ppm: 19.73 (Me-C\textsuperscript{5}), 23.32 (Me-C\textsuperscript{7}), 24.05 (C-7'), 26.49 (C-5'), 30.00 and 31.45 (2Me-C\textsuperscript{2}), 49.29 (C-3), 53.80 (C-7), 54.66 (C-3a), 60.65 (C-7a), 71.65 (C-2), 114.58 (C-9), 115.27 (C-12a), 117.76 (C-11), 126.88 (C-12), 132.11 (C-10), 137.27 (C-4), 144.78 (C-5), 146.30 (C-8a), 166.89 (C-12b), 197.98 (C-6); MS (EI) m/z (%): 350 [M]\textsuperscript{+} (100); Anal. Calcd for C\textsubscript{23}H\textsubscript{30}N\textsubscript{2}O: C 78.82, H 8.63, N 7.99; found: C 78.62, H 8.69, N 7.85.

**Data for 5i':** Pale yellow solid; R\textsubscript{f} 0.20 (hexane/isopropanol, 30:1); mp: 187-189°C; IR (film) ν: 3255, 2964, 2871, 1667, 1612 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}), δ, ppm, J/Hz: 0.90 (d, 3H, J = 6.4, Me-C\textsuperscript{5}), 0.96 (d, 3H, J = 6.9, Me-C\textsuperscript{5}), 1.08 (d, 3H, J = 6.4, Me-C\textsuperscript{7}), 1.43 (s, 3H, Me-C\textsuperscript{2}), 1.48 (s, 3H, Me-C\textsuperscript{2}), 1.99 (dsp, 1H, J = 11.2, 6.4, H-7'), 2.07 (dd, 1H, J = 11.2, 2.9, H-7), 2.16 (d, 1H, J = 12.9, H-3\textsuperscript{B}), 2.28 (d, 1H, J = 12.9, H-3\textsuperscript{A}), 2.82 (spd, 1H, J = 6.9, 1.1, H-5'), 3.98 (t, 1H, J = 2.5, H-7a), 4.25 (s, 1H, NH), 6.12 (dd, 1H, J = 2.3, 1.1, H-4), 6.49 (dd, 1H, J = 8.3, 1.0, H-9), 6.63 (ddd, 1H, J = 7.9, 7.0, 1.0, H-11), 7.10 (ddd, 1H, J = 8.3, 7.0, 1.5, H-10), 7.84 (dd, 1H, J = 7.9, 1.5, H-12); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}), δ, ppm: 20.98 (Me-C\textsuperscript{5}), 21.57 (Me-C\textsuperscript{7}), 21.91 and 21.94 (Me-C\textsuperscript{5}, Me-C\textsuperscript{7}), 26.26 (C-7'), 26.46 (C-5'), 29.79 and 31.78 (2Me-C\textsuperscript{2}), 51.10 (C-3), 53.28 (C-3a), 59.36 (C-7a), 61.05 (C-7), 71.65 (C-2), 114.13 (C-9), 114.20 (C-12a), 117.19 (C-11), 126.60 (C-12), 132.05 (C-10), 138.04 (C-4), 142.76 (C-5), 146.17 (C-8a), 166.50 (C-12b), 199.21 (C-6); MS (EI) m/z (%): 350 [M]\textsuperscript{+} (100); Anal. Calcd for C\textsubscript{23}H\textsubscript{30}N\textsubscript{2}O: C 78.82, H 8.63, N 7.99; found: C 78.68, H 8.64, N 7.95.

S11
1-(2-aminophenyl)-7,9-di-tert-butyl-3,3-dimethyl-2-azaspiro[4.5]deca-1,6,9-trien-8-one (4j), (3aS*,7R*,7aR*)-5,7-Di-tert-butyl-2,2-dimethyl-2,3,7a,8-tetrahydropyrrolo[3,2-l]acridin-6(7H)-one (5j'), and (3aS*,7R*,7aR*)-5,7,11-tri-tert-butyl-2,2-dimethyl-2,3,7a,8-tetrahydropyrrolo[3,2-l]acridin-6(7H)-one (7). Method A. The title compounds were prepared from 2,6-di-tert-butylphenol (416 mg, 2.0 mmol), isobutyric aldehyde (216 mg, 3.0 mmol), and 2-aminobenzonitrile (236 mg, 2.0 mmol) in a similar manner as described for the preparation of 5h/5h'. The crude mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate, 7:1) to give starting 2-aminobenzonitrile 3 (52 mg, 22 %), spirodienone 4j' (56 mg, 7 %) and 5j (36 mg, 5 %). Method B. 2,6-Di-tert-butyl-4-(1-hydroxy-2-methylpropyl)phenol 6 (556 mg, 2.0 mmol) and 2-aminobenzonitrile 3 (236 mg, 2.0 mmol) were combined in CH2Cl2 (1 ml) and the mixture was added dropwise to stirred concentrated sulfuric acid (92%, 1 ml, 17 mmol) at 5-7 °C. The reaction mixture was stirred at room temperature for 25 min and poured into a mixture of ice (25 g) and NH3 (aq) (7 mL). The product was extracted with CH2Cl2 (3×15 mL), and the combined organic layers were washed with water, dried over anhydrous Na2SO4, and filtered. The crude mixture was purified by column chromatography on silica gel (hexane/acetone, 7:1) to give 4j (100 mg, 13 %), a mixture of 5j' and 7 (120 mg) and pure 5j' (310 mg, 41 %). The mixture of 5j' and 7 (120 mg) was separated by column chromatography on silica gel (hexane/acetone, 15:1) to give pure compound 7 (60 mg, 7 %).

**Data for 4j**: Colorless solid; Rf 0.63 (hexane/acetone, 7:1); mp: 156-158 °C; IR (film) v: 3451, 3260, 2968, 2871, 1658, 1586, 1549 cm^-1; H NMR (300 MHz, CDCl3), δ, ppm, J/Hz: 1.23 (s, 18H, t-Bu-C7, t-Bu-C9), 1.48 (s, 6H, 2Me-C3), 2.06 (s, 2H, H-4), 6.39 (ddd, 1H, J = 8.1, 7.0, 1.2, H-5'), 6.54 (br s, 2H, NH2), 6.65 (dd, 1H, J = 8.3, 1.20, H-3'), 6.73 (s, 2H, H-6, H-10), 7.06 (ddd, 1H, J = 8.3, 7.0, 1.5, H-4'), 7.11 (dd, 1H, J = 8.1, 1.5, H-6'); C NMR (75 MHz, CDCl3), δ, ppm: 29.20 (6C, t-Bu-C7, t-Bu-C9), 31.22 (2Me-C3), 34.83 (C-7', C-9'), 50.02 (C-4), 61.18 (C-5), 71.80 (C-3), 114.53 (C-1'), 115.34 and 116.22 (C-3', C-5'), 129.50 and 131.13 (C-4', C-6'), 143.95 (C-6, C-10), 145.55 (C-2'), 149.16 (C-7, C-9), 168.38 (C-1), 185.78 (C-8); MS (EI) m/z (%): 378 [M]+ (11), 260 [M-H2NC6H4CN]+ (100); Anal. Calcd for C25H34N2O: C 79.32, H 9.05, N 7.40; found: C 79.38, H 8.99, N 7.34.

**Data for 5j'**: Pale yellow solid; Rf 0.37 (hexane/acetone, 7:1); mp: 217-218 °C. IR (film) v: 3383, 3260, 2960, 2871, 1658, 1614, 1520 cm^-1; H NMR (500 MHz, CDCl3), δ, ppm, J/Hz: 1.11 (s, 18H, t-Bu-C5, t-Bu-C7), 1.38 (s, 3H, Me-C2), 1.46 (s, 3H, Me-C2), 2.10 (d, 1H, J = 2.0, H-7), 2.07 (d, 1H, J = 12.6, H-38), 2.19 (d, 1H, J = 12.6, H-38), 3.76 (s, 1H, NH), 3.91 (t,
1H, \( J = 2.0, \) H-7a), 6.16 (d, 1H, \( J = 2.1, \) H-4), 6.48 (d, 1H, \( J = 8.3, \) H-9), 6.66 (ddd, 1H, \( J = 7.9, 7.0, 1.0, \) H-11), 7.14 (ddd, 1H, \( J = 8.3, 7.0, 1.4, \) H-10), 7.86 (dd, 1H, \( J = 7.9, 1.4, \) H-12); \(^{13}\text{C NMR} \) (126 MHz, CDCl\(_3\)), \( \delta, \) ppm: 29.31 and 29.36 (t-Bu-C\(^5\), t-Bu-C\(^7\)); 29.75 and 31.67 (2Me-C\(^2\)), 32.77 (C-7'), 34.89 (C-5'), 52.74 (C-3a), 52.97 (C-3), 58.65 (C-7a), 65.12 (C-7), 71.08 (C-2), 113.89 (C-12a), 113.96 (C-9), 117.42 (C-11), 126.78 (C-12), 132.23 (C-10), 138.41 (C-4), 146.02 (C-8a), 146.94 (C-5), 166.59 (C-12b), 199.71 (C-6); \textbf{MS} \) (EI) m/z (%): 378 [M]\(^+\) (100). \textbf{Anal. Calcd for} C\(_{25}\)H\(_{34}\)N\(_2\)O: C 79.32, H 9.05, N 7.40; found: C 79.09, H 9.27, N 7.44.

**Data for 7:** pale yellow solid; \( R_f \) 0.46 (hexane/acetone, 7:1); mp: 215-217 °C; \textbf{IR} \) (film) \( \nu \): 3378, 3269, 2958, 2871, 1664, 1617, 1506 cm\(^{-1}\); \(^1\text{H NMR} \) (500 MHz, CDCl\(_3\)), \( \delta, \) ppm, \( J/Hz:\)
1.11 (s, 9H, t-Bu), 1.12 (s, 9H, t-Bu), 1.29 (s, 9H, t-Bu-C\(^{11}\)), 1.37 (s, 3H, Me-C\(^2\)), 1.46 (s, 3H, Me-C\(^2\)), 2.02 (d, 1H, \( J = 12.4, \) H-3\(^B\)), 2.07 (d, 1H, \( J = 2.0, \) H-7), 2.13 (d, 1H, \( J = 12.4, \) H-3\(^A\)), 3.64 (s, 1H, NH), 3.85 (t, 1H, \( J = 2.0, \) H-7a), 6.17 (d, 1H, \( J = 2.0, \) H-4), 6.45 (d, 1H, \( J = 8.6, \) H-9), 7.22 (dd, 1H, \( J = 8.6, 2.3, \) H-10), 7.83 (d, 1H, \( J = 2.3, \) H-12); \(^{13}\text{C NMR} \) (126 MHz, CDCl\(_3\)), \( \delta, \) ppm: 29.29 and 29.34 (t-Bu-C\(^5\), t-Bu-C\(^7\)), 29.72 (Me-C\(^2\)), 31.41 (t-Bu-C\(^{11}\)), 31.66 (Me-C\(^2\)), 32.71 (C-7'), 34.08 (C-11'), 34.90 (C-5'), 52.99 (C-3a), 53.35 (C-3), 58.64 (C-7a), 65.28 (C-7), 70.98 (C-2), 113.50 (C-12a), 114.03 (C-9), 122.72 (C-12), 129.99 (C-10), 138.52 (C-4), 140.36 (C-11), 144.05 (C-8a), 147.15 (C-5), 166.96 (C-12b), 200.11 (C-6); \textbf{MS} \) (EI) m/z (%): 434 [M]\(^+\) (60), 419 [M-Me]\(^+\) (100). \textbf{Anal. Calcd for} C\(_{25}\)H\(_{34}\)N\(_2\)O: C 80.13, H 9.74, N 6.44; found: C 80.12, N 9.57, H 6.69.
3. ORTEP Drawing and Crystallographic Data

**Figure 1.**
ORTEP drawing of (±)-5h (CDCC No 988502)

**Figure 2.**
ORTEP drawing of 4i (CDCC No 988501)

**Figure 3.**
ORTEP drawing of (±)-5i (CDCC No 988503)

**Figure 4.**
ORTEP drawing of (±)-5j' (CDCC No 988504)
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<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 2₁/n</td>
<td>P 2₁/c</td>
<td>C 2/c</td>
<td>P 2₁/c</td>
</tr>
<tr>
<td>a, Å</td>
<td>12.2990(9)</td>
<td>9.5020(15)</td>
<td>19.2894(4)</td>
<td>9.7929(7)</td>
</tr>
<tr>
<td>b, Å</td>
<td>10.4923(8)</td>
<td>21.727(3)</td>
<td>9.7066(9)</td>
<td>9.9455(10)</td>
</tr>
<tr>
<td>c, Å</td>
<td>12.5948(12)</td>
<td>10.9938(11)</td>
<td>22.2610(18)</td>
<td>22.885(2)</td>
</tr>
<tr>
<td>α, º</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>β, º</td>
<td>97.493(7)</td>
<td>113.802(12)</td>
<td>98.072(13)</td>
<td>93.459(7)</td>
</tr>
<tr>
<td>γ, º</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>V, Å³</td>
<td>1611.4(2)</td>
<td>2076.7(5)</td>
<td>4126.7(5)</td>
<td>2224.8(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>ρ calcld, g/cm³</td>
<td>1.213</td>
<td>1.121</td>
<td>1.128</td>
<td>1.130</td>
</tr>
<tr>
<td>μ, mm⁻¹</td>
<td>0.075</td>
<td>0.068</td>
<td>0.069</td>
<td>0.068</td>
</tr>
<tr>
<td>F(000)</td>
<td>632</td>
<td>760</td>
<td>1520</td>
<td>824</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.92-28.28</td>
<td>3.00-26.38</td>
<td>2.90-26.40</td>
<td>2.66-26.41</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>8823</td>
<td>15767</td>
<td>9782</td>
<td>13376</td>
</tr>
<tr>
<td>Independent reflections (Rint)</td>
<td>3899 (0.0311)</td>
<td>4193 (0.0704)</td>
<td>4156 (0.0418)</td>
<td>4511 (0.0457)</td>
</tr>
<tr>
<td>Data / restraints / parameter</td>
<td>3899/0/231</td>
<td>4193/0/243</td>
<td>4156/0/257</td>
<td>4511/0/265</td>
</tr>
<tr>
<td>Goodness-of-Fit on F2</td>
<td>1.005</td>
<td>1.000</td>
<td>1.000</td>
<td>1.006</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R₁=0.0400</td>
<td>R₁=0.1344</td>
<td>R₁=0.1045</td>
<td>R₁=0.0989</td>
</tr>
<tr>
<td>wR²=0.0774</td>
<td>wR²=0.1562</td>
<td>wR²=0.0888</td>
<td>wR²=0.0885</td>
<td></td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁=0.0998</td>
<td>R₁=0.0600</td>
<td>R₁=0.0414</td>
<td>R₁=0.0440</td>
</tr>
<tr>
<td>wR²=0.0825</td>
<td>wR²=0.1426</td>
<td>wR²=0.0835</td>
<td>wR²=0.0817</td>
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</tr>
<tr>
<td>Completeness to theta (deg)</td>
<td>97.5 (28.28)</td>
<td>98.8 (26.38)</td>
<td>98.2 (26.40)</td>
<td>98.5 (26.41)</td>
</tr>
<tr>
<td>Largest diff. peak and hole, e·Å⁻³</td>
<td>0.134 and -0.140</td>
<td>0.344 and -0.206</td>
<td>0.182 and -0.176</td>
<td>0.192 and -0.187</td>
</tr>
</tbody>
</table>
4. $^1$H and $^{13}$C NMR Spectra

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 6.
\[13^C\text{ NMR spectrum (75 MHz, CDCl}_3\text{) of compound 6.}\]
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 5a.
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 5a.
\(^1\)H NMR spectrum (500 MHz, CDCl\(_3\)) of compound 5b.
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 5b.
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 5c.
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 5c.
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 5d.
$^{13}$C NMR spectrum (126 MHz, CDCl$_3$) of compound 5d.
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 5e.
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 5e.
1H NMR spectrum (500 MHz, CDCl₃) of compound 4f.
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 4f.
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 5f.
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 5f.
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 4g.
\(^{13}\text{C} \text{NMR spectrum (126 MHz, CDCl}_3\text{) of compound 4g.}\)
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 5g.
$^1$H NMR spectrum of compound 5g.
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 5h.
$^{13}$C NMR spectrum (126 MHz, CDCl$_3$) of compound 5h.
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of mixture of diastereomers 5h and 5h'.
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 4i.
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 4i.
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 5i.
$^{13}$C NMR spectrum (126 MHz, CDCl₃) of compound 5i.
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 5i'.
$^{13}$C NMR spectrum (126 MHz, CDCl$_3$) of compound 5i'.

S44
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 4j.
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 4j.
$^{1}$H NMR spectrum (500 MHz, CDCl$_3$) of compound 5j$^*$. 
$^{13}$C NMR spectrum (126 MHz, CDCl$_3$) of compound 5j'.

S48
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 7.
$^{13}$C NMR spectrum (126 MHz, CDCl$_3$) of compound 7.
5. References and notes
