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Chrysaorenes: Assembling Coronoid Hydrocarbons via the Fold-in Synthesis

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Supporting Information

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Experimental

General. Tetrahydrofuran, toluene and N,N-dimethylformamide were dried using a commercial solvent purification system. Dichloromethane was distilled from calcium hydride when used as a reaction solvent. All other solvents and reagents were used as received. Compounds **S1**¹, **S2**², **S3**³ and **S4**⁴ were prepared according to literature procedures. ¹H NMR spectra were recorded on high-field spectrometers (¹H frequency 500.13 or 600.13 MHz), equipped with broadband inverse gradient probeheads. Spectra were referenced to the residual solvent signals (chloroform-*d*, 7.24 ppm). ¹³C NMR spectra were recorded with ¹H broadband decoupling and referenced to solvent signals (¹³CDCl₃, 77.0 ppm). High resolution mass spectra were recorded using APCI or ESI ionization in the positive mode.

Computational methods. Density functional theory (DFT) calculations were performed using Gaussian 09.⁵ DFT geometry optimizations were carried out in unconstrained C_1 symmetry, using molecular mechanics or semiempirical models as starting geometries. X-ray geometries were used as initial models for **3**-Et and **4**-Et. DFT geometries were refined to meet standard convergence criteria, and the existence of a local minimum was verified by a normal mode frequency calculation. DFT calculations were performed using the hybrid functional B3LYP,^{6–8} and the 6-31G(d,p) basis set. Solvation effects were modeled using the IEFPCM formalism,⁹ with standard solvent parameterizations: chloroform (¹H and ¹³C NMR for **1–4**-Et), dichloromethane (TD-DFT for **1–4**-Et), and N,N-dimethylformamide (thermochemistry of the Yamamoto coupling). ¹H and ¹³C shieldings were calculated using the GIAO approach and referenced to the absolute TMS shieldings calculated at the same level of theory (31.7454 ppm for ¹H and 192.0973 ppm for ¹³C). NICS scans were performed with gas-phase calculated GIAO shieldings. Electronic transitions were calculated by means of time-dependent DFT (TD-DFT). All TD-DFT calculations were performed at the CAM-B3LYP/6-311+G(d,p)//6-31G(d,p) level of theory¹⁰ using dichloromethane solvation.

X-ray crystallography. X-ray quality crystals were grown by slow diffusion of methanol into a toluene solution of **3**, same method was used to get crystals of **4**. Diffraction measurements were performed on a κ-geometry Ruby PX diffractometer (ω scans) with graphite-monochromatized Mo K_α radiation. The data for **3** and **4** were collected at 100 K and 80 K respectively, corrected for Lorenz and polarization effects. Data collection, cell refinement, data reduction and analysis were carried out with the Xcalibur PX software, CRYSALIS CCD and CRYSALIS RED, respectively (Oxford Diffraction Ltd., Abignon, England, 2009). An analytical absorption correction was applied for the data of **3** and **4** with use of CRYSALIS RED. Both structures were solved by direct methods with the SHELXS-97 program and refined using SHELXL-97¹¹ with anisotropic thermal parameters for non-H atoms. In the final refinement cycles, all H atoms were treated as riding atoms in geometrically optimized positions. CCDC 1407282 and 1407283 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Photoluminescence. Photoluminescence excitation (PLE) spectra as well as decay kinetics (DEC) were taken with the FSL980-sm Fluorescence Spectrometer from Edinburgh Instruments Ltd. A 450 W Xenon arc lamp (PL and PLE) and a Super Continuum Fianium laser were used as excitation sources. Emission spectra were corrected for the recording system efficiency and excitation spectra were corrected for the incident light intensity. The quantum yield measurements were performed by using an Edinburgh Instruments integrating sphere equipped with a small elliptical mirror and a baffle plate for beam steering and shielding against directly detected light. For the measurement, the integrating

sphere replaces the standard sample holder inside the sample chamber. Calculations of quantum yields were made using the software provided by Edinburgh Instruments.

Synthesis



N,N'-(3,6-dibromo-9,9-diethyl-9H-fluorene-2,7-diyl)diacetamide (S5). In a 500 mL round-bottomed flask equipped with a stirring bar, compound **S4** (21.5 g, 63.9 mmol) was dissolved in dry N,N-dimethylformamide (250 mL) under nitrogen atmosphere. The solution was kept under dark and bromine (8.19 mL, 160 mmol) was added dropwise. The mixture was stirred under nitrogen for 20 hours. After that water (1 L) was added and a yellow-brown precipitate was formed. The mixture was filtered under reduced pressure and the precipitate was dried in vacuo. The resulting product did not require further purification (17.0 g, 86.4%). ¹H NMR (600 MHz, chloroform-*d*, 300 K): δ 8.37 s, 2H), δ 7.73 (s, 2H), δ 7.70 (s, 2H), δ 2.25 (s, 6H), δ 2.00 (q, 4H, ${}^{3}J$ = 7.3 Hz), δ 0.31 (t, 6H, ${}^{3}J$ = 7.3 Hz). ¹³C NMR (151 MHz, chloroform-*d*, 300 K): δ 168.16, 150.80, 136.98, 134.66, 126.31, 122.94, 116.36, 111.72, 56.82, 32.73, 32.35, 29.78, 25.15, 8.46, 8.36. HRMS (ESI+): *m/z*: [M + H]⁺ Calcd. for C₂₁H₂₃Br₂N₂O₂: 493.0133; Found 493.0121.



3,6-dibromo-9,9-diethyl-9H-fluorene-2,7-diamine (S6). To a 2000 mL round-bottomed flask equipped with a reflux condenser and a stirring bar compound **S5** (31.6 g, 63.9 mmol) was dissolved in methanol (1000 mL). Potassium hydroxide (57.4 g, 1020 mmol) was added to the mixture under nitrogen. The mixture was heated to 90 °C and stirred for 18 hours. The solvent was removed on a rotary evaporator and the product in the form of red-brown crystals was formed and used without further purification (26.0 g, 99.1 %) ¹**H NMR** (600 MHz, chloroform-*d*, 300 K): δ 7.53 (s, 2H), δ 6.65 (s, 2H), δ 4.06 (s, 4H), δ 1.85 (q, 4H, ³J = 7.4 Hz), δ 0.31 (t, 6H, ³J = 7.4 Hz). ¹³**C NMR** (151 MHz, chloroform-*d*, 300 K): δ 149.95, 142.29, 133.40, 122.61, 110.41, 108.11, 55.75, 33.04, 8.42. **HRMS** (ESI+): m/z: [M + H]⁺ Calcd. for C₁₇H₁₉Br₂N₂: 408.9910; Found 408.9913.



3,6-dibromo-9,9-diethyl-2,7-diiodo-9H-fluorene (S7). In a round-bottomed flask equipped with a magnetic stirring bar compound **S6** (26.0 g, 63.4 mmol) was suspended in a 10 % water solution of sulfuric acid. The suspension was cooled to room temperature and further cooled to 0 °C in an ice bath. Aqueous solution of sodium nitrite (17.5 g, 254 mmol in 90 mL of water) was added dropwise to the suspension and stirred for 45 min. To the solution potassium iodide (105.23 g, 634 mmol) dissolved in 90 mL of water was added slowly. The resulting solution was allowed to reach room temperature and was stirred for 1 hour. Aqueous solution of sodium sulphite (1 L) was added and the mixture was extracted with dichloromethane. The organic layers were combined, dried with anhydrous sodium sulphate, filtered and the solvent was removed on a rotary evaporator. The crude product was purified by column chromatography (silicagel, dichloromethane). The first fraction was

collected and concentrated on a rotary evaporator to yield yellow-brown crystals (25 g, 62.4 %). ¹**H NMR** (600 MHz, chloroform-*d*, 300 K): δ 7.89 (s, 2H), δ 7.77 (s, 2H), δ 1.93 (q, 4H, ³*J* = 7.4 Hz), δ 0.31 (t, 6H, ³*J* = 7.4 Hz). ¹³**C NMR** (151 MHz, chloroform-*d*, 300 K): δ 150.26, 134.72, 128.30, 124.09, 100.45, 56.22, 32.31, 8.86.



3,6-dibromo-9,9-diethyl-9H-fluorene-2,7-dicarbaldehyde (S8). In a 500 mL round-bottomed flask equipped with a stirring bar and septum compound **S7** (11.8 g, 18.7 mmol) was dissolved in dry tetrahydrofuran (300 mL) under nitrogen atmosphere. The solution was cooled in an acetone–liquid nitrogen bath to -78 °C and a solution of isopropylmagnesium chloride (19.61 mL, 39.2 mmol, 2 M solution in tetrahydrofuran) was added dropwise. After stirring for 15 minutes, dry N,N-dimethylformamide (5.78 mL, 74.7 mmol) was added and the solution was allowed to reach room temperature and was stirred for an additional hour. Aqueous solution of ammonium chloride was added and the reaction mixture was extracted with dichloromethane. The organic layers were combined, dried over anhydrous sodium sulphate, filtered and the solvent was removed on a rotary evaporator. The crude product was purified by column chromatography (silicagel, dichloromethane–hexanes = 2:1). The third fraction was collected and concentrated on a rotary evaporator to give orange crystals (5.38 g, 66.1 %) ¹**H NMR** (600 MHz, chloroform-*d*, 300 K): δ 10.43 (s, 2H), δ 7.99 (s, 2H), δ 7.90 (s, 2H), δ 2.07 (q, 4H, ³*J* = 7.4 Hz), δ 0.27 (t, 6H, ³*J* = 7.4 Hz). ¹³**C NMR** (151 MHz, chloroform-*d*, 300 K): δ 191.81, 151.12, 145.73, 133.26, 126.54, 126.33, 124.23, 56.90, 32.11, 8.41. **HRMS** (APCI): *m/z*: [M + H]⁺ Calcd. for C₁₉H₁₇Br₂O₂: 434.9590; Found 434.9595.



(3,6-dibromo-9,9-diethyl-9H-fluorene-2,7-diyl)dimethanol (S9). In a 50 mL round-bottomed flask equipped with a magnetic stirring bar compound S8 (500 mg, 1.2 mmol) and sodium borohydride (130 mg, 3.4 mmol) were suspended in dry tetrahydrofuran (25 mL). The mixture was stirred in room temperature overnight, after which a yellow precipitate was formed. Water (30 mL) was added and then the mixture was extracted with dichloromethane. Combined organic extracts were dried with anhydrous sodium sulphate and filtered. Solvents were removed on a rotary evaporator yielding an orange-brown crystals (482 mg, 95.5 %). The product was used without further purification. ¹H NMR (600 MHz, chloroform-d, 300 K): δ 7.80 (s, 2H), δ 7.42 (s, 2H), δ 4.81 (d, 4H, *J* = 6.4 Hz), δ 2.00 (q, 4H, ³*J* = 7.3 Hz), δ 0.27 (t, 6H, ³*J* = 7.3 Hz). ¹³C NMR (151 MHz, chloroform-d, 300 K): δ 149.78, 141.21, 138.78, 124.11, 123.30, 121.04, 65.45, 56.37, 32.45 8.48. HRMS (APCI): *m/z*: [M]⁺ Calcd. for C₁₉H₂₀Br₂O₂: 437.9825; Found 437.9771.



3,6-dibromo-2,7-bis(chloromethyl)-9,9-diethyl-9H-fluorene (S10). In a 50 mL round-bottomed flask equipped with a magnetic stirring bar compound **S9** (500 mg, 1.1 mmol) was dissolved in freshly distilled dichloromethane (15 mL) to which catalytic amounts of N,N-dimethylformamide (25 μ L) were added. With continuous stirring thionyl chloride (181 μ L, 2.5 mmol) was added to the reaction mixture. After one hour of stirring, the solvent and excess of thionyl chloride were removed on a rotary evaporator, yielding a brown crystals (520 mg, 96.0 %). The product was used without further purification. ¹H NMR (600 MHz, chloroform-*d*, 300 K): δ 7.86 (s, 2H), δ 7.41 (s, 2H), δ 4.76 (s, 4H), δ 2.00 (q, 4H, ³*J* = 7.3 Hz), δ 0.30 (t, 6H, ³*J* = 7.3 Hz). ¹³C NMR (151 MHz, chloroform-*d*, 300 K): δ 150.18, 141.75, 135.96, 125.32, 124.76, 122.93, 56.40, 46.67, 32.36, 8.48. HRMS (APCI): *m/z*: [M]⁺ Calcd. for C₁₉H₁₈Br₂Cl₂: 473.9147; Found 473.9290.



3,6-dibromo-2-chloromethyl-7-triphenylphosphine-9,9-diethyl-9H-fluorene (S11). In a 50 mL pressure tube equipped with a magnetic stirring bar compound **S10** (550 mg, 1.2 mmol) and triphenylphosphine (907 mg, 3.46 mmol) were dissolved in dry toluene (25 mL). The reaction mixture was sealed, heated at 120 °C and stirred for 12 hours, after which time a yellow precipitate was formed. The reaction mixture was cooled to room temperature, diluted with dichloromethane and the solvents were removed on a rotary evaporator. The precipitate was washed with hexane and dried, yielding yellow-white crystals (1.035 g, 89.5 %). ¹H NMR (600 MHz, chloroform-*d*, 300 K): δ 7.76 (t, 6H, ³J = 7.26 Hz), δ 7.69 (m, 12H), δ 7.60 (m, 12H), δ 7.59 (s, 2H), δ 7.27 (s, 2H), δ 5.80 (d, 4H, ³J = 14.4 Hz), δ 1.40 (q, 4H, ³J = 7.2 Hz), δ -0.18 (t, 6H, ³J = 7.2 Hz). ¹³C NMR (151 MHz, chloroform-*d*, 300 K): δ 150.27, 141.24, 135.11, 134.35, 130.18, 127.99, 126.98, 125.72, 124.38, 117.71, 117.15, 56.16, 31.47, 8.42. HRMS (ESI+): m/z: [M²⁺] Calcd. for C₅₅H₄₈Br₂P₂: 464.0793; Found 464.0799.



(3,3',3",6,6',6"-hexabromo-9,9',9",9"",9""9"""-hexaethyl)[2.2.2]-(2,7)-fluorenophanetriene (3-Et). To a 250 mL three-necked round-bottomed flask equipped with a reflux condenser, septum and syringe pump adapter were placed zinc powder (2250 mg, 34.4 mmol) and copper(I) iodide (210 mg, 1.1 mmol). The apparatus was filled with nitrogen and oxygen-free tetrahydrofuran (130 mL) was introduced through a syringe. Titanium tetrachloride (1.89 mL, 17.2 mmol) was added dropwise, the septum was replaced with a glass stopper and the reaction mixture was heated and stirred under reflux for 3 hours. Subsequently, a solution of compound **\$8** (100 mg, 0.23 mmol) in oxygen-free tetrahydrofuran (50 mL) was added to the reaction mixture using a syringe pump in 3 hours and the mixture was stirred under reflux for another 12 hours. After that time it was cooled down to room temperature. Aqueous ammonia (5%, 150 mL) was added and the mixture was stirred for 1 hour. Extraction with dichloromethane, followed by drying the combined organic layers over anhydrous sodium sulphate and removing the solvents on a rotary evaporator gave a yellow-green solid. It was purified using column chromatography (silicagel, dichloromethane/hexane = 1:10), yielding pale green crystals (16 mg, 17.3 %). ¹H NMR (500 MHz, chloroform-*d*, 300 K): δ 7.63 (s, 6H), δ 6.88 (s, 6H), δ 6.87 (s, 6H), δ 1.35 (q, 12H, ³J = 7.4 Hz), δ 0.11 (t, 18H, ³J = 7.4 Hz). ¹³C NMR (600 MHz, chloroformd, 300 K): δ 149.59, 140.18, 136.62, 132.43, 125.27, 123.64, 122.06, 54.78, 31.06, 8.72. HRMS (APCI+): *m*/*z*: [M]⁺ Calcd. for C₅₇H₄₈Br₆: 1205.8851; Found 1205.9023.



dichloromethane (80 mL). Aqueous sodium hydroxide (50%, 620 μ L) was added dropwise to the solution using a syringe. During the addition the mixture was kept under a nitrogen atmosphere and protected from light. After the addition, the solution was stirred for 1 hour. After that time the mixture was diluted with water and extracted with dichloromethane. Combined extracts were dried over anhydrous sodium sulphate, filtered and the solvent was removed on a rotary evaporator.

The crude material was purified using column chromatography (silicagel, dichloromethane/hexanes = 1:6), yielding pale green crystals (35 mg, 23.9 %). ¹H NMR (500 MHz, chloroform-*d*, 300 K): δ 7.82 (s,

8H), δ 7.01 (s, 8H), δ 6.77 (s, 8H), δ 1.42 (q, 16H, ${}^{3}J$ = 7.4 Hz), δ 0.02 (t, 24H, ${}^{3}J$ = 7.4 Hz). 13 **C NMR** (151 MHz, chloroform-*d*, 300 K): δ 149.63, 140.55, 136.18, 130.80, 124.83, 124.26, 123.01, 55.55, 31.30, 8.55. **HRMS** (APCI+): *m/z*: [M]⁺ Calcd. for C₇₆H₆₄Br₈: 1607.8490; Found 1607.8971.



[3]chrysaorene (1-Et). In a 50 mL Schlenk flask equipped with a magnetic stirring bar compound 3-Et (22 mg, 18.1 µmol) was placed and the vessel was capped with a septum. The atmosphere within the flask was then changed a few times to nitrogen, after which bis(1,5-cyclooctadiene)nickel(0) (45 mg, 0.16 mmol) and 2,2'-bibyridyl (26 mg, 0.16 mmol) were added in a glove-box. Dry N,Ndimethylformamide (7 mL) was then added to the vessel in a constant flow of nitrogen and the mixture was sealed with a glass stopper. After subsequent changing of the atmosphere to nitrogen one more time the reaction mixture was heated to 85 degrees and stirred for 18 hours. It was then cooled down to room temperature, diluted with water and extracted with dichloromethane. The combined organic extracts were dried over anhydrous sodium sulphate, filtered and the solvents were removed on a rotary evaporator. The crude mixture was filtered through a short silica plug to remove the solid impurities. Subsequent purification by column chromatography (silicagel, dichloromethane/hexane = 1:6) gave the product in a form of pale yellow solid (6.5 mg, 48.9 %). 1 H **NMR** (600 MHz, chloroform-*d*, 300 K): δ 9.27 (s, 6H), δ 7.63 (s, 6H), δ 7.61 (s, 6H), δ 2.31 (q, 6H, ³J = 7.4 Hz), δ 2.09 (q, 6H, ³J = 7.3 Hz), δ 1.19 (t, 9H, ³J = 7.4 Hz), δ -0.41 (t, 9H, ³J = 7.3 Hz). ¹³C NMR (151 MHz, chloroform-*d*, 300 K): δ 149.51, 141.79, 131.56, 130.94, 126.37, 123.19, 117.13, 59.40, 35.49, 29.80, 10.09, 8.26. HRMS (APCI+): *m*/*z*: [M + H]⁺ Calcd. for C₅₇H₄₉: 733.3829; Found 733.3834. UV-vis (dichloromethane, 295 K) λ [nm] (ϵ in M⁻¹cm⁻¹): 250 (7.61·10⁴), 281 (6.44·10⁴), 309 (4.27·10⁴), 316 (4.41·10⁴), 330 (3.42·10⁴), 348 (3.58·10⁴), 373 (1.48·10⁴), 396 (1.84·10⁴).



[4]chrysaorene (2-Et). In a 25 mL Schlenk flask equipped with a magnetic stirring bar compound 4-Et (15 mg, 9.3 μ mol) was placed and the vessel was capped with a septum. The atmosphere within the flask was then changed a few times to nitrogen, after which bis(1,5-cyclooctadiene)nickel(0) (31 mg, 111.0 µmol) and 2,2'-bibyridyl (17 mg, 111.0 µmol) were added in a glove-box. Dry N,Ndimethylformamide (5 mL) was then added to the vessel in a constant flow of nitrogen and the mixture was sealed with a glass stopper. After subsequent changing of the atmosphere to nitrogen one more time the reaction mixture was heated to 85 degrees and stirred for 18 hours. It was then cooled down to room temperature, diluted with water and extracted with dichloromethane. The combined organic extracts were dried over anhydrous sodium sulphate, filtered and the solvents were removed on a rotary evaporator. The crude mixture was filtered through a short silica plug to remove the solid impurities. Subsequent purification by column chromatography (silicagel, dichloromethane/hexane = 1:6) gave the product in a form of pale yellow solid (4 mg, 44.1 %). 1 H NMR (500 MHz, chloroform-d, 300 K): δ 9.70 (s, 8H), δ 7.91 (s, 8H), δ 7.84 (s, 8H), δ 2.30 (q, 16H, ³J = 7.4 Hz), δ 0.42 (t, 24H, ³J = 7.4 Hz). ¹³C NMR (151 MHz, chloroform-d, 300 K): δ 149.10, 141.22, 132.44, 130.84, 127.28, 123.08, 114.42, 54.30, 34.40, 8.39. HRMS (APCI+): m/z: [M + H]⁺ Calcd. for $C_{76}H_{65}$: 977.51; Found 977.53. **UV-vis** (dichloromethane, 295 K) λ [nm] (ϵ in M⁻¹cm⁻¹): 265 (2.44·10⁴), 296 (1.33·10⁴), 313 (1.67·10⁴), 319 (1.69·10⁴), 341 (2.06·10⁴), 366 (1.15·10⁴), 384 (1.26·10⁴), 398 $(6.99 \cdot 10^3).$



Scheme S1. Synthesis of compounds **S1-4-Et**. Reagents and conditions: a) fuming HNO₃ (20 equiv.), AcOH; b) N₂H₄ (4 equiv.), Pd/C (0.02 equiv.), EtOH; c) Ac₂O (30 equiv.), AcOH; d) Br₂ (2.5 equiv.), DMF; e) KOH (16 equiv.), MeOH; f) 1. H₂SO₄/H₂O, 2. NaNO₂ (4 equiv.), 3. KI (10 equiv.)/H₂O; g) 1. *i*-PrMgCl (2.1 equiv.)/THF, 2. DMF (4 equiv.); h) NaBH₄ (3 equiv.), THF; i) SOCl₂ (2.2 equiv.), DCM, DMF; j) PPh₃ (3 equiv.), toluene; k) TiCl₄ (75 equiv.), CuI (4.8 equiv.), Zn (150 equiv.), THF; I) NaOH_{aq} (65 equiv.), DCM.



Scheme S2. ¹H and ¹³C chemical shifts of **3-Et** and **4-Et** (full assignment based on data obtained from COSY, ROESY, HSQC and HMBC experiments).



Scheme S3. ¹H and ¹³C chemical shifts of **1-Et** and **2-Et** (full assignment based on data obtained from COSY, ROESY, HSQC and HMBC experiments).



Scheme S4. Macrocyclic conjugation pathways in **1** and **2**. [28]-, [32]-, [36]- and [40]annulene pathways in **2** are constructed by inclusion of outer parts of phenanthrene units, as shown for **1**.



Figure S1. Molecular structure of 3-Et (co-crystalizing solvent: dichloromethane also visible).



Figure S2. Molecular structure of 4-Et (co-crystalizing solvent: toluene also visible).



Figure S3. Correlation between ¹H NMR chemical shifts of **3-Et** derived from experiment (δ_{exptl} , 500 MHz, chloroform-*d*, 300 K) and theory (δ_{calcd} , GIAO-B3LYP/6-31G(d,p)/PCM(CHCl₃)). Signals in the experimental spectrum were assigned on the basis of 2D NMR data.



Figure S4. Correlation between ¹³C NMR chemical shifts of **3-Et** derived from experiment (δ_{exptl} , 600 MHz, chloroform-*d*, 300 K) and theory (δ_{calcd} , GIAO-B3LYP/6-31G(d,p)/PCM(CHCl₃)). Signals in the experimental spectrum were assigned on the basis of 2D NMR data. The calculated shift of carbon c does not include the relativistic effect of the attached Br atom.



Figure S5. Correlation between ¹H NMR chemical shifts of **4-Et** derived from experiment (δ_{exptl} , 500 MHz, chloroform-*d*, 300 K) and theory (δ_{calcd} , GIAO-B3LYP/6-31G(d,p)/PCM(CHCl₃)). Signals in the experimental spectrum were assigned on the basis of 2D NMR data.



Figure S6. Correlation between ¹³C NMR chemical shifts of **4-Et** derived from experiment 151 MHz, chloroform-*d*, 300 K) and theory (δ_{calcd} , GIAO-B3LYP/6-31G(d,p)/PCM(CHCl₃)). Signals in the experimental spectrum were assigned on the basis of 2D NMR data. The calculated shift of carbon c does not include the relativistic effect of the attached Br atom.



Figure S7. Correlation between ¹H NMR chemical shifts of **1-Et** derived from experiment (δ_{exptl} , 600 MHz, chloroform-*d*, 300 K) and theory (δ_{calcd} , GIAO-B3LYP/6-31G(d,p)/PCM(CHCl₃)). Signals in the experimental spectrum were assigned on the basis of 2D NMR data.



Figure S8. Correlation between ¹³C NMR chemical shifts of **1-Et** derived from experiment (δ_{exptl} , 151 MHz, chloroform-*d*, 300 K) and theory (δ_{calcd} , GIAO-B3LYP/6-31G(d,p)/PCM(CHCl₃)). Signals in the experimental spectrum were assigned on the basis of 2D NMR data.



Figure S9. Correlation between ¹H NMR chemical shifts of **2-Et** derived from experiment (δ_{exptl} , 600 MHz, chloroform-*d*, 300 K) and theory (δ_{calcd} , GIAO-B3LYP/6-31G(d,p)/PCM(CHCl₃)). Signals in the experimental spectrum were assigned on the basis of 2D NMR data.



Figure S10. Correlation between ¹³C NMR chemical shifts of **2-Et** derived from experiment (δ_{exptl} , 151 MHz, chloroform-*d*, 300 K) and theory (δ_{calcd} , GIAO-B3LYP/6-31G(d,p)/PCM(CHCl₃)). Signals in the experimental spectrum were assigned on the basis of 2D NMR data.



Figure S11. Decay traces of the emissions monitored at 437 nm (**1**-Et) and 447 nm (**2**-Et) under 395 nm excitation (Super Continuum Fianium Laser).



Figure S12. Quantum yield determinations for 1-Et (top) and 2-Et (bottom).



Figure S13. Chromaticity diagrams for **1**-Et (x = 0.16; y = 0.09 and u' = 0.17; v' = 0.22) and **2**-Et (x = 0.15; y = 0.1 and u' = 0.15; v' = 0.23).



Figure S14. Kohn–Sham frontier orbitals calculated for **1**-Et (left) and **2**-Et (right) at the PCM(DCM)/B3LYP/6-311+G(d,p)//6-31G(d,p) level of theory.



Figure S15. Comparison of DFT-optimized geometries of **2**-Et (blue) and **5**-Et (red, B3LYP/6-31G(d,p), gas phase).



Figure S16. NICS(1) scans for **2-Et**, **6-Et**, and phenanthrene. Nuclear shieldings were evaluated 1 Å above the ring plane using GIAO-B3LYP/6-31G(d,p).





Figure S17. DFT-optimized structure of 3-Et (B3LYP/6-31G(d,p)).





Figure S18. DFT-optimized structure of **4-Et** (B3LYP/6-31G(d,p)).

group	bond ^[b]	1-Et	2-Et	5-Et	∆(1 -Et – 5 -Et)	Δ (2 -Et – 5 -Et)
	ah	1.547	1.520	1.529	0.018	-0.009
	ab	1.385	1.371	1.375	0.010	-0.004
wi wa	bc	1.430	1.414	1.419	0.011	-0.005
rim	cg	1.438	1.430	1.433	0.005	-0.003
	gg'	1.368	1.357	1.361	0.007	-0.004
	mean				0.010	-0.005
	ff'	1.457	1.478	1.466	-0.009	0.012
hub	ef	1.376	1.390	1.384	-0.008	0.006
	de	1.406	1.419	1.414	-0.008	0.005
	dd'	1.458	1.465	1.460	-0.002	0.005
	mean				-0.007	0.007
spoke	cd	1.427	1.432	1.431	-0.004	0.001
	fa	1.416	1.422	1.421	-0.005	0.001
	mean				-0.005	0.001

Table S1. Bond length variation between chrysaorenes and the reference system 5-Et.^[a]

[a] B3LYP/6-31G(d,p) geometries. [b] Bond definitions:



Structure ^[a]	Functional	Basis set	Solvation	Code ^[b]	Energy ^[c]	ZPV ^[d]	lowest freq ^[e]	$\Delta G^{[f]}$
					[a.u.]	[a.u.]	[cm ⁻¹]	[a.u.]
1-Et	B3LYP	6-31G(d,p)	gas phase	c3Etcont	-2201.155124	0.879676	29.50	-2200.349383
	B3LYP	6-31G(d,p)	chloroform	c3EtCHCl3cont	-2201.161824	0.879472	29.52	-2200.356244
	CAM-B3LYP	6-31G(d,p)	DCM	c3Et_S0_CAM	-2199.875261	0.890989	29.80	-2199.057629
	CAM-B3LYP	6-311+G(d,p)	DCM		-2200.318806			
2-Et	B3LYP	6-31G(d,p)	gas phase	c4Et	-2934.960175	1.173886	7.44	-2933.880899
	B3LYP	6-31G(d,p)	chloroform	c4EtCHCl3	-2934.969275	1.173156	6.20	-2933.891240
	CAM-B3LYP	6-31G(d,p)	DCM	c4Et_S0_CAM	-2933.255625	1.188493	3.41	-2932.162641
	CAM-B3LYP	6-311+G(d,p)	DCM		-2933.843386			
3-Et	B3LYP	6-31G(d,p)	gas phase	3_Et_Xray	-17631.322441	0.882496	7.60	-17630.536224
	B3LYP	6-31G(d,p)	chloroform	3_Et_XrayCHCl3	-17631.330429	0.881911	9.22	-17630.544606
4-Et	B3LYP	6-31G(d,p)	gas phase	4_Et_Xrayf	-23508.440909	1.177296	3.82	-23507.390923
	B3LYP	6-31G(d,p)	chloroform	4_Et_XrayCHCl3	-23508.450612	1.176343	4.84	-23507.401682
5-Et	B3LYP	6-31G(d,p)	gas phase	hd2	-1392.444143	0.594712	20.31	-1391.910343
6-Et	B3LYP	6-31G(d,p)	gas phase	hd3	-2126.185352	0.888216	11.75	-2125.377818
7	B3LYP	6-31G(d,p)	gas phase	phen_Br2cont	-5682.927318	0.195174	20.53	-5682.776848
8	B3LYP	6-31G(d,p)	gas phase	phencont	-539.554443	0.194558	95.91	-539.394736

 Table S2. Computational data for DFT-optimized structures.

[a] As defined in Scheme 2. [b] Data set name (Cartesian coordinates available as *.pdb files). [c] Electronic energy. [d] Zero-point vibrational energy. [e] Lowest vibrational frequency. [f] Gibbs free energy.

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	No.	Energy (cm ⁻¹)	λ (nm)	f ^[a]	Major excitations ^[b]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	27684	361.2	0.000	H–1»LUMO (46%) HOMO»L+1 (46%)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	30217	330.9	0.351	H-2»LUMO (14%) H-1»L+1 (13%) H-1»L+2 (33%) HOMO»LUMO (13%)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	30219	330.9	0.351	H-2»L+1 (14%) H-1»LUMO (13%) HOMO»L+1 (13%) HOMO»L+2 (34%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4	32329	309.3	0.001	H-4%LUMO (18%) H-3%L+1 (19%) H-1%L+3 (16%) HOMO%L+4 (17%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5	32359	309.0	0.596	H–1»L+1 (23%) HOMO»LUMO (23%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	6	32360	309.0	0.596	H–1»LUMO (23%) HOMO»L+1 (23%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	7	34583	289.2	0.010	H–1»L+1 (42%) HOMO»LUMO (41%)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8	34753	287.7	0.000	H–2»L+2 (50%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	9	35397	282.5	0.111	H–4»L+1 (13%) H–3»LUMO (13%) HOMO»L+2 (31%) HOMO»L+5 (13%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10	35398	282.5	0.112	H-4»LUMO (13%) H-3»L+1 (13%) H-1»L+2 (31%) H-1»L+5 (13%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	11	36832	271.5	0.828	H–3»L+2 (23%) H–2»LUMO (41%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	12	36835	271.5	0.830	H–4»L+2 (23%) H–2»L+1 (41%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	13	38597	259.1	0.000	H–6»L+2 (25%) H–4»L+3 (14%) H–3»L+4 (14%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	14	39229	254.9	0.034	H–4»L+1 (10%) H–3»LUMO (10%) HOMO»L+5 (37%)
16 39445 253.5 0.126 H-4»LUMO (26%) H-3»L+1 (26%) H-1»L+3 (16%) HOMO»L+4 (16%) 17 39755 251.5 0.450 H-6»L+4 (10%) 18 39757 251.5 0.449 H-6»L+3 (10%) 18 39757 251.5 0.449 H-6»L+3 (10%) 19 40414 247.4 0.000 H-4»L+1 (20%) H-3»LUMO (20%) H-3»LUMO (20%) H-3%LUMO (20%)	15	39231	254.9	0.033	H–4»LUMO (10%) H–3»L+1 (10%) H–1»L+5 (37%)
17 39755 251.5 0.450 H-6»L+4 (10%) H-3»L+2 (17%) H-3»L+5 (16%) 18 39757 251.5 0.449 H-6»L+3 (10%) H-4»L+2 (17%) H-4»L+5 (16%) 19 40414 247.4 0.000 H-4»L+2 (20%) H-3»LUMO (20%)	16	39445	253.5	0.126	H–4»LUMO (26%) H–3»L+1 (26%) H–1»L+3 (16%) HOMO»L+4 (16%)
18 39757 251.5 0.449 H–6»L+3 (10%) H–4»L+2 (17%) H–4»L+5 (16%) 19 40414 247.4 0.000 H–4»L+1 (20%) H–3»LUMO (20%)	17	39755	251.5	0.450	H–6»L+4 (10%) H–3»L+2 (17%) H–3»L+5 (16%)
19 40414 247.4 0.000 H–4»L+1 (20%) H–3»LUMO (20%)	18	39757	251.5	0.449	H–6»L+3 (10%) H–4»L+2 (17%) H–4»L+5 (16%)
H–2»L+5 (22%)	19	40414	247.4	0.000	H–4»L+1 (20%) H–3»LUMO (20%) H–2»L+5 (22%)
20 41277 242.3 0.350	20	41277	242.3	0.350	
21 41279 242.3 0.349	21	41279	242.3	0.349	
22 41695 239.8 0.174 H–6»LUMO (44%) H–1»L+5 (17%)	22	41695	239.8	0.174	H–6»LUMO (44%) H–1»L+5 (17%)
23 41697 239.8 0.170 H–6»L+1 (45%) HOMO»L+5 (17%)	23	41697	239.8	0.170	H–6»L+1 (45%) HOMO»L+5 (17%)
24 43470 230.0 0.203 H–5»LUMO (45%) 25 43472 230.0 0.202 H–5»L+1 (45%)	24 25	43470 43472	230.0 230.0	0.203	H–5»LUNIU (45%) H–5»L+1 (45%)

Table S3. TD-DFT electronic transitions calculated for 1-E	Et.
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No.	Energy	λ	f ^[a]	Major
	(cm ⁻)	(nm)		excitations
26	43798	228.3	0.000	H–6»L+2 (10%)
				H–4»L+1 (10%)
				H–3»LUMO (10%)
				H–2»L+2 (28%)
27	44207	226.2	0.081	H–1»L+7 (26%)
				HOMO»L+7 (25%)
28	44210	226.2	0.081	H–1»L+7 (25%)
				HOMO»L+7 (26%)
29	44676	223.8	0.008	H–5»L+2 (56%)
30	44681	223.8	0.340	H–5»LUMO (10%)
				H–2»L+3 (24%)
31	44682	223.8	0.337	H–5»L+1 (10%)
				H–2»L+4 (23%)
32	45379	220.4	0.144	H–6»LUMO (14%)
				H–3»L+2 (26%)
				H–2»L+4 (11%)
33	45386	220.3	0.142	H–6»L+1 (14%)
				H–4»L+2 (26%)
				H=2*L+3 (11%)
34	45673	218.9	0.000	$H=6 \times 1 + 2 (30\%)$
0.	10070	210.5	0.000	$H_{-6} = (30, 3)$
35	46062	217 1	0.002	$H_{-1} \times I + 8 (11\%)$
55	10002	21/.1	0.002	$H_1 = 1 \times 1 + 11 (15\%)$
				$HOMO_{1+9}(11\%)$
				$HOMO \gg 1 + 12 (15\%)$
26	46207	216.0	0.260	HOMO = (55%)
27	40297	210.0	0.209	
20	40290	210.0	0.270	$H = 1 \times L^{+} 0 (33\%)$
20	40720	214.0	0.000	$H = 0 \times L + 2 (10\%)$
20	47065	212 E	0.000	$HOMO_{1} + 10(20\%)$
59	47005	212.5	0.000	$HOMO_{1+12}(17\%)$
40	47069	212 5	0.000	$HOIVIO \gg L+13(17%)$
40	47000	212.5	0.000	$H = 1 \times L + 10 (39\%)$
41	47762	211 6	0.002	$H = 1 \times L + 13 (17%)$
41	47203	211.0	0.003	$\Pi = 4 \times L + 4 (25\%)$
42	47264	211.0	0.000	H-3»L+3 (32%)
42	47264	211.6	0.003	H=4»L+3 (29%)
40	47045	244.2	0.005	H-3»L+4 (29%)
43	4/315	211.3	0.005	H-4»L+4 (37%)
	47500	240 F	0.040	H-3»L+3 (30%)
44	47506	210.5	0.018	H-5»L+5 (15%)
				H–1»L+16 (12%)
				HOMO»L+17 (12%)
45	47550	210.3	0.000	H–1»L+17 (12%)
				HOMO»L+16 (12%)
46	48006	208.3	0.079	H–5»L+3 (13%)
				H–3»L+5 (25%)
				H–2»L+4 (17%)
47	48008	208.3	0.079	H–5»L+4 (13%)
				H–4»L+5 (25%)
				H–2»L+3 (17%)
48	48231	207.3	0.000	H–2»L+7 (10%)
49	48814	204.9	0.013	H–4»L+7 (10%)
				HOMO»L+13 (12%)
50	48816	204.8	0.013	H–3»L+7 (10%)
				H–1»L+13 (12%)

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.

No.	Energy (cm ⁻¹)	λ (nm)	f ^[a]	Major excitations ^[b]
1	27464	364.1	0.000	H–2»L+2 (11%)
				H–1»L+1 (11%)
				HOMO»LUMO (67%)
2	30357	329.4	1.476	H–2»LUMO (11%)
				H–1»LUMO (29%)
				HOMO»L+1 (31%)
3	30357	329.4	1.476	H–2»LUMO (29%)
				H–1»LUMO (11%)
				HOMO»L+2 (31%)
4	30778	324.9	0.000	H–3»LUMO (21%)
-		200.0	0.000	HOMO»L+3 (30%)
5	32594	306.8	0.000	H=4»LUMO (29%)
				H=2»L+5 (10%)
				$\Pi = 1 \times L + 4 (10\%)$
6	277/2	205 /	0.451	$H_{5}(100) = 10000 = 100000 = 100000 = 100000000$
0	32743	303.4	0.451	$H=3\times101\times10$ (13%) $H=1\times1+3$ (11%)
				$HOMO \gg 1 + 4 (17\%)$
7	32743	305.4	0.451	$H=6 \times I \cup MO(15\%)$
				H–2»L+3 (11%)
				HOMO»L+5 (17%)
8	34634	288.7	0.000	H–7»LUMO (15%)
				H–4»L+3 (10%)
				H–2»L+1 (18%)
				H–1»L+2 (18%)
9	35256	283.6	0.000	H–3»L+3 (35%)
10	35733	279.9	0.134	H–2»LUMO (13%)
				H–1»L+3 (25%)
				HOMO»L+2 (10%)
11	35733	279.9	0.134	H–2»L+3 (25%)
				H–1»LUMO (13%)
10			0.000	HOMO»L+1 (10%)
12	36277	275.7	0.000	H-3»LUMO (30%)
10	27002	270.2	1 205	HUIVIU»L+3 (36%)
15	57002	270.5	1.295	$H=3\times L+1$ (11%) $H=2\times L+1MO$ (14%)
14	37002	270.3	1 295	$H_{-3} + 2 (11\%)$
14	57002	270.5	1.255	H-1»LUMO (14%)
15	37160	269.1	0.000	HOMO»L+6 (30%)
16	37559	266.2	0.000	H–2»L+1 (31%)
				H–1»L+2 (31%)
17	39296	254.5	0.000	H–3»L+6 (10%)
				H–2»L+2 (10%)
				H—1»L+1 (10%)
				HOMO»LUMO (11%)
18	39531	253.0	0.000	H–6»L+1 (20%)
				H–5»L+2 (20%)
				H–4»L+3 (12%)
				H–4»L+6 (11%)
19	39596	252.6	0.260	H-6»LUMO (12%)
				$HOMO_{NL} + 4 (17%)$
20	20506	2526	0.260	$H_6 = 11MO(200/)$
20	22220	252.0	0.200	H_5»[[]MO (12%)
				HOMO»I+5 (17%)
21	40255	248.4	0.000	H-4»LUMO (34%)
			0.000	H–2»L+5 (10%)
				H–1»L+4 (10%)
				HOMO»L+7 (16%)
22	40779	245.2	1.425	H–5»L+6 (12%)
				H–4»L+4 (11%)
23	40779	245.2	1.425	H–6»L+6 (12%)
				H–4»L+5 (11%)

No.	Energy	λ	f ^{laj}	Major
	(cm ^{−1})	(nm)		excitations ^[b]
24	41247	242.4	0.000	H–6»L+5 (12%)
				H–5»L+4 (12%)
				$H = 4 \times 1 + 3 (23\%)$
				$H=4 \times 1 + 6 (10\%)$
25	11222	2/10	0.000	$H_{2} + 4 (10\%)$
25	41555	241.9	0.000	$1 - 2 \times 1 + 4 (10 \%)$
				$H = 1 \times L + 3 (10\%)$
26	44.022	220.0	0.000	
26	41833	239.0	0.000	
				HOMO»L+6 (22%)
27	41948	238.4	0.000	H–6»L+2 (21%)
				H–5»L+1 (21%)
				H–3»L+6 (13%)
28	41950	238.4	0.049	H–1»L+3 (18%)
29	41950	238.4	0.049	H–2»L+3 (18%)
30	42959	232.8	0.315	H–1»L+7 (17%)
31	42959	232.8	0.315	H–2»L+7 (17%)
32	43157	231.7	0.000	H–3»LUMO (24%)
				H–2»L+2 (11%)
				H–1»L+1 (11%)
				HOMO»L+3 (14%)
33	43630	229.2	0.000	H–2»L+4 (24%)
				H–2»L+5 (10%)
				H–1»L+4 (10%)
				H–1»L+5 (24%)
34	43830	228.2	0.000	HOMO»L+8 (67%)
35	44243	226.0	0.259	H–1»L+3 (14%)
36	44243	226.0	0.259	H–2»L+3 (14%)
37	44386	225.3	0.000	H–7»LUMO (60%)
38	44892	222.8	0.092	H–6»LUMO (10%)
				HOMO»L+4 (12%)
39	44892	222.8	0.092	H–5»LUMO (10%)
				HOMO»L+5 (12%)
40	45020	222.1	0.000	H–7»L+3 (21%)
				HOMO»L+7 (38%)
41	45432	220.1	0.000	H–1»L+8 (29%)
				HOMO»L+10 (27%)
42	45432	220.1	0.000	H–2»L+8 (29%)
				HOMO»L+11 (27%)
43	45718	218.7	0.000	H–3»LUMO (10%)
				H–2»L+5 (15%)
				H–1»L+4 (15%)
				HOMO»L+6 (14%)
44	45744	218.6	0.000	H–6»L+1 (27%)
				H–5»L+2 (27%)
				$H=4 \times I \cup MO(27\%)$
45	45988	217.4	0 077	H=10 × 1 µ $MO(11%)$
15	15500	21/.1	0.077	$H_{-1} + 6 (25\%)$
46	45988	217.4	0.077	$H_{-9} \times UMO(11\%)$
40	43500	217.4	0.077	$H_{2} = 6 (25\%)$
17	46161	216.6	0 000	$H_{-3} = 3 (45\%)$
18	46211	210.0	0.000	H_3»I+7 (13%)
40	-0311	213.3	0.000	HOMO»I+9 (34%)
49	46427	215.4	0.000	HOMO»I+12 (52%)
45	40427	213.4	0.000	HOMO»I+23 (11%)
50	46916	213 1	0 194	H=7»I+1 (13%)
50	-0710	213.1	0.104	H-7»I+2 (11%)

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.

 Table S4. TD-DFT electronic transitions calculated for 2-Et.

Table S5. Crystal data and structure refinement for $\textbf{3-Et}{\cdot}CH_2Cl_2.$

Identification code	mm01a	
Empirical formula	$C_{57}H_{48}Br_6{\cdot}CH_2Cl_2$	
Formula weight	1297.35	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.600(4) Å	α= 106.28(5)°.
	b = 14.111(5) Å	β=94.05(4)°.
	c = 16.306(5) Å	$\gamma = 118.05(5)^{\circ}$.
Volume	2574(2) Å	
Z	2	
Density (calculated)	1.674 Mg/m ³	
Absorption coefficient	4.821 mm ⁻¹	
F(000)	1284	
Crystal size	$0.37 \ge 0.14 \ge 0.03 \text{ mm}^3$	
Theta range for data collection	2.87 to 30.59°.	
Index ranges	-19<=h<=17, -19<=k<=19, -13	<=l<=23
Reflections collected	20444	
Independent reflections	14059 [R(int) = 0.0424]	
Completeness to theta = 25.50°	99.6 %	
Absorption correction	Analytical	
Max. and min. transmission	0.867 and 0.381	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14059 / 0 / 595	
Goodness-of-fit on F ²	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0597, wR2 = 0.0951	
R indices (all data)	R1 = 0.1047, wR2 = 0.1138	
Largest diff. peak and hole	0.90 and -0.97 e. Å ⁻³	

Table S6. Crystal data and structure refinement for $4-Et \cdot C_7 H_8$.

Identification code	dstem1	
Empirical formula	$C_{76}H_{64}Br_8{\cdot}C_7H_8$	
Formula weight	1708.69	
Temperature	79(9) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c n	
Unit cell dimensions	$a = 29.202(12) \text{ Å}$ α	= 90°.
	$b = 17.637(1) \text{ Å}$ β =	= 90°.
	$c = 14.745(8) \text{ Å}$ $\gamma =$	= 90°.
Volume	7594(1) Å ³	
Z	4	
Density (calculated)	1.575 Mg/m ³	
Absorption coefficient	4.271 mm ⁻¹	
F(000)	3600	
Crystal size	0.53 x 0.44 x 0.38 mm ³	
Theta range for data collection	2.79 to 30.74°.	
Index ranges	-41<=h<=34, -14<=k<=25, -19<=	l<=20
Reflections collected	34296	
Independent reflections	10861 [R(int) = 0.0362]	
Completeness to theta = 25.50°	99.8 %	
Absorption correction	Analytical	
Max. and min. transmission	0.325 and 0.231	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10861 / 0 / 412	
Goodness-of-fit on F ²	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0496, $wR2 = 0.1165$	
R indices (all data)	R1 = 0.0837, $wR2 = 0.1342$	
Largest diff. peak and hole	2.893 and -0.701 e.Å ⁻³	



Figure S20. ¹³C NMR spectrum of S5 (chloroform-d, 151 MHz, 300 K, there are some solubility problems).





Figure S24. ¹³C NMR spectrum of S7 (chloroform-d, 151 MHz, 300 K).





Figure S26. ¹³C NMR spectrum of S8 (chloroform-d, 151 MHz, 300 K).



Figure S28. ¹³C NMR spectrum of S9 (chloroform-d, 151 MHz, 300 K).









Figure S34. ¹³C NMR spectrum of **3-Et** (chloroform-*d*, 151 MHz, 300 K).











Figure S41. High resolution mass spectrum of S5 (ESI+, top: experimental, bottom: simulated).



Figure S42. High resolution mass spectrum of S6 (ESI+, top: experimental, bottom: simulated).



Figure S43. High resolution mass spectrum of S8 (APCI+, top: experimental, bottom: simulated).







Figure S45. High resolution mass spectrum of S10 (APCI+, top: experimental, bottom: simulated).



Figure S46. High resolution mass spectrum of S11 (APCI+, top: experimental, bottom: simulated).



Figure S47. High resolution mass spectrum of 3-Et (APCI+, top: experimental, bottom: simulated).



Figure S48. High resolution mass spectrum of 4-Et (APCI+), top: experimental, bottom: simulated).



Figure S49. High resolution mass spectrum of 1-Et (APCI+, top: experimental, bottom: simulated).



Figure S50. High resolution mass spectrum of 2-Et (APCI+, top: experimental, bottom: simulated).

References

- (1) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30* (25), 7686–7691.
- (2) Li, X.; Xiao, Y.; Qian, X. Org. Lett. **2008**, *10* (13), 2885–2888.
- (3) Bavin, P. M. G. Org. Synth. **1960**, 40, 5.
- (4) Guo, L.; He, S.; Jian, T.; Lai, Y.; Liu, J.; Nargund, R.; Sebhat, I.; Ujjainwalla, F.; Ye, Z.; Young, J. Acylated Spiropiperidine Derivatives as Melanocortin-4 Receptor Agonists. WO/2004/089307, October 22, 2004.
- (5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09 Revision D.01*.
- (6) Becke, A. D. Phys. Rev. A 1988, 38 (6), 3098–3100.
- (7) Becke, A. D. J. Chem. Phys. 1993, 98 (7), 5648–5652.
- (8) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37 (2), 785–789.
- (9) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105* (8), 2999–3094.
- (10) Yanai, T.; Tew, D. P.; Handy, N. C. Chem. Phys. Lett. 2004, 393 (1–3), 51–57.
- (11) Sheldrick, G. M. Acta Crystallogr. A 2008, 64 (1), 112–122.