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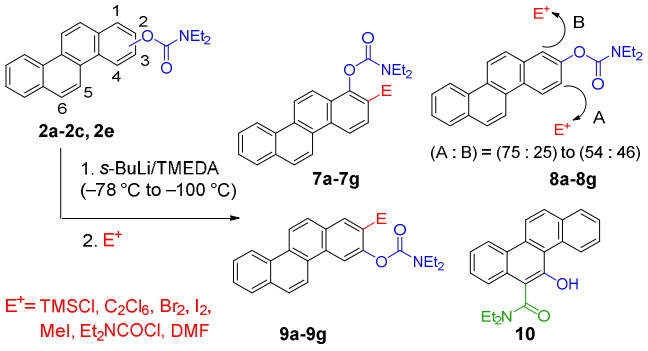
Directed *ortho* Metalation and Anionic *ortho* Fries Rearrangement of Polycyclic Aromatic *O*-Carbamates: Regioselective Synthesis of Substituted Chrysenes

Sindhu Kancherla[†], Marianne Lorentzen[†], Victor Snieckus[‡], Kåre B. Jørgensen[†*]

[†] Faculty of Science and Technology, University of Stavanger, N-4036 Stavanger, Norway; [‡] Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, ON K7L 3N6, Canada

KEYWORDS: Directed ortho Metalation (DoM), polycyclic aromatic hydrocarbons, chrysenes, anionic ortho Fries rearrangement (AoF)

ABSTRACT



A general method for the regioselective synthesis of a series of *ortho*-substituted chrysenyl *N*,*N*-diethyl-*O*-carbamates by the directed *ortho* metalation (D*o*M) strategy is reported. The starting *O*-carbamates were prepared from corresponding chrysenols, available by oxidative photochemical cyclization or directed remote metalation tactics. Chrysen-1-yl and chrysene-3-yl ring site selectivity of directed *ortho* metalation (D*o*M) and anionic *ortho* Fries rearrangement (A*o*F) protocols, with *s*-BuLi/TMEDA, followed by electrophilic quench using a selection of electrophiles, were observed leading to new chrysenyl derivatives. 5-Chrysenyl *N,N*-diethyl-*O*-carbamate underwent instant A*o*F rearrangement even at -100 °C to furnish chrysenyl *ortho*-hydroxycarboxamide. Iterative D*o*M reactions were carried out to gain insight in the regioselectivity factors.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are well-known carcinogenic and mutagenic pollutants in the environment[1,2] whose synthesis is of longstanding interest for the provision of analytical standards.[3,4] Currently, PAHs are also gaining substantial attention among material science and medicinal chemists. Thus, the synthesis of extended and helical polycyclic aromatic structures is of major interest due to their application in organic field-effect transistors (OFETs), photovoltaics, light-emitting diodes,[5,6] and

superconductors.[7, 8] The particular chrysene class of PAHs possess photophysical properties which have found utility as fluorescent OLEDs.[9] In the medicinal area, substituted chrysenes have been found to possess anticancer activity due to their intercalation with DNA[10] and have been shown to inhibit the functioning of topoisomerase II, a potentially advantageous property for cancer chemotherapy.[11]

Traditional synthetic approaches to PAHs involve a multitude of Lewis and Brønsted acid catalyzed S_EAr reactions,[12, 13] in which the Friedel-Craft acylation plays a major role.[14] Recently, new methodologies based on cooperative catalysis,[15] radical substitution,[16] and, significantly, transition metal catalyzed C-H activation,[17] have been developed. The directed *ortho* metalation (D*o*M) reaction has contributed new methodology for the construction of aromatic and heteroaromatic molecules,[18-20] in particular phenanthrenes.[21-23] Except for minor forays into small polyaromatic systems such as pyrene-1-carboxaldehyde,[24] 2-naphthyl-*O*-carbamates[25] and pyrene-1-carboxamide,[26] the D*o*M strategy has not been studied in relation to larger PAHs. The fundamental regioselectivity consequences of the D*o*M reaction for competitive sites has been studied in two or more DMG benzene derivatives.[27]

With the aim to contribute new synthetic methodology to this area, we report herein a D*o*M study on 1-, 2-, 3- and 5-chrysenyl *N,N*-diethyl-*O*-carbamates **2a**, **2b**, **2c**, and **2e**. The *N*,*N*-diethyl-*O*-carbamates were chosen in view of their very strong DMG power[18,19,27] and their recently introduced ability to undergo Suzuki-Miyaura cross coupling,[28,29] Schwarz reduction to phenols[30] and reductive hydrodecarbamoylation.[31] Thus we view that D*o*M reactions on larger polyaromatic skeletons offer considerable potential to further elaborate other and larger PAH skeletons of interest in material science areas.

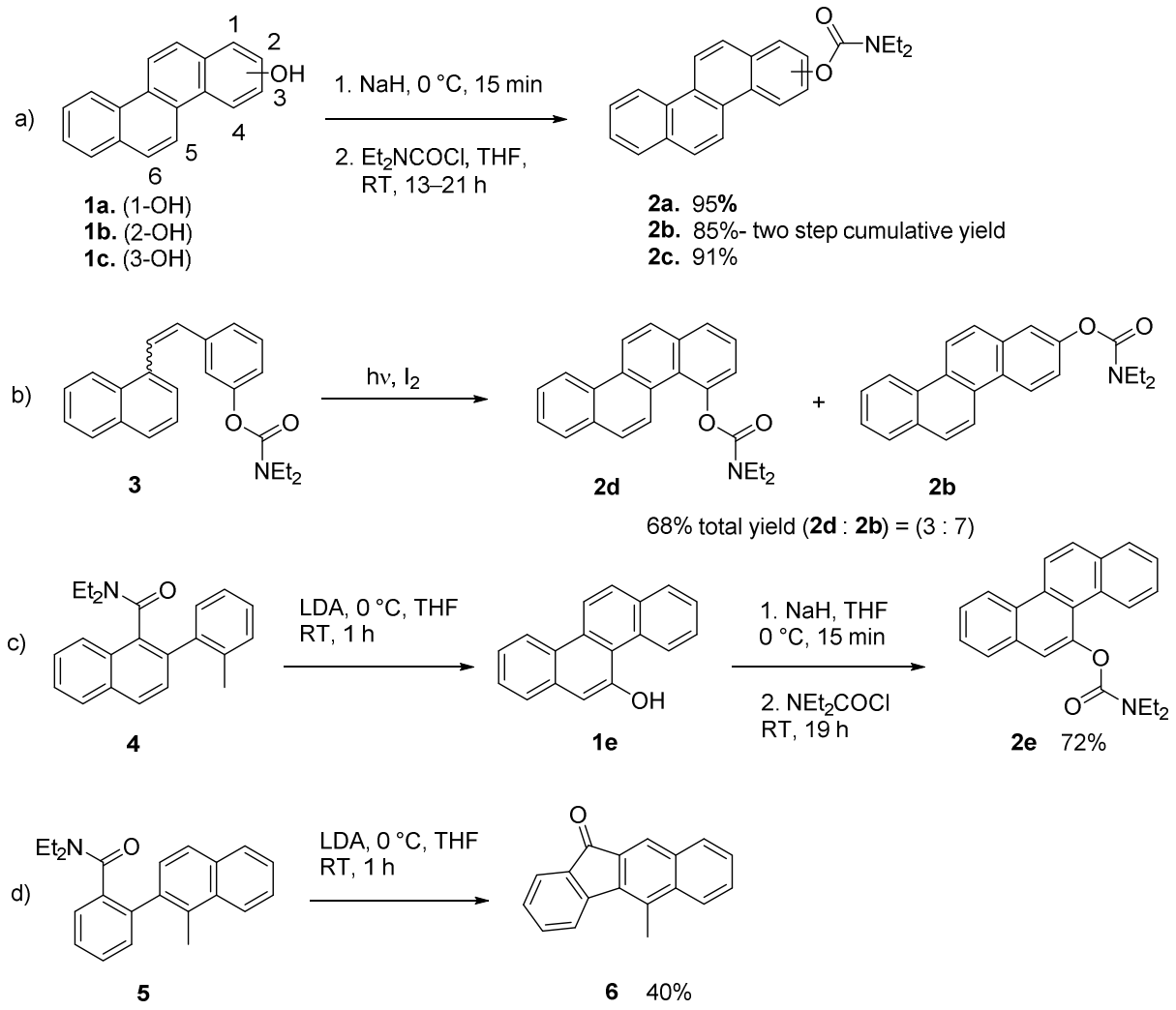
RESULTS AND DISCUSSION

To initiate the study, we used the photochemical oxidative cyclization of stilbenes to chrysenes[32-35] which has proven to be a reliable workhorse in the preparation of methoxychrysenes. The thus prepared methoxychrysenes, upon deprotection with BBr_3 furnished 1- and 3- chrysenols **1a** (96%) and **1c** (98%) in good to excellent yields (Scheme 1)[34] which**,** upon deprotonation with NaH and trapping with *N,N*-diethyl carbamoyl chloride afforded the O-carbamoyl chrysenes **2a** and **2c** in 95% and 91% yield, respectively (Scheme 1a). 2-Methoxychrysene, separated from 4-methoxychrysene by recrystallization from acetone, gave upon deprotection with BBr_3, a comparatively less soluble and unstable crude chrysenol **1b** which was immediately subjected to treatment with NaH and *N,N*-diethyl carbamoyl chloride to furnish the *O*-carbamoyl chrysene **2b** in 85% overall yield. Although 4-methoxychrysene was deprotected successfully to give chrysenol **1d**, attempts to incorporate the *N,N*-diethyl carbamate group were futile, likely due to steric crowding in the bay region.[2,36] Interestingly, the desired carbamate **2d** was obtained by the Mallory photocyclization route (Scheme 1b), albeit as a minor component of the mixture with **2b**, presumably also due to steric reasons. Unfortunately, chrysen-4-yl *N*,*N*-diethyl-O-carbamate (**2d**) could not be separated

from carbamoylchrysene **2b** by neither crystallization nor flash chromatography, and hence was not isolated (see Supporting Information).

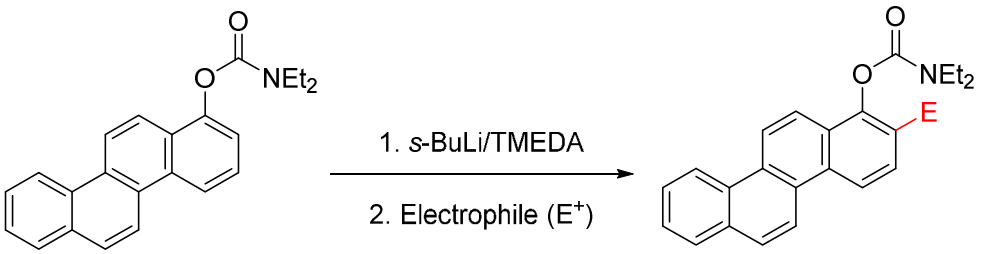
Molecules with phenolic rings which intersperse or bridge aromatic rings are available by the directed remote metalation (DreM) reaction.[23,37] Using this tactic, chrysen-5-yl *N,N*-diethyl-*O*-carbamate (**2e**) was prepared from the biaryl **4** (Scheme 1c).[38] However, the intermediate chrysenol **1e** was found to be highly unstable in air and required handling under N_2 and underwent rapid carbamoylation to give product **2e** in 72% overall yield. An attempt to prepare the 6-carbamoyl chrysene by the DreM protocol was thwarted by the fact that reaction of the requisite biaryl amide **5** afforded 5-methyl-11*H*-benzo[b]fluoren-11-one **6** rather than the expected product (Scheme 1d).

Scheme 1. Synthesis of Chrysenyl *N,N*-diethyl-*O*-carbamates (2a, 2b, 2c, 2e) and 5-methyl-11*H*-benzo[b]fluoren-11-one (6)



With four (**2a-2c, 2e**) of the six requisite regioisomeric chrysenyl *N*,*N*-diethyl-*O*-carbamates in hand, D*o*M studies were initiated and the results are summarized in Tables 1-4. Experiments were conducted under standard metalation conditions (*s*-BuLi/TMEDA, 30 min) followed by electrophilic quench with a selection of commonly used electrophiles.

Table 1. DoM reactions of Chrysene-1-yl *N*,*N*-diethyl-*O*-carbamates (2a)



2a **7a-7g**

Entry	E^+	Product	E	Yield %
1[a,b]	TMSCl	**7a**	TMS	93
2[a]	I_2	**7b**	I	94
3[a]	Br_2	**7c**	Br	86
4[a]	C_2Cl_6	**7d**	Cl	96
5[c]	MeI	**7e**	Me	quant.
6[c]	Et_2NCOCl	**7f**	$CONEt_2$	88
7[c]	DMF	**7g**	CHO[d]	65

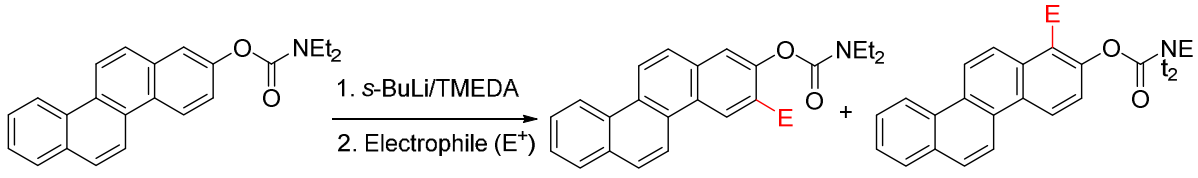
[a]1) 1.1 equiv *s*-BuLi/ TMEDA, −78 °C, 30 min; 2) 1.5 equiv E^+, −78 °C to rt., 1.5 h to 18 h; [b]TMSCl was added to the reaction mixture before *s*-BuLi; [c]1) 2 equiv *s*-BuLi/ TMEDA, −95 °C, 15 min; 2) 3 equiv E^+, -85 °C to rt., 3 - 4 h. [d]Decarbamoylation occurred during the reaction with DMF to give the chrysenol derivative.

In the first series (Table 1), chrysen-1-yl *N*,*N*-diethyl-*O*-carbamate (**2a**), upon metalation and subsequent quench with various electrophiles, afforded products **7a-g** in excellent to modest yields. In the case of using DMF as an electrophile (Entry 7, Table 1) decarbamoylation occurred to give 2-(hydroxy)chrysene-1-carbaldehyde (**7g**). In these reactions, no *peri*-substituted (C-12) products were observed. Possible reasons for the absence of *peri*-lithiated product may be the rotational orientation of DMG (steric factor) and the difference in the acidity of C-2 (electron-withdrawing effect of DMG) and C-12 (*peri*) hydrogens. Actually, ^{7}Li-^{1}H HOESY NMR studies of complexes of lithiated 1-naphthol have shown that the peri (C-8) hydrogen is in closer proximity to the prelithiated complex than C-2 hydrogen and exhibits a stronger agostic interaction with the alkyl lithium base.[39] However, possibly owing to the inductive strength of the DMG, attempts to *peri*-lithiate 1-napthamide by Clayden[40, 41] were either futile or gave low yields.

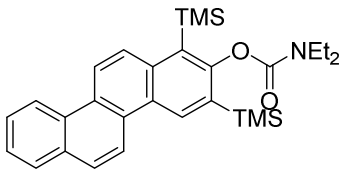
In pursuit of a molecule that will allow *peri*-lithiation, 2-(trimethylsilyl)chrysene-1-yl *N*,*N*-diethyl-*O*-carbamate (**7a**) in which the 2-position is blocked with a TMS-group,[42, 43] was subjected to a second metalation-deuteration sequence. As in the naphthyl case, starting material was recovered, conceivably indicating inability to achieve high rotamer populations in which the carbonyl is oriented towards the *peri*-hydrogen to effect deprotonation.

In addition to the successful results (Table 1), benzaldehyde, *p*-nitrobenzaldehyde, 2-methoxyethoxy methyl chloride and 2-methylbenzyl chloride electrophiles were tested but did not yield the expected products and led to the recovery of unreacted starting material. While benzaldehyde was previously used as an electrophile on benzyl[18] and napthyl carbamates[18, 25], it seemed to be unreactive with chrysenyl carbamates.

Table 2. DoM reactions on Chrysene-2-yl *N*,*N*-diethyl-*O*-carbamate (2b)



2b **8a-8g** **9a-9g**



10

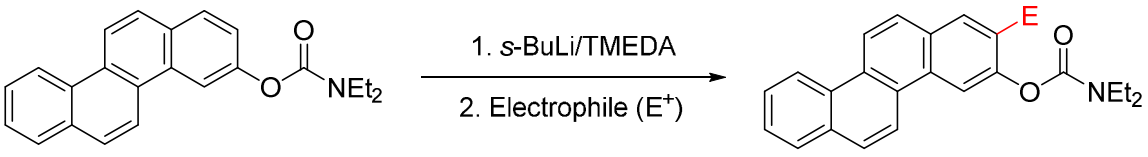
Entry	E^+	Product	E	Yield % (Ratio 8:9)[a]
1[b,c]	TMSCl	**8a : 9a**	TMS	27 (100 : 0)[d]
2[c,e]	TMSCl	**10**	1,3-diTMS	98%
3[b]	I_2	**8b : 9b**	I	68 (57 : 43)
4[b]	Br_2	**8c : 9c**	Br	67 (56 : 44)
5[b]	C_2Cl_6	**8d : 9d**	Cl	96 (59 : 41)
6[f]	MeI	**8e : 9e**	Me	79 (54 : 46)
7[f]	Et_2NCOCl	**8f : 9f**	$CONEt_2$	70 (75 : 25)
8[f]	DMF	**8g : 9g**	CHO[g]	64 (68 : 32)
9[h]	I_2	**8b**	I	89 (100 : 0)

[a]The products were isolated as mixture of two isomers and their ratio was determined by NMR analysis. [b]1) 1.1 equiv. *s*-BuLi/ TMEDA, −78 °C, 30 min; 2) 1.5 equiv E^+, −78 °C to rt., 1.5 - 18 h; [c]TMSCl was added to the reaction mixture before *s*-BuLi; [d]yield by NMR analysis; [e]2.5 equiv *s*-BuLi/ TMEDA, 3 equiv TMSCl; [f]1) 2 equiv *s*-BuLi/ TMEDA, −95 °C, 15 min; 2) 3 equiv E^+, -85 °C to rt., 3 - 4 h;

[g]Decarbamoylation occurred during reaction with DMF to give the chrysenol derivative; [h]1) 3 equiv. LiTMP, −78 °C, 1.5 h, 2) 3 equiv. I_2, −78 °C to rt, 5.5 h.

Chrysen-2-yl *N*,*N*-diethyl-*O*-carbamate (**2b**) was subjected to the same conditions as those used for chrysene-1-yl *N,N*-diethyl-*O*-carbamate (**2a**). As gleaned from Table 2, with the exception of the TMSCl electrophile, little regioselectivity for the C-1 and C-3 positions was observed for which brief comment is warranted. Rationalization of yields based on steric effects is difficult in view of the high complexity of the organolithium reactions involving aggregated lithiated species[44] and indeterminate mechanism(s)[37, 45, 46]. Rate of substitution of lithiated species may be competitive with exchange with alternate deprotonation sites as a function of electrophile. Thus, while the results with DMF and Et_2NCOCl (entries 7 and 8) may be rationalized based on steric effects, those with MeI and halogens are not consistent with a simple steric argument and may be related to change in mechanism. The TMSCl quench reactions (entries 1 and 2) were conducted under Martin conditions[47] which promote, in part, base-electrophile *in situ* compatibility which is reflected in the results: Using 1.5 equiv of TMSCl or large excess, both led to low yield of mono-silylated product **8a** with the recovery of unreacted **2b**, while 2.5 equiv of base-electrophile combination afforded almost quantitative yield of di-silylated product **10**. As observed, excess of base followed by quench with excess electrophile in all other cases (entries 5-7) led to monosubstituted products. As a rationalization of these results, a sequential deprotonation-silylation is suggested in which decomposition of TMSCl is sufficiently slow to allow double silylation of the derived C-3 anion.[18] Synthetically, the di-silylation result (entry 2) is similar to that achieved in benzamide[18,42,48] and naphthyl 2-O-carbamate[25] series and may be of synthetic value. The lack of C-1 vs C-3 regioselectivity using *s*-BuLi/TMEDA may be improved by change to a more sterically demanding base. Thus, using LiTMP metalation conditions and I_2 quench, the carbamate **2b** afforded 3-iodochrysen-2-yl *N,N*-diethyl-*O*-carbamate (**8b**) as a single regioisomer in 89% yield. An analogous selectivity was observed in experiments conducted on naphthyl 2-carbamate.[25]

Table 3. DoM reactions on Chrysene-3-yl *N,N*-diethyl-*O*-carbamates (2c)



2c **11a-11g**

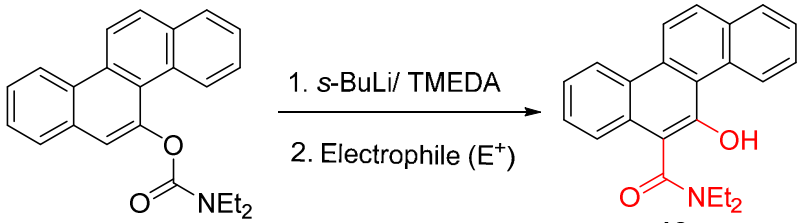
Entry	E^+	Product	E	Yield %
1[a,b]	TMSCl	**11a**	TMS	89
2[a]	I_2	**11b**	I	91
3[a]	Br_2	**11c**	Br	57[c]
4[a]	C_2Cl_6	**11d**	Cl	70[c]

5[d]	MeI	**11e**	Me	96
6[d]	Et_2NCOCl	**11f**	$CONEt_2$	88
7[d]	DMF	**11g**	CHO[e]	72

[a]1) 1.1 equiv *s*-BuLi/ TMEDA, −78 °C, 30 min; 2) 1.5 equiv E^+, −78 °C to rt., 1.5 h to 18 h; [b]TMSCl was added to the reaction mixture before *s*-BuLi; [c]Yield by NMR analysis; [d]1) 2 equiv *s*-BuLi/ TMEDA, −95 °C, 15 min; 2) 3 equiv E^+, -85 °C to rt., 3 - 4 h; [e]Decarbamoylation occurred during reaction with DMF to give the chrysenol derivative.

As expected, based on steric effects of the bay-region,[2, 36] chrysene-3-yl *N*,*N*-diethyl-*O*-carbamate (**2c**) afforded, using selected electrophiles, product **11a-11g** with complete regioselectivity. The Br_2 quench experiments (entry 3) required careful control of addition to avoid formation of dibrominated product (confirmed by HRMS analysis) and a complex mixture of products. Attempts to effect C-4 metalation of 2-(trimethyl silyl)chrysen-3-yl *N*,*N*-diethyl-*O*-carbamate (**11a**) also turned futile with the recovery of starting material when MeOD and MeI were used as electrophiles (HRMS analysis, see Supporting Information).

Table 4. DoM reactions on Chrysen-5-yl *N*,*N*-diethyl-*O*- carbamate (2e)



2e **12**

Entry	E^+	T °C	Yield %
1[a,b]	TMSCl	−78	75
2[c]	-	−100	79
3[d]	Br_2	−100	71

[a]1) 1.1 mmol *s*-BuLi/ TMEDA, −78 °C, 30 min, 2) 1.5 mmol E^+, −78 °C to rt; [b]TMSCl was added to the reaction mixture before *s*-BuLi; [c]1.1 mmol *s*-BuLi/ TMEDA, −100 °C, 1h; [d]1) 1.1 mmol *s*-BuLi/ TMEDA, −100 °C, 10 min; 2) 1.5 equiv E^+, −100 °C to rt.

Chrysen-5-yl *N*,*N*-diethyl-O-carbamate (**2e)** (Table 4), posits an interesting case since the opposite bay-hydrogen in C-4 position is expected to show strong hindrance in the orientation of the carbamoyl group towards the bay region. In the event, metalation under *in situ* TMSCl quench conditions at either −78 °C under (entry 1) or at −100°C (entry 2) resulted in extremely fast AoF rearrangement to cleanly afford amide **12**. In addition, an attempt to quench the reaction with Br_2 at −100 °C (entry 3) also gave compound **12**. The metalation of the 1- and 2- and 3-, 5-substituted chrysenyl derivatives showed individual characteristic color changes upon lithiation (see Supporting Information). The failure to inhibit the AoF

rearrangement by lowering the temperatures and variation of lithiation time suggests that significant steric and electronic factors[49, 50] of the K-region of chrysene are involved.

CONCLUSION

In conclusion, we have shown new D*o*M strategy using the powerful $OCONEt_2$ DMG for the chrysenyl O-carbamates **2a**, **2b**, **2c**, **2e** which leads to the efficient synthesis of disubstituted derivatives (Tables 1-4). Compound **2b** (Table 2) shows essentially no regioselective preference for the two *ortho* sites under standard *s*-BuLi/TMEDA conditions but indicates that LiTMP is a promising base for regioselectivity improvement. The availability of *peri*-metalation site is of no consequence for the D*o*M reaction (**2a**, Table 1) either directly or with 2-TMS protection. However, the K-region influence, of significance in consideration of carcinogenic effects[51, 52] affects the reactivity of the D*o*M reactions of **2c** (Table 3) and **2e** (Table 4) perhaps by combination of steric and electronic effects on the orientation of the carbamate group as a function of the rotational barriers. The present work provides an expansion of the D*o*M methodology for the preparation of substituted chrysenes (**7a-7g**, **8a-8g**, **9a-9g**, **10**, **11a-11g**, **12**). The utility for the D*o*M strategy described herein for the synthesis of other PAH type molecules may be anticipated.

EXPERIMENTAL SECTION

General Methods. All experiments were carried out in oven-dried glassware, using septa and syringes under dry-N_2 atmosphere and monitored by TLC (Merck silica gel 60 F_{254} plates) using UV light at 254 nm for detection. Purchased anhydrous solvents and chemical reagents were used without further purification, unless otherwise specified. *s*-BuLi was titrated periodically before use. The reagents were distilled and stored over molecular sieves before use. The products were purified by flash chromatography using silica gel (particle size: 40-60 µm. 60Å) with PE or heptane and EtOAc. ^{1}H and ^{13}C NMR spectra were either recorded on Bruker Avance 300 MHz or 400 MHz spectrometers with chemical shifts reported in ppm relative to internal TMS (δ = 0) or $CHCl_3$ (δ = 7.26), $CDCl_3$ (δ = 77.0). The multiplicities were recorded as singlet, s; doublet, d; triplet t; double doublet, dd; doublet of triplet, dt; triplet of doublet, td; quartet, q; multiplet, m; apparent, app; broad, br. IR spectra was obtained from KBr discs on an Agilent Cary 630 FTIR spectrometer. Mass spectra were obtained from ESI-TOF instruments at the University of Bergen and the University of Tromsø, Norway. All melting points were measured on Stuart Scientific melting point apparatus SMP3 and are uncorrected.

Synthesis of Chrysenols. Chrysenols **1a**-**1c** were synthesized by oxidative photo cyclization of stilbenes followed by demethylation with BBr_3, as previously described.[34]

General Procedure for the Synthesis of Chrysenyl *N,N*-diethyl-O-carbamate from Chrysenols. The chrysenol (1 mmol) in THF (2 mL) was added to a suspension of NaH (1.2 mmol) in THF (2 mL) at 0 °C. The reaction mixture was allowed to stir for 15 min and then warmed to rt before drop-wise addition of *N,N*-diethylcarbamoyl chloride (1.1 mmol). The mixture was stirred until complete reaction and quenched

with aq satd NH_4Cl solution (10 mL). The solution was extracted with Et_2O or EtOAc (3 x 10 mL) and the combined organic phase was washed with brine (3 x 10 mL), dried ($MgSO_4$), evaporated to dryness and the residue purified by gradient flash column chromatography (EtOAc and hexane).

*Chrysen-1-yl N,N-diethyl-O-carbamate (**2a**).* Following the general procedure, the reaction mixture was stirred for 13 h. Normal work-up (extraction with Et_2O) and purification by flash column chromatography (EtOAc:hexane 1:5) afforded product **2a** (886 mg , 95%) from chrysen-1-ol (**1a**) (668 mg, 2.73 mmol), as a white shiny powder, mp. 172.0−173.0 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.2 Hz, 1H), 8.76 (d, *J* = 9.2 Hz, 1H), 8.70 (d, *J* = 9.1 Hz, 1H), 8.65 (d, *J* = 8.6 Hz, 1H), 8.13 (d, *J* = 9.2 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 8.00 (dd, *J* = 1.3, 7.8 Hz, 1H), 7.74−7.63 (m, 3H), 7.46 (d, *J* = 7.7 Hz, 1H), 3.68 (q, *J* = 6.9 Hz, 2H), 3.50 (q, *J* = 6.9 Hz, 2H), 1.45 (t, *J* = 6.9 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 147.9, 132.2, 132.0, 130.4, 128.5, 128.2, 128.1, 127.6, 126.7, 126.5, 126.3, 126.0, 123.1, 121.7, 121.4, 120.4, 120.2, 118.9, 42.4, 42.1, 14.5, 13.5; FTIR (KBr, cm^{-1}) 2976, 2936, 1716, 1596, 1409, 1273, 1259; HRMS (ESI) m/z $[M + Na]^+$ for formula $C_{23}H_{21}NNaO_2$: calcd, 366.1470; found 366.1477.

*Chrysen-3-yl N,N-diethyl-O-carbamate (**2c**).* Following the general procedure, the reaction mixture was stirred for 14 h. Normal work-up (extraction with Et_2O) and purification by flash column chromatography (EtOAc:hexane 1:5, with 10% DCM) afforded product **2c** (7.76 g , 91%) from chrysen-3-ol (**1c**) (6.04 g, 24.70 mmol), as a white shiny powder, mp. 121.5−122.5 °C (EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.2 Hz, 1H), 8.67 (d, *J* = 9.0 Hz, 1H), 8.61 (d, *J* = 9.2 Hz, 1H), 8.48 (app d, *J* = 2.0 Hz 1H), 7.98 (d, *J* = 8.7 Hz, 2H), 7.97 (d, *J* = 8.9 Hz, 2H) 7.72−7.68 (m, 1H), 7.65−7.61 (m, 1H), 7.44 (dd, *J* = 2.2, 8.7 Hz, 1H), 3.55 (br. q, *J* = 6.8 Hz, 2H), 3.46 (br. q, *J* = 6.8 Hz, 2H) 1.35 (br. t, *J* = 6.9 Hz, 3H), 1.26 (br. t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 150.2, 132.2, 131.4, 130.5, 129.7, 129.6, 128.5, 128.4, 127.9, 127.2, 126.9, 126.6, 126.4, 123.2, 121.6, 121.4, 120.6, 115.0, 42.3, 42.0, 14.3, 13.4; FTIR (KBr, cm^{-1}) 2975, 1715, 1618, 1596, 1470, 1456, 1418, 1376, 1313, 1272, 1248; HRMS (ESI) m/z $[M + Na]^+$ for formula $C_{23}H_{21}NNaO_2$: calcd, 366.1470; found 366.1477.

*Chrysen-2-yl N,N-diethyl-O-carbamate (**2b**).*To a solution of 2-methoxychrysene (833 mg, 3.23 mmol) in DCM (30 mL) was added BBr_3 (4.84 mL, 4.84 mmol) at 0 °C. After stirring for 21 h, the reaction mixture was quenched with water (14 mL). The aqueous layer was extracted with EtOAc (3 x 30 mL), before the combined organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The crude chrysen-2-ol (**1b**) (3.23 mmol) in THF (15 mL) was added to a suspension of NaH (193 mg, 4.83 mmol) in THF (10 mL) at 0 °C. After 15 min. of stirring the mixture was warmed to rt before *N*,*N*- diethylcarbamoyl chloride (0.42 mL, 3.31 mmol) was added, and the reaction mixture was stirred overnight (21 h). After normal work-up (extraction with EtOAc), followed by flash column chromatography (EtOAc:PE 1:2, with 10% DCM), product **2b** (936 mg , 85% - two step) was obtained as a white shiny powder, mp. 189.0−190.0 °C (EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.9 Hz, 1H), 8.72 (d, *J* = 9.3 Hz, 1H), 8.67 (d, *J* = 9.2 Hz, 1H), 8.61−7.94 (m, 3H), 7.76 (app d, *J* = 2.3 Hz, 1 H), 7.73−7.61 (m, 2 H), 7.51 (dd, *J* = 2.4, 9.0 Hz, 1

H), 3.55−3.45 (m, 4H), 1.36−1.27 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3, 149.8, 132.9, 132.0, 130.5, 128.5, 128.2, 128.0, 127.8, 127.5, 126.9, 126.7, 126.3, 124.5, 123.0, 121.9, 121.7, 121.2, 119.4, 42.3, 42.0, 14.3, 13.4; FTIR (KBr, cm^{-1}) 2978, 1703, 1522, 1474, 1422, 1364, 1272; HRMS (ESI) m/z $[M + Na]^+$ for formula $C_{23}H_{21}NNaO_2$: calcd, 366.1470; found 366.1477.

Synthesis of Chrysenyl *N*,*N*-diethyl-*O*-carbamates by Directed remote Metalation (DreM).

*Chrysen-5-yl N,N-diethyl-O-carbamate (**2e**).* To a solution of diisopropylamine (DIPA) (1.26 mL, 8.99 mmol) in THF (15 mL) was added *n*-BuLi (4.26 mL, 8.95 mmol) at -5 ºC. Biphenyl **4**[38] (1.22 g, 3.85 mmol) in THF (8 mL) was added dropwise, and the reaction mixture stirred for 70 min at rt. Normal workup gave the chrysen-5-ol (**1e**) as a yellow solid in a complete reaction according to TLC. **1e** (3.85 mmol) was added to a suspension of NaH (0.258 g, 6.45 mmol) in THF (7 mL) at 0 ºC. *N*,*N*-diethylcarbamoyl chloride (0.5 mL, 3.95 mmol) was added at rt, and the reaction mixture stirred at rt for 18 h. Normal workup followed by flash column chromatography (EtOAc:hexane 1:6) afforded product **2e** as white shiny powder (953 mg, 72%), mp. 142.5−143.5 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14-9.11 (m, 1H), 8.73 (d, *J* = 9.0 Hz, 2 H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.97−7.95 (m, 1H), 7.92−7.89 (m, 1H), 7.68 (s, 1H), 7.67−7.57 (m, 4H), 3.78 (q, *J* = 7.0 Hz, 2H), 3.47 (q, *J* = 7.0 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 147.6, 133.0, 131.9, 131.0, 129.5, 128.9, 128.7, 128.4, 127.8, 126.8, 126.5, 126.4, 126.2, 126.15, 123.5, 123.3, 121.3, 120.5, 42.2, 41.9, 14.5, 13.4; FTIR (KBr, cm^{-1}) 2979, 2932, 1702, 1522, 1474, 1422, 1380, 1272; HRMS (ESI) m/z $[M + Na]^+$ for formula $C_{23}H_{21}NNaO_2$: calcd, 366.1470; found 366.1471.

*5-Methyl-11H-benzo[b]fluoren-11-one (**6**).* Lithium diisopropylamine (LDA) (4.65 mL, 6.46 mmol, 1.39 M in THF) was added to a precooled solution of biphenyl **5** (661 mg, 2.08 mmol) at 0 °C. The reaction mixture was stirred at rt for 1 h, before *tert*-butyldimethylsilyl chloride (1.0 M, 5.7 mL, 5.7 mmol) was added. The reaction mixture was stirred for 18 h and after normal work-up (extraction with Et_2O), followed by flash column chromatography (EtOAc:PE 1:9) afforded compound **6** (201 mg, 40%) of 5-methyl-11Hbenzo[*b*]fluoren-11-one (**6**) as an orange solid, mp. N/A; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.38−8.33 (m, 1H), 7.96−7.91 (m, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.60−7.51 (m, 3H), 7.47 (s, 1H), 7.46−7.40 (m, 1H), 7.25−7.20 (m, 1H), 2.63 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 194.7, 145.1, 141.0, 136.7, 136.4, 134.3, 131.26, 131.2, 128.8, 128.2, 128.0, 127.1, 125.6, 125.2, 123.8, 122.9, 120.5, 19.9; FTIR (KBr, cm^{-1}) 3049, 2981, 1709, 1621, 1606, 1583, 1468, 1424, 1400, 1272; HRMS (ESI) m/z $[M + H]^+$ for formula $C_{18}H_{13}O$: calcd, 245.0961; found 245.0959.

General procedure for the D*o*M Reaction on Chrysenyl *O*-carbamates.

To a solution of chrysenyl *N*,*N*-diethyl carbamate (1 mmol) dissolved in THF (2 mL) was added dry TMEDA (1.1 mmol). The solution was cooled to −78 °C before *s*-BuLi (1.1 mmol) was added slowly in drop-wise manner. After stirring for 30 min, the electrophile (1.5 mmol) was added and the reaction mixture was stirred and allowed to reach rt over 1.5 h to 18 h. The reaction mixture was quenched with aq

satd NH_4Cl solution (5 mL). The solution was extracted with EtOAc (3 x 15 mL) and the organic layer was washed with brine (3 x 15 mL) and dried ($MgSO_4$) followed by evaporation to dryness. The residue was purified by gradient flash column chromatography (EtOAc and PE) to obtain pure product.

*2-(Trimethysilyl)chrysene-1-yl N,N-diethyl-O-carbamate (**7a**).* According to the general procedure, **2a** (187 mg, 0.54 mmol) in THF (3 mL) was treated with *s*-BuLi (0.51 mL, 0.60 mmol), TMEDA (0.09 mL, 0.60 mmol) and TMSCl (0.10 mL, 0.79 mmol) at −78 °C for 1.5 h. Normal workup, followed by flash column chromatography (EtOAc:hexane 1:6) afforded product **7a** (209 mg, 93%) as a beige solid, mp. 158.0−159.5 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76−8.72 (m, 2H), 8.69 (d, *J* = 9.1 Hz, 1H), 8.63 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 9.1 Hz, 1H), 7.98 (dd, *J* = 1.0, 7.8 Hz, 1H), 7.91 (d, *J* = 9.3 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.71−7.67 (m, 1H), 7.64−7.61 (m, 1H), 3.85−3.39 (m, 4H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 153.2, 133.0, 132.3, 131.4, 130.4, 130.4, 129.0, 128.5, 128.3, 128.1, 127.5, 126.7, 126.5, 126.0, 123.2, 121.8, 121.5, 120.4, 120.35, 42.0, 41.8, 14.5, 13.3, 0.0; FTIR (KBr, cm^{-1}) 2971, 1709, 1615, 1584, 1474, 1418, 1390, 1349, 1270, 1247; HRMS (ESI) m/z $[M + Na]^+$ for formula $C_{26}H_{29}NNaO_2Si$: calcd, 438.1865; found 438.1860.

*2-Iodochrysen-1-yl N,N-diethyl-O-carbamate (**7b**).* According to the general procedure, **2a** (102 mg, 0.30 mmol) in THF (2.2 mL) was treated with *s*-BuLi (0.26 mL, 0.33 mmol), TMEDA (0.05 mL, 0.33 mmol) and iodine in THF (1 M, 0.6 mL, 0.6mmol) at −78 °C, and warmed to rt over 5.5 h. Normal workup, followed by flash column chromatography (EtOAc:hexane 1:6) afforded product **7b** (131 mg, 94%) as a beige solid, mp. 221.0−222.0 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 7.8 Hz, 1H), 8.54 (d, *J* = 9.0 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 7.98−7.92 (m, 4H), 7.69−7.66 (m, 1H), 7.63−7.60 (m, 1H), 3.76−3.47 (m, 4H), 1.48 (t, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 148.8, 135.3, 132.2, 131.7, 130.3 (2C), 128.5, 128.2, 127.9, 127.3, 126.8, 126.6, 123.1, 122.7, 122.3, 121.0, 120.4, 89.2, 42.5, 42.3, 14.7, 13.4; FTIR (KBr, cm^{-1}) 2972, 1723, 1587, 1469, 1419, 1392, 1367, 1270; HRMS (ESI) m/z $[M + Na]^+$ for formula $C_{23}H_{20}INNaO_2$: calcd, 492.0436; found 492.0434.

*2-Bromochrysen-1-yl N,N-diethyl-O-carbamate (**7c**).* According to the general procedure, **2a** (141 mg, 0.41 mmol) in THF (2.8 mL) was treated sequentially with *s*-BuLi (0.39 mL, 0.46mmol), TMEDA (0.07 mL, 0.47 mmol) and Br_2 (19.25 M, 0.03 mL, 0.58 mmol) at −78 °C, and warmed to rt over 16 h. Normal workup, followed by flash column chromatography (EtOAc:hexane 1:5) afforded product **7c** (149 mg, 86%) as a beige solid, mp. 211.0−212.0 °C (EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73−8.69 (m, 2H), 8.55 (d, *J* = 9.0 Hz, 1H), 8.44 (d, *J* = 9.1 Hz, 1H), 8.00 (d, *J* = 9.4 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.71−7.60 (m, 2H), 3.73−3.66 (m, 2H), 3.49 (app. d, *J* = 6.1 Hz, 2H), 1.47 (t, *J* = 7.0 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 145.4, 132.2, 130.9, 130.3, 129.9, 128.5, 128.2, 127.9, 127.88, 127.8, 126.9, 126.6, 123.1, 122.8, 122.0, 121.0, 120.2, 114.6, 42.6, 42.3, 14.5, 13.4; FTIR (KBr, cm^{-1}) 2975, 1725, 1591, 1471, 1417, 1394, 1267, 695; HRMS (ESI) m/z $[M + Na]^+$ for formula $C_{23}H_{20}BrNNaO_2$: calcd, 444.0575; found 444.0579.

*2-Chlorochrysen-1-yl N,N-diethyl-O-carbamate (**7d**).* According to the general procedure, **2a** (100 mg, 0.29 mmol) in THF (2.2 mL) was treated with *s*-BuLi (0.25 mL, 0.31 mmol), TMEDA (0.05 mL, 0.33 mmol) and Cl_3CCCl_3 (139 mg, 0.59 mmol) in THF (1 mL) at −78 °C, and warmed to rt over 6 h. Normal workup, followed by flash column chromatography (EtOAc:hexane 1:6) afforded product **7d** (108 mg, 96%) as a white solid, mp. 218.5−219.5 °C (EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74−8.69 (m, 2H), 8.56−8.49 (m, 2H), 8.02 (d, *J* = 9.3 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.71−7.60 (m, 3H), 3.68 (q, *J* = 7.0 Hz, 2H), 3.49 (q, *J* = 7.0 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 143.9, 132.1, 130.3, 128.5, 128.1, 127.9, 127.8, 127.7, 127.3, 126.9, 126.6, 124.9, 123.0, 122.8, 121.6, 121.0, 120.0, 42.6, 42.3, 14.4, 13.4; FTIR (KBr, cm^{-1}) 2976, 2933, 1724, 1594, 1471, 1419, 1397, 1382, 1268, 702; HRMS (ESI) m/z [M + Na]$^+$ for formula $C_{23}H_{20}ClNNaO_2$: calcd, 400.1080; found 400.1099.

*2-Methylchrysen-1-yl N,N-diethyl-O-carbamate (**7e**).* According to the general procedure, **2a** (111 mg, 0.32 mmol) in THF (2.2 mL) was treated with *s*-BuLi (0.57 mL, 0.65 mmol), TMEDA (0.10 mL, 0.65 mmol) and MeI (0.06 mL, 0.97 mmol) at −95 °C, and warmed to rt over 4 h. Normal workup, followed by flash column chromatography (EtOAc:PE 1:8) compound **7e** was isolated as a brown solid (116 mg, 100%), mp 179.5−180.6 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78-8.74 (m, 2H), 8.64 (d, *J* = 9.0 Hz, 1H), 8.53 (d, *J* = 8.7 Hz, 1H), 8.06 (d, *J* = 9.3 Hz, 1H), 8.00−7.95 (m, 2H), 7.73−7.69 (m, 1H), 7.66−7.62 (m, 1H), 7.55 (d, *J* = 8.6 Hz, 1H), 3.70 (q, *J* = 6.9 Hz, 2H), 3.53 (q, *J* = 6.9 Hz, 2H), 2.48 (s, 3H), 1.47 (t, *J* = 7.05 Hz, 3H), 1.33 (t, *J* = 7.04 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 145.6, 131.9, 130.4, 130.2, 129.1, 128.4, 128.1, 127.7, 127.5, 127.3, 126.5, 126.4, 126.1 122.9, 121.7, 121.2, 120.4, 120.0, 42.3, 42.0, 16.4, 14.5, 13.4; FTIR (KBr, cm^{-1}) 2980, 1714, 1475, 1418, 1397, 1271, 1256, 1184; HRMS (ESI) *m/z* [M + Na]$^+$ for formula $C_{24}H_{23}NNaO_2$: calcd, 380.1626; found, 380.1621.

*2-(N,N-Diethyl carbamoyl)chrysen-1-yl N,N-diethyl-O-carbamate (**7f**).* According to the general procedure, **2a** (100 mg, 0.29 mmol) in THF (2.2 mL) was treated with *s*-BuLi (0.52 mL, 0.58 mmol), TMEDA (0.09 mL, 0.58 mmol) and Et_2NCOCl (0.11 mL, 0.87 mmol) at −95 °C, and warmed to rt over 4 h. Normal workup, followed by flash column chromatography (EtOAc:PE 1:2) afforded compound **7f** as an off-white solid (113 mg, 88%), mp. 183.0−184.5 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77−8.72 (m, 2H), 8.65−8.63 (m, 2H), 8.06 (d, *J* = 9.3 Hz, 1H), 7.97 (br. d, *J* = 8.6 Hz, 1H), 7.71−7.67 (m, 1H), 7.65−7.61 (m, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 3.64−3.43 (m, 8H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.29−1.23 (m, 6H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 153.5, 144.1, 132.2, 131.8, 130.2, 128.4, 128.37, 127.9, 127.75, 127.7, 126.8, 126.7, 126.6, 123.7, 123.0, 122.3, 121.7, 120.7, 120.4, 42.8, 42.4, 42.3, 38.5, 14.4, 13.8, 13.4, 12.6; FTIR (KBr, cm^{-1}) 2975, 2934, 1716, 1633, 1472, 1420, 1383, 1366, 1270; HRMS (ESI) *m/z* [M + Na]$^+$ for formula $C_{28}H_{30}N_2NaO_3$: calcd, 465.2154 ; found, 465.2140.

*2-(Hydroxy)chrysene-1-carbaldehyde (**7g**).* According to the general procedure, **2a** (103 mg, 0.30 mmol) in THF (2.2 mL) was treated with *s*-BuLi (0.53 mL, 0.60 mmol), TMEDA (0.09 mL, 0.60 mmol) and DMF (0.07 mL, 0.90 mmol) at −95 °C, and warmed to rt over 3.5 h. Normal workup, followed by flash column

chromatography (EtOAc:PE 1:8) afforded compound **7g** as a yellow solid (52 mg, 65%, NMR yield), mp 179.0−180.6 °C (Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.48 (s, 1H), 10.06 (s, 1H), 8.82−8.77 (m, 2H), 8.63 (d, *J* = 9.1 Hz, 1H), 8.59 (d, *J* = 9.3 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 9.1 Hz, 1H), 8.00 (dd, *J* = 1.4, 7.9 Hz, 2H), 7.72, (d, *J* = 8.8 Hz, 1H), 7.77−7.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 161.2, 135.8, 132.7, 131.2, 130.2, 128.6, 127.9, 127.86, 127.4, 127.39, 127.0, 123.6, 122.7, 121.7, 121.6, 121.4, 115.1, 114.7; FTIR (KBr, cm^{-1}) 1646, 1627, 1588, 1460, 1384, 1320; HRMS (ESI) *m/z* [M - H]$^-$ for formula $C_{19}H_{11}O_2$: calcd, 271.0759; found, 271.0764.

*3-Iodochrysen-2-yl N,N-diethyl-O-carbamate (**8b**) and 1-Iodochrysen-2-yl N,N-diethyl-O-carbamate (**9b**).* According to the general procedure, **2b** (139 mg, 0.41 mmol) in THF (10 mL) was treated with *s*-BuLi (0.43 mL, 0.43 mmol), TMEDA (0.07 mL, 0.46 mmol) and iodine (0.6 mL, 0.6 mmol, 1.0 M in THF) at −78 °C, and warmed to rt over 5.5 h. Normal workup, followed by flash column chromatography (EtOAc:hexane 1:6) afforded a beige solid as a mixture of **8b** and **9b** (130 mg, 68%, 57:43), mp. 171.5−173.0 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H – **8b**), 8.71 (d, J = 9.0 Hz, 1H – **8b**, 1H – **9b**), 8.70 (d, J = 9.2 Hz, 1H - **9b**), 8.69−8.67 (m, 1H – **9b**), 8.64 (d, J = 9.1 Hz, 1H – **8b**), 8.58 (d, J = 9.1 Hz, 1H – **9b**), 8.50 (d, J = 9.1 Hz, 1H – **8b**), 8.32 (d, J = 9.3 Hz, 1H – **9b**), 7.96−7.93 (m, 1H – **8b**, 1H – **9b**), 7.77 (s, 1H – **8b**), 7.71−7.59 (m, 1H – **8b**, 1H – **9b**), 7.50 (d, J = 9.0 Hz, 1H – **9b**), 3.66−3.58 (m, 2H – **8b**, 2H – **9b**), 3.46 (q, J = 7.0 Hz, 2H – **8b**, 2H – **9b**), 1.42−1.37 (m, 3H – **8b** , 3H – **9b**), 1.27 (t, J = 7.0 Hz, 3H – **8b**, 3H – **9b**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.22, 153.2, 150.9, 149.0, 134.7, 134.1, 132.7, 132.1, 132.08, 130.9 (2C), 130.3, 130.2, 129.6, 128.9, 128.5, 128.46, 128.1, 128.0 (2C), 127.8, 126.9, 126.8, 126.76, 126.6, 126.5, 126.47, 124.7, 123.5, 123.05, 123.0, 122.4, 121.1, 120.8, 120.7, 96.0, 90.7, 42.4, 42.3, 42.1 (2C), 14.5, 14.4, 13.4 (2C); FTIR (KBr, cm^{-1}) 2978, 2933, 1713, 1591, 1473, 1416, 1380, 1313, 1272; HRMS (ESI) m/z [M + Na]$^+$ for formula $C_{23}H_{20}INNaO_2$: calcd, 492.0436; found 492.0434.

*3-Iodochrysen-2-yl N,N-diethyl-O-carbamate (**8b**).* The compound **2b** (100 mg, 0.29 mmol) in THF (3 mL) was treated with LiTMP (0.87 mmol prepared *in situ* by adding 0.87 mmol of *n*-BuLi to 0.96 mmol of 2,2,6,6-TMP in 1 mL THF at 0 °C) for 1.5 h and quenched with I_2 (0.87 mL , 0.87 mmol, 1.0 M in THF) at −78 °C, and warmed to rt over 5.5 h. Normal workup, followed by flash column chromatography (EtOAc:hexane 1:6) afforded **8b** (116 mg, 89%) as a white solid, mp. 171.8−172.8 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.61 (d, *J* = 9.0 Hz, 1H), 8.54 (d, *J* = 9.1 Hz, 1H), 8.39 (d, *J* = 9.1 Hz, 1H), 7.92 (app dd, J = 1.2, 7.7 Hz, 1H), 7.87 (d, *J* = 9.1 Hz, 1H), 7.78−7.75 (m, 1H), 7.75 (s, 1H), 7.66−7.58 (m, 2H), 3.61 (q, *J* = 7.2 Hz, 2H), 3.50 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 148.9, 134.5, 132.5, 131.9, 130.1, 129.4, 128.4, 127.8, 126.7, 126.5, 126.4, 126.3, 122.9, 122.3, 120.6, 120.57, 90.6, 42.3, 42.1, 14.4, 13.3; FTIR (KBr, cm^{-1}) 2974, 1714, 1473, 1416, 1380, 1244; HRMS (ESI) m/z [M + Na]$^+$ for formula $C_{23}H_{20}INNaO_2$: calcd, 492.0436; found 492.0434.

*3-Bromochrysen-2-yl N,N-diethyl-O-carbamate (**8c**) and 1-Bromochrysen-2-yl N,N-diethyl-O-carbamate (**9c**).* According to the general procedure, **2b** (89 mg, 0.26 mmol) in THF (6 mL) was treated with *s*-BuLi (0.38 mL, 0.27 mmol), TMEDA (0.04 mL, 0.27 mmol) and Br_2 (0.04 mL, 0.77 mmol) at −78 °C, and warmed to rt over 5 h. Normal workup, followed by flash column chromatography (EtOAc:hexane 1:4) afforded a mixture of **8c** and **9c** (73 mg, 67%, 56:44) as a beige solid, mp. 198.5−200.0 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H – **8c**), 8.70−8.65 (m, 1H – **8c**, 3H – **9c**), 8.61 (d, *J* = 9.2 Hz, 1H – **8c**), 8.53 (d, *J* = 9.0 Hz, 1H – **9c**), 8.45 (d, *J* = 9.0 Hz, 1H – **8c**), 8.38 (d, *J* = 9.4 Hz, 1H – **9c**), 7.95−7.91 (m, 2H – **8c**, 2H – **9c**), 7.82 (d, *J* = 9.3 Hz, 1H – **8c**), 7.81 (s, 1H – **8c**), 7.71−7.60 (m, 2H – **8c**, 2H – **9c**), 7.54 (d, *J* = 9.1 Hz, 1H – **9c**), 3.63−3.58 (m, 2H – **8c**, 2H – **9c**), 3.51−3.46 (q, *J* = 6.9 Hz, 2H – **8c**, 2H – **9c**), 1.43−1.39 (m, 3H – **8c**, 3H –**9c**), 1.31−1.28 (m, 3H – **8c**, 3H – **9c**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 153.19, 147.4, 146.5, 132.0, 131.8, 131.5, 130.2, 130.1, 129.2, 129.1, 128.5, 128.4, 128.1, 127.94, 127.9, 127.8, 127.77, 127.7, 126.9, 126.8, 126.7, 126.6, 126.5, 126.3, 125.5, 123.4, 123.0, 122.99, 122.95, 122.6, 122.2, 121.7, 121.0, 120.7, 116.24, 116.21, 42.4 (2C), 42.1 (2C), 14.3, 14.2, 13.4 (2C); FTIR (KBr, cm^{-1}) 2978, 2933, 1726, 1472, 1417, 1381, 1273, 1249; HRMS (ESI) m/z $[M + Na]^+$ for formula $C_{23}H_{20}BrNNaO_2$: calcd, 444.0575; found 444.0589.

*3-Chlorochrysen-2-yl N,N-diethyl-O-carbamate (**8d**) and 1-Chlorochrysen-2-yl N,N-diethyl-O-carbamate (**9d**).* According to the general procedure, **2b** (130 mg, 0.38 mmol) in THF (6 mL) was treated with *s*-BuLi (0.44 mL, 0.44 mmol), TMEDA (0.07 mL, 0.46 mmol) and Cl_3CCCl_3 (1.0 M, 0.57 mL, 0.57 mmol) at −78 °C, and warmed to rt over 16 h. Normal workup, followed by flash column chromatography (EtOAc:PE 1:2) afforded a mixture of **8d** and **9d** as an off-white solid (138 mg, 96%, 59:41), mp 184.5−185.5 °C (EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77−8.62 (m, 2H – **8d**, 3H – **9d**), 8.58 (d, *J* = 9.3 Hz, 1H – **9d**), 8.49 (d, *J* = 9.3 Hz, 1H – **8d**), 8.40 (d, *J* = 9.6 Hz, 1H – **9d**), 7.96−7.94 (m, 2H – **8d**, 2H – **9d**), 7.86 (d, *J* = 9.0 Hz, 1H – **8d**), 7.81 (s, 1H – **8d**), 7.72−7.59 (m, 2H – **8d**, 2H – **9d**), 7.55 (d, *J* = 9.1 Hz, 1H – **9d**), 3.60−3.53 (m, 2H – **8d**, 2H – **9d**), 3.45 (q, *J* = 6.9 Hz, 2H – **8d**, 2H – **9d**), 1.38−1.34 (m, 3H – **8d**, 3H – **9d**), 1.28−1.26 (m, 3H – **8d**, 3H – **9d**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4 (2C), 145.9, 145.6, 132.1, 132.07, 131.4, 130.3, 130.27, 130.2, 129.2, 128.8, 128.5, 128.49, 128.2, 127.9, 127.89, 127.8, 127.6, 127.1, 126.9, 126.8, 126.6, 126.55, 126.3, 124.7, 123.1, 123.0, 122.9, 122.8, 122.6, 122.5, 122.1, 122.0, 121.0, 120.8, 120.2, 42.5 (2C), 42.1 (2C), 14.2 (2C), 13.3 (2C); FTIR (KBr, cm^{-1}) 2978, 2934, 1731, 1472, 1419, 1381, 1274, 751; HRMS (ESI) m/z $[M + Na]^+$ for formula $C_{23}H_{20}ClNNaO_2$: calcd, 400.1080; found 400.1090.

*3-Methylchrysen-2-yl N,N-diethyl-O-carbamate (**8e**) and 1-Methylchrysen-2-yl N,N-diethyl-O-carbamate (**9e**).* According to the general procedure, **2b** (104 mg, 0.30 mmol) in THF (2.2 mL) was treated with *s*-BuLi (0.54 mL, 0.61 mmol), TMEDA (0.09 mL, 0.61 mmol) and MeI (0.06 mL, 0.91 mmol) at −95 °C, and warmed to rt over 4 h. Normal workup, followed by flash column chromatography (EtOAc:PE 1:8), the title compounds were isolated as a mixture **8e** and **9e** (85 mg, 79%, 54:46) as an off-white solid, mp 193.0−194.5 °C (EtOAc); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.77−8.71 (m, 1H – **8e**, 2H – **9e**), 8.68−8.63 (m, 2H – **8e**, 2H – **9e**), 8.59 (s, 1H−**8e**), 7.99−7.96 (m, 2H – **8e**, 2H – **9e**), 7.92 (d, *J* = 9.1 Hz, 1H – **8e**), 7.73

(s, 1H – **8e**), 7.72−7.68 (m, 1H – **8e**, 1H – **9e**), 7.66−7.61 (m, 1H – **8e**, 1H – **9e**), 3.59−3.56 (m, 2H – **8e**, 2H – **9e**), 3.49−3.47 (m, 2H – **8e**, 2H – **9e**), 2.54 (s, 3H – **8e**), 2.65 (s, 3H – **9e**), 1.38−1.35 (m, 3H – **8e**, 3H – **9e**), 1.30−1.27 (m, 3H – **8e**, 3H – **9e**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 154.0, 149.1, 147.6, 132.1, 131.9, 131.87, 131.5, 130.5, 130.4, 130.3, 128.5, 128.4, 128.3, 128.27, 127.8, 127.6, 127.4, 127.3, 127.1, 126.7, 126.6, 126.5, 126.2, 126.1, 125.5, 125.1, 123.1, 123.0, 122.9,122.0, 121.9, 121.5, 121.4, 121.2, 120.9, 119.9, 42.3 (2C), 41.9 (2C), 17.4, 14.4, 14.3, 13.4 (2C), 12.0; FTIR (KBr, cm^{-1}) 2976, 1720, 1420, 1273, 1246; HRMS (ESI) *m/z* $[M + H]^+$ for formula $C_{24}H_{24}O_2N$: calcd, 358.1807; found, 358.1805.

*3-(N,N-Diethylcarbamoyl)chrysen-2-yl N,N-diethyl-O-carbamate (**8f**) and 1-(N,N-Diethylcarbamoyl)chrysen-2-yl N,N-diethyl-O-carbamate (**9f**).* According to the general procedure, **2b** (107 mg, 0.31 mmol) in THF (2.2 mL) was treated with *s*-BuLi (0.55 mL, 0.62 mmol), TMEDA (0.09 mL, 0.62 mmol) and Et_2NCOCl (0.12 mL, 0.93 mmol) at −95 °C, and warmed to rt over 4 h. By normal workup, followed by flash column chromatography (EtOAc:PE 1:2), a mixture of compounds **8f** and **9f** were isolated as a beige solid (96 mg, 70%, 75:25), mp 181.5−182.5 °C (EtOAc); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.78−8.73 (m, 2H – **9f**), 8.71 (d, *J* = 8.2 Hz, 1H – **8f**), 8.70 (d, *J* = 9.1 Hz, 1H – **8f**), 8.67 (s, 1H – **8f**, 8.63 (d, *J* = 9.2 Hz, 1H – **9f**), 8.59 (d, *J* = 9.1 Hz, 1H – **8f**), 7.99−7.91 (m, 3H – **8f**, 2H – **9f**), 7.89 (s, 1H−**8f**), 7.69−7.59 (m, 2H – **8f**, 2H – **9f**), 3.83−3.07 (m, 8H – **8f**, 8H – **9f**), 1.39 (t, *J* = 7.1 Hz, 3H – **9f**), 1.33-1.25 (m, 6H – **8f**, 3H – **9f**), 1.22 (t, *J* = 7.1 Hz, 3H – **8f**, 3H – **9f**), 1.11 (t, *J* = 7.1 Hz, 3H- **8f**), 0.94 (t, *J* = 7.1 Hz, 3H – **9f**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 166.6, 153.5, 153.4, 145.7, 145.3, 132.8, 131.9, 130.3, 130.2, 130.1, 129.2, 128.4, 128.0, 127.9, 127.8, 127.75, 127.7, 127.5, 126.7, 126.6, 126.4, 126.37, 124.4, 123.4, 122.9, 122.86, 122.6, 122.4, 122.3, 121.8, 120.94, 120.91, 120.7, 42.9, 42.87, 42.2, 42.0, 38.9, 38.7, 14.1, 13.9, 13.8, 13.3, 12.9, 12.7; FTIR (KBr, cm^{-1}) 2971, 2932, 1714, 1637, 1474, 1420, 1271, 1246; HRMS (ESI) *m/z* $[M+Na]^+$ for formula $C_{28}H_{30}O_3N_2Na$: calcd, 465.2154; found, 465.2141.

*3-(Hydroxy)chrysene-2-carbaldehyde (**8g**) and 1-(Hydroxy)chrysene-2-carbaldehyde (**9g**).* According to the general procedure, **2b** (103 mg, 0.30 mmol) in THF (2.2 mL) was treated with *s*-BuLi (0.53 mL, 0.60 mmol), TMEDA (0.09 mL, 0.60 mmol) and DMF (0.07 mL, 0.90 mmol) at −95 °C, and warmed to rt over 3.5 hours. Normal workup, followed by flash column chromatography (EtOAc:PE 1:8) afforded a mixture of compound **8g** and **9g** as a yellow solid (53 mg, 64%, 68:32), mp 221.1−222.1 °C (Acetone); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 13.02 (s, 1H – **9g**), 10.99 (s, 1H – **9g**), 10.62 (s, 1H – **8g**), 10.22 (s, 1H – **8g**), 8.97 (s, 1H – **8g**), 8.96 (d, *J* = 9.6 Hz, 1H – **9g**), 8.88 (d, *J* = 9.6 Hz, 1H – **9g**), 8.78 (d, *J* = 9.3 Hz, 1H – **8g**), 8.75 (d, *J* = 8.4 Hz, 1H – **9g**), 8.72 (d, *J* = 8.4 Hz, 1H – **8g**), 8.62 (d, *J* = 9.0 Hz, 1H – **8g**), 8.57 (d, *J* = 9.0 Hz, 2H – **9g**), 8.06 (d, *J* = 8.9 Hz, 1H – **8g**), 8.04−7.99 (m, 2H – **9g**), 8.00 (app d, *J* = 9.4 Hz, 1H – **8g**), 7.86 (d, *J* = 9.1 Hz, 1H – **8g**), 7.76−7.72 (m, 1H – **9g**), 7.75−7.71 (m, 1H – **8g**), 7.68−7.64 (m, 1H – **9g**), 7.67−7.63 (m, 1H – **8g**), 7.44 (s, 1H – **8g**), 7.34 (d, *J* = 9.3 Hz, H – **9g**); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 196.8, 193.9, 157.2, 138.0, 133.8, 132.2, 131.9, 130.4, 128.8, 128.7 (2C), 128.6,128.5, 127.2, 126.9, 126.5, 126.0, 125.9, 124.7, 124.2, 122.8, 121.5, 120.5, 120.3, 118.8, 117.8, 113.5; FTIR (KBr, cm^{-1}) 2924, 1723, 1660,

1630, 1530, 1509, 1452, 1434, 1293, 1174, 818; HRMS (ESI) *m/z* $[M - H]^-$ for formula $C_{19}H_{11}O_2$: calcd, 271.0759; found, 271.0764.

*1,3-bis(Trimethylsilyl)chrysen-2-yl diethylcarbamate (**10**).* According to the general procedure, **2b** (71 mg, 0.21 mmol) in THF (2.0 mL) was treated with *s*-BuLi (0.46 mL, 0.53 mmol), TMEDA (0.03 mL, 0.41 mmol) and TMSCl (0.05 mL, 0.41 mmol) at −78 °C for 12 h. Normal workup, followed by flash column chromatography (EtOAc:PE 1:4) afforded product **10** (99 mg, 98%) as a colorless solid, mp. 166.4−167.1 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.80−8.74 (m, 3H), 8.42 (d, *J* = 9.5 Hz, 1H), 8.03−8.00 (m, 2H), 7.74−7.70 (m, 1H), 7.67−7.63 (m, 1H), 3.79−3.62 (m, 2H), 3.49−3.43 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.60 (s, 9H), 0.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 154.9, 138.0, 133.2, 132.0, 131.9, 130.4, 129.1, 128.9, 128.4, 127.9, 127.4, 127.3, 127.1, 126.6, 126.2, 123.0, 121.2, 121.18, 40.9, 40.7, 13.5, 12.8, 2.4, -0.4; FTIR (KBr, cm^{-1}) 2976, 2955, 2898, 1707, 1472, 1422, 1379, 1343, 1279, 1236; HRMS (ESI) m/z $[M + Na]^+$ for formula $C_{29}H_{37}NNaO_2Si_2$: calcd, 510.2261; found 510.2255.

*2-(Trimethysilyl)chrysene-3-yl N,N-diethyl-O-carbamate (**11a**).* According to the general procedure, **2c** (134 mg, 0.39 mmol) in THF (2.5 mL) was treated with *s*-BuLi (0.37 mL, 0.43 mmol), TMEDA (0.07 mL, 0.46 mmol) and TMSCl (0.07 mL, 0.55 mmol) at −78 °C for 1.5 h. Normal workup, followed by flash column chromatography (EtOAc:PE 1:4) afforded product **11a** (144 mg, 89%) as an off-white solid, mp. 106.0−107.0 °C (EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.2 Hz, 1H), 8.66 (t, *J* = 8.8 Hz, 2H), 8.41 (s, 1H), 8.12 (s, 1H), 8.02−7.97 (m, 3H), 7.73−7.64 (m, 2H), 3.62 (q, *J* = 7.1 Hz, 2H), 3.51 (q, *J* = 7.0 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.44 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 154.5, 136.3, 132.3, 132.29, 131.9, 130.4, 129.4, 128.5, 128.49, 127.7, 127.0, 126.9, 126.5, 126.4, 123.2, 121.6, 120.5, 115.5, 41.9, 41.6, 14.3, 13.3, -0.8; FTIR (KBr, cm^{-1}) 2961, 1699, 1467, 1420, 1310, 1271; HRMS (ESI) m/z $[M+Na]^+$ for formula $C_{26}H_{29}NNaO_2Si$: calcd, 438.1865; found 438.1858.

*2-Iodochrysen-3-yl N,N-diethyl-O-carbamate (**11b**).* According to the general procedure, **2c** (117 mg, 0.34 mmol) in THF (5 mL) was treated with *s*-BuLi (0.36 mL, 0.40mmol), TMEDA (0.06 mL, 0.40 mmol) and Iodine in THF (0.5 M, 1.0 mL, 0.5 mmol) at −78 °C, and warmed to rt over 18 h. Normal workup, followed by flash column chromatography (EtOAc:PE 1:2) afforded product **11b** (145 mg, 91%) as a beige solid, mp. 200.5−201.5 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.2 Hz, 1H), 8.60 (d, *J* = 9.1 Hz, 1H), 8.52 (d, *J* = 8.8 Hz, 1H), 8.51 (s, 1H), 8.41 (s, 1H), 7.97−7.93 (m, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.71−7.67 (m, 1H), 7.65−7.61 (m, 1H), 3.65 (q, *J* = 7.1 Hz, 2H), 3.50 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 149.4, 139.0, 132.3, 131.3, 131.2, 130.2, 128.5, 128.4, 127.6, 127.4, 126.7, 126.6, 125.5, 123.1, 121.6, 121.0, 116.7, 90.1, 42.4, 42.1, 14.4, 13.4; FTIR (KBr, cm^{-1}) 2973, 1723, 1469, 1417, 1380, 1318, 1275; HRMS (ESI) m/z $[M+Na]^+$ for formula $C_{23}H_{20}INNaO_2$: calcd, 492.0436; found 492.0428.

*2-Bromochrysen-3-yl N,N-diethyl-O-carbamate (**11c**).* According to the general procedure, **2c** (100 mg, 0.29 mmol) in THF (2.2 mL) was treated with *s*-BuLi (0.28 mL, 0.32 mmol), TMEDA (0.05 mL, 0.32 mmol) and Br_2 (0.02 mL, 0.44 mmol) at −78 °C for 16 h. Normal workup, followed by flash column chromatography (EtOAc:PE 1:4) afforded product **11c** (69.7 mg, 57%) as a beige solid, mp. 117.0−118.0 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.5 Hz, 1H), 8.63 (d, *J* = 9.3 Hz, 1H), 8.56 (s, 1H), 8.53 (d, *J* = 9.2 Hz, 1H), 8.19 (s, 1H), 7.97 (dd, *J* = 1.2 Hz, 7.8 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.83 (d, *J* = 9.1 Hz, 1H), 7.71−7.67 (m, 1H), 7.66−7.62 (m, 1H), 3.63 (q, *J* = 7.1 Hz, 2H), 3.49 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 146.9, 132.4, 132.3, 130.8, 130.4, 128.5, 128.3, 127.6, 127.5, 126.8, 126.6, 125.6, 123.1, 121.8, 121.1,117.1, 115.9, 42.4, 42.1, 14.3, 13.3; FTIR (KBr, cm^{-1}) 2972, 1722, 1470, 1417, 1380, 1318, 1274, 747; HRMS (ESI) m/z $[M + H]^+$ for formula $C_{23}H_{22}{}^{81}BrNNaO_2$: calcd, 446.0732; found 446.0548.

*2-Chlorochrysen-3-yl N,N-diethyl-O-carbamate (**11d**).* According to the general procedure, **2c** (102 mg, 0.30 mmol) in THF (2.2 mL) was treated with *s*-BuLi (0.30 mL, 0.33 mmol), TMEDA (0.05 mL, 0.33 mmol) and Cl_3CCCl_3 (106 mg, 0.45 mmol) in THF (1 mL) at −78 °C, and warmed to rt over 9 h. Normal workup, followed by flash column chromatography (EtOAc:hexane 1:9) afforded product **11d** as an orange solid (78 mg, 70%), mp. 184.5−185.5 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.4 Hz, 1H),8.58 (d, *J* = 9.1 Hz, 1H), 8.54 (s, 1H), 8.48 (d, *J* = 9.1 Hz, 1H), 7.98 (s, 1H), 7.96−7.91 (m, 2H), 7.78 (d, *J* = 9.1 Hz, 1H), 7.69−7.61 (m, 2H), 3.61 (q, *J* = 7.0 Hz, 2H), 3.50 (q, *J* = 6.9 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 146.0, 132.2, 130.4, 130.3, 129.8, 129.0, 128.5, 128.3, 127.53, 127.52, 126.8, 126.6, 126.5, 125.7, 123.1, 121.8, 121.1, 117.8, 42.5, 42.1, 14.2, 13.3; FTIR (KBr, cm^{-1}) 2975, 2936, 1724, 1471, 1419, 1381, 1318, 1276, 747; HRMS (ESI) m/z $[M + Na]^+$ for formula $C_{23}H_{20}ClNNaO_2$: calcd, 400.1080; found 400.1078.

*2-Methylchrysen-3-yl N,N-diethyl-O-carbamate (**11e**).* According to the general procedure, **2c** (100 mg, 0.29 mmol) in THF (2.2 mL) was treated with *s*-BuLi (0.52 mL, 0.58 mmol), TMEDA (0.09 mL, 0.58 mmol) and MeI (0.05 mL, 0.87 mmol) at −95 °C, and warmed to rt over 4 h. Normal workup, followed by flash column chromatography (EtOAc:PE 1:8), afforded compound **11e** as pale yellow solid (100 mg, 96%), mp. 166.2−167.0 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.3 Hz, 1H), 8.62 (d, *J* = 9.5 Hz, 2H), 8.47 (s, 1H), 8.00−7.96 (m, 2H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.80 (s, 1H), 7.72−7.68 (m, 1H), 7.65−7.61 (m, 1H), 3.59 (q, *J* = 6.8 Hz, 2H), 3.50 (q, *J* = 7.0 Hz, 2H), 2.48 (s, 3H), 1.39 (t, *J* = 7.7 Hz, 3H), 1.30 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 149.4, 132.0, 130.5, 130.3, 130.1, 130.0, 129.8, 128.4, 127.8, 127.0, 126.5, 126.4, 126.1, 123.0, 121.4, 120.6, 115.6, 42.3, 41.9, 16.7, 14.3, 13.4; FTIR (KBr, cm^{-1}) 2972, 1718, 1473, 1420, 1275, 1260; HRMS (ESI) *m/z* $[M+H]^+$ for formula $C_{24}H_{24}O_2N$: calcd, 358.1807; found, 358.1803.

*2-(N,N-Diethyl carbamoyl)chrysen-3-yl N,N-diethyl-O-carbamate (**11f**).* According to the general procedure, **2c** (102 mg, 0.30 mmol) in THF (2.2 mL) was treated with *s*-BuLi (0.53 mL, 0.59 mmol),

TMEDA (0.09 mL, 0.59 mmol) and Et_2NCOCl (0.11 mL, 0.89 mmol) at −95 °C, and warmed to rt over 4 h. Normal workup, followed by flash column chromatography (EtOAc:PE 1:2), afforded compound **11f** as colorless solid (116 mg, 88%), mp. 180.2−181.2 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.3 Hz, 1H), 8.65 (d, *J* = 9.1 Hz, 1H), 8.61 (s, 1H), 8.58 (d, *J* = 9.1 Hz, 1H), 7.97−7.92 (m, 2H), 7.89 (s, 1H), 7.70−7.65 (m, 1H), 7.64−7.60 (m, 1H), 3.92−3.13 (br m, 8H), 1.33−1.26 (m, 6H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 153.7, 146.1, 132.2, 131.3, 130.2, 130.1, 129.1, 128.5, 128.4, 127.5, 127.3, 126.6, 126.54, 126.51, 123.1, 121.3, 116.7, 42.9, 42.2, 42.0, 38.8, 14.1, 13.8, 13.3, 12.6; FTIR (KBr, cm^{-1}) 2978, 2933, 1719, 1630, 1472, 1420, 1382, 1347, 1317, 1295, 1272; HRMS (ESI) *m/z* $[M+Na]^+$ for formula $C_{28}H_{30}O_3N_2Na$: calcd, 465.2154; found, 465.2149

*2-(Hydroxy)chrysene-3-carbaldehyde (**11g**).* According to the general procedure, **2c** (1.08 g, 3.15 mmol) in THF (20 mL) was treated with *s*-BuLi (7.05 mL, 6.30 mmol), TMEDA (0.94 mL, 6.30 mmol) and DMF (0.73 mL, 9.44 mmol) at −95 °C, and warmed to rt over 3.5 h. Normal workup, followed by flash column chromatography (EtOAc:PE 1:8), afforded compound **11g** as yellow solid (1.23 g, 72%), mp. 230.5−231 5 °C (Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 10.13 (s, 1H), 8.74 (d, *J* = 8.1 Hz, 1H), 8.56 (t, *J* = 8.0 Hz, 2H), 8.20 (s, 2H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.95 (d, *J* = 9.1 Hz, 1H), 7.72−7.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 157.5, 136.8, 133.0, 130.8, 130.2, 128.7, 127.7, 127.4, 127.3, 127.0, 126.8, 125.8, 123.5, 121.6, 121.4, 119.9,109.2; FTIR (KBr, cm^{-1}) 3460, 1666, 1634, 1435, 1384, 1343; HRMS (ESI) *m/z* $[M - H]^-$ for formula $C_{19}H_{11}O_2$: calcd, 271.0759; found, 271.0764.

*N,N-Diethyl-5-hydroxychrysene-6-carboxamide (**12**).* According to the general procedure, **2e** (198 mg, 0.58 mmol) was treated with a precooled mixture of *s*-BuLi (0.1 mL, 0.67 mmol) and TMEDA (0.57 mL, 0.67 mmol) in THF (2.4 mL) at -98 °C. The mixture was warmed to rt overnight (17 h) and normal work-up procedures, followed by flash column chromatography (EtOAc:hexane 1:6) afforded *ortho*-Fries product **12** (156 mg, 79%) as beige solid, mp. 187.6−188.9 °C (Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 9.61 (d, *J* = 8.7 Hz, 1H), 8.31 (d, *J* = 9.2 Hz, 1H), 7.85−7.83 (m, 2H), 7.62 (dd, *J* = 0.6, 8.2 Hz, 1H), 7.53−7.49 (m, 1H), 7.45−7.38 (m, 2H), 7.28−7.24 (m, 1H), 3.46 (br s, 4H), 1.19 (br s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 151.7, 132.6, 130.9, 130.6, 129.1, 129.0, 128.8, 127.8, 127.0, 126.4, 125.9, 125.8, 124.0, 123.2, 123.1, 121.4, 120.5, 116.3, 41.8, 13.5; FTIR (KBr, cm^{-1}) 3469, 1598, 1582, 1491, 1429, 1379, 1314, 1343, 1240, 1200, 1125; HRMS (ESI) *m/z* $[M + H]^+$ for formula $C_{23}H_{22}NO_2$: calcd, 344.1651; found, 344.1652.

ASSOCIATED CONTENT

Supporting information

Supporting Information “This material is available free of charge via the Internet at http://pubs.acs.org.”

NMR spectra of the new compounds and HRMS of deuterium quench experiments (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: kare.b.jorgensen@uis.no

ORCID

Sindhu Kancherla: 0000-0001-7592-1179

Marianne Lorentzen:

Victor Snieckus: 0000-0002-6448-9832

Kåre B. Jørgensen: 0000-0003-0662-1839

Notes

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