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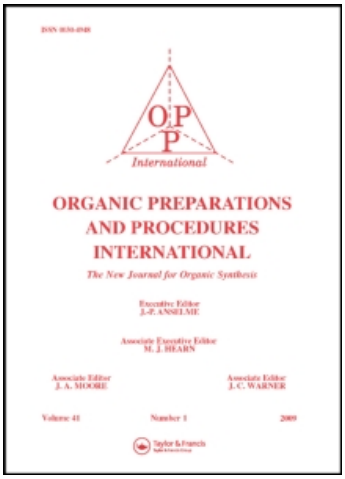

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SYNTHESIS OF SYMMETRICAL AND UNSYMMETRICAL DISUBSTITUTED α-PYRENYLMETHYL AND α-PERYLENYLMETHYL MALONATE AND CYANOACETATE ALLYL ESTERS

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SYNTHESIS OF SYMMETRICAL AND UNSYMMETRICAL DISUBSTITUTED α-PYRENYLMETHYL AND α-PERYLENYLMETHYL MALONATE AND CYANOACETATE ALLYL ESTERS

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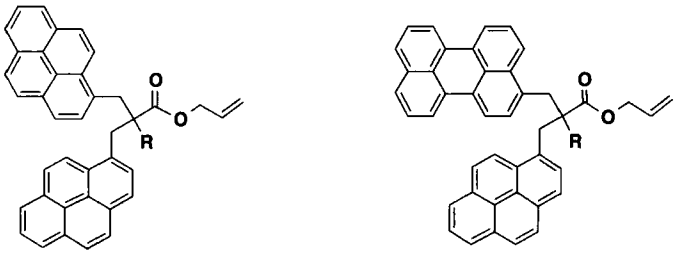
α-Alkylations of malonate and cyanoacetate derivatives have been well documented[1] due mainly to the many synthetic transformations of the resulting products. In most cases, the alkylating reagents are simple organic halides, tosylates or α,β-unsaturated compounds.[2-4] The analogous reactions with the chloromethyl derivatives of polycyclic aromatic compounds have received much less attention. In this paper, we describe the synthesis of the α-pyrenylmethyl and α-perylenylmethyl disubstituted (both symmetrical and unsymmetrical) malonate and cyanoacetate derivatives shown in Fig. 1.



1 a) R = $CO_2CH_2CH{=}CH_2$ b) R = CN **2**

Fig. 1

Many polycylic aromatic compounds and their derivatives have been examined and evaluated for their pharmaceutical and photochemical properties: recent examples are applications in mutation research,[5] structure-activity studies with DNA,[6] and in inter- and intramolecular charge transfer studies.[7,8]

A general procedure for the synthesis of the compounds of type **1a** and **1b** (i. e. with the same substituents at the α-position) involves the reaction of the appropriate chloromethyl derivatives of the aromatic compounds with anions of malonates or cyanoacetates.[1] 1-Chloromethylpyrene was

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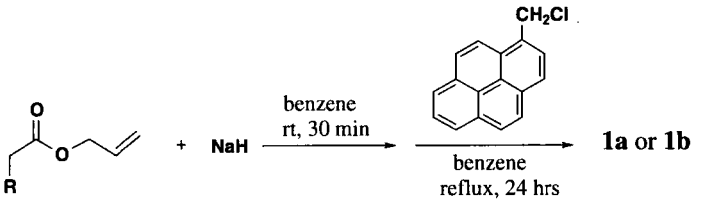
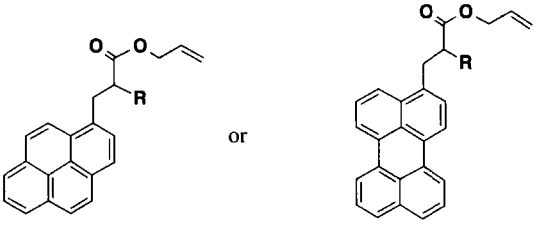
prepared by a two-step procedure:[5] reduction of 1-pyrene-carboxaldehyde with sodium borohydride, followed by chlorination with thionyl chloride afforded 1-chloromethylpyrene in an overall yield of 82%. Direct chloromethylation of pyrene with formaldehyde and concentrated hydrochloric acid in a mixture of glacial acetic acid and polyphosphoric acid[9] failed to give the expected product under several sets of conditions.

The reaction of 1-chloromethylpyrene with diallyl malonate or allyl cyanoacetate was carried out in refluxing benzene in the presence of sodium hydride (Scheme 1). Diallyl 2,2-*bis*(pyrenylmethyl)malonate (**1a**) and allyl 2-cyano-2,2-*bis*(pyrenylmethyl)acetate (**1b**) were thus prepared in 42% and 38% yields, respectively. Their structures were confirmed by their NMR spectra and elemental analyses (see Experimental Section).



Scheme 1

The synthesis of unsymmetrical compounds **2a** and **2b** required the preparation of the mono-substituted derivative **3** or **4** as the intermediate (Fig. 2).



3 **4**

a) R = $CO_2CH_2CH{=}CH_2$ b) R = CN

Fig. 2

Since pyrenecarboxaldehyde is commercially available and relatively inexpensive, we first attempted to synthesize diallyl 2-pyrenylmethylmalonate (**3a**). However, when 1-chloromethylpyrene was reacted with an excess of diallyl malonate under the conditions described above, the disubstituted compound **1a** was always produced as the major product. An alternative approach to the monosubstituted product **3a** was the Knoevenagel condensation of pyrenecarboxaldehyde with diallyl malonate followed by reduction of the resulting alkene derivative.

The reaction of pyrenecarboxaldehyde with diallyl malonate was carried out in refluxing benzene with piperidinium acetate as the catalyst to give the alkene derivative **5** in 91% yield. Reduction of α,β-unsaturated malonate derivatives has previously been achieved in a number of ways.[6]

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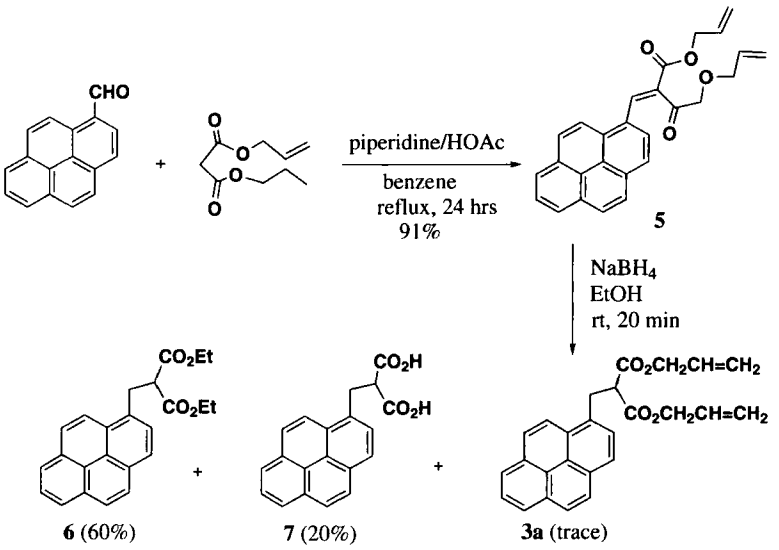

Scheme 2

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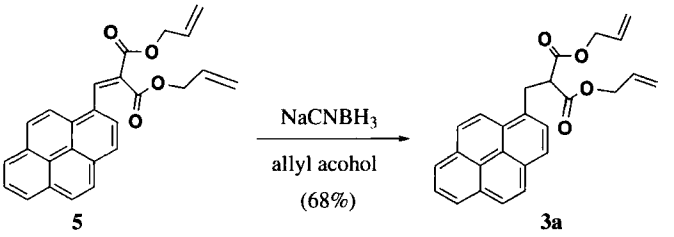
However, in this case, nucleophilic reducing agents must be employed to avoid the possible reduction of the two allyl double bonds in compound **5.** When **5** was treated with $NaBH_4$ in ethanol for only 20 min, diethyl pyrenylmethylmalonate **(6)** (60%) was produced along with pyrenylmethylmalonic acid **(7)** (ca. 20%) and only a trace of **3a** (Scheme 2). Clearly under these conditions, transesterification (with ethanol) and hydrolysis (upon aqueous work-up) of the reduced product was facile. To circumvent this, the reaction was repeated in allyl alcohol to give **3a** in 50% isolated yield along with some of the diacid **7**. The yield was improved to 68% by the use of $NaCNBH_3$, a much milder reducing agent (Scheme 3).



Scheme 3

3-Perylenecarboxaldehyde was prepared by the formylation of perylene with *N*-methylformanilide and $POCl_3$ in *o*-dichlorobenzene.[10] 3-Chloromethylperylene was prepared in a way analogous to that used for 1-chloromethylpyrene. It was insoluble in nearly all common solvents, and only slightly soluble in DMSO at room temperature. We first attempted the reaction of **3a** with 3-chloromethylperylene by using the general procedure for preparing **1a** and **1b.** Thus, a solution of **3a** in dry benzene was added to a suspension of NaH in the same solvent, and the mixture was stirred at

80° for 1 hr. 3-Chloromethylperylene was then added and the mixture refluxed overnight. After routine work-up, a nearly quantitative recovery of **3a** was obtained with no 3-chloromethylperylene observed. We then carried out the reaction in refluxing benzene but put 3-chloromethylperylene in a Soxhlet extractor in order to minimize its decomposition under alkaline conditions. However, after work-up, only a very small amount of a soluble yellow solid was obtained along with a large amount of insoluble materials. Although the NMR spectra of the soluble solid was consistent with the expected product **2a**, the extremely low yield (< 5%) made this approach synthetically unacceptable. The failure of this reaction was due mainly to the extremely poor solubility of 3-chloromethylperylene. The alternative approach to diallyl 2-perylenylmethyl-2-pyrenylmethylmalonate **(2a)** was the reaction of diallyl 2-perylenylmethylmalonate **(4a)** with 1-chloromethylpyrene, which has significantly better solubility in benzene and in other organic solvents.

The Knoevenagel condensation of 3-perylenecarboxaldehyde with diallyl malonate produced the corresponding alkene **9a** in 92% yield. Reduction of **9a** with $NaCNBH_3$ in allyl alcohol afforded diallyl 2-perylenylmethylmalonate **(4a)** in 62% yield. This was treated with NaH in dry toluene followed by reflux with 1-chloromethylpyrene to give diallyl 2-perylenylmethyl-2-pyrenylmethylmalonate **(2a)** in 28% yield. By using the same methodology, allyl 2-cyano-2-perylenylmethyl-2-pyrenylmethylacetate **(2b)** was synthesized in a yield of 31% (Scheme 4). Compounds **2a** and **2b** as well as the related intermediates were characterized by their NMR spectra and elemental analyses.

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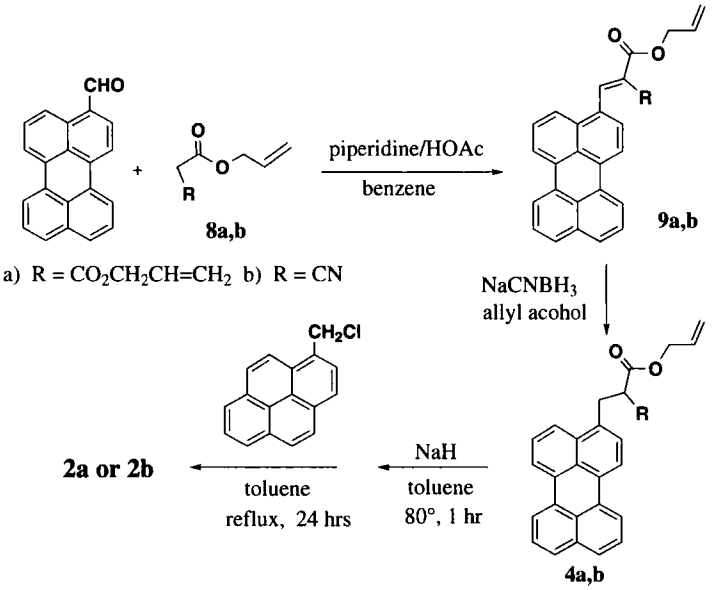

Scheme 4

The compounds here described are conveniently available for further synthetic purposes including the fabrication of advanced materials devices.

EXPERIMENTAL SECTION

Since the procedures involve the use of benzene and polycyclic aromatics, suitable safety precautions should be utilized, including the use of rubber gloves and adequate ventilation. Melting points were determined on a Bristoline hot-stage microscope and are uncorrected. ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer with TMS as internal reference. ^{13}C NMR spectra were recorded at 75 MHz on the same instrument using solvent peaks ($CDCl_3$, δ = 77.0 or DMSO-d_6, δ = 39.5 ppm) as references. Microanalyses were carried out using a Carlo Erba 1106 elemental analyser.

1-Hydroxymethylpyrene.- To a suspension of 1-pyrenecarboxaldehyde (9.6 g, 42 mmol) in ethanol (50 mL) was added $NaBH_4$ (2 g) and the mixture was stirred at room temperature for 6 hrs. Water (100 mL) was added and the mixture was extracted with ether (2 x 50 mL). The organic layer was dried over $MgSO_4$, and the solvent evaporated under reduced pressure to give a light-yellow solid which was recrystallized from ethyl acetate to afford prisms (8.3 g, 86%), mp. 125-126°, lit.[5] mp. 124-125°.

1-Chloromethylpyrene.- Thionyl chloride (15 mL, 200 mmol) was added dropwise to a suspension of 1-hydroxymethylpyrene (9.3 g, 40 mmol) in dry benzene (150 mL) at 0° and the mixture was stirred at room temperature overnight. Evaporation of the solvent under reduced pressure gave a creamy-white solid (9.6 g, 96%), mp. 146-148°, lit.[5] mp. 147-148°.

Diallyl 2,2-*bis*(Pyren-1-ylmethyl)malonate (1a).- Diallyl malonate (0.36 g, 2.0 mmol) was added to a stirred suspension of NaH (2.5 mmol) in dry benzene (5 mL). After 30 min, 1-chloromethylpyrene (0.5 g, 2.0 mmol) in benzene (20 mL) was added. The mixture was gently refluxed for 18 hrs, cooled to room temperature and washed with saturated aqueous NaCl (2 x 5 mL). The organic layer was dried over $MgSO_4$ and the solvent evaporated under reduced pressure to give the product, which was recrystallized from AcOEt/hexane to afford **1a** as white crystals (0.26 g, 42%), mp. 178-180°. ^{1}H NMR ($CDCl_3$): δ 8.23 (d, J = 9.3 Hz, 2H), 8.14-7.89 (m, 16H), 5.41-5.28 (m, 2H), 4.87-4.78 (m, 4H), 4.21 (s, 4H), 4.16 (dd, J = 5.8 and 1.2 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 170.8, 131.3, 130.8, 130.7, 130.6, 130.3, 130.1, 128.3, 127.4, 127.2, 127.0, 125.7, 125.0, 124.9, 124.7, 124.6, 123.2, 118.3, 66.1, 60.9, 36.6.

Anal. Calcd for $C_{43}H_{32}O_4$: C, 84.29; H, 5.26. Found: C, 84.13; H, 5.23

Allyl 2-Cyano-2,2-*bis*(pyrenylmethyl)acetate (1b).- The compound was prepared by the same method as **1a** (38%), mp. 181-183°. ^{1}H NMR ($CDCl_3$): δ 8.30 (d, J = 9.4 Hz, 2H), 8.17-7.93 (m, 16H), 5.26-5.13 (m, 1H), 4.73-4.61 (m, 2H), 4.27-4.00 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 168.5, 131.3, 131.1, 130.6, 129.9, 128.7, 127.8, 127.7, 127.6, 127.3, 126.0, 125.4, 125.1, 125.0, 124.8, 124.7, 123.2, 119.1, 118.7, 67.3, 53.2, 39.2.

Anal. Calcd for $C_{40}H_{27}NO_2$: C, 86.78; H, 4.92; N, 2.53. Found: C, 86.51; H, 4.95; N, 2.46

Diallyl 2-(Pyren-1-ylmethylene)malonate (5).- A mixture of 1-pyrenecarboxaldehyde (4.6 g, 20 mmol), diallyl malonate (4.1 g, 22 mmol) and catalytic amounts of piperidine and glacial HOAc was refluxed in benzene (150 mL) overnight. The water formed was collected in a Dean-Stark trap. Evaporation of the solvent under reduced pressure gave a yellow solid which was recrystallized from ethanol to afford the pure product as yellow plates (7.0 g, 89%), mp. 101-103°. ^{1}H NMR ($CDCl_3$): δ

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8.77 (s, 1H), 8.19-7.93 (m, 9H), 6.11-5.98 (m, 1H), 5.79-5.66 (m, 1H), 5.49-5.30 (m, 2H), 5.19-5.04 (m, 2H), 4.90-4.84 (m, 2H), 4.70-4.63 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 166.1, 163.7, 142.0, 132.7, 131.7, 131.1, 131.0, 130.5, 129.7, 128.7, 128.6, 127.8, 127.1, 127.0, 126.2, 126.1, 126.0, 125.9, 125.7, 124.5, 124.4, 124.2, 122.8, 119.0, 118.5, 66.1.

Anal. Calcd for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09. Found: C, 78.53; H, 5.02

Diallyl 2-(Perylen-3-ylmethylene)malonate (9a).- This material was prepared by the same method as **5**. The product precipitated from the solution upon cooling to afford **9a** which did not require further purification (92%), mp. 171-173°. ^1H NMR ($CDCl_3$): δ 8.35 (s, 1H), 8.12 (m, 4H), 7.73-7.58 (m, 3H), 7.50-7.35 (m, 4H), 6.10-5.97 (m, 1H), 5.84-5.70 (m, 1H), 5.49-5.11 (m, 4H), 4.83 (d, J = 5.4 Hz, 2H), 4.66 (d, J = 5.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 165.9, 163.6, 141.5, 134.3, 133.5, 132.6, 131.6, 131.5, 131.2, 130.6, 130.2, 129.5, 128.6, 128.4, 128.1, 127.5, 127.3, 127.2, 126.5, 126.4, 123.4, 121.0, 120.7, 120.5, 119.3, 119.0, 118.5, 66.1.

Anal. Calcd for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97. Found: C, 80.86; H, 4.89

Allyl 2-Cyano-2-(perylen-3-ylmethylene)acetate (9b).- This compound was similarly prepared. The product directly precipitated from the solution to give analytically pure **9b** (95%), mp. 185-187°. No suitable solvent was found for running the NMR spectra.

Anal. Calcd for $C_{27}H_{17}NO_2$: C, 83.70; H, 4.42; N, 3.62. Found: C, 83.54; H, 4.40; N, 3.57

Diallyl 2-(Pyren-1-ylmethyl)malonate (3a).- A mixture of diallyl 2-(pyrenylmethylene)malonate (**5**) (1 g, 2.5 mmol) and $NaCNBH_3$ (0.2 g, 3.1 mmol) in allyl alcohol (25 mL) was stirred at room temperature overnight. Aqueous HCl (2N) was then added until the pH of the solution reached 6-7. Chloroform (60 mL) was added and the solution was washed with saturated aqueous NaCl (2 x 10 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give a yellow oil which was purified by column chromatography (hexane : $CHCl_3$ = 2 : 1) to afford the pure product as a light-yellow oil (68%). ^1H NMR ($CDCl_3$): δ 8.28-7.76 (m, 9H), 5.68-5.53 (m, 2H), 5.07-4.91 (m, 4H), 4.50-4.34 (m, 4H), 3.90-3.78 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 168.4, 131.4, 131.3, 131.2, 130.6, 130.5, 128.7, 127.8, 127.7, 127.3, 127.0, 125.8, 125.1, 125.0, 124.8, 124.7, 122.6, 118.5, 66.0, 53.6, 32.2.

Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 78.21; H, 5.08

Diallyl 2-(Perylen-3-ylmethyl)malonate (4a).- This compound was prepared by the same method except that the reaction mixture was stirred at 60-70° overnight. The product was purified by column chromatography (hexane : $CHCl_3$ = 1 : 2) (64%), mp. 125-127°. ^1H NMR ($CDCl_3$): δ 8.17-7.98 (m, 4H), 7.82-7.60 (m, 3H), 7.52-7.30 (m, 4H), 5.90-5.76 (m, 2H), 5.30-5.18 (m, 4H), 4.70-4.56 (m, 4H), 3.91 (t, J = 7.6 Hz, 1H), 3.63 (d, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 168.5, 134.5, 133.1, 132.6, 131.9, 131.4, 131.1, 131.0, 130.5, 128.3, 128.0, 127.8, 127.6, 126.7, 122.8, 120.3, 120.1, 120.0, 119.7, 118.6, 66.1, 52.4, 32. 1.

Anal. Calcd for $C_{30}H_{24}O_4$: C, 80.34; H, 5.39. Found: C, 80.17; H, 5.38

Allyl 2-Cyano-2-(perylen-1-ylmethyl)malonate (4b).- This compound was similarly prepared and purified (53%), mp. 177-179°. ^1H NMR ($CDCl_3$): δ 8.16-7-92 (m, 4H), 7.60-7.58 (m, 3H), 7.49-7.30 (m, 4H), 5.93-5.80 (m, 1H), 5.40-5.24 (m, 2H), 4.75-4.65 (m, 2H), 3.90-3.81 (m, 1H), 3.74-

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3.63 (m, 1H), 3.43-3.30 (m. 1H). ^{13}C NMR ($CDCl_3$): δ 165.4, 134.3, 132.1, 132.0, 131.4, 130.7, 130.6, 130.3, 128.9, 127.9, 127.0, 126.4, 121.8, 120.4, 120.3, 120.2, 120.1, 119.72, 119.69, 119.6, 116.0, 67.3, 38.3, 33.3.

Anal. Calcd for $C_{27}H_{19}NO_2$: C, 83.27; H, 4.92; N, 3.60. Found: C, 83.21; H, 4.92; N, 3.49

Diallyl 2-(Peryien-3-ylmethy-2-pyren-1-ylmethyl)malonate (2a). - Diallyl (perylen-3-yl)methyl malonate (0.4 g, 0.9 mmol) was added to a suspension of NaH (50%, 1 equiv) in dry toluene (5 mL), and the mixture was stirred at 80° for 1-2 hrs. 1-Chloromethylpyrene (0.22 g, 0.9 mmol) in toluene (20 mL) was added in one portion and the mixture was gently refluxed for 24 hrs. Chloroform (50 mL) was added and the solution was washed with saturated aqueous NaCl (2 x 10 mL). The organic layer was dried ($MgSO_4$) and evaporated under reduced pressure to afford a yellow solid. Purification by column chromatography ($CHCl_3$: hexane = 2 : 1) gave the pure product as yellow microcrystals (0.17 g, 28%), mp. 95-98°. ^1H NMR ($CDCl_3$): δ 8.29-7.78 (m, 14H), 7.67-7.58 (m, 2H), 7.49-7.31 (m, 4H), 5.53-5.37 (m, 2H), 5.03-4.88 (m, 4H), 4.34-4.13 (m, 6H), 3.82 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 170.8, 134.5, 134.0, 132.6, 131.6, 131.3, 131.2, 131.1, 130.9, 130.6, 130.5, 130.4, 130.2, 130.1, 128.9, 128.4, 128.3, 127.7, 127.5, 127.4, 127.2, 127.1, 126.5, 126.2, 125.8, 125.0, 124.9, 124.8, 124.6, 123.5, 123.3, 120.2, 120.1, 120.0, 119.7, 118.4, 66.1, 60.2, 36.5, 36.1.

Anal. Calcd for $C_{47}H_{34}O_4$: C, 85.17; H, 5.17. Found: C, 85.30; H, 5.07

Allyl 2-Cyano-2-(perylen-3-yl)methyl-2-(pyren-1-ylmethyl)acetate (2b).- This compound was prepared and purified by the same method as for **2a** (31%), mp. 130-132°. ^1H NMR ($CDCl_3$): δ 8.24 (d, J = 9.3 Hz, 1H), 8.16-7.91 (m, 12H), 7.79 (d, J = 8.3 Hz, 1H), 7.62-7.55 (m, 2H), 7.48-7.31 (m, 4H), 5.33-5.20 (m, 1H), 4.87-4.72 (m, 2H), 4.26-4.21 (m, 2H), 4.08 (d, J = 7.1 Hz, 1H), 3.93 (d, J = 7.0 Hz, 1H), 3.80 (d, J = 7.2 Hz, 1H), 3.58 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 168.4, 134.4, 133.4, 131.6, 131.2, 131.1, 131.0, 130.9, 130.7, 130.5, 129.9, 129.85, 129.80, 129.1, 129.0, 128.6, 127.8, 127.77, 127.70, 127.6, 126.4, 125.9, 125.3, 125.1, 124.9, 124.7, 123.4, 123.1, 120.3, 120.27, 120.20, 119.6, 119.2, 118.8, 67.3, 52.5, 39.1, 38.9.

Anal. Calcd for $C_{44}H_{29}NO_2$: C, 87.54; H, 4.84; N, 2.32. Found: C, 87.61; H, 4.85; N, 2.05

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