Syntheses and Properties of Donor−Acceptor-Substituted Molecules with a Bicyclo[2.2.1]heptane, a Bicyclo[2.2.2]octane, and a Tricyclo[3.3.0.0^{3,7}]octane Spacer

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Starting from bicyclo[2.2.1]heptane-2,5-dione, bicyclo[2.2.2]octane-2,5-dione and tricyclo[3.3.0.0^{3,7}]octane-2,6-dione we were able to synthesize donor–acceptor-substituted derivatives by condensation reactions. The components for the condensations were propanedinitrile (**21**) for the acceptor part, and diethyl [(naphthalen-1-yl)methyl]phosphonate (**12**), diethyl [(anthracen-9-yl)methyl]phosphonate (**13**), and diethyl [(pyren-1-yl)methyl]phosphonate (**14**). To condense propanedinitrile we used the Knoevenagel condensation and for the phosphonates we used the Wittig–Horner–Emmons procedure. By means of NOESY NMR experiments the (*E*) configuration at the *exo* double bond of the donor–acceptor-substituted bicycles could be established. X-ray investigations on **22**, **24**, **27**, and **39** confirmed the (*E*) configuration at the *exo* double bond and yielded the molecular parameters. Fluorescence spectra provided evidence for efficient photoinduced electron transfer in only the naphthalene and pyrene derivatives **22** and **26**, but not in the analogous anthracene derivative **24** in accordance with estimates for ΔG_{et}.

Introduction

The past twenty years have seen a large amount of work on long-range electron-transfer processes. Experiments by several groups have established that the rate of transfer attenuates exponentially as a function of donor−acceptor distance.[1−3] Variation of the conformation of the saturated hydrocarbon spacer shows that the *trans* configuration[4,5] is more effective than other arrangements. These results agree well with the assumption that the strength of the through-bond coupling[6] is important for long-range electron-transfer processes.

Studies with photoelectron spectroscopy and electron transmission spectroscopy have shown that the strength of through-bond coupling can be modulated.[7,8] This coupling not only depends on the parameters cited above, but also on the p-character of the σ-bonds.[8] This encouraged us to synthesize a series of compounds in which the distance between the π-systems remains essentially constant with closely related configurations but different strain energies.

As a guide to select the appropriate σ-scaffold we used data from PE spectroscopy and force-field calculations. The systems we finally focused on were 2,5-dimethylidenebicyclo[2.2.2]octane (**1**), 2,5-dimethylidenebicyclo[2.2.1]heptane (**2**), and 2,5-dimethylidenetricyclo[3.3.0.0^{3,7}]octane (**3**, 2,5-stelladiene). In Figure 1 we have listed the calculated strain energies *SE* of **1**−**3** and the difference in the first two ionization energies (ΔI_π) determined by photoelectron-spectroscopic investigations.[9,10]

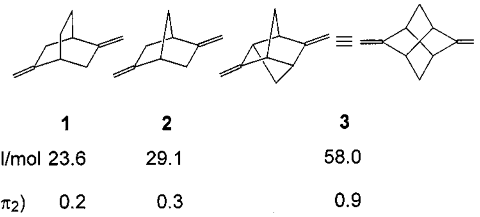

Figure 1. Comparison between the calculated strain energies (*SE*) and recorded differences of the first two ionization energies [$I(\pi_1-\pi_2)$] of **1**−**3**

It is seen that the energy difference ΔI_π increases with an increase in strain energy. The enlargement of the splitting is a measure of the increase of through-bond interaction. To probe if a similar increase is also found in the rates of electron transfer or charge recombination, we have synthesized a number of model compounds with **1**−**3** as scaffold.

Syntheses

The key compounds for attaching donor and acceptor substituents were the mono- and diketones of norbornane,[11] bicyclo[2.2.2]octane,[12] and stellane.[13] In the first series, we tested a number of donors and donor−acceptor combinations with stellane as scaffold. As the donor systems we used fluorene and xanthene, and as acceptor groups ester and cyano substituents.[14] The reaction products of stellanone and stellanedione with fluorene and xanthene (**4**−**7**) showed no or only a very weak fluorescence.

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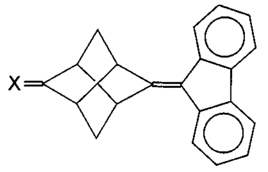
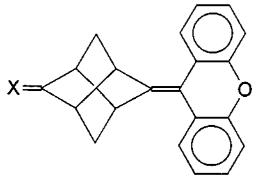
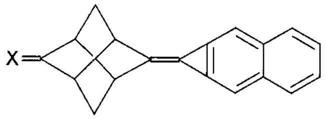
This observation was supported by investigations of the condensation products between cyclohexanone and fluorene and xanthene, respectively.[15]



X = H$_2$, O
4, **5**



X = H$_2$, O
6, **7**



X = H$_2$, O
8, **9**

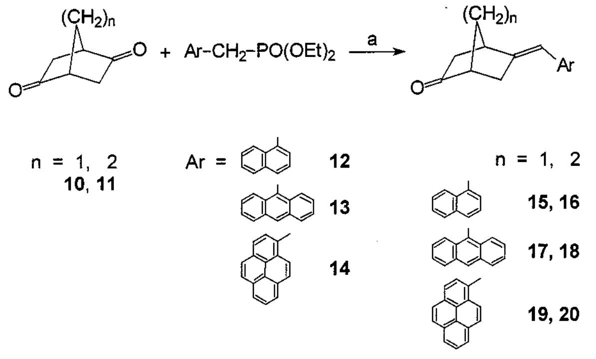
As a next generation of donor substituents we introduced the cyclopropa[*b*]naphthalene moiety[14] which was expected to have good fluorescence properties. A series of investigations on **8**, **9**, and related systems showed good fluorescence properties on the one hand but photolability on the other.[15]

We finally used extended π-systems such as vinylnaphthalene, vinylanthracene, and vinylpyrene as donors. The advantages of these groups include efficient fluorescence, low oxidation potential and photochemical stability. One disadvantage might be that diastereomers result when they are connected with the scaffolds **1** and **2**. As acceptor we used the dicyanomethylidene group which has been used in several systems[3–5] and provides a large negative driving force.

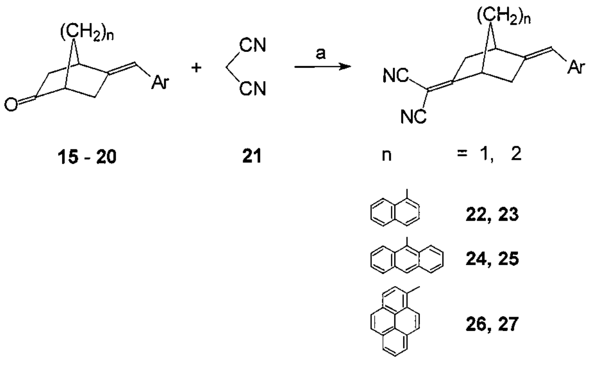
Donor−Acceptor-Substituted Derivatives of 1−3

To prepare the donor−acceptor-substituted derivatives of **1** and **2** we used the corresponding diketones **10**[11] and **11**[12] and carried out a Wittig−Horner−Emmons reaction with the readily available phosphonates **12**,[16] **13**,[17] and **14**[18] (Scheme 1). The monoketones **15−20** were obtained in moderate to good yields as shown in Scheme 1.

Heating **15−20** with propanedinitrile in the presence of ammonium acetate and acetic acid in toluene under reflux affords the donor−acceptor-substituted bicyclic systems **22−27**, respectively (Scheme 2). Yields of between 80 and 98% of the donor−acceptor-substituted bicyclic species **22−27** were obtained.

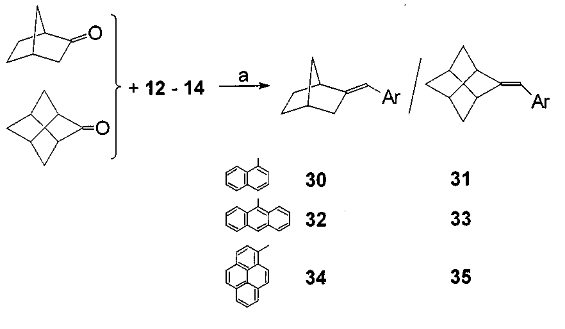


Scheme 1. Synthesis of **15−20**; a: LDA/THF



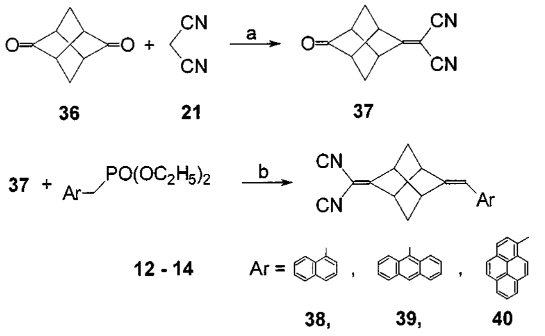
Scheme 2. Synthesis of **22−27**; a: NH$_4$OAc/HOAc/toluene

To derive the donor-substituted bicyclic and tricyclic derivatives **30−35** (Scheme 3) we proceeded analogously: The monoketones **28** and **29** were treated with the phosphonates **12−14** in a Wittig−Horner−Emmons olefination reaction. The yields of the tricyclic systems **31**, **33**, **35** varied between 30 and 40% while for the bicyclic derivatives **30**, **32**, and **34** the yields were above 70%.



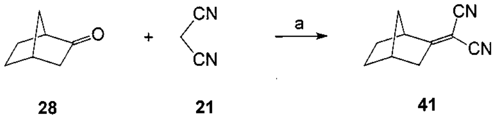
Scheme 3. Synthesis of **30−35**; a: LDA/THF

To obtain the 2,5-donor−acceptor-substituted stellanes **38−40** (Scheme 4), we first synthesized **37**[14] in a Knoevenagel condensation with the diketone **36** and propanedinitrile (**21**) in the presence of ammonium acetate/acetic acid. This affords **37** in 75% yield.[14]



Scheme 4. Synthesis of **37**−**40**; a: NH4OAc, HOAc/toluene; b: LDA/THF

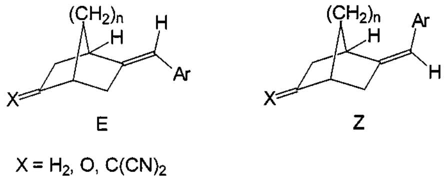
The reaction of **37** with the phosphonates **12**−**14** provides the 2,5-donor−acceptor-substituted stellane derivatives **38**−**40** in moderate yields. This route proved to be advantageous compared with the alternative. Reaction of **36** directly with **12**−**14** gave the corresponding monoketones which did not react with propanedinitrile. This result supports the observation that stellanone reacts with propanedinitrile to give the corresponding (tricyclo[3.3.0.0^{3,7}]octan-2-ylidene)propanedinitrile in only 2% yield.[14] For comparison we also synthesized (bicyclo[2.2.1]heptane-2-ylidene)propanedinitrile (**41**) from bicyclo[2.2.1]heptan-2-one and propanedinitrile by means of a Knoevenagel condensation (Scheme 5).

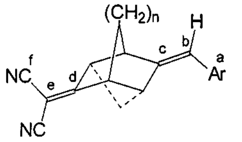


Scheme 5. Synthesis of **41**; a: NH4OAc, HOAc/toluene

Structural Investigations

In view of the electron-transfer studies, it was important to know the configuration at the *exo* double bond in **15**−**20**, **22**−**27**, **30**, **32**, and **34** as well as the distances between the π-systems separated by the σ-scaffold. To elucidate the configuration at the *exo* double bond we have carried out NMR investigations in solution. By means of NOESY NMR spectroscopy it was possible to determine if **15**−**20**, **22**−**27**, **30**, **32**, and **34** possess the (*E*) or (*Z*) configuration at the double bond. In all cases we found, for the isolated diastereomer, a coupling between the bridgehead proton and the neighboring olefinic proton which is only possible if the (*E*) configuration is present in solution.





For **22**−**24**, **27**, **31**, and **39** we were able to isolate single crystals. For **23** and **31** we found a disorder of the bicyclo[2.2.2]octane (60:40) and the stellane skeletons (65:35), respectively, and this hampered a more detailed analysis of the structural parameters. However, the (*E*) configuration at the olefinic double bond with the naphthalene unit in **23** could be determined without doubt. In Figure 2 we show the molecular structures of **22**, **27**, and **39**. In Table 1 we have listed the most relevant distances for **22**, **24**, **27**, and **39**. The transannular distances c−d are slightly longer in **39** (3.141 Å) than in the other three examples.

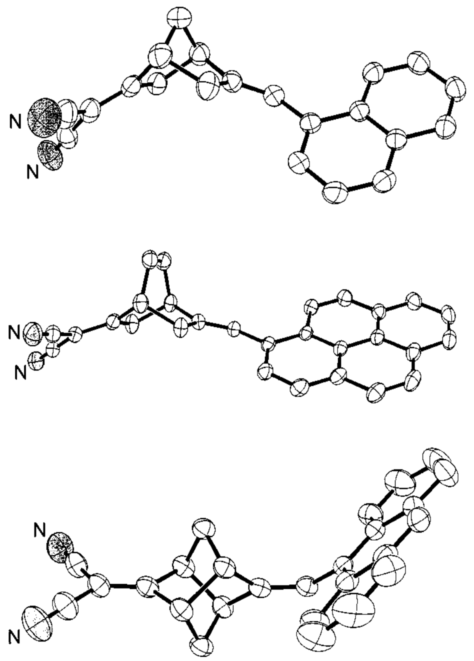


Figure 2. ORTEP plots (50% ellipsoid probability) of the molecular structures of **22** (top), **27** and **39** (bottom)

Table 1. Relevant distances [Å] of **22**, **24**, **27**, and **39**; for the definition of a−f see drawing in formula to the left

	22	**24**	**27**	**39**[a]
a−b	1.477(2)	1.485(5)	1.474(2)	1.486(2)
b−c	1.334(2)	1.321(3)	1.339(2)	1.327(2)
c−d	2.842(2)	2.803(3)	2.922(2)	3.142(2)
d−e	1.340(2)	1.340(4)	1.351(2)	1.339(2)
e−f	1.439(2)	1.454(4)	1.440(2)	1.438(2)
	1.442(2)	1.443(4)	1.451(2)	1.448(2)

[a] Averaged values of two independent molecules.

Fluorescence Spectra

The fluorescence spectra (Figure 3) of the donor moieties (vinylnaphthalene, vinylpyrene, and vinylanthracene) with attached bridge can easily be recorded owing to their relatively high fluorescence quantum yields. They show a small Stokes shift and some vibrational structure. The spectral distribution of the fluorescence of the locally excited states resembles that of the corresponding arenes without attached vinyl group, their lifetimes are, however, significantly reduced, for example, 350 ps for **30** in 2-methyl-THF. In the bridged donor−acceptor systems **22** and **26** the corresponding fluorescence from the locally excited states is significantly quenched. Thermodynamic considerations, for example, the estimate of the free enthalpy change upon formation of a charge separated state, suggest electron transfer to be an exergonic process with vinylnaphthalene and vinylpyrene as donors. In view of the strong electronic coupling and the shortness of the bridging element one can expect the rate for charge separation to be very high. Consequently, electron transfer should occur on a time-scale comparable to or even faster than the lifetime of the donor excited state. The created charge-separated (CT) state, $D^+{-}B{-}A^-$, can return to the electronic ground state by radiative recombination to yield a structureless emission with a large Stokes shift. The appearance of this emission (Figure 3) demonstrates that the synthesis of systems with efficient photoinduced electron transfer could be achieved with **22** and **26**. Estimates of the *p*olar *d*riving *f*orce[19] PDF = $e[E_{ox}(D) - E_{red}(A)] - E_{oo}$ predict that charge separation is not an exergonic process in compound **24** with vinylanthracene as donor and this is in contrast to the above results. Accordingly, the donor fluorescence is not quenched and no CT fluorescence is observed. A similar photophysical behavior (as demonstrated in Figure 3 for the derivatives with a norbornane bridge) is found for the analogous compounds with the other two types of bridging elements. The results including time-resolved spectroscopy in solvents of different polarity and/or temperature will be discussed extensively in a forthcoming publication.

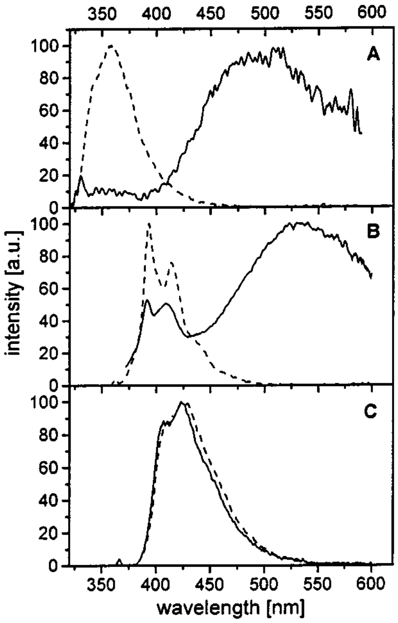


Figure 3. Comparison of the fluorescence spectra of the bridged electron donor−acceptor systems (—) **22** (A), **26** (B), and **24** (C) with those of the corresponding donors (---) **30** (A), **34** (B), and **32** (C) in ethyl acetate solvent ($c \approx 10^{-5}$ M); excitation wavelengths λ_{ex} = 300 nm (**22**), 364 nm (**26**), and 368 nm (**24**)

Conclusions

By using standard procedures, such as the Wittig−Horner−Emmons reaction and the Knoevenagel condensation we were able to synthesize donor−acceptor-substituted species with a bicyclo[2.2.1]heptane, a bicyclo[2.2.2]octane, and a tricyclo[3.3.0.0^{3,7}]octane skeleton. Structural investigations show the (*E*) configuration for all donor π-systems. The transannular distances between the *exo*-methylidene groups vary between 2.80 Å and 3.14 Å.

Experimental Section

General Methods: Moisture- and oxygen-sensitive reactions were conducted in oven-dried glassware under argon. THF was dried with sodium/benzophenone and distilled under argon before use, petroleum ether and diethyl ether were distilled before use. − Melting points are uncorrected. − Materials used for column chromatography were Silica gel 60 (Merck and Macherey−Nagel). − ^{1}H NMR and ^{13}C NMR spectra were measured with Bruker Avance 300 (^{1}H NMR at 300 MHz, ^{13}C NMR at 75.47 MHz) and Bruker Avance 500 (^{1}H NMR at 500 MHz, ^{13}C NMR at 125.77 MHz) spectrometers using the solvent as internal standard. − High-resolution mass spectra were recorded with a JEOL JMS-700. − UV/Vis spectra were obtained with a Hewlett−Packard 8452A spectrometer. − Elemental analyses were performed at the Mikroanalytisches Labor der Universität Heidelberg. − Fluorescence spectra were recorded with a Perkin−Elmer LS50 spectrometer with approximately 10^{-5} M solutions in ethyl acetate. − In the case of **17**, **18**, **25**, and **39** we were unable to record a melting point due to a slow decomposition on heating.

General Procedure for the Preparation of the Bicyclic Enones 15−20: To dry diisopropylamine (0.31 mL, 2.2 mmol) was added *n*-butyllithium (1.3 mL, 2 mmol, 1.6 M in *n*-hexane) at −78 °C. The mixture was stirred for 5 min, then dry THF (6 mL) was added. Phosphonate (2 mmol), dissolved in THF (4 mL), was then added and the mixture was stirred for 45 min. To this mixture was added a solution of the ketone (2.2 mmol) in THF (8 mL). After the addition was completed, cooling was stopped and the mixture was stirred for 2 d at room temp. For workup, water was added, and the aqueous phase was removed. The aqueous phase was extracted three times with dichloromethane. The combined organic solvents were dried with Na_2SO_4 and the solvent removed in vacuum. The crude product was purified by chromatography on silica gel with petroleum ether/diethyl ether (10:1).

(*E*)-5′-[(Naphthalen-1-yl)methylene]bicyclo[2.2.1]heptan-2′-one (15): Starting materials were bicyclo[2.2.1]heptane-2,5-dione (**10**) (274 mg, 2.2 mmol), diethyl [(naphthalen-1-yl)methyl]phosphonate (**12**) (576 mg, 2 mmol), diisopropylamine (0.3 mL, 2.2 mmol), *n*-butyllithium (1.3 mL, 1.6 M in *n*-hexane) and THF (18 mL). Yield 110 mg (20%) of **15** as a colorless solid, m.p. 95 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.88 (d, *J* = 10.0 Hz, 1 H), 1.94 (d, *J* =

10.4 Hz, 1 H), 2.16 (dd, 1 H, J_1 = 17.6 Hz, J_2 = 4.1 Hz), 2.36−2.41 (m, 2 H), 2.57 (d, J = 17.2 Hz, 1 H), 2.80 (d, J = 4.3 Hz, 1 H), 3.39 (s, 1 H), 7.08 (s, 1 H), 7.41−7.52 (m, 4 H), 7.74−7.76 (m, 1 H), 7.84−7.86 (m, 1 H), 8.01−8.03 (m, 1 H). − ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 32.5 (CH_2), 39.1 (CH_2), 45.8 (CH_2), 46.2 (CH), 51.2 (CH), 124.9 (CH), 126.0 (CH), 126.1 (CH), 126.4 (CH), 126.6 (CH), 127.9 (CH), 129.1 (CH), 129.2 (CH), 132.2 (C), 134.3 (C), 135.1 (C), 154.9 (C), 217.2 (CO). − HRMS (EI, 70 eV): [M$^+$] calcd. 248.1201; found 248.1200. − $C_{18}H_{16}O$ (248.1): calcd. C 87.06, H 6.49; found C 87.02, H 6.58.

(*E*)-5′-[(Naphthalen-1-yl)methylene]bicyclo[2.2.2]octan-2′-one (16): Starting materials were bicyclo[2.2.2]octane-2,5-dione (**11**) (607 mg, 4.4 mmol), diethyl [(naphthalen-1-yl)methyl]phosphonate (**12**) (1.4 g, 4 mmol), diisopropylamine (0.6 mL, 4.4 mmol), *n*-butyllithium (2.6 mL, 4 mmol, 1.6 M in *n*-hexane), and THF (36 mL). Yield: 130 mg (11%) of **16** as a colorless solid, m.p. 76 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85−1.93 (m, 3 H), 2.03−2.06 (m, 1 H), 2.43−2.58 (m, 4 H), 2.64 (m, 1 H), 3.01 (t, J = 2.7 Hz, 1 H), 6.88 (s, 1 H), 7.40 (d, J = 7.0 Hz, 1 H), 7.42 (t, J = 8.6 Hz, 1 H), 7.48−7.55 (m, 2 H), 7.75 (d, J = 8.0 Hz, 1 H), 7.82−7.84 (m, 1 H), 7.96−7.98 (m, 1 H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.8 (CH_2), 26.7 (CH_2), 31.7 (CH_2), 40.5 (CH), 44.8 (CH), 45.5 (CH_2), 121.3 (CH), 125.2 (CH), 126.0 (CH),126.5 (CH), 126.6 (CH), 127.9 (CH), 129.1 (CH), 132.3 (C), 134.3 (C), 134.9 (C), 143.4 (C), 216.7 (CO). − HRMS (EI, 70 eV): [M$^+$] calcd. 262.13658; found 262.13618. − $C_{19}H_{18}O$ (262.1): calcd. C 86.98, H 6.92; found C 86.73, H 6.99.

(E)-5′-[(Anthracen-9-yl)methylene]bicyclo[2.2.1]heptan-2′-one (17): Starting materials were bicyclo[2.2.1]heptane-2,5-dione (**10**) (248 mg, 2 mmol), phosphonate **13** (656 mg, 2 mmol), diisopropylamine (0.3 mL, 2.1 mmol), *n*-butyllithium (1.25 mL, 2 mmol, 1.6 M in *n*-hexane), and THF (15 mL). Yield: 208 mg (35%) of **17** as a yellow solid, R_f (silica gel; petroleum ether/diethyl ether, 1:1) = 0.36. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.75−1.88 (m, 2 H), 1.94−2.13 (m, 2 H), 2.30−2.48 (m, 2 H), 2.66−2.67 (d, 1 H), 3.58 (d, 1 H), 7.16 (s, 1 H), 7.44−7.49 (m, 4 H), 7.98−8.04 (m, 4 H), 8.08 (s, 2 H), 8.39 (s, 1 H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 32.2 (CH_2), 39.5 (CH_2), 45.4 (CH), 45.8 (CH_2), 50.9 (CH), 117.7 (CH), 125.8 (CH), 126.3 (CH), 126.8 (CH), 126.9 (CH), 129.5 (CH), 132.1 (C) 132.3 (C), 148.5 (C), 217.0 (CO). − HRMS (EI, 70 eV): [M$^+$] calcd. 298.13571; found 298.13577. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 258 (5.4), 336 (3.5), 352 (3.9), 370 (4.2), 388 (4.2) nm.

(*E*)-5′-[(Anthracen-9-yl)methylene]bicyclo[2.2.2]octan-2′-one (18): Starting materials were bicyclo[2.2.2]octane-2,5-dione (**11**) (276 mg, 2 mmol), phosphonate **13** (656 mg, 2 mmol), diisopropylamine (0.3 mL, 2.1 mmol), *n*-butyllithium (1.25 mL, 2 mmol, 1.6 M in *n*-hexane), and THF (15 mL). Yield: 35 mg (6%) of **18** as a yellow solid. R_f (silica gel; petroleum ether/diethyl ether, 1:1) = 0.38. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.83−1.98 (m, 3 H), 2.08−2.13 (m, 2 H), 2.14−2.20 (m, 1 H), 2.28−2.33 (m, 1 H), 2.50−2.57 (m, 1 H), 2.61−2.71 (m, 1 H), 3.21−3.24 (m, 1 H), 6.99 (s, 1 H), 7.45−7.50 (m, 4 H), 8.00−8.09 (m, 3 H), 8.11−8.19 (m, 1 H), 8.40 (s, 1 H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.8 (CH_2), 26.8 (CH_2), 31.2 (CH_2), 39.9 (CH), 44.5 (CH), 45.5 (CH_2), 119.8 (CH), 125.8 (CH), 125.9 (CH), 126.2 (CH), 126.4 (CH), 126.9 (CH), 129.5 (CH), 129.6 (CH),129.8 (C), 132.2 (C), 145.7 (C). 216.6 (CO). − UV/Vis: λ_{max} (log ε) = 258 (5.0), 336 (3.5), 350 (3.8), 368 (4.0), 390 (3.9) nm. − HRMS (EI, 70 eV) [M$^+$]: calcd. 312.1514; found 312.1510.

(*E*)-5′-[(Pyren-1-yl)methylene]bicyclo[2.2.1]heptan-2′-one (19): Starting materials were bicyclo[2.2.1]heptane-2,5-dione (**10**) (248 mg, 2 mmol), phosphonate **14** (704 mg, 2 mmol), diisopropylamine (0.3 mL, 2.1 mmol), *n*-butyllithium (1.25 mL, 2 mmol, 1.6 M in *n*-hexane). Yields: 200 mg (31%) of **19** as a yellow solid, m.p. 154 °C. − R_f (silica gel; petroleum ether/dichloromethane, 1:1) = 0.30. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.93−2.00 (m, 2 H), 2.21−2.26 (m, 1 H), 2.39- 2.43 (m, 1 H), 2.47−2.51 (d, 1 H), 2.62−2.66 (m, 1 H), 2.83−2.84 (d, 1 H), 3.46 (d, 1 H), 7.38 (s, 1 H), 7.95−7.97 (d, 1 H), 7.99−8.03 (t, 1 H), 8.04−8.06 (m, 2 H), 8.09−8.16 (m, 2 H), 8.17−8.19 (m, 2 H), 8.25−8.26 (d, 1 H). − ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 32.7 (CH_2), 39.1 (CH_2), 45.9 (CH_2), 46.5 (CH), 51.3 (CH), 108.2 (C), 119.4 (CH), 124.4 (CH), 125.3 (CH), 125.6 (C), 125.7 (CH), 125.8 (CH), 126.5 (CH), 126.6 (CH), 127.8 (CH), 128.0 (CH), 128.1 (CH), 129.1 (C), 130.7 (C), 131.6 (C), 132.1 (C), 132.7 (C), 146.4 (C), 217.2 (CO). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 246 (4.6), 282 (4.4), 332 (4.3), 348 (4.5), 364 (4.3) nm. − HRMS (EI, 70 eV) [M$^+$]: calcd. 322.13577; found 322.13499.

(*E*)-5-[(Pyren-1-yl)methylene]bicyclo[2.2.2]octan-2′-one (20): Starting materials were bicyclo[2.2.2]octane-2,5-dione (**11**) (276 mg, 2 mmol), phosphonate **14** (704 mg, 2 mmol), diisopropylamine (0.3 mL, 2 mmol), *n*-butyllithium (1.25 mL, 2 mmol, 1.6 M in *n*-hexane). Yield: 138 mg (21%) of **20** as a yellow solid, m.p. 52−56 °C. − R_f (silica gel; petroleum ether/diethyl ether, 1:1) = 0.32. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.88−2.00 (m, 3 H), 2.07−2.13 (m, 1 H), 2.45−2.47 (m, 1 H), 2.50−2.54 (m, 1 H), 2.58−2.64 (m, 2 H), 2.66−2.70 (m, 1 H), 3.09−3.10 (m, 1 H), 7.15 (s, 1 H), 7.91−7.93 (d, 1 H), 7.99−8.02 (m, 1 H), 8.05 (s, 2 H), 8.09−8.11 (m, 1 H), 8.13−8.15 (m, 1 H), 8.18−8.22 (m, 3 H). − ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 23.9 (CH_2), 26.7 (CH_2), 31.8 (CH_2), 40.6 (CH), 44.8 (CH), 45.6 (CH_2), 121.9 (CH), 124.7 (CH), 125.2 (CH), 125.6 (2C), 125.7 (CH), 125.8 (CH), 126.6 (CH), 127.1 (CH), 127.8 (CH), 128.1 (2CH), 129.2 (C), 130.9 (C), 131.6 (C), 132.1 (C), 132.7 (C), 143.9 (C), 216.7 (CO). − UV/Vis (CH_2Cl_2): λ_{max} (log ε): 246 (4.6), 270 (4.3), 280 (4.4), 332 (4.2), 346 (4.4) nm. − HRMS (EI, 70 eV) [M$^+$]: calcd. 336.15143; found 336.15125.

General Procedure for the Preparation of the Bicyclic Donor−Acceptor Species 22−27: A mixture of one of the bicyclic ketones **15**−**20** (0.7 mmol), propanedinitrile (**21**) (3.9 mmol), ammonium acetate (3 mmol), acetic acid (0.8 mmol), and toluene (10 mL) was heated under reflux for 4 h in a vessel with a separator for water. After cooling, the solution was poured into water, the organic phase was separated, and the water phase extracted twice with toluene. The combined organic phases were washed with an aqueous solution of $NaHCO_3$, dried with Na_2SO_4, and the solvent was removed in vacuum. The residue was chromatographed on silica gel with petroleum ether/diethyl ether.

(*E*)-{5-[(Naphthalen-1-yl)methylene]bicyclo[2.2.1]hept-2-ylidene}-propanedinitrile (22): Starting materials were toluene (10 mL) as solvent, **15** (180 mg, 0.7 mmol), propanedinitrile (230 mg, 3.9 mmol), ammonium acetate (256 mg, 3 mmol), and acetic acid (0.8 mL). Yield: 180 mg (84%) of **22** as a colorless solid, m.p. 138 °C. R_f [silica gel; petroleum ether (boiling range 30−40 °C)/diethyl ether, 2:1] = 0.25. − ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.77−1.95 (m, 2 H), 2.22−2.29 (m, 1 H), 2.67−2.88 (m, 3 H), 3.37 (d, J = 2.3 Hz, 1 H), 3.64 (d, J = 4.2 Hz, 1 H), 7.10 (s, 1 H), 7.37 (d, J = 7.0 Hz, 1 H), 7.42 (t, J = 8.0 Hz, 1 H), 7.48−7.55 (m, 2 H), 7.77 (d, J = 8.1 Hz, 1 H), 7.84−7.88 (m, 1 H), 7.96−7.99 (m, 1 H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 35.9 (CH_2), 41.1 (CH_2), 42.6 (CH_2), 46.9 (CH), 48.5 (CH), 80.8 (C), 112.2 (CN), 120.1 (CH), 124.7 (CH), 126.0 (CH), 126.6 (CH), 126.7 (CH), 128.2 (CH), 129.3 (CH), 132.1 (C), 134.3 (C), 134.4 (C), 143.7 (C), 191.3 (C). − UV/

Vis (CH_2Cl_2): λ_{max} (log ε) = 296 (4.0). − $C_{21}H_{16}N_2$ (296.4): calcd. C 85.11, H 5.44, N 9.45; found C 84.91, H 5.73, N 9.18.

(E)-{5-[(Naphthalen-1-yl)methylene]bicyclo[2.2.2]oct-2-ylidene}-propanedinitrile (23): Starting materials were **16** (190 mg, 0.7 mmol), propanedinitrile (**21**) (230 mg, 4 mmol), ammonium acetate (256 mg, 3 mmol), acetic acid (0.8 mL), and toluene (10 mL). Yield: 130 mg (58%) of **23** as a colorless solid; m.p. 143 °C. − R_f [silica gel, petroleum ether (boiling range 30−40 °C)/diethyl ether, 4:1] = 0.29. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.75−1.79 (m, 2 H), 1.92−2.03 (m, 2 H), 2.46 (dd, J_1 = 2.4 Hz, J_2 = 18.0 Hz, 1 H), 2.66 (d, J = 17.9 Hz, 1 H), 2.92 (t, J = 3.6 Hz, 2 H), 2.96 (t, J = 2.4 Hz, 1 H), 3.24 (t, J = 2.8 Hz, 1 H), 6.89 (s, 1 H), 7.34 (d, J = 7.0 Hz, 1 H), 7.45 (t, J = 7.4 Hz, 1 H), 7.50−7.53 (m, 2 H), 7.71 (d, J = 8.2 Hz, 1 H), 7.86−7.88 (m, 1 H), 7.93−7.95 (m, 1 H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.1 (CH_2), 26.3 (CH_2), 33.0 (CH_2), 38.1 (CH), 38.1 (CH), 38.8 (CH_2), 82.7 (C), 111.9 (CN), 112.0 (CN), 122.3 (CH), 125.0 (CH), 126.0 (CH), 126.6 (CH), 126.7 (CH), 128.2 (CH), 129.3 (CH), 132.1 (C), 134.2 (C), 134.3 (C), 141.6 (C), 190.4 (C). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 296 (3.6) nm. − $C_{22}H_{18}N_2$ (310.4): calcd. C 85.13, H 5.85, N 9.03; found C 84.85, H 5.94, N 9.04.

(E)-{5-[(Anthracen-9-yl)methylene]bicyclo[2.2.1]hept-2-ylidene}propanedinitrile (24): Starting materials were **17** (70 mg, 0.2 mmol), propanedinitrile (73 mg, 1 mmol), ammonium acetate (74 mg, 1 mmol), acetic acid (0.3 mL), and toluene (15 mL). Yield: 69 mg (87%) of **24** as a colorless solid, m.p. 154 °C. − R_f (silica gel; petroleum ether/diethyl ether, 1:1) = 0.34. − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.60 (m, 1 H), 1.85−1.87 (m, 1 H), 1.99−2.02 (m, 1 H), 2.27−2.30 (m, 1 H), 2.85−2.96 (m, 2 H), 3.51 (s, 1 H), 3.58 (s, 1 H), 7.18 (s, 1 H), 7.45−7.49 (m, 4 H), 7.97−8.03 (m, 4 H), 8.40 (s. 1 H). − ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 35.6 (CH_2), 41.5 (CH_2), 42.6 (CH_2), 46.1 (CH), 48.3 (CH), 80.7 (C), 111.9 (C), 112.2 (C), 119.0 (CH), 125.9 (CH), 126.5 (C), 127.3 (CH), 129.7 (2CH), 131.5 (C), 132.1 (C), 146.5 (C), 191.2 (C). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 258 (5.1), 357 (3.8), 370 (4.0), 388 (4.0) nm. − $C_{25}H_{18}N_2$ (346.4): calcd. C 86.68, H 5.24, N 8.09; found C 86.62, H 5.30, N 8.14.

(E)-{5-[(Anthracen-9-yl)methylene]bicyclo[2.2.2]oct-2-ylidene}propanedinitrile (25): Starting materials were **18** (70 mg, 0.2 mmol), propanedinitrile (74 mg, 1 mmol), ammonium acetate (69 mg, 1 mmol), acetic acid (0.3 mL), and toluene (15 mL). Yield: 61 mg (77%) of **25** as a yellow solid. − R_f (silica gel; petroleum ether/diethyl ether, 1:1) = 0.42. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.74−1.93 (m, 4 H), 2.09−2.16 (m, 2 H), 2.98−3.01 (m, 2 H), 3.05−3.07 (m, 1 H), 3.16−3.18 (m, 1 H), 7.00 (s, 1 H), 7.45−7.60 (m, 4 H), 7.93−8.09 (m, 4 H), 8.40 (s, 1 H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.2 (CH_2), 26.6 (CH_2), 32.4 (CH_2), 37.5 (CH), 37.8 (CH), 38.7 (CH_2), 82.7 (C), 111.8 (2C), 120.9 (CH), 125.9 (CH), 126.0 (CH), 126.5 (CH), 126.6 (CH), 172.2 (CH), 129.6 (CH), 129.7 (CH), 131.3 (C), 132.1 (C), 144.0 (C), 190.2 (C). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 250 (4.4), 258 (4.6), 318 (2.1), 334 (2.8), 350 (3.2), 368 (3.4), 388 (3.3) nm. − HRMS (EI, 70 eV) calcd. 360.1627; found 360.1638.

(E)-{5-[(Pyren-1-yl)methylene]bicyclo[2.2.1]hept-2-ylidene}propanedinitrile (26): Starting materials were **19** (107 mg, 0.3 mmol), propanedinitrile (**21**) (106 mg, 1.6 mmol), ammonium acetate (106 mg, 1.4 mmol), acetic acid (0.3 mL), and toluene (15 mL). Yield: 123 mg (100%) of **26** as a beige solid, m.p. 170 °C. − R_f (silica gel; petroleum ether/diethyl ether, 1:1) = 0.29. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.80−1.84 (m, 1 H), 1.95−2.00 (m, 1 H), 2.31−2.39 (m, 1 H), 2.73−2.92 (m, 3 H), 3.44 (m, 1 H), 3.67−3.68 (m, 1 H), 7.38 (s, 1 H), 7.89−7.92 (m, 1 H), 7.99−8.02 (m, 1 H), 8.04−8.07 (m, 2 H), 8.08−8.14 (m, 2 H), 8.18−8.23 (m, 3 H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 36.2 (CH_2), 41.2 (CH_2), 42.7 (CH_2), 47.2 (CH), 48.6 (CH), 80.8 (C), 112.1 (C), 112.2 (C), 120.5 (CH), 124.1 (CH), 125.3 (CH), 125.5 (C), 125.6 (C), 125.8 (CH), 126.0 (CH), 126.2 (CH), 126.7 (CH), 128.0 (2CH), 128.3 (CH), 129.1 (C), 131.1 (C), 131.5 (C), 131.9 (C), 132.1 (C), 144.0 (C), 191.3 (C). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 246 (4.5), 282 (4.3), 344 (4.1), 350 (4.3), 364 (4.2) nm. − $C_{27}H_{18}N_2$ (370.4): calcd. C 87.54, H 4.90, N 7.56; found C 87.34, H 5.09, N 7.56.

(E)-{5-[(Pyren-1-yl)methylene]bicyclo[2.2.2]oct-2-ylidene}propanedinitrile (27): Starting materials were **20** (110 mg, 0.3 mmol), propanedinitrile (**21**) (108 mg, 1.6 mmol), ammonium acetate (102 mg, 1.3 mmol), acetic acid (0.3 mL), and toluene (15 mL). Yield: 125 mg (99%) of **27** as a beige solid, m.p. 178 °C. − R_f (silica gel; diethyl ether) = 0.37. − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.75−1.86 (m, 2 H), 1.94−2.00 (m, 1 H), 2.08−2.13 (m, 1 H), 2.49−2.53 (m, 1 H), 2.69−2.72 (m, 1 H), 2.92−2.99 (m, 2 H), 3.03−3.04 (m. 1 H), 3.25−3.26 (m, 1 H), 7.16 (s, 1 H), 7.87−7.89 (m, 1 H), 8.00−8.21 (m, 8 H). − ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 25.2 (CH_2), 26.4 (CH_2), 33.1 (CH_2), 38.1 (CH), 38.2 (CH), 38.8 (CH_2), 82.8 (C), 111.9 (C), 112.0 (C), 122.8 (CH), 124.5 (CH), 125.2 (CH), 125.5 (C), 125.6 (C), 125.8 (CH), 126.0 (CH), 126.7 (CH), 126.9 (CH), 128.0 (2CH), 128.3 (CH), 129.2 (C), 131.1 (C), 131.6 (C), 131.9 (C), 132.0 (C), 142.0 (C), 190.3 (C). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 246 (4.4), 270 (4.1), 280 (4.2), 318 (3.6), 332 (4.0), 346 (4.2), 362 (4.0) nm. − $C_{28}H_{20}N_2$ (384.5): calcd. C 87.47, H 5.24, N 7.29; found C 87.26, H 5.33, N 7.21.

General Protocol for the Syntheses of 30−35: The syntheses of **30**−**35** were carried out analogously to those of **15**−**20**.

(E)-2-[(Naphthalen-1-yl)methylene]bicyclo[2.2.1]heptane (30): Starting materials were bicyclo[2.2.1]heptane-2-one (**28**) (242 mg, 2.2 mmol), phosphonate **12** (556 mg, 2 mmol), diisopropylamine (0.3 mL, 2.2 mmol), *n*-butyllithium (1.3 mL, 2 mmol, 1.6 M in *n*-hexane), and THF (18 mL). Yield: 380 mg (74%) of **30** as a colorless solid, m.p. 39 °C. − R_f [silica gel; petroleum ether (boiling range 30−40 °C)/diethyl ether, 4:1] = 0.36. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27−1.56 (m, 2 H), 1.59−1.65 (m, 2 H), 1.67−1.70 (m, 1 H), 1.76−1.84 (m, 1 H), 2.32 (d, J = 2.9 Hz, 1 H), 2.38 (d, J = 2.84 Hz, 1 H), 2.44 (s, 1 H), 2.99 (d, J = 3.4 Hz, 1 H), 6.88 (s, 1 H), 7.42−7.49 (m, 4 H), 7.70 (m, 1 H), 7.87 (m, 1 H), 8.11 (m, 1 H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 28.5 (CH_2), 30.1 (CH_2), 36.9 (CH), 37.7 (CH_2), 39.2 (CH_2), 47.2 (CH), 114.6 (CH), 124.2 (CH), 124.5 (CH), 125.4 (CH), 125.5 (CH), 125.5 (CH), 126.3 (CH), 128.4 (CH), 131.7 (C), 133.7 (C), 135.5 (C), 151.4 (C). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 302 (4.0) nm. − $C_{18}H_{18}$ (234.3): calcd. C 92.26, H 7.74; found C 92.03, H 7.82.

(E)-2-[(Naphthalen-1-yl)methylene]tricyclo[3.3.0.0^{3,7}]octane (31): Starting materials were stellanone (**29**) (366 mg, 3 mmol), phosphonate **12** (917 mg, 3.3 mmol), diisopropylamine (0.5 mL, 3.3 mmol), *n*-butyllithium (1.9 mL, 3 mmol, 1.6 M in *n*-hexane), and THF (20 mL). Yield: 291 mg (39%) of **31** as a white solid, m.p. 73 °C. − R_f (silica gel; petroleum ether/diethyl ether, 10: 1) = 0.58. − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.50−1.54 (m, 3 H), 1.60 (m, 3 H), 2.41 (s, 1 H), 2.54 (s, 1 H), 2.72 (s, 1 H), 2.92 (s, 1 H), 6.25 (s, 1 H), 7.38−7.39 (m, 1 H), 7.44−7.50 (m, 3 H), 7.72−7.73 (m, 1 H), 7.84−7.86 (m, 1 H), 8.09−8.11 (m, 1 H). − ^{13}C NMR (125.8 MHz; $CDCl_3$): δ = 36.7 (CH), 37.4 (CH), 39.4 (CH), 43.2 (CH), 45.1 (CH_2), 46.0 (CH_2), 46.5 (CH_2), 104.4 (CH), 125.5 (CH), 126.1 (CH), 126.2 (CH), 126.5 (2 CH), 126.9 (CH), 129.0 (CH), 132.8 (C), 134.3 (C), 136.4 (C), 161.7 (C). − UV/Vis (CD_2Cl_2): λ_{max} (log ε) = 232 (4.6), 300 (4.0) nm. − $C_{19}H_{18}$ (246.4): calcd. C 92.64, H 7.36; found C 92.45, H 7.35.

(E)-2-[(Anthracen-9-yl)methylene]bicyclo[2.2.1]heptane (32): Starting materials were norbornanone (**28**) (220 mg, 2 mmol), phosphonate **13** (656 mg, 2 mmol), diisopropylamine (0.3 mL, 2.1 mmol), *n*-butyllithium (1.25 mL, 2 mmol, 1.6 M in *n*-hexane), and THF (18 mL). Yield: 429 mg (76%) of **32** as a yellow solid, m.p. 110 °C. − R_f (silica gel; petroleum ether/diethyl ether, 1:1) = 0.62. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.25−1.37 (m, 1 H), 1.40−1.53 (m,2 H), 1.59−1.96 (m, 5 H), 2.30 (s, 1 H), 3.18−3.19 (m, 1 H), 6.90 (s, 1 H), 7.43−7.49 (m, 4 H), 7.98−8.03 (m, 2 H), 8.16−8.21 (m, 2 H), 8.36 (s, 1 H). − ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 29.1 (CH), 31.0 (CH$_2$), 37.3 (CH), 37.7 (CH$_2$), 40.3 (CH$_2$), 46.9 (CH), 114.0 (CH), 125.7 (CH), 125.7 (CH), 126.2 (CH), 127.0 (CH), 129.3 (CH), 130.0 (C), 132.2 (C), 134.2 (C), 154.1 (C). − UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε): 260 (5.1), 338 (3.5), 352 (3.8), 370 (3.9), 390 (3.9). − $C_{22}H_{20}$ (284.4): calcd. C 92.91, H 7.09; found 92.60, H 7.13.

(E)-2-[(Anthracen-9-yl)methylene]tricyclo[3.3.0.0^{3,7}]octane (33): Starting materials were stellanone (**29**) (366 mg, 3 mmol), phosphonate **13** (656 mg, 3 mmol), diisopropylamine (0.3 mL, 2 mmol), *n*-butyllithium (1.25 mL, 2 mmol, 1.6 M in *n*-hexane), and THF (18 mL). Yield: 192 mg (33%) of **33** as a yellow solid, m.p. 101 °C. − R_f (silica gel; petroleum ether/diethyl ether, 10:1) = 0.56. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.29−1.33 (m, 1 H), 1.42−1.55 (m, 1 H), 1.68−1.72 (m, 1 H), 1.94−1.99 (m, 1 H), 2.09 (m, 1 H), 2.37 (m, 1 H), 2.54 (m, 1 H), 2.91 (m, 1 H), 6.34 (s, 1 H), 7.42−7.48 (m, 4 H), 7.98−8.02 (m, 2 H), 8.25−8.28 (m, 2 H), 8.36 (s, 1 H). − ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 36.4 (CH), 37.5 (CH), 39.8 (CH), 43.3 (CH), 45.2 (CH$_2$), 46.0 (CH$_2$), 46.7 (CH$_2$), 102.5 (CH), 125.5 (CH), 125.6 (CH), 126.1 (CH), 127.3 (CH), 129.2 (C), 131.0 (C), 132.2 (C), 133.4 (C), 163.3 (C). − UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 260 (5.0), 354 (3.7), 370 (3.8), 388 (3.8) nm. − $C_{23}H_{20}$ (296.4): calcd. C 93.20, H 6.80; found C 93.02, H 6.74.

(E)-2-[(Pyren-1-yl)methylene]bicyclo[2.2.1]heptane (34): Starting materials were norbornanone (**28**) (165 mg, 1.5 mmol), phosphonate **14** (528 mg, 1.5 mmol), diisopropylamine (0.2 mL, 1.6 mmol), *n*-butyllithium (0.9 mL, 1.5 mmol, 1.6 M in *n*-hexane), and THF (15 mL). Yield: 344 mg (75%) of **34** as a yellow solid, m.p. 113. °C. − R_f (silica gel; petroleum ether/diethyl ether, 1:1) = 0.60. − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.35−1.41 (m, 1 H), 1.44−1.46 (m, 1 H), 1.59−1.62 (m, 2 H), 1.63−1.73 (m, 1 H), 1.84−1.89 (m, 1 H), 2.17−2.21 (m, 1 H), 2.43−2.44 (m, 1 H), 2.46−2.49 (m,1 H), 3.09 (m, 1 H), 7.20 (s, 1 H), 7.97−8.00 (m, 1 H), 8.03 (m, 2 H), 8.04−8.05 (m, 1 H), 8.07−8.09 (m, 1 H), 8.11−8.13 (m, 1 H), 8.15 (m, 1 H), 8.16−8.17 (m, 1 H), 8.34−8.36 (m, 1 H). − ^{13}C NMR (125.8 MHz, CDCl$_3$): δ = 29.2 (CH$_2$), 30.8 (CH$_2$), 37.7 (CH), 38.6 (CH$_2$), 39.9 (CH$_2$), 48.2 (CH), 115.9 (CH), 124.8 (CH), 125.2 (CH), 125.3 (CH), 125.5 (CH), 125.7 (2 C), 126.4 (CH), 126.6 (CH), 127.4 (CH), 127.6 (CH), 128.2 (CH), 129.0 (C), 130.3 (C), 131.7 (C), 132.2 (C), 134.2 (C), 152.8 (C). − UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 246 (4.7), 278 (4.6), 286 (4.6), 352 (4.6), 368 (4.5). − $C_{24}H_{20}$ (308.4): calcd. C 93.46, H 6.54; found C 93.48, H 6.51.

(E)-2-[(Pyren-1-yl)methylene]tricyclo[3.3.0.0^{3,7}]octane (35): Starting materials were stellanone (**29**) (244 mg, 2 mmol), phosphonate **14** (774 mg, 2.2 mmol), diisopropylamine (0.3 mL, 2.2 mmol), *n*-butyllithium (1.1 mL, 2 mmol, 1.6 M in *n*-hexane), and THF (15 mL). Yield: 192 mg (30%) of **35** as a yellow solid, m.p. 146 °C. − R_f (silica gel; petroleum ether/diethyl ether, 10:1) = 0.56. − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.53 −1.56 (m, 3 H), 1.64−1.72 (m, 3 H), 2.47 (s, 1 H), 2.57 (s, 1 H), 2.80 (s, 1 H), 3.01 (s, 1 H), 6.54 (s, 1 H), 7.94−8.08 (m, 5 H), 8.12−8.16 (m, 3 H), 8.32−8.34 (m, 1 H). − ^{13}C NMR (125.8 MHz, CDCl$_3$): δ = 36.8 (CH), 37.5 (CH), 39.6 (CH), 43.5 (CH), 45.2 (CH$_2$), 46.0 (CH$_2$), 46.5 (CH$_2$), 105.0 (CH), 125.1 (CH), 125.2 (CH), 125.3 (CH), 125.4 (CH), 125.6 (C), 125.7 (C), 126.4 (CH), 127.3 (CH), 127.5 (2CH), 128.1 (CH), 129.3 (C), 130.3 (C), 131.8 (C), 132.2 (C), 134.3 (C), 162.5 (C). − UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) =246 (4.1), 284 (4.0), 350 (3.0), 362 (4.0) nm. − $C_{25}H_{20}$ (320.4): calcd. C 93.71, H 6.29; found C 93.42, H 6.41.

General Remarks on the Syntheses of 38−40: The reaction of 2-[6-oxotricyclo[3.3.0.0^{3,7}]octan-2-ylidene]propanedinitrile (**37**) with the phosphonates **12**−**14** was carried out analogously to the protocol given for the preparation of **15**−**20**.

2-{6-[(Naphthalen-1-yl)methylene]tricyclo[3.3.0.0^{3,7}]oct-2-ylidene}-propanedinitrile (38): Starting materials were 2-(6-oxotricyclo[3.3.0.0^{3,7}]octan-2-ylidene)propanedinitrile (**37**) (553 mg, 3 mmol), phosphonate **12** (917 mg, 3.3 mmol), diisopropylamine (0.47 mL, 3.3 mmol), *n*-butyllithium (1.9 mL, 3 mmol, 1.6 M in *n*-hexane), and THF (15 mL). Yield: 213 mg (23%) of **38** as a colorless solid, m.p. 113 °C. − R_f (silica gel; petroleum ether/diethyl ether, 1:1) = 0.47. − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.71−1.73 (m, 1 H), 1.80−1.83 (m, 1 H), 1.91−1.97 (m, 2 H), 3.12 (s, 1 H), 3.24 (s, 2 H), 3.37 (s, 1 H), 6.69 (s, 1 H), 7.31 (d, 1 H), 7.44−7.47 (m, 1 H), 7.50−7.53 (m, 2 H), 7.79−7.80 (m, 1 H), 7.87−7.88 (m, 1 H), 7.99−8.01 (m, 1 H). − ^{13}C NMR (125.8 MHz, CDCl$_3$): δ = 40.9 (CH), 42.4 (CH$_2$), 42.9 (CH$_2$), 44.8 (CH), 45.4 (CH), 46.1 (CH), 72.0 (C), 111.9 (CH), 112.0 (CN), 112.1 (CN), 125.0 (CH), 126.1 (CH), 126.4 (CH), 126.7 (CH), 126.8 (CH), 128.3 (CH), 129.3 (CH), 132.5 (C), 134.3 (C), 134.9 (C), 154.3 (C), 195.8 (C). − UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 230 (4.6), 296 (4.1) nm. − $C_{22}H_{16}N_2$ (308.4): calcd. C 85.69, H 5.23, N 9.08; found C 85.62, H 5.28, N 8.95.

2-{6-[(Anthracen-9-yl)methylene]tricyclo[3.3.0.0^{3,7}]oct-2-ylidene}-propanedinitrile (39): Starting materials were **37** (276 mg, 1.5 mmol), phosphonate **13** (525 mg, 1.6 mmol), piperidine (0.2 mL, 1.6 mmol), *n*-butyllithium (1 mL, 1.6 mmol, 1.6 M in *n*-hexane), and THF (15 mL). Yield: 76 mg (15%) of **39** as a pale yellow substance which decomposes on warming. − R_f (silica gel; petroleum ether/diethyl ether, 1:1) = 0.43. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.54 (s, 1 H), 1.80−1.84 (m, 1 H), 1.91−1.95 (m, 1 H), 2.26−2.30 (m, 1 H), 2.44 (s, 1 H), 3.22 (s, 1 H), 3.32−3.39 (m, 2 H), 6.81 (s, 1 H), 7.48 (s, 4 H), 8.02−8.12 (m, 4 H), 8.42 (s, 1 H). − ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 41.2 (CH), 42.2 (CH$_2$), 43.0 (CH$_2$), 44.4 (CH), 44.6 (CH), 45.6 (CH), 110.0 (C), 111.9 (2C), 125.9 (CH), 126.2 (CH), 126.3 (CH), 127.2 (CH), 129.6 (CH), 130.9 (C), 132.1 (C), 156.4 (C), 195.6 (C). − UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 258 (5.0), 338 (3.4), 352 (3.7), 370 (3.8), 388 (3.8) nm. − HRMS (EI, 70 eV): calcd. 358.14700; found 358.14723.

2-{6-[(Pyrene-1-yl)methylene]tricyclo[3.3.0.0^{3,7}]oct-2-ylidene}propanedinitrile (40): Starting materials were **37** (221 mg, 1.2 mmol), phosphonate **14** (451 mg, 1.3 mmol), diisopropylamine (0.18 mL, 1.3 mmol), *n*-butyllithium (0.78 mL, 1.2 mmol, 1.6 M in *n*-hexane), and THF (13 mL). Yield: 21 mg (4.6%) of **40** as a pale yellow solid, m.p. 130 °C. − R_f (silica gel; petroleum ether/diethyl ether, 1:1) = 0.38. − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.73−1.76 (m, 1 H), 1.85−1.88 (m, 1 H), 1.96−1.99 (m, 1 H), 2.03−2.06 (m, 1 H), 3.19 (s, 1 H), 3.31 (m, 2 H), 3.40 (s, 1 H), 6.97 (s, 1 H), 7.85 (m, 1 H), 8.00−8.03 (m, 1 H), 8.06 (m, 2 H), 8.10−8.15 (m, 2 H), 8.19 (m, 2 H), 8.24 (m, 1 H). − ^{13}C NMR (125.8 MHz, CDCl$_3$): δ = 41.1 (CH), 42.4 (CH$_2$), 43.0 (CH$_2$), 44.6 (CH), 44.9 (CH), 45.4 (CH), 72.1 (C), 112.0 (CH), 112.1 (C), 112.4 (C), 124.4 (CH), 125.6 (C), 125.8 (CH), 126.0 (CH), 126.8 (CH), 127.2 (CH), 128.0 (C), 128.3

Table 2. Crystallographic data of **22**, **24**, **27**, and **39**

	22	**24**	**27**	**39**
Empirical formula	$C_{21}H_{16}N_2$	$C_{25}H_{18}N_2$	$C_{28}H_{20}N_2$	$C_{26}H_{18}N_2$
Molecular mass [g/mol]	296.4	346.4	384.5	358.4
Crystal size [mm]	0.38 × 0.34 × 0.24	0.62 × 0.21 × 0.06	0.36 × 0.20 × 0.16	0.50 × 0.32 × 0.32
Crystal color	colorless	yellow	yellow	yellow
Crystal shape	polyhedron	polyhedron	polyhedron	polyhedron
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a [Å]	8.7077(2)	17.7543(2)	9.3094(5)	9.044(3)
b [Å]	10.0298(1)	8.7942(2)	9.4929(5)	26.4122(8)
c [Å]	18.6124(5)	12.0276(1)	12.3892(6)	16.3152(5)
α [°]	90	90	78.215(1)	90
β [°]	90.568(2)	91.753(1)	84.443(1)	103.247(1)
γ [°]	90	90	66.519(1)	90
V [Å^3]	1625.46(6)	1877.05(5)	982.90(9)	3776.9(2)
$D_{\text{calcd.}}$ [g/cm^3]	1.21	1.23	1.30	1.26
Z	4	4	8	8
Temperature [K]	200(2)	200(2)	200(2)	200(2)
$h_{\text{min}}/h_{\text{max}}$	−9/9	−23/23	−12/12	−11/11
$k_{\text{min}}/k_{\text{max}}$	−7/11	−11/11	−12/12	−34/34
$l_{\text{min}}/l_{\text{max}}$	−21/18	−15/15	−16/16	−21/21
μ [mm^{-1}]	0.072	0.072	0.076	0.074
Refl. collected	6119	18819	16193	38466
Refl. unique	2559	4315	4500	8659
Refl. observed	2019	2474	3048	6007
Variables [$I > 2\sigma(I)$]	272	316	351	577
R (F)	0.037	0.063	0.048	0.049
Rw (F^2)	0.089	0.152	0.109	0.107
S (Gof) on F^2	1.03	1.03	1.03	1.03
$(\Delta)_{\text{max}}$ [eA^{-3}]	0.12	0.48	0.25	0.24
$(\Delta)_{\text{min}}$ [eA^{-3}]	−0.13	−0.22	−0.23	−0.19

(CH), 129.6 (C), 131.2 (C), 131.6 (C), 131.8 (C), 132.1 (C), 132.4 (C), 154.8 (C), 195.8 (C). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 246 (4.3), 274 (4.0), 282 (4.1), 330 (3.9), 348 (4.1), 358 (4.1) nm. − HRMS (EI, 70 eV): calcd. 382.1470; found 382.1490.

Syntheses of 2-(Bicyclo[2.2.1]heptane-2-ylidene)propanedinitrile (41): The Knoevenagel condensation was carried out in an analogous manner to the protocol used for the syntheses of **22**−**27**. Starting materials were bicyclo[2.2.1]heptan-2-one (**28**) (440 mg, 4 mmol), propanedinitrile (**21**) (1.4 g, 21 mmol), ammonium acetate (1.4 g, 18 mmol), acetic acid (4.2 mL), and toluene (50 mL). Yield: 516 mg (83%) of **41** as a colorless oil. − R_f [silica gel; petroleum ether (boiling range 30−40 °C)/diethyl ether, 4:1] = 0.24. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29−1.37 (m, 2 H), 1.56 (s, 2 H), 1.70−1.76 (m, 1 H), 1.93−1.98 (m, 1 H), 2.60 (d, J = 9.4 Hz, 1 H), 2.51 (d, J = 9.5 Hz, 1 H), 2.62 (s, 1 H), 3.41 (d, J = 3.5 Hz, 1 H). − ^{13}C NMR (125.8 MHz. $CDCl_3$): δ =27.4 (CH_2), 28.4 (CH_2), 37.2 (CH), 40.5 (CH_2), 42.2 (CH_2), 48.1 (CH), 79.2 (C), 112.4 (CN), 193.7 (C). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 244 (5.2) nm. − HRMS (EI, 70 eV): calcd. 158.0844; found 158.0833. − $C_{10}H_{10}N_2$ (158.2): calcd. C 75.92, H 6.37, N 17.71; found C 75.82, H 6.42, N 17.50.

X-Ray Diffraction Analyses: The reflections were collected with a Bruker Smart CCD diffractometer (Mo-K_α radiation, graphite monochromator). Intensities were corrected for Lorentz and polarization effects. The structures were solved by direct methods using SHELXS-97[20]. The structural parameters of the non-hydrogen atoms were refined anisotropically. Table 2 contains the crystallographic data and details of the refinement procedure. ORTEP drawings were obtained using the ORTEP-3 for Windows program[21] by L. Farrugia. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-155614 (**22**), -155615 (**24**), -155616 (**27**), -155617 (**39**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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