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Synthesis and spectroscopy of anthracene-containing linear and 'T'-shaped π-conjugated ligands

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Abstract

A range of new π-conjugated ethynyl- and diethynyl-benzene ligands has been synthesised and their spectroscopic characterisation carried out, most notably via IR and ^{1}H NMR. X-ray crystal structures were obtained for three of these ligands and one unusual ruthenium complex. Both the 4-ethynyl- and 2,5-diethynyl-benzene cores of these compounds have been functionalised through organic transformations by addition of an 9-anthracenyl. This has been attached via a range of linker moieties that vary in both their length and degree of π-conjugation. This has given rise to two groups of compounds with either a linear, e.g., 9-(2-(4-ethynylphenyl)ethynediyl)anthracene and 9-(2-(4-ethynylphenyl)ethyl)anthracene, or 'T'-shaped morphologies, e.g., 9-(2-(2,5-diethylnylphenyl)ethyl)anthracene.

Keywords: Metal-alkynyl; π-Conjugated ligands

1. Introduction

Considerable efforts have been made in preparing and characterising π-conjugated organic molecules with relatively high conductivities suitable as frameworks for future molecular electronic applications [1–3]. However, molecular conductors are not the sole requirement for preparing molecular analogues to modern electronic components. For this, molecular analogues to the fundamental unit of electronics, i.e. transistors, are required [4]. Such an analogue would have to appear schematically the same as a transistor, namely, possessing three terminals. One terminal would allow a signal to be received by the molecular transistor and translated into a modification of the properties of the molecule between the remaining two terminals. The signal should be applied via an additional moiety attached via a linker to the basic conductive framework, as this would allow variation of the switching signal with a minimised impact on the operation of the framework. This signalling 'antenna' moiety would take the form of a group that may interact with the macroscopic world by, for example, oxidation and reduction or by absorption of light, changing the properties of the conductive framework.

With these considerations in mind, we report herein a series of new π-conjugated ligands possessing a π-conjugated framework (the ethynyl benzene moieties) and an antenna group (anthracene). These two components are connected via a range of linkers that vary in their physical length, flexibility and electronic properties. In addition, trends in the spectroscopic data (^{1}H NMR, IR) are also analysed to obtain information about possible electronic communication, and the formation of an unusual ruthenium complex.

2. Results and discussion

2.1. Synthesis of linear ligands

In order to systematically examine the effects of an anthracene moiety upon a nearby π-conjugated ethynylbenzene ligand the two were covalently attached via a range of linker groups. These linkers vary both in physical length

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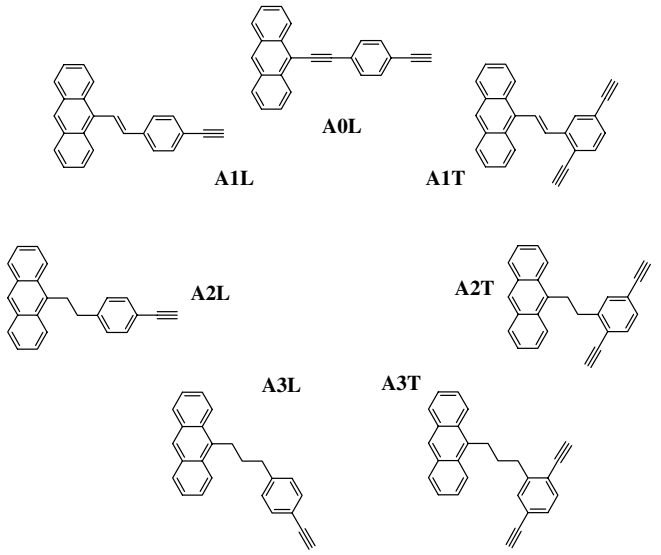

Fig. 1. Compound structures and abbreviations used throughout the following discussion: **A**, anthracene; **0**–**3**, length of linker moiety; **L**,**T**, linear or 'T'-shaped geometry.

and degree of unsaturation, giving rise to a range of anthracene-functionalised mono- and di-topic ligands, shown in Fig. 1. The labelling is due to 9-anthracene (**A**), the spacing unit may be either ethynyl, ethenyl, ethyl or propyl giving rise to the '**0**'–'**3**' parts, respectively (the numbering starts at '**0**' to give the ethyl and propyl species the more intuitive '**2**' and '**3**' labels). The core benzene ring may be either 4- or 2,5-substituted resulting in the ethynyl groups being either in line with, or as the crossbar of a '**T**' to the antenna moiety hence '**L**' (linear) or '**T**' abbreviations.

2.2. Synthesis of *A0L*

The synthesis of ligand **A0L**, 9-(4-ethynyl-phenylethynediyl)-anthracene, was straightforward due to its high symmetry. Thus, the ethynyl linker of **A0L** was prepared by simply coupling a 1.1:1 mixture of commercially available 1,4-diethynylbenzene and 9-bromoanthracene using Sonogashira conditions. A small amount of the expected disubstituted 1,4-di(2-(9-anthracenylethynediyl)-benzene) was formed but this was typically a minor product and the desired **A0L** could be obtained as a bright yellow crystalline solid via column chromatography. Further purification was possible by recrystallising from a DCM/hexane solution. This compound when in solution exhibited a strong blue fluorescence under ambient laboratory illumination, visible to the naked eye, which allowed a qualitative determination of the progress of the coupling reaction.

The ^{1}H NMR spectrum of **A0L** displayed the expected anthracene set of signals and those associated with the core phenyl ring and terminal acetylene. A singlet at 3.22 ppm is due to the terminal ethynyl proton, between 7.50 and 8.50 ppm are the aromatic resonances and working from low field to high field they are due to the protons on anthracene, i.e. a 4-position doublet, 10-position singlet, 1-position doublet. The remaining protons, anthracene 2- and 3-positions and the phenyl ring, give overlapping signals.

The IR spectrum recorded from a DCM solution of **A0L** showed both the terminal ethynyl carbon–proton and carbon–carbon stretches at 3296 and 2110 cm^{-1}, respectively. Uniquely, within this series of compounds, **A0L** displayed a second C≡C stretch at 2196 cm^{-1} due to the internal ethynyl group. The marked difference between the stretching frequencies of the two carbon–carbon triple bonds is due to a peculiarity associated with terminal acetylenes. This involves the vibrations of the carbon–proton bond coupling with those of the carbon–carbon bond, disproportionately lowering the apparent strength of the terminal triple bond [5].

2.3. Synthesis of *A1L*

Compound **A1L**, 9-[2-(4-ethynyl-phenyl)-vinyl]-anthracene, was prepared via a Wittig reaction, coupling the ylide derived from a 9-anthracene methylphosphonium salt and an ethynyl substituted benzaldehyde, to yield the desired *trans* carbon–carbon double bond linker. ^{1}H NMR spectroscopy showed two doublets at 7.95 and 6.94 ppm with equal $^3J_{H-H}$ coupling constants of approximately 16 Hz from the two ethenyl protons. Again this compound was isolated as a bright yellow solid, which crystallised very easily from a concentrated DCM solution. In contrast to **A0L**, **A1L** exhibited a strong green fluorescence, which was visibly weaker than that of **A0L**. In addition to the ethenyl proton signals, the ^{1}H NMR spectrum of this ligand also displayed the expected anthracene set of peaks between 7.50 and 8.50 ppm along with a peak at 3.17 ppm associated with the terminal acetylene. The *trans* geometry of the carbon linkages was confirmed by an X-ray crystal structure. Compound **A1L** (Fig. 2) crystallises with two independent molecules (**A** and **B**) in the asymmetric unit. Their conformations are virtually identical, a best-fit of the non-hydrogen atoms having a RMS deviation of only 0.14 Å. The small differences in conformation are in the torsional twists about the C(6)–C(9) and C(10)–C(11) which are 3° and 51° in one molecule and 14° and 48° in the other. As is observed in **A3L** (see later) there are no π–π stacking interactions involving either the phenyl or anthracene ring systems. There are, however, extensive C–H···π interactions between the two independent molecules (Fig. 3).

2.4. Synthesis of *A2L*

Compound **A2L**, 9-[2-(4-ethynyl-phenyl)-ethyl]-anthracene, was prepared via a Wittig reaction, as for **A1L**, followed by reduction of the central ethenyl linker to the ethyl analogue. This synthetic route required that the terminal ethynyl group was added, via a Sonogashira coupling of the aryl bromide with TMSA, following the reduction of the linker double bond (Fig. 4) rather than before

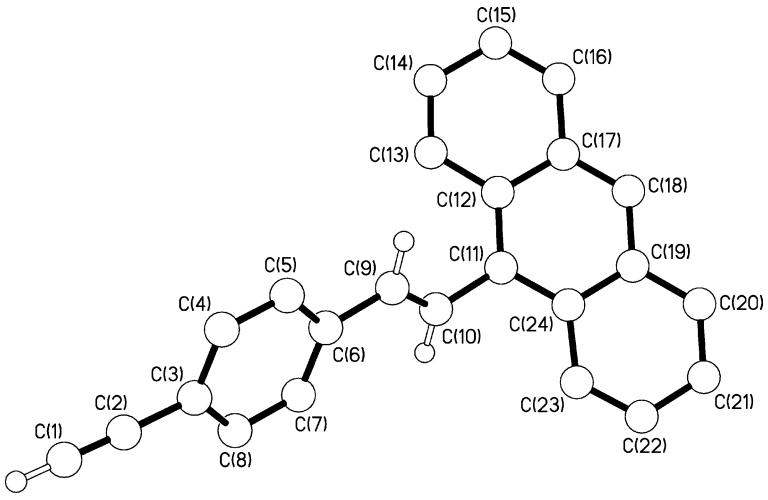

Fig. 2. One (**A**) of the pair of independent molecules in the structure of **A1L**. Selected bond lengths (Å) and bond angles (°) [values for the second independent molecule (**B**) in square parentheses]; C(6)–C(9) 1.476(5) [1.464(4)], C(9)–C(10) 1.307(4) [1.333(4)], C(10)–C(11) 1.477(5) [1.468(4)] and C(10)–C(9)–C(6) 128.3(3) [127.8(3)], C(9)–C(10)–C(11) 124.0(3) [123.8(3)].

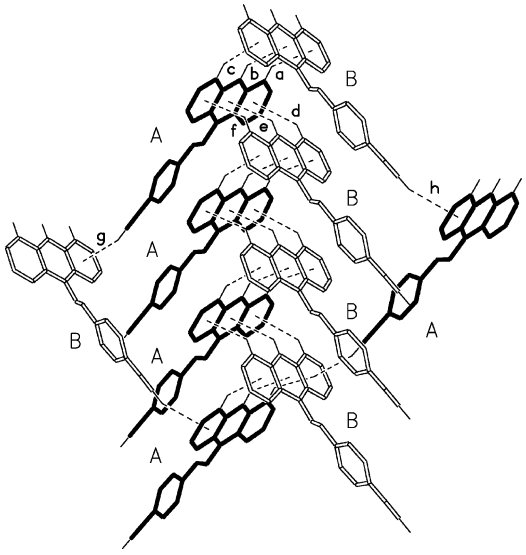

Fig. 3. The packing of the molecules in the structure of **A1L** showing the extensive C–H···π interactions. These interactions have: [H···π (Å), [C–H···π (°), (a) 2.99, 138; (b) 2.94, 141; (c) 2.68, 164; (d) 3.07, 144; (e) 2.98, 139; (f) 2.69, 137; (g) 2.62, 161; (h) 2.96, 145.

the Wittig reaction as for **A1L**. Initially, this reduction was attempted by dissolving a precursor to **A1L**, **A1PhBr**, 9-[2-(4-bromo-phenyl)-vinyl]-anthracene, in a mixture of methanol and diethyl ether followed by addition of magnesium turnings [6]. As the magnesium dissolved, liberating hydrogen gas, the colour of the initially yellow/fluorescent green solution diminished in intensity to be colourless after 30–60 min. Following an acidic workup and purification via column chromatography, compound **A2*PhBr**, 9-[2-(4-bromo-phenyl)-ethylidene]-9,10-dihydro-anthracene, was isolated. Notably this compound, whilst having been reduced to the required degree for **A2L**, had rearranged to yield a compound with a 9,10-dihydro-anthracenyl antenna rather than the desired 9-anthracenyl species. This rearrangement was apparent in the ^{1}H NMR spectrum of **A2*PhBr** in that the four characteristic anthracene peaks between 7 and 8 ppm had condensed to a single multiplet. Additionally, new proton peaks were observed; firstly, an ethylene resonance of integration 1 proton was observed at 6.16 ppm along with two new methylene resonances at 3.9 ppm with integration of 4 protons. The rearranged structure was confirmed by X-ray crystallographic analysis of a Ru(dppm)Cl complex, **A2*L**[**Ru**]. This complex was prepared in two steps by first forming the vinylidene species by addition of **A2*L** to a solution of $NaPF_6$ and $Ru(dppm)_2Cl_2$ in DCM. This complex was then deprotonated with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to yield the desired acetylide complex [7].

As revealed by the X-ray structure of **A2*L**[**Ru**], the ligand synthesis had not progressed as expected to give the anthracene containing compound **A2L** but a 10-hydroanthracene containing molecule instead. Complexation of the latter to the ruthenium centre is via the ethynyl carbon atom to give the complex illustrated in Fig. 5. The geometry at the metal centre is distorted octahedral with *cis* angles in the range 70.99(5)–108.96(5)°, the acute angles corresponding to the bite of the phosphine ligands (Table 1). The 'equatorial' RuP_4 atoms are coplanar to within 0.03 Å and the Cl···C(1) vector is inclined by ca. 83° to this plane. The Ru–P, Ru–Cl, Ru–C(1), C(1)≡C(2) and C(2)–C(3) bond lengths (Table 1), do not differ significantly from those observed in other related chloro-phenylacetylene-bis(bis(diphenylphosphino)methane)ruthenium containing complexes [8]. It is noteworthy that in these related complexes the Cl···C(ethynyl) vector is also significantly inclined to the normal of the RuP_4 plane. The only intermolecular packing interaction of note is a weak π–π stacking of the C(19)–C(24) rings of centrosymmetrically related molecules; the centroid···centroid and mean interplanar separations are 4.45 and 3.42 Å, respectively.

As the ligand rearrangement may have been due to either a specific problem with the method of reduction or

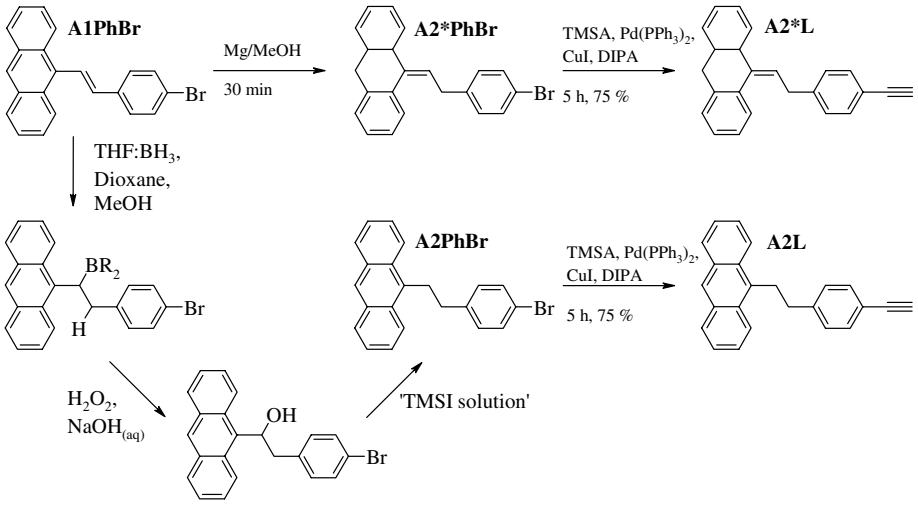

Fig. 4. Syntheses of **A2L** and **A2*L**. Notably, whilst only one isomer is shown above, the hydroboration of **A1PhBr** produced both regioisomers of the product borane, with the boron atom at both the anthracenyl and phenyl ends of the linker.

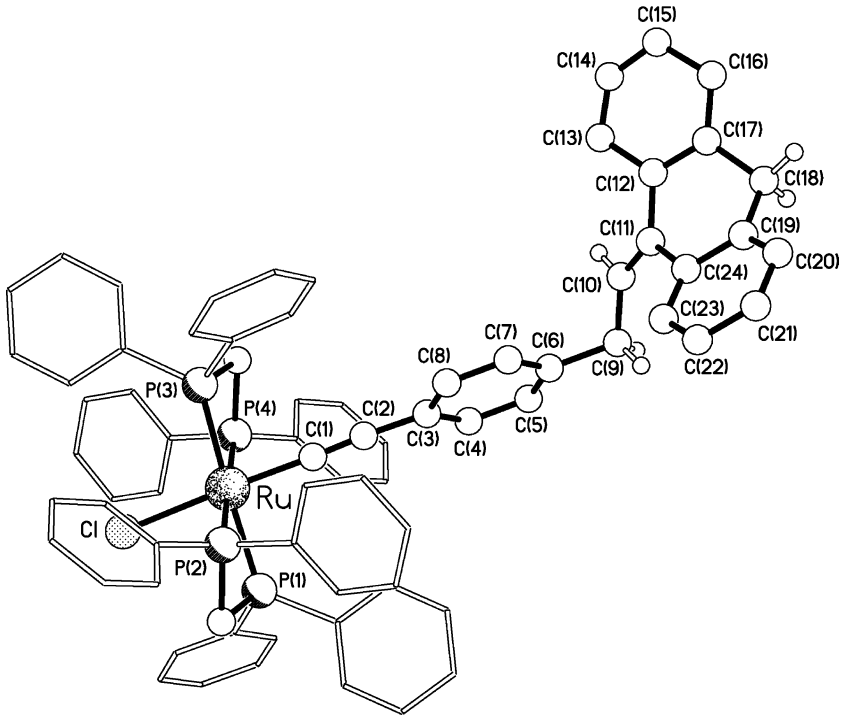

Fig. 5. Structure of compound **A2*L[Ru]**. Note the sp^3 hybridised C(18) and sp^2 hybridised C(10).

an intrinsic instability of the ethyl linker when placed between anthracenyl and phenyl rings, an alternative two-step reduction was developed (Fig. 4). In the event of the ethyl linker being intrinsically unstable, this would allow isolation of an intermediate compound with a reduced linker moiety. The two-step reduction took the form of first hydroborating the ethenyl linker of **A1PhBr** with a THF solution of freshly prepared $THF:BH_3$ [9,10], followed by an oxidative cleavage of the carbon–boron bond using aqueous solutions of potassium hydroxide and hydrogen peroxide. This yielded a mixture of regioisomers of the expected secondary alcohol, which were both reduced with trimethylsilyl iodide (TMSI) [11–13] to give **A2PhBr**, which was then converted to the desired **A2L** by coupling TMSA to the 4-position of the phenyl ring using Sonogashira conditions. The ligand **A2L** was isolated as a colourless oil, which solidified upon standing. The ^1H NMR spectrum for this compound showed the expected anthracene and ethynyl proton peaks. However, the peaks due to the ethyl linker's methylene protons were of particular interest. These were, rather than the expected triplets, relatively complex multiplets similar to triplet signals with additional internal fine structure – presumably due to restricted rotation around the linker bonds vide infra.

Table 1
Selected bond lengths (Å) and bond angles (°) for **A2*L[Ru]**

Ru–Cl	2.5033(11)	Ru–P(1)	2.3684(14)
Ru–P(2)	2.3269(13)	Ru–P(3)	2.3498(14)
Ru–P(4)	2.3124(13)	Ru–C(1)	1.999(5)
C(1)–C(2)	1.198(7)	C(2)–C(3)	1.450(7)
C(6)–C(9)	1.554(8)	C(9)–C(10)	1.440(11)
C(10)–C(11)	1.354(11)		
C(1)–Ru–P(4)	85.6(2)	C(1)–Ru–P(2)	93.0(2)
P(4)–Ru–P(2)	178.59(5)	C(1)–Ru–P(3)	82.9(2)
P(4)–Ru–P(3)	71.05(5)	P(2)–Ru–P(3)	108.96(5)
C(1)–Ru–P(1)	94.6(2)	P(4)–Ru–P(1)	108.94(5)
P(2)–Ru–P(1)	70.99(5)	P(3)–Ru–P(1)	177.54(4)
C(1)–Ru–Cl	178.02(14)	P(4)–Ru–Cl	95.63(5)
P(2)–Ru–Cl	85.77(5)	P(3)–Ru–Cl	98.95(4)
P(1)–Ru–Cl	83.51(4)	C(2)–C(1)–Ru	177.4(5)
C(1)–C(2)–C(3)	176.7(6)	C(10)–C(9)–C(6)	113.4(6)
C(11)–C(10)–C(9)	133.4(10)		

2.5. Synthesis of *A3L*

The propyl linker of compound **A3L** was prepared by coupling 9-acetylanthracene and 4-ethynylbenzaldehyde using sodium hydroxide in ethanol via an Aldol reaction [14]. This proceeded smoothly to yield the desired diaryl α,β-unsaturated ketone intermediate **A(enone)PhBr**. This unsaturated linker was reduced firstly to the secondary alcohol, by reaction of sodium borohydride in a dioxane/ethanol mixture [15], followed by reduction to the desired **A3L** using TMSI. **A3L** was also isolated as a colourless oil, which solidified upon standing. On this occasion, however, the compound solidified as a mat of needle-like crystals suitable for X-ray structure determination vide infra. The ^{1}H NMR spectrum for this compound showed some similarities to that of **A2L** with the addition of a third peak at 2.14 ppm due to the central methylene protons of the linker. However, in the case of **A3L** only the anthracenyl-methylene protons gave a complex multiplet signal while the other linker protons gave peaks with the expected multiplicities. This is rationalised in terms of less steric hindrance allowing greater rotational freedom of these methylene groups, and resulting in the idealised triplet and quintet splitting patterns (Table 2). A single crystal X-ray analysis showed compound **A3L** to have crystallised with two independent molecules **A** and **B** in the unit cell (Table 3). These molecules have distinctly different conformations, with in **A** the C–CH_2–CH_2–CH_2–C backbone linking the two ring systems having an all-*anti* conformation, whereas in **B** the conformation about one of these bonds [C(10′)–C(11′)] is *gauche* (Fig. 6). The torsional twists about the C(6)–C(9) and C(11)–C(12) bonds in **A** are ca. 68° and 86°, whilst their counterparts in **B** are ca.

Table 2
^{1}H NMR data for those ligands with linkers possessing protons pertaining to the behaviour of the individual methylene units within the linker

Ligand	Position of methylene in linker		
	Anthracenyl	Central	Phenyl
A1L	7.95 (16.6)	–	6.94 (16.5)
A2L	3.88 (m)	–	3.09 (m)
A3L	3.60 (pt)	2.14 (m)	2.88 (t)

$^3J_{H–H}$ coupling is noted for A1L and is shown in brackets, pt – pseudo triplet.

Table 3
Selected bond lengths (Å) and bond angles (°) for **A3L**

C(6)–C(9)	1.518(7)	C(6′)–C(9′)	1.564(8)
C(9)–C(10)	1.522(7)	C(9′)–C(10′)	1.478(9)
C(10)–C(11)	1.542(7)	C(10′)–C(11′)	1.522(8)
C(11)–C(12)	1.505(7)	C(11′)–C(12′)	1.503(7)
C(6)–C(9)–C(10)	112.5(4)	C(6′)–C(9′)–C(10′)	113.1(6)
C(9)–C(10)–C(11)	112.6(4)	C(9′)–C(10′)–C(11′)	110.5(6)
C(12)–C(11)–C(10)	111.0(4)	C(12′)–C(11′)–C(10′)	114.1(4)

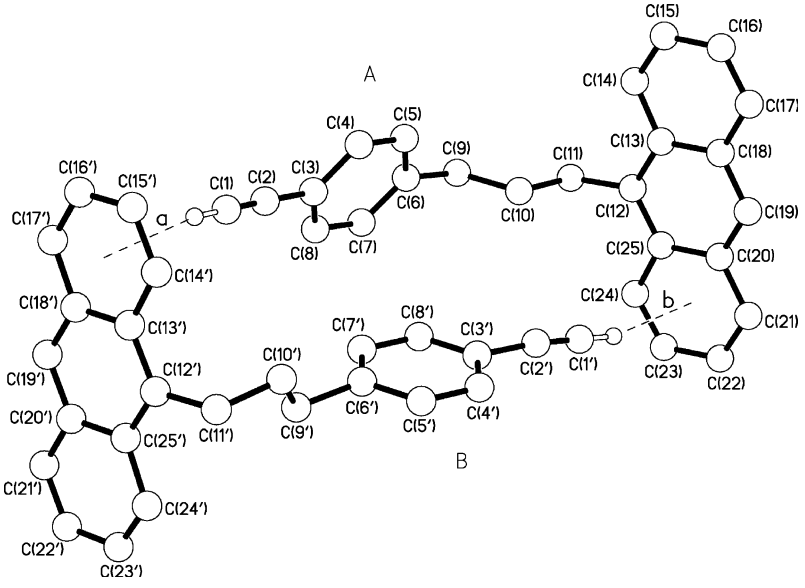

Fig. 6. The pair of independent molecules in the structure of **A3L**. The C–H···π interactions have: [H···π (Å), [C–H···π (°), (a) 2.61, 171; (b) 2.87, 164.

64° and 73°. Molecule **B** is disordered, there being a minor occupancy (30%) overlapping conformer where the signs of the torsional angles about the bonds linking the two ring systems are reversed. Surprisingly, there are no π–π stacking interactions involving either the phenyl or anthracene ring systems. The only intermolecular interactions of note are a pair of C–H···π interactions between the terminal ethynyl hydrogen atoms in molecules **A** and **B** and one of the C_6 rings of the anthracene units of **B** and **A**, respectively (Fig. 6).

3. Trends in the spectroscopic data for the anthracene-containing linear ligands

3.1. ^1H NMR of the terminal ethynyl and linker protons

It is worth noting spectroscopic trends in the behaviour of the linear ligands, **A(0–3)L**. Of particular interest is the effect the pendant anthracene has on the terminal acetylene groups and the extent that the central linker mediates this. ^{1}H NMR has been used to examine the acetylene protons for the ligands **A(0–3)L** and the data are displayed below (Table 4) (ethynylbenzene, **EB** was used as a standard aromatic substituted terminal acetylene for comparison). From these results, it is worthy of note that the acetylene protons of the ligands with saturated linkers **A(2–3)L** appear unaffected by the addition of a pendant anthracene, or indeed addition of the saturated linker. This is not so surprising as the saturated linker effectively insulates the ethynyl benzene moiety from the π-system of anthracene, which should otherwise interact strongly with the π-system of the ethynyl benzene core. However, this is not necessarily a trivial result, as although the alkyl linker cannot interact via π-conjugation with the core ethynyl benzene it is σ-electron donating and may have had an observable effect on the electronics of the core. Additionally, it is possible that such flexible linkers, especially in the case of **A3L**, might allow a through space, rather than through bond, interaction between the terminal acetylene and anthracene π-system. In contrast to the ^{1}H NMR spectra of **A(2–3)L**, those of the ligands with unsaturated linkers, **A(0–1)L**, show distinct variation of the ethynyl proton signal compared to that of **EB**. Both ligands possess extended π-systems throughout their structures allowing for a through-bond interaction between the anthracenyl and ethynyl groups to occur. However, in contrast to those ligands with saturated linkers, clearly the chemical shift of the terminal acetylenic protons in **A(0–1)L** should also be affected by the π-conjugated linker group. Therefore, to differentiate between the intrinsic effects of the linker groups from their ability to conduct the effect of the attached anthracene, comparisons of **A0L** and **A1L** with diethynylbenzene (**DEB**) and ethynylstyrene were made (Table 5). On initial examination of the data, it may be seen that the linker groups have relatively large different effects on the terminal ethynyl group. Comparison of **EB**, **DEB** and 4-ethynylstyrene shows that the inclusion of an additional ethynyl group causes a downfield shift of the ethynyl protons more than twice as large as that caused by the addition of an ethenyl group, +0.09 ppm vs. +0.04 ppm, respectively.

It is interesting to note that from the data shown in Table 5, the acetylenic proton shifts of **A0L** and **A1L** appear to be equally affected by the presence of an attached anthracene, approximately +0.06 ppm. It was thought that the two unsaturated linkers would provide different degrees of conjugation between antenna and core moieties. However, this unexpected result may have its origins in the differing flexibility of the two linkers in combination with their degree of unsaturation.

Table 4
Combined ^{1}H NMR data for **A(0–3)L** relating to the properties of the terminal acetylene groups in each case, compared with that of ethynylbenzene (**EB**)

Compound	Acetylene proton δ/ppm	Difference vs. MEB/ppm
EB	3.07	
A0L	3.22	0.15
A1L	3.17	0.10
A2L	3.07	0.00
A3L	3.07	0.00

Table 5
Comparison of the ^{1}H NMR acetylenic proton shifts of **A0L** and **A1L** with those of 1,4-diethynylbenzene and 4-ethynylstyrene, respectively

Compound	Acetylene proton δ/ppm	Difference vs. standard/ppm	Difference vs. **EB**/ppm
EB	3.07		
DEB	3.16		+0.09
A0L	3.22	+0.06	+0.15
4-Ethynylstyrene	3.11		+0.04
A1L	3.17	+0.06	+0.10

Additionally, comparisons of all the compounds are made with ethynylbenzene.

3.2. IR spectroscopy of the ethynyl groups

In addition to ^{1}H NMR, the IR behaviour of ligands **A(0–3)L**, in particular the ethynyl groups, was examined and is tabulated below (Table 6). In contrast to the ^{1}H NMR data collected for these ligands, there appears to be very lit-

Table 6
Combined IR data for **A(0–3)L** relating to the properties of the terminal acetylene groups in each case and compared with that of ethynylbenzene (EB)

Compound	ν≡CH/cm^{-1}	Difference vs. **EB**/cm^{-1}	νC≡C/cm^{-1}	Difference vs. **EB**/cm^{-1}
EB	3294		2111	
A0L	3296	+2	2110[a]	−1
A1L	3295	+1	2105	−6
A2L	3299	+5	[b]	[b]
A3L	3298	+4	2109	−2

[a] Internal C≡C bond stretch occurs at 2196.0 cm^{-1}.
[b] Peak too weak and not observed.

tle variation across the series of compounds associated with the ethynyl groups. The variation in the stretching frequency of the terminal acetylenic C–H bond varies by less than five wavenumbers between ethynylbenzene and the ligands. However, the ligands do seem to fall into two groups, based upon C–H stretching frequency, those with π-conjugated linkers and those with saturated hydrocarbon linkers. These two groups display C–H stretching frequencies approximately the same as, and 4 cm^{-1} higher in energy than the standard EB, respectively. The variation in the C≡C stretching frequency is slightly larger, however, as the peaks associated with these IR absorptions are typically very weak the error associated with their energies is greater than that for the C–H bond stretches.

3.3. 'T'-shaped ligand syntheses

Compounds 9-[2-(2,5-diethynyl-phenyl)-vinyl]-anthracene (**A1T**), 9-[2-(2,5-diethynyl-phenyl)-ethyl]-anthracene (**A2T**) and 9-[3-(2,5-diethynyl-phenyl)-propyl]-anthracene (**A3T**) were prepared as for their linear analogues, however, in these cases the required benzaldehyde precursor was not commercially available and was instead prepared via chromium(VI)oxide/sulphuric acid oxidation of 2,5-dibromotoluene [16]. This oxidation was carried out in a mixture of acetic acid and acetic anhydride in order to avoid over oxidation to 2,5-dibromobenzoic acid. The initial step yielded a diester, which was then hydrolysed by heating in a solution of H_2SO_4 in a mixture of water and ethanol to yield the desired aldehyde. This had the expected ^1H NMR resonances at 10.3, 8.0 and 7.6 ppm for the aldehyde and phenyl ring protons, respectively.

In addition to having to prepare the benzaldehyde precursor, the 'T'-shaped ligands displayed different behaviour than their linear analogues with respect to the coupling of TMSA to the core phenyl ring. In the case of the linear ligands this reaction proceeded smoothly, completing within 12 h and often in considerably less time. However, for the 'T'-shaped precursors this reaction proved to be unexpectedly troublesome, often resulting in only partial reaction despite extended reaction times and greater than stoichiometric quantities of TMSA. This difficulty is ascribed to the greater steric crowding associated with reaction *ortho* and *meta* rather than *para* to the antenna-linker group.

In its X-ray crystal structure determination, ligand **A1T** crystallises with only one independent molecule in the unit cell and has a conformation very similar to those observed for **2** (Fig. 7). The torsional twists about the C(2)–C(9) and C(10)–C(11) bonds are 17° and 50°, respectively, the phenyl and anthracene ring systems being mutually inclined by ca. 68° (cf. 52° and 61° for the two independent molecules of **A1L**). The intermolecular packing interactions are fairly complex; symmetry related molecules are linked by C–H···π interactions to form corrugated sheets (Fig. 8a) and adjacent sheets are linked by a combination of C–H···π and π–π stacking interactions (Fig. 8b).

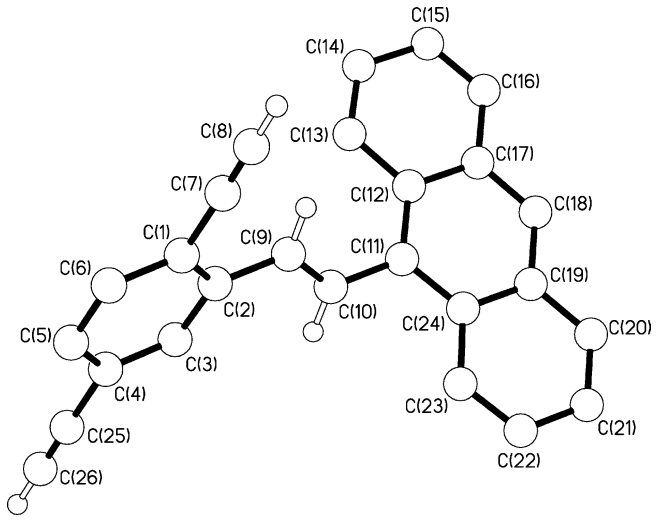

Fig. 7. The molecular structure of **A1T**. Selected bond lengths (Å) and bond angles (°); C(2)–C(9) 1.467(3), C(9)–C(10) 1.320(3), C(10)–C(11) 1.476(3), C(2)–C(9)–C(10) 125.8(2), C(9)–C(10)–C(11) 126.9(2).

4. Trends in the spectroscopic data for the the 'T'-shaped ligands A(1-3)T

4.1. ^1H NMR of the terminal ethynyl and linker protons

As for the linear ligands, it is useful to compare the spectral properties of this new set of 'T'-shaped ligands. Again, to gauge the effect of the linker upon communication between the antennae to the rest of the ligand, the ^1H NMR resonances associated with the ethynyl protons are of interest (Table 7). Worthwhile comparisons of these data include the variation of the peak positions relative to those of 1,4-diethynylbenzene, **DEB**. Such a comparison shows that the ppm values for the high field proton signals for all the ligands are quite similar to the single resonance from **DEB**. This suggests that the ethynyl protons associated with this high field peak are all likely to be in the *meta*-position to the linker, resulting in little communication between it and the antenna-linker moiety. This has indeed been confirmed by recording spectra of mono-ethynylated derivatives of **A2T** of known substitution pattern. Additionally, it is notable that the high field ethynyl protons of **A2T** and **A3T** are not exactly the same, as would be expected for a system where the only antenna-ethynyl proton communication is via the linker. This suggests that there may be some other, possibly through-space, interaction between the anthracene and/or linker group and the ethynyl group in either **A2T** or **A3T**. Additionally for **A(2–3)T** comparison of the low-field ethynyl proton resonances also shows some unusual patterns. Despite the apparently near identical electronic environments of the two sets of ethynyl groups, the low field resonance of **A2T** is significantly different from that of **A3T** (+0.32 and +0.11 ppm vs. **DEB**, respectively).

A possible explanation for this unexpected behaviour may involve one of the ethynyl protons in **A2T** being able

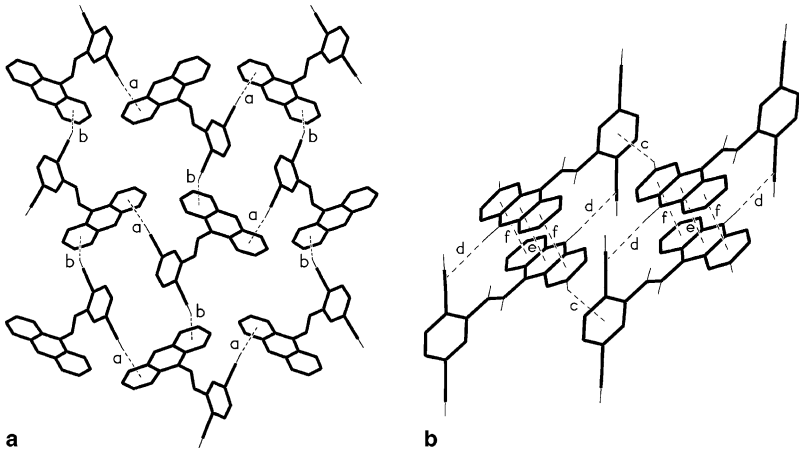

Fig. 8. (a) Part of one of the C–H···π linked corrugated sheets in the structure of **A1T**. (b) The C–H···π and π–π stacking interactions that link adjacent sheets. The C–H···π interactions have: [H···π] (Å), [C–H···π] (°), (a) 2.74, 163; (b) 3.00, 161; (c) 2.88, 143; (d) 3.01, 174. The π−π stacking interactions have centroid···centroid separations (e) and (f) of 3.85 Å and the mean interplanar separation between the anthracene rings is 3.60 Å.

Table 7
^{1}H NMR data associated with the ethynyl proton resonances for the 'T'-shaped ligands

Compound	High field acetylene proton δ/ppm	Low field acetylene proton δ/ppm	Peak separation/ppm
DEB		3.16	
A1T	3.25 (+0.09)	3.33 (+0.19)	0.08
A2T	3.22 (+0.06)[a]	3.48 (+0.32)[b]	0.26
A3T	3.16 (0.00)	3.25 (+0.11)	0.09

Numbers in parentheses are the differences between the ^{1}H NMR resonances due to each ligand and the standard 1,4-diethynylbenzene.
[a] Determined to be due to the *meta*-ethynyl group.
[b] Determined to be due to the *ortho*-ethynyl group.

to interact through space with the anthracene moiety. This interaction may take the form of a hydrogen bond between the ethynyl and anthracenyl groups. This type of bonding has already been observed in the X-ray structures of the anthracene containing ligands.

4.2. IR spectroscopy of the ethynyl groups

As for the linear ligands comparisons of the IR spectra of the 'T'-shaped ligands may also be made with particular respect to the ethynyl groups (Table 8). As for the linear ligands there is only a little variation in the IR peaks associated with the ethynyl groups. However, the slight decrease in stretching frequency of the C≡C group for all ligands relative to **DEB** may indicate a very small reduction in triple bond character for the ligands. Another notable feature is that despite the presence of two chemically distinct ethynyl groups, there is only one carbon–carbon triple bond and one ethynyl proton stretching frequency for all but one compound, **A2T**. In the case of **A2T** there appears to be a distinct shoulder on the peak associated with the carbon–carbon triple bond stretch. This is taken to be further supporting evidence for the anomalous variation in the two ethynyl groups of **A2T** vide supra.

Table 8
IR peaks associated with the ethynyl groups of the 'T'-shaped ligands

Compound	ν≡CH/cm^{-1}	Difference vs. **DEB**/cm^{-1}	νC≡C/cm^{-1}	Difference vs. **MEB**/cm^{-1}
DEB	3297		2111	
A1T	3300	+3	2105	−6
A2T	3297	0	2105/2108[a]	−6/−3
A3T	3298	+1	2107	−4

The differences in peak positions relative to those for diethynylbenzene (**DEB**) are also shown for comparison.
[a] Two values are given because, uniquely for **A2T** there were two peaks observed (a peak with a disinct shoulder).

5. Conclusions

A range of anthracene-functionalised 4-ethynyl- and 1,4-diethynylbenzene compounds have been prepared and characterised with respect to their solution state ^{1}H NMR and IR spectral properties. The linear and 'T-shaped' ligands were prepared via similar synthetic routes based upon the formation of the anthracene–phenyl ring linker via either Sonogashira, Wittig, or Aldol reactions. These initially formed linker moieties were further modified to yield the desired two- and three-carbon saturated and unsaturated hydrocarbon linkers. Sonogashira conditions were also used to couple terminal ethynyl groups to the core phenyl rings. In the preparation of the ethyl linker of **A2L** an unusual rearrangement of the anthracene moiety was observed. This involved the formation of an ethylidene-substituted 9,10-dihydro-anthracene group from a 9-ethenyl-anthracene precursor.

NMR analysis of the terminal ethynyl protons showed that the nature of the linker moiety has a significant effect on the degree of interaction between the anthracenyl antenna and the core ethynyl benzene moieties. Most notably, while the propyl and ethyl linkers should confer near identical electronic properties to their respective ligands ^{1}H NMR analysis shows that the terminal ethynyl protons

of **A2T** and **A3T** have different electronic environments. In addition to ^{1}H NMR and IR analysis it was observed that both the ligands possessing unsaturated and saturated linkers displayed a strong fluorescence, in the visible and near UV region, respectively. The detailed analysis of this fluorescent behaviour of both these groups of ligands, and their coordination to Pt metal centres will be presented in a forthcoming paper.

6. Experimental

6.1. General

All reactions were performed under a nitrogen atmosphere using standard schlenk techniques and all solvents were distilled over standard drying agents unless otherwise stated. All reagents were used as purchased from either Aldrich Chemical Company, Lancaster or Acros without purification. Silica gel (60 grade) was used for all column chromatographic separations ^{1}H NMR and ^{13}C NMR spectral were recorded using a Delta upgrade on a JEOL EX 270 MHz spectrometer. ^{1}H, ^{13}C and ^{31}P NMR chemical shifts are reported relative to $CDCl_3$ (residual proton impurities $^1H = \delta$ 7.26 ppm, $^{13}C = \delta$ 77 ppm) and H_3PO_4 ($^{31}P = \delta$ 0.00 ppm). Data are shown with assignments for which atoms are thought to be responsible for a particular peak. IR spectra were recorded on a Perkin–Elmer FT-IR spectrometer from samples in DCM solution. Analysis of IR spectra is limited for the most part to the effects of substitution on the strength of the carbon–carbon triple bond. Thus, the peaks quoted below refer to the carbon–proton and carbon–carbon stretches at approximately 3300 and 2100 cm^{-1}, respectively, UV–Vis spectra were recorded using a Thermo Electron Corporation Nicolet Evolution 100 absorption spectrometer. The absorption spectra are reported in terms of the wavelength of the peak absorptions and their intensities in parentheses. Mass spectra were recorded using a micromass Autospec Q spectrometer using an EI method. The spectra are reported in terms of the molecular ion and the most significant fragmentation peaks. Assignment of these peaks is based simply upon their m/z ratio and formulation of a reasonable fragmentation mechanism. The exception to this is for the assignment of the molecular ion peaks, which were additionally identified using a computerised isotope pattern predictor. X-ray structural analyses were carried out by Dr. Andrew J.P. White at the Chemical Crystallographic Laboratory, Imperial College. Elemental analyses were carried out by Stephen Boyer at the London Metropolitan University.

7. Synthesis of the linear anthracene-containing ligands

7.1. 9-(2-(4-Ethynylphenyl)ethynediyl)anthracene (*A0L*)

9-Bromoanthracene (257 mg, 1 mmol), dichlorobis(triphenylphosphine)palladium (7 mg, 0.01 mmol) and copper(I)iodide (3.9 mg, 0.02 mmol) were dissolved in DIPA cooled to 0 °C and stirred for 15 min. 1,4-Diethynyl benzene (189 mg, 1.5 mmol) was added and the mixture was heated to reflux for 15 h. The solvent was removed under vacuum and the resulting mixture was washed with 10% HCl solution (50 ml), water (50 ml), saturated sodium bicarbonate solution (50 ml) and water (50 ml). The trimethylsilyl-protected product was obtained pure from silica column chromatography (95:5 hexane:dichloromethane). Yield: 210 mg, 70%. ^{1}H NMR δ/ppm: 8.61 (2H d Anth), 8.42 (1H s 10-Anth), 8.00 (2H d Anth), 7.69 (2H d Anth), 7.53 (6H m 2/3-Anth + Ph), 3.22 (1H s a-CCH). ^{13}C NMR δ/ppm: 132.66, 132.22, 131.47, 131.18, 128.74, 128.08, 126.74, 126.63, 125.72, 124.10, 122.06, 116.84, 100.14, 88.40, 83.35, 79.04. Mass, m/z: 302 (M^+), 274 (–CCH), 124 (1,4-diethynylbenzene). IR/cm^{-1}: 3295.8 ν(CC–H), 2196.0 ν(ArC≡CAr′), 2109.9 ν(C≡CH). UV/nm: 10^{-5} M DCM. 428 (0.247), 404 (0.270), 313 (0.346), 299 (0.184), 266 (1.129). Elemental analysis: Calc. for $C_{24}H_{14}$: C, 95.33; H, 4.67. Found: C, 95.56, H, 4.63%.

7.2. 9-(2-(4-Ethylnylphenyl)ethenyl)anthracene (*A1L*)

7.2.1. 4-(2-Trimethylsilylethynyl)benzaldehyde

4-Trimethylsilylethynylbenzaldehyde was prepared from 4-bromobenzaldehyde (310 mg, 2 mmol) and trimethylsilyl acetylene (0.3 ml, 2.2 mmol), using a Heck coupling procedure as used for **A0L**. Silica column chromatography (DCM:hexane, 10:90) yielded the desired product. Yield: 360 mg, 89%. ^{1}H NMR δ/ppm: 9.86 (1H s C(O)H), 7.79 (2H d Ph), 7.57 (2H d Ph), 0.24 (9H s TMS). IR/cm^{-1}: 2158 ν(ArC≡CTMS).

7.2.2. 9-Bromomethylanthracene

9-Anthracene methanol (1248 mg, 6 mmol) was dissolved in dichloromethane (50 ml) and cooled in a dry ice/acetone bath with stirring. Boron tribromide (0.2 ml, 2 mmol) was added dropwise affording an initially green/blue suspension which turned brown. This was allowed to stir at −78 °C for 1 h and was then warmed to room temperature to complete the reaction. Water (10 ml) was then added, with stirring, to the cooled solution (−78 °C), which was then allowed to warm to room temperature. The organic layer was separated and washed with 10% aqueous HCl solution (20 ml), followed by water (20 ml), sodium bicarbonate solution (20 ml) and water and then dried over magnesium sulphate. Evaporation of the solvent yielded a product sufficiently pure for the next step. Yield: 1.45 g, 89%. ^{1}H NMR δ/ppm: 8.44 (1H s 10-Anth), 8.29 (2H d Anth-1), 8.00 (2H d Anth-4), 7.62 (2H m (pt) Anth-2/3), 7.48 (2H m (pt) Anth-3/2), 5.52 (2H s Anth-CH_2Br). Mass, m/z: 270/272 ($M^{+\ 79/81}$Br), 191 (Anth–Me).

7.2.3. 9-(Triphenylphosphoniumbromide)methylanthracene

9-Bromomethylanthracene (271 mg, 1 mmol) and triphenyl phosphine (288 mg, 1.1 mmol) were dissolved in toluene (50 ml) and heated to reflux with stirring for 3 h to yield a pale yellow suspension. The suspension was filtered off and

washed with several portions of diethyl ether to remove any unreacted starting material. The desired product was then obtained after recrystallisation from hot chloroform, as a cream powder. Yield: 455 mg, 85%. ^{1}H NMR δ/ppm: 8.27 (1H d 10-Anth), 7.79 (4H m Anth-1 and Anth-4), 7.49 (16H m Anth + Ph), 7.21 (2H m (pt) Anth-3/2), 7.15 (2H m (pt) Anth-2/3), 6.15 (2H d [$^2J_{H-P}$ 14 Hz] Anth-CH_2P).

9-(Triphenylphosphoniumbromide)methylanthracene (455 mg, 0.85 mmol) and potassium *tert*-butoxide (105 mg, 0.94 mmol) were dissolved in THF (50 ml) immediately forming a dark 'beetroot coloured' solution. This was allowed to stir at room temperature for 1 h to complete the formation of the ylide. A THF (20 ml) solution of 4-(2-trimethylsilylethynyl)benzaldehyde (122 mg, 0.94 mmol) was added and the reaction heated to reflux for 3 h yielding a yellow solution with a blue/green fluorescence. The mixture was cooled to room temperature and then washed with 10% aqueous HCl solution (20 ml), followed by water (20 ml), sodium bicarbonate solution (20 ml) and water (20 ml). The trimethylsilyl protected product was obtained pure after silica column chromatography (80:20, hexane:DCM). The trimethylsilyl group was then removed using potassium carbonate, as for 1,4-diethynyl benzene, to yield the desired product **A1L**. Yield. 155 mg, 60%. ^{1}H NMR δ/ppm: 8.42 (1H d 10-Anth), 8.31 (2H m 4-Anth), 8.00 (2H d 1-Anth), 7.95 (1H d [$^3J_{H-H}$ 16.6 Hz] C=C(H)-Anth), 7.59 (4H m Anth + Ph), 7.49 (4H m Anth + Ph), 6.94 (1H d [$^3J_{H-H}$ 16.5 Hz] C=C(H)–Ph) 3.18 (1H s CCH). ^{13}C NMR δ/ppm: 137.8, 136.6, 132.7, 132.4, 131.6, 129.8, 128.8, 126.8, 126.5, 126.3 , 125.9, 125.7, 125.3, 121.6, 83.8, 78.1. Mass, *m*/*z*: 304 (M^+), 202 (Anth–CH=CH), 176 (Anth). IR/cm^{-1}: 3294.9 ν(CC–H), 2105.2 ν(C≡4CH). UV/nm: 10^{-5} M DCM. 395 (0.120), 560 (1.055). Elemental analysis: Calc. for $C_{24}H_{16}$: C, 94.70; H, 5.30. Found: C, 94.53; H, 5.45%.

7.3. 9-(2-(4-Ethynylphenyl)ethyl)anthracene (*A2L*)

7.3.1. 9-(2-(4-Bromophenyl)ethenyl)anthracene

9-(2-(4-Bromophenyl)ethenyl)anthracene was prepared as for **A1L** using 4-bromobenzaldehyde rather than 4-(trimethylsilylethynyl) benzaldehyde in a Wittig reaction. ^{1}H NMR δ/ppm: 8.41 (1H s 10-Anth), 8.31 (2H m 4-Anth), 8.02 (2H d 1-Anth), 7.89 (1H d [$^3J_{H-H}$ 16.6 Hz] C=C(H)–Anth), 7.55 (4H m Anth + Ph), 7.49 (4H m Anth + Ph), 6.87 (1H d [$^3J_{H-H}$ 16.5 Hz] C=C(H)–Ph). Mass, *m*/*z*: 360/362 (M^+ + H $^{79/80}$Br), 282 (M^+–Br), 191 (Anth–Me), 179 (anth).

7.3.2. 9-(2-(4-Bromophenyl)-1l2-hydroxyethyl)anthracene

A solution of iodine (350 mg, 1.38 mmol) in THF (25 ml) was added slowly dropwise (60 min) to a cooled solution (0 °C) of sodium borohydride (132 mg, 3.5 mmol) in THF (25 ml). A THF solution (20 ml) of 9-(2-(4-bromo)ethenyl)anthracene (897.5 mg, 2.5 mmol) was added and the mixture stirred at room temperature for 1 h followed by heating to reflux for 4 h to complete the reaction. Water (2 ml) was added followed by addition of a mixture of aqueous hydrogen peroxide (6%, 25 ml) and sodium hydroxide (3 N, 5 ml) accompanied by an immediate darkening of the solution. Ether (50 ml) was then added and the organic layer was separated and washed with water (3 × 50 ml). The desired products were purified using silica column chromatography (80:20, hexane:DCM) to yield an almost equal mixture of the 1- and 2-hydroxyethyl derivative. Yield: 626 mg, 67%. ^{1}H NMR δ/ppm: 8.64 (1H br s C–OH), 8.43 (1H s 10-Anth), 8.28 (1H d Anth), 8.03 (2H d Anth) 7.55 (6H m Anth + Ph), 7.35 (1H d Anth), 7.20 (1H d Ph) 4.05 (1H m CH–O), 3.90 (1H m CH–O), 3.67 (2H m Anth–CH_2), 3.25 (2H m Ph–CH_2).

7.3.3. 9-(2-(4-Bromophenyl)ethyl)anthracene

A solution of 9-(2-(4-Bromophenyl)2′/1′-hydroxyethyl)anthracene (631 mg, 1.67 mmol) in hexane/dichloromethane (5 ml/15 ml) was added to the acetonitrile solution of freshly prepared TMSI and stirred at room temperature for 1 h. Water was then added and the product extracted with DCM. The organic layers were then washed with a saturated aqueous solution of sodium thiosulphate, to reduce the iodine by-product, followed by water (20 ml). The DCM solution was then dried over magnesium sulphate and evaporated to dryness in vacuo. The desired product was obtained from silica column chromatography (90:10, hexane:DCM). Yield: 0.49 mg, 81%. ^{1}H NMR δ/ppm: 8.38 (1H s 10-Anth), 8.24 (2H d Anth), 8.02 (2H d Anth) 7.50 (6H m Anth + Ph), 7.24 (2H d e-Ph), 3.87 (2H m h-CH_2), 3.04 (2H m g-CH_2). Mass, *m*/*z*: 362/360 (^{79}Br/^{81}Br M^+), 191 (Anth–Me).

9-(2-(4-Trimethylsilylethynylphenyl)ethyl)anthracene was prepared from 9-(2-(4-bromophenyl)ethyl)anthracene (0.49 mg, 1.36 mmol) and TMSA (0.19 ml, 1.49 mmol) using a Heck coupling reaction modified from that used for **A0L**. Yield: 68%. ^{1}H NMR δ/ppm: 8.37 (1H s 10-Anth), 8.26 (2H d Anth), 8.03 (2H d Anth) 7.49 (6H m Anth + Ph), 7.27 (2H d e-Ph), 3.88 (2H m h-CH_2), 3.08 (2H m g-CH_2). Mass, *m*/*z*: 378 (M^+), 281 (Anth-CH_2CH_2Ph), 203 (Anth-CH_2CH_2). The TMS protecting group was then removed using potassium carbonate as for 1,4-diethynylbenzne to yield **A2L**. Yield: 283 mg, Quant. ^{1}H NMR δ/ppm: 8.37 (1H s 10-Anth), 8.25 (2H d Anth), 8.02 (2H d Anth) 7.49 (6H m Anth + Ph), 7.31 (2H d e-Ph), 3.88 (2H m h-CH_2), 3.09 (2H m g-CH_2), 3.07 (1H s CCH). ^{13}C NMR δ/ppm: 143, 133, 132, 131, 129, 129, 128, 126, 126, 125, 124, 120, 84, 77 (hidden behind $CHCl_3$), 37, 30. Mass, *m*/*z*: 306 (M^+), 191 (Anth–Me). IR/cm^{-1}: 3298.7 ν(CC–H).UV/nm: DCM. 390 (0.060), 259 (0.903). Elemental analysis: Calc. for $C_{24}H_{18}$: C, 94.12; H, 5.58. Found: C, 93.90; H, 5.65.

7.4. 9-(3-(4-Ethylnylphenyl)propyl)anthracene (*A3L*)

7.4.1. 9-(3-(4-Bromophenyl)prop-2-enoneyl)anthracene

9-Acetylanthracene (440 mg, 2 mmol) and 4-bromobenzaldehyde were dissolved in non-distilled methanol fol-

lowed by three pellets of sodium hydroxide. The solution was briefly degassed, by cycling from a vacuum to nitrogen atmosphere four times, then stirred for 20 h. The resulting precipitate was filtered off and washed with water and small portions of methanol, yielding a product sufficiently pure for the next step. Yield: 718 mg, 93%. ^{1}H NMR δ/ppm: 8.54 (1H s Anth), 8.05 (2H m Anth), 7.88 (2H m Anth), 7.47 (6H m Anth + Ph), 7.26 (3H m Ph + C=CH), 7.15 (1H d C=CH).

7.4.2. 9-(3-(4-Bromophenyl)-1-hydroxypropyl)anthracene

9-(3-(4-Bromophenyl)prop-2-enoneyl)anthracene (718 mg, 1.85 mmol) was dissolved in a mixture of non-distilled dioxane (30 ml) and methanol (10 ml) followed by sodium borohydride (280 mg, 7.42 mmol). The mixture was briefly degassed as above and refluxed under nitrogen for 1 h. Water (10 ml) was then added to quench unreacted sodium borohydride and the solvent mixture was reduced in volume in vacuo. Ether was added and the organic layers washed with 10% aqueous HCl (20 ml), water (20 ml), saturated sodium bicarbonate solution (20 ml) and water (20 ml). The resulting oil was sufficiently pure for the next step. Yield: 704 mg, quantitative.

^{1}H NMR δ/ppm: 8.51 (1H br s OH), 8.39 (1H s Anth), 7.99 (2H m Anth), 7.42 (7H m Anth + Ph), 7.07 (2H d Ph), 6.22 (1H m Anth) 2.90 (1H m CH–O), 2.78 (3H m Ph–CH_2) 2.35 (1H m CH_2). Mass, *m*/*z*: 390/392 (^{79}Br/^{81}Br M^+), 205/208 (Anth–Me–OH), 178 (Anth).

7.4.3. 9-(3-(4-Bromophenyl)propyl)anthracene

TMSI (16.2 mmol) was prepared as for **A2L** into which 9-(3-(4-bromophenyl)-1-hydroxypropyl)anthracene (1.07 g, 2.7 mmol) was added as a hexane/DCM solution (5 ml/15 ml). The reaction was allowed to stir for 1 h at room temperature. Water (10 ml) was then added and the product extracted with DCM. The organic layers were then washed with a saturated aqueous solution of sodium thiosulphate, to reduce the iodine by-product, followed by water (20 ml). The DCM solution was then dried over magnesium sulphate and evaporated to dryness in vacuo. Silica column chromatography (80:20, hexane:DCM) yielded the desired product. Yield: 828 mg, 78%. ^{1}H NMR δ/ppm: 8.32 (1H s Anth), 8.12 (2H d Anth), 8.00 (2H d Anth), 7.44 (6H m Anth + Ph), 7.13 (2H m Ph), 3.60 (2H t Anth–CH_2), 2.83 (2H t Ph–CH_2), 2.11 (2H m CH_2). Mass, *m*/*z*: 374/376 (^{79}Br/^{81}Br M^+), 191 (Anth–Me), 178 (Anth).

9-(2-(4-Trimethylsilylethynylphenyl)propyl)anthracene was prepared from 9-(2-(4-bromophenyl)propyl)anthracene (845 mg, 2.25 mmol) and TMSA (0.34 ml, 2.48 mmol) using a Heck coupling reaction modified from that used for **A0L**. ^{1}H NMR δ/ppm: 8.33 (1H s 10-Anth), 8.12 (2H d Anth), 8.00 (2H d Anth), 7.46 (6H m Anth + Ph), 7.22 (2H m Anth), 3.59 (2H t i-CH_2), 2.88 (2H t g-CH_2), 2.13 (2H m h-CH_2), 0.30 (TMS). The protecting group was then removed using potassium carbonate as for 1,4-diethynylbenzne to yield the product **A3L**. ^{1}H NMR δ/ppm: 8.33 (1H s 10-Anth), 8.12 (2H d Anth), 8.00 (2H d Anth), 7.46 (6H m Anth + Ph), 7.22 (2H m Anth), 3.60 (2H t i-CH_2), 3.07 (1H s a-CCH), 2.88 (2H t g-CH_2), 2.14 (2H m h-CH_2). ^{13}C NMR δ/ppm: 143.0, 134.5, 132.2, 131.6, 129.5, 129.2, 128.5, 125.7, 125.5, 124.7, 124.2, 119.6, 83.8, 76.7. Mass, *m*/*z*: 320 (M^+), 191 (Anth–Me), 178 (Anth). IR/cm^{-1}: 3295.1 ν(CC–H), 2106.3 ν(C≡CH). UV/nm: 10^{-5} M DCM. 386 (0.112), 256 (1.484). Accurate mass Calc. for $C_{25}H_{20}$ 320.1554. Found: 320.156501%.

8. Synthesis of the 'T'-shaped anthracene-containing ligands

*8.1. 9-(2-(2,5-Diethynylphenyl)ethenyl)anthracene (**A1T**)*

8.1.1. 2,5-Dibromobenzaldehyde

2-5-Dibromotoluene (0.552 ml, 4 mmol) was dissolved in a mixture of acetic acid (10 ml) and acetic anhydride (26 ml) and cooled in an ice/water bath. Chromium(VI) oxide (996 mg, 10 mmol) and sulphuric acid (0.85 ml, 16 mmol) were then added to this vigorously stirred cooled solution, which was stirred for a further 1 h. The reaction mixture was then poured into ice/water (approx. 50 ml) and neutralised by careful addition of sodium bicarbonate with vigorous stirring. The diester product (see discussion) was filtered off and recrystallised from hot petroleum ether. Yield: 1098 mg, 75%. This was then dissolved in a mixture of water (10 ml) ethanol (20 ml) and sulphuric acid (1 ml) and heated to 75 °C for 80 min, upon cooling the desired product was filtered off, sufficiently pure for the next step. Yield: 637 mg, 80%. ^{1}H NMR δ/ppm: 10.27 (1H s C(O)H), 8.01 (1H d Ph), 7.55 (2H m Ph).

8.1.2. 2,5-Bis(trimethylsilylethynyl)benzaldehyde

2,5-Dibromobenzaldehyde (387 mg, 1.5 mmol) and TMSA (0.5 ml, 3.6 mmol) were coupled via a Sonogashira reaction and purified via silica column chromatography (DCM:hexane, 20:80) to yield the desired product. Yield: 357 mg, 80%. ^{1}H NMR δ/ppm: 10.47 (1H s C(O)H), 7.94 (1H s Ph), 7.50 (2H m Ph), 0.24 (18H s TMS).

9-(Triphenylposphoniumbromide)methylanthracene (343 mg, 0.64 mmol) and potassium *tert*-butoxide (78 mg, 0.71 mmol) were dissolved in THF (20 ml). This was allowed to stir at room temperature for 1 h to complete the formation of the ylide. A THF (20 ml) solution of 2,5-bis(trimethylsilylethynyl) benzaldehyde (202.6 mg, 0.68 mmol) was added and the reaction treated as for **A1L**. Mass, *m*/*z*: 472 (M^+), 454 (–Me), 441 ($-2\times$Me), 399 (–TMS), 302 ($-2\times$TMS).

The trimethylsilyl group was then removed using potassium carbonate, as for 1,4-diethynyl benzene, to yield the desired product **A1T**. ^{1}H NMR δ/ppm: 8.42 (1H s 10-Anth), 8.37 (2H m 4-Anth), 8.02 (5H m j + 1-Anth), 7.49 (7H m d,e,g + 2,3-Anth), 7.31 (1H d [$^3J_{H-H}$ 7.3 Hz] i), 3.33 (1H s a), 3.25 (1H s a′). ^{13}C NMR δ/ppm: 139.7, 134.3, 133.3, 132.1, 131.5, 130.8, 129.7, 128.7, 128.1, 126.8, 125.9, 125.7, 125.2, 122.9, 121.5, 83.8, 83.1, 81.5, 79.1. Mass, *m*/*z*: 328 (M^+), 304 (–CCH), 151 (–Anth). IR/cm^{-1}: 3299.7 ν(CC–H), 2105.4 ν(C≡CH). UV/nm: 10^{-5} M DCM. 392

(0.514), 249 (3.11). Elemental analysis: Calc. for $C_{26}H_{16}$: C, 95.12; H, 4.88. Found: C, 95.28; H, 4.68%.

8.2. 9-(2-(2,5-Diethylnylphenyl)ethyl)anthracene (*A2T*)

8.2.1. (2-(2,5-Dibromophenyl)ethenyl)anthracene

9-(Triphenylphosphoniumbromide)methylanthracene (3.198 g, 6 mmol) and potassium *tert*-butoxide (672 mg, 6 mmol) were dissolved in THF (50 ml). This was allowed to stir at room temperature for 1 h to complete the formation of the ylide. A THF (20 ml) solution of 2,5-dibromobenzaldehyde (1.584 g, 6 mmol) was added and the reaction treated as for **A1L**. Yield: 1.7 g, 65%. ^{1}H NMR δ/ppm: 8.42 (3H m Anth), 8.06 (5H m Anth), 7.84 (1H d [$^3J_{H-H}$ 7.3 Hz] CH–Anth), 7.49 (8H m Anth), 7.28 (3H m Anth + CH–Ph + Ph), 6.87 (1H dd Ph), 6.53 (1H d Ph).

8.2.2. (2-(2,5-Dibromophenyl)-2-hydroxyethyl)anthracene

THF–borane complex (from sodium borohydride (1.07 mmol) and iodine (0.482 mmol) in THF) was prepared as for **A2L** and added to (2-(2,5-dibromophenyl)ethenyl) anthracene (1 g, 2.3 mmol). The reaction and subsequent oxidation with alkaline hydrogen peroxide was performed as for **A2L**. Yield: 446 mg, 44% – mixture of isomers. Major by-product – starting olefin, 300 mg recovered. ^{1}H NMR δ/ppm: 8.73 (1H br s OH), 8.42 (1H s 10-Anth), 8.00 (2H d Anth), 7.45 (8H m Anth + Ph), 6.6 (1H dd Ph), 4.1–3.4 (2 × 3H m mixture of isomers of linker protons). Mass, *m*/*z*: 456 (M^+), 440 (–O), 376/378 ($M^+ - {}^{79}Br/{}^{81}Br$), 278 ($M^+$ − OH, Br).

8.2.3. (2-(2,5-Dibromophenyl)ethyl)anthracene

(2-(2,5-Dibromophenyl)-2-hydroxyethyl)anthracene (0.446 mg, 1 mmol) was treated with freshly prepared TMSI (appox. 6 mmol) in acetonitrile and worked up as for **A2L**. Silica column chromatography (DCM:hexane 10:90) yielded the desired product. Yield: 172 mg, 40%. ^{1}H NMR δ/ppm: 8.38 (2H d Anth), 8.33 (1H s Anth), 8.03 (2H d Anth), 7.48 (6H m Anth + Ph), 7.21 (1H m Ph), 3.88 (2H m Anth–CH_2), 3.16 (2H m Ph–CH_2).

(2-(2,5-Dibromophenyl)ethyl)anthracene (172 mg, 0.4 mmol) was coupled with TMSA (0.12 ml, 0.88 mmol) via a Sonogashira reaction as for **A0L**. Silica column chromatography (DCM:hexane, 10:90) yielded the desired bis-TMS protected product and a large (approx. 30%) amount of monosubstituted product. ^{1}H NMR δ/ppm: 8.41 (2H d Anth), 8.38 (1H s 10-Anth), 8.01 (2H d Anth), 7.51 (6H m Anth + Ph), 7.32 (2H m Anth), 3.91 (2H m j-CH_2), 3.23 (2H m i-CH_2) 0.29 (18 H s TMS). Mass, *m*/*z*: 474 (M^+), 459 (–Me), 401 (–TMS), 386 (–TMS, –Me), 191 (Anth–Me).

This was then deprotected with potassium carbonate as for **A0L**. Combined yield for Sonogashira and deprotection steps and formation of **A2T** 92.4 mg, 71% ^{1}H NMR δ/ppm. 8.44 (1H s 10-Anth), 8.40 (2H d 4-Anth), 8.03 (2H d 1-Anth), 7.50 (6H m 2,3-Anth + d,e), 7.35 (1H m g), 3.91 (2H m j) 3.48 (1H s a) 2.24 (2H m i), 2.23 (1H s a′). ^{13}C NMR δ/ppm: 144.0, 133.1, 132.5, 131.6, 129.8, 129.6, 129.2, 126.1, 125.5, 124.8, 124.3, 99.9, 83.2, 82.5, 78.9. Mass, *m*/*z*: 330 (M^+), 191 (Anth–Me), 179 (Anth). IR/cm^{-1}: 3296.6 ν(CC–H), 2107.5 ν(C≡CH). UV/nm: 10^{-5} M DCM. 391 (0.393), 370 (0.426), 275 (0.896), 251, (2.687). Elemental analysis: Calc. for $C_{26}H_{18}$: C, 94.55; H, 5.46. Found: C, 94.78; H, 5.81%.

8.3. 9-(2-(2,5-Diethynylphenyl)propyl)anthracene (*A3T*)

8.3.1. 9-(3-(2,5-Dibromophenyl)prop-2-enoneyl)anthracene

9-(3-(2,5-Dibromophenyl)prop-2-enoneyl)anthracene was prepared by reacting 9-acetylanthracene (634 mg, 2.88 mmol) with 2,5-dibromo benzaldehyde (637 mg, 2.4 mmol) as for **A3L**. Yield: 800 mg, 71%. ^{1}H NMR δ/ppm: 8.54 (1H s 10-Anth), 8.05 (2H m Anth), 7.90 (2H m Anth), 7.73 (1H d), 7.60 (1H d $^3J_{H-H}$ 16 Hz), 7.49 (4H m Anth + Ph), 7.34 (1H s Ph), 7.26 (1 H dd Ph), 7.13 (1H d $^3J_{H-H}$ 16 Hz).

8.3.2. 9-(3-(2,5-Dibromophenyl)-1-hydroxypropyl)anthracene

9-(3-(2,5-Dibromophenyl)prop-2-enoneyl)anthracene (800 mg, 1.7 mmol) was reduced to the anthracenyl alcohol with sodium borohydride (258.5 mg, 6.8 mmol) using a method analogous to that used for 9-(3-(4-bromophenyl)-1-hydroxypropyl)anthracene. Yield: 779 mg, 97%. ^{1}H NMR δ/ppm: 8.52 (1H s br OH), 8.30 (1H s 10-Anth), 7.94 (2H m Anth), 7.45 (4H m Anth), 7.30 (2H m Anth), 7.12 (1H m), 6.12 (1H m), 2.97 (1H m), 2.62 (3H m), 2.30 (1H m).

8.3.3. 9-(3-(2,5-Bromophenyl)propyl)anthracene

9-(3-(4-Bromophenyl)-1-hydroxypropyl)anthracene (779 mg, 1.66 mmol) was reduced to the propyl derivative using freshly prepared TMSI (10 mmol) as for **A3L**. Yield: 754 mg, Quantitative. ^{1}H NMR δ/ppm: 8.33 (1H s 10-Anth), 8.20 (2H d Anth), 7.99 (2H d Anth), 7.48 (6H m Anth + Ph), 7.19 (1H m Ph), 3.66 (2H t AnthCH_2), 2.96 (2H t PhCH_2), 2.13 (2H m R–CH_2–R′). Mass, *m*/*z*: 454 (M^+), 191 (Anth–Me).

9-(2-(2,5-Trimethylsilylethynylphenyl)propyl)anthracene was prepared from 9-(2-(2,5-bromophenyl)propyl)anthracene (726.7 mg, 1.6 mmol) and TMSA (0.51 ml, 3.65 mmol) using a Heck coupling reaction modified from that used for **A0L**. ^{1}H NMR δ/ppm: 8.35 (1H s 10-Anth), 8.22 (2H d Anth), 8.02 (2H d Anth), 7.48 (6H m Anth + Ph), 7.20 (1H m Ph), 3.69 (2H t AnthCH_2), 3.01 (2H m PhCH_2), 2.19 (2H m R–CH_2–R′), 0.31 (18H m TMS). Mass, *m*/*z*: 488 (M^+), 473 (–Me), 415 (–TMS), 400 (–TMS –Me), 191 (Anth–Me). The protecting groups were then removed using potassium carbonate as for 1,4-diethynylbenzene to yield **A3T**. ^{1}H NMR δ/ppm: 8.34 (1H s 10-Anth), 8.21 (2H d Anth), 8.02 (2H d Anth), 7.48 (6H m Anth + Ph), 7.32 (1H m Ph), 3.70 (2H t AnthCH_2), 3.25 (1H s CCH), 3.16 (1H s CCH), 3.02 (2H t PhCH_2), 2.19 (2H m R–CH_2–R′). ^{13}C NMR δ/ppm: 140.0, 129.8, 128.1, 127.6, 127.4, 127.3, 126.8, 124.8, 124.7, 124.4, 121.0, 120.7, 120.0, 119.6, 117.7, 117.5, 78.5,

77.8, 77.0, 74.0, 30.0, 26.9, 22.8. Mass, m/z: 344 (M^+), 191 (Anth–Me). IR/cm^{-1}: 3297.9 ν(C–H), 2107.0 ν(C≡CH). UV/nm: DCM, 391 (0.410), 371 (0.431), 275 (0.910), 251, (2.720). Acc. Mass. 344.155965 (Calc. 344.156501, $C_{27}H_{20}$).

Crystal data for ***A1L***. $C_{24}H_{16}$, $M = 304.37$, monoclinic, $P2_1/n$ (no. 14), $a = 14.7618(14)$ Å, $b = 6.0866(5)$ Å, $c = 37.489(3)$ Å, $\beta = 100.148(7)°$, $V = 3315.6(5)$ Å^3, $Z = 8$ (two independent molecules), $D_c = 1.219$ g cm^{-3}, μ(Cu Kα) = 0.523 mm^{-1}, $T = 293$ K, yellow needles; 4910 independent measured reflections, F^2 refinement, $R_1 = 0.062$, $wR_2 = 0.140$ for 3100 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 120°$], 434 parameters. CCDC 292095.

Crystal data for ***A3L***. $C_{25}H_{20}$, $M = 320.41$, monoclinic, $P2_1$ (no. 4), $a = 5.5422(13)$ Å, $b = 12.995(2)$ Å, $c = 25.041(4)$ Å, $\beta = 93.09(2)°$, $V = 1800.9(6)$ Å^3, $Z = 4$ (two independent molecules), $D_c = 1.182$ g cm^{-3}, μ(Mo Kα) = 0.067 mm^{-1}, $T = 203$ K, yellow hexagonal needles; 3336 independent measured reflections, F^2 refinement, $R_1 = 0.052$, $wR_2 = 0.115$ for 2195 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 50°$], 460 parameters. The absolute structure of **A3L** could not determined by either *R*-factor tests [$R_1^+ = 0.0522$, $R_1^- = 0.0522$] or by use of the Flack parameter [$x^+ = -9.99(999)$, $x^- = +9.99(999)$]. CCDC 292097.

Crystal data for ***A2*L[Ru]***, $M = 1210.63$, monoclinic, $C2/c$ (no. 15), $a = 24.3005(10)$ Å, $b = 9.8753(7)$ Å, $c = 51.476(3)$ Å, $\beta = 101.716(4)°$, $V = 12095.6(12)$ Å^3, $Z = 8$, $D_c = 1.330$ g cm^{-3}, μ(Cu Kα) = 3.833 mm^{-1}, $T = 293$ K, orange platy needles; 8329 independent measured reflections, F^2 refinement, $R_1 = 0.052$, $wR_2 = 0.122$ for 6518 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 120°$], 625 parameters. CCDC 292096.

Crystal data for ***A1T***. $C_{26}H_{16} \cdot 0.5CH_2Cl_2$, $M = 370.85$, monoclinic, $C2/c$ (no. 15), $a = 25.081(4)$ Å, $b = 8.7598(19)$ Å, $c = 19.273(3)$ Å, $\beta = 113.636(12)°$, $V = 3879.1(12)$ Å^3, $Z = 8$, $D_c = 1.270$ g cm^{-3}, μ(Cu Kα) = 1.780 mm^{-1}, $T = 293$ K, yellow needles; 2867 independent measured reflections, F^2 refinement, $R_1 = 0.050$, $wR_2 = 0.142$ for 2318 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 120°$], 263 parameters. CCDC 292098.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.12.024.

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