Unexpected iron(III) chloride-catalysed dimerisation of 1,1,3-trisubstituted-prop-2-yn-1-ols as an expedient route to highly conjugated indenes†

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A method to prepare highly conjugated indenes efficiently by iron(III) chloride-catalysed dimerisation of trisubstituted propargylic alcohols under very mild conditions at room temperature is described. The reactions are rapid and operationally straightforward, giving the indene products in good yields and regioselectivity.

Introduction

In addition to their versatility as building blocks in organic synthesis, indenes are an important class of carbocycles found in a myriad of compounds of biological and material interest.[1] Although this has led to many synthetic methods to this important carbocycle,[2] the number of literature examples still remains far fewer than those for structurally related heterocycles such as indoles and benzofurans. Moreover, many of the reported reactions have been shown to require high temperatures and/or prolonged reaction times. In this regard, the development of mild and efficient synthetic strategies that can make use of inexpensive and ecologically benign starting materials and catalysts for the synthesis of this class of compounds would be desirable.

Iron complexes have re-emerged as efficient Lewis acid catalysts in a variety of stereoselective C–X (X = C, N, O, S) bond formations in recent years.[3–5] When the electrophile in these reactions is an alcohol, they were shown not only to benefit from the nontoxic and inexpensive nature of the ubiquitous Group 8 metal but also the low cost of the substrate and formation of H_2O as potentially the only byproduct.[4,5] Added to this is the ease of preparing the starting alcohol that provided the possibility to introduce a wide variety of substitution patterns and a quaternary carbon centre through the use of a tertiary alcohol. As part of an ongoing program to develop such reactions,[5a,6] we unexpectedly found propargylic alcohols of the type **1** dimerised and gave the indene products **2** and **3** when treated with $FeCl_3$ under the mild conditions shown in route 1 in Scheme 1. The reactions were also shown to proceed with complete regioselectivity for substrates containing a sterically bulky alkyl group on the carbinol carbon, and such selectivities were dependent on the structural nature of this functional group. Interestingly, although indene formation from propargylic alcohols such as **1** has been described twice before in the literature, as shown in routes 2 and 3 in Scheme 1,[7] the structures of **2** and **3** are unprecedented. Additionally, while 1,2- and 1,3-migrations of acetoxy,[8] indole,[2h] silyl[7h] and sulfide[9] groups in the respective propargylic derivatives have been reported, the apparent 1,3-alkyl group migration observed in this reaction is not known. Herein, we report the discovery of this new iron-catalysed method for the synthesis of ethynyl-2-vinyl-1*H*-indenes from dimerisation of a variety of trisubstituted propargylic alcohols.

Results and discussion

We found that treating a solution of **1a** in CH_2Cl_2 and 4 Å MS with 5 mol% of $FeCl_3$ at room temperature for 0.5 h gave the best result (Table 1, entry 1). Under these conditions, the indenes **2a** and **3a** were obtained in respective yields of 65% and 7%, comparable to the yields and regioselectivities obtained for the analogous Au-catalysed reactions with propargylic acetates and indoles.[2h,2n] The regiochemistries of both indene products were determined by X-ray single crystal structure analysis (Fig. 1a and 1d).† Although requiring a longer reaction time of 2 h, the same yields of **2a** and **3a** were reproduced when the experiment was repeated at −78 °C (entry 2). In contrast, repeating the reaction in other solvents was found to be markedly less effective (entries 3–5). When toluene was employed as the solvent, the conjugated enyne side-product **7a** was furnished as the major product in 38% yield and the indene adducts as the minor products (entry 3). Similarly, performing the reaction in either THF or MeCN was found to result in only recovery of the starting alcohol in yields of 85–95%, along with **7a** in 7% yield when THF was used as the solvent (entries 4–5). On the other hand, an examination of other Lewis and Brønsted acid catalysts revealed that $InCl_3$, $ZnCl_2$ and $AuCl_3$ could also mediate the dimerisation of **1a** and give **2a** and **3a**, albeit in lower yields of 46–61 and 8–14%, respectively (entries 6–8). Formation of **7a** in yields of 3–8% was also afforded by the $ZnCl_2$- and $AuCl_3$-catalysed reactions. However, the absence of a catalyst, or switching to the metal triflates $Cu(OTf)_2$ and $Yb(OTf)_3$, or Brønsted acids *p*-TsOH or TfOH, was found to lead to no reaction based on ^{1}H NMR and TLC analysis of the crude mixtures (entries 9–13).

To define the scope of the present indene-forming procedure, we next turned our attentions to the reactions of a variety of propargylic alcohols **1** (Table 2). This revealed indene products **2b** and **3b**, and **2c** and **3c**, could be furnished in good overall

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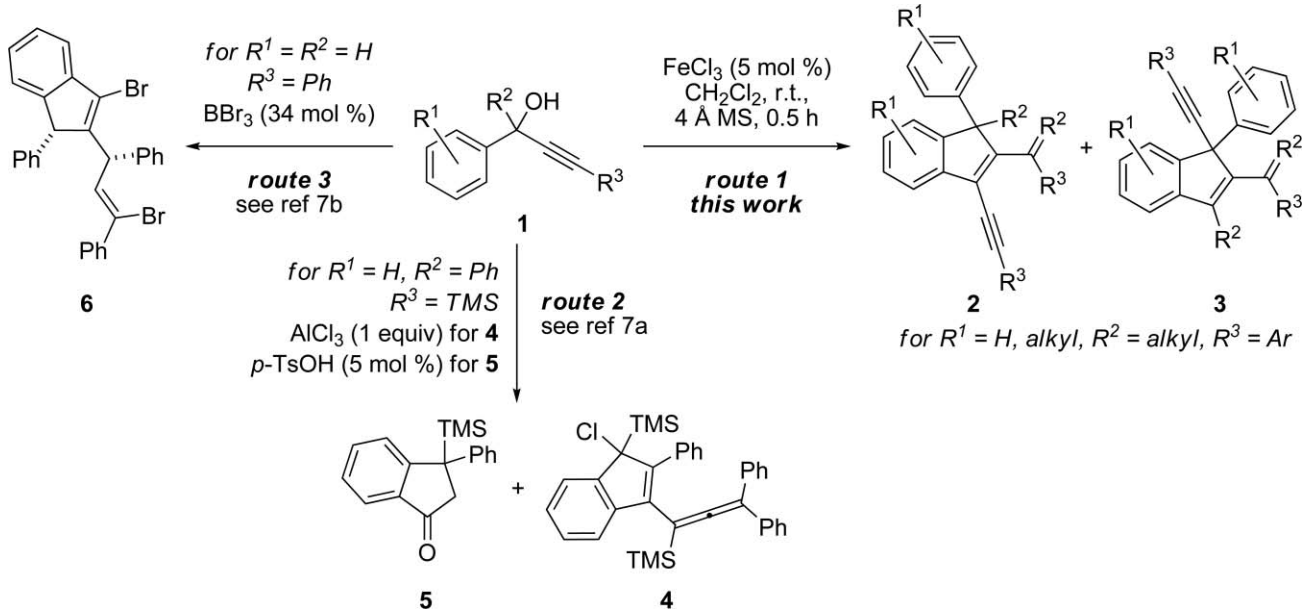
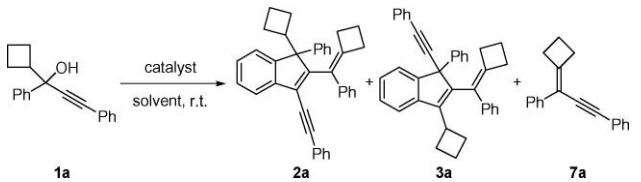
† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR data and spectra for compounds **1**, **7** and **8**, ^{1}H and ^{13}C NMR spectra for compounds **2** and **3** and HPLC measurements for the reaction of **1f**. CCDC reference numbers 726882–726885. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c003522j



Scheme 1 $FeCl_3$-catalysed formation of ethynyl-2-vinyl-1*H*-indenes from trisubstituted propargylic alcohols.

Table 1 Optimisation of the reaction conditions[a]



Entry	Catalyst	Solvent	Time/h	Yield (%) 2a	3a	7a
1	$FeCl_3$	CH_2Cl_2	0.5	65	7	—
2[b]	$FeCl_3$	CH_2Cl_2	2	65	7	—
3	$FeCl_3$	PhMe	15	23	7	38
4	$FeCl_3$	MeCN	15	—[c]	—	—
5	$FeCl_3$	THF	15	—	—	7
6	$AuCl_3$	CH_2Cl_2	0.5	50	8	3
7	$InCl_3$	CH_2Cl_2	0.5	61	11	—
8	$ZnCl_2$	CH_2Cl_2	15	46	14	8
9	$Cu(OTf)_2$	CH_2Cl_2	15	—[c]	—	—
10	$Yb(OTf)_3$	CH_2Cl_2	15	—[c]	—	—
11	*p*-TsOH	CH_2Cl_2	15	—[c]	—	—
12	TfOH	CH_2Cl_2	15	—[c]	—	—
13	—[d]	CH_2Cl_2	15	—[c]	—	—

[a] All reactions were performed at room temperature with 4 Å MS and catalyst : **1a** ratio of 1 : 20. [b] Reaction conducted at –78 °C. [c] No reaction based on ^{1}H NMR analysis of the crude reaction mixture. [d] Reaction conducted in the absence of a catalyst.

yields from 1-cyclobutylprop-2-yn-1-ols containing an electron-donating group at the acetylenic position. Although requiring a longer reaction time and catalyst loading of 10 mol% at 40 °C, the dimerisation process was also shown to be applicable to starting alcohols bearing an electron-withdrawing or thiophene group at this position. Under these slightly modified conditions, the indene adducts **2d** and **2e**, which was also structurally characterized by X-ray crystal analysis (Fig. 1b),† were afforded in lower yields of 22 and 24%, respectively. Interestingly, steric effects were also found to play a role since a more bulky *i*-Pr or cyclopentane unit in place of the cyclobutane group at the carbinol position in the starting alcohol were found to lead to no reaction. On the other hand, propargylic alcohols with a pendant $(CH_2)_nCH_3$ side chain where $n = 1$, 3 or 5 at the carbinol position as in **1f–h** and **1k** gave the corresponding indene products in good to excellent yields under the standard conditions. The enyne byproduct **7** was also obtained in yields of 3–26% for the reactions of **1b** and **1d–g** shown in Table 2. More notably, dimerisation of propargylic alcohols containing an *i*-Bu, Bn or phenethyl moiety at the carbinol position was shown to proceed with complete regioselectivity. A similar regioselective outcome was also found when we conducted the dimerisation of **1n** bearing a homoallylic functional group at the carbinol position of the starting alcohol. In each of these latter reactions, the indene adducts **2i–j** and **2l–n** were cleanly afforded as the sole product in yields of 61–78%. The structure of **2m** was also characterized by X-ray crystallographic analysis (Fig. 1c).† No minor products that could be attributed to either the indene regioisomer **3** or enyne byproduct **7** were detected based on TLC and ^{1}H NMR analysis of the crude mixtures. Varying the alkyl substituent at the carbinol position with a methyl group in place of the cyclobutane group was found to lead to oligomerization of the starting alcohol. Further control experiments also showed that no product formation could be detected for reactions with a proton or phenyl group instead of an alkyl group at the carbinol position of the starting material. In these reactions, either a mixture of decomposition products that could be identified by ^{1}H NMR analysis or recovery of the starting alcohol in addition to the Meyer–Schuster rearrangement product in respective yields of 41 and 26% was obtained.[10]

On the basis of the above results, it appears that the chemo- and regioselective outcomes of the reaction are dependent on the behaviour of the Lewis acid catalyst and the alkyl substitution pattern at the carbinol position. Although highly speculative, the apparent 1,3-alkyl group migration in products of the type **2** and **3**,[11] and the formation of the enyne byproduct **7** led us to

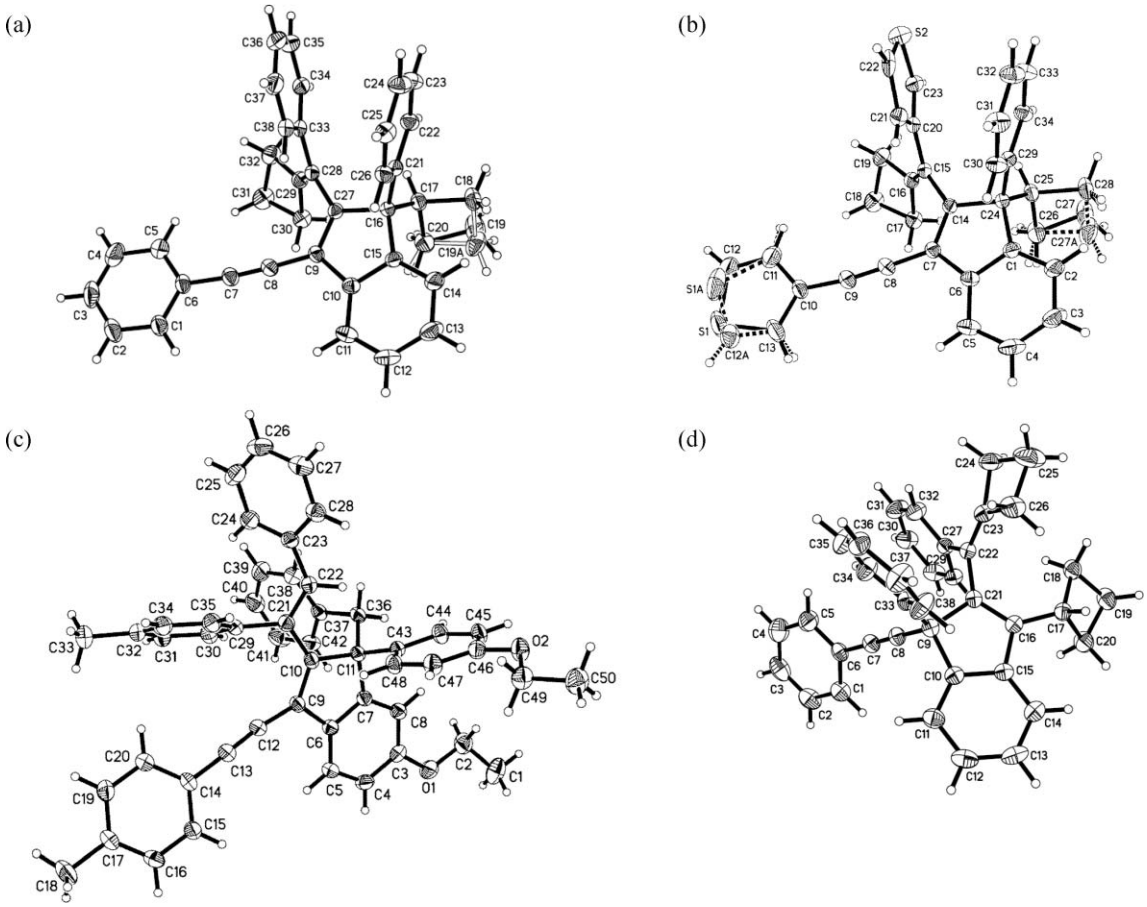


Fig. 1 ORTEP drawings of (a) **2a**, (b) **2e**, (c) **2m** and (d) **3a** with thermal ellipsoids at 50% probability levels.†

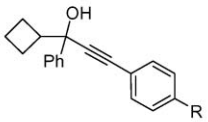
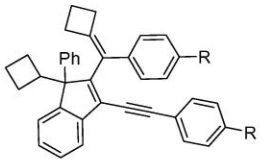
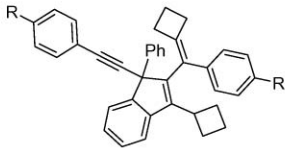
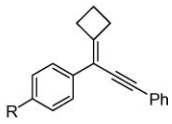
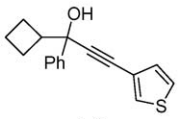
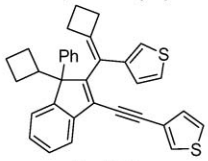
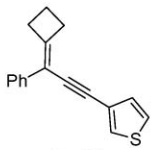
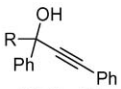
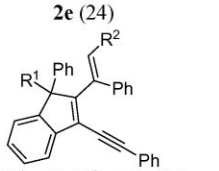
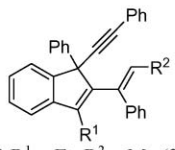
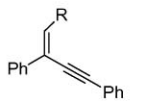
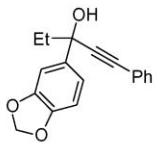
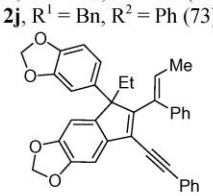
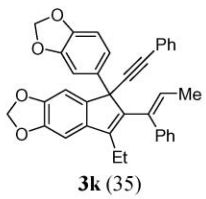
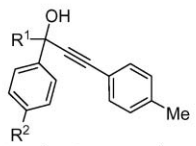
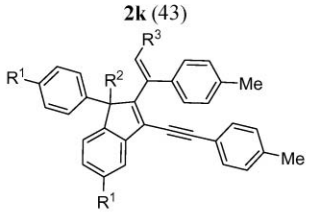
propose the mechanism outlined in Scheme 2 for the reaction of **1k**. This could involve activation of the alcohol substrate through coordination of the hydroxyl functional group to the $FeCl_3$ catalyst. This delivers the Fe(III)-coordinated intermediate **A** which undergoes elimination to give the putative alkynyl cation species **B** and its allenic resonance form **C**. Alkoxylation of carbocation **B**/**C** at the sterically less hindered carbon center by another molecule of **1k** and intramolecular Friedel–Crafts reaction would give the dimer **E**.[12] The reaction then proceeds *via* a second putative carbocation species **G** resulting from activation of the hydroxyl group of this newly formed dimer due to coordination to the metal catalyst and elimination of [Fe]–OH. This leads to intramolecular cyclization of the alkyne moiety to the resultant carbocation centre generated and concomitant 1,3-alkyl shift to furnish the cationic allylindene **H**.[13] We surmise that this C–C bond formation and 1,3-migration process could be concerted in character so as to avoid the possible formation of a highly reactive and unstable vinylic cation species.[14] Deprotonation at the methylene carbon center of the 1,3-migrated alkyl group in this indenyl cation species as shown in Scheme 2 would provide the indene regiosiomer **2k**. Alternatively, the aryl group in **H** could undergo a 1,4-migration to give the cationic indenyl regioisomer **I**, which deprotonates in a similar manner to that described above to provide the indene product **3k**.

The possible involvement of carbocation intermediates is also supported by our results for the dimerisation of enantioenriched **1f**. Under the experimental conditions described in Scheme 3, the indene products **2f** and **3f** were both obtained as a racemic mixture in 35% yield. What remains unclear is the origin of the product regioselectivities obtained in the present propargylic alcohol dimerisation process. One possible reason for the complete regioselectivities obtained for reactions of substrates containing an alkyl group with a bulky *i*Pr or Ph group or terminal C=C bond could be to prevent any unfavourable steric and/or stereoelectronic interactions arising between this group and the migrating aryl group in **H**. However, this is highly speculative and the exact reason(s) responsible for the unique regioselectivities observed require future theoretical and experimental studies.

Conclusions

In summary, a novel iron-catalysed route to highly conjugated indenes based on dimerisation of trisubstituted propargylic alcohols has been reported. This chemoselective carbocycle forming method was shown to proceed under very mild conditions at room temperature and provide product yields and regioselectivities comparable to those reported for the analogous reactions with propargylic acetates and indoles catalysed by gold salts.[2h,2n] In reactions where the substrate contained a sterically bulky alkyl group at the carbinol carbon, the indene-forming process was also shown to proceed with complete regioselectivity. Moreover, it makes use of alcohol substrates and an iron catalyst that are

Table 2 Iron(III) chloride-catalyzed dimerisation of **1b–n**[a]

Substrate	Product		
 **1b**, R = Me **1c**, R = $(CH_2)_4CH_3$ **1d**, R = Cl[b]	 **2b**, R = Me (55) **2c**, R = $(CH_2)_4CH_3$ (64) **2d**, R = Cl (22)	 **3b**, R = Me (10) **3c**, R = $(CH_2)_4CH_3$ (10)	 **7b**, R = Me (6) **7d**, R = Cl, (26)
 **1e**[c]	 **2e** (24)		 **7e** (3)
 **1f**, R = Et **1g**, R = *n*Bu **1h**, R = *n*Hex **1i**, R = *i*Bu **1j**, R = Bn	 **2f**, R^1 = Et, R^2 = Me (35) **2g**, R^1 = *n*Bu, R^2 = *n*Pr (55) **2h**, R^1 = *n*Hex, R^2 = *n*Pent (50) **2i**, R^1 = *i*Bu, R^2 = *i*Pr (78) **2j**, R^1 = Bn, R^2 = Ph (73)	 **3f**, R^1 = Et, R^2 = Me (35) **3g**, R^1 = *n*Bu, R^2 = *n*Pr (18) **3h**, R^1 = *n*Hex, R^2 = *n*Pent (15)	 **7f**, R = Me (9) **7g**, R = *n*Pr (6)
 **1k**	 **2k** (43)	 **3k** (35)	
 **1l**, R^1 = CH_2Bn, R^2 = H **1m**, R^1 = Bn, R^2 = OEt **1n**, R^1 = , R^2 = OEt	 **2l**, R^1 = H, R^2 = CH_2Bn, R^3 = Bn (61) **2m**, R^1 = OEt, R^2 = Bn, R^3 = Ph (69) **2n**, R^1 = OEt, R^2 =  , R^3 = allyl (71)		

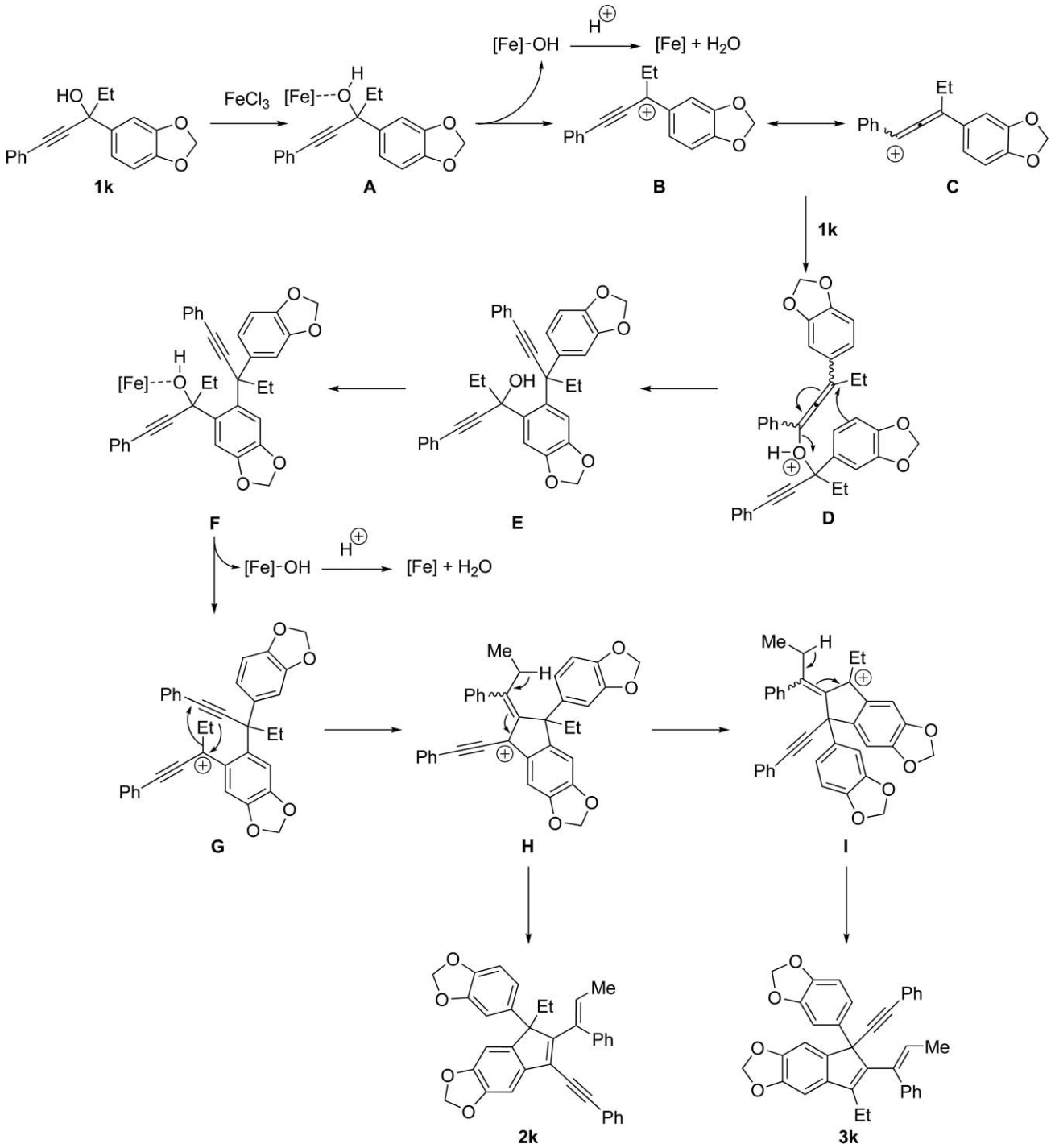
[a] All reactions were performed at room temperature for 0.5 h with 4 Å MS and $FeCl_3$: **1** ratio = 1 : 20; values denoted in parenthesis are isolated yields. [b] Reaction with 10 mol% $FeCl_3$ at 40 °C for 24 h. [c] Reaction with 10 mol% $FeCl_3$ at 40 °C for 2 h.

inexpensive, easily accessible and ecologically benign. Efforts are currently underway to explore the detailed mechanistic aspects of this reaction and how the method can be applied to natural product synthesis and as potential advanced functional materials in view of the nature of the substituents and high degree of conjugation in the indene products obtained.

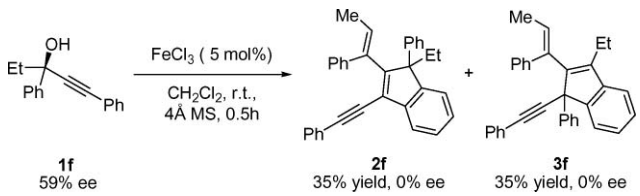
Experimental section

General details

Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Solvents were purified following standard literature procedures; CH_2Cl_2 was purified prior to use by passing through a PURESOLV™ Solvent Purification System. Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 pre-coated silica gel plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Unless otherwise stated, ^1H and ^{13}C NMR spectra were measured on Bruker Avance 400 MHz spectrometer. Chemical shifts (ppm) were recorded with respect to TMS in $CDCl_3$. Multiplicities were given as: s (singlet), bs (broad singlet), d (doublet), t (triplet), dd (doublet, doublet) or m (multiplets). The number of protons (*n*) for a given resonance is indicated by *n*H. Coupling constants are reported as a *J* value in Hz. Infrared



Scheme 2 Tentative mechanism for $FeCl_3$-catalysed formation of ethynyl-2-vinyl-1*H*-indenes from trisubstituted propargylic alcohols.



Scheme 3 $FeCl_3$-catalysed dimerisation of enantioenriched **1f**.

spectra were recorded on Shimadzu IR Prestige-21 FTIR Spectrometer. High Resolution Mass (HRMS) spectra were obtained using Finnigan MAT95XP LC/HRMS. Mass spectral data were reported in units of mass to charge (m/z). Enantioselectivities were determined by high performance liquid chromatography (HPLC) analysis on a Shimadzu (DGU-20A5/LC-20AD/SPD-M20A/RID-10(A) spectrometer employing a Daicel Chirapak AD-H or OJ-H column.

Representative experimental procedure for $FeCl_3$-catalysed preparation of vinyl-1*H*-indenes 2 and/or 3

To a solution of CH_2Cl_2 (3 mL) containing 1 (0.3 mmol) and 4 Å molecular sieves (200 mg), was added $FeCl_3$ (5 mol%). The mixture was stirred at room temperature and monitored by TLC analysis. On completion, the reaction mixture was filtered through Celite® and washed with CH_2Cl_2 (20 mL). The solvent was removed under reduced pressure and the residue was subjected to purification by flash column chromatography on silica gel (eluent: *n*-hexane–CH_2Cl_2 = 20 : 1 to 10 : 1) to give the title compound.

1-Cyclobutyl-2-(cyclobutylidene(phenyl)methyl)-1-phenyl-3-(phenylethynyl)-1*H*-indene (2a). White solid; R_f 0.59 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); m.p. 180–181 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.96–0.99 (m, 1H, C*H*$_2$), 1.40–1.59 (m, 3H, C*H*$_2$), 1.72–1.86 (m, 2H, C*H*$_2$), 2.04–2.09 (m, 3H, C*H*$_2$), 2.49–2.57 (m, 1H, C*H*$_2$), 2.71 (t, 2H, J = 7.6 Hz, C*H*$_2$), 3.13-3.19 (m, 1H, C*H*), 6.79 (d, 2H, J = 5.8 Hz, Ar-*H*), 7.00–7.13 (m, 8H, Ar-*H*), 7.23–7.52 (m, 8H, Ar-*H*), 7.68 (d, 2H, J = 7.4 Hz, Ar-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.1 (*C*H$_2$), 17.3 (*C*H$_2$), 23.5 (*C*H$_2$), 25.0 (*C*H$_2$), 32.0 (*C*H$_2$), 32.3 (*C*H$_2$), 38.3 (*C*H), 66.4 (Ph-*C*-CH), 84.4 (C≡C), 94.3 (C≡C), 120.3 (Ar–C), 122.1 (C=C), 123.7 (Ar–C), 125.0 (Ar–C), 125.7 (Ar–C), 125.9 (Ar–C), 126.2 (Ar–C), 126.7 (Ar–C), 127.2 (Ar–C), 127.6 (Ar–C), 127.7 (Ar–C), 128.2 (Ar–C), 128.3 (Ar–C), 128.4 (Ar–C), 131.8 (Ar–C), 138.5 (C=C), 140.9 (Ar–C), 144.3 (C=C), 145.9 (Ar–C), 149.1 (Ar–C), 158.4 (C=C); IR (NaCl, neat) ν: 2980, 2943,1653, 1597, 1511, 1443, 1265, 754 cm^{-1}; MS (ESI) m/z 489 [M + H]$^+$; HRMS (ESI) calcd. for $C_{38}H_{33}$ (M^+ + H): 489.2582, found: 489.2567.

1-Cyclobutyl-2-(cyclobutylidene(*p*-tolyl)methyl)-1-phenyl-3-(*p*-tolylethynyl)-1*H*-indene (2b). White solid; R_f 0.50 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); m.p. 87–89 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.90–0.96 (m, 1H, C*H*$_2$), 1.38–1.57 (m, 3H, C*H*$_2$), 1.67–1.82 (m, 2H, C*H*$_2$), 1.95–2.05 (m, 3H, C*H*$_2$), 2.26 (s, 3H, Ar–C*H*$_3$), 2.33 (s, 3H, Ar–C*H*$_3$), 2.41–2.49 (m, 1H, C*H*$_2$), 2.68 (s, 2H, C*H*$_2$), 3.08–3.16 (m, 1H, C*H*$_2$), 6.77 (d, 2H, J = 7.2 Hz, Ar-*H*), 6.90–7.03 (m, 7H, Ar-*H*), 7.11 (d, 2H, J = 7.8 Hz, Ar-*H*), 7.23-7.43 (m, 5H, Ar-*H*), 7.64 (d, 2H, J = 7.5 H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 17.1 (*C*H$_2$), 17.3 (*C*H$_2$), 21.2 (*C*H$_3$), 21.5 (*C*H$_3$), 23.5 (*C*H$_2$), 25.0 (*C*H$_2$), 32.0 (*C*H$_2$), 32.2 (*C*H$_2$), 38.3 (*C*H), 66.3 (Ph-*C*-CH), 83.8 (C≡C), 94.4 (C≡C), 120.2 (Ar–C), 120.6 (C=C), 122.1 (Ar–C), 124.9 (Ar–C), 125.6 (Ar–C), 126.0 (Ar–C), 126.5 (Ar–C), 127.2 (Ar–C), 127.6 (Ar–C), 128.1 (Ar–C), 128.3 (Ar–C), 129.1 (Ar–C), 131.7 (Ar–C), 135.3 (Ar–C), 135.6 (Ar–C), 138.3 (C=C), 141.1 (Ar–C), 144.4 (C=C), 145.2 (Ar–C), 149.1(Ar–C), 158.2 (C=C); IR (NaCl, neat) ν: 2978, 2941,1651, 1506, 816, 896 cm^{-1}; MS (ESI) m/z 517 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{40}H_{37}$ (M^+ + H): 517.2895, found: 517.2894.

1-Cyclobutyl-2-(cyclobutylidene(4-pentylphenyl)methyl)-3-((4-pentylphenyl)ethynyl)-1-phenyl-1*H*-indene (2c). Yellow oil; R_f 0.57 (eluent: *n*-hexane–CH_2Cl_2 = 4 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.87–1.00 (m, 7H, C*H*$_3$, C*H*$_2$), 1.26-1.44 (m, 10H, C*H*$_2$), 1.32–1.49 (m, 9H, C*H*$_2$), 1.55-1.62 (m, 6H, C*H*$_2$), 1.75–1.85 (m, 2H, C*H*$_2$), 2.05–2.14 (m, 3H, C*H*$_2$), 2.48-2.73 (m, 7H, C*H*$_2$), 3.08–3.19 (m, 1H, C*H*), 6.77 (d, 2H, J = 6.6 Hz, Ar-*H*), 6.88–6.99 (m, 7H, Ar-*H*), 7.12–7.44 (m, 7H, Ar-*H*), 7.66 (d, 1H, J = 7.4 Hz, Ar-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.1 (*C*H$_3$), 14.1 (*C*H$_3$), 17.2 (*C*H$_2$), 17.3 (*C*H$_2$), 22.6 (*C*H$_2$), 22.6 (*C*H$_2$), 23.6 (*C*H$_2$), 25.1 (*C*H$_2$), 31.0 (*C*H$_2$), 31.2 (*C*H$_2$), 31.5 (*C*H$_2$), 31.6 (*C*H$_2$), 32.1 (*C*H$_2$), 32.3 (*C*H$_2$), 35.7 (*C*H$_2$), 35.9 (*C*H$_2$), 38.4 (*C*H), 66.2 (Ph-*C*-CH), 83.9 (C≡C), 94.5 (C≡C), 120.2 (Ar–C), 120.9 (Ar–C), 122.1 (C=C), 124.9 (Ar–C), 125.6 (Ar–C), 126.0 (Ar–C), 126.7 (Ar–C), 127.2 (Ar–C), 127.6 (Ar–C), 128.1 (Ar–C), 128.3 (Ar–C), 128.5 (Ar–C), 131.7 (Ar–C), 135.8 (Ar–C), 140.3 (C=C), 141.1 (Ar–C), 143.3 (Ar–C), 144.4 (C=C), 145.0 (Ar–C), 149.2 (Ar–C), 158.2 (C=C); IR (NaCl, neat) ν: 2953, 2928, 1647, 1508, 1456, 752, 696 cm^{-1}; MS (ESI) m/z 629 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{48}H_{53}$ (M^+ + H): 629.4147, found: 629.4154.

2-((4-Chlorophenyl)(cyclobutylidene)methyl)-3-((4-chlorophenyl)ethynyl)-1-cyclobutyl-1-phenyl-1*H*-indene (2d). Pale yellow solid; R_f 0.50 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); m.p. 167–168 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.94–1.02 (m, 1H, C*H*$_2$), 1.45–1.66 (m, 3H, C*H*$_2$), 1.71–1.88 (m, 2H, C*H*$_2$), 2.06–2.23 (m, 3H, C*H*$_2$), 2.51–2.77 (m, 3H, C*H*$_2$), 3.16–3.22 (m, 1H, C*H*), 6.73 (d, 2H, J = 7.4 Hz, Ar-*H*), 6.88–7.06 (m, 7H, Ar-*H*), 7.25–7.46 (m, 8H, Ar-*H*), 7.64 (d, 2H, J = 7.4 Hz, Ar-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.1 (*C*H$_2$), 17.2 (*C*H$_2$), 23.4 (*C*H$_2$), 25.0 (*C*H$_2$), 32.2 (*C*H$_2$), 32.3 (*C*H$_2$), 38.2 (*C*H), 66.2 (Ph-*C*-CH), 85.2 (C≡C), 93.4 (C≡C), 120.2 (Ar–C), 121.9 (Ar–C), 122.1 (C=C), 125.0 (Ar–C), 125.8 (Ar–C), 125.9 (Ar–C), 126.2 (Ar–C), 127.3 (Ar–C), 127.7 (Ar–C), 127.7 (Ar–C), 128.2 (Ar–C), 128.7 (Ar–C), 129.4 (Ar–C), 131.5 (Ar–C), 132.9 (Ar–C), 134.3 (Ar–C), 136.8 (C=C), 140.6 (Ar–C), 143.8 (Ar–C), 146.6 (C=C), 149.1(Ar–C), 158.2 (C=C); IR (NaCl, neat) ν: 2998, 2931, 1498, 1321, 1108, 835 cm^{-1}; MS (ESI) m/z 557 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{38}H_{31}Cl_2$ (M^+ + H): 557.1803, found: 557.1812.

3-((1-Cyclobutyl-1-phenyl-3-(thiophen-3-ylethynyl)-1*H*-inden-2-yl)(cyclobutylidene) methyl)thiophene (2e). Pale yellow solid; R_f 0.36 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); m.p. 127–129 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.95–1.01 (m, 1H, C*H*$_2$), 1.45–1.64 (m, 1H, C*H*$_2$), 1.75–1.86 (m, 4H, C*H*$_2$), 2.05–2.11 (m, 2H, C*H*$_2$), 2.45–2.47 (m, 1H, C*H*$_2$), 2.71–2.79 (m, 1H, C*H*$_2$), 3.24–3.28 (m, 1H, C*H*), 6.70 (dd, 1H, J = 5.0, 1.1 Hz, Ar-*H*), 6.76 (dd, 1H, J = 2.8, 1.0 Hz, Ar-*H*), 6.80 (dd, 1H, J = 8.1, 2.0 Hz, Ar-*H*), 6.98-7.05 (m, 4H, Ar-*H*), 7.17 (dd, 1H, J = 5.0, 1.0 Hz, Ar-*H*), 7.27-7.49 (m, 5H, Ar-*H*), 7.64 (d, 2H, J = 7.5 Hz Ar-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.2 (*C*H$_2$), 17.2 (*C*H$_2$), 23.6 (*C*H$_2$), 25.1 (*C*H$_2$), 31.8 (*C*H$_2$), 32.5 (*C*H$_2$), 38.4 (*C*H), 66.3 (Ph-*C*-CH), 83.8 (C≡C), 89.6 (C≡C), 120.3 (Ar–C), 121.2 (Ar–C), 121.5 (C=C), 122.0 (Ar–C), 122.6 (Ar–C), 123.7 (Ar–C), 125.0 (Ar–C), 125.3 (Ar–C), 125.7 (Ar–C), 126.2 (Ar–C), 127.2 (Ar–C), 127.7 (Ar–C), 127.9 (Ar–C), 128.3 (Ar–C), 128.6 (Ar–C), 130.1 (Ar–C), 139.4 (C=C), 141.0 (Ar–C), 144.2 (C=C), 145.7 (Ar–C), 149.0 (Ar–C), 157.9 (C=C); IR (NaCl, neat) ν: 2977, 2941, 1653, 1636, 777, 696 cm^{-1}; MS (ESI) m/z 501 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{34}H_{29}S_2$ (M^+ + H): 501.1711, found: 501.1708.

(*E*)-1-Ethyl-1-phenyl-3-(phenylethynyl)-2-(1-phenylprop-1-enyl)-1*H*-indene (2f). Yellow oil; R_f 0.49 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.07 (t, 3H, J = 7.6 Hz, C*H*$_3$CH$_2$), 1.57 (d, 1H, J = 7.8 Hz, C*H*$_3$CH), 2.37-2.44 (m, 2H, CH$_2$C*H*$_2$CH$_3$), 5.75 (q, 1H, J = 7.0 Hz, C*H*CH$_3$), 7.09–7.35 (m, 19H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.3 (*C*H$_3$), 15.2 (*C*H$_3$), 19.6 (*C*H$_2$), 58.4 (Ph-*C*-CH$_2$), 84.5 (C≡C), 89.8 (C≡C), 119.7 (C=C), 123.7 (C=C), 126.3 (Ar–C), 126.5 (Ar–C), 126.6 (Ar–C), 126.6 (Ar–C), 127.3 (Ar–C), 127.7 (Ar–C), 127.7 (Ar–C),

128.0 (Ar–C), 128.2 (Ar–C), 128.3 (Ar–C), 129.6 (Ar–C), 131.8 (Ar–C), 136.0 (Ar–C), 139.9 (Ar–C), 140.8 (Ar–C), 141.5 (Ar–C), 143.8 (C=C), 147.9 (Ar–C), 151.3 (C=C); IR (NaCl, neat) *v*: 2993, 2921, 1654, 1490, 757, 693 cm^{-1}; MS (ESI) *m/z* 437 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{34}H_{29}$ (M^+ + H): 437.2269, found: 437.2243.

(*E*)-1-Butyl-1-phenyl-3-(phenylethynyl)-2-(1-phenylpent-1-enyl)-1*H*-indene (2g). Yellow oil; R_f 0.46 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.70 (t, 3H, J = 7.4 Hz, CH_3), 0.86 (t, 3H, J = 7.4 Hz, CH_3), 1.16–1.30 (m, 4H, CH_2), 1.38–1.50 (m, 2H, CH_2), 1.87–1.99 (m, 2H, CHCH_2), 2.27–2.32 (m, 2H, CH_2CH$_2$CH$_2$CH$_3$), 5.68 (t, 1H, J = 7.4 Hz, CH$_2$CH), 7.08-7.33 (m, 19H, Ar-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.6 (*C*H$_3$), 14.0 (*C*H$_3$), 23.0 (*C*H$_2$), 23.2 (*C*H$_2$), 26.3 (*C*H$_2$), 31.1 (*C*H$_2$CH), 31.1 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 58.6 (Ph-*C*-CH$_2$), 84.4 (C≡C), 90.0 (C≡C), 119.7 (C=C), 123.6 (C=C), 123.7 (Ar–C), 126.3 (Ar–C), 126.4 (Ar–C), 126.7 (Ar–C), 127.3 (Ar–C), 127.7 (Ar–C), 127.8 (Ar–C), 128.0 (Ar–C), 128.2 (Ar–C), 129.6 (Ar–C), 131.8 (Ar–C), 134.5 (Ar–C), 135.0 (Ar–C), 140.3 (Ar–C), 140.5 (Ar–C), 140.9 (Ar–C), 144.3 (C=C), 147.9 (Ar–C), 151.3 (C=C); IR (NaCl, neat) *v*: 3057, 2957, 2928, 2859, 1597, 1489, 1445, 1022, 754, 696 cm^{-1}; MS (ESI) *m/z* 493 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{38}H_{37}$ (M^++H): 493.2895, found: 493.2887.

(*E*)-1-Hexyl-1-phenyl-3-(phenylethynyl)-2-(1-phenylhept-1-enyl)-1*H*-indene (2h). Yellow oil; R_f 0.48 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.75(t, 3H, J = 7.2 Hz, CH_3), 0.88 (t, 3H, J = 7.1 Hz, CH_3), 1.02-1.51 (m, 18H, CH_2), 1.83-2.02 (m, 2H, CHCH_2CH$_2$), 2.29 (t, 2H, J = 7.6 Hz, CH_2), 5.68 (t, 1H, J = 7.5 Hz, CH$_2$CH), 7.08-7.33 (m, 19H, Ar-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.9 (*C*H$_3$), 14.1 (*C*H$_3$), 22.5 (*C*H$_2$), 22.7 (*C*H$_2$), 26.6 (*C*H$_2$), 28.9 (*C*H$_2$), 29.0 (*C*H$_2$), 29.5 (*C*H$_2$), 29.8 (*C*H$_2$), 31.1 (*C*H$_2$), 31.7 (*C*H$_2$), 58.5 (Ph-*C*-CH$_2$), 84.5 (C≡C), 90.0 (C≡C), 119.7 (C=C), 123.6 (Ar–C), 123.7(C=C), 126.3 (Ar–C), 126.4 (Ar–C), 126.7 (Ar–C), 127.3 (Ar–C), 127.7 (Ar–C), 127.7 (Ar–C), 128.0 (Ar–C), 128.2 (Ar–C), 129.6 (Ar–C), 131.8 (Ar–C), 134.8 (Ar–C), 134.8 (Ar–C), 140.3 (Ar–C), 140.5 (Ar–C), 140.9 (Ar–C), 144.3 (C=C), 147.9 (Ar–C), 151.2 (C=C); IR (NaCl, neat) *v*: 2955, 2926, 2855, 1597, 1489, 1028, 696 cm^{-1}; MS (ESI) *m/z* 549 [M]$^+$; HRMS (ESI) calcd. for $C_{42}H_{45}$ (M^+ + H): 549.3521, found: 549.3523.

(*E*)-1-*iso*-Butyl-2-(3-methyl-1-phenylbut-1-enyl)-1-phenyl-3-(phenylethynyl)-1*H*-indene (2i). Pale yellow oil; R_f 0.46 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.78 (d, 3H, J = 6.5 Hz, CH_3), 0.82 (d, 3H, J = 6.5 Hz, CH_3), 0.87 (d, 3H, J = 6.5 Hz, CH_3), 0.92 (d, 3H, J = 6.5 Hz, CH_3), 1.99-2.09 (m, 1H, CH$_3$CHCH), 2.18 (d, 2H, J = 7.3 Hz, CH_2), 2.34-2.43 (m, 1H, CH$_3$CH), 5.44 (d, 1H, J = 10.3 Hz, CHCH), 7.07-7.32 (m, 19H, Ar-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.0 (*C*H$_3$), 23.1 (*C*H$_3$), 23.1 (*C*H$_3$), 23.2 (*C*H$_3$), 28.0 (*C*H), 28.5 (*C*H), 35.0 (*C*HCH$_2$), 58.8 (Ph-*C*-CH$_2$), 84.8 (C≡C), 90.0 (C≡C), 120.0 (C=C), 123.7 (Ar–C), 123.7 (C=C), 126.2 (Ar–C), 126.4 (Ar–C), 126.7 (Ar–C), 126.9 (Ar–C), 127.3 (Ar–C), 127.7 (Ar–C), 127.7 (Ar–C), 128.0 (Ar–C), 128.1 (Ar–C), 129.4 (Ar–C), 131.8 (Ar–C), 132.2 (Ar–C), 139.5 (Ar–C), 140.2 (Ar–C), 140.8 (Ar–C), 142.2 (Ar–C), 144.9 (C=C), 149.2(Ar–C), 150.9 (C=C); IR (NaCl, neat) *v*: 2957, 2864, 1636, 1456, 752, 696 cm^{-1}; MS (ESI) *m/z* 493 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{38}H_{37}$ (M^+ + H): 493.2895, found: 493.2884.

(*E*)-1-Benzyl-2-(1,2-diphenylvinyl)-1-phenyl-3-(phenylethynyl)-1*H*-indene (2j). Grey oil; R_f 0.24 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.89 (q, 2H, J = 15.8 Hz, CH_2), 6.64 (s, 1H, CH), 6.75-7.36 (m, 29H, Ar-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 32.6 (*C*H$_2$), 58.9 (*C*-CH$_2$Ph), 84.8 (C≡C), 89.3 (C≡C), 121.0 (Ar–C), 123.5 (C=C), 123.7 (Ar–C), 126.1 (Ar–C), 126.7 (Ar–C), 126.8 (Ar–C), 126.9 (Ar–C), 126.9 (Ar–C), 127.2 (Ar–C), 127.5 (Ar–C), 127.8 (Ar–C), 127.9 (Ar–C), 127.9 (Ar–C), 128.1 (Ar–C), 128.2 (Ar–C), 128.4 (Ar–C), 128.5 (Ar–C), 129.6 (Ar–C), 130.0 (Ar–C), 131.9 (Ar–C), 132.4 (Ar–C), 136.5 (Ar–C), 137.1 (C=C), 139.1 (Ar–C), 139.5 (Ar–C), 140.4 (C=C), 143.9 (Ar–C), 150.7 (Ar–C), 151.2 (C=C); IR (NaCl, neat) *v*: 2991, 2918, 2089, 1636, 690 cm^{-1}; MS (ESI) *m/z* 561 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{44}H_{33}$ (M^+ + H): 561.2582, found: 561.2592.

(*E*)-5-(Benzo[*d*][1,3]dioxol-5-yl)-5-ethyl-7-(phenylethynyl)-6-(1-phenylprop-1-enyl)-5*H*-indeno[5,6-*d*][1,3]dioxole (2k). White solid; R_f 0.28 (eluent: *n*-hexane–CH_2Cl_2 = 3 : 1); m.p. 68–70 °C;^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.03 (t, 3 H, J = 7.5 Hz, CH$_2$CH_3), 1.60 (d, 3H, J = 7.0 Hz, CHCH_3), 2.33 (q, 2H, J = 7.4 Hz, CH$_3$CH_2), 5.77 (q, 1H, J = 7.0 Hz, CH$_3$CH), 5.88 (d, 2H, J = 8.1 Hz, OCH_2O), 5.92 (s, 2H, Ar-H), 6.59 (s, 1H, Ar-H), 6.65 (d, 1H, J = 8.1 Hz, Ar-H), 6.74 (s, 1H, Ar-H), 6.80 (s, 1H, Ar-H), 6.93 (d, 1H, J = 8.0 Hz, Ar-H), 7.09-7.30 (m, 10H, Ar-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.3 (CH$_2$*C*H$_3$), 15.2 (CH*C*H$_3$), 19.7 (CH$_3$*C*H$_2$), 57.6 (*C*-CH$_2$), 84.4 (C≡C), 89.7 (C≡C), 100.8 (C=C), 100.9 (O*C*H$_2$O), 101.1 (O*C*H$_2$O), 105.0 (Ar–C), 106.9 (Ar–C), 107.7 (Ar–C), 120.0 (Ar–C), 123.5 (C=C), 126.4 (Ar–C), 127.6 (Ar–C), 127.8 (Ar–C), 127.9 (Ar–C), 128.0 (Ar–C), 129.6 (Ar–C), 131.8 (Ar–C), 134.6 (Ar–C), 136.0 (Ar–C), 137.4(Ar–C), 139.9 (Ar–C), 141.0 (Ar–C), 145.1(C=C), 146.3 (Ar–C), 146.5(Ar–C), 147.0 (C=C), 147.3 (Ar–C), 147.4 (Ar–C); IR (NaCl, neat) *v*: 2982, 2937, 1672, 1513, 1235, 824 cm^{-1}; MS (ESI) *m/z* 525 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{36}H_{29}O_4$ (M^+ + H): 525.2066, found: 525.2057.

(*E*)-1-Phenethyl-1-phenyl-2-(3-phenyl-1-*p*-tolylprop-1-enyl)-3-(*p*-tolylethynyl)-1*H*-indene (2l). Pale yellow oil; R_f 0.44 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.26 (s, 3H, Ar–CH_3), 2.30 (s, 3H, Ar–CH_3), 2.65-2.88 (m, 4H, CH_2), 3.17-3.35 (m, 2H, CH_2CH$_2$), 5.72 (t, 1H, J = 7.7 Hz, CHCH$_2$), 6.84-7.43 (m, 27H, Ar-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.2 (Ar-*C*H$_3$), 21.5 (Ar-*C*H$_3$), 28.9 (CH$_2$*C*H$_2$), 34.9 (CH*C*H$_2$), 35.1 (CH$_2$*C*H$_2$), 58.5 (Ph-*C*-CH$_2$), 84.8 (C≡C), 88.7 (C≡C), 119.8 (C=C), 120.5 (Ar–C), 123.9 (C=C), 125.7 (Ar–C), 126.0 (Ar–C), 126.6 (Ar–C), 126.7 (Ar–C), 126.8 (Ar–C), 127.4 (Ar–C), 128.3 (Ar–C), 128.3 (Ar–C), 128.4 (Ar–C), 128.6 (Ar–C), 128.7 (Ar–C), 128.7 (Ar–C), 129.4 (Ar–C), 131.7 (Ar–C), 131.9 (Ar–C), 135.9 (Ar–C), 136.5 (Ar–C), 136.6 (Ar–C), 137.7 (Ar–C), 139.2 (Ar–C), 140.7 (Ar–C), 140.9 (Ar–C), 141.9 (Ar–C), 143.8 (C=C), 149.1 (Ar–C), 151.4 (C=C); IR (NaCl, neat) *v*: 2962, 2933, 1603, 1588, 1025, 717 cm^{-1}; MS (ESI) *m/z* 617 [M + H]$^+$; HRMS (ESI) calcd. for $C_{48}H_{41}$ (M^+ + H): 617.3208, found: 617.3201.

(*E*)-1-Benzyl-6-ethoxy-1-(4-ethoxyphenyl)-2-(2-phenyl-1-*p*-tolylvinyl)-3-(*p*-tolylethynyl)-1*H*-indene (2m). Pale yellow solid; R_f 0.38 (eluent: *n*-hexane–CH_2Cl_2 = 3 : 1); m.p. 191–192 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.38-1.52 (m, 6 H, CH_3CH$_2$), 2.25 (s, 3H, Ar–CH_3), 3.79 (d, 1H, J = 12.9 Hz, CH_2Ph), 3.98–4.05 (m, 5H, CH$_3$CH_2O, CH_2Ph), 6.51 (s, 1H, Ph-CH), 6.66–7.31(m,

25H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.9 (*C*H_3CH), 15.0 (*C*H_3CH), 21.3 (Ar-*C*H_3), 21.5 (Ar-*C*H_3), 42.5 (Ph-*C*H_2), 61.4 (*C*H_2Ph), 63.4 (CH_3*C*H_2O), 63.7 (CH_3*C*H_2O), 83.5 (C≡C), 101.0 (C≡C), 109.4 (Ar–C), 113.1 (Ar–C), 114.9 (Ar–C), 120.4 (C=C), 121.4 (Ar–C), 125.5 (Ar–C), 126.4 (C=C), 126.5 (Ar–C), 126.7 (Ar–C), 127.6 (Ar–C), 127.8 (Ar–C), 128.6 (Ar–C), 128.9 (Ar–C), 129.6 (Ar–C), 129.7 (Ar–C), 130.8 (Ar–C), 130.9 (Ar–C), 131.8 (Ar–C), 136.3 (Ar–C), 136.4 (Ar–C), 136.6 (Ar–C), 136.9 (Ar–C), 137.0 (Ar–C), 137.6 (Ar–C), 137.7 (Ar–C), 137.9 (Ar–C), 152.2 (C=C), 154.1(C=C), 157.6 (Ar–C), 158.8 (Ar–C); IR (NaCl, neat) *v*: 2978, 1651, 1506, 1246, 1045, 816, 694 cm^{-1}; MS (ESI) *m*/*z* 677 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{50}H_{45}O_2$ (M^+ + H): 677.3420, found: 677.3411.

(*E*)-1-(But-3-enyl)-6-ethoxy-1-(4-ethoxyphenyl)-3-(*p*-tolylethynyl)-2-(1-*p*-tolylpenta-1,4-dienyl)-1*H*-indene (2n). Pale brown oil; R_f 0.30 (eluent: *n*-hexane–CH_2Cl_2 = 3 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.33–1.40 (m, 6H, C*H*$_3$CH$_2$O), 1.84–1.91 (m, 1H, C*H*$_2$), 2.19–2.613 (m, 11H, C*H*$_2$, Ar–C*H*$_3$), 3.91–4.00 (m, 4H, CH$_3$C*H*$_2$O), 4.72–4.92 (m, 4H, CHC*H*$_2$), 5.60–5.75 (m, 3H, C*H*), 6.53 (d, 1H, *J* = 2.2 Hz, Ar-*H*), 6.72–6.80 (m, 3H, Ar-*H*), 6.98–7.24 (m, 10H, Ar-*H*), 7.39 (m, 1H, *J* = 8.2 Hz, Ar-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.9 (*C*H$_3$CH$_2$O), 14.9 (*C*H$_3$CH$_2$O), 21.2 (Ar-*C*H$_3$), 21.5 (Ar-*C*H$_3$), 27.9 (*C*H$_2$), 33.3 (*C*H$_2$), 35.6 (*C*H$_2$), 60.8 (*C*-CH$_2$), 63.4 (CH$_3$*C*H$_2$O), 63.6 (CH$_3$*C*H$_2$O), 83.6 (C≡C), 98.2 (C≡C), 109.0 (C=C), 112.6 (Ar–C), 114.3 (Ar–C), 114.4 (Ar–C), 114.7 (C=C), 120.5 (Ar–C), 121.0 (Ar–C), 122.6 (Ar–C), 127.1 (Ar–C), 128.5 (Ar–C), 128.8 (Ar–C), 129.9 (Ar–C), 131.0 (C=C), 131.8 (C=C), 136.0 (Ar–C), 136.1 (C=C), 136.5 (C=C), 136.7 (Ar–C), 137.4 (Ar–C), 138.0 (Ar–C), 138.8 (Ar–C), 153.6 (C=C), 153.8 (C=C), 157.4 (Ar–C), 158.6 (Ar–C); IR (NaCl, neat) *v*: 2978, 1607, 1508, 1248, 756 cm^{-1}; MS (ESI) *m*/*z* 605 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{44}H_{45}O_2$ (M^+ + H): 605.3420, found: 605.3413.

3-Cyclobutyl-2-(cyclobutylidene(phenyl)methyl)-1-phenyl-1-(phenylethynyl)-1*H*-indene (3a). White solid; R_f 0.41 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); m.p. 161–163 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.59–1.85 (m, 3H, C*H*$_2$), 1.90–1.97 (m, 1H, C*H*$_2$), 2.03–2.15 (m, 1H, C*H*$_2$), 2.23–2.38 (m, 3H, C*H*$_2$), 2.54–2.72 (m, 3H, C*H*$_2$), 2.84–2.89 (m, 1H, C*H*$_2$), 3.64–3.73 (m, 1H, C*H*), 6.93 (d, 2H, *J* = 7.2 Hz, Ar-*H*), 7.04–7.25 (m, 14H, Ar-*H*), 7.36–7.39 (m, 2H, Ar-*H*), 7.60 (d, 2H, *J* = 7.5 Hz, Ar-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.3 (*C*H$_2$), 19.2 (*C*H$_2$), 27.4 (*C*H$_2$), 27.8 (*C*H$_2$), 31.6 (*C*H$_2$), 32.5 (*C*H$_2$), 35.2 (C-*C*H), 58.4 (*C*-Ph), 84.2 (C≡C), 89.8 (C≡C), 120.7 (Ar–C), 123.5 (Ar–C), 124.3 (Ar–C), 125.7 (Ar–C), 126.0 (Ar–C), 126.6 (Ar–C), 127.3 (Ar–C), 127.4 (Ar–C), 127.5 (Ar–C), 127.6 (C=C), 127.7 (Ar–C), 128.0 (Ar–C), 131.7 (Ar–C), 139.2 (C=C), 140.8 (Ar–C), 141.2 (C=C), 144.1 (C=C), 144.2 (Ar–C), 145.0 (Ar–C), 150.4 (Ar–C); IR (NaCl, neat) *v*: 2983, 2933,1651, 1489, 754, 694 cm^{-1}; MS (ESI) *m*/*z* 489 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{38}H_{33}$ ([M + H]$^+$): 489.2582, found: 489.2579.

3-Cyclobutyl-2-(cyclobutylidene(*p*-tolyl)methyl)-1-phenyl-1-(*p*-tolylethynyl)-1*H*-indene (3b). Pale yellow oil; R_f 0.46 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.61–1.96 (m, 5H, C*H*$_2$), 2.02–2.39 (m, 9H, C*H*$_2$, Ar–C*H*$_3$), 2.51–2.66 (m, 3H, C*H*$_2$), 2.83–2.89 (m, 1H, C*H*$_2$), 3.63–3.72 (m, 1H, C*H*), 6.78 (d, 2H, *J* = 7.9 Hz, Ar-*H*), 6.93–7.00 (m, 4H, Ar-*H*), 7.10–7.38 (m, 10H, Ar-*H*), 7.58 (d, 2H, *J* = 7.6 Hz, Ar-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.2 (*C*H$_2$), 19.2 (*C*H$_2$), 21.0 (Ar-*C*H$_3$), 21.4 (Ar-*C*H$_3$), 27.4 (*C*H$_2$), 27.9 (*C*H$_2$), 31.5 (*C*H$_2$), 32.3 (*C*H$_2$), 35.3 (*C*H), 58.4 (*C*-Ph), 84.3 (C≡C), 89.0 (C≡C), 120.5 (Ar–C), 120.6 (Ar–C), 124.3 (Ar–C), 125.9 (Ar–C), 126.0 (Ar–C), 126.5 (Ar–C), 127.3 (Ar–C), 127.4 (Ar–C), 127.6 (C=C), 128.1 (Ar–C), 128.4 (Ar–C), 128.4 (Ar–C), 131.6 (Ar–C), 135.2 (Ar–C), 136.5 (Ar–C), 137.3 (Ar–C), 140.9 (C=C), 141.1 (C=C), 144.0 (Ar–C), 144.1 (C=C), 144.5 (Ar–C), 150.4 (Ar–C); IR (NaCl, neat) *v*: 2977, 2916, 2237, 1664, 1089, 751, 692 cm^{-1}; MS (ESI) *m*/*z* 517 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{40}H_{37}$ (M^+ + H): 517.2895, found: 517.2902.

3-Cyclobutyl-2-(cyclobutylidene(4-pentylphenyl)methyl)-1-((4-pentylphenyl)ethynyl)-1-phenyl-1*H*-indene (3c). White solid; R_f 0.52 (eluent: *n*-hexane–CH_2Cl_2 = 4 : 1); m.p. 90–91 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.85–0.92 (m, 6H, CH$_2$C*H*$_3$), 1.25–1.34 (m, 9H, C*H*$_2$), 1.54–1.67 (m, 5H, C*H*$_2$), 1.75–1.96 (m, 2H, C*H*$_2$), 2.04–2.37 (m, 4H, C*H*$_2$), 2.47–2.70 (m, 7H, C*H*$_2$), 2.85–2.87 (m, 1H, C*H*$_2$), 3.63–3.72 (m, 1H C*H*), 6.85 (d, 2H, *J* = 7.8 Hz, Ar-*H*), 6.92–7.36 (m, 14H, Ar-*H*), 7.59 (d, 2H, *J* = 7.6 Hz, Ar-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.0 (*C*H$_3$), 14.1 (*C*H$_3$), 17.3 (*C*H$_2$), 19.2 (*C*H$_2$), 22.5 (*C*H$_2$), 22.6 (*C*H$_2$), 27.4 (*C*H$_2$), 27.8 (*C*H$_2$), 30.9 (*C*H$_2$), 31.2 (*C*H$_2$), 31.4 (*C*H$_2$), 31.6 (*C*H$_2$), 31.8 (*C*H$_2$), 32.4 (*C*H$_2$), 35.2 (*C*H$_2$), 35.7 (*C*H$_2$), 35.8 (*C*H), 58.4 (*C*H-Ph), 84.2 (C≡C), 89.0 (C≡C), 120.6 (Ar–C), 120.8 (Ar–C), 124.3 (Ar–C), 125.9 (Ar–C), 126.5 (Ar–C), 127.2 (Ar–C), 127.4 (Ar–C), 127.5 (Ar–C), 127.6 (Ar–C), 127.8 (Ar–C), 127.9 (C=C), 131.5 (Ar–C), 136.6 (C=C), 140.3 (Ar–C), 140.9 (Ar–C), 141.1 (C=C), 142.4 (Ar–C), 144.0 (Ar–C), 144.1 (C=C), 144.5 (Ar–C), 150.5 (Ar–C); IR (NaCl, neat) *v*: 2979, 2918, 2089, 1634, 744, 696 cm^{-1}; MS (ESI) *m*/*z* 629 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{48}H_{53}$ (M^+ + H): 629.4147, found: 629.4145.

(*E*)-3-Ethyl-1-phenyl-1-(phenylethynyl)-2-(1-phenylprop-1-enyl)-1*H*-indene (3f). Yellow oil; R_f 0.45 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.55 (t, 3H, *J* = 7.2 Hz, CH$_2$C*H*$_3$), 1.49 (d, 1H, *J* = 7.1 Hz, CHC*H*$_3$), 2.37–2.45 (m, 1H, C*H*$_2$CH$_3$), 2.54–2.62 (m, 1H, C*H*$_2$CH$_3$), 5.82 (q, 1H, *J* = 7.1 Hz, CH$_3$C*H*), 6.95 (m, 1H, *J* = 7.4 Hz, Ar-*H*), 7.11–7.33 (m, 17H, Ar-*H*), 7.52 (m, 1H, *J* = 7.4 Hz, Ar-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 8.1 (*C*H$_3$CH$_2$), 15.6 (*C*H$_3$CH), 28.6 (*C*H$_2$), 62.2 (*C*-CH$_2$), 84.2 (C≡C), 98.3 (C≡C), 120.2 (C=C), 122.1 (Ar–C), 122.8 (Ar–C), 123.5 (Ar–C), 126.0 (Ar–C), 126.2 (Ar–C), 126.5 (Ar–C), 126.8 (Ar–C), 127.0 (Ar–C), 127.8 (Ar–C), 127.9 (Ar–C), 128.0 (Ar–C), 128.5 (Ar–C), 130.1 (Ar–C), 130.3 (Ar–C), 132.0 (C=C), 137.5 (Ar–C), 139.2 (Ar–C), 143.3 (C=C), 144.3 (Ar–C), 151.7 (C=C), 155.3 (Ar–C); IR (NaCl, neat) *v*: 3055, 2968, 1597, 1489, 1443, 1265, 756, 698 cm^{-1}; MS (ESI) *m*/*z* 437 [M + 1]$^+$; HRMS (ESI) calcd. for $C_{34}H_{29}$ (M^+ + H): 437.2269, found: 437.2261.

(*E*)-3-Butyl-1-phenyl-1-(phenylethynyl)-2-(1-phenylpent-1-enyl)-1*H*-indene (3g). Yellow oil; R_f 0.42 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.57–0.88 (m, 7H, C*H*$_3$, C*H*$_2$), 1.15–1.53 (m, 5H, C*H*$_2$), 1.82–1.86 (m, 2H, C*H*$_2$), 2.28–2.37 (m, 1H, C*H*$_2$), 2.43–2.50 (m, 1H, C*H*$_2$), 5.73 (t, 1H, *J* = 7.6 Hz, C*H*CH$_2$), 6.96 (d, 1H, *J* = 7.4 Hz, Ar-*H*), 7.10–7.31 (m, 17H, Ar-*H*), 7.52 (d, 1H, *J* = 7.5 Hz, Ar-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.5 (*C*H$_3$), 14.0 (*C*H$_3$), 22.8 (*C*H$_2$), 23.1 (*C*H$_2$), 25.4 (*C*H$_2$), 31.3 (CH*C*H$_2$), 35.7 (C*C*H$_2$), 61.7 (*C*CH$_2$), 84.2

(C≡C), 98.1 (C≡C), 120.2 (C=C), 122.0 (Ar–C), 122.4 (Ar–C), 123.5 (Ar–C), 126.1 (Ar–C), 126.2 (Ar–C), 126.4 (Ar–C), 126.7 (Ar–C), 127.0 (Ar–C), 127.7 (Ar–C), 127.9 (Ar–C), 128.0 (Ar–C), 128.4 (Ar–C), 130.2 (Ar–C), 132.0 (C=C), 136.3 (Ar–C), 136.4 (Ar–C), 139.3(Ar–C), 143.2 (Ar–C), 144.2 (C=C), 152.1 (C=C), 156.1(Ar–C); IR (NaCl, neat) *v*: 2957, 2859, 1645, 1488, 1456, 754, 698 cm^{-1}; MS (ESI) *m*/*z* 493 $[M + 1]^+$; HRMS (ESI) calcd. for $C_{38}H_{37}$ ($M^+ + H$): 493.2895, found: 493.2894.

(*E*)-3-Hexyl-1-phenyl-1-(phenylethynyl)-2-(1-phenylhept-1-enyl)-1*H*-indene (3h). Yellow oil; R_f 0.42 (eluent: *n*-hexane–CH_2Cl_2 = 6 : 1); ^1H NMR ($CDCl_3$, 400 MHz): δ 0.76 (t, 3H, J = 7.3 Hz, CH_3), 0.83 (t, 3H, J = 7.1 Hz, CH_3), 0.98–1.26 (m, 14H, CH_2), 1.84 (q, 2H, J = 7.2 Hz, CH_2), 2.29–2.37 (m, 1H, CH_2), 2.44–2.50 (m, 1H, CH_2), 5.72 (t, 1H, J = 7.6 Hz, CHCH$_2$), 6.96 (d, 1H, J = 7.4 Hz, Ar-*H*), 7.10–7.31 (m, 17H, Ar-*H*), 7.52 (d, 1H, J = 7.5 Hz, Ar-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.9 (*C*H$_3$), 14.1 (*C*H$_3$), 22.5 (*C*H$_2$), 22.6 (*C*H$_2$), 23.1 (*C*H$_2$), 29.2 (*C*H$_2$), 29.3 (*C*H$_2$), 29.8 (*C*H$_2$), 31.0 (*C*H$_2$), 31.6 (*C*H$_2$), 36.0 (C*C*H$_2$), 61.7 (*C*CH$_2$), 84.2 (C≡C), 98.1 (C≡C), 120.2 (C=C), 122.0 (Ar–C), 122.4 (Ar–C), 123.5 (Ar–C), 126.0 (Ar–C), 126.2 (Ar–C), 126.4 (Ar–C), 126.7 (Ar–C), 127.0 (Ar–C), 127.7 (Ar–C), 127.9 (Ar–C), 128.0 (Ar–C), 128.4 (Ar–C), 130.2 (Ar–C), 132.0 (C=C), 136.2 (Ar–C), 136.5 (Ar–C), 139.3 (Ar–C), 143.2 (C=C), 144.3 (C=C), 152.1 (Ar–C), 156.2 (Ar–C); IR (NaCl, neat) *v*: 2953, 2926, 2855, 1597, 1493, 1443, 754, 698 cm^{-1}; MS (ESI) *m*/*z* 549 $[M + 1]^+$; HRMS (ESI) calcd. For $C_{42}H_{45}$ ($M^+ + H$): 549.3521, found: 549.3506.

(*E*)-5-(Benzo[*d*][1,3]dioxol-5-yl)-7-ethyl-5-(phenylethynyl)-6-(1-phenylprop-1-enyl)-5*H*-indeno[5,6-*d*][1,3]dioxole (3k). Yellow solid; R_f 0.24 (eluent: *n*-hexane–CH_2Cl_2 = 3 : 1); m.p. 82–83 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.55 (t, 3 H, J = 7.1 Hz, CH_3CH$_2$), 1.50 (d, 3H, J = 7.1 Hz, CH_3CH), 2.27–2.43 (m, 2H, CH$_3$CH_2), 5.80 (q, 1H, J = 7.0 Hz, CH$_3$CH), 5.87–5.93 (m, 4H, OCH_2O), 6.45 (s, 1H, Ar-*H*), 6.52 (s, 1H, Ar-*H*), 6.67 (d, 1H, J = 8.2 Hz, Ar-*H*), 6.73 (d, 1H, J = 7.8 Hz, Ar-*H*), 6.98 (s, 1H, Ar-*H*), 7.16–7.33 (m, 10H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 8.0 (*C*H$_3$CH$_2$), 15.6 (*C*H$_3$CH), 29.0 (CH$_3$*C*H$_2$), 61.4 (*C*-C≡C), 84.0 (C≡C), 98.1 (C≡C), 100.8 (Ar–C), 101.0 (O*C*H$_2$O), 101.1 (O*C*H$_2$O), 103.2 (Ar–C), 106.9 (Ar–C), 108.0 (Ar–C), 118.5 (Ar–C), 122.2 (Ar–C), 123.3 (C=C), 127.0 (Ar–C), 127.8 (Ar–C), 127.9 (Ar–C), 129.0 (Ar–C), 130.3 (Ar–C), 132.0 (Ar–C), 136.9 (C=C), 137.4 (Ar–C), 138.1 (Ar–C), 139.2 (Ar–C), 145.9 (C=C), 145.9 (Ar–C), 146.8 (C=C), 147.0 (Ar–C), 147.8 (Ar–C), 154.4 (Ar–C); IR (NaCl, neat) *v*: 2975, 2915, 1654, 1527, 1033, 796 cm^{-1}; MS (ESI) *m*/*z* 525 $[M + 1]^+$; HRMS (ESI) calcd. for $C_{36}H_{29}O_4$ ($M^+ + H$): 525.2066, found: 525.2062.

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Notes and references

1 For a review, see: (*a*) H. Gao, J. A. Katzenellenbogen, R. Garg and C. Hansch, *Chem. Rev.*, 1999, **99**, 723; (*b*) For selected examples, see: N. J. Clegg, S. Paruthiyil, D. C. Leitman and T. S. Scanlan, *J. Med. Chem.*, 2005, **48**, 5989; (*c*) A. Korte, J. Legros and C. Bolm, *Synlett*, 2004, 2397; (*d*) I.-M. Karaguni, K.-H. Glüsenkamp, A. Langerak, C. Geisen, V. Ullrich, G. Winde, T. Möröy and O. Müller, *Bioorg. Med. Chem. Lett.*, 2002, **12**, 709; (*e*) J. Yang, M. V. Lakshmikantham, M. P. Cava, D. Lorcy and J. R. Bethelot, *J. Org. Chem.*, 2000, **65**, 6739; (*f*) O. J. Barber, O. A. Rakitin, M. B. Ros and T. Torroba, *Angew. Chem., Int. Ed.*, 1998, **37**, 296; (*g*) S. Hagishita, M. Yamada, K. Shirahase, T. Okada, Y. Murakami, Y. Ito, T. Matsuura, M. Wada and T. Kato, *J. Med. Chem.*, 1996, **39**, 3636; (*h*) J. Palm, K. P. Boegesoe and T. Liljefors, *J. Med. Chem.*, 1993, **36**, 2878; (*i*) D. T. Witiak, S. V. Kakodkar, G. E. Brunst, J. R. Baldwin and R. G. Rahwan, *J. Med. Chem.*, 1978, **21**, 1313.

2 For recent selected examples, see: (*a*) Z. A. Khan and T. Wirth, *Org. Lett.*, 2009, **11**, 229; (*b*) X. B. Zhou, H. M. Zhang, X. Xie and Y. Z. Li, *J. Org. Chem.*, 2008, **73**, 3958; (*c*) Z. B. Zhu and M. Shi, *Chem.–Eur. J.*, 2008, **14**, 10219; (*d*) F. R. Gou, H. P. Bi, L. N. Guo, Z. H. Guan, X. Y. Liu and Y. M. Liang, *J. Org. Chem.*, 2008, **73**, 3837; (*e*) W. L. Chen, J. Cao and X. Huang, *Org. Lett.*, 2008, **10**, 5537; (*f*) Y. T. Wu, M. Y. Kuo, Y. T. Chang, C. C. Shin, T. C. Wu, C. C. Tai, T. H. Cheng and W. S. Liu, *Angew. Chem., Int. Ed.*, 2008, **47**, 9891; (*g*) M. Miyamoto, Y. Harada, M. Tobisu and N. Chatani, *Org. Lett.*, 2008, **10**, 2975; (*h*) R. Sanz, D. Miguel and F. Rodriguez, *Angew. Chem., Int. Ed.*, 2008, **47**, 7354; (*i*) C. C. Liu, R. P. Korivi and C. H. Cheng, *Chem.–Eur. J.*, 2008, **14**, 9503; (*j*) H. P. Bi, X. Y. Liu, F. R. Gou, L. N. Guo, X. H. Duan and Y. M. Liang, *Org. Lett.*, 2007, **9**, 3527; (*k*) D. Zhang, Z. Liu, E. K. Yum and R. C. Larock, *J. Org. Chem.*, 2007, **72**, 251; (*l*) H. Tsukamoto, T. Ueno and Y. Kondo, *Org. Lett.*, 2007, **9**, 3033; (*m*) L. N. Guo, X. H. Duan, H. P. Bi, X. Y. Liu and Y. M. Liang, *J. Org. Chem.*, 2007, **72**, 1538; (*n*) N. Marion, S. Diez-Gonzalez, P. de Fremont, A. R. Noble and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2006, **45**, 3647; (*o*) G. B. Bajracharya, N. K. Pahadi, I. D. Gridnev and Y. Yamamoto, *J. Org. Chem.*, 2006, **71**, 6204; (*p*) X. H. Duan, L. N. Guo, H. P. Bi, X. Y. Liu and Y. M. Liang, *Org. Lett.*, 2006, **8**, 5777; (*q*) Y. Kuninobu, A. Kawata and K. Takai, *J. Am. Chem. Soc.*, 2005, **127**, 13498; (*r*) I. Nakamura, G. B. Bajracharya, Y. Mizushima and Y. Yamamoto, *Angew. Chem., Int. Ed.*, 2002, **41**, 4328.

3 For reviews on iron catalysis, see: (*a*) B. D. Sherry and A. Fürstner, *Acc. Chem. Res.*, 2008, **41**, 1500; (*b*) A. Fürstner, *Angew. Chem., Int. Ed.*, 2009, **48**, 1364; (*c*) S. Enthaler, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2008, **47**, 3317; (*d*) E. B. Bauer, *Curr. Org. Chem.*, 2008, **12**, 1341; (*e*) A. Correa, O. Garcia Mancheno and C. Bolm, *Chem. Soc. Rev.*, 2008, **37**, 1108; (*f*) C. Bolm, J. Legros, J. Le Paih and L. Zani, *Chem. Rev.*, 2004, **104**, 6217.

4 For reviews on the use of alcohols as pro-electrophiles, see: (*a*) M Bandini and M. Tragni, *Org. Biomol. Chem.*, 2009, **7**, 1501; (*b*) N Ljungdahl and N. Kann, *Angew. Chem., Int. Ed.*, 2009, **48**, 642; (*c*) J. Muzart, *Tetrahedron*, 2008, **64**, 5815; (*d*) J. Muzart, *Eur. J. Org. Chem.*, 2007, 3077; (*e*) J. Muzart, *Tetrahedron*, 2005, **61**, 4179; (*f*) Y. Tamaru, *Eur. J. Org. Chem.*, 2005, 2647.

5 (*a*) X. Zhang, W. Rao, Sally and Philip W. H. Chan, *Org. Biomol. Chem.*, 2009, **7**, 4186; (*b*) J. Wang, W. Huang, Z. Zhang, X. Xiang, R. Liu and X. Zhou, *J. Org. Chem.*, 2009, **74**, 3299; (*c*) J. Fan, C. Wan, G. Sun and Z. Wang, *J. Org. Chem.*, 2008, **73**, 8608; (*d*) W. Huang, P. Zheng, Z. Zhang, R. Liu, Z. Chen and X. Zhou, *J. Org. Chem.*, 2008, **73**, 6845; (*e*) W. Huang, Q. Shen, J. Wang and X. Zhou, *J. Org. Chem.*, 2008, **73**, 1586; (*f*) U. Jana, S. Maiti and S. Biswas, *Tetrahedron Lett.*, 2007, **48**, 7160; (*g*) D. Zhang and J. M. Ready, *J. Am. Chem. Soc.*, 2006, **128**, 15050; (*h*) Z.-P. Zhan, J.-L. Yu, H.-J. Liu, Y.-Y. Cui, R.-F. Yang, W.-Z. Yang and J.-P. Li, *J. Org. Chem.*, 2006, **71**, 8298; (*i*) P. O. Miranda, M. A. Ramirez, J. I. Padron and V. S. Martin, *Tetrahedron Lett.*, 2006, **47**, 283; (*j*) M. M. Heravi, F. K. Behbahani, R. H. Shoar and H. A. Oskooie, *Catal. Commun.*, 2006, **7**, 136; (*k*) P. R. Krishna, B. Lavanya, A. K. Mahalingam, V. V. R. Reddy and G. V. M. Sharma, *Lett. Org. Chem.*, 2005, **2**, 360; (*l*) I. Iovel, K. Mertins, J. Kischel, A. Zapf and M. Beller, *Angew. Chem., Int. Ed.*, 2005, **44**, 3913.

6 (*a*) P. Kothandaraman, W. Rao, S. J. Foo and P. W. H. Chan, *Angew. Chem., Int. Ed.*, 2010, **49**, 4619; (*b*) X. Zhang, W. T. Teo and P. W. H. Chan, *Org. Lett.*, 2009, **11**, 4990; (*c*) P. Kothandaraman, S. J. Foo and P. W. H. Chan, *J. Org. Chem.*, 2009, **74**, 5947; (*d*) S. R. Mothe and P. W. H. Chan, *J. Org. Chem.*, 2009, **74**, 5887; (*e*) W. Rao, X. Zhang, E. M. L. Sze and P. W. H. Chan, *J. Org. Chem.*, 2009, **74**, 1740; (*f*) P.

Kothandaraman, W. Rao, X. Zhang and P. W. H. Chan, *Tetrahedron*, 2009, **65**, 1833; (*g*) W. Rao and P. W. H. Chan, *Chem.–Eur. J.*, 2008, **14**, 10486; (*h*) W. Wu, W. Rao, Y. Q. Er, K. J. Loh, C. Y. Poh and P. W. H. Chan, *Tetrahedron Lett.*, 2008, **49**, 2620; W. Wu, W. Rao, Y. Q. Er, K. J. Loh, C. Y. Poh and P. W. H. Chan, *Tetrahedron Lett.*, 2008, **49**, 4981; (*i*) W. Rao and P. W. H. Chan, *Org. Biomol. Chem.*, 2008, **6**, 2426; (*j*) X. Zhang, W. Rao, and P. W. H. Chan, *Synlett* 2008, *Special Issue*, 2204.; (*k*) W. Rao, A. H. L. Tay, P. J. Goh, J. M. L. Choy, J. K. Ke and P. W. H. Chan, *Tetrahedron Lett.*, 2008, **49**, 122; W. Rao, A. H. L. Tay, P. J. Goh, J. M. L. Choy, J. K. Ke and P. W. H. Chan, *Tetrahedron Lett.*, 2008, **49**, 5115.

7 (*a*) V. Maraval, C. Duhayon, Y. Coppel and R. Chauvin, *Eur. J. Org. Chem.*, 2008, 5144; (*b*) A.-H. Feng, J.-Y. Chen, L.-M. Yang, G.-H. Lee, Y. Wang and T.-Y. Luh, *J. Org. Chem.*, 2001, **66**, 7922.

8 For a review, see: (*a*) N. Marion and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2007, **46**, 2750; For selected examples, see ref. 2n and: (*b*) P. Mauleon, J. L. Krinsky and F. D. Toste, *J. Am. Chem. Soc.*, 2009, **131**, 4513; (*c*) M. Uemura, L. D. Watson, M. Katsukawa and F. D. Toste, *J. Am. Chem. Soc.*, 2009, **131**, 3464; (*d*) L. D. Watson, S. Ritter and F. D. Toste, *J. Am. Chem. Soc.*, 2009, **131**, 2056; (*e*) N. D. Shapiro and F. D. Toste, *J. Am. Chem. Soc.*, 2008, **130**, 9244; (*f*) G. Li, G. Zhang and L. Zhang, *J. Am. Chem. Soc.*, 2008, **130**, 3740; (*g*) A. Correa, N. Marion, L. Fensterbank, M. Malacria, S. P. Nolan and L. Cavallo, *Angew. Chem., Int. Ed.*, 2008, **47**, 718; (*h*) C. H. M. Amijs, V. López-Carrillo and A. M. Echavarren, *Org. Lett.*, 2007, **9**, 4021; (*i*) J. Marco-Contelles and E. Soriano, *Chem.–Eur. J.*, 2007, **13**, 1350; (*j*) X. Shi, D. J. Gorin and F. D. Toste, *J. Am. Chem. Soc.*, 2005, **127**, 5802; (*k*) V. Mamane, T. Gress, H. Krause and A. Fürstner, *J. Am. Chem. Soc.*, 2004, **126**, 8654.

9 (*a*) X. Zhao, Z. Zhong, L. Peng, W. Zhang and J. Wang, *Chem. Commun.*, 2009, 2535; (*b*) L. Peng, X. Zhang, S. Zhang and J. Wang, *J. Org. Chem.*, 2007, **72**, 1192.

10 Please see the Electronic Supplementary Information for details†.

11 Apparent 1,3-alkyl migrations have also been proposed in other reactions, for selected examples see: (*a*) H.-H. Chou, H.-M. Wu, J.-D. Wu, T. W. Ly, N.-W. Jan, K.-S. Shia and H.-J. Liu, *Org. Lett.*, 2008, **10**, 121; (*b*) N. Dieltiens and C. V. Stevens, *Org. Lett.*, 2007, **9**, 465; (*c*) B. D. Smith, D. E. Alonso, J. T. Bien, J. D. Zielinski, S. L. Smith and K. J. Haller, *J. Org. Chem.*, 1993, **58**, 6493; (*d*) X. Coqueret, F. Bourelle-Wargnier and J. Chuche, *J. Org. Chem.*, 1985, **50**, 909; (*e*) M. Takahashi, N. Ishii, H. Suzuki, Y. Moro-Oka and T. Ikawa, *Chem. Lett.*, 1981, 1361; (*f*) H. Suzuki, H. Yashima, T. Hirose, M. Takahashi, Y. Moro-Oka and T. Ikawa, *Tetrahedron Lett.*, 1980, **21**, 4927; (*g*) K. Takagi and Y. Ogata, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1410.

12 For examples of Lewis acid-catalysed formation of propargylic cations and similar regioselectivities observed in these reactions, see ref. 4–7 and: (*a*) M. Yoshimatsu, T. Yamamoto, A. Sawa, T. Kato, G. Tanabe and O. Muraoka, *Org. Lett.*, 2009, **11**, 2952; (*b*) M. Yoshimatsu, T. Otani and A. Sawa, *Org. Lett.*, 2008, **10**, 4251; (*c*) T. Ishikawa, T. Aikawa, Y. Mori and S. Saito, *Org. Lett.*, 2003, **5**, 51; (*d*) T. Ishikawa, M. Okano, T. Aikawa and S. Saito, *J. Org. Chem.*, 2001, **66**, 4635.

13 The addition of an acetylenic moiety to a carbocation centre has also been proposed in other reactions, for selected examples see ref. 7a and (*a*) K. Kohno, K. Nakagawa, T. Yahagi, J.-C. Choi, H. Yasuda and T. Sakakura, *J. Am. Chem. Soc.*, 2009, **131**, 2784; (*b*) M.-L. Yao, T. R. Quick, Z. Wu, M. P. Quinn and G. W. Kabalka, *Org. Lett.*, 2009, **11**, 2647; (*c*) Z. Liu, J. Wang, Y. Zhao and B. Zhou, *Adv. Synth. Catal.*, 2009, **351**, 371; (*d*) T. Xu, Z. Yu and L. Wang, *Org. Lett.*, 2009, **11**, 2113; (*e*) S. Biswas, S. Maiti and U. Jana, *Eur. J. Org. Chem.*, 2009, 2354; (*f*) U. Jana, S. Biswas and S. Maiti, *Eur. J. Org. Chem.*, 2008, 5798; (*g*) R. Marcuzzi, G. Modena and G. Melloni, *J. Org. Chem.*, 1982, **47**, 4577; (*h*) R. Maroni, G. Melloni and G. Modena, *J. Chem. Soc., Perkin Trans. 1*, 1973, 2491.

14 For a review, see: (*a*) P. J. Stang, *J. Org. Chem.*, 2009, **74**, 2; (*b*) For selected examples, see: M. Slegt, R. Gronheid, D. Van der Vlugt, M. Ochiai, T. Okuyama, H. Zuilhof, H. S. Overkleeft and G. Lodder, *J. Org. Chem.*, 2006, **71**, 2227; (*c*) K. van Alem, G. Belder, G. Lodder and H. Zuilhof, *J. Org. Chem.*, 2005, **70**, 179; (*d*) M. Fujita, Y. Sakanishi, M. Nishii, H. Yamataka and T. Okuyama, *J. Org. Chem.*, 2002, **67**, 8130; (*e*) R. Pellicciari, B. Natalini, B. M. Sadeghpour, M. Marinozzi, J. P. Snyder, B. L. Williamson, J. T. Kuethe and A. Padwa, *J. Am. Chem. Soc.*, 1996, **118**, 1; (*f*) E. S. Krijnen and G. Lodder, *Tetrahedron Lett.*, 1993, **34**, 729; (*g*) S. Kobayashi, T. Nishi, I. Koyama and H. Taniguchi, *J. Chem. Soc., Chem. Commun.*, 1980, 103; (*h*) M. F. Ruasse and J.-E. Dubois, *J. Org. Chem.*, 1977, **42**, 2689.