1,3-Butadienyltributylphosphonium Bromide as a Conjunctive Reagent for the Synthesis of 1,3-Dienes from Carbonyl Compounds and Gilman Cuprates

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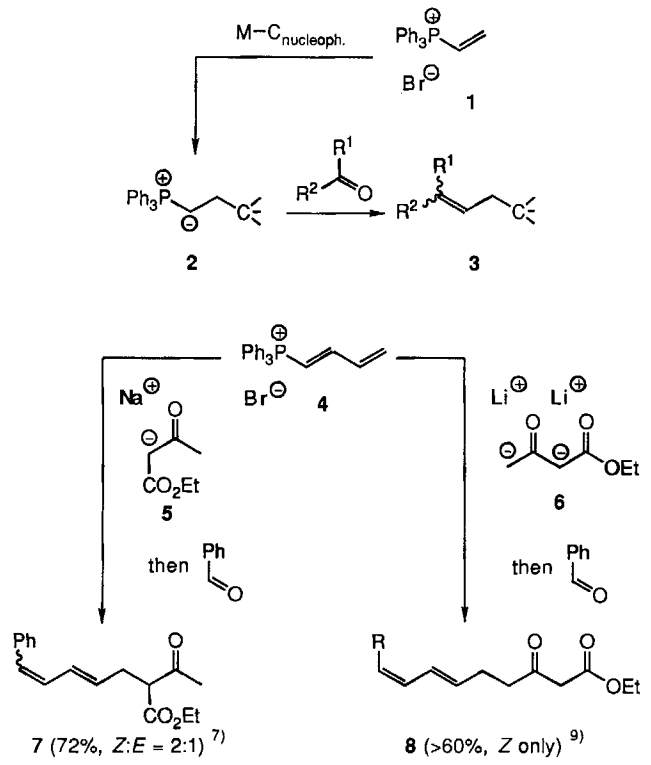
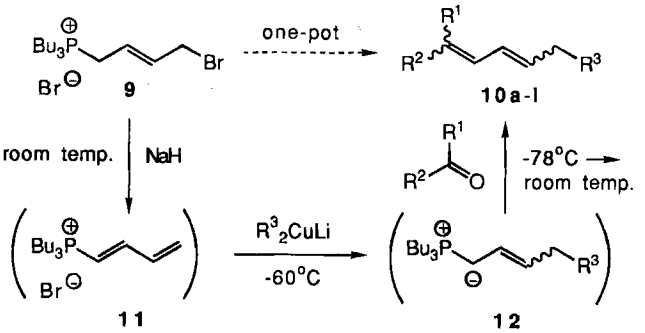
A one-pot non-stereoselective synthesis of 1,3-dienes from (4-bromo-2-butenyl)tributylphosphonium bromide (**9**), Gilman cuprates, and aldehydes or ketones is described. The yields of the dienes reach 79% or 63% when aldehydes and ketones are used, respectively. The pentadienylsilane **10k** is accessible similarly in 56% yield.

The Wittig reaction between a phosphorus ylide and a carbonyl compound is often used for the synthesis of olefins[1]. The ylide is nearly always generated by deprotonation of a phosphonium salt. Hence, the obtained olefin stems from *two* precursor molecules. *Three* components can be incorporated into olefins by a modified Wittig route: In this process, the ylide **2** is formed by the addition of a carbon nucleophile to Schweizer's reagent (**1**); subsequent intermolecular condensation of the ylide with the aldehydes or ketones provides olefins **3**. Examples pertinent to this protocol include reactions of Schweizer's reagent with PhLi[2], MeLi[2], diethyl ethylsodiomalonate[3], Bu_2CuLi[4], or (*Z*)-1-hexenyl lithiocuprate[5,6].

Concerning the synthesis of conjugated dienes, the butadienylphosphonium bromide **4**[7,8] – vinologous to **1** – can act as a conjunctive reagent according to *another three-components Wittig strategy* as demonstrated by Fuchs[7] and White[9]: By 1,4-addition of sodium acetoacetate (**5**) or dilithium acetoacetate (**6**) to **4** ylides are generated which, in turn, react with aldehydes to give dienes **7** and **8**, respectively.



In the present study we disclose that *Gilman cuprates are also amenable to such one-pot three-components syntheses of 1,3-dienes.* We have used the tributyl- (**11**) rather than the triphenylphosphonium bromide (**4**) as a Michael acceptor since the former is more soluble at −60°C in THF than the latter.



Compound **11** itself is obtained in situ from the (bromobutenyl)-phosphonium salt **9** by sodium hydride induced elimination of HBr. **11** reacts with Gilman cuprates at −60°C to form ylide intermediates **12** which are converted into dienes **10** by treatment with 1–2.5 equiv. of suitable carbonyl compounds (−78°C → room temp., 1–4 h).

The alkyl cuprates tBu_2CuLi, sBu_2CuLi, or Me_2CuLi are thus linked via the phosphonium salt to ketones to give dienes **10a–c** and **e** in 49–63% yield; treatment with the less reactive diallyl lithiocuprate furnishes 22 and 24% of trienes **10d** and **f**, respectively (cf. Table 1). Compounds **10a–f** contain one stereogenic C=C bond. This reveals a fairly constant 86:14 (**10b**) to 93:7 (**10a**) preference for the (*E*) isomer as concluded from the magnitude of the olefinic coupling constant in the major (14.0–15.0 Hz) vs. the minor isomer (9.9–11 Hz). This preference should reflect the (*E*)/(*Z*) ratio in the initially formed ylides; it is known that 2-alkenylphosphonium ylides olefinate carbonyl compounds with retention of configuration at their C2=C3 bond.

Similarly, *p*-anisaldehyde is transformed into conjugated dienes **10g–j** by starting from Gilman cuprates and the conjunctive re-

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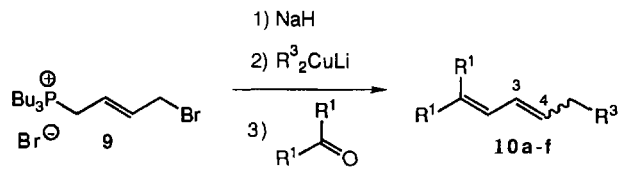
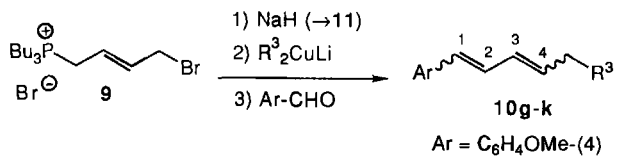
Table 1. 1,3-Dienes **10** from ketones



R^1 R^1 O	R^3	10	Yield	% *E*[a]	$J_{3,4}$ [Hz] *E*-10	$J_{3,4}$[Hz] *Z*-10
4-tBu-cyclo-hexanone	tBu	a	49%	93	14.9	
benzophenone	sBu	b	63%	86	15.0	11
benzophenone	tBu	c	61%	87	15.0	11
benzophenone	allyl	d	22%	87	14.5	9.9
fluorenone	Me	e	50%	91	14.0	10.7
fluorenone	allyl	f	24%	90	14.5	

[a] Determined by ^{1}H-NMR spectroscopy.

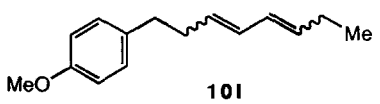
Table 2. 1,3-Dienes **10** from aldehydes



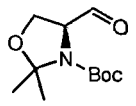
R^3	10	Yield	% 1*E*,3*E*[a]	$J_{1,2}$ [Hz] *E,E*-10	$J_{3,4}$[Hz] *E,E*-10
Me	g	55%	52	15.5	15.0
nBu	h	67%	40	15.6	15.1
sBu	i	55%	68	15.6	15.0
tBu	j	76%	79	15.6	14.7
$SiMe_2Ph$[b]	k	56%	70	15.6	15.0

[a] Determined by ^{1}H-NMR spectroscopy.- [b] From $(Me_2PhSi)_2Cu(CN)Li_2$.

agent **11**; **11** was again obtained in situ by HBr elimination from phosphonium salt **9** (cf. Table 2). Interestingly, the reaction with Fleming's silyl cuprate $(Me_2PhSi)_2Cu(CN)Li_2$[10] provides the pentadienylsilane **10k** also in satisfactory yield (56%). However, all dienes are obtained as mixtures of stereoisomers, the (*E,E*) fraction comprising between 40 (**10h**) and 79% (**10j**) of the material.



10l



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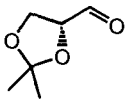

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Regrettably, enolizable aldehydes would not follow the novel procedure. The reaction of *p*-methoxyhydrocinnamaldehyde with the ylide resulting from treatment of **11** with Me_2CuLi affords just 11% of diene **10l**. Garner's aldehyde **13** or D-glyceraldehyde acetonide (**14**) – both of which have been expected to be quite reactive towards ylides because of their electron-withdrawing substituents *a* to the carbonyl group – yielded no dienes at all. Wether this failure may be due to a destruction of such aldehydes through electron transfer from RCu, which is formed along with the ylide upon 1,4-addition of R_2CuLi to **11**, has not yet been clarified.

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Experimental

^{1}H and ^{13}C NMR: Bruker AC 300, AC 250, AC 200 or WH 400; tetramethylsilane as internal standard in $CDCl_3$; coupling constants in Hz. – ^{31}P NMR (^{1}H-decoupled): Bruker AC 300 or WH 400; aq. H_3PO_4 as external standard; positive δ values refer to resonances upfield from the standard. – MS (EI): MAT CH7A or MAT 711. – IR: Perkin-Elmer 1420. – UV: Perkin Elmer 330; ε refers to units of $l \cdot mol^{-1} \cdot cm^{-1}$. – All reactions were performed in oven-dried (100°C) glassware under dry nitrogen. – All dienes were purified by flash chromatography[11] on silica gel 60 [particle size 0.040–0.063 mm, 230–400 mesh ASTM (Merck); particle size 0.030–0.060 mm (Baker)] layered on top of 1/2–1/3 of the volume of aluminium oxide [W200acid (Woelm)]; they were obtained initially as oils which upon standing turned into waxlike semisolids. The (*E*) isomers of **10a** and **10c** could be isolated from the corresponding (*E,Z*) mixtures by flash chromatography on silver-impregnated silica gel (Baker) (10 weight-% $AgNO_3$; obtained at room temperature by removing the solvent from a mixture of silica gel and a CH_3CN solution of $AgNO_3$ under reduced pressure).

[(E)-4-Bromo-2-butenyl]tributylphosphonium Bromide (**9**): PBu_3 (21.7 ml, 87.7 mmol, 1.0 equiv.) in a mixture of hexanes (130 ml) was added at 0°C to (*E*)-1,4-dibromobutene (19.0 g, 88.7 mmol) in a mixture of hexanes (700 ml) over a period of 7 h. The mixture was allowed to stand for 3 d; then the resulting precipitate was isolated by filtration, purified by several washings with ether, and dried to provide 22.0 g (60%) of a colorless powder (m.p. 74–75°C). – ^{1}H NMR (400 MHz): δ = 0.98 (t, *J* = 7.1, 3 CH_2CH_3), 1.49–1.63 (m, 3 $CH_2CH_2CH_3$), 2.43–2.50 (m, 3 PCH_2CH_2), 3.73 (dd, $^2J_{H,P}$ = 15.8, $J_{1,2}$ = 7.7, 1-H_2); 3.99 (dd, $J_{4,3}$ = 7.5, $J_{4,2}$ = 2.1, 4-H_2), 5.81 (dtd, $J_{3,2}$ = 15.0, $J_{3,4}$ = 7.7, $^4J_{H,P}$ = 4.6, 3-H), 6.21–6.30 (m, 2-H). – ^{31}P NMR (162 MHz): δ = 33.26.

$C_{16}H_{33}Br_2P$ (416.2) Calcd. C 46.17 H 7.99 Br 38.40 P 7.44
Found C 45.83 H 7.93 Br 37.63 P 7.53

[(1E)-1,3-Butadienyl]tributylphosphonium Bromide (**11**): **9** (2.22 g, 5.32 mmol) in CH_2Cl_2 (30 ml) was slowly added at room temp. to a suspension of NaH (460 mg, 19.2 mmol, 3.6 equiv.) in CH_2Cl_2 (10 ml). After stirring for 12 h, the mixture was transferred through a cannula into satd. aq. NH_4Br/concd. HBr (1:1) (25 ml). The organic phase was dried with $MgSO_4$ and concentrated in vacuo to give compound **11** as a yellow resin (1.92 g) contaminated with CH_2Cl_2; attempts to crystallize the product were unsuccessful. – ^{1}H NMR (300 MHz): δ = 0.71 (m_c, 3 CH_2CH_3), 1.28 (m_c, 3 $CH_2CH_2CH_3$), 2.26–2.43 (m, 3 PCH_2CH_2), 5.40 (d, $J_{4(cis),3}$ = 10.0, 4-H_{cis}), AB signal (δ_A = 5.61, δ_B = 6.36, $J_{A,B}$ = 16.9, in addition split by $J_{B,4(cis)} = J_{B,2}$ = 9.9, A: 4-H_{trans}, B: 3-H), 6.22 (dd, $^2J_{H,P} = J_{2,1}$ = 17.8, 1-H), 7.09 (ddd, $^3J_{H,P} = J_{1,2}$ = 17.9, $J_{2,3}$ = 10.3, 2-H). – ^{31}P NMR (121 MHz): δ = 28.20.

5-(Dimethylphenylsilyl)-1-(4-methoxyphenyl)-1,3-pentadiene (**10k**) (Representative Procedure for the Preparation of Dienes

10a–g, l): **11** (541 mg, 1.30 mmol) in THF (5 ml) was added at room temp. to NaH (159 mg, 6.62 mmol, 5.1 equiv.) suspended in THF (5 ml). After 14 h, an aliquot (1 ml) of supernatant liquid was removed and completeness of the conversion of **9** into **11** confirmed by ^{1}H-NMR spectroscopy (after workup with NH_4Br solution as described above). The residual liquid – including THF (3 ml) used for rinsing the remaining solid – was transferred dropwise through a cannula into a stirred solution of $(Me_2PhSi)_2Cu(CN)Li_2$ (1.30 mmol, 1.1 equiv., prepared as described in ref.[10]) in THF (5 ml) at –60°C. After 1.2 h *p*-anisaldehyde (0.18 ml, 1.48 mmol, 1.3 equiv.) in THF (5 ml) was added. Over a period of 2.7 h the temperature was raised from –60°C to room temp. The reaction mixture was quenched with satd. aq. NH_4Cl and conc. NH_3 (1:1) (4 ml). Flash chromatography [petroleum ether → petroleum ether:diethyl ether (25:1)] gave a colorless wax (204 mg, 56%) containing 70% (1*E*,3*E*)-**10k** besides isomers according to the ^{1}H-NMR integrals of the CH_3O singlets around δ = 3.8. – ^{1}H NMR (400 MHz): (1*E*,3*E*)-**10k**: δ = 0.23 [s, $Si(CH_3)_2$], 1.76 (dd, $J_{5,4}$ = 8.3, $J_{5,3}$ = 0.9, 5-H_2), 3.72 (s, CH_3O), AB signal (δ_A = 5.68, δ_B = 5.99, $J_{A,B}$ = 15.0, in addition split by $J_{A,5}$ = 7.9, $J_{B,2}$ = 10.4, A: 4-H, B: 3-H), AB signal (δ_A = 6.24, δ_B = 6.53, $J_{A,B}$ = 15.6, in addition split by $J_{B,3}$ = 10.3, A: 1-H, B: 2-H), 6.73–6.79 and 7.18–7.24 (2 m, $C_6H_4OCH_3$), 7.26–7.31 and 7.42–7.49 (2 m, C_6H_5). – MS (EI): *m/z* (%) = 308.1594 (68) [M^+] (calcd. for $^{12}C_{20}H_{24}OSi$: 308.1592), 309.1619 (23) [M^+ (^{13}C isotopomer)] (calcd. for $^{12}C_{19}{}^{13}C_1H_{24}OSi$: 309.1608), 135 (100) [$Me_2PhSi^+$].

1-(4-tert-Butylcyclohexylidene)-5,5-dimethyl-2-hexene (**10a**): 49% yield. – ^{1}H NMR (300 MHz): (2*E*)-**10a**: δ = 0.84 and 0.88 [2 s, 5-$(CH_3)_2$/6-H_3 and 4′-tC_4H_9], 0.92–1.30 (m, 3′-H_2, 5′-H_2), 1.70–1.92 and 2.00–2.14 (2 m, 2′-H_{ax}, 6′-H_{ax}, 4′-H), 1.96 (d, $J_{4,3}$ = 7.6, 4-H_2), 2.19–2.30 (m, 2′-H_{eq}), 2.82 (m_c, 6′-H_{eq}), AB signal (δ_A = 5.61, δ_B = 6.24, $J_{A,B}$ = 14.9, in addition split by $J_{A,4}$ = 7.5, $J_{B,1}$ = 10.8, A: 3-H, B: 2-H), 5.76 (d, $J_{1,2}$ = 10.8, 1-H). – ^{13}C NMR (63 MHz): (2*E*)-**10a**: δ = 27.52 and 29.24 [5-$(CH_3)_2$/C-6 and 4′-$C(CH_3)_3$], 28.26, 28.88, and 29.00 (C-3′, C-4′, C-5′), 31.11 and 32.38 [C-5 and 4′-$C(CH_3)_3$], 36.95, 47.39, and 48.31 (C-4, C-2′, C-6′), 121.58, 127.92, 129.24, and 140.87 (C-1, C-1′, C-2, C-3). – IR (film): $\tilde{\nu}$ = 3005 cm^{-1}, 2930 (s), 2850, 2820, 1465, 1430, 1380, 1355 (s), 1230, 960 (s). – UV (hexane): λ_{max} (lg ε) = 237 nm (4.30), 244 (4.35), 252 (4.17).

$C_{18}H_{32}$ (248.5) Calcd. C 87.02 H 12.98
Found C 86.90 H 13.05

6-Methyl-1,1-diphenyl-1,3-octadiene (**10b**): 63% yield. – ^{1}H NMR (400 MHz): (3*E*)-**10b**: δ = 0.85 (d, $J_{6\text{-}CH_3,6}$ = 6.6, 6-CH_3), 0.86 (t, $J_{8,7}$ = 7.3, 8-H_3), 1.08–1.53 (m, 6-H, 7-H_2), AB signal (δ_A = 1.90, δ_B = 2.07, $J_{A,B}$ = 13.9, in addition split by $J_{A,6}$ = $J_{A,4}$ = 7.1, $J_{A,3}$ = 1.2, $J_{B,6}$ = $J_{B,4}$ = 6.7, $J_{B,3}$ = 1.3, 5-H_2), AB signal (δ_A = 5.89, δ_B = 6.13, $J_{A,B}$ = 15.0, in addition split by $J_{A,5(A)}$ = $J_{A,5(B)}$ = 7.5, $J_{B,2}$ = 10.9, $J_{B,5(A)} \approx J_{B,5(B)} \approx$ 1.3, A: 4-H, B: 3-H), 6.68 (d, $J_{2,3}$ = 10.9, 2-H), 7.19–7.40 (m, Ph). – MS: *m/z* (%) = 276.1872 (89) [M^+] (calcd. for $^{12}C_{21}H_{24}$: 276.1866), 277.1907 (57) [M^+ (^{13}C isotopomer)] (calcd. for $^{12}C_{20}{}^{13}C_1H_{24}$: 277.1903), 219 (100) [$M^+ - C_4H_9$].

6,6-Dimethyl-1,1-diphenyl-1,3-heptadiene (**10c**): 61% yield. – (3*E*)-**10c**: m.p. 54–55°C. – ^{1}H NMR (300 MHz): δ = 0.88 [s, 6-$(CH_3)_2$/7-H_3], 1.94 (d, $J_{5,4}$ = 7.4, 5-H_2), AB signal (δ_A = 5.93, δ_B = 6.12, $J_{A,B}$ = 15.0, in addition split by $J_{A,5}$ = 7.6, $J_{B,2}$ = 10.8, A: 4-H, B: 3-H), 6.70 (d, $J_{2,3}$ = 10.7), 7.21–7.42 (m, Ph). – ^{13}C NMR (50 MHz): δ = 29.33 [6-$(CH_3)_2$/C-7], 31.45 (C-6), 47.47 (C-5), 127.01, 127.09, 127.40, 128.10, 128.40, 130.40, 130.53, 134.34, 140.06, 140.25, and 142.60 (sp^2 C). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3010, 2940 (s), 2850, 1580, 1480, 1460, 1430, 1355, 1240, 1070, 1030, 885, 780, 760 (s), 735, 720, 690 (s), 650, 640. – UV (hexane): λ_{max} = 228 nm (sh; 4.30), 291 (4.54). – (3*Z*)-**10c**: ^{1}H NMR (200 MHz): δ = 0.95 [s, 6-$(CH_3)_2$/7-H_3], 2.21 (dd, $J_{5,4}$ = 8.1, $J_{5,3}$ = 1.4, 5-H_2), 5.57 (dtd, $J_{4,3}$ = 11.1, $J_{4,5}$ = 8.1, $J_{4,2}$ = 1.1, 4-H), 6.18 (ddt, $J_{3,4}$ = $J_{3,2}$ = 11.3, $J_{3,5}$ = 1.4, 3-H), 6.95 (dd, $J_{2,3}$ = 11.5, $J_{2,4}$ = 1.1, 2-H), 7.16–7.42 (m, Ph). – ^{13}C NMR (50 MHz): δ = 29.39 [6-(CH_3)/C-7], 31.71 (C-6), 41.80 (C-5), 123.36, 124.85, 127.22, 127.64, 127.91, 128.07, 128.16, 130.59, 131.16, 142.22, and 142.83 (sp^2 C). – IR (film): $\tilde{\nu}$ = 3040 cm^{-1}, 3000, 2940 (s), 2890, 2850, 1585, 1485, 1465, 1435, 1380, 1355, 1230, 1070, 1025, 970, 900, 770, 760 (s), 730 (s), 695 (s), 630. – UV (hexane): λ_{max} = 230 nm (sh; 4.05), 293 (4.26).

$C_{21}H_{24}$ (276.4) Calcd. C 91.25 H 8.75
Found C 90.98 H 8.59

1,1-Diphenyl-1,3,7-octatriene (**10d**): 22% yield. – ^{1}H NMR (400 MHz): (3*E*)-**10d**: δ = 2.10–2.23 (m, 5-H_2, 6-H_2), 4.96 (dm_c, $J_{8(cis),7} \approx$ 10, 8-H_{cis}), superimposed in part by 5.00 (dm_c, $J_{8(trans),7} \approx$ 15, 8-H_{trans}), 5.79 (ddt, $J_{7,8(trans)}$ = 17.0, $J_{7,8(cis)}$ = 10.3, $J_{7,6}$ = 6.4, 7-H), AB signal (δ_A = 5.90, δ_B = 6.16, $J_{A,B}$ = 14.5, in addition split by $J_{A,5}$ = 6.5, $J_{B,2}$ = 10.9, $J_{B,5}$ = 1.3, A: 4-H, B: 3-H), 6.67 (d, $J_{2,3}$ = 10.9, 2-H), 7.20–7.41 (m, Ph). – MS: *m/z* (%) = 260.1570 (68) [M^+] (calcd. for $^{12}C_{20}H_{20}$: 260.1575), 261.1586 (15) [M^+(^{13}C isotopomer)] (calcd. for $^{12}C_{19}{}^{13}C_1H_{20}$: 261.1599), 219 (100) [$M^+$ – allyl].

9-(2-Pentenylidene)fluorene (**10e**): 50% yield. – ^{1}H NMR (400 MHz): (2′*E*)-**10e**: δ = 1.16 (t, $J_{5',4'}$ = 7.6, 5′-H_3), 2.36 (dqd, $J_{4',3'}$ = $J_{4',5'}$ = 7.3, $J_{4',2'}$ = 1.3, 4′-H_2), 6.27 (dt, $J_{3',2'}$ = 14.0, $J_{3',4'}$ = 6.9, 3′-H), 7.15–7.35 (m, 1′-H, 2′-H, 2-H, 3-H, 6-H, 7-H), 7.67–7.77 (m, 1-H, 4-H, 5-H), 7.94–8.00 (m, 8-H). – MS: *m/z* (%) = 232.1251 (52) [M^+] (calcd. for $^{12}C_{18}H_{16}$: 232.1250), 233.1287 (10) [M^+ (^{13}C isotopomer)] (calcd. for $^{12}C_{17}{}^{13}C_1H_{16}$: 233.1289), 203 (100) [$M^+$ – C_2H_5].

9-(2,6-Heptadienylidene)fluorene (**10f**): 24% yield. – ^{1}H NMR (400 MHz): (2′*E*)-**10f**: δ = 2.31 (br. dt, $J_{5',4'}$ = 6.8, $J_{5',6'}$ = 6.6, 5′-H_2), 2.45 (dt, $J_{4',5'}$ = 7.2, $J_{4',3'}$ = 7.1, 4′-H_2), 5.05 (ddt, $J_{7'(cis),6}$ = 10.2, $J_{7'(cis),7'(trans)} \approx J_{7'(cis),5'} \approx$ 1.4, 7′-H_{cis}), AB signal (δ_A = 5.11, δ_B = 5.89, $J_{A,B}$ = 17.1, in addition split by $J_{A,7'(cis)} \approx J_{A,5'} \approx$ 2, $J_{B,7'(cis)}$ = 10.3, $J_{B,5'}$ = 6.6, A: 7′-H_{trans}, B: 6′-H), 6.23 (dt, $J_{3',2'}$ = 14.5, $J_{3',4'}$ = 7.1, 3′-H), 7.16 (d, $J_{1',2'}$ = 11.8, 1′-H), 7.20–7.37 (m, 2′-H, 2-H, 3-H, 6-H, 7-H), 7.67–7.76 (m, 4-H, 5-H), 7.94–7.98 (m, 8-H). – MS: *m/z* (%) = 258.1403 (63) [M^+] (calcd. for $^{12}C_{20}H_{18}$: 258.1398), 259.1429 (15) [M^+ (^{13}C isotopomer)] (calcd. for $^{12}C_{19}{}^{13}C_1H_{18}$: 259.1416), 217 (100) [$M^+$ – allyl].

1-(4-Methoxyphenyl)-1,3-hexadiene (**10g**): 55% yield. – ^{1}H NMR (400 MHz): (1*E*,3*E*)-**10g**: δ = 1.04 (t, $J_{6,5}$ = 7.5, 6-H_3), 2.16 (br. dq, $J_{5,4}$ = 7.7, $J_{5,6} \approx$ 7, 5-H_2), 3.80 (s, CH_3O), AB signal (δ_A = 5.81, δ_B = 6.18, $J_{A,B}$ = 15.0, in addition split by $J_{A,5}$ = 6.7, $J_{B,2}$ = 10.7, and further unresolved splittings, A: 4-H, B: 3-H), AB signal (δ_A = 6.40, δ_B = 6.63, $J_{A,B}$ = 15.5, in addition split by $J_{B,3}$ = 10.1, A: 1-H, B: 2-H), 6.82–6.89 and 7.27–7.32 (2 m, Ph). – MS: *m/z* (%) = 188.1203 (100) [M^+] (calcd. for $^{12}C_{13}H_{16}O$: 188.1205), 189.1237 (41) [M^+ (^{13}C isotopomer)] (calcd. for $^{12}C_{12}{}^{13}C_1H_{16}O$: 189.1240).

$C_{13}H_{16}O$ (188.3) Calcd. C 82.94 H 8.57
Found C 82.60 H 8.81

1-(4-Methoxyphenyl)-1,3-nonadiene (**10h**): 67% yield. – ^{1}H NMR (300 MHz): (1*E*,3*E*)-**10h**: δ = 0.89 (br. t, $J_{9,8}$ = 6.9, 9-H_3), 1.26–1.49 (m, 6-H_2, 7-H_2, 8-H_2), 2.13 (dt, $J_{5,4}$ = $J_{5,6}$ = 6.9, 5-H_2), 3.80 (s, CH_3O), AB signal (δ_A = 5.78, δ_B = 6.18, $J_{A,B}$ = 15.1, in addition split by $J_{A,5}$ = 7.3, $J_{B,2}$ = 10.4, A: 4-H, B: 3-H), AB signal (δ_A = 6.39, δ_B = 6.63, $J_{A,B}$ = 15.6, in addition split by $J_{B,3}$ = 10.3, A: 1-H, B: 2-H), 6.83–6.87 and 7.29–7.33 (2 m, Ph).

$C_{16}H_{22}O$ (230.4) Calcd. C 83.43 H 9.63
Found C 83.37 H 9.78

1-(4-Methoxyphenyl)-6-methyl-1,3-octadiene (**10i**): 55% yield. – ^{1}H NMR (400 MHz): (1*E*,3*E*)-**10i**: δ = 0.88 (d, $J_{CH_3,6}$ = 6.5, 6-CH_3) superimposed by 0.88 (t, $J_{8,7}$ = 7.5, 8-H_3), 1.11–1.23 (m, 6-H or 7-H^1), 1.33–1.50 (m, 7-H^2 and 6-H or 7-H^1), AB signal (δ_A = 1.98, δ_B = 2.14, $J_{A,B}$ = 14.2, in addition split by $J_{A,4}$ = $J_{A,6}$ = 7.3, $J_{A,3} \approx$ 1, $J_{B,4} \approx J_{B,6} \approx$ 7, H_B shows unresolved small couplings, 5-H_2), 3.80 (s, CH_3O), AB signal (δ_A = 5.75, δ_B = 6.17, $J_{A,B}$ = 15.0, in addition split by $J_{A,5(A)} = J_{A,5(B)}$ = 7.5, $J_{B,2} \approx$ 10, H_B shows unresolved small couplings, A: 4-H, B: 3-H), AB signal (δ_A = 6.39, δ_B = 6.64, $J_{A,B}$ = 15.6, in addition split by $J_{B,3}$ = 10.3, A: 1-H, B: 2-H), 6.82–6.89 and 7.27–7.36 (2 m, Ph).

$C_{16}H_{22}O$ (230.4) Calcd. C 83.43 H 9.63
Found C 83.24 H 9.67

1-(4-Methoxyphenyl)-6,6-dimethyl-1,3-heptadiene (**10j**): 76% yield. – ^{1}H NMR (400 MHz): (1*E*,3*E*)-**10j**: δ = 0.91 [s, 6-$(CH_3)_2$/7-H_3], 2.01 (dd, $J_{5,4}$ = 7.7, $J_{5,3}$ = 1.0, 5-H_2), 3.80 (s, CH_3O), AB signal (δ_A = 5.80, δ_B = 6.15, $J_{A,B}$ = 14.7, in addition split by $J_{A,5}$ = 7.6, $J_{B,2}$ = 10.6, A: 4-H, B: 3-H), AB signal (δ_A = 6.40, δ_B = 6.65, $J_{A,B}$ = 15.6, in addition split by $J_{B,3}$ = 10.4, A: 1-H, B: 2-H), 6.82 to 6.89 and 7.27–7.36 (2 m, Ph).

$C_{16}H_{22}O$ (230.4) Calcd. C 83.43 H 9.63
Found C 83.77 H 9.96

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