Calcd for $C_4H_2F_6N_4$: C, 21.83; H, 0.92; F, 51.79; N, 25.46. Found: C, 21.81; H, 0.93; F, 51.86; N, 25.48.

2,5-Bis(trifluoromethyl)-1,3,4-oxadiazole (2a). By the procedure that we reported elsewhere,[2] **2a** was produced in 86% overall yield from ethyl trifluoroacetate and anhydrous hydrazine: bp 65 °C (lit.[10] bp 65 °C); ^{19}F NMR (CD_3OD) δ -67.1 (s). Anal. Calcd for $C_4F_6N_2O$: C, 23.32; F, 55.32; N, 13.60. Found: C, 23.17; F, 55.14; N, 13.57.

N^2-(α-Hydrazonotrifluoromethyl)-N^1-(trifluoroacetyl)hydrazine (4a). A solution of 25 g (750 mmol) of anhydrous hydrazine in 125 mL of absolute methanol was cooled to -42 °C (CH_3CN/CO_2 bath), and 25.0 g (121 mmol) of **2a** was added dropwise (neat) over a 30-min period. After the addition was complete, the reaction was stirred for an additional 60 min. The reaction was cooled to -78 °C (acetone/CO_2 bath), and 250 mL of 2.5 M HCl was added at such a rate that the internal temperature was maintained below -40 °C. The bath was removed, and the ice was allowed to melt as the reaction warmed to -10 °C where the pH was carefully adjusted to 6 with additional 2.5 M HCl. After being allowed to stand in the freezer (-10 °C) overnight, the product was filtered, giving 22.1 g (76%) of colorless **4a**: mp 127-128 °C dec; ^{19}F NMR (CD_3OD) δ -77.5 (s, anti $COCF_3$), -76.7 (s, syn $COCF_3$), -71.3 (s, anti $CNCF_3$), -69.3 (s, syn $CNCF_3$). Anal. Calcd for $C_4H_4F_6N_4O$: C, 20.18; H, 1.69; F, 47.88; N, 23.53. Found: C, 20.04; H, 1.75; F, 47.78; N, 23.44.

Acknowledgment. The support of Dr. Terry M. Balthazor in obtaining manuscript clearance is greatly appreciated.

Registry No. 1a, 103797-41-7; 2a, 1868-48-0; 4a, 118950-25-7; 6a, 67096-88-2.

Supplementary Material Available: Crystallographic data and table of atomic coordinates for 1a (13 pages). Ordering information is given on any current masthead page.

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A Short Route to 2,3-Bis(methylene)-7-oxabenzonorbornenes

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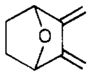
Bis(methylene)-7-oxanorbornenes **1**,[1] **2**,[2] and **3**[3] are dienes with theoretical interest[4] and synthetic[5] utility. Surprisingly, the benzo analogue **4** does not seem to have been prepared previously, although several naphtho analogues including **5** have been obtained as intermediates or byproducts in anthracycline syntheses from **3**.[5a,b,d,6]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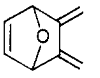
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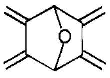
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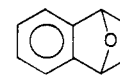
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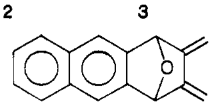
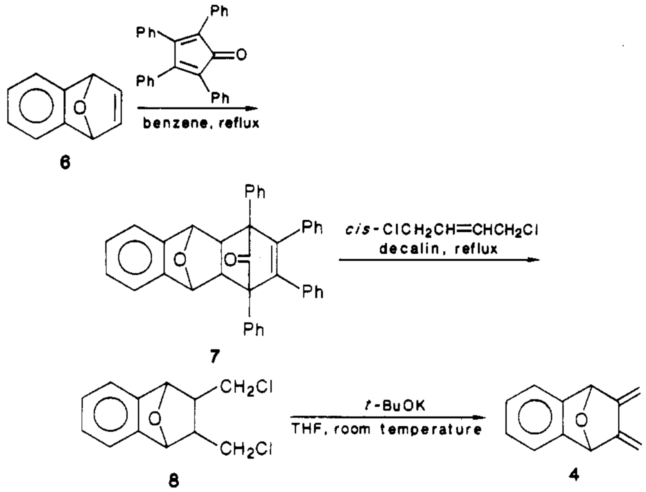

5

We report here a short general route to the title compounds, including the first synthesis of **4** and an improved synthesis of **5**. The methodology is illustrated by the synthesis of **4** from naphthalene 1,4-endoxide **6**. Treatment of **6** with tetraphenylcyclopentadienone (TPCPD) gave adduct **7**, a known precursor of isobenzofuran (IBF).[7] On heating **7** in decalin with *cis*-1,4-dichloro-2-butene (DCB), the IBF–DCB adduct **8** was obtained as a mixture of endo/exo isomers (89:11). This mixture was then dehydrohalogenated to give the desired **4**, mp 73–74 °C. The overall yield of **4** from **6** for the three steps was 65%; the only step that is not essentially quantitative is the isobenzofuran trapping (**7** → **8**). DCB has been used before as a dienophile with cyclopentadiene[1] and anthracene,[8] but does not react with furan or 1,3-cyclohexadiene;[1] as shown here, it is fairly effective toward isobenzofurans.



Tables I–III summarize our results. The only previously known final product is **5**[5b] (Table III), which was prepared by dehydrogenation of the benzyne monoadduct of **3** (18% yield, two steps, compared with 73% here for three steps).

The structures for all products are based on their method of synthesis and their spectral properties. Typical procedures and all physical constants for new compounds are given in the Experimental Section.

In summary, we describe here a general three-step synthesis of 2,3-bis(methylene)-7-oxabenzonorbornenes in 50–75% overall yield. The key step is the trapping of an isobenzofuran intermediate with 1,4-dichloro-2-butene. The product dienes should prove to be useful in linear acene synthesis and in other respects.

Experimental Section

General Procedures. NMR spectra (^1H and ^{13}C) were recorded on a Bruker WM 250-MHz spectrometer with $CDCl_3$ as solvent and $(CH_3)_4Si$ as the internal reference. Mass spectra were measured at 70 eV with a Finnigan 4000 spectrometer with the INCOS data system. Melting points (uncorrected) were determined on an electrothermal melting point apparatus (Fisher

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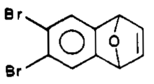
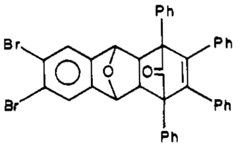
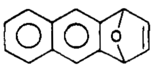
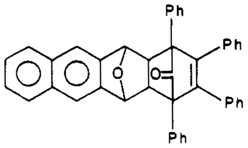
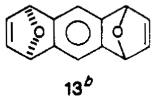
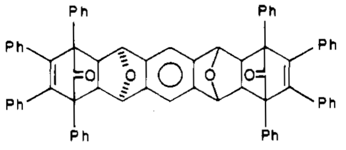
Table I. TPCPD Adducts of 1,4-Endoxides

endoxide	adduct	% yield
6	**7**	98
 **9**	 **10**	95
 **11**[a]	 **12**	96
 **13**[b]	 **14**	92

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Scientific). Anhydrous $MgSO_4$ was the drying agent throughout. Silica gel for chromatography was 230–400 mesh. Microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI.

Typical Procedure for Table I. Preparation of 10. A solution of endoxide **9**[8a] (3.02 g, 10 mmol) and tetraphenylcyclopentadienone (3.84 g, 10 mmol) in benzene (60 mL) was heated at reflux until the purple color disappeared (2 days), after which the benzene was removed (rotavap). Trituration of the residue with methanol gave a white solid, which was washed with methanol, dried, and recrystallized from benzene–methanol to give 6.52 g (95%) of **10** as a white solid, mp 198–200 °C: ^{1}H NMR δ 3.07 (s, 2 H), 5.75 (s, 2 H), 6.83–6.87 (m, 4 H), 6.91–7.01 (m, 6 H), 7.28–7.34 (m, 2 H), 7.36–7.38 (m, 8 H), 7.69 (s, 2 H); mass spectrum, *m/e* (relative intensity) 382 (32, M^+ for tetraphenylbenzene), 369 (8), 355 (10), 341 (7), 295 (20), 281 (18), 278 (17), 276 (31, M^+ for dibromoisobenzofuran), 274 (15), 221 (63), 207 (24), 169 (23), 147 (47), 73 (72), 44 (100). Anal. Calcd for $C_{39}H_{26}Br_2O_2$: C, 68.24; H, 3.82. Found: C, 68.09; H, 3.77.

Physical Data for New Compounds in Table I. For 12: mp 192–194 °C dec; ^{1}H NMR δ 3.18 (s, 2 H), 5.93 (s, 2 H), 6.93–7.03 (m, 10 H), 7.30–7.42 (m, 6 H), 7.47–7.52 (m, 6 H), 7.79 (s, 2 H), 7.87 (dd, 2 H); mass spectrum, *m/e* (relative intensity) 382 (44, M^+ for tetraphenylbenzene), 365 (5), 341 (5), 305 (11), 302 (12), 289 (16), 168 (100, M^+ for 2,3-isonaphthofuran), 139 (29), 77 (13). Anal. Calcd for $C_{43}H_{30}O_2$: C, 89.25; H, 5.22. Found: C, 89.17; H, 5.12. **For 14:** mp >280 °C dec; ^{1}H NMR δ 3.06 (s, 4 H), 5.84 (s, 4 H), 6.87–7.04 (m, 20 H), 7.27–7.52 (m, 20 H), 7.58 (s, 2 H); mass spectrum, *m/e* (relative intensity) 382 (100, M^+ for tetraphenylbenzene), 365 (9), 341 (10), 305 (15), 302 (17), 289 (20), 276 (6), 226 (3), 182 (8), 176 (6), 163 (5), 77 (6); IR (nujol) 1775, 1470, 1380 cm^{-1}. Anal. Calcd for $C_{72}H_{50}O_4$: C, 88.32; H, 5.15. Found: C, 88.31; H, 4.87.

Typical Procedure for Table II. Preparation of 16. To a refluxing solution of *cis*-1,4-dichloro-2-butene[9] (9 mL) in decalin (20 mL) under argon was added dropwise a solution of **10** (2.058 g, 3 mmol) in decalin (80 mL) over 1–1.5 h. After an additional 0.5 h at reflux, the solvent was removed by vacuum distillation and the residue was chromatographed over silica gel with benzene–hexane, 1:4, as the eluent to give the byproduct 1,2,3,4-tetraphenylbenzene. Increasing the eluent polarity gradually to benzene–hexane, 3:7, gave the minor product **16x** (0.099 g, 8%) as a colorless solid: mp 162–163 °C (recrystallized from 50–110 °C petroleum ether); ^{1}H NMR δ 2.25 (t, *J* = 5.2 Hz, 2 H), 3.57 (t, *J* = 10.6 Hz, 2 H), 3.74 (dd, *J* = 4.8, 10.7 Hz, 2 H), 5.34 (s, 2 H), 7.58 (s, 2 H); ^{13}C NMR δ 43.13, 46.97, 81.90, 123.20, 124.82, 145.43; mass spectrum, *m/e* (relative intensity) 402 (1), 400 (1, M^+), 367 (6), 365 (8), 363 (4), 278 (44), 276 (100, M^+ for dibromoisobenzofuran), 274 (53), 250 (4), 248 (6), 222 (5), 206 (4), 195 (7), 167 (14), 141 (15), 115 (13), 97 (11), 87 (14), 69 (21), 57 (27). Further elution gave **16n** (0.663 g, 55%) as a colorless solid: mp 143–144 °C (recrystallized from 50–110 °C petroleum ether); ^{1}H NMR δ 2.53 (t, *J* = 11.1 Hz, 2 H), 3.01 (dd, *J* = 5.0, 10.2 Hz, 2 H), 3.29 (dd, *J* = 5.2, 10.8 Hz, 2 H), 5.45 (d, *J* = 4.5 Hz, 2 H), 7.69 (s, 2 H); ^{13}C NMR δ 41.84, 44.09, 81.93, 123.65, 126.63, 143.16; mass spectrum, *m/e* (relative intensity) 402 (1), 400 (2, M^+), 367 (7), 365 (7), 363 (3), 329 (2), 278 (46), 276 (100, M^+ for dibromoisobenzofuran), 274 (52), 250 (4), 248 (5), 222 (5), 206 (4), 195 (7), 167 (16), 141 (18), 115 (14), 97 (16), 69 (34), 57 (45). Anal. Calcd for $C_{12}H_{10}Br_2Cl_2O$: C, 35.95; H, 2.51. Found: C, 35.89; H, 2.50.

Physical Data for New Compounds in Table II. For 15n: mp 68–69 °C (recrystallized from 35–60 °C petroleum ether); ^{1}H NMR δ 2.47 (t, 2 H), 2.99 (dd, 2 H), 3.21 (dd, 2 H), 5.48 (d, *J* = 4.3 Hz, 2 H), 7.26 (dd, 2 H), 7.42 (dd, 2 H); ^{13}C NMR δ 42.33, 44.42, 82.40, 121.55, 127.50, 142.07; mass spectrum, *m/e* (relative intensity) 244 (0.5, M^+), 242 (1), 207 (8), 171 (3), 143 (5), 128 (10), 118 (100, M^+ for isobenzofuran), 90 (9), 89 (12), 77 (4), 63 (7), 51 (6). Anal. Calcd for $C_{12}H_{12}Cl_2O$: C, 59.28; H, 4.97. Found: C, 59.16; H, 5.01. **For 15x:** mp 147–149 °C (recrystallized from CH_2Cl_2–petroleum ether); ^{1}H NMR δ 2.27 (t, 2 H), 3.64 (t, 2 H), 3.78 (dd, 2 H), 5.39 (s, 2 H), 7.22 (dd, 2 H), 7.32 (dd, 2 H); ^{13}C NMR δ 43.73, 47.23, 82.53, 119.35, 127.20, 144.46; mass spectrum, *m/e* (relative intensity) 244 (1, M^+), 242 (1), 207 (6), 171 (5), 143 (4), 118 (100, M^+ for isobenzofuran), 90 (10), 89 (15), 77 (6). **For 17n:** mp 109–110 °C (recrystallized from 35–60 °C petroleum ether); ^{1}H NMR δ 2.58 (t, 2 H), 3.06 (dd, 2 H), 3.25 (dd, 2 H), 5.60 (d, *J* = 4.6 Hz, 2 H), 7.52 (dd, 2 H), 7.81 (s, 2 H), 7.87 (dd, 2 H); ^{13}C NMR δ 42.19, 44.59, 82.36, 120.04, 126.31, 128.31, 132.86, 139.40; mass spectrum, *m/e* (relative intensity) 294 (3, M^+), 292 (4), 278 (6), 276 (14), 259 (7), 257 (22), 221 (8), 203 (7), 193 (10), 178 (16), 168 (100, M^+ for 2,3-isonaphthofuran), 140 (13), 139 (28), 113 (11), 97 (17), 81 (21), 69 (40), 57 (32). Anal. Calcd for $C_{16}H_{14}Cl_2O$: C, 65.55; H, 4.81. Found: C, 65.41; H, 4.75. **For 17x:** mp 171–172 °C (recrystallized from 35–60 °C petroleum ether); ^{1}H NMR δ 2.35 (t, 2 H), 3.64 (t, 2 H), 3.74 (dd, 2 H), 5.49 (s, 2 H), 7.47 (dd, 2 H), 7.68 (s, 2 H), 7.81 (dd, 2 H); ^{13}C NMR δ 43.40, 48.06, 82.41, 117.78, 126.09, 128.23, 132.89, 142.17; mass spectrum, *m/e* (relative intensity) 294 (4, M^+), 292 (5), 259 (7), 257 (23), 221 (5), 203 (6), 193 (10), 178 (18), 168 (100, M^+ for 2,3-isonaphthofuran), 140 (14), 139 (28), 115 (4), 89 (5), 75 (6). **For 18nn:** mp >280 °C (dec, recrystallized from $CHCl_3$–petroleum ether); ^{1}H NMR δ 2.43 (t, *J* = 11.0 Hz, 4 H), 3.01 (dd, *J* = 4.8, 10.3 Hz, 4 H), 3.23 (dd, *J* = 5.0, 10.7 Hz, 4H), 5.51 (d, *J* = 4.2 Hz, 4 H), 7.50 (s, 2 H); ^{13}C NMR δ 42.12, 44.32, 82.23, 115.35, 141.86; mass spectrum, *m/e* (relative intensity) 373 (3, $M^+ - Cl$), 371 (3), 284 (7), 282 (13), 247 (29), 211 (12), 193 (7), 183 (6), 165 (5), 158 (100, M^+ for benzodifuran), 141 (8), 128 (12), 115 (12), 102 (9), 77 (12), 55 (23). Anal. Calcd for $C_{18}H_{18}Cl_4O_2$: C, 52.97; H, 4.44. Found: C, 52.95; H, 4.41. **For 18nx:** mp 235–237 °C (recrystallized from $CHCl_3$–petroleum ether); ^{1}H NMR (peaks marked with an asterisk correspond to the *endo*-bis(chloromethyl) moiety) δ 2.23 (t, 2 H), 2.43* (t, 2 H), 3.01* (dd, 2 H), 3.24* (dd, 2 H), 3.63 (t, 2 H), 3.78 (dd, 2 H), 5.42 (s, 2 H), 5.49 (d, 2 H), 7.40 (s, 2 H); ^{13}C NMR δ 42.19,* 43.54, 44.32,* 47.07, 82.19,* 82.32, 113.41, 141.75,* 144.27; mass spectrum, *m/e* (relative intensity) 373 (8, $M^+ - Cl$), 371 (10), 284 (14), 282 (25), 249 (10), 247 (37), 211 (14), 193 (11), 183 (9), 158 (100, M^+ for benzodifuran), 141 (14), 128 (19), 115 (21), 102 (22), 89 (18), 75 (37), 53 (62). **For 18xx:** mp >250 °C dec; ^{1}H NMR δ 2.20 (t, *J* = 5.2 Hz, 4 H), 3.63 (t, *J* = 10.5 Hz, 4 H), 3.77 (dd, *J* = 4.9, 10.8 Hz, 4 H), 5.37 (s, 4 H), 7.28 (s, 2 H); ^{13}C NMR δ 43.59, 47.09, 82.34, 113.44, 144.29.

Typical Procedure for Table III. Preparation of 19. To an ice-cold solution of **16** (802 mg, 2 mmol) in anhydrous tetrahydrofuran (80 mL) under argon was added, in small portions, 1.12 g (10 mmol) of solid potassium *tert*-butoxide. After addition was complete, the mixture was stirred at room temperature overnight. The mixture was poured into water (200 mL) and ex-

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(9) Purchased from Aldrich Chemical Co.

Table II. Cycloadducts from Isobenzofuran Equivalents and DCB

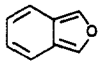
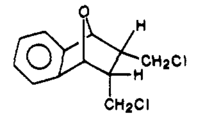
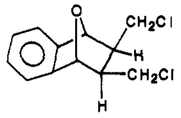
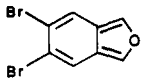
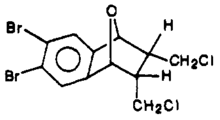
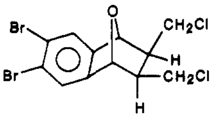
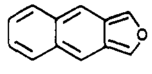
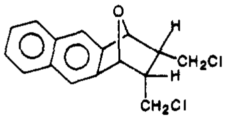
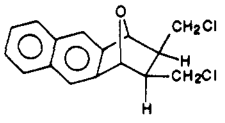
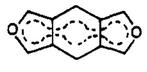
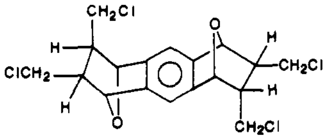
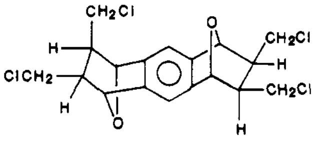
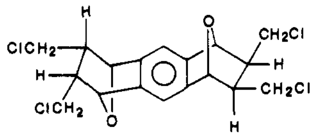
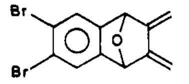
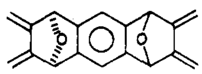
isobenzofuran equivalent	isobenzofuran	adducts (ratio)		% yield
7		 15n (89)	 15x (11)	69
10		 16n (87)	 16x (13)	63
12		 17n (90)	 17x (10)	78
14		 18nn (91)	 18nx (8)	54
		 18xx (1)		

Table III. Bis(methylene)oxabenzonorbornenes

bis(chloromethyl) substrate	product	% yield
15	4	96
16	 19	92
17	5	98
18nn	 20	90
18nx or 18xx	20	93

tracted with methylene chloride (3 × 80 mL). Combined organic layers were washed with water, dried, and concentrated to give, on recrystallization from 50–110 °C petroleum ether, 604 mg (92%) of **19** as a white solid, mp 149–151 °C; ^{1}H NMR δ 5.23 (s, 2 H), 5.34 (s, 2 H), 5.53 (s, 2 H), 7.57 (s, 2 H); ^{13}C NMR δ 83.07, 104.42, 123.17, 125.06, 143.04, 145.22; mass spectrum, *m/e* (relative intensity) 330 (16), 328 (29, M$^+$), 326 (15), 301 (10), 299 (21), 297 (12), 278 (11), 276 (23, M$^+$ for dibromoisobenzofuran), 274 (13), 249 (55), 247 (48), 221 (25), 219 (32), 167 (11), 140 (51), 139 (100), 113 (15), 87 (21), 69 (23). Anal. Calcd for $C_{12}H_8Br_2O$: C, 43.94; H, 2.46. Found: C, 44.11; H, 2.34.

Physical Data for Other Compounds in Table III. For 4: mp 73–74 °C (recrystallized from 35–60 °C petroleum ether); ^{1}H NMR δ 5.17 (s, 2 H), 5.28 (s, 2 H), 5.56 (s, 2 H), 7.15 (dd, 2 H), 7.28 (dd, 2 H); ^{13}C NMR δ 83.70, 103.27, 119.72 (overlapped peaks), 127.31, 144.33; mass spectrum, *m/e* (relative intensity) 170 (25, M$^+$), 169 (11), 141 (100), 118 (48, M$^+$ for isobenzofuran), 115 (44), 89 (21), 77 (12), 63 (24), 51 (19). Anal. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.80; H, 5.88. **For 5**: mp 135–137 °C (lit.[5b] mp 136–138 °C); ^{1}H NMR δ 5.24 (s, 2 H), 5.33 (s, 2 H), 5.70 (s, 2 H), 7.44 (dd, 2 H), 7.70 (s, 2 H), identical with that reported.[5b] **For 20**: mp >255 °C dec; ^{1}H NMR δ 5.18 (s, 4 H), 5.28 (s, 4 H), 5.52 (s, 4 H), 7.25 (s, 2 H); ^{13}C NMR δ 83.50, 103.35, 112.08, 143.97, 144.10; mass spectrum, *m/e* (relative intensity) 262 (100, M$^+$), 233 (94), 205 (98), 204 (71), 189 (62), 181 (47), 165 (29), 153 (63), 152 (74), 139 (21), 127 (13), 115 (12), 102 (13), 89 (24), 76 (23), 63 (29), 51 (30). Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.30; H, 5.43.

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Registry No. 4, 119273-69-7; 5, 73862-76-7; 6, 573-57-9; 7, 85798-64-7; 9, 106750-88-3; 10, 119273-70-0; 11, 22187-13-9; 12, 119273-71-1; 13, 87207-46-3; 14, 113451-37-9; 15n, 119273-72-2; 15x, 119363-66-5; 16n, 119273-73-3; 16x, 119363-67-6; 17n, 119273-74-4; 17x, 119363-68-7; 18nn, 119363-69-8; 18nx, 119363-70-1; 18xx, 119363-71-2; 19, 119273-75-5; 20, 119363-72-3; DCB, 1476-11-5; tetraphenylcyclopentadienone, 479-33-4.

Hydroboration of Terpenes. 10. An Improved Procedure for the Conversion of α-Pinene into β-Pinene in High Chemical and Optical Yield Using a Combination of the Schlosser Allylic Metalation of α-Pinene and Allylborane Chemistry

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Pyrolysis of β-pinene gives myrcene, an important raw material in the perfume industry. Furthermore, β-pinene

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[1] Visiting professor on a grant from the Dow Chemical Co.

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