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The Addition of sp^2- and sp-Hybridized Nucleophiles to a Bridgehead Bromoketone

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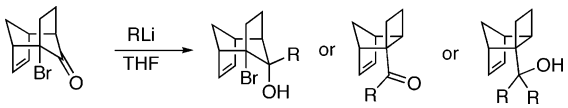


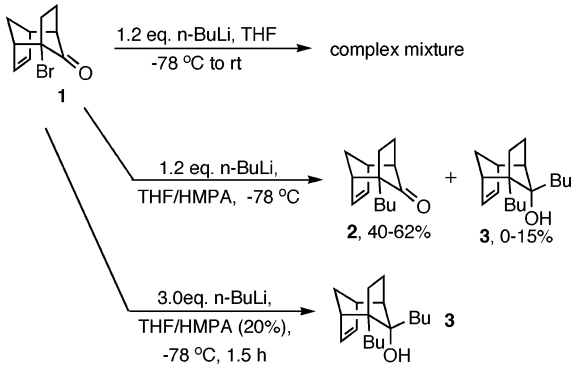
The reaction of various sp^2- and sp-hybridized organolithium species with bromoketone **1** is presented. In most cases, control over the course of the process is possible and products from simple addition, addition followed by a quasi-Favorskii rearrangement or addition, rearrangement, and addition can be selectively prepared.

During the course of our studies of the 4+3 cycloaddition reaction between cyclopentenyl oxyallylic species derived from polyhalogenated cyclopentanones,[1] we became interested in the chemistry of **1**, a cycloadduct obtained by the reaction of 2,5-dibromocyclopentanone with cyclopentadiene.

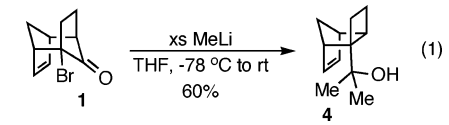
We recently reported the reaction of **1** with primary organolithium reagents.[2] A representative example of the results is shown in Scheme 1. In THF, the reaction of **1** with *n*-BuLi resulted in the formation of a complex mixture. The addition of HMPA surprisingly resulted in an unexpected pathway, with bromide substitution being favored over carbonyl addition when approximately stoichiometric amounts of organolithium reagent were used, affording **2** in reasonable yield. In the presence of excess organolithium, a product (**3**) was obtained that arose from both carbonyl addition and bromide substitution. While interesting, these results did not bode well for some of the plans we had for applying **1** to the synthesis of several natural products. We thus set out to see if other organolithium reagents could add to the carbonyl group of **1** without causing debromination, whether via substitution or halogen−metal exchange.

At the outset of this new study, we knew that at least one organolithium, methyllithium, would behave as desired. We had observed earlier that the reaction of **1** with this organolithium proceeded uneventfully to afford **4** in reasonable yield.[3] We thus anticipated that some degree of success should be possible.

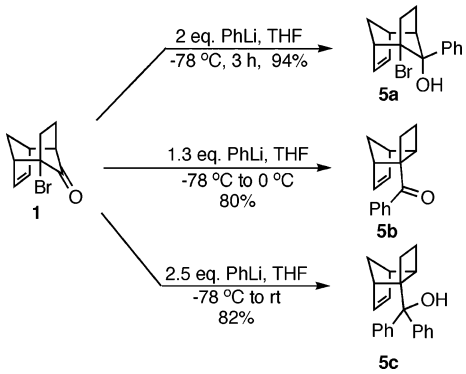
SCHEME 1



We began our study with phenyllithium. Exposure of **1** to 2 equiv of phenyllithium in THF at −78 °C for 3 h followed by aqueous workup afforded the addition product **5a** in 94% yield (Scheme 2). This indicated that the intermediate alkoxide formed in the addition process was stable with respect to quasi-Favorskii rearrangement, at least at low temperature.[4] We reasoned that using a smaller amount of phenyllithium and raising the temperature over the course of the process might result in an addition, quasi-Favorskii sequence. This was indeed the case. Treatment of **1** with 1.3 equiv of phenyllithium in THF at −78 °C followed by warming to 0 °C over 4 h gave the ketone **5b** in 80% yield along with 14% of recovered starting material. Finally, we combined both processes to conduct an addition−rearrangement−addition sequence. Using excess phenyllithium (2.5 equiv) and ultimately warming to room temperature gave the tertiary alcohol **5c** in 82% yield.



SCHEME 2



Other results are summarized in Table 1. 4-Methoxyphenyllithium could be added to **1** with control to produce

(1) (a) Harmata, M.; Bohnert, G. *Org. Lett*. **2001**, *5*, 59. (b) Harmata, M.; Rashatasakhon, P. *Org. Lett*. **2001**, *3*, 2533. (c) Harmata, M.; Rashatasakhon, P. *Tetrahedron Lett*. **2001**, *42*, 5593. (d) Harmata, M.; Shao, L.; Kürti, L.; Abeywardane, A. *Tetrahedron Lett*. **1999**, *40*, 1075.

(2) Harmata, M.; Wacharasindhu, S. *J. Chem. Soc., Chem Commun.* **2003**, 2492.

(3) Harmata, M.; Shao, L. *Synthesis* **1999**, 1534.

(4) For some synthetic applications of the quasi-Favorskii rearrangement, see: (a) Gambacorta, A.; Turchetta, S, S.; Bovicelli, P.; Botta, M. *Tetrahedron* **1991**, *47*, 9097. (b) Kraus, G. A.; Shi, J. *J. Org. Chem*. **1991**, *56*, 4147. (c) Kraus, G. A.; Shi, J. *J. Org. Chem*. **1990**, *56*, 5424.

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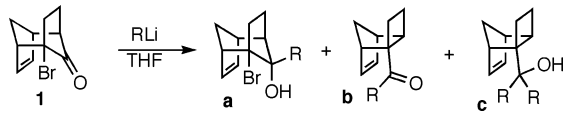
TABLE 1. Reactions of Organolithium Reagents with 1



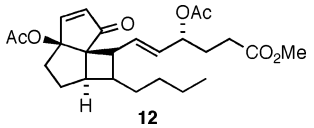
entry	RLi, equiv	T (°C)	time (h)	product	yield (%) a	yield (%) b	yield (%) c
1	phenyl, 2	−78	3	**5**	94	0	0
2	phenyl, 1.3	−78 to 0	4	**5**	0	80[a]	0
3	phenyl, 2.5	−78 to rt	4	**5**	0	0	82
4	4-methoxyphenyl, 2.2	−78	1	**6**	88	0	0
5	4-methoxyphenyl, 1.1	−78 to −30	0.5	**6**	0	72	0
6	4-methoxyphenyl, 2.2	−78 to rt	1	**6**	0	0	91
7	3-methoxyphenyl, 2.2	−78	1	**7**	64	20	0
8	3-methoxyphenyl, 2.2	−100	1	**7**	84	10	0
9	3-methoxyphenyl, 2.2	−78 to rt	1	**7**	0	0	93
10	2-furyl, 2.5	−78	1.5	**8**	63[b]	0	0
11	2-furyl, 2.5	−78	10	**8**	97	0	0
12	2-furyl, 1.2	−78 to −5	3	**8**	0	74	0
13	2-thienyl, 2.5	−78	3	**9**	97[c]	0	0
14	2-thienyl, 1.3	−78 to −5	1	**9**	0	44	14
15	2-thienyl, 2.2	−78 to rt	2	**9**	0	0	74
16	2-methylprop-1-enyl, 1.5	−78	2	**10**	90	0	0
17	2-methylprop-1-enyl, 1.5	−78 to −30	2.5	**10**	0	90[c]	0
18	2-phenylethynyl, 2.2	−78 to rt	5	**11**	0	25	61
19	2-phenylethynyl, 2.2	−78 to rt	48	**11**	0	0	71

[a] Plus 14% recovered starting material. [b] Plus 24% recovered starting material. [c] Solvent was diethyl ether.

three distinct products by using the procedure developed for phenyllithium (Table 1, entries 4−6). 3-Methoxyphenyllithium was subject to less control. Using the conditions that afforded simple addition for phenyllithium gave the expected addition product **7a** and the quasi-Favorskii product **7b** in a ratio of 3.2:1 (Table 1, entry 7). Conducting the reaction at lower temperature (−100 °C) improved the situation, giving a mixture of **7a** and **7b** in a ratio of 8.4:1 (Table 1, entry 8). But as expected, reacting **1** with excess 3-methoxyphenyllithium resulted in the formation of the tertiary alcohol **7c** in excellent yield (Table 1, entry 9). 2-Lithiofuran and 2-lithiothiophene were also used as nucleophiles. Simple carbonyl addition to **1** was possible with both reagents (Table 1, entries 10 and 13). However, with 2-lithiothiophene, addition to **1** did not take place at low temperature, but was successful in ether. The addition−quasi-Favorskii rearrangement sequence was also possible with both reagents (Table 1, entries 12 and 14). The possibility of forming a tertiary alcohol was only investigated with use of 2-lithiothiophene and this was successful (Table 1, entry 15).

Of particular interest for potential future applications was the addition of vinyllithium and alkynyllithium reagents to **1**. Only two systems were examined, but they demonstrate the feasibility of the reaction. Treatment of **1** with 2-methylprop-1-enyllithium at low temperature afforded the addition product **10a** in 90% yield (Table 1, entry 16). Similarly, when **1** was treated with an excess of the vinyllithium and the reaction mixture was allowed to warm to −30 °C, the ketone **10b** was obtained in 90% yield. 1-Lithiophenylacetylene reacted with **1** at −78 °C followed by warming to room temperature to afford a mixture of **11b** and **11c** in good yield. When stirring at room temperature was prolonged, **11c** could be isolated cleanly in 71% yield. At low temperature, addition to **1** was not observed.

In summary, we have shown that a selection of nucleophiles can add to the carbonyl group of **1** cleanly, in contrast to primary organolithium reagents. Controlling the reaction conditions allows for simple addition, addition followed by quasi-Favorskii rearrangement, or a sequence of addition−rearrangement and addition. This makes 2,5-dibromocyclopentanone a reasonably general equivalent of a wide variety of cyclobutenes in what would be a Diels−Alder reaction for such cyclobutenes. It is quite reasonable to assume that related cyclopentanones could assume such a role. Our goal is to take advantage of these results and use systems that will produce intermediates that might be parlayed into various interesting synthetic targets. In particular, we are interested in applying the chemistry to the prostanoid natural product, tricycloclavulone (**12**), whose unique



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carbocyclic core is an appealing challenge and should be accessible by using the chemistry discussed here.[5] Progress in these studies will be reported in due course.

Experimental Section

General Procedure for the Addition Reaction. To a cooled solution of bromoketone **1** (50 mg, 0.22 mmol) in THF (2.2 mL) at −78 °C was added PhLi (0.24 mL, 1.8 M, 0.44 mmol) dropwise. The mixture was stirred for 3 h, quenched with MeOH

(5) (a) Ito, H.; Hasegawa, M.; Takenaka, Y.; Kobayashi, T.; Iguchi, K. *J. Am. Chem. Soc.* **2004**, *126*, 4520. (b) Ito, Hi.; Kobayashi, T.; Hasegawa, M.; Iguchi, K. *Tetrahedron Lett.* **2003**, *44*, 1259. (c) Iwashima, M.; Terada, I.; Okamoto, K.; Iguchi, K. *J. Org. Chem.* **2002**, *67*, 2977.

(2 mL) at −78 °C, and warmed to room temperature. The mixture was diluted with distilled water, extracted by ether (3 × 10 mL), washed with brine (5 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography with 20% EtOAc/Hex to yield **5a** (63 mg, 94%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 7 Hz, 2H), 7.30−7.17 (m, 3H), 6.75−6.64 (m, 2H), 4.24 (s, 1H), 3.32−3.31 (m, 1H), 2.83 (s, 2H), 2.62−2.53 (m, 1H), 2.41-(d, J = 10.7 Hz, 2H), 2.31−2.22 (m, 1H), 1.62−1.39 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 146.3, 142.5, 138.6, 127.5, 126.7, 125.8, 87.7, 60.2, 45.2, 44.4, 44.2, 36.9, 28.3; IR (neat) 3554, 3056, 3019, 2953, 2900, 1956, 1891, 1805, 1486 cm^{-1}. Anal. Calcd for $C_{16}H_{17}BrO$: C, 62.96; H, 5.61. Found: C, 62.77; H, 5.55.

General Procedure for the Addition Reaction followed by Quasi-Favorskii Rearrangement. To a cooled solution of bromoketone **1** (50 mg, 0.22 mmol) in THF (2 mL) at −78 °C was added PhLi (0.15 mL, 1.8 M, 0.26 mmol) dropwise. After being stirred at −78 °C for 1 h, the reaction was warmed to 0 °C and stirred for an additional 4 h. It was then quenched with distilled water, extracted with ether (3 × 10 mL), washed with brine (5 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography with 20% EtOAc/Hex to yield a starting ketone **1** (14%) and ketone **5b** (39 mg, 80%) as a solid: mp 50−52 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.87−7.83 (m, 2H), 7.56−7.40 (m, 3H), 6.13−6.10 (m, 1H), 5.62−5.58 (m, 1H), 3.10 (d, J = 2.5 Hz, 1H), 2.77−2.98, (m, 2H), 2.44−2.30 (m, 1H), 2.20−2.24, (m, 3H), 1.51−1.37, (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 201.6, 136.4, 135.4, 132.4, 131.6, 128.8, 128.3, 57.3, 49.1, 45.4, 42.5, 39.1, 27.1, 19.2; IR (neat) 3530, 3060, 2970, 2847, 1666 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.57, H, 7.02.

General Procedure for the Addition, Rearrangement, and Addition Reaction. To a cooled solution of bromoketone **1** (100 mg, 0.44 mmol) in THF (4.4 mL) at −78 °C was added PhLi (0.15 mL, 1.8 M, 0.26 mmol) dropwise. After being stirred at −78 °C for 1 h, the reaction was then warmed to room temperature over 2 h and stirred for an additional 4 h. It was quenched with distilled water, extracted by ether (3 × 10 mL), washed with brine (5 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography with 5% EtOAc/Hex to yield alcohol **5c** (109 mg, 82%) as a solid: mp 82−84 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.47−1.17 (m, 10H), 6.30−6.26 (m, 1H), 5.97−5.93 (m, 1H), 2.73−2.64 (m, 4H), 2.08−1.93 (m, 2H), 1.82−1.71 (m, 1H), 1.60−1.51 (m, 1H) 1.29−1.14 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 146.9, 146.7, 138.2, 134.6, 127.8, 127.5, 127.3, 126.7, 126.5, 81.2, 58.3, 49.5, 46.5, 45.3, 39.6, 27.9, 19.7; IR (neat) 3525, 3501, 2998, 2966, 1486, 1442 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33. Found: C, 87.45, H, 7.22.

1-Bromo-9-(4-methoxyphenyl)tricyclo[4.2.1.1^{2,5}]dec-3-en-9-ol (6a): 88%, oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.84−7.79 (m, 2H), 6.84−6.78 (m, 2H), 6.75−6.64 (m, 2H), 4.14 (s, 1H), 3.79 (s, 3H), 3.31−3.30 (m, 1H), 2.83 (s, 1H), 2.57−2.05 (m, 3H), 1.63−127 (m, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 157.9, 142.4, 138.9, 138.5, 127.1, 112.7, 87.3, 72.9, 60.2, 55.1, 45.2, 44.5, 44.1, 37.1, 28.4; IR (neat) 3560, 3025, 2996, 1601, 1570 cm^{-1}; Anal. calcd for $C_{17}H_{19}BrO_2Na$ $[M + Na]^+$ 357.0460, found 357.0465.

(4-Methoxyphenyl)tricyclo[4.2.1.0^{2,5}]non-7-en-2-yl-methanone (6b): 72%, semisolid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87−7.82 (m, 2H), 6.94−6.89 (m, 2H), 6.13−6.10 (m, 1H), 5.62−5.59 (m, 1H), 3.86 (s, 3H), 3.08 (d, J = 1.2 Hz, 1H), 2.76 (s, 1H), 2.71−2.68 (m, 1H), 2.39−2.29 (m, 1H), 2.17−2.04 (m, 3H), 1.50−1.36 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 200.1, 162.8, 136.3, 131.6, 131.1, 128.1, 113.4, 56.9, 55.3, 49.3, 45.3, 42.5, 39.0, 27.3, 19.2; IR (neat) 3060, 2970, 2929, 2843, 1662, 1593 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.14, H, 7.19.

Bis(4-methoxyphenyl)tricyclo[4.2.1.0^{2,5}]non-7-en-2-yl-methanol (6c): 91%, oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39−7.30 (m, 4H), 6.94−6.78 (m, 4H), 6.33−6.30 (m, 1H), 6.01−5.98 (m, 1H), 3.85 (s, 3H), 3.79, (s, 3H), 2.73−2.63 (m, 4H), 2.11−1.95 (m, 2H), 1.80−1.62 (m, 2H), 1.32−1.29 (m, 1H), 1.22−1.19 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 158.1, 158.0, 139.7, 139.2, 138.1, 134.5, 132.1, 128.8, 128.2, 115.6, 112.8, 112.5, 80.6, 58.5, 55.3, 55.1, 55.0, 49.2, 46.5, 45.3, 39.5, 27.9, 19.7; IR (neat) 3534, 2953.5, 2835.4, 1613, 1499 cm^{-1}; HRMS calcd for $C_{24}H_{26}O_3Na$ $[M + Na]^+$ 385.1774, found 358.1764.

1-Bromo-9-(3-methoxyphenyl)tricyclo[4.2.1.1^{2,5}]dec-3-en-9-ol (7a): 84%, oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53−7.52 (m, 1H), 7.44−7.41 (m, 1H), 7.25−7.17 (m, 1H), 6.77−6.64 (m, 3H), 4.17 (s, 1H), 3.78 (s, 3H), 3.30 (s, 1H), 2.82 (s, 1H), 2.63−2.54 (s, 1H), 2.40 (d, J = 10.6 Hz, 2H), 2.30−2.31 (m, 1H), 1.65−1.61 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 158.7, 147.8, 142.5, 138.5, 128.5, 118.3, 112.2, 112.1, 87.6, 72.74, 60.3, 55.2, 45.1, 44.4,-44.1, 37.0, 28.3; IR (neat) 3546.4, 3015.2, 2966.1, 2900, 2835, 1601.1, 1585, 1495 cm^{-1}. Anal. Calcd for $C_{17}H_{19}BrO_2$: C, 60.91; H, 5.71. Found: C, 61.12; H, 5.90.

(3-Methoxyphenyl)tricyclo[4.2.1.0^{2,5}]non-7-en-2-yl-methanone (7b): 20%, oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.44−7.25 (m, 3H), 7.09−7.05 (m, 1H), 6.13−6.10 (m, 1H), 5.63−5.59 (m, 1H), 3.84 (s, 3H), 3.10 (s, 1H), 2.76 (s, 1H), 2.72−2.68 (m, 1H), 2.38−2.32 (m, 1H), 2.17−2.05 (m, 3H), 1.51−1.37 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 301.4, 159.6, 136.7, 136.4, 131.7, 129.2, 121.4, 118.7, 113.3, 57.4, 55.3, 49.2, 45.4, 42.5, 39.2, 27.2, 19.2; IR (neat) 3080, 2980, 1670, 1445 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.40; H, 7.29.

Bis(3-methoxyphenyl)tricyclo[4.2.1.0^{2,5}]non-7-en-2-yl-methanol (7c): 93%, solid, mp 103 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (t, J = 7.9 Hz, 1H), 7.15 (t, J = 8.8 Hz, 1H), 7.13−6.95 (m, 4H), 6.83−6.74 (m, 2H), 6.33−6.30, (m, 1H), 6.00−5.98 (m, 1H), 3.77 (d, J = 13.5 Hz, 6H), 2.75−2.66 (m, 4H), 2.08−1.97 (m, 2H), 1.78−1.60 (m, 2H), 1.29−1.16 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 159.2, 158.9, 148.4, 148.3, 138.4, 134.6, 128.3, 128.2, 120.5, 119.9, 114.1, 113.1, 11.78, 81.2, 58.3, 55.12, 55.0, 49.6, 46.5, 45.2, 39.8, 27.8, 19.9; IR (neat) 3530, 2962, 2835, 1932, 1854, 1760, 1597, 1580, 1486 cm^{-1}. Anal. Calcd for $C_{24}H_{26}O_3$: C, 79.53; H, 7.23. Found: C, 79.36; H, 7.37.

1-Bromo-9-furan-2-yltricyclo[4.2.1.1^{2,5}]dec-3-en-9-ol (8a): 97%, solid, mp 82−83 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, J = 1.5 Hz, 1H), 6.71−6.62 (m, 3H), 6.28−6.26 (m, 1H), 4.14 (s, 1H), 3.25−3.23 (m, 1H), 3.23−3.00 (m, 1H), 2.82−2.80 (m, 1H), 2.44−2.39 (m, 2H), 2.30−2.24 (m, 1H), 1.64−1.51 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 157.2, 142.3, 140.2, 138.6, 109.6, 105.8, 85.3, 70.7, 58.3, 45.1, 43.4, 43.0, 38.9, 28.4; IR (neat) 3538, 3141, 3043, 2958, 2884, 1503, 1462, 1335 cm^{-1}. Anal. Calcd for $C_{15}H_{15}BrO_2$: C, 56.97; H, 75.12. Found: C, 56.77; H, 5.32.

Furan-2-yltricyclo[4.2.1.0^{2,5}]non-7-en-2-yl-methanone (8b): 74%, oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.56 (t, J = 1.5 Hz, 1H), 7.13−7.11 (m, 1H), 6.53−6.51 (m, 1H), 6.12−6.08 (m, 1H), 5.77−5.73 (m, 1H), 3.14 (s, 1H), 2.76 (s, 1H), 2.97−2.64 (m, 1H), 2.43−1.95 (m, 4H), 1.53−1.25 (m, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 191.1, 151.9, 145.5, 136.3, 132.5, 117.1, 111.7, 56.8, 48.1, 45.4, 12.1, 38.7, 26.2, 19.2; IR (neat) 3129, 3060, 2970, 1670, 1568, 1466 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.28; H, 6.44.

1-Bromo-9-thiophen-2-yltricyclo[4.2.1.1^{2,5}]dec-3-en-9-ol (9a): 97%, solid, mp 51−52 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (dd, J = 1.2, 2.7 Hz, 1H), 7.17 (dd, J = 1.2, 3.9 Hz, 1H), 6.87−6.84 (m, 1H), 6.71−6.62 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 150.6, 142.3, 138.6, 125.0, 124.1, 124.0, 86.6, 72.8, 58.9, 46.0, 45.0, 43.9, 38.1, 29.2; IR (neat) 3542, 3011, 2953, 1495, 1217 cm^{-1}. Anal. Calcd for $C_{14}H_{15}BrOS$: C, 54.03; H, 4.86. Found: C, 53.96; H, 4.67.

Thiophen-2-yltricyclo[4.2.1.0^{2,5}]non-7-en-2-ylmethanone (9b): 44%, oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.64−7.57 (m, 2H), 7.12 (dd, J = 1.0, 3.7 Hz, 1H), 6.14−6.11 (m, 1H), 5.74−5.71 (m, 1H), 3.11 (s, 1H), 2.77 (m, 1H), 2.68−2.64 (m, 1H), 2.40−2.26 (m, 1H), 2.21−2.01 (m, 3H), 1.52−1.35 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 195.0, 142.5, 136.4, 132.5, 132.0, 131.6, 127.7, 5734, 49.4, 45.4, 42.4, 39.1, 27.2, 19.3. Anal. Calcd for $C_{14}H_{14}$-OS: C, 73.01; H, 6.13. Found: C, 72.95; H, 6.10.

Dithiophen-2-yltricyclo[4.2.1.0^{2,5}]non-7-en-2-ylmethanol (9c): 74%, solid, 105−107 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.25−7.21 (m, 2H), 7.04−6.98 (m, 2H), 6.90−6.85 (m, 2H), 6.35−6.32 (m, 1H), 6.19−6.16 (m, 1H), 3.33 (d, J = 0.7 Hz, 1H), 2.75 (m, 1H), 2.65−2.62 (m, 1H), 2.58 (s, 1H), 2.25−2.06 (m, 2H), 1.91−1.69 (m, 2H), 1.35−1.17 (m, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151.5, 151.4, 138.5, 134.8, 126.6, 126.0, 125.6, 124.9, 125.3, 123.0, 80.2, 58.9, 48.9, 46.6, 45.7, 39.7, 26.7, 19.8; IR (neat)

3501, 3011, 2996, 1478, 1429, 1213 cm^{-1}. Anal. Calcd for $C_{18}H_{18}OS_2$: C, 68.75; H, 5.77. Found: C, 68.66; H, 5.68.

1-Bromo-9-(2-methylpropenyl)tricyclo[4.2.1.1^{2,5}]dec-3-en-9-ol (10a): 90%, oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.64−6.51 (m, 2H), 5.53 (s, 1H), 3.81 (s, 1H), 3.14−3.12 (m, 1H), 2.70−2.60 (m, 2H), 2.34−2.18 (m, 3H), 1.94−1.87 (m, 1H), 1.80 (d, J = 0.75 Hz, 3H), 1.68 (d, J = 1.2 Hz, 3H), 1.59−1.44 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 142.2, 138.2, 135.3, 131.2, 85.8, 74.3, 56.6, 45.0, 43.5, 43.5, 38.6, 29.0, 26.8, 19.5; IR (neat) 3440, 3011, 2970, 2933, 2402, 1446 cm^{-1}. Anal. Calcd for $C_{14}H_{19}BrO$: C, 59.37; H, 6.76. Found: C, 59.45; H, 6.66.

3-Methyl-1-tricyclo[4.2.1.0^{2,5}]non-7-en-2-ylbut-2-en-1-one (10b): 90%, oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.13 (s, 1H), 6.12−5.81 (m, 2H), 2.85 (s, 1H), 2.70 (s, 1H), 2.42, (s, 1H), 2.20−2.05 (m, 5H), 2.05−1.87 (m, 4H), 1.87−1.66 (m, 1H), 1.48−1.31 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 202.5, 155.3, 135.7, 133.4, 121.2, 59.3, 47.0, 45.5, 42.0, 38.5, 27.8, 25.1, 20.7, 18.7; IR (neat) 3060, 2970, 2852, 1609 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.94; H, 8.70.

3-Phenyl-1-tricyclo[4.2.1.0^{2,5}]non-7-en-2-yl-propynone (11b): 25%, oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60−7.27 (m, 5H), 6.11−6.50 (m, 2H), 3.05 (s, 1H), 2.77 (s, 1H), 2.58−2.55 (m, 1H), 2.41−2.21 (m, 2H), 2.02 (d, J = 6.3 Hz, 1H), 1.89−1.79 (m, 1H), 1.51−1.26 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 190.5, 135.8, 134.3, 132.9, 130.4, 128.5, 120.3, 91.6, 86.8, 60.8, 40.5, 45.4, 42.0, 40.5, 25.0, 18.9; IR (neat) 3060, 2996, 2847, 2197, 1654 cm^{-1}; HRMS calcd for $C_{18}H_{16}O$ 248.1196, found 248.1209.

1-Phenyl-3-tricyclo[4.2.1.0^{2,5}]non-7-en-2-ylpenta-1,4-diyn-3-ol (11c): 71%, oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52−7.48 (m, 4H), 7.36−7.32 (m, 6H), 6.40−6.14 (m, 2H), 2.97 (d, J = 1.5 Hz, 1H), 2.73 (s, 1H), 2.47−2.58 (m, 2H), 2.37−2.31 (m, 2H), 2.15 (d, J = 9.3 Hz, 1H), 1.88−1.80 (m, 1H), 1.48−1.25 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 136.5, 134.8, 131.7, 128.4, 128.2, 128.1, 122.5, 122.4, 89.4, 89.5, 83.9, 83.0, 69.3, 58.6, 47.1, 46.0, 45.3, 40.0, 26.2. 20.0; IR (neat) 3472, 3051, 2839, 2222 cm^{-1}; HRMS calcd for $C_{26}H_{22}ONa$ $[M + Na]^+$ 373.1563, found 373.1554.

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Supporting Information Available: Copies of proton and carbon spectra for the products obtained. This material is available free of charge via the Internet at http://pubs.acs.org.

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