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# Ruthenium-Catalyzed Cascade Reactions of Diynes with Norbornadiene – Synthesis of Norbornene Derivatives[‡]

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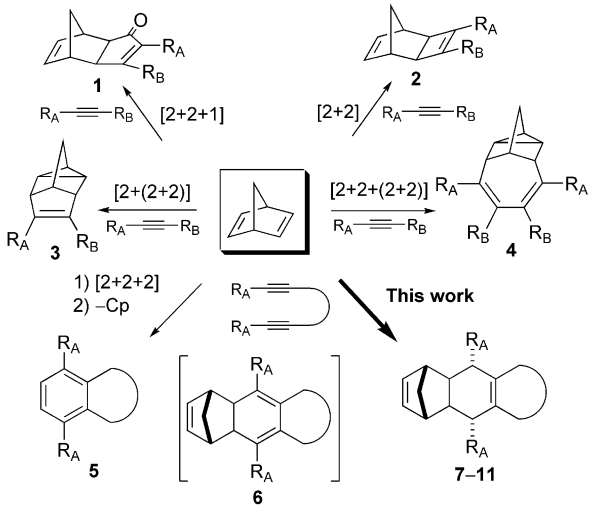
*Dedicated to Professor Pei-Lin Wu on the occasion of her 60th birthday*

**Keywords:** Norbornadiene / Norbornene / Cascade reaction / Ruthenium / Transfer hydrogenation / Cycloaddition

Norbornene derivatives **7**–**11** were prepared from norbornadiene and the corresponding diynes by Ru-catalyzed [(2+2)+2] cycloaddition and subsequent transfer hydrogenation. The structure and stereochemistry of the cycloadducts were confirmed by X-ray crystal analysis. This procedure provides high diastereoselectivity to generate norbornenes **7**–**11** in up to 82 % yield. The scope and limitations of this reaction were investigated. Compounds that contained the skeleton of 1,7-diaryl-1,6-heptadiynes were suitable starting materials. Additionly, **9h** was empolyed in the synthesis of polynorbornene **31** by ring-opening metathesis polymerization (ROMP). The number-average molecular weight ($M_n$) and polymer-distribution index (PDI) of this new polymer were determined to be 28.6 kDa and 1.35, respectively.

## Introduction

Norbornene is a bridged olefin with a rigid skeleton. The ring strain (17.6 kcal/mol)[1] makes the double bond in this molecule reactive. Norbornenes are suitable precursors for the ring-opening metathesis polymerization (ROMP)[2] because release of this ring strain drives this process. Therefore, norbornenes have been widely utilized in the synthesis of ROMP polynorbornenes. Norsorex®,[3] a polynorbornene, exhibits special properties, such as flexibility, bending and damping, and can be used for applications in fluid resistant devices and shock absorbers.[4] The preparation of norbornenes from norbornadiene (NBD) should be a simple and efficient method because the through-space interaction between the proximal olefins in NBD causes this compound to be more reactive than other simple alkenes and norbornenes.[5] Alkynes should be ideal reaction partners for NBD, and numerous examples have been reported (Scheme 1).[6] Pauson–Khand conditions yield cyclopentenone **1** by a formal [2+2+1] cycloaddition of NBD, an alkyne and CO.[7] The reaction of NBD and one alkyne molecule affords a formal [2+2] adduct **2**[8] or a homo-Diels–Alder product **3**,[9] depending on the catalysts and alkynes used. Tetracycles **4** can be obtained by a formal




Scheme 1. Metal-catalyzed/mediated reactions of NBD with alkynes. Cp = cyclopentadiene.

[‡] Metal-Catalyzed Reactions of Alkynes, IV. Part III: Y.-T. Wu, M.-Y. Kuo, Y.-T. Chang, C.-C. Shin, T.-C. Wu, C.-C. Tai, T.-H. Cheng, W.-S. Liu, *Angew. Chem.* **2008**, *120*, 10039–10042; *Angew. Chem. Int. Ed.* **2008**, *47*, 9891–9894. Part II: Y.-T. Wu, W.-C. Lin, C.-J. Liu, C.-Y. Wu, *Adv. Synth. Catal.* **2008**, *350*, 1841–1849.

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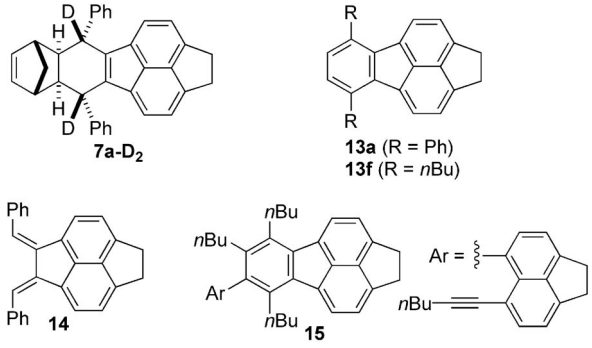
[2+2+(2+2)] cycloaddition of NBD and two alkynyl moieties under catalysis by a nickel(II)[10] or rhodium(I) complex.[11] NBD can also act as a "pre-alkyne".[12] A rhodium(I)-catalyzed [(2+2)+2] cycloaddition of NBD with a diyne form the intermediate **6**, which subsequently undergoes a thermal elimination of cyclopentadiene to give benzene derivatives **5**.[11] Recently, we observed that new cycloadducts **7**–**11** can be directly prepared with high diastereoselectivity from NBD and a diyne in a single pot. In this study, the reaction conditions are optimized, and the scope and limitations of this reaction are investigated.

## Results and Discussion

Limited systematic studies of the reaction conditions for the synthesis of norbornene derivative **7a** from diyne **12a** and NBD demonstrated that *i*PrOH and *p*-xylene both had key roles in this reaction (Table 1). In the absence of *i*PrOH, we isolated a mixture of **7a** (13%), **12a** (30%) and **13a** (3%, Table 1, Entry 1). However, a reaction in *i*PrOH was very inefficient, and we recovered most of the starting material **12a**. We also examined the catalytic abilities of some Ru complexes. In fact, $[RuCl_2Cp^*]_2$ (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) and $[RuCl_2(\eta^4\text{-NBD})]_\infty$ were efficient catalysts. Other complexes, such as $[RuCl_2(2,2'\text{-bipy})]\cdot 2H_2O$ and $[RuCl_2(\eta^6\text{-}p\text{-}MeC_6H_4iPr)]_2$, did not yield the desired cycloadduct **7a**. Notably, the commercially available polymer form, $[RuCl_2Cp^*]_\infty$,[13] was less reactive than its dimer analogue $[RuCl_2Cp^*]_2$. We had to conduct the reaction with 5 mol-% of catalyst $[RuCl_2Cp^*]_2$ in a mixed solvent of *p*-xylene and *i*PrOH at 130 °C for the best yield. Under the optimized reaction conditions, we obtained **7a** in 74% yield (Entry 3 in Table 1), and we did not observe other stereoisomers in significant amounts. The structure and stereochemistry of **7a** were determined from the 2D NMR spectra. The central cyclohexenyl ring in this compound is connected to the *exo* face of the norbornene moiety. The two phenyl substituents at C-5 and C-10 and 5a-H and 9a-H are all *cis* to each other.[14]

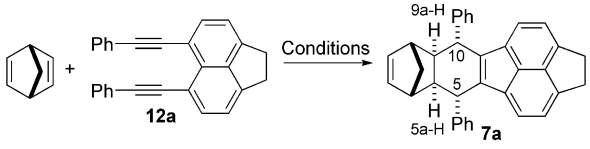
Compound **7** should be generated by transfer hydrogenation of the intermediate **6**, and *i*PrOH provided the two additional hydrogen atoms (5-H and 10-H) in **7a** (see Scheme 4).[15,16] A control experiment confirmed this hypothesis. When we performed a reaction in $[D_8]iPrOH$, we isolated cycloadduct **7a-D$_2$** with a 94% isotope purity (Scheme 2). Ru catalysts are well known to be very efficient in catalyzing the formation of a C–C bond[17] or transfer hydrogenation,[15] but both functions of a Ru catalyst in a reaction have never been reported before to the best of our knowledge. Additionally, **7a** contains six stereogenic centers and should be difficult to be produced by other synthetic methods. For example, the generation of **7a** by a Diels–Alder reaction[18,19] of diene **14**[20] with NBD is inefficient.




Scheme 2.

We investigated the reactivity of several diynes, such as 3,4-diethynylacenaphthalenes **12**, 3,4-diethynylfluoranthene **16** and 1,6-heptadiynes **17**–**19**, in the above-mentioned reaction. They provided cycloadducts **7**–**11** in 21–82% yield (Scheme 3 and Table 2). Both rigid and flexible diynes were suitable starting materials. Fluoranthenediyldiyne **16a** gave a lower yield than did acenaphthalenediyldiyne **12a**, perhaps because of its low solubility in the mixed solvent system. Among 1,6-hepatadiynes, heteroatom-unsubstituted

Table 1. Optimization of reaction conditions for the preparation of norbornene derivative **7a**.

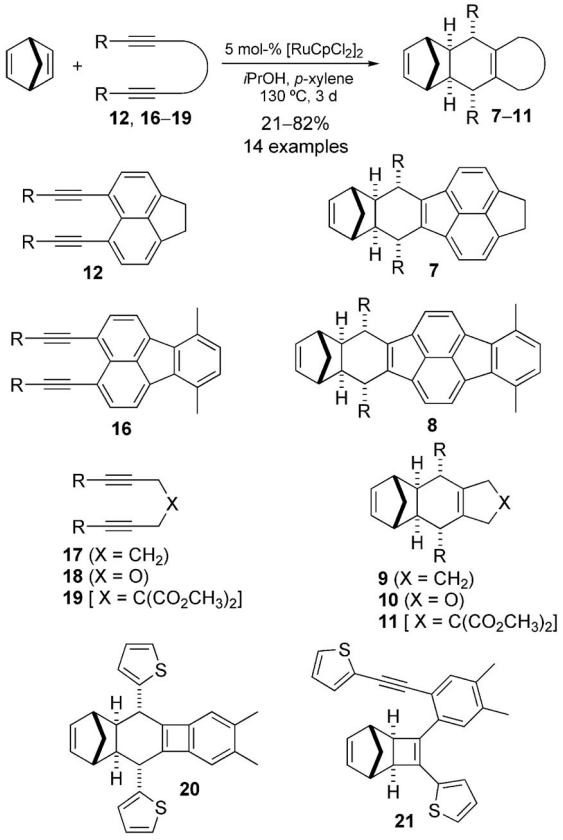



| Entry | Catalyst (mol-%) | Solvent[a] | Temp. [°C] | Time [h] | Yield [%] |
|---|---|---|---|---|---|
| 1 | $[RuCl_2Cp^*]_2$ (5) | A | 130 | 87 | 13[b] |
| 2 | $[RuCl_2Cp^*]_2$ (5) | B | 130 | 68 | trace[c] |
| 3 | $[RuCl_2Cp^*]_2$ (5) | C | 130 | 68 | 74 |
| 4 | $[RuCl_2Cp^*]_2$ (5) | C | 80 | 63 | 0[c] |
| 5 | $[RuCl_2Cp^*]_2$ (2.5) | C | 130 | 63 | 52 |
| 6 | $[RuCl_2Cp^*]_\infty$ (5) | C | 130 | 87 | 56 |
| 7 | $[RuCl_2(\eta^4\text{-NBD})]_\infty$ (5) | C | 130 | 63 | 70 |
| 8 | $[RuCl_2(2,2'\text{-bipy})]\cdot 2H_2O$ (10) | C | 130 | 63 | 0[c] |
| 9 | $[RuCl_2(\eta^4\text{-}p\text{-}MeC_6H_4iPr)]_2$ (5) | C | 130 | 63 | 0[c] |

[a] A: *p*-xylene, B: *i*PrOH, C: *p*-xylene + *i*PrOH. [b] 30% of **12a** and 3% of **13a** were also obtained. [c] Most of **12a** (>80%) was recovered.

**17** and **19** provided better results than their ether analogues **18**. The Thorpe–Ingold effect[21] was not important in this reaction because **17e** and **19e** gave the corresponding cycloadducts in similar yields (Entries 10 and 17 in Table 2). Apparently, only diaryl-substituted diynes could participate in this reaction. Terminal diyne **17j**[22] and dialkyl-substituted diyne **12f** did not furnish the desired cycloadducts. The former left the starting material unchanged, and the latter gave a mixture of **13f** and a formal [(2+2)+2] cycloadduct **15**. However, 1,7-bis(perfluorophenyl)-1,6-diyne **17i** did not yield norbornene **9i**, although 3,4,5-trifluorophenyl-substituted diyne **17e** gave cycloadduct **9e** in 59% yield (Entries 10 and 13 in Table 2).




Scheme 3. Synthesis of norbornenes **7**–**11**. For details, see Table 2.

As stated above, diynes that contain a 1,7-diaryl-1,6-heptadiyne skeleton are able to generate cycloadducts **7**–**11** with the formation of new five- and six-membered rings. Other species of alkynes did not produce the desired compounds. For example, 1,2-diphenylethyne gave cyclobutene **2** ($R_A$ = $R_B$ = Ph) in 46% yield. 1,2-Bis(2-thiophenylethynyl)-4,5-dimethylbenzene can be regarded as a monoalkyne in this reaction, forming the [2+2] cycloadduct **21** (56% yield), instead of **20** (Scheme 3). Under the reaction conditions used herein, 1,8-diphenyl-1,7-octadiyne did not yield the corresponding cycloadduct, and we recovered most of this starting material. X-ray diffraction analysis of cycloadducts **9e** and **9h** confirmed the structure and stereochemistry (Figure 1).[23]

Table 2. Synthesis of norbornenes **7**–**11**.

| Entry | Diyne | R | Product | Yield [%] |
|---|---|---|---|---|
| 1 | **12a** | Ph | **7a** | 74 |
| 2 | **12b** | 3,5-$(H_3C)_2C_6H_3$ | **7b** | 62 |
| 3 | **12c** | 4-$H_3CC_6H_4$ | **7c** | 34 |
| 4 | **12d** | 4-$FC_6H_4$ | **7d** | 38 |
| 5 | **12e** | 3,4,5-$F_3C_6H_2$ | **7e** | 53 |
| 6 | **12f** | *n*Bu | **7f** | 0[a] |
| 7 | **16a** | Ph | **8a** | 54 |
| 8 | **17a** | Ph | **9a** | 82 |
| 9 | **17d** | 4-$FC_6H_4$ | **9d** | 23 |
| 10 | **17e** | 3,4,5-$F_3C_6H_2$ | **9e** | 59 |
| 11 | **17g** | 4-$H_3CO_2CC_6H_4$ | **9g** | 52 |
| 12 | **17h** | 4-$F_3CC_6H_4$ | **9h** | 42 |
| 13 | **17i** | $C_6F_5$ | **9i** | 0[b] |
| 14 | **17j** | H | **9j** | 0[c] |
| 15 | **17k** | 4-$H_3COC_6H_4$ | **9k** | 51 |
| 16 | **18k** | 4-$H_3COC_6H_4$ | **10k** | 21 |
| 17 | **19e** | 3,4,5-$F_3C_6H_2$ | **11e** | 62 |

[a] A mixture of **13f** (15%) and **15** (30%) was obtained. [b] Most of **17i** remained unchanged. [c] Due to the low boiling point of diyne **17j**, it could not be recovered.

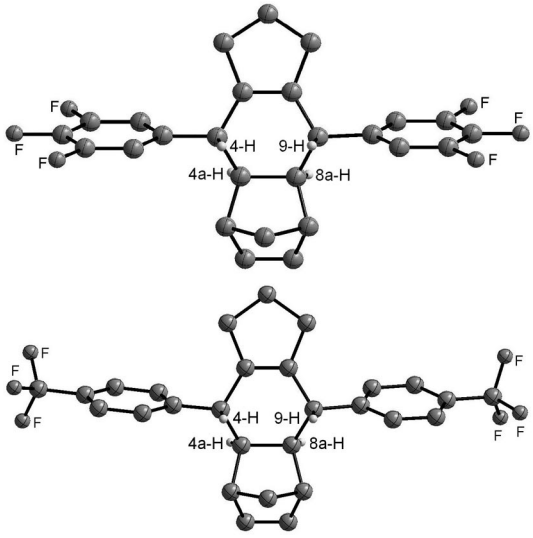
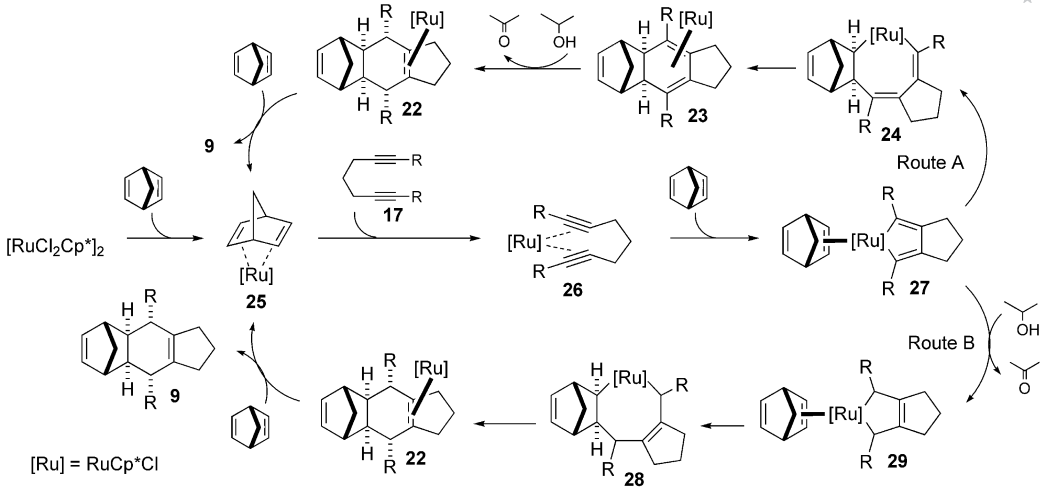



Figure 1. Molecular structures of **9e** (top) and **9h** (bottom), showing 50% probability ellipsoids. Except for 4-, 4a-, 8a- and 9-H, hydrogen atoms have been omitted for clarity.[23]

Based on the control experiment and the relevant literature, a possible mechanism of the formation of **9** was formulated as shown in Scheme 4. Initially, NBD reduces complex $[RuCl_2Cp^*]_2$ to generate the active catalyst **25**,[24] which then forms π complex **26** by the replacement of NBD with diyne **17**. The incorporation of a molecule of NBD leads complex **26** to rearrange to 1-ruthenacyclopentadiene **27**,[17a] where NBD provides its *exo* face as an $\eta^2$ ligand.[25,26] Subsequently, complex **27** inserts NBD to afford the σ complex **24** (route A). Reductive elimination yields 1,3-cyclohexadiene derivative **23**,[27] where the Ru fragment is *exo* to the norbornene moiety. Cyclopentadiene is not easily released from metal-stabilized intermediate **23**, which prefers to yield **22** by stereoselective transfer hydrogenation at the cyclohexadiene ring, and *i*PrOH is oxidized to ace-

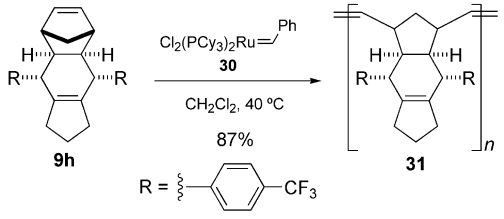
  




Scheme 4. Proposed mechanism of the reaction of diyne **17** and NBD.

tone. The substitution of **9** with NBD in **22** regenerates the active catalyst **25**. Alternatively, complex **27** can furnish **29** by transfer hydrogenation (route B). A coordinated NBD in **29** is inserted into the Ru moiety to form *exo*-**22**, which generates cycloadduct **9**, as in route A.

The preliminary study indicated that norbornene derivatives **9** were suitable precursors for ROMP. In the presence of the Grubbs' catalyst (**30**), **9h** underwent ROMP to form polynorbornene **31** in 87% yield (Scheme 5). We determined the number-averaged molecular weight ($M_n$) and the polymer-distribution index (PDI) of this new polymer to be 28.6 kDa and 1.35, respectively.




Scheme 5. Synthesis of ROMP polymer **31** from norbornene **9h**.

## Conclusions

This work elucidated a simple approach for preparing new norbornene derivatives **7**–**11** with high diastereoselectivity from diynes and NBD. One of the cycloadducts was used to form a new polynorbornene by ROMP. Further studies of the physical properties of functionalized polymers/copolymers and their applications are in progress.

## Experimental Section

**General:** $^1$H and $^{13}$C NMR spectra were recorded with a Bruker 300 (300 and 75.5 MHz) spectrometer. The assignments listed in the $^1$H and $^{13}$C NMR data below were supported by DEPT, NOESY, and COSY experiments. MS data were recorded with a Bruker Daltonics Apex II30 spectrometer. X-ray crystal-structure data were collected with a Stoe–Siemens-AED diffractometer. Melting points were determined with a Büchi B545 melting point apparatus and are uncorrected. The $M_n$ and PDI values were determined with a Waters Breeze GPC with HR3 and HR4 columns. Toluene and THF were used as the standard and the solvent, respectively.

**General Procedure for Preparation of Norbornene Derivatives:** A mixture of the respective diyne (0.30 mmol), $[RuCp^*Cl_2]_2$ (15.0 μmol), *p*-xylene (3 mL), NBD (0.5 mL) and *i*PrOH (0.5 mL) in a screw-capped Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was heated at 130 °C for ca. 68 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure, and the residue was subjected to chromatography on silica gel (or alumina). Elution with hexane/$CH_2Cl_2$ afforded the coupling product.

**(5α,5aα,9aα,10α)-5,10-Diphenyl-5,5a,6,9,9a,10-hexahydro-6β,9β-methanonaphtho[3,2-*k*]pyracene (7a):** Yield: 99.5 mg (74%) from **12a** (105 mg, 0.30 mmol), as a yellow solid, m.p. 256 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.60 (d, $^2J$ = 8.8 Hz, 1 H, CHC$H_2$CH), 2.12 (d, $^2J$ = 8.8 Hz, 1 H, CHC$H_2$CH), 2.31 (d, $^3J$ = 7.4 Hz, 2 H, 5a-H and 9a-H), 2.73 (s, 2 H, 6-H and 9-H), 3.32 (s, 4 H, 1-H and 2-H), 3.76 (d, $^3J$ = 7.4 Hz, 2 H, 5-H and 10-H), 6.05 (s, 2 H, 7-H and 8-H), 6.08 (d, $^3J$ = 6.9 Hz, 2 H, Ar-H), 6.97 (d, $^3J$ = 6.9 Hz, 2 H, Ar-H), 7.43–7.51 (m, 10 H, Ar-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 32.0 (C-1 and C-2), 43.8 (CHC$H_2$CH), 46.3 (C-6 and C-9), 48.6 (C-5 and C-10), 50.6 (C-5a and C-9a), 119.9 (CH), 125.5 (CH), 126.8 (CH), 127.1 ($C_{quat}$), 128.3 (CH), 129.7 (CH), 133.7 ($C_{quat}$), 134.1 ($C_{quat}$), 137.4 (C-7 and C-8), 141.3 ($C_{quat}$), 144.7 ($C_{quat}$), 145.6 ($C_{quat}$) ppm. MS (70 eV): *m*/*z* (%) = 448 (84) $[M]^+$, 381 (100) $[M - C_5H_7]^+$, 305 (97), 292 (68), 276 (42), 226 (24), 152 (25), 91 (54), 77 (37) $[C_6H_5]^+$. HRMS (EI): calcd. for $C_{35}H_{28}$ 448.2191; found 448.2181.

**(5α,5aα,9aα,10α)-5,10-Bis(3,5-dimethylphenyl)-5,5a,6,9,9a,10-hexahydro-6β,9β-methanonaphtho[3,2-*k*]pyracene (7b):** Yield: 76.8 mg (62%) from **12b** (101 mg, 0.25 mmol), as a yellow solid, m.p. 262–263 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.58 (d, $^2J$ = 8.8 Hz, 1 H, CHC$H_2$CH), 2.08 (d, $^2J$ = 8.8 Hz, 1 H, CHC$H_2$CH), 2.26 (d, $^3J$ = 7.7 Hz, 2 H, 5a-H and 9a-H), 2.37 (s, 12 H, $CH_3$), 2.74 (s, 2 H, 6-H and 9-H), 3.33 (s, 4 H, 1-H and 2-H), 3.65 (d, $^3J$ = 8.8 Hz, 2 H, 5-H and 10-H), 6.06 (s, 2 H, 7-H and 8-H), 6.13 (d, $^3J$ = 7.1 Hz, 2 H, Ar-H), 6.99 (d, $^3J$ = 7.1 Hz, 2 H, Ar-H), 7.04 (s, 2 H, Ar-H), 7.11 (s, 4 H, Ar-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$

= 21.4 ($CH_3$), 32.0 (C-1 and C-2), 43.8 (CH*C*$H_2$CH), 46.4 (C-6 and C-9), 48.4 (C-5 and C-10), 50.4 (C-5a and C-9a), 119.9 (CH), 125.5 (CH), 127.6 (2 CH), 128.3 (CH), 133.9 ($C_{quat}$), 137.4 (C-7 and C-8), 137.5 (4 $C_{quat}$), 141.4 ($C_{quat}$), 144.7 ($C_{quat}$), 145.3 ($C_{quat}$) ppm. MS (70 eV): *m/z* (%) = 504 (90) $[M]^+$, 438 (100) $[M - C_5H_6]^+$, 423 (28), 333 (67), 320 (61), 119 (24), 91 (49), 79 (28). HRMS (EI): calcd. for $C_{39}H_{36}$ 504.2817; found 504.2820.

**(5α,5aα,9aα,10α)-5,10-Bis(4-tolyl)-5,5a,6,9,9a,10-hexahydro-6β,9β-methanoacenaphtho[3,2-*k*]pyracene (7c):** Yield: 42.0 mg (34%), from **12c** (100 mg, 0.26 mmol), as a yellow solid, m.p. 280–281 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.58 (d, $^2J$ = 8.8 Hz, 1 H, CHC$H_2$CH), 2.10 (d, $^2J$ = 8.8 Hz, 1 H, CHC$H_2$CH), 2.27 (d, $^3J$ = 7.8 Hz, 2 H, 5a-H and 9a-H), 2.49 (s, 6 H, $CH_3$), 2.73 (s, 2 H, 6-H and 9-H), 3.33 (s, 4 H, 1-H and 2-H), 3.71 (d, $^3J$ = 7.8 Hz, 2 H, 5-H and 10-H), 6.06 (s, 2 H, 7-H and 8-H), 6.14 (d, $^3J$ = 7.0 Hz, 2 H, Ar-H), 7.00 (d, $^3J$ = 7.0 Hz, 2 H, Ar-H), 7.27 (d, $^3J$ = 7.7 Hz, 4 H, Ar-H), 7.40 (d, $^3J$ = 7.7 Hz, 4 H, Ar-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 21.3 ($CH_3$), 32.0 (C-1 and C-2), 43.9 (CH*C*$H_2$CH), 46.3 (C-6 and C-9), 48.1 (C-5 and C-10), 50.6 (C-5a and C-9a), 119.9 (CH), 125.5 (CH), 127.3 ($C_{quat}$), 129.0 (2 CH), 129.2 ($C_{quat}$), 129.6 (2 CH), 133.8 ($C_{quat}$), 134.3 ($C_{quat}$), 136.2 ($C_{quat}$), 137.4 (C-7 and C-8), 141.5 ($C_{quat}$), 141.7 ($C_{quat}$), 145.4 ($C_{quat}$) ppm. MS (70 eV): *m/z* (%) = 476 (100) $[M]^+$, 410 (72) $[M - C_5H_6]^+$, 395 (20), 319 (39), 306 (42), 105 (20), 91 (20), 66 (35) $[C_5H_6]^+$. HRMS (EI): calcd. for $C_{37}H_{32}$ 476.2504; found 476.2503.

**(5α,5aα,9aα,10α)-5,10-Bis(4-fluorophenyl)-5,5a,6,9,9a,10-hexahydro-6β,9β-methanoacenaphtho[3,2-*k*]pyracene (7d):** Yield: 46.6 mg (38%) from **12d** (100 mg, 0.26 mmol), as a yellow solid, m.p. 278–279 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.60 (d, $^2J$ = 8.7 Hz, 1 H, CHC$H_2$CH), 2.07 (d, $^2J$ = 8.7 Hz, 1 H, CHC$H_2$CH), 2.22 (d, $^3J$ = 7.5 Hz, 2 H, 5a-H and 9a-H), 2.69 (s, 2 H, 6-H and 9-H), 3.34 (s, 4 H, 1-H and 2-H), 3.74 (d, $^3J$ = 7.5 Hz, 2 H, 5-H and 10-H), 6.05 (s, 2 H, 7-H and 8-H), 6.13 (d, $^3J$ = 7.0 Hz, 2 H, Ar-H), 7.00 (d, $^3J$ = 7.0 Hz, 2 H, Ar-H), 7.14 (d, $^3J$ = 8.5 Hz, 2 H, Ar-H), 7.16 (d, $^3J$ = 8.5 Hz, 2 H, Ar-H), 7.46 (dd, $^3J_{H,F}$ = 5.6, $^3J$ = 7.5 Hz, 4 H, Ar-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 32.1 (C-1 and C-2), 43.8 (CH*C*$H_2$CH), 46.2 (C-6 and C-9), 47.8 (C-5 and C-10), 50.9 (C-5a and C-9a), 115.1 (CH), 115.4 (CH), 120.0 (CH), 125.6 (CH), 127.3 ($C_{quat}$), 130.9 (CH), 131.0 (CH), 133.5 ($C_{quat}$), 134.4 ($C_{quat}$), 137.4 (C-7 and C-8), 140.4 ($C_{quat}$), 141.1 ($C_{quat}$), 145.9 ($C_{quat}$), 162.0 (d, $^1J_{C,F}$ = 245 Hz, Ar-C, $C_{quat}$) ppm. $^{19}$F NMR (282.4 MHz, $CDCl_3$): $\delta$ = –116.5 (s) ppm. MS (70 eV): *m/z* (%) = 484/485/486/487 (100/37/8/1) $[M]^+$, 418 (71) $[M - C_5H_6]^+$, 375 (16), 323 (46), 310 (50). HRMS (EI): calcd. for $C_{35}H_{26}F_2$ 484.2003; found 484.1995.

**(5α,5aα,9aα,10α)-5,10-Bis(3,4,5-trifluorophenyl)-5,5a,6,9,9a,10-hexahydro-6β,9β-methanoacenaphtho[3,2-*k*]pyracene (7e):** Yield: 64.9 mg (53%), from **12e** (102 mg, 0.22 mmol), as a yellow solid, m.p. 272–273 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.65 (d, $^2J$ = 8.9 Hz, 1 H, CHC$H_2$CH), 1.98 (d, $^2J$ = 8.8 Hz, 1 H, CHC$H_2$CH), 2.14 (d, $^3J$ = 7.4 Hz, 2 H, 5a-H and 9a-H), 2.68 (s, 2 H, 6-H and 9-H), 3.38 (s, 4 H, 1-H and 2-H), 3.66 (d, $^3J$ = 7.3 Hz, 2 H, 5-H and 10-H), 6.08 (s, 2 H, 7-H and 8-H), 6.28 (d, $^3J$ = 7.0 Hz, 2 H, Ar-H), 7.08–7.16 (m, 6 H, Ar-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 32.2 (C-1 and C-2), 43.8 (CH*C*$H_2$CH), 46.1 (C-6 and C-9), 48.0 (C-5 and C-10), 50.6 (C-5a and C-9a), 113.4 (dd, $^2J_{C,F}$ = 14.3, $^3J_{C,F}$ = 6.2 Hz, CH), 120.3 and 125.6 (C-3, C-4, C-11, and C-12), 127.1 (m, $C_{quat}$), 132.6 (m, $C_{quat}$), 134.6 (m, $C_{quat}$), 137.2 (C-7 and C-8), 139.7 (m, $C_{quat}$), 140.8 (m, $C_{quat}$), 151.1 (ddd, $^3J_{C,F}$ = 3.8, $^2J_{C,F}$ = 9.2, $^1J_{C,F}$ = 249 Hz, $C_{quat}$) ppm. One $C_{quat}$ cannot be observed due to signals overlap. $^{19}$F NMR (282.4 MHz, $CDCl_3$): $\delta$ = –134.2 (dd, *J* = 8.5, 19.8 Hz, 2 F), –162.6 (m, 1 F) ppm. MS (70 eV): *m/z* (%) = 556 (90) $[M]^+$, 489 (92), 411 (19), 372 (23), 359 (100), 346 (51), 330 (17). HRMS (EI): calcd. for $C_{35}H_{22}F_6$ 556.1626; found 556.1616.

**(7α,7aα,11aα,12α)-1,4-Dimethyl-7,12-diphenyl-7,7a,8,11,11a,12-hexahydro-8β,11β-methanobenzo[*e*]naphtho[3,2-*k*]pyracene (8a):** Yield: 84.9 mg (54%) from **16a** (129 mg, 0.30 mmol), as a yellow solid, m.p. 291–292 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.56 (d, $^2J$ = 9.1 Hz, 1 H, CHC$H_2$CH), 2.02 (d, $^2J$ = 9.1 Hz, 1 H, CHC$H_2$CH), 2.17 (d, $^3J$ = 7.4 Hz, 2 H, 7a-H and 11a-H), 2.26 (s, 6 H, $CH_3$), 2.66 (s, 2 H, 8-H and 11-H), 3.47 (d, $^3J$ = 8.0 Hz, 2 H, 7-H and 12-H), 5.40 (d, $^3J$ = 6.9 Hz, 2 H, Ar-H), 6.01 (s, 2 H, 9-H and 10-H), 6.62 (s, 2 H, 2-H and 3-H), 6.76 (d, $^3J$ = 6.9 Hz, 2 H, Ar-H), 7.36–7.44 (m, 10 H, Ar-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 19.4 ($CH_3$), 43.8 (CH*C*$H_2$CH), 46.3 (C-8 and C-11), 48.1 (C-7 and C-12), 50.6 (C-7a and C-11a), 123.2 (CH), 125.1 (CH), 126.9 (CH), 128.3 (2 CH), 129.6 (2 CH), 130.4 (CH), 130.9 ($C_{quat}$), 132.5 ($C_{quat}$), 132.6 ($C_{quat}$), 137.4 (C-9 and C-10), 138.7 ($C_{quat}$), 139.0 ($C_{quat}$), 140.6 ($C_{quat}$), 143.9 ($C_{quat}$), 144.2 ($C_{quat}$) ppm. MS (70 eV): *m/z* (%) = 524 (90) $[M]^+$, 458 (33) $[M - C_5H_6]^+$, 443 (58), 368 (36), 236 (46), 123 (36), 109 (48), 97 (78), 91 (82), 83 (100), 77 (40) $[C_7H_5]^+$. HRMS (EI): calcd. for $C_{41}H_{32}$ 524.2504; found 524.2501.

**(4α,4aα,8aα,9α)-4,9-Diphenyl-2,3,4,4a,5,8,8a,9-octahydro-1*H*-5β,8β-methanocyclopenta[*b*]naphthalene (9a):** Yield: 114 mg (82%) from **17a** (100 mg, 0.41 mmol), as a white solid, m.p. 110–111 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.50 (d, $^2J$ = 8.4 Hz, 1 H, CHC$H_2$CH), 1.68–1.76 (m, 2 H, 2-H), 1.84–1.94 (m, 5 H, 1-H and 3-H), 2.16–2.23 (m, 2 H, 4a-H and 8a-H), 2.60 (s, 2 H, 5-H and 8-H), 3.08 (br. s, 2 H, 4-H and 9-H), 5.97 (s, 2 H, 6-H and 7-H), 7.22–7.29 (m, 6 H, Ph-H), 7.32–7.39 (m, 4 H, Ph-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 22.3 (C-2), 34.7 (C-1 and C-3), 43.8 (CH*C*$H_2$CH), 46.8 (C-5 and C-8), 48.8 (C-4 and C-9), 49.4 (C-4a and C-8a), 126.0 (CH), 128.2 (2 CH), 128.7 (2 CH), 137.1 (C-6 and C-7), 139.3 and 145.3 (C-3a, C-9a, $C_{quat}$, and C-Ar) ppm. MS (70 eV): *m/z* (%) = 338 (8) $[M]^+$, 272 (100), 243 (22), 165 (26), 115 (24), 91 (48), 66 (43). HRMS (EI): calcd. for $C_{26}H_{26}$ 338.2035; found 338.2029.

**(4α,4aα,8aα,9α)-4,9-Bis(4-fluorophenyl)-2,3,4,4a,5,8,8a,9-octahydro-1*H*-5β,8β-methanocyclopenta[*b*]naphthalene (9d):** Yield: 33.7 mg (23%) from **17d** (113 mg, 0.40 mmol), as a white solid, m.p. 136–137 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.48 (d, $^2J$ = 8.5 Hz, 1 H, CHC$H_2$CH), 1.68–1.77 (m, 2 H, 2-H), 1.83–1.91 (m, 5 H, 1-H and 3-H), 2.12–2.18 (m, 2 H, 4a-H and 8a-H), 2.55 (s, 2 H, 5-H and 8-H), 3.04 (d, $^3J$ = 4.8 Hz, 2 H, 4-H and 9-H), 5.96 (s, 2 H, 6-H and 7-H), 7.02 [apparent t (dd), $^3J$ = 8.5, $^3J_{H,F}$ = 8.5 Hz, 4 H, Ar-H], 7.15–7.21 (m, 4 H, Ar-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 22.3 (C-2), 34.6 (C-1 and C-3), 43.8 (CH*C*$H_2$CH), 46.7 (C-5 and C-8), 48.0 (C-4 and C-9), 49.6 (C-4a and C-8a), 114.9 (d, $^2J_{C,F}$ = 21 Hz, CH), 130.0 (d, $^3J_{C,F}$ = 7.7 Hz, CH), 137.1 (C-6 and C-7), 139.3 ($C_{quat}$, C-3a, and C-9a), 140.79 ($C_{quat}$), 140.80 ($C_{quat}$), 161.4 (d, $^1J_{C,F}$ = 244 Hz, $C_{quat}$) ppm. $^{19}$F NMR (282.4 MHz, $CDCl_3$): $\delta$ = –117.7 (s) ppm. MS (70 eV): *m/z* (%) = 374 (9) $[M]^+$, 308 (100), 280 (17), 199 (20), 183 (15), 109 (32), 84 (66), 57 (16). HRMS (EI): calcd. for $C_{26}H_{24}F_2$ 374.1846; found 374.1835.

**(4α,4aα,8aα,9α)-4,9-Bis(3,4,5-trifluorophenyl)-2,3,4,4a,5,8,8a,9-octahydro-1*H*-5β,8β-methanocyclopenta[*b*]naphthalene (9e):** Yield: 66.0 mg (59%) from **17e** (88.0 mg, 0.25 mmol), as colorless crystals (from $CH_2Cl_2$/MeOH), m.p. 160–161 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.52 (d, $^2J$ = 8.8 Hz, 1 H, CHC$H_2$CH), 1.73–1.86 (m, 5 H, H1, 2-H, and 3-H), 1.88–1.92 (m, 2 H, 1-H and 3-H), 2.03–2.20 (m, 2 H, 4a-H and 8a-H), 2.53 (s, 2 H, 5-H and 8-H), 2.95

(br. s, 2 H, 4-H and 9-H), 5.98 (s, 2 H, 6-H and 7-H), 6.82 (dd, $^4J_{H,F}$ = 7.1, $^3J_{H,F}$ = 7.4 Hz, 4 H, Ar-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 22.2 (C-2), 34.4 (C-1 and C-3), 43.9 (CH*C*H$_2$CH), 46.6 (C-5 and C-8), 48.3 (C-4 and C-9), 49.2 (C-4a and C-8a), 112.4 (dd, $^3J_{C,F}$ = 5.9, $^2J_{C,F}$ = 14.1 Hz, CH), 137.0 (C-6 and C-7), 138.2 (dm, $^1J_{C,F}$ = 250 Hz, $C_{quat}$), 138.8 (9a, C-3a), 141.1 (m, $C_{quat}$), 151.1 (ddd, $^3J_{C,F}$ = 4.0, $^2J_{C,F}$ = 9.9, $^1J_{C,F}$ = 250 Hz, $C_{quat}$) ppm. $^{19}$F NMR (282.4 MHz, $CDCl_3$): $\delta$ = –134.9 (dd, $J$ = 11.3, 19.7 Hz, 2 F), –163.8 (m, 1 F) ppm. MS (70 eV): *m*/*z* (%) = 446 (14) $[M]^+$, 380 (53), 351 (11), 235 (23), 221 (16), 219 (18), 201 (15), 195 (13), 169 (16), 145 (27), 91 (17). HRMS (EI): calcd. for $C_{26}H_{20}F_6$ 446.1469; found 446.1472.

**(4α,4aα,8aα,9α)-4,9-Bis[4-(methoxycarbonyl)phenyl]-2,3,4,4a,5,8,8a,9-octahydro-1*H*-5β,8β-methanocyclopenta[*b*]naphthalene (9g):** Yield: 66.3 mg (52%) from **17g** (102 mg, 0.28 mmol), as a white solid, m.p. 158–159 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.50 (d, $^2J$ = 8.8 Hz, 1 H, CHC*H*$_2$CH), 1.68–1.75 (m, 2 H, 2-H), 1.84–1.90 (m, 5 H, 1-H and 3-H), 2.11–2.19 (m, 2 H, 4a-H and 8a-H), 2.54 (s, 2 H, 5-H and 8-H), 3.12 (d, $^3J$ = 4.6 Hz, 2 H, 4-H and 9-H), 3.92 (s, 6 H, $OCH_3$), 5.93 (s, 2 H, 6-H and 7-H), 7.29 (d, $^3J$ = 8.3 Hz, 4 H, Ar-H), 8.02 (d, $^3J$ = 8.3 Hz, 4 H, Ar-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 22.3 (C-2), 34.5 (C-1 and C-3), 43.9 (CH*C*H$_2$CH), 46.7 (C-5 and C-8), 48.8 (C-4 and C-9), 49.3 (C-4a and C-8a), 52.0 ($CO_2C$H$_3$), 128.2 ($C_{quat}$), 128.8 (2 CH), 129.7 (2 CH), 137.0 (C-6 and C-7), 138.9 and 150.6 ($C_{quat}$, C-3a, C-9a, and C-Ar), 167.2 ($C_{quat}$, *C*O$_2$CH$_3$) ppm. MS (70 eV): *m*/*z* (%) = 454 (7) $[M]^+$, 423 (6) $[M - OCH_3]^+$, 388 (100) $[M - C_5H_6]^+$, 329 (23), 305 (14), 239 (12), 105 (23). HRMS (EI): calcd. for $C_{30}H_{30}O_4$ 454.2144; found 454.2142.

**(4α,4aα,8aα,9α)-4,9-Bis(4-trifluoromethylphenyl)-2,3,4,4a,5,8,8a,9-octahydro-1*H*-5β,8β-methanocyclopenta[*b*]naphthalene (9h):** Yield: 53.1 mg (42%) from **17h** (101 mg, 0.27 mmol), as colorless crystals (from $CH_2Cl_2$/MeOH), m.p. 171–172 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.52 (d, $^2J$ = 8.8 Hz, 1 H, CHC*H*$_2$CH), 1.68–1.78 (m, 2 H, 2-H), 1.85–1.90 (m, 5 H, 1-H and 3-H), 2.11–2.18 (m, 2 H, 4a-H and 8a-H), 2.55 (s, 2 H, 5-H and 8-H), 3.13 (d, $^3J$ = 4.7 Hz, 2 H, 4-H and 9-H), 5.95 (s, 2 H, 6-H and 7-H), 7.34 (d, $^3J$ = 7.8 Hz, 4 H, Ar-H), 7.60 (d, $^3J$ = 7.8 Hz, 4 H, Ar-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 22.3 (C-2), 34.5 (C-1 and C-3), 43.9 (CH*C*H$_2$CH), 46.6 (C-5 and C-8), 48.7 (C-4 and C-9), 49.4 (C-4a and C-8a), 124.3 (q, $^1J_{C,F}$ = 272 Hz, $CF_3$), 125.2 (q, $^3J_{C,F}$ = 3.8 Hz, CH), 128.5 (q, $^2J_{C,F}$ = 32.3 Hz, $C_{quat}$), 129.1 (CH), 137.1 (C-6 and C-7), 139.0 (C-3a and C-9a), 149.2 ($C_{quat}$) ppm. $^{19}$F NMR (282.4 MHz, $CDCl_3$): $\delta$ = –62.3 (s) ppm. MS (70 eV): *m*/*z* (%) = 474 (1) $[M]^+$, 408 (21), 159 (15), 127 (12), 91 (16), 66 (100). HRMS (EI): calcd. for $C_{28}H_{24}F_6$ 474.1782; found 474.1792.

**(4α,4aα,8aα,9α)-4,9-Bis(4-anisyl)-2,3,4,4a,5,8,8a,9-octahydro-1*H*-5β,8β-methanocyclopenta[*b*]naphthalene (9k):** Yield: 67.0 mg (51%) from **17k** (100 mg, 0.33 mmol), as a white solid, m.p. 200–201 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.45 (d, $^2J$ = 8.4 Hz, 1 H, CHC*H*$_2$CH), 1.63–1.72 (m, 2 H, 2-H), 1.81–1.88 (m, 5 H, 1-H and 3-H), 2.11–2.17 (m, 2 H, 4a-H and 8a-H), 2.55 (s, 2 H, 5-H and 8-H), 2.99 (d, $^3J$ = 4.7 Hz, 2 H, 4-H and 9-H), 3.82 (s, 6 H, $OCH_3$), 5.95 (s, 2 H, 6-H and 7-H), 6.87 (d, $^3J$ = 8.5 Hz, 4 H, Ar-H), 7.13 (d, $^3J$ = 8.5 Hz, 4 H, Ar-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 22.3 (C-2), 34.7 (C-1 and C-3), 43.8 (CH*C*H$_2$CH), 46.8 (C-5 and C-8), 47.9 (C-4 and C-9), 49.6 (C-4a and C-8a), 55.2 ($OCH_3$), 113.5 (2 CH), 129.7 (2 CH), 137.1 (C-6 and C-7), 137.5 and 139.4 ($C_{quat}$, C-3a, C-9a, and C-Ar), 157.9 ($C_{quat}$) ppm. MS (70 eV): *m*/*z* (%) = 398 (26) $[M]^+$, 332 (96) $[M - C_5H_6]^+$, 224 (24), 211 (32), 166 (23), 121 (100), 91 (32), 84 (46), 81 (62), 71 (35). HRMS (EI): calcd. for $C_{28}H_{30}O_2$ 398.2246; found 398.2248.

**(4α,4aα,8aα,9α)-4,9-Bis(4-anisyl)-1,3,4,4a,5,8,8a,9-octahydro-5β,8β-methanonaphtho[2,3-*c*]furane (10k):** Yield: 32.6 mg (21%), from **18k** (117 mg, 0.38 mmol), as a white solid, m.p. 214–215 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.52 (d, $^2J$ = 8.8 Hz, 1 H, CHC*H*$_2$CH), 1.83 (d, $^2J$ = 8.8 Hz, 1 H, CHC*H*$_2$CH), 1.89 (d, $^2J$ = 6.6 Hz, 2 H, 4a-H and 8a-H), 2.61 (s, 2 H, 5-H and 8-H), 3.03 (d, $^3J$ = 6.6 Hz, 2 H, 4-H and 9-H), 3.83 (s, 6 H, $OCH_3$), 4.21–4.25 (m, 2 H, 1-H and 3-H), 4.46–4.50 (m, 2 H, 1-H and 3-H), 5.96 (s, 2 H, 6-H and 7-H), 6.87 (d, $^3J$ = 8.5 Hz, 4 H, Ar-H), 7.15 (d, $^3J$ = 8.5 Hz, 4 H, Ar-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 43.9 (CH*C*H$_2$CH), 45.3 (C-5 and C-8), 46.5 (C-4 and C-9), 49.9 (C-4a and C-8a), 55.2 ($OCH_3$), 77.9 (C-1 and C-3), 113.8 (2 CH), 129.3 (2 CH), 135.7 and 136.4 ($C_{quat}$, C-3a, C-9a, and C-Ar), 137.1 (C-6 and C-7), 158.3 ($C_{quat}$) ppm. MS (70 eV): *m*/*z* (%) = 400 (27) $[M]^+$, 334 (61) $[M - C_5H_6]^+$, 303 (29), 273 (29), 226 (22), 165 (30), 152 (29), 145 (25), 128 (21), 121 (100), 115 (40), 107 (31), 91 (45), 77 (32). HRMS (EI): calcd. for $C_{27}H_{28}O_3$ 400.2038; found 400.2039.

**(4α,4aα,8aα,9α)-2,2-Bis(methoxycarbonyl)-4,9-bis(3,4,5-trifluorophenyl)-1,3,4,4a,5,8,8a,9-octahydro-5β,8β-methanocyclopenta[*b*]naphthalene (11e):** Yield: 89.5 mg (62%) from **19e** (121 mg, 0.26 mmol), as a white solid, m.p. 203–205 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.56 (d, $^2J$ = 9.1 Hz, 1 H, CHC*H*$_2$CH), 1.71 (d, $^2J$ = 9.1 Hz, 1 H, CHC*H*$_2$CH), 1.77 (d, $^3J$ = 6.9 Hz, 2 H, 4a-H and 8a-H), 2.54 (s, 2 H, 5-H and 8-H), 2.57 (d, $^2J$ = 16.2 Hz, 2 H, 1-H and 3-H), 2.81 (d, $^2J$ = 16.2 Hz, 2 H, 1-H and 3-H), 2.95 (d, $^3J$ = 6.9 Hz, 2 H, 4-H and 9-H), 3.65 (s, 3 H, $CO_2CH_3$), 3.72 (s, 3 H, $CO_2CH_3$), 5.97 (s, 2 H, 6-H and 7-H), 6.80–6.85 (m, 4 H, Ar-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 42.0 (C-1 and C-3), 43.9 (CH*C*H$_2$CH), 46.5 (C-5 and C-8), 47.6 (C-4 and C-9), 49.1 (C-4a and C-8a), 52.8 ($CO_2C$H$_3$), 52.9 ($CO_2C$H$_3$), 58.0 (C-2), 112.5 (dd, $^2J_{C,F}$ = 14.4, $^3J_{C,F}$ = 6.3 Hz, CH), 136.1 (C-3a and C-9a), 136.9 (C-6 and C-7), 140.1 (m, $C_{quat}$), 151.2 (dm, $^1J_{C,F}$ = 254 Hz, $C_{quat}$), 172.0 (*C*O$_2$CH$_3$), 172.1 (*C*O$_2$CH$_3$) ppm. $^{19}$F NMR (282.4 MHz, $CDCl_3$): $\delta$ = –134.2 (dd, $J$ = 5.6, 19.7 Hz, 2 F), –163.2 (m, 1 F) ppm. MS (70 eV): *m*/*z* (%) = 562 (4) $[M]^+$, 436 (48), 377 (60), 375 (22), 362 (14), 318 (10), 245 (13), 219 (17), 167 (21), 149 (80), 145 (51), 66 (100), 57 (29). HRMS (EI): calcd. for $C_{30}H_{24}F_6O_4$ 562.1579; found 562.1573.

**4-[4,5-Dimethyl-2-(2-thiophenylethynyl)phenyl]-3-(2-thiophenyl)tricyclo[4.2.1.0$^{2,5}$]nona-3,7-diene (21):** Yield: 68.9 mg (56%) from 4,5-dimethyl-1,2-bis(2-thiophenylethynyl)benzene (100 mg, 0.31 mmol), as a white solid. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.36 (d, $^2J$ = 9.2 Hz, 1 H, 9-H), 1.70 (d, $^2J$ = 9.2 Hz, 1 H, 9-H), 2.28 (s, 3 H, $CH_3$), 2.29 (s, 3 H, $CH_3$), 2.67 (s, 2 H, 1-H and 6-H), 2.84 (s, 1 H, 2-H or 5-H), 3.11 (d, $^3J$ = 3.4 Hz, 1 H, 2-H or 5-H), 6.20–6.24 (m, 2 H, 7-H and 8-H), 6.94 (dd, $^3J$ = 4.9, 5.0 Hz, 1 H, Ar-H), 6.97–7.02 (m, 2 H, Ar-H), 7.16–7.22 (m, 3 H, Ar-H), 7.35 (s, 1 H, Ar-H), 7.47 (s, 1 H, Ar-H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 19.4 ($CH_3$), 19.7 ($CH_3$), 39.4 and 39.9 (C-2 and C-5), 40.3 (C-9), 44.0 and 46.1 (C-1 and C-6), 85.7 and 93.7 (C≡C), 118.2 ($C_{quat}$), 123.6 ($C_{quat}$), 124.8 (CH), 125.4 (CH), 126.7 (CH), 126.9 (CH), 127.1 (CH), 129.0 (CH), 131.1 (CH), 133.7 (CH), 134.8 ($C_{quat}$), 135.8 (CH), 136.1 ($C_{quat}$), 136.2 (CH), 137.2 ($C_{quat}$), 138.2 ($C_{quat}$), 138.7 ($C_{quat}$) ppm. One $C_{quat}$ could not be observed due to signal overlap. MS (70 eV): *m*/*z* (%) = 410 (100) $[M]^+$, 395 (32) $[M - CH_3]^+$, 362 (16), 344 (24) $[M - C_5H_6]^+$, 329 (18), 318 (23), 311 (24), 295 (15), 135 (15), 108 (19), 97 (26). HRMS (EI): calcd. for $C_{27}H_{22}S_2$ 410.1163; found 410.1177. Note that **21** decomposes to 4,5-dimethyl-1,2-bis(2-thiophenylethynyl)benzene upon incubation at room temperature for a few weeks.

**Ring-Opening Metathesis Polymerization of 9h:** A solution of norbornene **9h** (71.0 mg, 0.15 mmol) in $CH_2Cl_2$ (4 mL) was treated

with the Grubbs' catalyst **30** (25.0 mg, 20.0 μmol), and the reaction mixture was heated at 40 °C under nitrogen for 30 min. Ethyl vinyl ether (0.5 mL) was added to the solution, and the mixture was stirred at the same temperature for 15 min. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was washed with MeOH to afford polynorbornene **31** (62.0 mg, 87%) as an off-white solid.

**Supporting Information** (see footnote on the first page of this article): Procedures for the preparation of the diynes and their analytic data.

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[22] ***Caution:*** The reaction of catalyst $[RuCl_2Cp^*]_2$ with neat dipropargyl ether under aerobic conditions could cause ignition.

[23] Crystals of **9e** and **9h** were grown from $CH_2Cl_2$/MeOH. Compound **9e**: $C_{28}H_{24}F_6$, triclinic crystals of space group *P*1, unit-cell dimensions: $a$ = 9.0375(10), $b$ = 10.8019(12), $c$ = 12.8635(14) Å, $\alpha$ = 74.999(2), $\beta$ = 72.041(2), $\gamma$ = 72.324(2)°, $V$ = 1119.1(2) Å$^3$, $Z$ = 2, crystal size: 0.45 × 0.45 × 0.15 mm. Compound **9h**: $C_{26}H_{20}F_6$, triclinic crystals of space group *P*1, unit-cell dimensions: $a$ = 6.8236(3), $b$ = 7.4049(3), $c$ = 36.375(6) Å, $\alpha$ = 102.834(3), $\beta$ = 107.013(3), $\gamma$ = 91.727(3)°, $V$ = 504.71(4) Å$^3$, $Z$ = 1, crystal size: 0.12 × 0.10 × 0.10 mm. CCDC-746967 (for **9e**) and -746968 (for **9h**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[24] It was reported that in the presence of ethanol and NBD, the $[RuCl_2Cp^*]_2$ complex can be easily reduced to form the active catalyst [RuCl($\eta^4$-NBD)Cp*]; see ref.[13]

[25] The *exo* stereoselectivity for [2+2] cycloadditions of NBD with alkynes has also been obtained previously; for details, see ref.[8]

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