Highly Regioselective Cyclotrimerization of 1-Perfluoroalkylenynes Catalyzed by Nickel

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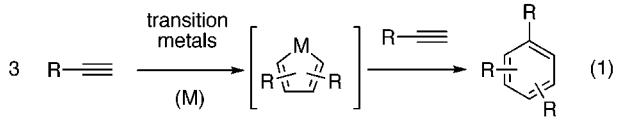
Received August 27, 2000

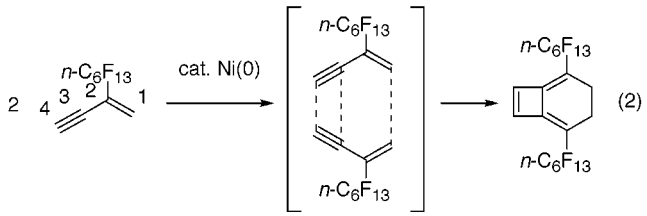
We report the highly regioselective cyclotrimerization of the 1-perfluoroalkylenynes in the presence of $Ni(PPh_3)_4$. The substituent effects on the reactivity of the enynes were investigated. We also succeeded in the nickel-catalyzed cocyclization of the 1-perfluoroalkylenynes with (trimethylsilyl)-acetylene. The possible structures of the intermediates of the cyclotrimerization and the reasons for the observed high regioselectivity were discussed.

Unsaturated hydrocarbons undergo various reactions in the presence of transition metal catalysts, and a large number of useful reactions has been developed.[1] Among them, the transition metal-catalyzed cyclotrimerization of alkynes is a well-known reaction (eq 1).[2] The previous studies have revealed that the high regioselectivity of the reaction was achieved mainly in the (partially) intramolecular reactions, and it is difficult to achieve high regioselectivity in the intermolecular reactions.

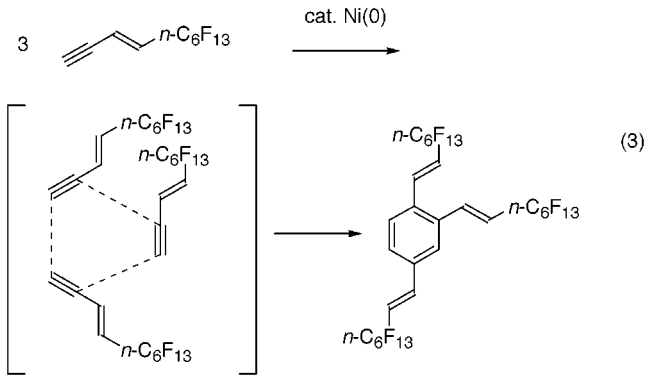


(1)

Recently, we reported the nickel-catalyzed zipper annulation of 2-substituted enynes and realized the unique reactivity of the electron-deficient enynes such as 2-perfluoroalkylenynes in the presence of nickel catalysts (eq 2).[3] To examine the effect of the substitution pattern on the reactivity of enynes, we carried out the reaction of 1-perfluoroalkylenynes in the presence of nickel catalysts and observed the formation of cyclotrimerized products. In this paper we report the highly regioselective cyclotrimerization of the 1-perfluoroalkylenynes in the presence of $Ni(PPh_3)_4$ (eq 3).



(2)



(3)

Results

Preparation of Fluorinated Enynes. The fluorinated enynes were prepared according to the procedures shown in Schemes 1−3. Thus, monosubstituted perfluoroalkylenyne **1a** and disubstituted perfluoroalkylenyne **1d** were prepared by the copper-mediated perfluorohexylation[4] of (*E*)-1,2-diiodoethylene **8**[5] followed by the Sonogashira coupling of the product **9** with alkynes (Scheme 1). Other disubstituted enynes (**1b**,**c**) were prepared from the iodoperfluoroolefins **12**, which were prepared by the transition metal-catalyzed addition of 1-iodoperfluorohexane to alkynes (Scheme 2).[6] The procedure described by Yamanaka et al.[7] was generally followed to prepare the 1-iodoperfluoroalkylolefin **16**, which was converted

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(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) Reviews: (a) Grothahn, D. B. Transition Metal Alkyne Complexes: Transition Metal-Catalyzed Cyclotrimerization. In *Comprehensive Organometallic Chemistry II*; Abel, E. W.; Stone, F. G. A.; Wilkinson, G., Eds., Hegedus, L. S., vol. Ed.; Pergamon: Oxford, 1995; Vol. 12, pp 741−770. (b) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49−92. (c) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081−1119. (d) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23(8)*, 539−644. (e) Maitlis, P. M. *J. Organomet. Chem.* **1980**, *200*, 161−176. (f) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93−99. (g) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901−2916. For recent related examples, see (h) Ozerov, O. V.; Ladipo, F. T.; Patrick, B. O. *J. Am. Chem. Soc.* **1999**, *121*, 7941−7942. (i) Sato, Y.; Ohshi, K.; Mori, M. *Tetrahedron Lett.* **1999**, *40*, 5231−5234.

(3) Saito, S.; Tanaka, T.; Koizumi, T.; Tsuboya, N.; Itagaki, H.; Kawasaki, T.; Endo, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 1810−1811.

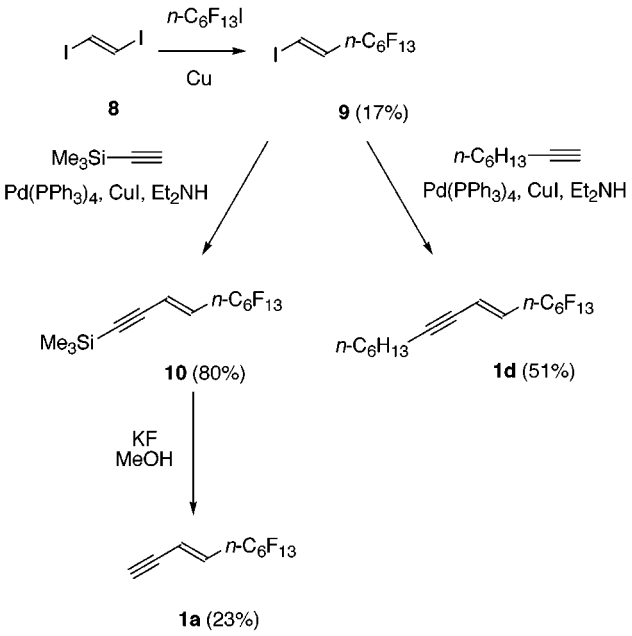
(4) Coe, P. L.; Milner, N. E.; Smith, J. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 654−656.

(5) Wright, M. E.; Lowe-Ma, C. K. *Organometallics* **1990**, *9*, 347−352.

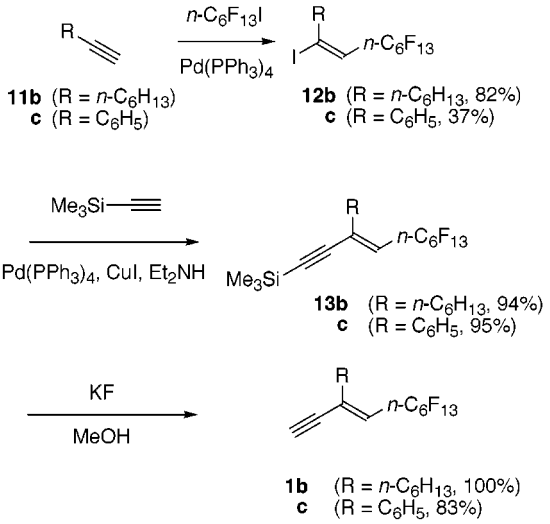
(6) Ishihara, T.; Kuroboshi, M.; Okada, Y. *Chem. Lett.* **1986**, 1895−1896.

10.1021/jo0056242 CCC: $20.00 © 2001 American Chemical Society
Published on Web 01/10/2001

Scheme 1



Scheme 2

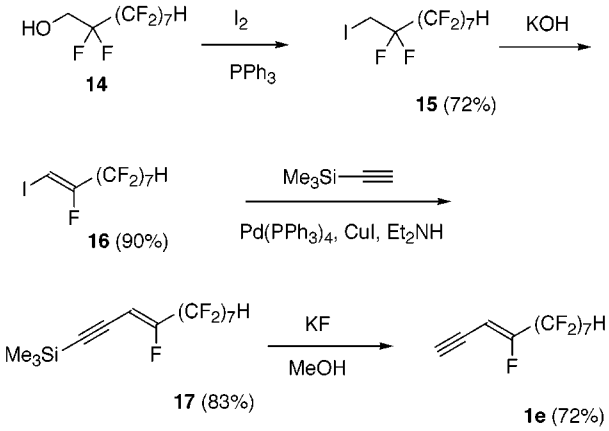


to 1-fluoro-1-perfluoroalkylenyne **17** by the Sonogashira coupling, followed by the deprotection of the trimethylsilyl group (Scheme 3). The fluoroenynes **1a**−**e** were subjected to the nickel-catalyzed reaction.

Ni(0)-Catalyzed Cyclotrimerization of Perfluorohexylenynes. (*E*)-1-Perfluorohexyl-1-butene-3-yne (**1a**) cyclotrimerized in the presence of a catalytic amount (10 mol %) of $Ni(PPh_3)_4$, which was prepared in situ from $Ni(cod)_2$ and PPh_3, to give the 1,2,4-trisubstituted benzene (**2a**) in good yield (Table 1, entry 1). The reaction proceeded in a highly regioselective manner, and only a trace amount of the isomeric 1,3,5-trisubstututed benzene (**3a**) was detected in the reaction mixture. The formation of a zipper annulation product (eq 2)[3] was not observed. We also carried out the reaction of disubstituted enynes such as **1b**−**d**, and the reaction of these enynes also proceeded (Table 1, entries 2−4). Thus, (*E*)-2-hexyl-1-perfluorohexyl-1-buten-3-yne (**1b**) cyclotrimerized to give

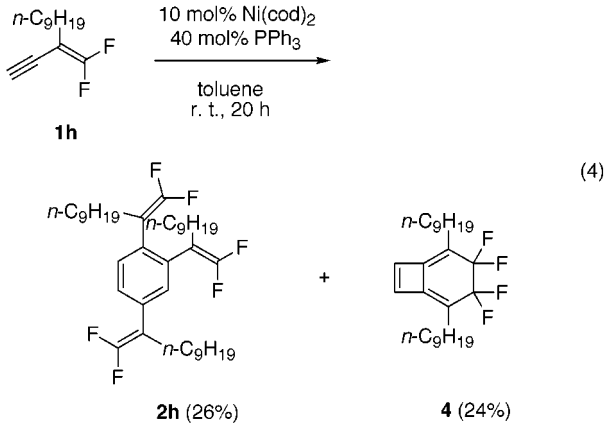
(7) Yamanaka, H.; Araki, T.; Kuwabara, M.; Fukunishi, K.; Nomura, M. *Nihon Kagaku Kaishi* **1986**, *10*, 1321−1328.

Scheme 3



2b, and (*E*)-2-phenyl-1-perfluorohexyl-1-buten-3-yne (**1c**) cyclotrimerized to give **2c**. Though the cyclotrimerization of a 2,4-disubstituted enyne (**1d**) proceeded in a highly regioselective manner, the reactivity of **1d** was low, and the reaction was carried out at 50 °C for 28.5 h (entry 4). The formation of isomeric benzenes was not observed in the reactions of **1b**−**d**.

To examine the effect of fluorine atom on the reactivity of conjugated enynes, we carried out the reaction of a 1-fluoroenyne and observed the regioselective formation of 1,2,4-trisubstituted benzenes. Thus, 1-fluoro-1-tetradecafluoropentyl-1-butene-3-yne (**1e**) cyclotrimerized in the presence of $Ni(PPh_3)_4$ to give 1,2,4-trisubstituted benzene **2e** in 78% yield (entry 5). Compared to the reaction of **1a**, the rate of this reaction was slower. The result is in contrast to the result of the reaction of 1,1-difluoroenyne **1h**: in the reaction of **1h**, the formation of a zipper annulation product **4**, together with the cyclotrimerized product **2h**, was observed (eq 4).[3]

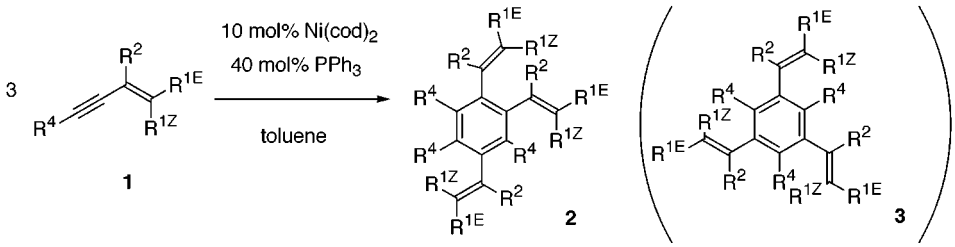


(4)

To examine the effect of other electron-withdrawing groups on the reactivity of enynes, we carried out the reaction of a cyanoenyne **1f**. The corresponding 1,2,4-trisubstituted benzene was isolated in a regioselective manner (entry 6). On the other hand, the formation of a significant amount of the 1,3,5-trisubstituted benzene **3**, together with the 1,2,4-trisubstituted benzene **2g**, was observed in the reaction of a methoxycarbonylenyne **1g** (entry 7). It is noteworthy that the [4 + 2] cycloaddition (benzannulation) of **1f** proceeded in the presence of $Pd(PPh_3)_4$.[8]

Ni(0)-Catalyzed Cocyclotrimerization of (*E*)-2-Hexyl-1-perfluorohexyl-1-buten-3-yne (1b) with

Table 1. Ni(0)-Catalyzed Regioselective Cyclotrimerization of Fluoroenynes

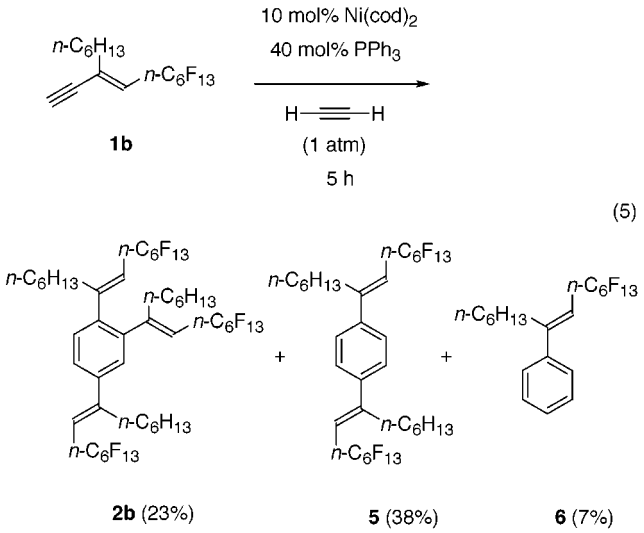


	enyne					reaction conditions			
entry		R^{1E}	R^{1Z}	R^2	R^4	temp (°C)	time (h)	product	yield (%)
1	**1a**	n-C_6F_{13}	H	H	H	rt	0.25	**2a**	65[a]
2	**1b**	n-C_6F_{13}	H	n-C_6H_{13}	H	rt	2	**2b**	88
3	**1c**	n-C_6F_{13}	H	Ph	H	rt	0.25	**2c**	67
4	**1d**	n-C_6F_{13}	H	H	n-C_6H_{13}	50	28.5	**2d**	47
5	**1e**	$(CF_2)_7H$	F	H	H	rt	5.5	**2e**	78
6	**1f**	CN	H	n-C_5H_{11}	H	rt	3.5	**2f**	79
7	**1g**	COOMe	H	H	n-C_6H_{13}	80	30	**2g**	60 (16)[b]

[a] A trace amount of isomeric 1,3,5-trisubstituted benzene **3a** was isolated. [b] Yield of the isomeric 1,3,5-trisubstituted benzene **3g**.

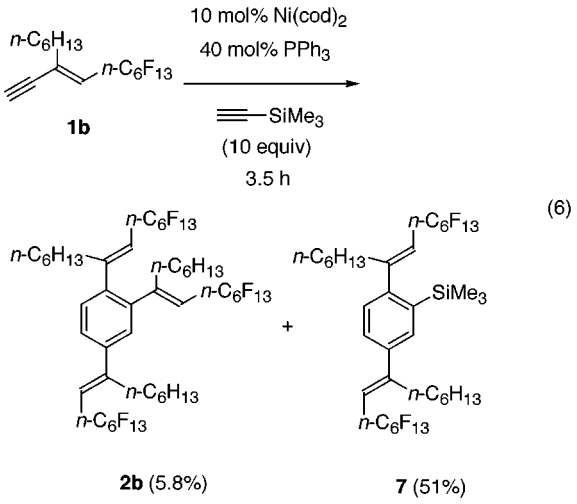
Alkynes. It is generally accepted that the cyclotrimerization proceeds via the matallacyclopentadiene intermediate, which was formed by the addition of two alkyne molecules to the metal complex.[2] The insertion (addition) of the third alkyne moiety occurs, and substituted benzene would be formed as the final product (eq 1). Since the regioselective formation of the trisubstituted benzenes was observed in the reactions we carried out, the metallacyclopentadiene intermediate would be formed regioselectively. However, the regiochemistry of the matallacyclopentadiene in this reaction was not clear. To determine the structure of the intermediate, which would be closely related to the intermediate of the zipper annulation reaction,[3] we carried out the cocyclotrimerization of (*E*)-2-hexyl-1-perfluorohexyl-1-buten-3-yne (**1b**) with alkynes.

We chose enyne **1b**, which is a moderately reactive enyne, as a substrate, and carried out the cocyclotrimerization in the presence of acetylene.[1i] Enyne **1b** cocyclotrimerized with acetylene (1 atm) in the presence of Ni catalyst, and the formation of a mixture of **2b**, **5** and **6** was observed (eq 5). Compound **5** was formed by the 2:1 cocyclotrimerization of **1b** with acetylene, while **6** was formed by the 1:2 cocyclotrimerization of **1b** with acetylene.



(5)

To isolate the cocyclodimerized product in a more selective manner, we used a less reactive alkyne as a substrate for the reaction. Compound **1b** (1 equiv) and (trimethylsilyl)acetylene (10 equiv) reacted in the presence of $Ni(PPh_3)_4$ (0.1 equiv) for 3.5 h and the formation of a cocyclotrimer **7** was observed (eq 6). It is noteworthy that **7** was the only cocyclotrimerized compound we isolated and other benzene derivatives were not isolated. Compound **7** was formed by the 2:1 cocyclotrimerization of **1b** with (trimethylsilyl)acetylene.



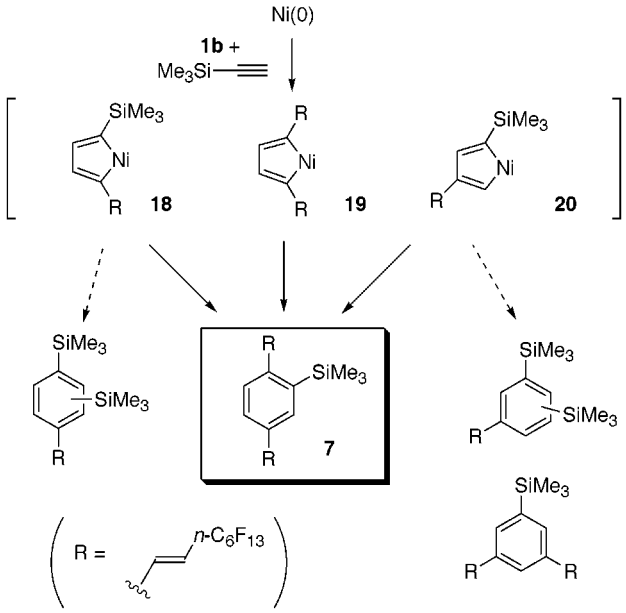
(6)

Discussions

It is difficult to achieve high regioselectivity in the intermolecular cyclotrimerization of alkynes, and successful examples have been reported in a limited number of reactions.[2] The Ni(0)-catalyzed cyclotrimerization of alkylenynes has been reported, and the formation of the cyclotrimerized compounds was observed, though the reaction was carried out at elevated temperatures (50−100 °C) and the isolated yields of cyclotrimerized products were low.[8] Our study revealed that the reaction of 1-perfluoroalkylenynes proceeded in highly regioselective manner, and the benzene derivatives are isolated in good

(8) Meriwether, L. S.; Colthup, G. W.; Kennerly, G. W.; Reusch, R. N. *J. Org. Chem.* **1961**, *26*, 5155−5163.

Scheme 4

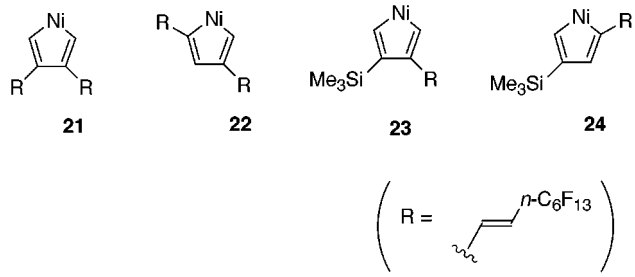


yields. The high reactivity of the conjugated enynes was also observed, and this result is in accordance with our postulation that the reactivity of the electron-deficient hydrocarbons is significantly enhanced in the Pd(0)- or Ni(0)-catalyzed reactions.[3,9]

Compared to the reaction of monosubstituted enyne **1a**, the reaction of disubstituted enyne **1b** proceeded more sluggishly (Table 1, entry 2). We assume that the reactivity of **1b** was reduced because an electron-donating group (alkyl group) was introduced to the enyne. Alternatively, the introduction of another substituent might have caused a steric repulsion between the catalyst and the substrate, which might have resulted in the lower rate of the reaction. On the other hand, when we introduced a phenyl group, which is a weak electron-withdrawing group, to the enyne, the electronic effect and the steric effect seem to be canceled out. As a result, the rate of reaction of phenylenyne **1c** was comparable to that of the monosubstituted enyne **1a**. The reactivity of **1d** was much lower compared to those of **1a**,**b**, probably because the substituent was directly attached to the "reactive" triple bond: the substituent would cause a stronger steric repulsion during the reaction (entry 4). It would also be possible to explain the low reactivity of **1g** in terms of the strong steric effect (entry 7). Generally, the reactivity of the perfluoroalkyl enynes seems to be higher than that of other electron-deficient enynes in this reaction (entry 3 vs 6, and entry 4 vs 7). The introduction of a fluorine atom resulted in the reduced reactivity of the enyne, probably because of the strong electron-donating ability of the fluorine atom through the resonance effect (entry 5).[10,11]

The high regioselectivity observed in the cyclotrimerization indicates that the intermediates were formed in highly regioselective manners. On the basis of the generally accepted mechanism of the cyclotrimerization reaction,[2] it is possible to attribute the high regioselectivity to the highly regioselective formation of the nickelacyclopentadienes. Considering the result of the reaction of **1b** with (trimethylsilyl)acetylene, the structure of the intermediate will be limited (Scheme 4). Several intermediates would be postulated as the intermediates of this reaction, though three of them could produce the cocyclodimerized product **7** which was isolated in the reaction. Metallacycles such as **21** and **22** would not give **7**, and the formation of **23** or **24** is unlikely because it is well-known that the Me_3Si group generally occupy the α-position of the metallacycles (Chart 1).[2d] Though we could not completely exclude the possibility of the formation of **18** or **20** as the intermediate of this reaction, we assume that **19** is the intermediate in this reaction since no 2:1 cocyclotrimerization of **1b** with (trimethylsilyl)acetylene was observed in this reaction: if **18** or **20** was formed in the reaction, the 2:1 cocyclotrimerization of **1b** with (trimethylsilyl)acetylene should occur (Scheme 4).[12,13] Thus, the structure of the intermediate would be **19**. The result of this reaction provided an indirect evidence for the structure of the metallacycle in the cyclotrimerization of **1b** and the zipper annulation of **1h** and 2-perfluorohexyl-1-butenyne.[3]

Chart 1



Though we expected that a bicyclic compound (zipper annulation product) similar to **4** would be isolated in the reactions of **1**, we did not detect the bicyclic compound in the reactions. We assume that the large steric hindrance between the 1-perfluoroalkyl group and the ligand (PPh_3) inhibited the reductive elimination of the Ni species from the nickelacycle (Scheme 5).[14,15]

The low regioselectivity was observed in the cyclotrimerization of a methoxycarbonylenyne **1g** (entry 7). We assume that the formation of the 1,3,5-trisubstituted benzene was induced by the relatively strong resonance effect of the methoxycarbonyl group.[16] Thus, the electronic structure of the triple bond of **1g** is different from other enynes because of the relatively strong resonance effect,[9,17] and the formation of the isomeric nickelacycle occurred. The nickelacycle similar to **27** would be formed

(9) (a) Saito, S.; Tsuboya, N.; Chounan, Y.; Nogami, T.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 7529−7532. (b) Saito, S.; Chounan, Y.; Nogami, T.; Fukushi, T.; Tsuboya, N.; Yamada, Y.; Kitahara, H.; Yamamoto, Y. *J. Org. Chem.* **2000**, *64*, 5350−5354.

(10) Field value (F) = 0.45, resonance value (R) = −0.39. The values shown in this paper were collected from ref 11.

(11) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

(12) This type of the reaction was observed in the cocyclotrimerization of **1b** with acetylene, which is a less sterically demanding alkyne (eq 5).

(13) Favorable electronic interaction would also be expected in the reaction of electron-deficient nickelacycle **19** with (trimethylsilyl)-acetylene.

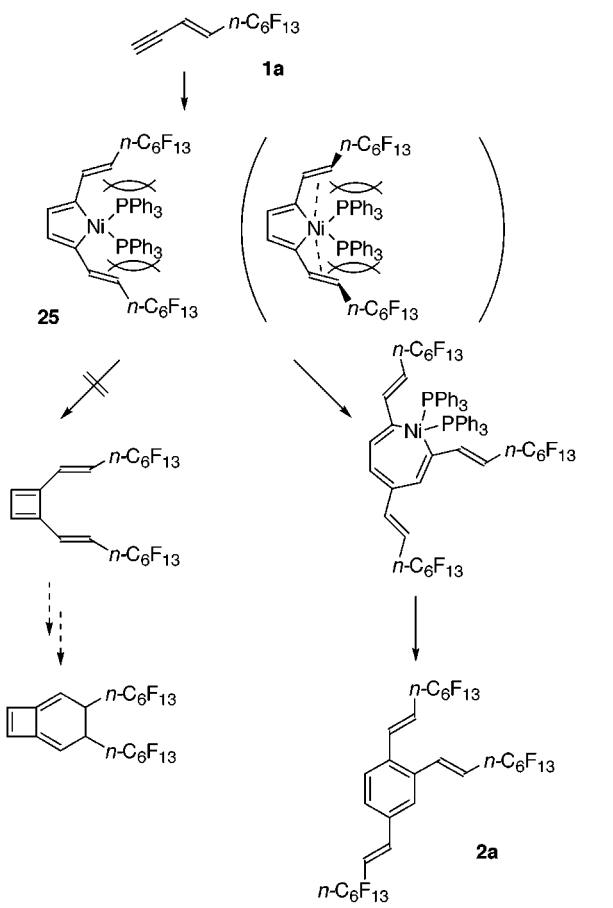
(14) In fact, we did not isolate the zipper annlation product in the Ni(0)-catalyzed reactions of various 1-substituted enynes except for **1h**.

(15) Alternatively, the result might be explained in terms of the smaller electronic effects of the substitutents attached to the C-1 position on the reactive triple bond.

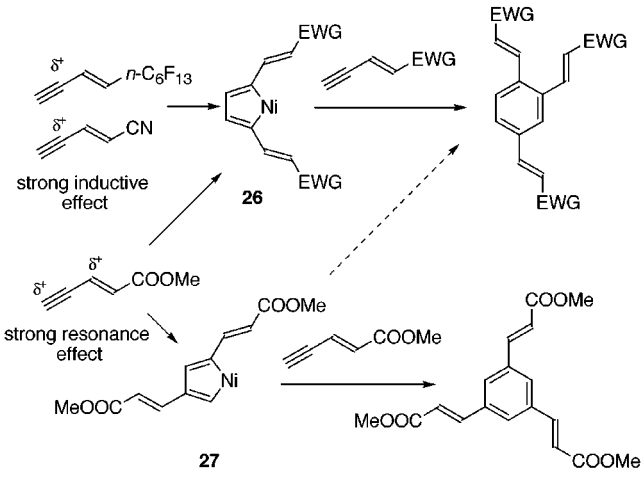
(16) Field value (F) = 0.34, resonance value (R) = 0.11.

(17) F = 0.42, R = 0.06 (values of $CF_2CF_2CF_3$). F = 0.51, R = 0.15 (values of CN).

Scheme 5



Scheme 6



in the reaction of **1g**, and the isomeric 1,3,5-trisubstituted benzene **3g** would be isolated (Scheme 6).[18]

Conclusions

We have shown that the Ni(0)-catalyzed cyclotrimerization of 1-perfluoroalkylenynes proceeded under mild conditions, and the 1,2,4-trisubstituted benzenes were isolated in high regioselectivity. We also carried out the cocyclization of an enyne with alkynes and isolated the cocyclotrimerized products. The high regioselectivity observed in these reactions was explained in terms of the highly regioselective formation of the nickelacycles.

Experimental Section

Compounds **1f**[9] and **1g**[19] were prepared according to the literature.

1-Iodo-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-(1*E*)-ethylene (9). The general procedure[4] was followed to prepare **9**. A mixture of perfluorohexyl iodide (29.0 g, 65 mmol), copper powder (9.7 g, 153 mmol), and (*E*)-1,2-diiodoethylene **8**[5] (30.8 g, 110 mmol) in DMF (45 mL) was heated at 120 °C for 71 h under an argon atmosphere. The cooled mixture was poured into ether, and the precipitate was removed by filtration. The filterate was washed with water, 10% aq Na_2SO_3 and brine. The organic layer was dried over $MgSO_4$ and evaporated. The mixture was cooled in a refrigerator, and the unreacted **8**, which crystallized out, was removed by filteration. The mixture was further purified by distillation (70 °C/33 mmHg) to give **9** (5.2 g, 17%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) 7.43−7.37 (m, 1H), 6.76−6.63 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 131.9 (dd, J_{C-F} = 24.0, 24.0 Hz), 123.5−104.3 (m), 91.1 (dd, J_{C-F} = 11.5, 11.5 Hz); IR (neat) 3080, 1614, 1366, 1292, 1240, 1202, 1146, 1121, 1067 cm^{-1}; HRMS Calcd for $C_8H_2F_{13}I$: 471.8992. Found: 471.8969. Anal. Calcd for $C_8H_2F_{13}I$: C, 20.36; H, 0.43. Found: C, 20.65; H, 0.60.

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluoro-1-trimethylsilyl-(3*E*)-buten-1-yne (10). To a mixture of $Pd(PPh_3)_4$ (60 mg, 0.052 mmol) and CuI (20 mg, 0.105 mol) was added a mixture of Et_2NH (4.8 mL, dried with KOH) and **9** (1.89 g, 4.0 mmol) under an argon atmosphere at room temperature. The temperature was raised to 40 °C, (trimethylsilyl)acetylene was added slowly, and the mixture was stirred for 20 min. The mixture was cooled, poured into iced water, and extracted with pentane. The combined organic layer was washed with 2 N aq HCl, dried over $MgSO_4$, and evaporated carefully to give a yellow oil. The oil was further purified by silica gel column chromatography (hexane) to give **10** (1.41 g, 80%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) 6.31−6.24 (m, 1H), 6.16−6.02 (m, 1H), 0.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 127.2 (dd, J_{C-F} = 22.7, 22.7 Hz), 123.4−104.2 (m) 120.9 (dd, J_{C-F} = 11.2, 11.2 Hz), 103.6, 99.3, −0.5; IR (neat) 2966, 2905, 2164, 1638, 1412, 1240, 1202, 1146, 1128, 1078, 1051 cm^{-1}; HRMS Calcd for $C_{13}H_{11}F_{13}Si$: 442.0421. Found: 442.0411. Anal. Calcd for $C_{13}H_{11}F_{13}Si$: C, 35.30; H, 2.51. Found: C, 35.48; H, 2.63.

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluoro-(3*E*)-buten-1-yne (1a). To a mixture of KF (0.45 g, 7.8 mmol) in MeOH (19 mL) was slowly added **10** (2.3 g, 5.2 mmol) at 0 °C under an argon atmosphere, and the mixture was kept stirring for 30 min. Water was added, and the mixture was extracted with pentane. The organic layer was washed with brine and dried over $MgSO_4$. Pentane was removed at normal pressure, and the residue was further purified by distillation to give **1a** (0.45 g, 23%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) 6.31−6.11 (m, 2H), 3.26 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) 128.7 (dd, J_{C-F} = 22.6, 22.6 Hz), 123.5−104.2 (m), 84.7 (m), 78.4; IR (neat) 3317, 1641, 1364, 1240, 1202, 1146, 1124, 1069 cm^{-1}; HRMS Calcd for $C_{10}H_3F_{13}$: 370.0027. Found: 370.0009. Anal. Calcd for $C_{10}H_3F_{13}$: C, 32.45; H, 0.82. Found: C, 32.29; H, 1.11.

1,1,2,2,3,3,4,4,5,5,6,6,6-Tridecafluoro-(7*E*)-hexadecen-9-yne (1d). To the mixture of $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) and CuI (5 mg, 0.026 mmol) was added a mixture of Et_2NH (1.2 mL, dried over KOH) and **10** (0.47 g, 1 mmol) under an argon atmosphere at 40 °C. Trimethylsilylacethlene was added slowly, and the mixture was stirred for 3 h. The mixture was cooled, poured into iced water, and extracted with pentane. The organic layer was washed with 2 N aq HCl, dried over $MgSO_4$, and evaporated to give an orange oil. The oil was further purified by silica gel column chromatography (hexane) to give **1d** (0.24 g, 51%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) 6.30−6.23 (m, 1H), 6.03−5.90 (m, 1H), 2.33 (dd, J = 6.5, 6.5 Hz, 2H), 1.56−1.49 (m, 2H), 1.38−1.23 (m, 6H), 0.88

(18) The increased steric effects could be another possible explanation for the observed low regioselectivity in the reaction of **1g**. We thank the referee for pointing out this possibility.

(19) Krause, N. *Chem. Ber.* **1990**, *123*, 2173−2180.

(dd, J = 6.8, 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 125.2 (dd, J_{C-F} = 22.4, 22.4 Hz), 121.7 (dd, J_{C-F} = 11.2, 11.2 Hz), 123.1−104.8 (m), 99.3, 76.2, 31.4, 28.6, 28.3, 22.6, 19.5, 13.9; IR (neat) 2963, 2936, 2864, 2224, 1639, 1472, 1458, 1364, 1240, 1202, 1146, 1121, 1065 cm^{-1}; HRMS Calcd for $C_{16}H_{15}F_{13}$: 454.0965. Found: 454.0982.

8-Iodo-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-(7*E*)-tetradecene (12b). The general procedure reported in a reference[6] was followed to prepare **12b**: yield 82%; colorless oil, bp 91 °C (1.9 mmHg).

1-Iodo-2-phenyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-(1*E*)-octene (12c). The general procedure reported in the reference[6] was followed to prepare **12c** (yield 37%) as a lemon yellow oil: bp 97 °C (1.9 mmHg); ^{1}H NMR (300 MHz, $CDCl_3$) 7.37−7.25 (m, 5H), 6.57 (dd, J = 13.5, 13.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 141.4, 129.3, 128.0, 127.0 (dd, J_{C-F} = 22.4, 22.4 Hz), 126.9, 124.1−105.7 (m), 112.8 (dd,J_{C-F} = 6.2, 6.2 Hz); IR (KBr) 1643, 1491, 1445, 1400, 1366, 1342, 1256, 1217, 1196, 1140, 1117, 1065, 1030 cm^{-1}. Anal. Calcd for $C_{14}H_6F_{13}I$: C, 30.68; H, 1.10. Found: C, 30.98; H, 1.34.

3-Hexyl-1-trimethylsilyl-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-(3*E*)-buten-1-yne (13b). To a mixture of Pd(PPh$_3$)$_4$ (105 mg, 0.091 mmol) and CuI (35 mg, 0.18 mmol) was added a mixture of Et_2NH (8.4 mL, dried over KOH) and **12b** (3.9 g, 7 mmol) under an argon atmosphere at 40 °C. Then trimethylsilylacethlene was added dropwise, and the mixture was stirred for 70 min. The mixture was cooled, poured into iced water, and extracted with hexane. The organic layer was washed with 2 N aq HCl, dried over $MgSO_4$, and evaporated to give an orange oil. The oil was further purified by silica gel column chromatography (hexane) to give **13b** (3.46 g, 94%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) 5.81 (dd, J = 15.6, 15.6 Hz, 1H), 2.33 (dd, J = 6.5, 6.5 Hz, 1H), 1.56−1.52 (m, 2H), 1.29(s, broad, 6H),0.90−0.85 (m, 3H), 0.19 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 139.0 (dd, J_{C-F} = 5.3, 5.3 Hz), 123.0−105.3 (m), 121.0 (dd, J_{C-F} = 23.3, 23.3 Hz), 103.9, 99.1, 32.3, 31.6, 28.8, 28.3, 22.5, 14.0, −0.4; IR (neat) 2963, 2934, 2864, 2152, 1628, 1456, 1364, 1313, 1240, 1202, 1146, 1121, 1105 cm^{-1}; HRMS Calcd for $C_{19}H_{23}F_{13}Si$: 526.1360. Found: 526.1359. Anal. Calcd for $C_{19}H_{23}F_{13}Si$: C, 43.34; H, 4.40. Found: C, 43.27; H, 4.48.

3-Phenyl-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-1-trimethylsilyl-(3*E*)-buten-1-yne (13c). The procedure for the preparation of **13b** was generally followed. The mixture was stirred for 40 min and worked up. Compound **13c** (yield 95%) was isolated as a pale lemon yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) 7.35 (s, 5H), 6.11 (dd, J = 15.1, 15.1 Hz, 1H), 0.18 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 137.0 (dd, J_{C-F} = 5.0, 5.0 Hz), 135.4, 128.9, 128.1 (dd, J_{C-F} = 2.8, 2.8 Hz), 128.0, 120.9 (dd, J_{C-F} = 20.8, 20.8 Hz), 119.5−107.3 (m), 104.0 (dd, J_{C-F} = 2.8, 2.8 Hz), 101.1; IR (neat) 3088, 3063, 3030, 2964, 2903, 2856, 2151, 1622, 1495, 1447, 1364, 1313, 1238, 1198, 1146, 1123 cm^{-1}. Anal. Calcd for $C_{19}H_{15}F_{13}Si$: C, 44.02; H, 2.92. Found: C, 43.93; H, 3.10.

2-Hexyl-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-(7*E*)-buten-9-yne (1b). The procedure for the preparation of **1a** was generally followed. The mixture was stirred at rt for 2 h, worked up, and purified to give **1b** (100% yield) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) 5.86 (dd, J = 15.5, 15.5 Hz, 1H), 3.10 (s, 1H), 2.35 (dd, J = 7.7, 7.7 Hz, 2H), 1.57 (dd, J = 7.2, 7.2 Hz, 2H) 1.33−1.25 (m, 6H), 0.89−0.85 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 138.2 (dd, J_{C-F} = 5.6, 5.6 Hz), 123.0−107.0 (m), 122.1 (dd, J_{C-F} = 23.3, 23.3 Hz), 82.8, 81.0, 32.3, 31.5, 28.8, 28.2, 22.5, 13.9; IR (neat) 3314, 2963, 2936, 2864, 2106, 1634, 1470, 1364, 1300, 1240, 1202, 1146, 1121, 1107 cm^{-1}; HRMS Calcd for $C_{16}H_{15}F_{13}$: 454.0965. Found: 454.0969. Anal. Calcd for $C_{16}H_{15}F_{13}$: C, 42.30; H, 3.33. Found: C, 42.23; H, 3.46.

3-Phenyl-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-(3*E*)-buten-1-yne (1c). The procedure for the preparation of **1a** was generally followed. The mixture was stirred at rt for 30 min, worked up, and purified to give **1c** (83% yield) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) 7.36 (s, 5H), 6.18 (dd, J = 15.0, 15.0 Hz, 1H), 3.30 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 136.2 (dd, J_{C-F} = 5.6, 4.3 Hz), 135.0, 129.2, 128.12, 128.05, 122.0 (dd, J_{C-F} = 21.2, 21.2 Hz), 119.6−106.6 (m), 83.1, 82.9; ^{19}F NMR (254 MHz, $CDCl_3$) −126.7 to −126.6 (m, 2F), −123.4 (m, 4F), −122.2 to −122.1 (m, 2F), −105.3 to −105.2 (m, 2F), −81.3 (dd, J = 9.2, 9.2 Hz, 3F); IR (neat) 3312, 3088, 3065, 3030, 2106, 1624, 1238, 1202, 1146, 1123, 1070 cm^{-1}; HRMS Calcd for $C_{16}H_7F_{13}$: 446.0339. Found: 446.0315. Anal. Calcd for $C_{16}H_7F_{13}$: C, 43.07; H, 1.58. Found: C, 43.12; H, 1.75.

1-Iodo-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluorononane (15). To a mixture of PPh_3 (59.0 g, 225 mmol) and 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro-1-nonanol **14** (64.8 g, 150 mmol) was added DMF (188 mL) under an argon atmosphere. To this mixture was slowly added a mixture of I_2 (57.1 g, 225 mmol) and DMF (150 mL) under 60 °C while stirring. When the addition was completed, the temperature was raised to 100 °C, and the mixture was stirred at this temperature for 18 h. Et_2O was added, and the organic layer was washed with Na_2SO_3 (10%, aqueous). The aqueous layer was extracted with Et_2O. The combined organic layer was washed with saturated brine, dried over Na_2SO_4, and evaporated. The resiude was further purified by silica gel column chromatography (hexane) to give **15** (58.5 g, 72%) as white powder: mp 23.9−24.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 6.04 (dddd, J = 52, 52, 5.1, 5.1, Hz, 1H), 3.61 (dd, J = 17.3, 17.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 118.4−105.4 (m), 107.6 (dddd, J_{C-F} = 255, 255, 31.5, 31.5 Hz), −4.3 (dd, J_{C-F} = 26.1, 26.1 Hz); IR (KBr) 1242, 1207, 1180, 1146 cm^{-1}; HRMS Calcd for $C_9H_3F_{16}I$: 541.9022. Found: 541.9022. Anal. Calcd for $C_9H_3F_{16}I$: C, 19.94; H, 0.56. Found: C, 19.96; H, 0.78.

1-Iodo-2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-pentadecafluoro-(1*Z*)-nonene (16). To a mixture of DMSO (40 mL) and **15** (21.5 g, 39.6 mmol) was added dropwise a solution of KOH (3.16 g) in Et_2O (40 mL) and for 30 min under an argon atmosphere, and the mixture was stirred for 50 min. Water was added, and the mixture was extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated. The residue was further purified by distillation to give **16** (18.7 g, 90%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) 6.64 (d, J = 30.8 Hz, 1H), 6.04 (dddd, J = 52, 52, 5.1, 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 152.4 (ddd, J_{C-F} = 264, 29.8, 29.8 Hz), 114.9−105.8 (m), 107.7 (dddd, J_{C-F} = 255, 255, 31.5, 31.5 Hz), 65.1 (m); IR (neat) 3107, 1663, 1402, 1315, 1265, 1207, 1146, 1070, 1011 cm^{-1}; HRMS Calcd for $C_9H_2F_{15}I$: 521.8960. Found: 521.8961. Anal. Calcd for $C_9H_2F_{15}I$: C, 20.71; H, 0.39. Found: C, 20.92; H, 0.50.

4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-Pentadecafluoro-1-trimethysilyl-(3*Z*)-undecen-1-yne (17). To a mixture of Pd(PPh$_3$)$_4$ (75 mg, 0.065 mmol) and CuI (25 mg, 0.13 mmol) was added a mixture of Et_2NH (6.0 mL, dried over KOH) and **16** (2.6 g, 5 mmol) under an argon atmosphere at 40 °C. Trimethylsilylacetylene was added slowly, and the mixture was stirred for 2 h. The mixture was cooled, poured into iced water, and extracted with pentane. The organic layer was washed with 2 N aq HCl, dried over $MgSO_4$, and evaporated to give brown oil. The oil was further purified by silica gel column chromatography (pentane) to give **17** (2.0 g, 83%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) 6.04 (dddd, J = 52, 52, 5.1, 5.1 Hz, 1H), 5.72 (d, J = 29 Hz, 1H), 0.21 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 153.7 (ddd, J_{C-F} = 277, 28.8, 28.8 Hz), 114.8−106.6 (m), 108.2, 107.7 (dddd, J_{C-F} = 255, 255, 31.6, 31.6 Hz), 97.5 (dd, J_{C-F} = 14.6, 5.9 Hz), 92.3, −0.7; IR (neat) 3076, 2966, 2905, 2156, 1672, 1402, 1356, 1256, 1209, 1167, 1146, 1065 cm^{-1}. Anal. Calcd for $C_{14}H_{11}F_{15}Si$: C, 34.16; H, 2.25. Found: C, 34.01; H, 2.18.

4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-Pentadecafluoro-(3*Z*)-undecen-1-yne (1e). The procedure for the preparation of **1a** was generally followed. The mixture was stirred at rt for 15 min, worked up, and purified to give **1e** (72% yield) as a pale yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) 6.04 (dddd, J = 52, 52, 5.1, 5.1 Hz, 1H), 5.72 (dd, J = 29.0, 2.6 Hz, 1H), 3.42 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 155.0 (ddd, J_{C-F} = 278, 28.9, 28.9 Hz), 115.1−106.7 (m), 107.8 (dddd, J_{C-F} = 255, 255, 31.6, 31.6 Hz), 96.6 (dd, J_{C-F} = 14.3, 6.2 Hz), 88.6 (d, J_{C-F} = 6.8 Hz), 71.9; ^{19}F NMR (254 MHz, $CDCl_3$) −137.5 (d, J = 55.5 Hz, 2F), −129.8 (s, 2F), −123.8 (m, 2F), −123.3 (m, 2F), −122.5 (m, 4F), −118.8 (dd, J = 24.0, 12.9 Hz, 2F), −113.9 (m, 1F); IR

(neat) 3315, 3086, 2124, 1678, 1402, 1358, 1207, 1167, 1146, 1040 cm^{-1}; HRMS Calcd for $C_{11}H_3F_{15}$: 419.9995. Found: 419.9980. Anal. Calcd for $C_{11}H_3F_{15}$: C, 31.45; H, 0.72. Found: C,31.22; H, 0.91.

Nickel(0)-Catalyzed Reaction of Conjugated Enynes. A Representative Procedure. To a dark red mixture of $Ni(cod)_2$ (13.8 mg, 0.05 mmol) and PPh_3 (53 mg, 0.2 mmol) in dry toluene (0.25 mL) was added a solution of **1a** (185 mg, 0.5 mmol) in dry toluene (0.25 mL) at room temperature, and the mixture was stirred for 15 min. The mixture was passed through a short alumina column (pentane) and evaporated. The residue was further purified by MPLC (hexane) to give **2a** (124 mg, 65%) as a pale yellow oil.

1,2,4-Tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-(1*E*)-octenyl)benzene (2a): pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.54−7.53 (m, 3H), 7.43−7.33 (m, 2H), 7.22−7.15 (m, 1H), 6.35−6.06 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 138.0 (dd, J_{C-F} = 9.4, 9.4 Hz), 136.5 (dd, J_{C-F} = 9.6, 9.6 Hz), 136.2 (dd, J_{C-F} = 9.7, 9.7 Hz), 135.3, 134.6, 134.1, 128.6, 128.5, 127.5, 123.4−104.6 (m); ^{19}F NMR (254 MHz, $CDCl_3$) −126.8 (s, 6F), −123.9 to −123.8 (m, 4F), −123.6 to −123.5 (m, 8F), −122.2 (s, 6F), −112.4 (s, 4F), −112.1 to −112.0 (m, 2F), −81.5 to −81.4 (m, 9F); IR (neat) 1655, 1364, 1238, 1200, 1146, 1121, 1067 cm^{-1}. Anal. Calcd for $C_{30}H_9F_{39}$: C, 32.45; H, 0.82. Found: C, 32.17; H, 1.06.

1,2,4-Tris(1-hexyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-(1*E*)-octenyl)benzene (2b): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.32 (dd, J = 8.0, 1.8 Hz, 1H), 7.17 (d, J = 8.1 Hz, 1H), 7.08 (d, J = 1.8 Hz, 1H), 5.63 (dd, J = 15.8, 15.8 Hz, 1H), 5.56 (dd, J = 15.2, 15.2 Hz, 2H), 2.70 (m, 2H), 2.56 (m, 4H), 1.27−1.19 (m, 24H), 0.87−0.77 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 157.5 (dd, J_{C-F} = 4.7, 4.7 Hz), 157.2 (dd, J_{C-F} = 4.7, 4.7 Hz), 155.5 (dd, J_{C-F} = 4.7, 4.7 Hz), 141.3, 139.6, 139.5, 130.1, 127.8, 126.8, 123.5−104.3 (m), 117.1, 117.0, 114.9, 32.3, 31.5−31.3 (m), 29.3, 29.2, 28.6, 28.5, 28.4, 22.5, 13.80, 13.77, 13.73; ^{19}F NMR (254 MHz, $CDCl_3$) −126.7 (m, 6F), −123.8 (m, 6F), −123.4 (m, 6F), −122.1 (m, 6F), −106.3 (m, 4F), −105.6 (dd, J = 29.6, 29.6 Hz, 2F), −81.4 to −81.2 (m, 9F); IR (neat) 2963, 2934, 2864, 1651, 1470, 1363, 1313, 1240, 1200, 1146, 1121, 1103 cm^{-1}. Anal. Calcd for $C_{48}H_{45}F_{39}$: C, 42.30; H, 3.33. Found: C, 42.30; H, 3.52.

1,2,4-Tris(1-phenyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-(1*E*)-octenyl)benzene (2c): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.37−7.09 (m, 14H), 6.80 (dd, J = 7.1 Hz, 2H), 6.68 (d, J = 7.5 Hz, 2H), 6.06 (dd, J = 14.5, 14.5 Hz, 1H), 5.81 (dd, J = 14.8, 14.8 Hz, 2H); ^{13} C NMR (75 MHz, $CDCl_3$) 153.9 (m), 153.4 (dd, J_{C-F} = 4.4, 3.7 Hz), 152.8 (dd, J_{C-F} = 4.4, 4.4 Hz), 141.9, 141.3, 141.0, 136.8, 136.7, 136.5, 130.9−127.8 (m), 123.4−104.7 (m); ^{19}F NMR (254 MHz, $CDCl_3$) −126.7 (m, 6F), −123.8 to −123.3 (m, 12F), −122.1 (m, 6F), −105.3 to −105.0 (m, 4F), −104.4 (dd, J = 25.9, 14.8 Hz, 2F), −81.4 to −81.3 (m, 9F); IR (neat) 3063, 3030, 1639, 1497, 1447, 1366, 1302, 1236, 1198, 1144, 1121, 1103, 1063 cm^{-1}. Anal. Calcd for $C_{48}H_{21}F_{39}$: C, 43.07; H, 1.58. Found: C, 43.31; H, 1.77.

3,5,6-Trihexyl-1,2,4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-(1*E*)-octenyl)benzene (2d): brown powder, mp 26.4−27.3 °C; ^{1}H NMR (300 MHz, CD_3COCD_3) 7.67−7.46 (m, 3H), 6.23−5.97 (m, 3H), 2.66−2.56 (m, 6H), 1.43−1.27 (m 24H), 0.88−0.85 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 139.8−130.8 (m), 123.4−106.3 (m), 31.5−29.4 (m), 22.6, 22.5, 13.9, 13.7; ^{19}F NMR (254 MHz, $CDCl_3$) −126.7 (m, 6F), −123.5 (m, 12F), −122.3 (m 6F), −112.9 (dd, J = 25.9, 11.1 Hz, 4F), −112.4 (m, 2F), −81.3 to −81.2 (m, 9F); IR (KBr) 2963, 2932, 2860, 1655, 1560, 1466, 1366, 1242, 1204, 1146, 1123, 1067 cm^{-1}. Anal. Calcd for $C_{48}H_{45}F_{39}$: C, 42.30; H, 3.33. Found: C, 42.16; H, 3.27.

1,2,4-Tris(2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-pentadecafluoro-(1*Z*)-nonenyl)benzene (2e): pale yellow powder, mp 73−74 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.80 (s, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.67 (dd, J = 8.3, 1.3 Hz,1H), 6.50 (d, J = 32.8 Hz, 1H), 6.47 (d, J = 33.0 Hz, 1H), 6.40 (d, J = 34.8 Hz, 1H), 6.04 (dddd, J = 52, 52, 5.1, 5.1 Hz, 1H), 6.03 (dddd, J = 52, 52, 5.1, 5.1 Hz, 2H); ^{13}C NMR (75 MHz, THF-d^8) 147.3 (ddd, J_{C-F} = 271, 28.3, 28.3 Hz), 147.2 (ddd, J_{C-F} = 270, 28.8, 28.8 Hz), 146.9 (ddd, J_{C-F} = 270, 28.6, 28.6 Hz), 132.3−130.4 (m), 116.2−105.5 (m); ^{19}F NMR (254 MHz, $CDCl_3$) −137.6 to −137.4 (m, 6F), −129.9 to −129.8 (m, 6F), −123.9 to −122.5 (m, 27F), −118.1 to −117.8 (m, 6F); IR (KBr) 3086, 3013, 1692, 1497, 1402, 1369, 1275, 1198, 1157, 1142, 1086, 1018 cm^{-1}. Anal. Calcd for $C_{33}H_9F_{45}$: C, 31.45; H, 0.72. Found: C, 31.27; H, 0.97.

(*E*)-3-[3,4-Bis{(*E*)-2-cyano-1-pentylvinyl}phenyl]-oct-2-enenitrile (2f): yellow powder (58.0 mg, 79%), mp 75.4−78.3 °C;^{1}H NMR (300 MHz, $CDCl_3$) 7.42 (dd, J = 8.0, 1.8 Hz, 1 H), 7.22 (d, J = 8.0 Hz, 1H), 7.16 (d, J = 1.8 Hz, 1H), 5.54 (s, 1H), 5.36 (s, 2H), 2.85 (t, J = 7.6 Hz, 2H), 2.70 (bs, 4H), 1.45−1.26 (m, 18H), 0.87−0.82 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 165.8, 165.4, 162.9, 138.8, 138.2, 137.7, 129.8, 127.1, 127.0, 117.0, 116.0, 115.8, 100.1, 99.9, 97.4, 35.5, 35.4, 33.6, 31.2, 31.1, 28.0, 27.7, 27.6, 22.14, 22.09, 13.74, 13.70; IR (KBr) 2953, 2928, 2860, 2214, 1609, 1468, 1456, 1404, 1379, 1325, 850, 826, 723 cm^{-1}; HRMS. Calcd for $C_{30}H_{39}N_3$: 441.3143. Found: 441.3147. Anal. Calcd for $C_{30}H_{39}N_3$: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.51; H, 9.12; N, 9.36.

(*E*)-3-[2,3,6-Trihexyl-4,5-bis{(*E*)-2-methoxycarbonylvinyl)phenyl]acrylic acid methyl ester (2g): yellow powder (58.1 mg, 60%); mp 48.7−50.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.84 (d, J = 16.3 Hz, 1H), 7.77 (d, J = 16.3 Hz, 1H), 7.72 (d, J = 16.3 Hz, 1H), 5.96 (d, J = 16.3 Hz, 1H), 5.88 (d, J = 16.3 Hz, 2H), 3.80 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 2.52 (bs, 6H), 1.35−1.22 (m, 24H), 0.86−0.81 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 166.51, 166.45, 166.38, 144.7, 144.4, 144.0, 139.5, 137.5, 136.9, 135.9, 134.1, 131.6, 125.3, 125.1, 124.5, 51.73, 51.68, 51.65, 31.31, 31.30, 31.2, 30.7, 30.5, 30.3, 30.1, 29.8, 29.7, 29.6, 29.2, 22.5, 22.4, 13.98, 13.95; IR (KBr) 2953, 2922, 2858, 1720, 1641, 1470, 1435, 1313, 1273, 1194, 1171, 1013, 986, 949, 858, 677 cm^{-1}; HRMS. Calcd for $C_{36}H_{54}O_6$: 582.3921. Found: 582.3886. Anal. Calcd for $C_{36}H_{54}O_6$: C, 74.19; H, 9.34. Found: C, 74.19; H, 9.40.

(*E*)-3-[2,4,6-Trihexyl-3,5-bis{(*E*)-2-methoxycarbonylvinyl}phenyl]acrylic acid methyl ester (3g): yellow powder (16.0 mg, 16%); mp 43.5−47.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.76 (d, J = 16.3 Hz, 3H), 5.91 (d, J = 16.3 Hz, 3H), 3.75 (s, 9H), 2.47−2.41 (m, 6H), 1.33−1.16 (m, 24H), 0.78 (t, J = 6.7 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 166.5, 144.3, 138.6, 132.9, 124.5, 51.8, 31.2, 31.0, 30.0, 29.3, 22.5, 14.0; IR (KBr) 2955, 2858, 1724, 1651, 1645, 1456, 1310, 1277, 1196, 1169, 989 cm^{-1}; HRMS. Calcd for $C_{36}H_{54}O_6$: 582.3921. Found: 582.3891. Anal. Calcd for $C_{36}H_{54}O_6$: C, 74.19; H, 9.34. Found: C, 74.26; H, 9.36.

1,2,4-Tris(1-nonyl-2,2-difluoroethylenyl)benzene (4): pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.27 (d, J = 7.5 Hz, 1H), 7.19 (d, J = 8.3 Hz, 1H), 7.14 (s, 1H), 2.39 (m, 2H), 2.24 (m, 4H), 1.26−1.24 (m, 42H), 0.87 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 157.6−149.3 (m), 133.5, 133.4, 132.2, 131.0, 130.8, 127.4 (dd, J_{C-F} = 3.1, 3.1 Hz), 92.2−91.4 (m), 31.9, 29.6, 29.3, 29.25, 29.19, 29.0, 28.2, 28.1, 27.8, 27.6, 27.5, 27.3, 22.7, 14.1; ^{19}F NMR (254 MHz, $CDCl_3$) −94.2 to −93.7 (m, 2F), −91.2 to −91.6 (d, J = 18.5 Hz, 2F), −90.2 to −90.0 (m, 2F); IR (neat) 2957, 2926, 2856, 1792, 1732, 1653, 1645, 1607 cm^{-1}; HRMS Calcd for $C_{39}H_{60}F_6$: 642.4596. Found: 642.4622. Anal. Calcd for $C_{39}H_{60}F_6$: C, 72.86; H, 9.41. Found: C, 72.94; H, 9.16.

Acknowledgment. This work was supported in part by the Japan Securities Scholarship Foundation, Shimadzu Foundation, and Japan Bioindustry Association.

JO0056242