JOC Article

A New Regioselective Heck Vinylation with Enamides. Synthesis and Investigation of Fluorous-Tagged Bidentate Ligands for Fast Separation

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Internal ligand-controlled Heck vinylations of enamides were performed with high regioselectivity and delivered moderate to good yields of dienamides. Controlled heating by microwave irradiation accelerated the palladium-catalyzed reactions, and full conversions were achieved after reaction times of only 15−30 min. New bidentate fluorous-tagged 1,3-bis(diphenylphosphino)propane ligands (F-dppp's) were synthesized and examined. The cationic vinylations of the enamides with F-dppp ligands rendered essentially the same α-selectivity and catalytic activity as in those vinylations where nonfluorous ligands were employed. After reaction, the fluorous-tagged ligand material was easily removed by convenient solid fluorous phase separation. The high selectivity, simplicity, and generality of the experimental procedure should make this approach to 2-acylamino-1,3-butadienes attractive.

Introduction

The palladium-catalyzed Heck coupling is a powerful tool in both organic and medicinal chemistry, and new applications and protocols are reported continuously.[1−6] Specifically, the coupling of vinyl halides (or pseudohalides) with olefins to provide 1,3-dienes constitutes an important subtype of the Heck reaction. In contrast to the wide range of available vinyl palladium precursors for this transformation, the olefinic substrates have so far mostly been limited to electron-deficient olefins.[1,3,5,6] Thus, there are only a few examples reported of successful preparations of the synthetically very useful electron-rich 1,3-dienes, despite the fact that electron-rich olefins have been extensively exploited in the related Heck arylation reaction.[4,7,8] We recently reported highly selective internal Heck vinylations of alkyl vinyl ethers where bidentate ligands controlled the regioselectivity.[9,10] Considering the fact that enamides are electron-rich, the obvious question arose whether a protocol that enabled also selective preparation of useful 2-acylamino-1,3-butadienes could be developed.

In modern synthetic chemistry laboratories protocols for high reaction speed and rapid purification are highly desired. To meet the first demand, controlled microwave synthesizers have been developed.[11−14] These heating devices can accelerate palladium-catalyzed transformations and reduce the reaction times from many hours down to a few minutes.[15] Among the variety of methods that have been used for improving the workup procedures of chemical reactions, fluorous techniques have attracted an increasing amount of attention due to quick liquid−liquid and solid−liquid extractions.[16,17] Recent investigations have showed that by shifting from liquid−liquid to solid−liquid extractions, the fluorine content on the tagged reagent or reactant can drastically be decreased without affecting the efficiency of the fluorous separation.[18]

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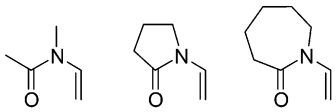
CHART 1

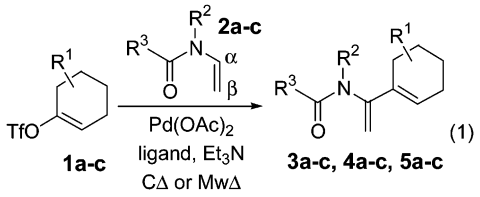


2a **2b** **2c**

This report is addressing the synthesis of dienamides and the impact of a set of catalytic palladium systems on the selective vinylic substitution of the α-hydrogen of three different *N*-alkylated enamides. We report herein (1) a new bidentate ligand-controlled, regioselective synthesis of 2-acylamino-1,3-butadienes, (2) the synthesis and examination of three fluorous-tagged dppp (F-dppp) derivatives, and (3) the effect of microwave heating (MwΔ).

Results

Internal Vinylations. The preparative results of the Heck reactions of three different vinyl triflates **1a**−**c** with the electron-rich enamides **2a**−**c** (Chart 1) are presented in eq 1 and Table 1. The triflates **1a**−**c** (1.0 equiv) were



(1)

mixed with 3 mol % $Pd(OAc)_2$ as palladium source, 9 mol % bidentate ligand,[19,20] 1.2 equiv triethylamine, and 2.5 equiv of the olefins **2a**−**c** in dry DMSO to give the dienamides **3**−**5**. Three different bidentate ligands were used in the reactions, dppp,[21] **6a** (F-dppp, *p*-C_4F_9), and *rac*-binap[21] (Table 1). The reactions were conducted under nitrogen at 60−70 °C with classic oil-bath heating (CΔ) overnight[22] or at 90 °C with 15−30 min of controlled microwave heating. Employing standard heating and dppp, high regioselectivity (α/β = 96/4) was obtained with triflate **1a** and olefin **2a** (entry 1). The enamide **2a** afforded a less selective mixture of regioisomers when the reaction time was reduced by heating to 90 °C (entry 2).[23] The relatively moderate yield (53%) of the dieneamide **3a** at 60 °C reaction temperature were attributed mainly to competing homocoupling of **1a** (the formation of bis-cyclohexenyls and oxidized derivatives). This competing side reaction was favored at low temperature, but by using microwave flash heating to 150 °C for 5 min nearly all homocoupling product formation was quelled. Unfortunately, the high reaction temperature was accompanied with a loss of α-selectivity (α/β = 80/20).[15] However, the isolated yield of branched **3a** in the 15 min microwave-heated reaction at 90 °C (51%, entry 2) was similar to entry 1 (53%) due to the counteracting effects of the temperature-suppressed homocoupling and the reduced α-selectivity. By application of exactly the same transformation with conventional heating at 90 °C, full conversion of **1a** was achieved after 1 h with a product pattern very similar to that encountered in the microwave reaction.[24]

Use of the identical reaction system with the cyclic enamides (**2b** and **2c**) improved yields but afforded a decreased selectivity for the branched **3b** and **3c** (entries 5, 7, and 8).[25]

With the objective to suppress the products derived from hydrogenolysis followed by aromatization (2-methoxynaphthalene formation) and homocoupling in the Heck vinylations of the more reactive **1b** and the enamides **2a**−**c**, the dppp ligand was displaced with *rac*-binap (entries 9−13).[10,26] The change in catalytic system reduced the byproduct formations and improved the yields of **4a**−**c** but resulted in a slightly slower vinylation. However, increasing the temperature to 70−90 °C did not adversely affect the desired α-selectivity (the α/β-ratio was constantly a very impressive >99/1). The low isolated yield of **4a** with microwave heating (45%, entry 10) was a consequence of a higher degree of hydrogenolysis followed by aromatization at the elevated temperature.

The progesterone dienyl triflate **1c** exhibited a similar reactivity as the vinyl triflate **1a**, but with a lower tendency to form the corresponding homocoupled byproduct. Compared to **1a**, the triflate **1c** was also less prone to form the terminal coupling products, and the use of the previously more demanding cyclic enamides **2b**-**c** did not reduce the regioselectivity.

Fluorous Couplings. When the fluorous F-dppp ligand **6a** was used in the vinylations of **1a** and **1c**, two conclusions become apparent. First, the performance was very similar to nonfluorous dppp, although the selectivity was slightly lower (Table 1, entries 3, 4, 6, and 16). Second, all free **6a**, palladium-complexed **6a**, and oxidized **6a** were easily removed from the reaction medium by direct solid fluorous phase separation using a 90% methanol−10% water eluting system.[27] The methanol was thereafter removed under reduced pressure and the salts were withdrawn by a water/ether extraction. Reso-

(18) Curran, D. P.; Luo, Z. *J. Am. Chem. Soc.* **1999**, *121*, 9069−9072.

(19) Amatore and Jutand have recently demonstrated that 3 equiv of dppp react with 1 equiv $Pd(OAc)_2$ to afford $Pd(0)(dppp)_2$ and dppp monoxide in DMF. Thus, 1 equiv or (3 mol % dppp) is consumed in the generation of the active Pd(0) catalyst.

(20) Amatore, C.; Jutand, A.; Thuilliez, A. *Organometallics* **2001**, *20*, 3241−3249.

(21) dppp = 1,3-bis(diphenylphosphino) propane, *rac*-binap = racemic-2, 2′-bis(diphenylphosphino)-1,1′-binaphthyl.

(22) Noncomplete consumption of the vinyl triflates (**1a**−**c**) was observed after 6 h by GC/MS.

(23) In an attempt to optimize the reaction further, we investigated 1,2,2,6,6-pentamethylpiperidine (PMP), diisopropylethylamine, dicyclohexane methylamine, proton sponge, or potassium carbonate as different bases, but with no significant effect on selectivity and rate. Exchanging $Pd(OAc)_2$ with Pd_2dba_3 as palladium source retarded the reaction rate drastically. The ligand 1,1′-bis(diphenylphosphino)-ferrocene (dppf) performed similar to dppp, but binap decreased the reaction rate with no effect on the selectivity. Applying the ionic liquid $bmimPF_6$ solvent retarded the reaction rate strongly.

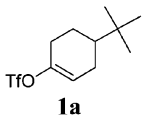
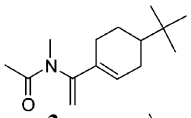
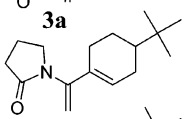
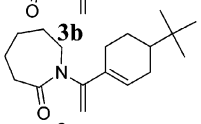
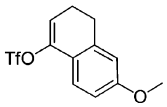
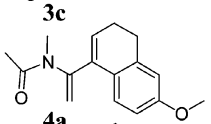
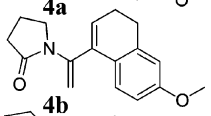
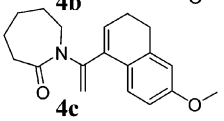
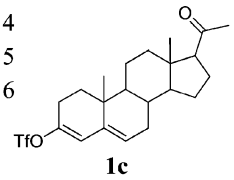
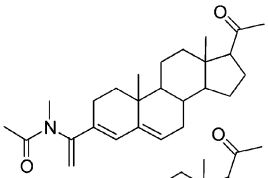
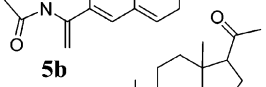
(24) When monitoring the reaction mixture at 0, 15, 30, 45, and 60 min, the product **3a**/homocoupling byproduct ratio increased significantly according to GC/MS.

(25) Employing 18.0 mol % instead of 9.0 mol % dppp at 60 °C resulted in a much slower (44 h) but equally selective internal vinylation of vinyl triflate **1a** (α/β = 92/8). Unfortunately, massive homocoupling reduced the yield of product **3b** (36% isolated yield).

(26) The use of dppp with **1b** under standard conditions (3 mol % $Pd(OAc)_2$, 9 mol % dppp) with classic heating afforded lower GC/MS yields of dienamide **4** due to competing hydrogenolysis followed by aromatization and homocoupling (44% yield of **4b** at 60 °C and 48% yield of **4c** at 60 °C). The α/β regioselectivities were in all cases >99/1.

(27) Curran, D. P. *Synlett* **2001**, 1488−1496.

TABLE 1. Internal Heck Vinylation of Enamides with Vinyl Triflates[a]

Entry	Vinyl triflate	Olefin	Reaction conditions: Ligand	Reaction conditions: CΔ / Mw	Product	α/β[b]	Isolated yield (%)[c]
1	 **1a**	**2a**	dppp	CΔ 18 h 60 °C	 **3a**	96/4	53
2		**2a**	dppp	MwΔ 15 min 90 °C		91/9	51
3		**2a**	F-dppp, **6a**	CΔ 18 h 60 °C		94/6	46
4		**2a**	F-dppp, **6a**	MwΔ 15 min 90 °C		90/10	46
5		**2b**	dppp	CΔ 24 h 60 °C	 **3b**	92/8	65
6		**2b**	F-dppp, **6a**	MwΔ 20 min 90 °C		87/13	63
7		**2c**	dppp	CΔ 18 h 60 °C	 **3c**	91/9	61
8		**2c**	dppp	MwΔ 15 min 90 °C		85/15	70
9	 **1b**	**2a**	binap	CΔ 18 h 70 °C	 **4a**	>99/1	58
10		**2a**	binap	MwΔ 30 min 90 °C		>99/1	45
11		**2b**	binap	CΔ 18 h 70 °C	 **4b**	>99/1	84
12		**2c**	binap	CΔ 18 h 70 °C	 **4c**	>99/1	83
13		**2c**	binap	MwΔ 30 min 90 °C		>99/1	71
14	 **1c**	**2a**	dppp	CΔ 18 h 60 °C	 **5a**	97/3	70
15		**2a**	dppp	MwΔ 30 min 90 °C		94/6	60
16		**2a**	F-dppp, **6a**	CΔ 18 h 60 °C		96/4	72
17		**2b**	dppp	CΔ 18 h 60 °C	 **5b**	94/6	78
18		**2c**	dppp	CΔ 18 h 60 °C	**5c**	96/4	70

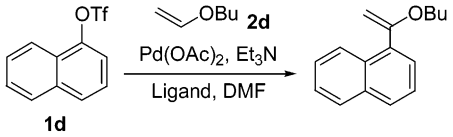
[a] Reaction conditions: The reactions were performed in 1.0 mmol scale with 1.0 equiv of **1a**−**c**, 2.5 equiv of **2a**−**c**, 3 mol % of $Pd(OAc)_2$, 9 mol % of the bidentate ligand, and 1.2 equiv of Et_3N in DMSO under N_2. [b] The regioselectivity (α/β = internal/terminal) was determined with ^1H NMR and GC/MS of the crude product mixture. [c] >95% pure of the internal product (**3**−**5**) according to GC/MS or LC/MS.

nances from the phosphine-based ligand could not be detected in neither ^{31}P nor ^1H NMR spectra of the crude product. Subsequent elution of the fluorous solid-phase cartridge with THF provided a complicated phosphine mixture according to ^{31}P NMR analysis. Attempts to reuse the isolated phosphine mixture as the catalytic system in a second vinylation with **1a** and **2b** furnished no Heck addition product under standard conditions. Similar observations were made in the previous work applying monodentate fluorous-tagged ligands, and the results suggest that the catalyst degrades during the course of the reaction.[28]

Selection of F-dppp Ligands. To improve the separation of the phosphine ligand from the reaction mixture, we initially studied three new fluorous-tagged dppp derivatives (**6a**−**c**, Table 2). These fluorous diphenylphosphinopropanes, with different fluorous content and tagging position on the phenyl groups, were initially investigated in both an internal arylation and in the herein reported Heck vinylation reaction (Tables 2 and 3). In the coupling between the electron-rich butyl vinyl ether (**2d**) with 1-naphthyl triflate (**1d**), **6a** (F-dppp *p*-C_4F_9) behaved similarly to the nonfluorous dppp (Table 2, entry 2). The arylation occurred smoothly in DMF with full conversion and excellent regiocontrol. Applying the phosphine ligands with heavier fluorous tails, **6b**,**c**, reduced the reaction rate and decreased the selectivity (entries 3

(28) Zhang, Q.; Luo, Z.; Curran, D. P. *J. Org. Chem.* **2000**, *65*, 8866−8873.

TABLE 2. Influence of Different F-dppp Ligands on the Arylation of Butyl Vinyl Ether[a]



entry	ligand	time (h)	α/β[b]	conv (%)[c]
1	dppp	5	>99/1	100
2	F-dppp *p*-C_4F_9, **6a**	5	>99/1	100
3	F-dppp *m*-C_6F_{13}, **6b**	84	60/40	83
4	F-dppp *p*-C_6F_{13}, **6c**	20	79/21	100
5	F-dppp *p*-C_6F_{13}, **6c**[d]	20	>99/1	100

[a] The reactions were performed in 0.1 mmol scale with 3 mol % of $Pd(OAc)_2$ and 6 mol % of the bidentate ligand in DMF at 80 °C. [b] The regioselectivity was determined with GC/MS. [c] Conversion of **1d** was determined with 2,3-dimethylnaphthalene as internal standard and GC/MS. [d] 9 mol % of **6c**.

TABLE 3. Influence of Different F-dppp Ligands on the Vinylation of 2a with 1a[a]

entry	ligand	time (h)	α/β[b]	conv (%)[c]
1	dppp	20	96/4	100
2	F-dppp *p*-C_4F_9, **6a**	20	96/4	100
3	F-dppp *m*-C_6F_{13}, **6b**	20	96/4	99
4	F-dppp *p*-C_6F_{13}, **6c**	20	96/4	100

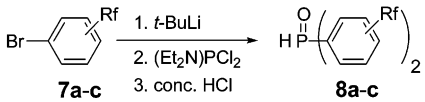
[a] The reactions were performed on 0.2 mmol scale with 3 mol % of $Pd(OAc)_2$ and 9 mol % of the bidentate ligand in DMSO at 60 °C. [b] The regioselectivity was determined with GC/MS. [c] Conversion of **2a** was determined with *o*-xylene as internal standard and GC/MS.

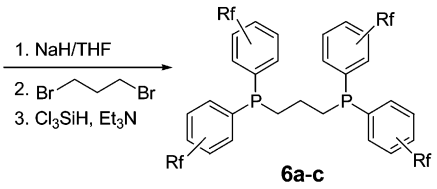
and 4). Thus, the regiocontrol and catalytic activity were lost when the C_6F_{13} tail was attached in the meta position to the phosphorus atom (ligand **6b**, entry 3).[29,30] Notably, in the case of para-substituted **6c**, full conversion of **1d** and higher α-selectivity could be achieved by increasing the ligand/palladium ratio (entry 5).

The internal vinylation with **1a** and **2a** in DMSO provided high regioselectivty and reactivity with both the nonfluorous and fluorous ligands **6a**−**c** (Table 3), but the competing vinyl triflate homocoupling process increased in the following order: dppp < **6a** < **6b** < **6c**. Thus, the lightly fluorinated ligand **6a** was selected for continued investigation due to this trend, but also because of preparative convenience, high activity, and good regiocontrol in the test reactions (Tables 2 and 3). The results from the 1.0 mmol scale vinylation of enamides **2a**,**b** are reported in Table 1.

Syntheses of F-dppp's. The preparation of fluorous diphenylphosphinopropanes started with the reaction of fluorinated aryllithium reagents derived from the corresponding fluorinated aryl bromides **7a**−**c**[28] with diethylphosphoramidous dichloride (Table 4). The reaction mixture was directly hydrolyzed with concentrated hydrogen chloride to give the fluorinated diarylphosphine oxides **8a**−**c** as white solids.[31] Alkylation of **8a**−**c** with

TABLE 4. Synthesis of Fluorous Diphenylphosphinopropanes (F-dppp's)





Rf	product yield (%)[a]	product yield (%)[b]
p-$CH_2CH_2C_4F_9$	**8a** (72%)	**6a** (56%)
m-$CH_2CH_2C_6F_{13}$	**8b** (61%)	**6b** (57%)
p-$CH_2CH_2C_6F_{13}$	**8c** (58%)	**6c** (62%)

[a] Isolated yield of **8a**−**c**, calculated from **7a**−**c**. [b] Isolated yield of **6a**−**c**, calculated from **8a**−**c**.

1,3-dibromopropane and reduction with trichlorosilane then provided the fluorous dppp's **6a**−**c** in 56−62% isolated yields.

Discussion

A few reports on metal-catalyzed synthesis of alkoxydienes and dienamides, primarily prepared for subsequent evaluation in Diels−Alder reactions, have appeared in the literature.[32−35] In view of the known difficulties in preparing the 2-acylamino-1,3-butadienes,[36] the reported direct Heck route from vinyl triflates and enamides constitutes a valuable new method.

We believe that this bidentate ligand-controlled vinylation is subject to strong electronic control.[2,4,6] Thus, in the presence of a strongly coordinating bidentate ligand, ionization occurs by dissociation of the weakly coordinating triflate counterion and a cationic π-complex is formed.[4] Internal vinylation then occurs by insertion of the palladium atom to the electron-rich β-carbon with subsequent generation of the internal carbon−carbon bond. The diene products **3**−**5** are thereafter liberated by β-elimination. The slightly lower regioselectivity with microwave heating is probably a consequence of the higher reaction temperature that destabilizes the ligand coordination to the palladium complex.[15]

The higher reaction rate in the vinylation of **2a** with **1a** under microwave heating at 90 °C, compared to the results of the classic heating method at the same temperature, is difficult to interpret. We speculate that the technical difficulties in correct temperature monitoring have contributed to this inconsistency.[11]

(29) In contrast to ligand **6c**, the regioselectivity in the reaction between **1d** and **2d** in DMF did not improve at higher concentrations of ligand **6b** (9 mol %). We speculate that the poor α/β-ratio in the arylation of **2d** with **6b** is a result of faster oxidation of **6b** to the corresponding dioxide in DMF than in DMSO (used in the vinylation reactions). Rapid oxidation of **6b** in $CDCl_3$ at room temperature furnished pure dioxide **9**; see the Experimental Section.

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The preparative vinylations at 60 °C provided significantly larger amounts of homocoupled bis-vinyl byproducts than experiments at higher temperature. These byproducts may be formed not only by direct homocoupling but also after hydrogenolysis of the vinyl triflate, producing the cyclic alkene, followed by a subsequent Heck coupling with an intact triflate **1**. The larger diene/homocoupled byproduct ratio observed at higher temperatures may thus originate from a predominance of enamide vinylation, as compared to the competing vinyl triflate reduction.

Conclusion

In summary, we have presented a novel palladium-catalyzed procedure for synthesis of 2-acylamino-1,3-butadienes from vinyl triflates and enamides. Although only a limited number of examples are provided here, we believe that the ease of operation and the high regioselectivity will prove to be useful in synthetic work. The fact that vinylations with fluorous ligands delivered branched products in useful yields proves that the cationic Heck cycle apparently can selectively operate also with this new catalytic system. The use of rapid microwave in-situ heating and fluorous solid phase purification combines strategic features for reducing both time and effort at both the reaction and separation stages. Employing fluorous solid-phase purification is a rapid and efficient method to completely remove the fluorous-tagged phosphine ligand before subsequent product isolation. We theorize that future work will also deliver protocols for recycling of new catalytic systems using microwave heating and fluorous technologies.

Experimental Section

General. All Heck coupling reactions were conducted in sealed process vials under nitrogen with magnetic stirring. The ^{1}H NMR and ^{13}C NMR spectra of the Heck coupling products were recorded at 270 and 68 MHz or at 400 and 100 MHz, respectively. The ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR of the fluorous diphenylphosphinopropane compounds were recorded at 300, 75, 282.5, and 121.5 MHz, respectively. Chemical shifts are reported as δ values (ppm) referenced to the following solvent signals: $CHCl_3$, δ 7.26; $CDCl_3$, δ 77.0; CH_3CN, δ 1.94; CD_3CN, δ 118.3. Mass spectra were recorded on a GC/MS, equipped with a 25 m × 0.20 mm or a 30 m × 0.25 mm capillary column, utilizing electron impact (EI) at an ionizing energy of 70 eV. RP/HPLC/MS was performed in ESI mode, on a C8 column (4.6 × 50 mm) using an CH_3CN/H_2O gradient with 0.05% HCOOH, employing UV (214, 255 nm) and MS detection. Fluorous solid-phase extractions were performed with fluorous SPE Cartridges (5 g, 10 cm^3) from Fluorous Technologies Inc. Column chromatography was performed using commercially available silica gel 60 (particle size 40−63 μm) or prepacked silica columns (average particle size 53 μm). The microwave heating was performed in a single-mode cavity producing controlled irradiation at 2450 MHz. Reaction temperature and pressure were determined using the built-in, on-line IR and pressure sensors.

Materials. All reagents were obtained from commercial sources and used without further purification. DMSO (H_2O < 0.01%) was used as received, but tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium benzophenone ketyl under nitrogen. The vinyl triflates **1a**−**c** are known compounds and were prepared by literature procedures.[37,38] The ^{1}H NMR data obtained for **1a** did not correspond to the literature data.[39] Triethylamine was distilled over potassium hydroxide. The fluorinated aryl bromides **7a**−**c** were prepared according to the previously described method.[28] All Heck vinylation reactions were performed using the appropriate choice of classic heating time and temperature, or microwave heating temperature and irradiation time, until the complete consumption of the starting vinyl triflates. The bis-vinyl and the oxidized bis-vinyl byproducts were detected by GC/MS and LC/MS.

General Procedure for Classic Synthesis of 2-Acylamino-1,3-butadienes (3−5, Table 1). A mixture of the vinyl triflate (1.0 mmol), enamide (2.5 mmol), triethylamine (0.121 g, 1.2 mmol), $Pd(OAc)_2$ (0.0067 g, 0.030 mmol), and bidentate ligand (0.090 mmol) was stirred in 4.0 mL of dry DMSO under N_2 in a sealed 2.0−5.0 mL Smith process vial (for reaction time and temperature, see Table 1). After complete conversion of the starting vinyl triflate as analyzed by GC/MS or LC/MS, the reaction mixture was allowed to cool.

Workup Method a. The reaction mixture containing dppp or *rac*-binap was poured into 0.1 M NaOH and extracted with diethyl ether. The combined organic layers were washed with brine and dried over potassium carbonate.

Workup Method b. When using fluorous-tagged **6a**, the reaction mixture was charged directly on to the fluorous reverse phase silica gel and the organic mixture was eluated with 200 mL, 90% methanol−10% water, to give an organic fraction. The methanol was then removed under reduced pressure and the salts were removed by ether extraction. The combined ether layers were washed with brine, dried over potassium carbonate, and concentrated. Subsequent elution of the fluorous silica gel with 50 mL of 100% methanol provided some of the homocoupled byproducts.

The product (**3**−**5**) was finally purified by column chromatography (hexane:ethyl acetate).

General Procedure for Microwave Heated Synthesis of 2-Acylamino-1,3-butadienes (3a−c, 4a,c, and 5a) (Table 1, Entries 2, 4, 6, 8, 10, 13, 15). The microwave-assisted vinylation was performed as described under General Procedure for Classic Synthesis of 2-Acylamino-1,3-butadienes, but with controlled microwave heating in a single-mode synthesizer. The products were purified as described for the conventionally heated products.

α-Arylation of Vinyl Ether 2d with Naphthyl Triflate 1d (Table 2). A mixture of **1d** (0.028 g, 0.10 mmol), **2d** (0.025 g, 0.25 mmol), triethylamine (0.012 g, 0.12 mmol), $Pd(OAc)_2$ (0.0007 g, 0.003 mmol), and bidentate ligand (0.006 mmol) was stirred at 80 °C, in 1.5 mL of dry DMF under N_2 in a sealed process vial (for reaction time and temperature see Table 2). The conversion was determined with 2,3-dimethyl naphthalene as internal standard.

α-Vinylation of Enamide 2a with Vinyl Triflate 1a (Table 3). The reaction of **1a** and **2a** was performed as described under General Procedure for Classic Synthesis of 2-Acylamino-1,3-butadienes but on a 0.2 mmol scale (for reaction time and temperature, see Table 3). The conversion was determined with *o*-xylene as internal standard.

4-*tert*-Butylcyclohex-1-enyl trifluoromethanesulfonate (1a): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.73−5.75 (m, 1H), 2.27−2.46 (m, 2H), 2.15−2.25 (m, 1H), 1.89−2.00 (m, 2H), 1.25−1.42 (m, 2H), 0.88 (s, 9H). The ^{1}H NMR data were confirmed with COSY and HETCOR.

***N*-[1-(4-*tert*-Butyl-1-cyclohexen-1-yl)vinyl]-*N*-methylacetamide (3a):** colorless oil; eluent hexane/ethyl acetate (8/2 v/v) with silica gel; ^{1}H NMR ($CDCl_3$) δ 5.80−5.85 (m, 1H), 5.17 (s, 1H), 4.96 (s, 1H), 3.01 (s, 3H), 3.06 (s, 3H), 2.26−2.32 (m, 1H), 2.07−2.20 (m, 2H), 1.94 (s, 3H), 1.83−1.98 (m, 2H), 1.12−1.31 (m, 2H), 0.87 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 170.8, 150.4, 131.5, 127.8, 110.2, 43.7, 35.9, 32.1, 27.2, 27.1, 26.6, 23.8, 21.2;

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MS *m/z* (relative intensity 70 eV) 235 (49, M^+), 220 (95), 56 (100). Anal. Calcd for $C_{15}H_{25}NO$: C, 76.55; H, 10.71; N, 5.95. Found: C, 76.37; H, 10.51; N, 5.69.

1-[1-(4-*tert*-Butyl-1-cyclohexen-1-yl)vinyl]-2-pyrrolidinone (3b): colorless oil; eluent hexane/ethyl acetate (8/2 v/v) with silica gel: ^{1}H NMR ($CDCl_3$) δ 5.74−5.76 (m, 1H), 5.18 (s, 1H), 4.93 (s, 1H), 3.46−3.56 (m, 2H), 2.47 (t, 2H, J = 8.1 Hz), 2.22−2,30 (m, 1H), 1.98−2.18 (m, 4H), 1.81−1.92 (m, 2H), 1.08−1.30 (m, 2H), 0.83 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 174.4, 144.9, 131.3, 126.5, 108.9, 50.4, 43.5, 32.1, 31.4, 27.1, 27.0, 26.7, 23.7, 18.6; MS *m/z* (relative intensity 70 eV) 247 (18, M^+), 190 (37), 86 (100). Anal. Calcd for $C_{16}H_{25}NO$: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.43; H, 9.97; N, 5.76.

1-[1-(4-*tert*-Butyl-1-cyclohexen-1-yl)vinyl]-2-azepanone (3c): colorless oil; eluent hexane/ethyl acetate (7/3 v/v) with silica gel; ^{1}H NMR ($CDCl_3$) δ 5.77−5.82 (m, 1H), 5.15 (s, 1H) 4.90 (s, 1H), 3.36−3.42 (m, 2H), 2.57−2.63 (m, 2H), 2.27−2,35 (m, 1H), 2.09−2.20 (m, 2H), 1.83−1.94 (m, 2H), 1.64−1.83 (m, 6H), 1.13−1.31 (m, 2H), 0.85 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 175.5, 150.4, 131.2, 126.5, 108.8, 52.1, 43.6, 37.5, 32.1, 30.1, 28.7, 27.14, 27.13, 26.6, 23.8, 23.5; MS *m/z* (relative intensity 70 eV) 275 (88, M^+), 218 (56), 96 (100). Anal. Calcd for $C_{18}H_{29}NO$: C, 78.49; H, 10.61; N, 5.09. Found: C, 78.17; H, 10.40; N, 5.21.

***N*-[1-(6-Methoxy-3,4-dihydro-1-naphthalenyl)vinyl]-*N*-methylacetamide (4a):**[40] colorless oil; eluent hexane/ethyl acetate (8/2 v/v) with silica gel; ^{1}H NMR ($CDCl_3$) δ 7.29 (d, 1H, J = 8.5 Hz), 6.77 (d, 1H, J = 2.7), 6.72 (dd 1H, J = 8.5, 2.7 Hz), 6.04 (t, 1H, J = 4.9 Hz), 5.35 (s, 1H), 5.18 (s, 1H), 3.81 (s, 3H), 3.06 (s, 3H), 2.71 (t, 2H, J = 7.7 Hz), 2.25−2.31 (m, 2H), 2.15 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.0, 158.7, 147.5, 139.2, 134.8, 126.7, 126.0, 125.9, 113.9, 112.4, 111.0, 55.2, 35.3, 28.5, 23.2, 21.9; MS *m/z* (relative intensity 70 eV) 257 (70, M^+), 214 (48), 56 (100); HRMS (EI+) calcd for $C_{16}H_{19}NO_2$ (M^+) 257.1416, found 257.1416.

1-[1-(6-Methoxy-3,4-dihydro-1-naphthalenyl)vinyl]-2-pyrrolidinone (4b):[40] colorless oil; eluent hexane/ethyl acetate (8/2 v/v) with silica gel; ^{1}H NMR ($CDCl_3$) δ 7.29 (d, 1H, J = 8.4 Hz), 6.77 (d, 1H, J = 2.6), 6.72 (dd 1H, J = 8.4, 2.6 Hz), 6.04 (t, 1H, J = 4.7 Hz), 5.40 (s, 1H), 5.10 (s, 1H), 3.78 (s, 3H), 3.35 (t, 2H, J = 7.0 Hz), 2.75 (t, 2H, J = 7.8 Hz), 2.41 (t, 2H, J = 8.1 Hz), 2.25−2.32 (m, 2H), 1.82−1.91 (m, 2H); ^{13}C NMR (CD_3CN) δ 174.4, 159.7, 144.6, 139.0, 137.5, 127.5, 127.0, 125.7, 114.4, 112.1, 104.9, 55.7, 49.0, 32.8, 28.8, 23.6, 18.6; MS *m/z* (relative intensity 70 eV) 269 (100, M^+), 254 (42), 184 (26). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.64; H, 6.95; N, 5.29.

1-[1-(6-Methoxy-3,4-dihydro-1-naphthalenyl)vinyl]-2-azepanone (4c):[40] colorless oil; eluent hexane/ethyl acetate (6/4 v/v) with silica gel; ^{1}H NMR (CD_3CN) δ 7.20 (d, 1H, J = 8.5 Hz), 6.75 (d, 1H, J = 2.7), 6.69 (dd 1H, J = 8.5, 2.7 Hz), 6.05 (t, 1H, J = 4.8 Hz), 5.22 (s, 1H), 5.09 (s, 1H), 3.74 (s, 3H), 3.36−3.40 (m, 2H), 2.68 (t, 2H, J = 7.8 Hz), 2.45−2.50 (m, 2H), 2.18−2.25 (m, 2H), 1.55−1.61 (m, 4H), 1.37−1.45 (m, 2H); ^{13}C NMR (CD_3CN) δ 175.7, 159.8, 148.2, 139.5, 137.6, 128.1, 127.4, 127.3, 114.3, 112.4, 112.0, 55.8, 50.3, 38.6, 29.1, 28.7, 24.1, 23.9; MS *m/z* (relative intensity 70 eV) 297 (100, M^+), 184 (24), 96 (41). Anal. Calcd for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80; N, 4.71. Found: C, 76.50; H, 7.99; N, 4.50.

***N*-Methyl-*N*-[1-(20-oxopregna-3,5-dien-3-yl)vinyl]acetamide (5a):** pale yellow solid; eluent hexane/ethyl acetate (7/3, v/v) with silica gel; ^{1}H NMR (CD_3CN) δ 5.96 (s, 1H), 5.59−5.63 (m, 1H), 5.33 (s, 1H), 5.12 (s, 1H), 2.95 (s, 3H), 2.56−2.61 (m 1H), 2.07 (s, 3H), 1.84 (s, 3H), 0.92 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (CD_3CN) δ 209.8, 170.6, 151.4, 142.6, 130.5, 128.4, 128.1, 112.4, 64.1, 57.7, 49.0, 44.6, 39.4, 36.2, 35.6, 34.4, 32.7, 32.5, 31.7, 25.0, 23.5, 23.4, 21.9, 21.4, 19.4, 13.6. Anal. Calcd for $C_{26}H_{37}NO_2$: C, 78.94; H, 8.43; N, 3.54. Found: C, 78.77; H, 9.51; N, 3.65.

(40) The products **4a**−**c** were unstable and oxidized easily to the 1-hydroxy-1,2-dihydronaphthalene analogues or to the aromatic naphthalene analogues, specially **4a**.

1-[1-(20-Oxopregna-3,5-dien-3-yl)vinyl]-2-pyrrolidinone (5b): pale yellow solid; eluent hexane/ethyl acetate (4/6, v/v) with silica gel; ^{1}H NMR ($CDCl_3$) δ 5.93 (s, 1H), 5.52−5.55 (m, 1H), 5.30 (s, 1H), 5.02 (s, 1H), 3.49−3.61 (m, 2H), 2.49−2.57 (m, 3H), 2.13 (s, 3H), 0.93 (s, 3H), 0.64 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 209.5, 174.6, 144.8, 141.4, 128.8, 127.0, 126.6, 110.0, 63.3, 57.0, 50.6, 48.0, 44.1, 38.8, 34.8, 33.6, 31.9, 31.7, 31.54, 31.46, 24.3, 23.0, 22.8, 21.1, 19.2, 18.7, 13.3. Anal. Calcd for $C_{27}H_{37}NO_2$: C, 79.56; H, 9.15; N, 3.44. Found: C, 79.44; H, 9.03; N, 3.47.

1-[1-(20-Oxopregna-3,5-dien-3-yl)vinyl]-2-azepanone (5c): pale yellow solid; eluent hexane/ethyl acetate (4/6, v/v) with silica gel; ^{1}H NMR ($CDCl_3$) δ 5.95 (s, 1H), 5.50−5.54 (m, 1H), 5.26 (s, 1H), 4.99 (s, 1H), 3.35−3.48 (m, 2H), 2.61−2.66 (m, 2H), 2.52−2.57 (m, 1H), 2.13 (s, 3H), 0.91 (s, 3H), 0.64 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 209.7, 175.6, 150.3, 141.6, 128.8, 127.1, 126.6, 110.1, 63.8, 57.1, 52.2, 48.1, 44.2, 38.9, 37.6, 34.9, 33.7, 32.1, 31.8, 31.7, 30.2, 28.7, 24.5, 23.7, 22.88, 22.87, 21.2, 19.2, 13.4. Anal. Calcd for $C_{29}H_{41}NO_2$: C, 79.95; H, 9.49; N, 3.22. Found: C, 79.75; H, 9.28; N, 3.18.

Bis[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)phenyl]-phosphine Oxide (8c). To a 250 mL, three-neck flask with *t*-BuLi (17.7 mL, 1.7 M in pentane, 30.0 mmol) at −78 °C was added dropwise a solution of 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phenyl bromide (**7c**, 7.54 g, 15.0 mmol) in dry diethyl ether (100 mL). After the addition was complete, the mixture was warmed to 0 °C in 30 min. Diethylphosphoramidous dichloride (1.0 mL, 13.5 mmol) was then added slowly to the reaction mixture at 0 °C. The resulting mixture was further stirred at 0 °C overnight. Concentrated aqueous hydrogen chloride (2.0 mL, 24.0 mmol) was then added and the mixture was stirred at room temperature for 4 h. The reaction was quenched by adding H_2O (50 mL). The ether layer was separated and the aqueous layer was further extracted with ether (50 mL) three times. The combined ether layers were washed with brine and dried over magnesium sulfate. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 10:1) and further purified by recrystallization from pentane to give product **8c** (4.68 g, 78%) as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (tt, J = 18.0, 8.7 Hz, 4H), 2.96−3.02 (m, 4H), 7.38 (dd, J = 8.1, 2.1 Hz, 4H), 7.67 (dd, J = 13.8, 8.1 Hz, 4H), 8.08 (d, J = 481.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.6, 32.5 (t, J_{FC} = 22.5 Hz), 105.2−121.3 (m, C_6F_{13}), 129.0 (d, J_{PC} = 12.0 Hz), 129.9 (d, J_{PC} = 105.0 Hz), 131.3 (d, J_{PC} = 11.5 Hz), 144.3; ^{19}F NMR (282.5 MHz, $CDCl_3$) δ −125.0 (4F), −122.3 (4F), −121.7 (4F), −120.7 (4F), −113.4 (4F), −79.6 (6F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 21.4 (s); FAB-MS *m/z* 895 $(M + H)^+$; HRMS (FAB) for $C_{28}H_{18}F_{26}OP$ $(M + H)^+$ calcd 895.0680, found 895.0672. Anal. Calcd for $C_{28}H_{18}F_{26}OP$: C, 37.60; H, 1.92. Found: C, 37.67; H, 1.96.

Bis[4-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)phenyl]phosphine Oxide (8a). This was synthesized in a manner similar to **8c**. Diethylphosphoramidous dichloride (1.0 mL, 6.87 mmol) and **7a** (5.60 g, 13.9 mmol) were used to yield **8a** (3.43 g, 72%) as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (tt, J = 18.1, 8.6 Hz, 4H), 2.96−3.02 (m, 4H), 7.37 (dd, J = 8.1, 2.1 Hz, 4H), 8.08 (d, J = 481.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.5, 32.3 (t, J_{FC} = 22.0 Hz), 104.7−123.5 (m, C_4F_9), 129.0 (d, J_{PC} = 13.0 Hz), 130.4, 131.3 (d, J_{PC} = 11.7 Hz), 144.2 (d, J_{PC} = 2.4 Hz); ^{19}F NMR (282.5 MHz, $CDCl_3$) δ −124.8 (4F), −123.2 (4F), −113.6 (4F), −79.8 (6F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 21.4 (s); EIMS *m/z* 694 (M^+), 447, 371; HRMS for $C_{24}H_{17}OF_{18}P$ calcd 694.0730, found 694.0742.

Bis[3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phenyl]-phosphine Oxide (8b).[31] This was synthesized in a manner similar to **8c**. Diethylphosphoramidous dichloride (0.86 g, 4.92 mmol) and **7b** (4.95 g, 9.84 mmol) were used to yield **8b** (2.68 g, 61%) as white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.25−2.45 (m, 4H), 2.51−2.56 (m, 4H), 7.46−7.75 (m, 8H), 8.10 (d, J = 480.0 Hz, 1H).

1,3-Bis{bis(4-[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-phenyl]phosphino}propane (6c). Bis[4-(3,3,4,4,5,5,6,6,7,7,-8,8,8-tridecafluoroocty)phenyl]phosphine oxide **8c** (2.38 g, 2.66 mmol) was dissolved in dry THF (15 mL) in a 50 mL three-neck flask. To this solution sodium hydride (0.106 g, 60% on oil, 2.66 mmol) was added at room temperature under argon. The resulting mixture was stirred at room temperature for 30 min. A solution of 1,3-dibromopropane (268.9 mg, 1.33 mmol) in THF (1 mL) was then added to the reaction solution slowly. The resulting mixture was stirred at room temperature for 4 h. The reaction was quenched by adding water. THF was partially removed under vacuum. The residue was extracted with ethyl acetate three times. The combined ethyl acetate layers were dried over magnesium sulfate. The solvent was then removed. The residue was dried under vacuum overnight before it was mixed with freshly distilled xylene (35 mL). To this mixture, trichlorosilane (1.1 mL) and triethylamine (1.5 mL) were added under argon. The mixture was stirred at 100 °C for 1 h, 110 °C for 1 h, and then refluxed for 6 h. The reaction solution was then cooled to room temperature and 30% sodium hydroxide aqueous solution (30 mL) was added. The resulting mixture was then stirred at 60 °C until both layers were clear. The organic layer was separated and the aqueous layer was further extracted with toluene three times. The combined organic layers were dried over magnesium sulfate. The solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 50:1) to give product **6c** (1.34 g, 56%) as white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63 (q, J = 6.6 Hz, 2H), 2.23 (t, J = 7.5 Hz, 4H), 2.38 (tt, J = 18.1, 9.3 Hz, 8H), 2.89−2.95 (m, 8H), 7.18 (d, J = 7.5 Hz, 8H), 7.33−7.37 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.4 (t, J = 16.5 Hz), 26.2, 29.6 (t, J = 11.6 Hz), 32.8 (t, J = 21.9 Hz), 104.7−123.0 (m, C_6F_{13}), 128.4 (d, J = 6.5 Hz), 133.2 (d, J = 18.5 Hz), 136.7 (d, J = 11.6 Hz), 139.8; ^{19}F NMR (282.5 MHz, $CDCl_3$) δ −124.8 (8F), −121.8 (8F), −121.5 (8F), −120.8 (8F), −113.7 (8F), −79.8 (12F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −18.2 (s); FAB-MS m/z 1797 $(M + H)^+$. Anal. Calcd for $C_{59}H_{38}F_{52}P_2$: C, 39.44; H, 2.13. Found: C, 39.63; H, 2.21.

1,3-Bis{bis-[4-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)phenyl]-phosphino}propane (6a). This was synthesized in a manner similar to **6c**. Compound **8a** (1.25 g, 1.80 mmol) was used to yield **8b** (0.642 g, 51%) as colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63 (q, J = 6.9 Hz, 2H), 2.23 (t, J = 7.2 Hz, 4H), 2.38 (tt, J = 18.0, 9.0 Hz, 8H), 2.89−2.95 (m, 8H), 7.18 (d, J = 7.8 Hz, 4H), 7.33−7.38 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.4, 26.4, 29.5 (t, J = 11.9 Hz), 32.8 (t, J = 21.7 Hz), 107.2−123.3 (m, C_4F_9), 128.7 (d, J = 7.1 Hz), 133.3 (d, J = 18.3 Hz), 136.1 (d, J = 9.0 Hz), 140.2; ^{19}F NMR (282.5 MHz, $CDCl_3$) δ −124.5 (8F), −123.3 (8F), −113.7 (8F), −79.9 (12F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −18.1 (s); EIMS m/z 1396 (M^+), 1073. Anal. Calcd for $C_{51}H_{38}F_{36}P_2$: C, 43.86; H, 2.74. Found: C, 43.80; H, 2.60.

1,3-Bis{bis[3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-phenyl]phosphino}propane (6b). This was synthesized in a manner similar to **6c**. Compound **8b** (0.81 g, 0.90 mmol) was used to yield **6b** (0.46 g, 57%) as colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.78−1.84 (m, 2H), 2.34−2.54 (m, 12H), 2.96−3.01 (m, 8H), 7.27−7.39 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.8 (t, J_{FC} = 17.4 Hz), 26.6, 29.7 (d, J_{PC} = 12.2 Hz), 33.0 (t, J_{FC} = 22.0 Hz), 105.0−121.6 (m, C_6F_{13}), 128.8, 129.1 (d, J_{PC} = 5.8 Hz), 131.1 (d, J_{PC} = 16.3 Hz), 133.1 (d, J_{PC} = 20.8 Hz), 139.4 (d, J_{PC} = 16.4 Hz), 139.7 (d, J_{PC} = 7.2 Hz); ^{19}F NMR (282.5 MHz, $CDCl_3$) δ −122.2 (8F), −119.2 (8F), −118.7 (8F), −117.7 (8F), −110.4 (8F), −77.4 (12F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −16.2 (s); FAB-MS m/z 1796 (M^+), 1373, 919. Anal. Calcd for $C_{59}H_{38}F_{52}P_2$: C, 39.44; H, 2.13. Found: C, 39.33; H, 2.32.

1,3-Bis{bis-[3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroocty)-phenyl]phosphinoxide}propane (9): dioxidized **6b**, pale red oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.91−2.10 (m, 2H), 2.21−2.58 (m, 12H), 2.83−3.01 (m, 8H), 7.33−7.70 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.8, 26.4 (t, J_{FC} = 4.3 Hz), 30.0 (d, J_{PC} = 71.0 Hz), 32.5 (t, J_{FC} = 22.0 Hz), 105.0−124.0 (m, C_6F_{13}), 128.8 (d, J_{PC} = 10.4 Hz), 129.1 (d, J_{PC} = 12.2 Hz), 130.6 (d, J_{PC} = 8.5 Hz), 132.0 (d, J_{PC} = 2.4 Hz), 133.0 (d, J_{PC} = 98.3 Hz), 140.0 (d, J_{PC} = 11.0 Hz); ^{19}F NMR (282.5 MHz, $CDCl_3$) δ −122.8 (8F), −120.0 (8F), −119.5 (8F), −118.5 (8F), −111.2 (8F), −77.4 (12F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 38.7 (s); HRMS (FAB) for $C_{59}H_{39}F_{52}O_2P_2$ $(M + H)^+$ calcd 1829.1595, found 1829.1590.

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