

# On the Tacticity of Polynorbornenes with 5,6-*endo* Pendant Groups That Contain Substituted Aryl Chromophores

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In memory of Yoshihiko Ito

**Abstract:** Two dimers and a series of polymers with 5,6-*endo* pendant aryl groups that contain different substituents at the *para* positions were synthesized. The conformation and stereochemistry of the dimers and polymers were determined by nonlinear optical analysis (EFISH) as well as UV/Vis and <sup>13</sup>C NMR spectroscopy. The chemical shifts of C7 for the polymers appeared as two peaks in the <sup>13</sup>C NMR

spectra when the substituents are electron-withdrawing groups. The percentage decrease in the relative extinction coefficient of the polymers,  $\epsilon_d$ , was linearly related to the Hammett constant  $\sigma$ . Polynorbornenes with electron-with-

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drawing substituents may adopt isotactic stereochemistry with all pendant groups aligned in one direction. The nature of the interactions between neighboring chromophores may be one of the most important factors in directing the stereoregularity and conformation of these polymers. The corresponding polymers derived from the *exo* isomers appeared to be less stereoregular.

## Introduction

We recently reported an unprecedented approach for the synthesis of DNA-like double-stranded polymer **2** by Grubbs I catalyst (**1**)-promoted ring-opening metathesis polymerization (ROMP) of bisnorbornene derivative **3** (Scheme 1).<sup>[1]</sup> The key to the success of this strategy lies in

the rigid rodlike structure and stereochemical homogeneity of the polymer. It has been shown that the single-stranded polynorbornenes **4** with dipolar pendant groups at the C5 and C6 positions<sup>[2]</sup> may adopt rigid rod structures.<sup>[3]</sup> The stereochemistry of simple polynorbornenes has been extensively examined, and it appears that the nature of the catalyst and the structure of the monomeric norbornenes may influence the tacticity and the double-bond configurations of the polymers.<sup>[4–11]</sup> To illustrate this, molybdenum-catalyzed ROMP of norbornenes gives mainly *cis* double bonds and isotactic selectivity.<sup>[7]</sup> Recently, ROMPs of norbornadiene diester and *exo,exo*-2,3-dicarbomethoxy-5-norbornene with a ruthenium catalyst reportedly gave isotactic polymers with mainly *trans* double bonds.<sup>[8]</sup> It has been shown that catalyst **1** yields predominantly *trans* double bonds in polynorbornenes.<sup>[9]</sup> However, the tacticity of the polymers varies with substrate.<sup>[4–11]</sup> <sup>13</sup>C NMR spectra have been widely used for the elucidation of the tacticity of these polymers.<sup>[10]</sup> Thus, polymer **4** was shown to assume mainly isotactic stereochemistry,<sup>[8]</sup> whereas **5** is atactic.<sup>[11]</sup> In a preliminary communication, we showed that **6** exhibits molecule-dependent nonlinear optical  $\beta_o$  values,<sup>[3]</sup> which may imply that **6** may adopt homogeneous stereochemistry and conformation. Although **5** and **6** are structurally similar with pendant *endo* nitrogen heterocycles, the imide ring in **5** and the pyrrolidine moiety in **6** may behave differently under these ruthenium-

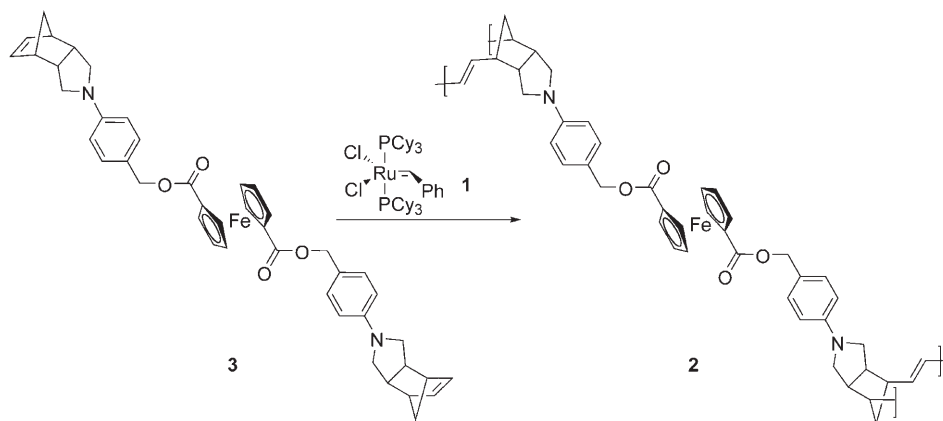
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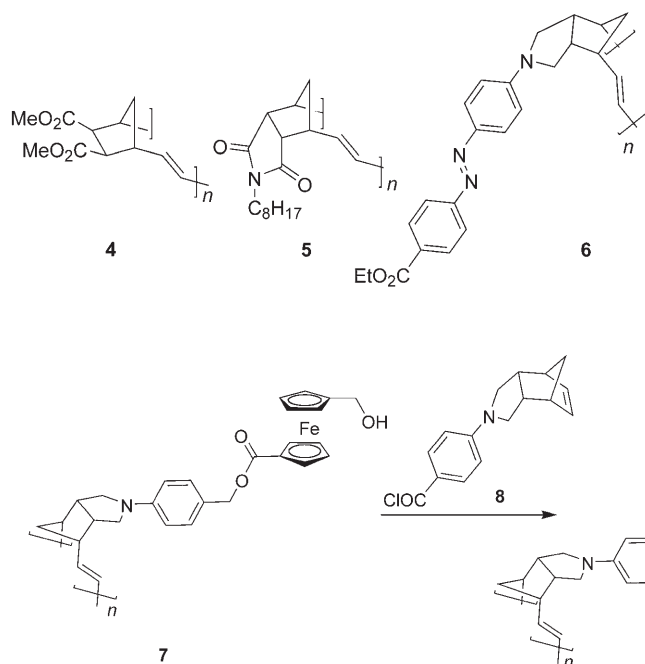
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Scheme 1. ROMP of **3** to give double-stranded polymer **2**. Cy=cyclohexyl.



Scheme 2. Replication of **7** to give complementary polymer **10**.

#### Abstract in Chinese:

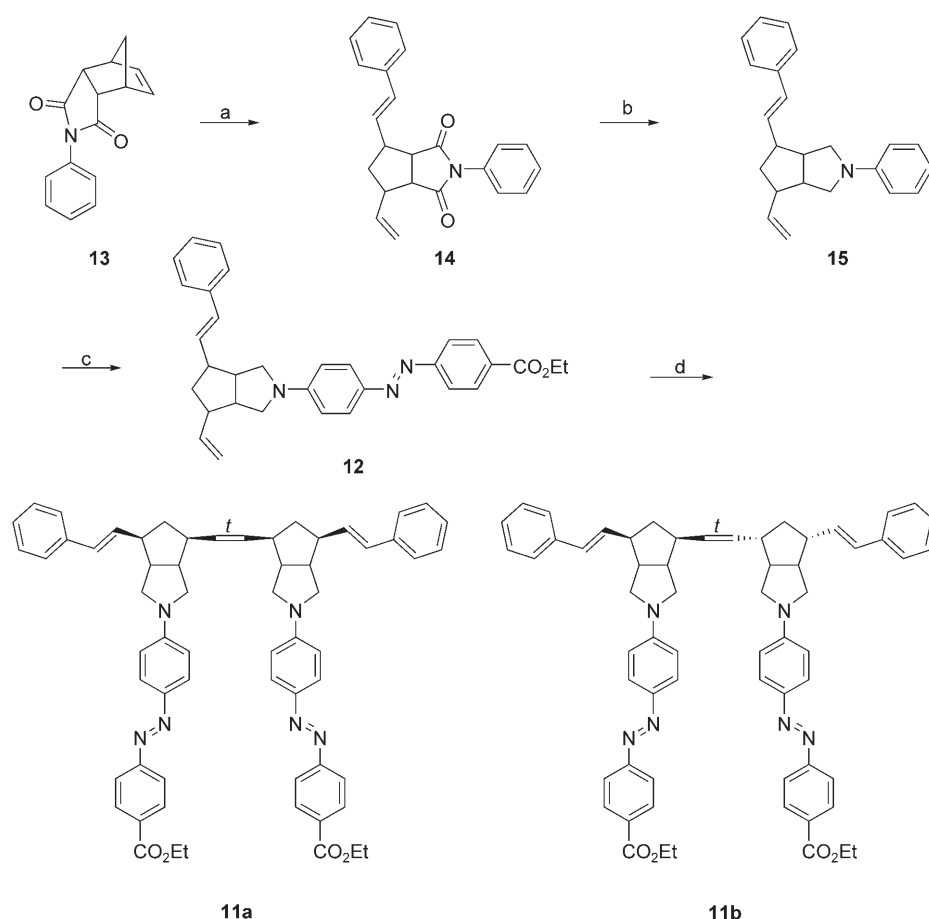
我們利用開環複分解聚合反應，合成了含5, 6-*endo*具不同取代基苯基的懸掛基團降冰片烯的二聚物和一系列的聚合物，透過非線性光學性質 (EFISH)，吸收光譜，以及碳譜確認其立體化學。從聚合物的碳譜中可以看出，當苯環有拉電子取代基時，C7的信號出現兩個峰。聚合物的相對消光係數減少的百分數  $\epsilon_r$  與 Hammett 常數  $\sigma$  成線性關係。含有吸電子取代基的降冰片烯聚合物可能採取全同立構的立體化學，且所有懸掛基團朝向同一方向。相鄰發色團之間的相互作用，可能是導致聚合物採取這種立體規整性的主要因素。

catalyzed conditions. Furthermore, the presence of the *N*-aryl pendant groups in **6** may be an important factor because they may interact with the neighboring aryl pendant group. It is envisaged that such interaction may depend on the nature of the aromatic rings. Hence, the substituent on these aryl pendant groups may influence the mode of these interactions. More recently, we found that single-stranded polymer **7** can serve as a template to accommodate monomeric norbornene moiety **8**, leading to **9**. ROMP of **9** followed by hydrolysis and esterification yields the corresponding complementary polymer **10** with an isotactic structure (Scheme 2).<sup>[12]</sup> This finding indicates that polynorbornenes such as **7** should adopt homogeneous tacticity. We now report a systematic investigation into the tacticity of **6** and its related polymers, which have a range of different aryl pendant groups.

## Results and Discussion

### Dimers

To begin, dimers **11** were synthesized according to Scheme 3. Notably, the Grubbs II catalyst was necessary to promote the cross-metathesis leading to **11**. The two stereoisomers (**11a**: 46%; **11b**: 25%) were separated and their photophysical properties were measured (Table 1). The absorption maxima for the dimers **11** and monomer **12** are similar. Interestingly, the  $\mu\beta$  values obtained by the EFISH (electric-field-induced second harmonic) method<sup>[13,14]</sup> for both **11a** and **11b** were significantly enhanced (Table 1). These results indicate that the pendant groups in **11a** and **11b** may align essentially toward a similar direction or adopt *syn* conformations. The IR absorption band at around 960 cm<sup>-1</sup> suggests that the double bonds in both **11a** and



Scheme 3. Synthesis of dimers **11**. a) Styrene, **1**, CH<sub>2</sub>Cl<sub>2</sub>, 24 h, 75%; b) LiAlH<sub>4</sub>, diethyl ether/CH<sub>2</sub>Cl<sub>2</sub> (2:1), 84%; c) ethyl 4-aminobenzoate, HNO<sub>2</sub>, 93%; d) **16**, CH<sub>2</sub>Cl<sub>2</sub>, 24 h, 71%. *t*=*trans* double bond.

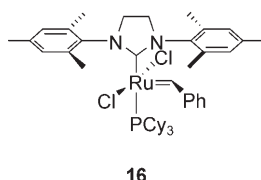


Table 1. Absorption maxima and EFISH<sup>[a]</sup> data of **11a**, **11b**, and **12**.

Compound	$\lambda_{\max}$ [nm] ( $\epsilon$ [g <sup>-1</sup> cm <sup>2</sup> ])	$\mu\beta^{[a]}$ [10 <sup>-46</sup> esu]	$\mu\beta_0^{[b]}$ [10 <sup>-46</sup> esu]	$\mu\beta_0$ ( <b>11</b> )/ $\mu\beta_0$ ( <b>12</b> )
<b>12</b>	441 (28.0)	3.8	2.7	1
<b>11a</b>	440 (27.4)	6.1	4.3	1.6
<b>11b</b>	400 (27.5)	5.3	3.8	1.4

[a] All  $\mu\beta$  values were measured in chloroform at 1907 nm. [b]  $\mu\beta_0$  values were deduced from the experimental values by using a two-level dispersion model.<sup>[13,14]</sup>

**11b** have a *trans* configuration. The large <sup>1</sup>H NMR coupling constant ( $J=15.1$  Hz) for the two olefinic protons of **11a** further supports this argument. The <sup>13</sup>C NMR spectrum for **11a** has seven pairs of signals at high field, whereas that for **11b** has only seven peaks. These results suggest that **11a** has C<sub>1</sub> symmetry and, therefore, is isotactic. On the other hand,

**11b** has C<sub>2</sub> symmetry and, hence, is syndiotactic.<sup>[15]</sup> These results provide a useful hint for the elucidation of the tacticity of the polymers as described later.

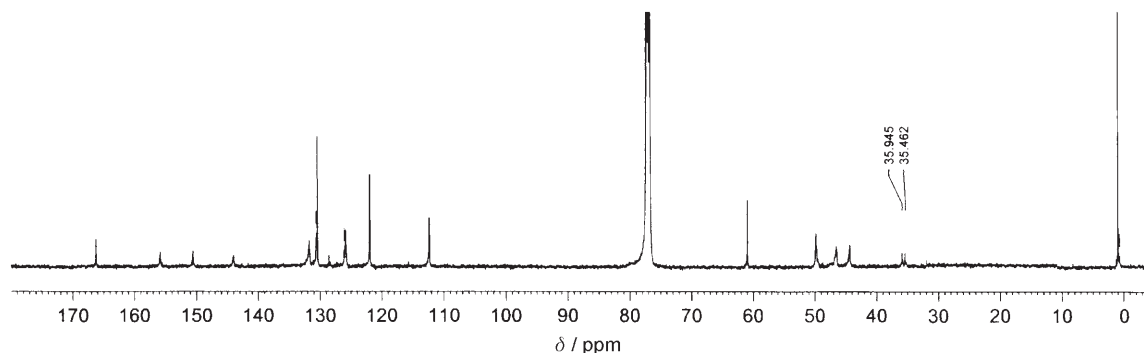
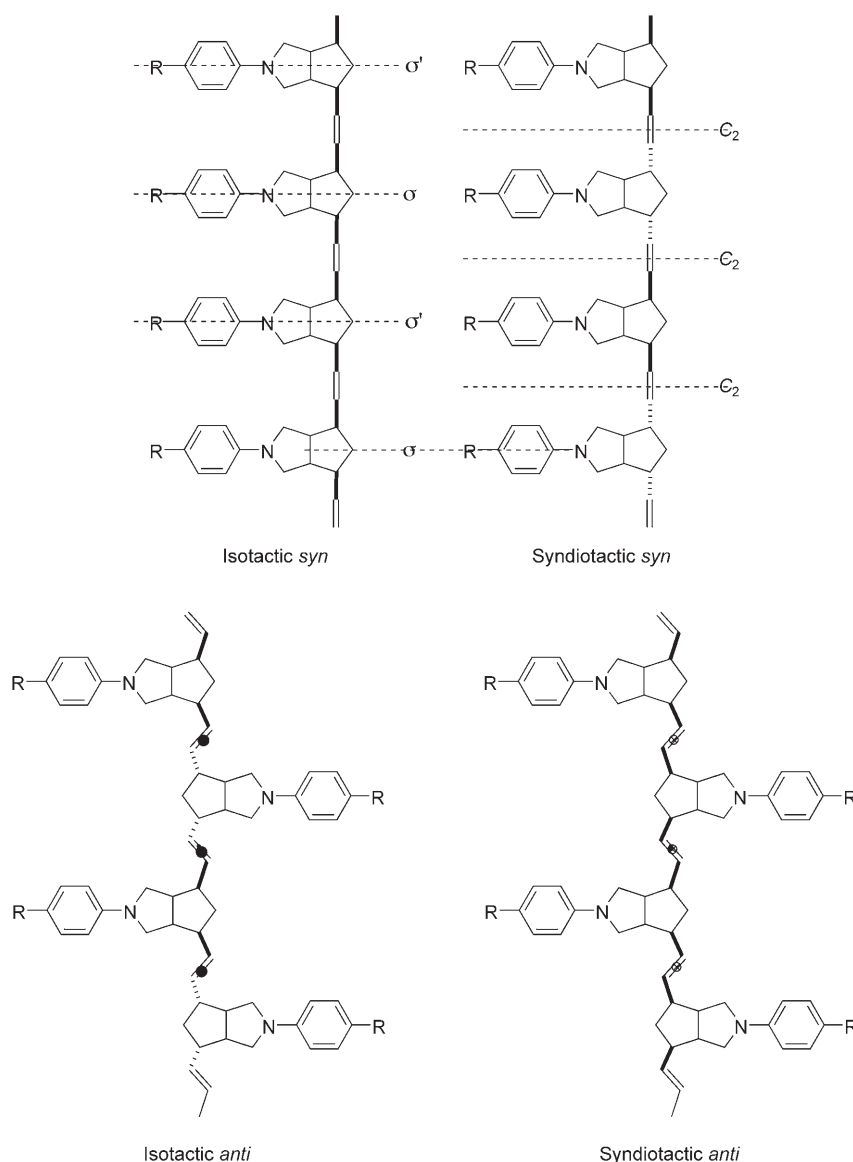
X-ray analysis of **14** suggested that the distance between the two olefinic moieties is 5–6 Å,<sup>[3b]</sup> and STM of **2** showed that the Fe–Fe distance is 5–5.5 Å.<sup>[1]</sup> It is therefore envisaged that each of the monomeric units in **2** and its related polymers may also occupy a similar amount of space. Rotation along the carbon–nitrogen bond in **11** may bring two neighboring arene moieties closer so that interaction between these chromophores might take place.

### Polymer 6

We previously showed that **6** may adopt homogeneous tacticity based on its spectroscopic data and nonlinear optical properties.<sup>[3]</sup> As described above, the stereochemistry of dimers **11** were established with the help of <sup>13</sup>C NMR spectroscopy. Interestingly, two peaks of equal intensity at 35.46 and 35.95 ppm attributed to C7<sup>[2]</sup> were observed in the <sup>13</sup>C NMR spectrum of **6** (Figure 1). This observation suggests that there are two

types of nonequivalent C7 atoms in **6**.

As described previously, polynorbornenes obtained by ROMP with the Grubbs I catalyst have double bonds in *trans* configurations.<sup>[3,9]</sup> The dipolar pendant groups are coherently aligned in the *syn* configuration.<sup>[3]</sup> Scheme 4 shows the possible structures of the isotactic and syndiotactic polymers **6**. For *syn* conformations, the syndiotactic structure has a C<sub>2</sub> symmetry axis bisecting the carbon–carbon double bond. As such, the environments for each of the neighboring monomeric units are the same, and only one set of <sup>13</sup>C NMR signals would be expected. In the isotactic structure, on the other hand, there is a plane of symmetry perpendicular to the polymeric backbone and bisecting each monomeric unit. However, the two planes of symmetry ( $\sigma$  and  $\sigma'$ ) in two neighboring units are different; therefore, two sets of <sup>13</sup>C NMR signals would be anticipated. For *anti* conformations, the isotactic structure has the center of inversion (*i*) at

Figure 1.  $^{13}\text{C}$  NMR spectrum of polymer **6**.Scheme 4. Possible conformations of isotactic and syndiotactic polymers **6**.

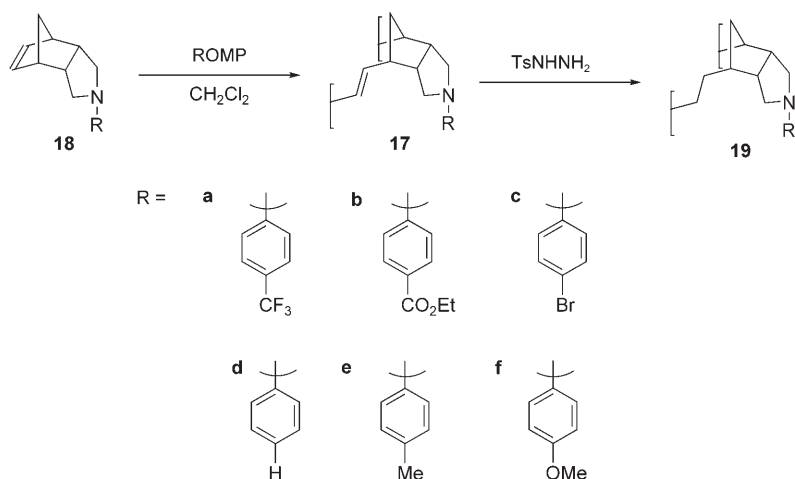
the center of the carbon–carbon double bond, whereas the syndiotactic form has the  $C_2$  rotation axis perpendicular to the polymeric backbone and orthogonal to the correspond-

ing  $C_2$  axis of the *syn* conformation. One might expect that both structures with *anti* conformation would show only one set of  $^{13}\text{C}$  NMR signals.

On the basis of this analysis, it seems likely that polymer **6** adopts isotactic stereochemistry. It is believed that interactions between pendant chromophores may play an important role in dictating the stereochemistry of the polynorbornenes. Interaction between these chromophores may depend on the relative electron demand of the aromatic rings. The substituents on these aryl pendant groups may influence the mode of such interactions, which may result in changes in the stereochemistry of the polymer. Accordingly, a series of polymers **17** with different substituents at the *para* position of the pendant phenyl groups were synthesized (Scheme 5). Different number-average molecular weights ( $M_n$ ) for **17** were obtained.<sup>[4,5]</sup> Table 2 summarizes the selected photophysical properties of these polymers.

#### Absorption Properties of **17**

As is the case with the polynorbornenes **6** with azo pendant groups,<sup>[3]</sup> the  $\lambda_{\text{max}}$  values of **17** also consistently appeared at shorter wavelengths relative to those of the corresponding monomers **18**, and the UV/Vis absorption profiles remained unchanged with changes in concentration. In gen-

Scheme 5. Synthesis of saturated polymer **19**. Ts = tosyl.Table 2. Absorption data of monomers **18a–f** and polymers **17a–f** of different molecular weights.

Compound <sup>[a]</sup>	$M_n$	PDI <sup>[b]</sup>	$n$	$\lambda_{\max}$ [nm]	$\epsilon$ [g <sup>-1</sup> cm <sup>2</sup> ]	$\epsilon_d$
<b>18a</b>	279		1	273	83.1	
<b>17a-1</b>	6999	1.17	25	270	43.5	47.6
<b>17a-2</b>	10901	1.18	39	270	27.7	66.7
<b>17a-3</b>	18114	1.31	65	270	16.0	80.7
<b>18b</b>	283		1	317	122.5	
<b>17b-1</b>	9888	1.20	35	313	103.7	15.3
<b>17b-2</b>	15658	1.32	55	313	98.8	19.3
<b>17b-3</b>	28152	1.49	99	313	98.4	19.6
<b>18c</b>	289		1	268	64.3	
<b>17c-1</b>	5531	1.13	19	265	41.8	35.0
<b>17c-2</b>	9593	1.35	25	265	36.1	43.8
<b>17c-3</b>	21421	1.05	74	265	32.6	49.3
<b>18d</b>	211		1	260	75.1	
<b>17d-1</b>	7669	1.13	36	256	61.1	18.6
<b>17d-2</b>	9958	1.25	47	256	57.3	23.6
<b>17d-3</b>	12485	1.17	59	256	55.9	25.5
<b>18e</b>	225		1	257	63.8	
<b>17e-1</b>	5249	1.11	23	255	56.6	11.2
<b>17e-2</b>	7236	1.15	32	255	55.6	12.9
<b>17e-3</b>	12985	1.06	58	255	55.5	13.0
<b>18f</b>	241		1	253	61.4	
<b>17f-1</b>	10041	1.52	42	251	55.7	9.2
<b>17f-2</b>	13048	1.42	54	251	54.9	10.7
<b>17f-3</b>	16253	1.33	67	251	54.3	11.5

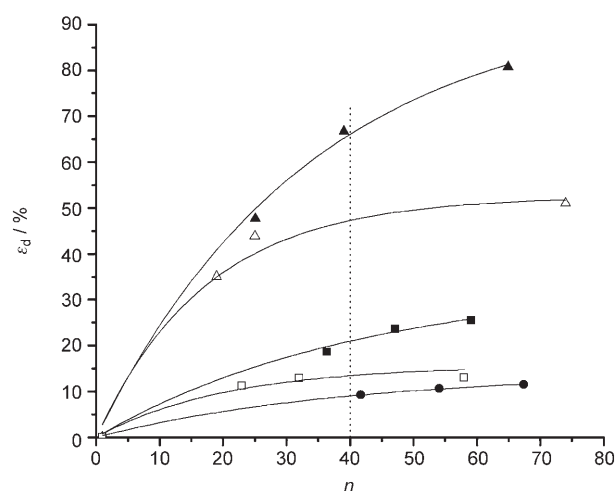
[a] Numbers after the dashes denote polymers of different  $M_n$ . [b] PDI = polydispersity index ( $M_w/M_n$ ).

eral, with the exception of **17b** and **18b**, monomers **18** and polymers **17** exhibited both *E* and *B* bands at 250–270 and 310–330 nm, respectively. These two bands, however, merged into one for **17b** and **18b** at around 313 nm. In all cases, the extinction coefficients (g<sup>-1</sup>cm<sup>2</sup>) of **17** decreased with an increase in the degree of polymerization. The percentage decrease in the relative extinction coefficient of the polymer,  $\epsilon_d$ , is defined in [Eq. (1)]:

$$\epsilon_d = [1 - (\epsilon_p/\epsilon_m)] \times 100 \quad (1)$$

in which  $\epsilon_p$  and  $\epsilon_m$  are the extinction coefficients (g<sup>-1</sup>cm<sup>2</sup>)

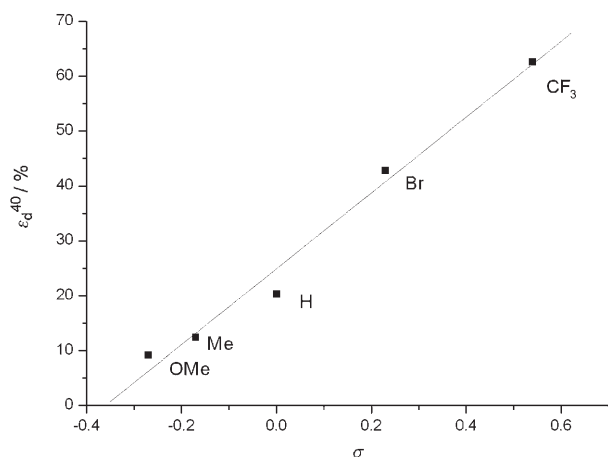
for **17** and the corresponding monomer **18**, respectively. The  $\epsilon_d$  values at 250–270 nm for **17a–f** were thus obtained, and the results are summarized in Table 2.<sup>[16]</sup> A plot of these  $\epsilon_d$  values of **17** for a given substituent against the average number of repeating units,  $n$  ( $15 < n < 99$ ), is shown in Figure 2.<sup>[16]</sup> Interestingly, the  $\epsilon_d$  values are larger for polymers with electron-withdrawing substituents and smaller for those with electron-donating substituents. From these plots, a

Figure 2. Plots of the  $\epsilon_d$  values of **17** against the average number of repeating units  $n$ . Substituents:  $\blacktriangle$  = CF<sub>3</sub>,  $\triangle$  = Br,  $\blacksquare$  = H,  $\square$  = Me,  $\bullet$  = OMe.

series of  $\epsilon_d^{40}$  values for **17a–f** with 40 repeating units were estimated by intra- or extrapolations (Figure 2, dotted line). As shown in Figure 3, the Hammett plot<sup>[17]</sup> of these  $\epsilon_d^{40}$  values gave a good linear relationship ( $R^2 = 0.992$ ). These results indicate that interchromophore interactions among the pendant groups of **17** are more important for those with electron-withdrawing rather than electron-donating substituents.

The pyrrolidine moiety in **17** is a strongly electron donating group. When the other substituent on the aromatic ring in **17** is also an electron-donating group, the aromatic rings would be highly electron-rich. As such, the modes of interaction between such electron-rich chromophores may be different from those with electron-withdrawing substituents. Such differences may lead to discrepancies in the  $\epsilon_d$  values due to the nature of the substituents.

It is known that substituents on phenylene ethynylene macrocycles and related cyclic conjugated systems may have

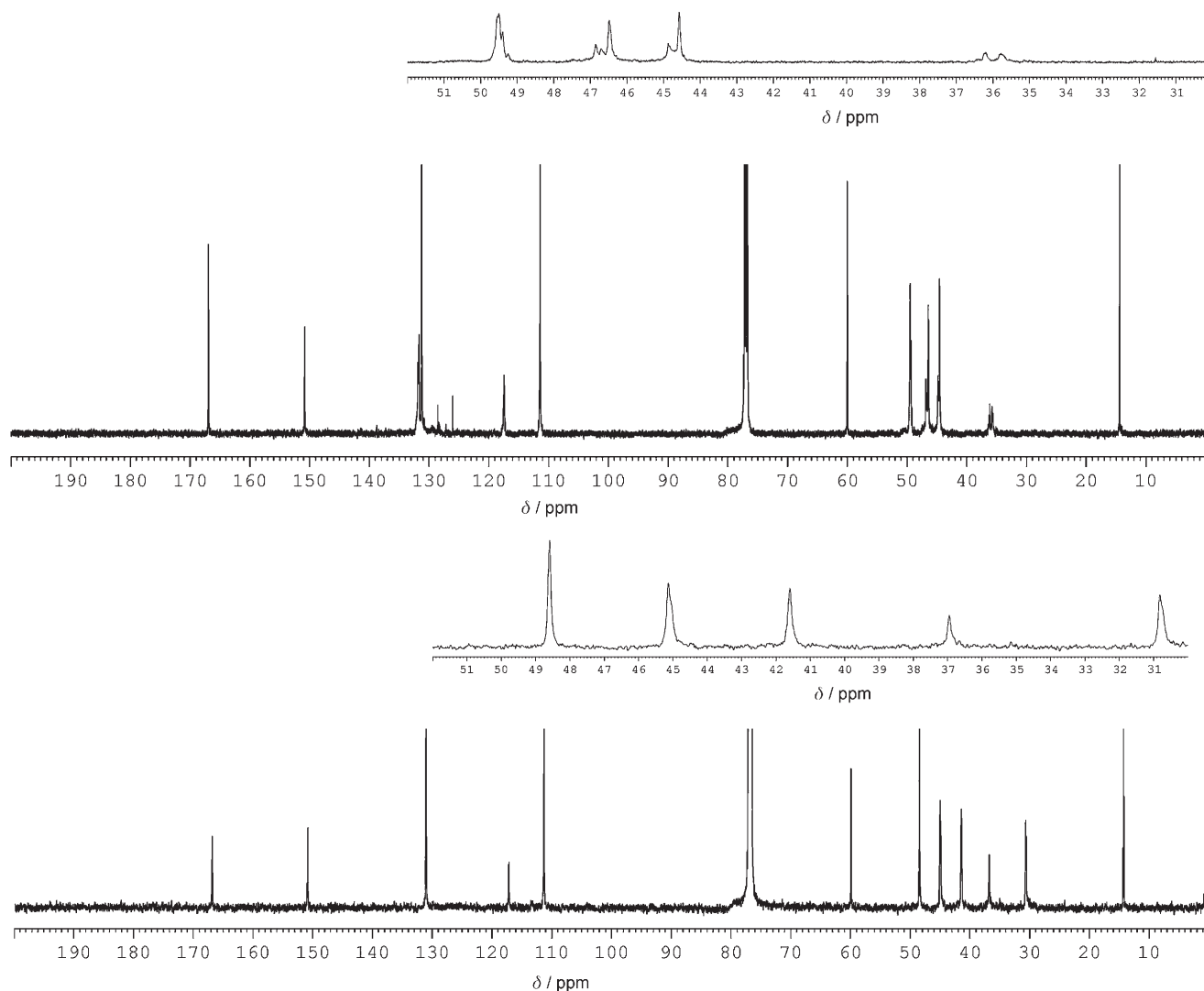
Figure 3. Hammett plot of the  $\epsilon_d^{40}$  values of **17**.

a direct influence on  $\pi$ -stacking tendency.<sup>[18,19]</sup> In general, electron-withdrawing groups such as the ester function may

favor  $\pi$ -stacking interactions, whereas such aggregation may become less favorable in those substrates with electron-donating substituents such as alkoxy groups.<sup>[19]</sup> Although the quantitative relationship remains to be clarified, our results on polynorbornenes may be compatible with those in the literature<sup>[18,19]</sup> in which interactions between the chromophores may be substituent-dependent. For electron-withdrawing substituents, such interactions may be more important. Therefore, the pendant chromophores in these polymers (e.g., **17a–c**) may align coherently in similar directions. Powder X-ray analysis of **17b** suggested that the polymer is amorphous, with a broad peak at  $2\theta = 18.76^\circ$ .

#### Effect of Substituent on the $^{13}\text{C}$ NMR Spectrum of **17**

Figure 4 shows the  $^{13}\text{C}$  NMR spectra of **17b** and the corresponding hydrogenated polymer **19b**. The simplicity of the spectrum for **19b** suggests that this polymer may adopt a single tacticity.<sup>[10,11]</sup> As with the spectrum of **6**, the high-field signals assigned to C7<sup>[2]</sup> for **17b** occur as two peaks of equal

Figure 4.  $^{13}\text{C}$  NMR spectra of a) **17b** and b) **19b**. Insets: Corresponding expanded high-field region.

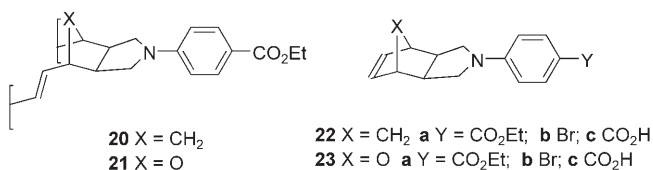


intensity at 35.75 and 36.21 ppm. These signals are independent of the degree of polymerization. In a similar manner, the signals for this carbon atom of **17a** (35.63 and 36.12 ppm) and **17c** (35.56 and 35.80 ppm) also show two peaks at high field. Interestingly, the separation of these two peaks ( $\Delta\delta$ ) is substituent-dependent. The more strongly electron withdrawing group gave a larger  $\Delta\delta$  value. On the other hand, the  $^{13}\text{C}$  NMR signals of C7 for **17d–f** with electron-donating substituents or hydrogen appeared as a single peak ( $\Delta\delta = 0$  ppm).

The change in  $\Delta\delta$  with substituents is interesting. For polymers **17a–c** with electron-withdrawing substituents,  $\pi$ -stacking interactions between neighboring aromatic chromophores may be significant. Accordingly, on the basis of the structures shown in Scheme 4, it seems likely that these polymers may adopt the isotactic structure with *syn* conformation. As the substituents become more electron-donating, such  $\pi$ -stacking tendencies would become less important. Interactions between two neighboring aromatic rings in such polymers (those with electron-donating substituents) may, therefore, be unfavorable. These tendencies may lead to conformational changes or even perturbation of the stereoregularities in polynorbornenes.

### Polymers from *exo*-Norbornene Derivatives

Polymers **20** and **21**, derived from the corresponding *exo* isomer **22a** and the corresponding furan adduct **23a**, respec-



tively, were prepared for comparison. Interestingly, both **20** and **21** may contain both *cis* and *trans* double bonds. Furthermore, the extinction coefficients of **20** and **21** are essentially the same as those of **22a** and **23a**, respectively. These results indicate that the stereoselectivity for polymerization of the *exo* derivatives of norbornene and related skeletons may not be as good as those of the corresponding *endo* isomers.

### Conclusions

A series of polynorbornenes with aryl substituents on the 5,6-*endo* pendant groups has been synthesized by Grubbs I catalyst mediated ROMP of the corresponding norbornene monomers. The tacticity of these polymers and the related dimers has been examined by UV/Vis and  $^{13}\text{C}$  NMR spectroscopy, and their nonlinear optical properties have been probed. The results suggest that polynorbornenes that contain aryl groups with electron-withdrawing substituents may

adopt isotactic stereochemistry with all the pendant groups aligned in one direction. Interaction between these chromophores may take place in these polymers. Such interaction may also be important in directing the stereochemistry of the polymer during the course of the ROMP process of norbornenes with aryl pendant groups. More importantly, the present work echoes our previous successful synthesis of double-stranded polymers<sup>[1]</sup> because of the nice coherent alignment of the pendant groups and the homogeneous tacticity in the polymerization of norbornene derivatives. The corresponding polymers derived from the *exo* isomers appeared less stereoregular.

## Experimental Section

### General

Gel permeation chromatography (GPC) was performed on a Waters GPC machine with an isocratic HPLC pump (1515) and a refractive-index detector (2414). THF was used as the eluent (flow rate = 1.0 mL min<sup>-1</sup>). Waters Styragel HR2, HR3, and HR4 columns (7.8 × 300 mm) were employed for determination of relative molecular weight with polystyrene as standard ( $M_n$  values ranged from 375 to 3.5 × 10<sup>6</sup>).

### EFISH Measurements

EFISH measurements were taken with a nonlinear optical spectrometer from SOPRA. The fundamental wavelength at 1907 nm is the first Stokes peak of a hydrogen Raman cell pumped by the 1064-nm light from a Q-switched Nd/YAG laser (Quantel YG 781, 10 pps, 8 ns, pulse). That light was passed through a linear polarizer and focused onto the EFISH cell. The polarizing dc voltage (parallel to the light polarization) used in this cell was 10 kV. The output light from the cell was passed through an interference filter to select the second harmonic (954 nm), which was detected with an R642 photomultiplier from Hamamatsu. Static  $\mu\beta_0$  values were deduced from the experimental values by using a two-level dispersion model. Each sample was measured with chloroform (CHCl<sub>3</sub>) as solvent, and the concentration was about 10<sup>-3</sup> M for monomers.

### Syntheses

**15**: Compound **14** (1.03 g, 3.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added slowly to a slurry of LiAlH<sub>4</sub> (0.68 g, 18 mmol) in Et<sub>2</sub>O (100 mL), and the mixture was stirred at room temperature for 1 h. Ethyl acetate (5 mL) was carefully added, water (1 mL) was then introduced, the resulting suspension was filtered, and the organic layer was evaporated in vacuo to give the residue, which was triturated repeatedly with CH<sub>2</sub>Cl<sub>2</sub>. The solution in CH<sub>2</sub>Cl<sub>2</sub> was dried (MgSO<sub>4</sub>) and filtered. The solvent was removed in vacuo to give **15** as a colorless liquid (0.79 g, 84%). IR (KBr):  $\tilde{\nu}$  = 3023, 2958, 2912, 2848, 1774, 1706, 1594, 1491, 1455, 1384, 1322, 1291, 1192, 1167, 107, 961, 921, 873, 815, 772, 755, 694, 622, 586 cm<sup>-1</sup>;  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.70 (q,  $J$  = 12.0 Hz, 1H), 1.96 (dt,  $J$  = 12.0, 5.9 Hz, 1H), 2.83–3.10 (m, 4H), 3.26 (brt,  $J$  = 6.9 Hz, 4H), 5.11 (d,  $J$  = 10.3 Hz, 1H), 5.15 (d,  $J$  = 17.2 Hz, 1H), 5.93 (ddd,  $J$  = 17.2, 10.3, 3.5 Hz, 1H), 6.30 (dd,  $J$  = 16.0, 7.2 Hz, 1H), 6.46 (d,  $J$  = 16.0 Hz, 1H), 6.69 (d,  $J$  = 8.2 Hz, 1H), 6.76 (t,  $J$  = 8.8 Hz, 1H), 7.23–7.36 ppm (m, 8H);  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 35.3, 45.5, 46.1, 46.2, 46.7, 50.3, 50.4, 113.4, 115.3, 116.8, 126.1, 127.1, 128.5, 129.1, 130.5, 131.1, 137.5, 139.1, 148.6 ppm; HRMS (FAB):  $m/z$  calcd for C<sub>23</sub>H<sub>25</sub>N: 315.1987 [M]<sup>+</sup>; found: 315.1989; elemental analysis: calcd (%) for C<sub>23</sub>H<sub>25</sub>N: C 87.57, H 7.99, N 4.44; found: C 87.99, H 7.64, N 4.20.

**12**: A solution of NaNO<sub>2</sub> (76 mg, 1.1 mmol) in a minimum amount of water was added to a mixture of ethyl 4-aminobenzoate (165 mg, 1.0 mmol) and HCl (5 mL, 50%) cooled to 5°C. After 3 min, **15** (315 mg, 1.0 mmol) in THF (5 mL) was added slowly, and stirring continued for 2 h. The reaction mixture was warmed to room temperature, neutralized with NaOAc, and stirred at room temperature overnight. CH<sub>2</sub>Cl<sub>2</sub>

(50 mL) was added, and the organic layer was washed with NaHCO<sub>3</sub> (5%, 3 × 100 mL) and brine (100 mL) and then dried (MgSO<sub>4</sub>). Removal of the solvent in vacuo and purification on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/hexane = 1:1) afforded **12** as a red solid (456 mg, 93%). M.p.: 191–192 °C; IR (KBr):  $\tilde{\nu}$  = 3076, 2976, 2951, 2935, 2859, 1713, 1598, 1513, 1478, 1421, 1366, 1273, 1170, 1135, 1107, 1012, 963, 910 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.40 (t, *J* = 7.0 Hz, 3H), 1.65 (q, *J* = 12.0 Hz, 1H), 1.99 (dt, *J* = 12.0, 5.9 Hz, 1H), 2.83–3.10 (m, 4H), 3.30–3.40 (m, 4H), 4.37 (q, *J* = 7.0 Hz, 2H), 5.07–5.11 (m, 2H), 5.93 (ddd, *J* = 17.2, 10.3, 3.5 Hz, 1H), 6.16 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.65 (d, *J* = 9.0 Hz, 2H), 7.19–7.32 (m, 5H), 8.16 ppm (d, *J* = 9.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.4, 35.3, 45.2, 45.9, 46.3, 46.8, 49.8, 50.0, 61.0, 112.5, 115.8, 121.9, 125.7, 126.1, 127.3, 128.6, 130.4, 130.5, 130.6, 131.0, 137.3, 138.8, 143.9, 150.6, 155.9, 166.4 ppm; HRMS (FAB): *m/z* calcd for C<sub>32</sub>H<sub>34</sub>N<sub>3</sub>O<sub>2</sub>: 492.2651 [*M* + H]<sup>+</sup>; found: 492.2650; elemental analysis: calcd (%) for C<sub>32</sub>H<sub>33</sub>N<sub>3</sub>O<sub>2</sub>: C 78.18, H 6.77, N 8.55; found: C 77.95, H 6.70, N 8.65.

**11**: Under argon, a solution of **12** (984 mg, 2 mmol) and **16** (169 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was heated under reflux for 24 h, cooled to room temperature, and the reaction was quenched with ethyl vinyl ether (1 mL). Removal of the solvent in vacuo followed by chromatographic purification (silica gel, EtOAc/hexane = 1:1) afforded **11a** (438 mg, 46%) and **11b** (239 mg, 25%). **11a**: M.p.: 210–211 °C; IR (KBr):  $\tilde{\nu}$  = 2949, 2831, 1711, 1597, 1523, 1384, 1282, 1135, 1131, 1111, 959, 857, 816 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.47 (t, *J* = 7.0 Hz, 6H), 1.67–2.00 (m, 4H), 2.95–3.10 (m, 8H), 3.30–3.40 (m, 8H), 4.43 (q, *J* = 7.0 Hz, 4H), 5.48 (d, *J* = 15.1 Hz, 2H), 6.19 (dd, *J* = 6.6, 15.8 Hz, 1H), 6.21 (dd, *J* = 7.5, 15.8 Hz, 1H), 6.43 (d, *J* = 15.8, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 7.22–7.40 (m, 10H), 7.79–8.01 (m, 8H), 8.10 ppm (d, *J* = 8.4 Hz, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.1, 35.4, 35.5, 44.3, 44.5, 44.9, 45.0, 46.1, 46.3, 46.6, 46.7, 48.7, 49.9, 61.1, 121.5, 126.0, 127.3, 128.3, 128.5, 128.7, 130.1, 130.4, 130.8, 131.7, 137.0, 143.6, 150.9, 166.1 ppm; HRMS (FAB<sup>+</sup>): *m/z* calcd for C<sub>62</sub>H<sub>62</sub>N<sub>6</sub>O<sub>4</sub>: 954.4833 [*M*]<sup>+</sup>; found: 954.4839; elemental analysis: calcd (%) for C<sub>62</sub>H<sub>62</sub>N<sub>6</sub>O<sub>4</sub>: C 77.96, H 6.54, N 8.80; found: C 78.15, H 6.77, N 8.64. **11b**: M.p.: 211–213 °C; IR (KBr):  $\tilde{\nu}$  = 2950, 2822, 1711, 1597, 1539, 1522, 1384, 1255, 1145, 1131, 1111, 960, 859, 820 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.47 (t, *J* = 7.0 Hz, 6H), 1.67–1.68 (m, 2H), 1.90–2.00 (m, 2H), 2.90–3.43 (m, 16H), 4.42 (q, *J* = 7.0 Hz, 4H), 5.45 (s, 2H), 6.15–6.17 (m, 2H), 6.40–6.52 (m, 2H), 6.71–6.80 (m, 4H), 7.22–7.49 (m, 10H), 7.79–8.01 (m, 8H), 8.10 ppm (d, *J* = 8.3 Hz, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.1, 35.8, 44.5, 45.0, 46.4, 46.9, 49.8, 49.9, 60.8, 112.7, 121.5, 126.0, 126.3, 127.1, 128.1, 128.4, 130.2, 130.5, 131.1, 131.7, 137.2, 143.5, 150.9, 166.0 ppm; HRMS (FAB<sup>+</sup>): *m/z* calcd for C<sub>62</sub>H<sub>62</sub>N<sub>6</sub>O<sub>4</sub>: 954.4833 [*M*]<sup>+</sup>; found: 954.4832.

**18a**: 4-(4-Trifluoromethylphenyl)-4-azatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-en-3,5-dione<sup>[20]</sup> (3.1 g, 10.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added slowly to a slurry of LiAlH<sub>4</sub> (2.3 g, 60.0 mmol) in Et<sub>2</sub>O (100 mL), and the mixture was stirred at room temperature for 1 h. Ethyl acetate (5 mL) was carefully added, water (10 mL) was then introduced, and the resulting suspension was filtered. The organic layer was evaporated in vacuo to give the residue, which was triturated repeatedly with CH<sub>2</sub>Cl<sub>2</sub>. The solution in CH<sub>2</sub>Cl<sub>2</sub> was dried (MgSO<sub>4</sub>) and filtered. The solvent was removed in vacuo to give **18a** as a white solid (1.73 g, 62%). M.p.: 165–166 °C; IR (KBr):  $\tilde{\nu}$  = 2935, 2830, 1718, 1702, 1609, 1523, 1410, 1330, 1160, 1129, 1108, 1069, 1058 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.52 (d, *J* = 8.0 Hz, 1H), 1.62 (d, *J* = 8.0 Hz, 1H), 2.92–3.28 (m, 8H), 6.16 (s, 2H), 6.42 (d, *J* = 8.5 Hz, 2H), 7.40 ppm (d, *J* = 8.5 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 45.4, 46.6, 50.4, 52.1, 111.0, 116.5 (q, *J* = 32.4 Hz), 124.3 (q, *J* = 107.4 Hz), 126.2, 129.6 (q, *J* = 114 Hz), 135.8, 149.3; HRMS (FAB<sup>+</sup>): *m/z* calcd for C<sub>16</sub>H<sub>16</sub>F<sub>3</sub>N: 279.1235 [*M*]<sup>+</sup>; found: 279.1237.

**18c**: In a manner similar to that described for the preparation of **18a**, the reaction of LiAlH<sub>4</sub> (2.3 g, 60.0 mmol) and (4-bromophenyl)-4-aza-tricyclo[5.2.1.0<sup>2,6</sup>]dec-8-en-3,5-dione (3.2 g, 10.0 mmol) afforded **18c** as white crystals (2.2 g, 77%). M.p.: 133–134 °C; IR (KBr):  $\tilde{\nu}$  = 2986, 2956, 2946, 2874, 2844, 1594, 1498, 1473, 1374, 1344, 1255, 1200, 1181, 808, 790 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.52 (d, *J* = 8.2 Hz, 1H), 1.62 (d, *J* = 8.2 Hz, 1H), 2.84–3.20 (m, 8H), 6.16 (s, 2H), 6.30 (d, *J* = 7.2 Hz, 2H),

7.25 ppm (d, *J* = 7.2 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 45.6, 46.5, 50.6, 52.2, 107.2, 113.4, 131.6, 135.8, 146.5 ppm; HRMS (FAB): *m/z* calcd for C<sub>15</sub>H<sub>16</sub><sup>79</sup>BrN: 289.0466 [*M*]<sup>+</sup>; found: 289.0467; elemental analysis: calcd (%) for C<sub>15</sub>H<sub>16</sub>BrN: C 62.08, H 5.56, N 4.83; found: C 61.87, H 5.03, N 4.76.

**18d**: In a manner similar to that described for the preparation of **18a**, the reaction of LiAlH<sub>4</sub> (4.6 g, 120.0 mmol) and 4-phenyl-4-azatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-en-3,5-dione<sup>[21]</sup> (4.8 g, 20.0 mmol) afforded **18d** as white crystals (3.2 g, 77%). M.p.: 88–89 °C (lit.: 93–94 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.50 (d, *J* = 8.2 Hz, 1H), 1.59 (d, *J* = 8.2 Hz, 1H), 2.87–2.90 (m, 2H), 2.96 (brs, 2H), 3.04–3.07 (m, 2H), 3.19–3.24 (m, 2H), 6.14 (s, 2H), 6.44 (d, *J* = 8.5 Hz, 2H), 6.62 (m, 1H), 7.18 ppm (d, *J* = 7.7 Hz, 2H); <sup>13</sup>C NMR (100 MHz):  $\delta$  = 45.5, 46.5, 50.5, 52.2, 111.9, 115.4, 129.0, 135.8, 147.7 ppm.

**18e**: In a manner similar to that described for the preparation of **18a**, the reaction of LiAlH<sub>4</sub> (2.3 g, 60.0 mmol) and 4-(4-tolyl)-4-azatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-en-3,5-dione<sup>[22]</sup> (2.5 g, 10.0 mmol) afforded **18e** as white crystals (1.5 g, 67%). M.p.: 103–105 °C; IR (KBr):  $\tilde{\nu}$  = 2954, 2863, 2843, 1619, 1561, 1473, 1367, 1348, 1202, 1180, 1132, 1033, 812, 794, 735, 716 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.54 (d, *J* = 8.1 Hz, 1H), 1.62 (d, *J* = 8.1 Hz, 1H), 2.28 (s, 3H), 2.90 (d, *J* = 9.3 Hz, 2H), 3.00 (s, 2H), 3.08 (brs, 2H), 3.24 (t, *J* = 8.6 Hz, 2H), 6.18 (s, 2H), 6.42 (d, *J* = 8.2 Hz, 2H), 7.05 ppm (d, *J* = 8.2 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 20.3, 45.6, 46.5, 50.8, 52.2, 112.0, 124.4, 129.6, 135.9, 145.9 ppm; HRMS (FAB<sup>+</sup>): *m/z* calcd for C<sub>16</sub>H<sub>19</sub>N: 225.1517 [*M*]<sup>+</sup>; found: 225.1517; elemental analysis: calcd (%) for C<sub>16</sub>H<sub>19</sub>N: C 85.28, H 8.50, N 6.22; found: C 85.77, H 8.43, N 6.46.

**18f**: In a manner similar to that described for the preparation of **18a**, the reaction of LiAlH<sub>4</sub> (2.3 g, 60.0 mmol) and 4-(4-anisyl)-4-azatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-en-3,5-dione (2.7 g, 10.0 mmol) afforded **18f** as white crystals (1.5 g, 60%). M.p.: 101–103 °C; IR (KBr):  $\tilde{\nu}$  = 2935, 2830, 1512, 1479, 1440, 1364, 1334, 1280, 1240, 1180, 1054 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.53 (d, *J* = 8.8 Hz, 1H), 1.62 (d, *J* = 8.8 Hz, 1H), 2.84 (d, *J* = 11.5 Hz, 2H), 2.97 (brs, 2H), 3.08 (brs, 2H), 3.22 (t, *J* = 9.6 Hz, 2H), 3.76 (s, 3H), 6.17 (s, 2H), 6.45 (d, *J* = 8.8 Hz, 2H), 6.83 ppm (d, *J* = 8.8 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 45.7, 46.3, 51.3, 52.3, 55.9, 113.0, 114.9, 135.9, 141.2, 153.9 ppm; HRMS (FAB<sup>+</sup>): *m/z* calcd for *m/z* C<sub>16</sub>H<sub>19</sub>NO: 241.1467 [*M*]<sup>+</sup>; found: 241.1469; elemental analysis: calcd (%) for C<sub>16</sub>H<sub>19</sub>NO: C 79.63, H 7.94, N 5.80; found: C 79.87, H 7.93, N 6.16.

**22b**: 4-(4-Bromophenyl)-4-aza-*exo*-tricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene-3,5-dione<sup>[11c]</sup> (14.0 g, 45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL) was added slowly to a suspension of LiAlH<sub>4</sub> (6.80 g, 180 mmol) in Et<sub>2</sub>O (250 mL), and the mixture was stirred at room temperature for 1 h. H<sub>2</sub>O (10 mL) and NaOH (10% in H<sub>2</sub>O, 5 mL) were then introduced, and the resulting suspension was filtered. The residue was triturated repeatedly with CH<sub>2</sub>Cl<sub>2</sub> and then filtered. The organic solution was dried (MgSO<sub>4</sub>) and filtered. The filtrate was evaporated in vacuo to give **22b** as a white solid (9.70 g, 72%). M.p.: 133–134 °C; IR (KBr):  $\tilde{\nu}$  = 3070, 2960, 2835, 1590, 1558, 1495, 1479, 1366, 1329, 1267, 1182, 811, 801, 709, 676 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.37 (dt, *J* = 9.0, 1.5 Hz, 1H), 1.56 (d, *J* = 9.0 Hz, 1H), 2.38–2.41 (m, 2H), 2.72–2.74 (m, 2H), 2.99 (dd, *J* = 9.6, 3.6 Hz, 2H), 3.32–3.42 (m, 2H), 6.16 (s, 2H), 6.42 (d, *J* = 9.0 Hz, 2H, 2 × phenyl-H), 7.28 ppm (d, *J* = 9.0 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 42.4, 44.5, 47.6, 52.9, 108.0, 114.0, 131.7, 137.7, 147.1 ppm; HRMS (MALDI): *m/z* calcd for C<sub>15</sub>H<sub>16</sub>BrN: 290.0544, found: 290.0539; elemental analysis: calcd (%) for C<sub>15</sub>H<sub>16</sub>BrN: C 62.08, H 5.56, N 4.83; found: C 62.52, H 5.56, N 4.63.

**22c**: *n*BuLi (13 mL, 2.5 M in hexane, 30 mmol) was added dropwise under argon to a solution of **22b** (5.80 g, 20 mmol) in dry THF (140 mL) cooled to –78 °C. After stirring at –78 °C for 1 h, excess CO<sub>2</sub> gas was bubbled into the solution until a white solid (≈ 2 h) was precipitated. The mixture was gradually warmed to room temperature, poured into a mixture of Et<sub>2</sub>O (200 mL) and H<sub>2</sub>O (200 mL), and filtered to give the filter cake and filtrate I. The filter cake was dissolved in aq. NaOH (10%, 1 L), and the solution was acidified with aq. HCl (10%) until pH 6 to give a precipitate, which was filtered. Additional solid was obtained from neutralization of filtrate I (10% HCl until pH 6). The combined solid was washed with Et<sub>2</sub>O (2 × 100 mL) to give **22c** as a white solid (4.59 g, 90%). M.p.: 278 °C



(decomp.); IR (KBr):  $\tilde{\nu}$  = 3060, 2962, 2850, 1664, 1599, 1554, 1525, 1477, 1420, 1384, 1328, 1288, 1180, 827, 775, 702, 670  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $[\text{D}_6]\text{DMSO}$  (dimethyl sulfoxide)):  $\delta$  = 1.27 (d,  $J$  = 9.0 Hz, 1H), 1.41 (d,  $J$  = 9.0 Hz, 1H), 2.33–2.41 (m, 2H), 2.75 (brs, 2H), 3.06–3.10 (m, 2H), 3.39–3.50 (m, 2H), 6.19 (s, 2H), 6.55 (d,  $J$  = 9.0 Hz, 2H), 7.75 (d,  $J$  = 9.0 Hz, 2H), 12.09 ppm (s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 42.4, 44.3, 47.5, 52.6, 111.8, 117.5, 134.0, 151.1, 168.0 ppm; HRMS (MALDI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{18}\text{NO}_2 + 1$ : 256.1338; found: 256.1332; elemental analysis: calcd (%) for  $\text{C}_{16}\text{H}_{17}\text{NO}_2$ : C 75.27, H 6.71, N 5.49; found: C 75.24, H 6.68, N 5.41.

**22a**: Oxalyl chloride (7.2 mL, 80 mmol) and *N,N*-dimethylformamide (DMF; 3 drops) were added to a suspension of **22c** (10.20 g, 40 mmol) in  $\text{CH}_2\text{Cl}_2$  (150 mL) at 0°C. The mixture was gradually warmed to room temperature and then stirred for 3 h. The solvent was removed in vacuo to give the corresponding acid chloride, which was dissolved in  $\text{CH}_2\text{Cl}_2$  (70 mL). EtOH (15 mL) was added to this solution, and the mixture was stirred at room temperature for 5 h. Water was introduced, and the organic layer was separated and washed with water and brine (200 mL) and then dried ( $\text{MgSO}_4$ ). The solvent was removed in vacuo to give **22a** as a white solid (10.30 g, 90%). M.p.: 123–124°C; UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 313 nm (90.8  $\text{g}^{-1}\text{cm}^2$ ); IR (KBr):  $\tilde{\nu}$  = 3053, 2974, 2958, 2875, 1701, 1691, 1612, 1556, 1525, 1473, 1386, 1369, 1280, 1181, 1104, 828, 771, 709, 699, 680  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.36 (t,  $J$  = 7.2 Hz, 3H), 1.38 (dt,  $J$  = 9.0, 1.5 Hz, 1H), 1.50 (d,  $J$  = 9.0 Hz, 1H), 2.41–2.44 (m, 2H), 2.75 (t,  $J$  = 1.8 Hz, 2H), 3.10 (dd,  $J$  = 10.2, 2.7 Hz, 2H), 3.44–3.55 (m, 2H), 4.31 (q,  $J$  = 7.2 Hz, 2H), 6.17 (t,  $J$  = 1.8 Hz, 2H), 6.49 (d,  $J$  = 9.0 Hz, 2H), 7.90 ppm (d,  $J$  = 9.0 Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.5, 42.3, 44.3, 47.7, 60.1, 111.2, 117.2, 131.2, 137.6, 150.9, 167.1 ppm; HRMS (MALDI):  $m/z$  calcd for  $\text{C}_{18}\text{H}_{21}\text{NO}_2 + 1$ : 284.1651; found: 284.1645; elemental analysis: calcd (%) for  $\text{C}_{18}\text{H}_{21}\text{NO}_2$ : C 76.29, H 7.47, N 4.94; found: C 76.02, H 7.26, N 4.67.

**23b**: 4-(4-Bromophenyl)-4-aza-10-oxa-*exo*-tricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene-3,5-dione<sup>[23]</sup> (9.60 g, 30 mmol) in  $\text{CH}_2\text{Cl}_2$  (150 mL) was added slowly to a slurry of  $\text{LiAlH}_4$  (6.80 g, 180 mmol) in Et<sub>2</sub>O (250 mL), and the mixture was stirred at room temperature for 4 h.  $\text{H}_2\text{O}$  (21 mL) and NaOH (10%, 7 mL) were then introduced, and the resulting suspension was filtered. The residue was triturated repeatedly with  $\text{CH}_2\text{Cl}_2$  and filtered. The organic solution was dried ( $\text{MgSO}_4$ ) and filtered, and the filtrate was evaporated in vacuo to give **23b** as a white solid (6.19 g, 71%). M.p.: 178–179°C; IR (KBr):  $\tilde{\nu}$  = 3072, 3000, 2956, 2830, 1590, 1494, 1473, 1369, 1183, 906, 701  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.56–2.60 (m, 2H), 3.02 (dd,  $J$  = 9.9, 3.6 Hz, 2H), 3.58 (t,  $J$  = 8.7 Hz, 2H), 4.80 (s, 2H), 6.41 (s, 2H), 6.46 (d,  $J$  = 8.4 Hz, 2H), 7.28 ppm (d,  $J$  = 8.4 Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 44.3, 52.0, 82.8, 108.7, 114.6, 131.7, 136.1, 147.4 ppm; HRMS (MALDI):  $m/z$  calcd for  $\text{C}_{14}\text{H}_{14}\text{ONBr} + 1$ : 292.0339; found: 292.0332; elemental analysis: calcd (%) for  $\text{C}_{14}\text{H}_{14}\text{BrNO}$ : C 57.55, H 4.83, N 4.79, Br 27.35; found: C 57.56, H 4.87, N 4.60, Br 27.48.

**23c**: In a manner similar to that described for the preparation of **22b**, **23b** (5.84 g, 20 mmol) gave **23c** as a white solid (5.0 g, 97%). M.p.: 276–277°C; IR (KBr):  $\tilde{\nu}$  = 3000, 2972, 2958, 2861, 2661, 2542, 1670, 1600, 1525, 1477, 1437, 1420, 1382, 1319, 1290, 1181, 905, 831, 695  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 2.52 (t,  $J$  = 4.2, 2H), 3.08–3.13 (m, 2H), 3.53–3.60 (m, 2H), 4.82 (s, 2H), 6.44 (s, 2H), 6.54 (d,  $J$  = 8.7, 2H), 7.28 (d,  $J$  = 8.7 Hz, 2H), 12.14 ppm (s); HRMS (MALDI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{NO}_3 + 1$ : 258.1130; found: 258.1125; elemental analysis: calcd (%) for  $\text{C}_{15}\text{H}_{15}\text{NO}_3$ : C 70.02, H 5.88, N 5.44; found: C 70.15, H 5.74, N 5.11.

**23a**: In a manner similar to that described for the preparation of **22a**, **23b** (4.6 g, 18 mmol) gave **23a** as a white solid (4.07 g, 79%). M.p.: 178–179°C; UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 310 nm (81.6  $\text{g}^{-1}\text{cm}^2$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.29 (t,  $J$  = 7.2 Hz, 3H), 2.51–2.55 (m, 2H), 3.08–3.13 (m, 2H), 3.56–3.60 (m, 2H), 4.24 (q,  $J$  = 7.2 Hz, 2H), 4.75 (s, 2H), 6.34 (s, 2H), 6.46 (d,  $J$  = 8.7 Hz, 2H), 7.83 ppm (d,  $J$  = 8.7 Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.5, 44.2, 51.6, 60.2, 83.1, 111.6, 117.6, 131.2, 136.1, 151.0, 167.1 ppm; HRMS (MALDI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{19}\text{NO}_3 + 1$ : 286.1440; found: 286.1438; elemental analysis: calcd (%) for  $\text{C}_{17}\text{H}_{19}\text{NO}_3$ : C 71.56, H 6.71, N 4.91; found: C 71.55, H 6.68, N 4.76.

**17a**: A solution of **18a** (307 mg, 1.1 mmol) and **1** (41 mg, 0.05 mmol) in  $\text{CH}_2\text{Cl}_2$  (3.6 mL) was stirred under argon at room temperature for

30 min, quenched with ethyl vinyl ether (1 mL), and poured into MeOH (20 mL). The solid was collected, redissolved in  $\text{CHCl}_3$  (1 mL), and reprecipitated by adding MeOH (20 mL). This procedure was repeated two or three times, and **17a** was collected as a grayish-white solid. (250 mg, 83%); IR (KBr):  $\tilde{\nu}$  = 2939, 2856, 1614, 1530, 1480, 1372, 1300, 1224, 1157, 1006, 1068, 963, 817  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.37 (br, 1H), 1.74 (br, 1H), 2.70–3.07 (m, 8H), 5.38 (br, 2H), 6.36 (br, 2H), 7.20 ppm (br, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 35.63, 36.12, 44.6, 46.3, 49.6, 111.8, 116.8, 126.0, 126.2, 131.7, 150.0 ppm; GPC (THF):  $M_n$  = 10800, PDI = 1.22; elemental analysis: calcd (%) for  $\text{C}_{16}\text{H}_{16}\text{F}_3\text{N}$ : C 68.80, H 5.77, N 5.01; found: C 68.33, H 6.03, N 5.01.

**17c**: In a manner similar to that described for the preparation of **17a**, **17c** was obtained as a white solid (253 mg, 86%). IR (KBr):  $\tilde{\nu}$  = 2986, 2874, 1594, 1498, 1473, 1374, 1344, 1183, 967, 808  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.40 (br, 1H), 1.77 (br, 1H), 2.73–3.10 (m, 8H), 5.40 (br, 2H), 6.39 (br, 2H), 7.20 ppm (br, 2H);  $^{13}\text{C}$  NMR (125 MHz):  $\delta$  = 35.6, 35.8, 44.6, 46.4, 50.1, 108.2, 114.5, 130.8, 131.7, 147.2 ppm; GPC (THF):  $M_n$  = 10300, PDI = 1.09; elemental analysis: calcd (%) for  $\text{C}_{15}\text{H}_{16}\text{BrN}$ : C 66.08, H 5.56, N 4.83; found: C 66.16, H 5.56, N 4.90.

**17d**: In a manner similar to that described for the preparation of **17a**, **17d** was obtained as a white solid (269 mg, 95%). IR (KBr):  $\tilde{\nu}$  = 2990, 2866, 1594, 1498, 1477, 1394, 1364, 1185, 966, 910, 814  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.46 (br, 1H), 1.76 (br, 1H), 2.70–3.48 (m, 8H), 5.46 (br, 2H), 6.67 (br, 3H), 7.20 ppm (br, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 35.8, 44.8, 46.4, 50.2, 113.1, 116.5, 129.0, 131.5, 148.6 ppm; GPC (THF):  $M_n$  = 9200, PDI = 1.44; elemental analysis: calcd (%) for  $\text{C}_{15}\text{H}_{17}\text{N}$ : C 85.26, H 8.11, N 6.63; found: C 84.32, H 8.69, N 6.02.

**17e**: In a manner similar to that described for the preparation of **17a**, **17e** was obtained as a white solid (110 mg, 90%). IR (KBr):  $\tilde{\nu}$  = 2935, 2829, 1512, 1479, 1440, 1364, 1334, 1280, 1240, 1179, 1039, 966, 814  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.48 (br, 1H), 1.73 (br, 1H), 2.23 (s, 3H), 2.70–3.10 (m, 8H), 5.49 (br, 2H), 6.55 (br, 2H), 7.00 ppm (br, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 20.0, 35.9, 45.0, 46.1, 50.1, 112.0, 124.4, 129.0, 131.2, 147.3 ppm; GPC (THF):  $M_n$  = 10800, PDI = 1.22; elemental analysis: calcd (%) for  $\text{C}_{16}\text{H}_{19}\text{NO}$ : C 85.28, H 8.50, N 6.22; found: C 85.65, H 8.16, N 5.99.

**17f**: In a manner similar to that described for the preparation of **17a**, **17f** was obtained as a white solid (132 mg, 91%). IR (KBr):  $\tilde{\nu}$  = 2915, 2819, 1500, 1421, 1364, 1334, 1280, 1227, 1221, 1179, 1033, 960, 803  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.48 (br, 1H), 1.73 (br, 1H), 2.70–3.14 (m, 8H), 3.71 (s, 3H), 5.50 (br, 2H), 6.55 (br, 2H), 6.77 ppm (br, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 35.7, 45.0, 46.3, 51.4, 55.7, 114.6, 114.7, 131.4, 143.8, 151.6 ppm; GPC (THF):  $M_n$  = 10500, PDI = 1.23; elemental analysis: calcd (%) for  $\text{C}_{16}\text{H}_{19}\text{NO}$ : C 79.63, H 7.94, N 5.8; found: C 78.65, H 8.16, N 5.91.

**19a**: A solution of **17a** (200 mg, 0.7 mmol) and *p*-tosylhydrazide (2 g, 10.9 mmol) in PhCl (10 mL) was stirred under argon at 120°C for 2 h and filtered. The hot filtrate was poured into methanol (50 mL). The mixture was centrifuged to collect the precipitate, which was washed several times with methanol and dried under vacuum to yield **19a** (90 mg, 45%) as a solid. IR (KBr):  $\tilde{\nu}$  = 2924, 1770, 1707, 1596, 1500, 1455, 1375, 1320, 1177, 1020  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.99–1.96 (m, 8H), 2.86 (br, 2H), 3.20 (br, 4H), 4.27 (br, 2H), 6.59 (br, 2H), 7.41 ppm (br, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 30.7, 37.0, 41.6, 45.1, 48.7, 111.7, 124.3, 126.3, 131.6, 149.3 ppm; elemental analysis: calcd (%) for  $\text{C}_{16}\text{H}_{18}\text{F}_3\text{N}$ : C 68.31, H 6.45, N 4.98; found: C 67.78, H 6.64, N 4.99.

**19c**: In a manner similar to that described for the preparation of **19a**, **17c** was obtained as a white solid (300 mg, 60%). IR (KBr):  $\tilde{\nu}$  = 2929, 2930, 2860, 1600, 1566, 1505, 1477, 1371, 1200, 1156, 900, 740, 725  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.91–1.92 (m, 8H), 2.82–3.15 (m, 6H), 6.67 (br, 2H), 7.20 ppm (br, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 30.6, 37.0, 41.8, 45.0, 49.4, 108.4, 114.7, 131.7, 147.3 ppm; elemental analysis: calcd (%) for  $\text{C}_{15}\text{H}_{18}\text{BrNO}$ : C 61.25, H 6.21, N 4.79; found: C 61.45, H 6.42, N 5.02.

**19d**: In a manner similar to that described for the preparation of **19a**, **17d** was obtained as a white solid (390 mg, 63%). IR (KBr):  $\tilde{\nu}$  = 2924, 2933, 2750, 1620, 1596, 1497, 1377, 1209, 1166, 900, 900, 740  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.95 (br, 1H), 1.23–1.95 (m, 7H), 2.83–

3.21 (m, 6H), 6.67 (br, 3H), 7.20 ppm (br, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 30.5, 37.0, 42.1, 45.0, 49.4, 113.4, 116.7, 129.0, 148.7 ppm; elemental analysis: calcd (%) for  $\text{C}_{15}\text{H}_{19}\text{N}$ : C 84.46, H 8.98, N 6.57; found: C 84.67, H 8.68, N 6.47.

**19e**: In a manner similar to that described for the preparation of **19a**, **19e** was obtained as a white solid (150 mg, 55%). IR (KBr):  $\tilde{\nu}$  = 2917, 2854, 1619, 1519, 1478, 1363, 1334, 1166, 802  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.91–1.88 (m, 8H), 2.33 (s, 3H), 2.78–3.14 (m, 6H), 6.57 (br, 2H), 7.00 ppm (br, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 20.3, 30.5, 36.9, 37.0, 42.4, 44.9, 49.8, 113.6, 125.7, 129.5, 146.9 ppm; elemental analysis: calcd (%) for  $\text{C}_{16}\text{H}_{21}\text{N}$ : C 84.53, H 9.31, N 6.16; found: C 84.98, H 9.59, N 6.01.

**19f**: In a manner similar to that described for the preparation of **19a**, **19f** was obtained as a white solid (290 mg, 59%). IR (KBr):  $\tilde{\nu}$  = 2944, 2963, 2829, 1600, 1519, 1478, 1363, 1334, 1166, 802  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.97 (br, 1H), 1.34–1.93 (m, 5H), 2.84–3.18 (m, 6H), 3.74 (s, 3H), 6.67 (br, 2H), 6.83 ppm (br, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 30.5, 36.95, 37.03, 42.4, 45.0, 50.5, 55.8, 114.7, 114.8, 144.0, 151.8 ppm; elemental analysis: calcd (%) for  $\text{C}_{16}\text{H}_{19}\text{NO}$ : C 78.97, H 8.70, N 6.57; found: C 79.55, H 8.90, N 6.98.

**20**: In a manner similar to that described for the preparation of **19a**, reaction of **22a** (566 mg, 2 mmol) and  $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}=\text{CHPh}]$  (41 mg, 0.05 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) gave **20** as a white solid (417 mg, 74%). UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 309 nm (89.9  $\text{g}^{-1}\text{cm}^2$ ); IR (KBr):  $\tilde{\nu}$  = 3053, 2974, 2931, 2848, 1702, 1607, 1560, 1522, 1478, 1381, 1365, 1276, 1180, 1103, 964, 829, 769, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.37 (brt,  $J$  = 7.2 Hz, 3H), 1.44 (br, 1H), 2.02 (br, 1H), 2.37 (br, 2H), 2.55 (br, 2H), 3.36 (br, 4H), 4.33 (brq,  $J$  = 7.2 Hz, 2H), 5.37 (br, 0.55H, *cis* double bond), 5.48 (brs, 1.40H, *trans* double bond), 6.50–6.62 (m, 2H), 7.85–7.94 ppm (m, 2H); GPC (THF):  $M_n$  = 41 700, PDI = 1.39; elemental analysis: calcd (%) for  $(\text{C}_{18}\text{H}_{21}\text{NO}_2)_n$ : C 76.29, H 7.47, N 4.94; found: C 76.37, H 7.43, N 4.59. With a different amount of catalyst, **20** of other  $M_n$  values (8500, 16900) were obtained, and  $\epsilon$  values were 89.2 and 90.4  $\text{g}^{-1}\text{cm}^2$ , respectively.

**21**: In a manner similar to that described for the preparation of **19a**, reaction of **23a** (570 mg, 2 mmol) and  $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}=\text{CHPh}]$  (122 mg, 0.15 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) gave **21** as a white solid (506 mg, 88%). UV/Vis  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 309 nm (81.8  $\text{g}^{-1}\text{cm}^2$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.29–1.40 (m, 3H), 2.75–2.83 (m, 2H), 3.16–3.61 (m, 4H), 4.13–4.36 (m, 2H), 4.44 (brs, 2H), 5.75–6.00 (m, 2H), 6.40–6.61 (m, 2H), 7.82–7.97 ppm (m, 2H); GPC (THF):  $M_n$  = 4100, PDI = 1.14; elemental analysis: calcd (%) for  $(\text{C}_{17}\text{H}_{19}\text{NO}_3)_n$ : C 71.56, H 6.71, N 4.91; found: C 71.42, H 6.83, N 4.62. When 10 mol % of the catalyst was used, **21** with  $M_n$  = 3800, PDI = 1.12 was obtained, and  $\epsilon$  was 79.1  $\text{g}^{-1}\text{cm}^2$  at  $\lambda_{\text{max}}$  = 307 nm.

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