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Simultaneous hydrogenation and hydroacylation of vinyl groups in polybutadiene by use of a rhodium catalyst

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Vinyl groups in phenyl-terminated polybutadiene (**1a**) containing 99% unsaturation (27% vinyl group, 73% internal olefin), and for which the average M_n is 3400, were simultaneously hydrogenated and hydroacylated with various aromatic or heteroaromatic primary alcohols in the presence of the catalytic system $RhCl_3.H_2O$, PPh_3 and 2-amino-4-picoline. Sterically less hindered alcohols, such as benzyl alcohol, showed greater reactivity than sterically more hindered alcohols, such as 2-naphthylmethanol and heteroaromatic primary alcohols. Vinyl groups in phenyl-terminated polybutadiene (**1b**) containing 99% unsaturation (45% vinyl group, 55% internal olefin) and for which the average M_n is 1300 also showed similar reactivity toward various primary alcohols under identical reaction conditions. © 1998 Elsevier Science Ltd.

(Keywords: polybutadiene; hydrogenation; hydroacylation)

Introduction

The chemical modification of an unsaturated polymer in the presence of a catalyst offers a potentially useful method for the synthesis of special polymers with desirable functional groups. In this method, the desirable functional groups can be introduced into available unsaturation sites in polymers. Polybutadiene is a good starting chemical material for this purpose because it is available, in various ranges of molecular weights, with different ratios in the vinyl group/internal olefin. The majority of these modifications are hydroformylation[1–4], aminomethylation[5,6], hydrocarboxylation[7,8], hydrosilation[9–11], and hydrogenation[12–16]. Hydroacylation of polybutadiene was also reported by hydroiminoacylation of polybutadiene with carboxaldimine, followed by hydrolysis of the resulting ketimine[17]. Since this indirect hydroacylation reaction requires several steps to achieve C–C bond coupling, direct intermolecular hydroacylation using 2-amino-3-picoline was developed[18]. However, application of this method to the polymer was found to be less efficient.

Recently, a new C–C bond-coupling method was invented for primary alcohols and 1-alkenes[19]. The primary alcohol reacted with 1-alkene in the presence of the catalyst system $RhCl_3.H_2O$, PPh_3 and 2-amino-4-picoline to give a ketone with the formation of alkane (*Figure 1*).

Initially, the primary alcohol is oxidized to an aldehyde with the reduction of 1-alkene to alkane by the rhodium catalyst. Subsequent hydroacylation of aldehyde and 1-alkene in the presence of the rhodium catalyst and 2-amino-4-picoline produces a ketone (*Figure 2*). Since the 1-alkene works as a hydrogen acceptor as well as a hydroacylation substrate, simultaneous hydrogenation and hydroacylation are possible for polybutadiene. In this paper we report a method for incorporating aromatic or heteroaromatic groups into the vinyl groups of the polybutadiene, while hydrogenating the vinyl groups and internal olefins of the polybutadiene.

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Experimental

In this experiment we chose two kinds of phenyl-terminated polybutadiene (PTPB): one (**1a**) contained 73% of the internal olefin (a) and 27% of the vinyl group (b), and the other (**1b**) 55% of the internal olefin and 45% of the vinyl group.† **1a** was reacted with benzyl alcohol (**2**) at 150°C for 24 h in the presence of a mixture of $RhCl_3.H_2O$ (10 mol%), PPh_3 (20 mol%) and 2-amino-4-picoline (100 mol%) (*Figure 3*).‡

After the reaction, the mixture was purified by column-chromatography to give the benzoyl group-impregnated polymer **5a** in 83% yield. Supplementary data relating to the compounds synthesized in this work are listed in Appendix A.

Results and discussion

The polymer **5a** was characterized by i.r., ^{1}H n.m.r. and ^{13}C spectroscopy. The i.r. band of the carbonyl peak in the benzoyl group appeared at 1687 cm^{-1}. The characteristic band of the vinyl group at 913 cm^{-1} disappeared completely while those of the trans-1,4-internal olefin at 968 cm^{-1} and the *cis*-1,4-internal olefin at 696 cm^{-1} remained. The ^{13}C n.m.r. spectra also showed the characteristic peaks of **5a**. While the signals of vinyl carbons at 143.0 and 114.2 ppm

† The ratio of the vinyl groups and internal olefins was calculated by measuring the integration of the vinylic CH_2 peak at 4.9–5.0 ppm, the internal –CH=CH– peak and the vinylic –CH= peak at 5.3–5.6 ppm. **1a** and **1b** were purchased from Aldrich Chemical Co. The vinyl content of the commercial PTPB (**1a,** labelled as 25% vinyl) was recalculated by ^{1}H NMR spectra to give 27% of the vinyl group, and the vinyl content of the commercial PTPB (**1b,** labelled as 45% vinyl) was recalculated as 45% vinyl.

‡ The following is an example of a typical experimental procedure: a screw-capped pressure vial (1 mL) was charged with 42.0 mg (0.2 mmol) PTPB **1a**, 4.5 mg (0.02 mmol) of $RhCl_3.H_2O$ (**3**), 10.5 mg(0.04 mmol) of triphenylphosphine, 21.6 mg (0.2 mmol) of 2-amino-4-picoline (**4**), 108 mg (1.0 mmol) of benzyl alcohol (**2**) and 184 mg (2.0 mmol) of toluene. The solution was flushed with nitrogen, and it was heated at 150°C for 24 h. After the reaction the mixture was purified by column chromatography (hexane:ethyl acetate = 5:2) to give 47.1 mg (83% yield based upon **1a**) of **5a**.

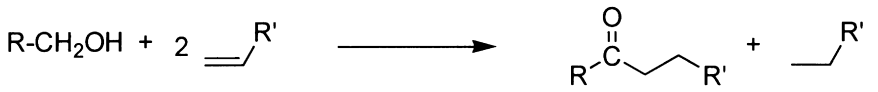


Figure 1 Hydrogen-transfer oxidation of primary alcohol to aldehyde and consecutive hydroacylation of 1-alkene

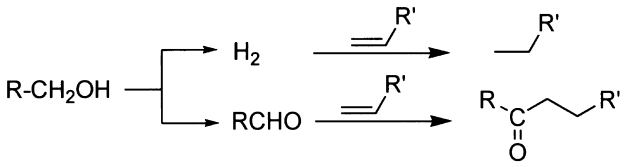


Figure 2 Presumed reaction mechanism

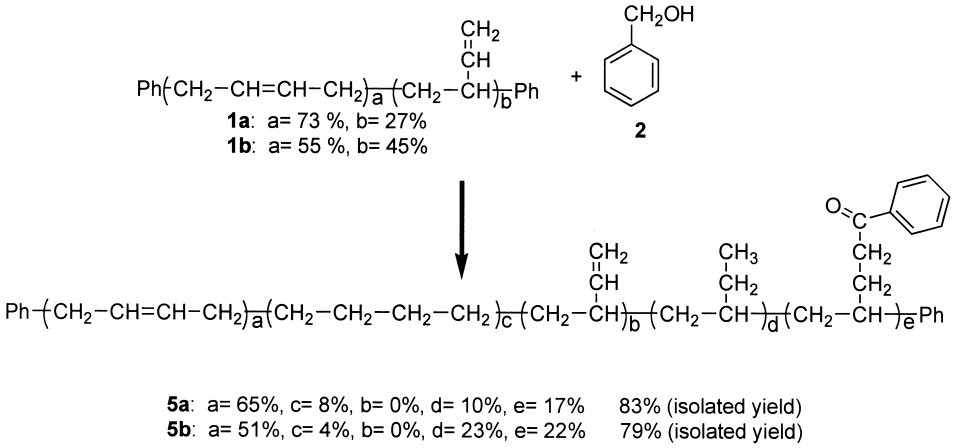


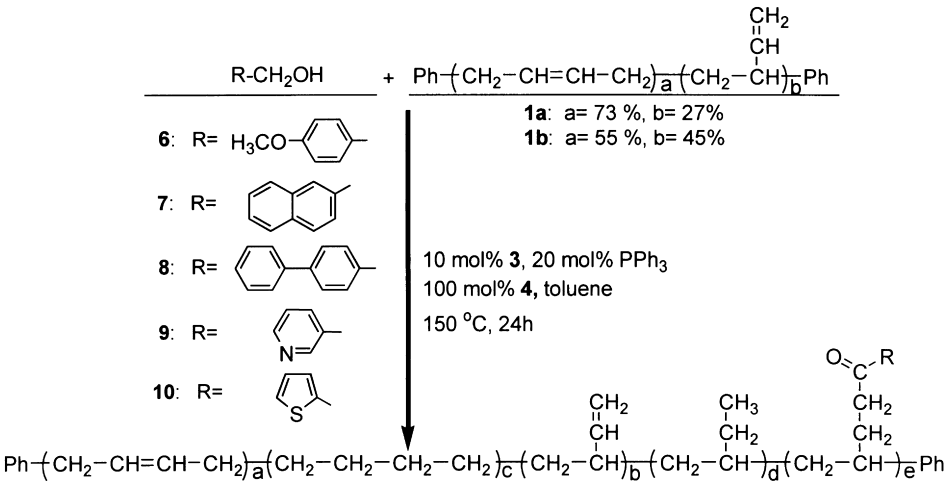
Figure 3 Reaction of polybutadiene and benzylalcohol in the presence of catalytic system of $RhCl_3.H_2O$, PPh_3 and 2-amino-4-picoline

in **1a** disappeared completely in **5a**, new peaks from the benzoylmethylene group appeared at 36.0 ppm for the α-CH_2 to the carbonyl group as well as 200.6 ppm for the carbonyl group. The ^{13}C n.m.r. chemical shift of the CH_3 peak of the ethyl group generated from the hydrogenation of the vinyl group appeared at 10.8 ppm. The amounts of hydrogenation (d) and hydroacylation (e) of the vinyl groups in **5a** could be directly determined by measuring the integrations of the CH_3 peak of the ethyl group at 0.83 ppm, and the α-CH_2 peak to the carbonyl group at 2.94 ppm that were not in the starting polymer **1a**. The amount of hydrogenation (c) of the internal olefin could be calculated by use of the equation; $(a + c)$: $(b + d + e) = 27$: 73 (a is the unreacted internal olefin and b is the unreacted vinyl group).§

While 10% of the vinyl groups and 8% of the internal olefins of **1a** were hydrogenated, 17% of the vinyl groups were hydroacylated. All the vinyl groups were either hydrogenated or hydroacylated. Although hydroacylation took place in the vinyl groups exclusively, hydrogenation occurred in the internal olefins as well as the vinyl groups. The internal olefin and vinyl group in **1a** showed different reactivities for hydrogenation (8%/10% for the internal olefin/vinyl group, respectively). The higher reactivity of the vinyl group compared to the internal olefin for hydrogenation could be explained by a steric difference between the vinyl group and the internal olefin. The catalyst may approach the vinyl group more easily than the internal olefin. A more dramatic effect appeared in **5b** formed from the reaction of **1b** with **2** under identical reaction conditions. Four percent of the internal olefin and 23% of the vinyl group in **1b** were hydrogenated, showing that the vinyl group is much more easily hydrogenated than the internal olefin. The amount (17%) of hydroacylation is similar to the total amount of hydrogenation (18%) in **5a**. However, in the case of **1b**, the amount of hydroacylation (22%) is less than that of hydrogenation (27%), which shows that hydroacylation is more sensitive to the steric hindrance than hydrogenation. The reason is probably that the bulky intermediate, iminoacylrhodium(III) hydride, may be involved in a catalytic cycle of hydroacylation while the sterically less hindered rhodium(III) hydride complex may be involved in hydrogenation. These trends can be seen in *Table 1*. When the reaction of **1a** and **2** was carried out with different concentrations of PPh_3 under 10 mol% of **3** and 100 mol% of **4** at 150°C for 6 h, 20 mol% of PPh_3 showed the best catalytic activity for this reaction as shown in entry 1 of *Table 2*. The excess use of PPh_3 may retard the coordination of the olefins in polybutadiene to the catalyst.

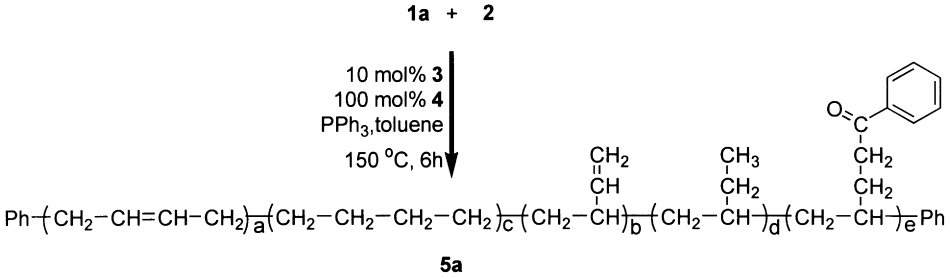
§ A is the area of 5.3–5.6 ppm (internal –CH=CH– and vinylic –CH); B is the area of 4.9–5.0 ppm (vinylic CH_2); D is the area of 0.83–0.88 ppm (CH_3 in ethyl group); E is the area of 2.88–3.06 ppm (α–CH_2 to CO); C = (73/27) × (B + 2/3D + E) − A + 1/2B (hydrogenated internal olefin; for the PTPB containing 45% of vinyl group, 55/45 was used instead of 73/27); C is derived from the equation, {(A − 1/2B) + C}: (B + 2/3D + E) = 73: 27; T = (A − 1/2B) + C + B + 2/3D + E (T is the sum of the area of unreacted internal olefin, hydrogenated internal olefin, unreacted vinyl group, hydrogenated vinyl group, and hydroacylated vinyl group), a (%) = (A − 1/2B)/T × 100, b (%) = B/T × 100, c (%) = C/T × 100, d (%) = (2D/3)/T × 100, e (%) = E/T × 100.

Table 1 Reaction of polybutadiene and various primary alcohols in the presence of the catalytic system $RhCl_3.H_2O$, PPh_3 and 2-amino-4-picoline



Entry	Product	R	Proportionality					Isolated yield
1	**11a**	H_3CO	$a = 68\%$	$c = 5\%$	$b = 0\%$	$d = 10\%$	$e = 17\%$	68%
2	**11b**		$a = 45\%$	$c = 10\%$	$b = 0\%$	$d = 22\%$	$e = 23\%$	70%
3	**12a**		$a = 64\%$	$c = 9\%$	$b = 2\%$	$d = 11\%$	$e = 14\%$	79%
4	**12b**		$a = 42\%$	$c = 13\%$	$b = 4\%$	$d = 23\%$	$e = 18\%$	75%
5	**13a**		$a = 59\%$	$c = 14\%$	$b = 1\%$	$d = 12\%$	$e = 14\%$	80%
6	**13b**		$a = 42\%$	$c = 13\%$	$b = 4\%$	$d = 24\%$	$e = 17\%$	84%
7	**14a**	N	$a = 72\%$	$c = 1\%$	$b = 5\%$	$d = 9\%$	$e = 13\%$	72%
8	**14b**		$a = 42\%$	$c = 13\%$	$b = 7\%$	$d = 27\%$	$e = 11\%$	80%
9	**15a**	S	$a = 63\%$	$c = 10\%$	$b = 4\%$	$d = 10\%$	$e = 13\%$	73%
10	**15b**		$a = 48\%$	$c = 7\%$	$b = 5\%$	$d = 19\%$	$e = 21\%$	75%

Table 2 Effect of the amount of PPh_3 on the hydrogenation and hydroacylation of polybutadiene (**1a**)



Entry	PPh_3	Proportionality				
1	20 mol%	$a = 72\%$	$c = 1\%$	$b = 3\%$	$d = 15\%$	$e = 9\%$
2	30 mol%	$a = 73\%$	$c = 0\%$	$b = 7\%$	$d = 12\%$	$e = 8\%$
3	50 mol%	$a = 72\%$	$c = 1\%$	$b = 13\%$	$d = 8\%$	$e = 6\%$

Conclusion

Simultaneous hydrogenation and hydroacylation of vinyl groups in preformed polybutadiene was achieved successfully, with aromatic or heteroaromatic primary alcohols in the presence of the rhodium catalyst and 2-amino-4-picoline.

Acknowledgements
This research was supported by the Korea Science and Engineering Foundation (Grant No. 961-0306-054-2) and the Ministry of Education (Project No. BSRI-97-3422).

APPENDIX A: SUPPLEMENTARY DATA

5a: ^{1}H n.m.r. (250 MHz, $CDCl_3$) δ (ppm) 7.95 (d, J = 7.5 Hz, 2,6-Hs in benzoyl group), 7.5–7.3 (m, 3,4,5-Hs in benzoyl group) 5.39 (br, –CH=CH–), 2.94 (br, α-CH_2 to CO), 2.1–1.2 (m, saturated CH_2 and CH), 0.83 (br, CH_3 in ethyl group); ^{13}C n.m.r. (62.9 MHz, $CDCl_3$) δ (ppm) 200.6 (C=O), 136.7 (1-C in benzoyl group), 132.8 (4-C in benzoyl group), 128.5, 128.0 (2, 3-Cs in benzoyl group), 36.0 (α-CH_2 to CO), 32.7–27.3 (saturated CH_2 and CH), 10.8 (CH_3); i.r. (neat) 3008, 2924, 2853, 1687 vs (C=O), 1598, 1449, 1356, 1274, 1214, 969, 740. 693 cm^{-1}; Anal. Calcd.

for $C_{324}H_{453}O_{10}$: C, 86.33; H, 10.13. Found: C, 85.67; H, 10.42%.

11a. ^{1}H n.m.r. (250 MHz, $CDCl_3$) δ (ppm) 7.94 (d, J = 7.5Hz, 2,6-Hs in 4-methoxybenzoyl group), 6.93 (d, J = 7.5Hz,3,5-Hs in 4-methoxybenzoyl group), 5.39 (br, –CH=CH–), 3.85 (s, 3Hs in 4-methoxy group) 2.88 (br, α-CH_2 to CO), 2.1–1.2 (m, saturated CH_2 and CH), 0.88 (br, CH_3 in ethyl group); ^{13}C n.m.r. (62.9 MHz, $CDCl_3$) δ (ppm) 200.9(C=O), 163.2 (4-C in 4-methoxybenzoyl group), 130.3 (2-C in 4-methoxybenzoyl group), 130.1 (1-C in 4-methoxybenzoyl group), 113.6 (3-C in 4-methoxybenzoyl group), 55.4 (C in 4-methoxy group), 35.6 (α-CH_2 to CO), 32.7–26.4 (saturated CH_2 and CH), 10.9 (CH_3); i.r. (neat) 2925, 2854, 1677 (C=O), 1603, 1512, 1453, 1256, 1177, 1038, 972, 834 cm^{-1}; Anal. Calcd. for $C_{324}H_{470}O_{20}$: C, 83.04; H, 10.12. Found: C, 82.16; H, 9.88%.

12a. ^{1}H n.m.r. (250 MHz, $CDCl_3$) δ (ppm) 8.45 (s, 1-H in naphthyl group), 8.0–7.6 (m, 3,4,5,6,7,8-Hs in naphthyl group), 5.39 (br, –CH=CH–), 4.97 (b, CH_2 in vinyl group), 3.06 (br, α-CH_2 to CO), 2.2–1.2 (m, saturated CH_2 and CH), 0.83 (br, CH_3 in ethyl group); ^{13}C n.m.r. (62.9 MHz, $CDCl_3$) δ (ppm) 199.4 (C=O), 135.4 (9-C in naphthyl group), 134.3 (2-C in naphthyl group), 132.5 (10-C in naphthyl group), 123.4 (3-C in naphthyl group), 129.5–125.6 (1,4,5,6,7,8-Cs and Cs in internal olefin), 36.0 (α-CH_2 to CO), 32.6–25.5 (saturated CH_2 and CH), 10.8 (CH_3);i.r. (neat) 3056, 2925, 2855, 1682 (C=O), 1451, 1362, 1281, 1181, 1069, 969, 911, 735 cm^{-1}; Anal. Calcd. for $C_{345}H_{462}O_8$: C, 87.46; H, 9.84. Found: C, 86.33; H, 9.68%.

13a. ^{1}H n.m.r. (250 MHz, $CDCl_3$) δ (ppm) 8.03 (d, J = 7.5 Hz, 2 Hs), 7.63–7.60 (m, 4 Hs), 7.46–7.41 (m, 3Hs), 5.39 (br,–CH=CH–), 4.97 (b, CH_2 in vinyl group), 2.96 (br, α-CH_2 to CO), 2.2–1.2 (m, saturated CH_2 and CH), 0.83 (br, CH_3 in ethyl group); ^{13}C n.m.r. (62.9 MHz, $CDCl_3$) δ (ppm) 200.2 (C=O), 145.5, 139.9, 135.7 (Cs in 4-biphenyl group), 129.95–127.2 (Cs in 4-biphenyl group and Cs in internal olefin), 36.0 (α-CH_2 to CO), 32.7–27.3 (saturated CH_2 and CH), 10.9 (CH_3); i.r. (neat) 2925, 2854, 1682 (C=O), 1605, 1449, 973, 910, 734, 698 cm^{-1}; Anal. Calcd. for $C_{362}H_{486}O_8$: C, 87.56; H, 9.87. Found: C, 85.34; H, 9.61%.

14a. ^{1}H n.m.r. (250 MHz, $CDCl_3$) δ (ppm) 9.16 (s, 2-H in pyridine ring), 8.76 (br, 6-H in pyridine ring), 8.23 (d, J = 7.5 Hz 4-H in pyridine ring), 7.44–7.39 (m, 5-H in pyridine ring), 5.39 (br, –CH=CH–), 4.96 (b, CH2 in vinyl group), 2.96 (br, α-CH_2 to CO), 2.2–1.2 (m, saturated CH_2 and CH), 0.83 (br, CH_3 in ethyl group); ^{13}C n.m.r. (62.9 MHz, $CDCl_3$) δ (ppm) 198.2 (C=O), 153.3 (2-C in pyridine ring), 149.6 (6-C in pyridine ring), 135.3 (4-C in pyridine ring), 132.1 (3-C in pyridine ring), 123.6 (5-C in pyridine ring), 36.2 (α-CH_2 to CO), 32.7–25.6 (saturated CH_2 and CH), 10.5 (CH_3); i.r. (neat) 3006, 2924, 2854, 1690 (C=O), 1585, 1447, 1269, 970, 737, 709 cm^{-1}; Anal. Calcd. for $C_{299}H_{421}O_8N_8$: C, 84.39; H, 9.96; N, 2.63. Found: C, 82.85; H, 9.79; N, 2.97%.

15a. ^{1}H n.m.r. (250 MHz, $CDCl_3$) δ (ppm) 7.70 (d, J = 2.5 Hz 3-H in thiophene ring), 7.61 (d, J = 2.5 Hz 5-H in thiophene ring), 7.11 (m, 4-H in thiophene ring), 5.40 (br, –CH=CH–), 4.97 (br, CH_2 in vinyl group), 2.87 (br, α-CH_2 to CO), 2.2–1.2 (m, saturated CH_2 and CH), 0.84 (br, CH_3 in ethyl group); ^{13}C n.m.r. (62.9 MHz, $CDCl_3$) δ (ppm) 193.6 (C=O), 144.4, 133.3, 131.6, 128.0 (Cs in thiophene ring), 36.9 (α-CH_2 to CO), 32.7–27.4 (saturated CH_2 and CH), 10.9 (CH_3); i.r. (neat) 3003, 2923, 2853, 1666 (C=O), 1453, 1417, 969, 723 cm^{-1}; Anal. Calcd. for $C_{291}H_{426}O_8S_8$: C, 81.11; H, 9.96; S, 5.96. Found: C,78.38; H, 9.39; S, 7.50%.

5b: ^{1}H n.m.r. (250 MHz, $CDCl_3$) δ (ppm) 7.96 (d, J = 7.5 Hz 2,6-Hs in benzoyl group), 7.51–7.43 (m, 3,4,5-Hs in benzoyl group) 5.36 (br, –CH=CH–), 2.93 (br, α-CH_2 to CO), 2.2–1.2 (m, saturated CH_2 and CH), 0.83 (br, CH_3 in ethyl group); ^{13}C n.m.r. (62.9 MHz, $CDCl_3$) δ (ppm) 200.6 (C=O), 137.0 (1-C in benzoyl group), 132.8 (4-C in benzoyl group), 128.5, 128.0 (2, 3-Cs in benzoyl group), 36.0 (α-CH_2 to CO), 32.6–27.2 (saturated CH_2 and CH), 10.8 (CH_3); i.r. (neat) 2925, 2856, 1687 vs (C=O), 1598, 1451, 1387, 1281, 1222, 970, 741, 693 cm^{-1}; Anal. Calcd. for $C_{129}H_{177}O_5$: C, 85.72; H, 9.85. Found: C, 84.67; H, 10.22%.

11b. ^{1}H n.m.r. (250 MHz, $CDCl_3$) δ (ppm) 7.94 (d, J = 7.5 Hz, 2,6-Hs in 4-methoxybenzoyl group), 6.93(d, J = 7.5 Hz, 3,5-Hs in 4-methoxybenzoyl group), 5.38 (br, –CH=CH–), 3.85 (s, 3 Hs in 4-methoxy group) 2.88 (br, α-CH_2 to CO), 2.1–1.2 (m, saturated CH_2 and CH), 0.83 (br, CH_3 in ethyl group); ^{13}C n.m.r. (62.9 MHz, $CDCl_3$) δ (ppm) 199.3 (C=O), 163.2 (4-C in 4-methoxybenzoyl group), 130.3 (2-C in 4-methoxybenzoyl group), 130.1 (1-C in 4-methoxybenzoyl group), 113.6 (3-C in 4-methoxybenzoyl group), 55.4 (C in 4-methoxy group), 35.6(α-CH_2 to CO), 32.6–27.3 (saturated CH_2 and CH), 10.7 (CH_3); i.r. (neat) 2925, 2855, 1677 (C=O), 1602, 1511, 1457, 1257, 1172, 1033, 972, 841, cm^{-1}; Anal. Calcd. for $C_{131}H_{190}O_{10}$: C, 81.37; H, 10.16. Found: C, 80.53; H, 9.75%.

12b. ^{1}H n.m.r. (250MHz, $CDCl_3$) δ (ppm) 8.45 (s, 1-H in naphthyl group), 8.0–7.5 (m, 3,4,5,6,7,8-Hs in naphthyl group), 5.38 (br, –CH=CH–), 4.98 (b, CH_2 in vinyl group), 3.06 (br, α-CH_2 to CO), 2.2–1.2 (m, saturated CH_2 and CH), 0.83 (br, CH_3 in ethyl group); ^{13}C n.m.r. (62.9 MHz, $CDCl_3$) δ (ppm) 200.5 (C=O), 135.4 (9-C in naphthyl group) 134.3 (2-C in naphthyl group), 132.5 (10-C in naphthyl group), 123.9 (3-C in naphthyl group) 129.9-125.8 (1,4,5,6,7,8-Cs and internal Cs), 36.0 (α-CH_2 to CO), 32.7–27.3 (saturated CH_2 and CH), 10.8 (CH_3); i.r. (neat) 3060, 2925, 2856, 1682 (C=O), 1458, 1368, 1282, 1190, 1070, 970, 913, 748 cm^{-1}; Anal. Calcd. for $C_{139}H_{183}O_4$: C, 87.07; H, 9.59. Found: C, 85.62; H, 9.54%.

13b. ^{1}H n.m.r. (250 MHz, $CDCl_3$) δ (ppm) 8.00 (br, 1H), 7.63–7.60 (m, 1H), 7.41 (br, 1H), 5.38 (br, –CH=CH–), 4.95 (b, CH_2 in vinyl group), 2.96 (br, α-CH_2 to CO), 2.2–1.2 (m, saturated CH_2 and CH), 0.83 (br, CH_3 in ethyl group); ^{13}C n.m.r. (62.9 MHz, $CDCl_3$) δ (ppm) 200.2 (C=O), 145.5, 139.9, 135.7 (Cs in 4-biphenyl group), 129.95–127.2 (Cs in 4-biphenyl group and Cs in internal olefin), 36.0(α-CH_2 to CO), 32.7–29.7 (saturated CH_2 and CH), 10.9 (CH_3); i.r. (neat) 2924, 2856, 1683 (C=O), 1605, 1452, 1070, 970, 913, 762, 696 cm^{-1}; Anal. Calcd. for $C_{144}H_{189}O_4$: C,87.15; H, 9.62. Found: C, 85.96; H, 9.73%.

14b. ^{1}H n.m.r. (250 MHz, $CDCl_3$) δ (ppm) 9.16 (s, 2-H in pyridine ring), 8.76 (br, 6-H in pyridine ring), 8.23 (d, J = 7.5 Hz 4-H in pyridine ring), 7.49–7.41 (m, 5-H in pyridine ring), 5.38 (br, –CH=CH–), 4.95 (b, CH_2 in vinyl group), 2.96 (br, α-CH_2 to CO), 2.2–1.2 (m, saturated CH_2 and CH), 0.83 (br, CH_3 in ethyl group); ^{13}C n.m.r. (62.9 MHz, $CDCl_3$) δ (ppm) 198.2 (C=O), 153.3 (2-C in pyridine ring), 149.6 (6-C in pyridine ring), 135.3 (4-C in pyridine ring), 132.1 (3-C in

pyridine ring), 123.6 (5-C in pyridine ring), 36.2 (α-CH_2 to CO), 32.7–25.6 (saturated CH_2 and CH), 10.5 (CH_3); i.r. (neat) 3006, 2924, 2854, 1690 (C=O), 1585, 1447, 1269, 970, 737, 709 cm^{-1}; Anal. Calcd. for $C_{111}H_{166}O_2N_2$: C, 85.45; H, 10.71; N, 1.79. Found: C, 80.14; H, 10.07; N, 2.00%.

15b. ^{1}H n.m.r. (250 MHz, $CDCl_3$) δ (ppm) 7.70 (br, 3-H in thiophene ring), 7.60 (br, 5-H in thiophene ring), 7.11 (br, 4-H in thiophene ring), 5.38 (br, –CH=CH–), 4.95 (br, CH_2 in vinyl group), 2.86 (br, α-CH_2 to CO), 2.2–1.2 (m, saturated CH_2 and CH), 0.83 (br, CH_3 in ethyl group); ^{13}C n.m.r. (62.9 MHz, $CDCl_3$) δ (ppm) 193.4(C=O), 144.4, 133.3, 131.6, 128.0 (Cs in thiophene ring), 36.4 (α-CH_2 to CO), 32.7–27.4 (saturated CH_2 and CH), 10.9 (CH_3); i.r. (neat) 2924, 2855, 1664 (C=O), 1451, 1416, 1361, 1236, 1065, 973, 913, 725 cm^{-1}; Anal. Calcd. for $C_{119}H_{166}O_5S_5$: C, 77.83; H, 9.10; S, 8.71. Found: C, 76.46; H, 9.28; S, 9.06%.

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