

can easily react with PbO to form PbO-Ta<sub>2</sub>O<sub>5</sub> related compounds, as expected from the corresponding phase diagram.<sup>12,13</sup> However, the pyrochlore phase is not formed with La<sup>3+</sup> contents 40 at.% and 50 at.%. This may be ascribed as the change of B-site compositions. For example, in Pb<sub>1-x</sub>La<sub>x</sub>(Mg<sub>(1-x)/3</sub>Ta<sub>(2-x)/3</sub>)O<sub>3</sub> for x=0.50, the pyrochlore phase is not observed because the 1:1 ordering promotes a more homogeneous distribution as in the case of Pb(Sc<sub>1/2</sub>Ta<sub>1/2</sub>)O<sub>3</sub>.

The Raman spectra for selected compositions are shown in Figure 5. For unmodified PMT, it exhibits the same feature as that for PMN.<sup>14</sup> The band at 290 cm<sup>-1</sup>, assigned to the O-B-O bending modes, are split to three band with increasing La<sup>3+</sup> content, which may be ascribed to the lowered local symmetry by the 1:1 ordering. The Raman spectrum for Pb<sub>1/2</sub>La<sub>1/2</sub>(Mg<sub>1/2</sub>Ta<sub>1/2</sub>)O<sub>3</sub>, having the highest degree of 1:1 ordering, has five relatively sharp Raman bands at ca. 798, 548, 432, 358, and 238 cm<sup>-1</sup>. This is very similar to those of ordered Pb(Yb<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub>, which has been known to have an ordered perovskite structure, except in the peak frequencies.<sup>5</sup> However, PBiMN ceramics show no changes with the Bi<sup>3+</sup> content is increased.

In conclusion, we suggest that the increase of the ordering can be explained as the effect of electrostatic charge compensation by incorporating La<sup>3+</sup> in PMT lattices. However, the effect of mechanical forces due to the reduction of unit cell volume and polarizability of A-site ion must be considered as in the case of PBiMN ceramics. In PLMT ceramics, the 1:1 ordering led to a mixture of Mg-rich region and Ta-rich region, resulting in the formation of pyrochlore phases.

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## Rhodium-Catalyzed Coupling Reaction of 2-Vinylquinolines with Terminal Alkenes via C-H Bond Activation

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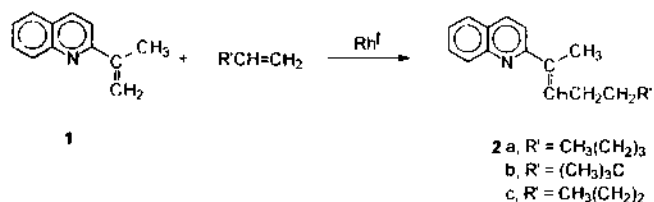
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The formation of C-C bonds by activation of C-H bonds is of particular value. Especially vinylic C-H bond activation of the alkenes has been investigated.<sup>1</sup> Alkylation at the vinylic position of alkenes via C-H bond activation by transition metal complexes has been reported by us,<sup>2</sup> Trost *et al.*<sup>3</sup> and Murai *et al.*<sup>4</sup> In this report, we describe that 2-vinylquinolines react with terminal alkenes at the β-position in the presence of the Rh(I) complex as a catalyst to give the highly selective cross coupled β-alkylated products.

2-Isopropenylquinoline **1** reacted with 1-hexene (3 equiv.) in the presence of Wilkinson complex (10 mol%) in toluene at 110 °C for 21 h to give the alkylated product **2a** as a mixture of *cis* and *trans* isomers in 65% yield (Run 1). The reaction rate was also found to be a function of the alkene concentration. The reaction rate increased as the alkene con-

centration: 10 equiv. and 20 equiv. of 1-hexene gave 86% and 94%, respectively (Run 3 and 5).

In the case of neohexene, **1** reacted with 5 equiv. of neohexene in the presence of Wilkinson complex (10 mol%) in toluene at 110 °C for 20 h to give the corresponding



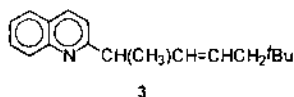
**Scheme 1.**

**Table 1.** Alkylation of 2-isopropenylquinoline with terminal alkenes<sup>a</sup>

Run	Alkene	Equiv.	Solvent	Reaction time (h)	Reaction temp. (°C)	Product	Yield <sup>b</sup>	Cis	Trans
1	1-hexene	3	toluene	21	110	2a	65	59	41
2	1-hexene	5	toluene	20	110	2a	68	60	40
3	1-hexene	10	toluene	20	110	2a	86	49	51
4	1-hexene	10	toluene	44	115-120	2a	89	33	67
5	1-hexene	20	toluene	20	115-120	2a	94	47	53
6	1-hexene	5	THF	20	120	2a	24 <sup>c</sup>	61	39
7	1-hexene <sup>d</sup>	5	THF	20	120	2a	45 <sup>e</sup>	26	74
8	neohexene	5	toluene	20	110	2b	87	64	36
9	neohexene	10	toluene	20	115-120	2b	>99 <sup>f</sup>	57	43
10	1-pentene	5	toluene	20	120-125	2c	>99	71	29

<sup>a</sup>Substrate: (Ph<sub>3</sub>P)<sub>3</sub>RhCl=1:0.1. <sup>b</sup>GC-yield. <sup>c</sup>Yield including isopropylquinoline (7%). <sup>d</sup>[(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>RhCl]<sub>2</sub> (5 mol%)/Cy<sub>3</sub>P (30 mol%) was used as a catalyst. <sup>e</sup>Yield including isopropylquinoline (32%). <sup>f</sup>Yield including the isomerized product (13%).

alkylated product **2b** in 87% GC yield (Run 8). Neohexene worked well than 1-hexene in the same reaction conditions. But, when the reaction time was prolonged to 44 h, the further isomerized products **3** were detected in the reaction mixture in a small amount; The structure of the isomerized product can be deduced from the identical molecular weight (253) with **2b** in mass spectrometer and the signals of CH [3.82 ppm (quintet)] and CCH<sub>3</sub> [1.49 ppm (doublet)] in <sup>1</sup>H NMR. The use of 10 equiv. of neohexene gave the alkylated product quantitatively together with the further isomerized product (13%); pure form of the further isomerized product could not be obtained because of difficulty of purification (Run 9). When 1-pentene was applied to this alkylation, the reaction proceeded fast even at 5 equiv. of 1-pentene to give the alkylated products **2c** quantitatively (Run 10).

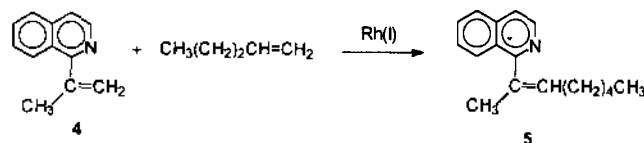


In order to compare the effects of phosphorus ligands in the alkylation of 2-isopropenylquinoline **1** with 1-hexene, the reaction was carried out in the presence of rhodium catalysts prepared *in situ* from chlorobis(cyclooctene)rhodium dimer, [(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>RhCl]<sub>2</sub> and various phosphorus ligands such as tricyclohexylphosphine (Cy<sub>3</sub>P), tri-*n*-butylphosphine, triphenylphosphine, trimethylphosphite and triphenylphosphite in toluene. Only triphenylphosphine worked well under the same reaction conditions as shown in Table 2.

The rate of the alkylation of vinylquinolines is slower than that of vinylpyridines under the same reaction con-

ditions: when 10 equiv. of 1-hexene is used, 2-isopropenylpyridine<sup>2b</sup> is about 5 times faster than 2-isopropenylquinoline. To know whether the steric effect or electronic effect on the coordination site, 2-isopropenylisoquinoline **4**, having the shape like 2-isopropenylpyridine on the coordination site, reacted with 1-pentene (5 equiv.) in the presence of Wilkinson complex (10 mol%) in toluene at 120-125 °C for 20 h to give **5** in 76% yield (*cis*:*trans*=28:72) (Scheme 2). The enhancement of the yield was not observed, maybe due to the electronic nature of substrates over the steric factor; quinoline (*pK<sub>a</sub>* 4.9) is more acidic than pyridine (*pK<sub>a</sub>* 5.2).<sup>5</sup>

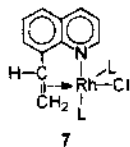
Finally, other catalytic system, [(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>RhCl]<sub>2</sub>/Cy<sub>3</sub>P in THF,<sup>2c</sup> which is the best catalytic system in the alkylation of 2-phenylpyridines with terminal alkenes, was applied to the alkylation of vinylquinolines. Substrate **1** reacted with 1-hexene (5 equiv.) in the presence of [(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>RhCl]<sub>2</sub> (5 mol%) and Cy<sub>3</sub>P (30 mol%) in THF at 125-130 °C for 20 h to give quantitatively the alkylated product **2a** as the *trans* isomer with trace amounts of the *cis* isomer (77% isolated yield, *trans*:*cis*= >99:1). Interestingly, in use of THF containing moisture, this reaction gave the hydrogenated product, 2-isopropylquinoline (32%) together with the alkylated products (Run 7 in Table 1). These results showed that moisture of the solvent affects deeply the catalyst for the

**Scheme 2.****Table 2.** Comparison of the ligand effect in alkylation of 2-isopropenylquinoline<sup>a</sup>

Run	Alkene	Equiv.	Ligand	Reaction time (h)	Reaction temp. (°C)	Yield <sup>b</sup>	Cis	Trans
1	1-hexene	5	Cy <sub>3</sub> P	20	110	35	33	67
2	1-hexene	5	<sup>n</sup> Bu <sub>3</sub> P	20	110	43	38	62
3	1-hexene	5	Ph <sub>3</sub> P	20	110	68	60	40
4	1-hexene	5	(MeO) <sub>3</sub> P	20	120	15	37	63
5	1-hexene	5	(PhO) <sub>3</sub> P	20	120	4	38	62

<sup>a</sup>Substrate: [(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>RhCl]<sub>2</sub>; phosphorus(III) ligand=1:0.05:0.3 in toluene. <sup>b</sup>GC-yield.

alkylation. 2-Vinylquinoline reacted with 1-hexene (5 equiv.) under this catalytic system to give the corresponding alkylated product **6** as the *trans* isomer in 26% isolated yields (THF, 125-130 °C, 20 h), while Wilkinson complex in toluene gave the trace amount of the alkylated product. In the case of 8-vinylquinoline, the coupled product was not detected; the starting material was only detected by GC-mass spectroscopy. No reaction occurs probably due to the formation of the stable intermediate **7**.<sup>6</sup>



In conclusion, we have found that the best catalytic system was  $[(C_8H_{14})_2RhCl]_2/Cy_3P$  in THF for the alkylation of the vinylic position of 2-vinylquinolines with terminal alkenes.

### Experimental

<sup>1</sup>H NMR spectra were recorded on Bruker AC-300F (300 MHz). The chemical shifts are reported in ppm relative to internal tetramethylsilane in CDCl<sub>3</sub>. <sup>13</sup>C NMR spectra were recorded on Bruker AC-300F (75 MHz). Infrared spectra were run on a Nicolet magna 550 FT-IR. Mass spectra were measured with a HP-5971A mass spectrometer equipped with a Hewlett-Packard 5890 series II gas chromatograph using electron impact method (70 eV). The silica gel used in column chromatography was obtained from Aldrich (Merck, 230-400 mesh). Analytical thin layer chromatography was performed on a glass plates (0.25 mm) coated with silica gel 60F 254 from Aldrich.

#### General procedure for the alkylation of 2-vinylquinolines

The catalytic system of Wilkinson complex; a screw-capped vial (2.5 mL) was charged with 33.85 mg (0.2 mmol) of **1** and 168.32 mg (2 mmol, 10 equiv.) of 1-hexene, and 18.5 mg (0.02 mmol, 10 mol%) of Wilkinson complex in 2 mL of toluene. The reaction mixture was heated at 115-120 °C for 44 h with stirring. The reaction mixture was concentrated under reduced pressure, and then purified by column chromatography on silica gel (EtOAc:Hexane=1:10) to give 37.6 mg (74%) of **2a** as a mixture of *trans* and *cis* isomers (*trans*:*cis*=67:33).

The catalytic system of  $[(C_8H_{14})_2RhCl]_2/Cy_3P$  in THF; A screw-capped vial (5 mL) was charged with 33.85 mg (0.2 mmol) of **1** and 84.16 mg (1 mmol, 5 equiv.) of 1-hexene, and 7.18 mg (0.01 mmol, 5 mol%) of  $[(C_8H_{14})_2RhCl]_2$  and 16.83 mg (0.06 mmol, 30 mol%) of Cy<sub>3</sub>P in 2.5 mL of THF (freshly dried with LiAlH<sub>4</sub>). The reaction mixture was heated at 125-130 °C for 20 h with stirring. The reaction mixture was concentrated under reduced pressure, and then purified by column chromatography on silica gel (EtOAc:Hexane=1:10) to give 39.08 mg (77%) of **2a** as the *trans* isomer.

**2-(2-Nonenyl)quinoline 2a** (*trans* isomer) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) 8.07-7.43 (6H, Hs in quinoline), 6.44 (t, 1H, *J*=7.28 Hz, =C-H), 2.32 (q, 2H, *J*=7.29 Hz, =C-CH<sub>2</sub>),

2.25 (s, 3H, =C-CH<sub>3</sub>), 1.54-1.25 (8H, -(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 0.90 (t, 3H, *J*=6.68 Hz, -CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 160.28, 147.66, 135.75, 133.93, 129.40, 129.20, 127.22, 126.83, 125.64, 118.48, 31.78, 29.30, 29.18, 29.15, 22.63, 14.31, 14.10; MS (*M/Z*) 128 (12.7), 156 (16.9), 167 (63.4), 168 (24.6), 180 (42.1), 181 (29.9), 182 (77.9, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>CH<sub>3</sub>), 183 (26.5), 194 (13.5), 196 (100, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-CH<sub>3</sub>), 197 (17.9), 210 (17.9, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 224 (12.4, M<sup>+</sup>-CH<sub>2</sub>CH<sub>3</sub>), 238 (11.0, M<sup>+</sup>-CH<sub>3</sub>), 252 (13.7, M<sup>+</sup>-1), 253 (38.2, M<sup>+</sup>); IR (NaCl) 3060 (w), 3039 (w), 2956 (s), 2926 (vs), 2855 (s), 1617 (m), 1599 (s), 1556 (w), 1504 (s), 1460 (w), 1427 (w), 1379 (w), 1364 (w), 823 (s), 754 (s); (*cis* isomer) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.11-7.31 (6H, Hs in quinoline), 5.73 (t, 1H, *J*=7.46 Hz, =C-H), 2.20 (s, 3H, =C-CH<sub>3</sub>), 2.11 (q, 2H, *J*=7.30 Hz, =C-CH<sub>2</sub>), 1.41-1.17 (8H, -(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 0.82 (t, 3H, *J*=7.14 Hz, -CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 160.86, 147.91, 135.71, 131.42, 129.40, 129.28, 127.39, 126.00, 121.60, 31.67, 29.84, 29.18, 28.96, 23.87, 22.56, 14.03; MS (*M/Z*) 128 (9.7), 156 (13.9), 167 (29.5), 168 (13.2), 180 (36.3), 181 (28.1), 182 (40.0, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 183 (15.0), 194 (11.5), 196 (100, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 197 (18.5), 210 (8.8, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 224 (3.4, M<sup>+</sup>-CH<sub>2</sub>CH<sub>3</sub>), 238 (10.3, M<sup>+</sup>-CH<sub>3</sub>), 253 (28.8, M<sup>+</sup>); IR (NaCl) 3058 (w), 3039 (w), 2957 (s), 2924 (vs), 2854 (s), 1597 (s), 1556 (w), 1502 (s), 1426 (w), 913 (s), 831 (s), 748 (s).

**2-(5,5-Dimethyl-2-hexenyl)quinoline 2b** (*trans* isomer) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.07-7.42 (6H, Hs in quinoline), 6.43 (t, 1H, *J*=7.96 Hz, =C-H), 2.32-2.19 (m, 2H, =C-CH<sub>2</sub>), 2.25 (s, 3H, =C-CH<sub>3</sub>), 1.43-1.38 (m, 2H, =C-CH<sub>2</sub>CH<sub>2</sub>), 0.95 (s, 9H, <sup>t</sup>Bu); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 160.29, 147.67, 135.78, 134.41, 129.41, 129.21, 127.23, 126.83, 125.65, 118.46, 43.43, 30.48, 29.31, 24.51, 14.20; MS (*M/Z*) 101 (2.8), 128 (7.8), 129 (3.8), 143 (4.3), 156 (3.9), 166 (5.5), 167 (37.6), 168 (10.7), 180 (25.3), 181 (22.0), 182 (49.0), 183 (7.9), 194 (8.4), 196 (100, M<sup>+</sup>-<sup>t</sup>Bu), 197 (17.5), 238 (15.7, M<sup>+</sup>-CH<sub>3</sub>), 253 (27.2, M<sup>+</sup>); IR (NaCl) 3060 (w), 3039 (w), 2954 (vs), 2906 (s), 2866 (m), 1617 (m), 1599 (s), 1557 (w), 1504 (s), 1474 (w), 1427 (w), 1364 (w), 823 (s), 756 (s); (*cis* isomer) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.09-7.31 (6H, Hs in quinoline), 5.73 (t, 1H, *J*=7.76 Hz, =C-H), 2.19 (s, 3H, =C-CH<sub>3</sub>), 2.08 (q, 2H, *J*=8.45 Hz, =C-CH<sub>2</sub>), 1.35-1.30 (m, 2H, =C-CH<sub>2</sub>CH<sub>2</sub>), 0.80 (s, 9H, <sup>t</sup>Bu); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) 160.87, 147.92, 135.71, 131.96, 129.41, 129.28, 127.40, 126.00, 121.50, 44.07, 30.35, 29.21, 24.59, 23.85; MS (*M/Z*) 101 (3.0), 128 (7.8), 129 (3.6), 143 (4.1), 156 (5.9), 157 (4.6), 166 (3.2), 167 (19.7), 168 (6.5), 180 (25.3), 181 (21.1), 182 (32.4), 183 (4.7), 194 (7.9), 196 (100, M<sup>+</sup>-<sup>t</sup>Bu), 197 (17.4), 238 (19.2, M<sup>+</sup>-CH<sub>3</sub>), 253 (14.2, M<sup>+</sup>); IR (NaCl) 3059 (w), 2955 (vs), 2866 (s), 1618 (w), 1599 (s), 1557 (w), 1502 (s), 1471 (w), 1427 (w), 1367 (w), 1305 (w), 830 (s), 756 (s).

**2-(2-Octenyl)quinoline 2c** (*trans* isomer) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.08-7.42 (6H, Hs in quinoline), 6.44 (t, 1H, *J*=7.3 Hz, =C-H), 2.32 (q, 2H, *J*=7.35 Hz, =C-CH<sub>2</sub>), 2.25 (s, 3H, =C-CH<sub>3</sub>), 1.60-1.45 (m, 2H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.45-1.30 (m, 4H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 0.91 (t, 3H, *J*=7.1 Hz, -CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) 160.28, 147.66, 135.75, 133.93, 129.41, 129.20, 127.22, 126.83, 125.65, 118.49, 31.68, 29.10, 29.02, 22.59, 14.31, 14.07; MS (*M/Z*) 128 (18.6), 143 (13.7), 156 (14.6), 167 (42.6), 168 (18.9), 180

(43.6), 181 (36.4), 182 (62.4, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 183 (22.1), 194 (10.2), 196 (100, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 197 (23.0), 210 (10.3, M<sup>+</sup>-CH<sub>2</sub>CH<sub>3</sub>), 224 (16.4, M<sup>+</sup>-CH<sub>3</sub>), 239 (34.0, M<sup>+</sup>); IR (NaCl)  $\nu$  3059 (w), 3039 (w), 2956 (s), 2926 (vs), 2856 (s), 1616 (m), 1599 (s), 1558 (m), 1503 (s), 1458 (w), 1426 (w), 1380 (w), 1304 (w), 1079 (w), 823 (s), 753 (s); (*cis* isomer) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  8.13-7.30 (6H, Hs in quinoline), 5.74 (t, 1H, *J*=7.64 Hz, =C-H), 2.20 (s, 3H, =C-CH<sub>3</sub>), 2.10 (q, 2H, *J*=7.14 Hz, =C-CH<sub>2</sub>), 1.42-1.29 (m, 2H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.29-1.15 (m, 4H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 0.83 (t, 3H, *J*=6.48 Hz, -CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  160.87, 147.92, 135.73, 131.44, 129.40, 129.29, 127.39, 126.02, 121.61, 31.49, 29.56, 29.16, 23.87, 22.48, 13.99; MS (M/Z) 128 (23.6), 143 (13.9), 156 (16.5), 167 (70.1), 168 (26.4), 180 (44.6), 181 (34.5), 182 (81.4, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>CH<sub>3</sub>), 183 (25.9), 194 (9.9), 196 (100, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 197 (18.9), 210 (17.4, M<sup>+</sup>-CH<sub>2</sub>CH<sub>3</sub>), 224 (13.1, M<sup>+</sup>-CH<sub>3</sub>), 239 (38.8, M<sup>+</sup>); IR (NaCl)  $\nu$  3059 (w), 2957 (s), 2926 (vs), 2856 (s), 1618 (m), 1598 (s), 1557 (w), 1503 (s), 1460 (w), 1428 (w), 1376 (w), 1140 (w), 1074 (w), 832 (s), 756 (s).

**2-(2-Octenyl)isoquinoline 5.** Spectral data were obtained from a mixture of the *trans* and *cis* isomers. (*trans* isomer) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  8.55-7.52 (6H, Hs in quinoline), 5.82 (t, 1H, *J*=7.38 Hz, =C-H), 2.15 (s, 3H, =C-CH<sub>3</sub>), 1.65 (q, 2H, *J*=7.42 Hz, =C-CH<sub>2</sub>), 1.35-1.20 (m, 2H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.20-1.05 (m, 4H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 0.76 (t, 3H, *J*=6.8 Hz, -CH<sub>3</sub>); MS (M/Z) 128 (9.1), 143 (7.6), 154 (11.5), 156 (8.3), 167 (33.0), 168 (12.1), 180 (38.2), 181 (39.0), 182 (34.8, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 183 (7.0), 194 (7.5), 196 (100, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 197 (16.9), 210 (4.2, M<sup>+</sup>-CH<sub>2</sub>CH<sub>3</sub>), 224 (2.1, M<sup>+</sup>-CH<sub>3</sub>), 239 (24.5, M<sup>+</sup>); (*cis* isomer) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  8.52-7.52 (6H, Hs in quinoline), 5.69 (t, 1H, *J*=7.11 Hz, =C-H), 2.34 (q, 2H, *J*=7.50 Hz, =C-CH<sub>2</sub>), 2.20 (s, 3H, =C-CH<sub>3</sub>), 1.60-1.47 (m, 2H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.46-1.33 (m, 4H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 0.92 (t, 3H, *J*=6.95 Hz, -CH<sub>3</sub>); MS (M/Z) 128 (13.7), 143 (11.9), 154 (22.1), 156 (11.0), 167 (71.8), 168 (40.1), 180 (46.7), 181 (42.6), 182 (95.5, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 183 (17.1), 194 (9.0), 196 (100, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 197 (16.1), 210 (14.8, M<sup>+</sup>-CH<sub>2</sub>CH<sub>3</sub>), 224 (12.1, M<sup>+</sup>-CH<sub>3</sub>), 238 (15.0, M<sup>+</sup>-1), 239 (38.8, M<sup>+</sup>).

**2-(1-Octenyl)quinoline 6** (*trans* isomer) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  8.07-7.43 (6H, Hs in quinoline), 6.83 (dt, 1H, *J*=15.9, 6.42 Hz, =C-H), 6.71 (d, 1H, *J*=15.9 Hz, =C-H), 2.32 (q, 2H, *J*=7.2 Hz, =C-CH<sub>2</sub>), 1.57-1.49 (m, 2H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.40-1.20 (m, 6H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 0.90 (t, 3H, *J*=6.7 Hz, -CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  156.50, 138.07, 136.11, 130.96, 129.47, 129.05, 127.38, 125.77, 118.65, 33.05, 31.70, 28.94, 28.84, 22.59, 14.08; MS (M/Z) 128 (10.2), 143 (27.5), 154 (6.4), 155 (11.8), 156 (21.8), 167 (70.3), 168 (73.0), 169 (25.8), 180 (20.3), 182 (100, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 183 (20.4), 196 (21.1, M<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>-CH<sub>3</sub>), 210 (27.7, M<sup>+</sup>-CH<sub>2</sub>CH<sub>3</sub>), 224 (5.6, M<sup>+</sup>-CH<sub>3</sub>), 238 (11.2, M<sup>+</sup>-1), 239 (25.9, M<sup>+</sup>); IR (NaCl)  $\nu$  3058 (w), 3039 (w), 2956 (s), 2927 (vs), 2855 (s), 1616 (m), 1598 (s), 1557 (w), 1504 (s), 1466 (w), 1427 (m), 1313 (w), 968 (s), 816 (w), 782 (w), 750 (s).

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## Facile Synthetic Method for 2,6-Di(aminomethyl)pyridine as Building Block for Macrocyclic Ligands

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Increasing interests of supramolecular chemistry have led to design new macrocyclic ligands for many purposes. 2,6-Di(aminomethyl)pyridine synthon as ligand site and building block was often utilized in many macrocyclic polyamine ligands.<sup>1-3</sup> However, direct incorporation of 2,6-

di(aminomethyl)pyridine moiety into macrocycles has barely been reported apparently because of synthetic difficulty of 2,6-di(aminomethyl)pyridine, **4**. Indirect incorporation of the moiety in the ligands was mostly done by reducing corresponding amides from 2,6-pyridinedicarbonyl chloride, **1**