

# Preparation of palladium complexes of 1,3-di(2-pyridyl)propane derivatives and their use in norbornene polymerization

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## Abstract

A variety of neutral palladium(II) complexes [Pd(L–L)Cl<sub>2</sub>] containing 1,3-di(2-pyridyl)propane (**1**), 1,3-bis(2-pyridyl)-2-pentylpropane (**2**), 1,3-bis(2-pyridyl)-2-phenylpropane (**3a**), 1,3-bis(2-pyridyl)-2-tolylpropane (**4**), and 1,3-bis(2-pyridyl)-2-ferrocenylpropane (**5**) as chelate ligands (L–L) have been synthesized. The crystal structures of 1,3-diphenyl-2,4-di-pyridin-2-yl-butan-1-ol (**3b**), **5**, [(**2**)PdCl<sub>2</sub>], [(**4**)PdCl<sub>2</sub>], and [(**5**)PdCl<sub>2</sub>] have been determined and show a square planar geometry at palladium(II). The neutral complexes were tested in the polymerization of norbornene and copolymerization of norbornene with norbornene derivatives. The complex bearing the pentyl group exhibited high reactivity to give up to  $5.9 \times 10^5$  in molecular weight for the homopolymerization. When [(**4**)PdCl<sub>2</sub>] or [(**5**)PdCl<sub>2</sub>] was used as a catalyst, homopolymers insoluble at 150 °C in trichlorobenzene were obtained. However, copolymerization of norbornene with norbornene derivatives **8a–d** catalyzed by [(**4**)PdCl<sub>2</sub>] gave soluble copolymers with molecular weights up to  $5.1 \times 10^5$ .

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**Keywords:** Neutral palladium(II) complexes; Norbornene; Polymerization; Dipyrityl

## 1. Introduction

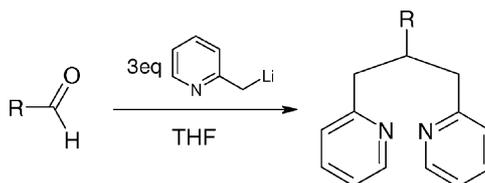
Recently, olefin polymerization by late transition metal complexes has attracted much attention [1]. A prime objective of such research on olefin polymerization is the design of catalysts capable of producing high molecular weight products. A number of neutral and cationic Pd complexes bearing chelating nitrogen ligands have received significant attention as catalysts for olefin polymerization. Previous studies were primarily devoted to complexes incorporating rigid chelating diimine [2], pyridylimine [3], bipyridine-type ligands [4], bis(pyrazolyl)methane ligand [5], tris(pyrazolyl)borata ligands [6], tridentate nitrogen ligands with varying N-heterocycles [7], or imidazole [8]. Recently, a ligand-deficient, cationic palladium(II)-based catalytic system was also reported [9]. During the course of our study on the design of catalysts, we were interested in investigating the coordination properties of a series of 1,3-di(2-pyridyl)propane-based ligands and in determining how electronic and steric factors of these ligands influ-

ence the reactivity at the metal center. We now report the synthesis and structural characterization of Pd(II) dichloride complexes bearing 1,3-di(2-pyridyl)propane derivatives. Their behavior in norbornene polymerization is also reported.

## 2. Results and discussion

### 2.1. Preparation of 1,3-di(2-pyridyl)propane derivatives

1,3-Di(2-pyridyl)propane derivatives **1–5**, which have the same organic structural frame except for R, have been prepared according to Eq. (1).



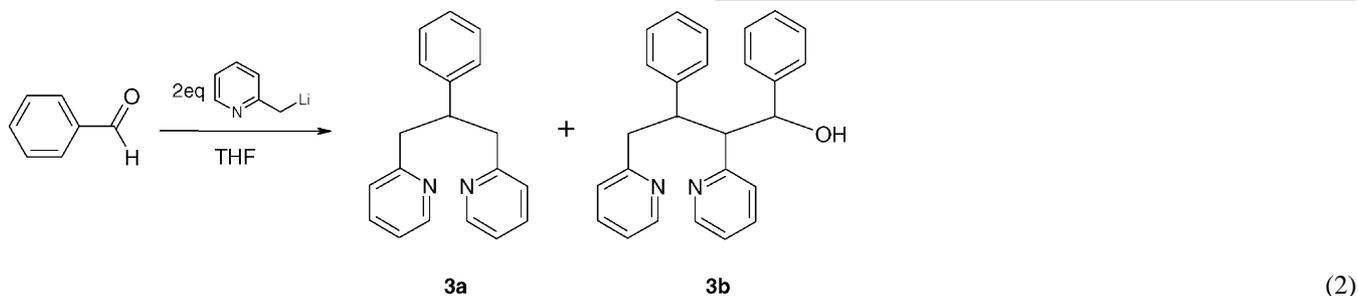
R : H, pentyl, Ph, tolyl, Fc

**1**   **2**   **3a**   **4**   **5**   (1)

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E-mail address: [ykchung@plaza.snu.ac.kr](mailto:ykchung@plaza.snu.ac.kr) (Y.K. Chung).

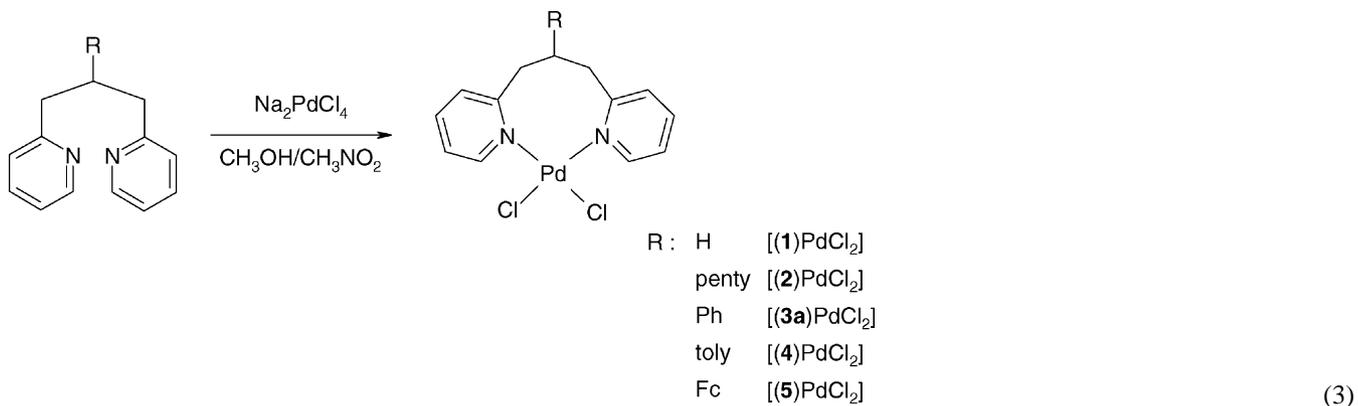
Compounds **1** and **3a** were already known [10,11], but their previous syntheses were somewhat different from ours. The yields for **2** and **5** were 63 and 89%, respectively. When benzaldehyde and *p*-tolualdehyde were used as aldehyde sources, the yields of **3a** and **4** were not so good presumably due to the formation of byproducts. When benzaldehyde reacted with lithiated 2-picoline, we observed the formation of **3a** and **3b** in 28 and 21% yields, respectively (Eq. (2)).



When *p*-nitrobenzaldehyde was used as an aldehyde source, the expected product was not obtained. Thus, the reaction seems to be quite sensitive to the electronic effect of the aldehyde used. The formation of **3b** and **5** was established by X-ray diffraction studies (Figs. 1 and 2). Selected crystallographic data, bond lengths, and bond angles are summarized in Tables 1 and 2.

## 2.2. Preparation of palladium(II) complexes

The Pd(II) complexes of [(1)PdCl<sub>2</sub>], [(2)PdCl<sub>2</sub>], [(3a)PdCl<sub>2</sub>], [(4)PdCl<sub>2</sub>], and [(5)PdCl<sub>2</sub>] were prepared in good yields (73–93%) by addition of 1 equivalent Na<sub>2</sub>PdCl<sub>4</sub> to the appropriate ligand in a solvent mixture of nitromethane and methanol (v/v, 1:1; Eq. (3)). A related palladium(II) complex of [(1)PdCl<sub>2</sub>] has been reported [12].



All the palladium complexes have been characterized by <sup>1</sup>H NMR spectroscopy and elemental analysis. They are very air-stable. Complex [(2)PdCl<sub>2</sub>] is quite soluble in a polar organic solvent, such as dichloromethane, methanol, nitromethane, and acetone, but other complexes are only slightly soluble in nitromethane. It seems that the introduction of a long alkyl chain, such as a pentyl group, dramatically improves the solubility of the palladium complex

in a polar organic solvent. Single crystals of [(2)PdCl<sub>2</sub>], [(4)PdCl<sub>2</sub>], and [(5)PdCl<sub>2</sub>] were grown and their structures were determined by X-ray diffraction studies. The molecular structures of [(2)PdCl<sub>2</sub>], [(4)PdCl<sub>2</sub>], and [(5)PdCl<sub>2</sub>] are shown in Figs. 3–5. Selected crystallographic data, bond lengths, and bond angles are summarized in Tables 1 and 2.

The structures are four coordinate, with ligation to the two pyridyl nitrogens and two chlorides. The geometry about the

palladium atom is best described as distorted square planar. The eight-membered chelate ring is not planar but puckered. The Pd–N bond distances were observed in the range of 2.024(4)–2.044(4) Å and those of Pd–Cl in the range of 2.282(2)–2.3025(10) Å. Due to the bichelating of the dipyridyl ligand, the bond angles of N1–Pd–N2 were in the range of 86.2(2)–87.73(14)° and the observed bond angles of Cl1–Pd–Cl2 in the range of 92.36(9)–93.41(4)°. The bond angles of N1–Pd–N2 are larger than those in other Pd(II) complexes with pyridinylimine and bipyridine chelating ligands [3,14] and the bond angles of Cl1–Pd–Cl2 are smaller than those in other Pd(II) complexes with pyridinylimine and bipyridine chelating ligands [3,15], respectively. The angles between the two pyridinyl rings for [(2)PdCl<sub>2</sub>], [(4)PdCl<sub>2</sub>], and [(5)PdCl<sub>2</sub>] were 86.71(20), 83.99(12), and 79.68(20)°,

respectively. In [(5)PdCl<sub>2</sub>], the two cyclopentadienyl rings are eclipsed.

## 2.3. Homopolymerization of Norbornene and Copolymerization of Norbornene with 7a–d and 8a–d

The palladium-based catalysts [(1)PdCl<sub>2</sub>], [(2)PdCl<sub>2</sub>], [(3a)PdCl<sub>2</sub>], [(4)PdCl<sub>2</sub>], and [(5)PdCl<sub>2</sub>] can be activated

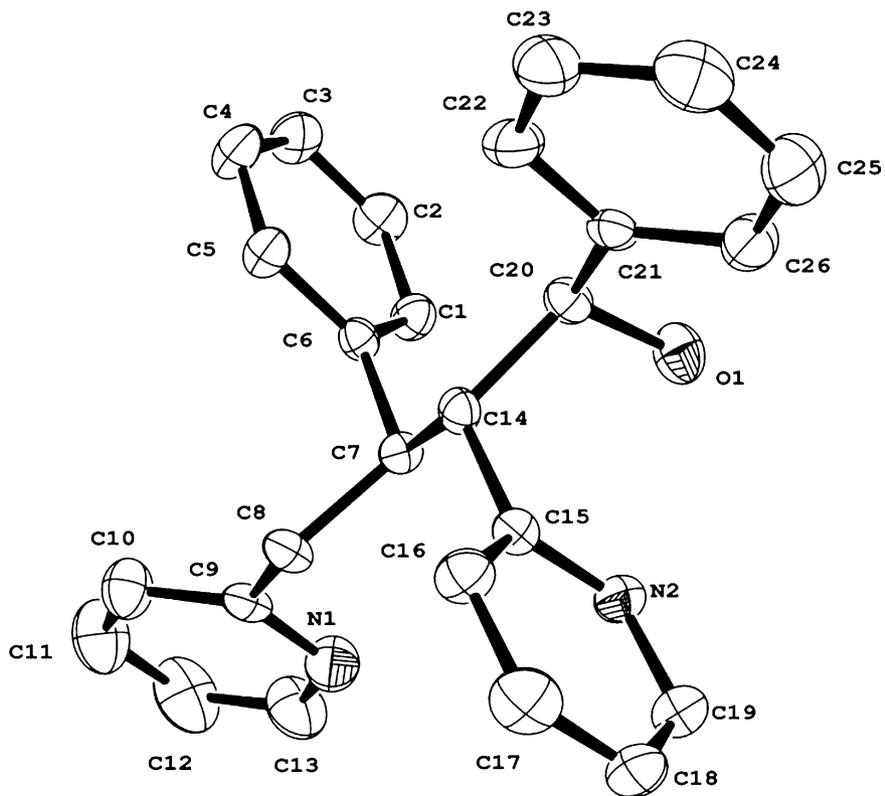
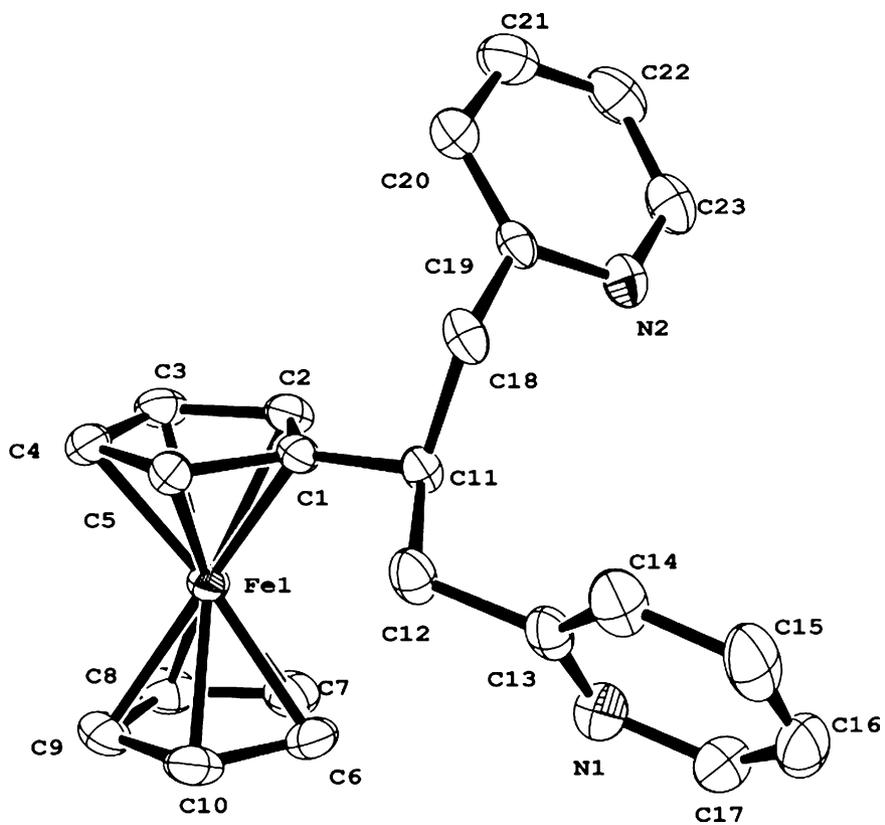
Fig. 1. ORTEP drawing of **3b** with 30% thermal ellipsoid.Fig. 2. ORTEP drawing of **5** with 30% thermal ellipsoid.

Table 1  
Crystal data and structure refinement for **3b**, **5**, [(2)PdCl<sub>2</sub>], [(4)PdCl<sub>2</sub>], and [(5)PdCl<sub>2</sub>]

	<b>3b</b>	<b>5</b>	[(2)PdCl <sub>2</sub> ]	[(4)PdCl <sub>2</sub> ]	[(5)PdCl <sub>2</sub> ]
Empirical formula	C <sub>26</sub> H <sub>24</sub> N <sub>2</sub> O	C <sub>23</sub> H <sub>22</sub> FeN <sub>2</sub>	C <sub>18</sub> H <sub>24</sub> Cl <sub>2</sub> N <sub>2</sub> Pd	C <sub>20</sub> H <sub>20</sub> Cl <sub>2</sub> N <sub>2</sub> Pd	C <sub>24</sub> H <sub>25</sub> Cl <sub>2</sub> FeN <sub>3</sub> O <sub>2</sub> Pd
Formula weight	380.47	382.28	445.69	465.68	620.62
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	14.342(3)	10.8813(3)	9.3084(3)	9.2050(5)	8.1797(4)
<i>b</i> (Å)	5.8334(7)	10.3638(2)	10.3100(5)	9.8800(6)	13.1367(6)
<i>c</i> (Å)	25.509(8)	16.6638(5)	10.9166(4)	21.3810(9)	23.0830(6)
$\alpha$ (°)	90	90	100.165(3)	90	90
$\beta$ (°)	105.62(2)	92.7324(15)	107.261(3)	90.630(3)	90
$\gamma$ (°)	90	90	102.132(3)	90	90
Volume (Å <sup>3</sup> )	2055.3(8)	1877.07(8)	945.59(6)	1944.39(18)	2480.37(18)
<i>Z</i>	4	4	2	4	4
<i>d</i> (calculated, mg/m <sup>3</sup> )	1.230	1.353	1.565	1.591	1.662
$\theta$ range (°)	1.66–24.96	2.19–27.45	2.02–27.46	2.21–27.49	1.76–27.48
No. of total collection	2863	7373	7608	5548	4740
No. of unique data	2757	4096	4274	4067	4740
No. of params refined	358	232	211	226	288
<i>R</i> 1	0.0533	0.0401	0.0421	0.0371	0.0601
<i>wR</i> 2	0.1175	0.1182	0.1285	0.1085	0.1595
GOF	0.993	1.222	1.137	1.194	1.069

Table 2  
Selected bond lengths (Å) and angles (°) for **3b**, **5**, [(2)PdCl<sub>2</sub>], [(4)PdCl<sub>2</sub>], and [(5)PdCl<sub>2</sub>]

<b>3b</b>	C(14)–C(20) 1.543(5) O(1)–C(20)–C(14) 111.0(3)	O(1)–C(20) 1.438(4) C(21)–C(20)–C(14) 111.6(3)	C(20)–C(21) 1.512(5)
<b>5</b>	Fe(1)–C(6) 2.031(2) N(1)–C(13) 1.334(4) C(5)–C(1)–Fe(1) 69.22(12) C(1)–C(11)–C(12) 112.15(17)	Fe(1)–C(1) 2.050(2) N(2)–C(19) 1.341(3) C(11)–C(1)–Fe(1) 128.15(15)	C(1)–C(11) 1.507(3) C(1)–C(2) 1.440(3)
[(2)PdCl <sub>2</sub> ]	Pd(1)–N(2) 2.034(4) Pd(1)–Cl(2) 2.2959(12) C(12)–C(14) 1.478(10) N(2)–Pd(1)–N(1) 87.73(14) N(2)–Pd(1)–Cl(2) 89.65(11) C(1)–N(1)–Pd(1) 117.6(3)	Pd(1)–N(1) 2.044(4) N(1)–C(5) 1.342(6) Cl(1)–Pd(1)–Cl(2) 92.87(6) N(1)–Pd(1)–Cl(1) 89.66(11) C(14)–C(12)–C(11) 112.3(11) C(5)–N(1)–Pd(1) 121.8(3)	Pd(1)–Cl(1) 2.2910(12) N(2)–C(6) 1.351(6)
[(4)PdCl <sub>2</sub> ]	Pd–N(1) 2.024(3) Pd–Cl(1) 2.3025(10) C(13)–C(14) 1.525(4) N(1)–Pd–Cl(2) 89.78(9) Cl(2)–Pd–Cl(1) 93.41(4) C(1)–N(1)–Pd 117.7(3)	Pd–N(2) 2.036(3) N(1)–C(5) 1.344(4) N(1)–Pd–N(2) 87.13(11) N(2)–Pd–Cl(1) 89.69(9) C(5)–N(1)–Pd 121.8(2) C(14)–C(13)–C(6) 110.0(3)	Pd–Cl(2) 2.2990(10) N(2)–C(11) 1.346(4)
[(5)PdCl <sub>2</sub> ]	Pd(1)–N(1) 2.025(6) Pd(1)–Cl(2) 2.283(2) C(1)–C(11) 1.495(8) N(1)–Pd(1)–N(2) 86.2(2) Cl(1)–Pd(1)–Cl(2) 92.36(9) C(2)–C(1)–C(11) 128.8(7) C(13)–N(1)–Pd(1) 122.7(4)	Pd(1)–N(2) 2.041(6) Fe(1)–C(1) 2.060(7) N(1)–C(13) 1.350(9) N(1)–Pd(1)–Cl(2) 91.51(18) N(2)–Pd(1)–Cl(1) 89.88(18) C(17)–N(1)–Pd(1) 117.5(5) C(1)–C(11)–C(12) 105.2(5)	Pd(1)–Cl(1) 2.282(2) Fe(1)–C(6) 2.062(9) N(2)–C(19) 1.341(9)

Table 3  
Norbornene homopolymerization result<sup>a</sup>

Catalyst	$M_w$	$M_n$	$M_w/M_n$	Yield (%) <sup>b</sup>
1 [(1)PdCl <sub>2</sub> ]	329000	112900	2.91	99
2 [(2)PdCl <sub>2</sub> ]	593600	216800	2.74	99
3 [(3a)PdCl <sub>2</sub> ]	457000	154100	2.97	99
4 <sup>c</sup> [(4)PdCl <sub>2</sub> ]	–	–	–	99
5 <sup>c</sup> [(5)PdCl <sub>2</sub> ]	–	–	–	99

<sup>a</sup> Reaction conditions: catalyst 0.1 mol%; MAO/catalyst = 1000; r.t., 5 min in toluene.

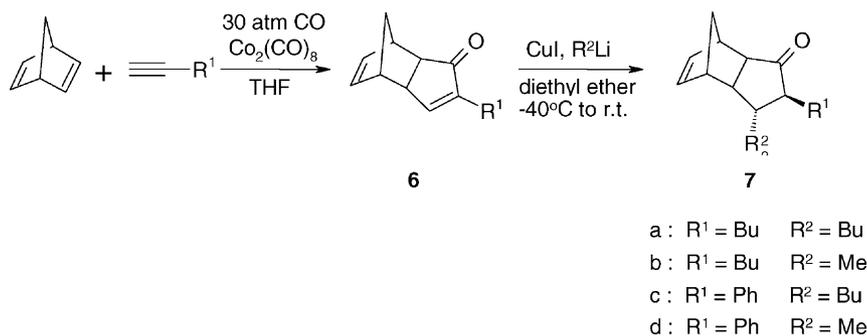
<sup>b</sup> Isolated yield.

<sup>c</sup> Insoluble polymer at 150 °C in 1,2,4-trichlorobenzene.

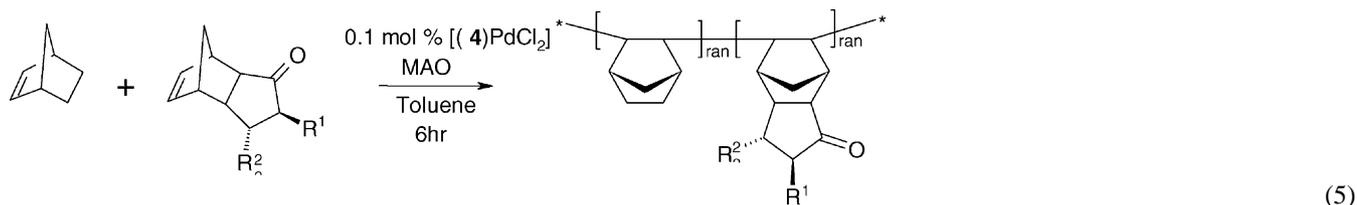
for norbornene polymerization with methylaluminumoxane. Polymerization results and conditions are summarized in Table 3.

The reaction was completed at room temperature within 5 min. Up to 100% monomer conversion was observed. Polymers obtained were white powdery solids. The molecular weights of the polynorbornenes were not determined at room temperature because of their insolubility. Instead, the molecular weights of the polynorbornenes were determined by the high temperature GPC in 1,2,4-trichlorobenzene at 150 °C. In the cases of [(1)PdCl<sub>2</sub>], [(2)PdCl<sub>2</sub>], and [(3a)PdCl<sub>2</sub>], molecular weights in the range of 330,000–590,000 were determined. For the other two cases, we could not achieve high temperature GPC data due to poor solubility.

Next, we prepared norbornene derivatives **7a–d** using the intermolecular Pauson–Khand reaction products to use them as monomers in the copolymerization with norbornene (Eq. (4)).



Syntheses of **7a–d** were previously reported by us [13]. We examined copolymerization of norbornene with **7a–d** using [(4)PdCl<sub>2</sub>] (0.1 mol%) as a catalyst in toluene for 6 h (Eq. (5) and Table 4).



The ratios of 1:1 and 5:1 of norbornene to **7a–d** were used. When the ratio of norbornene to **7a–d** was 1:1, formation of copolymers was not observed. When the ratio of norbornene

Table 4  
Copolymerization of norbornene and monomers with functionality<sup>a</sup>

Entry	Ratio <sup>b</sup>	Monomer	$M_w$	$M_n$	$M_w/M_n$	Yield (%) <sup>c</sup>
1	– <sup>d</sup>	<b>7a</b>	1700	1600	1.06	20
2	– <sup>d</sup>	<b>7b</b>	10500	5200	2.02	75
3	30:1 <sup>e</sup>	<b>7c</b>	17200	7100	2.42	83
4	15.5:1 <sup>e</sup>	<b>7d</b>	42700	11000	3.88	70

<sup>a</sup> Reaction conditions: [(4)PdCl<sub>2</sub>]-catalyst 0.1 mol%; MAO/catalyst = 1000; monomer ratio 1:5; r.t., 6 h in toluene.

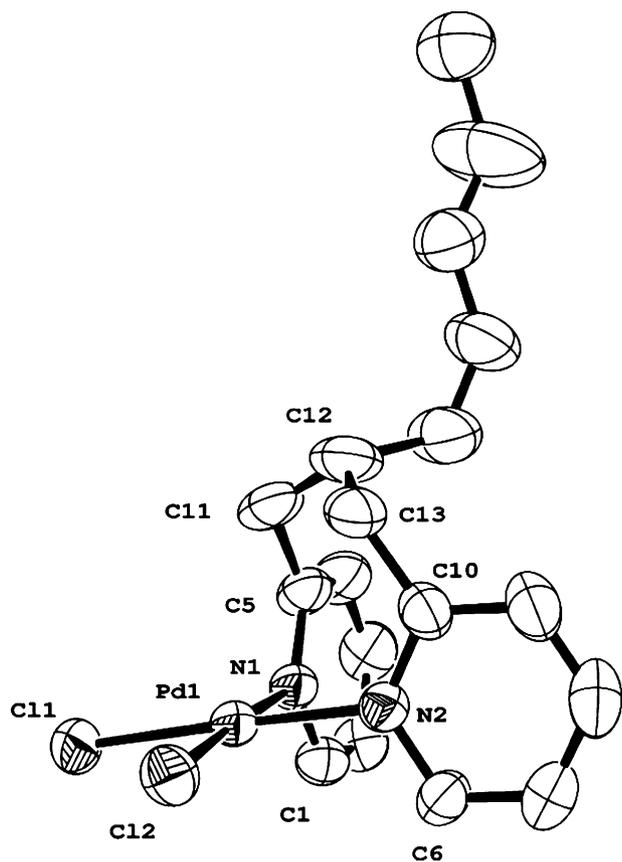
<sup>b</sup> Ratio calculated by [<sup>1</sup>H] NMR (norbornene: monomer **7**).

<sup>c</sup> Isolated yield.

<sup>d</sup> Cannot be calculated by [<sup>1</sup>H] NMR.

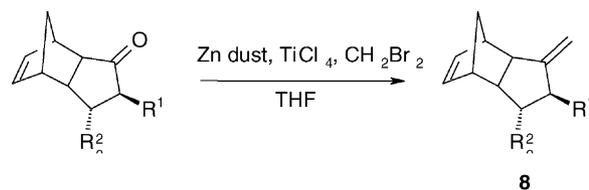
<sup>e</sup> Ratio calculated by [<sup>1</sup>H] NMR in 1,2-dichlorobenzene-d<sub>4</sub> at 150 °C.

to **7a–d** was 5:1, copolymers, showing a poor solubility in tetrahydrofuran (THF), chloroform, and dichloromethane, were formed in reasonable yields (70–83%) except for **7a** (20%). In the case of **7a** (entry 1), the molecular weight was only 1700. For **7b–d**, the molecular weight ranged from 10,500 to 42,700. The ratios of norbornene to **7c–d** in the copolymers were 30:1 and 15.5:1, respectively. Thus, the copolymers derived from **7c** or **7d** consisted of a large fraction of norbornene and a very small fraction of **7c–d**. The GPC profiles of the copolymers did not show a perfect uni-modal shape, but it looked like two humps, sometimes merged. The CDCl<sub>3</sub>-soluble parts of the copolymers derived from **7c** and **7d** showed that the ratios of norbornene to **7c** and **7d** were 10:1 and 5:1, respectively, meaning that the copolymers were composed of at least two kinds of polymers. Thus, the use of **7a–d** as a monomer in the copolymerization of norbornene was unsuccessful. The low contents

Fig. 3. ORTEP drawing of [(2)PdCl<sub>2</sub>] with 50% thermal ellipsoid.

of **7a–d** in the copolymers and the low molecular weight of the copolymers were presumably due to the polar functional group in **7a–d** as observed in other palladium(II)-catalyzed copolymerization with norbornene derivatives having polar functional groups [16]. Thus, we tried to remove a ketone group from **7a–d**.

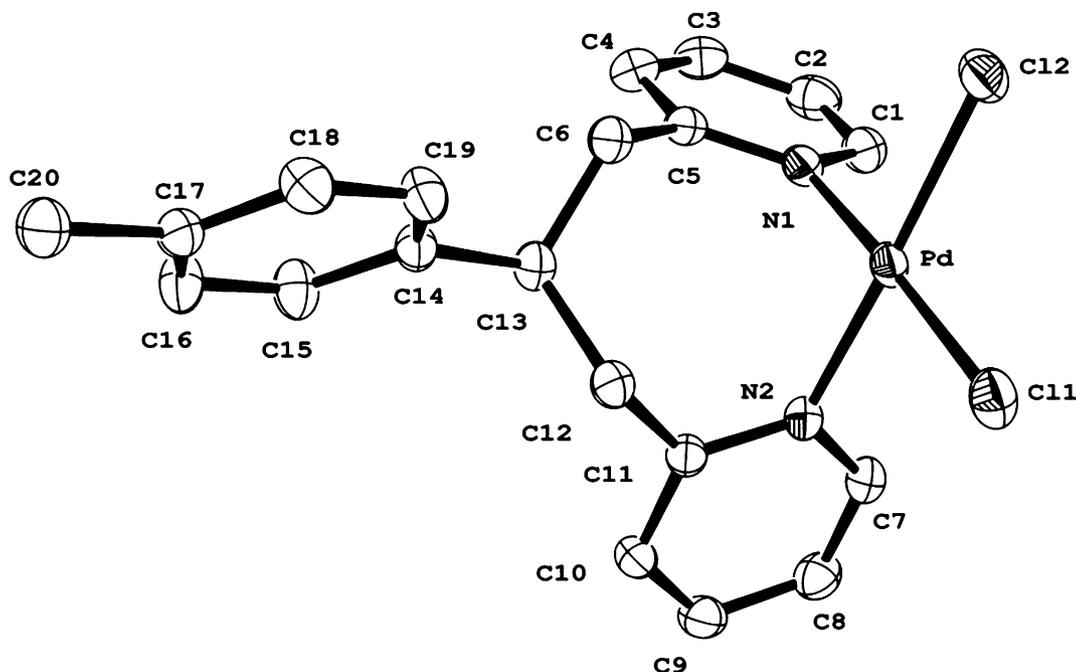
Compounds **8a–d** were prepared in high yields by the reaction of **7a–d** with zinc dust in the presence of TiCl<sub>4</sub> (Eq. (6)).



- a: R<sup>1</sup> = Bu R<sup>2</sup> = Bu  
 b: R<sup>1</sup> = Bu R<sup>2</sup> = Me  
 c: R<sup>1</sup> = Ph R<sup>2</sup> = Bu  
 d: R<sup>1</sup> = Ph R<sup>2</sup> = Me

(6)

We examined copolymerization of norbornene with **8a–d** using [(4)PdCl<sub>2</sub>] (0.1 mol%) as a catalyst in toluene for 1 h (Table 5). Ratios of 1:1 and 5:1 of norbornene to **8a–d** were used. Copolymers from the 1:1 ratio of norbornene to **8a–d**, which are soluble in THF, chloroform, and dichloromethane, were formed in reasonable yields (63–66%). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of a monomer and copolymer of **8a** are shown in Fig. 6. The <sup>1</sup>H NMR spectra showed that the actual ratios of norbornene to **8a–d** were 1.2:1, 2.4:1, 3.3:1, and 1.6:1 for **8a**, **8b**, **8c**, and **8d**, respectively. Thus, the compositions

Fig. 4. ORTEP drawing of [(4)PdCl<sub>2</sub>] with 30% thermal ellipsoid.

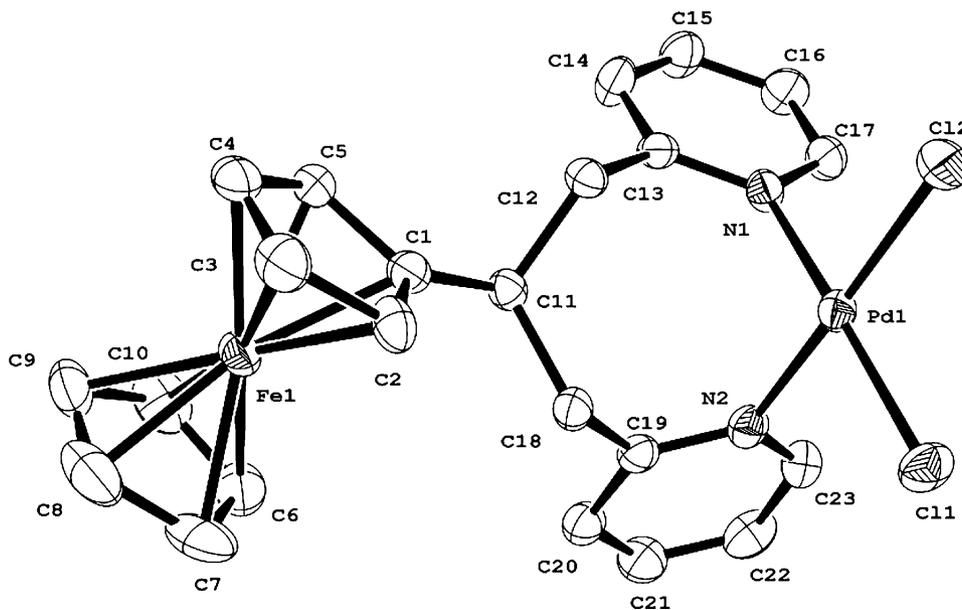


Fig. 5. ORTEP drawing of  $[(5)PdCl_2]$  with 30% thermal ellipsoid.

of copolymers for **8a** and **8d** were close to the ratios of the used reactants. According to GPC data, the molecular weight of the copolymers ranged from 96,200 to 332,600. When **8b** was used as a monomer, the highest molecular weight (332,600) was obtained. It seems that the molecular weight of the copolymers depended upon the bulkiness

of the monomer used. The order of the molecular weight of the copolymers was **8b** > **8d** > **8a** > **8c**. Copolymers from the 5:1 ratio of norbornene to **8a–d**, which are insoluble in organic solvents at room temperature, were formed in high yields (75–98%). The actual ratios of norbornene to **8a–d** were determined by high temperature  $^1H$  NMR

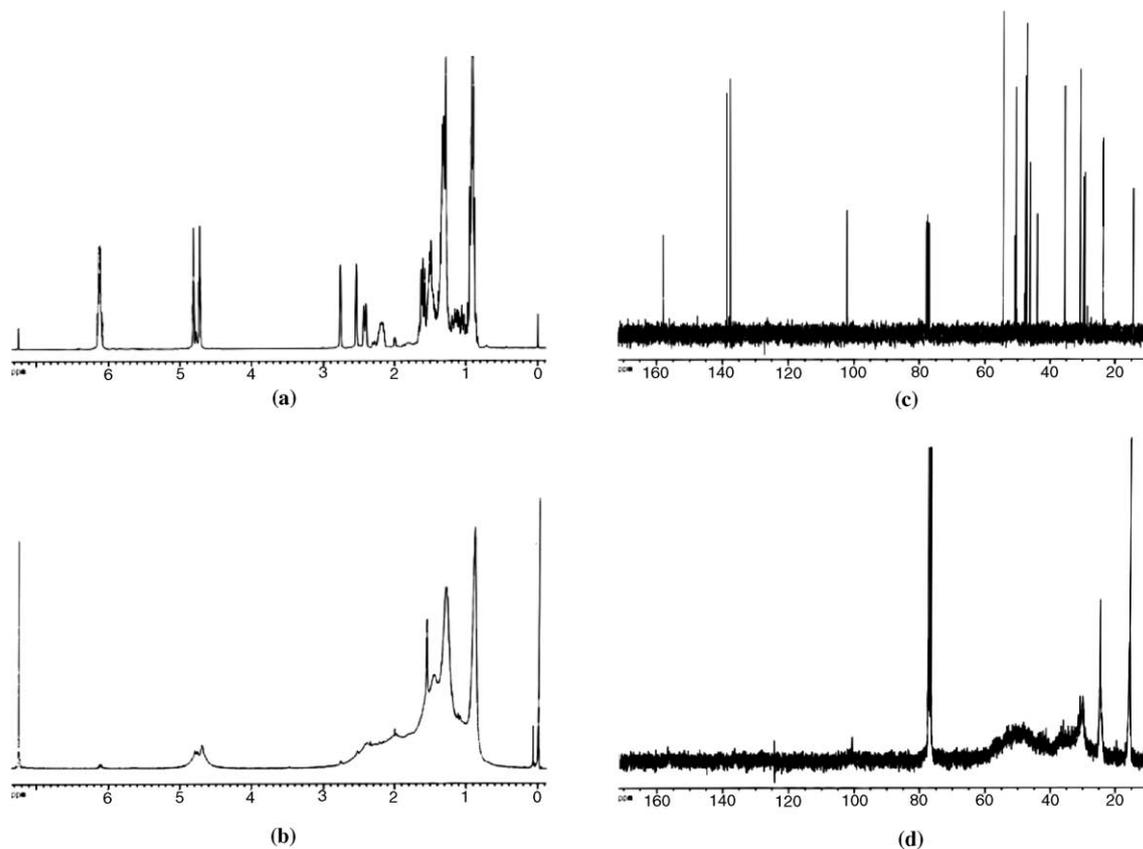


Fig. 6.  $^1H$  and  $^{13}C$  NMR spectra of: (a) and (c) monomer **8a**; and (b) and (d) copolymer of **8a** and norbornene with the ratio of 1:1.

Table 5  
Copolymerization of norbornene with new monomers<sup>a</sup>

Entry	Ratio <sup>b</sup>	Ratio <sup>c</sup>	Monomer	$M_w$	$M_n$	$M_w/M_n$	Yield (%) <sup>d</sup>
1	1:1	1.2:1	<b>8a</b>	125700	56700	2.22	63
2	5:1	5.3:1 <sup>e</sup>	<b>8a</b>	389500	161800	2.41	98
3	1:1	2.4:1	<b>8b</b>	332600	121300	2.74	66
4	5:1	7.6:1 <sup>e</sup>	<b>8b</b>	505600	176500	2.86	88
5	1:1	3.3:1	<b>8c</b>	96200	36000	2.67	66
6	5:1	7.2:1 <sup>e</sup>	<b>8c</b>	137400	53800	2.55	75
7	1:1	1.6:1	<b>8d</b>	162100	63800	2.54	66
8	5:1	5.5:1 <sup>e</sup>	<b>8d</b>	403000	172800	2.33	98

<sup>a</sup> Reaction conditions: [(4)PdCl<sub>2</sub>]-catalyst 0.1 mol%; MAO/catalyst = 1000; r.t., 1 h in toluene.

<sup>b</sup> Ratio of reactants (norbornene: monomer **8**).

<sup>c</sup> Ratio calculated by [<sup>1</sup>H] NMR.

<sup>d</sup> Isolated yield.

<sup>e</sup> Ratio calculated by [<sup>1</sup>H] NMR in 1,2-dichlorobenzene-d<sub>4</sub> at 150 °C.

spectroscopy in deuterated 1,2-dichlorobenzene. The ratios of norbornene to **8a–d** were 5.3:1, 7.6:1, 7.2:1, and 5.5:1 for **8a**, **8b**, **8c**, and **8d**, respectively. The high temperature GPC data show that the molecular weights of copolymers were from 137,400 to 505,600. When **8b** was used as a monomer, the highest molecular weight (505,600) was obtained. The order of the molecular weight of the copolymers was **8b** > **8d–a** > **8c**. Thus, the same trend was observed. Compared to the homopolymerization of norbornene by the same catalyst [(4)PdCl<sub>2</sub>], the introduction of **8a–d** to the polymer may relax the steric rigidity or regularity of the homopolymer and produces soluble copolymers of high molecular weight at room temperature or at high temperature depending upon the ratio of norbornene to **8a–d**.

The TGA and DSC study show that copolymers are stable up to 420 °C without noticeable loss of weight. Neither  $T_m$  nor  $T_g$  was observed in the range of 20–400 °C.

### 3. Conclusion

A very reactive catalyst system for vinyl-type polymerization of norbornene can be obtained by addition of MAO to Pd(II)–dipyridyl complexes. The polynorbornene is, however, insoluble in chlorobenzene. Copolymerization of norbornene and norbornene derivatives **8a–d** produces soluble copolymers in good yields. Due to the ease of structural variations of their ligand systems the Pd(II)–dipyridyl complexes might open the way to a new family of late transition metal cycloolefin polymerization catalysts.

## 4. Experimental

### 4.1. General

All manipulations of air- and/or moisture-sensitive compounds were carried out with use of standard Schlenk

or vacuum-line techniques. Freshly distilled, dry, and oxygen-free solvents were used throughout. <sup>1</sup>H NMR spectra were obtained with a Bruker 300 or 500 spectrometer. Elemental analyses were done at National Center for Inter-University Research Facilities, Seoul National University, Seoul. Molecular weight and molecular weight distributions were measured by gel permeation chromatography (GPC) relative to polystyrene standards. Thermal gravimetric analysis (TGA) was carried out on TA Instrument (TGA 2050; heating rate: 10 K/min). Infrared spectra were recorded on a JASCO FT/IR-660 spectrometer. Anhydrous toluene, tetrahydrofuran, diethyl ether, and dichloromethane were used. Methylalumoxane (MAO) was purchased as a solution in toluene from Akzo (10 wt.% of Al, MMAO type 4). Compound **1** was previously reported by Leonard and Boyer [10(a)], Sartoris and Pines [10(b)] and **3a** by Bloc and co-workers [11], and **7a–d** were prepared by the published procedure [13].

### 4.2. Synthesis of 1,3-di(2-pyridyl)propane derivatives

#### 4.2.1. Synthesis of **2**

Diisopropyl amine (3.8 ml, 2.7 mmol) and *n*-BuLi (11.4 ml, 2.5 M in hexane) were dissolved in 60 ml of THF in a Schlenk flask at –78 °C. After the solution was stirred for 30 min at –78 °C, 2-picoline (2.5 ml, 25 mmol) was added to it. The solution was allowed to warm to room temperature and stirred for 30 min. To the solution was added hexanal (1.0 ml, 8.3 mmol). The resulting solution was stirred overnight and quenched with water (100 ml). After washing with saturated NaHCO<sub>3</sub> (100 ml), CH<sub>2</sub>Cl<sub>2</sub> (100 ml) was added to extract the dipyridyl compound. The CH<sub>2</sub>Cl<sub>2</sub> layer was dried over anhydrous MgSO<sub>4</sub>, concentrated, and chromatographed on a silica gel column eluting with hexane and diethyl ether (1:1 (v/v)). Removal of the solvent gave the product in 63% yield (1.40 g, 5.2 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.50 (d, 4.9 Hz, 2H), 7.53 (t, 7.6 Hz, 2H), 7.13 (d, 7.7 Hz, 2H), 7.06 (t, 4.9 Hz, 2H), 2.78 (m, 4H), 2.50 (m, 1H), 1.34–1.17 (m, 8H), 0.82 (t, 6.8 Hz, 3H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 162.0, 149.9, 136.8, 124.5, 121.7, 43.6, 40.3, 34.2, 32.8, 27.0, 23.4, 14.9 ppm; HRMS  $M^+$  calculated: 268.1939; observed: 268.1923.

#### 4.2.2. Synthesis of **3a**

The same procedure as the synthesis of **2** was applied except for the use of benzaldehyde instead of hexanal and elution with diethyl ether and methanol (10:1 (v/v)) instead of hexane and diethyl ether (1:1 (v/v)). A mixture of **3a** and **3b** was obtained as products. Compounds **3a** and **3b** have quite similar  $R_f$  values in chromatography. To obtain pure **3a** and **3b**, a mixture of **3a** and **3b** was first separated from other compounds via a chromatography on a silica gel column eluting with diethyl ether and methanol (10:1 (v/v)). Compounds **3a** and **3b** have quite different solubilities in diethyl ether: **3a** is quite soluble but **3b** is insoluble. After removal of the solvent, the solid was put in diethyl ether

and the solution was stirred for 30 min. Filtration gave **3b** as a solid and **3a** could be obtained from the filtrate. The yields of **3a** and **3b** were 28 and 21%, respectively. **3a**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.45 (d, 3.2 Hz, 2H), 7.35 (t, 7.8 Hz, 2H), 7.11 (m, 5H), 6.93 (m, 4H), 3.73 (m, 1H), 3.19 (m, 4H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  161.0, 150.0, 144.7, 136.9, 129.1, 128.6, 127.1, 124.6, 121.9, 47.3, 45.8 ppm; HRMS  $M^+$  calculated: 274.1470, observed: 274.1472. **3b**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.62 (d, 4.8 Hz, 1H), 8.36 (d, 4.8 Hz, 1H), 7.41 (m, 3H), 7.28 (m, 2H), 7.17 (m, 2H), 7.07 (m, 3H), 6.85 (m, 4H), 6.72 (d, 7.8 Hz, 1H), 6.33 (d, 7.8 Hz, 1H), 4.68 (d, 9.0 Hz, 1H), 4.17 (td, 11.6, 4.3 Hz, 1H), 3.30 (d, 11.2 Hz, 1H), 2.93 (t, 13.3 Hz, 1H), 2.71 (dd, 13.7, 4.4 Hz, 1H) ppm. Analytically calculated for  $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}$ : C, 82.07; H, 6.36; N, 7.41. Found: C, 82.23; H, 6.48; N, 7.41.

#### 4.2.3. Synthesis of **4**

The same procedure as the synthesis of **2** was applied except for the use of *p*-tolualdehyde instead of hexanal and elution with diethyl ether and methanol (10:1 (v/v)) instead of hexane and diethyl ether (1:1 (v/v)). Yield: 36%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.47 (d, 4.9 Hz, 2H), 7.43 (t, 7.7 Hz, 2H), 7.03–6.93 (m, 8H), 3.70 (t, 7.0 Hz, 1H), 3.16 (m, 4H), 2.24 (s, 3H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  161.2, 150.0, 141.2, 136.9, 136.4, 129.8, 128.5, 124.6, 121.9, 46.8, 45.9, 22.0 ppm; HRMS  $M^+$  calculated: 288.1626; observed: 288.1622.

#### 4.2.4. Synthesis of **5**

The same procedure as the synthesis of **2** was applied except for the use of ferrocenecarboxaldehyde instead of hexanal and elution with diethyl ether instead of hexane and diethyl ether (1:1 (v/v)). Yield: 89%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.51 (d, 4.9 Hz, 2H), 7.49 (t, 7.7 Hz, 2H), 7.04 (m, 4H), 4.12 (s, 5H), 3.99 (s, 2H), 3.83 (s, 2H), 3.56 (m, 1H), 3.16 (dd, 13.5, 6.2 Hz, 2H), 2.96 (dd, 13.5, 8.0 Hz, 2H) ppm. Analytically calculated for  $\text{C}_{23}\text{H}_{22}\text{FeN}_2$ : C, 72.26; H, 5.80; N, 7.33. Found: C, 72.11; H, 5.82; N, 7.20.

### 4.3. Synthesis of palladium(II) complexes

#### 4.3.1. Synthesis of [(1)PdCl<sub>2</sub>]

Compound **1** (0.20 g, 1.0 mmol) was dissolved in a mixture solvent of methanol (5.0 ml) and nitromethane (5.0 ml) at room temperature.  $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$  (0.35 g) was added to the solution. In the beginning,  $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$  was completely dissolved in the solvent. After the solution was stirred for 1 h, precipitation started. After stirring for an additional 1 h, the precipitate was filtered, successively washed with methanol and water, and dried in vacuo. 0.85 g of the product (88%) was obtained.  $^1\text{H}$  NMR ( $\text{CD}_3\text{NO}_2$ )  $\delta$  8.89 (d, 4.8 Hz, 2H), 7.69 (t, 8.7 Hz, 2H), 7.34 (d, 8.2 Hz, 2H), 7.25 (t, 6.5 Hz, 2H), 4.70 (t, 13.1 Hz, 2H), 3.56 (d, 7.9 Hz, 2H), 2.91 (1H), 1.96 (1H) ppm (the splitting patterns of the peaks at 2.91 and 1.96 ppm were obscure due to the line-broadening). We could not take the  $^{13}\text{C}$  NMR spectrum because of its poor solubility in any deuterated solvents. Analytically calculated

for  $\text{C}_{13}\text{H}_{14}\text{Cl}_2\text{N}_2\text{Pd}$ : C, 41.57; H, 3.76; N, 7.46. Found: C, 41.45; H, 3.67; N, 7.17.

#### 4.3.2. Synthesis of [(2)PdCl<sub>2</sub>]

The same procedure as the synthesis of [(1)PdCl<sub>2</sub>] was applied. However, the precipitation did not occur within 2 h. After the solution was stirred 5 h, the solution was poured into excess diethyl ether to get precipitates. The precipitate was filtered, washed two times with water, and dried in vacuo. Yield: 90%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  9.14 (d, 5.3 Hz, 2H), 7.57 (t, 7.7 Hz, 2H), 7.24–7.16 (m, 4H), 4.87 (dd, 13.7, 9.8 Hz, 2H), 3.36 (t, 13.8 Hz, 2H), 1.86–1.31 (m, 8H), 0.98 (t, 6.8 Hz, 3H) ppm;  $^{13}\text{C}$  NMR ( $\text{DMSO-d}_6$ )  $\delta$  163.79, 152.17, 140.31, 127.41, 124.61, 47.47, 44.22, 32.44, 26.50, 23.00, 22.55, 14.95 ppm. Analytically calculated for  $\text{C}_{18}\text{H}_{24}\text{Cl}_2\text{N}_2\text{Pd}$ : C, 48.50; H, 5.43; N, 6.28. Found: C, 48.56; H, 5.39; N, 5.93.

#### 4.3.3. [(3a)PdCl<sub>2</sub>]

Yield: 73%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{NO}_2$ )  $\delta$  8.94 (d, 5.9 Hz, 2H), 7.70 (m, 4H), 7.50 (m, 4H), 7.29 (m, 3H), 5.18 (t, 13.2, 11.3 Hz, 2H), 3.63 (d, 13.7 Hz, 2H), 3.38 (m, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{DMSO-d}_6$ )  $\delta$  162.61, 153.39, 141.27, 129.32, 128.83, 127.39, 125.97, 124.94, 123.76, 48.68, 47.87 ppm. Analytically calculated for  $\text{C}_{19}\text{H}_{18}\text{Cl}_2\text{N}_2\text{Pd}$ : C, 50.52; H, 4.02; N, 6.25. Found: C, 50.13; H, 4.00; N, 6.20.

#### 4.3.4. [(4)PdCl<sub>2</sub>]

Yield: 93%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{NO}_2$ )  $\delta$  8.93 (d, 6.2 Hz, 2H), 7.73 (t, 7.5 Hz, 2H), 7.54 (d, 8.0, 2H), 7.44 (d, 7.4 Hz, 2H), 7.29 (m, 4H), 5.15 (m, 2H), 3.60 (d, 13.2 Hz, 2H), 3.30 (t, 10.8 Hz, 1H) ppm. We could not take the  $^{13}\text{C}$  NMR spectrum because of its poor solubility in any deuterated solvents. Analytically calculated for  $\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{N}_2\text{Pd}$ : C, 50.52; H, 4.02; N, 6.25. Found: C, 50.13; H, 4.00; N, 6.20.

#### 4.3.5. [(5)PdCl<sub>2</sub>]

Yield: 79%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{NO}_2$ )  $\delta$  8.91 (d, 4.0 Hz, 2H), 7.74 (t, 7.7 Hz, 2H), 7.45 (d, 7.6, 2H), 7.28 (t, 4.4 Hz, 2H), 4.93 (m, 2H), 3.89 (d, 13.3 Hz, 2H), 3.12 (m, 1H) ppm. (We could not assign the peak positions of  $\text{C}_p$  protons because of overlapping with the solvent peaks.)  $^{13}\text{C}$  NMR ( $\text{DMSO-d}_6$ )  $\delta$  162.68, 152.30, 140.40, 127.85, 126.29, 124.85, 96.12, 69.52, 68.45, 67.34, 48.74 ppm. Analytically calculated for  $\text{C}_{23}\text{H}_{22}\text{Cl}_2\text{FeN}_2\text{Pd}$ : C, 46.45; H, 4.06; N, 6.77. Found: C, 46.41; H, 3.87; N, 6.12.

### 4.4. Crystal structure determinations of **3b**, **5**, [(2)PdCl<sub>2</sub>], [(4)PdCl<sub>2</sub>], and [(5)PdCl<sub>2</sub>]

Single crystals of **3b** were grown by slow evaporation of **3b** in a solution mixture of methanol and dichloromethane, single crystals of **5** by slow diffusion of diethyl ether to a solution of **5** in dichloromethane, single crystals of [(2)PdCl<sub>2</sub>] by slow evaporation of diffusion of dichloromethane solution of [(2)PdCl<sub>2</sub>], single crystals of [(4)PdCl<sub>2</sub>] by slow diffusion

of methanol solution of  $\text{Na}_2\text{PdCl}_4$  to a nitromethane solution of **4**, and single crystals of [(**5**) $\text{PdCl}_2$ ] by slow diffusion of methanol solution of  $\text{Na}_2\text{PdCl}_4$  to a nitromethane solution of **5**, respectively. Diffraction for **3b** was measured by an Enraf–Nonius CAD4 automated diffractometer with an  $\omega/2\theta$  scan method. Unit cells were determined by centering 25 reflections in the appropriate  $2\theta$  range. Other relevant experimental details are listed in Table 1. Diffraction data for other compounds were collected on an Enraf–Nonius CCD single crystal X-ray diffractometer. The structures were solved by SHELXS-97 and refined by full-matrix least-squares with SHELXL-97 [14]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms in **3b** were found in Fourier map and refined. The other hydrogen atoms were refined isotropically using the riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 194993 194989, 194990, 194991 and 194992 for compound **3b**, **5**, [(**2**) $\text{PdCl}_2$ ], [(**4**) $\text{PdCl}_2$ ], and [(**5**) $\text{PdCl}_2$ ], respectively.

#### 4.5. Synthesis of norbornene derivatives **8a–d**

To a solution of Zn dust (4.8 g, 0.073 mol) and  $\text{CH}_2\text{Br}_2$  (2.5 ml) in 30 ml of THF at  $-40^\circ\text{C}$  was slowly added  $\text{TiCl}_4$  (2.0 ml, 0.019 mol). After the solution was stirred at  $5^\circ\text{C}$  for 3 days, a solution of **7a** (2.58 g, 9.9 mmol) in 20 ml of  $\text{CH}_2\text{Cl}_2$  was added. The resulting solution was stirred overnight and poured into 200 ml of aqueous saturated  $\text{NaHCO}_3$  solution. Extraction with diethyl ether followed by chromatography on a silica gel column eluting with hexane:diethyl ether (20:1 (v/v)) gave **8a** in 89% yield (2.28 g).

**8a**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.12 (m, 2H), 4.81 (t, 2.5 Hz, 1H), 4.72 (t, 2.5 Hz, 1H), 2.76 (s, 1H), 2.54 (s, 1H), 2.42 (d, 8.9 Hz, 1H), 2.17 (m, 1H), 1.61 (t, 7.3 Hz, 1H), 1.51–1.29 (m, 15H), 0.91 (m, 6 H) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  158.05, 138.65, 137.54, 102.08, 54.33, 50.78, 50.42, 47.53, 47.18, 46.24, 43.98, 35.48, 30.73, 29.59, 29.21, 23.83, 23.64, 14.52, 14.46 ppm; HRMS ( $M^+$ ) calculated: 258.2348, observed: 258.2351.

**8b**: Yield: 82%;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.05 (t, 1.9 Hz, 2H), 4.73 (t, 2.5 Hz, 1H), 4.65 (t, 2.6 Hz, 1H), 2.70 (s, 1H), 2.48 (s, 1H), 2.33 (d, 8.9 Hz, 1H), 2.02 (m, 1H), 1.48–1.43 (m, 3H), 1.27–1.22 (m, 6H), 0.99 (d, 2.3 Hz, 3H), 0.83 (t, 6.8 Hz, 3H) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  157.96, 138.60, 137.64, 102.06, 55.62, 52.39, 50.08, 45.96, 45.93, 44.16, 42.54, 29.30, 23.86, 19.74, 14.53 ppm; HRMS ( $M^+$ ) calculated: 216.1878; observed: 216.1874.

**8c**: Yield: 81%;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.31–7.13 (m, 5H), 6.18 (s, 2H), 4.85 (t, 2.7 Hz, 1H), 4.25 (t, 2.7 Hz, 1H), 3.33 (d, 11.7 Hz, 1H), 2.86 (s, 1H), 2.66 (s, 1H), 2.58 (d, 8.8 Hz, 1H), 2.20 (m, 1H), 1.77 (t, 8.4 Hz, 1H), 1.57 (d, 8.5 Hz, 1H), 1.40 (d, 7.3 Hz, 1H), 1.44–1.17 (m, 6H), 0.81 (t, 7.2 Hz, 3H) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  159.03, 142.23, 138.72, 137.78, 129.50, 128.60, 126.74, 105.31, 63.10, 50.65, 50.60,

50.58, 47.55, 46.27, 44.28, 35.26, 30.73, 23.48, 14.45 ppm; HRMS ( $M^+$ ) calculated: 278.2035, observed: 278.2036.

**8d**: Yield: 88%;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.32–7.13 (m, 5H), 6.17 (s, 2H), 4.86 (t, 2.4 Hz, 1H), 4.29 (t, 2.4 Hz, 1H), 3.26 (d, 10.9 Hz, 1H), 2.87 (s, 1H), 2.67 (s, 1H), 2.59 (d, 8.7 Hz, 1H), 1.71 (t, 8.3 Hz, 1H), 1.63 (m, 1H), 1.57 (d, 9.0 Hz, 1H), 1.42 (d, 8.7 Hz, 1H), 0.97 (d, 6.3 Hz, 3H) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  158.66, 141.69, 138.64, 137.86, 129.41, 128.62, 126.78, 105.33, 64.13, 51.97, 50.48, 46.12, 46.08, 45.89, 44.43, 19.13 ppm; HRMS ( $M^+$ ) calculated: 236.1565, observed: 236.1563.

#### 4.6. Homopolymerization of norbornene

##### 4.6.1. Typical procedures

In a glove box, to a solution of [(**1**) $\text{PdCl}_2$ ] (4.0 mg, 0.011 mmol) in 10 ml of toluene were added norbornene (1.0 g, 11 mmol) and MAO (7.0 ml). The reaction was completed within 5 min. The reaction flask was taken from the glove box and treated with MeOH to quench excess MAO. The synthesized polymer was added to a solution mixture of MeOH and HCl (1:1 (v/v)) and stirred for 30 min. Filtration followed by washing with MeOH gave polymers in a quantitative yield.

##### 4.7. Copolymerization of norbornene with **7a–d** and **8a–d**

##### 4.7.1. Typical procedures for the synthesis of 5:1 copolymer

In a glove box, to a solution of [(**4**) $\text{PdCl}_2$ ] (5.0 mg, 0.011 mmol) in 10 ml of toluene were added norbornene (1.0 g, 0.011 mol) and **8c** (0.60 g, 2.3 mmol). To the solution was added MAO (7.0 ml). The reaction flask was taken from the glove box and treated with MeOH to quench excess MAO. The synthesized polymer was added to a solution mixture of MeOH and HCl (1:1 (v/v)) and stirred for 30 min. Filtration followed by washing with MeOH gave polymers.

Entry 1 in Table 4:  $^1\text{H NMR}$  (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  2.9–2.2 [br m (2.38 maximum)], 2.2–1.7 [br m (2.05 maximum)], 1.7–1.5 [br m (1.59 maximum)], 1.5–1.2 [br m (1.39 maximum)], 1.20 (br s), 1.07 (br s), 0.96 (br s) ppm;  $^{13}\text{C NMR}$  (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  57–50 (br m), 58–40 (br m), 40–38 (br m), 37–35 (br m), 33–27 (br m), 17.5 (br s), 13.5 (br s) ppm; IR  $\nu_{\text{CO}}$ :  $1735.6\text{ cm}^{-1}$ .

Entry 2 in Table 4:  $^1\text{H NMR}$  (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  2.8–1.7 [br m (2.38 maximum)], 1.7–1.4 [br m (1.58 maximum)], 1.4–1.1 [br m (1.37 maximum)], 0.94 (br s) ppm;  $^{13}\text{C NMR}$  (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  56–54 (br m), 54–47 (br m), 47–37 (br m), 36–33 (br m), 32–25 (br m), 23–20 (br m), 15.2 (br s) ppm; IR  $\nu_{\text{CO}}$ :  $1744.3\text{ cm}^{-1}$ .

Entry 3 in Table 4:  $^1\text{H NMR}$  (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  7.3–7.0 (br m), 2.9–2.2 [br m (2.35 maximum)], 2.2–1.9 [br m (2.03 maximum)], 1.9–1.6 [br m (1.70 maximum)], 1.57 (br s), 1.33 (br s), 1.2–0.7 [br m

(1.01 maximum)] ppm;  $^{13}\text{C}$  NMR (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  128–126 (br m), 79.2 (br s), 58–50 (br m), 48–38 (br m), 36.1 (br s), 35–26 (br m), 22.8 (br s), 17.5 (br s), 13.4 (br s) ppm; IR  $\nu_{\text{CO}}$ :  $1747.2\text{ cm}^{-1}$ .

Entry 4 in Table 4:  $^1\text{H}$  NMR (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  7.3–7.0 (br m), 3.0–2.2 [br m (2.35 maximum)], 2.2–1.9 [br m (1.96 maximum)], 1.9–1.5 [br m (1.58 maximum)], 1.5–1.3 [br m (1.27 maximum)], 1.3–0.6 [br m (1.02 maximum)] ppm;  $^{13}\text{C}$  NMR (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  129–126 (br m), 78.3 (br m), 65.3 (br s), 60–48 (br m), 48–39 (br m), 38.1 (br s), 36.2 (br s), 35–26 (br m), 17.7 (br s) ppm; IR  $\nu_{\text{CO}}$ :  $1744.3\text{ cm}^{-1}$ .

#### 4.7.2. Typical procedures for the synthesis of 1:1 copolymer

To a solution of [(4)PdCl<sub>2</sub>] (5.0 mg, 0.011 mmol) in 10 ml of toluene were added norbornene (0.50 g, 0.011 mol) and **8c** (1.40 g, 5.5 mmol). To the solution was added MAO (7.0 ml). The reaction flask was taken from the dry box and treated with MeOH to quench excess MAO. The synthesized polymer was added to a solution mixture of MeOH and HCl (1:1 (v/v)) and stirred for 30 min. While the solution was stirring, the polymers became oily. Polymers were extracted with dichloromethane. Removal of the solvent followed by addition of methanol gave solids polymers.

Entry 1 in Table 5:  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  4.81 (br s), 4.72 (br s), 2.8–1.7 (br m), 1.7–1.5 [br m (1.6 maximum)], 1.5–1.4 [br m (1.47 maximum)], 1.4–1.0 (br m (1.31 maximum)), 0.9 (br s) ppm;  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  60–55 (br m), 55–38 (br m), 38–32 (br m), 32–27 (br m), 23.9 (br s), 14.5 (br s) ppm.

Entry 2 in Table 5:  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  4.8–4.6 (br m), 2.8–1.8 (br m), 1.8–1.4 [br m (1.46 maximum)], 1.4–1.1 [br m (1.25 maximum)], 1.05 (br s), 0.90 (br s) ppm;  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  60–54 (br m), 54–50 (br m), 50–39 (br m), 37–35 (br m), 33–28 (br m), 23.9 (br s), 20 (br m), 14.5 (br s) ppm.

Entry 3 in Table 5:  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  7.4–7.0 (br m), 4.86 (br s), 4.20 (br s), 3.2–1.7 (br m), 1.7–1.3 [br m (1.38 maximum)], 1.3–0.9 [br m (1.2 maximum)], 0.9–0.6 [br m (0.8 maximum)] ppm;  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  160.8 (br s), 130–122 (br m), 105.3 (br s), 61–50 (br m), 50–40 (br m), 38–35 (br m), 35–26 (br m), 23.5 (br s), 14.5 (br s) ppm.

Entry 4 in Table 5:  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  7.3–6.9 (br m), 4.85 (br s), 4.26 (br s), 3.1–1.8 (br m), 1.8–1.3 [br m (1.5 maximum)], 1.3–0.6 [br m (0.96 maximum)] ppm;  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  160.4 (br s), 130–125 (br m), 107.0 (br s), 62–60 (br m), 60–49 (br m), 49–38 (br m), 38–34 (br m), 34–30 (br m), 23.0 (br s) ppm.

Entry 5 in Table 5:  $^1\text{H}$  NMR (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  5.09 (br s), 4.89 (br s), 3.9–2.2 [br m (2.38 maximum)], 2.2–1.9 [br m (2.04 maximum)], 1.7 (br s), 1.6 (br s), 1.5–1.2 [br m (1.39 maximum)], 1.17 (br s), 1.05 (br s), 0.96 (br s) ppm;  $^{13}\text{C}$  NMR (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  54–48 (br m), 44–38 (br m), 33.7 (br s), 31.9 (br s), 30–26 (br m), 23.9 (br s), 20.8 (br s), 20.3 (br s), 11.5–10 (br m) ppm.

Entry 6 in Table 5:  $^1\text{H}$  NMR (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  4.97 (br s), 4.85 (br s), 2.9–2.2 [br m (2.38 maximum)], 2.2–1.9 [br m (2.06 maximum)], 1.9–1.4 [br m (1.59 maximum)], 1.37 (br s), 1.19 (br s), 0.95 (br s) ppm;  $^{13}\text{C}$  NMR (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  66–50 (br m), 50–47 (br m), 47–41 (br m), 36.3 (br s), 34–28 (br m), 26.3 (br s), 22.9 (br s), 21.2 (br s), 13.7–12.5 (br m) ppm.

Entry 7 in Table 5:  $^1\text{H}$  NMR (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  7.2–7.0 (br m), 5.03 (br s), 4.38 (br s), 3.0–2.1 [br m (2.37 maximum)], 2.1–1.7 [br m (1.89 maximum)], 1.7–1.4 [br m (1.58 maximum)], 1.4–1.0 [br m (1.34 maximum)], 1.0–0.7 [br m (0.81 maximum)] ppm;  $^{13}\text{C}$  NMR (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  127–122 (br m), 55–47 (br m), 44–37 (br m), 35–32 (br m), 31–26 (br m), 22–18 (br m), 11.6 (br s) ppm.

Entry 8 in Table 5:  $^1\text{H}$  NMR (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  7.2–6.9 (br m), 5.0 (br s), 4.4 (br s), 3.4–2.2 [br m (2.37 maximum)], 2.2–1.8 [br m (2.03 maximum)], 1.8–1.4 [br m (1.58 maximum)], 1.34 (br s), 1.3–0.9 [br m (1.20 maximum)] ppm;  $^{13}\text{C}$  NMR (1,2-dichlorobenzene- $d_4$  at  $150^\circ\text{C}$ ):  $\delta$  130–126 (br m), 55–50 (br m), 48–40 (br m), 36.3 (br s), 35–29 (br m), 21.6 (br s) ppm.

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