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Wagner–Meerwein Rearrangement of 4-Hydroxymethylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane to Pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane in Formic Acid

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The cationic rearrangement of 1-bromo-4-[hydroxybis(4-methoxyphenyl)methyl]pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-9-spiro-2′-[1,3]dioxolane (**1**) in formic acid gave 4-bromo-1-formyloxy-10,10-bis(4-methoxyphenyl)pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane-5-spiro-2′-[1,3]dioxolane in 27% yield along with 5-bromo-9-formyloxy-10,10-bis(4-methoxyphenyl)pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6-spiro-2′-[1,3]dioxolane in 55% yield. The reaction of **1** with *p*-toluenesulfonic acid or hydrochloric acid in methanol also afforded 4-bromo-1-methoxy-10,10-bis(4-methoxyphenyl)pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane-5-spiro-2′-[1,3]dioxolane together with 5-bromo-9-methoxy-10,10-bis(4-methoxyphenyl)pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6-spiro-2′-[1,3]dioxolane. With respect to migration of the C_4–C_5 bond in the pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (homocubane) skeleton to pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (D_{2h}-bishmocubane), a rearrangement into the bishomocubane system in driven by a concomitant release of strain; also, the stability of the 4-homocubanemethyl cation intermediate may play an important role in determining the course of the cage expansion into the D_{2h}-bishomocubane system. This reaction provides an attractive route for the synthesis of bishomocubane bridgehead alcohols and related compounds which are not easily accessible by other routes.

The principal structures of pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (cubane), pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (homocubane), pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (C_2-bishmocubane), and pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (D_{2h}-bishmocubane) are depicted together with their relative strain energies (SE), obtained by force field calculations (Chart 1).[1)] The driving force in a skeletal rearrangement of cubane to homocubane or homocubane to bishomocubane is the relief of about 40 kcal mol^{-1} of ring strain. In the regiospecific cationic rearrangement of the 4-hydroxymethylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (4-homocubanemethanol) system, force-field calculations show that migration of the C_3–C_4 bond (or the equivalent C_4–C_7 bond) to C_2-bishmocubane releases more strain energy than the migration of the central C_4–C_5 bond, which would lead D_{2h}-bishomocubane.[2)] These theoretical calculations are supported by experimental results that the cationic rearrangement of 1-bromo-4-(hydroxydiphenyl)methylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-9-spiro-2′-[1,3]dioxolane (**4**) and 1-bromo-4-(hydroxydimethyl)-methylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-9-spiro-2′-[1,3]dioxolane (**5**) leads to C_2-bishomocubane in good yields without giving D_{2h}-bishomocubane.[2,3)] In this paper we describe a new example of the formation of 4-bromo-1-formyloxy-10,10-bis(4-methoxyphenyl)pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane-5-spiro-2′-[1,3]dioxolane (**2a**) and its analogs (**2b**—**e**) by a cationic rearrangement of 1-bromo-4-[hydroxybis(4-methoxyphenyl)methyl]pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-9-spiro-2′-[1,3]dioxolane (**1**) in a variety of acids, such as formic acid, *p*-toluenesulfonic acid (*p*-TsOH), and hydrochloric acid.

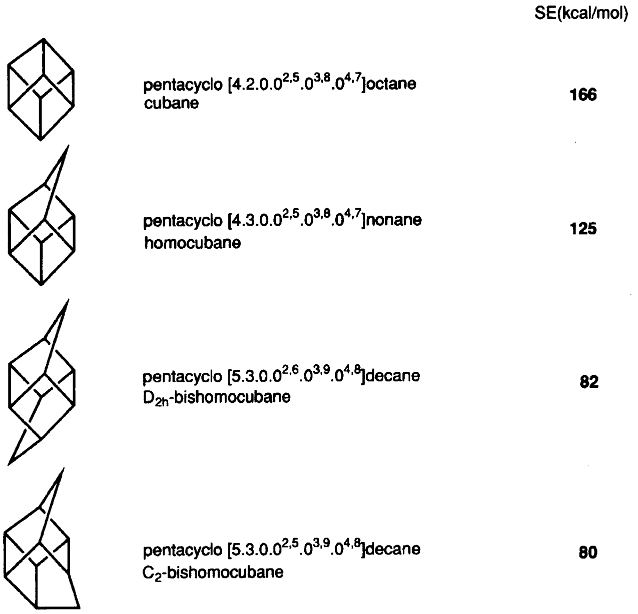


Chart 1.

Results and Discussion

4-Homocubanemethanol **1** was easily accessible from methyl 1-bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-9-spiro-2′-[1,3]dioxolane-4-carboxylate.[4)]

First, reactions were carried out in formic acid, which was known to be a solvent having a high Y value.[5)] The results are given in Table 1. When **1** was treated with formic acid, a mixture of **2a** and **3a** was obtained (Entry 1). The product ratio, 1/2.0 of **2**/**3**, was calculated from the yield of each compound. Interestingly, reaction of **1** with formic acid in dichloromethane gave rearranged chloro derivatives (**2c** and **3c**) along with rearranged formates (**2a** and **3a**) (Entry 2). Chloride ion

Table 1. Cationic Rearrangement of **1**

Entry	Conditions[a]		Product (% Yield)[e]		Product ratio of
	Acid/Solvent	Time/min			**2**/**3**[g]
1	HCOOH	15	**2a** (27),	**3a** (55)	1/2.0
2	HCOOH/$\mathrm{CH_2Cl_2}$[b]	15	**2a** (15), **2c** (4)	**3a** (31), **3c** (18)	1/2.6
3	HCOOH/MeOH[b]	15	**2a** (4), **2b** (9), **2d** (4)	**3a** (31), **3b** (2), **3d** (20)	1/3.1
4[d]	*p*-TsOH/MeOH	15	**2d** (21), **2e** (n.d.),[f]	**3d** (60), **3e** (8)	1/3.2
5[d]	*p*-TsOH/MeOH +$\mathrm{CH_2Cl_2}$[c]	15	**2d** (13), **2e** (n.d.),[f]	**3d** (69), **3e** (10)	1/6.1
6[d]	HCl/MeOH	15	**2c** (n.d.),[f], **2d** (14)	**3c** (14), **3d** (60)	1/5.3

a) Reactions were carried out at room temperature. b) A (1 : 1) mixture of HCOOH and $\mathrm{CH_2Cl_2}$ (or MeOH). c) A (1 : 1) mixture of MeOH and $\mathrm{CH_2Cl_2}$. d) 0.3 Molar amount of acid was employed in each experiment. e) Isolated yield. f) n. d.; Not detected. g) Product ratio was calculated from isolated yields of **2** and **3**.

as a nucleophile arises from hydrochloric acid, which is formed by a reaction of formic acid and dichloromethane.[6] The product ratio of **2**/**3** was 1/2.6. When **1** was treated with formic acid in methanol, a mixture of **2a**, **2b**, **2d**, **3a**, **3b**, and **3d** was produced (Entry 3). The rearranged hydroxy derivatives (**2b** and **3b**), which were hydrolysis products of **2a** and **3a**, were also prepared in quantitative yields by the alkaline hydrolysis of **2a** and **3a**. The reaction of **1** with a 0.3 molar amount of *p*-TsOH in methanol gave a mixture of **2d**, **3d**, and **3e** (Entry 4). In Entries 3 and 4, the product ratio of **2**/**3** is shown to be about 1/3, respectively, resulting in an increase in the yield of **3**. Upon the treatment of **1** with a 0.3 molar amount of *p*-TsOH in a (1 : 1) mixture of methanol and dichloromethane, a mixture of **2d**, **3d**, and **3e** in a product ratio of 1/6.1 in **2**/**3** was given without the formation of **2e** (Entry 5). The reaction of **1** with a 0.3 molar amount of hydrochloric acid in methanol gave a mixture of **2d**, **3c**, and **3d** in the product ratio of 1/5.3 in **2**/**3** (Entry 6). In this series, it was shown that the reaction of **1** with formic acid gave **2** in the highest yield.

The cationic rearrangement of **4** and **5** in formic acid has been reinvestigated.[7] The reaction of **4** with formic acid gave a mixture of D_{2h}- and C_2-bishomocubane derivatives in a product ratio of 1/3.5. On the other hand, a similar treatment of **5** with formic acid gave only C_2-bishomocubane.

Structure of D_{2h}- and C_2-Bishomocubanes. Compound **2d** was isolated as colorless prisms by recrystallization from acetonitrile, and was found to have the formula $\mathrm{C_{27}H_{27}BrO_5}$ based on elemental analysis and mass spectral data. In the proton nuclear magnetic resonance (^{1}H NMR) spectrum the symmetry in the structure of **2d** was characterized by two singlets for three methoxyl groups at δ=3.38 and 3.75 and symmetrical double–doublet protons for two benzene rings at δ=7.24 and 6.76. Four proton signals observed between δ=4.23 and 3.95 were assigned to the ethylene group of spiro[1,3]dioxolane ring. Two kinds of 2H multiplets at δ=3.02—3.00 and δ=2.98—2.96 were assigned to each proton of the 2- and 7-positions and the 3- and 8-positions. Another two kinds of 1H multiplets at δ=3.70—3.68 and δ=2.80—2.79 were assigned to each proton of the 9- and 6-positions. From a comparison with the signals of aliphatic protons of the C_2-bishomocubane derivatives reported in the literature,[2—4] **2d** was shown to have a D_{2h}-bishomocubane skeleton. The structure of **2d** was unambiguously established as being 4-bromo-1-methoxy-10,10-bis(4-methoxyphenyl)pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane-5-spiro-2′-[1,3]dioxolane by X-ray crystallography. X-Ray analytical data for **2d** are shown in Table 2, and its ORTEP drawing is given in Fig. 1. The structures of other derivatives **2** were determined based on their spectral data, compared with those of **2d**.

Compound **3d** was shown to have the composition $\mathrm{C_{27}H_{27}BrO_5}$ from an elemental analysis and mass-spectral data. In the ^{1}H NMR spectrum, **3d**, which was characterized by three signals for three different methoxyl groups at δ=3.74, 3.73, and 3.62 and double-doublet protons for two benzene rings at δ=7.36 and 6.75 and at δ=7.28 and 6.73, was shown to have an unsymmetrical structure. Four proton signals observed between δ=4.26 and 3.84 were assigned to the ethylene group of the spiro[1,3]dioxolane ring. Two kinds of 2H multiplets at δ=3.44—3.42 and δ=3.09—3.04 were as-

Table 2. Single-Crystal X-Ray Analytical Data of **2d**

Formula	$\mathrm{C_{27}H_{27}BrO_5}$
Crystal system	Monoclinic
Space group	$P2_1/n$
Cell parameter	a=19.617(3) Å
	b= 7.726(1) Å
	c=16.813(2) Å
	β=109.77(1) °
	V=2343 Å^3
Z value	4
D_{calcd}	1.450 g cm^{-3}
R (R_{w})	0.055 (0.060)
No. of Ref.	
Measured	5971
Used[a]	3011

a) $|F_{\mathrm{o}}|>3\sigma|F_{\mathrm{o}}|$.

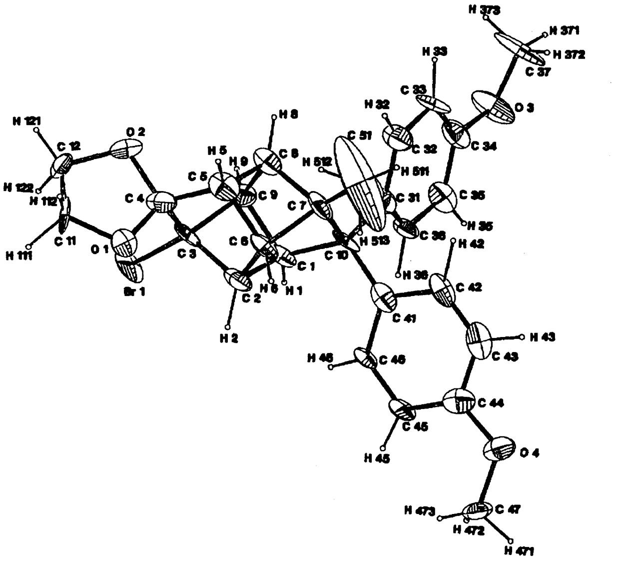


Fig. 1. ORTEP drawing of **2d**.

signed to each proton of the 1- and 8-positions and 3- and 4-positions. Another two kinds of 1H multiplets at δ=3.25—3.24 and δ=2.17—2.15 were assigned to each proton of the 2- and 7-positions. Thus, the structure of **3d** was assigned to 5-bromo-9-methoxy-10,10-bis(4-methoxyphenyl)pentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane-6-spiro-2′-[1,3]dioxolane, compared with those spectral data of the C_2-bishomocubane derivatives reported in the literature.[2—4] The structures of other derivatives **3** were determined in comparision with their spectral data with **3d**.

The cationic rearrangement of 4-homocubanemethanols to D_{2h}-bishomocubanes may be explained by the mechanism shown in Scheme 2.[8] Formic acid is known to be a solvent having a high *Y* value. Reflecting its high ionizing power, 4-homocubanemethanol **1** produces, comparatively, a stable 4-homocubanyl cation (**A**) bearing a *p*-methoxyphenyl group on the α-carbon. This cation is converted into bishomocubanyl cations (**B** and **C**) by a Wagner–Meerwein rearrangement. Both of the cations react with external nucleophiles to give respective D_{2h}- and C_2-bishomocubane derivatives. Although the rearrangement into the bishomocubane system is driven by a concomitant release of strain, the stability of the free carbocation intermediate **A** may play an important role in determining the course of the cage expansion into the D_{2h}-bishomocubane system. A detailed mechanistic study of this reaction remains to be made at the present time.

In conclusion, it may be pointed out that the cationic rearrangement of 4-homocubanemethanol **1** in formic acid provides an attractive route for the synthesis of D_{2h}-bishomocubane bridgehead alcohols and related compounds. These compounds are not easily accessible by other routes.

With respect to the formation of the D_{2h}-bishomocubane skeleton, our findings may indicate that: 1) the rearrangement into the bishomocubane system is mainly driven by a concomitant release of strain, and 2) the stability of the homocubanemethyl cation intermediate **A** plays an important role in determining the course of the cage expansion into the D_{2h}-bishomocubane system through a migration of the C_4–C_5 bond in the homocubane skeleton.

Experimental

The melting points were measured in a Gallenkamp melting-point apparatus, and are uncorrected. The IR spectra were recorded on a Hitachi 260-30 infrared spectrophotometer and ^{1}H NMR and ^{13}C NMR spectra were measured on Hitachi R-90 (90 MHz), JEOL JNM-EX 270 (270 MHz) and Bruker AM 360 (360 MHz) spectrometers with tetramethylsilane used as an internal standard. The chemical shifts are reported in ppm (δ), and the signals are described as s (singlet), d (doublet), t (triplet), m (multiplet), q (quartet), quin (quintet) or br (broad). All spectra are consistent with the assigned structures. Mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained on a JMS-DX 300 spectrometer operating at an ionization potential of 70 eV. Combustion analyses were performed on a Perkin–Elmer Model 240C elemental analyzer.

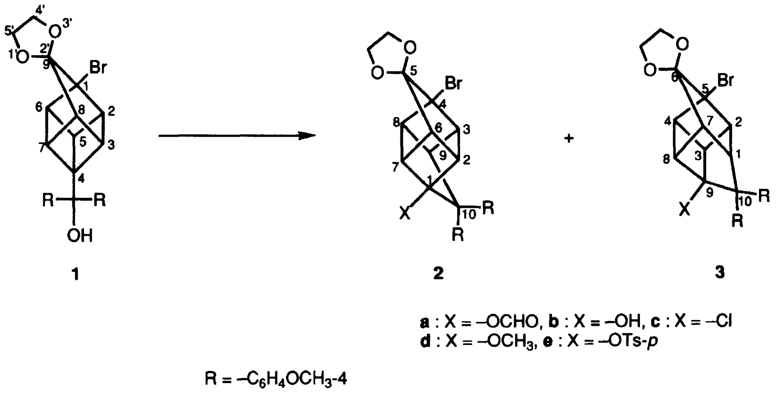
The solvents were dried over molecular sieves 4A overnight. The reagents employed in this study were commercially available.

1-Bromo-4-[hydroxybis(4-methoxyphenyl)methyl]pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane-9-spiro-2′-[1,3]dioxolane (1). Methyl 1-bromopentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane-9-spiro-2′-[1,3]dioxolane-4-carboxylate[4] (1.0 g, 3.19 mmol) was added to the Grignard reagent, prepared from 4-bromoanisole (1.3 g, 7.02 mmol) and Mg (171 mg, 7.02 mmol) in THF (20 ml). The mixture was refluxed for 1.5 h, poured into saturated aqueous NH_4Cl and extracted with Et_2O. The ethereal solution was dried over $MgSO_4$ and evaporated to give **1** as crystals, which were recrystallized from a mixture of $CHCl_3$ and hexane to give pure **1** as colorless prisms. Yield: 74%; mp 167.8—169.0 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=7.15-6.83 (8H, A_2B_2q, J=8.7 Hz), 4.22—4.18 (2H, m), 3.92—3.84 (2H, m), 3.79 (6H, s), 3.68—3.65 (1H, m), 3.59—3.52 (4H, m), 2.31—2.28 (1H, m), 1.96 (1H, s); ^{13}C NMR (90 MHz, $CDCl_3$) δ=158.7, 136.5, 128.4, 127.8, 124.1, 113.5, 66.0, 65.6, 58.3, 55.3, 46.2, 43.2, 43.1, 41.6; IR (CH_2ClCH_2Cl) 3600, 2960, 1615, 1515, 1450, 1425, 1315 cm^{-1}; MS m/z 496 (M^+). Found: C, 62.72; H, 4.91; Br, 15.84%. Calcd for $C_{26}H_{25}BrO_5$: C, 62.78; H, 5.06; Br, 16.06%.

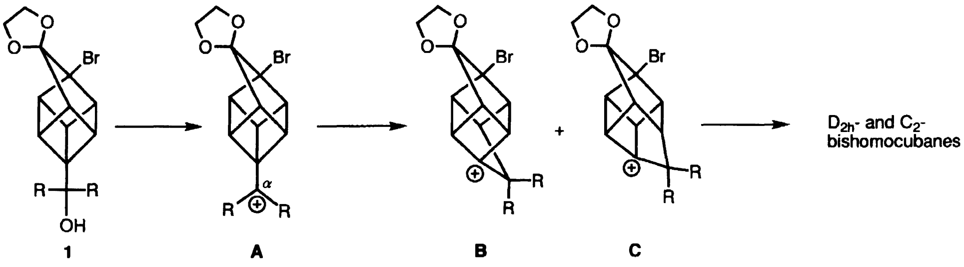
Reaction of 4-Homocubanemethanol 1 under a Variety of Conditions. A typical example is given to illustrate the general procedure. A mixture of **1** (100 mg, 0.200 mmol) and formic acid (2 ml) was stirred for 15 min at room temperature, poured into ice-water (10 ml) and extracted twice with each of CH_2Cl_2 (20 ml). The CH_2Cl_2 layer was dried over $MgSO_4$ and evaporated to give oily products. The products were purified by column or preparative thin-layer chromatographies. The results are given in Table 1.

Products **2** and **3** are summarized along with the elemental analysis in Table 3 and the ^{1}H and ^{13}C NMR spectral data of these compounds are given in Table 4.

Single-Crystal X-Ray Analysis of 2d. Com-



Scheme 1.



Scheme 2.

Table 3. D_{2h}- and C_2-Bishomocubanes (**2** and **3**)

Compd No.	Appearance	Mp°C	Recryst. solvt.[a]	Formula	Analysis Calcd (Found) C	H	Br	S
2a	Colorless needles	194.0—195.2	CH_2Cl_2–Hex	$C_{27}H_{25}BrO_6$	61.72 (61.74	4.80 4.52	15.21 15.52)	
2b	Pale yellow oil			$C_{26}H_{25}BrO_5$	HRMS 496.0884[b] (496.0870)			
2c	Colorless solids	190.5—191.5	CH_2Cl_2–Hex	$C_{26}H_{24}BrClO_4$	60.54 (60.72	4.69 4.54)		
2d	Colorless prisms	165.7—166.8	CH_3CN	$C_{27}H_{27}BrO_5$	63.42 (63.56	5.32 5.19	15.63 15.60)	
3a	Colorless solids	183.2—184.2	CH_2Cl_2–Hex	$C_{27}H_{25}BrO_6$	61.72 (61.96	4.80 4.58	15.21 15.33)	
3b	Colorless needles	131.5—132.8	$CHCl_3$–Hex	$C_{26}H_{25}BrO_5$	62.79 (62.83	5.07 4.98	16.07 16.16)	
3c	Colorless solids	182.4—183.4	CH_2Cl_2–Hex	$C_{26}H_{24}BrClO_4$	60.54 (60.73	4.69 4.45)		
3d	Colorless needles	206.1—207.2	CH_3CN	$C_{27}H_{27}BrO_5$	63.42 (63.35	5.32 5.32	15.63 15.75)	
3e	Colorless plates	224.8—225.8	CH_3CN	$C_{33}H_{31}BrSO_7$	60.83 (60.97	4.80 4.59	12.26 12.46	4.92 4.84)

a) Hex; Hexane. b) High-resolution mass spectrum.

pound **2d** was recrystallized from acetonitrile at room temperature to give colorless prisms. The diffracted intensities were recorded at room temperature on a Rigaku AFC-5FOS four-circle diffractometer (ω–2θ scan $2\theta < 55°$, Mo K_α, $\lambda = 0.71069$ Å). The structure was solved by direct method (MULTAN-84),[9] and refined by a block-diagonal least-squared method.[10] The final R-factor was determined by a procedure described in the literature.[11,12] The results are shown in Table 2 and an ORTEP drawing[13] of **2d** is depicted in Fig. 1.

We would like to express our thanks to the Material Analytical Center of the ISIR, Osaka University, for spectral measurements, microanalysis, and X-ray crystal analysis.

Table 4. ^{1}H and ^{13}C NMR Spectral Data of **2** and **3**

	^{1}H NMR spectra (360 MHz, CDCl$_3$) (ppm)	^{13}C NMR spectra (90 MHz, CDCl$_3$) (ppm)
2a	7.87 (1H, s), 7.14 (4H, d, *J*=9.0 Hz), 6.78 (4H, d, *J*=9.0 Hz), 4.20 (2H, m), 3.97 (2H, m), 3.79 (1H, m), 3.76 (6H, s), 3.26 (2H, dd, *J*=7.0, 5.0 Hz), 3.05 (2H, dd, *J*=7.0, 5.0 Hz), 2.95 (1H, m).	160.2, 158.4, 131.6, 129.4, 122.1, 113.9, 95.3, 66.2, 63.6, 63.5, 55.1, 50.9, 48.3, 45.6, 42.4.
2ba)	7.23 (4H, d, *J*=9.0 Hz), 6.78 (4H, d, *J*=9.0 Hz), 4.21—4.16 (2H, m), 3.97—3.92 (2H, m), 3.74 (6H, s), 3.75—3.70 (1H, m), 2.93 (2H, m), 2.88 (1H, m), 2.75 (2H, m), 2.39 (1H, s).	157.9, 132.8, 129.1, 122.4, 113.7, 90.1, 66.0, 64.4, 62.2, 55.1, 51.0, 47.7, 46.4, 42.2.
2c	7.21 (4H, d, *J*=9.0 Hz), 6.78 (4H, d, *J*=9.0 Hz), 4.20 (2H, m), 3.98 (2H, m), 3.79 (1H, m), 3.77 (6H, s), 3.04 (5H, m).	158.2, 132.0, 129.6, 121.7, 113.4, 77.8, 66.1, 64.8, 63.7, 55.1, 52.8, 50.5, 48.9, 42.6.
2d	7.24 (4H, d, *J*=9.0 Hz), 6.76 (4H, d, *J*=9.0 Hz), 4.23—4.20 (2H, m), 3.99—3.95 (2H, m), 3.75 (6H, s), 3.70—3.68 (1H, m), 3.38 (3H, s), 3.02—3.00 (2H, m), 2.98—2.96 (2H, m), 2.80—2.79 (1H, m).	157.9, 133.6, 129.6, 122.4, 113.4, 95.8, 66.1, 64.4, 62.6, 55.7, 55.1, 51.0, 48.0, 44.3, 43.4.
3a	8.29 (1H, s), 7.31 (2H, d, *J*=9.0 Hz), 7.12 (2H, d, *J*=9.0 Hz), 6.78 (2H, d, *J*=9.0 Hz), 6.76 (2H, d, *J*=9.0 Hz), 4.23—4.14 (2H, m), 3.98—3.87 (2H, m), 3.76 (3H, s), 3.75 (3H, s), 3.52 (2H, m), 3.41 (1H, m), 3.33 (1H, m), 2.98 (1H, m), 2.18 (1H, m).	159.1, 158.4, 157.9, 135.0, 132.4, 129.5, 129.0, 120.3 113.6, 113.5, 92.3, 66.2, 65.8, 65.6, 61.8, 55.2, 55.1, 50.5, 49.9, 49.1, 46.8, 45.0, 43.2.
3b	7.28 (2H, d, *J*=9.0 Hz), 7.26 (2H, d, *J*=9.0 Hz), 6.78 (2H, d, *J*=9.0 Hz), 6.77 (2H, d, *J*=9.0 Hz), 4.24—4.13 (2H, m), 3.99—3.87 (2H, m), 3.76 (3H, s), 3.75 (3H, s), 3.41 (1H, m), 3.28 (1H, m), 3.19 (2H, m), 2.70 (1H, m), 2.24 (1H, bs), 2.16 (1H, m).	158.1, 157.7, 135.8, 133.4, 129.2, 128.9, 120.2, 113.7, 113.6, 88.4, 66.1, 65.7, 63.5, 62.8, 55.2, 52.1, 49.4, 49.2, 46.1, 44.1, 42.9.
3c	7.34 (2H, d, *J*=9.0 Hz), 7.16 (2H, d, *J*=9.0 Hz), 6.78 (2H, d, *J*=9.0 Hz), 6.77 (2H, d, *J*=9.0 Hz), 4.24—4.13 (2H, m), 3.98—3.85 (2H, m), 3.77 (3H, s), 3.76 (3H, s), 3.45 (2H, m), 3.38 (1H, m), 3.29 (1H, m), 2.95 (1H, m), 2.18 (1H, m).	158.4, 157.9, 134.9, 131.9, 129.6, 129.3, 119.7, 113.4, 113.3, 75.0, 66.3, 66.2, 65.8, 61.6, 55.1, 53.5, 53.2, 50.6, 47.2, 46.5, 43.3.
3d	7.36 (2H, d, *J*=9.0 Hz), 7.28 (2H, d, *J*=9.0 Hz), 6.75 (2H, d, *J*=9.0 Hz), 6.73 (2H, d, *J*=9.0 Hz), 4.26—3.84 (4H, m), 3.74 (3H, s), 3.73 (3H, s), 3.62 (3H, s), 3.44—3.42 (2H, m), 3.25—3.24 (1H, m), 3.09—3.04 (2H, m), 2.17—2.15 (1H, m).	158.0, 157.5, 135.9, 133.7, 129.5, 129.2, 120.7, 113.3, 113.2, 94.4, 66.1, 65.7, 64.6, 62.7, 55.1, 55.0, 54.9, 51.6, 49.3, 46.7, 46.2, 44.1, 41.4.
3e	7.84 (2H, d, *J*=8.0 Hz), 7.32 (2H, d, *J*=8.0 Hz), 7.18 (2H, d, *J*=9.0 Hz), 7.09 (2H, d, *J*=9.0 Hz), 6.72 (2H, d, *J*=9.0 Hz), 6.70 (2H, d, *J*=9.0 Hz), 4.21—3.84 (4H, m), 3.83—3.81 (1H, m), 3.75 (3H, s), 3.74 (3H, s), 3.37—3.30 (3H, m), 3.12—3.09 (1H, m), 2.44 (3H, s), 2.19—2.17 (1H, m).	158.3, 157.8, 144.8, 134.9, 134.3, 131.7, 130.0, 129.3, 128.9, 127.6, 120.1, 113.5, 113.4, 96.8, 66.2, 66.1, 65.7, 61.6, 55.1, 50.2, 50.0, 49.1, 46.8, 46.5, 44.8, 42.8, 21.6.

a) ^{1}H NMR; 270 MHz, ^{13}C NMR; 67.5 MHz.

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