Tetrahedron 64 (2008) 11394–11403

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Preparation of fullerenol, fullerenone, and aminofullerene derivatives through selective cleavage of fullerene C–H, C–C, C–N, and C–O bonds in fullerene-mixed peroxide derivatives

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ARTICLE INFO

Article history:
Received 16 April 2008
Received in revised form 7 August 2008
Accepted 20 August 2008
Available online 26 August 2008

ABSTRACT

Various reactions of fullerene-mixed peroxides were investigated in an effort to explore the chemistry of functional groups on the fullerene surface. Amines convert fullerene peroxides into fullerene epoxides through S_N2' type reaction. Lewis acid catalyzed hydrolysis of fullerene epoxides led to vicinal fullerendiols, which may be oxidized into fullerendiones by diacetoxyiodobenzene (DIB). Alcohols and amines react with the adjacent dione to form acetal or hemiacetal groups through different mechanisms.

1. Introduction

Numerous reactions between pristine fullerene and various organic and inorganic compounds have been reported to form thousands of fullerene adducts.[1,2] Further functionalization of fullerene derivatives has been used by various groups to prepare compounds with potential applications.[3] The reactive functional groups in most of these further functionalization reactions are not directly attached onto the fullerene cage carbon atoms. Due to the unique spherical nature, functional groups connected directly on the fullerene cage usually show different reaction patterns from those in classical organic compounds. Well known functional group transformations in classical organic chemistry may not work or result in unexpected product when applied to fullerene chemistry. Successful transformation of functional groups bound directly onto a fullerene cage carbon atom is limited.[4–6] Much work is still needed to further develop the chemistry of fullerene functional groups attached to fullerene. Efficient transformation of functional groups on the fullerene surface can play an important role in the modification of fullerene skeleton and preparation of various cage modified fullerene derivatives such as cage-opened fullerenes[7] and heterofullerenes.[8]

We have reported the preparation of fullerene-mixed peroxides $C_{60}(OO^tBu)_n$.[9] The presence of *t*-butyl groups in these compounds greatly improves their solubility in common organic solvents such as chloroform, thus facilitating their purification by flash column chromatography and characterization by spectroscopic data. Single crystal X-ray analysis is also possible for some of these fullerene derivatives.[10] In an effort to explore the functional group chemistry in fullerene derivatives, we studied the chemistry of fullerene-mixed peroxides in detail. Here, we report the addition of hydroxylamine to $C_{60}(O)(OO^tBu)_4$ **1** and subsequent functional group transformations leading to the formation of fullerenol and cage-opened fullerene derivatives.

2. Results and discussion

Compound **1** was prepared from C_{60} and ^{t}BuOOH in the presence of catalytic amount of $FeCl_3$.[9] We have previously reported that addition of ammonia to **1** took place on the central pentagon with a 1,3-diene moiety (Scheme 1).[11] Only the 1,4-addition product **2** was observed. The structure of **2** was deduced from its spectroscopic data and the single crystal structure of its amide derivative **3**. The observed high regio-selectivity indicates that conjugation of the 1,3-diene moiety in **1** is similar to classical cyclopentadiene compounds.

2.1. Regio-selective addition of amines to fullerene derivatives

In classical organic reactions of 1,3-diene compounds, both 1,2- and 1,4-addition reactions may occur depending on the nature of the substrate and the addend. Steric hindrance around the central pentagon of **1** seems to favor the observed 1,4-addition. In an effort to extend the scope of the amine addition reaction, we treated **1**

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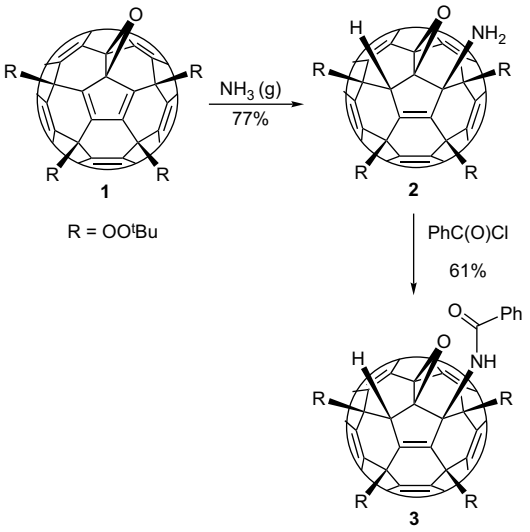
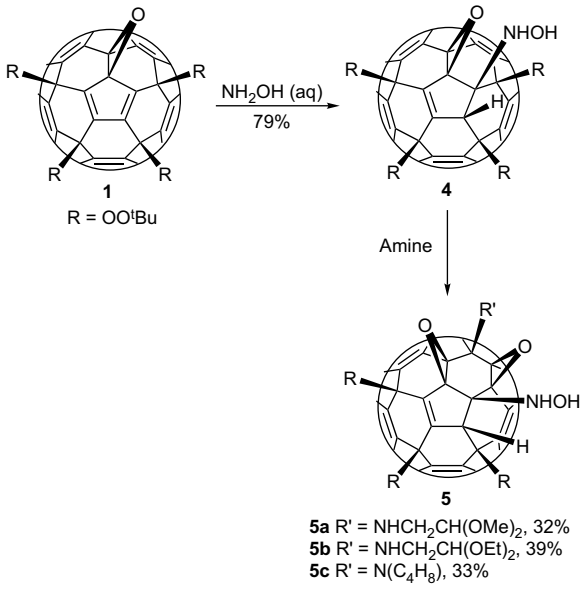
doi:10.1016/j.tet.2008.08.053



Scheme 1. Addition of ammonia to **1**.

with hydroxylamine (Scheme 2). To our surprise, the 1,2-addition product **4** was obtained as the only isolated product. The NMR spectrum of **4** is quite different from those of the 1,4-adducts **2** and **3**. For example, the H-bound sp^3 fullerene carbon appears at 47.5 and 49.8 ppm, respectively, for compounds **2** and **3**, whereas in compound **4**, it appears at 55.8 ppm.



Scheme 2. Preparation of hydroxylamine adducts.

To establish the structure of **4** as the 1,2-adduct, we tried various methods to grow single crystals but all the efforts failed. Addition of amines to **4** gave compounds **5**, which showed better crystallization property. Single crystal X-ray structures of both compounds **5b** and **5c** were obtained as shown in Figure 1. The structures clearly indicate that one of the four *tert*-butylperoxo groups was converted to an epoxide moiety on the same hexagon as the original epoxide. The hydroxylamino group and the fullerene hydrogen are adjacent to each other. In both compounds, bonding distances of the epoxide moiety at the 6,6-junction are shorter than that at the 5,6-junction.

The X-ray structures of **5b** and **5c** support the 1,2-addition pattern of hydroxylamine to **1** instead of the 1,4-addition pattern

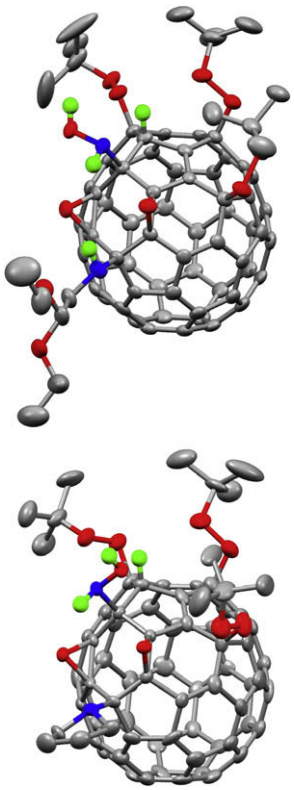


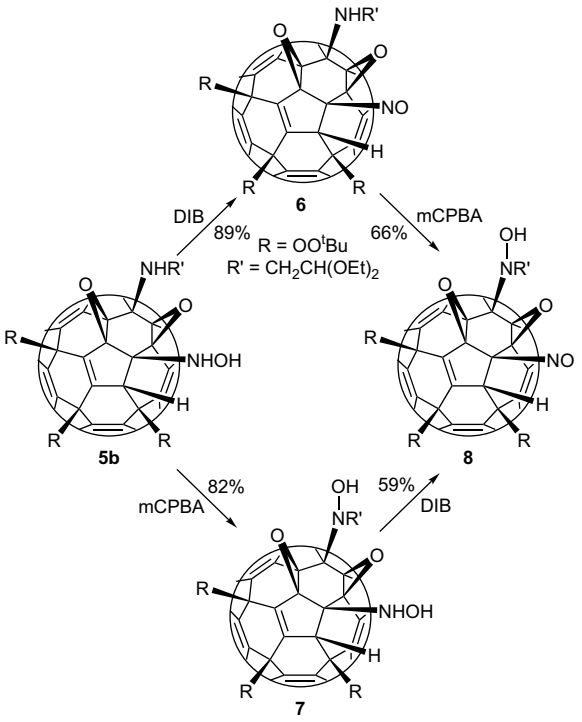
Figure 1. X-ray structures of **5b** (above) and **5c** (below). For clarity hydrogen atoms on the alkyl groups were omitted. Color scheme red=O, blue=N, green=H, grey=C.

observed for ammonia. It is unlikely that the 1,4-isomer rearranges into the 1,2-isomer during the conversion of **4** to **5**. A concerted 1,3-H shift is forbidden according to Woodward–Hoffman rules. A base catalyzed isomerization process can also be ruled out since the amines used here are not basic enough to deprotonate the fullerene hydrogen. In addition, chemical shifts of the H-bound sp^3 fullerene carbon are similar for compounds **4** (55.8 ppm) and **5a** (56.7 ppm, confirmed by DEPT), indicating that they have a similar structure. At present it is not clear why ammonia and hydroxylamine behave differently toward compound **1**.

Oxidation of **5b** occurs at the amino addends. *m*-Chloroperoxobenzoic acid oxidizes selectively the alkyl amino group $(EtO)_2CHCH_2NH$ into the alkylhydroxyl group $(EtO)_2CHCH_2N(OH)$. Whereas diacetoxyliodobenzene only oxidizes the hydroxylamino group into a nitrosyl group (Scheme 3). The conversion of **5b** to **8** could be carried out through either **6** or **7**, both of which have been isolated and fully characterized. Total yields of the two routes are comparable. DEPT spectra showed that the characteristic H-bound sp^3 fullerene carbon appears at 53.1, 56.5, and 53.3 ppm for compounds **6**, **7**, and **8**, respectively. These chemical shifts are close to those of **4** and **5a** mentioned above, indicating that their structures are similar.

2.2. Lewis acid catalyzed reactions of fullerene epoxide and peroxide groups

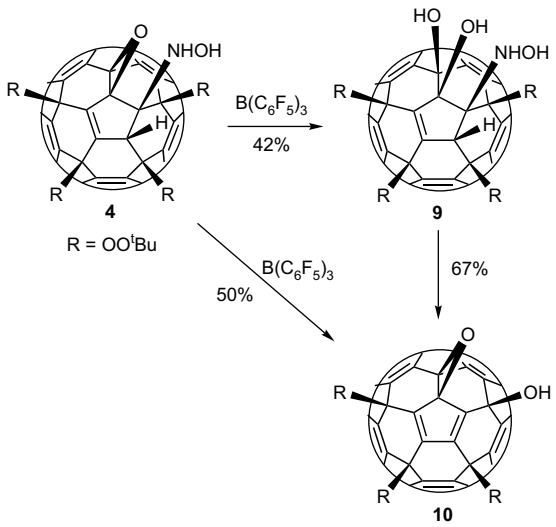
The epoxide moiety in compound **4** can be readily opened into the vicinal diol derivative **9** with tris(pentafluorophenyl)borane (Scheme 4). Diol **9** is stable for several hours. It decomposed completely to give compound **10** as the major product upon storage at rt for one day. Prolonged reaction of **4** with $B(C_6F_5)_3$ could also give **10** directly in moderate yield. Other Lewis acids such as $FeCl_3$ gave a complicated mixture of products when mixed with **4**.



Scheme 3. Oxidation reactions of **5b**.

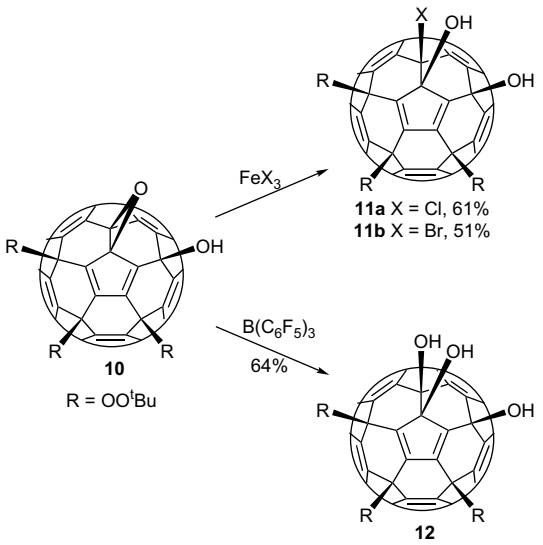
Formation of **10** results from elimination of the hydroxylamine and cleavage of a *tert*-butylperoxo O–O bond. It is difficult to understand the mechanism. Intramolecular H-bonding between the hydroxylamino group and the adjacent peroxo oxygen atoms may play a role in the process. Under the same conditions, compound **1** just gave the epoxide-opened diol derivative $C_{60}(OH)_2(OO^tBu)_4$, all the four *tert*-butylperoxo groups remained unchanged. Spectroscopic data of **10** are in agreement with the structure depicted in Scheme 4. The location of the hydroxyl group in **10** could not be determined directly from the NMR data. It was deduced from its further derivatization product compound **18b**, which was characterized by single crystal X-ray analysis (see the following section).

The epoxide moiety in compound **10** shows similar reactivity to that in compound **4**. Treating **10** with $B(C_6F_5)_3$ gave the triol



Scheme 4. Elimination of hydroxylamine from **4**.

derivative **12** (Scheme 5). Both ferric chloride and ferric bromide could also open the epoxide into the corresponding halohydrin derivative **11**. Regio-selectivity of the ferric halide reactions favored the hydroxyl group on the central pentagon and the halide on the outside. The same phenomenon has been observed before for the reaction of **1** with ferric chloride, which was confirmed by single crystal X-ray analysis data.[12a]



Scheme 5. Epoxide opening reactions.

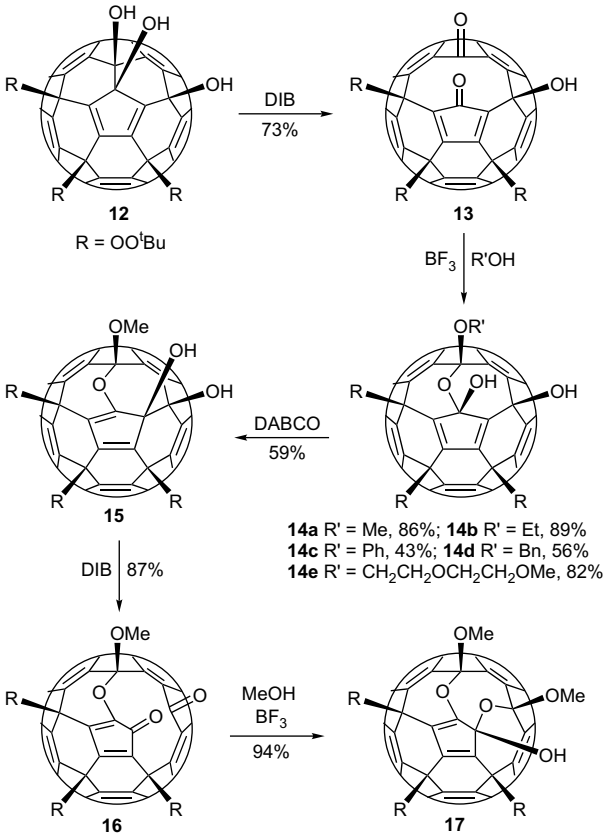
2.3. Cage-opening and closing reactions

Compound **12** is a good precursor for cage-opening reactions. We have reported that oxidation of the vicinal diol moiety in fullerene derivatives with DIB results in formation of cage-opened fullerene diketone derivatives.[10] As expected, oxidation of **12** with DIB led to compound **13** in good yield (Scheme 6). Formation of the two carbonyls is evident from the spectroscopic data. There are two carbonyl signals at 197.7 and 198.4 ppm on the ^{13}C NMR spectrum of **13**. The IR spectrum showed an intense C=O stretching band at 1747 cm^{-1}.

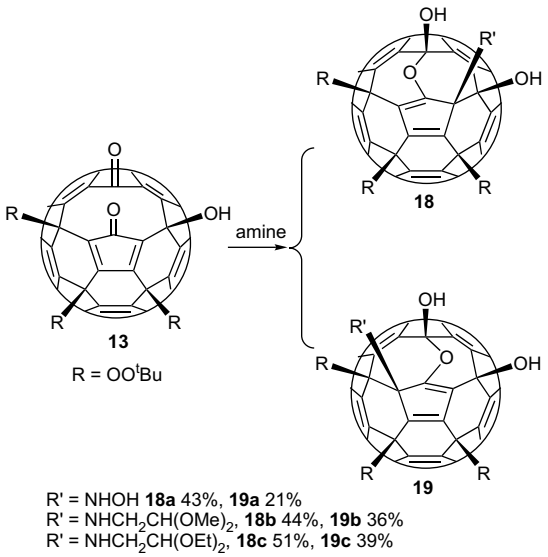
The two carbonyl groups in **13** readily form the hemiacetal and acetal moieties when treated with BF_3 in the presence of excess alcohol. The intense C=O stretching band of **13** disappeared in the IR spectrum of **14**. On the ^{13}C NMR spectrum of **14a**, there are two unique signals at 105.9 and 106.8 ppm due to the two hemiacetal and acetal fullerene carbons. Similar ^{13}C NMR chemical shifts are also observed for analogues **14b**–**14e**. Assignment of the hydroxyl group on the central pentagon is made on comparison to our previous result. In an analogous reaction with the symmetrical diketone derivative $C_{60}(O)_2(OO^tBu)_4$, we have shown by X-ray analysis data that location of the hemiacetal is on the central pentagon.[12b]

The hydroxyl group on the central pentagon of **14** shifted to the other hydroxyl group when treated with DABCO, forming compound **15** with a vicinal diol moiety. In the ^{13}C NMR spectrum of **15**, there is only one signal at 111.7 ppm corresponding to the fullerene acetal carbon. The base induced 1,5-shift of the OH group probably follows a deprotonation–migration–protonation sequence. Release of steric strain and H-bonding in the vicinal diol may provide the driving force for this rearrangement process. 'Walking' of oxygen atom on the central pentagon has been observed before for related compounds.[12c]

Just like the cage-opening reaction of **12**, the diol moiety of compound **15** can be oxidized to form compound **16** with two



Scheme 6. Reactions of fullerene OH and C=O groups.



Scheme 7. Amine induced formation of hemiacetal.

carbonyl groups. The presence of the acetal group improves the efficiency of the DIB reaction. Higher yield (87%) was obtained for **16** as compared to the 73% yield for **13**. The two carbonyl carbons of **16** appear at 192.5 and 195.6 ppm on the ^{13}C NMR spectrum. These shifts are at higher field than those of **13**, indicating less strain at the opening of **16** than that of **13**. The C=O stretching of **16** (1749 cm^{-1}) is essentially the same as that of **13**.

Treating **16** with BF_3 in the presence of methanol led to the cage closed product **17**. The reaction is the same as the conversion of **13** to **14**. On the ^{13}C NMR spectrum of **17**, there are three unique signals at 101.2, 108.1, and 113.1 ppm for the one hemiacetal and two acetal fullerene carbons. The two methoxy groups show similar chemical shifts on both the ^{1}H and the ^{13}C NMR spectra (3.8, 3.9, 53.9, and 53.2 ppm). These data also indicate that both methoxy groups are on the outside as depicted in Scheme 6.

2.4. Addition of amines to fullerenone 13

Addition of amines to **13** yields the hemiacetals **18** and **19** (Scheme 7). The two compounds are regio-isomers. Their structures are analogous to the methanol adduct **15**. But in the present case, the amines are on the central pentagon. Yields of compounds **18** with the amino group adjacent to the hydroxyl group are higher than those of **19** with the amino group next to the bulky *tert*-butylperoxo group. Secondary amines induced cleavage of the *tert*-butylperoxo groups and gave a complex mixture of products when added to **13**.

The single crystal X-ray structure of **18b** was obtained as shown in Figure 2. The five carbon atoms of the central pentagon and the bridging hemiacetal oxygen atom are planar. The pentagon containing the hemiacetal carbon adopts an envelope conformation with the hydroxyl bound carbon above the plane. The planarity of the central pentagon facilitates conjugation of the diene moiety. This may be the driving force for the DABCO catalyzed rearrangement of **14** to **15**. The bonding pattern of compound **15** is similar to **18b**. Simple modeling indicates that the central pentagon of **14** adopts a distorted structure with the hemiacetal sp^3 carbon above the plane.

Structural assignments of the other amino compounds **18a**, **18c**, and **19** were based on comparison of their spectroscopic data with those of **18b**. The ^{13}C NMR spectra convincingly verify their structural similarity. For example, the sp^3 fullerene carbons connecting the three OO^{t}Bu, OH, and NHR appear at 84.3, 81.9, 79.5, 78.6, and 71.8 ppm for **18b**. Compound **18c** showed exactly the

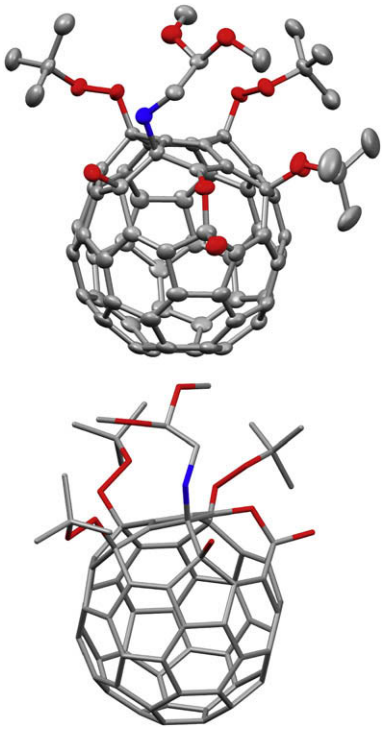
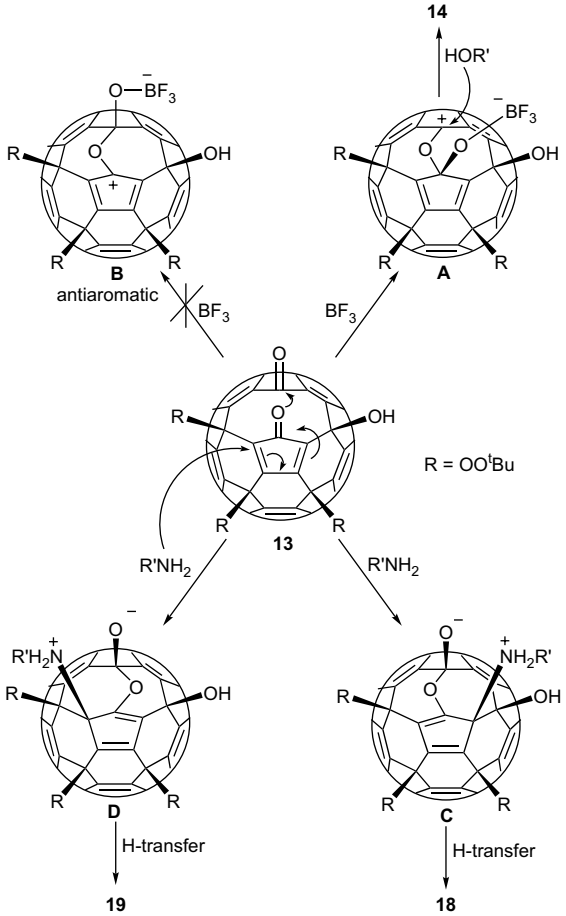


Figure 2. X-ray structure of **18b** (ellipsoid above and stick below). For clarity hydrogen atoms were omitted. Color scheme red=O, blue=N, grey=C.

same chemical shifts. Chemical shifts of the hydroxylamino adduct **18a** are slightly different, but the most downfield peak is still 84.4 ppm for these sp^3 fullerene carbons. For the isomeric compounds **19a**, **19b**, and **19c**, the biggest chemical shifts appear at 89.8, 90.8, and 90.8 ppm, respectively, for analogous sp^3 fullerene carbons.

To explain the different reaction patterns of amine and alcohol addition to the diketone derivative **13**, possible pathways are proposed in Scheme 8. Apparently, the nucleophilicity of alcohols is not strong enough for them to add directly to **13** since there was no reaction in the absence of Lewis acid. Aromaticity is a key factor in the regio-selective addition of alcohol to the fullerene acetal carbon on the outside pentagon. To form the other isomer with the alkoxyl group on the central pentagon would require the formation of the antiaromatic intermediate **B**. Amines are more nucleophilic than alcohols and add to the cyclopentadienone through a Michael addition type pathway. Steric hindrance in intermediate **C** should be smaller than that in **D**, thus higher yields of compounds **18** were obtained.



Scheme 8. Possible pathways of alcohol and amine additions.

3. Conclusion

The present work showed the formation and reactivity of various functional groups on the fullerene cage including amino, hydroxyl, epoxy, carbonyl, hemiacetal, and acetal groups. The results indicate that fullerene double bonds are more reactive at positions around the central pentagon in fullerene adducts with the cyclopentadienyl addition pattern. Both 1,2- and 1,4-adducts have been observed in the addition of amines to the central pentagon of compound **1**. Nucleophilic displacement reactions on the surface of the fullerene cage usually take place through an S_N2' or S_N1 mechanism. Aromaticity and local steric strain also play an important role in the selectivity pattern.

4. Experimental

4.1. General

NMR spectra were recorded on a Bruker ARX 400 spectrometer at rt (298 K). Chemical shifts are given in parts per million relative to TMS or $CDCl_3$ (for ^{13}C NMR). ESI-MS spectra were recorded on an LCQ Decaxp Plus Spectrometer with $CHCl_3/CH_3OH$ or $CDCl_3/CH_3OH$ as the solvent, and positive mode spectra were reported except when noted. FTIR spectra were recorded on a Nicolet Magna-IR 750 instrument in microscope mode. All reagents were used as-received. Reactions were performed under air at rt except where noted. Chromatographic purifications were carried out with 200–300 mesh silica gel.

Caution. Large amounts of peroxide are involved in some reactions, so care must be taken to avoid possible explosions.

*4.1.1. Compound **4***

An aqueous solution of $NH_2OH\cdot HCl$ (133 mg, 1.91 mmol in 1 mL of water) and K_2CO_3 (307 mg, 2.22 mmol) was added to a solution of compound **1** (100 mg, 0.092 mmol) in 20 mL of CH_2Cl_2. The flask was wrapped with aluminum foil. After stirring overnight at rt, the reaction was stopped. The product was purified by chromatography on a silica gel column eluting with toluene/ethyl acetate 10:1. Unreacted **1** was collected as the first band, **4** was collected as the second band (81 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$): δ=1.33 (s, 9H), 1.38 (s, 18H), 1.49 (s, 9H), 5.32 (s, 1H), 5.90 ppm (w, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=149.91, 149.47, 149.31, 149.12, 148.64, 148.56 (2C), 148.49, 148.29 (3C), 148.27 (2C), 148.10, 147.87 (2C), 147.79, 147.77, 147.72, 147.66, 147.49, 147.06, 146.95 (2C), 146.78, 146.43, 146.31, 146.19, 145.37, 145.11, 144.52, 144.60 (3C), 144.33 (2C), 144.01, 143.84, 143.47, 143.40, 143.38, 143.35, 143.23, 143.15, 142.77, 142.53, 142.32, 141.63, 140.54, 140.29, 138.28, 135.14, 90.69, 84.02, 83.02, 82.58, 81.89, 81.85, 81.62, 81.33, 80.84, 70.84, 63.42, 55.82, 26.73 ($3CH_3$), 26.72 ($3CH_3$), 26.67 ppm ($6CH_3$); FTIR (microscope): 3284, 2978, 2929, 2870, 1468, 1455, 1388, 1364, 1261, 1243, 1192, 1108, 1078, 1042, 1019, 876, 756 cm^{-1}; ESI-MS, *m*/*z* (%): 1126 (100) $[M+H]^+$.

*4.1.2. Compound **5a***

Aminoacetaldehyde dimethyl acetal (122 μL, 1.12 mmol) was added to a solution of **4** (122 mg, 0.11 mmol) in 25 mL of CH_2Cl_2. The mixture was stirred in dark at rt for 1 h. The solution was directly chromatographed on silica gel eluting with toluene/ethyl acetate 5:1. Unreacted **4** was collected as the first band, **5a** was collected as the second band (40 mg, 32%). ^1H NMR (400 MHz, $CDCl_3$): δ=1.32 (s, 9H), 1.36 (s, 9H), 1.47 (s, 9H), 3.28–3.40 (m, 2H), 3.45 (s, 6H), 4.67 (t, *J*=10.97 Hz, 1H), 5.12 (s, 1H), 5.52 ppm (w, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=150.25, 150.13, 149.69, 149.11, 149.00, 148.97, 148.88, 148.79, 148.48, 148.46 (2C), 148.42, 148.38 (2C), 148.30, 148.11, 148.03, 148.00, 147.45, 147.43, 147.28, 147.22, 147.13, 147.08, 147.04 (2C), 146.68, 146.00, 145.98, 145.41, 144.73, 144.60, 144.47, 144.19, 143.25, 143.22, 143.20 (2C), 143.16, 142.50, 142.10, 141.02, 140.99, 140.59, 140.50, 140.10, 139.61, 138.12, 136.48, 132.56, 103.44, 83.51, 82.35, 81.93, 81.67, 81.65, 80.92, 76.16, 74.15, 71.60, 67.16, 63.82, 61.32, 56.70, 53.81, 53.68, 45.27, 26.72 ($6CH_3$), 26.62 ppm ($3CH_3$); FTIR (microscope): 3321, 2979, 2931, 2833, 1457, 1388, 1364, 1192, 1133, 1111, 1083, 1065, 1016, 907, 875, 733 cm^{-1}; ESI-MS, *m*/*z* (%): 1179 (100) $[M+Na]^+$.

*4.1.3. Compound **5b***

Aminoacetaldehyde diethyl acetal (311 μL, 2.15 mmol) was added to a solution of **4** (242 mg, 0.22 mmol) in 40 mL of CH_2Cl_2. The mixture was stirred in dark at rt for 30 min. The solution was directly chromatographed on silica gel eluting with toluene/ethyl acetate 5:1. Unreacted **4** was collected as the first band and **5b** was collected as the second band (99 mg, 39%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.27 (t, J=14.03 Hz, 6H), 1.32 (s, 9H), 1.36 (s, 9H), 1.47 (s, 9H), 3.10–3.25 (w, 1H), 3.28–3.35 (m, 2H), 3.60–3.65 (m, 2H), 3.74–3.81 (m, 2H), 4.79 (t, J=11.14 Hz, 1H), 5.10 (s, 1H), 5.30 (s, 1H), 6.10–6.20 ppm (w, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=150.28, 150.14, 149.73, 149.14, 149.02, 149.01, 148.91, 148.81, 148.49 (3C), 148.44, 148.41 (2C), 148.35, 148.13, 148.09, 148.02, 147.48 (2C), 147.31, 147.22, 147.14, 147.10, 147.07, 147.01, 146.71, 146.08, 146.00, 145.46, 144.76, 144.62, 144.49, 144.20, 143.27, 143.24, 143.22 (2C), 143.19, 142.52, 142.11, 141.09, 140.98, 140.69, 140.57, 140.36, 139.59, 138.18, 136.45, 132.57, 101.85, 83.54, 82.38, 81.95, 81.69, 81.68, 80.94, 76.14, 74.24, 71.64, 67.18, 63.82, 62.12, 61.98, 61.36, 56.77, 46.14, 26.73 ($6CH_3$), 26.65 ($3CH_3$), 15.44 ppm ($2CH_3$); FTIR (microscope): 3327, 2976, 2927, 1451, 1365, 1192, 1128, 1111, 1064, 874 cm^{-1}; ESI-MS, m/z (%): 1185 (60) $[M+H]^+$, 1207 (100) $[M+Na]^+$.

Single crystals of compound **5b** were obtained from slow evaporation of its solution in $CDCl_3$ at 5 °C. Space group: $P2_1/C$, a=16.1755(2), b=46.6394(5), c=15.4678(2) Å, α=90.00, β=102.7592(4), γ=90.00. V=11,381 Å^3. Final R indices [$I>2\sigma(I)$]: R_1=0.0859, wR_2=0.2326. CCDC-669267.

*4.1.4. Compound **5c***

Aminoacetaldehyde diethyl acetal (15 μL, 0.19 mmol) was added to a solution of **4** (78 mg, 0.12 mmol) in 34 mL of CH_2Cl_2. The mixture was stirred in the dark at rt for 10 min. The solution was directly chromatographed on silica gel eluting with toluene/ethyl acetate 4:1. Unreacted **4** was collected as the first band and **5c** was collected as the second band (45 mg, 33%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.31 (s, 9H), 1.39 (s, 9H), 1.47 (s, 9H), 2.00 (w, 5H), 3.10–3.40 (w, 5H), 5.12 (s, 1H), 5.66 ppm (s, 1H); ^{13}C NMR was not obtained because of poor solubility. ESI-MS, m/z (%): 1123 (100) $[M+H]^+$. Anal. Calcd for $C_{76}H_{38}N_2O_9\cdot 2CDCl_3$: C 68.69; H 2.81; N 2.05. Found $C_{76}H_{38}N_2O_9\cdot 2CDCl_3$: C 68.28; H 3.21; N 2.02.

Single crystals of compound **5c** were obtained from slow evaporation of its solution in $CDCl_3$ at 5 °C. Space group: $P2_1/C$, a=14.3592(3), b=14.7852(2), c=15.7645(3) Å, α=71.9454(8), β=78.6218(7), γ=80.4127(6). V=3099.5 Å^3. Final R indices [$I>2\sigma(I)$]: R_1=0.0597, wR_2=0.1574. CCDC-679743.

*4.1.5. Compound **6***

DIB (diacetoxyliodobenzene, 26 mg, 0.081 mmol) was added to a solution of **5b** (48 mg, 0.041 mmol) in 24 mL of benzene. The mixture was stirred in dark at rt for 1 min. The product was purified by chromatography on a silica gel column eluting with toluene. Product **6** was collected as the first band (41 mg, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.19–1.25 (m, 6H), 1.23 (s, 9H), 1.44 (s, 9H), 1.45 (s, 9H), 2.58 (w, 1H), 3.20–3.35 (m, 2H), 3.54–3.59 (m, 2H), 3.69–3.75 (m, 2H), 4.43 (s, 1H), 4.74 ppm (t, J=11.19 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=150.36, 150.19, 149.80, 149.23, 149.09, 149.05, 148.85, 148.79, 148.52, 148.50, 148.47 (2C), 148.45, 148.42 (2C), 148.31, 148.22, 148.20, 148.03, 147.91, 147.50, 147.46, 147.34, 147.22, 147.11, 147.00, 146.32, 146.07, 144.71, 144.63 (2C), 144.48, 144.33, 144.15, 143.56, 143.26, 143.20, 143.17, 142.95, 142.62, 142.57, 141.54, 140.69, 140.53 (3C), 140.21, 138.26, 136.67, 133.32, 101.59, 94.79, 82.91, 82.69, 82.22, 81.97, 81.69, 81.07, 76.41, 72.87, 70.58, 65.06, 61.81, 61.77, 61.04, 53.15, 45.99, 26.71 ($3CH_3$), 26.67 ($3CH_3$), 26.55 ($3CH_3$), 15.32 ppm (CH_3); FTIR (microscope): 3490, 2977, 2929, 2873, 1729, 1668, 1573, 1458, 1387, 1365, 1288, 1261, 1245, 1191, 1122, 1091, 1067, 1018, 873 cm^{-1}; ESI-MS, m/z (%): 1205 (100) $[M+Na]^+$.

*4.1.6. Compound **7***

m-CPBA (9 mg, 0.037 mmol) was added to a solution of **5b** (22 mg, 0.019 mmol) in 11 mL of CH_2Cl_2. The mixture was stirred at rt for 5 min. A solution of 45 mg $Na_2S_2O_3$ and 25 mg K_2CO_3 in 11 mL of water was added to this mixture. The organic layer was separated, dried over Na_2SO_4, and filtered. The solvent was removed. The residue was purified by chromatography on a silica gel column eluting with toluene/ethyl acetate 10:1. Unreacted **5b** (trace) was collected as the first band. The eluent was then changed to toluene/ethyl acetate 2:1 and product **7** was collected (17 mg, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.26–1.30 (m, 6H), 1.32 (s, 9H), 1.36 (s, 9H), 1.47 (s, 9H), 3.50–3.60 (w, 2H), 3.63–3.69 (m, 2H), 3.81–3.87 (m, 2H), 5.13 (t, J=5.68 Hz, 1H), 5.14 (s, 1H), 5.83 (s, 1H), 6.25–6.50 (s, 1H), 7.13 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=150.32, 150.14 (2C), 149.67 (2C), 149.21, 149.04, 148.97, 148.89, 148.75, 148.59, 148.51, 148.45 (3C), 148.41, 148.39, 148.12, 148.10, 148.01, 147.80, 147.46, 147.44, 147.29 (2C), 147.24, 147.14, 147.05, 147.02, 146.19, 146.05, 145.54, 144.72, 144.61, 144.46, 144.17, 143.25, 143.16 (3C), 143.12, 142.02, 142.00, 141.19, 140.43, 140.32, 139.50, 138.14, 137.56, 132.41, 99.91, 83.60, 82.30, 81.94, 81.70, 81.62, 81.00, 76.24, 72.90, 70.38, 70.05, 66.67, 63.90, 61.13, 60.86, 56.51, 55.65, 26.73 ($6CH_3$), 26.64 ($3CH_3$), 15.33 (CH_3), 15.30 ppm (CH_3); FTIR (microscope): 3351, 2977, 2928, 1453, 1388, 1364, 1260, 1242, 1192, 1133, 1066, 1016, 875, 757 cm^{-1}; ESI-MS, m/z (%): 1201 (100) $[M+H]^+$, 1223 (40) $[M+Na]^+$.

*4.1.7. Compound **8***

Method 1: *m*-CPBA (7.50 mg, 0.031 mmol) was added to a solution of **6** (18 mg, 0.015 mmol) in 9 mL of CH_2Cl_2. The mixture was stirred in the dark at rt for 5 min. A solution of 38 mg $Na_2S_2O_3$ and 21 mg K_2CO_3 in 9 mL of water was added to this mixture. The organic layer was separated, dried over Na_2SO_4, and filtered. The solvent was removed. The residue was purified by chromatography on a silica gel column eluting with benzene/petroleum ether (boiling point 60–90 °C)/ethyl acetate (10:10:1). Unreacted **6** (trace) was collected as the first band, followed by product **8** (12 mg, 66%) as the second band. Method 2: DIB (11 mg, 0.034 mmol) was added to a solution of **7** (29 mg, 0.024 mmol) in 15 mL of benzene. The mixture was stirred in dark at rt for 2 min. The solution was purified by chromatography on a silica gel column eluting with benzene/petroleum ether (boiling point 60–90 °C)/ethyl acetate (10:10:1). Product **8** (17 mg, 59%) was collected as the first band. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.15–1.25 (m, 6H), 1.23 (s, 9H), 1.446 (s, 9H), 1.450 (s, 9H), 3.49 (d, J=5.31 Hz, 2H), 3.54–3.61 (m, 2H), 3.74–3.80 (m, 2H), 4.43 (s, 1H), 4.98 (t, J=11.12 Hz, 1H), 6.39 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=150.44, 150.20, 149.77, 149.28, 149.11, 149.02, 148.81, 148.78, 148.60, 148.48 (6C), 148.22, 148.10, 148.03, 147.99, 147.94, 147.56, 147.40, 147.39, 147.28, 147.19, 147.11, 146.30, 146.13, 144.69, 144.67, 144.63, 144.44, 144.33, 144.18, 143.60, 143.21, 143.18, 143.16, 142.81, 142.58, 142.11, 141.64, 141.10, 140.49, 140.35, 140.08, 138.10, 138.07, 137.56, 133.11, 99.88, 94.65, 82.92, 82.58, 82.23, 82.00, 81.68, 81.10, 76.60, 71.74, 69.44 (2C), 64.56, 61.15, 60.96, 55.45, 53.32, 26.72 ($3CH_3$), 26.66 ($3CH_3$), 26.55 ($3CH_3$), 15.24 (CH_3), 15.19 ppm (CH_3); FTIR (microscope): 3334, 2976, 2926, 2854, 1728, 1658, 1572, 1457, 1388, 1387, 1364, 1288, 1261, 1243, 1191, 1160, 1127, 1091, 1069, 1017, 874 cm^{-1}; ESI-MS, m/z (%): 1199 (100) $[M+H]^+$.

*4.1.8. Compound **9***

$(C_6F_5)_3B$ (5 mg, 0.0017 mmol) was added to a solution of **4** (48 mg, 0.043 mmol) in 12 mL of CH_2Cl_2. The mixture was stirred in dark at rt for 1 h. The solution was directly chromatographed on silica gel eluting with toluene/ethyl acetate 10:1. Unreacted **4**

(trace) was collected as the first band. The eluent was then changed to toluene/ethyl acetate 5:1. Product **9** was collected (20 mg, 42%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.38 (s, 9H), 1.41 (s, 18H), 1.46 (s, 9H), 4.36 (s, 1H), 4.93 (s, 1H), 5.93 ppm (s, 1H). Because compound **9** was not stable and changed to **10** slowly, ^{13}C NMR and MS spectra were not obtained.

4.1.9. Compound *10*

$(C_6F_5)_3B$ (55 mg, 0.019 mmol) was added to a solution of **4** (456 mg, 0.41 mmol) in 114 mL of commercial CH_2Cl_2 (used directly). The mixture was stirred in dark at 30 °C for 100 min. The solution was directly chromatographed on silica gel eluting with benzene/petroleum ether (boiling point 60–90 °C)/ethyl acetate (10:10:1). Product **10** was collected as a red band (208 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.44 (s, 9H), 1.47 (s, 9H), 1.50 (s, 9H), 3.40 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=152.33, 149.86, 149.65, 149.58, 149.51, 149.47, 148.71, 148.08, 147.99, 147.60, 147.58 (2C), 147.46, 147.40, 147.39, 147.30, 147.22, 147.14, 147.11, 147.07, 147.06, 146.96, 146.93, 146.87, 146.81 (2C), 146.77, 146.50, 146.36, 146.34, 146.11, 145.91, 145.45, 145.18, 144.96, 144.80 (2C), 144.62, 144.41, 144.37, 144.21, 144.16, 143.85, 143.81, 143.76, 143.71, 143.55, 143.30 (2C), 143.28, 141.99, 141.04, 140.74, 140.67, 85.13, 82.43, 82.01 (2C), 81.24, 80.51, 76.20, 76.04, 71.41, 26.85 ($3CH_3$), 26.80 ($3CH_3$), 26.71 ppm ($3CH_3$); FTIR (microscope): 3559, 3422, 2977, 2928, 2870, 1460, 1387, 1364, 1285, 1262, 1244, 1192, 1105, 1092, 1045, 1018, 860, 755 cm^{-1}; ESI-MS, *m*/*z* (%): 1043 (100) $[M+Na]^+$.

4.1.10. Compound *11a*

$FeCl_3$ (14 mg, 0.085 mmol) was added to a solution of **10** (107 mg, 0.10 mmol) in 11 mL of benzene. The mixture was stirred in the dark at rt for 10 min. The solution was chromatographed on silica gel eluting with benzene/petroleum ether (boiling point 60–90 °C)/ethyl acetate (10:10:1). Unreacted **10** (trace) was collected as the first band, followed by **11a** (67 mg, 61%) as the second band. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.50 (s, 9H), 1.52 (s, 18H), 3.59 (s, 1H), 4.90 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=156.73, 155.96, 153.44, 149.89, 149.05, 149.01, 148.98 (2C), 148.92, 148.83, 148.62, 148.56, 148.41, 148.34, 148.25, 148.23, 148.15, 148.11, 147.67, 147.48, 147.36 (2C), 147.25, 147.16, 147.15, 147.06, 146.96, 146.80, 145.86, 145.37, 145.26, 145.06, 144.87, 144.50, 144.49, 144.44, 144.30, 144.00, 143.65, 143.52, 143.49, 143.29, 143.21, 143.10, 143.06, 142.72, 142.68, 142.60, 142.55, 142.31, 141.28, 139.87, 137.42, 136.85, 83.56, 82.31, 81.94, 81.54, 81.47, 81.08, 80.13, 73.46, 69.75, 26.69 ($3CH_3$), 26.66 ($3CH_3$), 26.56 ppm ($3CH_3$). FTIR (microscope): 3521, 3392, 2979, 2930, 2869, 1457, 1388, 1364, 1262, 1242, 1191, 1149, 1100, 1049, 1023, 972, 868, 846, 757 cm^{-1}; ESI-MS, *m*/*z* (%): 1055 (100) $[M-H]^-$.

4.1.11. Compound *11b*

$FeBr_3$ (19 mg, 0.064 mmol) was added to a solution of **10** (65 mg, 0.064 mmol) in 6 mL of benzene. The mixture was stirred in the dark at rt for 10 min. The solution was chromatographed on silica gel eluting with benzene/petroleum ether (boiling point 60–90 °C)/ethyl acetate (10:10:1). Unreacted **10** (trace) was collected as the first band, followed by **11b** (36 mg, 51%) as the second band. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.49 (s, 9H), 1.51 (s, 9H), 1.54 (s, 9H), 3.51 (s, 1H), 4.97 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=156.64, 155.91, 153.73, 151.20, 150.11, 149.17, 149.13, 149.06, 148.98, 148.90, 148.71, 148.63, 148.56, 148.47, 148.40, 148.37, 148.34, 148.26, 147.75, 147.56, 147.46, 147.45, 147.36, 147.30, 147.20 (2C), 147.16, 146.99, 145.98, 145.47, 145.43, 145.27 (2C), 144.92, 144.65 (2C), 144.37, 144.06, 143.77, 143.68, 143.62, 143.46, 143.34, 142.93, 142.78, 142.69, 142.65, 142.47, 142.39, 142.34, 141.46, 139.94, 136.75, 136.67, 83.83, 82.44, 82.06, 81.72, 81.25, 81.22, 80.27, 73.62, 63.97, 26.89 ($3CH_3$), 26.80 ($3CH_3$), 26.69 ppm ($3CH_3$); FTIR (microscope): 3538, 3430, 2979, 2930, 2870, 1459, 1421, 1388, 1364, 1261, 1243, 1192, 1141, 1105, 1097, 1049, 1019, 898, 871, 756 cm^{-1}; ESI-MS, *m*/*z* (%): 1123 (100) $[M+NH_4]^+$.

4.1.12. Compound *12*

$(C_6F_5)_3B$ (29 mg, 0.010 mmol) was added to a solution of **10** (208 mg, 0.20 mmol) in 69 mL of CH_2Cl_2. The mixture was stirred in the dark at 30 °C for 40 min. The solution was chromatographed on silica gel eluting with toluene/ethyl acetate 10:1. Unreacted **10** was collected as the first band (trace). The eluent was then changed to toluene/ethyl acetate 2:1. Product **12** was collected (136 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.44 (s, 9H), 1.51 (s, 9H), 1.53 (s, 9H), 5.29 (s, 1H), 5.72 (s, 1H), 6.24 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=156.07, 154.83, 153.21, 149.51, 149.48, 149.20, 149.07, 149.04 (2C), 148.98, 148.72, 148.68, 148.63, 148.45, 148.42, 148.30 (2C), 148.19, 147.75, 147.58, 147.48, 147.41, 147.38 (2C), 147.35, 147.20, 147.07, 147.02, 145.92, 145.61, 145.37, 145.35, 145.29, 145.07, 144.82, 144.73, 144.56 (2C), 144.50, 144.14, 144.13, 144.04, 143.73, 143.55, 143.34 (2C), 142.98, 142.83, 142.81, 142.69, 141.28, 140.35, 137.99, 137.68, 82.95, 82.35, 82.07, 82.03, 81.40, 80.99, 80.32, 75.91, 73.50, 26.92 ($3CH_3$), 26.75 ($3CH_3$), 26.74 ppm ($3CH_3$); FTIR (microscope): 3343, 2979, 2930, 2871, 1459, 1420, 1388, 1364, 1263, 1243, 1191, 1144, 1092, 1049, 1027, 870, 756, 733 cm^{-1}; ESI-MS, *m*/*z* (%): 1056 (100) $[M+NH_4]^+$, 1061 (90) $[M+Na]^+$, 1077 (60) $[M+K]^+$.

4.1.13. Compound *13*

DIB (23 mg, 0.072 mmol) was added to a solution of **12** (37 mg, 0.036 mmol) in 18 mL of dry benzene. The mixture was stirred in the dark at 30 °C for 1 h. The solution was chromatographed on silica gel eluting with toluene/ethyl acetate 10:1. Product **13** was collected as the first band (27 mg, 73%), followed by unreacted **12** (trace) as the second band. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.41 (s, 9H), 1.43 (s, 9H), 1.45 (s, 9H), 4.02 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=198.44, 197.67, 154.08, 152.03, 149.79, 149.75, 149.69, 149.35, 149.32, 149.27, 148.96 (2C), 148.93, 148.80, 148.74, 148.72, 148.68, 148.49 (2C), 148.08, 147.95, 147.73, 147.45, 147.27, 146.97, 146.53, 146.40 (2C), 146.09, 145.17 (2C), 145.12, 145.08, 145.00, 144.95, 144.41, 144.38 (2C), 144.04, 143.96, 143.36, 143.26 (3C), 143.12, 143.01, 141.83, 141.63, 141.57, 141.36, 141.26, 140.87, 140.04, 138.09, 133.39, 131.48, 88.65, 82.51, 82.50, 82.27, 80.06, 78.31, 77.91, 26.64 ($6CH_3$), 26.54 ppm ($3CH_3$); FTIR (microscope): 3420, 2980, 2931, 2871, 1747, 1472, 1455, 1388, 1364, 1260, 1243, 1191, 1102, 1080, 1046, 1024, 1010, 868, 755, cm^{-1}; ESI-MS, *m*/*z* (%): 1037 (60) $[M+H]^+$, 1059 (60) $[M+Na]^+$, 1068 (50) $[M+K]^+$, 1082 (100) $[M+Me+MeO]^+$ (this peak is probably due to the formation of the dimethyl acetal since MeOH was added to measure the ESI-MS spectrum).

4.1.14. Compound *14a*

Methanol (486 μL, 10 mmol) and 1 M $BF_3{\cdot}Et_2O$ (204 μL, 0.20 mmol) were added to a solution of **13** (106 mg, 0.10 mmol) in 27 mL of dry CH_2Cl_2. The mixture was stirred in the dark at rt for 50 min and 2 mL of 2 M aqueous HCl was added to the mixture. The organic layer was separated, dried over Na_2SO_4, and filtered. The solvent was removed. The residue was chromatographed on silica gel eluting with toluene/ethyl acetate 10:1. Unreacted **13** (trace) was collected as the first band. The eluent was changed to toluene/ethyl acetate 1:1. Product **14a** was then collected (94 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.45 (s, 9H), 1.47 (s, 9H), 1.49 (s, 9H), 3.91 (s, 3H), 4.60–4.80 (w, 1H), 5.60–5.80 ppm (w, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=162.94, 162.05, 150.80, 149.69 (2C), 148.88, 148.86 (2C), 148.76, 148.58, 148.52, 148.44, 148.27, 148.25, 148.23, 148.15, 148.11, 148.05 (2C), 147.14, 147.07, 147.05, 146.99, 146.71 (2C), 146.65, 146.61, 146.20, 145.92, 145.83, 145.72, 145.49, 144.83, 144.81, 144.77, 144.63,

144.00, 143.90, 143.83, 143.79, 143.66, 143.40, 143.36, 143.02, 142.97, 142.88, 141.71, 141.59, 141.56, 141.49, 140.23, 139.10, 134.55, 133.18, 106.76, 105.87, 87.93, 82.41, 82.33, 81.90, 79.85, 79.12, 78.48, 54.12, 26.78 ($3CH_3$), 26.72 ($3CH_3$), 26.67 ppm ($3CH_3$); FTIR (microscope): 3364, 2978, 2928, 2868, 1455, 1378, 1364, 1242, 1210, 1193, 1160, 1105, 1090, 1060, 1020, 1009, 872, 756 cm^{-1}; ESI-MS, *m*/*z* (%): 1086 (100) $[M+NH_4]^+$.

4.1.15. Compound **14b**

Ethanol (326 μL, 5.50 mmol) and 1 M $BF_3 \cdot Et_2O$ (111 μL, 0.11 mmol) were added to a solution of **13** (58 mg, 0.055 mmol) in 15 mL of dry CH_2Cl_2. The mixture was stirred in the dark at rt for 50 min and 2 mL of 2 M aqueous HCl was added to the mixture. The organic layer was separated, dried over Na_2SO_4, and filtered. The solvent was removed. The residue was chromatographed on silica gel eluting with toluene/ethyl acetate 10:1. Unreacted **13** (trace) was collected as the first band. The eluent was changed to toluene/ethyl acetate 1:1. Product **14b** (54 mg, 89%). ^1H NMR (400 MHz, $CDCl_3$): δ=1.39 (t, *J*=14.10 Hz, 3H), 1.46 (s, 9H), 1.47 (s, 9H), 1.50 (s, 9H), 2.77 (s, 1H), 4.18–4.32 (w, 2H), 5.34 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=163.38, 161.79, 150.76, 149.69 (2C), 148.89, 148.86 (2C), 148.76, 148.58, 148.50, 148.43, 148.27, 148.26, 148.23, 148.15, 148.11, 148.05, 148.02, 147.13 (2C), 147.05, 147.02, 146.83, 146.72, 146.65, 146.58, 146.54, 146.47, 145.88, 145.86, 145.49, 145.88, 145.86, 145.49, 144.80, 144.78, 144.69, 144.63, 144.01, 143.91, 143.88, 143.81, 143.65, 143.38, 143.35, 143.01 (2C), 142.89, 141.72, 141.60, 141.54, 141.45, 140.28, 138.99, 134.17, 132.95, 106.67, 105.61, 87.86, 82.41, 82.25, 81.83, 79.83, 79.17, 78.43, 62.68, 26.79 ($6CH_3$), 26.72 ($3CH_3$), 15.63 ppm (CH_3); FTIR (microscope): 3376, 2979, 2929, 1472, 1454, 1388, 1364, 1264, 1245, 1213, 1192, 1159, 1104, 1091, 1041, 872, 756 cm^{-1}; ESI-MS, *m*/*z* (%): 1100 (100) $[M+NH_4]^+$, 1081 (100) $[M-Na]^-$, 1117 (80) $[M+Cl]^-$.

4.1.16. Compound **14c**

Phenol (37 μL, 0.42 mmol) and 1 M $BF_3 \cdot Et_2O$ (78 μL, 0.084 mmol) were added to a solution of **13** (87 mg, 0.084 mmol) in 17 mL of dry CH_2Cl_2. The mixture was stirred in the dark at rt for 2 min and 2 mL of 2 M aqueous HCl was added to the mixture. The organic layer was separated, dried over Na_2SO_4, and filtered. The solvent was removed. The residue was chromatographed on silica gel eluting with toluene/ethyl acetate 10:1. Unreacted **13** (trace) was collected as the first band, followed by product **14c** (41 mg, 43%) as the second band. ^1H NMR (400 MHz, $CDCl_3$): δ=1.44 (s, 9H), 1.475 (s, 9H), 1.481 (s, 9H), 4.62 (s, 1H), 5.88 (s, 1H), 7.08–7.12 (m, 1H), 7.32–7.36 (m, 2H), 7.55–7.57 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=162.47, 162.01, 155.52, 150.82, 149.70, 149.69, 148.89, 148.87 (2C), 148.79, 148.64, 148.55, 148.48, 148.26 (3C), 148.17 (2C), 148.12 (2C), 147.17, 147.08, 147.02, 146.80, 146.70, 146.64, 146.59, 146.51, 146.22, 145.82, 145.78, 145.55, 145.47, 145.20, 144.88, 144.80, 144.66, 144.01, 143.92, 143.89, 143.83, 143.69, 143.53, 143.41, 143.09, 143.01, 142.95, 141.63, 141.52, 141.50, 141.37, 140.25, 139.10, 134.63, 132.44, 129.36 (2C), 123.74, 120.21 (2C), 106.89, 106.42, 88.12, 82.59, 82.41, 82.39, 82.06, 80.08, 79.02, 78.49, 26.79 ($3CH_3$), 26.78 ($3CH_3$), 26.73 ppm ($3CH_3$); FTIR (microscope): 3404, 2978, 2929, 2869, 1591, 1489, 1455, 1388, 1365, 1247, 1214, 1194, 1159, 1086, 1040, 1016, 871, 755 cm^{-1}; ESI-MS, *m*/*z* (%): 1153 (100) $[M+Na]^+$.

4.1.17. Compound **14d**

Phenylmethanol (501 μL, 0.48 mmol) and 1 M $BF_3 \cdot Et_2O$ (96 μL, 0.096 mmol) were added to a solution of **13** (50 mg, 0.048 mmol) in 12 mL of dry CH_2Cl_2. The mixture was stirred in the dark at rt for 0.5 h and 2 mL of 2 M aqueous HCl was added to the mixture. The organic layer was separated, dried over Na_2SO_4, and filtered. The solvent was removed. The residue was washed with methanol to remove unreacted phenylmethanol. The washed residue was chromatographed on silica gel eluting with toluene/ethyl acetate 10:1. Unreacted **13** (trace) was collected as the first band, then followed by product **14d** (31 mg, 56%) as the second band. ^1H NMR (400 MHz, $CDCl_3$): δ=1.45 (s, 9H), 1.47 (s, 9H), 1.50 (s, 9H), 4.47 (s, 1H), 5.18–5.29 (two doublets, 2H), 5.55 (s, 1H), 7.28–7.33 (m, 3H), 7.42–7.44 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=163.37, 161.87, 150.78, 149.69 (2C), 148.88 (2C), 148.84, 148.76, 148.60, 148.52, 148.45, 148.28, 148.25, 148.23, 148.14, 148.12, 148.07, 148.05, 147.14, 147.10, 147.06, 146.97, 146.80, 146.70, 146.64, 146.45, 146.29, 146.08, 145.87, 145.76, 145.48, 144.82, 144.79, 144.71, 144.68, 144.03, 143.89 (2C), 143.81, 143.65, 143.36 (2C), 143.05, 143.03, 142.93, 141.66, 141.61, 141.56, 141.53, 140.23, 139.04, 137.25, 134.46, 133.16, 128.37 (2C), 128.19 (2C), 127.85, 106.77, 105.82, 87.88, 82.52, 82.32, 81.91, 79.90, 79.18, 78.45, 69.00, 26.80 ($6CH_3$), 26.72 ppm ($3CH_3$); FTIR (microscope): 3541, 3375, 2978, 2927, 2854, 1454, 1387, 1364, 1268, 1245, 1213, 1192, 1159, 1099, 1041, 1023, 872, 755 cm^{-1}; ESI-MS, *m*/*z* (%): 1162 (100) $[M+NH_4]^+$; 1143 (100) $[M-H]^-$ (negative mode).

4.1.18. Compound **14e**

2-(2-Methoxyethoxy)ethanol (64 μL, 0.54 mmol) and 1 M $BF_3 \cdot Et_2O$ (50 μL, 0.054 mmol) were added to a solution of **13** (56 mg, 0.054 mmol) in 11 mL of dry CH_2Cl_2. The mixture was stirred in the dark at rt for 1.5 h and 2 mL of 2 M aqueous HCl was added to the mixture. The organic layer was separated, dried over Na_2SO_4, and filtered. The solvent was removed. The residue was chromatographed on silica gel eluting with toluene/ethyl acetate 10:1. Unreacted **13** (trace) was collected as the first band. The eluent was changed to toluene/ethyl acetate 2:1. Product **14e** was then collected (51 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$): δ=1.43 (s, 9H), 1.47 (s, 9H), 1.48 (s, 9H), 3.42 (s, 3H), 3.58 (t, *J*=9.1 Hz, 2H), 3.68–3.79 (m, 2H), 3.86–3.89 (t, *J*=9.4 Hz, 2H), 4.36–4.39 (m, 2H), 5.12 (s, 1H), 6.15 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=162.73, 162.17, 150.71, 149.66, 149.64, 148.85 (3C), 148.76, 148.56, 148.48, 148.42, 148.26 (2C), 148.23, 148.17, 148.12, 148.04, 148.02, 147.18, 147.15, 147.05, 147.01 (2C), 146.68, 146.66, 146.57, 146.30, 145.90, 145.82, 145.65, 145.58, 145.11, 144.76, 144.72, 144.66, 144.03, 143.92, 143.72, 143.70, 143.68, 143.51, 143.29, 142.98, 142.84 (2C), 141.85, 141.56, 141.46, 141.40, 140.19, 139.33, 134.74, 133.04, 106.77, 105.73, 88.07, 82.19, 82.05, 81.85, 79.81, 79.05, 78.53, 71.96, 70.66, 70.31, 66.29, 59.01, 26.78 ($3CH_3$), 26.75 ($3CH_3$), 26.72 ppm ($3CH_3$); FTIR (microscope): 3344, 2978, 2926, 1454, 1387, 1364, 1269, 1245, 1193, 1157, 1145, 1095, 1043, 1020, 873, 756 cm^{-1}; ESI-MS, *m*/*z* (%): 1179 (100) $[M+Na]^+$.

4.1.19. Compound **15**

DABCO (10 mg, 0.092 mmol) was added to a solution of **14a** (49 mg, 0.046 mmol) in 10 mL of dry CH_2Cl_2. The mixture was stirred in the dark at rt for 3 h. The solution was chromatographed on silica gel eluting with benzene/petroleum ether (boiling point 60–90 °C)/ethyl acetate (10:10:1). Product **15** (29 mg, 59%) was collected as the second band. ^1H NMR (400 MHz, $CS_2/CDCl_3$=1:2): δ=1.41 (s, 9H), 1.44 (s, 9H), 1.46 (s, 9H), 3.92 (s, 3H), 5.22 (s, 1H), 5.63 ppm (s, 1H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$=1:2; all signals represent 1C except as noted): δ=159.96, 150.47, 149.80, 149.32, 149.23, 148.87 (2C), 148.72, 148.44, 148.40, 148.37, 148.20, 148.11, 148.04, 148.02, 147.89, 147.86, 147.78 (2C), 147.72, 147.54, 147.51, 147.39, 147.32, 146.75, 146.11, 145.42, 145.29, 145.11, 144.84, 144.68, 144.29, 144.17, 144.03, 143.70, 143.38, 143.35, 143.19, 143.12, 142.83, 142.75, 142.50, 142.39, 142.36, 142.17, 141.98, 141.74, 140.28, 139.64, 139.43, 139.31, 139.01, 137.74, 127.02, 111.69, 84.03, 83.61, 81.64, 81.57, 81.30, 79.70, 79.69, 78.73, 54.69, 26.60 ($6CH_3$), 26.58 ppm ($3CH_3$); FTIR (microscope): 3430, 2979, 2931, 1472, 1454, 1388, 1364, 1189, 1098, 1052, 1028, 909, 871, 733 cm^{-1}; ESI-MS, *m*/*z* (%): 1091 (100) $[M+Na]^+$; 1067 (100) $[M-H]^-$ (negative mode).

4.1.20. Compound ***16***

DIB (37 mg, 0.12 mmol) was added to a solution of **15** (62 mg, 0.058 mmol) in 31 mL of dry benzene. The mixture was stirred in the dark at 30 °C for 20 min. The solution was chromatographed on silica gel eluting with benzene/petroleum ether (boiling point 60–90 °C)/ethyl acetate (10:10:1). Product **16** was collected as the first band (54 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.37 (s, 9H), 1.39 (s, 9H), 1.41 (s, 9H), 3.94 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=195.60, 192.49, 155.65, 150.66, 150.09, 149.74, 149.60, 149.22, 149.17, 149.13, 149.08, 148.99, 148.90 (2C), 148.80, 148.68, 148.63, 148.40, 148.37, 148.22, 147.84, 147.72, 147.53, 147.28, 147.02, 145.85, 145.38, 145.32, 144.96, 144.91, 144.89, 144.53, 144.50, 143.71, 143.33, 143.29, 143.00, 142.70, 142.45, 142.24, 141.58, 141.23, 141.16, 141.02, 140.90, 140.88, 140.73, 140.41, 139.79, 139.37, 138.93, 138.68, 137.46, 135.32, 134.42, 127.87, 115.77, 88.74, 82.61, 82.27, 82.22, 82.16, 76.23, 55.63, 26.64 ($3CH_3$), 26.56 ($3CH_3$), 26.53 ppm ($3CH_3$); FTIR (microscope): 2979, 2928, 2852, 1749, 1659, 1457, 1388, 1365, 1261, 1243, 1191, 1158, 1142, 1105, 1079, 1043, 1024, 1002, 868, 756 cm^{-1}; ESI-MS, *m*/*z* (%): 1047 (100) $[M-OH]^+$.

4.1.21. Compound ***17***

Methanol (42 μL, 0.86 mmol) and 1 M $BF_3{\cdot}Et_2O$ (105 μL, 0.10 mmol) were added to a solution of **16** (54 mg, 0.051 mmol) in 5 mL of dry CH_2Cl_2. The mixture was stirred in the dark at rt for 20 min. The mixture was chromatographed on silica gel eluting with toluene/ethyl acetate–benzene/petroleum ether (boiling point 60–90 °C)/ethyl acetate (10:10:1). Unreacted **16** (trace) was collected as the first band. The eluent was changed to toluene/ethyl acetate 1:1. Product **17** was then collected (52 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.43 (s, 9H), 1.44 (s, 9H), 1.48 (s, 9H), 3.85 (s, 3H), 3.94 (s, 3H), 5.53 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=161.59, 150.72, 150.20, 149.53, 149.36, 149.05, 148.91, 148.85, 148.82, 148.79, 148.73, 148.42, 148.39, 148.35, 148.04, 147.99, 147.93, 147.86, 147.56, 147.36, 147.22, 147.01, 146.75, 146.62, 145.59, 145.17, 145.14, 145.04, 145.02, 144.58, 144.54, 144.14, 143.59, 143.34, 143.26, 143.17, 142.47, 142.08, 141.92, 141.90, 141.86, 141.67 (2C), 140.94, 140.81, 140.32, 140.05, 140.03, 139.90, 139.70, 138.95, 138.21, 135.28, 124.16, 113.12, 108.11, 101.23, 86.59, 83.39, 83.27, 82.01, 81.69, 77.55, 55.25, 53.94, 26.82 ($3CH_3$), 26.67 ppm ($6CH_3$); FTIR (microscope): 3497, 2979, 2932, 2831, 1456, 1388, 1365, 1261, 1242, 1191, 1172, 1088, 1050, 1028, 1003, 870, 757 cm^{-1}; ESI-MS, *m*/*z* (%): 1116 (100) $[M+NH_4]^+$, 1121 (100) $[M+Na]^+$; 1097 (100) $[M-H]^-$ (negative mode).

4.1.22. Compound ***18a***

An aqueous solution of $NH_2OH{\cdot}HCl$ (39 mg, 0.56 mmol in 0.5 mL of water) and K_2CO_3 (152 mg, 1.11 mmol) was added to a solution of compound **13** (115 mg, 0.11 mmol) in 23 mL of CH_2Cl_2, and the flask was wrapped with aluminum foil. After stirring for 20 min at rt, the solution was chromatographed on a silica gel eluting with toluene/ethyl acetate 10:1. Unreacted **13** (trace) was collected as the first band. The eluent was changed to toluene/ethyl acetate 2:1. Product **18a** was collected as the second band (25 mg, 21%). The eluent was changed to toluene/ethyl acetate 1:1. Product **19a** was collected as the third band (51 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.406 (s, 9H), 1.413 (s, 9H), 1.46 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=158.62, 151.00, 149.92, 149.89, 149.36 (3C), 149.02, 149.01, 148.70, 148.56, 148.37 (2C), 148.27, 148.18 (2C), 147.98, 147.90 (2C), 147.86, 147.78, 147.76, 147.72, 147.28, 147.12, 146.95, 146.46, 145.86, 145.59, 145.15, 144.94, 144.75, 144.68, 144.62, 144.33, 143.98 (2C), 143.86, 143.30, 143.13, 143.05, 142.73, 142.54, 142.50, 142.44, 142.11, 140.84, 140.39, 140.28, 139.89, 139.45, 139.04, 138.96, 136.99, 108.13, 84.38, 82.48, 82.20, 82.03, 81.90, 81.45, 78.53, 76.51, 26.74 ($3CH_3$), 26.73 ppm ($6CH_3$); FTIR (microscope): 3383, 2978, 2926, 2854, 1455, 1387, 1364, 1242, 1190, 1152, 1109, 1044, 1026, 954, 871, 793, 756 cm^{-1}; ESI-MS, *m*/*z* (%): 1170 (100) $[M+H]^+$.

4.1.23. Compound ***18b***

Aminoacetaldehyde dimethyl acetal (4.8 μL, 0.044 mmol) was added to a solution of **13** (48 mg, 0.046 mmol) in 24 mL of dry CH_2Cl_2. The mixture was stirred in the dark at rt for 5 min. The solution was chromatographed on silica gel eluting with toluene/ethyl acetate 5:1. Unreacted **13** (trace) was collected as the first band, then followed by product **18b** (19 mg, 36%) as the second band. The eluent was changed to toluene/ethyl acetate 2:1. Product **19b** was then collected (23 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.387 (s, 9H), 1.392 (s, 9H), 1.41 (s, 9H), 3.34–3.47 (m, 2H), 3.61 (s, 3H), 3.64 (s, 3H), 4.82 ppm (t, *J*=10.79 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=159.65, 151.10, 149.82, 149.35 (2C), 149.34, 149.02, 148.96, 148.73, 148.59, 148.31, 148.29, 148.18 (3C), 148.16, 148.00, 147.89 (2C), 147.79 (3C), 147.67, 147.64 (2C), 147.23, 146.91, 146.38, 146.02, 145.77, 145.58, 144.40, 144.30, 144.08, 144.04, 143.75, 143.39, 143.35, 143.05, 142.80, 142.53, 142.47, 142.40, 142.10, 142.06, 141.54, 140.68, 140.64, 140.36, 139.74, 139.51, 139.43, 137.38, 129.35, 108.15, 103.23, 84.33, 82.23, 81.90, 81.70, 81.55, 79.45, 78.68, 71.87, 54.93, 53.83, 47.12, 26.76 ($6CH_3$), 26.66 ppm ($3CH_3$); FTIR (microscope): 3282, 2979, 2930, 1455, 1387, 1364, 1243, 1191, 1153, 1106, 1084, 1022, 871, 756 cm^{-1}; ESI-MS, *m*/*z* (%): 1142 (100) $[M+H]^+$.

Single crystals of compound **18b** were obtained from slow evaporation of its solution in $CDCl_3$ at 5 °C. Space group: $P2_1/C$, a=15.8341(2), b=16.6776(2), c=27.5038(4) Å, α=90.00, β=124.7090(10), γ=90.00. V=5970.6 Å^3. Final R indices [$I>2\sigma(I)$]: R_1=0.0640, wR_2=0.1807. CCDC-679744.

4.1.24. Compound ***18c***

Aminoacetaldehyde diethyl acetal (10 μL, 0.069 mmol) was added to a solution of **13** (70 mg, 0.067 mmol) in 35 mL of dry CH_2Cl_2. The mixture was stirred in the dark at rt for 2 min. The solution was chromatographed on silica gel eluting with toluene/ethyl acetate 5:1. Unreacted **13** (trace) was collected as the first band, followed by product **18c** (31 mg, 39%) as the second band. The eluent was changed to toluene/ethyl acetate 2:1. Product **19c** was collected (40 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.35–1.39 (m, 6H), 1.37 (s, 9H), 1.39 (s, 9H), 1.42 (s, 9H), 3.44 (d, *J*=5.38 Hz, 2H), 3.77–3.84 (m, 2H), 3.89–3.95 (m, 2H), 4.91 ppm (t, *J*=10.71 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=160.19, 151.13, 149.79, 149.56, 149.33, 149.29, 148.98, 148.92, 148.68, 148.56, 148.27, 148.23, 148.15 (2C), 148.12, 147.96, 147.88, 147.85, 147.77, 147.75, 147.62, 147.60, 147.42, 147.20, 146.83, 146.34, 146.10, 145.61, 145.56, 145.08, 144.87, 144.32, 144.28, 144.03, 143.98, 143.73, 143.31, 143.29, 142.99, 142.83, 142.42, 142.39, 142.35, 142.17, 142.02, 141.43, 140.71, 140.38, 130.35, 139.79, 139.63, 139.40, 137.09, 129.14, 108.08, 101.52, 84.32, 82.08, 81.94, 81.65, 81.53, 79.55, 78.63, 71.81, 63.01, 62.55, 48.41, 26.73 ($3CH_3$), 26.70 ($6CH_3$), 15.57 (CH_3), 15.56 ppm (CH_3); FTIR (microscope): 3290, 2978, 2930, 1471, 1455, 1387, 1364, 1245, 1190, 1169, 1154, 1107, 1083, 1063, 1021, 1011, 908, 871, 733 cm^{-1}; ESI-MS, *m*/*z* (%): 1170 (100) $[M+H]^+$.

4.1.25. Compound ***19a***

See experimental procedure of **18a**. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$=1:2): δ=1.38 (s, 9H), 1.41 (s, 9H), 1.48 (s, 9H), 4.15 (s, 1H), 6.24 (s, 1H), 8.76 (s, 1H), 9.02 ppm (s, 1H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$=1:2; all signals represent 1C except as noted): δ=158.56, 149.86, 149.83, 149.47, 149.40, 149.03, 148.99, 148.87, 148.59, 148.39, 148.29 (2C), 148.22, 148.20, 148.16, 147.99, 147.91 (2C), 147.87 (3C), 147.63, 147.21, 147.09, 146.77, 146.23 (2C), 145.93, 145.76, 145.67, 145.35, 145.15, 144.95, 144.28, 144.24, 144.11, 143.67, 143.39, 143.16,

142.86, 142.82, 142.70, 142.56, 142.40, 142.11, 141.94, 140.24, 140.02 (2C), 139.82, 139.70, 139.53, 139.07, 130.30, 107.58, 89.79, 82.65, 82.30, 81.68, 81.50, 78.94, 77.01, 75.78, 26.78 ($3CH_3$), 26.70 ppm ($6CH_3$); FTIR (microscope): 3303, 2978, 2927, 2854, 1454, 1388, 1365, 1260, 1244, 1189, 1151, 1102, 1057, 1011, 871, 757 cm^{-1}; ESI-MS, *m*/*z* (%): 1170 (100) $[M+H]^+$.

4.1.26. Compound ***19b***

See experimental procedure of **18b**. ^1H NMR (400 MHz, $CDCl_3$): δ=1.33 (s, 9H), 1.37 (s, 9H), 1.42 (s, 9H), 3.29–3.34 (m, 1H), 3.56 (s, 3H), 3.57 (s, 3H), 4.93 ppm (t, *J*=11.40 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=159.21, 151.78, 149.83, 149.44, 149.32, 149.00, 148.93, 148.76, 148.57, 148.46, 148.35, 148.24, 148.16, 148.07, 148.04, 147.97, 147.85, 147.83, 147.80, 147.75, 147.64, 147.27, 147.14, 147.11, 146.56, 146.53, 146.23, 146.00, 145.87, 145.79, 145.70, 145.66, 144.80, 144.29, 144.25, 143.97, 143.72, 143.19, 143.17, 142.96, 142.62, 142.39 (2C), 142.31 (2C), 142.03, 140.10, 140.01, 139.97, 139.50, 139.10, 139.01, 138.55, 130.30, 107.55, 104.35, 90.80, 82.36, 82.20, 81.87, 81.46, 78.31, 75.70, 74.56, 54.07, 53.72, 44.80, 26.67 ppm ($9CH_3$); FTIR (microscope): 3350, 2978, 2930, 1455, 1388, 1364, 1190, 1109, 1066, 969, 871, 805, 757 cm^{-1}; ESI-MS, *m*/*z* (%): 1142 (100) $[M+H]^+$.

4.1.27. Compound ***19c***

See experimental procedure of **18c**. ^1H NMR (400 MHz, $CDCl_3$): δ=1.30–1.35 (m, 6H), 1.33 (s, 9H), 1.37 (s, 9H), 1.41 (s, 9H), 3.33–3.37 (m, 1H), 3.54–3.58 (m, 1H), 3.72–3.83 (m, 2H), 3.85–3.92 (m, 2H), 5.05 ppm (t, *J*=11.38 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C except as noted): δ=159.79, 151.93, 149.83, 149.43, 149.29, 148.98, 148.91, 148.74, 148.55, 148.45, 148.36, 148.23, 148.11, 148.05 (2C), 147.94, 147.85, 147.80, 147.78, 147.70, 147.63, 147.23, 147.11, 147.09, 146.62, 146.49 (2C), 145.95, 145.86 (2C), 145.71, 145.54, 144.82, 144.24 (2C), 143.94, 143.71, 143.21, 143.11, 142.95, 142.58, 142.36, 142.32, 142.12, 142.02, 142.00, 140.05, 140.03, 139.99 (2C), 139.30, 138.99, 138.65, 129.98, 107.41, 102.91, 90.85, 82.26, 82.21, 81.84, 81.39, 78.29, 75.77, 74.82, 62.56, 61.68, 45.50, 26.77 ($3CH_3$), 26.74 ($3CH_3$), 26.69 ($3CH_3$), 15.50 (CH_3), 15.46 ppm (CH_3); FTIR (microscope): 3559, 3358, 2977, 2929, 1473, 1454, 1387, 1365, 1261, 1245, 1190, 1146, 1100, 1062, 1024, 1008, 871, 757 cm^{-1}; ESI-MS, *m*/*z* (%): 1170 (100) $[M+H]^+$.

Acknowledgements

Financial support is provided by NNSFC (Grants 20632010, 20521202, and 20772004) and the Major State Basic Research Development Program (2006CB806201).

Supplementary data

Selected spectra for new compounds and crystallographic data in CIF format for compounds **5b**, **5c**, and **18b**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.08.053.

References and notes

1. (a) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317–324; (b) Martin, N. *Chem. Commun.* **2006**, 2093–2104; (c) Thilgen, C.; Diederich, F. *Chem. Rev.* **2006**, *106*, 5049–5135.
2. (a) Taylor, R. *Lecture Notes on Fullerene Chemistry, a Hand Book for Chemists*; Imperial College Press: London, 1999; (b) Hirsch, A. *Fullerenes: Chemistry and Reactions*; Wiley-VCH verlag GmbH & Co. KGaA: Weinheim, 2005.
3. For example: (a) the esterification reaction by Nierengarten, J.-F.; Herrmann, A.; Tykwinski, R. R.; Riittimann, M.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1997**, *80*, 293–316; (b) the amidation by Sijbesma, R.; Srdanov, G.; Wudl, F.; Castoro, J. A.; Wilkins, C.; Friedman, S. H.; DeCamp, D. L.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, 6510–6512; (c) the Click reactions by Iehl, J.; Freitas, R. P.; Delavaux-Nicot, B.; Nierengarten, J.-F. *Chem. Commun.* **2008**, 2450–2452; and also by Isobe, H.; Cho, K.; Solin, N.; Werz, D. B.; Seeberger, P. H.; Nakamura, E. *Org. Lett.* **2007**, *9*, 4611–4614. For more references of functionalization of fullerene derivatives, see Ref. 2.
4. (a) Lamparth, I.; Nuber, B.; Schick, G.; Skiebe, A.; Grosser, T.; Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2257–2259; (b) Hummelen, J. C.; Knight, B.; Pavlovich, J.; Gonzalez, R.; Wudl, F. *Science* **1995**, *269*, 1554–1556; (c) Arce, M.-J.; Viado, A. L.; An, Y.-Z.; Khan, S. I.; Rubin, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3775–3776; (d) Iwamatsu, S.-I.; Uozaki, T.; Kobayashi, K.; Re, S.; Nagase, S.; Murata, S. *J. Am. Chem. Soc.* **2004**, *126*, 2668–2669; (e) Vougioukalakis, G. C.; Prassides, K.; Orfanopoulos, M. *Org. Lett.* **2004**, *16*, 1245–1247; (f) Komatsu, K.; Murata, M.; Murata, Y. *Science* **2005**, *307*, 238–240.
5. (a) Qian, W. Y.; Bartberger, M. D.; Pastor, S. J.; Houk, K. N.; Wilkins, C. L.; Rubin, Y. *J. Am. Chem. Soc.* **2000**, *122*, 8333–8334; (b) Qian, W. Y.; Chuang, S.-C.; Amador, R. B.; Jarrosson, T.; Sander, M.; Pieniazek, S.; Khan, S. I.; Rubin, Y. *J. Am. Chem. Soc.* **2003**, *125*, 2066–2067.
6. (a) Chen, Z. X.; Wang, G. W. *J. Org. Chem.* **2005**, *70*, 2380–2383; (b) Matsuo, Y.; Iwashita, A.; Nakamura, E. *Organometallics* **2005**, *24*, 89–95; (c) Martin, N.; Altable, M.; Filippone, S.; Martin-Domenech, A.; Guell, M.; Sola, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1439–1442; (d) Tajima, Y.; Hara, T.; Honma, T.; Matsumoto, S.; Takeuchi, K. *Org. Lett.* **2006**, *8*, 3203–3205; (e) Thayumanavan, R.; Hawkins, B. C.; Keller, P. A.; Pyne, S. G.; Ball, G. E. *Org. Lett.* **2008**, *10*, 1315–1317.
7. (a) Rubin, Y. *Top. Curr. Chem.* **1999**, *199*, 67–92; (b) Iwamatsu, S.-I.; Murata, S. *Synlett* **2005**, 2117–2129; (c) Komatsu, K. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2285–2302.
8. (a) Hummelen, J. C.; Bellavia-Lund, C.; Wudl, F. *Top. Curr. Chem.* **1999**, *199*, 93–134; (b) Vostrowsky, O.; Hirsch, A. *Chem. Rev.* **2006**, *106*, 5191–5207.
9. Gan, L. B.; Huang, S. H.; Zhang, X.; Zhang, A. X.; Cheng, B. C.; Cheng, H.; Li, X. L.; Shang, G. *J. Am. Chem. Soc.* **2002**, *124*, 13384–13385.
10. Xiao, Z.; Yao, J. Y.; Yang, D. Z.; Wang, F. D.; Huang, S. H.; Gan, L. B.; Jia, Z. S.; Jiang, Z. P.; Yang, X. B.; Zheng, B.; Yuan, G.; Zhang, S. W.; Wang, Z. M. *J. Am. Chem. Soc.* **2007**, *129*, 16149–16162.
11. Hu, X. Q.; Jiang, Z. P.; Jia, Z. S.; Huang, S. H.; Yang, X. B.; Li, Y. L.; Gan, L. B.; Zhang, S. W.; Zhu, D. B. *Chem.—Eur. J.* **2007**, *13*, 1129–1141.
12. (a) Huang, S. H.; Yang, X. B.; Zhang, X.; Hu, X. Q.; Gan, L. B.; Zhang, S. W. *Synlett* **2006**, 1266–1268; (b) Huang, S. H.; Wang, F. D.; Gan, L. B.; Yuan, G.; Zhou, J.; Zhang, S. W. *Org. Lett.* **2006**, *8*, 277–279; (c) Jia, Z. S.; Zhang, X.; Zhang, G. H.; Huang, S. H.; Fang, H.; Hu, X. Q.; Li, Y. L.; Gan, L. B.; Zhang, S. W.; Zhu, D. B. *Chem.—Asian J.* **2007**, *2*, 290–300.