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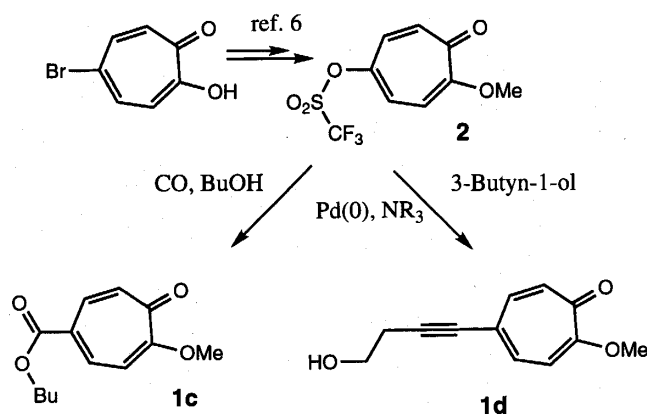
## High-Pressure Diels-Alder Reaction of [C<sub>60</sub>] Fullerene with Functionalized Troponone Derivatives

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By heating buckminsterfullerene, C<sub>60</sub>, with functionalized tropones having a C-substituent in toluene under high-pressure conditions (300 MPa) at 100°C, stable 1:1-Diels-Alder adducts were obtained in fairly good yields. The adduct obtained from 4-(2-methoxytropon-5-yl)butyn-1-ol was successfully esterified with succinic acid and β-indolecarboxylic acid.

Recently, we have carried out the high-pressure cycloaddition reactions between buckminsterfullerene (C<sub>60</sub>) and tropones<sup>1,2)</sup> to obtain the 1:1-[4+2] cycloadducts. Formation of L-B membrane system<sup>3)</sup> from a series of adducts of fluoroalkoxytropones<sup>4)</sup> prompted us to extend the reaction to several C-functionalized troponone derivatives, which should form chemically stable Diels-Alder adducts.

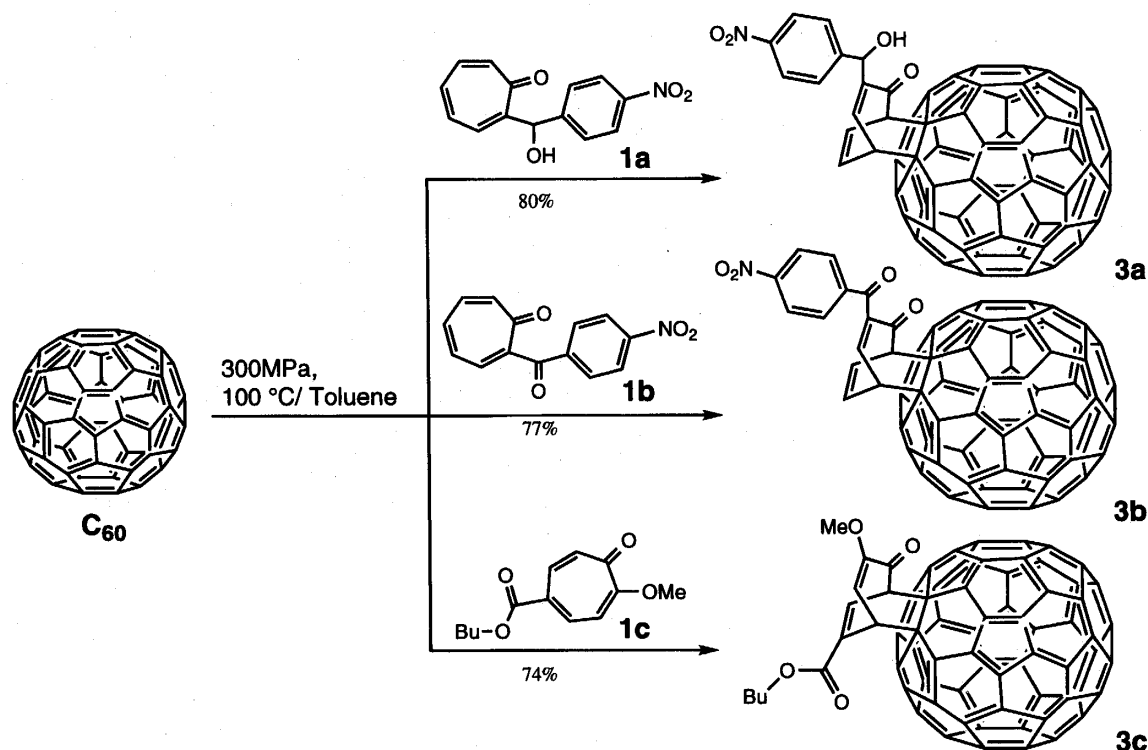
The tropones examined were 4-nitrophenyl(tropon-2-yl)methanol (**1a**),<sup>5)</sup> 2-(4-nitrobenzoyl)troponone (**1b**),<sup>5)</sup> butyl 2-methoxytropon-5-ylcarboxylate (**1c**), and 4-(2-methoxytropon-5-yl)-3-butyn-1-ol (**1d**). For preparation of C-functionalized tropones, the palladium(0)-mediated coupling reaction<sup>6)</sup> was also applicable; by condensation of 2-methoxy-5-(trifluoromesyloxy)troponone (**2**) with carbon monoxide in butanol afforded **1c** in 73% yield, and **2** with 3-butyn-1-ol gave **1d** in 95% yield.



Scheme 1

When a toluene solution of C<sub>60</sub><sup>7)</sup> and **1** (1: C<sub>60</sub> = 5: 2) was heated at 130°C, under 300 MPa for 36 h,<sup>8)</sup> a formation of single 1:1-products (**3a**, **3b**, and **3c**) was confirmed by HPLC analysis (YMC, R-ODS-5, S-5, 120A ODS, toluene/MeCN=1). Flush column chromatog-

raphy with silica gel afforded the analytical samples of the products as black powders.



Scheme 2

These **3** are stable both in the solid state and in solution. No cycloreversion occurred at room temperature, but they revealed the cycloreversion to the starting components at the temperature above 100 °C to their decomposition points. The <sup>1</sup>H NMR spectra of **3** showed the characteristic splitting patterns of the bicyclo[3.2.2]nona-3,6-dienone moiety with rather lower-field shifted signals ascribable to four olefinic and two methine proton signals than those of other representative derivatives.<sup>9)</sup> The UV-vis spectrum is quite similar to those of C<sub>60</sub> and reference compounds in literature.<sup>10)</sup> The <sup>13</sup>C NMR spectrum of **3c**, as a representative compound, was shown in Figure 1.

Similar high-pressure Diels-Alder reaction between C<sub>60</sub> and **1d** gave a 1:1-product (**3d**) in 78% yield. As **3d** has a reactive primary alcoholic group, a couple of reactions with it were performed; by heating with succinic anhydride, **3d** gave a monosuccinate (**4**) in 93% yield, while the DCC-mediated dehydrative condensation of **1d** with β-indolecarboxylic acid afforded an ester (**5**) in 87% yield. These facts offer a ready method for introduction of various functions into C<sub>60</sub> unit in viewpoints of molecular engineering and of physiological and biological interest.

Cosequently, **1d** is reactive towards various types of reagents, and it seems to be very promising for functionalizations of C<sub>60</sub>.

In conclusion, **1** having functional groups for further transformations smoothly afforded 1:1-Diels-Alder adducts with C<sub>60</sub>. Studies on this line are in underway.

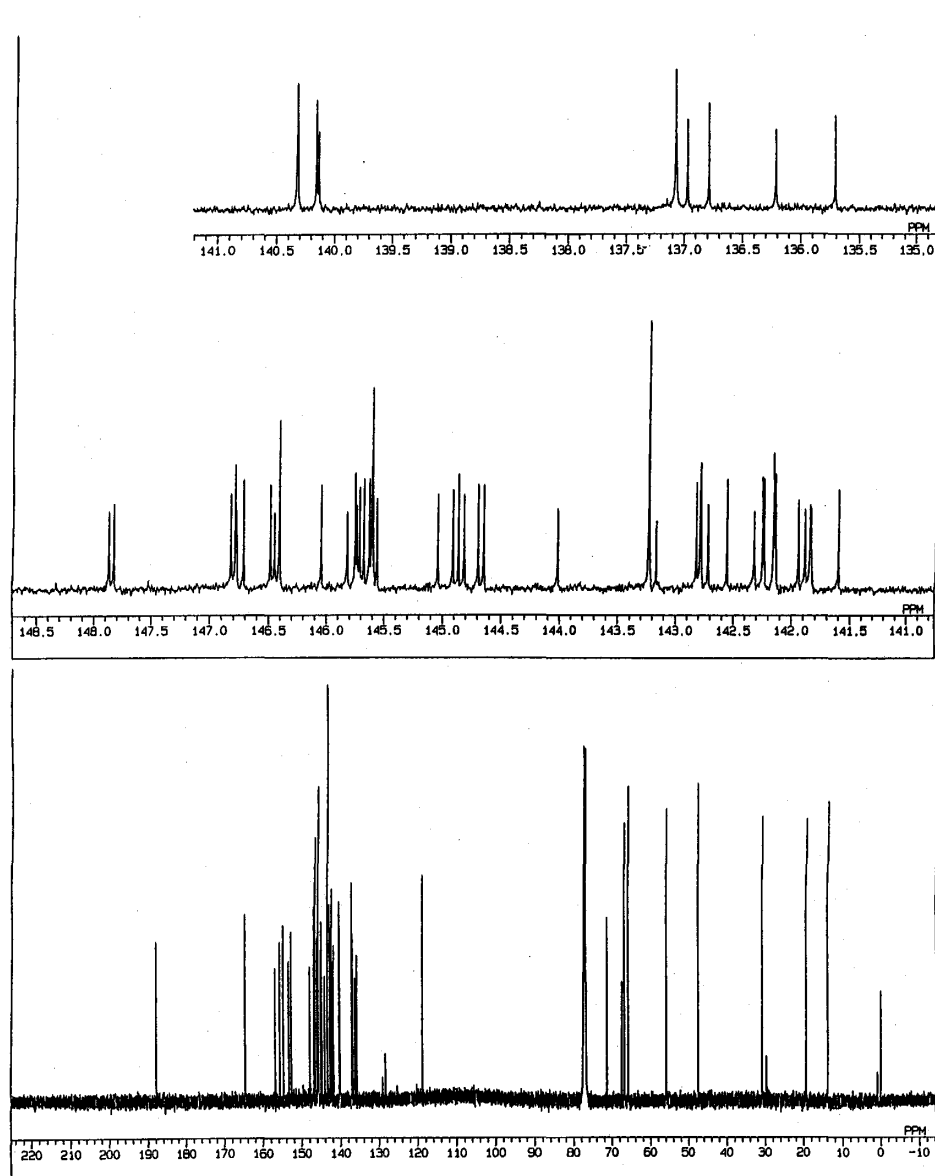
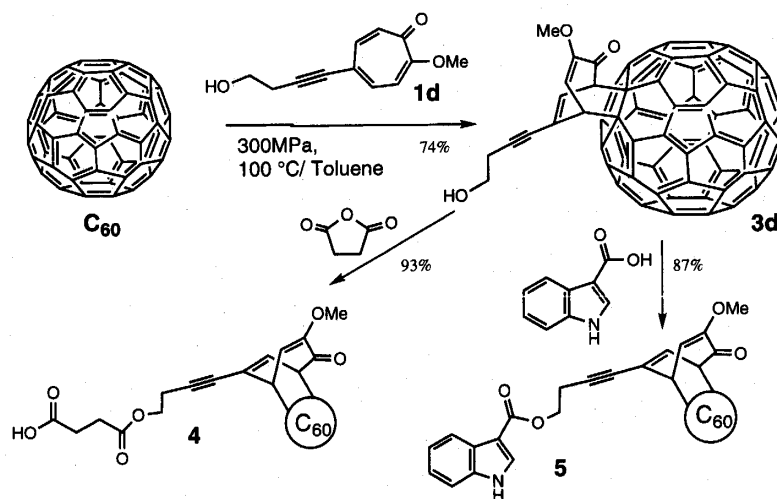


Figure 1.  $^{13}\text{C}$  NMR spectrum of **3c**



Scheme 3

## Experimental

**Preparation of Butyl 2-Methoxytropone-5-ylcarboxylate (1c).** A mixture of 2-methoxy-5-(trifluoromesyloxy) tropone (**2**, 100 mg, 0.35 mmol) and  $(\text{PPh}_3)_4\text{PdCl}_2$  (8 mg, 0.012 mmol) was dehydrated in vacuo. Then, to the mixture, CO and anhydrous BuOH (4 cm<sup>3</sup>) were introduced and stirred for 30 min at 0°C. The mixture was then treated with  $\text{Et}(\text{Me}_2\text{CH})_2\text{N}$  (45.6 mg, 0.35 mmol) at 60 °C for 23 h. The mixture was then poured into cold (0–5°C) 2M HCl and extracted with  $\text{CHCl}_3$ . After drying over  $\text{MgSO}_4$ , the organic layer was chromatographed on a silica-gel column to give **1c** [colorless crystals, mp 160 °C; 73%. Found:  $m/z$ , 368.0450 ( $\text{M}^+$ ). Calcd for  $\text{C}_{13}\text{H}_9\text{O}_2\text{F}_9$ :  $m/z$ , 368.0460 (M). <sup>1</sup>H NMR  $\delta$ =3.93 (3H, s), 4.02 (3H, s), 6.76 (1H, d,  $J$ =11 Hz), 7.23 (1H, d,  $J$ =13 Hz), 7.96 (1H, ddd,  $J$ =13, 2, 1 Hz), and 8.10 (1H, dd,  $J$ =11, 2 Hz)] which were used for the next step without purification.

**Preparation of 4-(2-methoxytropone-5-yl)-3-butyn-1-ol (1d).** A mixture of **2** (100mg, 0.35mmol),  $(\text{PPh}_3)_4\text{Pd}$  (5 mg, 0.0004 mmol), and CuI (3 mg, 0.016 mmol) was replaced by argon for 15 min. To this mixture was added was anhydrous benzene solution (10 cm<sup>3</sup>) of 3-butyn-1-ol (30 mg, 0.42 mmol) at room temperature and then  $\text{Et}_3\text{N}$  (80 mg, 0.58 mmol). The resultant mixture was stirred at room temperature for additional 6 h, poured into saturated aqueous  $\text{NaHCO}_3$ , and extracted with  $\text{CH}_2\text{Cl}_2$ . Flash chromatography of the organic layer afforded **1d** [yellow solid, 68 mg, 95%. Found:  $m/z$ , 368.0450 ( $\text{M}^+$ ). Calcd for  $\text{C}_{13}\text{H}_9\text{O}_2\text{F}_9$ :  $m/z$ , 368.0460 (M). <sup>1</sup>H NMR  $\delta$ =2.68 (2H, t,  $J$ =6.2 Hz), 3.83 (2H, t,  $J$ =6.2 Hz), 3.95 (3H, s), 6.64 (1H, d,  $J$ =10.6 Hz), 7.12 (1H, d,  $J$ =13.2 Hz), 7.24 (1H, dd,  $J$ =10.6, 1.1 Hz), and 7.27 (1H, d,  $J$ =13.2 Hz); <sup>13</sup>C NMR  $\delta$ =23.8, 56.4, 60.9, 83.7, 89.2, 111.9, 123.8, 135.8, 136.1, 139.3, 165.0, and 179.9; IR  $\nu$ : 2936, 2876, 1617, 1576, 1440, 1419, 1367, 1291, 1249, 1175, 1118, 1061, 1041, 980, 707, 656, 614, and 446 cm<sup>-1</sup>; MS  $m/z$ , 205 ( $\text{M}^+$ , 17.8), 173 (57.6), 155 (18.1), 145 (100), 130(6.8), and 115 (12.6)].

**Diels-Alder Reaction of C<sub>60</sub> with 1 (General Method).** A toluene solution (5 cm<sup>3</sup>) of C<sub>60</sub> (85%, 50 mg)<sup>7)</sup> and **1** (ca. 0.16 mmol) in a high-pressure furnace was heated at 100°C for 36 h. After cooling off the apparatus, the dark-colored mixture was chromatographed on a silica-gel column. Then, the fractions obtained from hexane-benzene (1: 1) was further purified with HPLC and recrystallized from benzene and CS<sub>2</sub> (1: 1) to give **3**. Each **3** showed a single spot on a thin-layer chromatogram.

**3a** [black powders, mp ca. 155°C (decomp), 80%. <sup>1</sup>H NMR  $\delta$ =3.86 (1H, d,  $J$ =7.0 Hz), 5.23 (1H, ddd,  $J$ =9.5, 7.3, 1.1 Hz), 5.25 ((2H, dd,  $J$ =7.7, 1.1 Hz), 5.90 (1H, d,  $J$ =7.0 Hz), 7.13 (1H, ddd,  $J$ =8.8, 7.7, 1.1 Hz), 7.45 (1H, ddd,  $J$ =8.8, 7.3, 1.1 Hz), 7.75 (2H, dd,  $J$ =7.0, 1.8 Hz), 7.79 (1H, d,  $J$ =9.5 Hz), and 8.23 (1H, dd,  $J$ =7.0, 1.8 Hz); IR  $\nu$ : 2920, 1658, 1639, 1603, 1519, 1428, 1345, 1185, 1032, 859, 751, and 527 cm<sup>-1</sup>; UV-vis  $\lambda$ max=405.4 nm ( $\epsilon$ =4920), 433.0 (3590), 458.2 (2630), 533.4 (1410), 606.1 (620), 632.3 (470), and 696.3 (280). M.W. Found:  $m/z$ , 978.0769 ( $[\text{M}+1]^+$ , 2.2), 720.0001 (100) (HR FAB-MS). Calcd for  $\text{C}_{74}\text{H}_{10}\text{O}_4\text{N}$ :  $\text{M}^+$ : 798.0766].

**3b** [black powders, mp ca. 155 °C(decomp), 77%. <sup>1</sup>H NMR  $\delta$ =5.37 (1H, ddd,  $J$ =9.2, 7.0, 1.1 Hz), 5.40 (2H, dd,  $J$ =7.7, 1.1 Hz), 7.25 (2H, ddd,  $J$ =9.5, 7.7, 1.1 Hz), 7.54 (1H, ddd,  $J$ =9.5, 7.0, 1.1 Hz), 8.13 (1H, d,  $J$ =9.2 Hz), 8.19 (2H, dd,  $J$ =7.2, 2.2 Hz), and 8.33 (1H, dd,  $J$ =7.2, 2.2 Hz); IR  $\nu$ : 2920, 1669, 1555, 1521, 1428, 1347, 1258, 1180, 752, 575, and 528 cm<sup>-1</sup>; UV-vis  $\lambda$ max=405.8 nm ( $\epsilon$ =5040), 432.6 (3600), 458.2 (2570), 533.4 (1420), 606.7 (610), 633.3 (460), and 696.0 (290). M.W. Found:  $m/z$ , 976.0602 ( $[\text{M}+1]^+$ , 2.0), 720.0001 (100) (HR FAB-MS). Calcd for  $\text{C}_{74}\text{H}_{10}\text{O}_4\text{N}$ :  $\text{M}^+$ : 796.0610].

**3c** [black powders, mp ca. 140 °C (decomp), 74%. <sup>1</sup>H NMR  $\delta$ =1.00 (3H, t,  $J$ =7.3 Hz), 1.50 (2H, sept,  $J$ =7.3 Hz), 1.75-1.86 (2H, tt,  $J$ =7.3, 6.6 Hz), 3.88 (3H, s), 4.40 (2H, t,  $J$ =6.6 Hz), 5.59 (1H, d,  $J$ =8.1 Hz), 5.81 (1H, dd,  $J$ =10.3, 1.5 Hz), 6.76 (1H, d,  $J$ =10.3 Hz), and

8.05 (1H, dd,  $J=8.1, 1.5$  Hz);  $^{13}\text{C}$  NMR  $\delta=13.79, 19.31, 30.76, 47.49, 55.89, 65.83, 66.84, 67.46, 71.25, 118.74, 135.71, 136.21, 136.79, 136.97, 137.07, 140.13, 140.15, 140.32$  (2C), 141.61, 141.84, 141.85, 141.89, 141.95, 142.14, 142.15, 142.16, 142.24, 142.25, 142.33, 142.56, 142.72, 142.79 (2C), 142.82, 143.23, 143.23 (2C), 144.02, 144.65, 144.70, 144.82, 144.87, 144.91, 145.02, 145.56, 145.60 (3C), 145.63, 145.68, 145.71, 145.74, 145.75, 145.82, 146.05, 146.41 (2C), 146.45, 146.48, 146.71, 146.77, 146.78, 146.82, 147.82, 147.87, 152.59, 153.23, 154.69, 155.61, 156.84, 164.53, and 187.78; IR  $\nu$ : 2952, 2924, 1713, 1686, 1650, 1622, 1460, 1428, 1377, 1238, 1150, 1096, 1061, 1003, 909, 821, 793, 729, 677, 553, and 526  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}=405.1$  nm ( $\epsilon=3890$ ), 432.3 (2740), 487.1 (1370), 541.1 (850), 607.0 (440), 633.6 (350), and 698.2 (300). M.W. Found:  $m/z, 957$  ( $[\text{M}+1]^+$ , 4.3), 720 (100) (FAB-MS)].

**3d** [black powders, mp ca. 140°C (decomp), 74%.  $^1\text{H}$  NMR  $\delta=2.80$  (2H, t,  $J=6.2$  Hz), 3.90 (2H, t,  $J=6.2$  Hz), 3.90 (3H, s), 5.12 (1H, dd,  $J=9.9, 1.5$  Hz), 5.41 (1H, d,  $J=8.1$  Hz), 6.74 (1H, d,  $J=9.9$  Hz), and 7.21 (1H, dt,  $J=8.1, 0.7$  Hz); IR  $\nu$ : 3480, 2922, 1680, 1624, 1461, 1428, 1374, 1241, 1182, 1151, 1051, 838, 829, 751, 672, 610, 576, 553, and 527  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}=405.8$  nm ( $\epsilon=5440$ ), 433.3 (3940), 460.8 (2750), 534.1 (1530), 607.7 (660), 633.9 (500), and 697.3 (320). Found:  $m/z, 925.0825$  ( $[\text{M}+1]^+$ ), 720.0002 (100) (HR FAB-MS). Calcd for  $\text{C}_{72}\text{H}_{13}\text{O}_3$ :  $\text{M}^+, 925.0865$ ].

**Reaction of Succinic Anhydride with 3d.** To a  $\text{CH}_2\text{Cl}_2$  solution of **3d** (6.5 mg, 0.007 mmol) was added succinic anhydride (5.5 mg, 0.055 mmol), DMAP (6.8 mg, 0.048 mmol) and pyridine (2 drops) at room temperature. The mixture was stirred under an  $\text{N}_2$  atmosphere for 24 h. The mixture was then heated in vacuo to remove the volatile material, and the residue was recrystallized from toluene and hexane to give **4** [brown powders, 6.5 mg, 93%. 74%.  $^1\text{H}$  NMR  $\delta=2.70$  (4H, m), 2.86 (2H, t,  $J=7.0$  Hz), 3.90 (3H, s), 4.35 (2H, t,  $J=7.0$  Hz), 5.12 (1H, dd,  $J=9.9, 1.5$  Hz), 5.40 (1H, d,  $J=7.7$  Hz), 6.76 (1H, d,  $J=9.9$  Hz), and 7.21 (1H, dt,  $J=7.7, 0.7$  Hz);  $^{13}\text{C}$  NMR  $\delta=20.42, 28.63, 29.03, 53.86, 55.88, 62.26, 66.30, 67.28, 70.96, 80.55, 92.46, 118.32, 124.10, 134.54, 135.88, 136.69, 136.72, 136.76, 140.09, 140.12, 140.18, 140.31, 141.55, 141.78, 141.83, 141.85, 141.90, 142.10, 142.17, 142.19, 142.23, 142.8, 142.32, 142.66, 142.69, 142.75, 142.77, 142.78, 143.20, 143.25, 144.11, 144.65, 144.66, 144.77, 144.78, 144.99, 145.08, 145.52, 145.59, 145.63, 145.65, 145.67$  (2C), 145.69, 145.70, 145.73, 145.78, 145.98, 146.38, 146.40, 146.46, 146.69, 146.71, 146.76, 146.78 (2C), 147.81, 147.82, 152.77, 154.65, 155.51, 152.24, 171.98, 188.52, and 189.68; IR  $\nu$ : 3460, 1730, 1681, 1647, 1404, 1260, 1155, 804, 753, 681, 575, and 52  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}=406.1$  nm ( $\epsilon=4770$ ), 433.3 (3500), 463.4 (2610), 534.4 (1520), 607.7 (780), 633.3 (650), and 696.0 (460). Found:  $m/z, 925.0825$  ( $[\text{M}+1]^+$ ), 720.0002 (100) (HR FAB-MS). Calcd for  $\text{C}_{72}\text{H}_{13}\text{O}_3$ :  $\text{M}^+, 925.0865$ ].

**Reaction of  $\beta$ -Indolecarboxylic Acid and 3d.** A mixture of **3d** (11 mg, 0.0119 mmol), DCC (2.5 mg, 0.0119 mmol), DMAP (0.3 mg) and  $\beta$ -indolecarboxylic Acid (1.4 mg, 0.012 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  and stirred for 24 h at room temperature. The mixture was then quenched with phosphate buffer (10  $\text{cm}^3$ ) and the organic layer was collected and dried over  $\text{MgSO}_4$ . Chromatography on a silica-gel column gave **5** [brown powders, 10 mg, 87%.  $^1\text{H}$  NMR  $\delta=3.02$  (2H, t,  $J=6.6$  Hz), 3.83 (3H, s), 4.61 (2H, t,  $J=6.6$  Hz), 5.05 (1H, dd,  $J=9.9, 1.5$  Hz), 5.38 (1H, d,  $J=7.7$  Hz), 6.63 (1H, d,  $J=10.3$  Hz), 7.13 (1H, ddd,  $J=8.1, 7.0, 1.1$  Hz), 7.19 (1H, dd,  $J=7.7, 1.5$  Hz), 7.27 (1H, d,  $J=1.1$  Hz), 7.31 (1H, dd,  $J=7.0, 1.1$  Hz), 7.36-7.41 (1H, m), 7.64 (1H, dd,  $J=8.1, 0.7$  Hz), and 8.91 (1H, br s)].

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  - 7) The sample was purchased from Kurita Co. Ltd., who provided the analytical figures, C<sub>60</sub>:C<sub>70</sub> = 80: 16.
  - 8) No appreciable reaction occurred under the atmospheric pressure.
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