Functional 2-benzyl-1,2-dihydro[60]fullerenes as acceptors for organic photovoltaics: facile synthesis and high photovoltaic performances

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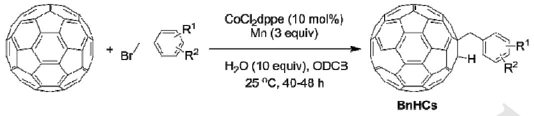

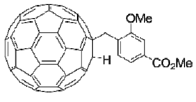

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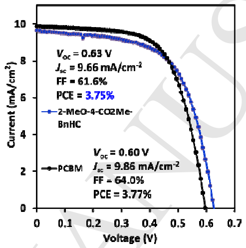

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Functional 2-benzyl-1,2-dihydro[60]fullerenes as acceptors for organic photovoltaics: facile synthesis and high photovoltaic performances

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ABSTRACT

A new series of functional 2-benzyl-1,2-dihydro[60]fullerenes, BnHCs, were synthesized efficiently via Co-catalyzed selective monofunctionalization of C_{60} with functional benzyl bromides. Photophysical and electrochemical properties of the new BnHCs were investigated. PSCs based on 2-MeO-4-CO_2Me-BnHC as new acceptor and P3HT as donor showed a power conversion efficiency of 3.75% which is comparable to that of PC_{61}BM under the same device conditions.

1. Introduction

Functional fullerenes are one of the most promising acceptors for the low band-gap polymer solar cells (PSCs) due to their high electron affinity and high electron mobility, and tunable solubility, energy level and packing structure.[1,2] Among them, PC_{61}BM ([6,6]-phenyl-C_{61}-butyric acid methyl ester) and its C_{70} analogue PC_{71}BM are the most representative acceptor materials which offer good solubility and high electron mobility.[3] In addition, most recently some new fullerene derivatives have been synthesized for PSC applications. For instance, bisfunctionalized 56 π-electron fullerenes such as bisPCBM, indene-C_{60} bisadduct, dihydronaphthyl-C_{60} bisadduct, di(4-methylphenyl)-methano-C_{60} bisadduct, 1,2-dihydromethano (CH_2)-modified PC_{61}BM, and thieno-*o*-quinodimethane-C_{60} bisadduct showed higher power conversion efficiencies (PCEs) for the PSCs based on P3HT (poly(3-hexylthiophene)) than that of PCBM.[4] To date, PCEs of 7-8% have already been reached for the PSCs based on the innovative low band-gap polymers as electron donors and PC_{61}BM or PC_{71}BM as an electron acceptor by optimization of the nanostructured morphology.[5] The design and efficient synthesis of new fullerene acceptors to replace PCBM are still needed to be compatible with the rapidly developed polymer donors for application in PSCs.

On the other hand, monofunctional fullerene derivatives have been paid less attention for PSCs application, while recently some advanced monofunctionalizations of fullerenes have been reported.[6] Recently, Lu and Tao *et al* synthesized new mono-fluorene-substituted hydrofullerene (C_{60}F) via Rh-catalyzed arylation.[7] However, even C_{60}F showed similar LUMO energy level to that of PC_{61}BM, it gave much lower PCE than that of

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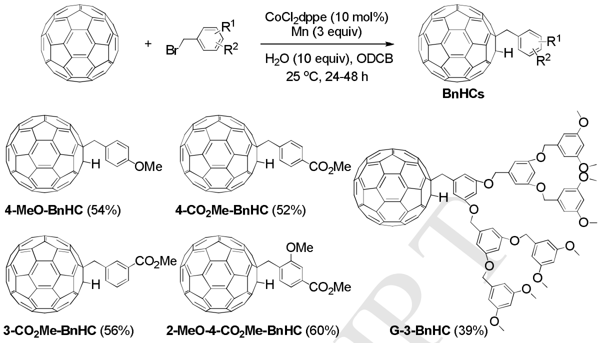
$PC_{61}BM$ when blended with PCDTBT (poly-(2,7-carbazole) derivative). Most recently, we reported an efficient Co-catalyzed monofunctionalization of C_{60} with active alkyl bromides.[6a] Various hydrofullerenes substituted with benzyl, allyl, and propargyl groups were obtained in good to high yields with high monoselectivity. Interestingly, during our study on electrochemical properties of these fullerene derivatives, we found that the LUMO level of 2-benzyl-1,2-dihydro[60]fullerene (BnHC) is almost similar to that of $PC_{61}BM$. This result led us to further design and synthesis of new BnHC derivatives for application in PSCs. Herein, we report the facile synthesis of a novel series of functional BnHCs, characterization of their photophysical and electrochemical properties, and evaluation of their PSC performances (Scheme 1). Functional BnHCs were synthesized efficiently through the Co-catalyzed monofunctionalization of C_{60} with commercially available benzyl bromide derivatives under mild reaction conditions. Among them, the PSC based on 2-MeO-4-CO_2Me-BnHC as acceptor showed a comparable PCE with the reference acceptor $PC_{61}BM$ under the same device conditions blending with P3HT as donor.

2. Results and discussion

BnHCs were prepared in one-step with good yields through our previously reported Co-catalyzed selective mono-benzylation of pristine C_{60} with functional benzyl bromides (Scheme 1).[8a] The reaction proceeds in the presence of $CoCl_2$dppe (dppe: diphenylphosphinoethane) catalyst and Mn reductant under argon atmosphere and neutral conditions at room temperature. The poor solubility BnHC prepared from benzyl bromide limits its application in solution-process solar cells. Several BnHC derivatives with various functional groups on phenyl ring were synthesized to improve their solubility as well as to investigate the influence of substituents on the energy levels and PSC performances. As shown in Scheme 1, a series of BnHCs such as 4-MeO-BnHC, 4-CO_2Me-BnHC, 3-CO_2Me-BnHC, and 2-MeO-4-CO_2Me-BnHC, were synthesized using 200-500 mg scale of C_{60} in 52-60% yields. In order to investigate the influence of solubility on morphology and performance in PSC device, the G3-dendrimer-substituted G3-BnHC was also prepared which has an excellent solubility in various organic solvents (>90mg/mL in *o*-dichlorobenzene (ODCB)). It is also worth noting that all the chemicals including C_{60}, functional benzyl bromides, and catalyst are commercially available. Although a very small amount of inseparable multiadducts was produced together with the recovered C_{60} (20-30%) in this large scale synthesis, the products were simply purified by silica gel chromatography using toluene and hexane as the eluents, especially for 4-CO_2Me-BnHC, 3-CO_2Me-BnHC, and 2-MeO-4-CO_2Me-BnHC due to the good polarity of methyl ester group, indicating its easy handling and low cost synthetic procedure. The functional BnHCs possess high solubility in chloroform, toluene, and ODCB comparable with that of $PC_{61}BM$.



Scheme 1. Co-catalyzed mono-functionalization of C_{60} for synthesis of BnHCs.

The UV-vis absorption spectra of the BnHCs and the reference $PC_{61}BM$ were measured in chloroform (Fig. 1). The absorption pattern of BnHCs in the 250-280 nm is not influenced by the varied functional groups on phenyl ring, and similar characteristic absorption as $PC_{61}BM$ are observed. BnHCs exhibit slightly enhanced absorption in the 280-330 nm region than that of $PC_{61}BM$, especially for 2-MeO-4-CO_2Me-BnHC. In the visible region from 400-500 nm, BnHCs show the same absorption spectra regardless of the varied functional groups, while they are stronger than that of $PC_{61}BM$ (Fig. 1, inset).

Table 1. Electrochemical reduction potentials[a] and LUMO energy levels[b] of BnHCs and $PC_{61}BM$.

compound	$E_{1/2}^1$/V	$E_{1/2}^2$/V	$E_{1/2}^3$/V	LUMO/eV
4-MeO-BnCH	-0.61	-1.01	-1.56	-3.55
4-CO_2Me-BnHC	-0.59	-0.98	-1.48	-3.57
3-CO_2Me-BnHC	-0.61	-0.98	-1.46	-3.55
2-MeO-4-CO_2Me-BnHC	-0.62	-1.01	-1.56	-3.54
G-3-BnHC	-0.60	-1.49	-1.49	-3.56
$PC_{61}BM$	-0.58	-0.98	-1.48	-3.58

[a] Potential values are versus Ag/AgCl reference electrode; reduction potential of ferrocene (0.64 V) is versus Ag/AgCl.

[b] The LUMO energy levels were estimated using the following equation: LUMO = $-(4.80+E_{1/2}^1-0.64)$ eV.

The LUMO energy levels of BnHCs and $PC_{61}BM$ were evaluated by the first reduction potentials measured by cyclic voltammetry (CV) (Fig. 1b and Table 1). BnHCs exhibit three pseudo-reversible reduction waves in the same manner as that of

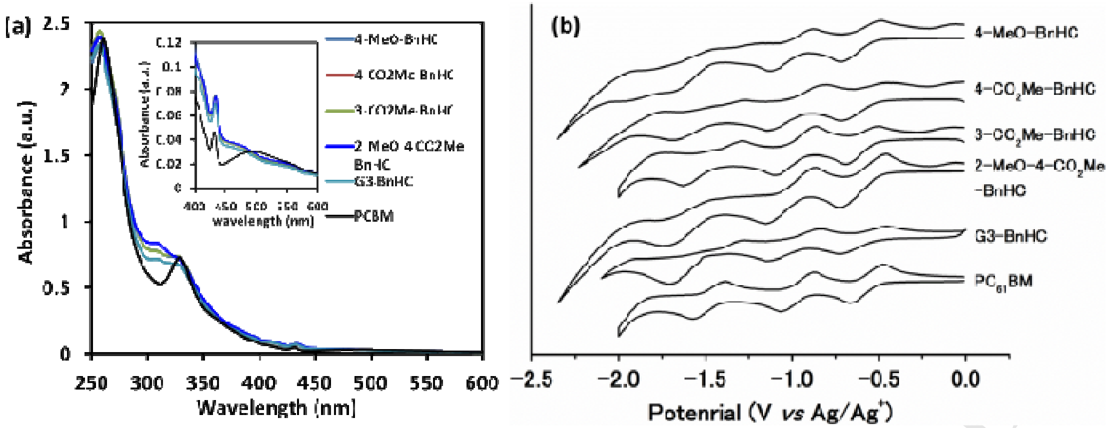


Figure 1. Photophysical and electrochemical properties of BnHCs and PC$_{61}$BM, (a) UV-vis absorption in chloroform, (b) cyclic voltammograms in ODCB solution with Bu_4NBF_4 as a supporting electrolyte (vs Ag/Ag$^+$).

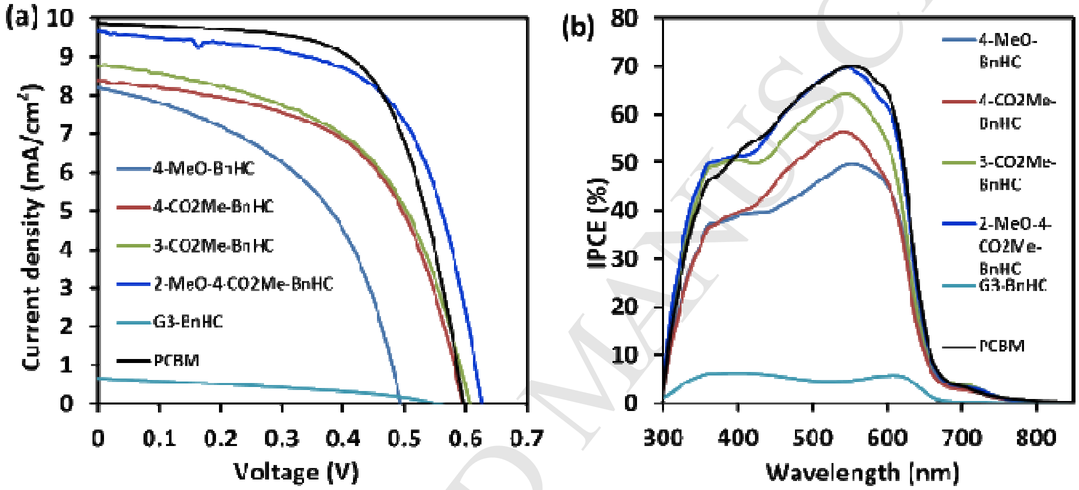


Figure 2. (a) Current density-voltage curves and (b) incident photon-to-current conversion efficiency.

PC$_{61}$BM. As aforementioned, BnHC without functional groups on phenyl ring shows a negative shift of the first reduction potential ($E_{1/2}^1$, -0.59 V) by 10 mV compared to PC$_{61}$BM. The BnHCs having an electron-donating or/and an electron-withdrawing group on phenyl ring, such as 4-MeO-BnHC, 4-CO$_2$Me-BnHC, 3-CO$_2$Me-BnHC, 2-MeO-4-CO$_2$Me-BnHC, and G-3-BnHC show a similar or slightly negative shifted $E_{1/2}^1$ than PC$_{61}$BM. The relatively higher LUMO energy levels of BnHCs are attributed to the presence of two sp^3 carbons between the aryl group and the C$_{60}$ cage that block the conjugation channel between both units. Since the open-circuit voltage (V_{oc}) of PSCs has an association with the energy difference between the LUMO of acceptor and the HOMO of donor,[8] it is expected that these soluble new BnHCs should be applicable as acceptors in PSCs.

PSCs based on new BnHCs as acceptors and the representative polymer P3HT as donor with thickness of about 200 nm were fabricated and characterized. The photovoltaic parameters for ITO/PEDOT:PSS(40 nm)/P3HT:BnHCs(w/w = 1/1)/LiF (1 nm)/Al (80 nm) under illumination with 100 mW cm^{-2} of AM 1.5 are summarized in Table 2. For comparison, the reference PSC device based on P3HT/PC$_{61}$BM was also fabricated. Fig. 2a shows the *J-V* curves and Fig. 2b shows the incident photon-to-current conversion efficiency (IPCE) spectra of the PSCs. Among the new BnHCs based devices, the 2-MeO-4-CO$_2$Me-BnHC device displays the highest PCE of 3.75%, which is comparable to that of the reference PC$_{61}$BM, 3.78%. It can be seen that, although the slightly lower J_{sc} and FF were obtained for 2-MeO-4-CO$_2$Me-BnHC device than that of the PC$_{61}$BM device, the V_{oc} value of 0.63 V is higher. The PCEs for other BnHCs with monofunctional group on phenyl ring such as 4-MeO-BnHC, 4-CO$_2$Me-BnHC, and 3-CO$_2$Me-BnHC are 2.39, 2.80, and 2.84%, respectively, which are lower than that of 2-MeO-4-CO$_2$Me-BnHC. Comparing with the PC$_{61}$BM device, the small increased LUMOs of BnHCs did not show significantly improved V_{oc}, and the lower J_{sc} and FF result in the lower or similar PCEs. In sharp contrast, although the PSC based on the bulky dendrimer-incorporated acceptor G3-BnHC showed a moderate V_{oc} value of 0.56 V, the J_{sc} and FF are much lower than that of other BnHCs devices, probably the bulky G3 dendrimer functional group inhibits the stacking of C$_{60}$ cages and hence decreases the electron transfer. The higher IPCE values of both 2-MeO-4-CO$_2$Me-BnHC and PC$_{61}$BM devices in the region from 350 to 650 nm than other BnHCs devices contribute to their higher J_{sc} values, suggesting their rather efficient photon-to-electron conversion processes.

Table 2. PSC performances based on P3HT and BnHCs acceptors (w/w = 1/1)[a]

acceptor	V_{oc} [V]	J_{sc} [mAcm^{-2}]	FF [%]	PCE [%]
4-MeO-BnCH	0.60	8.24	48.4	2.39
4-CO$_2$Me-BnHC	0.60	8.38	55.7	2.80
3-CO$_2$Me-BnHC	0.61	8.76	53.2	2.84

2-MeO-4-CO_2Me-BnHC	0.63	9.66	61.6	3.75
G-3-BnHC	0.56	0.66	36.6	0.13
$PC_{61}BM$	0.60	9.86	64.0	3.78

[a] Blend film was prepared using P3HT (20 mg) and BnHCs (20 mg) in 1,2-dichlorobenzene (1 mL); annealing temperature is 110 °C (10 min).

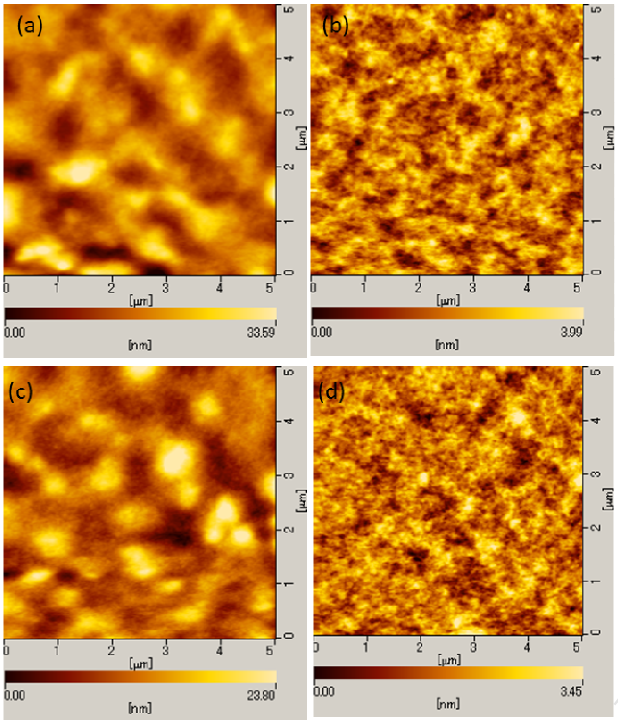


Figure 3. AFM images of P3HT donor with different BnHCs, (a) 4-MeO-BnHC, (b) 4-CO_2Me-BnHC, (c) 3-CO_2Me-BnHC, and (d) 2-MeO-4-CO_2Me-BnHC.

The surface morphologies of the BnHCs/P3HT active layer images observed by atomic force microscopy (AFM) show that, the surfaces of the active layers are homogeneous and display nanoscale phase separation (Figure 3). The root mean squares (RMS) were 5.25 nm for 4-MeO-BnHC, 0.63 nm for 4-CO_2Me-BnHC, 3.99 nm for 3-CO_2Me-BnHC, and 0.54 nm for 2-MeO-4-CO_2Me-BnHC, respectively, when blended with P3HT donor. Although the reason is not clear that PSCs based on 4-CO_2Me-BnHC and 3-CO_2Me-BnHC showed the similar performances despite their large difference roughness, it should be noted that 4-CO_2Me-BnHC has a lower solubility than 3-CO_2Me-BnHC in ODCB and chloroform. The RMSs indicate that the changing of functional groups on benzyl moiety influences the roughness of blend films. Moreover, the smoother surface based on 2-MeO-4-CO_2Me-BnHC/P3HT blend shows the highest photovoltaic performance among the BnHCs films, implying that the better interfacial contact of polymer donor and fullerene acceptor blend is a key on the improvement of the PSC performances. The morphology comprising of the dendrimer-bound G3-BnHC displays the largest RMS of 21.7 nm (Figure S2e), resulting in the lowest PCE due to the much lower J_{sc}.

3. Conclusion

In conclusion, we have efficiently synthesized a series of soluble electron acceptors BnHCs via Co-catalyzed highly selective mono-functionalization of C_{60} with commercially available functional benzyl bromides in one-step. Among the BnHCs, PSC based on 2-MeO-4-CO_2Me-BnHC as acceptor and P3HT as donor showed the highest PCE of 3.75% which is comparable to that of the reference acceptor $PC_{61}BM$. The high PCE is attributed to the improved nanoscale morphology of blend film rather than the slightly increased LUMO level. Considering the facile and low-cost synthetic method together with the high PSC performance, the new 2-MeO-4-CO_2Me-BnHC should be a promising candidate for employing as an electron acceptor in the PSC devices. Further investigations on molecular engineering of BnHC series, morphology optimization, and blending with other polymers to increase the PSC performances are in progress.

4. Experimental section

4.1. General information

^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL JMTC-270/54/SS (JASTEC, 400 MHz) spectrometers. ^{1}H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). ^{13}C NMR spectra reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. High-resolution mass spectra were obtained on a BRUKER APEXIII spectrometer. Preparative recycling HPLC was used a LC-2000 Plus instrument equipped with a Buckyprep column (4.6 mm x 250 mm, nakarai Tesque). HPLC analysis performed using toluene as an elution at 0.6 ml/min flow rate, detection at 320 nm in 4 °C or 18 °C. Column chromatography was carried out employing Silica gel 60 N (spherical, neutral, 40~100 μm, KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F_{254} (Merk). The thicknesses of the blend films and PEDOT:PSS layers were measured using an automatic micro figure measuring instrument (Surfcorder ET200, Kosaka Laboratory Ltd.). The current density–voltage (*J–V*) curves were measured using an ADCMT 6244 DC Voltage Current Source/Monitor under AM 1.5 solar-simulated light irradiation of 100 mW/cm^2 (OTENTO-SUN III, Bunkoh-Keiki Co.). IPCE was measured using a CEP-2000 system (Bunkoh-Keiki Co., Ltd.).

4.2. Materials

Anhydrous 1,2-dichlorobenzene (Aldrich), toluene, carbon disulfide, hexane, (WAKO), $CoCl_2$, Mn (Aldrich), methyl 4-(bromomethyl)-3-methoxybenzoate (TCL), single benzylic bromide group at the focal point of the third-generation dendrimer [G-3]-Br (Aldrich), [60]fullerene (Aldrich), regioregular poly(3-hexylthiophene) (P3HT, Luminescence Technology Corp.), PC61BM (Solenne), PEDOT:PSS (CLEVIOS P VP Al 4083, H. C. Starck) were purchased and used as received. The structures of BnHCs were determined by using ^{1}H NMR, ^{13}C NMR, high resolution mass (HRMS).

4.3. Fabrication of PSC device and characterization

The PSC device was fabricated in the configuration ITO/PEDOT:PSS/active layer/LiF/Al. The patterned ITO (conductivity: 10Ω/square) glass was precleaned in an ultrasonic bath of acetone and ethanol, and then treated in an ultraviolet-ozone chamber. A thin layer (40 nm) of PEDOT:PSS was spin coated on the ITO at 3000 rpm and subsequently dried at 110°C for 10 min on a hot plate under air. The substrate was transferred to an N_2 glovebox and then dried again at 110°C for 10 min on a hot plate. An ODCB solution of P3HT:PCBM (1:1, weight ratio, 210-260 nm) blend was subsequently spin coated onto the PEDOT:PSS surface, forming an active layer. The thicknesses of the blend films and PEDOT:PSS layers were measured using an automatic micro figure measuring instrument (Surfcorder ET200, Kosaka Laboratory Ltd.). The substrate with the active layer was dried at 110°C for 10 min in the N_2 glovebox. Finally, LiF (1 nm) and Al (80 nm) were deposited onto the active layer by means of conventional thermal evaporation at a chamber pressure lower than 5×10^{-4} Pa, which provided the devices with an active area of 2×2 mm^2. The current density–voltage (J–V) curves were measured using an ADCMT 6244 DC Voltage Current Source/Monitor under AM 1.5 solar-simulated light irradiation of 100 mW/cm^2 (OTENTO-SUN III, Bunkoh-Keiki Co.). IPCE was measured using a CEP-2000 system (Bunkoh-Keiki Co., Ltd.).

4.4. General procedure of Co-catalyzed hydroalkylation of C_{60} and benzyl bromides

A suspension of $CoCl_2$dppe (36.7 mg, 0.069 mmol), Mn (114 mg, 2.07 mmol), C_{60} (500 mg, 0.69 mmol), methyl 4-(bromomethyl)-3-methoxybenzoate (536 mg, 2.07 mmol), and H_2O (124 μL, 6.9 mmol) in ODCB (1,2-dichlorobenzene) (90 mL) was stirred for 48 h under Ar atmosphere at 25 ^{o}C. The reaction mixture was monitored by TLC and HPLC analysis (elution with toluene at 0.6 mL/min flow rate, detection at 320 nm). The mixture was filtered through a short florisil pad using ODCB as an eluent. After concentration, the residue was purified through silica gel chromatography using toluene as an eluent. After evaporation of toluene, the residue was washed with acetone and dried under vacuo, affording 2-MeO-4-CO_2Me-BnHC in 60% yield (373 mg).

4.5. Analytic data of 2-MeO-4-CO_2Me-BnHC

Dark brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ = 1/4) δ 3.94 (3H, s), 3.99 (3H, s),4.87 (2H, s), 6.69 (1H, s), 7.69 (1H, s), 7.76 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$ = 1/4) δ 46.43, 51.66, 55.09, 59.26, 65.24, 111.75, 121.94, 129.44, 130.82, 132.53, 135.06, 136.01, 139.46, 139.83, 141.16, 141.26, 141.48, 141.60, 141.63, 141.78, 142.18, 142.87, 144.18, 144.28, 144.93, 144.96, 145.07, 145.40, 145.68, 145.76, 145.80, 145.94, 146.00, 146.55, 146.87, 147.04, 153.33, 154.92, 157.55, 165.46; HRMS (ESI) calcd for $C_{70}H_{12}O_3Na$ $[M+Na]^+$: 923.06787, found 923.06789.

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