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# Retrocyclopropanation Reactions of Fullerenes: Complete Product Analyses

M. Ángeles Herranz, Charles T. Cox, Jr., and Luis Echegoyen*

*Department of Chemistry, Clemson University, Clemson, South Carolina 29634*

*luis@clemson.edu*

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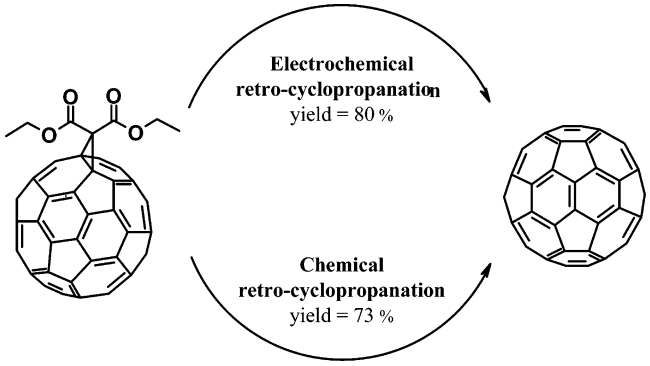
**Abstract:** Mono- and bis-pyrene malonates **1** and **2** were synthesized and reacted with $C_{60}$ to prepare the corresponding Bingel adducts **3** and **4**. These compounds were characterized electrochemically and exhibited the well-established retrocyclopropanation reaction when subjected to bulk electrolytic reductions. For the first time, it was possible to perform detailed product analyses after the retrocyclopropanation reactions, and these showed the presence of the original malonates **1** and **2** along with $C_{60}$, in reasonable yields, around 50%.

Of the various methods used to derivatize $C_{60}$ such as the Diels−Alder reaction,[1,2] diazocompound additions,[3] and azomethine ylide dipolar cycloadditions,[4] the Bingel reaction is one of the most commonly employed.[5] This reaction proceeds by addition of a stable α-halocarbanion to $C_{60}$ or directly from malonates in the presence of $I_2$[6] or $CBr_4$[7] and a base, resulting in the formation of a cyclopropane ring fused to the fullerene core at a [6,6]-junction. These cyclopropane rings are usually very stable,[8,9] although some exceptions have been reported.[10,11]

Under reductive conditions, the easy and efficient removal of the cyclopropane addends can occur either electrochemically[12−17] or chemically (see Scheme 1).[18,19]

**SCHEME 1. Retrocyclopropanation Reaction on $C_{60}$**




The initial finding was observed during electrolysis at the second reduction potential of diethyl 1,2-methano-[60]fullerene-61,61-dicarboxylate, where four electrons/molecule were transferred and pure $C_{60}$ was recovered in over 80% yield.[12] After this discovery, the electrochemical retrocyclopropanation reaction was applied to a large number of Bingel derivatives of $C_{60}$, $C_{70}$, $C_{76}$, $C_{78}$, and $C_{84}$.[12−15,20−22] Additional applications of the retrocyclopropanation reaction, acting in concert with the isomerization reaction, were also recently published.[20,22] Other methanofullerenes not of the Bingel-type were also found to be unstable after several reduction processes,[23−26] and under controlled potential electrolysis (CPE), they led to the isolation of [60]fullerene. For some of these monoadducts, electroreduction in THF provided regioisomeric bis-adducts with an isomeric distribution different from that obtained via the synthetic route.[24,25]

With the objective of understanding the mechanism that governs these processes, we have used digital simulations of the cyclic voltammetric results of some of these methanofullerenes,[27] and we have also recently proven how singly bonded dimers are formed as intermediates during retrocyclopronation reactions.[28] However, to date, no full product characterization has been

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**SCHEME 2. Synthesis of the Bingel Derivatives 3 and 4**

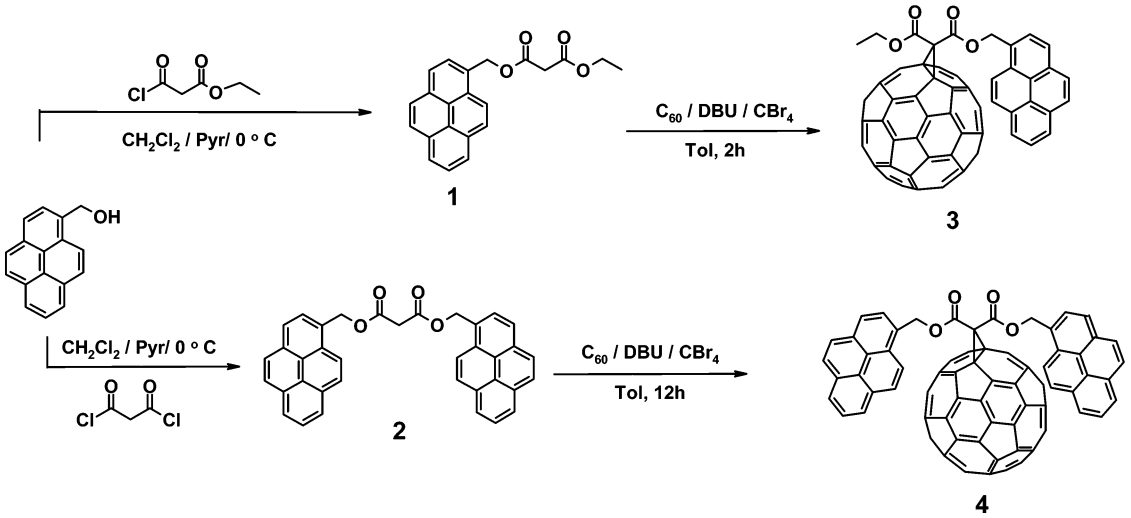


**TABLE 1. Redox Potentials of Methanofullerenes 3 and 4 vs Ferrocene in $CH_2Cl_2$ (mV)**

| compd | $E_1^{1/2}$ | $E_2^{1/2}$ | $E_3$[a] | $E_4$[a] |
|---|---|---|---|---|
| **3** | −1028 | −1402 | −1930 | |
| **4** | −1039 | −1384 | −1823 | −2080 |

[a] Electrochemically irreversible reductions, $E_{pc}$.

reported. While the $C_{60}$ resulting from retrocyclopropanation reactions is easily identified and purified from the reaction mixtures, no other products have been characterized so far, and the fate of the malonate group is currently not known, despite repeated attempts to isolate it. To improve the ability to track the fate of the organic addend in these reactions, fluorescent pyrene malonates were prepared in the present work and their electrochemical retrocyclopropanation reactions and corresponding product analyses were performed and are reported here.

Methanofullerenes **3** and **4** were prepared using a synthetic procedure that involves two steps, starting with commercially available 1-pyrenemethanol. The reaction sequences are presented in Scheme 2. We carried out the esterification reaction of 1-pyrenemethanol with 1 or 2 equiv of ethoxycarbonyl acetic acid chloride or malonic acid dichloride to form **1** or **2**, respectively, in $CH_2Cl_2$ at 0 °C under an argon atmosphere and in the presence of pyridine. The corresponding compounds **1** and **2** were formed in 30% yield, in agreement with the results for analogues obtained by similar methodologies for the formation of ((1-pyrenylmethoxy)carbonyl)alkanes.[29] Compounds **1** and **2** were isolated as pale yellow solids that were purified by column chromatography. All the compounds were characterized by analytical and spectroscopic methods (UV−vis, FTIR, $^1$H and $^{13}$C NMR, and MS) (see Experimental Section).

The Bingel derivatives **3** and **4** were prepared from the corresponding malonates by direct reaction with $C_{60}$ and $CBr_4$/DBU in toluene. They were purified by column chromatography, using carbon disulfide first to remove the unreacted $C_{60}$ and then toluene/chloroform 1/1 to isolate **3** (35% yield) and **4** (22% yield) as brown solids. Further purification of the compounds was carried out by repetitive centrifugation with hexane and methanol.

Compounds **3** and **4** show the characteristic absorption at 426 nm of [6,6]closed methanofullerenes. The $^{13}$C NMR spectra showed the presence of the fullerene $sp^3$ carbons at $\delta$ 71.44 and 68.09 for **3** and at $\delta$ 71.32 for **4** as well as the bridgehead carbon atom of the cyclopropane rings as a single signal at ∼52 ppm. Furthermore, the structures were confirmed by $^1$H NMR, FTIR, and mass spectrometry.

The electrochemistry of **3** and **4** was studied in $CH_2Cl_2$ as solvent. Potentials vs ferrocene are reported in Table 1, and the cyclic voltammograms (CVs) are presented in Figure 1. Methanofullerenes **3** and **4** exhibit

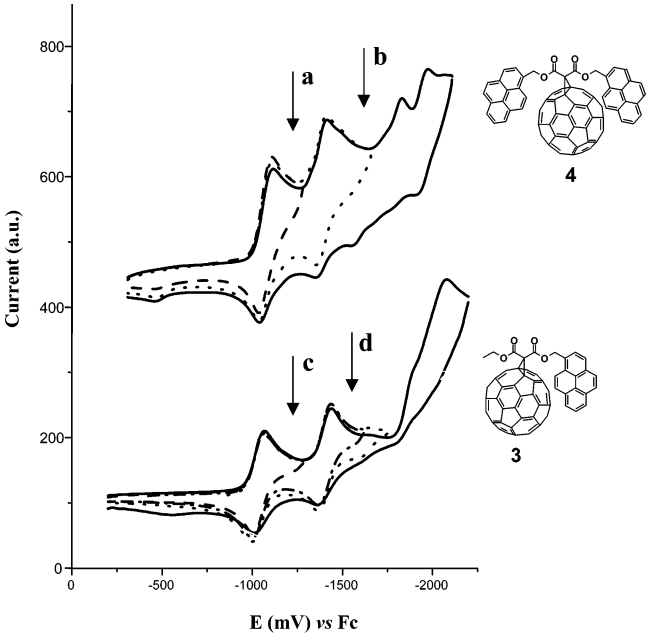


**FIGURE 1.** Cyclic voltammograms of the methanofullerenes **3** and **4** in dichloromethane.

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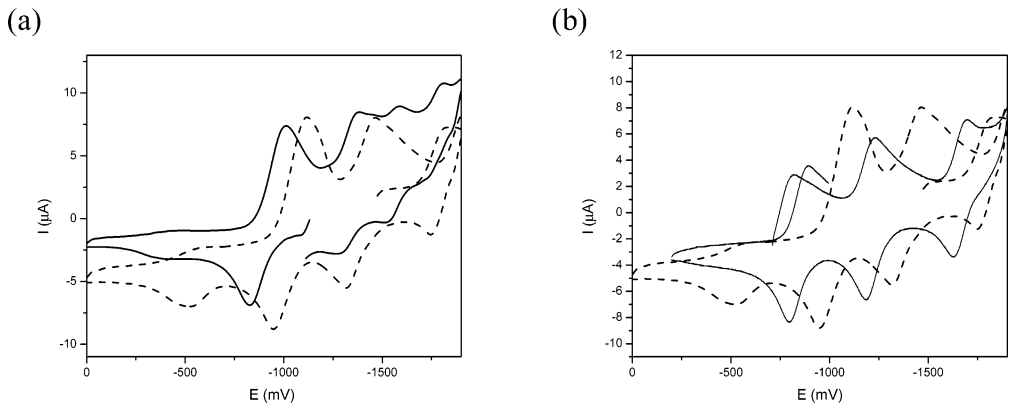


**FIGURE 2.** Reductive electrochemistry data for **4**. (a) (Solid line) cyclic voltammogram after 1e reduction; (dashed line) cyclic voltammogram after 2.2 e reduction. (b) (Dashed line) cyclic voltamogram after 2.2 e reduction; (solid line) cyclic voltammogram after reoxidation.

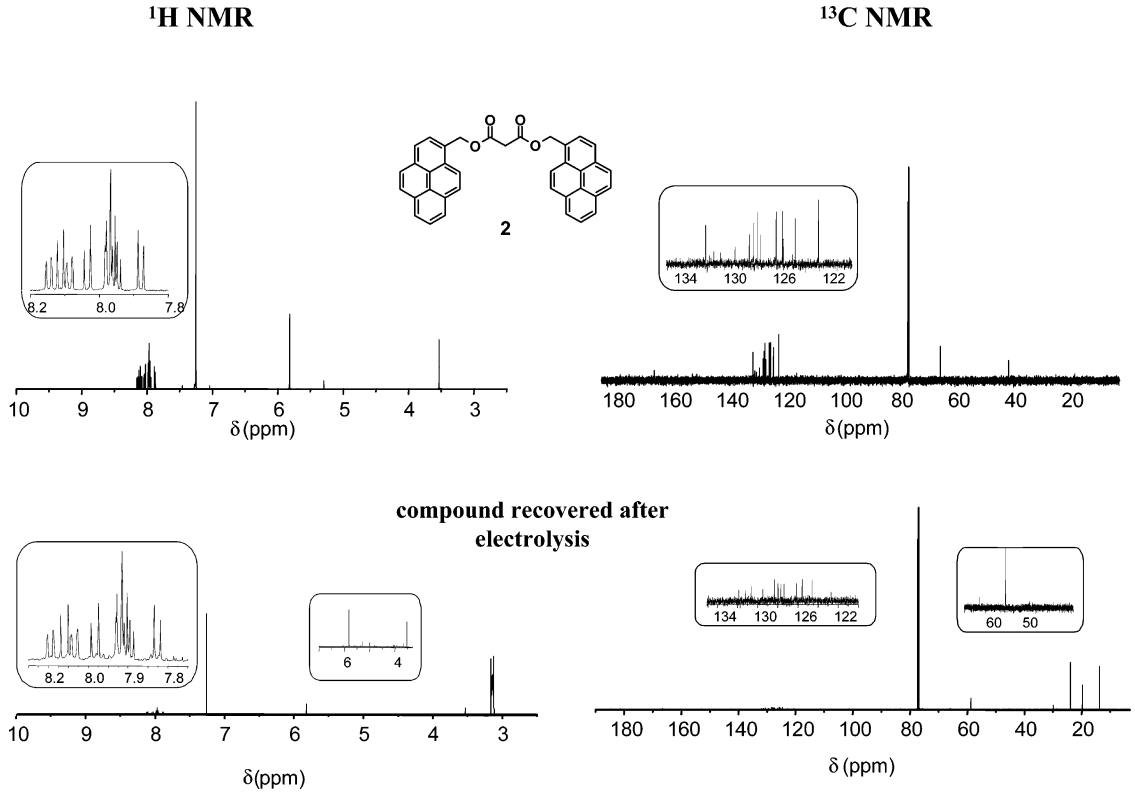


**FIGURE 3.** Comparative $^1$H NMR of **2** and the product obtained after purification of the solution resulting from bulk electrolysis of **4**.

similar electrochemical behavior, with two quasireversible fullerene-based reductions.[30] The third reduction is chemically irreversible, presumably due to the cleavage of one of the cyclopropane bonds connecting the addend to the $C_{60}$.

CPE under high vacuum conditions was performed after each reduction step at a potential 100 mV more cathodic than the corresponding reduction peak potential, at the positions pointed to by the arrows in Figure 1 for **3** and **4**. CPE after the first reduction step confirmed that 1e/methanofullerene was transferred (see Figure 2 for **4**). Reoxidation and purification of the products at this point showed mainly the recovery of the starting material, along with a small percent of $C_{60}$ (<5%).

CPE of **3** and **4** performed after the second reduction wave (arrows b and d in Figure 1) cause important voltammetric changes (see Figure 2 for **4**). After approximately 2.2e/molecule were transferred, the CV shows the appearance of a new redox couple approximately 500 mV more positive than the first fullerene-based reduction. We have recently shown that this intermediate is a singly bonded dimer formed by coupling between two $C_{60}$ adduct radical anions.[28] After oxidation at this stage, the cyclic voltammogram depicted in Figure 2b (solid line) is obtained, which corresponds to that of

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$C_{60}$. Careful chromatographic purification and analysis of the products yields approximately 48% of $C_{60}$, traces of a compound with close polarity to that of $C_{60}$ that is fluorescent, and 50% of another highly fluorescent product. The structure of the products was established spectroscopically.

A comparison between the NMR of malonate **2** and the main fluorescent product obtained after electrolysis of **4** is shown in Figure 3. The $^1$H and $^{13}$C NMR spectra are practically identical except for the intensity difference due to the small amount available from the electrolytic process. This definitively establishes that the product corresponds to **2**. MALDI-TOF spectrometry and UV−vis spectroscopy provided additional support, showing indistinguishable spectra for the electrolysis product and **2**.

In summary, we have prepared two pyrene-based methanofullerenes using the Bingel cyclopropanation reaction. Their electrochemical properties were studied by CV and CPE, and the retrocyclopropanation reaction was observed after the addition of approximately 2e/ starting fullerene molecule. A stable intermediate was observed that, on the basis of similar recent observations with other methanofullerenes, probably corresponds to a singly bonded dimeric structure between the fullerene cores.[28] For the first time, product analyses after electrolysis show the presence of the malonate addends along with $C_{60}$.

## Experimental Section

Electrochemical measurements were performed using an electrochemical cell designed to carry out CV and bulk electrolysis under high vacuum.[31] A 2−8 mg sample of fullerene methanoadducts **3** or **4** was used for each experiment, and 600 mg of the supporting electrolyte, $TBAPF_6$, were added into the electrolysis cell. The cell was degassed and pumped to $10^{-6}$ Torr. The solvent, methylene dichloride, which had also been degassed and pumped to the same pressure in the presence of calcium hydride, was then vapor-transferred into the cell. Prior to CPE, cyclic voltammetry was performed using a glassy carbon electrode to obtain the reduction potential versus a Ag wire pseudoreference electrode. The latter was separated from the bulk solution using a Vycor tip. CPE at 293 K was performed on a Pt mesh (100 mesh, 6.5 cm$^2$) working electrode. After reductive electrolysis, the solution was reoxidized at 0 V. The product mixture was then passed through a short column of $SiO_2$ and eluted first with carbon disulfide to remove $C_{60}$ and then with chloroform to elute the malonates. TLC, $^1$H and $^{13}$C NMR, UV−vis, and MALDI-TOF mass spectrometry were used to characterize the products.

**Syntheses of Malonates.** A solution of 1-pyrene methanol (1 g, 4.30 mmol) in methylene dichloride (100 mL) was prepared under an argon atmosphere. Pyridine (0.347 mL, 4.30 mmol) was then added to the solution dropwise and cooled in an ice bath as ethoxycarbonyl acetic acid chloride (0.551, 4.30 mmol) for **1** or malonic acid dichloride (0.245 mL, 4.30 mmol) for **4** was added dropwise over a 10 min period. The ice bath was removed after the solution was stirred for a 2 h period. The mixture was then stirred overnight at room temperature. Water was added and the residue extracted with $CH_2Cl_2$. The combined extracts were dried ($Na_2SO_4$) and filtered, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using hexane/ethyl acetate mixtures as eluent.

**Malonic Acid Ethyl Ester Pyren-1-yl Methyl Ester (1).** Yield: 27%. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 8.19−7.96 (9H, m), 5.83 (2H, s), 4.06 (2H, q, $J$ = 6.85 Hz), 3.37 (2H, s), 1.10 (3H, t, $J$ = 6.85 Hz). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 166.74, 166.65, 132.00, 131.27, 130.76, 128.41, 128.06, 128.00, 127.43, 126.22, 125.70, 125.62, 124.95, 124.70, 122.92, 65.87, 61.69, 41.77, 14.03. FTIR (PE): 1728, 1597, 1481, 1450, 1412, 1373, 1327, 1265, 1188, 1134, 1103 cm$^{-1}$. UV−vis ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$): 344 (4.40), 328 (4.40), 312 (4.12), 276 (4.58), 266 (4.22), 242 (5.52), 230 (5.30) nm. MS (EI), $m/z$: 346 ($M^+$).

**Malonic Acid Dipyren-1-yl Methyl Ester (2).** Yield: 29%. Mp: 178−180 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 8.16−7.93 (16H, m), 7.87 (2H, d, $J$ = 7.76 Hz), 5.82 (4H, s), 3.55 (2H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 166.36, 131.70, 131.06, 131.54, 129.69, 128.15, 127.49, 127.22, 125.96, 125.44, 125.30, 125.09, 124.44, 122.55, 65.73, 41.77. FTIR (PE) 1728, 1597, 1496, 1458, 1419, 1380, 1342, 1196, 1219, 1110 cm$^{-1}$. UV−vis ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$): 375 (3.38), 345 (4.86), 329 (4.72), 315 (4.36), 302 (3.98), 277 (4.88), 267 (4.67) nm. MS (EI) $m/z$: 532 ($M^+$); calcd exact mass (HR-EI) 532.1674, found 532.1681.

**Synthesis of Methanofullerenes.** A solution of $C_{60}$ (50 mg, 0.069 mmol) was prepared in toluene (50 mL) under an argon atmosphere. The corresponding malonate **1** or **2** (0.090 mmol), $CBr_4$ (30 mg, 0.090 mmol), and diazabicylo[4.2.0]undec-7-ene (DBU) (0.17 mL, 1.13 mmol) were then added in order. The DBU was added slowly over several minutes. The reaction was monitored using TLC ($SiO_2$/$CHCl_3$) and was allowed to react for two or 12 h in the case of **1** or **2**, respectively. Purification was achieved using column chromatography with silica as the stationary phase. Carbon disulfide was used to elute unreacted $C_{60}$, and then the product was eluted using $CHCl_3$. Further purification was accomplished by centrifugation using hexane and methanol.

**61-(Ethoxycarbonyl)-61-(pyren-1-yl methyloxycarbonyl)-1,2-methano[60]fullerene (3).** Yield: 35% (48% based on recovered $C_{60}$). Mp: >300 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 8.38 (2H, d, $J$ = 9.15 Hz), 8.19−7.89 (7H, m), 6.20 (2H, s), 4.31 (2H, q, $J$ = 7.30 Hz), 1.16 (3H, t, $J$ = 7.30 Hz). $^{13}$C NMR ($CDCl_3$, 500 MHz): $\delta$ 163.63, 163.61, 145.22, 142.12, 145.10, 145.05, 145.03, 144.79, 144.65, 144.60, 144.59, 144.16, 144.08, 143.85, 143.61, 143.02, 142.90, 142.88, 142.85, 142.71, 142.15, 142.13, 141.79, 141.43, 140.84, 140.59, 139.69, 137.96, 132.50, 131.23, 130.78, 130.29, 129.32, 128.64, 128.31, 127.78, 127.41, 126.33, 125.84, 125.74, 125.07, 124.76, 124.67123.29, 71.44, 68.09, 67.63, 63.57, 52.05, 14.06. FTIR (PE): 1743, 1596, 1465, 1365, 1319, 1226, 1203, 532 cm$^{-1}$. UV−vis ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$): 426 (3.65), 346 (4.72), 330 (4.77), 277 (4.99) nm. MS (FAB$^+$) $m/z$: 1065 ($M^+$).

**61-Bis(pyren-1-yl methyloxycarbonyl)-1,2-methano[60]-fullerene (4).** Yield: 22% (47% based on recovered $C_{60}$). Mp: >300 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 8.23 (2H, d, $J$ = 9.22 Hz), 8.12 (4H, m), 7.97 (12H, m), 6.06 (4H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 163.45, 145.03, 144.87, 144.65, 144.54, 144.19, 142.81, 142.75, 142.05, 141.45, 138.69, 132.18, 131.14, 130.65, 129.78, 128.45, 128.13, 127.41, 127.35, 126.20, 125.72, 125.65, 124.88, 124.62, 124.54, 124.46, 122.98, 71.32, 67.60, 51.96. FTIR (PE) 1743, 1597, 1466, 1365, 1311, 1226, 1203, 1064, 532 cm$^{-1}$. UV−vis ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$): 476 (3.56), 426 (3.61), 347 (4.82), 330 (4.81), 318 (4.67), 278 (5.02), 267 (5.04) nm. MS (FAB$^+$) $m/z$: 1251 ($M^+$).

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