Novel Synthesis of Benzenepolycarboxylates by Ruthenium-Catalyzed Cross-Benzannulation of Acetylenedicarboxylates with Allylic Compounds

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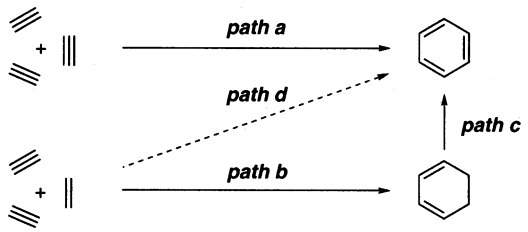
*Summary: A catalyst system consisting of Cp*RuCl-(cod)/PPh$_3$ [Cp* = pentamethylcyclopentadienyl, cod = 1,5-cyclooctadiene] for the novel cross-benzannulation of 2 equiv of dialkyl acetylenedicarboxylate with an allylic compound has been developed. As an example, the reaction of dimethyl acetylenedicarboxylate with allyl alcohol in the presence of 4 mol % Cp*RuCl(cod) and PPh$_3$ under reflux in toluene for 5 h gave tetramethyl 5-methyl-1,2,3,4-benzenetetracarboxylate in an isolated yield of 84%.*

Introduction

The transition metal complex catalyzed cyclotrimerization of alkynes has been extensively studied as a feasible method for constructing substituted aromatic nuclei (Scheme 1, path a).[1] The related cocyclization of two alkyne molecules with an alkene molecule can also be catalyzed by transition metals to generally give 1,3-cyclohexadiene derivatives (path b).[2] Both processes can be rationalized by assuming metallacyclopentadiene intermediates[3] via the oxidative cyclization of two alkyne molecules on low-valence transition metal catalysts, followed by insertion of an alkyne and/or an alkene, e.g., cobalt,[1a,2a−c] palladium,[4] titanium,[2d,e,5] and ruthenium[2f−h,6] catalysts. Although consecutive syntheses of benzene derivatives via 1,3-cyclohexadienes via a combination of the cocyclization reaction with dehydrogenation,[7] retro-Diels−Alder reaction,[8] or base-assisted oxidation[9] have been developed (paths b and c), methods for the direct synthesis of polysubstituted benzenes by the cocyclization of alkynes with alkenes, *so-called cross-benzannulation*, are quite limited (path d).[10] Recently, the palladium-catalyzed cross-benzannulation of alkynes with allylic compounds via a π-allylpalladium intermediate has been reported independently by tom Dieck[11a] and Tsukada.[11b] However, tom Dieck and co-workers only reported the reactions of dimethyl acetylenedicarboxylate with allyl formate and/or allyl acetate, and the yield and the selectivity of benzenetetracarboxylates were low. Tsukada and co-workers did not report the reaction using 3-buten-2-yl tosylate, even though they proposed a mechanism involving a π-allylpalladium intermediate. Further, the reaction of electron-deficient alkynes such as dimethyl

Scheme 1



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(2) For Co: (a) Macomber, D. W.; Verma, A. G.; Rogers, R. D. *Organometallics* **1988**, *7*, 1241. (b) Zhou, Z.; Battaglia, P.; Chiusoli, G. P.; Costa, M.; Nardelli, M.; Pelizzi, C.; Predieri, G. *J. Chem. Soc., Chem. Commun.* **1990**, 1632. (c) Chiusoli, G. P.; Costa, M.; Zhou, Z. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1399. For Ti: (d) Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1993**, *115*, 1581. (e) Johnson, E. S.; Balaich, G. J. Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 7685. For Ru: (f) Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Itoh, K. *J. Org. Chem.* **1998**, *63*, 9610. (g) Yamamoto, Y.; Kitahara, H.; Hattori, R.; Itoh, K. *Organometallics* **1998**, *17*, 1910. (h) Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Kawaguchi, H.; Tatsumi, K.; Itoh, K. *J. Am. Chem. Soc.* **2000**, *122*, 4310. For Rh: (i) Grigg, R.; Scott, R.; Stevenson, P. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1365. For Ni: (j) Chalk, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 5928. (k) Tsuda, T.; Mizuno, H.; Takeda, A.; Tobisawa, A. *Organometallics* **1997**, *16*, 932.

(3) For direct observation of cobaltacyclopentadienes and their related reactions in terms of the reaction mechanism for alkyne cyclotrimerization, see: (a) Diercks, R.; Eaton, B. E.; Gürtzgen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, *120*, 8247. Recently, pathways involving cascades of metathesis steps in ruthenium-catalyzed conversion of triynes to benzene derivatives have also been described. (b) Peters, J.-U.; Blechert, S. *Chem. Commun.* **1997**, 1983. (c) Witulski, B.; Stengel, T.; Fernández-Hernández, J. M. *Chem. Commun.* **2000**, 1965.

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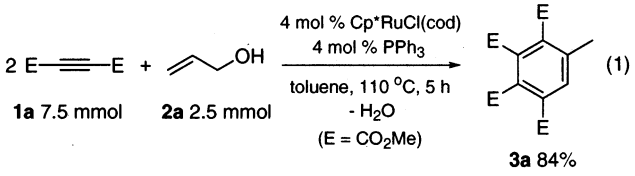
acetylenedicarboxylate with allylic tosylates was ineffective.

We previously reported the [2+2] cycloaddition of alkynes with 2-norbornenes[12] and the cyclocarbonylation of enynes (the intramolecular Pauson−Khand reaction)[13] catalyzed by ruthenium complexes, in which ruthenacyclopentenes are a key intermediate. On the basis of the results in these reactions, we further attempted the reaction of alkynes with functionalized alkenes such as allylic compounds in the presence of a ruthenium catalyst. Fortunately, a novel ruthenium-catalyzed intermolecular [2+2+2] cross-benzannulation of acetylenedicarboxylates with allylic compounds proceeded to give benzenetetracarboxylates directly in high yields instead of a normal cycloadduct of 1,3-cyclohexadienes. We report here the development of a new and highly active ruthenium catalyst system consisting of Cp*RuCl(cod)/PPh_3 [Cp* = pentamethylcyclopentadienyl, cod = 1,5-cyclooctadiene], which realized the rapid synthesis of benzenepolycarboxylates via a ruthenacyclopentene intermediate. The present reaction may complement the two palladium-catalyzed reactions mentioned above[11] and may be more synthetically useful since allylic alcohols can be used directly, although their mechanisms are completely different from one another.

Results and Discussion

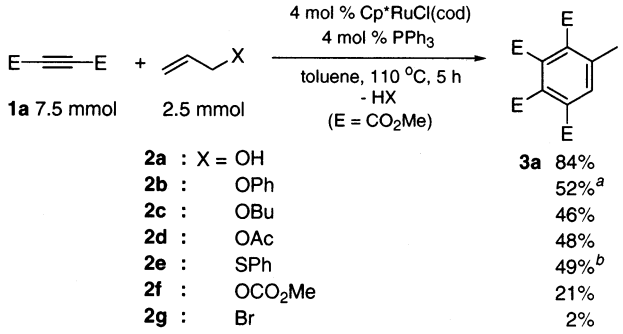
Treatment of dimethyl acetylenedicarboxylate (**1a**) with allyl alcohol (**2a**) in the presence of 4 mol % Cp*RuCl(cod) and PPh_3 under reflux in toluene for 5 h gave tetramethyl 5-methyl-1,2,3,4-benzenetetracarboxylate (**3a**) in an isolated yield of 84% (eq 1). No 1,3-cyclohexadiene derivative, which is a formal [2+2+2] cocyclization product of alkynes with an alkene, was detected.



(1)

First, the effects of the catalyst and the ligand were examined in the reaction of **1a** with **2a**. Among the catalysts examined, Cp*RuCl(cod) showed the highest catalytic activity (yield of **3a**, 54%). Addition of an equal amount of PPh_3 ligand with the ruthenium complex enhanced the catalytic activity to give **3a** in the best yield of 84%. Either increasing or decreasing the amount of PPh_3 resulted in low catalytic activity. NH_4PF_6 was used to generate the Cp^*Ru^+ species in the present reaction; however, almost no catalytic activity was observed, which suggests that the present reaction proceeds via a neutral ruthenium species possessing a chloride ligand. Other ruthenium catalysts, such as $CpRuCl(PPh_3)_2$ [Cp = cyclopentadienyl], (η^5-C_9H_7)$RuCl(PPh_3)_2$, $RuCl_2(PPh_3)_3$, $RuH_2(PPh_3)_4$, $Ru_3(CO)_{12}$, and Ru(η^4-cod)(η^6-cot) [cot = 1,3,5-cyclooctatriene] were totally ineffective. Other transition metal complexes such as $[RhCl(C_2H_4)_2]_2$,[7] $[Pd\{C_4(CO_2Me)_4\}]_n$,[4] $CpCo(CO)_2$,[1a] and $Ni(CO)_2(PPh_3)_2$,[2j,k] which showed high catalytic activity for the production of 1,3-cyclohexadienes by the normal cocyclization of two alkyne molecules with an alkene molecule, were also ineffective. No apparent solvent effect was observed, and **3a** was obtained in good yield in toluene (84%), 1,4-dioxane (64%), DMF (75%), and acetonitrile (75%). Interestingly, no positive effect of PPh_3 was observed in DMF, and **3a** was obtained in 76% yield in DMF without PPh_3, which suggests that DMF *itself* may serve as a suitable ligand for an active ruthenium species.

Scheme 2



[a] An equal amount of PhOH (52%) was obtained. [b] A mixture of PhSH and $(PhS)_2$ was obtained (total 50% yield).

The effect of the leaving group of allylic compounds (**2a**−**g**) is summarized in Scheme 2. In all cases, **1a** was completely consumed. Allyl alcohol **2a** gave the best result, which means that no protection of the hydroxy group was needed. The direct use of allylic alcohols as a building block for the construction of new carbon skeletons is highly economical in terms of atoms used.[14] In addition to **2a**, allyl phenyl ether (**2b**), allyl butyl ether (**2c**), allyl acetate (**2d**), and allyl phenyl sulfide (**2e**) also gave **3a** in good yield. Notably, an equal amount of phenol with **3a** in the reaction of **2b** with **1a** and a mixture of thiophenol and diphenyl disulfide in the reaction of **2e** with **1a** were obtained as byproducts, respectively. Unexpectedly, allyl methyl carbonate (**2f**) and allyl bromide (**2g**), which easily react with transition metal complexes to give π-allyl complexes, gave poor results, which strongly suggests that the present reaction does not involve a π-allylruthenium intermediate[15] (vide infra).

The cross-benzannulation of acetylenedicarboxylate **1** with several allylic alcohols **2** also proceeded smoothly by a catalyst system consisting of Cp*RuCl(cod)/PPh_3, and the results are summarized in Scheme 3. Generally, allylic alcohols bearing a substituent at the 1-position

(12) (a) Mitsudo, T.; Kokuryo, K.; Takegami, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 722. (b) Mitsudo, T.; Kokuryo, K.; Shinsugi, T.; Nakagawa, Y.; Watanabe, Y.; Takegami, Y. *J. Org. Chem.* **1979**, *44*, 4492. (c) Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580.

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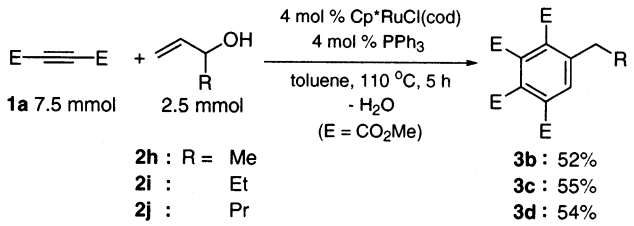
(15) Ruthenium-catalyzed reactions via a π-allyl ruthenium intermediate, see: (a) Matsushima, Y.; Onitsuka, K.; Kondo, T.; Mitsudo, T.; Takahashi, S. *J. Am. Chem. Soc.* **2001**, *123*, 10405. (b) Morisaki, Y.; Kondo, T.; Mitsudo, T. *Org. Lett.* **2000**, *2*, 949. (c) Kondo, T.; Morisaki, Y.; Uenoyama, S.; Wada, K.; Mitsudo, T. *J. Am. Chem. Soc.* **1999**, *121*, 8657. (d) Morisaki, Y.; Kondo, T.; Mitsudo, T. *Organometallics* **1999**, *18*, 4742. (e) Kondo, T.; Kodoi, K.; Nishinaga, E.; Okada, T.; Morisaki, Y.; Watanabe, Y.; Mitsudo, T. *J. Am. Chem. Soc.* **1998**, *120*, 5587. (f) Kondo, T.; Hiraishi, N.,; Morisaki, Y.; Wada, K.; Watanabe, Y.; Mitsudo, T. *Organometallics* **1998**, *17*, 2131. (g) Kondo, T.; Ono, H.; Satake, N.; Mitsudo, T.; Watanabe, Y. *Organometallics* **1995**, *14*, 1945, and references therein.

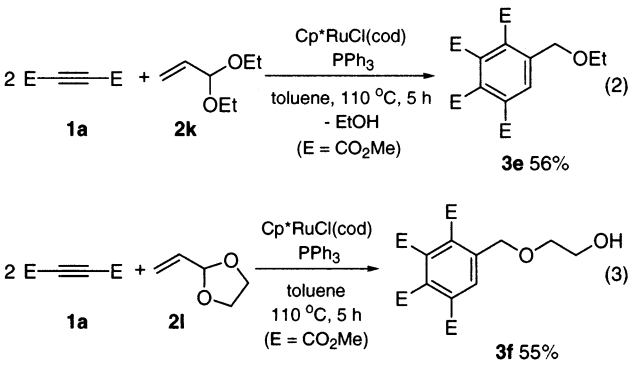
Scheme 3



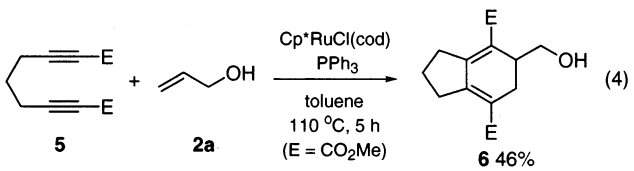
(**2h**−**j**) were suitable, and the corresponding products (**3b**−**d**) were obtained in good isolated yields.

No *cross*-benzannulation of **1a** with *trans*-crotyl alcohol, *cis*-2-pentene-1-ol, 2-methyl-3-butene-2-ol, or *β*-methallyl alcohol proceeded, and only hexamethyl 1,2,3,4,5,6-benzenehexacarboxylate (**4a**), a trimer of **1a**, was obtained. These results again exclude the likelihood of a mechanism involving a *π*-allylruthenium intermediate. Except for dimethyl acetylenedicarboxylate, other alkynes, such as methyl propiolate, methyl 2-butynoate, 4-octyne, and phenylacetylene, could not be used in the present reaction.

As a synthetic equivalent of allylic alcohols, several acetals such as **2k** and **2l** can be used in the present reaction. Reaction of **1a** with acrolein diethyl acetal (**2k**) gave the corresponding cross-benzannulation product **3e** via the elimination of ethanol (eq 2). Treatment of **1a** with a cyclic acetal, 2-vinyl-1,3-dioxolane (**2l**), gave **3f** via ring-opening of **2l**, in which a hydroxyl group remained (eq 3).

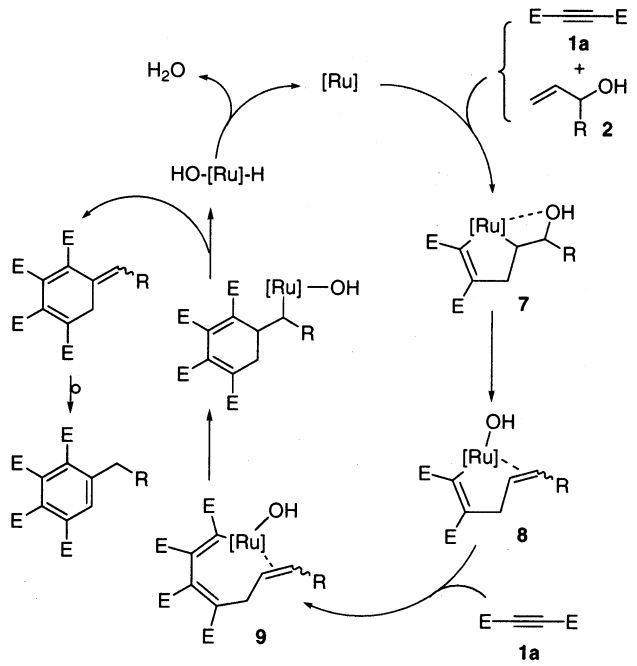


To investigate the intermediacy of a ruthenacyclopentadiene,[2f−h,6] the partially intramolecular cocyclization of diyne **5** with **2a** was examined (eq 4). In this reaction, the product was the normal 1,3-cyclohexadiene derivative **6**, not a benzene derivative. This result clearly indicates that the present reaction does not involve a ruthenacyclopentadiene intermediate.



Considering the results described above, the most plausible mechanism is illustrated in Scheme 4. Since the mechanisms involving a *π*-allyl ruthenium intermediate or a ruthenacyclopentadiene intermediate can be ruled out (vide supra), we now believe that a

Scheme 4



ruthenacyclopentene (**7**),[12,13,16] which is generated by oxidative cyclization of **1a** and allylic alcohol **2** on an active ruthenium center, is a key intermediate in the present reaction. The alkoxycarbonyl group (E, an electron-withdrawing group) decreased the electron density of the ruthenium center in **7**. This facilitates the intramolecular coordination of the hydroxyl group to ruthenium, which results in *β*-hydroxy elimination to form the intermediate **8**.[16c,17] Subsequent insertion of another molecule of **1a** into **8**, intramolecular insertion of a C=C bond in **9** into an alkenyl−ruthenium bond, and successive *β*-hydride elimination/isomerization would give the corresponding polysubstituted benzene derivatives.

In conclusion, we have described the first example of the ruthenium-catalyzed intermolecular [2+2+2] cross-benzannulation of dialkyl acetylenedicarboxylates with allylic compounds, which gave 1,2,3,4-benzenetetracarboxylates. These products may become important raw materials and/or components for the manufacture of heat-resistant polyamides and polyimides as well as esters for plasticizers, adhesives, and other functional polymers.[18]

Experimental Section

General Procedures. GLC analyses were performed on a Shimadzu GC-14B gas chromatograph with a glass column (2.8 mm i.d. × 3.0 m) packed with Silicone SE-30 (5% on Chromosorb W(AW-DMCS), 80−100 mesh). The ^{1}H (400 and/or 300) and ^{13}C NMR spectra (100 and/or 75) were obtained on JEOL

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(18) Weissermel, K.; Arpe, H.-J. In *Industrial Organic Chemistry*, 3rd ed.; VCH: Weinheim, 1997; Chapter 12, pp 314−317.

EX-400 and AL-300 spectrometers. Samples were analyzed in $CDCl_3$, and the chemical shift values were expressed relative to Me_4Si as an internal standard. IR spectra were obtained on a Nicolet Impact 410 spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials. The reagents used in this study were dried and purified before use by standard procedures. Compounds **2a**−**e**, **2g**−**j**, **2k**, and **2l** were obtained commercially and used after distillation. Compounds **2f**[19] and **5**[20] were prepared as described in the literature. $Ru_3(CO)_{12}$, $[RhCl(C_2H_4)_2]_2$, $CpCo(CO)_2$, and $Ni(CO)_2(PPh_3)_2$ were obtained commercially and used without further purification. Cp*RuCl(cod),[21] $CpRuCl(PPh_3)_2$,[22] (η^5-C_9H_7)$RuCl(PPh_3)_2$,[23] $RuCl_2(PPh_3)_3$,[24] $RuH_2(PPh_3)_4$,[25] Ru(η^4-cod)(η^6-cot),[26] and $[Pd\{C_4(CO_2Me)_4\}]_n$[27] were prepared as described in the literature.

General Procedure for Ruthenium-Catalyzed Cross-Benzannulation of Dimethyl Acetylenedicarboxylate (1a) with Allyl Alcohol (2a). A mixture of dimethyl acetylenedicarboxylate (**1a**) (7.5 mmol), allyl alcohol (**2a**) (2.5 mmol), Cp*RuCl(cod) (0.10 mmol), PPh_3 (0.10 mmol), and toluene (5.0 mL) was placed in a two-necked 20 mL Pyrex flask equipped with a magnetic stirring bar and a reflux condenser under an argon atmosphere. The mixture was then magnetically stirred at 110 °C for 5 h. After cooling, the reaction mixture was analyzed by GLC, and the products were isolated by Kugelrohr distillation.

Tetramethyl 5-methyl-1,2,3,4-benzenetetracarboxylate (3a): white solid; bp 150−160 °C (1.0 mmHg, Kugelrohr); mp 79−80 °C; IR (KBr) 3008, 2960, 2858, 1735 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.44 (s, 3H), 3.86 (s, 3H), 3.91 (s, 3H), 3.91 (s, 3H), 3.92 (s, 3H), 7.95 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.54, 52.70, 52.86, 52.86, 53.06, 129.67, 129.91, 133.02, 134.50, 137.00, 138.05, 165.08, 165.73, 167.47, 167.54; MS (EI) m/z 293 ($M^+ - OCH_3$). Anal. Calcd for $C_{15}H_{16}O_8$: C 55.56, H 4.97. Found: C 55.46, H 4.95.

Tetramethyl 5-ethyl-1,2,3,4-benzenetetracarboxylate (3b): white solid; bp 150−160 °C (1 mmHg, Kugelrohr); mp 83−84 °C; IR (KBr) 3011, 2989, 2960, 2893, 2850, 1735 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.25 (t, 3H, J = 7.49 Hz), 2.74 (q, 2H, J = 7.49 Hz), 3.86 (s, 3H), 3.91 (s, 3H), 3.92 (s, 3H), 3.92 (s, 3H), 7.98 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.10, 26.47, 52.66, 52.82, 52.82, 53.02, 129.60, 130.13, 133.00, 133.18, 136.60, 143.97, 165.11, 165.73, 167.47, 167.54; MS (EI) m/z 307 ($M^+ - OCH_3$). Anal. Calcd for $C_{16}H_{18}O_8$: C 56.80, H 5.36. Found: C 56.56, H 5.29.

Tetramethyl 5-propyl-1,2,3,4-benzenetetracarboxylate (3c): white solid; bp 160−170 °C (1.0 mmHg, Kugelrohr); mp 81−83 °C; IR (KBr) 3004, 2957, 2904, 2876, 2847, 1732 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.95 (t, 3H, J = 7.33 Hz), 1.64 (qt, 2H, J = 7.33, 7.82 Hz), 2.69 (t, 2H, J = 7.82 Hz), 3.86 (s, 3H), 3.90 (s, 3H), 3.92 (s, 3H), 3.92 (s, 3H), 7.96 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.74, 24.09, 35.19, 52.64, 52.84, 52.84, 53.04, 129.67, 129.85, 133.03, 133.84, 136.80, 142.58, 165.09, 165.77, 167.49, 167.58; MS (EI) m/z 321 ($M^+ - OCH_3$). Anal. Calcd for $C_{17}H_{20}O_8$: C 57.93, H 5.63. Found: C 57.95, H 5.72.

Tetramethyl 5-butyl-1,2,3,4-benzenetetracarboxylate (3d): white solid; bp 160−170 °C (1.0 mmHg, Kugelrohr); mp 84−85 °C; IR (neat) 3002, 2955, 2873, 1735 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.92 (t, 3H, J = 7.33 Hz), 1.36 (qt, 2H, J = 7.33, 7.33 Hz), 1.59 (tt, 2H, J = 7.81, 7.33 Hz), 2.71 (t, 2H, J = 7.81 Hz), 3.86 (s, 3H), 3.90 (s, 3H), 3.92 (s, 3H), 3.92 (s, 3H), 7.96 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.67, 22.34, 32.96, 33.04, 52.60, 52.82, 52.82, 53.01, 129.65, 129.87, 132.94, 133.78, 136.71, 142.82, 165.08, 165.75, 167.47, 167.54; MS (EI) m/z 335 ($M^+ - OCH_3$). Anal. Calcd for $C_{18}H_{22}O_8$: C 59.01, H 6.05. Found: C 58.96, H 5.86.

Tetramethyl 5-ethoxymethyl-1,2,3,4-benzenetetracarboxylate (3e): white solid; bp 160−170 °C (1.0 mmHg, Kugelrohr); mp 64−65 °C; IR (neat) 2976, 2954, 2876, 1732 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22 (t, 3H, J = 6.97 Hz), 3.51 (q, 2H, J = 6.97 Hz), 3.85 (s, 3H), 3.88 (s, 3H), 3.91 (s, 6H), 4.61 (s, 2H), 8.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.01, 52.79, 52.95, 52.95, 53.12, 66.45, 69.21, 130.27, 130.41, 131.84, 134.27, 135.30, 139.47, 165.03, 165.76, 166.88, 167.39; MS (EI) m/z 337 ($M^+ - OCH_3$). Anal. Calcd for $C_{17}H_{20}O_9$: C 55.43, H 5.47. Found: C 55.21, H 5.42.

Tetramethyl 5-(2-hydroxyethoxy)methyl-1,2,3,4-benzenetetracarboxylate (3f): pale yellow liquid; bp 200 °C (1 mmHg, Kugelrohr); IR (neat) 3455, 3013, 2956, 2887, 1754, 1737, 1731, 1715 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.16 (t, 1H, J = 6.25 Hz), 3.59 (t, 2H, J = 4.23 Hz), 3.74 (dt, 2H, J = 4.23, 6.25 Hz), 3.87 (s, 3H), 3.91 (s, 3H), 3.91 (s, 6H), 4.68 (s, 2H), 8.14 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) 53.01, 53.01, 53.01, 53.17, 61.69, 69.98, 72.23, 130.33, 130.60, 132.12, 134.61, 135.70, 138.63, 164.89, 165.63, 167.21, 167.25; MS (EI) m/z 352 ($M^+ - HOCH_3$). Anal. Calcd for $C_{17}H_{20}O_{10}$: C 53.13, H 5.25. Found: C 52.72, H 5.24.

Dimethyl 5-(hydroxymethyl)-2,3,5,6-tetrahydroindene-4,7-dicarboxylate (6): colorless liquid; bp 140−150 °C (1.0 mmHg, Kugelrohr); IR (neat) 3470, 2952, 2848, 1722 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.68−1.76 (m, 2H), 1.89 (s, 1H), 2.40 (dt, 2H, J = 14.16, 4.39 Hz), 2.63−2.71 (m, 2H), 2.80−2.88 (m, 2H), 2.92 (tt, 1H, J = 4.39, 5.86 Hz), 3.46 (dt, 2H, J = 67.38, 5.86 Hz), 3.68 (s, 3H), 3.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.24, 25.98, 31.87, 32.43, 36.18, 51.53, 51.69, 63.25, 121.86, 123.67, 151.67, 153.92, 167.86, 168.35; MS (EI) m/z 248 ($M^+ - H_2O$), 235 ($M^+ - OCH_3$). Anal. Calcd for $C_{14}H_{18}O_5$: C 63.15, H 6.81. Found: C 63.10, H 6.51.

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