Synthesis of *m*-Terphenyl Derivatives via Domino Diels–Alder/Retro-Diels–Alder Reaction of 1,3-Dienic δ-Sultones with Alkynes

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Dedicated to Dr. Margit Gruner on the occasion of her 65th birthday

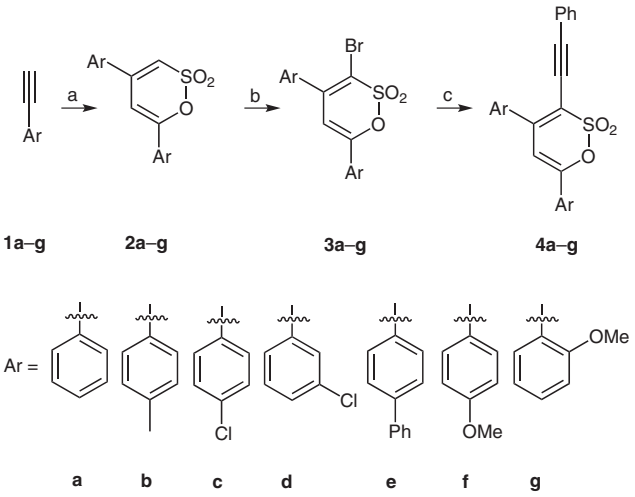
Abstract: A highly regioselective synthetic method based on the domino Diels–Alder/retro-Diels–Alder reaction (DA/RDA) of 1,3-dienic δ-sultones with alkynes provides substituted *m*-terphenyls by elimination of SO_3. A variety of δ-sultones and alkynes were examined to determine the scope of the reaction. The de novo synthesized aromatic products were obtained using thermal, microwave, and high-pressure activation.

Key words: *m*-terphenyls, sultones, Diels–Alder reaction, alkynes, high pressure

In the query to synthesize bioactive natural compounds and functional materials, *m*-terphenyl derivatives are important intermediates.[1] For this purpose it is essential to develop novel reactions leading to these compounds. The construction of the central benzene ring is a useful synthetic approach for substituted *m*-terphenyls.

Here we present a new regioselective synthesis of substituted *m*-terphenyls based on the domino Diels–Alder/retro-Diels–Alder (DA/RDA) reaction of 1,3-dienic δ-sultones with alkynes. The domino DA/RDA reactions of α-2*H*-pyranones[2–4] or 1,2-diazines[5–7] are known processes for the de novo construction of benzene derivatives. However, the transformation of δ-sultones embedding a 1,3-dienic moiety was only reported once from our group. In our example (Scheme 1),[8] we only used a 1,3-dienic δ-sultone with simple phenyl substituents, which has been inspired by an earlier proposed reaction scheme.[9] The potential of this reaction is now shown using a wide range of sultones and alkynes.

Starting from the functionalized arylacetylenes **1a**–**g**, δ-sultones **2a**–**g** were synthesized according to our method[10] with dioxane sulfotrioxide or trimethylsilyl chlorosulfonate as a sulfur trioxide source. The substituents at the benzene rings ranged over a broad variety of different inductive (I) and mesomeric (M) effects.



Scheme 1 Synthesis and functionalization of 1,3-dienic δ-sultones, including all residues processed. *Reagents and conditions*: a) SO_3 (1 equiv); b) Br_2 or NBS; c) **1a** and Sonogashira conditions.

Sultones **2a**–**g** were further functionalized with bromine at the carbon neighboring the sulfur atom resulting in the brominated sultones **3a**–**g**. This functionality was then used for a Sonogashira coupling[11] with phenylacetylene giving functionalized sultones **4a**–**g** (Scheme 1). We now have a large number of different 1,3-dienic δ-sultones in hand to consider a further study of the DA/RDA sequence (Scheme 2). When this strategy is applied to α-2*H*-pyranones, often dimethyl acetylenedicarboxylate (DMAD, **5**) was used as a dienophile,[12,13] resulting in derivatives of benzene-1,2-dicarboxylic acid via carbon dioxide extrusion. Other dienophiles were now explored in order to get more information about the regioselectivitiy of this cyclization. Thus, ethyl propiolate (**6**) and phenylacetylene (**1a**) were used as reasonable monosubstituted alkynes. To see, whether a heteroanalogous reaction for cyano groups is possible, the use of methyl cyanoformate (**7**) was also examined.

For all subsequent DA/RDA reactions it was decided to use three methods of activation. In addition to the classical thermal activation in a flask, the activation by microwave radiation as well as high pressure were also examined.

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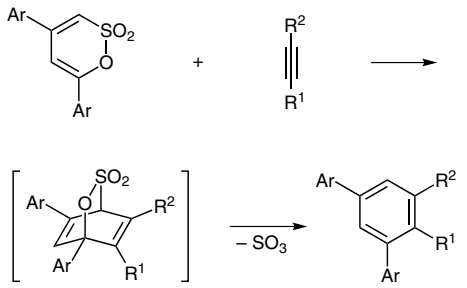
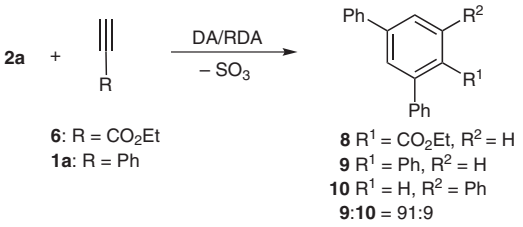


Scheme 2 Diels–Alder/retro-Diels–Alder reaction of 1,3-dienic δ-sultones with alkynes. Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 3-ClC_6H_4, 4-PhC_6H_4, 4-$MeOC_6H_4$, 2-$MeOC_6H_4$; R^1 = CO_2Me, CO_2Et, Ph; R^2 = CO_2Me, H.

The solvent-free method of microwave radiation has proved to be a modern way of reducing reaction times as well as increasing the yield in organic reactions,[14,15] thus amplifying reaction efficiency. Since high-pressure activation in liquid phase is a known method to realize Diels–Alder reactions,[16] it was also chosen for our approach. With α-2*H*-pyranones the activation of the DA/RDA with high pressure is not feasible due to the development of gaseous CO_2, slowing down or stopping the reaction. It is therefore only applicable on a limited number of substrates and may need reaction times over 300 hours.[17] In contrast, DA/RDA reactions of sultones lead to the elimination of SO_3, which may immediately react with the excess of the alkyne. Consequently, no gaseous products can be formed and high-pressure activation should be applicable.

Monosubstituted alkynes **6** and **1a** reacted with sultone **2a** to give one regioisomer predominantly. Interestingly, both gave the sterically more hindered 1,2,4-substituted terphenyls. While ethyl propiolate (**6**) gave only product **8**, phenylacetylene (**1a**) gave both, 1,2,4-triphenylbenzene (**9**) and 1,3,5-triphenylbenzene (**10**), in a 91:9 mixture (Scheme 3, Table 1). The mixture of both isomers could not be separated, but GC-MS revealed the ratio of both isomers, while ^{13}C NMR analysis showed, which isomer was predominant.[18] By replacing a carbon atom in the alkyne structure and testing the N-heteroanalogous **7** as a dienophile, no reaction was observed.



Scheme 3 Reaction of sultone **2a** with phenylacetylene (**1a**) and ethyl propiolate (**6**)

Considering the reactivity, both monofunctionalized acetylenes **6** and **1a** have to be discussed separately. Ethyl propiolate (**6**) showed a lower yield of cyclization product than DMAD (**5**) using comparable microwave irradiation (100 W). Interestingly, similar yields could be achieved using thermal activation, but no products were observed using high-pressure activation. Thus, the monocarboxylated alkyne **6** is in general less reactive than DMAD (**5**). In contrast, the reactivity of phenylacetylene (**1a**) cannot be judged as generally. Giving a lower yield under high-pressure activation, microwave and thermal activation resulted in unusually high yields of Diels–Alder products **9** and **10**. In combination, yields of more than 100% related to starting **2a** could be determined. Here, SO_3 leaving the starting sultone **2a** is recycled in situ, reacting with the excess of **1a** to form new sultone **2a**. Logically, these freshly formed molecules can now enter the DA/RDA sequence to form additional DA/RDA products **9** and **10**.

Comparing the results, the order of reactivity discovered by Kranjc and Kočevar[3] for a DA/RDA reaction of pyranones could be confirmed, if microwave radiation or thermal activation is applied. Using high-pressure activation, phenylacetylene (**1a**) shows a lower reactivity than DMAD (**5**) and therefore switches places in the reactivity scale (Figure 1).

Table 1 Reaction of Sultone **2a** with Phenylacetylene (**1a**) and Ethyl Propiolate (**6**)

Alkyne	Conditions	Temp (°C)	Time (h)	Conversion of **2a** (%)	Product, yield(%)
1a	MW 100 W	140	0.5	–	**9** + **10** (74)
1a	MW 300 W	150	0.5	–	**9** + **10** (130)[a]
1a	thermal	150	5	–	**9** + **10** (118)[a]
1a	1300 MPa	25	50	–	**9** + **10** (30)
6	MW 100 W	120	0.5	34	**8** (21)
6	MW 300 W	150	0.5	100	**8** (48)
6	thermal	150	8	100	**8** (54)
6	1300 MPa	25	24	0	–

[a] Yield related to **2a**, reaction with recycling of SO_3.

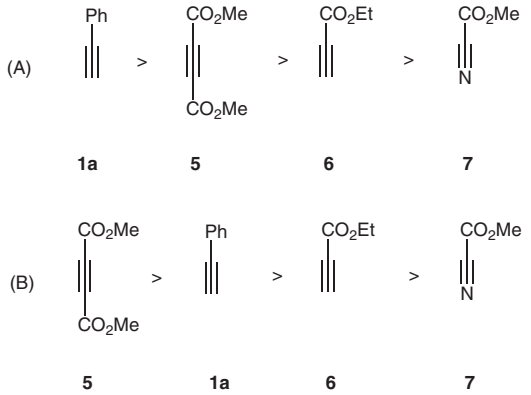


Figure 1 Reactivity scale of alkynes as dienophiles in the DA/RDA with 1,3-dienic δ-sultones for microwave assisted activation (A) and for high-pressure activation (B)

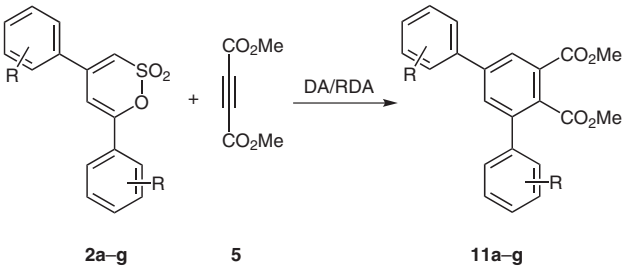
We suspect that any change in reactivity is due to the Diels–Alder step of the reaction, since the subsequent extrusion of SO_3 yields a stable benzene structure and should therefore not be rate-determining.

Since reactions with DMAD (**5**) supplied the most stable results and gave no further problems in the workup of the crude product, it was chosen as the dienophile for further studies with the sultones prepared.

To determine the scope of the DA/RDA reactivity, a further steric hindrance to the sultone was introduced, an α-substitution of the sulfur atom. The further functionalized sultones **3** and **4** were now applied as substrates in the explored DA/RDA reaction. As test substrates, the derivatives of the basic sultone **2a**, that is, 3-bromosultone **3a** and 3-phenylethynylsultone **4a**,[10] were chosen. Both substances were treated under similar conditions as for **2a**.

Unfortunately, in this case none of the methods of activation (thermal, microwave, high pressure) gave the desired terphenyl. With 3-bromosultone **3a**, the substrate was reisolated, while 3-phenylethynylsultone **4a** decomposed completely. These results show that a substitution in α position to sulfur within the sultone leads to a complete loss of DA/RDA reactivity. We suspect steric hindrance to suppress the desired reactivity of the functionalized sultones **3a** and **4a**.

As a logical subsequent step, now all remaining sultones **2b–g** were treated with DMAD (**5**) to give terphenyls **11a–g**, using all methods of activation (Scheme 4). The results for thermal, microwave, and high-pressure activation are all comprised in Table 2.



Scheme 4 Reaction of sultones **2a–g** with dimethyl acetylenedicarboxylate (**5**)

The yields of the synthesized terphenyl derivatives **11a–g** via DA/RDA of sultones **2a–g** with alkyne **5** reveal various properties of the reaction. First of all, it is obvious that there is only little dependency of the yield on the substituents at the adjacent phenyl rings. All yields of terphenyls **11a–d** are within a good range from 54–66%, for all activation methods. Here, the additional substituents of the phenyl rings adjacent to the sultone ring have only little influence on the DA/RDA reactivity of the central sultone ring.

Products with more than three phenyl ring chains can be also synthesized by this method. Thus, the diphenylacetylene **2e** gives the quinquiphenyl **11e** using the DA/RDA pathway. The structure of product **11e** was confirmed via X-ray crystal structure analysis (Figure 2).[19]

Table 2 Synthesis of *m*-Terphenyls **11a–g** under Thermal, Microwave, and High-Pressure Activation

Sultone	R	Product	Activation, yield (%)		
			Thermal	MW	High pressure
2a	H	**11a**	55[a,b]	54[a]	67
2b	4-Me	**11b**	60[c]	57	57
2c	4-Cl	**11c**	58[c]	61	63
2d	3-Cl	**11d**	66[c]	65	66
2e	4-Ph	**11e**	22[b]	24	54
2f	4-MeO	**11f**	44[c]	54	11
2g	2-MeO	**11g**	34[c]	34	24

[a] Mixture of 1,1′:3′,1″-terphenyl-4′,5′-dicarboxylic acid dimethyl ester **11a** and 1,1′:3′,1″-terphenyl-4′,5′-dicarboxylic acid anhydride 60:40 (mol/mol) for thermal activation and 74:26 (mol/mol) for microwave.
[b] Reaction temperature: 150 °C.
[c] Reaction temperature: 130 °C.

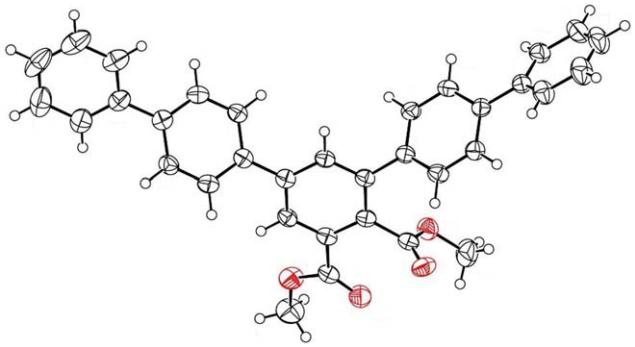


Figure 2 X-ray crystal structure of **11e**

For high-pressure activation, the resulting yields of **11a**–**e** are considerably higher than the yields for both methoxy substituted products **11f** and **11g**. Since both corresponding starting sultones **2f** and **2g** are unstable,[10] it is reasonable that this lack of yield is due to their instability. For microwave-assisted and thermal activation, the *o*-methoxy derivative **2g** gives the least amount of terphenylic product. Here, steric hindrance due to the methoxy group is the most probable reason for this behavior.

In summary, we have shown that 1,3-dienic δ-sultones react successfully with alkynes in the domino Diels–Alder/retro-Diels–Alder (DA/RDA) reaction. The synthesis of substituted *m*-terphenyls could be achieved with sultones **2a**–**g** and DMAD (**5**) or monosubstituted alkynes **1a** or **6** as dienophiles. As expected, an elimination of SO_3 occurs, which immediately reacts with excess of the alkyne. The synthesis under microwawe or thermal activation is carried out under solvent-free conditions. The activation using microwave radiation proved to be the most efficient way to start the reaction, while high-pressure activation is the cleanest way to perform this reaction. The reaction with monosubstituted alkynes **1a** or **6** gives 1,2,4-, but not 1,3,5-substituted central aromatic rings with high regioselectivity. A substitution at the adjacent phenyl rings in sultones **2b**–**g** shows only little influence on the reactivity of the sultones in the DA/RDA sequence.

Starting sultones **2a**–**g**, **3a**–**g**, and **4a**–**g** were synthesized according to our method.[8] All commercially available compounds were used as received, unless stated otherwise. Flash chromatography: Merck silica gel 60 (40–63 μm). TLC: Merck silica gel 60 F254 plates with UV detection of the spots. Solvent mixtures for chromatography are reported as vol/vol ratios. Melting points: Kleinfeld Labortechnik Electrothermal IA 9100 apparatus. ^{1}H and ^{13}C NMR: Bruker DRX-500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, $CDCl_3$, δ, ppm, calibrated to the residual resonance of the solvent, standard abbreviations). FT-IR spectra: Nicolet 205 and Nicolet Avatar 360 spectrometer (cm^{-1}, standard abbreviations). Mass spectra: HP 1100 Bruker Esquire Ion Trap (ESI/APCI, *m*/*z*, U = 10–50 V). Elemental analysis: Carlo Erba Instruments EA 1108 and Hekatech EA 3000. Hofer high-pressure apparatus (hydraulic press) up to 1400 MPa used for high-pressure experiments. Microwave apparatus was a CEM Discover System, model 908010.

m-Terphenyl Derivatives 11a–g from Sultones 2a–g; General Procedure 1, Thermal Preparation

Sultone **2** (0.30 mmol) was placed into a 5 mL round-bottomed flask, and dimethyl acetylenedicarboxylate (**5**, 390 mg, 2.75 mmol) was added. The resulting suspension was stirred under an argon atmosphere for 7.5 h under the conditions mentioned in Table 2. The resulting red-brown, highly viscous mixture solidified when it was cooled to r.t. It was purified by flash chromatography with pentane–EtOAc (5:1 for products **11a**–**e**, 3:1 for products **11f**, **11g**) under TLC control.

m-Terphenyl Derivatives 11a–g from Sultones 2a–g; General Procedure 2, Microwave Preparation

Sultone **2** (0.30 mmol) was placed into a microwave test tube and DMAD (**5**; 340 mg, 2.4 mmol) was added. The resulting suspension was placed in a microwave apparatus and exposed to the radiation (100 W, 20 min) with 5 min starting time and external cooling with N_2 gas. The resulting red-brown highly viscous crude product mixture was purified by flash chromatography with pentane–EtOAc (5:1 for products **11a**–**e**, 3:1 for products **11f**, **11g**) under TLC control.

m-Terphenyl Derivatives 11a–g from Sultones 2a–g; General Procedure 3, High Pressure Preparation

A solution of sultone **2** (0.30 mmol) in CH_2Cl_2 (10 mL) was transferred to a Teflon high-pressure test tube, and DMAD (**5**; 260 mg, 1.8 mmol) was added. The test tube was closed, inserted into the high-pressure apparatus, and subjected to a pressure of 1300 MPa at r.t. for 72 h. Then the high pressure was relieved, and the solvent was removed at reduced pressure. Product **11** was isolated from the resulting red-brown highly viscous mixture by flash chromatography with pentane–EtOAc (5:1 for products **11a**–**e**, 3:1 for products **11f**, **11g**) under TLC control.

General procedures 1–3 were also used for the experiments with sultones **2a**, **3a**, **4a** and dienophiles **1a**, **6**, and **7**.

Ethyl 1,1′:3′,1″-Terphenyl-4′-carboxylate (8)

Yields: see Table 1; pale yellow oil; R_f = 0.44 (pentane–EtOAc, 5:1).

^{1}H NMR: δ = 1.00 (t, *J* = 7.1 Hz, 3 H), 4.10 (q, *J* = 7.1 Hz, 2 H), 7.35–7.49 (m, 8 H), 7.58–7.67 (m, 4 H), 7.92 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR: δ = 13.7 (CH_3), 60.9 (CH_2), 125.7 (CH), 127.2 (CH), 127.3 (CH), 128.0 (CH), 128.1 (CH), 128.4 (CH), 128.9 (CH), 129.5 (CH), 129.8 (C), 130.5 (CH), 139.9 (C), 141.6 (C), 143.1 (C), 144.0 (C), 168.5 (C=O).

MS (ESI): *m*/*z* = 303 $[M + H]^+$.

GC-MS: *m*/*z* (%) = 302 (60, $[M]^+$), 257 (100, $[M - C_2H_5O]^+$), 228 (40, $[M - C_3H_6O_2]^+$).

1,2,4-Triphenylbenzene (9)

Yields: see Table 1; brown oil; R_f = 0.44 (pentane–EtOAc, 5:1).

^{1}H NMR: δ = 7.83–6.98 (m, 18 H).

^{13}C NMR: δ = 126.11 (CH), 126.51 (CH), 126.58 (CH), 127.13 (2 CH), 127.42 (CH), 127.89 (2 CH), 127.92 (2 CH), 128.82 (2 CH), 129.41 (CH), 129.86 (2 CH), 129.90 (2 CH), 131.09 (CH), 139.54 (C), 140.35 (C), 140.58 (C), 140.98 (C), 141.11 (C), 141.78 (C).

MS (ESI): δ = 323 $[M + NH_4]^+$.

Dimethyl 1,1′:3′,1″-Terphenyl-4′,5′-dicarboxylate (11a)

Yields: see Table 2; slowly crystallizing light yellow oil; mp 75–77 °C; R_f = 0.26 (pentane–EtOAc, 5:1).

IR (ATR): 636 (m), 697 (s), 744 (s), 760 (s), 781 (m), 794 (m), 844 (w), 896 (m), 973 (m), 1000 (w), 1058 (m), 1070 (s), 1118 (s), 1199 (s), 1237 (s, br), 1266 (s, br), 1341 (m), 1372 (w), 1429 (m), 1463 (m), 1497 (w), 1598 (m), 1724 (s, br), 2849 (w), 2950 (w), 3033 (w), 3062 cm^{-1} (w).

^{1}H NMR: δ = 3.70 (s, 3 H), 3.84 (s, 3 H), 7.39–7.45 (m, 6 H), 7.46–7.49 (m, 2 H), 7.64–7.66 (m, 2 H), 7.78 (d, *J* = 1.8 Hz, 1 H), 8.24 (d, *J* = 1.8 Hz, 1 H).

^{13}C NMR: δ = 52.23 (CH_3), 52.65 (CH_3), 127.18 (CH), 127.44 (CH), 127.95 (CH), 128.26 (CH), 128.31 (CH), 128.56 (CH), 128.73 (C), 128.97 (CH), 132.65 (CH), 133.32 (C), 139.01 (C), 139.22 (C), 141.14 (C), 142.17 (C), 166.15 (CO), 166.22 (C=O).

MS (ESI): *m*/*z* = 347 $[M + H]^+$, 710 $[2 M + NH_4]^+$, 715 $[2 M + Na]^+$.

Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 76.19; H, 5.36.

Dimethyl 4,4″-Dimethyl-1,1′:3′,1″-terphenyl-4′,5′-dicarboxylate (11b)

Yields: see Table 2; yellow solid; mp 98–100 °C; R_f = 0.32 (pentane–EtOAc, 5:1).

IR (ATR): 566 (m), 586 (w), 622 (w), 644 (w), 714 (w), 740 (m), 775 (s), 791 (s), 810 (s), 825 (m), 842 (w), 871 (w), 899 (w), 958 (m), 976 (w), 1068 (s), 1122 (s), 1191 (s), 1243 (s), 1278 (s), 1341 (m), 1434 (m) 1516 (w), 1562 (w), 1600 (w), 1636 (w), 1653 (w), 1685 (w), 1717 (s), 1771 (w), 1793 (w), 1829 (w), 1844 (w), 1870 (w), 1917 (w), 2116 (w), 2837 (w), 2916 (w), 2944 (w), 2992 (w), 3026 cm^{-1} (w).

^{1}H NMR: δ = 2.32 (s, 3 H), 2.33 (s, 3 H), 3.64 (s, 3 H), 3.86 (s, 3 H), 7.13–7.25 (m, 6 H), 7.46 (d, *J* = 8.1 Hz, 2 H), 7.66 (d, *J* = 1.9 Hz, 1 H), 8.11 (d, *J* = 1.9 Hz, 1 H).

^{13}C NMR: δ = 21.13 (CH_3), 21.20 (CH_3), 52.31 (CH_3), 52.62 (CH_3), 127.01 (2 CH), 127.04 (CH), 128.44 (2 CH), 128.72 (C), 129.06 (2 CH), 129.70 (2 CH), 132.49 (CH), 133.01 (C), 136.21 (C), 136.44 (C), 137.71 (C), 138.22 (C), 141.12 (C), 142.06 (C), 166.30 (C), 169.41 (C).

MS (ESI): *m*/*z* = 375 $[M + H]^+$, 392 $[M + NH_4]^+$.

Anal. Calcd for $C_{24}H_{18}O_4$: C, 76.99; H, 5.92. Found: C, 76.64; H, 5.65.

Dimethyl 4,4″-Dichloro-1,1′:3′,1″-terphenyl-4′,5′-dicarboxylate (11c)

Yields: see Table 2; yellow oil; R_f = 0.30 (pentane–EtOAc, 5:1).

IR (ATR): 566 (m), 619 (w), 645 (w), 693 (w), 755 (s), 774 (m), 792 (s), 827 (s), 902 (w), 974 (m), 1013 (s), 1067 (s), 1091 (s), 1120 (s), 1177 (m), 1199 (s), 1243 (s), 1264 (s), 1342 (m), 1433 (m), 1456 (w), 1494 (m), 1558 (w), 1603 (w), 1635 (w), 1652 (w), 1685 (w), 1723 (s), 1771 (w), 1828 (w), 1844 (w), 1869 (w), 1917 (w), 2951 cm^{-1} (w).

^{1}H NMR: δ = 3.64 (s, 3 H), 3.86 (s, 3 H), 7.39–7.25 (m, 6 H), 7.47–7.50 (m, 2 H), 7.60 (d, *J* = 1.9 Hz, 1 H), 8.11 (d, *J* = 1.9 Hz, 1 H).

^{13}C NMR: δ = 52.50 (CH_3), 52.77 (CH_3), 127.53 (CH), 128.42 (2 CH), 128.59 (2 CH), 129.00 (C), 129.22 (2 CH), 129.93 (2 CH), 132.21 (CH), 133.56 (C), 134.33 (C), 134.63 (C), 137.24 (C), 137.42 (C), 140.05 (C), 141.07 (C), 165.84 (C), 168.88 (C).

MS (ESI): *m*/*z* = 415 $[M + H]^+$, 432 $[M + NH_4]^+$, 437 $[M + Na]^+$.

Anal. Calcd for $C_{22}H_{16}Cl_2O_4$: C, 63.63; H, 3.88. Found: C, 63.45; H, 4.06.

Dimethyl 3,3″-Dichloro-1,1′:3′,1″-terphenyl-4′,5′-dicarboxylate (11d)

Yields: see Table 2; pale yellow oil; R_f = 0.29 (pentane–EtOAc, 5:1).

IR (ATR): 541 (w), 557 (w), 639 (w), 695 (s), 746 (m), 786 (s), 818 (w), 879 (m), 982 (w), 1067 (m), 1098 (m), 1123 (m), 1201 (m), 1242 (m), 1264 (m), 1339 (m), 1378 (w), 1433 (m), 1459 (m), 1476 (w), 1563 (w), 1594 (m), 1635 (w), 1651 (w), 1725 (s), 1772 (w), 1844 (m), 1917 (w), 2843 (w), 2951 (w), 3068 cm^{-1} (w).

^{1}H NMR: δ = 3.76 (s, 3 H), 3.98 (s, 3 H), 7.31–7.46 (m, 6 H), 7.53–7.56 (m, 1 H), 7.64 (s, 1 H), 7.73 (d, *J* = 1.8 Hz, 1 H), 8.24 (d, *J* = 1.8 Hz, 1 H).

^{13}C NMR: δ = 52.70 (CH_3), 52.77 (CH_3), 125.37 (CH), 126.80 (CH), 127.28 (CH), 127.85 (CH), 128.26 (CH), 128.43 (CH), 128.71 (CH), 129.07 (C), 129.62 (CH), 130.30 (CH), 132.30 (CH), 134.30 (C), 135.01 (C), 139.85 (C), 140.57 (C), 140.65 (C), 140.92 (C), 152.93 (C), 165.74 (C), 168.67 (C).

MS (ESI): *m*/*z* = 432 $[M + NH_4]^+$.

Anal. Calcd for $C_{22}H_{16}Cl_2O_4$: C, 63.63; H, 3.88. Found: C, 63.95; H, 4.16.

Dimethyl 1,1′:4′,1″:3″,1‴:4‴,1⁗-Quinquephenyl-4″,5″-dicarboxylate (11e)

Yields: see Table 2; pale yellow solid; mp 169 °C; R_f = 0.19 (pentane–EtOAc, 5:1).

IR (ATR): 544 (m), 561 (s), 626 (m), 651 (m), 694 (s), 721 (s), 746 (s), 762 (s), 795 (m), 835 (s), 870 (m), 902 (m), 954 (m), 968 (m), 1002 (m), 1022 (m), 1069 (m), 1116 (s), 1197 (m), 1238 (s), 1274 (s), 1341 (m), 1432 (m), 1458 (m), 1486 (m), 1516 (w), 1601 (m), 1636 (w), 1652 (m), 1682 (m), 1698 (m), 1723 (s), 1771 (w), 2030 (w), 2056 (w), 2853 (w), 2922 (w), 2947 (w), 2998 (w), 3029 cm^{-1} (w).

^{1}H NMR: δ = 3.75 (s, 3 H), 3.97 (s, 3 H), 7.38–7.41 (m, 2 H), 7.45–7.54 (m, 7 H), 7.64–7.71 (m, 6 H), 7.74 (d, *J* = 4.1 Hz, 3 H), 7.87 (d, *J* = 1.9 Hz, 1 H), 8.29 (d, *J* = 1.9 Hz, 1 H).

^{13}C NMR: δ = 52.48 (CH_3), 52.74 (CH_3), 127.08 (3 CH), 127.10 (3 CH), 127.39 (CH), 127.54 (CH), 127.60 (2 CH), 127.63 (CH), 127.75 (2 CH), 128.85 (2 CH), 128.88 (2 CH), 128.92 (C), 129.05 (2 CH), 132.53 (CH), 133.35 (C), 137.85 (C), 138.20 (C), 140.32 (C), 140.44 (C), 140.80 (C), 140.86 (C), 141.23 (C), 141.77 (C), 166.20 (C), 169.34 (C).

MS (ESI): *m*/*z* = 521 $[M + Na]^+$.

Anal. Calcd for $C_{34}H_{26}O_4$: C, 81.91; H, 5.26. Found: C, 81.72; H, 4.98.

Dimethyl 4,4″-Dimethoxy-1,1′:3′,1″-terphenyl-4′,5′-dicarboxylate (11f)

Yields: see Table 2; yellow oil; R_f = 0.29 (pentane–EtOAc, 3:1).

IR (ATR): 557 (m), 576 (w), 640 (w), 688 (w), 746 (m), 769 (m), 786 (m), 823 (s), 891 (w), 982 (m), 1024 (s), 1057 (m), 1071 (m), 1182 (m), 1176 (s), 1203 (m), 1239 (s), 1339 (w), 1391 (w), 1428 (m), 1458 (m), 1515 (m), 1541 (w), 1559 (w), 1577 (w), 1604 (m), 1652 (w), 1724 (s), 1773 (w), 1844 (w), 2055 (w), 2837 (w), 2951 (w), 3030 cm^{-1} (w).

^{1}H NMR: δ = 3.72 (s, 3 H), 3.85 (s, 3 H), 3.86 (s, 3 H), 3.94 (s, 3 H), 7.93–7.02 (m, 4 H), 7.35 (d, *J* = 8.9 Hz, 2 H), 7.58 (d, *J* = 8.9 Hz, 2 H), 7.70 (d, *J* = 1.9 Hz, 1 H), 8.15 (d, *J* = 1.9 Hz, 1 H).

^{13}C NMR: δ = 52.32 (CH_3), 52.58 (CH_3), 55.23 (CH_3), 55.35 (CH_3), 113.75 (2 CH), 114.40 (2 CH), 126.61 (CH), 128.27 (2 CH), 128.67 (C), 129.75 (2 CH), 131.51 (C), 131.71 (C), 132.18 (CH), 132.69 (C), 140.75 (C), 141.69 (C), 159.37 (C), 159.85 (C), 166.30 (C), 166.49 (C).

MS (ESI): *m*/*z* = 407 $[M + H]^+$, 424 $[M + NH_4]^+$.

Anal. Calcd for $C_{24}H_{22}O_6$: C, 70.92; H, 5.46. Found: C, 70.67; H, 5.52.

Dimethyl 2,2″-Dimethoxy-1,1′:3′,1″-terphenyl-4′,5′-dicarboxylate (11g)

Yields: see Table 2; yellow oil; R_f = 0.29 (pentane–EtOAc, 3:1).

IR (ATR): 570 (m), 632 (w), 751 (s), 794 (m), 826 (w), 851 (w), 874 (w), 903 (w), 934 (w), 973 (m), 1022 (s), 1044 (m), 1064 (m), 1107 (s), 1125 (s), 1174 (s), 1195 (s), 1244 (s), 1341 (m), 1395 (w), 1434 (m), 1459 (m), 1495 (m), 1578 (s), 1602 (w), 1635 (w), 1651 (w),

1685 (w), 1725 (s), 1771 (w), 1828 (w), 1844 (w), 1869 (w), 1918 (w), 2838 (w), 2950 (w), 2998 cm^{-1} (w).

^1H NMR: δ = 3.56 (s, 3 H), 3.67 (s, 3 H), 3.73 (s, 3 H), 3.82 (s, 3 H), 6.85–6.99 (m, 4 H), 7.17–7.20 (m, 1 H), 7.24–7.31 (m, 3 H), 7.61 (d, *J* = 2.0 Hz, 1 H), 8.03 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR: δ = 52.01 (CH_3), 52.47 (CH_3), 55.47 (CH_3), 55.58 (CH_3), 110.79 (CH), 111.30 (CH), 120.27 (CH), 120.90 (CH), 128.16 (C), 128.62 (C), 128.74 (C), 129.38 (CH), 129.43 (CH), 129.81 (CH), 130.77 (CH), 130.82 (CH), 133.13 (C), 135.97 (CH), 137.12 (C), 139.38 (C), 156.49 (C), 156.55 (C), 166.91 (C), 168.95 (C).

MS (ESI): *m*/*z* = 407 $[M + H]^+$, 424 $[M + NH_4]^+$.

Anal. Calcd for $C_{24}H_{22}O_6$: C, 70.92; H, 5.46. Found: C, 70.63; H, 5.70.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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(19) Crystallographic data for the structure **11e** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 869138. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or by writing to the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033; E-mail: deposit@ccdc.cam.ac.uk.

