Synthesis of Dimethyl Tetraarylphthalates by *Suzuki–Miyaura* Reactions of Dimethyl Tetrabromophthalate

by **Nadi Eleya**[a]), **Tamás Patonay**[b]), **Alexander Villinger**[a]), and **Peter Langer***[a])[c])

[a]) Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, D-18059 Rostock (fax: +381-4986412; e-mail: peter.langer@uni-rostock.de)

[b]) Department of Organic Chemistry, University of Debrecen, Egyetem tér 1, H-4032 Debrecen

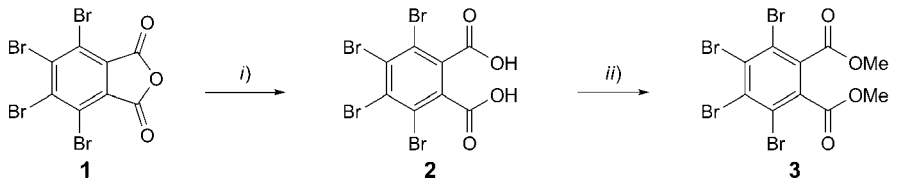
[c]) Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, D-18059 Rostock

Tetraarylphthalates were prepared by *Suzuki–Miyaura* reactions of dimethyl tetrabromophthalate.

Introduction. – *Beller* and co-workers reported the synthesis of substituted phthalates by domino reactions [1]. Phthalates have also been prepared by transition metal-catalyzed [2 + 2 + 2] cycloadditions of alkynes [2]. Several phthalate syntheses are based on the *Dields–Alder* reaction [3]. Hydroxylated phthalates are available by [4 + 2] cycloaddition of 1,3-bis(silyoxy)buta-1,3-dienes with dimethyl acetylene-1,3-dicarboxylate [4]. We have reported the synthesis of chlorinated, fluorinated, and arylsulfanyl-substituted phthalates by [4 + 2] cycloadditions of functionalized 1,3-bis(trimethylsilyloxy) 1,3-dienes with dimethyl acetylenedicarboxylate [5]. We have also reported the synthesis of hydroxylated phthalates by formal [3 + 3] cyclization reactions [6]. 4-Hydroxy- and 2,4-dihydroxyhomophthalates were prepared by [4 + 2] cycloaddition of 1,3-bis(silyoxy)buta-1,3-dienes with dimethyl allene-1,3-dicarboxylate [7]. Herein, we report a new and convenient approach to dimethyl tetraarylphthalates by fourfold *Suzuki–Miyaura* reaction of dimethyl tetrabromophthalate.

Results and Discussion. – Commercially available tetrabromophthalic anhydride (**1**) was converted to the corresponding diacid **2**, which was treated with *Hünig*'s base (EtN^iPr_2) and dimethyl sulfate in DMF to give dimethyl tetrabromophthalate (**3**; *Scheme*).

Scheme

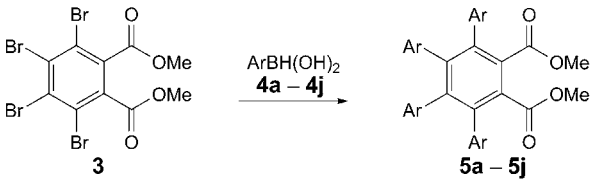


1 **2** **3**

i) KOH (2.0%), reflux (30 min), HCl (20%). *ii*) Me_2SO_4 (4.4 equiv.), EtN^iPr_2 (1.5 equiv.), DMF, 85°, 1 h.

The *Suzuki–Miyaura* reaction of **3** with arylboronic acids ($ArBH(OH)_2$) **4a – 4j** afforded the tetraarylphthalates **5a – 5j**, respectively, in 72 – 90% yields (*Table*). The best yield was obtained for **5f**, derived from the highly reactive, electron-rich 4-methoxyphenylboronic acid. Relatively low yield was obtained for product **5i** derived from an arylboronic acid containing an electron-withdrawing substituent. All attempts to achieve a position-selective reaction of **3** failed. The reaction of **3** with 2.0 equiv. of arylboronic acids resulted in the formation of complex mixtures.

Table. *Synthesis of Dimethyl Tetraarylphthalates* **5a – 5j**[a])



3 **5a – 5j**

4 and **5**	Ar	**5** [%][b])	**4** and **5**	Ar	**5** [%][b])
a	4-Me–C_6H_4	86	**f**	4-MeO–C_6H_4	90
b	3-Me–C_6H_4	85	**g**	4-F–C_6H_4	79
c	3,5-Me_2–C_6H_3	80	**h**	4-Cl–C_6H_4	77
d	4-Et–C_6H_4	79	**i**	4-F_3C–C_6H_4	73
e	4-^{t}Bu–C_6H_4	88	**j**	Ph	80

[a]) Reaction conditions: **4a – 4j** (4.5 equiv.), [$Pd(Ph_3P)_4$] (12 mol-%), K_2CO_3 (2M, 1 ml), 1,4-dioxane, 130°, 6 h. [b]) Yield of isolated product.

The structures of all products were confirmed by spectroscopic methods. The structure of **5c** was independently confirmed by an X-ray crystal-structure analysis (*Fig.*)[1]). The aryl groups are twisted out of plane, due to steric interaction. The vicinal CO_2Me groups possess an *anti*-arrangement of the two C=O groups, due to dipolar minimization.

In conclusion, we accomplished a novel synthesis of dimethyl tetraarylphthalates by, to the best of our knowledge, the first, *Suzuki–Miyaura* reactions of dimethyl tetrabromophthalate.

Experimental Part

General. Reactions were carried out under inert atmosphere (*Argon 4.6*) in order to simultaneously exclude O_2 and H_2O when appropriate. Pressure tubes were used to avoid condenser. Solvents for reactions were dried and distilled by standard methods, or purchased from *Merck®*, *Aldrich®*, *Acros Organics®*, and others, whenever exclusion of H_2O was desired. Solvents for liquid chromatography and

1) CCDC-887666 contains all crystallographic details of this publication and is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or can be ordered from the following address: Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk.

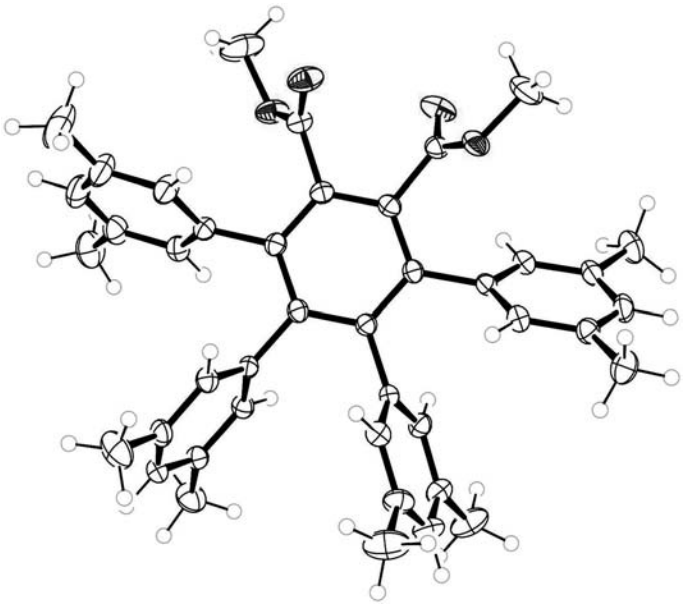


Figure. *ORTEP Plot of dimethyl 3,4,5,6-tetrakis(3,5-dimethylphenyl)benzene-1,2-dicarboxylate* (**5c**)

extraction were always distilled prior to use and partly reused after fractional distillation (heptane, AcOEt). TLC: *Merck Kieselgel 60 F254* on aluminium foil from *Macherey-Nagel*; detection was carried out under UV light at 254 nm and 365 nm, as colorizing reagent the following mixtures were used: 1–2/100 *p*-Anisaldehyde or vanillin, 10% glacial AcOH, 5% H_2SOH acid, 83–84% MeOH. Column Chromatography (CC): *Merck* silica gel *60* or *Macherey-Nagel* silica gel *60* (SiO_2, 0.063–0.200 mm, 70–230 mesh), the finer *Merck* silica gel *60* (0.040–0.063 mm, 230–400 mesh) was chosen when appropriate. M.p.: Micro heating table *HMK 67/1825 Kuestner* (*Büchi* Apparatus); *Leitz Labolux 12 Pol* with heating table *Mettler FP 90*; uncorrected. NMR Spectra: *Bruker AC 250*, *Bruker ARX 300*, *Bruker ARX 500*. For NMR characterization, the one-dimensional ^{1}H-NMR, H-decoupled ^{13}C-NMR, and DEPT 135 spectra were recorded. If necessary, other techniques (NOESY, COSY, HMQC, and HMBC) were applied as well. All NMR spectra presented in this work, were recorded in (D_6)DMSO and $CDCl_3$; δ in ppm rel. to Me_4Si or residual $CHCl_3$ as internal standard, *J* in Hz. MS: *AMD MS40*, *Varian MAT CH 7*, *MAT 731* (EI, 70 eV.), *Intecta AMD 402* (EI, 70 eV, and CI), *Finnigan MAT 95* (CI, 200 eV); in *m*/*z*. HR-MS: *Varian MAT 311*, *Intecta AMD 402*; in *m*/*z*. Elemental Analysis: *LECO CHNS-932 Thermoquest Flash EA 1112*. X-Ray crystal structure analysis: *Bruker X8Apex* diffractometer with CCD-Kamera (MoK_α und graphite monochromator, $\lambda = 0.71073$ Å) or *Bruker Apex Kappa-II* CCD diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.71073$).

Synthesis of Dimethyl 3,4,5,6-Tetrabromobenzene-1,2-dicarboxylate (**3**). To an aq. soln. of KOH (2%, 50 ml) was added **1** (0.5 g, 0.107 mmol). The mixture was heated under reflux for 30 min. After cooling to r.t., HCl (20%; 50 ml) was added, and the white precipitate was filtered and dried to give **2** (0.5 g, 96%). Then, Me_2SO_4 (0.58 g, 4.5 mmol) and EtN^iPr_2 (0.2 g, 1.56 mmol) were added to a soln. of **2** (0.5 g, 1.04 mmol) in DMF (50 ml). The mixture was heated for 1 h at 85°. After cooling to r.t., it was poured into ice-H_2O, and the white precipitate formed was filtered and dried to give **3** (0.5 g, 94%). M.p. 106–108°. IR (KBr): 3046*m*, 3017*m*, 2955*m*, 2845*m*, 1744*s*, 1721*s*, 1483*m*, 1432*m*, 1367*m*, 1330*m*, 1255*s*, 1236*s*, 1221*s*, 1147*s*, 1084*m*, 962*s*, 873*w*, 858*s*, 804*m*, 792*w*, 630*m*, 619*m*, 552*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.41 (*s*, 2 MeO). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 53.4 (MeO); 102.7; 132.3; 135.1; 135.1 (C); 165.1 (CO). GC/EI-MS (70 eV): 510 ($[M(^{79}Br_2{}^{81}Br_2)+1]^+$, 45), 508 ($[M(^{79}Br_3{}^{81}Br)+1]^+$, 29), 506 ($[M(^{79}Br_4)+1]^+$, 6),

483 (17), 481 (85), 480 (10), 479 (100), 477 (86), 475 (18). HR-EI-MS (70 eV): 505.700002 ($M(^{79}Br_4)^+$, $C_{10}H_6Br_4O_4^+$; calc. 505.69941); 507.697997 ($M(^{79}Br_3{}^{81}Br)^+$, $C_{10}H_6\ Br_4O_4^+$; calc. 507.69736); 509.6961 ($M(^{79}Br_2{}^{81}Br_2)^+$, $C_{10}H_6O_4^+$; calc. 509.69532).

General Procedure for Suzuki–Miyaura *Reactions.* A soln. of **3** (75 mg, 0.147 mmol), K_2CO_3 (2M, 1.0 ml), [$Pd(Ph_3P)_4$] (12 mol-%), and of $ArBH(OH_2$ (**4**; 4.5 equiv.) in 1,4-dioxane (4 ml) was stirred at 130° for 6 h under Ar in a *Schlenk* vessel. Then, H_2O (20 ml) and CH_2Cl_2 (25 ml) were added at 20°. Org. and aq. layers were separated, and the latter was extracted with CH_2Cl_2 (2 × 20 ml). The combined org. layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by (CC SiO_2; heptane/AcOEt).

Dimethyl 3,4,5,6-Tetrakis(4-methylphenyl)benzene-1,2-dicarboxylate (**5a**). From **3** (75 mg, 0.15 mmol), **4a** (90 mg, 0.66 mmol), [$Pd(Ph_3P)_4$] (20 mg, 12 mol-%, 0.021 mmol), K_2CO_3 (2M, 1.0 ml), and 1,4-dioxane (3 ml): **5a** (70 mg, 86%). White solid. M.p. 245–247°. IR (KBr): 3024*w*, 2952*w*, 2920*w*, 1738*s*, 1727*s*, 1513*m*, 1435*s*, 1340*s*, 1247*s*, 1221*s*, 1210*s*, 1189*s*, 1171*s*, 1149*m*, 1111*m*, 1060*m*, 969*s*, 806*m*, 791*s*, 756*w*, 727*s*, 541*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.01 (*s*, 2 Me); 2.15 (*s*, 2 Me); 3.41 (*s*, MeO); 6.43 (*d*, *J* = 7.8, 4 arom. H); 6.57 (*d*, *J* = 7.8, 4 arom. H); 6.82 (*s*, 8 arom. H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 21.0; 21.7 (Me); 52.1 (MeO); 127.5; 128.0; 129.5; 130.7 (CH); 132.0; 135.0; 135.8; 135.9; 136.0; 139.1; 143.3 (C); 168.9 (CO). GC/EI-MS (70 eV): 555 ([*M* + 1]$^+$, 51), 554 (M^+, 100), 491 (24), 464 (18), 433 (9), 262 (8). HR-EI-MS (70 eV): 554.245113 (M^+, $C_{38}H_{34}O_4^+$; calc.554.24516).

Dimethyl 3,4,5,6-Tetrakis(3-methylphenyl)benzene-1,2-dicarboxylate (**5b**). From **3** (75 mg, 0.15 mmol), **4b** (90 mg, 0.66 mmol), [$Pd(Ph_3P)_4$] (20 mg, 12 mol-%, 0.021 mmol), K_2CO_3 (2M, 1.0 ml), and 1,4-dioxane (4 ml): **5b** (69 mg, 85%) White solid. M.p. 170–173°. IR (KBr): 3098*w*, 3015*w*, 2947*w*, 2919*w*, 1740*s*, 1724*s*, 1605*m*, 1435*m*, 1344*m*, 1069*m*, 779*s*, 707*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.90 (*s*, 2 Me); 2.08 (*s*, 2 Me); 3.41 (*s*, MeO); 6.40–6.46 (*m*, 4 arom. H); 6.55–6.65 (*m*, 4 arom. H); 6.73–6.82 (*m*, 6 arom. H); 6.89–6.97 (*m*, 2 arom. H). ^{13}C-NMR (74.4 MHz, $CDCl_3$): 21.0; 21.2 (Me); 52.1 (MeO); 126.4; 126.8; 127.1; 127.4; 127.9; 130.5; 130.5; 131.7 (CH); 131.8; 135.9; 136.6; 138.5; 138.7; 139.1; 143.3 (C); 168.8 (CO). GC/EI-MS (70 eV): 555 ([*M* + H]$^+$, 38), 554(M^+, 100), 491 (30). HR-EI-MS (70 eV): 554.244093 (M^+, $C_{38}H_{34}O_4^+$; calc. 554.24516).

Dimethyl 3,4,5,6-Tetrakis(3,5-dimethylphenyl)benzene-1,2-dicarboxylate (**5c**). From **3** (75 mg, 0.15 mmol), **4c** (99 mg, 0.66 mmol), [$Pd(Ph_3P)_4$] (20 mg, 12 mol-%, 0.021 mmol), K_2CO_3 (2M, 1.0 ml), and 1,4-dioxane (4 ml): **5c** (71 mg, 80%). White solid. M.p. 205–207°. IR (KBr): 3022*w*, 3002*w*, 2943*w*, 1738*s*, 1722*s*, 1600*s*, 1434*m*, 1428*m*, 1377*m*, 1355*m*, 1297*m*, 1282*w*, 1246*s*, 1208*s*, 1197*s*, 1157*m*, 1145*m*, 1104*m*, 1099*m*, 1026*m*, 870*m*, 860*m*, 841*s*, 808*m*, 700*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.87 (*s*, 4 Me); 2.04 (*s*, 4 Me); 3.42 (*s*, 2 MeO); 6.23 (*m*, 4 arom. H); 6.35 (*m*, 2 arom. H); 6.57 (*m*, 4 arom. H); 6.61 (*m*, 2 arom. H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 20.8; 21.0 (Me); 52.0 (MeO); 127.0; 127.6; 128.0; 128.7 (CH); 131.4; 135.4; 136.2; 138.4; 138.6; 139.0; 143.5 (C); 168.9 (CO). GC/EI-MS (70 eV): 611 ([*M* + H]$^+$, 38), 610 (M^+, 100), 609 (50), 548 (20), 547 (59), 546 (47), 519 (9). HR-EI-MS (70 eV): 610.308341 (M^+, $C_{42}H_{42}O_4^+$; calc. 610.30776).

Dimethyl 3,4,5,6-Tetrakis(4-ethylphenyl)benzene-1,2-dicarboxylate (**5d**). From **3** (75 mg, 0.15 mmol), **4d** (99 mg, 0.66 mmol), [$Pd(Ph_3P)_4$] (20 mg, 12 mol-%, 0.021 mmol), K_2CO_3 (2M, 1.0 ml), and 1,4-dioxane (4 ml): **5d** (79 mg, 88%). Yellow solid. M.p. 132–134°. IR (KBr): 3437*w*, 3084*w*, 3048*w*, 3021*w*, 2960*m*, 2929*m*, 1725*s*, 1514*m*, 1451*m*, 1435*m*, 1326*s*, 1234*s*, 1206*m*, 1189*m*, 1165*m*, 1156*m*, 1114*m*, 1061*s*, 1049*m*, 1023*m*, 967*s*, 858*s*, 842*s*, 831*m*, 819*m*, 813*m*, 797*m*, 733*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.90–0.95 (*m*, 2 Me); 1.03–1.09 (*m*, 2 Me); 2.29 (*q*, *J* = 7.5, 15.1, 2 CH_2); 2.45 (*q*, *J* = 7.5, 15.1, 2 Me); 3.39 (*s*, 2 MeO); 6.47 (*d*, *J* = 8.1, 4 arom. H); 6.58 (*d*, *J* = 8.1, arom. H); 6.84 (*s*, 8 arom. H). ^{13}C-NMR (74.4 MHz, $CDCl_3$): 15.4; 15.5 (Me); 28.3; 28.4 (CH_2); 52.1 (MeO); 126.1; 126.7; 129.6; 130.8 (CH); 132.0; 136.1; 136.2; 139.1; 141.5; 142.4; 143.5 (C); 169.0 (CO). GC/EI-MS (70 eV): 610 (M^+, 100), 547 (8), 516 (9). HR-EI-MS (70 eV): 610.307662 (M^+, $C_{38}H_{34}O_4^+$; calc. 610.30776).

Dimethyl 3,4,5,6-Tetrakis[4-(1,1-dimethylethyl)phenyl]benzene-1,2-dicarboxylate (**5e**). From **3** (75 mg, 0.15 mmol), **4e** (117 mg, 0.66 mmol), [$Pd(Ph_3P)_4$] (20 mg, 12 mol-%, 0.021 mmol), K_2CO_3 (2M, 1.0 ml), and 1,4-dioxane (4 ml): **5e** (93 mg, 88%). White solid. M.p. 217–219°. IR (KBr): 3031*w*, 2951*s*, 2902*w*, 2866*w*, 1727*s*, 1511*m*, 1436*m*, 1392*m*, 1361*m*, 1341*m*, 1332*m*, 1269*m*, 1240*s*, 1223*s*, 1199*s*, 1172*s*, 1165s, 1122*m*, 1105*m*, 1066*s*, 1016*s*, 972*s*, 863*m*, 849*m*, 837*m*, 819*m*, 787*m*, 622*s*, 572*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.01 (*s*, 6 Me); 1.13 (*s*, 6 Me); 3.39 (*s*, 2 MeO); 6.47 (*d*, *J* = 8.5, 4 arom. H); 6.74 (*d*,

$J = 8.5$, 4 arom. H); 6.84 (*d*, $J = 8.5$, 4 arom. H); 7.02 (*d*, $J = 8.5$, 4 arom. H). ^{13}C-NMR (74.4 MHz, $CDCl_3$): 31.1; 31.2 (Me); 34.1; 34.3 (C); 52.1 (MeO); 123.3; 124.0; 129.4; 130.5 (CH); 131.7; 135.8; 135.9; 139.2; 143.6; 148.32; 149.2 (C); 169.0 (CO). GC/EI-MS (70 eV): 723 ($[M+H]^+$, 47), 722 (M^+, 100), 676 (11), 661 (12), 531 (23), 489 (11), 475 (14). HR-EI-MS (70 eV): 722.433526 (M^+, $C_{50}H_{58}O_4^+$; calc. 722.43296).

Dimethyl 3,4,5,6-Tetrakis(4-methoxyphenyl)benzene-1,2-dicarboxylate (**5f**). From **3** (75 mg, 0.147 mmol), **4f** (100 mg, 0.66 mmol), [$Pd(Ph_3P)_4$] (20 mg, 12 mol-%, 0.021 mmol), K_2CO_3 (2M, 1.0 ml), and 1,4-dioxane (4 ml): **5f** (81 mg, 90%). White solid. M.p. 253–255°. IR (KBr): 3039*w*, 3003*w*, 2952*w*, 1742*s*, 1721*s*, 1609*s*, 1575*m*, 1515*s*, 1461*m*, 1435*m*, 1417*m*, 1343*m*, 1306*w*, 1286*s*, 1237*s*, 1194*m*, 1174*s*, 1151*m*, 1109*m*, 1064*s*, 1029*s*, 968*m*, 794*s*, 546*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.43 (MeO); 3.54 (MeO); 3.64 (MeO); 6.34 (*d*, $J = 8.7$, 4 arom. H); 6.50 (*d*, $J = 8.7$, 4 arom. H); 6.60 (*d*, $J = 8.7$, 4 arom. H); 6.85 (*d*, $J = 8.7$, arom. H). ^{13}C-NMR (74.4 MHz, $CDCl_3$): 52.2; 54.9; 55.0 (MeO); 112.5; 112.9; 130.8 (CH); 131.3; 131.3 (C); 131.9 (CH); 132.1; 138.9; 143.3; 157.3; 158.1 (C); 168.9 (CO). GC/EI-MS (70 eV): 619 ($[M+H]^+$, 35), 618 (M^+, 100), 512 (8), 262 (14). HR-EI-MS (70 eV): 618.224059 (M^+, $C_{38}H_{34}O_8^+$; calc. 618.22482).

Dimethyl 3,4,5,6-Tetrakis(4-fluorophenyl)benzene-1,2-dicarboxylate (**5g**). From **3** (75 mg, 0.15 mmol), **4g** (92 mg, 0.66 mmol), [$Pd(Ph_3P)_4$] (20 mg, 12 mol-%, 0.021 mmol), K_2CO_3 (2M, 1.0 ml), and 1,4-dioxane (4 ml): **5g** (66 mg, 80%). White solid. M.p. 198–200°. IR (KBr): 3065*w*, 3052*w*, 3005*w*, 1740*s*, 1727*s*, 1604*s*, 1512*s*, 1439*s*, 1421*m*, 1395*m*, 1340*s*, 1256*s*, 1218*s*, 1197*s*, 1177*m*, 1162*s*, 1154*s*, 1095*s*, 1056*s*, 1013*m*, 967*s*, 860*m*, 845*m*, 829*s*, 803*s*, 545*s*, 530*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.45 (*s*, 2 MeO); 6.55 (*d*, $J = 7.0$, 8 arom. H); 6.75–6.80 (*m*, 4 arom. H); 6.88–6.93 (*m*, 4 arom. H). ^{13}C-NMR (74.4 MHz, $CDCl_3$): 52.4 (MeO); 113.7 (*d*, $J = 21.4$); 114.1 (*d*, $J = 21.4$); 130.6 (*d*, $J = 8.0$); 131.6 (*d*, $J = 8.0$, CH); 131.9; 133.5 (*d*, $J = 3.6$); 133.6 (*d*, $J = 3.6$); 138.0; 142.0; 160.4 (*d*, J(C,F) = 245.5, CF); 161.1 (*d*, J(C,F) = 245.5 Hz, CF); 167.6 (CO). GC/EI-MS (70 eV): 571 ($[M+H]^+$, 31), 570 (M^+, 100), 540 (15), 539 (47), 507 (22). HR-EI-MS (70 eV): 570.144951 (M^+, $C_{34}H_{22}F_4O_4^+$; calc. 570.14487).

Dimethyl 3,4,5,6-Tetrakis(4-chlorophenyl)benzene-1,2-dicarboxylate (**5h**). From **3** (75 mg, 0.15 mmol), **4h** (103 mg, 0.66 mmol), [$Pd(Ph_3P)_4$] (20 mg, 12 mol-%, 0.021 mmol), K_2CO_3 (2M, 1.0 ml), and 1,4-dioxane (4 ml): **5h** (72 mg, 77%). Yellow solid. M.p. 284–286°. IR (KBr): 3032*w*, 2993*w*, 2949*w*, 1744*s*, 1718*s*, 1492*s*, 1437*s*, 1393*m*, 1340*s*, 1332*s*, 1244*s*, 1223*s*, 1195*s*, 1171*s*, 1152*m*, 1089*s*, 1059*s*, 1013*s*, 966*m*, 914*m*, 862*s*, 834*s*, 813*s*, 782*s*, 752*s*, 743*s*, 732*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.45 (*s*, 2 MeO); 6.53 (*d*, $J = 8.5$, 4 arom. H); 6.82–6.88 (*m*, 8 arom. H); 7.06 (*d*, $J = 8.5$, arom. H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 51.5 (MeO); 126.7; 127.0; 129.8; 130.8 (CH); 131.6; 132.4; 135.3; 135.5; 137.4; 141.0 (C); 166.9 (CO). GC/EI-MS (70 eV): 640 ($M(^{35}Cl^{37}Cl_3)^+$, 10), 638 ($M(^{35}Cl_2{}^{37}Cl_2)^+$, 46), 636 ($M(^{35}Cl_3{}^{37}Cl)^+$, 100), 634 ($M(^{35}Cl_4)^+$, 68), 607 (11), 605 (22), 603 (17). HR-EI-MS (70 eV): 638.020486 (for $M(^{35}Cl_2{}^{37}Cl_2)^+$, $C_{34}H_{22}Cl_{44}^+$, calc. 638.02077), 636.021757 ($M(^{35}Cl^{37}Cl_3)^+$, $C_{34}H_{22}Cl_4O_4^+$; calc. 636.02372), 634.025016 ($M(^{35}Cl_3{}^{37}Cl)^+$, $C_{34}H_{22}Cl_4O_4^+$;calc. 634.0266).

Dimethyl 3,4,5,6-Tetrakis[4-(trifluoromethyl)phenyl]benzene-1,2-dicarboxylate (**5i**). From **3** (75 mg, 0.15 mmol), **4i** (125 mg, 0.66 mmol), [$Pd(Ph_3P)_4$] (20 mg, 12 mol-%, 0.021 mmol), K_2CO_3 (2M, 1.0 ml), and 1,4-dioxane (4 ml): **5i** (82 mg, 73%). White solid. M.p. 234–235°. IR (KBr): 2959*w*, 1737*s*, 1693*w*, 1617*m*, 1441*m*, 1405*m*, 1321*s*, 1243*m*, 1231*m*, 1158*s*, 1106*s*, 1064*s*, 1052*s*, 1018*s*, 971*m*, 890*w*, 883*w*, 869*m*, 847*m*, 825*m*, 814*m*, 797*m*, 711*m*, 703*m*, 613*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.43 (*s*, 2 MeO); 6.74 (*d*, $J =$ 8.0, 4 arom. H); 7.10 (*t*, $J = 8.1$, 16.5, 8 arom. H); 7.36 (*d*, $J = 8.1$, 4 arom. H). ^{13}C-NMR (74.4 MHz, $CDCl_3$): 52.6 (MeO); 123.5 (*q*, J(C,F) = 270.5, CF_3); 123.7 (*q*, J(C,F) = 270.5, CF_3); 124.4 (*d*, J(C,F) = 3.7, CH); 124.8 (*d*, J(C,F) = 3.7, CH); 129.2 (*q*, J(C,F) = 32.4, C); 129.7 (*q*, J(C,F) = 32.4, C); 129.9, 130.8 (CH); 138.6; 141.1; 141.4; 141.4; 141.7 (C); 167.5 (CO). ^{19}F-NMR (282.40 MHz, $CDCl_3$): −62.96; −62.81 (CF_3). GC/EI-MS (70 eV): 771 ($[M+H]^+$, 34), 770 (M^+, 94), 751 (11), 740 (35), 739 (100), 707 (12). HR-EI-MS (70 eV): 770.130669 (M^+, $C_{38}H_{22}F_{12}O_4^+$; calc. 770.13210).

Dimethyl 3,4,5,6-Tetraphenylbenzene-1,2-dicarboxylate (**5j**). From **3** (75 mg, 0.15 mmol), **4j** (80 mg, 0.66 mmol), [$Pd(Ph_3P)_4$] (20 mg, 12 mol-%, 0.021 mmol), K_2CO_3 (2M, 1.0 ml), and 1,4-dioxane (4 ml): **5j** (57 mg, 80%). White solid. M.p. 215–217°. IR (KBr): 3080*w*, 3052*w*, 3026*w*, 3004*w*, 2950*w*, 1720*s*, 1496*m*, 1440*m*, 1434*m*, 1410*m*, 1335*m*, 1241*s*, 1225*s*, 1196*m*, 1171*m*, 1158*m*, 1153*m*, 1065*s*, 1030*m*, 999*m*, 963*m*, 912*m*, 886*m*, 841*m*, 820*m*, 799*m*, 761*s*, 716s, 708*s*, 697*s*, 567*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.40 (*s*, 2 MeO); 6.60–6.64 (*m*, 4 arom. H); 6.76–6.78 (*m*, 6 arom. H); 6.94–6.98 (*m*, 4 arom. H); 7.01–7.04 (*m*, 6

arom. H). ^{13}C-NMR (74.4 MHz, $CDCl_3$): 52.2 (MeO); 125.9; 126.8; 126.9; 127.4; 129.7; 130.8 (CH); 132.2; 138.6; 138.7; 139.3; 143.2 (C); 168.7 (CO). GC/EI-MS (70 eV): 499 ($[M+H]^+$, 37), 498 (M^+, 100), 467 (16), 436 (13), 435 (38), 377 (11), 376 (11), 363 (8). HR-EI-MS (70 eV): 498.182831 (M^+, $C_{34}H_{26}O_4^+$; calc.498.18256).

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