

Supporting Information

Transition-Metal-Free Multicomponent Benzannulation Reactions for the Construction of Polysubstituted Benzene Derivatives

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Supporting Information

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Experimental Section

1. General Methods

All substrates and reagents were commercial and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200-300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1} . ^1H NMR spectra were determined at 25 °C on a Varian Mercury 600 MHz spectrometer. Chemical shifts are given in ppm relative to the internal standard of tetramethylsilane (TMS). HRMS were obtained on an Apex-Ultra MS equipped with an atmospheric-pressure chemical ionization (APCI) source or electrospray ionization (ESI) source. Melting points were determined using XT-4 apparatus and not corrected. The X-ray crystal-structure determinations were obtained on a Bruker APEX DUO CCD system.

2. General Experimental Details

General procedure for the synthesis of **4a-4l** and **5a-5k** (**4a** as example).

The mixture of ethyl benzoylacetate **1a** (192.1 mg, 1.0 mmol), trans- β -nitrostyrene **2a** (149.1 mg, 1.0 mmol), dimethyl acetylenedicarboxylate **3a** (142.1 mg, 1.0 mmol) and K_3PO_4 (636.9 mg, 3.0 mmol) was added in EtOAc (5 mL). Then, the resulting mixture was stirred at reflux for 2 h. After the reaction completed, and then added 100 mL water to the mixture, extracted with EtOAc three times (3×100 mL). Dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 8/1) to afford the desired product **4a**.

3. The Crystallographic Data

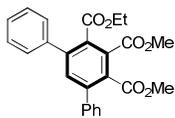
Table S1. The crystallographic data of **4a** (CCDC: 1415429).

Empirical formula	C ₂₂ H ₂₂ O ₆		Absorption coefficient	0.087 mm ⁻¹
Formula weight	418.43		F(000)	808
Temperature	296(2) K		Crystal size	0.20 x 0.20 x 0.20 mm ³
Wavelength	0.71073 Å		Reflections collected	7282
Crystal system	Triclinic		Independent reflections	5182 [R(int) = 0.0477]
Space group	P-1		Max. and min. transmission	0.9828 and 0.9828
Unit cell dimensions	a = 10.1670(17) Å	∠ = 68.165°	Refinement method Full	Full-matrix least-squares on F ²
	b = 11.5366(19) Å	∠ = 67.543°	Data / restraints / parameters	4178 / 43 / 314
	c = 11.951(2) Å	∠ = 79.903°	Goodness-of-fit on F ²	1.049
Volume	1201.7(3) Å ³		Final R indices [I>2σ(I)]	R1 = 0.0680, wR2 = 0.1885
Z	2		R indices (all data)	R1 = 0.0829, wR2 = 0.2095
Density (calculated)	1.156 Mg/m ³		Largest diff. peak and hole	0.510 and -0.290 e.Å ⁻³

Table S2. The crystallographic data of **6** (CCDC: 1415430).

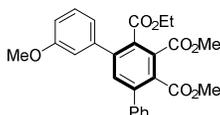
Empirical formula	C ₂₅ H ₂₅ NO ₉		Absorption coefficient	0.104 mm ⁻¹
Formula weight	483.46		F(000)	508
Temperature	298(2) K		Crystal size	0.20 x 0.20 x 0.20 mm ³
Wavelength	0.71073 Å		Reflections collected	5964
Crystal system	Triclinic		Independent reflections	2831 [R(int) = 0.0454]
Space group	P-1		Max. and min. transmission	
Unit cell dimensions	a = 10.930(9) Å	∠ = 113.763(11)°	Refinement method Full	Full-matrix least-squares on F ²
	b = 10.934(8) Å	∠ = 97.710(11)°	Data / restraints / parameters	2831 / 30 / 335
	c = 11.295(9) Å	∠ = 99.612(11)°	Goodness-of-fit on F ²	1.132
Volume	1187.3(17) Å ³		Final R indices [I>2sigma(I)]	R1 = 0.1281, wR2 = 0.3848
Z	2		R indices (all data)	R1 = 0.1482, wR2 = 0.4003
Density (calculated)	1.352 Mg/m ³		Largest diff. peak and hole	0.592 and -0.529 e.Å ⁻³

4. Spectroscopic Data



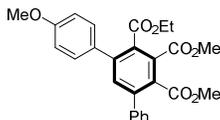
4'-ethyl 5',6'-dimethyl [1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**4a**):

Yield 89% (372.4 mg); White solid; m.p. 133–134 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.54 (s, 1H), 7.44 – 7.38 (m, 6H), 7.38 – 7.33 (m, 4H), 4.09 (q, $J = 7.2$ Hz, 2H), 3.88 (s, 3H), 3.63 (s, 3H), 1.02 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 168.1, 167.6, 166.9, 142.2, 142.0, 138.9, 138.8, 134.0, 132.1, 131.8, 130.7, 128.5, 128.4, 128.3, 128.2, 128.2, 61.6, 53.0, 52.5, 13.6; **IR (KBr, cm^{-1})**: 1729, 1594, 1452, 1441, 1434, 1347, 1278, 1250, 1242, 1226, 1187, 1147, 1069, 1020, 798, 759, 744, 705. **HRMS (ESI)**: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{22}\text{NaO}_6$: 441.1309; found: 441.1317.



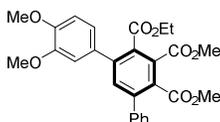
6'-ethyl 4',5'-dimethyl 3-methoxy-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**4b**):

Yield 72% (322.9 mg); White solid; m.p. 103–104 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.54 (s, 1H), 7.41 (t, $J = 7.2$ Hz, 3H), 7.36 (d, $J = 7.8$ Hz, 2H), 7.31 (t, $J = 7.8$ Hz, 1H), 6.98 – 6.92 (m, 2H), 6.90 (s, 1H), 4.11 (q, $J = 6.6$ Hz, 2H), 3.88 (s, 3H), 3.81 (s, 3H), 3.63 (s, 3H), 1.06 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 168.1, 167.6, 166.8, 159.5, 142.0, 142.0, 140.2, 138.8, 133.9, 132.0, 131.8, 130.7, 129.5, 128.5, 128.2, 128.2, 120.7, 114.1, 113.6, 61.7, 55.3, 53.0, 52.5, 13.6; **IR (KBr, cm^{-1})**: 1728, 1593, 1578, 1498, 1439, 1347, 1279, 1253, 1232, 1188, 1143, 1071, 1037, 1018, 978, 767, 703. **HRMS (ESI)**: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{O}_7$: 449.1595; found: 449.1597.



6'-ethyl 4',5'-dimethyl 4-methoxy-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**4c**):

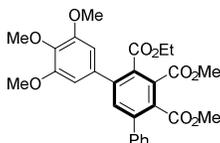
Yield 79% (354.3 mg); White solid; m.p. 136–137 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.51 (s, 1H), 7.40 (t, $J = 7.8$ Hz, 3H), 7.35 (d, $J = 6.6$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 6.94 (d, $J = 8.4$ Hz, 2H), 4.13 (q, $J = 7.2$ Hz, 2H), 3.88 (s, 3H), 3.84 (s, 3H), 3.62 (s, 3H), 1.09 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 168.2, 167.8, 166.9, 159.6, 141.9, 141.8, 138.9, 134.0, 132.0, 131.4, 131.2, 130.6, 129.5, 128.4, 128.2, 113.9, 61.6, 55.3, 53.0, 52.4, 13.7; **IR (KBr, cm^{-1})**: 1742, 1718, 1607, 1594, 1514, 1446, 1438, 1346, 1282, 1250, 1219, 1179, 1148, 1071, 1027, 1016, 841, 707. **HRMS (ESI)**: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{O}_7$: 449.1595; found: 449.1598.



6'-ethyl 4',5'-dimethyl 3,4-dimethoxy-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**4d**):

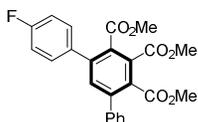
Yield 80% (354.3 mg); White solid; m.p. 127–129 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.54 (s, 1H), 7.45 – 7.39 (m, 3H), 7.36 (d, $J = 6.0$ Hz, 2H), 6.98 – 6.86 (m, 3H), 4.13 (q, $J = 7.2$ Hz,

2H), 3.92 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.63 (s, 3H), 1.09 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 168.1, 167.9, 166.8, 149.0, 148.7, 141.9, 141.8, 138.9, 133.9, 132.0, 131.5, 130.7, 128.5, 128.2, 128.2, 120.8, 111.5, 110.9, 61.7, 55.9, 55.9, 53.0, 52.5, 13.8; **IR** (KBr , cm^{-1}): 1733, 1714, 1593, 1519, 1466, 1439, 1421, 1348, 1260, 1246, 1227, 1179, 1146, 1108, 1075, 762, 702. **HRMS (ESI)**: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{26}\text{NaO}_8$: 501.1520; found: 501.1520.



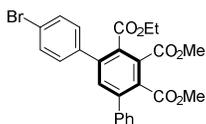
6'-ethyl 4',5'-dimethyl 3,4,5-trimethoxy-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**4e**):

Yield 83% (422.1 mg); White solid; m.p. 126–129 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.56 (s, 1H), 7.42 (t, $J = 7.2$ Hz, 3H), 7.37 (d, $J = 7.8$ Hz, 2H), 6.58 (s, 2H), 4.14 (q, $J = 7.2$ Hz, 2H), 3.89 (s, 2H), 3.88 (s, 3H), 3.85 (s, 5H), 3.63 (s, 3H), 1.08 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 168.0, 167.8, 166.8, 153.1, 142.0, 138.8, 137.9, 134.4, 133.7, 132.0, 131.7, 130.7, 128.5, 128.2, 128.1, 105.5, 61.8, 60.9, 56.1, 53.0, 52.5, 13.7; **IR** (KBr , cm^{-1}): 1735, 1584, 1506, 1464, 1449, 1439, 1416, 1360, 1299, 1277, 1233, 1211, 1187, 1125, 1106, 1087, 700. **HRMS (ESI)**: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{28}\text{NaO}_9$: 531.1626; found: 531.1632.



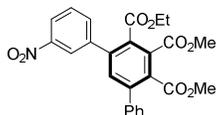
trimethyl 4-fluoro-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**4f**):

Yield 85% (359.0 mg); White solid; m.p. 174–175 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.51 (s, 1H), 7.44 – 7.38 (m, 3H), 7.38 – 7.30 (m, 4H), 7.11 (t, $J = 8.4$ Hz, 2H), 3.89 (s, 3H), 3.66 (s, 3H), 3.63 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 168.0, 166.6, 163.6, 161.9, 142.2, 141.0, 138.6, 134.7, 134.1, 132.1, 131.9, 130.5, 130.0, 130.0, 128.5, 128.3, 128.2, 115.6, 115.5, 53.1, 52.6, 52.5; **IR** (KBr , cm^{-1}): 1753, 1725, 1603, 1513, 1432, 1348, 1277, 1255, 1235, 1225, 1161, 1144, 1113, 1068, 855, 761, 703. **HRMS (ESI)**: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{20}\text{FO}_6$: 423.1238; found: 423.1230.



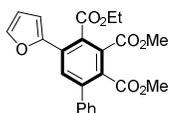
6'-ethyl 4',5'-dimethyl 4-bromo-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**4g**):

Yield 88% (436.6 mg); White solid; m.p. 143–144 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.54 (d, $J = 8.4$ Hz, 2H), 7.49 (s, 1H), 7.44 – 7.38 (m, 3H), 7.34 (d, $J = 6.6$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 4.12 (q, $J = 7.2$ Hz, 2H), 3.88 (s, 3H), 3.63 (s, 3H), 1.09 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 168.0, 167.3, 166.7, 142.2, 140.9, 138.6, 137.8, 133.8, 132.1, 131.9, 131.6, 130.8, 129.9, 128.5, 128.3, 128.1, 122.6, 61.8, 53.1, 52.5, 13.7; **IR** (KBr , cm^{-1}): 1744, 1732, 1595, 1490, 1437, 1406, 1348, 1289, 1230, 1185, 1145, 1111, 1010, 965, 821, 746, 700. **HRMS (ESI)**: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{21}\text{BrNaO}_6$: 519.0414; found: 519.0414.



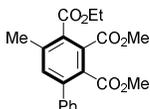
6'-ethyl 4',5'-dimethyl 3-nitro-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**4h**):

Yield 84% (389.3 mg); Yellow solid; m.p. 97–98 °C; ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.33 – 8.17 (m, 2H), 7.76 – 7.66 (m, 1H), 7.66 – 7.57 (m, 1H), 7.54 (s, 1H), 7.45 – 7.40 (m, 3H), 7.39 – 7.33 (m, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 3H), 3.65 (s, 2H), 1.12 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 167.7, 166.9, 166.4, 148.1, 142.5, 140.4, 139.5, 138.3, 134.4, 133.8, 132.9, 132.0, 131.1, 129.5, 128.6, 128.5, 128.2, 128.1, 123.4, 123.1, 62.0, 53.1, 52.6, 13.7; IR (KBr, cm⁻¹): 1741, 1632, 1594, 1530, 1439, 1352, 1222, 1146, 1108, 1017, 758, 736, 702, 687. HRMS (ESI): *m/z* [M+Na]⁺ calcd for C₂₅H₂₁NNaO₈: 486.1159; found: 486.1166.



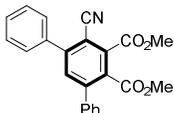
4-ethyl 2,3-dimethyl 5-(furan-2-yl)-[1,1'-biphenyl]-2,3,4-tricarboxylate (**4i**):

Yield 78% (318.6 mg); Yellow solid; m.p. 111–112 °C; ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.81 (s, 1H), 7.51 (s, 1H), 7.45 – 7.38 (m, 3H), 7.35 (d, *J* = 6.0 Hz, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 3.61 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 167.9, 167.8, 166.4, 150.1, 143.5, 142.1, 138.8, 131.9, 130.8, 130.5, 129.8, 129.5, 128.4, 128.2, 128.1, 112.0, 109.8, 62.0, 53.0, 52.4, 13.9; IR (KBr, cm⁻¹): 1740, 1600, 1436, 1331, 1294, 1282, 1256, 1241, 1229, 1212, 1187, 1173, 1165, 1139, 737, 710. HRMS (ESI): *m/z* [M+Na]⁺ calcd for C₂₃H₂₀NaO₇: 431.1101; found: 431.1101.



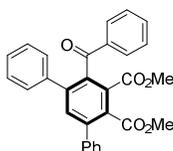
4-ethyl 2,3-dimethyl 5-methyl-[1,1'-biphenyl]-2,3,4-tricarboxylate (**4j**):

Yield 73% (260.2 mg); Yellow solid; m.p. 81–82 °C; ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.42 – 7.37 (m, 3H), 7.36 (s, 1H), 7.31 (d, *J* = 6.0 Hz, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.59 (s, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 168.2, 167.6, 166.9, 141.9, 139.0, 138.0, 134.6, 132.1, 130.8, 130.2, 128.3, 128.1, 128.0, 77.2, 77.0, 76.8, 61.7, 52.8, 52.3, 19.8, 14.0; IR (KBr, cm⁻¹): 3452, 1742, 1721, 1632, 1597, 1437, 1387, 1333, 1281, 1256, 1229, 1202, 1126, 1106, 1035, 1019, 764, 706. HRMS (ESI): *m/z* [M+Na]⁺ calcd for C₂₀H₂₀NaO₆: 379.1152; found: 379.1156.



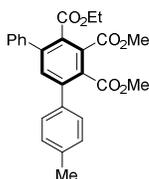
dimethyl 6'-cyano-[1,1':3',1''-terphenyl]-4',5'-dicarboxylate (**4k**):

Yield 54% (260.2 mg); White solid; m.p. 150–151 °C; ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.63 (s, 1H), 7.58 (d, *J* = 6.6 Hz, 2H), 7.54 – 7.48 (m, 3H), 7.47 – 7.41 (m, 3H), 7.41 – 7.33 (m, 2H), 4.02 (s, 3H), 3.65 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 167.1, 165.5, 147.9, 145.0, 138.1, 136.8, 136.3, 133.9, 132.2, 129.5, 128.9, 128.8, 128.7, 128.0, 115.8, 110.0, 109.3, 77.2, 77.0, 76.8, 53.5, 52.8; IR (KBr, cm⁻¹): 3449, 1739, 1717, 1632, 1591, 1450, 1431, 1386, 1349, 1288, 1243, 1126, 794, 752, 769, 705. HRMS (ESI): *m/z* [M+Na]⁺ calcd for C₂₃H₁₇NNaO₄: 394.1050; found: 394.1052.



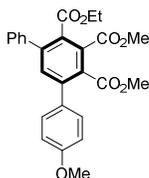
dimethyl 6'-cyano-[1,1':3',1''-terphenyl]-4',5'-dicarboxylate (**4I**):

Yield 67% (301.8 mg); Yellow solid; m.p. 199–200 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.64 (d, $J = 7.8$ Hz, 2H), 7.58 (s, 1H), 7.50 – 7.35 (m, 6H), 7.31 – 7.24 (m, 2H), 7.23 – 7.12 (m, 5H), 3.65 (s, 3H), 3.59 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 196.7, 168.4, 166.7, 142.1, 141.6, 138.8, 138.3, 137.2, 134.3, 133.0, 132.4, 130.7, 129.1, 129.0, 128.5, 128.2, 128.2, 128.2, 128.0, 52.7, 52.5; **IR (KBr, cm^{-1})**: 1737, 1726, 1661, 1596, 1449, 1429, 1288, 1276, 1250, 1216, 1177, 1129, 1070, 940, 709, 736, 699. **HRMS (ESI)**: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{29}\text{H}_{22}\text{NaO}_5$: 473.1359; found: 473.1359.



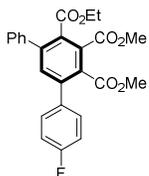
4'-ethyl 5',6'-dimethyl 4-methyl-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**5a**):

Yield 81% (350.3 mg); Yellow solid; m.p. 109–110 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.52 (s, 1H), 7.42 – 7.37 (m, 3H), 7.37 – 7.33 (m, 2H), 7.25 (d, $J = 8.4$ Hz, 3H), 7.21 (d, $J = 7.8$ Hz, 2H), 4.08 (q, $J = 7.2$ Hz, 2H), 3.88 (s, 3H), 3.66 (s, 3H), 2.39 (s, 3H), 1.01 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 168.2, 167.5, 166.8, 142.0, 141.9, 138.9, 138.0, 135.8, 133.9, 131.7, 131.5, 130.6, 129.1, 128.3, 128.1, 128.0, 127.9, 61.5, 52.9, 52.4, 21.1, 13.5; **IR (KBr, cm^{-1})**: 3449, 1737, 1632, 1593, 1434, 1385, 1348, 1279, 1245, 1220, 1189, 1144, 1108, 1016, 829, 758, 700. **HRMS (ESI)**: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{24}\text{NaO}_6$: 455.1465; found: 455.1470.



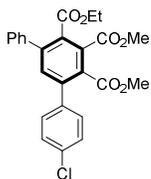
4'-ethyl 5',6'-dimethyl 4-methoxy-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**5b**):

Yield 83% (350.3 mg); White solid; m.p. 114–115 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.51 (s, 1H), 7.43 – 7.38 (m, 3H), 7.38 – 7.33 (m, 2H), 7.29 (d, $J = 8.4$ Hz, 2H), 6.94 (d, $J = 8.4$ Hz, 2H), 4.08 (q, $J = 7.2$ Hz, 2H), 3.88 (s, 3H), 3.84 (s, 3H), 3.67 (s, 3H), 1.01 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 168.4, 167.6, 166.9, 159.6, 142.1, 141.6, 139.0, 134.0, 131.6, 131.1, 130.7, 129.4, 128.4, 128.3, 128.1, 113.9, 61.6, 55.3, 53.0, 52.5, 13.6; **IR (KBr, cm^{-1})**: 3437, 1727, 1741, 1632, 1608, 1517, 1447, 1348, 1279, 1251, 1223, 1185, 1148, 1031, 1018, 761, 704. **HRMS (ESI)**: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{24}\text{NaO}_7$: 471.1414; found: 471.1412.



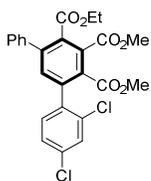
4'-ethyl 5',6'-dimethyl 4-fluoro-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**5c**):

Yield 85% (370.9 mg); White solid; m.p. 145–146 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.50 (s, 1H), 7.44 – 7.38 (m, 3H), 7.38 – 7.35 (m, 2H), 7.35 – 7.31 (m, 2H), 7.11 (t, $J = 8.4$ Hz, 2H), 4.09 (q, $J = 7.2$ Hz, 2H), 3.88 (s, 3H), 3.66 (s, 3H), 1.02 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 168.0, 167.5, 166.7, 163.5, 161.9, 142.2, 140.9, 138.8, 134.8, 134.0, 132.3, 131.8, 130.7, 130.0, 129.9, 128.4, 128.2, 128.2, 115.6, 115.4, 61.7, 53.0, 52.5, 13.6; **IR (KBr, cm^{-1})**: 3453, 1740, 1606, 1512, 1446, 1435, 1342, 1291, 1223, 1160, 1144, 1110, 972, 855, 757, 709, 541. **HRMS (ESI)**: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{21}\text{FNaO}_6$: 459.1214; found: 471.1215.



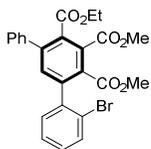
4'-ethyl 5',6'-dimethyl 4-chloro-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**5d**):

Yield 81% (365.2 mg); White solid; m.p. 146–147 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): 7.49 (s, 1H), 7.44 – 7.39 (m, 4H), 7.38 (s, 1H), 7.37 – 7.33 (m, 2H), 7.29 (d, $J = 8.4$ Hz, 2H), 4.09 (q, $J = 7.2$ Hz, 2H), 3.88 (s, 3H), 3.66 (s, 3H), 1.02 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 167.9, 167.4, 166.7, 142.3, 140.7, 138.7, 137.2, 134.5, 133.8, 132.4, 131.7, 130.8, 129.5, 128.7, 128.4, 128.2, 61.7, 53.0, 52.6, 13.6; **IR (KBr, cm^{-1})**: 3438, 1726, 1593, 1496, 1434, 1347, 1280, 1250, 1181, 1145, 1124, 1109, 1091, 1066, 1019, 967, 847, 750, 704. **HRMS (ESI)**: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{21}\text{ClNaO}_6$: 475.0919; found: 475.0926.



4'-ethyl 5',6'-dimethyl 2,4-dichloro-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**5e**):

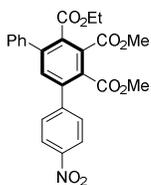
Yield 87% (424.0 mg); White solid; m.p. 165–166 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.48 (s, 1H), 7.41 (d, $J = 9.0$ Hz, 4H), 7.39 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 7.20 (d, $J = 8.4$ Hz, 1H), 4.11 (q, $J = 7.2$ Hz, 2H), 3.89 (s, 3H), 3.64 (s, 3H), 1.03 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 167.3, 166.8, 166.7, 142.4, 138.9, 138.5, 136.1, 134.8, 134.3, 133.6, 132.9, 131.6, 131.4, 129.3, 128.4, 128.3, 128.3, 126.9, 61.8, 53.0, 52.6, 13.6; **IR (KBr, cm^{-1})**: 3457, 1738, 1632, 1596, 1481, 1436, 1346, 1282, 1256, 1223, 1139, 1104, 1078, 1020, 780, 762, 700. **HRMS (ESI)**: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{20}\text{Cl}_2\text{NaO}_6$: 509.0529; found: 509.0527.



4'-ethyl 5',6'-dimethyl 2-bromo-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**5f**):

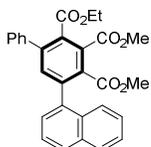
Yield 80% (397.8 mg); White solid; m.p. 152–153 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.64 (d, $J = 7.8$ Hz, 1H), 7.44 (s, 1H), 7.43 – 7.37 (m, 4H), 7.34 (t, $J = 7.8$ Hz, 1H), 7.24 (d, $J = 7.8$ Hz, 2H), 4.11 (q, $J = 7.2$ Hz, 2H), 3.88 (s, 3H), 3.59 (s, 3H), 1.04 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 167.5, 166.9, 166.9, 142.2, 141.5, 139.5, 138.7, 134.5, 132.6, 131.4, 131.2, 130.6, 129.6, 128.4, 128.3, 128.2, 127.0, 122.7, 61.8, 53.0, 52.5, 13.6; **IR (KBr, cm^{-1})**: 1739, 1721, 1445, 1435, 1400, 1347, 1275, 1248, 1183, 1148, 1112, 1026, 971, 764, 701, 746, 701. **HRMS**

(ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{22}BrO_6$: 497.0594; found: 497.0591.



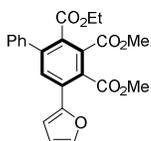
4'-ethyl 5',6'-dimethyl 4-nitro-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**5g**):

Yield 72% (333.6 mg); White solid; m.p. 175–176 °C; 1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.29 (d, $J = 9.0$ Hz, 2H), 7.53 (d, $J = 9.0$ Hz, 2H), 7.52 (s, 1H), 7.44 – 7.39 (m, 3H), 7.38 – 7.34 (m, 2H), 4.10 (q, $J = 7.2$ Hz, 2H), 3.90 (s, 3H), 3.67 (s, 3H), 1.03 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.4, 167.2, 166.5, 147.6, 145.4, 142.7, 139.7, 138.3, 133.6, 133.3, 131.5, 131.2, 129.3, 128.5, 128.5, 128.2, 123.7, 61.8, 53.2, 52.8, 13.6; IR (KBr, cm^{-1}): 3459, 1739, 1632, 1600, 1515, 1437, 1349, 1315, 1284, 1226, 1139, 1105, 1067, 1016, 857, 763, 745, 700. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{25}H_{21}NNaO_8$: 486.1159; found: 486.1160.



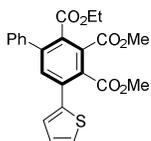
2-ethyl 3,4-dimethyl 5-(naphthalen-1-yl)-[1,1'-biphenyl]-2,3,4-tricarboxylate (**5h**):

Yield 81% (379.5 mg); White solid; m.p. 138–139 °C; 1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.88 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 8.4$ Hz, 1H), 7.57 (s, 1H), 7.52 – 7.45 (m, 2H), 7.44 – 7.40 (m, 1H), 7.39 (s, 5H), 7.35 (d, $J = 7.2$ Hz, 1H), 4.14 (q, $J = 7.2$ Hz, 2H), 3.89 (s, 3H), 3.32 (s, 3H), 1.06 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.6, 167.4, 166.9, 142.0, 140.9, 138.7, 136.3, 135.0, 133.3, 132.8, 132.4, 131.4, 131.0, 128.6, 128.4, 128.3, 128.2, 128.2, 126.7, 126.4, 126.0, 125.6, 124.9, 61.7, 53.0, 52.2, 13.7; IR (KBr, cm^{-1}): 3431, 1743, 1724, 1444, 1387, 1274, 1265, 1229, 1180, 1149, 1119, 1100, 1032, 793, 778, 764, 701. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{29}H_{24}NaO_6$: 491.1465; found: 491.1463.



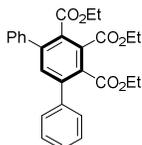
2-ethyl 3,4-dimethyl 5-(furan-2-yl)-[1,1'-biphenyl]-2,3,4-tricarboxylate (**5i**):

Yield 81% (310.4 mg); Yellow solid; m.p. 107–108 °C; 1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.81 (s, 1H), 7.51 (s, 1H), 7.44 – 7.39 (m, 3H), 7.39 – 7.30 (m, 2H), 6.67 (d, $J = 3.0$ Hz, 1H), 6.52 – 6.46 (m, 1H), 4.06 (q, $J = 7.2$ Hz, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 1.00 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 168.2, 167.3, 166.3, 149.9, 143.6, 142.2, 138.7, 132.1, 130.5, 130.3, 129.6, 129.0, 128.3, 128.1, 128.1, 111.9, 109.7, 61.5, 52.9, 52.7, 13.5; IR (KBr, cm^{-1}): 3444, 1727, 1632, 1595, 1436, 1337, 1248, 1165, 1140, 1171, 1020, 982, 903, 759, 733, 706, 595. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{20}NaO_7$: 431.1101; found: 431.1102.



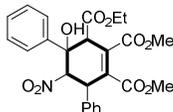
2-ethyl 3,4-dimethyl 5-(thiophen-2-yl)-[1,1'-biphenyl]-2,3,4-tricarboxylate (**5j**):

Yield 79% (335.4 mg); White solid; m.p. 112–114 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.63 (s, 1H), 7.44 – 7.38 (m, 4H), 7.38 – 7.32 (m, 2H), 7.14 (d, $J = 3.6$ Hz, 1H), 7.11 – 7.04 (m, 1H), 4.07 (q, $J = 7.2$ Hz, 2H), 3.88 (s, 3H), 3.77 (s, 3H), 1.01 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 168.0, 167.3, 166.4, 142.1, 139.3, 138.6, 134.2, 134.1, 132.5, 131.8, 130.2, 128.3, 128.2, 127.6, 127.3, 127.1, 61.6, 53.0, 52.6, 13.5; **IR (KBr, cm^{-1})**: 3438, 1740, 1725, 1594, 1446, 1437, 1321, 1293, 1248, 1236, 1293, 1276, 1178, 1134, 1019, 755, 733, 706. **HRMS (ESI)**: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{20}\text{NaO}_6\text{S}$: 447.0873; found: 447.0872.



triethyl [1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**5k**):

Yield 88% (392.9 mg); White solid; m.p. 146–147 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.52 (s, 1H), 7.44 – 7.38 (m, 6H), 7.38 – 7.34 (m, 4H), 4.35 (q, $J = 7.2$ Hz, 2H), 4.08 (q, $J = 7.2$ Hz, 4H), 1.34 (t, $J = 7.2$ Hz, 3H), 0.99 (t, $J = 7.2$ Hz, 6H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 167.6, 166.4, 142.0, 139.0, 133.7, 132.0, 130.9, 128.3, 128.3, 128.1, 77.2, 77.0, 76.8, 62.2, 61.5, 13.8, 13.4; **IR (KBr, cm^{-1})**: 2989, 1726, 1594, 1439, 1367, 1341, 1276, 1251, 1220, 1109, 1067, 1020, 796, 760, 746, 706. **HRMS (ESI)**: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{26}\text{NaO}_6$: 469.1622; found: 469.1618.



4'-ethyl

5',6'-dimethyl

-3'-hydroxy-2'-nitro-1',2',3',4'-tetrahydro-[1,1':3',1''-terphenyl]-4',5',6'-tricarboxylate (**6**):

Yield 29% (140.2 mg); Yellow solid; m.p. 177–178 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ (ppm) 7.52 – 7.43 (m, 2H), 7.42 – 7.30 (m, 8H), 6.13 (d, $J = 10.2$ Hz, 1H), 4.63 (d, $J = 10.8$ Hz, 1H), 4.10 (s, 1H), 4.03 – 3.90 (m, 2H), 3.78 (s, 1H), 3.73 (s, 3H), 3.44 (s, 3H), 0.90 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ (ppm) 169.8, 166.3, 165.3, 141.9, 138.9, 134.5, 129.1, 129.0, 128.9, 128.8, 126.4, 125.2, 90.2, 74.3, 61.8, 56.8, 52.7, 52.2, 48.2, 13.6; **IR (KBr, cm^{-1})**: 3514, 1724, 1654, 1550, 1437, 1274, 1200, 1075, 757, 703, 567. **HRMS (ESI)**: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{25}\text{NNaO}_6$: 506.1422; found: 506.1414.

5. Appendix: spectral copies of ^1H NMR, and ^{13}C NMR

