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A vicarious synthesis of unsymmetrical *meta*- and *para*-terphenyls from 2*H*-pyran-2-ones☆

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Abstract—An innovative synthesis of terphenyls functionalized with electron-withdrawing or -donating substituents is described and illustrated by carbanion-induced ring transformation of 2*H*-pyran-2-ones with 2-methoxyacetophenone in excellent yields. The existing protocols for the synthesis of terphenyls are generally inter- and intramolecular aryl–aryl cross couplings in the presence of metal complexes. In this letter, we report a potentially useful alternative to conventional metal-catalyzed cross-coupling reactions.

Symmetrical and unsymmetrical terphenyls functionalized with electron donor or acceptor groups are the main constituents of a large number of mushrooms belonging to the Thelephoraceae family.[1] Recently, numerous natural products having terphenyl architecture such as thelephorin,[2] terphenyllin,[3] terferol[4] and terprenin[5] have been reported to possess interesting biological properties. Several synthetic terphenyl derivatives have been designed as selective inhibitors for dihydroortate dehydrogenase[6] and cyclooxygenase[7] enzymes. Terphenyls containing acidic groups have recently been found to be potent insulin sensitizers.[8] Recently, Nozaki et al.[9] have identified a terphenyl-based novel auxin signaling inhibitor, terfestatin A, from *Streptomyces* sp. F40. Owing to their interesting optical[10] and electrical[11] properties, terphenyls find several industrial applications as liquid crystals, conducting polymers, heat storage and heat transfer agents, as textile dye carriers and as a laser dye. In addition, *meta*-terphenyls are ideal precursors in the design of cyclophanes and are useful as tectons in crystal engineering.[12]

Transition metal-catalyzed aryl–aryl cross coupling reactions are commonly employed for constructing biaryls. Palladium-catalyzed aryl–aryl cross-coupling between electrophilic aromatic dihalides $Ar(X)_2$ (X being generally Br, I and OTf) and two equivalents of organometallic species Ar–M (M being Mg, Ni, Zn, Sn and B) is a versatile synthetic method for the preparation of symmetrical and unsymmetrical terphenyls.[13] Of the various coupling reactions, the Pd-catalyzed Suzuki couplings[14] of a diverse array of haloarenes with arylboronic acids has gained wide popularity due to the commercial availability of several arylboronic acids and innocuous nature of the latter, easy work-up, and tolerance of the reactions to aqueous media. Symmetrical terphenyls have been prepared by double coupling reactions of aryl diboronic acids[15] with aryl halides and aryl distannanes[16] with aryl bromides. The classical approach for unsymmetrical terphenyls requires either the reactions of biaryl boronic acids with aromatic halides[17] or the stepwise chemoselective cross-couplings of aryl compounds containing two dissimilar reactive halides or triflates.[18] Recently non-C_2-symmetric substituted triphenylene compounds have been prepared using arylzinc halides.[19] Despite the wide synthetic potential of these metal-assisted cross-coupling reactions, they suffer from the requirements for expensive organometallic reagents/catalysts, harsh reaction conditions and undesired by-products. Thus, there exists a need to develop an expedient route for the synthesis of terphenyls that does not require specialized reagents or catalysts with flexibility of introducing the electron donor or acceptor groups in their molecular makeup.

Herein, we report a route for the synthesis of functionalized terphenyls through reaction of 2*H*-pyran-2-ones

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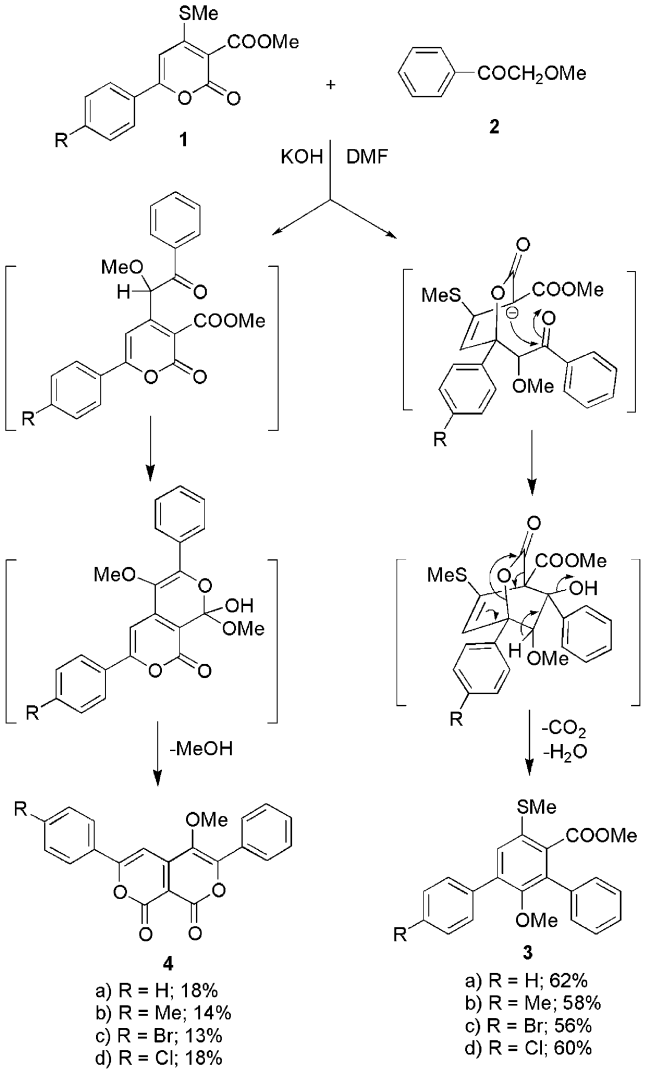
with 2-methoxyacetophenone in high yields without using an organometallic reagent or a catalyst. The advantage of the procedure lies in the creation of a 'middle' aryl ring through new carbon–carbon bond formation with flexibility of substituent variations in the terphenyl framework.

Our approach to **3a–d** is based on the ring transformation of 6-aryl-3-methoxycarbonyl-4-methylsulfanyl-2*H*-pyran-2-ones **1a–d** using 2-methoxyacetophenone **2** as a carbanion source. The 2*H*-pyran-2-ones **1a–d** precursors were prepared by the reaction of ethyl 2-carbomethoxy-3,3-di(methylsulfanyl)-acrylate[20] with substituted acetophenones under alkaline conditions in high yields. Lactones, **1a–d** have three electrophilic centres: C2, C4 and C6 in which the latter position is highly reactive towards nucleophiles due to the extended conjugation and the presence of the electron-withdrawing substitutent at position 3 of the pyran ring. Thus, stirring an equimolar mixture of **1a–d**, 2-methoxyacetophenone and powdered KOH in DMF for 9–12 h at room temperature yielded two products **3a–d** and **4a–d** (Scheme 1). The major nonpolar products were characterized as 2′-methoxy-5′-methylsulfanyl-[1,1′;3′,1″]terphenyl-4′-carboxylic acid methyl esters **3a–d** and the minor polar compounds as 4-methoxy-3,6-diarylpyrano[3,4-*c*]pyran-1,8-diones **4a–d** by spectroscopic analyses. In each case, compounds **3a–d** and **4a–d** were very different in polarity and could be separated very easily. The ^{1}H NMR spectrum of **3a** showed three singlets at δ 2.50, 3.06 and 3.56 for the SCH_3, OCH_3 and $COOCH_3$ protons, respectively. Two multiplets at δ 7.37–7.48 and 7.56–7.61 for nine and two protons, respectively, were attributed to aromatic protons. The IR spectrum showed a carbonyl peak at 1736 cm^{-1} due to the presence of an ester group. The molecular ion peak at 364 in the mass spectrum of **3a** confirmed the structure as 2′-methoxy-5′-methylsulfanyl-[1,1′;3′,1″]-terphenyl-4′-carboxylic acid methyl ester. In the ^{1}H NMR spectrum of **4a** two singlets at δ 3.69 and 7.07 were attributed to OCH_3 and aromatic methine protons, respectively. The absence of peaks for SCH_3 and $COOCH_3$ protons and the presence of two lactone–carbonyl peaks at 1703 and 1793 cm^{-1} in the IR spectrum confirmed the structure as 4-methoxy-3,6-diphenylpyrano[3,4-*c*]pyran-1,8-dione.



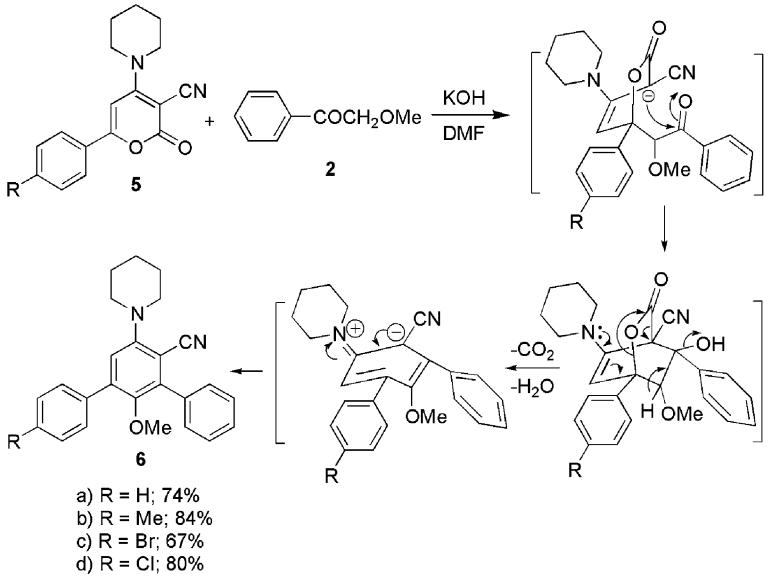
Scheme 1.

The pyrano[3,4-*c*]pyran-1,8-dione ring system has not been previously explored. Molecular orbital calculations, correlation of delocalization energies, π-bond order and π-charge density of different theoretical pyranopyrandiones have been reported.[21] Some interesting photochemical[22] and luminescence properties[23] have been reported for compounds with similar molecular architecture. Various natural and synthetic products having the basic scaffold of pyranopyrandiones have demonstrated anticancer[24] and antibacterial[25] activities.

The plausible reaction mechanisms for the formation of terphenyls and pyrano[3,4-*c*]pyran-1,8-diones are depicted in Scheme 1. The transformation of 6-aryl-2*H*-pyran-2-ones **1a–d** into terphenyls **3** is possibly initiated by attack of the carbanion generated from 2-methoxyacetophenone at position C6 of lactone **1**, followed by intramolecular cyclization involving the carbonyl functionality of **2** and C3 of the pyranone ring and elimination of carbon dioxide to yield **3a–d**.

Similarly, the formation of pyrano[3,4-*c*]pyran-1,8-diones could proceed through the attack of the carbanion at the less electrophilic position 4 with elimination of methyl mercaptan followed by intramolecular cyclization involving the carbonyl group and the carbomethoxy functionality of the 2*H*-pyran-2-one and elimination of methanol to yield products **4a–d** in smaller quantities.

In order to prepare terphenyls exclusively, we attempted to reduce the electrophilicity at position 4 of lactone **1** by replacing the methyl sulfanyl group with a secondary amine. With this consideration, we prepared 6-aryl-2-oxo-4-piperidin-1-yl-2*H*-pyran-3-carbonitriles (**5a–d**) in high yields by refluxing a solution of lactone **1** with piperidine in methanol for 6–8 h. The reaction of lactones **5a–d** and 2-methoxyacetophenone under the same reaction conditions as described in Scheme 1 gave



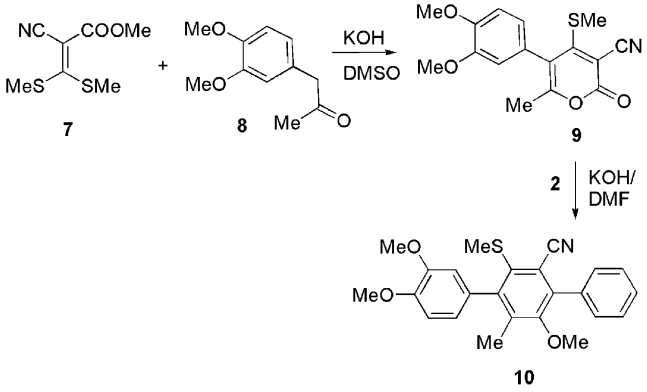
Scheme 2.

2′-methoxy-5′-piperidin-1-yl-[1,1′;3′,1″]terphenyl-4′-carbonitriles (**6a**–**d**) in high yields (Scheme 2). The terphenyls are the sole products of the reaction and were easily isolated by column chromatography and characterized by spectroscopic means. The possible reaction mechanism for the formation of terphenyls **6a**–**d** is depicted in Scheme 2.

A recent report by Luo and co-workers[26] demonstrated the potential applications of *para*-terphenyl derivatives containing cyano groups in organic light emitting diode (OLED) fabrication. It has been well documented that the introduction of alkoxy substituents in π-conjugated materials enhances the solubility of the polymer and the presence of the cyano group influences photophysical and electroluminescent properties by lowering the energy of the LUMO, thus exhibiting a relatively low threshold voltage and high quantum efficiency in LED devices.[27] The paucity of synthetic methodology for the preparation of *para*-terphenyls containing cyano groups prompted us to exploit our methodology for preparing *para*-terphenyls.

The starting material was synthesized by reacting an equimolar mixture of methyl 2-cyano-3,3-di(methylsulfanyl)acrylate[20] **7** and 3,4-dimethoxyphenylacetone **8** in dry DMSO to prepare 5-(3,4-dimethoxyphenyl)-6-methyl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitrile **9** in 89% yield (Scheme 3). The 2*H*-pyran-2-one **9** was then reacted with 2-methoxyacetophenone in the presence of a base to afford 6′,3″,4″-trimethoxy-5′-methyl-3′-methylsulfanyl-[1,1′;4′,1″]terphenyl-2′-carbonitrile **10** in 56% yield. This is a unique methodology for the construction of the *para*-terphenyl ring system under mild conditions, without using any organometallic reagents or catalysts. Data for all of the representative compounds are incorporated in the reference section.[28]

In summary, we have developed a new synthetic methodology for preparing functionalized *meta*- and *para*-terphenyls through the carbanion-induced ring transformation of 2*H*-pyran-2-ones, in good yields. The methodology is very simple, economical and does not require any specialized organometallic reagents or catalysts. This methodology is a potentially useful alternative to conventional metal-catalyzed cross-coupling reactions.



Scheme 3.

Acknowledgements

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28. General procedure for the synthesis of **3** and **4**: A mixture of 6-aryl-3-methoxycarbonyl-4-methylsulfanyl-2*H*-pyran-2-one **1** (1 mmol), 2-methoxyacetophenone **2** (1.1 mmol) and powdered KOH (1.2 mmol) in dry DMF (5 mL) was stirred at room temperature for 9–12 h. The reaction mixture was poured into ice water with vigorous stirring and neutralized with dilute HCl. The solid thus obtained was filtered and pure compounds were isolated by passing through a silica gel column using chloroform–hexane (1:2) as eluent; Compound **3a**: white solid; yield 62%; mp 146–148 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.50 (s, 3H, SCH_3), 3.06 (s, 3H, OCH_3), 3.56 (s, 3H, $COOCH_3$), 7.37–7.48 (m, 9H, ArH), 7.56–7.61 (m, 2H, ArH); IR (KBr) 1736 cm^{-1} (CO); MS (FAB) 364 (M^+); Anal. Calcd for $C_{22}H_{20}O_3S$: C, 72.5; H, 5.5%. Found: C, 72.2; H, 5.9%. Compound **3b**: White solid; yield 58%; mp 106–108 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.32 (s, 3H, CH_3), 2.40 (s, 3H, SCH_3), 2.98 (s, 3H, OCH_3), 3.46 (s, 3H, $COOCH_3$), 7.14–7.43 (m, 10H, ArH); IR (KBr) 1730 cm^{-1} (CO); MS (FAB) 378 (M^+). Compound **3c**: White solid; yield 56%; mp 148–150 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.50 (s, 3H, SCH_3), 3.06 (s, 3H, OCH_3), 3.55 (s, 3H, $COOCH_3$), 7.34 (s, 1H, ArH), 7.36–7.40 (m, 5H, ArH), 7.47 (d, 2H, $J = 8.4$ Hz, ArH), 7.57 (d, 2H, $J = 8.4$ Hz, ArH); IR (KBr) 1727 cm^{-1} (CO); MS (FAB) 444 (M^++2), 442 (M^+). Compound **3d**: White solid; yield 60%; mp 154–156 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.50 (s, 3H, SCH_3), 3.06 (s, 3H, OCH_3), 3.55 (s, 3H, $COOCH_3$), 7.34–7.43 (m, 8H, ArH), 7.51–7.56 (m, 2H, ArH); IR (KBr) 1727 cm^{-1} (CO); MS (FAB) 398 (M^+). Compound **4a**: Yellow solid; yield 18%; mp 260–262 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.69 (s, 3H, OCH_3), 7.07 (s, 1H, CH), 7.48–7.60 (m, 6H, ArH), 7.96–8.04 (m, 2H, ArH), 8.00–8.20 (m, 2H, ArH); IR (KBr) 1703, 1793 cm^{-1} (CO); MS (FAB) 347 (M^++1); Anal. Calcd for $C_{21}H_{14}O_5$: C, 72.8; H, 4.0%. Found: C, 72.3; H, 4.0%. Compound **4b**: Yellow solid; yield 14%; mp 219–220 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.45 (s, 3H, CH_3), 3.69 (s, 3H, OCH_3), 7.01 (s, 1H, CH), 7.33 (d, 2H, $J = 8.0$ Hz, ArH), 7.36–7.54 (m, 3H, ArH), 7.89 (d, 2H, $J = 8.0$ Hz, ArH), 8.10–8.14 (m, 2H, ArH); IR (KBr) 1710, 1779 cm^{-1} (CO); MS (FAB) 361 (M^++1). Compound **4c**: Yellow solid; yield 13%; mp 248–250 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.69 (s, 3H, OCH_3), 7.05 (s, 1H, CH), 7.50–7.56 (m, 3H, ArH), 7.68 (d, 2H, $J = 8.6$ Hz, ArH), 7.87 (d, 2H, $J = 8.6$ Hz, ArH), 8.10–8.16 (m, 2H, ArH); IR (KBr) 1718, 1769 cm^{-1} (CO); MS (FAB) 427, 425 (M^++1). Compound **4d**: Yellow solid; yield 18%; mp 258–260 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.69 (s, 3H, OCH_3), 7.04 (s, 1H, CH), 7.48–7.56 (m, 5H, ArH), 7.95 (d, 2H, $J = 8.4$ Hz, ArH), 8.11–8.16 (m, 2H, ArH); IR (KBr) 1721, 1770 cm^{-1} (CO); MS (FAB) 383, 381 (M^++1). Compound **6a**: White solid; yield 74%; mp 150–152 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.58–1.64 (m, 2H, CH_2), 1.73–1.82 (m, 4H, $2CH_2$), 3.03 (s, 3H, OCH_3), 3.12–3.18 (m, 4H, $2CH_2$), 6.99 (s, 1H, ArH), 7.38–7.61 (m, 10H, ArH); IR (KBr) 2217 cm^{-1} (CN); MS (FAB) 368 (M^+); Anal. Calcd for $C_{25}H_{24}N_2O$: C, 81.4; H, 6.5; N, 7.6%. Found: C, 81.0; H, 6.7; N, 7.5%. Compound **6b**: White solid; yield 84%; mp 108–110 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.57–1.63 (m, 2H, CH_2), 1.73–1.83 (m, 4H, $2CH_2$), 2.40 (s,

3H, CH_3), 3.03 (s, 3H, OCH_3), 3.11–3.17 (m, 4H, CH_2), 6.98 (s, 1H, ArH), 7.22–7.26 (m, 2H, ArH), 7.39–7.51 (m, 7H, ArH); IR (KBr) 2216 cm^{-1} (CN); MS (FAB) 382 (M^+). Compound **6c**: White solid; yield 67%; mp 163–164 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.57–1.64 (m, 2H, CH_2), 1.73–1.80 (m, 4H, $2CH_2$), 3.02 (s, 3H, OCH_3), 3.12–3.18 (m, 4H, $2CH_2$), 6.94 (s, 1H, ArH), 7.44–7.60 (m, 9H, ArH); IR (KBr) 2221 cm^{-1} (CN); MS (FAB) 448, 446 (M^+). Compound **6d**: White solid; yield 80%; mp 164–166 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.58–1.64 (m, 2H, CH_2), 1.74–1.85 (m, 4H, $2CH_2$), 3.02 (s, 3H, OCH_3), 3.12–3.18 (m, 4H, $2CH_2$), 6.94 (s, 1H, ArH), 7.39–7.56 (m, 9H, ArH); IR (KBr) 2216 cm^{-1} (CN); MS (FAB) 402 (M^+). Compound **10**: White solid; yield 56%; mp 133–134 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 2.10 (s, 3H, CH_3), 2.27 (s, 3H, SCH_3), 3.33 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 6.72 (s, 1H, ArH), 6.74 (d, 1H, $J = 8.0$ Hz, ArH), 6.98 (d, 1H, $J = 8.0$ Hz, ArH), 7.48–7.53 (m, 5H, ArH); IR (KBr) 2221 cm^{-1} (CN); MS (FAB) 406 (M^++1).