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One-Pot Regioselective Synthesis of *meta*-Terphenyls via [3 + 3] Annulation of Nitroallylic Acetates with Alkylidenemalononitriles

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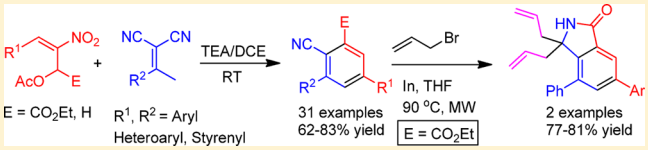
Supporting Information

ABSTRACT: A highly efficient one-pot method has been developed for the synthesis of *meta*-terphenyls via a regioselective [3 + 3] annulation-elimination sequence involving Morita–Baylis–Hillman (MBH) acetates of nitroalkenes and alkylidenemalononitriles. The reaction takes place in a regioselective manner under mild conditions (Et_3N, room temperature) to afford a wide variety of *meta*-terphenyls bearing aryl, heteroaryl and styrenyl groups. This novel [3 + 3] annulation takes advantage of the 1,3-bielectrophilic character of MBH acetates and 1,3-binucleophilic character of alkylidenemalononitriles and proceeds in a cascade fashion comprising an S_N2' substitution, intramolecular 6-*endo*-*trig* Michael addition and double elimination. Representative synthetic transformations of the products, for instance, to *meta*-terphenyl derived isoindolinones have also been demonstrated.



INTRODUCTION

Synthesis of polysubstituted benzene derivatives via various annulation strategies, viz [2 + 2 + 2], [3 + 3], [4 + 2] and [5 + 1], often performed under acid/base or transition metal catalyzed conditions, is well documented in the literature.[1] However, the scope of acid/base mediated annulations and conventional functionalization methods is curtailed by poor regioselectivity and requirement of harsh reaction conditions. Synthesis of terphenyls, a chain of three benzene rings, is of particular interest as these are part of many natural products present in the plant kingdom, e.g., mushrooms, and exhibit various biological activities such as anticoagulant, antithrombotic, immunosuppressant, lipoxygenase inhibitory, neuroprotective and cytotoxic activities.[2] While most of the terphenyl natural products are *para*-derivatives and few are *meta*, no *o*-terphenyl natural products are thus far reported in the literature.[2] The few *m*-terphenyls that were isolated from natural sources include trifucol **1** (from seaweed *Fucus vesiculosus*),[3] macranthol **2**, dunnialol **3**, simonsinol **4** (from Chinese flowering plant *Illicium macranthum*),[4] mulberrofuran R **5** (from mulberry tree *Morus ihou* Koidz.)[5] and dictyoterphenyl **6** (from the cellular slime mold *Dictyosteliumdiscoideum*).[6] Possible applications of *m*-terphenyl derivatives as ligands in catalysis[7] and as versatile synthetic materials[8] have been extensively explored in recent years (Figure 1).

Synthesis of *m*-terphenyls[9] has been achieved via metal catalyzed coupling,[6,10] multicomponent reactions, including cyclotrimerization,[11] [3 + 3] annulation[12,13] and Bronsted acid catalyzed cyclization.[14] As for [3 + 3] annulation, a four-step method involving base mediated annulation of chalcone with ethyl acetoacetate followed by hydrolysis and aromatization[12] and a one-pot base mediated synthesis involving chalcone and allyl *p*-tolyl sulfone[13] are known in the literature. While a single example is reported following the former multistep method, a mixture of *m*-terphenyls, with and without sulfone, is reported based on the latter method.

In the above scenario, we embarked on the idea of employing a [3 + 3] annulation strategy for the synthesis of *m*-terphenyls using the 1,3-bielectrophilic MBH acetate **7** and the 1,3-binucleophilic malononitrile derivative **8** as 3-carbon components. In recent years, we and others have extensively exploited the 1,3-bielectrophilic nature of **7** in the synthesis of a variety of heterocycles.[15] However, construction of carbocycles using **7** as the 3-carbon component received much less attention[16] and aromatic compounds have never been the targets of such approaches. Although malononitrile derivative **8** has been employed as a 4-carbon nucleophile–electrophile in [4 + 2] annulation with nitroalkenes,[17] and as a 3-carbon component in [3 + 2] annulations,[18] the role of **8** as a 3-carbon binucleophile in [3 + 3] annulation received much less attention[19] and has not been exploited, to our knowledge, in the synthesis of aromatics, particularly, terphenyls (Figure 2).

RESULTS AND DISCUSSION

At the outset, MBH acetate **7a** was treated with nitrile **8a** in the presence of different bases and in different solvents at room temperature (Table 1). While the reaction remained incomplete with 1 and 2 equiv of Et_3N in THF even after 48 h (entries 1–2), complete conversion was achieved upon increasing the amount of Et_3N to 3 and 4 equiv giving terphenyl **9a** in 60 and 65% yields, respectively (entries 3–4). Though there is only marginal difference in these yields (entries 3–4), further improvement in the yield to 73% and reaction time to 7 h was possible by changing the solvent to CH_2Cl_2 by using 4 equiv of Et_3N (entry 5). A hydrocarbon solvent such a toluene was not the best for our

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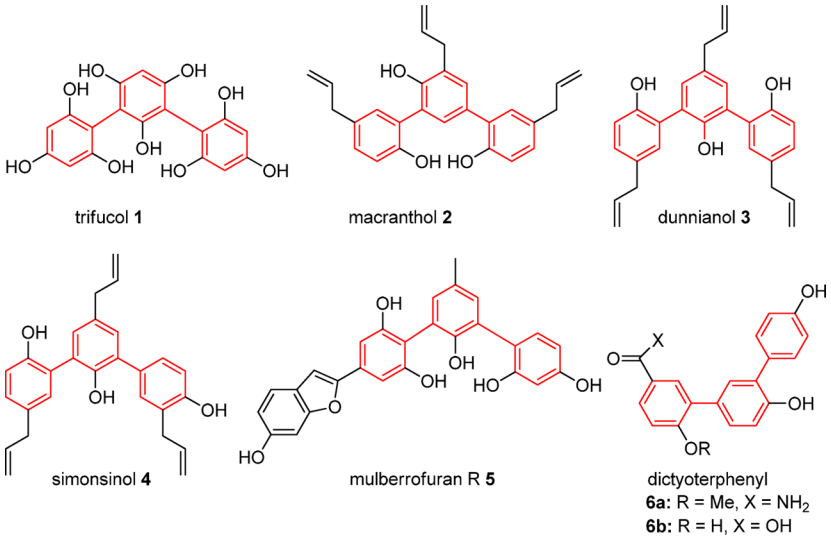


Figure 1. *m*-Terphenyl natural products.

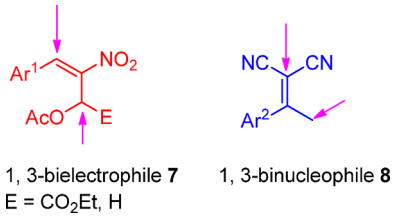


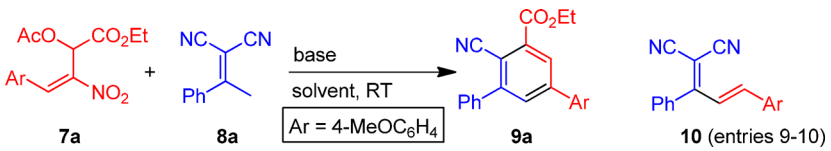
Figure 2. Proposed reactivity of MBH acetate 7 and alkylidenemalononitrile **8**.

reaction (entry 6). Although other amine bases such as DABCO and Huenig's base (entries 7–8) as well as inorganic bases such as K_2CO_3 and Cs_2CO_3 (entries 9–10) were screened, only DABCO provided the desired terphenyl **9a**, though in low yield (entry 7). Having found Et_3N to be the best base (entry 5), the yield and the reaction time were further improved, though marginally, from 73%, 7 h to 75%, 5 h, by changing the solvent from CH_2Cl_2 to $(CH_2)_2Cl_2$ (entries 5 and 11).

The above optimized conditions, viz Et_3N (4 equiv), $(CH_2)_2Cl_2$, room temperature, were then employed to investigate the scope of MBH acetates **7** using nitrile **8a** as the model binucleophile (Table 2). The reaction of nitrile **8a** with different MBH acetates **7a–k** proceeded well to provide cyanoesters **9a–k** in 65–78% yield (entries 1–11). No appreciable substituent effect was observed in these reactions as MBH acetates with electron rich aryl **7a–e** (entries 1–5), electron deficient aryl **7g** (entry 7), parent phenyl **7f** (entry 6), heteroaryl **7h–i** (entries 8–9) and styrenyl **7j** (entry 10) afforded the cyanoesters **9a–j** in good yields (70–78%) in 3–15 h. However, marginally lower yield was encountered with MBH acetate **7k** possessing unsubstituted styrenyl group (65%, entry 11) and only a complex mixture was isolated in the case of aliphatic MBH acetate **7m** (entry 12).

Subsequently, one of the MBH acetates **7h** was adopted to study the scope of nitriles **8** under our optimized conditions (Table 3). Nitriles with electron rich aryl **8b–d** (entries 1–3), electron poor aryl **8e–h** (entries 4–7), heteroaryl **8i** (entry 8)

Table 1. Optimization Studies for the Synthesis of Terphenyl 9a from Alkylidenemalononitrile 8a and MBH Acetate 7a



entry	base (equiv)	solvent	time (h)	% yield[a]
1	Et_3N (1)	THF	48	15[b]
2	Et_3N (2)	THF	48	40[b]
3	Et_3N (3)	THF	20	60
4	Et_3N (4)	THF	12	65
5	Et_3N (4)	DCM	7	73
6	Et_3N (4)	toluene	6	50
7	DABCO (4)	DCM	3	33
8	iPr_2EtN (4)	DCM	3	–[c]
9	K_2CO_3 (4)	DCM	1	–[d]
10	Cs_2CO_3 (4)	DCM	1	–[d]
11	**Et_3N (4)**	**DCE**	**5**	**75**

[a]Isolated yield after silica gel column chromatography. [b]Incomplete conversion. [c]Complex mixture. [d]Product **10** was formed in 68–70% yield presumably via elimination of *β*-nitroacrylate after the initial S_N2' reaction (see Scheme 1, vide infra).

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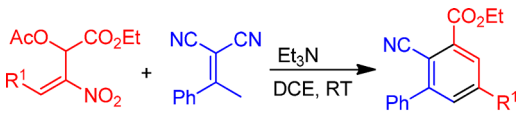
Table 2. Synthesis of 2-Cyano-3,5-disubstituted Benzoates 9 from Alkylidenemalononitrile 8a and MBH Acetates 7

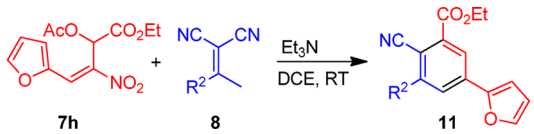


7 8a 9

entry	7	R^1	time (h)	9	% yield[a]
1	7a	4-OMeC_6H_4	5	9a	75
2	7b	2,4-$(OMe)_2C_6H_3$	10	9b	76
3	7c	3,4-$(OMe)_2C_6H_3$	12	9c	70
4	7d	5-Benzo[*d*][1,3]dioxole	15	9d	77
5	7e	4-MeC_6H_4	6	9e	76
6	7f	C_6H_5	6	9f	72
7	7g	4-FC_6H_4	10	9g	74
8	7h	2-Furyl	12	9h	78
9	7i	2-Thienyl	12	9i	76
10	7j	2-OMeC_6H_4CH=CH	3	9j	70
11	7k	C_6H_5CH=CH	4	9k	65
12	7l	Cyclohexyl	12	9l	–[b]

[a]Isolated yield after silica gel column chromatography. [b]Complex mixture.

Table 3. Synthesis of 2-Cyano-3,5-disubstituted Benzoates 11 from (Ethylidene)malononitriles 8 and MBH Acetate 7h



7h 8 11

entry	8	R^2	time (h)	11	% yield[a]
1	8b	4-MeC_6H_4	5	11b	79
2	8c	2-OMeC_6H_4	10	11c	80
3	8d	4-OMeC_6H_4	12	11d	76
4	8e	4-ClC_6H_4	12	11e	75
5	8f	4-BrC_6H_4	12	11f	83
6	8g	4-FC_6H_4	12	11g	79
7	8h	3-BrC_6H_4	15	11h	70
8	8i	2-Furyl	15	11i	69
9	8j	C_6H_5CH=CH	12	11j	76
10	8k	4-FC_6H_4CH=CH	15	11k	73

[a]Isolated yield after silica gel column chromatography.

and styrenyl **8j–k** (entries 9–10) groups reacted well with MBH acetate **7h** under our optimized conditions to furnish cyanoesters **11b–k** in good to excellent yield (69–83%). Again, no appreciable substituent effect was observed in these reactions except that the yield was marginally lower in the case of nitrile with a heteroaryl group **8i** (69%, entry 8) and an electron poor styrenyl group (73%, entry 10). The reaction time was consistently 12–15 h (entries 2–10) except for nitrile **8b** (entry 1).

Having investigated the scope of MBH acetate **7** and nitrile **8** in the synthesis of 2-cyano-3,5-disubstituted benzoates **9** and **11**, we subjected primary MBH acetates **12** to the Et_3N mediated reaction with nitrile **8** in anticipation that 2,4-diarylbenzonitrile **13** would be formed (Table 4). Thus, treatment of acetate **12a** with various nitriles **8a,b** and **8d** delivered 2,4-diarylbenzonitriles **13a–c** in 72–76% yield (entries 1–3). Interestingly, the reaction of **12a** with **8c** provided intermediate **14d** in 71% yield which did not undergo aromatization via elimination of HCN under our experimental conditions (entry 4). However, in a separate experiment, DBU (1.5 equiv) was added to the reaction mixture after complete conversion of **12a** and **8c** to **14d** and the resulting mixture was stirred for 1 h to achieve elimination of HCN from **14d** to form terphenyl **13d** in 62% yield (entry 4). Heteroaryl MBH acetates **12b,c** also reacted well with various nitriles **8a**, **8c,d** and **8f** leading to 2,4-diarylbenzonitriles **13e–h** in good to excellent yield (70–83%, entries 5–8). Finally, MBH acetates bearing an electron poor aryl group and parent phenyl group **12d** and **12e**, respectively, were also subjected to [3 + 3] annulation with a representative nitrile **8d** to afford terphenyls **13i** and **13j** in 73–77% yield (entries 9–10). Unlike in the case of secondary MBH acetates **7** where the reaction was complete in 15 h or less (Tables 2 and 3), the reaction times for primary MBH acetates **12** were long (1–4 d) which are attributable to the active role the electron withdrawing ester group played in the reaction of **7** (see Scheme 1, vide infra).

The structure of benzonitriles **9** and **11** were established by extensive spectral analysis. That the two protons in the central aromatic ring appearing, in general, as doublets at δ 8.20–8.40 and 7.70–7.90 are *meta* to each other was confirmed by their low coupling constants (J = 1.4–1.8 Hz). The regiochemistry was confirmed by ^{1}H–^{1}H 2D-NOESY experiment with **9a** in that the proton *ortho* to the ester group appearing at δ 8.26 had a positive NOE with only the anisyl protons whereas the *para*-proton exhibited NOE with both anisyl protons and phenyl protons (see the Supporting Information). Further unambiguous structural assignment was made by single crystal X-ray analysis of a representative product **11f** (see the Supporting Information). As for benzonitrile **13**, out of the three protons of the central aromatic ring appearing, in general, in a narrow range of 7.60–7.80, one appeared as a doublet with a small J value (1.5–1.8 Hz), another as a doublet with a large J value (7.7–8.2 Hz) and the third as a dd with a large and a small J value. This pattern was consistent with the regiochemistry in **13** which was further unambiguously established by ^{1}H–^{1}H 2D-COSY experiment with a representative compound **13g**. Thus, while the proton *ortho* to cyano group appeared at δ 7.73 as a doublet with a J value of 8.1 Hz, of the two *meta*-protons, one appeared as a doublet at δ 7.69 with a small J value (1.7 Hz) and the other as dd at δ 7.62 with large and small J values (8.1, 1.7 Hz). The observed unsymmetrical ^{1}H and ^{13}C NMR pattern of **9f**, **11i** and **13c** (Ar^1 = Ar^2) also ruled out regioisomers of terphenyls **9**, **11** or **13**. Structural and regiochemical assignment of intermediate **14d** was performed based on ^{1}H NMR and ^{1}H–^{1}H 2D-COSY spectra. The CH_2 protons of **14d** appeared as a doublet at δ 3.15 coupled only to one olefinic proton appearing at δ 6.21 with a J value of 4.3 Hz. Although the ^4J coupling of this olefinic proton with the other appearing at δ 6.74 is not measurable enough, the cross-peaks are clearly observed in the COSY spectrum (see the Supporting Information).

The proposed mechanism for the formation of benzonitrile **9**, **11** or **13** is outlined in Scheme 1. Deprotonation of the methyl group of nitrile **8** and addition of the resulting stabilized anion to MBH acetate **7** or **12** in a Michael fashion followed by elimination of the acetate in an overall S_N2' reaction generates intermediate **I**. Deprotonation at the allylic position of intermediate **I** generates a stabilized carbanion whose intramolecular Michael addition in a 6-*endo*-*trig* fashion to the newly formed nitroalkene moiety in **I** provides the cyclized product **II**. Finally, Et_3N mediated elimination of HNO_2 and HCN furnishes the aromatized product **9**, **11** or **13**. This overwhelming preference for the 6-*endo*-*trig* cyclization over 5-*exo*-*trig*

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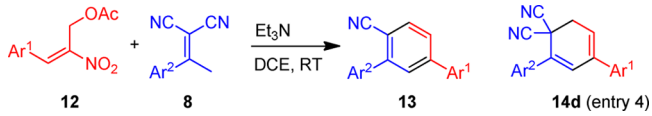
Table 4. Addition of Various Alkylidenemalononitriles 8 to MBH Acetates 12

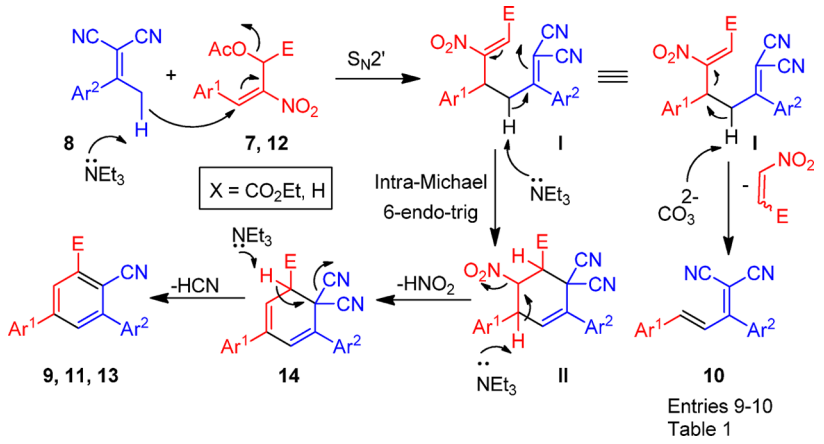


12 8 13 **14d** (entry 4)

entry	12	Ar^1	8	Ar^2	time (d)	13	% yield[a]
1	**12a**	4-$OMeC_6H_4$	**8a**	C_6H_5	3.0	**13a**	76
2	**12a**	4-$OMeC_6H_4$	**8b**	4-MeC_6H_4	1.0	**13b**	75[b]
3	**12a**	4-$OMeC_6H_4$	**8d**	4-$OMeC_6H_4$	4.0	**13c**	72
4	**12a**	4-$OMeC_6H_4$	**8c**	2-$OMeC_6H_4$	4.0	**13d**	62[c]
5	**12b**	2-Furyl	**8a**	C_6H_5	1.5	**13e**	79
6	**12c**	2-Thienyl	**8c**	2-$OMeC_6H_4$	4.0	**13f**	80
7	**12c**	2-Thienyl	**8d**	4-$OMeC_6H_4$	1.5	**13g**	83
8	**12c**	2-Thienyl	**8f**	4-BrC_6H_4	2.0	**13h**	70
9	**12d**	4-ClC_6H_4	**8d**	4-$OMeC_6H_4$	2.0	**13i**	77
10	**12e**	C_6H_5	**8d**	4-$OMeC_6H_4$	2.0	**13j**	73

[a]Isolated yield after silica gel column chromatography. [b]The reaction was carried out under microwave irradiation at 80 °C. [c]The intermediate **14d** (71% isolated yield) underwent elimination to form **13d** only after addition of DBU (1.5 equiv) and stirring at room temperature for 1 h.

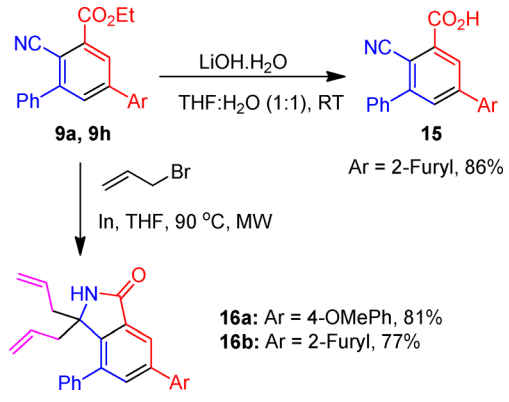
Scheme 1. Proposed Mechanism for the [3 + 3] Annulation of MBH Acetate 7 or 12 and Alkylidenemalononitrile 8



cyclization obviously arises from the possibility of aromatization of the initial cycloadduct **II**. In fact, this is for the first time, the S_N2' products of secondary MBH acetates **7** deviated from their normal cyclization mode of 5-*exo*-*trig* to 6-*endo*-*trig*.[15] Additional support for this mechanism emanated from the isolation of an intermediate in one case (**14d**, entry 4, Table 4). The reluctance of intermediate **14d** to undergo elimination to **13d** in the presence of Et_3N (pK_a 10.8) is attributable to the poor acidity of allylic proton in **14d** due to the *o*-OMe group. Therefore, a stronger base such as DBU (pK_a 12.0) was needed for elimination of HCN from **14d** (entry 4, Table 4). An alternate pathway followed by allylic anion derived from intermediate **I** in the presence of Bronsted bases (entries 9−10, Table 1) to form diene **10** is also shown in Scheme 1.

A representative terphenyl **9h** was subjected to LiOH mediated selective hydrolysis of the ester group under mild conditions to 2-cyano-3,5-diarylbenzoic acid **15** in excellent yield (86%, Scheme 2). Preferential reactivity of cyano group was demonstrated by indium mediated addition of allyl bromide to **9a** and **9h** under MW irradiation conditions. Interestingly, both **9a** and **9h** undergo a cascade double allylation−intramolecular lactamization under these conditions to generate synthetically useful isoindolinones **16a**,**b** in high yield (77−81%, Scheme 2).

Scheme 2. Selected Synthetic Transformations of Terphenyl



CONCLUSIONS

Polysubstituted *m*-terphenyls have been synthesized in high yield (62−83%) through a one-pot [3 + 3] annulation of Morita−Baylis−Hillman acetates of nitroalkenes and alkylidenemalononitrile in the presence of Et_3N at room temperature. The annulation takes place via a regioselective cascade S_N2'-intramolecular Michael reaction, which was confirmed by isolation of the intermediate cycloadduct, in one case, before

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aromatization and its subsequent transformation to the aromatized product. The scope of the reaction was demonstrated using nitroallylic acetates and alkylidenemalononitriles bearing aryl, heteroaryl and styrenyl groups at the β-position of the nitro/cyano group. Representative transformations of *meta*-terphenyl cyanoesters to corresponding carboxylic acids and isoindolinones have also been carried out.

EXPERIMENTAL SECTION

General Methods. The melting points recorded are uncorrected. NMR spectra were recorded with TMS as the internal standard for ^{1}H, ^{1}H decoupled ^{13}C, ^{13}C-APT, ^{1}H−^{1}H-2D-COSY and NOESY and $C_6H_5CF_3$ as the external standard for ^{19}F. The coupling constants (J values) are given in Hz. High resolution mass spectra were recorded under ESI Q-TOF conditions. X-ray data were collected on a diffractometer equipped with graphite monochromated Mo Kα radiation. The structure was solved by direct methods shelxs97 and refined by full-matrix least-squares against F^2 using SHELXL97 software. The secondary MBH acetates **7** (E = CO_2Et)[20] and the primary MBH acetates **11** (E = H)[21] were prepared from corresponding alcohols.[22,23] Malononitrile derivatives **8** were prepared from corresponding methyl ketone and malononitrile.[24]

General Procedure for the Synthesis of *m*-Terphenyls 9, 11, 13. To a stirred solution of MBH-acetate **7** or **12** (0.17 mmol) in DCE (3 mL) at rt, was added alkylidene malononitrile **8** (0.17 mmol) followed by triethylamine (0.1 mL, 69 mg, 0.68 mmol), and the completion of the reaction was monitored by TLC. The crude product was directly purified by silica gel column chromatography by eluting with 5−20% EtOAc−pet ether (gradient elution). In the case of entry 4, Table 4, the intermediate **14d** was either isolated or treated in situ with DBU (38 μL, 0.25 mmol) to afford **13d**.

Ethyl 4′-cyano-4-methoxy-[1,1′:3′,1″-terphenyl]-5′-carboxylate (9a). Pale yellow solid: yield 75%, 46 mg; mp 101 °C; IR (KBr, cm^{-1}) 3176 (vw), 2852 (vw), 2225 (w), 1726 (m), 1643 (vs), 1520 (w), 1457 (w), 1257 (m), 1171 (w), 1023 (w), 834 (w), 768 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 1.9 Hz, 1H), 7.81 (d, J = 1.9 Hz, 1H), 7.62 (d, J = 8.8 Hz, 2H), 7.57 (dd, J = 7.9, 1.5 Hz, 2H), 7.54−7.47 (m, 3H), 7.02 (d, J = 8.8 Hz, 2H), 4.51 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 160.7, 148.5, 144.6, 138.3, 134.9, 131.6, 130.6, 129.2, 129.1, 128.8, 128.7, 127.8, 117.0, 114.8, 109.0, 62.6, 55.6, 14.3; MS (ES$^+$, Ar) m/z (rel intensity) 375 ([M + H_2O]$^+$, 48), 358 (MH$^+$, 100), 312 (21); HRMS (ES$^+$, Ar) calcd for $C_{23}H_{20}NO_3$ (MH$^+$) 358.1443, found 358.1444. Confirmed by ^{1}H−^{1}H-2D-NOESY experiment.

Ethyl 4′-cyano-2,4-dimethoxy-[1,1′:3′,1″-terphenyl]-5′-carboxylate (9b). Dark yellow solid: yield 76%, 50 mg; mp 126 °C; IR (KBr, cm^{-1}) 2928 (m), 2224 (w), 1720 (vs), 1610 (vs), 1510 (m), 1465 (w), 1339 (m), 1306 (m), 1262 (m), 1209 (m), 1030 (m), 702 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 1.7 Hz, 1H), 7.81 (d, J = 1.7 Hz, 1H), 7.58 (dd, J = 8.0, 1.4 Hz, 2H), 7.52−7.46 (m, 3H), 7.31 (d, J = 8.3 Hz, 1H), 6.60 (dd, J = 8.3, 2.2 Hz, 1H), 6.58 (d, J = 2.2 Hz, 1H), 4.49 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 161.8, 157.8, 147.6, 142.7, 138.4, 134.6, 134.1, 131.5, 130.7, 129.3, 128.9, 128.7, 120.6, 117.2, 108.7, 105.3, 99.2, 62.4, 55.8, 55.7, 14.3; MS (ES$^+$, Ar) m/z (rel intensity) 426 (MK$^+$, 31), 425 ([M − 1]K$^+$, 45), 410 (MNa$^+$, 65), 388 (MH$^+$, 96), 360 (100), 342 (54), 298 (8), 279 (9), 213 (20), 196 (25); HRMS (ES$^+$, Ar) calcd for $C_{24}H_{22}NO_4$ (MH$^+$) 388.1549, found 388.1549.

Ethyl 4′-cyano-3,4-dimethoxy-[1,1′:3′,1″-terphenyl]-5′-carboxylate (9c). Dark yellow solid: yield 70%, 46 mg; mp 120 °C; IR (KBr, cm^{-1}) 2936 (m), 2223 (w), 1726 (m), 1596 (m), 1519 (m), 1464 (w), 1341 (w), 1264 (s), 1023 (m), 737 (w), 703 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, J = 1.9 Hz, 1H), 7.80 (d, J = 1.9 Hz, 1H), 7.58 (dd, J = 8.0, 1.5 Hz, 2H), 7.54−7.47 (m, 3H), 7.25 (dd, J = 8.4, 2.1 Hz, 1H), 7.14 (d, J = 2.1 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 4.52 (q, J = 7.1 Hz, 2H), 3.97 (s, 3H), 3.95 (s, 3H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 150.3, 149.7, 148.5, 144.9, 138.3, 134.9, 131.7, 131.1, 129.3, 129.2, 128.9, 127.9, 120.3, 116.9, 111.8, 110.4, 109.2, 62.6, 56.3, 56.2, 14 0.3; MS (ES$^+$, Ar) m/z (rel intensity) 388 (MH$^+$, 86), 360 (100), 342 (50); HRMS (ES$^+$, Ar) calcd for $C_{24}H_{22}NO_4$ (MH$^+$) 388.1549, found 388.1549.

Ethyl 5-(benzo[*d*][1,3]dioxol-5-yl)-2-cyano-[1,1′-biphenyl]-3-carboxylate (9d). Pale yellow solid: yield 77%, 49 mg; mp 104 °C; IR (KBr, cm^{-1}) 2988 (w), 2902 (w), 2225 (m), 1725 (s), 1597 (m), 1505 (m), 1494 (m), 1459 (m), 1446 (m), 1341 (m), 1250 (vs), 1229 (s), 1038 (s), 1016 (m), 929 (w), 734 (w), 702 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.77 (s, 1H), 7.57−7.49 (m, 5H), 7.15 (d, J = 8.1 Hz, 1H), 7.13 (s, 1H), 6.92 (d, J = 8.1 Hz, 1H), 6.04 (s, 2H), 4.51 (q, J = 7.0 Hz, 2H), 1.47 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 148.8, 148.5, 144.7, 138.1, 134.9, 132.4, 131.8, 129.17, 129.22, 128.8, 127.9, 121.6, 116.9, 109.3, 109.1, 107.7, 101.8, 62.6, 14.3; MS (ES$^+$, Ar) m/z (rel intensity) 410 (MK$^+$, 35), 394 (MNa$^+$, 100); HRMS (ES$^+$, Ar) calcd for $C_{23}H_{17}NO_4Na$ (MNa$^+$) 394.1050, found 394.1049.

Ethyl 4′-cyano-4-methyl-[1,1′:3′,1″-terphenyl]-5′-carboxylate (9e). Colorless solid: yield 76%, 44 mg; mp 102 °C; IR (KBr, cm^{-1}) 3027 (w), 2982 (m), 2923 (m), 2854 (w), 2225 (m), 1726 (vs), 1598 (m), 1458 (w), 1438 (w), 1369 (w), 1340 (w), 1280 (m), 1252 (s), 1175 (m), 1075 (m), 1014 (w), 820 (w), 788 (w), 702 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 1.9 Hz, 1H), 7.84 (d, J = 1.9 Hz, 1H), 7.59−7.56 (m, 4H), 7.54−7.48 (m, 3H), 7.31 (d, J = 7.9 Hz, 2H), 4.51 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 148.5, 145.0, 139.5, 138.2, 135.4, 134.9, 132.0, 130.1, 129.2, 129.1, 128.8, 128.1, 127.3, 117.0, 109.4, 62.6, 21.4, 14.3; MS (ES$^+$, Ar) m/z (rel intensity) 359 ([M + H_2O]$^+$, 57), 342 (MH$^+$, 100), 314 (46), 296 (30); HRMS (ES$^+$, Ar) calcd for $C_{23}H_{20}NO_2$ (MH$^+$) 342.1494, found 342.1508.

Ethyl 4′-cyano-[1,1′:3′,1″-terphenyl]-5′-carboxylate (9f). Colorless solid: yield 72%, 40 mg; mp 117 °C; IR (KBr, cm^{-1}) 2923 (m), 2226 (w), 1728 (s), 1599 (w), 1456 (w), 1339 (w), 1279 (m), 1249 (m), 1206 (w), 1076 (w), 765 (m), 701 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 1.9 Hz, 1H), 7.86 (d, J = 1.9 Hz, 1H), 7.68−7.65 (m, 2H), 7.58 (dd, J = 8.0, 1.6 Hz, 2H), 7.54−7.44 (m, 6H), 4.52 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 148.6, 145.1, 138.3, 138.1, 134.9, 132.3, 129.4, 129.3, 129.3, 129.2, 128.9, 128.4, 127.5, 116.9, 109.8, 62.6, 14.3; MS (ES$^+$, Ar) m/z (rel intensity) 366 (MK$^+$, 70), 350 (MNa$^+$, 85), 345 ([M + H_2O]$^+$, 75), 328 (MH$^+$, 100), 300 (38); HRMS (ES$^+$, Ar) calcd for $C_{22}H_{18}NO_2$ (MH$^+$) 328.1338, found 328.1334.

Ethyl 4′-cyano-4-fluoro-[1,1′:3′,1″-terphenyl]-5′-carboxylate (9g). Colorless solid: yield 74%, 43 mg; mp 101 °C; IR (KBr, cm^{-1}) 2925 (m), 2852 (w), 2225 (w), 1727 (vs), 1604 (m), 1514 (m), 1340 (w), 1280 (m), 1248 (s), 1162 (w), 1076 (w), 838 (m), 701 (w), 529 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 1.9 Hz, 1H), 7.81 (d, J = 1.9 Hz, 1H), 7.65 (dd, J = 8.7, 5.2 Hz, 2H), 7.57 (dd, J = 7.9, 1.7 Hz, 2H), 7.54−7.48 (m, 3H), 7.20 (t, J = 8.7 Hz, 2H), 4.52 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 163.6 (d, J_{C-F} = 249.8 Hz), 148.7, 144.0, 138.0, 135.0, 134.5 (d, J_{C-F} = 3.2 Hz), 132.1, 129.25, 129.34, 129.2 (d, J_{C-F} = 2.9 Hz), 128.9, 128.2, 116.8, 116.5 (d, J_{C-F} = 21.8 Hz), 109.9, 62.7, 14.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ −113.3; MS (ES$^+$, Ar) m/z (rel intensity) 346 (MH$^+$, 100), 319 (18), 318 (82), 300 (52), 274 (10), 213 (18), 196 (15); HRMS (ES$^+$, Ar) calcd for $C_{22}H_{17}NO_2F$ (MH$^+$) 346.1243, found 346.1229.

Ethyl 2-cyano-5-(furan-2-yl)-[1,1′-biphenyl]-3-carboxylate (9h). Pale yellow solid: yield 78%, 42 mg; mp 103 °C; IR (KBr, cm^{-1}) 2851 (vw), 2223 (m), 1725 (vs), 1608 (s), 1492 (vw), 1367 (w), 1333 (m), 1249 (m), 1199 (m), 1181 (m), 1073 (m), 1018 (s), 746 (s), 702 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 1.6 Hz, 1H), 7.89 (d, J = 1.6 Hz, 1H), 7.56−7.55 (m, 2H), 7.53−7.48 (m, 4H), 6.91 (d, J = 3.3 Hz, 1H), 6.56 (dd, J = 3.3, 1.7 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 151.4, 148.6, 144.3, 138.0, 135.0, 134.1, 129.17, 129.21, 128.8, 128.1, 124.7, 116.9, 112.6, 109.4, 109.1, 62.6, 14.3; MS (ES$^+$, Ar) m/z (rel intensity) 318 (MH$^+$, 100), 290 (71), 272 (88), 205 (25), 85 (25); HRMS (ES$^+$, Ar) calcd for $C_{20}H_{16}NO_3$ (MH$^+$) 318.1130, found 318.1122.

Ethyl 2-cyano-5-(thiophen-2-yl)-[1,1′-biphenyl]-3-carboxylate (9i). Pale yellow solid: yield 76%, 43 mg; mp 132 °C; IR (KBr, cm^{-1}) 3054 (w), 2988 (w), 2226 (w), 1728 (m), 1598 (w), 1422 (w), 1323 (w), 1266 (s), 738 (vs), 704 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 1.9 Hz, 1H), 7.83 (d, J = 1.9 Hz, 1H), 7.58−7.55 (m, 2H),

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7.54−7.49 (m, 4H), 7.44 (dd, J = 5.0, 0.8 Hz, 1H), 7.15 (dd, J = 5.0, 3.8 Hz, 1H), 4.52 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 148.7, 141.2, 138.2, 137.9, 135.1, 130.3, 129.15, 129.24, 128.8 (× 2), 127.9, 126.6, 126.1, 116.8, 109.3, 62.7, 14.3; MS (ES$^+$, Ar) m/z (rel intensity) 372 (MK^+, 10), 356 (MNa^+, 100), 301 (12), 193 (15), 148 (17), 102 (10); HRMS (ES$^+$, Ar) calcd for $C_{20}H_{15}NO_2SNa$ (MNa^+) 356.0716, found 356.0718.

Ethyl (*E*)-2-cyano-5-(2-methoxystyryl)-[1,1′-biphenyl]-3-carboxylate (9j). Pale yellow solid: yield 70%, 46 mg; mp 142 °C; IR (KBr, cm^{-1}) 3062 (vw), 2925 (m), 2851 (w), 2223 (m), 1726 (vs), 1593 (m), 1489 (m), 1464 (m), 1439 (m), 1369 (w), 1340 (w), 1249 (vs), 1199 (m), 1108 (w), 1074 (w), 1025 (s), 754 (s), 701 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 1.5 Hz, 1H), 7.75 (d, J = 1.5 Hz, 1H), 7.67 (d, J = 16.5 Hz, 1H), 7.61−7.46 (m, 6H), 7.32 (td, J = 8.4, 1.4 Hz, 1H), 7.18 (d, J = 16.5 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 3.91 (s, 3H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 157.5, 148.3, 142.1, 138.2, 134.7, 131.1, 130.2, 129.2, 129.1, 128.8 (× 2), 127.7, 127.2, 126.3, 125.1, 121.0, 117.1, 111.2, 109.0, 62.5, 55.6, 14.3; MS (ES$^+$, Ar) m/z (rel intensity) 422 (MK^+, 78), 415 ([M + MeOH]$^+$, 100), 406 (MNa^+, 92), 401 (41), 384 (24); HRMS (ES$^+$, Ar) calcd for $C_{25}H_{21}NO_3Na$ (MNa^+) 406.1414, found 406.1417.

Ethyl (*E*)-2-cyano-5-styryl-[1,1′-biphenyl]-3-carboxylate (9k). Pale yellow solid: yield 65%, 39 mg; mp 102 °C; IR (KBr, cm^{-1}) 2876 (m), 2223 (m), 1725 (vs), 1635 (s), 1593 (w), 1449 (w), 1369 (w), 1267 (s), 1199 (s), 1073 (m), 1021 (m), 963 (m), 751 (vs), 701 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 1.5 Hz, 1H), 7.74 (d, J = 1.5 Hz, 1H), 7.58−7.48 (m, 7H), 7.42−7.32 (m, 3H), 7.32 (d, J = 16.2 Hz, 1H), 7.15 (d, J = 16.2 Hz, 1H), 4.52 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 148.5, 141.4, 138.1, 136.2, 134.8, 133.8, 131.3, 129.2, 129.2, 129.16, 129.20, 128.8, 127.6, 127.2, 125.9, 117.0, 109.4, 62.6, 14.3; MS (ES$^+$, Ar) m/z (rel intensity) 392 (MK^+, 100), 376 (MNa^+, 32), 354 (41), 249 (9), 177 (13), 124 (8); HRMS (ES$^+$, Ar) calcd for $C_{24}H_{19}NO_2K$ (MK^+) 392.1047, found 392.1047.

Ethyl 2-cyano-5-(furan-2-yl)-4′-methyl-[1,1′-biphenyl]-3-carboxylate (11b). Pale yellow solid: yield 79%, 45 mg; mp 140 °C; IR (KBr, cm^{-1}) 2954 (s), 2923 (vs), 2856 (m), 2222 (w), 1731 (m), 1608 (m), 1461 (m), 1377 (w), 1260 (m), 1019 (m), 744 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 1.7 Hz, 1H), 7.88 (d, J = 1.7 Hz, 1H), 7.57 (d, J = 1.5 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 3.4 Hz, 1H), 6.56 (dd, J = 3.4, 1.5 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 151.4, 148.7, 144.3, 139.2, 135.1, 135.0, 134.0, 129.5, 129.0, 128.1, 124.5, 117.0, 112.6, 109.3, 109.0, 62.6, 21.5, 14.3; MS (ES$^+$, Ar) m/z (rel intensity) 354 (MNa^+, 65), 332 (MH^+, 100), 318 (22), 304 (74), 286 (92), 274 (40), 233 (83); HRMS (ES$^+$, Ar) calcd for $C_{21}H_{18}NO_3$ (MH^+) 332.1287, found 332.1280.

Ethyl 2-cyano-5-(furan-2-yl)-2′-methoxy-[1,1′-biphenyl]-3-carboxylate (11c). Pale yellow solid: yield 80%, 47 mg; mp 120 °C; IR (KBr, cm^{-1}) 2931 (w), 2225 (w), 1726 (s), 1608 (m), 1493 (w), 1464 (w), 1333 (w), 1254 (vs), 1021 (m), 753 (m); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, J = 1.4 Hz, 1H), 7.85 (d, J = 1.4 Hz, 1H), 7.55 (d, J = 1.5 Hz, 1H), 7.44 (td, J = 7.7, 1.3 Hz, 1H), 7.29−7.24 (m, 1H), 7.07 (t, J = 7.7 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H), 6.88 (d, J = 3.3 Hz, 1H), 6.54 (dd, J = 3.3, 1.5 Hz, 1H), 4.50 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 156.7, 151.6, 145.8, 144.1, 134.1, 133.9, 130.9, 130.8, 128.9, 127.2, 124.6, 120.9, 116.8, 112.5, 111.5, 111.3, 109.0, 62.5, 55.7, 14.3; MS (ES$^+$, Ar) m/z (rel intensity) 348 (MH^+, 100), 320 (27), 302 (64), 277 (8); HRMS (ES$^+$, Ar) calcd for $C_{21}H_{18}NO_4$ (MH^+) 348.1236, found 348.1233.

Ethyl 2-cyano-5-(furan-2-yl)-4′-methoxy-[1,1′-biphenyl]-3-carboxylate (11d). Pale yellow solid: yield 76%, 45 mg; mp 121 °C; IR (KBr, cm^{-1}) 2988 (w), 2839 (w), 2223 (m), 1726 (vs), 1609 (s), 1515 (m), 1335 (m), 1287 (m), 1254 (vs), 1182 (m), 1074 (m), 1022 (m), 836 (m), 739 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 1.3 Hz, 1H), 7.87 (d, J = 1.3 Hz, 1H), 7.55−7.58 (unresolved m, 1H), 7.51 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 3.4 Hz, 1H), 6.58−6.52 (m, 1H), 4.51 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 160.4, 151.4, 148.3, 144.3, 135.1, 134.0, 130.5, 130.3, 128.0, 124.3, 117.2, 114.3, 112.6, 109.3, 108.9, 62.6, 55.5, 14.3; MS (ES$^+$, Ar) m/z (rel intensity) 386 (MK^+, 45), 370 (MNa^+, 100); HRMS (ES$^+$, Ar) calcd for $C_{21}H_{17}NO_4Na$ (MNa^+) 370.1050, found 370.1049.

Ethyl 4′-chloro-2-cyano-5-(furan-2-yl)-[1,1′-biphenyl]-3-carboxylate (11e). Yellow solid: yield 75%, 45 mg; mp 171 °C; IR (KBr, cm^{-1}) 2936 (m), 1967 (m), 1728 (vs), 1608 (w), 1331 (w), 1249 (m), 1028 (m), 739 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 1.7 Hz, 1H), 7.86 (d, J = 1.7 Hz, 1H), 7.58 (d, J = 1.6 Hz, 1H), 7.53−7.47 (m, 4H), 6.93 (d, J = 3.5 Hz, 1H), 6.57 (dd, J = 3.5, 1.6 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 151.2, 147.4, 144.5, 136.4, 135.6, 135.1, 134.3, 130.6, 129.2, 127.9, 125.0, 116.8, 112.7, 109.6, 109.0, 62.7, 14.3; MS (ES$^+$, Ar) m/z (rel intensity) 354 ([M + 2]H$^+$, 8), 352 (MH^+, 24), 338 (15), 336 (77), 326 (20), 324 (71), 308 (15), 306 (60), 279 (100), 278 (73), 262 (25), 205 (49), 149 (12); HRMS (ES$^+$, Ar) calcd for $C_{20}H_{15}NO_3Cl$ (MH^+) 352.0740, found 352.0738.

Ethyl 4′-bromo-2-cyano-5-(furan-2-yl)-[1,1′-biphenyl]-3-carboxylate (11f). Yellow solid: yield 83%, 56 mg; mp 178 °C; IR (KBr, cm^{-1}) 2991 (vw), 2911 (vw), 2221 (w), 1728 (vs), 1609 (m), 1509 (w), 1367 (w), 1332 (m), 1293 (w), 1249 (s), 1072 (w), 1025 (m), 836 (m), 737 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 1.7 Hz, 1H), 7.85 (d, J = 1.7 Hz, 1H), 7.64 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 1.6 Hz, 1H), 7.43 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 3.4 Hz, 1H), 6.56 (dd, J = 3.4, 1.6 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 151.1, 147.4, 144.5, 136.9, 135.1, 134.3, 132.1, 130.8, 127.8, 125.0, 123.8, 116.8, 112.7, 109.6, 108.9, 62.7, 14.3; MS (ES$^+$, Ar) m/z (rel intensity) 398 ([MH+2]$^+$,100), 396 (MH^+, 80), 369 (97), 367 (100), 351 (63), 349 (60), 302 (18), 242 (55); HRMS (ES$^+$, Ar) calcd for $C_{20}H_{15}NO_3Br$ (MH^+) 396.0235, found 396.0239. Selected X-ray Data: $C_{20}H_{14}BrNO_3$, M = 396.23, Monoclinic, space group $P2(1)/n$, a = 7.446(3) Å, b = 7.600(3) Å, c = 29.561(11) Å, α = 90.00°, β = 97.206(10) °, γ = 90.00°, V = 1659.6(11) Å^3, D_c = 1.586 Mg/m^3, Z = 4, $F(000)$ = 800, λ = 0.71073 Å, μ = 2.496 mm^{-1}, Total/unique reflections = 11437/3001 [R(int) = 0.0752], T = 100(2) K, θ range = 3.02−25.34°. Final R [$I > 2\sigma(I)$]: $R1$ = 0.0403, $wR2$ = 0.0876. R (all data): $R1$ = 0.0513, $wR2$ = 0.0920.

Ethyl 2-cyano-4′-fluoro-5-(furan-2-yl)-[1,1′-biphenyl]-3-carboxylate (11g). Yellow liquid: yield 79%, 45 mg; IR (neat, cm^{-1}) 2926 (m), 2214 (w), 1731 (vs), 1609 (m), 1364 (w), 1333 (m), 1251 (s), 1067 (w), 1025 (m), 900 (w), 840 (m), 737 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 1.7 Hz, 1H), 7.87 (d, J = 1.7 Hz, 1H), 7.57 (d, J = 1.7 Hz, 1H), 7.54 (dd, J = 8.6, 5.2 Hz, 2H), 7.20 (t, J = 8.6 Hz, 2H), 6.93 (d, J = 3.4 Hz, 1H), 6.56 (dd, J = 3.4, 1.7 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.4 (d, J_{C-F} = 249.1 Hz), 151.2, 147.6, 144.4, 135.0, 134.2, 134.0 (d, J_{C-F} = 3.3 Hz), 131.1 (d, J_{C-F} = 8.5 Hz), 128.0, 124.8, 116.9, 115.9 (d, J_{C-F} = 21.8 Hz), 112.7, 109.5, 109.1, 62.7, 14.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ −113.4; MS (ES$^+$, Ar) m/z (rel intensity) 336 (MH^+, 27), 308 (84), 290 (100), 279 (25), 278 (19); HRMS (ES$^+$, Ar) calcd for $C_{20}H_{15}NO_3F$ (MH^+) 336.1036, found 336.1033.

Ethyl 3′-bromo-2-cyano-5-(furan-2-yl)-[1,1′-biphenyl]-3-carboxylate (11h). Pale yellow solid: yield 70%, 47 mg; mp 89 °C; IR (KBr, cm^{-1}) 2953 (m), 2922 (vs), 2850 (m), 2222 (w), 1724 (w), 1640 (br, s), 1555 (w), 1463 (w), 1077 (w), 1252 (w), 1019 (w), 755 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 1.8 Hz, 1H), 7.86 (d, J = 1.8 Hz, 1H), 7.67 (t, J = 1.7 Hz, 1H), 7.62 (dd, J = 7.9, 1.7 Hz, 1H), 7.58 (d, J = 1.4 Hz, 1H), 7.52 (dd, J = 7.9, 1.7 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 6.94 (d, J = 3.4 Hz, 1H), 6.57 (dd, J = 3.4, 1.4 Hz, 1H), 4.52 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 151.0, 146.9, 144.5, 139.9, 135.0, 134.2, 132.2, 132.0, 130.3, 127.85, 127.92, 125.1, 122.8, 116.5, 112.7, 109.7, 109.0, 62.7, 14.2; MS (ES$^+$, Ar) m/z (rel intensity) 436 ([MK+2]$^+$, 36), 434 (MK^+, 36), 420 ([MNa +2]$^+$, 100), 418 (MNa^+, 100), 415 (66), 413 (66); HRMS (ES$^+$, Ar) calcd for $C_{20}H_{14}NO_3BrNa$ (MNa^+) 418.0049, found 418.0049.

Ethyl 2-cyano-3,5-di(furan-2-yl)benzoate (11i). Colorless solid: yield 69%, 36 mg; mp 121 °C; IR (KBr, cm^{-1}) 2929 (w), 2221 (w), 1726 (s), 1607 (s), 1494 (m), 1367 (w), 1326 (m), 1297 (m), 1252 (vs), 1225 (m), 1073 (w), 1020 (s), 739 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 1.7 Hz, 1H), 8.19 (d, J = 1.7 Hz, 1H), 7.60 (d, J = 1.5 Hz, 1H),

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7.59 (d, J = 1.5 Hz, 1H), 7.53 (d, J = 3.4 Hz, 1H), 6.95 (d, J = 3.4 Hz, 1H), 6.60 (dd, J = 3.4, 1.5 Hz, 1H), 6.57 (dd, J = 3.4, 1.5 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 151.3, 149.1, 144.3, 143.8, 136.0, 135.6, 134.3, 124.06, 124.14, 117.4, 112.7, 112.6, 112.5, 109.4, 104.3, 62.6, 14.3; MS (ES^+, Ar) m/z (rel intensity) 330 (MNa^+, 100), 213 (11); HRMS (ES^+, Ar) calcd for $C_{18}H_{13}NO_4Na$ (MNa^+) 330.0737, found 330.0734.

Ethyl (*E*)-2-cyano-5-(furan-2-yl)-3-styrylbenzoate (11j). Pale yellow solid: yield 76%, 44 mg; mp 133 °C; IR (KBr, cm^{-1}) 2924 (m), 2852 (w), 2223 (w), 1726 (vs), 1634 (m), 1605 (m), 1369 (w), 1316 (w), 1316 (w), 1255 (w), 1021 (m), 964 (w), 754 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (ABq, J = 1.4 Hz, 2H), 7.66−7.60 (m, 4H), 7.43−7.33 (m, 4H), 6.95 (d, J = 3.4 Hz, 1H), 6.58 (dd, J = 3.4, 1.8 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 151.5, 144.2, 143.2, 136.1, 134.9, 134.5, 134.1, 129.3, 129.1, 127.5, 124.9, 124.0, 122.9, 116.4, 112.6, 109.2, 109.0, 62.6, 14.3; MS (ES^+, Ar) m/z (rel intensity) 389 ($[M + 2Na]^+$, 14), 382 (MK^+, 55), 366 (MNa^+, 100); HRMS (ES^+, Ar) calcd for $C_{22}H_{17}NO_3Na$ (MNa^+) 366.1101, found 366.1100.

Ethyl (*E*)-2-cyano-3-(4-fluorostyryl)-5-(furan-2-yl)benzoate (11k). Pale yellow solid: yield 73%, 45 mg; mp 154 °C; IR (KBr, cm^{-1}) 2989 (vw), 2216 (w), 1724 (s), 1635 (w), 1604 (m), 1508 (s), 1371 (w), 1259 (vs), 1231 (vs), 1028 (m), 738 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 4.0 Hz, 2H), 7.60−7.57 (m, 3H), 7.52 (d, J = 16.2 Hz, 1H), 7.29 (d, J = 16.2 Hz, 1H), 7.09 (t, J = 8.5 Hz, 2H), 6.94 (d, J = 3.3 Hz, 1H), 6.57 (dd, J = 3.3, 1.6 Hz, 1H), 4.50 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.3 (d, J_{C-F} = 249.6 Hz), 151.4, 144.3, 143.0, 134.4, 134.1, 133.6, 132.3 (d, J_{C-F} = 3.3 Hz), 129.2 (d, J_{C-F} = 8.2 Hz), 124.8, 123.7, 122.8, 116.4, 116.1 (d, J_{C-F} = 21.8 Hz), 112.6, 109.3, 108.9, 62.6, 14.3; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −111.7; MS (ES^+, Ar) m/z (rel intensity) 400 (MK^+, 64), 384 (MNa^+, 100), 379 (39), 362 (23), 347 (9), 291 (9); HRMS (ES^+, Ar) calcd for $C_{22}H_{16}FNO_3Na$ (MNa^+) 384.1006, found 384.1006.

4-Methoxy-[1,1′:3′,1″-terphenyl]-4′-carbonitrile (13a). Pale yellow liquid: yield 76%, 37 mg; IR (neat, cm^{-1}) 2924 (m), 2851 (w), 2221 (m), 1602 (vs), 1578 (w), 1518 (m), 1481 (w), 1294 (w), 1251 (vs), 1179 (m), 1027 (m), 824 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 1.7 Hz, 1H), 7.63−7.57 (m, 5H), 7.45−7.55 (m, 3H), 7.01 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 146.1, 145.4, 138.5, 134.3, 131.6, 128.9 (× 2), 128.6, 128.3, 125.7, 119.1, 114.7, 109.2, 55.6; MS (ES^+, Ar) m/z (rel intensity) 308 (MH^+, 100), 301 (31), 278 (29), 255 (8), 239 (9), 204 (19), 185 (22); HRMS (ES^+, Ar) calcd for $C_{20}H_{15}NONa$ (MNa^+) 308.1046, found 308.1049.

4-Methoxy-4″-methyl-[1,1′:3′,1″-terphenyl]-4′-carbonitrile (13b). Pale yellow solid: yield 75%, 38 mg; mp 86 °C; IR (KBr, cm^{-1}) 2925 (m), 2853 (w), 2221 (m), 1601 (s), 1519 (m), 1483 (m), 1293 (m), 1251 (vs), 1179 (m), 1036 (w), 821 (vs); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 1.8 Hz, 1H), 7.59 (dd, J = 8.0, 1.8 Hz, 1H), 7.58 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 146.1, 145.4, 138.9, 135.6, 134.3, 131.7, 129.6, 128.8, 128.6, 128.2, 125.5, 119.3, 114.7, 109.1, 55.6, 21.5; MS (ES^+, Ar) m/z (rel intensity) 338 (MK^+, 60), 322 (MNa^+, 100), 319 (53), 307 (26), 297 (21), 213 (19), 135 (14); HRMS (ES^+, Ar) calcd for $C_{21}H_{17}NONa$ (MNa^+) 322.1202, found 322.1203.

4,4″-Dimethoxy-[1,1′:3′,1″-terphenyl]-4′-carbonitrile (13c). Pale yellow liquid: yield 72%, 39 mg; IR (neat, cm^{-1}) 2957 (m), 2924 (s), 2851 (m), 2220 (m), 1608 (vs), 1600 (vs), 1578 (w), 1518 (s), 1482 (m), 1465 (w), 1291 (m), 1250 (s), 1178 (s), 1028 (s), 824 (vs), 758 (m), 536 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 1.5 Hz, 1H), 7.59−7.55 (m, 5H), 7.03 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 160.3, 145.8, 145.4, 134.3, 131.7, 130.9, 130.2, 128.6, 128.1, 125.3, 119.4, 114.7, 114.4, 109.0, 55.6, 55.5; MS (ES^+, Ar) m/z (rel intensity) 354 (MK^+, 10), 338 (MNa^+, 49), 301 (100), 132 (41), 102 (19); HRMS (ES^+, Ar) calcd for $C_{21}H_{17}NO_2Na$ (MNa^+) 338.1151, found 338.1158.

2″,4-Dimethoxy-[1,1′:3′,1″-terphenyl]-4′-carbonitrile (13d). Pale yellow liquid: yield 62%, 33 mg; IR (neat, cm^{-1}) 2929 (vs), 2857 (vs), 2223 (w), 1744 (s), 1683 (m), 1603 (s), 1580 (m), 1463 (vs), 1377 (m), 1291 (s), 1252 (vs), 1179 (m), 1162 (m), 1026 (m), 823 (m), 754 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 1.7 Hz, 1H), 7.60 (dd, J = 8.1, 1.7 Hz, 1H), 7.58 (d, J = 8.6 Hz, 2H), 7.44 (td, J = 7.5, 1.6 Hz, 1H), 7.32 (dd, J = 7.5, 1.6 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 7.00 (d, J = 8.6 Hz, 2H), 3.87 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 156.7, 145.0, 143.1, 133.4, 131.9, 131.1, 130.5, 129.1, 128.6, 127.6, 125.6, 121.0, 119.1, 114.6, 111.5, 111.4, 55.7, 55.6; MS (ES^+, Ar) m/z (rel intensity) 317 ($[MH+1]^+$, 48), 316 (MH^+, 100), 315 ($[MH - 1]^+$, 12); HRMS (ES^+, Ar) calcd for $C_{21}H_{18}NO_2$ (MH^+) 316.1332, found 316.1332.

5-(Furan-2-yl)-[1,1′-biphenyl]-2-carbonitrile (13e). Colorless solid: yield 79%, 33 mg; mp 98 °C; IR (KBr, cm^{-1}) 3107 (w), 3074 (w), 2958 (w), 2934 (w), 2837 (w), 2221 (s), 1609 (s), 1600 (s), 1515 (m), 1484 (m), 1295 (m), 1252 (vs), 1180 (m), 1028 (m), 833 (s), 736 (s), 705 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 1.6 Hz, 1H), 7.75, 7.70 (ABq, J = 8.2 Hz, the shielded half further split into d, 1.6 Hz, 2H), 7.61−7.58 (m, 2H), 7.54−7.44 (m, 4H), 6.84 (dd, J = 3.4, 0.6 Hz, 1H), 6.54 (dd, J = 3.4, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 146.2, 143.9, 138.2, 134.8, 134.3, 129.0, 128.87, 128.93, 125.0, 122.6, 119.0, 112.4, 109.4, 108.5; MS (ES^+, Ar) m/z (rel intensity) 268 (MK^+, 14), 247 ($[M + 2]^+$, 21), 246 (MH^+, 100), 214 (5), 158 (7); HRMS (ES^+, Ar) calcd for $C_{17}H_{12}NO$ (MH^+) 246.0919, found 246.0920.

2′-Methoxy-5-(thiophen-2-yl)-[1,1′-biphenyl]-2-carbonitrile (13f). Pale yellow liquid: yield 80%, 40 mg; IR (neat, cm^{-1}) 2924 (vs), 2853 (s), 2224 (m), 1600 (s), 1582 (w), 1496 (m), 1482 (m), 1463 (m), 1434 (m), 1283 (m), 1250 (s), 1024 (m), 821 (m), 755 (s), 703 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (ABq, J = 8.1 Hz, shielded half further split into d, J = 1.6 Hz, 2H), 7.68 (d, J = 1.6 Hz Hz, 1H), 7.47−7.44 (m, 1H), 7.43 (dd, J = 3.6, 1.1 Hz, 1H), 7.39 (dd, J = 5.1, 1.1 Hz, 1H), 7.31 (dd, J = 7.5, 1.7 Hz, 1H), 7.12 (dd, J = 5.1, 3.6 Hz, 1H), 7.10 (dd, J = 7.5, 1.0 Hz, 1H), 7.07−7.04 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 143.3, 142.4, 138.5, 133.5, 130.9, 130.7, 128.6, 128.0, 127.2, 127.0, 125.2, 124.5, 121.0, 118.8, 111.9, 111.5, 55.6; MS (ES^+, Ar) m/z (rel intensity) 330 (MK^+, 11), 319 (8), 317 (33), 314 (MNa^+, 100), 311 (4); HRMS (ES^+, Ar) calcd for $C_{18}H_{13}NOSNa$ (MNa^+) 314.0610, found 314.0610.

4′-Methoxy-5-(thiophen-2-yl)-[1,1′-biphenyl]-2-carbonitrile (13g). Pale yellow solid: yield 83%, 41 mg; mp 93 °C; IR (KBr, cm^{-1}) 3106 (vw), 2933 (vw), 2836 (vw), 2220 (m), 1600 (s), 1515 (m), 1483 (w), 1295 (m), 1251 (vs), 1180 (m), 1043 (w), 1028 (m), 832 (s), 736 (m), 736 (m), 705 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 1H), 7.69 (d, J = 1.7 Hz, 1H), 7.62 (dd, J = 8.1, 1.7 Hz, 1H), 7.55 (d, J = 8.7 Hz, 2H), 7.45 (dd, J = 3.6, 0.9 Hz, 1H), 7.40 (dd, J = 5.0, 0.9 Hz, 1H), 7.13 (dd, J = 5.0, 3.6 Hz, 1H), 7.04 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 146.0, 142.3, 138.7, 134.4, 130.4, 130.1, 128.7, 127.2, 126.9, 125.3, 124.2, 119.1, 114.4, 109.4, 55.5; MS (ES^+, Ar) m/z (rel intensity) 330 (MK, 18), 324 ($[MH+MeOH]^+$, 29), 314 (MNa^+, 100), 309 (9), 292 (11); HRMS (ES^+, Ar) calcd for $C_{18}H_{13}NOSNa$ (MNa^+) 314.0610, found 314.0610. Confirmed by ^{1}H−^{1}H COSY experiment.

4′-Bromo-5-(thiophen-2-yl)-[1,1′-biphenyl]-2-carbonitrile (13h). Colorless solid: yield 70%, 40 mg; mp 183 °C; IR (KBr, cm^{-1}) 3098 (vw), 2222 (s), 1601 (m), 1478 (m), 1269 (m), 1182 (w), 1074 (w), 837 (m), 818 (vs), 717 (vs); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.7 Hz, 1H), 7.68 (dd, J = 7.7, 1.8 Hz, 1H), 7.68 (d, J = 1.8 Hz, 1H), 7.65 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 7.46 (dd, J = 3.7, 0.9 Hz, 1H), 7.42 (dd, J = 5.0, 0.9 Hz, 1H), 7.14 (dd, J = 5.0, 3.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 142.0, 139.0, 137.0, 134.5, 132.2, 130.5, 128.8, 127.5, 126.9, 125.6, 125.0, 123.7, 118.6, 109.5; MS (ES^+, Ar) m/z (rel intensity) 364 ($[MNa+2]^+$, 100), 362 (MNa^+, 100), 341 (33), 339 (35); HRMS (ES^+, Ar) calcd for $C_{17}H_{10}BrNSNa$ (MNa^+) 361.9610, found 361.9609.

4-Chloro-4″-methoxy-[1,1′:3′,1″-terphenyl]-4′-carbonitrile (13i). Pale yellow solid: yield 77%, 42 mg; mp 145 °C; IR (KBr, cm^{-1}) 3054 (vw), 2937 (w), 2223 (m), 1601 (s), 1515 (s), 1478 (s), 1381 (m), 1294 (m), 1263 (s), 1251 (vs), 1178 (m), 1095 (w), 1033 (m), 1019 (w), 821 (vs), 809 (vs), 734 (w), 609 (w), 518 (m); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 1.5 Hz, 1H), 7.58

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(dd, J = 8.1, 1.5 Hz, 1H), 7.56 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 146.0, 144.5, 137.8, 135.1, 134.4, 130.5, 130.2, 129.5, 128.7, 128.5, 125.7, 119.1, 114.5, 110.1, 55.6; MS (ES$^+$, Ar) m/z (rel intensity) 360 ([MK+2]$^+$, 11), 345 ([M + 3]Na$^+$, 6), 344 ([M + 2]Na$^+$, 50), 343 ([M + 1]Na$^+$, 15), 342 (MNa$^+$, 100), 320 (3), 301 (6); HRMS (ES$^+$, Ar) calcd for $C_{20}H_{14}ClNONa$ (MNa$^+$) 342.0656, found 342.0656.

4″-Methoxy-[1,1′:3′,1″-terphenyl]-4′-carbonitrile (13j). Pale yellow liquid: yield 73%, 36 mg; IR (neat, cm^{-1}) 3053 (vw), 2924 (s), 2850 (w), 2221 (m), 1608 (s), 1601 (s), 1518 (s), 1483 (m), 1290 (s), 1251 (vs), 1178 (m), 1029 (m), 824 (s), 738 (vs), 704 (w), 535 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 1.6 Hz, 1H), 7.65−7.62 (m, 2H), 7.61 (dd, J = 8.0, 1.6 Hz, 1H), 7.57 (d, J = 8.7 Hz, 2H), 7.51−7.47 (m, 2H), 7.45−7.41 (m, 1H), 7.04 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 145.8, 145.8, 139.4, 134.3, 130.7, 130.2, 129.3, 128.8, 128.7, 127.4, 125.9, 119.2, 114.4, 109.7, 55.6; MS (ES$^+$, Ar) m/z (rel intensity) 326 ([MK+2]$^+$, 6), 309 ([M + 1]Na$^+$, 15), 308 (MNa$^+$, 100), 301 (9), 286 (MH$^+$, 9); HRMS (ES$^+$, Ar) calcd for $C_{20}H_{15}NONa$ (MNa$^+$) 308.1046, found 308.1047.

2″,4-Dimethoxy-[1,1′:3′,1″-terphenyl]-4′,4′(5′H)-dicarbonitrile (14d). Pale yellow solid: yield 71%, 41 mg; mp 117 °C; IR (KBr, cm^{-1}) 2958 (m), 2923 (vs), 2851 (m), 2222 (w), 1726 (m), 1606 (m), 1513 (m), 1488 (w), 1462 (m), 1250 (s), 1180 (m), 1120 (w), 1025 (s), 834 (w), 756 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, J = 7.7 Hz, 1H), 7.38 (d, J = 8.5 Hz, 2H), 7.31 (dd, J = 7.7, 1.5 Hz, 1H), 7.04−6.99 (m, 2H), 6.90 (d, J = 8.5 Hz, 2H), 6.74 (s, 1H), 6.21 (t, J = 4.3 Hz, 1H), 3.99 (s, 3H), 3.82 (s, 3H), 3.15 (d, J = 4.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 157.1, 137.6, 131.2, 130.6, 130.3, 128.9, 127.1, 125.7, 121.3, 116.4, 115.6, 114.3, 111.1, 55.5, 54.8, 35.6, 35.1; MS (ES$^+$, Ar) m/z (rel intensity) 381 (MK$^+$, 31), 365 (MNa$^+$, 100); HRMS (ES$^+$, Ar) calcd for $C_{22}H_{18}N_2O_2Na$ (MNa$^+$) 365.1260, found 365.1258. Confirmed by ^{1}H−^{1}H 2D-COSY experiment.

***(E)*-2-(3-(4-Methoxyphenyl)-1-phenylallylidene)malononitrile (10).**[25] To a stirred solution of MBH−acetate **7a** (0.17 mmol) in DCM (3 mL) at rt, was added alkylidene malononitrile **8** (0.17 mmol) followed by K_2CO_3 (94 mg, 0.68 mmol) or Cs_2CO_3 (222 mg, 0.68 mmol) and the completion of the reaction was monitored by TLC. The crude product was directly purified by silica gel column chromatography by eluting with 3−10% EtOAc-pet ether (gradient elution). Yellow solid: yield 68%, 32 mg (K_2CO_3, entry 9, Table 1), 70%, 37 mg (Cs_2CO_3, entry 10, Table 1); mp 119 °C (lit 125 °C,[25a] 129 °C[25b]); IR (KBr, cm^{-1}) 2925 (m), 2854 (w), 2221 (m), 1594 (s), 1569 (m), 1521 (s), 1255 (vs), 1175 (s), 1105 (w), 1027 (m), 834 (w), 762 (br m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.44 (m, 6H), 7.37 (d, J = 6.7 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 15.4 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.7, 162.9, 149.3, 133.5, 131.2, 131.0, 129.1, 129.0, 127.3, 122.4, 114.9, 113.9, 113.3, 80.8, 55.7; MS (ES$^+$, Ar) m/z (rel intensity) 328 ([MK+3]$^+$, 11), 327 ([MK+2]$^+$, 51), 310 ([MNa +1]$^+$, 23), 309 (MNa$^+$, 100), 304 (8); HRMS (ES$^+$, Ar) calcd for $C_{19}H_{14}N_2ONa$ (MNa$^+$) 309.0998, found 309.1000. IR and ^{1}H NMR data are broadly in agreement with literature.[25]

General Procedure for Selective Hydrolysis of Ester 9h. Lithium hydroxide (26 mg, 1.103 mmol, 7 equiv) was added to a stirred solution of cyanoester **9h** (50 mg, 0.158 mmol) in THF/water (1:1, 1 mL) at room temperature. After overnight stirring, the reaction mixture was poured into 1 N HCl and extracted with diethyl ether (3 × 10 mL). The combined organic extracts were washed with brine (10 mL), dried (Na_2SO_4), and concentrated in vacuo to give the title compound **15**.

2-Cyano-5-(furan-2-yl)-[1,1′-biphenyl]-3-carboxylic acid (15). Pale yellow solid: yield 86%, 39 mg; mp 223 °C; IR (KBr, cm^{-1}) 3647 (br, w), 2926 (br, s), 2223 (w), 1705 (s), 1604 (m), 1468 (m), 1295 (m), 934 (br, s), 695 (vs); ^{1}H NMR (400 MHz, DMSO) δ 13.97 (br s, 1H), 8.30 (unresolved, 1H), 8.00 (unresolved, 1H), 7.89 (unresolved, 1H), 7.58−7.52 (m, 5H), 7.41 (unresolved, 1H), 6.68 (unresolved, 1H); ^{13}C NMR (100 MHz, DMSO) δ 165.5, 150.4, 147.8, 145.2, 137.7, 135.8, 133.5, 129.1, 128.9, 128.5, 127.4, 123.6, 116.6, 112.9, 110.6, 107.9; MS (ES$^+$, Ar) m/z (rel intensity) 328 (MK$^+$, 23), 312 (MNa$^+$, 100), 301 (6); HRMS (ES$^+$, Ar) calcd for $C_{18}H_{11}NO_3Na$ (MNa$^+$) 312.0631, found 312.0634.

General Procedure for Synthesis of 4-Phenylisoindolin-1-one Derivatives 16. A stirred mixture of cyanoester **9** (0.140 mmol), allyl bromide (68 mg, 48 μL, 4.0 equiv, 0.56 mmol), and indium powder (32 mg, 2 equiv, 0.28 mmol) in THF (0.5 mL) was heated to 90 °C under microwave irradiation for 1−2 h. After completion of reaction, the crude product was directly purified by silica gel column chromatography by eluting with EtOAc−pet ether (gradient elution) to afford pure **16**.

3,3-Diallyl-6-(4-methoxyphenyl)-4-phenylisoindolin-1-one (16a). Off white solid: yield 81%, 45 mg; mp 181 °C; IR (KBr, cm^{-1}) 3206 (br, w), 3074 (vw), 2929 (vw), 2836 (vw), 1696 (vs), 1609 (w), 1519 (vw), 1468 (m), 1442 (w), 1360 (w), 1288 (w), 1250 (m), 1179 (w), 1030 (vw), 921 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 1.3 Hz, 1H), 7.60 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 1.3 Hz, 1H), 7.46−7.45 (m, 3H), 7.36−3.35 (m, 2H), 6.97 (d, J = 8.7 Hz, 2H), 5.46 (ddt, J = 17.2, 10.1, 7.0 Hz, 2H), 5.03−4.99 (m, 4H), 3.84 (s, 3H), 2.48 (dd, J = 14.3, 7.0 Hz, 2H), 2.36 (dd, J = 14.3, 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 159.7, 143.6, 141.0, 139.8, 138.7, 134.0, 132.5, 132.1, 132.0, 129.2, 128.4, 128.17, 128.22, 120.8, 119.6, 114.5, 65.6, 55.5, 42.5; MS (ES$^+$, Ar) m/z (rel intensity) 436 ([M + CH_3CN]$^+$, 30), 418 (MNa$^+$, 100); HRMS (ES$^+$, Ar) calcd for $C_{27}H_{25}NO_2Na$ (MNa$^+$) 418.1777, found 418.1779.

3,3-Diallyl-6-(furan-2-yl)-4-phenylisoindolin-1-one (16b). White solid: yield 77%, 38 mg; mp 218 °C; IR (KBr, cm^{-1}) 3183 (w), 3072 (w), 2899 (w), 1691 (vs), 1436 (vw), 1353 (w), 1254 (vw), 1017 (vw), 995 (w), 923 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 1.6 Hz, 1H), 7.67 (d, J = 1.6 Hz, 1H), 7.46−7.45 (m, 4H), 7.34−7.33 (m, 2H), 7.01−6.99 (br, 1H), 6.75 (dd, J = 3.3, 0.3 Hz, 1H), 6.48 (dd, J = 3.4, 1.8 Hz, 1H), 5.43 (ddt, J = 17.1, 10.1, 7.1 Hz, 2H), 5.01 (d, J = 17.1 Hz, 2H), 4.99 (d, J = 10.1 Hz, 2H), 2.44 (dd, J = 14.3, 7.1 Hz, 2H), 2.34 (dd, J = 14.3, 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 153.0, 144.0, 142.7, 139.5, 138.8, 134.1, 131.8, 131.2, 129.4, 129.1, 128.3 (×2), 119.6, 118.2, 112.0, 106.4, 65.9, 42.4; MS (ES$^+$, Ar) m/z (rel intensity) 394 (MK$^+$, 81), 378 (MNa$^+$, 100), 369 (6), 353 (8); HRMS (ES$^+$, Ar) calcd for $C_{24}H_{21}NO_2Na$ (MNa$^+$) 378.1464, found 378.1461.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of NMR spectra for all the new compounds as well as CIF for compound **11f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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