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Aerobic C–H Functionalization Using Pyrenedione as the Photocatalyst

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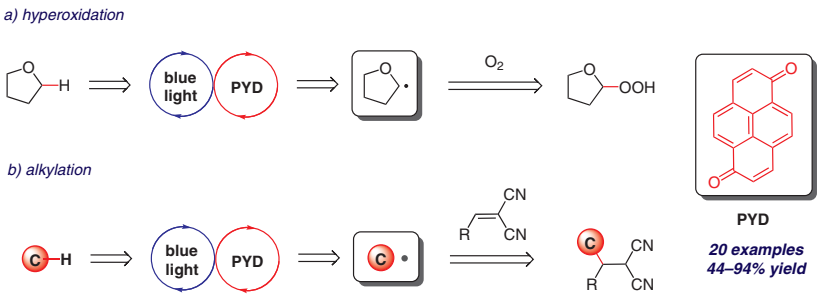

Received: 27.03.2020
Accepted after revision: 05.05.2020
Published online: 02.06.2020
DOI: 10.1055/s-0040-1707135; Art ID: ss-2020-z0165-fa

Abstract We disclose a visible-light-promoted aerobic alkylation of activated C(sp^3)–H bonds using pyrenedione (PYD) as the photocatalyst. Direct C–H bond alkylation of tetrahydrofuran with alkylidenemalononitriles is accomplished in over 90% yield in the presence of 5 mol% of PYD and 18 W blue LED light under ambient conditions. The substrate scope is extended to ethers, thioethers, and allylic C–H bonds in reactions with various electrophilic Michael acceptors. The catalytic turnover process is facilitated by oxygen. Our work represents the first example of using PYD as a photocatalyst to promote C(sp^3)–H alkylation, revealing the unique character of PYD as a novel organophotocatalyst.

Key words organophotocatalysts, pyrenedione, alkylation, tetrahydrofuran, visible light

Introduction

Direct functionalization of C(sp^3)–H bonds using unfunctionalized inert precursors has attracted intense interest in modern synthetic organic chemistry, thus greatly simplifying synthetic routes.[1–3] The development of visible-light photocatalysts over the past decade has enabled many novel methods for C(sp^3)–H activation under mild conditions that were previously impossible by other approaches.[4,5] Currently, the most widely used visible-light photocatalysts are based on Ir and Ru transition-metal complexes, which combine excellent visible-light-harvesting properties with rich redox chemistry due to metal-to-ligand charge transfer excited states.[6–8] However, their scarcity, high cost and low recyclability has impeded the wide application of transition-metal photocatalysts, especially on large scale.

From an economic point of view, ideal photocatalysts should be effective and robust, free of metal, and easily recyclable. Examples of such metal-free photocatalysts are Eosin Y,[9,10] acridinium salts[11,12] and rhodamine derivatives,[13] which have been extensively applied in a wide variety of reactions mediated by visible light. Due to their low cost, high absorption coefficients in the visible light region, and long excited state lifetime, they might represent good alternatives to transition-metal photocatalysts.

As a distinct class of photosensitizer, quinones occur naturally and are well known stoichiometric oxidants. Their potent hydrogen-abstracting and electron-accepting ability makes them potentially excellent photocatalysts for the activation of C–H bonds.[14] For example, Fukuzumi et al. discovered the photoredox catalytic conversion of benzene into phenol with DDQ under visible light irradiation.[15] Selective fluorination of inactivated C–H bonds using anthraquinone (AQN) as the photocatalyst was reported by Wong's group.[16] Recently, Arends disclosed an aerobic photocatalytic oxidation of alcohols with water-soluble sodium AQN sulfonate under visible light irradiation.[17] However, there are still several limitations that exist with quinone photocatalysts. Specifically, activation of AQN normally requires irradiation with UV light due to its poor absorption in the visible light region. The regeneration of DDQ in catalytic cycles is problematic and thus requires a high catalyst loading. Furthermore, the reaction scope applying AQN is limited. Therefore, the development of robust quinone catalysts with high catalytic performance, absorbing visible light as well as activating substrates efficiently, is in high demand.

Pyrenediones (PYDs) are a class of aromatic quinones with a pyrene backbone. Two isomers, namely 1,6-pyrenedione (1,6-PYD) and 1,8-pyrenedione (1,8-PYD), can be easily obtained on a large scale by the direct oxidation of pyrene with $K_2Cr_2O_7$.[18] PYD exhibits strong absorption in the visible light region.[19] Moreover, PYD displays excellent excited state oxidizing ability that is ideal for C–H activation.[19] We have previously demonstrated that the generation

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of H_2O_2 can be realized via a photocatalytic reaction between PYD and isopropanol, and its capability of in situ oxidizing organic compounds in a mild way.[19] We herein disclose the photooxidation of a series of C–H partners, including ethers and allylic compounds, by using 1,6-PYD as a photocatalyst under visible light irradiation. The aerobic alkylation of these C–H partners with electron-deficient alkenes has also been developed.

Results and Discussion

Design Strategy

Based on our preliminary findings, hydroperoxides were generated from various α-oxy and α-allylic C–H substrates with 1,6-PYD as the photocatalyst in the presence of visible light irradiation and an ambient atmosphere. Be-

Biographical Sketches

Yuannian Zhang has just completed her Ph.D. studies (March 2020) at Professor Dejian Huang's lab at the National University of Singapore. Her research is based on organophotocatalysis and the development of fluorescent probes in food analysis.

Xin Yang is a fourth year Ph.D. student at Professor Dejian Huang's lab at the National University of Singapore. His research involves the chemistry of flavonoids.

Jie Wu obtained his Ph.D. (organic chemistry) from Boston University and his research interests include continuous flow synthesis, photochemical synthesis, and automated synthesis.

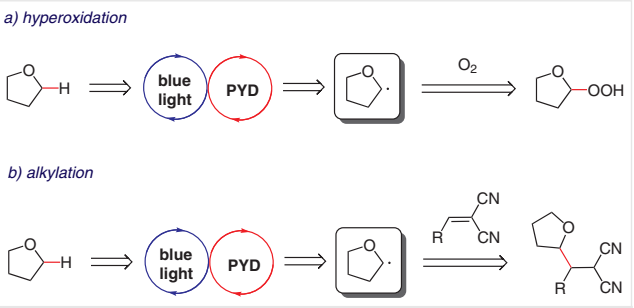
Dejian Huang obtained his Ph.D. (inorganic chemistry) from Indiana University and his research interests include catalysis and the chemistry of bioactive natural products.

cause of the high excited state oxidation potential of PYD (E^*_{red} = + 2.28 V vs SCE, MeCN), we proposed that ether/alkene radical cations were generated via visible-light induced single-electron transfer (SET), followed by a smooth deprotonation to form a transient α-oxy/allylic radical species. Triplet oxygen ($^3O_2$) could subsequently react with the α-oxy/allylic radical to accomplish the hydroperoxidation (Table 1, entries 1–4). Considering the ease of accessing α-oxy/allylic radicals upon irradiation in the presence of 1,6-PYD (Scheme 1, a), we envisioned that such radicals would participate in C–C bond formation with Michael acceptors, thereby furnishing direct alkylation of ether/allylic C(sp^3)–H bonds (Scheme 1, b).

Table 1 1,6-PYD-Photocatalyzed Hydroperoxidation of α-Oxy/Allylic C(sp^3)–H Bonds[a]

Entry	Substrate	Product	TON
1			110
2			90
3			80
4			160

[a] Reaction conditions: the ether or alkene (1 mL) was irradiated with 18 W blue LED light in the presence of 1,6-PYD (2.32 mg, 0.01 mmol) under an aerobic atmosphere. TON values were calculated based on analysis of the ^{1}H NMR spectra of the crude product mixtures using 1,3,5-trimethoxybenzene as an internal standard.



Scheme 1 Photocatalytic C–H functionalization by peroxidation or alkylation

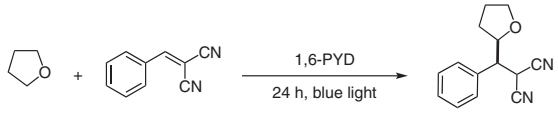
Reaction Optimization

To examine the feasibility of 1,6-PYD as a photocatalyst, a model reaction, the alkylation of C–H bonds via radical addition to an electron-deficient olefin, was selected. This convenient transformation represents an atom- and step-economical method for the formation of carbon–carbon bonds. We initially attempted the reaction mediated by 1,6-PYD using tetrahydrofuran (THF) as the C–H donor and solvent in the presence of an electron-deficient alkene and an alkylidenemalononitrile (AMN) **1a**, under air and an 18 W blue LED light (Table 2). In order to enhance the reaction efficiency, heating was applied using a water bath at 50 °C. Remarkably, 5 mol% of 1,6-PYD was able to catalyze this transformation to afford a 94% isolated yield of alkylation product **2a** in 24 hours (entry 3). An excellent yield (92%) was also obtained with 5 mol% of 1,8-PYD (entry 4). However, only a 28% yield was obtained in the absence of air, demonstrating the requirement of oxygen for the catalytic reaction (entry 6). This lower yield in the absence of oxygen might be attributed to the residual oxygen in the reaction system. To confirm that light and photocatalysts are indispensable components of this reaction, control experiments were conducted in the absence of either light or 1,6-PYD, with no product being formed under these conditions (entries 8 and 9). The performance of 1,6-PYD was also examined in acetone with 20 equivalents of THF, leading to, however, a relatively lower product yield of 50% (entry 2). Therefore, the C–H partner was applied as both the solvent and the reactant in subsequent experiments.

Scope of C–H Substrates and Michael Acceptors

We then evaluated the scope of the C–H partners for this convenient alkylation reaction using a catalytic amount of 1,6-PYD and alkylidene **1a** under visible-light irradiation.

Table 2 Optimization of the Reaction Conditions[a]

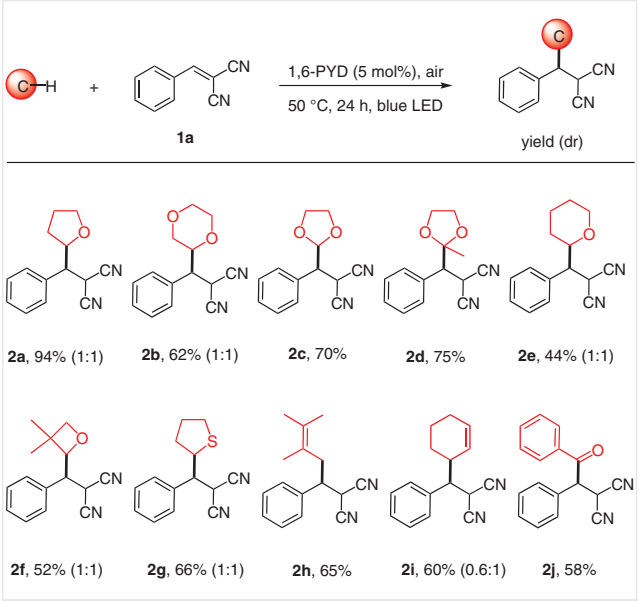


1a **2a**

Entry	Temp (°C)	PYD (mol%)	Atmosphere	Yield (%)[b]
1	30	5	air	62
2[c]	50	5	air	50
3	**50**	**5**	**air**	**94**
4[d]	**50**	**5**	**air**	**92**
5	50	5	O_2	84
6	50	5	argon	28
7	50	2	air	70
8	50	0	air	0
9[e]	50	5	air	0

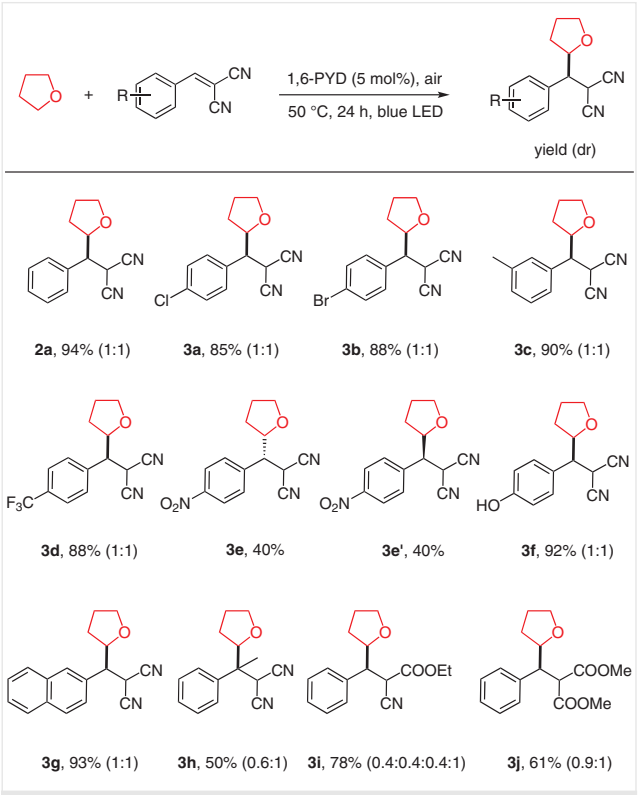
[a] Reaction conditions: **1a** (0.2 mmol), 1,6-PYD, THF as the solvent (2 mL), 18 W blue LED strip.
[b] Yields were determined from the ^{1}H NMR spectra of the crude product mixture using 1,3,5-trimethoxybenzene as an internal standard.
[c] Reaction performed with THF (20 equiv) in acetone (2 mL).
[d] 1,8-PYD was used as the photocatalyst.
[e] Reaction performed without light.

To our delight, a wide range of C–H bonds was readily accommodated. As depicted in Scheme 2, the use of ethers including 1,4-dioxane, tetrahydropyran, 1,3-dioxolane, 2-methyl-1,3-dioxolane and 3,3-dimethyloxetane gave the corresponding alkylation products **2b–f** in moderate to good yields ranging from 44–75%. A thioether, tetrahydrothiophene, reacted smoothly to afford product **2g** in 66% yield. Moreover, functionalized allylic substrates, including 2,3-dimethylbut-2-ene and cyclohexene, produced the coupling products **2h** and **2i** in moderate yields. Benzaldehyde was also well tolerated and afforded direct alkylation product **2j** in 58% yield.



Scheme 2 Reaction scope of the C–H partners. *Reagents and conditions*: **1a** (0.2 mmol), 1,6-PYD (0.01 mmol, 5 mol%), C–H partner as solvent (2 mL), 18 W blue LED strip, 50 °C, 24 h. Yields are of isolated products. Diastereomeric ratios are based on analysis of the ^{1}H NMR spectrum of the crude reaction mixtures.

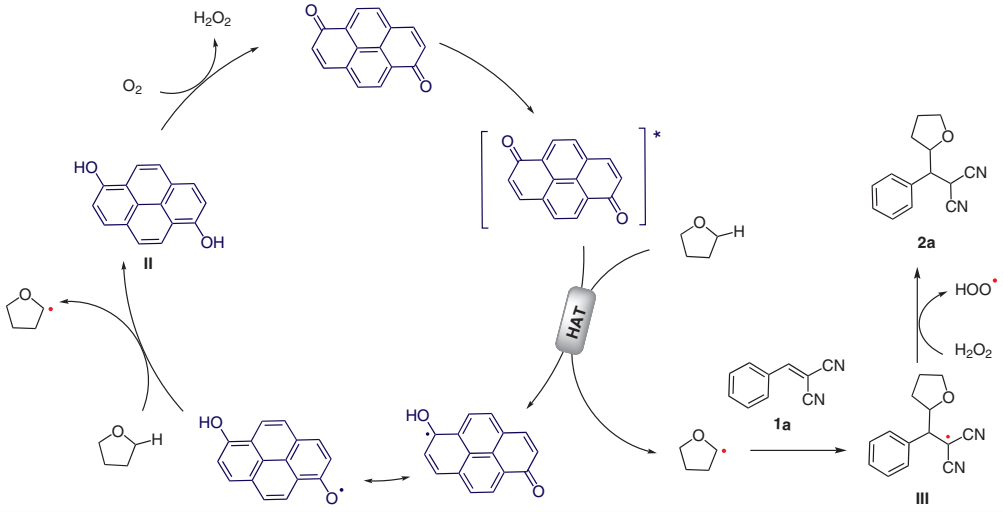
Further examination of the generality of this alkylation was evaluated with various AMN derivatives, demonstrating an extremely broad substrate scope (Scheme 3). A variety of electron-deficient and electron-rich aromatic rings on the Michael acceptors, even with functional groups such as phenols and aryl halides, participated in this coupling reaction smoothly, affording moderate to excellent yields (50–94%) of the expected products **3a–h** in 24 hours. Replacement of the nitrile groups on the malononitrile moiety with an ester, either one or two, was also applicable, giving products **3i** and **3j** in good yields. However, other Michael acceptors, including unsaturated aldehydes, ketones and amides, were unreactive.



Scheme 3 Reaction scope of the electron-deficient alkenes. *Reagents and conditions*: alkene (0.2 mmol), 1,6-PYD (0.01 mmol, 5 mol%), THF as the solvent (2 mL), 18 W blue LED strip, 50 °C, 24 h. Yields are of isolated products. Diastereomeric ratios are based on analysis of the ^{1}H NMR spectrum of the crude reaction mixtures.

Mechanistic Studies

The proposed mechanism is depicted in Scheme 4. Upon excitation by visible light, 1,6-PYD undergoes two sequential hydrogen atom abstractions from THF to deliver 1,6-PYDH_2 **II** and a THF α-oxy radical, which adds to the alkene to generate radical intermediate **III**. Triplet oxygen plays an essential role in the turnover step for regenerating 1,6-PYD, in which hydrogen peroxide was produced, resulting in the formation of **2a** by donating a hydrogen atom. We also questioned whether a hydrogen from the 1,6-PYDH_2 intermediate could be transferred directly to radical intermediate **III**.[20] However, as previously outlined, only a 28% yield of **2a** was generated in the absence of air (see Table 2), thus eliminating this possibility.



Scheme 4 Proposed photocatalytic mechanism for the alkylation

Several control experiments were conducted to gain insights into the reaction mechanism. Firstly, no alkylation product was obtained in the presence of radical scavengers such TEMPO, suggesting that a radical process was involved in the reaction. Secondly, the addition of the singlet oxygen quencher NaN_3 still afforded **2a** with 60% yield, which therefore excluded an energy-transfer pathway (see Scheme S1, Supporting Information). Furthermore, a light on/off experiment indicated that a radical chain reaction was unlikely (Figure 1, a). The magnitude of the kinetic isotope effect (KIE) given by k_H/k_D was 2.3, suggesting that hydrogen abstraction might be involved in the rate-limiting step (Figure 1, b, Scheme S2). A deuterium labelling study was also conducted to support the proposed catalytic mechanism (Scheme S3).

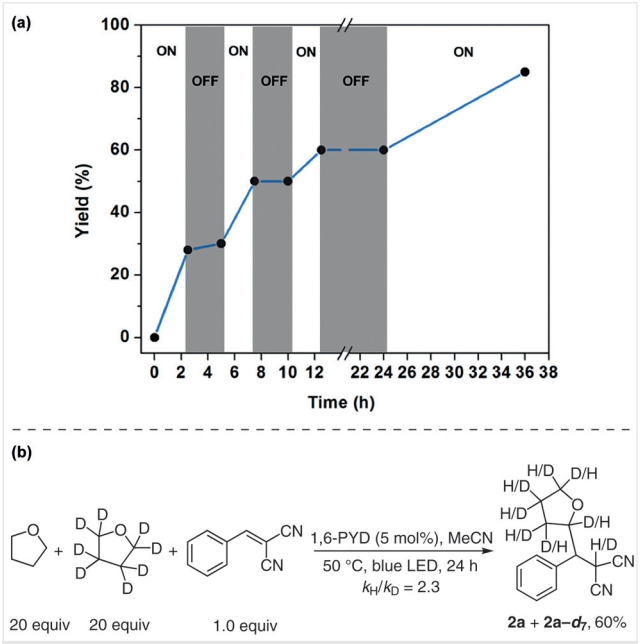


Figure 1 (a) Time profile of the transformation with light on/off over time. *Reagents and conditions*: **2a** (0.2 mmol), 1,6-PYD (0.01 mmol, 5 mol%), THF as the solvent (2 mL), 18 W blue LED strip, 50 °C. Yields were determined by analysis of the ^{1}H NMR spectra of the crude reaction mixtures. (b) Kinetic isotope effect experiments.

Conclusions

In conclusion, we have disclosed 1,6-PYD as an organophotocatalyst for the visible-light-promoted aerobic alkylation of electron-deficient alkenes. Direct C(sp^3)–H bond functionalization of ethers, thioethers, and allylic compounds with a wide variety of Michael acceptors has been accomplished with good to excellent yields of the products being obtained. The turnover process was facilitated by oxygen. This mild and metal-free protocol reveals a promising use of 1,6-PYD as a novel organophotocatalyst for C–H functionalization under an aerobic environment.

For general procedures on the PYD-catalyzed formation of hydroperoxides, see the supporting information. Chemicals and solvents were purchased from commercial suppliers and used as received without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVIII400 (400 MHZ) or Bruker AMX500 (500 MHz) spectrometers. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference for ^{1}H NMR ($CHCl_3$: 7.26 ppm) and $CDCl_3$ for ^{13}C NMR (at 77.0 ppm). Multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), br s (broad singlet). High-resolution mass spectrometry

was performed using a Bruker microTOF-Q II 1026 mass spectrometer. The blue LED strips (2 meters, 18 W) were purchased from InLEDs Pte Ltd (Singapore). The NMR data for compounds **2a**, **2b**, **2c**, **2e**, **2f**, **2g**, **2h**, **2i**, **2j** and **3h** were in accordance with those reported in the literature.[20]

PYD-Catalyzed Alkylation; General Procedure

Electron-deficient alkene **1** (0.2 mmol, 1.0 equiv) and 1,6-PYD (2.32 mg, 0.01 mmol, 5 mol%) were added to a 10 mL Pyrex tube equipped with a magnetic stir bar. The corresponding C–H partner as the reactant and solvent (2 mL) was added. Next, the reaction mixture was placed under a blue LED (2 meter strips, 18 W) and irradiated at 50 °C (water bath) for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography over silica gel by elution with hexane to hexane/ethyl acetate (10:1 to 2:1) to give the corresponding product.

2-[Phenyl(tetrahydrofuran-2-yl)methyl]malononitrile (2a)

Yield: 42.4 mg (94%); colorless oil; dr = 1:1.

Compound 2a′

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.35 (m, 8 H), 7.34–7.29 (m, 2 H), 4.54 (d, *J* = 4.1 Hz, 1 H), 4.46 (td, J = 7.1, 3.2 Hz, 1 H), 4.44–4.36 (m, 1 H), 4.39 (d, *J* = 10.7 Hz, 1 H), 4.00–3.92 (m, 1 H), 3.92–3.83 (m, 1 H), 3.75 (td, *J* = 6.4, 1.5 Hz, 2 H), 3.28 (dd, *J* = 10.6, 3.2 Hz, 1 H), 3.04 (dd, *J* = 10.3, 4.2 Hz, 1 H), 2.03–1.92 (m, 1 H), 1.98–1.87 (m, 3 H), 1.86–1.73 (m, 1 H), 1.50–1.34 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 134.45, 133.97, 129.29, 129.26, 129.24, 128.99, 128.96, 128.52, 112.32, 112.30, 112.26, 111.70, 78.06, 77.49, 68.85, 68.74, 50.67, 52.05, 30.37, 28.90, 27.36, 27.01, 25.80, 25.80.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{14}H_{13}N_2O$: 225.1033; found: 225.1034.

2-[(1,4-Dioxan-2-yl)(phenyl)methyl]malononitrile (2b)

Yield: 30.1 mg (62%); colorless oil; dr = 1:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 7.43 (d, *J* = 6.7 Hz, 3 H), 7.39–7.37 (m, 5 H), 7.34–7.31 (m, 2 H). 4.56 (d, *J* = 4.2 Hz, 1 H), 4.37 (d, *J* = 11.0 Hz, 1 H), 4.20–4.13 (m, 1 H), 4.10 (m, 1 H), 3.94–3.80 (m, 2 H), 3.88–3.80 (m, 2 H), 3.75 (dd, *J* = 11.8, 2.6 Hz, 1 H), 3.68 (dd, *J* = 11.8, 2.7 Hz, 1 H), 3.63–3.54 (m, 2 H), 3.51 (dd, *J* = 11.7, 2.5 Hz, 1 H), 3.44 (td, *J* = 11.7, 3.0 Hz, 1 H), 3.28 (dd, *J* = 11.0, 3.5 Hz, 1 H), 3.20 (dd, *J* = 11.7, 9.7 Hz, 1 H), 3.11 (dd, *J* = 10.8, 4.2 Hz, 1 H), 2.96 (dd, *J* = 11.6, 10.1 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 133.37, 132.54, 129.74, 129.57, 129.24, 129.18, 129.01, 128.36, 111.98, 111.96, 111.84, 111.48, 73.80, 73.75, 69.30, 68.92, 67.71, 67.18, 66.22, 66.21, 48.46, 48.37, 26.15, 26.06.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{14}H_{13}N_2O_2$: 241.0983; found: 241.0980.

2-[(1,3-Dioxolan-2-yl)(phenyl)methyl]malononitrile (2c)

Yield: 31.9 mg (70%); colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52–7.37 (m, 5 H), 5.25 (d, *J* = 3.1 Hz, 1 H), 4.31 (d, *J* = 6.6 Hz, 1 H), 4.15–4.04 (m, 2 H), 4.07–3.86 (m, 2 H), 3.52 (dd, *J* = 6.6, 3.1 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 133.12, 129.26, 129.16, 128.91, 111.99, 111.76, 102.86, 65.87, 65.00, 49.24, 24.23.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{13}H_{11}N_2O_2$: 227.0826; found: 227.0819.

2-[(2-Methyl-1,3-dioxolan-2-yl)(phenyl)methyl]malononitrile (2d)

Yield: 36.4 mg (75%); colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59–7.47 (m, 2 H), 7.41 (dd, *J* = 5.0, 2.0 Hz, 3 H), 4.41 (d, *J* = 5.9 Hz, 1 H), 4.24–4.16 (m, 1 H), 4.18–4.09 (m, 2 H), 4.09–4.01 (m, 1 H), 3.50 (d, *J* = 5.8 Hz, 1 H), 1.14 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 133.80, 129.55, 129.22, 129.11, 112.73, 112.33, 109.23, 65.27, 63.88, 53.99, 24.39, 22.65.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{14}H_{13}N_2O_2$: 241.0983; found: 241.0981.

2-[Phenyl(tetrahydro-2*H*-pyran-2-yl)methyl]malononitrile (2e)

Yield: 21.1 mg (44%); colorless oil; dr = 1:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 7.43–7.31 (m, 10 H), 4.63 (d, *J* = 4.3 Hz, 1 H), 4.38 (d, *J* = 11.1 Hz, 1 H), 4.13–4.04 (m, 2 H), 3.91–3.85 (m, 1 H), 3.76 (td, *J* = 10.7, 1.8 Hz, 1 H), 3.60–3.49 (m, 1 H) 3.48 (td, *J* = 11.6, 2.9 Hz, 1 H), 3.20 (dd, *J* = 10.9, 3.6 Hz, 1 H), 3.09 (dd, *J* = 10.3, 4.3 Hz, 1 H), 1.85–1.73 (m, 2 H), 1.59–1.34 (m, 8 H), 1.20–1.05 (m, 1 H), 1.04–0.92 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 134.49, 134.09, 129.39, 129.27, 129.18, 128.82, 128.78, 128.60, 112.55, 112.45, 112.34, 111.95, 76.44, 76.14, 69.22, 68.98, 52.18, 51.64, 29.60, 29.08, 26.46, 26.15, 25.59, 25.58, 22.99, 22.90.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{15}H_{15}N_2O$: 239.1190; found: 239.1197.

2-[(3,3-Dimethyloxetan-2-yl)(phenyl)methyl]malononitrile (2f)

Yield: 25.0 mg (52%); colorless oil; dr = 1:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 7.47–7.34 (m, 10 H), 4.99 (d, *J* = 11.0 Hz, 1 H), 4.97 (d, *J* = 8.4 Hz, 1 H), 4.40 (d, *J* = 5.6 Hz, 1 H), 4.33 (d, *J* = 5.5 Hz, 1 H), 4.31 (d, *J* = 3.6 Hz, 1 H), 4.15 (d, *J* = 5.6 Hz, 1 H), 3.98 (d, *J* = 5.5 Hz, 1 H), 3.94 (d, *J* = 6.4 Hz, 1 H), 3.58 (dd, *J* = 11.2, 3.7 Hz, 1 H), 3.54 (dd, *J* = 8.6, 6.5 Hz, 1 H), 1.39 (s, 3 H), 1.28 (s, 3 H), 1.13 (s, 3 H), 0.97 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 133.56, 132.37, 129.49, 129.32, 129.29, 129.27, 128.93, 128.63, 111.93, 111.34, 111.06, 111.03, 87.93, 87.13, 81.28, 80.77, 48.82, 47.48, 39.03, 38.40, 26.85, 26.70, 26.65, 25.97, 21.32, 21.22.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{15}H_{15}N_2O$: 239.1190; found: 239.1185.

2-[Phenyl(tetrahydrothiophen-2-yl)methyl]malononitrile (2g)

Yield: 31.9 mg (66%); colorless oil; dr = 1:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 7.54–7.33 (m, 10 H), 4.60 (d, *J* = 4.3 Hz, 1 H), 4.22 (d, *J* = 6.1 Hz, 1 H), 4.15–4.00 (m, 1 H), 4.02–3.87 (m, 1 H), 3.30 (dd, *J* = 9.2, 6.1 Hz, 1 H), 3.07–2.93 (m, 3 H), 2.87–2.73 (m, 2 H), 2.37 (dt, *J* = 11.7, 5.6 Hz, 1 H), 2.09–1.84 (m, 5 H), 1.74–1.58 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 136.18, 135.60, 129.31, 129.27, 129.25, 129.10, 128.31, 128.31, 112.00, 111.59, 111.50, 111.39, 53.87, 51.94, 50.26, 49.93, 35.71, 35.49, 33.13, 32.42, 31.10, 29.64, 29.61, 28.65.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{14}H_{13}N_2S$: 241.0805; found: 241.0798.

2-(3,4-Dimethyl-1-phenylpent-3-en-1-yl)malononitrile (2h)

Yield: 30.9 mg (65%); colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59–7.30 (m, 5 H), 3.96 (d, *J* = 5.1 Hz, 1 H), 3.34 (ddd, *J* = 8.8, 6.8, 5.1 Hz, 1 H), 2.94 (dd, *J* = 14.0, 8.7 Hz, 1 H), 2.50 (dd, *J* = 14.0, 6.8 Hz, 1 H), 1.70 (s, 3 H), 1.66 (s, 3 H), 1.62 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.14, 130.03, 128.98, 128.77, 127.92, 122.56, 112.43, 111.91, 45.39, 37.26, 28.50, 20.97, 20.64, 18.30.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{16}H_{17}N_2$: 237.1397; found: 237.1400.

2-[Cyclohex-2-en-1-yl(phenyl)methyl]malononitrile (2i)

Yield: 28.3 mg (60%); colorless oil; dr = 0.6:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 7.59–7.33 (m, 10 H), 6.04–5.92 (m, 1 H), 5.85–5.68 (m, 2 H), 5.59–4.87 (m, 1 H), 4.26 (d, *J* = 5.0 Hz, 1 H), 4.19 (d, *J* = 4.7 Hz, 1 H), 3.06 (dd, *J* = 10.6, 4.9 Hz, 1 H), 3.00–2.85 (m, 2 H), 2.85–2.76 (m, 1 H), 2.09–1.95 (m, 5 H), 1.88–1.78 (m, 1 H), 1.76–1.49 (m, 4 H), 1.42–1.31 (m, 1 H), 1.31–1.18 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 136.40, 136.31, 132.45, 130.16, 129.17, 128.89, 128.87, 128.52, 128.25, 126.34, 125.49, 112.15, 111.93, 111.79, 111.66, 51.34, 51.25, 37.06, 35.96, 27.71, 27.54, 27.46, 25.76, 25.11, 24.78, 21.18, 19.22.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{17}N_2$: 237.1386; found: 237.1382.

2-(2-Oxo-1,2-diphenylethyl)malononitrile (2j)

Yield: 30.2 mg (58%); colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 9.8 Hz, 2 H), 7.55 (t, *J* = 7.5 Hz, 1 H), 7.46–7.33 (m, 7 H), 5.10 (d, *J* = 8.5 Hz, 1 H), 4.54 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 193.05, 134.33, 133.78, 131.99, 129.97, 129.79, 129.18, 128.87, 128.55, 112.10, 111.54, 54.64, 26.76.

HRMS-ESI: *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{12}N_2NaO$: 283.0842; found: 283.0852.

2-[(4-Chlorophenyl)(tetrahydrofuran-2-yl)methyl]malononitrile (3a)

Yield: 44.2 mg (85%); colorless oil; dr = 1:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 7.43 (d, *J* = 8.5 Hz, 2 H), 7.39 (d, *J* = 8.5 Hz, 2 H), 7.35 (d, *J* = 8.5 Hz, 2 H), 7.30 (d, *J* = 8.7 Hz, 2 H), 4.57 (d, *J* = 4.1 Hz, 1 H), 4.46 (td, *J* = 7.4, 3.2 Hz, 1 H), 4.37 (d, *J* = 10.4 Hz, 1 H), 4.39–4.34 (m, 1 H), 3.97 (dt, *J* = 8.4, 6.5 Hz, 1 H), 3.89 (dt, *J* = 8.4, 6.7 Hz, 1 H), 3.77 (t, *J* = 6.9 Hz, 2 H), 3.30 (dd, *J* = 10.6, 3.2 Hz, 1 H), 3.05 (dd, *J* = 10.3, 4.1 Hz, 1 H), 2.07–1.89 (m, 4 H), 1.87–1.81 (m, 1 H), 1.55–1.43 (m, 2 H), 1.41–1.32 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 135.26, 135.00, 132.82, 132.42, 130.58, 129.80, 129.47, 129.18, 112.11, 112.03, 112.03, 111.45, 77.26, 68.80, 68.74, 51.31, 49.89, 30.27, 28.84, 27.19, 26.96, 25.73, 25.73.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{14}H_{12}ClN_2O$: 259.0644; found: 259.0642.

2-[(4-Bromophenyl)(tetrahydrofuran-2-yl)methyl]malononitrile (3b)

Yield: 53.3 mg (88%); colorless oil; dr = 1:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 7.58 (d, *J* = 8.4 Hz, 2 H), 7.54 (d, *J* = 8.3 Hz, 2 H), 7.29 (d, *J* = 8.5 Hz, 2 H), 7.23 (d, *J* = 8.4 Hz, 2 H), 4.57 (d, *J* = 4.1 Hz, 1 H), 4.45 (td, *J* = 7.4, 3.2 Hz, 1 H), 4.40–4.33 (m, 1 H), 4.36 (d, *J* = 10.6 Hz, 1 H), 3.97 (dt, *J* = 8.5, 6.5 Hz, 1 H), 3.89 (dt, *J* = 8.3, 6.7 Hz, 1 H), 3.77 (t, *J* = 6.8 Hz, 2 H), 3.29 (dd, *J* = 10.6, 3.2 Hz, 1 H), 3.04 (dd, *J* = 10.2, 4.1 Hz, 1 H), 2.07–1.84 (m, 4 H), 1.88–1.74 (m, 1 H), 1.55–1.40 (m, 2 H), 1.40–1.34 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 33.32, 132.93, 132.44, 132.15, 130.88, 130.09, 123.47, 123.23, 112.09, 112.02, 112.00, 111.43, 77.69, 77.22, 68.81, 68.75, 51.40, 49.98, 30.29, 28.85, 27.12, 26.89, 25.75, 25.74.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{14}H_{12}BrN_2O$: 303.0138; found: 303.0140.

2-[(Tetrahydrofuran-2-yl)(*m*-tolyl)methyl]malononitrile (3c)

Yield: 43.3 mg (90%); colorless oil; dr = 1:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 7.37–7.25 (m, 2 H), 7.25–7.17 (m, 4 H), 7.13 (d, *J* = 7.2 Hz, 2 H), 4.55 (d, *J* = 4.1 Hz, 1 H), 4.48 (td, *J* = 7.2, 3.3 Hz, 1 H), 4.46–4.36 (m, 1 H), 4.40 (d, *J* = 10.6 Hz, 1 H), 3.98 (dt, *J* = 8.5, 6.4 Hz, 1 H), 3.89 (dt, *J* = 8.5, 6.8 Hz, 1 H), 3.77 (t, *J* = 6.6 Hz, 2 H), 3.26 (dd, *J* = 10.6, 3.3 Hz, 1 H), 3.02 (dd, *J* = 10.3, 4.2 Hz, 1 H), 2.41 (s, 3 H), 2.39 (s, 3 H), 2.03–1.89 (m, 4 H), 1.86–1.78 (m, 1 H), 1.54–1.39 (m, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 138.94, 138.57, 134.38, 133.86, 129.95, 129.92, 129.64, 129.11, 129.05, 128.77, 126.09, 125.40, 112.36, 112.34, 112.33, 111.76, 78.08, 77.50, 68.80, 68.65, 51.83, 50.53, 30.29, 28.89, 27.29, 26.96, 25.80, 25.72, 21.41, 21.41.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{15}H_{15}N_2O$: 239.1190; found: 239.1194.

2-{(Tetrahydrofuran-2-yl)[4-(trifluoromethyl)phenyl]methyl}-malononitrile (3d)

Yield: 51.7 mg (88%); colorless oil; dr = 1:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 7.70 (d, *J* = 8.1 Hz, 2 H), 7.66 (d, *J* = 8.1 Hz, 2 H), 7.53 (d, *J* = 8.1 Hz, 2 H), 7.47 (d, *J* = 8.1 Hz, 2 H), 4.59 (d, *J* = 4.2 Hz, 1 H), 4.46 (td, *J* = 7.5, 3.3 Hz, 1 H), 4.43–4.35 (m, 1 H), 4.40 (d, *J* = 10.4 Hz, 1 H), 4.01–3.92 (m, 1 H), 3.88 (dt, *J* = 8.5, 6.7 Hz, 1 H), 3.76 (t, *J* = 6.8 Hz, 2 H), 3.37 (dd, *J* = 10.6, 3.3 Hz, 1 H), 3.11 (dd, *J* = 10.2, 4.1 Hz, 1 H), 2.00–1.89 (m, 4 H), 1.88–1.79 (m, 1 H), 1.51–1.40 (m, 2 H), 1.33 (ddt, *J* = 12.4, 8.7, 7.6 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 138.28, 138.02, 131.50 (q, *J* = 33.6 Hz), 131.23 (q, *J* = 33.4 Hz), 129.77, 129.05, 126.25 (q, *J* = 3.9 Hz), 125.92 (q, *J* = 3.6 Hz), 123.73 (q, *J* = 272.4 Hz), 123.68 (q, *J* = 272.1 Hz), 111.95, 111.86, 111.32, 77.65, 68.83, 68.82, 51.71, 50.25, 30.34, 28.91, 27.04, 26.89, 25.78, 25.75.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{15}H_{12}F_3N_2O$: 293.0907; found: 293.0912.

2-[(4-Nitrophenyl)(tetrahydrofuran-2-yl)methyl]malononitrile (3e)

Yield: 43.3 mg (80%); colorless oil; dr = 1:1.

Compound 3e

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 8.8 Hz, 2 H), 7.55 (d, *J* = 8.7 Hz, 2 H), 4.47 (td, *J* = 7.7, 3.3 Hz, 1 H), 4.41 (d, *J* = 10.5 Hz, 1 H), 3.77 (t, *J* = 6.9 Hz, 2 H), 3.44 (dd, *J* = 10.5, 3.3 Hz, 1 H), 2.12–1.99 (m, 1 H), 1.94–1.79 (m, 1 H), 1.56–1.42 (m, 1 H), 1.34–1.25 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.33, 141.20, 130.43, 124.08, 111,61, 111.56, 77.14, 68.88, 50.18, 28.98, 26.81, 26.75.

Compound 3e′

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 8.7 Hz, 2 H), 7.60 (d, *J* = 8.7 Hz, 2 H), 4.62 (d, *J* = 4.2 Hz, 1 H), 4.40 (dt, *J* = 10.2, 6.8 Hz, 1 H), 3.97 (dt, *J* = 8.7, 6.6 Hz, 1 H), 3.89 (dt, *J* = 8.6, 6.7 Hz, 1 H), 3.18 (dd, *J* = 10.1, 4.2 Hz, 1 H), 2.08–1.91 (m, 3 H), 1.48–1.36 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.48, 131.30, 129.70, 124.43, 111.74, 111.09, 77.51, 68.90, 51.65, 30.37, 26.90, 25.82.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{14}H_{12}N_3O_3$: 270.0884; found: 270.0880.

2-[(4-Hydroxyphenyl)(tetrahydrofuran-2-yl)methyl]malononitrile (3f)

Yield: 44.5 mg (92%); colorless oil; dr = 1:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 7.21 (d, *J* = 8.6 Hz, 2 H), 7.15 (d, *J* = 8.6 Hz, 2 H), 6.84 (d, *J* = 8.5 Hz, 2 H), 6.81 (d, *J* = 8.6 Hz, 2 H), 4.52 (d, *J* = 4.1 Hz, 1 H), 4.41 (td, *J* = 7.1, 3.2 Hz, 1 H), 4.38–4.29 (m, 1 H), 4.35 (d, *J* = 10.7 Hz, 1 H), 4.00–3.90 (m, 1 H), 3.90–3.80 (m, 1 H), 3.73 (td, *J* = 6.5, 1.7 Hz, 2 H), 3.21 (dd, *J* = 10.5, 3.2 Hz, 1 H), 2.97 (dd, *J* = 10.3, 4.1 Hz, 1 H), 1.96–1.83 (m, 5 H), 1.49–1.38 (m, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 156.83, 156.59, 130.45, 129.68, 125.91, 125.32, 116.11, 115.87, 112.47, 112.43, 112.39, 111.82, 78.15, 77.60, 68.67, 67.66, 51.23, 49.90, 30.27, 28.86, 27.58, 27.18, 25.74, 25.69.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{14}H_{13}N_2O_2$: 241.0983; found: 241.0975.

2-[Naphthalen-2-yl(tetrahydrofuran-2-yl)methyl]malononitrile (3g)

Yield: 51.3 mg (93%); colorless oil; dr = 1:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 8.11 (d, *J* = 8.6 Hz, 1 H), 8.03 (d, *J* = 8.6 Hz, 1 H), 8.00–7.86 (m, 4 H), 7.74 (d, *J* = 7.3 Hz, 1 H), 7.67–7.46 (m, 7 H), 4.73–4.48 (m, 3 H), 4.41 (dd, *J* = 10.8, 3.4 Hz, 1 H), 4.20–4.11 (m, 2 H), 4.09 (dt, *J* = 8.6, 6.6 Hz, 1 H), 3.95 (dt, *J* = 8.6, 6.9 Hz, 1 H), 3.84–3.72 (m, 3 H), 2.04–1.85 (m, 4 H), 1.80–1.73 (m, 1 H), 1.46–1.36 (m, 1 H), 1.33–1.25 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 34.07, 133.87, 132.43, 131.81, 131.03, 130.02, 129.51, 129.41, 129.40, 129.37, 129.35, 127.10, 127.08, 126.18, 125.97, 125.36, 125.21, 125.10, 121.96, 121.80, 112.58, 112.31, 112.16, 112.14, 79.37, 77.67, 68.81, 68.71, 60.34, 44.18, 30.22, 28.84, 27.19, 26.92, 25.95, 25.75.

HRMS-ESI: *m*/*z* [M – H]$^-$ calcd for $C_{18}H_{15}N_2O$: 275.1190; found: 275.1185.

2-[1-Phenyl-1-(tetrahydrofuran-2-yl)ethyl]malononitrile (3h)

Yield: 24.1 mg (50%); colorless oil; dr = 0.6:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 7.56–7.49 (m, 2 H), 7.47–7.31 (m, 8 H), 4.80 (s, 1 H), 4.67 (t, *J* = 7.3 Hz, 1 H), 4.28 (s, 1 H), 4.19 (t, *J* = 7.4 Hz, 1 H), 4.01–3.92 (m, 1 H), 3.92–3.83 (m, 1 H), 3.78–3.64 (m, 2 H), 1.99–1.70 (m, 5 H), 1.69 (s, 3 H), 1.58 (s, 3 H), 1.55–1.44 (m, 1 H), 1.37–1.27 (m, 1 H), 1.23–1.13 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 138.18, 136.69, 128.94, 128.68, 128.61, 128.44, 127.67, 126.63, 112.15, 112.14, 111.99, 82.56, 80.84, 69.46, 68.98, 48.25, 47.98, 34.37, 33.12, 27.26, 27.17, 26.28, 25.79, 19.44, 16.46.

HRMS-ESI: *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{16}N_2NaO$: 263.1155; found: 263.1563.

Ethyl 2-Cyano-3-phenyl-3-(tetrahydrofuran-2-yl)propanoate (3i)

Yield: 42.6 mg (78%); colorless oil; dr = 0.4:0.4:0.4:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ (mixture of four diastereomers) = 7.39–7.27 (m, 20 H), 4.68-4.55 (m, 2 H), 4.56–4.46 (m, 2 H), 4.39 (m, 1 H), 4.31 (d, *J* = 5.2 Hz, 1 H), 4.28–4.17 (m, 4 H), 4.10–4.03 (m, 4 H), 4.01–3.91 (m, 3 H), 3.89–3.80 (m, 4 H), 3.76–3.68 (m, 3 H), 3.43 (dd, *J* = 10.5, 3.2 Hz, 1 H), 3.39 (dd, *J* = 9.1, 5.4 Hz, 1 H), 3.31 (dd, *J* = 10.8, 3.3 Hz, 1 H), 3.24 (dd, *J* = 10.6, 5.2 Hz, 1 H), 1.95–1.82 (m, 12 H), 1.45–1.39 (m, 4 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 1.21 (t, *J* = 7.1 Hz, 3 H), 1.08 (t, *J* = 7.1 Hz, 3 H). 0.97 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (mixture of four diastereomers) = 165.67, 165.67, 165.59, 165.59, 136.19, 136.19, 135.56, 135.56, 129.69, 129.57, 129.25, 129.15, 129.01, 128.95, 128.77, 128.77, 128.62, 128.62, 128.27, 128.26, 128.21, 128.18, 128.15, 128.12, 79.23, 79.19, 79.00, 78.44, 68.62, 68.46, 68.42, 68.20, 62.83, 62.66, 62.43, 62.39, 51.18, 50.81, 50.21, 49.93, 42.99, 41.98, 41,47, 41.11, 30.36, 30.30, 29.45, 28.91, 25.82, 25.79, 25.74, 25.66, 13.88, 13.84, 13.79. 13.56.

HRMS-ESI: *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{19}NNaO_3$: 296.1257; found: 296.1255.

Dimethyl 2-[Phenyl(tetrahydrofuran-2-yl)methyl]malonate (3j)

Yield: 34.0 mg (61%); colorless oil; dr = 0.9:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 7.36–7.09 (m, 10 H), 4.37–4.10 (m, 2 H), 4.22 (d, *J* = 11.7 Hz, 1 H), 3.92 (d, *J* = 10.1 Hz, 1 H), 3.80 (s, 3 H), 3.76 (s, 3 H), 3.84–3.70 (m, 2 H), 3.71–3.60 (m, 2 H), 3.54 (dd, *J* = 11.7, 2.9 Hz, 1 H), 3.47 (t, *J* = 10.1 Hz, 1 H), 3.40 (s, 3 H), 3.39 (s, 3 H), 2.01–1.77 (m, 4 H), 1.75–1.61 (m, 2 H), 1.57–1.49 (m, 1 H), 1.47–1.37 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (mixture of two diastereomers) = 168.89, 168.87, 168.33, 168.26, 138.55, 137.29, 129.84, 128.65, 128.39, 127.87, 127.23, 127.06, 81.86, 78.87, 68.53, 68.01, 56.33, 54.69, 52.61, 52.47, 52.15, 52.09, 51.46, 49.23, 30.25, 28.75, 25.69, 25.25.

HRMS-ESI: *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{20}NaO_5$: 315.1203; found: 315.1198.

Funding Information

Funding was provided by the National University of Singapore, the Ministry of Education (MOE) of Singapore (MOE2014-T2-1-134, MOE2017-T2-2-081) and the Natural Science Foundation of Jiangsu Province, P. R. of China (BK20141219).

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1707135.

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