JOC The Journal of Organic Chemistry

Note

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b00433 • Publication Date (Web): 09 May 2019

ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Synthesis of Sterically Hindered *β*-Diketones via Condensation of Acid Chlorides with Enolates

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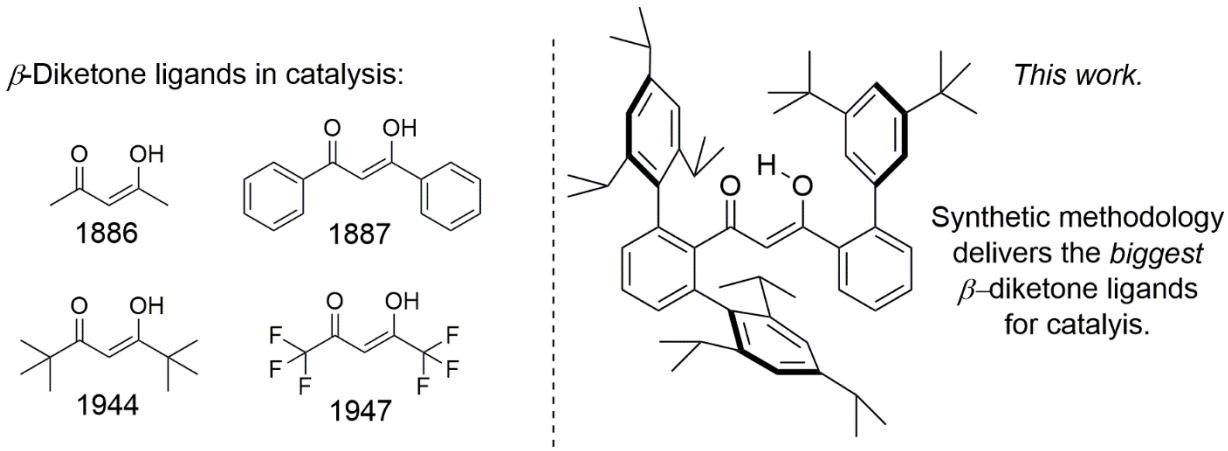
Supporting Information Placeholder



ABSTRACT: Bulky *β*-diketones have rarely exceeded dipivaloylmethane (DPM) in steric demand, largely due to synthetic limitations of the Claisen condensation. This work demonstrates hindered acid chlorides to be selective electrophiles in non-coordinating solvents for condensations with enolates. An improved synthesis of DPM is described (90% yield), and crowded *β*-diketones featuring bulky *o*-biphenyl or *m*-terphenyl fragments were prepared in good to excellent yields. These compounds are anticipated to have a steric profile far greater than that of DPM. General reaction conditions and mechanistic considerations are included.

Over the last fifty years, acetylacetonate (acac)-supported catalysts have proven capable of forming C–C bonds (*via* iron,[1–4] cobalt,[5] nickel,[6,7] and copper[8–10]), C–N bonds (*via* iron,[11] cobalt,[12] nickel,[13] and copper[14]), and C–O bonds (*via* iron,[15] cobalt,[16,17] nickel,[18] and copper[19]) to highlight select metals. These examples illustrate the generality of late, first-row metal catalysis using *β*-diketonates in carbon bond-forming reactions, which have developed in parallel to the second- and third-row transition metal catalysis. However, there is a renewed interest in these "base metal" catalysts due to sustainability, scalability, and other concerns of the "precious metal" catalysts.[20–22] In some cases, the larger dipivaloylmethane (DPM, **1**) offered a significant improvement in catalytic performance over

acac, and even choice reactivity over other ligand classes.[23–25] Unfortunately, synthetic challenges have limited exploration of sterically hindered β-diketonates.

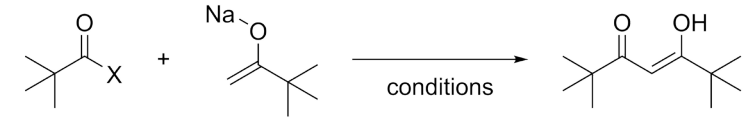
The synthesis of β-diketones is usually accomplished in good yields *via* the Claisen condensation.[26] Advancements have been made in increasing the efficiency of the coupling using soft enolization techniques of activated esters and methyl ketones.[27–29] Although these procedures are particularly robust and chemoselective,[28] the reactions are under thermodynamic control and specifically fail in preparing sterically hindered products.[27,30] Efforts to improve the yield of DPM syntheses often focus on changing the base or the ester substituent with modest improvement.[31–34] An efficient synthesis is highly desirable given this compound has applications in catalysis, metal refining, atomic layer deposition, precursor to heterocycles, and is notable for being the common "hindered β-diketone" of choice.[35–39] Other known methods for the synthesis of sterically hindered β-diketones include a double Friedel-Crafts acylation of malonyl dichloride,[40–42] the reaction of β,δ-triketones with pyrylium salts,[43] and treatment of acid chlorides with stoichiometric methyllithium.[44] In the last example, treating pivaloyl chloride **2** with methyllithium only produces DPM in 10% yield, instead providing 84% of the tertiary alcohol.

Other examples in the literature where acid chlorides are employed as electrophiles in condensations are rare.[44–46] Obtaining C-acylated products preferentially over the kinetically favored O-acylated products is a challenge.[47,48] This can be suppressed using excess enolate, which reduces the atom economy.[49] Nonetheless, the increased reactivity of acid chlorides can enable the construction of more crowded, decorated β-diketones, albeit in poor yields and with difficult separations.[50,51] Acid chlorides derived from *meta*-terphenyls show a remarkably slowed reactivity.[52] This very encumbering moiety has stabilized extremely reactive, low-coordinate metal complexes.[53–56] We have previously shown that a *m*-terphenyl appended to a β-diketone enables steric control of a metal's coordination sphere,[57] a historically difficult challenge for acac-type ligands.[58–60] Here we describe the preparation and synthetic considerations of a range of sterically hindered β-diketones.

Using DPM as a model compound, the reactivity of pivaloyl chloride **2** and methyl pivalate **3** with sodium pinacolonate **4** was investigated to shed light on their relative behavior in crowded environments (Table 1). Due to the sensitivity of acid chlorides to even weakly nucleophilic bases, it was advantageous to synthesize and isolate

the enolates free of residual solvents or conjugate acids. Treating pinacolone with an excess of sodium amide (1.5 equiv.) followed by filtration of residual base and removal of solvent *in vacuo* results in an isolation of **4** in 94% yield to produce 91 g of the tetrahydrofuran-adduct **4**. Two equivalents of the enolate **4** were treated with electrophiles **2** or **3** (1 M) at 0°C before warming, while varying the solvent, temperature, and reaction duration. DPM was conveniently isolated by subjecting the reaction mixture to aqueous work-up to remove residual pivalic acid followed by vacuum to remove pinacolone. The products were assayed by ^{1}H NMR to determine the purity. Reported crude yields have been corrected using the determined purity by mass.

Table 1. Comparative study of esters and acid chlorides in the preparation of dipivaloylmethane.



X = Cl **2**
OMe **3**

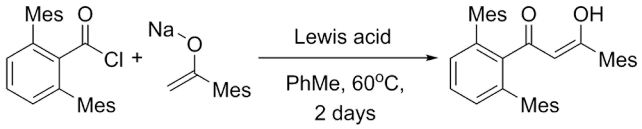
4 **1**

Entry	Solvent	Group X	Temperature (°C)	Time (hrs)	Crude Yield (%)	Purity (%)
1	PhMe	Cl	20	0.08	65	95
2		Cl	20	1	80	91
3		Cl	20	16	90	88
4		Cl	60	16	82	85
5		OMe	20	16	23	54
6		OMe	60	16	59	42
7	THF	Cl	20	1	78	84
8		Cl	20	16	80	83
9		Cl	60	16	77	91
10		OMe	20	16	18	59
11		OMe	60	16	49	37
12	DCM	Cl	20	1	84	96
13		Cl	20	16	83	94
14		Cl	40	16	65	93
15		OMe	20	16	23	69
16		OMe	40	16	34	50

After five minutes, DPM **4** was obtained from the acid chloride **1** in in 65% yield (Entry 1). Toluene, THF, and DCM each gave similar yields for the reaction with **1** after one hour (Entries 2, 7, 12), although toluene proved most effective when allowed to react overnight (Entry 3). In all solvents, the acid chloride condensations showed a

decreased yield when heated (Entries 4, 9, 14). Conversely, reactions with the ester **2** resulted in poor conversions at room temperature (Entries 5, 10, 15), which did improve upon heating (Entries 6, 11, 16). The best yield obtained is 90% for this reaction, using acid chloride **1** as the electrophile and toluene as the solvent. The method was proven on multi-gram scales, with an 88% yield obtained. While the O-acylation byproduct was observed in <1% in the preparation of DPM, this problematic impurity is more frequently observed with more sterically hindered acid chlorides and nucleophiles.

Table 2. Lewis acid screen for a hindered reaction.



5 **6** **7**

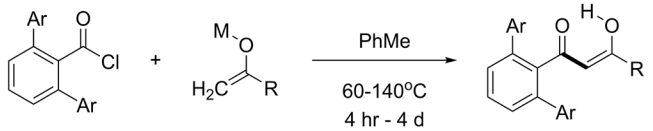
Entry	Lewis acid	Conversion (%)	C:O ratio (100:X)
1	LiCl	76	14
2	n/a (Na)	75	2
3	$MgSO_4$	63	20
4	$CuCl_2$	51	20
5	$ZnBr_2$	100	100

As steric bulk increases, the separation of large molecules which only differ by the transposition of oxygen and methylene linkages becomes increasingly intractable, requiring a two-step metalation/demetalation sequence or more preferably the inhibition of this by-product forming at all. The condensation of 2,6-dimesitylbenzoyl chloride **5** with the sodium enolate derived from trimethylacetophenone **6**, resulted in significant formation of the O-acylated product. Transmetalation with various Lewis acids was observed to improve the C/O acylation product ratio (Table 2). Zinc bromide resulted in the highest selectivity for the *β*-diketone product, and these conditions were employed to prepare **7** in >99% selectivity on multi-gram scales. In addition, the C/O-acylation selectivity is sensitive to the coordinating ability of the solvent.

For example, the preparation of **8** (Table 3) proceeds with high C-selectivity in toluene using zinc bromide with **3**, but same reaction and Lewis acid resulted in significant O-acylated product when performed in THF. In contrast, no solvent dependence was observed (PhMe, DCM, THF, Et_2O, hexanes) when sodium was employed as a Lewis acid in the high yielding synthesis of **8**. The condensations can be scaled up with no decrease in yields,

allowing the synthesis of **8** in over 40 grams. Furthermore, the reaction can be performed without the isolation of the enolate, obviating the need for a glovebox. This can be accomplished by swapping the ethereal solvent for a non-coordinating one after enolization prior to introducing the electrophile—affording **8** in typical yield and over 10-gram scale.

Table 3. *m*-Terphenyl β-diketones prepared using acid chlorides and enolate salts.



Entry	Aryl group (Ar)	Enolate group (R)	Lewis acid (M)	Isolated yield (%)
1 (**7**)	Mes	Mes	Zn	70
2 (**8**)	Mes	^{t}Bu	Na	92
3 (**9**)	Mes	3',5'-^{t}Bu$_2$Ph$_2$	Na	73
4 (**10**)	Mes	3',4',5'-(OMe)$_3$Ph	Na	65
6 (**11**)	TMP	^{t}Bu	Na	54
7 (**12**)	Trip	^{t}Bu	Na	75
8 (**13**)	Trip	3',5'-^{t}Bu$_2$Ph$_2$	Na	25

While steric bulk disfavors multiple acylation reactions to form triketones, as the size of each fragment increases the reaction favors C–O bond formation. The decreased steric hindrance of the lone pairs on oxygen relative to methylene of the enolate induce a steric preference (Figure 1a). In addition, the greater electronegativity of oxygen makes it the kinetically favored nucleophile. A Lewis acid bound to the oxygen of the enolate attenuates its nucleophilicity and increases its steric demand, improving both steric and electronic factors to increase the selectivity for C–C bond formation (Figure 1b). The Lewis acid pre-organizes the transition state by coordinating the oxygen of the enolate and the acyl chloride (Figure 1c). This weak interaction can be disrupted by the presence of coordinating solvents, thus rationalizing the observed solvent effect (Figure 1b). This effect has been demonstrated previously using strongly coordinating additives such as TMEDA to generate un-complexed enolate anions, resulting in the highly selective formation of O-acylation products (Figure 1d).[61] Therefore, control of the C/O-acylation selectivity seems determined by the promotion or interference of the metal-enolate complexes in solution.

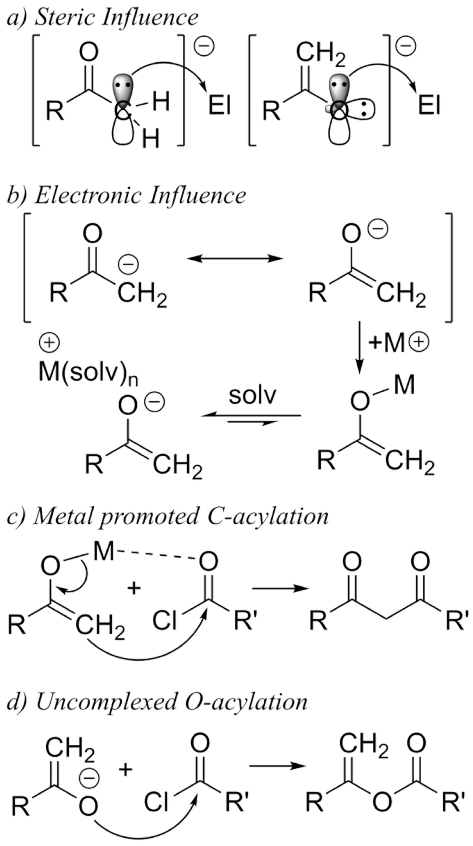


Figure 1. Factors which affect the C/O-acylation selectivity in acid chloride/enolate condensations.

An additional complication in preparing especially hindered *β*-diketones is the competing aldol condensation of the enolate nucleophile with the methyl ketone regenerated by deprotonation of the *β*-diketone product.[62,63] This reaction was most problematic in the preparation of **13**. In examples using 2,6-bis(2,4,6-triisopropylphenyl)benzoyl chloride as electrophile, the methyl ketones regenerated proved to be better electrophiles than the acid chloride. Lewis acids such as zinc and cadmium have been shown to prevent aldol condensation products.[64] Although in the case of **13**, no improvement was afforded by transmetalation to zinc. It is possible that either the zinc-enolate interaction shows diminished chemo-selectivity at the elevated temperatures required for the reaction or that sodium enolates transiently form which are capable of aldol condensation. Nevertheless, **13** can be isolated in 25% yield after purification by chromatography.

To better understand the crowding about the *β*-diketone moiety, single crystals of **9**, **12**, and **13** were grown and analyzed by X-ray diffraction. The structure of the most sterically hindered derivative, **13,** is presented below (Figure 2). **13** represents the most hindered *β*-diketone ever reported. Despite these results, accessing increasingly hindered *β*-diketone products is difficult because steric demands require higher temperatures and Lewis acids that can maintain their coordination in the extreme conditions. More reactive electrophiles are currently being investigated. Additionally, the condensation of secondary enolates have resulted in mixtures of C/O-acylation products, which is being probed with more effective Lewis acids.

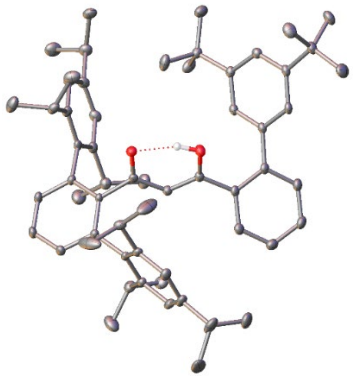


Figure 2. Crystal structure of the hindered *β*-diketone, **13**. Thermal ellipsoids drawn at the 50% probability level.

In summary, acid chlorides were found to be more effective electrophiles than corresponding esters in congested steric regimes. Reaction optimization for DPM has resulted in excellent yield and purity, which represents an improvement over the state of the art (90% vs. 65%). Application of this insight permitted the

preparation of sterically hindered examples which have proven to be synthetically challenging to date. The reactions of *m*-terphenyl acid chlorides require elevated temperatures (60–140°C) and increased times (4–96 hrs), standing in sharp contrast to typical acid chloride reaction conditions.[47] The reactions selectivity is sensitive to the identity of the Lewis acid and solvent. As a heuristic, it is preferable to employ the larger fragment as the electrophile to maximize the selectivity control, and similarly a smaller enolate seems a more competent nucleophile.

In a more specific context, the method described herein has been used to prepare a family of sterically hindered *β*-diketones that can function as ancillary ligands for transition metal catalysis. Work continues in our laboratory probing the novel coordination and catalytic chemistry of bulky acac-type metal complexes, especially of the first-row transition metals, a critical need identified in recent reports.[65,66]

EXPERIMENTAL SECTION

General Considerations

Syntheses were performed in a nitrogen-filled glovebox or in a fume hood using standard air-free Schlenk techniques. Organic reagents were purchased from Alfa Aesar, TCI Chemical, or Sigma Aldrich and used as received, except as noted below. Deuterated solvents were purchased from Cambridge Isotope Labs and stored over 4Å molecular sieves. All other solvents were purchased in anhydrous form from Sigma Aldrich and further dried with and stored over 4Å molecular sieves. 2,6-bis(2,4,6-trimethylphenyl)benzoyl chloride was prepared according to literature procedures.[67] Enolizations can be monitored by disappearance of ammonia emission upon N_2 sparging. Condensations may be monitored by withdrawing a 0.25 mL aliquot, shaking with ethyl acetate/1 M hydrochloric acid (1 mL each), removing the aqueous layer, concentrating the organics, and subjecting the residue to ^{1}H NMR analysis, using the 1H triplet at approximately 7.5 ppm as a diagnostic peak. NMR spectra were recorded on a Bruker Avance-III 300 NMR spectrometer (300 MHz) or 400 NMR spectrometer (400 MHz). IR were spectra recorded on an Agilent Cary 630 FTIR with ATR attachment. UV-Vis spectra were recorded on an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. High-Resolution Mass Spectrometry (HRMS) data were recorded at the University of Colorado Central Analytical Laboratory on a Waters Synapt G2 (ESI) by Dr. Danijel Djukavic or Mr. Duk Yi. X-ray crystal structures were recorded using a Bruker D8 Quest Eco three circle goniometer platform equipped with a Bruker APEX-II CCD detector, a graphite monochromator was employed for wavelength selection of the Mo Kα radiation (λ = 0.71073 A), and the data were processed using APEX III software provided by Bruker. Except as noted below, structures were solved by intrinsic phasing in SHELXT[68] and refined by standard difference Fourier techniques with SHELXL[69] within the OLEX2[70] software package. Hydrogen atoms were placed in calculated positions using the standard riding model and refined isotropically except as noted below.

Dipivaloylmethane (1)

To a 250 mL oven-dried one-neck round bottom flask equipped with a stirbar and septum is charged sodium 1-*tert*-butylethenolate (9.70 g, 50 mmol) and toluene (50 mL). The contents are cooled in an icebath to 0°C, and then pivaloyl chloride (3.05 mL, 25 mmol) is added in a single portion rapidly—dropwise addition results in ~60% yield. The contents are allowed to warmed to ambient over 16 hours. The vial is opened and 1 M hydrochloric acid (5 mL) is added. The color transitions from clear red-orange to yellow. The contents are stirred vigorously for about 15 minutes, allowed to settle, and the aqueous layer removed using a pipette. The organics are dried over sodium sulfate and concentrated to a pale-yellow oil, which is further dried *in vacuo* (4.05 g, 88%). Crude material may be purified by distillation or isolation as the copper(II) salt.[71] Spectroscopic data matches the previously reported (AIST, SDBS No.: 8580).

Sodium 1-*tert*-butylethenolate, THF adduct (4)

To an oven-dried 1000 mL one-neck round bottom flask equipped with a stirbar, addition funnel, and septum is charged sodium amide (24.4 g, 625 mmol) and tetrahydrofuran (250 mL). The flask is attached to a nitrogen manifold with adequate ventilation and heated to 40°C in an oil bath. Pinacolone (50.1 g, 500 mmol) is added dropwise over 2 hours. The contents are then allowed to react for 10 hours, and then allowed to cool to room temperature. Under an inert atmosphere, the grey suspension is diluted with diethyl ether (100 mL) and filtered through an oven-dried, medium-porosity frit, and the solvent is removed *in vacuo* to afford a white powder, which is further dried overnight (77.7 g, 80%). The product may develop a yellow patina after several months under nitrogen, with little to no loss of potency. ^{1}H NMR (400 MHz,

Benzene-d_6) δ 3.74 (s, 1H), 3.73 – 3.67 (m, 4H), 3.47 (s, 1H), 1.45 – 1.40 (m, 4H), 1.34 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 181.3, 128.3, 128.1, 127.8, 69.5, 68.4, 38.0, 30.1, 25.6.

Sodium 1-(2,4,6-trimethylphenyl)ethenolate, THF adduct (6)

To an oven-dried 250 mL one-neck round bottom flask equipped with a stirbar, addition funnel, and septum is charged sodium amide (3.9 g, 100 mmol) and tetrahydrofuran (100 mL). The flask is attached to a nitrogen manifold with adequate ventilation and heated to 60 °C in an oil bath. A solution of 2',4',6'-trimethylacetophenone (8.11 g, 50 mmol) is added dropwise over 1 hour. The contents are then heated to 60°C for 12 hours, and then allowed to cool to ambient. Large parallelepiped crystals form in the flask after reaching ambient temperature. Under an inert atmosphere, the grey suspension is diluted with diethyl ether (100 mL) and filtered through an oven-dried, medium-porosity frit, and the solvent is removed *in vacuo* to afford off-white microcrystalline material, which is further dried overnight (8.308 g, 65%). ^1H NMR (400 MHz, Benzene-d_6) δ 6.84 (s, 2H), 4.10 (d, J = 1.1 Hz, 1H), 3.69 (d, J = 1.1 Hz, 1H), 3.52 – 3.35 (m, 4H), 2.57 (s, 6H), 2.20 (s, 3H), 1.44 – 1.29 (m, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 170.4, 145.0, 134.4, 134.2, 128.3, 128.1, 128.1, 127.8, 78.0, 68.1, 25.6, 21.1, 20.5.

1-[2,6-Bis(2,4,6-trimethylphenyl)phenyl]-3-(2,4,6-trimethylphenyl)-propan-1,3-dione (7)

To an oven-dried 250 mL one-neck round bottom flask equipped with a stirbar and septum is charged sodium 1-(2,4,6-trimethylphenyl)ethenolate (4.8 g, 18.8 mmol), zinc bromide (6.32 g, 28.1 mmol), and toluene (50 mL). The flask is stirred and heated to 60°C in an oil bath for 30 minutes, and then 2,6-bis(2,4,6-trimethylphenyl)-benzoyl chloride (2.35 g, 6.3 mmol) is added in one portion. The contents are stirred for an additional 8 hours at 60°C, and then allowed to cool to room temperature. The flask is opened, 1 M hydrochloric acid (25 mL) is slowly added, followed by 5 M hydrochloric acid (25 mL), and the mixture is allowed to stir for 30 minutes. The color transitions from clear red-orange to opaque yellow. The mixture is then transferred to a separatory funnel, allowed to settle, and separated. The organics are concentrated to a thick, orange-colored oil and diluted with methanol (50 mL) is added, inducing precipitation of a fine powder. The suspension is stored in an icebath for 1 hour, filtered, and dried *in vacuo*. The crude material is purified by column chromatography (1.5% EtOAc/hexane isocratic) and obtained as a white, microcrystalline powder (2.2 g, 70%). m.p.: 215.7–216.8°C. ^1H NMR (400 MHz, Chloroform-*d*) δ 15.49 (s, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 7.6 Hz, 2H), 7.01 (s, 4H), 6.88 (s, 2H), 5.40 (s, 1H), 2.42 (s, 6H), 2.36 (s, 3H), 2.18 (s, 11H), 1.97 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 191.6, 187.9, 139.2, 138.5, 137.3, 137.0, 136.8, 136.1, 134.5, 134.5, 129.7, 128.8, 128.1, 128.0, 103.8, 77.5, 77.2, 76.8, 21.2, 21.1, 20.9, 18.6. IR (ν, cm^{-1}): 2947, 2918, 2858, 1618, 1577, 1454, 1380, 1275, 1041, 929, 854, 817, 791, 769, 743, 679, 590, 568, 538. UV-Vis (λ_{max}): 296 nm. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C36H39O2 503.2950; Found: 503.2965

1-[2,6-Bis(2,4,6-trimethylphenyl)phenyl]-4,4-dimethylpentan-1,3-dione (8)

To an oven-dried 500 mL one-neck round bottom flask equipped with a stirbar and septum is charged sodium 1-*tert*-butylethenolate (30.9 g, 159.2 mmol), 2,6-bis(2,4,6-trimethylphenyl)-benzoyl chloride (20 g, 53.1 mmol), and toluene (150 mL). The flask is stirred and heated to 60°C in an oil bath for 4 hours, and then allowed to cool to room temperature. The flask is opened, 1 M hydrochloric acid (150 mL) is slowly added, and the mixture is allowed to stir for 30 minutes. The color transitions from clear red-orange to yellow. The mixture is then transferred to a separatory funnel, allowed to settle and separated, and the aqueous layer is washed with ethyl acetate (100 mL). The combined organics are concentrated to a thick, orange-colored oil. 95:5 methanol/water (100 mL) is added and the mixture is triturated at 60°C for 15 minutes, inducing precipitation of a fine powder. The suspension is then stored in an icebath for 1 hour. The resultant colorless crystals are filtered, and dried *in vacuo* (21.63 g, 92%). Spectroscopic data matches the previously reported.[67]

1-[2,6-Bis(2,4,6-trimethylphenyl)phenyl]-3-[2-(3,5-di-*tert*-butylphenyl)phenyl]-propan-1,3-dione (9)

To an oven-dried 250 mL one-neck round bottom flask equipped with a stirbar and septum is charged sodium 1-[2-(3,5-di-*tert*-butylphenyl)phenyl]ethenolate (9.2 g, 21.07 mmol), 2,6-bis(2,4,6-trimethylphenyl)-benzoyl chloride (3.60 g, 9.58 mmol), and toluene (125 mL). The flask is stirred and heated to 60 °C in an oil bath for 16 hours, and then allowed to cool to room temperature. The flask is opened, 1 M hydrochloric acid (100 mL) is slowly added, and the mixture is allowed to stir for 30 minutes. The color transitions from clear red-orange to opaque yellow. The mixture is then transferred to a separatory funnel, allowed to settle and separated, and the aqueous is washed with toluene (50 mL). The combined organics are concentrated to a thick, orange-colored oil. 98:2 methanol/water (100 mL) is added and the mixture is triturate at 60 °C for 15 minutes, inducing precipitation of a fine powder. The suspension is then stored in an ice bath for 1 hour, filtered, and recrystallized from minimal 1:1 diethyl ether/ethanol and dried *in vacuo* (4.5 g, 73%). m.p.: 205.0–206.5°C. ^1H NMR (300 MHz, Chloroform-d) δ 14.76 (s, 1H), 7.50 (dd, J = 7.9, 7.3 Hz, 1H), 7.40 (td, J = 7.5, 1.3 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.21 (td, J = 7.5, 1.4 Hz, 1H), 7.14 (d, J = 7.6 Hz, 2H), 7.00 (d, J = 1.8 Hz, 2H), 6.87 (s, 4H), 6.66 (dd, J = 7.8, 1.3 Hz, 1H), 5.42 (s, 1H), 2.30 (s, 6H), 2.01 (s, 12H), 1.25 (s, 18H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 188.3, 187.5, 150.2, 142.4, 140.2, 140.0, 137.6, 136.5, 136.4, 136.1, 135.9, 130.8, 130.3, 129.9, 129.4, 129.2, 128.0, 126.3, 123.0, 120.7, 103.1, 34.7, 31.5, 21.1, 20.6. IR (ν, cm^{-1}): 2959, 2921, 2865, 1596, 1581, 1451, 1428, 1365, 1271, 1245, 1212, 1037, 880, 854, 821, 776, 743, 720, 642, 571, 545. UV-Vis (λ_{max}): 325 nm. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C47H53O2 649.4045; Found: 649.4047

1-[2,6-Bis(2,4,6-trimethylphenyl)phenyl]-3-(3,4,5-trimethoxyphenyl)-propan-1,3-dione (10)

To an oven-dried 20 mL vial equipped with a stirbar and cap is charged sodium 1-(3,4,5-trimethoxyphenyl)ethenolate (1.35 g, 4.44 mmol), 2,6-bis(2,4,6-trimethylphenyl)-benzoyl chloride (0.55 g, 1.46 mmol), and toluene (5 mL). The vial is stirred and heated to 60°C in an oil bath for 16 hours, and then allowed to cool to room temperature. The flask is opened, 5 M hydrochloric acid (2 mL) is slowly added, and the mixture is allowed to stir for 30 minutes. The color transitions from clear red-orange to opaque yellow over 2 minutes. The mixture is then transferred to a separatory funnel, allowed to settle, and separated, and the aqueous layer is washed with EtOAc (10 mL). The organics are concentrated to a thick, orange-colored oil and diluted with methanol (50 mL) is added, inducing precipitation of a fine powder from a deep red filtrate. The suspension is stored in an icebath for 1 hour, filtered, and dried *in vacuo*. The crude material is purified by trituation in acetone and obtained as an off-white powder (0.52 g, 65%). m.p.: 220.5–222.6°C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.62 (s, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 6.88 (s, 4H), 6.72 (s, 2H), 5.69 (s, 1H), 3.90 – 3.85 (m, 9H), 2.27 (s, 6H), 2.08 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 189.0, 183.4, 153.1, 141.6, 140.1, 137.6, 136.9, 136.7, 136.0, 131.0, 130.2, 129.4, 128.1, 104.3, 98.5, 77.5, 77.2, 76.8, 61.1, 56.3, 21.2, 20.9. IR (ν, cm^{-1}): 3000, 2940, 2921, 1581, 1503, 1462, 1413, 1380, 1335, 1238, 1186, 1171, 1130, 1000, 950, 855, 821, 791, 773, 736. UV-Vis (λ_{max}): 351 nm. HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C36H38O5Na 573.2617; Found: 573.2617

1-[2,6-Bis(2,4,5-trimethylphenyl)phenyl]-4,4-dimethylpentan-1,3-dione (11)

To an oven-dried 20 mL vial equipped with a stirbar and vial-cap is charged sodium 1-*tert*-butylethenolate (1.94 g, 10 mmol), 2,6-bis(2,4,5-trimethylphenyl)-benzoyl chloride (1.13 g, 3 mmol), and toluene (7.5 mL). The flask is stirred and heated to 60°C in an oil bath for 8 hours, and then allowed to cool to room temperature. The flask is opened, 1 M hydrochloric acid (2 mL) is slowly added, followed by 5 M hydrochloric acid (2 mL), and the mixture is allowed to stir for 30 minutes. The color transitions from clear red-orange to yellow. The mixture is then transferred to a separatory funnel, allowed to settle, and separated. The organics are concentrated to a thick, orange-colored oil and diluted with 98:2 methanol/water (2 mL) is added, inducing precipitation of a fine powder. The suspension is then stored in an icebath for 1 hour, filtered, and dried *in vacuo*. A second crop is obtained from the filtrates (716 mg, 54%). m.p.: 98.5–100.2°C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 14.93 (d, *J* = 8.7 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 2H), 6.99 (s, 2H), 6.96 (s, 2H), 5.23 (s, 1H), 2.25 (s, 6H), 2.21 (s, 6H), 2.13 (s, 3H), 2.11 (s, 3H), 0.86 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.5, 189.7, 189.5, 140.5, 138.2, 137.4, 135.6, 133.1, 131.2, 131.2, 130.9, 129.2, 128.6, 128.5, 100.2, 100.0, 77.5, 77.2, 76.8, 38.8, 26.9, 19.7, 19.5, 19.5, 19.2. IR (ν, cm^{-1}): 2970, 2921, 2869, 1584, 1506, 1450, 1365, 1286, 1234, 1130, 1104, 1022, 880, 858, 832, 810, 784, 702, 676, 478. UV-Vis (λ_{max}): 282 nm. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C31H37O2 441.2794; Found: 441.2797

1-[2,6-Bis(2,4,6-tri-*iso*-propylphenyl)phenyl]-4,4-dimethylpentan-1,3-dione (12)

To an oven-dried 100 mL one-neck round bottom flask equipped with a stirbar and septum is charged sodium 1-*tert*-butylethenolate (3.89 g, 20.1 mmol), 2,6-bis(2,4,6-tri-*iso*-propylphenyl)-benzoyl chloride (2.73 g, 5 mmol), and toluene (30 mL). The flask is stirred and heated to 60 C in an oil bath for 72 hours, and then allowed to cool to room temperature. The flask is opened, 1 M hydrochloric acid (50 mL) is slowly charged, and the mixture is allowed to stir for 30 minutes. The color transitions from clear red-orange to yellow. The mixture is then transferred to a separatory funnel, allowed to settle and separated, and the aqueous layer is washed with diethyl ether (50 mL). The combined organics are concentrated to a thick, orange-colored oil. 98:2 methanol/water (50 mL)is added and the mixture is triturated at 60 °C for 15 minutes, inducing precipitation of a fine powder. The suspension is then stored in an ice bath for 1 hour, filtered, and dried *in vacuo*. The crude material is purified by column chromatography (gradient 0–0.5% Et_2O/hexanes), and obtained as a white, microcrystalline powder (2.3 g, 75%). m.p.: 144.6–146.9°C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.46 (s, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.97 (s, 4H), 5.12 (s, 1H), 2.89 (hept, *J* = 6.9 Hz, 2H), 2.64 (hept, *J* = 6.8 Hz, 4H), 1.27 (d, *J* = 7.0 Hz, 12H), 1.12 (d, *J* = 6.9 Hz, 12H), 1.07 (d, *J* = 6.8 Hz, 16H), 0.76 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 203.6, 184.1, 148.0, 146.4, 139.8, 136.4, 135.6, 130.1, 128.4, 120.7, 99.7, 77.5, 77.2, 76.8, 40.0, 34.4, 30.8, 27.1, 25.6, 24.2, 23.2. IR (ν, cm^{-1}): 2959, 2929, 2869, 1607, 1584, 1461, 1432, 1383, 1365, 1324, 1286, 1234, 1126, 1104, 1055, 944, 880, 854, 813, 769, 653, 478. UV-Vis (λ_{max}): 282 nm. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C43H61O2 609.4672; Found: 609.4663.

1-[2,6-Bis(2,4,5-tri-*iso*-propylphenyl)phenyl]-3-[2-(3,5-di-*tert*-butylphenyl)phenyl]-propan-1,3-dione (13)

To an oven-dried 20 mL vial equipped with a stirbar and a vial-cap is charged sodium 1-[2-(3,5-di-*tert*-butylphenyl)phenyl]ethenolate (2.47 g, 7.47 mmol), 2,6-bis(2,4,6-tri-*iso*-propylphenyl)-benzoyl chloride (1 g, 1.87 mmol), and toluene (5 mL). The vial stirred and heated to 100°C in an oil bath for 72 hours, and then allowed to cool to ambient. The vial is opened and transferred to a separatory funnel. The mixture is quenched with 1 M hydrochloric acid (30 mL) and diluted with 20 mL of ethyl acetate. The color transitions from clear red-orange to opaque yellow when shaken. The aqueous is washed with ethyl acetate (10 mL). The combined organics are concentrated to a thick, orange-colored oil. 95:5 methanol/water (30 mL) is added and the mixture triturated at 60 °C for 15 minutes, inducing precipitation of a fine powder. The suspension is then stored in an ice bath for 1 hour, filtered, and recrystallized out of boiling methanol, filtered again, and washed with cold methanol, then dried *in vacuo* to yield a white, microcrystalline powder (380 mg, 25%). m.p.: 229.5–231.1 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.08 (s, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.36 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.14 (td, *J* = 7.6, 1.3 Hz, 1H), 7.02 (s, 4H), 6.99 (d, *J* = 1.8 Hz, 2H), 6.50 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.56 (s, 1H), 2.93 (hept, *J* = 6.9 Hz, 2H), 2.66 (hept, *J* = 6.7 Hz, 4H), 1.31 (d, *J* = 6.9 Hz, 12H), 1.21 (s, 18H), 1.09 (dd, *J* = 9.6, 6.8 Hz, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 189.1, 186.5, 150.1, 147.9, 146.5, 142.4, 140.0, 140.0, 136.7, 135.9, 135.6, 131.5, 130.5, 130.1, 129.9, 128.5, 126.4, 123.5, 120.8, 120.6, 104.3, 77.5, 77.2, 76.8, 34.9, 34.3, 31.6, 31.0, 25.7, 24.2, 23.4. IR (ν, cm^{-1}): 2959, 2933, 2869, 1599, 1566, 1465, 1387, 1365, 1320, 1242, 1108, 880, 772, 720, 642, 493. UV-Vis (λ_{max}): 305 nm, 320 nm. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C59H77O2 817.5923; Found: 817.5920

Bis[2-(3,5-di-*tert*-butylphenyl)benzoyl]methane (14)

To an oven-dried 20 mL vial equipped with a stirbar and septum is charged sodium amide (0.082 g, 2.00 mmol) and toluene (3 mL). The vial and septum are affixed using copper wire and the vial is attached to a nitrogen manifold with adequate ventilation, and a solution of 2'-(3,5-di-*tert*-butylphenyl)-acetophenone (0.339 g, 1.10 mmol) in toluene (1.1 mL) is added dropwise over 5 minutes. The contents are then heated to 80 °C stirred for an additional 10 minutes, after which a solution of methyl 2-(3,5-di-*tert*-butylphenyl)-benzoate (0.292 g, 0.90 mmol) in toluene (0.9 mL) is added dropwise over 5 minutes. The vial stirred at 80 °C for 16 hours, and then cooled to ambient. The mixture is quenched with 1 M hydrochloric acid (5 mL) and diluted with ethyl acetate (2 mL). The contents are allowed to stir for 30 minutes and then transferred to a separatory funnel and the aqueous layer washed with ethyl acetate (2 × 2 mL). The combined organics are dried over sodium sulfate and concentrated to a yellow powder. The crude material is purified by column chromatography (isocratic 2.5% EtOAc/hexanes) and obtained as a white powder (0.218 g, 36%). A similar yield is obtained when the reaction is carried out with the isolated enolate. m.p.: 170.3–171.6°C. ^{1}H NMR (400 MHz, Chloroform-d) δ 15.23 (s, 1H), 7.49 – 7.42 (m, 6H), 7.28 (ddd, J = 7.7, 6.7, 2.0 Hz, 2H), 7.20 (d, J = 1.8 Hz, 4H), 7.05 (ddd, J = 7.8, 1.3, 0.6 Hz, 2H), 5.41 (s, 1H), 1.32 (s, 36H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 188.6, 150.9, 142.2, 139.9, 136.7, 130.6, 130.4, 128.9, 127.0, 123.7, 121.4, 104.7, 77.5, 77.2, 76.8, 35.1, 31.6. IR (ν, cm^{-1}): 2962, 2903, 2865, 1596, 1469, 1428, 1365, 1249, 1208, 1063, 1033, 951, 903, 884, 810, 772, 717, 612, 553. UV-Vis (λ_{max}): 295 nm, 335 nm. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C43H53O2 601.4045; Found: 601.4045

2,6-Bis(2,4,5-trimethylphenyl)benzoyl chloride (15)

To an oven-dried 500 mL one-neck round bottom flask equipped with a stirbar, condenser, addition funnel, and septum is charged magnesium turnings (6.1 g, 250 mmol), tetrahydrofuran (200 mL), and 1,2-dibromoethane (0.5 mL, 5.7 mmol). The contents are heated to 60°C in an oil bath and stirred for at least 3 hours, at which point 1 mL of a solution of 2,4,5-trimethylbromobenzene (25.0 g, 125 mmol) in tetrahydrofuran (50 mL) is added through the addition funnel. After initiation of reaction, the heating is stopped, and the remainder of the solution is added dropwise at a rate which maintains reflux of flask contents. The solution is then reheated to 60 °C for 12 hours, and then cooled to ambient. The flask is capped with a fresh septum and stored until ready for use. To an oven-dried 500 mL two-neck round bottom flask equipped with a stirbar, addition funnel, and septum is charged 1,3-dichlorobenzene (5.71 mL, 20 mmol) and tetrahydrofuran (100 mL). The contents are cooled to −78 °C and *n*-butyllithium, 2.5 M in hexanes (20 mL, 50 mmol) is added dropwise over 30 minutes, forming a bright yellow solution which turns into a white suspension. The contents are stirred an additional 30 minutes before adding the pre-formed Grignard solution dropwise over several hours. Then the flask is allowed to warm to ambient, the addition funnel is replaced with a condenser, and the contents are heated to 60 °C for at least 12 hours. The now red solution is sparged with carbon dioxide gas for several days, during which it turns brown. After completion of the reaction (determined by ^{1}H NMR assay), the contents are cooled to ambient, slowly quenched using 1 M hydrochloric acid (100 mL) and 5 M hydrochloric acid (100 mL), and stirred vigorously for 30 minutes. The aqueous layer is separated and washed with diethyl ether (50 mL), and the combined organics are concentrated to an oil and passed through a silica plug using 10% ethyl acetate/hexane. The crude product is concentrated and dried *in vacuo* to remove traces of ethanol. To an oven-dried 250 mL one-neck round bottom flask equipped with a stirbar, condenser, and septum is charged the crude product, dichloromethane (100 mL), thionyl chloride (7.25 mL, 100 mmol), and pyridine (0.1 mL, 1.2 mmol). The contents are stirred and heated to reflux for at least 4 hours, cooled to ambient, and washed with deionized water (50 mL). The organics are diluted with hexane, concentrated to remove dichloromethane, and cooled to 0 °C for at least 1 hour. The product is filtered, washed with hexanes, and dried *in vacuo* to yield an off-white powder (10.5 g, 56%). m.p.: 145–148°C (decomp. at 125 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (q, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 2H), 7.08 (s, 1H), 7.06 (s, 1H), 7.04 (s, 1H), 7.00 (s, 1H), 2.29 (s, 6H), 2.27 (s, 3H), 2.26 (s, 3H), 2.20 (s, 3H), 2.13 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.0, 138.7, 138.5, 138.4, 136.7, 136.0, 135.9, 133.7, 133.6, 133.5, 131.6, 131.6, 131.2, 129.8, 129.5, 129.2, 77.5, 77.2, 76.8, 19.8, 19.6, 19.3. IR (ν, cm^{-1}): 3007, 2921, 2862, 1797, 1581, 1510, 1450, 1391, 1193, 1022, 1003, 884, 854, 769, 683, 616, 594, 475. UV-Vis (λ_{max}): 275 nm. HRMS (ESI-TOF) m/z: [M – Cl]+ Calcd for C25H25O 341.1900; Found: 349.1909

2,6-Bis(2,4,6-tri-*iso*-propylphenyl)benzoyl chloride (16)

To an oven-dried 500 mL one-neck round bottom flask equipped with a stirbar, condenser, addition funnel, and septum is charged magnesium turnings (4.8 g, 200 mmol), tetrahydrofuran (200 mL), and 1,2-dibromoethane (0.5 mL, 5.7 mmol). The contents are heated to 60°C in an oil bath and stirred for at least 3 hours, at which point 1 mL of a solution of 2,4,6-tri-*iso*-propylbromobenzene (28.3 g, 100 mmol) in tetrahydrofuran (10 mL) is added through the addition funnel. After initiation of reaction, the heating is stopped, and the remainder of the solution is added dropwise at a rate which maintains reflux of flask contents. The solution is then reheated to 60°C for 48 hours, and then cooled to ambient. The flask is capped with a fresh septum and stored until ready for use. To an oven-dried 500 mL two-neck round bottom flask equipped with a stirbar, addition funnel, and septum is charged 2,6-dichloroiodobenzene (10.24 g, 37.5 mmol) and ethyl magnesium bromide, 0.9 M in tetrahydrofuran (42 mL). The contents are stirred for 1 hour before adding the pre-formed Grignard solution. The flask is allowed to stir at ambient for at least 12 hours, the addition funnel is replaced with a condenser, and the contents are heated to 60 °C for at least 2 days. The now red solution is sparged with CO_2 gas for several days, during which it turns brown. After completion of the reaction (determined by ^{1}H NMR assay), the contents are cooled to ambient, diluted with diethyl ether (100 mL), slowly quenched using 1 M hydrochloric acid (50 mL) and 5 M hydrochloric acid (50 mL), and stirred vigorously for 15 minutes. The aqueous layer is separated and washed with diethyl ether (50 mL), and the combined organics are concentrated to a powder, triturated with ethanol, 95% (100 mL), and cooled to 0 °C for at least 1 hour. The crude product is filtered and washed with ethanol, 95% and hexanes, and dried *in vacuo* to remove traces of ethanol.

To an oven-dried 250 mL one-neck round bottom flask equipped with a stirbar, condenser, and septum is charged the crude product, dichloromethane (75 mL), thionyl chloride (3 mL, 41.3 mmol), and pyridine (0.1 mL, 1.2 mmol). The contents are stirred and heated to reflux for at least 4 hours, cooled to ambient, and washed with DI water (50 mL). The organics are diluted with hexane, concentrated to remove dichloromethane, and cooled to 0 °C for at least 1 hour. The product is filtered, washed with hexanes, and dried *in vacuo* to yield a white powder (9.59 g, 47%). m.p.: 205–210 °C (decomp. at 190 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.04 (s, 4H), 2.93 (hept, *J* = 6.9 Hz, 2H), 2.59 (hept, *J* = 6.8 Hz, 4H), 1.30 (d, *J* = 6.9 Hz, 12H), 1.23 (d, *J* = 6.8 Hz, 12H), 1.07 (d, *J* = 6.8 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.7, 149.2, 147.1, 146.6, 138.5, 137.1, 132.6, 129.8, 129.3, 128.0, 120.9, 120.6, 120.4, 77.5, 77.2, 76.8, 34.4, 31.1, 31.1, 30.5, 26.0, 24.4, 24.3, 24.2, 24.2, 22.7. IR (ν, cm^{-1}): 2959, 2933, 2869, 1793, 1610, 1573, 1461, 1383, 1365, 1190, 1175, 1108, 880, 858, 810, 772, 691, 653, 612, 497, 467. UV-Vis (λ_{max}): 280 nm. HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C37H49ClO 567.3370; Found: 567.3369

2'-(3,5-Di-*tert*-butylphenyl)acetophenone (17)

Under an inert atmosphere, to an oven-dried 500 mL one-neck round bottom flask equipped with a stirbar and septum is charged potassium carbonate (9.85 g, 71.24 mmol), bis(triphenylphosphino)palladium dichloride (0.250 g, 0.35 mmol, 1 mol%), and 3,5-di-*tert*-butylphenylboronic acid[72]. 3:1 tetrahydrofuran/water (90 mL) which has been sparged with nitrogen for 30 minutes is cannulated into the flask. The contents are stirred for 15 minutes, while the formed solution transitions from yellow through red to dark brown. 2'-Bromoacetophenone (4.80 mL, 35.6 mmol) is added via syringe, and the solution is heated to 60°C in an oil bath for 72 hours. The reaction progress may be followed by TLC on silica plates (10% EtOAc/hexanes). The solution is then cooled to room temperature and poured into a separatory funnel with 1 M hydrochloric acid (50 mL), and then washed with ethyl acetate (2 × 50 mL). The combined organics are dried over sodium sulfate, and concentrated to a brown oil containing trace palladium black. The crude material is purified by column chromatography (isocratic 2.5% EtOAc/hexanes) to yield a colorless to pale-yellow oil (9.2 g, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.49 (m, 2H), 7.47 – 7.43 (m, 2H), 7.41 (td, *J* = 7.4, 1.4 Hz, 1H), 7.19 (d, *J* = 1.8 Hz, 2H), 1.90 (s, 3H), 1.35 (s, 18H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.7, 151.4, 141.7, 141.4, 139.8, 130.7, 130.1, 127.9, 127.3, 123.6, 121.8, 77.5, 77.2, 76.8, 35.1, 31.6, 30.4. IR (ν, cm^{-1}): 2962, 2906, 2869, 1689, 1596, 1480, 1428, 1365, 1283, 1249, 1208, 903, 884, 761, 720, 642, 597, 571. UV-Vis (λ_{max}): 255 nm, 293 nm. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C22H29O 309.2218; Found: 309.2218

Methyl 2'-(3,5-di-*tert*-butylphenyl)benzoate (18)

Under an inert atmosphere, to an oven-dried 100 mL one-neck round bottom flask equipped with a stirbar and septum is charged potassium carbonate (5.53 g, 40 mmol), bis(triphenylphosphino)palladium dichloride (0.140 g, 0.2 mmol, 1 mol%), and 3,5-Di-*tert*-butylphenylboronic acid (4.9 g, 21 mmol). 3:1 tetrahydrofuran/water (50 mL) which has been sparged with nitrogen for 30 minutes is cannulated into the flask. The contents are stirred for 15 minutes, while the formed solution transitions from yellow through red to dark brown. Methyl 2-bromobenzoate (2.8 mL, 20 mmol) is charged via syringe, and the solution is heated to 65°C in an oil bath for 72 hours. The reaction progress may be followed by TLC on silica plates (10% EtOAc/hexanes). The solution is then cooled and poured into a separatory funnel with 1 M hydrochloric acid (70 mL), and then washed with ethyl acetate (2 × 25 mL). The combined organics are dried over sodium sulfate and concentrated to a brown oil with trace palladium black. The crude material is purified by column chromatography (isocratic 2.5% EtOAc/hexanes) to yield a colorless to pale-yellow oil (5.78 g, 89%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.77 – 7.72 (m, 1H), 7.55 – 7.50 (m, 1H), 7.46 – 7.43 (m, 1H), 7.42 – 7.37 (m, 2H), 7.18 (dd, J = 1.8, 0.6 Hz, 2H), 3.61 (d, J = 0.6 Hz, 3H), 1.36 (d, J = 0.7 Hz, 18H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.1, 150.6, 143.1, 140.3, 131.8, 131.1, 130.7, 129.4, 127.0, 122.8, 121.3, 77.5, 77.2, 76.8, 52.1, 35.0, 31.7. IR (ν, cm^{-1}): 2955, 2906, 2869, 1726, 1599, 1480, 1432, 1365, 1294, 1271, 1249, 1193, 1126, 1100, 1070, 1044, 970, 877, 776, 761, 717, 679, 638, 575. UV-Vis (λ_{max}): 250 nm, 285 nm. HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C22H28O2Na 347.1987; Found: 347.1983

Sodium 1-[2-(3,5-di-*tert*-butylphenyl)phenyl]ethenolate, THF adduct (19)

To an oven-dried 500 mL one-neck round bottom flask equipped with a stirbar, addition funnel, and septum is charged sodium amide (2.9 g, 74.6 mmol) and tetrahydrofuran (85 mL). The flask is attached to a nitrogen manifold with adequate ventilation and heated to 50°C in an oil bath. A solution of 2'-(3,5-di-*tert*-butylphenyl)-acetophenone (11.5 g, 37.3 mmol) in tetrahydrofuran (85 mL) is added dropwise over 1 hour. The contents are then reacted for 4 hours, and then allowed to cool to room temperature. Under an inert atmosphere, the yellow suspension is diluted with diethyl ether (50 mL) and filtered through an oven-dried, medium-porosity frit, and the solvent is removed *in vacuo*. The yellow foam is further dried overnight, and then ground into a powder (12.46 g, 83%). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.93 – 7.76 (m, 1H), 7.71 (s, 2H), 7.54 – 7.42 (m, 2H), 7.41 – 7.25 (m, 2H), 3.82 (s, 1H), 3.52 (s, 1H), 3.50 – 3.42 (m, 4H), 1.40 – 1.37 (m, 4H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6) δ 170.36, 150.65, 146.18, 143.07, 140.05, 131.19, 128.81, 128.30, 128.06, 127.82, 127.23, 126.75, 123.73, 123.49, 120.65, 81.46, 67.89, 35.27, 35.23, 35.19, 31.81, 31.75, 31.68, 25.72.

Sodium 1-(3,4,5-trimethoxyphenyl)ethenolate, bis-THF adduct (20)

To an oven-dried 100 mL one-neck round bottom flask equipped with a stirbar, addition funnel, and septum is charged sodium amide (0.8 g, 20 mmol) and tetrahydrofuran (20 mL). The flask is attached to a nitrogen manifold with adequate ventilation and heated to 60°C in an oil bath. A solution of 3',4',5'-trimethoxyacetophenone (2.10 g, 10 mmol) is added dropwise over 15 minutes. The contents are stirred at 60°C for 3 hours, and then allowed to cool to ambient, transitioning from a red solution to light yellow over 30 minutes. Under an inert atmosphere, the grey suspension is diluted with diethyl ether (100 mL) and filtered through an oven-dried, medium-porosity frit, and the

solvent is removed *in vacuo* to afford peach colored powder, which is further dried overnight (2.10 g, 69%). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.20 (s, 2H), 3.89 (s, 6H), 3.84 (s, 2H), 3.72 – 3.63 (m, 8H), 2.56 (s, 3H), 1.86 – 1.76 (m, 8H). Material insufficiently soluble to obtain the ^{13}C{^{1}H} spectrum.

ACKNOWLEDGMENT

This work was funded by laboratory startup funds provided by the University of Colorado, Boulder, CO.

ASSOCIATED CONTENT

Supporting Information

Full characterization data, including ^{1}H and ^{13}C NMR, IR, UV-Vis, HRMS, and selected crystal structure data are provided in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

Accession Codes

CCDC 1892445−1892447 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

Experimental work was conducted by ASC, with additional work by ATL, JXS, ESA, and MPM. Crystallography was conducted by SMK and MPM. The manuscript was prepared by ASC and MPM.

Notes

Any additional relevant notes should be placed here.

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