<i>tert</i>-Butoxide-Mediated Protodeformylative Decarbonylation of α-Quaternary Homobenzaldehydes


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Conflict of Interest: The authors declare that they have no conflict of interest.

Abstract: <i>tert</i>-butoxide mediates the Haller–Bauer-type (protodeformylative) decarbonylation of readily accessed α-quaternary homobenzaldehydes and related compounds at room temperature, generating cumene products. Both geminal dialkyl and geminal diaryl substituents are tolerated. <i>Gem</i>-<i>dimethyls</i> are sufficient for decarbonylation of polycyclic arenyl substrates whereas monocyclic aromatic homobenzaldehydes require cyclic <i>gem</i>-<i>diaryl</i> or <i>gem</i>-<i>di-alkyl</i> for significant decarbonylation.

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**tert-Butoxide-Mediated Protodeformylative Decarbonylation of α-Quaternary Homobenzaldehydes**

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The decarbonylation of aldehydes is an important C-C bond-cleaving reaction in synthesis and in nature.1,2 Chemosynthetic decarbonylations mediated by stoichiometric rhodium complexes were first developed by Tsuji and Wilkinson3 and are notable for their application in natural products total synthesis;4 flow-type and catalytic variants have been developed to lower the cost.5 Haller and Bauer popularized the base-mediated debenzoylation of aromatic ketones in the early 1900's;6 a room temperature Haller-Bauer-type tert-butoxide-mediated protodebenzoylation was used as the third step to achieve formal protodeformylation of non-enolizable aldehydes (Scheme 1A).7 Recently, Madsen and coworkers studied the mechanism of Haller-Bauer-type decarbonylations of enolizable aldehydes (Scheme 1B) as well as non-enolizable aldehyde substrates like 2,6-dichlorobenzaldehyde (not shown).8 Similar conditions are known to be capable of deformylating certain non-enolizable aldehydes like triphenylacetaldelyde9 despite benzaldehydes being especially sensitive to hydroxide-mediated Cannizzaro-type disproportionation into the alcohol and carboxylic acid.10 Other methods for formal protodeformylation of aldehydes have also been described.11-13 Of the single-pot approaches (specifically Wilkinson and Haller-Bauer-type), a mild and general decarbonylation of α-quaternary aldehydes has not been described. Herein, we show that a wide variety of readily accessed α-quaternary homobenzaldehydes are deformylated at ambient temperature using tert-butoxide in THF to afford isopropyl arene (cumene) derivatives (Scheme 1C).14 Mechanistically this presumably occurs via stabilized anion B generated from tert-butoxide adduct A.15

The impetus for developing this method stemmed from our interest in allene functionalization reactions of α-quaternary homobenzylstyrenes and related compounds,16 whereby we

**Abstract**

Tert-butoxide mediates the Haller–Bauer-type (protodeformylative) decarbonylation of readily accessed α-quaternary homobenzaldehydes and related compounds at room temperature, generating cumene products. Both geminal dialkyl and geminal diaryl substituents are tolerated. Gem-dimethyls are sufficient for decarbonylation of polycyclic arenyl substrates whereas monocyclic aromatic homobenzaldehydes require cyclic gem-dialkyls or gem-diaryls for significant decarbonylation.

**Key words**
dercarbonylation, C-C bond cleavage, protodeformylation, Haller–Bauer reaction, tert-butoxide, benzylic anion, cumenes

**Scheme 1** Comparison of Haller–Bauer-type aldehyde decarbonylation methods.

A. Paquette and coworkers' formal aldehyde decarbonylation protocol (1987).16

B. Examples of Haller–Bauer-type reactions from Madsen and coworkers' mechanistic study (2017).8

C. This work: tert-butoxide-mediated aldehyde decarbonylation and putative Haller–Bauer-type mechanism.
Scheme 2 Evaluation of the generality of the protodeformylation of α-quaternary homobenzaldehydes. *Reactions were conducted on 0.2 mmol of aldehyde unless otherwise noted, and yields refer to isolated yields unless otherwise noted. †Yield was determined by 1H NMR using 1,3,5-trimethoxybenzene as an internal standard. ‡Product is volatile under high vacuum. §Reaction was executed on 1.0 mmol scale of 3b.

Table 1 Optimization of aldehyde decarboxylation. Reactions were conducted on 0.1 mmol scale in 1.1 mL of solvent under an atmosphere of N2 unless otherwise noted. Conversions and yields were determined by 1H NMR using 1,3,5-trimethoxybenzene as an internal standard. (n.d. = not detected.) aFormulations of bases unless otherwise noted: KOt-Bu = 1.6 M solution in THF, KOH = solid; LDA = 2.0 M solution in THF/α-heptane/ethylbenzene; NaOt-Bu = 2.0 M in THF. bUsed solid KOt-Bu and DMF as solvent. cReaction was conducted open to air. dUsed 100% w/w of molecular sieves. eBase and 1.6 equiv of HOt-Bu sonicated for 5 minutes.

Table:<ref>
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<th>entry</th>
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<th>conv. (%)</th>
<th>yield (%)</th>
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<tr>
<td>1</td>
<td>KOt-Bu</td>
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<td>&gt;95</td>
<td>89</td>
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<td>2</td>
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<td>&gt;95</td>
<td>74</td>
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<td>air</td>
<td>&gt;95</td>
<td>17</td>
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<td>4</td>
<td>KOt-Bu</td>
<td>4 Å mol. sieves</td>
<td>&gt;95</td>
<td>70</td>
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<tr>
<td>5</td>
<td>KOt-Bu</td>
<td>TEMPO</td>
<td>78</td>
<td>62</td>
</tr>
<tr>
<td>6</td>
<td>NaOt-Bu</td>
<td>none</td>
<td>&gt;95</td>
<td>87</td>
</tr>
<tr>
<td>7</td>
<td>LDA</td>
<td>none</td>
<td>&gt;95</td>
<td>&lt;5</td>
</tr>
<tr>
<td>8</td>
<td>KOH</td>
<td>HOt-Bu</td>
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</tr>
<tr>
<td>9</td>
<td>KOH</td>
<td>none</td>
<td>&lt;5</td>
<td>n.d.</td>
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In terms of breadth of scope, phenyl analogues (1a–1c) afford lower yield than the optimized naphthyl substrate (Scheme 2A). In particular, cumene (2a) is only produced in 11% NMR yield; the yield improves significantly by substituting with a para-phenyl group, thereby accessing 2d in 67% yield. In revision, the para-trifluoromethyl analogue was prepared and protoformylated to afford a modest 20% yield of the corresponding cumene by 1H NMR although, as with other low-boiling cumenes, this is presumably an underestimate. Strained cyclic gem-dialkyl-containing substrates like α-cyclopropyl (1e) and α-cyclobutyl (1f) afford just 9% and 24% yield of their respective methine products, whereas cyclopropyl (1g) and cyclohexyl (1h) substrates are decarbonylated in useful yield (44% and 76%, respectively). Other monoaryl substrates evaluated include tetralin 1i and triphenylacetaldehyde 1j, both of which afford decarbonylation products in good yield (61% and 79%, respectively). tert-Butanol is a common byproduct after workup, potentially arising from hydrolysis of the implied tert-butylformate byproduct of C–C bond cleavage of intermediate A in Scheme 1C.

Fused bicyclic and tricyclic substrates afford generally excellent decarbonylation yields (Scheme 2B and 2C), presumably because the extended conjugation in these compounds affords a relatively stabilized benzylic anion. Among bicyclic arenes (Scheme 2B), cyclopentane-containing product 4a is accessed in double the yield as that of the analogous monocyclic arene 2g. A 1.0 mmol scale reaction of 1-naphthyl substrate 3b affords the highest decarbonylation yield that we observed in the study (93% of 4b). 2-Naphthyl and 4-benzofuranyl analogues (4c and 4d) are also accessed in good yield. In contrast, 3-benzofuranyl analogue 4e is not prepared efficiently and a significant amount of deamortized product 7 is formed (eq 1). A number of benzyl-protected 4-

[Diagram of 4-

4e, 18% 4h, 7.28%]

substituted indole analogues are also decarbonylated efficiently (3f–3j), as are a number of benzoxyphenyl substrates (3k–3n), with the exception of the 3-substituted analogue 3o, which may be prone to deamortization like 3e.

Finally, we evaluated four fused tricyclic arenes as shown in Scheme 2C, including carbazoles (5a and 5b), a dibenzo[b]thiophene (5c), and a dibenzofuran (5d), all of which afford the corresponding deamortized products (6a–6d) in good yield.

In conclusion, we have developed a tert-butoxide-mediated protoformylative decarbonylation of α-quaternary homocyclohexenones. The method enables efficient access to a variety of cumenes. Efforts to expand the scope and better understand the mechanism are ongoing in our lab.

Acknowledgment

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Supporting Information

YES (this text will be updated with links prior to publication)

References and Notes


(10) For the original Cannizzaro disproportionation reaction, see: (a) Cannizzaro, S. Liebig Ann. Chem. 1853, 81, 129. For a review, see: (b) Geissman, T. A. Org. React. 1944, 2, 94. For a relevant example, see: (c) DiBlase, S. A.; Gokel, G. W. J. Org. Chem. 1978, 43, 447.


(13) For a metal-free formal (two-pot) decarbonylation of tertiary aldehydes, see: (a) Ref. 5a. For a one-pot Pd-catalyzed tandem arylation/cyclization/migration between tertiary benzaldehydes and aryl iodides, see: (b) Gou, B.-B.; Yang, H.; Sun, H.-R.; Chen, J.; Wu, J.; Zhou, L. Org. Lett. 2019, 21, 80. For an example of a method involving the synthesis of tertiary benzaldehydes as synthetic intermediates, see: (c) Dehnen, L.; Zard, S. Z. J. Am. Chem. Soc. 2013, 135, 3808.


(15) Intermediate A is analogous to a ketone-derived intermediate invoked by Gilday and Paquette (ref. 7b). For a relevant study on benzyl anion formation via C–C bond cleavage analogous to A→B, see Cram, D. J.; Langemann, A.; Lwowski, W.; Kopecky, K. R. J. Am. Chem. Soc. 1959, 81, 5760.


(17) This substrate and many others herein were prepared in one step from the corresponding aryl bromide using a variant of the Pd-catalyzed α-methylene cross-coupling developed by Hartwig and co-workers. See Hama, T.; Liu, X.; Cukin, D. A.; Hartwig, J. F. J. Am. Chem. Soc. 2003, 125, 11176.

(18) A similar disparity between aprotic (ethereal) and protic (HO-t-Bu) solvents has been observed in tert-butoxide-mediated fragmentations of ketones. See: (a) Gassman, P. G.; Lamb, J. T.; Zalar, F. V. J. Am. Chem. Soc. 1967, 89, 946. (b) Cristol, S. J.; Freeman, P. K. J. Am. Chem. Soc. 1961, 83, 4427.

(19) As further mechanistic support, two deuterium labeling experiments (one employing deuterated aldehyde as substrate, the other employing δ4-THF as solvent) both afforded no detectable deuterium incorporation in the product.


(21) General Protodeformylation Procedure. An oven-dried 25 mL round bottom flask is charged with a PTFE-coated magnetic stir bar, fitted with a rubber septum, and purged with nitrogen for two minutes. Then, under ambient pressure of N2, 0.2 mL of KOt-Bu solution (1.6 M in THF, 0.3 mmol, 1.6 equiv) is added to the flask, and it is further diluted with 1.0 mL of anhydrous THF. To the flask, 1.0 mL of an anhydrous THF solution of aldehyde (0.2 M, 1.0 equiv) is added dropwise at room temperature. The mixture is then allowed to stir for five hours under ambient pressure of N2. The reaction is then diluted with EtOAc (2 mL), saturated aqueous NH4Cl (5 mL) is added, and the mixture is allowed to stir until the solution is decolorified. The aqueous layer is then extracted with EtOAc (5 mL) three times and the combined organic layers are washed with brine, dried over sodium sulfate, and concentrated in vacuo to afford crude decarbonylated product, which is then purified by silica gel chromatography.

(22) Characterization data of representative product 4b: Yield (1.0 mmol scale): 158 mg (93%); colorless oil. 'H NMR (500 MHz, CDCl3): δ = 8.16 (dd, J = 8.5, 1.2 Hz, 1H), 7.90–7.84 (m, 1H), 7.73 (dt, J = 7.8, 1.1 Hz, 1H), 7.62–7.38 (m, 4H), 3.79 (sept, J = 6.9 Hz, 1H). 14C NMR (125 MHz, CDCl3): δ = 144.6 (C), 133.9 (C), 131.3 (C), 128.9 (CH), 126.3 (CH), 125.7 (CH), 125.6 (CH), 125.2 (CH), 123.3 (CH), 121.7 (CH), 28.5 (C), 23.6 (CH3).
**tert-Butoxide-Mediated Protodeformylative Decarbonylation of α-Quaternary Homobenzaldehydes**

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**Table of Contents**

I. General Considerations .............................................................................................................. S2

II. General Approach to the Synthesis of Aldehydes .................................................................... S3

III. General Procedures for the Synthesis of Aldehydes ............................................................... S3

   A. General Procedure 1: Reduction-Oxidation of Carboxylic Acid or Ester ................... S3
   B. General Procedure 2: Pd-Catalyzed Cross-Coupling .................................................. S4
   C. Synthesis and Characterization of Aldehydes ............................................................. S4
   D. General Procedure 3: Benzyl Protection of Indolyl Aldehydes ................................ S16
   E. Synthesis and Characterization of Benzyl-Protected Indolyl Aldehydes .................. S17

IV. Decarbonylation .................................................................................................................... S20

   A. General Procedure 4: KOr-Bu Mediated Decarbonylation ........................................ S20
   B. Synthesis and Characterization of Decarbonylation Products .................................. S20

V. References .............................................................................................................................. S30

VI. NMR Spectra of Substrates ................................................................................................... S32
I. General Considerations

Silyl enol ethers were used as purchased from Gelest, Inc. A Mettler Toledo XS105 balance (minimum mass of 2 mg, repeatable to 0.1 mg) was used to measure mass. Flash column chromatography was performed using 40–63 μm 60 Å silica gel. NMR spectra were obtained on Agilent spectrometers. $^1$H NMR spectra were obtained at 400 or 500 MHz and referenced to the residual CHCl$_3$ singlet at 7.26 ppm unless otherwise noted. The abbreviations s, d, t, q, sept, dd, td, qd, and m stand for the resonance multiplicities singlet, doublet, triplet, quartet, septet, doublet of doublet, triplet of doublet, quartet of doublet, and multiplet, respectively (‘app.’ denotes apparent). $^{13}$C NMR spectra were obtained at 100 or 125 MHz and referenced to the center line of the CDCl$_3$ triplet at 77.2 ppm unless otherwise noted. Carbon atom degree of substitution was determined using $^1$H–$^{13}$C HSQC. $^{19}$F NMR spectra were obtained at 376 MHz subsequent to $^1$H NMR acquisition and were otherwise unreferenced. FT-IR analysis was performed on a Thermo-Nicolet 380 using a diamond GladiATR from Pike technologies. APCI/ESI HRMS data were obtained on an Agilent LC-TOF (NSF CHE-0541848). Glassware for all reactions was oven-dried at 145 °C and cooled in a desiccator prior to use.
II. General Approach to the Synthesis of Aldehydes

\[
\begin{align*}
\text{R} \quad \text{R} & \quad \text{LiAlH}_4 \quad \text{(x equiv)} \quad \text{Et}_2\text{O} \\
\text{R} \quad \text{O} & \quad 0 \quad \text{oC} \quad \text{rt, 1 h} \quad \text{PCC} \\
\text{R} \quad \text{OH} & \quad \text{DCM} \quad \text{R} \quad \text{R} \\
\text{R} = \text{Me}, \ x = 2.25 \text{ equiv}; \text{R} = \text{H}, \ x = 3.25 \text{ equiv}
\end{align*}
\]

III. General Procedures for the Synthesis of Aldehydes

A. General Procedure 1: Reduction-Oxidation of Carboxylic Acids or Esters

2-methyl-2-phenylpropanal 1a. To a dry 250 mL round bottom flask charged with a PTFE coated magnetic stir bar were added 2-methyl-2-phenylpropanoic acid (1.0 g, 6.1 mmol, 1.00 equiv) and diethyl ether (122 mL, 0.05 M). The solution was then cooled to 0 ºC and purged with nitrogen for 5 minutes. To the cold mixture was cautiously added LiAlH\(_4\) (753.4 mg, 3.25 equiv) in 4 portions over 10 minutes. The reaction was slowly warmed to room temperature and stirred for one hour. Once all carboxylic acid was consumed (monitored by TLC), the reaction was carefully quenched by addition of 1 M aqueous HCl (~10 mL) at 0 ºC. The primary alcohol intermediate was extracted with diethyl ether three times. The ether solution was dried over anhydrous magnesium sulfate before it was concentrated in vacuo. The crude product was then dissolved with DCM (24.5 mL, 0.25 M). The solution was chilled in an ice bath and allowed to purge with argon. To this inert gas-protected mixture, PCC (2.60 g, 2.0 equiv) was added. The reaction was allowed to stir at room temperature for 3 hours until all primary alcohol had been consumed as determined by TLC. The mixture was then diluted with EtOAc (20 mL) and the organic solution was filtered through a pad of Celite®. The combined liquid was dried over anhydrous sodium sulfate. All organic solvents were removed under reduced pressure and the residue was purified by flash column chromatography on SiO\(_2\) using hexanes:EtOAc (100:0→92:8) to afford aldehyde (701 mg, 77% yield), which was prone to decomposition over time.

\[\text{1H NMR (400 MHz, CDCl}_3\text{) } \delta: 9.50 \text{ (s, 1H),}
7.40-7.27 \text{ (m, 5H), 1.47 (s, 6H);}
\text{13C NMR (100 MHz, CDCl}_3\text{) } \delta: 202.3, 141.4, 129.0, 127.4, 126.8, 50.6, 22.6.\]

The spectral data matched those reported in the literature.
B. General procedure 2: Pd-catalyzed Cross-Coupling

2-(3,5-dimethoxyphenyl)-2-methylpropanal 1b. To a dry 50 mL round bottom flask charged with a PTFE-coated magnetic stir bar were added 396 mg of zinc fluoride (3.83 mmol, 1.50 equiv) and 147 mg of bis(dibenzylideneacetone) palladium (0) (0.26 mmol, 0.10 equiv). The reaction flask was then sealed with a rubber septum, degassed, and back-filled with nitrogen. Then 25.5 mL of DMF (0.1 M) and 554 mg of 1-bromo-3,5-dimethoxybenzene (2.55 mmol, 1.00 equiv) were added at room temperature. To this mixture were added 0.8 mL of a 1.0 M solution of tri-tert-butylphosphine in toluene (0.80 mmol, 0.31 equiv) and 0.7 mL of trimethyl((2-methylprop-1-en-1-yl)oxy)silane (3.83 mmol, 1.50 equiv) at the same time through syringe. The reaction mixture was heated to 85 °C and was allowed to stir in an N\textsubscript{2} atmosphere overnight. The reaction mixture was cooled to room temperature before filtration through Celite®, and the Celite® cake was washed with 15 mL of ethyl acetate. The filtrate was concentrated under reduced pressure. The crude product was purified by silica gel chromatography (100:0→85:15 hexanes:ethyl acetate) to afford 1b as a colorless oil (420 mg, 79%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 9.44 (s, 1H), 6.39 (s, 2H), 6.37 (s, 1H), 3.76 (s, 6H), 1.41 (s, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 201.8 (C=O), 161.1 (C), 143.6 (C), 105.1 (CH), 98.6 (CH), 55.3 (CH3), 50.5 (C), 24.0 (CH3). The spectral data matched those reported in the literature.\textsuperscript{1}

C. Synthesis and Characterization of Aldehydes

2-(4-Methoxyphenyl)-2-methylpropanal 1c. General procedure 1 was followed using 2.50 g of methyl 2-(4-methoxyphenyl)-2-methylpropanoate (12.0 mmol) and 1.03 g of LiAlH\textsubscript{4} (27.0 mmol) in 120 mL of Et\textsubscript{2}O. The crude isolate was then oxidized using 5.3 g of PCC (24 mmol) in 60 mL of DCM. Purification by flash column chromatography (100:0→80:20 hexanes:EtOAc) afforded 1c as light yellow oil. (1.65 g, 77% yield over two steps). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 9.44 (s, 1H), 7.19 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 3.78 (s, 3H), 1.43 (s, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 202.1 (C=O), 158.7 (C), 133.0 (C), 127.8 (CH), 114.2 (CH), 55.2 (CH3), 49.7 (C), 22.5 (CH3). The spectral data matched those reported in the literature.\textsuperscript{1}
2-(4-Trifluoromethylphenyl)-2-methylpropanal S8. General procedure 2 was followed using 500 mg of 4-bromobenzotrifluoride (2.22 mmol), 345 mg of zinc fluoride (3.33 mmol), 102 mg of tris(dibenzylideneacetone)dipalladium(0) (0.11 mmol), 0.4 mL (0.4 mmol) of a 1.0 M solution of tri-tert-butylphosphine in toluene, and 0.6 mL of trimethyl(2-methylprop-1-en-1-yl)oxy)silane (3.33 mmol) in 22 mL of DMF. Purification by silica gel chromatography (100:0→70:30 hexanes:benzene) afforded S8 (125 mg, 26% yield) as a colorless oil. The spectral data matched those reported by Cai and co-workers.\(^1\) \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 9.52 (s, 1H), 7.64 (d, \(J = 8.0\) Hz, 2H), 7.40 (d, \(J = 8.2\) Hz, 2H), 1.50 (s, 6H).

2-([1,1'-Biphenyl]-4-yl)-2-methylpropanal 1d. General procedure 1 was followed using 5.62 g of methyl 2-([1,1'-biphenyl]-4-yl)-2-methylpropanoate (22.1 mmol) and 1.89 g of LiAlH\(_4\) (49.7 mmol) in 220 mL of Et\(_2\)O. The crude isolate was then oxidized using 9.7 g of PCC (42.2 mmol) in 89 mL of DCM. Purification by flash column chromatography (100:0→80:20 hexanes:EtOAc) afforded 1d as a light yellow oil (3.0 g, 60% yield over two steps). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.64 (s, 1H), 7.77–7.65 (m, 3H), 7.55 (t, \(J = 7.5\) Hz, 1H), 7.48–7.45 (m, 5H), 1.61 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 202.0 (C=O), 140.6 (C), 140.3 (C), 140.2 (C), 129.0 (CH), 128.5 (CH), 127.7 (CH), 127.3 (CH), 127.2 (CH), 50.3(C), 22.62 (CH\(_3\)). The spectral data matched those reported in the literature.\(^1\)

2-([1,1'-biphenyl]-4-yl)-2-methylpropanal-1-d 1d-d. General procedure 1 was followed using 1.12 g of methyl 2-([1,1'-biphenyl]-4-yl)-2-methylpropanoate (4.42 mmol) and 378.5 mg of LiAlD\(_4\) (9.94 mmol) in 44.0 mL of Et\(_2\)O. The crude isolate was then oxidized using 1.94 g of PCC (8.44 mmol) in 17.8 mL of DCM. Purification by flash column chromatography (100:0→80:20 hexanes:EtOAc) afforded 1d-d as a light yellow oil (408.3 mg, 41% yield over two steps). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.68 – 7.56 (m, 4H), 7.46 (t, \(J = 7.7\) Hz, 2H), 7.41 – 7.33 (m, 3H), 7.30 – 7.23 (m, 3H), 7.18 – 7.10 (m, 3H), 1.70 (s, 6H).
1.52 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 201.8 (m, C=O), 140.5 (C), 140.2 (2C), 128.8 (CH), 127.5 (CH), 127.4 (CH), 127.2 (CH), 127.1 (CH), 50.1 (m, C), 22.5 (CH$_3$).

**1-phenylcyclopropane-1-carbaldehyde 1e.** General procedure 1 was followed using 486.57 mg of 1-phenylcyclopropane-1-carboxylic acid (3.0 mmol) and 370.01 mg of LiAlH$_4$ (9.75 mmol) in 30 mL of Et$_2$O. The crude isolate was then oxidized using 1.29 g of PCC (6.0 mmol) in 12 mL of DCM. Purification by flash column chromatography (100:0→95:5 hexanes:EtOAc) afforded 1f as a light yellow oil (179.81 mg, 41% over two steps). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.31 (s, 1H), 7.83 – 6.64 (m, 5H), 1.73 – 1.54 (m, 2H), 1.49 – 1.35 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 201.1 (C=O), 137.5 (C), 130.1 (CH), 128.6 (CH), 127.7 (CH), 37.5 (C), 16.2 (CH$_2$). The spectral data matched those reported in the literature.$^2$

![1e](image)

**1-Phenylcyclobutane-1-carbaldehyde 1f.** General procedure 1 was followed using 1.07 g of 1-phenylcyclobutane-1-carboxylic acid (6.1 mmol) and 0.753 g of LiAlH$_4$ (19.8 mmol) in 122 mL of Et$_2$O. The crude isolate was then oxidized using 2.72 g of PCC (12.2 mmol) in 25 mL of DCM. Purification by flash column chromatography (100:0→95:5 hexanes:EtOAc) afforded 1f as a light yellow oil (723.2 mg, 74% over two steps). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.55 (s, 1H), 7.41-7.37 (m, 2H), 7.28 (t, $J$ = 7.1 Hz, 1H), 7.17 (d, $J$ = 7.7 Hz, 2H), 2.78-2.70 (m, 2H), 2.46-2.38 (m, 2H), 2.08-1.88 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 199.4 (C=O), 130.9 (C), 128.8 (CH), 127.0 (CH), 126.4 (CH), 57.6 (C), 28.3 (CH$_2$), 15.8 (CH$_2$). The spectral data matched those reported in the literature.$^1$

![1f](image)

**1-Phenylcyclopentane-1-carbaldehyde 1g.** General procedure 1 was followed using 1.16 g of 1-phenylcyclopentane-1-carboxylic acid (6.1 mmol) and 0.753 g of LiAlH$_4$ (19.8 mmol) in 122 mL
of Et<sub>2</sub>O. The crude isolate was then oxidized using 2.72 g of PCC (12.2 mmol) in 25 mL of DCM. Purification by flash column chromatography (100:0→95:5 hexanes:E<sub>2</sub>OAc) afforded 1<sub>g</sub> as a light yellow oil (0.71 g, 67% over two steps). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ: 9.31 (s, 1H), 7.24–7.28 (m, 2H), 7.15–7.19 (m, 3H), 2.41–2.47 (m, 2H), 1.76–1.83 (m, 2H), 1.64–1.68 (m, 2H), 1.54–1.60 (m, 2H); <sup>1</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ: 200.6, 140.3, 128.7, 127.6, 127.1, 63.6, 32.3, 24.2. The spectral data matched those reported in the literature.<sup>1</sup>

<sup>1</sup><br>![1h](image_url)

**1-Phenylcyclohexane-1-carbaldehyde 1<sub>h</sub>.** General procedure 1 was followed using 1.25 g of 1-phenylcyclohexane-1-carboxylic acid (6.1 mmol) and 0.753 g of LiAlH<sub>4</sub> (19.8 mmol) in 122 mL of Et<sub>2</sub>O. The crude isolate was then oxidized using 2.72 g of PCC (12.2 mmol) in 25 mL of DCM. Purification by flash column chromatography (100:0→95:5 hexanes:E<sub>2</sub>OAc) afforded **1<sub>h</sub>** as a light yellow oil (0.90 g, 78% over two steps). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.38 (s, 1H), 7.41-7.31 (m, 4H), 7.30-7.24 (m, 1H), 2.38-2.26 (m, 2H), 1.91-1.80 (m, 2H), 1.73-1.57 (m, 3H), 1.56-1.43 (m, 2H), 1.37-1.26 (m, 1H); <sup>1</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 202.3 (C=O), 139.7 (C), 128.9 (CH), 127.2 (CH), 127.1 (CH), 54.4 (C), 31.3 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>), 22.8 (CH<sub>2</sub>). The spectral data matched those reported in the literature.<sup>1</sup>

<sup>1</sup><br>![1i](image_url)

**2-methyl-2-(5,6,7,8-tetrahydronaphthalen-1-yl)propanal 1<sub>i</sub>.** The general cross-coupling procedure 2 was followed using 538.3 mg of 5-bromo-1,2,3,4-tetrahydronaphthalene (2.55 mmol), 396.0 mg of zinc fluoride (3.83 mmol), 146.6 mg of bis(dibenzylideneacetone)palladium(0) (0.26 mmol), 0.8 mL (0.8 mmol) tri-tertbutylphosphine, and 0.7 mL of trimethyl((2-methylprop-1-en-1-yl)oxy)silane (3.83 mmol) in 25.5 mL of DMF. Purification by silica gel chromatography (100:0→70:30 hexanes: benzene) afforded **1<sub>j</sub>** (407.5 mg, 79% yield) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.65 (s, 1H), 7.36–7.15 (m, 2H), 7.09 (dd, J = 7.4, 1.4 Hz, 1H), 2.83 (t, J = 6.3 Hz, 2H), 2.49 (t, J = 6.0 Hz, 2H), 1.86 – 1.69 (m, 4H), 1.46 (s, 6H); <sup>1</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 204.7 (C=O), 140.3 (C), 139.1 (C), 136.6 (C), 128.9 (CH), 126.1 (CH), 124.1 (CH), 51.1 (C), 30.1 (CH<sub>2</sub>), 27.8 (CH<sub>2</sub>), 23.4 (CH<sub>3</sub>), 23.4 (CH<sub>3</sub>), 23.0 (CH<sub>3</sub>), 22.4 (CH<sub>2</sub>).
2,2,2-triphenylacetaldehyde 1j. General procedure 1 was followed using 1.50 g of 2,2,2-triphenylacetic acid (5.2 mmol) and 0.643 g of LiAlH$_4$ (16.9 mmol) in 104 mL of Et$_2$O. The crude isolate was then oxidized using 1.68 g of PCC (7.80 mmol) in 25 mL of DCM. Purification by flash column chromatography (100:0$\rightarrow$95:5 hexanes:EtOAc) afforded 1j as a light yellow powder (778.9 mg, 55% over two steps). The $^1$H NMR data matched those reported by Henderson and Heathcock.

1-(naphthalen-1-yl)cyclopentane-1-carbaldehyde 3a. General procedure 1 was followed using 1.20 g of 1-(naphthalen-1-yl)cyclopentane-1-carboxylic acid (5.0 mmol) and 0.62 g of LiAlH$_4$ (16.25 mmol) in 100 mL of Et$_2$O. The crude isolate was then oxidized using 2.16 g of PCC (10.0 mmol) in 25 mL of DCM. Purification by flash column chromatography (100:0$\rightarrow$95:5 hexanes:EtOAc) afforded 3a as a colorless oil (583.2 mg, 52% over two steps); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.49 (d, $J$ = 1.2 Hz, 1H), 7.94 – 7.73 (m, 3H), 7.60 (d, $J$ = 7.3 Hz, 1H), 7.54 – 7.44 (m, 3H), 2.66 (dd, $J$ = 12.7, 6.4 Hz, 2H), 2.14 (dd, $J$ = 13.4, 7.0 Hz, 2H), 1.86 – 1.65 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 201.8 (C=O), 129.1 (CH), 128.7 (CH), 126.1 (CH), 125.6 (CH), 125.4 (CH), 125.2 (CH), 124.7 (CH), 33.2 (CH$_2$), 24.8 (CH$_2$) (quaternary carbons were obscured).

2-methyl-2-(naphthalen-1-yl)propanol 3b. General procedure 2 was followed using 528.0 mg of 1-bromonaphthalene (2.55 mmol), 396.0 mg of zinc fluoride (3.83 mmol, 1.5 equiv), 146.6 mg of bis(dibenzylideneacetone)palladium(0) (0.26 mmol), 0.8 mL (0.8 mmol) tri-tertbutylphosphine, and 0.7 mL of trimethyl(2-methylprop-1-en-1-yl)oxy)silane (3.83 mmol) in 25.5 mL of DMF. Purification by silica gel chromatography (100:0$\rightarrow$80:20 hexanes: benzene) afforded 3m (429.8 g, 85% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.69 (s, 1H), 7.95 – 7.88 (m, 1H),
7.85 (dt, $J = 8.1$, 1.1 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.58 (dd, $J = 7.3$, 1.4 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.51 – 7.45 (m, 2H); 1H NMR (400 MHz, CDCl$_3$): $\delta$ 9.54 (s, 1H), 7.49 (d, $J = 8.3$ Hz, 1H), 7.33 (t, $J = 7.9$ Hz, 1H), 7.23 (d, $J = 7.6$ Hz, 1H), 6.71 (appr s, 1H), 1.56 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 202.4 (C=O), 155.3 (C), 144.8 (CH), 134.3 (C), 126.0 (C), 124.5 (CH), 120.1 (CH), 111.1 (CH), 105.9 (CH), 50.8 (C), 22.0 (CH$_3$); HRMS (ESI) m/z calculated for C$_{12}$H$_{13}$O$_2$ [M+H]$^+$: 189.0910, found: 189.0903. The spectral data matched those reported in the literature.$^4$

**2-methyl-2-(naphthalen-2-yl)propanal 3c.** General procedure 2 was followed using 528.0 mg of 2-bromonaphthalene (2.55 mmol), 396.0 mg of zinc fluoride (3.83 mmol, 1.5 equiv), 146.6 mg of bis(dibenzylideneacetone)palladium(0) (0.26 mmol), 0.8 mL (0.8 mmol) tri-tertbutylphosphine, and 0.7 mL of trimethyl(2-methylprop-1-en-1-yl)oxy)silane (3.83 mmol) in 25.5 mL of DMF. Purification by silica gel chromatography (100:0 → 80:20 hexanes: benzene) afforded 3c (450.0 g, 89% yield) as a colorless oil. The spectral data matched those reported in the literature.$^4$

**2-(Benzofuran-4-yl)-2-methylpropanal 3d.** The general cross-coupling procedure 2 was followed using 394.1 mg of 4-bromobenzofuran (2.00 mmol), 310.2 mg of zinc fluoride (3.0 mmol), 115.0 mg of bis(dibenzylideneacetone)palladium(0) (0.2 mmol), 0.60 mL of tri-tertbutylphosphine (0.60 mmol), and 0.6 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.0 mmol) in 20.0 mL of DMF. Purification by flash column chromatography (100:0 → 95:5 hexanes:benzene) afforded 3d (289.0 mg, 77% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.54 (s, 1H), 7.60 (appr s, 1H), 7.49 (d, $J = 8.3$ Hz, 1H), 7.33 (t, $J = 7.9$ Hz, 1H), 7.23 (d, $J = 7.6$ Hz, 1H), 6.71 (appr s, 1H), 1.56 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 202.4 (C=O), 155.3 (C), 144.8 (CH), 134.3 (C), 126.0 (C), 124.5 (CH), 120.1 (CH), 111.1 (CH), 105.9 (CH), 50.8 (C), 22.0 (CH$_3$); HRMS (ESI) m/z calculated for C$_{12}$H$_{13}$O$_2$ [M+H]$^+$: 189.0910, found: 189.0903. The spectral data matched those reported in the literature.$^5$
2-(Benzofuran-3-yl)-2-methylpropanal 3e. The general cross-coupling procedure 2 was followed using 394.1 mg of 3-bromobenzofuran (2.00 mmol), 310.2 mg of zinc fluoride (3.0 mmol), 115.0 mg of bis(dibenzylideneacetone)palladium(0) (0.2 mmol), 0.60 mL of tri-tert-butylphosphine (0.60 mmol), and 0.6 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.0 mmol) in 20.0 mL of DMF. Purification by flash column chromatography (100:0→95:5 hexanes:benzene) afforded 3e (243.9 mg, 65% yield) as a yellow oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 9.57 (s, 1H), 7.61 – 7.38 (m, 4H), 7.37 – 7.27 (m, 1H), 7.24 (q, J = 7.4, 6.4 Hz, 1H), 1.56 (s, 7H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 201.5 (C=O), 155.9 (C), 141.8 (CH), 126.0 (C), 124.6 (CH), 122.7 (CH), 121.7 (C), 120.8 (CH), 111.8 (CH), 45.9 (C), 21.4 (CH\textsubscript{3}).

2-(1H-Indol-4-yl)-2-methylpropanal S1. The general cross-coupling procedure 2 was followed using 535.1 mg of 4-bromoindole (2.55 mmol), 396.0 mg of zinc fluoride (3.83 mmol), 146.6 mg of bis(dibenzylideneacetone)palladium(0) (0.26 mmol), 0.8 mL of tri-tert-butylphosphine (0.80 mmol), and 0.7 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.83 mmol) in 25.5 mL of DMF. Purification by flash column chromatography (100:0→80:20 hexanes:benzene) afforded S1 as a colorless oil (405.8 mg, 85%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 9.62 (s, 1H), 8.38 (s, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.26 (app. t, J = 7.8 Hz, 1H), 7.18 (m, 1H), 7.14 (d, J = 7.4 Hz, 1H), 6.48–6.46 (m, 1H), 1.61 (s, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 204.2 (C=O), 136.4 (C), 133.5 (C), 126.3 (C), 124.4 (CH), 122.3 (CH), 117.4 (CH), 111.2 (CH), 102.2 (CH), 51.2 (C), 22.1 (CH\textsubscript{3}); ATR-FTIR (neat): 3409, 2971, 2933, 2809, 2709, 1717, 1611, 1503 cm\textsuperscript{-1}; HRMS (ESI) m/z calculated for C\textsubscript{12}H\textsubscript{14}NO [M+H]\textsuperscript{+} : 188.1070, found 188.1072. The spectral data matched those reported in the literature.\textsuperscript{5}
2-(7-Methoxy-1H-indol-4-yl)-2-methylpropanal S2. The general cross-coupling procedure 2 was followed using 500.0 mg of 4-bromo-7-methoxy-1H-indole (2.30 mmol), 356.7 mg of zinc fluoride (3.45 mmol), 132.2 mg of bis(dibenzylideneacetone)palladium(0) (0.23 mmol), 0.7 mL of tri-tert-butylphosphine (0.69 mmol), and 0.6 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.45 mmol) in 23.0 mL of DMF. Purification by flash column chromatography (100:0:0®92:3:5 hexanes:benzene:ethyl acetate) afforded S2 (284.8 mg, 57% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 9.57 (s, 1 H), 8.59 (s, br, 1 H), 7.16 (dd, $J = 3.2, 2.5$ Hz, 1H), 7.03 (d, $J = 8.0$ Hz, 1H), 6.68 (d, $J = 8.0$ Hz, 1H), 6.46 (dd, $J = 3.2, 2.2$ Hz, 1H), 3.98 (s, 3H), 1.58 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 203.8 (C=O), 146.0 (C), 127.3 (C), 126.7 (C), 125.8 (C), 123.7 (CH), 117.6 (CH), 102.5 (CH), 101.5 (CH), 55.3 (OCH$_3$), 50.4 (C), 22.0 (CH$_3$); HRMS (ESI) m/z calculated for C$_{13}$H$_{16}$NO$_2$ [M+H]$^+$ : 218.1176, found 218.1178. The spectral data matched those reported in the literature.$^5$

2-(7-Fluoro-1H-indol-4-yl)-2-methylpropanal S3. The general cross-coupling procedure 2 was followed using 513.2 mg of 4-bromo-7-fluoroindole (2.44 mmol), 378.4 mg of zinc fluoride (3.66 mmol), 140.3 mg of bis(dibenzylideneacetone)palladium(0) (0.24 mmol), 0.7 mL of tri-tert-butylphosphine (0.73 mmol), and 0.7 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.66 mmol) in 24.0 mL of DMF. Purification by flash column chromatography (100:0→80:20 hexanes:benzene) afforded S3 (345.5 mg, 69% yield) as colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 9.58 (s, 1 H), 8.82 (s, br, 1 H), 7.23 (t, $J = 2.8$ Hz, 1H), 7.04–7.01 (m, 1H), 6.96–6.93 (m, 1H), 6.50–6.49 (m, 1H), 1.59 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 203.8 (C=O), 146.0 (C), 127.3 (C), 126.7 (C), 125.8 (C), 123.7 (CH), 117.6 (CH), 102.5 (CH), 101.5 (CH), 55.3 (OCH$_3$), 50.4 (C), 22.0 (CH$_3$); HRMS (ESI) m/z calculated for C$_{12}$H$_{16}$FNO [M+H]$^+$ : 206.0976, found 206.0977. The spectral data matched those reported in the literature.$^5$
2-Methyl-2-(2-methyl-1H-indol-4-yl)propanal S4. The general cross-coupling procedure 2 was followed using 500.0 mg of 4-bromo-2-methyl-1H-indole (2.38 mmol), 369.1 mg of zinc fluoride (3.57 mmol), 136.9 mg of bis(dibenzylideneacetone)palladium(0) (0.24 mmol), 0.7 mL of tri-tert-butylphosphine (0.71 mmol), and 0.7 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.57 mmol) in 23.8 mL of DMF. Purification by flash column chromatography (100:0 80:20 hexanes:benzene) afforded S4 as a light yellow oil (273.0 mg, 57%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 9.58 (s, 1 H), 8.06 (s, 1 H), 7.27 (d, \(J = 8.1\) Hz, 1H), 7.16 (appr. t, \(J = 7.7\) Hz, 1H), 7.08 (dd, \(J = 7.4, 1.0\) Hz, 1H), 6.16 (s, 1H), 2.41 (s, 3H), 1.57 (s, 6H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): δ 204.2 (C=O), 136.6 (C), 135.4 (C), 132.4 (C), 127.5 (C), 121.3 (CH), 117.2 (CH), 110.3 (CH), 100.1 (CH), 51.1 (C), 22.0 (CH\(_3\)), 16.6 (CH\(_3\)); HRMS (ESI) m/z calculated for C\(_{13}\)H\(_{16}\)NO \([\text{M+H}]^+\): 202.1226, found 202.1229. The spectral data matched those reported in the literature.5

2-Methyl-2-(7-methyl-1H-indol-4-yl)propanal S5. The general cross-coupling procedure 2 was followed using 500.0 mg of 4-bromo-7-methyl-1H-indole (2.38 mmol), 369.1 mg of zinc fluoride (3.57 mmol), 136.9 mg of bis(dibenzylideneacetone)palladium(0) (0.24 mmol), 0.7 mL of tri-tert-butylphosphine (0.71 mmol), and 0.7 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.57 mmol) in 23.8 mL of DMF. Purification by flash column chromatography (100:0 90:10 hexanes:benzene) afforded S5 as a colorless oil (349.7 mg, 73%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 9.62 (s, 1 H), 8.71 (s, 1 H), 7.19–7.17 (m, 1H), 7.05 (appr. s, 2H), 6.50 (dd, \(J = 3.3, 1.9\) Hz, 1H), 2.49 (s, 3H), 1.59 (s, 6H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): δ 204.2 (C=O), 135.9 (C), 130.9 (C), 125.7 (C), 124.2 (CH), 122.5 (CH), 120.4 (C), 117.4 (CH), 102.3 (CH), 50.8 (C), 22.0 (CH\(_3\)), 16.6 (CH\(_3\)); ATR-FTIR (neat): 3472, 2963, 2920, 1711 cm\(^{-1}\); HRMS (ESI) m/z calculated for C\(_{13}\)H\(_{16}\)NO \([\text{M+H}]^+\): 202.1226, found 202.1228. The spectral data matched those reported in the literature.5
2-(Benzo[b]thiophen-4-yl)-2-methylpropanal 3k. The general cross-coupling procedure 2 was followed using 485.5 mg of 4-bromobenzo[b]thiophene (2.30 mmol), 356.7 mg of zinc fluoride (3.45 mmol), 132.3 mg of bis(dibenzylideneacetone)palladium(0) (0.23 mmol), 0.7 mL of tri-tert-butylphosphine (0.69 mmol), and 0.6 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.45 mmol) in 23.0 mL of DMF. Purification by flash column chromatography (100:0\textsuperscript{®}90:10 hexanes:benzene) afforded 3k (352.4 mg, 75% yield) as a colorless oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 9.58 (s, 1 H), 7.88 (td, \(J = 4.5, 0.9\) Hz, 1H), 7.46 (d, \(J = 5.7\) Hz, 1H), 7.40(dd, \(J = 4.6, 0.8\) Hz, 2H), 7.28 (dd, \(J = 5.7, 1.0\) Hz, 1H), 1.59 (s, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 203.5 (C=O), 141.2 (C), 137.6 (C), 136.4 (C), 126.8 (CH), 124.4 (CH), 122.6 (CH), 122.3 (CH), 121.9 (CH), 51.4 (C), 22.4 (CH\textsubscript{3}). The spectral data matched those reported in the literature.\textsuperscript{5}

2-(Benzo[b]thiophen-3-yl)-2-methylpropanal 3o. The general cross-coupling procedure 2 was followed using 485.5 mg of 3-bromobenzo[b]thiophene (2.30 mmol), 356.7 mg of zinc fluoride (3.45 mmol), 132.3 mg of bis(dibenzylideneacetone)palladium(0) (0.23 mmol), 0.7 mL of tri-tert-butylphosphine (0.69 mmol), and 0.6 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.45 mmol) in 23.0 mL of DMF. Purification by flash column chromatography (100:0\textsuperscript{®}90:10 hexanes:benzene) afforded 3o (293.7 mg, 63% yield) as a colorless oil. \textsuperscript{1}H NMR (400 MHz, Chloroform-d): \(\delta\) 9.54 (s, 1H), 7.99 – 7.77 (m, 1H), 7.75 – 7.54 (m, 1H), 7.41 – 7.30 (m, 3H), 1.60 (s, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 202.5 (C=O), 141.1 (C), 137.2 (C), 136.5 (C), 124.3 (CH), 124.2 (CH), 123.5 (CH), 123.2 (CH), 123.0 (CH), 49.3 (C), 22.0 (CH\textsubscript{3}).

2-(Benzo[b]thiophen-5-yl)-2-methylpropanal 3m. The general cross-coupling procedure 2 was followed using 485.5 mg of 5-bromobenzo[b]thiophene (2.30 mmol), 356.7 mg of zinc fluoride (3.45 mmol), 132.3 mg of bis(dibenzylideneacetone)palladium(0) (0.23 mmol), 0.7 mL of tri-tert-butylphosphine (0.69 mmol), and 0.6 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.45 mmol)
in 23.0 mL of DMF. Purification by flash column chromatography (100:0→90:10 hexanes:benzene) afforded \(3\text{m}\) (329.3 mg, 70% yield) as a colorless oil. \(^{1}\text{H} \text{NMR}\) (400 MHz, CDCl\(_3\)): \(\delta 9.54\) (s, 1H), 7.99 – 7.77 (m, 1H), 7.75 – 7.54 (m, 1H), 7.41 – 7.30 (m, 2H), 1.60 (s, 6H). \(^{13}\text{C} \text{NMR}\) (100 MHz, CDCl\(_3\)): \(\delta 202.2\) (C=O), 140.1 (C), 138.7 (C), 137.4 (C), 127.3 (CH), 123.9 (CH), 123.2 (CH), 122.9 (CH), 121.6 (CH), 50.4 (C), 22.7 (CH\(_3\)).

\[\text{2-(Benzo[b]thiophen-2-yl)-2-methylpropanal 3n.}\]

The general cross-coupling procedure was followed using 485.5 mg of 2-bromobenzo[b]thiophene (2.30 mmol), 356.7 mg of zinc fluoride (3.45 mmol), 132.3 mg of bis(dibenzylideneacetone)palladium(0) (0.23 mmol), 0.7 mL of tri-tert-butylphosphine (0.69 mmol), and 0.6 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.45 mmol) in 23.0 mL of DMF. Purification by flash column chromatography (100:0→90:10 hexanes:benzene) afforded \(3\text{n}\) (277.5 mg, 59% yield) as a colorless oil. \(^{1}\text{H} \text{NMR}\) (400 MHz, CDCl\(_3\)): \(\delta 9.56\) (s, 1H), 7.99 – 7.60 (m, 2H), 7.41 – 7.27 (m, 2H), 1.60 (s, 6H); \(^{13}\text{C} \text{NMR}\) (100 MHz, CDCl\(_3\)): \(\delta 199.7\) (C=O), 146.6 (C), 139.8 (C), 139.5 (C), 124.5 (CH), 124.3 (CH), 123.4 (CH), 122.2 (CH), 121.4 (CH), 49.4 (C), 23.3 (CH\(_3\)).

\[\text{2-(Benzo[b]thiophen-7-yl)-2-methylpropanal 3l.}\]

The general cross-coupling procedure was followed using 485.5 mg of 7-bromobenzo[b]thiophene (2.30 mmol), 356.7 mg of zinc fluoride (3.45 mmol), 132.3 mg of bis(dibenzylideneacetone)palladium(0) (0.23 mmol), 0.7 mL of tri-tert-butylphosphine (0.69 mmol), and 0.6 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.45 mmol) in 23.0 mL of DMF. Purification by flash column chromatography (100:0→90:10 hexanes:benzene) afforded \(3\text{l}\) (357.0 mg, 76% yield) as a colorless oil. \(^{1}\text{H} \text{NMR}\) (400 MHz, CDCl\(_3\)): \(\delta 9.62\) (s, 1H), 7.81 (dd, \(\text{J} = 7.8, 1.1\) Hz, 1H), 7.55 – 7.28 (m, 4H), 1.64 (s, 6H); \(^{13}\text{C} \text{NMR}\) (100 MHz, CDCl\(_3\)): \(\delta 202.3\) (C=O), 141.0 (C), 138.1 (C), 136.1 (C), 126.2 (CH), 124.7 (CH), 124.1 (CH), 123.5 (CH), 122.4 (CH), 51.6 (C), 21.3 (CH\(_3\)).
2-(9H-carbazol-4-yl)-2-methylpropanal S6. The general cross-coupling procedure 2 was followed using 492.2 mg of 4-bromo-9H-carbazole (2.00 mmol), 310.2 mg of zinc fluoride (3 mmol), 115.0 mg of bis(dibenzylideneacetone)palladium(0) (0.2 mmol), 0.60 mL of tri-tert-butylphosphine (0.60 mmol), and 0.6 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.0 mmol) in 20.0 mL of DMF. Purification by flash column chromatography (100:0→95:5 hexanes:benzene) afforded S6 (322.7 mg, 68% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.81 (s, 1H), 8.32 (s, 1H), 7.87 (d, $J$ = 8.2 Hz, 1H), 7.55 – 7.36 (m, 4H), 7.33 – 7.10 (m, 2H), 1.73 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 205.1 (C=O), 140.4 (C), 139.5 (C), 137.9 (C), 125.9 (CH), 125.5 (CH), 124.4 (CH), 121.1 (C), 121.0 (C), 119.5 (CH), 117.8 (CH), 110.5 (2CH), 51.3 (C), 22.8 (CH$_3$).

2-(9H-carbazol-1-yl)-2-methylpropanal S7. The general cross-coupling procedure 2 was followed using 492.2 mg of 1-bromo-9H-carbazole (2.00 mmol), 310.2 mg of zinc fluoride (3 mmol), 115.0 mg of bis(dibenzylideneacetone)palladium(0) (0.2 mmol), 0.60 mL of tri-tert-butylphosphine (0.60 mmol), and 0.6 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.0 mmol) in 20.0 mL of DMF. Purification by flash column chromatography (100:0→95:5 hexanes:benzene) afforded S7 (275.3 mg, 58% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.48 (s, 1H), 8.43 (s, 1H), 8.17 – 8.00 (m, 2H), 7.53 – 7.39 (m, 3H), 7.32 (t, $J$ = 7.7 Hz, 1H), 7.28 – 7.21 (m, 1H), 1.68 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 203.3 (C=O), 139.5 (C), 137.7 (C), 126.1 (CH), 124.4 (C), 123.3 (CH), 122.7 (C), 121.2 (C), 120.3 (CH), 120.2 (CH), 119.9 (CH), 119.6 (CH), 111.0 (CH). 49.8 (C), 21.1 (CH$_3$).
2-(dibenzo[b,d]furan-4-yl)-2-methylpropanal 5c. The general cross-coupling procedure 2 was followed using 494.2 mg of 4-bromodibenzo[b,d]furan (2.00 mmol), 310.2 mg of zinc fluoride (3 mmol), 115.0 mg of bis(dibenzylideneacetone)palladium(0) (0.2 mmol), 0.60 mL of tri-tert-butylphosphine (0.60 mmol), and 0.6 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.0 mmol) in 20.0 mL of DMF. Purification by flash column chromatography (100:0 → 95:5 hexanes:benzene) afforded 5c (367.0 mg, 77% yield) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 9.90 (s, 1H), 7.97 (dd, $J = 7.8, 1.3$ Hz, 1H), 7.93 (dd, $J = 6.7, 2.2$ Hz, 1H), 7.61 (d, $J = 8.3$ Hz, 1H), 7.48 (ddd, $J = 8.4, 7.3, 1.4$ Hz, 1H), 7.44 – 7.32 (m, 3H), 1.70 (s, 6H).

13C NMR (125 MHz, CDCl$_3$) δ 202.6 (C=O), 155.9 (C), 154.1 (C), 128.4 (C), 127.4 (CH), 126.7 (C), 124.8 (C), 124.7 (CH), 124.0 (C), 123.3 (CH), 123.0 (CH), 120.7 (CH), 120.1 (CH), 111.9 (CH), 49.3 (C), 22.0 (CH$_3$).

2-(dibenzo[b,d]thiophen-4-yl)-2-methylpropanal 5d. The general cross-coupling procedure 2 was followed using 526.3 mg of 4-bromodibenzo[b,d]thiophene (2.00 mmol), 310.2 mg of zinc fluoride (3 mmol), 115.0 mg of bis(dibenzylideneacetone)palladium(0) (0.2 mmol), 0.60 mL of tri-tert-butylphosphine (0.60 mmol), and 0.6 mL of trimethyl(2-methylprop-1-enyloxy)silane (3.0 mmol) in 20.0 mL of DMF. Purification by flash column chromatography (100:0 → 95:5 hexanes:benzene) afforded 5d (371.4 mg, 73% yield) as a light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 9.66 (s, 1H), 8.42 – 7.97 (m, 2H), 7.83 (dd, $J = 6.0, 3.2$ Hz, 1H), 7.52 (d, $J = 7.7$ Hz, 1H), 7.50 – 7.42 (m, 3H), 1.66 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 202.48 (C=O), 138.9 (C), 138.1 (C), 136.9 (C), 136.4 (C), 135.1 (C), 127.0 (CH), 125.0 (CH), 124.8 (CH), 124.5 (CH), 122.4 (CH), 121.6 (CH), 121.1 (CH), 51.7 (C), 21.3 (CH$_3$).

D. General procedure 3: Benzyl Protection of Indolyl Aldehydes

$\text{NaH, BnBr}$

DMF, 0°C–rt, 5h
2-(1-Benzyl-1H-indol-4-yl)-2-methylpropanal 3f. To a solution of aldehyde S1 (1.5 g, 8.0 mmol) in DMF (16.0 mL, 0.5M), 60 wt% NaH (480.0 mg, 1.5 eq.) was added in an ice bath through four portions. The slurry was allowed to stir at room temperature for 30 minutes before it was cooled to 0 °C. Benzyl bromide (2.0 g, 1.5 eq.) was diluted with DMF (1.0 mL) before it was added to the deprotonated indole solution through syringe. The reaction mixture was then allowed to stir at room temperature for overnight. After the complete consumption of the starting material indicated by TLC, the reaction was quenched by addition of saturated NaHCO₃ solution (10 mL) at 0 °C. The product was extracted with EtOAc three times and combined organic layers were washed with brine and dried over anhydrous sodium sulfate before it was concentrated under reduced pressure. The crude benzylated aldehyde was flushed through silica gel column with mixture of hexanes and ethyl acetate (hexanes:ethyl acetate, 100:0®90:10) to obtain pure aldehyde S7 (2.0 g, 89% yield) as light yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 9.64 (s, 1H), 7.38 – 7.21 (m, 5H), 7.17 – 7.13 (m, 4H), 6.49 (dd, J = 3.3, 0.7 Hz, 1H), 5.33 (s, 2H), 1.62 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 203.8 (C=O), 137.3 (C), 136.8 (C), 133.8 (C), 128.9 (CH), 128.4 (CH), 127.8 (CH), 127.1 (C), 127.0 (CH), 122.0 (CH), 117.2 (CH), 109.7 (CH), 101.3 (CH), 51.1 (C), 50.3 (CH₂), 22.1 (CH₃); ATR-FTIR (neat): 2970, 2931, 1722 cm⁻¹; HRMS (ESI) m/z calculated for C₁₉H₂₀NO [M+H]⁺: 278.1539, found 278.1539. The spectral data matched those reported in the literature.⁵

E. Synthesis and Characterization of Benzyl-Protected Indolyl Aldehydes

2-(1-benzyl-7-methoxy-1H-indol-4-yl)-2-methylpropanal 3g. The general procedure 3 was followed using 434.6 mg of S2 (2.0 mmol), 120.0 mg of 60 wt% NaH (3.0 mmol) and 514.0 mg of benzyl bromide (3.0 mmol in 1.0 mL DMF) in 10.0 mL DMF. Purification by flash column chromatography (100:0→90:10 hexanes: EtOAc) afforded benzylated indole 3g (436.5 mg, 71% yield) as colorless oil. ¹H NMR (400 MHz, CDCl₃): δ  9.57 (s, 1H), 7.33 – 7.24 (m, 3H), 7.16 – 7.10 (m, 2H), 7.06 – 6.97 (m, 2H), 6.66 (d, J = 8.1 Hz, 1H), 6.41 (d, J = 3.2 Hz, 1H), 5.64 (s, 2H), 3.86 (s, 3H), 1.58 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ  204.0 (C=O), 147.4 (C), 139.4 (C), 129.2 (CH), 129.1 (C), 128.5 (CH), 127.2 (CH), 126.8 (CH), 126.1 (C), 126.0 (C), 117.5 (CH), 102.5 (CH), 101.6 (CH), 55.3 (CH₃), 52.6 (CH₂), 50.4 (C), 22.0 (CH₃).
2-(1-benzyl-7-fluoro-1H-indol-4-yl)-2-methylpropanal 3h. The general procedure 3 was followed using 410.5 mg of S3 (2.0 mmol), 120.0 mg of 60 wt% NaH (3.0 mmol) and 514.0 mg of benzyl bromide (3.0 mmol in 1.0 mL DMF) in 10.0 mL of DMF. Purification by flash column chromatography (100:0→90:10 hexanes: EtOAc) afforded benzylated indole 3h (455.0 mg, 77% yield) as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 9.54 (s, 1H), 7.36 – 7.24 (m, 3H), 7.19 – 7.12 (m, 2H), 7.09 (d, $J = 3.3$ Hz, 1H), 6.98 (dd, $J = 8.2$, 4.2 Hz, 1H), 6.88 (dd, $J = 12.3$, 8.2 Hz, 1H), 6.42 (dd, $J = 3.3$, 2.4 Hz, 1H), 5.48 (s, 2H), 1.55 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 203.4 (C=O), 150.0 (d, $J = 244.5$ Hz, C), 137.9 (C), 130.8 (d, $J = 5.5$ Hz, C), 129.6 (CH), 129.2 (d, $J = 3.7$ Hz, C), 128.7 (CH), 128.1 (d, $J = 62.3$ Hz, C), 127.7 (CH), 126.9 (d, $J = 0.9$ Hz, CH), 117.4 (d, $J = 6.9$ Hz, CH), 107.3 (d, $J = 18.2$ Hz, CH), 102.3 (d, $J = 1.5$ Hz, CH), 52.2 (d, $J = 6.1$ Hz, CH$_2$), 50.5 (C), 22.0 (CH$_3$); $^{19}$F NMR (376 MHz, CDCl$_3$): δ –136.0.

2-(1-benzyl-2-methyl-1H-indol-4-yl)-2-methylpropanal 3i. General procedure 3 was followed using 403 mg of S4 (2.0 mmol), 120 mg of 60 wt% NaH (3.0 mmol) and 1.0 mL of a solution of 514 mg of benzyl bromide (3.0 mmol) in DMF and 10.0 mL DMF. Purification by flash column chromatography (100:0→90:10 hexanes: EtOAc) afforded benzylated indole 3i (466.2 mg, 80% yield) as colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 9.65 (s, 1H), 7.41 (s, 1H), 7.35 – 7.26 (m, 2H), 7.25 – 7.22 (m, 1H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.14 (dd, $J = 7.2$, 1.2 Hz, 1H), 7.02 (dd, $J = 8.1$, 1.4 Hz, 2H), 6.29 (s, 1H), 5.33 (s, 2H), 2.39 (d, $J = 1.0$ Hz, 3H), 1.64 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 203.9 (C=O), 137.6 (C), 136.9 (C), 132.3 (C), 128.8 (CH), 128.4 (C), 127.4 (CH), 126.5 (C), 126.0 (CH), 120.9 (CH), 117.0 (CH), 109.1 (CH), 100.1 (CH), 51.0 (C), 46.6 (CH$_2$), 21.9 (CH$_3$), 12.8 (CH$_3$).
2-(1-benzyl-7-methyl-1H-indol-4-yl)-2-methylpropanal 3j. The general procedure 3 was followed using 402.6 mg of S5 (2.0 mmol), 120.0 mg of 60 wt% NaH (3.0 mmol) and 514.0 mg of benzyl bromide (3.0 mmol in 1.0 mL DMF) in 10.0 mL DMF. Purification by flash column chromatography (100:0 → 90:10 hexanes: EtOAc) afforded benzylated indole 3j (437.1 mg, 75% yield) as colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 9.64 (s, 1H), 7.37 – 7.23 (m, 3H), 7.13 – 7.01 (m, 2H), 7.02 – 6.90 (m, 3H), 6.49 (d, $J$ = 3.3 Hz, 1H), 5.61 (s, 2H), 2.58 (s, 3H), 1.62 (s, 7H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 204.1 (C=O), 139.4 (C), 135.3 (C), 131.6 (C), 130.3 (CH), 128.9 (CH), 128.1 (C), 127.4 (CH), 125.5 (CH), 124.8 (CH), 121.0 (C), 117.4 (CH), 101.4 (CH), 52.3(C), 50.7 (CH$_2$), 22.0 (CH$_3$), 19.5 (CH$_3$).

2-(9H-carbazol-4-yl)-2-methylpropanal 5a. The general procedure 3 was followed using 474.6 mg of S6 (2.0 mmol), 120.0 mg of 60 wt% NaH (3.0 mmol) and 514.0 mg of benzyl bromide (3.0 mmol in 1.0 mL DMF) in 10.0 mL DMF. Purification by flash column chromatography (100:0 → 90:10 hexanes: EtOAc) afforded benzylated indole 5a (576.3 mg, 88% yield) as colorless oil; $^1$H NMR (500 MHz, CDCl$_3$): δ 9.94 (s, 1H), 8.07 (d, $J$ = 8.2 Hz, 1H), 7.61 – 7.47 (m, 4H), 7.42 – 7.16 (m, 7H), 5.60 (s, 2H), 1.85 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 205.1 (C=O), 141.7 (C), 140.8 (C), 138.1 (C), 137.0 (C), 128.9 (CH), 128.5 (C), 127.9 (C), 127.6 (CH), 126.4 (CH), 126.0 (CH), 125.7 (CH), 124.7 (CH), 121.0 (C), 119.4 (CH), 117.8 (CH), 108.9 (2CH), 51.4 (C), 46.6 (CH$_2$), 23.0 (CH$_3$).

2-(9-benzyl-9H-carbazol-1-yl)-2-methylpropanal 5b. The general procedure 3 was followed using 474.6 mg of S7 (2.0 mmol), 120.0 mg of 60 wt% NaH (3.0 mmol) and 514.0 mg of benzyl
bromide (3.0 mmol in 1.0 mL DMF) in 10.0 mL DMF. Purification by flash column chromatography (100:0→90:10 hexanes:EtOAc) afforded benzylated indole 5b (589.4 mg, 90% yield) as colorless oil; 1H NMR (400 MHz, CDCl3): δ 9.65 (s, 1H), 8.42 – 7.97 (m, 2H), 7.55 (dd, J = 7.7, 1.2 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.26 (td, J = 7.4, 1.0 Hz, 1H), 7.20 – 7.12 (m, 4H), 5.60 (s, 2H), 1.62 (s, 6H); 13C NMR (100 MHz, CDCl3): δ 204.5 (C=O), 141.7 (C), 139.4 (C), 137.2 (C), 128.6 (CH), 127.0 (CH), 126.2 (CH), 126.0 (C), 125.9 (C), 125.8 (CH), 125.6 (CH), 123.8 (C), 120.2 (CH), 120.0 (CH), 119.9 (CH), 119.7 (CH), 111.1 (CH), 50.8 (C), 49.7 (CH2), 24.5 (CH3).

IV. Decarbonylation Reactions

A. General procedure 4: KOr-Bu Mediated Decarbonylation

In a flame-dried 25 mL round bottom flask charged with a PTFE-coated magnetic stir bar was purged with nitrogen for 10 minutes. To the flask, 0.2 mL KOr-Bu solution (1.6 M in THF stock solution, 0.32 mmol, 1.6 equiv) was diluted with 1.0 mL of anhydrous THF. A pre-nitrogen-purged aldehyde 1d (0.2 mmol, 1 equiv) solution in 1.0 mL of THF was then added to the diluted KOr-Bu solution dropwise at room temperature. The mixture was then allowed to stir under nitrogen atmosphere (connected to bubbler) for five hours. The reaction was then diluted with EtOAc (2 mL) and quenched by addition of aqueous NH4Cl solution (5 mL), stirring until the solution decolorified. The aqueous layer was extracted with EtOAc (5 mL) three times and the combined organic layers were washed with brine and dried over sodium sulfate. The dried solution was concentrated under reduced pressure to afford crude decarbonylated hydrocarbon. The crude oil was then purified by silica gel chromatography.

B. Synthesis and Characterization of Decarbonylated Products

1-isopropyl-3,5-dimethoxybenzene 2b. The general protodeformylation procedure was followed using 41.7 mg of 1b (0.2 mmol) and 0.2 mL of KOr-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100:0→99:1 hexanes:ethyl acetate) to afford 2b as colorless oil (10.8 mg, 30%); 1H NMR (400 MHz, CDCl3) δ 6.46 (d, J = 2.4 Hz, 2H), 6.15 (s, 1H),...
3.83 (s, 6H), 2.90 (sept, $J = 6.9$ Hz, 1H), 1.30 (d, $J = 6.9$ Hz, 6H). The spectral data matched those reported in the literature.\(^6\)

**1-isopropyl-4-methoxybenzene 2c.** The general protodeformylation procedure was followed using 35.6 mg of 1c (0.2 mmol), 0.2 mL of KOr-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100:0→99:1 hexanes:ethyl acetate) to afford 2c as colorless oil (5.5 mg, 18%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.15 (d, $J = 8.2$ Hz, 2H), 6.85 (d, $J = 8.7$ Hz, 2H), 3.79 (s, 2H), 2.87 (sept, $J = 6.9$ Hz, 1H), 1.23 (d, $J = 6.9$ Hz, 6H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 157.6 (C), 141.0 (C), 127.2 (CH), 113.7 (CH), 55.2 (CH\(_3\)), 33.3 (C), 24.2 (CH\(_3\)). The spectral data matched those reported in the literature.\(^7\)

**4-isopropyl-1,1′-biphenyl 2d.** The general protodeformylation procedure was followed using 44.9 mg of 1d (0.2 mmol) and 0.2 mL of KOr-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100:0→99:1 hexanes:ethyl acetate) to afford 2d as colorless oil (26.3 mg, 67%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.15 (d, $J = 8.2$ Hz, 2H), 6.85 (d, $J = 8.7$ Hz, 2H), 3.79 (s, 2H), 2.87 (sept, $J = 6.9$ Hz, 1H), 1.23 (d, $J = 6.9$ Hz, 6H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 157.6 (C), 141.0 (C), 127.2 (CH), 113.7 (CH), 55.2 (CH\(_3\)), 33.3 (C), 24.2 (CH\(_3\)). The spectral data matched those reported in the literature.\(^8\)

4-isopropyl-1-(trifluoromethyl)benzene S9. The general protodeformylation procedure was followed using 43 mg of S8 (0.2 mmol) and 0.3 mL of a 1.0 M KOr-Bu solution (0.32 mmol) plus 1.9 mL of THF. The reaction was decolorized and assessed by crude \(^1\)H NMR, which showed approximately 20% yield of cumene S9 by comparison with the data reported by Percy and co-workers.\(^9\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.55 (d, $J = 8$ Hz, 2H), 7.34 (d, $J = 8$ Hz, 2H), 2.97 (sept, $J = 8$ Hz, 1H), 1.27 (d, $J = 8$ Hz, 6H).
cyclopropylbenzene 2e. The general protodeformylation procedure was followed using 23.6 mg of 1e (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100% hexanes) afforded hydrocarbon 2e in 9% NMR yield.

cyclobutylbenzene 2f. The general protodeformylation procedure was followed using 34.9 mg of 1f (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100% hexanes) afforded hydrocarbon 2f as colorless oil (12.9 mg, 44%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.37 – 7.12 (m, 5H), 3.55 (p, $J = 8.8$ Hz, 1H), 2.47 – 2.26 (m, 2H), 2.23 – 2.09 (m, 2H), 2.08 – 1.95 (m, 1H), 1.92 – 1.78 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.5 (C), 128.2 (CH), 127.1 (CH), 125.6 (CH), 45.9 (C), 34.6 (CH$_2$), 25.5 (CH$_2$). The spectral data matched those reported in the literature.$^{10}$

cyclopentylbenzene 2g. The general protodeformylation procedure was followed using 34.9 mg of 1g (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100% hexanes) afforded hydrocarbon 2g as colorless oil (12.9 mg, 44%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39 – 7.09 (m, 5H), 2.99 (tt, $J = 9.5$, 7.5 Hz, 1H), 2.21 – 1.86 (m, 2H), 1.81 (qdt, $J = 5.1$, 3.2, 1.5 Hz, 2H), 1.74 – 1.65 (m, 2H), 1.60 (dddd, $J = 12.1$, 6.3, 5.0, 3.9 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.5 (C), 128.2 (CH), 127.1 (CH), 125.6 (CH), 45.9 (C), 34.6 (CH$_2$), 25.5 (CH$_2$).

cyclohexylbenzene 2h. The general protodeformylation procedure was followed using 37.7 mg of 1h (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash
column chromatography (100% hexanes) afforded hydrocarbon 2h as colorless oil (24.4 mg, 76%); 
\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.39 – 7.05 (m, 5H), 2.50 (tt, \(J = 11.4, 3.5\) Hz, 1H), 1.95 – 1.81 (m, 4H), 1.49 – 1.21 (m, 6H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): δ 148.1 (C), 128.2 (CH), 126.8 (CH), 125.7 (CH), 44.5 (C), 34.5 (CH\(_2\)), 26.9 (CH\(_2\)), 26.2 (CH\(_2\)). The spectral data matched those reported in the literature.\(^{11}\)

![Structure 2i](image)

**5-isopropyl-1,2,3,4-tetrahydronaphthalene 2i.** The general protodeformylation procedure was followed using 40.5 mg of 1i (0.2 mmol) and 0.2 mL of KO\(\text{t}-\)Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100% hexanes) afforded hydrocarbon 2j as colorless oil (21.3 mg, 61%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.12 (d, \(J = 5.0\) Hz, 2H), 6.95 (t, \(J = 4.5\) Hz, 1H), 3.17 (sept, \(J = 6.8\) Hz, 1H), 2.80 (dt, \(J = 13.4, 6.4\) Hz, 4H), 2.05 – 1.63 (m, 4H), 1.24 (d, \(J = 6.8\) Hz, 6H) \(^13\)C NMR (100 MHz, CDCl\(_3\)): δ 146.9 (C), 137.2 (C), 134.0 (C), 126.9 (CH), 125.5 (CH), 122.1 (CH), 30.4 (CH\(_2\)), 28.2 (C), 25.8 (CH\(_2\)), 23.6 (CH\(_2\)), 23.4 (CH\(_3\)), 22.8 (CH\(_2\)).

![Structure 2j](image)

**triphenylmethane 2j.** The general protodeformylation procedure 3 was followed using 54.5 mg of 1j (0.2 mmol) and 0.2 mL of KO\(\text{t}-\)Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100% hexanes) afforded hydrocarbon 2i as white solid (38.6 mg, 79%).

![Structure 4a](image)

**1-cyclopentynaphthalene 4a.** The general protodeformylation procedure was followed using 44.9 mg of 3a (0.2 mmol) and 0.2 mL of KO\(\text{t}-\)Bu solution (0.32 mmol), and 2.0 mL of additional THF. Purification by flash column chromatography (100% hexanes) afforded hydrocarbon 4a as colorless oil (34.6 mg, 88%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.24–8.13 (m, 1H), 7.86 (dd, \(J = 7.7, 1.7\) Hz, 1H), 7.71 (dd, \(J = 5.6, 3.8\) Hz, 1H), 7.62–7.38 (m, 4H), 3.80 (p, \(J = 7.2, 6.6\) Hz, 1H), 2.37–2.10 (m, 2H), 2.10–1.63 (m, 6H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) δ 142.1 (C), 133.9 (C), 132.2 (C), 128.7 (CH), 126.2 (CH), 125.6 (CH), 125.5 (CH), 125.2 (CH), 123.9 (CH), 122.0 (CH), 41.2 (C), 33.6 (CH\(_2\)), 25.3 (CH\(_2\)).
1-isopropynaphthalene 4b. The general protodeformylation procedure was followed using 198 mg of 3b (1.0 mmol) and 1.0 mL of KOt-Bu solution (1.6 mmol), and 10 mL of additional THF. Purification by flash column chromatography (100% hexanes) afforded hydrocarbon 4b as colorless oil (158 mg, 93%); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.16 (dd, $J = 8.5$, 1.2 Hz, 1H), 7.90–7.84 (m, 1H), 7.73 (dt, $J = 7.8$, 1.1 Hz, 1H), 7.62–7.38 (m, 4H), 3.79 (sept, $J = 6.9$ Hz, 1H), 1.44 (d, $J = 6.9$ Hz, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 144.6 (C), 133.9 (C), 131.3 (C), 128.9 (CH), 126.3 (CH), 125.7 (CH), 125.6 (CH), 125.2 (CH), 123.3 (CH), 121.7 (CH), 28.5 (C), 23.6 (CH$_3$). The spectral data matched those reported in the literature.\textsuperscript{12}

2-isopropynaphthalene 4c. The general protodeformylation procedure was followed using 39.7 mg of 3c (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100% hexanes) afforded hydrocarbon 4c as colorless oil (25.6 mg, 75%); $^1$H NMR (400 MHz, CDCl$_3$); δ 7.87 – 7.72 (m, 3H), 7.67 – 7.60 (m, 1H), 7.52 – 7.32 (m, 3H), 3.08 (sept, $J = 6.9$ Hz, 1H), 1.35 (d, $J = 6.9$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.3 (C), 133.6 (C), 132.1 (C), 127.8 (CH), 127.5 (CH), 127.5 (CH), 125.8 (CH), 125.7 (CH), 125.0 (CH), 124.1 (CH), 34.2 (C), 23.9 (CH$_3$). The spectral data matched those reported in the literature.\textsuperscript{13}

4-isopropylbenzofuran 4d. The general protodeformylation procedure was followed using 37.6 mg of 3d (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100% hexanes) afforded hydrocarbon 4d as colorless oil (20.51 mg, 64%); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.61 (d, $J = 2.2$ Hz, 1H), 7.35 (dt, $J = 8.2$, 1.0 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.10 (dt, $J = 7.4$, 0.8 Hz, 1H), 6.85 (dd, $J = 2.2$, 1.0 Hz, 1H), 3.27 (sept, $J = 6.9$ Hz, 1H), 1.36 (d, $J = 7.0$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 155.0 (C), 144.2 (C), 142.0 (C), 124.3 (CH), 118.7 (CH), 108.9 (CH), 105.1 (2CH), 31.7 (C), 23.1 (CH$_3$).
3-isopropylbenzofuran 4e. The general protodeformylation procedure was followed using 37.6 mg of 3e (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100% hexanes) afforded hydrocarbon 4e as colorless oil (5.8 mg, 18%); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.63 – 7.59 (m, 1H), 7.47 (d, $J = 8.2$ Hz, 1H), 7.41 – 7.35 (m, 1H), 7.33 – 7.18 (m, 2H), 3.11 (pd, $J = 6.9$, 1.1 Hz, 1H), 1.38 (d, $J = 6.9$ Hz, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 155.6 (C), 139.7 (CH), 127.6 (C), 127.3 (C), 123.9 (CH), 122.0 (CH), 120.1 (CH), 111.5 (CH), 24.6 (C), 22.4 (CH$_3$).

3-(propan-2-ylidene)-2,3-dihydrobenzofuran 7. The general protodeformylation procedure was followed using 37.6 mg of 3e (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100:0→80:20 hexanes: benzene) afforded hydrocarbon 7 as colorless oil (9.0 mg, 28%); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.48 (dd, $J = 7.7$, 1.2 Hz, 1H), 7.11 (td, $J = 7.8$, 1.3 Hz, 1H), 6.98 – 6.66 (m, 2H), 5.33 – 4.65 (m, 2H), 2.06 (s, 3H), 1.77 (d, $J = 2.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 163.9 (C), 128.9 (C), 128.1 (CH), 126.6 (C), 123.6 (CH), 123.4 (C), 120.33 (CH), 109.9 (CH), 74.6 (CH$_2$), 23.3 (CH$_3$), 20.9 (CH$_3$).

1-benzyl-4-isopropyl-1H-indole 4f. The general protodeformylation procedure was followed using 55.5 mg of 3f (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100:0→90:10 hexanes: EtOAc) afforded hydrocarbon 4f as colorless oil (44.4 mg, 89%); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.41 – 7.22 (m, 4H), 7.21 – 7.09 (m, 4H), 7.02 (dd, $J = 4.8$, 3.4 Hz, 2H), 6.65 (d, $J = 3.2$ Hz, 2H), 5.33 (s, 2H), 3.42 (sept, $J = 6.9$ Hz, 1H), 1.42 (d, $J = 6.9$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 141.3 (C), 137.6 (C), 137.2 (C), 137.1 (C), 128.7 (CH), 127.6 (CH), 127.5 (CH), 126.9 (CH), 122.0 (CH), 115.2 (CH), 107.4 (CH), 100.1 (CH), 50.2 (CH$_2$), 31.2 (C), 23.2 (CH$_3$).
1-benzyl-4-isopropyl-7-methoxy-1H-indole 4g. The general protodeformylation procedure was followed using 61.5 mg of 3g (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100:0 → 85:15 hexanes: EtOAc) afforded hydrocarbon 4g as light yellow oil (45.3 mg, 81%); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.47 – 7.18 (m, 3H), 7.19 – 7.07 (m, 2H), 7.03 (d, $J = 3.2$ Hz, 1H), 6.86 (d, $J = 7.9$ Hz, 1H), 6.68 – 6.47 (m, 2H), 5.64 (s, 2H), 3.82 (s, 3H), 3.30 (sept, $J = 6.9$ Hz, 1H), 1.37 (d, $J = 6.9$ Hz, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 145.9 (C), 139.7 (C), 133.6 (C), 129.4 (C), 128.4 (CH), 127.8 (CH), 127.6 (C), 127.0 (CH), 126.8 (CH), 115.0 (CH), 102.7 (CH), 100.5 (CH), 55.4 (CH$_3$), 52.4 (CH$_2$), 30.5 (C), 23.5 (CH$_3$).

1-benzyl-7-fluoro-4-isopropyl-1H-indole 4h. The general protodeformylation procedure was followed using 59.017 mg of 3h (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100:0 → 90:10 hexanes: EtOAc) afforded hydrocarbon 4h as light yellow oil (38.0 mg, 71%); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.37 – 7.26 (m, 2H), 7.20 – 7.04 (m, 4H), 6.87 – 6.75 (m, 2H), 6.60 (dd, $J = 3.2$, 2.4 Hz, 1H), 5.48 (s, 2H), 3.31 (sept, $J = 7.0$ Hz, 1H), 1.35 (d, $J = 6.9$ Hz, 6H) $^{13}$C NMR (100 MHz, CDCl$_3$): δ 148.8 (d, $J = 240.5$ Hz, C), 138.3 (C), 136.8 (C), 131.0 (C), 129.5 (C), 128.8 (CH), 128.7 (CH), 127.5 (CH), 126.9 (CH), 115.09 (d, $J = 6.7$ Hz, CH), 107.26 (d, $J = 16.3$ Hz, CH), 101.1 (CH), 52.2 (CH$_2$), 30.6 (C), 23.2 (CH$_3$); $^{19}$F NMR (376 MHz, CDCl$_3$): -139.0.

1-benzyl-4-isopropyl-2-methyl-1H-indole 4i. The general protodeformylation procedure was followed using 58.3 mg of 3i (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL of THF. Purification by flash column chromatography (100:0 → 90:10 hexanes: EtOAc) afforded
hydrocarbon 4i as light yellow oil (38.5 mg, 73%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.36 – 7.18 (m, 3H), 7.12–6.94 (m, 5H), 6.46–6.33 (m, 1H), 5.30 (s, 2H), 3.35 (sept, $J = 6.9$ Hz, 1H), 2.39 (s, 3H), 1.40 (d, $J = 6.9$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 140.0 (C), 138.0 (C), 137.2 (C), 135.9 (C), 128.7 (CH), 127.2 (CH), 126.6 (C), 126.0 (CH), 121.0 (CH), 115.3 (CH), 107.0 (CH), 98.9 (CH), 46.6 (CH$_2$), 31.3 (C), 23.2 (CH$_3$), 12.8 (CH$_3$).

4j

1-benzyl-4-isopropyl-7-methyl-1H-indole 4j. The general protodeformylation procedure was followed using 58.3 mg of 3j (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL of THF. Purification by flash column chromatography (100:0 → 90:10 hexanes: EtOAc) afforded hydrocarbon 4j as light yellow oil (36.9 mg, 70%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.41 – 7.20 (m, 3H), 7.09 (d, $J = 3.2$ Hz, 1H), 7.01 – 6.96 (m, 2H), 6.91 (q, $J = 7.4$ Hz, 2H), 6.68 (d, $J = 3.3$ Hz, 1H), 5.61 (s, 2H), 3.42 (sept, $J = 6.9$ Hz, 1H), 2.54 (s, 3H), 1.43 (d, $J = 6.9$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.7 (C), 139.2 (C), 134.9 (C), 129.5, 128.8, 128.4, 127.3, 125.6 (CH), 124.8 (CH), 118.6, 115.3 (CH), 100.3 (CH), 52.2 (CH$_2$), 30.7 (C), 23.3 (CH$_3$), 19.4 (CH$_3$).

4k

4-isopropylbenzo[b]thiophene 4k. The general protodeformylation procedure was followed using 40.9 mg of 3k (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100% hexanes) afforded hydrocarbon 4k as colorless oil (25.0 mg, 71%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.74 (d, $J = 7.9$ Hz, 1H), 7.50 (dd, $J = 5.6$, 0.8 Hz, 1H), 7.44 (d, $J = 5.6$ Hz, 1H), 7.32 (t, $J = 7.7$ Hz, 1H), 7.28 – 7.17 (m, 1H), 3.49 (sept, $J = 6.9$ Hz, 1H), 1.38 (d, $J = 6.9$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.7 (C), 139.9 (C), 138.0 (C), 125.6 (CH), 124.5 (CH), 121.7 (CH), 120.0 (CH), 119.9 (CH), 31.3 (C), 23.3 (CH$_3$).
3-isopropylbenzo[b]thiophene 4o. The general protodeformylation procedure was followed using 40.9 mg of 3o (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100% hexanes) afforded impure 4o as colorless oil (16.9 mg, 27%, determined by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.89 – 7.83 (m, 1H), 7.80 (dt, $J$ = 8.2, 0.9 Hz, 1H), 7.45 – 7.27 (m, 3H), 7.19 – 7.06 (m, 3H), 3.31 (pd, $J$ = 6.9, 1.0 Hz, 1H), 1.38 (d, $J$ = 6.8 Hz, 7H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 130.3 (C), 129.1 (C), 127.7 (C), 124.1 (CH), 123.7 (CH), 122.9 (CH), 121.9 (CH), 118.9 (CH), 27.8 (C), 22.8 (CH$_3$).

5-isopropylbenzo[b]thiophene 4m. The general protodeformylation procedure was followed using 40.9 mg of 3m (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100% hexanes) afforded hydrocarbon 4m as colorless oil (24.7 mg, 70%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80 (d, $J$ = 8.3 Hz, 1H), 7.67 (d, $J$ = 1.7 Hz, 1H), 7.41 (d, $J$ = 5.4 Hz, 1H), 7.29 (dd, $J$ = 5.4, 0.8 Hz, 1H), 7.24 (d, $J$ = 1.7 Hz, 1H), 3.04 (sept, $J$ = 6.9 Hz, 1H), 1.32 (d, $J$ = 6.9 Hz, 7H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.1 (C), 139.9 (C), 137.2 (C), 126.4 (CH), 123.7 (CH), 123.7 (CH), 122.2 (CH), 120.8 (CH), 34.1 (C), 24.3 (CH$_3$).

2-isopropylbenzo[b]thiophene 4n. The general protodeformylation procedure was followed using 40.9 mg of 3n (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100% hexanes) afforded hydrocarbon 4n as colorless oil (28.2 mg, 80%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.86 – 7.72 (m, 1H), 7.68 (dt, $J$ = 7.8, 0.8 Hz, 1H), 7.44 – 7.16 (m, 2H), 7.03 (d, $J$ = 1.0 Hz, 1H), 3.26 (septd, $J$ = 6.8, 1.1 Hz, 1H), 1.41 (d, $J$ = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.1 (C), 140.1 (C), 138.8 (C), 124.0 (CH), 123.4 (CH), 122.8 (CH), 122.2 (CH), 118.2 (CH), 30.6 (C), 24.4 (CH$_3$).
7-isopropylbenzo[b]thiophene 4l. The general protodeformylation procedure was followed using 40.9 mg of 3l (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100% hexanes) afforded hydrocarbon 4l as colorless oil (22.2 mg, 63%); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.68 (dd, $J$ = 7.9, 1.1 Hz, 1H), 7.43 (d, $J$ = 5.5 Hz, 1H), 7.40 - 7.32 (m, 2H), 7.24 (dd, $J$ = 7.4, 1.0 Hz, 1H), 3.27 (sept, $J$ = 6.9 Hz, 1H), 1.42 (d, $J$ = 6.9 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 142.8 (C), 139.7 (C), 138.8 (C), 125.5 (CH), 124.8 (CH), 124.6 (CH), 121.3 (CH), 119.9 (CH), 33.4 (C), 22.6 (CH$_3$).

9-benzyl-4-isopropyl-9H-carbazole 6a. The general protodeformylation procedure was followed using 65.5 mg of 5a (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100:0 → 90:10 hexanes: EtOAc) afforded hydrocarbon 6a as colorless oil (45.2 mg, 69%); $^1$H NMR (400 MHz, CDCl$_3$): δ 8.31 (d, $J$ = 8.0 Hz, 1H), 7.57 - 7.38 (m, 4H), 7.35 - 7.12 (m, 7H), 5.55 (s, 2H), 4.07 (sept, $J$ = 7.0 Hz, 1H), 1.57 (d, $J$ = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 144.7 (C), 141.0 (C), 140.7 (C), 137.3 (C), 128.8 (CH), 127.4 (CH), 126.4 (CH), 126.0 (CH), 125.1 (CH), 123.2 (CH), 122.8 (C), 120.4 (C), 119.2 (CH), 115.3 (CH), 108.8 (CH), 106.5 (CH), 46.5 (CH$_2$), 30.4 (C), 22.7 (CH$_3$).

9-benzyl-1-isopropyl-9H-carbazole 6b. The general protodeformylation procedure was followed using 65.5 mg of 5b (0.2 mmol) and 0.2 mL of KOt-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100:0 → 90:10 hexanes: EtOAc) afforded hydrocarbon 6b as colorless oil (41.3 mg, 63%); $^1$H NMR (400 MHz, CDCl$_3$): δ 8.13 (d, $J$ = 7.7 Hz, 1H), 8.02 (dd, $J$ = 7.6, 1.3 Hz, 1H), 7.51 - 7.15 (m, 9H), 7.11 - 7.00 (m, 1H), 5.74 (s, 2H), 3.57 (sept, $J$ = 6.8 Hz, 1H), 1.27 (d, $J$ = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 141.9 (C), 138.5 (C), 132.3 (C), 128.8 (CH), 128.7 (C), 127.2 (CH), 125.9 (CH), 125.6 (CH), 124.3 (C), 123.5
6c. The general protodeformylation procedure was followed using 47.7 mg of 5c (0.2 mmol) and 0.2 mL of KOr-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100:0→90:10 hexanes: EtOAc) afforded hydrocarbon 6c as colorless oil (34.5 mg, 82%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.96 (ddd, \(J = 7.7, 1.4, 0.7\) Hz, 1H), 7.80 (dd, \(J = 7.3, 1.7\) Hz, 1H), 7.66 – 7.55 (m, 1H), 7.46 (ddd, \(J = 8.3, 7.3, 1.4\) Hz, 1H), 7.39 – 7.24 (m, 3H), 3.59 (sept, \(J = 6.9\) Hz, 1H), 1.45 (d, \(J = 6.9\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 156.0 (C), 154.1 (C), 132.8 (C), 126.8 (CH), 124.6 (C), 124.0 (CH), 123.9 (C), 122.8 (CH), 122.5 (CH), 120.6 (CH), 118.0 (CH), 111.6 (CH), 28.7 (C), 22.6 (CH\(_3\)).

6d. The general protodeformylation procedure was followed using 50.9 mg of 5d (0.2 mmol) and 0.2 mL of KOr-Bu solution (0.32 mmol) in 2.0 mL THF. Purification by flash column chromatography (100:0→90:10 hexanes: EtOAc) afforded hydrocarbon 6d as colorless oil (38 mg, 84%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.22 – 8.09 (m, 1H), 8.01 (dd, \(J = 7.8, 1.2\) Hz, 1H), 7.92 – 7.82 (m, 1H), 7.52 – 7.39 (m, 3H), 7.36 (dt, \(J = 7.4, 0.9\) Hz, 1H), 3.25 (sept, \(J = 6.9\) Hz, 1H), 1.43 (d, \(J = 6.9\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 143.0 (C), 139.0 (C), 138.5 (C), 136.2 (C), 135.6 (C), 126.5 (CH), 125.0 (CH), 124.2 (CH), 122.7 (CH), 122.6 (CH), 121.6 (CH), 119.2 (CH), 33.5 (C), 22.5 (CH\(_3\)).

V. References

1d-D
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$\text{H NMR (400 MHz, CDCl}_3\)$

$\text{KOr-Bu (1.6 equiv) THF, rt, 5 h then saturated aq. NH}_4\text{Cl}$

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