Supporting Information

Functionalization of Styrenes by Copper-Catalyzed Borylation/ortho-Cyanation and Silver-Catalyzed Annulation Processes
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Supporting information

Table of Contents

I. General Information ...........................................................................................................01
II. Preparation of Substrates ...............................................................................................02
III. Copper-Catalyzed Borylation / ortho-Cyanation .......................................................03
IV. Silver-Mediated Cyclization .........................................................................................15

1H NMR and 13C NMR Spectra

I. General Information

Unless otherwise noted, all reactions were conducted in oven-dried vials with magnetic stirring under an atmosphere of dry nitrogen. Solvents were purified under nitrogen using a solvent purification system (Innovative Technology, inc., Model #SPS-400-3 and PS-400-3). IMesCuCl (Aldrich), all N-heterocyclic carbene salts (Aldrich), lithium tert-butoxide (Strem Chemicals, Inc.) were stored and weighed in an inert atmosphere glovebox. Analytical thin layer chromatography (TLC) was performed on SiliaPlate TLC 60Å F-254 (250 μm silica gel) and compounds were visualized with phosphomolybdic acid, ceric ammonium molybdate, or aqueous KMnO4 stain. Flash column chromatography was performed using SiliaFlash® P60 (230-400 mesh) silica gel.

1H-Nuclear Magnetic Resonance (1H-NMR) and 13C Nuclear Magnetic Resonance (13C-NMR) spectra were recorded on Varian MR 400, Vnmrs 500, INOVA 500 and Vnmrs 700 MHz. NMR spectra were recorded in deuterated chloroform (CDCl3) at rt unless otherwise stated. The NMR data were presented as follows: chemical shift in ppm with the proton signal of the residual of chloroform (δ 7.26 for 1H-NMR) and (δ = 77.0 ppm for 13C-NMR) as internal standards, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet, br. = broad), coupling constant (J/Hz), integration. High resolution mass spectra were recorded on a VG 70-250-s spectrometer manufactured by Micromass Corp. (Manchester UK) at the University of Michigan Mass Spectrometry Laboratory. IR spectra were collected on a Spectrum BX FTIR from Perkin-Elmer and reported in unit of cm⁻¹.
II. Preparation of Substrates

The following styrenes were purchased and used as received: styrene, 4-fluorostyrene, 4-chlorostyrene, 4-methylstyrene, 4-tert-butylstyrene, 4-phenylstyrene, 3-methylstyrene, 3-bromostyrene, 3-vinylanisole, 2-methylstyrene and 2-vinylnaphthalene.

The following styrenes were prepared by the literature procedure: tert-butylidimethyl((4-vinylbenzyl)oxy)silane, 1 1-(diethoxymethyl)-4-vinylbenzene, 2 1-(prop-1-en-1-yl)-4-vinylbenzene, 3 tert-butylidimethyl(3-vinylbenzyl)oxy)silane, 4 tert-butyl 5-vinyl-1H-indole-1-carboxylate, 5 tert-butyl 2-vinyl-1H-pyrrole-1-carboxylate 6 and 3-Vinylestrone.7 All characterization data are in accordance with the literature.

N-cyano-4-methyl-N-phenylbenzenesulfonamide (NCTS, 1) was prepared according to the known procedure.8

**tert-Butyl 3-vinyl-9H-carbazole-9-carboxylate**

![Chemical Structure](image)

In glove box, to an oven-dried 20-mL microwave tube was added potassium vinyltrifluoroborate (0.7 g, 5.0 mmol), PdCl₂ (17.7 mg, 0.1 mmol), PPh₃ (78.6 mg, 0.3 mmol), Cs₂CO₃ (4.9 g, 15.0 mmol) and tert-butyl 3-bromo-9H-carbazole-9-carboxylate (1.7 g, 5.0 mmol). The microwave tube was sealed with a cap and taken outside the glove box. Under N₂, THF/H₂O (9:1) (10 mL) were added. The resulting solution was stirred at 85 °C for 40 h, then cooled to rt and diluted with H₂O. The mixture was extracted with DCM, dried with Na₂SO₄, filtered, and concentrated, and the residue was chromatographed on

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silica gel (20:1 hexane/EtOAc), to afford 1.14 g (78%) of tert-butyl 3-vinyl-9H-carbazole-9-carboxylate as a colorless oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.31 (d, \(J = 8.4\) Hz, 1H), 8.26 (d, \(J = 8.6\) Hz, 1H), 8.04 – 7.95 (m, 2H), 7.56 (dd, \(J = 8.7, 1.8\) Hz, 1H), 7.48 (m, 1H), 7.37 (m, 1H), 6.89 (dd, \(J = 17.6, 10.9\) Hz, 1H), 5.85 (dd, \(J = 17.6, 1.0\) Hz, 1H), 5.30 (dd, \(J = 10.9, 0.9\) Hz, 1H), 1.78 (s, 9H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 151.0, 138.8, 138.1, 136.8, 132.7, 127.1, 126.0, 125.7, 125.3, 123.0, 119.6, 117.2, 116.3, 116.2, 112.9, 83.9, 28.4.

HRMS (ESI) calculated for C\(_{19}\)H\(_{19}\)NNaO\(_2\) [M+Na]\(^+\): 316.1308, found: 316.1306.

IR (neat, cm\(^{-1}\)): 2978, 1722, 1450, 1354, 1304, 1153, 748.

III. Copper-Catalyzed Borylation / \textit{ortho}-Cyanation

\begin{align*}
\text{IMesCuCl} & \quad & \text{B}_{2}\text{pin}_2 & \quad & \text{CN} & \quad & \text{OH} \\
\text{LiO-t-Bu, THF} & \quad & \text{4 Å MS, 12 h} & \quad & \text{CN} & \quad & \text{CN} \\
\end{align*}

**General Procedure A.** In glove box, to an oven-dried 10-mL vial was added IMesCuCl (12.1 mg, 0.03 mmol, 10 mol %), LiO-t-Bu (48.0 mg, 0.6 mmol, 2.0 eq), 4 Å molecular sieves (50.0 mg) and anhydrous THF (0.3 mL). The resulting solution was stirred for 15 min at rt. The B\(_2\)pin\(_2\) (114.3 mg, 0.45 mmol, 1.5 eq) was then added. After stirring for 30 min at rt, the solution of styrene (0.3 mmol) and \textit{N}-cyano-\textit{N}-phenyl-\textit{p}-toluenesulfonamide \(\mathbf{1}\) (NCTS, 163.2 mg, 0.6 mmol) in THF (0.5 mL) was then added by syringe (10 min). The resulting solution was stirred overnight and diluted with ethyl acetate, filtered through a silica gel pad, concentrated in vacuo, and the residue was purified by silica gel flash chromatography to afford cyanoborylated product.

**General Procedure B.** To a 10-mL vial was added the cyanoborylated product, NaOH (5.0 eq, 60.0 mg) and THF (1 mL). The resulting mixture was cooled to 0 °C followed by addition of 30% H\(_2\)O\(_2\) (5.0 eq, 170.0 mg), dropwise. The reaction mixture was allowed to warm to rt and stir for 2 hours. The reaction mixture was then diluted with H\(_2\)O, extracted with ethyl acetate, dried with MgSO\(_4\), filtered, and concentrated, and the residue was chromatographed on silica gel to afford the desired alcohol.
2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a colorless oil from styrene (31.2 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B_{2}pin_{2} (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 64.8 mg, 84% yield).

\[ {^1}H \text{ NMR} \text{ (500 MHz, CDCl}_3 \text{) } \delta 7.60 (dd, J = 7.7, 1.1 \text{ Hz}, 1H), 7.50 (td, J = 7.7, 1.4 \text{ Hz}, 1H), 7.39 (d, J = 7.8 \text{ Hz}, 1H), 7.26 (dd, J = 7.6, 1.1 \text{ Hz}, 1H), 2.98 (t, J = 10.0 \text{ Hz}, 2H), 1.24 (m, 14H). \]

\[ {^{13}}C \text{ NMR} \text{ (125 MHz, CDCl}_3 \text{) } \delta 148.3, 132.7, 132.6, 128.9, 126.2, 118.1, 112.1, 83.3, 28.6, 24.8. \]

HRMS (EI) calculated for C_{15}H_{20}BNO_{2} [M+]: 257.1587, found: 257.1594.

IR (neat, cm\(^{-1}\)): 2979, 2223, 1370, 1319, 1142, 848, 761.

5-Fluoro-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a white solid from 4-fluorostyrene (36.6 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B_{2}pin_{2} (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 66.8 mg, 81% yield).

\[ {^1}H \text{ NMR} \text{ (500 MHz, CDCl}_3 \text{) } \delta 7.35 (dd, J = 8.7, 5.3 \text{ Hz}, 1H), 7.27 (dd, J = 8.1, 2.7 \text{ Hz}, 1H), 7.20 (td, J = 8.4, 2.7 \text{ Hz}, 1H), 2.93 (t, J = 8.0 \text{ Hz}, 2H), 1.21 (s, 12H), 1.21 \text{–} 1.15 (m, 2H). \]

\[ {^{13}}C \text{ NMR} \text{ (125 MHz, CDCl}_3 \text{) } \delta 160.2 (d, J = 246.3 \text{ Hz}), 144.3 (d, J = 3.8 \text{ Hz}), 130.80 (d, J = 7.5 \text{ Hz}), 120.2 (d, J = 21.3 \text{ Hz}), 119.1 (d, J = 23.8 \text{ Hz}), 116.9 (d, J = 2.5 \text{ Hz}), 113.2 (d, J = 8.6 \text{ Hz}), 83.4, 27.9, 24.8. \]

HRMS (EI) calculated for C_{16}H_{19}BFNO_{2} [M+] : 275.1493, found: 275.1496.

IR (neat, cm\(^{-1}\)): 2980, 2234, 1371, 1320, 1142, 840.
5-Chloro-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a white solid from 4-chlorostyrene (41.6 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), Bpin₂ (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 39.3 mg, 45%).

^1H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 2.3 Hz, 1H), 7.45 (dd, J = 8.4, 2.2 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 2.93 (t, J = 8.1 Hz, 2H), 1.22 (s, 12H), 1.17 (t, J = 8.1 Hz, 2H).

^13C NMR (125 MHz, CDCl₃) δ 146.8, 132.9, 132.1, 130.4, 116.8, 113.6, 83.4, 28.1, 24.8.

HRMS (EI) calculated for C₁₅H₁₉BClNO₂ [M⁺]: 291.1197, found: 291.1203.

IR (neat, cm⁻¹): 2979, 2227, 1371, 1321, 1142, 848.

5-Methyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a white solid from 4-methylstyrene (35.5 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), Bpin₂ (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 65.9 mg, 81% yield).

^1H NMR (400 MHz, CDCl₃) δ 7.36 (s, 1H), 7.29 – 7.20 (m, 2H), 2.89 (t, J = 8.1 Hz, 2H), 2.31 (s, 3H), 1.20 (s, 12H), 1.15 (m, J = 8.4 Hz, 2H).

^13C NMR (100 MHz, CDCl₃) δ 145.3, 135.9, 133.5, 132.9, 128.8, 118.3, 111.9, 83.2, 28.1, 24.8, 20.6.


IR (neat, cm⁻¹): 2976, 2224, 1371, 1318, 1142, 848.
5-(tert-Butyl)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a colorless oil from 4-tert-butylstyrene (48.0 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), Bpin₂ (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 78.9 mg, 84% yield).

\[ \text{H NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ 7.55 \ (d, \ J = 2.1 \text{ Hz}, 1\text{H}), 7.48 \ (dd, \ J = 8.2, 2.1 \text{ Hz}, 1\text{H}), 7.29 - 7.23 \ (m, 1\text{H}), 2.90 \ (t, \ J = 8.1 \text{ Hz}, 2\text{H}), 1.28 \ (s, 9\text{H}), 1.22 - 1.15 \ (m, 15\text{H}). \]

\[ \text{C NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta \ 149.3, 145.2, 130.0, 129.5, 128.6, 118.6, 111.7, 83.3, 34.5, 31.1, 28.0, 24.8. \]


\[ \text{IR (neat, cm}^{-1}) : 2973, 2222, 1371, 1320, 1142, 841, 737. \]

4-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-[1,1'-biphenyl]-3-carbonitrile was prepared as a colorless oil from 4-phenylstyrene (54.0 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), Bpin₂ (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol), 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 78.9 mg, 79% yield).

\[ \text{H NMR} \ (500 \text{ MHz, CDCl}_3) \ \delta \ 7.81 \ (d, \ J = 1.9 \text{ Hz}, 1\text{H}), 7.72 \ (dd, \ J = 8.1, 2.0 \text{ Hz}, 1\text{H}), 7.57 - 7.54 \ (m, 2\text{H}), 7.49 - 7.44 \ (m, 3\text{H}), 7.42 - 7.38 \ (m, 2\text{H}), 3.02 \ (m, 2\text{H}), 1.27 - 1.22 \ (m, 14\text{H}). \]

\[ \text{C NMR} \ (125 \text{ MHz, CDCl}_3) \ \delta \ 147.0, 139.4, 138.9, 131.3, 131.1, 129.4, 129.0, 128.0, 126.8, 117.9, 112.6, 83.3, 28.3, 24.8. \]

HRMS (EI) calculated for C₂₁H₂₄BNO₂ [M⁺]: 333.1900, found: 333.1908.

\[ \text{IR (neat, cm}^{-1}) : 2977, 2204, 1371, 1320, 1142, 762. \]
5-(((tert-Butyldimethylsilyl)oxy)methyl)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as colorless oil from tert-butyldimethyl(4-vinylbenzyl)oxy)silane (74.4 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B2pin₂ (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 15:1 hexane/EtOAc, 86.6 mg, 72% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.55 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 8.1 Hz, 1H), 4.71 (s, 2H), 2.95 (t, J = 8.2 Hz, 2H), 1.23 (s, 12H), 1.21 – 1.17 (m, 2H), 0.94 (s, 9H), 0.11 (s, 6H).

¹³C NMR (125 MHz, CDCl₃) δ 146.8, 139.8, 130.3, 130.1, 128.8, 118.3, 111.9, 83.3, 63.8, 28.3, 25.9, 24.8, 18.3, -5.3.

HRMS (ESI) calculated for C₂₂H₃₆BNNaO₃Si [M+Na]+: 424.2450, found: 424.245.

IR (neat, cm⁻¹): 2930, 2225, 1371, 1320, 1143, 836.

5-((Diethoxymethyl)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a colorless oil from 1-(diethoxymethyl)-4-vinylbenzene (61.8 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B₂pin₂ (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 87.2 mg, 81% yield).

¹H NMR (500 MHz, C₆D₆) δ 7.64 (d, J = 1.7 Hz, 1H), 7.43 (dd, J = 8.1, 1.6 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H), 5.19 (s, 1H), 3.37 – 3.28 (m, 2H), 3.28 – 3.18 (m, 2H), 3.00 (t, J = 8.0 Hz, 2H), 1.24 (t, J = 8.0 Hz, 2H), 1.02 (t, J = 7.1 Hz, 6H), 0.97 (s, 12H).

¹³C NMR (125 MHz, C₆D₆) δ 148.0, 137.8, 131.0, 130.5, 128.6, 117.8, 112.5, 99.8, 82.8, 60.3, 28.5, 24.5, 14.9.


IR (neat, cm⁻¹): 2976, 2224, 1372, 1328, 1143, 1055, 848.
2-(2-Hydroxyethyl)-5-(prop-1-en-1-yl)benzonitrile was prepared as colorless oil from 1-(prop-1-en-1-yl)-4-vinylbenzene (E/Z = 1:1, 43.2 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B₂pin₂ (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol), 4 Å molecular sieves (50.0 mg), NaOH (60.0 mg) and 30% H₂O₂ (170.0 mg) following the above general procedure A and B (eluent: 5:1 hexane/EtOAc, 36.5 mg, 65% yield for 2 steps, E/Z = 1/2).

^1H NMR (500 MHz, CDCl₃, E isomer): δ 7.56 (d, J = 1.9 Hz, 1H), 7.47 (dd, J = 8.1, 1.9 Hz, 1H), 7.31 (d, J = 8.1 Hz, 1H), 6.39 – 6.31 (m, 1H), 6.27 (dq, J = 15.8, 6.2 Hz, 1H), 3.91 (d, J = 6.5 Hz, 2H), 3.05 (d, J = 6.5 Hz, 2H), 1.87 (d, J = 1.8 Hz, 3H).

^1H NMR (500 MHz, CDCl₃, Z isomer): 7.55 (d, J = 1.9 Hz, 1H), 7.44 (dd, J = 8.0, 1.9 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 6.39 – 6.31 (m, 1H), 5.88 (dq, J = 11.6, 7.2 Hz, 1H), 3.96 – 3.93 (m, 2H), 3.09 (t, J = 6.6 Hz, 2H), 1.89 (dd, J = 6.4, 1.5 Hz, 3H).

^13C NMR (125 MHz, CDCl₃, E/Z isomers) δ 140.6, 140.4, 137.2, 136.7, 133.1, 132.8, 130.5, 130.2, 129.98, 129.97, 129.0, 128.8, 128.1, 127.5, 118.2, 113.0, 112.7, 62.6, 37.4, 37.4, 18.5, 14.6.


IR (neat, cm⁻¹): 3416, 2942, 2225, 1495, 1044, 840.

4-Methyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a colorless oil from 3-methylstyrene (35.5 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B₂pin₂ (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 52.8 mg, 65% yield).

^1H NMR (500 MHz, CDCl₃) δ 7.46 (d, J = 7.9 Hz, 1H), 7.17 (s, 1H), 7.05 (d, J = 7.9 Hz, 1H), 2.92 (t, 2 J = 8.0 Hz, H), 2.36 (s, 3H), 1.25 – 1.14 (m, 14H).
\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 148.2, 143.3, 132.6, 129.7, 127.0, 118.4, 109.1, 83.3, 28.5, 24.8, 21.8.

HRMS (EI) calculated for C\(_{15}\)H\(_{22}\)BNO\(_2\) [M\(^+\)]: 271.1744, found: 271.1749.

IR (neat, cm\(^{-1}\)): 2977, 2222, 1370, 1316, 1142, 847, 731.

4-(((tert-Butyldimethylsilyloxy)methyl)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a colorless oil from tert-butyldimethyl((3-vinylbenzyl)oxy)silane (74.4 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B\(_2\)pin\(_2\) (114.3 mg, 0.45 mmol), LiO\(^-\)t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 15:1 hexane/EtOAc, 80.6 mg, 67% yield).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.54 (d, \(J = 7.9\) Hz, 1H), 7.30 (s, 1H), 7.22 (d, \(J = 7.9\) Hz, 1H), 4.73 (s, 2H), 2.95 (t, 2H), 1.24 – 1.16 (m, 14H), 0.93 (s, 9H), 0.09 (s, 6H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 148.2, 146.7, 132.7, 126.1, 123.5, 118.3, 110.4, 83.3, 64.3, 28.6, 25.9, 24.8, -5.3.

HRMS (ESI) calculated for C\(_{22}\)H\(_{36}\)BNNaO\(_3\)Si [M+Na\(^+\)]: 424.2450, found: 424.2451.

IR (neat, cm\(^{-1}\)): 2930, 2223, 1371, 1319, 1143, 836.

4-Bromo-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a white solid from 3-bromostyrene (54.3 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B\(_2\)pin\(_2\) (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 78.4 mg, 78% yield).
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J = 1.8$ Hz, 1H), 7.45 – 7.38 (m, 2H), 2.93 (t, $J = 7.9$ Hz, 2H), 1.22 (s, 12H), 1.20 – 1.15 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 150.1, 133.8, 132.5, 129.6, 127.6, 117.3, 111.1, 83.4, 28.5, 24.8.

HRMS (ESI) calculated for C$_{15}$H$_{20}$BBrNO$_2$ [M+H]$^+$: 336.0765, found: 336.0767.

IR (neat, cm$^{-1}$): 2977, 2225, 1370, 1322, 1142, 846.

2-(2-Hydroxyethyl)-4-methoxybenzonitrile was prepared as a colorless oil from 3-vinylanisole (40.3 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B$_2$pin$_2$ (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol), 4 Å molecular sieves (50.0 mg), NaOH (60.0 mg) and 30% H$_2$O$_2$ (170.0 mg) following the above general procedure A and B (eluent: 5:1 hexane/EtOAc, 37.7 mg, 71% yield for 2 steps).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J = 8.6$ Hz, 1H), 6.89 (d, $J = 2.3$ Hz, 1H), 6.83 (dd, $J = 8.6, 2.4$ Hz, 1H), 3.94 (t, $J = 6.5$ Hz, 2H), 3.85 (s, 3H), 3.06 (t, $J = 6.4$ Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 162.8, 144.8, 134.6, 116.0, 112.7, 109.1, 104.5, 62.5, 55.5, 37.9.

HRMS (ESI) calculated for C$_{10}$H$_{12}$NO$_2$ [M+H]$^+$: 178.0863, found: 178.0862.

IR (neat, cm$^{-1}$): 3444, 2943, 2219, 1605, 1248, 1040, 820.

3-Methyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a white solid from 2-methylstyrene (35.5 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B$_2$pin$_2$ (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 54.5 mg, 67% yield).
\textbf{1H NMR} (500 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 7.14 (t, $J = 7.7$ Hz, 1H), 2.94 (t, $J = 8.5$ Hz, 2H), 2.37 (s, 3H), 1.25 (s, 15H), 1.08 (t, $J = 8.5$ Hz, 3H).

\textbf{13C NMR} (125 MHz, CDCl$_3$) $\delta$ 146.8, 137.0, 134.6, 130.7, 126.1, 118.6, 112.4, 83.3, 26.1, 24.8.

\textbf{HRMS} (EI) calculated for C$_{15}$H$_{22}$BNO$_2$ [M$^+$]: 271.1744, found: 271.1745.

\textbf{IR} (neat, cm$^{-1}$): 2980, 2224, 1370, 1324, 1145, 850, 786.

6-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-2,3-dihydro-1H-indene-5-carbonitrile (5) was prepared as a colorless oil from 5-vinyl-2,3-dihydro-1H-indene (43.2 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B$_2$pin$_2$ (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 50.8 mg, 57% yield).

\textbf{1H NMR} (500 MHz, CDCl$_3$) $\delta$ 7.41 (s, 1H), 7.21 (s, 1H), 2.93 – 2.87 (m, 6H), 2.07 (q, $J = 7.5$ Hz, 2H), 1.23 (s, 12H), 1.16 (t, $J = 8.5$ Hz, 2H).

\textbf{13C NMR} (175 MHz, CDCl$_3$) $\delta$ 150.1, 146.6, 142.3, 128.2, 124.9, 118.9, 109.4, 83.2, 33.2, 32.1, 28.5, 25.3, 24.8.


\textbf{IR} (neat, cm$^{-1}$): 2977, 2220, 1370, 1326, 1144, 968.

\begin{center}
\includegraphics[width=0.5\textwidth]{image}
\end{center}

 tert-Butyl (2-(3-cyano-1H-pyrrol-2-yl)ethyl) carbonate (6) was prepared as a pale yellow solid from tert-butyl 2-vinyl-1H-pyrrole-1-carboxylate (57.9 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B$_2$pin$_2$ (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol), 4 Å molecular sieves (50.0 mg), NaOH (60.0 mg) and 30% H$_2$O$_2$ (170.0 mg) following the above general procedure A and B (eluent: 10:1 hexane/EtOAc, 53.1 mg, 75% yield for 2 steps).
\( ^1 \)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.79 (s, 1H), 6.68 (t, \( J = 2.8 \) Hz, 1H), 6.38 (t, \( J = 2.9 \) Hz, 1H), 4.31 (t, \( J = 5.9 \) Hz, 2H), 3.12 (t, \( J = 5.9 \) Hz, 2H), 1.49 (s, 9H).

\( ^{13} \)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 153.0, 137.5, 118.3, 111.3, 91.9, 83.0, 65.5, 27.7, 26.2.

HRMS (ESI) calculated for C\(_{12}\)H\(_{16}\)N\(_2\)NaO\(_3\) \([\text{M+Na}]^+\): 259.1053, found: 259.1051.

IR (neat, cm\(^{-1}\)): 3308, 2981, 2220, 1741, 1279, 1162, 839.

2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1-naphthonitrile (7) was prepared as a colorless oil from 2-vinylnaphthalene (45.2 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B\(_2\)pin\(_2\) (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 76.4 mg, 83% yield). The data is in accordance with the literature.\(^9\)

tert-Butyl 4-cyano-5-(2-hydroxyethyl)-1H-indole-1-carboxylate (8) was prepared as a colorless oil from tert-butyl 5-vinyl-1H-indole-1-carboxylate (72.9 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B\(_2\)pin\(_2\) (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol), 4 Å molecular sieves (50.0 mg), NaOH (60.0 mg) and 30% H\(_2\)O\(_2\) (170.0 mg) following the above general procedure A and B (eluent: 3:1 hexane/EtOAc, 53.2 mg, 62% yield for 2 steps).

\( ^1 \)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.30 (d, \( J = 8.5 \) Hz, 1H), 7.72 (d, \( J = 3.7 \) Hz, 1H), 7.29 (d, \( J = 8.6 \) Hz, 1H), 6.77 – 6.72 (m, 1H), 3.96 (t, \( J = 6.5 \) Hz, 2H), 3.19 (t, \( J = 6.5 \) Hz, 2H), 1.67 (s, 9H), 1.62-1.55 (m, 1H).

\[ ^{13}C \text{NMR} \ (125 \text{ MHz, CDCl}_3) \ \delta \ 149.0, 137.8, 132.9, 128.5, 125.8, 119.5, 117.1, 110.0, 105.5, 103.8, 84.8, 63.1, 37.7, 28.1. \]

**HRMS (ESI)** calculated for C\textsubscript{16}H\textsubscript{22}N\textsubscript{3}O\textsubscript{3} [M+NH\textsubscript{4}]\textsuperscript{+}: 304.1656, found: 304.1655.

**IR** (neat, cm\textsuperscript{-1}): 3440, 2977, 2222, 1737, 1350, 1286, 1151, 1119, 1040, 767.

**tert-Butyl 4-cyano-3-(2-hydroxyethyl)-9H-carbazole-9-carboxylate (9)** was prepared as a white solid from *tert*-butyl 3-vinyl-9H-carbazole-9-carboxylate (87.9 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B\textsubscript{2}pin\textsubscript{2} (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol), 4 Å molecular sieves (50.0 mg), NaOH (60.0 mg) and 30% H\textsubscript{2}O\textsubscript{2} (170.0 mg) following the above general procedure A (eluent: 3:1 hexane/EtOAc, 71.6 mg, 71% yield for 2 steps).

\[ ^{1}H \text{NMR} \ (500 \text{ MHz, CDCl}_3) \ \delta \ 8.60 \ (d, \ J = 7.9 \text{ Hz}, 1\text{H}), \ 8.51 \ (d, \ J = 8.6 \text{ Hz}, 1\text{H}), \ 8.30 \ (d, \ J = 8.5 \text{ Hz}, 1\text{H}), \ 7.56 \ (t, \ J = 7.9 \text{ Hz}, 1\text{H}), \ 7.45 \ (d, \ J = 8.6 \text{ Hz}, 1\text{H}), \ 7.42 \ (t, \ J = 7.6 \text{ Hz}, 1\text{H}), \ 4.01 \ (t, \ J = 6.5 \text{ Hz}, 2\text{H}), \ 3.25 \ (t, \ J = 6.5 \text{ Hz}, 2\text{H}), \ 1.82 – 1.69 \ (m, 10\text{H}). \]

\[ ^{13}C \text{NMR} \ (125 \text{ MHz, CDCl}_3) \ \delta \ 150.5, 139.0, 138.2, 137.3, 128.8, 128.2, 126.7, 123.6, 123.1, 121.3, 120.4, 117.4, 116.1, 103.8, 84.9, 63.0, 37.4, 28.3. \]

**HRMS (ESI)** calculated for C\textsubscript{20}H\textsubscript{24}N\textsubscript{3}O\textsubscript{3} [M+NH\textsubscript{4}]\textsuperscript{+}: 354.1812, found: 354.1812.

**IR** (neat, cm\textsuperscript{-1}): 3445, 2976, 2221, 1727, 1319, 1152, 746.

\[ 2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)dibenzo[b,d]furan-1-carbonitrile (10) \] was prepared as a white solid from 2-vinyl dibenzo[b,d]furan (58.2 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B\textsubscript{2}pin\textsubscript{2} (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 73.9 mg, 71% yield).
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.43 (d, $J = 7.8$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.59 (d, $J = 8.1$ Hz, 1H), 7.55 (t, $J = 7.7$ Hz, 1H), 7.44 (d, $J = 8.4$ Hz, 2H), 3.12 (t, $J = 8.0$ Hz, 2H), 1.31 – 1.25 (t, $J = 8.4$ Hz, 2H), 1.23 (s, 12H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.8, 154.0, 143.8, 128.7, 127.4, 125.8, 123.4, 122.1, 121.9, 116.7, 115.9, 111.8, 103.7, 83.3, 28.4, 24.8.

HRMS (ESI) calculated for C$_{21}$H$_{22}$BNO$_3$K [M+K]$^+$: 386.1324, found: 386.1329.

IR (neat, cm$^{-1}$): 2977, 2206, 1370, 1320, 1141, 848, 748.

Compound 11 was prepared as a white solid from 3-vinylestrone (84.0 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B$_2$pin$_2$ (114.3 mg, 0.45 mmol), LiO-t-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (elutnet: 15:1 hexane/EtOAc), 79.2 mg, 61% yield.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.48 (s, 1H), 7.07 (s, 1H), 2.97 – 2.82 (m, 4H), 2.51 (dd, $J = 19.1$, 8.7 Hz, 1H), 2.37 (m, 1H), 2.25 (m, 1H), 2.15 (m, 1H), 2.08 – 1.95 (m, 3H), 1.66 – 1.43 (m, 6H), 1.23 (s, 12H), 1.16 (t, $J = 9.0$ Hz, 2H), 0.91 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 220.3, 145.3, 142.0, 138.2, 129.8, 129.4, 118.6, 109.3, 83.3, 50.3, 47.8, 43.7, 37.8, 35.8, 31.3, 29.5, 28.0, 26.1, 25.5, 24.8, 24.8, 21.5, 13.8.


IR (neat, cm$^{-1}$): 2930, 2221, 1739, 1372, 1145, 848.
IV. Silver-mediated cyclization

![Chemical structure](image)

**General Procedure C:** To a thick-walled tube was added AgNO₃ (17.0 mg, 0.1 mmol), cyanoborylated product (0.1 mmol), and Selectfluor (106.0 mg, 0.3 mmol). The tube was sealed with a cap, evacuated and filled with nitrogen. Dichloromethane (0.2 mL), water (0.5 mL), and TFA (0.3 mL) were added successively at rt. The resulting mixture was then stirred at 50 °C overnight, then cooled to rt and filtered through a silica gel pad. The mixture was washed with aqueous saturated NaHCO₃ solution and brine, dried with Na₂SO₄, filtered, and concentrated, and the residue was chromatographed on silica gel to afford cyclopentannulated product.

2,3-Dihydro-1H-inden-1-one (14) was prepared as a white solid from 2 (table 1, entry 1, 25.7 mg, 0.1 mmol), AgNO₃ (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol) following the above general procedure C (eluent: 10:1 hexane/Et₂O, 9.8 mg, 74% yield). The characterization data is in accordance with the literature.¹⁰

4-Methyl-2,3-dihydro-1H-inden-1-one (15) was prepared as a white solid from 3-methyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (table 1, entry 14, 27.1 mg, 0.1 mmol), AgNO₃ (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol)

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following the above general procedure C (eluent: 10:1 hexane/Et₂O, 9.8 mg, 67% yield). The characterization data is in accordance with the literature.¹¹

5-Methyl-2,3-dihydro-1H-inden-1-one (16) was prepared as a white solid from 4-methyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (table 1, entry 10, 27.1 mg, 0.1 mmol), AgNO₃ (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol) following the above general procedure C (eluent: 10:1 hexane/Et₂O, 9.5 mg, 65% yield). The characterization data is in accordance with the literature.¹²

6-(tert-Butyl)-2,3-dihydro-1H-inden-1-one (17) was prepared as a white solid from 5-(tert-butyl)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (table 1, entry 5, 31.3 mg, 0.1 mmol), AgNO₃ (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol) following the above general procedure C (eluent: 10:1 hexane/Et₂O, 13.2 mg, 70% yield). The characterization data is in accordance with the literature.¹³

5-Bromo-2,3-dihydro-1H-inden-1-one (18) was prepared as a white solid from 4-bromo-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (table 1, entry 12, 33.6 mg, 0.1 mmol), AgNO₃ (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol)

following the above general procedure C (eluent: 2:1 hexane/dichloromethane, 14.5 mg, 70% yield). The characterization data is in accordance with the literature.\textsuperscript{14}

\begin{center}
\includegraphics[width=0.2\textwidth]{image1}
\end{center}

6-Fluoro-2,3-dihydro-1H-inden-1-one (19) was prepared as a pale yellow solid from 5-fluoro-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (table 1, entry 2, 27.5 mg, 0.1 mmol), AgNO\textsubscript{3} (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol) following the above general procedure C (eluent: 2:1 hexane/dichloromethane, 5.6 mg, 37% yield). The characterization data is in accordance with the literature.\textsuperscript{12}

\begin{center}
\includegraphics[width=0.2\textwidth]{image2}
\end{center}

3,5,6,7-Tetrahydro-s-indacen-1(2H)-one (20) was prepared as a white solid from 6-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-2,3-dihydro-1H-indene-5-carbonitrile (table 2, 5, 27.5 mg, 0.1 mmol), AgNO\textsubscript{3} (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol) following the above general procedure C (eluent: 10:1 hexane/ethyl acetate, 9.1 mg, 53% yield). The characterization data is in accordance with the literature.\textsuperscript{15}

\begin{center}
\includegraphics[width=0.2\textwidth]{image3}
\end{center}

2,3-Dihydro-1H-cyclopenta[a]naphthalen-1-one (21) was prepared as a white solid from 2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1-naphthonitrile (table 2, 5, 30.7 mg, 0.1 mmol), AgNO\textsubscript{3} (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol)

following the above general procedure C (eluent: 10:1 hexane/Et₂O, 11.3 mg, 62% yield). The characterization data is in accordance with the literature.\textsuperscript{16}

\begin{center}
\includegraphics[width=0.2\textwidth]{image}
\end{center}

\textbf{2,3-Dihydro-1H-indeno[5,4-b]benzofuran-1-one (22)} was prepared as a pale yellow solid from 10 (34.7 mg, 0.1 mmol), AgNO\textsubscript{3} (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol) following the above general procedure C (eluent: 2:1 hexane/dichloromethane, 13.5 mg, 61% yield).

\textbf{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.92 (d, \(J = 7.5\) Hz, 1H), 7.80 (d, \(J = 8.4\) Hz, 1H), 7.60 (d, \(J = 8.3\) Hz, 1H), 7.54 (td, \(J = 8.3, 7.8, 1.3\) Hz, 1H), 7.51 (d, \(J = 8.4\) Hz, 1H), 7.44 – 7.39 (m, 1H), 3.31 (t, \(J = 5.5\) Hz, 2H), 2.88 – 2.83 (m, 2H).

\textbf{\textsuperscript{13}C NMR} (125 MHz, CDCl\textsubscript{3}) \(\delta\) 206.8, 157.1, 155.6, 151.3, 132.2, 128.5, 126.1, 124.2, 123.2, 123.1, 121.1, 117.7, 111.3, 37.01, 26.57.

\textbf{HRMS} (ESI) calculated for C\textsubscript{15}H\textsubscript{11}O\textsubscript{2} [M+H]\textsuperscript{+}: 223.0754, found: 223.0753.

\textbf{IR} (neat, cm\textsuperscript{-1}): 2970, 1701, 1439, 1268, 1204, 756.

\begin{center}
\includegraphics[width=0.2\textwidth]{image}
\end{center}

Compound 23 was prepared as a white solid from 9 (43.3 mg, 0.1 mmol), AgNO\textsubscript{3} (8.5 mg, 0.05 mmol) and Selectfluor (106.0 mg, 0.3 mmol) following the above general procedure C (eluent: 5:1 hexane/EtOAc, 12.9 mg, 42% yield).

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.70 (s, 1H), 7.21 (s, 1H), 3.12 – 2.95 (m, 4H), 2.72 – 2.63 (m, 2H), 2.56 – 2.46 (m, 2H), 2.39 – 2.27 (m, 1H), 2.20 – 1.97 (m, 4H), 1.65 – 1.47 (m, 6H), 0.91 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 220.5, 206.9, 152.7, 144.8, 139.8, 135.1, 126.8, 120.3, 50.5, 47.9, 44.2, 37.9, 36.5, 35.8, 31.4, 30.1, 26.2, 25.7, 25.2, 21.6, 13.8.

**HRMS** (ESI) calculated for C$_{21}$H$_{25}$O$_2$ [M+H]$^+$: 309.1849, found: 309.1852.

**IR** (neat, cm$^{-1}$): 2925, 1737, 1702, 1250, 735.
CN

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