Supporting Information

for

Copper-Catalyzed Oxidative Ring Closure and Carboarylation of 2-Ethynyl-Anilides

by

Ádám Sinai, Ádám Mészáros, Tamás Gáti, Veronika Kudar, Anna Palló, Zoltán Novák*
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Mesityl(phenyl)iodonium trifluoromethanesulfonate (2a)...................................................... 83
1. General Information

$^1$H-NMR and $^{13}$C-NMR spectra were recorded on a Bruker Avance-250 spectrometer operating at 250 MHz and 62.5 MHz using DMSO-$d_6$ or CDCl$_3$ as solvent. Chemical shifts are given in ppm relative to TMS for CDCl$_3$, or the residual solvent peak of DMSO as internal standards. Coupling constants ($J$) are reported in Hertz (Hz). Infrared spectra were recorded on Bruker Alpha spectrometer on a single-reflection diamond ATR spectrometer as solids or thin films. In the IR spectra, only the strongest/structurally most important peaks (n, cm$^{-1}$) are listed. HRMS were measured on an Agilent Technologies 6210 Time of Flight mass spectrometer. Melting points were recorded on Büchi 501 apparatus and are reported uncorrected. All solvents used were distilled using standard methods. 1,2-dichloroethane were distilled from calcium hydride. All mixed solvent systems are reported as v/v solutions. All reactions were monitored by TLC using Merck DC pre coated TLC plates with 0.25 mm Kieselgel 60 F$_{254}$. Visualization was performed with a 254 nm UV lamp. Commercially available Cu(OTf)$_2$ was dried at 100 °C under high vacuum and was stored under argon. M-CPBA was dried under high vacuum at room temperature and was stored under argon. All other chemicals were used as received without further purification.
2. Optimization studies

![Chemical structures](image)

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<th>Conversion / %</th>
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<td>7</td>
<td>Cu(OTf)₂</td>
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<td>100 (78% isolated)</td>
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<td>THF</td>
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3. Single crystal X-ray measurements

The molecular structure of compound 3j. The displacement ellipsoids are drawn at the 50% probability level, and heteroatoms are shaded.

Single crystal X-ray measurements of 3j: C_{25}H_{22}N_{2}O_{3}, Mr = 398.45, yellow, prism, size: 0.32 × 0.13 × 0.11 mm. The data were collected on a Rigaku R-Axis RAPID image plate diffractometer (graphite monochromated Cu-Kα radiation, λ = 1.54187 Å) at 93(2) K. Monoclinic space group P 2_1/c, a = 5.9898(1) Å, b = 19.4167(5) Å, c = 18.1253(4) Å, β = 98.273(1)º, V = 2086.07(8) Å³. Intensity data were collected at T = 93(2) K in the range of 6.72 ≤ θ ≤ 55.08, Z = 4, F(000) = 840, D_{calcd} = 1.269 Mg/m³, µ = 0.675 mm⁻¹. A total of 9647 reflections were collected, of which 2451 were unique (R_{int} = 0.0775). A numerical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.949 and 0.844). The structure was solved by direct methods (and subsequent difference syntheses). Anisotropic full-matrix least-squares refinement on F² for all non-hydrogen atoms yielded R₁ = 0.0713 and wR² = 0.1392 for [I>2σ(I)] and R₁ = 0.1272 and wR² = 0.1590 for all intensity data (number of parameters = 274, goodness-of-fit = 1.052). Hydrogen atomic positions were calculated from assumed geometries and refined by the riding model. The maximum and minimum residual electron density in the final difference map was 0.196 and -0.193 e.Å⁻³.

Single crystal X-ray measurements of 3aa: C_{25}H_{21}F_{2}NO, Mr = 389.43, colourless, prism, size: 0.37 × 0.14 × 0.10 mm. The data were collected on a Rigaku R-Axis RAPID image plate diffractometer (graphite monochromated Cu-Kα radiation, λ = 1.54187 Å) at 93(2) K. Triclinic space group P -1, a = 6.0188(2) Å, b = 9.7294(3) Å, c = 17.4629(6) Å, α = 75.170(2)º, β = 88.700(2)º, γ = 85.311(2)º, V = 985.24(6) Å³. Intensity data were collected at T = 93(2) K

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1 CrystalClear SM 1.4.0 (Rigaku/MSC Inc., 2008)
in the range of \(7.38 \leq \theta \leq 51.14\), \(Z = 2\), \(F(000) = 408\), \(D_{\text{calcd}} = 1.313\) Mg/m\(^3\), \(\mu = 0.758\) mm\(^{-1}\). A total of 6765 reflections were collected, of which 1936 were unique \((R_{\text{int}} = 0.0549)^a\). A numerical absorption correction was applied\(^b\) to the data (the minimum and maximum transmission factors were 0.949 and 0.828). The structure was solved by direct methods\(^c\) (and subsequent difference syntheses). Anisotropic full-matrix least-squares refinement\(^d\) on \(F^2\) for all non-hydrogen atoms yielded \(R_1 = 0.0741\) and \(wR^2 = 0.1748\) for \([I > 2\sigma(I)]\) and \(R_1 = 0.1251\) and \(wR^2 = 0.2521\) for all intensity data (number of parameters = 266, goodness-of-fit = 1.228). Hydrogen atomic positions were calculated from assumed geometries and refined by the riding model. The maximum and minimum residual electron density in the final difference map was 0.322 and -0.364 e\(\cdot\)\(\text{Å}^3\).

CCDC 936170 and CCDC 936171 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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<th>Identification code</th>
<th>3j</th>
<th>3aa</th>
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<td>C_{25}H_{21}F_{2}NO</td>
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<td>Formula weight</td>
<td>398.45</td>
<td>389.43</td>
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<td>Temperature</td>
<td>93(2) K</td>
<td>93(2) K</td>
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<tr>
<td>Wavelength</td>
<td>1.54187 Å</td>
<td>1.54187 Å</td>
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<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P 2_{1}/c</td>
<td>Triclinic, P -1</td>
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<td>Unit cell dimensions</td>
<td>a = 5.98980(10) Å, b = 19.4167(5) Å, c = 18.1253(4) Å, α = 90 °, β = 98.273(1) °, γ = 90 °</td>
<td>a = 6.0188(2) Å, b = 9.7294(3) Å, c = 17.4629(6) Å, α = 75.170(2) °, β = 88.700(2) °, γ = 85.311(2) °</td>
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<tr>
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<td>2086.07(8) Å³</td>
<td>985.24(6) Å³</td>
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<tr>
<td>Z</td>
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<td>2</td>
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<td>Calculated density</td>
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<td>1.313 Mg/m³</td>
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<td>0.758 mm⁻¹</td>
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<td>F(000)</td>
<td>840</td>
<td>408</td>
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<td>Crystal size</td>
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<td>0.37 x 0.14 x 0.10 mm</td>
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<td>Theta range for data collection</td>
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<td>Reflections collected / unique</td>
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<td>6765 / 1936 [R_{int} = 0.0549]</td>
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<td>91.8 % (θ = 51.14)</td>
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<td>Numerical</td>
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<td>0.949 and 0.828</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
<td>Full-matrix least-squares on F²</td>
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<td>Goodness-of-fit on F²</td>
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<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R_I = 0.0713, wR² = 0.1392</td>
<td>R_I = 0.0741, wR² = 0.1748</td>
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<td>R indices (all data)</td>
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<td>R_I = 0.1251, wR² = 0.2521</td>
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<td>Extinction coefficient</td>
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<td>Largest diff. peak and hole</td>
<td>0.196 and -0.193 e.Å⁻³</td>
<td>0.322 and -0.364 e.Å⁻³</td>
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Table 2. Selected Interatomic Distances and Angles of \textbf{3j} and \textbf{3aa}

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<td>1.229(4)</td>
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<td>1.386(7)</td>
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<td>1.424(6)</td>
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**Torsion angles (deg.)**

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<th>Torsion Angle</th>
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<td>6.6(6)</td>
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4. Isomerization studies

\[
\text{one isomer, one isomer, one isomer, one isomer, minor:major 1:10, minor:major 1:10}
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<tr>
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**Note:** 1.2:1 not significant
5. Synthesis and Analytical Data of 2-Iodoanilides

2-Iodoanilides were synthetised from 2-iodoaniline and the appropriate acyl chloride according to the modified procedure of Zhdankin.

**General procedure for the synthesis of N-(2-iodophenyl)pivalamides**

2-iodoaniline (32.853 g, 150 mmol) and triethylamine (24.11 ml, 173 mmol) were solubilised in 400 ml diethyl ether, and cooled to 0 °C. A solution of pivaloyl chloride (20.32 ml, 165 mmol) and diethyl ether (120 ml) was added dropwise. The reaction mixture was stirred at room temperature for 24 h. The precipitated triethylamine hydrochloride was filtered, and the filtrate was concentrated under reduced pressure. The crude product was recrystallised from ethanol/water 95/5.

**N-(2-iodophenyl)pivalamide (i1)**

Prepared according to the general procedure from 2-iodoaniline and pivaloyl chloride. Recrystallised from ethanol/water 95/5 to give a white solid (38.864 g, 128.2 mmol, 85%). M. p. 61-62 °C; Rf: 0.66 (hexanes/ethyl acetate = 5/1); \(^1^H\) NMR (250 MHz, CDCl\(_3\)): \(\delta\) 8.29 (dd, 1H, \(J = 8.4\) Hz and 1.4 Hz), 7.80 (bs, 1H), 7.76 (dd, 1H, \(J = 7.9\) Hz and 1.4 Hz), 7.33 (td, \(J = 8.4\) Hz and 1.3 Hz), 6.82 (td, 1H, \(J = 7.9\) Hz and 1.6 Hz), 1.37 (s, 9H); \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)): \(\delta\) 176.7, 138.6, 129.2, 125.6, 124.8, 121.7, 90.0, 40.1, 27.6; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 3261, 2960, 1640, 1499, 1459, 1365, 1173, 1017, 926, 739, 615, 435; HRMS m/z; [M+H]\(^+\) calculated for C\(_{11}\)H\(_{14}\)INO: 304.0193; found: 304.0188.

**N-(4-fluoro-2-iodophenyl)pivalamide (i2)**

Prepared according to the general procedure from 4-fluoro-2-iodoaniline (472 µl, 4 mmol) and trimethylacetyl chloride (739 µl, 6 mmol) in the presence of triethylamine (836 µ, 6 mmol) in diethyl ether (15 ml) for 28 h. Recrystallised from ethanol/water 95/5 to give a white solid (721 mg, 2.25 mmol, 56%). M. p. 112-113 °C; Rf: 0.41 (hexanes/ethyl acetate = 7/1); \(^1^H\) NMR (250 MHz, CDCl\(_3\)): \(\delta\) 8.18 (dd, 1H, \(J = 9.1\) Hz and 5.5 Hz), 7.67 (bs, 1H), 7.48 (dd, 1H, \(J = 7.7\) Hz and 2.8 Hz), 7.07 (td, 1H, \(J = 9.0\) Hz and 2.8 Hz), 1.35 (s, 9H); \(^{13}\)C
NMR (62.5 MHz, CDCl$_3$): $\delta$ 176.8, 158.6 ($d, J = 248.7$ Hz), 135.0 ($d, J = 3.1$ Hz), 125.3 ($d, J = 24.9$ Hz), 122.8 ($d, J = 7.7$ Hz), 116.1 ($d, J = 21.6$ Hz), 89.7 ($d, J = 8.3$ Hz), 40.1, 27.8; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 3287, 2968, 1646, 1591, 1482, 1255, 1192, 1031, 856, 801, 591, 523, 442; HRMS m/z [M+H]$^+$ calculated for C$_{14}$H$_{13}$FINO: 322.0099; found: 322.0107.

Methyl 4-iodo-3-pivalamidobenzoate (i3)

Prepared according to the general procedure from methyl 3-amino-4-iodobenzoate (416 mg, 1.5 mmol) and trimethylacetyl chloride (462 µl, 3.75 mmol) in the presence of triethylamine (522 µl, 6 mmol) in 1,4-dioxane (15 ml) at 45°C for 22 h. Recrystallised from ethanol/ water 95/ 5 to give a white solid (373 mg, 1.03 mmol, 69%). M. p. 126-127 °C; Rf: 0.32 (hexanes/ ethyl acetate = 7/ 1); $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 8.87 ($d, 1H, J = 2.0$ Hz), 7.86 ($s, 1H$), 7.83 (s, 1H), 7.48 (dd, 1H, $J = 8.3$ Hz and 2.0 Hz), 3.89 ($s, 3H$), 1.37 ($s, 9H$); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 177.0, 166.4, 138.9, 138.7, 131.5, 126.5, 122.3, 96.0, 52.5, 40.3, 27.7; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 3339, 2951, 1718, 1667, 1567, 1521, 1408, 1319, 1164, 757, 570; HRMS m/z [M+H]$^+$ calculated for C$_{13}$H$_{16}$INO: 362.0248; found: 362.0254.

N-(5-chloro-2-iodophenyl)pivalamide (i4)

Prepared according to the general procedure from 5-chloro-2-iodoaniline (1.014 g, 4 mmol) and trimethylacetyl chloride (1.232 ml, 10 mmol) in the presence of triethylamine (1.394 ml, 10 mmol) in 1,4-dioxane (25 ml) at 45°C for 24 h. Recrystallised from ethanol/ water 95/ 5 to give a white solid (959 mg, 2.84 mmol, 71%). M. p. 78-79 °C; Rf: 0.56 (hexanes/ ethyl acetate = 7/ 1); $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 8.35 ($d, 1H, J = 2.5$ Hz), 7.45 (bs, 1H), 7.59 (d, 1H, $J = 8.5$ Hz), 6.76 (dd, 1H, $J = 8.5$ Hz and 2.5 Hz), 1.29 (s, 9H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 177.0, 139.3, 139.2, 135.6, 125.7, 121.5, 86.7, 40.4, 27.7; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 3318, 2965, 1667, 1562, 1506, 1389, 1189, 1092, 1014, 872, 798, 584, 438; HRMS m/z [M+H]$^+$ calculated for C$_{11}$H$_{13}$ClINO: 337.9803; found: 337.9795.
6. Synthesis and Analytical Data of 2-Arylethynylpivalanilides

2-Phenylethynylanilides were synthetised in a Sonogashira reaction from the appropriate 2-iodoanilide and phenyacetylene, and 2-arylethynylpivalanilides were synthetised in a sequential Sonogashira coupling from N-(2-iodophenyl)pivalamide, 2-methylbut-3-yn-2-ol and the appropriate iodoarenes according to the general method of Kotschy.6

General procedure for the synthesis of N-(2-(phenylethynyl)aryl)pivalamides

N-(2-iodoaryl)pivalamide (5 mmol), PdCl$_2$(PPh$_3$)$_2$ (175 mg, 0.25 mmol, 5 mol%) and CuI (48 mg, 0.25 mmol, 5 mol%) were placed in a round bottomed flask, then the flask was sealed with rubber septa, evacuated and charged with argon. Diisopropylamine (20 ml) was added to the flask followed by phenylacetylene (824 µl, 7.5 mmol). The reaction mixture was stirred under argon at 50 °C until the disappearance of the starting material (TLC check, 0.5 – 2 h). The reaction mixture was cooled to room temperature, diluted with diethyl ether (20 ml), neutralised with 1 M HCl, the aqueous phase was extracted with diethyl ether (20 ml). The combined organic phases were washed with water (40 ml), dried over Na$_2$SO$_4$ and evaporated in vacuo. The crude residue was purified by column chromatography.

N-(2-(phenylethynyl)phenyl)pivalamide (1a)

Prepared according to the general procedure for 2 h. Purified by column chromatography on silica gel with hexane/ ethyl acetate 40/1 to give a pale yellow solid (919 mg, 3.31 mmol, 66%).

M. p. 61-62 °C; Rf: 0.43 (hexanes/ ethyl acetate = 10/1); $^1$H NMR (250 MHz, CDCl$_3$): δ 8.50 (d, 1H, $J = 8.4$ Hz), 8.46 (bs, 1H), 7.60 – 7.47 (m, 3H), 7.44 – 7.30 (m, 4H), 7.06 (td, 1H, $J =$ 7.6 Hz and 0.9 Hz), 1.37 (s, 9H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 176.7, 139.3, 131.7, 131.5, 129.9, 129.0, 128.7, 123.3, 122.4, 119.2, 112.1, 96.5, 84.5, 40.3, 27.8; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 3400, 2966, 1682, 1578, 1521, 1445, 1304, 1156, 752, 686, 602; HRMS m/z [M+H]$^+$ Calculated for C$_{20}$H$_{21}$NO: 292.1696; found 292.1699.

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S19
N-(4-fluoro-2-(phenylethynyl)phenyl)pivalamide (1b)

Prepared according to the general procedure from N-(4-fluoro-2-iodophenyl)pivalamide (321.1 mg, 1 mmol) and phenylacetylene (165 µl, 1.5 mmol) with PdCl$_2$(PPh$_3$)$_2$ (35.1 mg, 0.05 mmol) and CuI (9.5 mg, 0.05 mmol) in diisopropylamine (8 ml) for 6 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 50/1 to give a pale yellow solid (272 mg, 0.92 mmol, 92%).

M. p. 77-78 °C; Rf: 0.54 (hexanes/ethyl acetate = 7/1); $^1$H NMR (250 MHz, CDCl$_3$): δ 8.44 (dd, 1H, $J$ = 9.2 Hz and 5.2 Hz), 8.34 (bs, 1H), 7.55-7.51 (m, 2H), 7.41-7.39 (m, 3H), 7.19 (dd, 1H, $J$ = 8.7 Hz and 3.0 Hz), 7.06 (td, 1H, $J$ = 9.2 Hz and 3.0 Hz), 1.36 (s, 9H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 176.4, 156.0, 135.5 (d, $J$ = 2.8 Hz), 131.4, 129.2, 128.6, 121.8, 120.7 (d, $J$ = 8.3 Hz), 117.7 (d, $J$ = 24.4 Hz), 116.6 (d, $J$ = 22.1 Hz), 113.5 (d, $J$ = 9.7 Hz), 97.1, 83.4 (d, $J$ = 3.2 Hz), 40.0, 27.6; IR $\nu_{max}$/cm$^{-1}$ (solid): 3401, 2959, 1679, 1519, 1415, 1296, 1187, 1150, 953, 872, 828, 754, 690, 590, 525; HRMS m/z [M+H]$^+$ Calculated for C$_{19}$H$_{18}$FNO 296.1445; found 296.1451.

methyl 4-(phenylethynyl)-3-pivalamidobenzoate (1c)

Prepared according to the general procedure from methyl 4-ido-3-pivalamidobenzoate (180.6 mg, 0.5 mmol) and phenylacetylene (82.4 µl, 0.75 mmol) with PdCl$_2$(PPh$_3$)$_2$ (17.5 mg, 0.025 mmol) and CuI (4.8 mg, 0.025 mmol) in diisopropylamine (5 ml) for 2 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 5/1 to give a pale yellow solid (138 mg, 0.41 mmol, 82%).

M. p. 138-139 °C; Rf: 0.46 (hexanes/ethyl acetate = 5/1); $^1$H NMR (250 MHz, CDCl$_3$): δ 9.12 (d, 1H, $J$ = 1.6 Hz), 8.45 (bs, 1H), 7.75 (dd, 1H $J$ = 8.1 Hz and 1.6 Hz), 7.56-7.51 (m, 3H), 7.41 (d, 2H, $J$ = 2.4 Hz), 7.39 (t, 1H, $J$ = 1.1 Hz), 3.90 (s, 3H), 1.37 (s, 9H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 176.7, 166.4, 139.0, 131.4, 130.9, 129.3, 128.7, 124.3, 121.7, 119.9, 116.3, 98.8, 83.8, 52.2, 40.2, 27.6; IR $\nu_{max}$/cm$^{-1}$ (solid): 3410, 2951, 1721, 1697, 1568, 1527, 1422, 1283, 1232, 1144, 1116, 754, 690, 584, 478; HRMS m/z [M+H]$^+$ Calculated for C$_{21}$H$_{21}$NO$_3$ 336.1594; found 336.1596.
N-(5-chloro-2-(phenylethynyl)phenyl)pivalamide (1d)

Prepared according to the general procedure from N-(5-chloro-2-iodophenyl)pivalamide (337.6 mg, 1 mmol) and phenylacetylene (165 µl, 1.5 mmol) with PdCl₂(PPh₃)₂ (35.1 mg, 0.05 mmol) and CuI (9.5 mg, 0.05 mmol) in diisopropylamine (8 ml) for 2 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 50/1 to give a pale yellow solid (293 mg, 0.94 mmol, 94%).

M. p. 97-98 °C; Rf: 0.57 (hexanes/ethyl acetate = 7/1); \(^1\)H NMR (250 MHz, CDCl₃): δ 8.61 (d, 1H, \(J = 2.1\) Hz), 8.44 (bs, 1H), 7.54 (d, 1H, \(J = 2.7\) Hz), 7.51 (d, 1H, \(J = 3.6\) Hz), 7.42-7.38 (m, 4H), 7.04 (dd, 1H, \(J = 8.4\) Hz and 2.1 Hz), 1.36 (s, 9H); \(^1^3\)C NMR (62.5 MHz, CDCl₃): δ 176.7, 139.9, 135.6, 132.1, 131.3, 129.1, 128.6, 123.3, 121.9, 119.2, 110.3, 97.2, 83.5, 40.2, 27.5; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 3412, 2953, 1684, 1567, 1509, 1415, 1215, 1109, 912, 880, 805, 753, 686, 594; HRMS m/z [M+H]+ Calculated for C₁₉H₁₈ClNO: 312.1150; found 312.1155.

General procedure for the one-pot synthesis of 2-arylethynylpivalanilides

N-(2-iodophenyl)pivalamide (1.516 g, 5 mmol), PdCl₂(PPh₃)₂ (105 mg, 0.15 mmol, 3 mol%) and CuI (29 mg, 0.15 mmol, 3 mol%) were placed in a round bottomed flask, then the flask was sealed with rubber septa, evacuated and charged with argon. Next diisopropylamine (20 ml) was added to the flask followed by 2-methyl-but-3-yn-2-ol (533 µl, 5.5 mmol). The reaction mixture was stirred under argon at room temperature for 30 minutes (TLC check). Then KOH (1.403 g, 25 mmol) and the appropriate aryl halide (5.5 mmol) was added to the reaction mixture, and it was stirred at 110°C for the indicated time. The reaction mixture was cooled to room temperature, diluted with diethyl ether (20 ml), neutralised with 1 M HCl, the aqueous phase was extracted with diethyl ether (20 ml). The combined organic phases were washed with water (40 ml), dried over Na₂SO₄ and evaporated in vacuo. The crude residue was purified by column chromatography.

N-(2-((4-methoxyphenyl)ethynyl)phenyl)pivalamide (1e)

Prepared according to the general procedure from N-(2-iodophenyl)pivalamide and 4-iodoanisole (1.287 g, 5.5 mmol) for 2 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 10/1 to give a yellow solid (823 mg, 2.68 mmol, 54%).
N-(2-((2-methylphenyl)ethynyl)phenyl)pivalamide (1f)

Prepared according to the general procedure from N-(2-iodophenyl)pivalamide and 2-iodotoluene (700 µl, 5.5 mmol) for 1 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 25/1 to give a yellow oil (882 mg, 3.02 mmol, 61%).

Rf: 0.53 (hexanes/ethyl acetate = 7/1); \(^1\)H NMR (250 MHz, CDCl\(_3\)): δ 8.36 (d, 1H, 8.4 Hz), 8.28 (bs, 1H), 7.35 (td, 2H, 7.6 Hz and 1.4 Hz), 7.21 (td, 1H, 7.1 Hz and 1.6 Hz), 7.15-7.02 (m, 3H), 6.91 (td, 1H, J = 7.6 Hz and 1.1 Hz), 2.39 (s, 3H), 1.20 (s, 9H); \(^1\)^3C NMR (62.5 MHz, CDCl\(_3\)): δ 176.7, 140.1, 139.0, 131.8, 131.7, 129.84, 129.8, 129.1, 125.9, 123.3, 122.2, 119.2, 112.3, 95.4, 88.2, 40.2, 27.7, 20.9; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (thin film): 3410, 2960, 1684, 1577, 1513, 1445, 1303, 1156, 750; HRMS m/z [M+H]^+ Calculated for C\(_{20}\)H\(_{21}\)NO: 292.1696; found 292.1706.

N-(2-((3-methylphenyl)ethynyl)phenyl)pivalamide (1g)

Prepared according to the general procedure from N-(2-iodophenyl)pivalamide and 3-iodotoluene (706 µl, 5.5 mmol) for 2 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 50/1 to give a pale yellow solid (842 mg, 2.89 mmol, 58%).

M. p. 62-63 °C; Rf: 0.55 (hexanes/ethyl acetate = 7/1); \(^1\)H NMR (250 MHz, CDCl\(_3\)): δ 8.35 (d, 1H, 8.4 Hz), 7.35 (dd, 1H, J = 7.7 Hz and 1.4 Hz), 7.24-7.21 (m, 2H), 7.18-7.04 (m, 3H), 6.92 (td, 1H, J = 7.6 Hz and 1.1 Hz), 2.23 (s, 3H), 1.23 (s, 9H) (one peak NH missing due to overlap); \(^1\)^3C NMR (62.5 MHz, CDCl\(_3\)): δ 176.7, 139.3, 138.5, 132.1, 131.6, 129.9, 129.8, 128.62, 128.55, 123.3, 122.2, 119.2, 112.2, 95.6, 84.2, 40.3, 27.8, 21.4; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 3414, 2964, 1684, 1577, 1513, 1443, 1303, 1152, 757, 686, 574, 440; HRMS m/z [M+H]^+ Calculated for C\(_{20}\)H\(_{21}\)NO: 292.1696; found 292.1706.
N-(2-((4-methylphenyl)ethynyl)phenyl)pivalamide (1h)

Prepared according to the general procedure from N-(2-iodophenyl)pivalamide and 4-iodotoluene (1.199 g, 5.5 mmol) for 2.5 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 75/1 to give a pale yellow solid (940 mg, 3.23 mmol, 65%).

M. p. 90-91 °C; Rf: 0.41 (hexanes/ethyl acetate = 7/1); $^1$H NMR (250 MHz, CDCl$_3$): δ 8.49 (d, 1H, $J = 8.4$ Hz), 7.49 (dd, 1H, $J = 7.7$ Hz and 1.4 Hz), 7.43 (d, 2H, $J = 8.1$ Hz), 7.34 (td, 1H, $J = 7.3$ Hz and 1.4 Hz), 7.20 (d, 2H, $J = 8.1$ Hz), 7.06 (t, 1H, $J = 7.4$ Hz), 2.39 (s, 3H), 1.37 (s, 9H) (one peak NH missing due to overlap); $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 176.7, 139.3, 139.2, 131.6, 131.4, 129.7, 129.5, 123.3, 119.4, 119.1, 112.3, 96.8, 83.9, 40.3, 27.8, 21.6; IR $\nu_{\max}$/cm$^{-1}$ (solid): 3410, 2968, 1679, 1575, 1509, 1445, 1304, 1161, 812, 764, 588, 476; HRMS m/z [M+H]$^+$ Calculated for C$_{20}$H$_{21}$NO: 292.1696; found 292.1694.

N-(2-((2-bromophenyl)ethynyl)phenyl)pivalamide (1i)

Prepared according to the general procedure from N-(2-iodophenyl)pivalamide and 1-bromo-2-iodobenzene (706 µl, 5.5 mmol) for 1.5 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 100/1 to give a pale yellow solid (1220 mg, 3.42 mmol, 69%).

M. p. 58-59 °C; Rf: 0.52 (hexanes/ethyl acetate = 7/1); $^1$H NMR (250 MHz, CDCl$_3$): δ 8.41 (d, 1H, 8.4 Hz), 8.31 (bs, 1H), 7.55 (dd, 1H, $J = 7.9$ Hz and 1.1 Hz), 7.46 (ddd, 2H, $J = 7.6$ Hz and 2.9 Hz and 1.8 Hz), 7.32-7.24 (m, 2H), 7.14 (td, 1H, $J = 7.9$ Hz and 1.6 Hz), 6.99 (td, 1H, $J = 7.4$ Hz and 1.1 Hz), 1.26 (s, 9H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 176.9, 139.4, 133.4, 132.7, 132.2, 130.3, 130.2, 127.4, 125.4, 124.7, 123.3, 119.5, 111.7, 94.7, 89.0, 40.2, 27.8; IR $\nu_{\max}$/cm$^{-1}$ (solid): 3413, 2952, 1677, 1575, 1514, 1443, 1304, 1162, 1024, 920, 749, 546; HRMS m/z [M+H]$^+$ Calculated for C$_{19}$H$_{18}$BrNO: 356.0645; found 356.0638.
N-(2-((3-bromophenyl)ethynyl)phenyl)pivalamide (1j)

Prepared according to the general procedure from N-(2-iodophenyl)pivalamide and 1-bromo-3-iodobenzene (702 µl, 5.5 mmol) for 2.5 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 50/1 to give a pale yellow solid (1278 mg, 3.59 mmol, 72%).

M. p. 74-75 °C; Rf: 0.51 (hexanes/ethyl acetate = 7/1); \(^1\)H NMR (250 MHz, CDCl\(_3\)): δ 8.34 (d, 1H, \(J = 8.5\) Hz), 8.23 (bs, 1H), 7.53 (t, 1H, \(J = 1.6\) Hz), 7.40-7.29 (m, 3H), 7.23 (td, 1H, \(J = 7.4\) Hz and 1.4 Hz), 7.11 (t, 1H, \(J = 7.9\) Hz), 6.93 (td, 1H, \(J = 7.4\) Hz and 1.1 Hz), 1.23 (s, 9H); \(^13\)C NMR (62.5 MHz, CDCl\(_3\)): δ 176.6, 139.4, 134.2, 132.1, 131.8, 130.3, 130.2, 129.9, 124.4, 123.4, 122.5, 119.3, 111.6, 94.8, 85.9, 40.3, 27.8; IR \(v_{\text{max}}/\text{cm}^{-1}\) (solid): 3398, 2969, 1672, 1579, 1520, 1523, 1446, 1304, 1160, 1068, 1008, 821, 751, 594, 476; HRMS m/z [M+H]+ Calculated for C\(_{19}\)H\(_{18}\)BrNO: 356.0645; found 356.0649.

N-(2-((4-bromophenyl)ethynyl)phenyl)pivalamide (1k)

Prepared according to the general procedure from N-(2-iodophenyl)pivalamide and 1-bromo-4-iodobenzene (1.556 g, 5.5 mmol) for 0.75 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 50/1 to give a pale yellow solid (1461 mg, 4.10 mmol, 82%).

M. p. 97-98 °C; Rf: 0.49 (hexanes/ethyl acetate = 7/1); \(^1\)H NMR (250 MHz, CDCl\(_3\)): δ 8.47 (d, 1H, \(J = 8.2\) Hz), 8.37 (bs, 1H), 7.55-7.47 (m, 3H), 7.39-7.33 (m, 3H), 7.06 (td, 1H, \(J = 7.6\) Hz and 1.1 Hz), 1.35 (s, 9H); \(^13\)C NMR (62.5 MHz, CDCl\(_3\)): δ 176.6, 139.3, 132.8, 132.1, 131.7, 130.2, 128.4, 123.4, 121.4, 119.4, 111.8, 95.4, 85.8, 40.3, 27.8; IR \(v_{\text{max}}/\text{cm}^{-1}\) (solid): 3386, 2924, 1673, 1574, 1518, 1441, 1302, 1160, 1068, 1008, 821, 751, 594, 476; HRMS m/z [M+H]+ Calculated for C\(_{19}\)H\(_{18}\)BrNO: 356.0645; found 356.0646.

N-(2-((4-fluorophenyl)ethynyl)phenyl)pivalamide (1l)
Prepared according to the general procedure from N-(2-iodophenyl)pivalamide and 1-fluoro-4-iodobenzene (634 µl, 5.5 mmol) for 1.5 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 30/1 to give a pale yellow solid (849 mg, 2.90 mmol, 58%).

M. p. 98-100 °C; Rf: 0.45 (hexanes/ethyl acetate = 7/1) 1H NMR (250 MHz, CDCl3): δ 8.48 (d, 1H, J = 8.4 Hz), 8.40 (bs, 1H), 7.53-7.46 (m, 3H), 7.35 (td, 1H, J = 7.8 Hz and 1.4 Hz), 7.12-7.02 (m, 3H), 1.36 (s, 9H); 13C NMR (62.5 MHz, CDCl3): δ 176.6, 162.9 (d, J = 250.9 Hz), 139.3, 133.4 (d, J = 8.4 Hz), 131.6, 130.0, 123.3, 119.3, 118.5 (d, J = 3.6 Hz), 116.1 (d, J = 22.2 Hz), 111.9, 95.4, 84.3, 40.2, 27.8; IR νmax/cm−1 (solid): 3394, 2964, 1677, 1575, 1504, 1448, 1307, 1218, 1156, 829, 749, 597; HRMS m/z [M+H]+ Calculated for C19H18FNO: 296.1445; found 296.1442.

N-(2-((4-nitrophenyl)ethynyl)phenyl)pivalamide (1m)

Prepared according to the general procedure from N-(2-iodophenyl)pivalamide and 1-iodo-4-nitrobenzene (1.370 g, 5.5 mmol) for 1.5 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 15/1 to give a yellow solid (271 mg, 0.84 mmol, 17%).

M. p. 141-142 °C; Rf: 0.31 (hexanes/ethyl acetate = 7/1) 1H NMR (250 MHz, CDCl3): δ 8.47 (d, 1H, J = 8.4 Hz), 8.30 (bs, 1H), 8.25 (d, 2H, J = 8.8 Hz), 7.65 (d, 2H, J = 8.8 Hz), 7.52 (dd, 1H, J = 7.7 Hz and 1.4 Hz), 7.40 (td, 1H, J = 8.7 Hz and 1.4 Hz), 7.09 (td, 1H, J = 7.6 Hz and 0.9 Hz), 1.37 (s, 9H); 13C NMR (62.5 MHz, CDCl3): δ 176.6, 147.4, 139.5, 132.1, 132.1, 131.0, 129.2, 124.0, 123.5, 119.6, 111.0, 94.4, 89.8, 40.3, 27.7; IR νmax/cm−1 (solid): 3416, 2203, 1687, 1592, 1514, 1442, 1338, 844, 744, 577, 478; HRMS m/z [M+H]+ Calculated for C19H18N2O3: 323.1390; found 323.1403.

N-(2-((4-chlorophenyl)ethynyl)phenyl)pivalamide (1n)

Prepared according to the general procedure from N-(2-iodophenyl)pivalamide and 1-chloro-4-iodobenzene (1.311 g, 5.5 mmol) for 3 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 75/1 to give a yellow solid (1188 mg, 3.81 mmol, 76%).

M. p. 85-86 °C; Rf: 0.53 (hexanes/ethyl acetate = 7/1) 1H NMR (250 MHz, CDCl3): δ 8.48 (d, 1H, J = 8.4 Hz), 8.38 (bs, 1H), 7.50-7.42 (m, 3H), 7.39-7.33 (m, 3H), 7.06 (td, 1H, J = 7.6 Hz and 1.1 Hz), 1.36 (s, 9H); 13C NMR (62.5 MHz, CDCl3): δ 176.6, 139.3, 135.1, 132.7, 131.7, 130.2, 129.1, 123.4, 120.9, 119.3, 111.8, 95.3, 85.6, 40.3, 27.8; IR νmax/cm−1 (solid):
N-(2-((3-(trifluoromethyl)phenyl)ethynyl)phenyl)pivalamide (1o)

Prepared according to the general procedure from N-(2-iodophenyl)pivalamide and 1-iodo-3-trifluoromethylbenzene (772 µl, 5.5 mmol) for 2.5 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 50/1 to give a yellow solid (625 mg, 1.81 mmol, 36%).

M. p. 82-83 °C; Rf: 0.47 (hexanes/ethyl acetate = 7/1) 1H NMR (250 MHz, CDCl3): δ 8.49 (d, 1H, J = 8.3 Hz), 8.37 (s, 1H), 7.79 (s, 1H), 7.66 (dd, 2H, J = 13.3 Hz and 7.8 Hz), 7.52 (t, 2H, J = 7.5 Hz), 7.38 (t, 1H, J = 7.9 Hz), 7.08 (t, 1H, J = 7.6 Hz), 1.37 (s, 9H); 13C NMR (62.5 MHz, CDCl3): δ 176.7, 139.5, 134.4, 131.9, 131.7, 130.5, 129.4, 128.28 (q, J = 3.9 Hz), 125.9, 125.5 (q, J = 3.6 Hz), 123.5, 121.5, 119.5, 111.5, 94.8, 86.3, 40.3, 27.8; IR νmax/cm⁻¹ (solid): 3408, 2960, 1677, 1577, 1517, 1447, 1336, 1304, 1158, 1122, 1068, 888, 759, 688, 601; HRMS m/z [M+H]+ Calculated for C19H18ClNO: 312.1150; found 312.1163.

N-(2-((naphthalen-1-ylethynyl)phenyl)pivalamide (1p)

Prepared according to the general procedure from N-(2-iodophenyl)pivalamide and 1-iodonaphthalene (803 µl, 5.5 mmol) for 3 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 50/1 to give a yellow solid (907 mg, 2.77 mmol, 55%).

M. p. 89-91 °C; Rf: 0.42 (hexanes/ethyl acetate = 7/1) 1H NMR (250 MHz, CDCl3): δ 8.55 (d, 1H, J = 8.0 Hz), 8.41 (d, 1H, J = 7.6 Hz), 7.91 (d, 2H, J = 8.5 Hz), 7.77 (dd, 1H, J = 7.1 Hz and 0.8 Hz), 7.61 (ddd, 3H, J = 8.1 Hz and 7.3 Hz and 1.4 Hz), 7.50 (dd, 1H, J = 8.1 Hz and 7.3 Hz), 7.45 – 7.36 (m, 1H), 7.12 (td, 1H, J = 7.6 Hz and 1.0 HzH), 1.34 (s, 9H) (one peak, NH is missing due to overlap); 13C NMR (62.5 MHz, CDCl3): δ 176.8, 139.4, 133.4, 133.1, 131.9, 130.5, 130.1, 129.6, 128.6, 127.2, 126.8, 126.1, 125.4, 123.4, 120.1, 119.4, 112.3, 94.6, 89.3, 40.3, 27.8; IR νmax/cm⁻¹ (solid): 3401, 2960, 1686, 1578, 1514, 1442, 1304, 1151, 798, 773, 744, 591, 547, 432; HRMS m/z [M+H]+ Calculated for C20H18F3NO: 346.1413; found: 346.1424.
ethyl 4-{(2-pivalamidophenyl)ethynyl}benzoate\(^7\) (1q)

N-(2-iodophenyl)pivalamide (606.3 mg, 2.0 mmol), PdCl\(_2\)(PPh\(_3\))\(_2\) (42.1 mg, 0.06 mmol, 3 mol\%) and CuI (11.4 mg, 0.06 mmol, 3 mol\%) were placed in a round bottomed flask, then the flask was sealed with rubber septa, evacuated and charged with argon. Diisopropylamine (10 ml) was added to the flask, the reaction mixture was stirred, and ethynyltrimethylsilane (311 µl, 2.2 mmol, 1.1 eq.) was added dropwise. The reaction mixture was stirred under argon at room temperature until the disappearance of the starting material (TLC check, 0.5 h). Then tetrabutylammonium fluoride hydrate (575 mg, 2.2 mmol) and ethyl 4-iodobenzoate (607.4 µl, 2.2 mmol) was added to the reaction mixture, and it was stirred at room temperature for 4 h. The reaction mixture was diluted with diethyl ether (15 ml), neutralised with 1 M HCl, the aqueous phase was extracted with diethyl ether (2*15 ml). The combined organic phases were washed with water (2*20 ml), dried over Na\(_2\)SO\(_4\) and evaporated in vacuo. The crude residue was purified column chromatography on silica gel with hexane/ ethyl acetate 20/1 to give an off-white solid (239 mg, 0.68 mmol, 34%).

M. p. 93-94 °C; Rf: 0.33 (hexanes/ ethyl acetate = 7/1); \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta\) 8.47 (d, 1H, \(J = 8.4\) Hz), 8.38 (s, 1H), 8.06 (d, 2H, \(J = 8.4\) Hz), 7.57 (d, 2H, \(J = 8.3\) Hz), 7.50 (dd, 1H, \(J = 7.6\) Hz and 1.3 Hz), 7.38 (dd, 1H, \(J = 11.3, 4.5\) Hz), 7.07 (t, 1 H, \(J = 7.6\) Hz), 4.39 (q, 2H, \(J = 7.1\) Hz), 1.40 (t, 3H, \(J = 7.1\) Hz), 1.36 (s, 9H); \(^13\)C NMR (62.5 MHz, CDCl\(_3\)): \(\delta\) 176.7, 165.9, 139.4, 131.8, 131.3, 130.6, 130.4, 129.8, 126.9, 123.4, 119.4, 111.6, 95.7, 87.4, 77.7, 77.2, 76.7, 61.4, 40.3, 27.8, 14.4; IR \(\nu_{max}/\text{cm}^{-1}\) (solid): 3408, 2960, 1677, 1577, 1517, 1447, 1336, 1304, 1158, 1122, 1068, 888, 759, 688, 601; HRMS m/z [M+H]\(^+\) Calculated for C\(_{22}\)H\(_{23}\)NO\(_3\): 350.1751; found 350.1753.

diluted with diethyl ether (20 ml), neutralised with 1 M HCl, the aqueous phase was extracted with diethyl ether (20 ml). The combined organic phases were washed with 5% NaHCO₃ solution (20 ml), with water (2*20 ml), dried over Na₂SO₄ and evaporated in vacuo. The crude residue was purified by column chromatography on silica gel with hexane/ethyl acetate 15/1. The product was obtained as an off white solid (1023 mg, 3.97 mmol, 80%). M. p. 65-67 °C; Rf: 0.60 (hexanes/ethyl acetate = 7/1); $^1$H NMR (250 MHz, CDCl₃): δ 8.43 (d, 1H, $J = 8.4$ Hz), 8.39 (s, 1H), 7.36 (dd, 1H, $J = 7.7$ Hz and 1.2 Hz), 7.32 – 7.23 (m, 1H), 2.51 (t, 2H, $J = 6.9$ Hz), 1.63 (dt, 2H, $J = 14.6$ Hz and 7.1 Hz), 1.48 (dt, 2H, $J = 14.0$ Hz and 7.0 Hz), 1.34 (s, 9H), 0.96 (t, 3H, $J = 7.2$ Hz); $^{13}$C NMR (62.5 MHz, CDCl₃): δ 176.6, 139.3, 131.5, 129.0, 123.1, 118.9, 112.8, 97.9, 76.2, 40.2, 31.0, 27.7, 22.2, 19.3, 13.7; IR ν$_{\text{max}}$/cm$^{-1}$ (solid): 3404, 2956, 2870, 1677, 1578, 1516, 1442, 1304, 1154, 761, 736, 597; HRMS m/z [M+H]$^+$ Calculated for C$_{17}$H$_{23}$NO: 258.1852; found 258.1852.

**Synthesis of 2-(phenylethynyl)aniline (1s)**

![Structure of 2-(phenylethynyl)aniline](image)

2-idoaniline (1.095 g, 5 mmol), PdCl$_2$(PPh$_3$)$_2$ (70.2 mg, 0.1 mmol, 2 mol%) and CuI (9.5 mg, 0.05 mmol, 1 mol%) were placed in a round bottomed flask, then the flask was sealed with rubber septa, evacuated and charged with argon. Diisopropylamine (20 ml) was added to the flask followed by phenylacetylene (824 µl, 7.5 mmol). The reaction mixture was stirred under argon at room temperature until the disappearance of the starting material (TLC check, 1 h). The reaction mixture was diluted with diethyl ether (20 ml), neutralised with 1 M HCl, the aqueous phase was extracted with diethyl ether (2*20 ml). The combined organic phases were washed with water (2*20 ml), dried over MgSO₄ and evaporated in vacuo. The crude residue was purified by column chromatography on silica gel with hexane/ethyl acetate 25/1. The product was obtained as a white solid (770 mg, 3.98 mmol, 80%). M. p. 92-93 °C; Rf: 0.47 (hexanes/ethyl acetate = 5/1); $^1$H NMR (250 MHz, CDCl₃): δ 7.57 (d, 1H, $J = 4.4$ Hz), 7.55 (d, 1H, $J = 2.0$ Hz), 7.44 – 7.34 (m, 4H), 7.21 – 7.13 (m, 1H), 6.80 – 6.71 (m, 2H), 4.23 (s, 2H); $^{13}$C NMR (62.5 MHz, CDCl₃): δ 147.9, 132.3, 131.6, 129.8, 128.5, 128.3, 123.4, 118.1, 114.5, 108.0, 94.8, 86.0; IR ν$_{\text{max}}$/cm$^{-1}$ (solid): 3462, 2956, 1611, 1482, 1453, 1309, 1258, 744, 688, 479;

**General procedure for the synthesis of 2-phenylethynylanilides**

2-(phenylethynyl)aniline (154.6 mg, 0.8 mmol) and triethylamine (122.8 µl, 0.88 mmol, 1.1 eq.) were solubilised in dichloromethane (5 ml), and cooled to 0 °C. A solution of benzoyl chloride (0.88 mmol, 1.1 eq.) in dichloromethane (2 ml) was added dropwise. The reaction was stirred at room temperature for 8 – 24 hours (TLC check). The reaction mixture was poured into water (20 ml), extracted with dichloromethane (3*15 ml). The combined organic
phases were washed with brine (2*20 ml), dried over MgSO$_4$ and evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel.

**N-(2-(phenylethynyl)phenyl)benzamide (1t)**

Prepared according to the general procedure with benzoyl chloride (102.2 µl, 0.88 mmol) for 8 hours. Purified by column chromatography on silica gel with hexane/ethyl acetate 10/1 to afford a yellow solid (216 mg, 0.72 mmol, 91%).

M. p. 112-113 °C; Rf: 0.46 (hexanes/ethyl acetate = 10/1); $^1$H NMR (250 MHz, CDCl$_3$): δ 8.86 (s, 1H), 8.54 (d, 1H, $J$ = 8.3 Hz), 7.87 (d, 2H, $J$ = 7.1 Hz), 7.48 – 7.24 (m, 10H), 7.02 (t, 1H, $J$ = 7.6 Hz); $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 165.2, 139.2, 135.0, 132.2, 131.6, 131.5, 130.0, 129.1, 129.0, 128.8, 128.4, 127.1, 123.7, 122.4, 119.3, 112.4, 97.1, 84.6; IR ν$_{max}$/cm$^{-1}$ (solid): 3294, 1650, 1574, 1521, 1489, 1443, 1309, 749, 686, 627, 485; HRMS m/z [M+H]$^+$ Calculated for C$_{21}$H$_{15}$NO: 298.1232; found: 298.1226.

**4-nitro-N-(2-(phenylethynyl)phenyl)benzamide (1u)**

Prepared according to the general procedure with 4-nitrobenzoyl chloride (163.5 mg, 0.88 mmol) for 24 hours. Purified by column chromatography on silica gel with hexane/ethyl acetate 5/1 to afford a yellow solid (190 mg, 0.55 mmol, 69%).

M. p. 172-173 °C; Rf: 0.41 (hexanes/ethyl acetate = 5/1); $^1$H NMR (250 MHz, CDCl$_3$): δ 8.92 (s, 1H), 8.57 (d, 1H, $J$ = 8.3 Hz), 8.32 (d, 2H, $J$ = 8.8 Hz), 8.10 (d, 2H, $J$ = 8.8 Hz), 7.60 – 7.54 (m, 1H), 7.53 – 7.45 (m, 2H), 7.45 – 7.35 (m, 4H), 7.17 (td, 1H, $J$ = 7.6 Hz and 0.8 Hz); $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 163.0, 140.5, 138.5, 131.8, 131.5, 130.1, 129.5, 129.0, 128.3, 124.5, 124.3, 122.1, 119.5, 112.8, 97.5, 84.3; IR ν$_{max}$/cm$^{-1}$ (solid): 3282, 1652, 1577, 1531, 1509, 1448, 1347, 1312, 851, 757, 713, 688, 642, 482; HRMS m/z [M+H]$^+$ Calculated for C$_{21}$H$_{14}$N$_2$O$_3$: 343.1077; found 343.1079.
4-methoxy-N-(2-(phenylethynyl)phenyl)benzamide (1v)

Prepared according to the general procedure with 4-nitrobenzoyl chloride (119.2 mg, 0.88 mmol) for 18 hours. Purified by column chromatography on silica gel with hexane/ethyl acetate 10/1 to afford a yellow solid (250 mg, 0.76 mmol, 95%).
M. p. 113-114 °C; Rf: 0.31 (hexanes/ethyl acetate = 5/1); $^1$H NMR (250 MHz, CDCl$_3$): δ 8.87 (s, 1H), 8.62 (d, 1H, $J$ = 8.3 Hz), 7.93 (d, 2H, $J$ = 8.8 Hz), 7.61 – 7.49 (m, 3H), 7.40 (dd, 4H, $J$ = 3.8 Hz and 2.6 Hz), 7.10 (td, 1H, $J$ = 7.6 Hz and 0.8 Hz), 6.96 (d, 2H, $J$ = 8.8 Hz), 3.87 (s, 3H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 164.7, 162.8, 139.5, 131.6, 131.5, 130.0, 129.1, 129.0, 128.8, 127.3, 123.4, 122.5, 119.2, 114.2, 112.2, 97.0, 84.8, 55.6; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 3418, 1676, 1604, 1577, 1504, 1443, 1303, 1243, 1171, 1019, 837, 754, 686, 539, 474; HRMS m/z [M+H]$^+$ Calculated for C$_{22}$H$_{17}$NO$_2$: 328.1332; found 328.1334.

N-(2-(phenylethynyl)phenyl)acetamide (1w)

Prepared according to the general procedure with acetyl chloride (85.4 µl, 1.2 mmol, 1.5 eq.) for 8 hours. Purified by column chromatography on silica gel with hexane/ethyl acetate 5/1 to afford a yellow solid (184 mg, 0.78 mmol, 97%).
M. p. 121-122 °C; Rf: 0.22 (hexanes/ethyl acetate = 5/1); 1H NMR (250 MHz, CDCl$_3$): δ 8.42 (d, 1H, $J$ = 8.3 Hz), 7.99 (s, 1H), 7.60 – 7.52 (m, 2H), 7.50 (dd, 1H, $J$ = 7.8 and 1.4 Hz), 7.44 – 7.37 (m, 3H), 7.36 – 7.30 (m, 1H), 7.08 (t, 1H, $J$ = 7.5 Hz), 2.25 (s, 3H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 168.3, 139.0, 131.8, 131.6, 129.9, 129.1, 128.7, 123.5, 122.5, 119.5, 96.5, 84.4, 25.1; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 3302, 1660, 1577, 1528, 1492, 1445, 1367, 1302, 750, 685, 649, 600, 553, 483; HRMS m/z [M+H]$^+$ Calculated for C$_{16}$H$_{13}$NO: 236.1070; found 236.1078.
6. Synthesis and Analytical Data of Iodonium Salts

Aryl-mesityliodonium triflates were synthetised in a one-pot procedure from the appropriate iodoarene and mesitylene according to the geneearal method of Olofsson.\(^8\)

**General procedure for the one-pot synthesis of aryl-mesityliodonium triflates**

\(m\)-Chloroperbenzoic acid (65% active oxidant, 1.320 g, 5.0 mmol) and the appropriate iodoarene (4.5 mmol) were dissolved in CH\(_2\)Cl\(_2\) (20 ml). Mesitylene (696 µl, 5.0 mmol) was added and the solution was cooled to 0 °C. Trifluoromethanesulfonic acid (825 µl, 5.5 mmol) was added dropwise over 5 and the reaction mixture was allowed to warm to room temperature over 2h. The volatile components were removed in vacuo/ evaporated under reduced pressure and the resulting material was suspended in Et\(_2\)O (20 ml). The suspension was stored at -20 °C for 2h. The resulting crystals were filtered under reduced pressure and were washed on the filter with Et\(_2\)O to give the appropriate aryl-mesityliodonium triflate as a solid, which was dried at 100 °C under vacuum.

**Mesityl(phenyl)iodonium trifluoromethanesulfonate (2a)**

![Image of 2a]

Prepared according to the general procedure from iodobenzene. The product was obtained as a white solid (1.436 g, 3.04 mmol, 68%). M. p. 147-148 °C; \(^1^H\) NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 7.99 (d, 2H, \(J = 7.8\) Hz), 7.64 (t, 1H, \(J = 7.3\) Hz), 7.50 (t, 2H, \(J = 7.6\) Hz), 7.22 (s, 2H), 2.60 (s, 6H), 2.29 (s, 3H); \(^1^C\) NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 143.2, 141.6, 134.6, 131.9, 131.8, 129.8, 122.6, 114.6, 26.3, 20.6; IR \(v_{\text{max}}/\text{cm}^{-1}\) (solid): 1443, 1246, 1157, 1025, 856, 742, 632, 572, 515, 454; HRMS m/z [M-OTf]\(^+\) Calculated for C\(_{15}\)H\(_{16}\)I: 323.0291; found 323.0289.

**2-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (2b)**

![Image of 2b]

Prepared according to the general procedure from 2-iodotoluene. The product was obtained as a white solid (2.023 g, 4.16 mmol, 93%). M. p. 166-167 °C; \(^1^H\) NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 7.97 (d, 1H, \(J = 8.0\) Hz), 7.55 (d, 2H, \(J = 4.3\) Hz), 7.26 (dd, 1H, \(J = 8.3\) Hz and 4.1 Hz), 7.21 (s, 2H), 2.57 (s, 9H), 2.29 (s, 3H); \(^1^C\) NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 143.0, 141.7, 140.8, 136.8, 132.5, 131.9, 130.0, 129.4, 121.9, 118.6, 26.2, 24.4, 20.5; IR \(v_{\text{max}}/\text{cm}^{-1}\) (solid): 1467,

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3-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (2c)

Prepared according to the general procedure from 3-iodotoluene. The product was obtained as a white solid (1.587 g, 3.26 mmol, 73%). M. p. 171-172 °C; \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 7.86 (s, 1H), 7.77 (d, 1H, \(J = 7.7\) Hz), 7.45 (d, 1H, \(J = 7.5\) Hz), 7.38 (t, 1H, \(J = 7.7\) Hz), 7.21 (s, 2H), 2.61 (s, 6H), 2.32 (s, 3H), 2.29 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 143.1, 142.0, 141.6, 134.6, 132.5, 131.7, 131.6, 129.8, 122.4, 114.3, 26.3, 20.7, 20.5; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 1455, 1275, 1245, 1156, 1025, 634, 516; HRMS m/z [M-O\(\text{OTf}\)]\(^+\) Calculated for C\(_{16}\)H\(_{18}\)I: 337.0448; found 337.0443.

4-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (2d)

Prepared according to the general procedure from 4-iodotoluene. The product was obtained as a white solid (2.072 g, 4.26 mmol, 95%). M. p. 183-184 °C; \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 7.87 (d, 2H, \(J = 8.2\) Hz), 7.31 (d, 2H, \(J = 8.1\) Hz), 7.20 (s, 2H), 2.60 (s, 6H), 2.32 (s, 3H), 2.28 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 143.0, 142.3, 141.5, 134.5, 132.5, 129.7, 122.7, 110.9, 26.3, 20.8, 20.5; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 1452, 1246, 1157, 1024, 804, 632, 481; HRMS m/z [M-O\(\text{OTf}\)]\(^+\) Calculated for C\(_{16}\)H\(_{18}\)I: 337.0448; found 337.0444.

2-bromophenyl(mesityl)iodonium trifluoromethanesulfonate (2e)

Prepared according to the general procedure from 2-bromiodobenzene. The product was obtained as an off-white solid (1.645 g, 2.98 mmol, 66%). M. p. 167-168 °C; \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 8.18 (dd, 1H, \(J = 7.9\) Hz and 1.4 Hz), 7.95 (dd, 1H, \(J = 7.9\) Hz and 1.4 Hz), 7.59 (td, 1H, \(J = 7.7\) Hz and 1.5 Hz), 7.47 (td, 1H, \(J = 7.7\) Hz and 1.4 Hz), 7.22 (s, 2H), 2.62 (s, 6H), 2.29 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 143.3, 141.9, 139.1, 134.3, 134.2, 130.5, 130.1, 126.6, 123.0, 119.5, 26.4, 20.5; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 1442, 1276, 1241,
1160, 1025, 757, 631, 516; HRMS m/z [M-O Tf]+ Calculated for C_{15}H_{15}BrI: 400.9396; found 400.9386.

3-bromophenyl(mesityl)iodonium trifluoromethanesulfonate (2f)

Prepared according to the general procedure from 3-bromoiodobenzene. The product was obtained as an off-white solid (1.353 g, 2.45 mmol, 55%). M. p. 173-174 °C; ¥H NMR (250 MHz, DMSO-d6): δ 8.29 (s, 1H), 7.90 (d, 1H, $J = 8.0$ Hz), 7.84 (d, 1H, $J = 8.1$ Hz), 7.44 (t, 1H, $J = 8.0$ Hz), 7.23 (s, 2H), 2.60 (s, 6H), 2.30 (s, 3H); ¥C NMR (62.5 MHz, DMSO-d6): δ 143.4, 141.8, 136.2, 134.8, 133.6, 133.2, 129.9, 123.5, 122.7, 115.0, 26.4, 20.6; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 1454, 1222, 1024, 797, 634, 516; HRMS m/z [M-O Tf]+ Calculated for C_{15}H_{15}BrI: 400.9396; found 400.9402.

4-bromophenyl(mesityl)iodonium trifluoromethanesulfonate (2g)

Prepared according to the general procedure from 4-bromoiodobenzene. The product was obtained as a white solid (1.690 g, 3.07 mmol, 68%). M. p. 179-180 °C; ¥H NMR (250 MHz, DMSO-d6): δ 7.90 (d, 2H, $J = 8.5$ Hz), 7.70 (d, 2H, $J = 8.5$ Hz), 7.22 (s, 2H), 2.59 (s, 6H), 2.29 (s, 3H); ¥C NMR (62.5 MHz, DMSO-d6): δ 143.3, 141.6, 136.4, 134.7, 129.9, 125.8, 122.8, 113.1, 26.3, 20.6; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 1473, 1245, 1232, 1024, 807, 631, 518, 475; HRMS m/z [M-O Tf]+ Calculated for C_{15}H_{15}BrI: 400.9396; found 400.9402.

2-fluorophenyl(mesityl)iodonium trifluoromethanesulfonate (2h)

Prepared according to the general procedure from 2-fluoroiodobenzene. The product was obtained as an off-white solid (0.948 g, 1.93 mmol, 43%). M. p. 161-162 °C; ¥H NMR (250 MHz, DMSO-d6): δ 8.28 (dd, 1H, $J = 7.7$ Hz and 6.1 Hz and 1.5 Hz), 7.72 (tdd, 1H, $J = 7.2$ Hz and 5.7 Hz and 1.5 Hz), 7.56 (td, 1H, $J = 8.7$ Hz and 1.3 Hz), 7.35 (td, 1H, $J = 8.0$ Hz and 1.3 Hz), 7.20 (s, 2H), 2.62 (s, 6H), 2.27 (s, 3H); ¥C NMR (62.5 MHz, DMSO-d6): δ 159.57 (d, $J = 248.7$ Hz), 143.3, 141.6, 137.5, 135.43 (d, $J = 8.3$ Hz), 129.9, 127.6, 122.8, 117.18 (d, $J = 22.4$ Hz), 101.55 (d, $J = 23.6$ Hz), 26.1 (d, $J = 1.9$ Hz), 20.5; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 1476, 1279, 1236, 1161, 1027, 770, 635, 515; HRMS m/z [M-O Tf]+ Calculated for C_{15}H_{15}F1: 341.0197; found 341.0194.
4-fluorophenyl(mesityl)iodonium trifluoromethanesulfonate (2i)

Prepared according to the general procedure from 4-fluoroiodobenzene. The product was obtained as an off-white solid (1.133 g, 2.31 mmol, 51%). M. p. 178-179 °C; \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 8.06 (dd, 2H, \(J = 8.0\) Hz and 5.1 Hz), 7.37 (t, 2H, \(J = 8.6\) Hz), 7.22 (s, 2H), 2.60 (s, 6H), 2.29 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 161.8, 143.2, 141.6, 137.4 (d, \(J = 8.8\) Hz), 129.9, 123.0, 119.3 (d, \(J = 22.8\) Hz), 108.69 (d, \(J = 3.0\) Hz), 26.3, 20.6; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 1575, 1483, 1224, 1168, 1024, 849, 632, 508; HRMS m/z \([\text{M-OTf}]^+\) Calculated for C\(_{15}\)H\(_{15}\)FI: 341.0197; found 341.0195.

4-nitrophenyl(mesityl)iodonium trifluoromethanesulfonate (2j)

Prepared according to the general procedure from 4-iodonitrobenzene with the modification that all the reagents except the trifluoromethanesulfonic acid were stirred together at room temperature for 24h before the addition of the acid. The product was obtained as a white solid (0.919 g, 1.78 mmol, 40%). M. p. 207-208 °C; \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 8.26 (d, 2H, \(J = 9.1\) Hz), 8.18 (d, 2H, \(J = 9.1\) Hz), 7.25 (s, 2H), 2.59 (s, 6H), 2.31 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 149.3, 143.6, 141.8, 135.6, 130.0, 126.3, 122.8, 120.8, 26.3, 20.6; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 1534, 1483, 1242, 1157, 1024, 846, 735, 632, 574, 519, 454; HRMS m/z \([\text{M-OTf}]^+\) Calculated for C\(_{15}\)H\(_{15}\)INO\(_2\): 368.0142; found 368.0139.

2-trifluoromethylphenyl(mesityl)iodonium trifluoromethanesulfonate (2k)

Prepared according to the general procedure from 1-iodo-2-(trifluoromethyl)benzene. The product was obtained as an off-white solid (1.113 g, 2.06 mmol, 46%). M. p. 180-181 °C; \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 8.50 (d, 1H, \(J = 7.8\) Hz), 8.05 (d, 1H, \(J = 7.6\) Hz), 7.80 (t, 1H, \(J = 7.6\) Hz), 7.23 (s, 2H), 7.23 (s, 6H), 2.30 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 143.5, 142.1, 140.4, 135.8, 133.2, 130.2, 129.4 (m), 124.8, 123.2, 109.7, 26.1, 20.5; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 1588, 1431, 1309, 1244, 1164, 1132, 1024, 773, 632, 516; HRMS m/z \([\text{M-OTf}]^+\) Calculated for C\(_{16}\)H\(_{15}\)F\(_3\)I: 391.0165; found 391.0160.
3-trifluoromethylphenyl(mesityl)iodonium trifluoromethanesulfonate (2l)

Prepared according to the general procedure from 1-iodo-3-(trifluoromethyl)benzene. The product was obtained as an off-white solid (1.278 g, 2.37 mmol, 53%). M. p. 186-187 °C; \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 8.48 (s, 1H), 8.11 (d, 1H, \(J = 8.1\) Hz), 8.00 (d, 1H, \(J = 7.9\) Hz), 7.69 (t, 1H, \(J = 8.0\) Hz), 7.23 (s, 2H), 2.59 (s, 6H), 2.29 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 143.5, 141.8, 138.1, 132.9, 131.7, 131.2 (d, \(J = 4.2\) Hz), 130.0, 122.7, 114.8, 26.4, 20.6; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 1422, 1241, 1166, 1127, 1024, 804, 681, 634, 516; HRMS m/z [M-OTf]^+ Calculated for C\(_{16}\)H\(_{15}\)F\(_3\)I: 391.0165; found 391.0163.

(2-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (2m)

Prepared according to the general procedure from 1-chloro-2-iodobenzene. The product was obtained as an off-white solid (1.411 g, 2.78 mmol, 62%). M. p. 167-168 °C; \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 8.27 (dd, 1H, \(J = 8.0\) Hz and 1.2 Hz), 7.82 (dd, 1H, \(J = 8.0\) Hz and 1.4 Hz), 7.68 (td, 1H, \(J = 7.9\) Hz and 1.3 Hz), 7.45 (td, 1H, \(J = 8.0\) Hz and 1.4 Hz), 7.21 (s, 2H), 2.62 (s, 6H), 2.28 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 143.3, 141.9, 139.0, 135.8, 134.4, 130.8, 130.2, 130.0, 122.7, 116.5, 26.2, 20.5; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 1449, 1276, 1239, 1160, 759, 631, 516, 432; HRMS m/z [M-OTf]^+ Calculated for C\(_{15}\)H\(_{15}\)ClI: 356.9901; found 356.9899.

(4-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (2n)

Prepared according to the general procedure from 1-chloro-4-iodobenzene. The product was obtained as a white solid (1.367 g, 2.70 mmol, 60%). M. p. 177-178 °C; \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 7.98 (d, 2H, \(J = 8.7\) Hz), 7.57 (d, 2H, \(J = 8.7\) Hz), 7.23 (s, 2H), 2.59 (s, 6H), 2.29 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 143.3, 141.6, 137.0, 136.3, 131.8, 129.9, 122.8, 112.3, 26.3, 20.5; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 1473, 1245, 1163, 1024, 807, 631, 516; HRMS m/z [M-OTf]^+ Calculated for C\(_{15}\)H\(_{15}\)ClI: 356.9901; found 356.9901.
(2-(ethoxycarbonyl)phenyl)(mesityl)iodonium trifluoromethanesulfonate (2o)

Prepared according to the general procedure from ethyl 2-iodobenzoate with the exception that 3-chloroperoxybenzoic, acid, mesitylene and the aryl iodide were stirred together at room temperature for 4 hours before the addition of the trifluoromethanesulfonic acid. The product was obtained as a white solid (0.835 g, 1.53 mmol, 34%). M. p. 169-170 °C; $^1$H NMR (250 MHz, DMSO-d$_6$): $\delta$ 8.34 (dd, 1H, $J = 7.2$ Hz and 1.9 Hz), 7.88 – 7.68 (m, 2H), 7.41 (s, 2H), 6.89 (d, 1H, $J = 7.5$ Hz), 4.53 (q, 2H, $J = 7.1$ HzH), 2.52 (s, 6H), 2.43 (s, 3H), 1.43 (t, 3H, $J = 7.1$ Hz); $^{13}$C NMR (62.5 MHz, DMSO-d$_6$): $\delta$ 167.4, 144.6, 143.3, 137.3, 132.9, 131.4, 130.1, 128.5, 127.6, 117.8, 113.5, 63.8, 26.1, 20.7, 13.9; IR $\nu_{max}$/cm$^{-1}$ (solid): 1673, 1310, 1272, 1246, 1222, 1154, 1027, 753, 637, 515; HRMS m/z [M+OTf]$^+$ Calculated for C$_{18}$H$_{20}$IO$_2$: 395.0502; found: 395.0511.

(4-(ethoxycarbonyl)phenyl)(mesityl)iodonium trifluoromethanesulfonate (2p)

Prepared according to the general procedure from ethyl 4-iodobenzoate with the exception that 3-chloroperoxybenzoic acid, mesitylene and the aryl iodide were stirred together at room temperature for 4 hours before the addition of the trifluoromethanesulfonic acid. The product was obtained as a white solid (1.159 g, 2.13 mmol, 47%). M. p. 174-175 °C; $^1$H NMR (250 MHz, DMSO-d$_6$): $\delta$ 8.09 (d, 2H, $J = 8.6$ Hz), 7.99 (d, 2H, $J = 8.5$ Hz), 7.24 (s, 2H), 4.31 (q, 2H, $J = 7.1$ Hz), 2.59 (s, 6H), 2.30 (s, 3H), 1.30 (t, 3H, $J = 7.1$ Hz); $^{13}$C NMR (62.5 MHz, DMSO-d$_6$): $\delta$ 164.5, 143.4, 141.7, 134.7, 132.7, 131.9, 129.9, 122.6, 119.3, 61.4, 26.3, 20.5, 14.0; IR $\nu_{max}$/cm$^{-1}$ (solid): 1723, 1584, 1458, 1395, 1272, 1238, 1161, 1103, 1025, 849, 753, 634, 516; HRMS m/z [M+OTf]$^+$ Calculated for C$_{18}$H$_{20}$IO$_2$: 395.0502; found 395.0504.

(4-acetylphenyl)(mesityl)iodonium trifluoromethanesulfonate (2q)

Prepared according to the general procedure from 1-acetyl-4-iodobenzene. The product was obtained as an off-white solid (0.689 g, 1.34 mmol, 30%). M. p. 183-185 °C; $^1$H NMR (250 MHz, DMSO-d$_6$): 8.09 (d, 2H, $J = 8.2$ Hz), 7.98 (d, 2H, $J = 8.3$ Hz), 7.24 (s, 2H), 2.60 (s, 6H), 2.58 (s, 3H), 2.30 (s, 3H); $^{13}$C NMR (62.5 MHz, DMSO-d$_6$): $\delta$ 197.2, 143.4, 141.7, 138.9, 134.6, 131.0, 129.9, 122.7, 119.2, 26.8, 26.3, 20.5; IR $\nu_{max}$/cm$^{-1}$ (solid): 1693, 1577,
1391, 1236, 1170, 1022, 825, 631, 516; HRMS m/z [M-OTf]⁺ Calculated for C₁₇H₁₈IO: 365.0397; found 365.0400.
7. Synthesis and Analytical Data of 4-diarylmethylene-4H-benzoxazines

General procedure for the synthesis of 4-diarylmethylene-4H-benzoxazines

N-(2-(phenylethynyl)phenyl)pivalamide (0.35 mmol), aryl(mesityl)iodonium trifluoromethanesulfonate (0.42 mmol, 1.2 eq.) and copper(II) trifluoromethanesulfonate (12.7 mg, 0.035 mmol, 10 mol%) were placed in a 4 ml vial, which was sealed with rubber septa, evacuated then charged with argon. 1,2-dichloroethane (3 ml) was added, and the reaction mixture was stirred at 50°C for the indicated time. The reaction mixture was diluted with CH$_2$Cl$_2$ (15 ml), washed twice with saturated sodium bicarbonate solution (15 ml), the aqueous phase was extracted with CH$_2$Cl$_2$ (15 ml), and the combined organic phases were dried over magnesium sulphate and evaporated in vacuo. The crude product was purified by column chromatography.

2-tert-butyl-4-(diphenylmethylene)-4H-benzo[d][1,3]oxazine (3a)

Prepared according to the general procedure from N-(2-(phenylethynyl)phenyl)pivalamide (97.1 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg, 0.42 mmol) for 12 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane to give a pale yellow solid (72.7 mg, 0.206 mmol, 59%).

M. p. 168 – 170 °C; $^1$H NMR (DMSO-$d_6$, 500 MHz): δ 7.42-7.32 (m, 5H), 7.31-7.21 (m, 6H), 7.13 (dm, 1H, $J = 7.9$ Hz), 6.89-6.83 (m, 1H), 6.51 (dm, 1H, $J = 8.0$ Hz), 1.04 (s, 9H); $^{13}$C (DMSO-$d_6$, 125 MHz): δ 166.1, 140.6, 140.4, 139.9, 139.4, 130.2, 130.1, 129.34, 129.27, 127.8, 127.7, 126.8, 126.2, 126.1, 125.5, 120.7, 120.4, 36.8, 27.0. IR $\nu_{max}$/cm$^{-1}$ (solid): 2975, 1640, 1615, 1597, 1456, 1219, 1136, 1061, 751, 696, 613; HRMS m/z [M+H]$^+$ Calculated for C$_{25}$H$_{23}$NO: 353.1852 found 353.1856.

$^1$H δ [ppm] + NOESY
$^{13}\text{C} \delta \text{ [ppm]}$

HMBC $^{1}\text{H} \rightarrow ^{13}\text{C}$

$^{1}\text{H}/^{15}\text{N}$-HMBC $^{1}\text{H} \rightarrow ^{15}\text{N}$ [ppm] (indirect standard for liquid ammonia = 0 ppm)
4-((4-methylphenyl)(phenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3b)

Prepared according to the general procedure from N-(2-((4-methylphenyl)ethynyl)phenyl)pivalamide (102.0 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg 0.42 mmol) for 12 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane/ethyl acetate 100/1 to give a pale yellow solid (83.1 mg, 0.226 mmol, 65%). Isomer ratio E/Z = 2/3 (from $^1$H NMR).

Prepared according to the general procedure from N-(2-(phenylethynyl)phenyl)pivalamide (97.1 mg, 0.35 mmol) with 4-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (204.2 mg 0.42 mmol) for 12 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane/ethyl acetate 200/1 to give a pale yellow solid (88.5 mg, 0.241 mmol, 69%). Isomer ratio E/Z = 3/2 (from $^1$H NMR).

M. p. 108 – 110 °C; Rf: 0.73 (hexanes/ethyl acetate = 7/1); $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 7.21 (m, 5H), 7.15 (m, 3H), 7.12 – 7.05 (m, 5H), 7.02 (d, 4H, J = 8.7 Hz), 6.77 – 6.64 (m, 2H), 6.61 (d, 1H, J = 8.0 Hz), 6.51 (d, 1H, J = 8.0 Hz), 2.27 (s, 2H), 2.26 (s, 3H), 1.05 (s, 9H), 1.02 (s, 6H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 167.24, 167.22, 141.4, 140.9, 140.3, 137.6, 137.2, 137.1, 136.4, 130.9, 130.7, 130.0, 129.9, 129.8, 129.7, 129.0, 128.4, 127.7, 127.4, 127.0, 126.7, 126.0, 125.6, 121.84, 121.80, 120.75, 120.72, 37.30, 37.27, 27.6, 27.5, 21.41; IR
\( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 2959, 2925, 1636, 1594, 1275, 1219, 1140, 1059, 828, 761, 695; HRMS \text{m/z [M+H]}^+ \) Calculated for \( \text{C}_{26}\text{H}_{25}\text{NO} \): 368.2009; found 368.2016.

\((E,Z)-2\text{-tert-butyl-4-((3-methylphenyl)(phenyl)methylene)-4H-benzo}[d][1,3]\text{oxazine (3c)}\)

![Chemical structure of (E,Z)-2-tert-butyl-4-((3-methylphenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine (3c)](image)

Prepared according to the general procedure from \( \text{N-(2-(3-methylphenyl)ethynyl)phenyl)pivalamide (102.0 mg, 0.35 mmol)} \) with \( \text{mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg 0.42 mmol)} \) for 12 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane to give a yellow solid (81.2 mg, 0.221 mmol, 63%). Isomer ratio \( E/Z = 2/3 \) (from \( ^1\text{H NMR} \)).

M. p. 126 - 128 °C; \( ^1\text{H NMR} \) (250 MHz, CDCl\(_3\)): \( \delta \) 7.24 – 7.22 (m, 5H), 7.21 – 7.13 (m, 4H), 7.10 – 7.09 (m, 6H), 7.04 – 6.92 (m, 4H), 6.77 – 6.66 (m, 2H), 6.54 (t, 2H, \( J = 9.1 \text{ Hz} \)), 2.24 (s, 3H), 2.20 (s, 2H), 1.04 (s, 3H), 1.03 (s, 6H); \( ^{13}\text{C NMR} \) (62.5 MHz, CDCl\(_3\)): \( \delta \) 167.3, 167.2, 141.5, 141.3, 140.7, 139.9, 138.7, 137.0, 131.4, 130.9, 130.8, 130.0, 129.8, 129.1, 128.9, 128.3, 127.82, 127.75, 127.7, 127.6, 127.5, 127.1, 127.0, 126.7, 126.0, 125.59, 125.56, 121.7, 120.9, 37.3, 27.5, 21.6, 21.5; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 3055, 3017, 2972, 2928, 2865, 1639, 1597, 1455, 1219, 1139, 1062, 760, 699, 615; HRMS \text{m/z [M-OTf]}^+ \) Calculated for \( \text{C}_{26}\text{H}_{25}\text{NO} \): 368.2009; found 368.2009.

\((E,Z)-2\text{-tert-butyl-4-((2-methylphenyl)(phenyl)methylene)-4H-benzo}[d][1,3]\text{oxazine (3d)}\)

![Chemical structure of (E,Z)-2-tert-butyl-4-((2-methylphenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine (3d)](image)

Prepared according to the general procedure from \( \text{N-(2-(2-methylphenyl)ethynyl)phenyl)pivalamide (97.1 mg, 0.35 mmol)} \) with \( \text{(3-methylphenyl)(mesityl) iodonium trifluoromethanesulfonate (204.2 mg 0.42 mmol)} \) for 12 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane to give a yellow solid (76.2 mg, 0.27 mmol, 59%). Isomer ratio \( E/Z = 3/2 \) (from \( ^1\text{H NMR} \)).

M. p. 126 - 128 °C; Rf: 0.67 (hexanes/ethyl acetate = 7/1); \( ^1\text{H NMR} \) (250 MHz, CDCl\(_3\)): \( \delta \) 7.24 – 7.22 (m, 5H), 7.21 – 7.13 (m, 4H), 7.10 – 7.09 (m, 6H), 7.04 – 6.92 (m, 4H), 6.77 – 6.66 (m, 2H), 6.54 (t, 2H, \( J = 9.1 \text{ Hz} \)), 2.24 (s, 3H), 2.20 (s, 2H), 1.04 (s, 3H), 1.03 (s, 6H); \( ^{13}\text{C NMR} \) (62.5 MHz, CDCl\(_3\)): \( \delta \) 167.3, 167.2, 141.5, 141.3, 140.7, 139.9, 138.7, 137.0, 131.4, 130.9, 130.8, 130.0, 129.8, 129.1, 128.9, 128.3, 127.82, 127.75, 127.7, 127.6, 127.5, 127.1, 127.0, 126.7, 126.0, 125.59, 125.56, 121.7, 120.9, 37.3, 27.5, 21.6, 21.5; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 3055, 3017, 2972, 2928, 2865, 1639, 1597, 1455, 1219, 1139, 1062, 760, 699, 615; HRMS \text{m/z [M-OTf]}^+ \) Calculated for \( \text{C}_{26}\text{H}_{25}\text{NO} \): 368.2009; found 368.2009.
Rf: 0.73 (hexanes/ethyl acetate = 7/1); $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 7.24 (t, 3H, $J$ = 6.2 Hz), 7.21 – 7.03 (m, 18H), 6.77 – 6.74 (m, 1H), 6.66 (ddd, 1H, $J$ = 8.6 Hz and 6.3 Hz and 2.4 Hz), 6.33 (d, 1H, $J$ = 7.8 Hz), 2.24 (s, 2H), 2.01 (s, 3H), 1.07 (s, 9H), 0.90 (s, 7H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 167.4, 167.1, 141.8, 141.48, 141.4, 141.0, 139.9, 139.7, 139.0, 137.8, 136.6, 131.2, 131.0, 130.1, 130.0, 129.8, 129.7, 128.9, 128.0, 127.7, 127.3, 127.1, 126.8, 126.6, 126.4, 126.1, 126.0, 125.8, 125.7, 122.0, 121.1, 119.9, 119.4, 37.4, 37.2, 27.5, 27.2, 20.05, 19.89; IR $\nu_{max}$/cm$^{-1}$ (thin film): 3058, 3018, 2970, 2928, 2867, 1642, 1598, 1456, 1273, 1218, 1139, 1061, 1029, 751, 698, 615; HRMS m/z [M+H]$^+$ Calculated for C$_{26}$H$_{25}$NO: 368.2009; found 368.2013.

*(E,Z)-4-((4-bromophenyl)(phenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3e)*

Prepared according to the general procedure from N-(2-(phenylethynyl)phenyl)pivalamide (97.1 mg, 0.35 mmol) with (4-bromophenyl)(mesityl)iodonium trifluoromethanesulfonate (231.5 mg 0.42 mmol) for 20 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane to give a yellow solid (57.4 mg, 0.133 mmol, 38%). Isomer ratio E/Z = 9/4 (from $^1$H NMR).

Prepared according to the general procedure from N-(2-((4-bromophenyl)ethynyl)phenyl)pivalamide (106.9 mg, 0.30 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (170.0 mg 0.36 mmol) for 20 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane to give a yellow solid (72.0 mg, 0.17 mmol, 56%). Isomer ratio E/Z = 4/9 (from $^1$H NMR).

M. p. 120 – 122 °C; Rf: 0.64 (hexanes/ethyl acetate = 7/1); $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 7.36 (dd, 3H, $J$ = 8.5 Hz and 2.1 Hz), 7.25 – 7.16 (m, 7H), 7.15 – 7.10 (m, 5H), 7.06 (d, 2H, $J$ = 8.3 Hz), 6.79 (dd, 1H, $J$ = 8.4 Hz and 6.2 Hz and 2.4 Hz), 6.74 – 6.67 (m, 1H), 6.63 (d, 1H, $J$ = 7.9 Hz), 6.53 (d, 1H, $J$ = 8.0 Hz), 1.07 (s, 4H), 1.02 (s, 9H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 167.1, 142.1, 141.5, 139.8, 139.7, 132.9, 132.3, 131.8, 131.0, 130.2, 130.1, 129.2, 127.9, 127.0, 126.9, 126.2, 125.8, 125.8, 121.6, 121.2, 120.6, 119.5, 37.31, 37.29, 27.58, 27.46; $\nu_{max}$/cm$^{-1}$ (solid): 2962, 2925, 1639, 1599, 1484, 1455, 1219, 1137, 1059, 1010, 831, 757, 696, 613, 503; HRMS m/z [M-OTf]$^+$ Calculated for C$_{25}$H$_{22}$BrNO: 432.0958; found 432.0957.
(E,Z)-4-((3-bromophenyl)(phenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3f)

Prepared according to the general procedure from N-(2-(3-bromophenyl)ethynyl)phenyl)pivalamide (124.7 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg 0.42 mmol) for 20 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane to give a yellow solid (59.9 mg, 0.138 mmol, 40%). Isomer ratio E/ Z = 4/ 9 (from $^1$H NMR).

Prepared according to the general procedure from N-(2-(phenylethynyl)phenyl)pivalamide (97.1 mg, 0.35 mmol) with (3-bromophenyl)(mesityl)iodonium trifluoromethanesulfonate (231.5 mg 0.42 mmol) for 20 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane to give a yellow solid (74.9 mg, 0.173 mmol, 50%). Isomer ratio E/ Z = 9/ 4 (from $^1$H NMR).

M. p. 128 – 130 °C; Rf: 0.76 (hexanes/ ethyl acetate = 7/ 1); $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 7.50 (s, 1H), 7.37 – 7.33 (m, 2H), 7.28-7.21 (m, 6H), 7.18 – 7.06 (m, 9H), 6.77 (ddd, 1H, $J = 8.5$ Hz and 5.6 Hz and 3.0 Hz), 6.70 (dd, 1H, $J = 8.3$ Hz and 4.1 Hz), 6.59 (d, 1H, $J = 7.9$ Hz), 6.52 (d, 1H, $J = 8.0$ Hz), 1.07 (s, 4H), 1.02 (s, 9H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 167.0, 166.8, 142.9, 142.5, 142.4, 142.1, 141.4, 141.3, 140.0, 139.5, 133.8, 133.1, 130.9, 130.6, 130.3, 130.1, 129.7, 129.6, 129.4, 129.3, 128.5, 127.9, 127.8, 127.1, 127.0, 126.9, 126.2, 126.1, 125.9, 123.0, 121.8, 121.0, 119.2, 119.0, 37.32, 37.29, 27.54, 27.46; IR $\nu_{max}$/cm$^{-1}$ (solid): 3064, 2959, 1642, 1604, 1455, 1219, 1134, 1062, 756, 695, 615; HRMS m/z [M-OTf]$^+$ Calculated for C25H22BrNO: 432.0958; found 432.0953.

(E,Z)-4-((2-bromophenyl)(phenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3g)

Prepared according to the general procedure from N-(2-(2-bromophenyl)ethynyl)phenyl)pivalamide (124.7 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg 0.42 mmol) for 20 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane to give a yellow oil (63.7 mg, 0.147 mmol, 42%). Isomer ratio E/ Z = 1/ 3 (from $^1$H NMR).

Rf: 0.73 (hexanes/ ethyl acetate = 7/ 1); $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 7.54 (d, 1H, $J = 7.8$ Hz), 7.30 (m,3H), 7.23 (m, 5H), 7.18 – 7.09 (m, 6H), 7.03 (t, 1H, $J = 8.5$ Hz), 6.81 – 6.68 (m, 2H), 6.39 (d, 1H, $J = 8.2$ Hz), 1.06 (s, 3H), 0.94 (s, 9H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$
(E,Z)-2-tert-butyl-4-((4-chlorophenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine (3h)

Prepared according to the general procedure from N-(2-((4-chlorophenyl)ethynyl)phenyl)pivalamide (109.1 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg 0.42 mmol) for 16 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane/ethyl acetate 100/1 to give a pale yellow solid (86 mg, 0.22 mmol, 63%). Isomer ratio E/Z = 5/2 (from $^1$H NMR).

Prepared according to the general procedure from N-(2-(phenylethynyl)phenyl)pivalamide (97.1 mg, 0.35 mmol) with (4-chlorophenyl)(mesityl) iodonium trifluoromethanesulfonate (212.8 mg 0.42 mmol) for 24 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane/dichloromethane acetate 50/1 to give a pale yellow solid (79 mg, 0.204 mmol, 58%). Isomer ratio E/Z = 9/5 (from $^1$H NMR).

M. p. 120 – 122 °C; Rf: 0.70 (hexanes/ethyl acetate = 7/1); $^1$H NMR (250 MHz, CDCl$_3$): δ 7.25 – 7.16 (m, 11H), 7.15 – 7.05 (m, 7H), 6.76 (dt, 1H, $J = 8.5$ Hz and $4.2$ Hz), 6.69 (dd, 1H, $J = 8.3$ Hz 4.7 Hz), 6.61 (d, 1H, $J = 8.0$ Hz), 6.52 (d, 1H, $J = 8.0$ Hz), 1.05 (s, 5H), 1.01 (s, 9H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 167.1, 166.8, 142.2, 142.1, 141.4, 141.3, 140.3, 139.7, 139.2, 138.6, 133.4, 132.32, 131.4, 130.9, 130.2, 130.1, 130.0, 129.3, 129.2, 128.0, 127.9, 127.7, 127.0, 126.9, 126.2, 126.1, 125.82, 125.76, 121.3, 121.2, 119.5, 119.3, 37.3, 27.6, 27.5; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 2695, 1638, 1594, 1487, 1455, 1219, 1140, 1087, 1059, 1015, 832, 757, 698, 614, 505; HRMS m/z [M+H]$^+$ Calculated for C$_{25}$H$_{22}$ClNO: 388.1463; found 388.1467.

(E,Z)-2-tert-butyl-4-((4-fluorophenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine (3i)

\[\text{Formula Image}\]
Prepared according to the general procedure from N-(2-(4-fluorophenylethynyl)phenyl)pivalamide (103.4 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg 0.42 mmol) for 12 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane/ dichloromethane 75/1 to give a pale yellow solid (70 mg, 0.19 mmol, 54%). Isomer ratio E/ Z = 1/2 (from 1H NMR).

Prepared according to the general procedure from N-(2-(phenylethynyl)phenyl)pivalamide (97.1 mg, 0.35 mmol) with (4-fluorophenyl)(mesityl) iodonium trifluoromethanesulfonate (205.9 mg 0.42 mmol) for 20 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane/ dichloromethane 75/1 to give a yellow solid (71 mg, 0.19 mmol, 55%). Isomer ratio E/ Z = 2/1 (from 1H NMR).

M. p. 136 – 138 °C; Rf: 0.69 (hexanes/ ethyl acetate = 7/1); 1H NMR (250 MHz, CDCl3): δ 7.29 – 7.18 (m, 4H), 7.18 – 7.06 (m, 5H), 6.92 (t, 2H, J = 8.6 Hz), 6.72 (ddd, 1H, J = 11.6 Hz and 8.3 Hz and 4.4 Hz), 6.54 (t, 1H, J = 7.3 Hz), 1.04 (s, 3H), 1.02 (s, 6H); 13C NMR (62.5 MHz, CDCl3): δ 167.0 (d, J = 9.9 Hz), 164.3, 160.4, 141.9, 141.4 (d, J = 9.1 Hz), 140.2 (d, J = 36.7 Hz), 136.5, 132.6 (d, J = 7.9 Hz), 131.7 (d, J = 7.8 Hz), 130.9, 130.06, 129.99, 129.2, 127.9, 127.7, 126.9 (d, J = 7.1 Hz), 125.9 (d, J = 19.0 Hz), 121.4, 119.6 (d, J = 4.3 Hz), 116.1 (d, J = 21.3 Hz), 114.7 (d, J = 21.4 Hz), 37.3, 27.51, 27.46; IR νmax/cm-1 (solid): 3063, 2973, 2929, 2865, 1640, 1598, 1504, 1456, 1219, 1134, 1059, 837, 756, 695, 590, 518; HRMS m/z [M-OTf]+ Calculated for C25H22FNO: 372.1758; found 372.1759.

2-tert-butyl-4-((4-nitrophenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine (3j)

Prepared according to the general procedure from N-(2-(4-nitrophenylethynyl)phenyl)pivalamide (112.8 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg 0.42 mmol) for 17 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane/ ethyl acetate 75/1 to give a bright yellow solid (48 mg, 0.12 mmol, 34%). Isomer ratio E/ Z = 2/7 (from 1H NMR).

M. p. °C; Rf: 0.69 (hexanes/ ethyl acetate = 7/1); 1H NMR (250 MHz, CDCl3): δ 8.11 (d, 2H, J = 8.4 Hz), 7.42 (d, 2H, J = 8.6 Hz), 7.34 – 7.26 (m, 3H), 7.23 – 7.11 (m, 4H), 6.77 (t, 1H, J = 6.2 Hz), 6.57 (d, 1H, J = 8.0 Hz), 1.09 (s, 7H), 1.05 (s, 2H); 13C NMR (62.5 MHz, CDCl3): δ 166.2, 147.2, 146.2, 144.12, 141.4, 139.7, 131.9, 131.1, 130.5, 130.06, 129.8, 129.0, 128.22, 128.20, 127.5, 127.3, 126.9, 126.4, 126.2, 126.1, 124.2, 123.2, 120.6, 118.2, 37.4, 27.6, 27.5; IR νmax/cm-1 (solid): 3061, 2958, 2922, 2851, 1639, 1578, 1511, 1455, 1337, 1272, 1218, 1139, 1061, 849, 756, 698, 611; HRMS m/z [M-OTf]+ Calculated for C25H22N2O3: 399.1703; found 399.1701.
2-tert-butyl-4-((4-methoxyphenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine (3k)

Prepared according to the general procedure from N-(2-((4-methoxyphenyl)ethynyl)phenyl)pivalamide (92.2 mg, 0.30 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (170.0 mg 0.35 mmol) for 4 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 30/1 to give a yellow oil (55 mg, 0.143 mmol, 48%). Isomer ratio E/Z = 1/2 (from 1H NMR). Rf: 0.61 (hexanes/ethyl acetate = 7/1); 1H NMR (250 MHz, CDCl₃): δ 7.24 – 7.19 (m, 5H), 7.19 – 7.12 (m, 5H), 7.11 – 7.05 (m, 4H), 6.77 (d, 3H, J = 8.8 Hz), 6.72 – 6.59 (m, 1.5H), 6.50 (d, 1H, J = 8.0 Hz), 3.74 (s, 1.5H), 3.73 (s, 3H), 1.07 (s, 9H), 1.02 (s, 4.5H); 13C NMR (62.5 MHz, CDCl₃): δ 167.3, 158.4, 141.3, 141.1, 140.9, 132.6, 132.0, 131.3, 131.0, 130.0, 129.8, 129.7, 129.0, 127.7, 127.5, 127.0, 126.03, 125.95, 125.61, 125.55, 122.0, 121.9, 120.5, 114.5, 113.1, 55.4, 37.33, 37.27, 27.6, 27.5; IR νmax/cm⁻¹ (thin film): 3058, 3031, 2958, 2925, 2853, 1639, 1601, 1509, 1456, 1245, 1218, 1171, 1137, 1032, 834, 749, 699, 594, 537; HRMS m/z [M-OOTf]+ Calculated for C₂₆H₂₅NO₂: 384.1958; found 384.1963.

(E,Z)-ethyl 4-((2-tert-butyl-4H-benzo[d][1,3]oxazin-4-ylidene)(phenyl)methyl)benzoate (3l)

Prepared according to the general procedure from ethyl 4-((2-pivalamidophenyl)ethynyl)benzoate (104.8 mg, 0.3 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (196.0 mg 0.36 mmol) for 20 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 50/1 to give a yellow solid (86 mg, 0.20 mmol, 67%). Isomer ratio E/Z = 3/1 (from 1H NMR). M. p. 142 – 145 °C; Rf: 0.49 (hexanes/ethyl acetate = 7/1); 1H NMR (250 MHz, CDCl₃): δ 7.90 (d, 2H, J = 8.2 Hz), 7.30 – 7.08 (m, 9H), 6.72 (td, 1H, J = 8.1 Hz and 4.0 Hz), 6.56 (t,
1H, \( J = 8.2 \) Hz), 4.29 (q, 2H, \( J = 7.1 \) Hz), 1.30 (t, 3H, \( J = 7.0 \) Hz), 1.02 (s, 9H); \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)): \( \delta \) 166.9, 166.5, 145.8, 142.5, 141.4, 139.5, 131.0, 130.3, 130.2, 130.1, 130.0, 129.4, 129.2, 129.1, 127.9, 127.8, 127.1, 127.0, 126.2, 125.8, 121.0, 119.7, 61.1, 37.3, 27.5, 27.4, 14.5; IR \( \nu_{\text{max}} \text{/cm}^{-1} \) (solid): 2979, 2934, 1714, 1638, 1601, 1455, 1275, 1141, 1102, 1062, 1018, 757, 699; HRMS m/z [M+H]\(^+\) Calculated for C\(_{28}\)H\(_{27}\)NO\(_3\): 426.2064; found 426.2067.

(E,Z)-2-tert-butyl-4-(naphthalen-1-yl(phenyl)methylene)-4H-benzo[d][1,3]oxazine (3m)

Prepared according to the general procedure from N-(2-(naphthalen-1-ylethynyl)phenyl)pivalamide (98.3 mg, 0.30 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (170.0 mg 0.36 mmol) for 18 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 35/1 to give a yellow oil (96 mg, 0.24 mmol, 79%). Isomer ratio E/Z = 1/1 (from 1H NMR).

Rf: 0.65 (hexanes/ethyl acetate = 7/1); \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta \) 8.11 – 7.64 (m, 5H), 7.35 – 7.13 (m, 19H), 7.06 – 6.88 (m, 5H), 6.78 (d, 1H, \( J = 2.9 \) Hz), 6.42 (t, 1H, \( J = 7.9 \) Hz), 6.11 (d, 1H, \( J = 7.3 \) Hz), 1.10 (s, 9H), 0.57 (s, 9H); \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)): \( \delta \) 167.2, 166.9, 142.9, 142.3, 141.6, 141.0, 140.4, 139.7, 138.7, 137.8, 134.5, 133.9, 132.7, 131.9, 130.3, 129.8, 129.7, 129.5, 129.0, 128.7, 128.5, 128.4, 128.3, 127.8, 127.5, 127.3, 126.9, 126.8, 126.7, 126.6, 126.5, 126.2, 126.1, 125.9, 125.7, 125.7, 125.6, 121.5, 120.8, 118.1, 117.8, 37.4, 37.0, 27.6, 27.0; IR \( \nu_{\text{max}} \text{/cm}^{-1} \) (thin film): 3056, 2970, 1639, 1598, 1456, 1218, 1136, 1061, 906, 760, 732, 696; HRMS m/z [M+H]\(^+\) Calculated for C\(_{29}\)H\(_{25}\)NO: 404.2009; found 404.2011.

2-tert-butyl-4-(1-phenylpentylidene)-4H-benzo[d][1,3]oxazine (3n)

Prepared according to the general procedure from N-(2-(hex-1-ynyl)phenyl)pivalamide (77.2 mg, 0.3 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (170.0 mg 0.36 mmol) for 16 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 50/1 to give an almost white solid (74 mg, 0.22 mmol, 74%).

M. p. 64 – 66 °C; Rf: 0.76 (hexanes/ethyl acetate = 7/1); \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta \) 7.29 – 7.20 (m, 3H), 7.13 (dd, 2H, \( J = 7.7 \) Hz and 1.7 Hz), 7.07 – 6.96 (m, 2H), 6.60 (t, 1H, \( J = 7.3 \) Hz), 6.28 (d, 1H, \( J = 7.6 \) Hz), 2.52 – 2.43 (m, 2H), 1.29 (s, 11H) (due to overlap), 0.86 – 0.78
2-tert-butyl-4-(diphenylmethylene)-6-fluoro-4H-benzo[d][1,3]oxazine (3o)

Prepared according to the general procedure from N-(4-fluoro-2-(phenylethynyl)phenyl)pivalamide (103.4 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg 0.42 mmol) for 16 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane/ dichloromethane 100/1 to give a pale yellow solid (91 mg, 0.25 mmol, 70%).
M. p. 115 – 117 °C; Rf: 0.71 (hexanes/ethyl acetate = 7/1); $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 7.28 – 7.19 (m, 7H), 7.19 – 7.12 (m, 3H), 7.05 (dd, 1H, $J = 8.7$ Hz and 5.6 Hz), 6.77 (td, 1H, $J = 8.4$ Hz and 2.8 Hz), 6.15 (dd, 1H, $J = 10.4$ Hz 2.8 Hz), 1.02 (s, 9H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 166.5 (d, $J = 1.8$ Hz), 162.20, 158.31, 140.8 (d, $J = 3.3$ Hz), 139.8 (d, $J = 19.7$ Hz), 137.6 (d, $J = 2.5$ Hz), 130.6, 129.9, 129.3, 128.0, 127.8, 127.2 (d, $J = 8.5$ Hz), 127.0, 123.0 (d, $J = 9.4$ Hz), 121.8, 116.9 (d, $J = 23.0$ Hz), 113.3 (d, $J = 26.2$ Hz), 37.3, 27.5; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 2953, 1639, 1476, 1214, 1184, 1059, 873, 824, 751, 695, 631, 510; HRMS m/z $[M+H]^+$ Calculated for C$_{25}$H$_{22}$FNO: 372.1758; found 372.1764.

2-tert-butyl-7-chloro-4-(diphenylmethylene)-4H-benzo[d][1,3]oxazine (3p)

Prepared according to the general procedure from N-(5-chloro-2-(phenylethynyl)phenyl)pivalamide (109.1 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg 0.42 mmol) for 17 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane/ dichloromethane 50/1 to give a pale yellow solid (97 mg, 0.25 mmol, 71%).
M. p. 134 – 136 °C; Rf: 0.79 (hexanes/ethyl acetate = 7/1); $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 7.38 – 7.30 (m, 7H), 7.30 – 7.23 (m, 3H), 7.22 (d, 1H, $J = 2.2$ Hz), 6.78 (dd, 1H, $J = 8.6$ Hz and 2.2 Hz), 6.55 (d, 1H, $J = 8.6$ Hz), 1.14 (s, 9H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 168.3,
142.8, 140.9, 140.3, 139.7, 135.3, 130.8, 129.9, 129.2, 128.0, 127.8, 127.0, 126.1, 125.6, 121.4, 120.2, 37.4, 27.4; IR ν\textsubscript{max}/cm\textsuperscript{-1} (solid): 2959, 1638, 1589, 1441, 1214, 1140, 1051, 879, 811, 754, 692, 617, 535; HRMS m/z [M+H]\textsuperscript{+} Calculated for C\textsubscript{25}H\textsubscript{22}ClNO: 388.1463; found 388.1464.

methyl 2-tert-butyl-4-(diphenylmethylene)-4H-benzo[d][1,3]oxazine-7-carboxylate (3q)

Prepared according to the general procedure from methyl 4-((phenylethynyl)-3-pivalamidobenzoate (33.5 mg, 0.1 mmol) with mesityl (phenyl)iodonium trifluoromethanesulfonate (56.7 mg 0.12 mmol) for 12 h. Purified by column chromatography on Brockmann II. type neutral alumina with hexane/ethyl acetate 75/1 to give a yellow solid (18 mg, 0.044 mmol, 44%).

M. p. 126 – 128 °C; Rf: 0.51 (hexanes/ethyl acetate = 5/1); \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}): δ 7.82 (d, 1H, J = 1.6 Hz), 7.43 (dd, 1H, J = 8.3 Hz and 1.8 Hz), 7.32 – 7.30 (m, 7H), 7.25 – 7.20 (m, 3H), 6.63 (d, 1H, J = 8.3 Hz), 3.85 (s, 3H), 1.10 (s, 9H); \textsuperscript{13}C NMR (62.5 MHz, CDCl\textsubscript{3}): δ 167.9, 166.4, 141.5, 140.07, 139.6, 131.1, 130.8, 130.0, 129.3, 128.9, 128.0, 127.9, 127.2, 127.0, 126.8, 126.8, 126.2, 123.3, 52.3, 37.4, 27.4; IR ν\textsubscript{max}/cm\textsuperscript{-1} (solid): 2955, 1720, 1638, 1612, 1436, 1204, 1141, 1090, 1051, 759, 693, 618; HRMS m/z [M+H]\textsuperscript{+} Calculated for C\textsubscript{27}H\textsubscript{25}NO\textsubscript{3}: 412.1907; found 412.1917.

2-tert-butyl-4-(diphenylmethylene)-7-methoxy-4H-benzo[d][1,3]oxazine (3r)

Prepared according to the general procedure from N-(5-methoxy-2-(phenylethynyl)phenyl)pivalamide (30.7 mg, 0.1 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (56.7 mg 0.12 mmol) for 12 h. Purified by column chromatography on Brockmann II. type neutral alumina with hexane/ethyl acetate 100/1 to give a yellow oil (23 mg, 0.06 mmol, 60%).

Rf: 0.53 (hexanes/ethyl acetate = 7/1); \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}): δ 7.24 – 7.18 (m, 8H), 7.17 – 7.09 (m, 2H), 6.63 (d, 1H, J = 2.6 Hz), 6.47 (d, 1H, J = 8.8 Hz), 6.30 (dd, 1H, J = 8.9 Hz and 2.7 Hz), 3.70 (s, 3H), 1.04 (s, 9H); \textsuperscript{13}C NMR (62.5 MHz, CDCl\textsubscript{3}): δ 161.0, 143.1, 141.8, 141.0, 131.0, 129.3, 129.1, 128.9, 128.2, 127.8, 127.3, 126.5, 118.4, 114.1, 113.6, 109.2, 55.5, 37.4, 27.5; IR ν\textsubscript{max}/cm\textsuperscript{-1} (thin film): 2959, 2925, 2853, 1606, 1643, 1442,
1275, 1143, 1058, 756, 699; HRMS m/z [M-OTf]+ Calculated for C_{26}H_{23}NO₂: 384.1958; found 384.1960.

**4-(diphenylmethylene)-2-methyl-4H-benzo[d][1,3]oxazine (3s)**

[Chemical structure image]

Prepared according to the general procedure from N-(2-(phenylethynyl)phenyl)acetamide (70.6 mg, 0.3 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (170.0 mg, 0.36 mmol) for 18 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 10/1 to give an almost white solid (78 mg, 0.25 mmol, 83%).

M. p. 120 – 122 °C; Rf: 0.56 (hexanes/ethyl acetate = 3/1); \(^1\)H NMR (250 MHz, CDCl₃): \(\delta\) 7.29 – 7.21 (m, 7H), 7.19 – 7.12 (m, 3H), 7.10 – 7.01 (m, 2H), 6.70 (t, 1H, \(J = 7.4\) Hz), 6.48 (d, 1H, \(J = 8.3\) Hz), 2.03 (s, 3H); \(^13\)C NMR (62.5 MHz, CDCl₃): \(\delta\) 159.1, 141.4, 140.9, 140.7, 139.9, 131.0, 130.0, 129.9, 129.2, 127.9, 127.7, 127.2, 126.8, 126.2, 125.1, 121.4, 120.8, 21.1; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 1650, 1616, 1597, 1439, 1377, 1242, 1175, 1072, 1028, 988, 751, 699, 614; HRMS m/z [M+H]+ Calculated for C_{22}H_{17}NO: 312.1383; found 312.1386.

**4-(diphenylmethylene)-2-phenyl-4H-benzo[d][1,3]oxazine (3t)**

[Chemical structure image]

Prepared according to the general procedure from N-(2-(phenylethynyl)phenyl)benzamide (89.2 mg, 0.3 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (170.0 mg, 0.36 mmol) for 16 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 75/1 to give a bright yellow solid (90 mg, 0.24 mmol, 80%).

M. p. 187 – 189 °C; Rf: 0.64 (hexanes/ethyl acetate = 7/1); \(^1\)H NMR (250 MHz, CDCl₃): \(\delta\) 7.79 (d, 2H, \(J = 7.4\) Hz), 7.35 – 7.19 (m, 14H), 7.11 (t, 1H, \(J = 7.5\) Hz), 6.72 (t, 1H, \(J = 7.6\) Hz), 6.58 (d, 1H, \(J = 7.8\) Hz); \(^13\)C NMR (62.5 MHz, CDCl₃): \(\delta\) 156.2, 141.6, 141.5, 140.6, 140.1, 131.7, 131.2, 130.9, 130.1, 129.2, 128.4, 128.1, 128.0, 127.7, 127.2, 127.1, 126.4, 126.0, 122.0, 121.5; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 3055, 1738, 1633, 1612, 1591, 1574, 1449, 1243, 1069, 1024, 753, 688, 614; HRMS m/z [M+H]+ Calculated for C_{27}H_{19}NO: 374.1539; found 374.1542.
4-(diphenylmethylene)-2-(4-methoxyphenyl)-4H-benzo[d][1,3]oxazine (3u)

Prepared according to the general procedure from 4-methoxy-N-(2-(phenylethynyl)phenyl)benzamide (98.2 mg, 0.3 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (170.0 mg 0.36 mmol) for 16 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 25/1 to give a yellow solid (106 mg, 0.26 mmol, 88%).

M. p. 158 – 160 °C; Rf: 0.42 (hexanes/ethyl acetate = 7/1); \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta\) 7.72 (d, 2H, \(J = 8.9\) Hz), 7.30 (dt, 5H, \(J = 15.2\) Hz and 4.6 Hz), 7.21 (s, 4H), 7.16 (d, 2H, \(J = 7.5\) Hz), 7.12 – 7.05 (m, 1H), 6.71 (d, 2H, \(J = 8.9\) Hz), 6.69 – 6.64 (m, 1H), 6.57 (d, 1H, \(J = 7.9\) Hz), 3.68 (s, 3H); \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)): \(\delta\) 162.6, 156.0, 141.9, 141.6, 140.2, 140.0, 139.8, 137.0, 130.7, 130.3, 129.9, 129.1, 128.0, 127.6, 127.2, 127.0, 125.9, 125.7, 123.6, 121.7, 121.2, 113.7, 55.4; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 2965, 1633, 1589, 1509, 1456, 1406, 1402, 130.9, 130.1, 130.0, 129.9, 129.1, 128.0, 127.6, 127.2, 127.0, 125.9, 125.7, 123.6, 121.7, 113.7, 55.4; HRMS m/z [M+H]^+ Calculated for C\(_{28}\)H\(_{21}\)NO\(_2\): 404.1645; found 404.1650.

4-(diphenylmethylene)-2-(4-nitrophenyl)-4H-benzo[d][1,3]oxazine (3v)

Prepared according to the general procedure from 4-nitro-N-(2-(phenylethynyl)phenyl)benzamide (102.7 mg, 0.3 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (170.0 mg 0.36 mmol) for 16 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 75/1 to give a bright orange solid (66 mg, 0.16 mmol, 53%).

M. p. 208 – 210 °C; Rf: 0.57 (hexanes/ethyl acetate = 7/1); \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta\) 8.06 (d, 2H, \(J = 8.8\) Hz), 7.90 (d, 2H, \(J = 8.8\) Hz), 7.32 – 7.12 (m, 12H), 6.78 (t, 1H, \(J = 7.5\) Hz), 6.60 (d, 1H, \(J = 7.9\) Hz); \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)): \(\delta\) 154.0, 149.6, 141.0, 140.8, 140.0, 139.8, 137.0, 130.3, 129.9, 129.3, 128.9, 128.2, 127.9, 127.5, 127.3, 126.5, 123.5, 122.3, 122.0; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 3073, 1638, 1591, 1517, 1344, 1276, 861, 776, 757, 698, 618; HRMS m/z [M+H]^+ Calculated for C\(_{27}\)H\(_{18}\)N\(_2\)O\(_3\): 419.1390; found 419.1393.
4-(bis(4-methylphenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3w)

Prepared according to the general procedure from N-(2-((4-methylphenyl)ethynyl)phenyl)pivalamide (102.0 mg, 0.35 mmol) with 4-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (204.2 mg 0.42 mmol) for 12 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane/ethyl acetate 200/1 to give a pale yellow solid (59.2 mg, 0.16 mmol, 44%).

M. p. 137 – 139 °C; Rf: 0.72 (hexanes/ethyl acetate = 7/1); 1H NMR (250 MHz, CDCl3): δ 7.21 – 7.15 (m, 4H), 7.10 (m, 6H), 6.80 (ddd, 1H, J = 8.5 Hz and 5.3 Hz and 3.4 Hz), 6.65 (d, 1H, J = 7.9 Hz), 2.36 (s, 3H), 2.35 (s, 3H), 1.13 (s, 9H); 13C NMR (62.5 MHz, CDCl3): δ 167.3, 141.3, 141.1, 137.8, 137.3, 137.2, 136.4, 130.8, 129.9, 129.8, 129.6, 128.4, 127.0, 125.9, 125.5, 122.0, 120.7, 37.28, 27.5, 21.45, 21.43; IR νmax/cm⁻¹ (solid): 2958, 2921, 1638, 1602, 1509, 1455, 1273, 1219, 1137, 1059, 1021, 818, 754, 583, 472; HRMS m/z [M+H]+ Calculated for C27H27NO: 382.2186; found 382.2188.

4-(bis(3-methylphenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3x)

Prepared according to the general procedure from N-(2-((3-methylphenyl)ethynyl)phenyl)pivalamide (102.0 mg, 0.35 mmol) with (3-methylphenyl)(mesityl)iodonium trifluoromethanesulfonate (204.2 mg 0.42 mmol) for 12 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane to give a yellow solid (47.2 mg, 0.124 mmol, 35%).

M. p. 104 – 107 °C; Rf: 0.79 (hexanes/ethyl acetate = 7/1); 1H NMR (250 MHz, CDCl3): δ 7.24 – 7.17 (m, 5H), 7.13 – 7.09 (m, 3H), 7.08 – 7.04 (m, 2H), 6.81 (dt, 1H, J = 8.6 Hz and 4.4 Hz), 6.64 (d, 1H, J = 8.0 Hz), 2.34 (s, 3H), 2.30 (s, 3H), 1.14 (s, 9H); 13C NMR (62.5 MHz, CDCl3): δ 167.2, 141.4, 141.3, 140.5, 140.0, 138.7, 137.0, 131.4, 130.7, 129.8, 128.9, 128.3, 127.8, 127.6, 127.5, 127.03, 127.00, 126.0, 125.6, 121.8, 120.9, 37.3, 27.5, 21.6, 21.5; IR νmax/cm⁻¹ (solid): 3033, 2958, 2924, 1642, 1598, 1456, 1218, 1137, 1063, 771, 754, 705; HRMS m/z [M-OTf]+ Calculated for C27H27NO: 382.2165; found 382.2167.
4-(bis(3-bromophenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3y)

Prepared according to the general procedure from N-(2-(3-bromophenyl)ethynyl)phenyl)pivalamide (124.7 mg, 0.35 mmol) with (3-bromophenyl)(mesityl)iodonium trifluoromethanesulfonate (231.5 mg 0.42 mmol) for 20 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane to give a yellow solid (87.0 mg, 0.170 mmol, 49%).

M. p. 150 – 152 °C; Rf: 0.74 (hexanes/ethyl acetate = 7/1); \( ^1 \)H NMR (250 MHz, CDCl\(_3\)): δ 7.48 (t, 1H, \( J = 1.6 \) Hz), 7.40 – 7.34 (m, 1H), 7.33 – 7.25 (m, 2H), 7.16 – 7.04 (m, 6H), 6.78 (ddd, 1H, \( J = 8.5 \) Hz and 6.0 Hz and 2.8 Hz), 6.56 (d, 1H, \( J = 7.9 \) Hz), 1.06 (s, 9H); \( ^{13} \)C NMR (62.5 MHz, CDCl\(_3\)): δ 166.6, 143.3, 142.2, 141.5, 141.4, 133.8, 133.1, 131.0, 130.8, 130.7, 130.0, 129.6, 129.5, 128.5, 126.9, 126.3, 126.1, 123.2, 122.0, 120.5, 117.4, 37.3, 27.5; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 2965, 2929, 1646, 1605, 1470, 1455, 1415, 1272, 1219, 1137, 1062, 780, 760, 710, 679; HRMS m/z [M-O\( \text{OTf} \)]\(^+\) Calculated for C\(_{25}\)H\(_{21}\)Br\(_2\)NO: 510.0063; found 510.0063.

4-(bis(3-bromophenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3z)

Prepared according to the general procedure from N-(2-(4-bromophenyl)ethynyl)phenyl)pivalamide (124.7 mg, 0.35 mmol) with (4-bromophenyl)(mesityl)iodonium trifluoromethanesulfonate (231.5 mg 0.42 mmol) for 20 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane yellow solid (74.6 mg, 0.146 mmol, 42%).

M. p. 146 – 148 °C; \( ^1 \)H NMR (250 MHz, CDCl\(_3\)): δ 7.37 (d, 4H, \( J = 8.4 \) Hz), 7.17 – 6.99 (m, 6H), 6.84 – 6.76 (m, 1H), 6.62 (d, 1H, \( J = 7.9 \) Hz), 1.07 (s, 9H); \( ^{13} \)C NMR (62.5 MHz, CDCl\(_3\)): δ 167.0, 142.5, 141.3, 139.3, 138.6, 132.7, 132.4, 131.8, 131.0, 130.5, 130.0, 126.9, 126.3, 125.9, 121.8, 120.8 (d, \( J = 2.5 \) Hz), 118.0, 37.3, 27.5; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 2965, 2929, 1646, 1605, 1555, 1470, 1455, 1415, 1272, 1219, 1137, 1062, 780, 760, 710, 679; HRMS m/z [M+H]\(^+\) Calculated for C\(_{25}\)H\(_{21}\)Br\(_2\)NO: 510.0022; found 510.0019.
4-(bis(4-fluorophenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3aa)

Prepared according to the general procedure from N-(2-((4-fluorophenyl)ethynyl)phenyl)pivalamide (103.4 mg, 0.35 mmol) with (4-fluorophenyl)(mesityl)iodonium trifluoromethanesulfonate (205.9 mg, 0.42 mmol) for 17 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane/dichloromethane 75/1 to give a pale yellow solid (62 mg, 0.16 mmol, 46%).

M. p. °C; Rf: 0.72 (hexanes/ethyl acetate = 7/1); $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 7.33 – 7.16 (m, 6H), 7.02 (t, 4H, $J$ = 7.9 Hz), 6.88 – 6.80 (m, 1H), 6.63 (d, 1H, $J$ = 7.9 Hz), 1.12 (s, 9H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 167.0, 163.7 ($J$ = 55.9 Hz), 160.4 ($J$ = 55.0 Hz), 141.7 ($J$ = 51.9 Hz), 136.4 ($J$ = 3.5 Hz), 132.8 ($J$ = 3.4 Hz), 135.9 ($J$ = 3.5 Hz), 131.7 ($J$ = 7.9 Hz), 137.2, 126.8, 126.2, 125.8, 121.3, 118.5, 116.2 ($J$ = 21.4 Hz), 114.8 ($J$ = 21.4 Hz); IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 2960, 2921, 2851, 1643, 1597, 1503, 1455, 1219, 1137, 1061, 832, 759, 578, 519; HRMS m/z [M+OTf]$^{+}$ Calculated for C$_{25}$H$_{21}$F$_2$NO: 390.1664; found 390.1664.

4-(bis(4-chlorophenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3bb)

Prepared according to the general procedure from N-(2-((4-chlorophenyl)ethynyl)phenyl)pivalamide (109.1 mg, 0.35 mmol) with (4-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (212.8 mg, 0.42 mmol) for 16 h. Purified by column chromatography on Brockmann II type neutral alumina with hexane/ethyl acetate 100/1 to give a yellow solid (123 mg, 0.29 mmol, 83%).

M. p. 155 – 157 °C; Rf: 0.72 (hexanes/ethyl acetate = 7/1); $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 7.35 – 7.26 (m, 4H), 7.22 (d, 4H, $J$ = 6.4 Hz), 7.16 (d, 2H, $J$ = 8.5 Hz), 6.87 (t, 1H, $J$ = 7.0 Hz), 6.67 (d, 1H, $J$ = 7.9 Hz), 1.13 (s, 9H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 166.8, 142.6, 141.4, 138.9, 138.2, 133.7, 132.7, 132.4, 131.4, 130.4, 129.5, 128.1, 126.9, 126.3, 126.0, 121.0, 118.1, 37.3, 27.6; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 2963, 2921, 2851, 1643, 1597, 1503, 1455, 1219, 1137, 1061, 832, 759, 578, 519; HRMS m/z [M+H]$^{+}$ Calculated for C$_{25}$H$_{21}$Cl$_2$NO: 422.1073; found 422.1085.
(E,Z)-1-(4-((2-tert-butyl-4H-benzo[d][1,3]oxazin-4-ylidene)(phenyl)methyl)phenyl)ethanone (3cc)

Prepared according to the general procedure from N-(2-(phenylethynyl)phenyl)pivalamide (83.2 mg, 0.30 mmol) with (4-acetylphenyl)(mesityl)iodonium trifluoromethanesulfonate (18515 mg 0.36 mmol) for 36 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 10/1 to give a yellow solid (68 mg, 0.17 mmol, 57%). Isomer ratio E/Z = 3/1 (from 1H NMR).

M. p. 133 – 135 °C; Rf: 0.35 (hexanes/ethyl acetate = 7/1); 1H NMR (250 MHz, CDCl3): δ 7.81 (d, 2H, J = 7.6 Hz), 7.36 – 7.08 (m, 9H), 6.81 – 6.66 (m, 1H), 6.59 (d, 1H, J = 7.9 Hz), 2.51 (s, 3H), 1.02 (s, 9H); 13C NMR (62.5 MHz, CDCl3): δ 197.7, 166.9, 146.1, 142.6, 141.5, 139.5, 136.1, 131.2, 130.4, 130.1, 129.0, 128.0, 127.1, 126.9, 126.2, 125.9, 125.0, 119.6, 37.3, 27.4, 26.7; IR νmax/cm⁻¹ (solid): 2970, 1674, 1639, 1598, 1455, 1268, 1139, 1061, 838, 760, 695, 615; HRMS m/z [M+H]+ Calulated for C27H25NO2: 396.1958; found 396.1964.

(E,Z)-2-tert-butyl-4-(phenyl(3-(trifluoromethyl)phenyl)methylene)-4H-benzo[d][1,3]-oxazine (3dd)

Prepared according to the general procedure from N-(2-(phenylethynyl)phenyl)pivalamide (83.2 mg, 0.30 mmol) with mesityl(3-(trifluoromethyl)phenyl)iodonium trifluoromethanesulfonate (194.5 mg 0.36 mmol) for 18 h. Purified by column chromatography on silica gel with hexane/ethyl acetate 40/1 to give a yellow oil (98 mg, 0.23 mmol, 78%). Isomer ratio E/Z = 1/1 (from GC-MS).

M. p. 133 – 135 °C; Rf: 0.60 (hexanes/ethyl acetate = 7/1); 1H NMR (250 MHz, CDCl3): δ 7.47 – 7.33 (m, 3H), 7.28 – 7.11 (m, 8H), 6.78 – 6.69 (m, 1H), 6.52 (dd, 1H, J = 14.2 Hz and 8.0 Hz), 1.02 (s, 9H); 13C NMR (62.5 MHz, CDCl3): δ 167.0, 142.7, 141.7, 141.5, 141.3, 140.9, 140.00, 139.4, 134.5, 133.1, 131.8, 131.1, 131.0, 130.6, 130.4, 130.1, 129.5, 129.4, 128.4, 128.0, 127.9, 127.8, 127.2, 127.1, 126.7, 126.2, 126.0, 125.9, 124.3 (q, J = 7.3 Hz), 124.29, 124.24, 124.18, 121.0, 120.9, 119.3, 37.32, 37.26, 27.46, 27.44; IR νmax/cm⁻¹ (thin
film): 2972, 1643, 1597, 1456, 1320, 1259, 1218, 1164, 1119, 756, 696; HRMS m/z [M+H]^+ 
Calculated for C_{26}H_{22}F_{3}NO: 422.1726; found 422.1733.
8. NMR spectra

N-(2-iodophenyl)pivalamide (i1)
N-(4-fluoro-2-iodophenyl)pivalamide (i2)
Methyl 4-iodo-3-pivalamidobenzoate (i3)
N-(5-chloro-2-iodophenyl)pivalamide (i4)
N-(2-(phenylethynyl)phenyl)pivalamide (1a)
N-(4-fluoro-2-(phenylethynyl)phenyl)pivalamide (1b)
methyl 4-(phenylethynyl)-3-pivalamidobenzoate (1c)
N-(5-chloro-2-(phenylethynyl)phenyl)pivalamide (1d)
N-(2-((4-methoxyphenyl)ethynyl)phenyl)pivalamide (1e)
N-(2-((2-methylphenyl)ethynyl)phenyl)pivalamide (1f)
N-(2-((3-methylphenyl)ethynyl)phenyl)pivalamide (1g)
N-(2-((4-methylphenyl)ethynyl)phenyl)pivalamide (1h)
N-(2-((2-bromophenyl)ethynyl)phenyl)pivalamide (1i)
N-(2-((3-bromophenyl)ethynyl)phenyl)pivalamide (1j)
N-(2-((4-fluorophenyl)ethynyl)phenyl)pivalamide (1l)
N-(2-((4-nitrophenyl)ethynyl)phenyl)pivalamide (1m)
N-(2-((4-chlorophenyl)ethynyl)phenyl)pivalamide (1n)
N-(2-((3-(trifluoromethyl)phenyl)ethynyl)phenyl)pivalamide (1o)
N-(2-(naphthalen-1-ylethynyl)phenyl)pivalamide (1p)
Ethyl 4-((2-pivalamidophenyl)ethynyl)benzoate\textsuperscript{9} (1q)


S77
N-(2-(hex-1-ynyl)phenyl)pivalamide (1r)
N-(2-(phenylethynyl)phenyl)benzamide (1t)
4-nitro-N-(2-(phenylethynyl)phenyl)benzamide (1u)
4-methoxy-N-(2-(phenylethynyl)phenyl)benzamide (1v)
N-(2-(phenylethynyl)phenyl)acetamide (1w)
Mesityl(phenyl)iodonium trifluoromethanesulfonate (2a)
2-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (2b)
3-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (2c)
4-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (2d)
2-bromophenyl(mesityl)iodonium trifluoromethanesulfonate (2e)
3-bromophenyl(mesityl)iodonium trifluoromethanesulfonate (2f)
4-bromophenyl(mesityl)iodonium trifluoromethanesulfonate (2g)
2-fluorophenyl(mesityl)iodonium trifluoromethanesulfonate (2h)
4-fluorophenyl(mesityl)iodonium trifluoromethanesulfonate (2i)
4-nitrophenyl(mesityl)iodonium trifluoromethanesulfonate (2j)
2-trifluoromethylphenyl(mesityl)iodonium trifluoromethanesulfonate (2k)
3-trifluoromethylphenyl(mesityl)iodonium trifluoromethanesulfonate (2l)
(2-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (2m)
(4-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (2n)
(2-(ethoxycarbonyl)phenyl)(mesityl)iodonium trifluoromethanesulfonate (2o)
(4-(ethoxycarbonyl)phenyl)(mesityl)iodonium trifluoromethanesulfonate (2p)
(4-acetylphenyl)(mesityl)iodonium trifluoromethanesulfonate (2q)
2-tert-butyl-4-(diphenylmethylene)-4H-benzo[d][1,3]oxazine (3a)
4-((4-methylphenyl)(phenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3b)
(E,Z)-2-tert-butyl-4-((3-methylphenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine (3c)
(E,Z)-2-tert-butyl-4-((2-methylphenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine (3d)
(E,Z)-4-((4-bromophenyl)(phenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3e)
(E,Z)-4-((3-bromophenyl)(phenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3f)
(E,Z)-4-((2-bromophenyl)(phenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3g)
(E,Z)-2-tert-butyl-4-((4-chlorophenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine (3h)
(E,Z)-2-tert-butyl-4-((4-fluorophenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine (3i)
2-tert-butyl-4-((4-nitrophenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine (3j)
2-tert-butyl-4-((4-methoxyphenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine (3k)
(E,Z)-ethyl 4-((2-tert-butyl-4H-benzo[d][1,3]oxazin-4-ylidene)(phenyl)methyl)benzoate (3l)
(E,Z)-2-tert-butyl-4-(naphthalen-1-yl(phenyl)methylene)-4H-benzo[d][1,3]oxazine (3m)
2-tert-butyl-4-(1-phenylpentylidene)-4H-benzo[d][1,3]oxazine (3n)
2-tert-butyl-4-(diphenylmethylene)-6-fluoro-4H-benzo[d][1,3]oxazine (3o)
2-tert-butyl-7-chloro-4-(diphenylmethylene)-4H-benzo[d][1,3]oxazine (3p)
methyl 2-tert-butyl-4-(diphenylmethylene)-4H-benzod[1,3]oxazine-7-carboxylate (3q)
2-tert-butyl-4-(diphenylmethylene)-7-methoxy-4H-benzo[d][1,3]oxazine (3r)
4-(diphenylmethylene)-2-methyl-4H-benzo[d][1,3]oxazine (3s)
4-(diphenylmethylene)-2-phenyl-4H-benzo[d][1,3]oxazine (3t)
4-(diphenylmethylene)-2-(4-methoxyphenyl)-4H-benzo[d][1,3]oxazine (3u)
4-(diphenylmethylene)-2-(4-nitrophenyl)-4H-benzo[d][1,3]oxazine (3v)
4-(bis(4-methylphenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3w)
4-(bis(3-methylphenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3x)
4-(bis(3-bromophenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3y)
4-(bis(3-bromophenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3z)
4-(bis(4-fluorophenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3aa)
4-(bis(4-chlorophenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine (3bb)
(E,Z)-1-(4-((2-tert-butyl-4H-benzo[d][1,3]oxazin-4-ylidene)(phenyl)methyl)-phenyl)ethanone (3cc)
(E,Z)-2-tert-butyl-4-(phenyl(3-(trifluoromethyl)phenyl)methylene)-4H-benzo[d][1,3]-oxazine (3dd)