Supporting Information

for

*Copper-Catalyzed Oxidative Ring Closure of ortho-Cyanoanilides with Hypervalent Iodonium Salts: Arylation – Ring Closure Approach to Iminobenzoxazines*

by

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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 Buchi 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 F254. 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 of the ring closing reaction of compound 1a

![Chemical structures and reaction scheme]

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* product mixture was formed
2. Synthesis and analytical data of 2-cyanoanilides

N-(2-cyanophenyl)acetamides were synthesized from 2-aminobenzonitrile derivative and the appropriate acyl chloride or anhydride according to the modified procedure of Fagnou.¹

General procedure for the synthesis of N-(2-cyanophenyl)acetamides

2-aminobenzonitrile (1.00 g, 8.47 mmol) was added to a 100 ml round bottom flask fitted with a rubber septum then the system was charged with argon. Dichloromethane (25 ml) was added under argon atmosphere then acetic anhydride (1.30 g, 12.7 mmol, 1.20 ml) was added dropwise. The reaction mixture was stirred at room temperature for 24 h. The reaction mixture was washed with saturated sodium hydrogen carbonate solution (3 x 20 ml), with brine (2 x 20 ml), dried over anhydrous sodium sulfate, filtered and evaporated to yield white or yellow solids.

N-(2-cyanophenyl)acetamide (1a)²

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{CN}
\end{array}
\]

Prepared according to the general procedure from 2-aminobenzonitrile and acetic anhydride. After evaporation of the solvent under reduced pressure the product was afforded as a white solid (1.21 g, 7.59 mmol, 90%). \( R_f = 0.45 \) (hexane-ethyl acetate, 3:1). \(^1\)H NMR (250 MHz, CDCl₃): \( \delta \) 8.29 (d, \( J = 8.8 \) Hz, 1H), 7.71 (br s, 1H), 7.57 – 7.44 (m, 2H), 7.10 (t, \( J = 7.9 \) Hz, 1H), 2.20 (s, 3H); \(^{13}\)C NMR (62.5 MHz, CDCl₃): \( \delta \) 169.08, 140.92, 134.55, 132.66, 124.54, 121.92, 116.79, 102.37, 25.05; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 3322, 2229, 1710, 1579, 1523, 1445, 1372, 1293, 1252, 1229, 751, 634, 599, 575, 535, 495, 475.

N-(5-chloro-2-cyanophenyl)acetamide (1l)³

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{N} \\
\text{CN}
\end{array}
\]

Prepared according to the general procedure from 2-aminobenzonitrile and acetic anhydride. After evaporation of the solvent under reduced pressure the product was afforded as a white solid (1.21 g, 7.59 mmol, 90%). \( R_f = 0.35 \) (hexane-ethyl acetate, 7:3). \(^1\)H NMR (250 MHz, DMSO-d₆): \( \delta \) 10.30 (br s, 1H), 7.83 (d, \( J = 8.4 \) Hz, 1H), 7.76 (d, \( J = 1.9 \) Hz, 1H), 7.39 (dd, \( J = 8.4, 2.0 \) Hz, 1H), 2.11 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-d₆): \( \delta \) 169.36, 142.00, 134.55, 132.66, 124.54, 121.92, 116.47, 105.35, 25.05; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 3332, 2918, 1710, 1579, 1523, 1445, 1372, 1293, 1252, 1229, 751, 634, 599, 575, 535, 495, 475.

S4
N-(4-chloro-2-cyanophenyl)acetamide (1m)\(^4\)

![Chemical structure](image)

Prepared according to the general procedure from 2-amino-4-chlorobenzonitrile (250 mg, 1.64 mmol) and acetic anhydride (251 mg, 2.46 mmol, 232 µl) in 8 ml dichloromethane. The reaction mixture was stirred at room temperature for 4 days. The product was obtained as a white solid (234 mg, 1.21 mmol, 73%). \(R_f = 0.30\) (hexane-ethyl acetate, 7:3). \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 10.24 (s, 1H), 7.96 (d, \(J = 2.1\) Hz, 1H), 7.72 (dd, \(J = 8.8, 2.2\) Hz, 1H), 7.60 (d, \(J = 8.8\) Hz, 1H), 2.09 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 169.15, 139.73, 134.18, 132.76, 129.48, 127.18, 115.96, 108.74, 23.53; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 3340, 2228, 1698, 1583, 1516, 1288, 833, 646, 574, 489, 437.

**General procedure for the synthesis of N-(2-cyanophenyl)amides**

N-(2-cyanophenyl)amides were synthesized from 2-aminobenzonitrile and the appropriate acyl chloride or anhydride according to the modified procedure of Zhdankin.\(^5\)

2-aminobenzonitrile (1.00 g; 8.47 mmol) and triethylamine (9.73-19.1 mmol, 1.15-2.25 eq.) were dissolved in 50-80 ml dichloromethane and cooled to 0°C. A solution of acyl chloride (9.73-19.1 mmol, 1.15-2.25 eq.) and dichloromethane (7 ml) was added dropwise then the resulted mixture was stirred at room temperature for the appropriate time. After that the pH of the reaction mixture was adjusted to 7-8 with saturated sodium hydrogen carbonate solution, the separated organic layer was washed with distilled water (3 x 50 ml) and with brine (2 x 50 ml), dried over anhydrous magnesium sulfate, filtered and evaporated. Purification of the crude product afforded the appropriate amides as white or yellow solids.

N-(2-cyanophenyl)pivalamide (1b)\(^6\)

![Chemical structure](image)

Prepared according to the general procedure from 2-aminobenzonitrile (1.00 g; 8.47 mmol), triethylamine (985 mg, 9.73 mmol, 1.36 ml, 1.15 eq.) and pivaloyl chloride (1.17 g, 9.73 mmol, 1.20 ml) in 80 ml dichloromethane. The reaction mixture was stirred at room temperature for 2 days. Purification of the crude product by column chromatography on silica gel afforded the product as a white solid. (925 mg, 4.58 mmol, 54%). \(R_f = 0.60\) (hexane-ethyl acetate, 3:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta\) 8.36 (d, \(J = 8.5\) Hz, 1H), 7.90 (br s, 1H), 7.51 (t, \(J = 7.4\) Hz, 2H), 7.09 (t, \(J = 7.4\) Hz, 1H), 1.29 (s, 9H); \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)): \(\delta\) 177.33, 141.16, 134.55, 132.32, 124.29, 121.42, 116.77, 102.39, 40.57, 27.84; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 3329, 2973, 2229, 1666, 1509, 1447, 1296, 1163, 755, 613.
N-(2-cyanophenyl)benzamide (1c)

Prepared according to the general procedure from 2-aminobenzonitrile (1.00 g; 8.47 mmol), triethylamine (1.29 g, 12.7 mmol, 1.77 ml, 1.50 eq.) and benzoyl chloride (1.78 g, 12.7 mmol, 1.47 ml, 1.50 eq.) in 80 ml dichloromethane. The reaction mixture was stirred at room temperature for 2 days. Recrystallization of the crude product from ethanol gave a white solid (992 mg, 4.47 mmol, 53%). \(R_f = 0.35\) (hexane-ethyl acetate, 5:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta 8.49 (d, J = 8.3 \text{ Hz}, 1\text{H}), 8.36 (\text{br s}, 1\text{H}), 7.86 (d, J = 7.2 \text{ Hz}, 2\text{H}), 7.59 – 7.41 (m, 5\text{H}), 7.13 (t, J = 7.5 \text{ Hz}, 1\text{H}); \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)): \(\delta 165.89, 141.03, 134.68, 134.09, 133.02, 132.59, 129.45, 127.61, 124.68, 121.69, 116.84, 102.73;\) IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 3285, 2231, 1649, 1601, 1508, 1481, 1436, 1310, 1286, 1261, 1245, 794, 708, 686, 675, 488.

N-(2-cyanophenyl)-2,2,2-trifluoroacetamide (1d)

2-aminobenzonitrile (1.00 g; 8.47 mmol) was dissolved in 45 ml dichloromethane then 2,2,2-trifluoroacetic anhydride (2.13 g; 10.2 mmol; 1.43 ml) was added dropwise. The reaction mixture was stirred at room temperature overnight. After that the pH of the reaction mixture was adjusted to 7-8 with saturated sodium hydrogen carbonate, the separated organic layer was washed with distilled water (1 x 50 ml) and with brine (1 x 50 ml), dried over anhydrous magnesium sulfate, filtered and evaporated. The product was obtained as a white crystalline solid after recrystallization from toluene (1.15 g, 5.37 mmol, 63%). \(R_f = 0.40\) (hexane-ethyl acetate, 3:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)): 8.38 (br s, 1H), 8.22 (d, \(J = 8.6 \text{ Hz}, 1\text{H}), 7.62 \) (d, \(J = 6.2 \text{ Hz}, 2\text{H}), 7.29 (t, \(J = 7.5 \text{ Hz}, 1\text{H}); \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)): \(\delta 156.60, 155.99, 155.38, 154.77, 137.63, 134.80, 133.24, 127.04, 123.02, 118.07, 115.76, 113.48, 104.92;\) IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 3263, 2229, 1714, 1546, 1286, 1251, 1203, 1156, 1094, 917, 763, 716, 653, 494.

2-Chloro-N-(2-cyanophenyl)acetamide (1e)

Prepared according to the general procedure from 2-aminobenzonitrile (1.00 g; 8.47 mmol), triethylamine (1.07 g, 10.6 mmol, 1.48 ml, 1.25 eq.) and chloroacetyl chloride (1.20 g, 10.6
mmol, 842 µl, 1.25 eq.) in 50 ml dichloromethane. The reaction mixture was stirred at room temperature for 2 days. Purification of the crude product by column chromatography on silica gel afforded the product as a white solid. (909 mg, 4.69 mmol, 55%). \( R_f = 0.30 \) (hexane-ethyl acetate, 3:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)): δ 8.79 (br s, 1H), 8.30 (d, \( J = 8.8 \) Hz, 1H), 7.57 – 7.52 (m, 2H), 7.17 (t, \( J = 7.6 \) Hz, 1H), 4.18 (s, 2H); \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)): δ 164.80, 139.64, 134.62, 132.83, 125.48, 121.55, 116.20, 103.30, 43.31; IR ν\(_{\text{max}}/\text{cm}^{-1}\) (solid): 3313, 2229, 1698, 1604, 1535, 1446, 1402, 1250, 766, 619, 495.

4-Chloro-N-(2-cyanophenyl)benzamide (1f)

Prepared according to the general procedure from 2-aminobenzonitrile (1.00 g; 8.47 mmol), triethylamine (1.29 g, 12.7 mmol, 1.77 ml, 1.50 eq.) and 4-chlorobenzoyl chloride (2.22 g, 12.7 mmol, 1.63 ml, 1.50 eq.) in 50 ml dichloromethane. The reaction mixture was stirred at room temperature for 24 h. The product was obtained as a white solid after recrystallization from ethanol (1.34 g, 5.23 mmol, 62%). \( R_f = 0.45 \) (hexane-ethyl acetate, 4:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)): δ 8.46 (d, \( J = 7.3 \) Hz, 1H), 8.29 (s, 1H), 7.90 (dd, \( J = 48.9, 6.6 \) Hz, 4H), 7.68 – 7.28 (m, 4H), 7.17 (d, \( J = 6.5 \) Hz, 1H). \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)): δ 164.82, 161.68, 141.81, 140.75, 139.49, 134.77, 132.63, 132.28, 129.76, 129.06, 127.43, 124.93, 121.70, 116.81, 102.77; IR ν\(_{\text{max}}/\text{cm}^{-1}\) (solid): 3282, 2223, 1653, 1590, 1579, 1523, 1485, 1445, 1307, 1091, 1007, 855, 754, 649, 622, 537, 500, 483, 470.

N-(2-cyanophenyl)-4-nitrobenzamide (1g)

Prepared according to the general procedure from 2-aminobenzonitrile (1.00 g; 8.47 mmol), triethylamine (1.93 g, 19.0 mmol, 2.66 ml, 2.25 eq.) and 4-nitrobenzoyl chloride (3.53 g, 19.0 mmol, 2.25 eq.) in 50 ml dichloromethane. The reaction mixture was stirred at room temperature for 2 days. Purification of the crude product by column chromatography on silica gel then recrystallization from 2-propanol afforded a yellow solid (223 mg, 0.835 mmol, 26%). \( R_f = 0.30 \) (hexane-ethyl acetate, 7:3). \(^1\)H NMR (250 MHz, DMSO-d\(_6\)): δ 10.97 (br s, 1H), 8.26-7.60 (m, 8H); \(^{13}\)C NMR (62.5 MHz, DMSO-d\(_6\)): δ 170.80, 149.85, 140.90, 139.41, 135.36, 134.48, 131.18, 130.49, 130.30, 124.24, 124.13, 111.80; IR ν\(_{\text{max}}/\text{cm}^{-1}\) (solid): 3113, 2232, 1676, 1524, 1334, 1316, 1228, 1143, 1109, 911, 859, 847, 765, 718, 702, 439.
N-(2-cyanophenyl)-4-fluorobenzamide (1h)\(^7\)

![Structure of N-(2-cyanophenyl)-4-fluorobenzamide](image1)

Prepared according to the general procedure from 2-aminobenzonitrile (1.00 g; 8.47 mmol), triethylamine (1.93 g, 19.0 mmol, 2.66 ml, 2.25 eq.) and 4-fluorobenzoyl chloride (3.02 g, 19.0 mmol, 2.25 ml, 2.25 eq.) in 50 ml dichloromethane. The reaction mixture was stirred at room temperature for 24 h. The product was obtained as a white crystalline solid after recrystallization from ethanol then from toluene (368 mg, 1.53 mmol, 37\%). \(R_f = 0.50\) (hexane-ethyl acetate, 4:1). \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 10.66 (s, 1H), 8.07 – 7.42 (m, 1H); \(^13\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 166.72, 164.93, 140.62, 134.16, 133.48, 131.02, 130.87, 130.33, 127.21, 126.79, 117.28, 116.13, 115.78, 109.72; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 3278, 2225, 1652, 1601, 1579, 1525, 1504, 1444, 1310, 1296, 1224, 762, 620, 501.

N-(2-cyanophenyl)-4-methoxybenzamide (1i)\(^7\)

![Structure of N-(2-cyanophenyl)-4-methoxybenzamide](image2)

Prepared according to the general procedure from 2-aminobenzonitrile (1.00 g; 8.47 mmol), triethylamine (1.93 g, 19.0 mmol, 2.66 ml, 2.25 eq.) and 4-methoxybenzoyl chloride (3.25 g, 19.0 mmol, 2.58 ml, 2.25 eq.) in 50 ml dichloromethane. The reaction mixture was stirred at room temperature for 2 days. The product was obtained as a white crystalline solid after recrystallization from ethanol (1.19 g, 4.72 mmol, 56\%). \(R_f = 0.80\) (hexane-ethyl acetate, 3:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta\) 8.50 (d, \(J = 8.3\) Hz, 1H), 8.28 (br s, 1H), 7.83 (d, \(J = 8.5\) Hz, 2H), 7.55 (t, \(J = 8.2\) Hz, 2H), 7.11 (t, \(J = 7.5\) Hz, 1H), 6.92 (d, \(J = 8.4\) Hz, 2H), 3.80 (s, 3H); \(^13\)C NMR (62.5 MHz, CDCl\(_3\)): \(\delta\) 165.31, 163.50, 141.30, 134.70, 132.52, 129.60, 126.21, 124.36, 121.43, 116.98, 114.66, 102.34, 55.93; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 3277, 2227, 1649, 1605, 1579, 1525, 1508, 1444, 1302, 1251, 1176, 1022, 840, 762, 623, 503.

N-(2-cyanophenyl)cyclohexanecarboxamide (1j)\(^12\)

![Structure of N-(2-cyanophenyl)cyclohexanecarboxamide](image3)

Prepared according to the general procedure from 2-aminobenzonitrile (1.00 g; 8.47 mmol), triethylamine (1.29 g, 12.7 mmol, 1.77 ml, 1.50 eq.) and cyclohexanecarbonyl chloride (1.86
g, 12.7 mmol, 1.71 ml, 1.50 eq.) in 50 ml dichloromethane. The reaction mixture was stirred at room temperature for 2 days. The product was obtained as a white crystalline solid after recrystallization from ethanol (1.20 g, 5.26 mmol, 62%). $R_f = 0.60$ (hexane-ethyl acetate, 7:3). $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 8.33 (d, $J = 7.2$ Hz, 1H), 7.67 (s, 1H), 7.50 (s, 2H), 7.08 (s, 1H), 2.27 (s, 1H), 2.09 – 0.96 (m 10H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 175.04, 141.09, 134.55, 132.52, 124.31, 121.71, 116.85, 102.26, 46.76, 29.91, 25.92; IR $\nu_{max}$/cm$^{-1}$ (solid): 3294, 2925, 2852, 2230, 1664, 1602, 1511, 1492, 1447, 1437, 1250, 1198, 955, 776, 759, 671, 489.

$\text{N-(2-cyanophenyl)cinnamamide (1k)}$

Prepared according to the general procedure from 2-aminobenzonitrile (1.00 g, 8.47 mmol), triethylamine (1.29 g, 12.7 mmol, 1.77 ml, 1.50 eq.) and cinnamoyl chloride (2.12 g, 12.7 mmol, 1.50 eq.) in 50 ml dichloromethane. The reaction mixture was stirred at room temperature for 24 h. The product was obtained as a white crystalline solid after recrystallization from ethanol then from toluene (550 mg, 2.22 mmol, 50%). $R_f = 0.50$ (hexane-ethyl acetate, 7:3). $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 8.57 (d, $J = 7.7$ Hz, 1H), 7.94 (s, 1H), 7.81 (d, $J = 15.0$ Hz, 1H), 7.60 (d, $J = 6.5$ Hz, 4H), 7.41 (s, 3H), 7.26 – 7.08 (m, 1H), 6.67 (d, $J = 15.3$ Hz, 1H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 164.58, 144.45, 141.19, 134.68, 134.60, 132.75, 130.86, 129.38, 128.63, 124.52, 121.83, 120.26, 116.98, 102.22; IR $\nu_{max}$/cm$^{-1}$ (solid): 3341, 2226, 1686, 1634, 1583, 1531, 1448, 1290, 1155, 976, 763, 710, 620, 550, 483.

$\text{N-(3-cyanothiophen-2-yl)acetamide (1n)}$

Prepared according to the general procedure for the synthesis of $\text{N-(2-cyanophenyl)amides}$ from 2 -aminothiophene-3-carbonitrile (261 mg, 2.10 mmol), triethylamine (319 mg, 3.15 mmol, 440 µl, 1.50 eq.) and acetyl chloride (247 mg, 3.15 mmol, 224 µl, 1.50 eq.) in 12 ml dichloromethane. The reaction mixture was stirred at room temperature for 18 h. The product was obtained as a yellow crystalline solid after recrystallization from ethanol (161 mg, 0.970 mmol, 46%). $R_f = 0.40$ (hexane-ethyl acetate, 7:3). $^1$H NMR (250 MHz, DMSO-d$_6$): $\delta$ 11.66 (s, 1H), 7.11 (s, 2H), 2.19 (s, 3H); $^{13}$C NMR (62.5 MHz, DMSO): $\delta$ 168.72, 149.75, 125.03, 119.01, 115.16, 92.13, 22.76; IR $\nu_{max}$/cm$^{-1}$ (solid): 3269, 2217, 1692, 1545, 1496, 1363, 1280, 1238, 730, 720, 685, 670, 638, 593, 535, 486.
3. Synthesis and analytical data of cyclic β-enaminonitriles

β-enaminonitriles were synthesized from the appropriate dinitrile and potassium tert-butoxide according to the modified procedure of Ma et al.\textsuperscript{15}

2-aminocyclopent-1-ene-1-carbonitrile (1o')\textsuperscript{15}

\begin{center}
\includegraphics[width=0.2\textwidth]{2-aminocyclopent-1-ene-1-carbonitrile}
\end{center}

A mixture of powdered \textsuperscript{t}BuOK (3.36 g; 30.0 mmol) and adiponitrile (2.70 g, 25.0 mmol, 2.84 ml) in toluene (40 ml) was stirred at room temperature overnight. Solvent was removed under reduced pressure, than distilled water was added to the reaction mixture and the product was extracted with dichloromethane (4 x 40 ml), the combined organics were washed with brine (1 x 100 ml), dried over anhydrous sodium sulfate, filtered and evaporated. The residual yellow solid was recrystallized from MeOH to give 2-aminocyclopent-1-ene-1-carbonitrile as a white solid (1.15 g; 10.6 mmol; 43%). \textit{R} \textsubscript{f} = 0.30 (hexane-ethyl acetate, 7:3). \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}): δ 4.54 (s, 1H), 2.44 (s, 2H), 1.86 (s, 1H). \textsuperscript{13}C NMR (62.5 MHz, CDCl\textsubscript{3}): δ=163.01, 119.50, 74.48, 34.63, 31.60, 22.36; IR \textit{ν}\textsubscript{max}/cm\textsuperscript{-1} (solid): 3434, 3346, 2947, 2172, 1636, 1604, 1401, 1209, 1147, 887, 492, 468, 448.  

2-amino-1-cyclohexene-1-carbonitrile (1p')\textsuperscript{15}

\begin{center}
\includegraphics[width=0.2\textwidth]{2-amino-1-cyclohexene-1-carbonitrile}
\end{center}

A mixture of powdered \textsuperscript{t}BuOK (6.73 g; 60.0 mmol) and pimelonitrile (6.11 g; 50.0 mmol; 6.43 ml) was kept at 80 °C for 3 h then at room temperature overnight. Distilled water was added to the reaction mixture and the product was extracted with ether (3 x 40 ml), dried over anhydrous magnesium sulfate, filtered and evaporated. The residual yellow solid was recrystallized from MeOH to give 2-amino-1-cyclohexene-1-carbonitrile as a white solid (1.32 g; 10.8 mmol; 22%). \textit{R} \textsubscript{f} = 0.40 (hexane-ethyl acetate, 7:3). \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}): δ 4.28 (s, 2H), 2.12 (s, 4H), 1.59 (s, 4H); \textsuperscript{13}C NMR (62.5 MHz, CDCl\textsubscript{3}): δ 156.66, 121.33, 74.30, 28.54, 24.64, 22.36, 21.98; IR \textit{ν}\textsubscript{max}/cm\textsuperscript{-1} (solid): 3421, 3348, 3232, 2947, 2172, 1636, 1604, 1410, 490, 457.
2-aminocyclohept-1-ene-1-carbonitrile (1q')

A mixture of powdered tBuOK (3.36 g; 60.0 mmol) and 1,6-dicyanohexane (3.41 g, 25.0 mmol, 3.57 ml) in toluene (40 ml) was stirréd at 100°C for 2 days. Solvent was removed under reduced pressure, than distilled water was added to the reaction mixture and the product was extracted with dichloromethane (4 x 40 ml), the combined organics were washed with brine (1 x 100 ml), dried over anhydrous sodium sulfate, filtered and evaporated. Purification of the crude product by column chromatography on silica gel afforded the product as a yellow solid (825 mg, 6.07 mmol, 24%). The obtained product (not totally pure) was brought into the next step (acylation) without further purification. $R_f = 0.74$ (hexane-ethyl acetate, 1:1). $^1$H NMR (250 MHz, CDCl₃): $\delta$ 4.50 (s, 2H), 2.74-2.08 (m, 6H), 1.91 – 1.32 (m, 9H); $^{13}$C NMR (62.5 MHz, CDCl₃): $\delta$ 164.61, 122.78, 120.02, 76.02, 35.69, 32.14, 28.88, 28.42, 28.19, 25.74, 25.40, 17.41, IR $\nu_{max}$/cm$^{-1}$ (solid): 3464, 3360, 2925, 2852, 2246, 2173, 1634, 1596, 1448, 1192.
4. Synthesis and analytical data of cyclic β-acetylaminoacrylonitriles

β-acetylaminoacrylonitriles were synthesized from the appropriate cyclic β-enaminonitrile and acetic anhydride according to the modified procedure of Ma et al.\textsuperscript{15}

**General procedure for the synthesis of β-acetylaminoacrylonitriles**

To a solution of cyclic-β-enaminonitrile (4.09 mmol) in pyridine (5 ml), acetic anhydride (8.19 mmol, 2.0 eq.) was added. The reaction mixture was heated at reflux for 16 h and cooled to room temperature. It was then poured onto 2 molar hydrochloric acid solution and extracted with chloroform (5 x 10 ml). The combined organics were washed with distilled water (2 x 50 ml), with brine (1 x 50 ml), dried over anhydrous sodium sulfate, filtered and evaporated. Purification of the crude product by column chromatography on silica gel afforded the product as a solid.

**N-(2-cyanocyclopent-1-en-1-yl)acetamide (1o)\textsuperscript{15}**

![Image](image1)

Prepared according to the general procedure from 2-aminocyclopent-1-ene-1-carbonitrile (1o') (811 mg, 7.50 mmol) and acetic anhydride (1.53 g, 15.0 mmol, 1.42 ml). Purification of the crude product by column chromatography on silica gel afforded the product as a grey solid (884 mg, 5.90 mmol, 79%). \( R_f = 0.60 \) (hexane-ethyl acetate, 1:1). \( ^1\text{H} \text{NMR} (250 \text{ MHz, CCl}_3) \): \( \delta \) 8.54 (s, 1H), 3.26 – 2.88 (m, 2H), 2.54 – 2.36 (m, 2H), 2.06 (s, 3H), 1.99 – 1.83 (m, 2H). \( ^1\text{C} \text{NMR} (62.5 \text{ MHz, CCl}_3) \): \( \delta \) 169.00, 157.45, 116.99, 87.50, 34.11, 30.46, 24.33, 22.52; \( \text{IR } v_{\text{max}}/\text{cm}^{-1} \) (solid): 3276, 2202, 1713, 1631, 1510, 1367, 1230, 1203, 995, 740, 604, 522, 467.

**N-(2-cyanocyclohex-1-en-1-yl)acetamide (1p)\textsuperscript{15}**

![Image](image2)

Prepared according to the general procedure from 2-amino-1-cyclohexene-1-carbonitrile (1p') (500 mg, 4.09 mmol) and acetic anhydride (836 mg, 8.19 mmol, 774 µl). Purification of the crude product by column chromatography on silica gel afforded the product as a white solid (260 mg, 1.59 mmol, 39%). \( R_f = 0.30 \) (hexane-ethyl acetate, 3:2). \( ^1\text{H} \text{NMR} (250 \text{ MHz, CCl}_3) \): \( \delta \) 7.61 (s, 1H), 2.73 (s, 2H), 2.21 (s, 2H), 2.05 (s, 3H), 1.60 (s, 4H); \( ^1\text{C} \text{NMR} (62.5 \text{ MHz, CCl}_3) \): \( \delta \) 168.83, 152.19, 118.44, 91.38, 28.14, 25.96, 24.93, 21.78, 21.36; \( \text{IR} \)
\( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 3230, 3148, 2932, 2210, 1667, 1520, 1440, 1422, 1366, 1281, 1267, 1229, 1032, 756, 583, 430.

**N-(2-cyanocyclohept-1-en-1-yl)acetamide (1q)**

![Chemical Structure](image)

Prepared according to the general procedure from 2-aminocyclohept-1-ene-1-carbonitrile (1q') (732 mg, 5.38 mmol) and acetic anhydride (1.10 g, 10.8 mmol, 1016 µl). Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (160 mg, 0.899 mmol, 17%). M. p. 112-114 °C. \( R_f = 0.35 \) (hexane-ethyl acetate, 7:3). \(^1\)H NMR (250 MHz, CDCl\(_3\)): 7.75 (s, 1H), 2.82 – 2.56 (m, 2H), 2.39 – 2.23 (m, 3H), 2.05 (s, 3H), 1.78 – 1.40 (m, 5H). \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)) δ 169.57, 158.83, 119.27, 99.71, 32.10, 31.96, 29.74, 26.55, 24.84, 24.55. IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 3223, 2997, 2932, 2919, 2852, 2203, 1657, 1627, 1517, 1445, 1366, 1350, 1289, 1275, 1264, 1044, 998, 880, 725, 692, 665, 610; HRMS m/z [M-H]\(^+\) Calculated for C\(_{16}\)H\(_{15}\)N\(_2\)O: 179.1179; found: 179.1186.
5. Synthesis and analytical data of diaryl iodonium triflates

Aryl-mesityliodonium triflates (2a-2m) were synthesized in a one-pot procedure from the appropriate iodoarene and mesitylene according to the modified procedure\textsuperscript{17} of Olofsson.\textsuperscript{18}

General procedure for the one-pot synthesis of aryl-mesityliodonium triflates\textsuperscript{17}

\( m \)-Chloroperbenzoic acid (65% active oxidant, 1.32 g, 5.00 mmol) and the appropriate iodoarene (4.50 mmol) were dissolved in dichloromethane (20 ml). Mesitylene (696 µl, 5.00 mmol) was added and the solution was cooled to 0 °C. Trifluoromethanesulfonic acid (825 mg, 486 µl, 5.50 mmol) was added dropwise in 5 min and the resulting reaction mixture was allowed to warm to room temperature over 2h. The volatile components were removed under reduced pressure and the resulting material was suspended in diethyl ether (40 ml). The suspension was stored at -20 °C for 2 h. The resulting crystals were filtered off and were washed with ether to give the appropriate aryl-mesityliodonium triflate as a solid, which was dried at 100 °C under vacuum.

Mesityl(phenyl)iodonium trifluoromethanesulfonate (2a)\textsuperscript{17}

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, \( J = 7.7 \) Hz), 7.64 (t, 1H, \( J = 7.3 \) Hz), 7.50 (t, 2H, \( J = 7.4 \) Hz), 7.22 (s, 2H), 2.60 (s, 6H), 2.29 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\( d_6 \)): \( \delta \) 143.1, 141.5, 134.5, 131.8, 131.7, 129.7, 122.5, 114.5, 26.2, 20.5; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (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)\textsuperscript{17}

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, \( J = 7.9 \) Hz), 7.55 (d, 2H, \( J = 4.4 \) Hz), 7.26 (m, 1H, \( J = 4.3 \)Hz), 7.21 (s, 2H), 2.57 (s, 9H), 2.29 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\( d_6 \)): \( \delta \) 142.9, 141.6, 140.7, 136.7, 132.4, 131.8, 129.9, 129.3, 121.8, 118.5, 26.1, 24.4, 20.4; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 1467, 1245,
1156, 1027, 855, 634, 516; HRMS m/z [M-OTf]+ Calculated for C_{16}H_{18}I: 337.0448; found 337.0443.

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-$d_6$): $\delta$ 7.87 (s, 1H), 7.78 (d, 1H, $J = 7.6$ Hz), 7.45 (d, 1H, $J = 7.6$ 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-$d_6$): $\delta$ 143.0, 141.9, 141.5, 134.6, 132.5, 131.6, 131.5, 129.7, 122.4, 114.3, 26.3, 20.7, 20.4; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 1455, 1275, 1245, 1156, 1025, 634, 516; HRMS m/z [M-OTf]+ Calculated for C_{16}H_{18}I: 337.0448; found 337.0440.

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-$d_6$): $\delta$ 7.88 (d, 2H, $J = 8.4$ Hz), 7.30 (d, 2H, $J = 8.2$ Hz), 7.20 (s, 2H), 2.60 (s, 6H), 2.32 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (62.5 MHz, DMSO-$d_6$): $\delta$ 142.9, 142.2, 141.4, 134.5, 132.4, 129.7, 122.7, 110.8, 26.2, 20.7, 20.4; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 1452, 1246, 1157, 1024, 804, 632, 481; HRMS m/z [M-OTf]+ Calculated for C_{16}H_{18}I: 337.0448; found 337.0444.

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

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, $J = 8.1$ Hz and 1.3 Hz), 7.82 (dd, 1H, $J = 8.1$ Hz and 1.4 Hz), 7.68 (td, 1H, $J = 7.9$ Hz and 1.4 Hz), 7.45 (td, 1H, $J = 7.9$ Hz and 1.4 Hz), 7.21 (s, 2H),
2.62 (s, 6H), 2.28 (s, 3H); $^{13}$C NMR (62.5 MHz, DMSO-$d_6$): δ 143.2, 141.8, 138.9, 135.7, 134.3, 130.7, 130.0 (d, $J = 7.8$ Hz), 122.6, 116.4, 26.1, 20.4; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 1449, 1276, 1239, 1160, 1024, 759, 631, 516, 432; HRMS m/z [M-OTf]$^+$ Calculated for C$_{15}$H$_{15}$I: 356.9901; found 356.9899.

(4-Chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (2f)$^{17}$

![Chemical Structure]

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-$d_6$): δ 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-$d_6$): δ 143.2, 141.5, 136.9, 136.2, 131.7, 129.8, 122.7, 112.2, 26.2, 20.4; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 1473, 1245, 1163, 1024, 807, 631, 516; HRMS m/z [M-OTf]$^+$ Calculated for C$_{15}$H$_{15}$I: 356.9901; found 356.9901.

3-Bromophenyl(mesityl)iodonium trifluoromethanesulfonate (2g)$^{17}$

![Chemical Structure]

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. 167-168 °C; $^1$H NMR (250 MHz, DMSO-$d_6$): δ 8.18 (dd, 1H, $J = 7.9$ and 1.4 Hz), 7.95 (dd, 1H, $J = 7.9$ and 1.4 Hz), 7.59 (td, 1H, $J = 7.9$ and 1.4 Hz), 7.47 (td, 1H, $J = 7.9$ and 1.4 Hz), 7.22 (s, 2H) 2.62 (s, 6H), 2.29 (s, 3H); $^{13}$C NMR (62.5 MHz, DMSO-$d_6$): δ 143.2, 141.8, 139.0, 134.1, 130.4, 130.0, 126.5, 119.4, 26.3, 20.4; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 1442, 1276, 1241, 1160, 1025, 757, 631, 516; HRMS m/z [M-OTf]$^+$ Calculated for C$_{15}$H$_{15}$BrI: 400.9396; found 400.9386.
3-Bromophenyl(mesityl)iodonium trifluoromethanesulfonate (2h)\textsuperscript{17}

\[
\begin{array}{c}
\text{OSO}_2\text{CF}_3 \\
\text{Br} \\
\text{Br} \\
\text{Br}
\end{array}
\]

Prepared according to the general procedure from 3-bromiodobenzene. The product was obtained as an off-white solid (1.353 g, 55%). M. p. 173-174 °C; \textsuperscript{1}H NMR (250 MHz, DMSO-\textit{d}_6): δ 8.29 (s, 1H), 7.90 (d, 1H, \textit{J} = 8.1 Hz), 7.84 (d, 1H, \textit{J} = 7.4 Hz), 7.44 (t, 1H, \textit{J} = 7.9), 7.23 (s, 2H), 2.60 (s, 6H), 2.30 (s, 3H); \textsuperscript{13}C NMR (62.5 MHz, DMSO-\textit{d}_6): δ 144.0, 143.3, 141.7, 136.1, 134.7, 133.5, 133.1, 129.8, 123.4, 122.6, 114.9, 26.3, 20.5; IR \nu_{\text{max}}/\text{cm}^{-1} (solid): 1454, 1222, 1024, 797, 634, 516; HRMS m/z [M-OTf]\textsuperscript{+} Calculated for C\textsubscript{15}H\textsubscript{15}BrI: 400.9396; found: 400.9402.

4-Bromophenyl(mesityl)iodonium trifluoromethanesulfonate (2i)\textsuperscript{17}

\[
\begin{array}{c}
\text{OSO}_2\text{CF}_3 \\
\text{Br} \\
\text{Br}
\end{array}
\]

Prepared according to the general procedure from 4-bromiodobenzene. The product was obtained as a white solid (1.690 g, 68%). M. p. 179-180 °C; \textsuperscript{1}H NMR (250 MHz, DMSO-\textit{d}_6): δ 7.90 (d, 2H, \textit{J} = 8.5 Hz), 7.70 (d, 2H, \textit{J} = 8.5 Hz), 7.22 (s, 2H), 2.60 (s, 6H), 2.29 (s, 3H); \textsuperscript{13}C NMR (62.5 MHz, DMSO-\textit{d}_6): δ 143.2, 141.5, 136.3, 134.6, 129.8, 125.7, 122.7, 113.0, 26.2, 20.5; IR \nu_{\text{max}}/\text{cm}^{-1} (solid): 1473, 1245, 1232, 1024, 807, 631, 518, 475; HRMS m/z [M-OTf]\textsuperscript{+} Calculated for C\textsubscript{15}H\textsubscript{15}BrI: 400.9396; found: 400.9399.

2-Fluorophenyl(mesityl)iodonium trifluoromethanesulfonate (2j)\textsuperscript{17}

\[
\begin{array}{c}
\text{OSO}_2\text{CF}_3 \\
\text{Br} \\
\text{F}
\end{array}
\]

Prepared according to the general procedure from 2-fluoroiodobenzene. The product was obtained as an off-white solid (0.948 g, 43%). M. p. 161-162 °C; \textsuperscript{1}H NMR (250 MHz, DMSO-\textit{d}_6): δ 8.27 (m, 1H), 7.72 (m, 1H), 7.56 (td, 1H, \textit{J} = 8.8 Hz and 1.3 Hz), 7.35 (td, 1H, \textit{J} = 7.9 Hz and 1.3 Hz), 7.20 (s, 2H), 2.62 (s, 6H), 2.27 (s, 3H); \textsuperscript{13}C NMR (62.5 MHz, DMSO-\textit{d}_6): δ 143.2, 141.5, 137.4, 135.3 (d, \textit{J} = 8.3 Hz), 129.8, 127.5 (d, \textit{J} = 2.6 Hz), 122.7, 117.3, 116.9, 101.6, 101.3, 26.0, 20.4; IR \nu_{\text{max}}/\text{cm}^{-1} (solid): 1476, 1279, 1236, 1161, 1027, 770, 635, 515; HRMS m/z [M-OTf]\textsuperscript{+} Calculated for C\textsubscript{15}H\textsubscript{15}FI: 341.0197; found: 341.0194.
4-Fluorophenyl(mesityl)iodonium trifluoromethanesulfonate (2k)\textsuperscript{17}

![Structure](image)

Prepared according to the general procedure from 4-fluoroiodobenzene. The product was obtained as an off-white solid (1.13 g, 51%). M. p. 178-179 °C; \textsuperscript{1}H NMR (250 MHz, DMSO-\textit{d}_6): \(\delta\) 7.37 (t, 2H, \(J = 8.7 \text{ Hz}\)), 7.22 (s, 2H), 2.60 (s, 6H), 2.29 (s, 3H); \textsuperscript{13}C NMR (62.5 MHz, DMSO-\textit{d}_6): \(\delta\) 143.1, 141.5, 137.4, 137.2, 129.7, 119.4, 119.0, 26.2, 20.5; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 1575, 1483, 1224, 1168, 1024, 849, 632, 508; HRMS m/z [M-OTf]\textsuperscript{+} Calculated for C\textsubscript{15}H\textsubscript{15}FI: 341.0197; found: 341.0195.

(2-(Ethoxycarbonyl)phenyl)(mesityl)iodonium trifluoromethanesulfonate (2l)\textsuperscript{17}

![Structure](image)

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, 34%). M. p. 169-170 °C; \textsuperscript{1}H NMR (250 MHz, DMSO-\textit{d}_6): \(\delta\) 8.33 (dd, 1H, \(J = 7.2 \text{ Hz}\) and 1.9 HzH), 7.86 – 7.69 (m, 2H), 7.40 (s, 2H), 6.89 (d, 1H, \(J = 7.4 \text{ Hz}\)), 4.52 (q, 2H, \(J = 7.1 \text{ Hz}\)), 2.52 (s, 6H), 2.42 (s, 3H), 1.42 (t, 3H, \(J = 7.1 \text{ Hz}\)); \textsuperscript{13}C NMR (62.5 MHz, DMSO-\textit{d}_6): \(\delta\) 167.4, 144.6, 143.3, 137.3, 132.9, 131.4, 130.1, 128.6, 127.7, 117.8, 113.5, 63.8, 40.5, 26.1, 20.7, 13.9; IR \(\nu_{\text{max}}/\text{cm}^{-1}\) (solid): 1673, 1310, 1272, 1246, 1222, 1154, 1027, 753, 637, 515; HRMS m/z [M-OTf]\textsuperscript{+} Calculated for C\textsubscript{18}H\textsubscript{20}IO\textsubscript{2}: 395.0502; found: 395.0511.

(4-(Ethoxycarbonyl)phenyl)(mesityl)iodonium trifluoromethanesulfonate (2m)\textsuperscript{17}

![Structure](image)

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, 47%). M. p. 174-175 °C; \textsuperscript{1}H NMR (250 MHz, DMSO-
$d_6$: $\delta$ 8.09 (d, 2H, $J = 8.4$ Hz), 7.99 (d, 2H, $J = 8.4$ Hz), 7.24 (s, 2H), 4.31 (q, 2H, $J = 6.9$ Hz), 2.59 (s, 2H), 2.30 (s, 1H), 1.29 (t, 3H, $J = 7.0$ 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 $\nu_{\text{max}}$/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.
6. Synthesis and analytical data of imino-1,3-benzoxazines

General procedure for the synthesis of (Z)-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-ylidene)anilines

N-(2-cyanophenyl)acetamide (1a) (80.1 mg, 0.500 mmol), diaryl iodonium salt (0.600 mmol, 1.2 eq.) and copper(II)triflate (18.08 mg; 0.050 mmol, 10 mol%) were added to a 4 ml vial then the system was charged with argon. Solvent (1,2-dichloroethane or ethyl acetate, 1000 μl) was added under argon atmosphere then the reaction mixture was stirred at 75°C for the appropriate time. Saturated sodium hydrogen carbonate solution (10 ml) was added to the mixture, the aqueous layer was extracted with dichloromethane (4 x 10 ml) the combined organics were dried over anhydrous sodium sulfate, filtered and evaporated. Purification of the crude products by column chromatography on silica gel afforded the products as solids.

(Z)-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3a)

Prepared according to the general procedure from N-(2-cyanophenyl)acetamide (1a) and phenyl(mesityl) iodonium trifluoromethanesulfonate (2a) (283 mg, 0.600 mmol). Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (60.0 mg, 0.254 mmol, 51%). M. p. 142 - 145 °C. \( R_f = 0.30 \) (hexane-ethyl acetate, 3:2). \(^1\)H NMR (250 MHz, CDCl\(_3\)): δ 8.19 (d, \( J = 7.9 \) Hz, 1H), 7.78 – 7.55 (m, 2H), 7.55 – 7.28 (m, 4H), 7.19 (d, \( J = 6.8 \) Hz, 2H), 2.16 (s, 3H); \(^1\)C NMR (62.5 MHz, CDCl\(_3\)): δ 162.64, 154.61, 147.88, 138.17, 134.96, 130.38, 129.67, 128.43, 127.45, 127.16, 127.02, 121.19, 24.76; IR \( \nu_{\max} \)/cm\(^{-1}\) (solid): 2923, 1676, 1606, 1585, 1572, 1470, 1265, 1116, 760, 692, 659, 622, 507.

(Z)-2-methyl-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3b)

Prepared according to the general procedure from N-(2-cyanophenyl)acetamide (1a) and 2-methylphenyl(mesityl) iodonium trifluoromethanesulfonate (2b) (292 mg, 0.600 mmol). Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (66.5 mg, 0.266 mmol, 53%). M. p. 115-117 °C. \( R_f = 0.35 \) (hexane-
ethyl acetate, 2:1). $^1$H NMR (250 MHz, CDCl$_3$): δ 8.27 (d, $J = 8.0$ Hz, 1H), 7.82 – 7.60 (m, 2H), 7.53 – 7.28 (m, 4H), 7.15 (d, $J = 6.2$ Hz, 1H), 2.17 (s, 3H), 2.11 (s, 3H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 162.01, 154.70, 148.05, 137.22, 135.74, 134.96, 131.91, 129.96, 128.33, 128.03, 127.49, 127.18, 126.98, 121.14, 24.24, 17.77; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 2921, 1673, 1607, 1597, 1567, 1468, 1325, 1279, 1269, 1123, 776, 759, 720, 702, 657, 458; HRMS m/z [M+H]$^+$ Calculated for C$_{16}$H$_{15}$N$_2$O: 251.1179; found 251.1175.

(Z)-3-methyl-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3c)

Prepared according to the general procedure from N-(2-cyanophenyl)acetamide (1a) and 3-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (2c) (292 mg, 0.600 mmol). Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (77.0 mg, 0.308 mmol, 62%). M. p. 96-98 °C. $R_f = 0.25$ (hexane-ethyl acetate, 2:1). $^1$H NMR (250 MHz, CDCl$_3$): δ 8.26 (d, $J = 7.9$ Hz, 1H), 7.89 – 7.57 (m, 2H), 7.44 (dd, $J = 11.8$, 7.7 Hz, 2H), 7.30 (d, $J = 7.7$ Hz, 1H), 7.06 (d, $J = 7.5$ Hz, 2H), 2.42 (s, 3H), 2.24 (s, 3H). $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 162.68, 154.72, 147.89, 140.51, 138.08, 134.90, 130.46, 130.15, 128.88, 127.43, 127.13, 126.95, 125.33, 121.20, 24.72, 21.72; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 2923, 2249, 1673, 1596, 1584, 1584, 1567, 1471, 1376, 1340, 1320, 1278, 726, 694, 659, 646, 630, 444; HRMS m/z [M+H]$^+$ Calculated for C$_{16}$H$_{15}$N$_2$O: 251.1179; found 251.1180.

(Z)-4-methyl-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3d)

Prepared according to the general procedure from N-(2-cyanophenyl)acetamide (1a) and 4-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (2d) (292 mg, 0.600 mmol). Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (70.5 mg, 0.282 mmol, 56%). M. p. 145-146 °C. $R_f = 0.30$ (hexane-ethyl acetate, 2:1). $^1$H NMR (250 MHz, CDCl$_3$): δ 8.24 (d, $J = 7.7$ Hz, 1H), 7.88 – 7.68 (m, 1H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.42 (t, $J = 7.3$ Hz, 1H), 7.33 (d, $J = 7.8$ Hz, 2H), 7.13 (d, $J = 7.9$ Hz, 2H), 2.42 (s, 3H), 2.23 (s, 3H). $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 162.71, 154.85, 147.89, 139.66, 135.51, 134.85, 131.01, 128.09, 127.43, 127.13, 126.90, 121.20, 24.76, 21.64;
IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 2922, 1680, 1605, 1589, 1566, 1512, 1468, 1342, 1321, 1267, 1109, 817, 776, 697, 615, 520; HRMS m/z [M+H]$^+$ Calculated for $C_{16}H_{15}N_2O$: 251.1179; found 251.1180.

(Z)-4-chloro-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3e)

Prepared according to the general procedure from N-(2-cyanophenyl)acetamide (1a) and (4-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (2f) (304 mg, 0.600 mmol). Purification of the crude product by column chromatography on silica gel afforded the product as a white solid (71.5 mg, 0.265 mmol, 53%). M. p. 153-155 °C. $R_f$ = 0.28 (hexane-ethyl acetate, 7:3). $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 8.18 (d, $J$ = 7.4 Hz, 1H), 7.81 – 7.67 (m, 1H), 7.62 (d, $J$ = 7.7 Hz, 1H), 7.50 (d, $J$ = 7.8 Hz, 2H), 7.45 – 7.33 (m, 1H), 7.19 (d, $J$ = 7.8 Hz, 2H), 2.21 (s, 3H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 162.46, 154.05, 147.74, 136.61, 135.70, 135.08, 130.64, 129.92, 127.36, 127.22, 127.14, 120.96, 24.75; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 3094, 2923, 1685, 1602, 1590, 1571, 1466, 1343, 1330, 1268, 1110, 1087, 1036, 864, 827, 764, 695, 629, 513, 444; HRMS m/z [M+H]$^+$ Calculated for $C_{15}H_{12}ClN_2O$: 271.0633; found 271.0629.

(Z)-3-bromo-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3f)

Prepared according to the general procedure from N-(2-cyanophenyl)acetamide (1a) and 3-bromophenyl(mesityl)iodonium trifluoromethanesulfonate (2h) (331 mg, 0.600 mmol). Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (78.0 mg, 0.248 mmol, 50%). M. p. 124-126 °C. $R_f$ = 0.22 (hexane-ethyl acetate, 2:1). $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 8.15 (dd, $J$ = 7.9, 0.8 Hz, 1H), 7.81 – 7.67 (m, 1H), 7.62 – 7.52 (m, 2H), 7.43 – 7.36 (m, 2H), 7.33 (d, $J$ = 8.0 Hz, 1H), 7.18 – 7.10 (m, 1H), 2.17 (s, 3H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 162.41, 153.96, 147.67, 139.27, 135.18, 132.98, 131.74, 131.59, 128.41, 127.39, 127.37, 127.23, 127.22, 123.67, 120.93, 24.69; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 3612, 2923, 1665, 1604, 1569, 1340, 1327, 1273, 1254, 765, 691, 420; HRMS m/z [M+H]$^+$ Calculated for $C_{15}H_{12}BrN_2O$: 315.0128; found 315.0124.
(Z)-4-bromo-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3g)

Prepared according to the general procedure from N-(2-cyanophenyl)acetamide (1a) and 4-bromophenyl(mesityl)iodonium trifluoromethanesulfonate (2i) (331 mg, 0.600 mmol). Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (76.0 mg, 0.242 mmol, 48%). M. p. 166-168 °C. $R_f = 0.24$ (hexane-ethyl acetate, 2:1). $^1$H NMR (250 MHz, CDCl$_3$): δ 8.12 (d, $J = 7.9$ Hz, 1H), 7.71 – 7.62 (m, 1H), 7.62 – 7.52 (m, 3H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.11 – 7.01 (m, 2H), 2.14 (s, 3H). $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 162.43, 153.98, 147.74, 137.14, 135.11, 133.65, 130.23, 127.39, 127.23, 127.17, 123.82, 120.95, 24.76; IR $\nu_{max}$/cm$^{-1}$ (solid): 2923, 1678, 1601, 1572, 1491, 1467, 1343, 1267, 1015, 822, 763, 692, 626, 508; HRMS m/z [M+H]$^+$ Calculated for C$_{15}$H$_{12}$BrN$_2$O: 315.0128; found 315.0124.

(Z)-N-(4H-benzo[d][1,3]oxazin-4-ylidene)-4-fluoroaniline (3h)

Prepared according to the general procedure from N-(2-cyanophenyl)acetamide (1a) and 4-fluorophenyl(mesityl)iodonium trifluoromethanesulfonate (2k) (294 mg, 0.600 mmol). Purification of the crude product by column chromatography on silica gel afforded the product as a brown solid (60.0 mg, 0.236 mmol, 47%). M. p. 128-130 °C. $R_f = 0.30$ (hexane-ethyl acetate, 2:1). $^1$H NMR (250 MHz, CDCl$_3$): δ 8.14 (dd, $J = 7.9$, 1.0 Hz, 1H), 7.73 – 7.62 (m, 1H), 7.58 (d, $J = 8.1$ Hz, 1H), 7.43 – 7.30 (m, 1H), 7.16 (d, $J = 6.0$ Hz, 4H), 2.15 (s, 3H). $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 165.10, 162.65, 161.13, 154.44, 147.72, 135.08, 133.95, 130.38, 130.24, 127.39, 127.17, 121.00, 117.62, 117.26, 24.72; IR $\nu_{max}$/cm$^{-1}$ (solid): 3051, 2923, 1675, 1609, 1592, 1505, 1469, 1269, 1208, 849, 765, 693, 649, 612, 524, 507; HRMS m/z [M+H]$^+$ Calculated for C$_{15}$H$_{12}$FNN$_2$O: 255.0928; found 255.0924.
(Z)-ethyl-2-(4H-benzo[d][1,3]oxazin-4-ylideneamino)benzoate (3i)

Prepared according to the general procedure from N-(2-cyanophenyl)acetamide (1a) and (2-(ethoxycarbonyl)phenyl)(mesityl)iodonium trifluoromethanesulfonate (2l) (326 mg, 0.600 mmol). Purification of the crude product by column chromatography on silica gel afforded the product as a brown solid (75.5 mg, 0.245 mmol, 49%). M. p. 120-122 °C. \( R_f = 0.40 \) (hexane-ethyl acetate, 1:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta \) 8.16 (d, \( J = 7.6 \) Hz, 1H), 7.72 – 7.58 (m, 2H), 7.52 (td, \( J = 7.7, 1.2 \) Hz, 1H), 7.44 – 7.30 (m, 1H), 7.23 (dd, \( J = 7.7, 1.0 \) Hz, 1H), 4.04 (q, \( J = 7.1 \) Hz, 2H), 2.12 (s, 3H), 0.89 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)) \( \delta \) 164.87, 162.72, 154.55, 147.92, 138.17, 134.96, 134.32, 132.89, 130.23, 130.03, 128.84, 127.32, 127.09, 126.88, 121.05, 61.88, 24.31, 13.96; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 2985, 1711, 1678, 1607, 1594, 1569, 1470, 1291, 1258, 1119, 1084, 1018, 780, 756, 696, 622, 515; HRMS m/z [M+H]\(^+\) Calculated for C\(_{18}\)H\(_{17}\)N\(_2\)O\(_3\): 309.1234; found 309.1231.

(Z)-ethyl-4-(4H-benzo[d][1,3]oxazin-4-ylideneamino)benzoate (3j)

Prepared according to the general procedure from N-(2-cyanophenyl)acetamide (1a) and (4-(ethoxycarbonyl)phenyl)(mesityl)iodonium trifluoromethanesulfonate (2m) (326 mg, 0.600 mmol). Purification of the crude product by column chromatography on silica gel afforded the product as an orange solid (80.0 mg, 0.260 mmol, 52%). M. p. 166-168 °C. \( R_f = 0.40 \) (hexane-ethyl acetate, 5:3). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 8.15 (d, \( J = 8.1 \) Hz, 1H), 7.68 (t, \( J = 7.4 \) Hz, 1H), 7.37 (t, \( J = 7.4 \) Hz, 1H), 7.28 (d, \( J = 8.2 \) Hz, 1H), 4.33 (q, \( J = 14.1, 7.0 \) Hz, 2H), 2.14 (s, 3H), 1.33 (t, \( J = 7.1 \) Hz, 3H); \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)) \( \delta \) 165.86, 162.36, 153.72, 147.77, 142.07, 135.11, 131.85, 131.65, 128.73, 127.36, 127.25, 127.17, 120.97, 61.77, 24.66, 14.68 ; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 2923, 1709, 1678, 1590, 1569, 1344, 1268, 1104, 1019, 770, 699, 662, 627, 505; HRMS m/z [M+H]\(^+\) Calculated for C\(_{18}\)H\(_{17}\)N\(_2\)O\(_3\): 309.1234; found 309.1232.
General procedure for the synthesis of (Z)-2-(substituted)-N-phenyl-4H-benzo[d][1,3]oxazin-4-imines

N-(2-cyanophenyl)amide (0.500 mmol), mesityl(phenyl)iodonium trifluoromethanesulfonate (2a) (283 mg, 0.600 mmol, 1.2 eq.) and copper(II)triflate (18.08 mg; 0.050 mmol, 10 mol%) were added to a 4 ml vial then the system was charged with argon. Solvent (1,2-dichloroethane or ethyl acetate, 1000 μl) was added under argon atmosphere then the reaction mixture was stirred at 75°C for the appropriate time. Saturated sodium hydrogen carbonate solution (10 ml) was added to the mixture, the aqueous layer was extracted with dichloromethane (4 x 10 ml) the combined organics were dried over anhydrous sodium sulfate, filtered and evaporated. Purification of the crude products by column chromatography on silica gel afforded the products as solids.

(Z)-2-(tert-butyl)-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3k)

Prepared according to the general procedure from N-(2-cyanophenyl)pivalamide (1b) (101 mg, 0.500 mmol) and mesityl(phenyl)iodonium trifluoromethanesulfonate (2a). Purification of the crude product by column chromatography on silica gel afforded the product as a white solid (58.3 mg, 0.210 mmol, 42%). M. p. 56-57 °C. Rf = 0.40 (hexane-ethyl acetate, 15:1). 1H NMR (250 MHz, CDCl3); δ 8.15 (d, J = 7.7 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.42 – 7.19 (m, 5H), 7.05 (d, J = 8.2 Hz, 3H), 1.14 (s, 9H). 13C NMR (62.5 MHz, CDCl3); δ 166.34, 147.14, 146.12, 143.11, 133.90, 129.02, 128.29, 126.88, 126.64, 124.35, 122.82, 119.60, 38.26, 27.99, IR νmax/cm⁻¹ (solid): 2974, 2932, 1664, 1635, 1606, 1490, 1463, 1197, 1114, 1052, 1017, 773, 744, 696, 671, 582; HRMS m/z [M+H]+ Calculated for C18H19N2O: 279.1492; found 279.1492.
**(Z)-2-(chloromethyl)-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3l)**

Prepared according to the general procedure from 2-chloro-N-(2-cyanophenyl)acetamide (1e) (97.0 mg, 0.500 mmol) and mesityl(phenyl)iodonium trifluoromethanesulfonate (2a). Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (62.0 mg, 0.230 mmol, 46%). M. p. 150 - 151 °C. $R_f = 0.25$ (hexane-ethyl acetate, 3:1). $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 8.21 (d, $J = 6.4$ Hz, 1H), 7.71 (s, 2H), 7.48 (s, 4H), 7.29 (s, 2H), 4.19 (s, 2H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 162.45, 151.92, 147.37, 136.34, 135.22, 130.25, 129.10, 128.36, 128.10, 127.59, 121.66, 43.97; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 2922, 1682, 1602, 1587, 1568, 1471, 1278, 1256, 1085, 1072, 1012, 779, 762, 752, 691, 639, 608, 506; HRMS m/z [M+H]$^+$ Calculated for C$_{15}$H$_{12}$ClN$_2$O: 271.0633; found 271.0629.

**(Z)-N-phenyl-2-(trifluoromethyl)-4H-benzo[d][1,3]oxazin-4-imine (3m)**

Prepared according to the general procedure from N-(2-cyanophenyl)-2,2,2-trifluoroacetamide (1d) (107 mg, 0.500 mmol) and mesityl(phenyl)iodonium trifluoromethanesulfonate (2a). Purification of the crude product by column chromatography on silica gel afforded the product as a white solid (27.0 mg, 0.093 mmol, 18%). M. p. 70-71 °C. $R_f = 0.60$ (hexane-ethyl acetate, 10:1). $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 8.23 (d, $J = 7.1$ Hz, 1H), 7.60 (t, $J = 7.5$ Hz, 1H), 7.55 – 7.40 (m, 2H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.25 – 7.02 (m, $J = 20.1$, 6.8 Hz, 3H). $^{13}$C NMR (63 MHz, CDCl$_3$) $\delta$ 143.81, 142.44, 140.35, 134.43, 131.05, 129.26, 128.09, 127.46, 125.72, 123.49, 121.07; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 1690, 1216, 1152, 1112, 1037, 1004, 945, 903, 773, 748, 725, 695, 664, 564, 502; HRMS m/z [M+H]$^+$ Calculated for C$_{15}$H$_{10}$F$_3$N$_2$O: 291.07; found.
(Z)-N-(2-phenyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3n)

Prepared according to the general procedure from N-(2-cyanophenyl)benzamide (1c) (111 mg, 0.500 mmol) and mesityl(phenyl)iodonium triflouromethanesulfonate (2a). Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (58.0 mg, 0.195 mmol, 39%). M. p. 120-121 °C. \( R_f = 0.35 \) (hexane-ethyl acetate, 15:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta \) 8.22 (dd, \( J = 7.8, 1.1 \) Hz, 1H), 8.00 – 7.81 (m, 2H), 7.63 – 7.50 (m, 1H), 7.50 – 7.24 (m, 7H), 7.23 – 7.06 (m, 3H); \(^13\)C NMR (62.5 MHz, CDCl\(_3\)): \( \delta \) 155.33, 146.52, 146.01, 143.42, 134.12, 132.52, 131.06, 129.25, 128.98, 128.58, 128.29, 127.18, 126.92, 124.61, 122.75, 119.88; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 3057, 2921, 1679, 1625, 1594, 1573, 1463, 1248, 1197, 1064, 1044, 1026, 1016, 775, 766, 737, 688, 669, 583, 556, 539.

(Z)-2-(4-chlorophenyl)-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3o)

Prepared according to the general procedure from 4-chloro-N-(2-cyanophenyl)benzamide (1f) (128 mg, 0.500 mmol) and mesityl(phenyl)iodonium triflouromethanesulfonate (2a). Purification of the crude product by column chromatography on silica gel afforded the product as a white solid (78.0 mg, 0.235 mmol, 47%). M. p. 158-160 °C. \( R_f = 0.35 \) (hexane-ethyl acetate, 15:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta \) 8.28 (d, \( J = 6.6 \) Hz, 1H), 7.91 (d, \( J = 7.1 \) Hz, 2H), 7.61 (d, \( J = 6.5 \) Hz, 1H), 7.57 – 7.29 (m, 6H), 7.23 (d, \( J = 4.9 \) Hz, 3H); \(^13\)C NMR (62.5 MHz, CDCl\(_3\)): \( \delta \) 154.39, 149.69, 146.18, 145.91, 143.18, 138.85, 134.16, 129.53, 129.29, 128.75, 128.31, 127.18, 126.95, 124.71, 122.66, 119.81; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 3057, 3016, 1681, 1621, 1591, 1568, 1485, 1475, 1463, 1252, 1086, 1069, 1047, 847, 777, 745, 718, 693, 668, 540, 464; HRMS m/z [M+H]\(^+\) Calculated for \( \text{C}_{20}\text{H}_{14}\text{ClN}_2\text{O} \): 333.0789; found 333.0781.
(Z)-2-(4-nitrophenyl)-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3p)

![Chemical structure]

Prepared according to the general procedure from N-(2-cyanophenyl)-4-nitrobenzamide (1g) (134 mg, 0.500 mmol) and mesityl(phenyl)iodonium trifluoromethanesulfonate (2a). Purification of the crude product by column chromatography on silica gel afforded the product as a white solid (90.0 mg, 0.262 mmol, 52%). M. p. 220-222 °C. Rf = 0.40 (hexane-ethyl acetate, 10:1). 1H NMR (500 MHz, DMSO): δ 8.35 (d, J = 8.8 Hz, 1H), 8.24 (d, J = 7.6 Hz, 1H), 8.12 (d, J = 8.7 Hz, 1H), 7.80 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.21 (t, J = 7.3 Hz, 1H). 13C NMR (125 MHz, DMSO): δ 153.39, 149.89, 145.64, 145.43, 142.53, 136.66, 134.76, 129.76, 129.37, 129.07, 127.42, 126.60, 124.81, 124.47, 122.79, 119.83; IR νmax/cm⁻¹ (solid): 2917, 1678, 1592, 1519, 1486, 1345, 1315, 1252, 1236, 1071, 1047, 1011, 863, 845, 776, 743, 709, 698, 668, 537; HRMS m/z [M+H]+ Calculated for C20H14N3O3: 334.1030; found 334.1024.

(Z)-2-(4-fluorophenyl)-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3q)

![Chemical structure]

Prepared according to the general procedure from N-(2-cyanophenyl)-4-fluorobenzamide (1h) (120 mg, 0.500 mmol) and mesityl(phenyl)iodonium trifluoromethanesulfonate (2a). Purification of the crude product by column chromatography on silica gel afforded the product as a white solid. (73.0 mg, 0.231 mmol, 46%). M. p. 136-138 °C. Rf = 0.35 (hexane-ethyl acetate, 15:1). 1H NMR (250 MHz, CDCl3): δ 8.29 (d, J = 7.4 Hz, 1H), 8.00 (t, J = 5.6 Hz, 2H), 7.75 – 7.58 (m, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.2 Hz, 3H), 7.23 (d, J = 6.7 Hz, 3H), 7.08 (t, J = 8.2 Hz, 2H); 13C NMR (62.5 MHz, CDCl3): δ 154.41, 146.33, 145.97, 143.30, 134.18, 130.68, 130.54, 129.28, 128.60, 127.10, 126.93, 124.67, 122.62, 119.71, 116.36, 116.01; IR νmax/cm⁻¹ (solid): 3032, 2922, 1681, 1623, 1591, 1576, 1505, 1485, 1474, 1251, 1236, 1222, 1198, 1151, 1068, 1052, 1014, 849, 771, 734, 692, 668, 539, 520; HRMS m/z [M+H]+ Calculated for C20H14F2N2O: 317.1085; found 317.1082.
(Z)-2-(4-methoxyphenyl)-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3r)

Prepared according to the general procedure from N-(2-cyanophenyl)-4-methoxybenzamide (1i) (126 mg, 0.500 mmol) and mesityl(phenyl)iodonium trifluoromethanesulfonate (2a). Purification of the crude product by column chromatography on silica gel afforded the product as a white solid. (85.2 mg, 0.260 mmol, 52%). M. p. 158-160 °C. R_f = 0.30 (hexane-ethyl acetate, 10:1). ^1H NMR (250 MHz, CDCl_3): δ 8.16 (d, J = 7.2 Hz, 1H), 7.82 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 6.7 Hz, 1H), 7.43 – 7.21 (m, J = 16.6, 7.8 Hz, 4H), 7.22 – 6.99 (m, 3H), 6.76 (d, J = 7.5 Hz, 2H), 3.70 (s, 3H); ^13C NMR (62.5 MHz, CDCl_3): δ 163.23, 155.25, 146.73, 146.20, 143.75, 134.05, 130.17, 129.23, 128.33, 128.03, 126.86, 124.52, 123.39, 122.82, 119.60, 114.37, 55.79; IR ν_max/cm^-1 (solid): 3058, 2933, 1668 , 1619, 1593, 1568, 1509, 1486, 1465, 1420, 1245, 1168, 1118, 1069, 1050, 1028, 1016, 764, 736, 693, 670, 542; HRMS m/z [M+H]^+ Calculated for C_{21}H_{17}N_2O_2: 329.1285; found 329.1082.

(Z)-N-phenyl-2-((E)-styryl)-4H-benzo[d][1,3]oxazin-4-imine (3s)

Prepared according to the general procedure from N-(2-cyanophenyl)cinnamamide (1k) (124 mg, 0.500 mmol) and mesityl(phenyl)iodonium trifluoromethanesulfonate (2a). Purification of the crude product by column chromatography on silica gel afforded the product as a yellow solid. (61.2 mg, 0.189 mmol, 38%). M. p. 105-107 °C. R_f = 0.32 (hexane-ethyl acetate, 10:1). ^1H NMR (250 MHz, CDCl_3): δ 8.13 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.40 – 7.03 (m, 13H), 6.51 (d, J = 16.1 Hz, 1H); ^13C NMR (62.5 MHz, CDCl_3): δ 155.70, 146.31, 146.00, 143.64, 141.43, 135.11, 134.13, 130.47, 129.32, 129.18, 128.57, 128.29, 126.96, 126.95, 124.74, 123.03, 119.86, 119.53; IR ν_max/cm^-1 (solid): 3023, 2922, 1665, 1632, 1590, 1570, 1487, 1463, 1446, 1247, 1196, 1051, 1021, 984, 971, 769, 752, 687, 667, 481; HRMS m/z [M+H]^+ Calculated for C_{22}H_{17}N_2O: 325.1335; found 325.1331.
General procedure for the synthesis of (Z)-chloro-2-methyl-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine

N-(chboro-2-cyanophenyl)acetamide (97.3 mg, 0.500 mmol), mesityl(phenyl)iodonium trifluoromethanesulfonate (2a) (283 mg, 0.600 mmol, 1.2 eq.) and copper(II)triflate (18.08 mg; 0.050 mmol, 10 mol%) were added to a 4 ml vial then the system was charged with argon. Solvent (1,2-dichloroethane or ethyl acetate, 1000 μl) was added under argon atmosphere then the reaction mixture was stirred at 75°C for the appropriate time. Saturated sodium hydrogen carbonate solution (10 ml) was added to the mixture, the aqueous layer was extracted with dichloromethane (4 x 10 ml) the combined organics were dried over anhydrous sodium sulfate, filtered and evaporated. Purification of the crude products by column chromatography on silica gel afforded the products as solids.

(Z)-7-chloro-2-methyl-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3t)

Prepared according to the general procedure from N-(5-chloro-2-cyanophenyl)acetamide (1l) and mesityl(phenyl)iodonium trifluoromethanesulfonate (2a). Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid. (67.5 mg, 0.250 mmol, 50%). M. p. 153-155 °C. Rf = 0.30 (hexane-ethyl acetate, 3:1). 1H NMR (250 MHz, CDCl3): δ 8.16 (d, J = 7.1 Hz, 1H), 7.59 (d, J = 30.8 Hz, 4H), 7.39 (d, J = 6.0 Hz, 1H), 7.26 (s, 2H), 2.23 (s, 3H). 13C NMR (62.5 MHz, CDCl3): δ 162.02, 156.04, 148.86, 141.07, 137.86, 130.47, 129.83, 128.91, 128.33, 127.60, 126.83, 119.65, 24.85; IR νmax/cm⁻¹ (solid): 2922, 1679, 1601, 1583, 1561, 1429, 1342, 1317, 1270, 1070, 896, 874, 830, 776, 761, 699, 689, 680, 586; HRMS m/z [M+H]^+ Calculated for C15H12ClN2O: 271.0633; found 271.0633.

(Z)-6-chloro-2-methyl-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3u)

Prepared according to the general procedure from N-(4-chloro-2-cyanophenyl)acetamide (1m) and mesityl(phenyl)iodonium trifluoromethanesulfonate (2a). Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid. (66.5
mg, 0.246 mmol, 45%). M. p. 162-164 °C. $R_f = 0.30$ (hexane-ethyl acetate, 2:1). $^1$H NMR (250 MHz, CDCl$_3$): $\delta$: 8.11 (s, 1H), 7.78 – 7.33 (m, 5H), 7.18 (s, 2H), 2.14 (s, 3H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 161.61, 154.97, 146.38, 137.85, 135.34, 132.70, 130.49, 129.85, 128.91, 128.31, 126.70, 122.24, 24.78; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 2922, 1688, 1587, 1566, 1470, 1340, 1313, 1269, 821, 765, 718, 697, 684, 640, 538; HRMS m/z [M+H]$^+$ Calculated for C$_{15}$H$_{12}$ClN$_2$O: 271.0633; found 271.0634.

(Z)-2-methyl-N-phenyl-4H-thieno[2,3-d][1,3]oxazin-4-imine (3v)

N-(3-cyanothiophen-2-yl)acetamide (1n) (83.1 mg, 0.500 mmol), mesityl(phenyl)iodonium trifluoromethanesulfonate (2a) (283 mg, 0.600 mmol, 1.2 eq.) and copper(II)triflate (18.08 mg; 0.050 mmol, 10 mol%) were added to a 4 ml vial then the system was charged with argon. Solvent (1,2-dichloroethane or ethyl acetate, 1000 μl) was added under argon atmosphere then the reaction mixture was stirred at 75°C for the appropriate time. Saturated sodium hydrogen carbonate solution (10 ml) was added to the mixture, the aqueous layer was extracted with dichloromethane (4 x 10 ml) the combined organics were dried over anhydrous sodium sulfate, filtered and evaporated. Purification of the crude product by column chromatography on silica gel afforded the products as a yellow oil (58.0 mg, 0.240 mmol, 48%). $R_f = 0.30$ (hexane-ethyl acetate, 7:3). $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 7.65 – 7.48 (m, 3H), 7.44 (d, $J = 5.8$ Hz, 1H), 7.32 – 7.21 (m, 2H), 7.18 (d, $J = 5.8$ Hz, 1H), 2.22 (s, 3H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 163.92, 159.10, 155.25, 137.94, 130.45, 129.78, 128.31, 122.96, 122.92, 24.64; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 3083, 2924, 1674, 1553, 1513, 1489, 1417, 1286, 1256, 737, 697, 626; HRMS m/z [M+H]$^+$ Calculated for C$_{13}$H$_{11}$N$_2$OS: 243.0587; found 243.0586.

(Z)-2-methyl-N-phenyl-6,7-dihydrocyclopenta[d][1,3]oxazin-4(5H)-imine (3w)

N-(2-cyanocyclopent-1-en-1-yl)acetamide (1o) (75.1 mg; 0.500 mmol), mesityl(phenyl)iodonium trifluoromethanesulfonate (2a) (283 mg, 0.600 mmol, 1.2 eq.) and copper(II)triflate (18.08 mg; 0.050 mmol, 10 mol%) were added to a 4 ml vial then the system was charged with argon. Solvent (1,2-dichloroethane or ethyl acetate, 1000 μl) was added under argon atmosphere then the reaction mixture was stirred at 75°C for the appropriate
time. Saturated sodium hydrogen carbonate solution (10 ml) was added to the mixture, the aqueous layer was extracted with dichloromethane (4 x 10 ml) the combined organics were dried over anhydrous sodium sulfate, filtered and evaporated. Purification of the crude product by column chromatography on silica gel afforded the product as a brown solid. (60.2 mg, 0.266 mmol, 53%). M. p. 124-126 °C. Rf = 0.28 (hexane-ethyl acetate, 1:4). 1H NMR (250 MHz, CDCl3): δ 7.55 – 7.29 (m, 3H), 7.11 (d, J = 6.8 Hz, 2H), 2.94 – 2.61 (m, 4H), 2.07 (s, 3H), 2.00 (dd, J = 15.2, 7.6 Hz, 2H); 13C NMR (62.5 MHz, CDCl3): δ=168.06, 161.19, 159.11, 138.18, 130.32, 129.55, 127.97, 123.01, 35.36, 28.22, 24.56, 21.64; IR νmax/cm⁻¹ (solid): 2923, 1687, 1517, 1493, 1430, 1367, 1258, 1092, 766, 758, 724, 696, 648, 500; HRMS m/z [M+H]^+ Calculated for C14H15N2O: 227.1179; found 227.1174.

(Z)-2-methyl-N-phenyl-5,6,7,8-tetrahydro-4H-benzo[d][1,3]oxazin-4-imine (3x)

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\text{N-(2-cyanocyclohex-1-en-1-yl)acetamide (1p)} \quad (82.1 \text{ mg}; 0.500 \text{ mmol}), \text{mesityl(phenyl)iodonium trifluoromethanesulfonate (2a) (283 mg, 0.600 mmol, 1.2 eq.) and copper(II)triflate (18.08 mg; 0.050 mmol, 10 mol%) were added to a 4 ml vial then the system was charged with argon. Solvent (1,2-dichloroethane or ethyl acetate, 1000 μl) was added under argon atmosphere then the reaction mixture was stirred at 75°C for the appropriate time. Saturated sodium hydrogen carbonate solution (10 ml) was added to the mixture, the aqueous layer was extracted with dichloromethane (4 x 10 ml) the combined organics were dried over anhydrous sodium sulfate, filtered and evaporated. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid. (56.7 mg, 0.236 mmol, 47%). M. p. 142-144 °C. Rf = 0.35 (hexane-ethyl acetate, 1:2). 1H NMR (250 MHz, CDCl3): δ 7.56 – 7.28 (m, 3H), 7.11 (d, J = 7.4 Hz, 2H), 2.70 – 2.50 (m, 2H), 2.49 – 2.34 (m, 2H), 2.05 (s, 3H), 1.86 – 1.55 (m, 4H); 13C NMR (62.5 MHz, CDCl3): δ 163.02, 159.51, 155.39, 138.12, 130.29, 129.51, 127.98, 120.28, 31.90, 24.10, 22.72, 22.64, 22.17; IR νmax/cm⁻¹ (solid): 2926, 1687, 1517, 1493, 1430, 1367, 1258, 1196, 1135, 768, 754, 693, 502; HRMS m/z [M+H]^+ Calculated for C15H17N2O: 241.1335; found 241.1338.
(Z)-2-methyl-N-phenyl-6,7,8,9-tetrahydrocyclohepta[d][1,3]oxazin-4(5H)-imine (3y)

N-(2-cyanocyclohept-1-en-1-yl)acetamide (1q) (127 mg; 0,500 mmol), mesityl(phenyl)iodonium trifluoromethanesulfonate (2a) (283 mg, 0.600 mmol, 1.2 eq.) and copper(II)triflate (18,08 mg; 0,050 mmol, 10 mol%) were added to a 4 ml vial then the system was charged with argon. Solvent (1,2-dichloroethane or ethyl acetate, 1000 μl) was added under argon atmosphere then the reaction mixture was stirred at 75°C for the appropriate time. Saturated sodium hydrogen carbonate solution (10 ml) was added to the mixture, the aqueous layer was extracted with dichloromethane (4 x 10 ml) the combined organics were dried over anhydrous sodium sulfate, filtered and evaporated. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (348.0 mg, 0,134 mmol, 27%). M. p. 90-92 °C. $R_f = 0.28$ (hexane-ethyl acetate, 1:21). $^1$H NMR (250 MHz, CDCl$_3$): δ 7.42 (s, 1H), 7.12 (s, 1H), 2.72 (s, 1H), 2.04 (s, 1H), 1.90 – 1.38 (m, 2H). $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 165.47, 163.25, 155.48, 138.52, 130.28, 129.49, 127.86, 124.80, 38.55, 32.66, 26.77, 25.74, 24.92, 24.20.; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 2921, 2851, 1655, 1600, 1592, 1539, 1487, 1437, 1398, 1381, 1361, 1254, 1104, 958, 789, 751, 694, 506; HRMS m/z [M+H]$^+$ Calculated for C$_{15}$H$_{17}$N$_2$O: 255.1492; found: 255.1492.
7. NMR spectras

N-(2-cyanocyclohept-1-en-1-yl)acetamide (1q)
(Z)-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3a)
(Z)-2-methyl-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3b)
(Z)-3-methyl-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-yldene)aniline (3c)
(Z)-4-methyl-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3d)
(Z)-4-chloro-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3e)
(Z)-3-bromo-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3f)
(Z)-4-bromo-N-(2-methyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3g)
(Z)-N-(4H-benzo[d][1,3]oxazin-4-ylidene)-4-fluoroaniline (3h)
(Z)-ethyl 2-(4H-benzo[d][1,3]oxazin-4-ylideneamino)benzoate (3i)
(Z)-ethyl-4-(4H-benzo[d][1,3]oxazin-4-ylideneamino)benzoate (3j)
(Z)-2-(tert-butyl)-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3k)
(Z)-2-(chloromethyl)-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3l)
(Z)-N-phenyl-2-(trifluoromethyl)-4H-benzo[d][1,3]oxazin-4-imine (3m)
(Z)-N-(2-phenyl-4H-benzo[d][1,3]oxazin-4-ylidene)aniline (3n)
(Z)-2-(4-chlorophenyl)-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3o)
(Z)-2-(4-nitrophenyl)-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3p)
(Z)-2-(4-fluorophenyl)-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3q)
(Z)-2-(4-methoxyphenyl)-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3r)
(Z)-7-chloro-2-methyl-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3t)
(Z)-6-chloro-2-methyl-N-phenyl-4H-benzo[d][1,3]oxazin-4-imine (3u)
(Z)-2-methyl-N-phenyl-4H-thieno[2,3-d][1,3]oxazin-4-imine (3v)
(Z)-2-methyl-N-phenyl-6,7-dihydrocyclopenta[d][1,3]oxazin-4(5H)-imine (3w)
(Z)-2-methyl-N-phenyl-5,6,7,8-tetrahydro-4H-benzo[d][1,3]oxazin-4-imine (3x)
(Z)-2-methyl-N-phenyl-6,7,8,9-tetrahydrocyclohepta[d][1,3]oxazin-4(5H)-imine (3y)
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