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Harnessing triaryloxonium ions for aryne generation

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Supplementary Information

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1 General Information:

Reagents were purchased from major commercial suppliers and were used without further purification. Anhydrous reaction solvents (CH_2Cl_2, 1,4-dioxane, DMF, THF, PhMe, Et_3N, *i*-Pr_2NH) were obtained from an MBraun SPS5 solvent purification system having been dried over activated alumina columns. All other solvents were used without prior drying. Unless specified, the synthetic reactions were carried out without using dried glassware or an inert atmosphere. The glassware for reactions conducted using an inert atmosphere was flame-dried under vacuum and then placed under N_2 unless H_2O was used as a solvent in the procedure. Solvents were degassed by sparging with Argon for 10 minutes as stated in the procedures. Reactions were heated using a DrySyn® heating block and contact thermometer. Room Temperature (r.t.) is defined as 20-25 °C.

Reactions were monitored by Thin Layer Chromatography (TLC) using silica gel on pre-coated 0.25 mm aluminium sheets (Merck Kieselgel 60 F_{254}) and visualized with UV irradiation (λ = 254 nm) followed by a basic $KMnO_4$ solution. Flash column chromatography was carried out on Silica Gel 60 (0.043-0.063 nm, VWR) under pressure (0.2-0.4 bar) from the house N_2 supply. An UltrawaveU1250D Ultrasonic water bath (50-60 Hz) was used for sonication.

NMR spectra were recorded on Bruker AVIII/AVIIIHD (700, 600, 500 and 400 MHz (^{1}H)) and Bruker NEO (600 MHz (^{1}H)) spectrometers in the deuterated solvent specified. NMR data are reported as chemical shifts (δ) and quoted in parts per million (ppm). ^{1}H NMR were referenced to the non-deuterated residual solvent peak, ^{13}C NMR were referenced to the residual solvent peak and ^{19}F NMR were referenced externally to $CFCl_3$ = 0 ppm. Chemical shifts are quoted in ppm with splitting assigned as singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), sextet (sext), and multiplet (m) or combinations of the above. The abbreviation br is used to denote broad signals. Coupling constants, *J*, are measured to the nearest 0.1 Hz and are presented as observed. NMR Spectra were processed using MestReNova 11.0 and where spectra are assigned, this was carried out with the aid of COSY, HSQC and HMBC experiments.

Melting points (M.P.) were determined using a Reichert melting point apparatus and are uncorrected. Unless otherwise stated, the solid material analysed was obtained from *in vacuo* removal of the solvent system used for flash column chromatography. Fourier Transform Infra-red spectra were recorded on a Bruker Tensor 27 FTIR spectrometer equipped with a diamond ATR module. Absorption maxima (n_{max}) are reported in wavenumbers (cm^{-1}) for the range 3500 – 600 cm^{-1}. Low-resolution mass spectra were recorded on a Micro Mass LCT Premier spectrometer under conditions of electrospray ionization (ESI). High resolution mass spectra using electrospray ionization (ESI) were recorded on a Thermo Exactive orbitrap spectrometer equipped with a Waters Acquity LC system. High resolution mass spectra using atmospheric pressure chemical ionization (APCI) or electron ionization (EI) were recorded on

an Agilent 7200 Accurate Mass Q-TOF GC-MS spectrometer connected to a 7890 GC system DIP solid/liquid state thermal probe and a CTC Analytics HTS PAL Sample Manager. Optical rotations were recorded on a Schmidt-Haensch Unipol L2000 polarimeter at 25 °C using 589 nm radiation. Concentrations are quoted in g/100 mL and $[\alpha]_D^{25}$ values are quoted in [° mL g^{-1} dm^{-1}]. Compound names were generated using ChemDraw 20.1.1 in accordance with the guidelines stipulated by the International Union of Pure and Applied Chemistry (IUPAC).

2 General Procedures:

General Procedure A for the S_NAr reaction with fluoroarenes: (2-20 mmol)

K_2CO_3 (2 eq.) was added to a solution of the appropriate fluoroarene (1 eq.) and 2-bromo-4,6-dimethylphenol (1 eq.) in DMF (2.5 mL/mmol) and the reaction mixture heated to 110 °C for 16 h. The reaction mixture was cooled, H_2O (5 mL/mmol) was added and the reaction mixture was extracted (Et_2O, 3 × 10 mL/mmol). The combined organic layers were washed (H_2O, 10 mL/mmol), dried ($MgSO_4$) and concentrated *in vacuo*.

General Procedure B for S_NAr reaction with phenols: (2-4 mmol)

K_2CO_3 (2 eq.) was added to a solution of *the appropriate phenol* (1 eq.) and 1-bromo-2-chloro-3-methyl-5-nitrobenzene (1 eq.) in DMF (2.5 mL/mmol) and the reaction mixture heated to 110 ℃. After 16 h, the reaction mixture was cooled, H_2O (5 mL/mmol) was added and the reaction mixture was extracted (Et_2O, 3 × 10 mL/mmol). The combined organic layers were washed (H_2O, 10 mL/mmol), dried ($MgSO_4$) and concentrated *in vacuo*.

General Procedure C for cross coupling of aryl bromides: (2-4 mmol)

The *appropriate aryl bromide* (1 eq.) as a solid or a solution in PhMe or CH_2Cl_2, 2,4-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, 158, (1.5 eq.) as a solution in PhMe (6 mL/mmol) and water (10 mL/mmol) were sequentially added to Pd(dppf)Cl_2·CH_2Cl_2 (5 mol%) and Na_2CO_3 (4 eq.) in PhMe (4 mL/mmol) under N_2 at r.t.. Argon was bubbled through the solution for 5 mins and the reaction mixture was heated to 95 ℃. After 24 h, the reaction mixture was extracted (CH_2Cl_2, 3 × 10 mL/mmol), dried ($MgSO_4$) and concentrated *in vacuo*.

General Procedure D for hydrogenation, acetylation and cross coupling of aryl bromides: (2-4 mmol)

H_2 was sparged through a solution of *the appropriate aryl bromide* (1.00 mmol, 1 eq.)and Pd/C (10 wt%, 2.5 mol%) and EtOAc (5 mL/mmol) under N_2 for 5 mins and kept under a H_2 pressure (1 atm). After 16 h, N_2 was sparged through the solution for 10 mins, the reaction was filtered (Celite®, 1 mL/mmol) and concentrated *in vacuo*. The crude residue was dissolved in CH_2Cl_2 (5 mL/mmol) and Ac_2O (3 eq.) was added. After 4 h, $NaHCO_3$ (sat. aq., 15 mL/mmol) was added and the mixture was extracted (CH_2Cl_2, 3 × 5 mL/mmol). The organic extracts were washed ($NaHCO_3$, sat. aq., 10 mL/mmol), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue, as a solid or a solution in PhMe or CH_2Cl_2, 2,4-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, **2**, (1.50 eq.) as a solution in PhMe (6 mL/mmol) and water (10 mL/mmol) were sequentially added to Pd(dppf)Cl_2·CH_2Cl_2 (5 mol%) and Na_2CO_3 (4 eq.) in PhMe (4 mL/mmol) under N_2 at r.t.. Argon was bubbled through the solution for 5 mins and the reaction mixture was heated to 95 ℃. After 24 h, the reaction mixture was extracted (CH_2Cl_2, 3 × 10 mL/mmol), dried ($MgSO_4$) and concentrated *in vacuo*.

General Procedure E for formation of oxonium ions :

t-BuONO (5 eq.) was added to a solution of *the appropriate aniline* (1 eq.) and HBF_4 (48% aq., 5 eq.) in CH_2Cl_2:IPA (1:1, 4 mL/mmol) at 0 ℃. After 1 h, the reaction mixture was diluted (CH_2Cl_2, 5 mL/mmol), washed (H_2O, 2 mL/mmol) and warmed to 30 ℃. After 36-48 h, the solvent was removed by a steady stream of N_2 and Et_2O (5 mL/mmol) was added resulting in a solid precipitate. The Et_2O layer was passed through Celite® (1 mL/mmol). The solid precipitate was washed, and the solvent passed through Celite® (Et_2O, 4 x 1 mL/mmol). The solid was dissolved in MeCN (4-12 mL/mmol), passed through Celite® and eluted (MeCN, 4 × 5 mL/mmol). The solvent was removed by a steady stream of N_2 or *in vacuo* at r.t. to give the desired oxonium ion.

General Procedure F for formation of oxonium ions from biaryl triazenes:

HBF_4 (48% aq., 10 eq.) was added to a solution of *the appropriate triazene* (1 eq.) in CH_2Cl_2:IPA (1:1, 4 mL/mmol) at 0 ℃. After 4 mins, the solution was washed (H_2O, 6 mL/mmol) and HBF_4 (48% aq., 10 eq.) was added. After a further 5 mins, the solution was washed (H_2O, 3 mL), diluted (CH_2Cl_2, 3 mL) and stirred at 30 ℃. After 36 h, the solvent was removed by a steady stream of N_2 and Et_2O (5 mL/mmol) was added resulting in a solid precipitate. The Et_2O layer was passed through Celite® (1 mL/mmol). The solid precipitate was washed and the solvent passed through Celite® (Et_2O, 4 x 1 mL/mmol). The solid was dissolved in MeCN (4-12 mL/mmol), passed through Celite® and eluted (MeCN, 4 × 5 mL/mmol). The solvent was removed by a steady stream of N_2 or *in vacuo* at r.t. to give the desired oxonium ion.

General Procedure G for the trapping of arynes with furan:
The *appropriate oxonium ion* (1 eq.) was dissolved in MeCN (2mL/mmol) in an oven-dried vial. Furan (5 eq.) and K_3PO_4 (5 eq.) were added sequentially, and the reaction mixture stirred (600 rpm) at r.t. for 16 h. Once complete, the reaction mixture was filtered through Celite® (1 mL/mmol), eluted (CH_2Cl_2, 4 × 2 mL/mmol) and concentrated *in vacuo*.

3 Experimental Procedures:

3.1 S_NAr Precursors

2-Bromo-4,6-dimethylphenol, S1:

A solution of bromine (4.41 mL, 13.76 g, 8.61 mmol, 1.05 eq.) in CH_2Cl_2 (20 mL) was added *via* a pressure equalising dropping funnel over 5 minutes to a stirred solution of 4,6-dimethylphenol (9.89 mL, 10.00 g, 8.20 mmol, 1 eq.) in CH_2Cl_2 (40 mL) at 0 °C. Once the addition was complete, the reaction was warmed to r.t.. After 1 h, Na_2SO_3 (sat. aq., 30 mL) was added and the aqueous layer was extracted (CH_2Cl_2, 30 mL). The combined organics were dried ($MgSO_4$) and concentrated *in vacuo* to give the title compound as a pale yellow oil (16.25 g, 99 %).

^{1}H (400 MHz, $CDCl_3$) δ_H = 7.16 – 7.10 (m, 1H, H_3), 6.93 – 6.86 (m, 1H, H_5), 5.46 (s, 1H, OH), 2.30 (s, 3H, H_7), 2.26 (s, 3H, H_8).
^{13}C (101 MHz, $CDCl_3$) δ_C = 148.2 (C_1), 131.2 (C_5), 130.7 (C_{Ar}), 129.5 (C_3), 125.5 (C_{Ar}), 109.8 (C_6), 20.2 (C_8), 16.7 (C_7).
IR (neat) ν_{max}/cm^{-1} = 3516, 2921, 1482, 1378, 1323, 1288, 1250, 1231, 1209, 1189, 1112, 989, 958, 849, 822, 763, 714
HRMS (EI$^+$): m/z calculated for $C_8H_9{}^{79}BrO^+$ $[M]^+$ = 199.9831; m/z found = 199.9837. Δ = 3.40 ppm.

2-Bromo-6-methyl-4-nitroaniline, S2:

A solution of bromine (3.41 mL, 10.62 g, 6.65 mmol, 1.00 eq.) in MeOH (20 mL) was added *via* a pressure equalising dropping funnel over 5 minutes to a stirred solution of 2-methyl-4-nitroaniline (10.12 g, 6.65 mmol, 1 eq.) in MeOH (500 mL) at 0 °C. Once the addition was complete, the reaction was warmed to r.t.. After 1 h, the solid precipitate was collected by suction filtration, washed (MeOH, 2 × 15 mL) and dried to give the title compound as a bright yellow solid (11.16 g, 73 %).

m.p. = 176-177 °C (MeOH).
^{1}H (400 MHz, DMSO-d$_6$) δ_H = 8.12 (d, *J* = 2.6 Hz, 1H, H_5), 7.92 – 7.86 (m, 1H, H_3), 6.47 (s, 2H, NH), 2.22 (s, 3H, H_7).
^{13}C (101 MHz, DMSO-d$_6$) δ_C = 150.4 (C_4), 135.9 (C_1), 126.6 (C_5), 125.0 (C_3), 122.1 (C_2), 105.1 (C_6), 18.4 (C_7).
IR (neat) ν_{max}/cm^{-1} **=** 3487, 3385, 2922, 2359, 1617, 1480, 1298, 1279, 1203, 1103, 1037, 900, 821, 745, 701.
HRMS (ESI$^+$): m/z calculated for $C_7H_8O_2N_2$ $[M+H]^+$ = 230.9764; m/z found = 230.9764. Δ = -1.15 ppm.

1-Bromo-2-chloro-3-methyl-5-nitrobenzene, S3:

Two reactions of identical scale were carried out simultaneously for convenience: ^{t}BuONO (4.10 mL, 3.56 g, 34.51 mmol, 1.60 eq.) was added to a stirred suspension of anhydrous $CuCl_2$ (3.86 g, 28.71 mmol, 1.33 eq.) in MeCN (250 mL). To this dark suspension, 2-bromo-6-methyl-4-nitroaniline, (5 g, 21.64 mmol, 1.00 eq.) was slowly added over 30 mins. After 2 h, H_2O (500 mL) was added to each reaction and the combined reaction mixtures were extracted (Et_2O, 3 × 400 mL). The combined organic layers were washed (H_2O, 500 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (CH_2Cl_2:Pentane, 10:90) to give the title compound as a white solid (9.01 g, 83%).

m.p. = 91-92 °C.
^{1}H (500 MHz, CDCl$_3$) δ_H = 8.34 (d, *J* = 2.5 Hz, 1H, H_6), 8.10 – 8.03 (m, 1H, H_4), 2.55 (s, 3H, H_7).
^{13}C (126 MHz, CDCl$_3$) δ_C = 146.0, 141.8, 139.9, 126.3, 124.2, 123.7, 22.1.
IR (neat) ν_{max}/cm^{-1} **=** 3107, 2361, 1514, 1457, 1415, 1390, 1338, 1288, 1234, 1059, 941, 900,

871, 840, 760, 740, 695, 659.
HRMS (EI$^+$): m/z calculated for $C_7H_5O_2NBrCl$ [M-e^-]$^+$ = 248.9192; m/z found = 248.9187. Δ = -2.85 ppm.

3.2 S_NAr reactions

Derivatization of 1-bromo-3,5-dimethyl-2-(4-nitrophenoxy)benzene, 1a:

A solution of **1-bromo-3,5-dimethyl-2-(4-nitrophenoxy)benzene**, **1a** (4.00 g, 12.50 mmol, 1.00 eq.) and suspended 10% Pd/C (330 mg, 0.31 mmol, 2.5 mol%) in EtOAc (40 mL) under N_2 was purged with H_2 for 5 mins. A H_2 balloon was fitted and the reaction stirred at r.t.. After 16 h, N_2 was bubbled through the suspension for 5 minutes, the reaction mixture was filtered through Celite® (10 mL) and eluted (EtOAc, 2 × 10 mL). The crude reaction mixture was concentrated *in vacuo* and the resulting 4-(2-bromo-4,6-dimethylphenoxy)aniline, **1ab** was used without further purification.

1-bromo-3,5-dimethyl-2-(4-nitrophenoxy)benzene, 1a:

1a was prepared according to **General Procedure A** on a 20 mmol scale using 2-bromo-4,6-dimethylphenol, **S1**, (4.02 g, 20.00 mmol, 1.00 eq.), 1-fluoro-4-nitrobenzene (2.92 g, 20.00 mmol, 1.00 eq.) and K_2CO_3 (5.52 g, 40.00 mmol, 2.00 eq.) in DMF (50 mL). No further purification was required to give the titled compound as a bright yellow solid (5.93 g, 92 %).

m.p. = 74-76 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 8.24 – 8.18 (m, 2H, H_{11}), 7.36 – 7.32 (m, 1H, H_5), 7.10 – 7.05 (m, 1H, H_3), 6.93 – 6.86 (m, 2H, H_{10}), 2.36 (s, 3H, H_8), 2.16 (s, 3H, H_7).
^{13}C (126 MHz, $CDCl_3$) δ_C = 162.3 (C_9), 146.7 (C_2), 142.6 (C_{12}), 137.5 (C_{Ar}), 132.8 (C_{Ar}), 132.0 (C_6), 131.7 (C_4), 126.2 (C_{11}), 116.6 (C_1), 115.2 (C_{10}), 20.7 (C_8), 16.8 (C_7).

IR (film) ν_{max}/cm^{-1} = 1610, 1590, 1515, 1489, 1469, 1340, 1278, 1235, 1164, 1110, 1038, 909, 871, 847, 815, 781, 748, 722, 686, 644, 619.
HRMS ($APCl^-$): m/z calculated for $C_{14}H_{11}{}^{79}BrNO_3$ $[M-H]^-$ = 319.9928; m/z found = 319.9918 . Δ = -3.00 ppm.

4-(2-Bromo-4,6-dimethylphenoxy)aniline, 1ab:

EtOAc (40 mL) was added to a mixture of 1-bromo-3,5-dimethyl-2-(4-nitrophenoxy)benzene, **1a**, (4.00 g, 12.5 mmol, 1 eq.) and Pd/C (10 wt%, 330 mg, 0.31 mmol, 2.5 mol%) under N_2. The reaction was purged with H_2 and stirred under a positive pressure of H_2. After 24 h, N_2 was bubbled through the solution for 10 mins and then filtered through Celite® (10 mL). The Celite® was eluted (EtOAc, 2 × 10 mL) and the organic fractions were concentrated *in vacuo* to obtain the title compound as an off-white solid (3.37 g, 92%).

m.p. = 68-69 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 7.30 (d, *J* = 2.1 Hz, 1H, H_5), 7.01 (d, *J* = 2.1 Hz, 1H, H_3), 6.63 (s, 4H, H_{11}, H_{10}), 3.54 – 3.22 (br s, 2H, NH), 2.33 (s, 3H, H_8), 2.16 (s, 3H, H_7).
^{13}C (126 MHz, $CDCl_3$) δ_C = 150.6 (C_9), 148.2 (C_1), 140.8 (C_{12}), 136.0 (C_{Ar}), 133.5 (C_{Ar}), 131.6 (C_5), 131.4 (C_3), 117.6 (C_6), 116.5 ($C_{11/10}$), 115.7 ($C_{11/10}$), 20.7 (C_8), 17.1 (C_7).
FTIR (film) ν_{max}/cm^{-1} =3363, 2919, 2850, 1624, 1504, 1470, 1321, 1278, 1216, 1197, 1164, 1123, 1009, 907, 863, 824, 800, 729, 647.
HRMS (ESI^+): m/z calculated for $C_{14}H_{15}{}^{79}BrNO^+$ $[M+H]^+$ = 292.0332; m/z found = 292.0335. Δ = 1.32 ppm.

***N*-(4-(2-Bromo-4,6-dimethylphenoxy)phenyl)acetamide, 1b:**

Ac_2O (0.44 mL, 473 mg, 4.64 mmol, 1.50 eq.) was added to a solution of 4-(2-bromo-4,6-dimethylphenoxy)aniline, **1ab**, (900 mg, 3.09 mmol, 1.00 eq.) in CH_2Cl_2 (20 mL) at r.t.. After 16 h, water (20 mL) and $NaHCO_3$ (sat. aq., 20 mL) were sequentially added and the reaction mixture was extracted (CH_2Cl_2, 3 × 15 mL). The combined organic extracts were washed ($NaHCO_3$, sat. aq., 20 mL), dried ($MgSO_4$) and concentrated *in vacuo*. No further purification was required to give the title compound, **1b** as a white solid (1.01 g, 98%).
m.p. = 142-144 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.40 – 7.35 (m, 3H, NH, H_{11}), 7.29 – 7.27 (m, 1H, H_5), 7.01 – 6.98 (m, 1H, H_3), 6.74 – 6.71 (m, 2H, H_9), 2.31 (s, 3H, H_{14}), 2.15 (s, 3H, H_8), 2.12 (s, 3H, H_7).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 168.5 (C_{13}), 154.2 (C_5), 147.6 (C_1), 136.5 (C_{Ar}), 133.4 (C_{Ar}), 132.0 (C_{12}), 131.7 (C_5), 131.5 (C_3), 122.0 (C_{11}), 117.3 (C_6), 115.2 (C_{12}), 24.4 (C_{14}), 20.7 (C_5), 17.0 (C_3).
FTIR (film) ν_{max}/cm^{-1} = 3294, 2923, 1660, 1608, 1547, 1504, 1470, 1410, 1371, 1316, 1280, 1214, 1166, 1123, 1014, 909, 868, 830, 810, 732.
HRMS (ESI$^+$): m/z calculated for $C_{16}H_{17}{}^{79}BrNO_2^+$ $[M+H]^+$ = 334.0437; m/z found = 334.0438. Δ = 0.13 ppm.

Ethyl 4-(2-bromo-6-methyl-4-nitrophenoxy)benzoate, 1c:

1c was prepared according to **General Procedure B** on a 4.00 mmol scale using 1-bromo-2-chloro-3-methyl-5-nitrobenzene, **S3**, (1.00 g, 4.00 mmol, 1.00 eq.), ethyl 4-hydroxybenzoate (664 mg, 4.00 mmol, 1.00 eq.) and K_2CO_3 (1.11 g, 8.00 mmol, 2.00 eq.) in DMF (10 mL). The crude residue was purified by flash column chromatography (EtOAc:Pentane, 10:90, R_f = 0.2) to give the title compound as a bright yellow solid (1.05 g, 69 %).

m.p. = 97-100 °C (Et_2O).
^{1}H (500 MHz, $CDCl_3$) δ_H = 8.39 (d, 2.5 Hz, 1H, H_6), 8.14 (m, 1H, H_4), 8.05 – 7.98 (m, 2H, H_{10}), 6.84 – 6.77 (m, 2H, H_9), 4.35 (q, *J* = 7.1 Hz, 2H, H_{13}), 2.28 (s, 3H, H_7), 1.37 (t, *J* = 7.1 Hz, 3H, H_{14}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 165.9 (C_{12}), 159.6 (C_8), 154.8 (C_2), 145.3 (C_5), 135.2 (C_{11}), 132.1 (C_{10}), 127.2 (C_6), 125.9 (C_4), 125.5 (C_3), 118.3 (C_1), 114.8 (C_9), 61.1 (C_{13}), 17.4 (C_7), 14.5 (C_{14}).
IR (film) ν_{max}/cm^{-1} **=** 2981, 2885, 1713, 1605, 1577, 1527, 1503, 1461, 1434, 1417, 1393, 1367, 1344, 1307, 1278, 1258, 1218, 1163, 1109, 1095, 1015, 969, 945, 898, 867, 852, 801, 767, 743, 695, 637.
HRMS (ESI$^+$): m/z calculated for $C_{16}H_{15}O_5NBr^+$ $[M+H]^+$ = 380.0128; m/z found = 380.0130, Δ = 0.46 ppm.

1-(4-(2-Bromo-4,6-dimethylphenoxy)phenyl)ethan-1-one, 1d:

1d was prepared according to **General procedure A** on a 5 mmol scale using 2-bromo-4,6-dimethylphenol, **S1**, (1.05 g, 5.00 mmol, 1.00 eq.), 4-fluoroacetophenone (691 mg, 5.00 mmol, 1 eq.) and K_2CO_3 (1.38 g, 10.00 mmol, 2.00 eq.) in DMF (12.5 mL). The crude residue was purified by flash column chromatography (Et_2O:Pentane, 7:93, R_f = 0.25) to give the titled compound as a pale yellow solid (550 mg, 35%).

m.p. = 63-65 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 7.96 – 7.88 (m, 2H, H_{11}), 7.33 – 7.29 (m, 1H, $H_{5/3}$), 7.05 – 7.01 (m, 1H, $H_{5/3}$), 6.86 – 6.80 (m, 2H, H_{10}), 2.55 (s, 3H, H_{14}), 2.33 (s, 3H, H_8), 2.13 (s, 3H, H_7);
^{13}C (126 MHz, $CDCl_3$) δ_C = 196.8 (C_{13}), 161.2 (C_9), 147.0 (C_1), 137.0 (C_{Ar}), 133.1 (C_{Ar}), 131.9 (C_5), 131.6 (C_5), 131.6 (C_{12}), 130.9 (C_{11}), 117.0 (C_6), 114.8 (C_{10}), 26.5 (C_{14}), 20.7 (C_8), 16.9 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 2922, 1678, 1595, 1502, 1471, 1416, 1357, 1301, 1266, 1230, 1218, 1163, 1123, 1009, 957, 864, 836, 819, 784, 630.
HRMS (ESI$^+$): m/z calculated for $C_{16}H_{16}BrO_2^+$ $[M+H]^+$ = 319.0328; found m/z = 319.0329 Δ = 0.34 ppm.

4-(2-Bromo-4,6-dimethylphenoxy)benzaldehyde, 1e:

1e was prepared according to **General Procedure A** on a 20.00 mmol scale using 2-bromo-4,6-dimethylphenol, **S1**, (4.02 g, 20.00 mmol, 1.00 eq.), 4-fluorobenzaldehyde (2.14 mL, 2.48 g, 20.00 mmol, 1.00 eq.) and K_2CO_3 (5.53 g, 40.00 mmol, 2.00 eq.) in DMF (50 mL). The crude residue was purified by flash column chromatography (Et_2O:Pentane, 5:95 to 14:86, R_f = 0.3) to give the title compound as a white solid (3.48 g, 57%).

m.p. = 55-57 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 9.90 (s, 1H), 7.86 – 7.79 (m, 2H), 7.33 – 7.29 (m, 1H), 7.06 – 7.01 (m, 1H), 6.94 – 6.87 (m, 2H), 2.33 (s, 3H), 2.13 (s, 3H).
^{13}C (126 MHz, $CDCl_3$) δ_C = 190.7 (C_{13}), 162.2 (C_9), 146.8 (C_1), 137.1 (C_{Ar}), 132.9 (C_{Ar}), 132.1 (C_{11}), 131.8 (C_5), 131.5 (C_3), 131.0 (C_{12}), 116.7 (C_6), 115.4 (C_{10}), 20.6 (C_8), 16.8 (C_7).

IR (film) ν_{max}/cm^{-1} **=** 2922, 2736, 2361, 1695, 1606, 1596, 1584, 1502, 1470, 1391, 1299, 1279, 1232, 1154, 1122, 1105, 868, 831, 805, 711, 648, 618.
HRMS (ESI^+): m/z calculated for $C_{15}H_{14}{}^{79}BrO_2^+$ $[M+H]^+$ = 305.0172; m/z found = 305.0172. Δ = 0.14 ppm.

1-Bromo-2-(4-chlorophenoxy)-3,5-dimethylbenzene, 1f:

4-(2-Bromo-4,6-dimethylphenoxy)aniline, **1ab**, (1.40 g, 4.81 mmol, 1.00 eq.) was added to a solution of $CuCl_2$ (840 mg, 6.25 mmol, 1.30 eq.) and ^{t}BuONO (0.91 mL, 779 mg, 1.60 eq.) in MeCN (30 mL) at r.t.. After 2 h, water (30 mL) was added and the reaction mixture was extracted (Et_2O 3 × 30 mL). The combined organic extracts were washed (H_2O, 30 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (*n*-pentane, R_f = 0.5) to give the title compound as a white solid (818 mg, 55%).

m.p. = 64-66 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 7.30 – 7.28 (m, 1H, H_5), 7.24 – 7.19 (m, 2H, H_{11}), 7.02 – 7.00 (m, 1H, H_3), 6.74 – 6.70 (m, 2H, H_{10}), 2.32 (s, 3H, H_8), 2.12 (s, 3H, H_7).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 156.1 (C_9), 147.4 (C_1), 136.7 (C_{Ar}), 133.3 (C_{Ar}), 131.8 (C_5), 131.5 (C_3), 129.7 (C_{11}), 126.9 (C_{12}), 117.2 (C_6), 116.3 (C_{10}), 20.7 (C_8), 16.9 (C_7).
FTIR (film) ν_{max}/cm^{-1} = 1542, 1485, 1472, 1318, 1283, 1227, 1163, 1122, 1093, 1009, 854, 825, 729, 650.
HRMS (EI^+): m/z calculated for $C_{14}H_{12}$ $^{79}Br^{35}ClO^+$ $[M]^+$ = 309.9755; m/z found = 309.976. Δ = +2.12 ppm.

1-Bromo-3,5-dimethyl-2-(4-(methylsulfonyl)phenoxy)benzene, 1g:

1g was prepared according to **General Procedure A** on a 5.00 mmol scale using 2-bromo-4,6-dimethylphenol, **S1**, (1.01 g, 5.00 mmol, 1.00 eq.), 4-fluorophenyl methyl sulfone (871 mg, 5.00 mmol, 1.00 eq.) and K_2CO_3 (1.38 g, 10.00 mmol, 2.00 eq.) in DMF (12.5 mL). The crude residue was purified by flash column chromatography (EtOAc:Pentane, 10:90 to 20:80, R_f = 0.25). The title compound was obtained as an inseparable mixture (1:2, **1g**:4-fluorophenyl

methyl sulfone) and was used without further purification (1.12 g comprising 565 mg, 32%).

(4-(2-Bromo-4,6-dimethylphenoxy)phenyl)methanol, 1h:

$NaBH_4$ (75.7 mg, 2.00 mmol, 1 eq.) was added to a solution of 4-(2-bromo-4,6-dimethylphenoxy)benzaldehyde, **1e,** (610 mg, 2.00 mmol, 1.00 eq.) in THF/MeOH (2:1, 6 mL). After 1 h, the reaction was concentrated *in vacuo*. H_2O (10 mL) was added and the reaction mixture was extracted (EtOAc, 3 × 10 mL). The organic extracts were washed (H_2O, 10 mL), dried ($MgSO_4$) and concentrated *in vacuo* to give the title compound as a white solid (615 mg, quant.).

m.p. = 62-64 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 7.34 – 7.31 (m, 1H, H_5), 7.31 – 7.27 (m, 2H, H_{11}), 7.05 – 7.02 (m, 1H, H_3), 6.83 – 6.77 (m, 2H, H_{10}), 4.64 (s, 2H, H_{13}), 2.35 (s, 3H, H_8), 2.16 (s, 3H, H_7).
^{13}C (126 MHz, $CDCl_3$) δ_C = 156.9 (C_9), 147.5 (C_1), 136.4 ($C_{4/2}$), 134.3 (C_{12}), 133.3 ($C_{4/2}$), 131.6 (C_5), 131.4 (C_3), 128.8 (C_{11}), 117.2 (C_6), 114.9 (C_{10}), 65.0 (C_{13}), 20.6 (C_8), 16.9 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 3329, 2922, 1737, 1612, 1569, 1506, 1471, 1379, 1278, 1217, 1165, 1123, 1010, 864, 852, 821, 796, 725.
HRMS (ESI^+): m/z calculated for $C_{15}H_{14}BrO$ $[M\text{-}OH]^+$ = 289.0223; m/z found = 289.0224. Δ = 0.35 ppm.

4-(2-Bromo-6-methyl-4-nitrophenoxy)-1,1'-biphenyl, 1i:

1i was prepared according to **General Procedure B** on a 4.00 mmol scale using 1-bromo-2-chloro-3-methyl-5-nitrobenzene, **S3**, (1.00 g, 4.00 mmol, 1.00 eq.), [1,1'-biphenyl]-4-ol (680 mg, 4.00 mmol, 1 eq.) and K_2CO_3 (1.11 g, 8.00 mmol, 2.00 eq.) in DMF (10 mL). The crude residue was purified by flash column chromatography (Et_2O:Pentane, 2:98, R_f = 0.4) to give the title compound as a white solid (1.12 g, 73%).

m.p. = 140-143 °C.

^{1}H (500 MHz, $CDCl_3$) δ_H = 8.42 (dd, *J* = 2.7, 1.0 Hz, 1H, H_1), 8.15 (dd, *J* = 2.8, 0.9 Hz, 1H, H_4), 7.57 – 7.50 (m, 4H, H_{10}, H_{11}), 7.43 (dd, *J* = 8.5, 7.0 Hz, 2H, H_{14}), 7.37 – 7.30 (m, 1H, H_{15}), 6.89 – 6.82 (m, 2H, H_{13}), 2.33 (s, 3H, H_7).
^{13}C (126 MHz, $CDCl_3$) δ_C = 155.8 (C_8), 155.5 (C_2), 145.1 (C_5), 140.3 (C_{11}), 136.2 (C_{12}), 135.4 (C_3), 129.0 (C_{13}), 128.8 ($C_{9/10}$), 127.3 ($C_{9/10}$), 127.1 (C_{15}), 127.0 (C_6), 125.9 (C_4), 118.6 (C_1), 115.4 (C_{13}), 17.6 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 2922, 2360, 1607, 1525, 1484, 1459, 1344, 1258, 1216, 1168, 1090, 1006, 946, 897, 865, 841, 803, 763, 742, 724, 698, 623.
HRMS (APCl$^-$): m/z calculated for $C_{19}H_{13}O_3NBr$ [M-H]$^-$ = 382.0084; m/z found = 382.2215. Δ = -2.20 ppm

1-Bromo-3-methyl-5-nitro-2-phenoxybenzene, 1j:

1j was prepared according to **General Procedure B** on a 4.00 mmol scale using 1-bromo-2-chloro-3-methyl-5-nitrobenzene, **S3**, (1.00 g, 4 mmol, 1.00 eq.), phenol (376 mg, 4.00 mmol, 1.00 eq.) and K_2CO_3 (1.11 g, 8.00 mmol, 2.00 eq.) in DMF (10 mL). The crude residue was purified by flash column chromatography (Et_2O:Pentane, 1:100, R_f = 0.5) to give the title compound as a bright yellow solid (900 mg, 73 %).

m.p. = 44-46 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 8.40 (d, *J* = 2.7 Hz, 1H, H_6), 8.13 (d, *J* = 2.7 Hz, 1H, H_4), 7.35 – 7.27 (m, 2H, H_{10}), 7.11 – 7.04 (m, 1H, H_{11}), 6.81 – 6.75 (m, 2H, H_9), 2.29 (s, 3H, H_7).
^{13}C (126 MHz, $CDCl_3$) δ_C = 156.3 (C_8), 155.5 (C_2), 145.0 (C_5), 135.4 (C_3), 130.1 (C_{10}), 127.1 (C_6), 125.8 (C_4), 123.0 (C_{11}), 118.6 (C_1), 115.1 (C_9), 17.5 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 3087, 2363, 1592, 1575, 1525, 1490, 1458, 1344, 1291, 1260, 1213, 1195, 1165, 1090, 946, 898, 861, 842, 799, 748, 689, 619.
HRMS (APCl$^-$): m/z calculated for $C_{13}H_9BrO_3N$ [M-H]$^-$ = 305.9771; m/z found = 305.9763. Δ = -2.64 ppm.

1-Bromo-3,5-dimethyl-2-(2-nitrophenoxy)benzene, 1k:

1k was prepared according to **General Procedure A** on a 10 mmol scale using 2-bromo-4,6-dimethylphenol, **S1**, (2.01 g, 10.00 mmol, 1.00 eq.), 1-fluoro-2-nitrobenzene (1.41 g, 10.00 mmol, 1.00 eq.) and K_2CO_3 (2.76 g, 20.00 mmol, 2.00 eq.) in DMF (25 mL). No further purification was required to give the titled compound as a bright yellow solid (2.88 g, 89 %).

m.p. = 74-76 °C (Et_2O).
^{1}H (500 MHz, $CDCl_3$) δ_H = 7.97 (dd, *J* = 8.0, 1.5 Hz, 1H, H_{13}), 7.39 (ddd, *J* = 8.0, 7.5, 1.5 Hz, 1H, H_{12}), 7.34 – 7.28 (m, 1H, H_5), 7.10 (ddd, *J* = 8.5, 7.5, 1.0 Hz, 1H, H_{11}), 7.06 – 7.02 (m, 1H, H_3), 6.57 (dd, *J* = 8.5, 1.0 Hz, 1H, H_{10}), 2.33 (s, 3H, H_8), 2.18 (s, 3H, H_7).
^{13}C (126 MHz, $CDCl_3$) δ_C = 150.6 (C_9), 146.5 (C_1), 139.3 (C_{14}), 137.4 (C_{Ar}), 134.2 (C_{12}), 133.1 (C_{Ar}), 132.0 (C_5), 131.7 (C_3), 126.2 (C_{13}), 121.8 (C_{11}), 116.7 (C_6), 115.5 (C_{10}), 20.8 (C_8), 16.8 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 1609, 1525, 1470, 1347, 1280, 1238, 1204, 1162, 1122, 877, 841, 818, 774, 740, 661.
HRMS (ESI$^+$): m/z calculated for $C_{14}H_{13}{}^{79}BrNO_3{}^+$ $[M+H]^+$ = 322.0073; m/z found 322.0074 . Δ = 0.16 ppm

2-(2-Bromo-4,6-dimethylphenoxy)benzonitrile, 1l:

1l was prepared according to **General Procedure A** on a 10 mmol scale using 2-bromo-4,6-dimethylphenol, **S1**, (1.01 g, 5.00 mmol, 1.00 eq.), 2-fluorobenzonitrile (0.54 mL, 0.61 g, 5.00 mmol, 1.00 eq.) and K_2CO_3 (1.38 g, 10.00 mmol, 2.00 eq.) in DMF (12 mL). The crude residue was purified by flash column chromatography (Et_2O:Pentane, 4:96, R_f = 0.2) to give the title compound as a white solid (770 mg, 51%).

m.p. = 89-90 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 7.67 (dd, *J* = 7.7, 1.7 Hz, 1H, H_{13}), 7.40 (ddd, *J* = 8.9, 7.6, 1.7 Hz, 1H, H_{11}), 7.32 – 7.29 (m, 1H, H_5), 7.08 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 1H, H_{12}), 7.05 – 7.02 (m, 1H, H_3), 6.48 (d, *J* = 8.5 Hz, 1H, H_{10}), 2.33 (s, 3H, H_8), 2.17 (s, 3H, H_7).

^{13}C (126 MHz, $CDCl_3$) δ_C = 159.1 (C_9), 146.9 (C_1), 137.5 (C_{Ar}), 134.4 (C_{11}), 134.2 (C_{13}), 133.1 (C_{Ar}), 132.1 (C_5), 131.7 (C_3), 122.3 (C_{12}), 116.9 (C_{Ar}), 116.2 (C_{14}), 113.8 (C_{Ar}), 102.2 (C_{Ar}), 20.9 (C_8), 16.9 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 2922, 2359, 2229, 1601, 1579, 1485, 1470, 1447, 1380, 1281, 1239, 1205, 1161, 1124, 1103, 1037, 991, 871, 853, 821, 783, 756, 724.
HRMS (ESI$^+$): m/z calculated for $C_{15}H_{13}{}^{79}BrNO^+$ $[M+H]^+$ = 302.0175; m/z found = 302.0175 . Δ = 0.15 ppm

1-Bromo-3-methyl-5-nitro-2-(o-tolyloxy)benzene, 1m:

1m was prepared according to **General Procedure B** using 1-bromo-2-chloro-3-methyl-5-nitrobenzene, **S3**, (1.00 g, 4.00 mmol, 1 eq.), *o*-cresol (432 mg, 4.00 mmol, 1.00 eq.) and K_2CO_3 (1.11 g, 8.00 mmol, 2.00 eq.) in DMF (10 mL). The crude residue was purified by flash column chromatography (2:98, Et_2O, pentane, R_f = 0.3) to give the title compound as a white solid (966 mg, 75%).

m.p. = 101-103 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 8.42 (d, *J* = 2.8 Hz, 1H, H_5), 8.20 – 8.13 (m, 1H, H_3), 7.33 – 7.26 (m, 1H, H_{12}), 7.09 – 6.96 (m, 2H, H_{11}, H_{10}), 6.24 (dd, *J* = 7.9, 1.4 Hz, 1H, H_9), 2.48 (s, 3H, H_{14}), 2.31 (s, 3H, H_7).
^{13}C (126 MHz, $CDCl_3$) δ_C = 156.1 (C_8), 154.4 (C_1), 144.8 (C_5), 135.2 (C_2), 131.7 (C_{12}), 127.1 (C_4), 127.0 (C_{13}), 126.8 ($C_{11/10}$), 125.7 ($C_{11/10}$), 122.8 (C_3), 118.4 (C_7), 112.2 (C_6), 17.3 (C_9), 16.4 (C_{14}).
IR (film) ν_{max}/cm^{-1} = 3087, 2359, 1575, 1525, 1489, 1460, 1433, 1379, 1343, 1301, 1259, 1224, 1176, 1113, 1090, 1044, 945, 898, 868, 842, 790, 746, 686.
HRMS: not found by ESI, APCl or EI.

2-(2-Bromo-4,6-dimethylphenoxy)benzaldehyde, 1na:

1na was prepared according to General Procedure B on a 15.00 mmol scale using 2-bromo-4,6-dimethylphenol, **S 1**, (3.02 g, 15.00 mmol, 1.00 eq.), 2-fluorobenzaldehyde (1.58 mL, 1.86 g, 15.00 mmol, 1.00 eq.) and K_2CO_3 (4.15 g, 30.00 mmol, 2.00 eq.) in DMF (37.5 mL). The crude residue was purified by flash column chromatography (Et_2O:Pentane, 4:96 to 7:93, R_f = 0.2) to give the title compound as a white solid (1.51

g, 33%).
m.p. = 76-77 °C.

^{1}H (500 MHz, $CDCl_3$) δ_H = 10.78 (s, 1H, H_{15}), 7.96 (dd, J = 7.5, 1.9 Hz, 1H, H_{13}), 7.42 (ddd, J = 8.5, 7.5, 1.9 Hz, 1H, H_{11}), 7.36 – 7.32 (m, 1H, H_5), 7.11 (dd, J = 7.5, 7.5 Hz, 1H, H_{12}), 7.09 – 7.05 (m, 1H, H_3), 6.48 (d, J = 8.5 Hz, 1H, H_{10}), 2.36 (s, 3H, H_8), 2.21 (s, 3H, H_7).
^{13}C (126 MHz, $CDCl_3$) δ_C = 189.6 (C_{15}), 159.9 (C_9) 147.0 (C_1), 137.3 (C_{Ar}), 136.0 (C_{11}), 133.3 (C_{Ar}), 132.1 (C_5), 131.6 (C_3), 128.8 (C_{13}), 124.8 (C_{14}), 122.3 (C_{12}), 117.1 (C_6), 113.9 (C_{10}), 20.8 (C_8), 17.1 (C_7).
IR (film) ν_{max}/cm^{-1} = 2922, 2858, 2359, 1689, 1600, 1581, 1471, 1454, 1435, 1395, 1304, 1279, 1231, 1211, 1187, 1155, 1124, 1097, 1036, 990, 958, 869, 852, 827, 812, 783, 755, 715, 647.
HRMS (ESI$^+$): *m/z* calculated for $C_{15}H_{14}{}^{79}BrO^+$, $[M+H]^+$ = 305.0172; *m/z* found = 305.0173. Δ = 0.44 ppm.

2-(2-Bromo-4,6-dimethylphenoxy)phenol, 1nb:

Prepared according to a modified literature procedure.[4] *m*-CPBA (77%, 1.84 g, 8.22 mmol, 2.50 eq.) was added to a solution of 2-(2-bromo-4,6-dimethylphenoxy)benzaldehyde, **1na**, (1.00 g, 3.29 mmol, 1.00 eq.) in $CHCl_3$ (20 mL) at r.t.. After 24 h, the reaction mixture was washed (Na_2SO_3, sat. aq., 20 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was dissolved in MeOH (20 mL) and concentrated HCl (1 drop) was added. After 30 mins, the reaction was concentrated *in vacuo* and the crude residue was purified by flash column chromatography (Et_2O:Pentane, 4:96, R_f = 0.3) to give the title compound as a white solid (740 g, 77%).

m.p. = 76-78 °C.
^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 7.32 – 7.28 (m, 1H, H_5), 7.08 – 6.99 (m, 2H, H_{13}, H_3), 6.94 (ddd, *J* = 7.8, 7.7, 1.5 Hz, 1H, H_{12}), 6.71 (ddd, *J* = 7.8, 7.5, 1.6 Hz, 1H, H_{11}), 6.36 (dd, *J* = 8.1, 1.5 Hz, 1H, H_{10}), 5.86 (s, 1H, OH), 2.33 (s, 3H, H_8), 2.18 (s, 3H, H_7).
^{13}C NMR (126 MHz, $CDCl_3$): δ_C = 147.3 (C_1), 145.4 (C_{14}), 144.4 (C_9), 136.8 (C_{Ar}), 133.3 (C_{Ar}), 131.8 (C_5), 131.4 (C_3), 123.0 (C_{12}), 120.3 (C_{11}), 117.0 (C_6), 115.8 (C_{13}), 113.0 (C_{10}), 20.7 (C_8), 16.8 (C_7).
IR (film) ν_{max}/cm^{-1} = 3525, 1605, 1494, 1471, 1354, 1279, 1257, 1204, 1176, 1124, 1096, 1032, 874, 852, 824, 798, 782, 743.
HRMS (APCI$^+$): *m/z* calculated for $C_{14}H_{13}{}^{79}BrO_2^+$, $[M]^+$ = 292.0093; *m/z* found = 292.0093. Δ = -0.11 ppm.

1-Bromo-2-(2-methoxyphenoxy)-3,5-dimethylbenzene, 1n:

MeI (0.223 mL, 508 mg, 3.59 mmol, 1.50 eq.) was added to a solution of 2-(2-bromo-4,6-dimethylphenoxy)phenol, **1nb**, (700 mg, 2.39 mmol, 1.00 eq.) and K_2CO_3 (396 mg,2.87 mmol, 1.20 eq.) in DMF (5 mL) at r.t.. After 2 h, H_2O (10 mL) was added and the reaction mixture was extracted (Et_2O, 3 × 20 mL). The organic extracts were washed (H_2O, 20 mL), dried ($MgSO_4$), concentrated *in vacuo* to give the title compound as a white solid (701 mg, 96%).

m.p. = 83-84 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 7.30 – 7.26 (m, 1H, H_5), 7.03 – 6.99 (m, 2H, H_{13} H_3), 6.96 (ddd, *J* = 8.1, 7.3, 1.5 Hz, 1H, H_{12}), 6.76 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H, H_{11}), 6.36 (dd, *J* = 8.0, 1.5 Hz, 1H, H_{10}), 3.98 (s, 3H, H_{15}), 2.31 (s, 3H, H_8), 2.15 (s, 3H, H_7).
^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 148.8 (C_{14}), 147.9 (C_1), 146.7 (C_9), 136.2 ($C_{4/2}$), 133.3 ($C_{4/2}$), 131.7 (C_5), 131.4 (C_3), 122.2 (C_{12}), 120.9 (C_{11}), 117.3 (C_6), 113.6 (C_{10}), 112.7 (C_{13}), 56.4 (C_{15}), 20.7 (C_8), 16.8 (C_7).
FTIR (film) ν_{max}/cm^{-1} = 2922, 1600, 1499, 1454, 1323, 1278, 1251, 1213, 1175, 1126, 1114, 1047, 1029, 853, 819, 781, 742, 612.
HRMS (ESI$^+$): *m/z* calculated for $C_{15}H_{15}{}^{79}BrNaO_2{}^+$ $[M+Na]^+$ = 329.0148; m/z found = 329.0148. Δ = 0.00 ppm.

1-(2-Bromo-6-methyl-4-nitrophenoxy)naphthalene, 1o:

1o was prepared according to **General Procedure B** using 1-bromo-2-chloro-3-methyl-5-nitrobenzene, **S3**, (500 mg, 2.00 mmol, 1.00 eq.), 1-naphthol (288 mg, 2.00 mmol, 1.00 eq.) and K_2CO_3 (553 mg, 4.00 mmol, 2.00 eq.) in DMF (5 mL). The crude residue was purified by flash column chromatography (2:98, Et_2O:pentane, R_f = 0.4) to give the title compound as a bright yellow solid (566 mg, 79%).

m.p. = 126-128 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 8.53 – 8.45 (m, 2H, H_{16}, H_5), 8.21 (d, *J* = 2.7 Hz, 1H, H_3), 7.96 – 7.89 (m, 1H, H_{14}), 7.68 – 7.58 (m, 3H, H_{15}, H_{11}, H_{13})), 7.32 – 7.25 (m, 1H, H_{10}), 6.33 (dd, *J* =

7.6, 1.0 Hz, 1H, H_9), 2.33 (s, 3H, H_7).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 155.9 (C_1), 152.0 (C_8), 145.1 (C_4), 135.4 (C_{Ar}), 135.1 (C_{Ar}), 127.9 (C_{14}), 127.2 (C_5), 127.1 ($C_{11/13/15}$), 126.3 ($C_{11/13/15}$), 125.8 (C_3), 125.5 (C_{10}), 124.9 (C_{Ar}), 122.9 ($C_{11/13/15}$), 121.9 (C_{16}), 118.6 (C_6), 106.8 (C_9), 17.3 (C_7).
FTIR (film) ν_{max}/cm^{-1} = 2359, 1598, 1573, 1526, 1460, 1434, 1391, 1343, 1297, 1257, 1228, 1210, 1177, 1155, 1092, 1078, 1043, 1015, 945, 898, 844, 792, 770, 742, 719, 685.
HRMS (APCI$^-$): m/z calculated for $C_{17}H_{11}{}^{79}BrNO_3^-$ [M-H] = 355.9928; m/z found = 355.9918. Δ = -2.87 ppm.

1-Bromo-2-(3-fluorophenoxy)-3-methyl-5-nitrobenzene, 1p:

1p was prepared according to **General Procedure B** using 1-bromo-2-chloro-3-methyl-5-nitrobenzene, **S3**, (500 mg, 2.00 mmol, 1.00 eq.), 3-fluorophenol (0.181 mL, 224 mg, 2.00 mmol, 1 eq.) and K_2CO_3 (552 mg, 8.00 mmol, 2.00 eq.) in DMF (5 mL). The crude residue was purified by flash column chromatography (2:98, Et_2O, pentane, R_f = 0.3) to give the title compound as a white solid (370 mg, 57%).

m.p. = 84-86 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 8.42 (d, *J* = 2.7 Hz, 1H, H_5), 8.19 – 8.15 (m, 1H, H_3), 7.33 – 7.24 (m, 1H, H_{10}), 6.82 (dddd, *J* = 8.3, 8.3, 2.4, 0.9 Hz, 1H, H_{11}), 6.60 – 6.52 (m, 2H, H_{13}, H_9), 2.32 (s, 3H, H_7).
^{13}C (126 MHz, $CDCl_3$) δ_C = 163.70 (d, *J* = 247.5 Hz, C_{12}), 157.21 (d, *J* = 10.8 Hz, C_8), 154.8 (C_1), 145.2 (C_4), 135.2 (C_2), 130.9 (d, *J* = 9.8 Hz, C_{10}), 110.6 (d, *J* = 3.1 Hz, C_9), 110.0 (d, *J* = 21.3 Hz, C_{11}), 103.18 (d, *J* = 25.8 Hz, C_{13}), 17.3 (C_7).
^{19}F NMR (471 MHz, $CDCl_3$) δ_F = -110.2.
IR (film) ν_{max}/cm^{-1} = 3089, 1601, 1523, 1486, 1460, 1343, 1309, 1262, 1209, 1177, 1118, 1090, 1004, 959, 899, 846, 815, 767, 741, 677.
HRMS: Not found by ESI, APCI or EI.

1-Bromo-3-methyl-5-nitro-2-(3-(trifluoromethyl)phenoxy)benzene, 1q:

1q was prepared according to **General Procedure B** using 1-bromo-2- chloro-3-methyl-5-

nitrobenzene, **S3**, (500 mg, 2.00 mmol, 1.00 eq.), 3-(trifluoromethyl)phenol (0.36 mL, 486 mg, 2.00 mmol, 1.00 eq.) and K_2CO_3 (552 mg, 4.00 mmol, 2.00 eq.) in DMF (5 mL). The crude residue was purified by flash column chromatography (10:90, CH_2Cl_2, pentane, R_f = 0.2) to give the title compound as a white solid (568 mg, 76%).

m.p. = 100-102 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 8.41 (d, *J* = 2.7 Hz, 1H, H_5), 8.16 (d, *J* = 2.7 Hz, 1H, H_3), 7.43 (dd, *J* = 8.0, 8.0 Hz, 1H, H_{10}), 7.35 (d, *J* = 8.0 Hz, 1H, H_{11}), 7.07 (d, *J* = 2.5 Hz, 1H, H_{13}), 6.91 (dd, *J* = 8.0, 2.5 Hz, 1H, H_9), 2.30 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 156.2 (C_8), 154.5 (C_1), 145.3 (C_4), 135.1 (C_2), 132.6 (q, *J* = 32.8 Hz, C_{12}), 130.6 (C_{10}), 127.2 (C_5), 125.9 (C_3), 123.5 (q, *J* = 272.5 Hz, C_{14}), 119.8 (q, *J* = 3.9 Hz, C_{11}), 118.2 (C_6), 118.0 (C_9), 112.2 (q, *J* = 4.0 Hz, C_{13}), 17.3 (C_7).
^{19}F NMR (471 MHz, $CDCl_3$) δ_F = -62.7.
FTIR (film) ν_{max}/cm^{-1} = 2926, 1603, 1519, 1489, 1448, 1430, 1378, 1347, 1330, 1316, 1280, 1259, 1216, 1193, 1160, 1118, 1090, 1062, 1001, 945, 907, 867, 843, 821, 794, 762, 741, 694, 648.
HRMS (APCI$^-$): m/z calculated for $C_{14}H_8$ $^{79}BrF_3NO^+$ $[M-H]^-$ = 373.9645; m/z found = 373.9637. Δ = -2.26 ppm.

1-Bromo-2-(3-(tert-butyl)phenoxy)-3-methyl-5-nitrobenzene, 1r:

1r was prepared according to **General Procedure B** on a 4.00 mmol scale using 1-bromo-2-chloro-3-methyl-5-nitrobenzene, **S3**, (1.00 g, 4.00 mmol, 1.00 eq.), 3-(tert-butyl)phenol (601 mg, 4.00 mmol, 1.00 eq.) and K_2CO_3 (1.11 g, 8.00 mmol, 2.00 eq.) in DMF (10 mL). The crude residue was purified by flash column chromatography (Et_2O:Pentane, 1:100, R_f = 0.8) to give the title compound as a bright yellow solid (1.28 g, 88%).

m.p. = 70-74 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 8.40 (d, *J* = 2.7 Hz, 1H, H_6), 8.13 (d, *J* = 2.7 Hz, 1H, H_4), 7.20 (t, *J* = 8.0 Hz, 1H, H_{12}), 7.11 (ddd, *J* = 7.9, 1.8, 0.9 Hz, 1H, H_{11}), 6.94 (dd, *J* = 2.6, 1.8 Hz, 1H, H_9), 6.46 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H, H_{13}), 2.29 (t, *J* = 0.8 Hz, 3H, H_7), 1.30 (s, 9H, H_{15}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 156.2 (C_8), 155.7 (C_2), 154.0 (C_{10}), 144.9 (C_5), 135.3 (C_3), 129.4 (C_{12}), 127.0 (C_6), 125.8 (C_4), 120.1 (C_{11}), 118.6 (C_1), 112.9 (C_9), 111.4 (C_{13}), 34.9 (C_{14}), 31.4 (C_{15}), 17.6 (C_7).

IR (film) ν_{max}/cm^{-1} **=** 3090, 2964, 2867, 2363, 2156, 1605, 1573, 1527, 1485, 1460, 1431, 1343, 1260, 1213, 1189, 1113, 1089, 947, 921, 897, 872, 844, 802, 781, 759, 742, 716, 699, 667.
HRMS (EI^+): m/z calculated for $C_{17}H_{18}O_3NBr$ $[M-e^-]^+$ = 363.0470; m/z found = 363.0465. Δ = -3.72 ppm.

Methyl (E)-3-(4-hydroxyphenyl)acrylate, 1s:

1s was prepared according to **General Procedure B** on a 4.00 mmol scale using 1-bromo-2-chloro-3-methyl-5-nitrobenzene, **S3**, (1.00 g, 4.00 mmol, 1.00 eq.), 3-(tert-butyl)phenol (713 mg, 4.00 mmol, 1.00 eq.) and K_2CO_3 (1.11 g, 8.00 mmol, 2.00 eq.) in DMF (10 mL). The crude residue was purified by flash column chromatography (EtOAc:Pentane, 5:95, R_f = 0.3) to give the title compound as a yellow solid (1.02 g, 65%).

m.p. = 128-131 °C (Et_2O).
^{1}H (500 MHz, $CDCl_3$) δ_H = 8.37 (dd, *J* = 2.7, 0.7 Hz, 1H, H_2), 8.13 (dd, *J* = 2.8, 0.8 Hz, 1H, H_4), 7.62 (d, *J* = 16.0 Hz, 1H, H_{12}), 7.51 – 7.44 (m, 2H, H_{10}), 6.81 – 6.76 (m, 2H, H_9), 6.33 (d, *J* = 16.0 Hz, 1H, H_{13}), 3.77 (s, 3H, H_{15}), 2.28 (s, 3H, H_7).
^{13}C (126 MHz, $CDCl_3$) δ_C = 167.4 (C_{14}), 157.7 (C_8), 154.9 (C_2), 145.2 (C_5), 143.7 (C_{12}), 135.2 (C_3), 130.1 (C_{10}), 129.5 (C_{11}), 127.1 (C_6), 125.8 (C_4), 118.3 (C_1), 116.9 (C_{13}), 115.5 (C_9), 51.8 (C_{15}), 17.4 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 2981, 2885, 1713, 1605, 1577, 1527, 1503, 1461, 1434, 1417, 1393, 1367, 1344, 1307, 1278, 1258, 1218, 1163, 1109, 1095, 1015, 969, 945, 898, 867, 852, 801, 767, 743, 695, 637.
HRMS ($APCI^-$): m/z calculated for $C_{17}H_{13}{}^{79}BrO_5N$ $[M-H]^-$ = 389.9983; m/z found = 389.9970. Δ = -0.41 ppm.

Methyl 3-(4-(2-bromo-6-methyl-4-nitrophenoxy)phenyl)propanoate, 1t:

1t was prepared according to **General Procedure B** on a 4.00 mmol scale using 1-bromo-2-chloro-3-methyl-5-nitrobenzene, **S3**, (1.00 g, 4.00 mmol, 1.00 eq.), methyl 3-(4-hydroxyphenyl)propanoate (721 mg, 4.00 mmol, 1.00 eq.) and K_2CO_3 (1.11 g, 8.00 mmol, 2.00

eq.) in DMF (10 mL). The crude residue was purified by flash column chromatography (Et_2O:Pentane, 6:94, R_f = 0.8) to give the title compound as a bright yellow solid (1.24 g, 79%).

m.p. = 45-47 °C (Et_2O).
^{1}H (500 MHz, $CDCl_3$) δ_H = 8.38 (d, *J* = 2.8 Hz, 1H, H_6), 8.12 (dd, *J* = 2.7, 0.9 Hz, 1H, H_4), 7.15 – 7.09 (m, 2H, H_{10}), 6.72 – 6.67 (m, 2H, H_9), 3.67 (s, 3H, H_{15}), 2.91 (t, *J* = 7.8 Hz, 2H, H_{12}), 2.61 (t, *J* = 7.8 Hz, 2H, H_{13}), 2.27 (d, *J* = 0.7 Hz, 3H, H_7).
^{13}C (126 MHz, $CDCl_3$) δ_C = 173.4 (C_{14}), 155.6 (C_2), 154.9 (C_8), 145.0 (C_5), 135.3 ($C_{3/11}$), 135.2 ($C_{3/11}$), 129.9 (C_{10}), 127.1 (C_6), 125.8 (C_4), 118.6 (C_1), 115.1 (C_9), 51.8 (C_{15}), 35.9 (C_{13}), 30.2 (C_{12}), 17.5 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 3661, 2981, 1737, 1609, 1527, 1506, 1460, 1436, 1344, 1295, 1260, 1216, 1198, 1167, 1091, 1015, 946, 899, 865, 843, 743.
HRMS ($APCl^-$): m/z calculated for $C_{17}H_{15}O_5NBr$ $[M-H]^-$ = 392.0139, m/z found = 392.0137. Δ = -0.62 ppm.

N-(4-(2-bromo-6-methyl-4-nitrophenoxy)-3-methoxybenzyl)-8-methylnonanamide, 1u:

Capsaicin (900 mg, 2.94 mmol, 1.00 eq.) and Pd/C (10%, 78 mg, 2.5 mol%) were added to an RBF. Following evacuation and backfilling of N_2 x 3, EtOH (6 mL) was added. The mixture was purged with H_2 using a 3-skin balloon and an exit needle. After 5 minutes the balloon was replaced with a fresh H_2 balloon and the exit needle was removed. After stirring overnight, the reaction monitored by TLC. Then the reaction was sparged with N_2 and the solution was filtered through Celite® and eluted (EtOH, 4 x 4 mL) and concentrated *in vacuo*. The crude residue was used without further purification.
1u was prepared according to **General Procedure B** on a 2.00 mmol scale using 1-bromo-2-chloro-3-methyl-5-nitrobenzene, **S3**, (501 mg, 2.00 mmol, 1.00 eq.), and the crude residue containing N-(4-hydroxy-3-methoxybenzyl)-8-methylnonanamide--methane (615 mg, 2.00 mmol, 1.00 eq.) and K_2CO_3 (553 mg, 4.00 mmol, 2.00 eq.) in DMF (5 mL). The crude residue was purified by flash column chromatography (EtOAc:Pentane, 40:60, R_f = 0.2) to give the title compound as a yellow solid (875 g, 84%).

m.p. = 78-80 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 8.36 (m, 1H, H_{21}), 8.10 (qd, *J* = 1.8, 0.9 Hz, 1H, H_{23}), 6.95 (d, *J* = 2.0 Hz, 1H, H_3), 6.67 (m, 1H, H_5), 6.28 (dd, *J* = 8.2, 1.5 Hz, 1H, H_6), 5.81 (s, 1H, H_9), 4.39 (m, 2.4 Hz, 2H, H_8), 3.94 (d, *J* = 1.9 Hz, 3H, H_7), 2.27 (d, *J* = 1.7 Hz, 3H, H_{25}), 2.21 (t, *J* = 7.6 Hz, 2H, H_{11}),

1.64 (m, 2H, H_{12}), 1.53 – 1.44 (m, 1H, H_{17}), 1.36 – 1.19 (m, 6H, H_{13}, H_{14}, H_{15}), 1.16 – 1.09 (m, 2H, H_{16}), 0.84 (m, 6H, H_{18}).

^{13}C (126 MHz, $CDCl_3$) δ_C = 173.2 (d, *J* = 2.1 Hz, C_{10}), 156.0 (C_{19}), 149.1 (d, *J* = 2.3 Hz, C_1), 144.9 (d, *J* = 2.1 Hz, C_2), 144.8 (d, *J* = 2.5 Hz, C_{22}), 135.0 (C_{24}), 134.2 (C_4), 127.1 (C_{21}), 125.8 (C_{23}), 120.0 (d, *J* = 1.9 Hz, C_5), 118.1 (C_{24}), 114.0 (C_6), 112.7 (d, *J* = 2.1 Hz, C_3), 56.4 (C_7), 43.3 (C_8), 39.1 (C_{16}), 36.9 (d, *J* = 2.6 Hz, C_{11}), 29.7 (C_{13}), 29.5 (C_{14}), 28.1 (C_{17}), 27.4 (C_{15}), 25.9 (C_{12}), 22.7 (C_{18}), 17.3 (C_{25}).

IR (film) ν_{max}/cm^{-1} **=** 3287, 3085, 2954, 2927, 2855, 2360, 2342, 1645, 1600, 1527, 1509, 1462, 1433, 1420, 1341, 1257, 1213, 1176, 1154, 1128, 1091, 1036, 946, 897, 852, 840, 793, 742, 685, 655, 643.

HRMS (ESI$^+$): m/z calculated for $C_{25}H_{34}O_5N_2Br$ $[M+H]^+$ = 521.1646; m/z found = 521.1642. Δ = -0.61 ppm.

Propyl 2',4'-difluoro-4-hydroxy-[1,1'-biphenyl]-3-carboxylate, 1va:

1va was prepared according to a literature procedure[1]. Carbonyl diimidizole (1.30 g, 8 mmol, 1.00 eq.) was added to a solution of diflunisal **23** (2.00 g, 8.00 mmol, 1.00 eq.) in DMF (40 mL). The reaction mixture was stirred at 50 °C. After 2 h *n*-PrOH (1.80 mL, 24.00 mmol, 3.00 eq.) was added dropwise and the resultant mixture was stirred at 50 °C. After 3 h the mixture was cooled to r.t. and H_2O (50 mL) was added and extracted with Et_2O (2 x 50 mL). The organic layer was washed with $NaHCO_3$ (sat. aq., 20 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (EtOAc:Pentane, 2:98, R_f = 0.7) to give the title compound as a white solid (968 mg, 42%).

m.p. = 40-42 °C.

^{1}H (500 MHz, $CDCl_3$) δ = 10.94 (s, 1H, H_7), 7.99 (dd, *J* = 2.5, 1.5 Hz, 1H, H_3), 7.58 (dt, *J* = 8.5, 2.0 Hz, 1H, H_5), 7.36 (td, *J* = 8.5, 6.5 Hz, 1H, H_{17}), 7.05 (d, *J* = 8.5 Hz, 1H, H_2), 6.94 (tdd, *J* = 8.0, 2.5, 1.0 Hz, 1H, H_{16}), 6.90 (ddd, *J* = 10.5, 8.5, 2.5 Hz, 1H, H_{14}), 4.34 (t, *J* = 6.5 Hz, 2H, H_9), 1.82 (m, 2H, H_{10}), 1.05 (t, *J* = 7.5 Hz, 3H, H_{11}).

^{13}C (126 MHz, $CDCl_3$) δ = 170.1 (C_8), 163.1 (dd, *J* = 249.0, 12.0 Hz, C_{15}), 161.4 (C_1), 159.8 (dd, *J* = 250.0, 12.0 Hz, C_{13}), 136.1 (d, *J* = 3.0 Hz, C_5), 131.1 (dd, *J* = 9.5, 4.5 Hz, C_{17}), 130.2 (d, *J* = 3.0 Hz, C_3), 126.0 (C_4), 124.3 (dd, *J* = 13.5, 3.0 Hz, C_{12}), 117.9 (C_2), 112.8 (C_2), 111.7 (dd, *J* = 21.0, 4.0 Hz (C_{16}), 104.8 – 104.0 (m, C_{14}), 67.2 (C_9), 22.1 (C_{10}), 10.5 (C_{11}).

^{19}F NMR (470 MHz, DMSO) δ_F = -111.5 (d, *J* = 7.1 Hz), -113.7 (d, *J* = 7.6 Hz).

IR (film) ν_{max}/cm^{-1} **=** 3657, 2982, 2971, 2883, 2360, 1676, 1617, 1591, 1513, 1484, 1398, 1334, 1291, 1267, 1252, 1225, 1205, 1141, 1091, 969, 939, 850, 815, 795, 730, 668, 633, 628, 613.

HRMS (ESI$^+$): calculated for $C_{16}H_{15}O_3F_2$, $[M+H]^+$ = 293.0985; m/z found 293.0985, Δ = 0.35 ppm.

Propyl 4-(2-bromo-6-methyl-4-nitrophenoxy)-2',4'-difluoro-[1,1'-biphenyl]-3-carboxylate, 1v:

1v was prepared according to **General Procedure B** on a 2.00 mmol scale using 1-bromo-2-chloro-3-methyl-5-nitrobenzene, **S3**, (501 mg, 2.00 mmol, 1.00 eq.), **1va** (585 mg, 2.00 mmol, 1.00 eq.) and K_2CO_3 (553 mg g, 4.00 mmol, 2 eq.) in DMF (5 mL). The crude residue was purified by flash column chromatography (Et_2O:Pentane, 1:99, R_f = 0.2) to give the title compound as a yellow oil (409 mg, 40%).

^{1}H (500 MHz, $CDCl_3$) δ = 8.41 (d, *J* = 2.7 Hz, 1H, H_{22}), 8.16 (dd, *J* = 2.7, 0.9 Hz, 1H, H_{24}), 8.08 (dd, *J* = 2.4, 1.1 Hz, 1H, H_3), 7.50 – 7.46 (m, 1H, H_5), 7.40 (td, *J* = 8.7, 6.3 Hz, 1H, H_{17}), 6.99 – 6.94 (m, 1H, H_4), 6.91 (ddd, *J* = 11.0, 8.8, 2.6 Hz, 1H, H_{14}), 6.44 (m, 1H, H_{16}), 4.35 (t, *J* = 6.6 Hz, 2H, H_9), 2.36 (s, 3H, H_{26}), 1.81 (qn, *J* = 7.1 Hz, 2H, H_{10}), 1.03 (t, *J* = 7.4 Hz, 3H, H_{11}).
^{13}C (126 MHz, $CDCl_3$) δ = 165.5 (C_8), 162.6 (dd, *J* = 249.7, 11.9 Hz, C_{15}), 159.8 (dd, *J* = 250.7, 11.9 Hz, C_{13}), 155.1 (C_{20}), 154.8 (C_1), 145.3 (C_{23}), 135.2 (C_{25}), 133.8 (d, *J* = 3.5 Hz, C_5), 132.8 (d, *J* = 2.7 Hz, C_3), 131.3 (dd, *J* = 9.5, 4.7 Hz, C_{17}), 129.7 (C_4), 127.2 (C_{22}), 125.9 (C_{24}), 123.6 (dd, *J* = 13.4, 3.9 Hz, C_{12}), 121.0 (C_2), 118.3 (C_{21}), 114.1 (C_6), 112.0 (dd, *J* = 21.2, 3.7 Hz, C_{16}), 104.7 (t, *J* = 25.9 Hz, C_{14}), 67.2 (C_9), 22.3 (C_{10}), 17.4 (C_{26}), 10.7 (C_{11}).
^{19}F NMR (470 MHz, DMSO) δ_F = -110.7 (d, *J* = 7.8 Hz), -113.5 (d, *J* = 7.5 Hz).
IR (film) ν_{max}/cm^{-1} **=** 3089, 2971, 2360, 2343, 1728, 1610, 1583, 1528, 1485, 1462, 1434, 1404, 1344, 1317, 1294, 1261, 1221, 1178, 1142, 1103, 1090, 1081, 1040, 969, 946, 898, 880, 849, 813, 784, 758, 742, 664, 660, 653, 645, 638, 634, 628, 616, 610.
HRMS (ESI$^+$): m/z calculated for $C_{23}H_{19}O_5NBrF_2$ $[M+H]^+$ = 506.0409; m/z found = 506.0411. Δ = 0.37 ppm.

3.3 Cross Coupling Precursors

2,4-Dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, 2:

2 was prepared according to a modified literature procedure[2]. 1,4- Dioxane (120 mL) was added to a mixture of 2-bromo-4,6-dimethylaniline (3.00 g, 15.00 mmol, 1.00 eq.), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (366 mg, 0.45 mmol, 3 mol%), KOAc (4.41 g, 45.00 mmol, 3.00 eq.) and B_2Pin_2 (5.71 g, 22.50 mmol, 1.50 eq.) under N_2. Argon was bubbled through the mixture for 5 mins and the reaction was heated to 95 °C. After 24 h, H_2O (100 mL) was added. The resulting mixture was extracted (CH_2Cl_2, 3 × 50 mL), the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was suspended in pentane (100 mL), filtered through Celite® (20 mL), eluted (pentane, 3 × 30 mL) and concentrated *in vacuo*.

2 was stored in solid form and used without further purification assuming 100% conversion.

The crude solid was dissolved in PhMe (52 mL) to give a total solution volume of 60 mL. The solution was stored at 0 °C and used within 2 weeks of being made.

1-((2-Bromo-4,6-dimethylphenyl)diazenyl)pyrrolidine, C1:

Prepared according to a modified literature procedure[3]. $NaNO_2$ (414 mg, 6.00 mmol, 1.20 eq.) was added to a solution of 2-bromo-4,6-dimethylaniline (1.00 g, 5.00 mmol, 1 eq.) and HCl (37%, aq., 4.11 mL, 50.00 mmol, 10 eq.) in H_2O:MeCN (2:3, 25 mL) at 0 °C. After 30 mins, the reaction mixture was added to a solution of pyrrolidine (0.52 mL, 605 mg, 8.50 mmol, 1.7 eq.) and K_2CO_3 (6.90 g, 50.00 mmol, 10 eq.) in H_2O:MeCN (1:2, 60 mL) at 0 °C. Once the addition was complete the reaction was warmed to r.t. and extracted (Et_2O, 2 × 40 mL). The organic extracts were washed (brine, 2 × 30 mL), dried ($MgSO_4$) and concentrated *in vacuo* to give the title compound as a bright yellow oil (1.34 g, 95%).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 7.25 – 7.23 (m, 1H, H_6), 6.93 – 6.90 (m, 1H, H_4), 3.87 – 3.68 (br, m, 4H, H_9), 2.26 (s, 3H, H_8), 2.18 (s, 3H, H_7), 2.09 – 2.01 (br, m, 4H, H_{10}).

^{13}C (126 MHz, $CDCl_3$) δ_C = 146.0 (C_2), 135.4 (C_3), 131.8 (C_5), 130.9 (C_6), 130.8 (C_4), 117.1 (C_1), 50.8 (br, C_9), 46.5 (br, $C_{9'}$), 23.9 (C_{10}), 20.5 (C_8), 18.9 (C_7).
IR (film) ν_{max}/cm^{-1} = 2870, 2361, 1558, 1421, 1319, 1264, 1210, 1161, 1108, 1029, 850, 815, 733, 668.
HRMS (ESI^+): *m/z* calculated for $C_{12}H_{17}{}^{79}BrN_3{}^+$, $[M+H]^+$ = 282.0611; *m/z* found = 282.0601. Δ = -3.71 ppm.

3.5 Cross Coupling

3,3',5,5'-Tetramethyl-2'-(4-nitrophenoxy)-[1,1'-biphenyl]-2-amine, 3a:

3a was prepared according to **General Procedure C** using 1-bromo-3,5-dimethyl-2-(4-nitrophenoxy)benzene (2.00 g, 6.23 mmol, 1.00 eq.), 2,4-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, **2**, (9.35 mmol, 1.50 eq.) in PhMe (38 mL), H_2O (60 mL), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (254 mg, 0.31 mmol, 5 mol%) and Na_2CO_3 (2.64 g, 24.92 mmol, 4.00 eq.) in PhMe (22 mL). The crude residue was purified by flash column chromatography (EtOAc:Pentane, 7:93, R_f = 0.2). The crude product was suspended in IPA (20 mL) and H_2O (40 mL) was added. The solid precipitate was collected by suction filtration to give the title compound as a bright yellow solid (1.43 g, 63%).

m.p. = 149-150 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.04 – 7.96 (m, 2H, H_{11}), 7.14 – 7.10 (m, 1H, H_3), 7.05 (m, 1H, H_5), 6.75 – 6.72 (m, 1H, H_{16}), 6.70 (m, 2H, H_{10}), 6.57 (d, *J* = 2.1 Hz, 1H, H_{18}), 2.37 (s, 3H, H_8), 2.17 (s, 3H, H_7), 2.11 (s, 3H, H_{19}), 2.07 (s, 3H, H_{20}). NH_2 not observed.
^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 163.1 (C_9), 147.6 (C_1), 141.9 (C_{12}), 138.7 (br, C_{14}), 136.2 (C_{Ar}), 132.7 (C_6), 131.8 (C_3), 131.4 (C_{16}), 130.7 (C_{Ar}), 130.5 (C_5), 128.7 (C_{18}), 127.3 (br, C_{Ar}), 125.5 (C_{11}), 123.2 (br, C_{13}), 122.8 (br, C_{Ar}), 115.3 (C_{10}), 20.9 (C_8), 20.2 (C_{20}), 17.8 (C_{19}), 16.4 (C_7).
IR (film) ν_{max}/cm^{-1} = 3385, 2920, 2342, 1588, 1512, 1488, 1340, 1240, 1197, 1163, 1111, 870, 849, 750.
HRMS (ESI$^+$) = m/z calculated for $C_{22}H_{23}N_2O_3^+$ $[M+H]^+$ = 363.1703; m/z found = 363.1700. Δ = -0.93 ppm.

***N*-(4-((2'-Amino-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-yl)oxy)phenyl)acetamide, 3b:**

3b was prepared according to **General Procedure D** using *N*-(4-(2-bromo-4,6-dimethylphenoxy)phenyl)acetamide **1b** (832 mg, 2.50 mmol, 1 eq.) as a solid, 2,4-dimethyl-6-

(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, **2**, (3.75 mmol, 1.5 eq.) in PhMe (15 mL), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (102 mg, 0.12 mmol, 5 mol%), Na_2CO_3 (1.05 g, 10.00 mmol, 4 eq.) in PhMe (10 mL) and H_2O (25 mL). The crude residue was purified by flash column chromatography (EtOAc:Pentane, 50:50 to 60:40, R_f = 0.2) to give the title compound as a white solid (430 mg, 46%).

m.p. = 169-170 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.32 (s, 1H, NH), 7.17 (d, *J* = 8.6 Hz, 2H, H_{11}), 7.06 (d, *J* = 2.2 Hz, 1H, H_3), 6.99 (d, *J* = 2.2 Hz, 1H, H_5), 6.73 (d, *J* = 2.1 Hz, 1H, H_{18}), 6.63 (d, *J* = 2.1 Hz, 1H, H_{20}), 6.54 (d, *J* = 8.5 Hz, 2H, H_{10}), 3.35 (br s, 2H, NH_2), 2.34 (s, 3H, H_8), 2.15 (s, 3H, H_7), 2.10 (s, 3H, H_{21}), 2.09 (s, 3H, H_{22}), 2.05 (s, 3H, H_{14}).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 168.3 (C_{13}), 155.1 (C_9), 148.6 (C_1), 139.1 (C_{16}), 135.2 (C_{Ar}), 133.3 (C_6), 131.9 (C_{12}), 131.7 (C_3), 131.5 (C_{Ar}), 130.5 (C_{18}, C_5), 129.0 (C_{20}), 127.1 (C_{Ar}), 124.4 (C_{15}), 122.8 (C_{Ar}), 121.5 (C_{11}), 115.5 (C_{10}), 24.4 (C_{14}), 20.9 (C_8), 20.4 (C_{22}), 17.9 (C_{21}), 16.7 (C_7).
FTIR (film) ν_{max}/cm^{-1} = 3649, 3366, 2920, 1663, 1607, 1541, 1505, 1410, 1372, 1313, 1213, 1166, 1014, 862, 837, 754.
HRMS (ESI$^+$): m/z calculated for $C_{24}H_{27}N_2O_2^+$ $[M+H]^+$ = 375.2067; m/z found = 375.2065. Δ = -0.51 ppm.

Ethyl 4-((5-acetamido-2'-amino-3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)benzoate, 3c:

3c was prepared according to **General Procedure D** using **1c** (760mg, 2.0 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (EtOAc:pentane, 50:50, R*f*= 0.2) to give the title compound as a brown solid (507 mg, 59%).

m.p. = 157-159 °C (Et_2O).
^{1}H (500 MHz, $CDCl_3$) δ_H = 7.83 – 7.77 (m, 2H, H_{13}), 7.64 (d, *J* = 2.7 Hz, 1H, H_4), 7.43 (s, 1H, H_8), 7.16 (d, *J* = 2.5 Hz, 1H, H_6), 6.74 – 6.70 (m, 1H, H_{21}), 6.66 – 6.59 (m, 2H, H_{12}), 6.57 (d, *J* = 2.1 Hz, 1H, H_{23}), 4.30 (q, *J* = 7.1 Hz, 2H, H_{16}), 3.05 (s, 2H, H_{24}), 2.17 (s, 3H, H_7), 2.16 (s, 3H, H_{10}), 2.08 (s, 3H, H_{25}), 2.06 (s, 3H, H_{26}), 1.34 (t, *J* = 7.1 Hz, 3H, H_{17}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 168.5 (C_9), 166.4 (C_{15}), 161.9 (C_{11}), 146.6 (C_2), 139.5 (C_{19}), 135.6 (C_5), 134.0 (C_{22}), 133.0 (C_3), 131.4 (C_{13}), 130.8 (C_{21}), 128.8 (C_{23}), 126.9 (C_{20}), 123.7 (C_{14}), 122.8 (C_{18}),

122.6 (C_4), 121.2 (C_6), 114.9 (C_{12}), 60.8 (C_{16}), 24.6 (C_{10}), 20.3 (C_{26}), 17.9 (C_{25}), 17.0 (C_7), 14.5 (C_{17}). One aromatic carbon was not observed.
IR (film) ν_{max}/cm^{-1} **=** 3311, 2978, 2927, 1711, 1605, 1551, 1504, 1469, 1419, 1368, 1276, 1231, 1197, 1161, 1101, 1015, 862, 768, 695, 645, 617.
HRMS (ESI$^+$) = m/z calculated for $C_{26}H_{29}N_2O_4^+$ $[M+H]^+$ = 433.2122; m/z found = 433.2126. Δ = 0.86 ppm.

1-(4-((3,3',5,5'-Tetramethyl-2'-(pyrrolidin-1-yldiazenyl)-[1,1'-biphenyl]-2-yl)oxy)phenyl)ethan-1-one, 3d: [1]

1,4-Dioxane (10 mL) was added to a mixture of 1-(4-(2-bromo-4,6-dimethylphenoxy)phenyl)ethan-1-one, **1d**, (479 mg, 1.50 mmol, 1 eq.), Pd(dppf)Cl_2·CH_2Cl_2 (37 mg, 0.045 mmol, 3 mol%), KOAc (442 mg, 4.50 mmol, 3 eq.) and B_2Pin_2 (571 mg, 2.25 mmol, 1.5 eq.) under N_2. Argon was bubbled through the mixture for 5 mins and it was heated to 95 °C. After 24 h, H_2O (20 mL) was added. The resulting mixture was extracted (CH_2Cl_2, 3 × 10 mL), the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was suspended in pentane (20 mL), filtered through Celite® (5 mL), eluted (pentane, 3 × 10 mL) and concentrated *in vacuo*. The crude residue was used without further purification.
The crude reaction mixture in PhMe (5 mL), 1-((2-bromo-4,6-dimethylphenyl)diazenyl) pyrrolidine, **C1**, (633 mg, 2.25 mmol, 1.50 eq.) in PhMe (5 mL) and H_2O (17 mL) were sequentially added to a mixture of Pd(dppf)Cl_2·CH_2Cl_2 (69 mg, 0.085 mmol, 5 mol%) and Na_2CO_3 (720 mg, 6.80 mmol, 4.00 eq.) in PhMe (7 mL) under N_2. Argon was bubbled through the mixture for 5 mins and it was heated to 95 °C. After 16 h, the reaction mixture was extracted (CH_2Cl_2, 3 × 10 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (EtOAc:Pentane, 6:94, R_f = 0.2) to give the title compound as a viscous colourless oil (373 mg, 56%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.75 – 7.68 (m, 2H, H_{11}), 6.95 (d, *J* = 2.3 Hz, 1H, H_3), 6.90 (d, *J* = 2.2 Hz, 1H, H_5), 6.83 (d, *J* = 2.1 Hz, 1H, H_{18}), 6.78 (d, *J* = 2.0 Hz, 1H, H_{20}), 6.73 – 6.67 (m, 2H, H_{10}), 3.54 – 3.46 (m, 4H, H_{23}), 2.48 (s, 3H, H_{14}), 2.30 (s, 3H, $H_{22/8}$), 2.18 (s, 3H, H_{21}), 2.14 (s, 3H,

[1] We employ a different method to make oxonium ions bearing reactive carbonyl groups (aldehyde **4e** and ketone **4d**) as the standard cross-coupling method between aniline-containing pinacol borane **2** and biaryl ethers bearing an aldehyde **1e** and a ketone **1d** is unsuccessful. This is most likely as a consequence of condensation between these groups. As a consequence, we employ a masked diazonium salt (an amino triazene) which is successful in the cross-coupling and enables us to circumvent the chemoselectivity issue we observe.

$H_{22/8}$), 2.06 (s, 3H, H_7), 1.91 – 1.87 (m, 4H, H_{24}).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 197.0 (C_{13}), 162.4 (C_9), 147.4 (C_1), 146.0 (C_{16}), 135.2 (C_6), 134.0 (C_{Ar}), 133.3 (C_{Ar}), 131.4 (C_5), 130.9 (C_{18}), 130.7 (C_{Ar}), 130.5 (C_{Ar}), 130.4 (C_{12}), 130.2 (C_{11}), 130.1 (C_3), 129.9 (C_{Ar}), 129.1 (C_{20}), 115.4 (C_{10}), 48.4 (br, C_{23}), 26.4 (C_{14}), 24.1 (C_{24}), 20.9 ($C_{22/8}$), 20.9 ($C_{22/8}$), 18.6 (C_{21}), 16.6 (C_7).

FTIR (film) ν_{max}/cm^{-1} = 2921, 2361, 1734, 1677, 1653, 1594, 1559, 1541, 1505, 1430, 1357, 1323, 1267, 1235, 1164, 1124, 957, 858, 837, 729.

HRMS (ESI$^+$): m/z calculated for $C_{24}H_{23}O^+$ $[M-C_4H_8N_3]^+$ = 343.1693; m/z found = 343.1694. Δ = 0.52 ppm.

4-((3,3',5,5'-Tetramethyl-2'-(pyrrolidin-1-yldiazenyl)-[1,1'-biphenyl]-2-yl)oxy) benzaldehyde, 3e:

1,4-Dioxane (10 mL) was added to a mixture of 4-(2-bromo-4,6-dimethylphenoxy)benzaldehyde, **1e** (456 mg, 1.50 mmol, 1 eq.), Pd(dppf)Cl_2·CH_2Cl_2 (37 mg, 0.045 mmol, 3 mol%), KOAc (442 mg, 4.50 mmol, 3 eq.) and B_2Pin_2 (571 mg, 2.25 mmol, 1,5 eq.) under N_2. Argon was bubbled through the mixture for 5 mins and it was heated to 95 °C. After 24 h, H_2O (20 mL) was added. The resulting mixture was extracted (CH_2Cl_2, 3 × 10 mL), the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was suspended in pentane (20 mL), filtered through Celite® (5 mL), eluted (pentane, 3 × 10 mL) and concentrated *in vacuo*. The crude residue was used without further purification.

The crude reaction mixture in PhMe (5 mL), 1-((2-bromo-4,6-dimethylphenyl)diazenyl) pyrrolidine, **C1**, (633 mg, 2.25 mmol, 1.50 eq.) in PhMe (5 mL) and H_2O (17mL) were sequentially added to a mixture of Pd(dppf)Cl_2·CH_2Cl_2 (69 mg, 0.085 mmol, 5 mol%) and Na_2CO_3 (720 mg, 6.80 mmol, 4.00 eq.) in PhMe (7 mL) under N_2. Argon was bubbled through the mixture for 5 mins and it was heated to 95 °C. After 16 h, the reaction mixture was extracted (CH_2Cl_2, 3 × 10 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (EtOAc:Pentane, 6:94, R_f = 0.2) to give the title compound as a viscous colourless oil (275 mg, 43%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 9.78 (s, 1H, H_{13}), 7.65 – 7.57 (m, 2H, H_{11}), 6.98 – 6.95 (m, 1H, H_3), 6.93 – 6.90 (m, 1H, H_5), 6.83 – 6.80 (m, 1H, H_{17}), 6.79 – 6.75 (m, 3H, H_{19}, H_{10}), 3.54 – 3.46 (m, 4H, H_{22}), 2.30 (s, 3H, $H_{21/8}$), 2.18 (s, 3H, H_{20}), 2.13 (s, 3H, $H_{21/8}$), 2.07 (s, 3H, H_7), 1.95 – 1.84

(m, 4H, H_{23}).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 190.9 (C_{13}), 163.4 (C_9), 147.1 (C_1), 145.8 (C_{15}), 135.0 (C_6), 134.1 (C_{Ar}), 133.3 (C_{Ar}), 131.5 (C_{10}), 131.3 (C_5), 130.8 (C_{17}), 130.6 (C_{Ar}), 130.2 (C_{Ar}), 130.1 (C_{12}), 130.0 (C_3), 129.6 (C_{Ar}), 129.0 (C_{19}), 115.9 (C_{11}), 48.5 (br, C_{22}), 23.9 (C_{23}), 20.8 ($C_{21/8}$), 20.7 ($C_{21/8}$), 18.5 (C_{20}), 16.5 (C_7).

IR (film) ν_{max}/cm^{-1} = 2919, 2865, 2359, 1698, 1606, 1594, 1580, 1503, 1471, 1427, 1324, 1299, 1266, 1234, 1212, 1198, 1155, 1124, 1106, 866, 860, 833, 757.

HRMS (ESI$^+$) = m/z calculated for $C_{23}H_{21}O_2^+$ $[M-C_4H_8N_3]^+$ = 329.1536; m/z found = 329.1534. Δ = -0.78 ppm.

2'-(4-Chlorophenoxy)-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-amine, 3f:

3f was prepared according to **General Procedure C** using 1-bromo-2-(4-chloro-phenoxy)-3,5-dimethylbenzene, **1f**, (527 mg, 1.70 mmol, 1 eq.) as a solid, 2,4-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, **2**, (2.55 mmol, 1.5 eq.) in PhMe (10 mL), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (69 mg, 0.085 mmol, 5 mol%), Na_2CO_3 (720 mg, 6.80 mmol, 4 eq.) in PhMe (7 mL) and H_2O (17 mL). The crude residue was purified by flash column chromatography (Et_2O:Pentane, 5:95, R_f = 0.3) to give the title compound as a white solid (440 mg, 74%).

m.p. = 74-75 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.10 – 7.06 (m, 1H, H_3), 7.06 – 6.99 (m, 3H, H_{11}, H_5), 6.77 – 6.74 (m, 1H, H_{16}), 6.60 – 6.57 (m, 1H, H_{18}), 6.56 – 6.52 (m, 2H, H_{10}), 3.28 (br, s, 2H, NH_2), 2.36 (s, 3H, H_8), 2.17 (s, 3H, H_7), 2.12 (s, 3H, H_{19}), 2.10 (s, 3H, H_{20}).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 157.1 (C_9), 148.6 (C_1), 139.3 (C_{14}), 135.4 (C_{Ar}), 133.2 (C_{Ar}), 131.8 (C_{Ar}), 131.7 (C_3), 130.5 (C_5, C_{16}), 129.1 (C_{11}), 129.0 (C_{18}), 127.0 (C_{Ar}), 126.1 (C_{12}), 123.9 (C_{Ar}), 122.6 (C_{Ar}), 116.7 (C_{10}), 20.9 (C_8), 20.4 (C_{20}), 17.9 (C_{19}), 16.7 (C_7).

IR (film) ν_{max}/cm^{-1} = 2920, 1622, 1485, 1280, 1225, 1162, 1094, 1009, 858, 827.

HRMS (ESI$^+$): m/z calculated for $C_{22}H_{23}{}^{35}ClNO_2^+$ $[M+H]^+$ = 352.1463; m/z found = 352.1461. Δ = -0.43 ppm.

3,3',5,5'-Tetramethyl-2'-(4-(methylsulfonyl)phenoxy)-[1,1'-biphenyl]-2-amine, 3g:

3g was prepared according to **General procedure C** using 1-bromo-3,5-dimethyl-2-(4-(methylsulfonyl)phenoxy)benzene, **1g**, as a 1:2 mixture with 1- fluoro-4-(methyl sulfonyl)benzene (703 mg, 1.00 mmol, 1.00 eq.). The crude reside was purified by flash column chromatography (EtOAc:Pentane, 15:85 to 30:70, R_f = 0.3) to give the title compound as a viscous oil (283 mg, 72%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H = δ 7.70 – 7.63 (m, 2H, H_{11}), 7.11 (d, *J* = 2.2 Hz, 1H, H_3), 7.04 (d, *J* = 2.2 Hz, 1H, H_5), 6.77 – 6.74 (m, 2H, H_{10}), 6.73 (d, *J* = 2.0 Hz, 1H, H_{17}), 6.56 (d, *J* = 2.1 Hz, 1H, H_{19}), 2.96 (s, 3H, H_{13}), 2.37 (s, 3H, H_8), 2.17 (s, 3H, H_7), 2.11 (s, 3H, H_{20}), 2.07 (s, 3H, H_{21}). NH_2 was not observed.
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 162.4 (C_9), 147.8 (C_1), 138.9 (br, C_{15}), 136.1 (C_{Ar}), 132.9 (C_{12}), 132.9 (C_6), 131.9 (C_3), 131.5 (C_{Ar}), 130.7 (C_{17}), 130.6 (C_5), 129.3 (C_{11}), 128.9 (C_{19}), 127.2 (br, C_{Ar}), 123.5 (C_{14}), 122.9 (br, C_{Ar}), 115.9 (C_{10}), 44.8 (C_{13}), 21.0 (C_8), 20.4 (C_{21}), 17.9 (C_{20}), 16.6 (C_7).
IR (film) ν_{max}/cm^{-1} = 2981, 2918, 1624, 1588, 1487, 1410, 1380, 1315, 1293, 1237, 1199, 1146, 1091, 1012, 957, 859, 839, 770, 628.
HRMS (ESI$^+$): m/z calculated for $C_{23}H_{26}NO_3S^+$ $[M+H]^+$ = 396.1628; m/z found = 396.1625. Δ = -0.64 ppm.

(4-((2'-Amino-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-yl)oxy)phenyl)methanol, 3h:

3h was prepared according to **General procedure C** using (4-(2-bromo-4,6-dimethyl phenoxy)phenyl)methanol, **1h**, (306 mg, 1.00 mmol, 1 eq.). The crude reside was purified by flash column chromatography (EtOAc:Pentane, 20:80, R_f = 0.2) to give the title compound as a viscous oil (285 mg, 82%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.09 – 7.03 (m, 3H, H_{11}, H_3), 7.00 (d, *J* = 2.3 Hz, 1H, H_5), 6.73

(d, J = 2.1 Hz, 1H, H_{17}), 6.63 (s, 1H, H_{19}), 6.61 – 6.55 (m, 2H, H_{10}), 4.48 (s, 2H, H_{13}), 2.35 (s, 3H, H_8), 2.15 (s, 3H, H_7), 2.11 (s, 3H, H_{20}), 2.08 (s, 3H, H_{21}). NH_2 and OH were not observed.
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 157.9 (C_9), 148.5 (C_1), 138.7 (C_{15}), 135.1 (C_{Ar}), 133.7 (C_{12}), 133.2 (C_6), 131.9 (C_{Ar}), 131.7 (C_3), 130.4 (C_{17}, C_5), 129.1 (C_{19}), 128.3 (C_{11}), 127.4 (C_{Ar}), 124.6 (C_{14}), 123.0 (C_{Ar}), 115.3 (C_{10}), 64.8 (C_{13}), 20.9 (C_8), 20.4 (C_{21}), 17.9 (C_{20}), 16.7 (C_7).
FTIR (film) ν_{max}/cm^{-1} = 3380, 2921, 2852, 1611, 1506, 1468, 1368, 1220, 1164, 1108, 1010, 949, 860, 831, 732.
HRMS (ESI$^+$): m/z calculated for $C_{23}H_{26}NO_2^+$ $[M+H]^+$ = 348.1958; m/z found = 348.1958. Δ = -0.01 ppm.

N-(6-([1,1'-biphenyl]-4-yloxy)-2'-amino-3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl)acetamide, 3i:

3i was prepared according to **General Procedure D** using **1i** (768 mg, 2.0 mmol, 1 eq.). The crude residue was purified by flash column chromatography (EtOAc:pentane, 40:60, R*f*= 0.10) to give the title compound as a white solid (332 mg, 38%).
m.p. = 154-156 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 7.66 (d, J = 2.6 Hz, 1H, H_4), 7.49 – 7.43 (m, 2H, H_{16}), 7.38 (dd, J = 8.5, 7.0 Hz, 2H, H_{17}), 7.33 – 7.30 (m, 2H, H_{13}), 7.29 – 7.27 (m, 1H, H_{18}), 7.18 (s, 1H, H_8), 7.13 (d, J = 2.5 Hz, 1H, H_6), 6.74 (d, J = 2.1 Hz, 1H, H_{22}), 6.69 – 6.63 (m, 2H, H_{12}), 6.62 (d, J = 2.1 Hz, 1H, H_{24}), 2.24 (s, 3H, H_7), 2.18 (s, 3H, H_{10}), 2.10 (s, 3H, H_{26}), 2.06 (s, 3H, H_{27}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 168.3 (C_9), 158.0 (C_{11}), 147.6 (C_2), 140.9 (C_{13}), 139.6 (C_{20}), 135.1 (C_5), 134.5 (C_{15}), 134.2 (C_{19}), 133.3 (C_3), 130.7 (C_{22}), 129.0 (C_{24}), 128.8 (C_{17}), 127.9 (C_{13}), 126.9 (C_{23}), 126.8 (C_{13}), 123.3 (C_1), 122.6 (C_{18}), 122.6 (C_{16}, C_{23}), 121.2 (C_6), 115.8 (C_{12}), 24.7 (C_{10}), 20.4 (C_{27}), 17.9 (C_{26}), 17.2 (C_7). One aromatic carbon was not observed.
IR (film) ν_{max}/cm^{-1} **=** 3661, 2981, 2885, 2361, 2341, 2015, 1609, 1462, 1382, 1252, 1148, 1073, 954, 751, 668, 619.
HRMS (ESI$^+$): m/z calculated for $C_{29}H_{29}O_2N_2$ $[M+H]^+$ = 437.2224; m/z found = 437.2222. Δ = -0.27 ppm.

***N*-(2'-Amino-3',5,5'-trimethyl-6-phenoxy-[1,1'-biphenyl]-3-yl)acetamide, 3j:**

3j was prepared according to **General Procedure D** using **1j** (616 mg, 2.0 mmol, 1 eq.). The crude residue was purified by flash column chromatography (EtOAc:pentane, 40:60, R*f*= 0.10) to give the title compound as a brown solid (559 mg, 63%).

m.p. = 133-135 °C (Et_2O)

^{1}H (500 MHz, $CDCl_3$) δ_H = 7.62 (d, *J* = 3.00 Hz, 1H, H_4), 7.32 (s, 1H, H_8), 7.11 (d, *J* = 3.00 Hz, 1H, H_6), 7.10 – 7.06 (m, 2H, H_{12}), 6.87 – 6.80 (m, 1H, H_{14}), 6.73 (d, *J* = 2.00 Hz, 1H, H_{18}), 6.62 – 6.57 (m, 3H, H_{13}, H_{20}), 3.44 (s, 2H, H_{21}), 2.19 (s, 3H, H_7), 2.15 (s, 3H, H_{10}), 2.09 (s, 3H, H_{22}), 2.06 (s, 3H, H_{23}).

^{13}C (126 MHz, $CDCl_3$) δ_C = 168.4 (C_9), 158.3 (C_{11}), 147.4 (C_2), 139.6 (C_{16}), 135.0 (C_5), 134.2 (C_1), 133.3 (C_3), 130.6 (C_{18}), 129.2 (C_{13}), 129.0 (C_{20}), 126.8 (C_{19}), 123.4 (C_{15}), 122.6 (C_4), 122.5 (C_{17}), 121.4 (C_{14}), 121.2 (C_6), 115.4 (C_{12}), 24.6 (C_{10}), 20.4 (C_{23}), 17.9 (C_{22}), 17.1 (C_7).

IR (film) ν_{max}/cm^{-1} **=** 3301, 2920, 2850, 2370, 2337, 2136, 2066, 2042, 2016, 1966, 1667, 1601, 1552, 1489, 1471, 1370, 1218, 1164, 1035, 856, 751, 690, 666.

HRMS (MSS$^+$): m/z calculated for $C_{23}H_{25}O_2N_2$ $[M+H]^+$ = 361.1911; m/z found = 361.1905. Δ = -1.65 ppm.

3,3',5,5'-Tetramethyl-2'-(2-nitrophenoxy)-[1,1'-biphenyl]-2-amine, 3k:

3k was prepared according to General Procedure C using 1-bromo-3,5- dimethyl-2-(2-nitrophenoxy)benzene, **1k**, (2.61 g, 8.00 mmol, 1.00 eq.), 2,4-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, 158, (12.00 mmol, 1.5 eq.) in PhMe (48 mL), H_2O (80 mL), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (327 mg, 0.4 mmol, 5mol%) and Na_2CO_3 (3.39 g, 32.00 mmol, 4 eq.) in PhMe (20 mL). The crude residue was purified by flash column chromatography (EtOAc :Pentane, 7:93, R_f = 0.3). The crude product was suspended in IPA (20 mL) and H_2O (40 mL) was added. The solid precipitate was collected to give the title compound as a bright yellow solid (1.86 g, 64%).

m.p. = = 128-130 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ_H = 7.70 (dd, *J* = 8.1, 1.7 Hz, 1H, H_{13}), 7.24(ddd, *J* = 8.7, 7.4, 1.7 Hz, 1H, H_{11}), 7.14 – 7.10 (m, 1H, H_3), 7.03 (d, *J* = 2.3 Hz, 1H, H_5), 6.87 (ddd, *J* = 8.4, 7.4, 1.2 Hz, 1H, H_{12}), 6.72 – 6.69 (m, 1H, H_{18}), 6.56 (dd, *J* = 8.5, 1.2 Hz, 1H, H_{10}), 6.53 (s, 1H, H_{16}), 3.86 (br s, 2H, NH), 2.37 (s, 3H, H_8), 2.26 (s, 3H, H_7), 2.10 (s, 3H, H_{21}), 2.05 (s, 3H, H_{22}).

^{13}C NMR (151 MHz, $CDCl_3$): δ_C = 151.6 (C_9), 147.4 (C_1), 139.0 (br, C_{20}), 138.7 (C_{14}), 136.2 (C_{Ar}), 133.6 (C_{11}), 132.7 (C_{Ar}), 131.6 (C_3), 131.4 (C_{15}), 130.6 (C_{18}), (C_5), 128.8 (C_{16}), 127.3 (C_{Ar}), 125.5 (C_{13}), 123.3 (C_{Ar}), 120.9 (C_{12}), 116.4 (C_{10}), 20.9 (C_8), 20.2 (C_{22}), 17.7 (C_{21}), 16.3 (C_7). One quaternary carbon was not observed.

FTIR (film) ν_{max}/cm^{-1} = 3447, 2920, 2277, 1607, 1523, 1474, 1347, 1308, 1239, 1196, 1159, 1039, 861, 837, 775, 739.

HRMS (ESI$^+$): *m/z* calculated for $C_{22}H_{23}N_2O^+$, $[M+H]^+$ = 363.1703; *m/z* found = 363.1701. *Δ* = -0.59 ppm.

2-((2'-Amino-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-yl)oxy)benzonitrile, 3l:

3l was prepared according to **General Procedure C** using 2-(2-bromo-4,6-dimethylphenoxy)benzonitrile, **1l**, (301 mg, 1.00 mmol, 1.00 eq.) and PhMe. The crude residue was purified by flash column chromatography (EtOAc :Pentane, 10:90, R_f = 0.3). The crude product was suspended in IPA (5 mL) and H_2O (5 mL) was added. The precipitate was collected by suction filtration to give the title compound as a white solid (230 g, 67%).

m.p. = 128-130 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.33 (dd, *J* = 7.7, 1.7 Hz, 1H, H_{13}), 7.24 (ddd, *J* = 8.5, 7.5, 1.7 Hz, 1H, H_{11}), 7.13 – 7.09 (m, 1H, H_3), 7.03 (d, *J* = 2.2 Hz, 1H, H_5), 6.84 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 1H, H_{12}), 6.73 – 6.69 (m, 1H, H_{19}), 6.52 (br s, 1H, H_{21}), 6.47 (d, *J* = 8.5 Hz, 1H, H_{10}), 3.78 (s, 2H, NH_2), 2.36 (s, 3H, H_8), 2.25 (s, 3H, H_7), 2.14 (s, 3H, H_{22}), 2.06 (s, 3H, H_{23}).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 160.0 (C_9), 147.8 (C_1), 139.3 (br, C_{17}), 136.2 (C_{Ar}), 133.6 (C_{11}), 133.3 (C_{13}), 132.8 (C_{Ar}), 131.6 (C_{Ar}), 131.5 (C_3), 130.7 (C_{19}, C_5), 129.1 (C_{21}), 127.3 (br, C_{Ar}), 123.4 (C_{16}), 121.4 (C_{12}), 116.3 (C_{15}), 114.5 (C_{10}), 101.6 (C_{14}), 21.0 (C_8), 20.3 (C_{23}), 17.9 (C_{22}), 16.5 (C_7). One quaternary carbon was not observed.
FTIR (film) ν_{max}/cm^{-1} = 3383, 2920, 2360, 2228, 1600, 1484, 1448, 1280, 1241, 1198, 1158,

861, 756.
HRMS (ESI$^+$): m/z calculated for $C_{23}H_{23}N_2O^+$ $[M+H]^+$ = 343.1805; m/z found = 343.1804. Δ = -0.38 ppm.

***N*-(2'-Amino-3',5,5'-trimethyl-6-(*o*-tolyloxy)-[1,1'-biphenyl]-3-yl)acetamide, 3m:**

3m was prepared according to **General Procedure D** using 1-bromo-3-methyl-5-nitro-2-(*o*-tolyloxy)benzene, **1m**, (357 mg, 1.00 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (EtOAc:Pentane, 40:60 to 60:40, R_f = 0.2) to give the title compound as a white solid (247 mg, 66%).

m.p. = 154-155 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.66 (d, *J* = 2.6 Hz, 1H, H_3), 7.22 (s, 1H, NH), 7.11 (d, *J* = 2.6 Hz, 1H, H_5), 7.00 – 6.93 (m, 1H, H_{12}), 6.88 (ddd, *J* = 8.2, 7.8, 1.8 Hz, 1H, H_{10}), 6.76 – 6.69 (m, 2H, H_{20}, H_{11}), 6.57 (br s, 1H, H_{22}), 6.28 (dd, *J* = 8.1, 1.2 Hz, 1H, H_9), 2.21 (s, 3H, H_7), 2.17 (s, 3H, H_{16}), 2.09 – 2.06 (m, 6H, H_{24}, H_{23}), 2.05 (s, 3H, H_{14}). NH_2 was not observed.
^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 168.4 (C_{15}), 156.5 (C_8), 147.8 (C_1), 139.6 (C_{18}), 134.9 (C_{Ar}), 134.1 (br, C_{Ar}), 133.4 (C_{Ar}), 130.7 (C_{12}), 130.5 (C_{20}), 129.1 (C_{22}), 126.7, 126.4 (C_{10}), 123.4 (br, C_{Ar}), 122.4 (C_3), 121.1 (C_5), 121.1 (C_{11}), 112.8 (C_9), 25.0 (C_{16}), 20.3 ($C_{24/23}$), 17.9 ($C_{24/23}$), 16.9 (C_7), 16.0 (C_{14}). Two quaternary carbons were not observed.
FTIR (film) ν_{max}/cm^{-1} = 3268, 2921, 2277, 1665, 1602, 1552, 1487, 1469, 1431, 1371, 1300, 1226, 1203, 1183, 1114, 1036, 909, 861, 731, 647.
HRMS (ESI$^+$): m/z calculated for $C_{24}H_{27}N_2O_2^+$ $[M+H]^+$ = 375.2067; m/z found = 375.2068. Δ = 0.38 ppm.

2'-(2-Methoxyphenoxy)-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-amine, 3n:

3n was prepared according to **General Procedure C** using 1-bromo-2-(2-methoxyphenoxy)-3,5-dimethylbenzene, **1n**, (512 mg, 1.7 mmol, 1.00 eq.) as a solid, 2,4-dimethyl-6-(4,4,5,5-

tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, **1n**, (2.55 mmol, 1.50 eq.) in PhMe (10 mL), Pd(dppf)Cl_2·CH_2Cl_2 (69 mg, 0.085 mmol, 5 mol%), Na_2CO_3 (720 mg, 6.8 mmol, 4 eq.) in PhMe (7 mL) and H_2O (17 mL). The crude residue was purified by flash column chromatography (Et_2O:Pentane, 20:80, R_f = 0.2) to give the title compound as a white solid (320 mg, 54%).

m.p. = 156-158 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.08 (d, *J* = 2.2 Hz, 1H, H_3), 6.99 (d, *J* = 2.2 Hz, 1H, H_5), 6.77 (td, *J* = 7.7, 1.5 Hz, 1H, H_{11}), 6.71 (d, *J* = 2.0 Hz, 1H, H_{19}), 6.68 (dd, *J* = 8.0, 1.5 Hz, 1H, H_{10}), 6.64 (td, *J* = 7.7, 1.6 Hz, 1H, H_{12}), 6.57 (d, *J* = 2.0 Hz, 1H, H_{21}), 6.39 (dd, *J* = 8.0, 1.6 Hz, 1H, H_{13}), 3.69 (s, 3H, H_{15}), 3.56 (br, 2H, NH_2), 2.34 (s, 3H, H_8), 2.25 (s, 3H, H_7), 2.11 (s, 3H, H_{22}), 2.06 (s, 3H, H_{23}).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 149.5 (C_9), 149.0 (C_{14}), 148.1 (C_1), 138.6 (C_{17}), 134.9 (C_{Ar}), 132.6 (C_6), 132.1 (C_{Ar}), 131.5 (C_3), 130.5 (C_5), 130.2 (C_{19}), 129.1 (C_{21}), 127.5 (C_{Ar}), 124.7 (C_{16}), 123.0 (C_{Ar}), 121.7 (C_{11}), 120.5 (C_{12}), 115.0 (C_{13}), 112.3 (C_{10}), 56.1 (C_{15}), 20.9 (C_8), 20.4 (C_{23}), 18.0 (C_{22}), 16.6 (C_7).
FTIR (film) ν_{max}/cm^{-1} = 3376, 2919, 2361, 2342, 1559, 1500, 1457, 1252, 1212, 1177, 1154, 1116, 1047, 1030, 858, 743.
HRMS (ESI$^+$): m/z calculated for $C_{22}H_{26}NO_2^+$ $[M+H]^+$ = 348.1958; m/z found = 348.1952. Δ = -1.85 ppm.

***N*-(2'-Amino-3',5,5'-trimethyl-6-(naphthalen-1-yloxy)-[1,1'-biphenyl]-3-yl)acetamide, 3o:**

3o was prepared according to **General Procedure D** using 1-(2-bromo-6-methyl-4-nitrophenoxy)naphthalene, **1o**, (357 mg, 1.00 mmol, 1 eq.). The crude residue was purified by flash column chromatography (EtOAc:Pentane, 50:50 to 60:40, R_f = 0.25) to give the title compound as a viscous oil (357 mg, 87%).

m.p. = 127 °C (dec.).
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 8.26 (d, *J* = 7.8 Hz, 1H, H_{16}), 7.76 – 7.68 (m, 2H, H_{13}, H_3), 7.48 – 7.40 (m, 2H, H_{15}, H_{14}), 7.40 – 7.26 (m, 2H, C_{11}), 7.20 (s, 1H, H_5), 7.15 (t, *J* = 7.9 Hz, 1H, H_{10}), 6.66 (br s, 1H, H_{25}), 6.54 (s, 1H, H_{23}), 6.38 (d, *J* = 7.7 Hz, 1H, H_9), 3.16 (br s, 2H, NH_2), 2.24 (s, 3H, H_7), 2.19 (s, 3H, H_{19}), 2.02 – 1.94 (m, 6H, H_{27}, H_{26}).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 168.4 (C_{18}), 154.0 (C_8), 147.6 (C_1), 139.3 (C_{21}), 135.0 (C_{Ar}), 134.4 (C_{12}), 133.2 (C_{Ar}), 130.4 (C_{23}), 128.9 (C_{25}), 127.2 (C_{13}), 126.6 (C_{Ar}), 126.2 ($C_{15/14}$), 125.3

(C_{10}), 125.1 (C_{Ar}), 124.9 ($C_{15/14}$), 122.5 (C_3), 122.4 (C_{Ar}), 121.9 (C_{16}), 121.1 (C_5), 121.0 (C_{11}), 107.3 (C_9), 24.5 (C_{19}), 20.1 ($C_{27/26}$), 17.7 ($C_{27/26}$), 16.8 (C_7). Two quaternary carbons were not observed.

FTIR (film) ν_{max}/cm^{-1} = 3299, 3054, 2922, 2856, 2275, 1665, 1599, 1552, 1461, 1392, 1261, 1229, 1204, 1160, 1109, 1080, 1044, 1016, 909, 862, 791, 770, 732, 646.

HRMS (ESI$^+$): m/z calculated for $C_{27}H_{27}N_2O_2^+$ $[M+H]^+$ = 411.2067; m/z found = 411.2068. Δ = 0.29 ppm

***N* -(2'-Amino-6-(3-fluorophenoxy)-3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl)acetamide, 3p:**

3p was prepared according to **General Procedure D** using 1-bromo-2- (3-fluoro phenoxy)-3-methyl-5-nitrobenzene, **1p**, (326 mg, 1.00 mmol, 1 eq.). The crude residue was purified by flash column chromatography (EtOAc:Pentane, 50:50 to 60:40, R_f = 0.25) to give the title compound as a viscous oil (257 mg, 68%).

m.p. = 152-153 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.63 (d, *J* = 2.7 Hz, 1H, H_3), 7.27 (br s, 1H, NH), 7.14 (d, *J* = 2.7 Hz, 1H, H_5), 7.02 (td, *J* = 8.3, 6.7 Hz, 1H, H_{10}), 6.77 – 6.72 (m, 1H, H_{19}), 6.59 (d, *J* = 2.1 Hz, 1H, H_{21}), 6.54 (td, *J* = 8.3, 2.5 Hz, 1H, H_{11}), 6.42 – 6.35 (m, 1H, H_9), 6.31 (dt, *J* = 10.7, 2.4 Hz, 1H, H_{13}), 2.20 (s, 3H, H_7), 2.17 (s, 3H, H_{15}), 2.10 (s, 3H, H_{22}), 2.07 (s, 3H, H_{23}). NH_2 was not observed.

^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 168.3 (C_{14}), 163.3 (d, *J* = 245.2 Hz, C_{12}), 159.4 (d, *J* = 10.5 Hz, C_8), 146.9 (C_1), 139.4 (C_{17}), 135.2 (C_{Ar}), 134.0 (C_6), 133.0 (C_{Ar}), 130.6 (C_{19}), 129.8 (d, *J* = 9.9 Hz, H_{10}), 128.8 (C_{21}), 126.7 (C_{Ar}), 122.9 (C_{Ar}), 122.4 (C_3), 122.4 (C_{16}), 121.0 (C_5), 111.0 (d, *J* = 3.0 Hz, H_9), 108.2 (d, *J* = 21.4 Hz, H_{11}), 103.1 (d, *J* = 25.4 Hz, H_{12}), 24.6 (C_{15}), 20.2 (C_{23}), 17.8 (C_{22}), 16.9 (C_7).

^{19}F NMR (377 MHz, $CDCl_3$) δ_F = -112.1.

FTIR (film) ν_{max}/cm^{-1} = 3295, 2922, 2856, 2275, 1665, 1609, 1552, 1484, 1446, 1370, 1302, 1262, 1202, 1165, 1119, 1035, 960, 909, 862, 767, 732, 679.

HRMS (ESI$^+$): m/z calculated for $C_{23}H_{24}FN_2O^+$ $[M+H]^+$ = 379.1816; m/z found = 379.1817. Δ = 0.10 ppm.

***N*-(2'-Amino-3',5,5'-trimethyl-6-(3-(trifluoromethyl)phenoxy)-[1,1'-biphenyl]-3-yl) acetamide, 3q:**

3q was prepared according to **General Procedure D** using 1-bromo-3- methyl-5-nitro-2-(3-(trifluoromethyl)phenoxy)benzene, **1q**, (387 mg, 1.00 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (EtOAc:Pentane, 40:60 to 60:40, R_f = 0.3) to give the title compound as a viscous oil (338 mg, 88%).

m.p. = 115-116 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 7.63 (d, *J* = 2.9 Hz, 1H, H_3), 7.56 – 7.51 (m, 1H, NH), 7.19 – 7.13 (m, 2H, H_{10}, H_5), 7.06 (d, *J* = 7.4 Hz, 1H, H_{11}), 6.80 – 6.78 (m, 1H, H_{13}), 6.78 – 6.75 (m, 1H, H_9), 6.69 (d, *J* = 2.1 Hz, 1H, H_{20}), 6.53 (d, *J* = 2.1 Hz, 1H, H_{22}), 3.41 (s, 2H, NH_2), 2.21 (s, 3H, H_7), 2.13 (s, 3H, H_{16}), 2.05 (s, 3H, H_{23}), 2.04 (s, 3H, H_{24}).
^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 168.5 (C_{15}), 158.1 (C_8), 146.9 (C_1), 139.3 (C_{18}), 135.4 (C_{Ar}), 133.6 (C_6), 132.8 (C_{Ar}), 131.3 (q, *J* = 32.5 Hz, C_{12}), 130.6 (C_{20}), 129.5 (C_{10}), 128.8 (C_{22}), 126.8 (C_{Ar}), 123.8 (q, *J* = 272.3 Hz, C_{14}), 122.7 (C_{Ar}), 122.5 (C_3), 122.4 (C_{Ar}), 121.1 (C_5), 118.8 (C_9), 118.1 (q, *J* = 3.9 Hz, C_{11}), 112.3 (q, *J* = 3.9 Hz, C_{13}), 24.5 (C_{16}), 20.1 (C_{24}), 17.6 (C_{23}), 16.8 (C_7).
^{19}F NMR (377 MHz, $CDCl_3$) δ_F = -62.7.
FTIR (film) ν_{max}/cm^{-1} = 2924, 1666, 1602, 1554, 1472, 1448, 1326, 1283, 1216, 1192, 1167, 1125, 1093, 1063, 1034, 909, 864, 790, 732, 697, 656.
HRMS (ESI$^+$): m/z calculated for $C_{24}H_{24}F_3N_2O^+$ $[M+H]^+$ = 429.1784; m/z found = 429.1783. Δ = -0.29 ppm

***N*-(2'-Amino-6-(3-(tert-butyl)phenoxy)-3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl)acetamide, 3r:**

3r was prepared according to **General Procedure D** using **1r** (729 mg, 2.0 mmol, 1 eq.). The crude residue was purified by flash column chromatography (EtOAc:pentane, 40:60, R*f*= 0.10) to give the title compound as a brown solid (449 mg, 54%).
m.p. = 64-66 °C (Et_2O)

^{1}H (500 MHz, $CDCl_3$) δ_H = 7.61 (d, *J* = 2.7 Hz, 1H, H_4), 7.39 (s, 1H, H_8), 7.10 (d, *J* = 2.7 Hz, 1H, H_6), 6.99 (t, *J* = 7.9 Hz, 1H, H_{12}), 6.84 (ddd, *J* = 7.8, 1.8, 0.9 Hz, 1H, H_{14}), 6.69 (d, *J* = 2.0 Hz, 1H, H_{22}), 6.59 (t, *J* = 2.2 Hz, 1H, H_{15}), 6.55 (d, *J* = 2.1 Hz, 1H, H_{24}), 6.38 (ddd, *J* = 8.1, 2.5, 0.9 Hz, 1H, H_{16}), 3.14 (s, 2H, H_{25}), 2.23 (s, 3H, H_7), 2.14 (s, 3H, H_{10}), 2.07 (s, 3H, H_{26}), 2.04 (s, 3H, H_{27}), 1.16 (s, 9H, H_{18}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 168.5 (C_9), 158.2 (C_{11}), 152.6 (C_{13}), 148.1 (C_2), 139.5 (C_{20}), 134.9 (C_5), 134.0 (C_{19}), 133.2 (C_3), 130.6 (C_{22}), 129.1 (C_{24}), 128.5 (C_{12}), 126.7 (C_{23}), 123.7 (C_1), 122.4 (C_{21}), 122.4 (C_4), 121.1 (C_6), 118.6 (C_{14}), 113.2 (C_{15}), 112.5 (C_{16}), 34.7 (C_{17}), 31.3 (C_{18}), 24.6 (C_{10}), 20.3 (C_{27}), 17.9 (C_{26}), 17.1 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 3648, 2981, 2885, 2360, 2341, 1668, 1604, 1552, 1473, 1382, 1252, 1214, 1152, 1073, 954, 863.
HRMS (ESI$^+$): m/z calculated for $C_{27}H_{33}O_2N_2$ $[M+H]^+$ =417.2537; m/z found = 417.2549. Δ = 3.06 ppm

Methyl (E)-3-(4-((5-acetamido-2'-amino-3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)phenyl)acrylate, 3s:

Methyl (E)-3-(4-hydroxyphenyl)acrylate, **1r** (484 mg, 2.00 mmol, 1.00 eq.) was dissolved in EtOH (7.00 mL). Fe (335 mg, 6.00 mmol, 3.00 eq.), NH_4Cl (53 mg, 1.00 mmol, 0.50 eq.) and H_2O (1.8 mL) were sequentially added to the solution. The reaction mixture was heated to 85 °C for 1 h. The reaction mixture was cooled to r.t. and filtered through Celite® (10 mL), eluted (EtOH:CH_2Cl_2, 1:1, 3 × 5 mL) and concentrated *in vacuo*. The crude residue was dissolved in EtOAc (20 mL) and the mixture was washed with H_2O (2 x 5 mL) and sat. aq. NaCl (1 x 5 mL), dried ($MgSO_4$) and concentrated *in vacuo*.
Using this crude residue, **3s** was prepared according to **General Procedure D**. The crude residue was purified by flash column chromatography (EtOAc:pentane, 40:60, R*f*= 0.10) to give the title compound as a brown solid (448 mg, 50%).

m.p. = 167-169 °C (Et_2O)
^{1}H (500 MHz, $CDCl_3$) δ_H = 7.65 (s, 1H, H_4), 7.55 (d, *J* = 16.0 Hz, 1H, H_{15}), 7.28 (m, 2H, H_{12}), 7.15 (s, 1H, H_6), 6.73 (d, *J* = 1.9 Hz, 1H, H_{23}), 6.61 (d, *J* = 8.5 Hz, 2H, H_{13}), 6.57 (d, *J* = 2.1 Hz, 1H, H_{25}), 6.23 (d, *J* = 16.0 Hz, 1H, H_{16}), 3.77 (s, 3H, H_{19}), 2.2 (s, 3H, H_7), 2.19 (s, 3H, H_{10}), 2.09 (s, 3H, H_{27}), 2.05 (s, 3H, H_{28}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 168.4 (C_9), 167.8 (C_{17}), 160.1 (C_{11}), 147.0 (C_2), 144.5 (C_{15}), 139.5 (C_{21}), 135.3 (C_5), 134.1 (C_{20}), 133.1 (C_3), 130.8 (C_{23}), 129.5 (C_{13}), 128.9 (C_{25}), 127.9 (C_{14}), 126.9 (C_{24}), 122.9 (C_1), 122.6 (C_{22}), 122.6 (C_4), 121.2 (C_6), 115.8 (C_{13}), 115.6 (C_{12}), 51.7 (C_{19}), 24.8 (C_{10}), 20.4 (C_{28}), 17.9 (C_{27}), 17.1 (C_7).

IR (film) ν_{max}/cm^{-1} **=** 3310, 2947, 1713, 1632, 1602, 1551, 1505, 1470, 1434, 1369, 1325, 1276, 1229, 1197, 1166, 1107, 1035, 982, 864, 831, 735, 702, 610.
HRMS (ESI$^+$): m/z calculated for $C_{27}H_{29}O_4N_2$ $[M+H]^+$ = 445.2122; m/z found = 445.2118. Δ = -0.95 ppm.

Methyl 3-(4-((5-acetamido-2'-amino-3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)phenyl)propanoate, 3t:

3t was prepared according to **General Procedure D** using **1t** (788 mg, 2.0 mmol, 1 eq.). The crude residue was purified by flash column chromatography (EtOAc:pentane, 40:60, R*f*= 0.10) to give the title compound as a brown solid (490 mg, 55%).

m.p. = 51-54 °C (Et_2O)
^{1}H (500 MHz, $CDCl_3$) δ_H = 7.67 – 7.55 (m, 2H, H_4, H_8), 7.11 (d, *J* = 2.3 Hz, 1H, H_6), 6.89 (d, *J* = 8.4 Hz, 2H, H_{13}), 6.72 (d, *J* = 2.1 Hz, 1H, H_{22}), 6.56 (d, *J* = 2.1 Hz, 1H, H_{24}), 6.52 – 6.46 (m, 2H, H_{12}), 3.63 (s, 3H, H_{18}), 3.44 – 3.23 (m, 2H, H_{25}), 2.79 (t, *J* = 7.8 Hz, 2H, H_{15}), 2.51 (t, *J* = 7.9 Hz, 2H, H_{16}), 2.16 (s, 3H, H_7), 2.12 (s, 3H, H_{10}), 2.08 (s, 3H, H_{26}), 2.05 (s, 3H, H_{27}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 173.5 (C_{17}), 168.6 (C_9), 156.8 (C_{11}), 147.5 (C_2), 139.5 (C_{20}), 135.1 (C_5), 134.1 (C_{19}), 133.3 (C_{14}), 133.1 (C_3), 130.5 (C_{22}), 129.0 (C_{24}), 128.9 (C_{13}), 126.7 (C_{23}), 123.5 (C_{21}), 122.6 (C_4), 122.4 (C_1), 121.2 (C_6), 115.4 (C_{12}), 51.7 (C_{18}), 36.0 (C_{16}), 30.1 (C_{15}), 24.5 (C_{10}), 20.3 (C_{27}), 17.9 (C_{26}), 17.1 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 3658, 3376, 2981, 2020, 1712, 1610, 1549, 1506, 1469, 1369, 1288, 1255, 1222, 1168, 1103, 1072, 955, 873, 847, 768, 699, 640, 619, 610.
HRMS (ESI$^+$): m/z calculated for $C_{27}H_{31}O_4N_2$ $[M+H]^+$ = 447.2278; m/z found = 447.2272. Δ = -1.41 ppm.

N-(4-((5-Acetamido-2'-amino-3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)-3-methoxybenzyl)-8-methylnonanamide, 3u:

3u was prepared according to **General Procedure D** using **1u** (526 mg, 0.98 mmol, 1 eq.). The crude residue was purified by flash column chromatography (EtOAc:pentane, 50:50, R*f*= 0.2) to give the title compound as a brown solid (236 mg, 41%).

m.p. = 78-82 °C.

^{1}H (500 MHz, $CDCl_3$) δ_H = 8.05 (s, 1H, H_{25}), 7.54 (d, *J* = 2.7 Hz, 1H, H_{23}), 7.13 (d, *J* = 2.7 Hz, 1H, H_{21}), 6.66 (d, *J* = 2.1 Hz, 1H, H_{32}), 6.57 (d, *J* = 2.0 Hz, 1H, H_3), 6.56 – 6.51 (m, 1H, H_{34}), 6.46 (dd, *J* = 8.2, 2.0 Hz, 1H, H_5), 6.27 (d, *J* = 8.2 Hz, 1H, H_6), 5.84 (t, *J* = 5.5 Hz, 1H, H_9), 4.19 (d, *J* = 4.9 Hz, 2H, H_8), 3.63 (s, 3H, H_7), 3.38 (s, 2H, H_{35}), 2.16 (s, 3H, H_{28}), 2.12 (t, *J* = 7.6 Hz, 2H, H_{11}), 2.06 (s, 3H, H_{27}), 2.02 (s, 3H, H_{36}), 2.01 (s, 3H, H_{37}), 1.59 (p, *J* = 7.6 Hz, 2H, H_{12}), 1.48 (hept, *J* = 6.7 Hz, 1H, H_{17}), 1.32 – 1.18 (m, 6H, H_{13}, H_{14}, H_{15}), 1.12 (q, *J* = 6.9 Hz, 2H, H_{16}), 0.83 (d, *J* = 6.9 Hz, 6H, H_{18}).

^{13}C (126 MHz, $CDCl_3$) δ_C = 173.1 (C_{10}), 168.8 (C_{26}), 148.9 (C_2), 147.8 (C_{19}), 147.3 (C_1), 139.6 (C_{30}), 135.3 (C_{22}), 133.5 ($C_{20/29}$), 132.8 (C_{24}), 131.9 (C_4), 130.3 (C_{32}), 129.0 (C_{34}), 126.5 (C_{33}), 123.4 ($C_{20/29}$), 122.4 (C_{23}), 122.4 (C_{31}), 121.2 (C_{21}), 119.7 (C_5), 114.7 (C_6), 112.0 (C_3), 56.0 (C_7), 43.3 (C_8), 39.0 (C_{16}), 36.8 (C_{13}), 29.7 (C_{15}), 29.4 (C_{16}), 28.0 (C_{17}), 27.3 (C_{15}), 25.9 (C_{14}), 24.3 (C_{27}), 22.7 (C_{18}), 20.3 (C_{37}), 17.8 (C_{36}), 16.8 (C_{28}).

IR (film) ν_{max}/cm^{-1} **=** 3291, 2925, 2855, 2360, 2341, 1645, 1600, 1551, 1509, 1467, 1421, 1368, 1265, 1215, 1160, 1128, 1035, 909, 863, 813, 731, 647.

HRMS (ESI$^+$): m/z calculated for $C_{35}H_{48}O_4N_3$ $[M+H]^+$ = 574.3639; m/z found = 574.3635. Δ = -0.71 ppm

Propyl 4-((5-acetamido-2'-amino-3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)-2',4'-difluoro-[1,1'-biphenyl]-3-carboxylate, 3v:

3v was prepared according to **General Procedure D** using **1v** (506 mg, 1.00 mmol, 1 eq.). The crude residue was purified by flash column chromatography (EtOAc:pentane, 50:50, R*f*= 0.1) to give the title compound as a yellow solid (253 mg, 45%).

m.p. = 80-82 °C.

^{1}H (500 MHz, $CDCl_3$) δ = 8.27 (s, 1H, H_{26}), 7.85 – 7.82 (m, 1H, H_3), 7.59 (d, *J* = 3.0 Hz, 1H, H_{21}), 7.29 (d, *J* = 8.5 Hz, 2H, H_5, H_{16}), 7.20 (s, 1H, H_{23}), 6.94 – 6.89 (m, 1H, H_{15}), 6.87 (ddd, *J* = 11.0, 8.5, 2.5 Hz, 1H, H_{13}), 6.72 (s, 1H, H_{32}), 6.61 (s, 1H, H_{34}), 6.50 (d, *J* = 8.5 Hz, 1H, H_6), 4.27 (t, *J* = 6.5 Hz, 2H, H_8), 3.79 (s, 2H, NH_2), 2.21 (s, 3H, H_{25}), 2.12 (s, 3H, H_{28}), 2.11 – 1.99 (m, 2 x 3H, H_{36}, H_{37}), 1.79 (m, 2H, H_9), 1.04 (t, *J* = 7.5 Hz, 3H, H_{10}).

^{13}C (126 MHz, $CDCl_3$) δ = 168.9 (d, *J* = 2.5 Hz, C_{27}), 165.5 (C_7), 162.2 (dd, *J* = 249.0, 11.5 Hz, C_{14}), 159.7 (dd, *J* = 250.0, 12.0 Hz, C_{12}), 157.3 (C_1), 146.4 (C_{19}), 139.2 (C_{30}), 135.8 (C_{22}), 133.6 (C_{Ar}), 133.4 (C_5), 132.5 (C_{20}), 132.0 (d, *J* = 2.5 Hz, C_3), 131.1 (dd, *J* = 9.5, 4.5 Hz, C_{16}), 130.8 (C_{25}), 129.2 (C_{34}), 127.7 (C_4), 127.3 (C_{Ar}), 123.9 (dd, *J* = 13.5, 4.0 Hz, C_{11}), 123.3 (C_{Ar}), 122.6 (C_{21}), 121.5 (C_{23}), 119.6 (C_2), 115.2 (C_6), 111.7 (dd, *J* = 21.0, 3.5 Hz, C_{15}), 104.4 (t, *J* = 26.0 Hz, C_{13}), 66.6 (C_8), 24.3 (C_{28}), 22.2 (C_9), 20.3 ($C_{36/37}$), 17.8 ($C_{36/37}$), 16.8 (C_{25}), 10.7 (C_{10}).

^{19}F NMR (470 MHz, DMSO) δ_F = -111.4 (d, *J* = 7.2 Hz), -113.6 (d, *J* = 7.2 Hz).

IR (film) ν_{max}/cm^{-1} **=** 3651, 2982, 2971, 2883, 2359, 2343, 1685, 1617, 1558, 1473, 1382, 1251, 1151, 1079, 957, 815, 668, 653, 645, 638, 632, 628, 619.

HRMS (ESI$^+$): m/z calculated for $C_{33}H_{33}O_4N_2F_2$ $[M+H]^+$ = 559.2403; m/z found = 559.2399. Δ = -0.65 ppm.

3.6 Oxonium Ion Formation

2,4,6,8-Tetramethyl-5-(4-nitrophenyl)-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4a:

4a was prepared according to **General Procedure E** using 3,3',5,5'- tetramethyl-2'-(2-nitrophenoxy)-[1,1'-biphenyl]-2-amine, **3a**, (1.40 g, 3.87 mmol, 1.00 eq.) to give the title compound as a tan solid (1.10 g, 65%).

m.p. = 204 ˚C (MeCN, dec.).
^{1}H NMR (500 MHz, CD_3CN) δ_H = 8.49 – 8.42 (m, 2H, H_{10}), 8.04 – 7.98 (m, 2H, H_{11}), 7.93 – 7.89 (m, 2H, H_5), 7.34 – 7.30 (m, 2H, H_3), 2.51 (s, 6H, H_8), 2.13 (s, 6H, H_7).
^{13}C NMR (126 MHz, CD_3CN) δ_C = 162.3 (C_9), 161.4 (C_1), 150.4 (C_{12}), 143.4 (C_{Ar}), 135.5 (C_3), 128.5 (C_{10}), 124.7 (C_{Ar}), 124.2 (C_{Ar}), 123.8 (C_{11}), 122.7 (C_5), 21.1 (C_8), 16.7 (C_7).
^{19}F NMR (471 MHz, CD_3CN) δ_F = -151.8.
FTIR (film) ν_{max}/cm^{-1} = 3071, 1581, 1538, 1479, 1356, 1309, 1048, 1036, 1001, 859, 781, 738, 675.
HRMS (ESI$^+$): m/z calculated for $C_{22}H_{20}NO_3^+$ $[M]^+$ = 346.1438; m/z found = 346.1437. Δ = -0.32 ppm.

5-(4-Acetamidophenyl)-2,4,6,8-tetramethyl-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4b:

4b was prepared according to **General Procedure E** using *N* -(4- ((2'-amino-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-yl)oxy)phenyl)acetamide, **3b** (187 mg, 0.50 mmol, 1.00 eq.) to give the title compound as a tan solid (202 mg, 92%).

m.p. = 172 ˚C (MeCN, dec.).
^{1}H NMR (500 MHz, CD_3CN) δ_H = 8.81 (s, 1H, NH), 7.87 – 7.86 (m, 2H, H_5), 7.85 – 7.81 (m, 2H, H_{11}), 7.67 – 7.61 (m, 2H, H_{10}), 7.31 – 7.26 (m, 2H, H_3), 2.49 (s, 6H, H_8), 2.11 (s, 6H, H_7), 2.10 (s, 3H, H_{14}).
^{13}C NMR (126 MHz, CD_3CN) δ_C = 170.3 (C_{13}), 160.6 (C_1), 155.1 (C_9), 143.3 (C_{12}), 142.7 (C_{Ar}), 135.3 (C_3), 124.7 (C_{Ar}), 124.1 (C_{Ar}), 122.5 (C_{10}), 122.2 (C_5), 121.5 (C_{11}), 24.4 (C_{14}), 21.0 (C_8), 16.8 (C_7).

^{19}F NMR (377 MHz, CD_3CN) δ_F = -151.8.
FTIR (film) ν_{max}/cm^{-1} = 3370, 1706, 1588, 1536, 1494, 1461, 1405, 1304, 1257, 1170, 1063, 1008, 853, 622.
HRMS (ESI$^+$): m/z calculated for $C_{24}H_{24}NO_2^+$ $[M]^+$ = 358.1802; m/z found = 358.1802. Δ = -0.01 ppm.

2-Acetamido-5-(4-(ethoxycarbonyl)phenyl)-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, 4c:

4c was prepared according to **General Procedure E** using ethyl 4-((5-acetamido-2'-amino-3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)benzoate, **3c** (216 mg, 0.50 mmol, 1.00 eq.) to give the title compound as a red solid (166 mg, 66%).

m.p. = 186-188 °C
^{1}H (500 MHz, $CDCl_3$) δ_H = 8.82 (s, 1H, H_8), 8.43 (d, *J* = 2.4 Hz, 1H, H_6), 8.27 – 8.21 (m, 2H, H_{13}), 7.92 (d, *J* = 1.9 Hz, 1H, H_{23}), 7.90 – 7.83 (m, 2H, H_{12}), 7.47 – 7.43 (m, 1H, H_4), 7.30 (d, *J* = 2.0 Hz, 1H, H_{21}), 4.38 (q, *J* = 7.1 Hz, 2H, H_{16}), 2.49 (s, 3H, H_{25}), 2.13 (s, 3H, H_{10}), 2.11 (s, 6H, H_7, H_{24}), 1.36 (t, *J* = 7.1 Hz, 3H, H_{17}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 170.4 (C_9), 165.0 (C_{15}), 162.8 (C_{11}), 161.4 (C_{19}), 157.9 (C_2), 143.2 (C_5), 142.6 (C_{22}), 135.7 (C_{14}), 135.3 (C_{21}), 133.9 (C_{13}), 126.0 (C_{Ar}), 125.1 (C_{Ar}), 124.8 (C_4), 124.3 (C_{Ar}), 124.3 (C_{Ar}), 122.7 (C_{23}), 122.4 (C_{12}), 111.6 (C_6), 63.0 (C_{16}), 24.5 (C_{10}), 21.1 (C_{25}), 17.1 ($C_{7/24}$), 16.8 ($C_{7/24}$), 14.4 (C_{17}).
^{19}F (377 MHz, CD_3CN) δ_F = -151.7.
IR (film) ν_{max}/cm^{-1} **=** 3649, 2999, 2981, 2885, 2230, 2197, 2159, 2086, 2023, 2004, 1460, 1394, 1381, 252, 1150, 1071.
HRMS (ESI$^+$): m/z calculated for $C_{26}H_{26}O_4N$ $[M+H]^+$ = 416.1856; m/z found = 416.1853. Δ = -0.72 ppm

5-(4-Acetylphenyl)-2,4,6,8-tetramethyl-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4d:

4d was prepared according to **General Procedure F** using 1-(4- ((3,3',5,5'-tetramethyl-2'-(pyrrolidin-1-yldiazenyl)-[1,1'-biphenyl]-2-yl)oxy)phenyl)ethan- 1-one, **3d**, (220 mg, 0.50 mmol, 1.00 eq.) to give the title compound as a tan solid (152 mg, 71%).

m.p. = 185 ˚C (MeCN, dec.).
^{1}H NMR (500 MHz, CD_3CN) δ_H = 8.22 – 8.15 (m, 2H, H_{11}), 7.92 – 7.89 (m, 2H, H_5), 7.87 – 7.83 (m, 2H, H_{10}), 7.32 – 7.28 (m, 2H, H_3), 2.62 (s, 3H, H_{14}), 2.50 (s, 6H, H_8), 2.11 (s, 6H, H_7).
^{13}C NMR (126 MHz, CD_3CN) δ_C = 197.1 (C_{13}), 162.4 (C_9), 161.0 (C_1), 143.1 (C_{Ar}), 140.9 (C_{12}), 135.4 (C_3), 132.8 (C_{11}), 124.7 (C_{Ar}), 124.3 (C_{Ar}), 122.5 (C_{10}), 122.3 (C_5), 27.3 (C_{14}), 21.1 (C_8), 16.8 (C_7).
^{19}F NMR (377 MHz, CD_3CN) δ_F = -151.8.
FTIR (film) ν_{max}/cm^{-1} = 3066, 1696, 1585, 1460, 1409, 1359, 1259, 1054, 1000, 957, 856, 706, 620.
HRMS (ESI$^+$): m/z calculated for $C_{24}H_{23}O_2^+$ $[M]^+$ = 343.1693; m/z found = 343.1693. Δ = -0.07 ppm.

5-(4-Formylphenyl)-2,4,6,8-tetramethyl-5*H* dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4e:

4e was prepared according to **General Procedure F** using 4- ((3,3',5,5'-tetramethyl-2'-(pyrrolidin-1-yldiazenyl)-[1,1'-biphenyl]-2-yl)oxy) benzaldehyde, **3e**, (214 mg, 0.50 mmol, 1.00 eq.) to give the title compound as a white solid (166 mg, 80%).

m.p. = 182 ˚C (MeCN, dec.).
^{1}H NMR (500 MHz, CD_3CN) δ_H = 10.09 (s, 1H, H_{13}), 8.20 – 8.13 (m, 2H, H_{11}), 7.97 – 7.92 (m, 2H, H_{10}), 7.91 – 7.89 (m, 2H, H_5), 7.33 – 7.29 (m, 2H, H_3), 2.50 (s, 6H, H_8), 2.11 (s, 6H, H_7).
^{13}C NMR (126 MHz, CD_3CN) δ_C = 191.6 (C_{13}), 162.9 (C_9), 161.1 (C_1), 143.1 (C_{Ar}), 139.8 (C_{12}), 135.4 (C_3), 133.7 (C_{11}), 124.7 (C_{Ar}), 124.3 (C_{Ar}), 123.0 (C_{10}), 122.5 (C_5), 21.1 (C_8), 16.8 (C_7).
^{19}F NMR (471 MHz, CD_3CN) δ_F = -151.8.
FTIR (film) ν_{max}/cm^{-1} = 2926, 2854, 2359, 1707, 1607, 1586, 1488, 1460, 1386, 1198, 1061, 1033,

1001, 854, 818, 734, 697, 648, 621.
HRMS (ESI$^+$): m/z calculated for $C_{23}H_{21}O_2^+$ $[M]^+$ = 329.1536; m/z found = 329.1533. Δ = -0.87 ppm.

5-(4-Chlorophenyl)-2,4,6,8-tetramethyl-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4f:

4f was prepared according to **General Procedure E** using 2'- (4-chlorophenoxy)-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-amine, **3f**, (174 mg, 0.50 mmol, 1.00 eq.) to give the title compound as a white solid (184 mg, 87%).

m.p. = 205 ˚C (MeCN, dec.).
^{1}H NMR (500 MHz, CD_3CN) δ_H = 7.91 – 7.86 (m, 2H, H_5), 7.79 – 7.72 (m, 2H, $H_{10/11}$), 7.72 – 7.64 (m, 2H, $H_{10/11}$), 7.32 – 7.27 (m, 2H, H_3), 2.50 (s, 6H, H_8), 2.13 (s, 6H, H_7).
^{13}C NMR (126 MHz, CD_3CN) δ_C = 161.0 (C_1), 158.6 (C_9), 143.0 (C_{Ar}), 138.7 (C_{12}), 135.4 (C_3), 132.8 ($C_{10/11}$), 124.7 (C_{Ar}), 124.1 (C_{Ar}), 123.6 ($C_{10/11}$), 122.4 (C_5), 21.0 (C_8), 16.8 (C_7).
^{19}F NMR (377 MHz, CD_3CN) δ_F = -151.8.
FTIR (film) ν_{max}/cm^{-1} = 3104, 1606, 1477, 1460, 1406, 1384, 1046, 999, 879, 846, 732, 705, 620.
HRMS (ESI$^+$): m/z calculated for $C_{22}H_{20}$ $^{35}ClO^+$ $[M]^+$ = 335.1197; m/z found = 335.1200. Δ = 0.81 ppm.

2,4,6,8-Tetramethyl-5-(4-(methylsulfonyl)phenyl)-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4g:

4g was prepared according to **General Procedure E** using 3,3',5,5'- tetramethyl-2'-(4-(methylsulfonyl)phenoxy)-[1,1'-biphenyl]-2-amine, **3g**, (197 mg, 0.50 mmol, 1.00 eq.) to give the title compound as a white solid (180 mg, 77%).

m.p. = 227 ˚C (MeCN, dec.).
^{1}H NMR (500 MHz, CD_3CN) δ_H = 8.22 – 8.16 (m, 2H, H_{11}), 8.02 – 7.96 (m, 2H, H_{10}), 7.93 – 7.89 (m, 2H, H_5), 7.34 – 7.29 (m, 2H, H_3), 3.14 (s, 3H, H_{13}), 2.50 (s, 6H, H_8), 2.14 (s, 6H, H_7).

^{13}C NMR (126 MHz, CD_3CN) δ_C = 162.2 (C_9), 161.2 (C_1), 145.2 (C_{12}), 143.1 (C_{Ar}), 135.2 (C_3), 132.4 (C_{11}), 124.6 (C_{Ar}), 124.1 (C_{Ar}), 123.2 (C_{10}), 122.4 (C_5), 44.1 (C_{13}), 20.9 (C_8), 16.6 (C_7).
^{19}F NMR (377 MHz, CD_3CN) δ_F = -151.7.
FTIR (film) ν_{max}/cm^{-1} = 2925, 2360, 1559, 1458, 1386, 1319, 1297, 1154, 1061, 1003, 961, 869, 779, 619.
HRMS (ESI$^+$): m/z calculated for $C_{23}H_{23}O_3S^+$ $[M]^+$ = 379.1362; m/z found = 379.1360. Δ = -0.51 ppm.

5-(4-(Hydroxymethyl)phenyl)-2,4,6,8-tetramethyl-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4h:

4h was prepared according to **General Procedure E** using (4-((2'- amino-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-yl)oxy)phenyl)methanol, **4h**, (173 mg,0.50 mmol, 1.00 eq.) to give the title compound as a tan solid (153 mg, 73%).

m.p. = 279 ˚C (MeCN, dec.).
^{1}H NMR (700 MHz, CD_3CN) δ_H =7.89 – 7.87 (m, 2H, H_5), 7.71 – 7.66 (m, 2H, H_{10}), 7.63 – 7.58 (m, 2H, H_{11}), 7.30 – 7.28 (m, 2H, H_3), 4.68 (s, 2H, H_{13}), 3.54 (s, 1H, OH), 2.50 (s, 6H, H_8), 2.10 (s, 6H, H_7).
^{13}C NMR (176 MHz, CD_3CN) δ_C = 159.8 (C_1), 158.5 (C_9), 147.3 (C_{12}), 141.8 (C_{Ar}), 134.4 (C_3), 129.1 (C_{11}), 123.8 (C_{Ar}), 123.3 (C_{Ar}), 121.4 (C_5), 120.6 (C_{10}), 62.2 (C_{13}), 20.1 (C_8), 15.9 (C_7).
^{19}F NMR (471 MHz, CD_3CN) δ_F = -151.8.
FTIR (film) ν_{max}/cm^{-1} = 3067, 2359, 1602, 1490, 1458, 1387, 1282, 1060, 1001, 861, 843, 765, 734, 621.
HRMS (ESI$^+$): m/z calculated for $C_{23}H_{23}O_2^+$ $[M]^+$ = 331.1693; m/z found = 331.1690. Δ = -0.83 ppm.

5-([1,1'-biphenyl]-4-yl)-2-acetamido-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, 4i:

4i was prepared according to **General Procedure E** using n-(6-([1,1'-biphenyl]-4-yloxy)-2'-amino-3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl)acetamide**, 3i** (218 mg, 0.5 mmol, 1.00 eq.) to give the title compound as a red solid (187 mg, 74 %).

m.p. = 191-194 °C (CH_3CN)

^{1}H (500 MHz, $CDCl_3$) δ_H = 8.79 (s, 1H, H_8), 8.45 (d, *J* = 2.3 Hz, 1H, H_6), 7.96 – 7.93 (m, 1H, H_{24}), 7.92 – 7.86 (m, 2H, $H_{12/13}$), 7.84 – 7.77 (m, 2H, $H_{12/13}$), 7.71 – 7.66 (m, 2H, H_{16}), 7.55 – 7.50 (m, 2H, H_{17}), 7.49 – 7.46 (m, 1H, H_{18}), 7.46 – 7.44 (m, 1H, H_4), 7.34 – 7.30 (m, 1H, H_{22}), 2.50 (s, 3H, H_{26}), 2.17 (s, 3H, H_7), 2.17 (s, 3H, H_{25}), 2.14 (s, 3H, H_{10}).

^{13}C (126 MHz, $CDCl_3$) δ_C = 170.4 (C_9), 161.2 (C_{20}), 160.3 (C_{11}), 157.8 (C_2), 146.0 (C_{15}), 143.0 (C_{23}), 142.4 (C_5), 138.9 (C_{14}), 135.6 (C_{22}), 131.0 ($C_{12/13}$), 130.2 (C_{17}), 129.9 (C_{18}), 128.4 (C_{16}), 126.0 (C_{Ar}), 125.1 (C_{Ar}), 124.8 (C_{Ar}), 124.4 (C_{Ar}), 124.3 (C_4), 122.6 (C_{24}), 122.1 ($C_{12/13}$), 111.6 (C_6), 24.4 (C_{10}), 21.1 (C_{26}), 17.2 ($C_{7/25}$), 16.9 ($C_{7/25}$).

^{19}F (377 MHz, CD_3CN) δ_F = 151.5 (s).

IR (film) ν_{max}/cm^{-1} **=** 3788, 3662, 2981, 2886, 2356, 1583, 1550, 1462, 1382, 1252, 1152, 1073, 955, 749.

HRMS (ESI$^+$):m/z calculated for $C_{29}H_{29}O_2N$ $[M]^+$ = 420.1958; m/z found = 420.1945. Δ = -2.99 ppm.

2-acetamido-4,6,8-trimethyl-5-phenyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, 4j:

4j was prepared according to **General Procedure E** using n-(2'-amino-3',5,5'-trimethyl-6-phenoxy-[1,1'-biphenyl]-3-yl)acetamide, **3j** (375 mg, 1.0 mmol, 1 eq.) to give the title compound as an orange solid (354 mg, 82%).

m.p. = 189-192 °C (CH_3CN)

^{1}H (500 MHz, $CDCl_3$) δ_H = 8.76 (s, 1H, H_8), 8.43 (d, *J* = 2.4 Hz, 1H, H_6), 7.95 – 7.90 (m, 1H, H_{20}), 7.78 – 7.65 (m, 5H, H_{12-14}), 7.43 (dd, *J* = 2.4, 1.0 Hz, 1H, H_4), 7.30 (dd, *J* = 2.0, 1.0 Hz, 1H, H_{18}), 2.49 (s, 3H, H_{22}), 2.13 (s, 3H, H_{10}), 2.09 (s, 3H, H_7), 2.09 (s, 3H, H_{21}).

^{13}C (126 MHz, $CDCl_3$) δ_C = 170.3 (C_9), 161.1 (C_{11}), 161.0 (C_{16}), 157.7 (C_2), 142.9 (C_5), 142.4 (C_{19}), 135.6 (C_{18}), 133.5 (C_{14}), 132.9 (C_{12}), 125.9 (C_{Ar}), 125.1 (C_{Ar}), 124.8 (C_{Ar}), 124.4 (C_{Ar}), 124.3 (C_4), 122.6 (C_{20}), 121.8 (C_{13}), 111.5 (C_6), 24.4 (C_{10}), 21.0 (C_{22}), 17.1 ($C_{7/21}$), 16.8 ($C_{7/21}$).

^{19}F (377 MHz, CD_3CN) δ_F = -151.7 (s).

IR (film) ν_{max}/cm^{-1} **=** 3661, 3356, 2981, 2888, 1691, 1553, 1462, 1383, 1259, 1150, 1072, 955, 859, 805, 736, 694, 635, 610.

HRMS (ESI$^+$):m/z calculated for $C_{23}H_{22}O_2N$ $[M]^+$ = 344.1645; m/z found = 344.1644. Δ = -0.22 ppm.

2,4,6,8-tetramethyl-5-(2-nitrophenyl)-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, 4k:

4k was prepared according to **General Procedure E** using 3,3',5,5'- tetramethyl-2'-(2-nitrophenoxy)-[1,1'-biphenyl]-2-amine, **3k**, (1.81 g, 5.00 mmol, 1.00 eq.) to give the title compound as a tan solid (1.85 g, 85%).

m.p. = 191 ˚C (MeCN, dec.).
^{1}H NMR (500 MHz, CD_3CN) δ_H = 8.57 – 8.54 (m, 1H, $H_{10/13}$), 8.12 – 8.05 (m, 2H, H_{11}, H_{12}), 7.97 – 7.94 (m, 3H, H_5, $H_{10/13}$), 7.34 – 7.30 (m, 2H, H_3), 2.51 (s, 6H, H_8), 1.96 (s, 6H, H_7).
^{13}C NMR (126 MHz, CD_3CN) δ_C = 159.8 (C_1), 148.1 (C_9), 141.8 (C_{Ar}), 140.4 (C_{14}), 138.7 ($C_{11/12}$), 135.2 (C_3), 134.9 ($C_{11/12}$), 128.9 ($C_{10/13}$), 125.0 ($C_{10/13}$), 122.7 (C_{Ar}), 122.4 (C_{Ar}), 121.9 (C_5), 20.0 (C_8), 15.2 (C_7).
^{19}F NMR (377 MHz, CD_3CN) δ_F = -151.8.
FTIR (film) ν_{max}/cm^{-1} = 3100, 1584, 1541, 1452, 1390, 1358, 1057, 1031, 873, 842, 808, 734, 692, 620.
HRMS (ESI$^+$): m/z calculated for $C_{22}H_{20}NO_3^+$ $[M]^+$ = 346.1438; m/z found = 346.1438. Δ = -0.10 ppm.

5-(2-Cyanophenyl)-2,4,6,8-tetramethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, 4l:

4l was prepared according to **General Procedure E** using 2-((2'- amino-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-yl)oxy)benzonitrile, **3l**, (171 mg, 0.50 mmol, 1.00 eq.) to give the title compound as a white solid (142 mg, 69%).

m.p. = 58-59 ˚C.
^{1}H NMR (500 MHz, CD_3CN) δ_H = 8.14 – 8.10 (m, 1H, H_{Ar}), 8.04 – 8.01 (m, 2H, H_{Ar}), 7.98 – 7.92 (m, 3H, H_5, H_{Ar}), 7.37 – 7.33 (m, 2H, H_3), 2.52 (s, 6H, H_8), 2.10 (s, 6H, H_7).
^{13}C NMR (126 MHz, CD_3CN) δ_C = 161.6 (C_1), 157.6 (C_9), 143.4 (C_{Ar}), 138.4 (C_{Ar}), 137.8 (C_{Ar}), 135.8 (C_3), 134.5 (C_{Ar}), 124.7 (C_{Ar}), 124.3 (C_{Ar}), 124.3 (C_{Ar}), 122.6 (C_5), 112.5 ($C_{14/15}$), 107.1 ($C_{14/15}$), 21.0 (C_8), 16.5 (C_7).
^{19}F NMR (471 MHz, CD_3CN) δ_F = -146.4.

FTIR (film) ν_{max}/cm^{-1} = 2981, 1612, 1549, 1483, 1444, 1383, 1059, 1037, 868, 802, 733, 699, 619.
HRMS (ESI$^+$): m/z calculated for $C_{23}H_{22}NO^+$ $[M]^+$ = 326.1539; m/z found = 326.1539. Δ = 0.06 ppm.

2-Acetamido-4,6,8-trimethyl-5-(o-tolyl)-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4m:

4m was prepared according to **General Procedure E** using *N* -(2'- amino-3',5,5'-trimethyl-6-(*o*-tolyloxy)-[1,1'-biphenyl]-3-yl)acetamide, **3m**, (187 mg, 0.50 mmol, 1.00 eq.) to give the title compound as a tan solid (169 mg, 72%).

m.p. = 168 ˚C (MeCN, dec.).
^{1}H NMR (500 MHz, CD_3CN) δ_H = 8.77 (br, s, 1H, NH), 8.46 (d, *J* = 2.4 Hz,1H, H_5), 7.97 – 7.93 (m, 1H, H_{22}), 7.68 (ddd, *J* = 8.2, 6.6, 1.8 Hz, 1H, H_{11}), 7.63 –7.58 (m, 1H, H_{12}), 7.52 – 7.44 (m, 3H, H_{10}, H_9, H_3), 7.34 – 7.29 (m, 1H, H_{20}), 2.50 (s, 3H, H_{24}), 2.43 (s, 3H, H_{14}), 2.14 (s, 3H, H_{16}), 2.01 – 1.98 (m, 6H, H_{23}, H_7).
^{13}C NMR (126 MHz, CD_3CN) δ_C = 170.3 (C_{15}), 159.7 (C_{18}), 158.8 (C_8), 156.3 (C_1), 142.5 (C_{Ar}), 142.0 (C_{Ar}), 135.9 (C_{20}), 134.9 (C_{12}), 133.5 (C_{11}), 132.0 (C_{Ar}), 131.0 (C_{10}), 125.2 (C_{Ar}), 124.7 ($C_{3/Ar}$), 124.6 ($C_{3/Ar}$), 124.0 (C_{Ar}), 124.0 (C_{Ar}), 122.5 (C_{22}), 122.0 (C_9), 111.5 (C_5), 24.4 (C_{16}), 20.9 (C_{24}), 16.5 (C_7), 16.2 (C_{23}), 16.1 (C_{14}).
^{19}F NMR (377 MHz, CD_3CN) δ_F = -151.7.
FTIR (film) ν_{max}/cm^{-1} = 3360, 1697, 1639, 1559, 1488, 1460, 1385, 1284, 1258, 1060, 1015, 869, 806, 764, 696, 660, 619.
HRMS (ESI$^+$): m/z calculated for $C_{24}H_{24}NO_2^+$ $[M]^+$ = 358.1802; m/z found = 358.1800. Δ = -0.54 ppm.

5-(2-Methoxyphenyl)-2,4,6,8-tetramethyl-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4n:

4n was prepared according to **General Procedure E** using 2'-(2- methoxyphenoxy)-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-amine, **3n**, (176 mg, 0.50 mmol, 1.00 eq.) to give the title compound

as a tan solid (198 mg, 95%).

m.p. = 191 ˚C (MeCN, dec.).
^{1}H NMR (500 MHz, CD_3CN) δ_H = 7.88 – 7.84 (m, 2H, H_5), 7.72 (ddd, *J* = 8.8, 7.5, 1.5 Hz, 1H, H_{12}), 7.67 (dd, *J* = 8.5, 1.5 Hz, 1H, H_{10}), 7.39 (dd, *J* = 8.5, 1.5 Hz, 1H, H_{13}), 7.31 – 7.25 (m, 2H, H_3), 7.19 (ddd, *J* = 8.8, 7.5, 1.5 Hz, 1H, H_{11}), 3.83 (s, 3H, H_{15}), 2.49 (s, 6H, H_8), 2.06 (s, 6H, H_7).
^{13}C NMR (126 MHz, CD_3CN) δ_C = 160.1 (C_1), 151.3 (C_{14}), 147.4 (C_9), 142.2 (C_{Ar}), 135.2 (C_3), 134.9 (C_{12}), 123.9 (C_{Ar}), 123.9 (C_{Ar}), 123.5 (C_{10}), 123.1 (C_{11}), 122.1 (C_5), 116.5 (C_{10}), 57.7 (C_{15}), 21.0 (C_8), 15.8 (C_7).
^{19}F NMR (471 MHz, CD_3CN) δ_F = –151.8.
FTIR (film) ν_{max}/cm^{-1} = 1620, 1496, 1454, 1387, 1290, 1261, 1034, 1006, 861, 794, 782, 757, 703, 673, 621.
HRMS (ESI$^+$): m/z calculated for $C_{23}H_{23}O_2^+$ [M]$^+$ = 331.1693; m/z found = 331.1691. Δ = -0.49 ppm.

1-Acetamido-4,6,8-trimethyl-5-(naphthalen-1-yl))-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4o:

4o was prepared according to **General Procedure E** using *N*-(2'- amino-3',5,5'-trimethyl-6-(naphthalen-1-yloxy)-[1,1'-biphenyl]-3-yl)acetamide, **3o**, (205 mg, 0.50 mmol, 1.00 eq.) and 1:1 CH_2Cl_2:MeCN elution (5 × 1.5 mL) to give the title compound as a tan solid (154 mg, 64%).

m.p. = 188 ˚C (MeCN, dec.).
^{1}H NMR (500 MHz, CD_3CN) δ_H = 8.77 (s, 1H, NH), 8.53 (d, *J* = 2.4 Hz, 1H, H_5), 8.36 – 8.28 (m, 2H, H_{16}, H_{11}), 8.25 (dd, *J* = 8.2, 1.4 Hz, 1H, H_{13}), 8.03 – 7.99 (m, 1H, H_{25}), 7.89 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H, H_{15}), 7.85 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H, H_{14}), 7.69 (dd, *J* = 8.1, 1.1 Hz, 1H, H_9), 7.63 (dd, *J* = 8.0, 8.0 Hz, 1H, H_{10}), 7.38 (dd, *J* = 2.4, 1.0 Hz, 1H, H_3), 7.29 – 7.25 (m, 1H, H_{23}), 2.51 (s, 3H, H_{27}), 2.16 – 2.11 (m, 3H, H_{19}), 1.73 – 1.68 (m, 6H, H_{26}, H_7).
^{13}C NMR (126 MHz, CD_3CN) δ_C = 170.1 (C_{18}), 161.4 (C_{21}), 157.9 (C_1), 156.0 (C_8), 142.4 (C_{Ar}), 141.8 (C_{Ar}), 135.7 (C_{12}), 135.6 (C_{23}), 133.8 (C_{11}), 131.0 (C_{15}), 130.0 (C_{13}), 129.7 (C_{14}), 126.7 (C_{10}), 125.4 (C_{Ar}), 125.2 (C_{Ar}), 124.6 (C_{17}), 124.3 (C_3), 124.0 (C_{Ar}), 123.9 (C_{Ar}), 122.5 (C_{25}), 120.2 (C_{16}), 119.5 (C_9), 111.4 (C_5), 24.2 (C_{19}), 20.7 (C_{27}), 16.8 (C_7), 16.5 (C_{26}).
^{19}F NMR (377 MHz, CD_3CN) δ_C = -151.8.
FTIR (film) ν_{max}/cm^{-1} = 3339, 1696, 1638, 1559, 1488, 1448, 1383, 1284, 1258, 1056, 956, 868, 815, 765, 727, 626.
HRMS (ESI$^+$): m/z calculated for $C_{27}H_{24}NO_2^+$ [M]$^+$ = 394.1802; m/z found = 394.1804. Δ = 0.67 ppm.

2-Acetamido-5-(3-fluorophenyl)-4,6,8-trimethyl–5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4p:

4p was prepared according to **General Procedure E** using *N*-(2'-amino-6-(3-fluorophenoxy)-3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl)acetamide, **3p**, (189 mg, 0.50 mmol, 1 eq.) to give the title compound as a tan solid (153 mg, 68%).

m.p. = 182 ˚C (MeCN, dec.).
^{1}H NMR (700 MHz, CD_3CN) δ_H = 8.77 (s, 1H, NH), 8.45 – 8.42 (m, 1H, H_5), 7.94 – 7.92 (m, 1H, H_{21}), 7.77 – 7.71 (m, 2H, H_{10}, H_9), 7.61 – 7.56 (m, 1H, H_{13}), 7.55 – 7.50 (m, 1H, H_{11}), 7.46 – 7.43 (m, 1H, H_3), 7.33 – 7.30 (m, 1H, H_{19}), 2.50 (s, 3H, H_{23}), 2.17 – 2.12 (m, 9H, H_{22}, H_{15}, H_7).
^{13}C NMR (176 MHz, CD_3CN) δ_C = 169.4 (C_{14}), 162.7 (d, *J* = 254.3 Hz, C_{12}), 160.5 (C_{17}), 158.8 (d, *J* = 10.9 Hz, C_8), 157.1 (C_1), 142.2 (C_{Ar}), 141.5 (C_{Ar}), 134.7 (C_{Ar}), 133.0 (d, *J* = 9.5 Hz, C_{10}), 125.0 (C_{Ar}), 124.1 (C_{21}), 123.9 (C_{Ar}), 123.3 (C_3), 123.3 (C_{Ar}), 121.7 (C_{21}), 120.1 (d, *J* = 21.0 Hz, C_{11}), 117.6 (d, *J* = 4.4 Hz, C_9) 110.7 (C_5), 109.6 (d, *J* = 28.0 Hz, C_{13}), 23.5 (C_{Me}), 20.1 (C_{23}), 16.1 (C_{Me}), 15.8 (C_{Me}).
^{19}F NMR (471 MHz, CD_3CN) δ_F = -106.0, -151.7 (BF_4^-).
FTIR (film) ν_{max}/cm^{-1} = 3102, 2359, 1698, 1642, 1621, 1559, 1529, 1488, 1448, 1386, 1349, 1327, 1285, 1260, 1229, 1175, 1128, 1093, 1064, 1052, 997, 910, 871, 799, 765, 742, 699, 673, 621.
HRMS (ESI$^+$): m/z calculated for $C_{23}H_{21}FNO_2^+$ $[M]^+$ = 362.1551; m/z found = 362.1551. Δ = 0.02 ppm.

2-Acetamido-4,6,8-trimethyl-5-(3-(trifluoromethyl)phenyl)-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4q:

4q was prepared according to **General Procedure E** using *N*-(2'-amino-3',5,5'-trimethyl-6-(3-(trifluoromethyl)phenoxy)-[1,1'-biphenyl]-3-yl)acetamide, **3q**, (214 mg, 0.50 mmol, 1.00 eq.) to give the title compound as a tan solid (155 mg, 62%).

m.p. = 197 ˚C (MeCN, dec.).
^{1}H NMR (500 MHz, CD_3CN) δ_H = 8.79 (br, s, 1H, NH), 8.45 (d, *J* = 2.4 Hz, 1H, H_5), 8.13 (dd, *J* = 8.6, 2.9 Hz, 1H, H_9), 8.11 – 8.08 (m, 1H, C_{13}), 8.08 – 8.05 (m, 1H, H_{11}), 7.94 – 7.93 (m, 1H, H_{22}), 7.93 – 7.88 (m, 1H, H_{10}), 7.45 (dd, *J* = 2.4, 1.0 Hz, 1H, H_3), 7.33 – 7.29 (m, 1H, H_{20}), 2.50 (s, 3H, H_{24}), 2.14 (s, 3H, H_{16}), 2.11 – 2.07 (m, 2 x 3H, H_{23}, H_7).
^{13}C NMR (126 MHz, CD_3CN) δ_C = 170.1 (C_{15}), 161.4 (C_{18}), 159.6 (C_8), 158.0 (C_1), 143.1 (C_{Ar}), 142.4 (C_{Ar}), 135.4 (C_{10}), 134.1 (C_{20}), 134.1 (q, *J* = 34.6 Hz, C_{12}), 130.4 (q, *J* = 3.7 Hz, C_{11}), 126.2 (C_9), 125.6 (C_{Ar}), 124.9 (C_{Ar}), 124.4 (C_{Ar}), 124.1 (C_{Ar}), 124.1 (C_3), 123.2 (q, *J* = 272.5 Hz, C_{14}), 122.6 (C_{22}), 119.2 (q, *J* = 3.8 Hz, C_{13}), 111.5 (C_5), 24.2 (C_{16}), 20.8 (C_{24}), 16.8 (C_{23}), 16.5 (C_{23}).
^{19}F NMR (377 MHz, CD_3CN) δ_F = -63.3, -151.6 (BF_4^-).
FTIR (film) ν_{max}/cm^{-1} = 3361, 3080, 1696, 1642, 1559, 1489, 1443, 1387, 1322,1282, 1260, 1179, 1137, 1053, 931, 874, 816, 729, 697, 655, 639.
HRMS (ESI$^+$): m/z calculated for $C_{24}H_{21}F_3NO_2^+$ $[M]^+$ = 412.1519; m/z found = 412.1520. Δ = 0.29 ppm.

2-Acetamido-5-(3-(*tert*-butyl)phenyl)-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, 4r:

4r was prepared according to **General Procedure E** using n-(2'-amino-6-(3-(tert-butyl)phenoxy)-3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl)acetamide, **3r** (313 mg, 0.75 mmol, 1.00 eq.) to give the title compound as a red solid (202 mg, 55%).

m.p. = 138-141 °C (CH_3CN).
^{1}H (500 MHz, $CDCl_3$) δ_H = 8.78 (s, 1H, H_8), 8.42 (d, *J* = 2.4 Hz, 1H, H_6), 7.98 (dd, *J* = 2.90, 1.7 Hz, 1H, H_{12}), 7.91 (d, *J* = 2.0 Hz, 1H, H_{22}), 7.76 (ddd, *J* = 7.8, 1.6, 0.8 Hz, 1H, H_{14}), 7.56 (dd, *J* = 8.6, 7.9 Hz, 1H, H_{15}), 7.43 (dd, *J* = 2.4, 1.0 Hz, 1H, H_4), 7.35 (ddd, *J* = 8.7, 2.9, 0.8 Hz, 1H, H_{16}), 7.29 (d, *J* = 1.9 Hz, 1H, H_{24}), 2.49 (s, 3H, H_{26}), 2.13 (s, 3H, H_{10}), 2.07 (s, 6H, H_7, H_{25}), 1.33 (s, 9H, H_{18}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 170.4 (C_9), 161.3 (C_{20}), 160.6 (C_{11}), 157.4 (C_2), 157.2 (C_{13}), 142.8 (C_{23}), 142.2 (C_5), 135.6 (C_{24}), 132.6 (C_{15}), 130.1 (C_{14}), 125.8 (C_{Ar}), 125.1 (C_{Ar}), 124.7 (C_{Ar}), 124.4 (C_{Ar}), 124.3 (C_4), 122.5 (C_{22}), 119.6 (C_{12}), 118.2 (C_{16}), 111.5 (C_6), 36.4 (C_{17}), 31.0 (C_{18}), 24.5 (C_{10}), 21.0 (C_{26}), 17.1 ($C_{7/25}$), 16.8 ($C_{7/25}$).
^{19}F NMR (377 MHz, CD_3CN) δ_F = -151.7.

IR (film) ν_{max}/cm^{-1} **=** 3662, 3360, 2980, 2884, 2361, 2342, 1703, 1563, 1462, 1383, 1260, 1073, 954, 873, 807, 764.
HRMS (ESI$^+$): m/z calculated for $C_{27}H_{30}O_2N$ $[M]^+$ =400.2271; m/z found = 400.2264. Δ = -1.66 ppm.

(*E*)-2-Acetamido-5-(4-(3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, 4s:

4s was prepared according to **General Procedure E** using methyl (E)-3-(4-((5-acetamido-2'-amino-3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)phenyl)acrylate, **3s** (333 mg, 0.75 mmol, 1.00 eq.) to give the title compound as a red solid (283 mg, 73 %).

m.p. = 180-183 °C (CH_3CN).
^{1}H (500 MHz, $CDCl_3$) δ_H = 8.76 (s, 1H, H_8), 8.44 (d, *J* = 2.4 Hz, 1H, H_6), 7.93 (d, *J* = 1.9 Hz, 1H, H_{24}), 7.90 – 7.83 (m, 2H, H_{13}), 7.81 – 7.74 (m, 2H, H_{12}), 7.71 (d, *J* = 16.1 Hz, 1H, H_{15}), 7.43 (dd, *J* = 2.5, 1.0 Hz, 1H, H_4), 7.30 (dt, *J* = 1.9, 0.8 Hz, 1H, H_{22}), 6.64 (d, *J* = 16.1 Hz, 1H, H_{16}), 3.77 (s, 3H, H_{18}), 2.49 (s, 3H, H_{26}), 2.14 (s, 3H, H_{10}), 2.13 (s, 3H, H_7), 2.12 (s, 3H, H_{25}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 170.4 (C_9), 167.2 (C_{17}), 161.3 (C_{20}), 161.0 (C_{11}), 157.8 (C_2), 143.1 (C_5), 142.5 (C_{23}), 141.9 (C_{15}), 139.6 (C_{14}), 135.6 (C_{22}), 132.2 (C_{13}), 125.9 (C_{Ar}), 125.1 (C_{Ar}), 124.8 (C_{Ar}), 124.4 (C_{Ar}), 124.2 (C_{Ar}), 123.3 (C_{16}), 122.7 (C_{24}), 122.4 (C_{12}), 111.6 (C_6), 52.6 (C_{18}), 24.4 (C_{10}), 21.0 (C_{26}), 17.1 ($C_{7/25}$), 16.8 ($C_{7/25}$).
^{19}F NMR (377 MHz, CD_3CN) δ_F = -151.7.
IR (film) ν_{max}/cm^{-1} **=** 3662, 2981, 2888, 2361, 2340, 1462, 1382, 1252, 1145, 1074, 954, 763, 668.
HRMS (ESI$^+$): m/z calculated for $C_{27}H_{26}O_4N$ $[M]^+$ = 428.1856; m/z found = 428.1852. Δ = -1.13 ppm.

2-Acetamido-5-(4-(3-methoxy-3-oxopropyl)phenyl)-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, 4t:

4t was prepared according to **General Procedure E** using methyl 3-(4-((5-acetamido-2'-amino-3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)phenyl)propanoate, **3t** (223 mg, 0.5 mmol, 1.00 eq.) to give the title compound as a red solid (193 mg, 74 %).

m.p. = 98-102 °C (CH_3CN).
^{1}H (500 MHz, $CDCl_3$) δ_H = 8.74 (s, 1H, H_8), 8.42 (d, *J* = 2.3 Hz, 1H, H_6), 7.94 – 7.90 (m, 1H, H_{24}), 7.67 – 7.62 (m, 2H, H_{12}), 7.52 – 7.48 (m, 2H, H_{13}), 7.42 (dd, *J* = 2.5, 0.9 Hz, 1H, H_4), 7.29 (dd, *J* = 2.0, 0.9 Hz, 1H, H_{22}), 3.59 (s, 3H, H_{18}), 3.01 (t, *J* = 7.6 Hz, 2H, H_{15}), 2.65 (t, *J* = 7.5 Hz, 2H, H_{16}), 2.49 (s, 3H, H_{26}), 2.13 (s, 3H, H_{10}), 2.09 (s, 3H, H_7), 2.08 (s, 3H, H_{25}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 173.5 (C_{17}), 170.3 (C_9), 161.0 (C_{20}), 159.4 (C_{11}), 157.6 (C_2), 147.3 (C_{14}), 142.9 (C_{23}), 142.3 (C_5), 135.6 (C_{22}), 132.6 (C_{13}), 125.9 (C_{Ar}), 125.0 (C_{Ar}), 124.7 (C_{Ar}), 124.3 (C_{Ar}), 124.2 (C_4), 122.5 (C_{24}), 121.6 (C_{12}), 111.5 (C_6), 52.1 (C_{18}), 35.6 (C_{16}), 30.9 (C_{15}), 24.4 (C_{10}), 21.0 (C_{10}), 17.1 ($C_{7/25}$), 16.8 ($C_{7/25}$).
^{19}F NMR (377 MHz, CD_3CN) δ_F = -151.7.
IR (film) ν_{max}/cm^{-1} **=** 3649, 2981, 2884, 2362, 1734, 1559, 1490, 1459, 1384, 1253, 1150, 1071, 955, 855, 624.
HRMS (ESI$^+$): m/z calculated for $C_{27}H_{28}O_4N$ $[M]^+$ = 430.2013; m/z found = 430.2013. Δ = 0.07 ppm.

2-acetamido-5-(2-methoxy-4-((8-methylnonanamido)methyl)phenyl)-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, 4u:

4u was prepared according to **General Procedure E** using n-(4-((5-acetamido-2'-amino-3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)-3-methoxybenzyl)-8-methylnonanamide, **3u**, (215 mg, 0.38 mmol, 1.00 eq.) to give the title compound as a red solid (211 mg, 86 %).

m.p. = 140-145 °C.

^{1}H (500 MHz, CD_3CN) δ = 8.76 (s, 1H, H_8), 8.39 (d, *J* = 2.2 Hz, 1H, H_6), 7.89 (d, *J* = 1.9 Hz, 1H, H_{16}), 7.58 (d, *J* = 8.7 Hz, 1H, H_{24}), 7.44 (d, *J* = 2.3 Hz, 1H, H_4), 7.37 (s, 1H, H_{21}), 7.28 (s, 1H, H_{14}), 7.10 – 7.01 (m, 1H, H_{23}), 4.45 (d, *J* = 6.0 Hz, 2H, H_{26}), 3.83 (s, 3H, H_{25}), 2.48 (s, 3H_{18}), 2.28 (t, *J* = 7.5 Hz, 1H, H_{29}), 2.13 (s, 3H, H_{10}), 2.06 (s, 3H, $H_{7/17}$), 2.06 (s, 2H, $H_{7/17}$), 1.59 (p, *J* = 7.2 Hz, 2H, H_{30}), 1.55 – 1.42 (m, 1H, H_{35}), 1.26 (m, 6H, H_{31}, H_{32}, H_{33}), 1.19 – 1.07 (m, 2H, H_{34}), 0.84 (d, *J* = 6.6 Hz, 6H, H_{36}).

^{13}C (126 MHz, CD_3CN) δ = 175.7 (C_{28}), 170.3 (C_9), 160.6 (C_{12}), 157.2 (C_2), 151.0 (C_{20}), 146.8 (C_{19}), 146.3 (C_{22}), 142.4 (C_{15}), 141.9 (C_5), 135.5 (C_{14}), 125.0 (C_{Ar}), 124.6 (C_{Ar}), 124.2 (C_{Ar}), 123.9 (C_{Ar}), 123.8 (C_4), 123.1 (C_{Ar}), 122.4 (C_{16}), 121.6 (C_{23}), 115.2 (C_{24}), 111.4 (C_6), 57.8 (C_{25}), 43.5 (C_{26}), 39.6 (C_{34}), 36.3 (C_{29}), 30.2 (C_{31}), 29.8 (C_{32}), 28.7 (C_{33}), 27.9 (C_{35}), 26.5 (C_{30}), 24.4 (C_{10}), 22.9 (C_{36}), 21.0 (C_{18}), 16.1 ($C_{7/17}$), 15.8 ($C_{7/17}$).

^{19}F NMR (377 MHz, CD_3CN) δ_F = -151.5.

IR (film) ν_{max}/cm^{-1} **=** 3368, 2928, 2360, 2342, 1644, 1619, 1559, 1492, 1464, 1424, 1385, 1266, 1066, 1040, 870, 729, 701, 669, 642, 619.

HRMS (ESI$^+$): m/z calculated for $C_{35}H_{45}O_4N_2$ $[M]^+$ = 557.3374; m/z found, = 557.3367. Δ = -1.28 ppm.

2-Acetamido-5-(2',4'-difluoro-3-(propoxycarbonyl)-[1,1'-biphenyl]-4-yl)-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, 4v:

4v was prepared according to **General Procedure E** using propyl 4-((5-acetamido-2'-amino-3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)-2',4'-difluoro-[1,1'-biphenyl]-3-carboxylate, **3v**, (152 mg, 0.27 mmol, 1.00 eq.) to give the title compound as a red solid (73 mg, 43 %).

m.p. = 204-206 °C.

^{1}H (500 MHz, CD_3CN) δ = 8.82 (d, *J* = 4.5 Hz, 1H, H_{26}), 8.48 – 8.43 (m, 2H, H_3, H_{23}), 8.01 (ddd, *J* = 9.0, 2.5, 1.0 Hz, 1H, H_5), 7.95 (q, *J* = 2.5 Hz, 1H, H_{31}), 7.74 (d, *J* = 9.0 Hz, 1H, H_6), 7.67 (td, *J* = 9.0, 6.5 Hz, 1H, H_{16}), 7.49 (d, *J* = 2.5 Hz, 1H, H_{21}), 7.32 (s, 1H, H_{33}), 7.21 – 7.11 (m, 2H, H_{13}, H_{16}), 4.27 (t, *J* = 6.5 Hz, 2H, H_8), 2.51 – 2.48 (m, 3H, H_{35}), 2.14 (s, 3H, H_{28}), 2.02 (2 x s, 2 x 3H, H_{25}, H_{36}), 1.66 – 1.56 (m, 2H, H_9), 0.82 (t, *J* = 7.5 Hz, 3H, H_{10}).

^{13}C (126 MHz, CD_3CN) δ = 170.4 (C_{27}), 164.5 (dd, *J* = 250.0, 12.0 Hz, $C_{12/14}$), 162.8 (C_7), 160.2 (C_1), 156.8 (C_{29}), 156.0 (C_{19}), 142.5 (C_{32}), 142.0 (C_{22}), 140.9 (C_4), 137.7 (d, *J* = 3.5 Hz, C_5), 136.1 (C_{33}), 134.6 (d, *J* = 4.0 Hz, C_3), 133.3 (dd, *J* = 10.0, 4.0 Hz, C_{16}), 125.9 (C_2), 124.8 (C_{Ar}), 124.7 (C_{Ar}), 124.4 (d, *J* = 2.0

Hz, C_{21}), 124.2 (C_{Ar}), 123.7 (C_{Ar}), 123.6 (C_6), 122.7 (C_{31}), 122.6 (dd, *J* = 13.0, 3.8 Hz, C_{11}), 113.4 (dd, *J* = 21.5, 3.5 Hz, C_{15}), 111.7 (C_{23}), 105.6 (t, *J* = 26.5 Hz, C_{13}), 69.6 (C_8), 24.4 (C_{28}), 22.3 (C_9), 20.9 (C_{35}), 16.8 ($C_{25/36}$), 16.5 ($C_{25/36}$), 10.4 (C_{10}).

^{19}F NMR (377 MHz, CD_3CN) δ_F = -109.16 – -109.51 (m), -114.32 (dd, *J* = 15.7, 7.2 Hz), -151.2.

IR (film) ν_{max}/cm^{-1} **=** 3648, 2982, 2971, 2883, 2360, 2343, 2261, 1726, 1701, 1653, 1617, 1559, 1511, 1473, 1386, 1319, 1259, 1226, 1146, 1068, 1037, 969, 857, 730, 697, 668, 638, 628, 613.

HRMS (ESI$^+$): m/z calculated for $C_{33}H_{30}O_4NF_2$ $[M]^+$ = 542.2137; m/z found = 542.2132, Δ = -1.01 ppm.

3.7 Trapping reactions with furan

Optimization of aryne generation & trapping conditions

Entry	Base	Yield (%)[a]
1	K_3PO_4	>95
2	K_2CO_3	>95
3	KOAc	83[b]
4	$NaHCO_3$	n.r.
5	DIPEA	25[c]
6	2,6-lutidine	n.r.

Table S1: Optimisation of the aryne generation conditions on a 0.03 mmol scale. [a] conversion determined by quantitative ^{1}H NMR using CH_2Br_2 (0.015 mmol) as an internal standard. [b] 6% remaining **4a**. [c] 25% remaining **4a**.

6-Nitro-1,4-dihydro-1,4-epoxynaphthalene, 5a:

5a was prepared according to **General Procedure G** using oxonium 2,4,6,8-Tetramethyl-5-(4-nitrophenyl)-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4a**, (433 mg, 1.00 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:Pentane, 15:85, R_f = 0.3) to give the title compound as a white solid (189 mg, 99%).

m.p. = 108-109 ˚C.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.04 (d, *J* = 2.0 Hz, 1H, H_7), 7.98 (dd, *J* = 7.8, 2.0 Hz, 1H, H_9), 7.36 (d, *J* = 7.8 Hz, 1H, H_{10}), 7.10 (dd, *J* = 5.5, 1.9 Hz, 1H, $H_{3/4}$), 7.05 (dd, *J* = 5.5, 1.9 Hz, 1H, $H_{3/4}$), 5.83 – 5.78 (m, 2H, H_2, H_5).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 156.6 (C_1), 151.4 (C_6), 145.9 (C_8), 143.6 ($C_{3/4}$), 142.5 ($C_{3/4}$), 122.5 (C_9), 120.2 (C_{10}), 115.4 (C_7), 82.2 ($C_{2/5}$), 82.2 ($C_{2/5}$).
FTIR (film) ν_{max}/cm^{-1} = 3097, 1604, 1517, 1447, 1344, 1280, 1140, 1060, 991, 872, 848, 794, 753, 735, 699, 672, 640.
HRMS (APCI$^-$): m/z calculated for $C_{10}H_6NO_3^+$ $[M-H]^-$ = 188.0353; m/z found = 188.0342. Δ = -6.20 ppm.

***N* -(1,4-Dihydro-1,4-epoxynaphthalen-6-yl)acetamide, 5b:**

5b was prepared according to **General Procedure G** using 5-(4-acetamidophenyl)-2,4,6,8-tetramethyl-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4b**, (134 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (EtOAc:Pentane, 50:50, R_f = 0.2) to give the title compound as a tan solid (55 mg, 91%).

m.p. = 128-129 ˚C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.57 (s, 2H, H_7, NH), 7.13 (d, *J* = 7.6 Hz, 1H, H_{10}), 7.01 – 6.96 (m, 2H, H_4, H_3), 6.96 – 6.91 (m, 1H, H_9), 5.67 (s, 1H, H_2), 5.65 (s, 1H, H_5), 2.11 (s, 3H, H_{12}).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 168.7 (C_{11}), 150.4 (C_6), 144.8 (C_1), 143.2 (C_3), 142.7 (C_4), 135.2 (C_8), 120.3 (C_{10}), 115.8 (C_9), 114.0 (C_7), 82.5 (C_5), 82.2 (C_2), 24.6 (C_{12}).
FTIR (film) ν_{max}/cm^{-1} = 3299, 2361, 1663, 1609, 1546, 1468, 1417, 1373, 1350, 1280, 1196, 1089, 1039, 988, 910, 867, 850, 837, 730, 698, 646.
HRMS (ESI$^+$): m/z calculated for $C_{12}H_{12}NO_2^+$ $[M+H]^+$ = 202.0863; m/z found = 202.0865. Δ = 1.32 ppm.
Ethyl 1,4-dihydro-1,4-epoxynaphthalene-6-carboxylate, 5c:

5c was prepared according to **General procedure G** using 2-acetamido-5-(4-(ethoxycarbonyl)phenyl)-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, **4c**, (151 mg, 0.30 mmol, 1 eq.). The crude residue was purified by flash column chromatography (Et_2O:*n*-pentane, 40:60, R_f = 0.5) to give the title compound as a yellow oil (61 mg, 94%).

^{1}H (500 MHz, $CDCl_3$) δ_H = 7.87 (dt, *J* = 7.2, 0.8 Hz, 1H, H_{10}), 7.76 (dd, *J* = 7.4, 1.4 Hz, 1H, H_8), 7.29 (dt, *J* = 7.4, 0.8 Hz, 1H, H_7), 7.04 (dd, *J* = 5.6, 1.9 Hz, 1H, H_3), 7.00 (dd, *J* = 5.6, 1.9 Hz, 1H, H_4), 5.75 (dt, *J* = 1.8, 0.8 Hz, 1H, H_5), 5.73 (dt, *J* = 1.8, 0.8 Hz, 1H, H_4), 4.34 (q, *J* = 7.1 Hz, 2H, H_{12}), 1.37 (t, *J* = 7.1 Hz, 3H, H_{13}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 166.5 (C_{10}), 154.4 (C_1), 149.6 (C_6), 143.4 (C_3), 142.5 (C_4), 128.1 (C_8), 127.7 (C_9), 120.7 (C_{10}), 120.0 (C_7), 82.2 ($C_{4/5}$), 82.2 ($C_{4/5}$), 61.0 (C_{12}), 14.4 (C_{13}).
IR (film) ν_{max}/cm^{-1} **=** 2981, 2928, 1710, 1617, 1595, 1464, 1420, 1390, 1367, 1349, 1287, 1254, 1193, 1168, 1141, 1102, 1072, 1020, 994, 912, 873, 846, 794, 768, 750, 742, 698, 664, 640.
HRMS (ESI$^+$): m/z calculated for $C_{13}H_{13}O_3$ $[M+H]^+$ = 217.0859; m/z found = 217.0860. Δ = 0.29 ppm.

1-(1,4-Dihydro-1,4-epoxynaphthalen-6-yl)ethan-1-one, 5d:

5d was prepared according to **General Procedure G** using 5-(4-acetylphenyl)- 2,4,6,8-tetramethyl-5H-dibenzo[*b*,*d*]furan-5-ium, **4d**, (129 mg, 0.5 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (EtOAc:pentane, 20:80, R_f = 0.2) to give the title compound as a white solid (53 mg, 96%).

m.p. = 108-109 ˚C.
^{1}H NMR (500 MHz, CD_3CN) δ_H = 7.84 – 7.80 (m, 1H, H_7), 7.65 (dd, *J* = 7.4, 1.5 Hz, 1H, H_9), 7.35 – 7.28 (m, 1H, H_{10}), 7.06 (dd, *J* = 5.5, 1.9 Hz, 1H, H_3), 7.01 (dd, *J* = 5.5, 1.9 Hz, 1H, H_4), 5.80 – 5.73 (m, 2H, H_2, H_5), 2.56 (s, 3H, H_{12}).
^{13}C NMR (126 MHz, CD_3CN) δ_C = 197.7 (C_{11}), 154.6 (C_1), 149.9 (C_6), 143.5 (C_3), 142.4 (C_4), 134.8 (C_8), 127.5 (C_9), 120.1 (C_{10}), 119.3 (C_7), 82.3 ($C_{2/5}$), 82.2 ($C_{2/5}$), 26.9 (C_{12}).
FTIR (film) ν_{max}/cm^{-1} = 3012, 1732, 1676, 1617, 1583, 1547, 1456, 1418, 1359, 1282, 1251, 1200, 1164, 1106, 993, 966, 872, 849, 749, 706, 650, 631.
HRMS (ESI$^+$): m/z calculated for $C_{12}H_{11}O_2^+$ $[M+H]^+$ = 187.0754; m/z found = 187.0757. Δ = 1.59 ppm.

1,4-Dihydro-1,4-epoxynaphthalene-6-carbaldehyde, 5e:

5e was prepared according to **General Procedure G** using 5-(4-formylphenyl)- 2,4,6,8-tetramethyl-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4e**, (125 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:pentane, 20:80, R_f = 0.2) to give the title compound as a colourless oil (48 mg, 93%).

^{1}H NMR (500 MHz, CD_3CN) δ_H = 9.94 (s, 1H, H_{11}), 7.73 (d, *J* = 1.3 Hz, 1H, H_7), 7.54 (dd, *J* = 7.2, 1.3 Hz, 1H, H_9), 7.39 (d, *J* = 7.2 Hz, 1H, H_{10}), 7.07 (dd, *J* = 5.5, 1.9 Hz, 1H, $H_{3/4}$), 7.02 (dd, *J* = 5.5, 1.9 Hz, 1H, $H_{3/4}$), 5.80 – 5.74 (m, 2H, H_2, H_5).
^{13}C NMR (126 MHz, CD_3CN) δ_C = 191.9 (C_{11}), 156.3 (C_1), 150.4 (C_6), 143.5 ($C_{3/4}$), 142.3 ($C_{3/4}$), 134.4 (C_8), 131.2 (C_9), 120.5 (C_{10}), 118.8 (C_7), 82.2 ($C_{2/5}$), 82.1 ($C_{2/5}$).
FTIR (film) ν_{max}/cm^{-1} = 3016, 2833, 2770, 2728, 1686, 1616, 1589, 1457, 1422, 1349, 1280, 1209, 1194, 1157, 1120, 1086, 1072, 992, 931, 872, 851, 839, 827, 770, 748, 699, 667, 642, 631.
HRMS (APCI$^-$): m/z calculated for $C_{11}H_7O_2^-$ $[M-H]^-$ = 171.0452; m/z found = 171.0441. Δ = -6.43 ppm.

6-Chloro-1,4-dihydro-1,4-epoxynaphthalene, 5f:

5f was prepared according to **General Procedure G** using 5-(4-chlorophenyl)- 2,4,6,8-tetramethyl-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4f**, (127 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:pentane, 0:100 to 10:90, R_f = 0.4) to give the title compound as a colourless oil (50 mg, 94%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.23 (d, *J* = 1.9 Hz, 1H, H_7), 7.15 (d, *J* = 7.6 Hz, 1H, H_{10}), 7.03 (dd, *J* = 5.5, 1.8 Hz, 1H, ($H_{4/3}$), 7.01 (dd, *J* = 5.6, 1.8 Hz, 1H, ($H_{4/3}$), 6.95 (dd, *J* = 7.5, 1.8 Hz, 1H, H_9), 5.73 – 5.67 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 151.5 (C_6), 147.7 (C_1), 143.3 ($C_{4/3}$), 142.7 ($C_{4/3}$), 130.8 (C_8), 124.7 (C_9), 121.4 (C_7), 121.1 (C_{10}), 82.3 ($C_{5/2}$), 82.2 ($C_{5/2}$).
FTIR (film) ν_{max}/cm^{-1} = 3014, 2360, 1590, 1441, 1407, 1328, 1280, 1193, 1165,
1140, 1100, 1059, 992, 951, 866, 849, 823, 807, 749, 697, 682, 641.
HRMS: Not found by ESI, APCI or EI.

6-(Methylsulfonyl)-1,4-dihydro-1,4-epoxynaphthalene, 5g:

5g was prepared according to **General Procedure G** using 2,4,6,8-tetramethyl-5- (4-(methylsulfonyl)phenyl)-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4g**, (140 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (EtOAc:Pentane, 40:60, R_f = 0.2) to give the title compound as a tan solid (63 mg, 94%).

m.p. = 136-138 ˚C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.75 (d, *J* = 1.6 Hz, 1H, H_7), 7.65 (dd, *J* = 7.5, 1.6 Hz, 1H, H_9), 7.40 (d, *J* = 7.5 Hz, 1H, H_{10}), 7.08 (dd, *J* = 5.5, 1.8 Hz, 1H, H_3), 7.04 (dd, *J* = 5.5, 1.8 Hz, 1H, H_4), 5.81 – 5.76 (m, 2H, H_2, H_5), 3.02 (s, 3H, H_{11}).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 155.8 (C_1), 151.3 (C_6), 143.4 (C_3), 142.6 (C_4), 137.7 (C_8), 126.3 (C_9), 120.6 (C_{10}), 118.6 (C_7), 82.2 ($C_{2/5}$), 82.2 ($C_{2/5}$), 44.8 (C_{11}).
FTIR (film) ν_{max}/cm^{-1} = 3019, 2926, 1409, 1301, 1278, 1155, 1128, 1104, 1057, 993, 961, 871, 850, 814, 764, 748, 700, 642, 607.
HRMS (ESI$^+$): m/z calculated for $C_{11}H_{10}NaO_3S^+$ $[M+Na]^+$ = 245.0243; m/z found = 245.0245. Δ = 0.80 ppm.

(1,4-Dihydro-1,4-epoxynaphthalen-6-yl)methanol, 5h:

5h was prepared according to **General Procedure G** using 5-(4-(hydroxymethyl) phenyl)-2,4,6,8-tetramethyl-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4h**, (126 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (EtOAc:Pentane, 40:60, R_f = 0.2) to give the title compound as a colourless oil (50 mg, 96%).

^{1}H NMR (400 MHz, CD_3CN) δ_H = 7.19 – 7.16 (m, 1H, H_7), 7.12 (d, *J* = 7.2 Hz, 1H, H_{10}), 6.97 – 6.89 (m, 2H, H_3, H_4), 6.86 (dd, *J* = 7.2, 1.4 Hz, 1H, H_9), 5.65 – 5.58 (m, 2H, H_2, H_5), 4.50 (s, 2H, H_{11}), 2.07 (s, 1H, OH).
^{13}C NMR (176 MHz, CD_3CN) δ_C = 149.8 (C_6), 148.6 (C_1), 143.1 ($C_{3/4}$), 143.0 ($C_{3/4}$), 138.1 (C_8), 123.9 (C_9), 120.2 (C_{10}), 119.6 (C_7), 82.4 ($C_{2/5}$), 82.3 ($C_{2/5}$), 65.4 (C_{11}).
FTIR (film) ν_{max}/cm^{-1} = 3384, 3011, 2872, 2361, 1422, 1280, 1210, 1164, 1122, 1086, 988, 869, 849, 750, 697, 639.
HRMS (ESI$^+$): m/z calculated for $C_{11}H_{11}O_2$ $[M+H]^+$ = 175.0754; m/z found = 175.0755. Δ = 0.74 ppm.

6-phenyl-1,4-dihydro-1,4-epoxynaphthalene, 5i:

5i was prepared according to **General procedure G** using 5-([1,1'-biphenyl]-4-yl)-2-acetamido-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, **4i,** (152 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:*n*-pentane, 10:90, R_f = 0.8) to give the title compound as a pale yellow oil (57 mg, 86%).

^{1}H (500 MHz, $CDCl_3$) δ_H = 7.59 – 7.53 (m, 2H, H_{12}), 7.51 (d, *J* = 1.5 Hz, 1H, H_{10}), 7.44 (dd, *J* = 8.4, 6.9 Hz, 2H, H_{13}), 7.37 – 7.34 (m, 1H, H_{14}), 7.33 (d, *J* = 7.5 Hz, 1H, H_7), 7.22 (dd, *J* = 7.3, 1.6 Hz, 1H, H_8), 7.11 – 7.05 (m, 2H, H_3, H_4), 5.79 (d, *J* = 4.0 Hz, 2H, H_2, H_5).
^{13}C (126 MHz, $CDCl_3$) δ_C = 150.0 (C_1), 148.1 (C_6), 143.1 ($C_{3/4}$), 143.1 ($C_{3/4}$), 141.4 (C_{11}), 138.7 (C_9), 128.8 (C_{13}), 127.3 (C_{12}), 127.3 (C_{14}), 124.1 (C_8), 120.5 (C_7), 119.7 (C_{10}), 82.5 ($C_{2/5}$), 82.3 ($C_{2/5}$).
IR (film) ν_{max}/cm^{-1} **=** 3791, 3661, 2981, 2887, 2358, 1659, 1588, 1549, 1462, 1382, 1252, 1153, 1073, 954, 750.
HRMS (ESI$^+$): m/z calculated for $C_{16}H_{13}O$ $[M+H]^+$ = 221.0961; m/z found = 221.0963. Δ = 0.93 ppm.

1,4-dihydro-1,4-epoxynaphthalene, 5j:

5j was prepared according to **General Procedure G** using 2-acetamido-4,6,8-trimethyl-5-phenyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, **4j**, (129 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:*n*-pentane, 10:90, R_f = 0.8) to give the title compound as a pale yellow solid (35 mg, 81%).

m.p. = 53-54 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 7.32 – 7.24 (m, 2H, H_5), 7.06 (t, *J* = 1.0 Hz, 2H, H_3), 7.00 (dd, *J* = 5.1, 3.0 Hz, 2H, H_4), 5.74 (t, *J* = 1.0 Hz, 2H, H_2).
^{13}C (126 MHz, $CDCl_3$) δ_C = 149.1 (C_1), 143.2 (C_3), 125.1 (C_4), 120.4 (C_5), 82.5 (C_2).
IR (film) ν_{max}/cm^{-1} **=** 3314, 3053, 2927, 2852, 1596, 1580, 1517, 1455, 1386, 1363, 1278, 1197, 1132, 1084, 1044, 1015, 991, 871, 846, 795, 773, 760, 741, 691, 636.
HRMS (ESI$^+$): m/z calculated for $C_{10}H_9O$ $[M+H]^+$ = 145.0648; m/z found = 145.0649. Δ = 0.47 ppm.

6-Nitro-1,4-dihydro-1,4-epoxynaphthalene, 5k:

5k was prepared according to **General Procedure G** using 2,4,6,8 tetramethyl- 5-(2-nitrophenyl)-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **5k**, (129 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:pentane, 20:80, R_f = 0.3) to give the title compound as a tan solid (52 mg, 91%).

m.p. = 99-100 ˚C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.72 (d, *J* = 8.4 Hz, 1H, H_9), 7.49 (d, *J* = 6.9 Hz, 1H, H_7), 7.19 – 7.10 (m, 3H, H_8, H_3, H_4), 6.51 – 6.47 (m, 1H, H_2), 5.85 – 5.81 (m, 1H, H_5).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 152.7 (C_6), 146.9 (C_1), 144.5 (C_4), 142.6 (C_{10}), 142.2 (C_3), 126.9 (C_8), 125.0 (C_7), 119.5 (C_9), 82.8 (C_2), 82.1 (C_5).
FTIR (film) ν_{max}/cm^{-1} = 2360, 1523, 1454, 1349, 1279, 1131, 1049, 1013, 877, 861, 842, 810, 789, 767, 743, 711, 650.
HRMS (ESI$^-$): m/z calculated for $C_{10}H_6NO_3^-$ $[M-H]^-$ = 188.0353; m/z found = 188.0344. Δ = -4.80 ppm.

1,4-dihydro-1,4-epoxynaphthalene-5-carbonitrile, 5l:

5l was prepared according to **General Procedure G** using 5-(2-cyanophenyl)-2,4,6,8-tetramethyl-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4l**, (124 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:*n*-pentane, 15:85, R_f = 0.2) to give the title compound as a pale yellow solid (49 mg, 97%).

m.p. = 58-59 ˚C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.42 (d, *J* = 7.1 Hz, 1H, H_7), 7.19 (dd, *J* = 7.9, 0.9 Hz, 1H, H_9), 7.12 – 7.05 (m, 3H, H_8, H_4, H_3), 5.95 (dd, *J* = 1.0, 1.0 Hz, 1H, H_2), 5.79 (dd, *J* = 1.1, 1.1 Hz, 1H, H_5).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 154.7 (C_1), 150.9 (C_6), 143.9 (C_4), 142.4 (C_3), 127.3 (C_9), 126.3 (C_8), 124.0 (C_7), 116.9 (C_{11}), 105.2 (C_{10}), 82.6 (C_5), 81.6 (C_2).
FTIR (film) ν_{max}/cm^{-1} = 2918, 2359, 2228, 1604, 1463, 1416, 1351, 1281, 1195, 1136, 1082, 1045, 1016, 961, 931, 873, 857, 821, 797, 779, 746, 721, 658.
HRMS (APCI$^-$): m/z calculated for $C_{11}H_6NO_2^+$ $[M-H]^-$ = 168.0455; m/z found = 168.0444. Δ = -6.41 ppm.

5-Methyl-1,4-dihydro-1,4-epoxynaphthalene, 5m:

5m was prepared according to **General Procedure G** using 2-acetamido-4,6,8-trimethyl-5-(o-tolyl)-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4m**, (133.5 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (CH_2Cl_2, R_f = 0.7) to give the title compound as a viscous oil (45 mg, 95%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.09 (d, *J* = 7.0 Hz, 1H, H_7), 7.06 – 7.01 (m, 2H, H_3, H_4)), 6.91 – 6.85 (m, 1H, H_8), 6.80 – 6.75 (m, 1H, H_9), 5.83 – 5.79 (m, 1H, H_2), 5.73 – 5.68 (m, 1H, H_5), 2.32 (s, 3H, H_{11}).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 148.7 (C_6), 147.4 (C_1), 143.2 ($C_{3/4}$), 142.8 ($C_{3/4}$), 130.1 (C_{10}), 126.8 (C_9), 125.1 (C_8), 117.9 (C_7), 82.7 (C_5), 81.0 (C_5), 18.2 (C_{11}).
FTIR (film) ν_{max}/cm^{-1} = 3010, 2921, 1615, 1471, 1379, 1280, 1231, 1176, 1135, 1083, 1030, 979, 926, 871, 855, 823, 791, 771, 746, 718, 658, 621.
HRMS (ESI$^+$): m/z calculated for $C_{11}H_{11}O^+$ $[M+H]^+$ = 159.0804; m/z found = 159.0806. Δ = 1.17 ppm.

5-Methoxy-1,4-dihydro-1,4-epoxynaphthalene, 5n:

5n was prepared according to **General Procedure G** using 5-(2-methoxyphenyl)- 2,4,6,8-tetramethyl-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4n**, (125 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:Pentane, 5:95 to 8:92, R_f = 0.2) to give the title compound as a pale yellow oil (51 mg, 98%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.08 (dd, *J* = 5.6, 1.8 Hz, 1H, H_3), 7.03 (dd, *J* = 5.5, 1.9 Hz, 1H, H_4), 6.99 – 6.92 (m, 2H, H_8, H_7), 6.60 (dd, *J* = 8.1, 0.9 Hz, 1H, H_9), 5.98 – 5.94 (m, 1H, H_2), 5.73 – 5.69 (m, 1H, H_5), 3.83 (s, 3H, H_{11}).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 153.1 (C_{10}), 151.7 (C_6), 143.2 (C_3), 143.0 (C_4), 135.2 (C_1), 127.1 (C_8), 113.8 (C_7), 110.4 (C_9), 82.7 (C_5), 80.2 (C_2), 55.8 (C_{11}).
FTIR (film) ν_{max}/cm^{-1} = 3014, 2837, 2361, 1616, 1597, 1478, 1440, 1263, 1176, 1133, 1091, 1065, 999, 922, 855, 822, 791, 771, 738, 721, 667, 625.
HRMS (APCI$^+$): m/z calculated for $C_{11}H_{11}O_2^+$ $[M+H]^+$ = 175.0754; m/z found = 175.0756. Δ = 1.61 ppm.

1,4-Dihydro-1,4-epoxyphenanthrene, 5o:

5o was prepared according to **General Procedure G** using 2- acetamido-4,6,8-trimethyl-5-(naphthalen-1-yl))-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4o**, (144 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:pentane, 10:90, R_f = 0.2) to give the title compound as a pale yellow solid (56.8 mg, 97%).

m.p. = 84-85 ˚C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.84 (d, *J* = 8.0 Hz, 1H, H_{10}), 7.81 (d, *J* = 8.0 Hz, 1H, H_{13}), 7.58 (d, *J* = 7.9 Hz, 1H, H_8), 7.54 (d, *J* = 7.9 Hz, 1H, H_7), 7.46 (ddd, *J* = 8.0, 6.7, 1.3 Hz, 1H, H_{12}), 7.38 (ddd, *J* = 8.0, 6.7, 1.3 Hz, 1H, H_{11}), 7.23 – 7.18 (m, 2H, H_3, H_4), 6.28 – 6.25 (m, 1H, H_2), 5.95 – 5.90 (m, 1H, H_5).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 148.4 (C_6), 148.0 (C_1), 145.0 (C_4), 143.5 (C_3), 131.9 (C_9), 128.9 (C_{10}), 127.8 (C_{14}), 126.3 (C_{12}), 125.5 (C_8), 125.3 (C_{11}), 122.8 (C_{13}), 119.4 (C_7), 83.5 (C_5), 81.4 (C_2).
FTIR (film) ν_{max}/cm^{-1} = 3051, 3008, 2921, 1519, 1365, 1278, 1185, 1149, 1041, 1004, 960, 923, 858, 824, 809, 778, 747, 718, 685, 665, 638.

HRMS (APCI$^+$): m/z calculated for $C_{14}H_{11}O^+$ $[M+H]^+$ = 195.0804; m/z found = 195.0808. Δ = 1.73 ppm.

5-Fluoro-1,4-dihydro-1,4-epoxynaphthalene, 5p:

5p was prepared according to **General Procedure G** using 2-acetamido-5-(3-fluorophenyl)-4,6,8-trimethyl–5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate **4p** (134 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:pentane, 10:90, R_f = 0.2) to give the title compound as a viscous oil (48 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.09 – 7.02 (m, 3H, H_3, H_4, H_7), 6.97 (ddd, *J* = 8.4, 7.0, 4.6 Hz, 1H, H_8), 6.69 (ddd, *J* = 8.4, 8.4, 0.8 Hz, 1H, H_9), 6.00 – 5.95 (m, 1H, H_2), 5.78 – 5.71 (m, 1H, H_5).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 156.0 (d, *J* = 246.5 Hz, C_{10}), 152.9 (d, *J* = 4.5 Hz, C_6), 143.2 (C_4), 142.7 (C_3), 133.7 (d, *J* = 20.9 Hz, C_1), 127.7 (d, *J* = 5.9 Hz, C_8), 116.5 (d, *J* = 2.7 Hz, C_7), 114.0 (d, *J* = 22.2 Hz, C_9), 82.6 C_5), 79.6 (C_2).
^{19}F NMR (471 MHz, $CDCl_3$) δ_F = -120.8.
FTIR (film) ν_{max}/cm^{-1} = 3022, 2361, 1633, 1599, 1468, 1280, 1234, 1192, 1177, 1136, 1083, 964, 939, 871, 857, 828, 793, 773, 735, 721, 663, 618.
HRMS: not found by ESI, APCI or EI.

5-(Trifluoromethyl)-1,4-dihydro-1,4-epoxynaphthalene, 5q:

5q was prepared according to **General Procedure G** using 2-acetamido- 4,6,8-trimethyl-5-(3-(trifluoromethyl)phenyl)-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4q**, (149 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:pentane, 10:90, R_f = 0.2) to give the title compound as a viscous oil (57.2 mg, 84%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.39 (d, *J* = 7.1 Hz, 1H, H_7), 7.18 (d, *J* = 8.0 Hz, 1H, H_9), 7.12 – 7.08 (m, 1H, H_8), 7.07 (dd, *J* = 5.6, 1.8 Hz, 1H, H_4), 7.04 (dd, *J* = 5.6, 1.8 Hz, 1H, H_3), 6.03 – 5.99 (m, 1H, H_2), 5.80 – 5.75 (m, 1H, H_5).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 150.6 (C_6), 148.0 (q, *J* = 2.7 Hz, C_1), 143.8 (C_4), 142.6 (C_3), 125.8 (C_8), 124.1 (q, *J* = 272.7 Hz, C_{11}), 123.7 (q, *J* = 33.4 Hz, C_{10}), 123.0 (C_7), 121.2 (q, *J* = 4.0 Hz, C_9), 82.1 (C_5), 81.6 (q, *J* = 1.9 Hz, C_2).
^{19}F NMR (377 MHz, $CDCl_3$) δ_F = -60.8.

FTIR (film) ν_{max}/cm^{-1} = 1615, 1423, 1355, 1320, 1281, 1259, 1164, 1120, 1101, 1047, 1006, 957, 901, 877, 858, 818, 799, 782, 750, 730, 700, 658, 633.
HRMS (EI$^+$): m/z calculated for $C_{11}H_7F_3O^+$ $[M]^+$ = 212.04435; m/z found = 212.0449. Δ = +2.6 ppm.

6-(tert-butyl)-1,4-dihydro-1,4-epoxynaphthalene, 5r:

5r was prepared according to **General procedure G** using 2-acetamido-5-(3-(*tert*-butyl)phenyl)-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, **4r**, (146 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:*n*-pentane, 15:85, R_f = 0.7) to give the title compound as a pale yellow oil (52 mg, 87%).

^{1}H (500 MHz, $CDCl_3$) δ_H = 7.35 (d, *J* = 1.7 Hz, 1H, H_{10}), 7.18 (d, *J* = 7.5 Hz, 1H, H_7), 7.03 (d, *J* = 0.9 Hz, 2H, H_3, H_4), 6.99 (dd, *J* = 7.5, 1.7 Hz, 1H, H_8), 5.70 (t, *J* = 1.1 Hz, 2H, H_2, H_5), 1.31 (s, 9H, H_{12}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 149.0 (C_1), 148.4 (C_9), 146.0 (C_6), 143.1 ($C_{3/4}$), 143.0 ($C_{3/4}$), 121.3 (C_8), 119.7 (C_7), 118.3 (C_{10}), 82.6 ($C_{2/5}$), 82.3 ($C_{2/5}$), 34.8 (C_{11}), 31.6 (C_{12}).
IR (film) ν_{max}/cm^{-1} **=** 3012, 2960, 2360, 2342, 1723, 1477, 1409, 1364, 1262, 1099, 1018, 989, 870, 851, 838, 750, 730, 698, 668, 655, 633.
HRMS (ESI$^+$): m/z calculated for $C_{14}H_{17}O$ $[M+H]^+$ = 201.1274; m/z found = 201.1277. Δ = 1.31 ppm.

Methyl (E)-3-(1,4-dihydro-1,4-epoxynaphthalen-6-yl)acrylate, 5s:

5s was prepared according to **General procedure G** using (*E*)-2-acetamido-5-(4-(3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, **4s**, (155 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:*n*-pentane, 30:70, R_f = 0.4) to give the title compound as a pale yellow oil (59 mg, 86%).

^{1}H (500 MHz, $CDCl_3$) δ_H = 7.65 (d, *J* = 16.0 Hz, 1H, H_{11}), 7.44 (t, *J* = 1.0 Hz, 1H, H_{10}), 7.25 (d, *J* = 7.3 Hz, 1H, H_7), 7.12 (dd, *J* = 7.4, 1.5 Hz, 1H, H_8), 7.06 – 6.98 (m, 2H, H_3, H_4), 6.37 (d, *J* = 16.0 Hz, 1H, H_{12}), 5.72 (m, 2H, H_2, H_5), 3.79 (s, 3H, H_{14}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 167.6 (C_{13}), 151.6 (C_6), 150.1 (C_1), 144.9 (C_{11}), 143.1 ($C_{3/4}$), 142.7 ($C_{3/4}$), 131.8 (C_9), 127.1 (C_8), 120.6 (C_7), 118.7 (C_{10}), 117.3 (C_{12}), 82.2 (C_4, C_5), 51.8 (C_{14}).
IR (film) ν_{max}/cm^{-1} **=** 3775, 3660, 2981, 2888, 1711, 1639, 1549, 1462, 1382, 1263, 1169, 1073, 955, 836, 750, 700.

HRMS (ESI$^+$): m/z calculated for $C_{14}H_{13}O_3$ $[M+H]^+$ = 229.0859; m/z found = 229.0862. Δ = 1.27 ppm.

Methyl 3-(1,4-dihydro-1,4-epoxynaphthalen-6-yl)propanoate, 5t:

5t was prepared according to **General procedure G** using 2-acetamido-5-(4-(3-methoxy-3-oxopropyl)phenyl)-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, **4t**, (155 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:*n*-pentane, 40:60, R_f = 0.6) to give the title compound as a pale yellow oil (37 mg, 54%).

^{1}H (500 MHz, $CDCl_3$) δ_H = 7.15 (d, *J* = 7.2 Hz, 1H, H_7), 7.11 (d, *J* = 1.5 Hz, 1H, H_{10}), 7.03 – 6.99 (m, 2H, H_3, H_4), 6.79 (dd, *J* = 7.2, 1.5 Hz, 1H, H_8), 5.71 – 5.66 (m, 2H, H_2, H_5), 3.66 (s, 3H, H_{14}), 2.89 (t, *J* = 7.9 Hz, 2H, H_{11}), 2.59 (t, *J* = 8.0 Hz, 2H, H_{12}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 173.4 (C_{13}), 149.7 (C_1), 147.1 (C_6), 143.2 ($C_{3/4}$), 142.9 ($C_{3/4}$), 137.7 (C_9), 124.7 (C_8), 120.9 (C_{10}), 120.3 (C_7), 82.4 ($C_{2/5}$), 82.3 ($C_{2/5}$), 51.7 (C_{14}), 35.9 (C_{12}), 30.9 (C_{11}).
IR (film) ν_{max}/cm^{-1} **=** 3011, 2952, 2241, 2186, 2160, 2007, 1734, 1436, 1366, 1281, 1198, 1168, 1088, 989, 870, 850, 749, 697, 643, 611.
HRMS (ESI$^+$): m/z calculated for $C_{14}H_{15}O_3$ $[M+H]^+$ = 231.1016; m/z found = 231.1018. Δ = 0.89 ppm.

***N*-((8-Methoxy-1,4-dihydro-1,4-epoxynaphthalen-6-yl)methyl)-8-methylnonanamide, 5u:**

5u was prepared according to **General procedure F** using, 2-acetamido-5-(2-methoxy-4-((8-methylnonanamido)methyl)phenyl)-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, **4u**, (61 mg, 0.10 mmol, 1.00 eq.). The crude residue was purified by semi-preparative HPLC (YMC AAmylose-SA (10 x 250 mm), 15% EtOH/Hexane, 5 mL/min) to give the title compound as a colourless oil (11 mg, 31%).

^{1}H (500 MHz, $CDCl_3$) δ = 7.05 (dd, *J* = 5.5, 1.8 Hz, 1H, H_8), 7.00 (dd, *J* = 5.6, 1.8 Hz, 1H, H_7), 6.86 (s, 1H, H_4), 6.50 (s, 1H, H_2), 5.94 – 5.90 (m, 1H, H_9), 5.65 (m, 2H, H_4, H_{15}), 4.36 (dd, *J* = 5.7, 1.6 Hz, 2H, H_{12}), 3.81 (s, 3H, H_{11}), 2.19 (t, *J* = 7.6 Hz, 2H, H_{15}), 1.64 (m, 2H, H_{16}), 1.51 (m, 1H, H_{21}), 1.37 – 1.21 (m, 6H, H_{17}, H_{18}, H_{19}), 1.14 (m, 2H, H_{20}), 0.86 (d, *J* = 6.6 Hz, 6H, H_{22}).

^{13}C (126 MHz, $CDCl_3$) δ = 173.0 (C_{14}), 153.0 (C_5), 152.6 (C_1), 143.2 (C_8), 142.9 (C_7), 138.1 (C_3), 134.6 (C_{10}), 113.7 (C_4), 110.4 (C_2), 82.6 (C_6), 80.2 (C_9), 56.0 (C_{11}), 43.7 (C_{12}), 39.1 (C_{20}), 37.0 (C_{15}), 29.8 (C_{17}), 29.5 (C_{18}), 28.1 (C_{21}), 27.4 (C_{16}), 25.9 (C_{16}), 22.8 (C_{22}).
IR (film) ν_{max}/cm^{-1} **=** 3855, 3725, 3650, 3297, 2981, 2929, 2889, 2361, 2342, 1647, 1605, 1541, 1463, 1383, 1293, 1252, 1146, 1071, 1000, 955, 850, 818, 745, 711, 685, 669, 656, 643, 617.
HRMS (ESI$^+$) = m/z calculated for $C_{22}H_{32}NO_3$ $[M+H]^+$ = 358.2377; m/z found = 358.2373. Δ = -1.03 ppm.

Propyl 7-(2,4-difluorophenyl)-1,4-dihydro-1,4-epoxynaphthalene-5-carboxylate, 5v:

5v was prepared according to **General procedure G** using 2-acetamido-5-(2',4'-difluoro-3-(propoxycarbonyl)-[1,1'-biphenyl]-4-yl)-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, **4v**, (63 mg, 0.10 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:*n*-pentane, 10:90, R_f = 0.4) to give the title compound as a pale yellow oil (30 mg, 88%).

^{1}H (500 MHz, $CDCl_3$) δ_H = 7.68 (t, *J* = 1.2 Hz, 1H, H_3), 7.53 (d, *J* = 1.7 Hz, 1H, H_5), 7.39 (td, *J* = 8.7, 6.4 Hz, 1H, H_{20}), 7.10 (m, 2H, H_8, H_9), 6.95 (tdd, *J* = 8.0, 2.3, 1.0 Hz, 1H, H_{19}), 6.91 (ddd, *J* = 10.5, 8.8, 2.6 Hz, 1H, H_{17}), 6.40 (dt, *J* = 1.8, 0.8 Hz, 1H, H_{10}), 5.79 (t, *J* = 1.3 Hz, 1H, H_7), 4.33 (t, *J* = 6.6 Hz, 2H, H_{12}), 1.88 – 1.76 (m, 2H, H_{13}), 1.06 (t, *J* = 7.4 Hz, 3H, H_{14}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 165.9 (C_{11}), 162.6 (dd, *J* = 249.6, 11.9 Hz, C_{18}), 159.9 (dd, *J* = 250.7, 11.9 Hz, C_{16}), 151.8 (C_1), 150.8 (C_6), 143.9 (C_9), 142.5 (C_8), 132.5 (C_4), 131.6 (dd, *J* = 9.6, 4.7 Hz, C_{20}), 126.1 (d, *J* = 2.3 Hz, C_3), 124.6 (t, *J* = 3.3 Hz, C_5), 124.5 (d, *J* = 3.8 Hz, C_{15}), 124.3 (C_2), 111.8 (dd, *J* = 21.0, 3.8 Hz, C_{19}), 104.6 (t, *J* = 26.0 Hz, C_{17}), 82.9 (C_7), 82.0 (C_{10}), 67.0 (C_{12}), 22.3 (C_{13}), 10.8 (C_{14}).
^{19}F NMR (377 MHz, CD_3CN) δ_F = -110.7 (d, *J* = 7.5 Hz), -113.2 (d, *J* = 7.5 Hz).
IR (film) ν_{max}/cm^{-1} **=** 3080, 2917, 2849, 2360, 2341, 1716, 1619, 1591, 1509, 1453, 1428, 1353, 1280, 1266, 1217, 1180, 1141, 1118, 1097, 1058, 1042, 1018, 969, 947, 910, 873, 846, 815, 786, 729, 694, 649, 623, 607.
HRMS (ESI$^+$) = m/z calculated for $C_{20}H_{17}F_2O_3$ $[M+H]^+$ = 343.1140; m/z found = 343.1137. Δ = -0.9 ppm.

3.8 Pyrimidine Oxonium Synthesis

Ethyl 2-(2-bromo-4,6-dimethylphenoxy)acetate, 6a:

2-Bromo-4,6-dimethylphenol **S1** (20.10 g, 100.00 mmol, 1.00 eq.) was dissolved in acetone (300 mL). Ethyl 2-bromoacetate (13.32 mL, 120.00 mmol, 1.20 eq.) and K_2CO_3 (27.64 g, 200.00 mmol, 2.00 eq.) were added sequentially and the mixture was stirred at 56 °C. After 16 h the mixture was cooled to r.t., filtered and concentrated *in vacuo* to afford the desired product as an orange oil (28.00 g, 98%).

^{1}H (500 MHz, $CDCl_3$) δ_H = 7.20 – 7.17 (m, 1H, H_6), 6.92 (m, 1H, H_4), 4.51 (s, 2H, H_9), 4.30 (q, *J* = 7.2 Hz, 1H, H_{11}), 2.31 (s, 3H, H_7), 2.25 (s, 3H, H_8), 1.33 (t, *J* = 7.1 Hz, 3H, H_{12}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 168.8 (C_{10}), 151.5 (C_2), 135.7 (C_5), 132.9 (C_3), 131.5 (C_6), 131.3 (C_4), 116.5 (C_1), 69.5 (C_9), 61.4 (C_{11}), 20.6 (C_8), 16.7 (C_7), 14.4 (C_{12}).
IR (film) ν_{max}/cm^{-1} **=** 3650, 2981, 2361, 2339, 1764, 1740, 1603, 1559, 1474, 1436, 1380, 1278, 1201, 1127, 1069, 852, 828, 790, 689, 626.
HRMS (ESI$^+$) = *m/z* calculated for $C_{12}H_{16}O_3Br$, $[M+H]^+$ = 287.0277; *m/z* found = 287.0278 found, Δ = 0.13 ppm.

5-(2-Bromo-4,6-dimethylphenoxy)-2-(tert-butyl)pyrimidin-4(3H)-one, 6b:

6b was prepared according to a modified literature procedure[4]. A solution of NaH (60% in oil, 440 mg, 11.00 mmol, 1.10 eq.) in anhydrous Et_2O (6 mL) was cooled to 0 °C. Ethyl formate (0.80 mL, 10.00 mmol, 1.00 eq.) and ethyl 2-(2-bromo-4,6-dimethylphenoxy)acetate **6a** (2.87 g, 10.00 mmol, 1.00 eq.) were sequentially added and the mixture was stirred at r.t.. After 18 h the solution was washed with pentane (100 mL) and recrystalised with anhydrous Et_2O. The pale orange precipitate was used without further purification. The crude precipitate was added to a mixture of pivalimidamide hydrochloride (1.50 g, 11.00 mmol, 1.10 eq.), K_2CO_3 (1.52 g, 11.00 mmol, 1.10 eq.) and CH_3CN (30 mL). The mixture was stirred at 82 °C for 16 h and then concentrated *in vacuo*. The crude residue was purified by flash column chromatography (Et_2O:pentane, 10:90, R*f*= 0.1) to give the title compound as a pale yellow solid (1.69 g, 48%).
m.p. = 202-203 °C.

^{1}H (500 MHz, $CDCl_3$) δ_H = 11.32 (s, 1H, H_{11}), 7.25 (d, *J* = 2.0 Hz, 1H, H_6), 7.14 (s, 1H, H_{13}), 6.99 – 6.97 (m, 1H, H_4), 2.29 (s, 3H, H_8), 2.22 (s, 3H, H_7), 1.34 (s, 9H, H_{15}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 161.2 (C_{12}), 158.5 (C_{10}), 147.3 (C_3), 142.6 (C_9), 136.8 (C_5), 134.3 (C_{13}), 132.5 (C_2), 131.8 (C_6), 131.4 (C_4), 116.1 (C_1), 37.2 (C_{14}), 28.5 (C_{15}), 20.7 (C_8), 16.8 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 3853, 3839, 3802, 3735, 3676, 3650, 2981, 2361, 2341, 1734, 1671, 1594, 1559, 1541, 1507, 1473, 1395, 1279, 1237, 1211, 1139, 1067, 979, 844, 804, 752, 669, 627, 618.
HRMS (ESI$^+$) = calculated for $C_{16}H_{20}BrO_2N_2$ [M+H]$^+$ = 351.0703; *m/z* found = 351.0705, Δ = 0.65 ppm.

5-(2-Bromo-4,6-dimethylphenoxy)-2-(tert-butyl)-4-methoxypyrimidine, 6c:

5-(2-bromo-4,6-dimethylphenoxy)-2-(tert-butyl)pyrimidin-4(3H)-one **6b** (1.97 g, 5.61 mmol, 1.00 eq.) was added to a flame dried RBF and dissolved in anhydrous DMF (14.00 mL). K_2CO_3 (1.55 g, 11.22 mmol, 2.00 eq.) and MeI (0.53 mL, 8.42 mmol, 1.50 eq.) were added sequentially and the mixture was stirred at r.t. for 16 h. H_2O (20 mL) was added and the organic layer was washed with EtOAc (3 x 50 mL). The combined organic layers were dried over ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (Et_2O:pentane, 10:90, R*f*= 0.9) to give the title compound as a yellow solid (1.58 g, 77%).

m.p. = 80-83 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 7.26 (s, 1H, C_{12}), 7.04 (d, *J* = 2.0 Hz, 1H, C_6), 6.78 – 6.74 (m, 1H, C_4), 3.90 (s, 3H, C_{13}), 2.07 (s, 3H, C_8), 1.94 (s, 3H, C_7), 1.13 (s, 9H, C_{15}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 169.6 (C_{11}), 158.6 (C_{10}), 147.0 (C_2), 138.9 (C_{12}), 137.7 (C_9), 136.9 (C_5), 132.5 (C_3), 131.7 (C_6), 131.3 (C_4), 116.3 (C_1), 53.8 (C_{13}), 38.9 (C_{14}), 29.6 (C_{15}), 20.6 (C_8), 16.6 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 2958, 2361, 2340, 1569, 1479, 1416, 1394, 1370, 1328, 1278, 1234, 1209, 1178, 1154, 1121, 1017, 937, 853, 825, 810, 781.
HRMS (ESI$^+$) = calculated for $C_{17}H_{22}O_2N_2Br$ [M+H]$^+$ = 365.0859; *m/z* found = 365.0860, Δ = 0.22 ppm.

2'-((2-(Tert-butyl)-4-methoxypyrimidin-5-yl)oxy)-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-amine, 6d:

6d was prepared according to a **General Procedure C** using 5-(2-bromo-4,6-dimethylphenoxy)-2-(tert-butyl)-4-methoxypyrimidine, **6c** (2.00 g, 5.48 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (EtOAc:pentane, 14:86, R*f*= 0.20) to give the title compound as a pale yellow solid (1.04 g, 47%).

m.p. = 94-99 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 7.53 (s, 1H, H_{12}), 7.06 (dt, *J* = 2.3, 0.8 Hz, 1H, H_4), 6.94 (d, *J* = 2.3 Hz, 1H, H_6), 6.70 (m, H_{21}), 6.54 (d, *J* = 2.1 Hz, 1H, H_{19}), 3.83 (s, 3H, H_{13}), 3.40 (s, 2H, H_{22}), 2.32 (s, 3H, H_8), 2.29 (s, 3H, H_7), 2.08 (s, 3H, H_{24}), 2.06 (s, 3H, H_{23}), 1.26 (s, 9H, H_{15}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 169.1 (C_{11}), 158.8 (C_{10}), 149.7 (C_2), 141.2 (C_{12}), 139.6 (C_{17}), 139.1 (C_9), 135.2 (C_5), 131.7 (C_{16}), 131.4 (C_4), 131.2 (C_3), 130.4 (C_6), 130.3 (C_{21}), 128.8 (C_{19}), 126.6 (C_{20}), 123.1 (C_1), 122.2 (C_{18}), 53.5 (C_{23}), 38.8 (C_{14}), 29.6 (C_{15}), 20.9 (C_8), 20.3 (C_{24}), 17.8 (C_{23}), 16.5 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 3649, 3382, 2980, 2360, 2342, 1623, 1567, 1479, 1416, 1392, 1379, 1326, 1238, 1204, 1178, 1148, 1018, 940, 860, 795, 748, 722, 670, 657, 648, 633, 618.
HRMS (ESI$^+$) = calculated for $C_{25}H_{32}O_2N_3$ $[M+H]^+$ = 406.2489; *m/z* found = 406.2485, Δ = -1.06 ppm.

5-(2-(tert-Butyl)-4-methoxypyrimidin-5-yl)-2,4,6,8-tetramethyl-5H-dibenzo[b,d]furan-5-ium tetrafluoroborate, 6:

6e was prepared according to **General Procedure E** using 2'-((2-(tert-butyl)-4-methoxypyrimidin-5-yl)oxy)-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-amine, **6d**, (487 mg, 1.20 mmol, 1.00 eq.) to give the title compound as an orange solid (271 mg, 50%).

m.p. = 184-186 °C.
^{1}H (500 MHz, CD_3CN) δ_H = 9.05 (s, 1H, H_{10}), 7.97 – 7.77 (m, 2H, H_6), 7.42 – 7.14 (m, 2H, H_4), 3.93 (s, 3H, H_{12}), 2.50 (s, 6H, H_8), 2.17 (s, 6H, H_7), 1.40 (s, 9H, H_{14}).
^{13}C (126 MHz, CD_3CN) δ_C = 181.7 (C_{11}), 161.1 (C_2), 158.9 (C_{10}), 151.9 (C_{12}), 142.9 (C_9), 141.5 (C_5), 135.3 (C_4), 124.0 (C_3), 123.8 (C_1), 122.5 (C_6), 56.4 (C_{12}), 41.0 (C_{13}), 29.5 (C_{14}), 21.1 (C_8), 16.2 (C_7).

^{19}F NMR (377 MHz, CD_3CN) δ_F = -151.8.
IR (film) ν_{max}/cm^{-1} **=** 3853, 3734, 3650, 3211, 2981, 2359, 2338, 1587, 1484, 1459, 1412, 1395, 1324, 1234, 1168, 1060, 993, 958, 856, 816, 749, 715, 669, 657, 626.
HRMS (ESI$^+$) = calculated for $C_{25}H_{29}O_2N_2$ [M]$^+$ = 389.2224; *m/z* found = 389.2224, Δ = 0.15 ppm.

3.9 Pyrimidyne Trapping Reactions

2-(tert-Butyl)-4-methoxy-5,8-dihydro-5,8-epoxyquinazoline, 7:

6 (95 mg, 0.20 mmol, 1.00 eq.) was dissolved in MeCN:furan (1:2, 6 mL) in an oven-dried vial. K_3PO_4 (212.27, 1.00 mmol, 5.00 eq.) was then added and the reaction mixture stirred (600 rpm) at r.t. for 16 h. Once complete, the reaction mixture was filtered through Celite® (1 mL/mmol), eluted (CH_2Cl_2, 4 × 2 mL/mmol) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (Et_2O:*n*-pentane, 1:99, R_f = 0.2) to give the title compound as a pale yellow oil (18 mg, 39%).

^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 7.11 (dd, *J* = 5.5, 1.8 Hz, 1H, H_6), 7.09 (dd, *J* = 5.5, 1.9 Hz, 1H, H_7), 5.91 – 5.87 (m, 1H, H_5), 5.59 (dd, *J* = 2.0, 0.9 Hz, 1H, H_8), 3.96 (s, 3H, H_9), 1.36 (s, 9H, H_{11}).
^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 184.8 (C_2), 174.7 (C_3), 160.0 (C_2), 144.4 (C_6), 141.8 (C_7), 120.8 (C_1), 83.0 (C_8), 79.4 (C_5), 53.3 (C_9), 39.5 (C_{10}), 29.8 (C_{11}).
IR (film) ν_{max}/cm^{-1} **=** 2958, 2360, 1612, 1579, 1483, 1460, 1400, 1369, 1280, 1253, 1235, 1120, 1092, 1069, 998, 912.
HRMS (ESI$^+$) = calculated for $C_{13}H_{17}N_2O_2^+$ [M+H]$^+$ = 233.1285; *m/z* found = 233.1282, Δ = -1.22 ppm.

2-(tert-butyl)-4-ethoxy-6-methoxypyrimidine, 8:

6 (95 mg, 0.20 mmol, 1.00 eq.) was dissolved in MeCN:EtOH (1:2, 6 mL) in an oven-dried vial. K_3PO_4 (212.27, 1.00 mmol, 5.00 eq.) was then added and the reaction mixture stirred (600 rpm) at r.t. for 16 h. Once complete, the reaction mixture was filtered through Celite® (1 mL/mmol), eluted (CH_2Cl_2, 4 × 2 mL/mmol) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (*n*-pentane, R_f = 0.2) to give the title compound as a colourless oil (16 mg, 38%).

^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 5.80 (s, 1H, H_1), 4.36 (q, *J* = 7.0 Hz, 2H, H_8), 3.92 (s, 3H, H_5), 1.38 (t, *J* = 7.1 Hz, 3H, H_9), 1.34 (s, 9H, H_7).
^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 176.9 (C_3), 171.3 (C_2), 171.0 (C_4), 86.3 (C_3), 62.4 (C_8), 53.8 (C_5), 39.5 (C_6), 14.7 (C_9).
IR (film) ν_{max}/cm^{-1} **=** 2961, 2360, 2341, 1589, 1465, 1424, 1390, 1347, 1259, 1230, 1186, 1167, 1060, 1026, 991, 942, 833, 735, 639.
HRMS (ESI$^+$) = calculated for $C_{11}H_{19}N_2O_2$ $[M+H]^+$ = 211.1441; *m/z* found = 211.1140 , Δ = - 0.29 ppm.

2-(tert-Butyl)-4-methoxy-6-(1H-pyrazol-1-yl)pyrimidine, **9:**

6 (95 mg, 0.20 mmol, 1.00 eq.) and pyrazole (68 mg, 0.10 mmol, 5.00 eq.) were dissolved in MeCN (4 mL) in an oven-dried vial. K_3PO_4 (212 mg, 1.00 mmol, 5.00 eq.) was then added and the reaction mixture stirred (600 rpm) at r.t. for 16 h. Once complete, the reaction mixture was filtered through Celite® (1 mL/mmol), eluted (CH_2Cl_2, 4 × 2 mL/mmol) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (Et_2O:*n*-pentane, 1:9, R_f = 0.2) to give the title compound a white solid (24 mg, 55%).

m.p. = 65-66 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 8.61 (dd, *J* = 2.5, 1.0 Hz, 1H, H_{11}), 7.74 (dd, *J* = 1.5, 1.0 Hz, 1H, H_9), 7.05 (s, 1H, H_5), 6.45 (dd, *J* = 2.5, 1.5 Hz, 1H, H_{10}), 4.01 (s, 3H, H_6), 1.40 (s, 9H, H_8).
^{13}C (126 MHz, $CDCl_3$) δ_C = 177.4 (C_3), 171.5 (C_1), 158.2 (C_4), 143.0 (C_9), 128.0 (C_{11}), 108.0 (C_{10}), 90.2 (C_5), 54.1 (C_4), 39.6 (C_7), 29.9 (C_8).
IR (film) ν_{max}/cm^{-1} **=** 2960, 2361, 1593, 1573, 1524, 1474, 1459, 1439, 1408, 1396, 1367, 1300, 1257, 1214, 1107, 1060, 1039, 990, 950, 915, 847, 839, 785, 760, 648.
HRMS (ESI$^+$): calculated for $C_{12}H_{17}N_4O^+$ $[M+H]^+$ = 233.1397; *m/z* found = 233.1400, Δ = 1.34 ppm.

2-(tert-butyl)-6-methoxy-N-methyl-N-phenylpyrimidin-4-amine, **10**:

6 (95 mg, 0.20 mmol, 1.00 eq.) and N-methyl aniline (108 µL, 107 mg, 1.00 mmol, 5.00 eq.) were dissolved in MeCN (4 mL) in an oven-dried vial. K_3PO_4 (212 mg, 1.00 mmol, 5.00 eq.) was then added and the reaction mixture stirred (600 rpm) at r.t. for 16 h. Once complete, the reaction mixture was filtered through Celite® (1 mL/mmol), eluted (CH_2Cl_2, 4 × 2 mL/mmol) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (Et_2O:*n*-pentane, 1:9, R_f = 0.2) to give the title compound a yellow oil (13 mg, 24%).

^{1}H (500 MHz, $CDCl_3$) δ_H = 7.46 – 7.39 (m, 2H, H_{11}), 7.31 – 7.21 (m, 3H, H_{10}, H_{12}), 5.48 (s, 1H, H_4), 3.83 (s, 3H, H_5), 3.52 (s, 3H, H_8), 1.38 (s, 9H, H_7).
^{13}C (126 MHz, $CDCl_3$) δ_H = 176.5 (C_2), 170.4 (C_1), 164.5 (C_3), 145.6 (C_9), 130.0 (C_{11}), 127.2 (C_{10}), 126.6 (C_{12}), 83.5 (C_4), 53.4 (C_5), 39.7 (C_6), 38.0 (C_8), 29.7 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 3648, 2982, 2971, 2883, 2360, 2343, 2261, 1726, 1701, 1653, 1617, 1559, 1511, 1473, 1386, 1319, 1259, 1226, 1146, 1068, 1037, 969, 857, 730, 697, 668, 638, 628, 613.
HRMS (ESI$^+$): calculated for $C_{16}H_{22}N_3O^+$ $[M+H]^+$ = 272.1757; *m/z* found = 272.1755, Δ = -0.74 ppm.

3.10 Aryne Trapping Reactions

5-Nitro-9-(propan-2-ylidene)-1,4-dihydro-1,4-methanonaphthalene, **11**:

K_3PO_4 (318 mg, 1.50 mmol, 5.00 eq.) was added to a solution of 6,6-dimethylfulvene (72 μL, 63.7 mg, 0.60 mmol, 2.00 eq.) and 2,4,6,8-tetramethyl-5-(2-nitrophenyl)-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4k**, (129 mg, 0.30 mmol, 1.00 eq.) in MeCN (6 mL) under N_2. After 16 h, the reaction was filtered through Celite® (3 mL), eluted (CH_2Cl_2, 3 × 10 mL) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (Et_2O:Pentane, 2:98, R_f = 0.4) to give the title compound as a tan solid (40 mg, 59%).

m.p. = 85-86 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.70 (dd, *J* = 8.5, 0.9 Hz, 1H, H_3), 7.44 (d, *J* = 7.1 Hz, 1H, H_5), 7.07 (dd, *J* = 8.4, 7.1 Hz, 1H, H_4), 7.03 – 6.95 (m, 2H, H_9, H_8), 5.37 – 5.32 (m, 1H, $H_{10/7}$), 4.50 – 4.45 (m, 1H, $H_{10/7}$), 1.57 (s, 3H, $H_{14/13}$), 1.57 (s, 3H, $H_{14/13}$).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 160.0 (C_{12}), 154.5 (C_6), 147.5 (C_1), 144.3 ($C_{9/8}$), 143.1 (C_2), 142.1 ($C_{9/8}$), 125.5 (C_4), 125.4 (C_5), 119.5 (C_3), 105.9 (C_{11}), 50.7 ($C_{10/7}$), 50.6 ($C_{10/7}$), 19.3 ($C_{14/13}$), 19.1 ($C_{14/13}$).
FTIR (film) ν_{max}/cm^{-1} = 2915, 1721, 1521, 1448, 1343, 1225, 1164, 1047, 935, 866, 848, 810, 796, 739, 696.
HRMS (APCI$^+$): m/z calculated for $C_{14}H_{14}O_2N$ $[M+H]^+$ = 228.1019; m/z found = 228.1022. Δ = 1.41 ppm.

2,3-Diphenyl-2,3-dihydrobenzo[*d*]isoxazole-4-carbonitrile, **12**:

K_3PO_4 (318 mg, 1.50 mmol, 5.00 eq.) was added to a solution of (*Z*)-*N*,1-diphenylmethanimine oxide, (118 mg, 0.60 mmol, 2.00 eq.) and 5-(2-cyanophenyl)-2,4,6,8- tetramethyl-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4l**, (124 mg, 0.30 mmol, 1.00 eq.) in MeCN (6 mL) under N_2. After 16 h, the reaction was filtered through Celite® (3 mL), eluted (CH_2Cl_2, 3 × 10 mL) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (EtOAc:pentane, 5:95, R_f = 0.2) to give the title compound as a colourless oil (64 mg, 71%).

^{1}H NMR (500 MHz, CD_3CN) δ_H = 7.56 – 7.52 (m, 2H, H_{10}), 7.46 – 7.41 (m, 3H, H_{12}, H_{11}), 7.37 – 7.33

(m, 2H, H_{15}), 7.27 – 7.23 (m, 1H, H_{16}), 7.19 – 7.15 (m, 2H, H_{14}), 7.02 (dd, *J* = 8.2, 1.1 Hz, 1H, C_3), 6.97 (dd, *J* = 7.8, 1.1 Hz, 1H, H_5), 6.87 – 6.79 (m, 2H, H_8, H_4).
^{13}C NMR (126 MHz, CD_3CN) δ_C = 152.5 (C_6), 141.0 ($C_{13/1}$), 140.9 ($C_{13/1}$), 138.3 (C_9), 131.3 (C_{12}), 130.3 (C_{15}), 129.9 (C_{11}), 128.5 (C_{10}), 128.0 (C_{16}), 126.5 (C_{14}), 125.6 (C_3), 121.8 (C_4), 117.0 (C_7), 112.2 (C_5), 103.1 (C_8), 92.5 (C_2).
FTIR (film) ν_{max}/cm^{-1} = 2359, 2224, 1672, 1601, 1581, 1495, 1474, 1453, 1393, 1370, 1336, 1276, 1221, 1196, 1176, 1158, 1093, 1069, 1046, 1027, 966, 846, 817, 759, 725, 695, 666, 619.
HRMS (ESI$^+$): m/z calculated for $C_{20}H_{15}N_2O^+$ $[M+H]^+$ = 299.1179; *m/z* found = 299.1182. Δ = 1.12 ppm.
Regiochemistry assignment based on literature precedent.[5]

(4a*S*,8b*S*)-8-Nitro-3,4,4a,8b-tetrahydro-2*H* -benzo[3,4]cyclobuta[1,2-*b*]pyran, 13:

K_3PO_4 (318 mg, 1.50 mmol, 5.00 eq.) was added to a solution of 2,4,6,8-tetramethyl-5-(2-nitrophenyl)-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4k**, (129 mg, 0.3 mmol, 1.00 eq.) and 3,4-Dihydro-2*H* -pyran (137 *μ*L, 126 mg, 1.50 mmol, 5 eq.) in MeCN (6 mL). After 16 h, the reaction was filtered through Celite® (1.5 mL), eluted (CH_2Cl_2, 4 × 5 mL) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (Et_2O:Pentane, 6:94, R_f = 0.2) to give the title compound as a pale yellow oil (61 mg, 92%).

^{1}H NMR (700 MHz, $CDCl_3$) δ_H = 7.99 (d, *J* = 8.3 Hz, 1H, H_3), 7.51 (dd, *J* = 7.8, 7.8 Hz, 1H, H_4), 7.47 (d, *J* = 7.3 Hz, 1H, H_5), 5.40 (d, *J* = 4.9 Hz, 1H, H_{11}), 3.87 – 3.73 (m, 3H, H_{10}, H_7), 2.27 – 2.19 (m, 1H, H_8), 1.95 (ddt, *J* = 12.5, 7.3, 5.2 Hz, 1H, H_8), 1.65 – 1.57 (m, 1H, H_9), 1.46 – 1.38 (m, 1H, H_9).
^{13}C NMR (176 MHz, $CDCl_3$) δ_C = 150.2 (C_6), 143.4 (C_2), 141.6 (C_1), 130.9 (C_4), 129.4 (C_5), 122.0 (C_3), 73.4 (C_{11}), 62.6 (C_{10}), 44.1 (C_7), 23.1 (C_8), 19.7 (C_9).
FTIR (film) ν_{max}/cm^{-1} = 2943, 2870, 1523, 1455, 1348, 1248, 1221, 1188, 1156, 1098, 1076, 1042, 949, 908, 885, 803, 737, 681, 639.
HRMS (ESI$^+$): m/z calculated for $C_{11}H_{11}NNaO_3^+$ $[M+Na]^+$ = 228.0631; *m/z* found = 228.0633. Δ = 0.99 ppm.
Data in accord with the literature.[6]

1-Benzyl-1H-benzo[d][1,2,3]triazole, 14:

2-Acetamido-4,6,8-trimethyl-5-phenyl-5H-dibenzo[b,d]furan-5-ium tetrafluoroborate, **4j**, (194 mg, 0.30 mmol, 1.00 eq.) was dissolved in MeCN (6 mL) in an oven-dried vial. Benzyl azide (188 µL, 1.50 mmol, 5 eq.) and K_3PO_4 (318 mg, 1.50 mmol, 5.00 eq.) were added sequentially and the reaction mixture stirred (600 rpm) at r.t. for 16 h. Once complete, the reaction mixture was filtered through Celite® (2 mL), eluted (CH_2Cl_2, 4 × 5 mL) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (EtOAc:*n*-pentane, 10:90, R_f = 0.3) to give the title compound as a pale yellow solid (53 mg, 84%).

m.p. = 82-92 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H 8.08 (d, *J* = 8.2 Hz, 1H, H_1), 7.41 (dd, *J* = 2.5, 0.5 Hz, 1H, H_3), 7.37 (dd, *J* = 8.1, 1.6 Hz, 2H, H_2, H_4), 7.36 – 7.31 (m, 3H, H_{10}, H_{11}), 7.28 (dq, *J* = 7.8, 1.7 Hz, 2H, H_9), 5.86 (s, 2H, H_7).
^{13}C (126 MHz, $CDCl_3$) δ_C = 146.2 (C_1), 134.8 (C_8), 133.0 (C_5), 129.2 (C_{10}), 128.7 (C_{11}), 127.8 (C_9), 127.7 (C_3), 124.3 (C_4), 120.2 (C_1), 109.9 (C_2), 52.6 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 3821, 3735, 3628, 3032, 2980, 2918, 2850, 2360, 2341, 1717, 1615, 1523, 1496, 1456, 1386, 1263, 1226, 1159, 1094, 1071, 1028, 1001, 949, 914, 773, 747, 723, 696, 669, 623.
HRMS (ESI$^+$): m/z calculated for $C_{13}H_{12}N_3$ $[M+H]^+$ = 210.1026; *m/z* found = 210.1027. Δ = 0.78 ppm. Data in accord with the literature.[7]

2,2-Dimethyl-5-nitro-2*H* -chromene, 15:

K_3PO_4 (318 mg, 1.50 mmol, 5.00 eq.) was added to a solution of 2,4,6,8-tetramethyl- 5-(2-nitrophenyl)-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4k**, (129 mg, 0.30 mmol, 1.00 eq.) and 3-methyl-2-butenal (145 *µ*L, 126 mg, 1.50 mmol, 5.00 eq.) in MeCN (6 mL). After 16 h, the reaction was filtered through Celite® (1.5 mL), eluted (CH_2Cl_2, 4 × 5 mL) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (Et_2O:pentane, 2:98, R_f = 0.4) to give the title compound as a pale yellow oil (58 mg, 94%).

^{1}H NMR (700 MHz, $CDCl_3$) δ_H =7.44 (dd, *J* = 8.2, 1.2 Hz, 1H, H_3), 7.12 (dd, *J* = 8.2, 8.2 Hz, 1H, H_4), 6.97

(ddd, J = 8.1, 1.0, 1.0 Hz, 1H, H_5), 6.87 (dd, J = 10.2, 0.8 Hz, 1H, H_9), 5.80 (d, J = 10.2 Hz, 1H, H_8), 1.39 (s, 6H, H_{10}).

^{13}C NMR (176 MHz, $CDCl_3$) δ_C = 154.2 (C_6), 146.1 (C_2), 134.5 (C_8), 128.3 (C_4), 121.9 (C_5), 117.5 (C_9), 117.0 (C_3), 116.0 (C_1), 76.2 (C_7), 27.6 (C_{10}).

FTIR (film) ν_{max}/cm^{-1} = 2979, 2360, 1609, 1521, 1453, 1363, 1343, 1310, 1275,1206, 1165, 1119, 1074, 997, 892, 856, 824, 808, 779, 760, 735, 707, 688.

HRMS (ESI$^+$): m/z calculated for $C_{22}H_{23}N_2O_6^+$ $[2M+H]^+$ = 411.1551; *m/z* found= 411.1550. Δ = -0.16 ppm.

Data in accord with the literature.[8]

1,4-Dimethyl-6-nitro-1,2,3,4-tetrahydro-5*H* -benzo[*e*][1,4]diazepin-5-one, 16:

K_3PO_4 (318 mg, 1.50 mmol, 5.00 eq.) was added to a solution of 2,4,6,8-tetramethyl- 5-(2-nitrophenyl)-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4k**, (129 mg, 0.30 mmol, 1.00 eq.) in DMI (6 mL). After 16 h, the reaction was filtered through Celite® (1.5 mL), eluted (CH_2Cl_2, 4 × 5 mL) and concentrated *in vacuo*. The DMI was removed by distillation (110 °C at 7 mbar) and the crude residue was purified by flash column chromatography (EtOAc:CH_2Cl_2, 5:95 to 15:85, R_f = 0.3) to give the title compound as a bright yellow solid (26 mg, 37%).

m.p. = 177-179 °C. ($CHCl_3$).

^{1}H NMR (700 MHz, $CDCl_3$) δ_H = 7.44 – 7.37 (m, 2H, H_4, H_3), 7.09 – 7.05 (m, 1H, H_5), 3.59 (t, J = 5.7 Hz, 2H, H_8), 3.32 (t, J = 5.7 Hz, 2H, H_7), 3.21 (s, 3H, H_{10}), 2.86 (s, 3H, H_{11}).

^{13}C NMR (176 MHz, $CDCl_3$) δ_C = 166.4 (C_9), 150.3 (C_2), 147.2 (C_6), 131.1 (C_4), 124.8 (C_1), 122.1 (C_5), 116.9 (C_3), 57.0 (C_8), 48.1 (C_7), 40.4 (C_{11}), 33.8 (C_{10}).

FTIR (film) ν_{max}/cm^{-1} = 2946, 2361, 1650, 1607, 1528, 1489, 1456, 1431, 1399, 1359, 1304, 1263, 1189, 1120, 1095, 1059, 931, 852, 815, 769, 724, 664.

HRMS (ESI$^+$): m/z calculated for $C_{11}H_{14}N_3O_3^+$ $[M+H]^+$ = 236.1030; *m/z* found = 236.1030. Δ = 0.12 ppm.

Data in accord with the literature.[9]

1-(2-nitrophenyl)-1H-pyrazole, 17:

K_3PO_4 (318 mg, 1.50 mmol, 5.00 eq.) was added to a solution of 2,4,6,8-tetramethyl- 5-(2-nitrophenyl)-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4k**, (129 mg, 0.30 mmol, 1.00 eq.) and pyrazole (102 mg, 1.50 mmol, 5.00 eq.) in MeCN (6 mL). After 16 h, the reaction was filtered through Celite® (1.5 mL), eluted (CH_2Cl_2, 4 × 5 mL) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (Et_2O:pentane, 5:95, R_f = 0.4) to give the title compound as a white solid (54 mg, 87%).

m.p. = 60-62 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.56 (dt, *J* = 2.8, 1.4 Hz, 1H, $H_{2/6}$), 8.15 – 8.11 (m, 1H, H_3), 8.11 – 8.06 (m, 1H, H_4), 8.02 (d, *J* = 2.6 Hz, 1H, H_7), 7.77 (d, *J* = 1.9 Hz, 1H, H_9), 7.63 (td, *J* = 8.1, 0.8 Hz, 1H, $H_{2/6}$), 6.56 – 6.52 (m, 1H, H_8).
^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 149.1 (C_1), 142.3 (C_7), 141.1 (C_6), 130.6 ($C_{2/5}$), 127.0 (C_7), 124.6 (C_4), 120.9 (C_3), 113.8 ($C_{2/5}$), 109.0 (C_8).
IR (film) ν_{max}/cm^{-1} **=** 3119, 2360, 1622, 1534, 1492, 1392, 1352, 1265, 1200, 1128, 1040, 945, 912, 869, 800, 737, 668, 668.
HRMS (ESI$^+$): *m/z* calculated for $C_9H_8N_3O_2$ $[M+H]^+$ = 190.0611; *m/z* found = 190.0609, Δ = -1.26 ppm.
Data in accord with the literature.[10]

N-methyl-2-nitro-N-phenylaniline, 18:

K_3PO_4 (318 mg, 1.50 mmol, 5.00 eq.) was added to a solution of 2,4,6,8-tetramethyl- 5-(2-nitrophenyl)-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4k**, (129 mg, 0.30 mmol, 1.00 eq.) and N-methyl aniline (162 μL, 161 mg, 1.50 mmol, 5.00 eq.) in MeCN (6 mL). After 16 h, the reaction was filtered through Celite® (1.5 mL), eluted (CH_2Cl_2, 4 × 5 mL) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (Et_2O:pentane, 2:98, R_f = 0.4) to give the title compound as a bright orange oil (54 mg, 74%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.65 (t, *J* = 2.4 Hz, 1H, H_6), 7.62 (ddd, *J* = 8.1, 2.2, 0.9 Hz, 1H, H_2), 7.45 – 7.36 (m, 2H, H_{10}), 7.29 (t, *J* = 8.2 Hz, 1H, H_3), 7.23 – 7.16 (m, 3H, H_9, H_{11}), 7.09 (ddd, *J* = 8.4, 2.5, 0.9 Hz, 1H, H_4), 3.37 (s, 3H, H_7).
^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 149.9 (C_6), 149.3 (C_1), 147.5 (C_8), 130.0 (C_{10}), 129.4 (C_3), 125.2 (C_{11}), 125.0 (C_9), 121.5 (C_4), 113.1 (C_2), 109.6 (C_5), 40.4 (C_7).
IR (film) ν_{max}/cm^{-1} **=** 2360, 1619, 1595, 1571, 1529, 1496, 1351, 1254, 1135, 1090, 991, 913, 840, 736, 701, 669.
HRMS (ESI$^+$): *m/z* calculated for $C_{13}H_{12}N_2O_2$ $[M+H]^+$ = 229.0972; *m/z* found = 229.0970, Δ = -0.76 ppm.

2'-nitro-1,2,3,4-tetrahydro-1,1'-biphenyl, 19:

K_3PO_4 (318 mg, 1.50 mmol, 5.00 eq.) was added to a solution of 2,4,6,8-tetramethyl-5-(2-nitrophenyl)-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4k**, (129 mg, 0.30 mmol, 1.00 eq.) and cyclohexene (174 *µ*L, 144 mg, 1.50 mmol, 5.00 eq.) in MeCN (6 mL). After 16 h, the reaction was filtered through Celite® (1.5 mL), eluted (CH_2Cl_2, 4 × 5 mL) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (Et_2O:pentane, 2:98, R_f = 0.4) to give the title compound as a pale yellow oil (41 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.14 – 8.03 (m, 2H, H_2, H_6), 7.55 (dt, *J* = 7.6, 1.4 Hz, 1H, H_4), 7.45 (t, *J* = 7.8 Hz, 1H, H_3), 5.98 (m, 1H, H_9), 5.73 – 5.64 (m, 1H, H_8), 3.52 (ddp, *J* = 8.2, 5.5, 2.8 Hz, 1H, H_7), 2.12 (tdd, *J* = 8.1, 6.8, 4.2 Hz, 2H, H_{10}), 2.09 – 2.01 (m, 1H, H_{12}), 1.80 – 1.47 (m, 3H, H_{11}, $H_{12'}$).
^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 148.9 ($C_{1/5}$), 148.5 ($C_{1/5}$), 134.2 (C_4), 130.0 (C_9), 129.3 (C_3), 128.6 (C_8), 122.8 (C_6), 121.3 (C_2), 41.6 (C_7), 32.5 (C_{12}), 25.0 (C_{10}), 20.9 (C_{11}).
IR (film) ν_{max}/cm^{-1} **=** 3022, 2935, 2360, 1531, 1447, 1353, 1266, 1084, 910, 866, 835, 808, 738, 705, 688, 667.
HRMS (ESI$^+$): *m/z* calculated for $C_{12}H_{14}NO_2$ $[M+H]^+$ = 204.1019; *m/z* found = 204.1013, Δ = -2.75 ppm.
Data in accord with the literature.[11]

1,8-di(furan-2-yl)naphthalene, 20a:

20a was synthesised according to a modified literature procedure[12]. Under an inert atmosphere *n*-BuLi in hexane (1.23 mL, 1.6 M, 30.60 mmol, 10.20 eq.) was added dropwise to a stirred solution furan in THF (3.69 mL, 0.6 M, 30.60 mmol, 10.2 eq.) at 0 °C. After 30 minute the mixture was slowly added over a stirred mixture of $InCl_3$ (2.26 g 10.20 mmol, 3.40 eq.) in THF (11 mL) at -78 °C under an inert atmosphere. After 30 minutes the solution was slowly warmed to r.t. and was slowly added to a refluxing solution of 1,8-dibromonapthalene (856 mg, 3 mmol, 1 eq.) and $PdCl_2(dppf)\cdot CH_2Cl_2$ (123 mg, 0.15 mmol, 5 mol%) in THF (100 mL) and refluxed. After 18 h the mixture was cooled to r.t., MeOH (1 mL) was added and the mixture was concentrated *in vacuo*. The mixture was dissolved in Et_2O (20 mL) and washed with HCl (10 %, 20 mL) and aq. sat. $NaHCO_3$ (20 mL). The organic phase was dried over $MgSO_4$, filtered, and evaporated *in vacuo*. The crude residue was purified by flash column chromatography (pentane, R_f = 0.5) to give the title compound as a yellow solid (374 mg, 72%).

m.p. = 77-80 °C.

^{1}H (400 MHz, $CDCl_3$) δ_H = 7.92 (dd, *J* = 8.0, 1.5 Hz, 2H, H_4), 7.67 (dt, *J* = 7.0, 1.5 Hz, 2H, H_2), 7.54 (dd, *J* = 8.0, 7.0 Hz, 2H, H_3), 7.17 (dt, *J* = 2.0, 1.0 Hz, 2H, H_8), 6.22 (ddd, *J* = 3.5, 2.0, 1.0 Hz, 2H, H_9), 6.13 (dt, *J* = 3.5, 1.0 Hz, 2H, H_{10}).

^{13}C (126 MHz, $CDCl_3$) δ_C = 154.5 (C_7), 141.6 (C_8), 135.1 (C_{Ar}), 130.3 (C_8), 129.4 (C_4), 128.9 (C_{Ar}), 128.8 (C_{Ar}), 125.2 (C_3), 111.0 (C_2), 107.3 (C_{10}).

IR (film) ν_{max}/cm^{-1} **=** 3649, 3054, 2981, 2362, 1717, 1560, 1508, 1496, 1457, 1363, 1264, 1223, 1184, 1157, 1112, 1076, 1014, 984, 940, 898, 885, 829, 801, 770, 726, 706, 686.

HRMS (ESI$^+$) = calculated for $C_{18}H_{13}O_2^+$ $[M+H]^+$ = 261.0910; m/z found = 261.0912, Δ = 0.81 ppm.

Data in accord with the literature.[11]

3b1,6a-dihydro-6H,7H-3b,6:7,11b-diepoxybenzo[a]perylene, 20:

2-Acetamido-4,6,8-trimethyl-5-phenyl-5H-dibenzo[b,d]furan-5-ium tetrafluoroborate, **4j**, (194 mg, 0.45 mmol, 1.50 eq.) was dissolved in MeCN (6 mL) in an oven-dried vial. 1,8-di(furan-2-yl)naphthalene (78 mg, 0.30 mmol, 1.00 eq.) and K_3PO_4 (318 mg, 1.50 mmol, 5.00 eq.) were added sequentially and the reaction mixture stirred (600 rpm) at r.t. for 16 h. Once complete, the reaction mixture was filtered through Celite® (2 mL), eluted (CH_2Cl_2, 4 × 5 mL) and concentrated *in vacuo*.

The crude residue was purified by flash column chromatography (EtOAc:toulene, 30:70, R_f = 0.2) to give the title compound as a brown solid (67 mg, 66%).

m.p. = 177-179 °C.
^{1}H (500 MHz, $CDCl_3$) δ_H = 7.94 (td, *J* = 8.3, 1.3 Hz, 2H, H_4, H_{10}), 7.87 (dd, *J* = 7.1, 1.3 Hz, 1H, $H_{5/9}$), 7.75 (dd, *J* = 7.0, 1.3 Hz, 1H, $H_{5/90}$), 7.54 (ddd, *J* = 10.7, 8.2, 7.0 Hz, 2H, H_1, H_3), 7.30 – 7.28 (m, 1H, H_{16}), 7.20 – 7.17 (m, 1H, H_{13}), 7.17 – 7.12 (m, 2H, H_{14}, H_{15}), 6.70 (d, *J* = 5.6 Hz, 1H, H_{22}), 6.65 (dd, *J* = 5.6, 1.8 Hz, 1H, H_{21}), 5.38 (s, 1H, H_{18}), 5.16 (d, *J* = 1.7 Hz, 1H, H_{20}), 2.39 – 2.32 (m, 2H, H_{19}, H_{24}).
^{13}C (126 MHz, $CDCl_3$) δ_C = 148.6 (C_{12}), 147.8 (C_{17}), 140.4 (C_{21}), 140.0 (C_{22}), 134.2 (C_2), 130.7 (C_{Ar}), 130.3 ($C_{4/10}$), 130.3 ($C_{4/10}$), 129.8 (C_{Ar}), 128.8 ($C_{5/9}$), 128.4 ($C_{5/9}$), 128.1 (C_{Ar}), 126.8 ($C_{14/15}$), 126.8 ($C_{14/15}$), 126.0 ($C_{1/3}$), 125.9 ($C_{1/3}$), 120.0 (C_{13}), 119.8 (C_{16}), 86.0 (C_{23}), 86.0 (C_{11}), 82.2 (C_{20}), 80.8 (C_{18}), 53.6 (C_{19}), 51.1 (C_{24}).
IR (film) ν_{max}/cm^{-1} **=** 3664, 3301, 2981, 2360, 2339, 2040, 1660, 1564, 1484, 1379, 1326, 1264, 1183, 1126, 1029, 966, 859, 828, 754, 625.
HRMS (ESI$^+$): m/z calculated for $C_{24}H_{17}O_2$ $[M+H]^+$ = 337.1223; m/z found = 337.1223. Δ = 0.11 ppm. Data in accord with the literature.[11]

(9*r*,10*r*)-2-Nitro-9,10-dihydro-9,10-[1,2]benzenoanthracene, 21:

K_3PO_4 (318 mg, 1.50 mmol, 5.00 eq.) was added to a solution of 2,4,6,8-tetramethyl-5-(4-nitrophenyl)-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4a** (129 mg, 0.30 mmol, 1.00 eq.) and anthracene (267 mg, 1.50 mmol, 5.00 eq.) in MeCN (6 mL). After 16 h, the reaction was filtered through Celite® (1.5 mL), eluted (CH_2Cl_2, 4 × 5 mL) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (CH_2Cl_2:pentane, 10:90 to 30:70, R_f = 0.25) to give the title compound as a pale yellow solid (75 mg, 83%).

m.p. = >250 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.22 (d, *J* = 2.2 Hz, 1H, H_{10}), 7.93 (dd, *J* = 8.1, 2.2 Hz, 1H, H_{12}), 7.50 (d, *J* = 8.1 Hz, 1H, H_{13}), 7.47 – 7.39 (m, 4H, H_{Ar}), 7.12 – 7.00 (m, 4H, H_{Ar}), 5.58 – 5.53 (m, 2H, H_8, H_1).
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 152.6 (C_{Ar}), 147.2 (C_{Ar}), 145.6 (C_{Ar}), 144.1 (C_{Ar}), 143.7 (C_{Ar}), 126.0 (C_{Ar}), 125.9 (C_{Ar}), 124.2 (C_{Ar}), 124.1 (C_{Ar}), 124.1 (C_{13}), 121.6 (C_{12}), 118.8 (C_{10}), 54.1 ($C_{8/1}$), 53.9 ($C_{8/1}$).
FTIR (film) ν_{max}/cm^{-1} = 3068, 2361, 1593, 1517, 1459, 1340, 1275, 1194, 1166, 1070, 1021, 908, 891, 836, 801, 749, 738, 709, 653, 637, 628, 611.
HRMS (APCI$^-$): m/z calculated for $C_{20}H_{13}NO_2^-$, $[M+e^-]^-$ = 299.0952; m/z found = 299.0946. Δ = -1.94 ppm.

4 Kinetic isotope effect investigation

Intramolecular isotope effect: method from Beak *et al*, *J. Am. Chem. Soc.* **121**, 7553–7558 (1999).

For an intramolecular isotope effect, if isotopically pure monodeuterated starting material was available, the isotope effect would be given by the ratio of d_0 to d_1 in the product. The reaction below proceeds to completion (>98% isolated yield of product), and hence we can calculate the isotope effect by correcting for the presence of (20%) undeuterated starting material **23**, which unambiguously leads to (20%) undeuterated product **24**.

d_1 product yield:	50%
corrected d_0 product yield: 50% - 20% =	30%

$$\left(\frac{k_H}{k_D}\right) = \left(\frac{[\mathbf{24}-d_1]}{[\mathbf{24}-d_0]}\right) = \frac{5}{3} = 1.67.$$

4-Fluorobenzonitrile-3-*d*, 22:

n-BuLi (1.6 M in hexanes, 6.87 mL, 11.00 mmol, 1.10 eq.) was added to a solution of *i*-Pr_2NH (1.68 mL, 1.21 g, 12.00 mmol, 1.20 eq.) in THF (50 mL) at –78 °C under N_2. Once the addition was complete, the reaction was warmed to r.t. for 5 mins and cooled back to –78 °C. 4-Fluorobenzonitrile (1.21 g, 10.00 mmol, 1.00 eq.) in THF (10 mL) was added dropwise to the stirred reaction mixture.[78] After 1 h at –78 °C, D_2O (2 mL) in THF (10 mL) was slowly added. After 10 minutes, the reaction was warmed to r.t., HCl (3 M, aq., 40 mL) was added and the mixture was extracted with Et_2O (5 × 30 mL). The combined organic extracts were washed with HCl (3M, aq., 30 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (5:95, Et_2O:pentane, R_f = 0.5) to give the title compound with 80% D incorporation as a white solid (696 mg, 57%).

m.p. = 34-35 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.71 – 7.65 (m, 2H, H_5, H_3), 7.22 – 7.13 (m, 1.2H, H_6, H_2).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = Major: 165.2 (d, *J* = 256.6 Hz, C_1), 134.9 (d, *J* = 9.3 Hz, $C_{5/3}$), 134.8 (d, *J* = 9.2 Hz, $C_{5/3}$), 118.2 (C_7), 117.08 (d, *J* = 22.5 Hz, C_2), 116.9 (d, 1:1:1 t (I = 1), *J* = 25.4, 22.4 Hz,

C_6), 108.82 – 108.73 (m, C_4).
Minor: 165.3 (d, J = 256.8 Hz, C_1). All other resonances are obscured by the major isomer.
^{19}F NMR (471 MHz, $CDCl_3$) δ_F = Major: -102.7. Minor: -102.4.
FTIR (film) ν_{max}/cm^{-1} = 3107, 2232, 1597, 1507, 1488, 1394, 1275, 1230, 1185, 1163, 1136, 1031, 913, 828, 737, 684, 673.
HRMS: not found by ESI, APCI or EI.

4-(2-Bromo-4,6-dimethylphenoxy)benzonitrile-3-*d*, 23a:

Bromide was prepared according to General Procedure B on a 5 mmol scale using 2-bromo-4,6-dimethylphenol (1.05 g, 5.00 mmol, 1 eq.), 4-fluorobenzonitrile-3-*d*, **22**, (610 mg, 5.00 mmol, 1 eq.) and K_2CO_3 (1.38 g, 10.00 mmol, 2 eq.) in DMF (12.5 mL). The crude residue was purified by flash column chromatography (Et_2O:pentane, 5:95, R_f = 0.4) to give the title compound with 80% D incorporation as a white solid (1.28 g, 85%).

m.p. = 64-65 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.61 – 7.55 (m, 2H, H_3, H_5), 7.33 – 7.28 (m, 1H, H_{12}), 7.05 – 7.02 (m, 1H, H_{10}), 6.88 – 6.83 (m, 1.2H, H_2, H_6), 2.33 (s, 3H, H_{15}), 2.12 (s, 3H, H_{14}).
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = Major: 160.5 (C_1), 146.5 (C_8), 137.3 ($C_{10/11}$), 134.3 ($C_{3/5}$), 134.2 ($C_{3/5}$), 132.8 ($C_{10/11}$), 131.9 (C_{12}), 131.5 (C_{10}), 118.9 (C_7), 116.7 (C_{13}), 115.8 (C_2), 115.5 (1:1:1 t (I = 1), J = 25.1 Hz C_6), 105.5 (C_4), 20.6 (C_{15}), 16.7 (C_{14}). Minor: 160.6 (C_1). All other resonances are obscured by the major isomer.
FTIR (film) ν_{max}/cm^{-1} = 2360, 2227, 1596, 1559, 1469, 1398, 1279, 1234, 1166, 1122, 1030, 855, 826, 784, 738.
HRMS (APCI$^+$): m/z calculated for calculated for $C_{15}H_{13}{}^2H^{79}BrON^+$, $[M+H]^+$ = 303.0328; m/z found = 303.0328. Δ = 0.30 ppm.

4-((2'-Amino-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-yl)oxy)benzonitrile-3-*d*, 23b:

23b was prepared according to **General Procedure D** using 4-(2-bromo- 4,6-dimethyl-phenoxy)benzonitrile-3-d, **23a**, (303 mg, 1.00 mmol, 1.00 eq.) added as a solid. The crude residue was purified by flash column chromatography (EtOAc:Pentane, 8:92 to 10:90, R_f = 0.25) to give the title compound as a white solid (303 mg, 88%).

m.p. = 120-121 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.41 – 7.35 (m, 2H, H_3, H_5), 7.13 – 7.09 (m, 1H, H_{10}), 7.05 – 7.01 (m, 1H, H_{12}), 6.76 – 6.72 (m, 1H, H_{19}), 6.71 – 6.65 (m, 1.2H, H_2, H_6), 6.56 – 6.52 (m, 1H, H_{17}), 2.36 (s, 3H, H_{15}), 2.16 (s, 3H, H_{14}), 2.11 (s, 3H, H_{22}), 2.07 (s, 3H, H_{23}). NH_2 was not observed.
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = Major: 161.7 (C_1), 147.8 (C_8), 139.0 (C_{21}), 136.2 (C_{Ar}), 133.9 ($C_{3/5}$), 133.8 ($C_{3/5}$), 133.0 (C_{20}), 131.9 (C_{10}), 131.7 (C_{Ar}), 130.8 (C_{19}), 130.7 (C_{12}), 128.9 (C_{17}), 127.3 (C_{Ar}), 123.5 (C_9), 122.9 (C_{Ar}), 119.3 (C_7), 116.2 (C_2), 116.0 (1:1:1 t (I = 1), J = 24.7 Hz, C_6), 104.7 (C_4), 21.1 (C_{15}), 20.5 (C_{23}), 18.0 (C_{22}), 16.7 (C_{14}). Minor: 161.7 (C_1). All other resonances were obscured by the major isomer.
FTIR (film) ν_{max}/cm^{-1} = 2921, 2361, 2225, 1653, 1596, 1559, 1541, 1481, 1277, 1237, 1199, 1150, 1013, 912, 860, 834, 733.
HRMS (ESI$^+$): m/z calculated for $C_{23}H_{22}{}^2HON_2^+$, $[M+H]^+$ = 344.1868; m/z found = 344.1866. Δ = -0.53 ppm.

5-(4-Cyanophenyl-2-*d*)-2,4,6,8-tetramethyl-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 23:

23 was prepared according to **General Procedure F** using 4-((2'- amino-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-yl)oxy)benzonitrile-3-*d*, **23b**, (172 mg, 0.50 mmol, 1.00 eq.) to give the title compound as a pale yellow solid (181 mg, 87%).

m.p. = 226 °C (dec.).
^{1}H NMR (500 MHz, CD_3CN) δ_H = 8.06 – 8.02 (m, 2H, H_3, H_5), 7.94 – 7.91 (m, 1H, H_2, H_6), 7.91 – 7.88 (m, 2H, H_{12}), 7.32 – 7.30 (m, 2H, H_{10}), 2.50 (s, 6H, H_{15}), 2.11 (s, 6H, H_{14}).
^{13}C NMR (126 MHz, CD_3CN) δ_C = Major: 161.7 (C_1), 161.3 (C_8), 143.3 (C_{Ar}), 137.3 ($C_{3/5}$), 137.2 ($C_{3/5}$), 135.4 (C_{10}), 124.7 (C_{Ar}), 124.2 (C_{Ar}), 123.3 (C_2), 123.2 (1:1:1 t (I = 1), *J* = 26.5 Hz, C_6) 122.6 (C_{12}), 117.4 ($C_{7/Ar}$), 117.4 ($C_{7/Ar}$, 21.1 (C_{15}), 16.7 (C_{14}). Minor: 161.8 (C_1). All other resonances are obscured by the major isomer.
^{19}F NMR (377 MHz, CD_3CN) δ_F = -151.8.
FTIR (film) ν_{max}/cm^{-1} = 3102, 2240, 1606, 1487, 1462, 1386, 1289, 1057 (br), 1008, 909, 870, 840, 734, 704, 619.
HRMS (ESI$^+$): m/z calculated for calculated for $C_{23}H_{19}{}^{2}HON^+$, $[M]^+$ = 327.1602; m/z found = 327.1598. Δ = -1.21 ppm.

1,4-Dihydro-1,4-epoxynaphthalene-6-carbonitrile-8-*d*, 24:

24 was prepared according to **General Procedure G** using 5-(4-cyanophenyl- 2-*d*)-2,4,6,8-tetramethyl-5*H*`-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **23**, (124 mg, 0.30 mmol, 1.00 eq.). The crude residue was purified by flash column chromatography (Et_2O:pentane, 20:80, R_f = 0.25) to give the title compound as a white solid (50.2 mg, 98%).

m.p. = 82-84 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.48 – 7.44 (m, 1H, H_3), 7.37 – 7.31 (m, 1.5H, H_6, H_5), 7.06 (dd, *J* = 5.5, 2.0 Hz, 1H, $H_{10/9}$), 7.03 (dd, *J* = 5.5, 2.0 Hz, 1H, $H_{10/9}$), 5.78 – 5.75 (m, 2H, H_{11}, H_8).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 154.6 (C_1), 154.5 ($C_{1'}$), 150.5 (C_2), 143.1 ($C_{10/9}$), 142.6 ($C_{10/9}$), 130.9 (C_5), 130.8 ($C_{5'}$), 122.8 (C_3), 120.7 ($C_{6'}$), 120.4 (1:1:1 t (I = 1), *J* = 25.2 Hz, C_6), 119.1 (C_7), 108.8 (C_4), 82.1 (C_8), 82.1 ($C_{8'}$), 81.9 (C_{11}).
FTIR (film) ν_{max}/cm^{-1} = 3018, 2226, 1614, 1456, 1417, 1398, 1280, 1178, 1079, 997, 871, 852, 839, 821, 749, 701, 645, 615.
HRMS (ESI$^+$): *m/z* calculated for calculated for $C_{11}H_6NO^+$, $[M-D]^+$ = 168.0439; m/z found = 168.0455. Δ = 2.93 ppm. *m/z* calculated for calculated for $C_{11}H_5DNO^-$, $[M-H]^+$ = 169.0518; m/z found = 169.0502. Δ = -2.53 ppm.

5 Computational details

All calculations were performed with Gaussian 16 revision C.01[13]. Geometry optimizations were done at the dispersion-corrected range-separated ωB97X-D functional[14] along with the 6-31+G(d,p) basis set[15]. Single point energy corrections were performed with the same functional and def2-QZVPP basis set[16]. Harmonic vibrational frequencies were evaluated to confirm all stationary point structures as minima or first-order saddle points. Transition structures (TSs) were confirmed to possess a single imaginary frequency, and Intrinsic Reaction Coordinate (IRC)[17] calculations further identified the connecting intermediates. Solvation effects were incorporated in all calculations through a continuum solvation model (Solvation Model based on Density, SMD)[18] describing acetonitrile (ε = 35.68). A quasi-harmonic correction to vibrational entropies[19] was incorporated along with a conversion to 1M standard state to the computed thermochemical data using the *Goodvibes* program[20]. Natural bond orbital (NBO) analysis was performed on stationary point structures using NBO 6.0[21].

Key structural and electronic parameters of onium and zwitterion intermediates:

	Internal angles (°) IM1	Internal angles (°) IM2		Bond lengths (Å) IM1	Bond lengths (Å) IM2
C1	125.55	133.66	O-C1	1.45	1.61
C2	116.97	114.40	C1-C2	1.38	1.38
C3	119.46	118.21	C2 -C3	1.38	1.38
C4	121.50	121.53	C3 -C4	1.40	1.40
C5	119.40	122.53	C4 -C5	1.39	1.40
C6	117.09	109.65	C5-C6	1.38	1.41
O	105.68	105.77	C6-C1	1.37	1.34
C7	108.60	109.55	O-C7	1.46	1.43
C8	108.52	107.53	C7-C8	1.38	1.38
C9	108.52	107.53	C8-C9	1.45	1.45
C10	108.60	109.55	C9-C10	1.38	1.38
			C10-O	1.46	1.43

	Internal angles (°)		Bond lengths (Å)	
C1	123.45		I-C1	2.11
C2	117.72		C1-C2	1.38
C3	120.28		C2 -C3	1.39
C4	120.52		C3 -C4	1.39
C5	120.30		C4 -C5	1.39
C6	117.70		C5-C6	1.39
I	96.96		C6-C1	1.39
C7	123.57		I-C7	2.15
C8	117.55		C7-C8	1.38
C9	120.57		C8-C9	1.39
C10	120.19		C9-C10	1.39
C11	120.57		C10-C11	1.39
C12	117.55		C11-C12	1.39
			C12-C7	1.38

Figure S1. Structural parameters and computed natural charges for **IM1**, **IM2** and diphenyliodonium ion at the ωB97X-D/6-31+G(d,p), LANL2DZ(I) level of theory with SMD CH_3CN solvation.

Comparison with benzyne generation from a diaryliodonium: Based on literature use of *t*-butoxide base, we computed the TS for *ortho*-C–H abstraction from diphenyl iodonium. In this case, concerted C–I abstraction occurs resulting in a single elementary step for benzyne formation (Figure S2).

Figure S2. Computed Gibbs free energy profile for benzyne formation from the diphenyliodonium ion at the ωB97X-D/6-31+G(d,p), LANL2DZ(I) level of theory with SMD CH_3CN solvation.

Structures of stationary points not shown in the main text: starting oxonium ion (**IM1**) and Diels-Alder **TS3**

Figure S3. Optimized geometries of aryl oxonium **IM1** and Diels-Alder **TS3**.

NBO analysis: We obtained second-order perturbative estimates of donor-acceptor (i.e., bond-antibond) interactions in the NBO basis, comparing the results obtained for oxonium ion **IM1**, the zwitterionic intermediate **IM2** formed after deprotonation, and the diphenyliodonium ion. These data show that the σ^*_{C1-O} orbital acts as a good acceptor, particularly in stabilizing the formation of intermediate **IM2** (**Table S1**, **Table S2**). Similar stabilizing delocalizations into both σ^*_{C-I} antibonds are observed in diphenyliodonium, but to a much lesser extent.

Table S2. Comparison of select hyperconjugative (σ-σ*) donor-acceptor delocalization energies (kcal/mol) into the C_1–X σ* antibonding orbital of **IM1**, **IM2** and diphenyliodonium.

Delocalization	Energy	Delocalization	Energy	Delocalization	Energy
C_{11}–C_{12}σ → C_1–Oσ*	10.2	C_{11}–C_{12}σ → C_1–Oσ*	8.9	C_5–C_6σ → C_1–Iσ*	5.8
C_{13}–C_{14}σ → C_1–Oσ*	10.2	C_{13}–C_{14}σ → C_1–Oσ*	8.9	C_7–C_8σ → C_1–Iσ*	4.1
C_5–C_6σ → C_1–Oσ*	7.3	C_4–C_5σ → C_1–Oσ*	17.2	C_2–C_3σ → C_1–Iσ*	6.2
C_6–Hσ → C_1–Oσ*	2.6				
C_2–C_3σ → C_1–Oσ*	7.2	C_2–C_3σ → C_1–Oσ*	8.3	C_{11}–C_{12}σ → C_7–Iσ*	5.7
C_2–Hσ→ C_1–Oσ*	2.5	C_2–Hσ → C_1–Oσ*	3.1	C_8–C_9σ → C_7–Iσ*	5.7

The negative charge formed on C6 in **IM2** following deprotonation is stabilized by further conjugative delocalization, as evident from the results of NBO analysis summarized in Table S2.

Table S3. Comparison of select conjugative (*n*-σ*) donor-acceptor delocalization energies (kcal/mol) into the C_1–X σ* antibonding orbital in **IM2**.

Delocalization	Energy (kcal/mol)
n → C_1–Oσ*	26.4
n → C_4–C_5σ*	12.6
n → C_1–C_2σ*	15.1
n → C_5–Hσ*	2.9

Table S4. Computed Gibbs Free Energies (in kcal/mol) for the conversion of oxonium **IM1** to **P** at L1(SMD$_{(CH3CN)}$/ωB97X-D/6-31+G**) and L2 (/SMD$_{(CH3CN)}$/ωB97X-D/Def2-QZVPP/SMD$_{(CH3CN)}$/ωB97X-D/6-31+G**)

Stationary Points	**L1**	**L2**	**L3**
IM1	0.0	0.0	0.0
TS1	9.9	10.6	9.7
IM2	8.3	7.9	7.3
TS2	10.6	9.3	8.8
IM3	-10.2	-15.2	-14.5
TS3	-3.1	-7.6	-7.0
P	-70.3	-70.9	-70.7

Table S5. Computed Gibbs Free Energies (in kcal/mol) for benzyne formation from diphenyliodonium at L1(SMD$_{(CH3CN)}$/ωB97X-D/6-31+G**) and L2 (SMD$_{(CH3CN)}$/ωB97X-D/Def2-QZVPP/SMD$_{(CH3CN)}$/ωB97X-D/6-31+G**)

Stationary Points	**L1**	**L2**	**L3**
IM1_I	0.0	0.0	0.0
TS1_I	0.6	3.4	2.9
IM2_I	-14.6	-6.0	-6.3

Cartesian Coordinates of stationary points for the conversion of aryloxonium ion **IM1** to Diels-Alder adduct **P**. Absolute electronic Energies in atomic units.

53
IM1 Energy: -3460.194813

C	-0.31735	2.27853	-0.70485
C	-0.32239	2.26413	0.75367
O	-1.10255	0.23246	0.00211
C	-0.75624	1.01611	1.16533
C	-0.77716	0.54401	2.46274
C	0.10297	3.17322	1.71644
C	-0.35873	1.49700	3.40356
C	0.06709	2.79173	3.06158
H	0.46948	4.15265	1.42551
H	-0.34102	1.19997	4.44948
C	-0.74670	1.03804	-1.14381
C	-0.75573	0.58998	-2.44976
C	-0.33323	1.56220	-3.36908
C	0.11343	3.20690	-1.64679
C	0.08649	2.85132	-2.99954
H	-0.30684	1.28495	-4.42022
H	0.47635	4.18109	-1.33455
C	-1.08325	-0.81754	-2.85691
H	-0.58917	-1.52814	-2.18283
H	-2.16172	-1.00249	-2.82111
H	-0.74478	-0.99398	-3.88046
C	-1.11475	-0.86920	2.84228
H	-2.19356	-1.04872	2.79442
H	-0.62045	-1.57270	2.16229
H	-0.78514	-1.06650	3.86492

53
TS1 Energy: -3460.170762

C	3.51635	-0.64874	-0.48477
C	3.33525	-0.39383	0.93786
O	1.37526	0.14793	-0.15440
C	2.04625	0.07472	1.12903
C	1.47353	0.39128	2.35067
C	4.16402	-0.56580	2.04239
C	2.34414	0.21057	3.43231
C	3.66412	-0.25172	3.30679
H	5.17494	-0.94086	1.91780
H	1.96322	0.43439	4.42570
C	2.33335	-0.33377	-1.13412
C	2.08538	-0.50244	-2.48744
C	3.18867	-1.00263	-3.19099
C	4.58270	-1.15309	-1.22263
C	4.42042	-1.32220	-2.59793
H	3.07044	-1.16249	-4.25996
H	5.51536	-1.41314	-0.73197
C	0.78562	-0.21111	-3.18145
H	-0.06428	-0.62652	-2.63272
H	0.62421	0.86708	-3.27739
H	0.80334	-0.64298	-4.18433
C	0.06234	0.86636	2.54424
H	-0.05486	1.88527	2.15790
H	-0.64891	0.20611	2.03049
H	-0.17491	0.87538	3.61080

C	0.51087	3.83663	-4.05671
H	1.22516	4.56100	-3.65690
H	0.96638	3.32967	-4.91162
H	-0.35739	4.39370	-4.42633
C	0.48808	3.75463	4.14051
H	0.95696	3.23116	4.97813
H	1.19030	4.49763	3.75382
H	-0.38365	4.29097	4.53192
C	-2.41469	-0.39942	-0.00871
C	-2.40585	-1.77594	-0.02796
C	-3.53344	0.40957	0.00130
C	-3.64648	-2.40472	-0.03853
H	-1.43400	-2.28599	-0.03697
C	-4.76635	-0.22995	-0.00931
H	-3.45618	1.49129	0.01689
C	-4.81364	-1.63062	-0.02934
H	-3.71059	-3.48702	-0.05431
H	-5.68149	0.35073	-0.00243
C	-6.09341	-2.28643	-0.04061
N	-7.12480	-2.81575	-0.04964
P	1.82198	-1.73635	-0.03635
O	0.45953	-2.47219	-0.09292
O	2.70237	-2.05801	-1.30761
O	2.64732	-2.14249	1.24789
O	1.62228	-0.17330	0.01049
K	4.67749	-3.12279	-0.02057
K	2.55140	0.23797	2.35646
K	2.59302	0.37342	-2.29534

53

IM2 Energy: -3460.176208

C	0.34038	2.81468	-0.58479
C	0.57749	2.53159	0.82108
O	-0.84389	0.94906	-0.00514
C	-0.17162	1.41583	1.16978
C	-0.20703	0.84676	2.43840
C	1.38497	3.14723	1.77649
C	0.60629	1.50743	3.36906
C	1.39506	2.63290	3.07285
H	1.98652	4.01095	1.51125
H	0.63188	1.10947	4.38030
C	-0.53971	1.86152	-1.07385
C	-0.99850	1.80147	-2.38509
C	-0.49153	2.82543	-3.19408
C	0.82693	3.80829	-1.43070
C	0.40121	3.81730	-2.75604
H	-0.80951	2.84199	-4.23365
H	1.52066	4.55511	-1.05737
C	-1.93136	0.77395	-2.96403
H	-1.54171	-0.23685	-2.82389
H	-2.91998	0.81714	-2.49874
H	-2.04953	0.95589	-4.03432
C	-0.96839	-0.38591	2.82938
H	-2.04905	-0.24522	2.74586
H	-0.65978	-1.20035	2.17209
H	-0.73186	-0.64958	3.86217
C	0.88031	4.86876	-3.72244
H	1.61289	5.53094	-3.25458
C	5.54375	-1.84961	-3.45178
H	6.40511	-2.13276	-2.84196
H	5.22155	-2.72597	-4.02292
H	5.86946	-1.09143	-4.17168
C	4.52260	-0.39877	4.53580
H	3.99528	-0.95320	5.31803
H	5.45360	-0.92312	4.30700
H	4.77789	0.58423	4.94604
C	0.66715	1.45141	-0.46846
C	-0.66904	1.33697	-0.72806
C	1.47925	2.57040	-0.44141
C	-1.26584	2.58071	-0.99274
H	-1.32971	0.06446	-0.83945
C	0.84770	3.78017	-0.69814
H	2.54264	2.52294	-0.22836
C	-0.52889	3.77546	-0.96872
H	-2.32479	2.63406	-1.24090
H	1.40913	4.70739	-0.69020
C	-1.19437	5.02167	-1.23336
N	-1.74085	6.02281	-1.44548
P	-3.02900	-1.21718	0.05619
O	-1.82525	-0.98265	-0.99374
O	-3.51267	-2.66954	-0.17008
O	-4.15410	-0.17486	-0.18562
O	-2.39452	-1.03034	1.46517
K	-5.96518	-1.97348	-0.82281
K	-3.30066	1.43554	1.73524
K	-0.78386	-3.09108	0.56181

53

TS2 Energy: -3460.171142

C	-1.78565	-2.34784	-0.55640
C	-1.85851	-1.96557	0.84105
O	0.17010	-1.31748	0.01963
C	-0.64236	-1.36285	1.15949
C	-0.33793	-0.86661	2.42820
C	-2.86437	-2.07596	1.80343
C	-1.36730	-1.00653	3.36590
C	-2.61619	-1.59346	3.08667
H	-3.81780	-2.53064	1.55163
H	-1.18858	-0.62660	4.36905
C	-0.53525	-1.94771	-1.01991
C	-0.10492	-2.13965	-2.33347
C	-1.03727	-2.78307	-3.15303
C	-2.68915	-2.98010	-1.41006
C	-2.30958	-3.20591	-2.72870
H	-0.75580	-2.95986	-4.18866
H	-3.66552	-3.28701	-1.04681
C	1.22324	-1.71204	-2.89500
H	1.38659	-0.63970	-2.76235
H	2.05499	-2.23671	-2.41656
H	1.25613	-1.93224	-3.96443
C	0.94843	-0.18876	2.79980
H	1.79469	-0.88121	2.77844
H	1.13287	0.62150	2.09277
H	0.87061	0.22704	3.80682
C	-3.23575	-3.88519	-3.70473
H	-4.17610	-4.16863	-3.22497

H	1.34382	4.40835	-4.60079
H	0.04354	5.47995	-4.07660
C	2.22803	3.27087	4.15336
H	2.73749	2.51443	4.75739
H	2.97813	3.94228	3.72842
H	1.59329	3.85653	4.82734
C	-2.17189	0.20404	0.05844
C	-2.11322	-1.11637	-0.28456
C	-3.22294	1.01731	0.44188
C	-3.39772	-1.69499	-0.20477
H	-0.33181	-1.27127	-1.05820
C	-4.46140	0.39426	0.51365
H	-3.09900	2.07011	0.67518
C	-4.53597	-0.96861	0.18825
H	-3.54854	-2.74334	-0.46224
H	-5.34594	0.94680	0.80948
C	-5.80829	-1.63390	0.25268
N	-6.82951	-2.18291	0.30218
P	1.65215	-2.00854	-0.49959
O	0.58577	-1.17798	-1.43231
O	3.03672	-1.40808	-0.81080
O	1.54106	-3.49864	-0.89522
O	1.21839	-1.77789	0.96479
K	4.00242	-3.64779	-1.83807
K	-0.61819	-3.73306	0.75345
K	3.01745	0.09582	1.42826

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Dibenzofuran Energy: -694.427441

C	0.72653	-0.61234	-0.00004
C	-0.72653	-0.61234	-0.00005
O	0.00000	1.56168	-0.00003
C	-1.09530	0.73474	-0.00003
C	-2.41697	1.17675	0.00003
C	-1.71746	-1.59998	0.00000
C	-3.37626	0.16512	0.00006
C	-3.05401	-1.20905	0.00005
H	-1.44914	-2.65288	0.00000
H	-4.42602	0.45205	0.00013
C	1.09530	0.73474	-0.00003
C	2.41697	1.17675	-0.00001
C	3.37626	0.16513	0.00000
C	1.71747	-1.59998	-0.00003
C	3.05401	-1.20905	-0.00000
H	4.42603	0.45204	0.00002
H	1.44914	-2.65288	-0.00005
C	-2.76105	2.63930	0.00005
H	-2.34788	3.14090	0.88175
H	-2.34821	3.14084	-0.88183
H	-3.84453	2.78115	0.00025
C	2.76103	2.63931	-0.00003
H	-3.46772	-3.22502	-4.54720
H	-2.77564	-4.78963	-4.11629
C	-3.65656	-1.69439	4.17219
H	-3.77957	-0.73854	4.69088
H	-4.62514	-1.99347	3.76383
H	-3.36072	-2.43693	4.92124
C	2.06594	-1.21254	0.07652
C	2.54155	-0.04633	-0.26295
C	2.51568	-2.44446	0.46020
C	3.95314	-0.09118	-0.21238
H	0.83808	0.90071	-1.11274
C	3.91158	-2.44739	0.50838
H	1.90884	-3.30908	0.69768
C	4.61319	-1.27458	0.17294
H	4.56061	0.77284	-0.47563
H	4.44291	-3.34756	0.79743
C	6.04926	-1.28772	0.21995
N	7.20881	-1.28617	0.25526
P	-0.44320	2.56051	-0.53455
O	0.02366	1.29359	-1.48453
O	-1.93546	2.76458	-0.84707
O	0.42962	3.77210	-0.92685
O	-0.18381	2.11876	0.92001
K	-1.59307	5.17514	-1.89567
K	2.31286	3.05040	0.88377
K	-2.67599	1.32618	1.34134

11

P Energy: -323.053409

C	2.12431	0.20155	0.00002
C	1.46800	1.26120	0.00002
C	1.70492	-1.11234	-0.00001
C	0.08935	1.34216	-0.00002
C	0.30045	-1.14330	-0.00001
H	2.31270	-2.00786	-0.00000
C	-0.47344	0.04086	-0.00001
H	-0.52271	2.23630	-0.00001
H	-0.20661	-2.10345	0.00000
C	-1.90529	-0.08121	0.00000
N	-3.06188	-0.16835	0.00001

9

Furan Energy: -229.963678

C	1.09332	-0.34850	-0.00029
C	0.71801	0.95709	0.00018
C	-0.71803	0.95707	-0.00013
C	-1.09331	-0.34853	-0.00017
O	0.00001	-1.15463	0.00038
H	2.05118	-0.84685	-0.00042
H	1.37698	1.81401	0.00033
H	-1.37702	1.81398	-0.00022
H	-2.05116	-0.84689	-0.00025

H	2.34815	3.14083	-0.88191
H	2.34788	3.14092	0.88167
H	3.84451	2.78118	0.00013
C	-4.16373	-2.23159	-0.00005
H	-3.76364	-3.24916	0.00116
H	-4.80436	-2.11793	0.88123
H	-4.80276	-2.11945	-0.88269
C	4.16373	-2.23158	0.00008
H	3.76364	-3.24916	-0.00037
H	4.80389	-2.11842	-0.88161
H	4.80324	-2.11895	0.88231

20

TS3 Energy: -553.022417

C	1.99391	-1.40499	0.74517
C	2.52691	-1.27132	-0.49902
C	2.22437	-0.15701	1.41061
C	2.87760	0.63131	0.51526
O	3.07752	-0.04027	-0.64691
H	1.93403	0.11899	2.41461
H	3.26057	1.64003	0.55477
C	-0.71824	2.00812	0.18679
C	-0.01234	1.37122	-0.81302
C	-0.24340	0.29719	-1.40370
C	-1.32143	-0.52994	-1.15806
C	-2.12938	0.01405	-0.12897
C	-1.84255	1.23742	0.52187
H	-0.48197	2.94481	0.67523
H	-1.56054	-1.46803	-1.64526
H	-2.50989	1.58683	1.30393
H	1.49229	-2.27882	1.13673
H	2.60112	-1.93189	-1.34989
C	-3.29930	-0.71492	0.27583
N	-4.24181	-1.31092	0.59553

9

K_3PO_4H Energy: -2442.678163

H	0.00511	-0.72124	2.83102
P	0.00008	0.02561	0.77427
O	0.00068	0.15353	2.42393
O	-0.00127	1.48396	0.28766
O	-1.27463	-0.74003	0.36314
O	1.27575	-0.73823	0.36255
K	-2.44834	1.37104	-0.74212
K	0.00173	-2.79476	-0.72264
K	2.44606	1.37442	-0.74279

20

P Energy: -553.138951

C	2.36683	-1.05417	0.96013
C	1.63795	-1.22842	-0.38005
C	2.66902	0.24225	1.03294
C	2.12687	0.85964	-0.26513
O	2.31365	-0.23761	-1.17972
H	3.12359	0.79994	1.84152
H	2.58504	1.77626	-0.62868
C	-0.37071	1.79438	0.01282
C	0.59979	0.82900	-0.14943
C	0.28020	-0.53536	-0.22649
C	-1.01760	-0.97540	-0.14550
C	-2.01870	0.01219	0.01285
C	-1.70581	1.37183	0.09106
H	-0.12564	2.84975	0.07367
H	-1.28190	-2.02624	-0.20185
H	-2.50183	2.09943	0.20924
H	2.51103	-1.83693	1.69359
H	1.65173	-2.20896	-0.84957
C	-3.39284	-0.39377	0.09150
N	-4.50303	-0.72649	0.15595

Coordinates of Stationary Points for the Conversion of Diphenyliodonium ion **IM1-I** to Benzyne and the Total Electronic Energy (in Hartree)

37

IM1-I Energy: -707.439350

C	-1.85975	-2.28714	-0.17122
C	-0.74949	-1.55974	0.23374
C	-0.57793	-1.09296	1.52623
C	-2.84852	-2.55181	0.77574
C	-1.58054	-1.36922	2.45662
C	-2.71121	-2.09319	2.08467
H	-3.72958	-3.11174	0.47879
H	-1.47138	-1.00461	3.47304
C	2.01803	0.07249	-0.05563
C	1.65381	1.39696	0.11838
C	3.14511	-0.52346	0.50106
C	2.49791	2.17353	0.91777
H	0.70258	1.77125	-0.33310
C	3.96688	0.28155	1.28815

37

TS1-I Energy: -707.434459

C	-2.01548	-2.18077	-0.17405
C	-0.84883	-1.57428	0.27338
C	-0.69950	-1.08048	1.56010
C	-3.08190	-2.28902	0.71788
C	-1.78123	-1.19533	2.43408
C	-2.96717	-1.79561	2.01654
H	-4.00536	-2.75279	0.38594
H	-1.68820	-0.80596	3.44296
C	1.97686	0.03755	0.00379
C	1.53177	1.33171	0.02821
C	3.10341	-0.50332	0.61799
C	2.35406	2.18698	0.78867
H	0.40449	1.71719	-0.57219
C	3.88393	0.38998	1.34877

H	3.37901	-1.56970	0.33794
C	3.64197	1.62384	1.49457
H	2.24995	3.21723	1.08878
H	4.85591	-0.14555	1.74129
O	-0.90218	1.83356	-1.09102
H	-3.48867	-2.29628	2.81414
H	0.29341	-0.51629	1.81618
H	4.28688	2.24243	2.11165
I	0.73006	-1.13764	-1.25297
H	-1.97210	-2.63079	-1.19409
C	-1.93602	2.38581	-0.38315
C	-1.49639	2.76463	1.05627
H	-2.30993	3.20215	1.65218
H	-1.13311	1.87136	1.58018
H	-0.67425	3.49128	1.01833
C	-3.12122	1.39426	-0.26324
H	-3.98743	1.81872	0.26528
H	-3.44591	1.08856	-1.26603
H	-2.80048	0.49440	0.27508
C	-2.45870	3.67178	-1.07159
H	-2.79767	3.43254	-2.08755
H	-3.29234	4.14475	-0.53203
H	-1.64426	4.40272	-1.15467
H	3.36576	-1.55328	0.54555
C	3.50520	1.73403	1.43199
H	2.08107	3.23766	0.87499
H	4.77721	0.03324	1.85246
O	-0.63978	1.99422	-1.21731
H	-3.80456	-1.87543	2.70245
H	0.21821	-0.60191	1.88423
H	4.11635	2.42675	2.00477
I	0.75503	-1.39523	-1.12627
H	-2.10937	-2.54745	-1.19078
C	-1.69749	2.54838	-0.50168
C	-1.28351	2.90596	0.94159
H	-2.11513	3.35708	1.49724
H	-0.95974	2.01008	1.48458
H	-0.45030	3.61903	0.93665
C	-2.87153	1.55149	-0.43712
H	-3.75109	1.97417	0.06707
H	-3.16457	1.25590	-1.45164
H	-2.56807	0.64870	0.10394
C	-2.17359	3.83137	-1.20849
H	-2.47554	3.59936	-2.23680
H	-3.02473	4.29975	-0.69623
H	-1.35483	4.55935	-1.25425

37

IM2-I Energy: -707.459379

C	0.27570	-2.15050	1.41270
C	0.96567	-1.04797	0.91365
C	0.96419	0.16966	1.58776
C	-0.41814	-2.02774	2.61627
C	0.26273	0.27897	2.78890
C	-0.42618	-0.81626	3.30592
H	-0.95712	-2.88483	3.00900
H	0.25731	1.22867	3.31552
C	0.47603	2.37853	-1.29108
C	-0.63959	2.36293	-0.72995
C	1.66431	2.99374	-0.97043
C	-0.89391	3.05841	0.45280
H	-2.41727	1.18542	-1.45440
C	1.47329	3.72119	0.22308
H	2.60578	2.95415	-1.50318
C	0.24263	3.75128	0.90601
H	-1.83707	3.07384	0.98752
H	2.31652	4.27505	0.62729
O	-3.27770	0.75274	-1.54801
H	-0.97109	-0.72552	4.24056
H	1.49764	1.02630	1.18968
H	0.16991	4.32842	1.82400
I	2.04619	-1.23227	-0.90348
H	0.27735	-3.09388	0.87718
C	-3.23511	-0.48373	-0.82036
C	-2.94584	-0.20503	0.65629
H	-2.99318	-1.12856	1.24239
H	-1.94325	0.21897	0.78311
H	-3.67821	0.50157	1.06150
C	-2.15288	-1.38804	-1.41383
H	-2.10868	-2.34586	-0.88394

H	-2.35525	-1.58390	-2.47213
H	-1.16832	-0.91346	-1.33217
C	-4.61734	-1.10372	-0.99317
H	-4.83390	-1.26752	-2.05398
H	-4.67303	-2.06690	-0.47576
H	-5.38814	-0.44404	-0.58088

6 Crystallographic Information

Single crystal X-ray diffraction studies were carried out by Owen A. Smith using a (Rigaku) Oxford Diffraction/Agilent Supernova A diffractometer (Cu Kα radiation, λ = 1.54184 Å) within the Department of Chemistry, University of Oxford. Single crystals were mounted using the oil-drop method in perfluoropolyether oil on a MiTeGen 200 µm loop and flash-cooled to 150 K using an Oxford CryoSystems CryoStream N_2 open-flow cooling device.[22] The raw frame data were reduced using CrysalisPro. SuperFlip[23] embedded within CRYSTALS[24,25] was used to obtain an ab initio solution. The structure refinement suite, CRYSTALS was used to optimise each of the structures by full-matrix least-squares. In general, hydrogen atoms were visible in the difference Fourier map, but were placed at geometric positions and refined as part of a separate block before inclusion in the final refinement using a riding model.[26] Compounds **4a**, **4k** and **6** exhibited signs of disorder which was modelled using a split site model as per the CIF.

Raw frame data, reduced intensity data and final CIF files for all structures are available on request.

2,4,6,8-Tetramethyl-5-(4-nitrophenyl)-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, **4a**:

CCDC 2109776. $C_{22}H_{20}BF_4NO_3$: Yellow blocks were grown by vapour diffusion of Et_2O into a solution of **4a** (5 mg) in acetone (0.6 mL) over 48 h.

Crystal System	Monoclinic
Space Group	P 2_1/c
Unit Cell Dimensions	a = 12.5037(3) Å α = 90°
	b = 10.5734(2) Å β = 101.975(2)°
	c = 15.9053(4) Å γ = 90°
Volume	2057.03(8) Å^3
Z Density (Calculated)	1.399 Mg m^{-3}
Absorption Coefficient	0.994 mm^{-1}
Crystal Size	0.07 × 0.13 × 0.15 mm^3
Theta range for data collection	3.613 to 76.208°
Index Ranges	-15<=h<=15, -13<=k<=13, -17<=l<=19
Reflections Collected	21741
Independent Reflections	4268 [R(int)] = 0.041]
Completeness to theta = 74.684°	99.7 %
Absorption Correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.9996
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.1054
R indices (all data)	R1 = 0.0512, wR2 = 0.1172

2-Acetamido-4,6,8-trimethyl-5-phenyl-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4j:

CCDC 2109774. $C_{23}H_{22}BF_4NO_2$: Crystals of X-ray quality were grown by vapour diffusion of Et_2O into a solution of **4j** (5 mg) in CH_2Cl_2 (0.6 mL).

Crystal System	Monoclinic
Space Group	P 2_1/c
Unit Cell Dimensions	a = 7.9272(2) Å α = 90°
	b = 13.0127(3) Å β = 97.1934(19)°
	c = 19.8955(4) Å γ = 90°
Volume	2036.15(8) Å^3
Z	4
Density (Calculated)	1.407 Mg m^{-3}
Absorption Coefficient	0.962 mm^{-1}
Crystal Size	0.03 × 0.08 × 0.21 mm^3
Theta range for data collection	4.069 to 76.334°
Index Ranges	-9<=h<=9, -16<=k<=16, -21<=l<=24
Reflections Collected	22777
Independent Reflections	4231 [R(int)] = 0.042]
Completeness to theta = 74.808°	99.8%
Absorption Correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.0000
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.1060
R indices (all data)	R1 = 0.0515, wR2 = 0.1185

2,4,6,8-tetramethyl-5-(2-nitrophenyl)-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, 4k:

CCDC 2251371. $C_{22}H_{20}BF_4NO_3$: Crystals of X-ray quality were grown by vapour diffusion of Et_2O into a solution of **4k** (5 mg) in CH_2Cl_2 (0.6 mL).

Crystal System	Orthorhombic
Space Group	Pbca
Unit Cell Dimensions	a = 13.2608(2) Å α = 90°
	b = 13.8324(2) Å β = 90°
	c = 22.1520(3) Å γ = 90°
Volume	4063.31(10) Å^3
Z	8
Density (Calculated)	1.416 Mg m^{-3}
Absorption Coefficient	1.006 mm^{-1}
Crystal Size	0.12 × 0.15 × 0.20 mm^3
Theta range for data collection	3.991 to 76.079°
Index Ranges	-11<=h<=16, -15<=k<=17, -27<=l<=19
Reflections Collected	22796
Independent Reflections	4204 [R(int)] = 0.037]
Completeness to theta = 73.796°	99.7%
Absorption Correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.9912
Final R indices [I>2sigma(I)]	R1 = 0.0526, wR2 = 0.1433
R indices (all data)	R1 = 0.0610, wR2 = 0.1547

5-(2-Cyanophenyl)-2,4,6,8-tetramethyl-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4l:

CCDC 2109775. $C_{23}H_{20}BF_4NO$: Crystals of X-ray quality were grown by vapour diffusion of Et_2O into a solution of **4l** (5 mg) in MeCN (0.6 mL).

Crystal System	Monoclinic
Space Group	P 2_1
Unit Cell Dimensions	a = 7.9170(1) Å α = 90°
	b = 14.4039(2) Å β = 98.7111(12)°
	c = 9.1419(1) Å γ = 90°
Volume	1030.48(2) Å^3
Z	2
Density (Calculated)	1.332 Mg m^{-3}
Absorption Coefficient	0.891 mm^{-1}
Crystal Size	0.04 × 0.10 × 0.11 mm^3
Theta range for data collection	4.894 to 76.324°
Index Ranges	-9<=h<=9 , -18<=k<=18 , -11<=l<=11
Reflections Collected	22487
Independent Reflections	4268 [R(int)] = 0.026]
Completeness to theta = 76.324°	99.5%
Absorption Correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.0000
Final R indices [I>2sigma(I)]	R1 = 0.0421, wR2 = 0.1198
R indices (all data)	R1 = 0.0432, wR2 = 0.1224

5-(2-(tert-Butyl)-4-methoxypyrimidin-5-yl)-2,4,6,8-tetramethyl-5H-dibenzo[b,d]furan-5-ium tetrafluoroborate, 6:

CCDC 2251372. $C_{25}H_{29}BF_4N_2O_2$: Crystals of X-ray quality were grown by vapour diffusion of Et_2O into a solution of **6** (5 mg) in CH_2Cl_2 (0.6 mL).

Crystal System	Monoclinic
Space Group	P 2_1/c
Unit Cell Dimensions	a = 11.8067(1) Å α = 90°
	b = 11.8614(1) Å β = 97.1934(19)°
	c = 19.3444(2) Å γ = 90°
Volume	2699.33(4) Å^3
Z	4
Density (Calculated)	1.273 Mg m^{-3}
Absorption Coefficient	0.831 mm^{-1}
Crystal Size	0.30 × 0.32 × 0.35 mm^3
Theta range for data collection	3.757 to 76.143°
Index Ranges	-10<=h<=14, -14<=k<=14, -24<=l<=24
Reflections Collected	32228
Independent Reflections	5598 [R(int)] = 0.031]
Completeness to theta = 74.620°	99.7%
Absorption Correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.0011
Final R indices [I>2sigma(I)]	R1 = 0.0529, wR2 = 0.1373
R indices (all data)	R1 = 0.0566, wR2 = 0.1420

7 NMR Spectra

2-bromo-4,6-dimethylphenol, S1:

2-Bromo-6-methyl-4-nitroaniline, S2:

1-Bromo-2-chloro-3-methyl-5-nitrobenzene, S3:

1-((2-Bromo-4,6-dimethylphenyl)diazenyl)pyrrolidine, C1:

1-bromo-3,5-dimethyl-2-(2-cyanophenoxy)benzene, 1a:

4-(2-Bromo-4,6-dimethylphenoxy)aniline, 1ab:

***N*-(4-(2-Bromo-4,6-dimethylphenoxy)phenyl)acetamide, 1b:**

Ethyl 4-(2-bromo-6-methyl-4-nitrophenoxy)benzoate, 1c:

1-(4-(2-bromo-4,6-dimethylphenoxy)phenyl)ethan-1-one, 1d:

4-(2-bromo-4,6-dimethylphenoxy)benzaldehyde, 1e:

1-bromo-2-(4-chlorophenoxy)-3,5-dimethylbenzene, 1f:

(4-(2-bromo-4,6-dimethylphenoxy)phenyl)methanol, 1h:

4-(2-bromo-6-methyl-4-nitrophenoxy)-1,1'-biphenyl, 1i:

1-Bromo-3-methyl-5-nitro-2-phenoxybenzene, 1j:

1-bromo-3,5-dimethyl-2-(2-nitrophenoxy)benzene, 1k:

2-(2-bromo-4,6-dimethylphenoxy)benzonitrile, 1l:

1-bromo-3-methyl-5-nitro-2-(o-tolyloxy)benzene, 1m:

2-(2-Bromo-4,6-dimethylphenoxy)benzaldehyde, 1na:

2-(2-Bromo-4,6-dimethylphenoxy)phenol, 1nb:

1-Bromo-2-(2-methoxyphenoxy)-3,5-dimethylbenzene, 1n:

1-(2-Bromo-6-methyl-4-nitrophenoxy)naphthalene, 1o:

1-bromo-2-(3-fluorophenoxy)-3-methyl-5-nitrobenzene, 1p:

-110.2
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-22
ppm

1-bromo-3-methyl-5-nitro-2-(3-(trifluoromethyl)phenoxy)benzene, 1q:

-62.7
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
ppm

1-bromo-2-(3-(tert-butyl)phenoxy)-3-methyl-5-nitrobenzene, 1r:

methyl (E)-3-(4-hydroxyphenyl)acrylate, 1s:

methyl 3-(4-(2-bromo-6-methyl-4-nitrophenoxy)phenyl)propanoate, 1t:

N-(4-(2-bromo-6-methyl-4-nitrophenoxy)-3-methoxybenzyl)-8-methylnonanamide, 1u:

Propyl 2',4'-difluoro-4-hydroxy-[1,1'-biphenyl]-3-carboxylate, 1va:

-111.5
-111.5
-113.7
-113.7
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

Propyl 4-(2-bromo-6-methyl-4-nitrophenoxy)-2',4'-difluoro-[1,1'-biphenyl]-3-carboxylate, 1v:

-110.7
-110.7
-113.5
-113.5
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

3,3',5,5'-Tetramethyl-2'-(4-nitrophenoxy)-[1,1'-biphenyl]-2-amine, 3a:

***N*-(4-((2'-Amino-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-yl)oxy)phenyl)acetamide, 3b:**

***N*-(2'-amino-6-(3-(dimethylamino)phenoxy)-3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl)acetamide, 3c:**

1-(4-((3,3',5,5'-tetramethyl-2'-(pyrrolidin-1-yldiazenyl)-[1,1'-biphenyl]-2-yl)oxy)phenyl)ethan-1-one, 3d:

4-((3,3’,5,5’-Tetramethyl-2’-(pyrrolidin-1-yldiazenyl)-[1,1’-biphenyl]-2-yl)oxy) benzaldehyde, 3e:

1-Bromo-2-(4-chlorophenoxy)-3,5-dimethylbenzene, 3f:

3,3',5,5'-Tetramethyl-2'-(4-(methylsulfonyl)phenoxy)-[1,1'-biphenyl]-2-amine, 3g:

(4-((2'-Amino-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-yl)oxy)phenyl)methanol, 3h:

***N*-(6-([1,1'-biphenyl]-4-yloxy)-2'-amino-3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl)acetamide, 3i:**

N-(2'-amino-3',5,5'-trimethyl-6-phenoxy-[1,1'-biphenyl]-3-yl)acetamide, 3j:

3,3',5,5'-tetramethyl-2'-(2-nitrophenoxy)-[1,1'-biphenyl]-2-amine, 3k:

2-((2'-Amino-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-yl)oxy)benzonitrile, 3l:

***N*-(2'-amino-3',5,5'-trimethyl-6-(o-tolyloxy)-[1,1'-biphenyl]-3-yl)acetamide, 3m:**

2’-(2-Methoxyphenoxy)-3,3’,5,5’-tetramethyl-[1,1’-biphenyl]-2-amine, 3n:

***N*-(2'-Amino-3',5,5'-trimethyl-6-(naphthalen-1-yloxy)-[1,1'-biphenyl]-3-yl)acetamide, 3o:**

N **-(2'-Amino-6-(3-fluorophenoxy)-3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl)acetamide, 3p:**

-112.1
-112.1
-112.1
-112.1
-112.1
-112.2
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
ppm

N **-(2'-Amino-3',5,5'-trimethyl-6-(3-(trifluoromethyl)phenoxy)-[1,1'-biphenyl]-3-yl) acetamide, 3q:**

-62.7
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
ppm

***N*-(2'-amino-6-(3-(tert-butyl)phenoxy)-3',5,5'-trimethyl-[1,1'-biphenyl]-3-yl)acetamide, 3r:**

Methyl 3-(4-((5-acetamido-2'-amino-3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)phenyl)propanoate, 3s:

Methyl 3-(4-((5-acetamido-2'-amino-3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)phenyl)propanoate, 3t:

N-(4-((5-acetamido-2'-amino-3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)-3-methoxybenzyl)-8-methylnonanamide, 3u:

Propyl 4-((5-acetamido-2'-amino-3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)-2',4'-difluoro-[1,1'-biphenyl]-3-carboxylate, 3v:

-111.4
-111.4
-113.6
-113.6
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

2,4,6,8-Tetramethyl-5-(4-nitrophenyl)-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4a:

-151.8
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

5-(4-Acetamidophenyl)-2,4,6,8-tetramethyl-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4b:

-151.8
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
ppm

2-acetamido-5-(4-(ethoxycarbonyl)phenyl)-4,6,8-trimethyl-5H-dibenzo[b,d]furan-5-ium tetrafluoroborate, 4c:

151.7
4.00
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

5-(4-Acetylphenyl)-2,4,6,8-tetramethyl-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4d:

-151.9
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
ppm

5-(4-Formylphenyl)-2,4,6,8-tetramethyl-5*H* dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4e:

-151.8
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

5-(4-Chlorophenyl)-2,4,6,8-tetramethyl-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4f:

-151.8
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
ppm

2,4,6,8-Tetramethyl-5-(4-(methylsulfonyl)phenyl)-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4g:

-151.7
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
ppm

5-(4-(Hydroxymethyl)phenyl)-2,4,6,8-tetramethyl-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4h:

-151.8
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

5-([1,1'-biphenyl]-4-yl)-2-acetamido-4,6,8-trimethyl-5H-dibenzo[b,d]furan-5-ium tetrafluoroborate, 4i:

-151.5
4.00
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

2-acetamido-4,6,8-trimethyl-5-phenyl-5H-dibenzo[b,d]furan-5-ium tetrafluoroborate, 4j:

-151.7
4.00
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

2,4,6,8-tetramethyl-5-(2-nitrophenyl)-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, 4k:

-151.8
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
ppm

5-(2-Cyanophenyl)-2,4,6,8-tetramethyl-5H-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4l:

-146.4
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

2-Acetamido-4,6,8-trimethyl-5-(o-tolyl)-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4m:

-151.7
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
ppm

5-(2-Methoxyphenyl)-2,4,6,8-tetramethyl-5H-dibenzo[b,d]furan-5-ium tetrafluoroborate, 4n:

-151.8
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
ppm

1-Acetamido-4,6,8-trimethyl-5-(naphthalen-1-yl))-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4o:

-151.8
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
ppm

2-Acetamido-5-(3-fluorophenyl)-4,6,8-trimethyl–5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4p:

-106.0
-151.7
0.62
4.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

2-Acetamido-4,6,8-trimethyl-5-(3-(trifluoromethyl)phenyl)-5*H*-dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 4q:

-63.3
-151.6
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
ppm

2-acetamido-5-(3-(tert-butyl)phenyl)-4,6,8-trimethyl-5H-dibenzo[b,d]furan-5-ium tetrafluoroborate, 4r:

-151.7
4.00
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

(*E*)-2-acetamido-5-(4-(3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-4,6,8-trimethyl-5H-dibenzo[b,d]furan-5-ium tetrafluoroborate, 4s:

151.7
4.07
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

2-Acetamido-5-(4-(3-methoxy-3-oxopropyl)phenyl)-4,6,8-trimethyl-5H-dibenzo[b,d]furan-5-ium tetrafluoroborate, 4t:

151.7
4.07
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

2-acetamido-5-(2-methoxy-4-((8-methylnonanamido)methyl)phenyl)-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, 4u:

-151.6
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

2-Acetamido-5-(2',4'-difluoro-3-(propoxycarbonyl)-[1,1'-biphenyl]-4-yl)-4,6,8-trimethyl-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate, 4v:

109.4
109.5
109.5
114.3
114.3
114.3
114.3
114.3
114.4
114.4
151.5
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

6-Nitro-1,4-dihydro-1,4-epoxynaphthalene, 5a:

N **-(1,4-Dihydro-1,4-epoxynaphthalen-6-yl)acetamide, 5b:**

Ethyl 1,4-dihydro-1,4-epoxynaphthalene-6-carboxylate, 5c:

1-(1,4-Dihydro-1,4-epoxynaphthalen-6-yl)ethan-1-one, 5d:

1,4-Dihydro-1,4-epoxynaphthalene-6-carbaldehyde, 5e:

6-Chloro-1,4-dihydro-1,4-epoxynaphthalene, 5f:

6-(Methylsulfonyl)-1,4-dihydro-1,4-epoxynaphthalene, 5g:

(1,4-Dihydro-1,4-epoxynaphthalen-6-yl)methanol, 5h:

6-phenyl-1,4-dihydro-1,4-epoxynaphthalene, 5i:

1,4-dihydro-1,4-epoxynaphthalene, 5j:

6-Nitro-1,4-dihydro-1,4-epoxynaphthalene, 5k:

1,4-dihydro-1,4-epoxynaphthalene-5-carbonitrile, 5l:

5-Methyl-1,4-dihydro-1,4-epoxynaphthalene, 5m:

5-Methoxy-1,4-dihydro-1,4-epoxynaphthalene, 5n:

1,4-Dihydro-1,4-epoxyphenanthrene, 5o:

5-Fluoro-1,4-dihydro-1,4-epoxynaphthalene, 5p:

-120.8
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

5-(Trifluoromethyl)-1,4-dihydro-1,4-epoxynaphthalene, 5q:

-60.8
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
ppm

6-(tert-butyl)-1,4-dihydro-1,4-epoxynaphthalene, 5r:

Methyl (E)-3-(1,4-dihydro-1,4-epoxynaphthalen-6-yl)acrylate, 5t:

methyl 3-(1,4-dihydro-1,4-epoxynaphthalen-6-yl)propanoate, 5t:

^{13}C NMR (101MHz, $CDCl_3$):

N-((8-methoxy-1,4-dihydro-1,4-epoxynaphthalen-6-yl)methyl)-8-methylnonanamide, 5u:

Propyl 7-(2,4-difluorophenyl)-1,4-dihydro-1,4-epoxynaphthalene-5-carboxylate, 5v:

110.7
110.7
110.7
110.8
113.2
113.2
113.2
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

Ethyl 2-(2-bromo-4,6-dimethylphenoxy)acetate, 6a:

5-(2-bromo-4,6-dimethylphenoxy)-2-(tert-butyl)pyrimidin-4(3H)-one, 6b:

5-(2-Bromo-4,6-dimethylphenoxy)-2-(tert-butyl)-4-methoxypyrimidine, 6c:

2'-((2-(Tert-butyl)-4-methoxypyrimidin-5-yl)oxy)-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-amine, 6d:

5-(2-(Tert-butyl)-4-methoxypyrimidin-5-yl)-2,4,6,8-tetramethyl-5H-dibenzo[b,d]furan-5-ium tetrafluoroborate, 6:

151.8
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

2-(tert-butyl)-4-methoxy-5,8-dihydro-5,8-epoxyquinazoline, 7:

2-(tert-butyl)-4-ethoxy-6-methoxypyrimidine, 8:

2-(tert-butyl)-4-methoxy-6-(1H-pyrazol-1-yl)pyrimidine, 9:

2-(tert-butyl)-6-methoxy-N-methyl-N-phenylpyrimidin-4-amine, 10:

5-Nitro-9-(propan-2-ylidene)-1,4-dihydro-1,4-methanonaphthalene, 11:

2,3-Diphenyl-2,3-dihydrobenzo[*d*]isoxazole-4-carbonitrile, 12:

(4a*S*,8b*S*)-8-Nitro-3,4,4a,8b-tetrahydro-2*H* -benzo[3,4]cyclobuta[1,2-*b*]pyran, 13:

1-Benzyl-1H-benzo[d][1,2,3]triazole, 14:

2,2-Dimethyl-5-nitro-2*H* -chromene, 15:

1,4-Dimethyl-6-nitro-1,2,3,4-tetrahydro-5*H* -benzo[*e*][1,4]diazepin-5-one, 16:

1-(3-nitrophenyl)-1*H*-pyrazole, 17:

***N*-methyl-3-nitro-*N*-phenylaniline, 18:**

2'-nitro-1,2,3,4-tetrahydro-1,1'-biphenyl, 19:

1,8-di(furan-2-yl)naphthalene, 20a:

3b1,6a-dihydro-6H,7H-3b,6:7,11b-diepoxybenzo[a]perylene, 20:

(9*r*,10*r*)-2-Nitro-9,10-dihydro-9,10-[1,2]benzenoanthracene, 21:

4-Fluorobenzonitrile-3-*d*, 22:

-102.4
-102.7
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

4-(2-Bromo-4,6-dimethylphenoxy)benzonitrile-3-*d*, 23a:

4-((2'-Amino-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2-yl)oxy)benzonitrile-3-*d*, 23b:

5-(4-Cyanophenyl-2-*d*)-2,4,6,8-tetramethyl-5*H* -dibenzo[*b*,*d*]furan-5-ium tetrafluoroborate, 23:

-151.8
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
ppm

1,4-Dihydro-1,4-epoxynaphthalene-6-carbonitrile-8-*d*, 24:

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