SUPPORTING INFORMATION

Convenient, scalable and flexible method for the preparation of imidazolium salts with previously inaccessible substitution patterns

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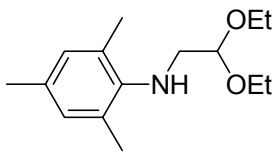
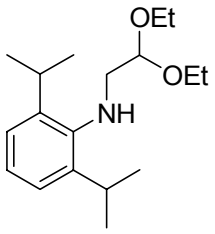
General: All reactions were carried out in flame-dried glassware under Ar. The solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg-anthracene), CH_2Cl_2 (P_4O_{10}), MeCN, Et_3N (CaH_2), MeOH (Mg), DMF (Desmodur®, dibutyltin dilaurate), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker DPX 300 or AV 400 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale. Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received unless stated otherwise.

***N*-(2,2-Diethoxyethyl)mesitylamine.** *n*-BuLi (1.6 M in hexane, 64 mL, 103 mmol) was added to a solution of 2,4,6-trimethylaniline (13.2 mL, 94 mmol) in THF (150 mL) at 0°C. After the addition was complete, the mixture was stirred for 30 min at ambient temperature before bromoacetaldehyde diethylacetal (15.6 mL, 103 mmol) was added. The reaction mixture was stirred overnight before the solution was poured into a mixture of sat. aq. $NaHCO_3$ and H_2O (200 mL, 1/1). The layers were separated, the



aqueous phase was extracted with *tert*-butyl methyl ether (2 x 150 mL), the combined organic layers were washed with water (100 mL) and brine (150 mL), dried over $MgSO_4$, filtered, and the filtrate was evaporated. Distillation of the residue furnished the title compound as a yellow oil (21.0 g, 89%); bp: 105°C / 0.05 torr; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.81 (s, 2H), 4.60 (t, *J* = 5.5 Hz, 1H), 3.72 (dt, *J* = 9.4, 7.0 Hz, 2H), 3.56 (dt, *J* = 9.3, 7.0 Hz, 2H), 3.07 (d, *J* = 5.7 Hz, 2H), 2.27 (s, 6H), 2.22 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 129.1, 129.0, 101.4, 62.0, 50.4, 20.2, 17.9, 15.0; IR (neat): $\tilde{\nu}$ = 2974, 2915, 1485, 1443, 1372, 1347, 1304, 1230, 1123, 1061, 959, 941, 852, 738 cm^{-1}; MS (EI): *m/z* (%): 251 (57) $[M]^+$, 206 (20), 148 (100), 103 (100), 75 (54), 47 (29); elemental analysis *calcd.* (%) for $C_{15}H_{25}NO_2$: C 71.67, H 10.02, N 5.57; *found*: C 71.75, H 10.01, N 5.46.

***N*-(2,2-Diethoxyethyl)-2,6-diisopropylaniline.** *n*-BuLi (1.6 M in hexane, 52 mL, 82 mmol) was added to a solution of 2,6-diisopropylaniline (14.0 mL, 75 mmol) in THF (150 mL) at 0°C. Once the addition was complete, the mixture was stirred for 30 min at ambient temperature before bromoacetaldehyde diethylacetal (12.4 mL, 82 mmol) was added. After stirring overnight, the solution was poured into a mixture of sat. aq. $NaHCO_3$ and H_2O (200 mL, 1/1). The layers were separated, the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 150 mL), the combined organic layers were washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$, filtered, and the filtrate was evaporated. Distillation of the residue afforded the title compound as a yellow oil (18.2 g, 82%); bp: 115°C / 0.05 torr; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10-7.03 (m, 3H), 4.68 (t, *J* = 5.5 Hz, 1H), 3.76 (tt, *J* = 7.0, 5.2 Hz, 2H), 3.58 (qd, *J* = 9.3, 7.0 Hz, 2H), 3.31 (sept, *J* = 6.8 Hz, 2H), 3.01 (d, *J* = 5.5 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 6H), 1.24 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.9, 142.2, 123.6, 123.5, 102.2, 62.7, 53.8, 27.5, 24.2, 15.4; IR (neat): $\tilde{\nu}$ = 2962, 2869,1739,1620, 1445, 1372, 1247, 1226, 1124, 1060, 941, 858, 803, 754 cm^{-1}; MS (EI): *m/z* (%): 293 (33) $[M]^+$, 190 (55), 160 (19), 103 (100), 75 (31), 47 (15); elemental analysis *calcd.* (%) for $C_{18}H_{31}NO_2$: C 73.67, H 10.65, N 4.77; *found*: C 73.81, H 10.60, N 4.86.



Representative procedure for the synthesis of α-(alkyl/arylamino)ketones 5. In a typical experiment, a mixture of 3-hydroxybutan-2-one (7.04 g, 80 mmol), the amine R^1–NH_2 (40 mmol), toluene (150 mL) and two drops of concentrated HCl was stirred for 3 h at reflux with azeotropic removal of water using a Dean-Stark trap. After cooling the mixture to ambient temperature, the solvent was evaporated and the residue purified by flash chromatography (hexanes/EtOAc) to afford the desired α–aminoketone **5**. The analytical and spectroscopic data of the products thus formed are compiled below:

3-(Phenylamino)butan-2-one: Yellow solid (84 %). mp = 51-52 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (t, 2H, *J* = 7.4 Hz), 6.73 (t, 1H, *J* = 7.4 Hz), 6.54 (d, 2H, *J* = 7.8 Hz), 4.38 (br s, 1H), 4.05 (c, 1H, *J* = 7.0 Hz), 2.19 (s, 3H), 1.40 (d, 3H, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.2, 146.5, 129.4, 117.9, 113.0, 58.6, 25.8, 17.9. IR (KBr): $\tilde{\nu}$ = 3355, 3079, 1713, 1602, 1581, 1512, 1428, 1359, 1319, 1282, 1141, 754, 698 cm^{-1}. HRMS *calcd.* for $C_{10}H_{13}NO$: 163.0997; *found* 163.0998; elemental analysis *calcd.* (%) for $C_{10}H_{13}NO$: C 73.59, H 8.03, N 8.59; *found* C 73.60, H 7.97, N 8.56.

3-(Mesitylamino)butan-2-one: Pale yellow oil (79 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.79 (s, 2H), 4.05 (q,1H, *J* = 7.0 Hz), 3.97 (br s, 1H), 2.25 (s, 6H), 2.21 (s, 3H), 2.19 (s, 3H), 1.25 (d, 3H, *J* = 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.0, 141.5, 130.9, 129.8, 129.0, 61.2, 27.5, 20.5, 18.8, 18.3. IR (KBr): $\tilde{\nu}$ = 3252, 2970, 2917, 1717, 1609, 1478, 1436, 1359, 1211, 1146, 1122, 1012, 856, 727 cm^{-1}. HRMS *calcd.* for $C_{13}H_{19}NO$: 205.1467; *found* 205.1467; elemental analysis *calcd.* (%) for $C_{13}H_{19}NO$: C 76.06, H 9.33, N 6.82; *found* C 76.21, H 9.51, N 6.80.

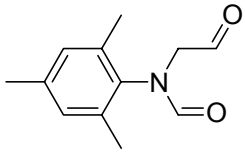
3-(3',4',5'-Trimethoxyphenylamino)butan-2-one: Pale yellow oil (67 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.80 (s, 2H), 4.41 (br s, 1H), 4.10-3.95 (m, 1H), 3.81 (s, 6H), 3.75 (s, 3H), 2.21 (s, 3H), 1.41 (d, 3H, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.5, 154.1, 143.3, 130.4, 90.6, 61.1, 59.1, 55.9, 53.5, 25.6, 18.0. IR (KBr): $\tilde{\nu}$ = 3372, 2937, 2841, 1712, 1610, 1509, 1453, 1413, 1355, 1235, 1186, 1125, 1012, 808, 777 cm^{-1}. HRMS *calcd.* for $C_{13}H_{19}NO_4Na$: 276.1206; *found* 276.1204; elemental analysis *calcd.* (%) for $C_{13}H_{19}NO_4$: C 61.64, H 7.56, N 5.53; *found* C 61.51, H 7.83, N 5.25.

3-(1'-Adamantylamino)butan-2-one: Pale yellow oil (41%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.55 (q, 1H, *J* = 7.1 Hz), 2.21 (s, 3H), 2.03 (br s, 3H), 1.78 (br s, 1H), 1.70-1.45 (m, 12H), 1.19 (d, 3H, *J* = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.2, 55.5, 50.9, 43.2, 36.6, 29.5, 26.1, 21.1. IR (KBr): $\tilde{\nu}$ = 3304, 2905, 2848, 1713, 1452, 1356, 1148, 1100, 726, 693 cm^{-1}. HRMS *calcd.* for $C_{14}H_{23}NONa$: 244.1672; *found* 244.1672; elemental analysis *calcd.* (%) for $C_{14}H_{23}NO$: C 75.97, H 10.47, N 6.33; *found* C 75.83, H 10.40, N 6.27.

2-(*p*-Tolylamino)cyclohexanone: White solid (63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98 (d, 2H, *J* = 8.0 Hz), 6.53 (d, 2H, *J* = 9.2 Hz), 4.84 (br s, 1H), 3.96 (dd, 1H, *J* = 12.2, 5.8 Hz), 2.82-2.54 (m, 2H), 2.47-2.33 (m, 1H), 2.23 (s, 3H), 2.20-2.10 (m, 1H), 1.96-1.88 (m, 1H), 1.85-1.63

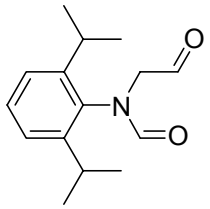
(m, 2H), 1.50-1.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.6, 144.3, 129.8, 126.8, 113.2, 62.2, 41.2, 35.9, 28.1, 24.1, 20.4. IR (KBr): $\tilde{\nu}$ = 3369, 2935, 2864, 1705, 1616, 1526, 1308, 813 cm^{-1}. HRMS *calcd.* for $C_{13}H_{17}NONa$: 226.1202; *found* 226.1200; elemental analysis *calcd.* (%) for $C_{13}H_{17}NO$: C 76.81, H 8.43, N 6.89; *found* C 77.00, H 8.52, N 6.76.

***N*-Mesityl-*N*-(2-oxoethyl)formamide.** A mixture of acetic anhydride (7.5 mL, 80 mmol) and formic acid (7.5 mL, 200 mmol) was stirred at ambient temperature for 2 h before it was added to an ice-cooled solution of *N-(*2,2-diethoxyethyl)mesitylamine (10.11 g, 40.2 mmol) in THF (150 mL) at such a rate that the internal temperature remained below 5°C. Once the addition was complete, the ice bath was removed and stirring was continued for 30 min. The resulting mixture was poured into a solution of NaOH (10%, 200 mL), the aqueous phase was extracted with *tert*-butyl methyl ether (150 mL), the combined organic layers were washed with brine (150 mL), dried over $MgSO_4$ and the solvents were evaporated.



Formic acid (100 mL, 2.5 mL/mmol) was then added to the residue at 0°C and the resulting mixture was stirred at ambient temperature for 3 h before all volatile materials were distilled off. The crude product was dissolved in *tert*-butyl methyl ether (300 mL) and successively washed with sat. aq. $NaHCO_3$ (2 x 150 mL) and brine (150 mL), before the organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 4/1 → 2/1) to give a yellow oil which can be further purified by Kugelrohr distillation, affording the title compound as a colorless oil which slowly crystallized upon standing (4.50 g, 55%); mp = 39-40°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.77 (s, 1H), 8.16 (s, 1H), 6.96 (s, 2H), 4.15 (s, 2H), 2.30 (s, 3H), 2.25 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.2, 163.9, 138.9, 136.2, 129.8, 56.4, 20.9, 18.3; IR (neat): $\tilde{\nu}$ = 2922, 2880, 1726, 1655, 1486, 1443, 1378, 1347, 1276, 1214, 1047, 998, 857 cm^{-1}; MS (EI): *m/z* (%): 205 (20) [M]$^+$, 177 (49), 148 (100), 120 (26), 105 (13), 77 (13); elemental analysis *calcd.* (%) for $C_{12}H_{15}NO_2$: C 70.22, H 7.37, N 6.82; *found*: C 69.97, H 7.31, N 6.75.

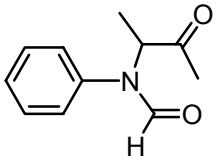
N-(2,6-Diisopropylphenyl)-N-(2-oxoethyl)formamide. A mixture of acetic anhydride (5.6 mL, 60 mmol) and formic acid (5.6 mL, 150 mmol) was stirred for 2 h at ambient temperature before the mixture was slowly added to a solution of *N*-(2,2-diethoxyethyl)-2,6-diisopropylaniline (8.87 g, 30.2 mmol) in THF (150 mL) at 0°C. The resulting mixture was stirred for 5 h at ambient temperature before the reaction was quenched with aq. NaOH (10%, 150 mL). The layers were separated, the aqueous phase was extracted with *tert*-butyl methyl ether (100 mL) and the



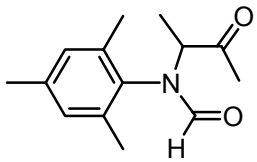
combined organic phases were washed with brine (100 mL) and dried over $MgSO_4$. After removal of the solvents, formic acid (75 mL) was added to the remainder at 0°C and the resulting mixture was kept at ambient temperature for 2.5 h before all volatile materials were distilled off. The residue was dissolved in *tert*-butyl methyl ether (250 mL) and the organic layer was washed with sat. aq. $NaHCO_3$ (2 x 100 mL) and brine (150 mL) before being dried over Na_2SO_4 and evaporated. Kugelrohr distillation of the residue followed by crystallization of the resulting material from EtOH (10 mL) furnished the desired product as a colorless solid (3.81 g, 51%); mp = 83-84°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.83 (t, *J* = 1.3 Hz, 1H), 8.22 (s,1H), 7.44-7.40 (m, 1H), 7.28-7.24 (m, 2H), 4.18 (d, *J* = 1.3 Hz, 2H), 3.10 (sept, *J* = 6.8 Hz, 2H), 1.23 (d, *J* = 6.8, 6H), 1.22 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.8, 163.9, 147.4, 135.0, 130.0, 124.6, 57.7, 28.3, 24.6, 24.0; IR (neat): $\tilde{\nu}$ = 3072, 2966, 2870, 2811, 2715, 1741, 1659, 1589, 1466, 1454, 1381, 1327, 1286, 1204, 1057, 1042, 933, 869, 812 cm^{-1}; MS (EI): *m/z* (%): 247 (23) $[M]^+$, 214 (100), 204 (14), 176 (14), 160 (14), 148 (12), 132 (13), 91 (11), 43 (13); elemental analysis *calcd.* (%) for $C_{15}H_{21}NO_2$: C 72.84, H 8.56, N 5.66; *found*: C 72.81, H 8.49, N 5.57.

General procedure for the formylation of α-(alkyl/arylamino)ketones (5→6): In a typical experiment, a mixture of the α-(alkyl/arylamino)ketone **5** (10 mmol), acetic formic anhydride (1.32 g, 15 mmol)[1] and THF (5 mL) was stirred overnight. For work up, all volatile materials were evaporated and the residue purified by flash chromatography (hexanes/EtOAc) to afford the desired formamide **6**. The analytical and spectroscopic data of the products thus formed are compiled below:

***N*-Formyl-3-(phenylamino)butan-2-one:** Colorless oil (91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (s, 1H), 7.46-7.33 (m, 3H), 7.22-7.17 (m, 2H), 4.87 (q,1H, *J* = 7.3 Hz), 2.29 (s, 3H), 1.35 (d, 3H, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.3, 162.6, 139.1, 129.7, 127.9, 126.2, 60.3, 26.8, 13.7. IR (KBr): $\tilde{\nu}$ = 2990, 2940, 2881, 1722, 1675, 1595, 1496, 1456, 1357, 1294, 1260, 1185, 1094, 772, 746, 700, 557 cm^{-1}. HRMS *calcd.* for $C_{11}H_{13}NO_2$: 191.0946; *found* 191.0944; elemental analysis *calcd.* (%) for $C_{11}H_{13}NO$: C 69.09, H 6.85, N 7.32; *found* C 68.89, H 6.92, N 7.38.



***N*-Formyl-3-(mesitylamino)butan-2-one:** Pale yellow solid (84%). mp = 98-99 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (s, 1H), 6.96 (s, 1H), 6.92 (s, 1H), 4.52 (q,1H, *J* = 7.4 Hz), 2.41 (s, 3H), 2.38 (s, 3H), 2.27 (s, 3H), 2.15 (s, 3H), 0.98 (d, 3H, *J* = 7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.4, 163.6, 138.8, 137.8, 133.1, 129.6, 129.0, 59.4, 27.8, 20.9, 18.9, 18.6, 13.6. IR (KBr): $\tilde{\nu}$ = 2988, 2916, 1719,



[1] L. I. Krimen, *Org. Synth*. 1970, **50**, 1.

1657, 1486, 1452, 1319, 1304, 1251, 1166 cm^{-1}. HRMS *calcd.* for $C_{14}H_{19}NO_2Na$: 256.1308; *found* 256.1308; elemental analysis *calcd.* (%) for $C_{14}H_{19}NO_2$: C 72.07, H 8.21, N 6.00; *found* C 71.96, H 8.19, N 5.95.

***N*-Formyl-3-(3',4',5'-trimethoxyphenylamino)butan-2-one:** Pale yellow solid (92 %). mp = 94-95 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 1H), 6.47 (s, 2H), 4.89 (q,1H, *J* = 7.4 Hz), 3.86 (s, 9H), 2.30 (s, 3H), 1.34 (d, 3H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.6, 162.6, 153.6, 137.9, 134.5, 104.8, 60.9, 60.1, 56.3, 27.0, 13.8. IR (KBr): $\tilde{\nu}$ = 3072, 2991, 2965, 2894, 1730, 1677, 1594, 1505, 1470, 1450, 1363, 1278, 1243, 1126, 1004, 815, 766, 736 cm^{-1}. HRMS *calcd.* for $C_{14}H_{19}NO_5Na$: 304.1155; *found* 304.1153; elemental analysis *calcd.* (%) for $C_{14}H_{19}NO_5$: C 59.78, H 6.81, N 4.98; *found* C 60.02, H 6.67, N 4.85.

***N*-Formyl-3-(1'-adamantylamino)butan-2-one:** Pale yellow solid (93%). mp = 106-107 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1H), 3.63 (q, 1H, *J* = 6.7 Hz), 2.23 (br s, 3H), 2.15 (s, 3H), 2.06-1.91 (m, 6H), 1.78-1.63 (m, 6H), 1.48 (d, 3H, *J* = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.3, 160.7, 57.2, 57.0, 42.4, 35.8, 29.4, 26.4, 15.4. IR (KBr): $\tilde{\nu}$ = 2910, 2857, 1715, 1647, 1382, 1367, 1247, 1091 cm^{-1}. HRMS *calcd.* for $C_{15}H_{23}NO_2Na$: 272.1621; *found* 272.1621; elemental analysis *calcd.* (%) for $C_{15}H_{23}NO_2$: C 72.25, H 9.30, N 5.62; *found* C 72.35, H 9.26, N 5.54.

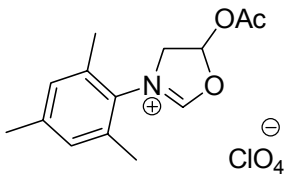
***N*-Formyl-2-(*p*-tolylamino)cyclohexanone:** White solid (88%). mp = 127-128 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 1H), 7.22-7.12 (m, 4H), 4.98 (dd, 1H, *J* = 12.2, 5.7 Hz), 2.63-2.54 (m, 1H), 2.52-2.41 (m, 1H), 2.36 (s, 3H), 2.13-1.99 (m, 2H), 1.98-1.91 (m, 1H), 1.84-1.67 (m, 2H), 1.66-1.51(m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.2, 163.0, 138.1, 136.4, 129.9, 128.1, 62.8, 41.2, 31.1, 26.4, 24.7, 21.0. IR (KBr): $\tilde{\nu}$ = 2941, 2905, 2864, 1720, 1673, 1607, 1515, 1378, 1339, 1277, 1240, 1203, 826 cm^{-1}. HRMS *calcd.* for $C_{14}H_{17}NO_2Na$: 254.1151; *found* 254.1151; elemental analysis *calcd.* (%) for $C_{14}H_{17}NO_2$: C 72.70, H 7.41, N 6.06; *found* C 72.82, H 7.45, N 5.91.

Standard procedure for the preparation of 4,5-unsubstituted 4*H*,5*H*-imidazolium salts 12 (R^4 = R^5 = H). The respective *N*-aryl-*N*-(2-oxoethyl)formamide (1 mmol) was dissolved in acetic anhydride (1 mL) and $HClO_4$ (100 µL, 70 % *w/w* in water, 1.15 equiv) or $HBF_4{\cdot}OEt_2$ (158 µL, 1.15 equiv) was slowly added at ambient temperature. A small increase of the temperature can be detected during the addition. The mixture was stirred overnight before Et_2O (5 mL) was introduced to precipitate compound **10**. The solvent was removed using a pipette and the remaining solid was washed with Et_2O (3 x

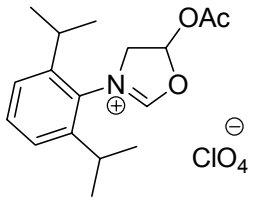
3 mL). A suspension of this solid in toluene (4 mL) was reacted with the amine R^2–NH_2 of choice (1.5 mmol) for 3-4 hours, during which course the formation of a precipitate or the separation of a second phase was observed. Stirring was discontinued, the toluene phase was removed with a pipette and the residue was triturated with Et_2O (3 x 3 mL). Toluene (4 mL) was added to the remainder before 48% aq. HBF_4 or 70% aq. $HClO_4$ (1 equiv) was introduced. The mixture was stirred at 80°C overnight before the solvent was evaporated and the residue was taken up in CH_2Cl_2 (~ 4-5 mL) (if a precipitate appears at that point, it is filtered off prior to further processing). NH_3 (0.35 mL, 7 M in MeOH, 2.5 equiv) was then added to the clear solution and the precipitate of NH_4ClO_4 (or NH_4BF_4) was filtered off through a small plug of Celite. Evaporation of the filtrate, and precipitation and washing of the final product with Et_2O provided the corresponding imidazolium salt **12** as an analytically pure powder.

The following compounds were prepared by this method:

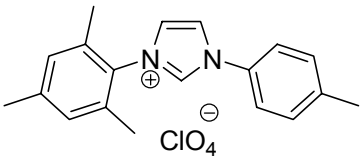
1-Mesityl-3-acetoxyoxazolinium perchlorate: White powder (92%); ^{1}H NMR (400 MHz, CD_3CN): δ 8.86 (br s, 1H), 7.36 (ddd, J = 7.0, 3.1, 1.2 Hz, 1H), 7.12 (s, 2H), 4.70 (tdd, J = 14.3, 7.0, 1.8 Hz, 1H), 4.30 (dd, J = 14.3, 3.1 Hz, 1H), 2.34 (s, 3H), 2.28 (s, 6H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, CD_3CN): δ 169.0, 168.1, 143.1, 135.8, 130.9, 128.0, 100.8, 56.1, 21.0, 20.6, 17.5; IR (KBr): 3103, 3021, 2980, 2927, 1780, 1677, 1636, 1388, 1362, 1182, 1099, 943, 852, 744, 625 cm^{-1}; MS (ESI): *m/z* (%): 248 (100) $[M - ClO_4]^+$, 206 (68); HRMS (EI): *m/z* : *calcd.* for $C_{14}H_{18}NO_3$: 248.128117, *found*: 248.127880.



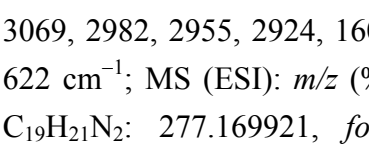
1-(2,6-Diisopropylphenyl)-3-acetoxyoxazolinium perchlorate: White powder (98%). Crystallization from CH_3CN/Et_2O furnished colorless crystals suitable for crystal structure analysis; ^{1}H NMR (400 MHz, CD_3CN): δ 8.95 (m, 1H), 7.61 (m, 1H), 7.44 (d, J = 7.9 Hz, 2H), 7.36 (dd, J = 7.0, 3.1 Hz, 1H), 4.69 (ddd, J= 14.1, 7.0, 1.9 Hz, 1H), 4.28 (ddd, J = 14.4, 3.1, 1.2 Hz, 1H), 2.89 (sept, J = 6.8 Hz, 1H), 2.82 (sept, J = 6.8 Hz, 1H), 2.23 (s, 3H), 1.31 (d, J = 6.8 Hz, 3H), 1.28 (d, J = 6.8 Hz, 3H), 1.26 (d, J = 6.8 Hz, 3H), 1.24 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, CD_3CN): δ 168.9, 167.9, 146.6, 146.4, 133.4, 127.3, 126.3, 126.2, 100.8, 58.6, 29.3, 29.2, 24.6, 24.5, 24.3, 24., 20.6; IR (KBr): 3057, 2972, 2932, 2873, 1793, 1638, 1467, 1394, 1366, 1179, 1091, 939, 851, 810, 759, 715, 625 cm^{-1}; MS (ESI): *m/z* (%): 290 (90) $[M - ClO_4]^+$, 248 (100); HRMS (EI): *m/z*: *calcd.* for $C_{17}H_{24}NO_3$: 290.175070, *found*: 290.174833.



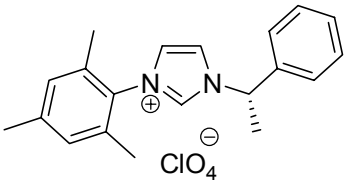
1-Mesityl-3-(p-tolyl)imidazolium perchlorate: Off-white powder (215 mg, 59 %); mp = 216-218 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.25 (t, *J* = 1.6 Hz, 1H), 7.94 (t, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 1.6 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.03 (s, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 141.4, 135.0, 134.1, 131.2, 130.0, 124.8, 122.3, 122.1, 21.2, 21.1, 17.5; IR (KBr): $\tilde{\nu}$ = 3183, 3147, 3069, 2982, 2955, 2924, 1607, 1545, 1514, 1487, 1460, 1447, 1239, 1107, 1088, 822, 622 cm^{-1}; MS (ESI): *m/z* (%): 277.0 (100) $[M - ClO_4]^+$; HRMS (EI): *m/z*: *calcd.* for $C_{19}H_{21}N_2$: 277.169921, *found*: 277.170043; elemental analysis *calcd.* (%) for $C_{19}H_{21}ClN_2O_4$: C 60.56, H 5.62, N 7.43; *found*: C 60.77, H 5.56, N 7.40.



1-Mesityl-3-(p-tolyl)imidazolium tetrafluoroborate: White powder (230 mg, 56%); mp = 181-183 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (t, *J* = 1.6 Hz, 1H), 8.03 (t, *J* = 1.8 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 1.6 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.97 (s, 2H), 2.38 (s, 3H), 2.31 (s, 3H), 2.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 140.9, 134.6, 134.1, 131.8, 131.0, 130.6, 129.7, 124.9, 122.5, 121.9, 21.1, 21.0, 17.3; IR (KBr): $\tilde{\nu}$ = 3153, 3072, 2983, 2956, 2926, 2868, 1609, 1546, 1515, 1488, 1461, 1447, 1385, 1240, 1061, 822, 748, 669, 521 cm^{-1}; MS (ESI): *m/z* (%): 277.0 (100) $[M - BF_4]^+$; HRMS (EI): *m/z*: *calcd.* for $C_{19}H_{21}N_2$: 277.169921, *found*: 277.170065.



1-Mesityl-3-((*S*)-1-phenylethyl)imidazolium perchlorate: Pale orange powder (225 mg, 64%); mp = 139-140 °C; $[\alpha]_D^{20} = -34.2$ (*c* 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (t, *J* = 1.5 Hz, 1H), 7.59 (t, *J* = 1.8 Hz, 1H), 7.46-7.37 (m, 5H), 7.21 (t, *J* = 1.8 Hz, 1H), 6.97 (s, 2H), 6.07 (q, *J* = 7.0 Hz, 1H), 2.31 (s, 3H), 2.04 (s, 3H), 2.03 (d, *J* = 7.0 Hz, 3H), 1.7 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.3, 137.7, 136.0, 134.3, 134.1, 130.5, 129.8, 129.7, 129.6, 129.5, 126.9, 123.9, 121.5, 60.3, 21.0, 20.8, 17.2; IR (KBr): $\tilde{\nu}$ = 3165, 3138, 3089, 2983, 2925, 1608, 1548, 1484, 1457, 1385, 1289, 1191, 1159, 1097, 857, 829, 75, 702, 603 cm^{-1}; MS (ESI): *m/z* (%): 291.0 (100) $[M - ClO_4]^+$, 186.9 (95); HRMS (EI): *calcd.* for $C_{20}H_{23}N_2$: 291.185573, *found*: 291.185535; elemental analysis *calcd.* (%) for $C_{20}H_{23}ClN_2O_4$: C 61.46, H 5.93, N 7.17; *found*: C 61.58, H 5.97, N 7.11.



1-(2,6-Diisopropylphenyl)-3-(mesityl)imidazolium perchlorate: Starting from 213 mg of *N*-mesityl-*N*-(2-oxoethyl)formamide (1.04 mmol) the product was obtained as a white powder (340 mg, 73%). Starting from 247 mg of *N*-(2,6-diisopropylphenyl)-*N*-(2-oxoethyl)formamide (1.00 mmol) the product was obtained as a white powder (405 mg, 91%); mp = 244-246 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.95 (t, *J* = 1.6 Hz, 1H), 7.65 (d, *J* = 1.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.02 (s, 2H), 2.36 (sept, *J* = 6.8 Hz, 2H), 2.32 (s, 3H), 2.09 (s, 6H), 1.21 (d, *J* = 6.8 Hz, 6H), 1.18 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.0, 141.4, 137.5, 133.8, 132.0, 130.2, 130.0, 129.8, 126.1, 125.2, 124.6, 28.9, 24.1, 23.9, 21.1, 17.1; IR (KBr): 3157, 3110, 3042, 2967, 2930, 2873, 1610, 1548, 1462, 1389, 1368, 1332, 1250, 1213, 1172, 1092, 934, 872, 808, 760, 677, 624 cm^{-1}; MS (ESI): *m/z* (%): 347.1 (100) $[M - ClO_4]^+$; HRMS (EI): *calcd.* for $C_{24}H_{31}N_2$: 347.248174, *found*: 347.248487; elemental analysis *calcd.* (%) for $C_{24}H_{31}ClN_2O_4$: C 64.49, H 6.99, N 6.27; *found*: C 64.50, H 6.87, N 6.27.

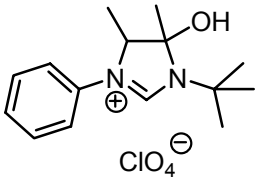
1-(2,6-Diisopropylphenyl)-3-(mesityl)imidazolium tetrafluoroborate: White powder (323 mg, 75%); mp = 248-249 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.85 (t, *J* = 1.6 Hz, 1H), 7.63 (d, *J* = 1.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.02 (s, 2H), 2.35 (sept, *J* = 6.8 Hz, 2H), 2.33 (s, 3H), 2.09 (s, 6H), 1.20 (d, *J* = 6.8 Hz, 6H), 1.16 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.0, 141.4, 137.3, 133.9, 132.0, 130.2, 130.0, 129.9, 126.2, 125.2, 124.6, 28.9, 24.1, 23.9, 21.1, 17.0; IR (KBr): $\tilde{\nu}$ = , 3161, 3124, 2968, 2931, 2873, 1611, 1532, 1463, 1215, 1056, 935, 809, 761, 678 cm^{-1}; MS (ESI): *m/z* (%): 347.1 (100) $[M - BF_4]^+$; HRMS (EI): *calcd.* for $C_{24}H_{31}N_2$: 347.248169, found: 347.248070; elemental analysis *calcd.* (%) for $C_{24}H_{31}BF_4N_2$: C 66.37, H 7.19, N 6.45; *found*: C 66.27, H 7.14, N 6.35.

1-(2,6-Diisopropylphenyl)-3(adamantyl)imidazolium perchlorate: White powder (381 mg, 82%); mp = 244-246 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (t, *J* = 1.6 Hz, 1H), 7.9 (t, *J* = 1.8 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 1.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.34 (br s, 3H), 2.30 (br s, 6H), 2.21 (sept, *J* = 6.8 Hz, 2H), 1.81 (br q, *J* = 12.7 Hz, 6H), 1.19 (d, *J* = 6.8 Hz, 6H), 1.14 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.2, 134.4, 131.8, 130.3, 125.0, 124.5, 120.2, 61.7, 42.6, 35.1, 29.5, 28.7, 24.3, 24.0; ; IR (KBr): 3152, 2968, 2912, 2867, 1540, 1460, 1366, 1309, 1254, 1175, 1084, 804, 759, 623 cm^{-1}; MS (ESI): *m/z* (%): 363.2 (100) $[M - ClO_4]^+$; HRMS (EI): *calcd.* for $C_{25}H_{35}N_2$:

363.279476, *found*: 363.279201; elemental analysis *calcd.* (%) for $C_{25}H_{35}ClN_2O_4$: C 64.85, H 7.62, N 6.05; *found*: C 64.76, H 7.57, N 5.97.

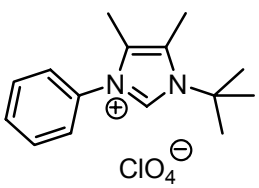
General procedure for the "one pot" synthesis of non-symmetric 4,5-disubstituted imidazolium salts 12 (R^4, $R^5 \neq$ H): A 50 mL Schlenk flask was charged under argon with the corresponding formylaminoketone (1 mmol) and acetic anhydride (1.5 mL). 70% aq. $HClO_4$ (100 µL) or 48% aq. HBF_4 (138 µL) were added dropwise to this mixture at such a rate as to keep the temperature below 50 ºC. Once the addition was complete, the mixture was stirred for 3 h at ambient temperature. For work up, Et_2O (10 mL) was added causing the precipitation of compound **10** as an oil or as a crystalline solid. The supernatant organic phase was removed via canula and the precipitate was rinsed with Et_2O (2 x 5 mL) before it was suspended in toluene (2 mL). The desired amine R^2–NH_2 (1.5 mmol) was then added to this suspension in one portion and the resulting mixture was stirred for 3 h during which time the 4-hydroxy-imidazolinium salts **11** separates. The precipitate was filtered off and was washed with Et_2O (2 x 5 mL) before it was suspended in toluene (2 mL) and acetic anhydride (2 mL) containing a catalytic amount of either 70% aq. $HClO_4$ or 48% aq. HBF_4. The resulting mixture is stirred at 80°C overnight. After evaporation of the solvents, the crude imidazolium salts were triturated with Et_2O and the resulting suspension was placed in a ultrasonic cleaning bath for ca. 20 min. During this time the desired compound **12** precipitated as a white or pale brown solid which was filtered off and dried *in vacuo*. The analytical and spectroscopic data of the resulting products are compiled below:

1-Phenyl-3-*t*-butyl-4-hydroxy-4,5-dimethyl-4,5-dihydroimidazolium perchlorate:



White solid (96 %). mp = 141-142 ºC. ^{1}H NMR (400 MHz, acetone-d_6): δ = 8.37 (s, 1H), 7.43-7.22 (m, 5H), 6.34 (br s, 1H), 4.68 (q,1H, *J* = 6.8 Hz), 1.43 (s, 9H), 1.38 (s, 3H), 1.28 (d, 3H, *J* = 6.8 Hz). ^{13}C NMR (75 MHz, acetone-d_6): δ = 153.3, 138.9, 131.0, 128.6, 124.3, 67.1, 59.4, 53.8, 28.3, 27.1, 12.6. IR (KBr): $\tilde{\nu}$ = 3421, 2981, 2917, 2839, 2635, 1624, 1595, 1552, 1402, 1296, 1279, 1216, 1194, 1094, 791, 693, 623 cm^{-1}; HRMS (EI): *calcd.* for $C_{15}H_{23}N_2O^+$: 247.1805, *found*: 247.1805; elemental analysis *calcd.* (%) for $C_{15}H_{23}ClN_2O_5$: C 51.95, H 6.68, N 8.08; *found* C 52.10, H 6.64, N, 8.15.

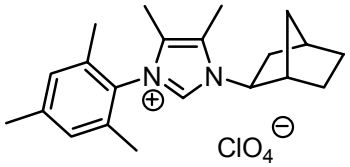
1-Phenyl-3-*t*-butyl-4,5-dimethylimidazolium perchlorate: Colorless needles (91%).



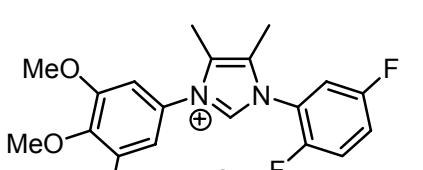
mp = 106-107 ºC. ^{1}H NMR (400 MHz, acetone-d_6): δ = 9.05 (s, 1H), 7.67 (br s, 5H), 2.63 (s, 3H), 2.22 (s, 3H), 1.86 (s, 9H). ^{13}C NMR (100 MHz, acetone-d_6): δ = 135.3, 134.9, 131.8, 131.2, 130.7, 128.4, 127.8, 62.8, 30.1, 12.4, 9.5. IR (KBr): $\tilde{\nu}$ = 3153, 3080, 2991, 1600, 1555, 1466, 1227, 1094, 774, 697, 622 cm^{-1}.

HRMS *calcd.* for $C_{15}H_{21}N_2^+$: 229.1699; *found* 229.1699; elemental analysis *calcd.* (%) for $C_{15}H_{21}ClN_2O_4$: C 54.79, H 6.44, N 8.52; *found* C 54.81, H 6.45, N 8.52.

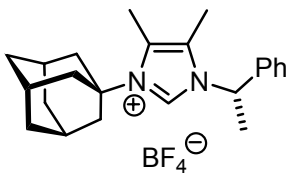
1-(Bicyclo[2.2.1]heptanyl)-3-mesityl-4,5-dimethylimidazolium perchlorate: Light yellow solid (84%). mp = 187-188 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (s, 1H), 7.02 (s, 2H), 4.37-7.29 (m, 1H), 2.78 (d, 1H, *J* = 4.5 Hz), 7.09 (br s, 1H), 2.42 (s, 3H), 2.34 (s, 3H), 2.20-2.10 (m, 1H), 1.99 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H), 1.84-1.71 (m, 2H), 1.63-1.54 (s, 1H), 1.53-1.37 (m, 2H), 1.33-1.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.1, 135.1, 134.8, 131.0, 129.8, 129.7, 129.0, 128.4, 128.1, 61.5, 41.7, 39.5, 36.8, 35.8, 27.8, 27.0, 21.2, 17.4, 9.4, 8.2. IR (KBr): $\tilde{\nu}$ = 3126, 2961, 2877, 1546, 1456, 1219, 1097, 623; HRMS *calcd.* for $C_{21}H_{29}N_2^+$: 309.2325; *found* 309.2325; elemental analysis *calcd.* (%) for $C_{21}H_{29}ClN_2O_4$: C 61.68, H 7.15, N 6.85; *found* C 61.60, H 7.18, N 6.80.



1-(3',4',5'-Trimethoxyphenyl)-3-(2',5'-difluoro)-4,5-dimethylimidazolium tetrafluoroborate: Pink foam (31%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (s, 1H), 7.67-7.60 (m, 1H), 7.38-7.24 (m, 2H), 6.87 (s, 2H), 3.87 (s, 9H), 2.24 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8 (d, $J_{C\text{-}F}$ = 246 Hz), 154.0, 152.8 (d, $J_{C\text{-}F}$ = 249 Hz), 139.6, 134.8, 128.6, 128.3, 121.3 (dd, $J_{C\text{-}F}$ = 15.0, 10.0 Hz), 120.1 (dd, $J_{C\text{-}F}$ = 23.6, 7.8 Hz), 118.1 (dd, $J_{C\text{-}F}$ = 21.3, 8.7 Hz), 116.8 (d, $J_{C\text{-}F}$ = 27.1 Hz), 103.9, 60.9, 56.6, 9.1, 8.6. IR (KBr): $\tilde{\nu}$ = 3138, 3082, 2978, 1603, 1555, 1506, 1470, 1427, 1236, 1128, 1061, 831, 772, 661, 521; HRMS *calcd.* for $C_{20}H_{21}N_2O_3F_2^+$: 375.1515; *found* 375.1512; elemental analysis *calcd.* (%) for $C_{20}H_{21}BF_6N_2$: C 51.97, H 4.58, N 6.06; *found* C 51.86, H 4.69, N 6.02.



(*S*)-1-Adamantyl-3-(1'-phenylethyl)-4,5-dimethylimidazolium tetrafluoroborate: White solid (59%). mp = 187-188 ºC. $[\alpha]_D^{20}$ = +59.4 (*c* 1.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 1H), 7.42-7.23 (m, 3H), 7.25-7.14 (m, 2H), 5.59-5.51 (q,1H, *J* = 7.0 Hz), 2.47 (s, 3H), 2.31 (s, 9H), 2.00 (s, 3H), 1.97 (d, 3H, *J* = 7.0 Hz), 1.78 (br s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 131.2, 129.4, 129.1, 128.7, 127.3, 126.2, 62.8, 58.6, 41.2, 35.3, 29.6, 21.0, 12.2, 8.8. IR (KBr): $\tilde{\nu}$ = 3174, 2914, 2855, 1625, 1544, 1496, 1456, 1308, 1246, 1179, 1070, 773, 708, 578, 521; HRMS *calcd.* for $C_{23}H_{31}N_2^+$: 335.2482; *found* 335.2485; elemental analysis *calcd.* (%) for $C_{23}H_{31}BN_2F_4$: C 65.41, H 7.40, N 6.63; *found* C 65.29, H 7.35, N 6.53.



1-(*p*-Tolyl)-3-(1'-adamantyl)-4,5,6,7-tetrahydrobenzimidazolium perchlorate: Pale yellow solid (88%). mp = 160-161 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1H), 7.44 (d, 2H, *J* = 8.2 Hz), 7.34 (d, 2H, *J* = 8.2 Hz), 3.02-2.97 (m, 2H), 2.54-2.47 (m, 2H), 2.42 (s, 3H), 2.37-2.28 (m, 9H), 1.99-1.90 (m, 2H), 1.90-1.82 (m, 2H), 1.75 (br s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.9, 131.9, 131.6, 130.7, 129.5, 125.5, 62.8, 41.2, 35.4, 29.6, 24.5, 22.3, 21.3, 21.2, 21.0. IR (KBr): $\tilde{\nu}$ = 3129, 2955, 1552, 1455, 1220, 1061, 819, 710, 571, 522; HRMS *calcd.* for $C_{24}H_{31}N_2^+$: 347.2482; *found* 347.2484; elemental analysis *calcd.* (%) for $C_{24}H_{31}ClN_2O_4$: C 64.49, H 6.99, N 6.27; *found* C 64.71, H 6.80, N 5.98.

X-ray Crystallography

X-ray diffraction data were collected at low temperature in a cold nitrogen gas stream using Bruker AXS CCD diffractometers (KappaCCD for **10** and **11**, and Proteum X8 for **12**). Structures were solved by direct methods (SHELXS-97) and were refined using full matrix least-squares based on F^2 (SHELXL-97). Hydrogen atoms were placed at geometrically idealized positions and refined using constraints (riding model), highest residual electron density peak were < 0.6 e^- $Å^{-3}$. The *tert*-butyl group in **11** is disordered over two positions at a ratio of 40:60 and was refined using distance restraints to maintain a C_3 symmetric geometry. Hydrogen atoms attached to the two partially occupied parts of this group were prevented from occupying physically unreasonable positions using the BUMP restraint. Complete lists of atom co-ordinates and anisotropic displacement parameters as well as tables of bond lengths and bond angles are available as CIF from the Cambridge Crystallographic Data Centre quoting the reference no. CCDC 602506 (**10**), CCDC 602504 (**11**), CCDC 602505 (**12**).

Crystal data for compound 10 (R^1 = 2,6-di-isopropylphenyl; R^4 = R^5 = H)): $C_{17}H_{24}ClNO_7$, M = 389.82, colorless, crystal dimensions 0.26 x 0.08 x 0.08 mm, triclinic $P\bar{1}$ (no. 2), at 100 K a = 9.5374(10), b = 10.5798(14), c = 10.6445(14) Å , α = 73.132(5), β = 87.076(6), γ = 69.773(5)°, U = 963.0(2) $Å^3$, Z = 2, ρ = 1.344 Mg m^{-3}, μ = 0.236 mm^{-1}, λ = 0.71073 Å. Data collection to θ_{max} = 33.74°, 84.6% completeness, 14693 reflections measured, 6512 unique (R_{int} = 0.101). Refinement converged at $R(F)$ = 0.091 and $wR(F^2)$ = 0.234 (all data).

Crystal data for compound 11 (R^1 = Ph, R^2 = *tert*-Bu, R^4 = R^5 = Me): $C_{15}H_{23}ClN_2O_5$, M = 346.80, colorless, crystal dimensions 0.24 x 0.20 x 0.10 mm, monoclinic $P2_1/n$ (no. 14), at 100 K a = 11.5277(4), b = 8.3692(3), c = 17.3259(6) Å , α = 90, β = 97.388(2), γ = 90°, U = 1657.68(10) $Å^3$, Z = 4, ρ = 1.390 Mg m^{-3}, μ = 0.257 mm^{-1}, λ = 0.71073 Å. Data collection to θ_{max} = 31.49°, 99.5% completeness, 37427 reflections measured, 5490 unique (R_{int} = 0.110). Refinement converged at $R(F)$ = 0.077 and $wR(F^2)$ = 0.200 (all data).

Crystal data for compound 12 (R^1 = mesityl, R^2 = 2,6-di-isopropylphenyl, R^4 = R^5 = H): $C_{24}H_{31}ClN_2O_4$, M = 446.96, colorless, crystal dimensions 0.15 x 0.12 x 0.05 mm, triclinic $P\bar{1}$ (no. 2), at 100 K a = 9.5248(2), b = 9.5297(2), c = 15.4459(4) Å , α = 80.3070(10), β = 88.7100(10), γ = 60.7890(10)°, U = 1203.33(5) $Å^3$, Z = 2, ρ = 1.234 Mg m^{-3}, μ = 1.659 mm^{-1}, λ = 1.54178 Å. Data collection to θ_{max} = 68.03°, 93.7% completeness, 24652 reflections measured, 4125 unique (R_{int} = 0.048). Refinement converged at $R(F)$ = 0.038, and $wR(F^2)$ = 0.104 (all data).

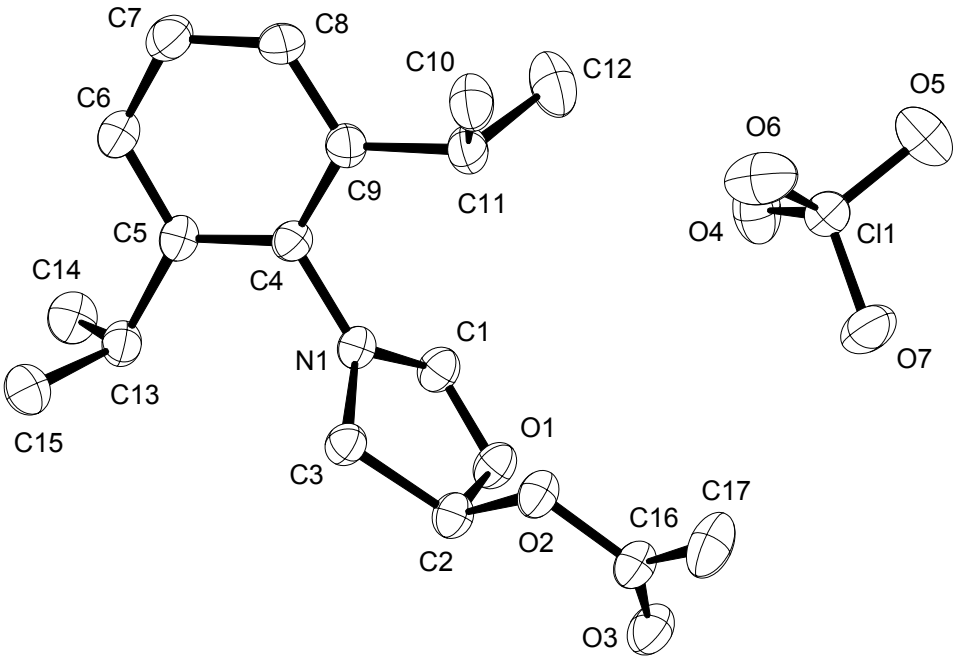


Fig. 1: Molecular structure of **10** from single crystal X-ray structure determination. Anisotropic displacement parameter ellipsoids are shown at 50% probability and hydrogen atoms have been omitted.

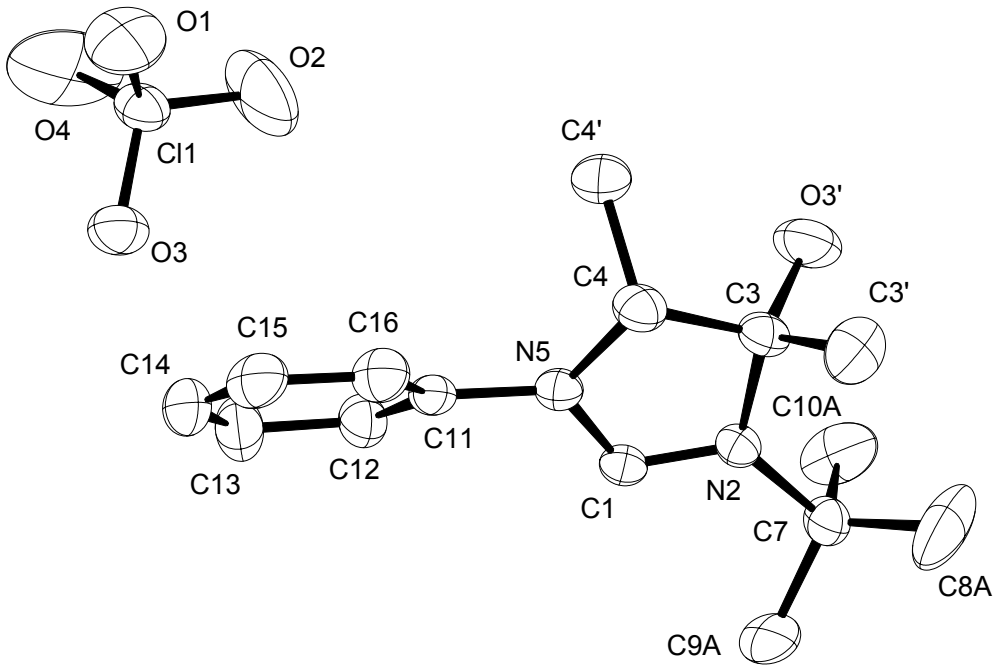


Fig. 2: Molecular structure of **11** from single crystal X-ray structure determination. Anisotropic displacement parameter ellipsoids are shown at 50% probability and hydrogen atoms have been omitted. The *tert*-butyl group is disordered over two positions at a ratio of 40:60.

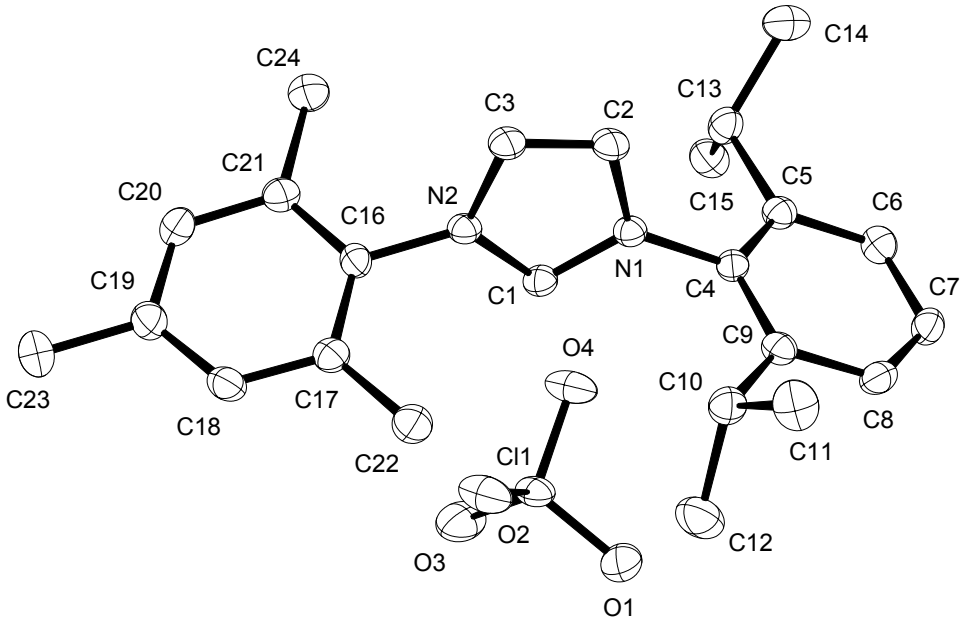


Fig. 3: Molecular structure of **12** from single crystal X-ray structure determination. Anisotropic displacement parameter ellipsoids are shown at 50% probability and hydrogen atoms have been omitted. The *tert*-butyl group is disordered over two positions at a ratio of 40:60.