Electronic Supplementary Information

Ortho-directed Functionalization of Arenes using Magnesate Bases

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General Information

THF was distilled from benzophenone/Na and used immediately. Water content of the solvent was estimated by the modified Karl Fisher method (less than 60 ppm water). IR spectra were obtained as potassium bromide pellets with a Perkin Elmer Paragon 500 spectrometer. Absorption bands are given in cm$^{-1}$. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded in CDCl$_3$ with a Bruker Avance 300 spectrometer ($^1$H at 300MHz, $^{13}$C at 75.4MHz and $^{19}$F at 282.5MHz). Chemical shift $\delta$ were reported in ppm relative to the residual solvent peak ($^1$H, $\delta$=7.26 or $^{13}$C, $\delta$=77.16). Melting points (°C) were measured on a Kofler hot-stage (± 2°C) and are uncorrected. Elemental analyses were performed on a Carlo Erba 1106 apparatus or CE Instrument EA 1110 and measurement accuracy is around ± 0.4% on carbon. Column chromatography was performed using silica gel (mesh size 60-80 µM).

Commercially available (4,4’dimethyloxazolin-2-yl)benzene 1a, 1,4-dimethoxybenzene 1m and anisole 1l were used without further purification.

Preparation of benzene derivatives 1b-k

Synthesis of oxazolinylbenzenes 1b-c.$^{1a}$

Zinc chloride (300 mg, 2 mmol) was placed in a 250 mL round bottom flask, melted three times under high pressure and allowed to cool to room temperature under N$_2$ before a solution of 4-chlorobenzonitrile (20 mmol) (respectively 4-methoxybenzonitrile) and 2-amino-2-methylpropane-1-ol (2.87 mL, 30 mmol) in dry chlorobenzene (40 mL) was added. The resulting mixture was refluxed for 48h. The volatiles were removed under vacuum and water (30 mL) was added. The aqueous layer was extracted with CH$_2$Cl$_2$ and the combined organic extracts were washed with water, brine, dried (MgSO$_4$) and concentrated in vacuum. The crude product was purified by flash chromatography on silica gel to give 4-chloro-2’-oxazolinylbenzene 1b (3.9g, 92%) and 1c (3.4g, 83% yields). All analyses are in accordance with those described in literature.$^{1b}$

Synthesis of N-tert-butylbenzamides 1d-f and N-cumylbenzamides 1g-i.$^{2a}$

A solution of benzoic chloride (10 mmol) (respectively 4-chlorobenzoyl chloride, 4-methoxybenzoyl chloride) in THF (30 mL) was added dropwise at 0°C to a solution of tert-butylamine (20 mmol) or cumylamine$^{2b}$ in THF (30 mL). After stirring 18h, aq.K$_2$CO$_3$ (2 mL, 2M) was added. The mixture was extracted with Et$_2$O (20 mL) and the combined organic extracts were washed water and dried (MgSO$_4$). After filtration, solvents were removed in vacuum to afford crude N-tert-butylbenzamide 1d-f and N-cumylbenzamide 1g-i which was purified by flash chromatography on silica gel to give 4-chloro-2’-oxazolinylbenzene 1b (3.9g, 92%) and 1c (3.4g, 83% yields). All analyses are in accordance with those described in literature.$^{1b}$


chloro-N-cumylbenzamide 1h (2.2 g, 81%), 4-methoxy-N-cumylbenzamide 1f (2.3 g, 84%) as white solids. All analyses of products 1d, 3a 1e, 3b 1f, 3c 1g, 3d 1i 3e are in accordance with those reported in literature data. All analysis of the new compound 1h is given in the characterization data section.

Synthesis of N-pivaloylaniline 1k

A solution of trimethylacetylchloride (6.97 mL, 50 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (30 mL) was added dropwise at 0°C to a solution of aniline (4.55 mL, 50 mmol) and triethylamine (8.7 mL, 60 mmol). The resulting mixture was stirred overnight at room temperature. The solvents are removed under vacuum and the crude product was purified by chromatography on silica gel using EtOAc and petroleum ether as eluents to give pivaloylaminobenzene 1k (8.6 g, 97%) as a white solid. All analyses of product 1k is given in the characterization data section.

General Experimental Procedures of Magnesation-Functionalization Reactions

General procedure for preparation of lithium butylmagnesate bases (procedure 1):

To a suspension of magnesium turning (0.0486 g, 2.0 mmol) in THF (10 mL) was added 1,2-dibromoethane (0.17 mL, 2.0 mmol) under N\textsubscript{2}. The mixture was refluxed for 1 h to afford a magnesium dibromide (MgBr\textsubscript{2}) as a colourless solution. After cooling at 0°C, the n-butyllithium (6 mmol or 8 mmol respectively, 2.5 M in hexanes) was added dropwise and the resulted mixture was stirred at the same temperature for 1 h to give a solution of Bu\textsubscript{3}MgLi and Bu\textsubscript{4}MgLi\textsubscript{2} (0.2 M) respectively.

General procedure for magnesation of benzene derivatives 1a-m (procedure 2):

Benzene derivatives 1a-c (4.8 mmol), 1d-i (3.6 mmol), 1k (2 mmol) and 1l-m (6.4 mmol) were added dropwise at room temperature to a selected freshly prepared solution of Bu\textsubscript{3}MgLi or Bu\textsubscript{4}MgLi\textsubscript{2} (see Table 1) (2 mmol) in THF following the above procedure 1. The resulted mixture was stirred at room temperature or at reflux (see Table 1) over a 2 h period before the subsequent introduction of the adequate reagents for electrophilic trapping or cross-coupling reactions (The magnesation was previously evaluated by carrying out D\textsubscript{2}O-trapping experiments followed by \textsuperscript{1}H NMR analysis of the crude of the deprotonation).


**General procedure for iodination of benzene derivatives 1a-m (procedure 3):**

To a solution of arylmagnesate in THF (10 mL) under N₂, prepared by treatment of 1a-m with a butylmagnesate base following the above general magnesation procedure 2, was added a solution of I₂ (6 or 8 mmol using Bu₃MgLi or Bu₄MgLi₂ respectively) in THF (10 mL) at room temperature. After a 2h stirring period, satd. aq.NH₄Cl (1 mL) and satd.aq.Na₂S₂O₃ (5 mL) solutions were successively added. The mixture was then extracted with Et₂O (10 mL) and the combined organic phase were washed with water (10 mL) and brine (10 mL), dried (MgSO₄) and evaporated under vacuum to give crude iodoaromatics 2a-m. Procedure of purification and all analysis are reported in the next ‘characterization data products’ section.

**General procedure for alkylation of benzene derivatives 1a-m (procedure 4):**

To a solution of arylmagnesate in THF (10 mL) under N₂, prepared by treatment of 1a-m with a butylmagnesate base following the above general magnesation procedure 2, was added dropwise propylene oxide (6 mmol or 8 mmol respectively) at room temperature. After 2h stirring at room temperature, satd.aq.NH₄Cl was added (1mL) and MgSO₄ was added. After filtration, the solvent was removed under vacuum to give crude hydroxymethylaromatics 3a-e. Procedure of purification and all analysis are reported in the next ‘characterization data products’ section

**General procedure for (hetero)arylation and vinylation of benzene derivatives 1a-m (procedure 5):**

To a solution of arylmagnesate in THF (10 mL) under N₂, prepared by treatment of 1a-m with a butylmagnesate base following the above general magnesation procedure 2, cross-coupling partner (2-bromopyridine, 3-iodopyridine, 3-bromoquinoline and 1-methylbromoethene) (6 mmol or 8 mmol respectively) and [1,1’-Bis(diphenyl phosphino)ferrocene]palladium (II) chloride (5 mol%) were added. After refluxing for 18h., satd.aq.NH₄Cl (1 mL) was then added and the resulted mixture was then filtered on Celite washed with Et₂O (40 mL). The solution was dried over MgSO₄, and after filtration solvents were removed to give crude arylated and vinylated aromatics 4a-d, 5a-d, 6a-b, 7a-d. Procedure of purification and all analysis are reported in the next ‘characterization data products’ section

**General procedure for oxydation of benzene derivatives 1a-m (procedure 6):**

Dried oxygene (O₂ gas passed through a drying system consisting on a sulphuric acid buller followed by a cartridge of KOH and ends with a silica guard) was bubbled without flow control at room temperature for 10 min into a solution arylmagnesate in THF (10 mL) prepared by treatment of 1a-m with a butylmagnesate base following the above general magnesation procedure 2. satd.aq.Na₂S₂O₃ (0.5 mL) and satd. aq.NH₄Cl (0.5 mL) solutions were successively added and after 5 min stirring, MgSO₄ was added. After filtration, the
solvent was removed under vacuum to give crude alcohols 8a-d. Procedure of purification and all analysis are reported in the next ‘characterization data products’ section.

**General procedure for fluorination of benzene derivatives 1a-m (procedure 7):**

To a solution of arylmagnesate in THF (10 mL) under N₂, prepared by treatment of 1a-m with a butylmagnesate base following the above general magnesation procedure 2, was added dropwise at room temperature a solution of N-fluorobenzenesulfonymid (NFSi) (6 mmol or 8 mmol respectively) in THF (6 mL). After 30 min stirring, sadt.aq.NH₄Cl (1 mL) was added. The mixture was extracted with Et₂O (20 mL) and the combined organic phases were washed with aq.NaOH (20mL of 0.5 M solution), water (20mL) and brine (20 mL), dried over MgSO₄. After filtration, the solvent was removed under vacuum to give crude fluoroaromatics 9a-e. Procedure of purification and all analysis are reported in the next ‘characterization data products’ section.

**Characterization Data of Products**

**4-Chloro-N-cumylbenzamide (1h)**

Crude 1h was prepared according the above reported general synthesis of benzamides and purified by column chromatography on silica gel (AcOEt/PE 2:8, Rf = 0.4) to give a white solid (mp = 198-199°C). ¹H NMR (CDCl₃) δ 7.72-7.67 (m, 2H), 7.46-7.33 (m, 6H), 7.28-7.23 (m, 1H), 6.35 (br s, 1H), 1.82 (s, 6H); ¹³C NMR (CDCl₃) δ 165.5, 146.7, 137.7, 133.8, 128.9, 128.7, 128.4, 127.0, 124.8, 56.6, 29.21; IR (KBr) ν 3277, 3060, 2978, 2364, 1634, 1594, 1534, 1486, 1196, 1013, 848, 762, 695; Anal. calcd. for C₁₆H₁₆ClNO : C, 70.20; H, 5.89; N, 5.12. Found: C, 70.42; H, 5.91; N, 4.95.

**2-Iodo-2'-oxazolinylbenzene (2a)**

Crude 2a was prepared according to the above procedure 3 using Bu₃MgLi as base and purified by flash chromatography to give an oil (1.0g, 75%). All analyses are in accordance with those reported in literature.⁵a

**4-Chloro-2-iodo-2'-oxazolinylbenzene (2b)**

Crude 2b was prepared according to the general procedure 3 using Bu₃MgLi as base and purified by flash chromatography (1.1g, 68%). All analyses are in accordance with those reported in literature.⁵b

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2-Iodo-4-methoxy-2'-oxazolinylbenzene (2c)

Crude 2c was prepared according to the general procedure 3 using Bu₃MgLi as base and purified by flash chromatography (1.1g, 71%). All analyses are in accordance with those reported in literature.⁵

2-Iodo-N-tert-butylbenzamide (2d)

Crude 2d was prepared according to the general procedure 3 using Bu₄MgLi₂ as base and purified by flash chromatography (AcOEt/PE 1:9, Rf = 0.11) as a white solid (0.9g, 82%), mp 124-125°C. ¹H NMR (CDCl₃) δ 7.84-7.82 (m, 1H), 7.40-7.33 (m, 2H), 7.09-7.04 (m, 1H), 5.52 (br s, 1H) 1.49 (s, 9H); ¹³C NMR (CDCl₃) δ 168.8, 143.3, 139.7, 130.8, 128.2, 128.1, 92.5, 52.3, 28.8; IR (KBr) ν 3243, 3070, 2971, 1639, 1588, 1555, 1331, 1224, 1014, 881, 749, 719, 677, 637; Anal. calcd. for C₁₁H₁₄INO: C, 43.58; H, 4.66; N, 4.62. Found: C, 43.60; H, 4.60; N, 4.65.

4-Chloro-2-iodo-N-tert-butylbenzamide (2e)

Crude 2e was prepared according to the general procedure 3 using Bu₄MgLi₂ as base and purified by flash chromatography (AcOEt/PE 2:8, Rf = 0.46) as a white solid (0.9g, 76%), mp= 142-143 °C. ¹H NMR (CDCl₃) δ 7.83 (d, J=1.8Hz, 1H), 7.36-7.29 (m, 2H), 5.52 (br s, 1H), 1.48 (s, 9H). ¹³C NMR (CDCl₃) δ 167.9, 141.6, 139.0, 135.6, 128.8, 128.4, 92.7, 52.4, 28.7; IR (KBr) ν 3255, 2964, 1637, 1553, 1365, 1224, 1095, 822, 572; Anal. calcd. for C₁₁H₁₃ClINO: C, 39.14; H, 3.88; N, 4.15. Found : C, 39.23 ; H, 3.67 ; N, 4.15.

2-Iodo-4-methoxy-N-tert-butylbenzamide (2f)

Crude 2f was prepared according to the general procedure 3 using Bu₄MgLi₂ as base and purified by flash chromatography (AcOEt/PE 2:8, Rf = 0.3) as a white solid (1g, 84%), mp = 82-83 °C. ¹H NMR (CDCl₃) δ 7.35 (s, 1H), 7.33 (dd, J=8.4Hz, J=2.7Hz, 1H), 6.87 (dd, J=8.7Hz, J=2.4Hz, 1H), 5.56 (br s, 1H), 3.79 (s, 3H), 1.47 (s, 9H). ¹³C NMR (CDCl₃) δ 168.5, 160.3, 135.6, 129.2, 124.9, 114.0, 92.9, 55.6, 52.1, 28.8 IR (KBr) ν 3275, 2967, 1633, 1594, 1485, 1295, 1223, 1026, 887, 837, 820, 685; Anal. calcd. for C₁₂H₁₆INO₂ : C, 43.26; H, 4.84; N, 4.20. Found : C, 43.34 ; H, 4.78 ; N, 4.23.

2-Iodo-N-cumylbenzamide (2g)

Crude 2g was prepared according to the general procedure 3 using Bu₄MgLi₂ as base and purified by flash chromatography (AcOEt/PE 2:8, Rf = 0.2) as an orange solid (1.2g, 88%), mp= 122-123°C. ¹H NMR (CDCl₃) δ 7.86-7.83
(m, 1H), 7.54-7.51 (m, 2H), 7.43-7.34 (m, 4H), 7.29-7.23 (m, 1H), 7.10-7.05 (m, 1H), 6.04 (br s, 1H), 1.85 (s, 6H); $^{13}$C NMR (CDCl$_3$) δ 168.2, 146.6, 142.8, 139.9, 131.0, 128.6, 128.4, 128.2, 127.0, 125.0, 92.4, 56.3, 28.9; IR (KBr) ν 3312, 3059, 2987, 2933, 1649, 1583, 1526, 1309, 1194, 1017, 751, 694, 561; Anal. calcd. for C$_{16}$H$_{16}$INO : C, 52.62; H, 4.42; N, 3.84. Found : C, 52.62; H, 4.52; N, 3.65.

4-Chloro-2-iodo-N-cumylbenzamide (2h)

Crude 2h was prepared according to the general procedure 3 using Bu$_4$MgLi$_2$ as base and purified by flash chromatography (AcOEt/PE 2:8, Rf = 0.4) as a white solid (1.2g, 82%), mp = 132-133 °C. $^1$H NMR (CDCl$_3$) δ 7.85-7.84 (m, 1H), 7.52-7.48 (m, 2H), 7.39-7.34 (m, 4H), 7.29-7.24 (m, 1H), 6.01 (br s, 1H), 1.85 (s, 6H); $^{13}$C NMR (CDCl$_3$) δ 167.3, 146.4, 141.1, 139.1, 135.7, 129.0, 128.5, 128.4, 126.9, 125.0, 92.6, 56.9, 28.8; IR (KBr) ν 3230, 3058, 2976, 1640, 1577, 1552, 1322, 1097, 1029, 767, 703; Anal. calcd. for C$_{16}$H$_{15}$ClINO : C, 48.08; H, 3.78; N, 3.50. Found : C, 48.12; H, 3.53; N, 3.73.

2-Iodo-4-methoxy-N-cumylbenzamide (2i)

Crude 2h was prepared according to the general procedure 3 using Bu$_4$MgLi$_2$ as base and purified by flash chromatography (AcOEt/PE 2:8, Rf = 0.2) as a white solid (1.2g, 87%), mp = 121-122 °C. $^1$H NMR (CDCl$_3$) δ 7.53-7.50 (m, 2H), 7.39-7.23 (m, 5H), 6.90-6.87 (m, 1H), 6.14 (br s, 1H), 3.80 (s, 3H), 1.84 (s, 6H); $^{13}$C NMR (CDCl$_3$) δ 167.9, 160.6, 146.7, 135.1, 129.6, 128.5, 126.9, 125.0, 114.1, 92.9, 56.8, 55.7, 29.0 IR (KBr) ν 3230, 3058, 2976, 1640, 1577, 1552, 1322, 1097, 1034, 817, 761, 701, 549; Anal. calcd. for C$_{17}$H$_{18}$INO$_2$ : C, 51.66; H, 4.59; N, 3.54. Found : C, 51.76; H, 4.48; N, 3.33.

2-Iodo-pivaloylaminobenzene (2k)

Crude 2f was prepared according to the general procedure 3 using Bu$_4$MgLi$_2$ as base and purified by flash chromatography (AcOEt/PE 2:8, Rf = 0.4) as yellow solid (0.4g, 70%). All analyses are in accordance with those reported in literature.$^{5c}$

1,4-Dimethoxy-2-Iodobenzene (2m)

Crude 2m was prepared according to the general procedure 3 using Bu$_4$MgLi$_2$ as base and purified by flash chromatography (AcOEt/PE 2:8, Rf = 0.7) flash chromatography (1.5g, 91%). All analyses are in accordance with those reported in literature.$^{5d}$
2-(2'-Hydroxypropyl)-2'-oxazolinylbenzene (3a)

Crude 3a was prepared according to the general procedure 4 using Bu$_3$MgLi as base and purified by flash chromatography (AcOEt/PE 6:4, Rf = 0.4) as a pale yellow oil (0.6g, 55%). $^1$H NMR (CDCl$_3$) $\delta$ 7.75-7.72 (m, 1H), 7.43-7.37 (m, 1H), 7.28-7.23 (m, 2H), 6.37 (br s, 1H), 4.12 (s, 1H), 4.11 (s, 1H), 4.1-4.04 (m, 1H), 3.16-3.02 (m, 2H), 1.41 (s, 3H), 1.40 (s, 3H), 1.30 (d, $J$=6.3Hz, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 162.9, 140.0, 131.6, 130.7, 129.4, 127.3, 126.0, 78.9, 69.4, 67.8, 42.4, 28.5, 28.2, 24.4; IR (KBr) $\nu$ 3288, 2966, 2928, 2870, 1645, 1355, 1313, 1059, 744; Anal. calcd. for C$_{14}$H$_{19}$NO$_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 71.97; H, 8.12; N, 6.13.

2-(2'-Hydroxypropyl)-N-tert-butylbenzamide (3b)

Crude 3b was prepared according to the general procedure 4 using Bu$_4$MgLi$_2$ as base and purified by flash chromatography (AcOEt/PE 3:7, Rf = 0.2) as a white solid (0.4g, 42%), mp = 99-100°C. $^1$H NMR (CDCl$_3$) $\delta$ 7.40-7.34 (m, 2H), 7.26-7.20 (m, 2H), 6.19 (br s, 1H), 4.31 (d, $J$=4.8Hz, 1H), 4.08-3.97 (m, 1H), 2.90-2.77 (m, 2H), 1.46 (s, 9H), 1.31 (d, $J$=6.3Hz, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 170.1, 138.0, 137.3, 130.8, 129.9, 127.3, 126.3, 69.0, 52.0, 42.1, 28.8, 24.3; IR (KBr) $\nu$ 3288, 3069, 2965, 2926, 1632, 1598, 1580, 1554, 1451, 1427, 1365, 1331, 1226, 1125, 745; Anal. calcd. for C$_{14}$H$_{21}$NO$_2$: C, 71.46; H, 8.99; N, 5.95. Found: C, 71.46; H, 9.03; N, 5.96.

2-(2'-Hydroxypropyl)-N-cumylbenzamide (3c)

Crude 3c was prepared according to the general procedure 4 using Bu$_4$MgLi$_2$ as base and purified by flash chromatography (AcOEt/PE 1:1, Rf = 0.4) as a white solid (0.7g, 61%), mp= 115-116°C. $^1$H NMR (CDCl$_3$) $\delta$ 7.49-7.46 (m, 3H), 7.42-7.33 (m, 3H), 7.28-7.24 (m, 3H), 6.69 (br s, 1H), 4.00-3.96 (m, 2H), 2.90-2.77 (m, 2H), 1.83 (s, 3H), 1.80 (s, 3H) 1.26 (d, $J$=6.0Hz, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 169.6, 146.7, 137.5, 130.9, 130.1, 128.4, 127.4, 126.7, 126.4, 124.9, 69.1, 56.5, 42.1, 29.4, 29.0, 24.2; IR (KBr) $\nu$ 3345, 3059, 2965, 2927, 2873, 1632, 1598, 1580, 1554, 1451, 1427, 1365, 1331, 1226, 1125, 745; Anal. calcd. for C$_{19}$H$_{23}$NO$_2$: C, 76.73; H, 7.80; N, 4.71. Found: C,76.70; H, 7.85; N, 3.69.

2-(2'-Hydroxypropyl)-anisole (3d)

Crude 3d was prepared according to the general procedure 4 using Bu$_4$MgLi$_2$ as base and purified by flash chromatography (AcOEt/PE 2:8, Rf = 0.3) as limpid oil (0.6g, 57%). All analyses are in accordance with those reported in
2-(2'-Hydroxypropyl)-pivaloylaminobenzene (3e)

Crude 3e was prepared according to the general procedure 4 using Bu₄MgLi₂ as base and purified by flash chromatography (AcOEt/PE 2:8, Rf = 0.2) as a white solid (0.2g, 50%), mp 101°C. ¹H NMR (CDCl₃) δ 9.03 (br s, 1H), 7.82-7.79 (m, 1H), 7.26-7.21 (m, 1H), 7.13-7.04 (m, 2H), 4.18-4.10 (m, 1H), 2.80-2.63 (m, 2H), 2.10 (br s, 1H), 1.31 (s, 9H), 1.28 (s, 3H); ¹³C NMR (CDCl₃) δ 177.6, 137.1, 131.1, 131.0, 126.9, 124.6, 124.5, 70.0, 40.8, 39.6, 27.8, 23.9; IR (KBr) ν 3326, 2961, 2926, 2867, 1638, 1552, 1310, 1201, 1132, 1070, 799, 733, 678; Anal. calcd. for C₁₄H₂₁NO₂: C, 71.46; H, 8.99; N, 5.95. Found : C, 71.39 ; H , 8.99 ; N, 6.03.

2-Hydroxy-2'-oxazolinylbenzene (8a)

Crude 8a was prepared according to the general procedure 6 using Bu₃MgLi as base and purified by flash chromatography (AcOEt/PE 1:9, Rf = 0.5) as limpid oil (0.5g, 55%). All analyses are in accordance with those reported in literature.

2-Hydroxy-N-tert-butylbenzamide (8b)

Crude 8b was prepared according to the general procedure 6 using Bu₄MgLi₂ as base and purified by flash chromatography (AcOEt/PE 1:9, Rf = 0.3) as a white solid (0.3g, 37%), mp= 82-83°C. ¹H NMR (CDCl₃) δ 12.50 (br s, 1H), 7.39-7.33 (m, 1H), 7.27 (dd, J=8.1Hz, J=1.5Hz, 1H), 6.96 (dd, J=8.4Hz, J=1.2Hz, 1H), 6.84-6.79 (m, 1H), 6.10 (br s, 1H), 1.48 (s, 9H); ¹³C NMR (CDCl₃) δ 169.9, 161.7, 133.9, 125.4, 118.7, 118.5, 115.2, 52.2, 28.9; IR (KBr) ν 3343, 2969, 2722, 1606, 1573, 1500, 1457, 1390, 1364, 1325, 1321, 1157, 891, 754, 648; Anal. calcd. for C₁₁H₁₅NO₂: C, 68.37; H, 7.82; N, 7.25. Found : C, 68.13; H, 7.80; N, 7.17.

2-Hydroxy-N-cumylbenzamide (8c)

Crude 8c was prepared according to the general procedure 6 using Bu₄MgLi₂ as base and purified by flash chromatography (AcOEt/PE 2:8, Rf = 0.3) as a white solid (0.2g, 23%), mp= 181-182°C. ¹H NMR (CDCl₃) δ 12.21 (br s, 1H), 7.46-7.34 (m, 6H), 7.30-7.24 (m, 1H), 6.96 (dd, J=7.8Hz, J=1.2Hz, 1H), 6.86 (ddd, J=8.4Hz, J=7.5Hz, J=12Hz, 1H), 6.57 (br s, 1H), 1.82 (s, 6H); ¹³C NMR (CDCl₃) δ 169.4, 161.8, 146.3, 134.2, 128.7, 127.1, 125.5, 124.6, 118.8, 118.7, 114.8, 56.7, 29.4; IR (KBr) ν


3336, 3086, 2961, 2712, 1629, 1495, 1384, 1363, 1322, 1240, 1208, 1095, 757, 698; Anal. calcd. for C_{16}H_{17}NO_{2}: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.18; H, 6.69; N, 5.14.

2-Hydroxypivaloylaminobenzene (8e)

Crude 8e was prepared according to the general procedure 6 using Bu_{4}MgLi as base and purified by flash chromatography (AcOEt/PE 1:9, Rf = 0.1) as a white solid (0.2 g, 42%). All analyses are in accordance with those reported in literature.\(^7b\)

1-Fluoro-2-(4,4'-dimethyloxazolin-2-yl)benzene (9a)

Crude 9a was prepared according to the general procedure 7 using Bu_{3}MgLi as base and purified by flash chromatography (AcOEt/PE 1:9, Rf = 0.1) as limpid oil (0.4 g, 43%). All analyses are in accordance with those reported in literature.\(^8a\)

2-Fluoro-N-tert-butylbenzamide (9b)

Crude 9b was prepared according to the general procedure 7 using Bu_{4}MgLi as base and purified by flash chromatography (AcOEt/PE 5:95, Rf = 0.2) as a yellow solid (0.5 g, 65%), mp = 34-35°C. \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 8.01 (ddd, \(J\) = 9.6 Hz, \(J\) = 7.8 Hz, \(J\) = 1.8 Hz, 1H), 7.43-7.36 (m, 1H), 7.20 (ddd, \(J\) = 8.4 Hz, \(J\) = 7.8 Hz, \(J\) = 0.9 Hz, 1H), 7.05 (ddd, \(J\) = 12.3 Hz, \(J\) = 8.4 Hz, \(J\) = 0.9 Hz, 1H), 6.58 (br s, 1H), 1.45 (s, 9H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 162.3 (\(J\) = 3.0 Hz), 160.4 (\(J\) = 245.8 Hz), 132.9 (\(J\) = 9.0 Hz), 131.8 (\(J\) = 2.3 Hz), 124.7 (\(J\) = 3.8 Hz), 122.4 (\(J\) = 12.1 Hz), 115.9 (\(J\) = 24.9 Hz), 51.8, 28.9; \(^{19}\)F NMR (CDCl\(_3\)) \(\delta\) -113; IR (KBr) \(\nu\) 3277, 2970, 1639, 1615, 1538, 1487, 1449, 1364, 1324, 1227, 754; Anal. calcd. for C\(_{11}\)H\(_{14}\)FNO: C, 67.67; H, 7.23; N, 7.17. Found: C, 67.62; H, 7.17; N, 7.06.

2-Fluoro-4-methoxy-N-tert-butylbenzamide (9c)

Crude 9c was prepared according to the general procedure 7 using Bu_{4}MgLi as base and purified by flash chromatography (AcOEt/PE 2:8, Rf = 0.2) as an yellow oil (0.5 g, 65%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 8.04-7.98 (m, 1H), 6.71 (dd, \(J\) = 8.7 Hz, \(J\) = 2.4 Hz, 1H), 6.59 (dd, \(J\) = 14.1 Hz, \(J\) = 2.4 Hz, 1H), 6.50 (br s, 1H), 3.83 (s, 3H), 1.46 (s, 9H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 163.0 (\(J\) = 6 Hz), 162.2 (\(J\) = 3.8 Hz), 161.5 (\(J\) = 263.9 Hz), 132.9 (\(J\) = 4.5 Hz), 114.6 (\(J\) = 12.1 Hz), 110.5 (\(J\) = 2.3 Hz), 101.5 (\(J\) = 29.4 Hz), 55.8, 51.6, 28.9; \(^{19}\)F NMR (CDCl\(_3\)) \(\delta\) -111; IR (KBr) \(\nu\) 3466, 2967, 1665, 1621, 1535, 1500, 1455, 1281, 1268, 1221, 1155, 1104; Anal. calcd. for C\(_{12}\)H\(_{16}\)FNO\(_2\): C, 63.98; H, 7.16; N, 6.22. Found: C, 64.05; H, 7.13; N, 6.34.

2-Fluoro-N-cumylbenzamide (9d)

Crude 9d was prepared according to the general procedure 7 using Bu₄MgLi₂ as base and purified by flash chromatography (AcOEt/PE 1:9, Rf = 0.2) as a pale yellow solid (0.6g, 69%), mp= 49-50°C. ¹H NMR (CDCl₃) δ 8.02 (ddd, J=9.6Hz, J=7.8Hz, J=1.8Hz, 1H), 7.50-7.42 (m, 3H), 7.38-7.32 (m, 2H), 7.27-7.21 (m, 2H), 7.13 (ddd, J=11.4Hz, J=8.4Hz, J=0.9Hz, 1H), 7.09 (br s, 1H), 1.82 (s, 6H); ¹³C NMR (CDCl₃) δ 161.9 (J=3.8Hz), 160.4 (J=245.8Hz), 146.7, 146.3, 133.1 (J=9.0Hz), 131.9 (J=9.0Hz), 131.9 (J=2.3Hz), 128.4, 126.6, 124.7 (J=3.8Hz), 124.7, 121.9 (J=12.1Hz), 115.9 (J=24.9Hz), 56.3, 29.3; ¹⁹F NMR (CDCl₃) δ -116; IR (KBr) ν 3462, 3311, 3061, 2976, 1667, 1651, 1614, 1520, 14 80, 1450, 1302, 757, 698; Anal. calcd. for C₁₆H₁₆FNO : C, 74.69; H, 6.27; N, 5.44. Found : C, 70.64; H, 6.25; N, 4.51.

1-(4,4’-dimethyloxazolin-2-yl)-2-(pyridin-2-yl)benzene (4a)

Crude 4a was prepared according to the general procedure 5 using Bu₃MgLi as base and purified by flash chromatography (AcOEt/PE 7:3, Rf = 0.2) as a red oil (0.5g, 40%). ¹H NMR (CDCl₃) δ 8.65 (d, J=4.8Hz, 1H), 7.78 (dd, J=7.8 Hz, J=1.5Hz, 1H), 7.59 (dd, J=7.8Hz, J=1.5Hz, 1H), 7.52 (ddd, J=8.7Hz, J=7.2Hz, J=1.2Hz, 1H), 7.48–7.40 (m, 2H), 7.26–7.23 (m, 1H), 3.83 (s, 2H), 1.30  (s, 6H); ¹³C NMR (CDCl₃) δ 163.1, 158.2, 148.6, 140.1, 135.6, 130.1, 129.8, 129.4, 127.8, 127.6, 122.7, 121.6, 79.0, 67.1, 27.6; IR (KBr) ν 2966, 1656, 1587, 1463, 1426, 1312, 1037, 750; Anal. calcd. for C₁₆H₁₆N₂O : C, 76.16; H, 6.39; N, 11.1. Found : C, 75.97; H, 6.35; N, 11.00.

1-Chloro-4-(4,4’-dimethyloxazolin-2-yl)-5-(pyridine-2-yl)benzene (4b)

Crude 4b was prepared according to the general procedure 5 using Bu₃MgLi as base and purified by flash chromatography (AcOEt/PE 1:1, Rf = 0.2) as a yellow solid (0.7g, 53%), mp = 94-95°C. ¹H NMR (CDCl₃) δ 8.67-8.64 (m, 1H), 7.77-7.71 (m, 1H), 7.64-7.61 (m, 1H), 7.53-7.40 (m, 2H), 7.29–7.24 (m, 1H), 3.83 (s, 2H), 1.30 (s, 6H); ¹³C NMR (CDCl₃) δ 157.2, 149.1, 142.1, 136.3, 135.9, 131.5, 129.9, 128.1, 126.5, 126.4, 123.0, 122.3, 79.4, 67.6, 27.9; IR (KBr) ν 2978, 2965, 2925, 1581, 1588, 1466, 1427, 1398, 1348, 1311, 1102, 1072, 1034, 842, 793, 756; Anal. calcd. for C₁₆H₁₅ClN₂O : C, 67.02; H, 5.29; N, 9.77. Found : C, 67.05; H, 5.27; N, 9.83.

2-(pyridin-2-yl)-N-tert-butylbenzamide (4c)

Crude 4c was prepared according to the general procedure 5 using Bu₄MgLi₂ as base and purified by flash chromatography (AcOEt/PE 4:6, Rf = 0.2) as a white solid (0.3g, 36%), mp = 94-95°C. ¹H NMR (CDCl₃) δ 8.67-8.65 (m, 1H), 7.77-7.71 (m, 1H), 7.64-7.61 (m, 1H), 7.53-7.40 (m,
4-H), 7.29 (dd, J=5.1Hz, J=1.2Hz, 1H), 5.67 (br s, 1H), 1.21 (s, 9H); $^{13}$C NMR (CDCl$_3$) $\delta$ 169.0, 158.7, 149.2, 138.5, 137.6, 136.6, 129.8, 129.7, 128.7, 128.4, 124.3, 122.5, 51.6, 51.2, 28.5; IR (KBr) 3306, 3047, 2962, 2924, 1638, 1590, 1546, 755; Anal. calcd. for C$_{16}$H$_{18}$N$_2$O : C, 75.56; H, 7.13; N, 11.01. Found : C, 75.56; H, 7.10; N, 11.06.

4-Methoxy-2-(pyridin-2-yl)-N-tert-butylbenzamide (4d)

Crude 4d was prepared according to the general procedure 5 using Bu$_4$MgLi$_2$ as base and purified by flash chromatography (AcOEt/PE 1:1, Rf = 0.2) as an yellow solid (0.4g, 41%), mp = 99-100°C. $^1$H NMR (CDCl$_3$) $\delta$ 8.66 (m, 1H), 7.74 (ddd, $J$=7.5Hz, $J$=7.5Hz, $J$=1.5Hz, 1H), 7.61 (d, $J$=8.4Hz, 1H), 7.47 (d, $J$=7.8Hz, 1H), 7.30 (ddd, $J$=7.5Hz, $J$=4.8Hz, $J$=0.9Hz, 1H), 6.99 (d, $J$=2.7Hz, 1H), 6.96 (dd, $J$=8.4Hz, $J$=2.7Hz, 1H), 5.61 (br s, 1H), 3.85 (s, 3H), 1.17 (s, 9H); $^{13}$C NMR (CDCl$_3$) $\delta$ 168.3, 160.2, 158.5, 149.0, 140.0, 136.4, 130.2, 129.9, 124.1, 122.4, 114.6 114.1, 55.3, 51.2, 28.2; IR (KBr) 3315, 1642, 1542, 1479, 1319, 1293, 1216, 1180, 1034; Anal. calcd. for C$_{17}$H$_{20}$N$_2$O$_2$ : C, 71.81; H, 7.09; N, 9.85. Found : C, 71.55; H, 6.91; N, 9.69.

1-(4,4'-dimethyloxazolin-2-yl)-2-(pyridin-3-yl)benzene (5a)

Crude 5a was prepared according to the general procedure 5 using Bu$_3$MgLi as base and purified by flash chromatography (AcOEt/PE 6:4, Rf = 0.2) as an yellow solid (0.6g, 52%), mp = 96-97°C. $^1$H NMR (CDCl$_3$) $\delta$ 8.60 (d, $J$=1.8Hz, 1H), 8.56 (dd, $J$=4.8Hz, $J$=1.5Hz, 1H), 7.80 (dd, $J$=7.5Hz, $J$=1.2Hz, 1H), 7.68 (ddd, $J$=7.8Hz, $J$=5.7Hz, $J$=1.8Hz, 1H), 7.51 (ddd, $J$=9Hz, $J$=7.5Hz, $J$=1.5Hz, 1H), 7.42 (dd, J=8.1Hz, J=2.1Hz, 1H), 7.30 (ddd, J=9Hz, J=7.5Hz, J=1.5Hz, 1H), 7.36–7.28 (m, 2H), 3.82 (s, 2H), 1.26 (s, 6H); $^{13}$C NMR (CDCl$_3$) $\delta$ 163.1, 149.3, 148.4, 138.2, 137.0, 135.7, 130.5, 130.4, 128.1, 128.0, 122.9, 79.4, 67.8, 28.1; IR (KBr) v 2961, 2926, 2885, 1651, 1591, 1473, 1437, 1413, 1348, 1300, 1068, 1039, 1028, 968, 816, 776, 698; Anal. calcd. for C$_{16}$H$_{16}$N$_2$O : C, 76.16; H, 6.39; N, 11.1. Found : C, 76.10; H, 6.50; N, 11.87.

4-chloro-2-(pyridin-3-yl)-N-tert-butylbenzamide (5b)

Crude 5b was prepared according to the general procedure 5 using Bu$_4$MgLi$_2$ as base and purified by flash chromatography (AcOEt/PE 1:1, Rf = 0.3) as an yellow solid (0.5g, 52%), mp = 172-173°C. $^1$H NMR (CDCl$_3$) $\delta$ 8.67-8.65 (m, 2H), 7.78-7.75 (m, 1H), 7.59(d, 8.4Hz, 1H), 7.42 (dd, J=8.1Hz, J=2.1Hz, 1H), 7.30-7.28 (m, 2H), 5.08 (br s, 1H), 1.18 (s, 9H); $^{13}$C NMR (CDCl$_3$) $\delta$ 167.3, 149.3, 149.1, 137.5, 136.2, 135.9, 135.8, 134.9, 130.0 (2C), 128.4, 123.3, 52.0, 28.4. IR (KBr) 3220, 3055, 1633, 1590, 1563, 1474, 1455, 1411, 1362, 1324,
1219, 1097, 1014, 848, 708; Anal. calcd. for C$_{16}$H$_{17}$ClN$_2$O: C, 66.55; H, 5.93; N, 9.7. Found: C, 66.13; H, 6.01; N, 9.65.

4-Chloro-2-(pyridin-3-yl)-N-cumylbenzamide (5c)

Crude 5c was prepared according to the general procedure 5 using Bu$_4$MgLi$_2$ as base and purified by flash chromatography (AcOEt/Pe 3:7, Rf = 0.1) as an yellow solid (0.7g, 58%), mp= 181-182°C. $^1$H NMR (CDCl$_3$) δ 8.70 (m, 1H), 7.77 (d, J=7.8Hz, 1H), 7.61 (d, J=8.1Hz, 1H), 7.42 (ddd, J=10.5Hz, J=8.4Hz, J=2.1Hz, 1H), 7.36-7.35 (m, 2H), 7.29-7.20 (m, 4H), 7.11-7.08 (m, 2H), 5.54 (br s, 1H), 1.56 (s, 6H); $^{13}$C NMR (CDCl$_3$) δ 167.0, 149.3, 149.2, 146.3, 137.6, 136.4, 136.0, 135.6, 130.1, 130.0, 128.5, 128.4, 126.9, 124.6, 56.7, 28.2; IR (KBr) 3285, 1643, 1542, 1314, 764, 701, 558; Anal. calcd. for C$_{21}$H$_{19}$ClN$_2$O: C, 71.89; H, 5.46; N, 7.98. Found: C, 72.00; H, 5.43; N, 7.96.

2-(3'-pyridyl)-anisole (5d)

Crude 5b was prepared according to the general procedure 5 using Bu$_4$MgLi$_2$ as base and purified by flash chromatography (AcOEt/PE 2:8, Rf = 0.2) as a limpid oil (0.6g, 51%). All analyses are in accordance with those reported in literature.

4-Chloro-1-(4,4'-dimethyloxazolin-2-yl)-2-(quinolin-3-yl)benzene (6a)

Crude 6a was prepared according to the general procedure 5 using Bu$_3$MgLi as base and purified by flash chromatography (AcOEt/PE 1:1, Rf = 0.4) as a white solid (1g, 62%), mp = 92-93°C. $^1$H NMR (CDCl$_3$) δ 8.86 (d, J=2.1Hz, 1H), 8.14-8.11 (m, 2H), 7.85-7.81 (m, 2H), 7.76-7.70 (m, 1H), 7.59-7.54 (m, 1H), 7.46-7.41 (m, 2H), 3.79 (s, 2H), 1.24 (s, 6H); $^{13}$C NMR (CDCl$_3$) δ 162.1, 150.6, 147.3, 140.0, 136.9, 134.5, 133.2, 132.0, 130.9, 129.8, 129.4, 128.2, 128.1, 127.7, 127.1, 126.6, 79.5, 67.9, 28.1; IR (KBr) 2964, 1667, 1305, 1099, 1037, 898, 745; Anal. calcd. for C$_{20}$H$_{17}$ClN$_2$O: C, 71.32; H, 5.09; N, 8.32. Found: C, 70.97; H, 5.11; N, 8.33.

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4-Chloro-2-(quinolin-3-yl)-N-tert-butylbenzamide (6b)

Crude 6b was prepared according to the general procedure 5 using Bu₄MgLi₂ as base and purified by flash chromatography (AcOEt/PE 3:7, Rf = 0.2) as an yellow solid (0.5g, 42%), mp = 171-172°C. ¹H NMR (CDCl₃) δ 8.95 (d, J = 2.4Hz, 1H), 8.24 (d, J = 2.1Hz, 1H), 8.16 (d, J = 8.4Hz, 1H), 7.85 (d, J = 8.4Hz, 1H), 7.80-7.75 (m, 1H), 7.65–7.58 (m, 2H), 7.47–7.43 (m, 2H), 5.18 (br s, 1H), 1.12 (s, 9H); ¹³C NMR (CDCl₃) δ 167.5, 150.0, 147.3, 137.5 136.0, 135.9, 135.3, 131.9, 130.2, 130.1, 130.0, 129.2, 128.3, 128.0, 127.4, 127.4, 51.9, 28.3; IR (KBr) 3246, 2967, 1664, 1593, 1547, 1455, 1310, 1227, 759; Anal. calcd. for C₂₀H₁₉ClN₂O : C, 70.90; H, 5.65; N, 8.27. Found : C, 70.89; H , 5.67; N, 8.25 .

1-(4,4’-dimethyloxazolin-2-yl)-2-propenyl-benzene (7a)

Crude 7a was prepared according to the general procedure 5 using Bu₄MgLi₂ as base and was purified by flash chromatography to give a mixture of 7a and the starting material (3:2, 66%). All analyses are in accordance with those reported in literature.⁹b

2-Propenyl-N-tert-butylbenzamide (7b)

Crude 7b was prepared according to the general procedure 5 using Bu₄MgLi₂ as base and purified by flash chromatography (AcOEt/PE 3:7, Rf = 0.18) as an white solid (0.5g, 67%), mp = 77-78°C. All analyses are in accordance with those reported in literature.⁹c

2-Propenyl-N-cumylbenzamide (7c)

Crude 7c was prepared according to the general procedure 5 using Bu₄MgLi₂ as base and purified by flash chromatography (AcOEt/PE 2:8, Rf = 0.4) as a white solid (0.7, 67%), mp = 100-101°C. ¹H NMR (CDCl₃) δ 7.67-7.64 (m, 1H), 7.46-7.43 (m, 2H), 7.40-7.28 (m, 4H), 7.25-7.18 (m, 3H), 6.48 (br s, 1H), 5.23 (s, 1H), 5.09 (s, 1H), 2.12 (s, 3H), 1.80 (s, 6H); ¹³C NMR (CDCl₃) δ 167.9, 146.7, 146.5, 141.7, 134.8, 130.1, 128.8, 128.6, 128.4, 127.5, 126.8, 124.9, 115.9, 56.4, 28.5, 24.8; IR (KBr) 3275, 2972, 1644, 1532, 1316, 890, 765, 699; Anal. calcd. for C₁₉H₂₁NO : C, 81.68 ; H, 7.58 ; N, 5.01. Found : C, 81.70; H, 7.54; N, 5.03.

2-Propenyl-anisole 7d

Crude 7d was prepared according to the general procedure 5 using Bu₄MgLi₂ as base and purified by flash chromatography (AcOEt/PE 3:7, Rf = 0.18) as a limpid oil (0.6g, 66%). All analyses are in accordance with those reported in literature.⁹d
$^1$H, $^{13}$C and $^{19}$F NMR Spectra of Product

[Chemical structure images]

Supplementary Material (ESI) for Chemical Communications
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