Phosphane-free Suzuki–Miyaura Coupling of Aryl Imidazolesulfonates with Arylboronic Acids and Potassium Aryltrifluoroborates under Aqueous Conditions

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1. **General**

Unless otherwise noted all commercial reagents and solvents were used without further purification. Melting points were determined with a Reichert Thermovar hot plate apparatus and are uncorrected. IR spectra were recorded on a Nicolet 510 P-FT. $^1$H-NMR (300 or 400 MHz) and $^{13}$C-NMR (75 or 100 MHz) spectra were obtained on a Bruker AC-300 and Bruker AC-400, respectively, using CDCl$_3$ as solvent and TMS as internal standard, unless otherwise stated. Low-resolution electron impact (EI) mass spectra were obtained at 70 eV on an Agilent 5973 Network Mass selective detector. Analytical TLC was performed on Merck aluminum sheets with silica gel 60 F$_{254}$. Silica gel 60, (0.04-0.06 mm) was employed for flash chromatography. Microwave reactions were performed with a CEM Discover Synthesis Unit (CEM Corp., Matthews, NC) with a continuous focused microwave power delivery system in glass vessels (10 ml) sealed with a septum under magnetic stirring. The temperature of the reaction mixture inside the vessel was monitored using a calibrated infrared temperature control under the reaction vessel.

2. **Synthesis of 1,1´-Sulfonyldiimidazole.$^1$**

To a 0 ºC solution of imidazole (20.0 g, 294 mmol) in anhydrous CH$_2$Cl$_2$ (210 mL), cooled to 0ºC, was added a solution of sulfuryl chloride (5.0 ml, 61.6 mmol) in anhydrous CH$_2$Cl$_2$ (28 mL), drop-wise. The reaction mixture was allowed to warm to ambient temperature and stirred for 16 hours. The reaction mixture was filtered, the solvent evaporated under reduced pressure, and the resulting solid crystallized from isopropyl alcohol (100 mL). The obtained white needles were filtered, washed with cold isopropyl alcohol and dried under reduced pressure to afford 10.59 g of pure 1,1´-sulfonyldiimidazole (87%).

3. **Synthesis of tert-Butyl Naphthalen-1-yl Carbonate (2aa).**

Under Ar atmosphere, a 100 mL round bottom flask was charged with 1-naphthol (1 g, 6.94 mmol, 1 equiv), DMAP (0.086 g, 0.694 mmol, 0.1 equiv), Et$_3$N (1.07 mL, 7.64 mmol, 1.1 equiv) and anhydrous CH$_2$Cl$_2$ (23 mL). Then, a solution of Boc$_2$O (1.66 g, 7.46 mmol, 1.1 equiv) in anhydrous CH$_2$Cl$_2$ (10 mL) was added dropwise via cannula. The resulting solution was stirred for 15 min. Then, the solution was transferred to a separatory funnel and NaHSO$_4$ (20 mL, 0.5 M) was added. The layers were separated and the aqueous layer was washed with CH$_2$Cl$_2$ (3 × 20 mL), washed with brine (20 mL), dried over MgSO$_4$, and concentrated under reduced pressure. The
crude residue was purified by flash chromatography (Hexane/EtOAc: 3/1) to obtain 1.61 g of compound 2aa (95% yield).

4. Synthesis of Naphthalene-1-yl Dimethylcarbamate (2ab).

Under Ar atmosphere, a round bottom flask charged with NaH (0.4 g, 16.67 mmol, 1.2 equiv, 60% dispersion in oil), cooled to 0°C. Then, a solution of 1-naphthol (2 g, 13.88 mmol, 1 equiv) in anhydrous DME (45 mL) was added dropwise via cannula. The resulting solution was stirred at r.t. for 10 min, and then cooled to 0 °C. A solution of dimethyl carbamoyl chloride (1.80 g, 16.76 mmol, 1.2 equiv) in anhydrous DME (10mL) was then added dropwise via cannula to the vessel. The reaction was warmed to rt, allowed to stir for 11 h, and then quenched with water. The solvent was removed under reduced pressure, and the solid material was dissolved in Et₂O (50 mL) and H₂O (15 mL), and transferred to a separatory funnel. The layers were separated, and the organic layer was washed with 1 M KOH (15 mL), then H₂O (15 mL). The combined aqueous layers were extracted with Et₂O (3 × 20 mL), washed with brine (15 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (Hexane/EtOAc: 4/1) to obtain 2.75 g of compound 2ab (92% yield).

5. Synthesis of Naphthalen-2-yl Bis(2-oxooazolidin-3-yl)phosphinate (2ac).

Under Ar atmosphere, a 100 mL round bottom flask was charged with 2-naphthol (0.2 g, 1.39 mmol, 1 equiv), bis(2-oxo-3-oxazolidinyl)phosphinic chloride (0.35 g, 1.39 mmol, 1 equiv) and anhydrous CH₂Cl₂ (7 mL). The obtained mixture was cooled to 0 °C. Then, Et₃N (0.19 mL, 1.39 mmol, 1 equiv) was added dropwise. The reaction was allowed to stir to r.t. Then, the reaction mixture was transferred to a separatory funnel and NaHSO₄ (20 mL, 0.5 M) was added. The layers were separated and the aqueous layer was washed with EtOAc. The combined organic layers were then washed with brine (20 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude residue was purified by flash chromatography to obtain 0.311 g of compound 2ac (62% yield).
6. Synthesis of Naphthalene-1-yl Dimethylsulfamate (2ad).

Under Ar atmosphere, a 100 mL round bottom flask was charged with NaH (0.4 g, 16.67 mmol, 1.2 equiv, 60% dispersion in oil), was cooled to 0 ºC. Then, a solution of 1-naphthol (2 g, 13.88 mmol, 1 equiv) in anhydrous DME (45 mL) was added dropwise via cannula. The resulting solution was stirred at r.t. for 10 min, and then cooled back to 0 ºC. A solution of dimethyl sulfamoyl chloride (2.39 g, 16.67 mmol, 1.2 equiv) in anhydrous DME (10 mL) was then added dropwise via cannula to the vessel. The reaction was warmed to rt, allowed to stir for 11 h, and then quenched carefully with water. The solvent was removed under reduced pressure, and the solid material was dissolved in Et₂O (50 mL) and H₂O (15 mL), and transferred to a separatory funnel. The layers were separated, and the organic layer was washed in this order, with 1 M KOH (15 mL), and H₂O (15 mL). The combined aqueous layers were extracted with Et₂O (3 × 20 mL). The combined organic layers were then washed with brine (15 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (Hexane/EtOAc: 4/1) to obtain 2.54 g of compound 2ad (85% yield).


A 100 mL round bottom flask was charged with 1-naphthol (1 g, 6.94 mmol, 1 equiv), 1,1'-N,N'-sulfonyldiimidazole (2.75 g, 13.88 mmol, 2 equiv), and cesium carbonate (1.13 g, 3.47 mmol, 0.5 equiv) in THF (20 mL). The reaction was stirred at r.t. for 4-16 h. When the reaction was complete (TLC), the solvent was evaporated and EtOAc was added to the obtained solution which was cooled at 0 ºC. Then a saturated aqueous NH₄Cl was added. The layers were separated and the aqueous layer was washed with EtOAc (2 × 20 mL). The combined organic extracts were washed with water (1 × 20 mL), followed by brine (1 × 20 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude residue was purified by flash chromatography.

8. Typical Procedure for the Suzuki Coupling with Conventional Heating.

A 10 mL round bottom flask was charged with naphthalen-1-yl-1H-imidazole-1-sulfonate (0.024 g, 0.1 mmol, 1 equiv), 4-tolyboronic acid (0.020 g, 0.15 mmol, 1.5 equiv), KOH (0.011 g, 0.2 mmol, 2 equiv), TBAB (0.016 g, 0.05 mmol, 20 mol%) catalyst 1a (0.00029 g, 1 mol% Pd) a MeOH/H₂O mixture (3/1, 4 mL). The reaction was
allowed to stir at 110 °C, during 24 h. Then, the solution was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The organic layers were washed with H₂O (3 × 10 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (EtOAc/hexane: 4/1) to obtain 0.017 g of the corresponding pure coupling compound 3b in 90% yield.


A 10 mL MW vessel was charged with naphthalen-1-yl-1H-imidazole-1-sulfonate (0.024 g, 0.1 mmol, 1 equiv), phenylboronic acid (0.018 g, 0.15 mmol), KOH (0.011 g, 0.2 mmol), TBAB (0.016 g, 0.05 mmol), catalyst 1b (0.00041 g, 1 mol % Pd), a MeOH/H₂O mixture (3/1, 2 mL) were added. The vessel was sealed with pressure lock, and the mixture was heated in air at 110 °C by a MW irradiation of 40 W for 30 min in a CEM Discover MW reactor. The reaction mixture was extracted with EtOAc (3 × 10 mL), and the organic layers were washed with H₂O (3 × 10 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (EtOAc/hexane: 3/1) to obtain 0.018 g of the corresponding pure coupling compound 3a in 99% yield.

10. Typical Procedure for the One Pot Suzuki Coupling.

A 10 mL round bottom flask was charged with 1-naphthol (0.144 g, 1 mmol), Cs₂CO₃ (0.163 g, 0.5 mmol), 1,1'-sulfonyldiimidazole (0.297 g, 1.5 mmol) and THF (5 mL). The reaction was stirred until completion (monitored by TLC). Then the solvent was evaporated and in the same reaction flask phenylboronic acid (0.183 g, 1.5 mmol), KOH (0.112 g, 2 mmol), TBAB (0.006 g, 0.02 mmol), catalyst 1b (0.0041 g, 1 mol % Pd) a MeOH/H₂O mixture (3/1, 4 mL) were added. After 24 h, the reaction mixture was extracted with EtOAc (3 × 10 mL), and the organic layers were washed with H₂O (3 × 10 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (EtOAc/hexane: 3/1) to obtain 0.145 g of the corresponding pure coupling compound 3a in 71% yield.
11. Physical and spectroscopic data:

**tert-Butyl Naphthalen-1-yl Carbonate (2aa).** Yield 95%; Yellow oil; R<sub>f</sub> 0.91 (hexane/EtOAc: 3/1); IR (neat) υ (cm<sup>-1</sup>) 3059, 2981, 2934, 2872, 1760, 1739, 1600, 1510, 1462, 1393, 1371, 1274, 1256, 1229, 1142, 1093, 1047, 784, 772; δ<sub>H</sub> (400 MHz) 7.97-7.95 (m, 1H), 7.86 (dd, J = 7.2, 2.8 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.55-7.48 (m, 2H), 7.46 (t, J = 8 Hz, 1H), 7.31 (dd, J = 7.6, 0.8 Hz, 1H), 1.59 (s, 9H); δ<sub>C</sub> 151.8, 146.7, 134.4, 127.7, 126.7, 126.20, 126.16, 125.7, 125.1, 120.8, 117.5, 83.2, 27.4; MS (m/z, %) 245 (M<sup>+</sup>+1, 18), 244 (M<sup>+</sup>, 100), 185 (17), 145 (31), 144 (100), 127 (36), 116 (14), 115 (85), 89 (11), 57 (100).

**Naphthalene-1-yl Dimethylcarbamate (2ab).** Yield 92%; Pale brown solid; m.p. 73-74 °C (hexane); R<sub>f</sub> 0.59 (hexane/EtOAc: 4/1); IR (neat) υ (cm<sup>-1</sup>) 3053, 2932, 1727, 1595, 1486, 1461, 1378, 1256, 1228, 1162, 1078, 1044, 994, 868, 797, 769; δ<sub>H</sub> 7.93 (dd, J = 9, 3 Hz, 1H), 7.86-7.83 (m, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.50-7.42 (m, 3H), 7.28 (dd, J = 7.5, 0.9 Hz, 1H), 3.24 (s, 3H), 3.06 (s, 3H); δ<sub>C</sub> 154.8, 147.2, 134.5, 127.8, 127.3, 126.2, 125.4, 125.3, 121.2, 118.1, 36.8, 36.5; MS (m/z, %) 216 (M<sup>+</sup>+1, 23), 215 (M<sup>+</sup>, 100), 143 (10), 127 (21), 116 (13), 115 (100), 89 (21), 73 (21), 72 (100), 63 (16).
Naphthalen-2-yl Bis(2-oxooazolidin-3-yl)phosphinate (2ac). Yield 62%; White solid; m.p. 285-286 °C (hexane); IR (neat) ν (cm⁻¹) 3497, 3414, 3055, 3021, 2932, 1774, 1633, 1598, 1509, 1487, 1482, 1390, 1384, 1294, 1202, 1158, 982, 764, 611; δ H 7.86 (dd, J = 8.8, 5.2 Hz, 3H), 7.78 (s, 1H), 7.56-7.40 (m, 2H), 7.42 (dd, J = 7.6, 1.2 Hz, 1H), 4.53-4.40 (m, 4H), 4.21 (dd, J = 8.8, 6.4 Hz, 2H), 4.1 (dd, J = 7.6, 1.6 Hz, 2H); δ C 156.1, 156.0, 146.2, 146.1, 133.7, 131.5, 130.5, 127.8, 127.7, 127.2, 126.2, 120.0, 119.9, 117.6, 117.5, 64.7, 64.6, 45.61, 45.58; MS (m/z, %) 363 (M⁺+1, 18), 362 (M⁺, 100), 281 (21), 213 (33), 208 (14), 207 (58), 191 (11), 190 (10), 169 (20), 168 (19), 167 (10), 154 (26), 144 (25), 141 (12), 127 (25), 115 (44), 77 (10), 73 (10).

Naphthalene-1-yl Dimethylsulfamate (2ad). Yield 85%; Pale brown solid; m.p. 73-76 °C (hexane); Rf 0.33; IR (KBr) ν (cm⁻¹) 3053, 2984, 2935, 1595, 1370, 1221, 1179, 977, 881, 809, 767, 698; δ H 8.21 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 8 Hz, 1H), 7.62-7.54 (m, 3H), 7.48 (t, J = 8 Hz, 1H), 3.08 (s, 6H); δ C 146.1, 134.8, 127.9, 127.1, 126.8, 126.6, 125.4, 121.5, 117.8; MS (m/z, %) 247 (M⁺, 251), 158 (10), 144 (19), 143 (72), 116 (11), 115 (100).

Naphthalen-1-yl-1H-imidazole-1-sulfonate (2ae). Yield 76%; White solid; m.p. 101 °C (hexane); Rf 0.39 (hexane/EtOAc: 2/1); IR (KBr) ν (cm⁻¹) 3132, 3092, 1425, 1208, 1161, 1063, 907, 816, 773, 624; δ H 7.91-7.79 (m, 4H), 7.60-7.55 (m, 2H), 7.42 (t, J = 7.8 Hz, 1H), 7.32 (s, 1H), 7.13 (s, 1H), 7.01 (d, J = 7.5 Hz, 1H); δ C 145.3, 137.4, 134.8, 131.3, 128.7, 128.0, 127.7, 127.4, 126.4, 125.1, 120.4, 118.4, 117.8; MS (m/z, %) 274 (M⁺, 56), 144 (15), 143 (86), 116 (11), 115 (100).

Phenyl-1H-imidazole-1-sulfonate (2be). Yield 98%; Colorless oil; Rf 0.34 (hexane/EtOAc: 3/1); IR (neat) ν (cm⁻¹) 3125, 1585, 1524, 1485, 1420, 1204, 1135,
1050, 877, 784, 688; \( \delta_H \) 7.73 (s, 1H), 7.41-7.35 (m, 3H), 7.31 (s, 1H), 7.17 (s, 1H), 6.97-6.90 (m, 2H); \( \delta_C \) 149.0, 137.5, 131.4, 130.3, 128.7, 121.3, 118.3; MS (m/z, %) 225 (M^\text{+1} + 10), 224 (M^+, 78), 144 (16), 132 (15), 131 (12), 117 (70), 94 (77), 93 (59), 77 (15), 67 (10), 65 (100).

\[ \text{Me-} \overset{\text{SO}_2\text{Im}}{\text{O}} \]

\text{p-Tolyi-1H-imidazole-1-sulfonate (2ce).} \text{ Yield 86%; Pale yellow oil; } R_f 0.32 \text{ (hexane/EtOAc: 4/1); IR (neat) } \nu (\text{cm}^{-1}) 3427, 3130, 2927, 1598, 1524, 1502, 1459, 1427, 1345, 1208, 1160, 1159, 1096, 1051, 995, 882, 830, 611; \delta_H 7.71 (s, 1H), 7.29 (s, 1H), 7.15 (dd, \text{J} = 9.6, 2.4 Hz, 3H), 6.80 (dd, \text{J} = 6.8, 1.6 Hz, 2H); \delta_C 146.9, 138.7, 137.5, 131.2, 130.7, 120.9, 118.3, 20.9; MS (m/z, %) 238 (M^+, 50), 158 (14), 131 (31), 108 (32), 107 (100), 79 (38), 78 (14), 77 (49).

\[ \text{Me} \overset{\text{SO}_2\text{Im}}{\text{Me}} \]

\text{3,5-Dimethylphenyl-1H-imidazole-1-sulfonate (2de).} \text{ Yield 90%; Colorless solid; m.p. 47-48 °C (hexane); } R_f 0.32 \text{ (hexane/EtOAc: 3/1); IR (KBr) } \nu (\text{cm}^{-1}) 3407, 3156, 3133, 2923, 2252, 1618, 1589, 1428, 1205, 1158, 1118, 1052, 908, 732; \delta_H 7.74 (s, 1H), 7.30 (d, \text{J} = 1.2 Hz, 1H), 7.16 (d, \text{J} = 1.2 Hz, 1H), 6.95 (s, 1H), 6.51 (s, 2H), 2.26 (s, 3H); \delta_C 148.9, 140.3, 137.5, 131.0, 130.0, 118.5, 118.3, 21.0; MS (m/z, %) 253 (M^+1,22), 252 (M^+, 100), 188 (55), 187 (16), 160 (20), 159 (27), 146 (15), 145 (48), 132 (10), 122 (83), 121 (100), 120 (18), 107 (15), 105 (13), 103 (10), 93 (71), 92 (100), 91 (100), 79 (15), 78 (28), 77 (100), 69 (11), 67 (19), 65 (23), 53 (22), 51 (16). HRMS calcd for C_{11}H_{12}N_{2}O_{3}S 252.0569 found 252.0561.

\[ \text{CF}_2\overset{\text{SO}_2\text{Im}}{\text{CF}} \]

\text{4-(Trifluoromethyl)phenyl-1H-imidazole-1-sulfonate (2ee).} \text{ Yield 76%; Colorless oil; } R_f 0.37 \text{ (hexane/EtOAc: 3/1); IR (neat) } \nu (\text{cm}^{-1}) 3405, 2922, 2852, 1614, 1424, 1416, 1325, 1211, 1165, 1144, 1065, 1058; \delta_H 7.78 (s, 1H), 7.67 (d, \text{J} = 8.7 Hz, 2H), 7.33 (s, 1H), 7.21 (s, 1H), 7.08 (d, \text{J} = 9 Hz, 2H); \delta_C 150.9, 137.4, 131.6, 131.1 (q, \text{J} = 33.4 Hz), 127.86, 127.81, 127.77 (q, \text{J} = 3.5 Hz), 127.71, 123.1 (q, \text{J} = 272 Hz), 122.1, 118.3,
115.4; MS (m/z, %) 293 (M'+1, 11), 292 (M', 100), 273 (15), 205 (22), 200 (14), 185 (78), 173 (12), 172 (12), 162 (85), 161 (31), 145 (20), 143 (10), 133 (97), 132 (16), 131 (13), 114 (17), 113 (36), 83 (23), 67 (45), 63 (15). HRMS calcd for C_{10}H_{7}F_{3}N_{2}O_{3}S 292.0129 found 292.0149.

2-(Trifluoromethyl)phenyl-1H-imidazole-1-sulfonate (2fe). Yield 73%; Light yellow oil; R_f 0.50 (hexane/EtOAc: 2/1); IR (neat) υ (cm⁻¹) 2915, 2849, 1615, 1433, 1318, 1192, 1152, 1050, 881, 779, 729; δ_H 7.92 (s, 1H), 7.72 (d, J = 7.6, 1H), 7.63 (t, J = 7.2, 1H), 7.48 (t, J = 8.4, 1H), 7.35 (br.s, 1H), 7.25 (d, J = 8.4, 1H), 7.18 (br.s, 1H); δ_C 146.2, 137.2, 133.9, 132.6 (q, J = 31.4 Hz), 131.4, 128.3, 128.2 (q, J = 5.2 Hz), 128.1, 123.4 (q, J = 7.8 Hz), 121.8 (q, J = 272 Hz); MS (m/z, %) 293 (M'+1, 13), 292 (M', 100), 200 (12), 185 (75), 173 (10), 172 (10), 162 (80), 161 (26), 145 (15), 133 (86), 132 (13), 114 (14), 113 (37), 83 (23), 67 (48). HRMS calcd for C_{10}H_{7}F_{3}N_{2}O_{3}S 292.0129 found 292.0156.

2,6-Dimethylphenyl-1H-imidazole-1-sulfonate (2ge). Yield 90%; White solid; m.p. 56-58 °C; R_f 0.42 (hexane/EtOAc: 3/1); IR (KBr) υ (cm⁻¹) 3113, 3123, 2968, 2927, 1472, 1419, 1211, 1166, 1052, 893, 779, 624; δ_H 7.91 (br.s, 1H), 7.36-7.35 (br.s, 1H), 7.22-7.06 (m, 4H); 2.08 (s, 6H), δ_C 147.7, 137.0, 131.5, 131.2, 129.7, 127.8, 118.5, 16.1; MS (m/z, %) 252 (M', 5), 172 (35), 120 (41), 91 (38), 77 (33); Calcd for C_{11}H_{12}N_{2}O_{3}S: C: 52.37, H: 4.79, N: 11.10, S: 12.71; found C: 52.48, H: 4.73; N: 10.74; S: 13.60.

1-Phenylnaphthalene (3a). Yield 99%; White solid; R_f 0.87 (hexane); m.p. 40-41 °C (hexane); IR (KBr) υ (cm⁻¹) 3056, 2952, 2925, 2848, 1724, 1593, 1493, 1397, 1277, 1069, 804, 777, 703; δ_H 7.94-7.88 (m, 3H), 7.57-7.50 (m, 6H), 7.49-7.43 (m, 3H); δ_C
140.8, 140.3, 133.8, 131.6, 130.1, 128.3, 127.6, 127.2, 126.9, 126.0, 125.8, 125.4; MS (m/z, %) 205 (M'+1, 16), 204 (M', 98), 203 (M'-1, 100), 202 (61), 201 (11), 200 (12), 101 (18).

1-(p-Tolyl)naphthalene (3b). Yield 90%; White solid; Rf 0.72 (hexane); m.p. 52-53 °C (hexane); IR (KBr) ν (cm⁻¹) 3045, 2919, 2862, 1590, 1504, 1394, 1023, 800; δH 8.00-7.89 (m, 3H), 7.59-7.54 (m, 2H), 7.55-7.45 (m, 4H), 7.36 (d, J = 8 Hz, 2H); 2.51 (s, 3H); δC 140.3, 137.9, 136.9, 133.9, 131.8, 130.0, 129.5, 129.0, 128.3, 127.5, 126.9, 126.1, 125.9, 125.7, 125.4, 21.26; MS (m/z, %) 219 (M'+1, 18), 218 (M', 100), 217 (M'-1, 31), 215 (17), 203 (60), 202 (56), 108 (11).

1-(4-Methoxyphenyl)naphthalene (3c). Yield 75%; White Solid; m.p. 116-117 °C (hexane); Rf 0.15 (hexane); IR (KBr) ν (cm⁻¹) 3043, 2990, 2995, 2825, 1607, 1502, 1390, 1242, 1168, 1102, 1028, 842, 803, 779, 568; δH 7.96-7.92 (m, 2H), 7.87 (d, J = 8 Hz, 1H), 7.54-7.42(m, 6H), 7.06 (d, J = 8.8 Hz, 2H), 3.92 (s, 3H); δC 158.9, 139.9, 133.8, 133.1, 131.8, 131.1, 128.2, 127.3, 126.9, 126.1, 125.9, 125.7, 125.4, 113.7, 55.4; MS (m/z, %) 235 (M'+1, 19), 234 (M'), 219 (29), 191(17), 190 (23), 189 (36).

1-[4-(Trifluoromethyl)phenyl]naphthalene (3d). Yield 66%; White solid; m.p. 48-49 °C (hexane); Rf 0.34 (hexane); IR (KBr) ν (cm⁻¹) 3068, 3045, 1616, 1404, 1323, 1166, 1123, 1069, 1019, 850, 804, 700; δH 8.09-7.99 (m, 3H), 7.90 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.69-7.57 (m, 3H), 7.54 (d, J = 8.4 Hz, 1H); δC 144, 6, 138.6, 134.0, 131.4, 130.5, 129.6 (q, J = 32.4 Hz), 128.6, 128.5, 127.7, 127.2, 126.6, 126.2,
125.6, 125.5, 125.4, 125.3 (q, \( J = 3.4 \text{ Hz} \)), 123.2 (q, \( J = 272 \text{ Hz} \)); MS (m/z, %) 273 (\( M^+1, 18 \)), 272 (\( M^* \), 100), 271 (\( M^*-1, 23 \)), 251 (15), 203 (50), 202 (54).

4-Methyl-1,1'-biphenyl (3e).\(^9\) Yield 90%; White solid; m.p. 46 °C (hexane); R\(_f\) 0.40 (hexane); \( \delta^H \) 7.58 (dd, \( J = 8.4, 1.5 \text{ Hz} \), 2H), 7.49 (d, \( J = 8.1 \text{ Hz} \), 2H), 7.43 (t, \( J = 7.2 \text{ Hz} \), 2H), 7.32 (t, \( J = 9.3 \text{ Hz} \), 1H), 7.24 (d, \( J = 8.4 \text{ Hz} \), 2H), 2.39 (s, 3H); \( \delta^C \) 141.1, 138.3, 137.0, 129.4, 128.7, 126.9, 21.1; MS (m/z, %) 169 (\( M^+1, 13\% \)), 168 (\( M^* \), 100), 167 (\( M^*-1, 66 \)), 164 (28), 152 (17), 151 (24).

3,5-Dimethyl-1,1'-biphenyl (3f).\(^10\) Yield 88%; Colorless oil; R\(_f\) 0.74 (hexane); IR (neat) \( \nu \) (cm\(^{-1} \)) 3054, 3013, 2948, 2915, 2842, 1460, 1439, 1374, 1010, 766, 705; \( \delta^H \) 7.62-7.55 (m, 2H), 7.47-7.30 (m, 3H), 7.23 (d, \( J = 14.1 \text{ Hz} \), 2H), 2.38 (s, 6H); \( \delta^C \) 141.4, 141.1, 138.2, 128.9, 128.7, 128.6, 127.22, 127.16, 127.1, 125.1, 21.4; MS (m/z, %): 183 (\( M^+1, 17 \)), 182 (\( M^* \), 100), 181 (\( M^*-1, 20 \)), 167 (62), 166 (19), 165 (43), 152 (17).

4-(Trifluoromethyl)-1,1'-biphenyl (3g).\(^11\) Yield 81%; White solid; R\(_f\) 0.70 (hexane); m.p. 96-97 °C (hexane); IR (KBr) \( \nu \) (cm\(^{-1} \)) 3431, 3083, 2921, 2850, 2359, 1959, 1925, 1614, 1570, 1490, 1406, 1343, 1162, 1113, 1074, 843, 767, 728; \( \delta^H \) 7.69 (s, 4H), 7.60-7.58 (m, 2H), 7.49-7.38 (m, 3H); \( \delta^C \) 144.7, 139.8, 129.0 (q, \( J = 32 \text{ Hz} \)), 128.2, 127.4, 127.3, 125.72, 125.68 (q, \( J = 3.6 \text{ Hz} \)), 123 (q, \( J = 272 \text{ Hz} \)); MS (m/z, %) 223 (\( M^+1, 15 \)), 222 (\( M^* \), 100), 203 (10), 202 (12), 153 (17), 152 (29).
2-(Trifluoromethyl)-1,1′-biphenyl (3h). Yield 78%; White solid; R\text{f} 0.70 (hexane); m.p. 15 °C (hexane); IR (KBr) ν (cm\(^{-1}\)) 3065, 2926, 1483, 1316, 1171, 1072, 768, 654; δ\text{H} 7.74 (d, J = 7.8 Hz, 1H), 7.61-7.52 (m, 1H), 7.48-7.31 (m, 7H); δ\text{C} 141.4, 139.8, 132.0, 131.2, 128.9, 128.7 (q, J = 32.6 Hz), 127.7, 127.6, 127.3, 127.1, 126.1 (q, J = 10.6 Hz), 126.04, 125.97, 125.91 (q, J = 272 Hz); MS (m/z, %) 223 (\text{M}^+1, 18), 222 (\text{M}^+, 100), 203 (15), 202 (14), 153 (21), 152 (35).

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2,6-Dimethylbiphenyl (3i). Yield 53%; Colorless oil; R\text{f} 0.74 (hexane); IR (neat) ν (cm\(^{-1}\)) 3054, 3013, 2948, 2915, 2842, 1460, 1439, 1374, 1010, 766, 705; δ\text{H} 7.52-7.38 (m, 3H), 7.28-7.16 (m, 5H), 2.10 (s, 6H); δ\text{C} 141.9, 141.4, 136.1, 129.1, 128.4, 127.3, 127.2, 127.0, 20.9; MS (m/z, %): 183 (\text{M}^+1, 14), 182 (\text{M}^+, 92), 168 (14), 167 (100), 166 (29), 165 (51), 152 (22).

12. References


\(\text{(2aa)Tert-butyl naphthalen-1-yl carbonate}\)
(2ab) Naphthalen-2-yl dimethylcarbamate
(2ac) Naphthalen-2-yl bis(2-oxooxazolidin-3-yl)phosphinate
(2ad) Naphthalen-1-yl dimethylsulfamate
(2be) Phenyl 1H-imidazole-1-sulfonate
Me-\(\text{OSO}_3\text{Im}\)

\((2\text{ce}) \text{\(\rho\)-Tolyl \(1\)H-imidazole-1-sulfonate}\)
(2de) 3,5-Dimethylphenyl 1H-imidazole-1-sulfonate
(2ee) 4-(Trifluoromethyl)phenyl 1H-imidazole-1-sulfonate
(2fe) 2-(Trifluoromethyl)phenyl 1H-imidazole-1-sulfonate
(2ge) 2,6-Dimethylphenyl 1H-imidazole-1-sulfonate
(3c) 1-(4-Methoxyphenyl)naphthalene
(3d) 1-(4-(Trifluoromethyl)phenyl)naphthalene
(3i) 2,6-Dimethyl-1,1'-biphenyl

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