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A Strategy for the Synthesis of 2,3-Disubstituted Indoles Starting from *N*-(*o*-Halophenyl)allenamides

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General remarks

All reactions were performed using oven-dried glasswares under an atmosphere of argon. Anhydrous THF was purchased from Kanto Chemicals Inc. and distilled from Na/benzophenone immediately prior to use. Anhydrous DMF was purchased from Kanto Chemicals, Co. Inc. and used as received. CH_3CN, methanol, and toluene were distilled from CaH_2 under an atmosphere of argon. HMPA was distilled from CaH_2 under reduced pressure. Tetrakis(triphenylphosphine)palladium(0) was prepared according to the literature procedure (D. R. Coulson, *Inorg. Synth.*, **1972**, *13*, 121) and stored under argon at −20 °C. All other chemicals were purchased at the highest commercial grade and used as received. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} pre-coated glass plates (0.25 mm-thickness). Flash column chromatography was carried out using Fuji Silysia silica gel BW-300 (200-400 mesh). ^1H and ^{13}C NMR spectra were recorded on a Varian Unity INOVA-500 or INOVA-600 spectrometer. Chemical shift values are reported in δ (ppm) downfield from tetramethylsilane with reference to internal residual solvent [^1H NMR: $CHCl_3$ (7.24); ^{13}C NMR: $CDCl_3$ (77.0)]. Coupling constants (*J*) are reported in hertz (Hz). Multiplicities of signals are designated as follows: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. EI mass spectra were measured on a JEOL JMS-700 spectrometer and ESI-TOF mass spectra were recorded on a Bruker microTOFfocus spectrometer.

Representative experimental procedures for the synthesis of α-functionalised allenamides

To a solution of *i*-Pr_2NH (0.310 mL, 2.21 mmol) in THF (5 mL) cooled at 0 °C was

added dropwise *n*-BuLi (1.58 M solution in hexane, 1.27 mL, 2.01 mmol). After being stirred at 0 °C for 0.5 h, the solution was cooled to −78 °C. To this solution was added a solution of allenamide **8** (357.0 mg, 1.00 mmol) in THF (5 mL + 2 mL rinse), and the resultant solution was stirred at −78 °C for 1 h. To this solution was added dropwise MeI (0.310 mL, 4.98 mmol). After being stirred at −78 °C for 3.5 h, the reaction was quenched with H_2O and extracted with EtOAc. The organic layer was washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography (silica gel, 5% diethyl ether/hexane) gave allenamide **9a** (281.9 mg, 76%) as a colourless oil. **9a**: ^{1}H NMR (300 MHz, C_6D_6) δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5, 1H), 6.86 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.44 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.79—4.65 (m, 2H), 2.17 (brs, 3H), 1.40 (s, 9H); HRMS (EI) calcd for $C_{15}H_{18}INO_2$ [M^+] 371.0382, found 371.0388. Due to its unstability, this material was not fully characterised and used in the next reaction immediately.

Representative experimental procedures for the carbopalladation/anion capture cascade
For aryl and alkenyl boronic acid capture [Table 1, Table 3 (entries 1-5), Table 4], the synthesis of compound **10** is representative. To a solution of **8** (74.9 mg, 0.2098 mmol) in ethanol (3 mL) were added 3 M aqueous Cs_2CO_3 (0.210 mL, 0.630 mmol), $PhB(OH)_2$ (28.1 mg, 0.230 mmol) and $Pd_2(dba)_3$ (9.6 mg, 0.010 mmol). The resultant mixture was heated at 70 °C for 1.5 h. After cooling to room temperature, the resultant mixture was diluted with EtOAc, washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography (silica gel, 5% Et_2O/hexane) gave **10** (63.2 mg, 98%) as a colorless oil.

For alkylborane capture [Table 2, Table 3 entries 6-8], the synthesis of compound **12** is representative. The alkylborane was prepared *in situ* by hydroboration of the corresponding olefin (59.2 mg, 0.269 mmol) with 9-BBN (0.5 M solution in THF, 1.34 mL, 0.670 mmol) at room temperature for 2 h. To this solution was added 3 M aqueous Cs_2CO_3 (0.220 mL, 0.660 mmol), and the resultant mixture was stirred at room temperature for 15 min before dilution with DMF (3 mL). To this mixture were added **8** (80.0 mg, 0.224 mmol) and $PdCl_2(dppf)\cdot CH_2Cl_2$ (18.3 mg, 0.0224 mmol). After being stirred at 50 °C for 20 h, the mixture was diluted with EtOAc, washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography (silica gel, 6% Et_2O/hexane) gave **12** (53.1 mg, 53%) as a colorless oil.

*Selected spectroscopic data for compounds **10**, **12-26**, and **28-34**.*

Compound **10**: IR (neat) ν_{max}/cm^{-1} 2979, 1731, 1453, 1368, 1254, 1158, 1082, 746; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (br, 1H), 7.48 (d, J = 7.0 Hz, 1H), 7.41 (br, 1H), 7.36—7.32 (m, 5H), 7.26—7.21 (m, 2H), 4.08 (s, 2H), 1.70 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 139.6, 135.6, 130.5, 128.6 (× 2), 128.4 (× 2), 126.2, 124.3, 123.5, 123.3, 120.0, 119.3, 115.2, 83.4, 31.3, 28.1 (× 3); HRMS (EI) calcd for $C_{20}H_{21}NO_2$ [M^+] 307.1560, found 307.1578.

Compound **12**: IR (neat) ν_{max}/cm^{-1} 2930, 2855, 1730, 1513, 1454, 1375, 1251, 1160, 1098, 746; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (br, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.37 (br, 1H), 7.32 (dd, J = 8.0, 7.5 Hz, 1H), 7.29—7.23 (m, 3H), 6.90 (d, J = 8.5 Hz, 2H), 4.44 (s, 2H), 3.80 (s, 3H), 3.45 (t, J = 6.5 Hz, 2H), 2.68 (t, J = 7.0 Hz, 2H), 1.75—1.59 (m, 13H), 1.46—1.35 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 149.8, 135.4, 130.8, 130.7, 129.1 (× 2), 124.0, 122.13, 122.08, 121.3, 118.9, 115.1, 113.6 (× 2), 83.1, 72.4, 70.1, 55.1, 29.7, 29.4, 29.2, 29.1, 28.1 (× 3), 26.1, 24.8; HRMS (ESI) calcd for $C_{28}H_{37}NO_4Na$ [$(M + Na)^+$] 474.2620, found 474.2623.

Compound **13**: IR (neat) ν_{max}/cm^{-1} 3028, 2918, 1599, 1448, 1367, 1173, 1121, 975, 741, 672, 574; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 1H), 7.31—7.15 (m, 10H), 4.00 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 138.9, 135.5, 135.2, 130.8, 129.7 (× 2), 128.6 (× 2), 128.5 (× 2), 126.7 (× 2), 126.4, 124.7, 123.9, 123.0, 122.4, 119.7, 113.7, 31.3, 21.5; HRMS (ESI) calcd for $C_{22}H_{19}NO_2SNa$ [$(M + Na)^+$] 384.1034, found 384.1034.

Compound **14**: IR (neat) ν_{max}/cm^{-1} 3054, 2919, 1598, 1491, 1446, 1367, 1279, 1173, 1122, 975, 809, 747, 669, 574; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.33—7.27 (m, 3H), 7.24—7.22 (m, 2H), 7.20—7.15 (m, 3H), 7.12 (d, J = 8.5 Hz, 2H), 3.95 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 137.4, 135.4, 135.1, 132.1, 130.5, 129.9 (× 2), 129.8 (× 2), 128.6 (× 2), 126.7 (× 2), 124.8, 123.9, 123.1, 121.8, 119.6, 113.8, 30.7, 21.5; HRMS (ESI) calcd for $C_{22}H_{18}ClNO_2SNa$ [$(M + Na)^+$] 418.0644, found 418.0670.

Compound **15**: IR (neat) ν_{max}/cm^{-1} 3027, 1598, 1446, 1367, 1278, 1173, 1122, 969, 745, 669, 576; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 7.5 Hz, 1H), 7.39 (s, 1H), 7.33—7.29 (m, 5H), 7.22—7.18 (m, 4H), 6.49 (d, J = 16.0 Hz, 1H), 6.36 (dt, J = 16.0, 7.0 Hz, 1H), 3.58 (d, J = 7.0 Hz, 2H), 2.32

(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 137.1, 135.4, 135.3, 131.6, 130.8, 129.8 (× 2), 128.5 (× 2), 127.3, 126.9, 126.7 (× 2), 126.1 (× 2), 124.7, 123.2, 123.0, 121.2, 119.7, 113.7, 28.6, 21.5; HRMS (ESI) calcd for $C_{24}H_{21}NO_2SNa$ [$(M + Na)^+$] 410.1191, found 410.1217.

Compound **16**: IR (neat) ν_{max}/cm^{-1} 2978, 1730, 1610, 1512, 1453, 1368, 1251, 1158, 1081, 746; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (br, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.35 (br, 1H), 7.31 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.24—7.18 (m, 3H), 6.85 (d, *J* = 7.5 Hz, 2H), 3.99 (s, 2H), 3.79 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 149.8, 135.6, 131.7, 130.5, 129.5 (× 2), 124.2, 123.4, 122.3, 120.5, 119.3, 115.2, 113.8 (× 2), 83.3, 55.2, 30.5, 28.2 (× 3); HRMS (ESI) calcd for $C_{21}H_{23}NO_3Na$ [$(M + Na)^+$] 360.1576, found 360.1568.

Compound **17**: IR (neat) ν_{max}/cm^{-1} 2978, 1731, 1452, 1371, 1257, 1157, 1081, 746; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (br, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.46 (br, 1H), 7.31 (dd, J = 8.0, 7.5 Hz, 1H), 7.21 (dd, *J* = 7.5, 7.0 Hz, 1H), 7.14 (dd, *J* = 5.0, 1.5 Hz, 1H), 6.92 (m, 1H), 6.88 (m, 1H), 4.24 (s, 2H), 1.67 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 142.7, 135.6, 130.1, 126.8, 125.1, 124.4, 123.7, 123.5, 122.4, 119.5, 119.2, 115.2, 83.5, 28.2, 25.7; HRMS (ESI) calcd for $C_{18}H_{19}NO_2SNa$ [$(M + Na)^+$] 336.1034, found 336.1039.

Compound **18**: IR (neat) ν_{max}/cm^{-1} 2977, 2929, 1713, 1453, 1369, 1314, 1254, 1160, 1083, 1019, 745; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (br, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.36 (br, 1H), 7.34—7.18 (m, 8H), 3.04—2.99 (m, 4H), 1.67 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 141.8, 135.6, 130.6, 128.40 (× 2), 128.38 (× 2), 126.0, 124.2, 122.4, 122.3, 120.6, 118.9, 115.2, 83.3, 35.6, 28.2 (× 3), 27.0; HRMS (EI) calcd for $C_{21}H_{23}NO_2$ [M^+] 321.1721, found 321.1732.

Compound **19**: IR (neat) ν_{max}/cm^{-1} 2976, 1731, 1454, 1376, 1254, 1160, 1092, 746; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (br, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.35 (br, 1H), 7.29 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.21 (dd, *J* = 8.0, 7.5 Hz, 1H), 4.51 (t, *J* = 5.0 Hz, 1H), 3.62 (m, 2H), 3.48 (m, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 1.82—1.74 (m, 2H), 1.74—1.68 (m, 2H), 1.65 (s, 9H), 1.19 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 135.5, 130.6, 124.1, 122.3, 122.2, 120.8, 118.9, 115.2, 102.7, 83.2, 60.9 (× 2), 33.3, 28.2 (× 3), 24.6, 24.3, 15.3 (× 2); HRMS (ESI) calcd for $C_{21}H_{31}NO_4Na$ [$(M + Na)^+$] 384.2151, found 384.2153.

Compound **20**: IR (neat) ν_{max}/cm^{-1} 2974, 1447, 1369, 1173, 1122, 974, 747, 670, 576; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.31 (s, 1H), 7.27 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.22—7.13 (m, 3H), 4.49 (m, 1H), 3.63—3.57 (m, 2H), 3.48—3.42 (m, 2H), 2.67—2.64 (m, 2H), 2.29 (s, 3H), 1.78—1.69 (m, 2H), 1.69—1.63 (m, 2H), 1.18 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 135.3, 135.2, 131.0, 129.7, 126.7, 124.5, 123.1, 122.9, 122.6, 119.4, 113.7, 102.6, 61.0 (× 2), 33.2, 24.6, 23.9, 21.5, 15.3 (× 2); HRMS (EI) calcd for $C_{23}H_{29}NO_4S$ [M^+] 415.1817, found 415.1820.

Compound **21**: IR (neat) ν_{max}/cm^{-1} 2978, 2930, 1729, 1457, 1358, 1227, 1135, 746; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.27—7.14 (m, 7H), 4.05 (s, 2H), 2.60 (s, 3H), 1.70 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8, 140.3, 135.8, 134.0, 130.1, 128.4 (× 2), 128.1 (× 2), 125.9, 123.3, 122.4, 118.2, 116.8, 115.3, 83.5, 29.8, 28.3 (× 3), 14.1; HRMS (ESI) calcd for $C_{21}H_{23}NO_2Na$ [$(M + Na)^+$] 344.1626, found 344.1625.

Compound **22**: IR (neat) ν_{max}/cm^{-1} 3028, 2979, 2928, 1729, 1455, 1328, 1230, 1132, 845, 744; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.32 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.29—7.16 (m, 9H), 7.09 (d, *J* = 6.5 Hz, 2H), 4.56 (s, 2H), 4.13 (s, 2H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 139.9, 139.6, 136.4, 134.8, 129.7, 128.3 (× 2), 128.22 (× 2), 128.18 (× 2), 127.7 (× 2), 126.0, 125.8, 123.8, 122.5, 118.8, 115.5, 83.6, 32.1, 30.0, 27.8 (× 3) (one quaternary carbon missing probably due to overlapping); HRMS (ESI) calcd for $C_{27}H_{27}NO_2Na$ [$(M + Na)^+$] 420.1939, found 420.1949.

Compound **23**: IR (neat) ν_{max}/cm^{-1} 2977, 2930, 1729, 1455, 1327, 1230, 1133, 962, 846, 745; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.30—7.21 (m, 4H), 7.14 (d, *J* = 7.5, 7.0 Hz, 1H), 7.05 (d, *J* = 7.0 Hz, 2H), 5.51—5.49 (m, 2H), 4.45 (s, 2H), 3.40 (d, *J* = 4.5 Hz, 2H), 1.59 (d, *J* = 4.5 Hz, 3H), 1.42 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 139.8, 136.3, 133.9, 129.7, 128.5, 128.1 (× 2), 128.8 (× 2), 125.9, 125.7, 123.7, 122.3, 118.8, 118.6, 115.5, 83.5, 32.0, 27.8 (× 3), 27.3, 17.7; HRMS (ESI) calcd for $C_{24}H_{27}NO_2Na$ [$(M + Na)^+$] 384.1939, found 384.1942.

Compound **24**: IR (neat) ν_{max}/cm^{-1} 2978, 1727, 1449, 1363, 1242, 1161, 1109, 848, 745; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H),

7.28—7.23 (m, 4H), 7.17—7.16 (m, 2H), 7.11 (dd, *J* = 8.0, 7.5 Hz, 1H), 4.28 (s, 2H), 1.74 (s, 9H), 0.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 140.6, 137.6, 137.3, 132.0, 129.7, 128.3 (× 2), 128.1 (× 2), 125.8, 124.6, 122.1, 119.5, 115.2, 83.6, 31.0, 28.3 (× 3), 2.2 (× 3); HRMS (EI) calcd for $C_{23}H_{29}NO_2Si$ [M^+] 379.1968, found 379.1970.

Compound **25**: IR (neat) ν_{max}/cm^{-1} 3624, 3418, 2978, 1713, 1449, 1372, 1246, 1160, 1111, 840, 745; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.30 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.26—7.23 (m, 2H), 7.19—7.14 (m, 4H), 4.39 (s, 2H), 2.76 (br, 1H), 1.74 (s, 9H), 0.47 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.4, 140.7, 136.7, 136.5, 132.3, 130.2, 128.4 (× 2), 127.9 (× 2), 125.9, 125.0, 122.5, 119.7, 115.3, 84.6, 30.7, 28.2 (× 3), 2.27 (× 2); HRMS (EI) calcd for $C_{22}H_{27}NO_3Si$ [M^+] 381.1760, found 381.1764.

Compound **26**: IR (neat) ν_{max}/cm^{-1} 2975, 1730, 1458, 1366, 1324, 1136, 1062, 746; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 1H), 7.22—7.16 (m, 2H), 4.47 (m, 1H), 3.59 (dq, *J* = 14.0, 7.0 Hz, 2H), 3.44 (dq, *J* = 14.0, 7.0 Hz, 2H), 2.67 (m, 2H), 2.51 (s, 3H), 1.66 (s, 9H), 1.65 (m, 4H), 1.16 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.8, 135.7, 133.0, 130.0, 123.1, 122.2, 118.2, 117.8, 115.3, 102.8, 83.2, 60.9, 33.2, 28.3 (× 3), 25.2, 23.6, 15.3, 14.0; HRMS (ESI) calcd for $C_{22}H_{33}NO_4Na$ [$(M + Na)^+$] 398.2307, found 398.2330.

Compound **28**: IR (neat) ν_{max}/cm^{-1} 2979, 1735, 1445, 1352, 1313, 1247, 1155, 1094, 745; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.24—7.14 (m, 6H), 7.11 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.13 (s, 2H), 1.72 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 139.0, 138.2, 129.7, 128.5, 128.4, 128.3, 126.2, 124.3, 122.6, 118.8, 115.5, 85.0, 80.0, 33.8, 28.3 (× 3); HRMS (EI) calcd for $C_{20}H_{20}INO_2$ [M^+] 433.0539, found 433.0543.

Compound **29**: IR (neat) ν_{max}/cm^{-1} 2980, 1733, 1435, 1330, 1241, 1157, 1102, 749; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.39 (dd, J = 8.5, 7.0 Hz, 1H), 7.30—7.26 (m, 4H), 7.22—7.18 (m, 2H), 4.22 (s, 2H), 3.92 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 149.3, 139.2, 136.8, 128.5, 128.45 (× 2), 128.42 (× 2), 127.3, 126.6, 126.2, 125.0, 123.0, 120.7, 115.0, 84.4, 52.2, 30.3, 27.9 (× 3); HRMS (EI) calcd for $C_{22}H_{23}NO_4$ [M^+] 365.1627, found 365.1633.

Compound **30**: IR (neat) ν_{max}/cm^{-1} 2979, 1732, 1602, 1519, 1453, 1346, 1235, 1150,

1068, 854, 750; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26—8.23 (m, 3H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.41—7.35 (m, 2H), 7.24—7.20 (m, 3H), 7.16 (m, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 3.91 (s, 2H), 1.32 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 147.0, 141.0, 139.6, 136.8, 134.1, 130.5 (× 2), 129.5, 128.5 (× 2), 128.0 (× 2), 126.2, 125.4, 123.2, 123.1 (× 2), 120.7, 119.8, 115.5, 84.0, 30.1, 27.7 (× 3); HRMS (EI) calcd for $C_{26}H_{24}N_2O_4$ [M^+] 428.1736, found 428.1736.

Compound **31**: IR (neat) ν_{max}/cm^{-1} 3029, 1597, 1447, 1372, 1316, 1173, 1089, 975, 814, 749, 671, 574; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.36 (s, 1H), 7.28—7.22 (m, 4H), 7.12 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.39 (s, 2H), 2.35 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 144.8, 134.9, 134.6 (× 2), 129.9 (× 2), 129.6, 129.5 (× 2), 128.5 (× 2), 127.2, 126.8 (× 2), 125.0, 123.4, 119.5, 113.4, 110.2, 53.5, 21.6; HRMS (EI) calcd for $C_{23}H_{21}NO_4S_2$ [M^+] 439.0912, found 439.0912.

Compound **32**: IR (neat) ν_{max}/cm^{-1} 2979, 2099, 1735, 1453, 1372, 1258, 1157, 1088, 747; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (br, 1H), 7.62 (br, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.36 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.28 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.46 (s, 2H), 1.68 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 135.8, 129.0, 124.92, 124.87, 122.9, 119.0, 115.4, 114.7, 84.0, 46.1, 28.1 (× 3); HRMS (EI) calcd for $C_{14}H_{16}N_4O_2$ [M^+] 272.1273, found 272.1277.

Compound **33**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (br, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.35 (br, 1H), 7.29 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.21 (dd, *J* = 7.5 Hz, 1H), 6.03 (m, 1H), 5.18 (dd, *J* = 17.0, 2.0 Hz, 1H), 5.11 (dd, *J* = 10.0, 1.5 Hz, 1H), 3.44 (dd, *J* = 7.0, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 135.8, 135.6, 130.5, 124.3, 122.8, 122.3, 119.2, 119.0, 116.2, 115.2, 83.3, 29.5, 28.2 (× 3); HRMS (EI) calcd for $C_{16}H_{19}NO_2$ [M^+] 257.1410, found 257.1418.

Compound **34**: IR (neat) ν_{max}/cm^{-1} 2979, 1735, 1453, 1370, 1257, 1157, 1084, 1018, 747; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (br, 1H), 7.57 (br, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.32 (dd, *J* = 7.5, 7.0 Hz, 1H), 7.24 (dd, *J* = 8.0, 7.0 Hz, 1H), 3.71 (s, 2H), 3.70 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 149.5, 135.3, 130.0, 124.5, 124.4, 122.6, 118.9, 115.2, 113.0, 83.5, 52.1, 30.8, 28.1 (× 3); HRMS (ESI) calcd for $C_{16}H_{19}NO_4Na$ [$(M + Na)^+$] 312.1212, found 312.1196.